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Brønsted Base-catalyzed Imino-Ene-Type Allylation Reactions Using Unactivated Alkenes

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Supporting Information

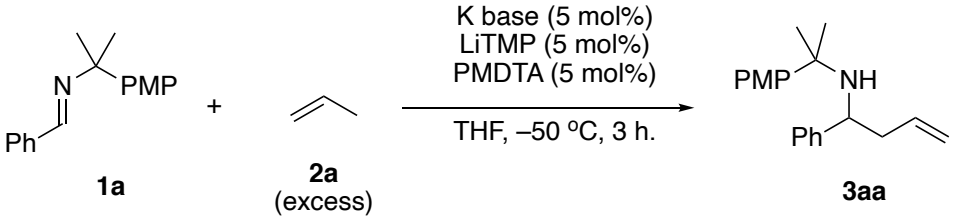
Contents

I. Supporting experiments

1. Effect of potassium bases for the imino-ene-type reaction.

Effect of the potassium base structure was examined (Table S1). Not only KO^{t}Bu but also KHMDS was a good potassium base for the reaction, and the desired product was obtained in quantitative yield (entry 2). On the other hand, potassium benzoate was found to be ineffective (entry 3). It might be due to less basic nature of potassium benzoate compared to the other successful potassium bases.

Table S1. Effect of potassium bases



1a + **2a** (excess) → **3aa**

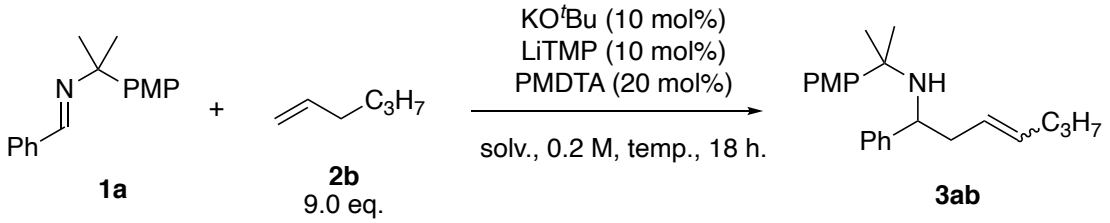
Entry	K base	Yield[a] (%)
1	KO^{t}Bu	quant.
2	KHMDS	quant.
3	KOCOPh	5

[a] Yield was determined by ^{1}H NMR analysis.

2. Optimization of reaction conditions in the allylation reactions of other alkenes

Other simple alkenes such as 1-hexene were tried for the reaction as pronucleophiles (Table S2). In the presence of 10 mol% of KO^{t}Bu, LiTMP and 20 mol% of PMDTA as a ligand, the catalytic addition reaction of 1-hexene **2b** with imine **1a** was conducted in CPME at –40 ºC to afford the desired homoallylic amine **3ab** in 73% yield with 75/25 of *E/Z* selectivity (entry 1). It should be mentioned that there was no branched product detected, and some byproducts were formed in the reaction. By ^{1}H NMR and mass spectroscopic analysis, it was assumed that the byproducts were the isomers of the desired product, and it could be formed from the product *via* a migration of the double bond under the strongly basic condition (Scheme S1), and also it was suggested that the *E/Z* isomerization of the products also could proceed via this pathway. To increase the yield and improve the *E/Z* selectivity, further optimization of the reaction conditions was performed. The reaction at lower temperature (–78 ºC) gave the product in similar level

Table S2. Optimization of reaction conditions of hexene **2b** with alkylimine **1a**

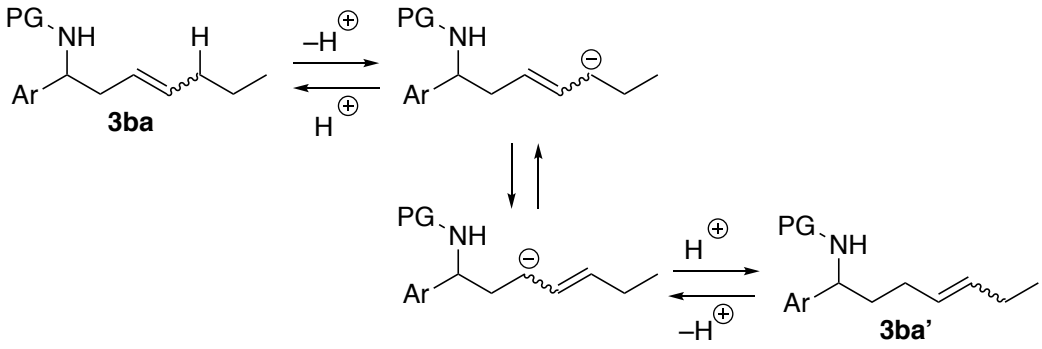


Entry	Solv.	Temp. (ºC)	Yield[a] (%)	*E*/*Z*[b]
1	CPME	–40	80 (73)	75/25
2	CPME	–78	69	59/41
3	THF	–78	63	43/57
4	CPME	–20	78	76/24

[a] Yield was determined by ^{1}H NMR analysis of the crude mixture. Isolated yield was shown in the parenthesis. [b] *E*/*Z* ratio was determined by ^{1}H NMR analysis of the crude mixture.

of yield with lower *E/Z* selectivity (entry 2). Furthermore, the reaction in THF as a solvent gave the product in 63% yield with reversed *E/Z* selectivity (43/57, entry 3). The reaction at higher temperature (–20 ºC) gave the desired compound in 78% yield with almost comparable *E/Z* selectivity (76/24, entry 4), and it was found that the byproduct formation was accelerated at this higher reaction temperature. It was assumed that the equilibrium between *E*- and *Z*-product lead the *E/Z* selectivity of the reaction to be moderate.

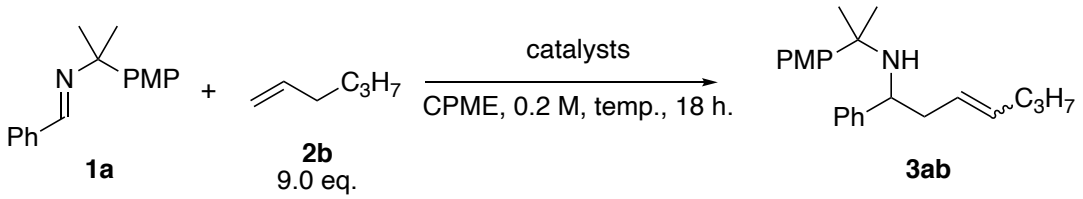
Scheme S1. Possible pathway for byproduct formation



To suppress the isomerization and improve the *E/Z* ratio, investigation of the catalysts was undertaken (Table S3). Firstly, KCH_2TMS was used as a catalyst instead of KO^{t}Bu and LiTMP; however, no improvement of the *E/Z* ratio was observed (entry 2). To tune the basicity and nucleophilicity of the anionic species, NaO^{t}Bu was utilized instead of

KO^{t}Bu. Although only 8% of the product was obtained in the reaction at –40 ºC (entry 3), the reaction catalyzed by 10 mol% of NaO^{t}Bu, LiTMP and 20 mol% of PMDTA at 0 ºC proceeded to afford the desired product in 43% yield with higher *E/Z* ratio (entry 4, *E/Z* = 81/19). It should be noted that there was almost no byproduct such as isomers as mentioned before. This result implied that appropriate basicity and nucleophilicity of the sodium-based intermediate could suppress the isomerization of the product. The reaction using LiO^{t}Bu instead of NaO^{t}Bu did not show any reaction due to lower basicity (entry 5).

Table S3. Catalyst screening



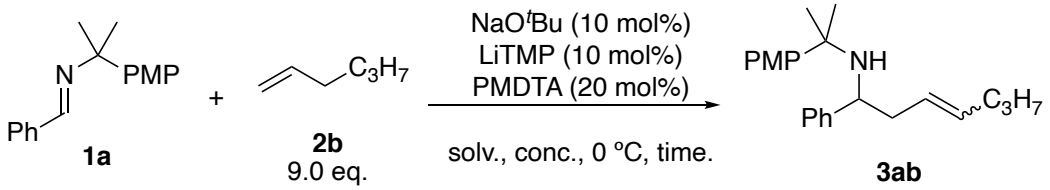
Entry	Catalyst	Temp. (ºC)	Yield[a] (%)	*E*/*Z*[b]
1	KO^{t}Bu (10 mol%) LiTMP (10 mol%) PMDTA (20 mol%)	–40	80 (73)	75/25
2	KCH_2TMS (10 mol%) PMDTA (10 mol%)	–40	78	71/19
3	NaO^{t}Bu (10 mol%) LiTMP (10 mol%) PMDTA (20 mol%)	–40	8	56/44
4	NaO^{t}Bu (10 mol%) LiTMP (10 mol%) PMDTA (20 mol%)	0	43	81/19
5	LiO^{t}Bu (10 mol%) LiTMP (10 mol%) PMDTA (20 mol%)	0	trace	--

[a] Yield was determined by ^{1}H NMR analysis of the crude mixture. Isolated yield was shown in the parenthesis. [b] *E*/*Z* ratio was determined by ^{1}H NMR analysis of the crude mixture.

Further optimization of the reaction condition using NaO^{t}Bu/LiTMP system was carried out (Table S4). Reducing the amounts of 1-hexene (2.0 eq.) showed low reactivity

with similar *E/Z* selectivity (entry 2). Then, the concentration of the reaction was increased to 0.4 M to give the product in higher yield (entry 3). Prolonging of the reaction time showed a subtle improvement of the yield of the product (entry 4). Next, other solvents were examined for the reaction. The reaction in THF showed almost comparable yield and *E/Z* selectivity compared with the reaction in CPME (entry 5). On the other hand, the reaction in Et_2O gave the product in lower yield with lower *E/Z* selectivity compared to the reaction in CPME or THF (entry 6). To improve the reactivity, the concentration of the reactions was again increased to 0.8 M to give the product in 89% with higher *E/Z* selectivity (entry 7). On the other hand, the reaction in much higher concentration (1.2 M) gave lower *E/Z* selectivity (entry 8). These results implied that a subtle change of the solvent system could affect the *E/Z* selectivity. The reaction using TMEDA instead of PMDTA gave the product in almost similar yield with higher *E/Z* selectivity (entry 9). Finally, the amounts of 1-hexene were reduced for the reaction to give lower reactivity and *E/Z* selectivity (entries 10,11).

Table S4. Optimization of reaction condition for NaO^{t}Bu/LiTMP-catalyzed reaction



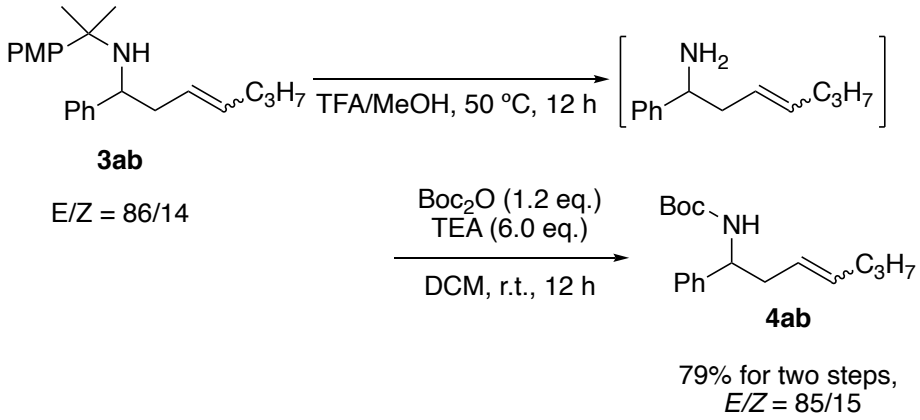
Entry	Solv.	Conc. (M)	Time (h)	Yield[a] (%)	*E/Z*[b]
1	CPME	0.2	18	43	81/19
2[c]	CPME	0.2	18	21	79/21
3	CPME	0.4	18	57	82/18
4	CPME	0.4	24	65	81/19
5	THF	0.4	24	67	80/20
6	Et_2O	0.4	24	37	78/22
7	CPME	0.8	24	89	87/13
8	CPME	1.2	24	90	81/19
9[d]	CPME	0.8	24	90 (89)[e]	91/9
10[d][f]	CPME	0.8	24	80	86/14
11[d][g]	CPME	0.8	24	80	86/14

[a] Yield was determined by ^{1}H NMR analysis of the crude mixture. [b] *E/Z* ratio was determined by ^{1}H NMR analysis of the crude mixture. [c] 2.0 eq. of **1b** were used. [d] TMEDA was used instead of PMDTA. [e] Isolated yield was shown in the parenthesis.

[f] 5.0 eq. of 1-hexene were used. [g] 3.0 eq. of 1-hexene were used.

Determination of *E*/*Z* structure of **3ab** was conducted by a comparison with the literature known compound after transformation (Scheme S2). The protecting group of the product **3ab** on a nitrogen atom was removed easily by an acid treatment to form the unprotected amine, followed by protection by Boc_2O to form the Boc-protected amine **4ab** in 79% yield for two steps with the same diastereomer ratio as the starting material. The structure of **3ab** was determined by a comparison of ^{1}H and ^{13}C NMR spectra of **4ab** and reported ones.

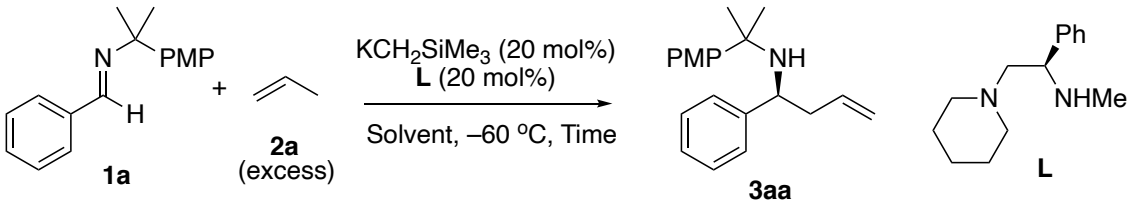
Scheme S2.



3. Optimization of the chiral strong base catalyst system in catalytic asymmetric imino-ene-type allylation reaction

First, screening of solvent was conducted (Table S5). Yields were good use of ether solvent, however, enantioselectivity was very low (entries 1,2). Coordination of solvent to potassium is not effective. Therefore, cumene which is nonpolar solvent was used and moderate enantioselectivity was observed (entry 3).

Table S5 Screening of solvent for the asymmetric reaction

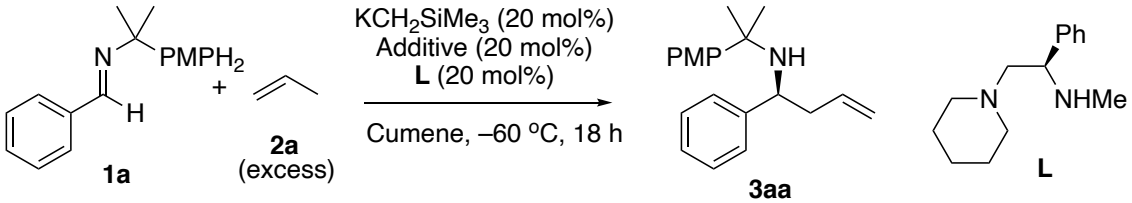


Entry	Solv.	Time [h]	Yield [%]	ee [%]
1[a]	TBME	15	90	5
2[a]	CPME	15	97	3
3	Cumene	18	68	40

[a] 15 h and 10 mol% of KCH_2SiMe_3 and 10 mol% of L1 were used.

Next, additive screening was conducted. LiO^{t}Bu improved reactivity and enantioselectivity although KO^{t}Bu had no effect for the reaction (Table S6, entries 2,3). Then, lithium, potassium, **L**, *tert*-Butoxide mixed system was good for enantioselectivity. To check effect of the anion, alkali metal amides were used as an additive. LiTMP had low effect (entry 4). LiHMDS or NaHMDS suppressed the reaction (entries 5,6). Surprisingly, KHMDS critically improved the enantioselectivity (entry 7). In addition, less amount of KHMDS improved the reactivity (entry 8). This was the best result.

Table S6 Screening of additive for asymmetric reactions



Entry	Additive	Yield [%]	ee [%]
1	—	77	40
2	LiO^{t}Bu	92	65
3	KO^{t}Bu	71	42
4	LiTMP	86	33
5	LiHMDS	NR	—
6	NaHMDS	NR	—
7	KHMDS	35	86
8[a]	KHMDS	96	80
9[b]	KHMDS	96	83

[a] KHMDS 6.7 mol%, [b] KHMDS 5 mol%

II. Experimental Section

1. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with JEOL JNM-ECA500 and JNM-ECX600 spectrometers in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (δ = 0 ppm) for ^{1}H NMR, and $CDCl_3$ served as internal standard (δ = 77.0 ppm) for ^{13}C NMR. Benzotrifluoride (BTF) served as internal standard (δ = –63.72 ppm) for ^{19}F NMR. IR spectra were measured with a JASCO FT/IR-4200 spectrometer. High-performance liquid chromatography was carried out using followed apparatuses; SHIMADZU LC-20AB (liquid chromatograph), SHIMADZU SPD-M20A (Photo diode array detector). Optical rotations were recorded on JASCO P-2100. Column chromatography was conducted on Silica gel 60N (spherical, neutral, Kanto Chem. Co., Inc.) and preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Potassium bis(trimethylsilyl)amide (KHMDS) was purchased from Aldrich Co., Ltd.. Potassium *tert*-butoxide (KO^{t}Bu), sodium *tert*-butoxide (NaO^{t}Bu) and lithium *tert*-butoxide (LiO^{t}Bu) were purchased from Wako Pure Chemical Industrials, Ltd. Lithium 2,2,6,6-tetramethylpiperizide (LiTMP) was prepared according to a literature. [1] (Trimethylsilyl)methyl potassium (KCH_2TMS) was prepared according to a reported procedure. [2] *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDTA) were purchased from Tokyo Chemical Industry Co., Ltd.. Propylene was purchased from Sumitomo Seika Chemicals Co., Ltd.. The other alkenes were purchased from Tokyo Chemical Industry Co., Ltd., and purified by distillation with CaH_2. Imines were prepared according to a literature.[3] Physical data of imine **1d** and **1i** were shown below. **2f**[4] and **2g**[5] were prepared according to literatures. **L1** was prepared according to a literature.[6]

Typical procedure of catalytic allylation reaction of imine 2a using propene 1a (Table 1, entry 10)

KO^{t}Bu (3.4 mg, 3.0 x 10^{-2} mmol), LiTMP (4.5 mg, 3.0 x 10^{-2} mmol) and imine **1a** (152.4 mg, 6.0 x 10^{-1} mmol) were placed in a flame-dried 20 mL flask inside a glove box fulfilled with argon, and the whole system was cooled to –78 ºC. Then, propylene (800 mL as a gas, regulated by a mass flow controller, ca 2.5 mL as a liquid) was introduced to the flask, followed by addition of THF (0.75 mL), PMDTA (5.2 mg, 3.0 x 10^{-2} mmol) via well-dried syringe. The whole reaction mixture was warmed to –50 ºC, and stirred for 3 h. The reaction was quenched by adding water (2.0 mL) and extracted with DCM (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product obtained was purified by PTLC (Et_2O/DCM) to afford the desired product **3aa** (172.6 mg, 0.584 mmol, 97% yield).

Typical procedure of catalytic allylation reaction of imine 1a using 1-hexene 2b (Table 3)

NaO^{t}Bu (2.9 mg, 3.0 x 10^{-2} mmol), LiTMP (4.4 mg, 3.0 x 10^{-2} mmol) and imine **1a** (76.2

mg, 3.0 x 10^{-1} mmol) were placed in a flame-dried 20 mL flask inside a glove box fulfilled with argon, and the whole system was cooled to –78 ºC. Then, 1-hexene (337 μL, 2.7 mmol), CPME (0.375 mL) and TMEDA (8.9 μL, 6.0 x 10^{-2} mmol) was successively added via well-dried syringe. The whole reaction mixture was warmed to 0 ºC, and stirred for 24 h. The reaction was quenched by adding water (2.0 mL) and extracted with DCM (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product obtained was purified by PTLC (Hexane/EtOAc) to afford the desired product **3ab** (90.4 mg, 0.268 mmol, 89% yield, *E/Z* = 91/9).

Procedure of the deprotection of the product 3aa (Scheme 2)

Homoallylic amine **3aa** (25.5 mg, 8.6 x 10^{-2} mmol) was placed in a 20 mL flask, then TFA (3.0 mL) was added to the flask. The reaction mixture was warmed to 50 ºC, and stirred for 3 h, followed by addition of MeOH (3 mL). After stirring for 2 h, the reaction temperature was cooled to r.t., then Et_2O (20 mL) was added to the reaction mixture. The ammonium salt of the product was extracted with 4M aq. HCl (20 mL x 5), then combined water layers were basified by addition of NaOH pellet to pH ~14, followed by extraction with DCM (20 mL x 5). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the desired deprotected amine **4aa** was obtained (11.4 mg, 7.7 x 10^{-2} mmol, 90% yield).

Procedure of the deprotection/Boc-protection of the product 3ab

Homoallylic amine **3ab** (83.2 mg, 2.5 x 10^{-2} mmol, *E/Z* = 86/14) was placed in a 20 mL flask, then TFA (10 mL) was added to the flask. The reaction mixture was warmed to 50 ºC, and stirred for 12 h, followed by addition of MeOH (5 mL). After stirring for 1h, the reaction temperature was cooled to r.t., then the reaction mixture was poured into 4M NaOH aq. to basify the mixture. The mixture was extracted by DCM (20 mL x 5), then combined organic layers were dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was placed in a 50 mL flask, then DCM (2 mL) and TEA (200 μ L, 1.5 mmol, 6.0 eq.) was successively added. After cooling the mixture, Boc_2O (72.3 mg, 2.9 mmol, 1.2 eq.) was added as DCM solution (3 mL), then the reaction mixture was stirred at r.t.. After 12 h, the reaction was quenched by adding water (5.0 mL) and extracted with DCM (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product obtained was purified by PTLC (DCM) to afford the desired product **4ab** (56.8 mg, 0.196 mmol, 79% yield, *E/Z* = 85/15).

Procedure of hydrogenation of the product 3ab (Scheme 2)

Homoallylic amine **3ab** (65.3 mg, 1.9 x 10^{-2} mmol, *E/Z* = 80/20) and Pt/C (5% w/w, 37.8 mg) were placed in a 10 mL flask. To the reaction vessel, MeOH (3.0 mL) was added. A balloon fulfilled with a H_2 gas was set to the reaction vessel, and the reaction atmosphere

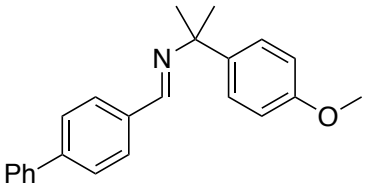
was replaced with a H_2 gas by evacuation/refill cycles. After stirring for 1.5 h, the reaction mixture was filtered over a pad of Celite, and the filtrate was concentrated under reduced pressure. The crude product obtained was purified by PTLC (Hexane/EtOAc) to afford the desired product **5ab** (61.8 mg, 0.182 mmol, 94% yield).

Typical procedure of catalytic asymmetric allylation reaction of imine 1a using propene 2a (Scheme 3)

KCH_2TMS (7.6 mg, 6.0 x 10^{-2} mmol) and KHMDS (3.0 mg, 1.5 x 10^{-2} mmol) were placed in a flame-dried 20 mL flask inside a glove box fulfilled with argon, and the whole system was cooled to –78 ºC. Then, propylene (400 mL as a gas, regulated by a mass flow controller) was introduced to the flask, followed by addition of **L** (13.1 mg, 6.0 x 10^{-2} mmol), which were put in another dried tube fulfilled with argon, was added to the reaction mixture via cannula with cumene (0.2 mL). The reaction temperature was increased to –50 ºC, and the mixture was stirred for 30 min for a catalyst preparation. After that, the reaction temperature was cooled to –60 ºC, and imine **1a** (76.0 mg, 3.0 x 10^{-2} mmol), which were put in another dried tube fulfilled with argon, was added to the reaction mixture via cannula with extra cumene (0.4 mL), then the whole reaction mixture was stirred for 18 h at the same temperature. The reaction was quenched by adding water (2.0 mL) and extracted with DCM (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product obtained was purified by PTLC (Et_2O/DCM) to afford the desired product **3aa** (85.8 mg, 0.290 mmol, 96% yield, 83% ee).

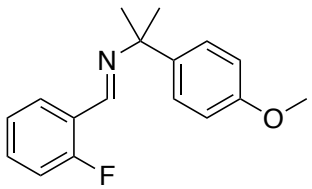
Physical data of employed and obtained compounds

(*E*)-1-([1,1'-biphenyl]-4-yl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)methanimine (1d);



Colorless solid; Mp: 88-89 ºC; IR (neat, cm^{-1}); 418, 558, 769, 811, 832, 1035, 1246, 1508, 1559; HRMS (DART) calcd for $C_{23}H_{24}NO$ $[M + H]^+$ 330.18524. found: 330.18627;^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.19 (1H, s), 7.84 (2H, d, *J* = 8.25 Hz), 7.64-7.61 (4H, m), 7.46-7.44 (2H, m), 7.37-7.36 (3H, m), 6.89-6.88 (2H, m), 3.81 (3H, s), 1.65 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.1, 156.7, 143.1, 140.6, 140.2, 135.9, 128.8, 128.5, 127.6, 127.4, 127.2, 127.1, 113.5, 62.3, 55.2, 29.9.

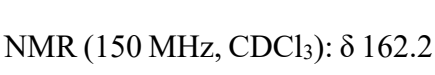
(*E*)-1-(2-fluorophenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)methanimine (1i);



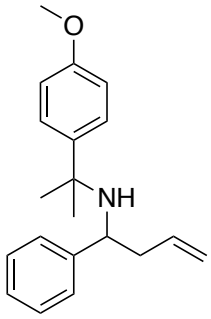
Colorless oil; IR (neat, cm^{-1}); 455, 562, 756, 789, 808, 828, 1033, 1095, 1178, 1243, 1279, 1298, 1455, 1843, 1510, 1580, 1612, 1636, 2971; HRMS (DART) calcd for $C_{17}H_{19}FNO$ $[M + H]^+$ 272.14452. found: 272.14642 ;^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.51 (1H, s), 8.10-8.08 (1H, m), 7.37-7.34 (3H, m), 7.17-7.16 (1H, m), 7.06-7.04 (1H, m), 6.88-6.86 (2H, m), 3.79 (3H, s), 1.64 (6H, s); ^{13}C

NMR (150 MHz, $CDCl_3$): δ 162.2 ($J_{C\text{-}F}$ = 249-95 Hz), 158.0, 150.1 ($J_{C\text{-}F}$ = 4.31 Hz), 139.9, 131.8 ($J_{C\text{-}F}$ = 8.61 Hz), 127.5, 127.1, 124.5 ($J_{C\text{-}F}$ = 8.61 Hz), 124.2 ($J_{C\text{-}F}$ = 2.88 Hz), 115.5 ($J_{C\text{-}F}$ = 20.12 Hz), 113.4, 62.6, 55.1, 29.7; ^{19}F NMR ($CDCl_3$, 465 MHz): δ –123.4.

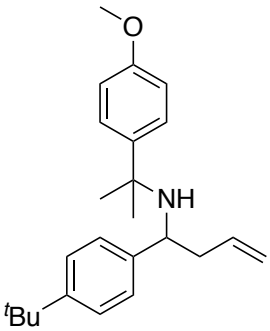
10-(methoxymethoxy)dec-1-ene (2h)[7] Colorless oil; IR (neat, cm^{-1}); 909, 993, 1043, 1111, 1148, 2854, 2926; HRMS (DART) calcd for $C_{12}H_{25}O_2$ $[M + H]^+$ 201.18546. found: 201.18486; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.84-5.77 (1H, m), 5.00 (1H, d, J = 17.16 Hz), 4.92 (1H, d, J = 10.32 Hz), 4.62 (2H, s), 3.51 (2H, t, J = 6.90 Hz), 3.36 (3H, s), 2.05-2.00 (2H, m), 1.61-1.56 (2H, m), 1.39-1.29 (10H, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.1, 114.1, 96.3, 67.8, 55.0, 33.7, 29.7, 29.4, 29.3, 29.0, 28.8, 26.1.



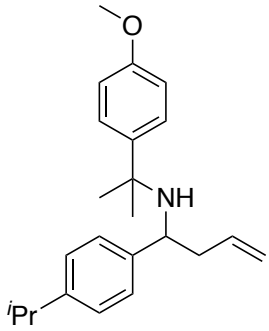
***N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylbut-3-en-1-amine (3aa);** Colorless oil; IR (neat, cm^{-1}); 549, 699, 759, 828, 915, 1035, 1179, 1249, 1298, 1362, 1380, 1510, 1690; HRMS (DART) calcd for $C_{20}H_{26}NO$ $[M + H]^+$ 296.20089. found: 296.19842; HPLC analysis using ULTRON ES-PhCD column (20 mM KH_2PO_4 aq./MeCN = 7/3, 1.5 mL/min, 210 nm, t_R = 11.9 min (minor), 15.7 min (major)); $[\alpha]_D^{25}$ = –71.89 (c 0.27, $CHCl_3$, 83% ee); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.22 (2H, d, J = 8.50 Hz), 7.20-7.15 (4H, m), 7.11-7.09 (1H, m), 6.77 (2H, d, J = 8.50 Hz), 5.48-5.40 (1H, m), 4.96-4.94 (2H, m), 3.74 (3H, s), 3.36 (1H, dd, J = 7.65, 5.95 Hz), 2.18-2.14 (2H, m), 1.67 (1H, br), 1.25 (3H, s), 1.11 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 147.4, 140.5, 136.0, 128.0, 127.2, 127.1, 126.3, 117.5 ,113.1, 57.2, 56.0, 55.2, 44.9, 32.1, 28.2.



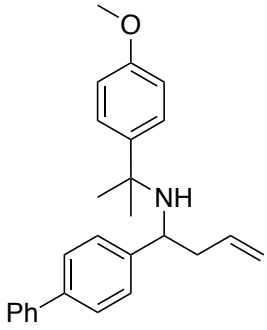
1-(4-(*tert*-butyl)phenyl)-N-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3ba); Colorless oil; IR (neat, cm^{-1}); 566, 634, 735, 826, 915, 1036, 1109, 1178, 1249, 1299, 1362, 1463, 1510, 1609, 2961; HRMS (DART) calcd for $C_{24}H_{34}NO$ $[M + H]^+$ 352.26349. found: 352.26659; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.29-7.27 (2H, m), 7.24-7.23 (2H, m), 7.13 (2H, d, J = 8.25 Hz), 6.81 (2H, d, J = 8.94 Hz), 5.55-5.48 (1H, m), 5.02-5.01 (2H, m), 3.80 (3H, s), 3.41 (1H, dd, J = 7.90, 5.84 Hz), 2.28-2.17 (2H, m), 1.78 (1H, br), 1.33 (3H, s), 1.30 (9H, s), 1.20 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 149.0, 144.0, 140.5, 136.3, 127.2, 126.6, 124.8, 117.3, 113.0, 56.8, 55.9, 55.2, 44.7, 34.3, 31.9, 31.4, 28.5.



1-(4-isopropylphenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3ca);

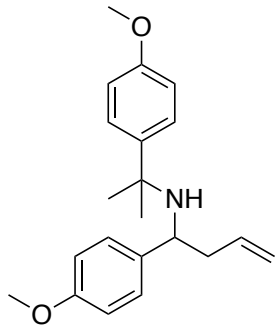


Colorless oil; IR (neat, cm^{-1}); 565, 826, 915, 1036, 1176, 1249, 1296, 1362, 1380, 1462, 1510, 1609, 2958; HRMS (DART) calcd for $C_{23}H_{32}NO$ $[M + H]^+$ 338.24784. found: 338.24342; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.29-7.28 (2H, m), 7.13 (2H, d, J = 8.25 Hz), 7.08 (2H, d, J = 8.25 Hz), 6.82 (2H, d, J = 8.94 Hz), 5.55-5.48 (1H, m), 5.02-5.01 (2H, m), 3.81 (3H, s), 3.40 (1H, dd, J = 7.90, 5.84 Hz), 2.89-2.84 (1H, m), 2.25-2.20 (2H, m), 1.60 (1H, br), 1.33 (3H, s), 1.23 (6H, d, J = 6.87 Hz), 1.19 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 146.8, 144.5, 140.5, 136.3, 127.2, 126.9, 125.9, 117.3, 113.0, 57.0, 56.0, 55.2, 44.8, 33.6, 32.0, 28.4, 24.1.



