Syntheses of α-CF3-α-quaternary ketones via *p*-quinone methides and their derivatization to compounds with successively congested stereogenic centers

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General information

Most of reactions where an organic solvent was employed were performed under argon with magnetic stirring using a flame-dried glassware. Unless otherwise noted, materials were obtained from commercial suppliers including anhydrous THF, Et_2O, and CH_2Cl_2, and were used without further purification. DMSO was freshly dried prior to the reaction over 4Å MS which was activated by irradiating with a microwave for 1 min and heating under vacuum for 1 h. The substrates **2** were prepared as our previous report[1]. Indole-3-carboxaldehyde[2], 4-(benzyloxy)butanal[3], methyl 5-oxopentanoate[4] were prepared according to the previous reports.

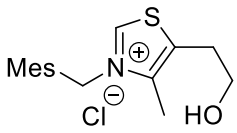
Analytical thin-layer chromatography (TLC) was routinely used for monitoring reactions by generally using a mixture of hexane and ethyl acetate. Spherical neutral silica gel (63–210 μm) was employed for usual column chromatography. All diasteroselectivity were determined by ^{19}F NMR at the crude stage.

^1H (300.40 MHz), ^{13}C (75.45 Hz), and ^{19}F (282.65 Hz) NMR spectra were recorded in $CDCl_3$ unless otherwise noted, and chemical shifts were reported in parts per million (ppm), downfield from internal tetramethylsilane (Me_4Si: δ 0.00, for ^1H and ^{13}C) or hexafluorobenzene (C_6F_6: δ –163.00 for ^{19}F). Data were tabulated in the following order: number of protons or fluorines, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet; b, broad peak), coupling constants in Hertz. In the case of ^{13}C NMR, because it is difficult to observe perfluoroalkyl carbon atoms even after long time data acquisition due to multiple coupling, these data are not shown. Infrared (IR) spectra were reported in wave numbers (cm^{-1}). High resolution mass spectrometry was performed by the positive ionization mode. Melting points were measured by Differential Scanning Calorimetry.

Synthesis of *pre*-NHC catalysts

pre-NHC catalysis A[5], C[6] and D[7] were prepared according to the previous reports. However, because no required data for *pre*-NHC cat. B was found in the previous report,[8] we dealt with only this compound as new.

pre-NHC B



To a pressure tight glass tube were added 2-(chloromethyl)-1,3,5-trimethylbenzene (0.3412 g, 0.3989 mmol), 5-(2-hydroxyethyl)-4-methylthiazol (0.2902 g, 2.027 mmol), and MeCN (2 mL), and the

mixture was stirred for 24 h at 80 °C. After the volatiles were removed by evaporation, the residue was washed with MeCN to afford the desired product as a white solid (0.4121 g, 1.321, 66%).

m.p.: 176.0 °C.

^{1}H NMR (DMSO-d_6): δ 2.18 (s, 6H), 2.28 (s, 3H), 2.61 (s, 3H), 3.06 (t, J = 5.1 Hz, 2H), 3.65 (t, J = 5.1 Hz, 2H), 5.50 (s, 1H), 7.04 (s, 2H), 8.95 (s, 1H).

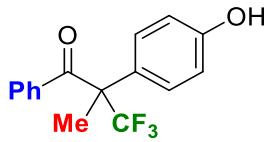
^{13}C NMR (DMSO-d_6): δ 11.6, 19.1, 20.7, 29.4, 51.3, 59.6, 125.1, 129.7, 135.9, 138.7, 139.4, 142.2, 154.1.

IR (KBr) ν 3282, 3223, 3096, 2906, 2862, 1612, 1591, 1490, 1428, 1337 cm^{-1}.

HRMS (FAB+, *m/z*): [M–Cl]$^{+}$ Calcd for $C_{16}H_{22}NOS$, 276.1422; Found, 276.1416.

General procedure for the synthesis of ketones containing α-quaternary carbons with a CF_3 group

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-phenylpropan-1-one. (3aa) (GP1)



To a test tube under an argon atmosphere were introduced **2a** (0.1684 g, 0.4000 mmol), benzaldehyde (0.0636 g, 0.0599 mmol, 1.5 eq.), *pre*-NHC **A** (0.0108 g, 0.0400 mmol, 10 mol%) and 4.0 mL of DMSO, where K_2CO_3 (0.0056 g, 0.040 mmol, 10 mol%) was added. This reaction mixture was stirred for 2 h at 50 °C (see Table 2). After cooling to 30 °C, KF (0.0350 g, 0.602 mmol, 1.5 eq.) was added to the reaction mixture which was further stirred for 0.5 h at the same temperature. After quenching with sat. NH_4Cl aq., the reaction mixture was extracted three times with Et_2O and the combined organic phase was dried over anhydrous Na_2SO_4. After filtration, evaporation of the volatiles afforded a crude material which was purified by silica gel column chromatography using AcOEt:hexane=3:1 to 1:1 as an eluent to furnish 0.0983 g (0.335 mmol) of the desired product **3aa** in 84% yield as a white solid.

Rf = 0.23 (hexane:AcOEt = 3:1).

m.p.: 139.5 °C.

^{1}H NMR: δ 1.92 (s, 3H), 4.99 (brs, 1H), 6.87-6.92 (m, 2H), 7.23-7.28 (m, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.40-7.46 (m, 3H).

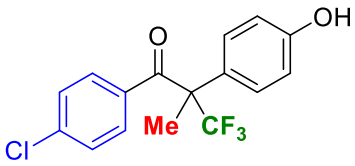
^{13}C NMR (acetone-d_6): δ 18.7 (q, J = 2.5 Hz), 60.0 (q, J = 23.0 Hz), 116.8, 125.6, 127.0 (q, J = 283.3 Hz), 129.1, 130.4, 133.4, 135.8 (q, J = 1.8 Hz), 159.0, 196.0.

^{19}F NMR: δ –73.40 (s).

IR (KBr) ν 3463, 3078, 3015, 2994, 2952, 1672, 1593, 1518, 1439, 1283 cm^{-1}.

HRMS (FAB+, *m/z*): [M]$^{+}$ Calcd for $C_{16}H_{13}F_3O_2$, 294.0868; Found, 294.0877.

1-(4-Chlorophenyl)-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methylpropan-1-one. (3ab)



Following to **GP1**, *p*-chlorobenzaldehyde (0.0845 g, 0.601 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.1118 g, 0.3401 mmol, 85%).

Rf = 0.20 (hexane:AcOEt = 3:1).

m.p.: 128.5 °C.

^{1}H NMR: δ 1.90 (s, 3H), 5.11 (brs, 1H), 6.86-6.91 (m, 2H), 7.21-7.25 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.37-7.42 (m, 2H).

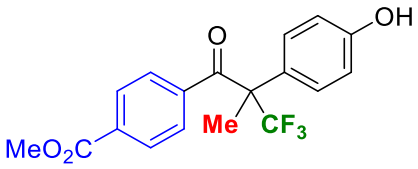
^{13}C NMR: δ 18.7 (q, *J* = 2.5 Hz), 59.3 (q, *J* = 23.6 Hz), 116.2, 125.6 (q, *J* = 283.9 Hz), 126.0, 128.6, 129.5, 131.3, 133.0, 139.2, 156.4, 195.1.

^{19}F NMR: δ –73.37 (s).

IR (KBr) ν 3109, 3030, 2899, 2828, 1698, 1590, 1518, 1458, 1391, 1257 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{20}H_{22}F_3O_3$, 329.0556; Found, 329.0570.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-1-(4-methoxycarbonylphenyl)-2-methylpropan-1-one. (3ac)



Following to **GP1**, methyl *p*-formylbenzoate (0.0986 g, 0.601 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.0792 g, 0.225 mmol, 56%).

Rf = 0.17 (hexane:AcOEt = 3:1).

m.p.: 108.3 °C.

^{1}H NMR: δ 1.90 (s, 3H), 3.90 (s, 3H), 5.34 (brs, 1H), 6.88-6.93 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.45-7.49 (m, 2H), 7.91 (d, *J* = 8.7 Hz, 2H).

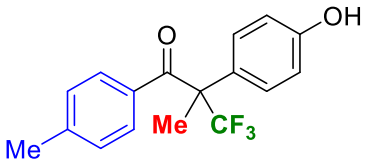
^{13}C NMR (acetone-d_6): δ 18.4 (q, *J* = 2.5 Hz), 52.7, 60.1 (q, *J* = 23.0 Hz), 116.9, 125.0 (q, *J* = 1.0 Hz), 126.9 (q, *J* = 282.5 Hz), 130.0, 130.5, 134.2, 139.5 (q, *J* = 1.9 Hz), 159.2, 166.2, 195.9.

^{19}F NMR: δ –71.75 (s).

IR (KBr) ν 3454, 3257, 2995, 2956, 1723, 1706, 1687, 1516, 1280, 1175 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{18}H_{16}F_3O_4$, 353.1001; Found, 353.1008.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-(4-methylphenyl)propan-1-one. (**3ae**)



Following to **GP1**, *p*-tolualdehyde (0.0817 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.0908 g, 0.2945 mmol, 74%).

Rf = 0.42 (hexane:AcOEt = 2:1).

m.p.: 139.8 °C.

^{1}H NMR: δ 1.92 (s, 3H), 2.31 (s, 3H), 5.09 (brs, 1H), 6.86-6.90 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.35-7.39 (m, 2H).

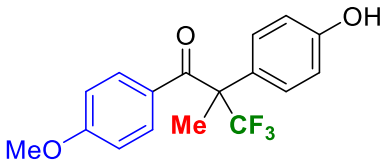
^{13}C NMR: δ 18.8 (q, *J* = 2.5 Hz), 21.5, 59.2 (q, *J* = 22.7 Hz), 113.4, 116.0, 125.8 (q, *J* = 283.5 Hz), 126.5, 128.9, 129.6, 130.1, 143.7, 156.3, 196.0.

^{19}F NMR: δ –73.40 (s).

IR (KBr) ν 3358, 3054, 3008, 2920, 1671, 1608, 1515, 1285, 1238, 973 cm^{-1}.

HRMS (FAB+, *m/z*): [M+H]$^{+}$ Calcd for $C_{17}H_{16}F_3O_2$, 309.1102; Found, 309.1101.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-1-(4-methoxyphenyl)-2-methylpropan-1-one. (3af)



Following to **GP1**, *p*-anisaldehyde (0.0817 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow oil (0.0728 g, 0.224 mmol, 56%).

^{1}H NMR: δ 1.93 (s, 3H), 3.79 (s, 3H), 5.06 (brs, 1H), 6.70-6.75 (m, 2H), 6.85-6.89 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.47-7.50 (m, 2H).

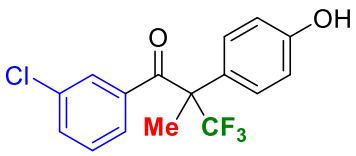
^{13}C NMR: δ 19.0 (q, *J* = 2.5 Hz), 55.3, 59.2 (q, *J* = 22.9 Hz), 113.4, 116.0, 125.8 (q, *J* = 281.9 Hz), 126.6, 127.1, 129.5, 132.5, 156.4, 163.0, 195.1.

^{19}F NMR: δ –73.28 (s).

IR ($CHCl_3$) ν 3427, 3038, 2956, 1674, 1572, 1559, 1512, 1266, 1174, 972 cm^{-1}.

HRMS (FAB+, *m/z*): [M+H]$^{+}$ Calcd for $C_{17}H_{16}F_3O_3$, 325.1252; Found, 325.1270.

1-(3-Chlorophenyl)-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methylpropan-1-one. (3ag)



Following to **GP1**, methyl *m*-chlorobenzaldehyde (0.0843 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde and the reaction mixture was stirred for 4 h at 30 °C to afford the desired product as a yellow oil (0.1174 g, 0.3571 mmol, 89%).

Rf = 0.20 (hexane:AcOEt = 3:1).

^{1}H NMR: δ 1.90 (s, 3H), 5.12 (brs, 1H), 6.88-6.93 (m, 2H), 7.14-7.20 (m, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.40 (dt, *J* = 6.9, 2.1 Hz, 1H),7.50-7.51 (m, 1H).

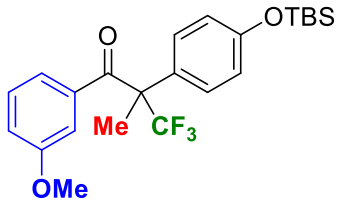
^{13}C NMR: δ 18.4 (q, *J* = 2.4 Hz), 59.3 (q, *J* = 23.7 Hz), 116.3, 125.4, 125.6 (q, *J* = 283.9 Hz), 127.8, 129.5, 129.8, 132.7, 134.5, 136.4, 156.6, 195.3.

^{19}F NMR: δ –73.77 (s).

IR ($CHCl_3$) ν 3443, 3071, 3025, 2957, 1690, 1613, 1515, 1283, 1234, 1182 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{16}H_{16}F_3O_2Cl$, 329.0556; Found, 329.0570.

2-[4-[{(1,1-Dimethylethyl)dimethylsilyl}oxy]phenyl]-3,3,3-trifluoro-1-(3-methoxyphenyl)-2-methylpropan-1-one. (3ai)



Following to **GP1**, *m*-anisaldehyde (0.0817 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde. After cooling to 30 °C and quenched with sat. NH_4Cl aq, the reaction mixture was extracted three times with Et_2O, and the combined organic phase was washed with sat. NaCl aq. . After drying over anhydrous Na_2SO_4, evaporation of the volatiles afforded a crude material which was introduced to a 30 mL round-bottomed flask with imidazole (0.0544 g, 0.799 mmol, 1.5 eq.) and CH_2Cl_2 (0.8 mL). To this solution was added TBSCl (0.0906 g, 0.601 mmol, 1.5 eq.) at 30 °C, and the mixture was stirred for 1 h at that temperature. After the reaction mixture was quenched with sat. NH_4Cl aq. and usual workup, the crude product was purified by column chromatography (hexane:AcOEt = 10:1) to give the desired product as a colorless oil (0.1283 g, 0.2925 mmol, 73%).

Rf = 0.23 (hexane:AcOEt = 10:1).

^{1}H NMR: δ 0.21 (s, 6H), 0.98 (s, 9H), 1.91 (s, 3H), 3.68 (s, 3H), 6.87-6.92 (m, 3H), 6.95 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.06 (s, 1H), 7.11 (t, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H).

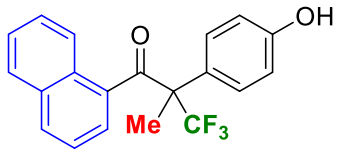
^{13}C NMR: δ –4.5, 18.2, 18.6 (q, *J* = 2.5 Hz), 25.6, 55.1, 59.3 (q, *J* = 23.6 Hz), 114.3, 119.0, 120.6, 122.3, 125.8 (q, *J* = 283.3 Hz), 127.0, 129.0, 129.4, 136.2, 156.3, 159.2, 195.5.

^{19}F NMR: δ –73.32 (s).

IR ($CHCl_3$) ν 2957, 2932, 289 6, 2859, 1688, 1596, 1511, 1277, 1260, 1178 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{23}H_{30}F_3O_3Si$, 439.1916; Found, 439.1906.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-(1-naphthyl)propan-1-one. (3aj)



Following to **GP1**, 1-naphthaldehyde (0.0939 g, 0.601 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow oil (0.1167 g, 0.3389 mmol, 85%).

Rf = 0.17 (hexane:AcOEt = 3:1).

^{1}H NMR: δ 1.99 (s, 3H), 5.32 (brs, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.44-7.57 (m, 3H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.98 (s, 1H).

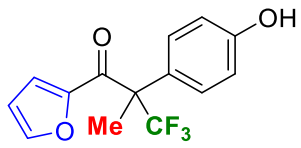
^{13}C NMR: δ 18.7 (q, *J* = 2.5 Hz), 59.4 (q, *J* = 23.7 Hz), 116.2, 125.2, 125.8 (q, *J* = 285.6 Hz), 126.2, 126.7, 127.5, 127.9, 128.7, 129.60, 129.62, 131.96, 131.99, 135.0, 156.6, 196.6.

^{19}F NMR: δ –73.27 (s).

IR ($CHCl_3$) ν 3436, 3059, 3028, 2957, 1680, 1515, 1465, 1283, 1179, 1160 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{20}H_{16}F_3O_2$, 345.1102; Found, 345.1122.

3,3,3-Trifluoro-1-(2-franyl)-2-(4-hydroxyphenyl)-2-methylpropan-1-one. (3ak)



Following to **GP1**, furfural (0.0576 g, 0.599 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.0947 g, 0.333 mmol, 83%).

Rf = 0.13 (hexane:AcOEt = 3:1).

m.p.: 191.5 °C.

^{1}H NMR: δ 1.99 (q, *J* = 0.6 Hz, 3H), 4.98 (s, 1H), 6.35 (dd, *J* = 3.6, 1.5 Hz, 1H), 6.75 (dd, *J* = 3.6, 0.6 Hz, 1H), 6.81-6.86 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 3.6, 0.6 Hz, 1H).

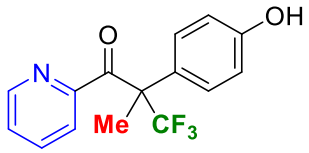
^{13}C NMR (acetone-d_6): δ 18.1 (q, *J* = 3.1 Hz), 59.3 (q, *J* = 22.9 Hz), 112.8, 116.4, 120.9, 125.9, 126.9 (q, *J* = 282.7 Hz), 130.4, 147.7, 150.8, 158.7, 184.6.

^{19}F NMR: δ –72.86 (s).

IR (KBr) ν 3345, 3142, 3033, 2956, 1899, 1656, 1519, 1454, 1292, 1179 cm^{-1}.

HRMS (FAB+, *m/z*): $[M]^+$ Calcd for $C_{14}H_{11}F_3O_3$, 294.0660; Found, 284.0687.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-(2-pyridyl)propan-1-one. (3al)



Following to **GP1**, 2-pyridinecarboxaldehyde (0.0646 g, 0.603 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.1064 g, 0.3604 mmol, 90%).

Rf = 0.17 (hexane:AcOEt = 3:1).

m.p.: 183.1 °C.

^{1}H NMR: δ 1.91 (s, 3H), 6.81 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.42 (dd, *J* = 7.8, 4.8 Hz, 1H), 8.08 (d, *J* = 6.6 Hz, 1H), 8.36 (s, 1H), 8.64 (d, *J* = 4.8 Hz, 1H).

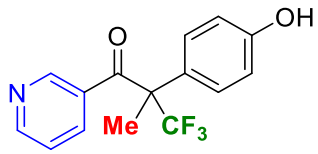
^{13}C NMR: δ 18.5 (q, *J* = 2.3 Hz), 59.4 (q, *J* = 23.7 Hz), 116.4, 123.9, 124.2, 125.4 (q, *J* = 283.3 Hz), 129.5, 131.6, 138.5, 149.6, 151.5, 157.9, 193.9.

^{19}F NMR: δ –73.15 (s).

IR (KBr) ν 3109, 3030, 2899, 2828, 1698, 1590, 1518, 1458, 1390, 1154 cm^{-1}.

HRMS (FAB+, *m/z*): $[M]^+$ Calcd for $C_{15}H_{12}F_3NO_2$, 295.0820; Found, 295.0833.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-(3-pyridyl)propan-1-one. (3am)



Following to **GP1**, 3-pyridinecarboxaldehyde (0.0642 g, 0.599 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.0566 g, 0.192 mmol, 48%).

Rf = 0.37 (hexane:AcOEt = 2:1).

m.p.: 144.2 °C.

^{1}H NMR: δ 2.25 (s, 3H), 4.86 (brs, 1H), 6.74-6.77 (m, 2H), 7.20-7.28 (m, 3H), 7.76 (dt, *J* = 1.8, 7.8 Hz, 1H), 8.06 (dt, *J* = 8.1, 0.9 Hz, 1H), 8.30 (ddd, *J* = 4.8 1.8, 0.9 Hz, 1H).

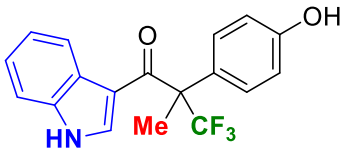
^{13}C NMR (acetone-d_6): δ 17.9 (q, *J* = 3.1 Hz), 59.9 (q, *J* = 23.0 Hz), 116.0, 125.0, 126.7, 127.2 (q, *J* = 283.3 Hz), 130.0, 137.9, 148.8, 149.6, 153.1, 158.0, 196.0.

^{19}F NMR: δ –73.65 (s).

IR (KBr) ν 3367, 3064, 2999, 2946, 2800, 1695, 1599, 1512, 1284, 1188 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{15}H_{13}F_3NO_2$, 296.0898; Found, 296.0924.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-1-(1*H*-indol-3-yl)-2-methylpropan-1-one (3an)



Following to **GP1**, indole-3-carboxaldehyde (0.0871 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.1080 g, 0.3240 mmol, 81%).

Rf = 0.42 (hexane:AcOEt = 2:1).

m.p.: 172.3 °C.

^{1}H NMR: δ 2.23 (s, 3H), 5.15 (brs, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.82-6.87 (m, 2H), 7.01 (ddd, *J* = 8.6, 7.2, 1.2 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.22 (dt, *J* = 7.8, 0.9 Hz, 1H), 8.13 (d, *J* = 0.9 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 10.11 (s, 1H).

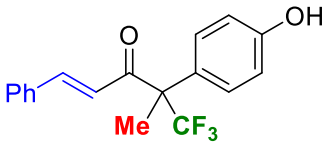
^{13}C NMR: δ 24.5, 67.7 (q, *J* = 28.6 Hz), 114.9, 116.1, 118.7, 121.7, 123.2, 124.1, 125.4 (q, *J* = 285.8 Hz), 125.8, 127.2, 128.0, 137.0, 138.6, 156.9, 185.8.

^{19}F NMR: δ –73.40 (s).

IR (KBr) ν 3348, 3140, 2999, 2821, 1649, 1543, 1517, 1446, 1247, 1183 cm^{-1}.

HRMS (FAB+, *m/z*): [M+H]$^{+}$ Calcd for $C_{18}H_{14}F_3NO_2$, 333.0977; Found, 333.0986.

5,5,5-Trifluoro-4-(4-hydroxyphenyl)-4-methyl-1-phenylprop-1-en-3-one (3ao)



Following to **GP1**, cinnamaldehyde (0.0793 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a yellow solid (0.0612 g, 0.189 mmol, 47%).

Rf = 0.27 (hexane:AcOEt = 3:1).

m.p.: 134.1 °C.

^{1}H NMR: δ 1.83 (s, 3H), 6.49 (d, *J* = 15.3 Hz, 1H), 6.85-6.90 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.33-7.43 (m, 5H), 7.76 (d, *J* = 15.6 Hz, 1H).

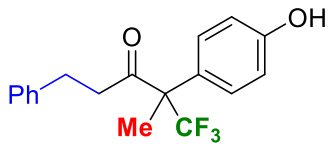
^{13}C NMR: δ 17.6 (q, *J* = 2.9 Hz), 59.4 (q, *J* = 23.6 Hz), 116.0, 121.3, 125.7, 125.8 (q, *J* = 284.6 Hz), 128.5, 128.8, 129.7, 130.9, 134.0, 144.8, 156.3, 194.3.

^{19}F NMR: δ –71.91 (s).

IR (KBr) ν 3441, 3020, 2926, 1684, 1602, 1516, 1279, 1156, 1035, 826 cm^{-1}.

HRMS (FAB+, *m/z*): [M+H]$^{+}$ Calcd for $C_{18}H_{16}F_3O_2$, 321.1102; Found, 321.1130.

1,1,1-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-5-phenyl-3-pentanone (3aq)



Following to **GP1**, 3-phenylpropionaldehyde (0.0805 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a white solid (0.1025 g, 0.2923 mmol, 80%).

Rf = 0.30 (hexane:AcOEt = 3:1).

m.p.: 68.4 °C.

^{1}H NMR: δ 1.69 (s, 3H), 2.49-2.68 (m, 2H), 2.78-2.97 (m, 2H), 5.17 (m, 1H), 6.77-6.81 (m, 2H), 7.03-7.07 (m, 4H), 715-7.26 (m, 3H).

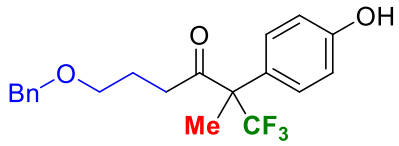
^{13}C NMR: δ 17.0 (q, J = 3.1 Hz), 30.0, 40.0 (q, J = 1.9 Hz), 60.1 (q, J = 23.6 Hz), 115.8, 125.4, 125.7 (q, J = 283.3 Hz), 126.2, 128.4, 129.1, 140.2, 156.1, 204.9.

^{19}F NMR: δ –71.90 (s).

IR (KBr) ν 3109, 3030, 2899, 2828, 1698, 1590, 1518, 1458, 1390, 1154 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{18}H_{18}F_3O_2$, 323.1259; Found, 323.1260.

6-Benzyloxy-1,1,1-trifluoro-2-(4-hydroxyphenyl)-2-methyl-3-hexanone (3ar)



Following to **GP1**, 4-(benzyloxy)butanal (0.0805 g, 0.600 mmol, 1.5 eq.) was used instead of benzaldehyde to afford the desired product as a colorless liquid (0.1025 g, 0.2923 mmol, 80%).

Rf = 0.30 (hexane:AcOEt = 3:1).

^{1}H NMR: δ 1.76-1.97 (m, 5H), 2.31-2.52 (m 2H), 3.34-3.48 (m, 2H), 4.48 (s, 2H), 5.04 (brs, 1H), 6.80-6.85 (m, 2H), 7.17-7.35 (m, 7H).

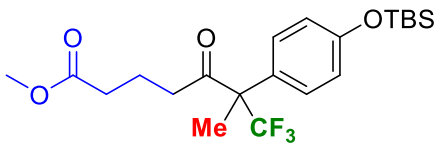
^{13}C NMR: δ 17.2 (q, J = 2.4 Hz), 23.8, 34.7, 60.1 (q, J = 23.6 Hz), 68.9, 72.7, 115.8, 125.4, 125.7 (q, J = 283.3 Hz), 127.4, 128.4, 129.0, 137.7, 156.3, 205.5.

^{19}F NMR: δ –71.90 (s).

IR ($CHCl_3$) ν 3380, 3031, 2934, 2867, 1718, 1613, 1516, 1279, 1160, 1084 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{20}H_{22}F_3O_3$, 367.1521; Found, 367.1528.

Methyl 6-[4-[{(1,1-Dimethylethyl)dimethylsilyl}oxy]phenyl]-7,7,7-trifluoro-6-methyl-5-oxoheptanoate (3as)



Following to **GP1**, methyl 5-oxopentanoate (0.1556 g, 1.196 mmol, 3.0 eq.) was used instead of benzaldehyde. After cooling to 30 °C and quenched with sat. NH_4Cl aq., the reaction mixture was extracted three times with Et_2O and the combined organic phase was washed with sat. NaCl aq. which was dried over anhydrous Na_2SO_4. After filtration, evaporation of the volatiles afforded a crude material. To a 30 mL round-bottomed flask were added this crude material, imidazole (0.0547 g, 0.803 mmol, 1.5 eq.) and CH_2Cl_2 (0.8 mL), where TBSCl (0.0906 g, 0.601 mmol, 1.5 eq.) was introduced at 30 °C. After stirring for 1 h, to the mixture was further added imidazole (0.054 g, 0.799 mmol, 1.5 eq.) and TBSCl (0.0910 g, 0.604 mmol, 1.5 eq.) once more and the mixture stirred at 30 °C for 1 h for completion of the reaction. The reaction mixture was quenched with sat. NH_4Claq. and extracted with CH_2Cl_2 three times. After usual workup, the crude product was purified by column chromatography (hexane:AcOEt = 10:1) to give the desired product as a colorless oil (0.1211 g, 0.2800 mmol, 70%).

Rf = 0.16 (hexane:AcOEt = 10:1).

^{1}H NMR: δ 0.21 (s, 6H), 0.98 (s, 9H), 1.76 (s, 3H), 2.16-2.46 (m, 4H), 3.61 (s, 3H), 6.83-6.88 (m, 2H), 7.15 (d, J = 8.4 Hz, 2H).

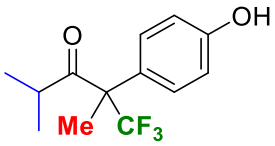
^{13}C NMR: δ –4.51, 17.3 (q, J = 1.9 Hz), 17.9, 18.1, 19.1, 25.5, 32.6, 36.8 (q, J = 1.9 Hz) 51.4, 60.1 (q, J = 23.6 Hz), 120.3, 125.7 (q, J = 283.8 Hz), 126.4, 128.7, 156.0, 173.3, 204.1.

^{19}F NMR: δ –71.65 (s).

IR ($CHCl_3$) ν 3031, 2955, 2829, 2859, 1725, 1609, 1512, 1472, 1273, 1162 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{21}H_{32}F_3O_4Si$, 433.2022; Found, 433.2043.

1,1,1-Trifluoro-2-(4-hydroxyphenyl)-2,4-dimethyl-3-pentanone (3at)



Following to **GP1**, isobutyraldehyde (0.0870 g, 1.21 mmol, 3.0 eq.) was used instead of benzaldehyde to afford the desired product as a white solid (0.571 g, 0.219 mmol, 55%).

Rf = 0.20 (hexane:AcOEt = 3:1).

m.p.: 139.5 °C.

^{1}H NMR: δ 0.94 (d, J = 7.5 Hz, 3H), 1.05 (d, J = 7.5 Hz, 3H), 1.81 (s, 3H), 2.60 (sept, J = 7.5 Hz, 1H), 5.21 (brs, 1H), 6.85-6.90 (m, 2H), 7.22 (d, J = 9.0 Hz, 2H)

^{13}C NMR: δ 16.6 (q, J = 2.4 Hz), 20.9, 21.2, 36.5, 60.7 (q, J = 23.7 Hz), 115.8, 124.7, 125.7 (q, J =

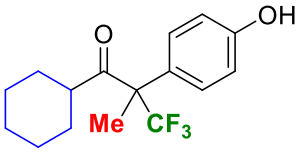
283.8 Hz), 129.5, 156.4, 210.8.

^{19}F NMR: δ –71.94 (s).

IR (KBr) ν 3459, 3384, 2974, 2938, 2880, 1705, 1603, 1517, 1279, 1151 cm^{-1}.

HRMS (FAB+, *m/z*): [M]$^{+}$ Calcd for $C_{13}H_{15}F_3O_2$, 260.1024; Found, 260.1021.

1-Cyclohexyl-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methylpropan-1-one (3au)



Following to **GP1**, cyclohexanecarboxaldehyde (0.1346 g, 1.20 mmol, 3.0 eq.) was used instead of benzaldehyde, and the crude product was purified by column chromatography (hexane:AcOEt = 3:1) and the resultant solid was washed with hexane to afford the desired product as a white solid basically as a pure condition (0.0463 g, 0.154 mmol, 39%).

m.p.: 141.3 °C.

Rf = 0.20 (hexane:AcOEt = 3:1).

^{1}H NMR: δ 0.91–1.27 (m, 3H), 1.35–1.72 (m, 7H), 1.80 (tt, *J* = 11.1, 3.6 Hz, 1H), 5.26 (brs, 1H), 6.86-6.91 (m, 2H), 7.23 (d, *J* = 8.7 Hz, 2H).

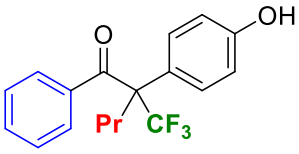
^{13}C NMR: δ 16.6 (q, *J* = 2.5 Hz), 25.26, 25.33, 25.4, 30.5, 31.2, 47.1, 60.6 (q, *J* = 23.0 Hz), 115.7, 124.8, 125.7 (q, *J* = 283.9 Hz), 129.5, 156.2, 209.1.

^{19}F NMR: δ –71.98 (s).

IR (KBr) ν 3415, 2998, 2937, 1893, 1702, 1614, 1593, 1517, 1448, 1162 cm^{-1}.

HRMS (FAB+, *m/z*): [M]$^{+}$ Calcd for $C_{16}H_{19}F_3O_2$, 300.1337; Found, 300.1350.

2-(4-Hydroxyphenyl)-1-phenyl-2-(trifluoromethyl)-1-pentanone. (3ba)



Following to **GP1**, **2b** (0.1792 g, 0.3995 mmol) was used instead of **2a** and the reaction mixture was stirred at 50 °C for 4 h to afford the desired product as a white solid (0.0442 g, 0. 137 mmol, 32%).

Rf = 0.20 (hexane:AcOEt = 3:1).

m.p.: 148.9 °C.

^{1}H NMR: δ 0.77 (t, *J* = 7.2 Hz, 3H), 0.97-1.11 (m, 1H), 1.54-1.67 (m, 1H), 2.29 (tm, *J* = 13.2 Hz, 1H), 2.59 (ddd, *J* = 14.7 , 12.9, 4.8 Hz, 1H), 4.80 (brs, 1H), 6.86 (d, *J* = 8.7 Hz , 2H), 7.23-7.29 (m, 4H), 7.40-7.48 (m, 3H).

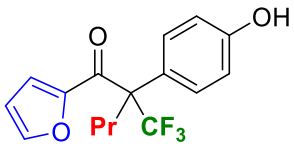
^{13}C NMR: δ 14.7, 18.1 (q, *J* = 2.5 Hz), 35.7, 62.9 (q, *J* = 21.8 Hz), 115.9, 125.9 (q, *J* = 282.8 Hz), 127.4, 128.2, 129.5, 129.9,132.7, 135.6, 156.2, 195.9.

^{19}F NMR: δ –69.65 (s).

IR (KBr) ν 3393, 3071, 2969, 2881, 1667, 1602, 1515, 1448, 1280, 1224 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{18}H_{18}F_3O_2$, 323.1259; Found, 323.1252.

1-(2-Franyl)-2-(4-hydroxyphenyl)-2-(trifluoromethyl)-1-pentanone. (3bk)



Following to **GP1**, **2b** (0.1792 g, 0.3995 mmol) and furfural (0.0576 g, 0.599 mmol, 1.5 eq.) were used instead of benzaldehyde and **2a** and the reaction mixture was stirred at 50 °C for 4 h to afford the desired product as a brown solid (0.0368 g, 0.130 mmol, 32%).

Rf = 0.23 (hexane:AcOEt = 2:1).

m.p.: 143.2 °C.

^{1}H NMR: δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.10-1.21 (m, 1H), 1.59-1.72 (m, 1H), 2.41-2.59 (m, 2H), 4.97 (brs, 1H), 6.36 (dd, *J* = 3.6, 1.5 Hz, 1H), 6.74 (dd, *J* = 3.6, 0.6 Hz, 1H), 6.79-6.84 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 3.6, 0.6 Hz, 1H).

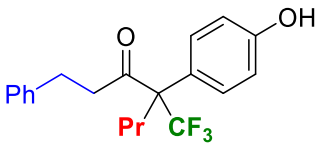
^{13}C NMR: δ 14.9, 19.1 (q, *J* = 2.5 Hz), 35.6, 62.8 (q, *J* = 22.0 Hz), 112.8, 116.2, 120.2, 126.9, 127.1 (q, *J* = 290.8 Hz), 130.6, 147.6, 151.7, 158.5, 184.2.

^{19}F NMR: δ –69.65 (s).

IR (KBr) ν 3375, 3144, 2970, 2881, 1657, 1517, 1453, 1275, 1228, 1165 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{16}H_{16}F_3O_3$, 313.1052; Found, 313.1047.

4-(4-Hydroxyphenyl)-1-phenyl-4-(trifluoromethyl)-3-heptanone (3bq)



Following to **GP1**, 3-phenylpropionaldehyde (0.0806 g, 0.600 mmol, 1.5 eq.) and **2b** (0.1792 g, 0.3995 mmol) were used instead of benzaldehyde and **2a** and the reaction mixture was stirred at 50 °C for 6 h to afford the desired product as a white solid (0.1258 g, 0.3590 mmol, 90%).

Rf = 0.37 (hexane:AcOEt = 3:1).

m.p.: 147.1 °C.

^{1}H NMR: δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.10-1.29 (m, 1H), 1.38-1.53 (m, 1H), 2.03 (brt, *J* = 12.9 Hz, 2H),

2.28 (t, J = 12.9 Hz, 1H), 2.29 (t, J = 12.9 Hz, 1H), 2.57 (dt, J = 17.7, 7.8 Hz, 1H), 2.64 (dt, J = 17.4, 7.8 Hz, 1H), 2.89 (t, J = 7.8 Hz, 2H), 4.99 (brs, 1H), 6.76 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 6.9 Hz, 2H) 7.15-7.24 (m, 3H).

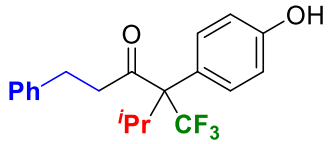
^{13}C NMR (acetone-d_6): δ 15.0, 19.0 (q, J = 2.5 Hz), 30.3, 34.7, 40.9 (q, J = 1.9 Hz), 64.5 (q, J = 22.4 Hz), 116.3, 128.2, 126.7, 127.1 (q, J = 284.2 Hz), 129.0, 129.3, 130.4, 141.7, 158.4, 204.1.

^{19}F NMR: δ –67.11 (s).

IR (KBr) ν 3477, 3026, 2971, 2881, 2880, 1715, 1603, 1513, 1219, 1172 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{20}H_{22}F_3O_2$, 351.1572; Found, 351.1557.

4-(4-Hydroxyphenyl)-5-methyl-1-phenyl-4-(trifluoromethyl)-3-hexanone (3cq)



Following to **GP1**, 3-phenylpropionaldehyde (0.0806 g, 0.600 mmol, 1.5 eq.) and **2c** (0.1792 g, 0.3995 mmol) were used instead of benzaldehyde and **2a** and the reaction mixture was stirred at 50 °C for 6 h to afford the desired product as a white solid (0.1004 g, 0.2865 mmol, 72%).

Rf = 0.40 (hexane:AcOEt = 3:1).

m.p.: 97.9 °C.

^{1}H NMR: δ 0.84 (d, J = 6.9 Hz, 3H), 1.07 (d, J = 6.9 Hz, 3H), 2.60 (sept, J = 6.6 Hz, 1H), 2.71 (t, J = 6.9 Hz, 2H), 2.85 (dt, J = 14.1, 7.8 Hz, 1H), 2.92 (dt, J = 14.4, 7.8 Hz, 1H), 4.97 (brs, 1H), 6.71-6.78 (m, 2H), 6.89 (d, J = 8.4 Hz, 2H), 7.07-7.13 (m, 2H) 7.14-7.26 (m, 3H).

^{13}C NMR: δ 18.7, 19.4, 30.0, 33.5, 41.9, 68.1 (q, J = 22.9 Hz), 115.7, 126.1, 126.9 (q, J = 290.8 Hz), 127.0, 128.3, 128.5, 128.8, 140.5, 155.0, 203.3.

