Electric Supplementary Information for the article entitled

Synthesis and fluorescence properties of *N*-methyl-1,2-dihyroquinoline-3-carboxylate derivatives: Light-emitting compounds in organic solvent, in neat form, and in water

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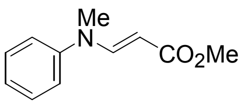
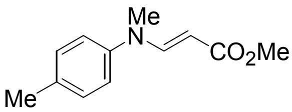
General Infromation: Melting points were determined with Yanaco MP-J3 and values were uncorrected. ^{1}H and ^{13}C NMR measurements were performed on a Varian GEMINI 2000 (300 MHz) spectrometer. Chemical shifts (δ) of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane (δ = 0) or DMSO-d_5 (δ = 2.49) as an internal standard. Multiplicities are indicated as s (singlet), bs (broadened singlet), d (doublet), t (triplet), m (multiplet), and coupling constants (*J*) are reported in Hz unit. Chemical shifts (δ) of ^{13}C NMR (75 MHz) were expressed in parts per million downfield or upfield from $CDCl_3$ (δ = 77.0) or DMSO-d_6 (δ = 39.6) (as an internal standard. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer in KBr disk or on NaCl plate. Absorption spectra were measured with quartz cell (1 cm × 1 cm)on a JASCO V570 spectrophotometer. Fluorescence spectra in solution were measured with quartz cell (1 cm × 1 cm) on a JASCO FP-6600 spectrofluorometer. Fluorescence spectra in neat form were measured with glass plates sandwiched the compound. Absolute fluorescence quantum yield was measured with the integrating sphere unit. Elemental analyses (EA) were carried out on a Perkin-Elmer 2400CHN or an Exeter Analytical, Inc. CE-440 in Analytical Chemical Center of Chiba University. Mass spectra were carried out on a JEOL JMS-AX500, a JMS-HX110, or THERMO Scientific Exactive in Analytical Chemical Center of Chiba University. Analytical thin-layer chromatography (TLC) was performed on glass plates pre-coated with silica gel (layer thickness 0.25 mm). Column chromatography was performed on 70-230 mesh silica gel. The commercially available materials were purchased from Aldrich Chemical Co., Tokyo Kasei Chemical Industry Co., Wako Pure Chemical Co., Kanto Chemical Co., and Nacalai Tesque Inc. Anhydrous CH_3CN was distilled from sodium hydride and was stored with MS 3Å. The reactions were performed under nitrogen atmosphere otherwise noted.

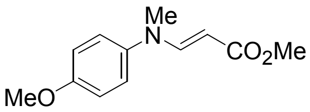
Typical Procedure for the Preparation of Methyl 3-(Aryl(methyl)amino)acrylates.



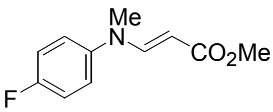
(*E*)-Methyl 3-(Methyl(phenyl)amino)acrylate (3a):[1] To a solution of *N*-methylaniline (0.537 g, 5.01 mmol) in MeOH (10 mL) was added methyl 2-propynoate (0.428 g, 5.09 mmol) at room temperature under air atmosphere. The mixture was stirred for 4 d and was concentrated under reduced pressure to give (*E*)-methyl 3-(methyl(phenyl)amino)acrylates (**3a**) (0.967 g, 5.05 mmol) as brown oil quantitatively. The compound was used to next reaction without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.25 (s, 3H), 3.71 (s, 3H), 4.94 (d, 1H, *J* = 13.2 Hz), 7.12 (t, 1H, *J* = 7.6 Hz), 7.13 (d, 2H, *J* = 7.1 Hz), 7.35 (t, 2H, *J* = 7.6 Hz), 7.94 (d, 1H, *J* = 13.2 Hz);[2] ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.5, 50.7, 89.9, 119.8 (2C), 124.2, 129.4 (2C), 146.5, 148.5, 169.5.



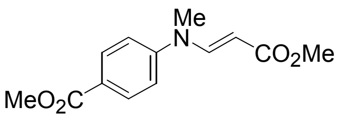
(*E*)-Methyl 3-(Methyl(4-tolyl)amino)acrylate (3b): The titled compound was prepared for 5 d quantitatively according to a procedure similar to that mentioned in **3a**: Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 3.22 (s, 3H), 3.70 (s, 3H), 4.89 (d, 1H, *J* = 13.1 Hz), 7.02 (d, 2H, *J* = 8.5 Hz), 7.21 (d, 2H, *J* = 8.2 Hz), 7.90 (d, 1H, *J* = 13.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 36.7, 50.7, 89.2, 119.9 (2C), 129.9 (2C), 133.9, 144.2, 148.8, 169.6; IR (neat): 2949, 1694, 1622, 1597, 1510, 1438, 1336, 1264, 1224, 1161, 1126, 1039, 985, 833, 800, 690 cm^{-1}. EA Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%. Found: C, 70.23; H, 7.33; N, 6.83%.



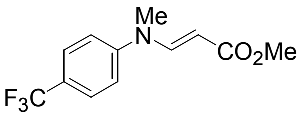
(*E*)-Methyl 3-(Methyl(4-methoxyphenyl)amino)acrylate (3c): The titled compound (*E*/*Z* = 91 : 9) was prepared for 2 d quantitatively according to a procedure similar to that mentioned in **3a**: Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.21 (s, 3H), 3.70 (s, 3H), 3.80 (s, 3H), 4.84 (d, 1H, *J* = 13.2 Hz), 6.88 (d, 2H, *J* = 9.0 Hz), 7.06 (d, 2H, *J* = 9.0 Hz), 7.82 (d, 1H, *J* = 13.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.5, 50.6, 55.5, 88.5, 114.5 (2C), 122.0 (2C), 140.1, 149.5, 156.7, 169.7; IR (neat): 2948, 2909, 2837, 1695, 1622, 1603, 1513, 1438, 1340, 1246, 1160, 1127, 1037, 985, 831, 796, 688 cm^{-1}. EA Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33%. Found: C, 64.98; H, 6.86; N, 6.26%.



(*E*)-Methyl 3-((4-Fluorophenyl)methylamino)acrylate (3d): The titled compound was prepared for 3 d quantitatively according to a procedure similar to that mentioned in **3a**: Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.22 (s, 3H), 3.71 (s, 3H), 4.91 (s, 1H, *J* = 13.2 Hz), 7.01-7.12 (m, 4H), 7.83 (d, 1H, *J* = 13.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.1, 50.7, 89.7, 116.0 (d, 2C, $J_{C\text{-}C2\text{-}F}$ = 22.7 Hz), 121.8 (d, 2C, $J_{C\text{-}C\text{-}F}$ = 8.2 Hz), 142.8 (d, $J_{C\text{-}C3\text{-}F}$ = 2.9 Hz), 148.8, 159.5 (d, $J_{C\text{-}F}$ = 244.3 Hz), 169.5; IR (neat): 2950, 1696, 1618, 1597, 1510, 1438, 1336, 1264, 1224, 1162, 1126, 1039, 986, 828, 801, 690 cm^{-1}. EA Calcd for $C_{11}H_{12}FNO_2$: C, 63.15; H, 5.78; N, 6.69%. Found: C, 63.02; H, 5.35; N, 6.67%.

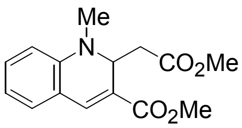


(*E*)-Methyl 3-((4-Methoxycarbonylphenyl)methylamino)acrylate (3e): The titled compound was prepared for 6 d in 87% yield purified by column chromatography after according to a procedure similar to that mentioned in **3a**: Colorless needle crystals; m.p. 117.6–118.7 °C (hexane-chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.28 (s, 3H), 3.73 (s, 3H), 3.91 (s, 3H), 5.09 (d, 1H, *J* = 13.2 Hz), 7.16 (d, 2H, *J* = 8.9 Hz), 8.02 (d, 1H, *J* = 13.2 Hz), 8.03 (d, 2H, *J* = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.7, 51.0, 52.0, 92.7, 118.0 (2C), 125.0, 131.2 (2C), 146.8, 149.7, 166.4, 169.1; IR (KBr): 2993, 2954, 1717, 1628, 1591, 1516, 1427, 1314, 1258, 1169, 1139, 1113, 1028, 977, 841, 804, 765, 695 cm^{-1}. EA Calcd for $C_{13}H_{15}NO_4 \cdot 0.1H_2O$: C, 62.19; H, 6.10; N, 5.58%. Found: C, 62.11; H, 5.96; N, 5.54%.

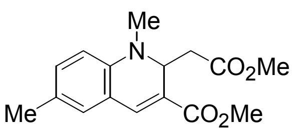


(*E*)-Methyl 3-(Methyl(4-trifluoromethylphenyl)amino)acrylate (3f): The titled compound was prepared for 4 d at 40 °C in 66% yield purified by column chromatography after according to a procedure similar to that mentioned in **3a**: colorless needle crystals; m.p. 78.7–79.5 °C (hexane-chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.27 (s, 3H), 3.73 (s, 3H), 5.07 (d, 1H, J = 13.3 Hz), 7.21 (d, 2H, J = 8.5 Hz), 7.60 (d, 2H, J = 8.5 Hz), 7.98 (d, 1H, J = 13.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.9, 51.0, 92.6, 118.7 (2C), 124.0 (q, $J_{C\text{-}F}$ = 271.5 Hz), 125.8 (q, $J_{C\text{-}C\text{-}F}$ = 32.8 Hz), 126.7 (q, 2C, $J_{C\text{-}C2\text{-}F}$ = 3.6 Hz), 147.0, 148.9, 169.1; IR (KBr): 3001, 2955, 1699, 1594, 1522, 1437, 1385, 1323, 1266, 1165, 1106, 1073, 1036, 980, 963, 933, 830, 808, 760 cm^{-1}. HRMS (ESI): Calcd for $C_{12}H_{12}F_3NNaO_2$ ($[M+Na]^+$): 282.0718. Found: 282.0712.

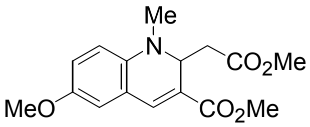
Typical Procedure for the Formation of Methyl 1-Methyl-1,2-dihydroquinoline-3-carboxylate Derivatives (2).



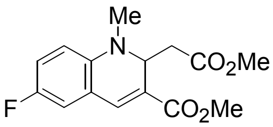
Methyl 2-(Methoxycarbonylmethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylate (2a): To a solution of methyl 3-(methyl(phenyl)amino)acrylate (**3a**) (0.208 g, 1.09 mmol) in anhydrous CH_3CN (10 mL) was added I_2 (84.1 mg, 0.331 mmol) at room temperature under nitrogen atmosphere. To the mixture was added EtSH (39.0 mg, 0.628 mmol). The resultant mixture was stirred for 1 d at that temperature. EtOAc (10 mL) was added to the reaction mixture, and it was washed with saturated aqueous Na_2SO_3 (10 mL × 4). The aquous layer was extracted with EtOAc (5 mL x 2). The combined organic layer was dried with Na_2SO_4. After filtration and evaporation, the residue was subject to column chromatography on SiO_2 (chloroform : ethyl acetate = 15 : 1) to give methyl 2-(methoxycarbonylmethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylate (**2a**) (0.121 g, 0.440 mmol) in 81% yield as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (dd, 1H, J = 5.3 and 13.6 Hz), 2.52 (dd, 1H, J = 6.3 and 13.6 Hz), 3.02 (s, 3H), 3.53 (s, 3H), 3.81 (s, 3H), 4.94 (dd, 1H, J = 5.4 and 6.2 Hz), 6.56 (d, 1H, J = 8.2 Hz), 6.70 (dd, 1H, J = 6.7 and 7,4 Hz), 7.12 (dd, 1H, J = 1.4 and 7.5 Hz), 7.24 (dt, 1H, J = 1.5 and 6.9 Hz), 7.49 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.3 (2C), 51.7, 51.8, 56.8, 111.9, 117.4, 120.2, 122.2, 129.7, 132.1, 135.3, 145.1, 165.7, 171.6; IR (neat): 2950, 1738, 1733, 1704, 1699, 1634, 1600, 1494, 1353, 1324, 1305, 1248, 1203, 1161, 1079, 1032, 1013, 986, 768, 750 cm^{-1}. EA Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09%. Found: C, 65.39; H, 6.19; N, 5.03%.



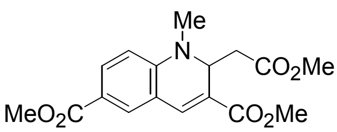
Methyl 2-(Methoxycarbonylmethyl)-1,6-dimethyl-1,2-dihydroquinoline-3-carboxylate (2b): The titled compound was prepared for 1 d in 66% yield according to a procedure similar to that mentioned in **2a**: Yellow needle crystals; m.p. 49.8–52.3 °C (hexane-chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.37 (dd, 1H, *J* = 5.2 and 13.6 Hz), 2.51 (dd, 1H, *J* = 6.5 and 13.5 Hz), 2.99 (s, 3H), 3.54 (s, 3H), 3.80 (s, 3H), 4.90 (t, 1H, *J* = 5.9 Hz), 6.48 (d, 1H, *J* = 8.2 Hz), 6.94 (s, 1H), 7.06 (d, 1H, *J* = 8.8 Hz), 7.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.1, 36.9, 37.3, 51.7, 51.8, 56.8, 112.0, 120.3, 122.4, 126.5, 130.0, 132.9, 135.3, 143.0, 165.8, 171.7; IR (KBr): 2950, 1734, 1685, 1624, 1559, 1525, 1490, 1437, 1319, 1241, 1194, 1075, 871, 747 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{19}NNaO_4$ ($[M+Na]^+$): 312.1206. Found: 312.1197.



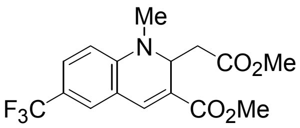
Methyl 6-(Methoxy)-2-(methoxycarbonylmethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylate (2c): The titled compound was prepared for 1 d in 49% yield according to a procedure similar to that mentioned in **2a**: Orange needle crystals; m.p. 67.2–69.3 °C (hexane-chloroform-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (dd, 1H, *J* = 5.5 and 13.7 Hz), 2.51 (dd, 1H, *J* = 6.6 and 13.5 Hz), 2.98 (s, 3H), 3.54 (s, 3H), 3.76 (s, 3H), 3.81 (s, 3H), 4.88 (t, 1H, *J* =5.9 Hz), 6.53 (d, 1H, *J* = 8.7 Hz), 6.72 (d, 1H, *J* = 2.8 Hz), 6.87 (dd, 1H, *J* = 2.9 and 8.8 Hz), 7.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.6, 37.4, 51.7, 51.8, 55.9, 56.7, 113.2, 114.0, 118.7, 121.1, 123.5, 135.0, 139.7, 151.8, 165.7, 171.7; IR (KBr): 2994, 2950, 1733, 1700, 1637, 1567, 1497, 1435, 1239, 1208, 1188, 1167, 1084, 1037, 808, 768, 730, 690 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{19}NNaO_5$ ($[M+Na]^+$): 328.1155. Found: 328.1149.



Methyl 6-Fluoro-2-(methoxycarbonylmethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylate (2d): The titled compound was prepared for 4 d in 70% yield according to a procedure similar to that mentioned in **2a**: Orange needle crystals; m.p. 67.8–68.3 °C (hexane-chloroform-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (dd, 1H, *J* = 5.2 and 13.7 Hz), 2.50 (dd, 1H, *J* = 6.5 and 13.7 Hz), 3.00 (s, 3H), 3.54 (s, 3H), 3.82 (s, 3H), 4.91 (dd, 1H, *J* = 5.5 and 6.2 Hz), 6.49 (dd, 1H, *J* = 8.9 Hz and $J_{H\text{-}C3\text{-}F}$ = 4.5 Hz), 6.85 (dd, 1H, *J* = 2.9 Hz and $J_{H\text{-}C2\text{-}F}$ = 8.5 Hz), 6.96 (ddd, 1H, *J* = 3.0, 8.8 Hz, and $J_{H\text{-}C2\text{-}F}$ = 8.8 Hz), 7.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.9, 37.6, 51.7, 51.9, 56.7, 112.9 (d, $J_{C\text{-}C2\text{-}F}$ = 7.1 Hz), 115.1 (d, $J_{C\text{-}C\text{-}F}$ = 19.1 Hz), 118.5 (d, $J_{C\text{-}C\text{-}F}$ = 22.9 Hz), 121.0 (d, $J_{C\text{-}C2\text{-}F}$ = 8.0 Hz), 124.1, 134.2 (d, $J_{C\text{-}C3\text{-}F}$ = 2.6 Hz), 141.5, 155.4 (d, $J_{C\text{-}F}$ = 235.9 Hz), 165.4, 171.4 ; IR (KBr): 2952, 2925, 2852, 1733, 1704, 1640, 1572, 1496, 1435, 1348, 1288, 1270, 1234, 1208, 1152, 1083, 1032,1016, 986, 963, 925, 866, 808, 768, 735, 696 cm^{-1}. HRMS (ESI): Calcd for $C_{15}H_{16}FNNaO_4$ ($[M+Na]^+$): 316.0956. Found: 316.0956.

