Supporting Information For

Silver-Catalyzed Vinylogous Fluorination of Vinyldiazoacetates

Changming Qin and Huw M. L. Davies*

Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322.
Email: hmdavie@emory.edu

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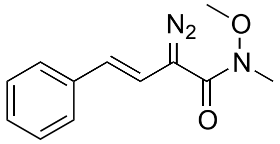
(1) General Method

All reactions were conducted in flame-dried 35 mL heavy wall cylindrical and round bottom vessels or borosilicate glass (purchased from Chemglass) under an inert atmosphere of dry Argon. All reagents were used as received from commercial suppliers. Farnesol (F203-25G), Cholesterol (C75209-25g), Deoxo-Fluor and DAST were purchased from Sigma-Aldrich. (+)-Dehydsroisoandrosterone (70793-25g) was purchased from AK Scientific, Inc. Dichloromethane was obtained from drying columns (Grubbs type solvent purifier) and was degassed using freeze-pump-thaw degassing. Flash chromatography was performed on silica gel 60 (230-400 mesh). Thin layer chromatography (TLC) was performed on aluminum backed plates, pre-coated with silica gel (0.25 mm, 60 F_{254}) which were developed using standard visualizing agents: UV fluorescence (254 nm) and permanganate. ^{1}H NMR spectra were recorded on Varian Nuclear Magnetic Resonance spectrometers at 400 MHz. Tetramethylsilane (TMS) was used as an internal standard ($\delta = 0.00$). The NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, and br = broad), integration and coupling constants in Hz. ^{13}C NMR spectra were recorded at 100 MHz using the given solvent as an internal standard ($CDCl_3$, δ =77.0). ^{13}C NMR spectra were obtained with complete proton decoupling and ^{19}F NMR spectra were recorded at 376.3 MHz, using trichlorofluoromethane as an internal standard ($CDCl_3$, δ =0.0). Mass spectral determinations were carried out by FTMS+p-NSI or APCI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}.

(2) Procedure for Vinyldiazo Compound Synthesis

Vinyldiazo acetates **3a-q** were synthesized according to the previous procedures.[1] The other vinyldiazo compounds were synthesized by the following procedure.



(*E*)-2-diazo-N-methoxy-N-methyl-4-phenylbut-3-enamide (**3e**)

To a stirred solution of (*E*)-N-methoxy-N-methyl-4-phenylbut-3-enamide (3.7 g, 14.8 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (7.1 g, 29.6 mmol, 2.0 equiv.) in acetonitrile (100 mL) under Argon atmosphere, DBU (6.6 mL, 44.4 mmol, 3.0 equiv.) was added dropwise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed (pentane/diethyl ether) to afford the corresponding (*E*)-2-diazo-N-methoxy-N-methyl-4-phenylbut-3-enamide **3e** (1.6 g, 47%) as a red-orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 136.9, 128.6, 126.8, 125.9, 121.6, 113.6, 61.4, 34.3; IR (neat): 2935, 2072, 1636, 1619, 1448, 1407, 1378, 1203; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{14}O_2N_3$ $(M+H)^+$ 232.10805 found 232.10796.

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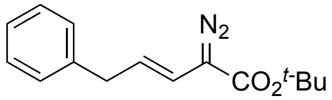
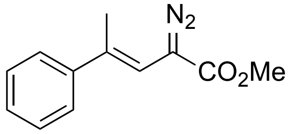
[1] Manning, J. R.; Davies, H. M. L. *Organic Synthesis*, **2007**, *84*, 334.



(*E*)-tert-butyl 2-diazo-5-phenylpent-3-enoate (**3r**)

To a stirred solution of (*E*)-tert-butyl 5-phenylpent-3-enoate (1.2 g, 5.0 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (6.1 g, 25.0 mmol, 5.0 equiv.) in acetonitrile (30 mL) under Argon atmosphere, DBU (6.0 mL, 40.0 mmol, 8.0 equiv.) was added drop-wise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by flash chromatography (pentane/diethyl ether) to afford the corresponding (*E*)-tert-butyl 2-diazo-5-phenylpent-3-enoate (**3r**) (800 mg, 62%) as a yellow-red oil.

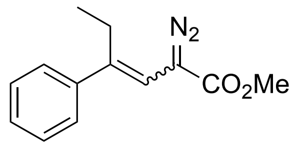
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.18 (m, 5H), 5.81 (d, *J* = 15.6 Hz, 1H), 5.45-5.38 (m, 1H), 3.48 (d, *J* = 7.2 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 140.1, 128.5, 126.2, 125.4, 123.2, 113.8, 81.8, 39.2, 28.3; IR (neat): 2978, 2078, 1698, 1369, 1161, 1118; HRMS (FTMS+p-NSI) calcd for $C_{15}H_{19}O_2N_2$ $(M+H)^+$ 259.14410 found 259.14390.



(*E*)-methyl 2-diazo-4-phenylpent-3-enoate (**5a**)

To a stirred solution of (*E*)-methyl 4-phenylpent-3-enoate (1.9 g, 10.0 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (3.7 g, 15.0 mmol, 1.5 equiv.) in acetonitrile (50 mL) under Argon atmosphere, DBU (3.0 mL, 20.0 mmol, 2.0 equiv.) was added drop-wise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by flash chromatography (pentane/diethyl ether) to afford the corresponding (*E*)-methyl 2-diazo-4-phenylpent-3-enoate (**5a**) (1.55 g, 72%) as a yellow-red oil.

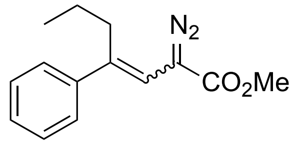
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.26 (m, 5H), 5.99 (s, 1H), 3.83 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.4, 134.5, 128.2, 127.2, 125.7, 108.9, 52.2, 16.8; IR (neat): 2952, 2077, 1705, 1436, 1241, 1113; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{12}O_2N_2Na$ $(M+Na)^+$ 239.07910 found 239.07896.



Methyl 2-diazo-4-phenylhex-3-enoate (**5b**)

To a stirred solution of methyl 4-phenylhex-3-enoate (632 mg, 3.1 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.3 g, 9.3 mmol, 3.0 equiv.) in acetonitrile (25 mL) under Argon atmosphere, DBU (2.8 mL, 18.6 mmol, 6.0 equiv.) was added drop-wise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by flash chromatography (pentane/diethyl ether) to afford the corresponding methyl 2-diazo-4-phenylhex-3-enoate (**5b**) (*E/Z* = 8.3/1, 442 mg, 62%) as a yellow-red oil.

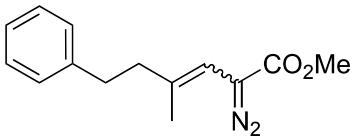
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.24 (m, 5H), 5.85 (s, 1H), 3.82 (s, 3H), 2.55-2.50 (q, 2H), 1.00 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 141.6, 140.9, 128.3, 127.3, 126.2, 108.3, 52.3, 23.6, 13.2; IR (neat): 2968, 2077, 1707, 1436, 1254, 1117; HRMS (FTMS+p-NSI) calcd for $C_{13}H_{14}O_2N_2Na$ $(M+Na)^+$ 253.09475 found 254.09473.



Methyl 2-diazo-4-phenylhept-3-enoate (**5c**)

To a stirred solution of methyl 4-phenylhept-3-enoate (510 mg, 2.34 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.14 g, 4.68 mmol, 2.0 equiv.) in acetonitrile (15 mL) under Argon atmosphere, DBU (1.4 mL, 9.4 mmol, 4.0 equiv.) was added drop-wise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by flash chromatography (pentane/diethyl ether) to afford the corresponding methyl 2-diazo-4-phenylhept-3-enoate (**5c**) (*E/Z* = 10/1, 442 mg, 62%) as a yellow-red oil.

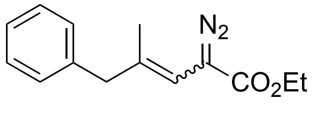
^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.24 (m, 5H), 5.87 (s, 1H), 3.82 (s, 3H), 2.47 (t, *J* = 8.0 Hz, 2H), 1.42-1.35 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.7, 128.3, 127.2, 126.1, 108.9, 52.3, 32.4, 21.9, 13.9; IR (neat): 2957, 2873, 2075, 1706, 1436, 1359, 1243, 1118, 1096, 759, 697; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{16}O_2N_2Na$ $(M+Na)^+$ 267.11040 found 267.11004.



Methyl 2-diazo-4-methyl-6-phenylhex-3-enoate (**5d**)

To a stirred solution of methyl 4-methyl-6-phenylhex-3-enoate (567 mg, 2.6 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.9 g, 7.8 mmol, 3.0 equiv.) in acetonitrile (20 mL) under Argon atmosphere, DBU (2.4 mL, 15.6 mmol, 6.0 equiv.) was added drop-wise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by flash chromatography (pentane/diethyl ether) to afford the corresponding methyl 2-diazo-4-methyl-6-phenylhex-3-enoate (**5d**) (*E/Z* = 1.4/1, 425 mg, 67%) as a yellow-red oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.14 (m, 9.2H, *E/Z* mixture), 5.45 (s, 0.72H, *Z* isomer), 5.42 (s, 1H, *E* isomer), 3.75 (s, 4.9H, *E/Z* mixture), 2.74 (t, *J* = 8.0 Hz, 2H, *E* isomer), 2.69 (t, *J* = 8.0 Hz, 1.4H, *Z* isomer), 2.42 (t, *J* = 8.8 Hz, 2H, *E* isomer), 2.30 (t, *J* = 8.8 Hz, 1.4H, *Z* isomer), 1.89 (s, 2.1H, *Z* isomer), 1.70 (s, 3H, *E* isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 141.4, 141.1, 138.4, 137.7, 128.3, 128.2, 128.1, 125.9, 125.8, 107.0, 106.7, 51.9, 41.8, 35.1, 34.5, 33.7, 23.9, 17.5; IR (neat): 3027, 2950, 2073, 1703, 1436, 1287, 1194; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{17}O_2N_2$ $(M+H)^+$ 245.12845 found 245.12845.