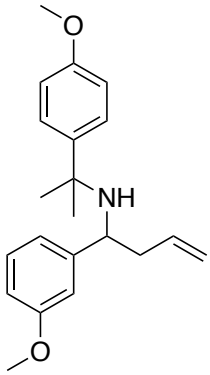
1-([1,1'-biphenyl]-4-yl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3da); Colorless oil; IR (neat, cm^{-1}); 565, 696, 732, 765, 828, 913, 1035, 1178, 1248, 1298, 1362, 1379, 1485, 1510, 1609, 2973; HRMS (DART) calcd for $C_{26}H_{30}NO$ $[M + H]^+$ 372.23219. found: 372.23012; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.59 (2H, d, J = 8.25 Hz), 7.48 (2H, d, J = 8.25 Hz), 7.41 (2H, t, J = 7.22 Hz), 7.31-7.30 (5H, m), 6.83 (2H, d, J = 8.94 Hz), 5.56-5.52 (1H, m), 5.05-5.03 (2H, m), 3.79 (3H, s), 3.48 (1H, dd, J = 7.90, 5.84 Hz), 2.32-2.21 (2H, m), 1.82 (1H, s), 1.35 (3H, s), 1.23 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 146.5, 141.1, 141.1, 140.4, 139.1, 135.9, 128.6, 127.4, 127.2, 126.9, 126.7, 117.6, 113.1, 56.9, 56.0, 55.2, 44.8, 32.0, 28.4.

1-(4-methoxyphenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3ea);



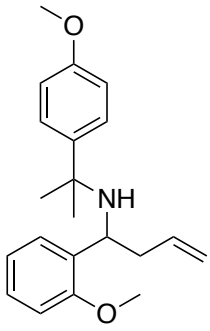
Colorless oil; IR (neat, cm^{-1}); 551, 826, 915, 1033, 1241, 1299, 1360, 1379, 1463, 1508, 1609; HRMS (DART) calcd for $C_{21}H_{28}NO_2$ $[M + H]^+$ 326.21146. found: 326.21480; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.30-7.27 (2H, m), 7.14-7.13 (2H, m), 6.83 (2H, d, J = 8.25 Hz), 6.79 (2H, d, J = 8.94 Hz), 5.53-5.47 (1H, m), 5.01-5.00 (2H, m), 3.81 (3H, s), 3.78 (3H, s), 3.38 (1H, dd, J = 7.56, 6.19 Hz), 2.23-2.20 (2H, m), 1.79 (1H, s), 1.32 (3H, s), 1.18 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.1, 157.8, 140.4, 139.3, 136.1, 128.0, 127.2, 117.3, 113.3, 113.1, 56.6, 56.0, 55.2, 55.1, 44.9, 32.1, 28.2.

1-(3-methoxyphenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3fa);



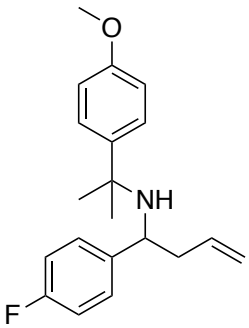
Colorless oil; IR (neat, cm^{-1}); 566, 701, 779, 828, 915, 1035, 1178, 1249, 1380, 1435, 1463, 1510, 1599, 1609, 2834, 2964; HRMS (DART) calcd for $C_{21}H_{28}NO_2$ $[M + H]^+$ 326.21146. found: 326,20984; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.30 (2H, d, J = 8.94 Hz), 7.16 (1H, t, J = 7.56 Hz), 6.83 (4H, t, J = 6.19 Hz), 6.72 (1H, d, J = 8.25 Hz), 5.54-5.47 (1H, m), 5.03-5.01 (2H, m), 3.81 (3H, s), 3.79 (3H, s), 3.40 (1H, dd, J = 7.56, 6.19 Hz), 2.26-2.21 (2H, m), 1.78 (1H, br), 1.33 (3H, s), 1.21 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.4, 157.9, 149.2, 140.4, 135.9, 128.9, 127.2, 119.5, 117.5, 113.1, 112.6, 111.7, 57.2, 56.0, 55.2, 55.1, 44.7, 32.0, 28.1.

1-(2-methoxyphenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3ga);



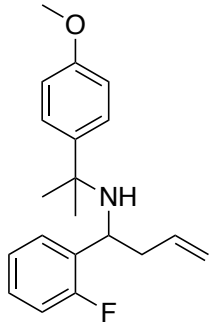
Colorless oil; IR (neat, cm^{-1}); 561, 752, 799, 828, 912, 1031, 1176, 1233, 1438, 1462, 1486, 1510, 1599, 1609, 2961; HRMS (DART) calcd for $C_{21}H_{28}NO_2$ $[M + H]^+$ 326.21146. found: 326.21087; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.39 (1H, d, J = 6.87 Hz), 7.34 (2H, d, J = 8.94 Hz), 7.13 (1H, t, J = 7.90 Hz), 6.88 (1H, t, J = 7.56 Hz), 6.80 (2H, d, J = 8.94 Hz), 6.76 (1H, d, J = 8.25 Hz), 5.57-5.53 (1H, m), 4.96-4.94 (2H, m), 3.91 (1H, t, J = 6.87 Hz), 3.80 (3H, s), 3.76 (3H, s), 2.34-2.29 (1H, m), 2.23-2.22 (1H, m), 1.29 (3H, s), 1.24 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.7, 156.2, 141.0, 136.7, 135.3, 128.5, 127.2, 126.9, 120.2, 116.6, 112.9, 110.2, 55.8, 55.2, 55.2, 55.1, 42.9, 31.5, 28.4.

1-(4-fluorophenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3ha);



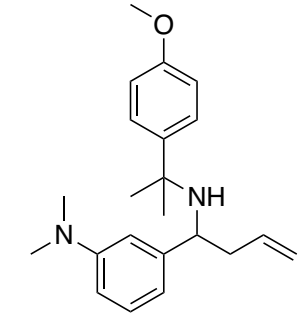
Colorless oil; IR (neat, cm^{-1}); 544, 828, 916, 1035, 1152, 1179, 1218, 1296, 1380, 1506, 1603; HRMS (DART) calcd for $C_{20}H_{25}FNO$ $[M + H]^+$ 314.19147. found: 314.19112; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.28-7.25 (2H, m), 7.20-7.18 (2H, m), 6.91 (2H, t, J = 8.94 Hz), 6.82 (2H, d, J = 8.25 Hz), 5.52-5.45 (1H, m), 5.02-5.00 (2H, m), 3.80 (3H, s), 3.42 (1H, dd, J = 7.90, 5.84 Hz), 2.23-2.16 (2H, m), 1.76 (1H, s), 1.32 (3H, s), 1.17 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.5 ($J_{C\text{-}F}$ = 241.28 Hz), 157.9, 143.0 ($J_{C\text{-}F}$ = 2.88 Hz), 140.2, 135.7, 128.4 ($J_{C\text{-}F}$ = 7.17 Hz), 127.2, 117.8, 114.6 ($J_{C\text{-}F}$ = 21.54 Hz), 113.1, 56.5, 56.0, 55.2, 44.9, 32.0, 28.3; ^{19}F NMR ($CDCl_3$, 465 MHz): δ –118.2.

1-(2-fluorophenyl)-*N*-(2-(4-methoxyphenyl)propan-2-yl)but-3-en-1-amine (3ia);
Colorless oil; IR (neat, cm^{-1}); 755, 828, 916, 1033, 1178, 1249, 1299, 1380, 1453, 1485, 1510, 1583, 1610; HRMS (DART) calcd for $C_{20}H_{25}FNO$ $[M + H]^+$ 314.19147. found: 314.19180; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.48-7.47 (1H, m), 7.34-7.31 (2H, m), 7.15-7.11 (1H, m), 7.06 (1H, t, J = 7.56 Hz), 6.91-6.89 (1H, m), 6.82-6.79 (2H, m), 5.55-5.49



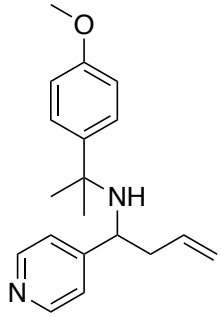
(1H, m), 4.99-4.98 (2H, m), 3.87 (1H, dd, J = 7.90, 5.84 Hz), 3.80 (3H, s), 2.29-2.24 (2H, m), 1.32 (3H, s), 1.25 (3H, s).; ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.8 ($J_{C\text{-}F}$ = 242.73 Hz), 157.9, 140.3, 135.5, 134.0 ($J_{C\text{-}F}$ = 12.93 Hz), 129.1 ($J_{C\text{-}F}$ = 5.75 Hz), 127.5 ($J_{C\text{-}F}$ = 8.62 Hz), 127.1, 123.7 ($J_{C\text{-}F}$ = 2.88 Hz), 117.5, 114.8 ($J_{C\text{-}F}$ = 21.54 Hz), 113.1, 55.9, 55.1, 50.0, 43.2, 31.4, 28.2; ^{19}F NMR ($CDCl_3$, 465 MHz): δ –121.5.

4-(1-((2-(4-methoxyphenyl)propan-2-yl)amino)but-3-en-1-yl)-*N*,*N*-dimethylaniline (3ja); Colorless oil; IR (neat, cm^{-1}); 549, 816, 828, 912, 946, 1035, 1176, 1248, 1298, 1343, 1510, 1612, 2973; HRMS (DART) calcd for $C_{22}H_{31}N_2O$ $[M + H]^+$ 339.24309. found: 339.24358; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.30 (2H, d, J = 8.94 Hz), 7.08 (2H, d, J = 8.94 Hz), 6.84 (2H, d, J = 8.94 Hz), 6.65 (2H, d, J = 8.94 Hz), 5.54-5.49 (1H, m), 5.01-4.99 (2H, m), 3.81 (3H, s), 3.34 (1H, t, J = 7.22 Hz), 2.91 (6H, s), 2.25-2.20 (2H, m), 1.77 (1H, br), 1.33 (3H, s), 1.20 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 149.3, 140.6, 136.5, 135.1, 127.7, 127.2, 117.0, 113.0, 112.4, 56.6, 56.0, 55.2, 44.8, 40.7, 32.2, 28.3.



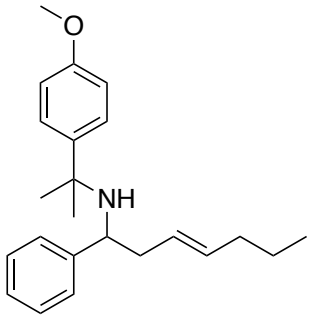
3-(1-((2-(4-methoxyphenyl)propan-2-yl)amino)but-3-en-1-yl)-*N*,*N*-dimethylaniline (3ka); Colorless oil; IR (neat, cm^{-1}); 701, 775, 800, 828, 914, 994, 1034, 1178, 1250, 1300, 1348, 1438, 1511, 1602; HRMS (DART) calcd for $C_{22}H_{31}N_2O$ $[M + H]^+$ 339.24364. found: 339.24323;^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31-7.30 (2H, m), 7.14-7.11 (1H, m), 6.84-6.82 (2H, m), 6.63-6.61 (2H, m), 6.58-6.56 (1H, m), 5.54-5.51 (1H, m), 5.03-4.99 (2H, m), 3.80 (3H, s), 3.36-3.35 (1H, m), 2.92 (6H, s), 2.27-2.23 (2H, m), 1.34 (3H, s), 1.23 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 150.5, 148.1, 140.6, 136.4, 128.6, 127.2, 117.2, 115.7, 113.1, 111.7, 110.8, 57.7, 56.1, 55.2, 44.8, 40.7, 32.0, 28.2.

***N*-(2-(4-methoxyphenyl)propan-2-yl)-1-(pyridin-4-yl)but-3-en-1-amine (3la);**



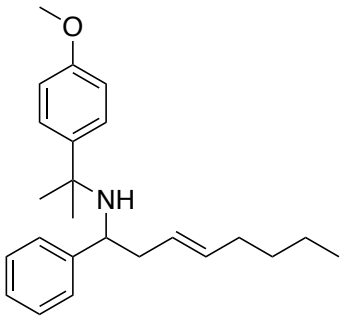
Colorless oil; IR (neat, cm^{-1}); 558, 828, 918, 992, 1033, 1178, 1246, 1298, 1380, 1410, 1510, 1596; HRMS (DART) calcd for $C_{19}H_{25}N_2O$ $[M + H]^+$ 297.19614. found: 297.19312; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.46-8.45 (2H, m), 7.28-7.25 (2H, m), 7.21-7.20 (2H, m), 6.81 (2H, d, *J* = 9.07 Hz), 5.51-5.43 (1H, m), 5.06-5.02 (2H, m), 3.80 (3H, s), 3.44 (1H, dd, *J* = 8.22, 5.38 Hz), 2.25-2.13 (2H, m), 1.91 (1H, br), 1.33 (3H, s), 1.20 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.0, 156.6, 149.4, 139.7, 134.8, 127.1, 122.4, 118.4, 113.1, 56.2, 56.1, 55.2, 44.1, 31.6, 28.3.

***N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylhept-3-en-1-amine (3ab, *E/Z* = 91/9);**

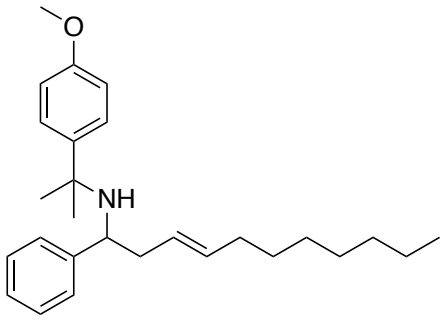


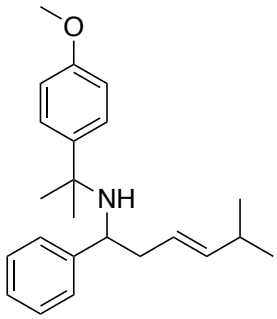
Colorless oil; IR (neat, cm^{-1}); 556, 701, 828, 971, 1036, 1179, 1249, 1453, 1510, 1609, 2927, 2957; HRMS (DART) calcd for $C_{23}H_{32}NO$ $[M + H]^+$ 338.24784. found: 338.24698; ^1H NMR ($CDCl_3$, 600 MHz, major): δ 7.30-7.22 (6H, m), 7.17-7.14 (1H, m), 6.83-6.81 (2H, m), 5.45-5.40 (1H, m), 5.12-5.09 (1H, m), 3.81 (3H, s), 3.36 (1H, dd, *J* = 8.28, 4.58 Hz), 2.16-2.11 (2H, m), 1.98-1.94 (2H, m), 1.82 (1H, s), 1.36-1.33 (5H, m), 1.16 (3H, s), 0.88 (3H, t, *J* = 7.56 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, major): δ 157.8, 147.8, 140.5, 133.7, 127.9, 127.5, 127.2, 127.0, 126.1, 113.0, 57.4, 56.0, 55.2, 43.7, 34.7, 32.2, 28.0, 22.5, 13.7.

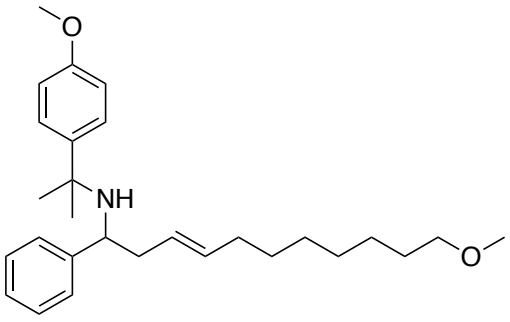
***N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenyloct-3-en-1-amine (3ac, *E/Z* = 91/9);**

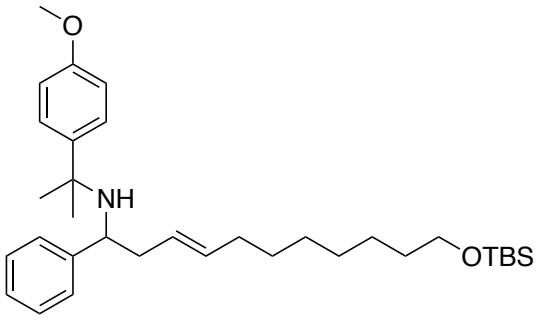


Colorless oil; IR (neat, cm^{-1}); 556, 699, 828, 971, 1036, 1178, 1249, 1298, 1379, 1510, 1609, 2926, 2957; HRMS (DART) calcd for $C_{24}H_{34}NO$ $[M + H]^+$ 352.26349. found: 352.26524; ^1H NMR ($CDCl_3$, 600 MHz, major): δ 7.31-7.22 (6H, m), 7.17-7.14 (1H, m), 6.83-6.83 (2H, m), 5.45-5.40 (1H, m), 5.13-5.08 (1H, m), 3.80 (3H, s), 3.36 (1H, dd, *J* = 8.28, 4.86 Hz), 2.17-2.09 (2H, m), 1.98 (2H, t, *J* = 5.84 Hz), 1.82 (1H, br), 1.32-1.29 (7H, m), 1.16 (3H, s), 0.89 (3H, t, *J* = 7.22 Hz).; ^{13}C NMR (150 MHz, $CDCl_3$, major): δ 157.8, 147.8, 140.5, 133.9, 127.9, 127.3, 127.2, 127.0, 126.1, 113.0, 57.4, 56.0, 55.2, 43.7, 32.3, 32.2, 31.5, 28.0, 22.2, 13.9.

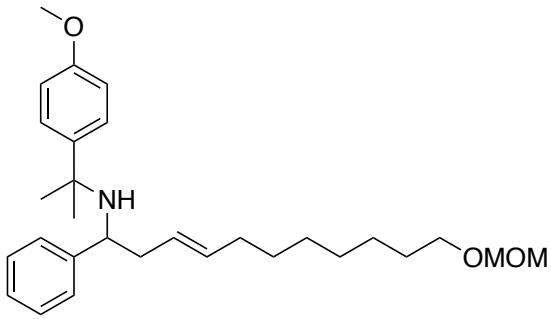
***N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylundec-3-en-1-amine (3ad, *E/Z* = 90/10);** 
Colorless oil; IR (neat, cm^{-1}); 556, 699, 828, 971, 1036, 1179, 1249, 1299, 1453, 1510, 1609, 2853, 2924; HRMS (DART) calcd for $C_{27}H_{40}NO$ $[M + H]^+$ 394.31044. found: 394.30924; ^1H NMR ($CDCl_3$, 600 MHz, major): δ 7.31-7.14 (7H, m), 6.83 (2H, d, *J* = 11.68 Hz), 5.46-5.41 (1H, m), 5.11-5.08 (1H, m), 3.80 (3H, s), 3.36 (1H, dd, *J* = 8.28, 4.86 Hz), 2.17-2.09 (2H, m), 1.98-1.96 (2H, m), 1.82 (1H, s), 1.31-1.27 (13H, m), 1.16 (3H, s), 0.88 (3H, t, *J* = 7.22 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, detectable peaks): δ 157.8, 147.8, 140.5, 134.0, 127.9, 127.3, 127.2, 127.1, 127.1, 127.0, 126.1, 113.1, 113.0, 57.4, 56.0, 55.2, 43.7, 32.6, 32.3, 31.8, 29.4, 29.2, 29.2, 28.0, 22.7, 14.1.

***N*-(2-(4-methoxyphenyl)propan-2-yl)-5-methyl-1-phenylhex-3-en-1-amine (3ae, *E/Z* = 83/17);** 
Colorless oil; IR (neat, cm^{-1}); 555, 699, 828, 973, 1036, 1179, 1249, 1299, 1362, 1380, 1463, 1510, 1609, 2957; HRMS (DART) calcd for $C_{23}H_{32}NO$ $[M + H]^+$ 338.24784. found: 338.24770; ^1H NMR ($CDCl_3$, 600 MHz, major): δ7.31-7.14 (7H, m), 6.84-6.82 (2H, m), 5.41 (1H, dd, *J* = 15.46, 6.53 Hz), 5.10-5.05 (1H, m), 3.81 (3H, s), 3.35 (1H, dd, *J* = 8.94, 5.52 Hz), 2.25-2.24 (1H, m), 2.15-2.09 (2H, m), 1.79 (1H, br), 1.32 (3H, s), 1.15 (3H, s), 0.98 (3H, d, *J* = 6.87 Hz), 0.95 (3H, d, *J* = 6.87 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, detectable peaks): δ 157.8, 147.9, 141.1, 140.5, 127.9, 127.2, 127.0, 126.1, 124.3, 113.1, 113.0, 57.5, 56.0, 55.2, 43.6, 32.3, 31.0, 28.1, 22.5, 22.5.

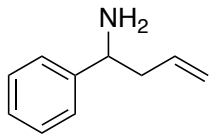
11-methoxy-*N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylundec-3-en-1-amine (3af, *E/Z* = 90/10); 
Colorless oil; IR (neat, cm^{-1}); 556, 701, 828, 971, 1036, 1116, 1179, 1249, 1299, 1510, 1609, 2926; HRMS (DART) calcd for $C_{28}H_{42}NO_2$ $[M + H]^+$ 424.32155. found: 424.32145; ^1H NMR ($CDCl_3$, 600 MHz, major): δ 7.31-7.21 (6H, m), 7.17-7.15 (1H, m), 6.83 (2H, d, *J* = 8.94 Hz), 5.42-5.39 (1H, m), 5.12-5.06 (1H, m), 3.81 (3H, s), 3.36 (3H, m), 3.33 (3H, s), 2.17-2.09 (2H, m), 1.98-1.96 (2H, m), 1.82 (1H, br), 1.58-1.53 (2H, m), 1.34-1.28 (11H, m), 1.16 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, detectable peaks): δ 157.8, 147.8, 140.5, 133.8, 127.8, 127.8, 127.3, 127.1, 127.0, 126.1, 113.0, 113.0, 72.8, 58.5, 57.4, 56.0, 55.1, 43.6, 32.5, 32.2, 29.6, 29.3, 29.1, 28.0, 26.0.

11-((*tert*-butyldimethylsilyl)oxy)-*N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylundec-3-en-1-amine (3ag, *E/Z* = 89/11); 

Colorless oil; IR (neat, cm^{-1}); 556, 659, 701, 774, 828, 971, 1038, 1095, 1179, 1249, 1462, 1510, 1610, 2854, 2927; HRMS (DART) calcd for $C_{33}H_{54}NO_2Si$ $[M + H]^+$ 524.39238. found: 524.39008; ^1H NMR ($CDCl_3$, 600 MHz, major): δ 7.24-7.20 (6H, m), 7.11-7.10 (1H, m), 6.78 (2H, d, *J* = 8.25 Hz), 5.40-5.35 (1H, m), 5.06-5.04 (1H, m), 3.76 (3H, s), 3.55 (2H, t, *J* = 6.53 Hz), 3.31 (1H, dd, *J* = 8.22, 4.80 Hz), 2.12-2.05 (2H, m), 1.94-1.91 (2H, m), 1.75 (1H, br), 1.47-1.46 (2H, m), 1.27-1.24 (11H, m), 1.11 (3H, s), 0.85 (9H, s), 0.00 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$, detectable peaks): δ 157.8, 147.7, 140.5, 133.9, 127.9, 127.3, 127.1, 127.0, 126.1, 113.0, 72.8, 63.3, 57.4, 56.0, 55.1, 43.6, 32.9, 32.5, 32.2, 29.3, 29.3, 28.0, 25.9, 25.7, 18.3, –5.2.

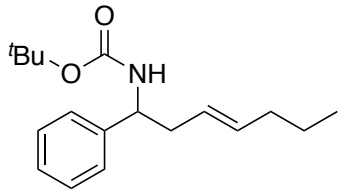
11-(methoxymethoxy)-*N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylundec-3-en-1-amine (3ah, *E/Z* = 92/8); 

Colorless oil; IR (neat, cm^{-1}); 558, 701, 732, 758, 828, 916, 971, 1036, 1109, 1143, 1179, 1249, 1453, 1510, 1609, 2927; HRMS (DART) calcd for $C_{29}H_{44}NO_3$ $[M + H]^+$ 454.33212. found: 454.33283; ^1H NMR ($CDCl_3$, 600 MHz, major): δ 7.29-7.23 (6H, m), 7.17-7.14 (1H, m), 6.82 (2H, d, *J* = 8.94 Hz), 5.44-5.39 (1H, m), 5.12-5.07 (1H, m), 4.62 (2H, s), 3.81 (3H, s), 3.51 (2H, t, *J* = 6.87 Hz), 3.37-3.34 (4H, m), 2.17-2.09 (2H, m), 1.99-1.95 (2H, m), 1.61-1.56 (2H, m), 1.35-1.28 (11H, m), 1.16 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, detectable peaks): δ 157.8, 147.7, 140.4, 133.8, 127.8, 127.3, 127.1, 127.0, 126.1, 112.9, 96.3, 67.7, 57.3, 55.9, 55.1, 55.0, 43.6, 32.4, 32.2, 29.7, 29.3, 29.2, 29.1, 28.0, 26.1.

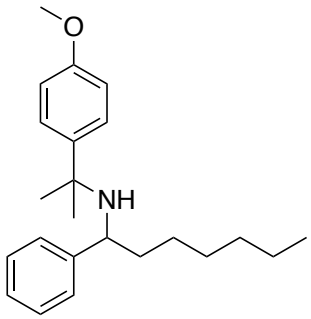
1-phenylbut-3-en-1-amine (4aa); 

Colorless oil; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.26 (4H, m), 7.20-7.16 (1H, m), 5.72-5.65 (1H, m), 5.06-5.02 (2H, m), 3.93-3.92 (1H, m), 2.41-2.39 (1H, m), 2.31-2.26 (1H, m), 1.44 (2H, br); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.9, 135.4, 128.4, 126.9, 126.3, 117.6, 55.4, 44.2. Data are in accordance with a literature.[8]

***tert*-butyl (1-phenylhept-3-en-1-yl)carbamate (4ab, *E/Z* = 78/22);** White solid; ^{1}H NMR ($CDCl_3$, 600 MHz, major): δ 7.32-7.31 (2H, m), 7.27-7.22 (3H, m), 5.51-5.46 (1H, m), 5.28-5.26 (1H, m), 4.88 (1H, br), 4.68 (1H, br), 2.45-2.43 (2H, m), 1.97-1.95 (2H, m), 1.37-1.32 (11H, m), 0.85 (3H, t, *J* = 7.56 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, major): δ 155.2, 142.6, 134.3, 128.4, 126.9, 126.2, 125.3, 79.3, 54.3, 40.1, 34.6, 28.3, 22.6, 22.4, 13.5. Data are in accordance with a literature.[9]



***N*-(2-(4-methoxyphenyl)propan-2-yl)-1-phenylheptan-1-amine (5ab);** Colorless oil; IR (neat, cm^{-1}); 556, 699, 761, 828, 1036, 1178, 1249, 1299, 1453, 1510, 1609, 2854, 2927; HRMS (DART) calcd for $C_{23}H_{34}NO$ $[M + H]^+$ 340.26349. found: 340.26320; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31 (2H, d, *J* = 8.94 Hz), 7.23 (2H, t, *J* = 7.56 Hz), 7.16-7.15 (3H, m), 6.83 (2H, d, *J* = 8.25 Hz), 3.80 (3H, s), 3.33 (1H, t, *J* = 6.87 Hz), 1.65 (1H, br), 1.55-1.46 (2H, m), 1.33 (3H, s), 1.19-1.17 (5H, m), 1.13-1.09 (5H, m), 0.94-0.91 (1H, m), 0.82 (3H, t, *J* = 6.87 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 147.9, 140.6, 127.9, 127.1, 127.1, 126.1, 113.1, 58.0, 56.1, 55.2, 40.3, 32.0, 31.7, 29.1, 28.6, 26.3, 22.5, 14.0.



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III. NMR and HPLC charts

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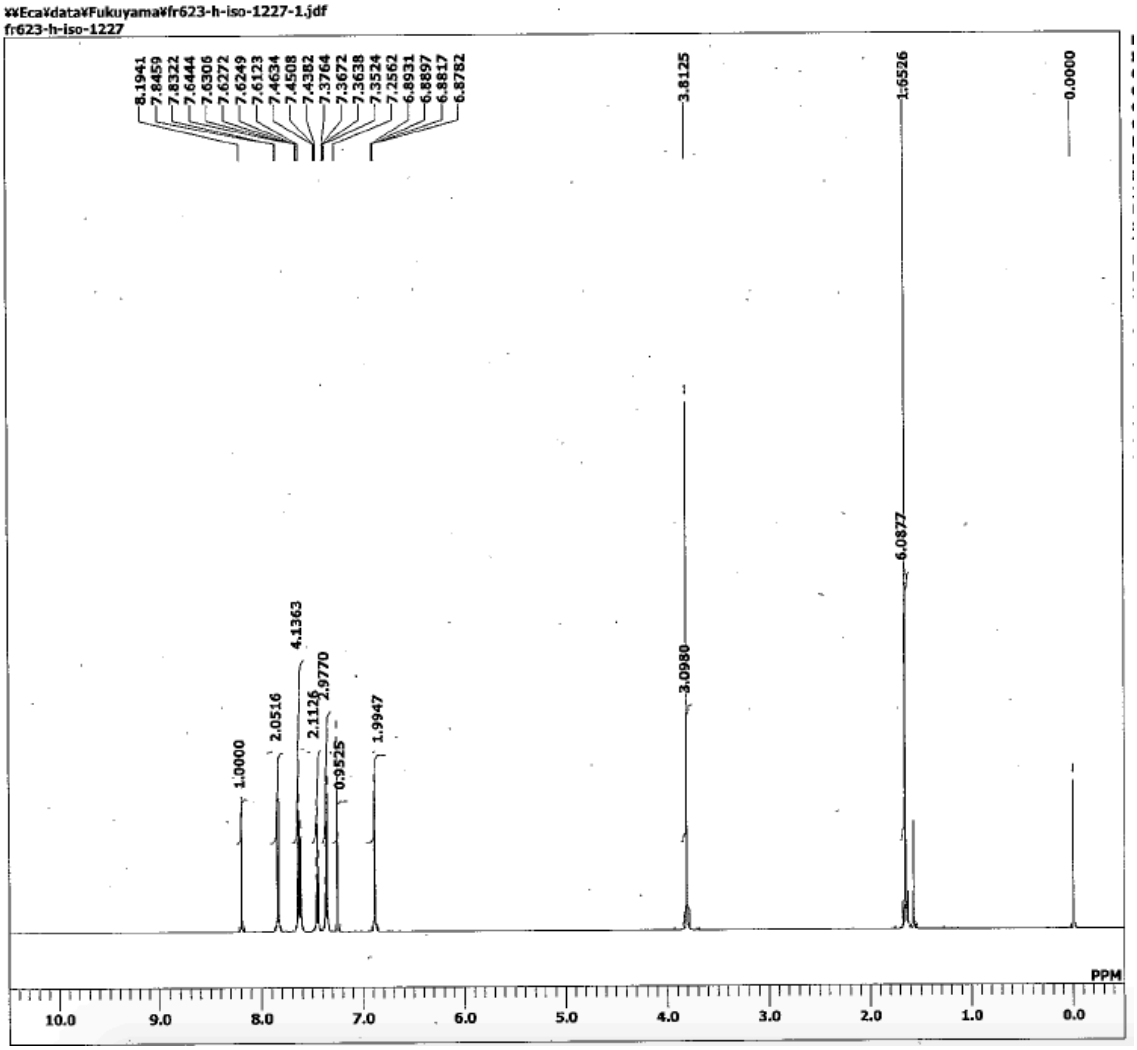

