Efficient Photolytic C–H Bond Functionalization of Alkylbenzene with Hypervalent Iodine(III) Reagent

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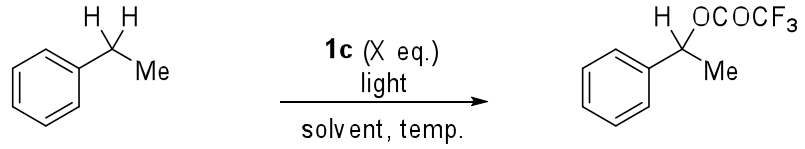
General Information

[1]1H NMR spectra were measured on JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. Infared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. High-resolution mass spectra (HRMS) were performed on Brucker microTOF and Thermo Exactive plus. VBL-SL 150-UU(400) was used as 400 nm LED lamp. The products were purified by flash column chromatography on silica gel (Kanto Chemical silica gel 60 N, neutral, spherical, 40-50 μm) or Merck precoated preparative thin layer chromatography (PLC) plate (silica gel 60 GF254, 0.5 mm). Iodine(III) reagents **1b-d** were prepared according to the literature procedure.[1,2] Substrates **4l**, **4m**, **4n** and **4o** were prepared according to the literature procedure.[3] Commercially available reagents were purchased from Wako, Sigma Aldrich, TCI and Alfa-aesar chemicals and used as received.

Optimization of Reaction Condition using Ethylbenzene 4a with 1c.

The effect of the amount of **1c** and solvents were summarized in Table S1 (entries 1-7). Decreasing the amount of **1c** to 1 equiv or 1.2 equiv resulted in lower yields of **7a** in 53% and 75% respectively (entries 2 and 3). Other solvents, such as trifluoroethanol, chloroform or tetrachloromethane, were found to be less satisfactory than benzene in term of chemical yield (entries 4-6). We also tested the reaction of **4a** with **1c** by the thermal decomposition approach instead of the photolysis (entries 7-10). However, the desired product was not observed, even when the reaction was carried out at 150 °C (entry 10).

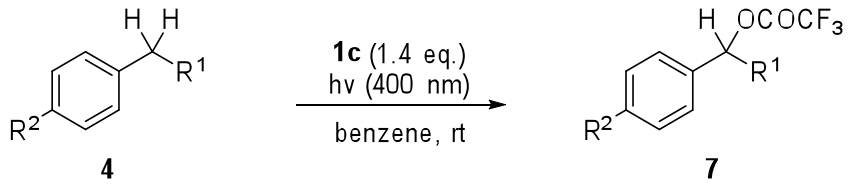
Table S1.



4a **7a**

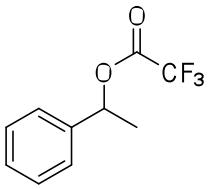
entry	reagent **1c** (eq.)	light	temp.	solvent	% yield
1	1.4	400 nm	RT	benzene	98
2	1.0	400 nm	RT	benzene	53
3	1.2	400 nm	RT	benzene	75
4	1.4	400 nm	RT	CF_3CH_2OH	16
5	1.4	400 nm	RT	CH_3Cl	75
6	1.4	400 nm	RT	CCl_4	48
7	1.4	no light	RT	benzene	no reaction
8	1.4	no light	50 °C	benzene	no reaction
9	1.4	no light	80 °C	benzene	trace
10	1.4	no light	150 °C	benzene	trace

General Procedure for the Direct Trifluoroacetoxylation of Alkylbenzenes (4) (Table 2)



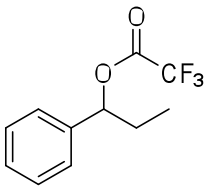
To a stirred solution of alkylbenzene (**4**) (0.5 mmol) in benzene (1.0 mL) was added **1c** (301 mg, 0.7 mmol) at room temperature. The reaction mixture was then stirred for 12 h under visible light (400 nm). The crude product was analyzed directly by NMR spectroscopy to determine the yield by using 1,1,2,2-tetrachloroethane as an internal standard. The residue was purified by flash column chromatography on silica gel to afford the corresponding product for analytical use.

1-Phenylethyl Trifluoroacetate (7a)



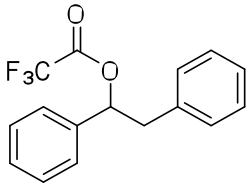
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.34 (5H, m, Ar*H*), 6.03 (1H, q, J = 6.5 Hz, ArC*H*), 1.68 (3H, d, J = 6.5 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8 (q, $J_{C\text{-}F}$ = 42.1 Hz), 139.1, 128.9, 128.8, 126.1, 114.6 (q, $J_{C\text{-}F}$ = 286.1Hz), 77.2, 21.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.2; IR (neat) 2991, 1781, 1378, 1220, 1149, 1056, 760, 670 cm^{-1}; HRMS calculated for $C_{10}H_9F_3O_2Na$: *m/z* 241.0447 ([M + Na]$^+$), found: *m/z* 241.0448 ([M + Na]$^+$).

1-Phenylpropyl Trifluoroacetate (7b)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.33 (5H, m, Ar*H*), 5.81 (1H, dd, J = 7.4, 6.2 Hz, ArC*H*), 2.12-2.03 (1H, m, C*H*HCH$_3$), 1.99-1.91 (1H, m, CH*H*CH$_3$), 0.95 (3H, t, J = 7.4 Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9 (q, $J_{C\text{-}F}$ = 43.1 Hz), 138.0, 128.8, 128.7, 126.5, 114.6 (q, $J_{C\text{-}F}$ = 287.3 Hz), 82.1, 29.0, 9.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.0; IR (neat) 2976, 1781, 1219, 1151, 753, 697 cm^{-1}; HRMS calculated for $C_{11}H_{11}F_3O_2Na$: *m/z* 255.0603 ([M + Na]$^+$), found: *m/z* 255.0604 ([M + Na]$^+$).

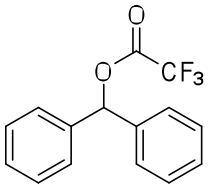
1,2-Diphenylethyl Trifluoroacetate (7c)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.23 (8H, m, Ar*H*), 7.12 (2H, d, J = 6.8 Hz, Ar*H*), 6.05 (1H, dd, J = 8.2, 5.7 Hz, ArC*H*CH$_2$), 3.30 (1H, dd, J = 14.0, 8.4 Hz, ArCHC*H*H), 3.16 (1H, dd, J = 14.2, 5.7 Hz, ArCHCH*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5 (q, $J_{C\text{-}F}$

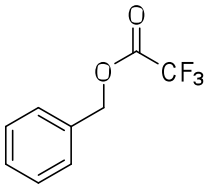
= 42.1 Hz), 137.6, 135.6, 129.6, 128.9, 128.7, 128.5, 127.1, 126.6, 114.5 (q, $J_{C\text{-}F}$ = 286.1 Hz), 81.1, 42.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.1; IR (neat) 3033, 1782, 1219, 1151, 758, 696 cm^{-1}; HRMS calculated for $C_{16}H_{13}F_3O_2Na$: *m/z* 317.0760 ([M + Na]$^+$), found: *m/z* 317.0760 ([M + Na]$^+$).

Benzhydryl Trifluoroacetate (7d)



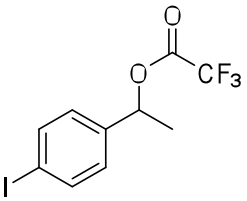
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.33 (10H, m, Ar*H*), 6.99 (1H, s, ArC*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6 (q, $J_{C\text{-}F}$ = 42.5 Hz), 137.9, 128.84, 128.80, 127.1, 114.6 (q, $J_{C\text{-}F}$ = 286.1 Hz), 81.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –74.9; IR (neat) 3035, 1782, 1221, 1151, 697 cm^{-1}; HRMS calculated for $C_{15}H_{11}F_3O_2Na$: *m/z* 303.0603 ([M + Na]$^+$), found: *m/z* 303.0601 ([M + Na]$^+$).

Benzyl Trifluoroacetate (7e)



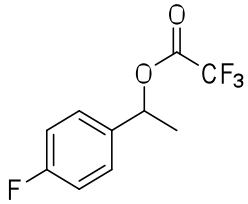
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.37 (5H, m, Ar*H*), 5.36 (2H, s, ArCH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3 (q, $J_{C\text{-}F}$ = 42.1 Hz), 133.5, 129.1, 128.7, 128.5, 114.7 (q, $J_{C\text{-}F}$ = 285.3 Hz), 69.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –74.8; IR (neat) 1781, 1345, 1217, 1136, 729, 695 cm^{-1}; HRMS calculated for $C_9H_7F_3O_2Na$: *m/z* 227.0290 ([M + Na]$^+$), found: *m/z* 227.0289 ([M + Na]$^+$).

1-(4-Iodophenyl)ethyl Trifluoroacetate (7f)



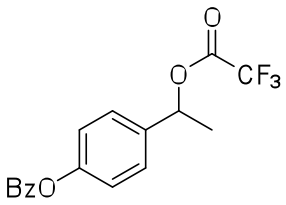
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (2H, d, *J* = 8.2 Hz, Ar*H*), 7.12 (2H, d, *J* = 8.2 Hz, Ar*H*), 5.96 (1H, q, *J* = 6.6 Hz, ArC*H*), 1.65 (3H, d, *J* = 6.6 Hz, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7 (q, $J_{C\text{-}F}$ = 42.1 Hz), 138.7, 138.0, 128.0, 114.5 (q, $J_{C\text{-}F}$ = 287.3 Hz), 94.6, 76.5, 21.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.2; IR (neat) 2988, 1784, 1221, 1156 cm^{-1}; HRMS calculated for $C_{10}H_8IF_3O_2Na$: *m/z* 366.9413 ([M + Na]$^+$), found: *m/z* 366.9416 ([M + Na]$^+$).

1-(4-Fluorophenyl)ethyl Trifluoroacetate (7g)



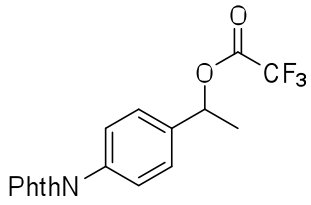
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (2H, m, Ar*H*), 7.08 (2H, m, Ar*H*), 6.01 (1H, q, *J* = 6.5 Hz, ArC*H*), 1.67 (3H, d, *J* = 6.5 Hz, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 248.9 Hz), 156.8 (q, $J_{C\text{-}F}$ = 42.5 Hz), 134.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz), 114.5 (q, $J_{C\text{-}F}$ = 286.1 Hz), 76.5, 21.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –112.5, –75.2; IR (neat) 2992, 1781, 1515, 1221, 1150, 1055, 835 cm^{-1}; HRMS calculated for $C_{10}H_8F_4O_2Na$: *m/z* 259.0353 ([M + Na]$^+$), found: *m/z* 259.0353 ([M + Na]$^+$).

4-(1-(Trifluoroacetoxy)ethyl)phenyl Benzoate (7h)



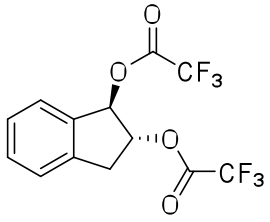
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (2H, d, J = 7.7 Hz, Ar*H*COO), 7.65 (1H, t, J = 7.7 Hz, Ar*H*COO), 7.53 (2H, t, J = 7.7 Hz, Ar*H*COO), 7.46 (2H, d, J = 8.5 Hz, Ar*H*), 7.25 (2 H, d, J = 8.5 Hz, Ar*H*), 6.07 (1H, q, J = 6.6 Hz, ArC*H*), 1.70 (3H, d, J = 6.8 Hz, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 156.7 (q, $J_{C\text{-}F}$ = 42.1 Hz), 151.2, 136.6, 133.7, 130.2, 129.3, 128.6, 127.5, 122.1, 114. 5 (q, $J_{C\text{-}F}$ = 285.7 Hz), 76.6, 21.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.1; IR (neat) 2988, 1782, 1741, 1715, 1511, 1265, 1214, 1158, 1055, 707 cm^{-1}; HRMS calculated for $C_{17}H_{13}F_3O_4Na$: *m/z* 361.0658 ([M + Na]$^+$), found: *m/z* 361.0660 ([M + Na]$^+$).

1-(4-(1,3-dioxoisoindolin-2-yl)phenyl)ethyl Trifluoroacetate (7i)



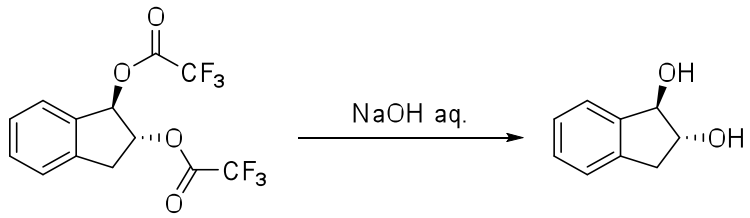
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (2H, dd, J = 5.4, 3.1 Hz, Ar*H*CON), 7.81 (2H, dd, J = 5.4, 3.1 Hz, Ar*H*CON), 7.53 (2H, d, J = 8.8 Hz, Ar*H*), 7.50 (2H, d, J = 8.5 Hz, Ar*H*), 6.09 (1H, q, J = 6.6 Hz, ArC*H*), 1.71 (3H, d, J = 6.5 Hz, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 157.0 (q, $J_{C\text{-}F}$ = 42.5 Hz), 139.0, 134.8, 132.4, 131.9, 127.2, 127.0, 124.1, 114. 7 (q, $J_{C\text{-}F}$ = 286.1 Hz), 76.8, 22.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.0; IR (neat) 1782, 1716, 1519, 1376, 1219, 1155, 1056, 908, 728, 716 cm^{-1}; HRMS calculated for $C_{18}H_{12}F_3NO_4Na$: *m/z* 386.0611 ([M + Na]$^+$), found: *m/z* 386.0617 ([M + Na]$^+$).

***trans*-2,3-Dihydro-1*H*-indene-1,2-diyl Bis(2,2,2-trifluoroacetate) (7j)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.31 (4H, m, Ar*H*), 6.48 (1H, d, J = 3.1 Hz, ArC*H*CH), 5.73 (1H, ddd, J = 7.5, 4.5, 3.1 Hz, CHC*H*CH$_2$), 3.71 (1H, dd, J = 17.0, 7.4 Hz, ArC*H*H), 3.12 (1H, dd, J = 17.0, 4.5 Hz, ArCH*H*); ^{13}C NMR (125 MHz, CDCl3) δ 157.1 (q, $J_{C\text{-}F}$ = 44.0 Hz), 157.0 (q, $J_{C\text{-}F}$ = 44.1 Hz), 139.8, 135.0, 131.0, 128.4, 125.8, 125.3, 114.4 (q, $J_{C\text{-}F}$ = 286.1 Hz), 114.3 (q, $J_{C\text{-}F}$ = 286.1 Hz), 84.1, 81.6, 36.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –74.75, –74.70; IR (neat) 1787, 1226, 1169, 1140 cm^{-1}.

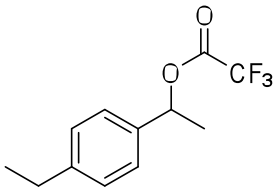
Determination of relative stereochemistry of 2,3-Dihydro-1*H*-indene-1,2-diyl Bis(2,2,2-trifluoroacetate) (7j).