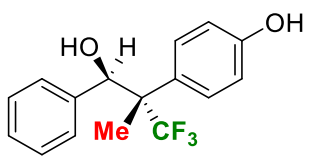
^{19}F NMR: δ –69.65 (s).

IR (KBr) ν 3421, 3029, 2991, 2945, 1707, 1606, 1516, 1448, 1274, 1126 cm^{-1}.

HRMS (FAB+, *m/z*): $[M+H]^+$ Calcd for $C_{20}H_{22}F_3O_2$, 351.1572; Found, 351.1586.

Synthetic application of 3a

(1*R, 2*S**)-3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-pheny-1-propanol (6aa-major)**



Reduction with DIBAL

To a two-necked round-bottomed flask were added **3aa** (0.1177 g, 0.4000 mmol) and CH_2Cl_2 (10 mL), where DIBAL (a 1.0 *M* hexane solution, 1.2 mL, 1.2 mmol, 3.0 eq.) was introduced slowly at –80 °C, and the mixture was stirred for 3 h at the same temperature. The reaction mixture was quenched with 1 *M* HCl aq. and extracted with CH_2Cl_2 three times. After usual workup, the crude product was purified by column chromatography (hexane:AcOEt = 2:1) to successfully separate the desired stereoisomeric products both as a white solid (major product (0.0599 g, 0.202 mmol, 50%), minor product (0.0265 g, 0.089 mmol, 22%)).

Reduction with BuLi (**GP2**)

To a two-necked round-bottomed flask were added **3aa** (0.1177 g, 0.4000 mmol) and Et_2O (4 mL), where BuLi (a 2.80 *M* hexane solution, 0.42 mL, 1.18 mmol, 1.2 eq.) was introduced slowly at –80 °C, and the mixture was stirred for 1 h at the same temperature. Then, the mixture was warmed up to 30 °C. After stirring for 1 h at the same temperature, the reaction mixture was quenched with sat. NH_4Cl aq. and extracted with AcOEt three times. After usual workup, the crude product was purified by column chromatography (hexane:AcOEt = 2:1) to stereospecifically give the desired product (the same as the major compound of the DIBAL reduction) as a white solid (0.0863 g, 0.291 mmol, 73%).

The major compound

Rf = 0.30 (hexane:AcOEt = 2:1).

m.p.: 132.3 °C.

^{1}H NMR: δ 1.45 (s, 3H), 1.90 (s, 1H), 5.00 (brs, 1H), 5.31 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.18-7.19 (m, 2H), 7.28-7.30 (m, 3H), 7.52 (d, *J* = 8.7 Hz, 2H).

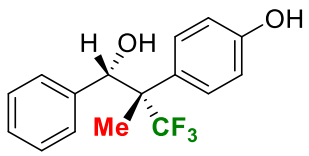
^{13}C NMR (acetone-d_6) : δ 16.4 (q, *J* = 2.5 Hz), 52.7 (q, *J* = 21.7 Hz), 76.9, 115.3, 127.8, 128.0. 128.3, 129.2, 131.03, 131.01 (q, *J* = 284.3 Hz) 141.9, 157.8.

^{19}F NMR: δ –69.95 (s).

IR (KBr) ν 3391, 3275, 3034, 2964, 2930, 1685, 1614, 1516, 1267, 1162 cm^{-1}.

HRMS (FAB+, *m/z*): $[M]^+$ Calcd for $C_{16}H_{15}F_3O_2$, 296.1024; Found, 296.1003.

(1*S, 2*S**)-3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-pheny-1-propanol (6aa-minor)**



Rf = 0.40 (hexane:AcOEt = 2:1).

m.p.: 127.4 °C.

^{1}H NMR: δ 1.50 (s, 3H), 2.22 (d, *J* = 3.3 Hz, 1H), 4.85 (brs, 1H), 5.45 (d, *J* = 3.0 Hz, 1H), 6.73-6.78

(m, 2H), 6.87 (d, J = 6.6 Hz, 2H), 7.07-7.15 (m, 3H), 7.19 (d, J = 8.7 Hz, 2H).

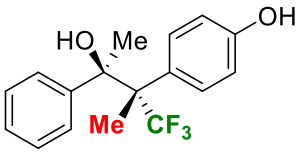
^{13}C NMR (acetone-d_6) : δ 12.6 (q, J = 3.1 Hz), 53.4 (q, J = 22.4 Hz), 76.9, 115.6, 127.6, 127.7. 128.6, 129.1, 129.6 (q, J = 285.6 Hz), 129.8 (q, J = 1.9 Hz), 141.5, 157.7.

^{19}F NMR: δ –68.56 (s)

IR (KBr) ν 3510, 3297, 3035, 2941, 2902, 1610, 1596, 1516, 1261, 1147 cm^{-1}.

HRMS (FAB+, *m/z*): $[M]^-$ Calcd for $C_{16}H_{15}F_3O_2$, 296.1024; Found, 296.1011.

(2*R, 3*S**)-4,4,4-Trifluoro-2-(4-hydroxyphenyl)-2,3-dimethyl-1-pheny1butanol (7aa)**



Following to **GP2**, MeLi-LiBr (a 3.0 *M* Et_2O solution, 0.40 mL, 1.2 mmol, 3.0 eq.) was used instead of BuLi. The mixture was purified by column chromatography (hexane:AcOEt = 2:1) to give a product as a solid with some contamination, and washing with hexane gave the desired product as a white solid basically as a pure condition (0.1013 g, 0.3264 mmol, 82%).

Rf = 0.37 (hexane:AcOEt = 2:1).

m.p.: 138.6 °C.

^{1}H NMR: δ 1.48 (s, 3H), 1.83 (q, J = 1.5 Hz, 3H), 2.07 (s, 1H), 4.92 (brs, 1H), 6.70-6.76 (m, 2H), 7.01-7.05 (m, 2H), 7.17-7.26 (m, 5H).

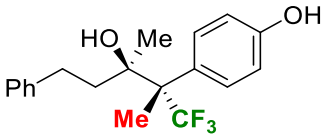
^{13}C NMR: δ 18.3 (q, J = 3.7 Hz), 27.3 (q, J = 2.5 Hz), 56.3 (q, J = 21.2 Hz), 77.1, 114.5, 127.2, 127.3, 128.5, 129.9 (q, J = 286.3 Hz), 131.5 (q, J = 1.8 Hz), 146.2, 157.3.

^{19}F NMR: δ –63.18 (s).

IR (KBr) ν 3468, 3327, 3079, 3015, 2987, 1614, 1590, 1517, 1169, 1144 cm^{-1}.

HRMS (FAB–, *m/z*): $[M–H]^-$ Calcd for $C_{17}H_{16}F_3O_2$, 309.1102; Found, 309.1074.

(2*S, 3*R**)-1,1,1-Trifluoro-2-(4-hydroxyphenyl)-2,3-dimethyl-5-phenyl-3-pentanol (7aq)**



Following to **GP2**, MeLi-LiBr (a 3.0 *M* Et_2O solution, 0.40 ml, 1.2 mmol, 3.0 eq.) and **3aq** (0.1289 g, 0.3999 mmol) were used instead of BuLi and **3aa** to afford the desired product as a white solid (0.0568 g, 0.168 mmol, 42%).

Moreover, **3aq** was recovered (0.0621 g, 0.193 mmol, 48%).

Rf = 0.20 (hexane:AcOEt = 2:1).

m.p.: 119.6 °C.

^{1}H NMR: δ 1.39 (s, 3H), 1.45 (s, 1H), 1.62 (s, 3H), 2.56-2.75 (m, 2H), 6.82 (d, *J* = 9.0 Hz, 2 H), 7.04-7.08 (m, 4H), 7.14-7.26 (m, 3H). 7.45 (d, *J* = 8.1 Hz, 2 H)

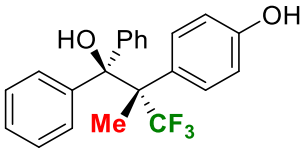
^{13}C NMR: δ 17.3 (q, *J* = 0.8 Hz), 23.1 (q, *J* = 2.5 Hz), 29.8, 38.9 (q, *J* = 1.8 Hz), 56.2 (q, *J* = 21.8 Hz), 75.5, 114.9, 125.8, 127.3, 128.5, 128.7 (q, *J* = 286.3 Hz), 130.3, 130.6, 142.2, 155.0.

^{19}F NMR: δ –63.18 (s).

IR (KBr) ν 3605, 3363, 3032, 2975, 2928, 1612, 1515, 1455, 1254, 1144 cm^{-1}.

HRMS (FAB–, *m/z*): [M]$^-$ Calcd for $C_{19}H_{21}F_3O_2$, 333.1494; Found, 333.1497.

3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1,1-dipheny-1-propanol (8aa) (GP3)



To a two-necked round-bottomed flask were added bromobenzene (0.2071 g, 1.319 mmol, 3.3 eq.) and Et_2O (1.2 mL), where BuLi (a 2.80 *M* hexane solution, 0.42 mL, 1.2 mmol, 3.0 eq.) was introduced slowly at 0 °C, and the mixture was stirred for 1 h at the same temperature. To this mixture was added a solution of **1a** (0.1178 g, 0.4003 mmol) in Et_2O (2.8 mL) via a syringe at –80 °C and the mixture was stirred for 1 h at the same temperature. Then, the mixture was warmed up to 30 °C. After, stirring for 2 h at the same temperature and the reaction mixture was quenched with sat. NH_4Cl aq. and extracted with AcOEt three times. After usual workup, the crude product was purified by column chromatography (hexane:AcOEt = 2:1) to give the desired product as a colorless oil (0.1057 g, 0.2838 mmol, 71%).

Rf = 0.37 (hexane:AcOEt = 2:1).

m.p.: 146.6 °C.

^{1}H NMR: δ 1.73 (s, 3H), 2.92 (s, 1H), 4.84 (s, 1H), 6.67-6.72 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.16-7.19 (m, 2H), 7.26-7.33 (m, 6H), 7.46-7.50 (m, 2H).

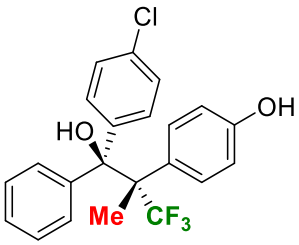
^{13}C NMR (acetone-d_6): δ 19.6, 57.9 (q, *J* = 21.1 Hz), 82.6, 114.6, 127.2, 127.4, 127.6, 127.8, 128.8, 129.4 (q, *J* = 285.2 Hz), 130.0, 132.4, 145.2, 146.2, 157.6.

^{19}F NMR: δ –63.23 (s).

IR (KBr) ν 3538, 3391, 3072, 3032, 2972, 1605, 1514, 1441, 1253, 1160 cm^{-1}.

HRMS (FAB+, *m/z*): [M]$^+$ Calcd for $C_{12}H_{19}F_3O_2$, 372.1337; Found, 372.1360.

(1*S, 2*S**)-1-(4-Chlorophenyl)-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-pheny-1-propanol (9aa)**



Following to **GP3**, 1-bromo-4-chlorobenzene (0.2529 g, 1.321 mmol, 3.3 eq.) was used instead of bromobenzene and the reaction mixture was stirred –80 °C for 1 h and then, the mixture was warmed up to 0 °C and stirred for 4 h at the same temperature to afford the desired product as a white solid (0.1336 g, 0.3370 mmol, 84%).

Rf = 0.20 (hexane:AcOEt = 4:1).

m.p.: 117.7 °C.

^{1}H NMR: δ 1.72 (s, 3H), 2.91 (s, 1H), 4.83 (brs, 1H), 6.71 (d, *J* = 9.0 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 7.17-7.29 (m, 7H), 7.41 (d, *J* = 8.7 Hz, 2H).

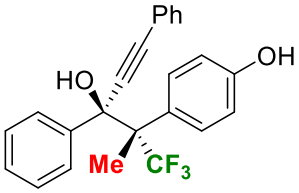
^{13}C NMR: δ 19.4, 57.0 (q, *J* = 21.7 Hz), 81.4, 114.3,127.2, 127.4, 127.5, 128.1 (q, *J* = 287.0 Hz), 128.4, 128.6, 129.5, 131.5, 133.2, 142.3, 143.1, 155.1.

^{19}F NMR: δ –63.32 (s).

IR (KBr) ν 3565, 3392, 3064, 3041, 3015, 1652, 1591, 1516, 1281, 1000 cm^{-1}.

HRMS (FAB–, *m/z*): $[M–H]^-$ Calcd for $C_{18}H_{17}F_3O_2Cl$, 405.0869; Found, 405.0842.

(3*S, 4*S**)-5,5,5-Trifluoro-4-(4-hydroxyphenyl)-4-methyl-3-phenyl-1-phenylpent-1-yn-3-ol (10aa)**



Following to **GP3**, ethynylbenzene (0.1298 g, 1.271 mmol, 3.2 eq.) was used instead of bromobenzene to afford the desired product as a pale brown oil as an inseparable diastereomeric mixture (0.1336 g, 0.3370 mmol, *dr* = 92:8, 84%).

Rf = 0.33 (hexane:AcOEt = 2:1).

The major compound

^{1}H NMR: δ 1.74 (s, 3H), 2.92 (s, 1H), 4.85 (s, 1H), 6.67-6.72 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.16-7.19 (m, 2H), 7.25-7.33 (m, 6H), 7.46-7.50 (m, 2H).

^{13}C NMR (acetone-d_6): δ 18.5 (q, *J* = 2.3 Hz), 57.0 (q, *J* = 21.8 Hz), 76.8, 87.6, 92.1, 114.6, 123.5, 127.2, 128.3, 129.1,129.2 (q, *J* = 280.1 Hz) 129.3, 129.4, 130.4, 131.8, 132.1, 142.5, 157.7.

^{19}F NMR: δ –64.16 (s).

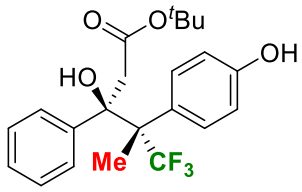
The minor compound

^{19}F NMR: δ –63.78 (s).

IR ($CHCl_3$) ν 3585, 3393, 3088, 3036, 3008, 1615, 1597, 1517, 1267, 1152 cm^{-1}.

HRMS (FAB–, *m/z*): $[M–H]^-$ Calcd for $C_{24}H_{18}F_3O_2$, 395.1259; Found, 395.1269.

(3*S, 4*S**)-*tert*-Butyl 5,5,5-trifluoro-3-hydroxyl-4-(4-hydroxyphenyl)-4-methyl-3-phenylpentanoate (11aa)**



A solution of **3aa** (0.1177 g, 0.4000 mmol) in THF (2 mL) was added to a mixture containing the enolate from *t*-butyl acetate (0.1559 g, 1.342 mmol, 3.4 eq.) and LDA (prepared from diisopropylamine (0.19 mL, 1.3 mmol, 3.4 eq.) and BuLi (a 2.80 *M* hexane solution, 0.43 mL, 1.2 mmol, 3.0 eq.)) in THF (2 mL) at –80 °C for 1 h), and then the mixture was stirred for 1 h at that temperature. Then, the mixture was warmed up to 30 °C and stirring was continued for 2 h at the same temperature. After quenching with sat. NH_4Cl aq., the reaction mixture was extracted with AcOEt three times. After usual workup, the crude product was purified by column chromatography (hexane:AcOEt = 2:1) to give the desired product as a pale brown oil as an inseparable diastereomeric mixture (0.1416 g, 0.3450 mmol, *dr* = 93:7, 86%).

Rf = 0.40 (hexane:AcOEt = 2:1).

The major compound

^{1}H NMR: δ 1.14 (s, 9H), 1.56 (s, 3H), 1.60 (s, 1H), 2.75 (d, *J* = 15.6 Hz, 1H), 3.36 (d, *J* = 15.6 Hz, 1H) 4.80 (s, 1H), 6.73 (d, *J* = 9.0 Hz, 2H), 7.18 (s, 5H), 7.29 (d, *J* = 9.3 Hz, 2H).

^{13}C NMR: δ 17.2 (q, *J* = 3.7 Hz), 27.5, 43.4, 55.9 (q, *J* = 21.7 Hz), 77.7, 82.5, 114.0, 127.0, 127.3, 127.8, 128.0, 128.2 (q, *J* = 286.3 Hz), 130.8, 142.0, 155.0, 172.3.

^{19}F NMR: δ –63.00 (s).

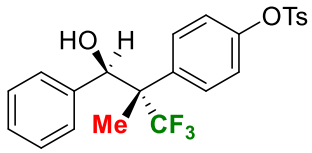
The minor compound

^{19}F NMR: δ –62.81 (s).

IR ($CHCl_3$) ν 3592, 3436, 3025, 3010, 2982, 1704, 1616, 1518, 1256, 1152 cm^{-1}.

HRMS (FAB+, *m/z*): $[M]^+$ Calcd for $C_{22}H_{26}F_3O_4$, 411.1783; Found, 411.1788.

(1*R, 2*S**)-3,3,3-Trifluoro-2-methyl-1-pheny-2-[4-{(toluenesulfonyl)oxy}phenyl]-1-propanol (12aa)**



To a test tube under an argon atmosphere were introduced **6aa** (0.0561g, 0.189 mmol), DMAP (0.0269 g, 0.220 mmol, 1.2 eq.), and 4.0 mL of CH_2Cl_2, where TsCl (0.0420 g, 0.220 mmol, 1.2 eq.) was added at 0 °C. This reaction mixture was stirred for 3 h at 30 °C. After quenching with sat. NH_4Cl aq., the reaction mixture was extracted three times with the mixture of CH_2Cl_2 and the combined organic phase was dried over anhydrous Na_2SO_4. After filtration, evaporation of the volatiles afforded a crude material which was purified by silica gel column chromatography using AcOEt:hexane = 2:1 to furnish 0.0685 g (0.152 mmol) of the desired product **12aa** in 80% yield as a white solid.

m.p.: 131.8 °C.

^{1}H NMR: δ 1.44 (s, 3H), 1.92 (d, J = 3.0 Hz, 1H), 2.47 (s, 3H), 5.27 (d, J = 3.0 Hz, 1H), 7.02 (d, J = 9.0 Hz, 2H), 7.05 (d, J = 9.0 Hz, 2H), 7.24-7.29 (m, 3H), 7.33 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 7.5 Hz, 2H).

^{13}C NMR: δ 15.7 (q, J = 2.6 Hz), 21.7, 52.6 (q, J = 23.0 Hz), 76.4, 121.8, 127.4 (q, J = 282.8 Hz), 127.7, 127.9, 128.3, 128.4, 129.7, 130.1, 132.2, 134.7, 138.9, 145.5, 149.3.

^{19}F NMR: δ –69.85 (s).

IR (KBr) ν 3570, 3066, 2990, 2900, 1920, 1597, 1505, 1368, 1186, 1159 cm^{-1}.

HRMS (FAB–, *m/z*): $[M]^-$ Calcd for $C_{23}H_{21}F_3O_4S$, 450.1113; Found, 450.1124.

X-Ray crystallographic data of the compounds

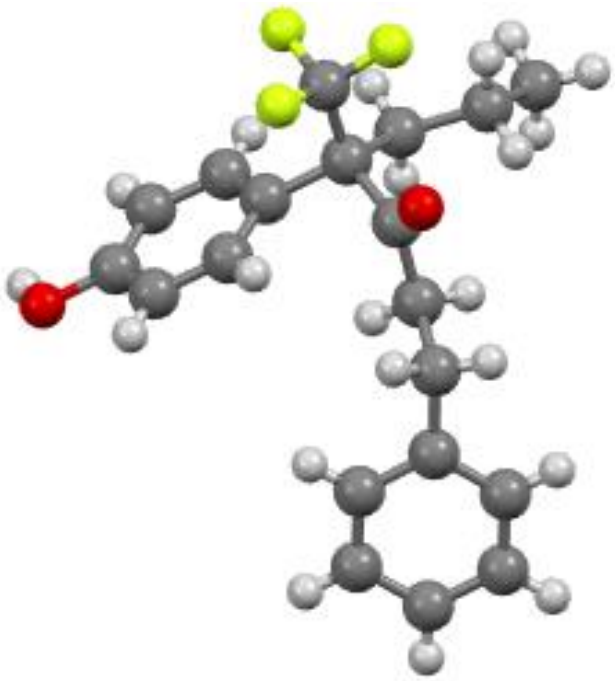


Table 1. Crystal data and structure refinement for C:.

Identification code	**3bq**	
Empirical formula	C20 H21 F3 O2	
Formula weight	350.37	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.8717(3) Å	α= 90°.
	b = 10.7087(3) Å	β= 95.029(2)°.
	c = 15.1761(4) Å	γ = 90°.
Volume	1760.03(8) $Å^3$	
Z	4	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	736	
Crystal size	0.130 x 0.130 x 0.110 mm^3	
Theta range for data collection	2.675 to 25.490°.	

Index ranges	-13<=h<=13, -12<=k<=12, -18<=l<=18
Reflections collected	20387
Independent reflections	3265 [R(int) = 0.0239]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.75069
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3265 / 0 / 228
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0890
R indices (all data)	R1 = 0.0365, wR2 = 0.0915
Extinction coefficient	n/a
Largest diff. peak and hole	0.272 and -0.186 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for C:. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1098(1)	5434(2)	4268(1)	46(1)
C(2)	1994(1)	5863(2)	3635(1)	38(1)
C(3)	3170(1)	6427(1)	4092(1)	25(1)
C(4)	4175(1)	6835(1)	3480(1)	21(1)
C(5)	3755(1)	8004(1)	2951(1)	28(1)
F(1)	4603(1)	8399(1)	2425(1)	38(1)
F(2)	3546(1)	8959(1)	3488(1)	42(1)
F(3)	2704(1)	7848(1)	2424(1)	37(1)
C(6)	5402(1)	7168(1)	4012(1)	21(1)
C(7)	6521(1)	7002(1)	3640(1)	24(1)
C(8)	7636(1)	7303(1)	4103(1)	27(1)
C(9)	7651(1)	7807(1)	4950(1)	27(1)
C(10)	6547(1)	8007(1)	5322(1)	28(1)
C(11)	5435(1)	7683(1)	4857(1)	25(1)
O(1)	8777(1)	8101(1)	5364(1)	40(1)
C(12)	4378(1)	5740(1)	2845(1)	22(1)
O(2)	4123(1)	5817(1)	2053(1)	31(1)
C(13)	4892(1)	4543(1)	3256(1)	24(1)
C(14)	5548(1)	3745(1)	2601(1)	30(1)
C(15)	6337(1)	2742(1)	3063(1)	25(1)
C(16)	5938(1)	1512(1)	3106(1)	30(1)
C(17)	6664(1)	610(1)	3556(1)	38(1)
C(18)	7807(1)	926(1)	3965(1)	38(1)
C(19)	8223(1)	2142(1)	3919(1)	37(1)
C(20)	7493(1)	3043(1)	3475(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for C:.

C(1)-C(2)	1.499(2)
C(1)-H(1)	0.9800
C(1)-H(2)	0.9800
C(1)-H(3)	0.9800
C(2)-C(3)	1.5249(17)
C(2)-H(4)	0.9900
C(2)-H(5)	0.9900
C(3)-C(4)	1.5583(16)
C(3)-H(6)	0.9900
C(3)-H(7)	0.9900
C(4)-C(5)	1.5343(16)
C(4)-C(6)	1.5394(15)
C(4)-C(12)	1.5464(16)
C(5)-F(1)	1.3392(16)
C(5)-F(2)	1.3405(15)
C(5)-F(3)	1.3458(14)
C(6)-C(11)	1.3937(16)
C(6)-C(7)	1.3962(17)
C(7)-C(8)	1.3851(17)
C(7)-H(8)	0.9500
C(8)-C(9)	1.3921(18)
C(8)-H(9)	0.9500
C(9)-O(1)	1.3628(15)
C(9)-C(10)	1.3871(19)
C(10)-C(11)	1.3897(18)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
O(1)-H(12)	0.8400
C(12)-O(2)	1.2120(14)
C(12)-C(13)	1.5105(16)
C(13)-C(14)	1.5328(17)
C(13)-H(13)	0.9900
C(13)-H(14)	0.9900
C(14)-C(15)	1.5088(17)

C(14)-H(15)	0.9900
C(14)-H(16)	0.9900
C(15)-C(16)	1.3903(19)
C(15)-C(20)	1.3913(18)
C(16)-C(17)	1.388(2)
C(16)-H(17)	0.9500
C(17)-C(18)	1.382(2)
C(17)-H(18)	0.9500
C(18)-C(19)	1.382(2)
C(18)-H(19)	0.9500
C(19)-C(20)	1.386(2)
C(19)-H(20)	0.9500
C(20)-H(21)	0.9500

C(2)-C(1)-H(1)	109.5
C(2)-C(1)-H(2)	109.5
H(1)-C(1)-H(2)	109.5
C(2)-C(1)-H(3)	109.5
H(1)-C(1)-H(3)	109.5
H(2)-C(1)-H(3)	109.5
C(1)-C(2)-C(3)	113.32(12)
C(1)-C(2)-H(4)	108.9
C(3)-C(2)-H(4)	108.9
C(1)-C(2)-H(5)	108.9
C(3)-C(2)-H(5)	108.9
H(4)-C(2)-H(5)	107.7
C(2)-C(3)-C(4)	116.37(10)
C(2)-C(3)-H(6)	108.2
C(4)-C(3)-H(6)	108.2
C(2)-C(3)-H(7)	108.2
C(4)-C(3)-H(7)	108.2
H(6)-C(3)-H(7)	107.3
C(5)-C(4)-C(6)	106.90(9)
C(5)-C(4)-C(12)	110.16(9)
C(6)-C(4)-C(12)	109.79(9)
C(5)-C(4)-C(3)	110.39(10)

C(6)-C(4)-C(3)	111.90(9)
C(12)-C(4)-C(3)	107.72(9)
F(1)-C(5)-F(2)	106.44(10)
F(1)-C(5)-F(3)	106.16(10)
F(2)-C(5)-F(3)	105.97(10)
F(1)-C(5)-C(4)	112.37(10)
F(2)-C(5)-C(4)	111.27(10)
F(3)-C(5)-C(4)	114.09(10)
C(11)-C(6)-C(7)	118.02(11)
C(11)-C(6)-C(4)	121.69(10)
C(7)-C(6)-C(4)	120.25(10)
C(8)-C(7)-C(6)	121.31(11)
C(8)-C(7)-H(8)	119.3
C(6)-C(7)-H(8)	119.3
C(7)-C(8)-C(9)	119.84(11)
C(7)-C(8)-H(9)	120.1
C(9)-C(8)-H(9)	120.1
O(1)-C(9)-C(10)	123.39(11)
O(1)-C(9)-C(8)	116.91(11)
C(10)-C(9)-C(8)	119.69(11)
C(9)-C(10)-C(11)	119.99(11)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(10)-C(11)-C(6)	121.12(11)
C(10)-C(11)-H(11)	119.4
C(6)-C(11)-H(11)	119.4
C(9)-O(1)-H(12)	109.5
O(2)-C(12)-C(13)	120.79(11)
O(2)-C(12)-C(4)	122.20(11)
C(13)-C(12)-C(4)	117.00(9)
C(12)-C(13)-C(14)	112.42(10)
C(12)-C(13)-H(13)	109.1
C(14)-C(13)-H(13)	109.1
C(12)-C(13)-H(14)	109.1
C(14)-C(13)-H(14)	109.1
H(13)-C(13)-H(14)	107.9

C(15)-C(14)-C(13)	111.94(10)
C(15)-C(14)-H(15)	109.2
C(13)-C(14)-H(15)	109.2
C(15)-C(14)-H(16)	109.2
C(13)-C(14)-H(16)	109.2
H(15)-C(14)-H(16)	107.9
C(16)-C(15)-C(20)	118.13(12)
C(16)-C(15)-C(14)	121.98(12)
C(20)-C(15)-C(14)	119.88(12)
C(17)-C(16)-C(15)	121.08(12)
C(17)-C(16)-H(17)	119.5
C(15)-C(16)-H(17)	119.5
C(18)-C(17)-C(16)	120.04(13)
C(18)-C(17)-H(18)	120.0
C(16)-C(17)-H(18)	120.0
C(17)-C(18)-C(19)	119.57(13)
C(17)-C(18)-H(19)	120.2
C(19)-C(18)-H(19)	120.2
C(18)-C(19)-C(20)	120.27(13)
C(18)-C(19)-H(20)	119.9
C(20)-C(19)-H(20)	119.9
C(19)-C(20)-C(15)	120.90(13)
C(19)-C(20)-H(21)	119.5
C(15)-C(20)-H(21)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C:. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	35(1)	59(1)	45(1)	-8(1)	9(1)	-16(1)
C(2)	28(1)	55(1)	33(1)	-6(1)	2(1)	-11(1)
C(3)	22(1)	30(1)	22(1)	-2(1)	2(1)	1(1)
C(4)	21(1)	23(1)	19(1)	1(1)	-2(1)	2(1)
C(5)	28(1)	27(1)	28(1)	1(1)	-5(1)	3(1)
F(1)	38(1)	36(1)	38(1)	17(1)	-1(1)	-1(1)
F(2)	54(1)	27(1)	44(1)	-4(1)	-7(1)	14(1)
F(3)	31(1)	37(1)	40(1)	7(1)	-14(1)	6(1)
C(6)	23(1)	21(1)	18(1)	2(1)	-2(1)	1(1)
C(7)	26(1)	27(1)	18(1)	0(1)	0(1)	1(1)
C(8)	22(1)	35(1)	23(1)	-1(1)	1(1)	1(1)
C(9)	25(1)	33(1)	22(1)	1(1)	-6(1)	-2(1)
C(10)	32(1)	34(1)	18(1)	-4(1)	-1(1)	0(1)
C(11)	25(1)	30(1)	21(1)	-1(1)	2(1)	2(1)
O(1)	25(1)	64(1)	28(1)	-12(1)	-7(1)	-4(1)
C(12)	17(1)	27(1)	20(1)	1(1)	0(1)	-1(1)
O(2)	36(1)	36(1)	18(1)	0(1)	-5(1)	6(1)
C(13)	27(1)	24(1)	20(1)	1(1)	2(1)	1(1)
C(14)	35(1)	31(1)	23(1)	0(1)	3(1)	8(1)
C(15)	26(1)	30(1)	20(1)	-3(1)	6(1)	5(1)
C(16)	28(1)	32(1)	31(1)	-4(1)	1(1)	0(1)
C(17)	43(1)	28(1)	42(1)	1(1)	3(1)	4(1)
C(18)	41(1)	40(1)	31(1)	0(1)	-1(1)	18(1)
C(19)	26(1)	50(1)	34(1)	-12(1)	-3(1)	8(1)
C(20)	30(1)	32(1)	35(1)	-7(1)	4(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for C:.

	x	y	z	U(eq)
H(1)	1500	4821	4678	69
H(2)	381	5049	3938	69
H(3)	828	6151	4603	69
H(4)	1585	6493	3232	46
H(5)	2218	5144	3272	46
H(6)	3542	5809	4521	30
H(7)	2938	7166	4433	30
H(8)	6517	6676	3058	28
H(9)	8389	7167	3844	32
H(10)	6552	8366	5895	34
H(11)	4684	7815	5120	30
H(12)	8686	8395	5867	60
H(13)	4209	4053	3475	28
H(14)	5482	4749	3769	28
H(15)	4923	3351	2175	36
H(16)	6073	4290	2264	36
H(17)	5156	1285	2823	36
H(18)	6374	-225	3583	45
H(19)	8304	311	4276	45
H(20)	9012	2361	4194	45
H(21)	7786	3877	3451	39

Table 6. Torsion angles [°] for C:.

C(1)-C(2)-C(3)-C(4)	177.06(13)
C(2)-C(3)-C(4)-C(5)	71.32(14)
C(2)-C(3)-C(4)-C(6)	-169.76(11)
C(2)-C(3)-C(4)-C(12)	-49.00(14)
C(6)-C(4)-C(5)-F(1)	57.06(13)
C(12)-C(4)-C(5)-F(1)	-62.18(13)
C(3)-C(4)-C(5)-F(1)	178.98(10)
C(6)-C(4)-C(5)-F(2)	-62.20(13)
C(12)-C(4)-C(5)-F(2)	178.57(10)
C(3)-C(4)-C(5)-F(2)	59.73(13)
C(6)-C(4)-C(5)-F(3)	177.97(10)
C(12)-C(4)-C(5)-F(3)	58.74(13)
C(3)-C(4)-C(5)-F(3)	-60.10(13)
C(5)-C(4)-C(6)-C(11)	89.21(13)
C(12)-C(4)-C(6)-C(11)	-151.32(11)
C(3)-C(4)-C(6)-C(11)	-31.76(15)
C(5)-C(4)-C(6)-C(7)	-88.32(13)
C(12)-C(4)-C(6)-C(7)	31.15(14)
C(3)-C(4)-C(6)-C(7)	150.71(11)
C(11)-C(6)-C(7)-C(8)	1.87(18)
C(4)-C(6)-C(7)-C(8)	179.49(11)
C(6)-C(7)-C(8)-C(9)	-1.38(19)
C(7)-C(8)-C(9)-O(1)	-179.05(12)
C(7)-C(8)-C(9)-C(10)	-0.2(2)
O(1)-C(9)-C(10)-C(11)	180.00(12)
C(8)-C(9)-C(10)-C(11)	1.2(2)
C(9)-C(10)-C(11)-C(6)	-0.7(2)
C(7)-C(6)-C(11)-C(10)	-0.83(18)
C(4)-C(6)-C(11)-C(10)	-178.41(11)
C(5)-C(4)-C(12)-O(2)	-5.75(15)
C(6)-C(4)-C(12)-O(2)	-123.21(12)
C(3)-C(4)-C(12)-O(2)	114.71(12)
C(5)-C(4)-C(12)-C(13)	175.29(10)
C(6)-C(4)-C(12)-C(13)	57.83(13)

C(3)-C(4)-C(12)-C(13)	-64.25(12)
O(2)-C(12)-C(13)-C(14)	24.88(16)
C(4)-C(12)-C(13)-C(14)	-156.15(10)
C(12)-C(13)-C(14)-C(15)	164.96(10)
C(13)-C(14)-C(15)-C(16)	99.89(14)
C(13)-C(14)-C(15)-C(20)	-79.07(15)
C(20)-C(15)-C(16)-C(17)	0.81(19)
C(14)-C(15)-C(16)-C(17)	-178.17(12)
C(15)-C(16)-C(17)-C(18)	-0.5(2)
C(16)-C(17)-C(18)-C(19)	-0.3(2)
C(17)-C(18)-C(19)-C(20)	0.7(2)
C(18)-C(19)-C(20)-C(15)	-0.4(2)
C(16)-C(15)-C(20)-C(19)	-0.38(19)
C(14)-C(15)-C(20)-C(19)	178.62(12)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for C: [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(12)...O(2)#1	0.84	2.01	2.8083(13)	159.3

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,z+1/2

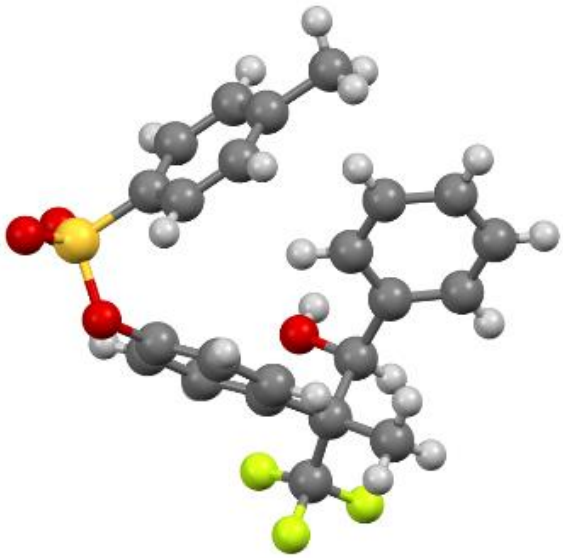


Table 1. Crystal data and structure refinement for C:.

Identification code	**12aa**	
Empirical formula	C23 H21 F3 O4 S	
Formula weight	450.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.8943(4) Å	α= 90°.
	b = 9.9889(3) Å	β= 99.237(3)°.
	c = 15.0537(4) Å	γ = 90°.
Volume	2062.19(10) $Å^3$	
Z	4	
Density (calculated)	1.451 Mg/m^3	
Absorption coefficient	0.212 mm^{-1}	
F(000)	936	
Crystal size	0.090 x 0.080 x 0.060 mm^3	
Theta range for data collection	2.457 to 25.499°.	
Index ranges	-16<=h<=16, -12<=k<=12, -18<=l<=18	
Reflections collected	24059	
Independent reflections	3833 [R(int) = 0.0270]	

Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.84658
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3833 / 0 / 283
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0890
R indices (all data)	R1 = 0.0352, wR2 = 0.0912
Extinction coefficient	n/a
Largest diff. peak and hole	0.256 and -0.354 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for C:. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	8347(1)	5623(1)	3897(1)	32(1)
F(1)	5175(1)	7053(1)	7290(1)	55(1)
F(2)	5033(1)	5825(1)	8425(1)	54(1)
O(1)	8601(1)	6085(1)	4927(1)	33(1)
F(3)	6410(1)	6744(1)	8322(1)	60(1)
O(2)	7426(1)	6177(1)	3510(1)	41(1)
O(3)	9207(1)	5977(1)	3549(1)	45(1)
O(4)	4596(1)	4975(1)	6136(1)	48(1)
C(1)	6670(1)	5260(1)	6738(1)	26(1)
C(2)	7926(1)	5810(1)	5520(1)	28(1)
C(3)	5244(1)	2767(1)	6552(1)	28(1)
C(4)	7573(1)	4626(1)	6799(1)	31(1)
C(5)	8230(1)	3878(2)	3955(1)	30(1)
C(6)	5954(1)	4871(1)	7377(1)	30(1)
C(7)	8202(1)	4889(2)	6189(1)	32(1)
C(8)	7053(1)	6498(1)	5449(1)	31(1)
C(9)	6427(1)	6210(1)	6056(1)	30(1)
C(10)	5731(1)	2575(2)	5823(1)	35(1)
C(11)	5022(1)	4158(2)	6865(1)	33(1)
C(12)	8040(1)	1110(2)	4021(1)	38(1)
C(13)	6424(1)	3939(2)	8144(1)	37(1)
C(14)	7368(1)	3282(2)	3560(1)	36(1)
C(15)	9006(1)	3112(2)	4376(1)	38(1)
C(16)	4970(1)	1653(2)	7004(1)	38(1)
C(17)	5640(1)	6132(2)	7839(1)	41(1)
C(18)	7284(1)	1902(2)	3593(1)	41(1)
C(19)	5710(1)	196(2)	6050(1)	47(1)
C(20)	5204(1)	371(2)	6754(1)	44(1)
C(21)	8902(1)	1742(2)	4409(1)	41(1)
C(22)	5968(1)	1288(2)	5584(1)	46(1)

C(23)	7918(2)	-382(2)	4067(2)	55(1)

Table 3. Bond lengths [Å] and angles [°] for C:.