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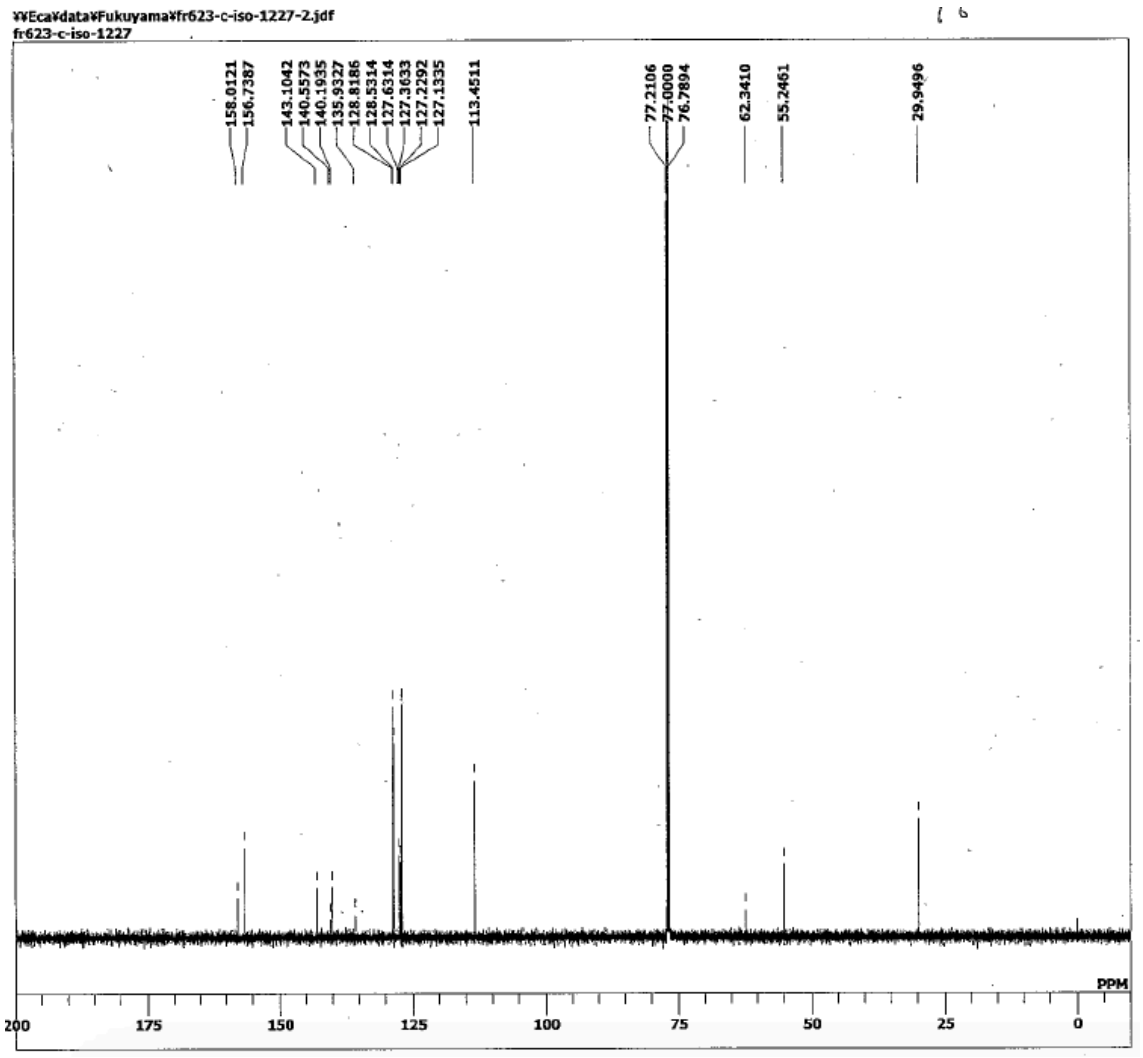
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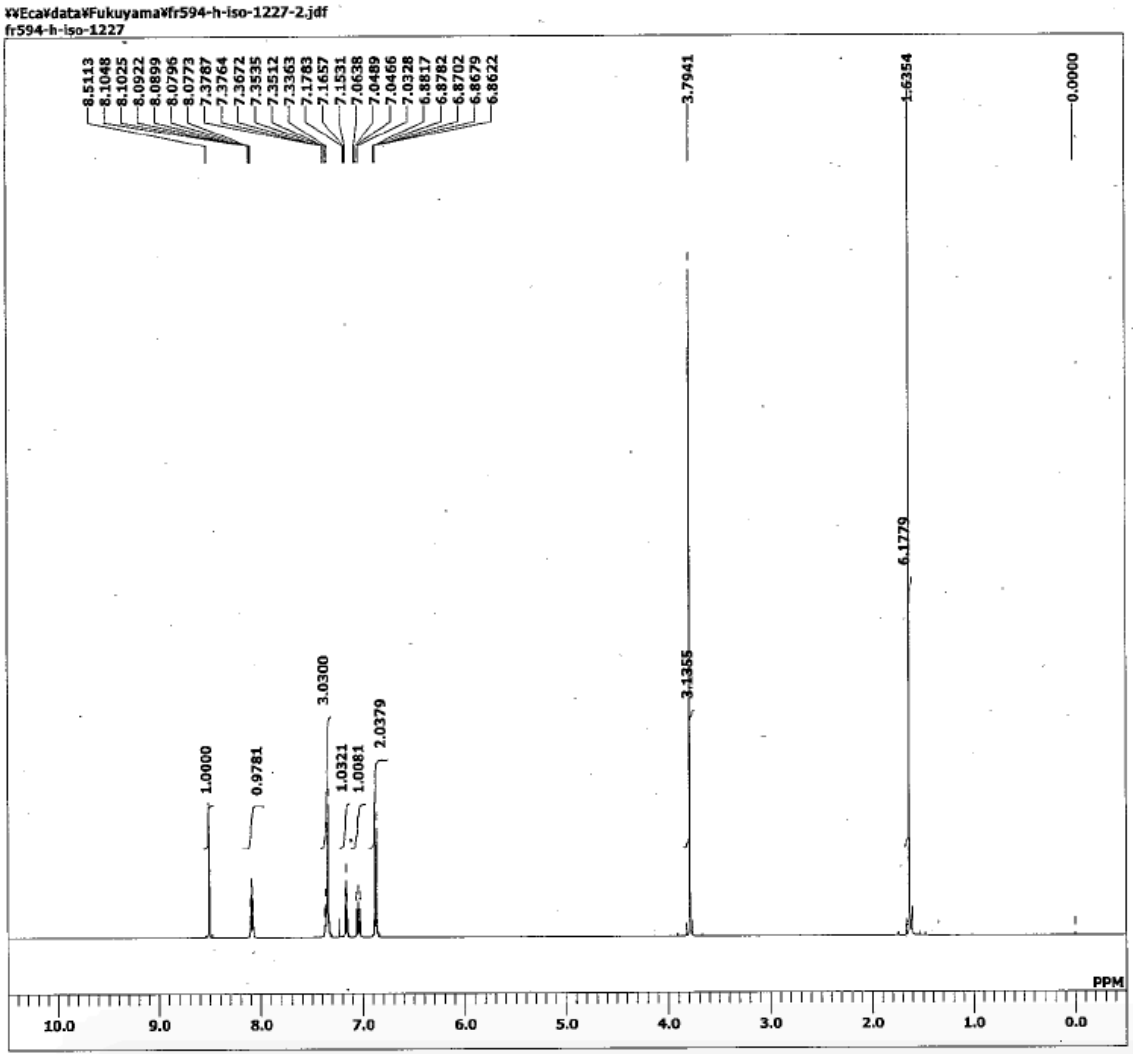
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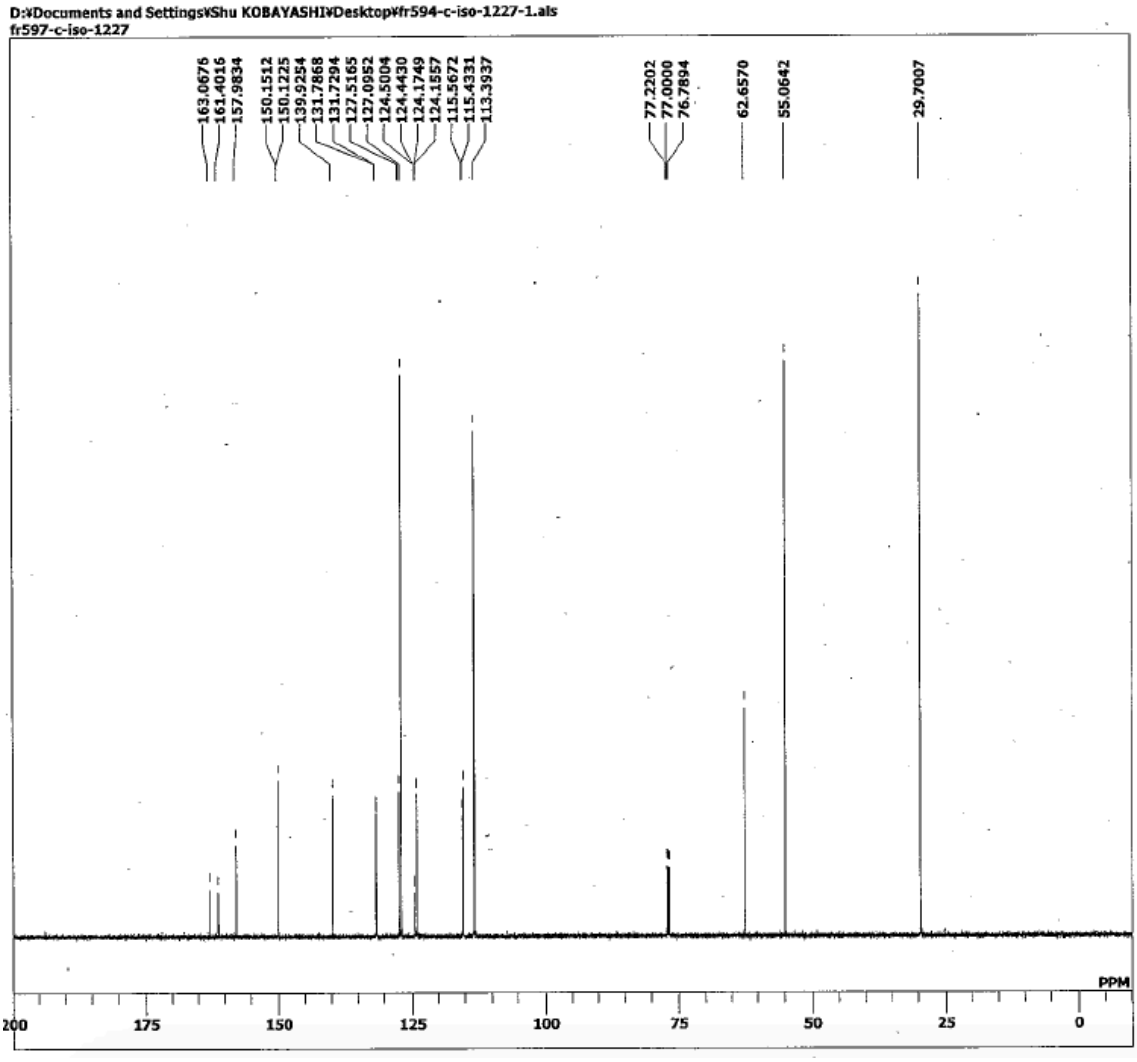
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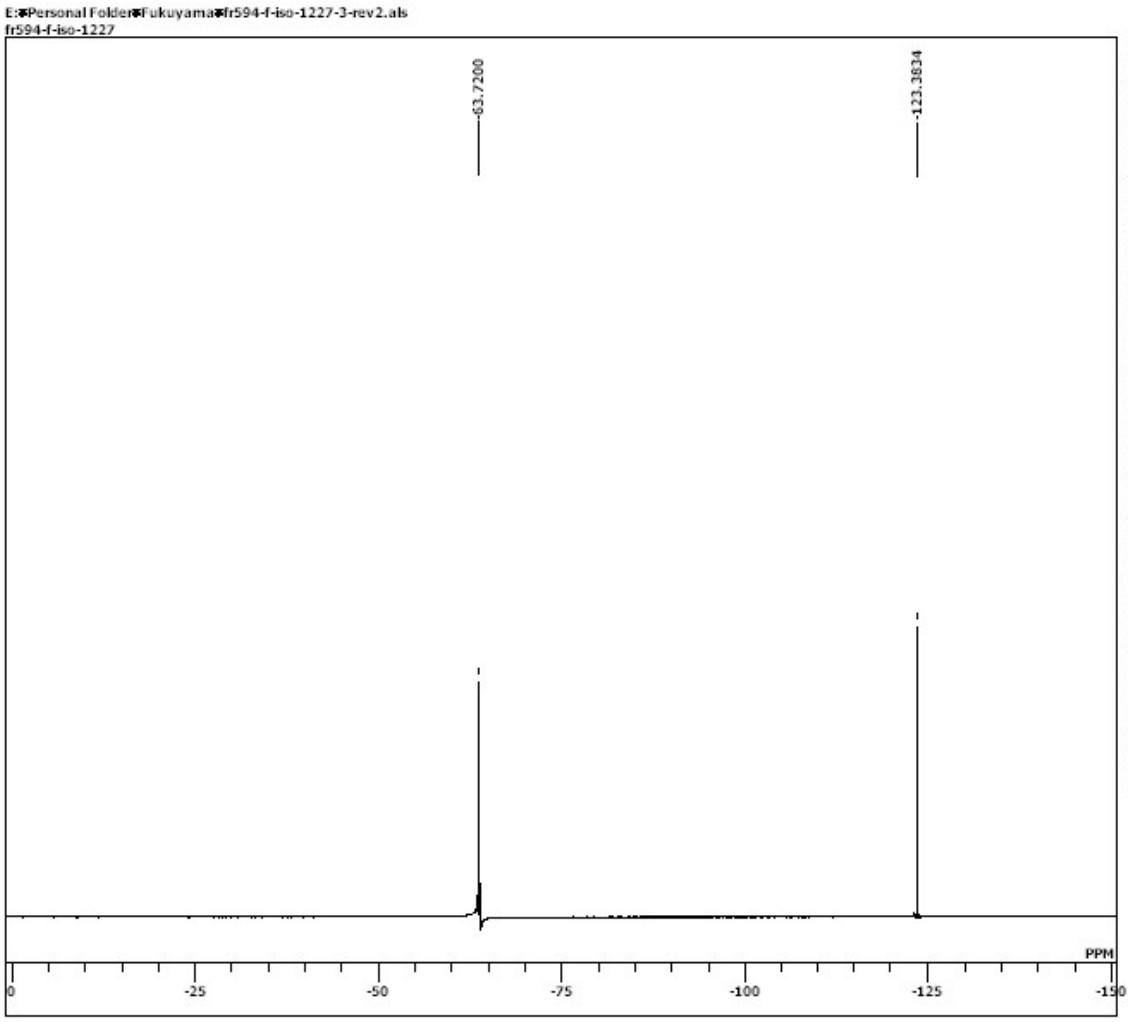
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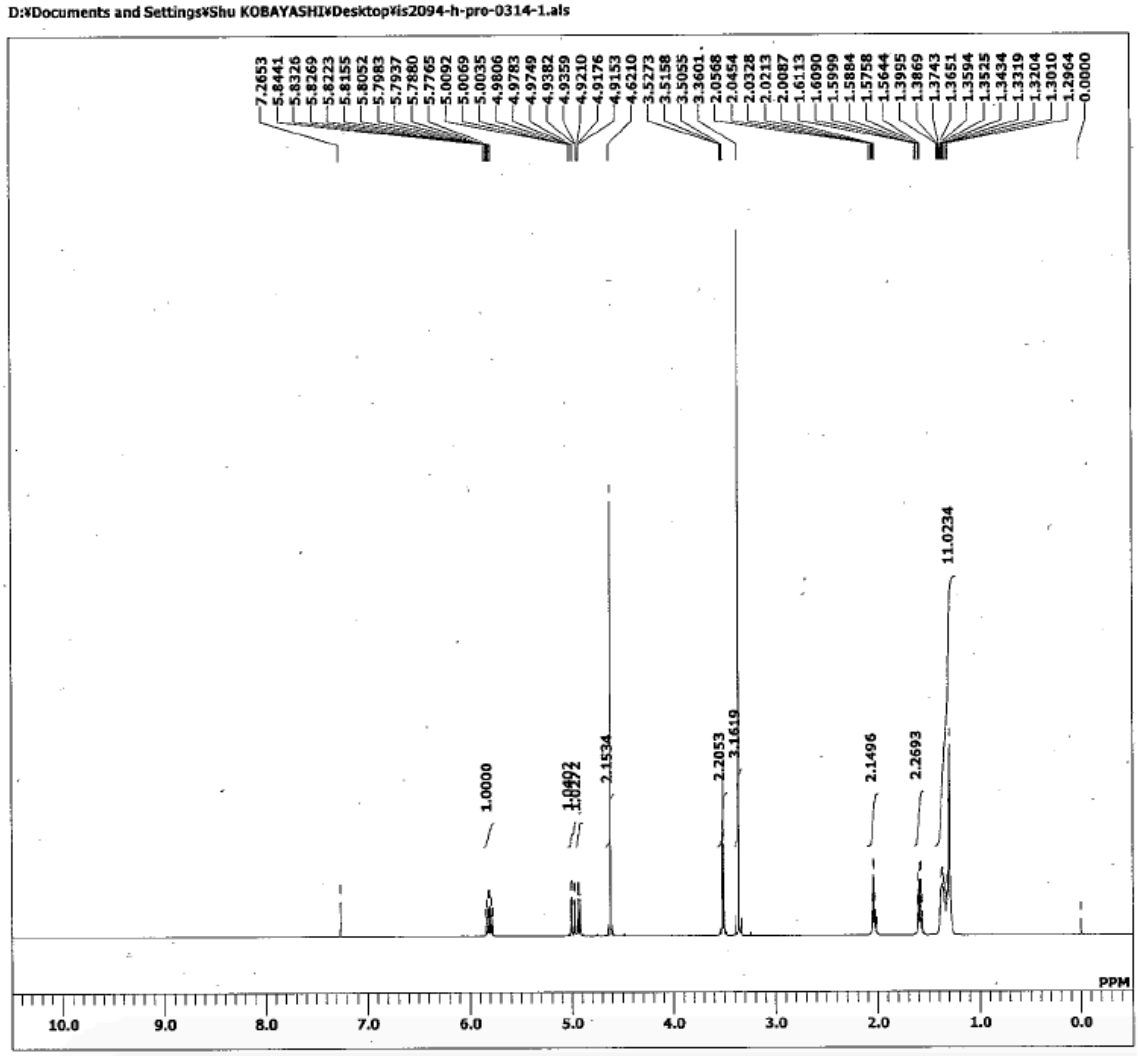
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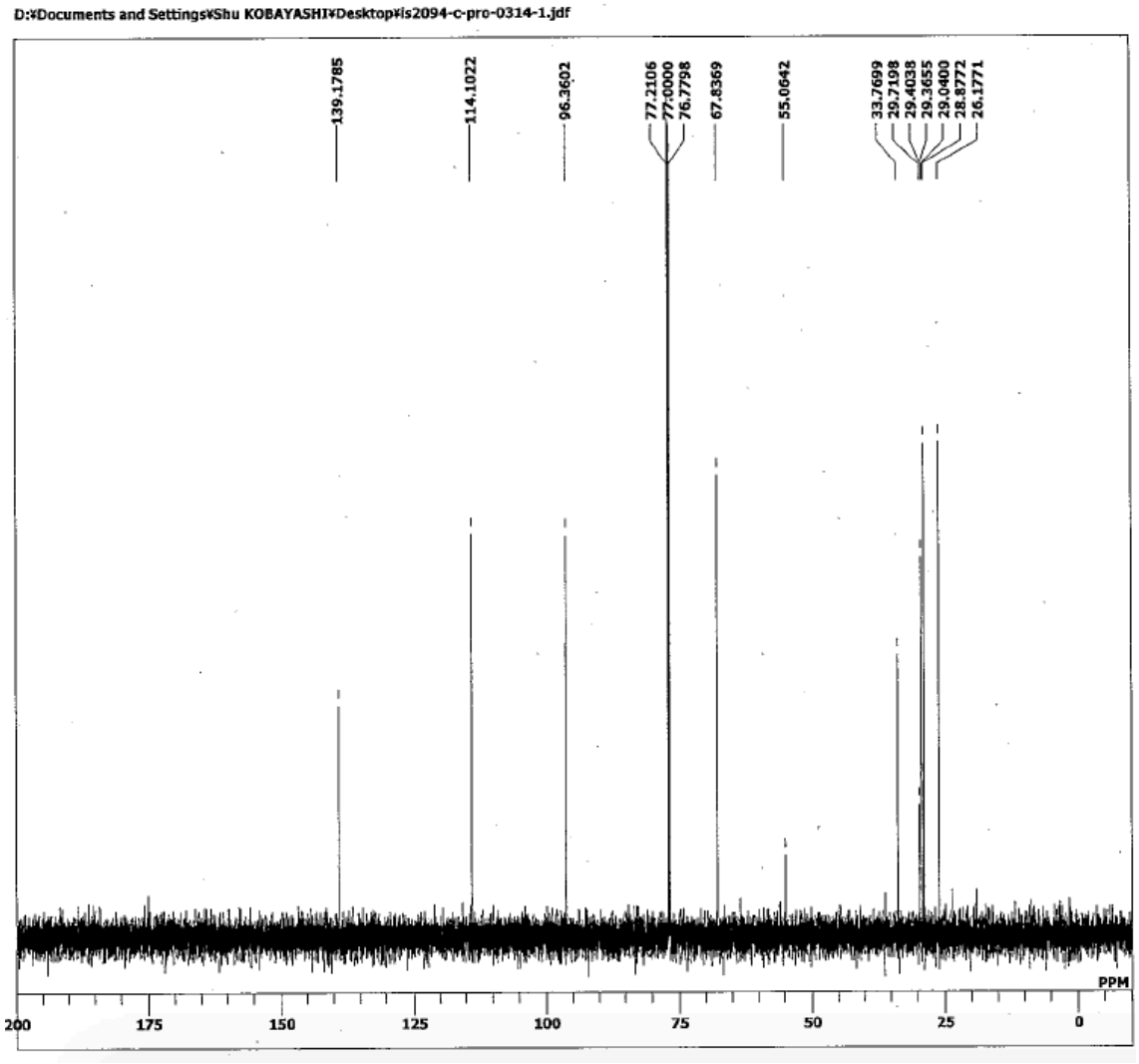
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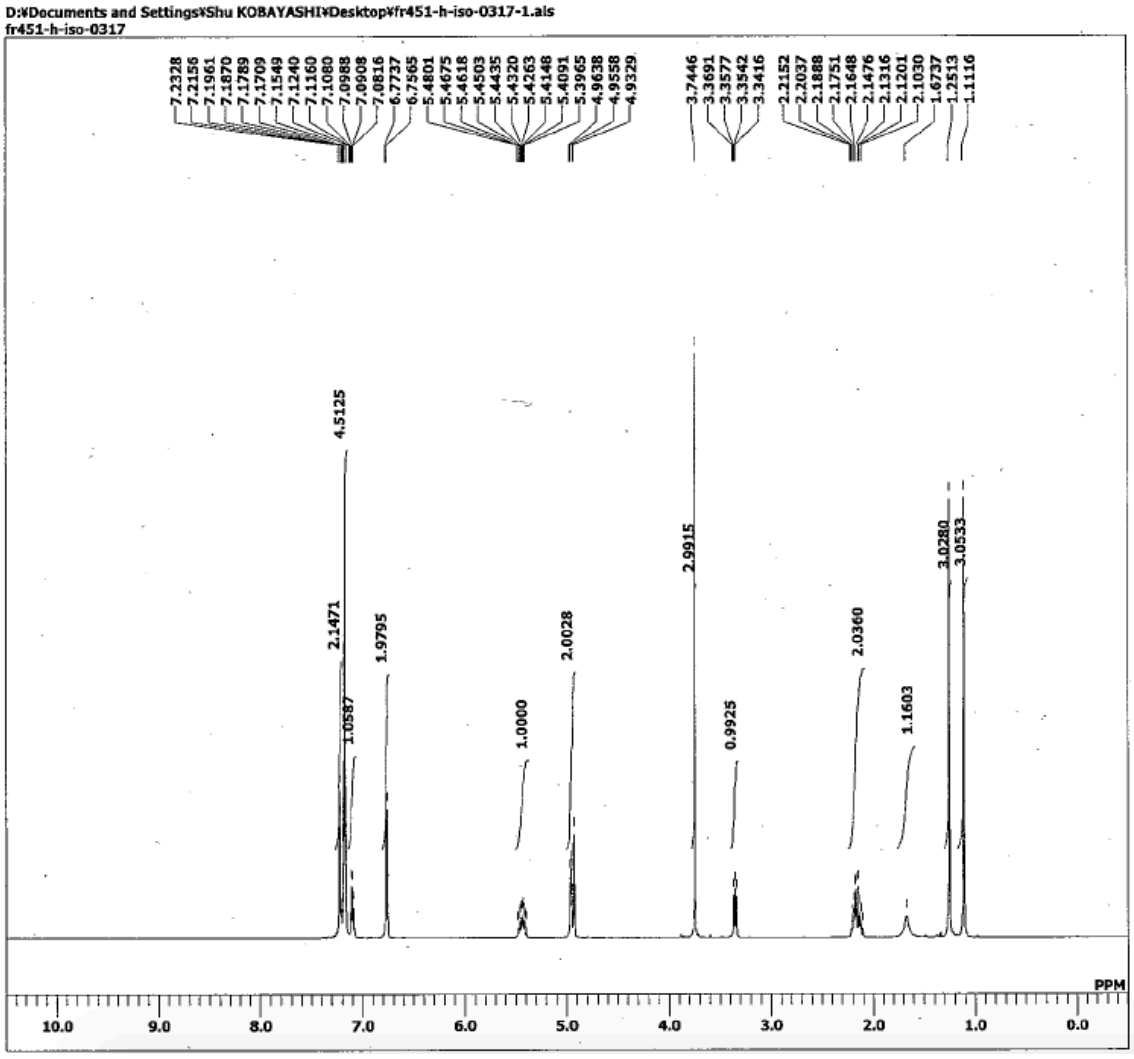
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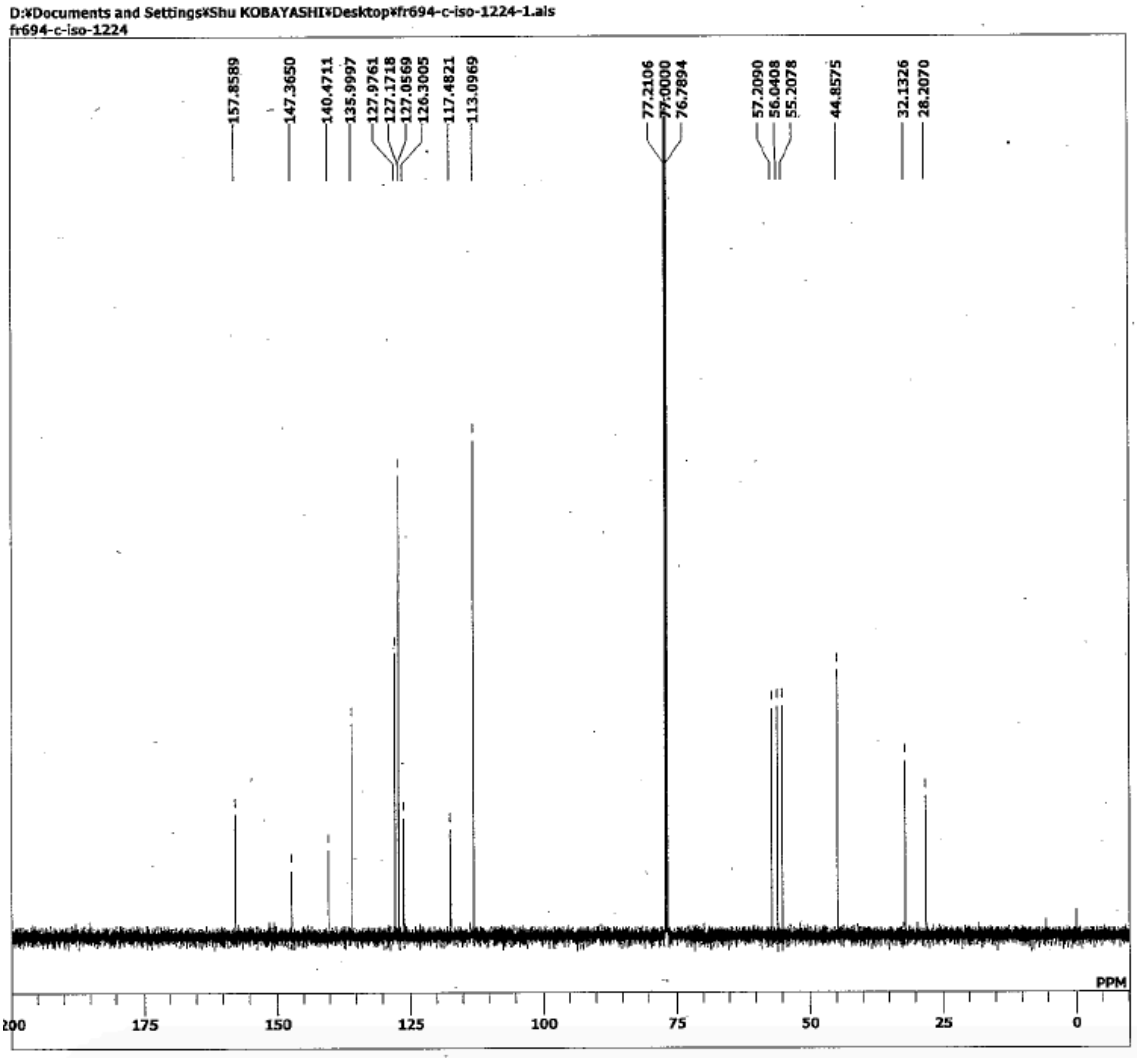
3aa-C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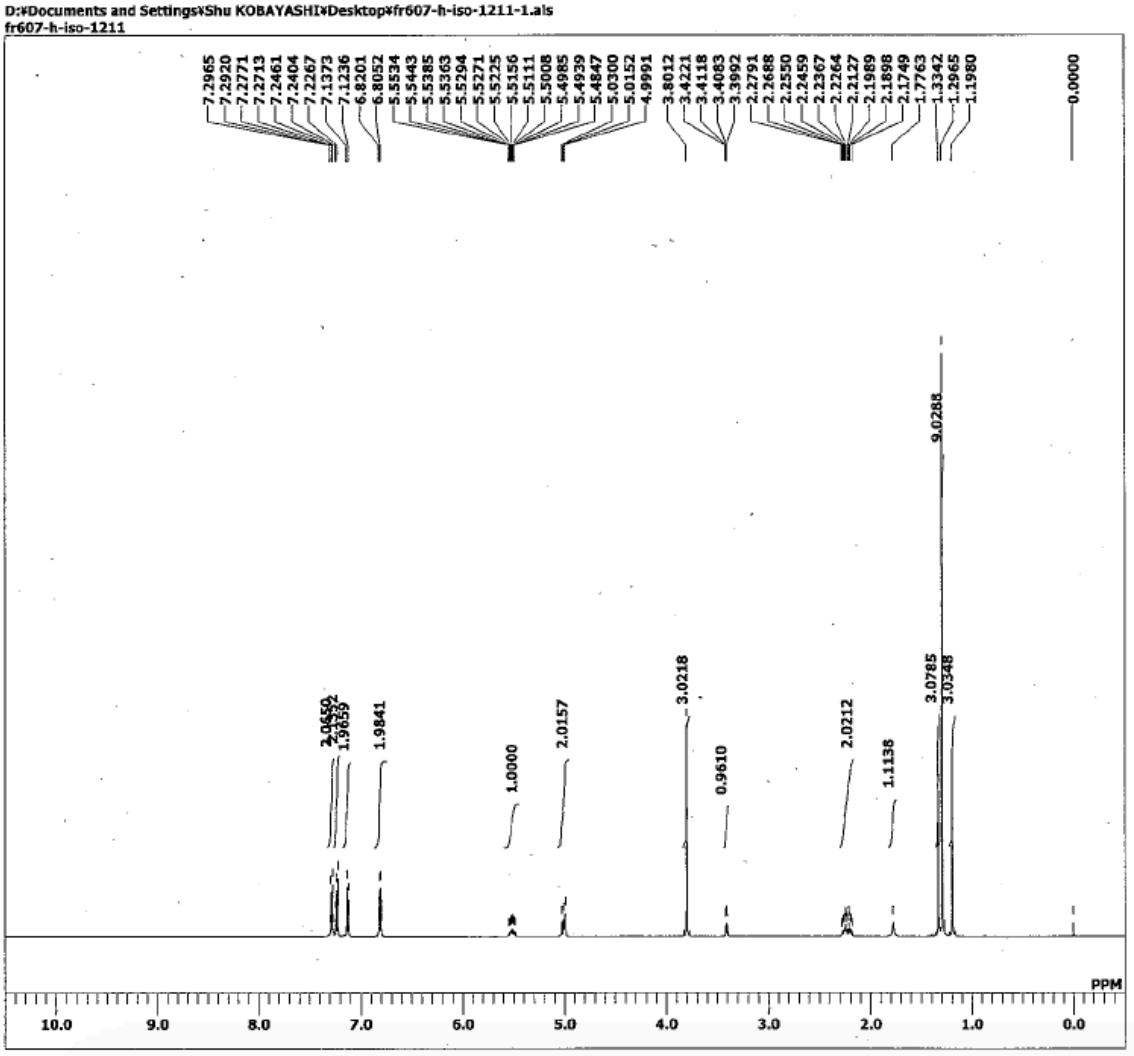
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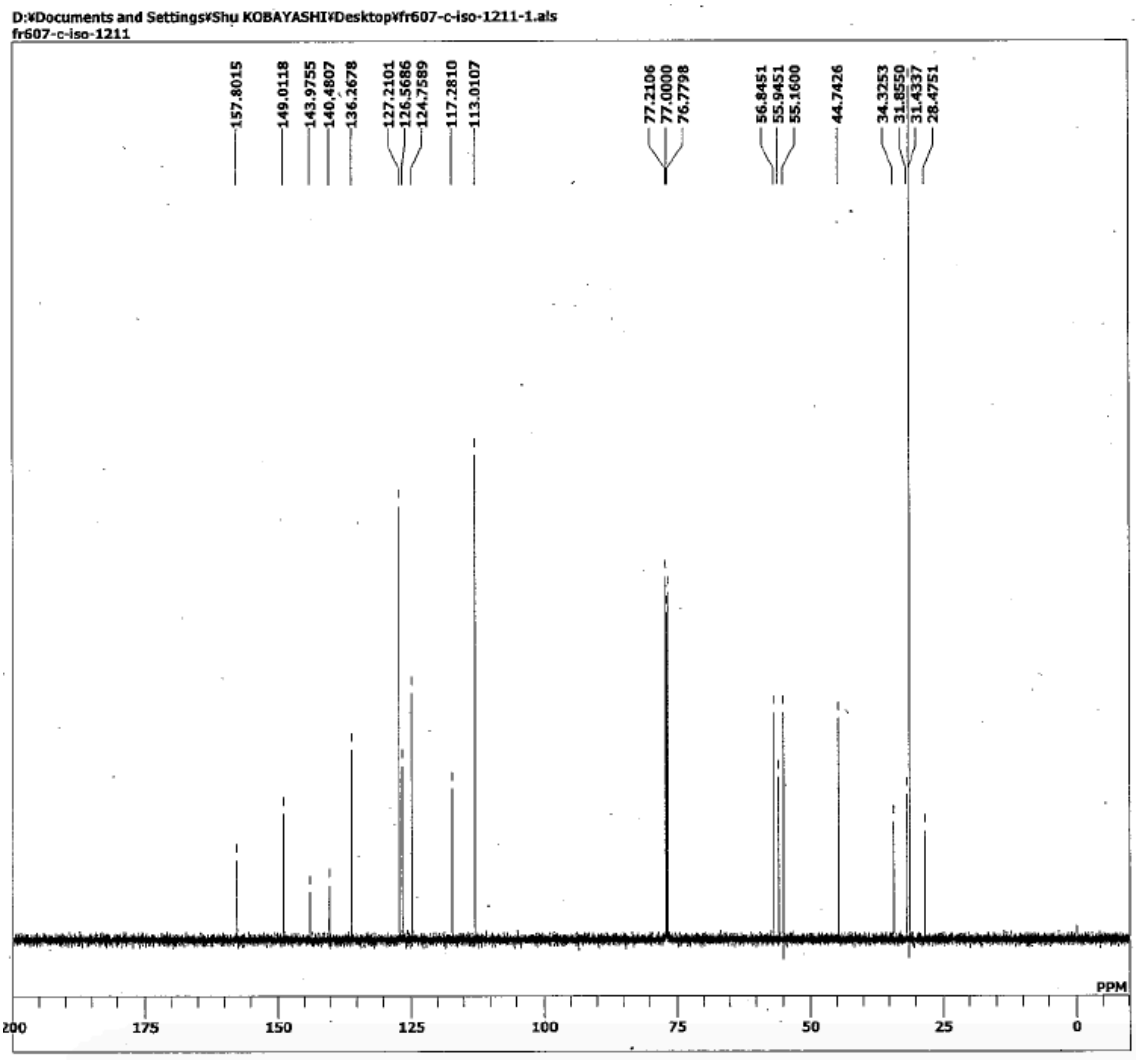
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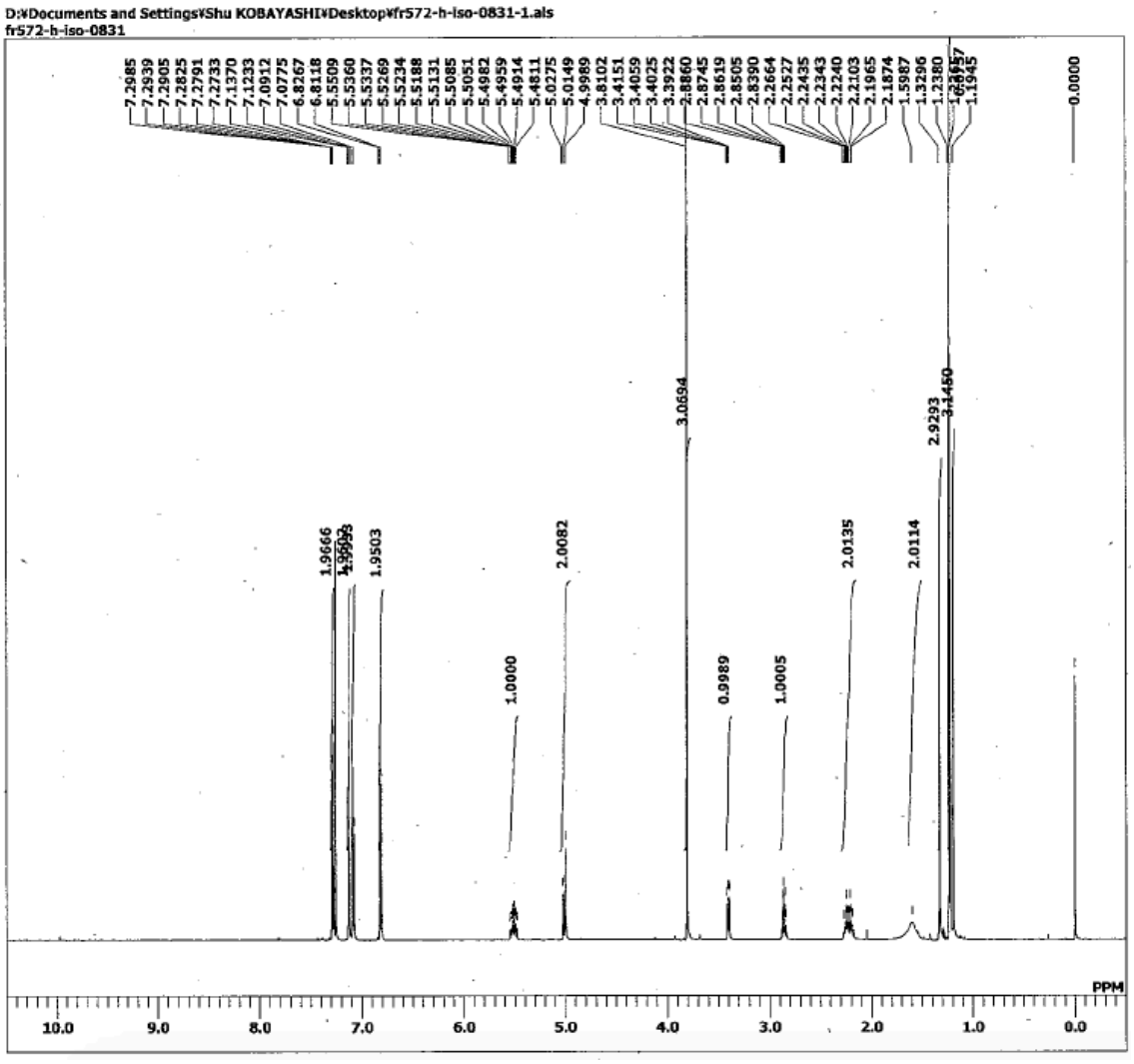