7j

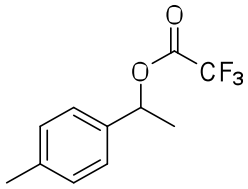
To a stirred solution of **7j** in benzene (1.0 mL) was added 1 M NaOH (2.0 mL) at room temperature. After stirring for 1 h at room temperature, the reaction mixture was extracted with EtOAc, and washed with water. The combined organic layers were dried over Na_2SO_4. After the removal of solvents under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford a *trans*-2,3-Dihydro-1*H*-indene-1,2-diol. [4] The relative stereochemistry of **7j** was determined to be *trans* configuration by the comparison with [1]1H NMR spectrum of the literature.[4]

1-(4-Ethylphenyl)ethyl Trifluoroacetate (7n)



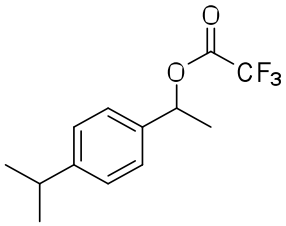
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 8.2 Hz, Ar*H*), 7.23 (2H, d, J = 8.2 Hz, Ar*H*), 6.05 (1H, q, J = 6.5 Hz, ArC*H*OCOCF$_3$), 2.67 (2H, q, J = 7.7 Hz, ArCH_2), 1.67 (3H, d, J = 6.5 Hz, $CF_3CO_2CHCH_3$), 1.25 (3H, t, J = 7.7 Hz, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8 (q, $J_{C\text{-}F}$ = 42.1 Hz), 145.1, 136.3, 128.3 126.3, 114.5 (q, $J_{C\text{-}F}$ = 286.1 Hz), 77.2, 28.6, 21.6, 15.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.2; IR (neat) 2970, 1780, 1221, 1156, 1058, 831, 733 cm^{-1}; HRMS calculated for $C_{12}H_{13}F_3O_2Na$: *m/z* 269.0760 ([M + Na]$^+$), found: *m/z* 269.0755 ([M + Na]$^+$).

1-(4-Methylphenyl)ethyl Trifluoroacetate (7p)



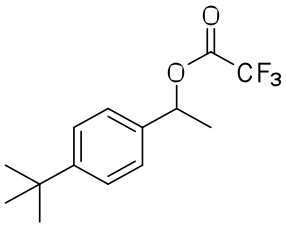
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (2H, d, J = 7.9 Hz, Ar*H*), 7.19 (2H, d, J = 7.9 Hz, Ar*H*), 6.00 (1H, q, J = 6.6 Hz, ArC*H*), 2.36 (3H, s, ArCH_3), 1.66 (3H, d, J = 6.5 Hz, CHCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7 (q, $J_{C\text{-}F}$ = 42.1 Hz), 138.7, 136.3, 129.4, 126.1, 114.7 (q, $J_{C\text{-}F}$ = 287.3 Hz), 77.2, 21.3, 20.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.2; IR (neat) 2990, 1779, 1219, 1151, 1054, 815 cm^{-1}; HRMS calculated for $C_{11}H_{11}F_3O_2Na$: *m/z* 255.0603 ([M + Na]$^+$), found: *m/z* 255.0602 ([M + Na]$^+$).

1-(4-Isopropylphenyl)ethyl Trifluoroacetate (7q)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 8.2 Hz, Ar*H*), 7.24 (2H, d, J = 8.2 Hz, Ar*H*), 6.02 (1H, q, J = 6.5 Hz, ArC*H*OCOCF$_3$), 2.91 (1H, m, ArC*H*(CH$_3$)$_2$), 1.66 (3H, d, J = 6.5 Hz, $CF_3CO_2CHCH_3$), 1.25 (6H, d, J = 6.5 Hz, ArCH(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9 (q, $J_{C\text{-}F}$ = 42.1 Hz), 149.7, 136.4, 126.9, 126.3, 114.6 (q, $J_{C\text{-}F}$ = 285.7 Hz),

77.2, 33.9, 23.9, 21.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.2; IR (neat) 2963, 1781, 1220, 1151, 1060, 823 cm^{-1}; HRMS calculated for $C_{13}H_{15}F_3O_2Na$: *m/z* 283.0916 ([M + Na]$^+$), found: *m/z* 283.0912 ([M + Na]$^+$).

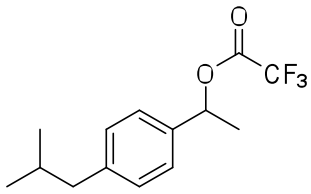


1-(4-(*tert*-Butyl)phenyl)ethyl Trifluoroacetate (7r)

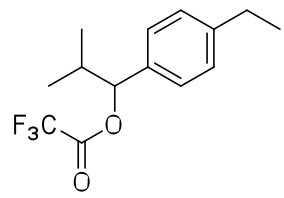
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (2H, d, *J* = 8.2 Hz, Ar*H*), 7.31 (2H, d, *J* = 8.2 Hz, Ar*H*), 6.03 (1H, q, *J* = 6.5 Hz, ArC*H*), 1.67 (3H, d, *J* = 6.5 Hz, CHCH_3), 1.32 (9H, s, C(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9 (q, $J_{C\text{-}F}$ = 42.1 Hz), 152.0, 136.2, 126.1, 125.8, 114.8 (q, $J_{C\text{-}F}$ = 286.1 Hz), 77.2, 34.7, 31.3, 21.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.1; IR (neat) 2966, 1781, 1219, 1151, 1054, 830 cm^{-1}; HRMS calculated for $C_{14}H_{17}F_3O_2Na$: *m/z* 297.1073 ([M + Na]$^+$), found: *m/z* 297.1078 ([M + Na]$^+$).

1-(4-Isobutylphenyl)ethyl Trifluoroacetate (7s)

7q was obtained as the mixture of **7q** and 1-(4-Ethylphenyl)-2-methylpropyl trifluoroacetate.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (2H, d, *J* = 7.9 Hz, Ar*H*), 7.16 (2H, d, *J* = 7.9 Hz, Ar*H*), 6.02 (1H, q, *J* = 6.8 Hz, ArC*H*), 2.48 (2H, d, *J* = 7.1 Hz, ArCH_2), 1.91-1.83 (1H, m, C*H*(CH$_3$)$_2$), 1.67 (3H, d, *J* = 6.8 Hz, ArCHCH_3), 0.90 (6H, d, *J* = 6.5 Hz, CH(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8 (q, $J_{C\text{-}F}$ = 41.7 Hz), 142.6, 136.3, 129.5, 126.0, 114.6 (q, $J_{C\text{-}F}$ = 286.1 Hz), 77.2, 45.1, 30.2, 22.3, 21.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –75.2; IR (neat) 2962, 1782, 1222, 1159, 906, 732 cm^{-1}; HRMS calculated for $C_{14}H_{17}F_3O_2Na$: *m/z* 297.1073 ([M + Na]$^+$), found: *m/z* 297.1070 ([M + Na]$^+$).



1-(4-Ethylphenyl)-2-methylpropyl Trifluoroacetate

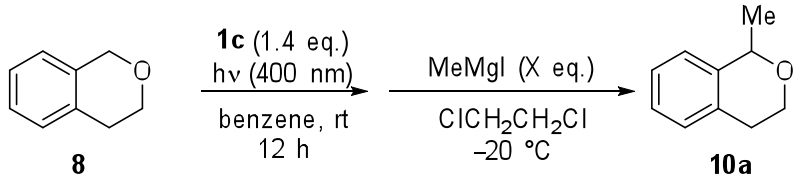
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (2H, d, *J* = 8.2 Hz, Ar*H*), 7.19 (2H, d, *J* = 8.2 Hz, Ar*H*), 5.55 (1H, d, *J* = 7.9 Hz, ArC*H*), 2.65 (2H, q, *J* = 7.6 Hz, ArCH_2), 2.22 (1H, m), 1.24 (3H, t, *J* = 7.8 Hz, ArCH$_2$CH_3), 1.02 (3H, d, *J* = 6.5 Hz, CH(CH_3)$_2$), 0.83 (3H, d, *J* = 6.8 Hz, CH(CH_3)$_2$)

Optimization of Direct C-H Functionalization of Isochromane

We examined the addition of nucleophiles after the photoreaction of isochroman. The addition of 1 equiv MeMgI to the reaction mixture gave the desired product **10** albeit in

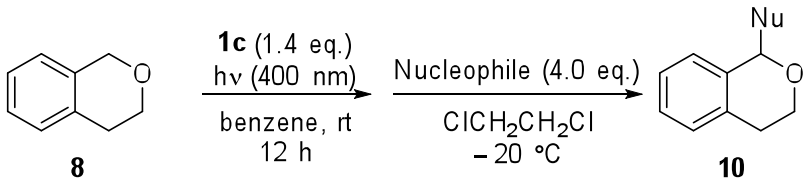
only 23% yield (entry 1). Improvement of the yield was observed by using 4.0 equiv MeMgI, affording **10** in 72% yield (entry 3).

Table S2. Direct C-H Functionalization of Isochromane (**8**).



entry	MeMgI (eq.)	% yield
1	1.0	23
2	2.0	41
3	4.0	72

General Procedure for Functionalization with Isochromane (8) (Table 3)



To a stirred solution of isochromane (**8**) (62.8 μL, 0.5 mmol) in benzene (1.0 mL) was added **1c** (301 mg, 0.7 mmol) at room temperature under visible light (400 nm). Afrer stirring for 12 h, to the reaction mixture were added dichloroethane (1.0 mL) and nucleophile (2.0 mmol) at – 20 ˚C. The reaction mixture was stirred for 6 h at –20 ˚C. After the removal of solvents under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford the corresponding product.

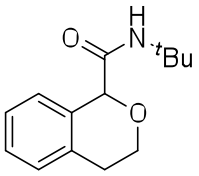
The spectral data of **10a-c** and **10f-g** were consistent with previously reported data.[5]

Procedure for Amidation of Isochromane (8)

To a stirred solution of **8** (62.8 μL, 0.5 mmol) in benzene (1.0 mL) was added **1c** (301 mg, 0.7 mmol) at room temperature under visible light (400 nm). Afrer stirring for 12 h, to the reaction mixture were added benzene (4.0 mL) and isocyanide (0.75 mmol) at room temperature. The reaction mixture was stirred for 6 h at room temperature. After

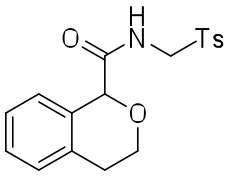
the removal of solvents under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford the corresponding product.

***N*-(*tert*-Butyl)isochromane-1-carboxamide (10d)**



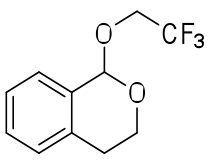
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.70 (1H, m, Ar*H*), 7.22-7.18 (2H, m, Ar*H*), 7.11-7.09 (1H, m, Ar*H*), 6.47 (1H, br, N*H*), 5.04 (1H, s, ArC*H*CONH), 4.20-4.16 (1H, m, $ArCH_2CH$*H*), 3.86 (1H, td, J = 10.6, 3.7 Hz, $ArCH_2CH$*H*), 3.07-3.00 (1H, m, $ArCH$*H*CH_2), 2.73 (1H, dt, J = 16.2, 3.3 Hz, ArC*H*HCH_2), 1.34 (9H, s, $C(CH_3)_3$): ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 132.6, 132.3, 128.6, 127.1, 126.3, 126.0, 76.9, 63.9, 50.8, 28.6, 28.5; IR (neat) 3411, 2967, 1675, 1517, 1453, 1364, 1226, 1105, 748 cm^{-1}; HRMS calculated for $C_{14}H_{19}NO_2Na$: *m/z* 256.1308 ($[M + Na]^+$), found: *m/z* 256.1308 ($[M + Na]^+$).

***N*-(Tosylmethyl)isochromane-1-carboxamide (10e)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (2H, d, J = 8.2 Hz, SO_2ArH) 7.49-7.46 (1H, m, Ar*H*), 7.31 (1H, d, J = 7.9 Hz, Ar*H*), 7.24-7.21 (1H, m, Ar*H*), 7.14-7.11 (1H, m, Ar*H*), 7.08 (2H, d, J = 8.2 Hz, SO_2ArH), 5.06 (1H, s, ArC*H*CONH), 4.78 (1H, dd, J = 14.0, 7.9 Hz, CONHCH*H*), 4.52 (1H, dd, J = 14.0, 6.2 Hz, CONHC*H*H), 4.27-4.23 (1H, m, $ArCH_2CH$*H*), 3.80 (1H, td, J = 11.1, 3.1 Hz, $ArCH_2CH$H), 3.13-3.06 (1H, m, $ArCH$*H*CH_2), 2.73-2.69 (1H, m, ArC*H*HCH_2), 2.36 (3H, s, $ArCH_3$): ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 145.1, 133.2, 132.9, 130.8, 129.7, 128.7, 128.6, 127.3, 126.3, 125.9, 75.9, 64.0, 59.5, 28.6, 21.7; IR (neat) 3349, 2927, 1695, 1507, 1321, 1289, 1144, 1111, 1085, 753 cm^{-1}; HRMS calculated for $C_{18}H_{19}NO_4SNa$: *m/z* 368.0927 ($[M + Na]^+$), found: *m/z* 368.0933 ($[M + Na]^+$).

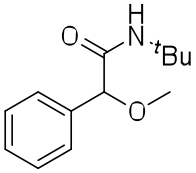
1-(Trifluoroethoxy)isochromane (10h)



To a stirred solution of isochromane (**8**) (62.8 µL, 0.5 mmol) in trifluoroethanole (1.0 mL) was added **1c** (301 mg, 0.7 mmol) at room temperature under visible light (400 nm). After stirring for 12 h, solvents was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the isochromane **10 h**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.23 (3H, m, Ar*H*), 7.15-7.14 (1H, m, Ar*H*), 5.66 (1H, s, $ArCHOCH_2CF_3$), 4.15-4.09 (3H, m, CF_3CH_2O, $ArCH_2CH$*H*), 3.96-3.92 (1H, m, $ArCH_2CH$*H*), 3.08-3.01 (1H, m, $ArCH$*H*CH_2), 2.66-2.62 (1H, m, ArC*H*HCH_2): ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.1, 132.5, 128.7, 128.5, 127.7, 126.6, 124.2 (q, $J_{C\text{-}F}$ = 280.1 Hz), 97.3, 64.4 (q, $J_{C\text{-}F}$ = 34.8 Hz), 58.3, 27.8; ^{19}F

NMR (470 MHz, $CDCl_3$) δ –73.8; IR (neat) 2892, 1274, 1153, 1077, 1062, 999, 981, 746 cm^{-1}; HRMS calculated for $C_{11}H_{11}F_3O_2Na$: *m/z* 255.0603 ($[M + Na]^+$), found: *m/z* 255.0601 ($[M + Na]^+$).

***N*-(*tert*-butyl)-2-methoxy-2-phenylacetamide (12)**



^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (5H, m, Ar*H*), 6.6 (1H, br, N*H*), 4.49 (1H, s, ArC*H*OCH_3), 3.3 (3H, s, OCH_3), 1.36 (9H, s, $NHC(CH_3)_3$): ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 137.3, 128.4, 128.2, 127.0, 84.1, 57.0, 50.8, 28.7; IR (neat) 3407, 2968, 1671, 1521, 1454, 1366, 1195, 1100, 908, 729, 697 cm^{-1}; HRMS calculated for $C_{13}H_{19}NO_2Na$: *m/z* 244.1308 ($[M + Na]^+$), found: *m/z* 244.1301 ($[M + Na]^+$).

References

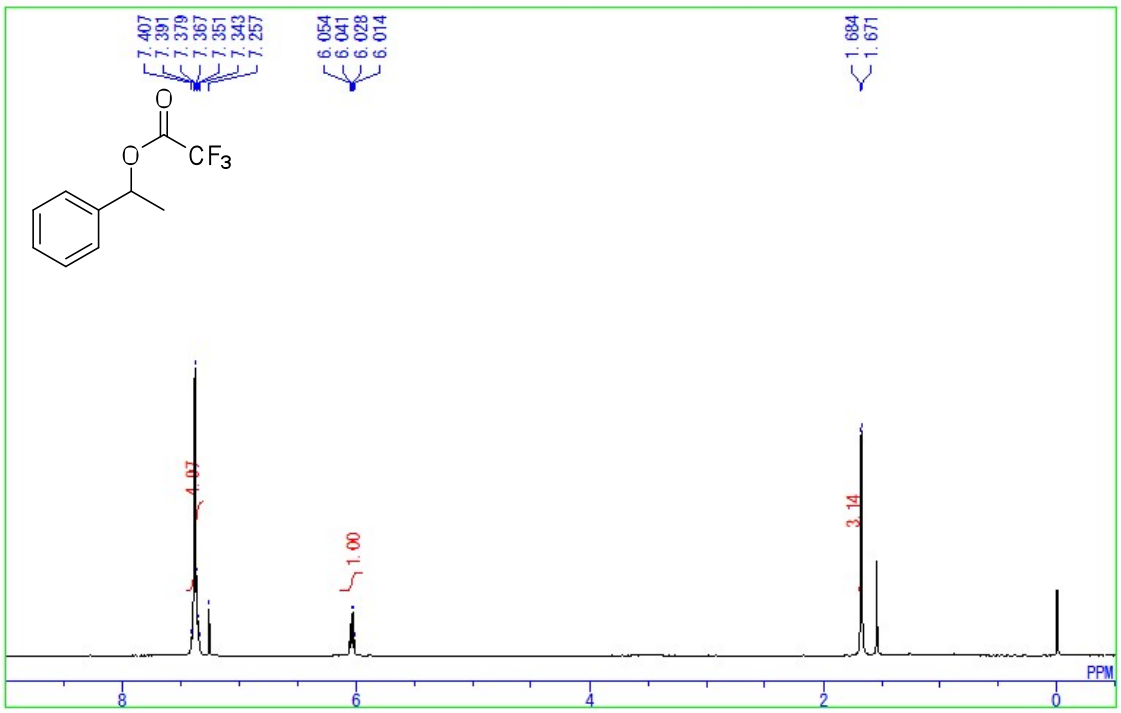
[1] S. A. Moteki, A. Usui, S. Selvakumar, T. Zhang, K. Maruoka, *Angew. Chem. Int. Ed.* 2014, **53**, 11060.

