Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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Contents

A. General information

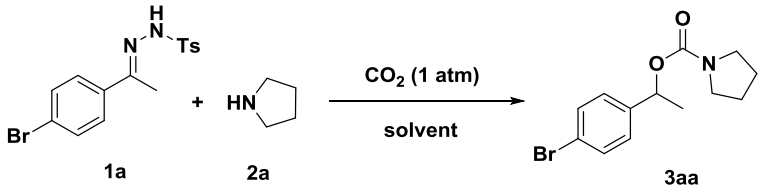
All solvents were obtained by passing through activated alumina columns of solvent purification systems from Glass Contour. n-Hexane and ethyl acetate were used without further purification. Reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, and TCI and were used as received. CO_2 (purity >99.999) was used. Reactions were carried out in a flame-dried glassware equipped with a stirring bar and capped with a rubber septum under CO_2, unless otherwise indicated. Elevated temperatures were maintained in thermostat-controlled oil baths. The TLC plate was carried out on 0.25 mm E. Merck silica gel plates (60F-254) visualized by UV-light (254 nm) and treatment with acidic *p*-anisaldehyde and $KMnO_4$ stain followed by gentle heating. Workup procedures were done in air. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^1H and ^{13}C NMR spectra were recorded with Varian spectrometer (400 MHz) spectrometer. ^1H NMR spectra were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, brs = broad singlet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.16 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.

B. General procedure for the preparation of organic carbamates

Reactions were performed in a tube schlenk equipped with a stirring bar and capped with a rubber septum and the followings were placed in the tube in order: 10 mmol of amine was added and tube was charged with CO_2 by balloon for 30 seconds. Then, 1 mmol of N-Tosylhydrazone and 1.5mL of CH_3NO_2 (Nitromethane) were put into the schlenk. The mixture was stirred at 80 ^oC for 18 h and CO_2 was provided by balloon (1 atm). After the completion of the reaction, the solvent was removed under reduced pressure. The crude residue was separated by column chromatography on silica gel with n-hexane and ethyl acetate to afford carbamates. The carbamate products were characterized by ^1H NMR, ^{13}C NMR, and HRMS.

C. Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions[a]



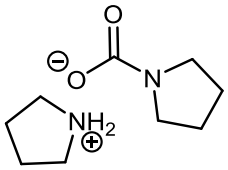
Entry	Additive	Base	Solvent	Temperature(°C)	Time(h)	Yield[b]
1	Poly(NHC), $ZnBr_2$	DBU	DMF	80	18	57
2	$ZnBr_2$	-	DMF	80	18	59
3	-	-	DMF	80	18	57
4	-	-	1,4-dioxane	80	18	60
5	-	-	Toluene	80	18	61
6	-	-	THF	80	18	60
7	-	-	DCE	80	18	26
8	-	-	-	80	18	62
9	-	-	-	50	18	19
10	-	-	-	r.t.	18	N.R.
11	-	-	-	80	6	62
12	-	-	-	80	3	60
13	-	-	-	80	2	61
14	-	-	-	80	1	51
15	-	-	-	90	2	60
16	-	-	-	100	2	55
17	-	-	CH_3NO_2	80	18	75
18[c]	-	-	CH_3NO_2	80	18	68
19[d]	-	-	CH_3NO_2	80	18	55
20	-	-	CH_3NO_2	80	6	71
21	-	-	CH_3NO_2	80	3	70
22	-	-	CH_3NO_2	80	2	67
23	-	-	CH_3NO_2	100	2	64
24[e]	-	-	MeCN/H_2O	80	18	63

[a] Reaction conditions: 1 mmol **1c**, 10 mmol **2a**, 1.5 mL solvent, 5 mol% additive, 20 mol% base, 1.5 ml solvent, under 1 atm CO_2. [b] Isolated yield. [c] 7 Equiv and [d] 5 equiv of pyrrolidine were used [e]MeCN/H_2O (v/v, 3.0 mL: 0.2 mL)

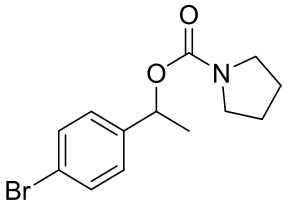
D. Gram-scale experiment

Reactions were performed in 50-mL flame-dried, two-necked schlenk flask equipped with a stirring bar and capped with a rubber septum and the followings were placed in the schlenk in order: 50 mmol of Pyrrolidine (**2a**, 4.1mL) was added and tube was charged with CO_2 by balloon for 30 seconds. Then, 5 mmol of N'-(1-(4-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (**1a**, 1.84g) and 7.5mL of CH_3NO_2 (Nitromethane) were put into the schlenk. The mixture was stirred at 80^{o}C for 18 h and CO_2 was provided by balloon (1 atm). After the completion of the reaction, the solvent was removed under reduced pressure. The crude residue was separated by column chromatography on silica gel with n-hexane and ethyl acetate (1.074g, 72% isolated yield).

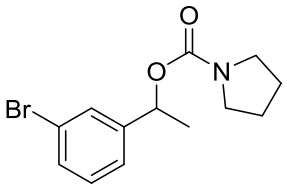
E. Characterization data for isolated products



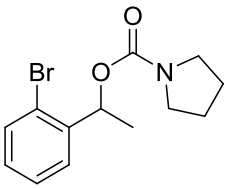
Pyrrolidin-1-ium pyrrolidine-1-carboxylate:[2)]
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 2 H), 3.15 (d, *J* = 57.8 Hz, 8 H), 1.78 (d, *J* = 26.8 Hz, 8 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.8, 46.1, 44.6, 25.8, 24.8 ppm.



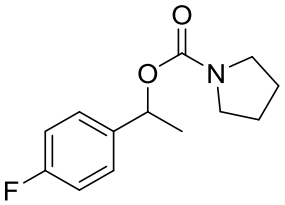
1-(4-Bromophenyl)ethyl pyrrolidine-1-carboxylate(**3aa**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 5.77 (q, *J* = 6.6 Hz, 1 H), 3.39 (dd, *J* = 13.6, 6.8 Hz, 4 H), 1.86 (dd, *J* = 11.0, 4.9 Hz, 4 H), 1.51 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.9, 141.5, 131.2, 127.4, 121.0, 71.5, 45.8, 45.5, 25.4, 24.6, 22.5 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}BrNO_2$]: 297.0364, found: 297.0361; pale yellow oil.



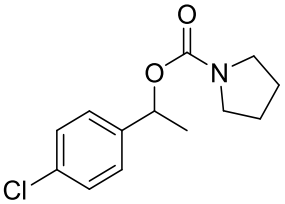
1-(3-Bromophenyl)ethyl pyrrolidine-1-carboxylate (**3ba**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1 H), 7.29 (d, *J* = 7.9 Hz, 1 H), 7.18 (d, *J* = 7.7 Hz, 1 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 5.69 (q, *J* = 6.6 Hz, 1 H), 3.37 – 3.24 (m, 4 H), 1.76 (dt, *J* = 11.9, 6.2 Hz, 4 H), 1.42 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.0, 145.0, 130.4, 129.9, 128.8, 124.5, 122.4, 71.6, 46.1, 45.7, 25.6, 24.8, 22.9 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}BrNO_2$]: 297.0364, found: 297.0362; pale yellow oil.



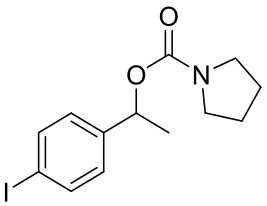
1-(2-Bromophenyl)ethyl pyrrolidine-1-carboxylate (**3ca**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 7.7 Hz, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 6.02 (q, *J* = 6.5 Hz, 1 H), 3.41 – 3.26 (m, 4 H), 1.84 – 1.71 (m, 4 H), 1.43 (d, *J* = 6.5 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**154.0, 142.2, 132.7, 128.7, 127.6, 126.7, 121.5, 71.8, 46.1, 45.7, 25.7, 24.9, 21.8 ppm. **HRMS (FAB^+)** calc. for [$C_{13}H_{16}BrNO_2$]: 298.0443, found: 298.0439; pale yellow oil.



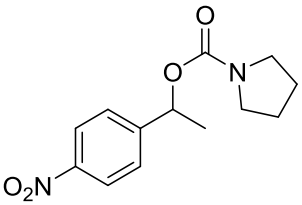
1-(4-Fluorophenyl)ethyl pyrrolidine-1-carboxylate(**3da**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 2 H), 6.91 (t, *J* = 7.9 Hz, 2 H), 5.72 (q, *J* = 6.2 Hz, 1 H), 3.36 – 3.22 (m, 4 H), 1.75 (brs, 4 H), 1.43 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.0 (d, *J* = 245.4 Hz), 154.2, 138.5 (d, *J* = 3.1 Hz), 127.5 (d, *J* = 8.1 Hz), 115.0 (d, *J* = 21.4 Hz), 71.7, 46.0, 45.6, 25.5, 24.8, 22.8 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}FNO_2$]: 237.1165, found:237.1166; yellow oil.



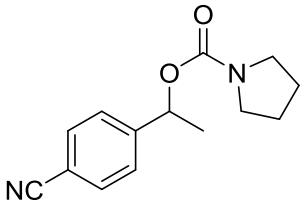
1-(4-Chlorophenyl)ethyl pyrrolidine-1-carboxylate(**3ea**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (brs, 4 H), 5.69 (q, *J* = 6.5 Hz, 1 H), 3.34 – 3.22 (m, 4 H), 1.74 (d, *J* = 4.8 Hz, 4 H), 1.41 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 141.2, 133.0, 128.4, 127.2, 71.7, 46.0, 45.6, 25.6, 24.8, 22.7 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}ClNO_2$]: 253.0870, found: 253.0871; pale yellow oil.



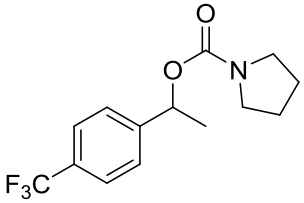
1-(4-Iodophenyl)ethyl pyrrolidine-1-carboxylate(**3fa**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2 H), 7.02 (d, *J* = 8.2 Hz, 2 H), 5.67 (q, *J* = 6.5 Hz, 1 H), 3.30 (d, *J* = 16.9 Hz, 4 H), 1.76 (d, *J* = 3.0 Hz, 4 H), 1.42 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 142.4, 137.3, 127.8, 92.9, 71.8, 46.0, 45.7, 25.6, 24.8, 22.7 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}INO_2$]: 345.0226, found: 345.0226; pale yellow oil.



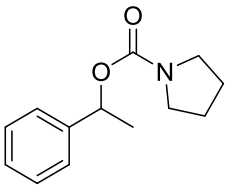
1-(4-Nitrophenyl)ethyl pyrrolidine-1-carboxylate(**3ga**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 2 H), 7.44 (d, *J* = 8.5 Hz, 2 H), 5.81 (q, *J* = 6.5 Hz, 1 H), 3.42 – 3.26 (m, 4 H), 1.81 (dd, *J* = 15.3, 5.9 Hz, 4 H), 1.48 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.0, 150.3, 147.4, 126.6, 123.8, 71.6, 46.3, 45.9, 25.8, 25.0, 22.9 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}N_2O_4$]: 264.1110, found:264.1113; yellow oil.



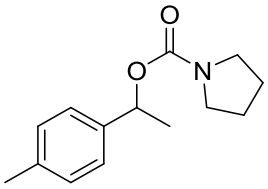
1-(4-Cyanophenyl)ethyl pyrrolidine-1-carboxylate(**3ha**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 5.75 (q, *J* = 6.6 Hz, 1 H), 3.40 – 3.25 (m, 4 H), 1.86 – 1.74 (m, 4 H), 1.45 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.9, 148.1, 132.2, 126.4, 118.7, 111.1, 71.6, 46.1, 45.7, 25.6, 24.8, 22.7 ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{16}N_2O_2$]: 244.1212, found: 244.1211; pale yellow oil.



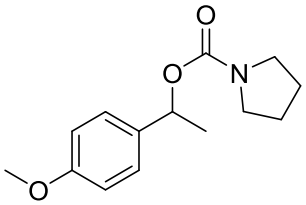
1-(4-(Trifluoromethyl)phenyl)ethyl pyrrolidine-1-carboxylate(**3ia**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 5.84 (q, *J* = 6.6 Hz, 1 H), 3.46 – 3.31 (m, 4 H), 1.88 – 1.80 (m, 4 H), 1.52 (d, *J* = 6.6 Hz, 3 H) ppm.**^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 146.9, 129.6 (q, *J* = 32.3 Hz), 126.1, 125.4 (q, *J* = 3.8 Hz), 122.8, 71.9, 46.1, 45.8, 25.7, 24.9, 22.9ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{16}F_3NO_2$]: 287.1133, found: 287.1135; pale yellow oil.



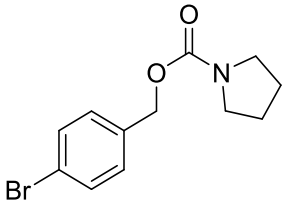
1-Phenylethyl pyrrolidine-1-carboxylate(**3ja**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4 H), 7.13 – 7.17 (m, 1 H), 5.74 (q, *J* = 6.6 Hz, 1 H), 3.35 – 3.22 (m, 4 H), 1.79 – 1.67 (m, 4 H), 1.44 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 142.6, 128.3, 127.4, 125.7, 72.4, 46.0, 45.6, 25.6, 24.8, 22.9 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{17}NO_2$]: 219.1259, found: 219.1260; pale yellow oil.



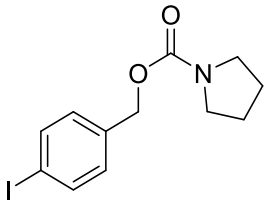
1-(p-Tolyl)ethyl pyrrolidine-1-carboxylate(**3ka**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.9 Hz, 2 H), 7.06 (d, *J* = 7.8 Hz, 2 H), 5.72 (q, *J* = 6.5 Hz, 1 H), 3.36 – 3.24 (m, 4 H), 2.25 (s, 3 H), 1.76 (brs, 4 H), 1.44 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.5, 139.8, 137.1, 129.1, 125.9, 72.4, 46.1, 45.7, 25.7, 25.0, 22.9, 21.1 ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{19}NO_2$]: 233.1416, found: 233.1419; pale yellow oil.



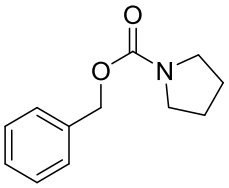
1-(4-Methoxyphenyl)ethyl pyrrolidine-1-carboxylate (**3la**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 5.71 (q, *J* = 6.6 Hz, 1 H), 3.69 (s, 3 H), 3.35 – 3.21 (m, 4 H), 1.82 – 1.67 (m, 4 H), 1.44 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9, 154.5, 134.8, 127.3, 113.7, 72.2, 55.2, 46.0, 45.7, 25.7, 24.9, 22.7 ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{19}NO_3$]: 249.1365, found: 249.1367; yellow oil.



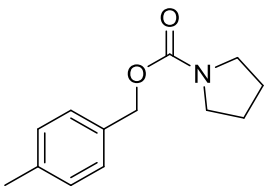
4-Bromobenzyl pyrrolidine-1-carboxylate (**3ma**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 4.98 (s, 2 H), 3.35 – 3.23 (m, 4 H), 1.73 – 1.79 (m, 4 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.5, 136.1, 131.4, 129.4, 121.7, 65.6, 46.2, 45.7, 25.6, 24.8 ppm. **HRMS (EI^+)** calc. for [$C_{12}H_{14}BrNO_2$]: 283.0208, found: 283.0212; pale yellow oil.



4-Iodobenzyl pyrrolidine-1-carboxylate (**3na**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2 H), 7.02 (d, *J* = 8.1 Hz, 2 H), 4.97 (s, 2 H), 3.33 – 3.24 (m, 4 H), 1.76 (brs, 4 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4, 137.3, 136.7, 129.6, 93.3, 65.7, 46.1, 45.7, 25.6, 24.8 ppm. **HRMS (EI^+)** calc. for [$C_{12}H_{14}INO_2$]: 331.0069, found: 331.0070; yellow oil.

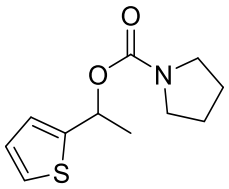


Benzyl pyrrolidine-1-carboxylate (**3oa**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5 H), 5.05 (s, 2 H), 3.35 – 3.26 (m, 4 H), 1.80 – 1.72 (m, 4 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.9, 137.1, 128.4, 127.8, 127.8, 66.5, 46.2, 45.8, 25.7, 24.9 ppm. **HRMS (EI^+)** calc. for [$C_{12}H_{15}NO_2$]: 205.1103, found: 205.1103; pale yellow oil.

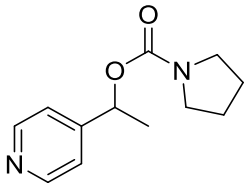


4-Methylbenzyl pyrrolidine-1-carboxylate (**3pa**):

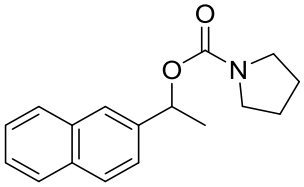
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.6 Hz, 2 H), 7.02 (d, *J* = 7.6 Hz, 2 H), 4.97 (s, 2 H), 3.22 – 3.27 (m, 4 H), 2.21 (s, 3 H), 1.70 – 1.68 (m, 4 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 137.2, 133.9, 128.8, 127.7, 66.2, 45.9, 45.5, 25.4, 24.7, 20.9 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{17}NO_2$]: 219.1259, found: 219.1257; pale yellow oil.



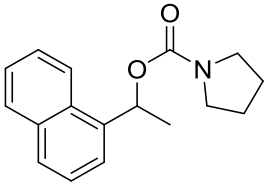
1-(Thiophen-2-yl)ethyl pyrrolidine-1-carboxylate (**3qa**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.0 Hz, 1 H), 6.95 (d, *J* = 3.4 Hz, 1 H), 6.86 (dd, *J* = 5.0, 3.5 Hz, 1 H), 6.01 (q, *J* = 6.5 Hz, 1 H), 3.33 – 3.24 (m, 4 H), 1.79 – 1.71 (m, 4 H), 1.56 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.2, 145.8, 126.5, 124.7, 124.5, 68.1, 46.1, 45.7, 25.6, 24.9, 22.7 ppm. **HRMS (EI^+)** calc. for [$C_{11}H_{15}NO_2S$]: 225.0823, found: 225.0824; yellow oil.



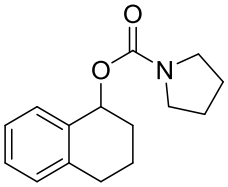
1-(Pyridin-4-yl)ethyl pyrrolidine-1-carboxylate (**3ra**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 4.6, 1.4 Hz, 2 H), 7.18 (dd, *J* = 4.6, 1.1 Hz, 2 H), 5.72 (q, *J* = 6.7 Hz, 1 H), 3.41 – 3.27 (m, 4 H), 1.86 – 1.75 (m, 4 H), 1.45 (d, *J* = 6.7 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.9, 151.5, 149.8, 120.5, 70.9, 46.1, 45.7, 25.6, 24.8, 22.5 ppm. **HRMS (EI^+)** calc. for [$C_{12}H_{16}N_2O_2$]: 220.1212, found: 220.1213; yellow oil.



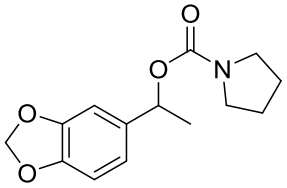
1-(Naphthalen-2-yl)ethyl pyrrolidine-1-carboxylate (**3sa**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.74 (m, 4 H), 7.45 – 7.30 (m, 3 H), 5.92 (q, *J* = 6.6 Hz, 1 H), 3.39 – 3.24 (m, 4 H), 1.80 – 1.69 (m, 4 H), 1.54 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4, 140.0, 133.1, 132.8, 128.1, 127.9, 127.5, 126.0, 125.8, 124.6, 124.1, 72.6, 46.0, 45.7, 25.6, 24.8, 22.8 ppm. **HRMS (EI^+)** calc. for [$C_{17}H_{19}NO_2$]: 269.1416, found: 269.1415; pale yellow oil.



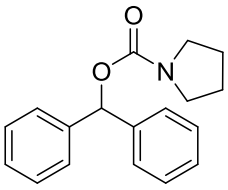
1-(Naphthalen-1-yl)ethyl pyrrolidine-1-carboxylate (**3ta**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 1 H), 7.73 (d, *J* = 7.8 Hz, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.49 (d, *J* = 7.0 Hz, 1 H), 7.42 – 7.37 (m, 1 H), 7.37 – 7.28 (m, 2 H), 6.48 (q, *J* = 6.6 Hz, 1 H), 3.24 – 3.39 (m, 4 H), 1.69 – 1.74 (m, 4 H), 1.60 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4, 138.4, 133.8, 130.2, 128.7, 128.1, 126.0, 125.5, 125.3, 123.5, 123.1, 70.1, 46.1, 45.8, 25.6, 24.9, 22.5 ppm. **HRMS (EI^+)** calc. for [$C_{17}H_{19}NO_2$]: 269.1416, found: 269.1418; pale yellow oil.



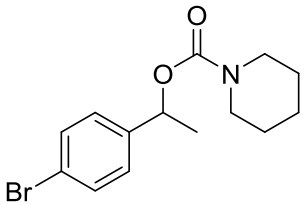
1,2,3,4-Tetrahydronaphthalen-1-yl pyrrolidine-1-carboxylate (**3ua**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.2 Hz, 1 H), 7.10 – 7.03 (m, 2 H), 6.99 (d, *J* = 6.8 Hz, 1 H), 5.78 – 5.79 (m, 1 H), 3.32 (brs, 2 H), 3.18 (brs, 2 H), 2.76 – 2.72 (m, 1 H), 2.66 – 2.63 (m, 1 H), 1.91 – 1.84 (m, 3 H), 1.72 (brs, 5 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.8, 137.5, 135.5, 129.2, 128.7, 127.5, 125.7, 70.2, 46.0, 45.6, 29.5, 28.9, 25.5, 24.8, 18.9 ppm. **HRMS (EI^+)** calc. for [$C_{15}H_{19}NO_2$]: 245.1416, found: 245.1413; pale yellow oil.



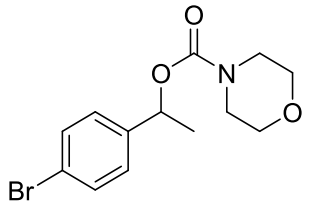
1-(Benzo[d][1,3]dioxol-5-yl)ethyl pyrrolidine-1-carboxylate (**3va**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (m, 2 H), 6.67 (d, *J* = 7.9 Hz, 1 H), 5.84 (s, 2 H), 5.65 (q, *J* = 6.6 Hz, 1 H), 3.35 – 3.23 (m, 4 H), 1.81 – 1.69 (m, 4 H), 1.41 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 147.6, 146.8, 136.7, 119.4, 108.0, 106.5, 100.9, 72.3, 46.0, 45.7, 25.7, 24.9, 22.9 ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{17}NO_4$]: 263.1158, found: 263.1158; yellow oil.



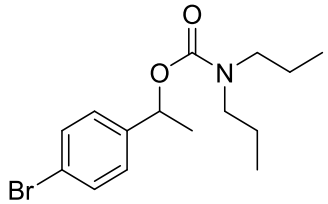
Benzhydryl pyrrolidine-1-carboxylate (**3wa**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.4 Hz, 4 H), 7.23 (t, *J* = 7.4 Hz, 4 H), 7.16 (t, *J* = 7.1 Hz, 2 H), 6.76 (s, 1 H), 3.42 (t, *J* = 6.6 Hz, 2 H), 3.30 (t, *J* = 6.6 Hz, 2 H), 1.81 – 1.72 (m, 4 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 141.2, 128.4, 127.6, 127.0, 77.2, 46.3, 45.9, 25.7, 24.9 ppm. **HRMS (EI^+)** calc. for [$C_{18}H_{19}NO_2$]: 281.1416, found: 281.1415; m.p. = 125 °C; white solid.



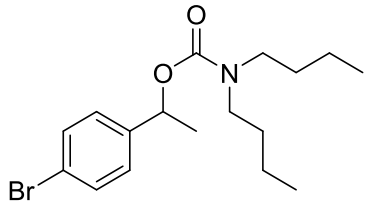
1-(4-Bromophenyl)ethyl piperidine-1-carboxylate (**3ab**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 5.75 (q, *J* = 6.6 Hz, 1 H), 3.42 (brs, 4 H), 1.58 (d, *J* = 8.4 Hz, 6 H), 1.50 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.7, 141.9, 131.6, 127.6, 121.4, 72.3, 44.9, 25.7, 24.4, 22.7 ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{18}BrNO_2$]: 311.0521, found: 311.0520; yellow oil.



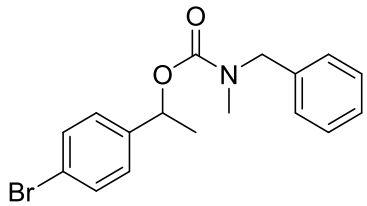
1-(4-Bromophenyl)ethyl morpholine-4-carboxylate (**3ac**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 5.76 (q, *J* = 6.6 Hz, 1 H), 3.63 (d, *J* = 4.7 Hz, 4 H), 3.47 (brs, 4 H), 1.51 (d, *J* = 6.6 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 141.3, 131.7, 127.7, 121.7, 72.9, 66.6, 44.2, 22.6 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{16}BrNO_3$]: 313.0314, found: 313.0310; pale yellow oil.



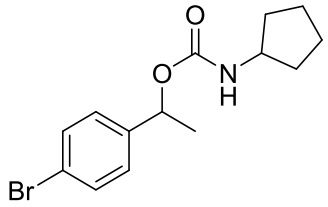
1-(4-Bromophenyl)ethyl dipropylcarbamate (**3ad**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.6 Hz, 2 H), 7.21 (d, *J* = 6.8 Hz, 2 H), 5.74 (q, *J* = 6.5 Hz, 1 H), 3.17 (brs, 4 H), 1.57 – 1.51 (m, 4 H), 1.5 – 1.48 (m, 3 H), 0.86 – 0.88 (m, 6 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.6, 141.9, 131.6, 127.7, 121.4, 72.2, 49.3, 48.7, 22.7, 22.0, 21.4, 11.4 ppm. **HRMS (EI^+)** calc. for [$C_{15}H_{22}BrNO_2$]: 327.0834, found: 327.0836; pale yellow oil.



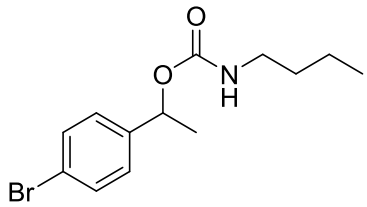
1-(4-Bromophenyl)ethyl dibutylcarbamate (**3ae**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 5.74 (q, *J* = 6.6 Hz, 1 H), 3.20 (brs, 4 H), 1.59 – 1.41 (m, 7 H), 1.29 (d, *J* = 6.7 Hz, 4 H), 0.97 – 0.82 (m, 6 H)**^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.5, 141.8, 131.5, 127.7, 121.3, 72.2, 47.3, 46.6, 30.9, 30.3, 22.7, 20.1, 13.9 ppm. **HRMS (EI^+)** calc. for [$C_{17}H_{26}BrNO_2$]: 355.1147, found: 355.1147; pale yellow oil.



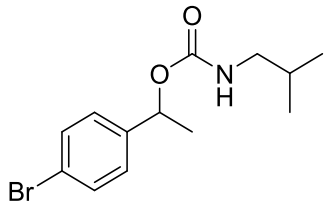
1-(4-Bromophenyl)ethyl benzyl(methyl)carbamate (**3af**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 2 H), 7.22 (m, 7 H), 5.82 (q, *J* = 6.5 Hz, 1 H), 4.54 – 4.38 (m, 2 H), 2.88 (s, 3 H), 1.50 – 1.54 (m, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.6, 141.5, 137.5, 131.6, 128.6, 127.7, 127.4, 127.2, 121.5, 72.8, 52.5, 52.4, 34.6, 33.6, 22.8 ppm. **HRMS (EI^+)** calc. for [$C_{17}H_{18}BrNO_2$]: 347.0521, found: 347.0518; pale yellow oil.



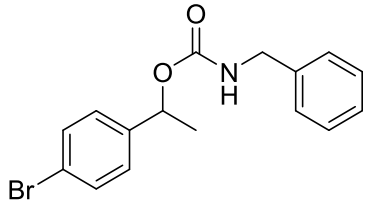
1-(4-Bromophenyl)ethyl cyclopentylcarbamate (**3ag**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 5.71 (q, *J* = 6.2 Hz, 1 H), 4.62 (brs, 1 H), 3.99 – 3.86 (m, 1 H), 1.92 (d, *J* = 6.5 Hz, 2 H), 1.68 – 1.60 (m, 2 H), 1.53 – 1.58 (m, 2 H), 1.47 (d, *J* = 6.3 Hz, 3 H), 1.42 – 1.29 (m, 2 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.3, 141.5, 131.6, 127.8, 121.6, 71.8, 52.8, 34.6, 33.3, 24.2, 23.6, 22.5 ppm. **HRMS (EI^+)** calc. for [$C_{14}H_{18}BrNO_2$]: 311.0521, found: 311.0522; m.p. = 86 °C; white solid



1-(4-Bromophenyl)ethyl butylcarbamate (**3ah**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 5.72 (q, *J* =6.3 Hz, 1 H), 4.86 (brs, 1 H), 3.22 – 3.04 (m, 2 H), 1.53 – 1.39 (m, 5 H), 1.35 – 1.25 (m, 2 H), 0.89 (t, *J* = 7.3 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.8, 141.4, 131.5, 127.7, 121.5, 71.8, 40.7, 32.0, 22.4, 19.9, 13.7 ppm. **HRMS (EI^+)** calc. for [$C_{13}H_{18}BrNO_2$]: 299.0521, found: 299.0521; pale yellow oil.