S(1)-O(3)	1.4249(11)
S(1)-O(2)	1.4300(11)
S(1)-O(1)	1.6019(11)
S(1)-C(5)	1.7531(16)
F(1)-C(17)	1.333(2)
F(2)-C(17)	1.3499(18)
O(1)-C(2)	1.4221(16)
F(3)-C(17)	1.340(2)
O(4)-C(11)	1.4179(19)
O(4)-H(1)	0.8400
C(1)-C(4)	1.395(2)
C(1)-C(9)	1.399(2)
C(1)-C(6)	1.5410(19)
C(2)-C(7)	1.372(2)
C(2)-C(8)	1.384(2)
C(3)-C(16)	1.389(2)
C(3)-C(10)	1.391(2)
C(3)-C(11)	1.5142(19)
C(4)-C(7)	1.391(2)
C(4)-H(2)	0.9500
C(5)-C(14)	1.384(2)
C(5)-C(15)	1.389(2)
C(6)-C(17)	1.536(2)
C(6)-C(13)	1.543(2)
C(6)-C(11)	1.5675(19)
C(7)-H(3)	0.9500
C(8)-C(9)	1.389(2)
C(8)-H(4)	0.9500
C(9)-H(5)	0.9500
C(10)-C(22)	1.388(2)
C(10)-H(6)	0.9500
C(11)-H(7)	1.0000
C(12)-C(18)	1.388(2)
C(12)-C(21)	1.396(2)

C(12)-C(23)	1.503(2)
C(13)-H(8)	0.9800
C(13)-H(9)	0.9800
C(13)-H(10)	0.9800
C(14)-C(18)	1.386(2)
C(14)-H(11)	0.9500
C(15)-C(21)	1.378(2)
C(15)-H(12)	0.9500
C(16)-C(20)	1.388(2)
C(16)-H(13)	0.9500
C(18)-H(14)	0.9500
C(19)-C(20)	1.373(3)
C(19)-C(22)	1.375(3)
C(19)-H(15)	0.9500
C(20)-H(16)	0.9500
C(21)-H(17)	0.9500
C(22)-H(18)	0.9500
C(23)-H(19)	0.9800
C(23)-H(20)	0.9800
C(23)-H(21)	0.9800

O(3)-S(1)-O(2)	120.18(7)
O(3)-S(1)-O(1)	102.46(6)
O(2)-S(1)-O(1)	109.09(6)
O(3)-S(1)-C(5)	110.77(7)
O(2)-S(1)-C(5)	108.79(7)
O(1)-S(1)-C(5)	104.26(6)
C(2)-O(1)-S(1)	119.10(8)
C(11)-O(4)-H(1)	109.5
C(4)-C(1)-C(9)	117.73(13)
C(4)-C(1)-C(6)	120.50(12)
C(9)-C(1)-C(6)	121.71(12)
C(7)-C(2)-C(8)	121.92(13)
C(7)-C(2)-O(1)	117.09(12)
C(8)-C(2)-O(1)	120.90(12)
C(16)-C(3)-C(10)	118.78(14)

C(16)-C(3)-C(11)	119.80(13)
C(10)-C(3)-C(11)	121.41(13)
C(7)-C(4)-C(1)	121.61(13)
C(7)-C(4)-H(2)	119.2
C(1)-C(4)-H(2)	119.2
C(14)-C(5)-C(15)	120.92(15)
C(14)-C(5)-S(1)	119.09(11)
C(15)-C(5)-S(1)	119.97(11)
C(17)-C(6)-C(1)	109.51(11)
C(17)-C(6)-C(13)	105.82(12)
C(1)-C(6)-C(13)	112.41(12)
C(17)-C(6)-C(11)	108.88(12)
C(1)-C(6)-C(11)	111.87(11)
C(13)-C(6)-C(11)	108.12(12)
C(2)-C(7)-C(4)	118.68(13)
C(2)-C(7)-H(3)	120.7
C(4)-C(7)-H(3)	120.7
C(2)-C(8)-C(9)	118.64(13)
C(2)-C(8)-H(4)	120.7
C(9)-C(8)-H(4)	120.7
C(8)-C(9)-C(1)	121.38(13)
C(8)-C(9)-H(5)	119.3
C(1)-C(9)-H(5)	119.3
C(22)-C(10)-C(3)	119.86(14)
C(22)-C(10)-H(6)	120.1
C(3)-C(10)-H(6)	120.1
O(4)-C(11)-C(3)	111.58(13)
O(4)-C(11)-C(6)	109.21(12)
C(3)-C(11)-C(6)	112.13(11)
O(4)-C(11)-H(7)	107.9
C(3)-C(11)-H(7)	107.9
C(6)-C(11)-H(7)	107.9
C(18)-C(12)-C(21)	118.09(15)
C(18)-C(12)-C(23)	120.30(16)
C(21)-C(12)-C(23)	121.60(16)
C(6)-C(13)-H(8)	109.5

C(6)-C(13)-H(9)	109.5
H(8)-C(13)-H(9)	109.5
C(6)-C(13)-H(10)	109.5
H(8)-C(13)-H(10)	109.5
H(9)-C(13)-H(10)	109.5
C(5)-C(14)-C(18)	118.97(14)
C(5)-C(14)-H(11)	120.5
C(18)-C(14)-H(11)	120.5
C(21)-C(15)-C(5)	119.03(14)
C(21)-C(15)-H(12)	120.5
C(5)-C(15)-H(12)	120.5
C(20)-C(16)-C(3)	120.78(15)
C(20)-C(16)-H(13)	119.6
C(3)-C(16)-H(13)	119.6
F(1)-C(17)-F(3)	106.70(13)
F(1)-C(17)-F(2)	105.67(13)
F(3)-C(17)-F(2)	106.13(13)
F(1)-C(17)-C(6)	115.44(13)
F(3)-C(17)-C(6)	111.11(13)
F(2)-C(17)-C(6)	111.20(12)
C(14)-C(18)-C(12)	121.50(15)
C(14)-C(18)-H(14)	119.2
C(12)-C(18)-H(14)	119.2
C(20)-C(19)-C(22)	119.99(15)
C(20)-C(19)-H(15)	120.0
C(22)-C(19)-H(15)	120.0
C(19)-C(20)-C(16)	119.85(16)
C(19)-C(20)-H(16)	120.1
C(16)-C(20)-H(16)	120.1
C(15)-C(21)-C(12)	121.47(15)
C(15)-C(21)-H(17)	119.3
C(12)-C(21)-H(17)	119.3
C(19)-C(22)-C(10)	120.68(16)
C(19)-C(22)-H(18)	119.7
C(10)-C(22)-H(18)	119.7
C(12)-C(23)-H(19)	109.5

C(12)-C(23)-H(20)	109.5
H(19)-C(23)-H(20)	109.5
C(12)-C(23)-H(21)	109.5
H(19)-C(23)-H(21)	109.5
H(20)-C(23)-H(21)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C:. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	29(1)	38(1)	31(1)	4(1)	11(1)	-1(1)
F(1)	76(1)	30(1)	69(1)	-2(1)	37(1)	12(1)
F(2)	70(1)	42(1)	61(1)	-12(1)	43(1)	-7(1)
O(1)	27(1)	38(1)	35(1)	-2(1)	10(1)	-7(1)
F(3)	71(1)	47(1)	68(1)	-29(1)	25(1)	-24(1)
O(2)	40(1)	45(1)	37(1)	6(1)	5(1)	6(1)
O(3)	41(1)	53(1)	46(1)	6(1)	22(1)	-6(1)
O(4)	29(1)	35(1)	74(1)	2(1)	-6(1)	5(1)
C(1)	26(1)	24(1)	30(1)	-5(1)	6(1)	-4(1)
C(2)	26(1)	28(1)	30(1)	-4(1)	8(1)	-5(1)
C(3)	25(1)	27(1)	33(1)	-2(1)	3(1)	-3(1)
C(4)	30(1)	31(1)	32(1)	2(1)	5(1)	2(1)
C(5)	27(1)	38(1)	27(1)	-2(1)	10(1)	0(1)
C(6)	31(1)	26(1)	35(1)	-4(1)	11(1)	-3(1)
C(7)	25(1)	36(1)	35(1)	-1(1)	4(1)	3(1)
C(8)	32(1)	26(1)	33(1)	2(1)	6(1)	1(1)
C(9)	28(1)	27(1)	36(1)	-2(1)	7(1)	3(1)
C(10)	39(1)	33(1)	33(1)	-3(1)	7(1)	-7(1)
C(11)	26(1)	29(1)	46(1)	-4(1)	11(1)	-2(1)
C(12)	43(1)	40(1)	35(1)	-6(1)	19(1)	0(1)
C(13)	40(1)	40(1)	32(1)	1(1)	9(1)	-8(1)
C(14)	28(1)	45(1)	36(1)	-2(1)	4(1)	2(1)
C(15)	27(1)	44(1)	42(1)	-2(1)	3(1)	1(1)
C(16)	42(1)	34(1)	38(1)	-2(1)	10(1)	-11(1)
C(17)	49(1)	32(1)	47(1)	-10(1)	24(1)	-8(1)
C(18)	34(1)	47(1)	41(1)	-10(1)	7(1)	-7(1)
C(19)	47(1)	29(1)	62(1)	-13(1)	-2(1)	2(1)
C(20)	52(1)	29(1)	48(1)	3(1)	-3(1)	-10(1)
C(21)	37(1)	44(1)	42(1)	1(1)	7(1)	8(1)
C(22)	49(1)	46(1)	47(1)	-18(1)	14(1)	-4(1)
C(23)	63(1)	40(1)	68(1)	-7(1)	26(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for C:.

	x	y	z	U(eq)
H(1)	4048	4663	5915	72
H(2)	7762	3998	7269	37
H(3)	8811	4440	6234	38
H(4)	6885	7155	4994	37
H(5)	5821	6667	6007	36
H(6)	5900	3322	5489	42
H(7)	4543	4069	7290	40
H(8)	6985	4390	8498	56
H(9)	6642	3112	7887	56
H(10)	5944	3723	8533	56
H(11)	6841	3812	3271	44
H(12)	9600	3526	4637	45
H(13)	4620	1770	7491	45
H(14)	6696	1488	3317	49
H(15)	5882	-680	5885	57
H(16)	5013	-384	7068	53
H(17)	9428	1215	4702	49
H(18)	6312	1161	5094	56
H(19)	7292	-588	4258	83
H(20)	8450	-759	4502	83
H(21)	7933	-773	3472	83

Table 6. Torsion angles [°] for C:.

O(3)-S(1)-O(1)-C(2)	-175.92(10)
O(2)-S(1)-O(1)-C(2)	55.68(12)
C(5)-S(1)-O(1)-C(2)	-60.39(11)
S(1)-O(1)-C(2)-C(7)	111.66(12)
S(1)-O(1)-C(2)-C(8)	-71.59(15)
C(9)-C(1)-C(4)-C(7)	-2.0(2)
C(6)-C(1)-C(4)-C(7)	175.24(13)
O(3)-S(1)-C(5)-C(14)	-127.41(12)
O(2)-S(1)-C(5)-C(14)	6.76(13)
O(1)-S(1)-C(5)-C(14)	123.05(11)
O(3)-S(1)-C(5)-C(15)	51.13(14)
O(2)-S(1)-C(5)-C(15)	-174.69(11)
O(1)-S(1)-C(5)-C(15)	-58.41(13)
C(4)-C(1)-C(6)-C(17)	127.19(14)
C(9)-C(1)-C(6)-C(17)	-55.69(17)
C(4)-C(1)-C(6)-C(13)	9.87(18)
C(9)-C(1)-C(6)-C(13)	-173.01(12)
C(4)-C(1)-C(6)-C(11)	-112.00(14)
C(9)-C(1)-C(6)-C(11)	65.12(16)
C(8)-C(2)-C(7)-C(4)	1.3(2)
O(1)-C(2)-C(7)-C(4)	178.00(12)
C(1)-C(4)-C(7)-C(2)	0.9(2)
C(7)-C(2)-C(8)-C(9)	-2.2(2)
O(1)-C(2)-C(8)-C(9)	-178.78(12)
C(2)-C(8)-C(9)-C(1)	1.0(2)
C(4)-C(1)-C(9)-C(8)	1.1(2)
C(6)-C(1)-C(9)-C(8)	-176.14(12)
C(16)-C(3)-C(10)-C(22)	-2.6(2)
C(11)-C(3)-C(10)-C(22)	176.54(14)
C(16)-C(3)-C(11)-O(4)	-132.39(14)
C(10)-C(3)-C(11)-O(4)	48.50(18)
C(16)-C(3)-C(11)-C(6)	104.75(15)
C(10)-C(3)-C(11)-C(6)	-74.37(17)
C(17)-C(6)-C(11)-O(4)	67.49(15)

C(1)-C(6)-C(11)-O(4)	-53.68(15)
C(13)-C(6)-C(11)-O(4)	-177.98(12)
C(17)-C(6)-C(11)-C(3)	-168.32(12)
C(1)-C(6)-C(11)-C(3)	70.51(15)
C(13)-C(6)-C(11)-C(3)	-53.79(16)
C(15)-C(5)-C(14)-C(18)	0.3(2)
S(1)-C(5)-C(14)-C(18)	178.87(12)
C(14)-C(5)-C(15)-C(21)	-1.1(2)
S(1)-C(5)-C(15)-C(21)	-179.60(12)
C(10)-C(3)-C(16)-C(20)	2.0(2)
C(11)-C(3)-C(16)-C(20)	-177.17(14)
C(1)-C(6)-C(17)-F(1)	61.39(17)
C(13)-C(6)-C(17)-F(1)	-177.22(12)
C(11)-C(6)-C(17)-F(1)	-61.21(17)
C(1)-C(6)-C(17)-F(3)	-60.27(17)
C(13)-C(6)-C(17)-F(3)	61.12(16)
C(11)-C(6)-C(17)-F(3)	177.13(12)
C(1)-C(6)-C(17)-F(2)	-178.25(13)
C(13)-C(6)-C(17)-F(2)	-56.86(17)
C(11)-C(6)-C(17)-F(2)	59.15(17)
C(5)-C(14)-C(18)-C(12)	0.7(2)
C(21)-C(12)-C(18)-C(14)	-1.0(2)
C(23)-C(12)-C(18)-C(14)	178.36(15)
C(22)-C(19)-C(20)-C(16)	-1.3(3)
C(3)-C(16)-C(20)-C(19)	0.0(2)
C(5)-C(15)-C(21)-C(12)	0.8(2)
C(18)-C(12)-C(21)-C(15)	0.3(2)
C(23)-C(12)-C(21)-C(15)	-179.13(15)
C(20)-C(19)-C(22)-C(10)	0.7(3)
C(3)-C(10)-C(22)-C(19)	1.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for C: [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(1)...O(2)#1	0.84	2.49	3.1584(17)	136.8
C(14)-H(11)...O(4)#1	0.95	2.61	3.3291(19)	132.6
C(15)-H(12)...O(1)#2	0.95	2.51	3.4167(17)	159.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1

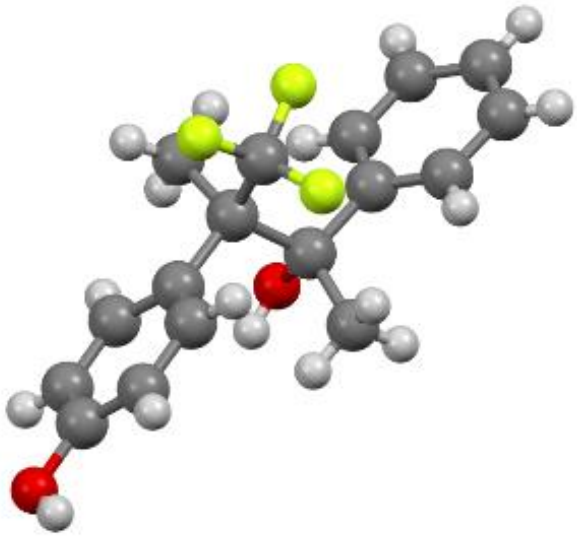


Table 1. Crystal data and structure refinement for C:.

Identification code	**7aa**	
Empirical formula	C17 H17 F3 O2	
Formula weight	310.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 24.3360(11) Å	α= 90°.
	b = 7.1684(3) Å	β= 90°.
	c = 16.7513(8) Å	γ = 90°.
Volume	2922.3(2) $Å^3$	
Z	8	
Density (calculated)	1.411 Mg/m^3	
Absorption coefficient	0.117 mm^{-1}	
F(000)	1296	
Crystal size	0.220 x 0.190 x 0.130 mm^3	
Theta range for data collection	2.432 to 25.499°.	
Index ranges	-25<=h<=29, -8<=k<=8, -20<=l<=19	
Reflections collected	20991	

Independent reflections	2724 [R(int) = 0.0608]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.24460
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2724 / 0 / 203
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0935
R indices (all data)	R1 = 0.0468, wR2 = 0.0989
Extinction coefficient	n/a
Largest diff. peak and hole	0.200 and -0.260 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for C:. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3138(1)	5003(1)	7133(1)	39(1)
F(2)	2889(1)	3058(1)	6236(1)	40(1)
F(3)	3310(1)	5581(1)	5907(1)	44(1)
O(1)	4800(1)	1270(2)	3497(1)	32(1)
O(2)	4385(1)	891(2)	7262(1)	32(1)
C(1)	4095(1)	2793(2)	5683(1)	22(1)
C(2)	3542(1)	1704(2)	7847(1)	23(1)
C(3)	4552(1)	1788(2)	4199(1)	25(1)
C(4)	3867(1)	3258(2)	6520(1)	23(1)
C(5)	3831(1)	1389(2)	7049(1)	23(1)
C(6)	3988(1)	1835(2)	4300(1)	28(1)
C(7)	3767(1)	2314(2)	5035(1)	28(1)
C(8)	3820(1)	2533(2)	8482(1)	28(1)
C(9)	3003(1)	1139(2)	7972(1)	30(1)
C(10)	4661(1)	2788(2)	5555(1)	29(1)
C(11)	4887(1)	2285(2)	4829(1)	31(1)
C(12)	3304(1)	4194(2)	6450(1)	30(1)
C(13)	3566(1)	2799(2)	9210(1)	33(1)
C(14)	3028(1)	2226(2)	9325(1)	35(1)
C(15)	4237(1)	4726(2)	6928(1)	34(1)
C(16)	3588(1)	-257(2)	6591(1)	34(1)
C(17)	2748(1)	1395(2)	8704(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for C:.

F(1)-C(12)	1.3452(17)
F(2)-C(12)	1.3450(19)
F(3)-C(12)	1.3473(18)
O(1)-C(3)	1.3732(17)
O(1)-H(1)	0.8400
O(2)-C(5)	1.4401(17)
O(2)-H(2)	0.8400
C(1)-C(7)	1.391(2)
C(1)-C(10)	1.394(2)
C(1)-C(4)	1.5437(19)
C(2)-C(9)	1.389(2)
C(2)-C(8)	1.395(2)
C(2)-C(5)	1.5272(19)
C(3)-C(11)	1.380(2)
C(3)-C(6)	1.382(2)
C(4)-C(12)	1.531(2)
C(4)-C(15)	1.544(2)
C(4)-C(5)	1.6088(19)
C(5)-C(16)	1.526(2)
C(6)-C(7)	1.387(2)
C(6)-H(3)	0.9500
C(7)-H(4)	0.9500
C(8)-C(13)	1.380(2)
C(8)-H(5)	0.9500
C(9)-C(17)	1.385(2)
C(9)-H(6)	0.9500
C(10)-C(11)	1.383(2)
C(10)-H(7)	0.9500
C(11)-H(8)	0.9500
C(13)-C(14)	1.386(2)
C(13)-H(9)	0.9500
C(14)-C(17)	1.379(2)
C(14)-H(10)	0.9500
C(15)-H(11)	0.9800

C(15)-H(12)	0.9800
C(15)-H(13)	0.9800
C(16)-H(14)	0.9800
C(16)-H(15)	0.9800
C(16)-H(16)	0.9800
C(17)-H(17)	0.9500

C(3)-O(1)-H(1)	109.5
C(5)-O(2)-H(2)	109.5
C(7)-C(1)-C(10)	116.50(13)
C(7)-C(1)-C(4)	123.82(12)
C(10)-C(1)-C(4)	119.65(13)
C(9)-C(2)-C(8)	117.83(14)
C(9)-C(2)-C(5)	121.60(13)
C(8)-C(2)-C(5)	120.55(13)
O(1)-C(3)-C(11)	117.61(13)
O(1)-C(3)-C(6)	123.27(13)
C(11)-C(3)-C(6)	119.11(13)
C(12)-C(4)-C(15)	104.89(12)
C(12)-C(4)-C(1)	110.23(12)
C(15)-C(4)-C(1)	109.89(12)
C(12)-C(4)-C(5)	110.96(12)
C(15)-C(4)-C(5)	110.88(12)
C(1)-C(4)-C(5)	109.89(11)
O(2)-C(5)-C(16)	107.15(12)
O(2)-C(5)-C(2)	104.53(11)
C(16)-C(5)-C(2)	112.08(12)
O(2)-C(5)-C(4)	106.91(11)
C(16)-C(5)-C(4)	112.90(12)
C(2)-C(5)-C(4)	112.61(11)
C(3)-C(6)-C(7)	120.04(14)
C(3)-C(6)-H(3)	120.0
C(7)-C(6)-H(3)	120.0
C(6)-C(7)-C(1)	122.06(13)
C(6)-C(7)-H(4)	119.0
C(1)-C(7)-H(4)	119.0

C(13)-C(8)-C(2)	121.07(14)
C(13)-C(8)-H(5)	119.5
C(2)-C(8)-H(5)	119.5
C(17)-C(9)-C(2)	121.13(15)
C(17)-C(9)-H(6)	119.4
C(2)-C(9)-H(6)	119.4
C(11)-C(10)-C(1)	121.99(14)
C(11)-C(10)-H(7)	119.0
C(1)-C(10)-H(7)	119.0
C(3)-C(11)-C(10)	120.25(14)
C(3)-C(11)-H(8)	119.9
C(10)-C(11)-H(8)	119.9
F(2)-C(12)-F(1)	105.29(12)
F(2)-C(12)-F(3)	105.97(13)
F(1)-C(12)-F(3)	105.09(12)
F(2)-C(12)-C(4)	115.24(13)
F(1)-C(12)-C(4)	113.04(13)
F(3)-C(12)-C(4)	111.42(12)
C(8)-C(13)-C(14)	120.36(15)
C(8)-C(13)-H(9)	119.8
C(14)-C(13)-H(9)	119.8
C(17)-C(14)-C(13)	119.25(15)
C(17)-C(14)-H(10)	120.4
C(13)-C(14)-H(10)	120.4
C(4)-C(15)-H(11)	109.5
C(4)-C(15)-H(12)	109.5
H(11)-C(15)-H(12)	109.5
C(4)-C(15)-H(13)	109.5
H(11)-C(15)-H(13)	109.5
H(12)-C(15)-H(13)	109.5
C(5)-C(16)-H(14)	109.5
C(5)-C(16)-H(15)	109.5
H(14)-C(16)-H(15)	109.5
C(5)-C(16)-H(16)	109.5
H(14)-C(16)-H(16)	109.5
H(15)-C(16)-H(16)	109.5

C(14)-C(17)-C(9)	120.37(15)
C(14)-C(17)-H(17)	119.8
C(9)-C(17)-H(17)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C:. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	46(1)	40(1)	30(1)	1(1)	14(1)	17(1)
F(2)	24(1)	55(1)	39(1)	1(1)	1(1)	6(1)
F(3)	58(1)	40(1)	33(1)	13(1)	13(1)	22(1)
O(1)	30(1)	44(1)	23(1)	-10(1)	5(1)	-2(1)
O(2)	28(1)	46(1)	22(1)	0(1)	3(1)	16(1)
C(1)	24(1)	22(1)	21(1)	0(1)	2(1)	2(1)
C(2)	25(1)	23(1)	22(1)	2(1)	0(1)	3(1)
C(3)	29(1)	24(1)	21(1)	-3(1)	5(1)	0(1)
C(4)	24(1)	24(1)	21(1)	-1(1)	2(1)	1(1)
C(5)	24(1)	25(1)	22(1)	0(1)	-1(1)	4(1)
C(6)	28(1)	35(1)	23(1)	-5(1)	-5(1)	3(1)
C(7)	20(1)	35(1)	29(1)	-4(1)	0(1)	4(1)
C(8)	23(1)	34(1)	26(1)	-2(1)	1(1)	1(1)
C(9)	28(1)	32(1)	30(1)	2(1)	0(1)	-4(1)
C(10)	26(1)	38(1)	23(1)	-6(1)	-1(1)	-4(1)
C(11)	22(1)	42(1)	29(1)	-7(1)	5(1)	-4(1)
C(12)	34(1)	33(1)	24(1)	4(1)	7(1)	7(1)
C(13)	36(1)	40(1)	24(1)	-7(1)	0(1)	4(1)
C(14)	38(1)	40(1)	28(1)	0(1)	12(1)	6(1)
C(15)	42(1)	32(1)	27(1)	-8(1)	9(1)	-9(1)
C(16)	47(1)	25(1)	29(1)	-2(1)	2(1)	-1(1)
C(17)	27(1)	40(1)	39(1)	3(1)	9(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for C:.

	x	y	z	U(eq)
H(1)	4567	771	3195	49
H(2)	4546	447	6861	48
H(3)	3753	1538	3866	34
H(4)	3379	2314	5097	34
H(5)	4190	2922	8414	33
H(6)	2805	568	7549	36
H(7)	4898	3140	5979	35
H(8)	5275	2281	4763	37
H(9)	3761	3378	9634	40
H(10)	2853	2403	9827	43
H(11)	4291	5786	6567	50
H(12)	4594	4167	7055	50
H(13)	4061	5158	7420	50
H(14)	3825	-557	6136	51
H(15)	3220	70	6399	51
H(16)	3564	-1342	6945	51
H(17)	2380	996	8778	42

Table 6. Torsion angles [°] for C:.

C(7)-C(1)-C(4)-C(12)	-32.40(19)
C(10)-C(1)-C(4)-C(12)	149.59(14)
C(7)-C(1)-C(4)-C(15)	-147.53(14)
C(10)-C(1)-C(4)-C(15)	34.46(18)
C(7)-C(1)-C(4)-C(5)	90.20(16)
C(10)-C(1)-C(4)-C(5)	-87.82(16)
C(9)-C(2)-C(5)-O(2)	-141.33(14)
C(8)-C(2)-C(5)-O(2)	37.08(17)
C(9)-C(2)-C(5)-C(16)	-25.61(19)
C(8)-C(2)-C(5)-C(16)	152.79(14)
C(9)-C(2)-C(5)-C(4)	102.99(16)
C(8)-C(2)-C(5)-C(4)	-78.61(16)
C(12)-C(4)-C(5)-O(2)	-164.85(11)
C(15)-C(4)-C(5)-O(2)	-48.71(15)
C(1)-C(4)-C(5)-O(2)	72.98(13)
C(12)-C(4)-C(5)-C(16)	77.57(15)
C(15)-C(4)-C(5)-C(16)	-166.29(13)
C(1)-C(4)-C(5)-C(16)	-44.60(16)
C(12)-C(4)-C(5)-C(2)	-50.61(16)
C(15)-C(4)-C(5)-C(2)	65.54(15)
C(1)-C(4)-C(5)-C(2)	-172.78(11)
O(1)-C(3)-C(6)-C(7)	177.87(14)
C(11)-C(3)-C(6)-C(7)	-2.2(2)
C(3)-C(6)-C(7)-C(1)	1.3(2)
C(10)-C(1)-C(7)-C(6)	0.6(2)
C(4)-C(1)-C(7)-C(6)	-177.42(14)
C(9)-C(2)-C(8)-C(13)	-0.5(2)
C(5)-C(2)-C(8)-C(13)	-179.00(14)
C(8)-C(2)-C(9)-C(17)	0.1(2)
C(5)-C(2)-C(9)-C(17)	178.57(14)
C(7)-C(1)-C(10)-C(11)	-1.7(2)
C(4)-C(1)-C(10)-C(11)	176.49(14)
O(1)-C(3)-C(11)-C(10)	-178.86(14)
C(6)-C(3)-C(11)-C(10)	1.2(2)

C(1)-C(10)-C(11)-C(3)	0.8(2)
C(15)-C(4)-C(12)-F(2)	-169.00(12)
C(1)-C(4)-C(12)-F(2)	72.76(15)
C(5)-C(4)-C(12)-F(2)	-49.21(16)
C(15)-C(4)-C(12)-F(1)	-47.85(16)
C(1)-C(4)-C(12)-F(1)	-166.10(12)
C(5)-C(4)-C(12)-F(1)	71.93(16)
C(15)-C(4)-C(12)-F(3)	70.23(15)
C(1)-C(4)-C(12)-F(3)	-48.02(17)
C(5)-C(4)-C(12)-F(3)	-169.99(12)
C(2)-C(8)-C(13)-C(14)	0.6(2)
C(8)-C(13)-C(14)-C(17)	-0.3(2)
C(13)-C(14)-C(17)-C(9)	-0.1(2)
C(2)-C(9)-C(17)-C(14)	0.2(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for C: [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84	2.02	2.7761(15)	150.2
O(2)-H(2)...O(1)#2	0.84	2.10	2.8186(14)	143.6
C(16)-H(15)...F(2)	0.98	2.30	2.9821(19)	125.5

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z-1/2 #2 -x+1,-y,-z+1

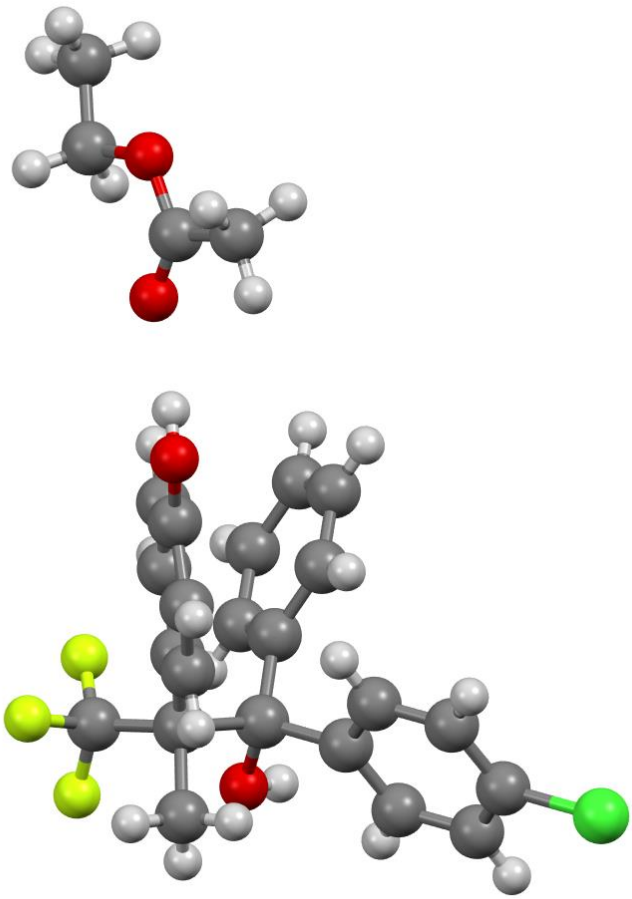


Table 1. Crystal data and structure refinement for C:.

Identification code	**9aa**	
Empirical formula	C26 H26 Cl F3 O4	
Formula weight	494.92	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.0518(6) Å	α= 90°.
	b = 11.0358(4) Å	β= 103.931(5)°.
	c = 18.5393(9) Å	γ = 90°.
Volume	2393.22(19) $Å^3$	
Z	4	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	0.214 mm^{-1}	

F(000)	1032
Crystal size	0.210 x 0.180 x 0.110 mm^3
Theta range for data collection	2.602 to 25.495°.
Index ranges	-14<=h<=13, -13<=k<=13, -22<=l<=22
Reflections collected	28431
Independent reflections	4433 [R(int) = 0.0376]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.76561
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4433 / 0 / 312
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1285
R indices (all data)	R1 = 0.0523, wR2 = 0.1330
Extinction coefficient	n/a
Largest diff. peak and hole	0.726 and -0.389 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for C:. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	4483(1)	13109(1)	2156(1)	47(1)
C(1)	4649(2)	11624(2)	1875(1)	31(1)
C(2)	4338(2)	11342(2)	1130(1)	32(1)
C(3)	4474(2)	10159(2)	905(1)	27(1)
C(4)	4910(2)	9242(2)	1410(1)	22(1)
C(5)	5240(2)	9572(2)	2163(1)	28(1)
C(6)	5116(2)	10749(2)	2395(1)	32(1)
C(7)	4980(2)	7931(2)	1121(1)	22(1)
O(1)	4811(1)	7961(1)	334(1)	26(1)
C(8)	4026(2)	7151(2)	1314(1)	25(1)
C(9)	3680(2)	7270(2)	1978(1)	32(1)
C(10)	2803(2)	6581(2)	2123(1)	43(1)
C(11)	2233(2)	5757(2)	1605(2)	54(1)
C(12)	2553(2)	5628(2)	942(2)	50(1)
C(13)	3438(2)	6314(2)	796(1)	34(1)
C(14)	6260(2)	7408(2)	1394(1)	23(1)
C(15)	7071(2)	8343(2)	1170(1)	30(1)
C(16)	6433(2)	6233(2)	977(1)	29(1)
F(1)	7473(1)	5754(1)	1285(1)	40(1)
F(2)	5681(1)	5350(1)	994(1)	38(1)
F(3)	6430(1)	6394(1)	260(1)	45(1)
C(17)	6606(2)	7122(2)	2230(1)	22(1)
C(18)	7460(2)	7783(2)	2712(1)	25(1)
C(19)	7772(2)	7544(2)	3470(1)	28(1)
C(20)	7231(2)	6628(2)	3761(1)	26(1)
C(21)	6386(2)	5942(2)	3295(1)	25(1)
C(22)	6088(2)	6185(2)	2538(1)	23(1)
O(2)	7557(1)	6423(2)	4513(1)	36(1)
C(27)	6564(3)	5553(3)	6174(1)	55(1)
O(5)	6368(2)	4623(2)	4982(1)	46(1)

C(24)	6308(2)	4553(2)	5623(1)	39(1)
O(4)	5972(2)	3551(2)	5901(1)	62(1)
C(25)	5683(5)	2502(3)	5398(2)	102(2)
C(26)	5075(3)	1634(3)	5718(2)	82(1)

Table 3. Bond lengths [Å] and angles [°] for C:.