[2] S. Spyroudis, A. Varvoglis, *Synthesis* 1975, 445.

[3] A. Ono, N. Suzuki, J. Kamimura, *Synthesis* 1987, 736.

[4] L. Emmanuvel, T. M. A. Shaikh, A. Sudalai, *Org. Lett.* 2005, **7**, 5071.

[5] W. Muramatsu, K. Nakano, *Org. Lett.* 2014, **16**, 2042.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4
2
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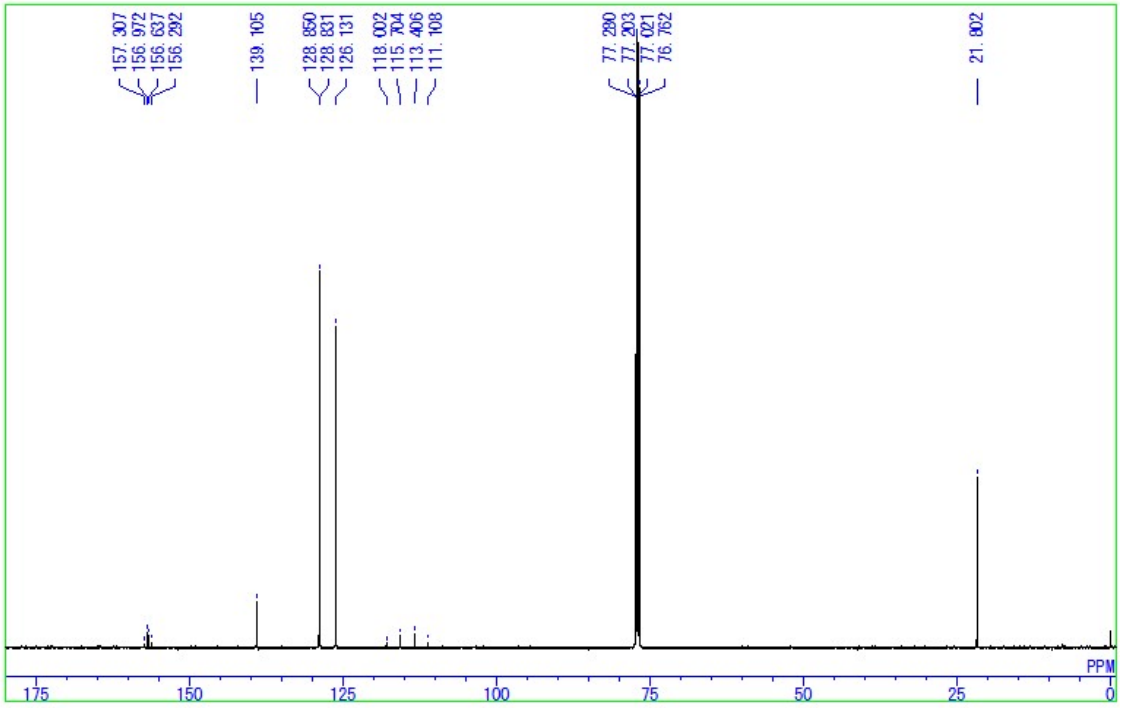
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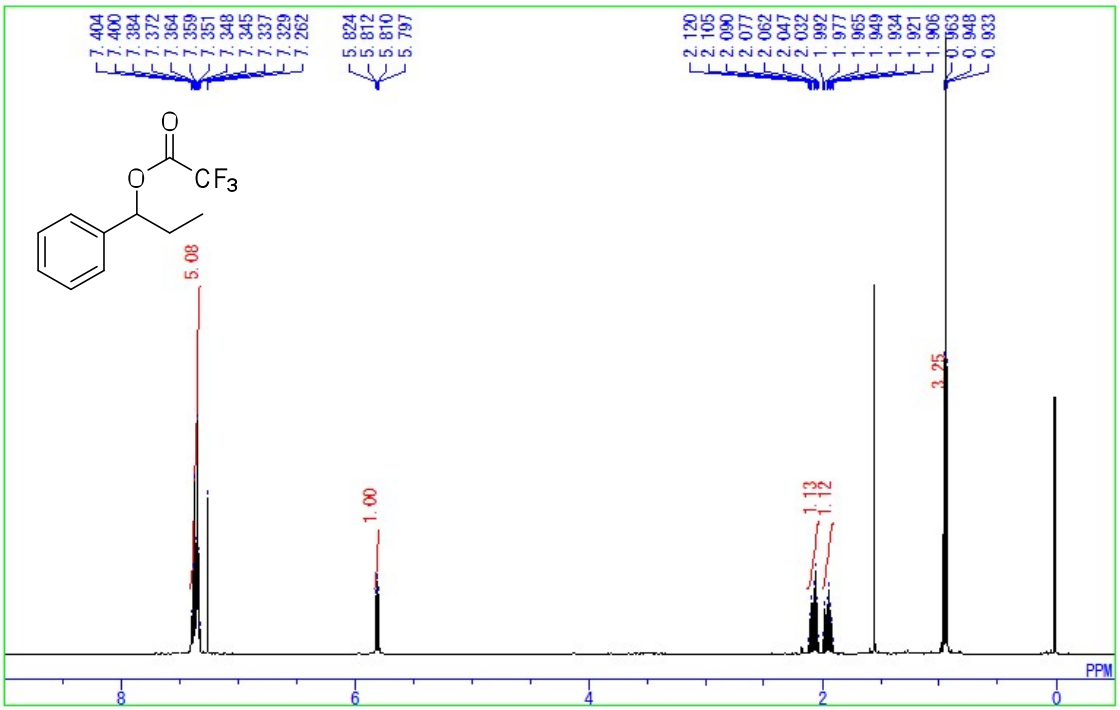
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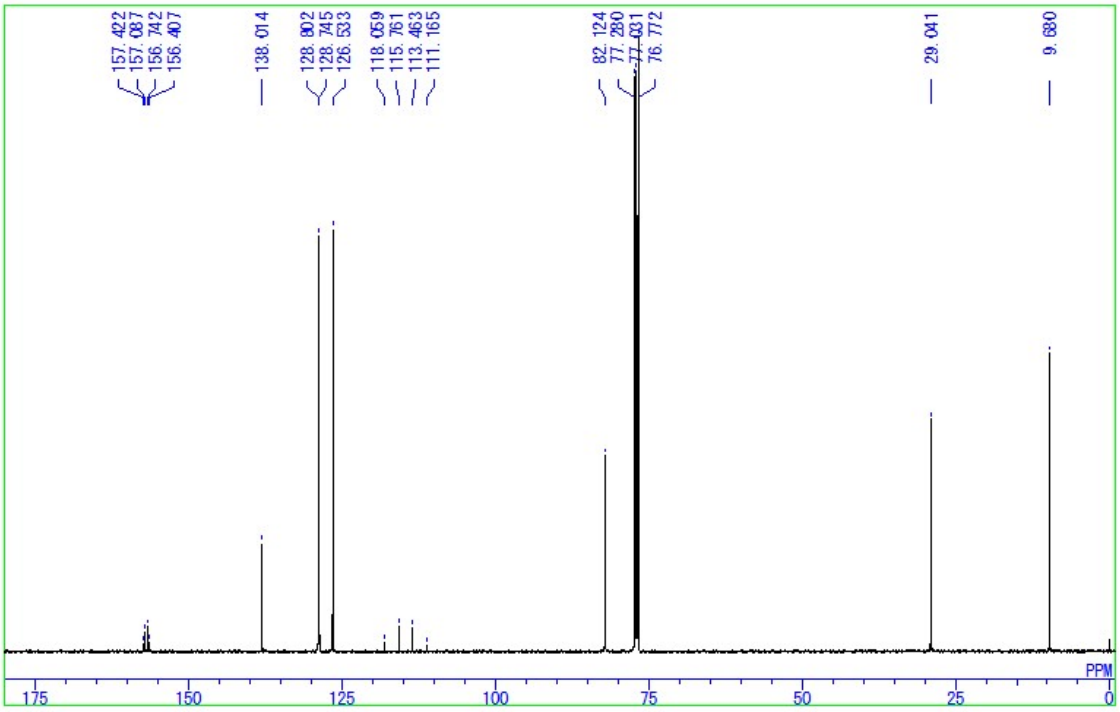