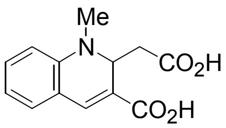


Dimethyl 2-(Methoxycarbonylmethyl)-1-methyl-1,2-dihydroquinoline-3,6-dicarboxylate (2e): The titled compound was prepared for 4 d in 73% yield according to a procedure similar to that mentioned in **2a**: Yellow needle crystals; m.p. 67.2–69.3 °C (hexane-chloroform-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (dd, 1H, J = 5.0 and 13.9 Hz), 2.54 (dd, 1H, J = 6.1 and 14.0 Hz), 3.08 (s, 3H), 3.50 (s, 3H), 3.82 (s, 3H), 3.86 (s, 3H), 4.99 (dd, 1H, J = 5.2 and 5.9 Hz), 6.54 (d, 2H, J = 8.7 Hz), 7.50 (s, 1H), 7.78 (d, 1H, J = 2.0 Hz), 7.89 (dd, 1H, J = 2.1 and 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.6, 38.3, 51.7, 51.8, 52.0, 57.2, 111.1, 118.7, 119.1, 122.4, 131.5, 133.7, 135.0, 148.6, 165.3, 166.7, 171.1; IR (KBr): 2995, 2952, 2847, 1733, 1704, 1699, 1640, 1606, 1559, 1506, 1436, 1332, 1310, 1274, 1249, 1198, 1114, 1082, 1016, 986, 934, 825, 767 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{19}NNaO_6$ ($[M+Na]^+$): 356.1105. Found: 356.1097.

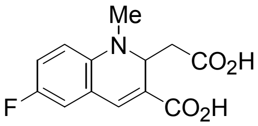


Methyl 2-(Methoxycarbonylmethyl)-1-methyl-6-(trifluoromethyl)-1,2-dihydroquinoline-3-carboxylate (2f): The titled compound was prepared for 4 d at 40 °C in 66% yield according to a procedure similar to that mentioned in **2a**: Yellow needle crystals; m.p. 51.0–53.1 °C (hexane-chloroform-ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (dd, 1H, J = 5.3 and 13.8 Hz), 2.53 (dd, 1H, J = 6.2 and 13.8 Hz), 3.07 (s, 3H), 3.52 (s, 3H), 3.82 (s, 3H), 4.98 (dd, 1H, J = 5.3 and 6.2 Hz), 6.59 (d, 1H, J = 8.5 Hz), 7.33 (d, 1H, J = 1.2 Hz), 7.44 (dd, 1H, J = 1.8 and 8.8 Hz), 7.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.6, 38.0, 51.7, 52.0, 57.0, 111.6, 119.1 (q, $J_{C\text{-}C2\text{-}F}$ = 33 Hz), 119.5, 123.3, 124.5 (q, $J_{C\text{-}F}$ = 270.5 Hz), 126.6 (q, $J_{C\text{-}C2\text{-}F}$ = 3.8 Hz), 128.7 (q, $J_{C\text{-}C2\text{-}F}$ = 3.6 Hz), 134.4, 147.3, 165.2, 171.1; IR (KBr): 2956, 1734, 1714, 1639, 1568, 1511, 1440, 1330, 1278, 1244, 1195, 1138, 1106, 1035, 1009, 961, 911, 863, 810, 765, 743 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{16}F_3NNaO_4$ ($[M+Na]^+$): 366.0924. Found: 366.0914.

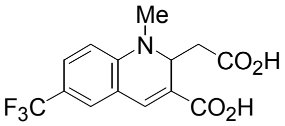
Typical Procedure for Hydrolysis of 2.



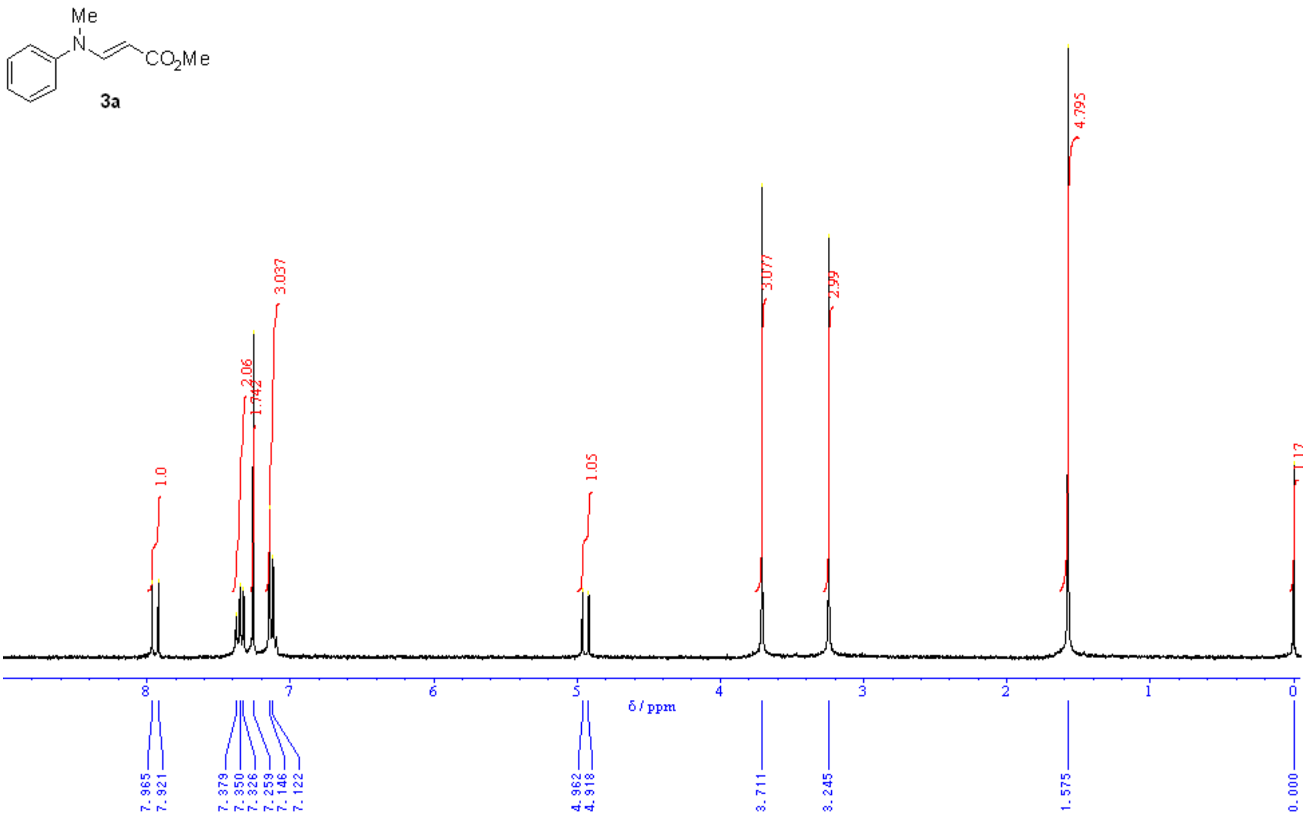
2-(Carboxymethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylic Acid (4a): To a solution of methyl 2-(methoxycarbonylmethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylate (**2a**) (55.0 mg, 0.200 mmol) in THF (1 mL) was added 1 M aqueous solution of KOH (1 mL). The mixture was stirred for 2 h at room temperature under air atmosphere. The reaction mixture was added water 5 mL and was washed with $CHCl_3$ (5 mL × 4). The aqueous layer was added 1 M aqueous HCl (2 mL) to acidify to pH 1~2. After extraction with $CHCl_3$ (5 mL × 9), the extracted organic layer was dried with Na_2SO_4 and was concentrated under reduced pressure to give 2-(carboxymethyl)-1-methyl-1,2-dihydroquinoline-3-carboxylic acid (**4a**) (49.1 mg, 1.99 mmol) in 99% yield as yellow solid. m.p. 120.8–121.1 °C (hexane-chloroform); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.16 (dd, 1H, J = 4.3 and 14.0 Hz), 2.32 (dd, 1H, J = 7.4 and 14.0 Hz), 2.94 (s, 3H), 4.80 (dd, 1H, J = 4.3 and 7.3 Hz), 6.59 (d, 1H, J = 8.6 Hz), 6.64 (t, 1H, J = 7.3 Hz), 7.19 (d, 1H, J = 7.4 Hz), 7.19 (t, 1H, J = 6.7 Hz), 7.38 (s, 1H), 12.33 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.1, 37.5, 56.2, 111.9, 116.9, 120.1, 123.7, 129.5, 131.9, 134.0, 144.9, 166.2, 172.3; IR (KBr): 2950(br), 2400(br), 1695, 1684, 1653, 1559, 1540, 1507, 1490, 1457, 1436, 1266, 1204, 1161, 750 cm^{-1}. HRMS (ESI): Calcd for $C_{13}H_{13}NNaO_4$ ($[M+Na]^+$): 270.0737. Found: 270.0725.

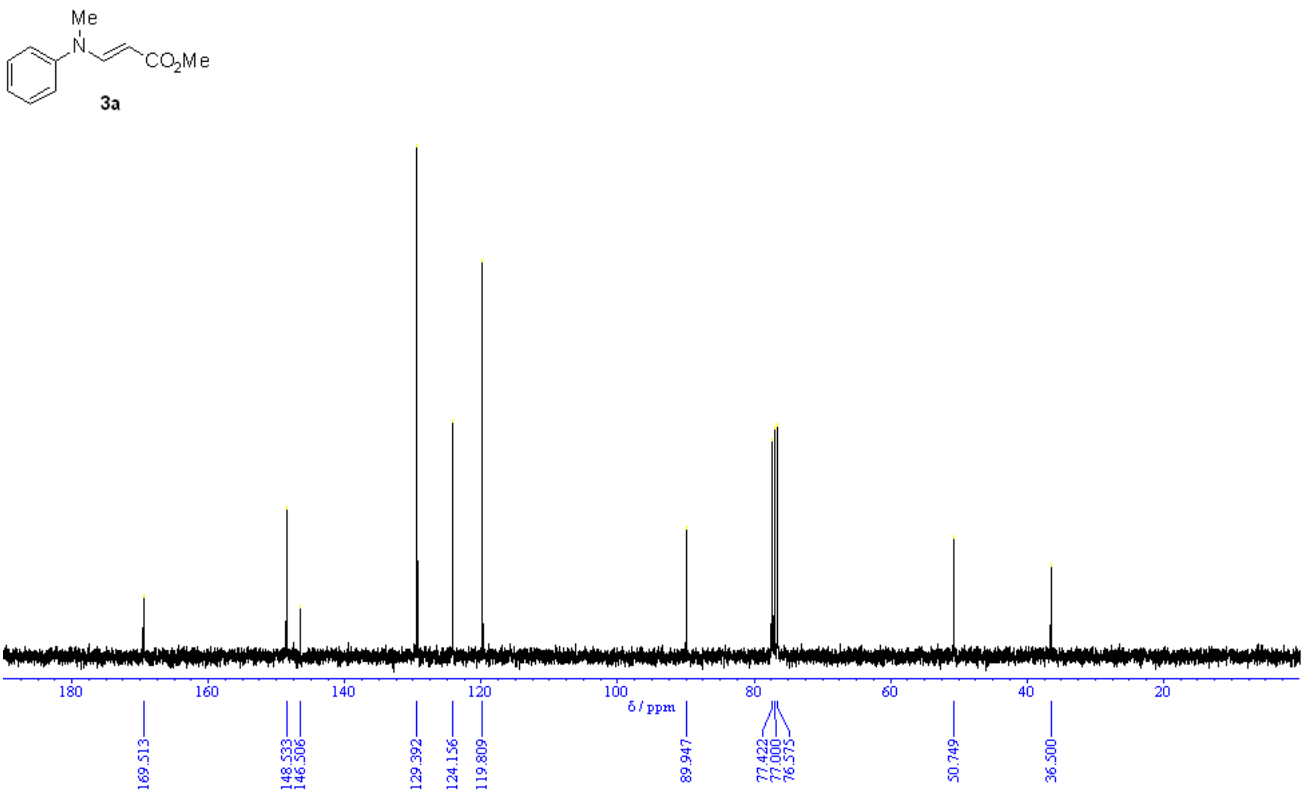


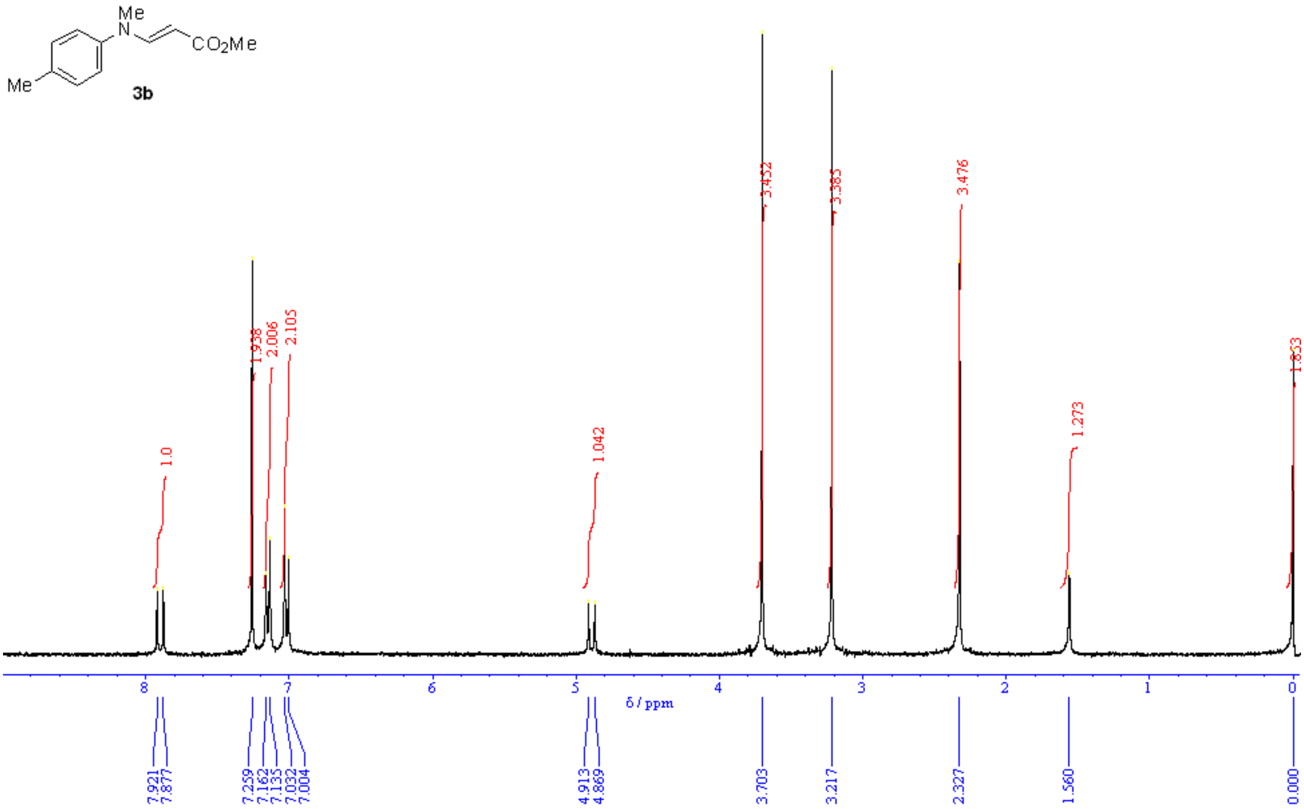
2-(Carboxymethyl)-6-fluoro-1-methyl-1,2-dihydroquinoline-3-carboxylic Acid (4d): The titled compound was prepared in 85% yield according to a procedure similar to that mentioned in **4a**: Yellow solid; m.p. 128.1–129.5 °C (hexane-chloroform); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.15 (dd, 1H, J = 4.4 and 14.0 Hz), 2.31 (dd, 1H, J = 7.3 and 14.0 Hz), 2.92 (s, 3H), 4.78 (dd, 1H, J = 4.4 and 7.2 Hz), 6.57 (dd, 1H, J = 9.0 Hz and $J_{H\text{-}C3\text{-}F}$ = 4.5 Hz), 7.04 (ddd, 1H, J = 3.0, 8.8 Hz, and $J_{H\text{-}C2\text{-}F}$ = 8.8 Hz), 7.13 (dd, 1H, J = 3.0 Hz and $J_{H\text{-}C2\text{-}F}$ = 9.0 Hz), 7.38 (s, 1H), 12.38 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.1, 37.3, 56.2, 113.0 (d, $J_{C\text{-}C2\text{-}F}$ = 8.1 Hz), 115.0 (d, $J_{C\text{-}C\text{-}F}$ = 22.5 Hz), 118.0 (d, $J_{C\text{-}C\text{-}F}$ = 22.8 Hz), 121.1 (d, $J_{C\text{-}C2\text{-}F}$ = 8.3 Hz), 125.7, 133.0 (d, $J_{C\text{-}C3\text{-}F}$ = 2.3 Hz), 141.6, 154.7 (d, $J_{C\text{-}F}$ = 232.6 Hz), 166.1, 172.3; IR (KBr) 2890(br), 2400(br), 1695, 1653, 1646, 1568, 1496, 1418, 1312, 1235, 1207, 1161, 973, 805 cm^{-1}. HRMS (ESI): Calcd for $C_{13}H_{12}FNNaO_4$ ([M+Na]$^{+}$): 288.0643. Found: 288.0630.