1-(4-Bromophenyl)ethyl isobutylcarbamate (**3ai**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 5.72 (q, *J* = 6.5 Hz, 1 H), 4.93 (brs, 1 H), 3.02 – 2.89 (m, 2 H), 1.66 – 1.74 (m, 1 H), 1.47 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.7 Hz, 6 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.9, 141.4, 131.5, 127.7, 121.4, 71.8, 48.4, 28.7, 22.3, 19.9 ppm. **HRMS (EI^+)** calcfor [$C_{13}H_{18}BrNO_2$]: 299.0521, found: 299.0522; yellow oil.

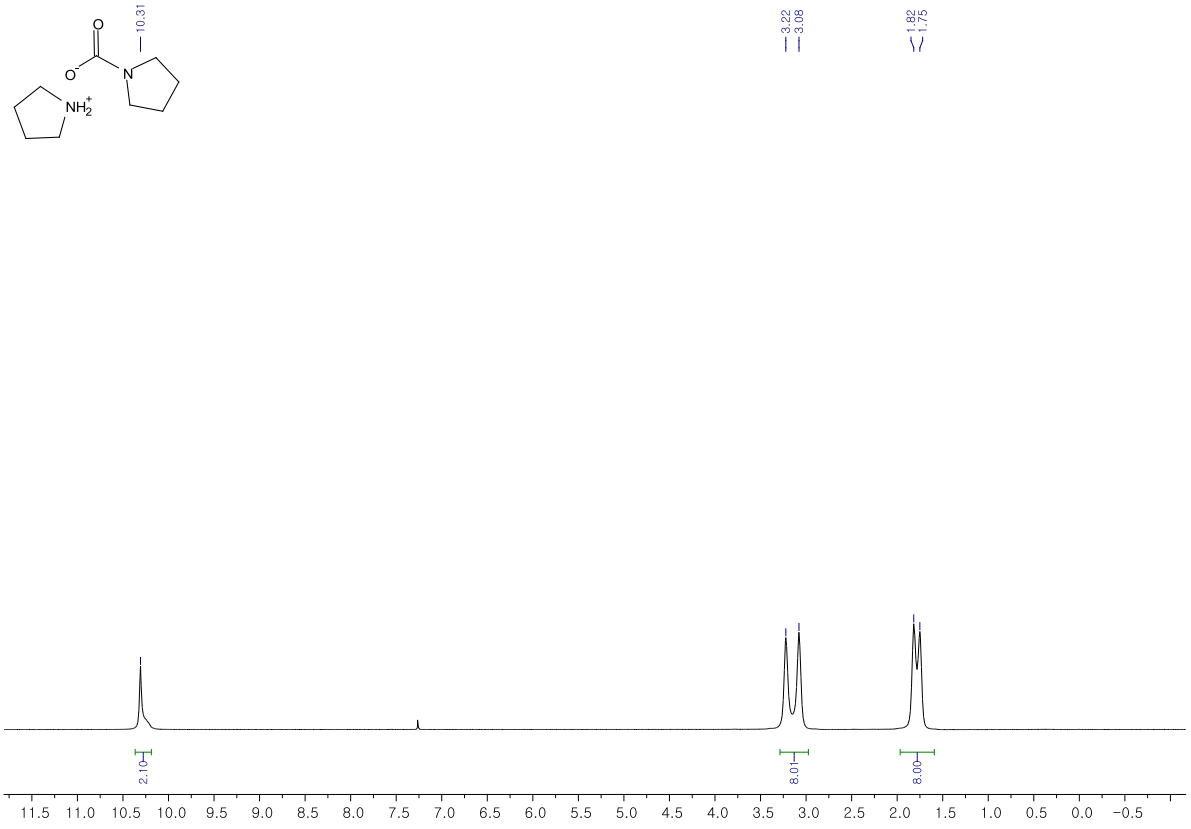


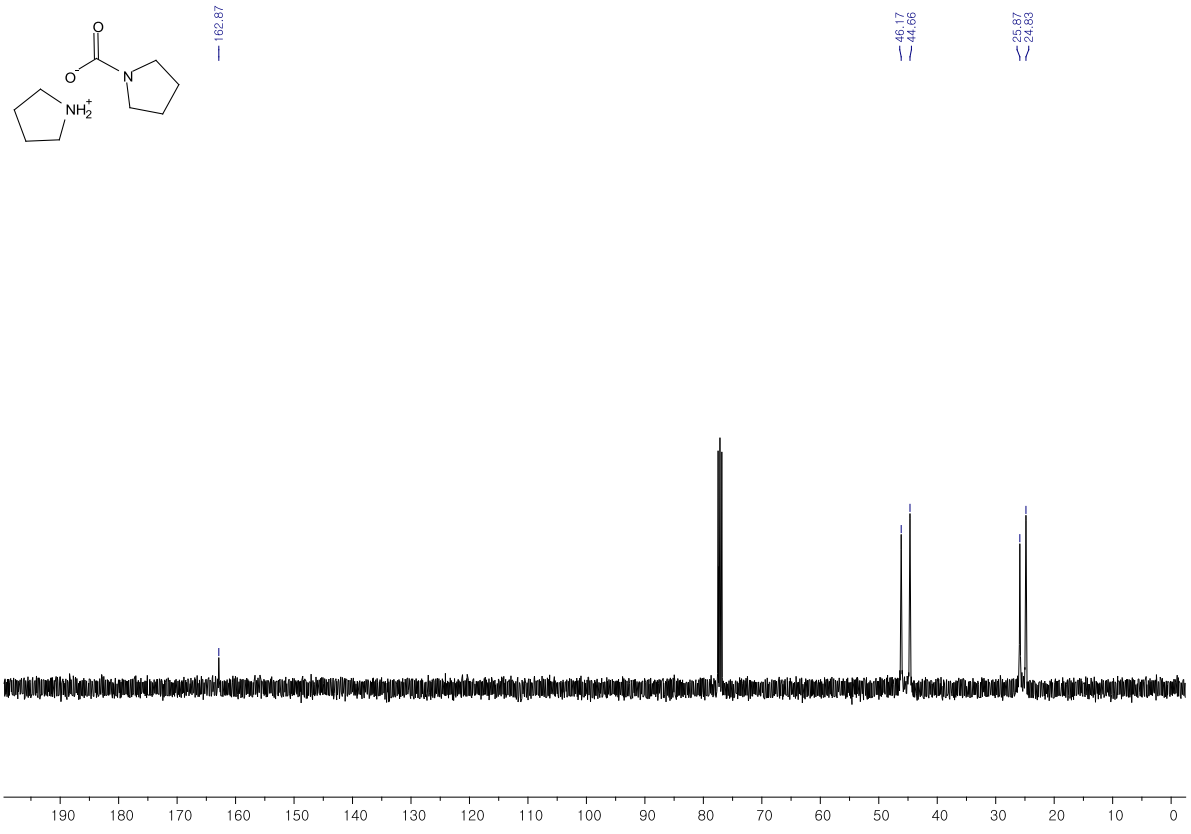
1-(4-Bromophenyl)ethyl benzylcarbamate (**3aj**):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 2 H), 7.20 (m, 7 H), 5.69 (q, *J* = 6.6 Hz, 1 H), 5.06 (brs, 1 H), 4.31 – 4.20 (m, 2 H), 1.43 (d, *J* = 6.5 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.8, 141.3, 138.4, 131.6, 128.7, 127.8, 127.5, 121.6, 72.3, 45.1, 22.4 ppm. **HRMS (EI^+)** calc. for [$C_{16}H_{16}BrNO_2$]: 333.0364, found: 333.0363; m.p. = 103 °C; white solid.

F. References

1. W. Xiong, C. Qi, H. He, L. Ouyang, M. Zhang, H. Jiang, *Angew. Chem., Int. Ed.* **2015**, 54, 3084.
2. (a)T. Horibe, N. Mase, *Org. Lett*, **2013**, 15, 1854. (b) Q-W Song, Z-H Zhou, H. Yin, L-N He, *ChemSusChem*, **2015**, 8, 3967.

