Supporting Information

Organocatalytic Nucleophilic Substitution Reaction of *gem*-Difluoroalkenes with Ketene Silyl Acetals

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General Information

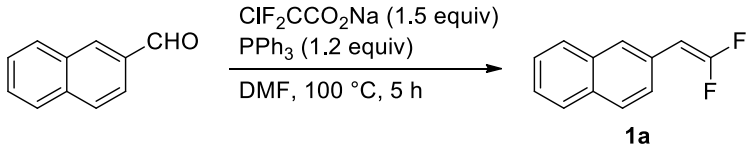
Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{19}F NMR spectra were recorded on a JEOL JNM-ECA600 (565 MHz) spectrometer. Chemical shifts are reported in ppm from the $C_6F_5CF_3$ (-67.2 ppm) resonance as the external standard. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dimethylketene Methyl Trimethylsilyl Acetal (**2a**) was purchased from Tokyo Chemical Industry Co., LTD. Dichloromethane, tetrahydrofuran, diethyl ether and toluene were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system" (water content: dichloromethane <10 ppm; tetrahydrofuran <10 ppm; diethyl ether <50 ppm; toluene < 1 ppm). Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under argon atmosphere.

Experimental Procedure

Procedure for Preparation of *gem*-Difluoroalkenes 1.

Synthesis of *gem*-Difluoroalkenes **1a-1k**.[1]

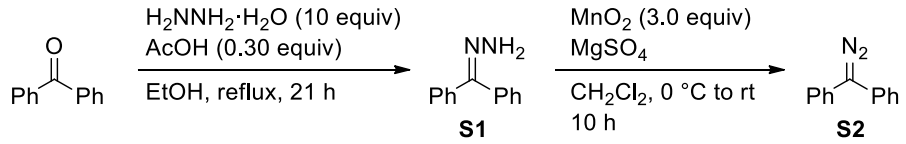


Synthesis of **1a** is representative.

A solution of sodium chlorodifluoroacetate (4.6 g, 30 mmol) in DMF (10 mL) was added dropwise to a solution of 2-naphthaldehyde (3.1 g, 20 mmol) and triphenylphosphine (6.3 g, 24 mmol) in DMF (30 mL) at 100 °C. The resulting mixture was stirred at that temperature for 5 h. The reaction was quenched with H_2O at 0 °C, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane) to provide **1a** (3.0 g, 16 mmol, 78%) as a white solid.

Synthesis of **1l**.[2]

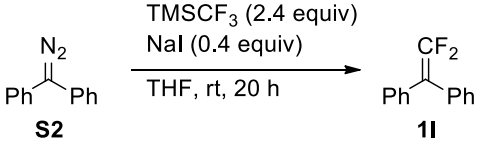
*Synthesis of **S2***.



A mixture of benzophenone (1.1 g, 6.0 mmol), hydrazine monohydrate (2.9 mL, 60 mmol), and acetic acid (0.10 mL, 1.8 mmol) was stirred at 100 °C for 21 h. After cooled to room temperature, solvent and volatile materials were removed under reduced pressure to afford **S1** (1.2 g, 6.0 mmol, quant) as a white solid. **S1** was used without further purification in the next step.

To a mixture of **S1** (1.1 g, 5.4 mmol) and $MgSO_4$ (0.48 g) in CH_2Cl_2 (14 mL) was added MnO_2 (1.4 g, 16 mmol) at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 10 h. After filtration followed by concentration under reduced pressure, the residue was purified by silica-gel column chromatography (hexane/AcOEt = 50:1 with 5% Et_3N) to provide **S2** (0.59 g, 3.1 mmol, 57%) as a purple solid.

*Synthesis of **1l**.*

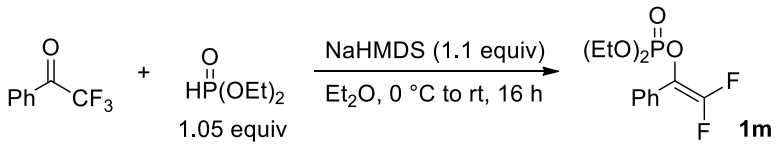


Trimethyl(trifluoromethyl)silane (1.1 mL, 7.5 mmol) was added to a mixture of **S2** (0.59 g, 3.1 mmol) and NaI

[1] Sakaguchi, H.; Uetake, Y.; Ohashi, M.; Niwa, T.; Ogoshi, S.; Hosoya, T. *J. Am. Chem. Soc.* **2017**, *139*, 12855.
[2] Tang, H.-J.; Lin, L.-Z.; Feng, C.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2017**, *56*, 9872.

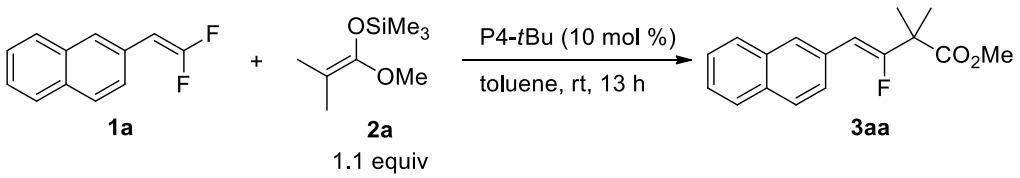
(0.18 g, 1.2 mmol) in THF (31 mL). After stirred at room temperature for 20 h, the reaction was quenched with H_2O, and the product was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane with 5% Et_3N) to provide **1a** (0.36 g, 1.7 mmol, 55%) as a colorless oil.

Synthesis of **1m**.



To a solution of 2,2,2-trifluoroacetophenone (2.5 mL, 18 mmol) and diethyl phosphite (2.4 mL, 19 mmol) in Et_2O (25 mL) was added a solution of NaHMDS in THF (1.9 M, 11 mL, 20 mL) at 0 °C. The resulting solution was allowed to warm to room temperature and stirred at that temperature for 16 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane/AcOEt = 3:2) to furnish **1m** (2.0 g, 7.0 mmol, 39%) as a colorless oil.

General Procedure for Organocatalytic Nucleophilic Substitution of *gem*-Difluoroalkenes with Ketene Silyl Acetals.



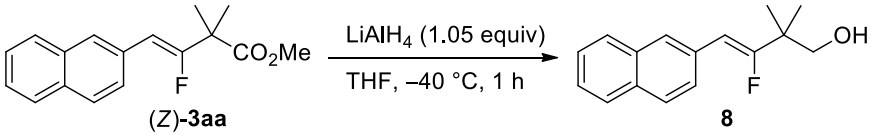
The reaction of **1a** with **2a** is representative (Table 1, entry 1).

To a solution of **1a** (18 mg, 0.10 mmol) and **2a** (23 μL, 0.11 mmol) in toluene (1.0 mL) was added a solution of P4-*t*Bu in hexane (0.80 M, 13 μL, 0.010 mmol). The resulting mixture was stirred at room temperature for 13 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane/AcOEt = 10:1) to provide **3aa** (23 mg, 0.096 mmol, 96%) as a white solid.

*Gram-Scale Synthesis of **3aa***

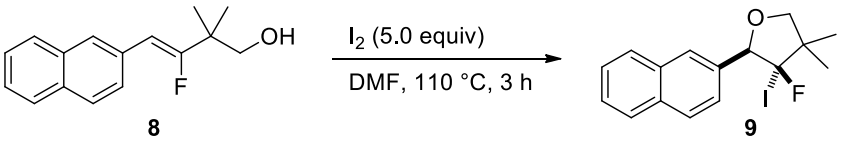
To a solution of **1a** (2.9 g, 15.5 mmol) and **2a** (3.6 mL, 17.8 mmol) in toluene (25 mL) was added a solution of P4-*t*Bu in hexane (0.80 M, 0.70 mL, 0.56 mmol). The resulting mixture was stirred at room temperature for 12 h. The reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane/AcOEt = 10:1) to provide (*Z*)-**3aa** (3.9 g, 14.5 mmol, 93%) as a white solid.

Procedure for Transformation of (*Z*)-3aa into 8 (Scheme 5a).



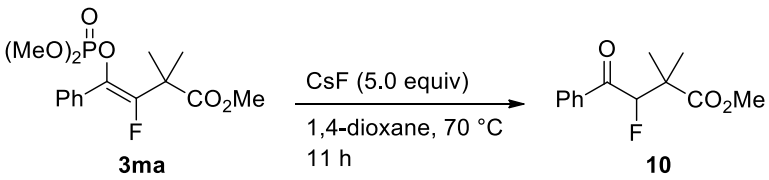
To a solution of (*Z*)-**3aa** (1.4 g, 5.0 mmol) in THF (8.0 mL) was added dropwise a solution of $LiAlH_4$ (0.20 g, 5.3 mmol) in THF (16 mL) at -40 °C. After stirred at that temperature for 1 h, the reaction was quenched with sat. aq. potassium sodium tartrate, and the product was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane/AcOEt = 4:1) to provide **8** (1.1 g, 4.7 mmol, 93%) as a white solid.

Procedure for Transformation of 8 into 9 (Scheme 5b).



A mixture of **8** (24 mg, 0.097 mmol) and iodine (0.13 g, 0.50 mmol) in DMF (1.0 mL) was stirred at 110 °C for 3 h. After cooled to room temperature, the reaction was quenched with sat. aq. $Na_2S_2O_3$, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane/AcOEt = 10:1) to provide **9** (26 mg, 0.069 mmol, 71%) as a white solid.

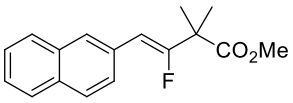
Procedure for Transformation of 3ma into 10 (Scheme 5c).



A mixture of **3ma** (35 mg, 0.10 mmol) and CsF (76 mg, 0.50 mmol) in 1,4-dioxane (1.0 mL) was stirred at 70 °C for 11 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH_4Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica-gel column chromatography (hexane/AcOEt = 10:1) to provide **10** (21 mg, 0.087 mmol, 87%) as a yellow oil.

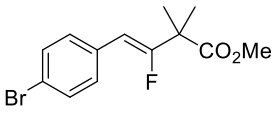
Analytical Data

(*Z*)-Methyl 3-fluoro-2,2-dimethyl-4-(naphthalene-2-yl)but-3-enoate (3aa):



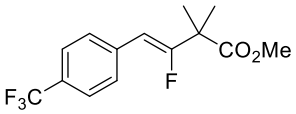
26 mg, 96%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.53 (s, 6H), 3.75 (s, 3H), 5.84 (d, *J* = 40.2 Hz, 1H), 7.42-7.48 (m, 2H), 7.66 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.78–7.80 (m, 2H), 7.94 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.5 (d, *J* = 3.0 Hz), 46.9 (d, *J* = 24.5 Hz), 52.6, 105.4 (d, *J* = 8.6 Hz), 125.9, 126.1, 126.7 (d, *J* = 8.7 Hz), 127.5, 127.8 (d, *J* = 7.2 Hz), 127.9, 128.0, 130.6, 132.4, 133.4, 162.3 (d, *J* = 266.4 Hz), 174.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -106.3 (d, *J* = 40.1 Hz); IR (ATR): 3057, 2986, 2952, 2851, 1739, 1683, 1630, 1598, 1508, 1255, 1149, 1074, 864 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}FO_2$ $[M+Na]^+$ 295.1105, Found 295.1105; m.p. 62.5-63.5 °C.

(*Z*)-Methyl 4-(4-bromophenyl)-3-fluoro-2,2-dimethylbut-3-enoate (3ba):



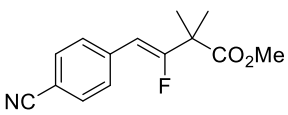
25 mg, 84%; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.48 (s, 6H), 3.74 (s, 3H), 5.62 (d, *J* = 39.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4 (d, *J* = 2.9 Hz), 46.9 (d, *J* = 24.5 Hz), 52.7, 104.4 (d, *J* = 8.2 Hz), 121.0 (d, *J* = 2.9 Hz), 130.2 (d, *J* = 7.1 Hz), 131.5, 132.0, 162.6 (d, *J* = 267.2 Hz), 174.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -105.5 (d, *J* = 38.2 Hz); IR (ATR): 2990, 2952, 1743, 1687, 1490, 1254, 1195, 1150, 1075, 1011, 868 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}BrFO_2$ $[M+Na]^+$ 323.0053, Found 323.0054.

(*Z*)-Methyl 3-fluoro-2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)but-3-enoate (3ca):



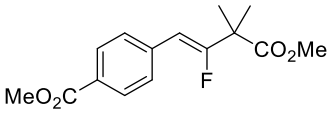
24 mg, 81%; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.51 (s, 6H), 3.75 (s, 3H), 5.72 (d, *J* = 39.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4 (d, *J* = 2.9 Hz), 46.9 (d, *J* = 25.8 Hz), 52.7, 104.3 (d, *J* = 8.6 Hz), 124.1 (q, *J* = 271.5 Hz), 125.3 (q, *J* = 3.6 Hz), 128.9 (d, *J* = 8.6 Hz), 129.0 (q, *J* = 34.5 Hz), 136.7, 163.7 (d, *J* = 270.0 Hz), 174.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -103.5 (d, *J* = 38.4 Hz, 1F), -62.5 (s, 3F); IR (ATR): 2989, 2957, 1741, 1685, 1618, 1323, 1255, 1113, 1067, 1016, 864 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{14}F_4O_2$ $[M+Na]^+$ 313.0822, Found 313.0822.

(*Z*)-Methyl 4-(4-cyanophenyl)-3-fluoro-2,2-dimethylbut-3-enoate (3da):



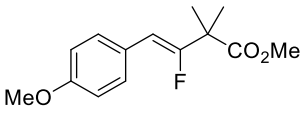
20 mg, 80%; white crystal; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.50 (s, 6H), 3.75 (s, 3H), 5.71 (d, *J* = 38.4 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.61 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.3 (d, *J* = 2.9 Hz), 47.0 (d, *J* = 24.5 Hz), 52.8, 104.3 (d, *J* = 7.1 Hz), 110.4 (d, *J* = 2.3 Hz), 118.9, 129.1 (d, *J* = 7.2 Hz), 132.2, 137.8, 164.6 (d, *J* = 272.3 Hz), 173.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -101.3 (d, *J* = 37.9 Hz); IR (ATR): 2991, 2954, 2914, 2843, 2226, 1743, 1686, 1606, 1507, 1255, 1151, 1078, 870 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{14}FNO_2$ $[M+Na]^+$ 270.0901, Found 270.0901; m.p. 89.5-90.5 °C.

(*Z*)-Methyl 4-(3-fluoro-4-(4-methoxycarbonyl)phenyl)-2,2-dimethylbut-3-enoate (3ea):



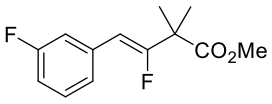
20 mg, 72%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.50 (s, 6H), 3.74 (s, 3H), 3.91 (s, 3H), 5.73 (d, *J* = 39.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4 (d, *J* = 2.9 Hz), 47.0 (d, *J* = 24.5 Hz), 52.1, 52.7, 104.7 (d, *J* = 8.6 Hz), 128.5, 128.6 (d, *J* = 8.7 Hz), 129.7, 137.7 (d, *J* = 2.9 Hz), 163.7 (d, *J* = 270.8 Hz), 166.8, 174.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -102.9 (d, *J* = 37.9 Hz); IR (ATR): 2953, 1745, 1723, 1681, 1610, 1508, 1434, 1281, 1187, 1150, 1111, 1077, 871 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{17}FO_4$ $[M+Na]^+$ 303.1003, Found 303.1003; m.p. 63.5-64.5 °C.

Methyl 3-fluoro-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (3fa):



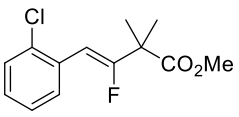
22 mg, 89%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) **(*Z*)-isomer** δ 1.48 (s, 6H), 3.73 (s, 3H), 3.81 (s, 3H), 5.61 (d, *J* = 40.2 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), **(*E*)-isomer** δ 1.38 (d, *J* = 1.2 Hz, 6H), 3.33 (s, 3H), 3.79 (s, 3H), 6.30 (d, *J* = 24.6 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) **(*Z*)-isomer** δ 23.4 (d, *J* = 2.9 Hz), 46.7 (d, *J* = 25.8 Hz), 52.5, 55.2, 104.6 (d, *J* = 10.1 Hz), 113.8, 125.8, 129.9 (d, *J* = 7.2 Hz), 158.6, 160.7 (d, *J* = 264.3 Hz), 174.7, **(*E*)-isomer** δ 24.4 (d, *J* = 2.9 Hz), 46.1 (d, *J* = 27.3 Hz), 52.0, 55.2, 108.1 (d, *J* = 31.5 Hz), 113.4, 125.2 (d, *J* = 14.4 Hz), 130.3 (d, *J* = 2.3 Hz), 158.6, 161.0 (d, *J* = 249.9 Hz), 174.3 (d, *J* = 5.7 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) **(*Z*)-isomer** δ -109.6 (d, *J* = 40.7 Hz), **(*E*)-isomer** δ -104.6 (d, *J* = 23.7 Hz); IR (ATR): 2991, 2953, 2839, 1740, 1609, 1514, 1253, 1149 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{17}FO_3$ $[M+Na]^+$ 275.1054, Found 275.1054.

(*Z*)-Methyl 3-fluoro-4-(3-fluorophenyl)-2,2-dimethylbut-3-enoate (3ga):



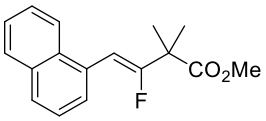
20 mg, 83%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.49 (s, 6H), 3.74 (s, 3H), 5.66 (d, *J* = 39.0 Hz, 1H), 6.93 (dddd, *J* = 8.4, 8.4, 3.0, 1.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.26-7.30 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4 (d, *J* = 2.9 Hz), 46.9 (d, *J* = 24.5 Hz), 52.7, 104.5 (dd, *J* = 8.6, 2.9 Hz), 114.1 (d, *J* = 21.6 Hz), 115.4 (dd, *J* = 21.6, 10.1 Hz), 124.5 (dd, *J* = 7.2, 2.9 Hz), 129.7 (d, *J* = 10.2 Hz), 135.2 (d, *J* = 10.1 Hz), 162.8 (d, *J* = 242.7 Hz), 162.9 (d, *J* = 268.5 Hz), 174.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.2 (m), -104.6 (d, *J* = 38.4 Hz); IR (ATR): 2990, 2954, 1742, 1685, 1615, 1584, 1445, 1259, 1151, 1075, 862 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}F_2O_2$ $[M+Na]^+$ 263.0854, Found 263.0854.

(*Z*)-Methyl 4-(2-chlorophenyl)-3-fluoro-2,2-dimethylbut-3-enoate (3ha):



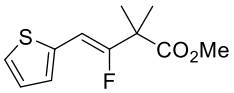
23 mg, 91%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.52 (s, 6H), 3.75 (s, 3H), 6.11 (d, *J* = 39.0 Hz, 1H), 7.17 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4 (d, *J* = 4.4 Hz), 47.1 (d, *J* = 24.3 Hz), 52.6, 101.4 (d, *J* = 8.6 Hz), 126.7, 128.3, 129.4, 130.4 (d, *J* = 11.6 Hz), 131.0 (d, *J* = 2.9 Hz), 132.9, 163.1 (d, *J* = 269.4 Hz), 174.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -106.5 (d, *J* = 37.9 Hz); IR (ATR): 3068, 2987, 2952, 2882, 2844, 1739, 1684, 1469, 1439, 1252, 1147, 1076, 870 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}ClFO_2$ $[M+Na]^+$ 279.0559, Found 279.0559.

(*Z*)-Methyl 3-fluoro-2,2-dimethyl-4-(naphthalen-1-yl)but-3-enoate (3ia):



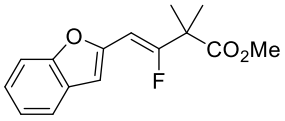
24 mg, 87%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.59 (s, 6H), 3.78 (s, 3H), 6.33 (d, *J* = 37.2 Hz, 1H), 7.47 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.8, 1.8 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.5 (d, *J* = 2.9 Hz), 47.0 (d, *J* = 25.8 Hz), 52.6, 102.1 (d, *J* = 10.1 Hz), 124.1, 125.4, 125.6, 126.0, 127.3 (d, *J* = 7.1 Hz), 127.8, 128.6, 129.2, 131.4, 133.6, 162.5 (d, *J* = 264.3 Hz), 174.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -107.6 (d, *J* = 35.6 Hz); IR (ATR): 2987, 2952, 1742, 1688, 1542, 1508, 1261, 1150, 1089, 1072 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}FO_2$ $[M+Na]^+$ 295.1105, Found 295.1105; m.p. 34.5-35.5 °C.

(*Z*)-Methyl 3-fluoro-2,2-dimethyl-4-(thiophen-2-yl)but-3-enoate (3ja):



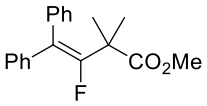
19 mg, 84%; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.48 (s, 6H), 3.73 (s, 3H), 6.01 (d, *J* = 38.4 Hz, 1H), 7.00 (m, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 7.27 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.3 (d, *J* = 3.6 Hz), 46.4 (d, *J* = 24.3 Hz), 52.7, 100.2 (d, *J* = 13.1 Hz), 125.7 (d, *J* = 8.6 Hz), 126.6 (d, *J* = 8.6 Hz), 126.7 (d, *J* = 4.4 Hz), 135.3 (d, *J* = 4.4 Hz), 160.7 (d, *J* = 265.7 Hz), 174.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -103.7 (d, *J* = 38.4 Hz); IR (ATR): 2986, 2952, 1741, 1682, 1472, 1259, 1149, 865 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{13}FO_2S$ $[M+Na]^+$ 251.0513, Found 251.0512.