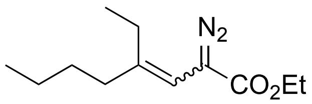


Ethyl 2-diazo-4-methyl-5-phenylpent-3-enoate (**5e**)

To a solution of ethyl diazoacetate (1.2 equiv., 3.1 mmol, 15% in toluene, 2.36 g) in anhydrous acetonitrile (10 mL), at room temperature, under Argon atmosphere, was added successively a solution of DBU (3.0 equiv., 7.74 mmol, 1.2 mL) in anhydrous acetonitrile (1.0 mL) and 2-methyl-3-phenylpropanal (2.58 mmol, 383 mg, 1.0 equiv.) in anhydrous acetonitrile (2.0 mL). The resulting mixture was stirring overnight. The reaction was quenched with saturated sodium bicarbonate and then extracted with diethyl ether. The solvent was removed by evaporation under reduced pressure and the crude product was purified by flash chromatography to give ethyl 2-diazo-3-hydroxy-4-methyl-5-phenylpentanoate (543 mg, 2.1 mmol, 81%).

To a solution of ethyl 2-diazo-3-hydroxy-4-methyl-5-phenylpentanoate (543 mg, 2.1 mmol) and Et_3N (10.5 mmol, 1.5 mL, 5.0 equiv.) in 15 mL dichloromethane at 0 ^oC, was slowly added a solution of $POCl_3$ (966 mg, 6.3 mmol, 3.0 equiv.) in 5 mL dichloromethane over 30 minutes. The resulting solution was warmed to room temperature and stirred overnight. The solution was quenched by saturated sodium bicarbonate and extracted with diethyl ether. The crude product was purified by flash chromatography (pentane/ether) to give the ethyl 2-diazo-4-methyl-5-phenylpent-3-enoate (**5e**) (*E/Z* = 10/1, 313 mg, 61%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.12 (m, 5.8H, *E/Z* mixture), 5.64 (s, 0.15H, *Z* isomer), 5.56 (s, 1H, *E* isomer), 4.27 (q, *J* = 8.0 Hz, 2H, *E* isomer), 3.44 (s, 2H, *E* isomer), 3.40 (s, 0.3 H, *Z* isomer), 1.78 (s, 0.5H, *Z* isomer), 1.61 (s, 3H, *E* isomer), 1.29 (t, *J* = 8.0 Hz, 3H, *E* isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 138.9, 136.7, 128.8, 128.4, 128.3, 126.3, 108.2, 108.1, 60.9, 46.3, 38.7, 23.9, 16.9, 14.4; IR (neat): 3027, 2979, 2072, 1694, 1601, 1494, 1453, 1368, 1275, 1182, 1101, 1027, 850, 729, 698; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{17}O_2N_2$ $(M+H)^+$ 245.12845 found 245.12830.

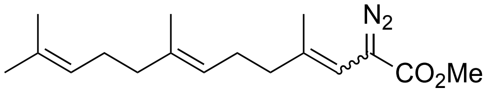


Ethyl 2-diazo-4-ethyloct-3-enoate (**5f**)

To a solution of ethyl diazoacetate (1.2 equiv., 6.0 mmol, 15% in toluene, 4.6 g) in anhydrous acetonitrile (10 mL), at room temperature, under Argon atmosphere, was added successively a solution of DBU (3.0 equiv., 15 mmol, 2.23 mL) in anhydrous acetonitrile (1.0 mL) and 2-ethylhexanal (5.0 mmol, 641 mg, 1.0 equiv.) in anhydrous acetonitrile (2.0 mL). The resulting mixture was stirring overnight. The reaction was quenched with saturated sodium bicarbonate and then extracted with diethyl ether. The solvent was removed by evaporation under reduced pressure and the crude product was purified by flash chromatography to give ethyl 2-diazo-4-ethyl-3-hydroxyoctanoate (847 mg, 3.5 mmol, 70%).

To a solution of ethyl 2-diazo-4-ethyl-3-hydroxyoctanoate (847 mg, 3.5 mmol) and Et_3N (17.5 mmol, 2.44 mL, 5 equiv.) in dichloromethane (15 mL) at 0 ^oC, was slowly added a solution of $POCl_3$ (1.6 g, 10.5 mmol, 3.0 equiv.) in dichloromethane (5 mL) over 30 minutes. The resulting solution was warmed to room temperature and stirred overnight. The solution was quenched by saturated sodium bicarbonate and extracted with diethyl ether. The crude product was purified by flash chromatography (pentane/ether) to give the ethyl 2-diazo-4-ethyloct-3-enoate (**5f**) as a yellow-red oil (*E/Z* = 10/1, 533 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.37 (s, 1H), 4.26 (q, *J* = 8.0 Hz, 2H), 2.18-2.11 (m, 2H), 2.08-2.01 (m, 2H), 1.45-1.27 (m, 7H), 1.08-0.97 (m, 3H), 0.91 (t, *J* = 8.0 Hz, 3H); ^{13}C

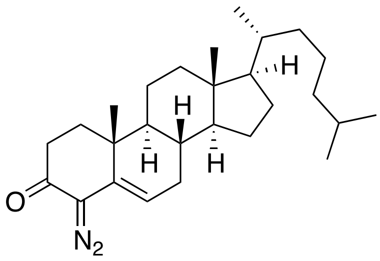
NMR (100 MHz, $CDCl_3$) δ166.7, 143.9, 143.8, 105.2, 104.6, 60.7, 36.6, 30.8, 30.2, 30.1, 23.9, 22.7, 22.2, 14.2, 13.7, 13.6, 12.4, 12.3; IR (neat): 2962, 2932, 2874, 2072, 1702, 1464, 1369, 1275, 1178, 1117, 1090, 736; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{20}O_2N_2Na$ $(M+Na)^+$ 247.14170 found 247.14138



Methyl 2-diazo-4,8,12-trimethyltrideca-3,7,11-trienoate (**5g**)

To a stirred solution of methyl 4,8,12-trimethyltrideca-3,7,11-trienoate (164.2 mg, 1.0 mmol, 1.0 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.22 g, 5.0 mmol, 5.0 equiv.) in dry acetonitrile (10 mL) under Argon atmosphere, DBU (1.5 mL, 10 mmol, 10.0 equiv.) was added dropwise at 0 °C. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with pentane, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed (pentane/diethyl ether) to afford the corresponding methyl 2-diazo-4,8,12-trimethyltrideca-3,7,11-trienoate (**5g**) (151 mg, 52%) as a red oil.

^1H NMR (400 MHz, $CDCl_3$): δ 5.42 (s, 1H), 5.11-5.07 (m, 2H), 3.78 (s, 3H), 2.16-1.85 (m, 8H), 1.69-1.59 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 154.8, 139.3, 139.2, 138.6, 138.5, 136.1, 135.9, 135.8, 135.7, 135.4, 131.6, 131.3, 124.2, 124.1, 123.9, 123.8, 123.3, 123.1, 119.2, 106.6, 106.5, 106.2, 52.0, 51.3, 40.3, 40.0, 39.6, 35.9, 33.2, 32.9, 31.9, 29.7, 26.6, 26.5, 26.4, 25.9, 25.7, 25.6, 25.4, 23.9, 23.3, 19.3, 17.6, 17.5, 16.0; IR (neat): 2923, 2855, 2073, 1708, 1436, 1285, 1194, 1108; HRMS (FTMS+p-NSI) calcd for $C_{17}H_{27}O_2N_2$ $(M+H)^+$ 291.20670 found 291.20671.

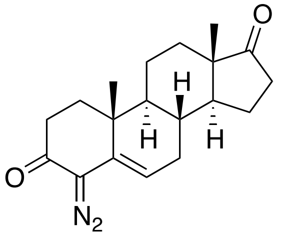


*(8S,9S,10R,13R,14S,17R)-4-diazo-10,13-dimethyl-17-((R)-6-methylheptan-2-yl) 4,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (**7**)*

To a stirred solution of cholesterol (1.94 g, 5.0 mmol, 1.0 equiv.) in dichloromethane (80 mL) at room temperature, a few drops a saturated sodium bicarbonate was added, followed by addition of Dess-Martin oxidant (5.3g, 12.5 mmol, 2.5 equiv.) in several portions in 20 minutes. Then, the reaction was stirred at room temperature for 2 hours, and was quenched by a solution of sodium bicarbonate. The crude mixture was extracted with ether, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed (pentane/diethyl ether) to afford the ketone product (1.3g, 3.4 mmol, 68% yield).

To a solution of the ketone product (1.3 g, 3.4 mmol, 1.0 equiv.) in dry dichromethane (80 mL) at 0 °C under Argon atmosphere, was added *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (8.3 g, 34 mmol, 10.0 equiv.) was added in one pot, followed DBU (10 mL, 68 mmol, 20 equiv.) was added dropwise at 0 °C under Argon atmosphere. The reaction mixture was then stirring overnight. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with ether, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed (pentane/diethyl ether) to afford the corresponding **7** (348.5 mg, 25%) as a red-orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24-5.22 (m, 1H), 2.60-2.50 (m, 2H), 2.27-2.19 (dt, *J* = 5.2, 18.4 Hz, 1H), 1.88-1.00 (m, 25H), 0.91 (d, *J* = 6.0 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 1H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 128.4, 116.5, 69.9, 59.6, 56.4, 55.9, 47.9, 42.2, 39.4, 39.3, 36.8, 36.0, 35.7, 33.9, 31.7, 31.3, 28.1, 27.9, 24.1, 23.7, 22.8, 22.5, 21.2, 20.7, 18.6, 11.8; IR (neat): 2947, 2867, 2062, 1602, 1346, 1286; HRMS (FTMS+p-NSI) calcd for $C_{27}H_{42}ON_2Na$ $(M+Na)^+$ 433.31894 found 433.31859.