G. NMR Spectra





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O
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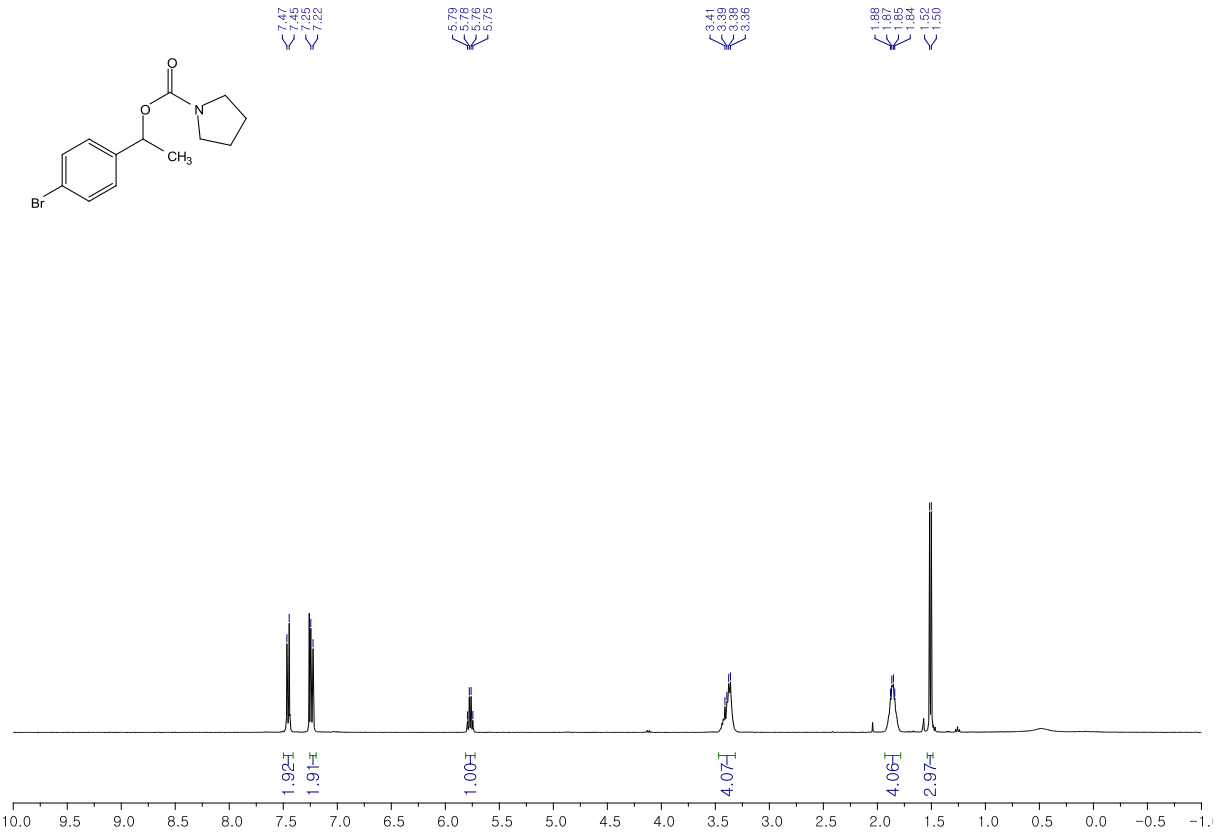
CH3
Br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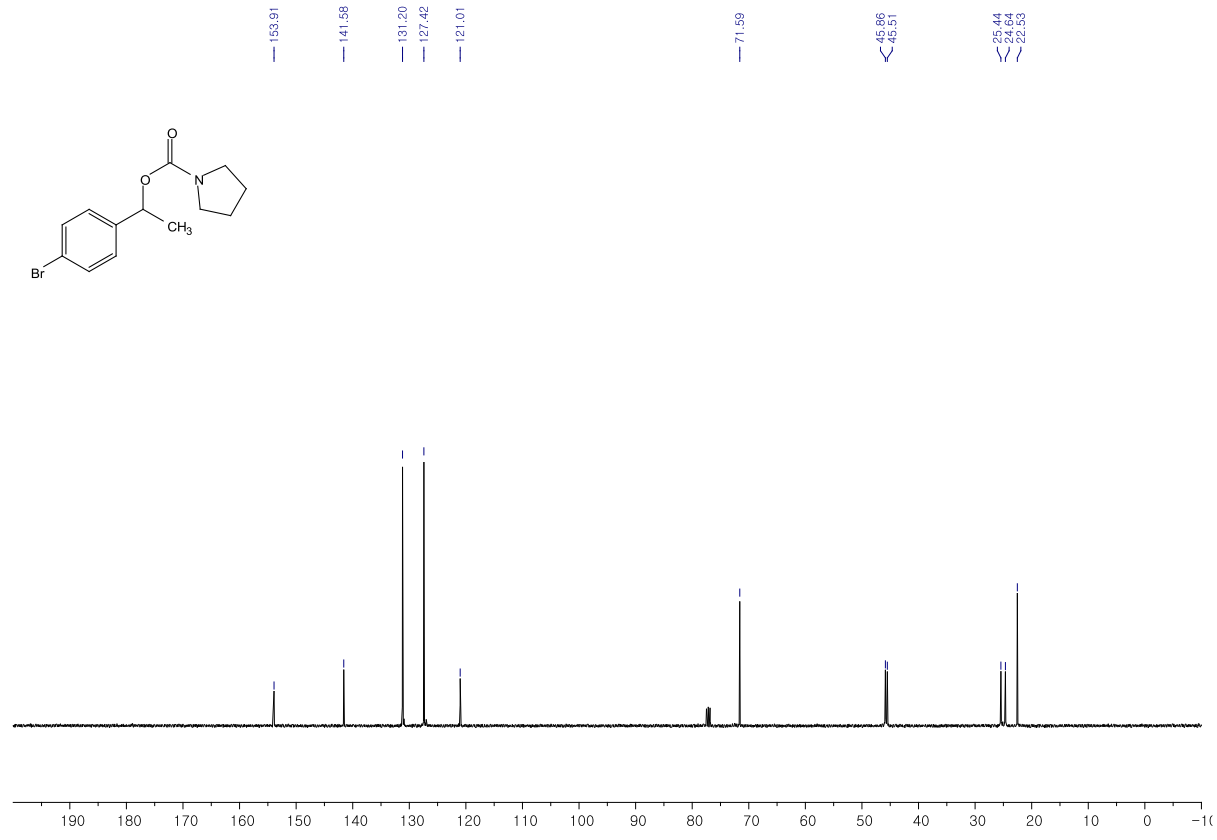
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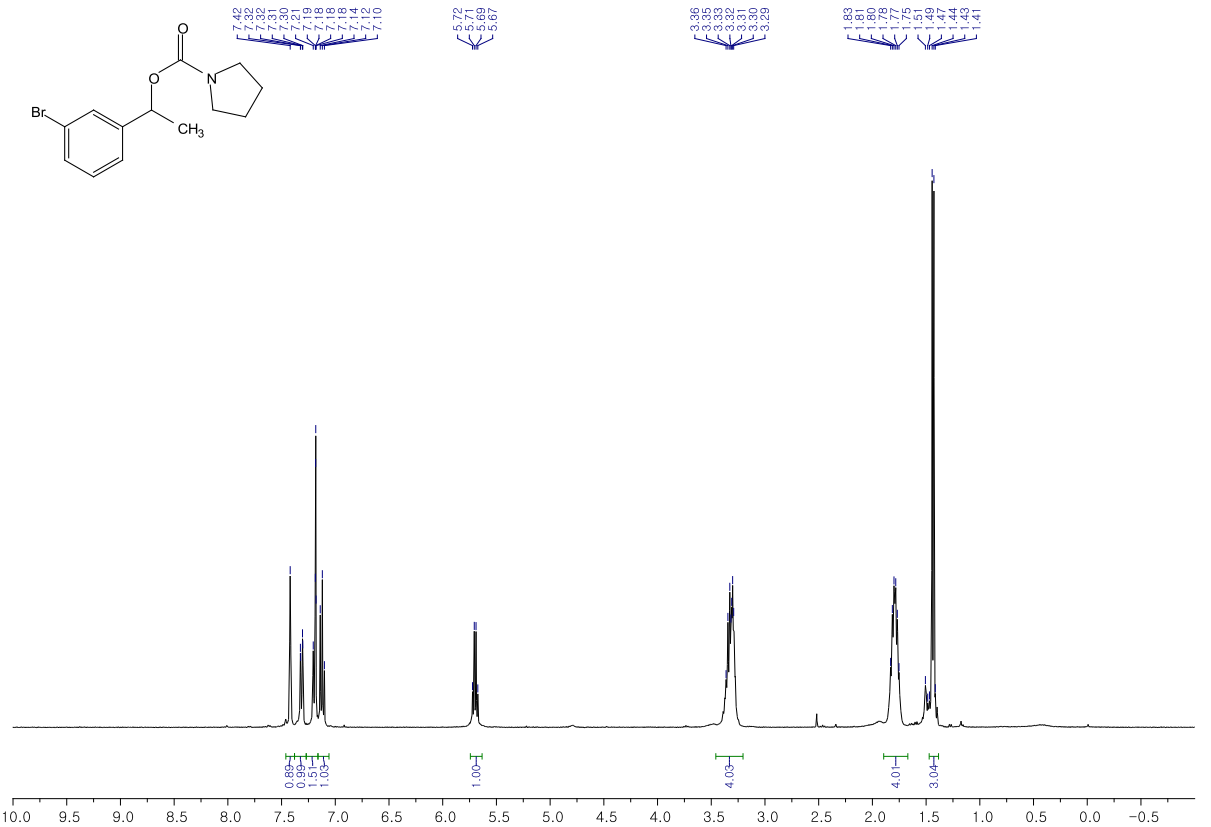
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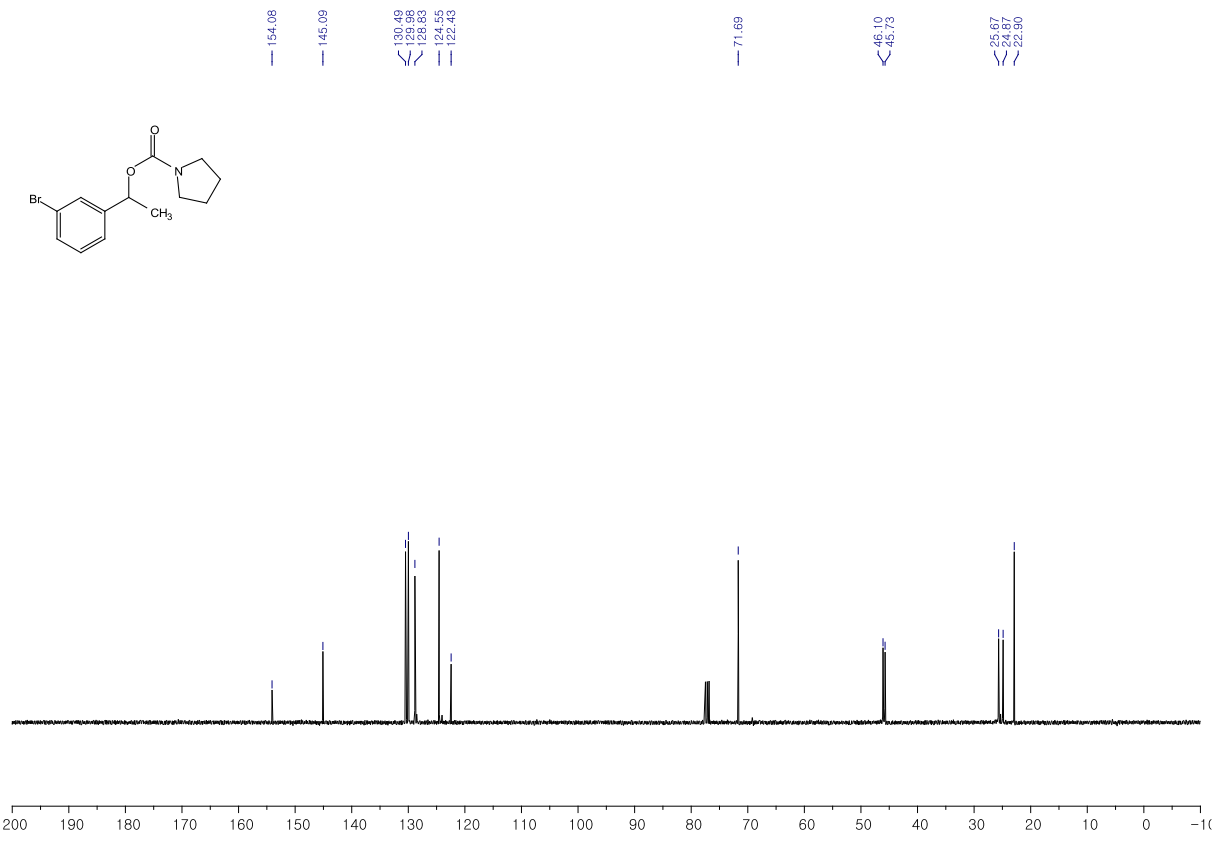
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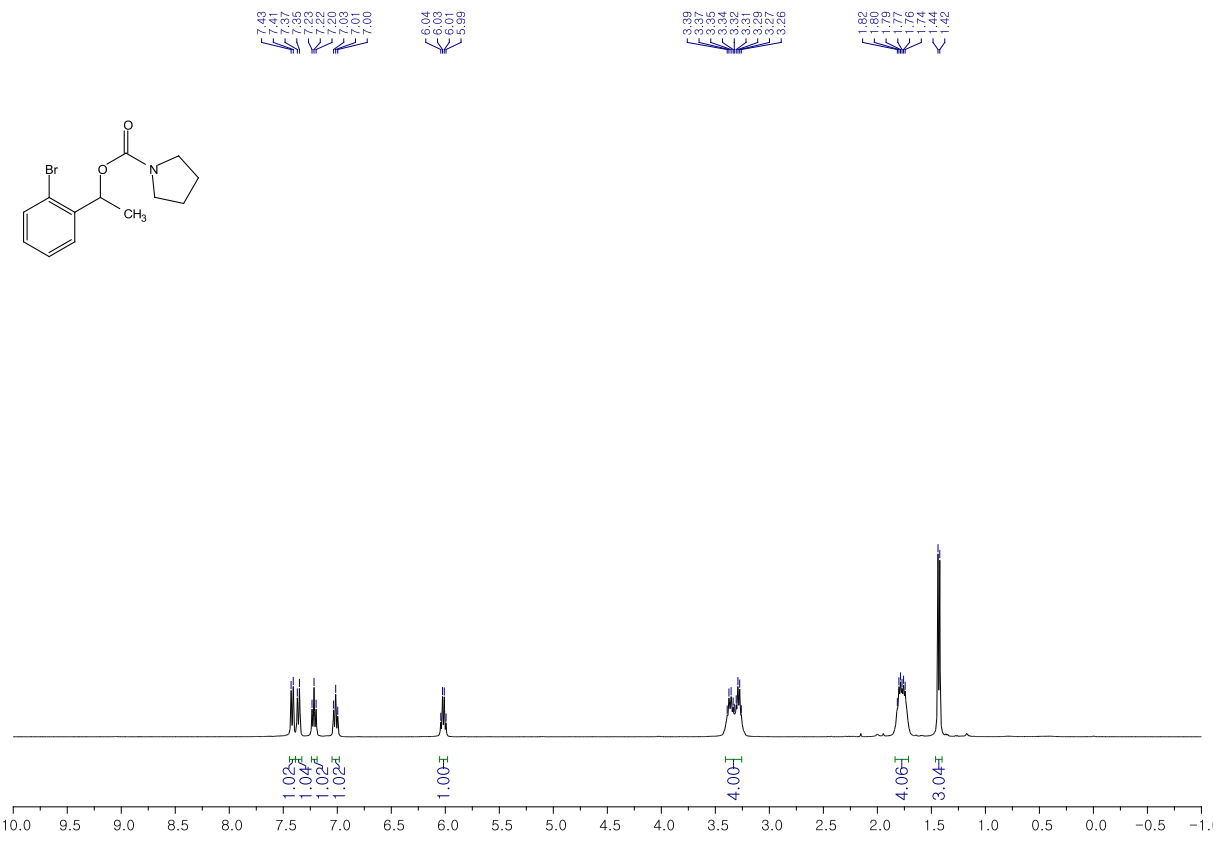
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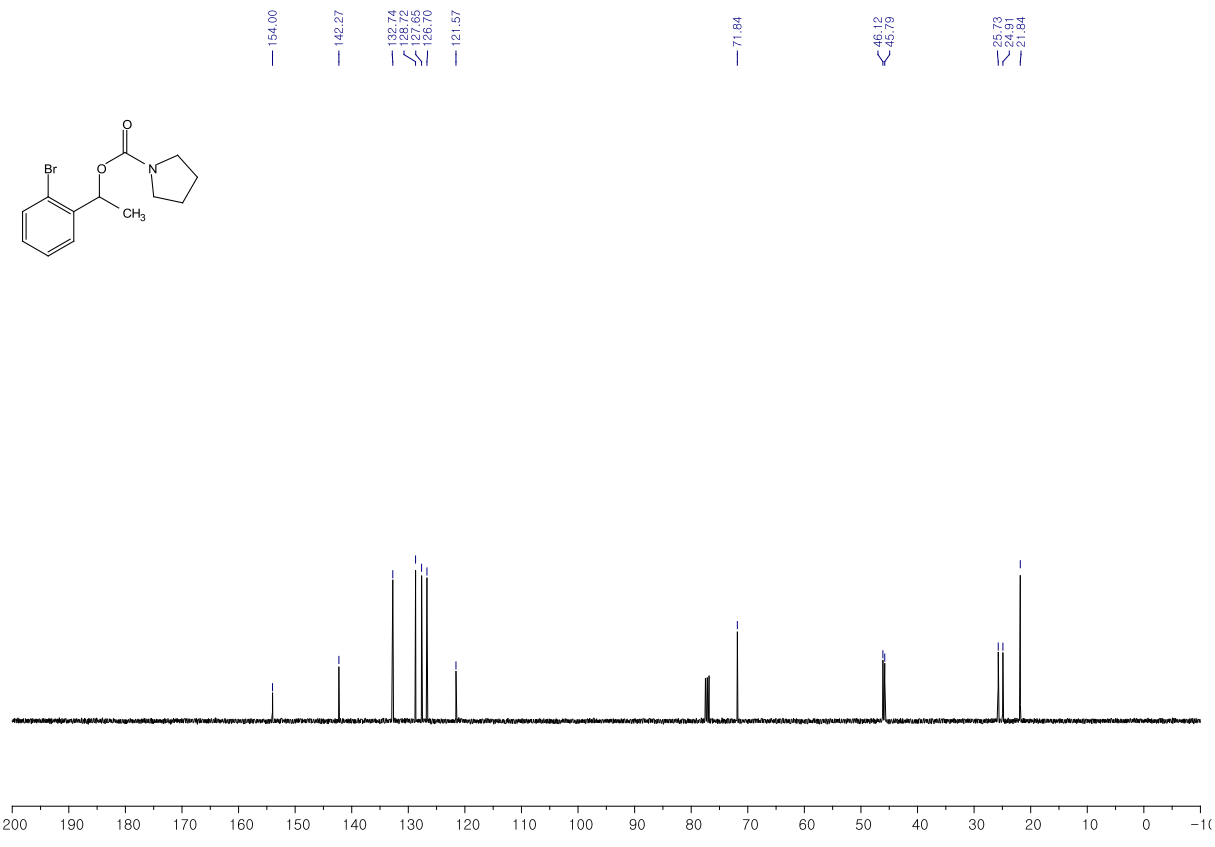
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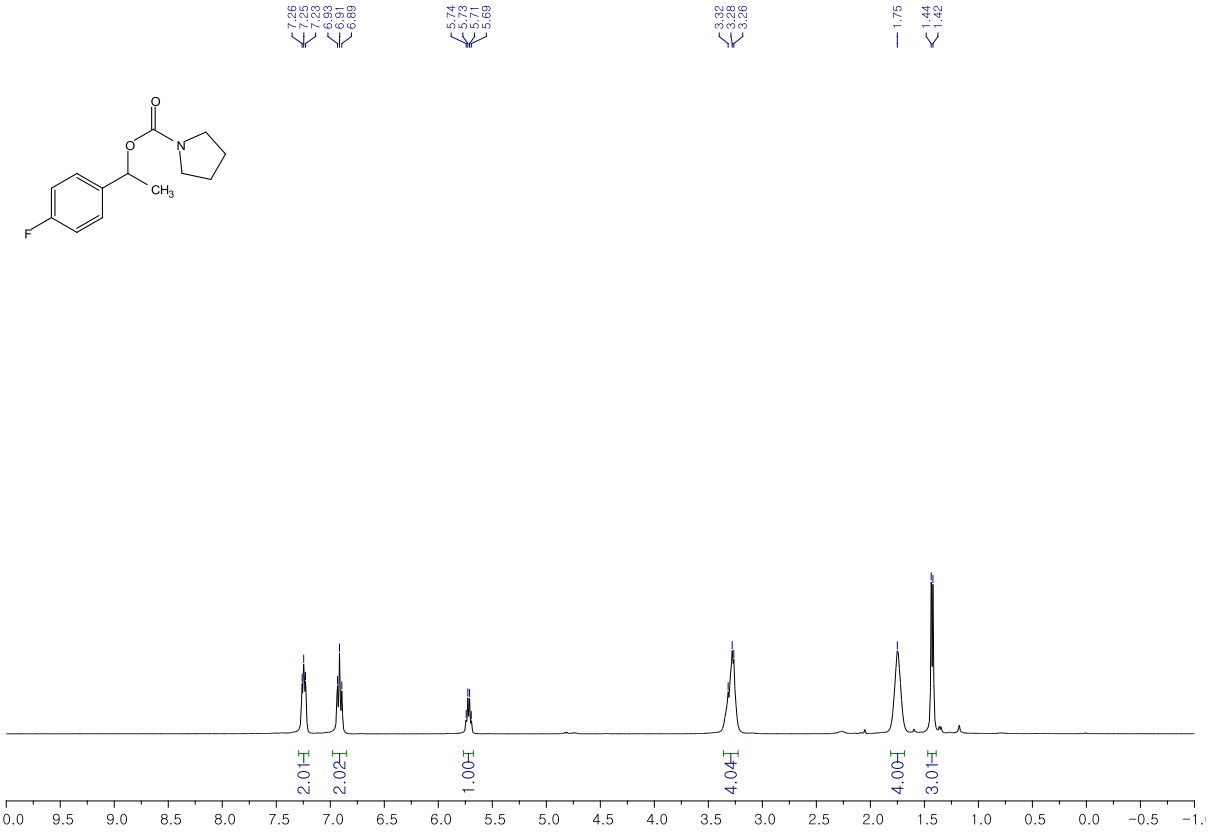
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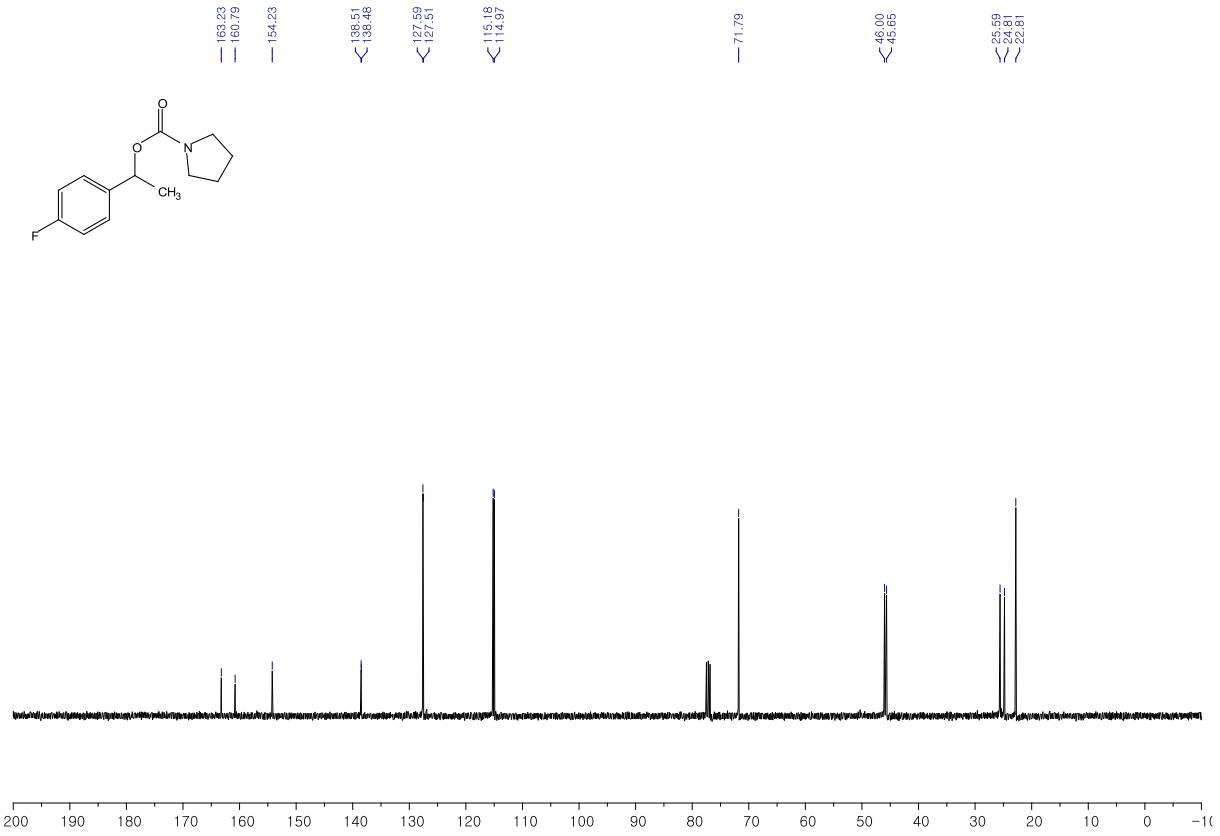
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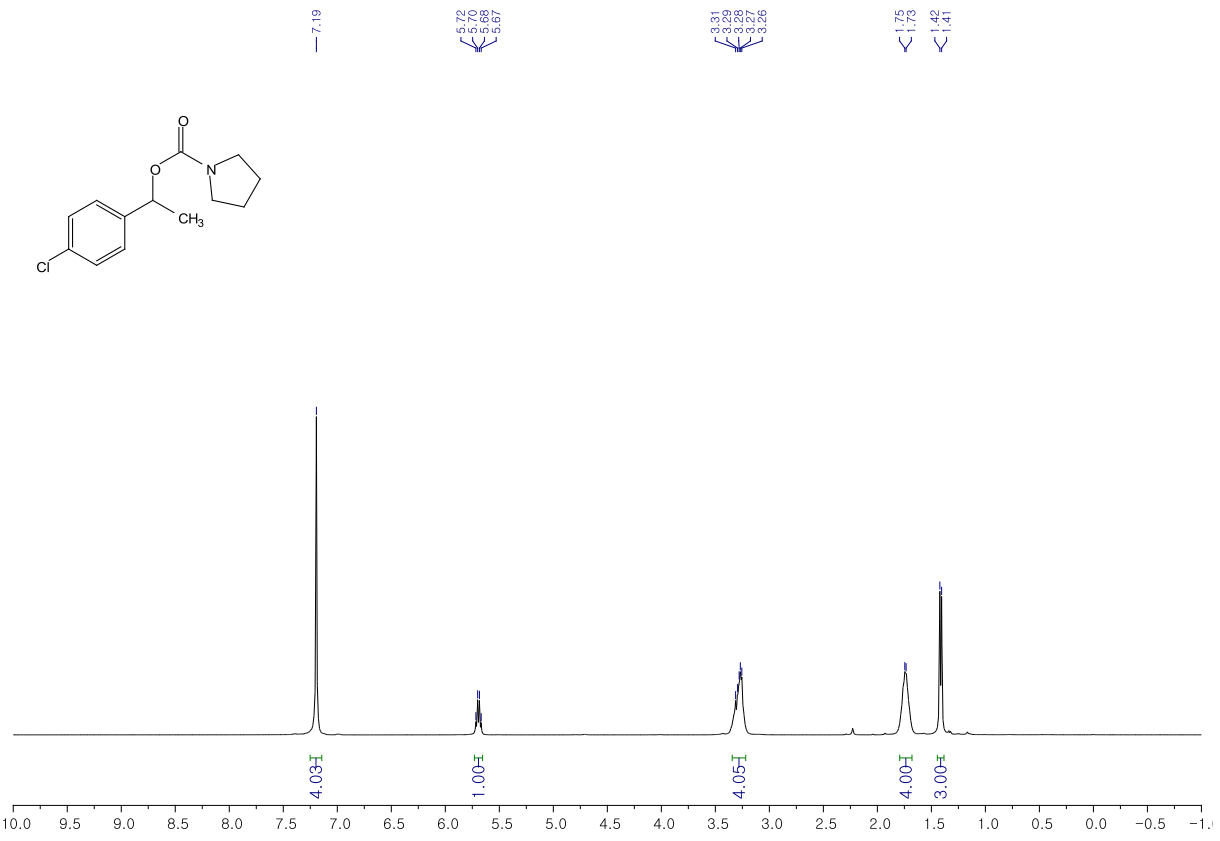
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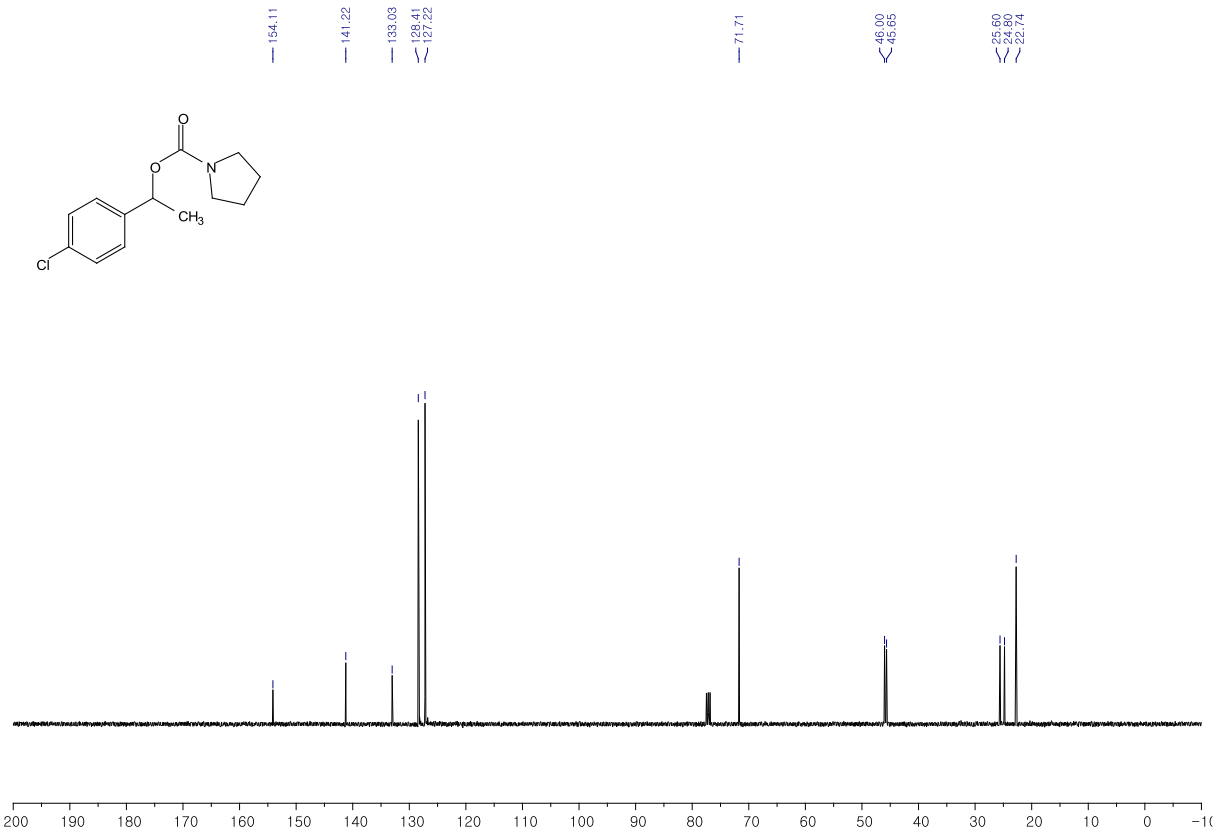
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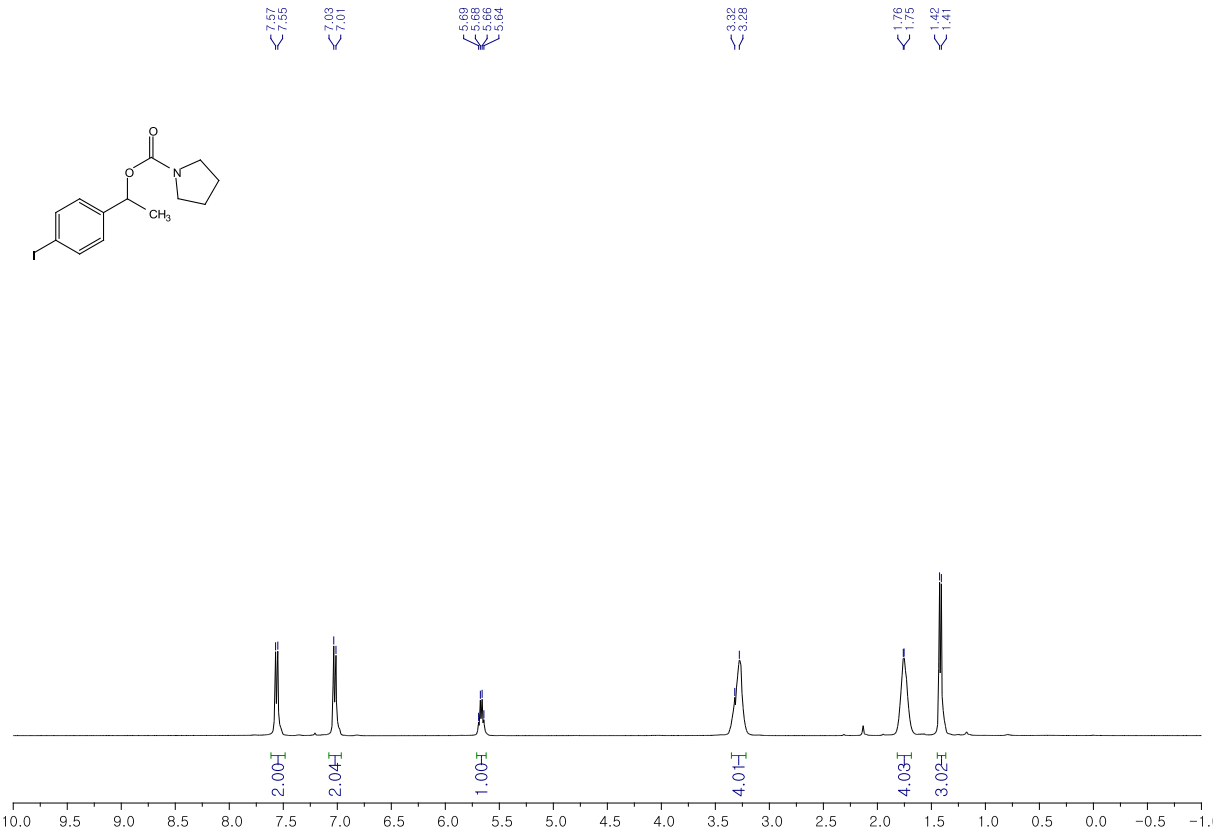