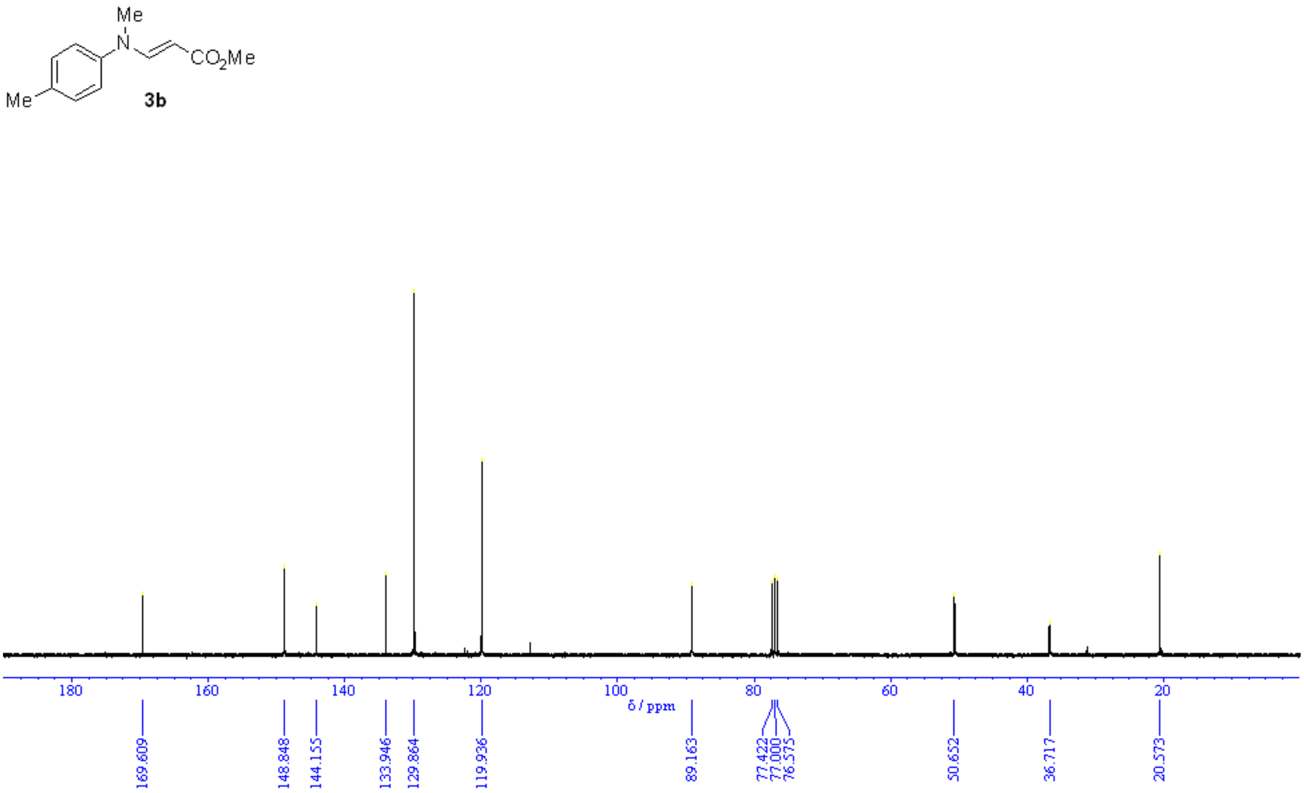
2-(Carboxymethyl)-6-fluoro-1-methyl-1,2-dihydroquinoline-3-carboxylic Acid (4f): The titled compound was prepared in 98% yield according to a procedure similar to that mentioned in **4a**: Green solid; m.p. 141.2–143.1 °C (hexane-chloroform); ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.29 (dd, 1H, J = 4.7 and 14.0 Hz), 2.35 (dd, 1H, J = 6.0 and 14.2 Hz), 3.00 (s, 3H), 4.88 (dd, 1H, J = 5.1 and 5.9 Hz), 6.69 (d, 1H, J = 8.8 Hz), 7.45 (dd, 1H, J = 2.0 and 8.7 Hz), 7.48 (s, 1H), 7.54 (d, 1H, J = 1.8 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.3, 38.4, 56.6, 117.7, 116.8 (q, $J_{C\text{-}C\text{-}F}$ = 32.4 Hz), 119.7, 125.00, 125.02 (q, $J_{C\text{-}C\text{-}F}$ = 270.4 Hz), 126.3 (q, $J_{C\text{-}C2\text{-}F}$ = 3.7 Hz), 128.3 (q, $J_{C\text{-}C2\text{-}F}$ = 3.3 Hz), 133.2, 147.6, 166.0, 172.2; IR (KBr): 2970(br), 2400(br), 1699, 1653, 1647, 1617, 1559, 1540, 1521, 1507, 1457, 1447, 1419, 1329, 1196, 1164, 1142, 1109, 1070, 817 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{12}F_3NNaO_4$ ([M+Na]$^{+}$): 338.0611. Found: 338.0602.



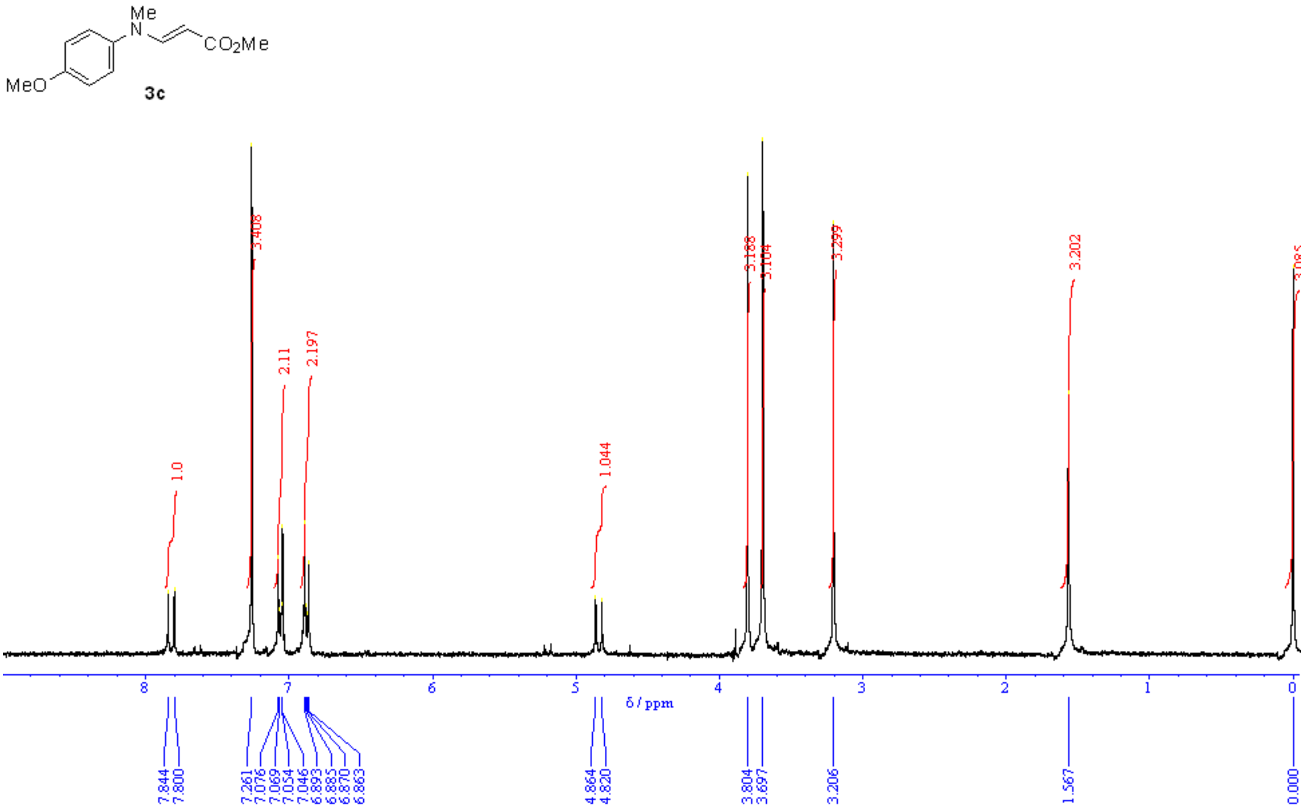




3b



3b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N
CO2Me
MeO
3c
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3.408
2.11
2.197
1.044
3.188
3.104
3.299
3.202
δ / ppm
8
7
6
5
4
3
2
1
0
7.844
7.800
7.261
7.076
7.069
7.054
7.046
6.893
6.885
6.870
6.863
4.864
4.820
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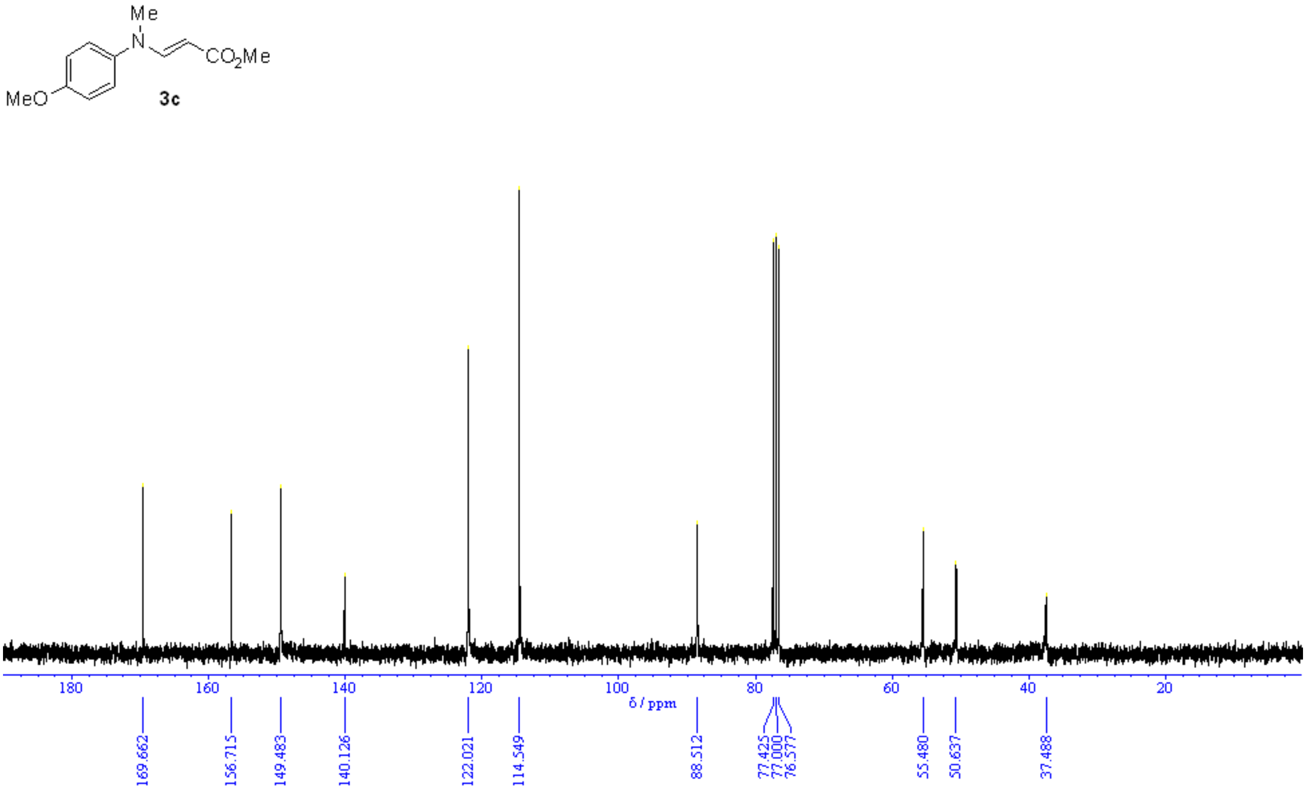
3.206
1.567
0.000