(8R,9S,10R,13S,14S)-4-diazo-10,13-dimethyl-7,8,9,10,11,12,13,14,15,16-decahydro-1H-cyclopenta[a]phenanthrene-3,17(2H,4H)-dione (**9**)

To a stirred solution of (+)-dehydsroisoandrosterone (2.88 g, 10.0 mmol, 1.0 equiv.) in dichloromethane (100 mL) at room temperature, a few drops a saturated sodium bicarbonate was added, followed by addition of Dess-Martin oxidant (10.6 g, 25 mmol, 2.5 equiv.) in several portions in 30 minutes. Then, the reaction was stirred at room temperature for 1.5 hours, and was quenched by a solution of sodium bicarbonate. The crude mixture was extracted with ether, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed (pentane/diethyl ether) to afford the ketone product (2.22 g, 7.8 mmol, 78% yield).

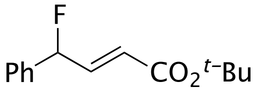
To a solution of the ketone product (2.22 g, 7.8 mmol, 1.0 equiv.) in dry acetonitrile (100 mL) 0 °C under Argon atmosphere, was added 3-(azidosulfonyl)benzoic acid (5.3 g, 23.4 mmol, 3.0 equiv.) was added in one pot, followed DBU (5.8 mL, 39 mmol, 5.0 equiv.)

was added dropwise at 0 °C under Argon atmosphere. The reaction mixture was then stirring over 2 hours at 0 °C. Then, saturated aqueous ammonium chloride was added. The crude mixture was extracted with ether, washed by brine, dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and chromatographed (pentane/diethyl ether) to afford the corresponding **9** (1.5 g, 62%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.04-5.02 (m, 1H), 2.33-2.15 (m, 4H), 1.97-1.56 (m, 7H), 147-0.99 (m, 6H), 0.94 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.4, 192.5, 129.8, 114.2, 72.6, 51.6, 48.5, 47.6, 35.9, 35.6, 33.5, 32.4, 31.4, 31.2, 30.0, 21.9, 20.6, 19.5, 13.8; IR (neat): 2945, 2867, 2078, 1739, 1633, 1339, 1264, 1229, 1142; HRMS (FTMS+p-APCI) calcd for $C_{19}H_{25}O_2N_2$ $(M+H)^+$ 313.19105 found 313.19071.

(3) General Procedure for Silver Catalyzed Fluorination of Vinylcarbenoids

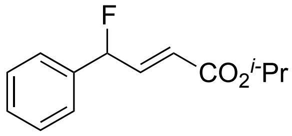
An oven-dried 35 mL heavy wall cylindrical and round bottom vessels containing a Teflon-coated oval stir bar is fitted with a rubber septum and allowed to cool to room temperature under vacuum. At room temperature (25 °C), silver acetate (6.6 mg, 10 mol%) is added and the flask, wrapped with aluminum foil to avoid light, is connected to a vacuum line *via* a needle inserted through the septum. The flask is evacuated then back-filled with Argon. This process is repeated three times. Et_3N-3HF in dry DCM (2.0 mL) is introduced *via* syringe under a positive Argon pressure. Then, diazo compound (0.4 mmol) is added drop-wise *via* syringe under refluxing over 1.0 hour under Argon atmosphere, and the syringe was rinsed with dry DCM (0.5-1.0 mL) and transferred to the reaction. The resulting solution was refluxed another one hour. The oil bath is removed and the suspension is cooled to room temperature and is quenched by saturated sodium bicarbonate and extracted with diethyl ether (50 mLx4). The combined organic solvent was removed by evaporation under reduced pressure and the crude products were purified (pentane/diethyl ether) by flash chromatography.



(*E*)-tert-butyl 4-fluoro-4-phenylbut-2-enoate (**2**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-tert-butyl 2-diazo-4-phenylbut-3-enoate (0.4 mmol, 97.6 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^1H NMR and purified by flash column chromatography to afford product **2** as a colorless oil (85.1 mg, 90% yield).

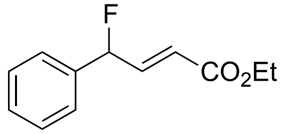
^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.35 (m, 5H), 6.96 (ddd, *J* = 4.8, 16.0, 19.0 Hz, 1H), 6.11-6.10 (m, 0.5H), 6.08-6.06 (m, 1H), 5.95-5.93 (m, 0.5H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 142.8 (d, ^2J = 22.3 Hz), 137.5 (d, ^2J = 20.1 Hz), 129.1, 128.8, 126.6 (d, ^3J = 5.2 Hz), 123.4 (^3J = 9.7 Hz), 91.9 (d, ^1J = 173.4 Hz), 80.9, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.3 (q, *J* = 22.3, 47.8 Hz); IR (neat): 2979, 1714, 1660, 1368, 1309, 1254, 1151, 978; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{17}O_2FNa$ $(M+Na)^+$ 259.11048 found 259.11055.



(*E*)-isopropyl 4-fluoro-4-phenylbut-2-enoate (**4a**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-isopropyl 2-diazo-4-phenylbut-3-enoate (0.4 mmol, 92.0 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^1H NMR and purified by flash column chromatography to afford product **4a** as a colorless oil (81.6 mg, 92% yield).

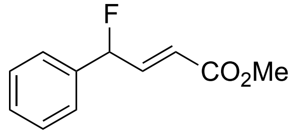
^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 5H), 7.04 (ddd, *J* = 4.4, 15.6, 18.8 Hz, 1H), 6.16 (dt, *J* = 1.6, 15.6 Hz, 1H), 6.03 (dq, *J* = 1.6, 4.4, 47.2 Hz, 1H), 5.12-5.06 (m, 1H), 1.28 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 143.2 (d, ^2J = 22.3 Hz), 136.8 (d, ^2J = 20.1 Hz), 129.2, 128.8, 126.6 (d, ^3J = 5.2 Hz), 122.0 (d, ^3J = 10.4 Hz), 91.8 (d, ^1J = 174.1 Hz), 68.2, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.7 (q, *J* = 47.8, 19.2 Hz); IR (neat): 2927, 2850, 1726, 1665, 1450, 1436, 1310, 1272, 1169, 1040, 981; HRMS (FTMS+p-NSI) calcd for $C_{13}H_{15}O_2FNa$ $(M+Na)^+$ 245.09483 found 245.09478.



(*E*)-ethyl 4-fluoro-4-phenylbut-2-enoate (**4b**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-ethyl 2-diazo-4-phenylbut-3-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^1H NMR and purified by flash column chromatography to afford product **4b** as a colorless oil (76.3 mg, 92% yield).

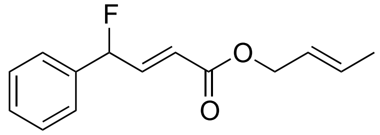
^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.35 (m, 5H), 7.06 (ddd, *J* = 4.4, 16.0, 20.0 Hz, 1H), 6.19 (dt, *J* = 1.6, 15.6 Hz, 1H), 6.03 (dq, *J* = 2.0, 4.8, 47.2 Hz, 1H), 4.25-4.20 (m, 2H), 1.31 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 144.0 (d, ^2J = 21.6 Hz), 136.7 (d, ^2J = 20.1 Hz), 129.2, 128.8, 126.6 (d, ^3J = 5.9 Hz), 121.5 (d, ^3J = 10.4 Hz), 91.8 (d, ^1J = 174.2 Hz), 60.7, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.7 (q, J = 47.8, 19.2 Hz); IR (neat): 2984, 1721, 1663, 1304, 1268, 1177, 979; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{13}O_2FNa$ $(M+Na)^+$ 231.07918 found 231.07912.



(*E*)-methyl 4-fluoro-4-phenylbut-2-enoate (**4c**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using ((*E*)-methyl 2-diazo-4-phenylbut-3-enoate (0.4 mmol, 80.8 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4c** as a colorless oil (73.2 mg, 94% yield).

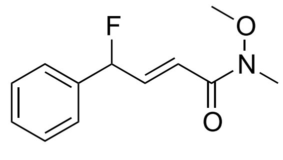
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.35 (m, 5H), 7.06 (ddd, J = 4.4, 16.0, 20.0 Hz, 1H), 6.20 (dt, J = 1.6, 15.6 Hz, 1H), 6.03 (dq, J = 2.0, 4.8, 47.2 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 144.3 (d, ^2J = 21.6 Hz), 136.6 (d, ^2J = 20.1 Hz), 129.2, 128.8, 126.6 (d, ^3J = 5.2 Hz), 120.9 (d, ^3J = 10.5 Hz), 91.7 (d, ^1J = 174.1 Hz), 51.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.9 (q, J = 47.4, 18.8 Hz); IR (neat): 2953, 1727, 1667, 1436, 1308, 1278, 979; HRMS (FTMS+p-NSI) calcd for $C_{11}H_{11}O_2FNa$ $(M+Na)^+$ 217.06353 found 217.06347.



(*E*)-(*E*)-but-2-en-1-yl 4-fluoro-4-phenylbut-2-enoate (**4d**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-(*E*)-but-2-en-1-yl 2-diazo-4-phenylbut-3-enoate (0.4 mmol, 96.8 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4d** as a colorless oil (79.6 mg, 85% yield).