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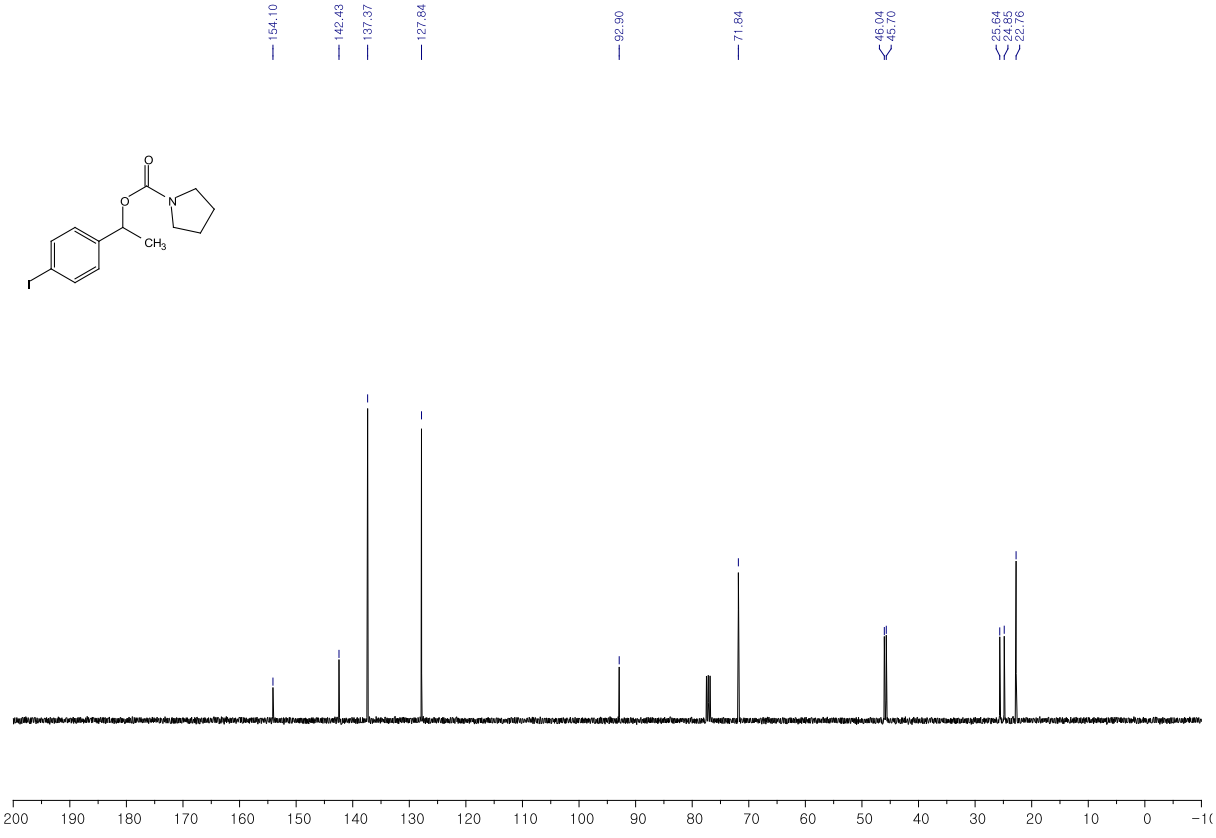
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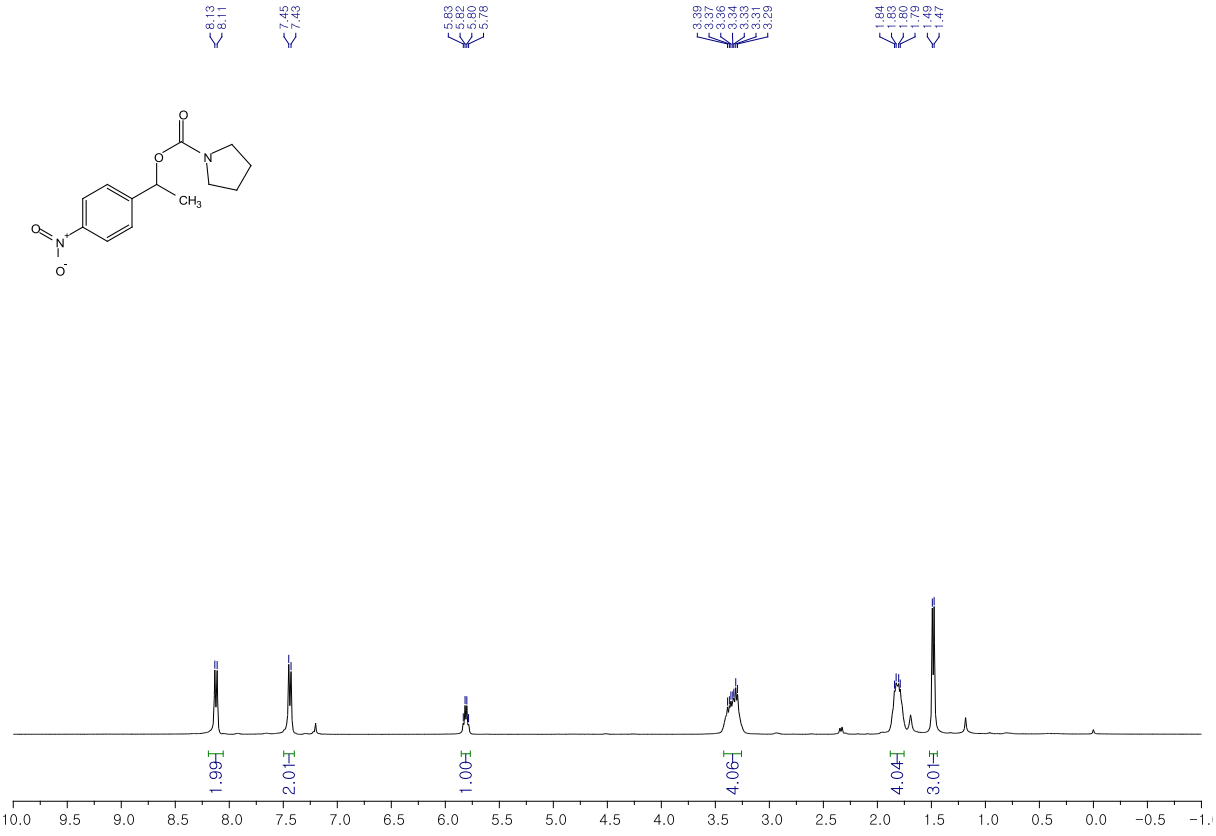
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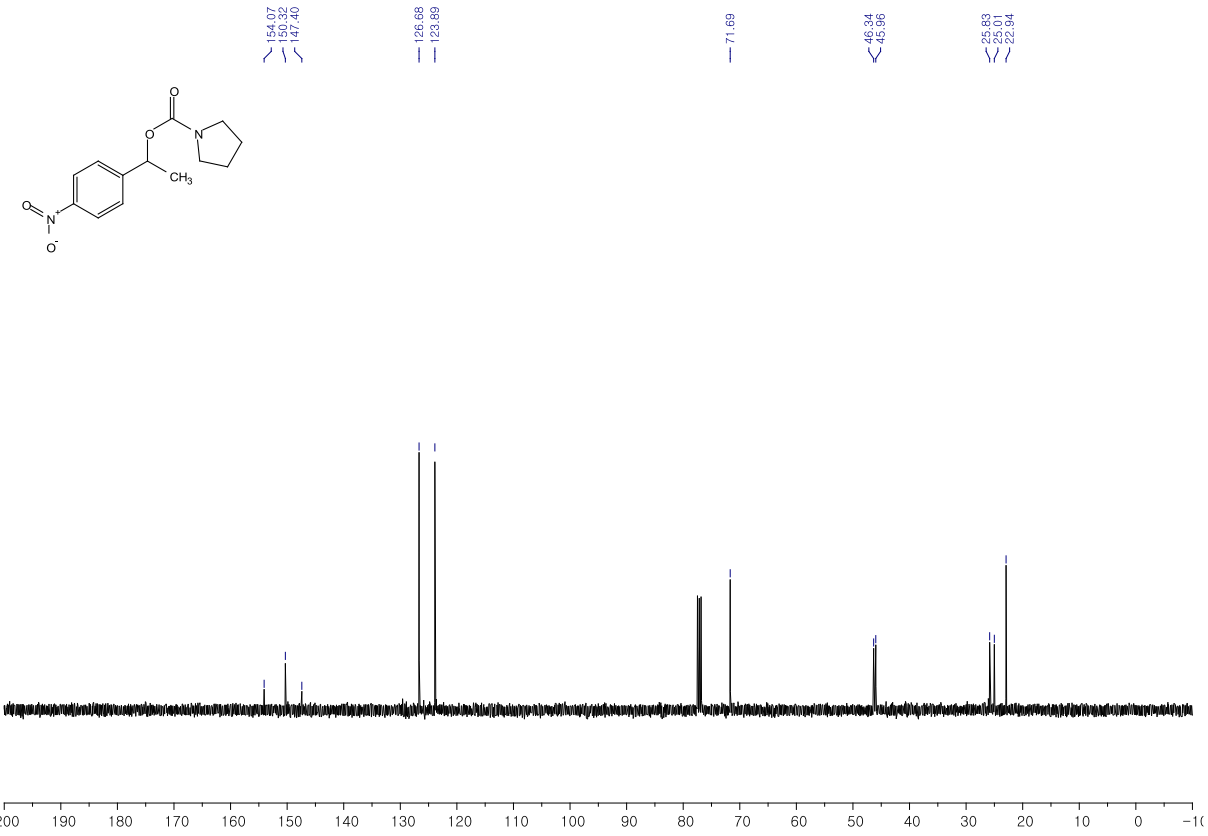
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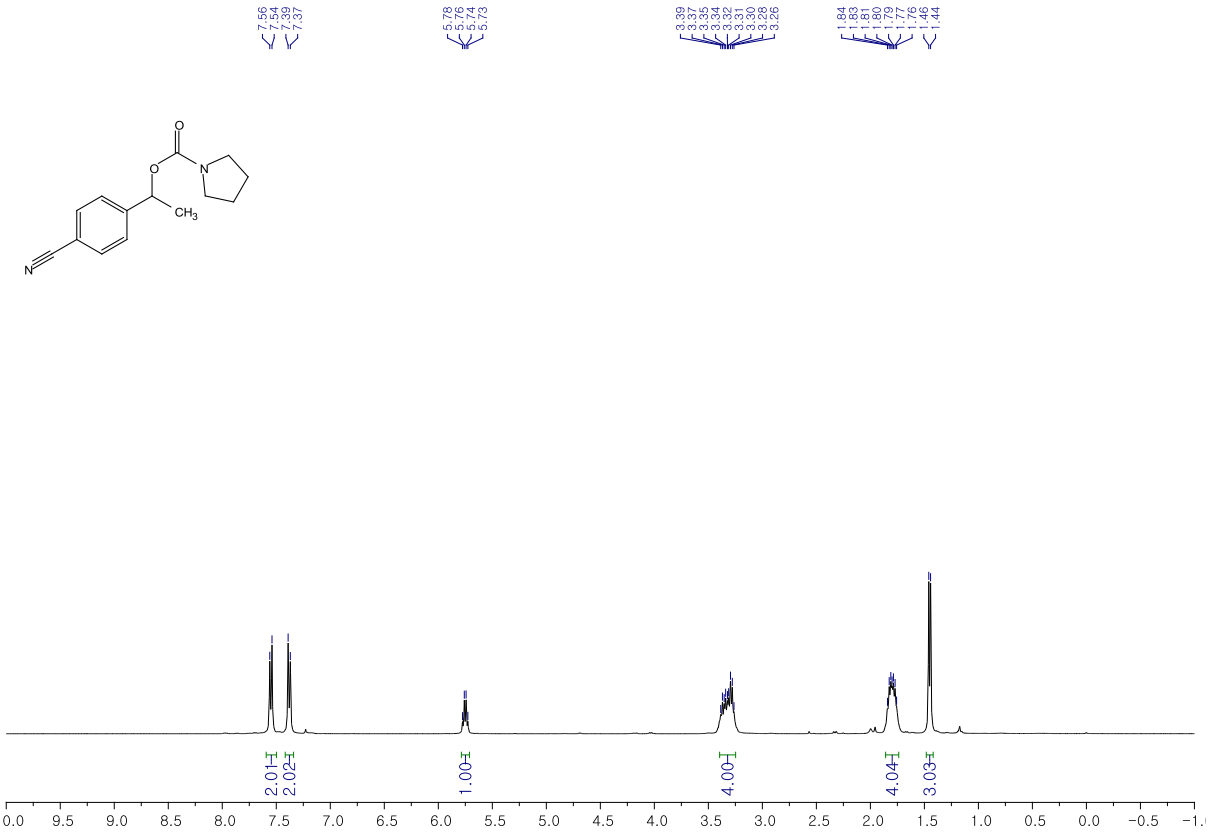
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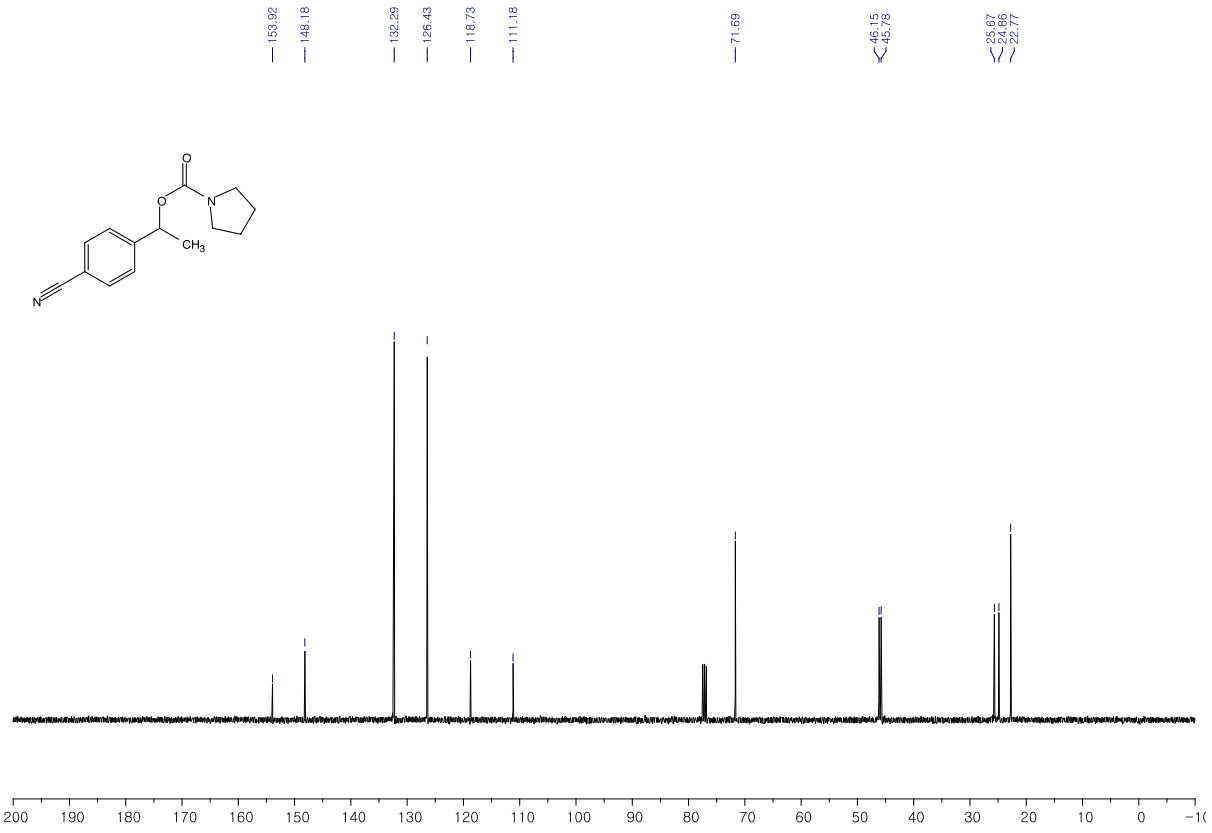
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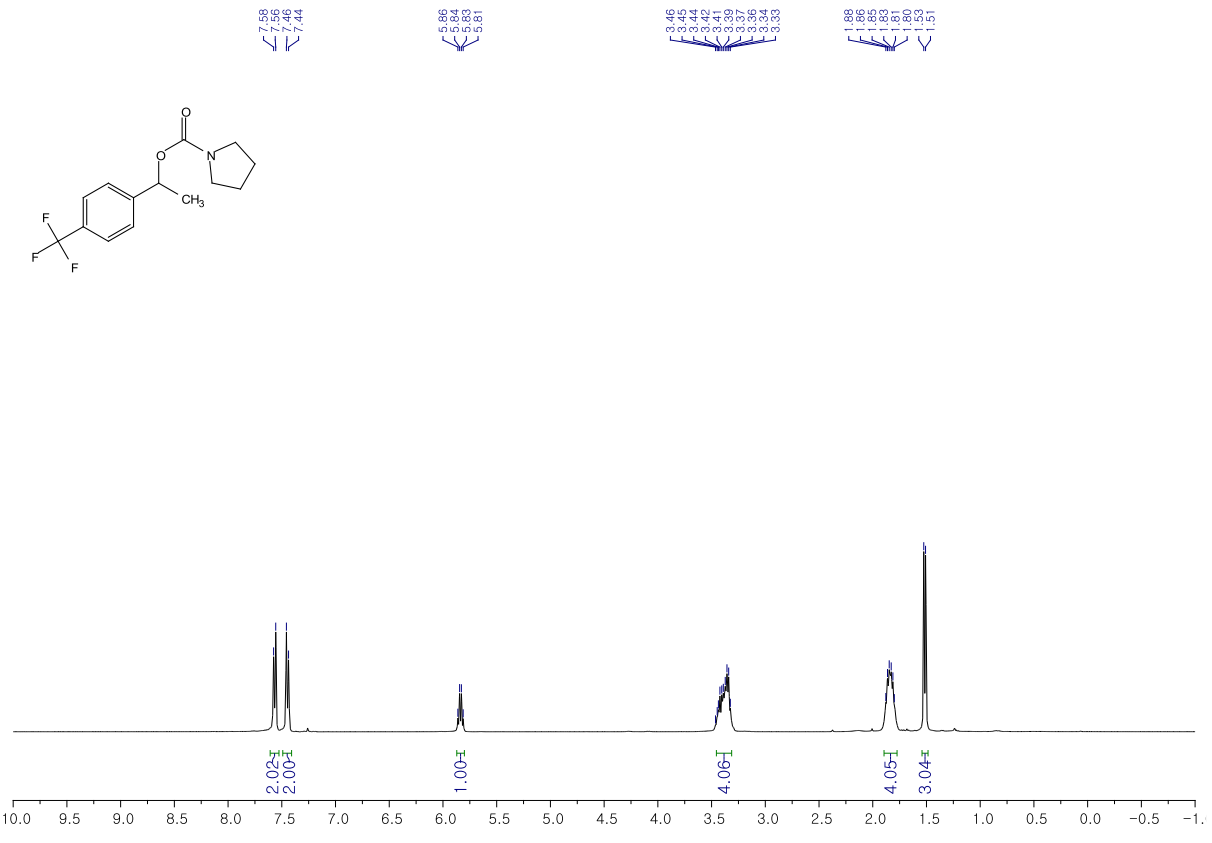
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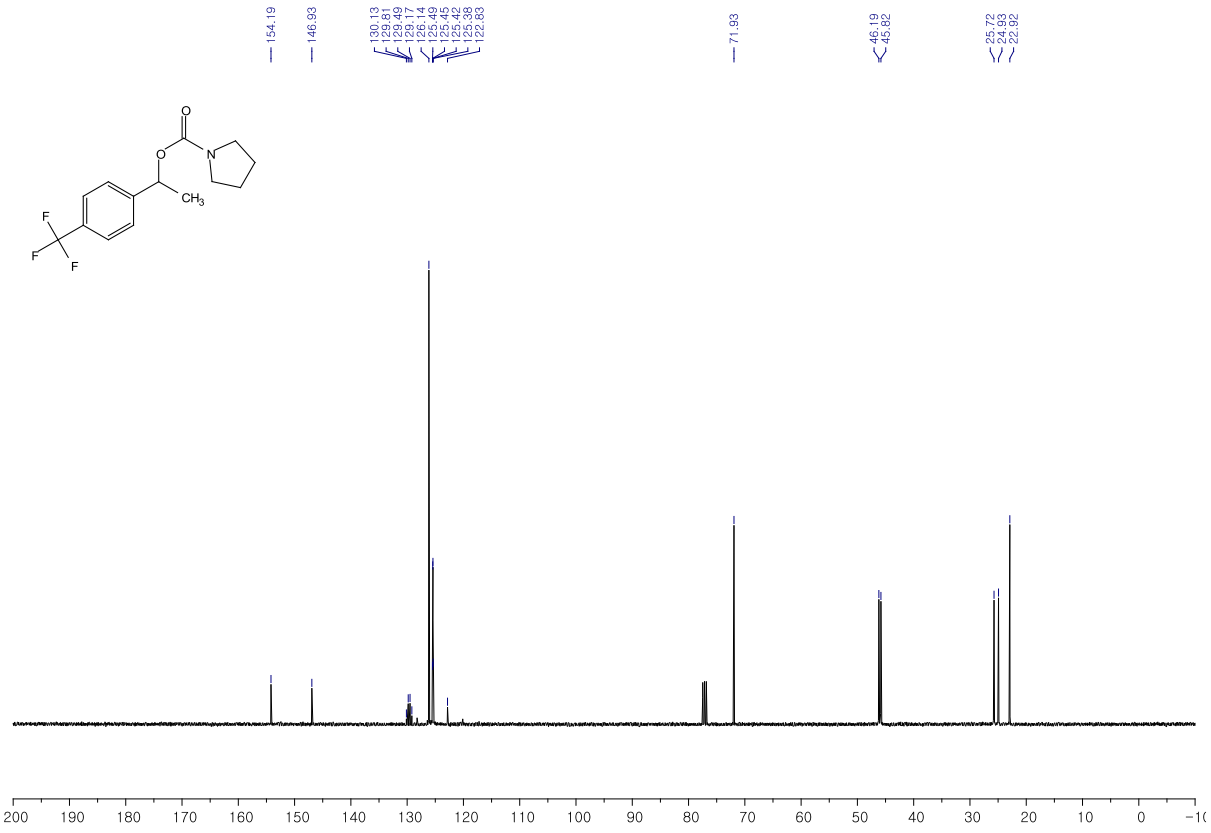
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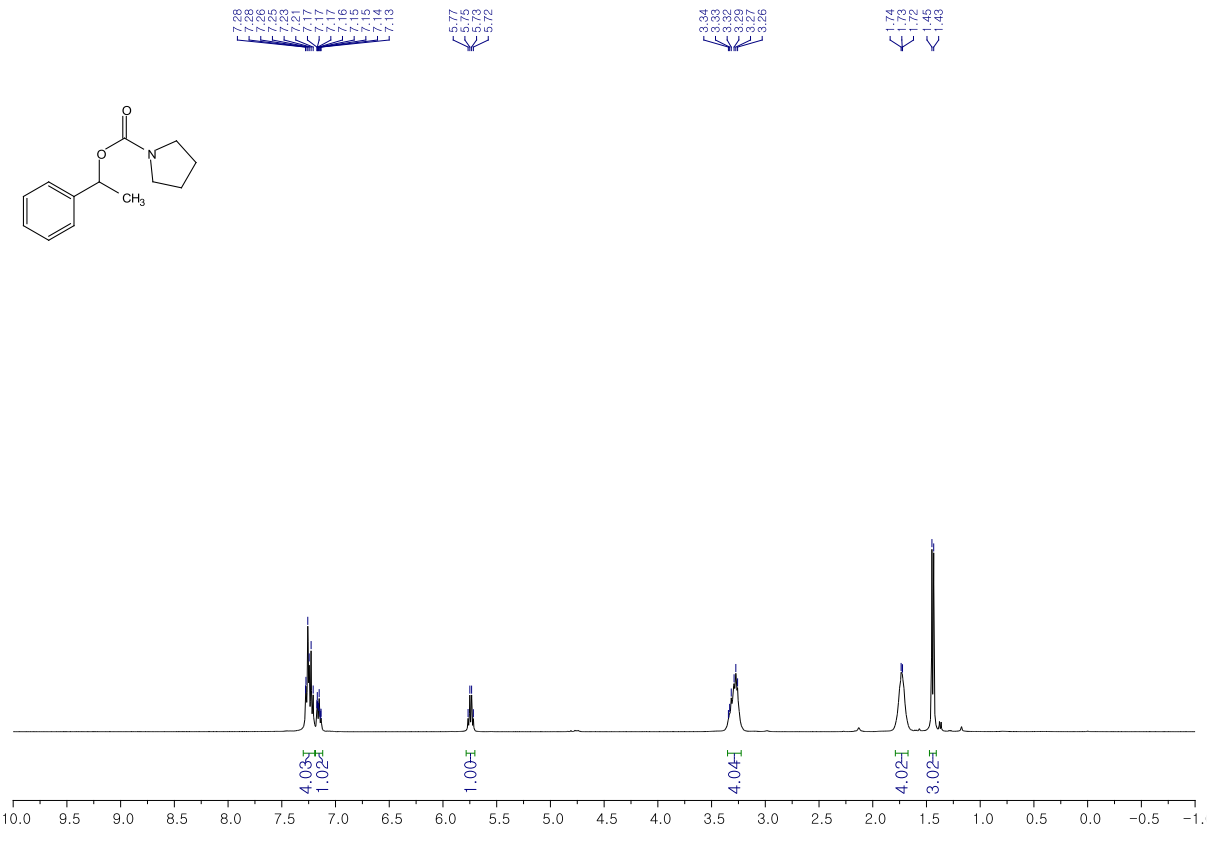
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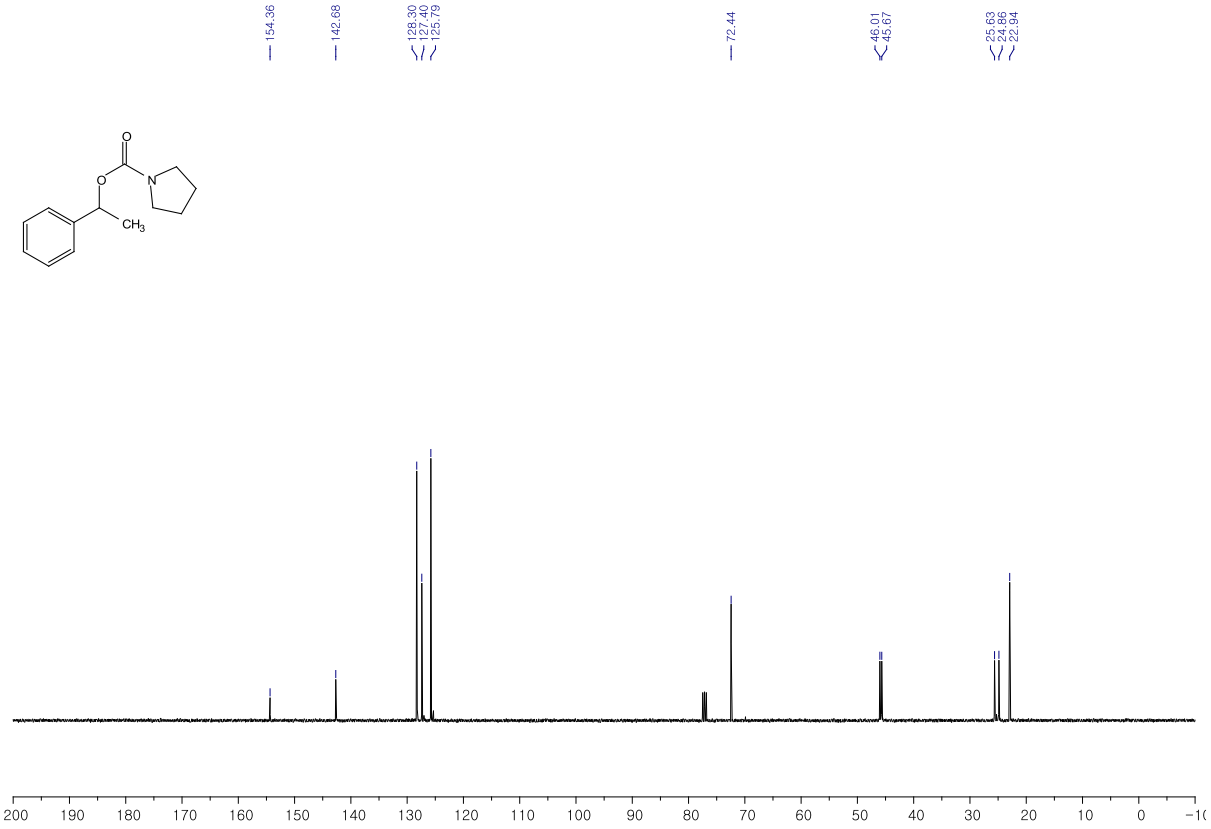
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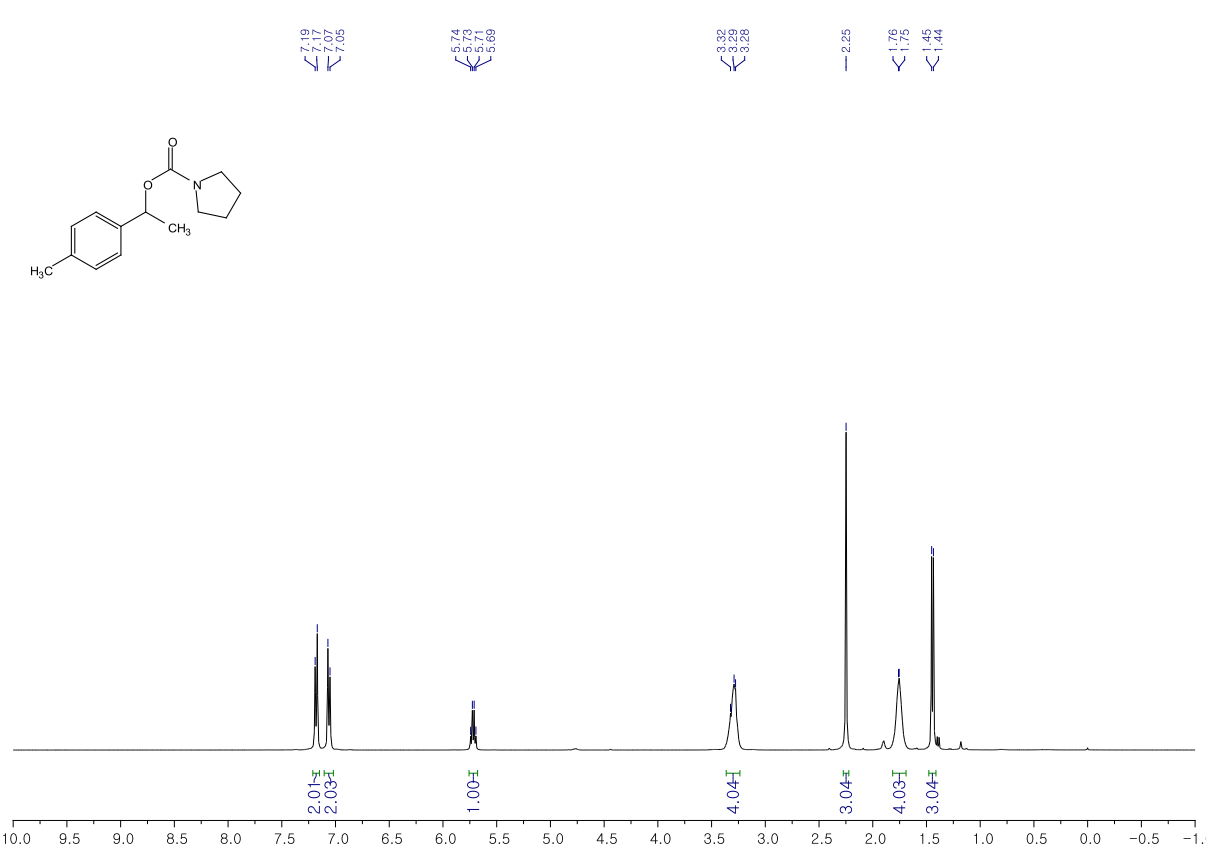
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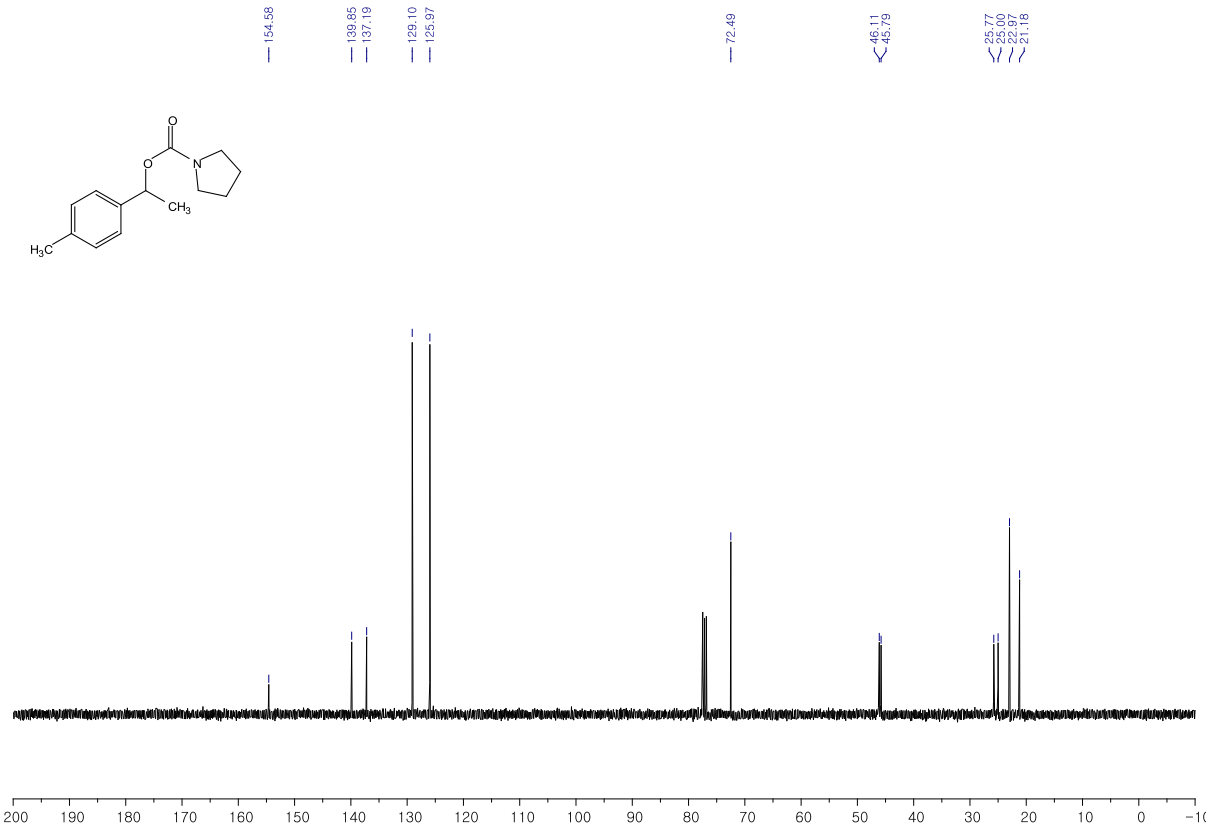
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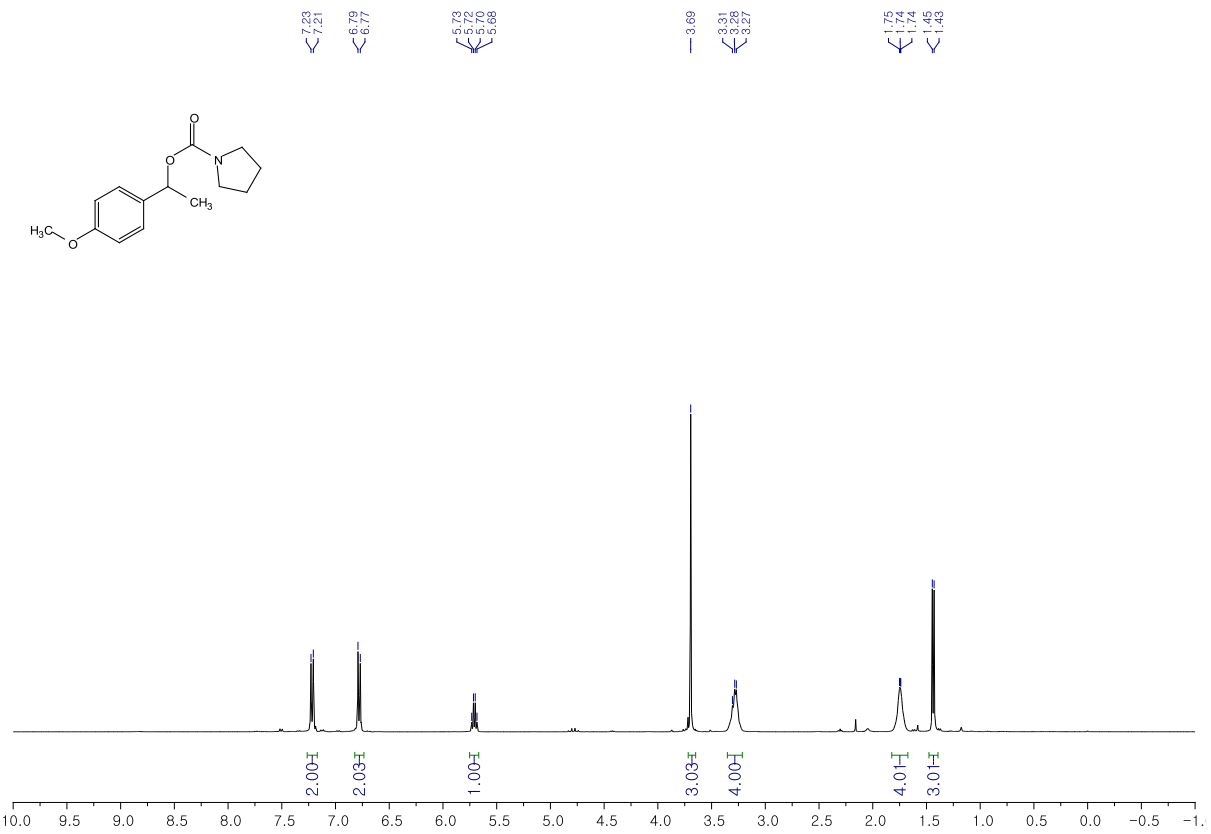
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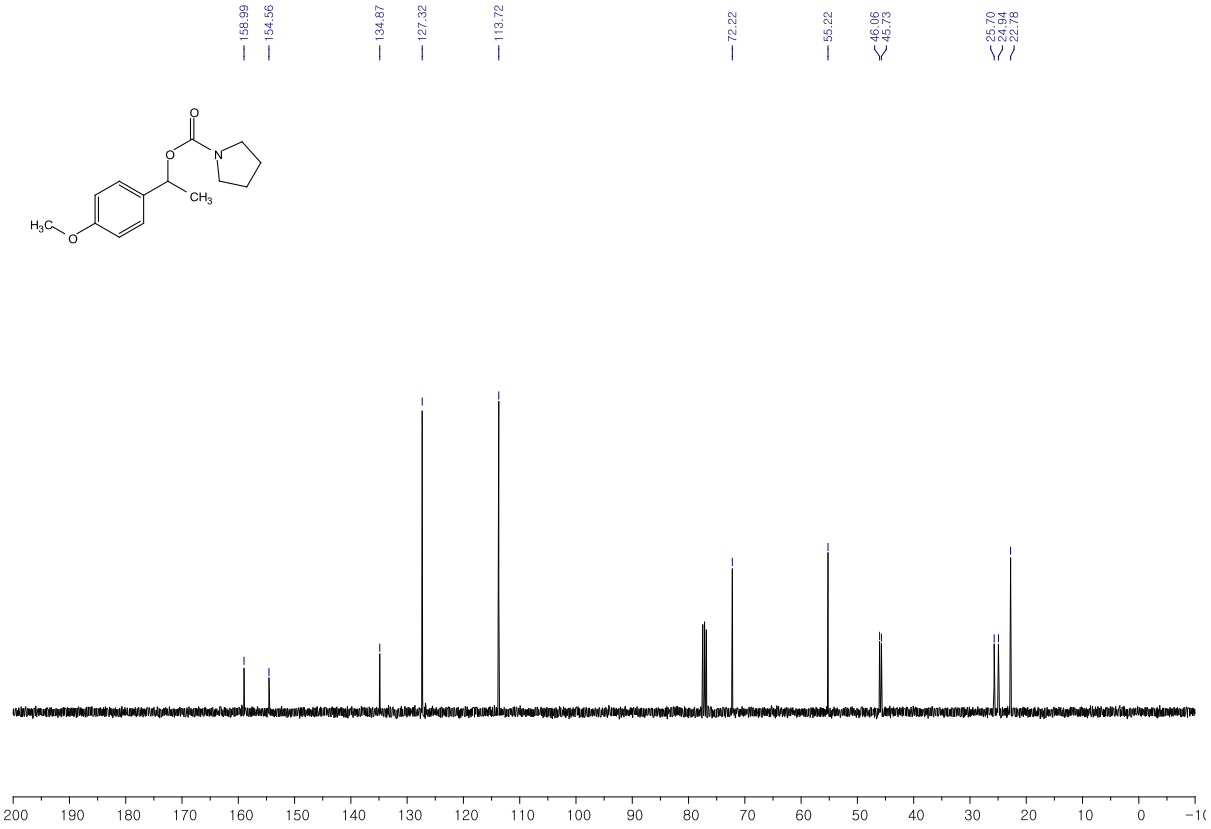