(*Z*)-Methyl 4-(benzofuran-2-yl)-3-fluoro-2,2-dimethylbut-3-enoate (3ka):



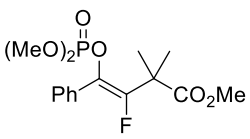
22 mg, 83%; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.51 (s, 6H), 3.75 (s, 3H), 5.92 (d, *J* = 37.8 Hz, 1H), 6.91 (s, 1H), 7.21 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.26 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.2, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.2 (d, *J* = 3.0 Hz), 46.7 (d, *J* = 23.1 Hz), 52.8, 96.8 (d, *J* = 11.6 Hz), 106.0 (d, *J* = 11.4 Hz), 110.9, 120.9, 122.9, 124.3, 129.0, 150.2, 153.9, 163.6 (d, *J* = 271.5 Hz), 174.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.1 (d, *J* = 37.9 Hz); IR (ATR): 2988, 2953, 1742, 1685, 1452, 1258, 1149, 1077, 962, 865 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{15}FO_3[M+Na]^+$ 285.0897, Found 285.0897.

Methyl 3-fluoro-2,2-dimethyl-4,4-diphenylbut-3-enoate (3la):



28 mg, 95%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.38 (d, *J* = 1.2 Hz, 6H), 3.57 (s, 3H), 7.17-7.24 (m, 5H), 7.26-7.33 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.1 (d, *J* = 3.6 Hz), 47.1 (d, *J* = 28.7 Hz), 52.0, 121.3 (d, *J* = 18.8 Hz), 127.0, 127.6, 127.9, 128.1, 129.4 (d, *J* = 4.4 Hz), 130.7 (d, *J* = 2.9 Hz), 137.2 (d, *J* = 8.6 Hz), 138.4, 157.2 (d, *J* = 257.7 Hz), 174.5 (d, *J* = 5.7 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -106.9 (s); IR (ATR): 2925, 2854, 1742, 1654, 1494, 1468, 1460, 1388, 1272, 1195, 1150 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{19}FO_2$ $[M+Na]^+$ 321.1261, Found 321.1261; m.p. 76.5-77.5 °C.

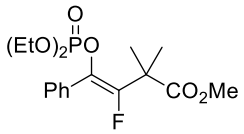
(*E*)-Methyl 4-((dimethoxyphosphoryl)oxy)-3-fluoro-2,2-dimethyl-4-phenyl-3-enoate (3ma):



30 mg, 87%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.55 (d, *J* = 2.4 Hz, 6H), 3.55 (d, *J* = 11.4 Hz, 6H), 3.78 (s, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.40 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.52

(d, *J* = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4 (d, *J* = 5.9 Hz), 45.3 (d, *J* = 24.5 Hz), 52.5, 54.7 (d, *J* = 5.7 Hz), 128.0, 128.6 (d, *J* = 3.6 Hz), 129.0, 131.3, 134.2 (dd, *J* = 50.3, 7.2 Hz), 154.7 (dd, *J* = 249.9, 11.2 Hz), 174.5 (d, *J* = 4.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -138.2 (d, *J* = 9.6 Hz); IR (ATR): 2990, 2957, 2857, 1739, 1446, 1281, 1135, 1044, 899, 852 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{20}FO_6P$ $[M+Na]^+$ 369.0874, Found 369.0874.

(*E*)-Methyl 4-((diethoxyphosphoryl)oxy)-3-fluoro-2,2-dimethyl-4-phenyl-3-enoate (3ma'):

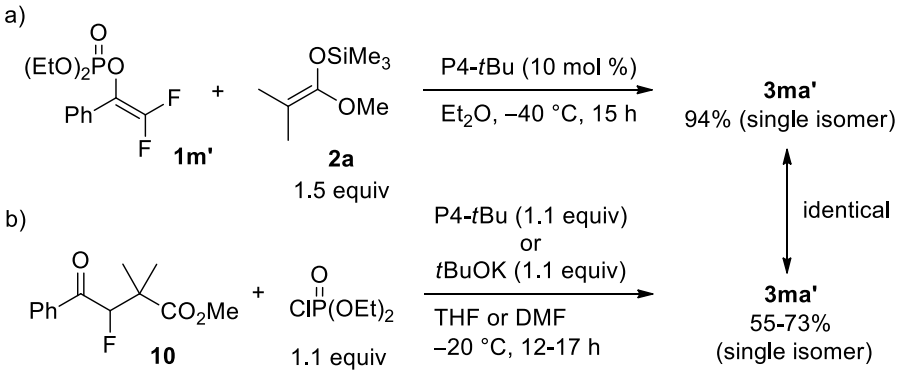


31 mg, 83%; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.15 (td, *J* = 7.2, 1.2 Hz, 6H), 1.56 (d, *J* = 1.8 Hz, 6H), 3.77 (s, 3H), 3.84 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 2H), 3.97 (ddq, *J* = 10.2, 7.2, 7.2 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8 (d, *J* = 6.5 Hz), 23.5 (d, *J* = 5.1 Hz), 45.4 (d, *J* = 24.5 Hz), 52.5, 64.3 (d, *J* = 5.9 Hz), 127.8, 128.7 (d, *J* = 4.4 Hz), 128.8, 131.6 (d, *J* = 3.0 Hz), 134.3 (dd, *J* = 48.9, 7.2 Hz), 154.7 (dd, *J* = 249.9, 10.1 Hz), 174.5 (d, *J* = 4.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -138.1 (d, *J* = 6.8 Hz); IR (ATR): 2986, 2952, 1739, 1445, 1273, 1134, 1024, 984, 889 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{24}FO_6P$ $[M+Na]^+$ 397.1187, Found 397.1187.

*Determination of the Configuration of Alkenylphosphate **3ma***

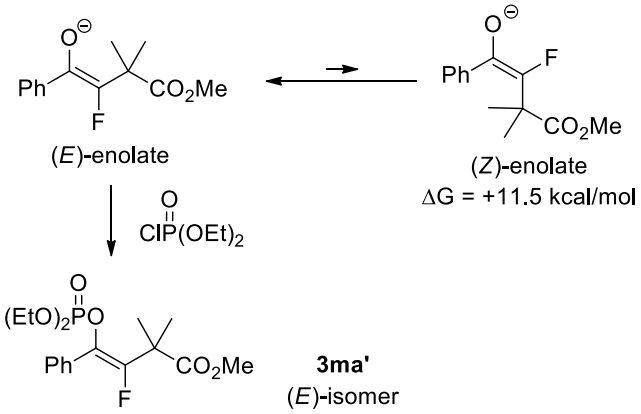
In this substitution reaction, alkenylphosphate **3ma** and its analog **3ma'** were obtained as a single isomer (Table 2, entry 12, and Scheme S1a). The NOE analysis of those compounds did not give any information about the configuration. Therefore, we attempted the synthesis of a mixture of stereoisomers of **3ma'** from ketone **10** by treating with diethyl chlorophosphate in the presence of *t*BuOK or P4-*t*Bu in DMF or THF (Scheme S1b). However, under these reaction conditions, only the identical isomer of **3ma'** was obtained.

Scheme S1.



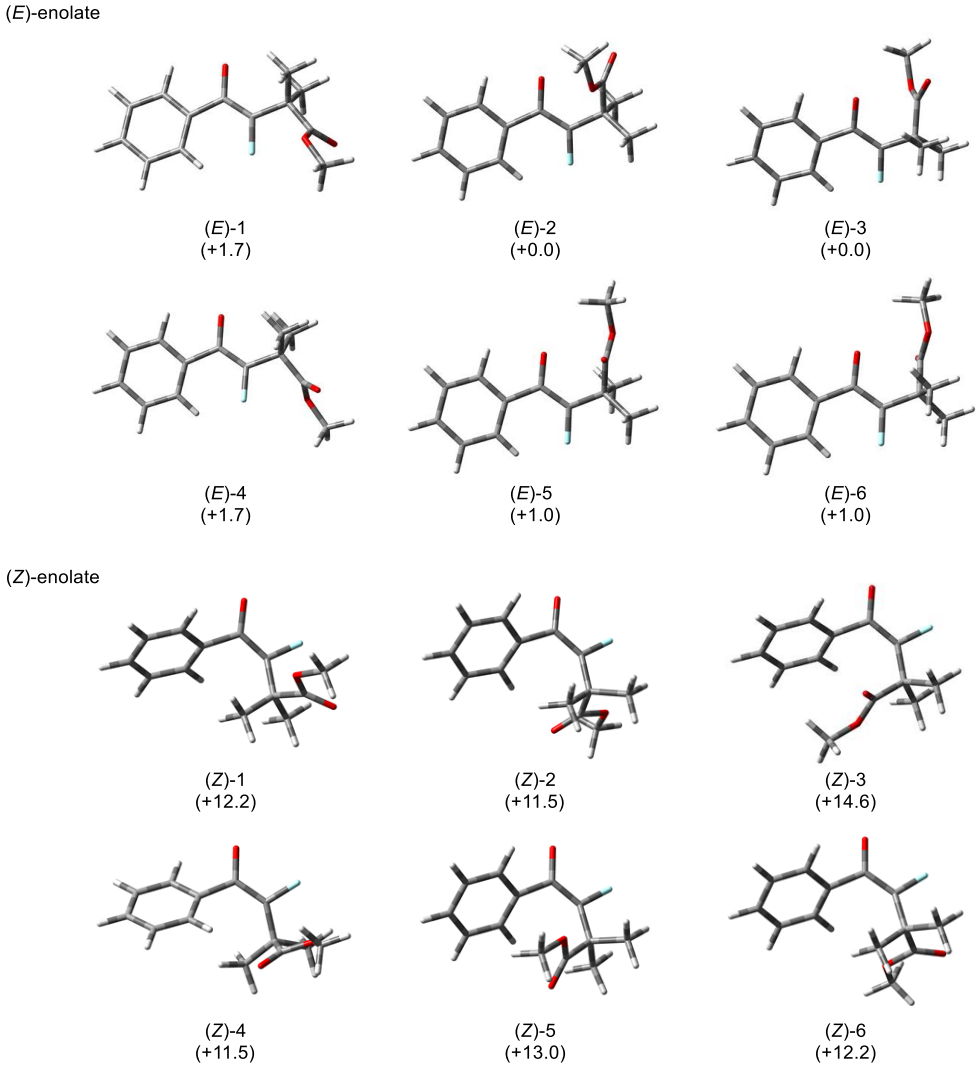
We assumed that the obtained isomer would be formed from the thermodynamically favored enolate of ketone **10**, and thus compared the Gibbs free energy of (*E*)- and (*Z*)-enolates of **10** by using DFT calculation. As a result, the Gibbs free energy difference (ΔG) between (*E*)- and (*Z*)-enolates was found to be 11.5 kcal/mol, suggesting (*E*)-enolate would be energetically favored. Based on the experimental evidence and the result of DFT calculation, we concluded the configuration of alkenylphosphate **3ma** would be *E* (Scheme S2).

Scheme S2.



The geometries were fully optimized using the B3LYP/6-31G(d) methods in gas-phase. A variety of initial structures generated from a series of conformation of enolate were thoroughly explored (Figure S1).

Figure S1.



Complete References of Gaussian 16

Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

Cartesian coordinates

(*E*)-2

B3LYP/6-31g(d); E(RB3LYP) = -829.346156 hartree
Sum of electronic and thermal Free Energies= -829.146868 hartree
Thermal correction to Gibbs Free Energy= 0.199287 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.055967	-0.775655	-0.851187
2	6	0	2.676909	-0.874689	-0.651298
3	6	0	1.984752	0.069088	0.135147
4	6	0	2.748050	1.109310	0.702094
5	6	0	4.123100	1.207759	0.503137
6	6	0	4.793388	0.262377	-0.278014
7	1	0	4.559457	-1.522422	-1.465207
8	1	0	2.133732	-1.687894	-1.110141
9	1	0	2.197452	1.826724	1.301915
10	1	0	4.678798	2.027192	0.959277
11	1	0	5.868526	0.333065	-0.438110
12	6	0	0.492582	0.116464	0.455322
13	8	0	0.098863	1.117891	1.166540
14	6	0	-0.382078	-0.853512	-0.002525
15	9	0	0.084633	-1.942138	-0.737771
16	6	0	-1.872010	-0.842510	0.309131
17	6	0	-2.073728	-0.873358	1.853997
18	1	0	-3.132208	-0.988180	2.108542
19	1	0	-1.482092	-1.710564	2.231126
20	1	0	-1.693004	0.051001	2.305832
21	6	0	-2.531576	-2.117158	-0.301266
22	1	0	-1.938445	-2.968595	0.043131
23	1	0	-3.574807	-2.213142	0.016851
24	1	0	-2.498429	-2.078541	-1.397380
25	6	0	-2.720866	0.336491	-0.182010
26	8	0	-3.927266	0.393372	-0.005107
27	8	0	-2.060012	1.356999	-0.784153
28	6	0	-2.883270	2.447598	-1.195668
29	1	0	-3.399428	2.899218	-0.342681
30	1	0	-2.203403	3.168671	-1.653525
31	1	0	-3.637858	2.123397	-1.919089

(*E*)-3

B3LYP/6-31g(d); E(RB3LYP) = -829.346156 hartree
Sum of electronic and thermal Free Energies= -829.146867 hartree
Thermal correction to Gibbs Free Energy= 0.199289 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.090878	-0.877768	-0.596133
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3	6	0	-1.956011	0.066141	0.130335
4	6	0	-2.666966	1.215837	0.528905
5	6	0	-4.046770	1.321334	0.370635
6	6	0	-4.775167	0.271817	-0.196092
7	1	0	-4.640610	-1.708397	-1.038890
8	1	0	-2.206451	-1.886707	-0.754871
9	1	0	-2.072247	2.011474	0.965825
10	1	0	-4.560712	2.227691	0.691126
11	1	0	-5.854430	0.347166	-0.322840
12	6	0	-0.450534	0.120964	0.379045
13	8	0	-0.012125	1.186430	0.958944
14	6	0	0.386897	-0.918200	0.012497
15	9	0	-0.116687	-2.038943	-0.646177
16	6	0	1.892560	-0.889647	0.234552
17	6	0	2.560422	-2.000081	-0.630980
18	1	0	3.627676	-2.085565	-0.402904
19	1	0	2.032017	-2.930293	-0.410373
20	1	0	2.437063	-1.776429	-1.697895
21	6	0	2.193733	-1.184874	1.736043
22	1	0	1.652261	-2.101008	1.986769
23	1	0	3.268306	-1.306580	1.906995
24	1	0	1.825504	-0.367560	2.368863
25	6	0	2.663930	0.393885	-0.096137
26	8	0	3.864575	0.503816	0.094386
27	8	0	1.958075	1.401434	-0.668287
28	6	0	2.720866	2.563929	-0.989622
29	1	0	3.520600	2.330247	-1.699400
30	1	0	2.010894	3.263981	-1.434218
31	1	0	3.175154	2.999647	-0.094289

(*Z*)-2

B3LYP/6-31g(d); E(RB3LYP) = -829.327938 hartree
Sum of electronic and thermal Free Energies= -829.128546 hartree
Thermal correction to Gibbs Free Energy= 0.199392 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	-1.737081	0.358025	-0.296463
4	6	0	-2.974774	0.804723	0.196613
5	6	0	-4.025661	-0.080387	0.424838
6	6	0	-3.880258	-1.441104	0.125900
7	1	0	-2.555104	-2.946085	-0.668727
8	1	0	-0.680270	-1.349267	-1.046814
9	1	0	-3.090144	1.869577	0.378509
10	1	0	-4.968317	0.287876	0.828044
11	1	0	-4.705148	-2.132322	0.290703
12	6	0	-0.675004	1.392800	-0.623990
13	8	0	-1.095780	2.379285	-1.304223
14	6	0	0.653414	1.145697	-0.285533
15	9	0	1.550547	2.123179	-0.775275
16	6	0	1.363391	0.448867	0.855411
17	6	0	0.363458	0.075982	1.976296
18	1	0	0.819798	-0.561845	2.744586
19	1	0	-0.002719	0.996285	2.444825
20	1	0	-0.488163	-0.458931	1.549192
21	6	0	2.563317	1.198109	1.474239
22	1	0	2.234885	2.102157	1.991198
23	1	0	3.061715	0.551401	2.209391
24	1	0	3.290408	1.488485	0.713014
25	6	0	1.918603	-0.876330	0.285634
26	8	0	1.606786	-2.000243	0.630076
27	8	0	2.850581	-0.663727	-0.682602
28	6	0	3.349735	-1.840863	-1.309015
29	1	0	2.539032	-2.402403	-1.783882
30	1	0	4.061685	-1.497145	-2.062843
31	1	0	3.848387	-2.497064	-0.586191

(*Z*)-4

B3LYP/6-31g(d); E(RB3LYP) = -829.343199 hartree
Sum of electronic and thermal Free Energies= 0.199027 hartree
Thermal correction to Gibbs Free Energy= -829.144172 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.605116	-1.337235	-0.573437
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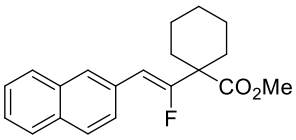
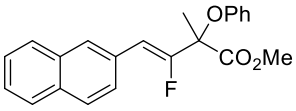
3	6	0	-1.970167	0.419043	-0.117161
4	6	0	-2.797466	0.861854	0.928804
5	6	0	-3.980388	0.198999	1.246903
6	6	0	-4.392421	-0.909474	0.496186
7	1	0	-3.927589	-2.180219	-1.183567
8	1	0	-1.803209	-0.994134	-1.720214
9	1	0	-2.490730	1.751420	1.471845
10	1	0	-4.593387	0.549484	2.076472
11	1	0	-5.323687	-1.420639	0.734597
12	6	0	-0.753737	1.253573	-0.477572
13	8	0	-0.985005	2.497407	-0.588538
14	6	0	0.451018	0.620613	-0.774614
15	9	0	1.455079	1.506223	-1.230380
16	6	0	1.167103	-0.619203	-0.283215
17	6	0	1.768262	-1.410672	-1.469585
18	1	0	2.419601	-2.228862	-1.135424
19	1	0	0.950434	-1.825062	-2.069585
20	1	0	2.357040	-0.740643	-2.100625
21	6	0	0.343612	-1.579382	0.602253
22	1	0	-0.457901	-2.049268	0.028492
23	1	0	0.995322	-2.376169	0.986291
24	1	0	-0.107145	-1.056923	1.448598
25	6	0	2.351824	-0.130808	0.581053
26	8	0	2.281528	0.526089	1.602129
27	8	0	3.551120	-0.510970	0.062949
28	6	0	4.686025	-0.162889	0.849097
29	1	0	4.625053	-0.617562	1.842889
30	1	0	5.552132	-0.552364	0.309246
31	1	0	4.770161	0.923418	0.969870

(*Z*)-Methyl 1-(1-fluoro-2-(naphthalen-2-yl)vinyl)cyclohexanecarboxylate (3ab):



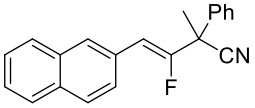
18 mg, 58%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.38-1.44 (m, 1H), 1.48-1.58 (m, 3H), 1.66-1.73 (m, 2H), 1.80-1.88 (m, 2H), 2.22-2.28 (m, 2H), 3.76 (s, 3H), 5.83 (d, *J* = 40.8 Hz, 1H), 7.42-7.48 (m, 2H), 7.65 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.78-7.80 (m, 3H), 7.94 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.7, 25.5, 31.6 (d, *J* = 2.9 Hz), 51.5 (d, *J* = 23.0 Hz), 52.5, 106.9 (d, *J* = 8.7 Hz), 125.9, 126.1, 126.7 (d, *J* = 8.6 Hz), 127.5, 127.7 (d, *J* = 8.6 Hz), 127.9, 128.0, 130.8, 132.4, 133.4, 161.1 (d, *J* = 270.0 Hz), 173.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.3 (d, *J* = 40.7 Hz); IR (ATR): 3058, 2940, 2860, 1735, 1677, 1454, 1311, 1222, 1132, 1016 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{21}FO_2$ $[M+Na]^+$ 335.1418, Found 335.1418; m.p. 67.5-68.5 °C.

(*Z*)-Methyl 3-fluoro-2-methyl-4-(naphthalen-2-yl)-2-phenoxybut-3-enoate (3ac):



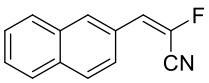
22 mg, 62%; green oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.79 (s, 3H), 3.86 (s, 3H), 6.26 (d, *J* = 39.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.27 (dd, *J* = 8.4, 7.8 Hz, 2H), 7.45-7.49 (m, 2H), 7.69 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.79-7.83 (m, 3H), 7.97 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8, 53.2, 81.6 (d, *J* = 30.2 Hz), 108.5 (d, *J* = 5.7 Hz), 121.3, 123.9, 126.25, 126.31, 126.7 (d, *J* = 7.2 Hz), 127.5, 128.1, 128.2, 128.5 (d, *J* = 7.2 Hz), 129.3, 129.7 (d, *J* = 2.9 Hz), 132.7, 133.3, 154.1, 156.7 (d, *J* = 267.2 Hz), 170.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.6 (d, *J* = 40.7 Hz); IR (ATR): 3059, 2952, 1693, 1656, 1595, 1489, 1455, 1285, 1223, 1116 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}FO_3$ $[M+Na]^+$ 373.1210, Found 373.1211.

(*Z*)-3-Fluoro-2-methyl-4-(naphthalen-2-yl)-2-phenylbut-3-enenitrile (5):



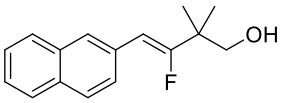
22 mg, 73%; white crystal; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.06 (s, 3H), 6.20 (d, *J* = 37.8 Hz, 1H), 7.40 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.45 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.46-7.49 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.65 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.78-7.83 (m, 3H), 7.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.8, 45.7 (d, *J* = 30.5 Hz), 108.4 (d, *J* = 7.2 Hz), 120.3 (d, *J* = 4.4 Hz), 126.2, 126.3 (d, *J*, 7.2 Hz), 126.4, 126.5, 127.6, 128.1, 128.2, 128.5 (d, *J* = 7.2 Hz), 128.8, 129.2, 129.3 (d, *J* = 3.0 Hz), 132.8, 133.2, 136.8, 156.5 (d, *J* = 268.7 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.9 (d, *J* = 38.4 Hz); IR (ATR): 3060, 2998, 1683, 1599, 1505, 1495, 1448, 1377, 1367, 1062, 901 cm^{-1}; HRMS (APCI) Calcd for $C_{21}H_{16}FN$ $[M+Na]^+$ 324.1159, Found 324.1159; m.p. 92.5-93.5 °C.