Me
N
CO2Me
MeO
3c
δ / ppm
180
160
140
120
100
80
60
40
20
169.662
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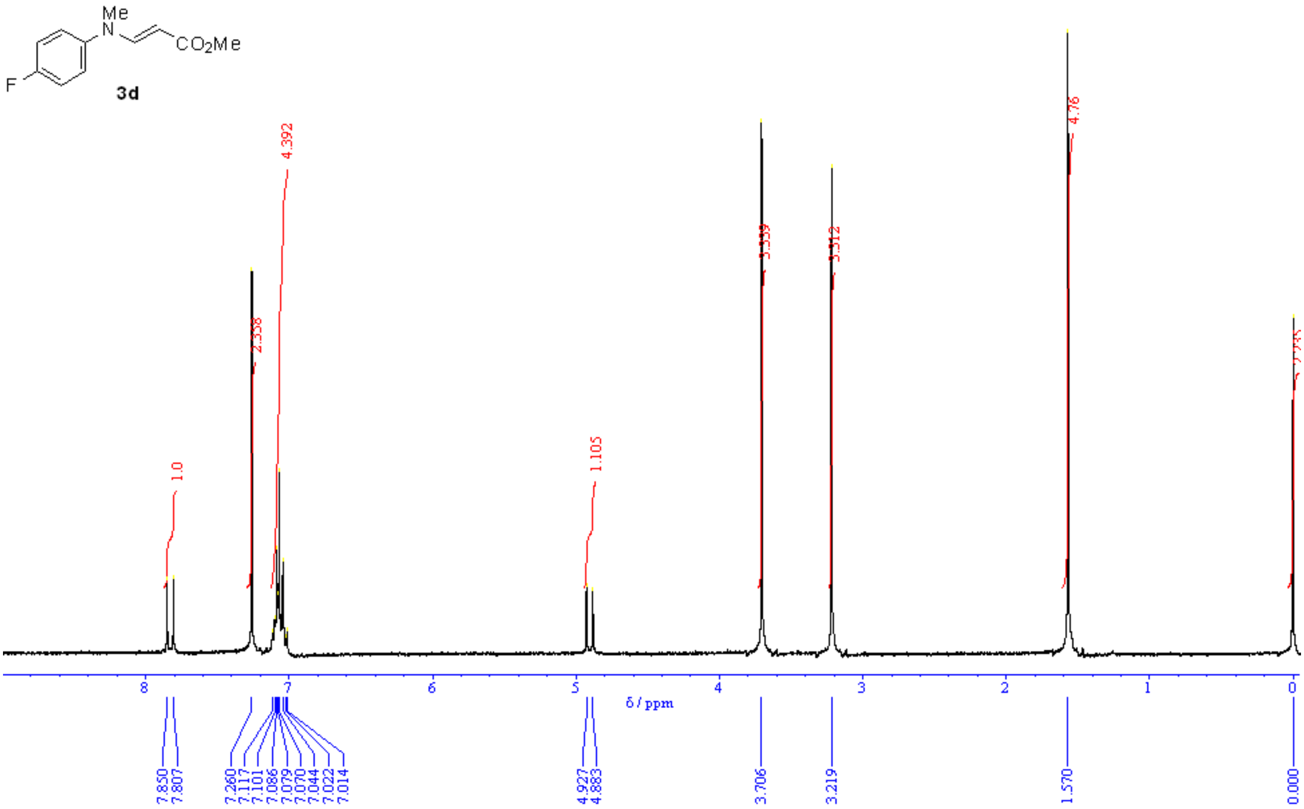
140.126
122.021
114.549
88.512
77.425
77.000
76.577
55.480
50.637
37.488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CO2Me
F
3d
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2.338
4.392
1.105
3.339
3.312
4.76
8
7
6
5
4
3
2
1
0
δ / ppm
7.850
7.807
7.260
7.117
7.101
7.086
7.079
7.070
7.044
7.022
7.014
4.927
4.883
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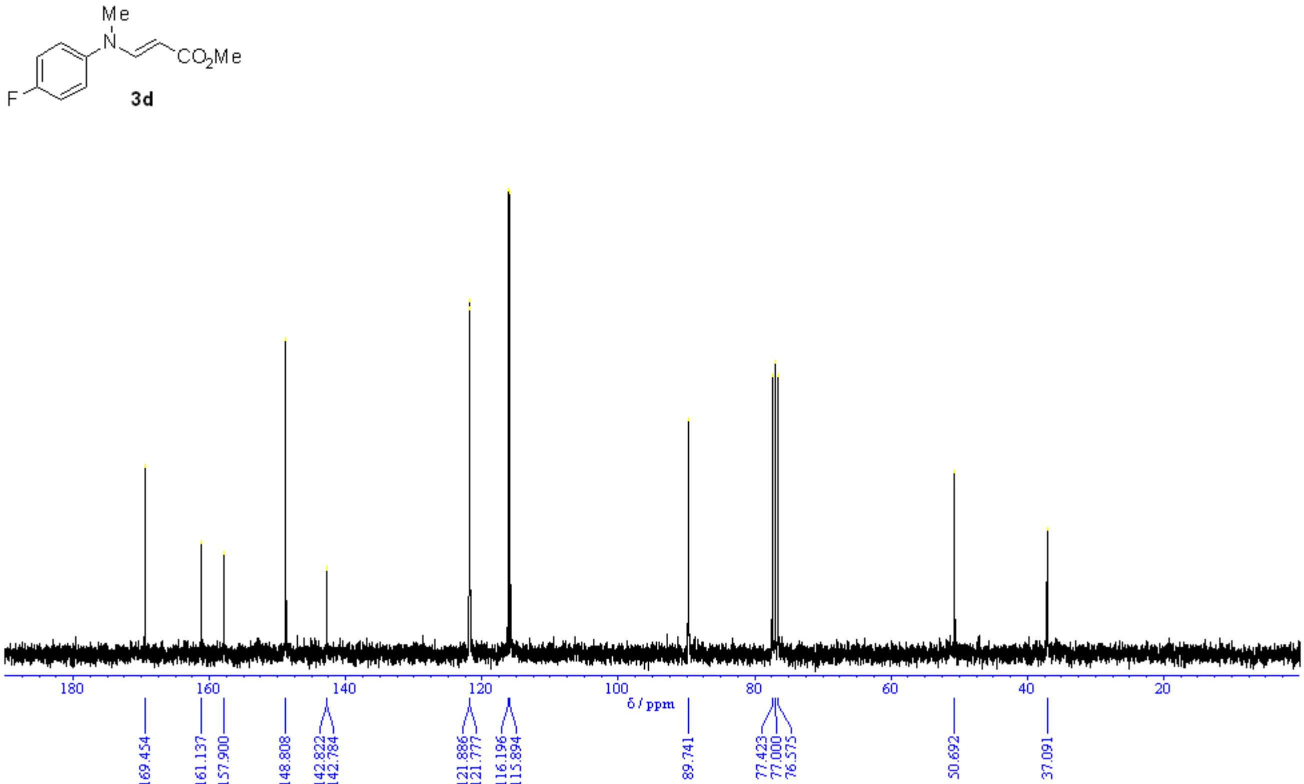
3.219
1.570
0.000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N
CO2Me
F
3d
180
160
140
120
100
80
60
40
20
δ / ppm
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157.900
148.808
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121.777
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115.894
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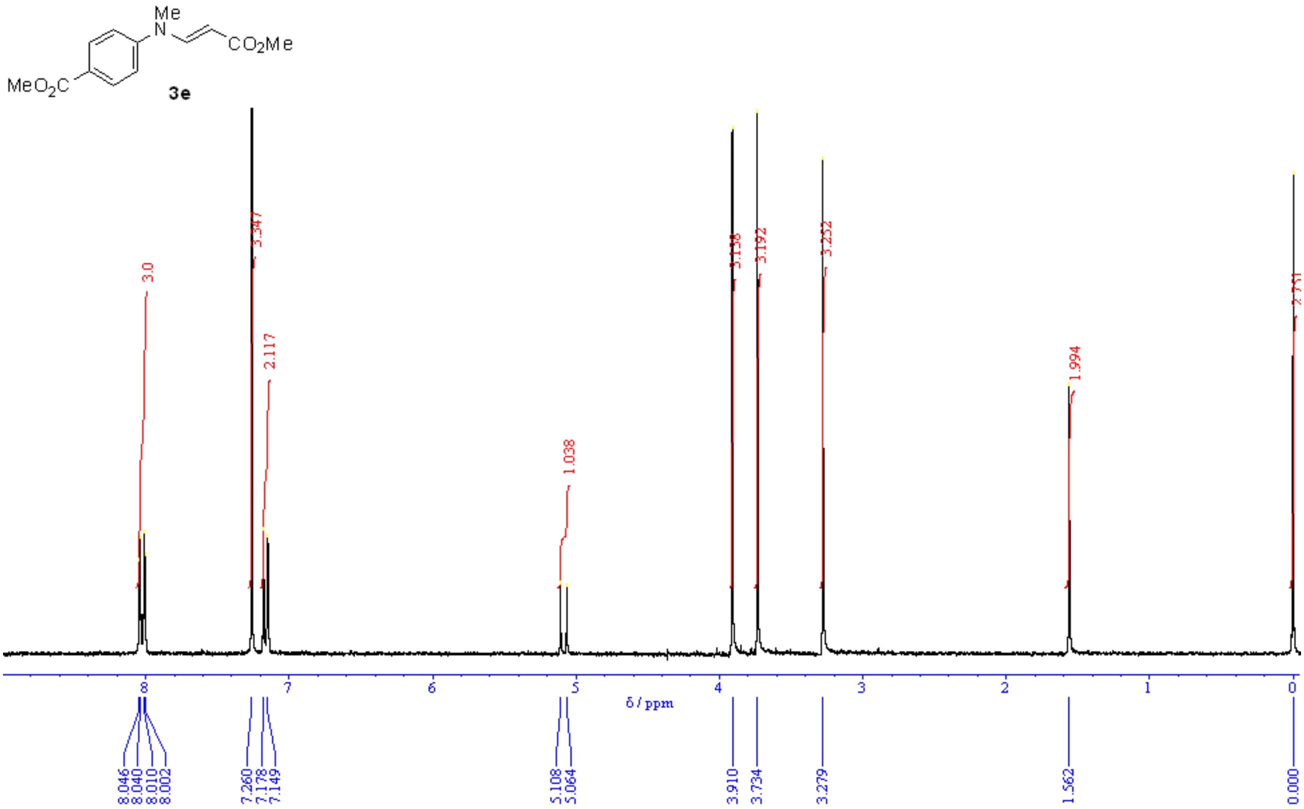
77.423
77.000
76.575
50.692
37.091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CO2Me
MeO2C
3e
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1.038
3.138
3.192
3.252
1.994
2.711
δ / ppm
8.046
8.040
8.010
8.002
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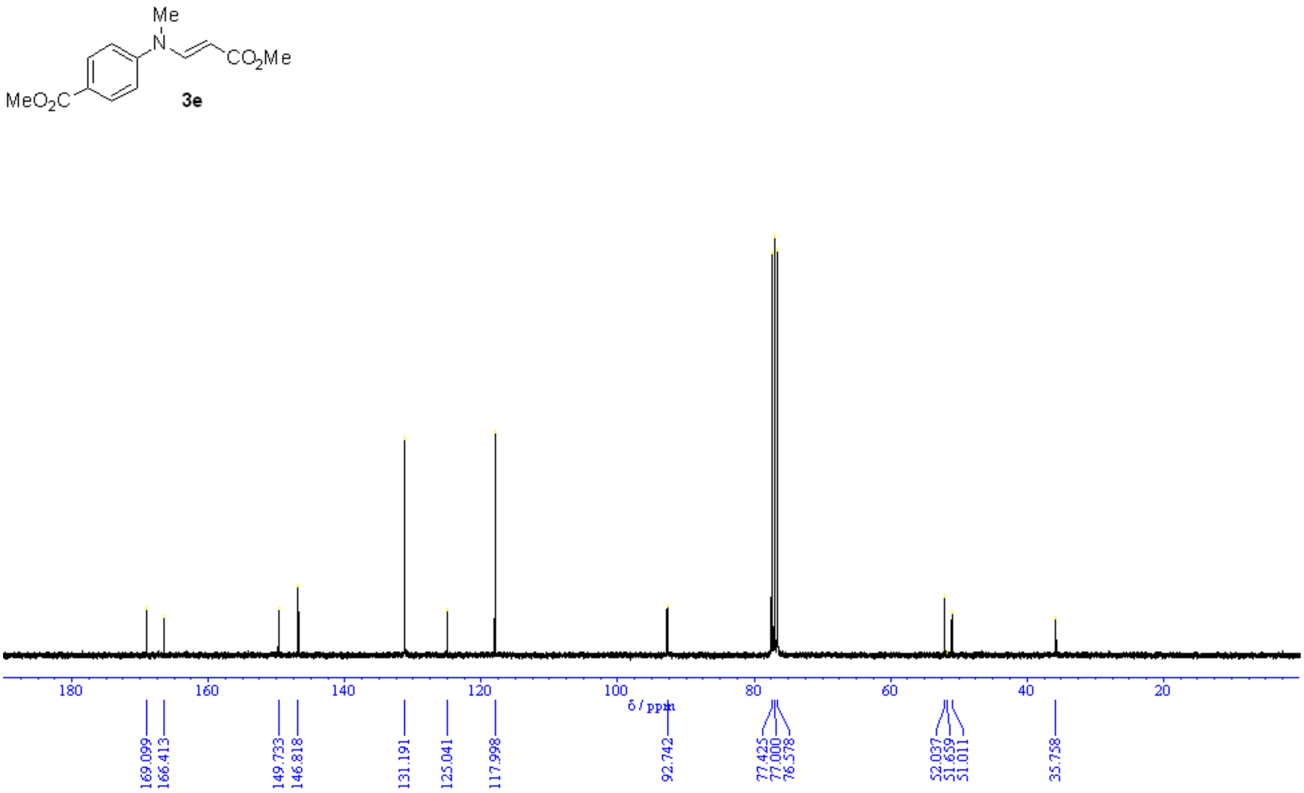
7.178
7.149
5.108
5.064
3.910
3.734
3.279
1.562
0.000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N
CO2Me
MeO2C
3e
δ / ppm
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149.733
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131.191
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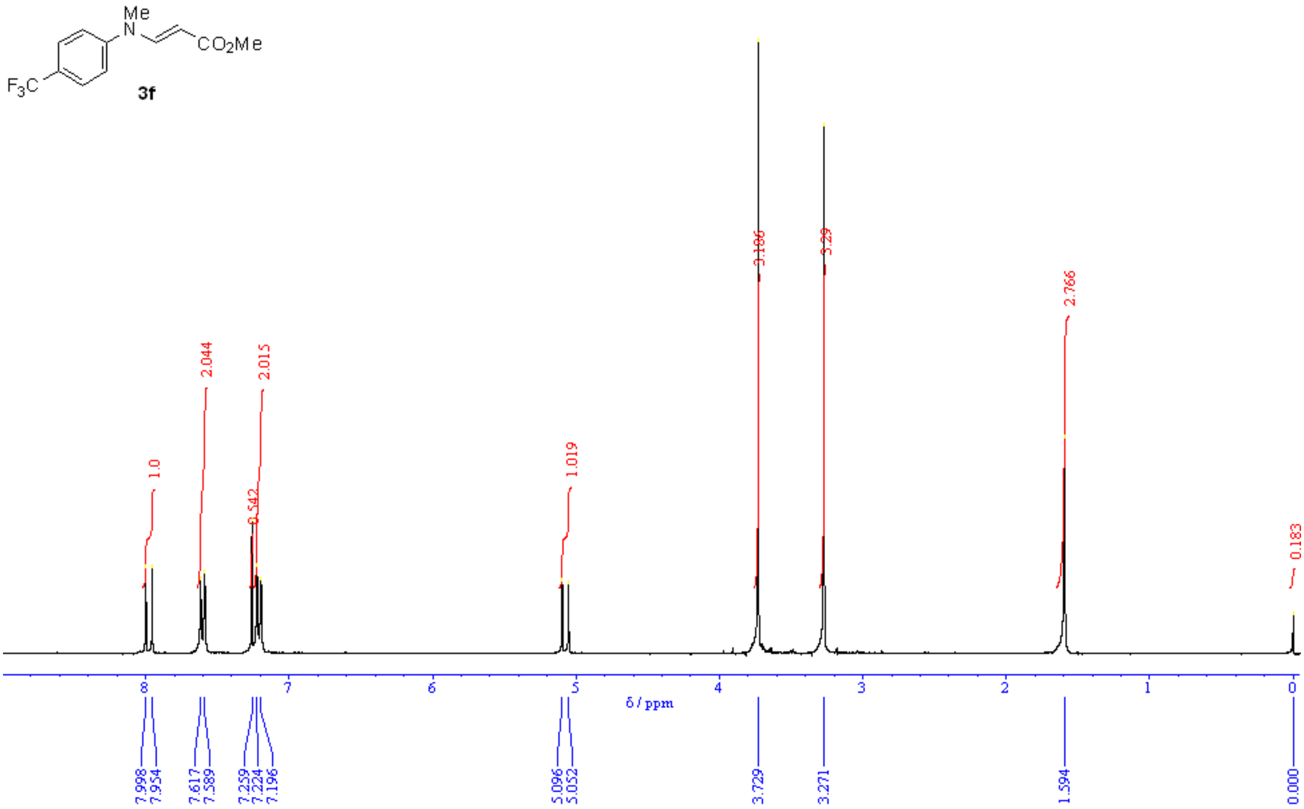
117.998
92.742
77.425
77.000
76.578
52.037
51.659
51.011
35.758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CO2Me
F3C
3f
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2.044
0.542
2.015
1.019
3.186
3.29
2.766
0.183
δ / ppm
7.998
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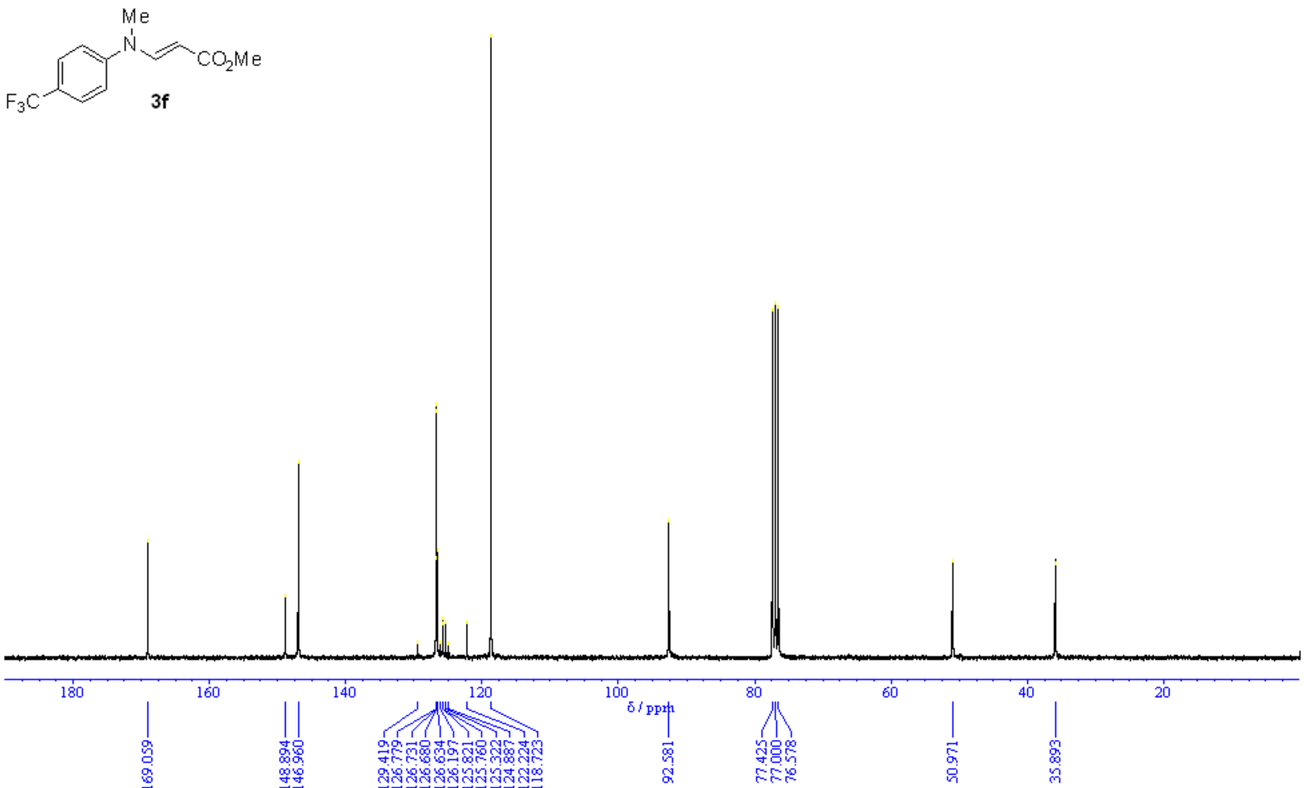
7.589
7.259
7.224
7.196
5.096
5.052
3.729
3.271
1.594
0.000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CO2Me
F3C
3f
δ / ppm
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146.960
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126.731
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126.634
126.197
125.821
125.760
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124.887
122.224
118.723
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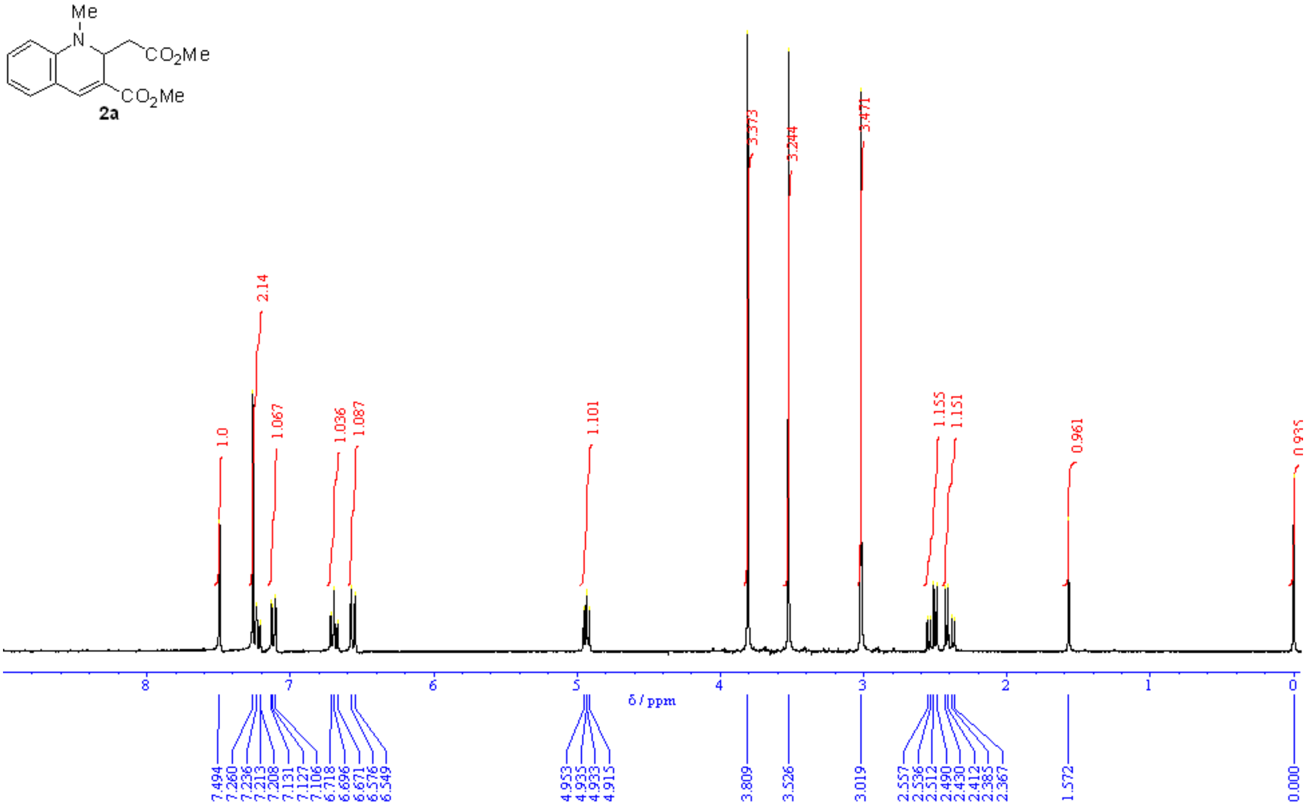
77.425
77.000
76.578
50.971
35.893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CO2Me
CO2Me
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1.036
1.087
1.101
3.373
3.244
3.471
1.155
1.151
0.961
8
7
6
5
δ / ppm
4
3
2
1
0
7.494
7.260
7.236
7.213
7.208
7.131
7.127
7.106
6.718
6.696
6.671
6.576
6.549
4.953
4.935
4.933
4.915
3.809
3.526
3.019
2.557
2.536
2.512
2.490
2.430
2.412
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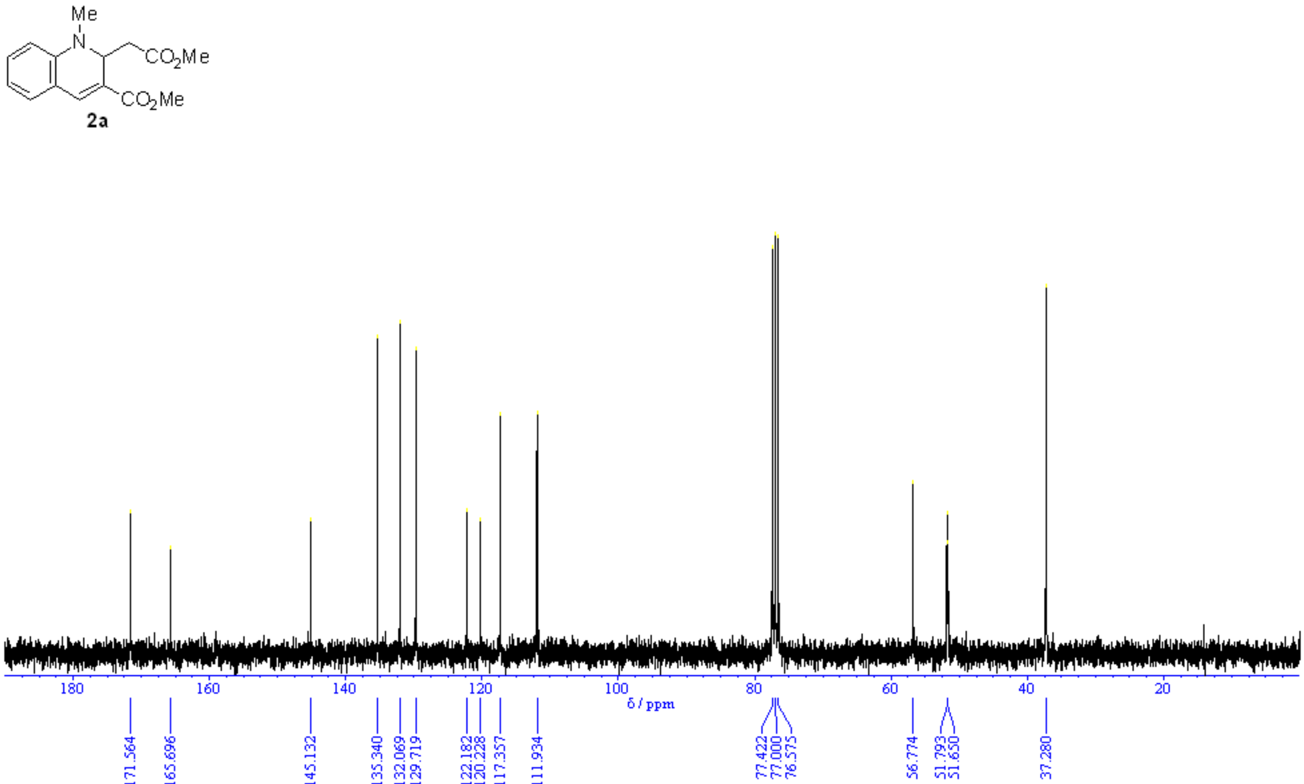
2.367
1.572
0.000