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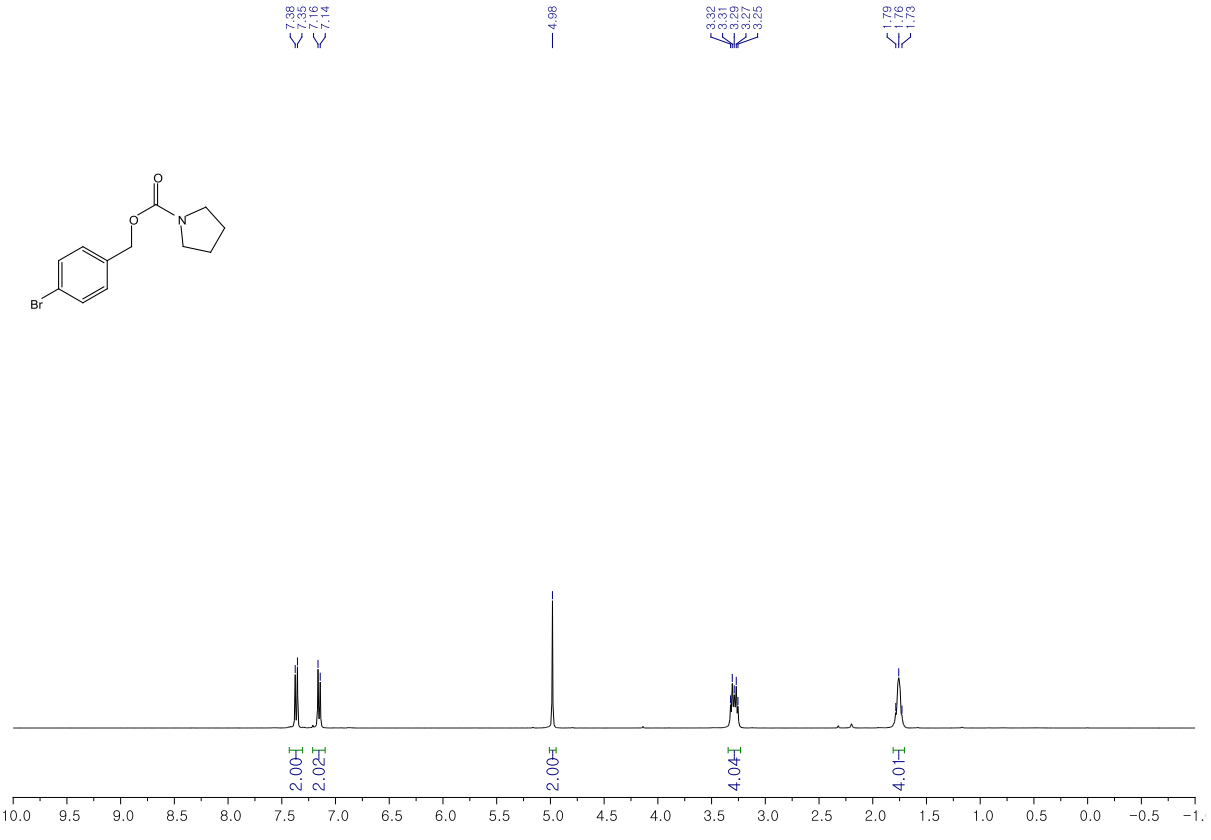
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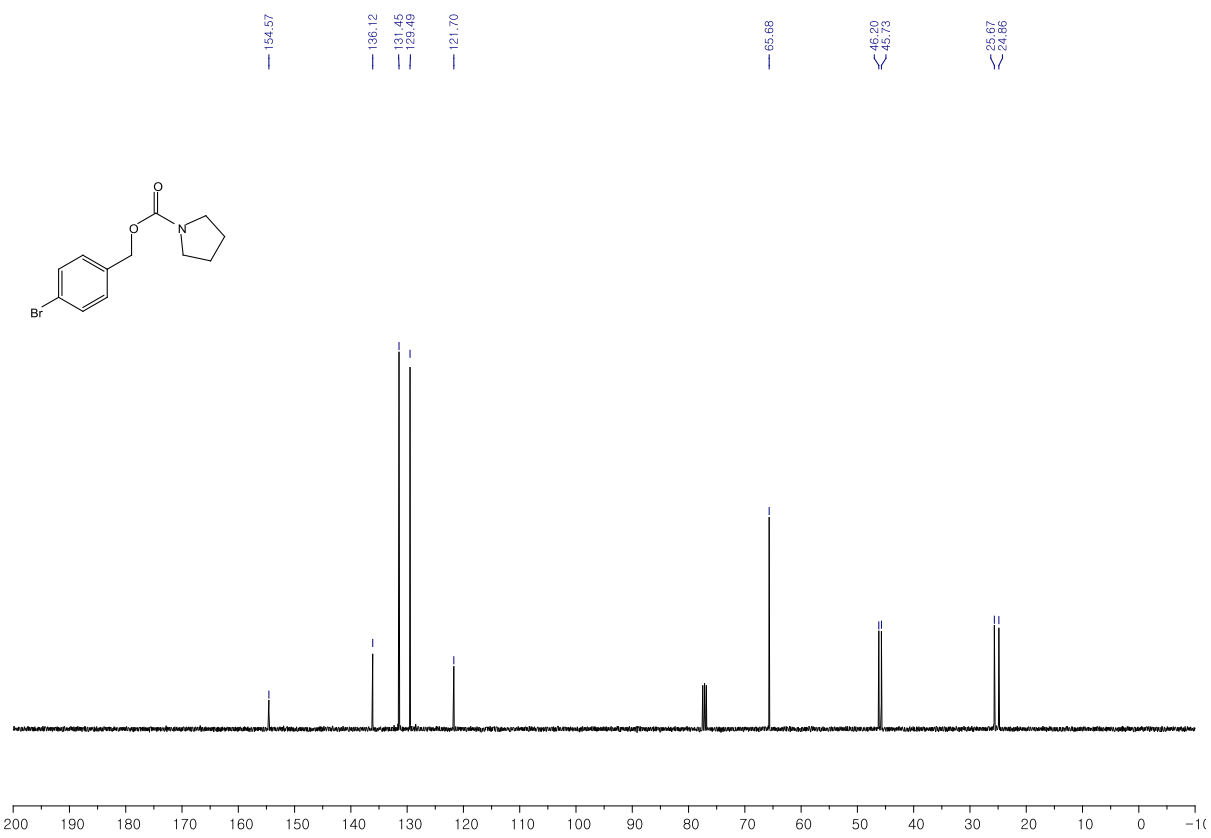
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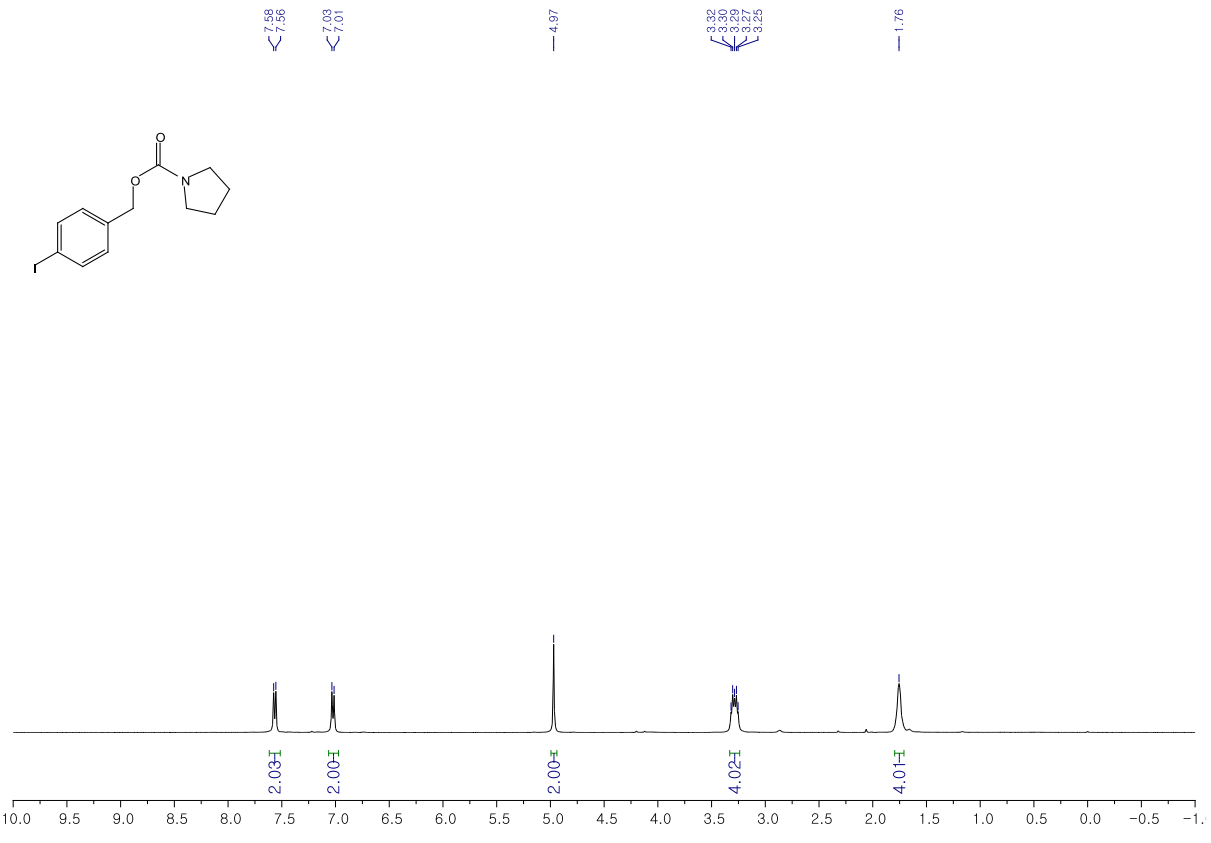
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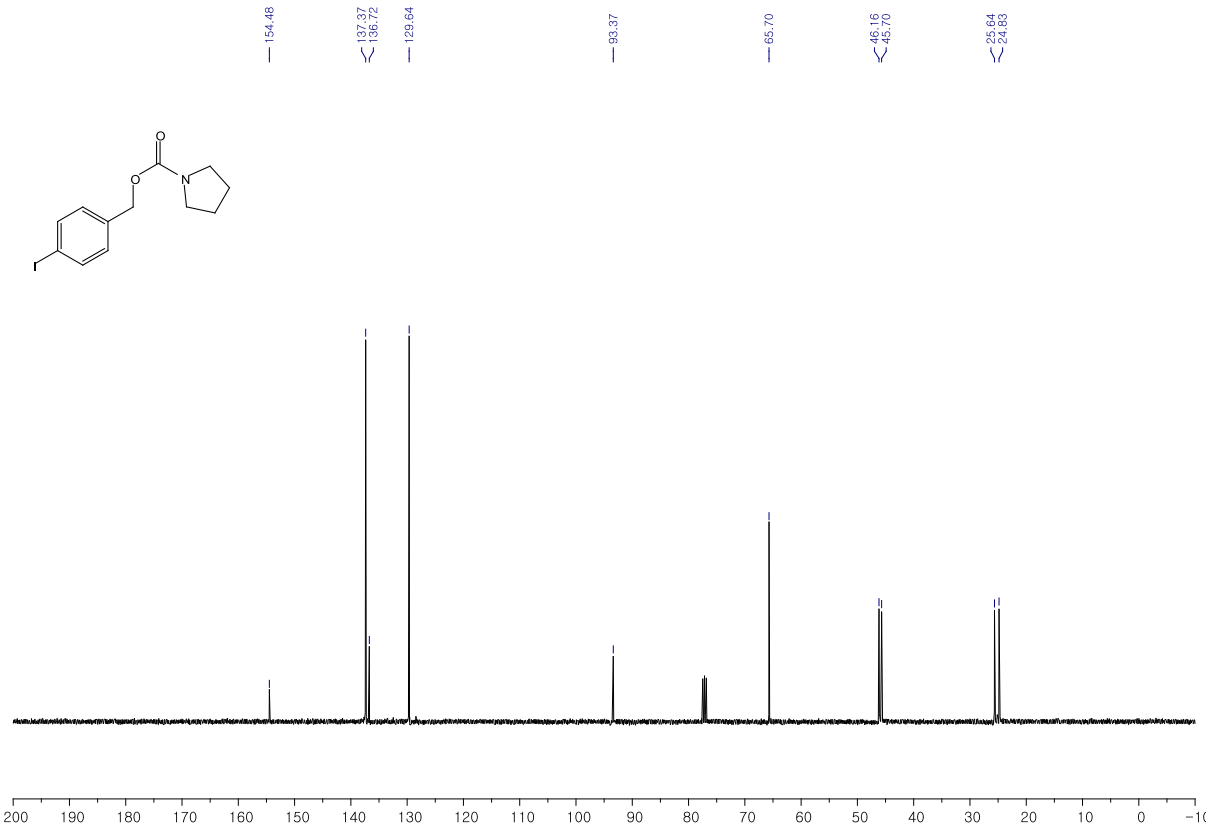
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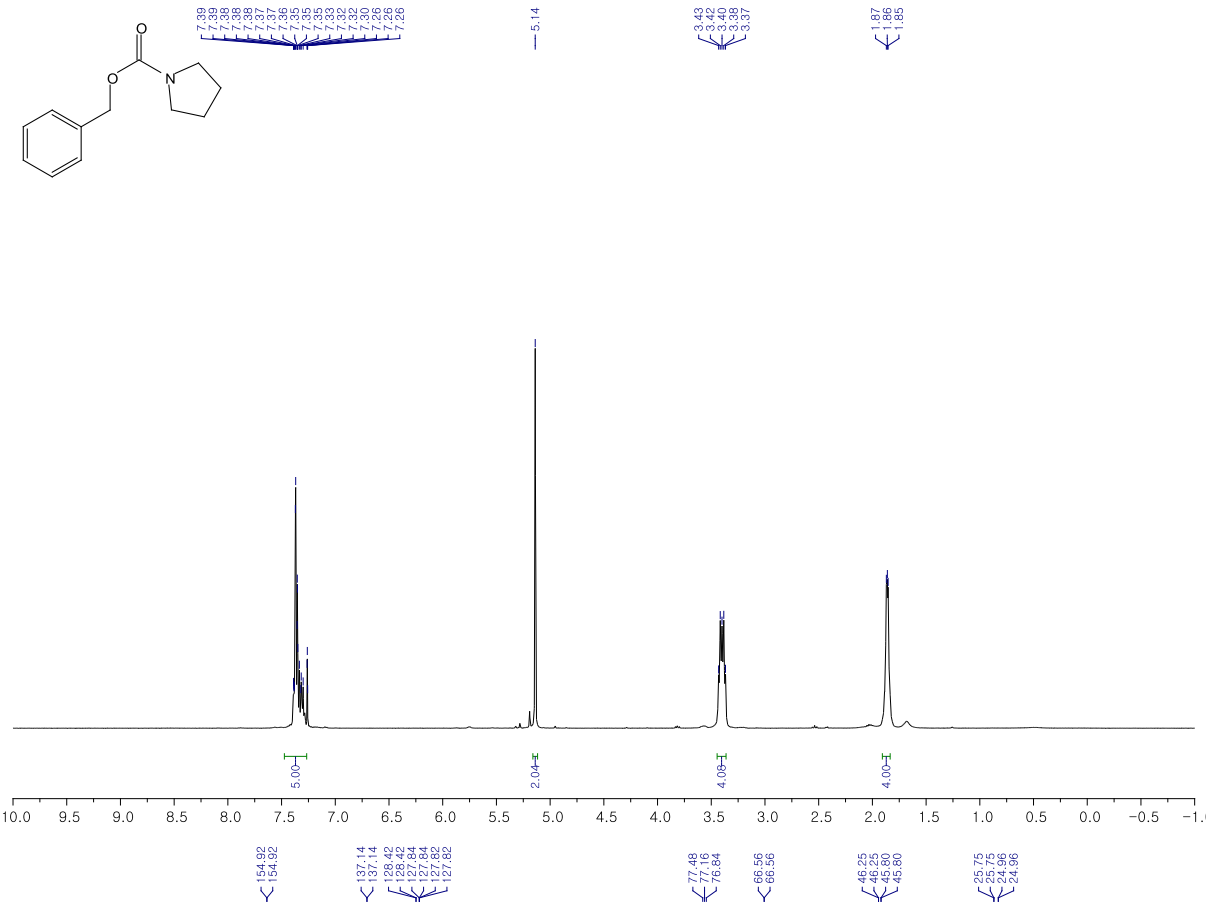
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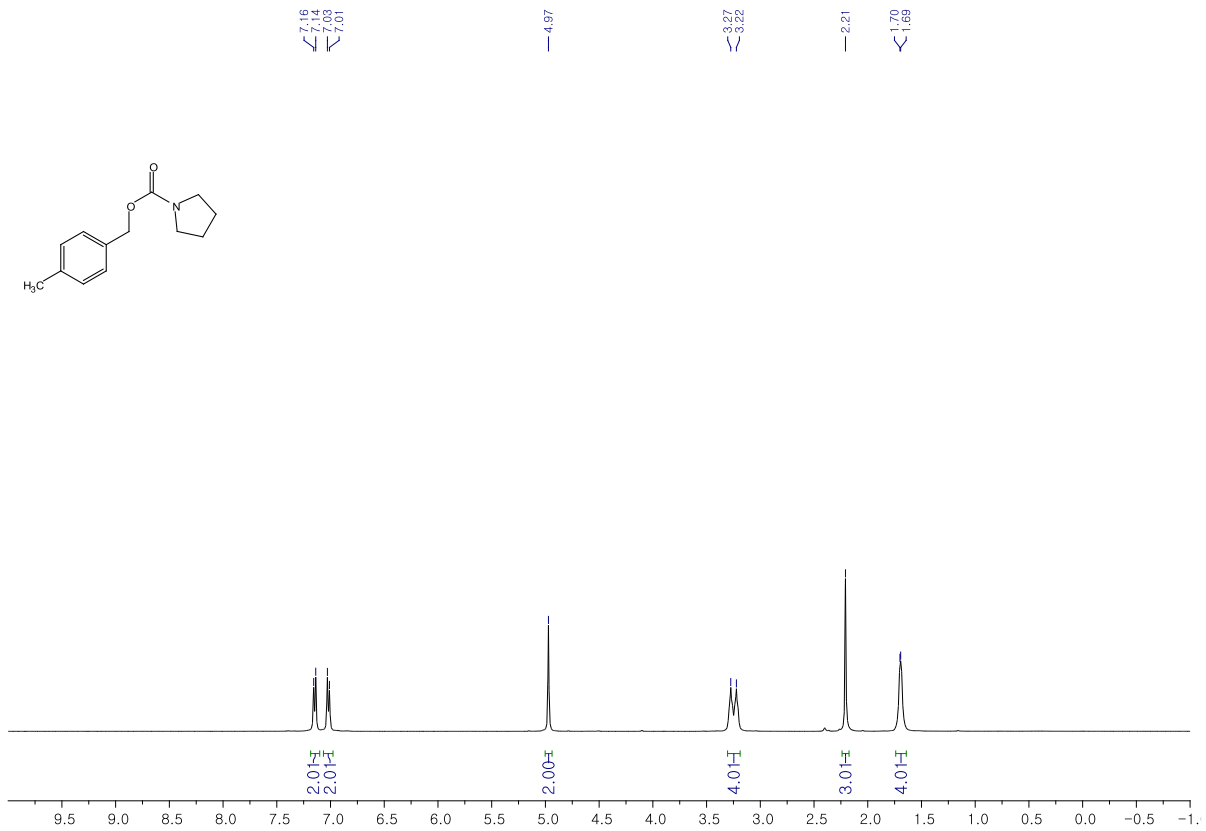
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4.01H
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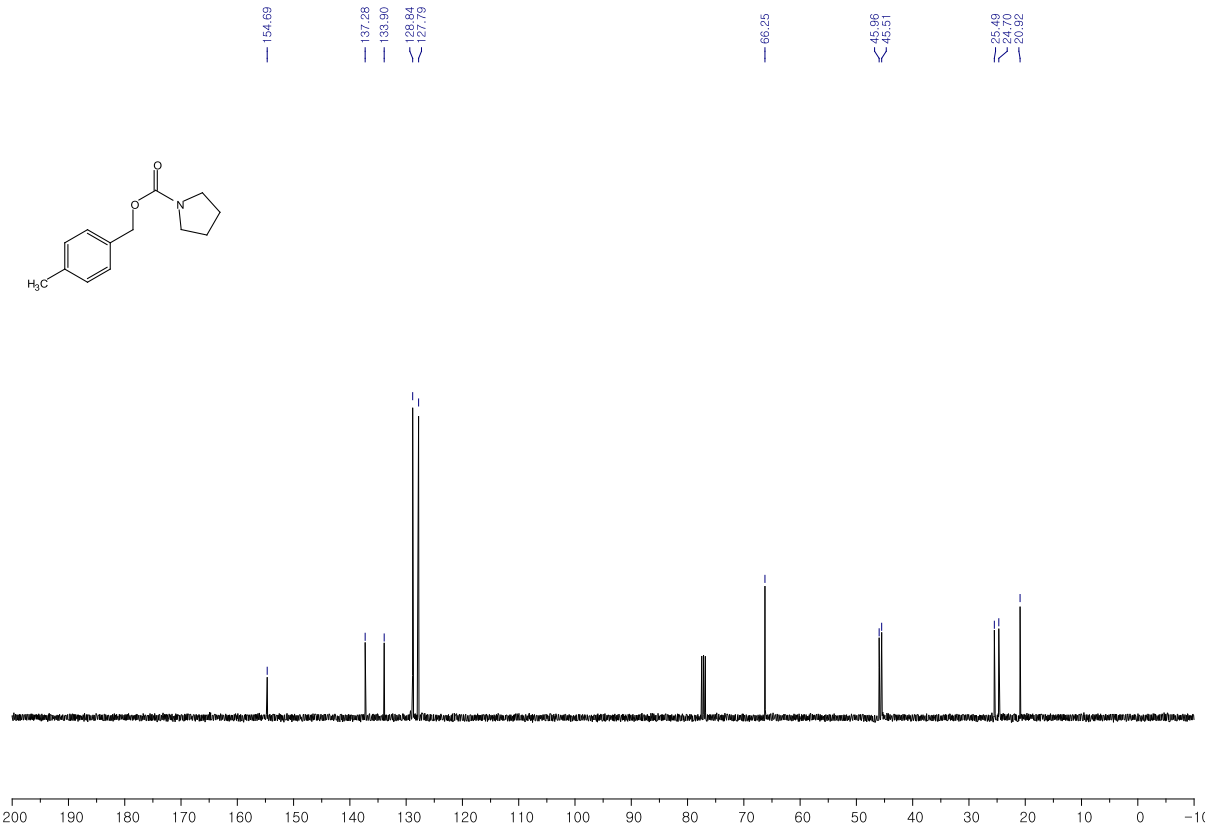
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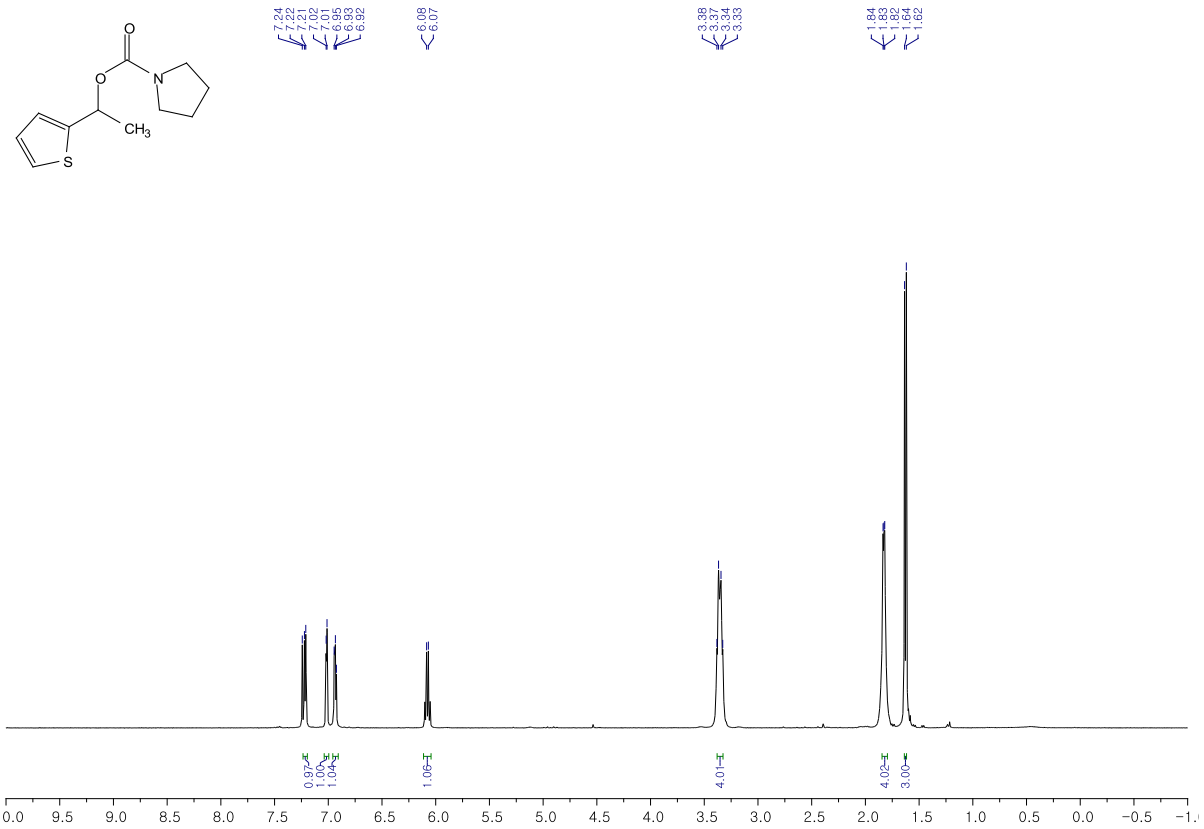
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1.04
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3.00
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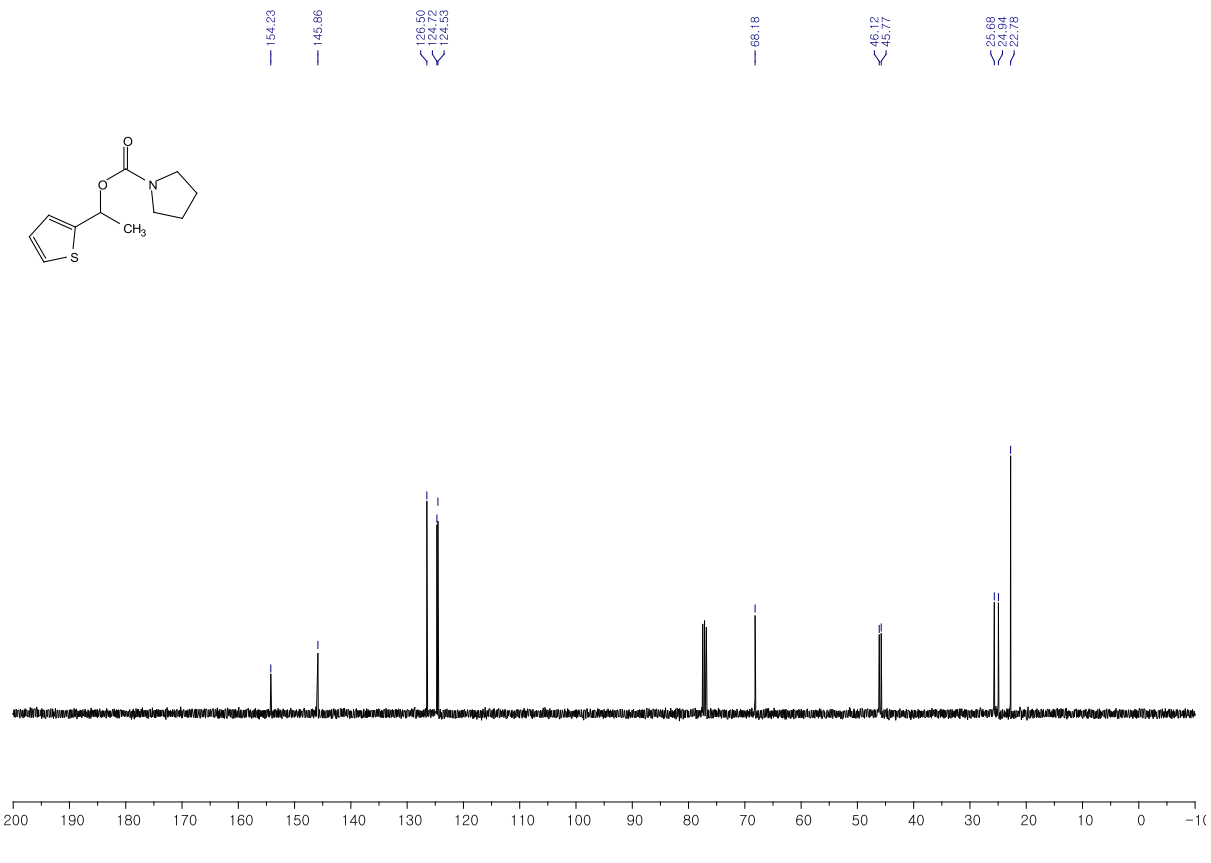
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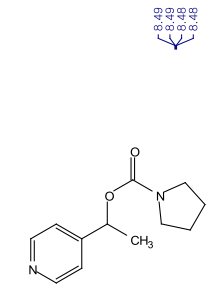