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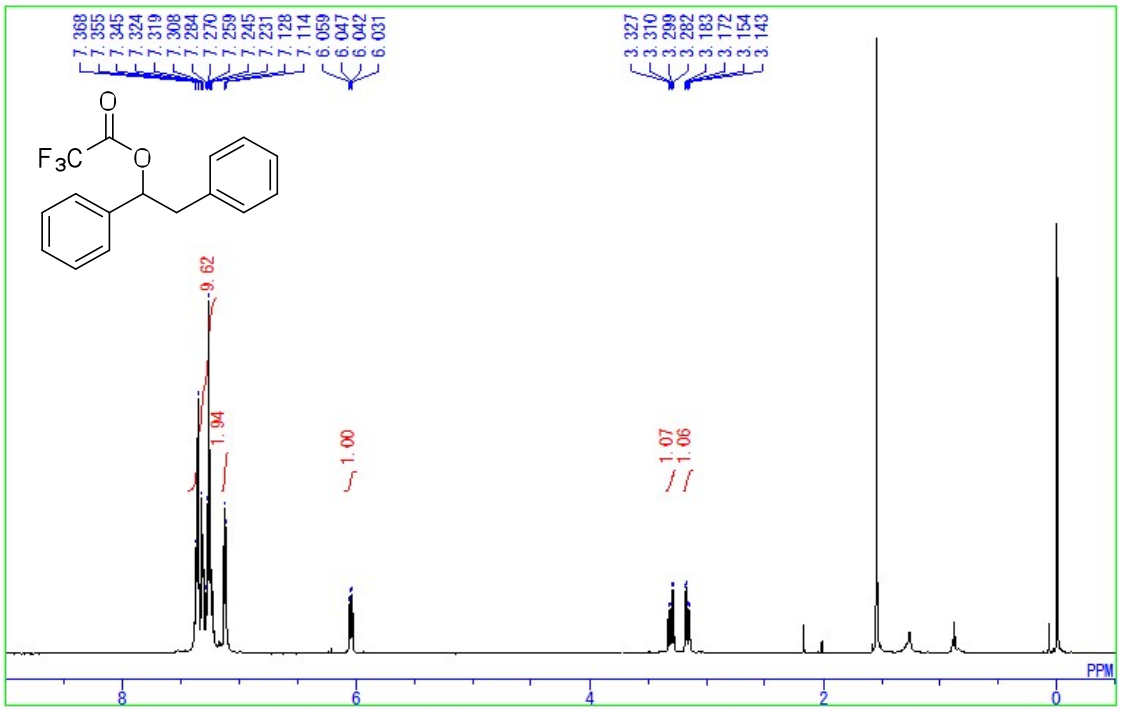
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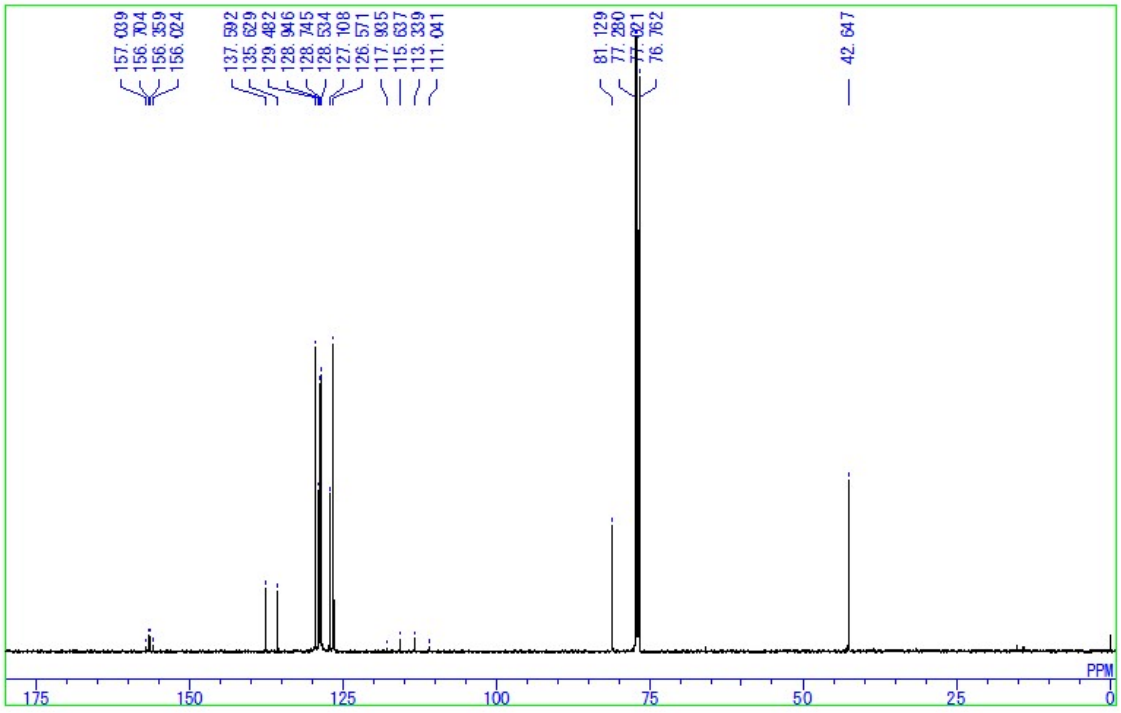
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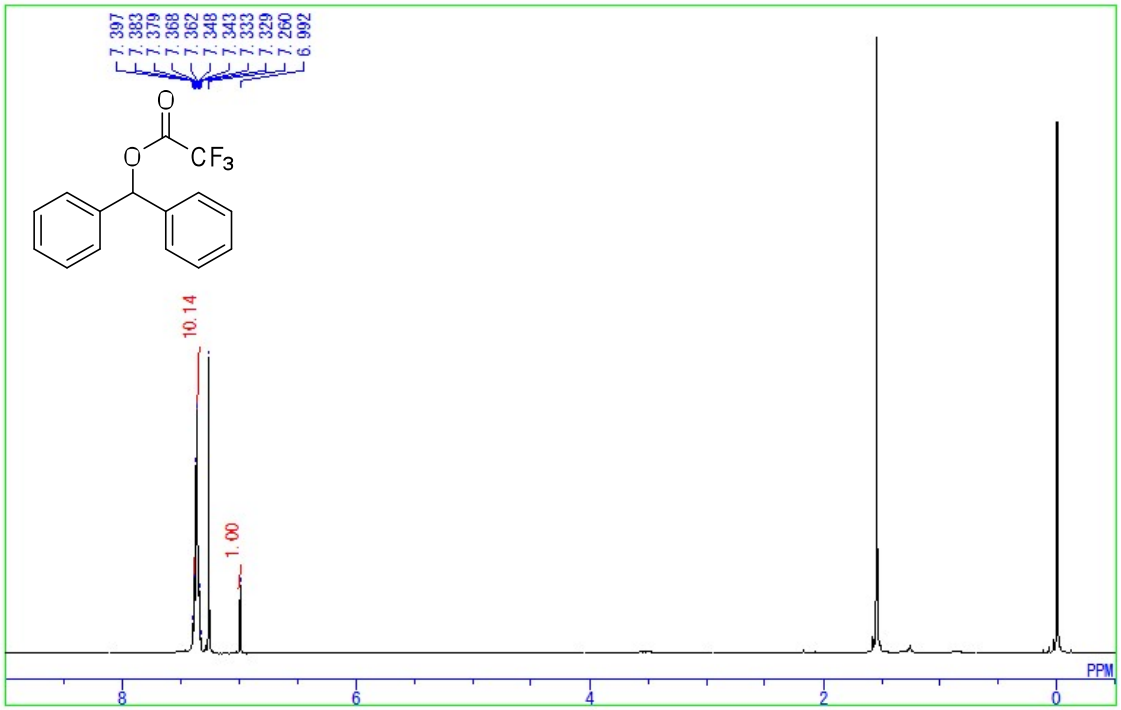
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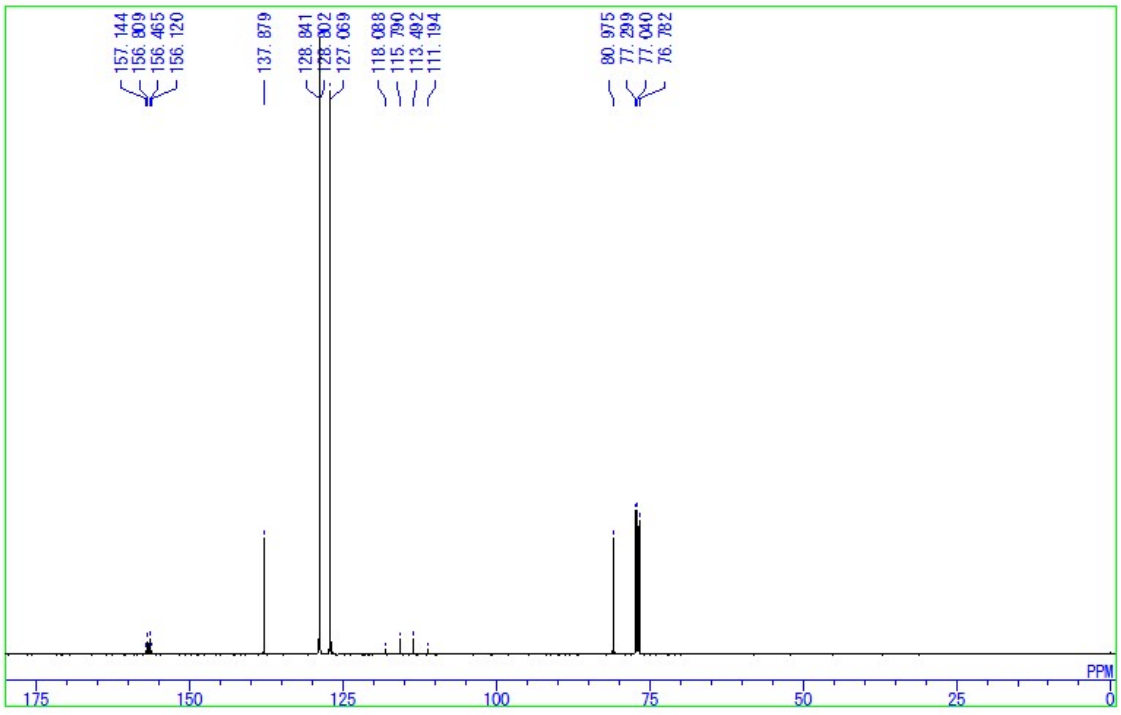
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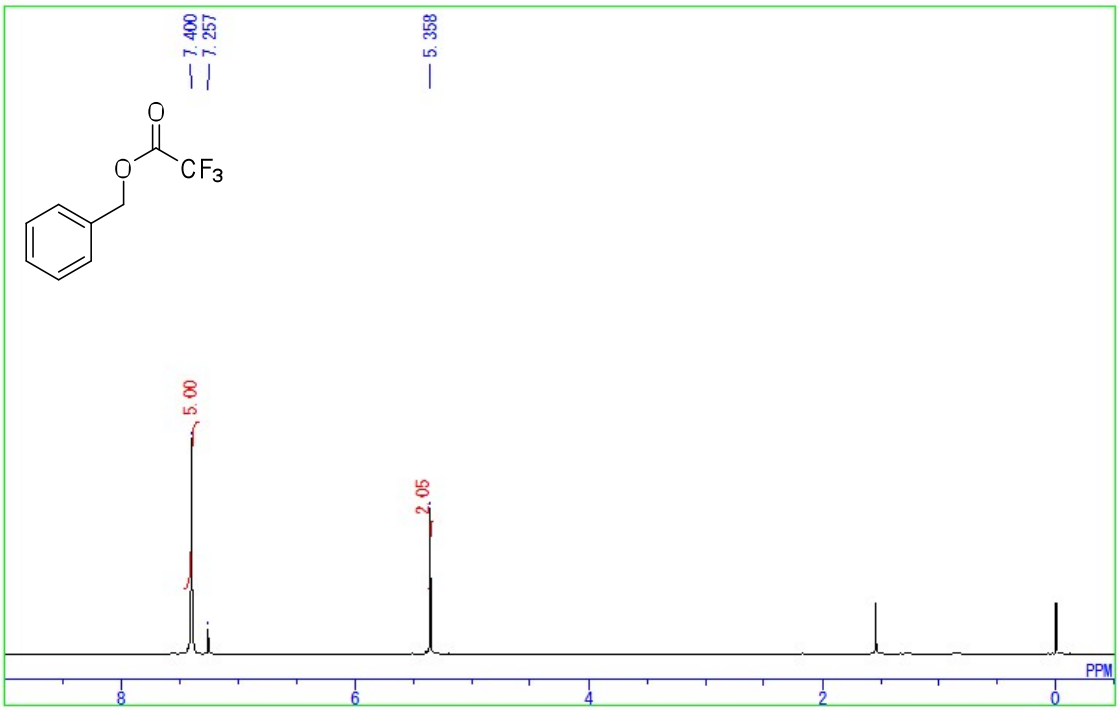
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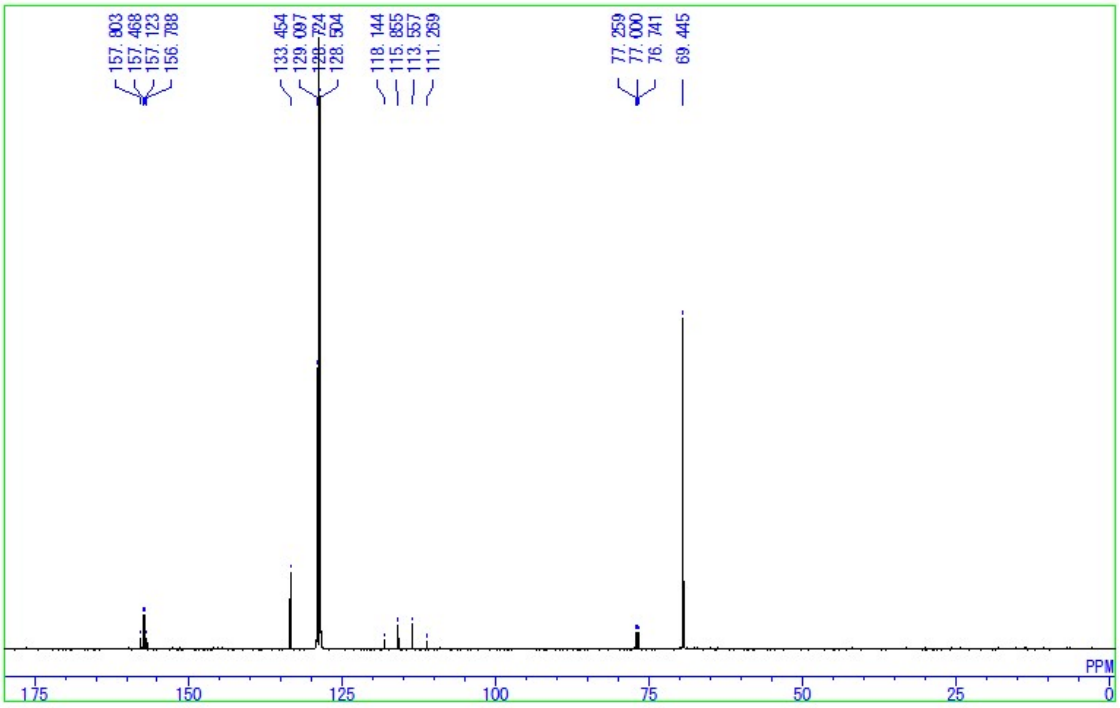
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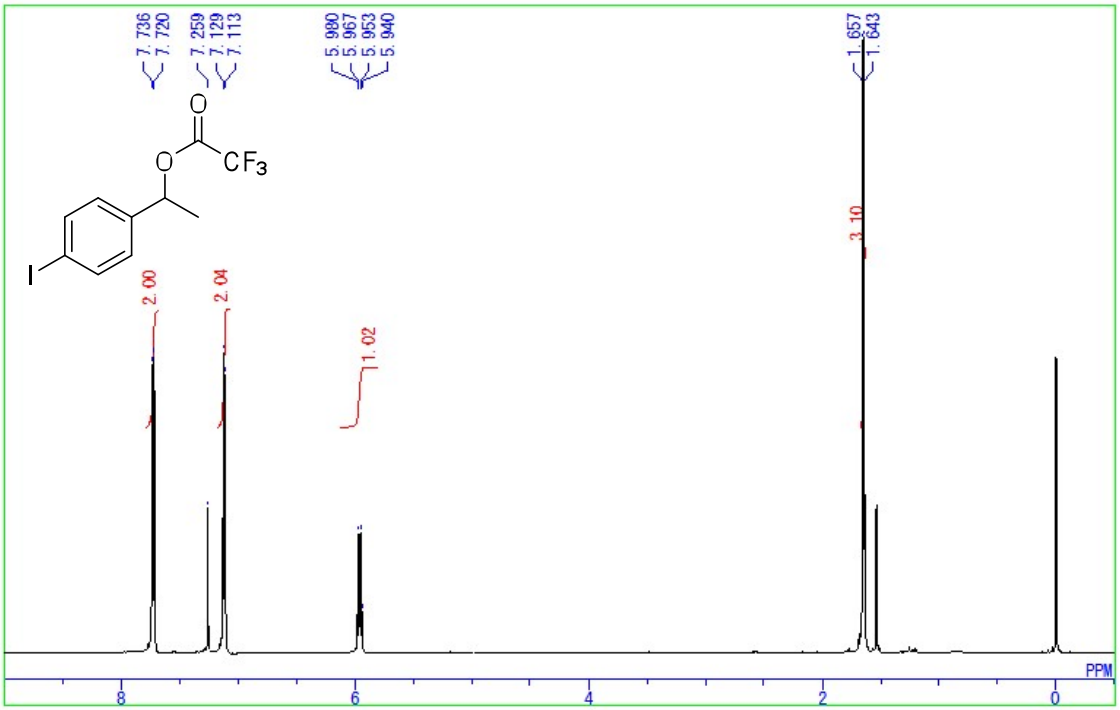