Cl(1)-C(1)	1.746(2)
C(1)-C(2)	1.377(3)
C(1)-C(6)	1.384(3)
C(2)-C(3)	1.392(3)
C(2)-H(1)	0.9500
C(3)-C(4)	1.393(3)
C(3)-H(2)	0.9500
C(4)-C(5)	1.405(3)
C(4)-C(7)	1.553(3)
C(5)-C(6)	1.388(3)
C(5)-H(3)	0.9500
C(6)-H(4)	0.9500
C(7)-O(1)	1.424(2)
C(7)-C(8)	1.545(3)
C(7)-C(14)	1.609(2)
O(1)-H(5)	0.8400
C(8)-C(13)	1.397(3)
C(8)-C(9)	1.398(3)
C(9)-C(10)	1.381(3)
C(9)-H(6)	0.9500
C(10)-C(11)	1.379(4)
C(10)-H(7)	0.9500
C(11)-C(12)	1.384(4)
C(11)-H(8)	0.9500
C(12)-C(13)	1.386(3)
C(12)-H(9)	0.9500
C(13)-H(10)	0.9500
C(14)-C(17)	1.538(2)
C(14)-C(15)	1.546(3)
C(14)-C(16)	1.550(3)
C(15)-H(11)	0.9800
C(15)-H(12)	0.9800
C(15)-H(13)	0.9800
C(16)-F(2)	1.336(2)

C(16)-F(3)	1.339(2)
C(16)-F(1)	1.353(2)
C(17)-C(18)	1.395(3)
C(17)-C(22)	1.399(3)
C(18)-C(19)	1.388(3)
C(18)-H(14)	0.9500
C(19)-C(20)	1.381(3)
C(19)-H(15)	0.9500
C(20)-O(2)	1.374(2)
C(20)-C(21)	1.390(3)
C(21)-C(22)	1.387(3)
C(21)-H(16)	0.9500
C(22)-H(17)	0.9500
O(2)-H(18)	0.8400
C(27)-C(24)	1.484(3)
C(27)-H(19)	0.9800
C(27)-H(20)	0.9800
C(27)-H(21)	0.9800
O(5)-C(24)	1.210(3)
C(24)-O(4)	1.324(3)
O(4)-C(25)	1.475(4)
C(25)-C(26)	1.420(5)
C(25)-H(26)	0.9900
C(25)-H(27)	0.9900
C(26)-H(23)	0.9800
C(26)-H(24)	0.9800
C(26)-H(25)	0.9800

C(2)-C(1)-C(6)	120.50(18)
C(2)-C(1)-Cl(1)	119.22(16)
C(6)-C(1)-Cl(1)	120.26(16)
C(1)-C(2)-C(3)	119.30(18)
C(1)-C(2)-H(1)	120.3
C(3)-C(2)-H(1)	120.3
C(2)-C(3)-C(4)	122.16(17)
C(2)-C(3)-H(2)	118.9

C(4)-C(3)-H(2)	118.9
C(3)-C(4)-C(5)	116.80(17)
C(3)-C(4)-C(7)	119.22(16)
C(5)-C(4)-C(7)	123.96(16)
C(6)-C(5)-C(4)	121.59(18)
C(6)-C(5)-H(3)	119.2
C(4)-C(5)-H(3)	119.2
C(1)-C(6)-C(5)	119.61(18)
C(1)-C(6)-H(4)	120.2
C(5)-C(6)-H(4)	120.2
O(1)-C(7)-C(8)	108.61(14)
O(1)-C(7)-C(4)	109.01(14)
C(8)-C(7)-C(4)	109.49(14)
O(1)-C(7)-C(14)	102.73(13)
C(8)-C(7)-C(14)	115.96(14)
C(4)-C(7)-C(14)	110.67(14)
C(7)-O(1)-H(5)	109.5
C(13)-C(8)-C(9)	117.23(18)
C(13)-C(8)-C(7)	119.47(16)
C(9)-C(8)-C(7)	123.24(17)
C(10)-C(9)-C(8)	121.7(2)
C(10)-C(9)-H(6)	119.2
C(8)-C(9)-H(6)	119.2
C(11)-C(10)-C(9)	120.3(2)
C(11)-C(10)-H(7)	119.9
C(9)-C(10)-H(7)	119.9
C(10)-C(11)-C(12)	119.2(2)
C(10)-C(11)-H(8)	120.4
C(12)-C(11)-H(8)	120.4
C(11)-C(12)-C(13)	120.6(2)
C(11)-C(12)-H(9)	119.7
C(13)-C(12)-H(9)	119.7
C(12)-C(13)-C(8)	121.0(2)
C(12)-C(13)-H(10)	119.5
C(8)-C(13)-H(10)	119.5
C(17)-C(14)-C(15)	111.90(15)

C(17)-C(14)-C(16)	107.15(15)
C(15)-C(14)-C(16)	104.72(15)
C(17)-C(14)-C(7)	113.40(14)
C(15)-C(14)-C(7)	107.24(14)
C(16)-C(14)-C(7)	112.14(15)
C(14)-C(15)-H(11)	109.5
C(14)-C(15)-H(12)	109.5
H(11)-C(15)-H(12)	109.5
C(14)-C(15)-H(13)	109.5
H(11)-C(15)-H(13)	109.5
H(12)-C(15)-H(13)	109.5
F(2)-C(16)-F(3)	106.25(16)
F(2)-C(16)-F(1)	105.60(16)
F(3)-C(16)-F(1)	104.59(15)
F(2)-C(16)-C(14)	115.18(16)
F(3)-C(16)-C(14)	114.55(16)
F(1)-C(16)-C(14)	109.79(16)
C(18)-C(17)-C(22)	117.24(16)
C(18)-C(17)-C(14)	121.14(16)
C(22)-C(17)-C(14)	121.61(16)
C(19)-C(18)-C(17)	121.79(17)
C(19)-C(18)-H(14)	119.1
C(17)-C(18)-H(14)	119.1
C(20)-C(19)-C(18)	119.72(17)
C(20)-C(19)-H(15)	120.1
C(18)-C(19)-H(15)	120.1
O(2)-C(20)-C(19)	118.10(17)
O(2)-C(20)-C(21)	121.94(18)
C(19)-C(20)-C(21)	119.96(16)
C(22)-C(21)-C(20)	119.73(17)
C(22)-C(21)-H(16)	120.1
C(20)-C(21)-H(16)	120.1
C(21)-C(22)-C(17)	121.54(17)
C(21)-C(22)-H(17)	119.2
C(17)-C(22)-H(17)	119.2
C(20)-O(2)-H(18)	109.5

C(24)-C(27)-H(19)	109.5
C(24)-C(27)-H(20)	109.5
H(19)-C(27)-H(20)	109.5
C(24)-C(27)-H(21)	109.5
H(19)-C(27)-H(21)	109.5
H(20)-C(27)-H(21)	109.5
O(5)-C(24)-O(4)	122.1(2)
O(5)-C(24)-C(27)	125.2(2)
O(4)-C(24)-C(27)	112.7(2)
C(24)-O(4)-C(25)	117.2(2)
C(26)-C(25)-O(4)	109.4(3)
C(26)-C(25)-H(26)	109.8
O(4)-C(25)-H(26)	109.8
C(26)-C(25)-H(27)	109.8
O(4)-C(25)-H(27)	109.8
H(26)-C(25)-H(27)	108.2
C(25)-C(26)-H(23)	109.5
C(25)-C(26)-H(24)	109.5
H(23)-C(26)-H(24)	109.5
C(25)-C(26)-H(25)	109.5
H(23)-C(26)-H(25)	109.5
H(24)-C(26)-H(25)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C:. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	54(1)	27(1)	67(1)	-11(1)	28(1)	-3(1)
C(1)	29(1)	24(1)	41(1)	-4(1)	14(1)	-3(1)
C(2)	34(1)	26(1)	37(1)	7(1)	11(1)	2(1)
C(3)	30(1)	29(1)	23(1)	4(1)	6(1)	-1(1)
C(4)	21(1)	25(1)	22(1)	1(1)	5(1)	-1(1)
C(5)	28(1)	32(1)	21(1)	1(1)	1(1)	5(1)
C(6)	30(1)	36(1)	28(1)	-9(1)	5(1)	-1(1)
C(7)	23(1)	26(1)	14(1)	3(1)	3(1)	1(1)
O(1)	28(1)	33(1)	14(1)	1(1)	3(1)	1(1)
C(8)	22(1)	26(1)	25(1)	6(1)	4(1)	3(1)
C(9)	31(1)	36(1)	30(1)	9(1)	10(1)	5(1)
C(10)	38(1)	50(1)	47(1)	16(1)	22(1)	6(1)
C(11)	38(1)	50(2)	79(2)	13(1)	25(1)	-9(1)
C(12)	40(1)	44(1)	66(2)	-2(1)	9(1)	-15(1)
C(13)	31(1)	34(1)	36(1)	-1(1)	5(1)	-5(1)
C(14)	24(1)	26(1)	21(1)	2(1)	6(1)	1(1)
C(15)	26(1)	36(1)	30(1)	7(1)	9(1)	-2(1)
C(16)	31(1)	32(1)	25(1)	1(1)	7(1)	6(1)
F(1)	34(1)	41(1)	44(1)	-2(1)	6(1)	13(1)
F(2)	41(1)	30(1)	42(1)	-10(1)	9(1)	-3(1)
F(3)	64(1)	49(1)	26(1)	0(1)	17(1)	17(1)
C(17)	20(1)	22(1)	21(1)	2(1)	3(1)	3(1)
C(18)	22(1)	24(1)	28(1)	3(1)	4(1)	-2(1)
C(19)	24(1)	29(1)	26(1)	-3(1)	-3(1)	-1(1)
C(20)	24(1)	32(1)	18(1)	1(1)	0(1)	6(1)
C(21)	22(1)	27(1)	24(1)	6(1)	4(1)	1(1)
C(22)	20(1)	23(1)	24(1)	2(1)	1(1)	0(1)
O(2)	35(1)	50(1)	19(1)	5(1)	-2(1)	-3(1)
C(27)	65(2)	61(2)	42(1)	-9(1)	17(1)	-15(1)
O(5)	50(1)	59(1)	32(1)	3(1)	14(1)	-3(1)
C(24)	38(1)	46(1)	35(1)	4(1)	13(1)	3(1)

O(4)	105(2)	42(1)	49(1)	2(1)	40(1)	-1(1)
C(25)	195(5)	47(2)	85(3)	-10(2)	72(3)	-4(2)
C(26)	62(2)	62(2)	123(3)	-26(2)	21(2)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for C:.

	x	y	z	U(eq)
H(1)	4032	11948	774	38
H(2)	4264	9971	390	32
H(3)	5555	8974	2523	34
H(4)	5350	10954	2907	38
H(5)	4123	8119	137	38
H(6)	4058	7840	2339	38
H(7)	2591	6674	2582	51
H(8)	1626	5285	1703	65
H(9)	2164	5063	582	61
H(10)	3647	6214	337	41
H(11)	7044	9103	1439	45
H(12)	6829	8493	634	45
H(13)	7853	8026	1294	45
H(14)	7838	8413	2517	30
H(15)	8355	8009	3786	33
H(16)	6015	5310	3493	30
H(17)	5518	5704	2223	28
H(18)	7135	5889	4629	54
H(19)	6832	6263	5946	83
H(20)	7160	5293	6605	83
H(21)	5871	5764	6333	83
H(26)	5207	2770	4911	123
H(27)	6391	2133	5315	123
H(23)	5549	1372	6199	123
H(24)	4888	934	5387	123
H(25)	4368	1999	5790	123

Table 6. Torsion angles [°] for C:.

C(6)-C(1)-C(2)-C(3)	1.3(3)
Cl(1)-C(1)-C(2)-C(3)	179.70(15)
C(1)-C(2)-C(3)-C(4)	0.5(3)
C(2)-C(3)-C(4)-C(5)	-1.7(3)
C(2)-C(3)-C(4)-C(7)	176.88(17)
C(3)-C(4)-C(5)-C(6)	1.2(3)
C(7)-C(4)-C(5)-C(6)	-177.32(17)
C(2)-C(1)-C(6)-C(5)	-1.8(3)
Cl(1)-C(1)-C(6)-C(5)	179.82(15)
C(4)-C(5)-C(6)-C(1)	0.5(3)
C(3)-C(4)-C(7)-O(1)	13.5(2)
C(5)-C(4)-C(7)-O(1)	-168.02(16)
C(3)-C(4)-C(7)-C(8)	-105.21(18)
C(5)-C(4)-C(7)-C(8)	73.3(2)
C(3)-C(4)-C(7)-C(14)	125.76(17)
C(5)-C(4)-C(7)-C(14)	-55.7(2)
O(1)-C(7)-C(8)-C(13)	21.1(2)
C(4)-C(7)-C(8)-C(13)	140.03(18)
C(14)-C(7)-C(8)-C(13)	-93.9(2)
O(1)-C(7)-C(8)-C(9)	-156.28(17)
C(4)-C(7)-C(8)-C(9)	-37.3(2)
C(14)-C(7)-C(8)-C(9)	88.7(2)
C(13)-C(8)-C(9)-C(10)	0.8(3)
C(7)-C(8)-C(9)-C(10)	178.22(19)
C(8)-C(9)-C(10)-C(11)	-0.7(3)
C(9)-C(10)-C(11)-C(12)	0.3(4)
C(10)-C(11)-C(12)-C(13)	0.1(4)
C(11)-C(12)-C(13)-C(8)	0.0(4)
C(9)-C(8)-C(13)-C(12)	-0.4(3)
C(7)-C(8)-C(13)-C(12)	-178.0(2)
O(1)-C(7)-C(14)-C(17)	-172.27(14)
C(8)-C(7)-C(14)-C(17)	-54.0(2)
C(4)-C(7)-C(14)-C(17)	71.49(18)
O(1)-C(7)-C(14)-C(15)	63.69(17)

C(8)-C(7)-C(14)-C(15)	-178.02(15)
C(4)-C(7)-C(14)-C(15)	-52.55(18)
O(1)-C(7)-C(14)-C(16)	-50.73(18)
C(8)-C(7)-C(14)-C(16)	67.55(19)
C(4)-C(7)-C(14)-C(16)	-166.98(14)
C(17)-C(14)-C(16)-F(2)	71.24(19)
C(15)-C(14)-C(16)-F(2)	-169.77(15)
C(7)-C(14)-C(16)-F(2)	-53.8(2)
C(17)-C(14)-C(16)-F(3)	-165.07(15)
C(15)-C(14)-C(16)-F(3)	-46.1(2)
C(7)-C(14)-C(16)-F(3)	69.9(2)
C(17)-C(14)-C(16)-F(1)	-47.8(2)
C(15)-C(14)-C(16)-F(1)	71.23(18)
C(7)-C(14)-C(16)-F(1)	-172.81(14)
C(15)-C(14)-C(17)-C(18)	8.1(2)
C(16)-C(14)-C(17)-C(18)	122.31(18)
C(7)-C(14)-C(17)-C(18)	-113.41(19)
C(15)-C(14)-C(17)-C(22)	-171.31(17)
C(16)-C(14)-C(17)-C(22)	-57.1(2)
C(7)-C(14)-C(17)-C(22)	67.2(2)
C(22)-C(17)-C(18)-C(19)	-1.4(3)
C(14)-C(17)-C(18)-C(19)	179.25(17)
C(17)-C(18)-C(19)-C(20)	0.2(3)
C(18)-C(19)-C(20)-O(2)	-179.60(17)
C(18)-C(19)-C(20)-C(21)	0.6(3)
O(2)-C(20)-C(21)-C(22)	-179.99(17)
C(19)-C(20)-C(21)-C(22)	-0.2(3)
C(20)-C(21)-C(22)-C(17)	-1.0(3)
C(18)-C(17)-C(22)-C(21)	1.8(3)
C(14)-C(17)-C(22)-C(21)	-178.84(16)
O(5)-C(24)-O(4)-C(25)	0.7(4)
C(27)-C(24)-O(4)-C(25)	179.4(3)
C(24)-O(4)-C(25)-C(26)	-165.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for C: [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(1)...F(3)#1	0.95	2.61	3.550(2)	169.3
O(1)-H(5)...O(2)#2	0.84	2.03	2.8578(19)	170.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z #2 x-1/2,-y+3/2,z-1/2

Computational study

DFT calculations were performed by the Gaussian 09 program using the B3LYP/6-311++G** level of theory, and stationary points were confirmed by the frequency calculation with 0 negative frequency. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

1 with a Me group as R^1, E = –722.10528297 hartree, no negative frequency,
HOMO –7.262 eV, LUMO –3.372 eV

	Coordinates (Å)		
	X	Y	Z
C1	3.0950618	–0.2297607	0.0006503
C2	2.0610064	–1.2776761	0.0000579
C3	0.7473633	–0.9855411	–0.0000022
C4	0.2554357	0.3956353	0.0001281
C5	1.2809206	1.4399877	–0.0000604
C6	2.5964873	1.1572672	–0.0000451
H7	2.4116130	–2.3033171	–0.0001282
H8	0.0316151	–1.7947193	–0.0001350
H9	0.9711211	2.4761383	–0.0003198
H10	3.3457331	1.9406728	–0.0003489
O11	4.2925326	–0.4901126	–0.0004420
C12	–1.0750041	0.7036553	0.0001467

C13	–1.6633012	2.0851940	0.0002915
H14	–2.3035214	2.2299408	0.8760349
H15	–0.9059881	2.8629177	0.0011792
H16	–2.3022917	2.2306963	–0.8762405
C17	–2.1156721	–0.4077398	–0.0000570
F18	–2.0191393	–1.2097069	1.0886369
F19	–3.3716479	0.0856035	–0.0005919
F20	–2.0183603	–1.2100699	–1.0883966

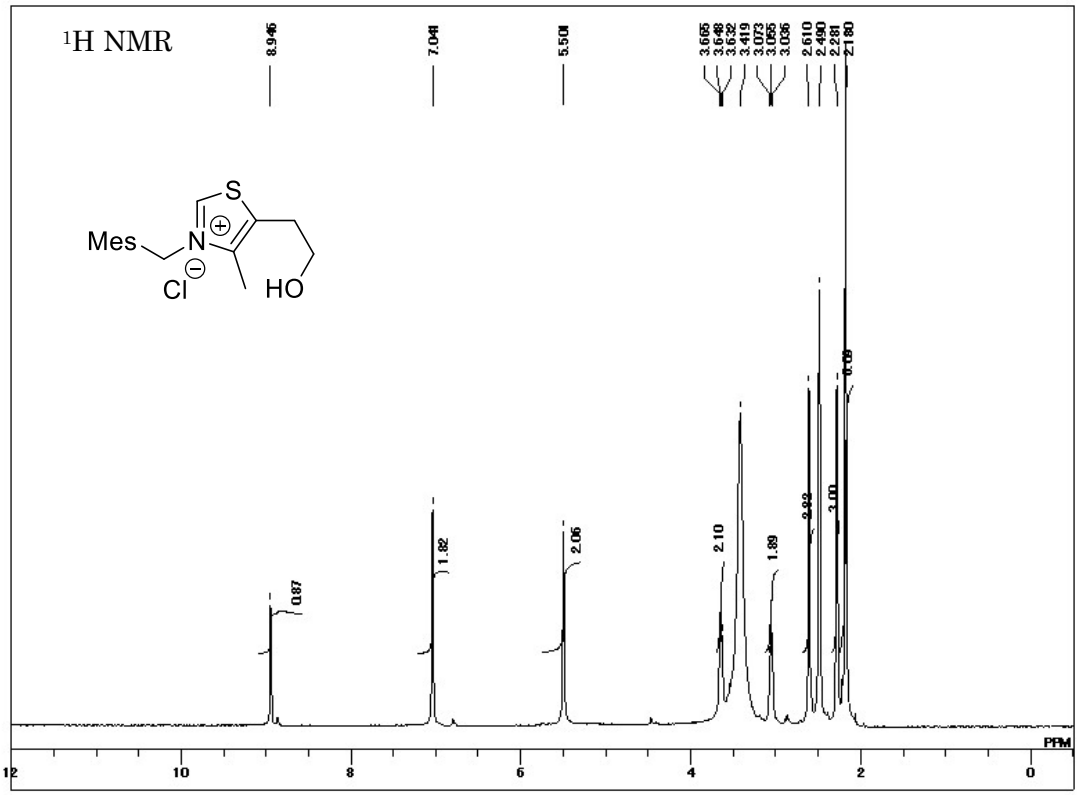
1 with a Ph group as R^1, E = –913.88559866 hartree, no negative frequency,
HOMO –7.129 eV, LUMO –3.441 eV

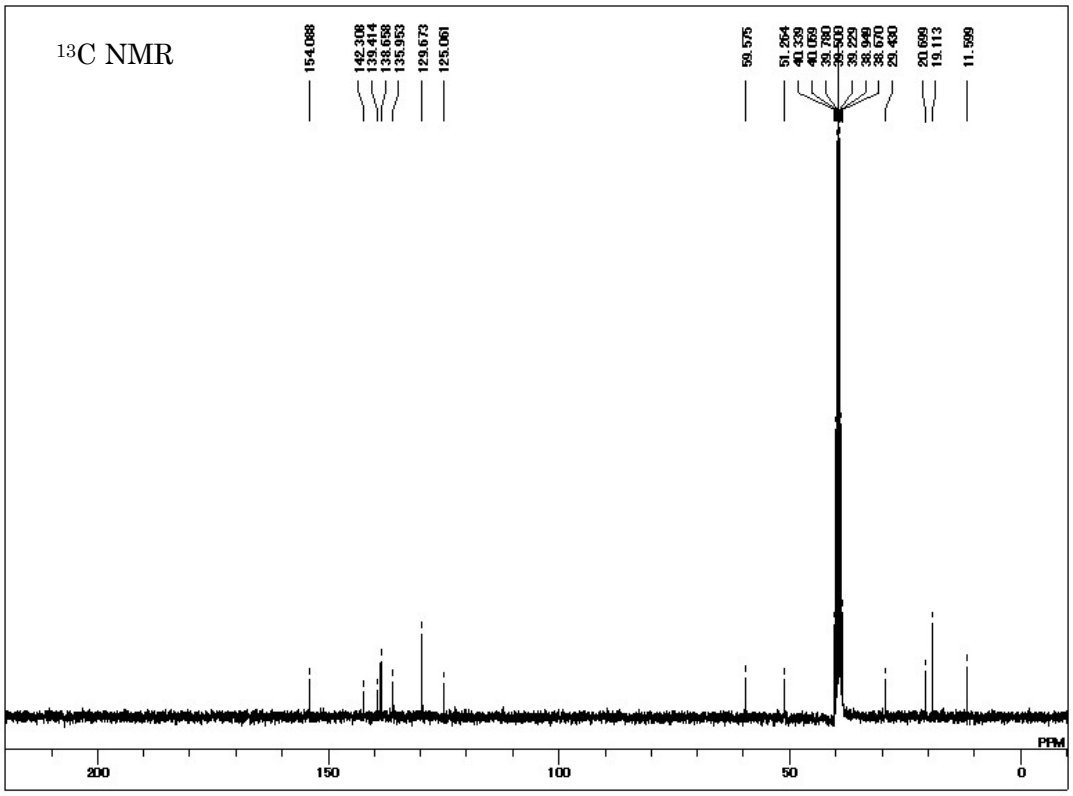
	Coordinates (Å)		
	X	Y	Z
C1	–3.6671820	–1.0880535	–0.1026871
C2	–3.4200050	0.3555640	0.0612600
C3	–2.1769295	0.8711285	0.0795088
C4	–0.9889711	0.0236126	–0.0448923
C5	–1.2281051	–1.4071679	–0.2401109
C6	–2.4684718	–1.9283744	–0.2696471
H7	–4.2953269	0.9855116	0.1704391
H8	–2.0494955	1.9364604	0.2083093
H9	–0.3691673	–2.0486526	–0.3872426
H10	–2.6374573	–2.9867245	–0.4320398
O11	–4.7991940	–1.5580046	–0.1116343
C12	0.2878457	0.5129465	–0.0021695
C13	0.5288853	2.0135928	0.0950881
F14	0.0305584	2.5296134	1.2481029
F15	1.8358062	2.3270391	0.0693712
F16	–0.0544277	2.6996594	–0.9204618
C17	1.4982091	–0.3501320	–0.0046004
C18	2.4389559	–0.2788834	–1.0425257
C19	1.7190927	–1.2495903	1.0481684

C20	3.5598368	−1.1024531	−1.0351512
H21	2.2858862	0.4116502	−1.8635765
C22	2.8492979	−2.0636657	1.0589854
H23	1.0087317	−1.2980826	1.8654394
C24	3.7698651	−1.9949908	0.0159083
H25	4.2714109	−1.0459826	−1.8508635
H26	3.0094805	−2.7478615	1.8843299
H27	4.6481131	−2.6302888	0.0223601

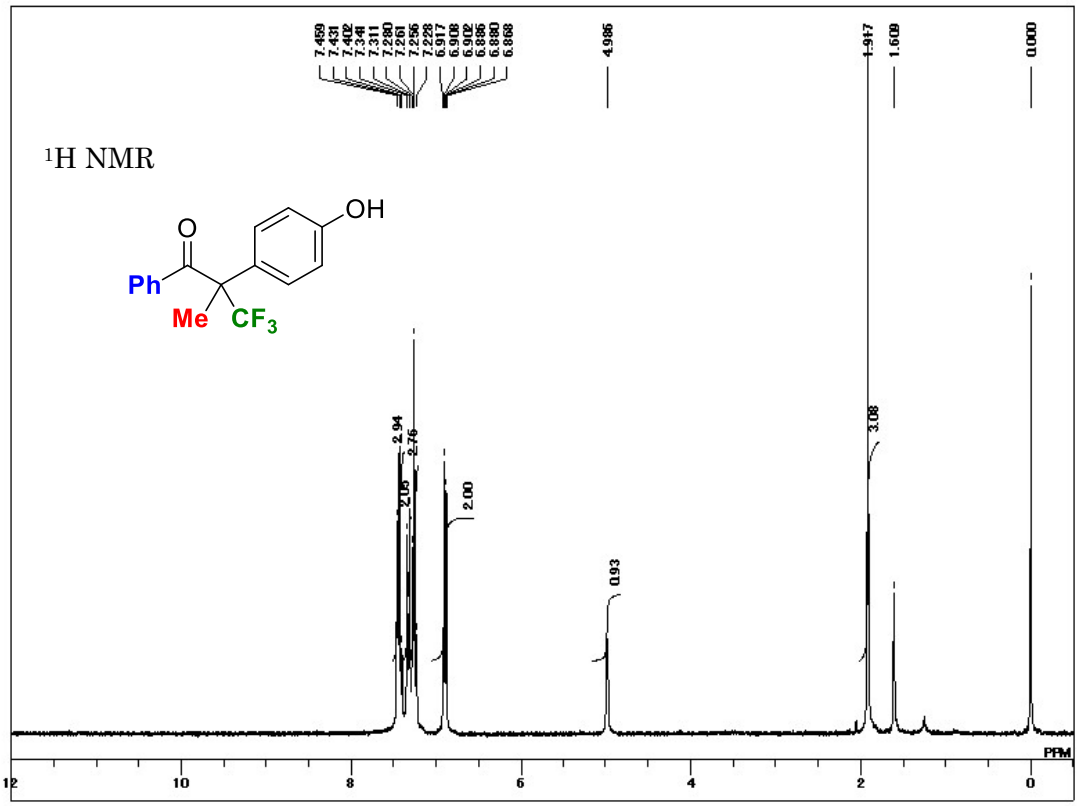
^{1}H and ^{13} C NMR spectrums

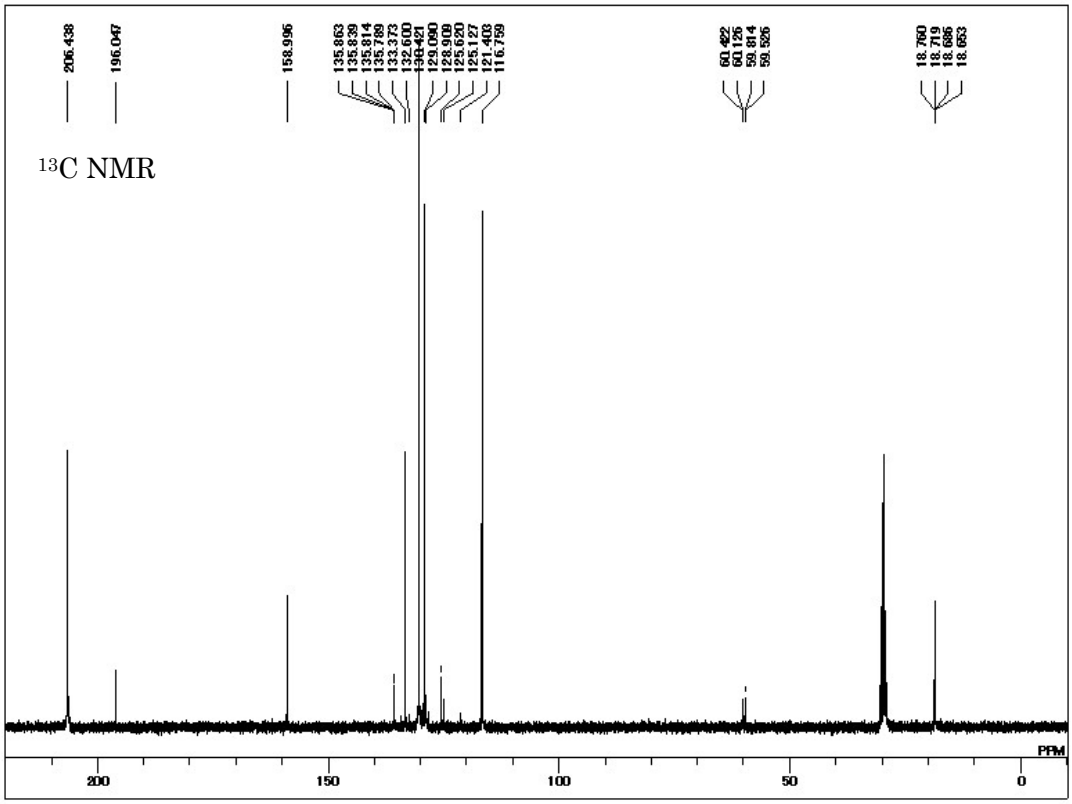
***pre*-NHC B**



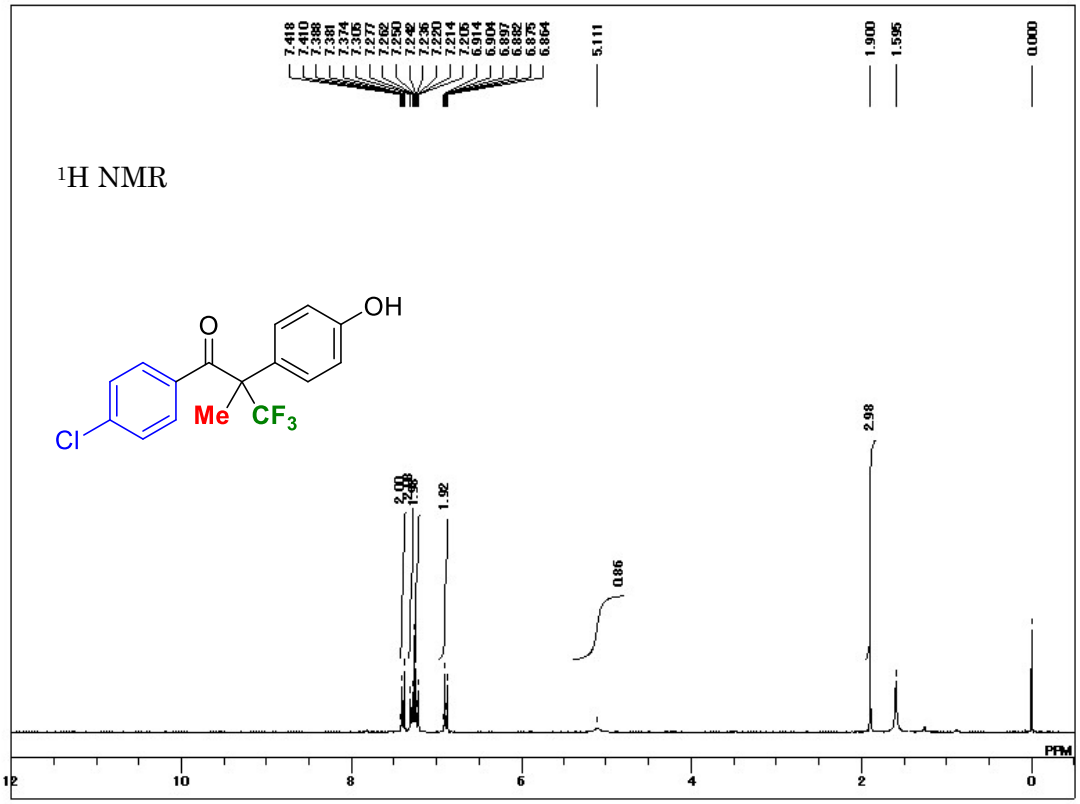


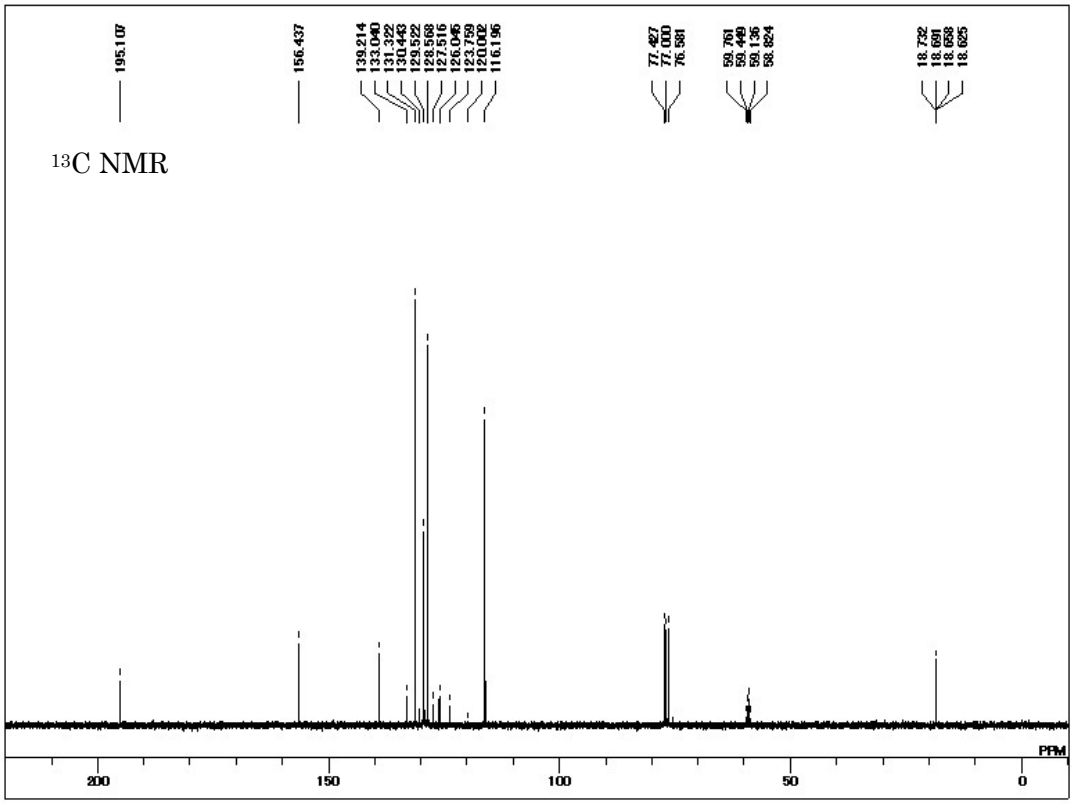
3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-phenylpropan-1-one. (3aa)



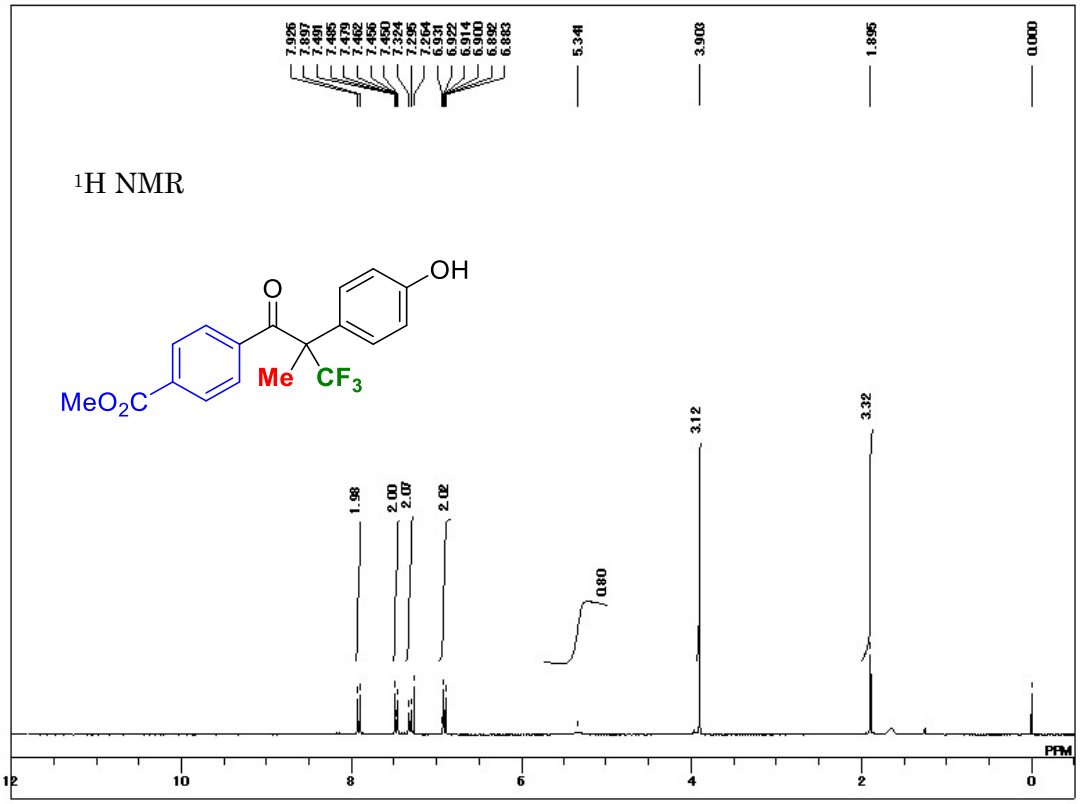


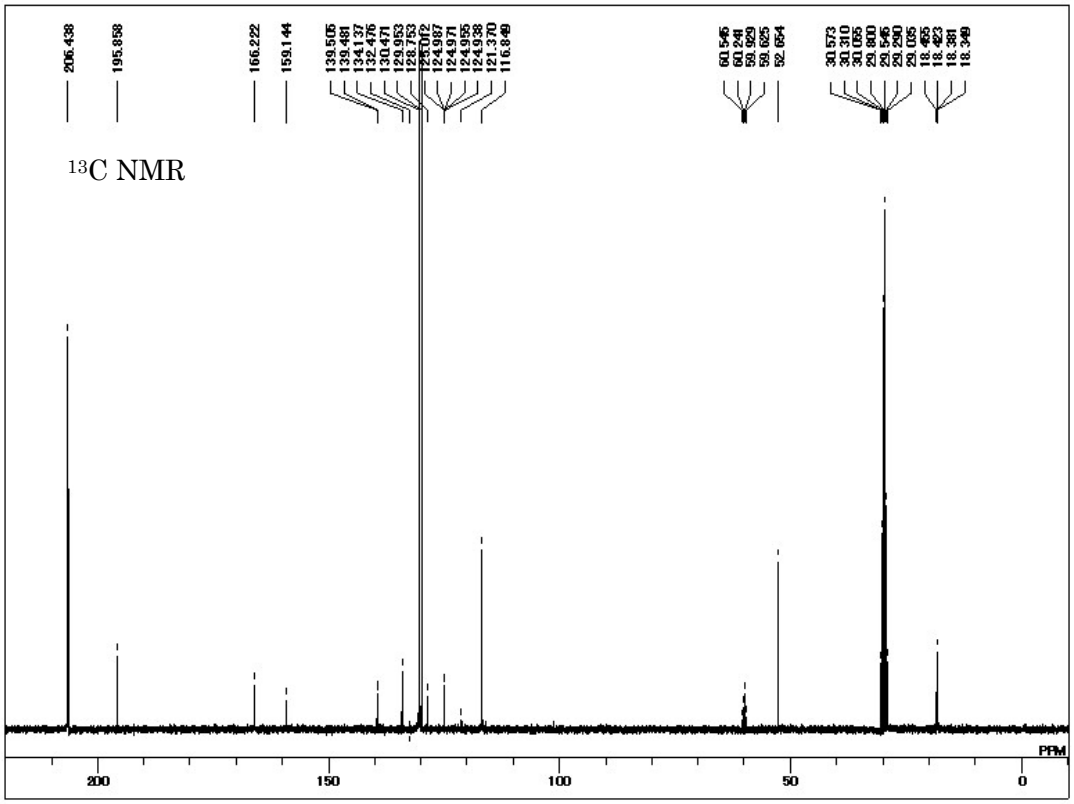
1-(4-Chlorophenyl)-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methylpropan-1-one. (3ab)