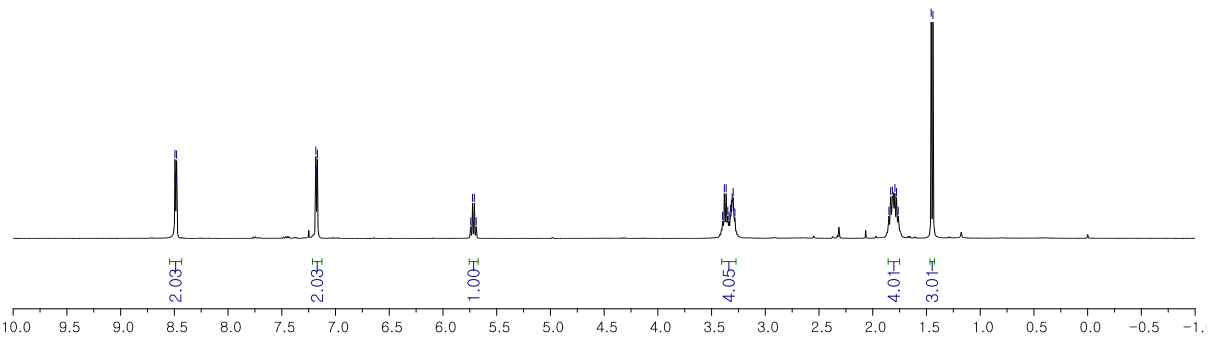

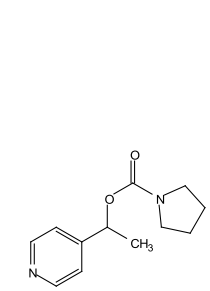

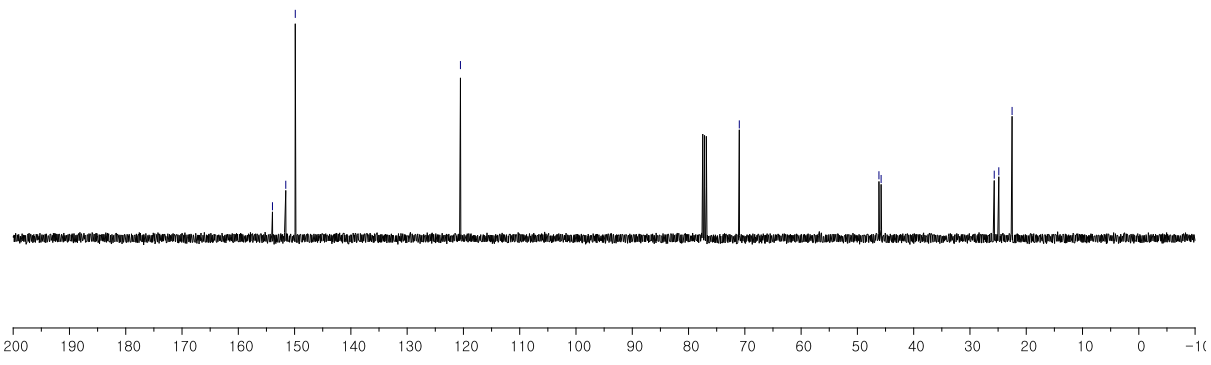

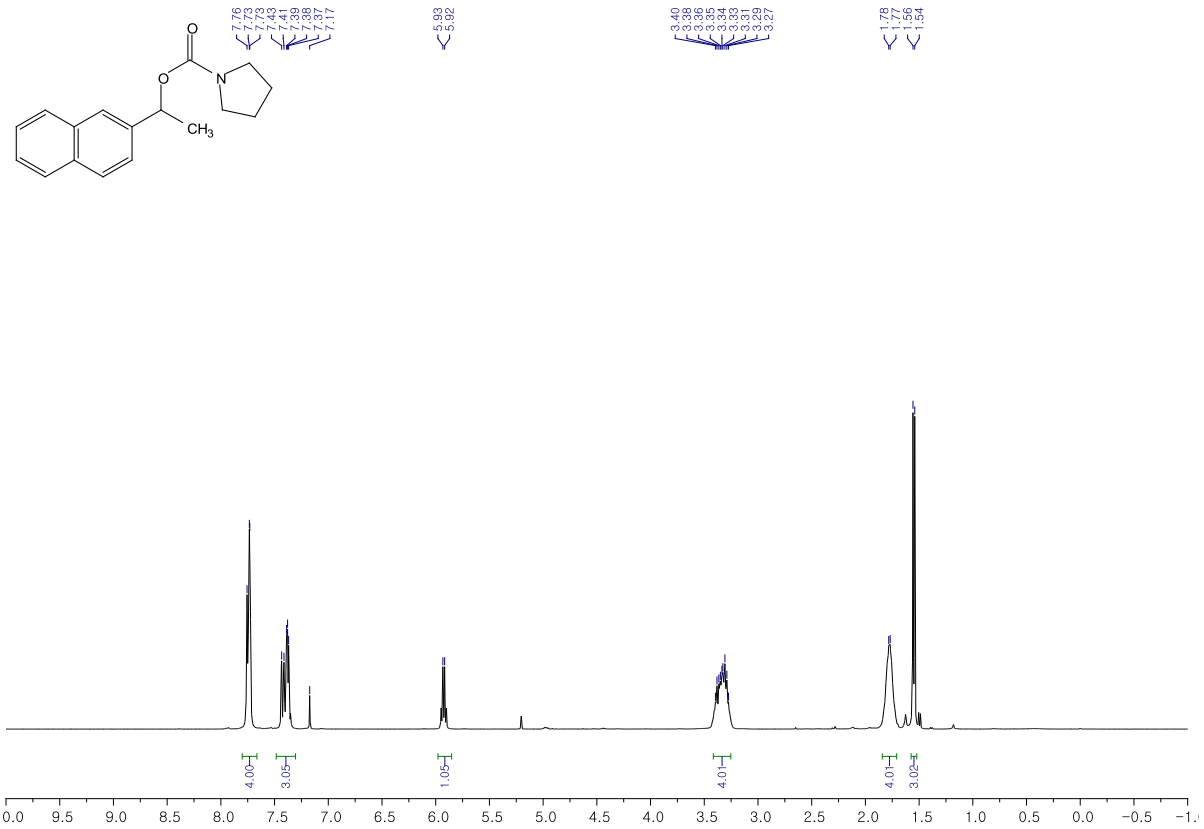
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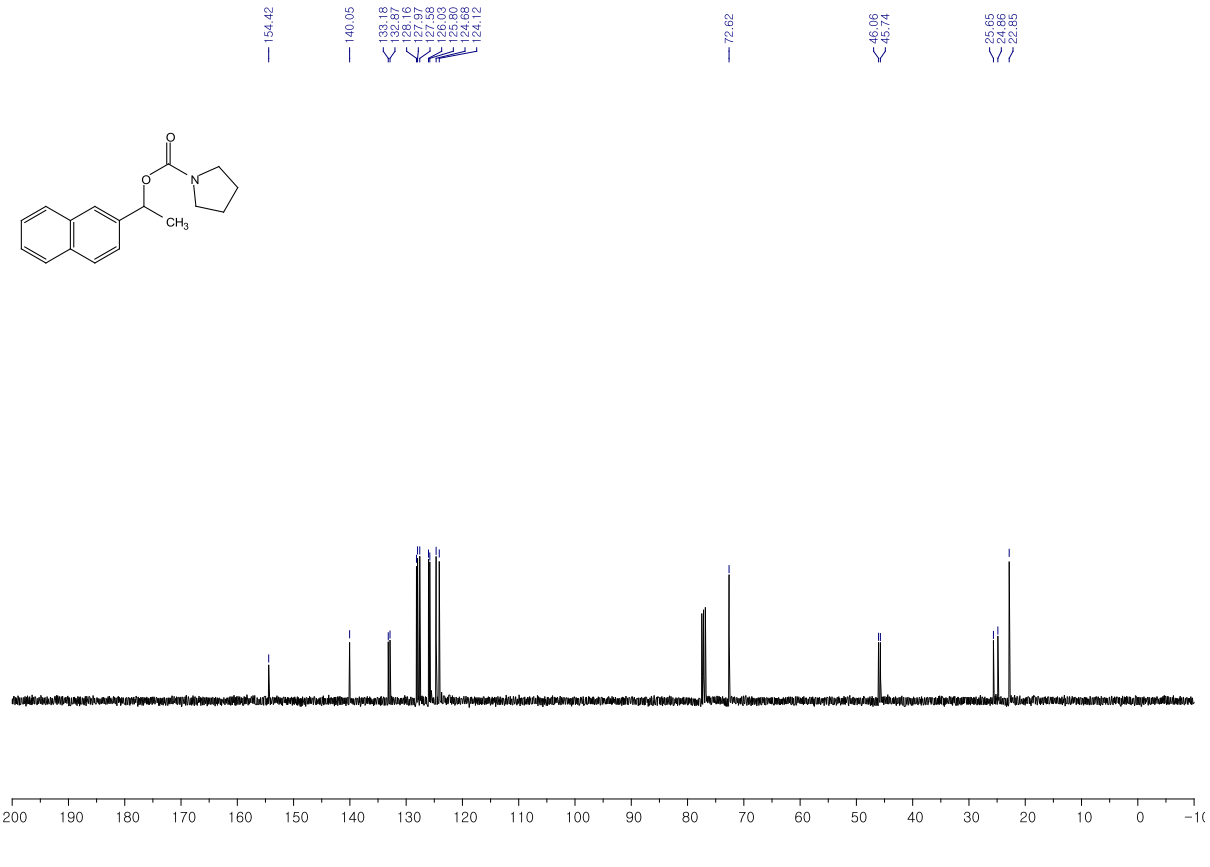
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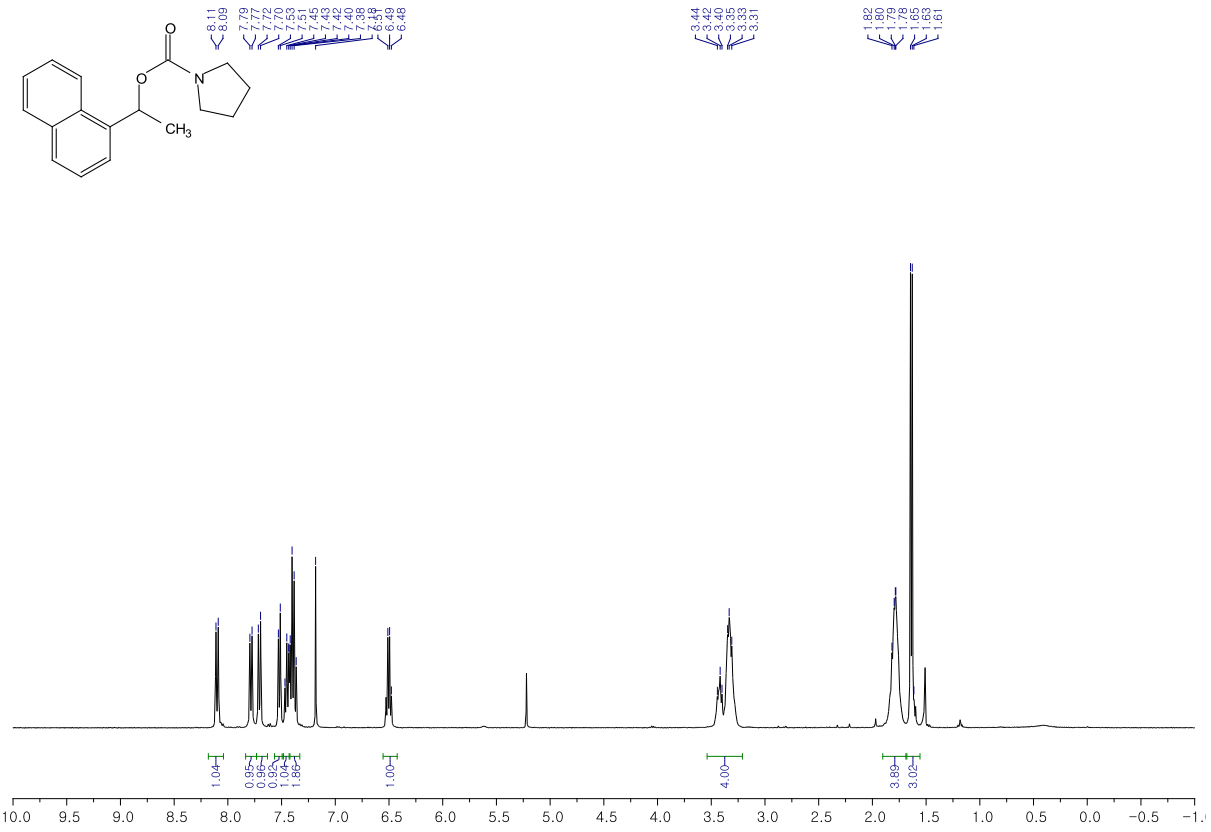
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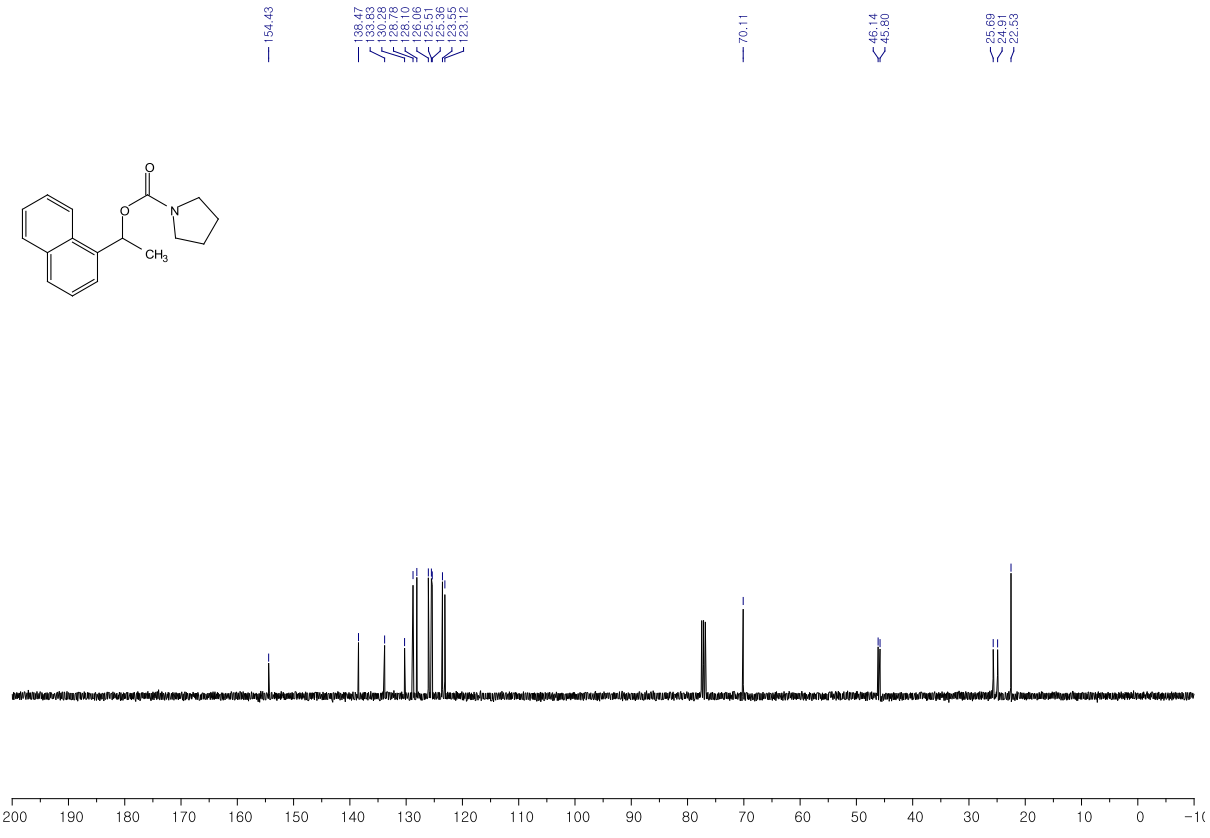
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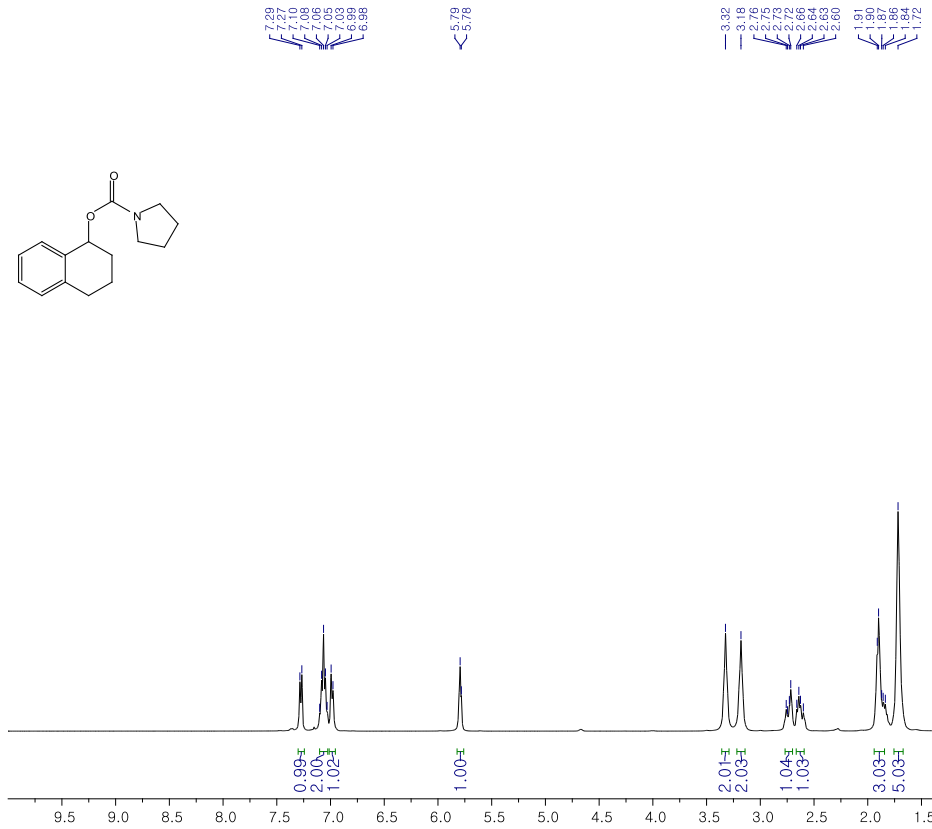
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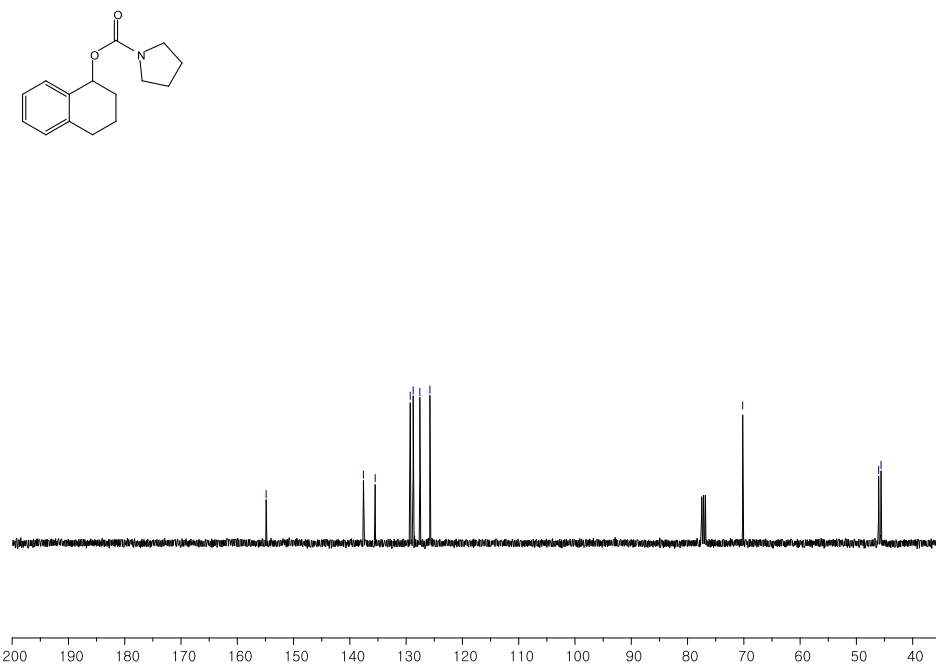
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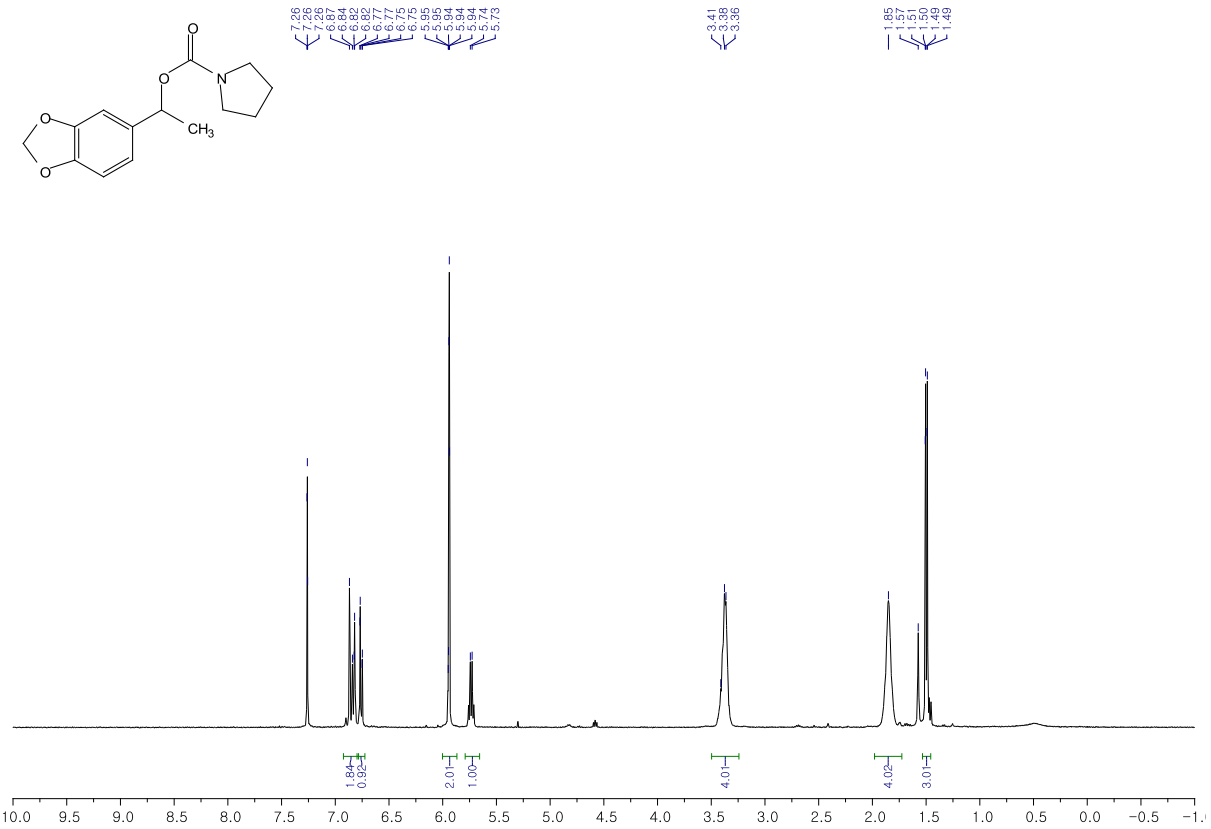
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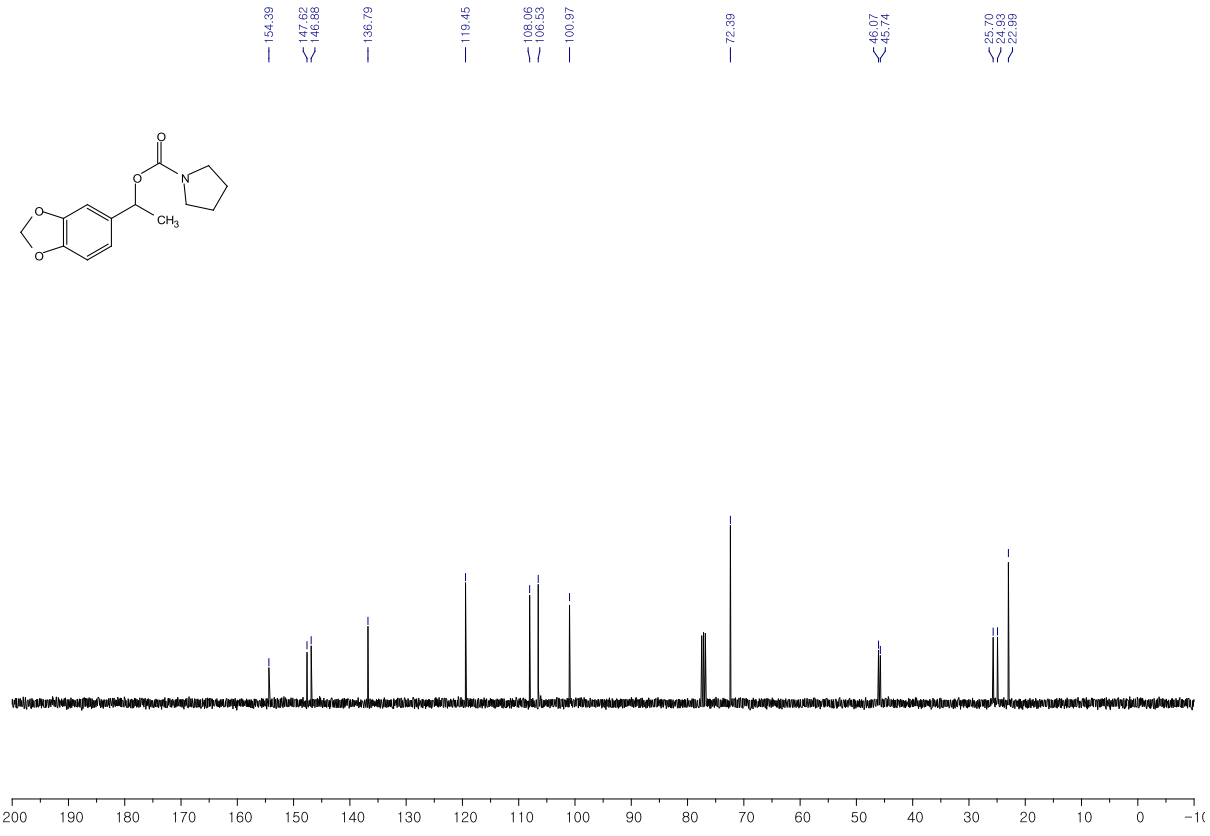
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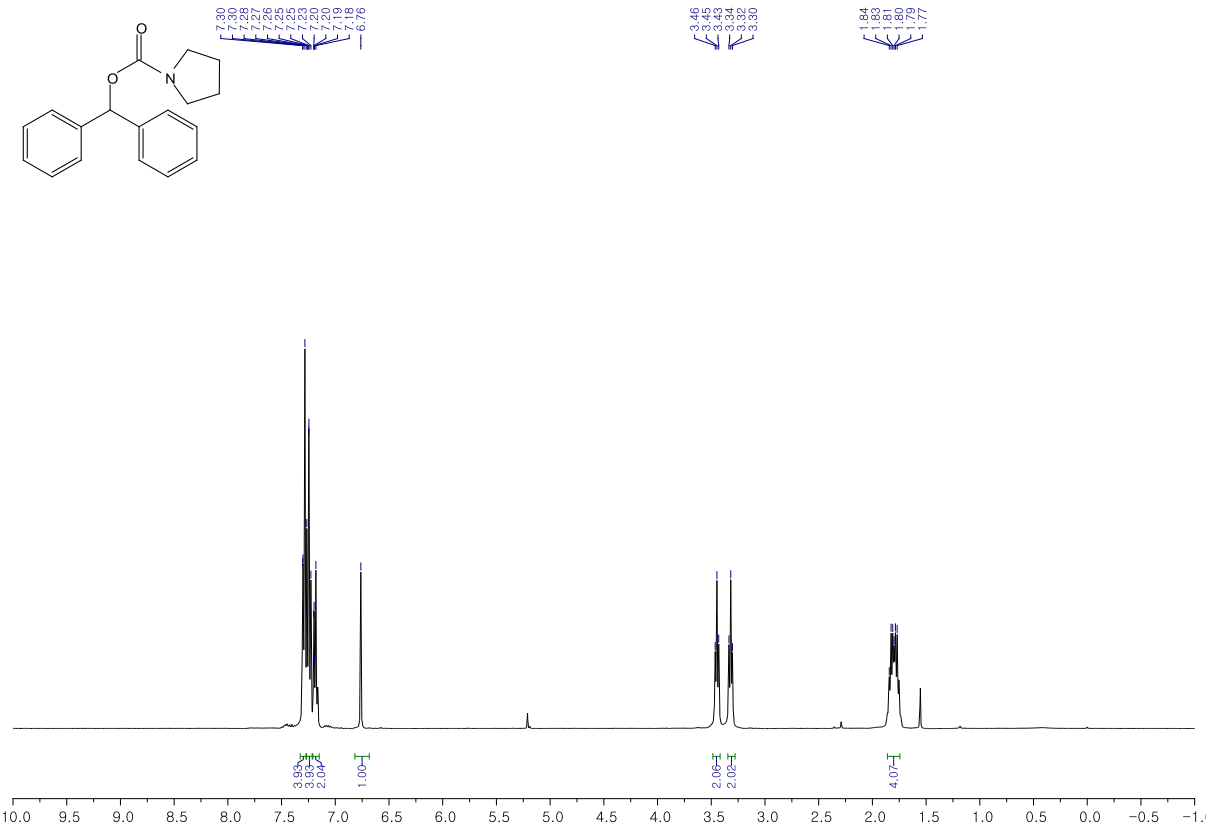
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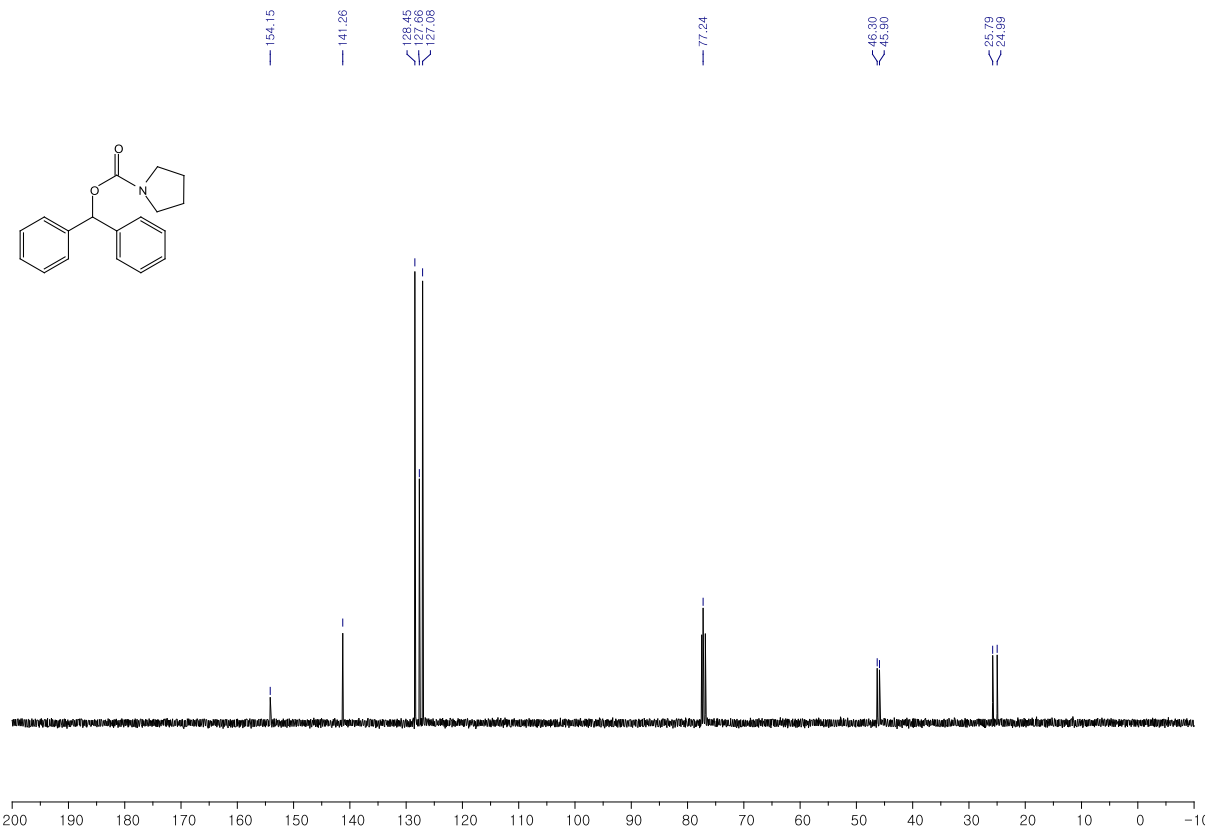
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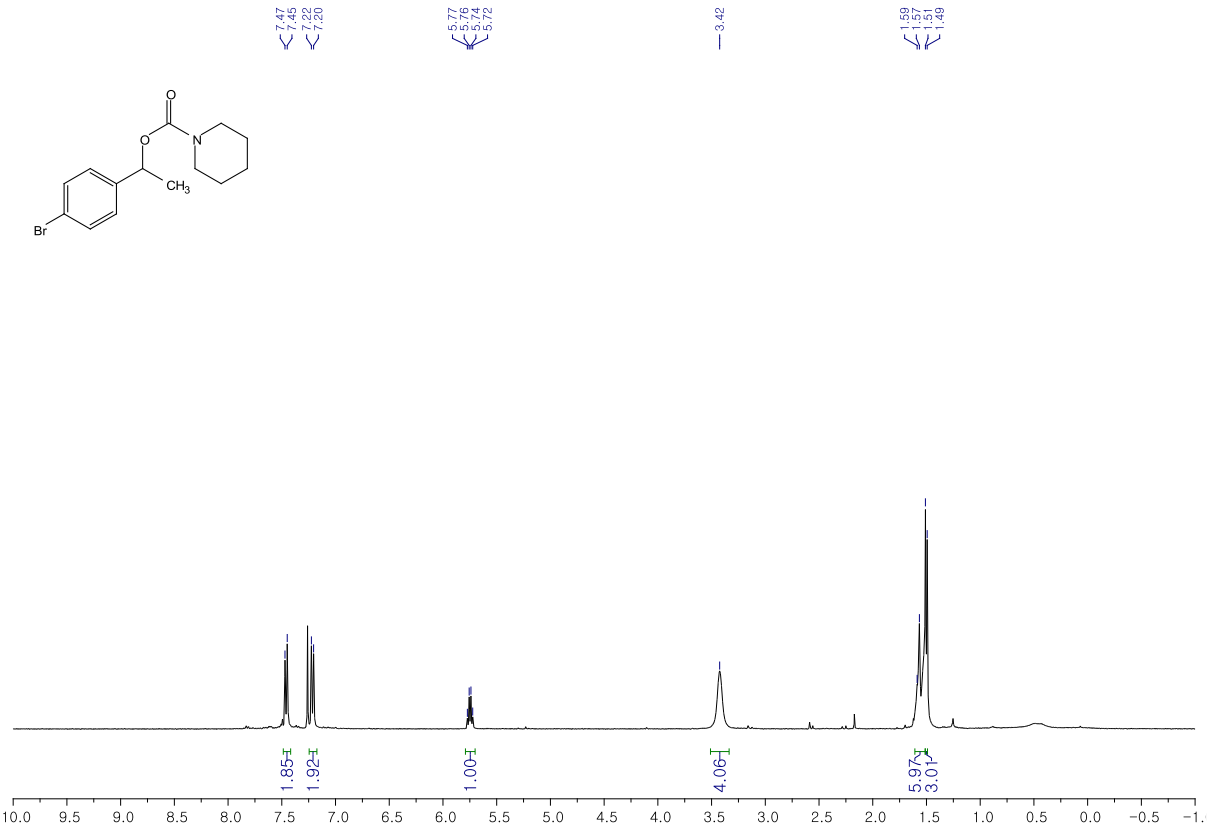
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10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.