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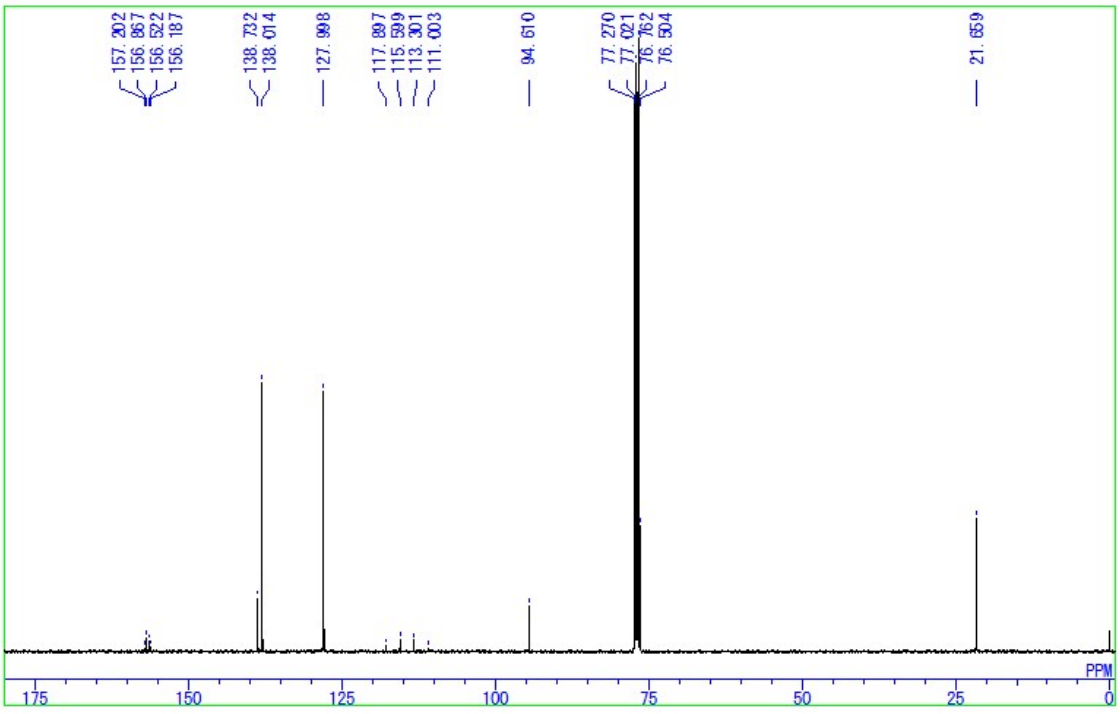
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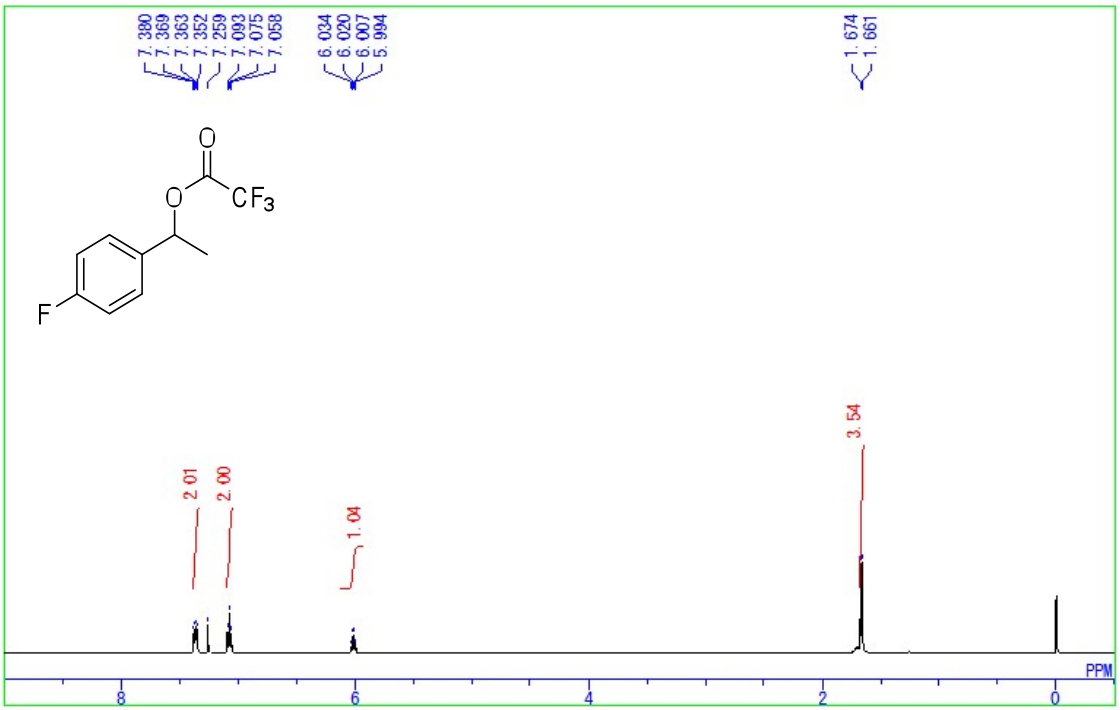
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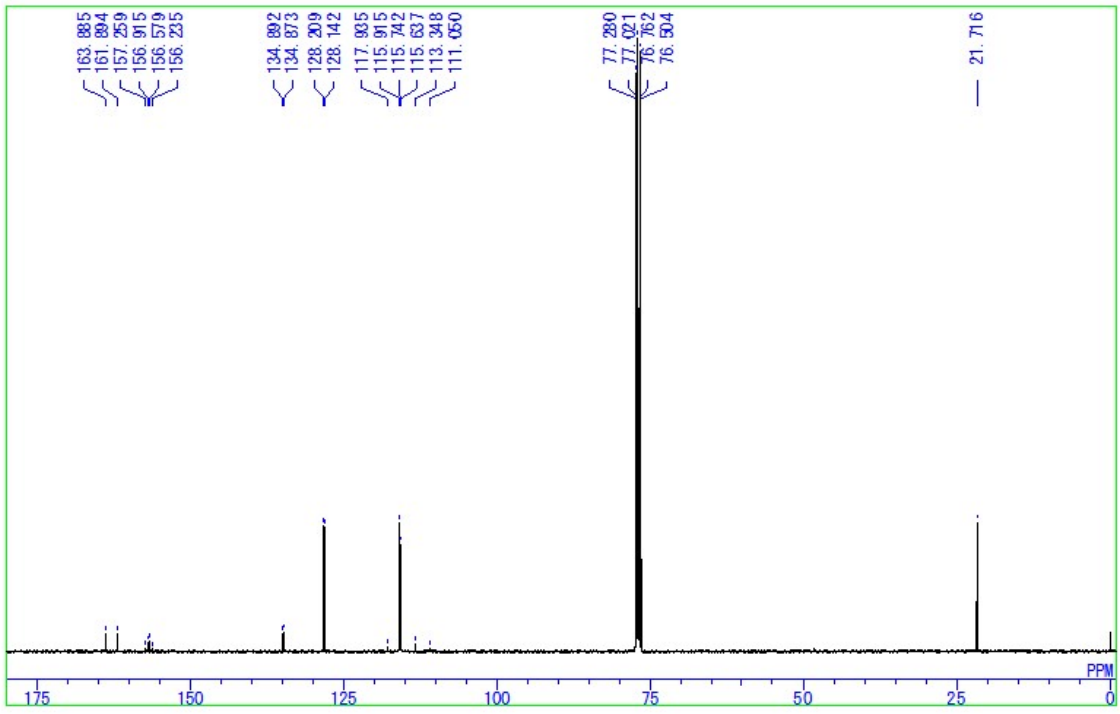
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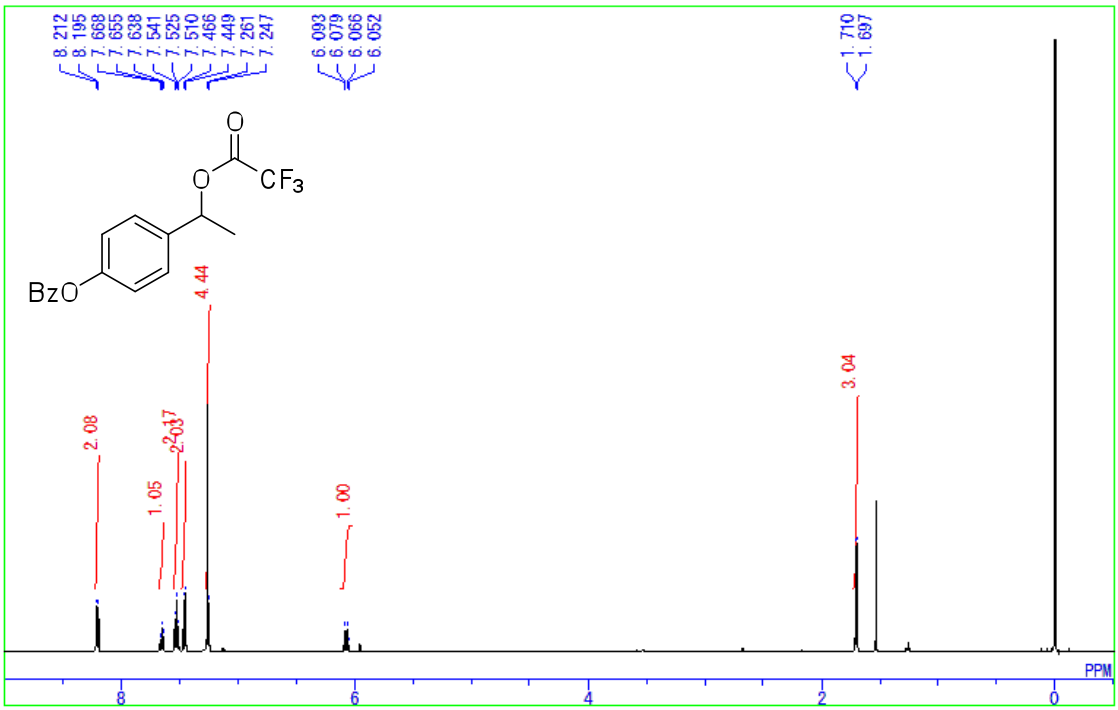
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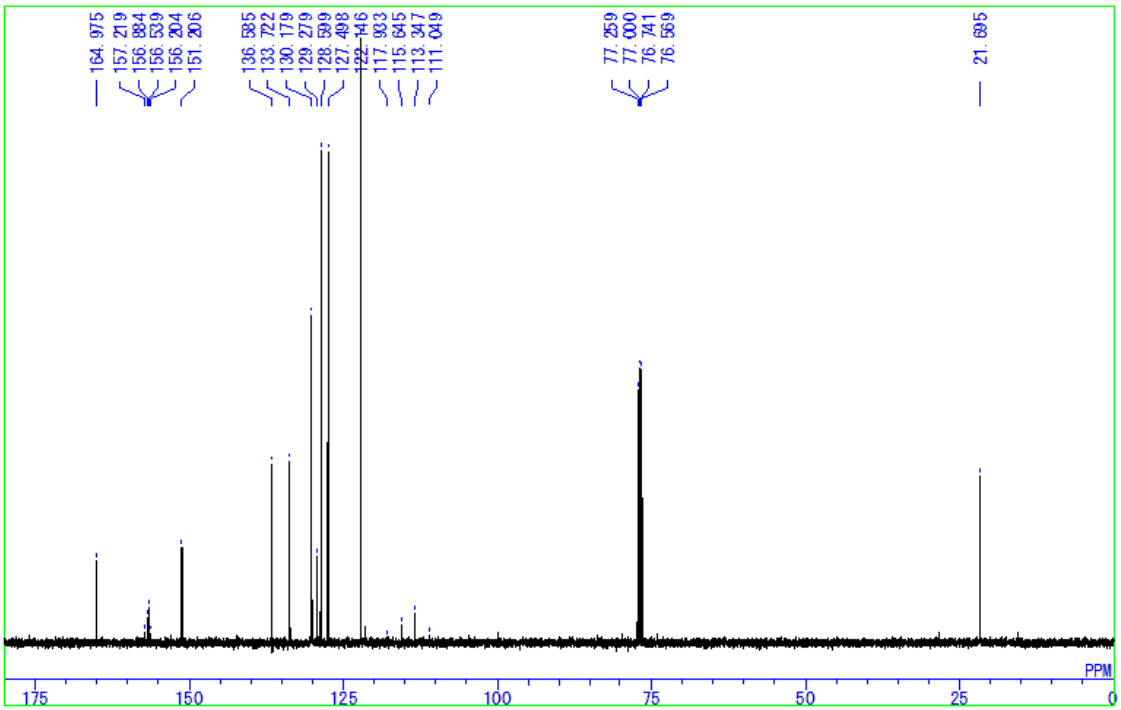
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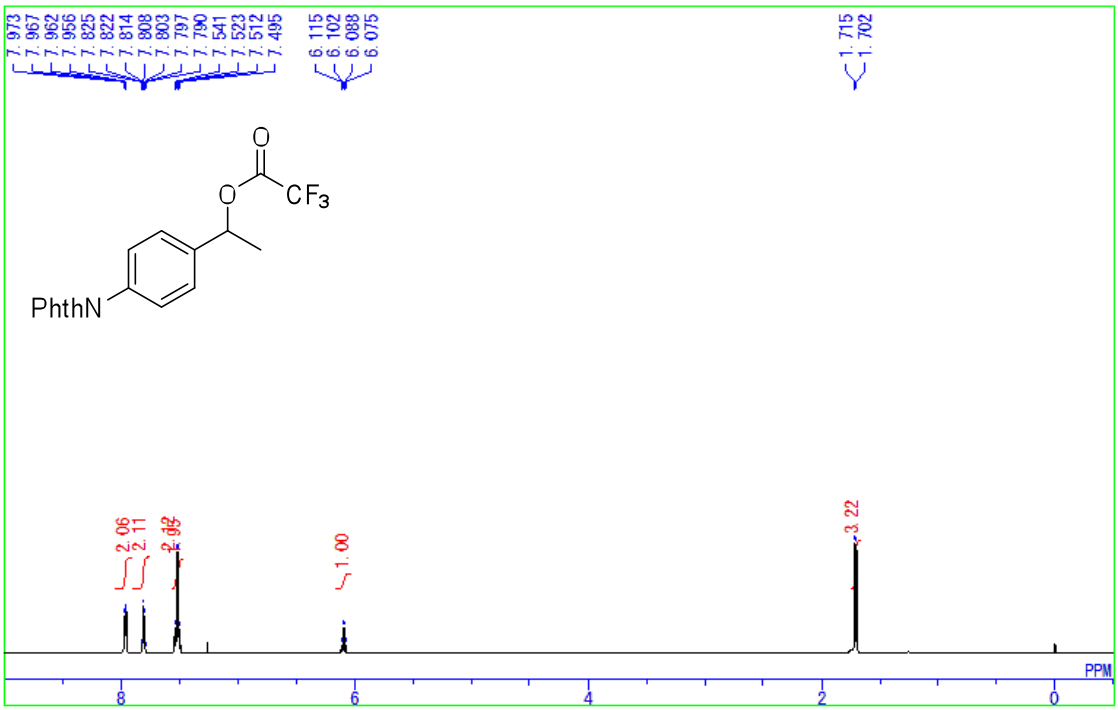
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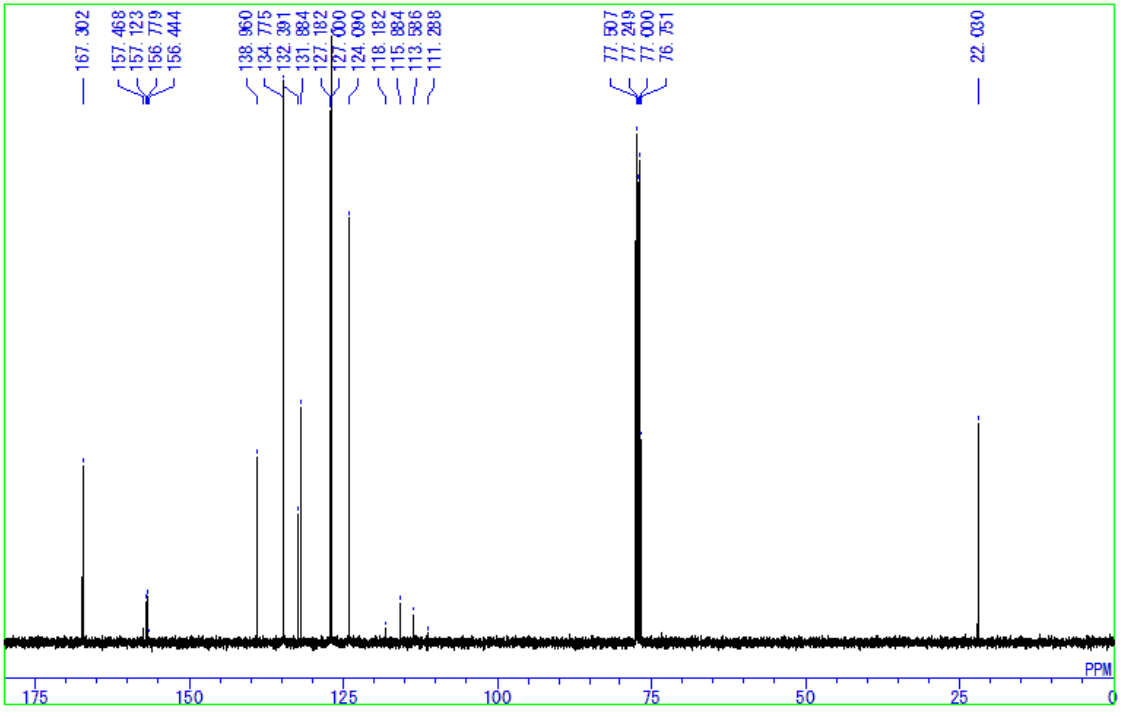