(*E*)-2-Fluoro-3-(naphthalen-2-yl)acrylonitrile (7):



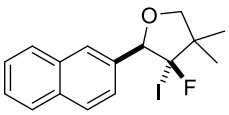
14 mg, 72%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 16.8 Hz, 1H), 7.54 (ddd, *J* = 7.2, 7.2, 1.8 Hz, 1H), 7.56 (ddd, *J* = 7.8, 7.2, 1.8 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 8.00 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 112.7 (d, *J* = 47.4 Hz), 124.1, 125.5 (d, *J* = 7.1 Hz), 126.2 (d, *J* = 24.5 Hz), 127.0, 127.7, 127.8, 128.4, 129.1, 129.5 (d, *J* = 4.4 Hz), 131.2 (d, *J* = 237.0 Hz), 133.0, 134.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -121.9 (d, *J* = 17.0 Hz); IR (ATR): 3063, 3031, 2925, 2857, 2224, 1454, 1362, 1274, 1185, 1142, 1071, 912, 818 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_8FN$ $[M]^+$ 197.0635, Found 197.0635; m.p. 87.5-88.5 °C.

(*Z*)-3-Fluoro-2,2-dimethyl-4-(naphthalen-2-yl)but-3-en-1-ol (8):



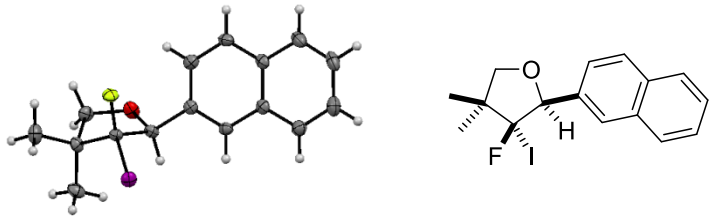
23 mg, 93%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.26 (s, 6H), 1.50 (br, 1H), 3.62 (d, J = 6.6 Hz, 2H), 5.78 (d, J = 41.4 Hz, 1H), 7.42-7.47 (m, 2H), 7.66 (dd, J = 7.2, 1.8 Hz, 1H), 7.78-7.80 (m, 3H), 7.94 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.3 (d, J = 2.1 Hz), 41.4 (d, J = 23.0 Hz), 69.1, 106.0 (d, J = 8.7 Hz), 125.8, 126.1, 126.7 (d, J = 7.2 Hz), 127.50, 127.52 (d, J = 7.2 Hz), 127.9, 128.0, 131.0, 132.3, 133.4, 164.6 (d, J = 267.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.5 (d, J = 42.9 Hz); IR (ATR): 3280, 3055, 2973, 2935, 2877, 2368, 2340, 1506, 1464, 1392, 1362, 1317, 1055, 898, 857, 827 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{17}FO$ $[M+Na]^+$ 267.1156, Found 267.1155; m.p. 99.5-100.5 °C.

(2*R,3*S**)-3-Fluoro-3-iodo-4,4-dimethyl-2-(naphthalen-2-yl)tetrahydrofuran (9):**

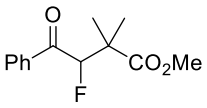


26 mg, 71%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.37 (s, 3H), 3.98 (d, J = 7.8 Hz, 1H), 4.17 (d, J = 7.8 Hz, 1H), 5.59 (d, J = 27.6 Hz, 1H) 7.48-7.51 (m, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.84-7.87 (m, 2H), 7.88-7.90 (m, 1H), 7.97 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.2 (d, J = 7.2 Hz), 30.0 (d, J = 2.9 Hz), 50.0 (d, J = 17.3 Hz) 75.4, 89.6 (d, J = 20.1 Hz), 101.6 (d, J = 265.7 Hz), 126.0, 126.17, 126.19, 127.5, 127.7, 128.2 (2C), 132.0 (d, J = 2.9 Hz), 132.9, 133.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.4 (d, J = 26.0 Hz); IR (ATR): 3056, 2972, 2937, 2878, 1603, 1509, 1466, 1393, 1371, 1055 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}FIO$ $[M+Na]^+$ 393.0122, Found 393.0122; m.p. 149.5-150.5 °C.

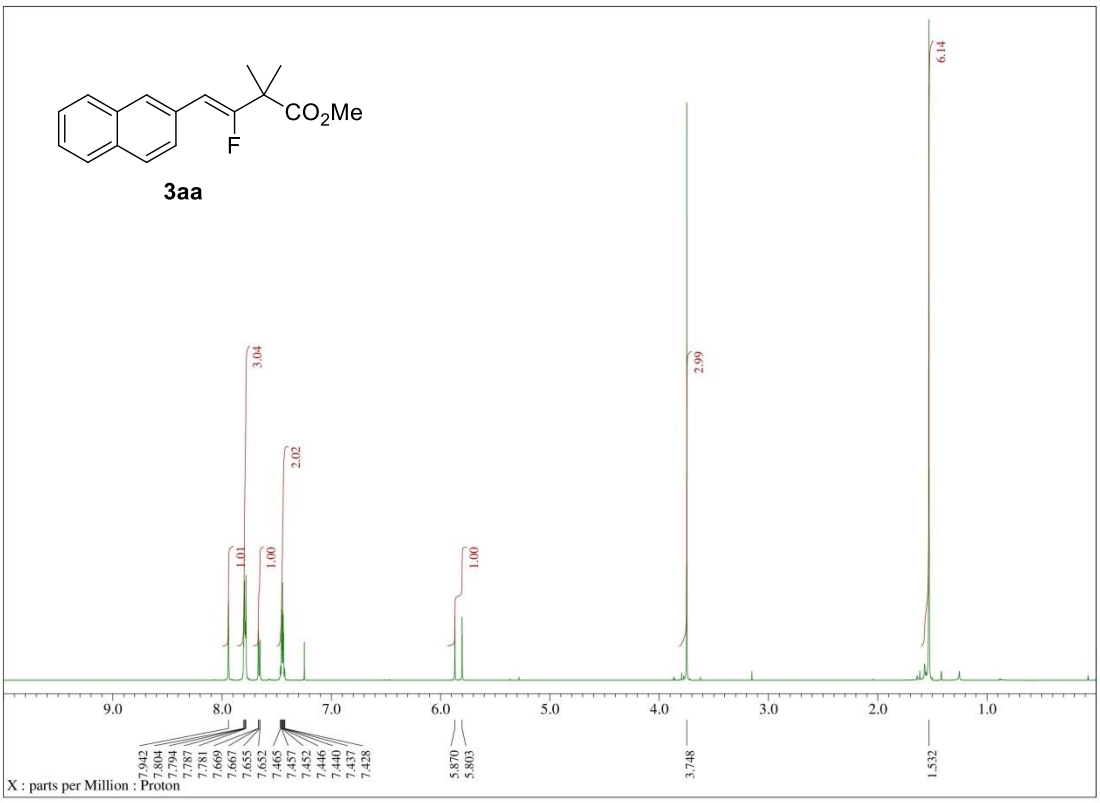
Figure S2. ORTEP diagram of **9**. CCDC No. 1890181. Recrystallization from CH_3CN/ethanol.



Methyl 3-fluoro-2,2-dimethyl-4-oxo-4-phenylbutanoate (10):