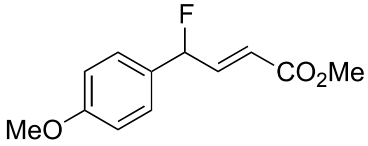
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.31 (m, 5H), 7.06 (ddd, J = 4.0, 15.6, 19.2 Hz, 1H), 6.19 (d, J = 15.6 Hz, 1H), 6.08 (dd, J = 4.4, 47.6 Hz, 1H), 5.86-5.79 (m, 1H), 5.66-5.89 (m, 1H), 4.60 (d, J = 6.8 Hz, 2H), 1.74 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 144.5 (d, ^2J = 22.3 Hz), 136.9 (d, ^2J = 20.0 Hz), 132.1, 129.5, 129.1, 126.9 (d, ^3J = 5.2 Hz), 125.0, 121.6 (d, ^3J = 9.7 Hz), 91.1 (d, ^1J = 174.1 Hz), 65.8, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.8 (q, J = 47.4, 18.8 Hz); IR (neat): 2919, 1722, 1662, 1455, 1305, 1264, 1168, 968, 697; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{15}O_2FNa$ $(M+Na)^+$ 257.09483 found 257.09474.



(*E*)-4-fluoro-N-methoxy-N-methyl-4-phenylbut-2-enamide (**4e**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-2-diazo-N-methoxy-N-methyl-4-phenylbut-3-enamide (0.4 mmol, 92.4 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4e** as a colorless oil (53.5 mg, 60% yield).

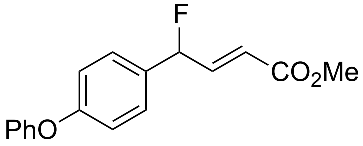
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.31 (m, 5H), 7.08 (ddd, *J* = 4.4, 15.6, 20.0 Hz, 1H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.08 (dq, *J* = 1.6, 4.4, 47.6 Hz, 1H), 3.74 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 142.7 (d, ^2J = 20.8 Hz), 136.9 (d, ^2J = 19.3 Hz), 129.1, 128.7, 126.7 (d, ^3J = 6.0 Hz), 118.6 (d, ^3J = 9.7 Hz), 92.3 (d, ^1J = 174.1 Hz), 61.9, 32.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.7 (q, *J* = 47.4, 20.7 Hz); IR (neat): 2937, 1667, 1637, 1456, 1418, 1384, 1179, 1119, 1003, 701; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{15}O_2FN$ $(M+H)^+$ 224.10813 found 224.10800.



(*E*)-methyl 4-fluoro-4-(4-methoxyphenyl)but-2-enoate (**4f**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-(4-methoxyphenyl)but-3-enoate (0.4 mmol, 92.8 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). Dry product is unstable over 2 hours under vacuum line condition and also decomposed upon on silica gel column (yield based on NMR using dibromomethane as internal standard, 96% yield). The crude residue were analyzed by ^{1}H NMR and ^{13}C NMR. The spectra are attached.

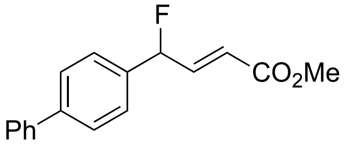
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.06 (ddd, *J* = 4.0, 16.0, 20.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.19 (dt, *J* = 1.6, 16.0 Hz, 1H), 5.98 (dq, *J* = 1.6, 4.4, 47.6 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.6, 160.7, 144.8 (d, ^2J = 23.1 Hz), 129.3, 128.9, 120.9 (d, ^3J = 9.7 Hz), 114.3, 91.8 (d, ^1J = 173.4 Hz), 55.6, 52.1; ^{19}F NMR (376 MHz, CDCl$_3$) δ -168.2 (q, *J* = 47.4, 18.8 Hz); IR (neat): 2953, 2840, 1726, 1662, 1611, 1514, 1437, 1306, 1251, 1173, 1033, 834; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{14}O_3F$ $(M+H)^+$ 225.09215 found 225.09108.



(*E*)-methyl 4-fluoro-4-(4-phenoxyphenyl)but-2-enoate (**4g**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-(4-phenoxyphenyl)but-3-enoate (0.4 mmol, 117.6 mg, 1.0 equiv.) and Et$_3$N-3HF (322 mg, 5.0 equiv.). Product is unstable on silica gel column (yield was based on NMR using dibromomethane as internal standard, 95% yield).

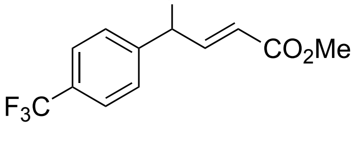
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39-7.31 (m, 4H), 7.17-7.11 (m, 1H), 7.10-7.02 (m, 5H), 6.21 (dt, *J* = 1.6, 15.6 Hz, 1H), 6.01 (dq, *J* = 1.6, 4.4, 47.6 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.3, 158.4, 156.5, 144.3 (d, ^2J = 22.3 Hz), 130.1 (d, ^2J = 20.1 Hz), 129.9, 128.6 (d, ^3J = 5.2 Hz), 123.8, 121.0 (d, ^3J = 9.6 Hz), 119.3, 118.7, 92.4 (d, ^1J = 173.4 Hz), 51.9; ^{19}F NMR (376 MHz, CDCl$_3$) δ -170.3 (q, *J* = 47.8, 19.2 Hz); IR (neat): 2951, 1727, 1664, 1589, 1507, 1489, 1239, 1168, 1074, 980, 870; HRMS (FTMS+p-NSI) calcd for $C_{17}H_{15}O_3FNa$ $(M+Na)^+$ 309.08974 found 309.08970.



(*E*)-methyl 4-([1,1'-biphenyl]-4-yl)-4-fluorobut-2-enoate (**4h**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 4-([1,1'-biphenyl]-4-yl)-2-diazobut-3-enoate (0.4 mmol, 111.24 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4h** as a white solid (93.6 mg, 87% yield).

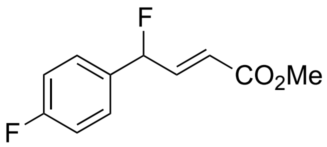
Mp: 60-62 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.59 (m, 4H), 7.50-7.37 (m, 5H), 7.12 (ddd, *J* = 4.8, 15.8, 19.6 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 6.01 (dd, *J* = 3.6, 46.8 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 144.3 (d, ^2J = 22.3 Hz), 142.3, 140.3, 135.5 (d, ^2J = 20.1 Hz), 128.8, 127.7, 127.6, 127.1 (d, ^3J = 3.0 Hz), 121.0 (d, ^3J = 10.4 Hz), 91.6 (d, ^1J = 174.1 Hz), 51.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.3 (q, *J* = 45.9, 17.3 Hz); IR (neat): 3031, 2951, 1727, 1664, 1487, 1436, 1307, 1273, 1171, 1077, 979, 766, 698; HRMS (FTMS+p-NSI) calcd for $C_{17}H_{15}O_2FNa$ $(M+Na)^+$ 293.09483 found 293.09475.



(*E*)-methyl 4-fluoro-4-(4-(trifluoromethyl)phenyl)but-2-enoate (**4i**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (0.4 mmol, 108.0 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^1H NMR and purified by flash column chromatography to afford product **4i** as a white solid (66.0 mg, 63% yield).

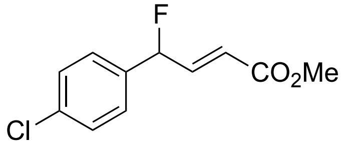
Mp: 42-44 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.03 (ddd, *J* = 4.0, 16.0, 19.6 Hz, 1H), 6.20 (dt, *J* = 1.6, 15.8 Hz, 1H), 6.09 (dd, *J* = 3.6, 46.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 143.2 (^2J = 21.6 Hz), 140.5 (^2J = 20.8 Hz), 131.3 (q, *J* = 32.8 Hz), 126.6 (d, ^3J = 5.9 Hz), 125.8 (d, ^3J = 3.7 Hz), 121.8 (d, ^3J = 10.4 Hz), 90.9 (d, ^1J = 175.6 Hz), 51.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2 (s), -177.7 (q, *J* = 45.9, 19.2 Hz); IR (neat): 2956, 1727, 1665, 1621, 1438, 1417, 1324, 1167, 1126, 1067, 979, 844; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{11}O_2F_4$ $(M+H)^+$ 263.06897 found 263.06900.



(*E*)-methyl 4-fluoro-4-(4-fluorophenyl)but-2-enoate (**4j**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-(4-fluorophenyl)but-3-enoate (0.4 mmol, 88.0 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^1H NMR and purified by flash column chromatography to afford product **4j** as a light yellow oil (73.6 mg, 87% yield).

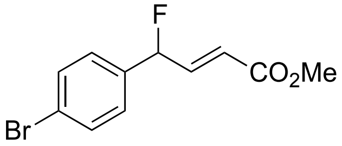
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36-7.32 (m, 2H), 7.12-6.99 (m, 3H), 6.19 (dt, *J* = 1.6, 15.6 Hz, 1H), 6.01 (dq, *J* = 4.4, 46.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.2, 163.1 (d, ^1J = 247.0 Hz), 143.9 (d, ^2J = 21.6 Hz), 132.4 (d, ^2J = 23.8 Hz), 128.82, 128.77, 128.74, 128.69, 121.2 (d, ^3J = 10.4 Hz), 115.8 (d, ^2J = 21.5 Hz), 91.1 (d, ^1J = 174.1 Hz), 51.9; ^{19}F NMR (376 MHz, CDCl$_3$) δ -112.2 (m), -171.5 (q, *J* = 47.3, 18.8 Hz); IR (neat): 2956, 1728, 1662, 1513, 1437, 1279, 1227, 1172, 839; HRMS (FTMS+p-NSI) calcd for $C_{11}H_{11}O_2F_2$ (M+H)$^+$ 213.07216 found 213.07205.



(*E*)-methyl 4-(4-chlorophenyl)-4-fluorobut-2-enoate (**4k**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 4-(4-chlorophenyl)-2-diazobut-3-enoate (0.4 mmol, 94.4 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4k** as a light yellow oil (77.6 mg, 85% yield).