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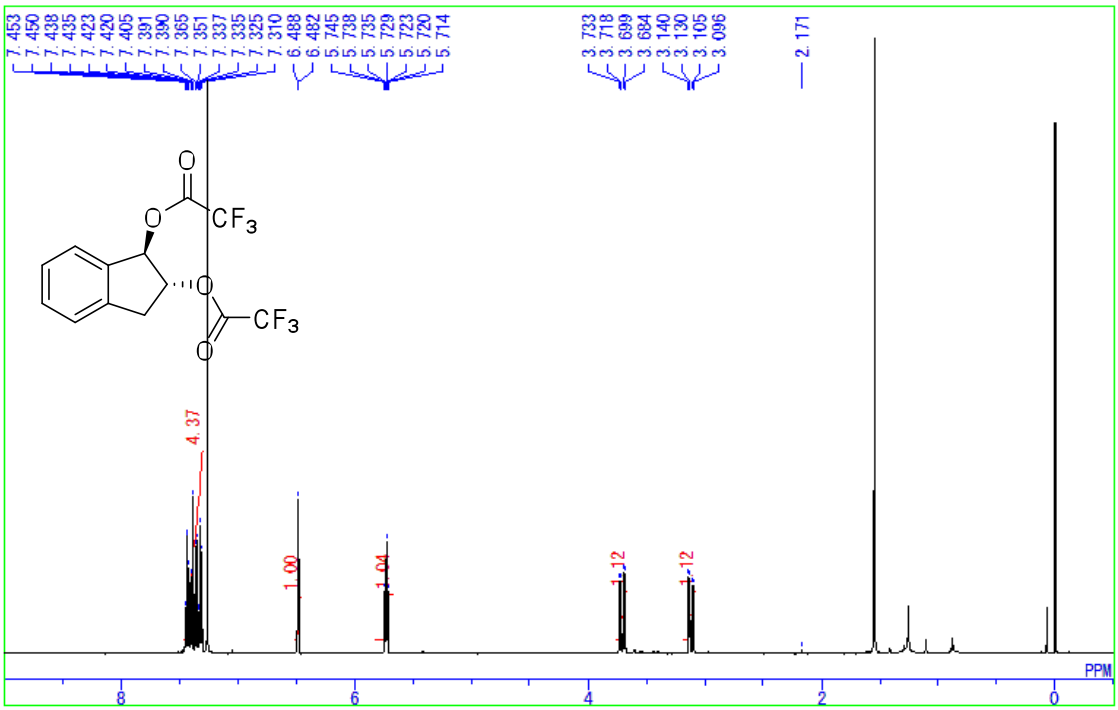
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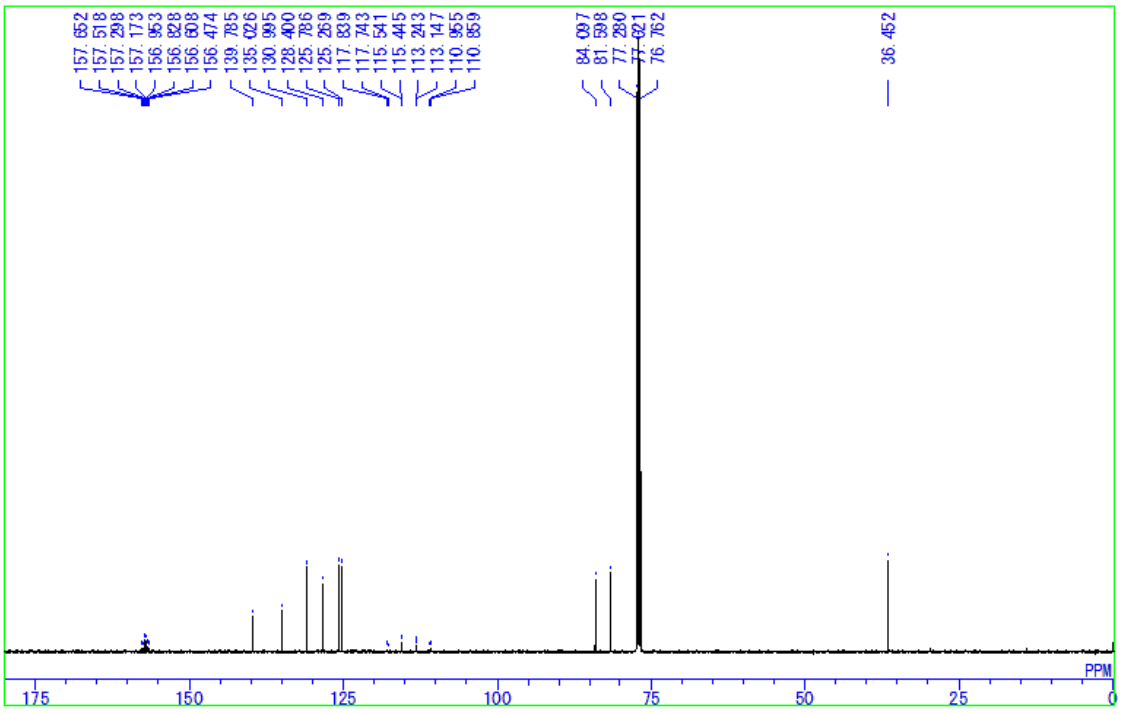
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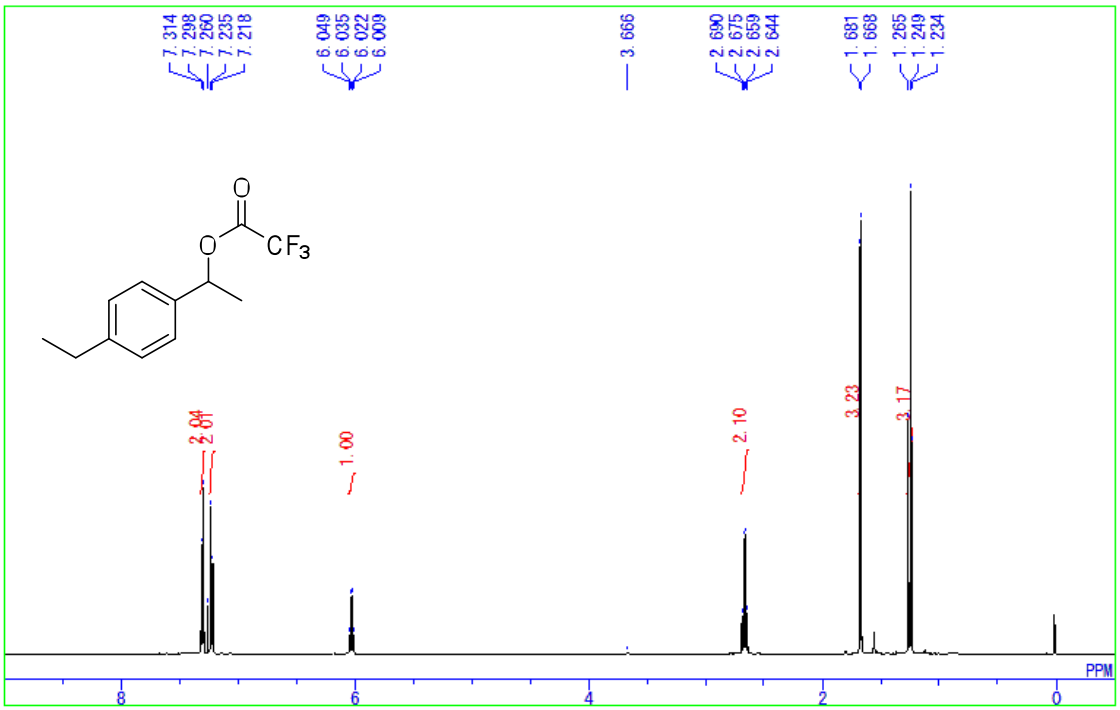
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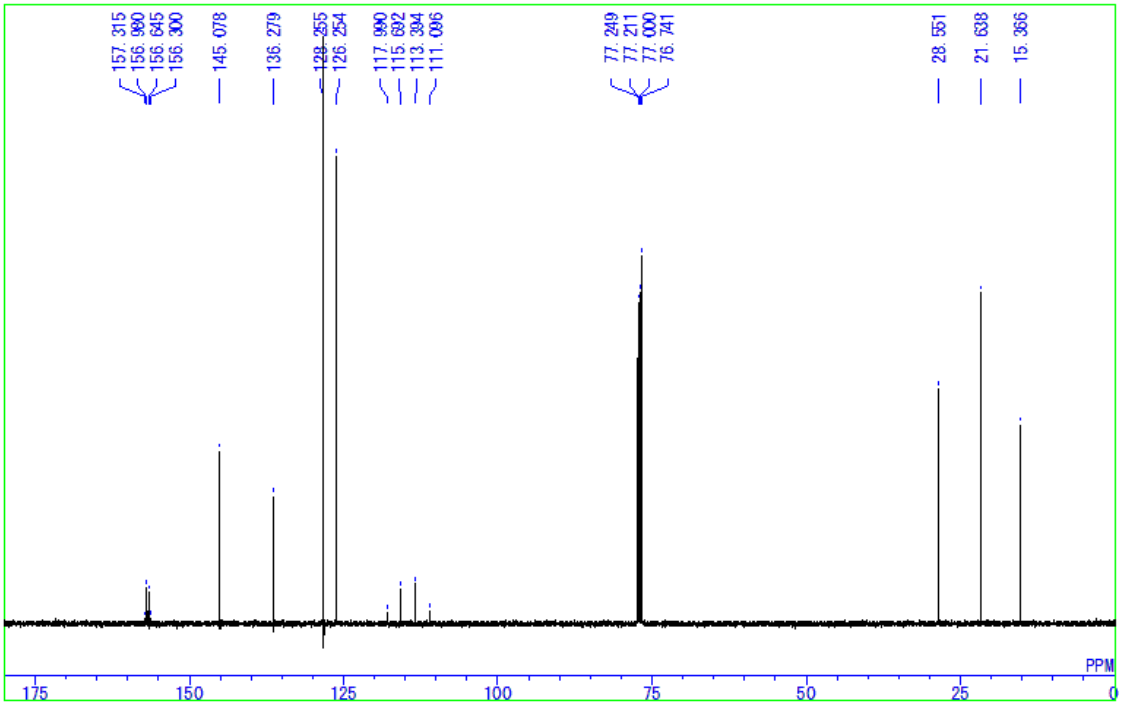
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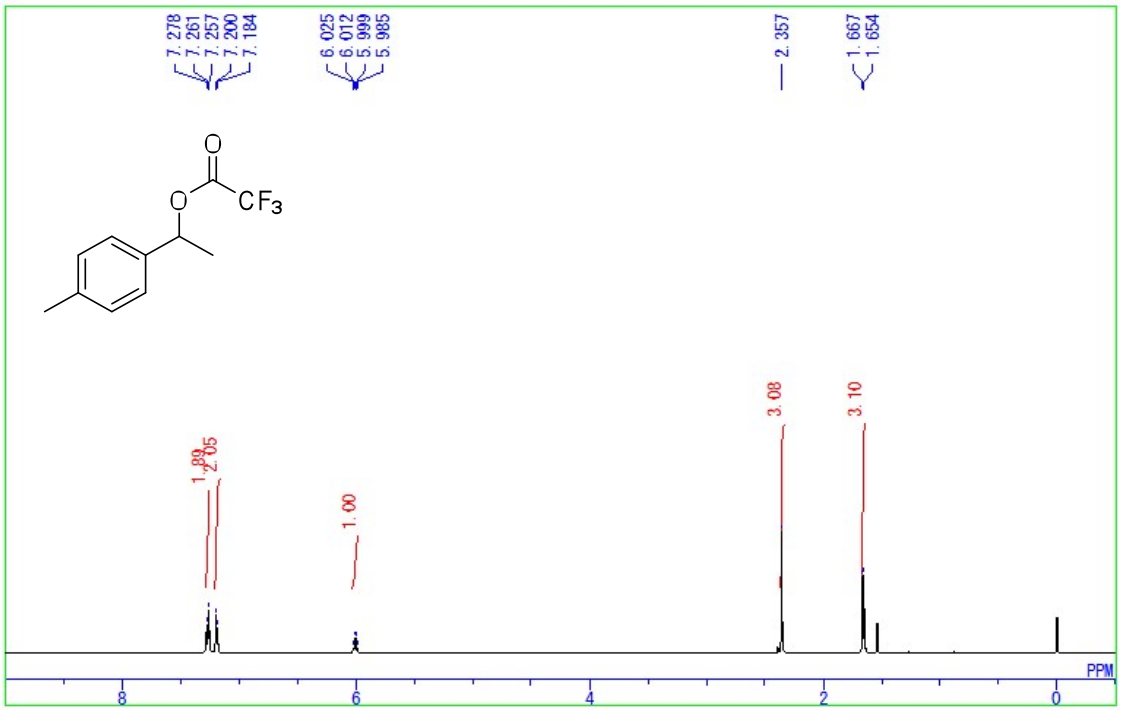
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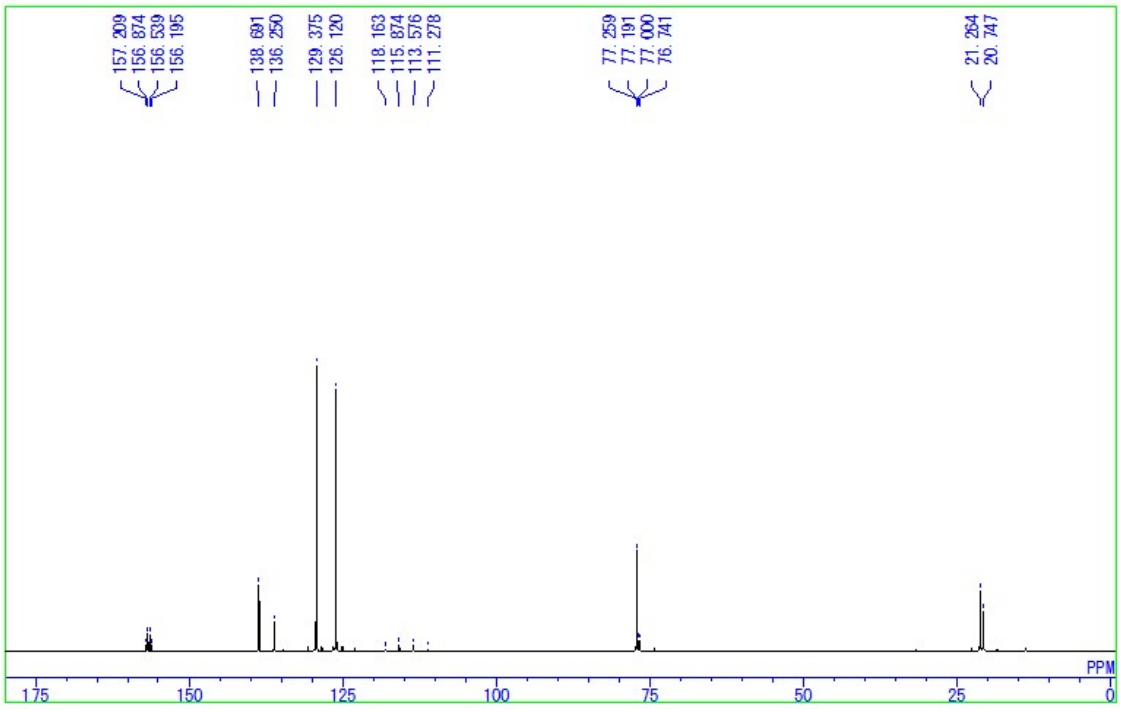
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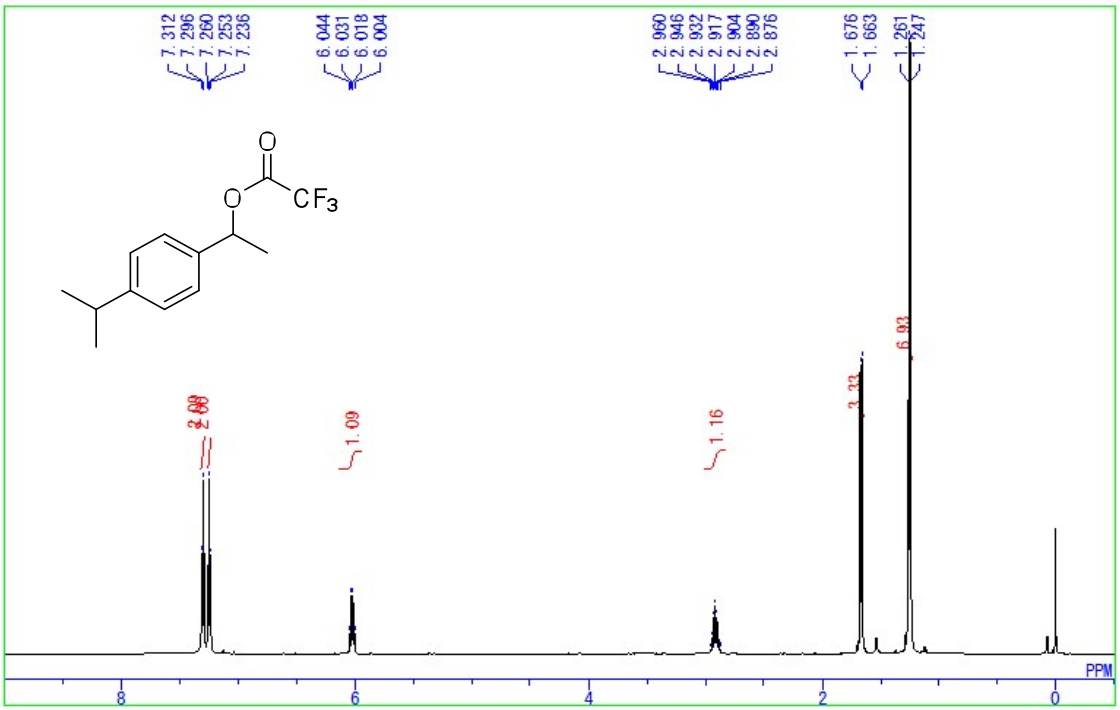