25 mg, 87%; yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27 (d, J = 1.2 Hz, 3H), 1.41 (d, J = 1.2 Hz, 3H), 3.67 (s, 3H), 5.74 (d, J = 46.8 Hz, 1H), 7.48 (dd, J = 8.4, 8.4 Hz, 2H), 7.60 (t, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1 (d, J = 3.6 Hz), 23.0 (d, J = 4.2 Hz), 45.6 (d, J = 20.1 Hz), 52.2, 96.2 (d, J = 188.3 Hz), 128.5, 129.3 (d, J = 4.4 Hz) 133.7, 135.6, 175.0 (d, J = 7.2 Hz), 195.7 (d, J = 21.6 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -194.0 (d, J = 47.5 Hz); IR (ATR): 3063, 2989, 2952, 2882, 1741, 1697, 1598, 1449, 1272, 1250, 1155, 1136, 1034 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{15}FO_3$ $[M+Na]^+$ 261.0897, Found 261.0897.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7.465
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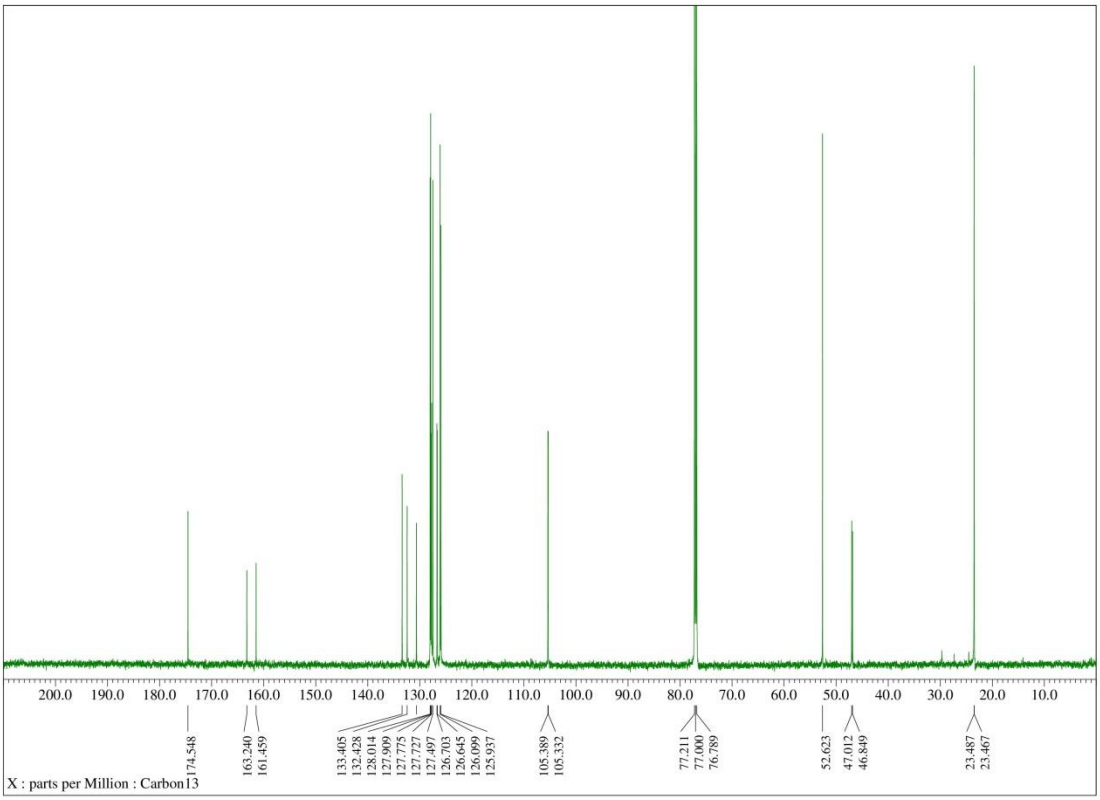
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133.405
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127.909
127.775
127.727
127.497
126.703
126.645
126.099
125.937
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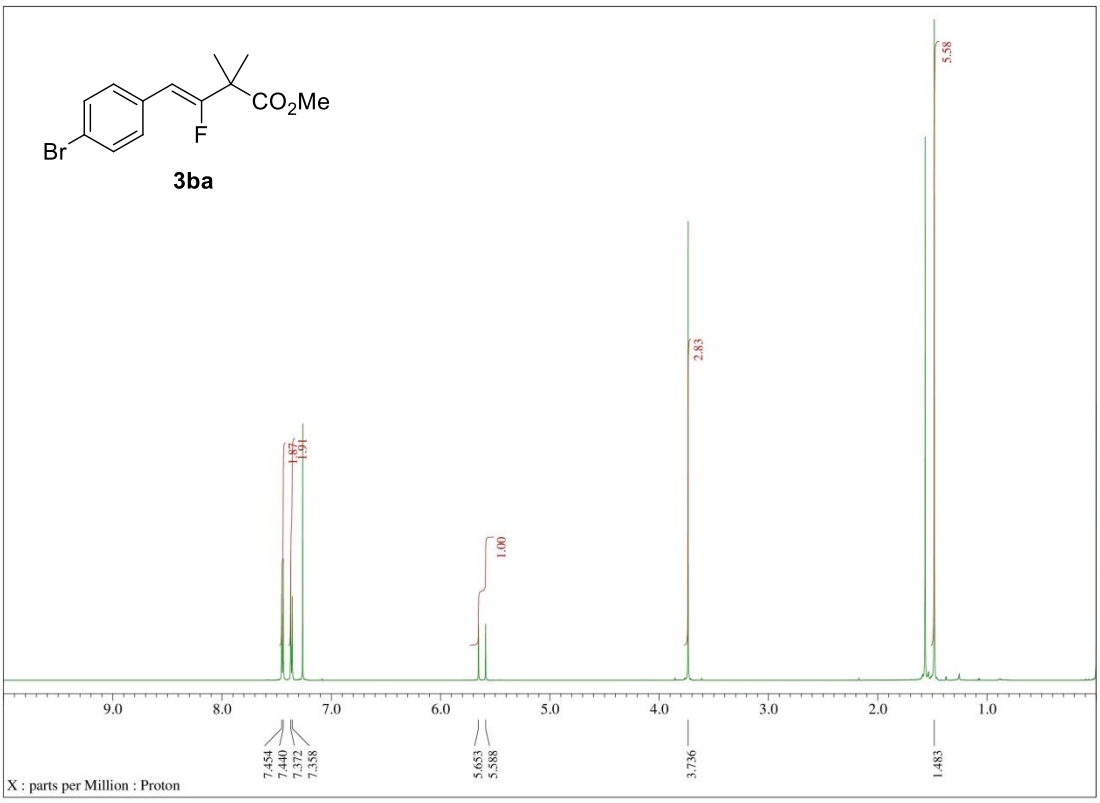
23.467
X : parts per Million : Carbon13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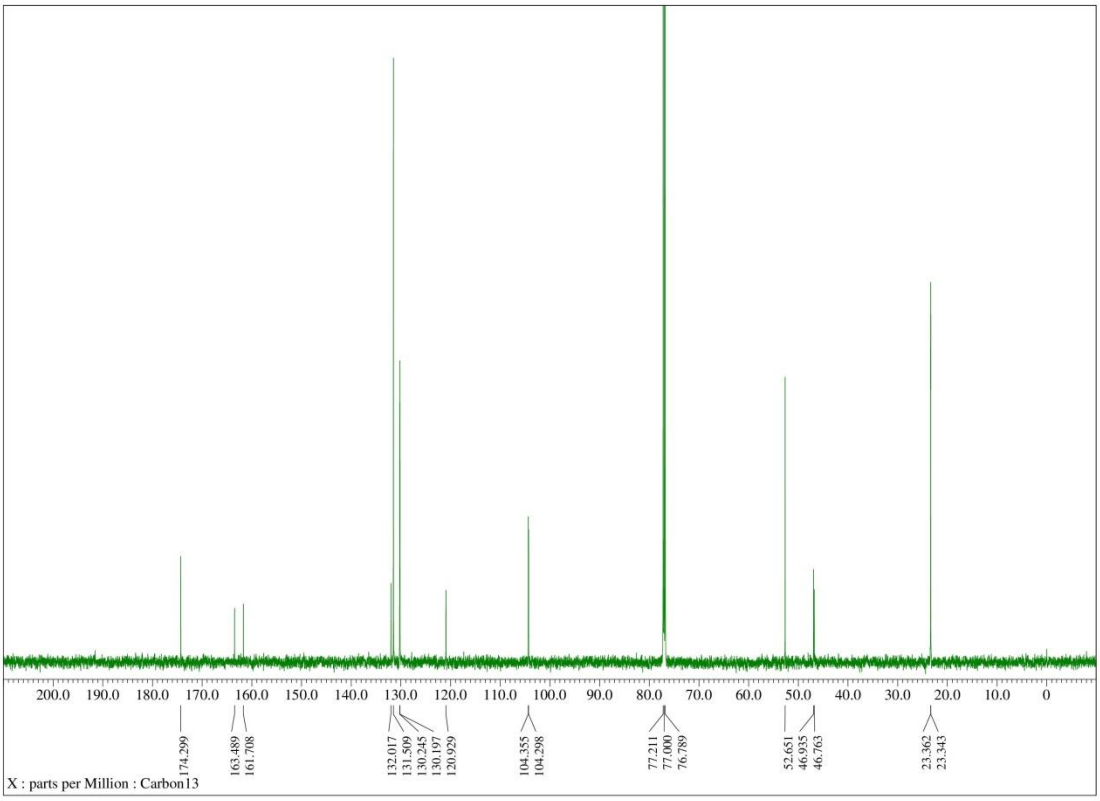
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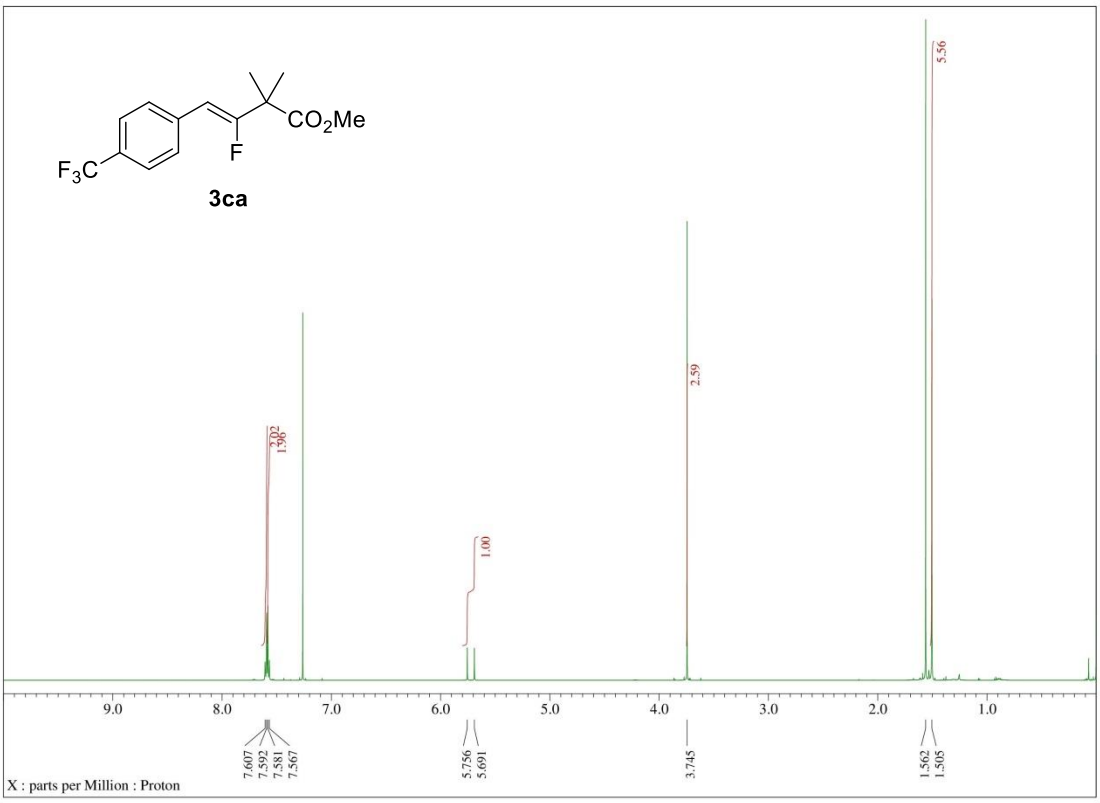
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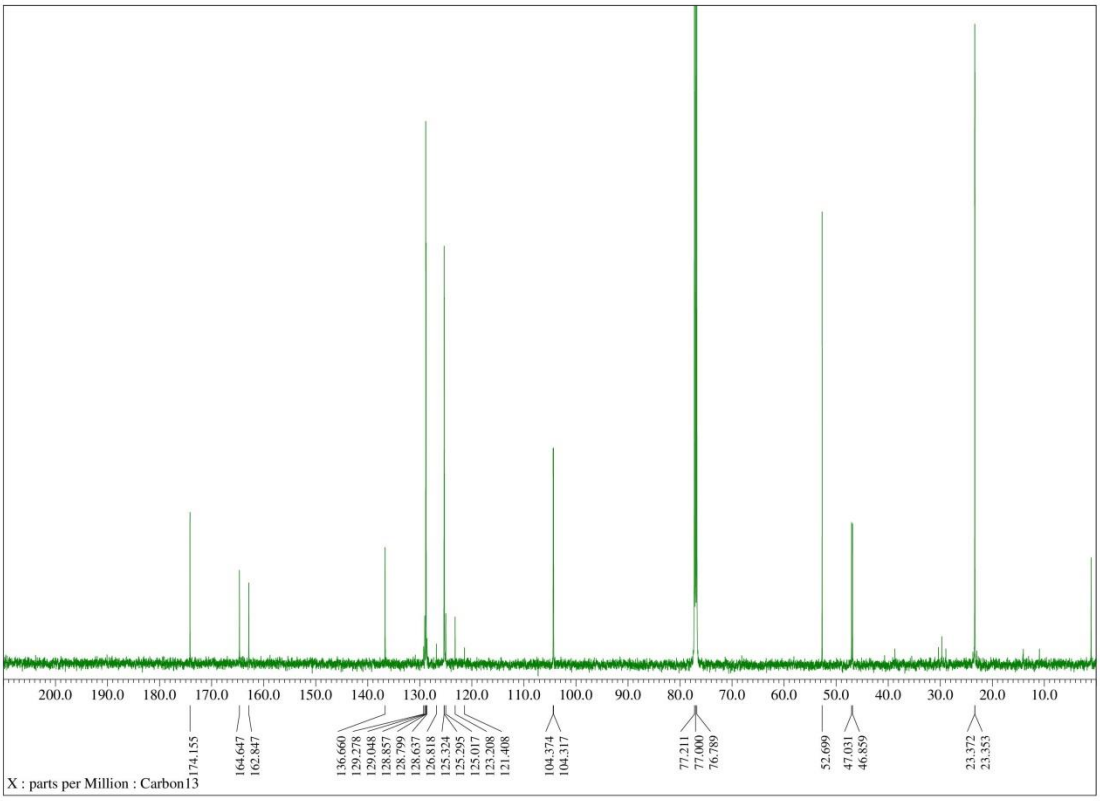
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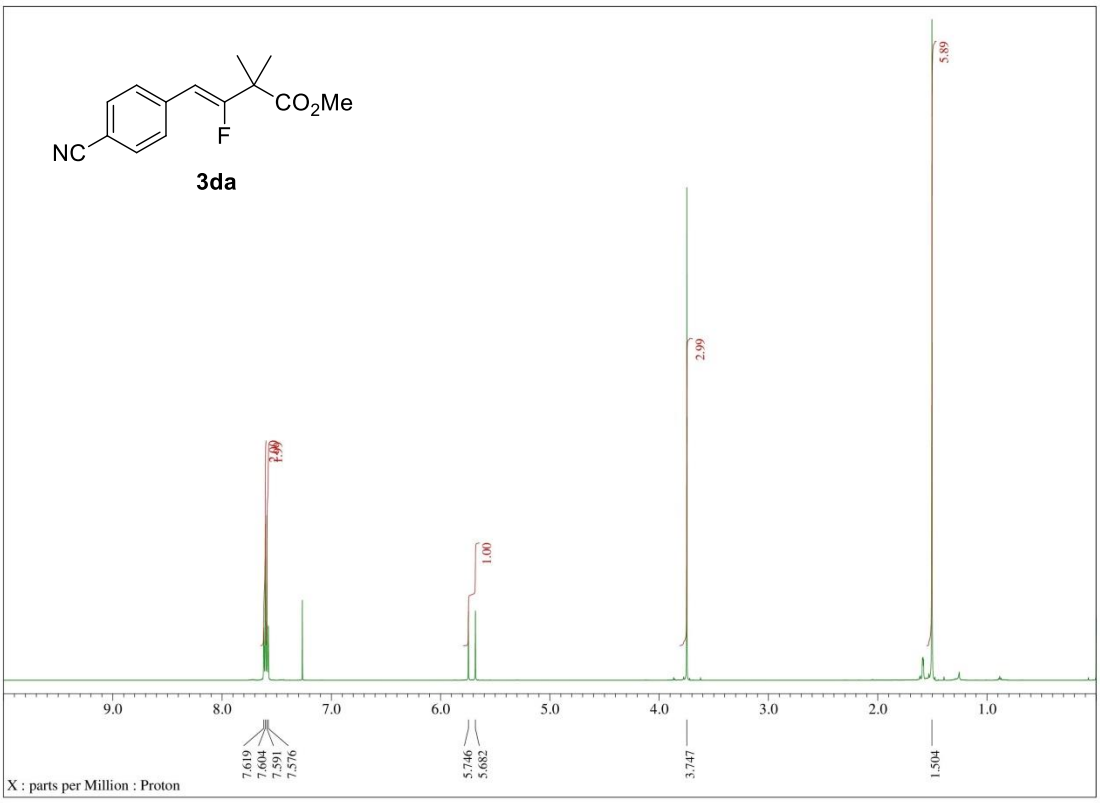
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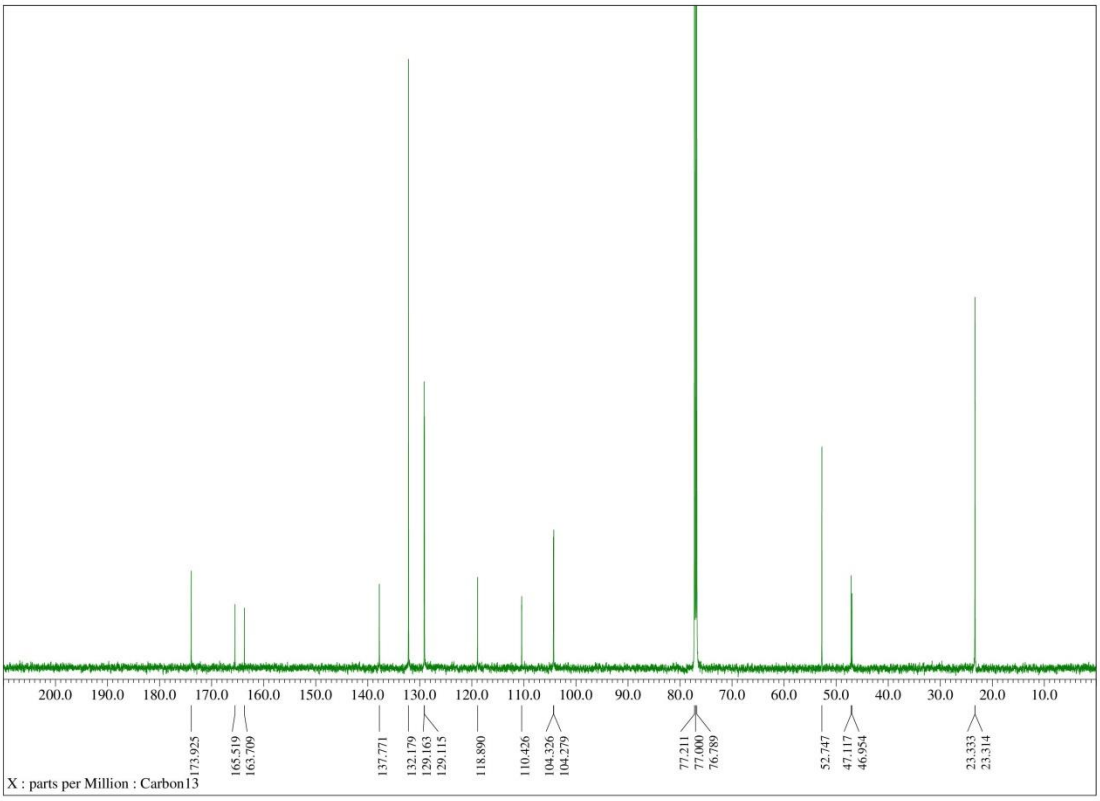
X : parts per Million : Proton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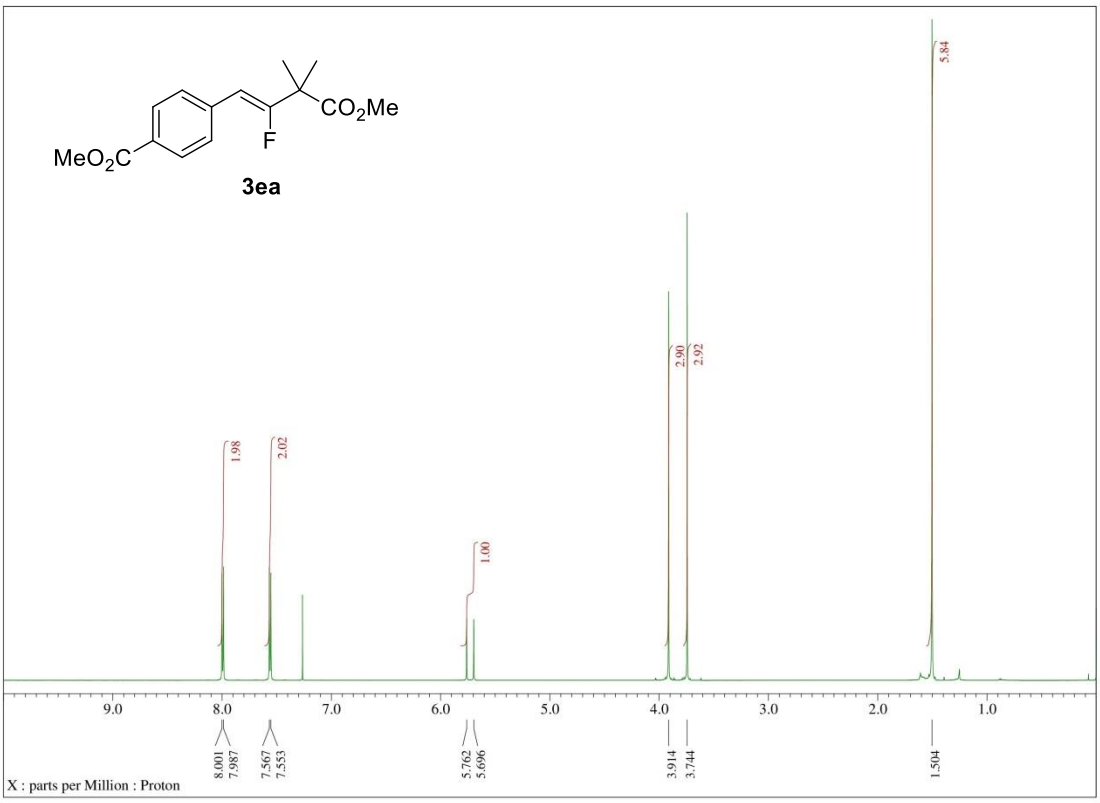
X : parts per Million : Carbon13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4.0
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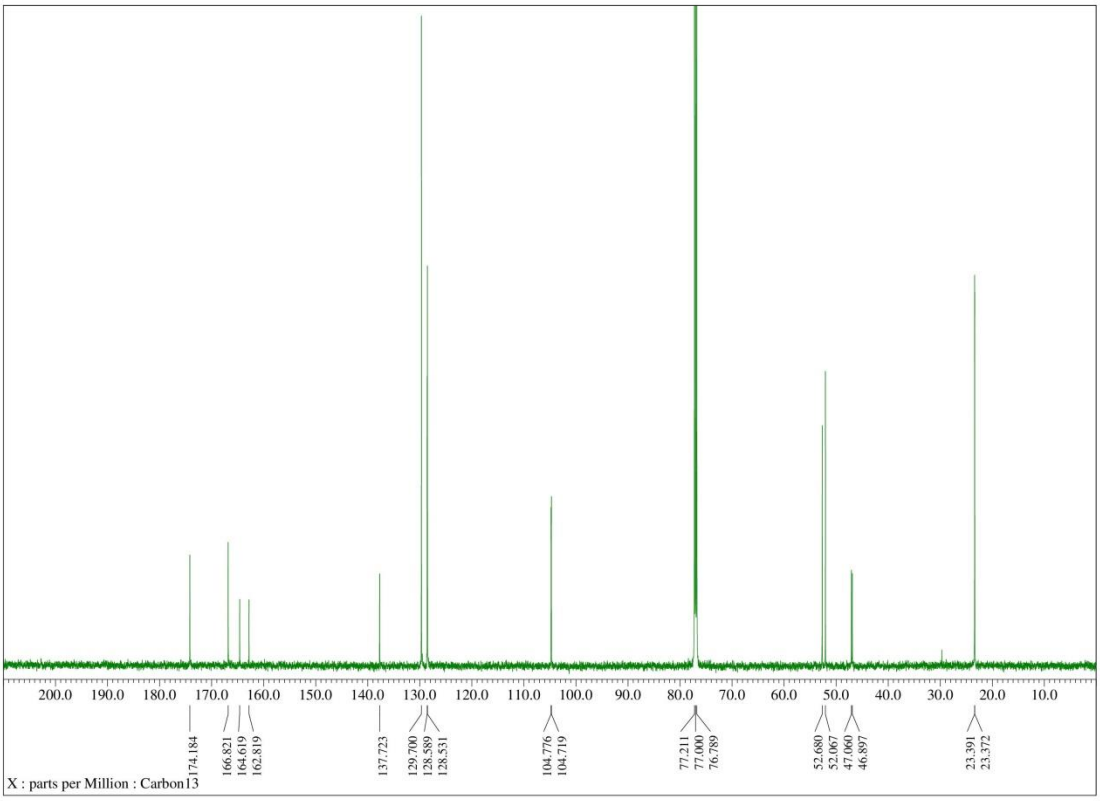
1.504
X : parts per Million : Proton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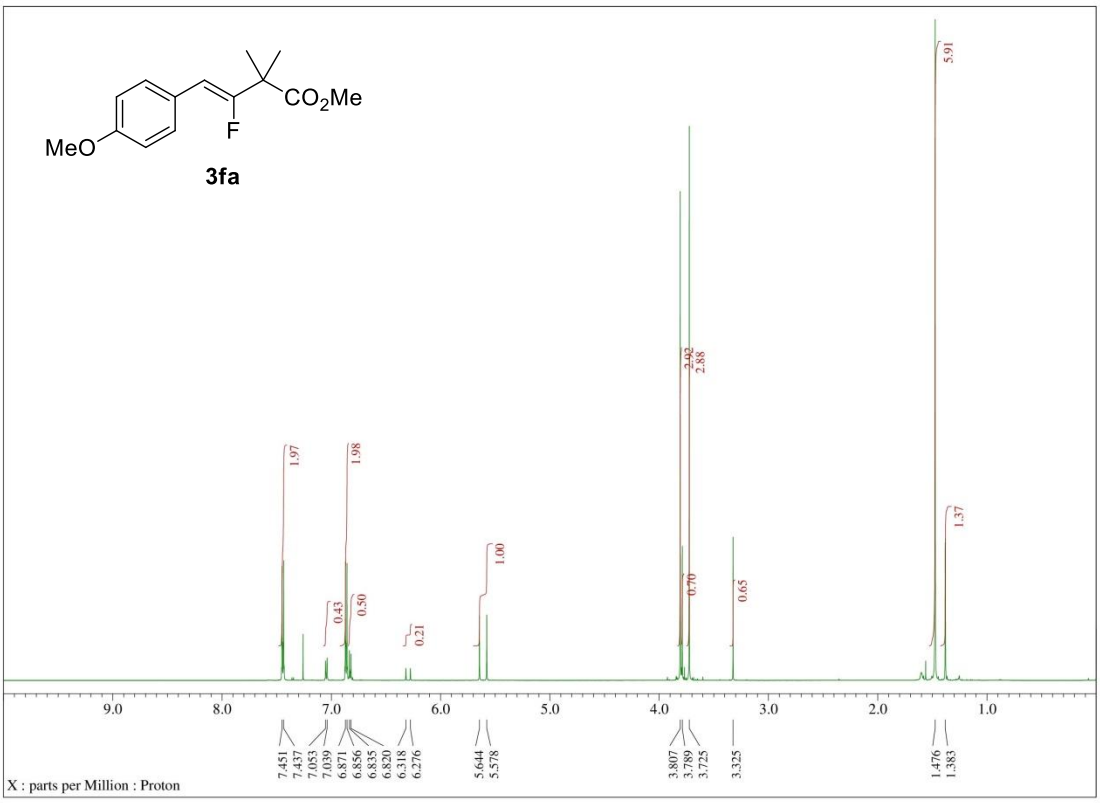
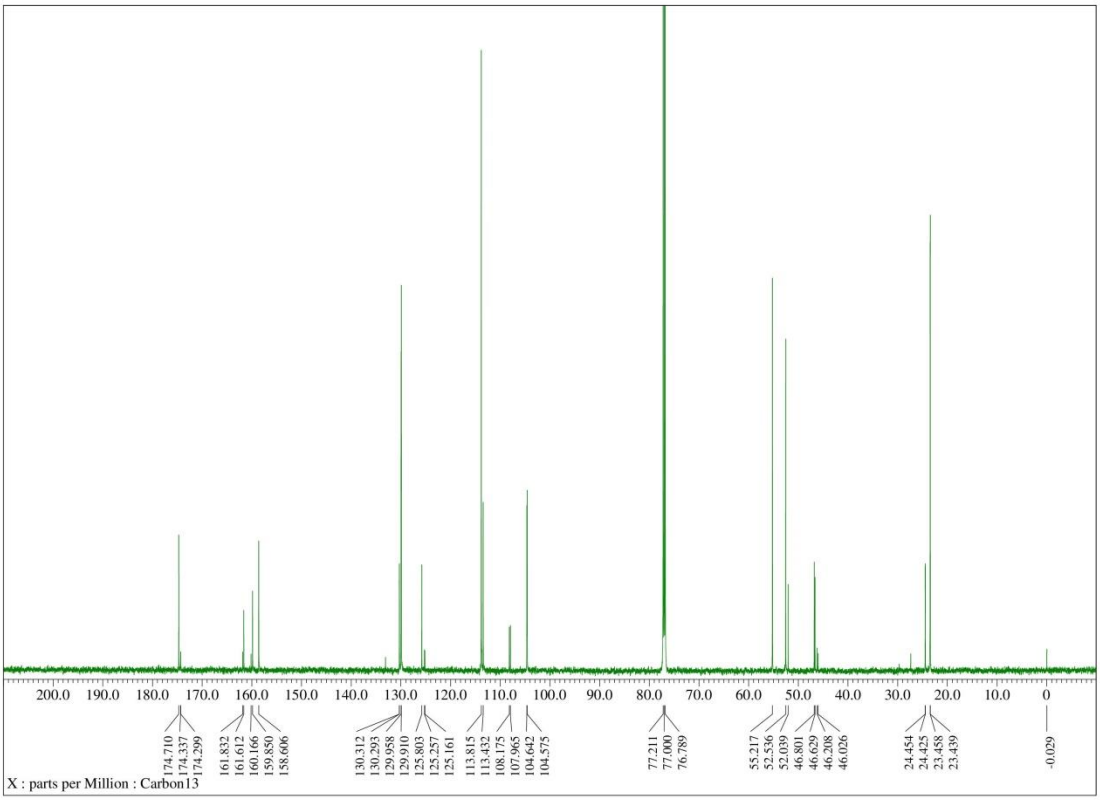
47.060
46.897
23.391
23.372
X : parts per Million : Carbon13


MeO
F
CO2Me
3fa
5.91
2.92
2.88
1.97
1.98
1.00
1.37
0.70
0.65
0.43
0.50
0.21
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.451
7.437
7.053
7.039
6.871
6.856
6.835
6.820
6.318
6.276
5.644
5.578
3.807
3.789
3.725
3.325
1.476
1.383
X : parts per Million : Proton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110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.710
174.337
174.299
161.832
161.612
160.166
159.850
158.606
130.312
130.293
129.958
129.910
125.803
125.257
125.161
113.815
113.432
108.175
107.965
104.642
104.575
77.211
77.000
76.789
55.217
52.536
52.039
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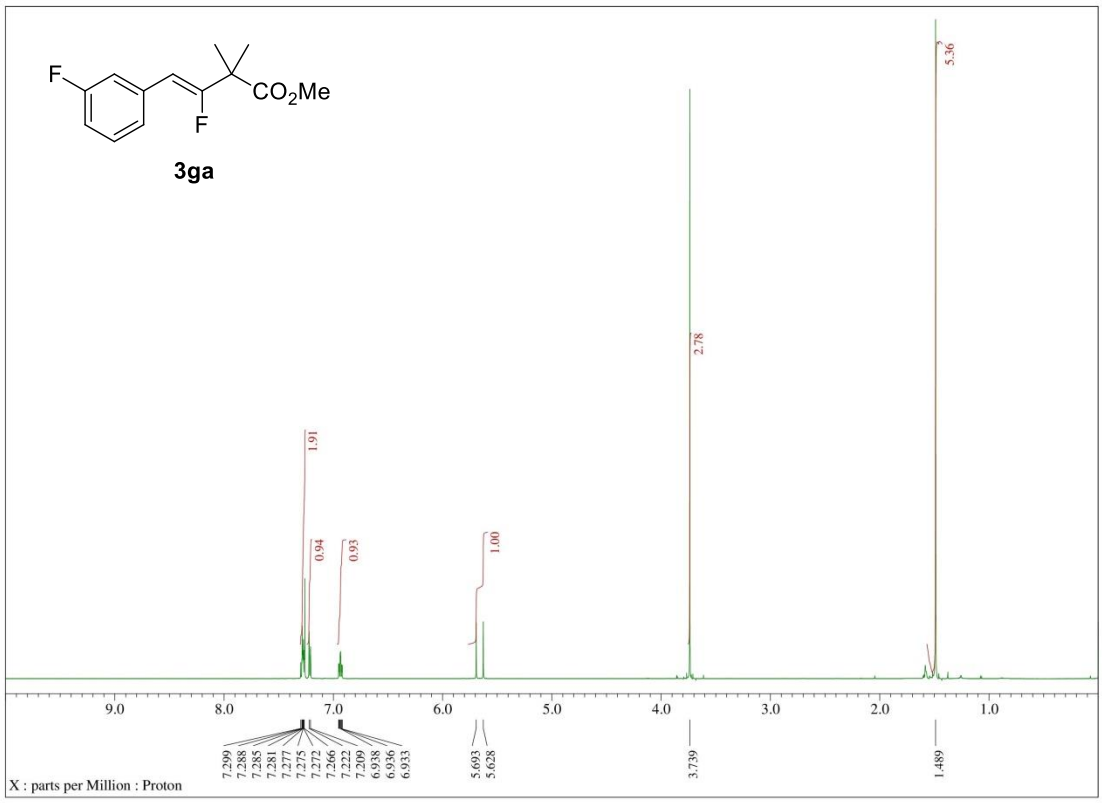
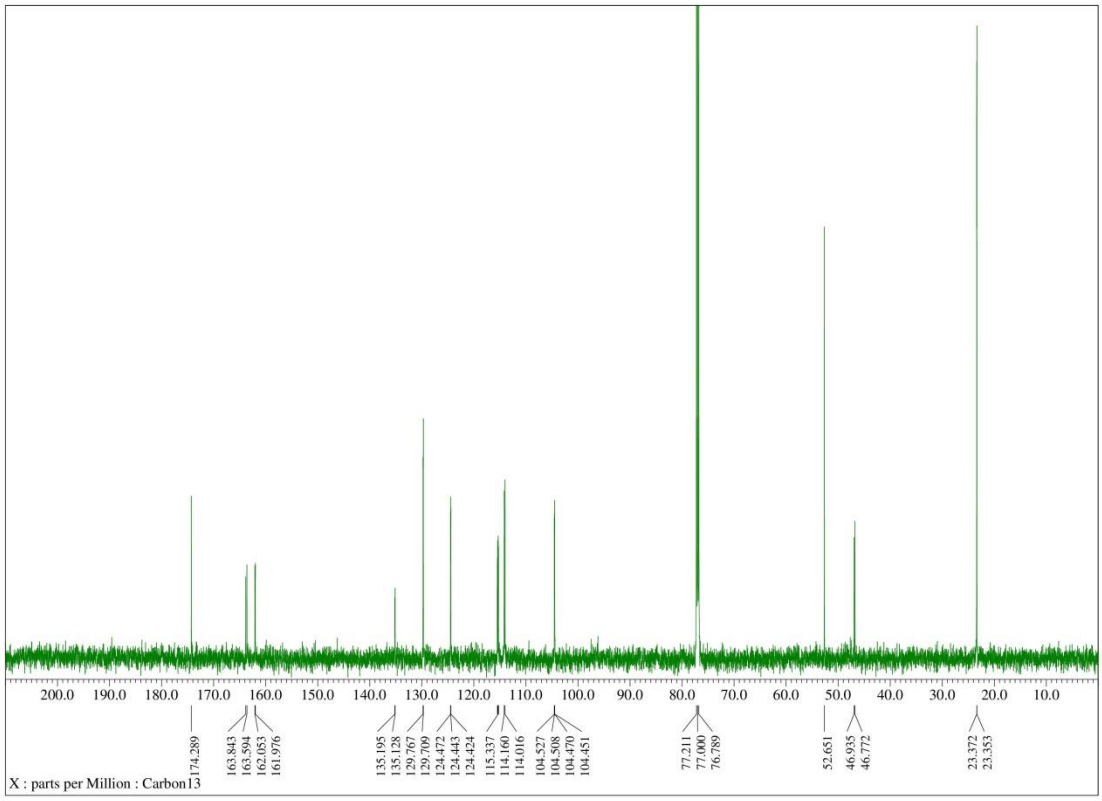
46.629
46.208
46.026
24.454
24.425
23.458
23.439
-0.029
X : parts per Million : Carbon13