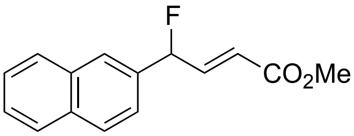
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (d, *J* = 8.0, 2H), 7.26 (d, *J* = 8.0, 2H), 6.99 (ddd, *J* = 4.4, 16.0, 20.0 Hz, 1H), 6.15 (dt, *J* = 1.6, 15.6 Hz, 1H), 5.97 (dd, *J* = 4.4, 46.8 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.0, 143.6 (d, ^2J = 21.5 Hz), 135.1 (d, ^2J = 19.3 Hz), 129.1, 128.0, 127.9, 121.3 (d, ^3J = 9.6 Hz), 91.0 (d, ^1J = 174.9 Hz), 51.9; ^{19}F NMR (376 MHz, CDCl$_3$) δ -174.0 (q, *J* = 47.8, 19.2 Hz); IR (neat): 2952, 1723, 1663, 1597, 1493, 1436, 1274, 1197, 1079, 1016, 978, 830; HRMS (FTMS+p-NSI) calcd for $C_{11}H_{10}O_2ClFNa$ (M+Na)$^+$ 251.02456 found 251.02459.



(*E*)-methyl 4-(4-bromophenyl)-4-fluorobut-2-enoate (**4l**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 4-(4-bromophenyl)-2-diazobut-3-enoate (0.4 mmol, 111.9 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column to afford product **4l** as a colorless oil (96.5 mg, 89% yield).

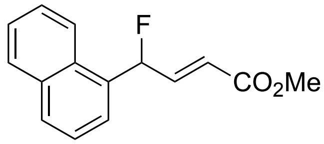
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0, 2H), 7.24 (d, *J* = 8.0, 2H), 7.01 (ddd, *J* = 4.4, 16.0, 20.0 Hz, 1H), 6.18 (dt, *J* = 1.6, 15.6 Hz, 1H), 5.98 (dq, *J* = 2.0, 4.4, 47.2 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 143.6 (d, ^2J = 22.3 Hz), 135.6 (d, ^2J = 20.1 Hz), 132.0, 128.2 (d, ^3J = 5.9 Hz), 121.4 (d, ^3J = 9.7 Hz), 123.4, 91.0 (d, ^1J = 174.9 Hz), 51.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -174.5 (q, *J* = 47.8, 19.2 Hz); IR (neat): 2951, 1727, 1663, 1593, 1449, 1436, 1310, 1277, 1171, 1071, 1012, 979, 829; HRMS (FTMS+p-NSI) calcd for $C_{11}H_{10}O_2BrFNa$ $(M+Na)^+$ 294.97404 found 294.97400.



(*E*)-methyl 4-fluoro-4-(naphthalen-2-yl)but-2-enoate (**4m**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-(naphthalen-2-yl)but-3-enoate (0.4 mmol, 100.8 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4m** as a colorless oil (78.0 mg, 80% yield).

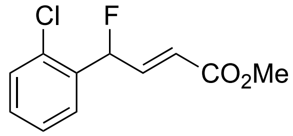
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.83 (m, 4H), 7.55-7.52 (m, 2H), 7.47-7.44 (m, 1H), 7.16 (ddd, *J* = 3.6, 16.0, 18.8 Hz, 1H), 6.28-6.13 (m, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 144.3 (d, ^2J = 21.6 Hz), 133.9 (d, ^2J = 19.3 Hz), 133.5, 133.0, 128.9, 128.2, 127.8, 126.8, 126.6, 126.2 (d, ^3J = 7.4 Hz), 123.8 (d, ^3J = 4.5 Hz), 121.2 (d, ^3J = 10.4 Hz), 91.9 (d, ^1J = 174.9 Hz), 51.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.5 (q, *J* = 47.8, 19.2 Hz); IR (neat): 3058, 2951, 1725, 1663, 1509, 1436, 1307, 1273, 1171, 1076, 1018, 980, 820; HRMS (FTMS+p-NSI) calcd for $C_{15}H_{13}O_2$ $(M-HF+H)^+$ 225.09155 found 225.09085.



(*E*)-methyl 4-fluoro-4-(naphthalen-1-yl)but-2-enoate (**4n**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-(naphthalen-1-yl)but-3-enoate (0.4 mmol, 100.8 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4n** as a colorless oil (81.2 mg, 83% yield).

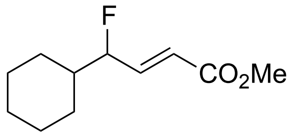
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 2H), 7.61-7.48 (m, 4H), 7.28 (ddd, *J* = 4.4, 16.0, 18.8 Hz, 1H), 6.73 (dq, *J* = 2.0, 3.6, 46.4 Hz, 1H), 6.28 (dt, *J* = 1.6, 15.6 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 144.3 (d, ^2J = 21.5 Hz), 133.8, 132.3 (d, ^2J = 17.9 Hz), 130.3, 130.0, 128.9, 126.8, 126.1, 125.3, 125.2, 123.2, 121.6 (d, ^3J = 9.7 Hz), 89.9 (d, ^1J = 174.1 Hz), 51.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -175.9 (q, *J* = 45.9, 18.8 Hz); IR (neat): 2951, 1725, 1663, 1511, 1436, 1309, 1274, 1173, 978, 781; HRMS (FTMS+p-NSI) calcd for $C_{15}H_{14}O_2F$ $(M+H)^+$ 245.09723 found 245.09728.



(*E*)-methyl 4-(2-chlorophenyl)-4-fluorobut-2-enoate (**4o**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 4-(2-chlorophenyl)-2-diazobut-3-enoate (0.4 mmol, 94.4 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4o** as a colorless oil (67.4 mg, 74% yield).

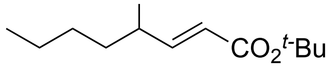
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.29 (m, 4H), 7.06 (ddd, *J* = 4.0, 15.6, 19.2 Hz, 1H), 6.44 (dq, *J* = 1.6, 4.0, 46.0 Hz, 1H), 6.19 (dt, *J* = 1.6, 15.6 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 142.8 (d, ^2J = 21.6 Hz), 134.6 (d, ^2J = 21.6 Hz), 131.8 (d, ^3J = 5.2 Hz), 130.2, 129.7, 127.4, 127.3, 121.3 (d, ^3J = 10.5 Hz), 88.3 (d, ^1J = 174.8 Hz), 51.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -182.6 (q, *J* = 45.9, 19.2 Hz); IR (neat): 2952, 1727, 1663, 1478, 1437, 1308, 1276, 1196, 1172, 979, 754; HRMS (FTMS+p-NSI) calcd for $C_{11}H_{11}O_2FCl$ $(M+H)^+$ 229.04261 found 229.04249.



(*E*)-methyl 4-cyclohexyl-4-fluorobut-2-enoate (**4p**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 4-cyclohexyl-2-diazobut-3-enoate (0.4 mmol, 94.4 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^1H NMR and purified by flash column chromatography to afford product **4p** as a colorless oil (68.0 mg, 85% yield).

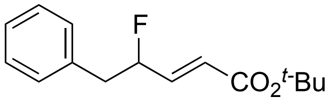
^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (ddd, *J* = 4.0, 15.6, 20.8 Hz, 1H), 6.06 (d, *J* = 15.6 Hz, 1H), 4.85 (dt, *J* = 4.0, 47.6 Hz, 1H), 3.76 (s, 3H), 1.78-1.63 (m, 6H), 1.27-1.05 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.4 (d, ^2J = 19.4 Hz), 121.1 (d, ^3J = 11.1 Hz), 94.9 (d, ^1J = 174.9 Hz), 51.7, 42.2 (d, ^2J = 20.1 Hz), 28.2 (d, ^3J = 3.7 Hz), 27.2 (d, ^3J = 5.2 Hz), 26.1, 25.8, 25.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.8 (m); IR (neat): 2927, 2850, 1726, 1665, 1450, 1436, 1310, 1272, 1169, 1040, 981; HRMS (FTMS+p-NSI) calcd for $C_{11}H_{18}O_2F$ $(M+H)^+$ 201.12853 found 201.12846.



(*E*)-tert-butyl 4-fluorooct-2-enoate (**4q**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-tert-butyl 2-diazoo-3-enoate (0.4 mmol, 89.6 mg, 1.0 equiv.) and Et$_3$N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4r** as a colorless oil (74.3 mg, 86% yield).

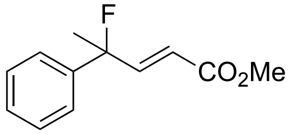
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.80 (ddd, J = 4.4, 15.6, 19.2 Hz, 1H), 5.97 (dm, J = 15.6 Hz, 1H), 5.14-4.98 (m, 1H), 1.78-1.66 (m, 2H), 1.51 (s, 9H), 1.47-1.33 (m, 4H), 0.92 (t, ^3J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.3, 143.9 (d, ^2J = 18.6 Hz), 122.8 (d, ^3J = 11.1 Hz), 91.4 (d, ^1J = 171.8 Hz), 80.7, 34.4 (d, ^2J = 20.8 Hz), 28.1, 26.6 (d, ^3J = 3.8 Hz), 22.4, 13.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ -183.8 (m); IR (neat): 2960, 2935, 2874, 1717, 1664, 1458, 1368, 1315, 1285, 1154, 980; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{22}O_2F$ (M+H)$^+$ 217.15983 found 217.15974.



(*E*)-tert-butyl 4-fluoro-5-phenylpent-2-enoate (**4r**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-tert-butyl 2-diazo-5-phenylpent-3-enoate (0.4 mmol, 103.2 mg, 1.0 equiv.) and Et$_3$N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **4r** as a colorless oil (81.1 mg, 81% yield).