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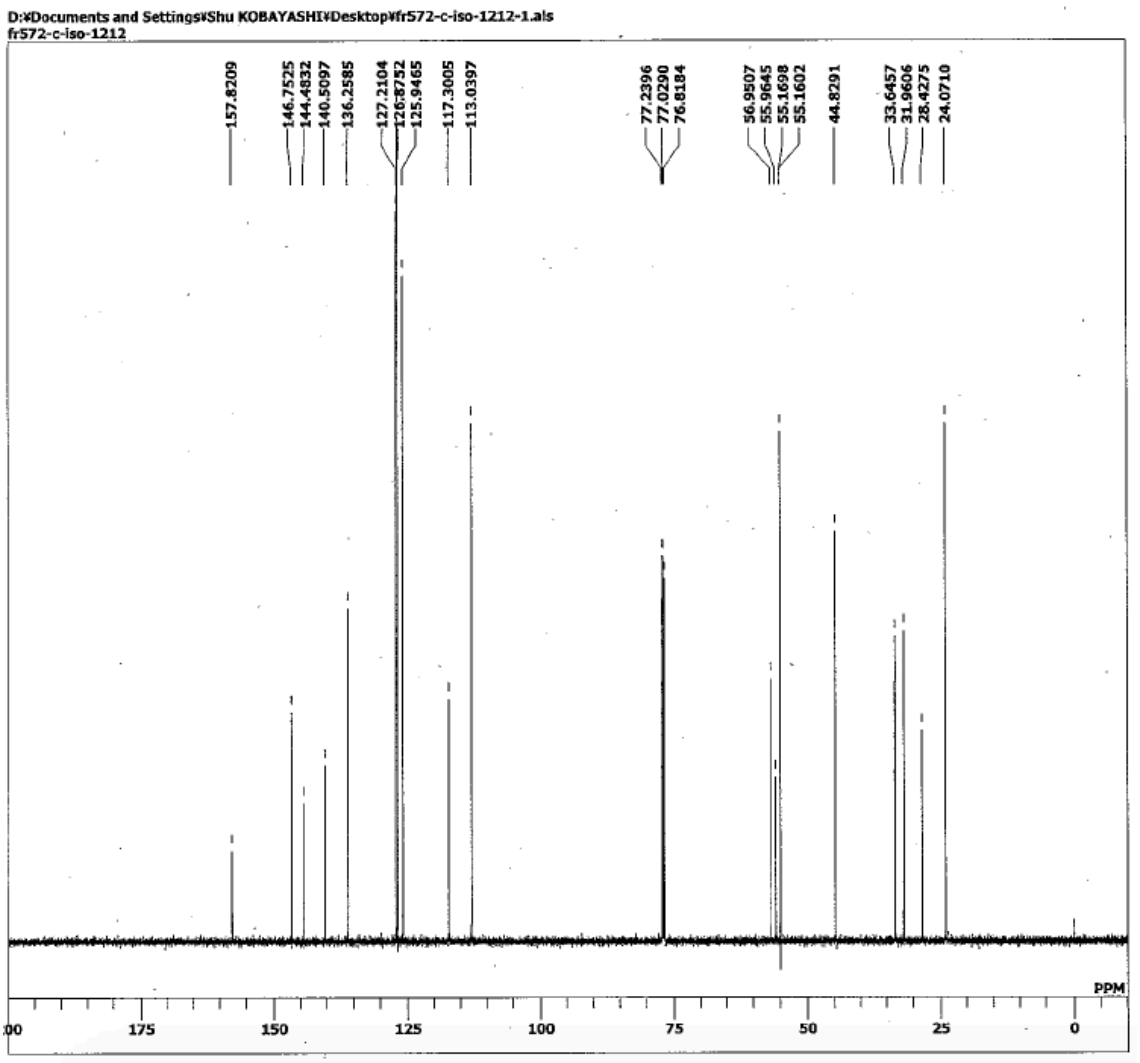
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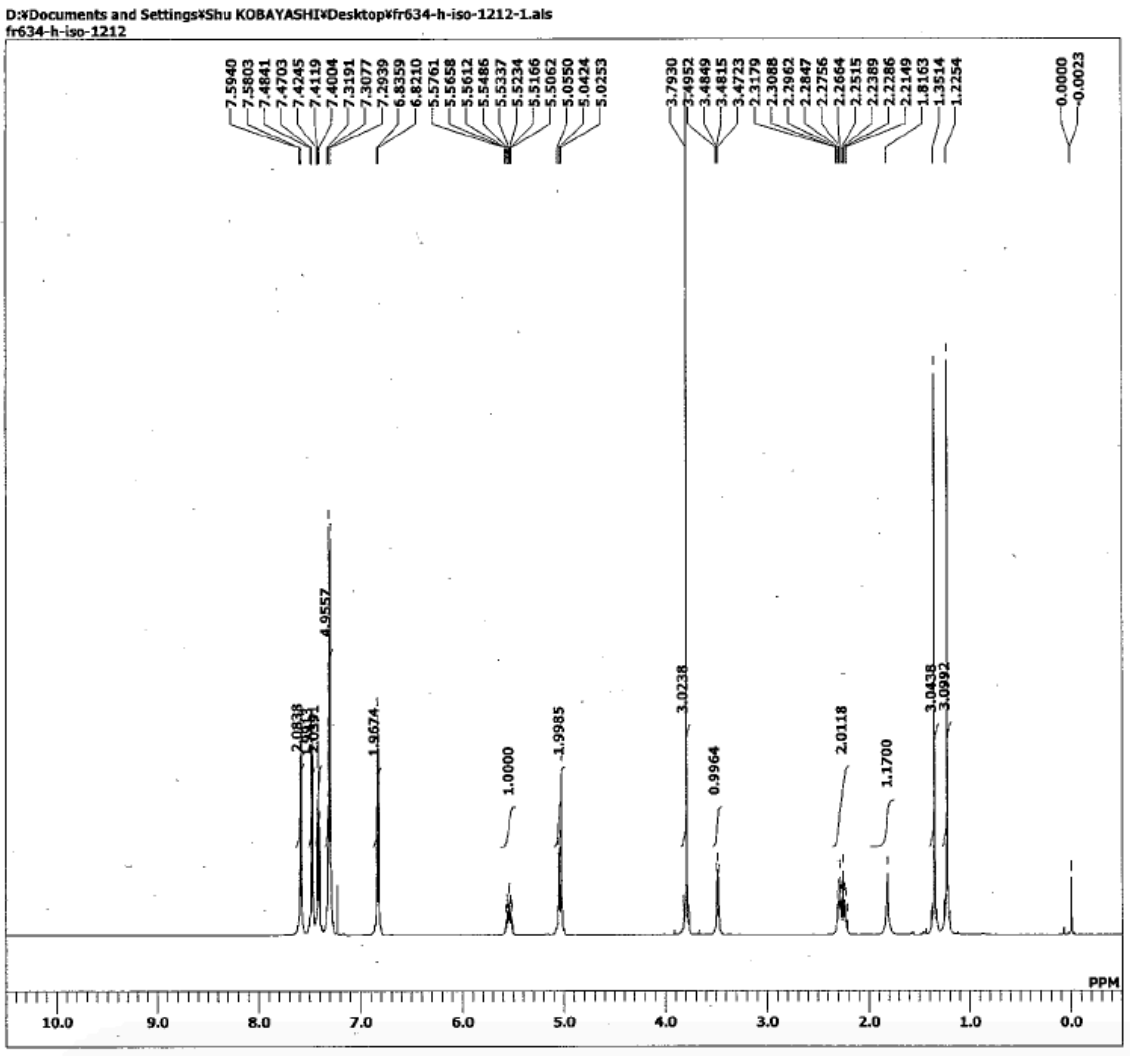
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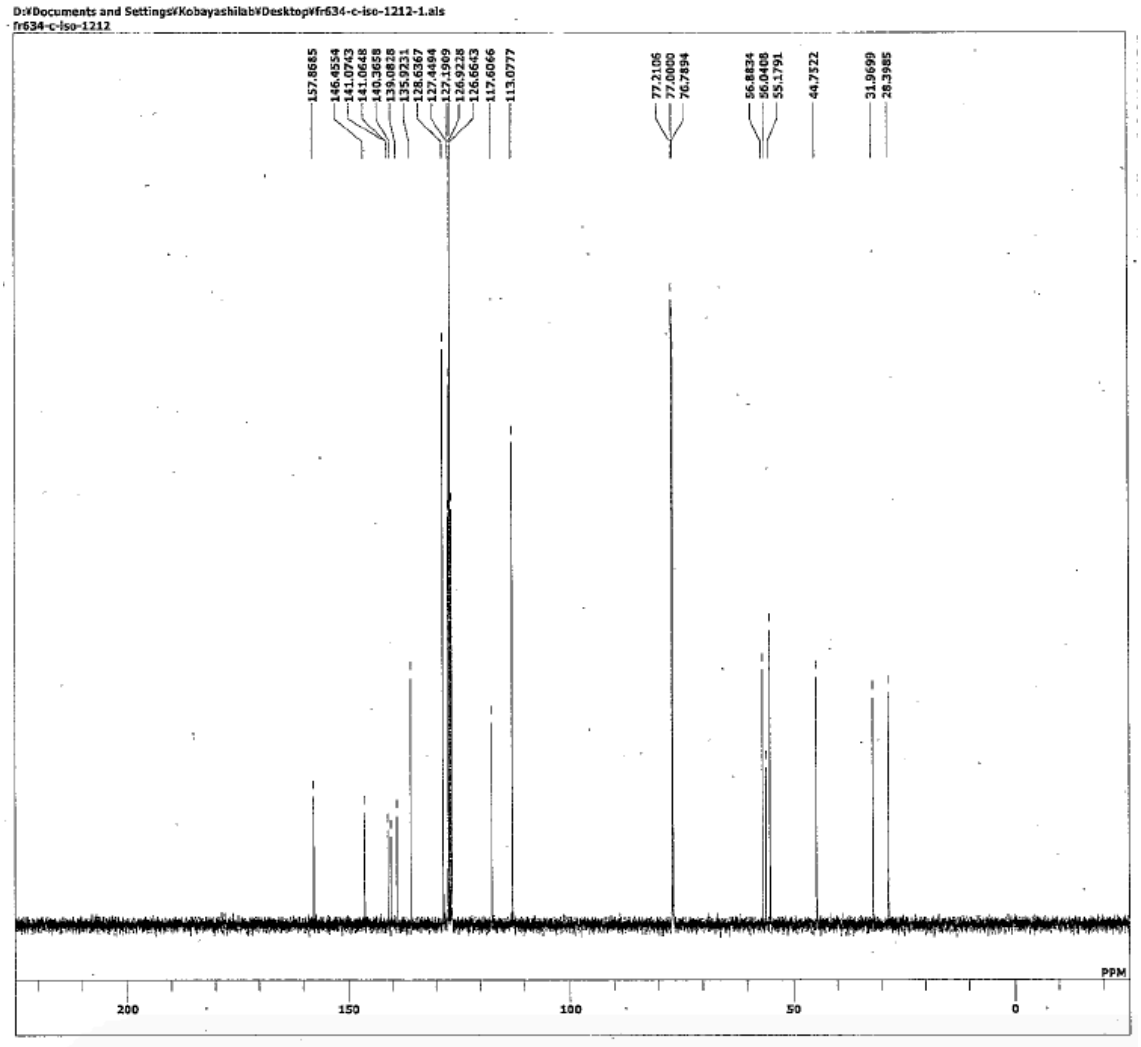
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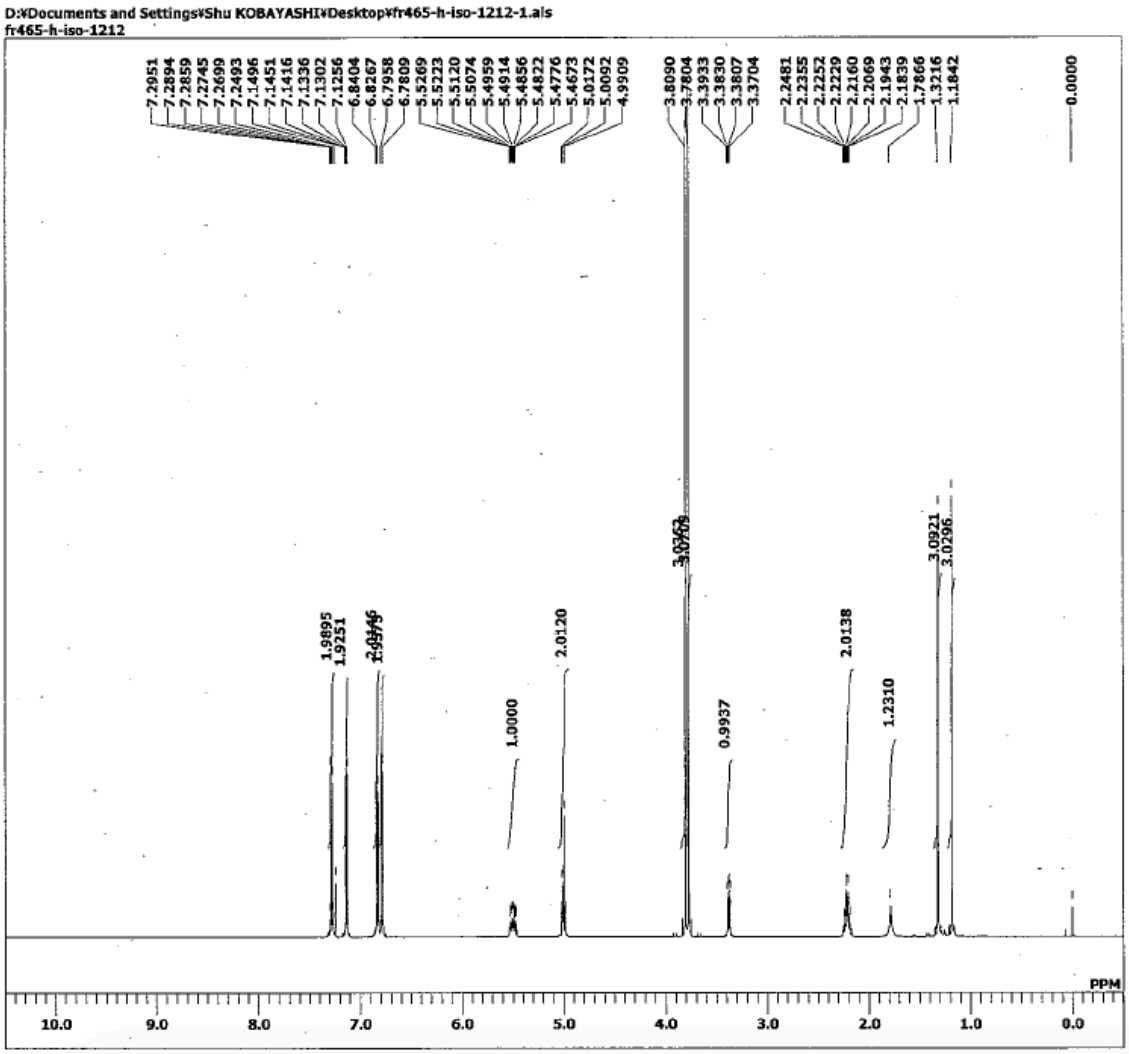
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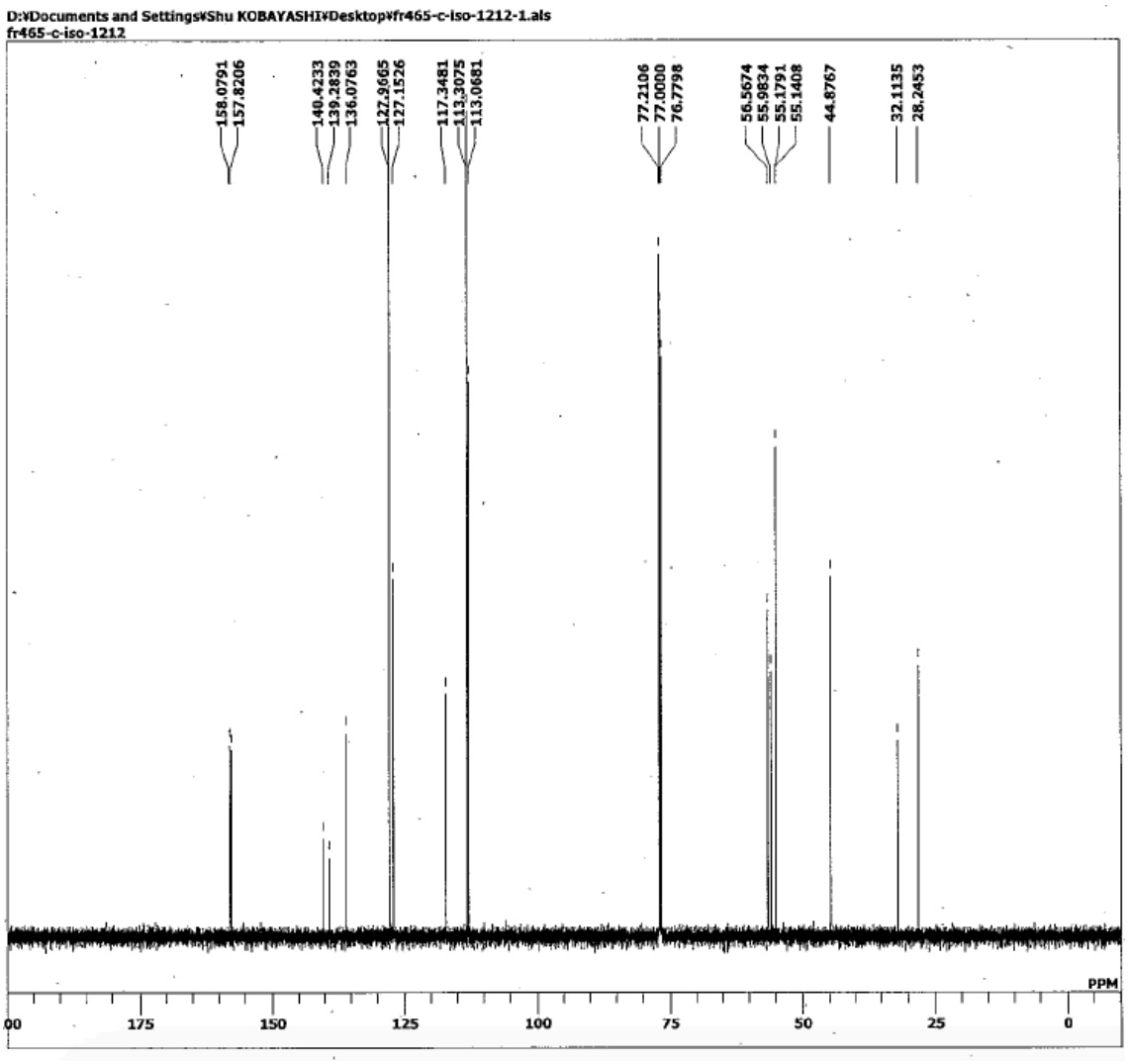
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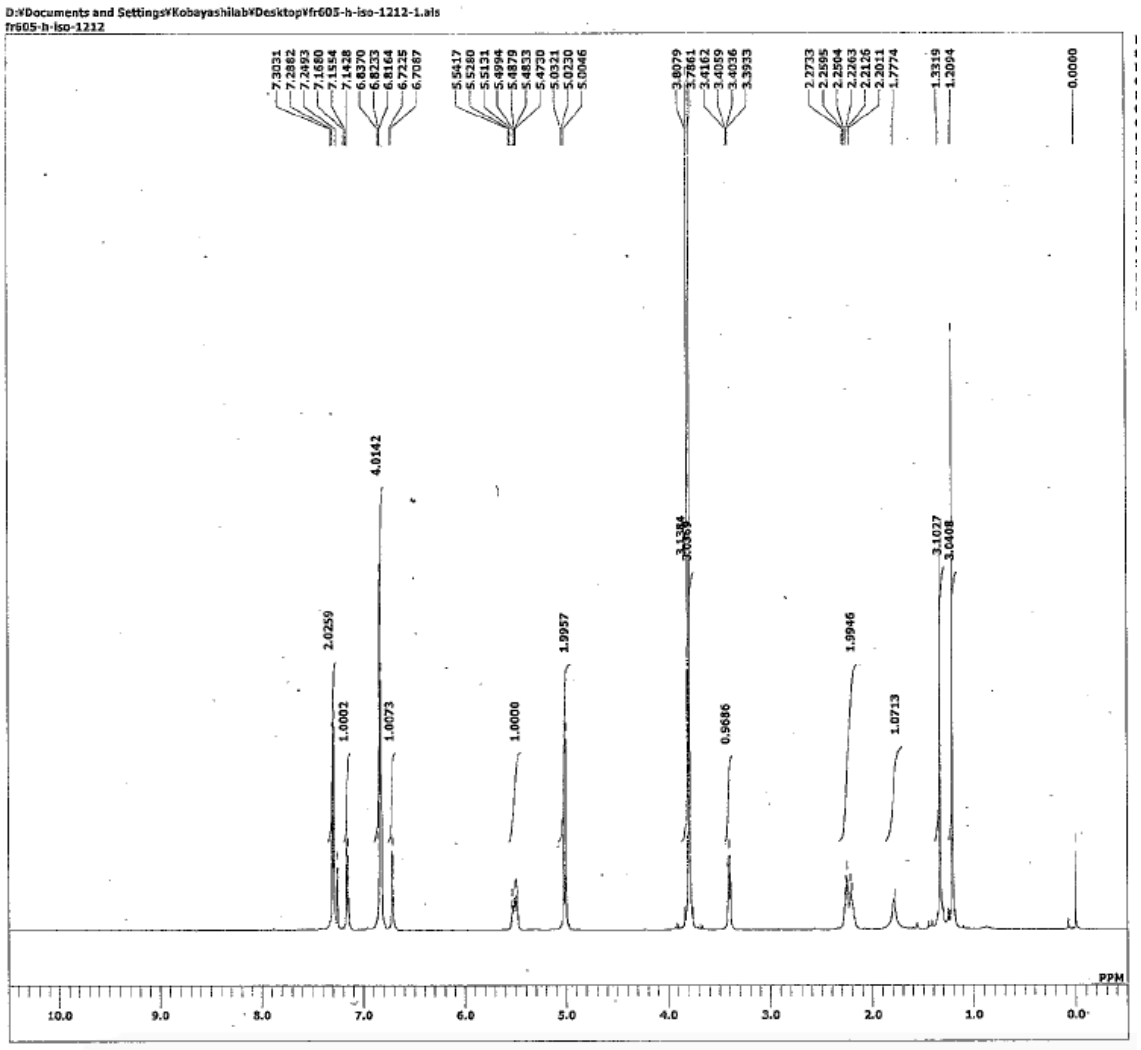
3fa-H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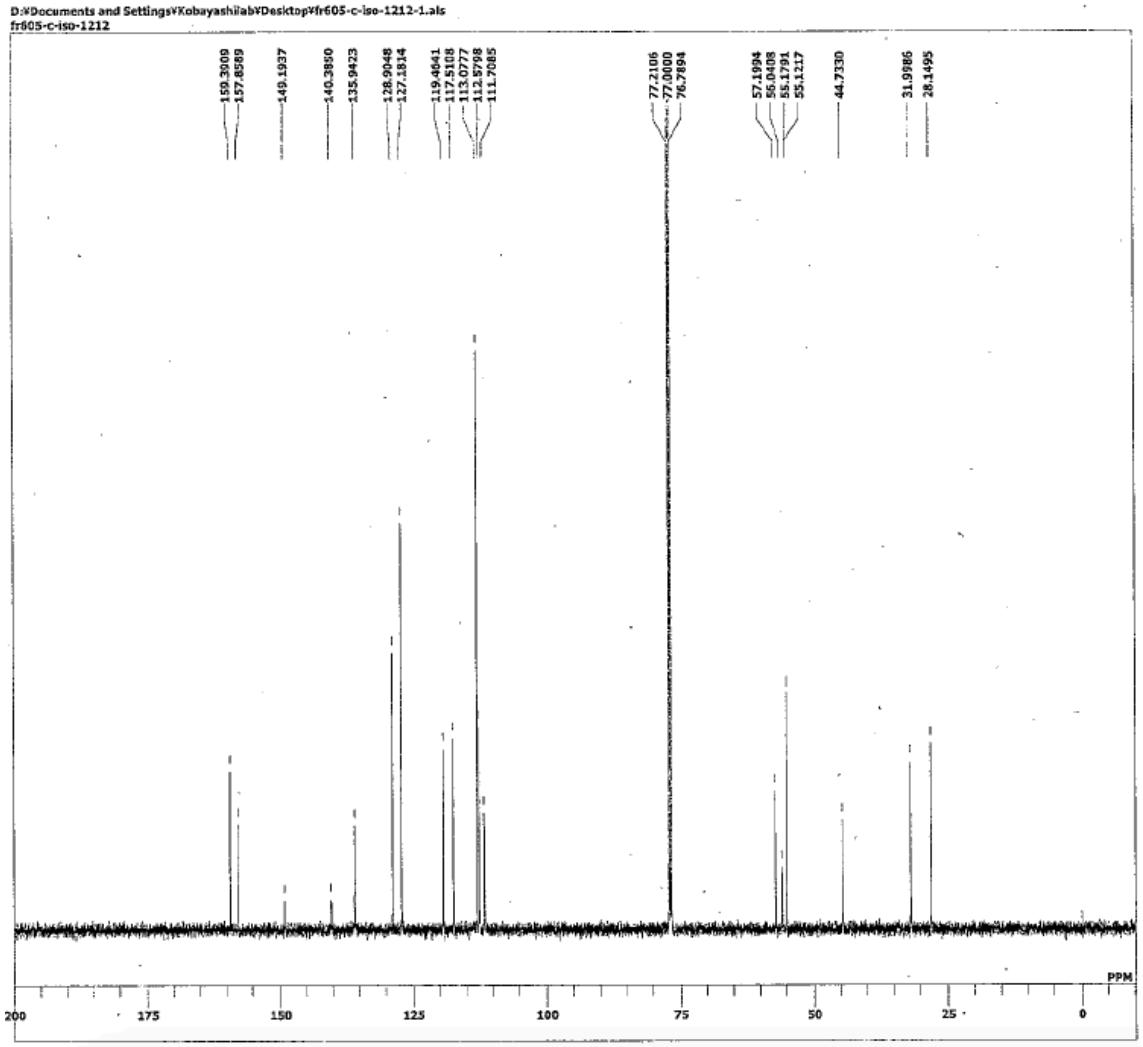
3fa-C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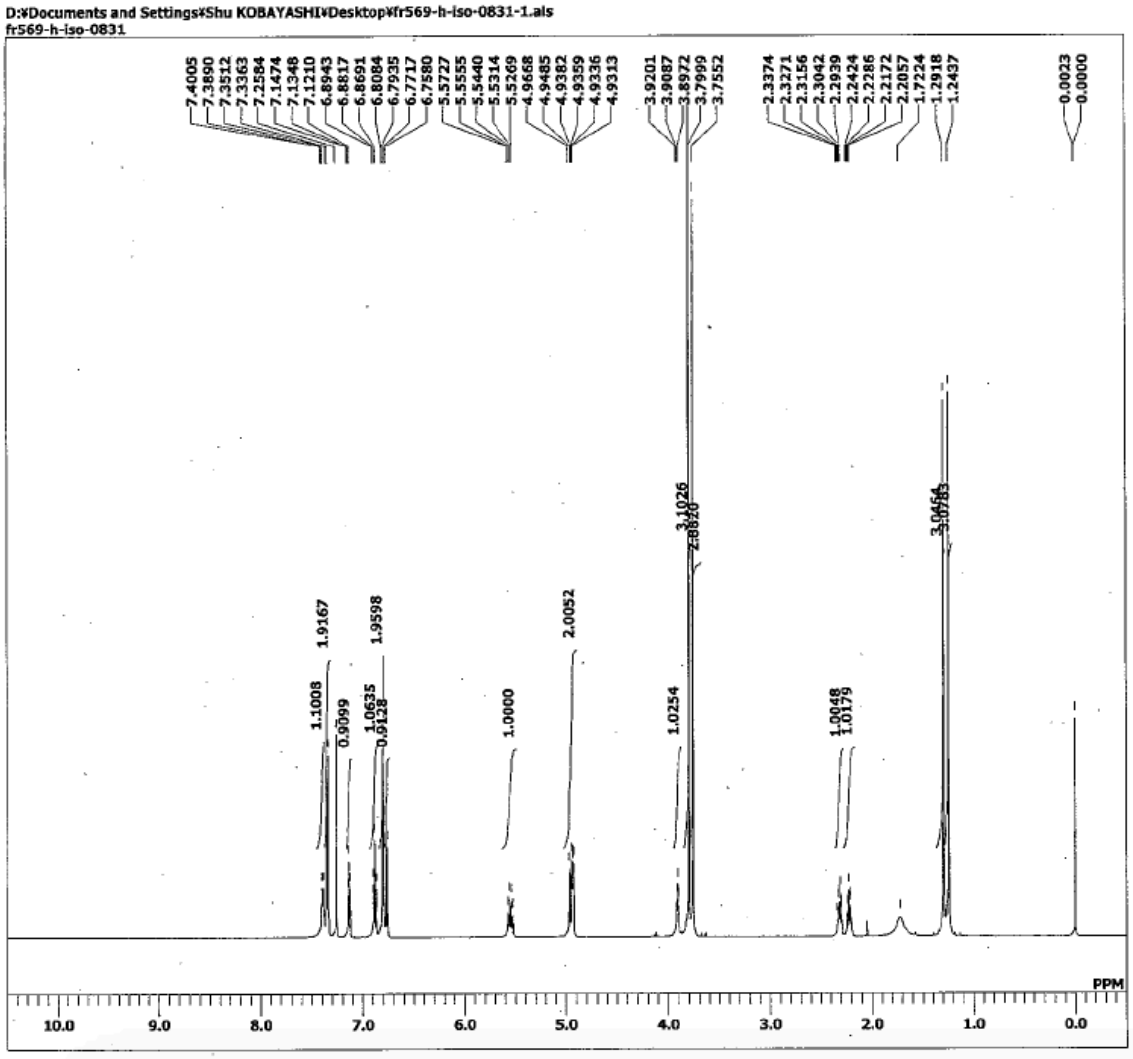
3ga-H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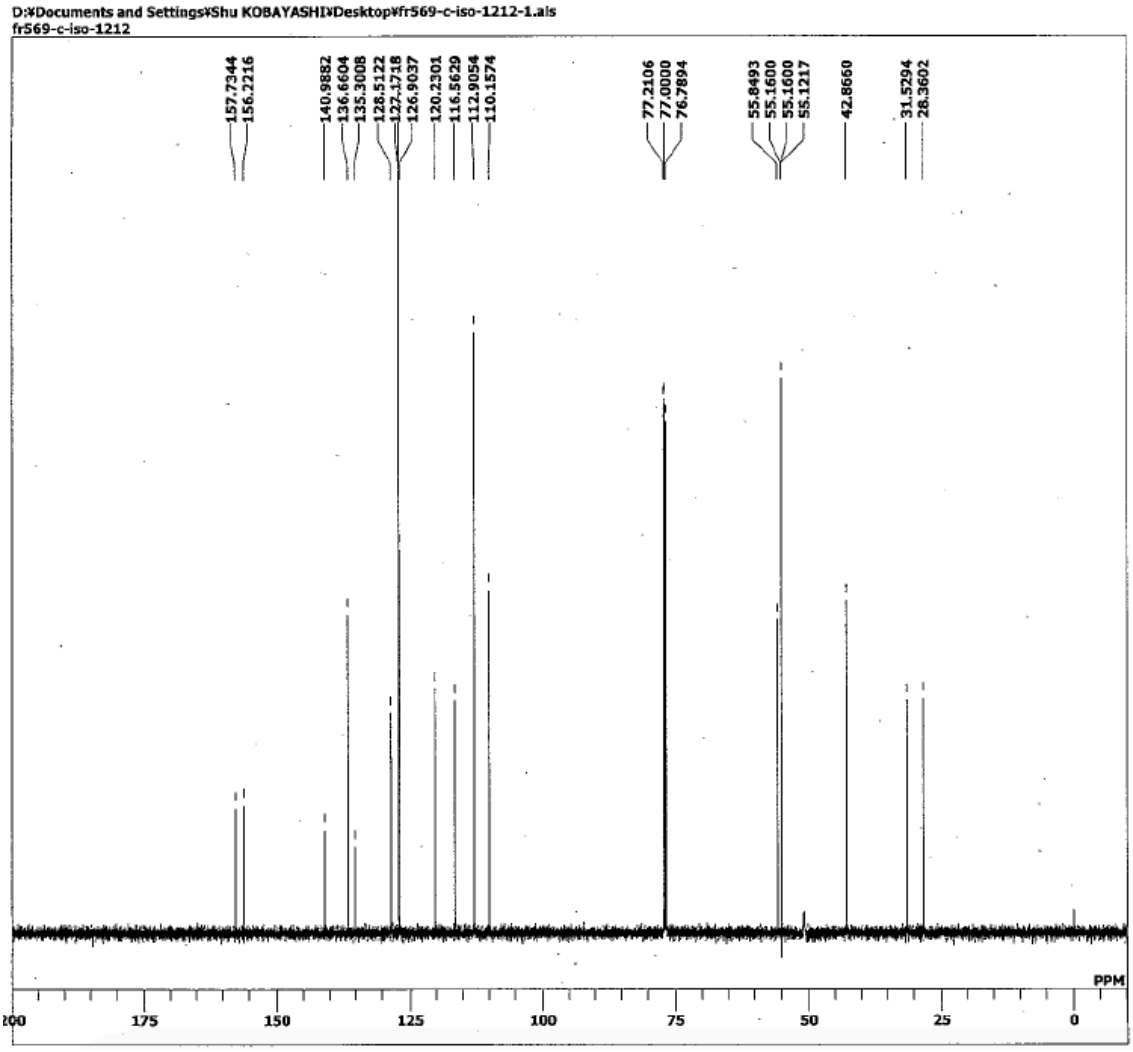
3ga-C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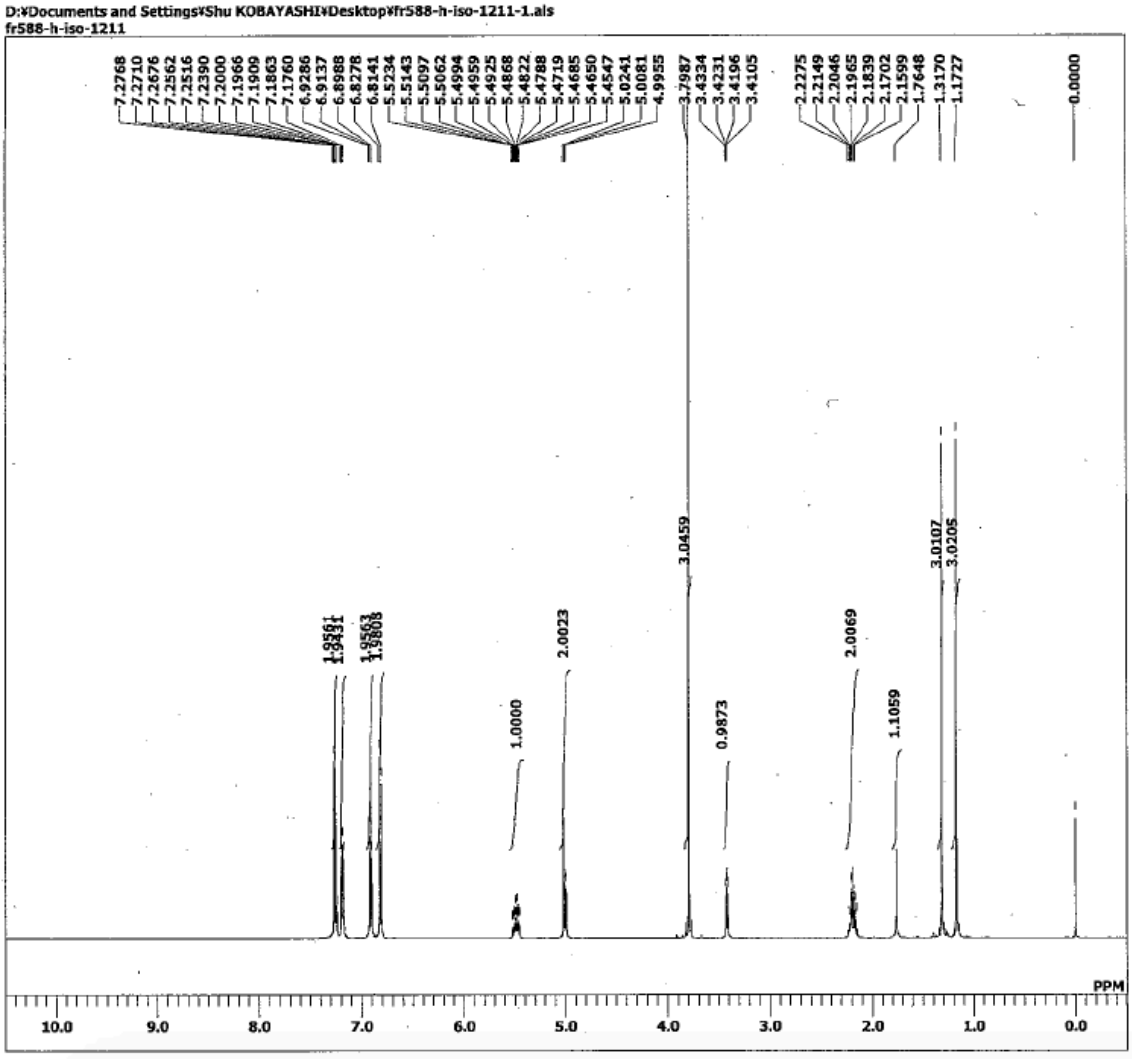
3ha-H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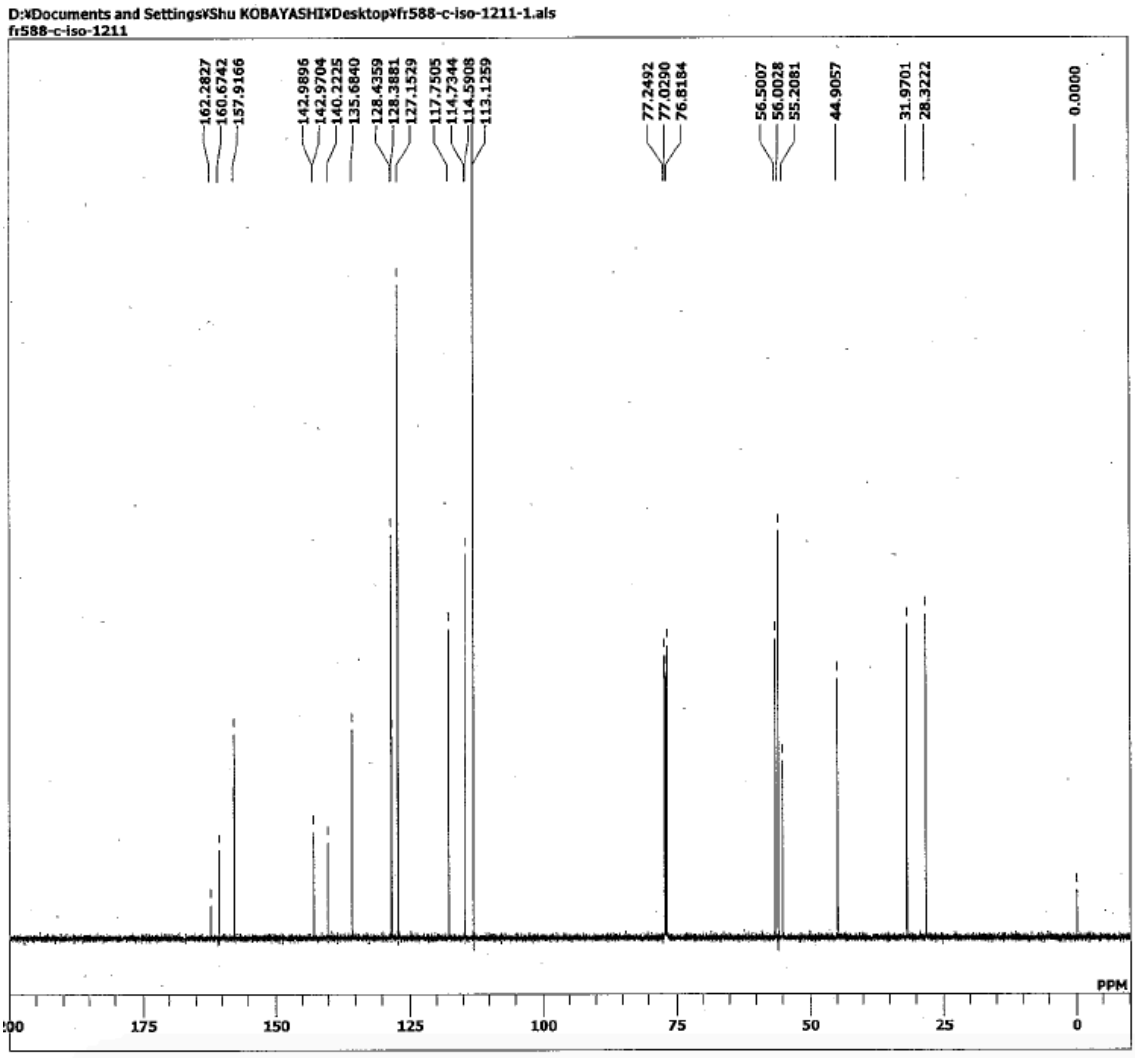