F
CO2Me
F
3ga
5.36
2.78
1.91
0.94
0.93
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.299
7.288
7.285
7.281
7.277
7.275
7.272
7.266
7.222
7.209
6.938
6.936
6.933
5.693
5.628
3.739
1.489
X : parts per Million : Proton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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
174.289
163.843
163.594
162.053
161.976
135.195
135.128
129.767
129.709
124.472
124.443
124.424
115.337
114.160
114.016
104.527
104.508
104.470
104.451
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77.000
76.789
52.651
46.935
46.772
23.372
23.353
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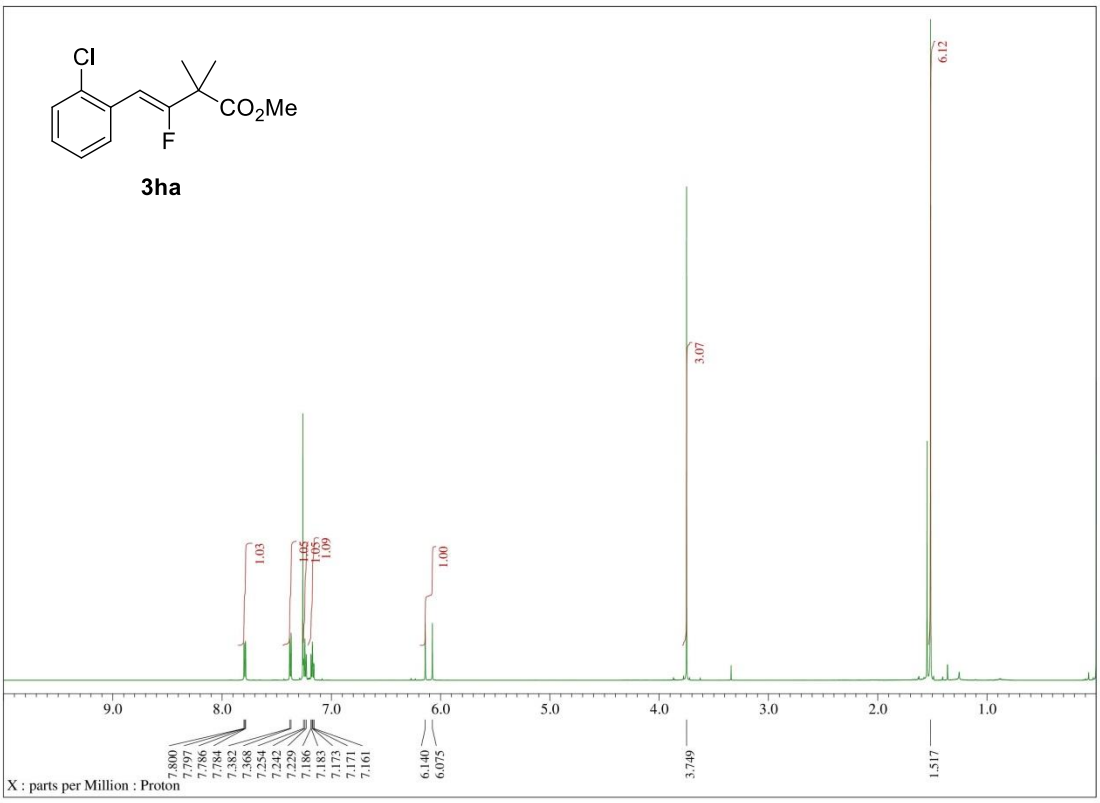
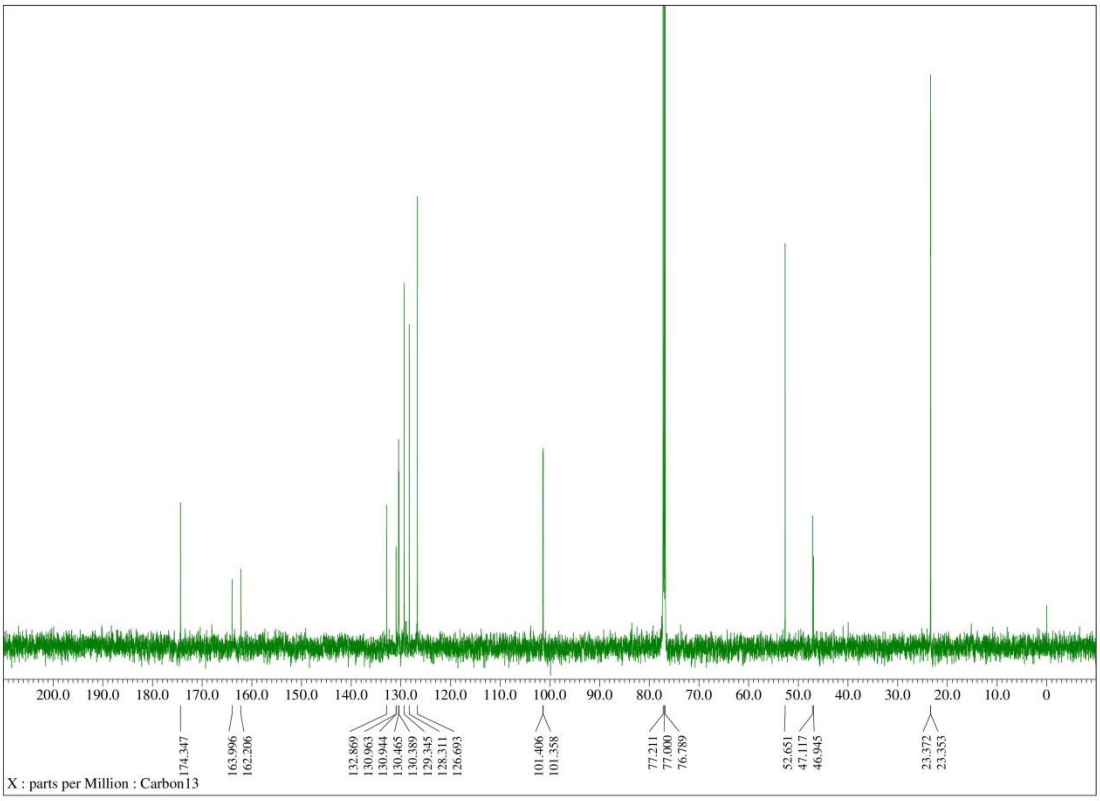
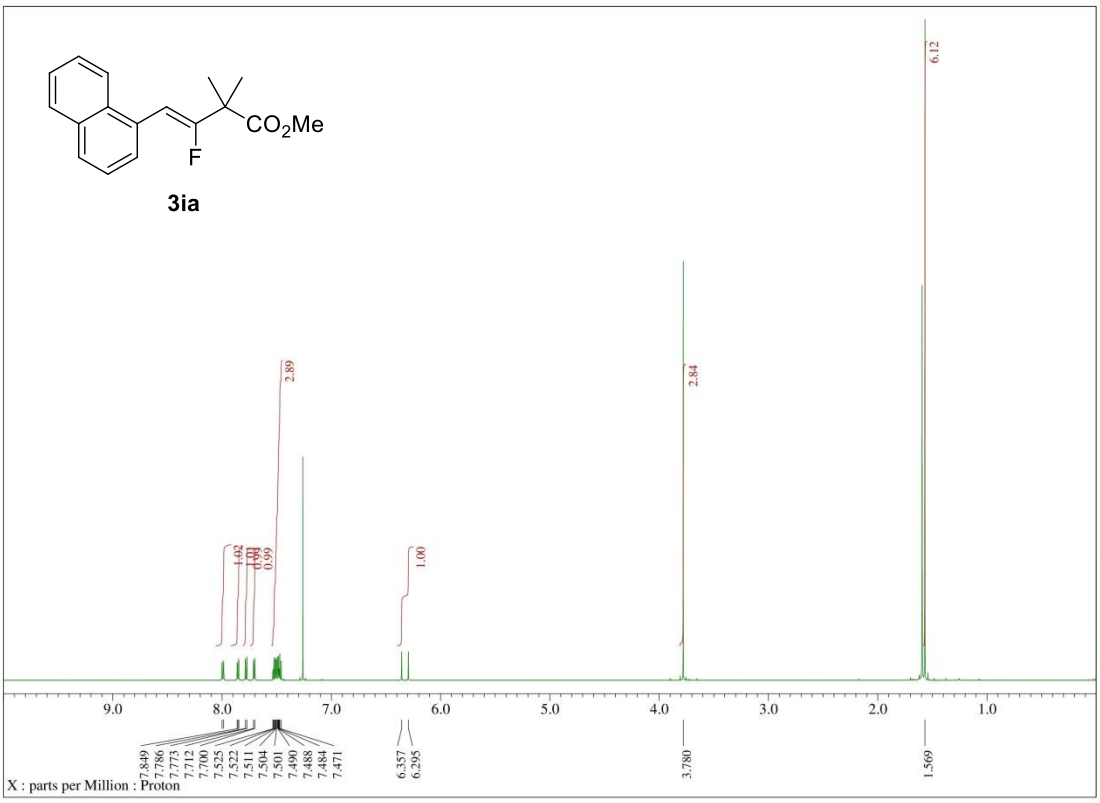
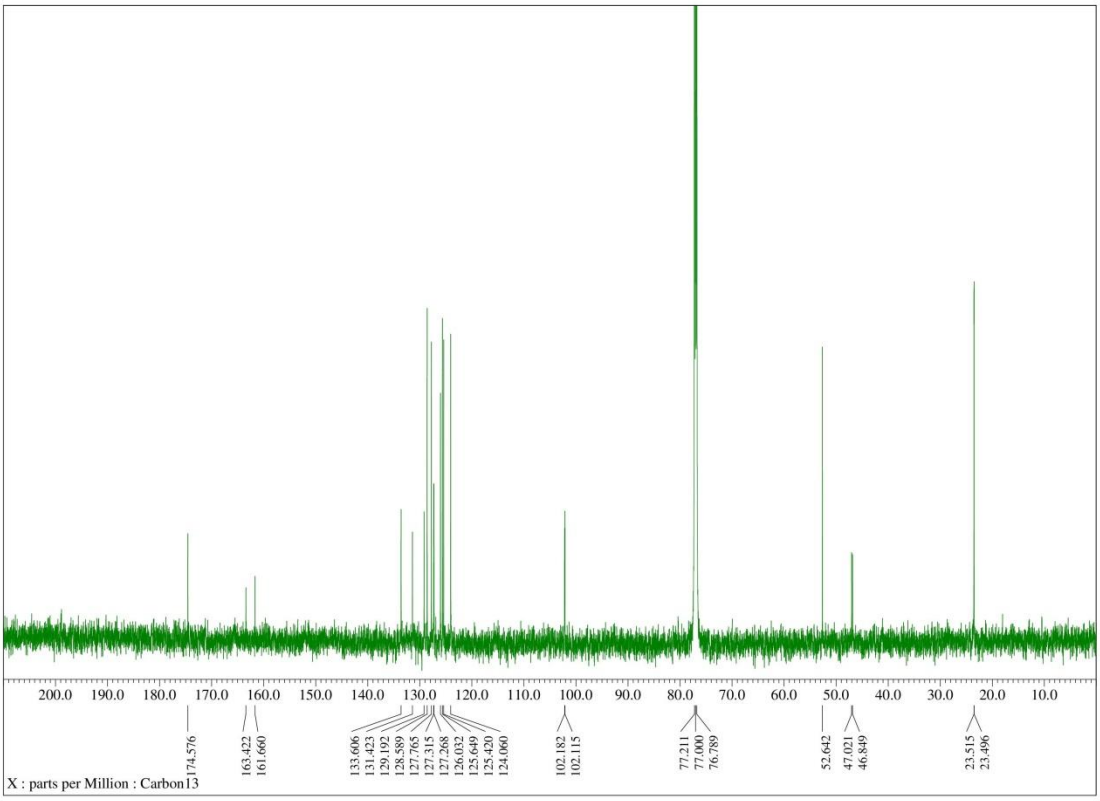