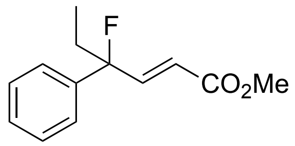
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34-7.14 (m, 5H), 6.82 (ddd, J = 4.4, 15.6, 20.0 Hz, 1H), 5.99 (dm, J = 15.6 Hz, 1H), 5.31-5.15 (m, 1H), 3.09-2.90 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.1, 142.9 (d, ^2J = 18.6 Hz), 135.7 (d, ^3J = 4.4 Hz), 129.4, 128.5, 126.9, 123.5 (d, ^3J = 10.4 Hz), 91.7 (d, ^1J = 175.6 Hz), 80.8, 41.4 (d, ^2J = 22.3 Hz), 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -182.0 (m); IR (neat): 2978, 1713, 1662, 1455, 1367, 1312, 1285, 1255, 1149, 1089, 977, 699; HRMS (FTMS+p-NSI) calcd for $C_{15}H_{20}O_2F$ $(M+H)^+$ 251.14418 found 251.14402.



(*E*)-methyl 4-fluoro-4-phenylpent-2-enoate (**6a**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-phenylpent-3-enoate (0.4 mmol, 86.4 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **6a** as a colorless oil (75.6 mg, 91% yield).

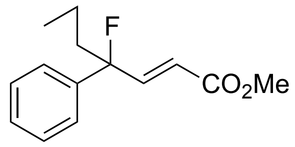
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 5H), 7.13 (dd, *J* = 15.6, 20.8 Hz, 1H), 6.13 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H), 1.84 (d, *J* = 20.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 149.1 (d, ^2J = 23.1 Hz), 141.3 (d, ^2J = 22.3 Hz), 128.6, 128.2, 124.5 (d, ^3J = 8.2 Hz), 118.8 (d, ^3J = 10.4 Hz), 95.1 (d, ^1J = 175.6 Hz), 51.8, 26.5 (d, ^2J = 24.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.4 (m); IR (neat): 2989, 2952, 1724, 1663, 1496, 1435, 1375, 1309, 1279, 1196, 1172, 763, 698; HRMS (FTMS+p-APCI) calcd for $C_{12}H_{14}O_2F$ $(M+H)^+$ 209.09723 found 209.09717.



<u>(*E*)-methyl 4-fluoro-4-phenylhex-2-enoate (**6b**)</u>

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-Methyl 2-diazo-4-phenylhex-3-enoate (0.4 mmol, 92.0 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **6b** as a colorless oil (72.8 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.31 (m, 5H), 7.12 (dd, *J* = 15.6, 21.6 Hz, 1H), 6.14 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 2.16-2.04 (m, 2H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.4 d, ^2J = 20.9 Hz), 140.6 (d, ^2J = 22.3 Hz), 128.5, 127.9, 124.5 (^3J = 8.9 Hz), 119.1 (d, ^3J = 10.5 Hz), 97.6 (d, ^1J = 180.8 Hz), 51.7, 32.7 (d, ^2J = 23.8 Hz), 7.41 (d, ^3J = 4.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -163.2 (q, *J* = 22.6, 45.5 Hz); IR (neat): 2977, 2949, 1728, 1661, 1436, 1311, 1274, 1195, 1172, 698; HRMS (FTMS+p-NSI) calcd for $C_{13}H_{15}O_2FNa$ $(M+Na)^+$ 245.09483 found 245.09485.

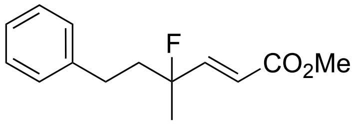


<u>(*E*)-methyl 4-fluoro-4-phenylhept-2-enoate (**6c**)</u>

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using (*E*)-methyl 2-diazo-4-phenylhept-3-enoate (0.4 mmol, 97.6 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H

NMR and purified by flash column chromatography to afford product **6c** as a colorless oil (72.8 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.31 (m, 5H), 7.12 (dd, *J* = 15.6, 21.6 Hz, 1H), 6.13 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 2.09-1.98 (m, 2H), 1.44-1.32 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.6 (^2J = 21.6 Hz), 141.1 (d, ^2J = 22.4 Hz), 128.5, 127.8, 124.4 (d, ^3J = 8.9 Hz), 118.9 (d, ^3J = 11.2 Hz), 97.5 (d, ^1J = 180.1 Hz), 51.7, 41.9 (d, ^2J = 23.0 Hz), 16.5 (d, ^3J = 10.1 Hz), 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -160.8 (q, *J* = 22.9, 45.5 Hz); IR (neat): 2961, 2875, 1724, 1661, 1495, 14351309, 1275, 1194, 1171, 979, 919, 852, 763, 698; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{17}O_2FNa$ $(M+Na)^+$ 259.11048 found 259.11030.

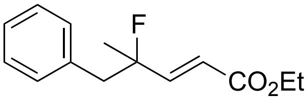


(*E*)-methyl 4-fluoro-4-methyl-6-phenylhex-2-enoate (**6d**)

Prepared according to the general procedure for sliver acetate-catalyzed fluorination of vinylcarbenoids using methyl 2-diazo-4-methyl-6-phenylhex-3-enoate (0.4 mmol, 97.6 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **6d** as a colorless oil (84.1 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.16 (m, 5H), 6.93 (dd, *J* = 15.6, 21.6 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 3.77 (s, 3H), 2.77-2.57 (m, 2H), 2.13-1.84 (m, 2H), 1.51 (d, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 149.1 (d, ^2J = 20.8 Hz), 141.2, 128.5, 128.2, 126.0, 119.4 (d, ^3J = 10.4 Hz), 95.2 (d, ^1J = 175.6 Hz), 51.8, 41.7 (d, ^2J = 22.3

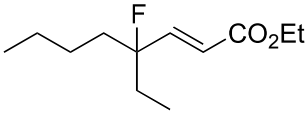
Hz), 29.7 (d, ^3J = 3.7 Hz), 25.5 (d, ^2J = 24.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -153.1 (m); IR (neat): 3027, 2951, 1726, 1664, 1497, 1435, 1313, 1274, 1198, 1165, 698; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{17}O_2FNa$ $(M+Na)^+$ 259.11048 found 259.11034.



(*E*)-ethyl 4-fluoro-4-methyl-5-phenylpent-2-enoate (**6e**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using ethyl 2-diazo-4-methyl-5-phenylpent-3-enoate (0.4 mmol, 97.6 mg, 1.0 equiv.) and Et_3N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **6e** as a colorless oil (75.5 mg, 80% yield).

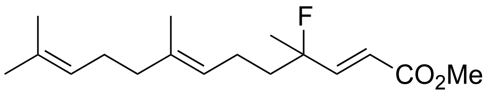
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.19 (m, 5H), 6.94 (dd, *J* = 15.6, 20.8 Hz, 1H), 5.99 (d, *J* = 15.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.09-2.93 (m, 2H), 1.42 (d, *J* = 21.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 148.8 (d, ^2J = 21.1 Hz), 134.9, 130.4, 128.9, 128.2, 126.9, 119.8 (d, ^3J = 10.4 Hz), 95.0 (d, ^1J = 177.1 Hz), 60.5, 46.2 (d, ^2J = 23.1 Hz), 24.5 (d, ^2J = 23.8 Hz), 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -149.3 (m); IR (neat): 2983, 2933, 1720, 1662, 1454, 1367, 1306, 1282, 1180, 1091, 1032, 982, 700; HRMS (FTMS+p-NSI) calcd for $C_{14}H_{18}O_2F$ $(M+H)^+$ 237.12853 found 237.12953.



(*E*)-ethyl 4-ethyl-4-fluorooct-2-enoate (**6f**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using ethyl 2-diazo-4-ethyloct-3-enoate (0.4 mmol, 89.6 mg, 1.0 equiv.) and Et$_3$N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **6f** as a colorless oil (76.0 mg, 88% yield).

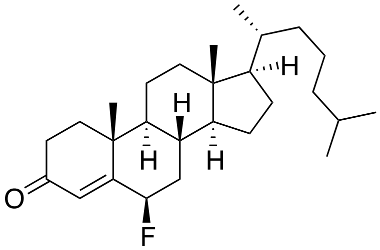
^{1}H NMR (400 MHz, CDCl$_3$): δ 6.80 (dd, J = 15.6, 20.8 Hz, 1H), 6.03 (d, J = 15.6 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.83-1.59 (m, 4H), 1.40-1.23 (m, 8H), 0.93-0.87 (m, 7H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.3, 148.4 (d, ^2J = 20.1 Hz), 120.4 (d, ^3J = 10.4 Hz), 97.9 (d, ^1J = 178.0 Hz), 60.5, 37.9 (d, ^2J = 23.1 Hz), 31.4 (d, ^2J = 23.8 Hz), 25.3 (d, ^3J = 4.5 Hz), 22.8, 14.0 (d, ^2J = 29.8 Hz), 7.50 (d, ^3J = 5.2 Hz); ^{19}F NMR (376 MHz, CDCl$_3$) δ -163.2 (m); IR (neat): 2959, 2941, 2874, 1722, 1662, 1465, 1367, 1305, 1268, 1179, 1038, 983; HRMS (FTMS+p-NSI) calcd for $C_{12}H_{21}O_2FNa$ (M+Na)$^+$ 239.14178 found 239.14178.



(2*E*)-methyl 4-fluoro-4,8,12-trimethyltrideca-2,7,11-trienoate (**6g**)

Prepared according to the general procedure for silver acetate-catalyzed fluorination of vinylcarbenoids using methyl 2-diazo-4,8,12-trimethyltrideca-3,7,11-trienoate (0.4 mmol, 116.0 mg, 1.0 equiv.) and Et$_3$N-3HF (322 mg, 5.0 equiv.). The crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **6g** as a colorless oil (95.9 mg, 85% yield).