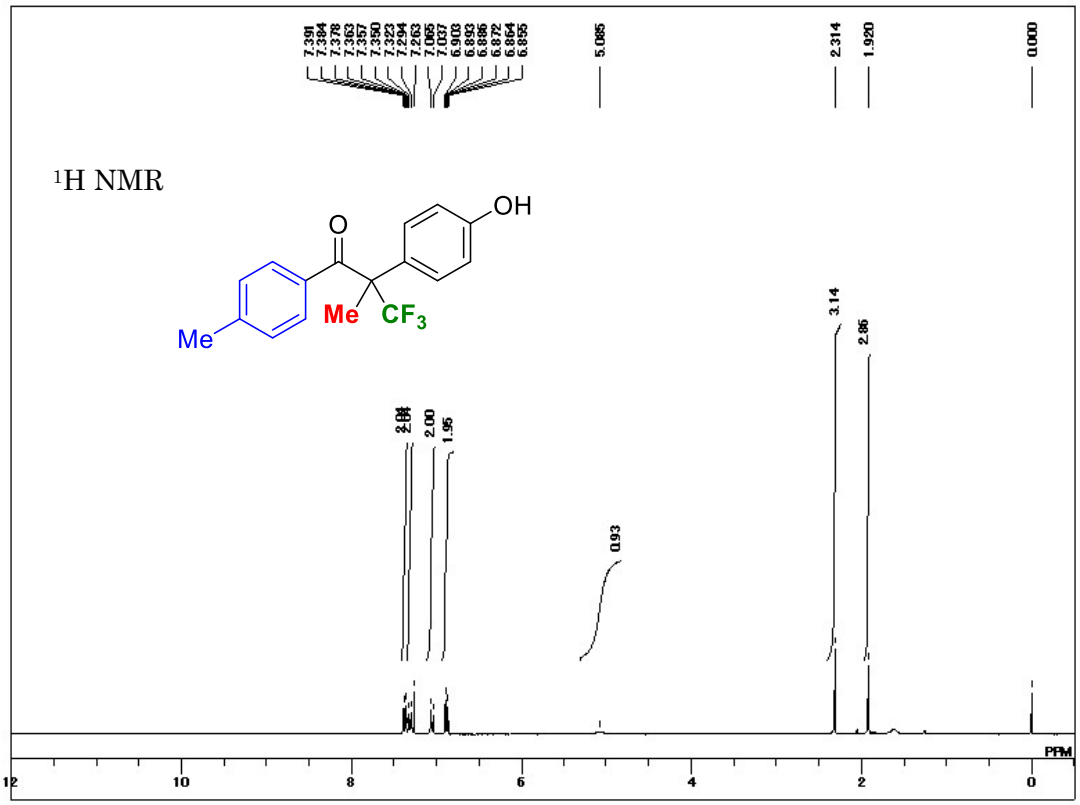


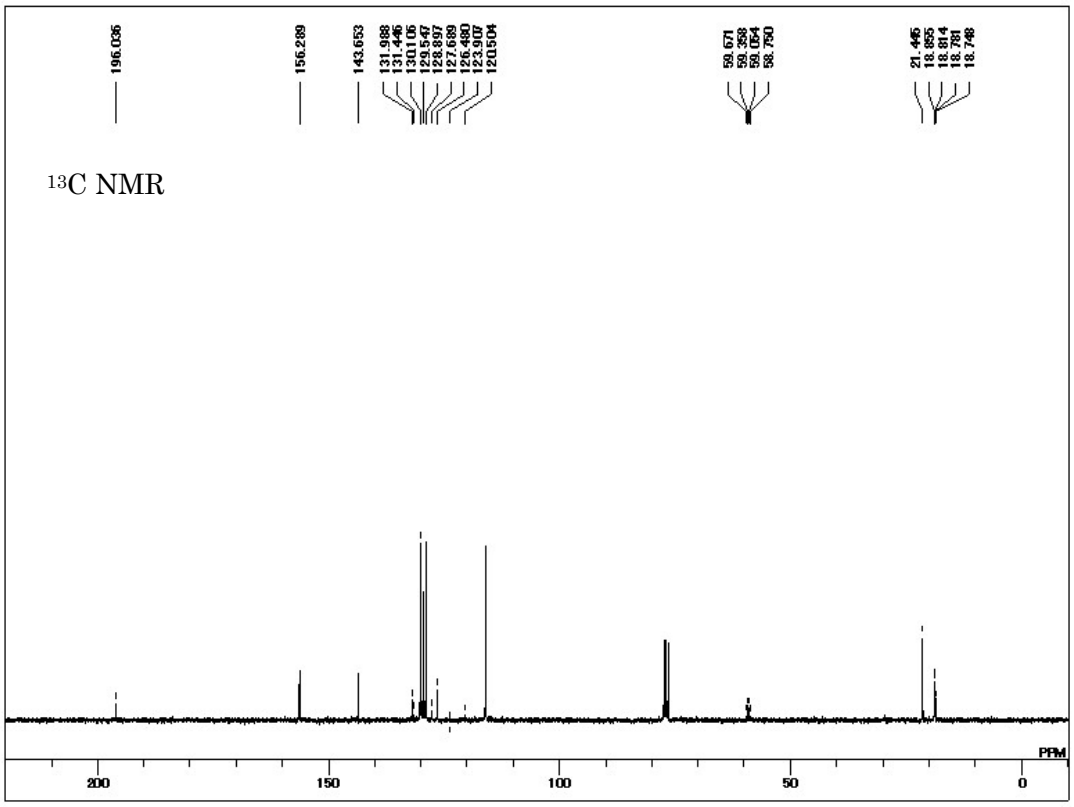
3,3,3-Trifluoro-2-(4-hydroxyphenyl)-1-(4-methoxycarbonylphenyl)-2-methylpropan-1-one. (3ac)



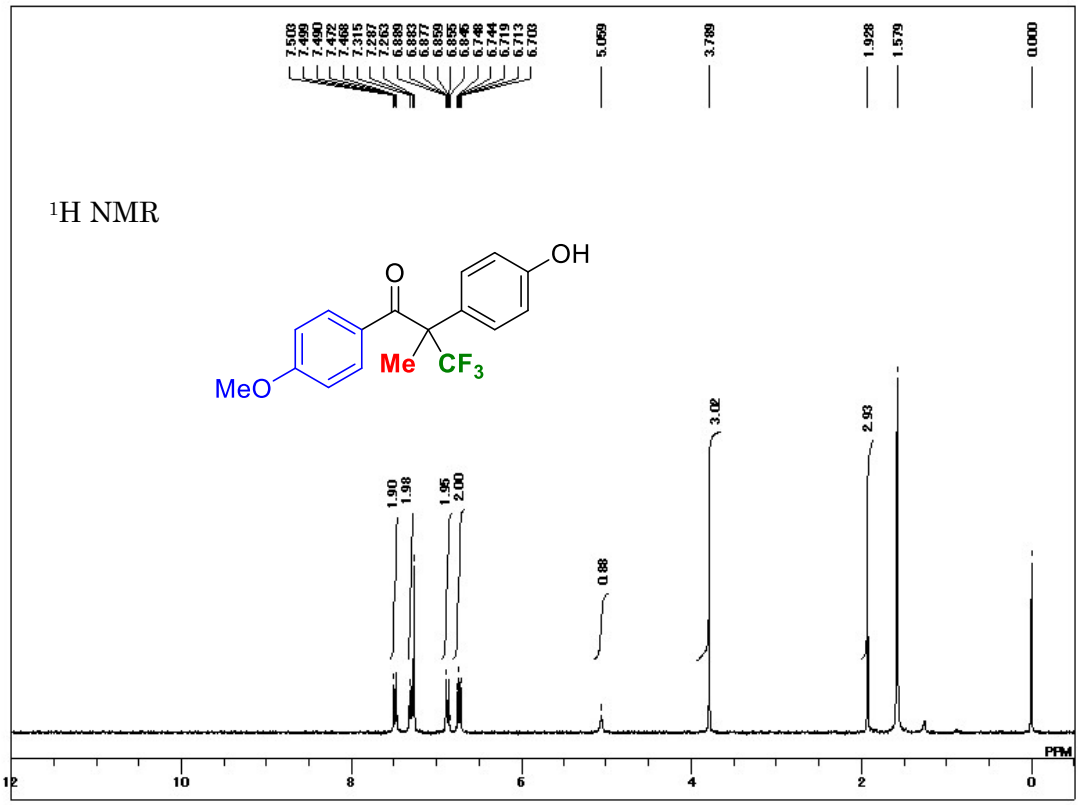


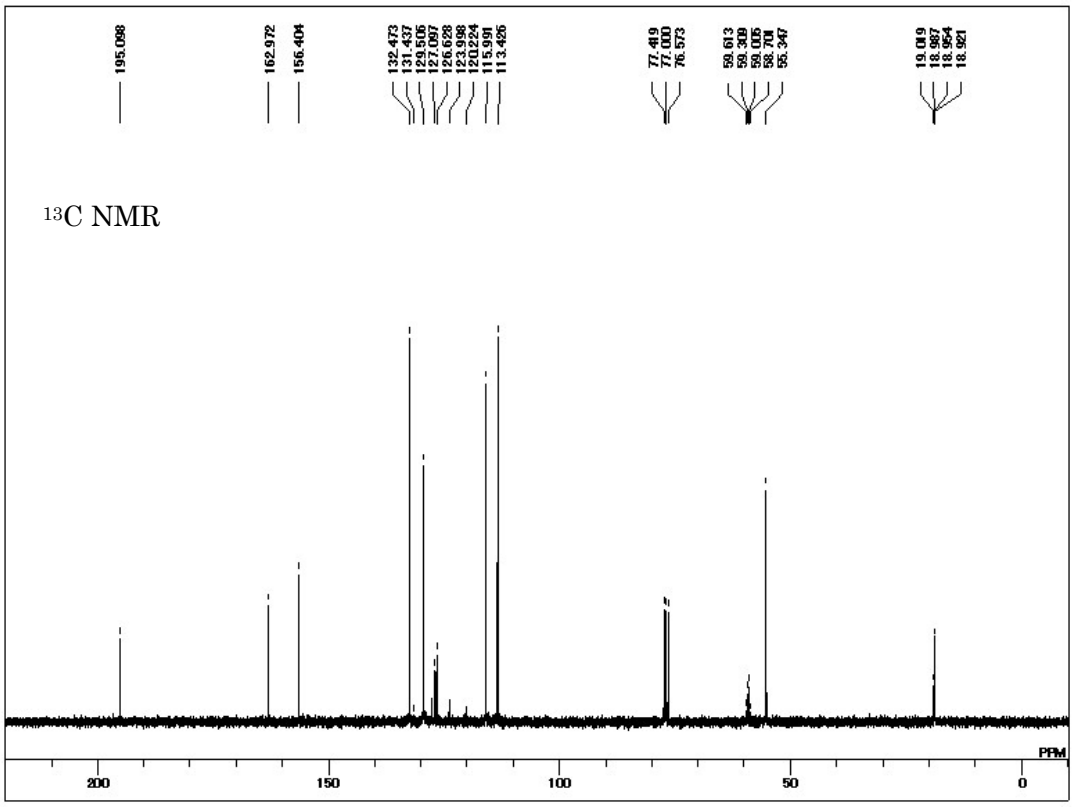
3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-(4-methylphenyl)propan-1-one. (**3ae**)



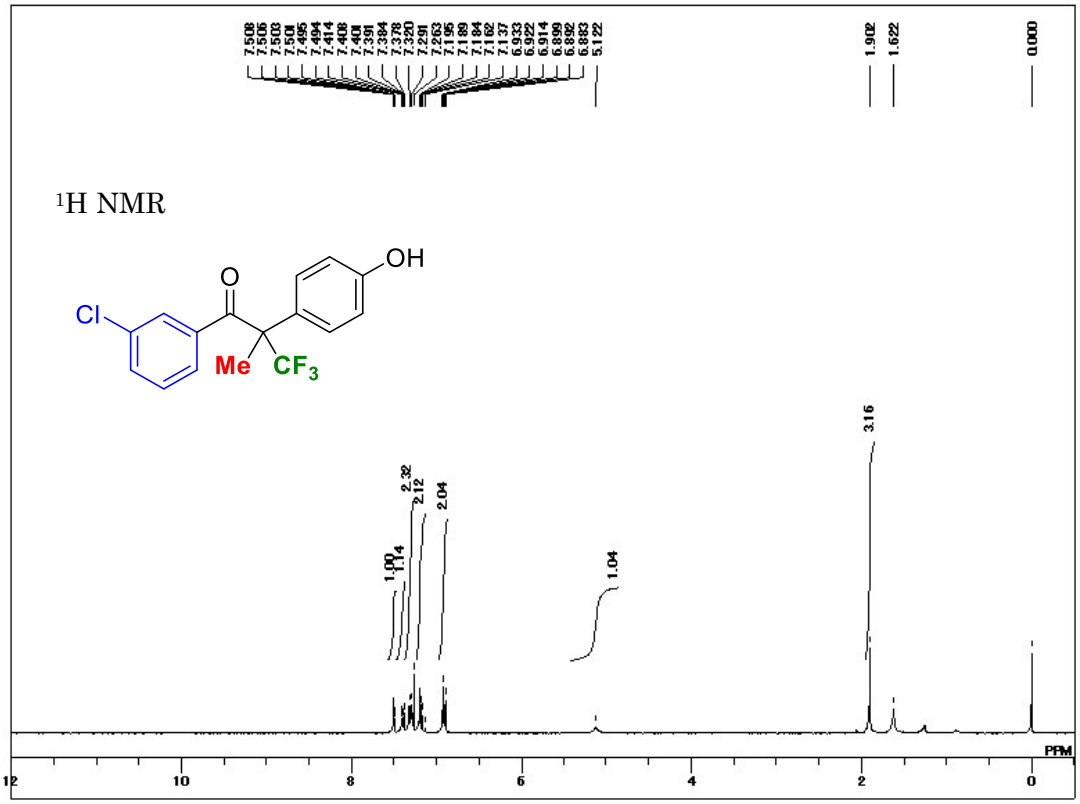


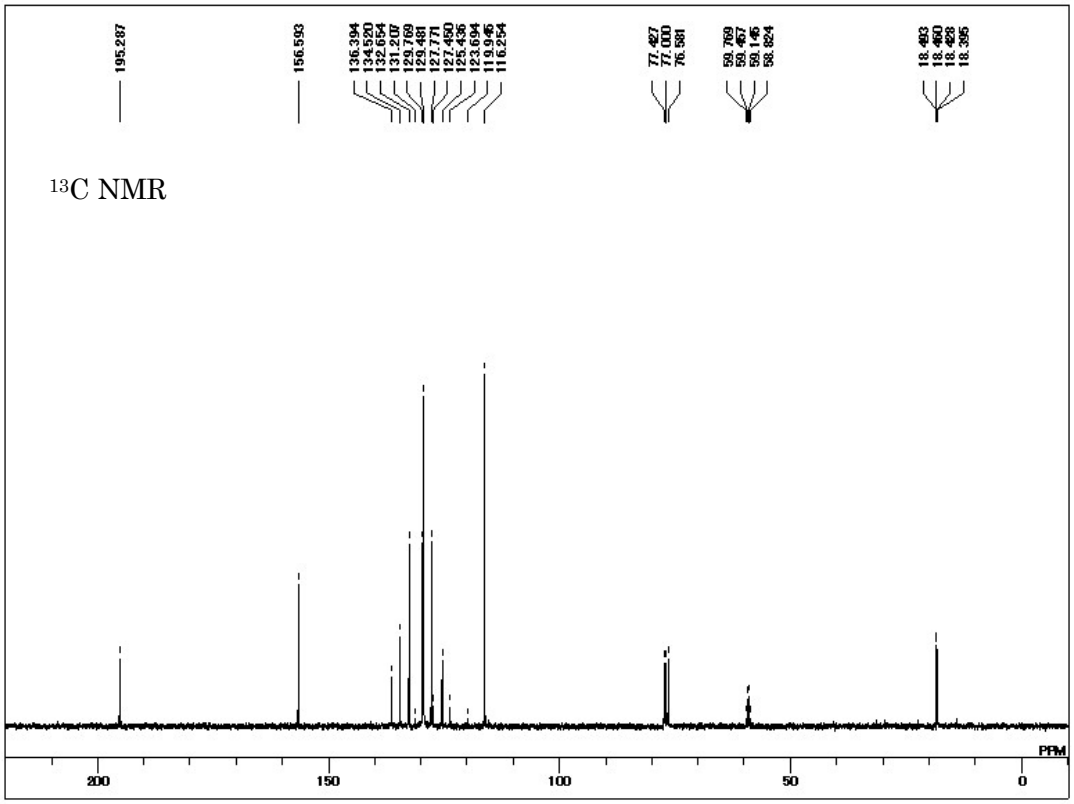
3,3,3-Trifluoro-2-(4-hydroxyphenyl)-1-(4-methoxyphenyl)-2-methylpropan-1-one. (3af)



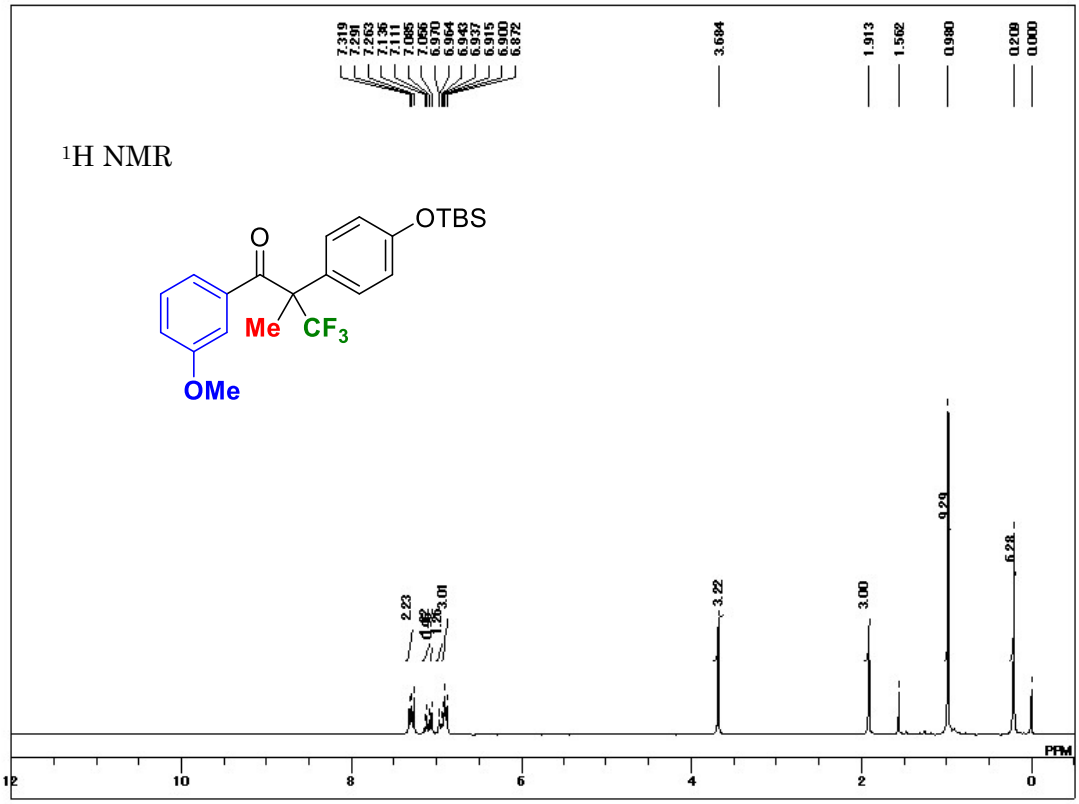


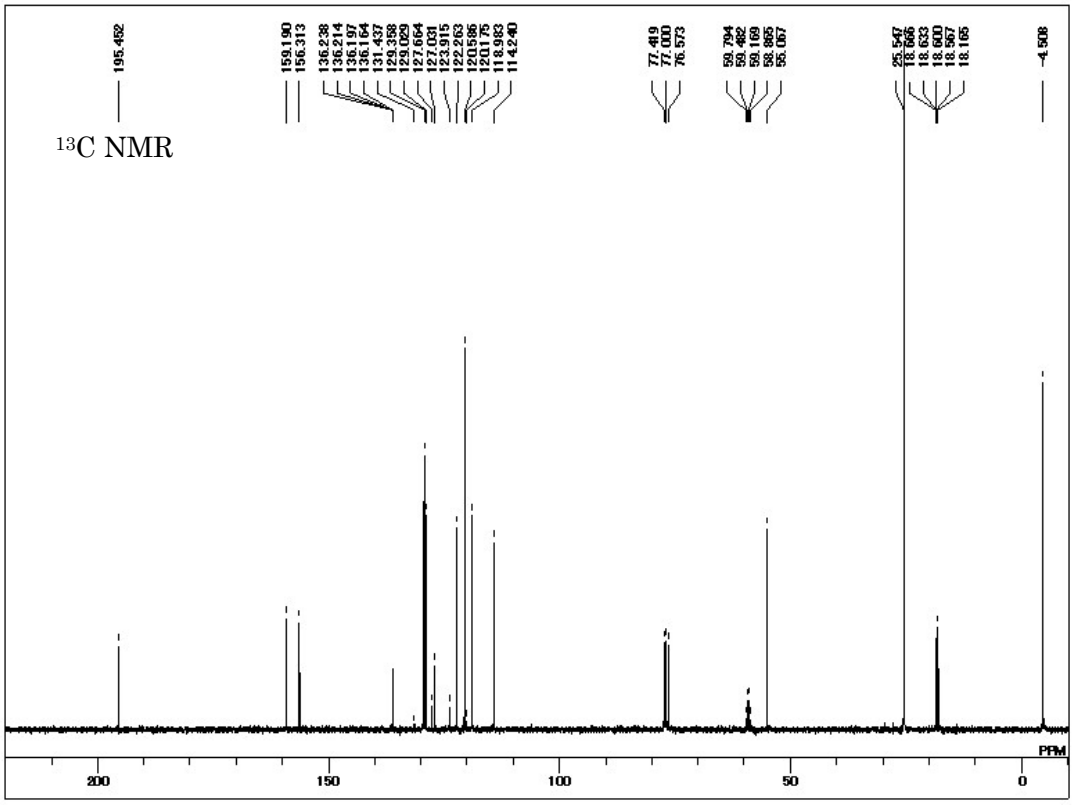
1-(3-Chlorophenyl)-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methylpropan-1-one. (3ag)



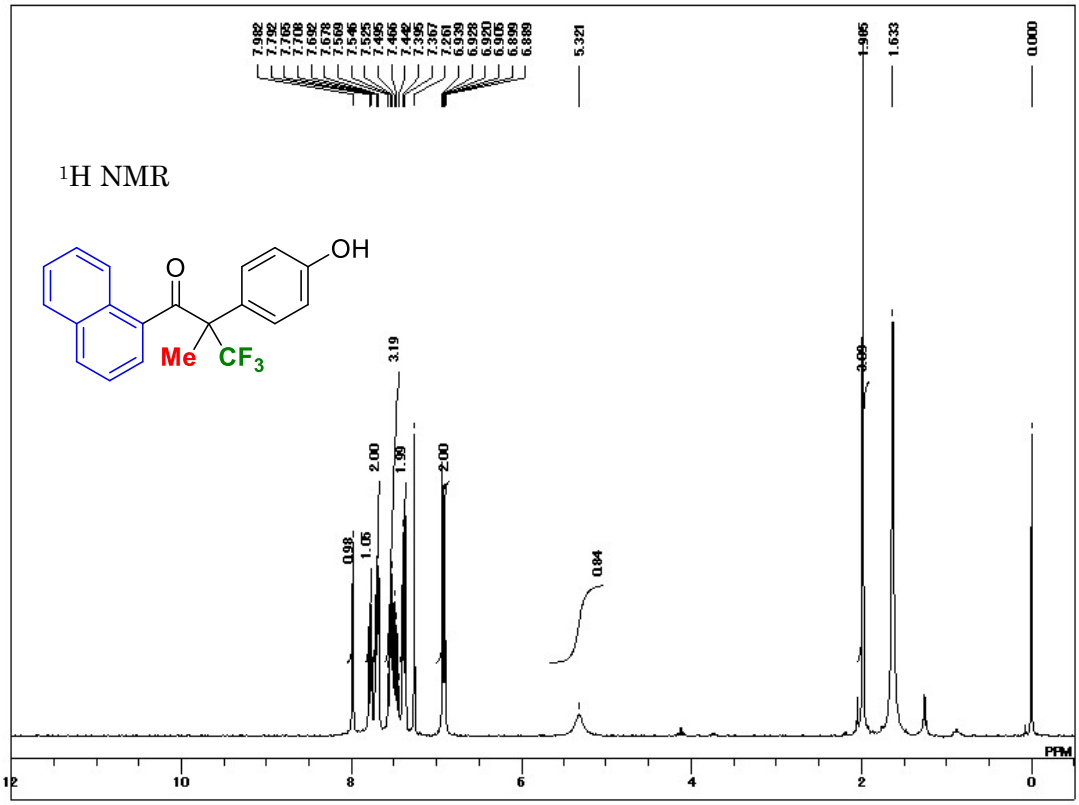


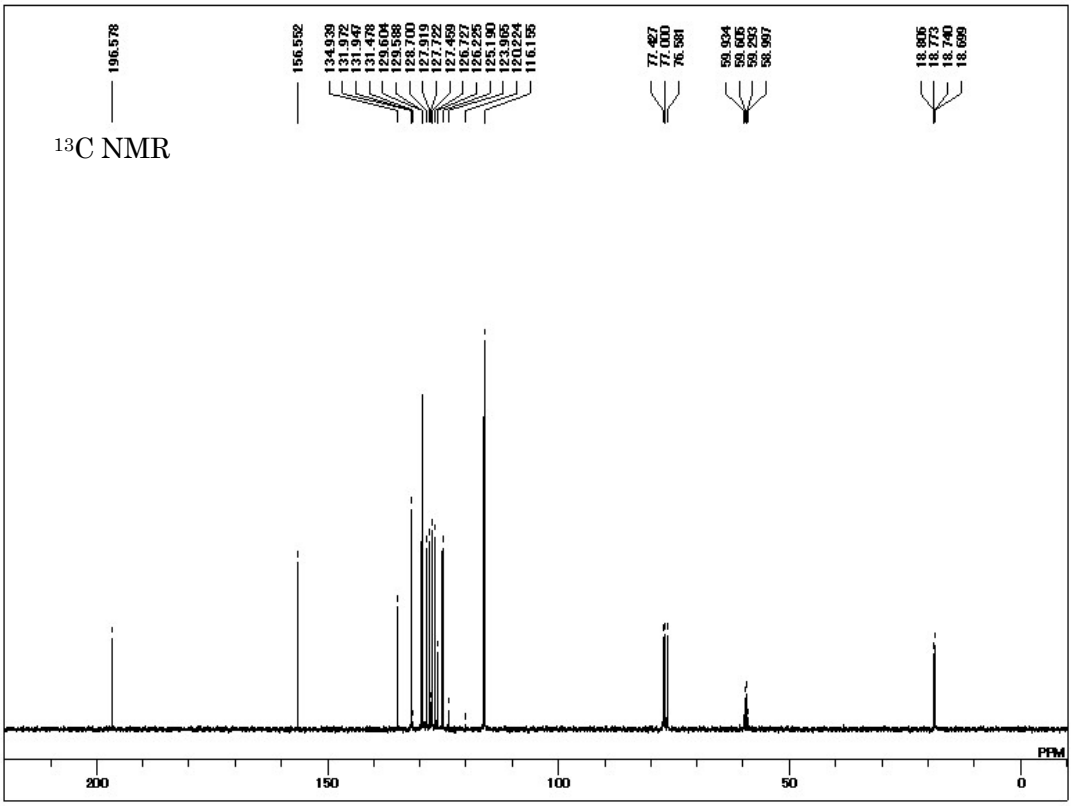
2-[4-[{(1,1-Dimethylethyl)dimethylsilyl}oxy]phenyl]-3,3,3-trifluoro-1-(3-methoxyphenyl)-2-methylpropan-1-one. (3ai)





3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-(1-naphthyl)propan-1-one. (3aj)





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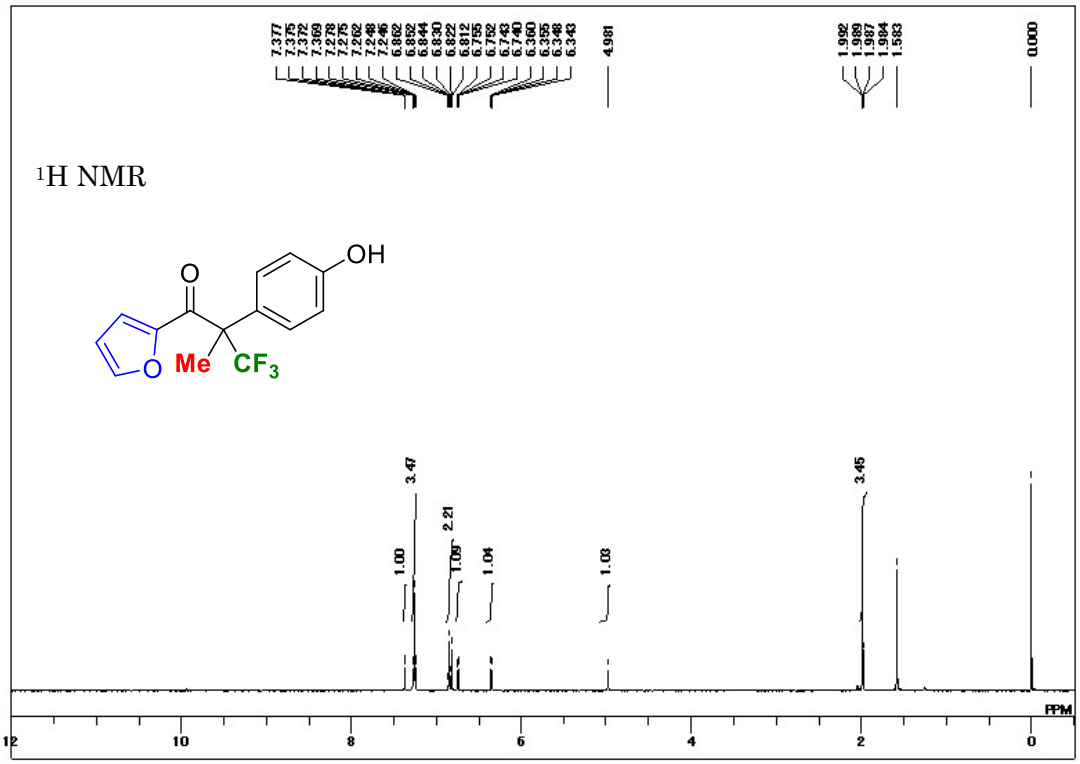

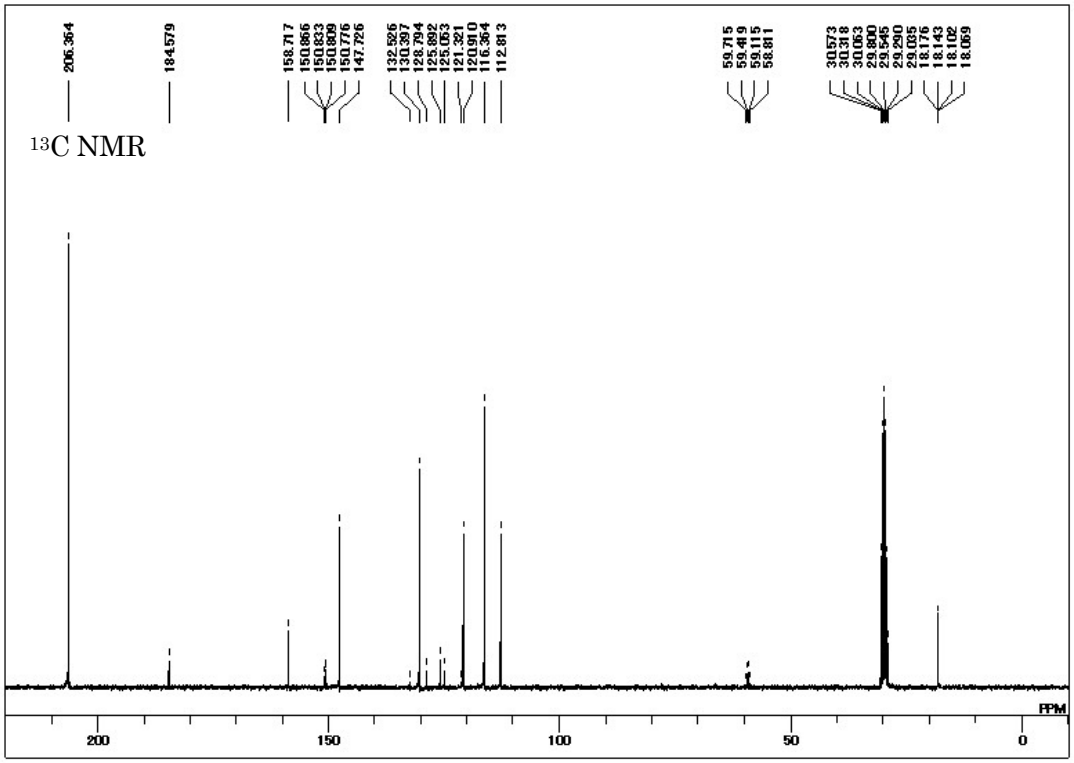

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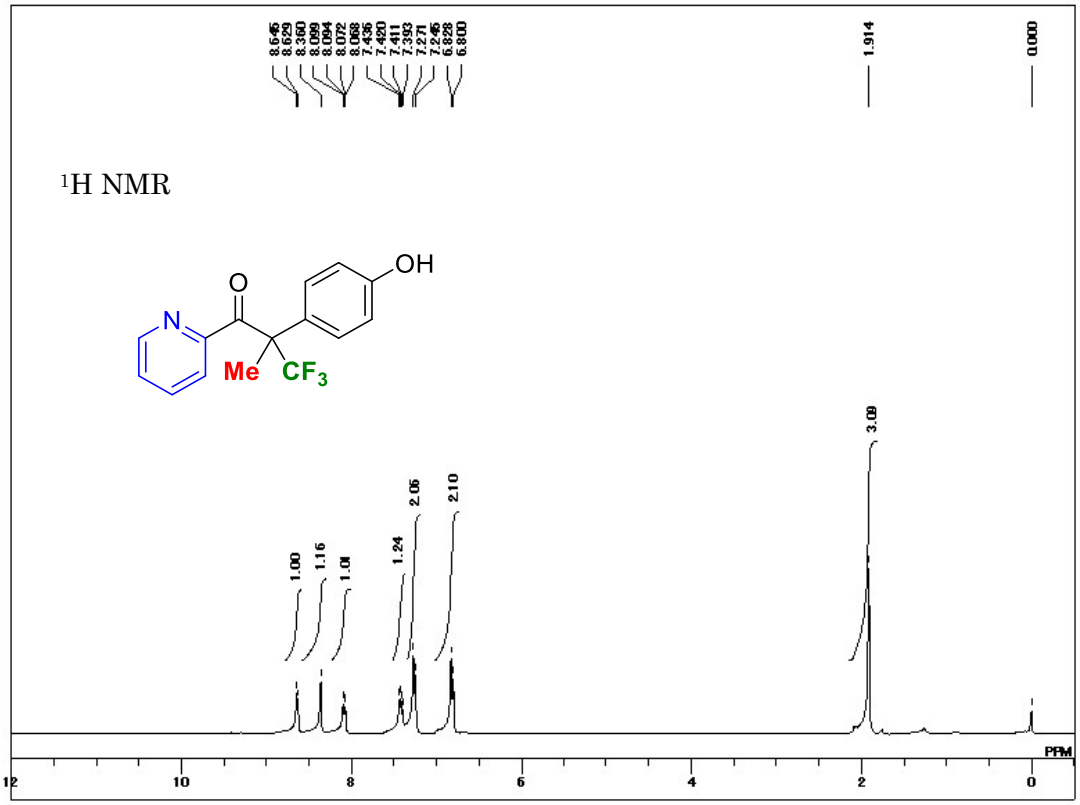