Cl
CO2Me
F
3ha
6.12
3.07
1.03
1.00
X : parts per Million : Proton


X : parts per Million : Carbon13


CO2Me
F
3ia
6.12
2.89
2.84
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.849
7.786
7.773
7.712
7.700
7.525
7.522
7.511
7.504
7.501
7.490
7.488
7.484
7.471
6.357
6.295
3.780
1.569
X : parts per Million : Proton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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
174.576
163.422
161.660
133.606
131.423
129.192
128.589
127.765
127.315
127.268
126.032
125.649
125.420
124.060
102.182
102.115
77.211
77.000
76.789
52.642
47.021
46.849
23.515
23.496
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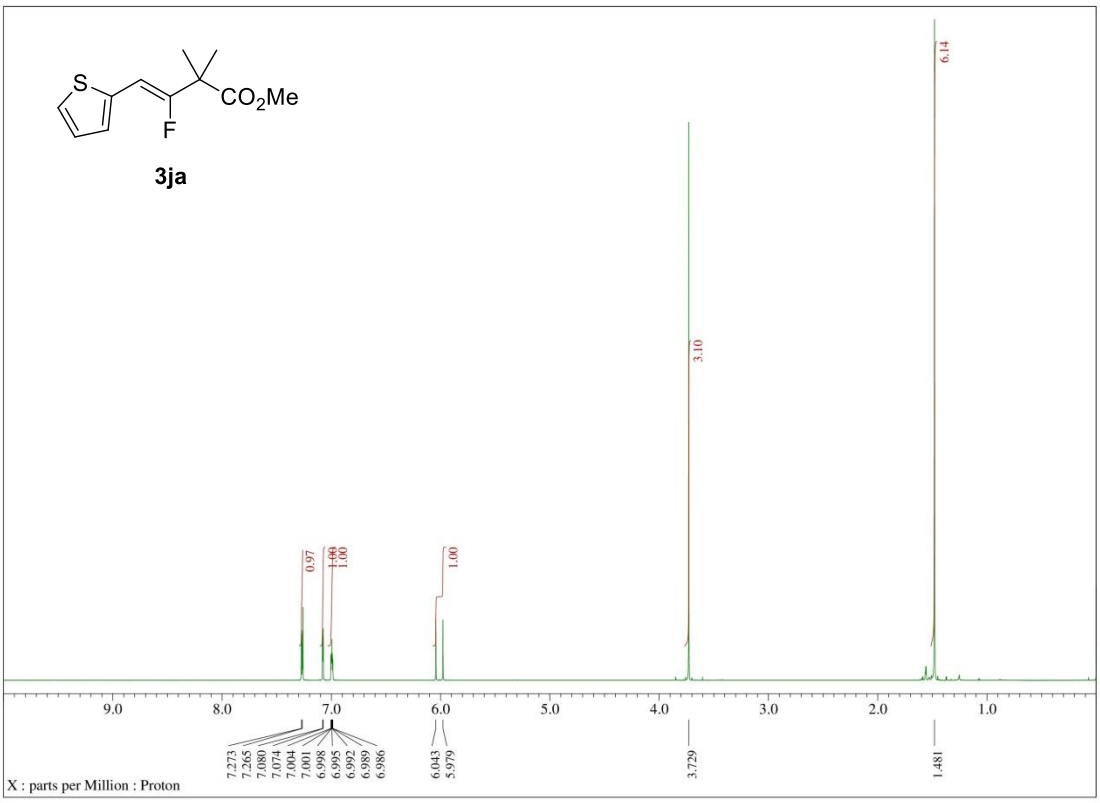
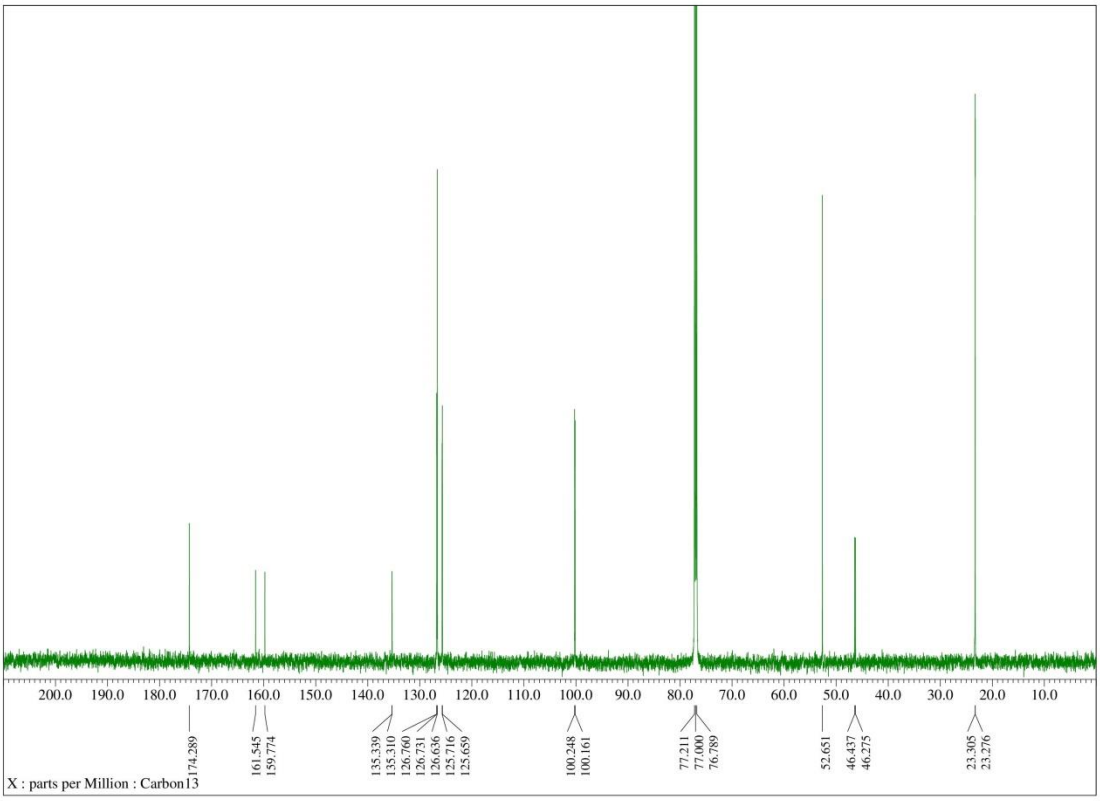
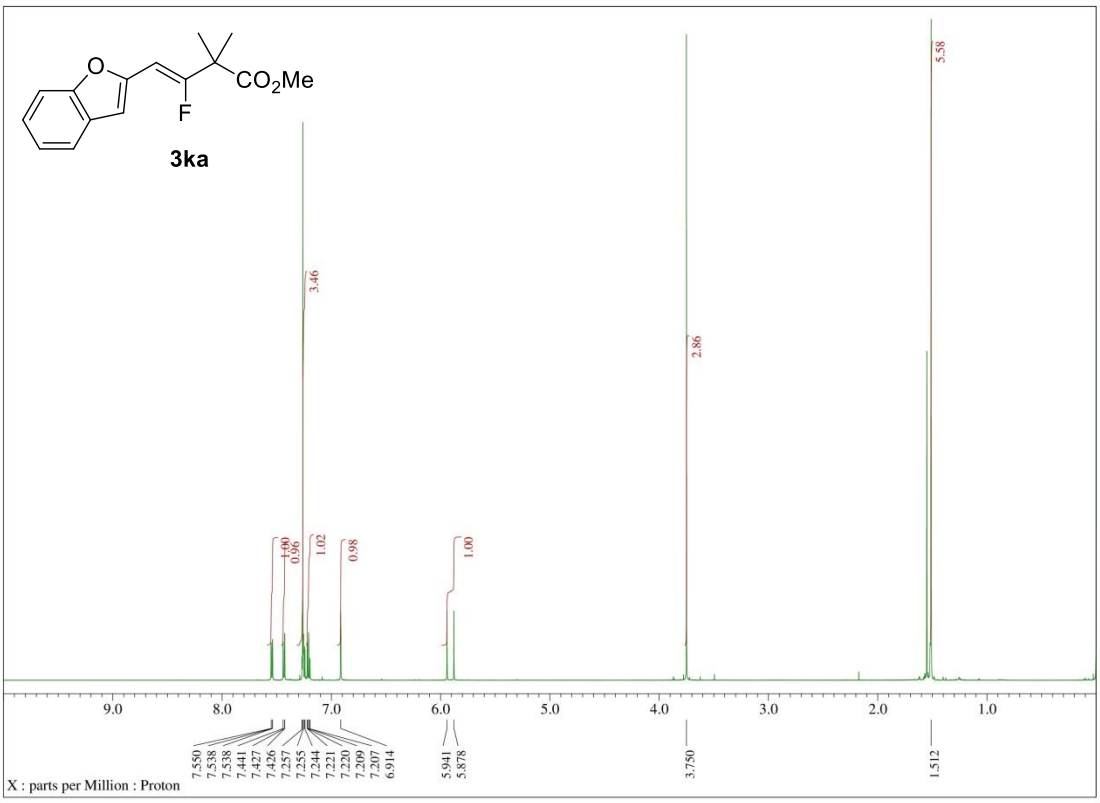
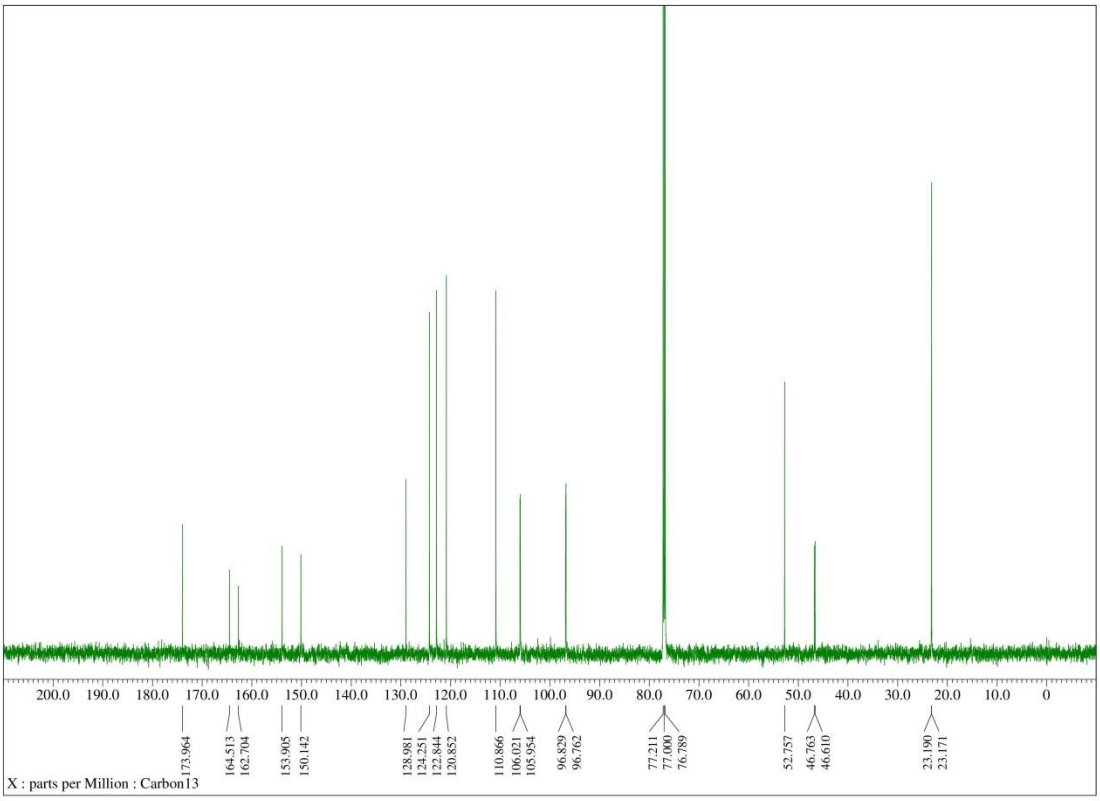
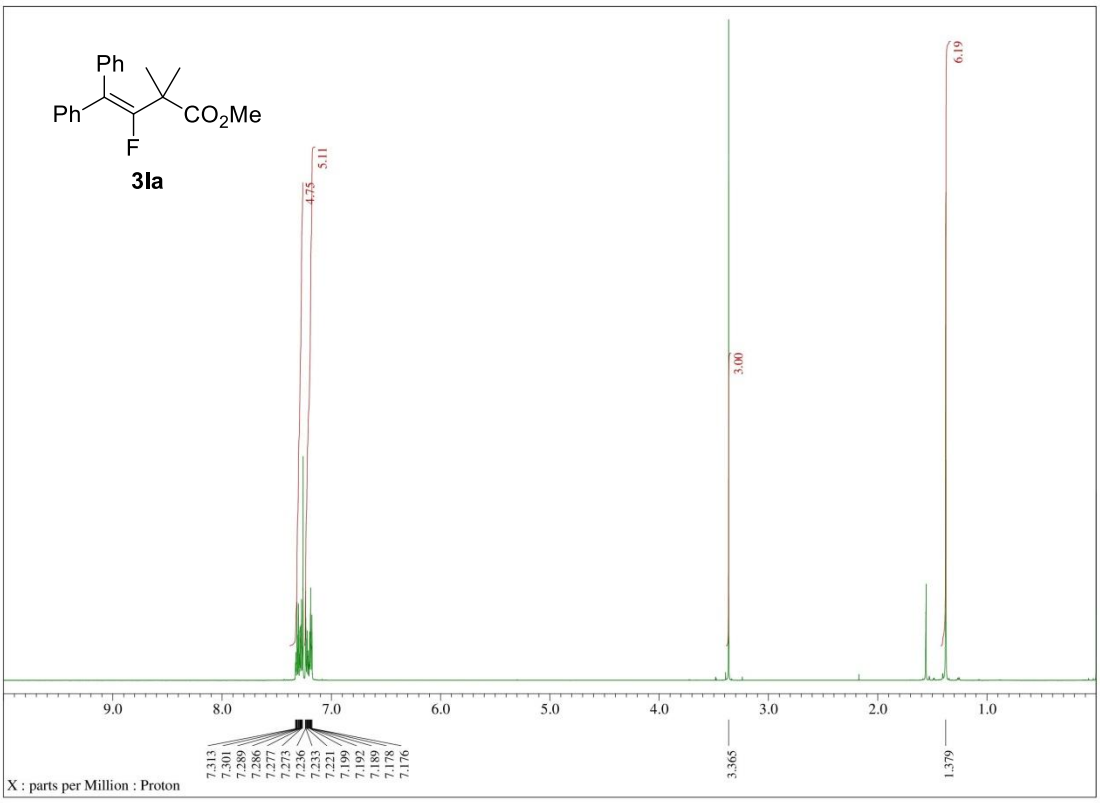
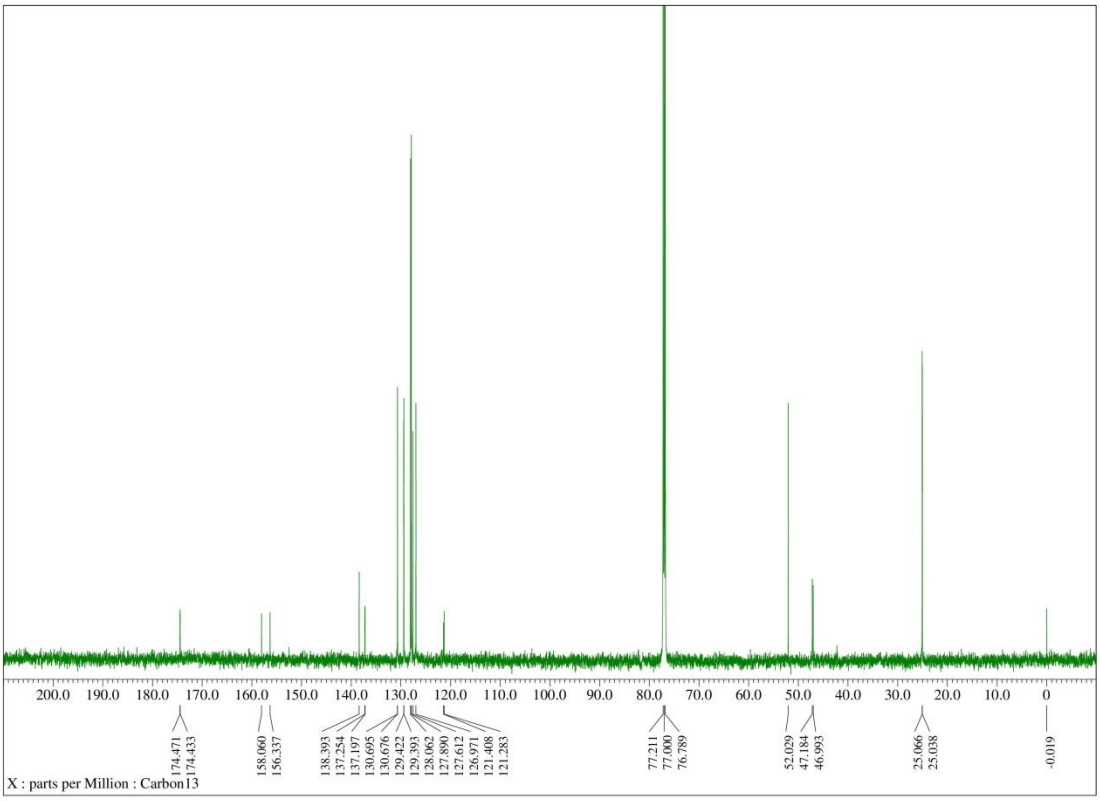

S
CO2Me
F
3ja
6.14
3.10
0.97
1.00
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.273
7.265
7.080
7.074
7.004
7.001
6.998
6.995
6.992
6.989
6.986
6.043
5.979
3.729
1.481
X : parts per Million : Proton


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
174.289
161.545
159.774
135.339
135.310
126.760
126.731
126.636
125.716
125.659
100.248
100.161
77.211
77.000
76.789
52.651
46.437
46.275
23.305
23.276
X : parts per Million : Carbon13


O
CO2Me
F
3ka
3.46
2.86
5.58
1.00
0.96
1.02
0.98
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.550
7.538
7.538
7.441
7.427
7.426
7.257
7.255
7.244
7.221
7.220
7.209
7.207
6.914
5.941
5.878
3.750
1.512
X : parts per Million : Proton


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.964
164.513
162.704
153.905
150.142
128.981
124.251
122.844
120.852
110.866
106.021
105.954
96.829
96.762
77.211
77.000
76.789
52.757
46.763
46.610
23.190
23.171
X : parts per Million : Carbon13


Ph
Ph
CO2Me
F
3la
5.11
4.75
3.00
6.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.313
7.301
7.289
7.286
7.277
7.273
7.236
7.233
7.221
7.199
7.192
7.189
7.178
7.176
3.365
1.379
X : parts per Million : Proton


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.471
174.433
158.060
156.337
138.393
137.254
137.197
130.695
130.676
129.422
129.393
128.062
127.890
127.612
126.971
121.408
121.283
77.211
77.000
76.789
52.029
47.184
46.993
25.066
25.038
-0.019
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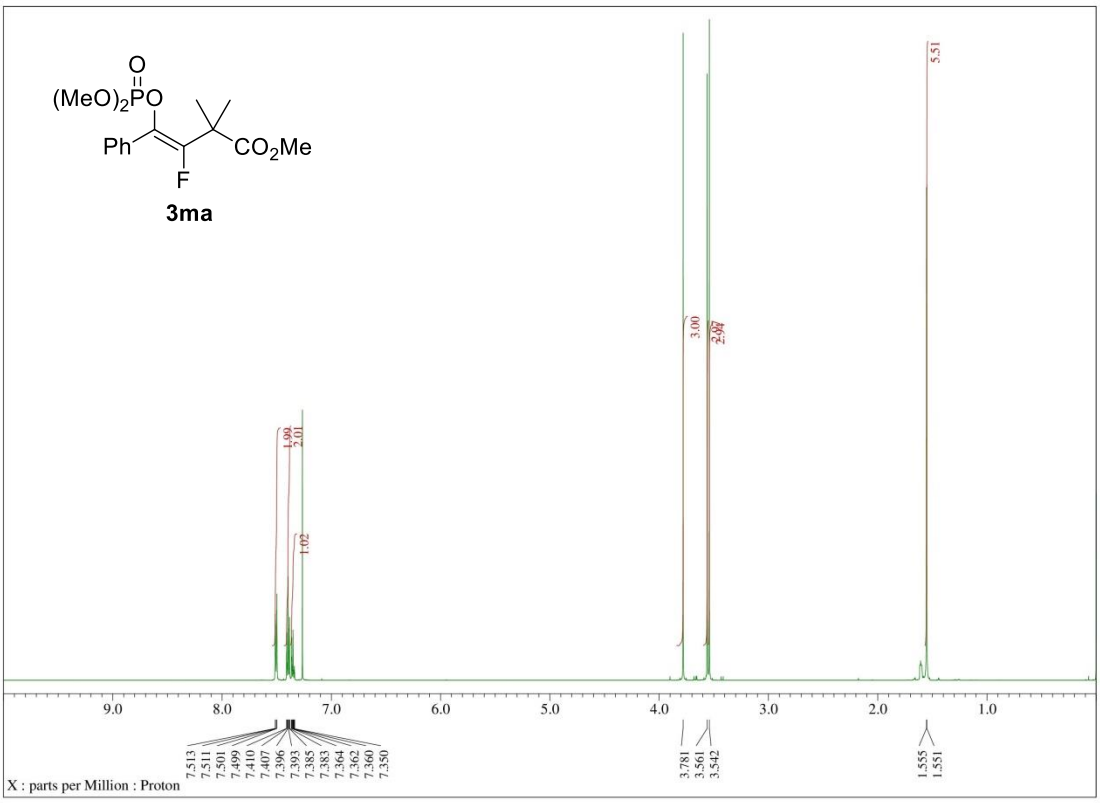
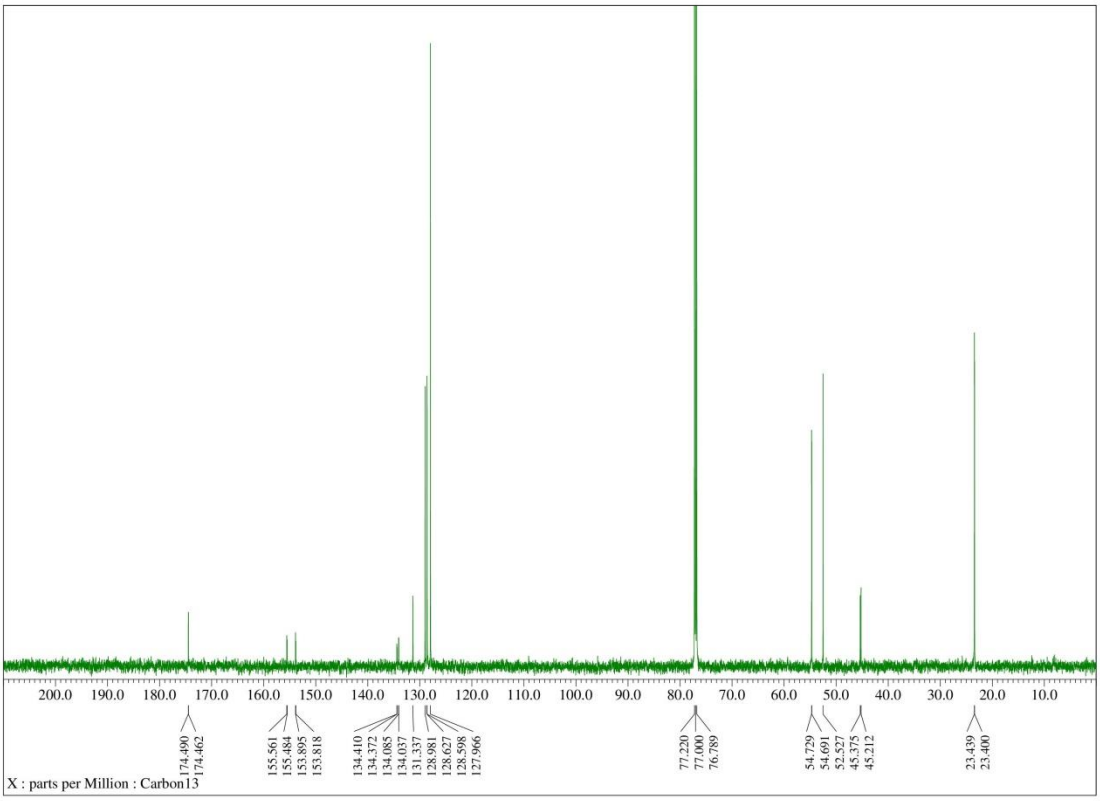
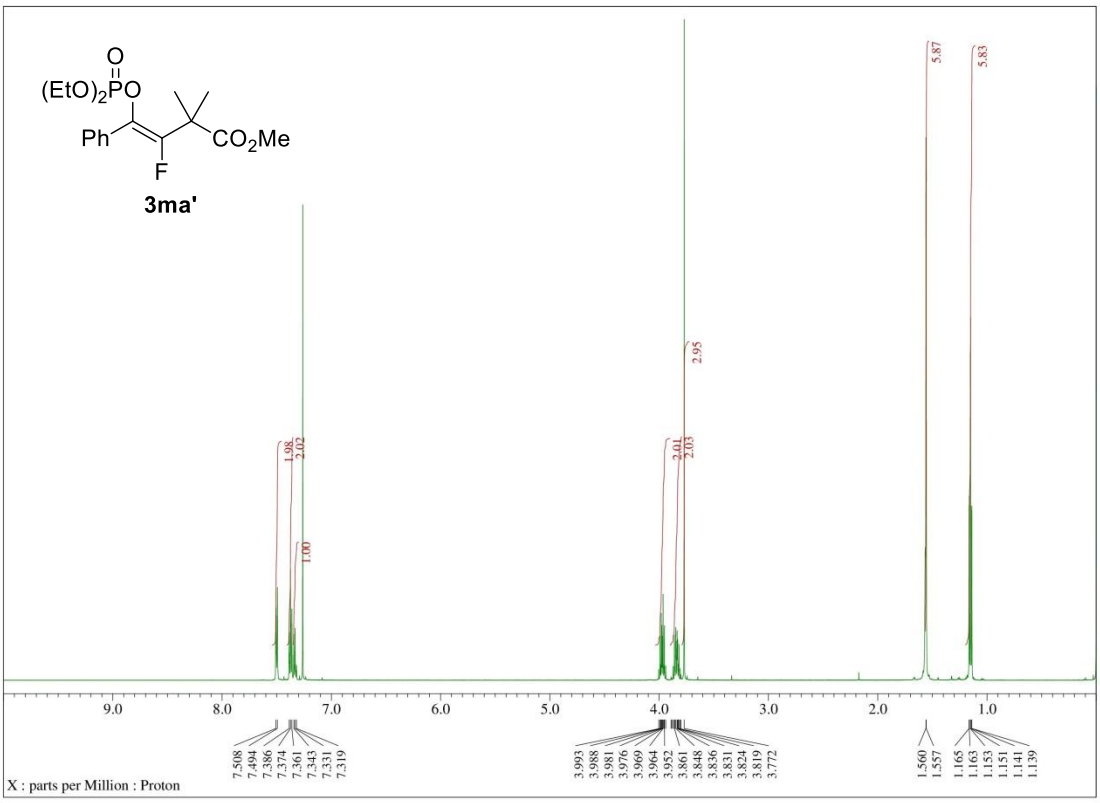
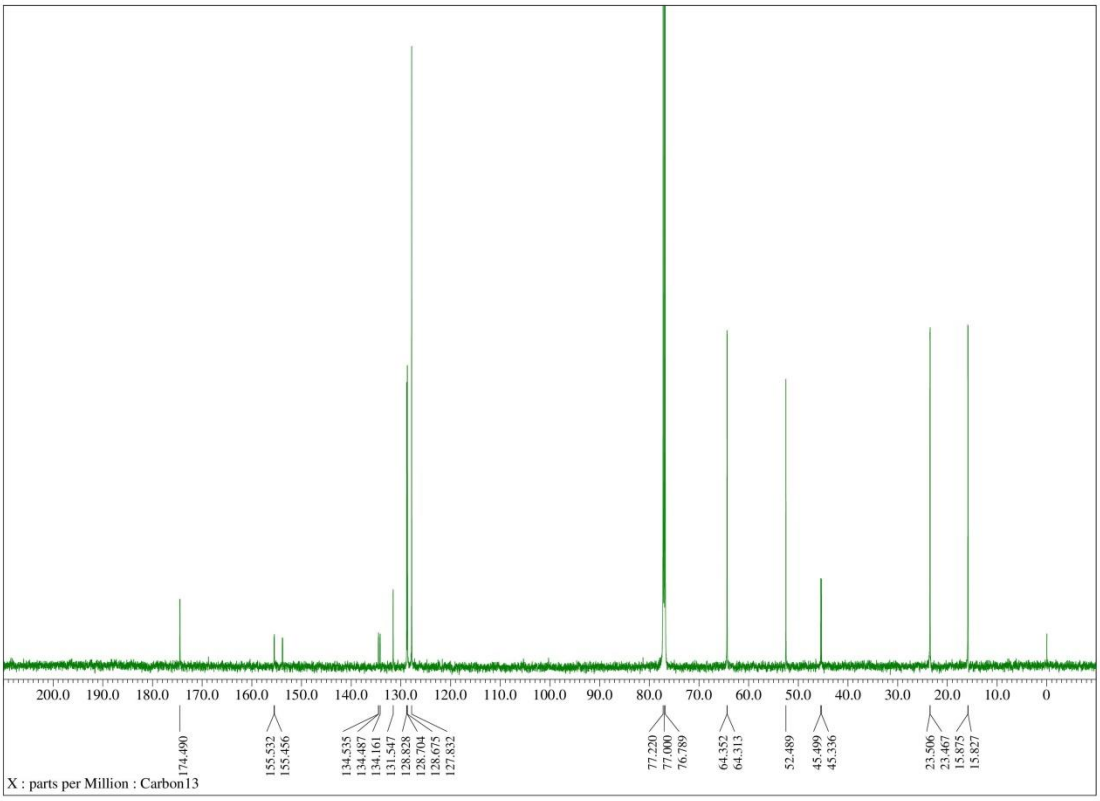
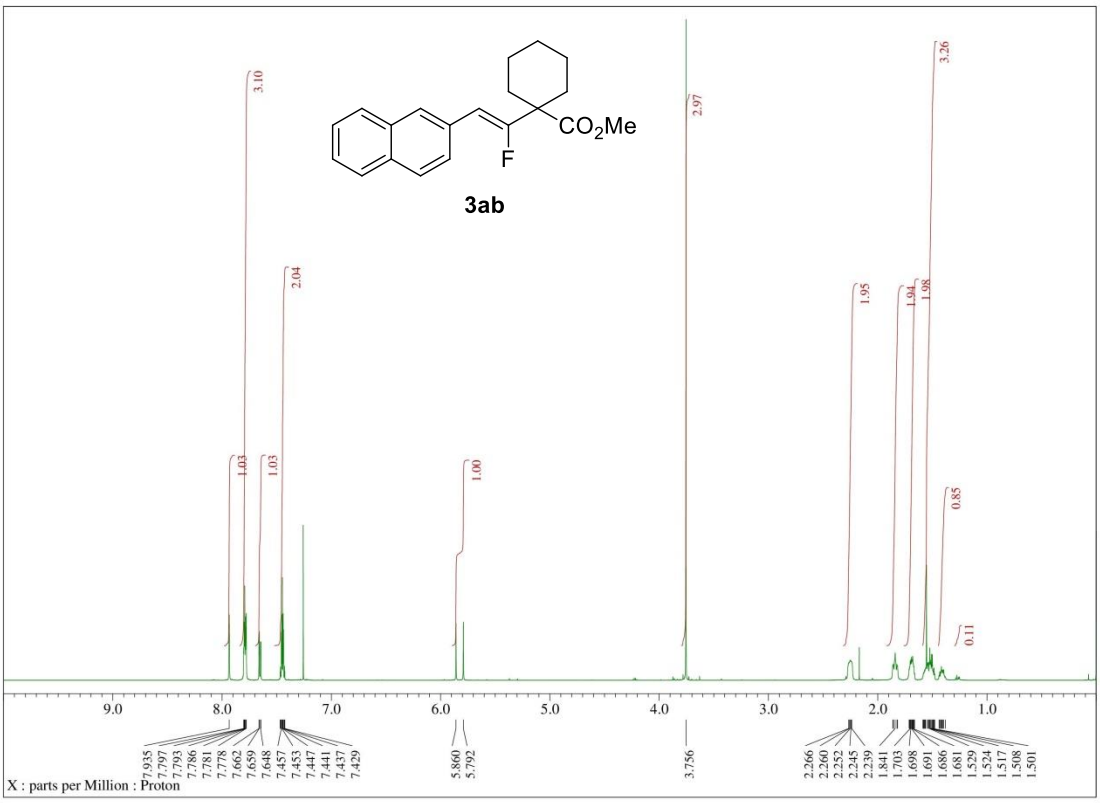
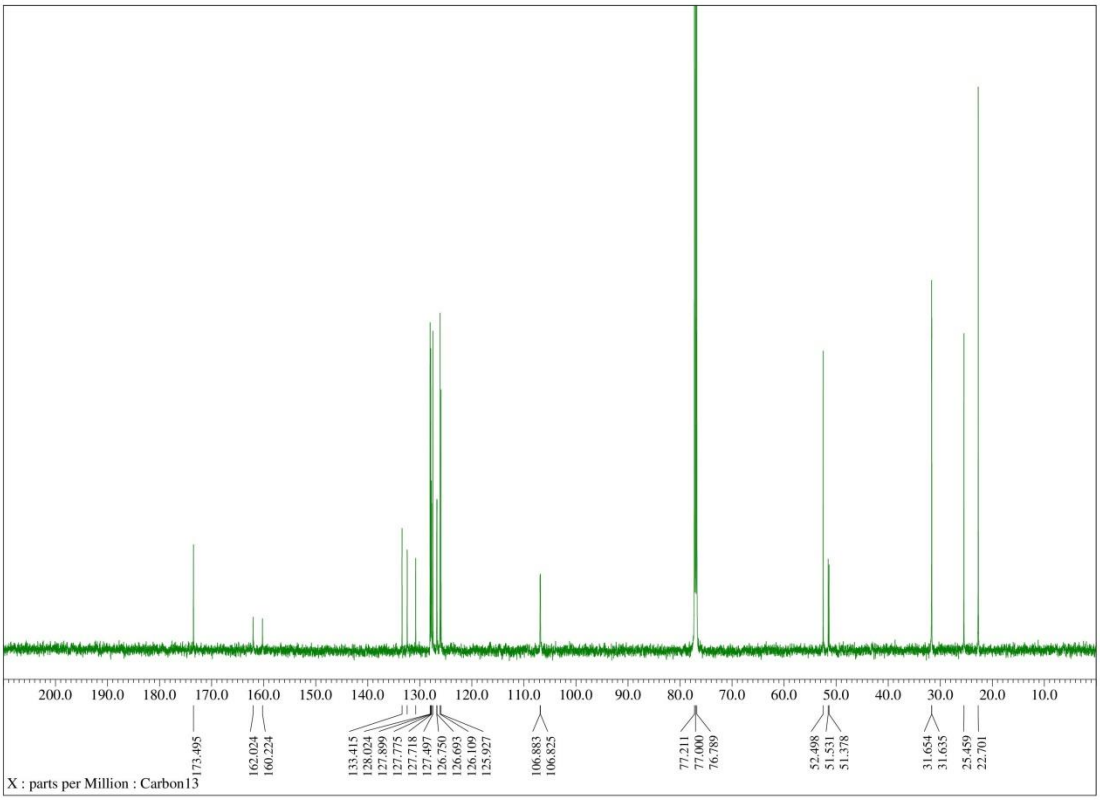