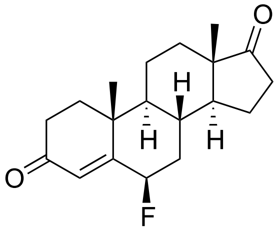
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-6.84 (ddm, *J* = 15.6, 20.8 Hz, 1H), 6.07-6.02 (dm, *J* = 15.6 Hz, 1H), 5.09-5.05 (m, 2H), 3.76 (s, 3H), 2.07-1.94 (m, 6H), 1.82-1.58 (m, 11H), 1.48-1.42 (dm, *J* = 21.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 149.5 (d, ^2J = 20.1 Hz), 136.0 (d, ^3J = 8.9 Hz), 131.6, 131.3, 124.2, 124.1, 123.9, 123.0, 119.0 (d, ^3J = 10.4 Hz), 95.2 (d, ^1J = 174.9 Hz), 51.7, 40.2, 40.0, 39.0, 39.6, 31.8, 26.6, 26.4, 25.7, 25.6, 25.4 (d, ^2J = 24.5 Hz), 23.3, 22.04, 21.99, 21.92, 21.87, 17.58 (d, ^3J = 10.4 Hz), 15.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.3 (m); IR (neat): 2969, 2915, 2874, 1729, 1664, 1435, 1376, 1312, 1272, 1197, 1165, 979, 907; HRMS (FTMS+p-NSI) calcd for $C_{17}H_{28}O_2F$ $(M+H)^+$ 283.20678 found 283.20668.



(6R,8S,9S,10R,13R,14S,17R)-6-fluoro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (**8**)

Prepared according to the general procedure using silver triflate-catalyzed fluorination of vinylcarbenoids using steroid diazo **7** (0.4 mmol, 116.0 mg, 1.0 equiv.) and Et_3N-3HF (644 mg, 10.0 equiv.). The reaction was refluxing under Argon for another 2 hours after diazo addition and the crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **8** as a white solid (90.1 mg, 56% yield).

Mp: 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (d, *J* = 4.8 Hz, 1H), 4.99 (dt, *J* = 2.8, 48.4 Hz, 1H), 2.60-2.50 (m, 1H), 2.42-2.37 (m, 1H), 2.24-2.17 (m, 1H), 2.09-2.04 (m, 1H), 1.94-1.82 (m, 2H), 1.77-1.69 (m, 1H), 1.62-1.47 (m, 4H), 1.43-0.99 (m, 17H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 6H), 0.733 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 162.1 (d, ^{2}J = 12.6 Hz), 128.2 (d, ^{3}J = 8.9 Hz), 93.5 (d, ^{1}J = 165.1 Hz), 56.0, 55.7, 53.2, 42.4, 39.4, 37.8, 37.4, 37.2, 36.8, 36.0, 35.7, 34.2, 29.9, 28.1, 27.9, 23.9, 23.8, 22.8, 22.5, 20.8, 18.6, 18.3, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -165.7 (m); IR (neat): 2935, 2868, 1686, 1467, 1380, 1331, 1267, 1191; HRMS (FTMS+p-APCI) calcd for $C_{27}H_{44}OF$ $(M+H)^+$ 403.33707 found 403.33640.

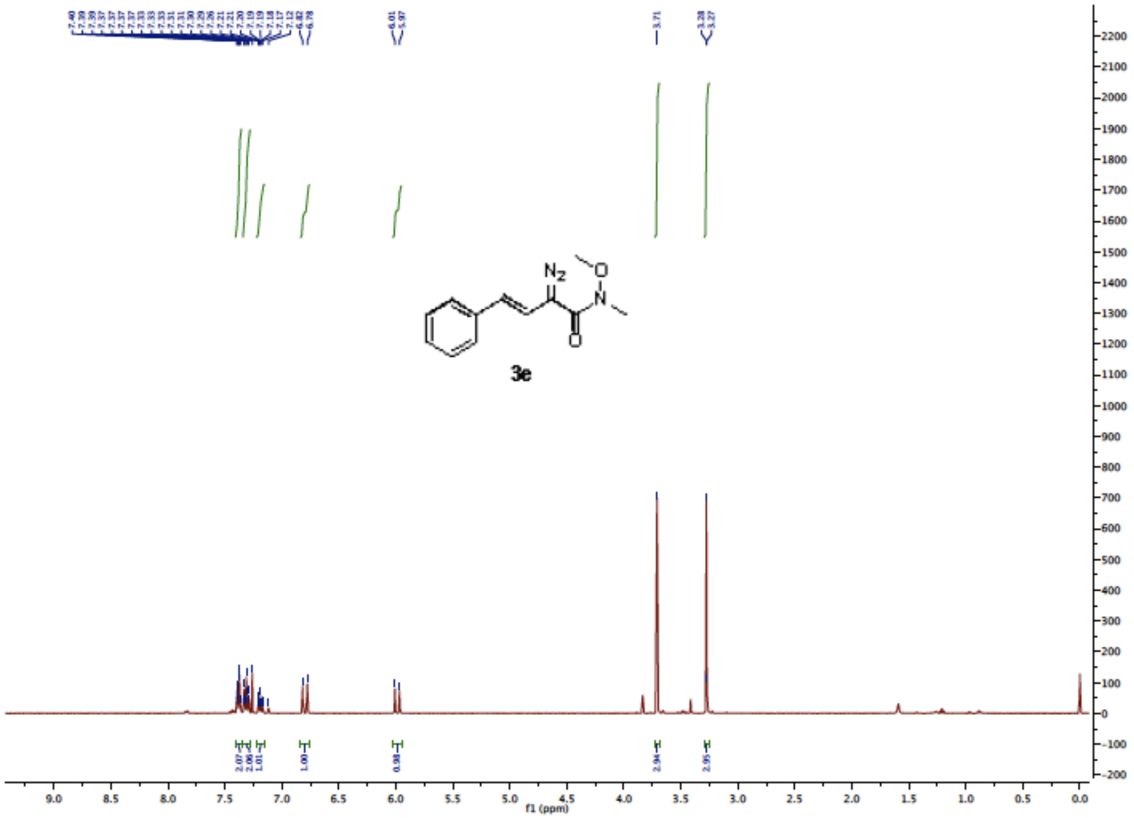


(6R,8R,9S,10R,13S,14S)-6-fluoro-10,13-dimethyl-7,8,9,10,11,12,13,14,15,16-decahydro-1H-cyclopenta[a]phenanthrene-3,17(2H,6H)-dione (**10**)

Prepared according to the general procedure using silver triflate-catalyzed fluorination of vinylcarbenoids using steroid diazo **9** (0.4 mmol, 124.8 mg, 1.0 equiv.) and Et_3N-3HF (644 mg, 10.0 equiv.). The reaction was refluxing under Argon for another 2 hours after diazo addition and the crude residue was analyzed by ^{1}H NMR and purified by flash column chromatography to afford product **8** as a white solid (72.8 mg, 60% yield).

Mp: 130-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (d, *J* = 4.8 Hz, 1H), 5.05 (dt, *J* = 2.8, 48.4 Hz, 1H), 2.62-2.31 (m, 5H), 2.18-1.63 (m, 10H), 1.34 (s, 3H), 1.11-0.97 (m, 2H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.1, 199.6, 161.1 (d, ^{2}J = 12.0 Hz), 128.6 (d, ^{3}J = 8.9 Hz), 93.0 (d, ^{1}J = 166.6 Hz), 53.2, 50.6, 47.6, 37.8, 36.8, 36.2, 35.9, 35.6, 34.1, 31.1, 29.6, 21.6, 20.1, 18.4, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -166.1 (m);