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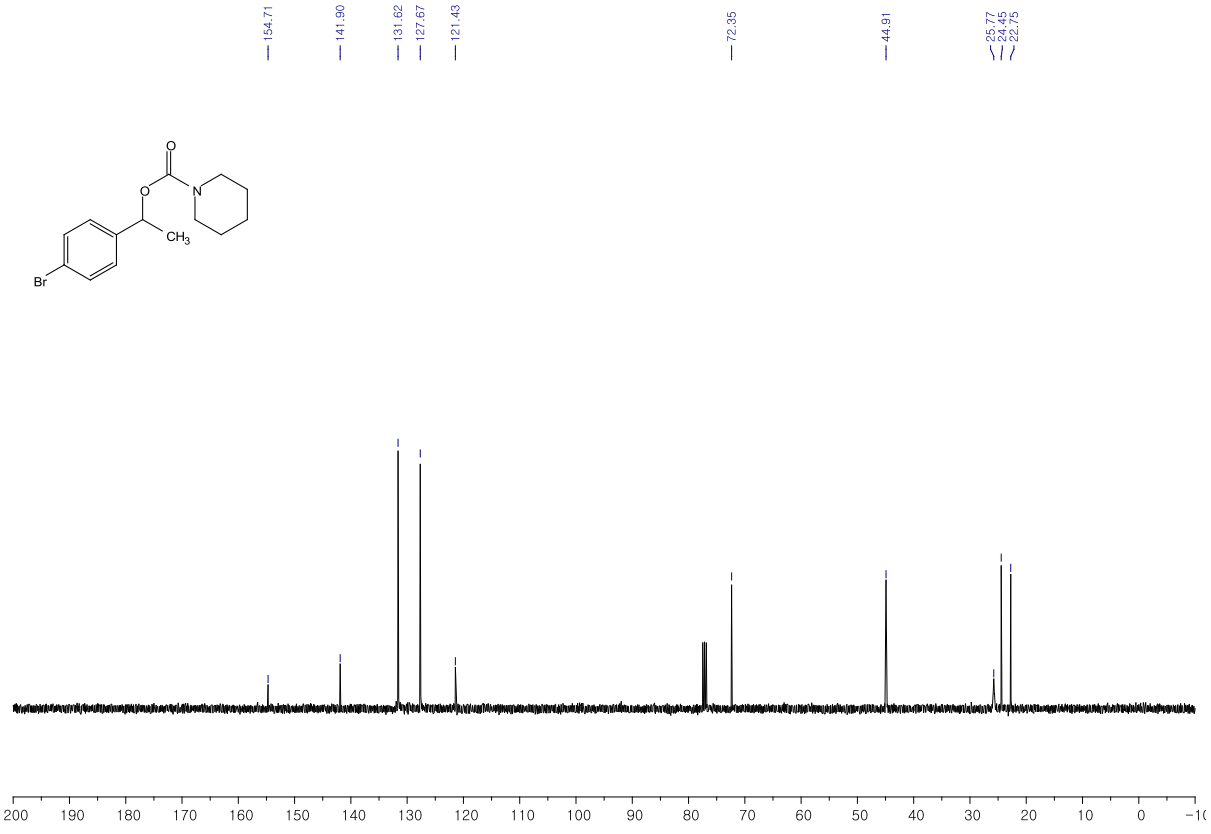
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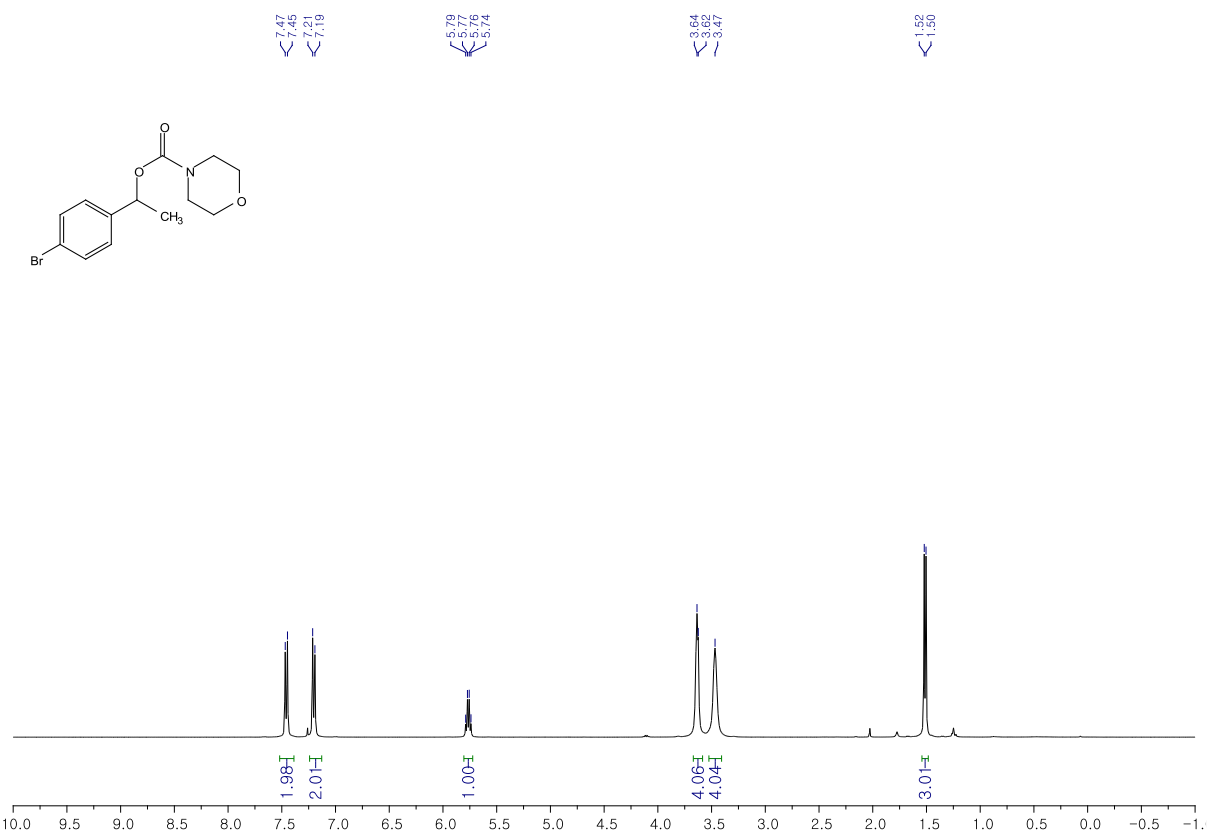
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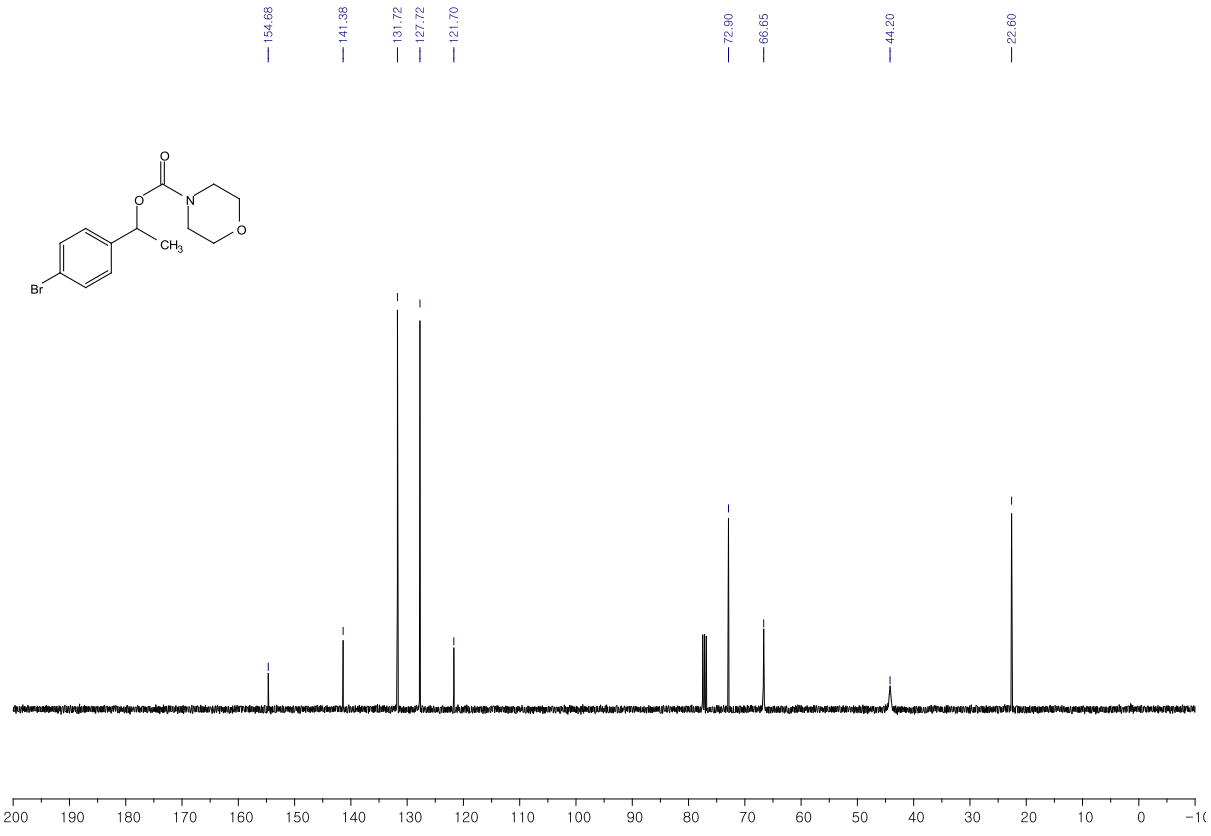
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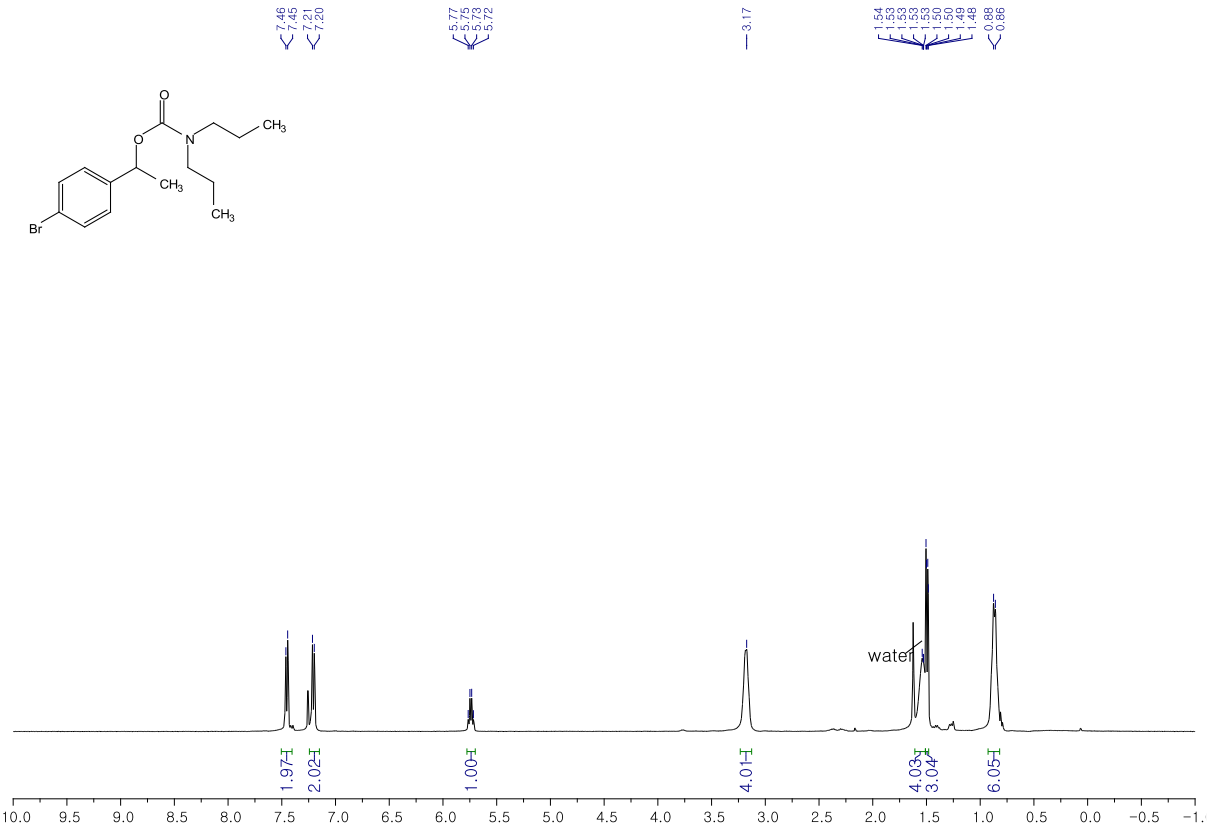
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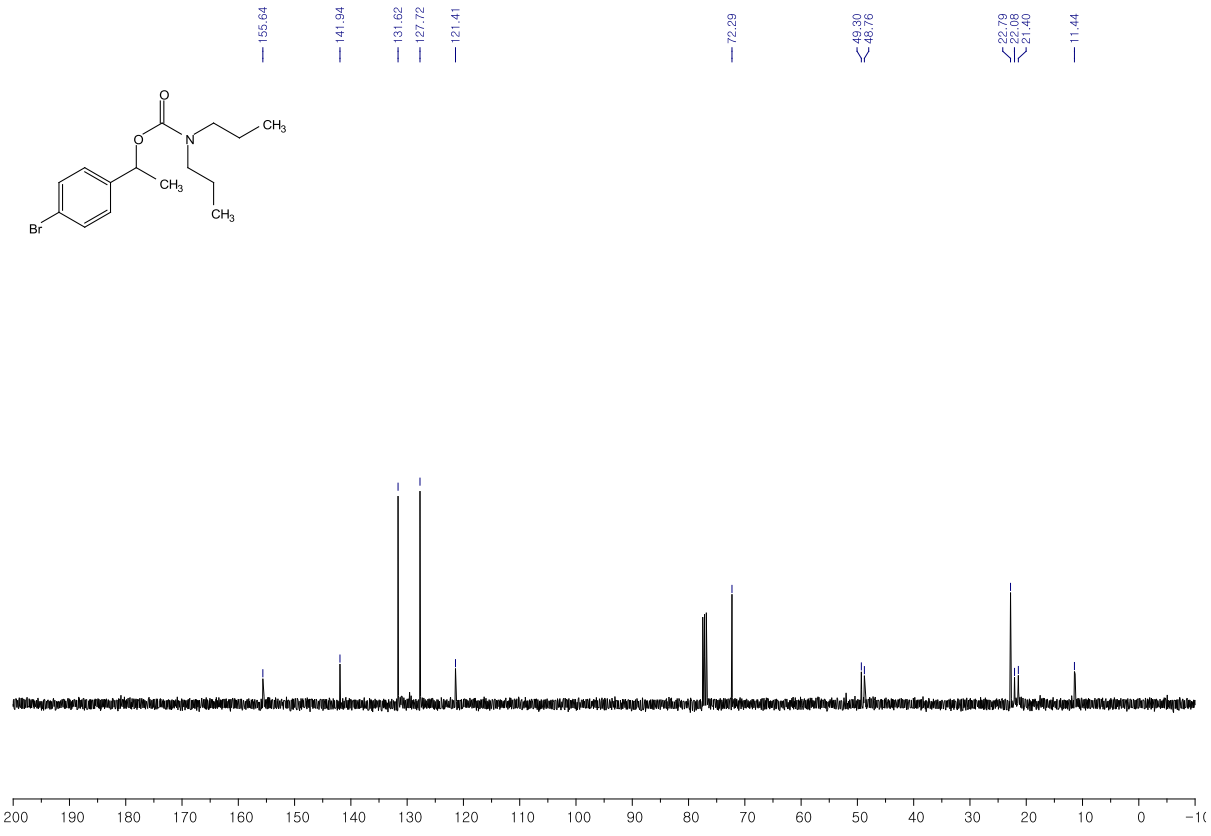
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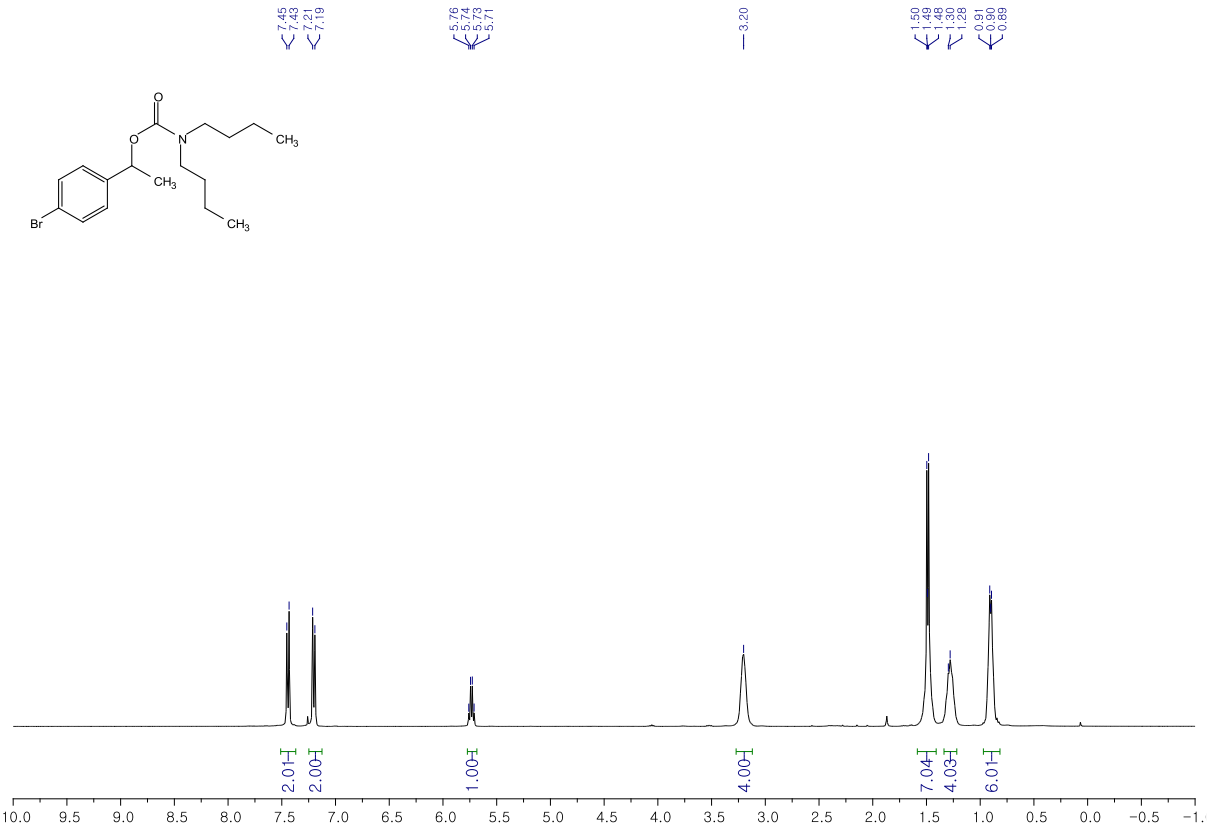
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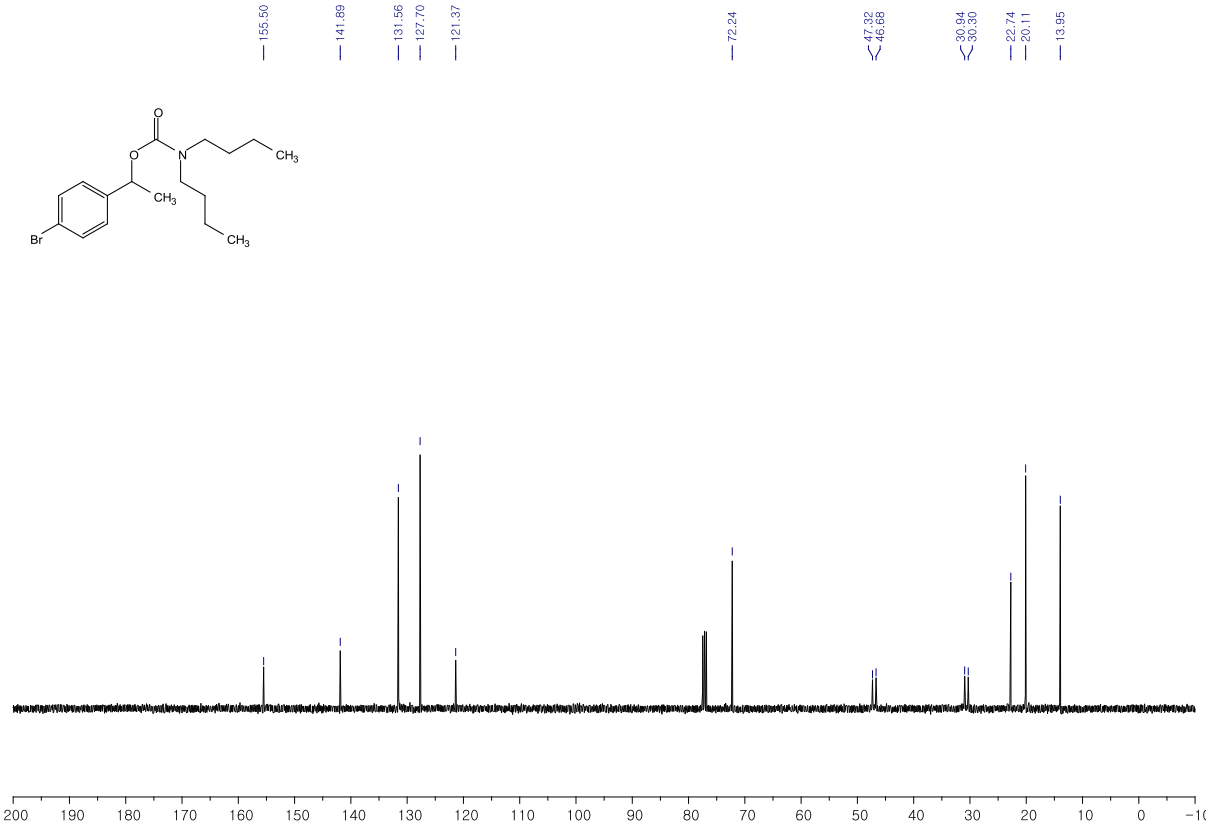
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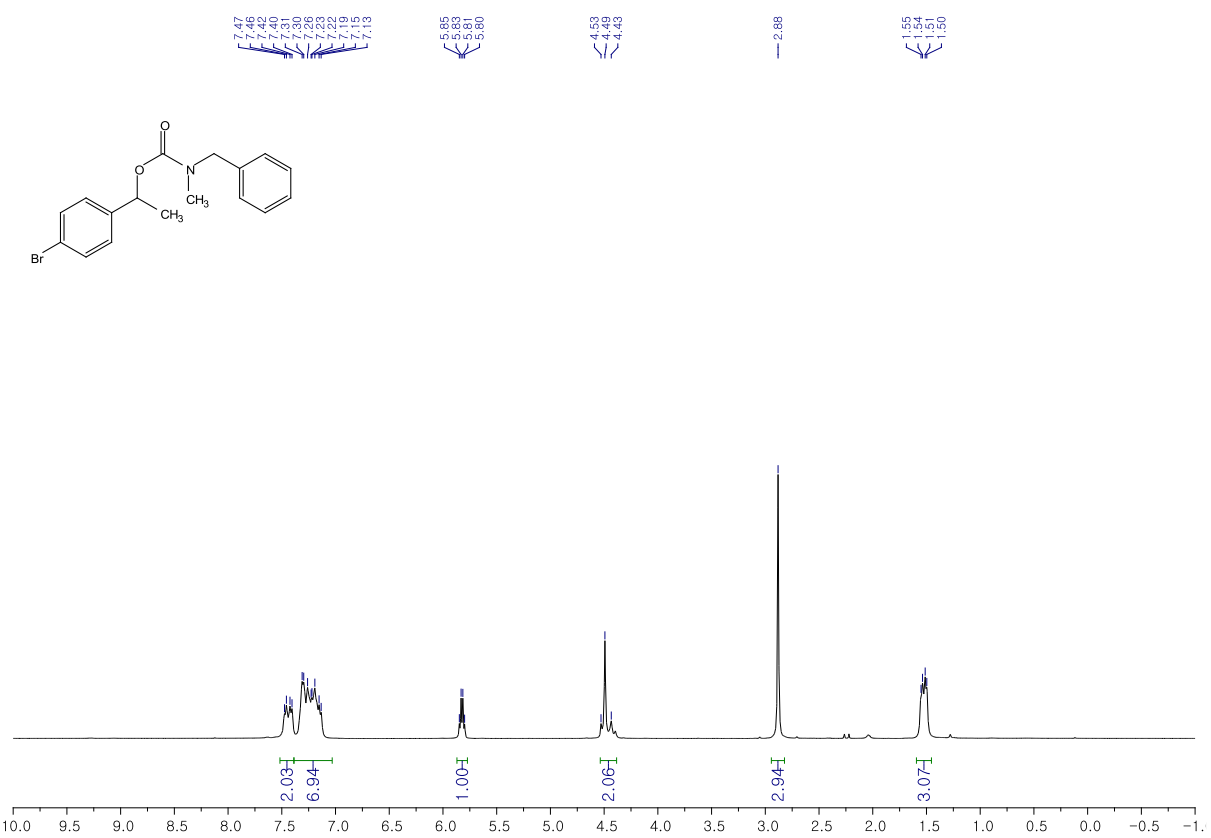
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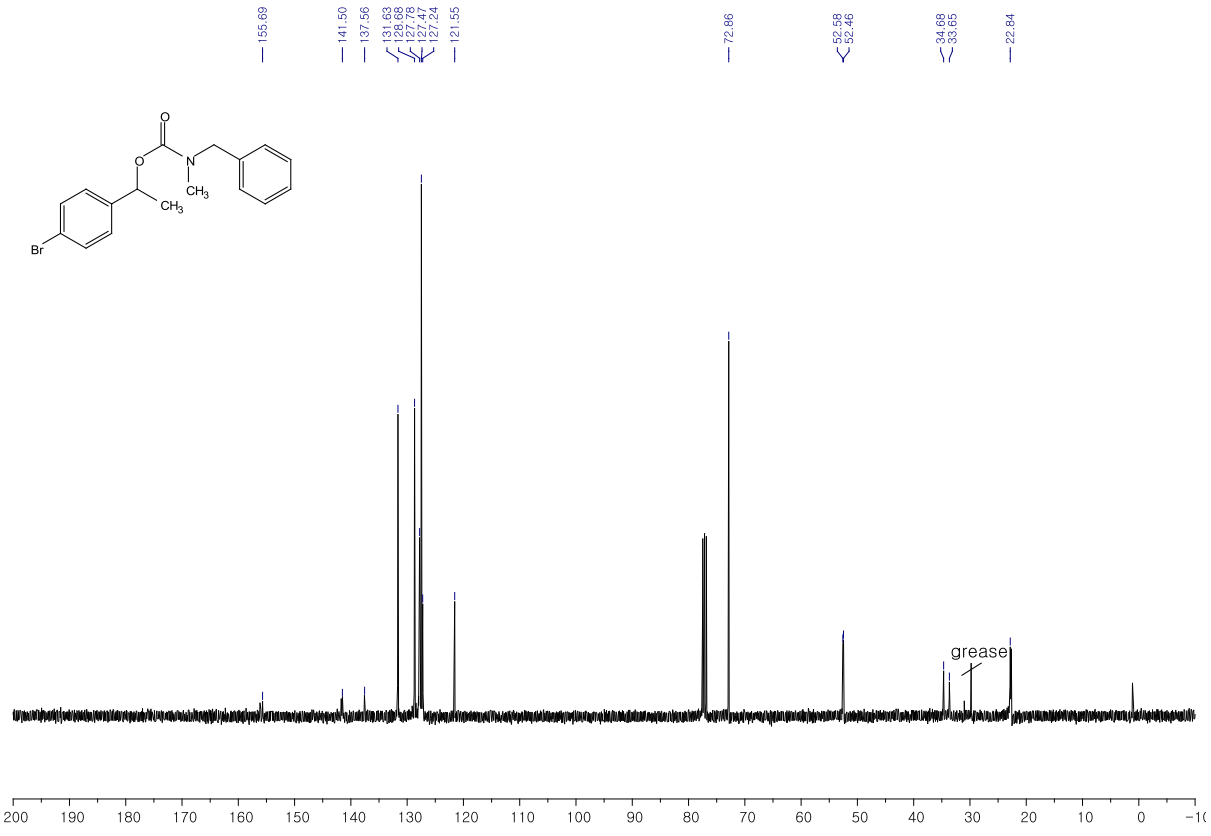