3ha-C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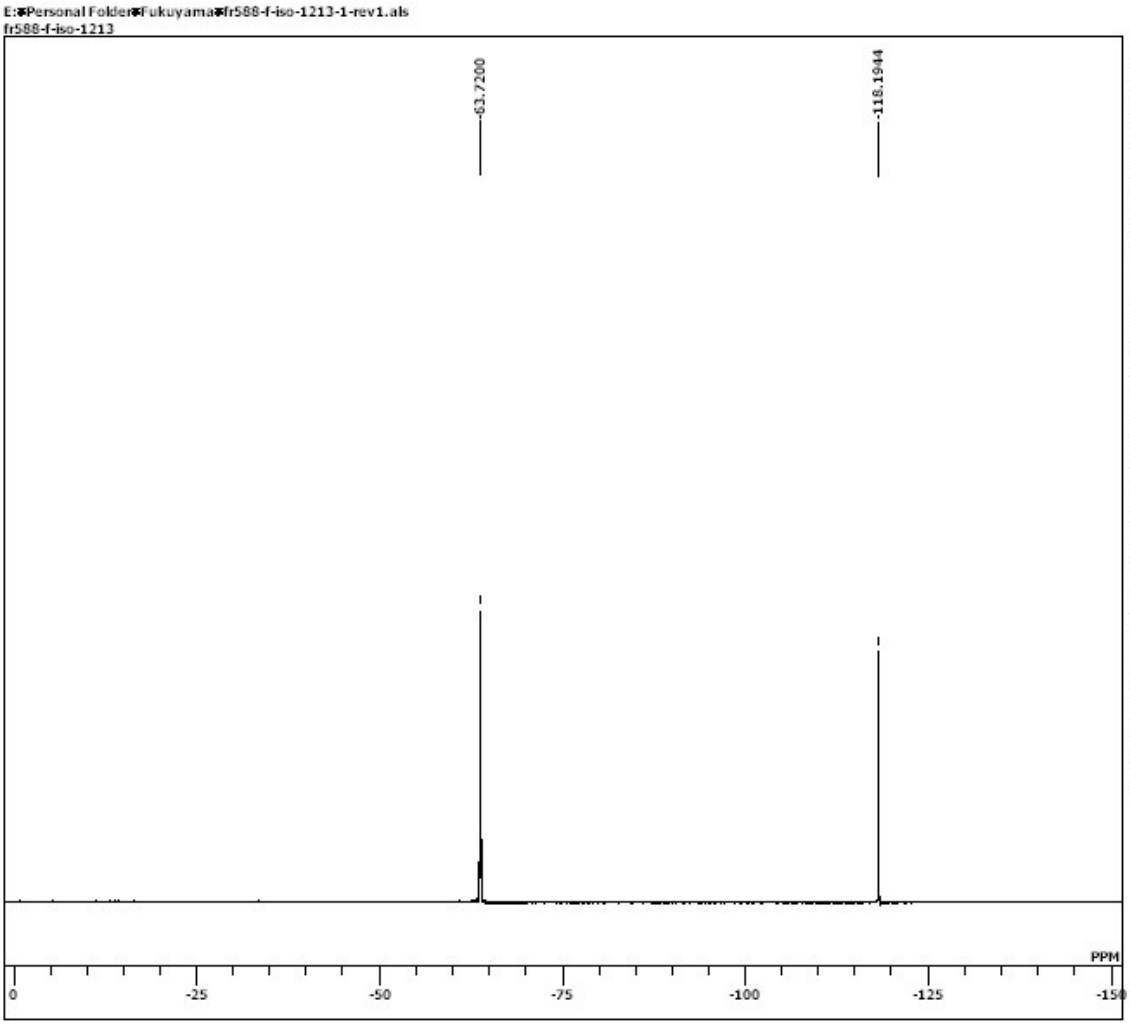
3ha-F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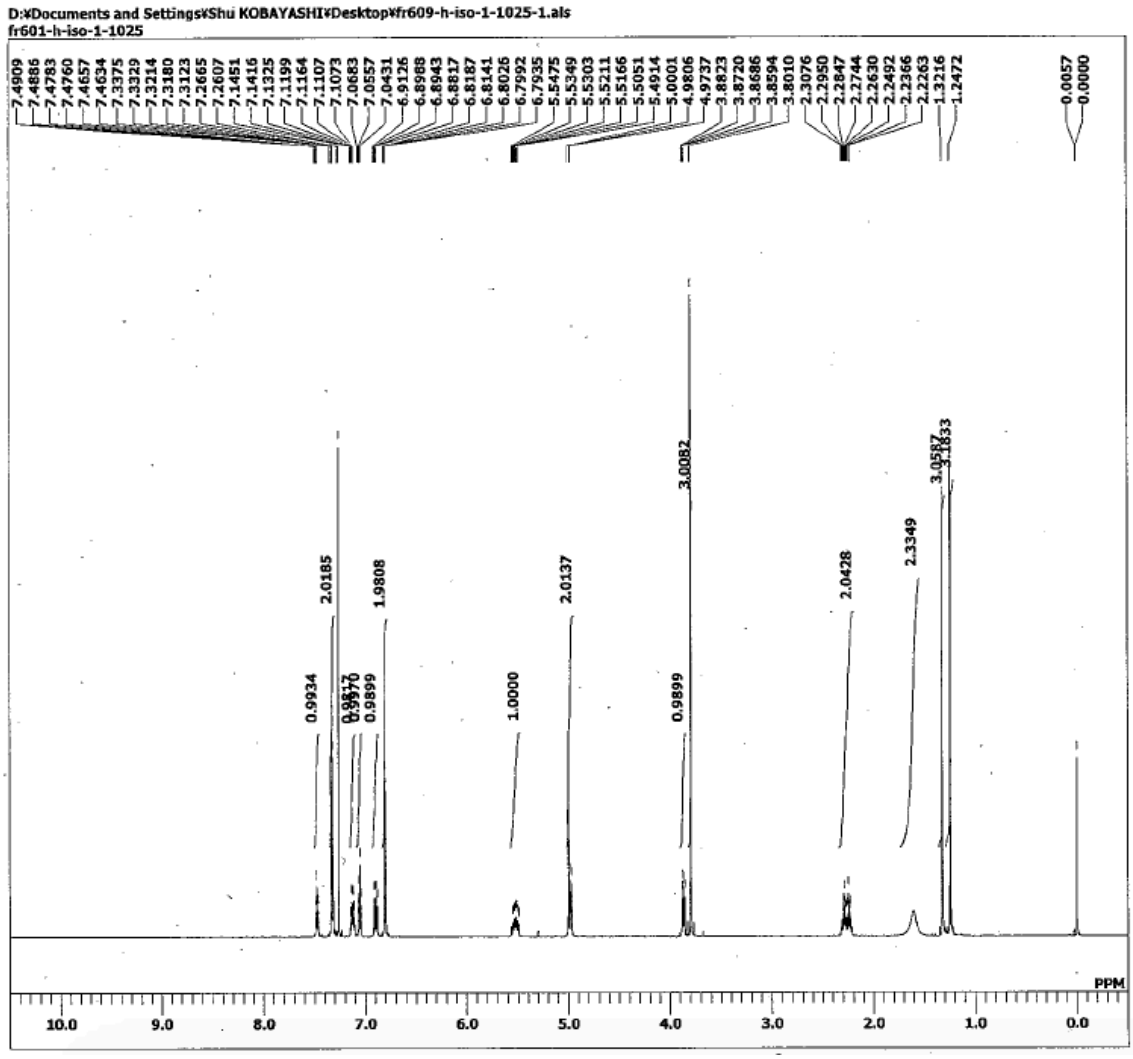
3ia-H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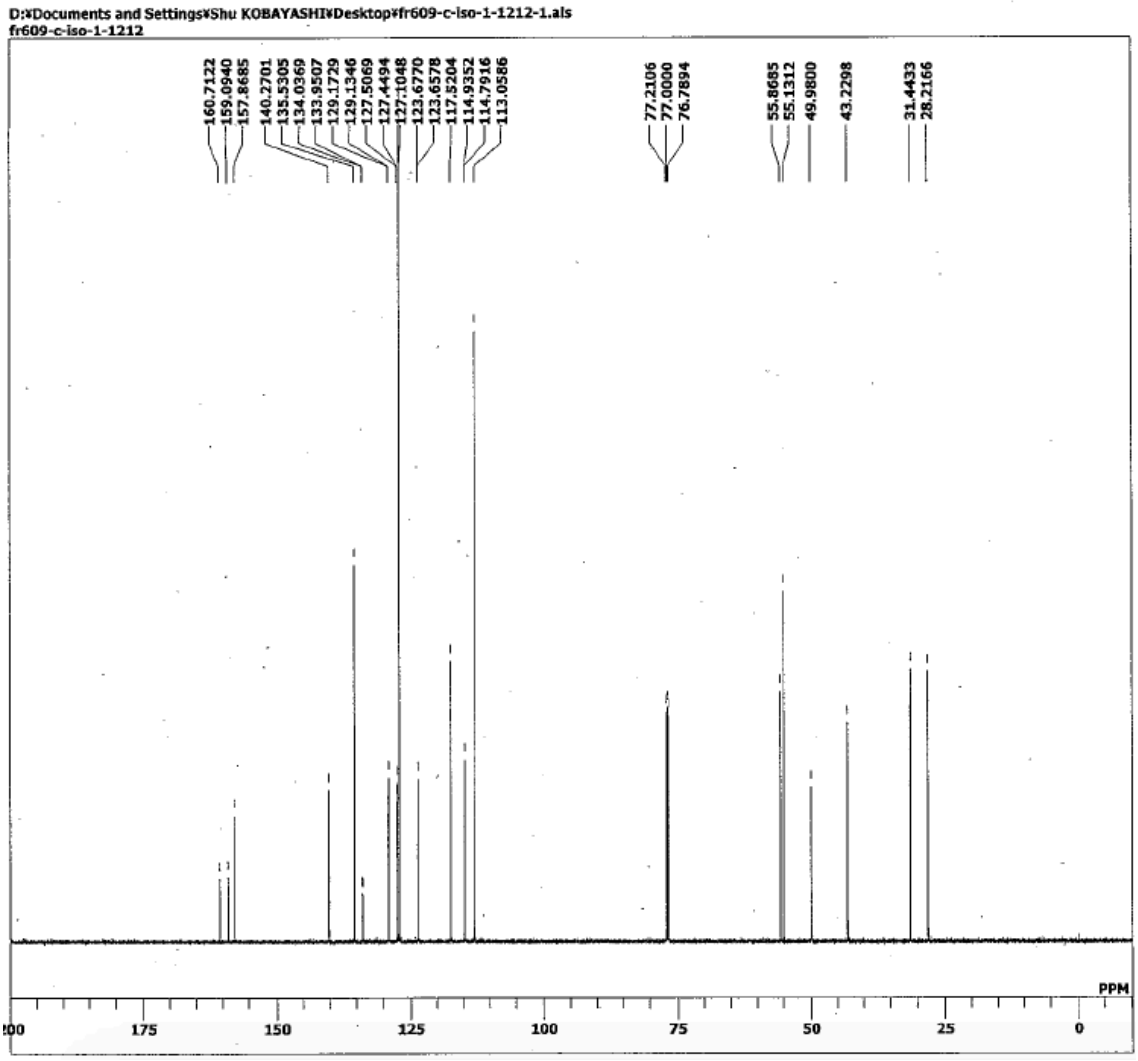
3ia-C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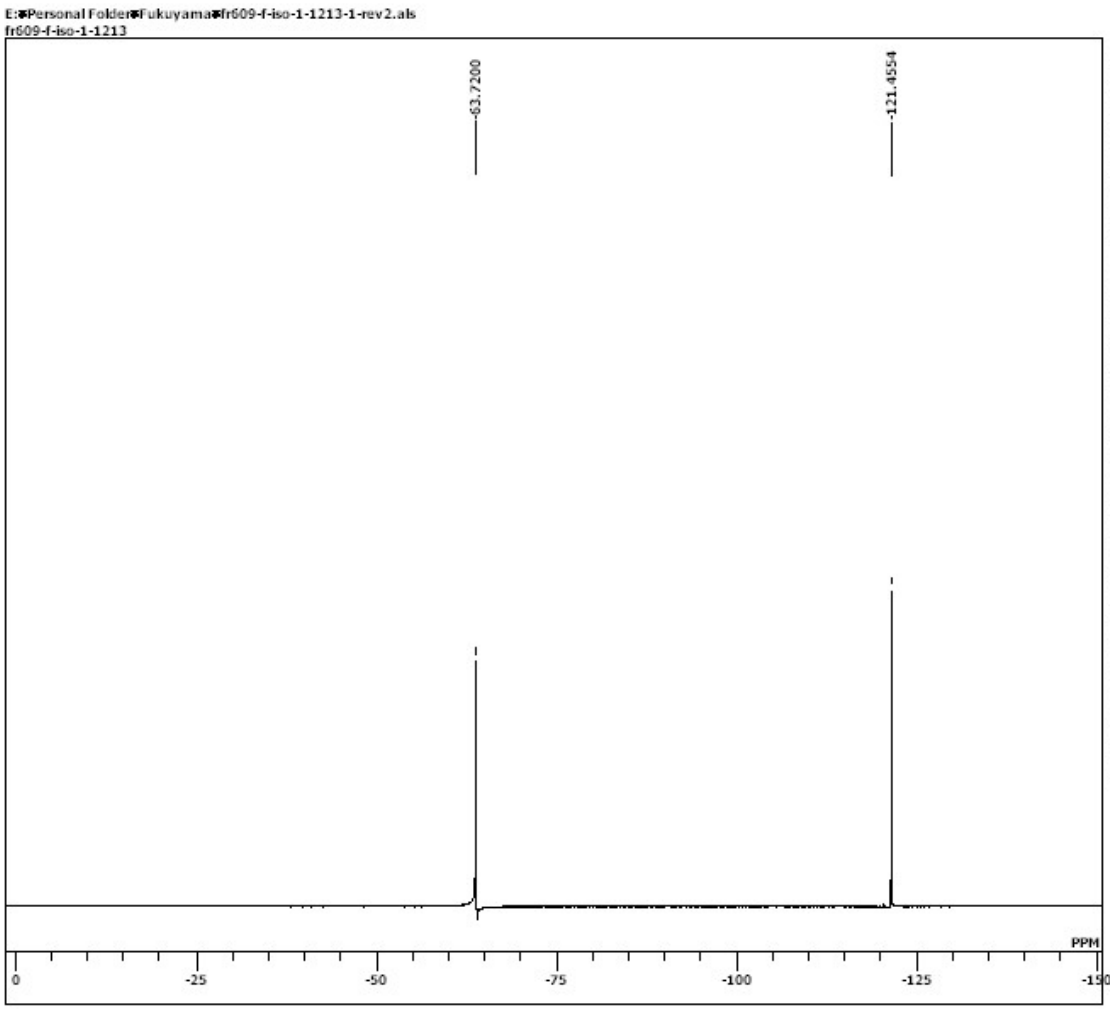
3ia-F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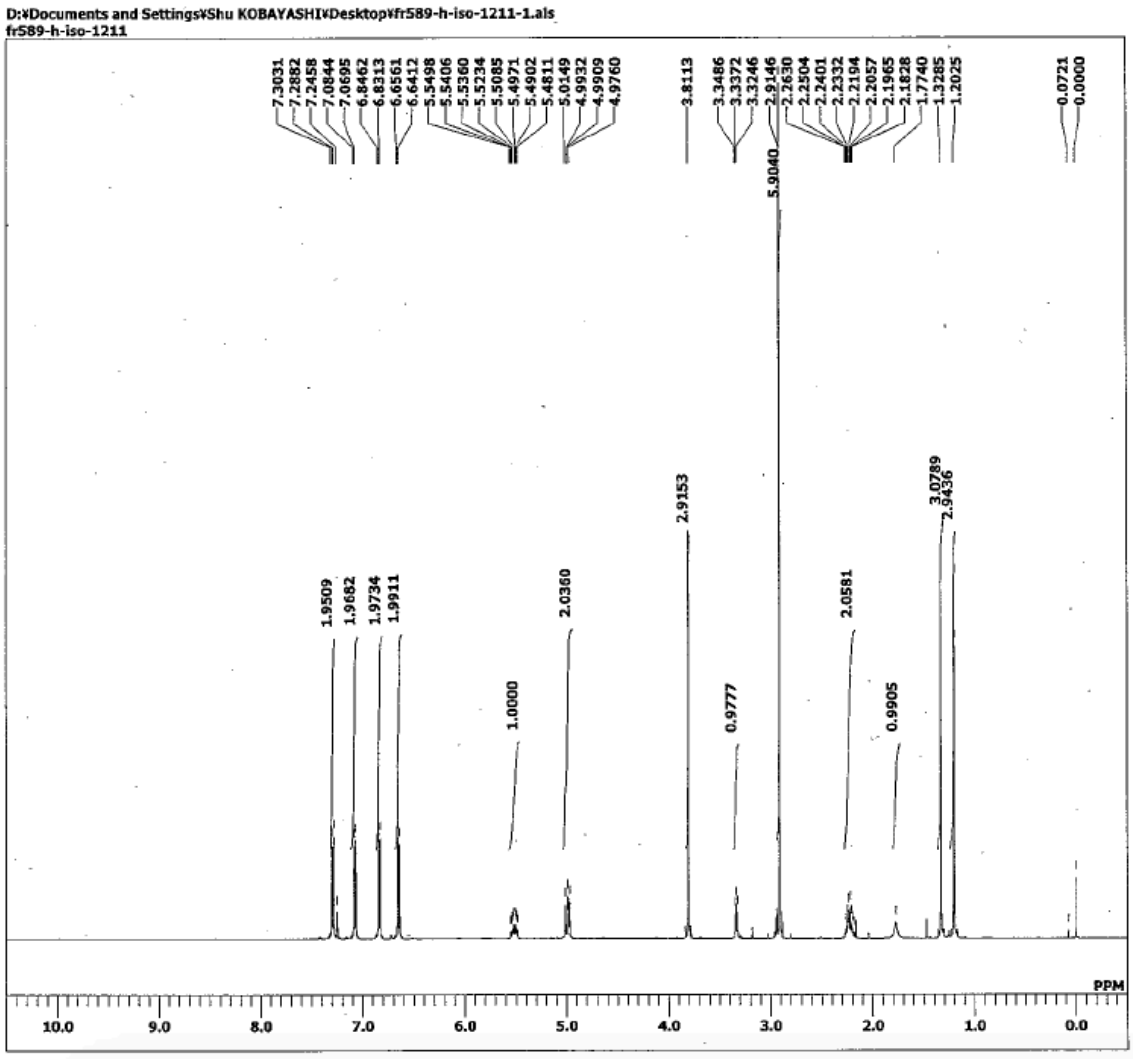
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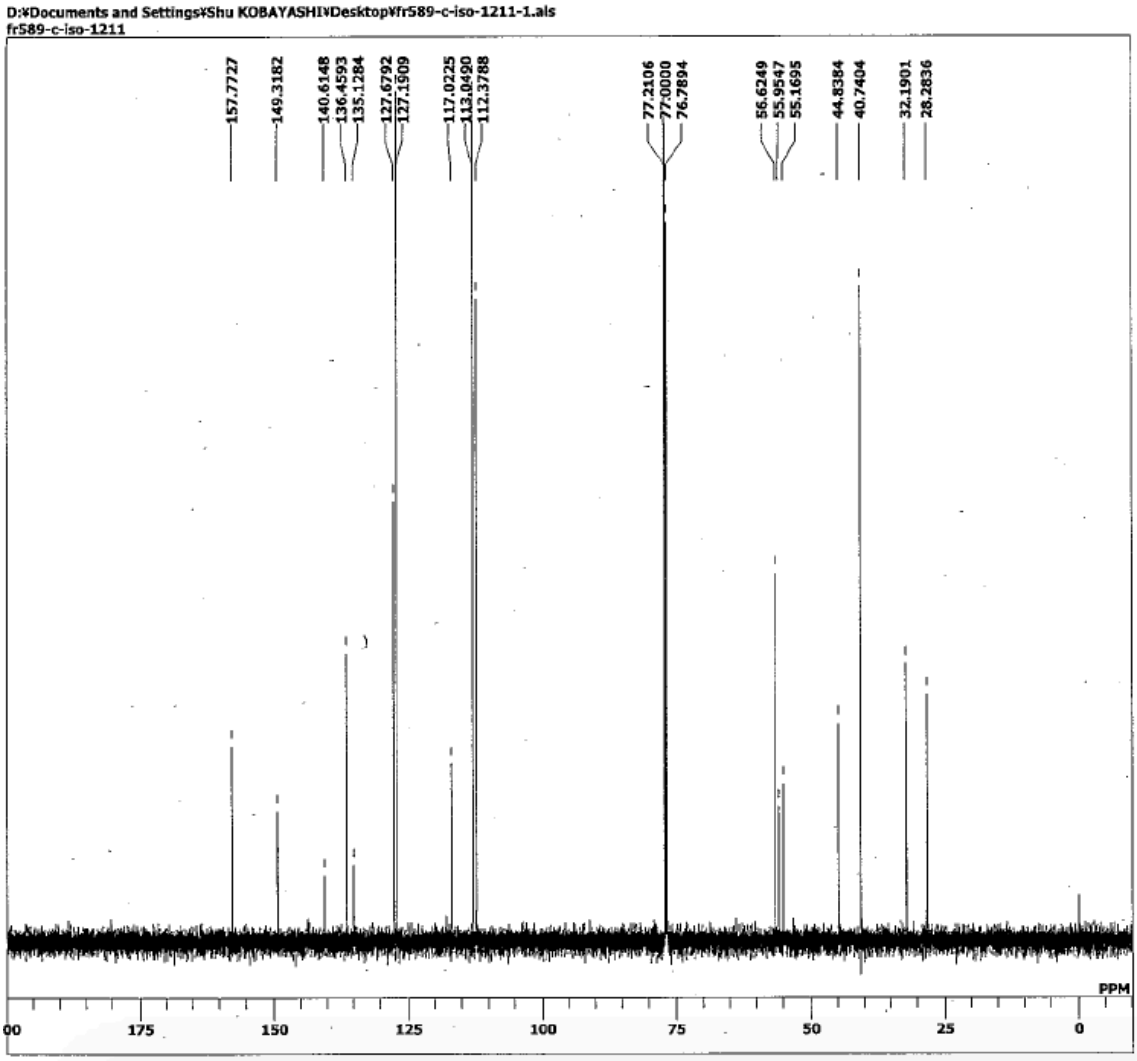
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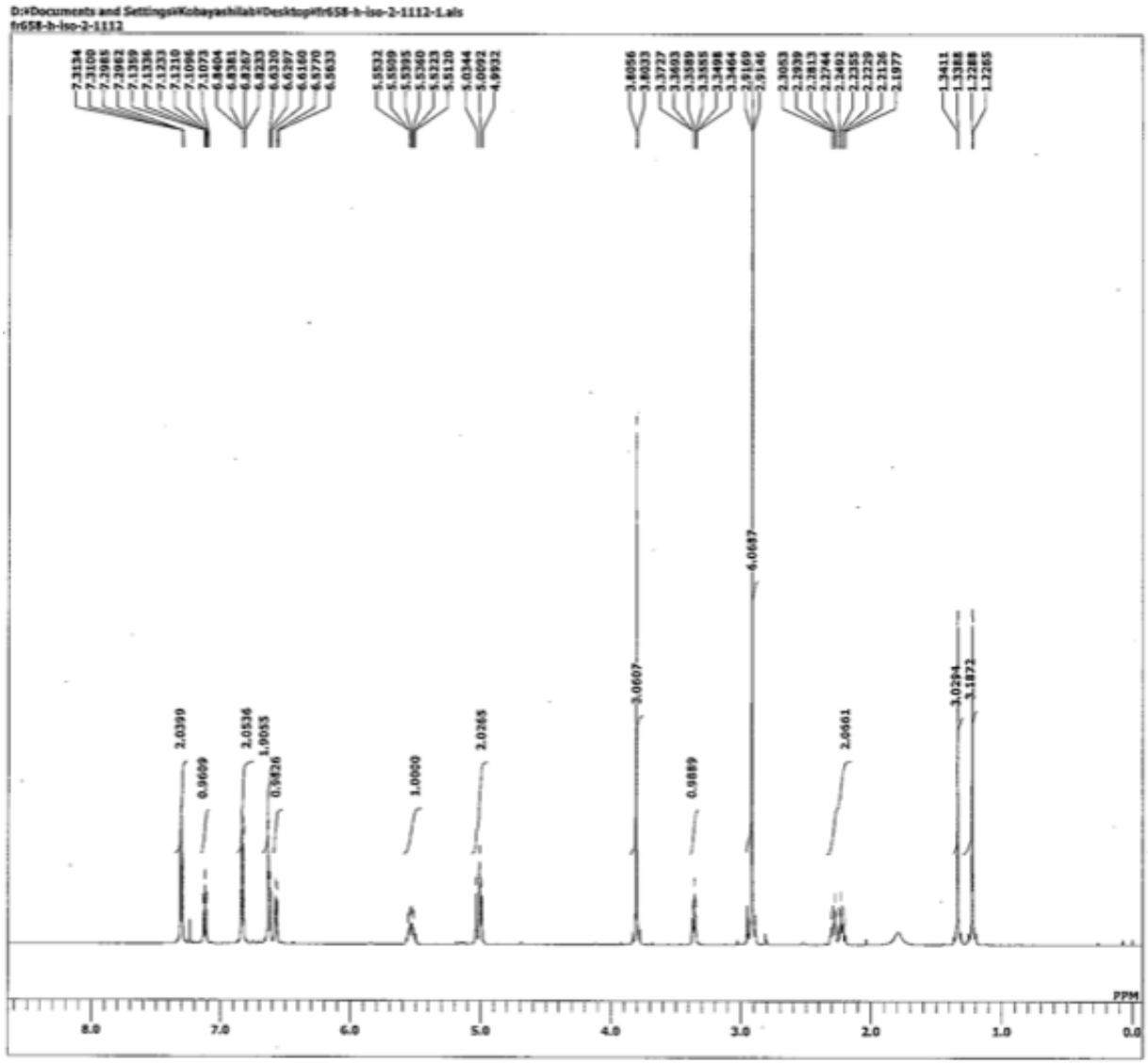
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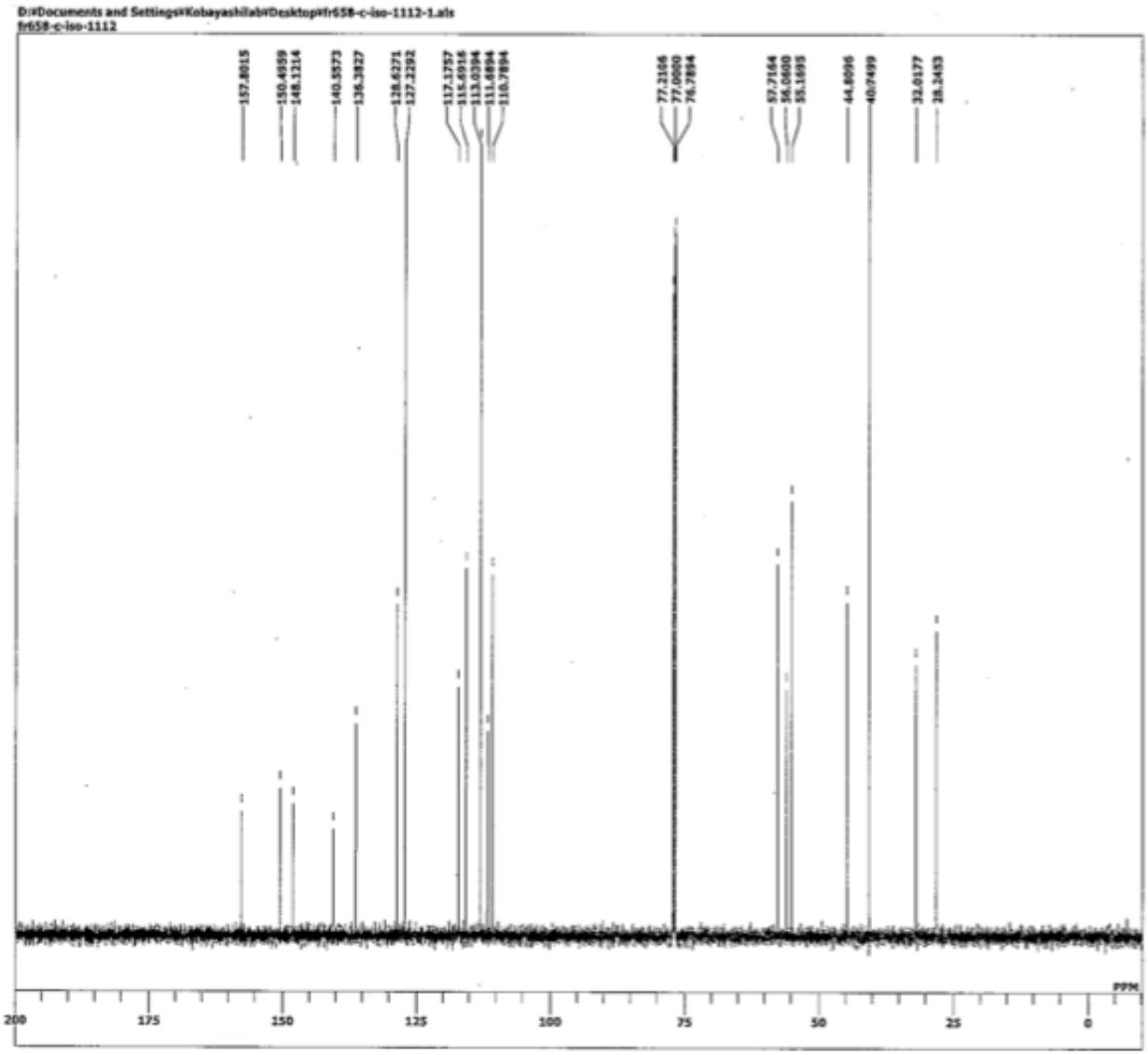
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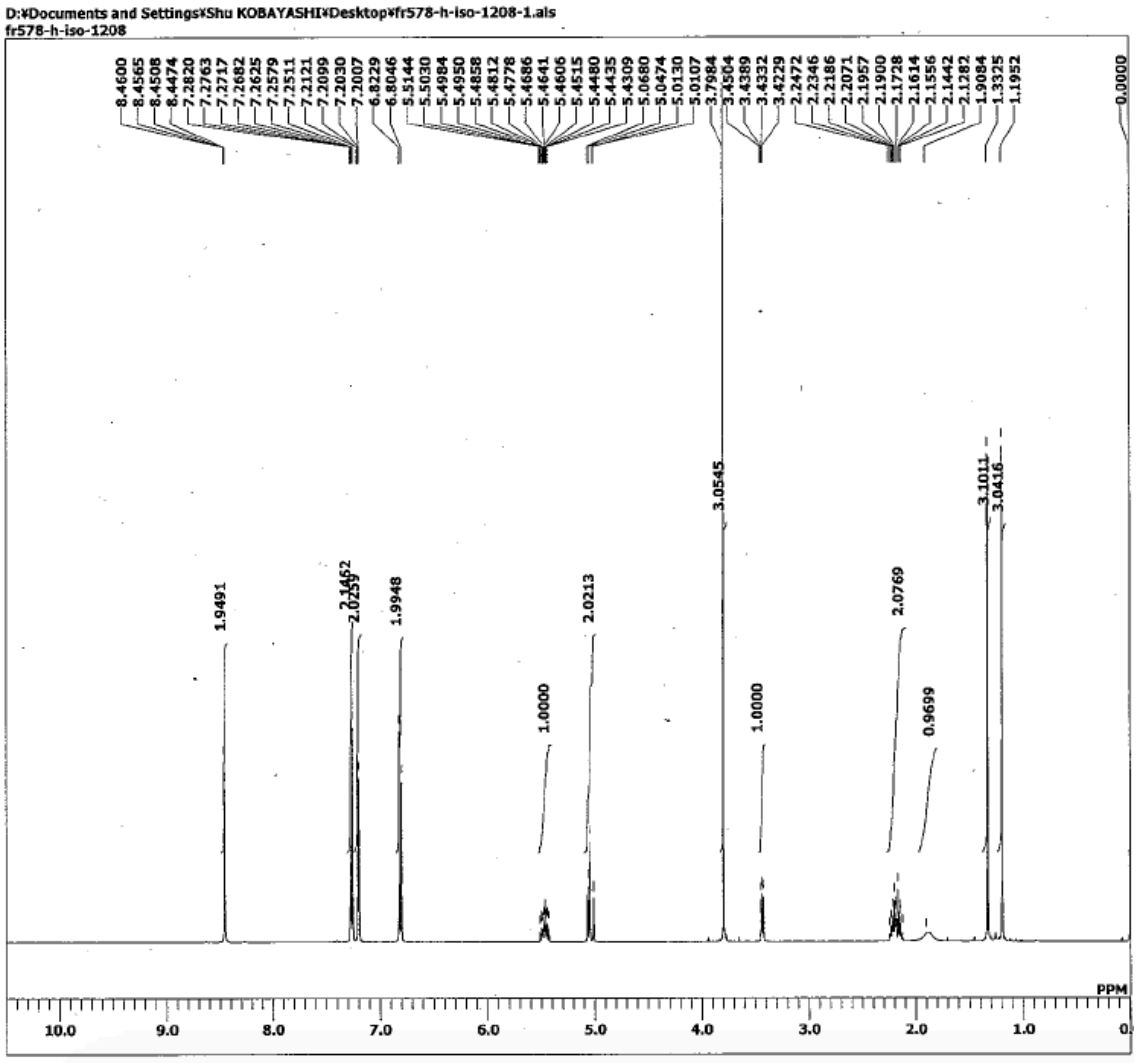
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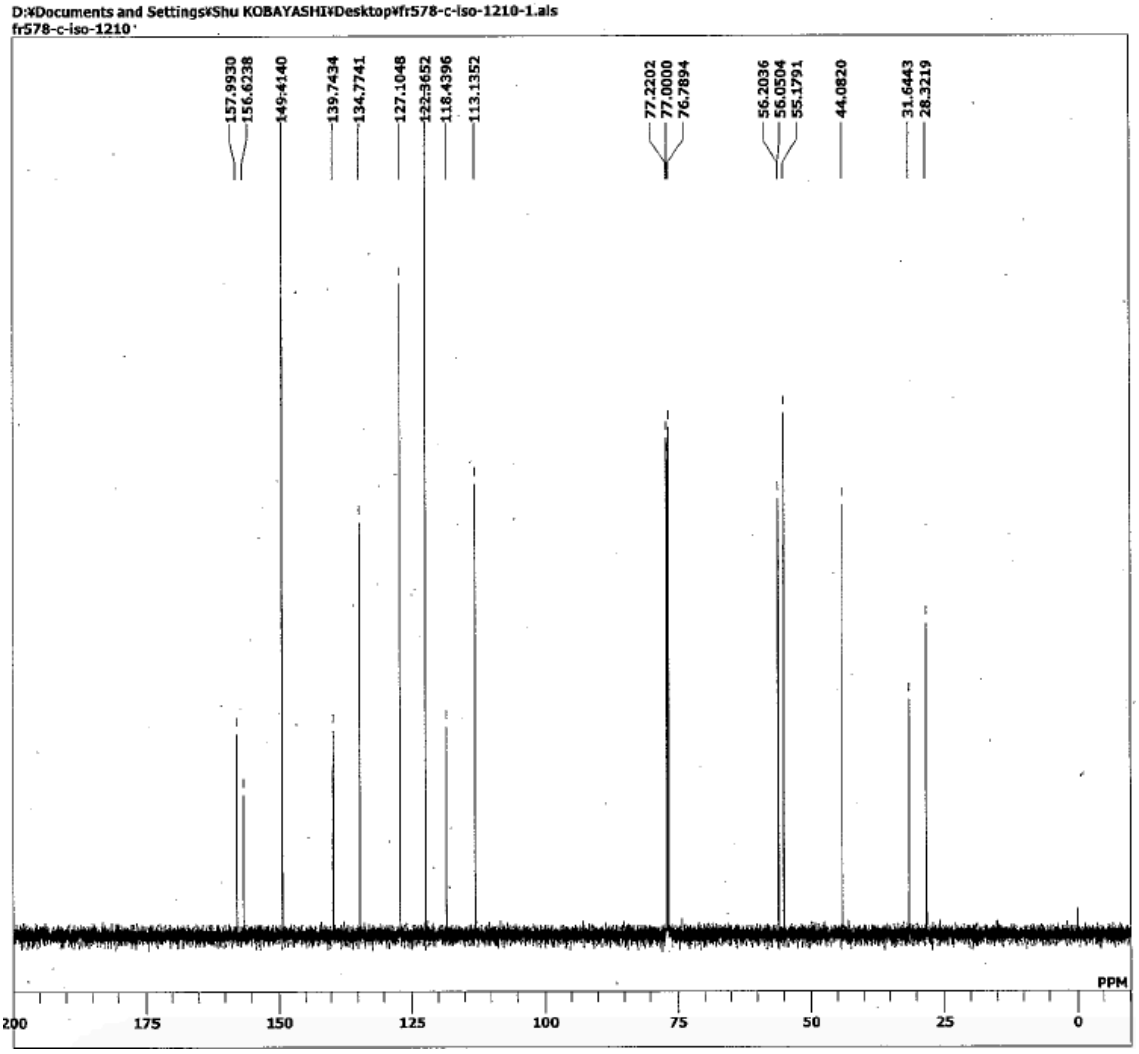
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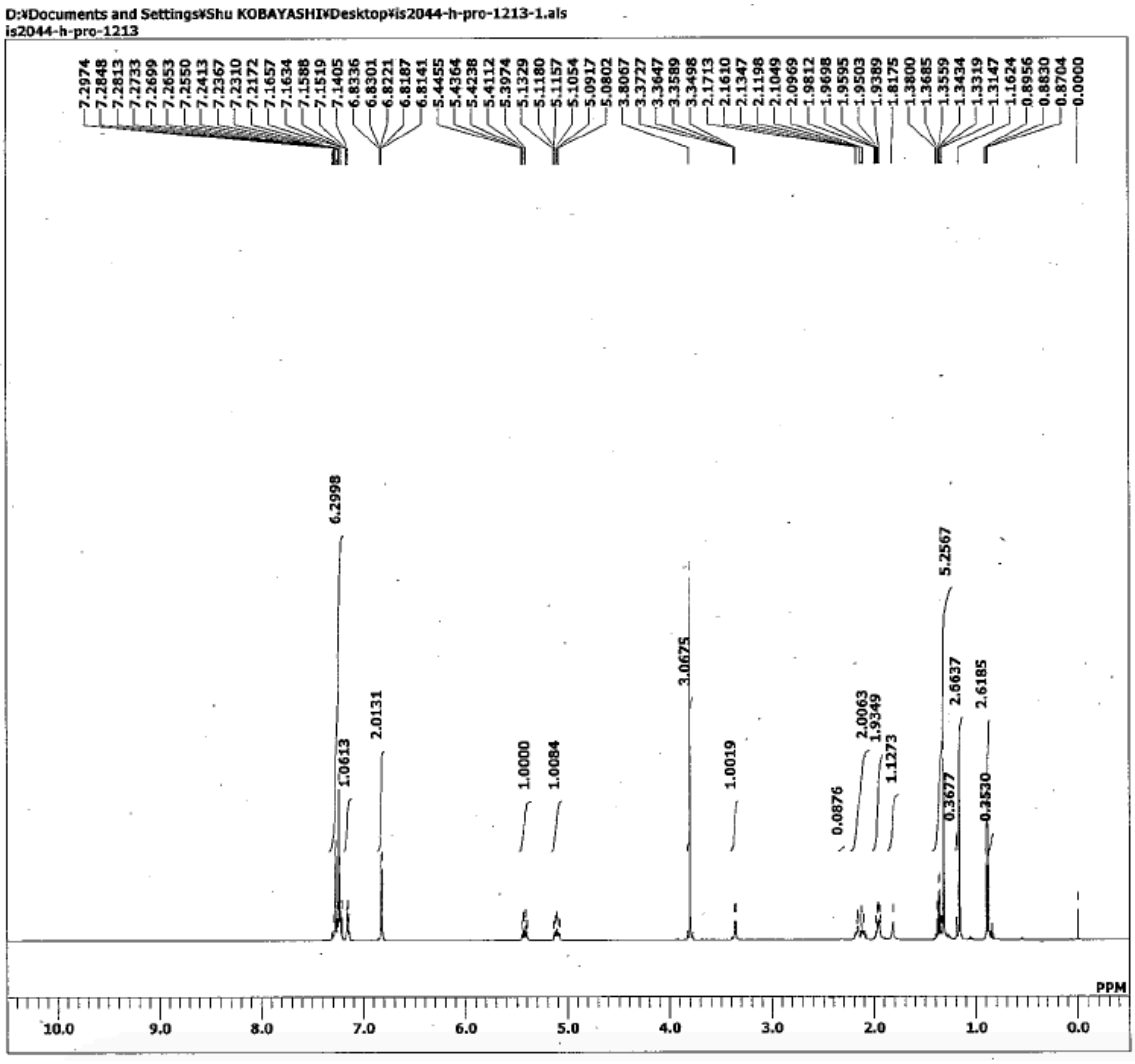