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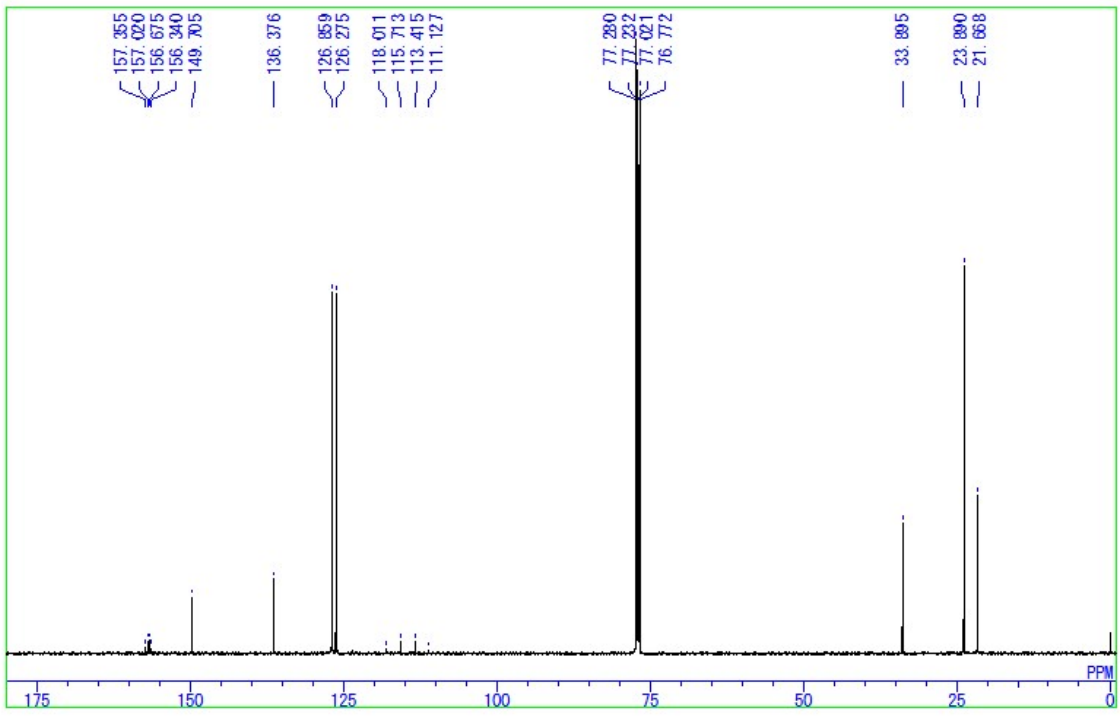
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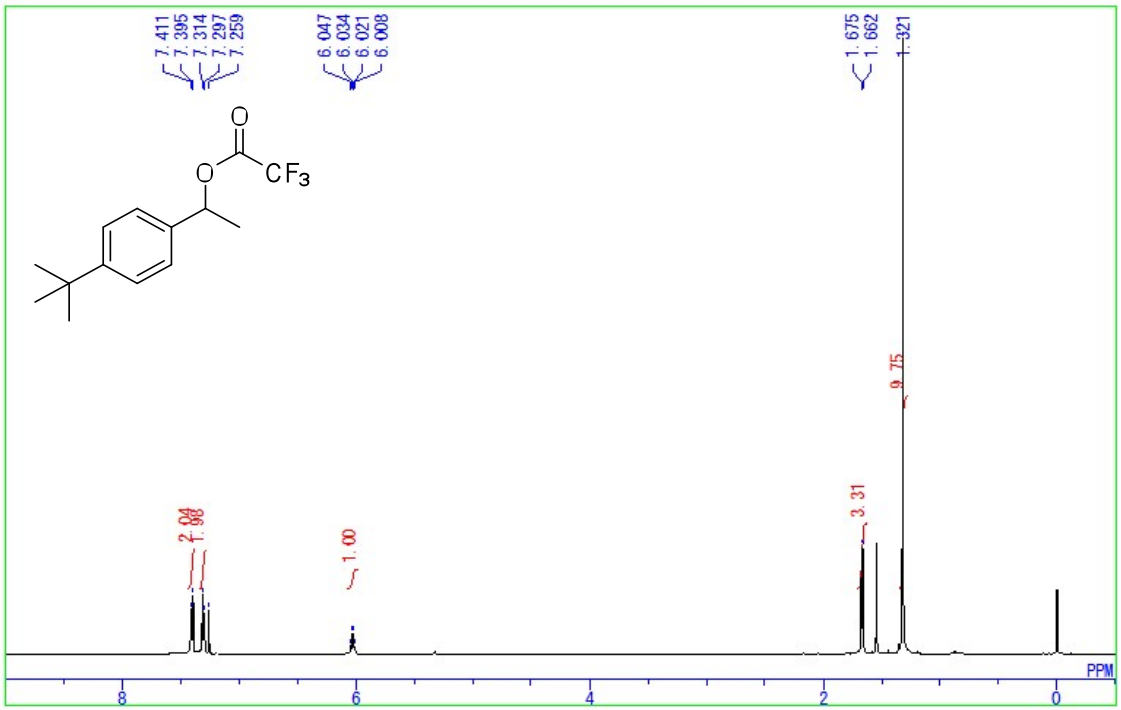
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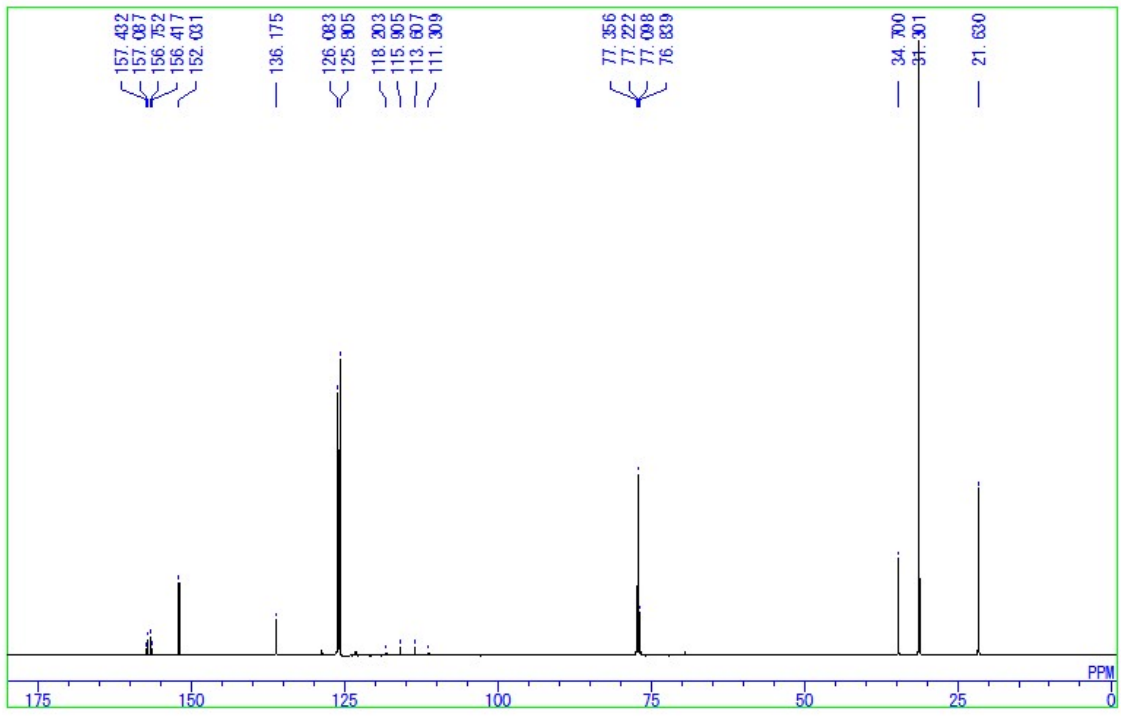
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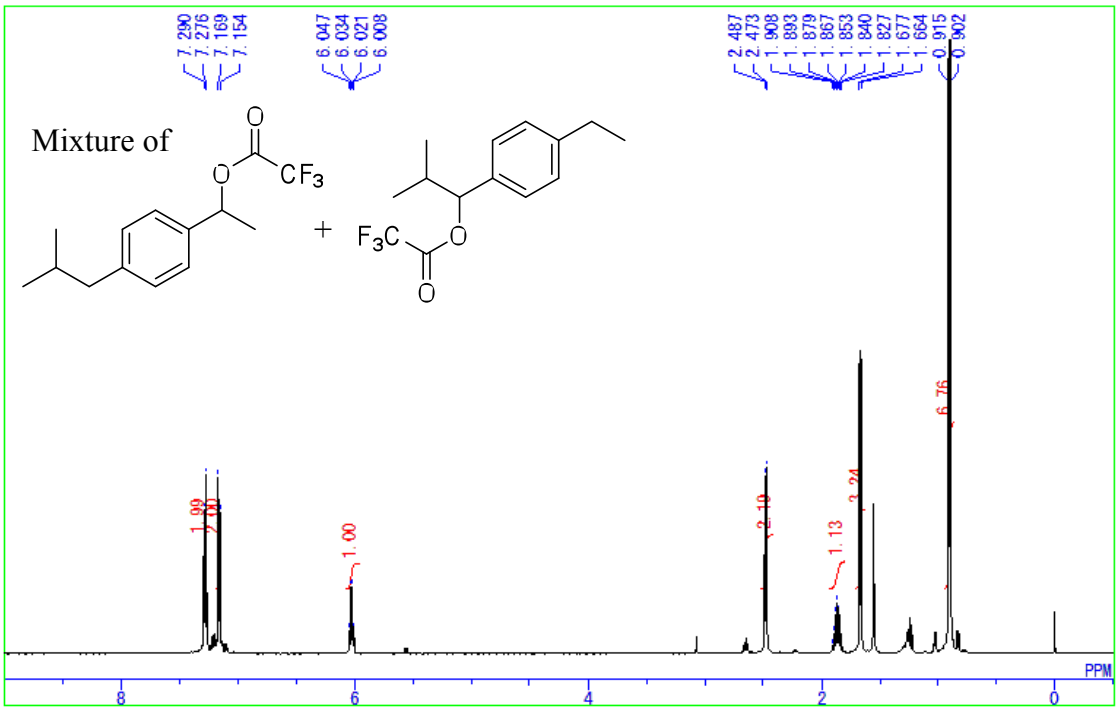
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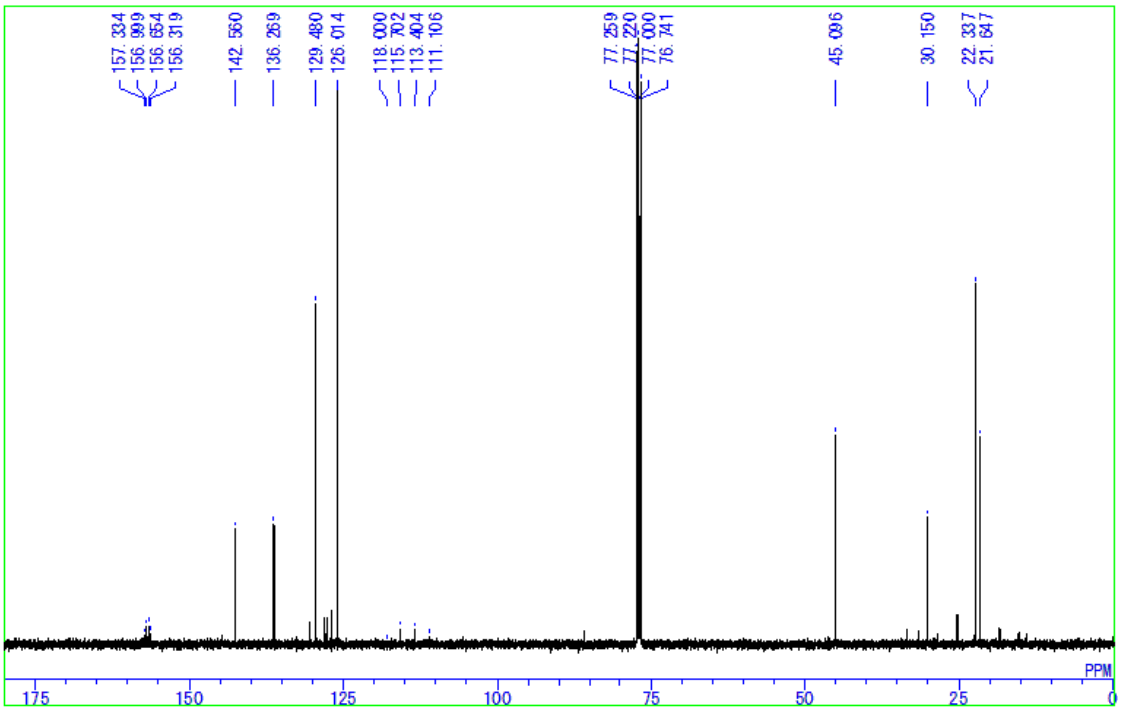
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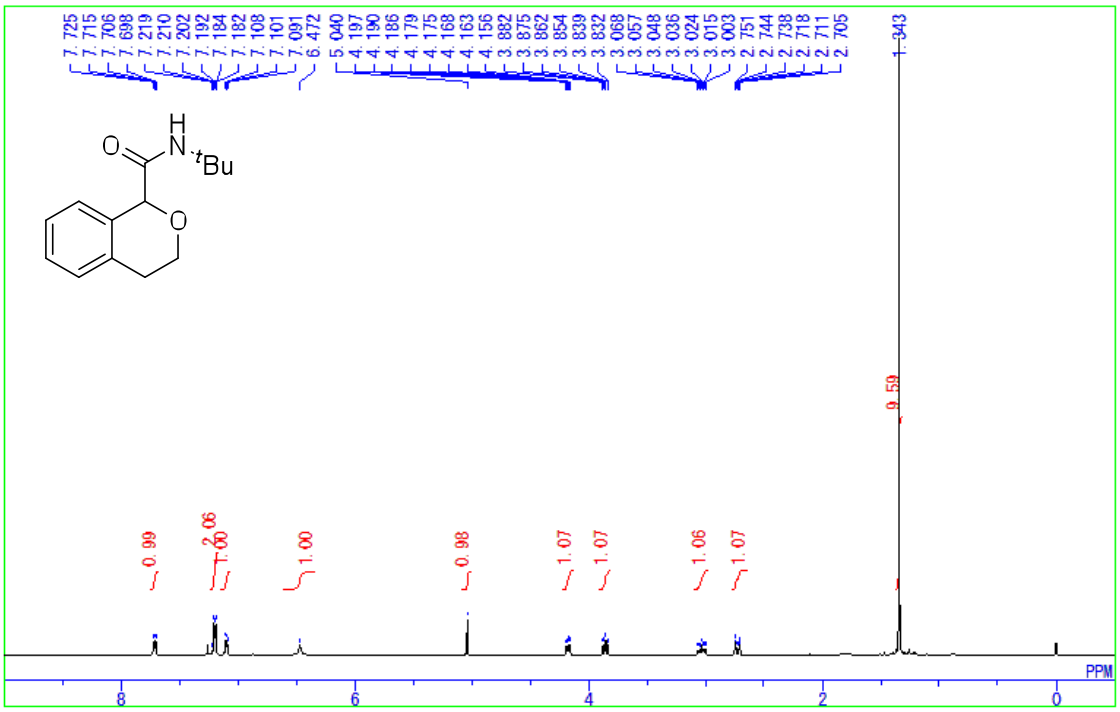
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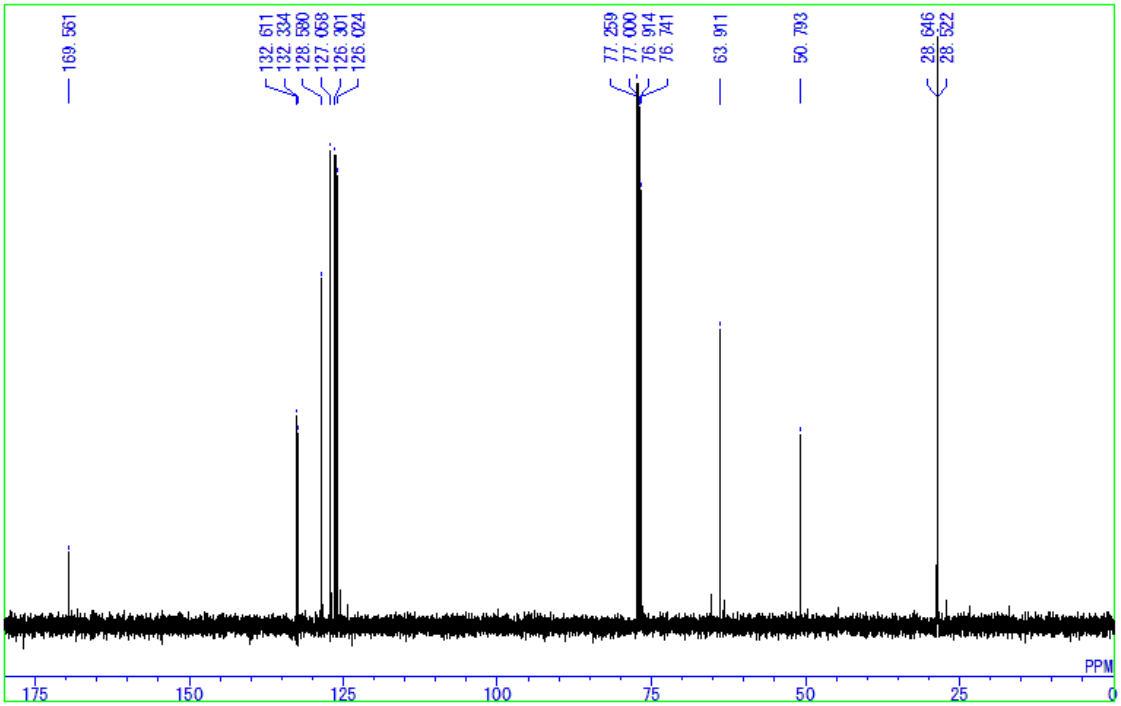