Me
N
CO2Me
CO2Me
2a
180
160
140
120
100
δ / ppm
80
60
40
20
171.564
165.696
145.132
135.340
132.069
129.719
122.182
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117.357
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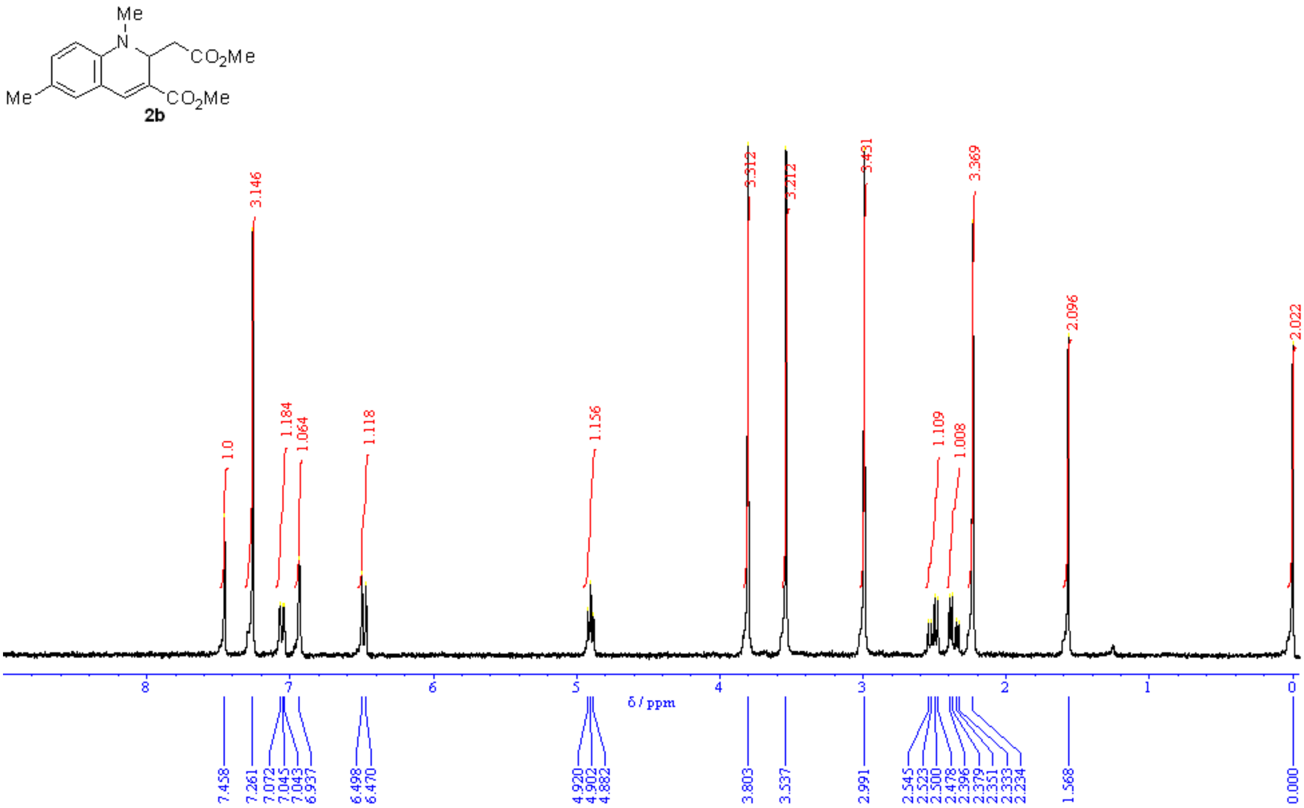
77.000
76.575
56.774
51.793
51.650
37.280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CO2Me
Me
CO2Me
2b
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1.064
1.118
1.156
3.312
3.212
3.431
1.109
1.008
3.369
2.096
2.022
δ / ppm
7.458
7.261
7.072
7.045
7.043
6.937
6.498
6.470
4.920
4.902
4.882
3.803
3.537
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2.234
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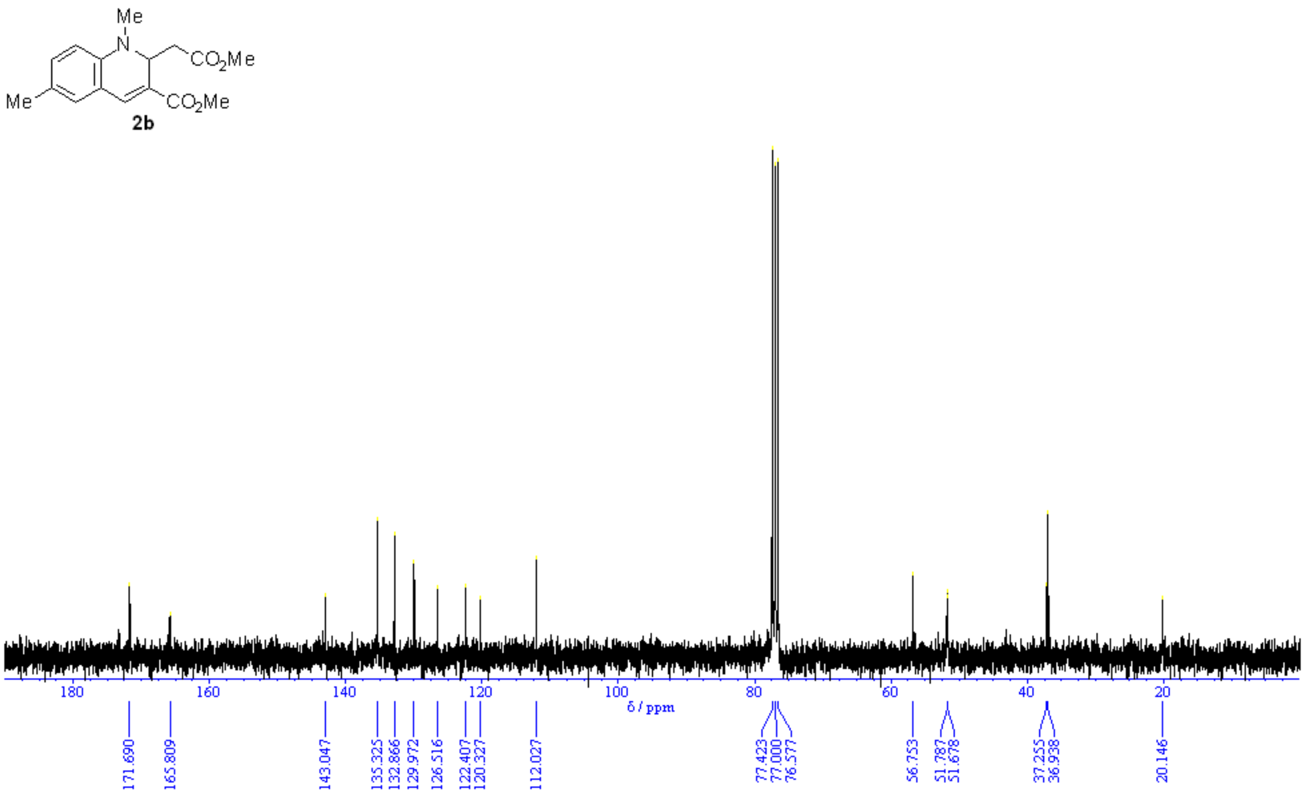
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N
CO2Me
Me
CO2Me
2b
δ / ppm
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126.516
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77.000
76.577
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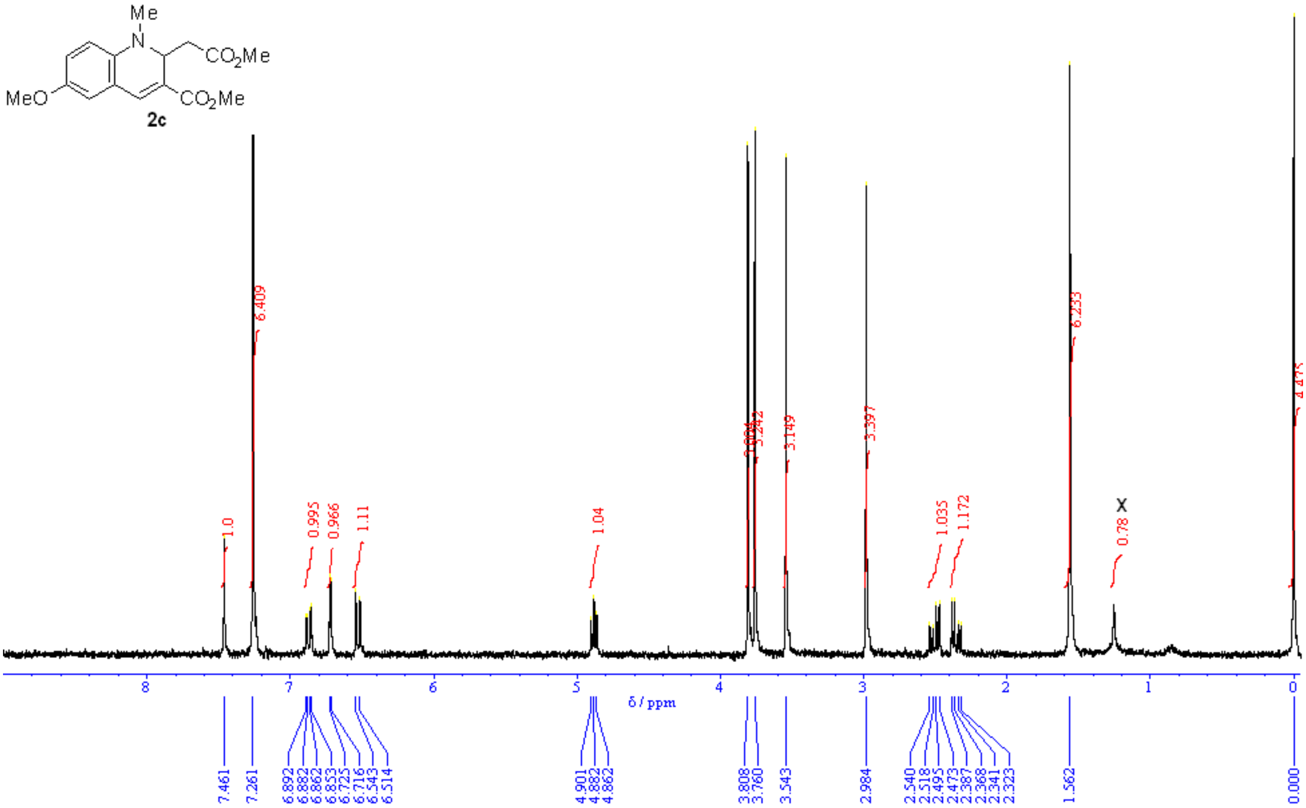
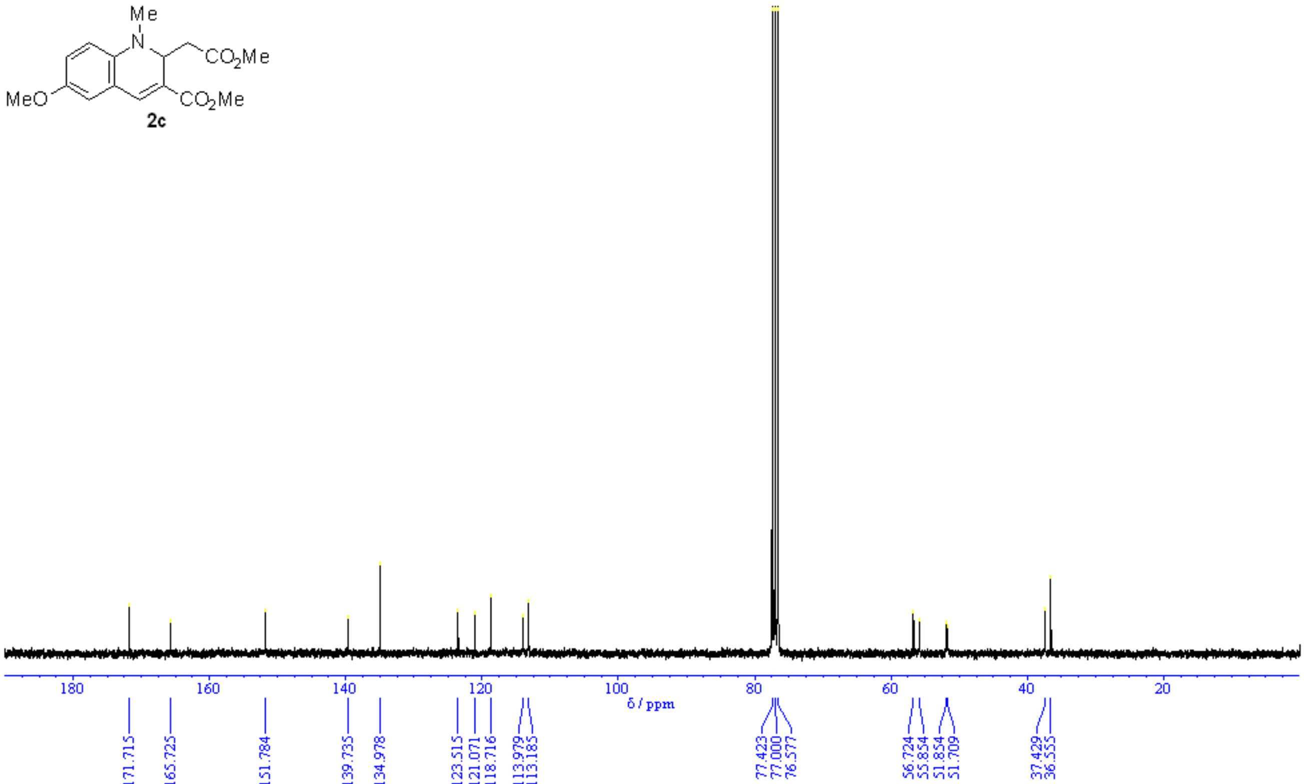
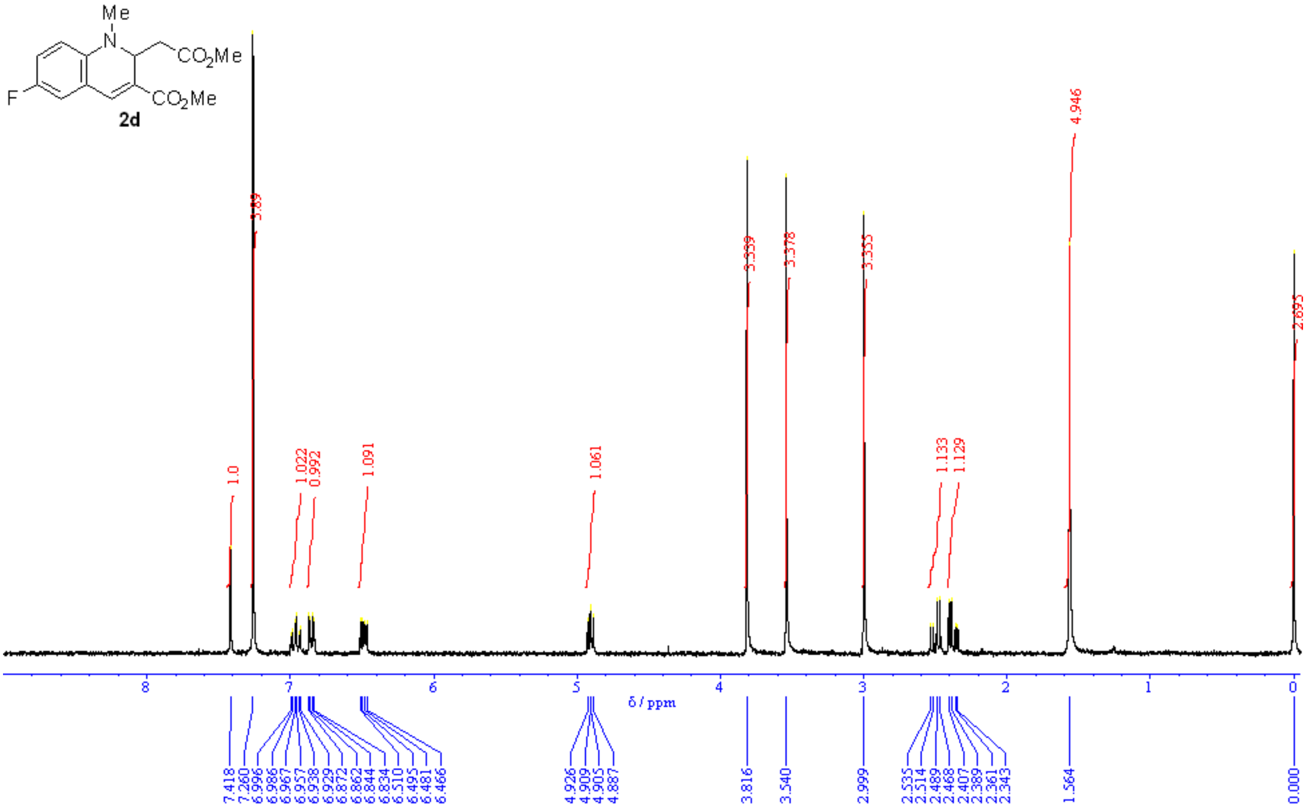
51.678
37.255
36.938
20.146