3ab-H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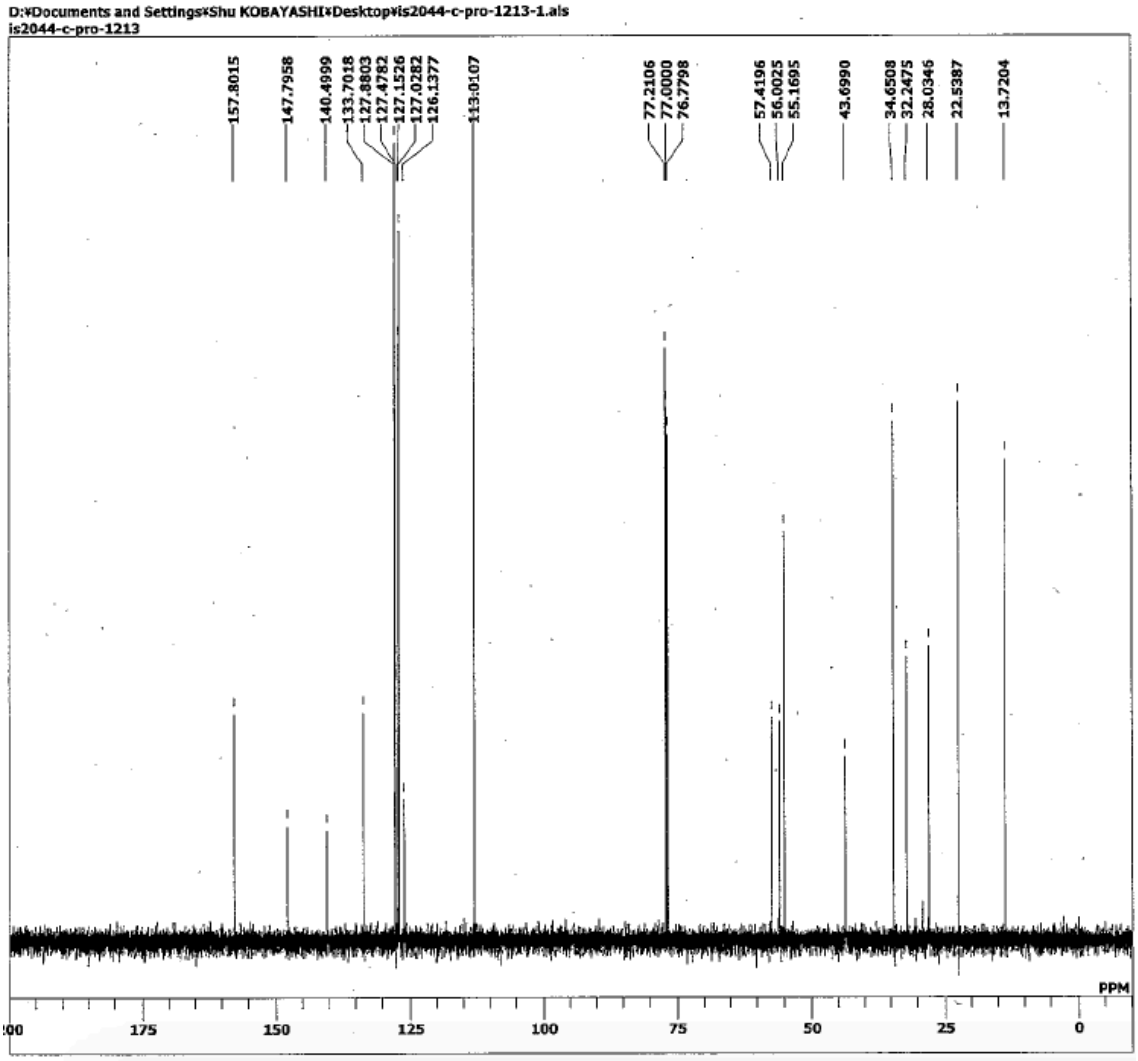
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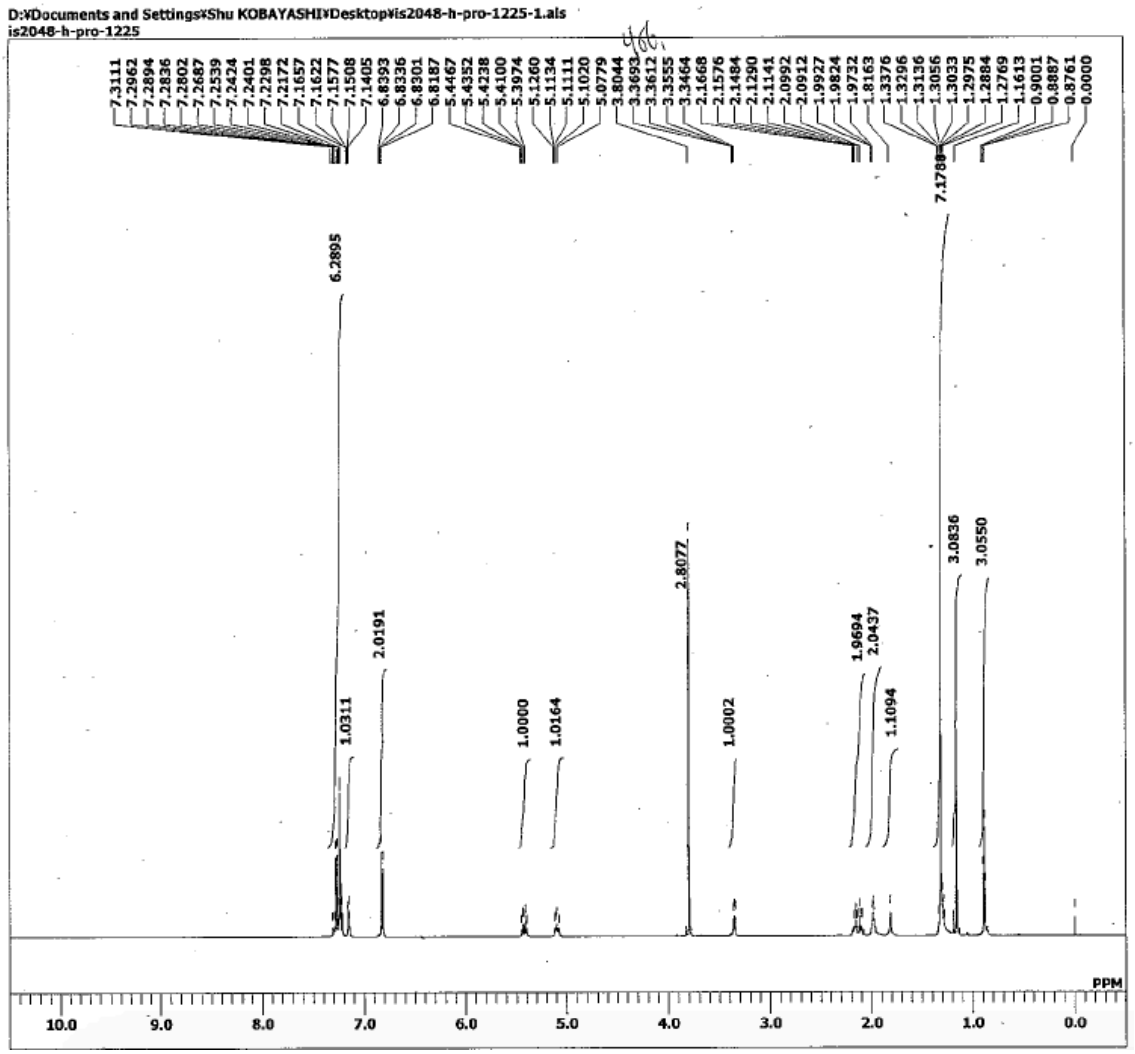
3ac-H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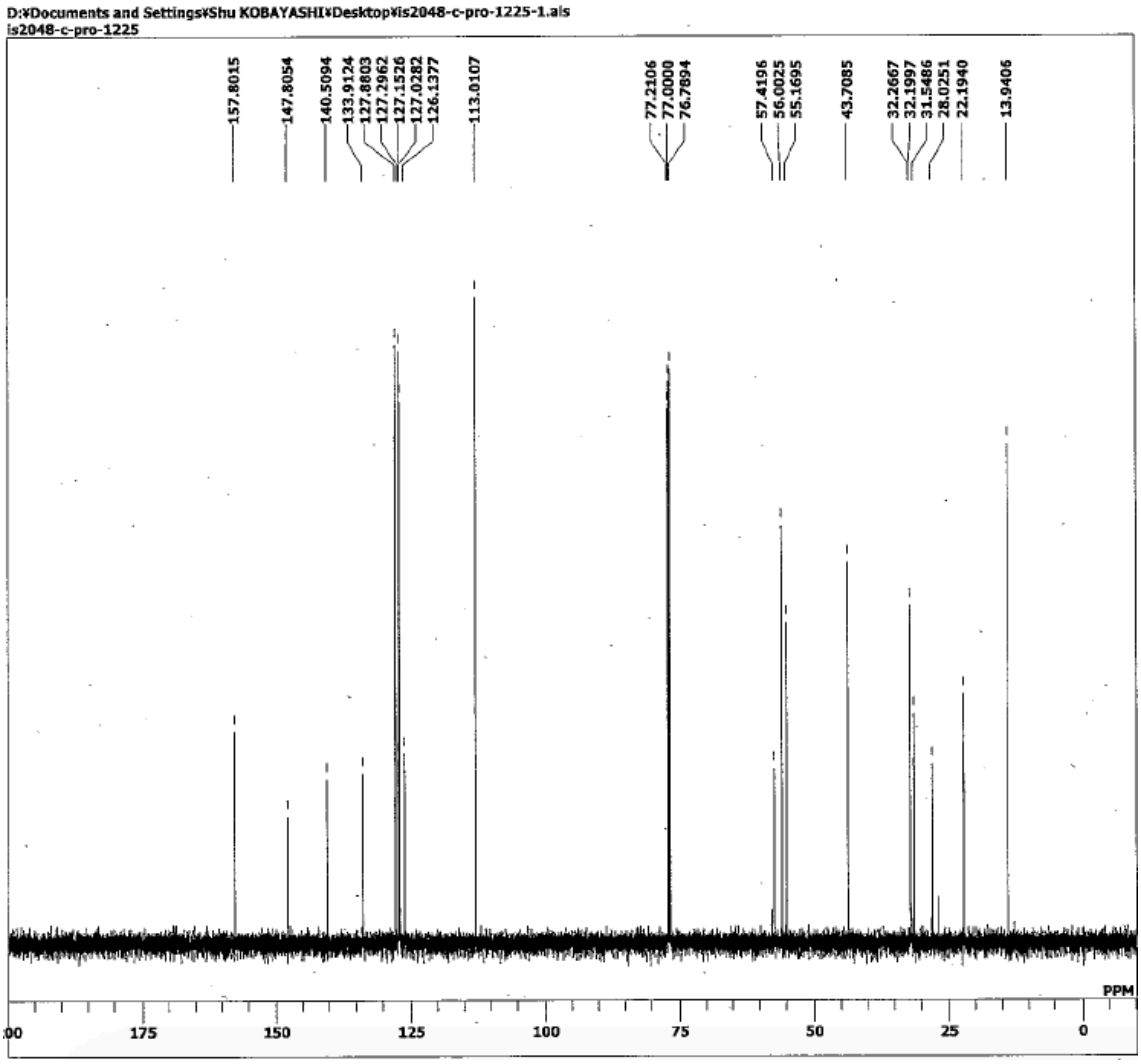
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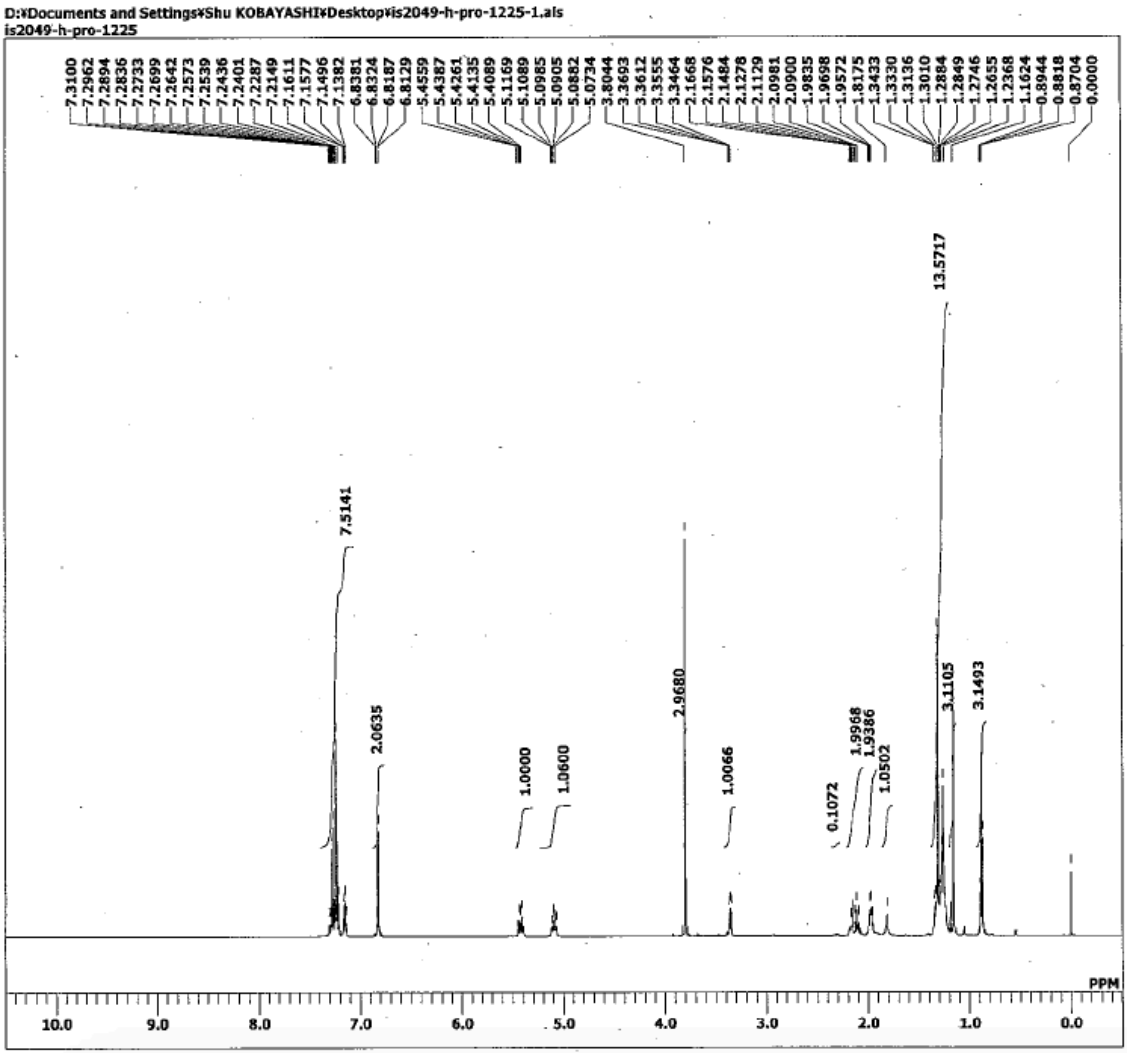
3ad-H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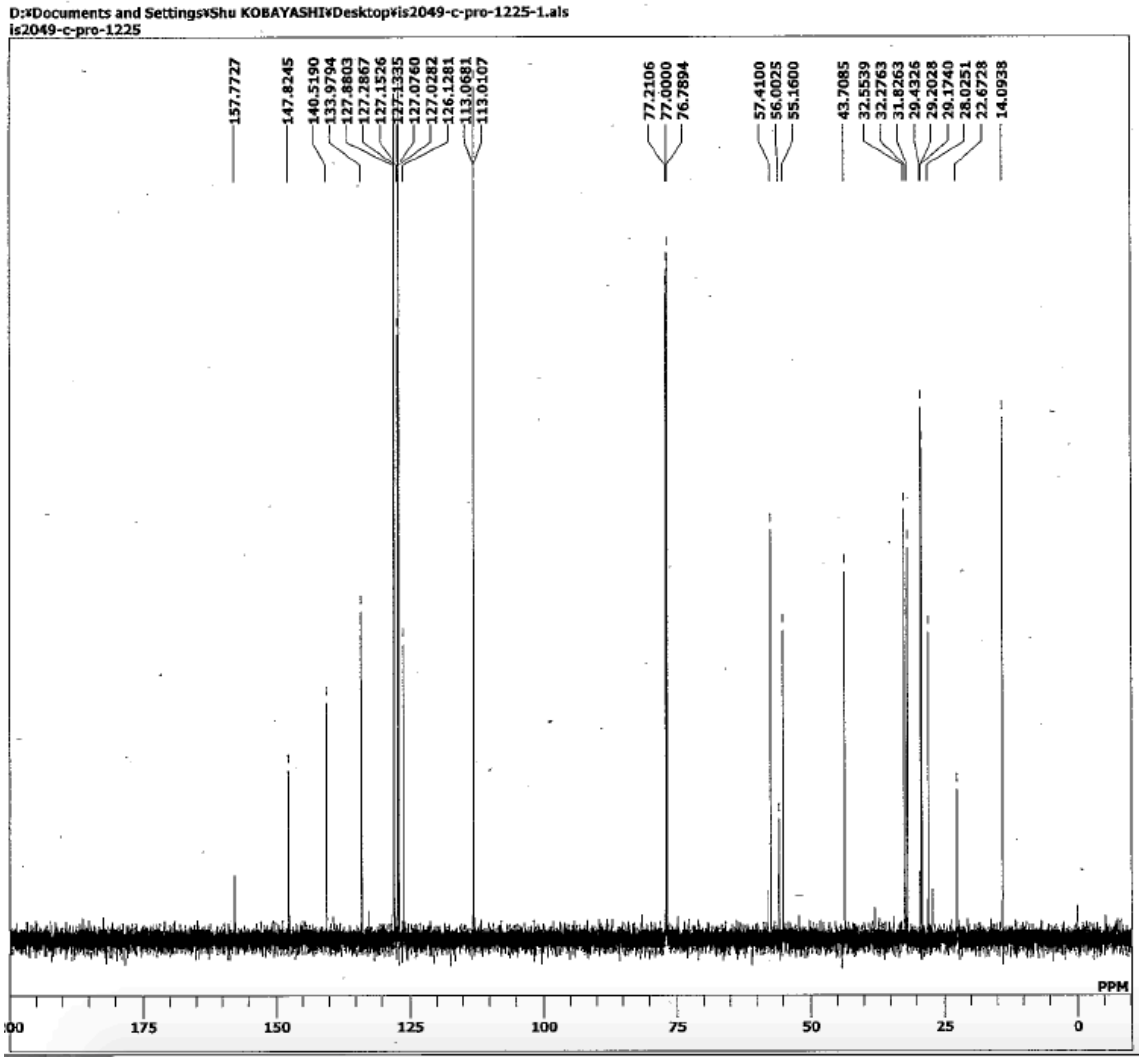
3ad-C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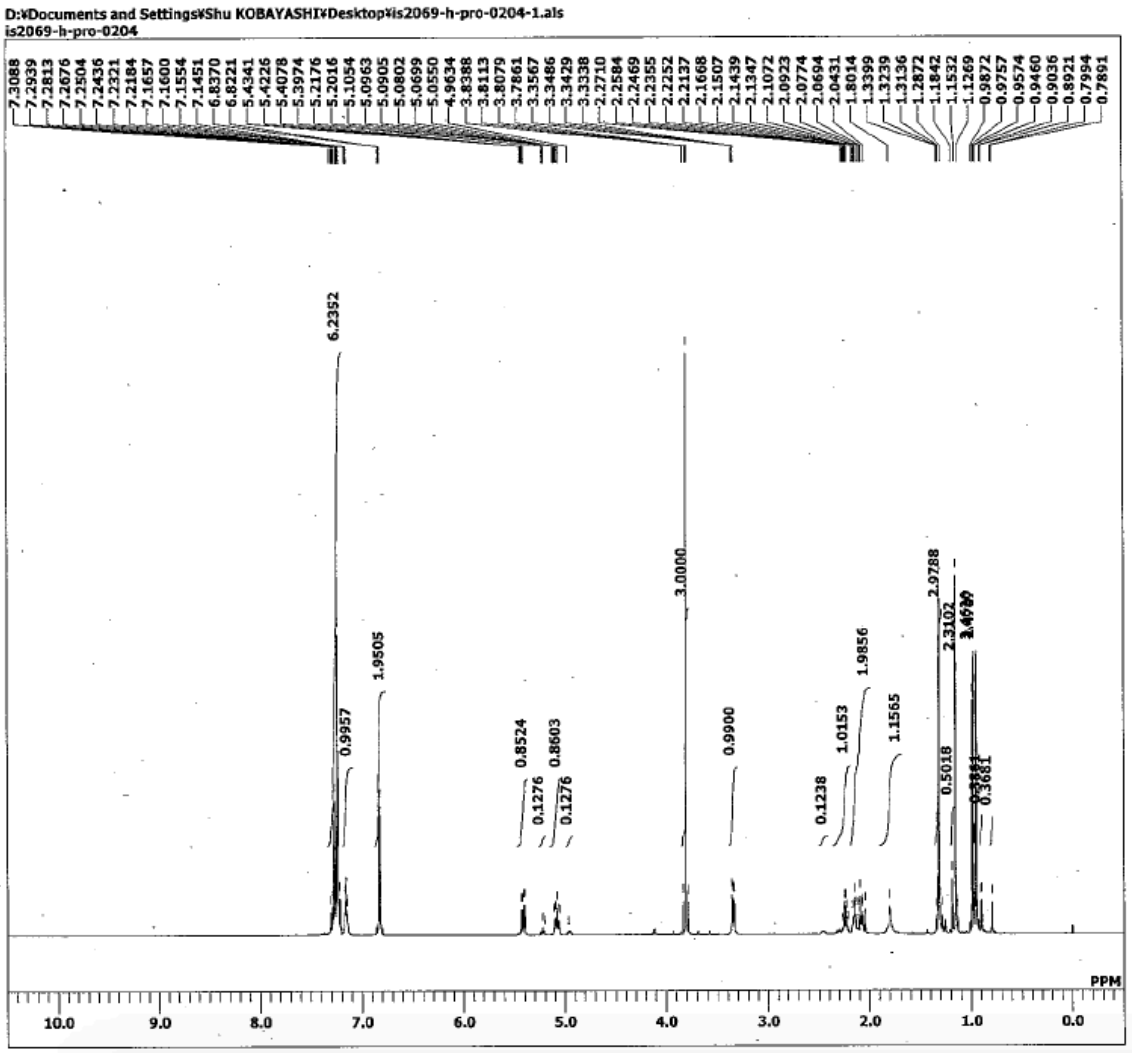
3ae-H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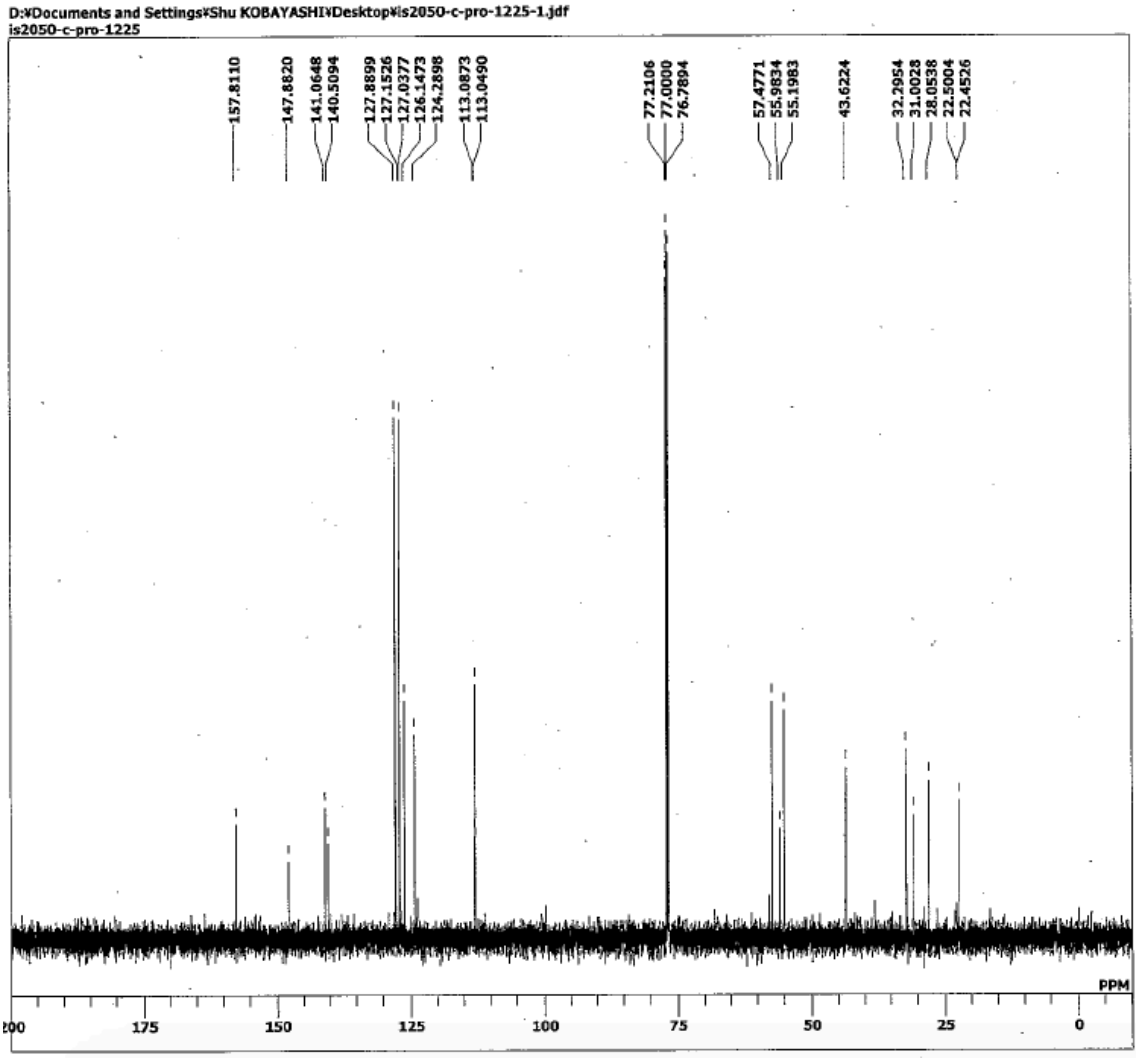
3ae-C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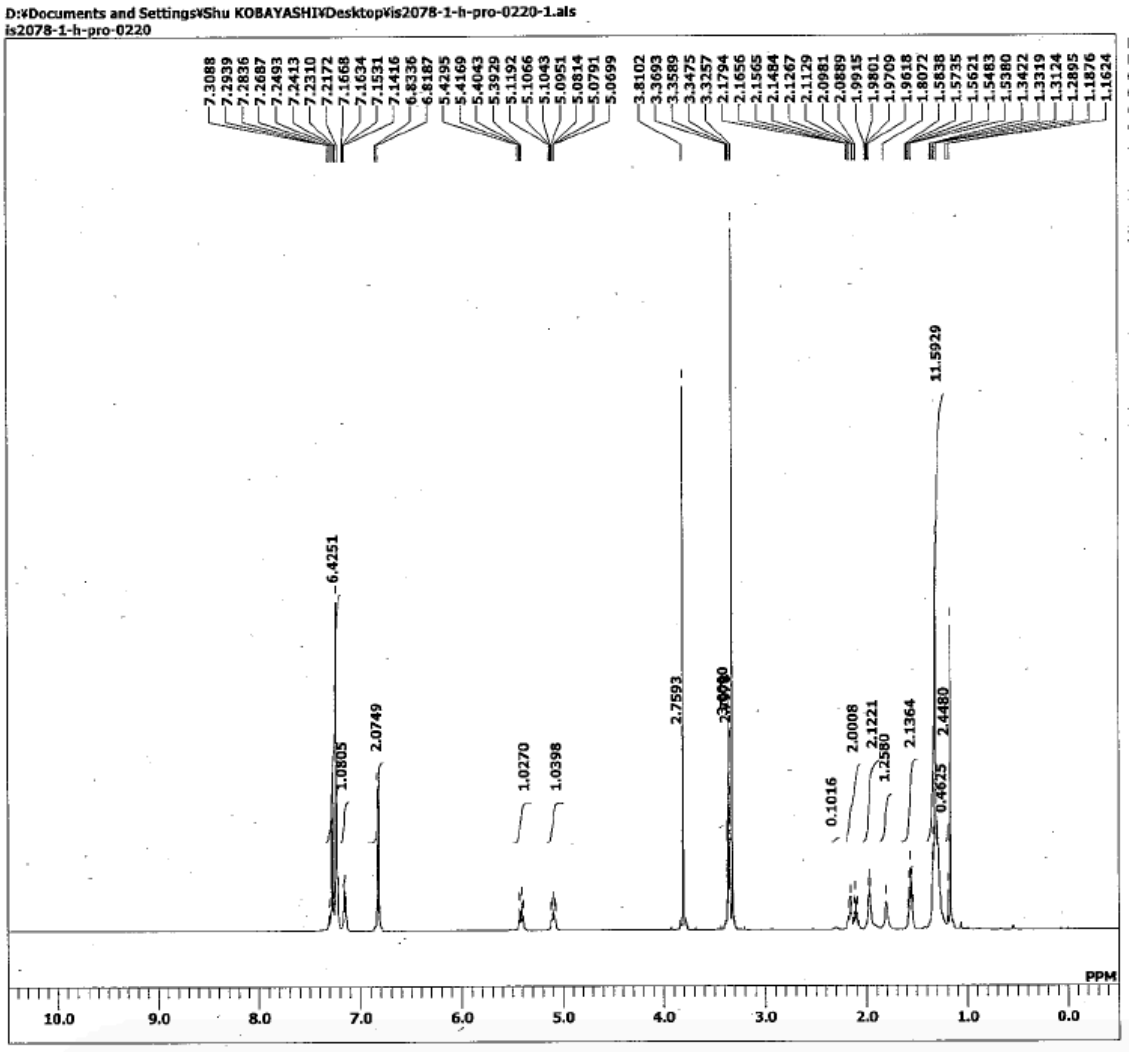
3af-H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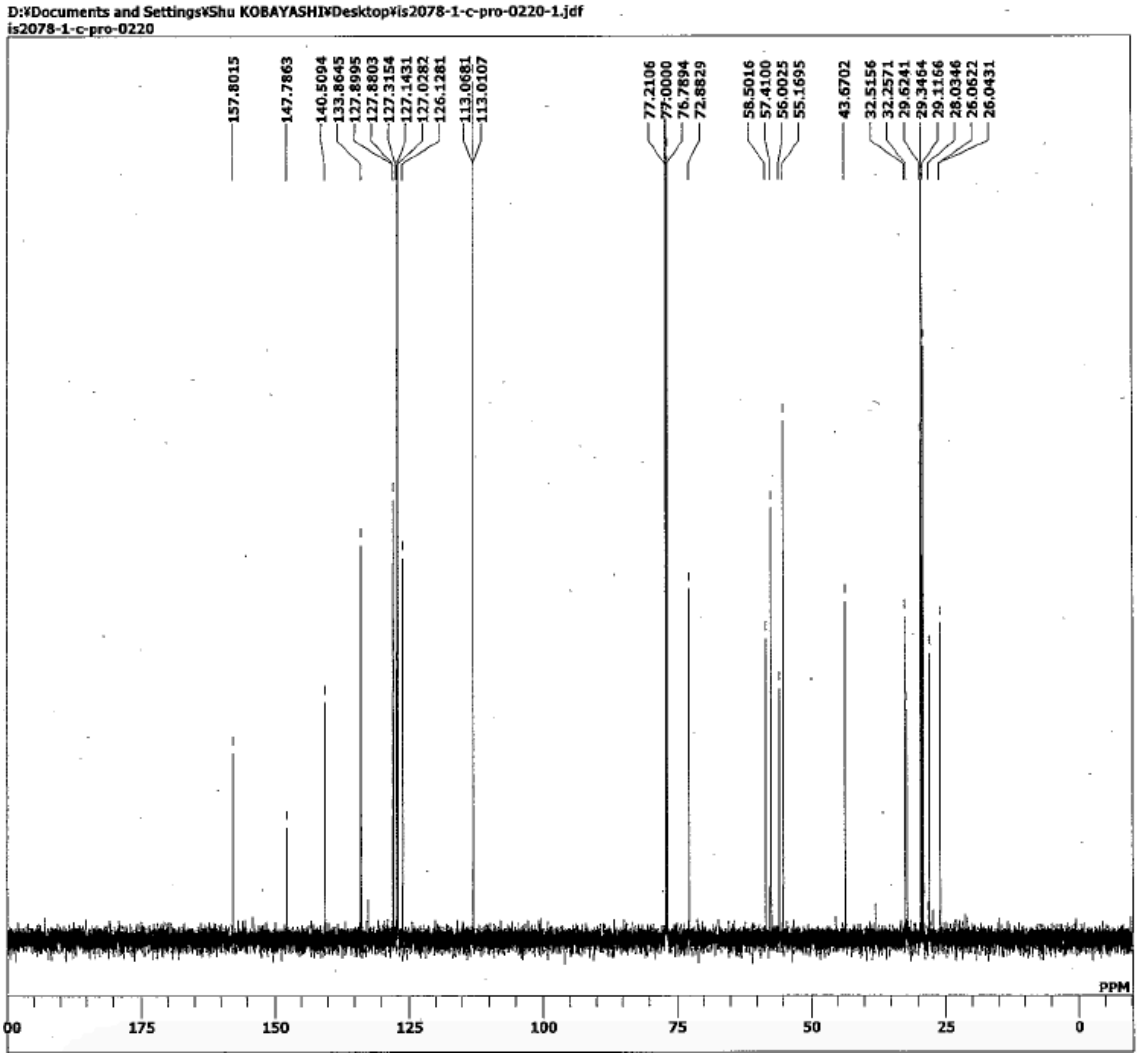
3af-C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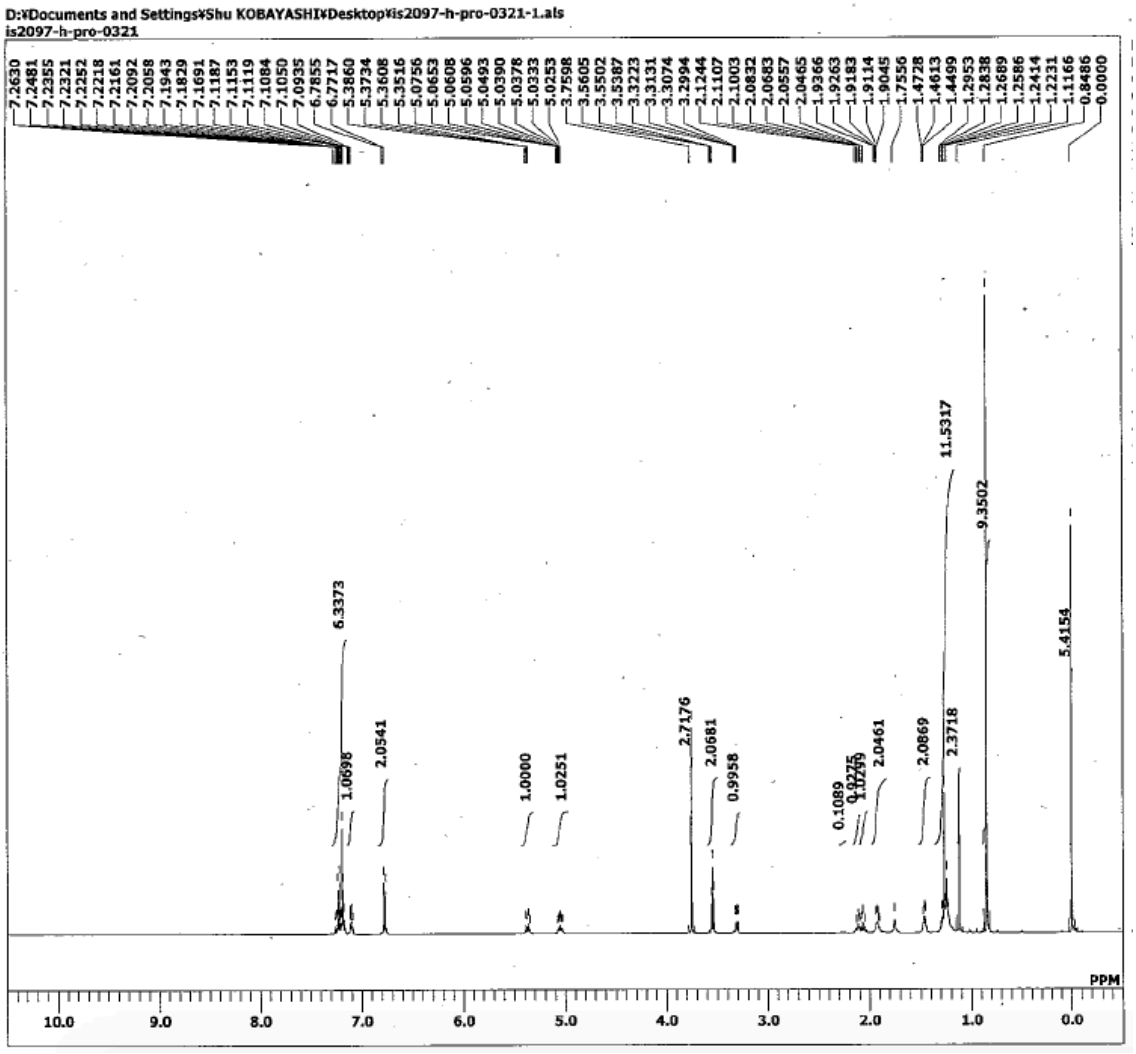
3ag-H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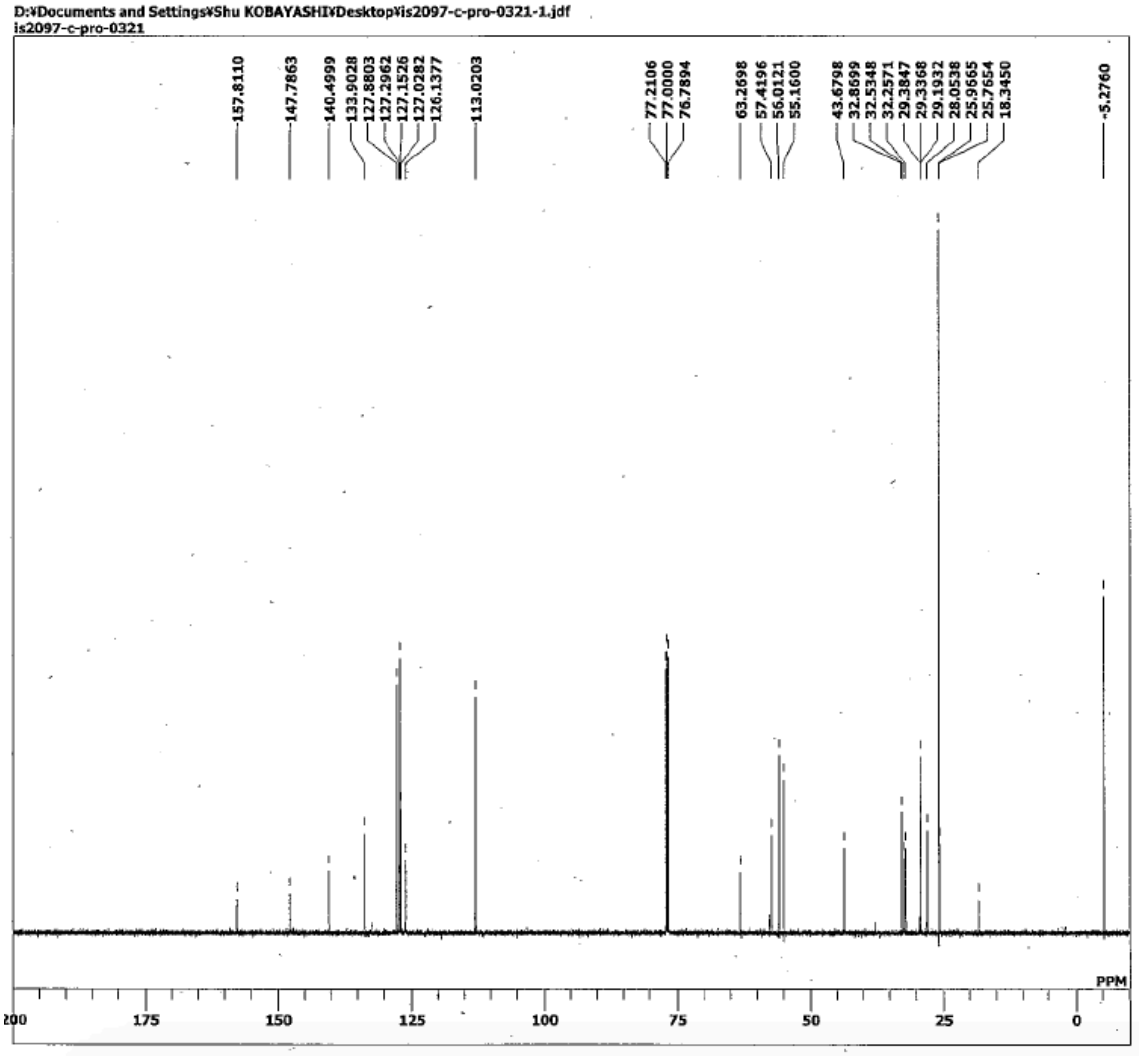