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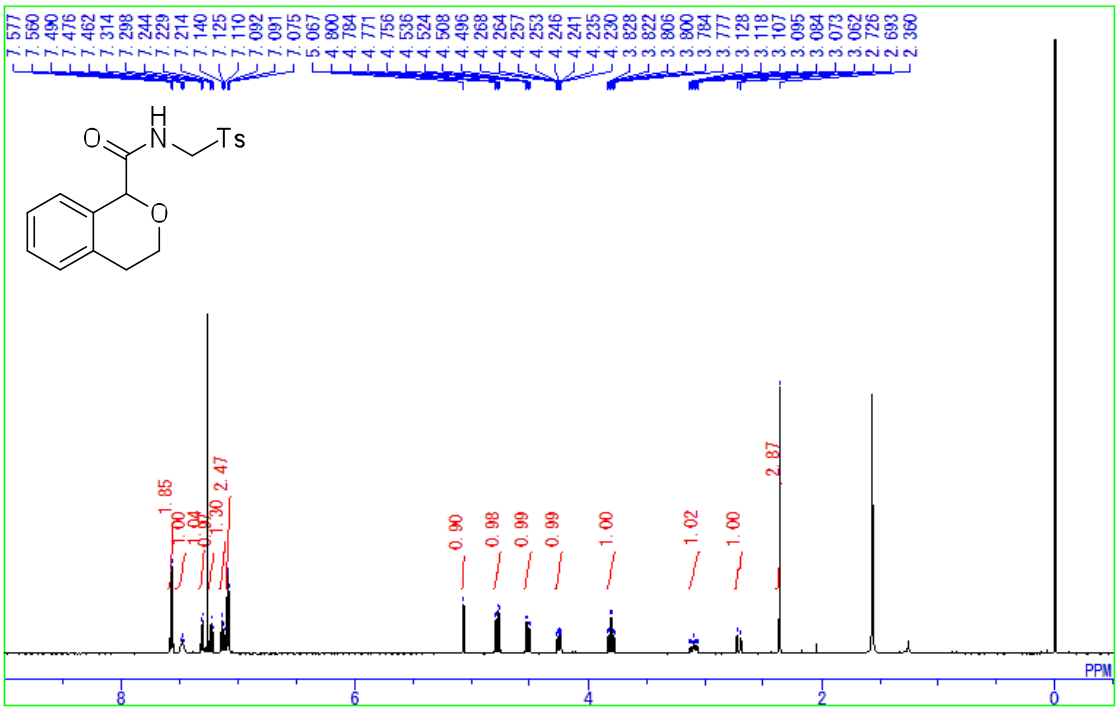
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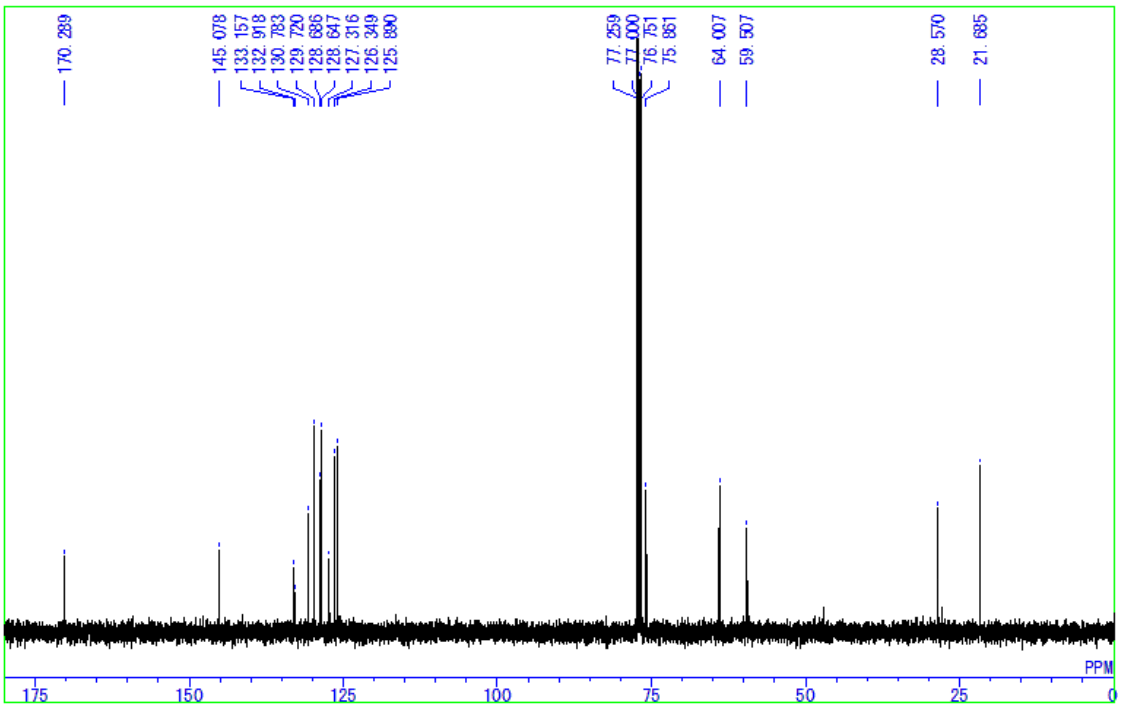
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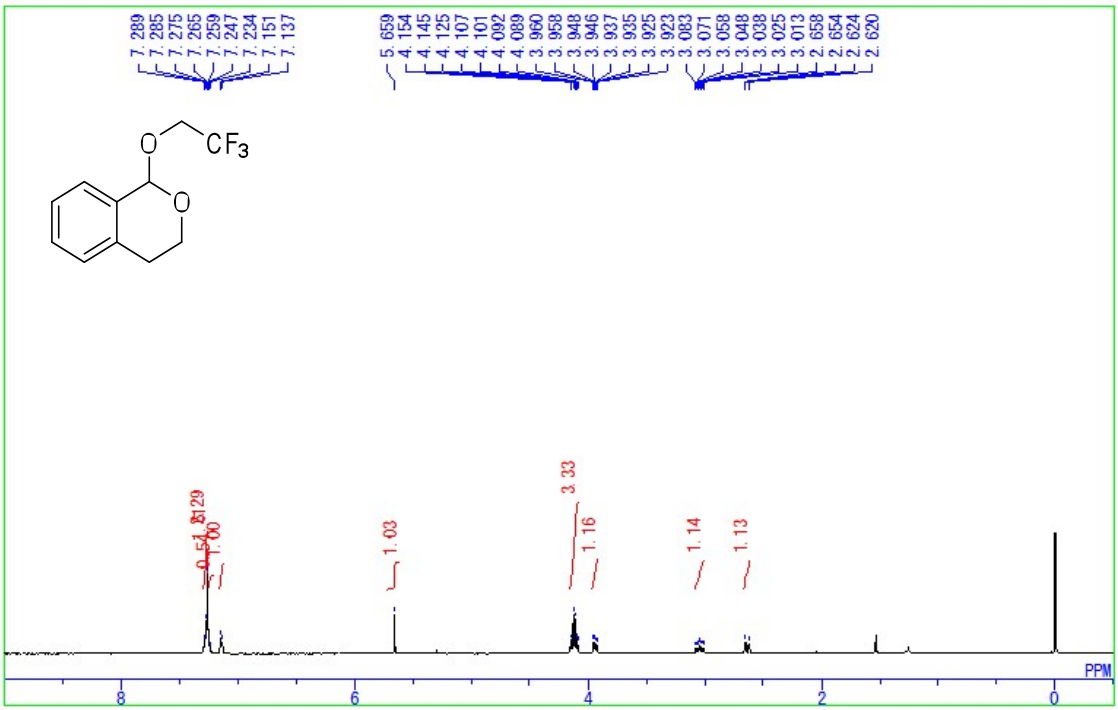
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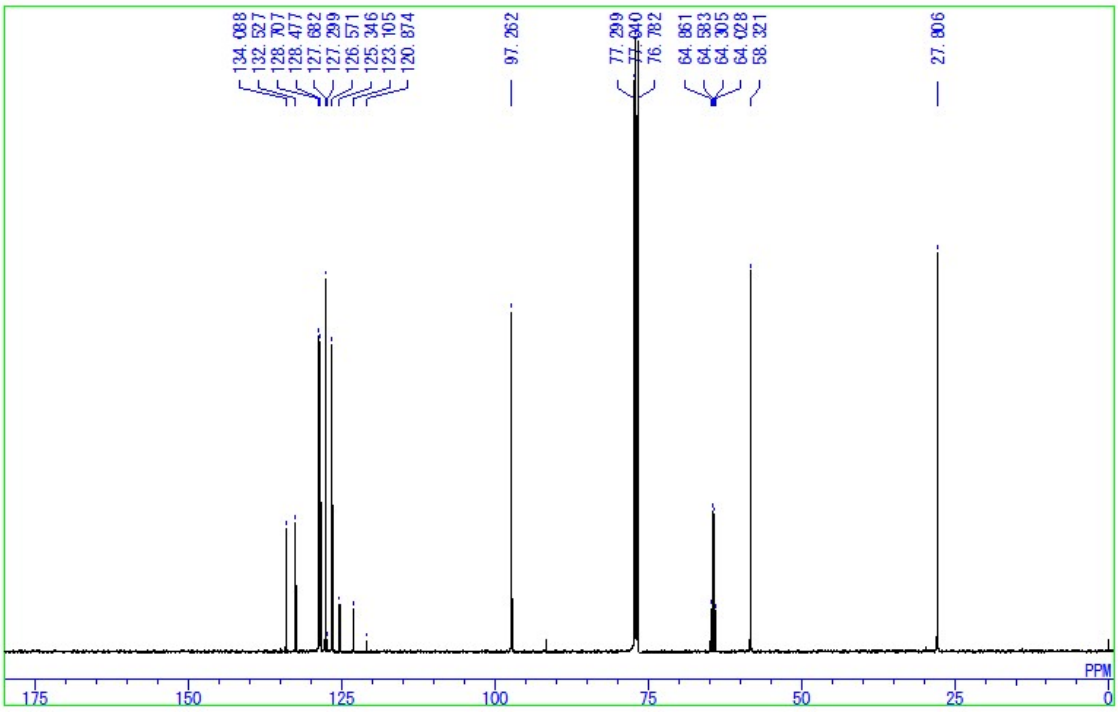
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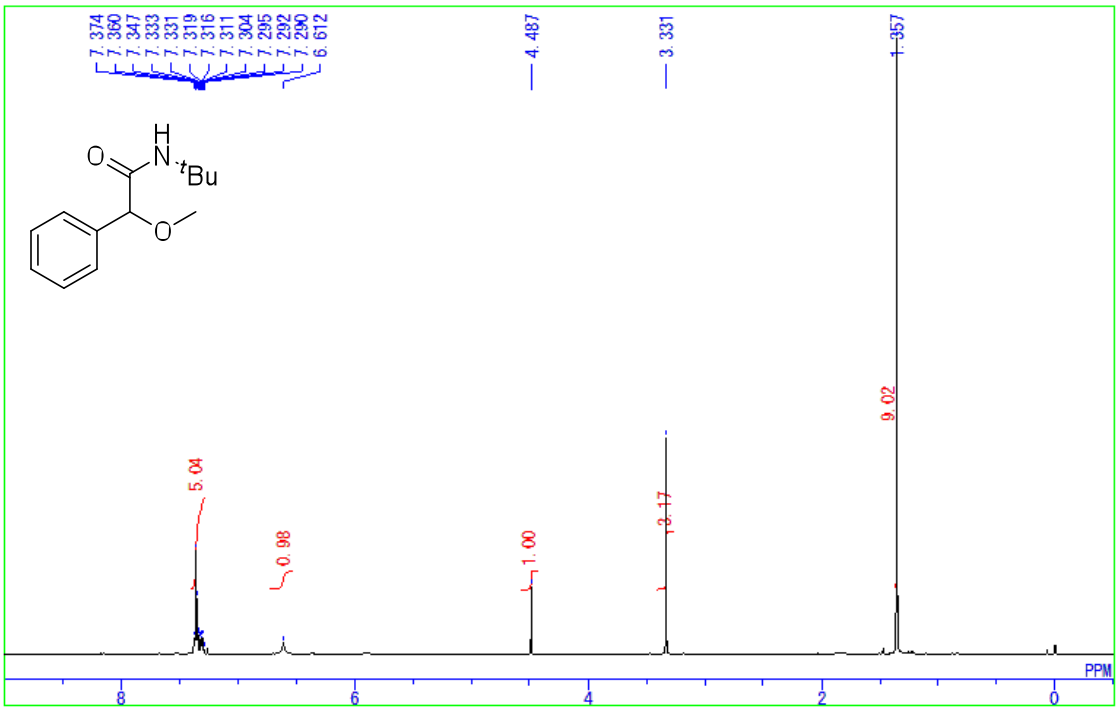
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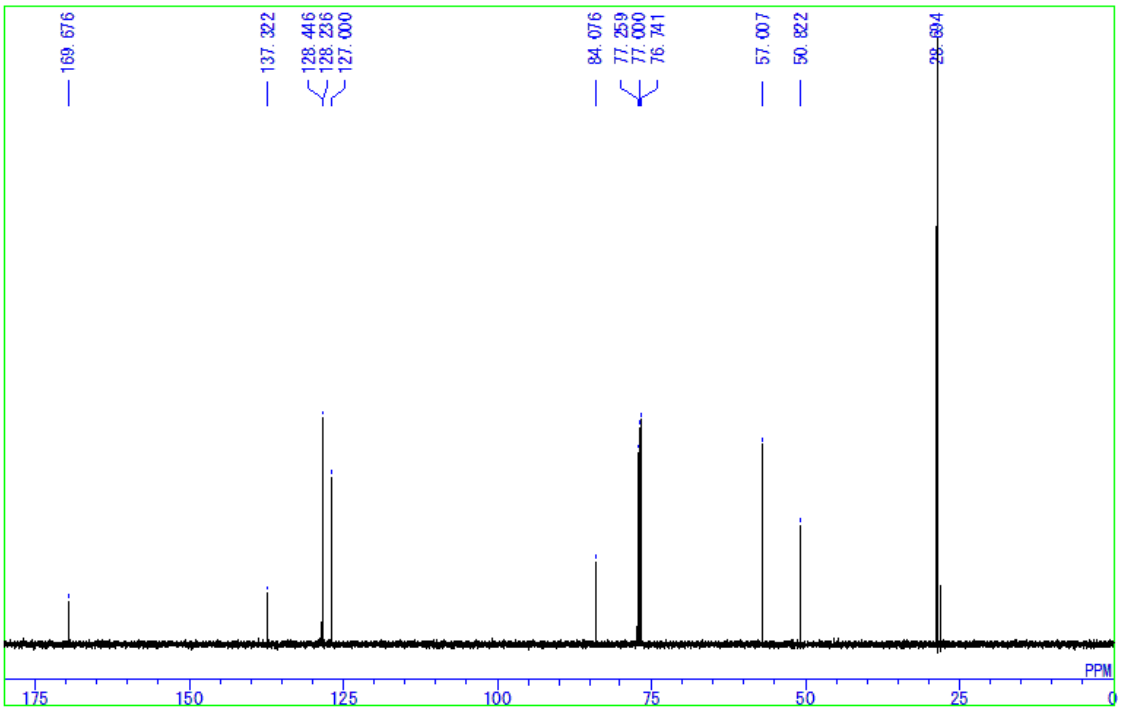
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