O
(MeO)2PO
Ph
CO2Me
F
3ma
5.51
3.00
2.97
2.94
1.99
2.01
1.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.513
7.511
7.501
7.499
7.410
7.407
7.396
7.393
7.385
7.383
7.364
7.362
7.360
7.350
3.781
3.561
3.542
1.555
1.551
X : parts per Million : Proton


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
174.490
174.462
155.561
155.484
153.895
153.818
134.410
134.372
134.085
134.037
131.337
128.981
128.627
128.598
127.966
77.220
77.000
76.789
54.729
54.691
52.527
45.375
45.212
23.439
23.400
X : parts per Million : Carbon13


O
(EtO)2PO
Ph
CO2Me
F
3ma'
5.87
5.83
2.95
1.98
2.02
2.01
2.03
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.508
7.494
7.386
7.374
7.361
7.343
7.331
7.319
3.993
3.988
3.981
3.976
3.969
3.964
3.952
3.861
3.848
3.836
3.831
3.824
3.819
3.772
1.560
1.557
1.165
1.163
1.153
1.151
1.141
1.139
X : parts per Million : Proton


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.490
155.532
155.456
134.535
134.487
134.161
131.547
128.828
128.704
128.675
127.832
77.220
77.000
76.789
64.352
64.313
52.489
45.499
45.336
23.506
23.467
15.875
15.827
X : parts per Million : Carbon13


CO2Me
F
3ab
3.10
2.04
1.03
1.03
1.00
2.97
1.95
1.94
1.98
3.26
0.85
0.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.935
7.797
7.793
7.786
7.781
7.778
7.662
7.659
7.648
7.457
7.453
7.447
7.441
7.437
7.429
5.860
5.792
3.756
2.266
2.260
2.252
2.245
2.239
1.841
1.703
1.698
1.691
1.686
1.681
1.529
1.524
1.517
1.508
1.501
X : parts per Million : Proton


200.0
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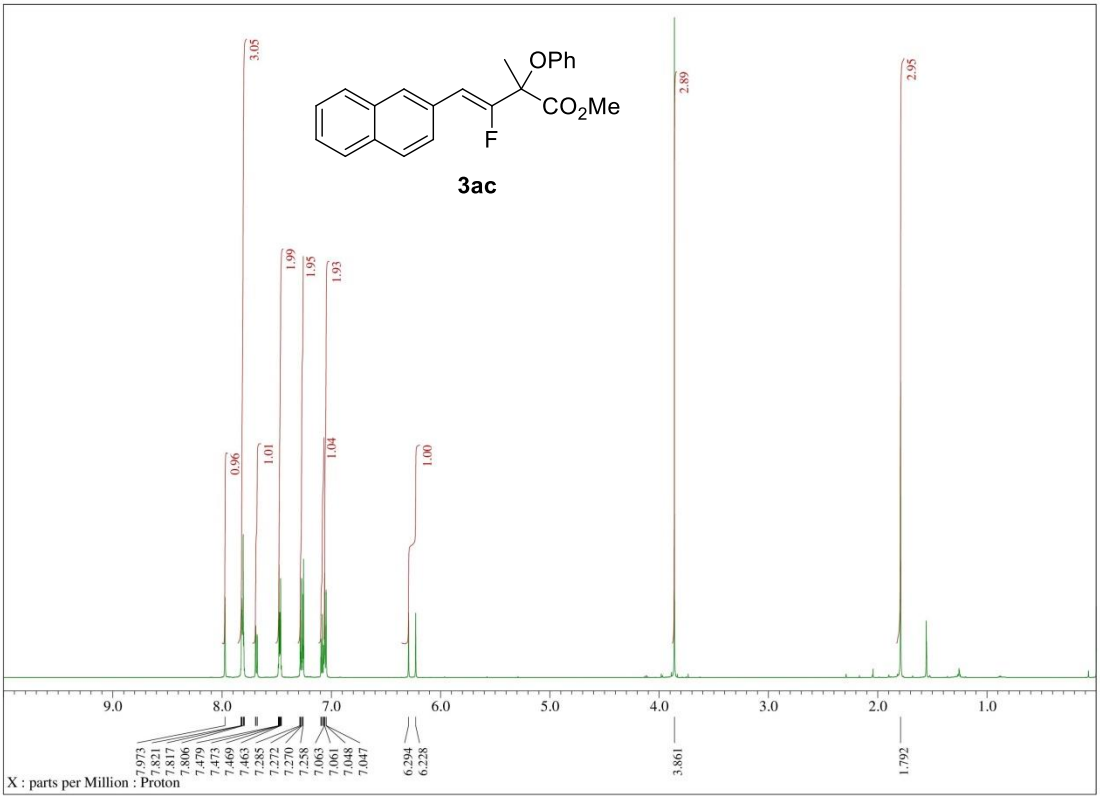
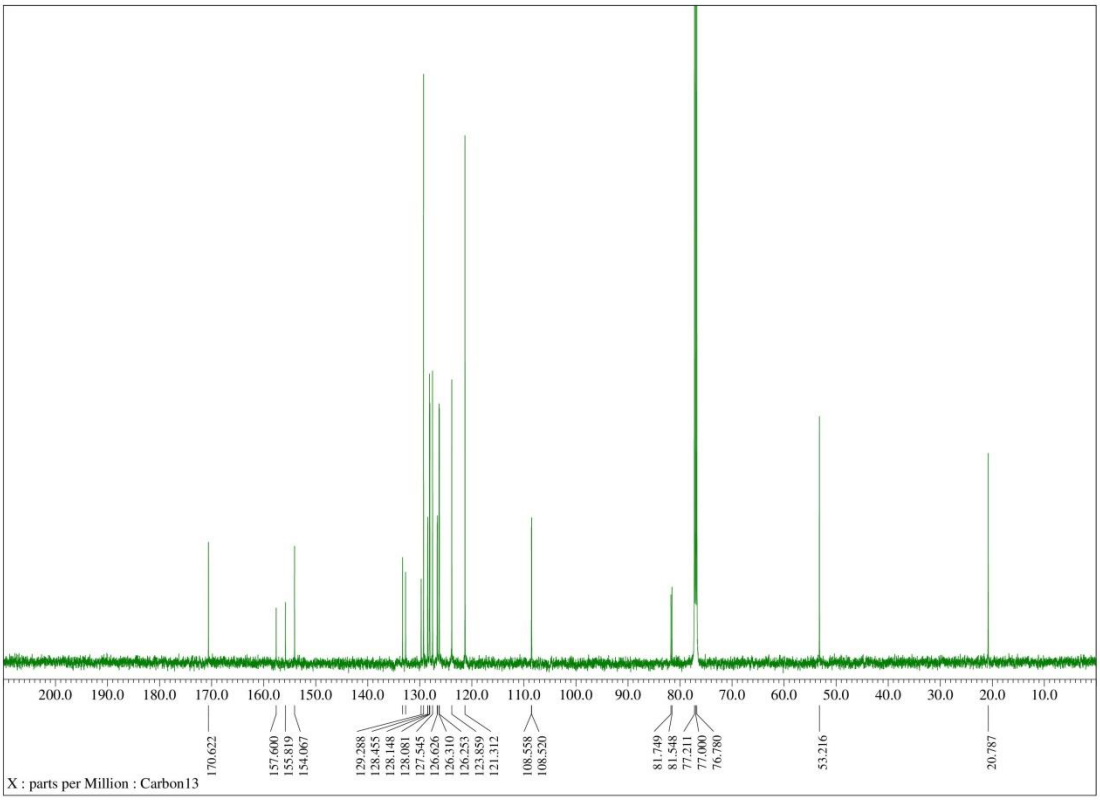
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
173.495
162.024
160.224
133.415
128.024
127.899
127.775
127.718
127.497
126.750
126.693
126.109
125.927
106.883
106.825
77.211
77.000
76.789
52.498
51.531
51.378
31.654
31.635
25.459
22.701
X : parts per Million : Carbon13


OPh
CO2Me
F
3ac
3.05
2.89
2.95
1.99
1.95
1.93
0.96
1.01
1.04
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.973
7.821
7.817
7.806
7.479
7.473
7.469
7.463
7.285
7.272
7.270
7.258
7.063
7.061
7.048
7.047
6.294
6.228
3.861
1.792
X : parts per Million : Proton


200.0
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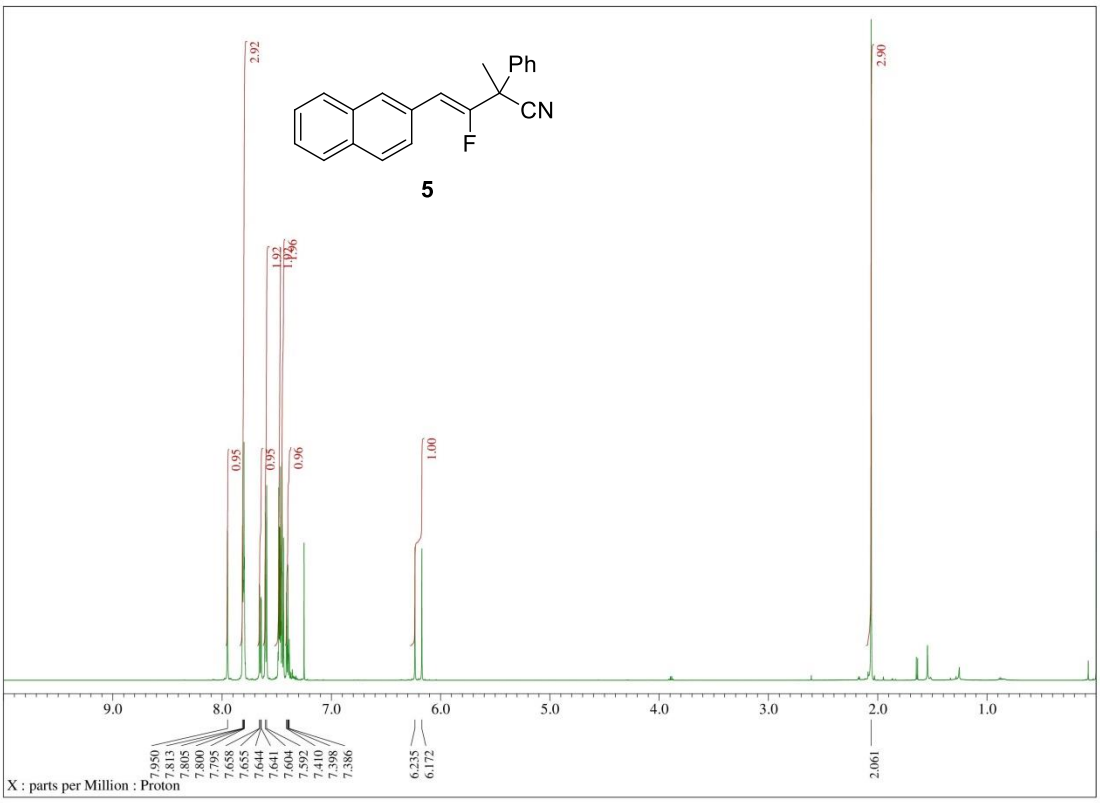
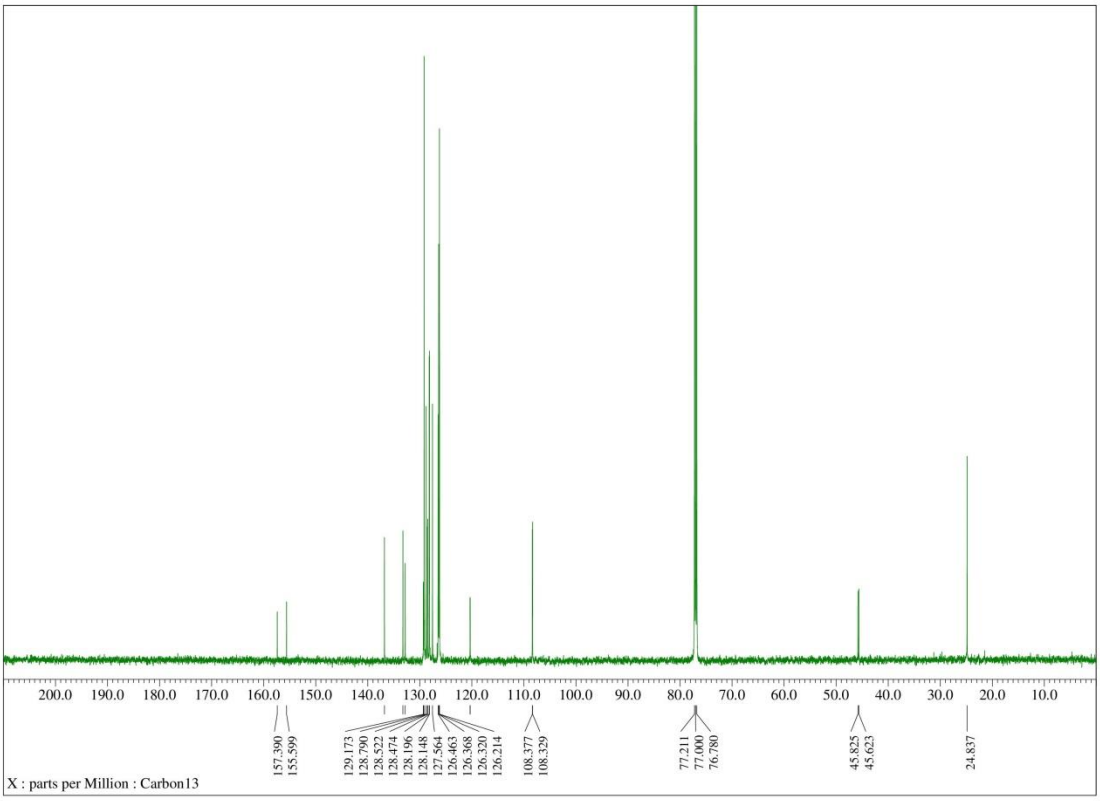
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
170.622
157.600
155.819
154.067
129.288
128.455
128.148
128.081
127.545
126.626
126.310
126.253
123.859
121.312
108.558
108.520
81.749
81.548
77.211
77.000
76.780
53.216
20.787
X : parts per Million : Carbon13


Ph
CN
F
5
2.92
2.90
1.92
1.96
0.95
0.95
0.96
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.950
7.813
7.805
7.800
7.795
7.658
7.655
7.644
7.641
7.604
7.592
7.410
7.398
7.386
6.235
6.172
2.061
X : parts per Million : Proton


200.0
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170.0
160.0
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120.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
157.390
155.599
129.173
128.790
128.522
128.474
128.196
128.148
127.564
126.463
126.368
126.320
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108.329
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77.000
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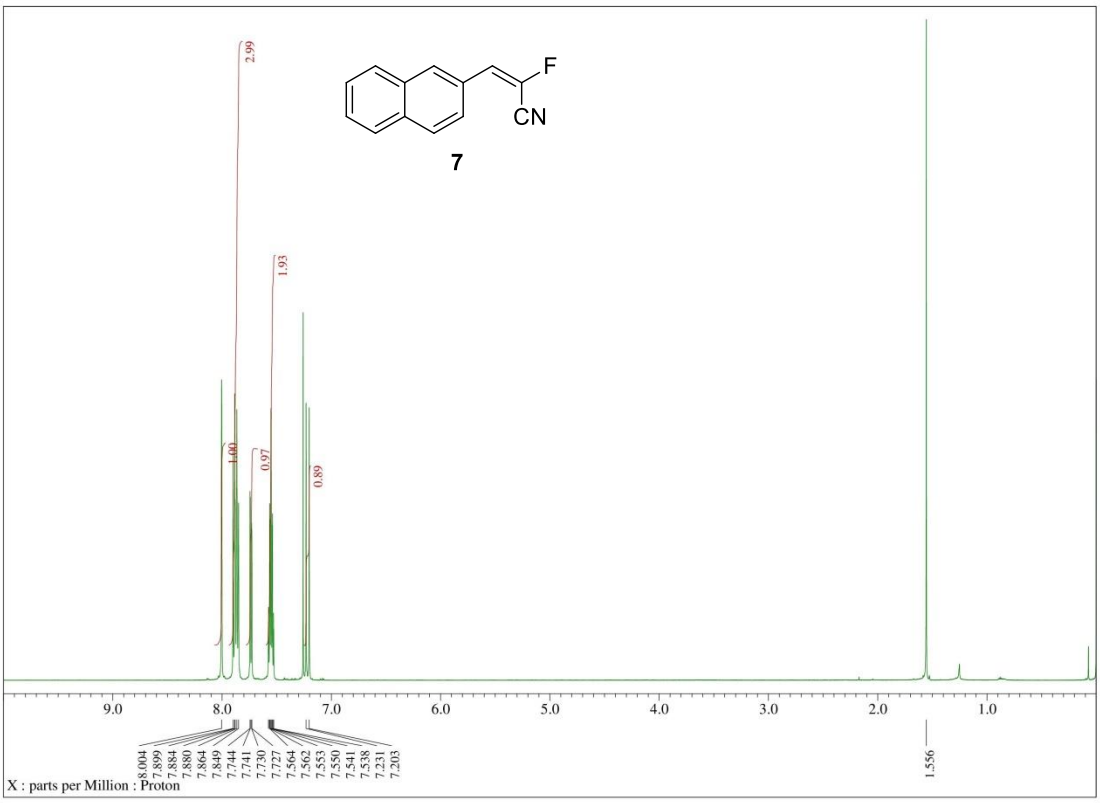
45.623
24.837
X : parts per Million : Carbon13