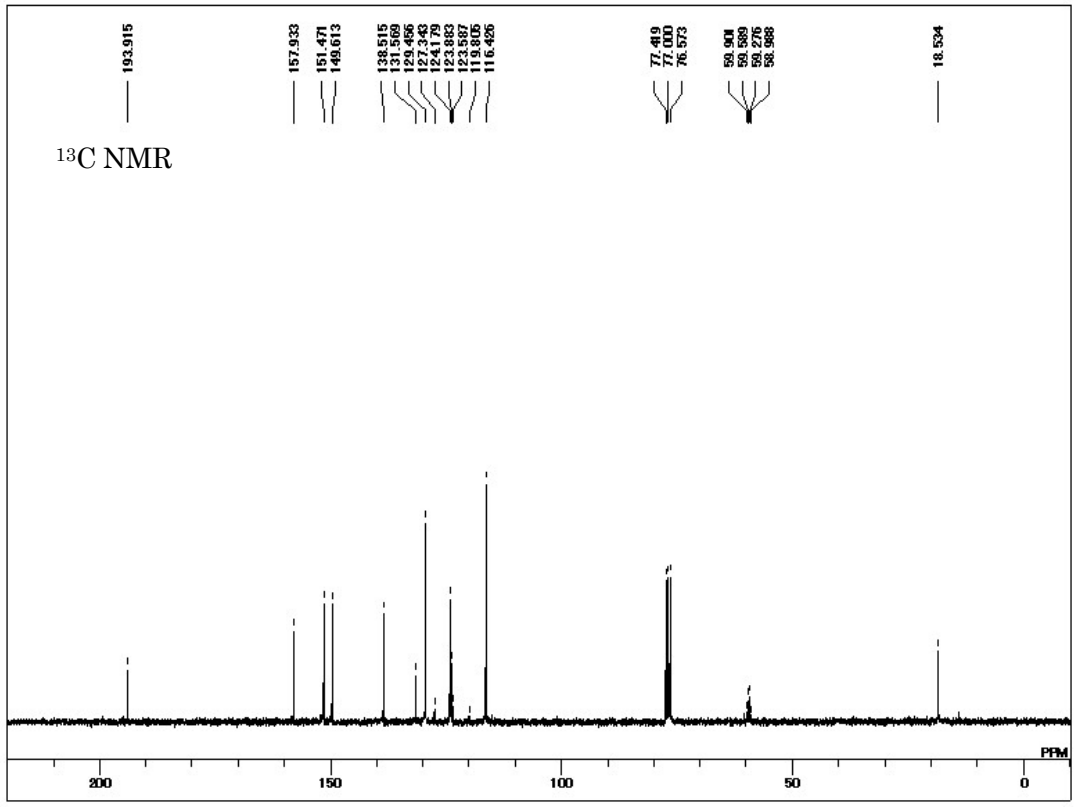

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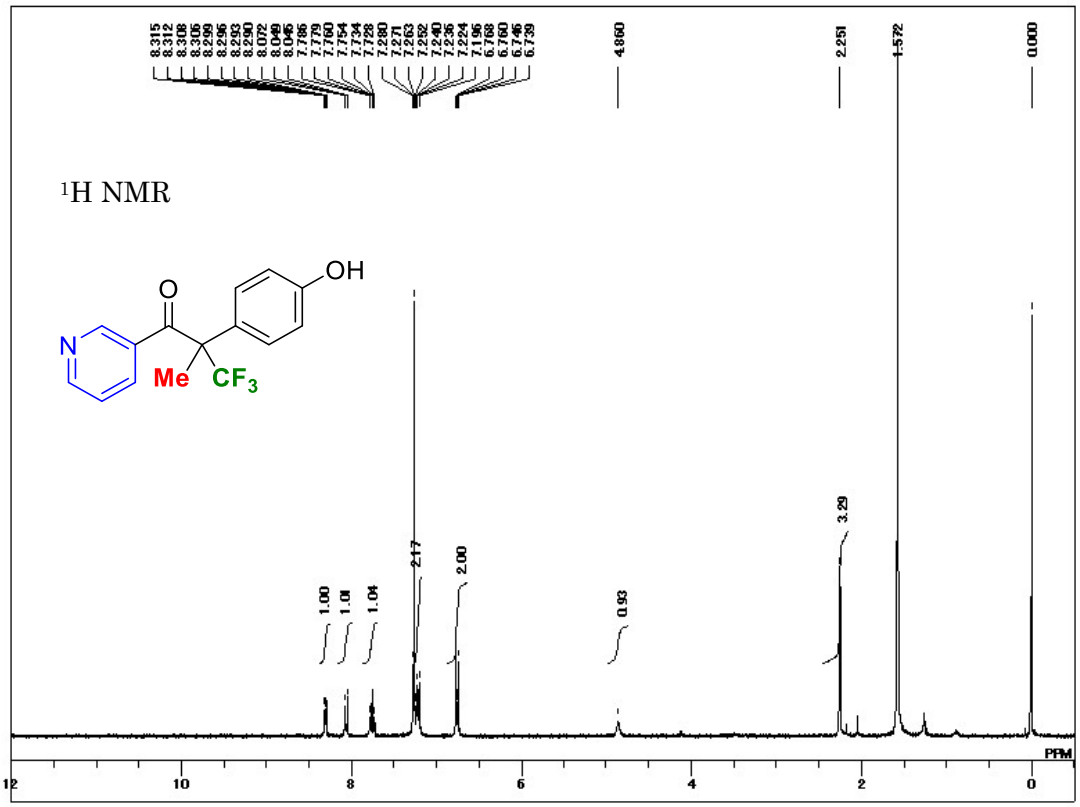
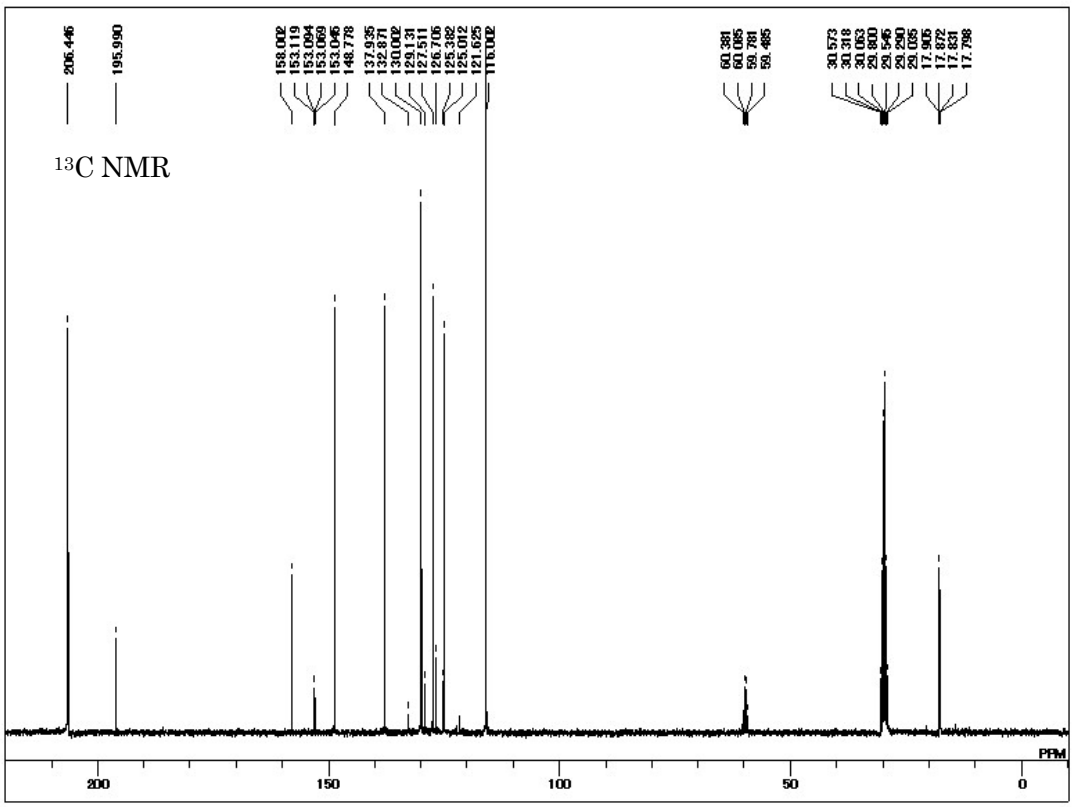
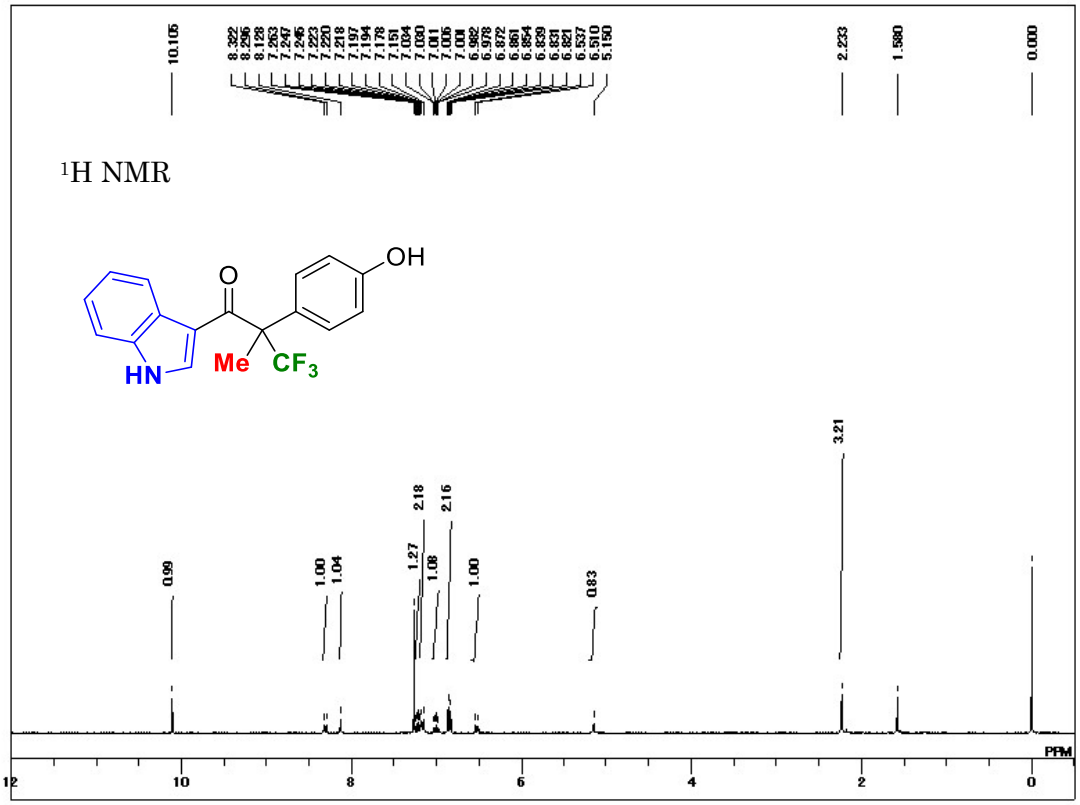
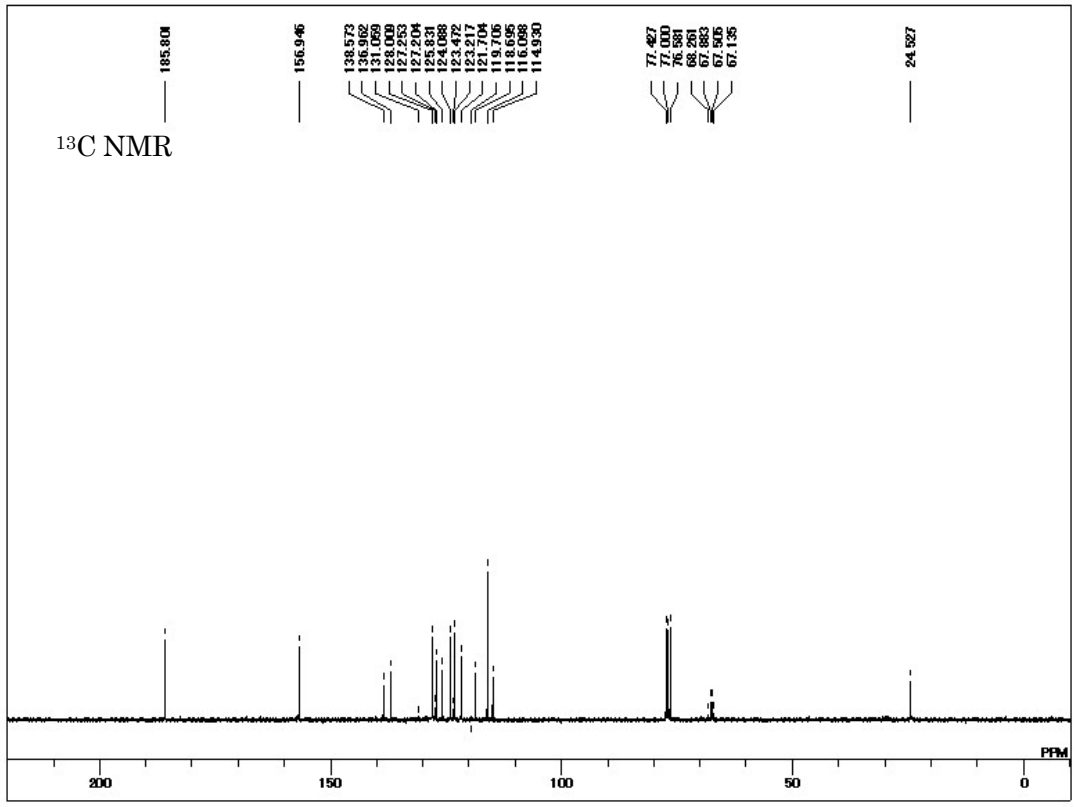


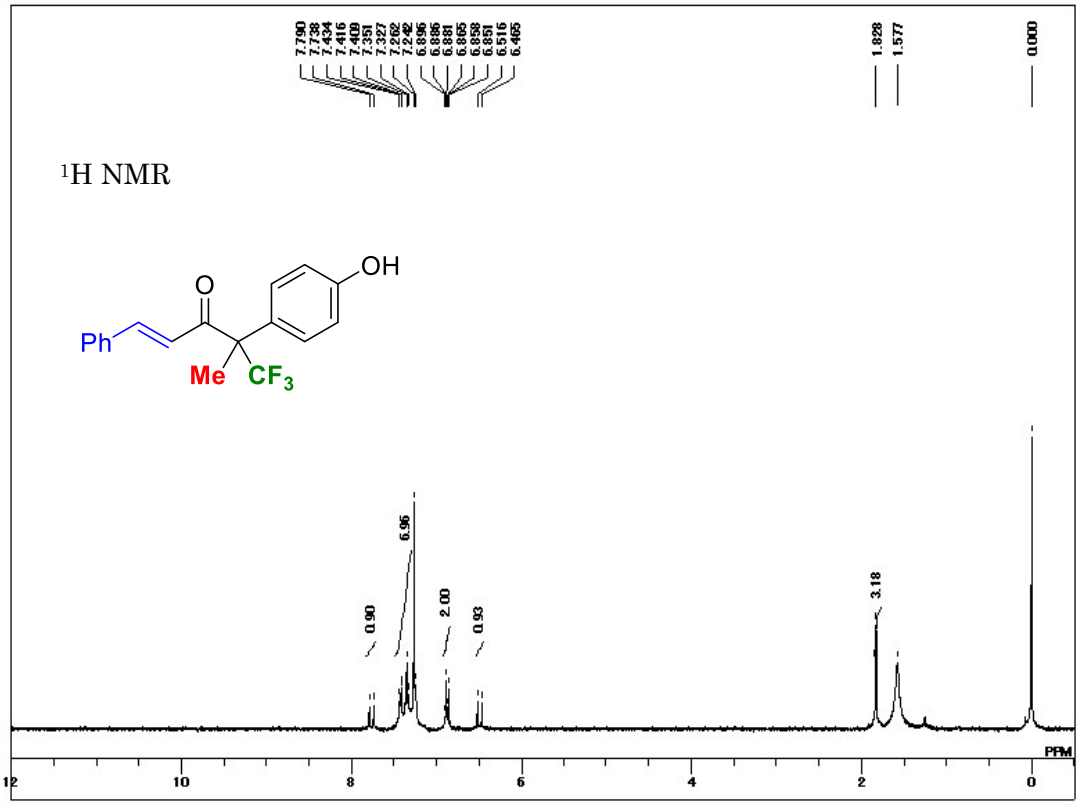


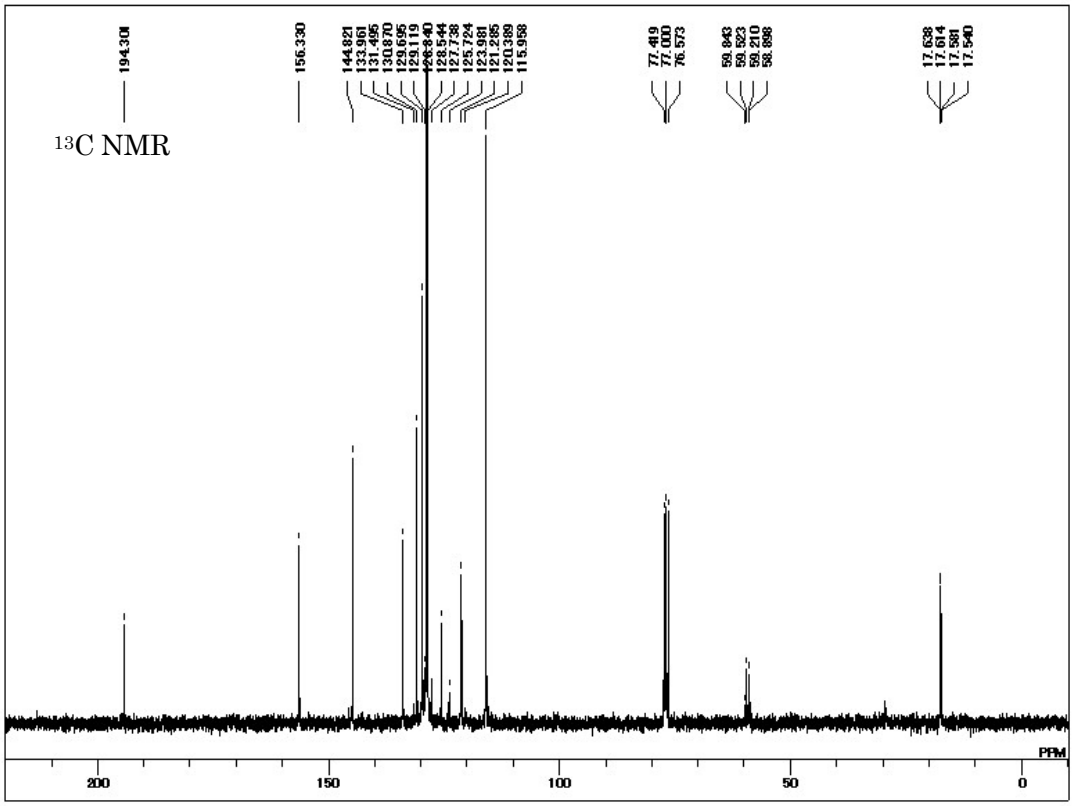
3,3,3-Trifluoro-2-(4-hydroxyphenyl)-1-(1*H*-indol-3-yl)-2-methylpropan-1-one (3an)



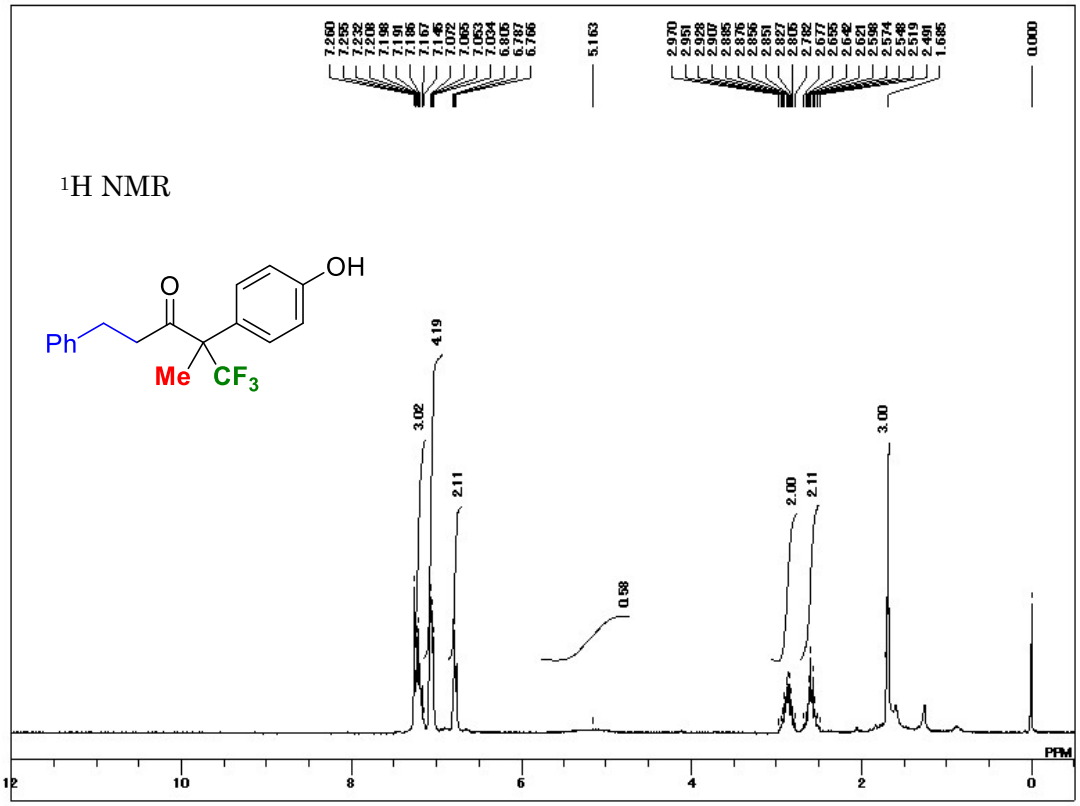


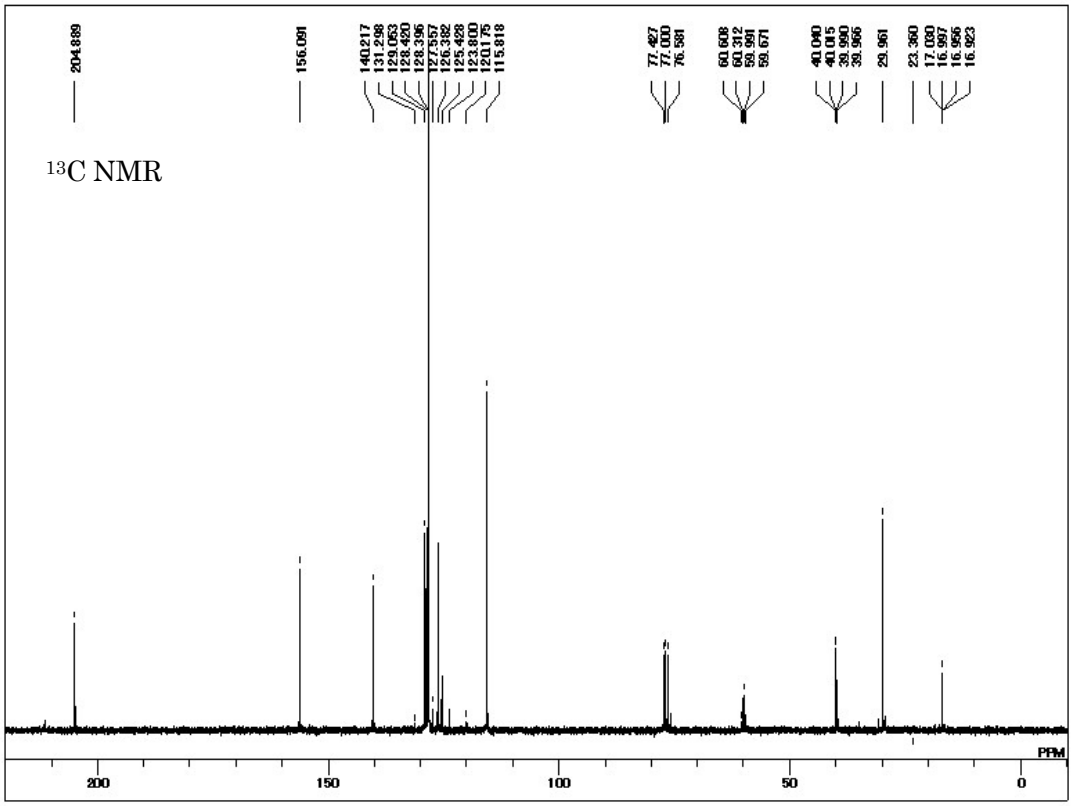
5,5,5-Trifluoro-4-(4-hydroxyphenyl)-4-methyl-1-phenylprop-1-en-3-one (3ao)



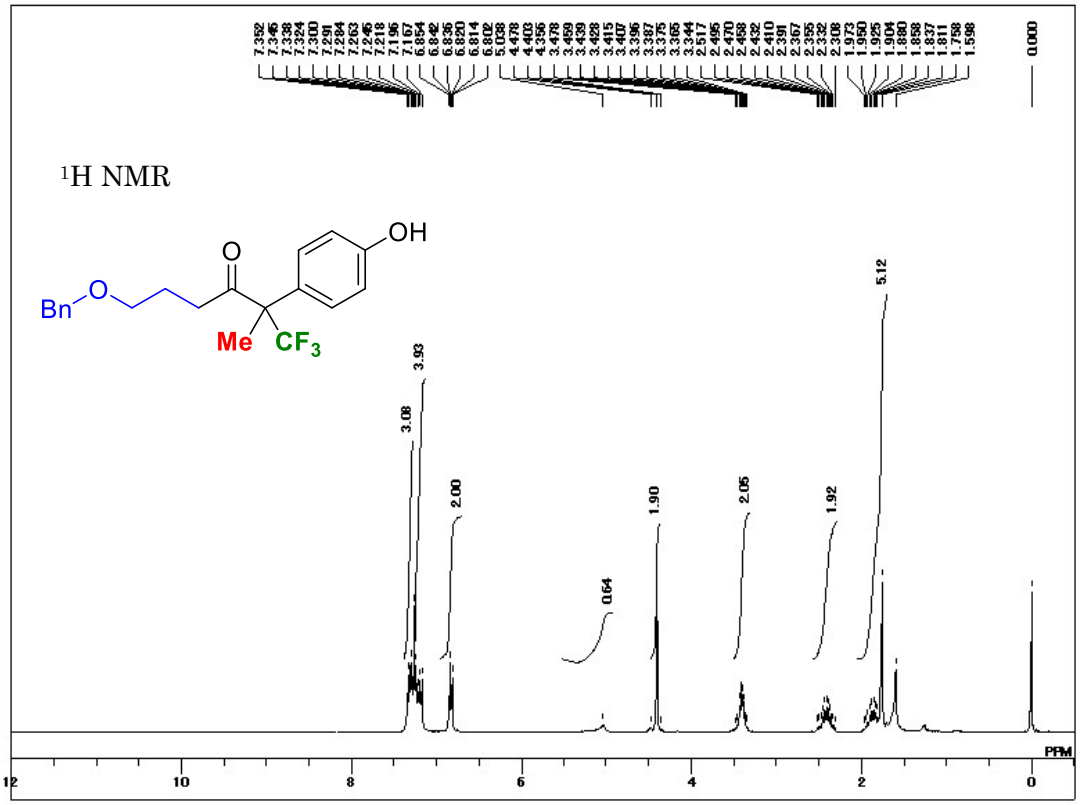


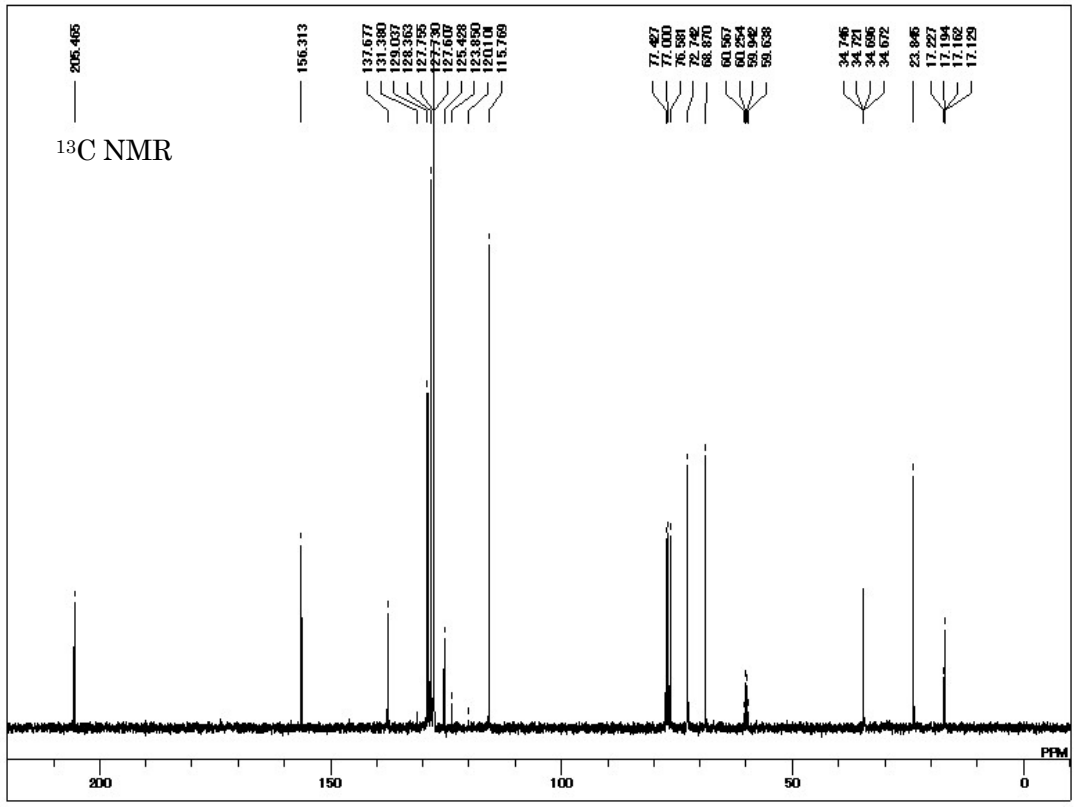
1,1,1-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-5-phenylpentan-3-one (3aq)



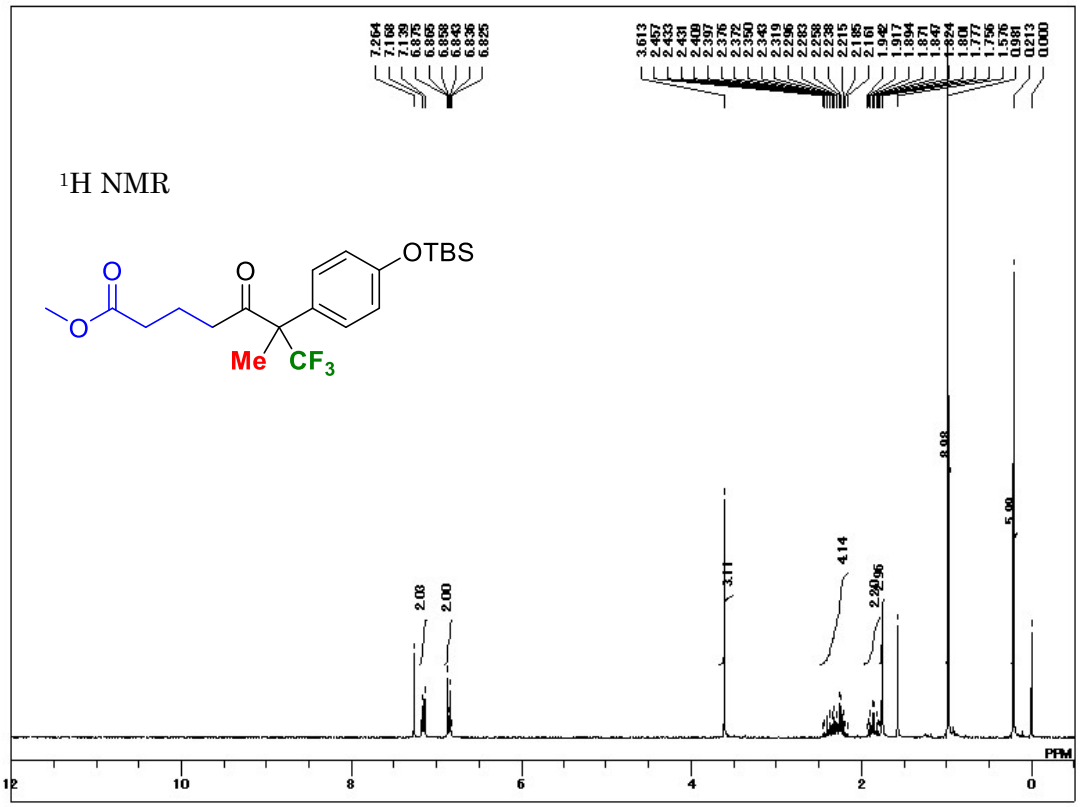


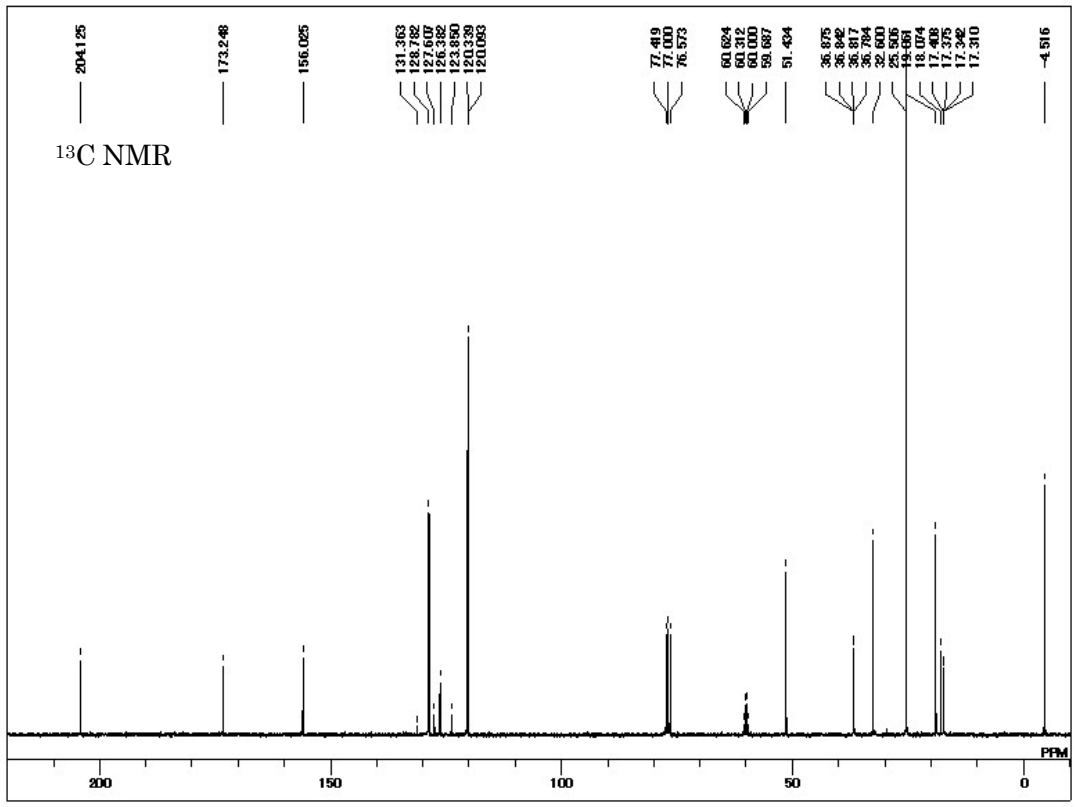
6-Benzyloxy-1,1,1-trifluoro-2-(4-hydroxyphenyl)-2-methylhexan-3-one (3ar)



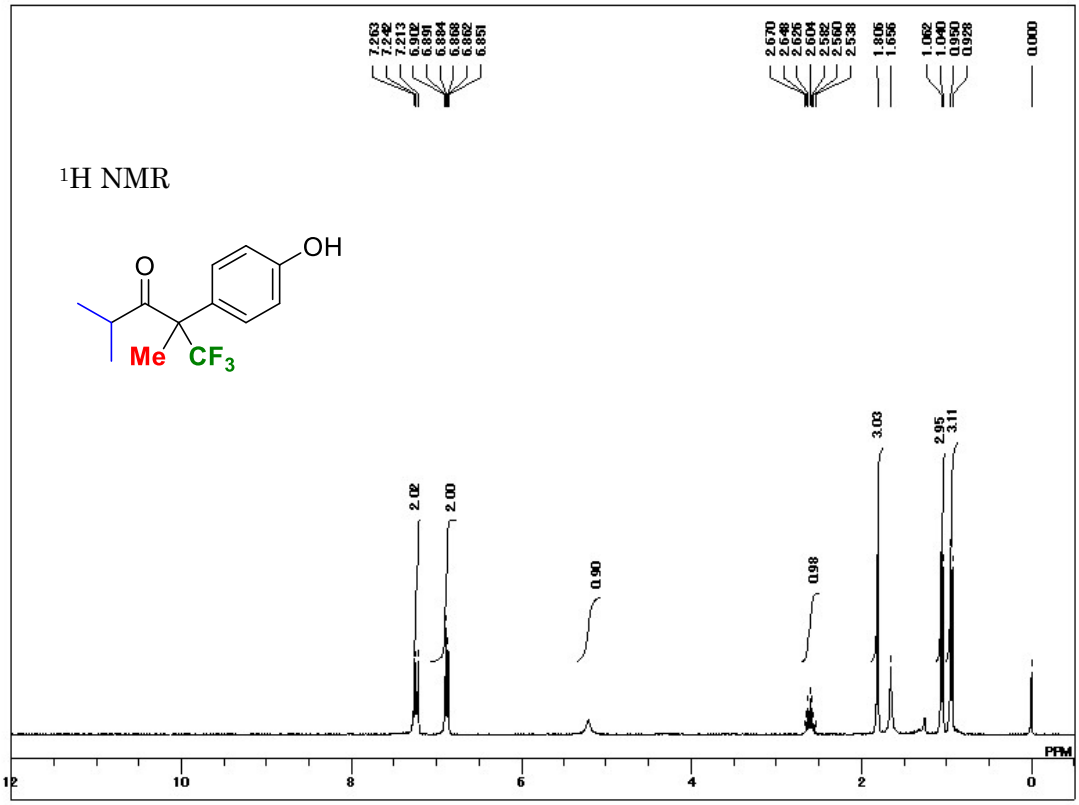


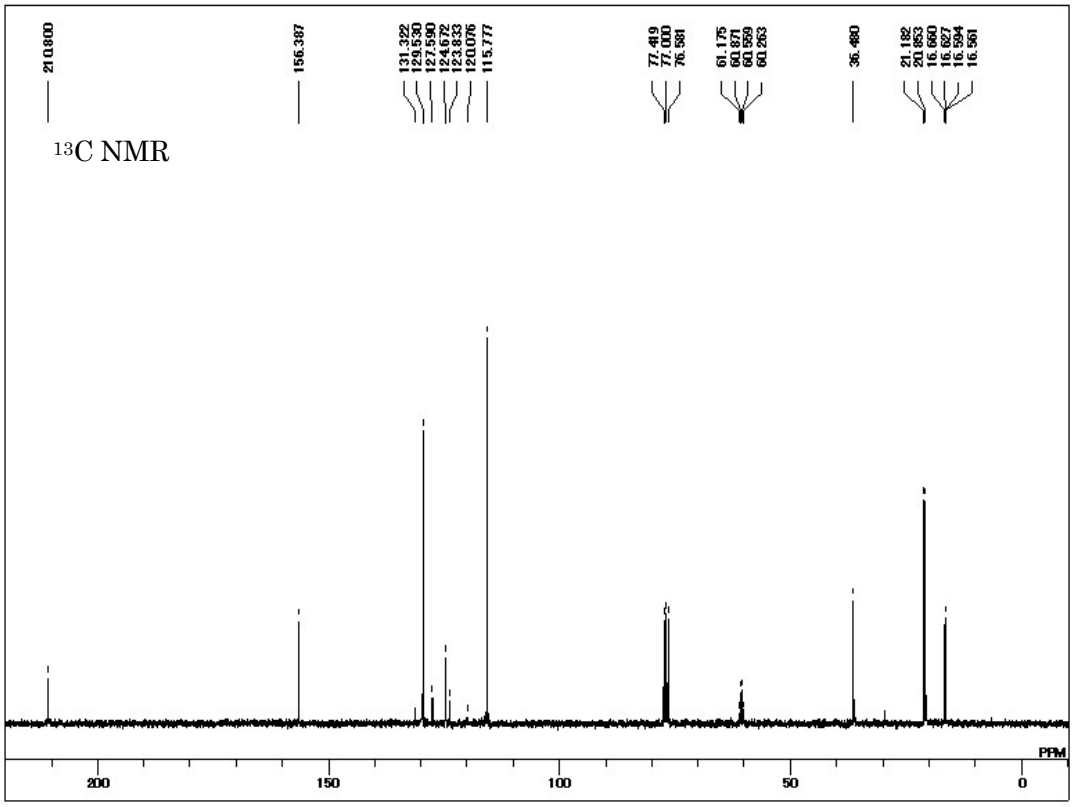
Methyl 7,7,7-trifluoro-6-(4-hydroxyphenyl)-6-methyl-5-oxoheptanoate (3as)