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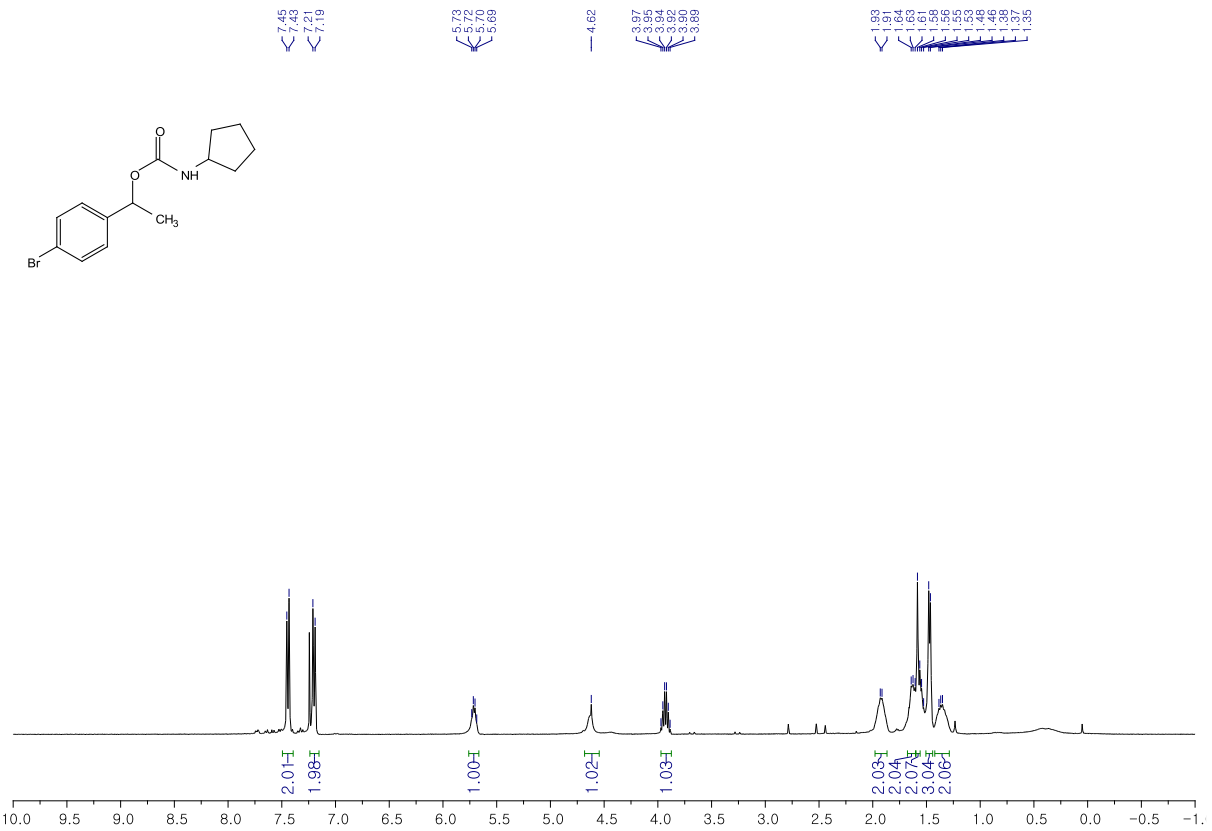
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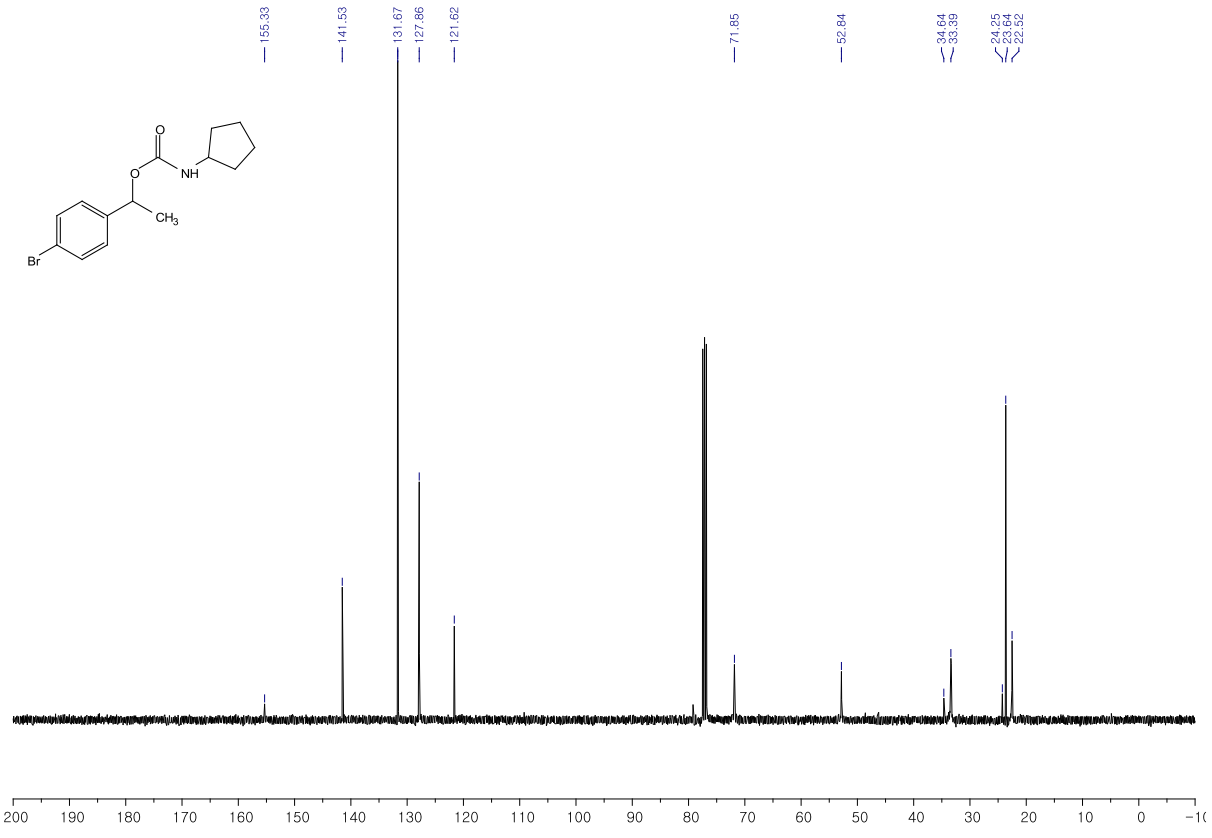
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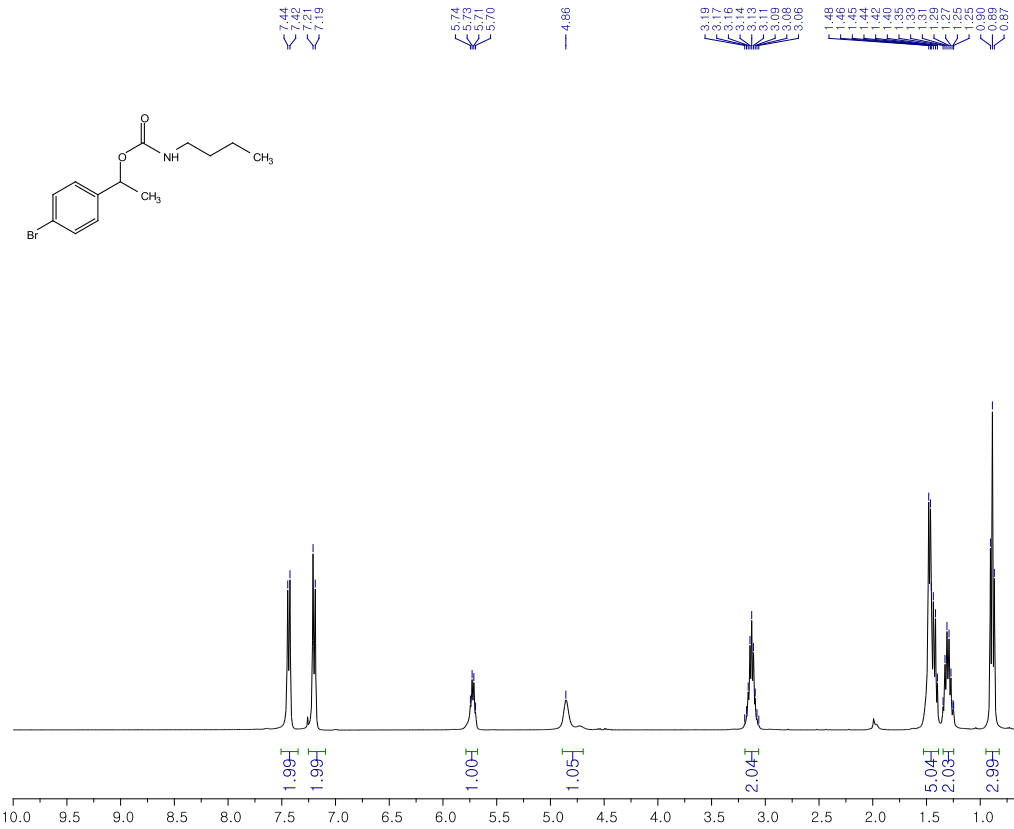
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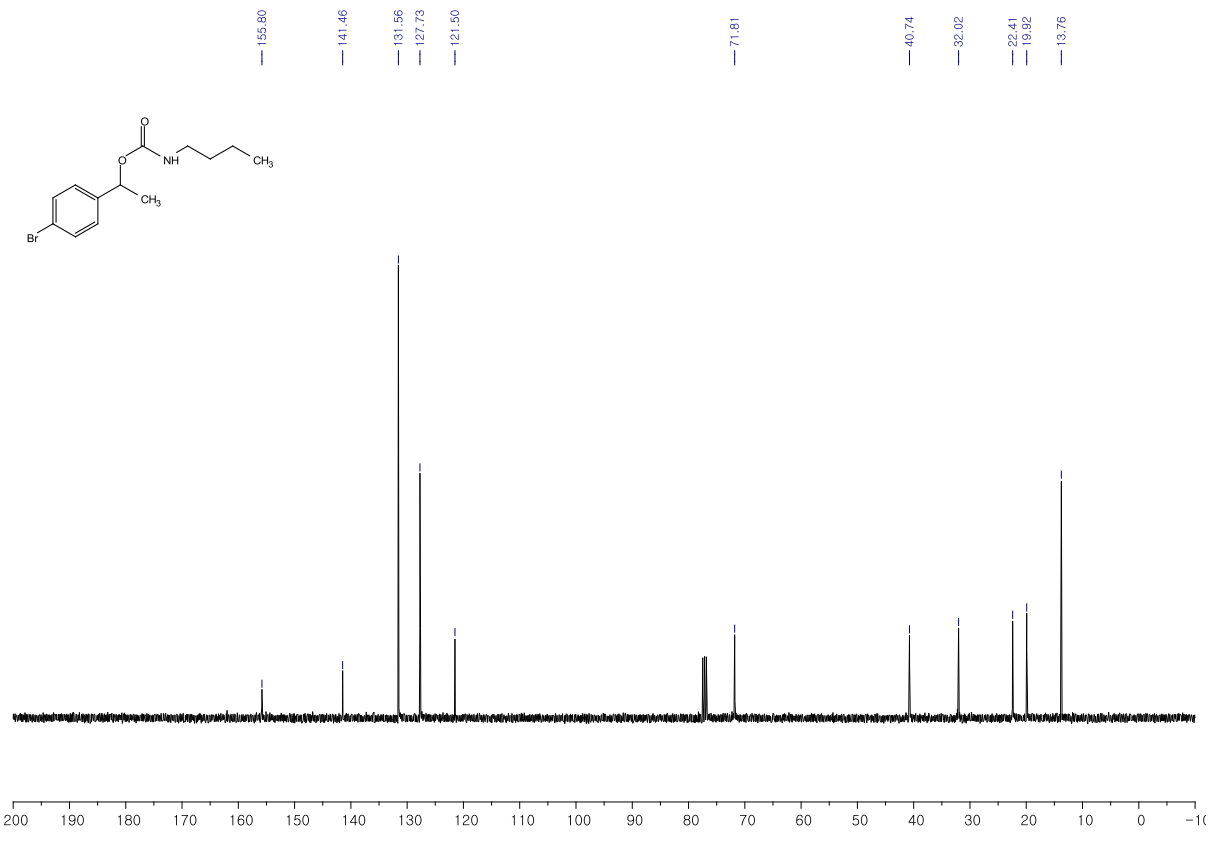
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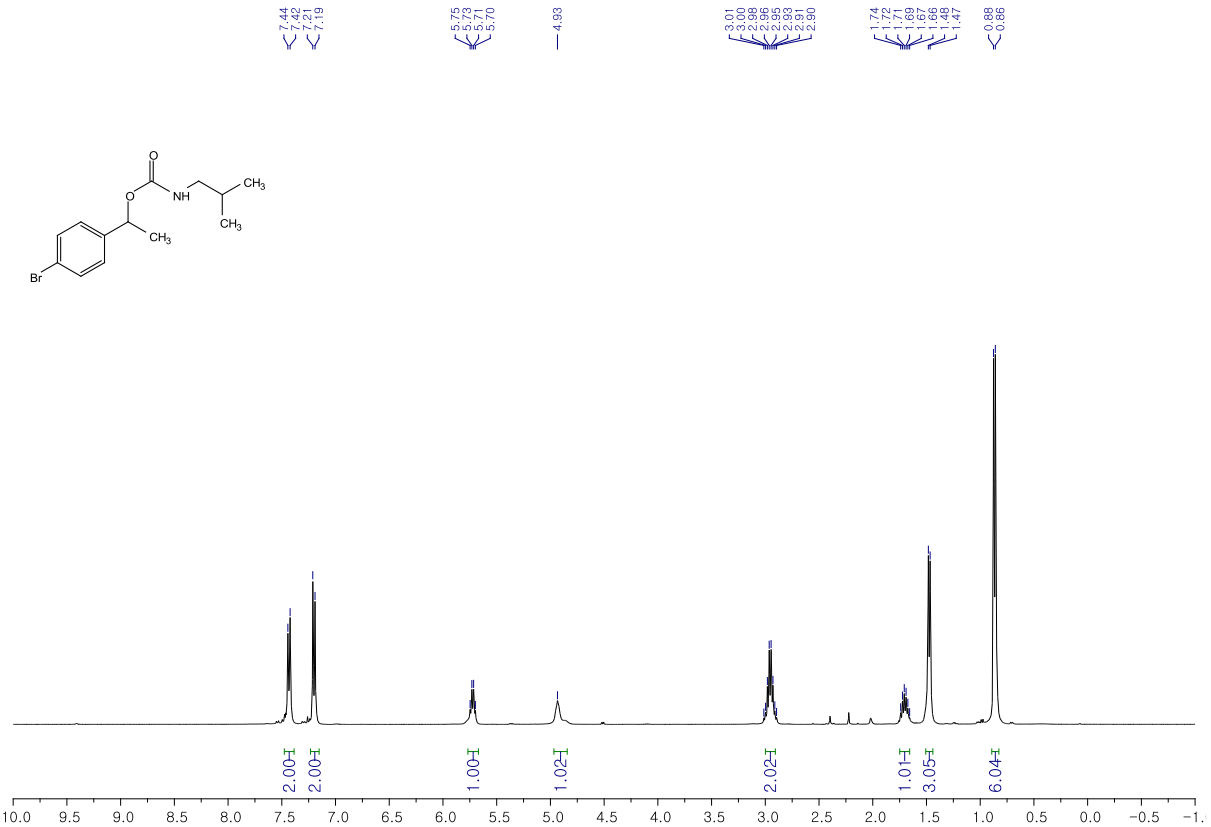
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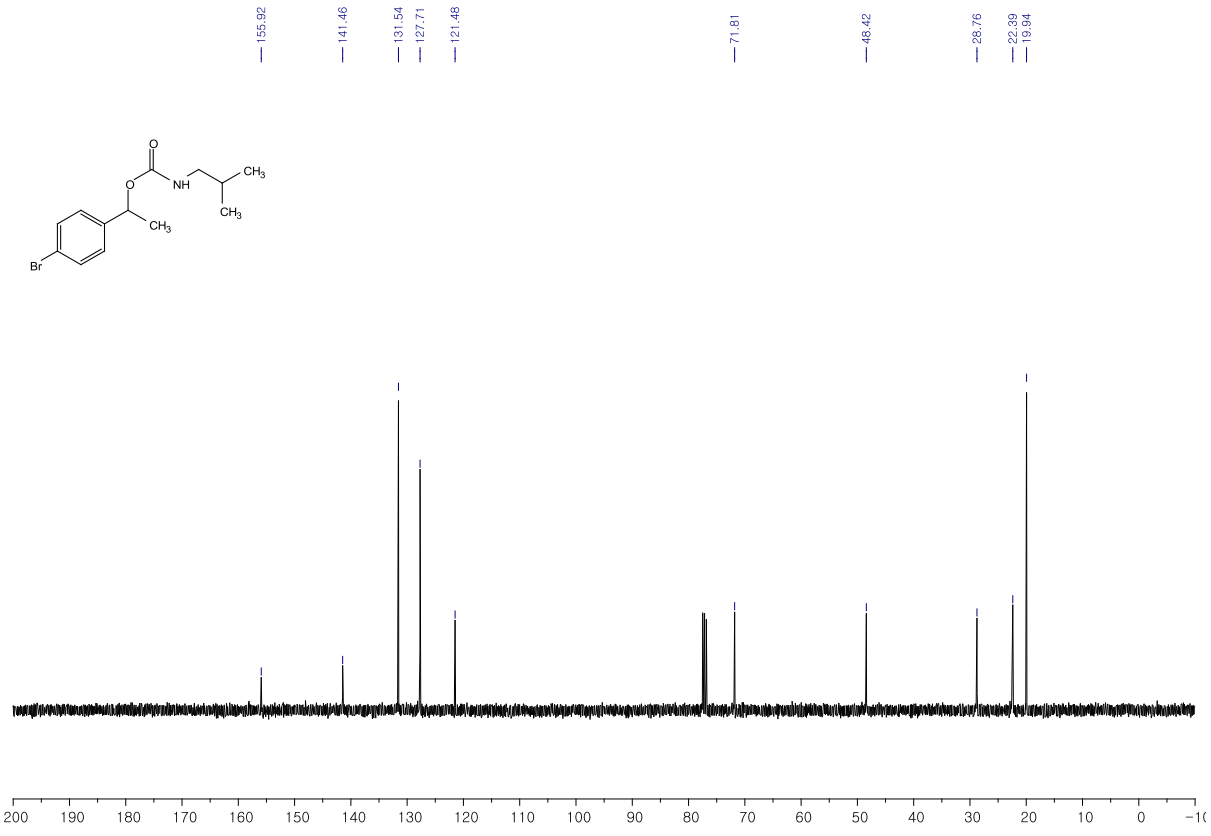
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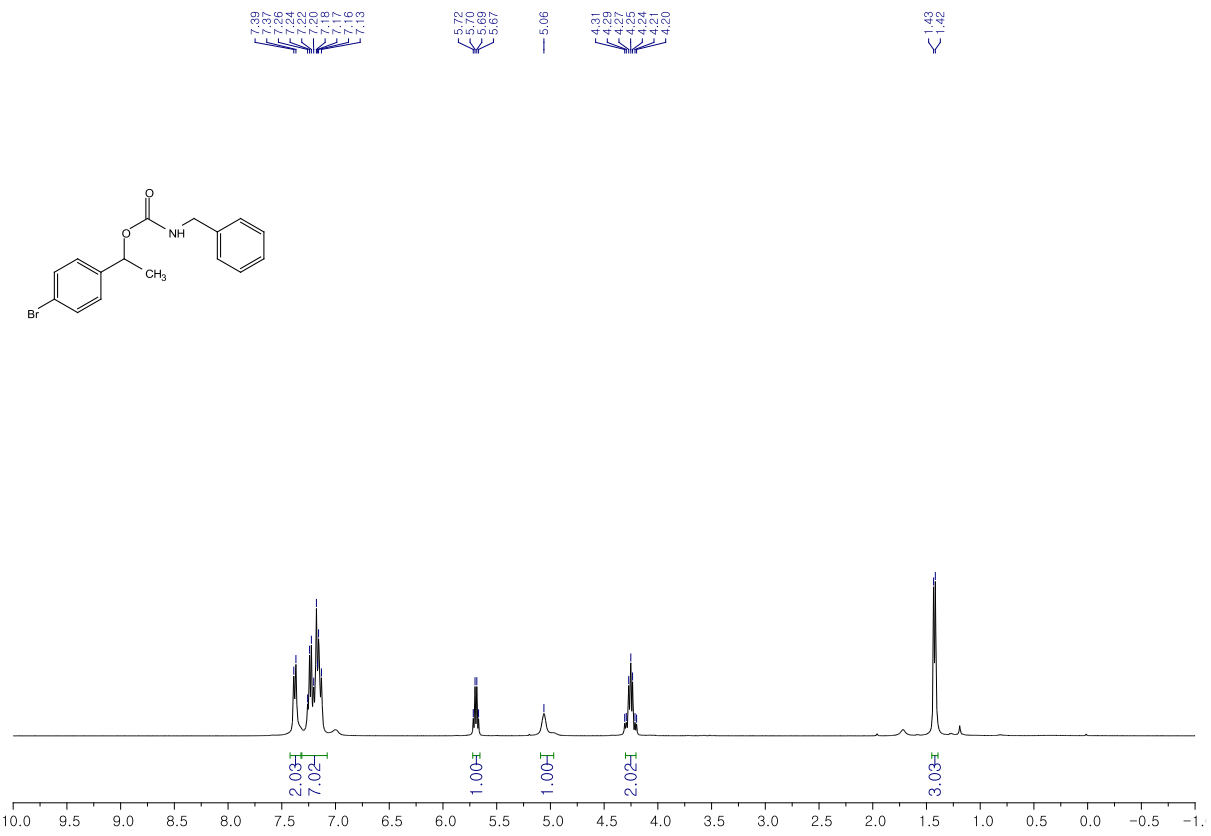
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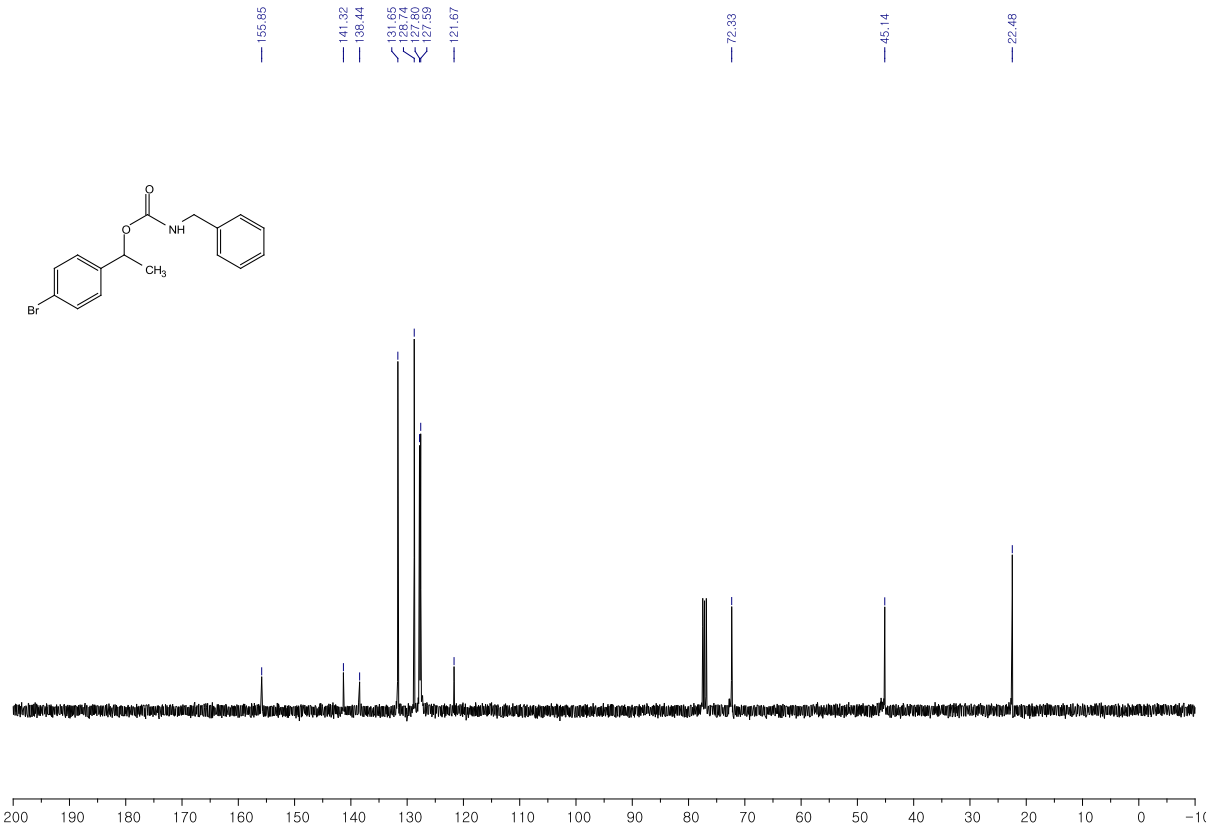
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