2c
δ / ppm


2c
δ / ppm


Me
N
CO_2Me
CO_2Me
F
2d
δ / ppm
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6.957
6.938
6.929
6.872
6.862
6.844
6.834
6.510
6.495
6.481
6.466
4.926
4.909
4.905
4.887
3.816
3.540
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2.514
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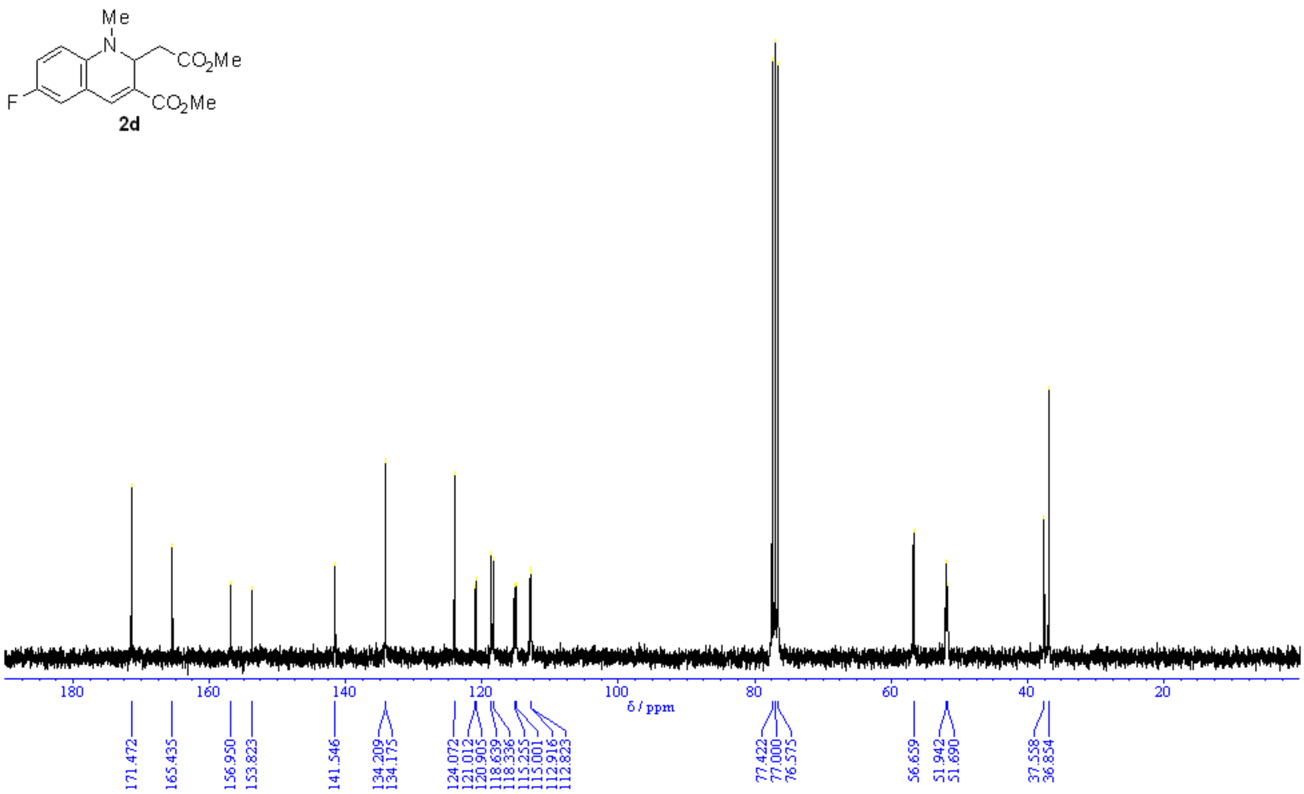
1.564
0.000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N
CO_2Me
CO_2Me
F
2d
δ / ppm
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141.546
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134.175
124.072
121.012
120.905
118.639
118.336
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77.000
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56.659
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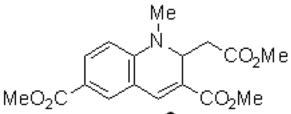
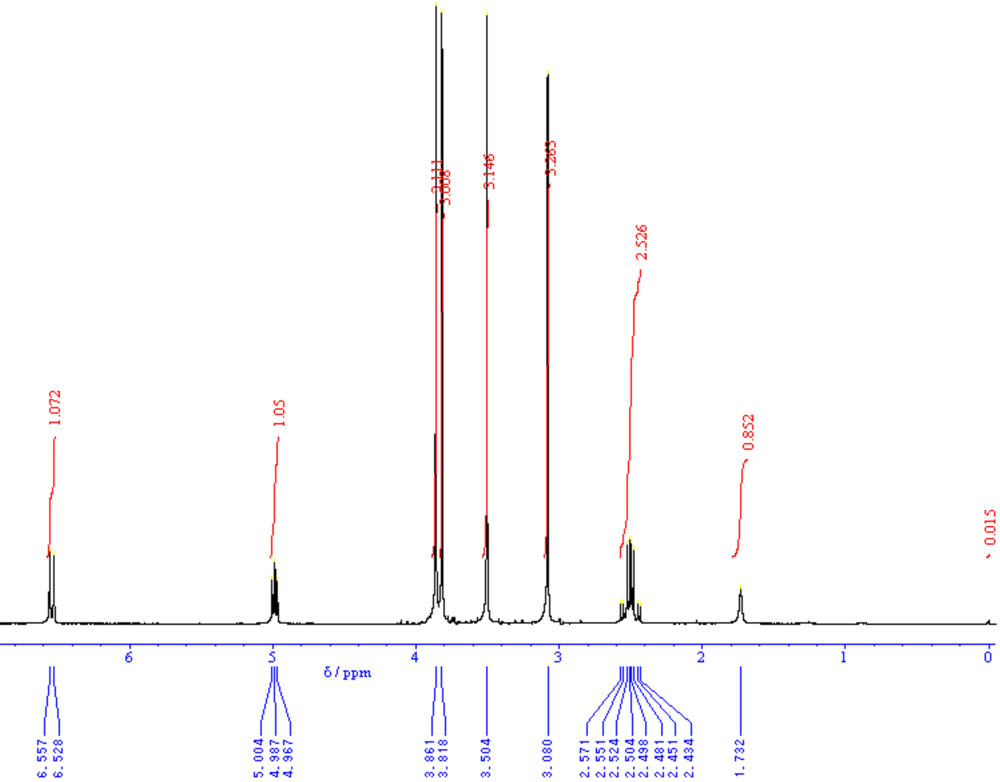
51.690
37.558
36.854