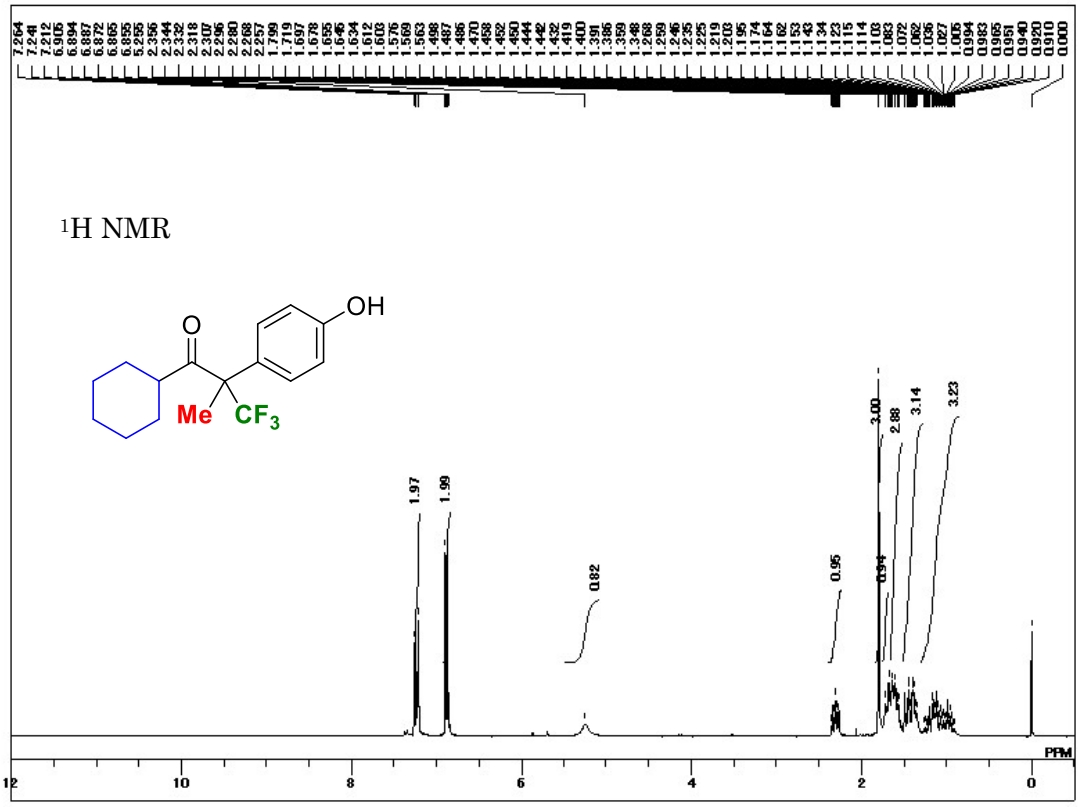


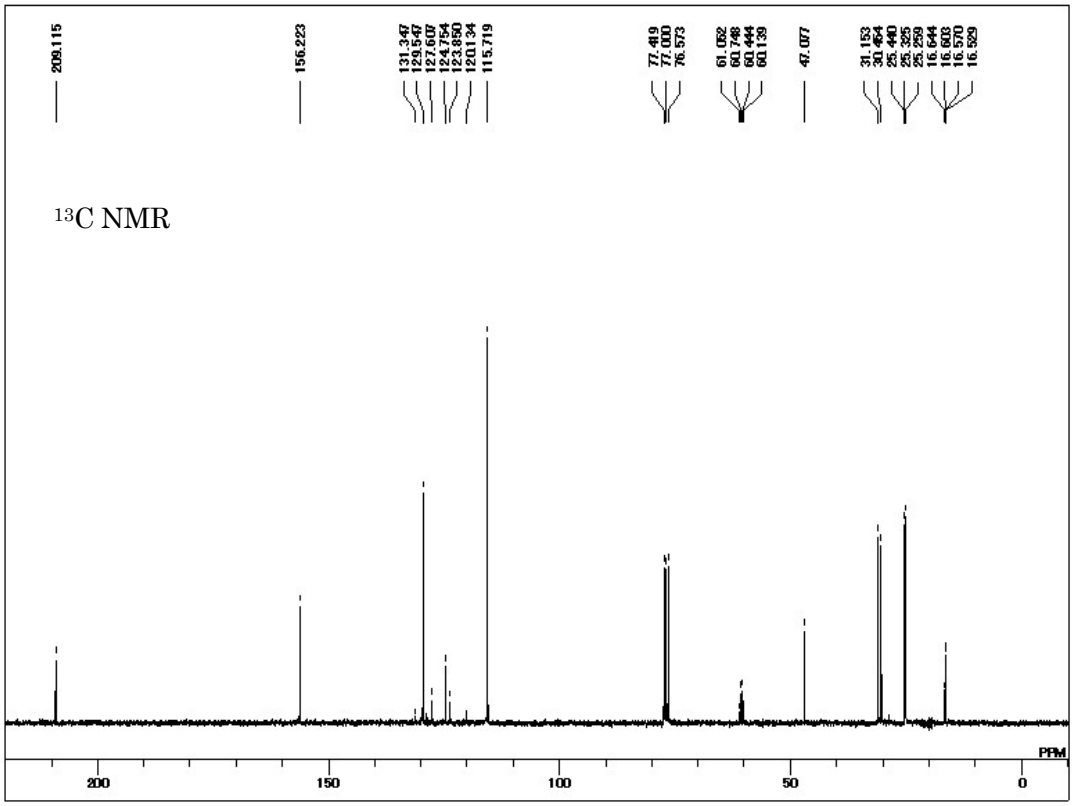
1,1,1-Trifluoro-2-(4-hydroxyphenyl)-2,4-dimethylpentan-3-one (3at)



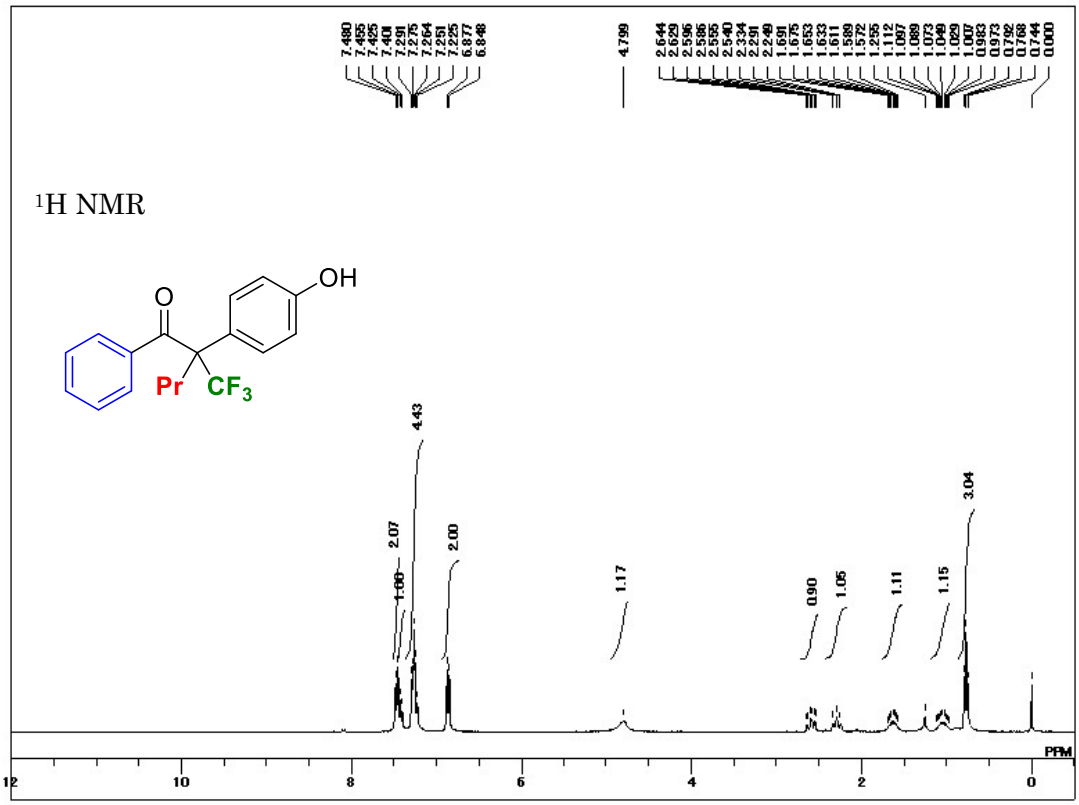


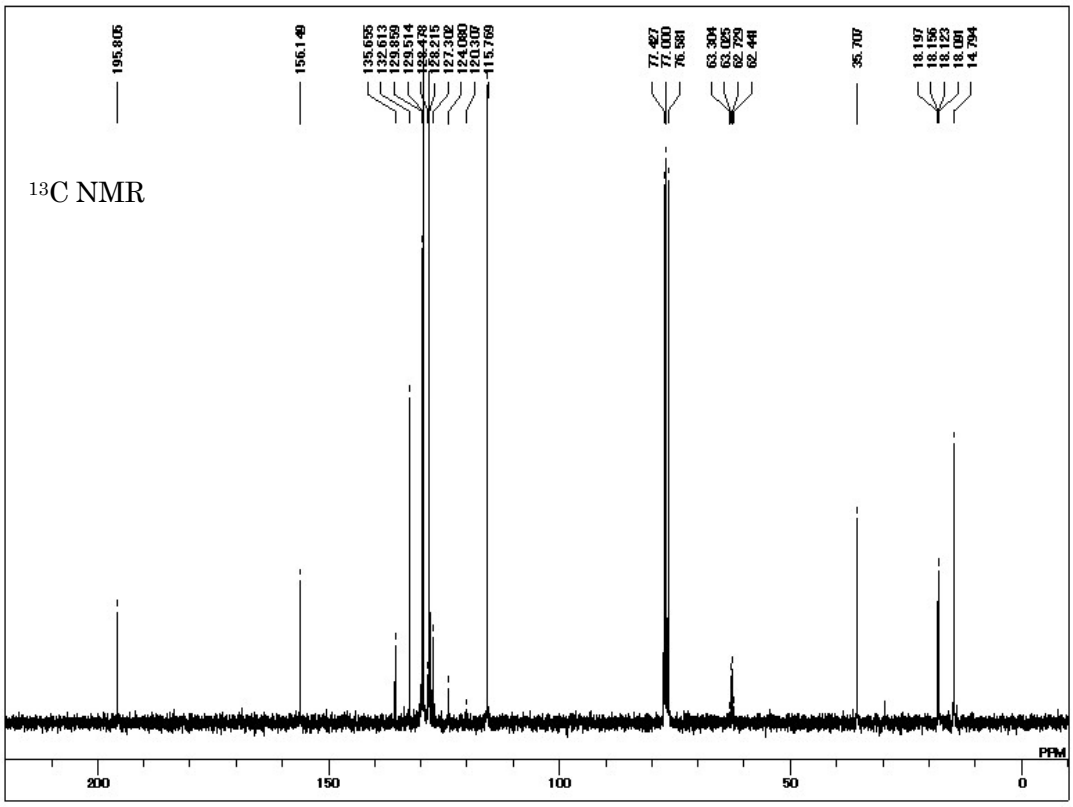
1-Cyclohexyl-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methylpropan-1-one (3au)



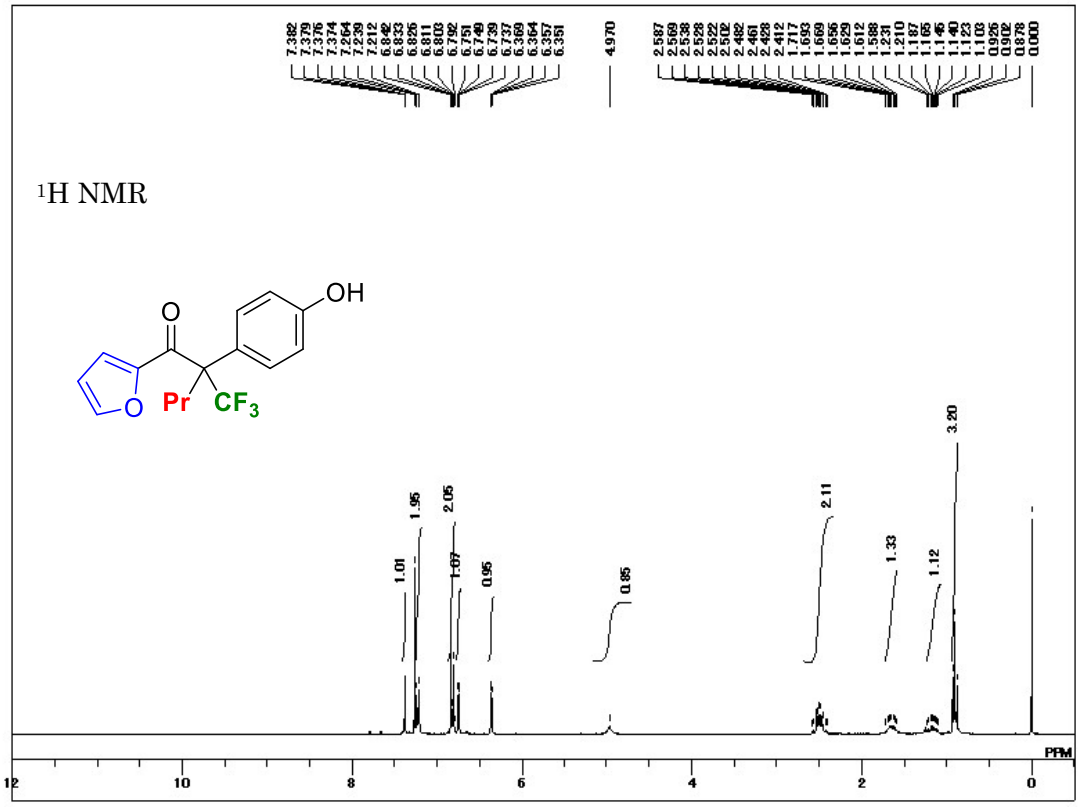


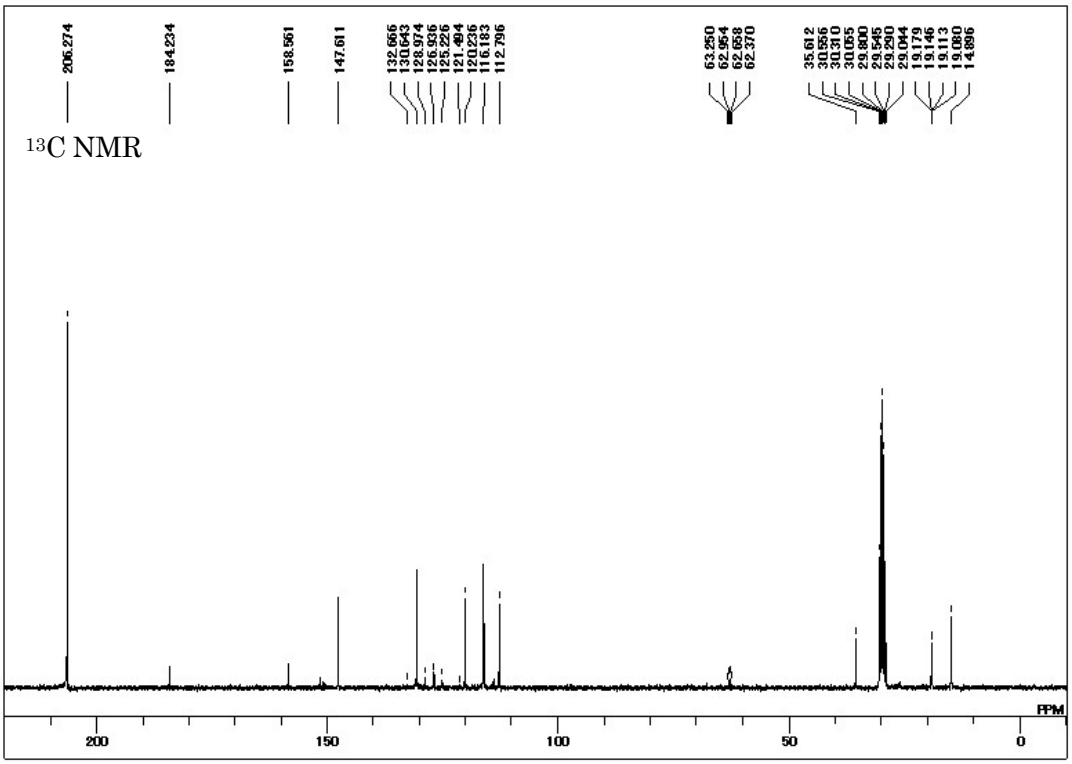
2-(4-Hydroxyphenyl)-1-phenyl-2-(trifluoromethyl)pentan-1-one. (3ba)



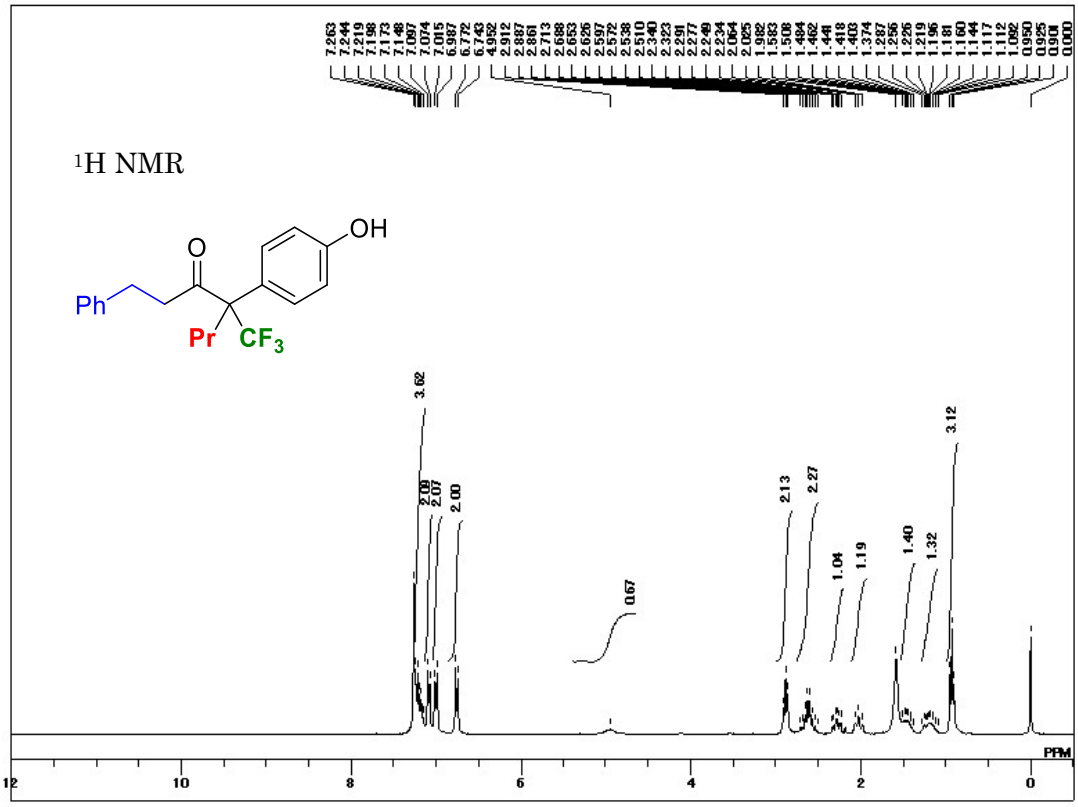


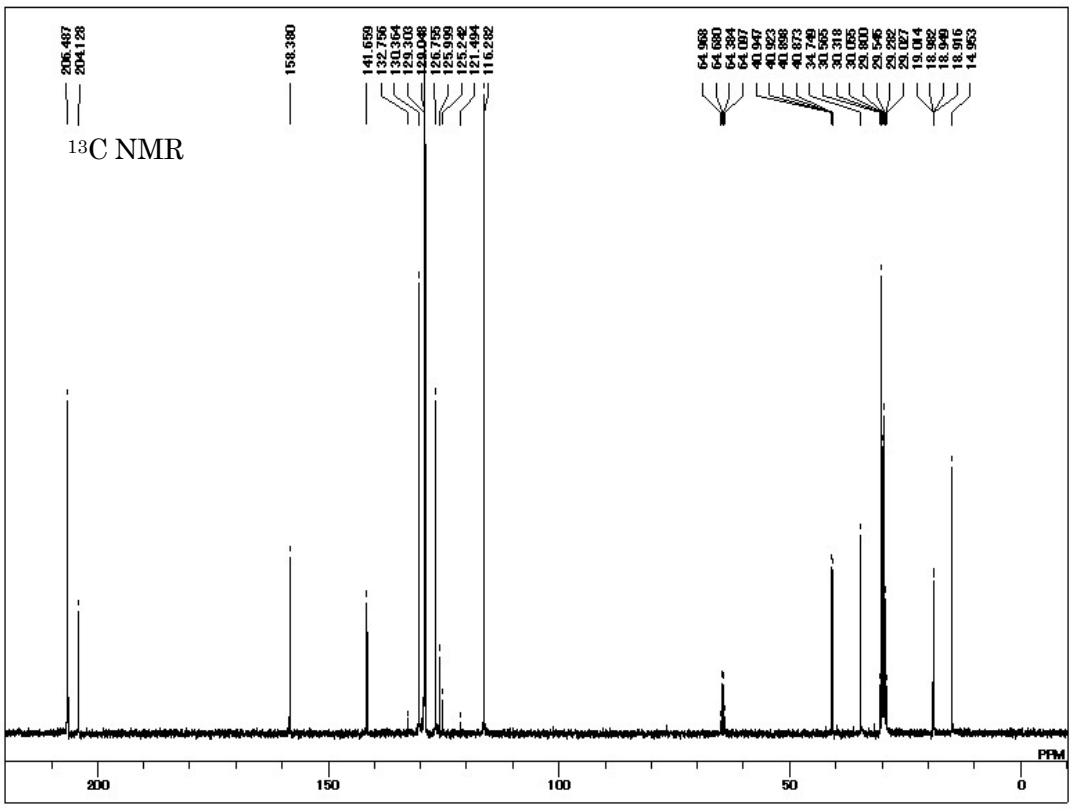
1-(2-Franyl)-2-(4-hydroxyphenyl)-2-(trifluoromethyl)pentan-1-one. (3bk)



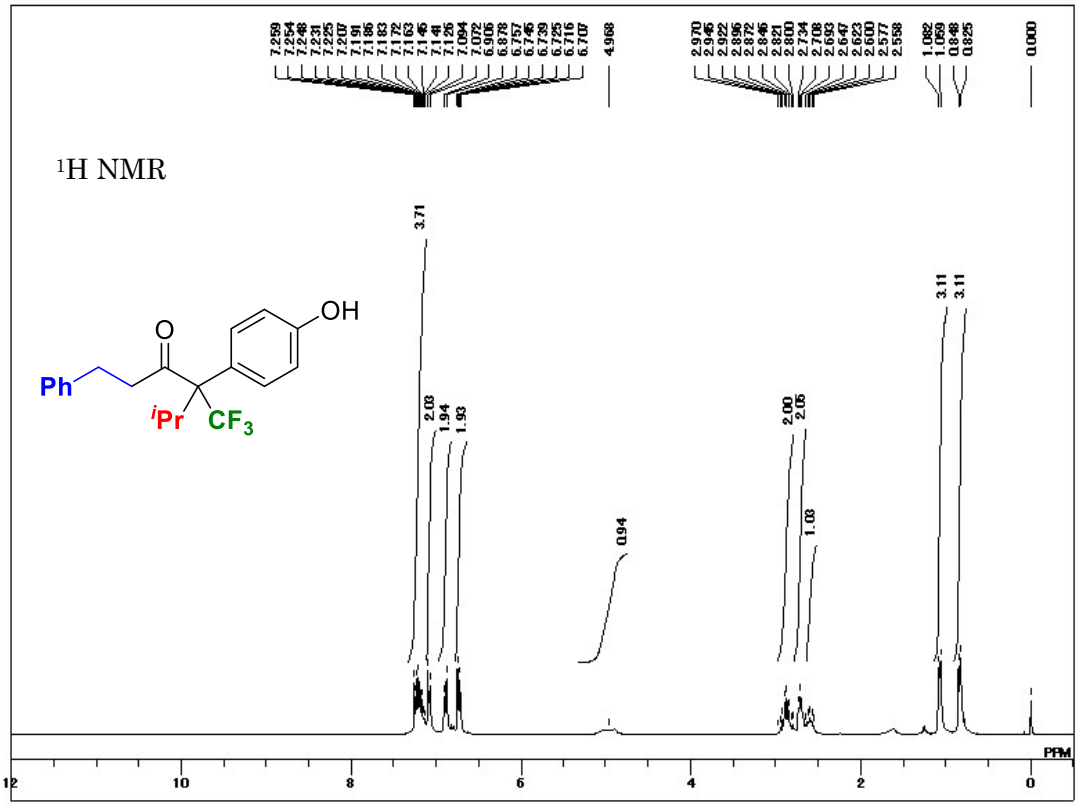


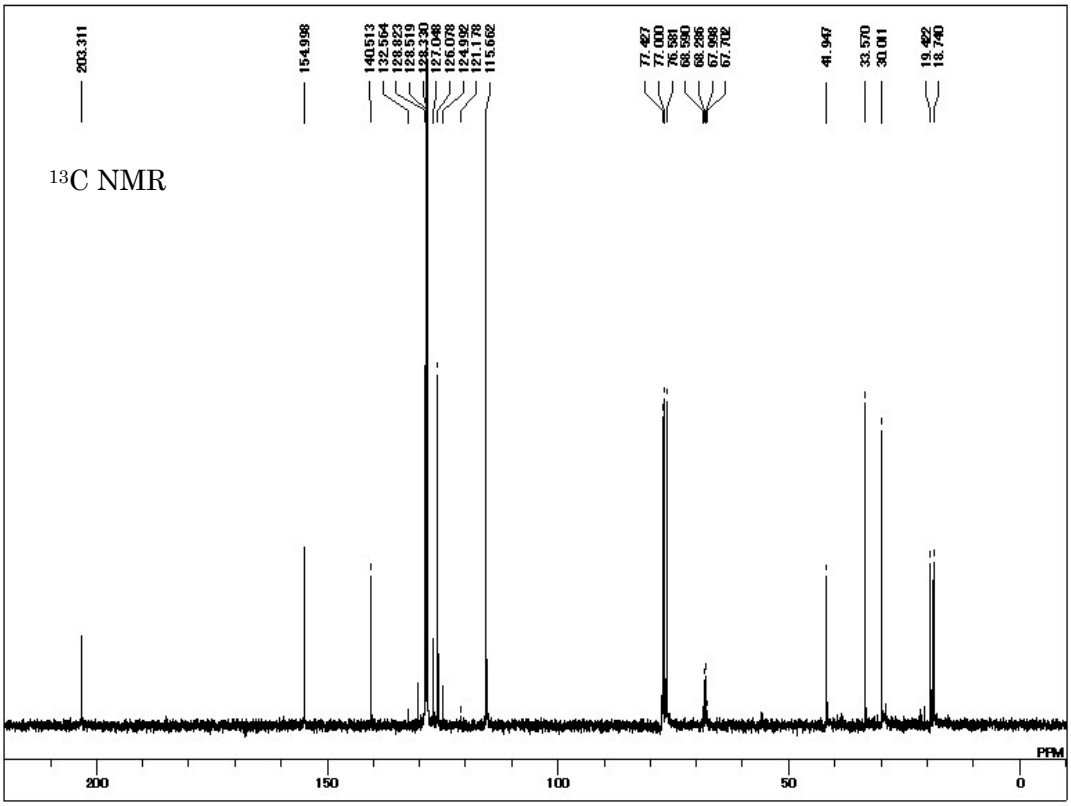
4-(4-Hydroxyphenyl)-1-phenyl-4-(trifluoromethyl)heptan-3-one (3bq)



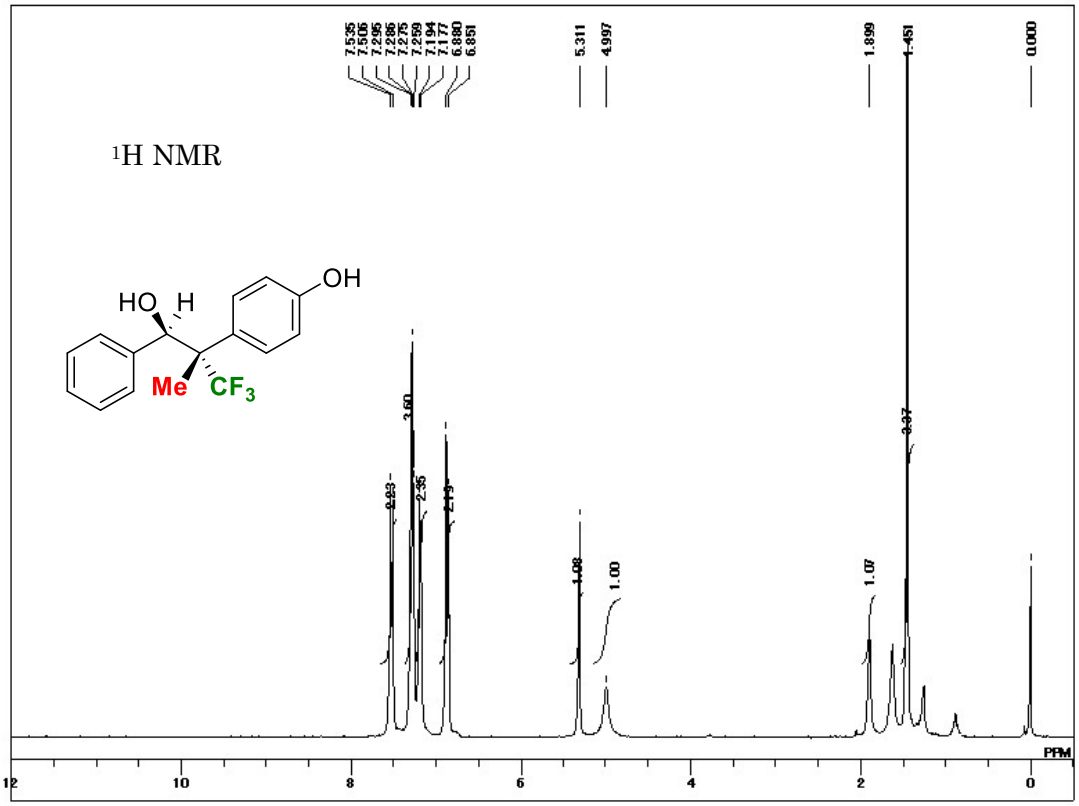


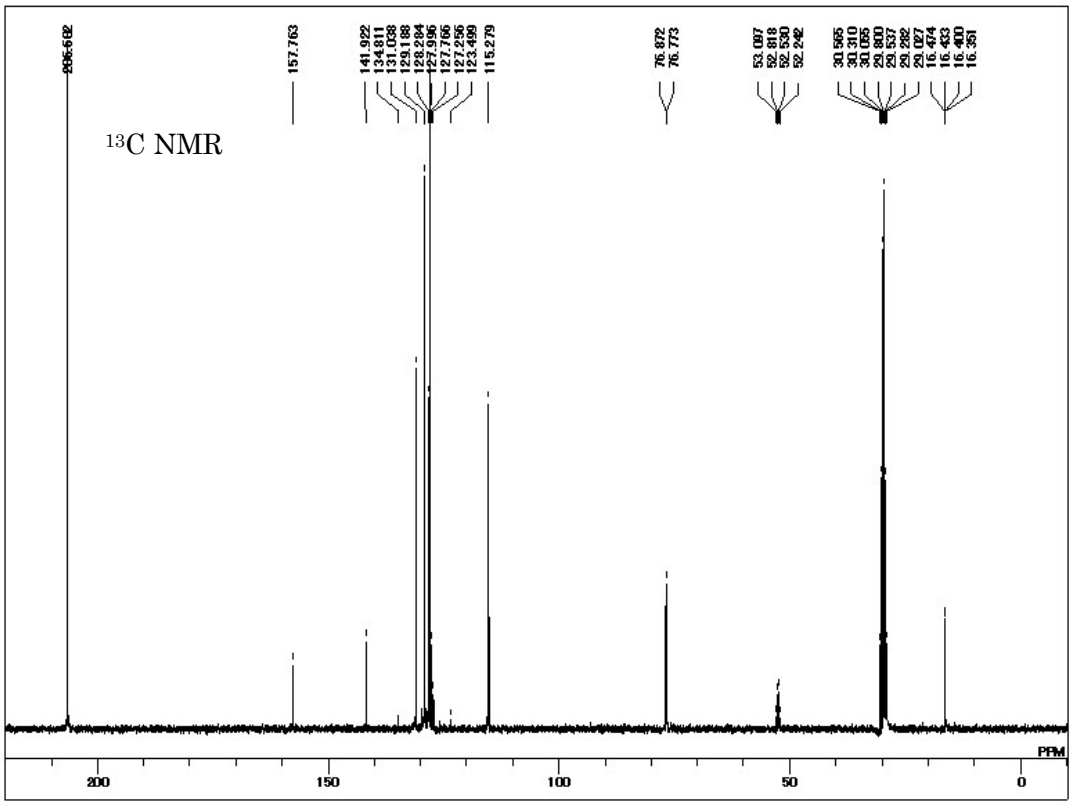
4-(4-Hydroxyphenyl)-5-methyl-1-phenyl-4-(trifluoromethyl)-3-hexanone (3cq)



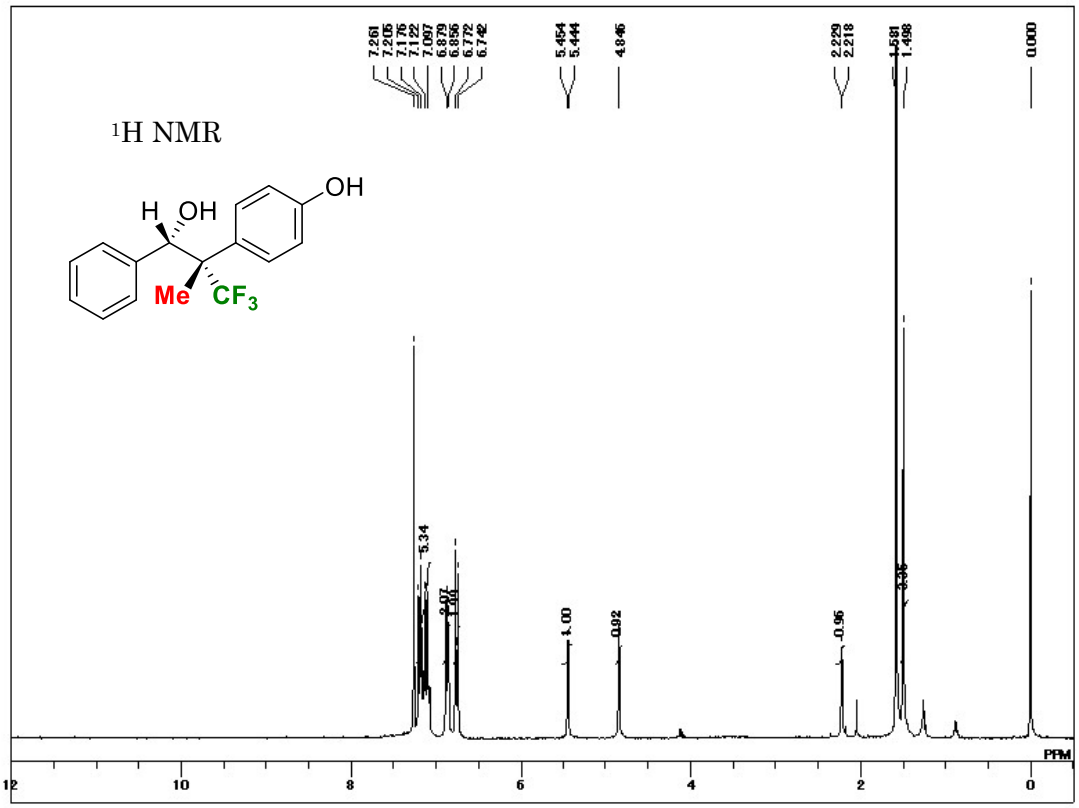


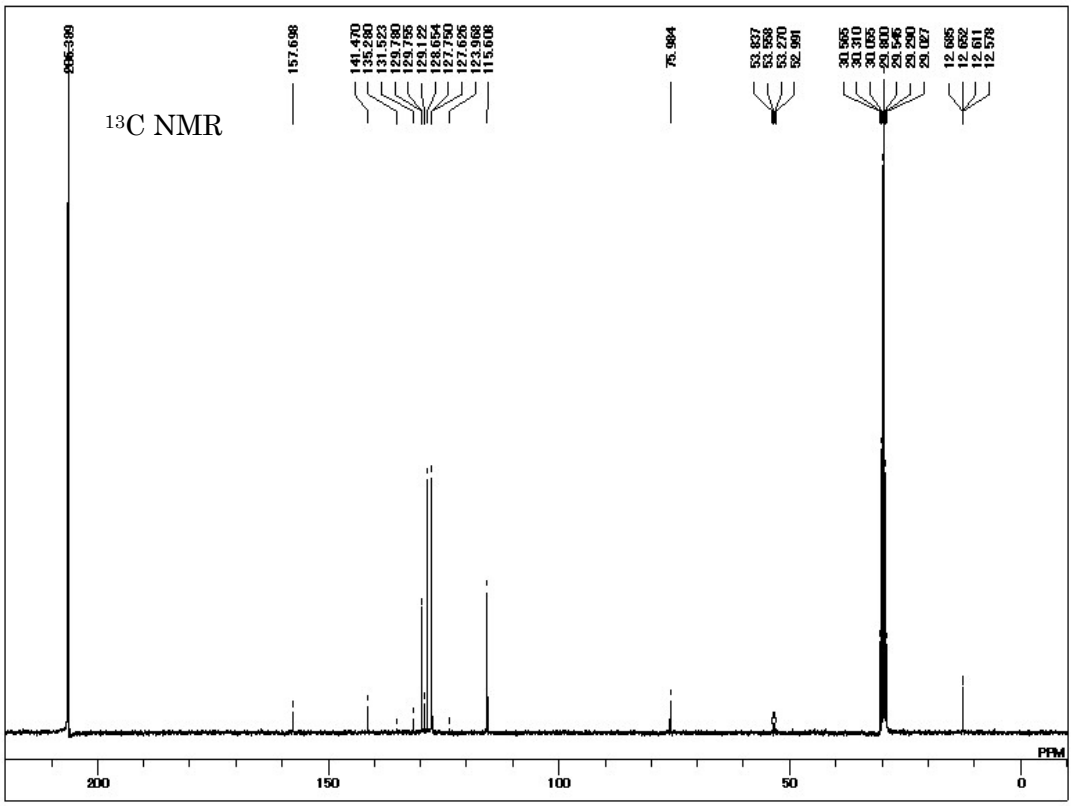
(1*R, 2*S**)-3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-pheny-1-propanol (6aa-major)**