F
CN
7
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1.00
0.97
0.89
9.0
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6.0
5.0
4.0
3.0
2.0
1.0
8.004
7.899
7.884
7.880
7.864
7.849
7.744
7.741
7.730
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7.550
7.541
7.538
7.231
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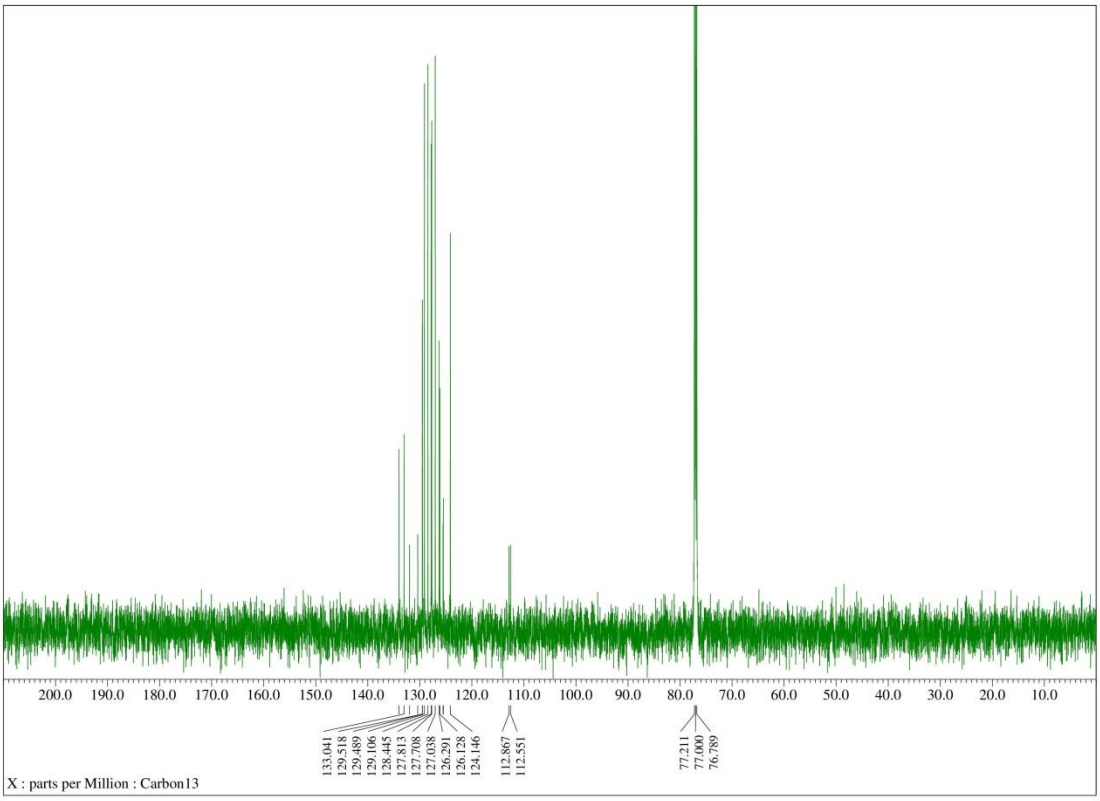
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150.0
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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
133.041
129.518
129.489
129.106
128.445
127.813
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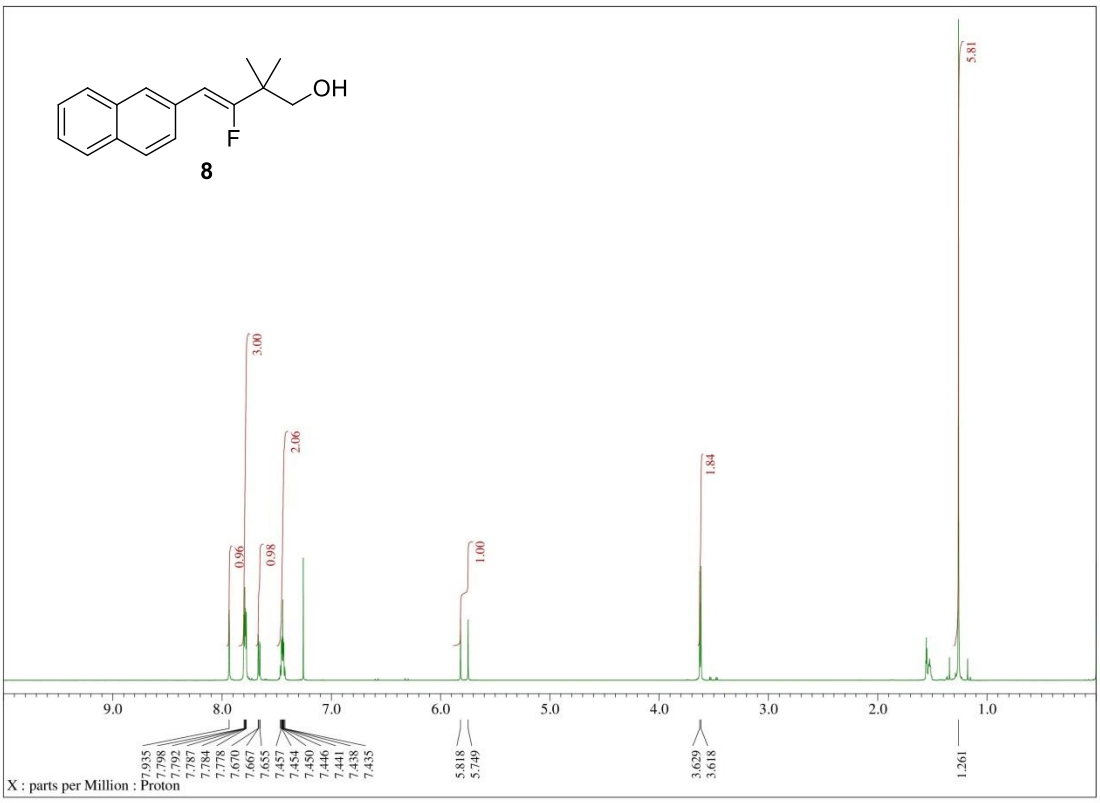
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F
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0.98
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6.0
5.0
4.0
3.0
2.0
1.0
7.935
7.798
7.792
7.787
7.784
7.778
7.670
7.667
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7.454
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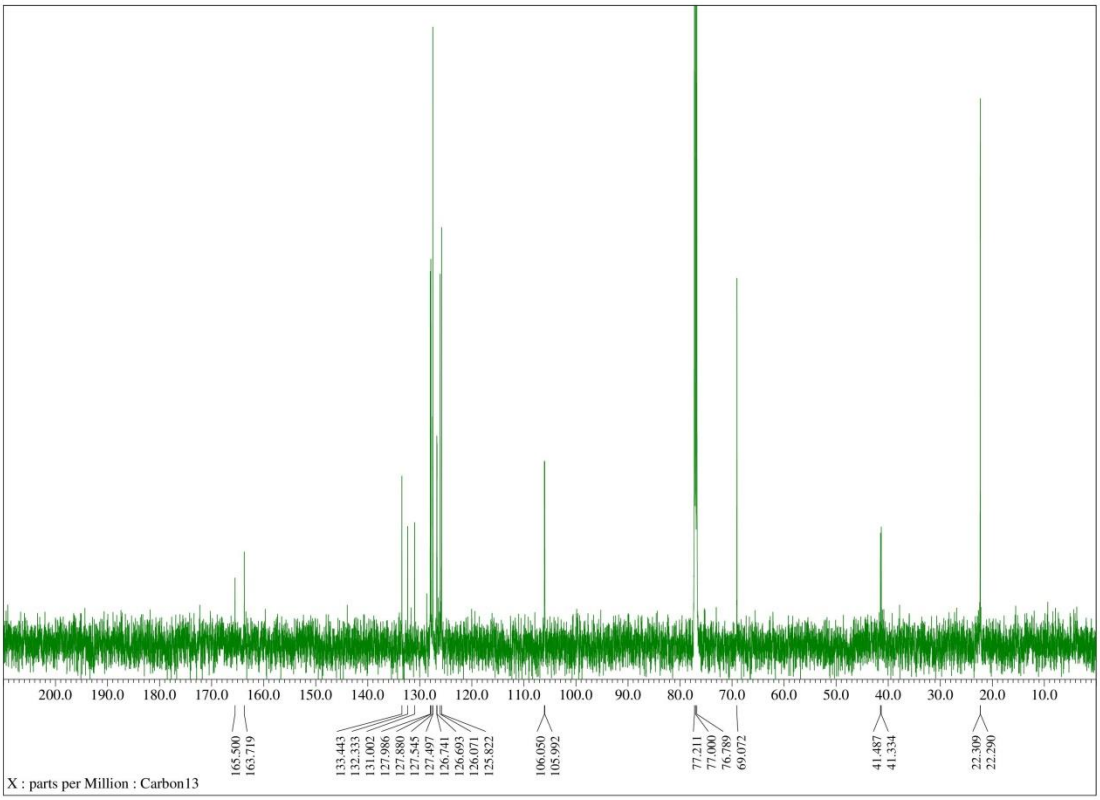
X : parts per Million : Proton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80.0
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60.0
50.0
40.0
30.0
20.0
10.0
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133.443
132.333
131.002
127.986
127.880
127.545
127.497
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126.693
126.071
125.822
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76.789
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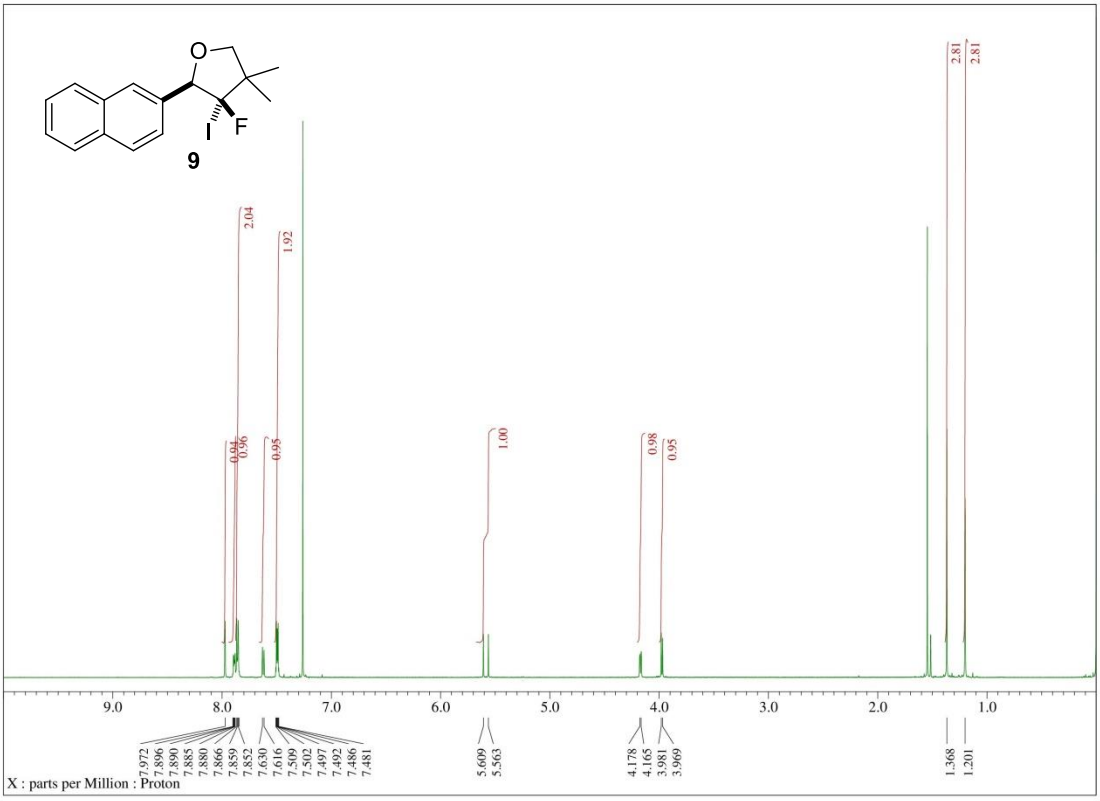
O
I
F
9
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0.96
0.95
1.00
0.98
0.95
2.81
2.81
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.972
7.896
7.890
7.885
7.880
7.866
7.859
7.852
7.630
7.616
7.509
7.502
7.497
7.492
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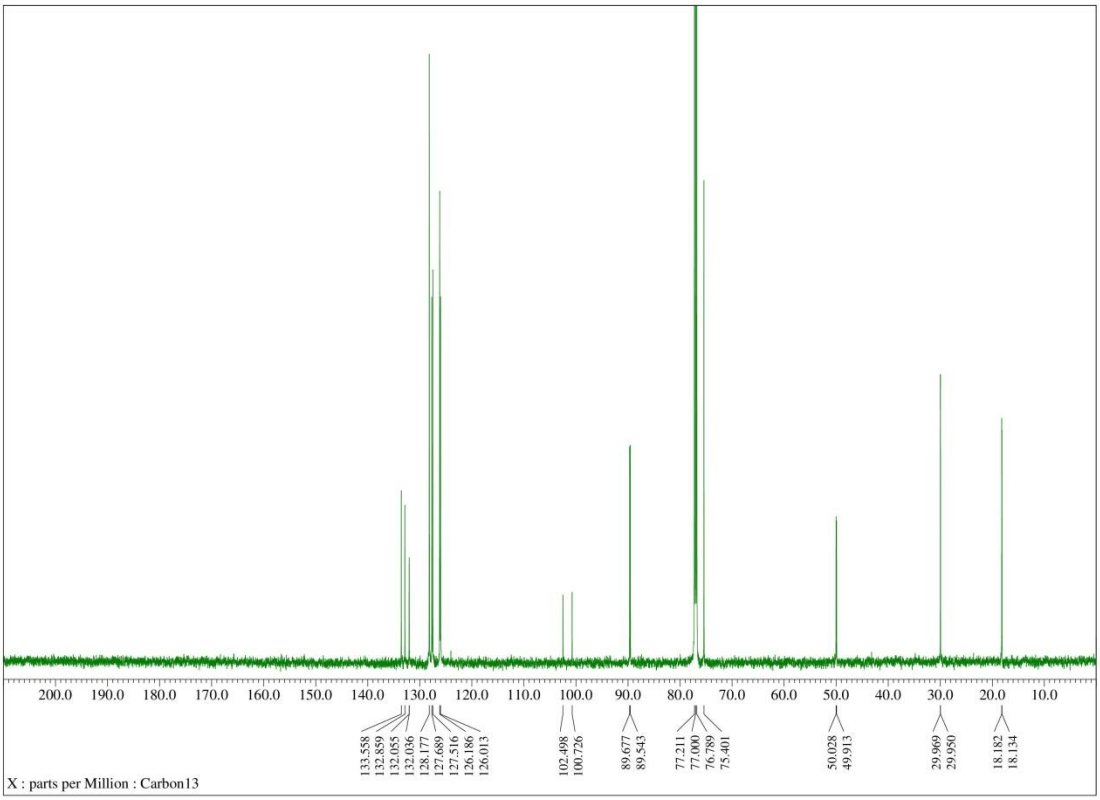
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140.0
130.0
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110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
133.558
132.859
132.055
132.036
128.177
127.689
127.516
126.186
126.013
102.498
100.726
89.677
89.543
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29.969
29.950
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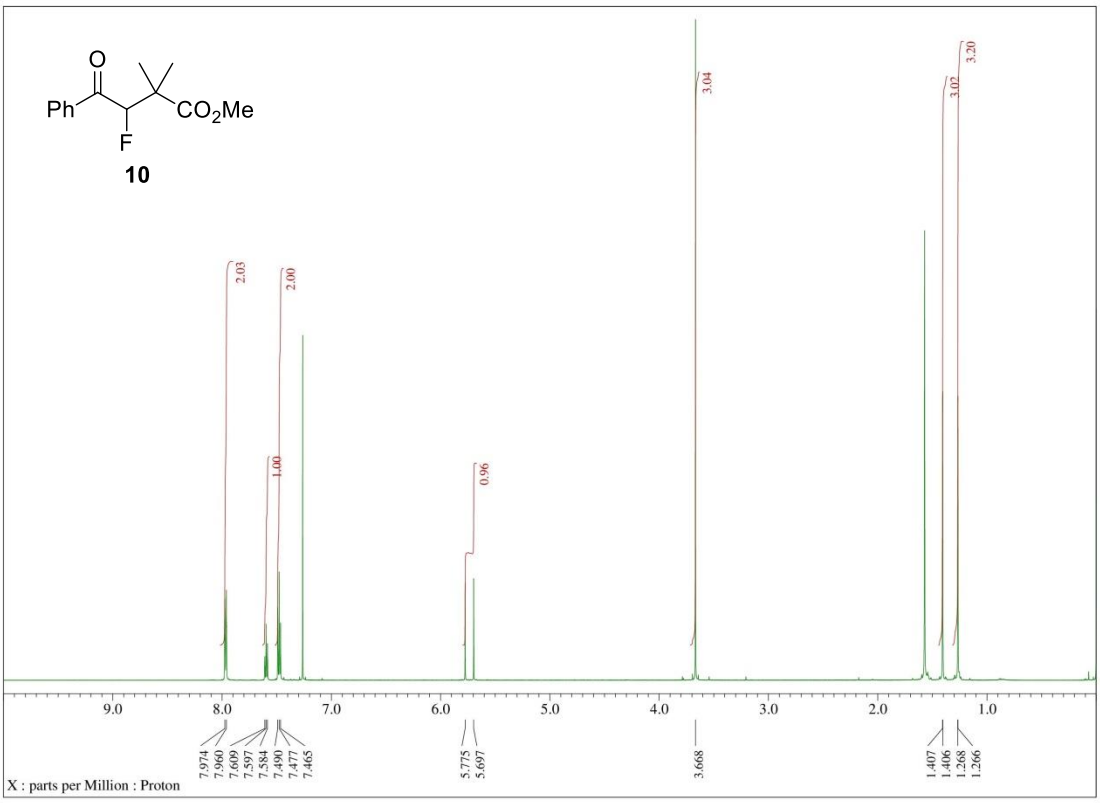
18.134
X : parts per Million : Carbon13


O
Ph
CO2Me
F
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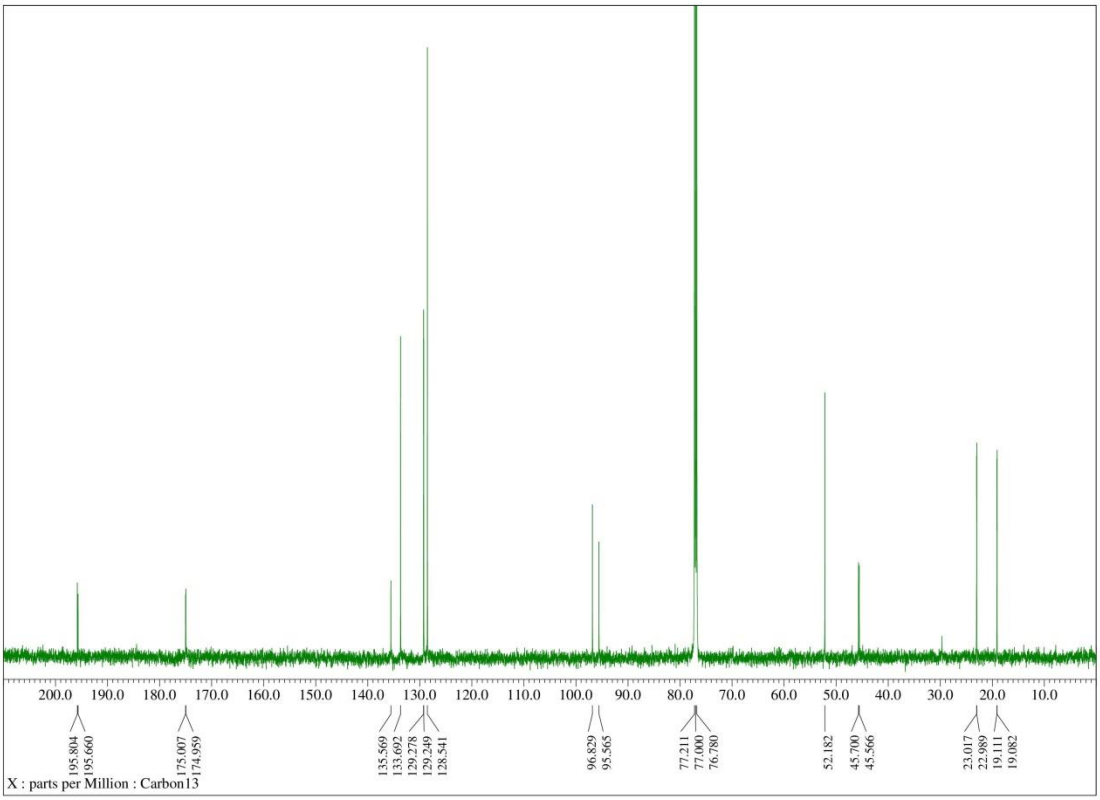
2.03
2.00
1.00
0.96
3.04
3.02
3.20
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.974
7.960
7.609
7.597
7.584
7.490
7.477
7.465
5.775
5.697
3.668
1.407
1.406
1.268
1.266
X : parts per Million : Proton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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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195.660
175.007
174.959
135.569
133.692
129.278
129.249
128.541
96.829
95.565
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77.000
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45.566
23.017
22.989
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X : parts per Million : Carbon13