3ag-C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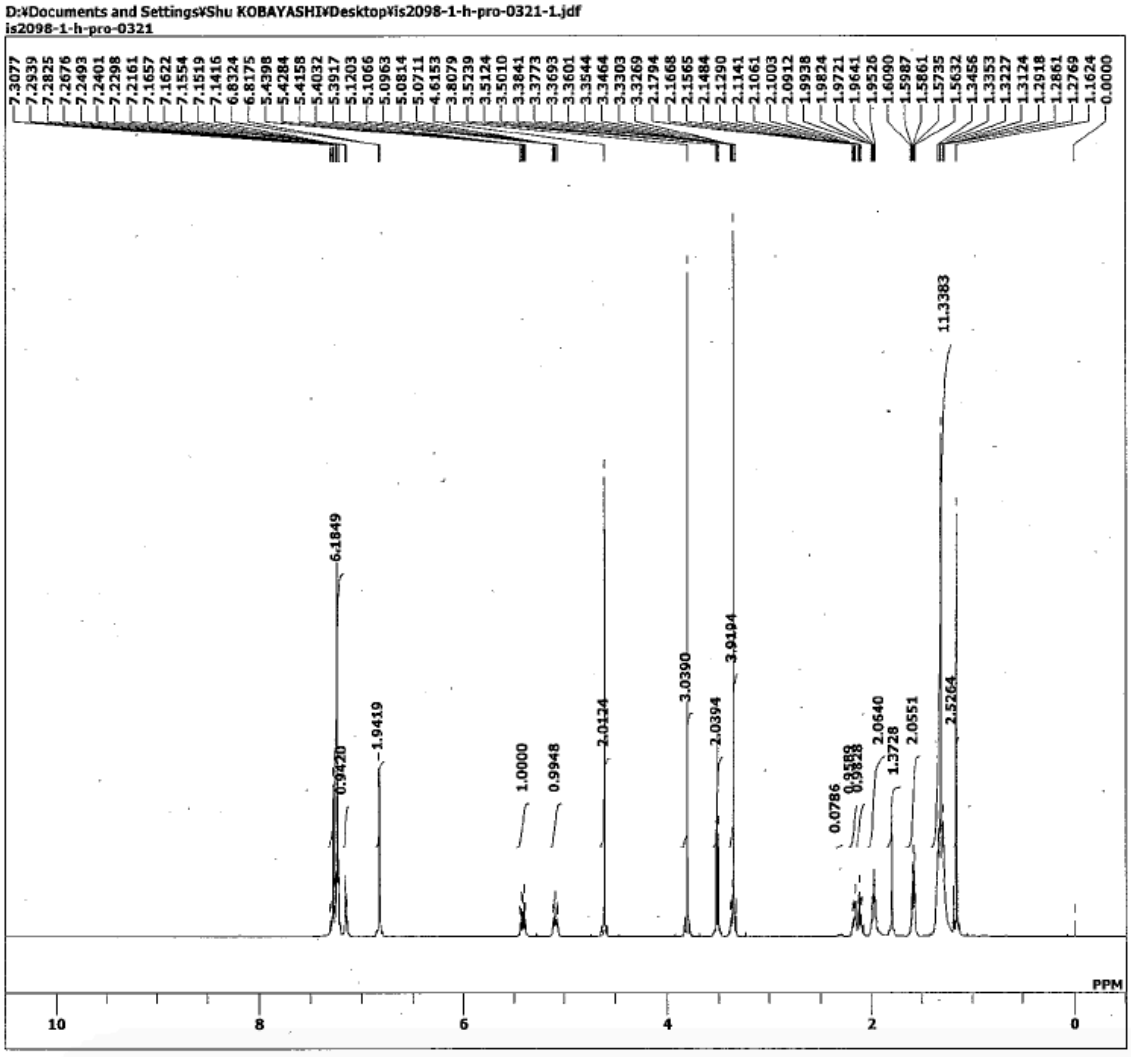
3ah-H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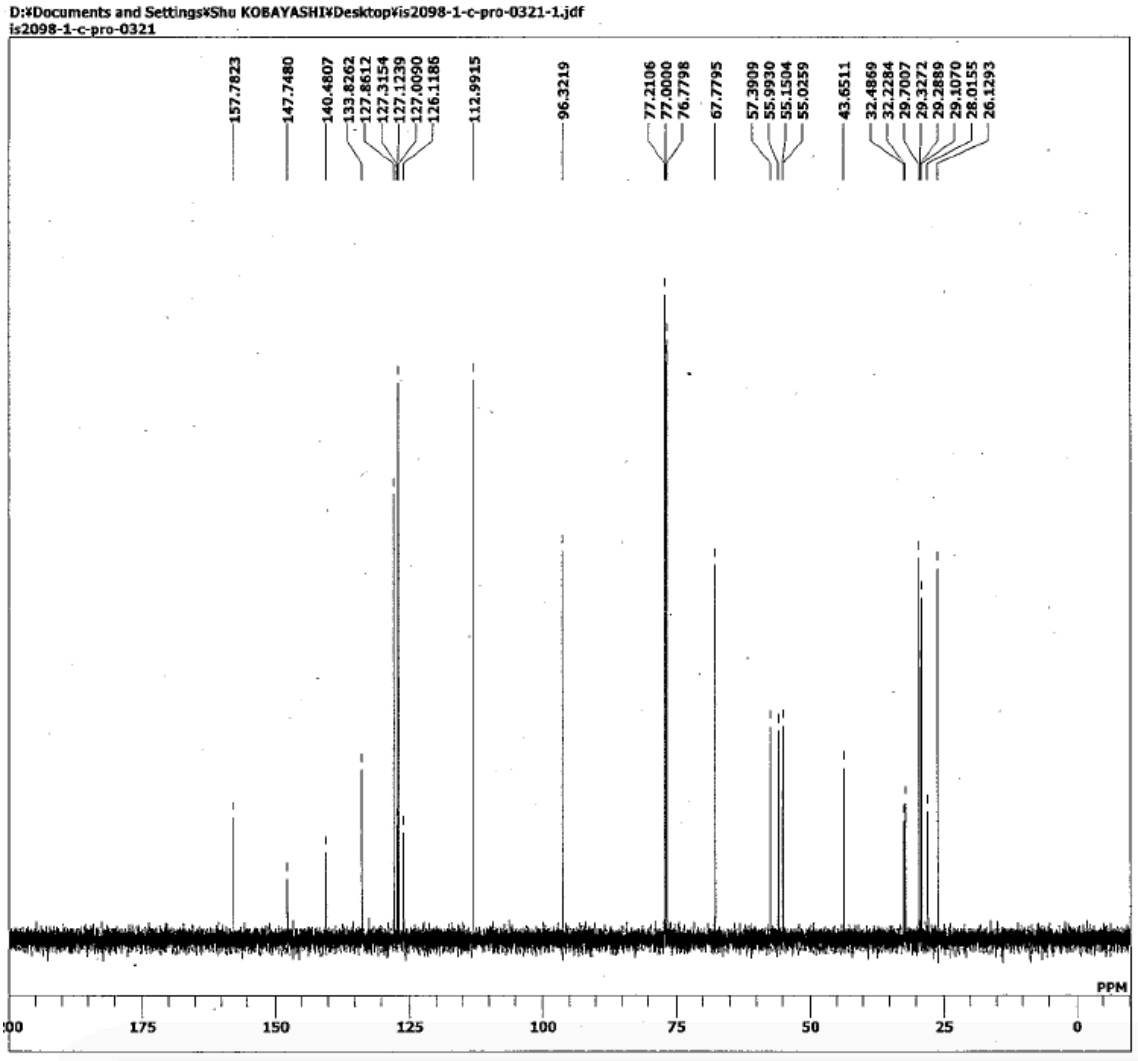
3ah-C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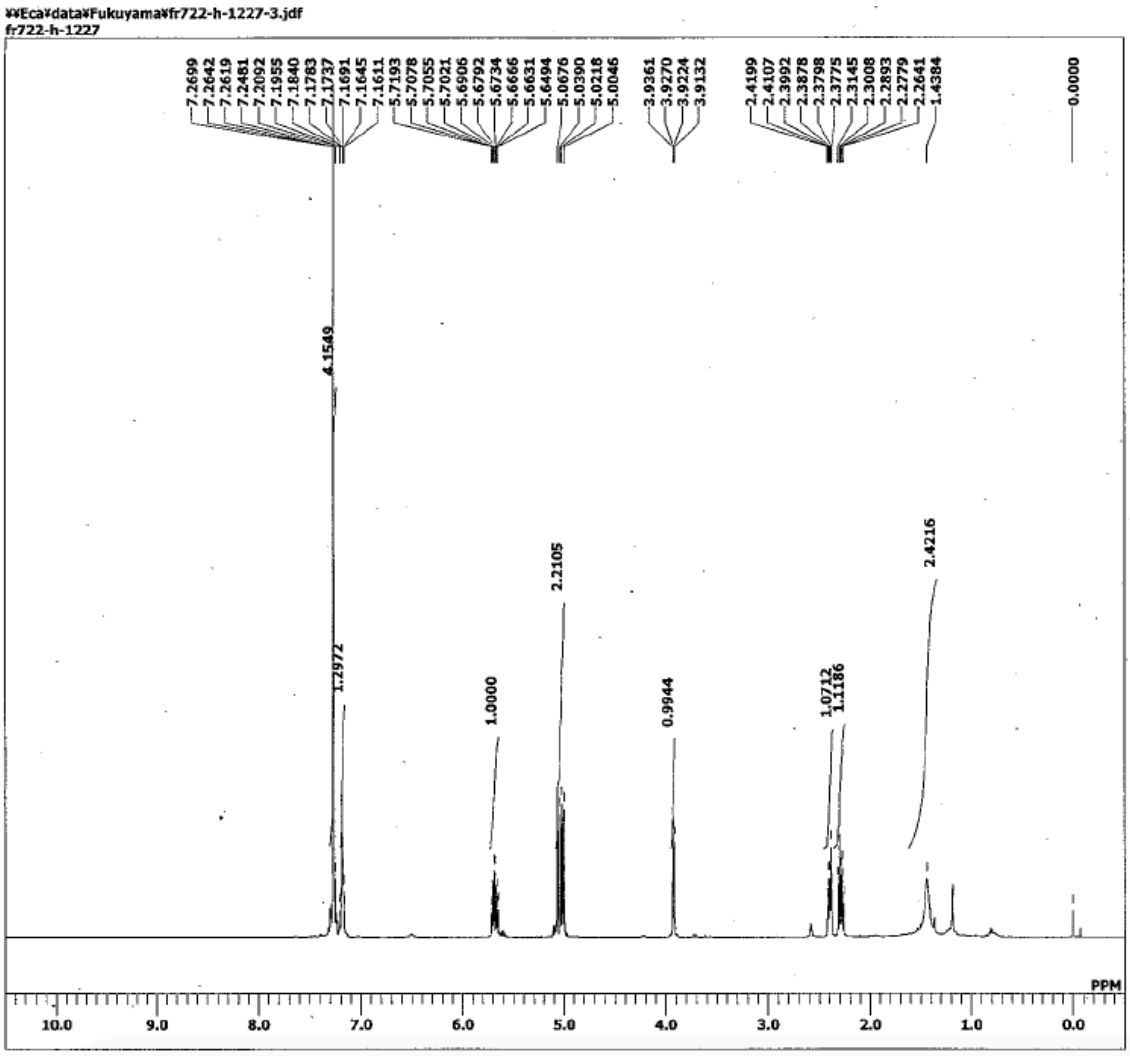
4aa-H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5.7055
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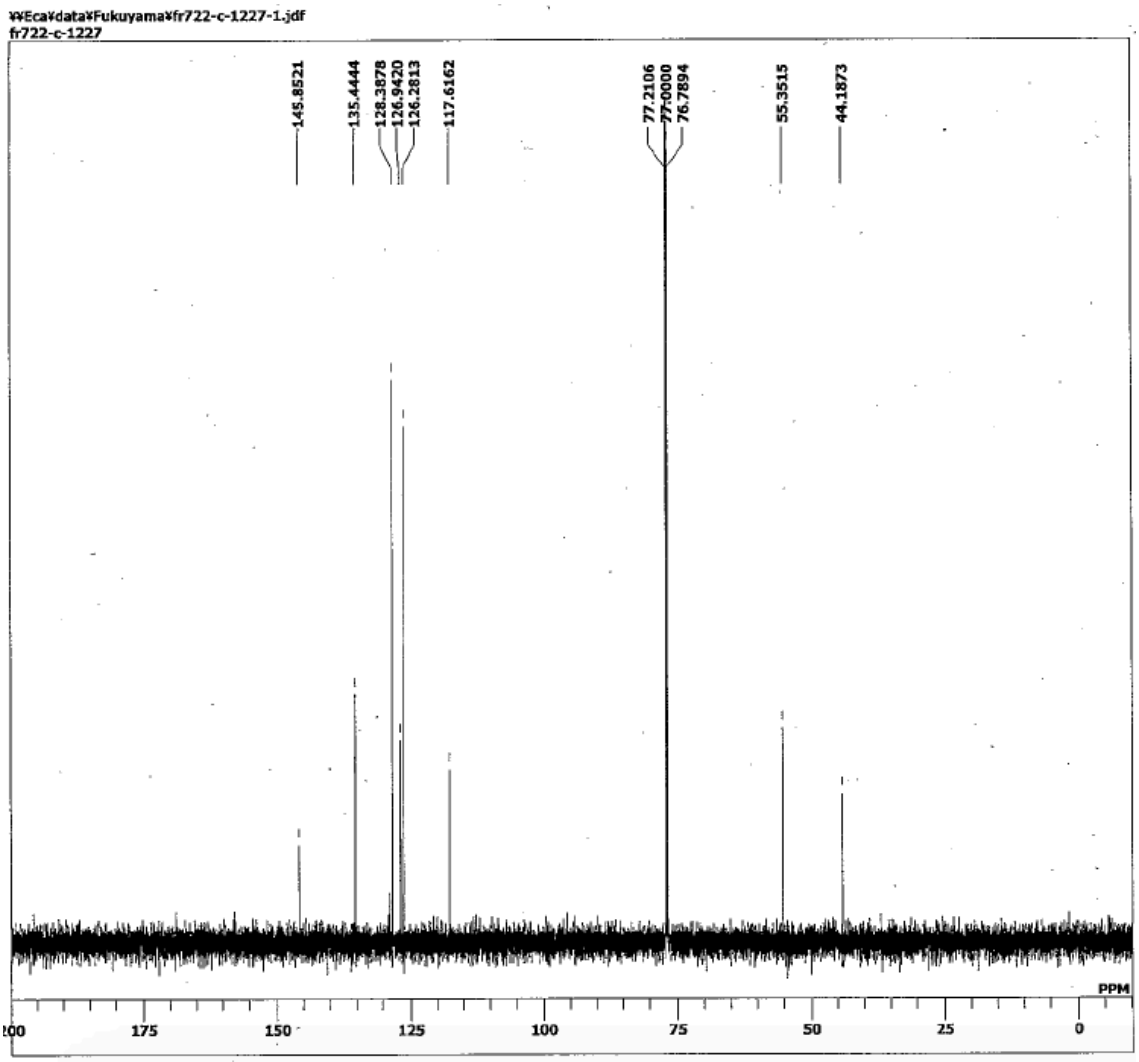
4aa-C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125
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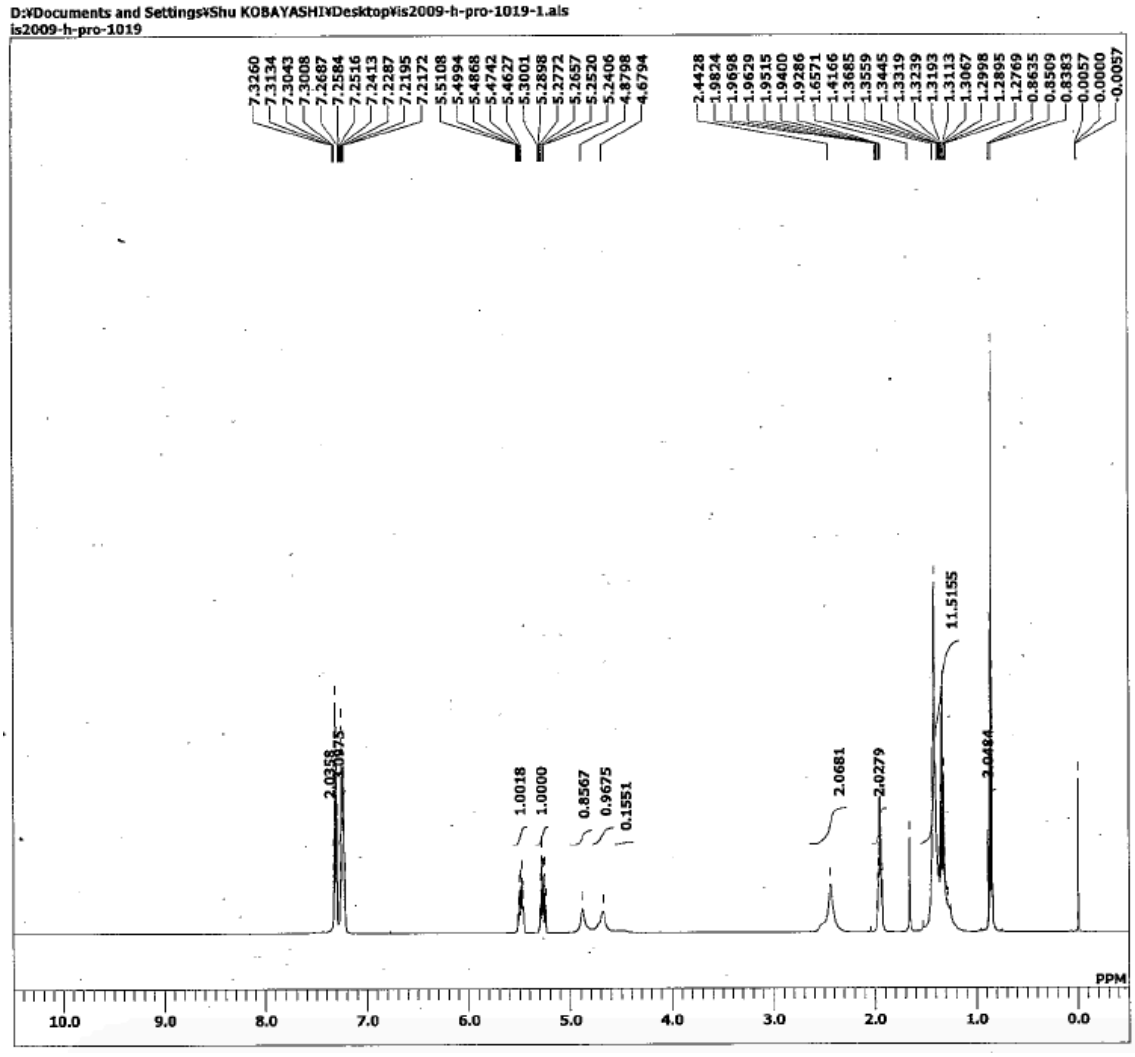
4ab-H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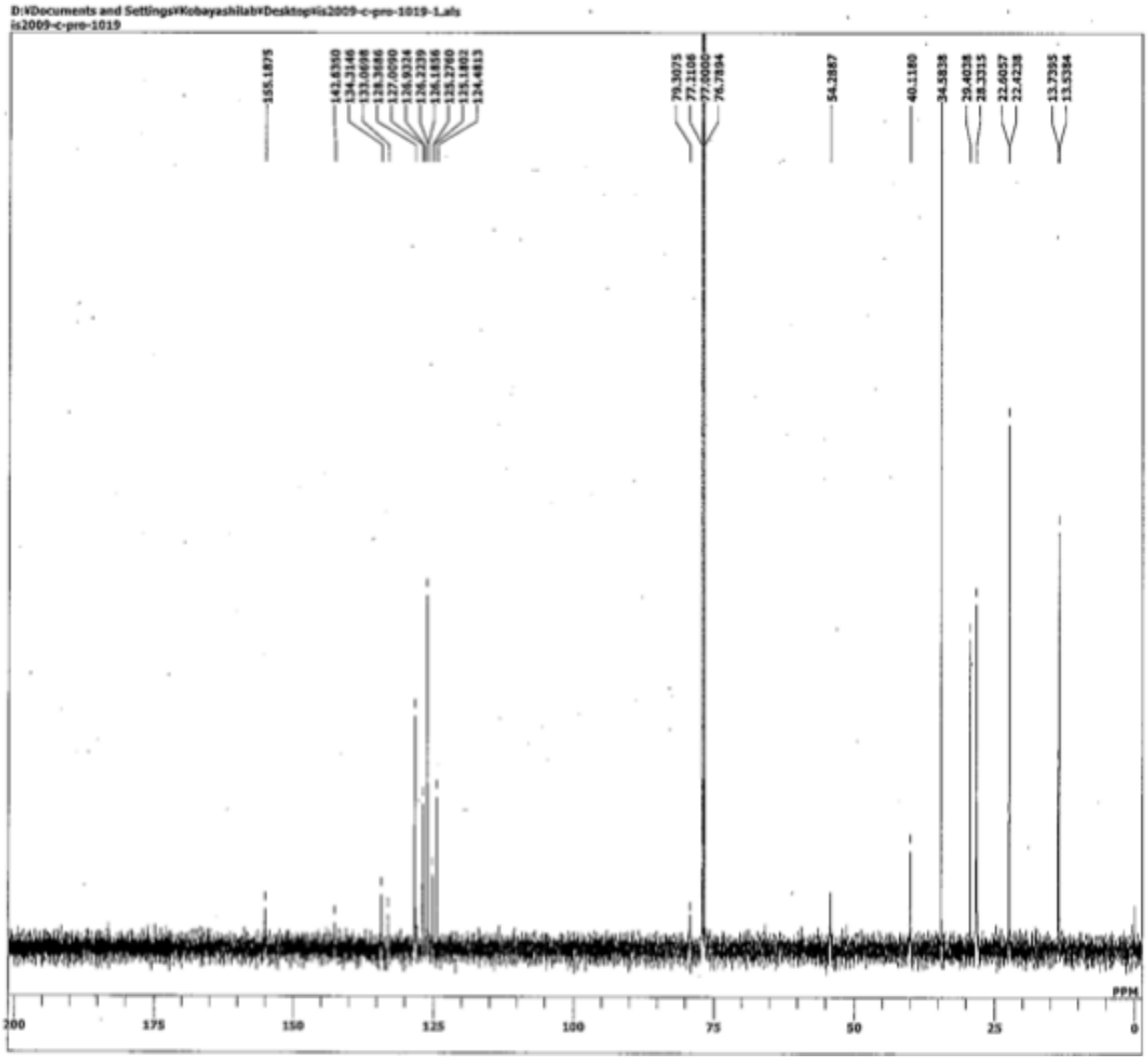
4ab-C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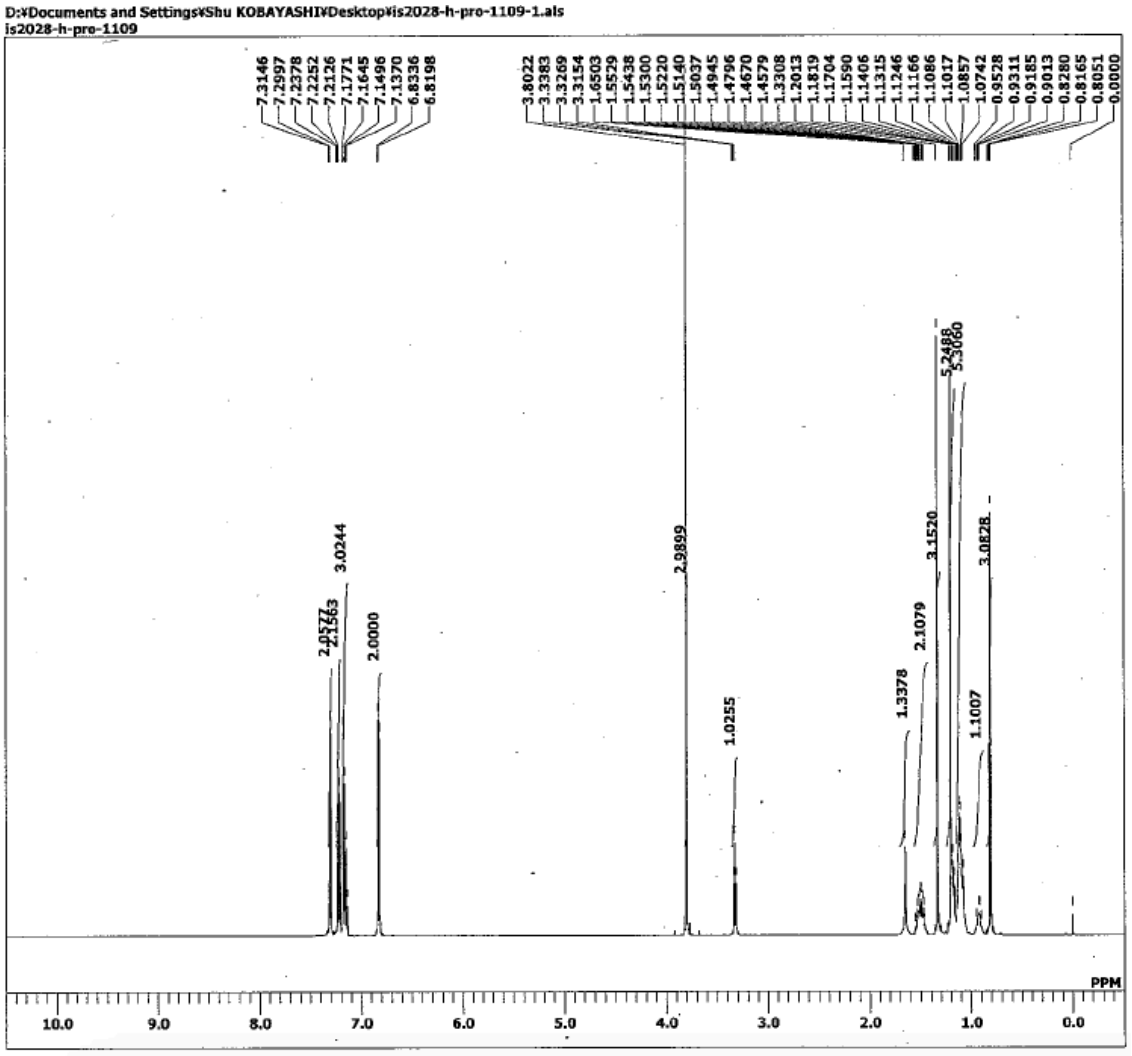
5ab-H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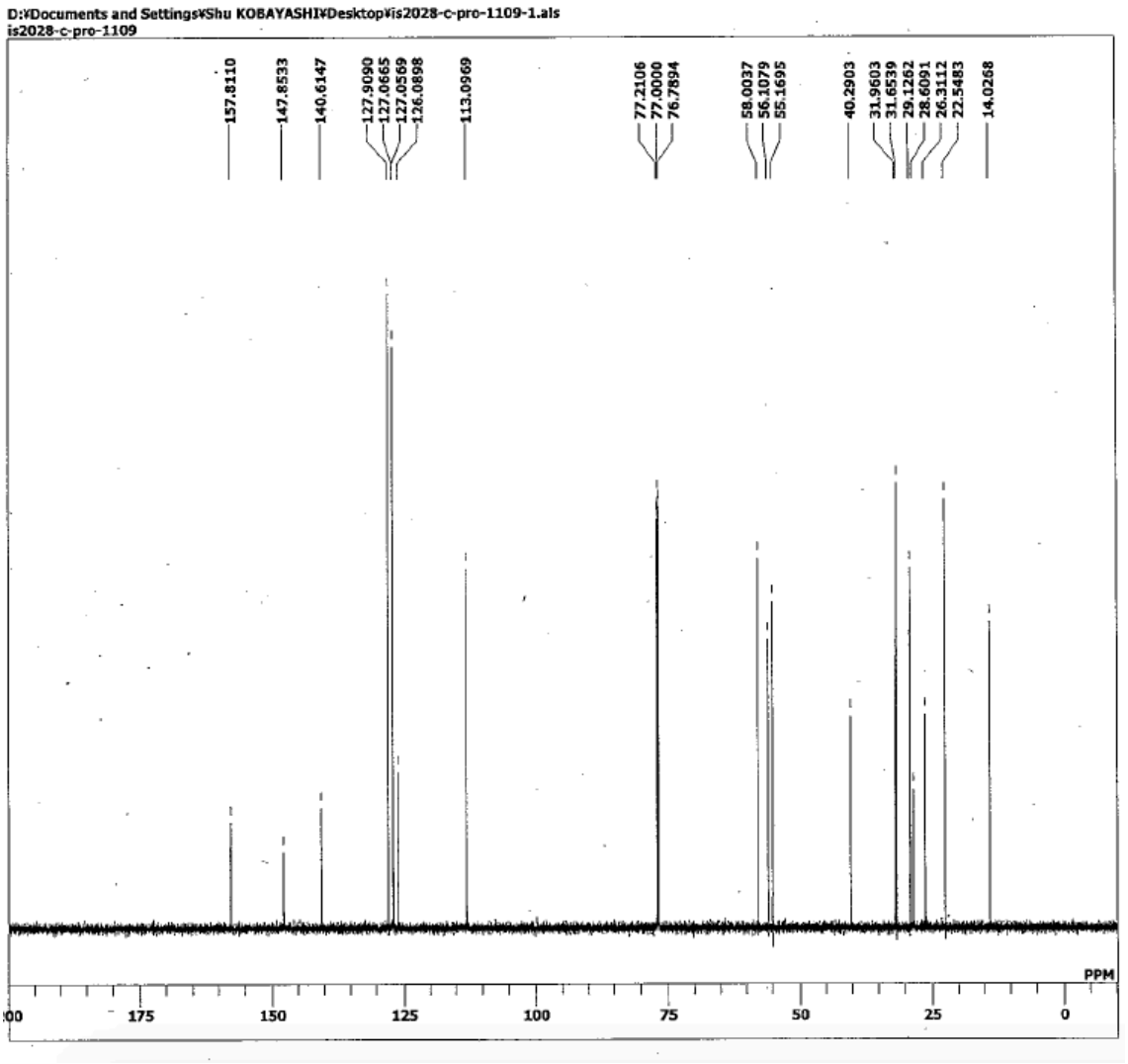
5ab-C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PPM
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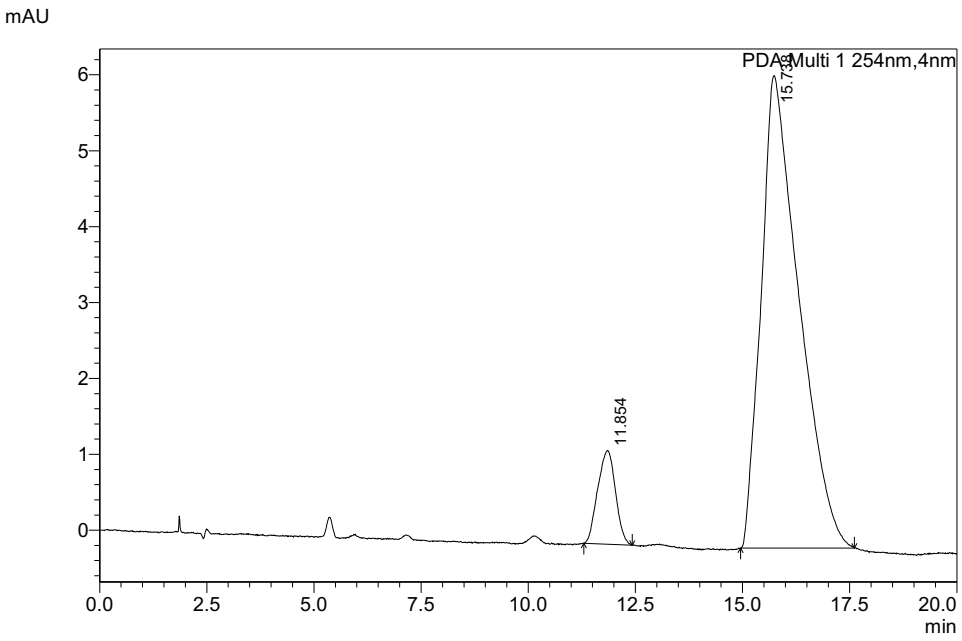
HPLC chart for **3aa**