Me
N
CO2Me
MeO2C
CO2Me

2e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0.145
1.072
1.05
3.111
3.008
3.146
3.263
2.526
0.852
0.015
8
7
6
5
δ / ppm
4
3
2
1
0
7.906
7.899
7.877
7.870
7.787
7.780
7.499
7.271
6.557
6.528
5.004
4.987
4.967
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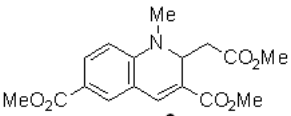
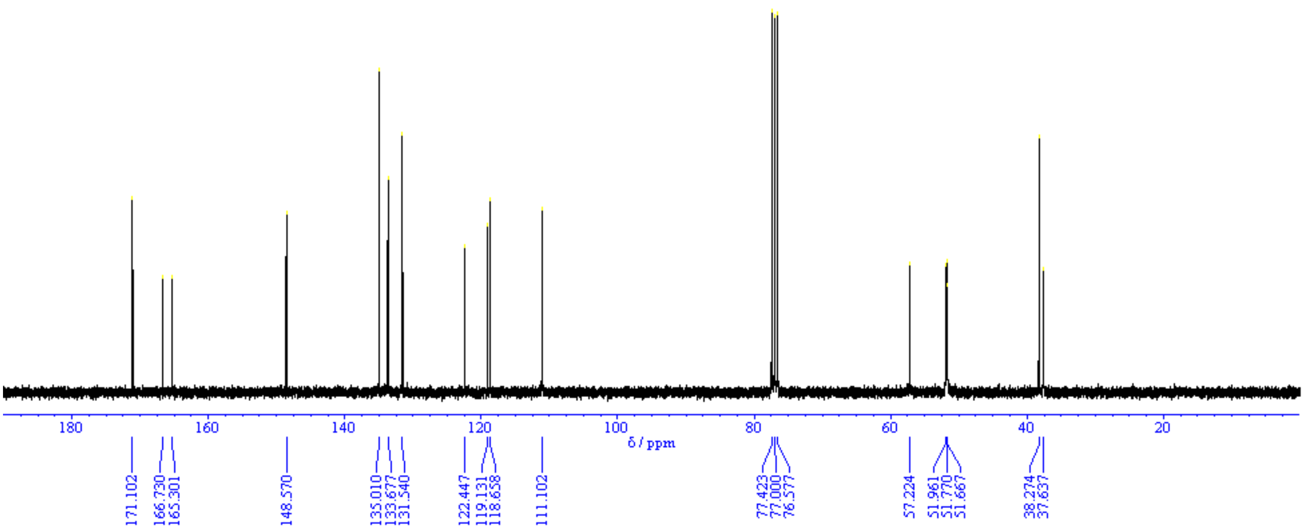
2.451
2.434
1.732


Me
N
CO2Me
MeO2C
CO2Me

2e


180
160
140
120
100
δ / ppm
80
60
40
20
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166.730
165.301
148.570
135.010
133.677
131.540
122.447
119.131
118.658
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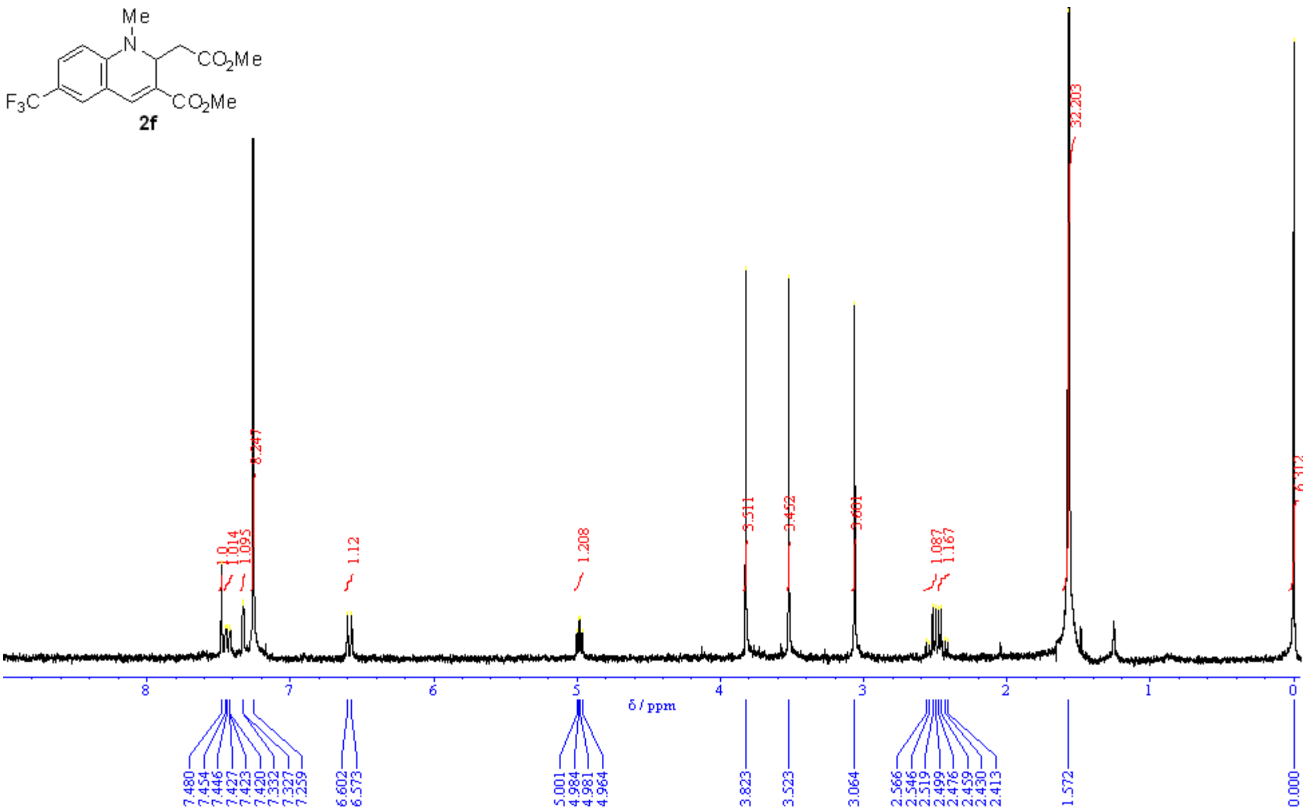
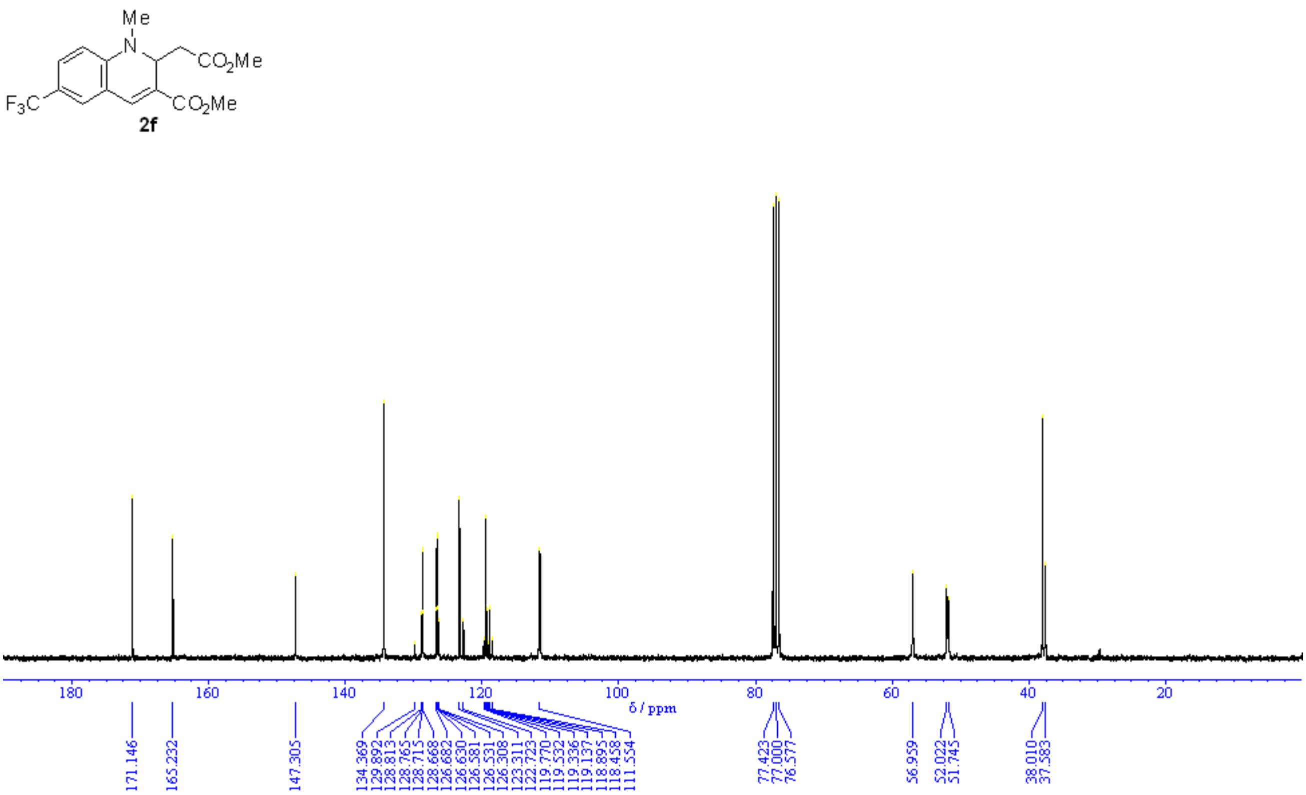
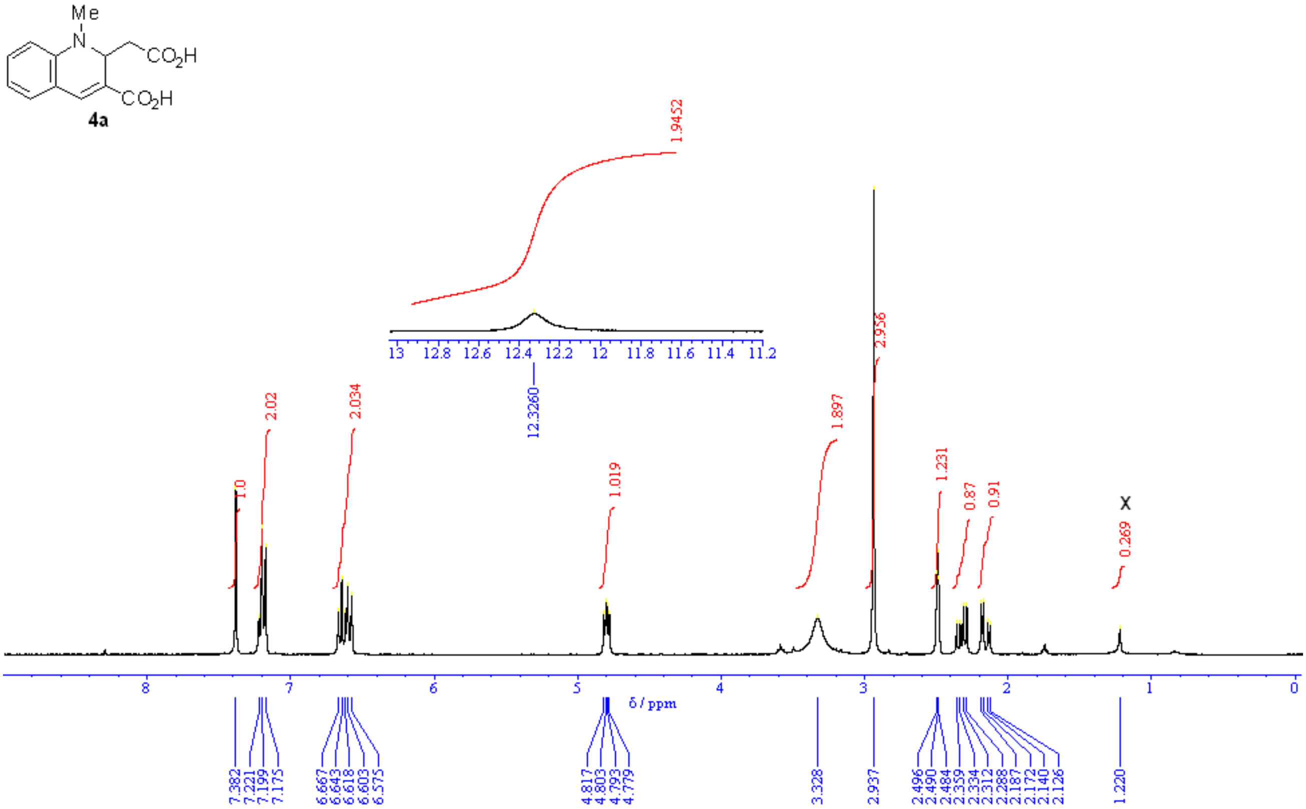
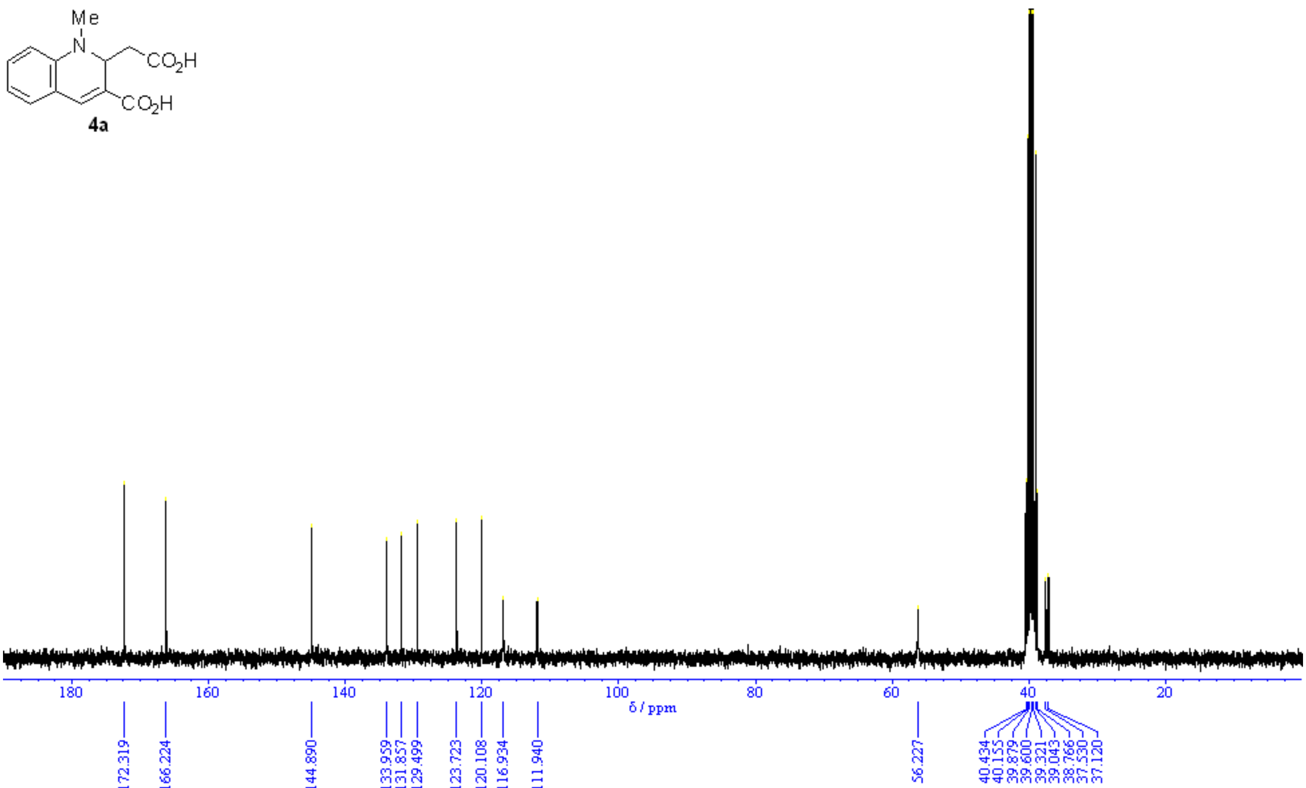
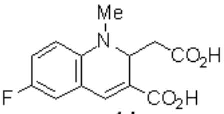
77.423
77.000
76.577
57.224
51.961
51.770
51.667
38.274
37.637