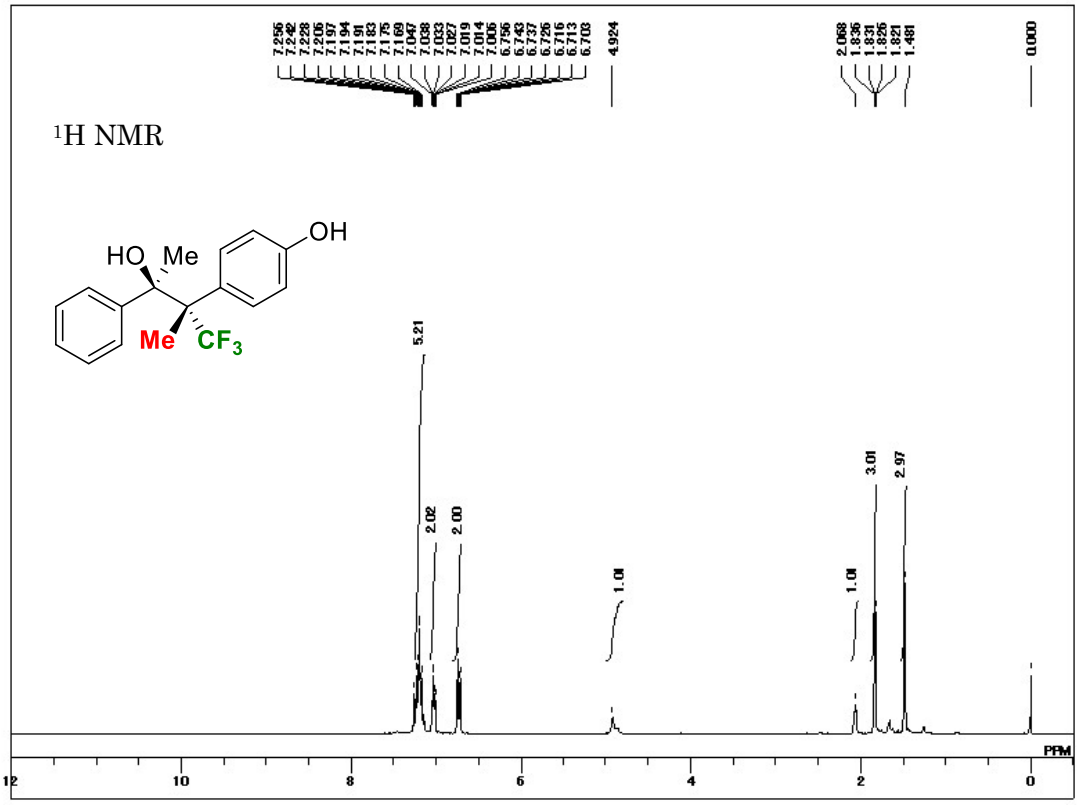


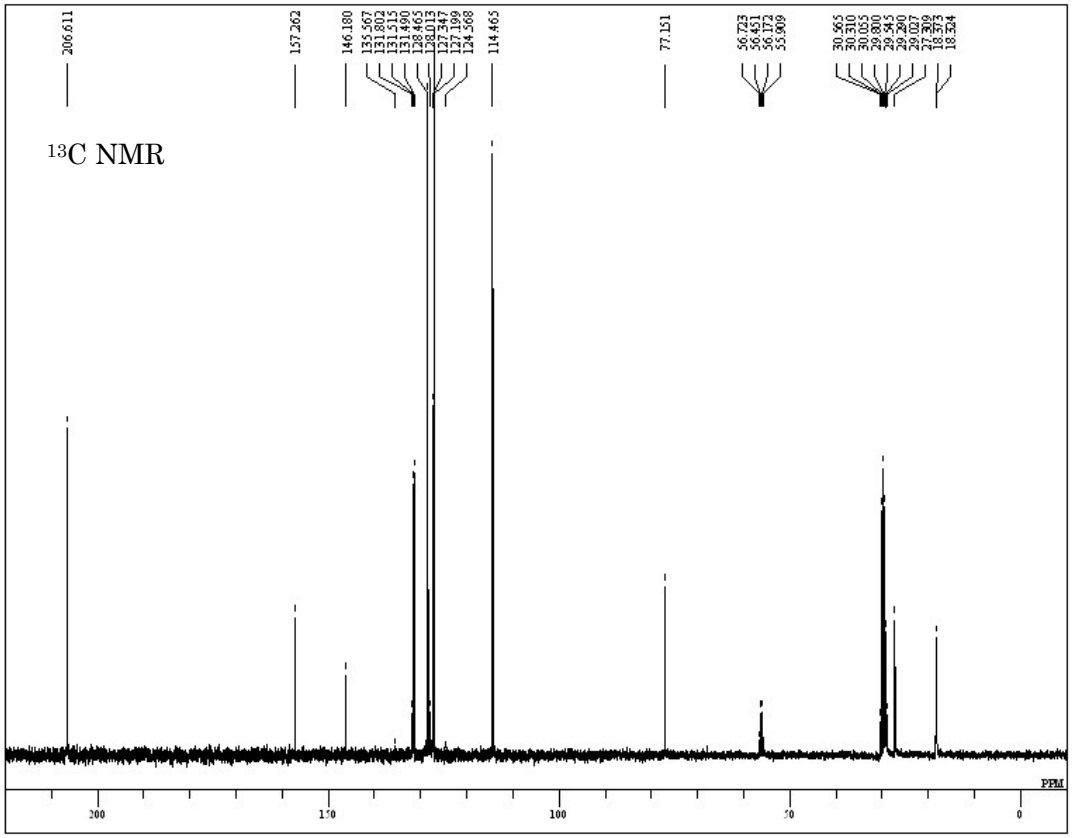
(1*S, 2*S**)-3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-pheny-1-propanol (6aa-minor)**



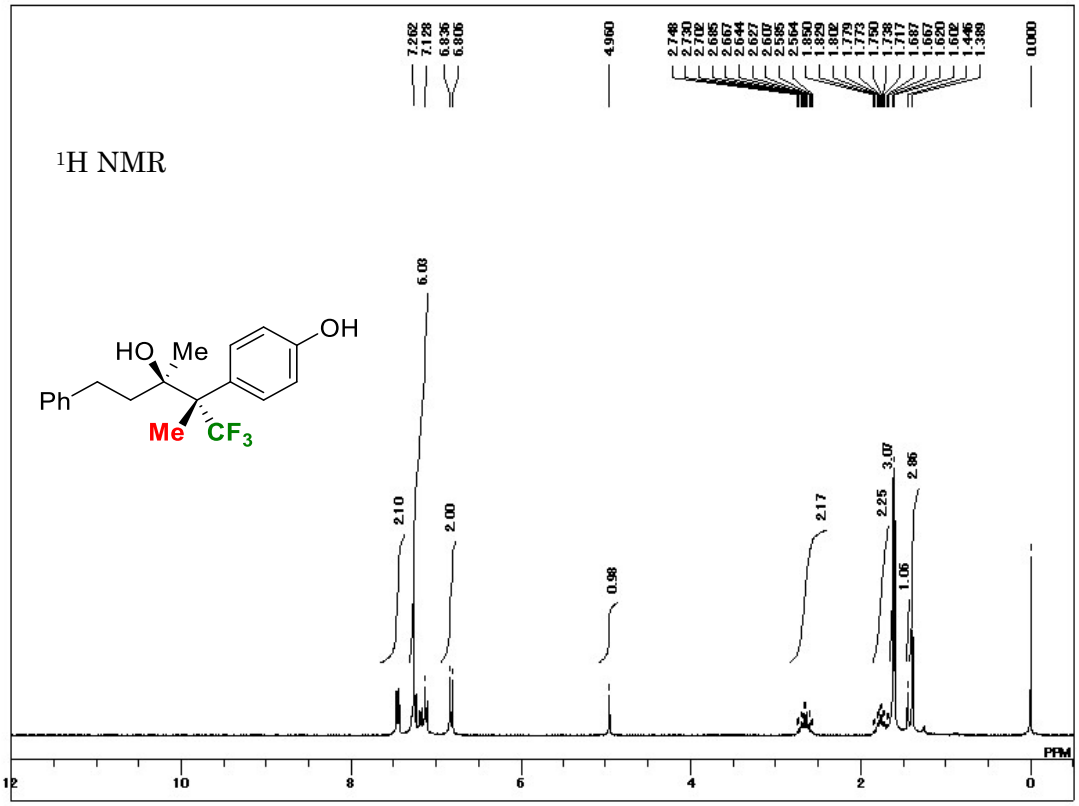


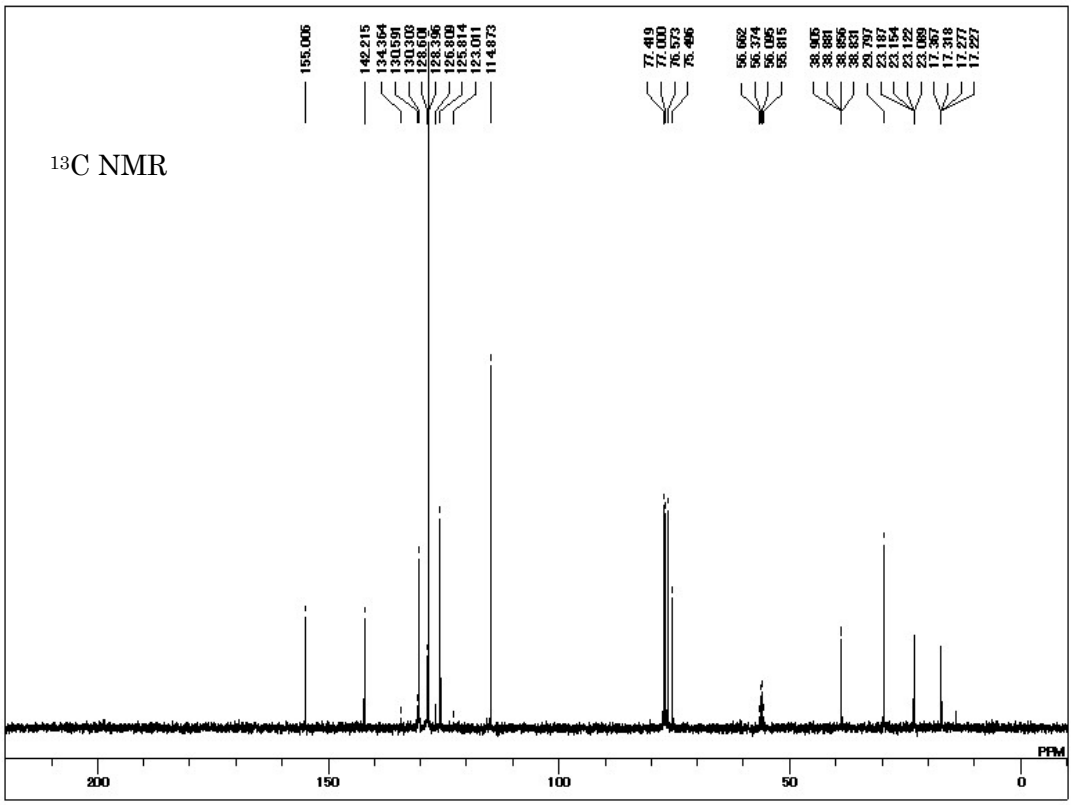
(2*R, 3*S**)-4,4,4-Trifluoro-2-(4-hydroxyphenyl)-2,3-dimethyl-1-pheny1butanol (7aa)**



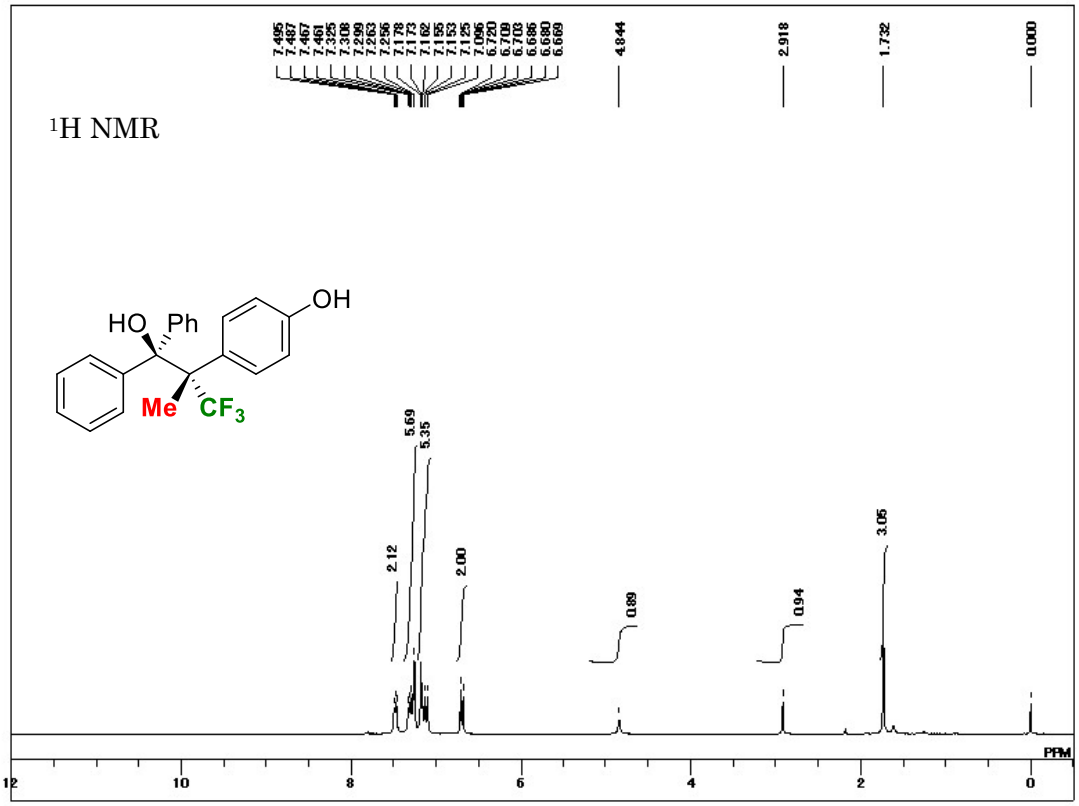


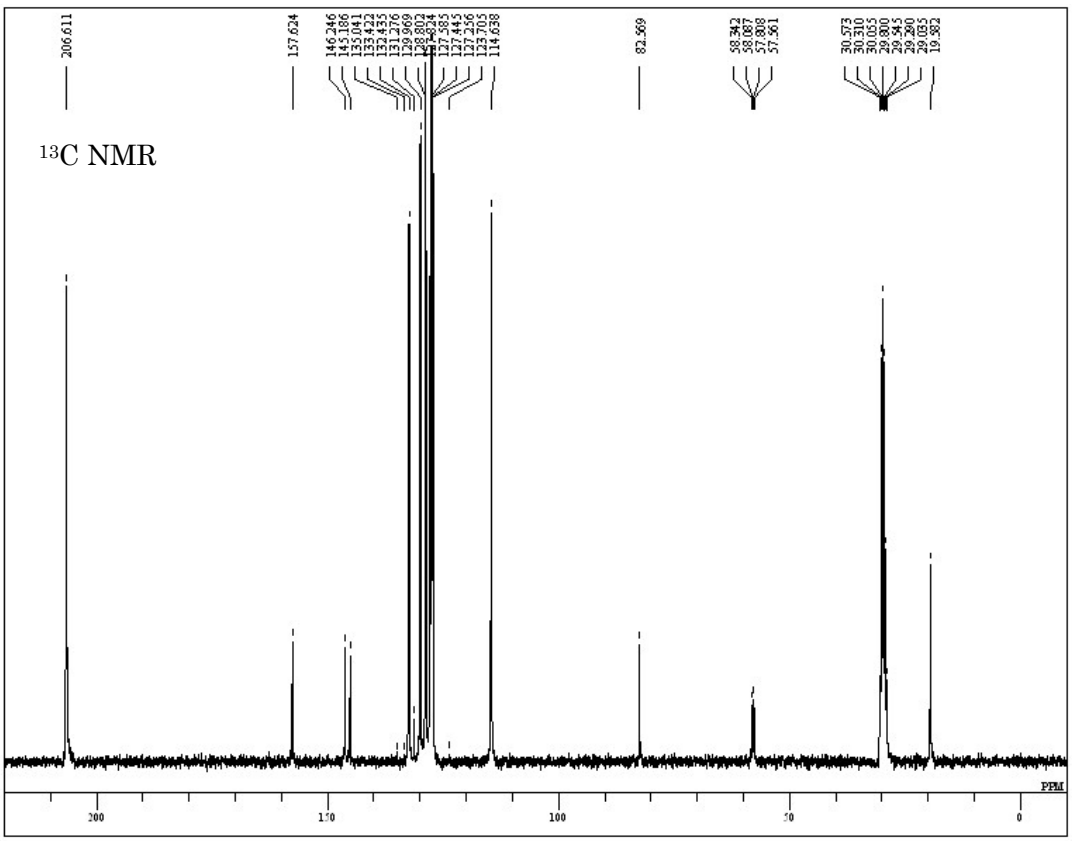
(2*S, 3*R**)-1,1,1-Trifluoro-2-(4-hydroxyphenyl)-2,3-dimethyl-5-phenyl-3-pentanol (7aq)**



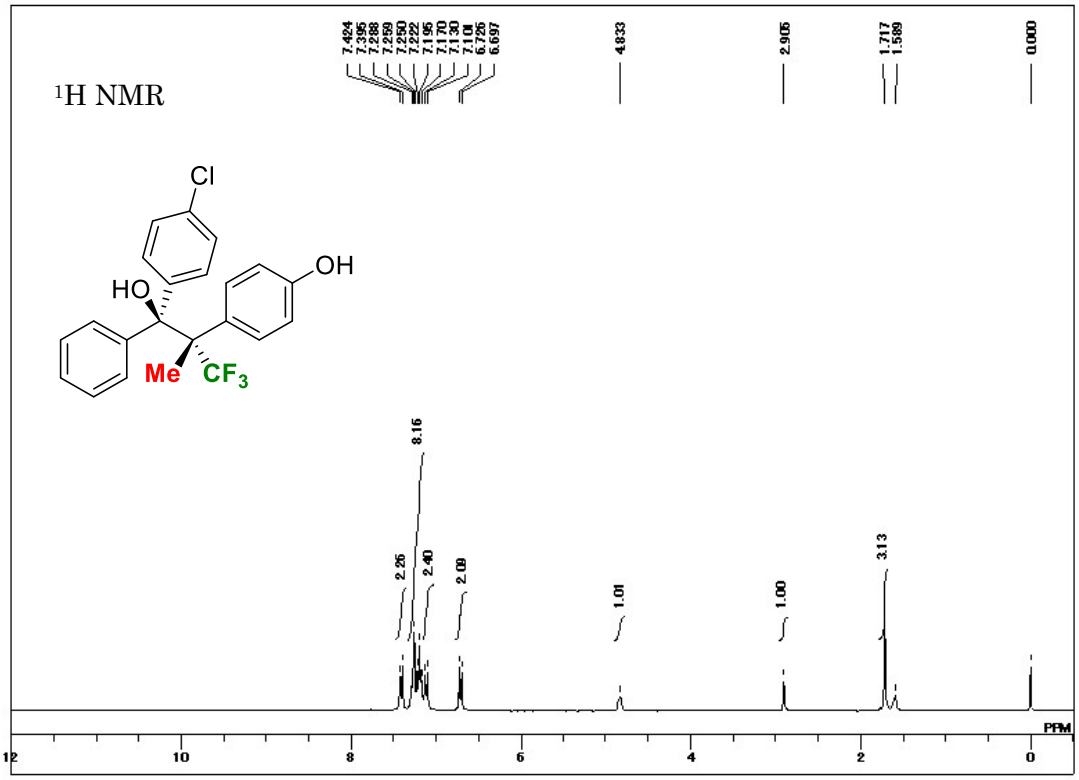


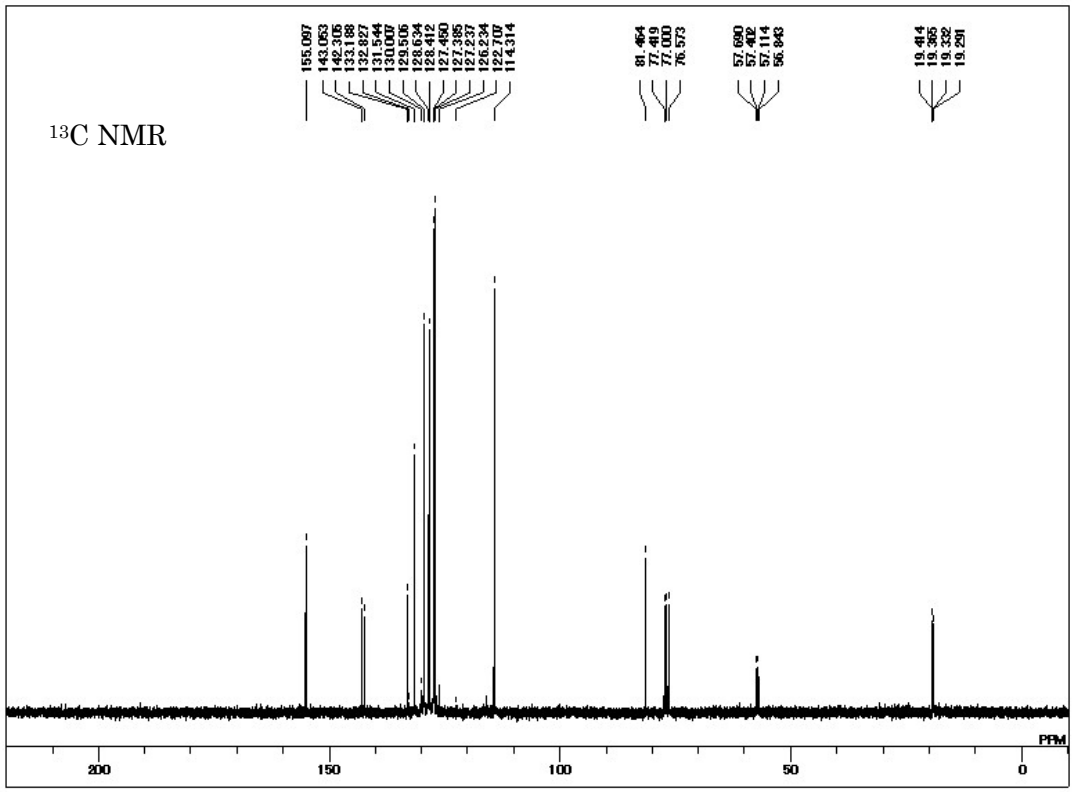
3,3,3-Trifluoro-2-(4-hydroxyphenyl)-2-methyl-1,1-dipheny-1-propanol (8aa)



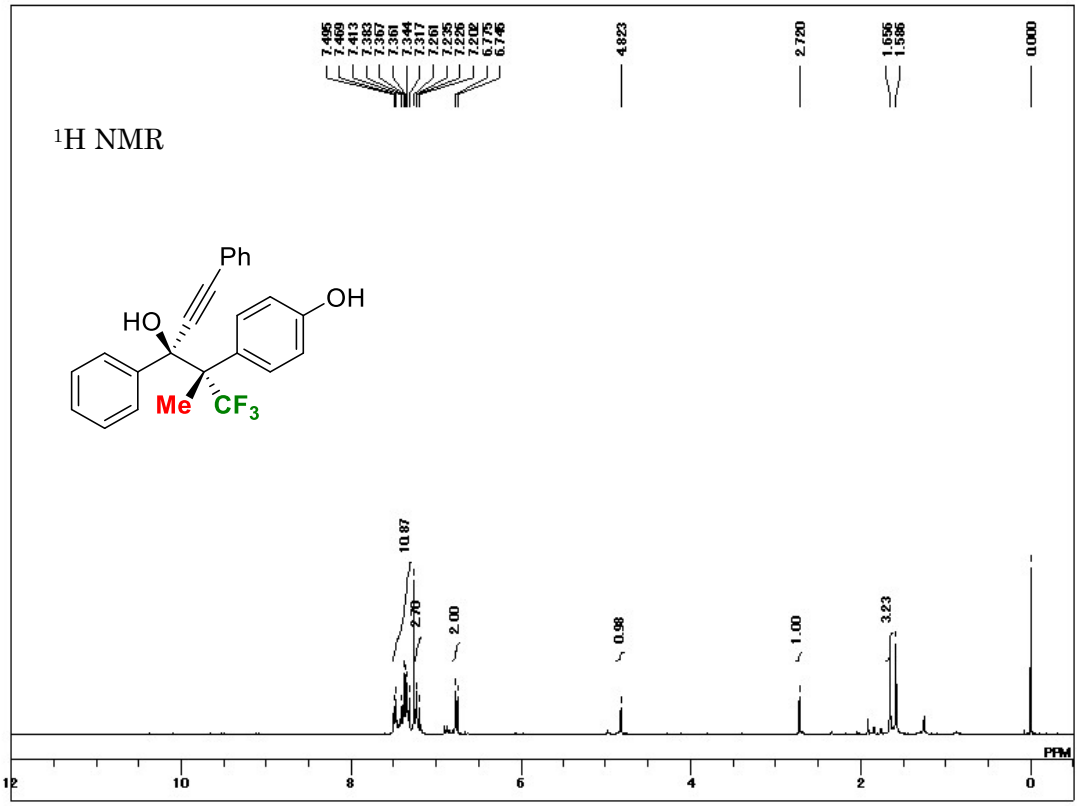


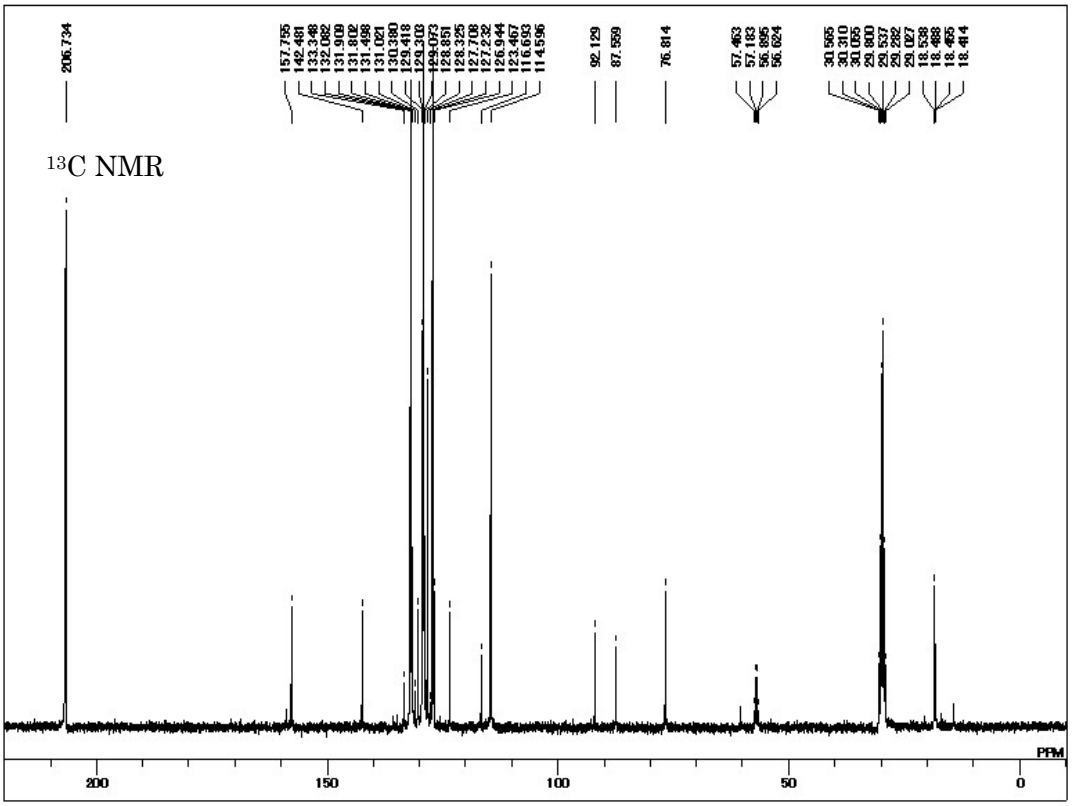
(1*S, 2*S**)-1-(4-Chlorophenyl)-3,3,3-trifluoro-2-(4-hydroxyphenyl)-2-methyl-1-pheny-1-propanol (9aa)**



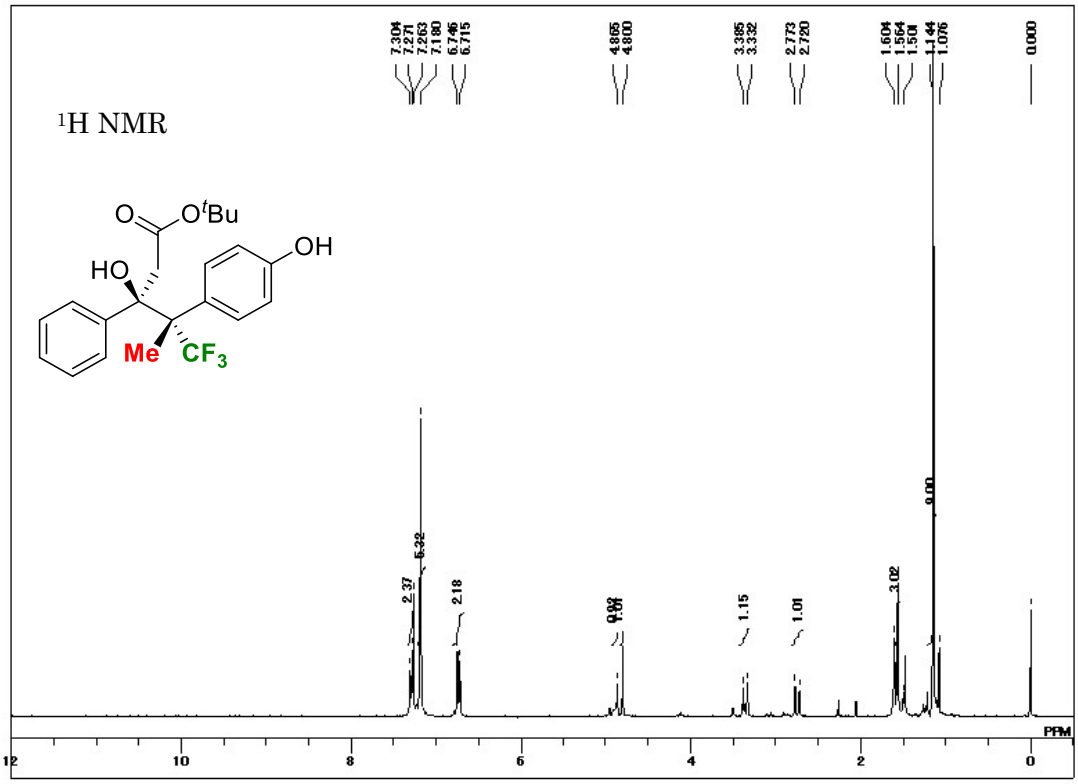


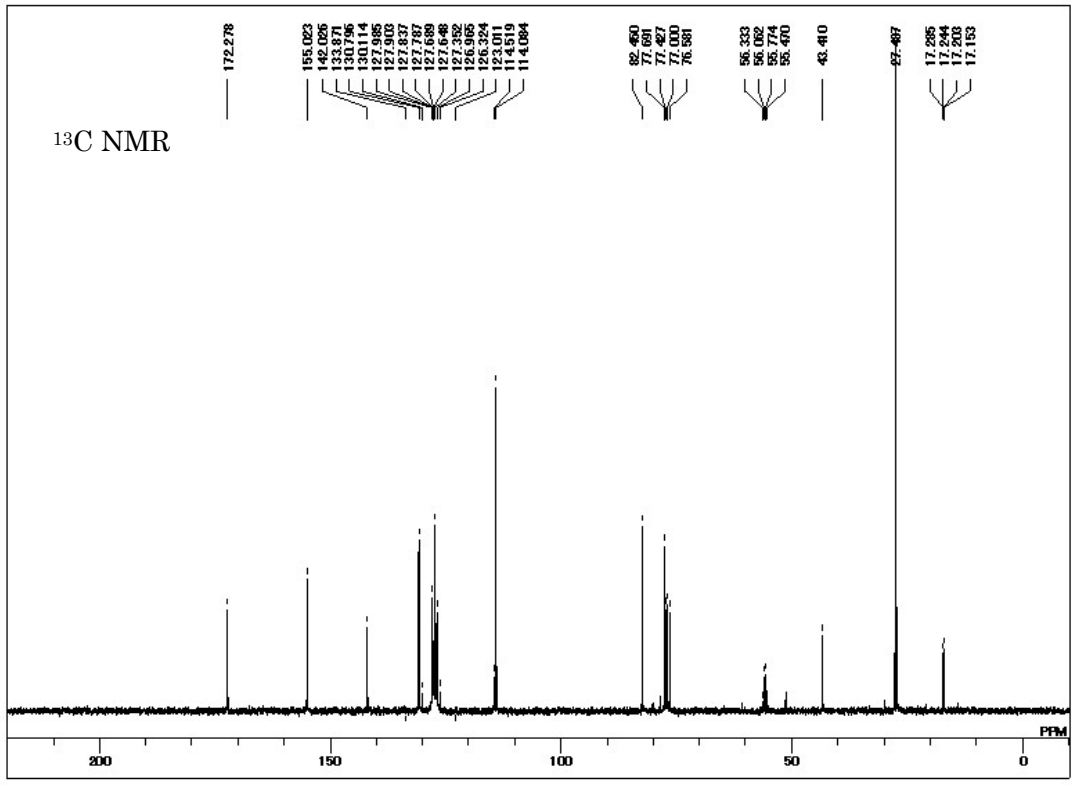
(3*S, 4*S**)-5,5,5-Trifluoro-4-(4-hydroxyphenyl)-4-methyl-3-phenyl-1-phenylpent-1-yn-3-ol (10aa)**



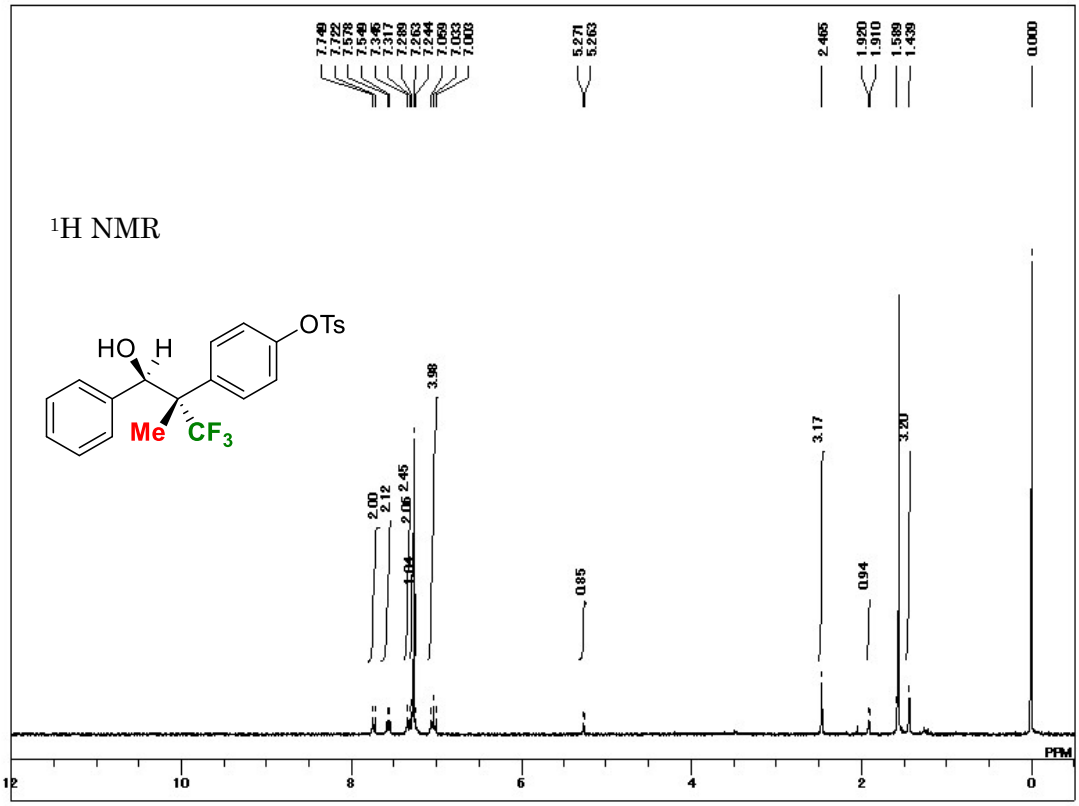


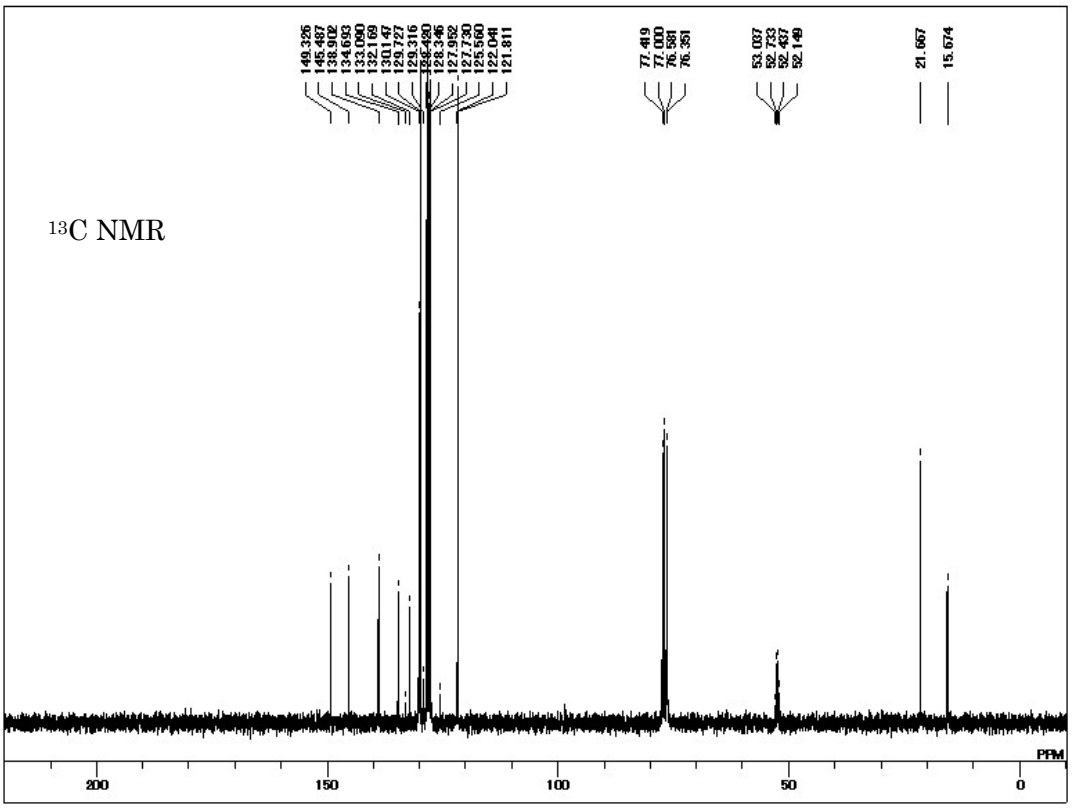
(3*S, 4*S**)-*tert*-Butyl 5,5,5-trifluoro-3-hydroxyl-4-(4-hydroxyphenyl)-4-methyl-3-phenylpentanoate (11aa)**





(1*R, 2*S**)-3,3,3-Trifluoro-2-methyl-1-pheny-2-[4-{(toluenesulfonyl)oxy}phenyl]-1-propanol (12aa)**





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