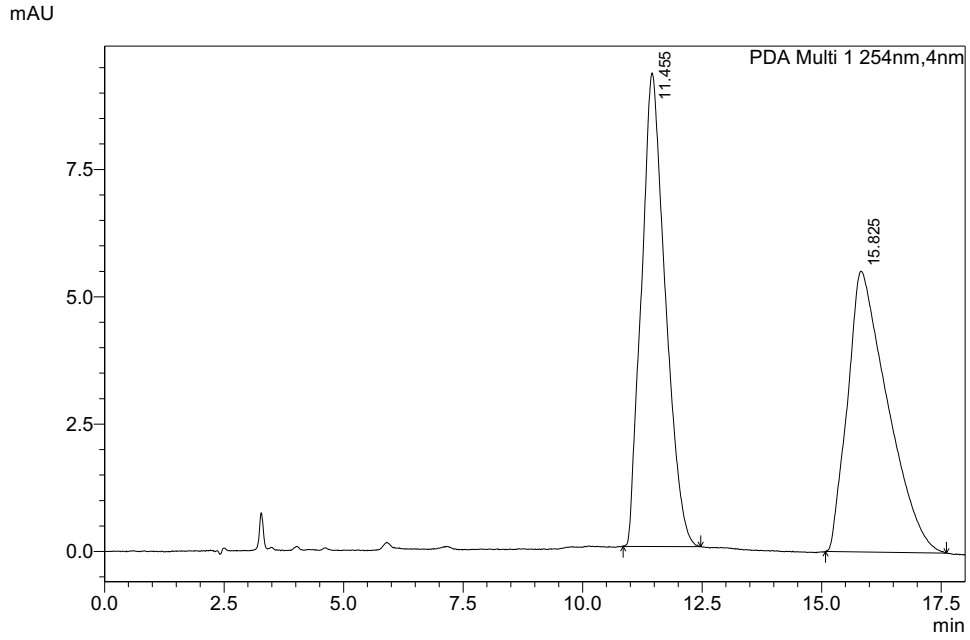


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.854	35573	1235	8.539
2	15.738	381005	6223	91.461
Total		416578	7459	100.000

rac-**3aa**



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.455	322880	9296	50.195
2	15.825	320372	5515	49.805
Total		643252	14811	100.000