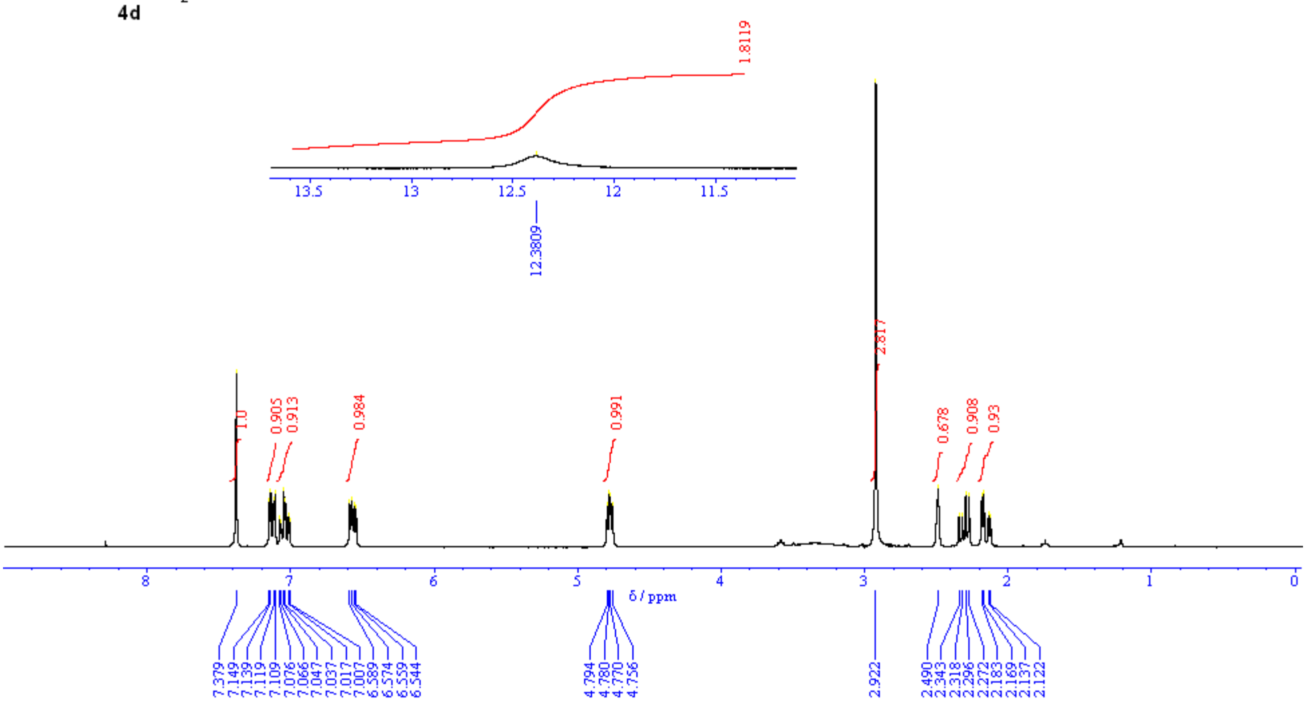







Me
N
CO2H
F
CO2H

4d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13
12.5
12
11.5
12.3809
1.0
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0.913
0.984
0.991
2.817
0.678
0.908
0.93
8
7
6
5
4
3
2
1
0
δ / ppm
7.379
7.149
7.139
7.119
7.109
7.076
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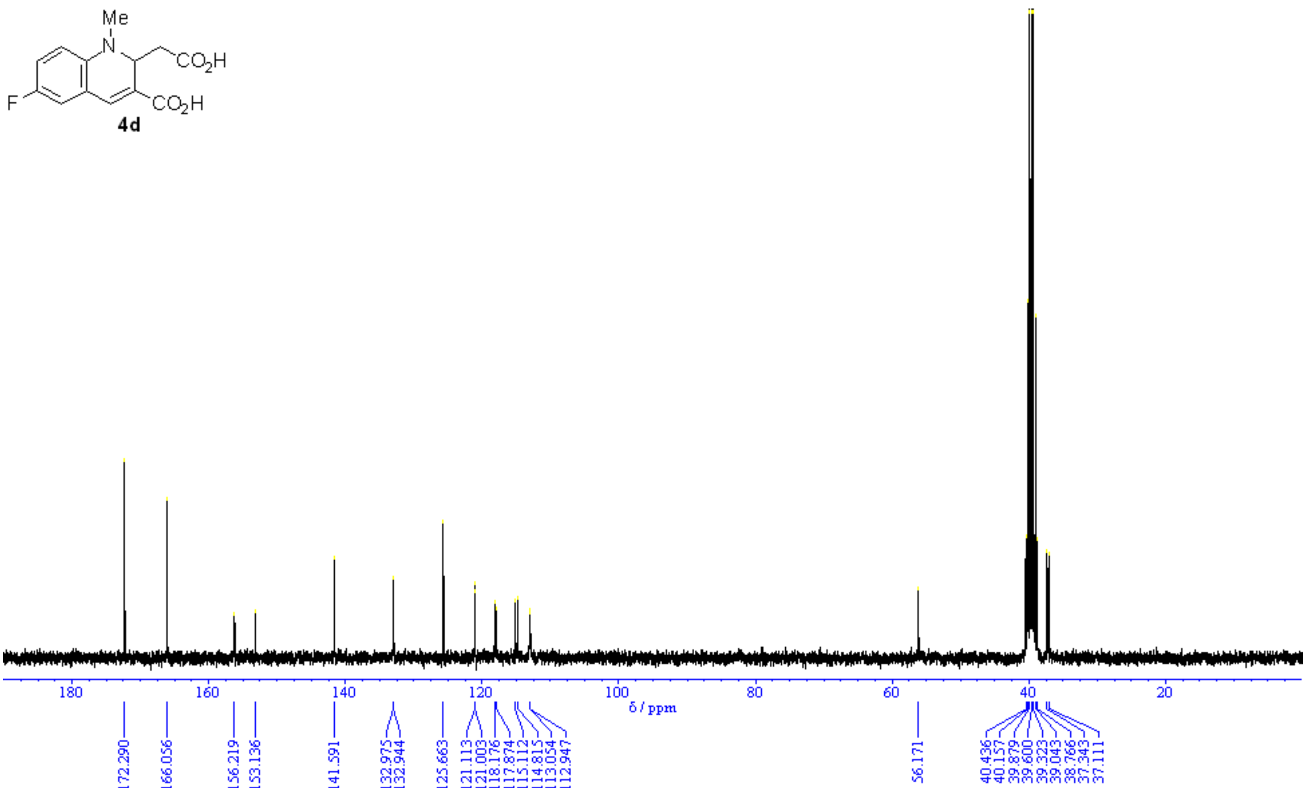
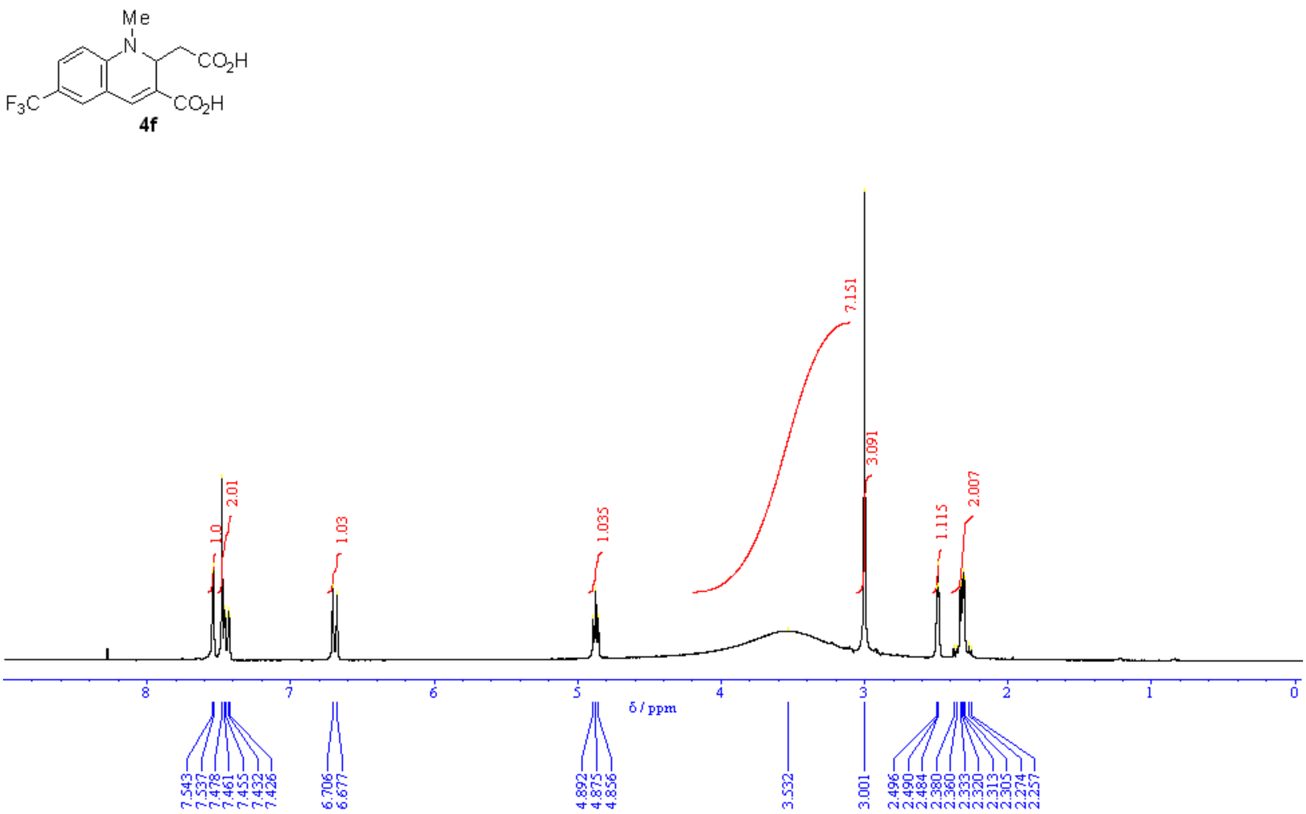
7.037
7.017
7.007
6.589
6.574
6.559
6.544
4.794
4.780
4.770
4.756
2.922
2.490
2.343
2.318
2.296
2.272
2.183
2.169
2.137
2.122


Me
N
CO2H
F
CO2H

4d

180
160
140
120
100
80
60
40
20
δ / ppm
172.290
166.056
156.219
153.136
141.591
132.975
132.944
125.663
121.113
121.003
118.176
117.874
115.112
114.815
113.054
112.947
56.171
40.436
40.157
39.879
39.600
39.323
39.043
38.766
37.343
37.111



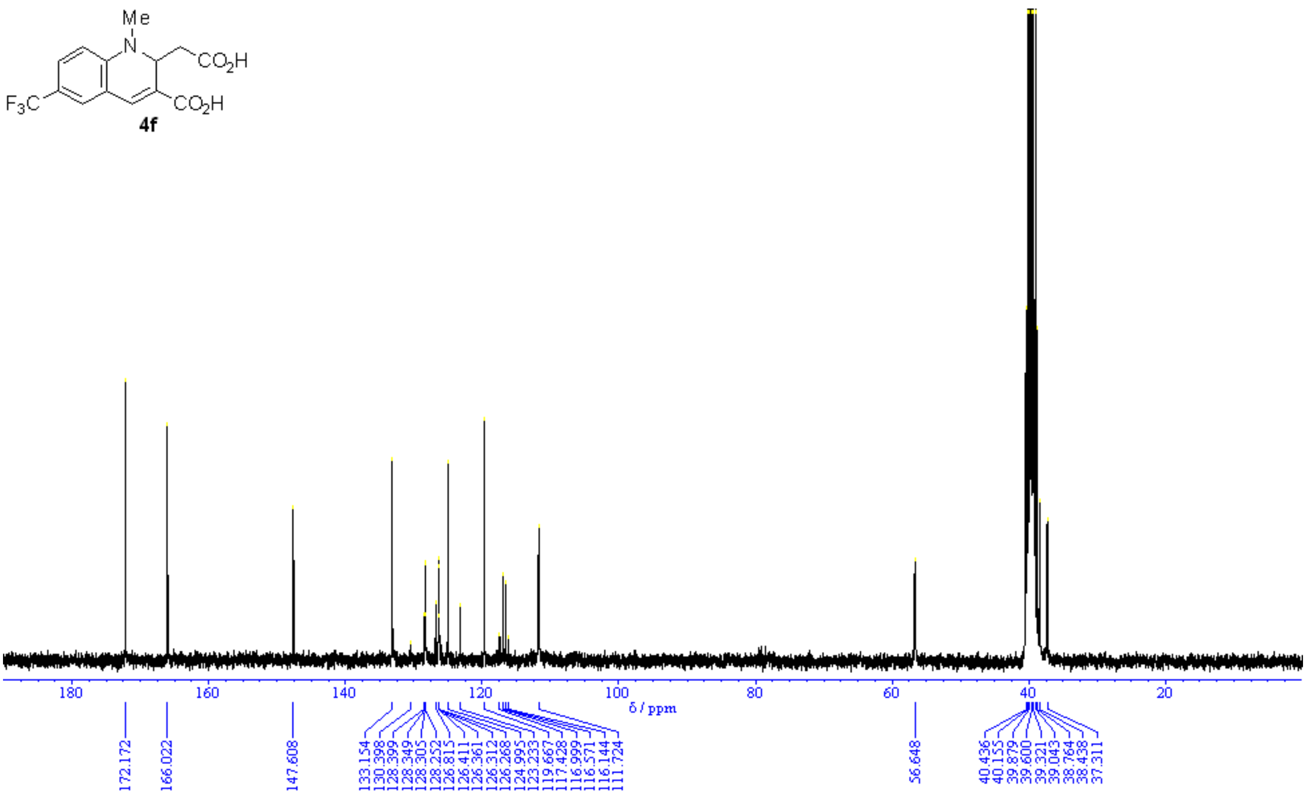
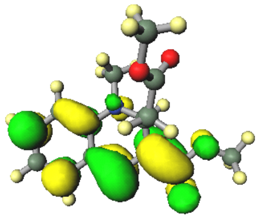
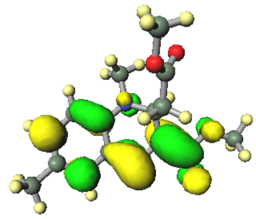
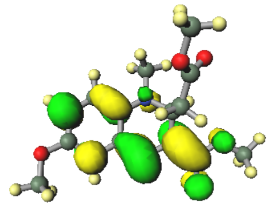
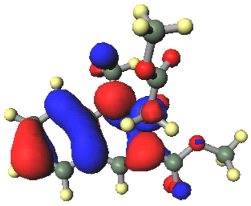
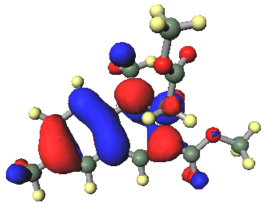
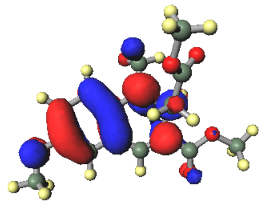
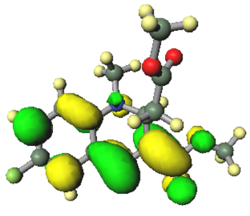
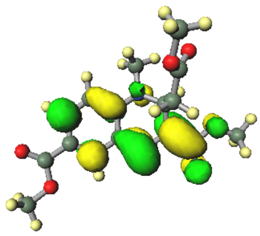
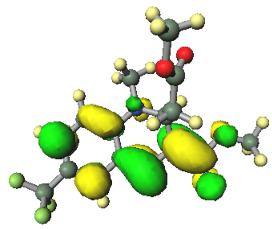
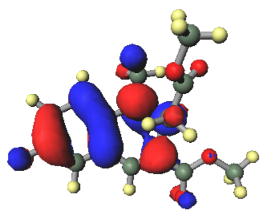
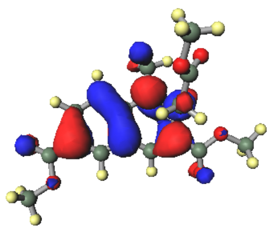
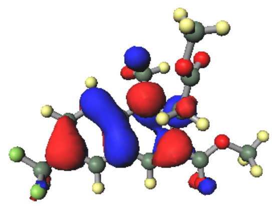


Table S1 Summary of TD-DFT calculation with B3LYP/6-31+G*.

Compound	**2a**	**2b**	**2c**
Subtituent (G)	H	Me	OMe
Orbital of LUMO			
Energy level of LUMO [eV]	-1.8961	-1.8602	-1.9013
Orbital of HOMO			
Energy level of HOMO [eV]	-5.5201	-5.3862	-5.2012
λ_{max} (calcd) [nm]	410.65	421.09	448.33
λ_{max} (exp.) [nm]	411.5	422	439.5
Compound	**2d**	**2e**	**2f**
Subtituent (G)	F	CO_2Me	CF_3
Orbital of LUMO			
Energy level of LUMO [eV]	-2.1083	-2.0602	-2.2240
Orbital of HOMO			
Energy level of HOMO [eV]	-5.6020	-5.7900	-5.9568
λ_{max} (calcd) [nm]	426.25	397.72	399.31
λ_{max} (exp.) in THF [nm]	424	405.5	403

References

1 A. Padwa and L. Zhi, *J. Am. Chem. Soc.*, 1990, **112**, 2037–2038.

2 J. J. Bozel and L. S. Hegedus, *J Org. Chem.*, 1981, **46**, 2561–2563.