IR (neat): 2945, 1737, 1684, 1455, 1377, 1329, 1268, 1229, 1012; HRMS (FTMS+p-APCI) calcd for $C_{19}H_{26}O_2F$ $(M+H)^+$ 305.19113 found 305.19109.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N_2
O
N
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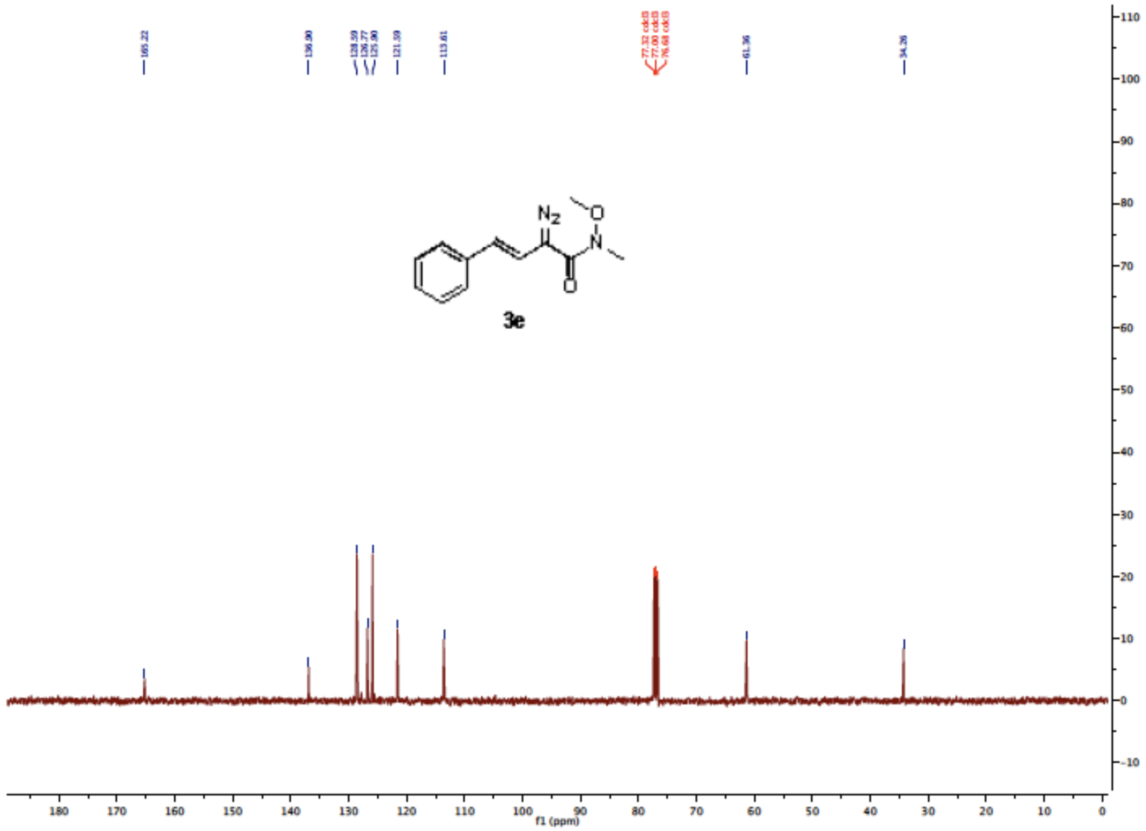
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N
3e
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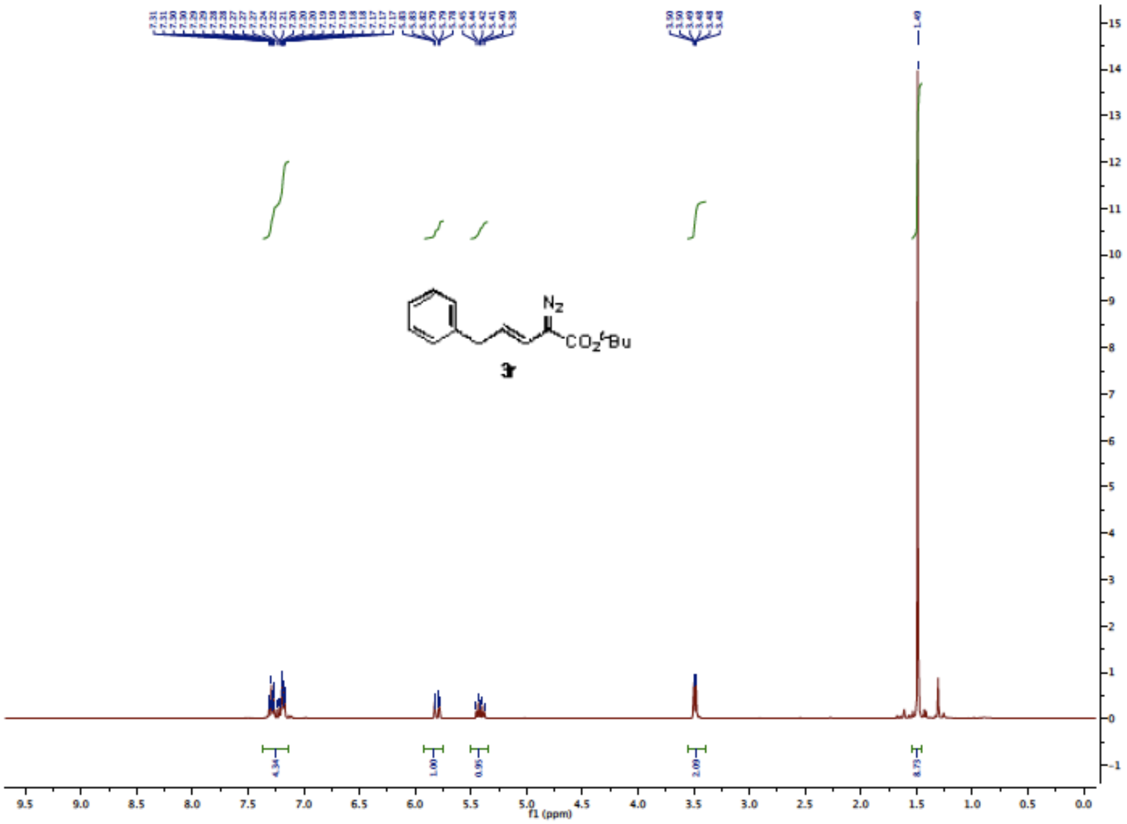
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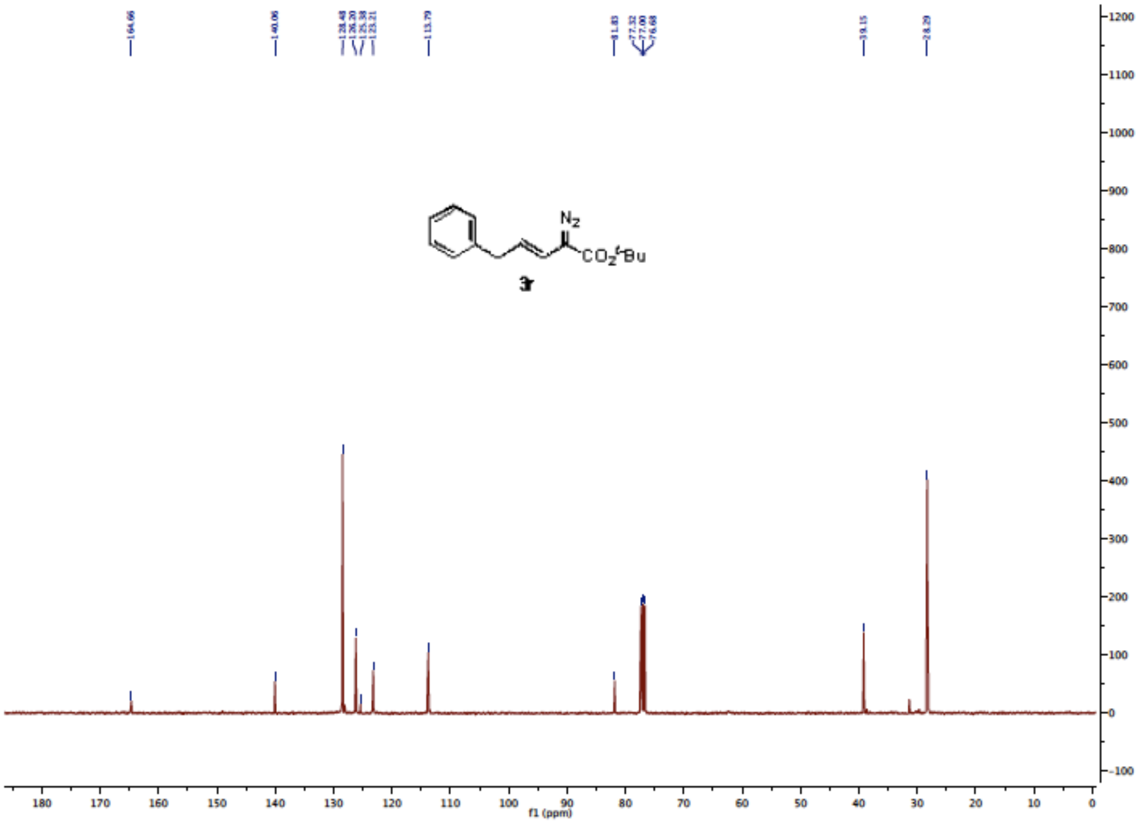
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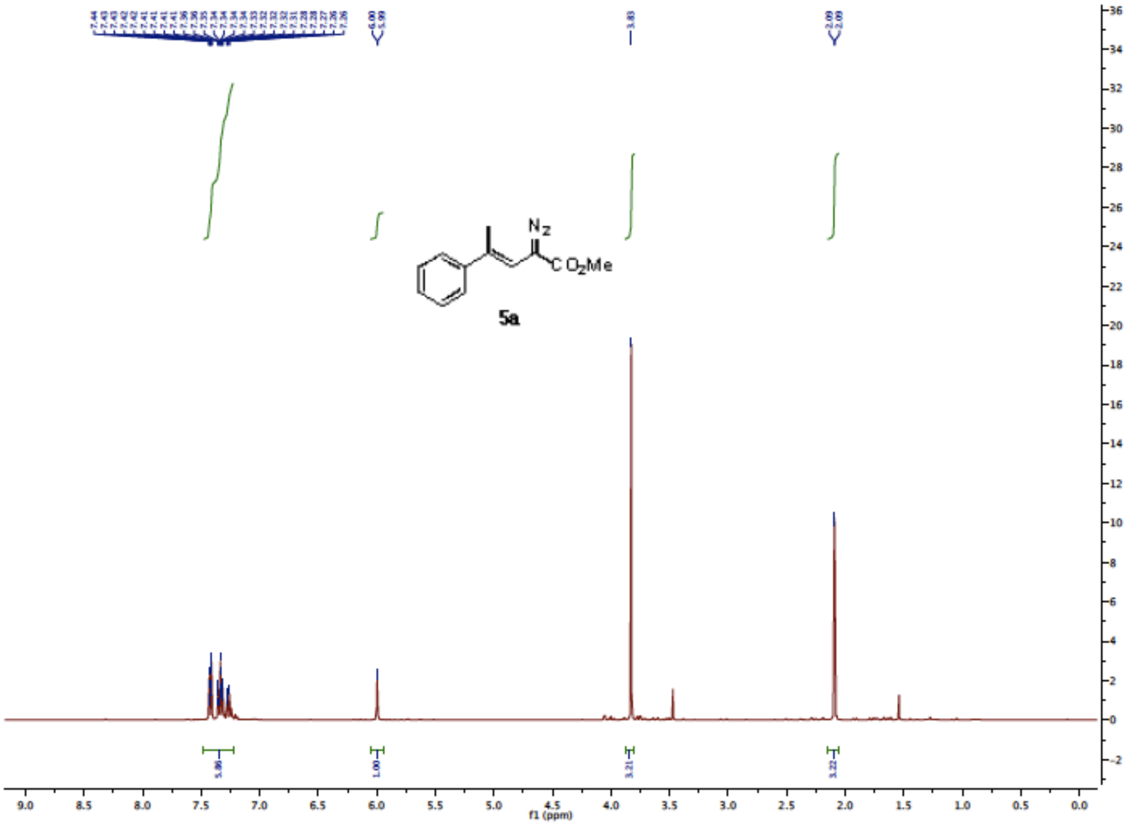
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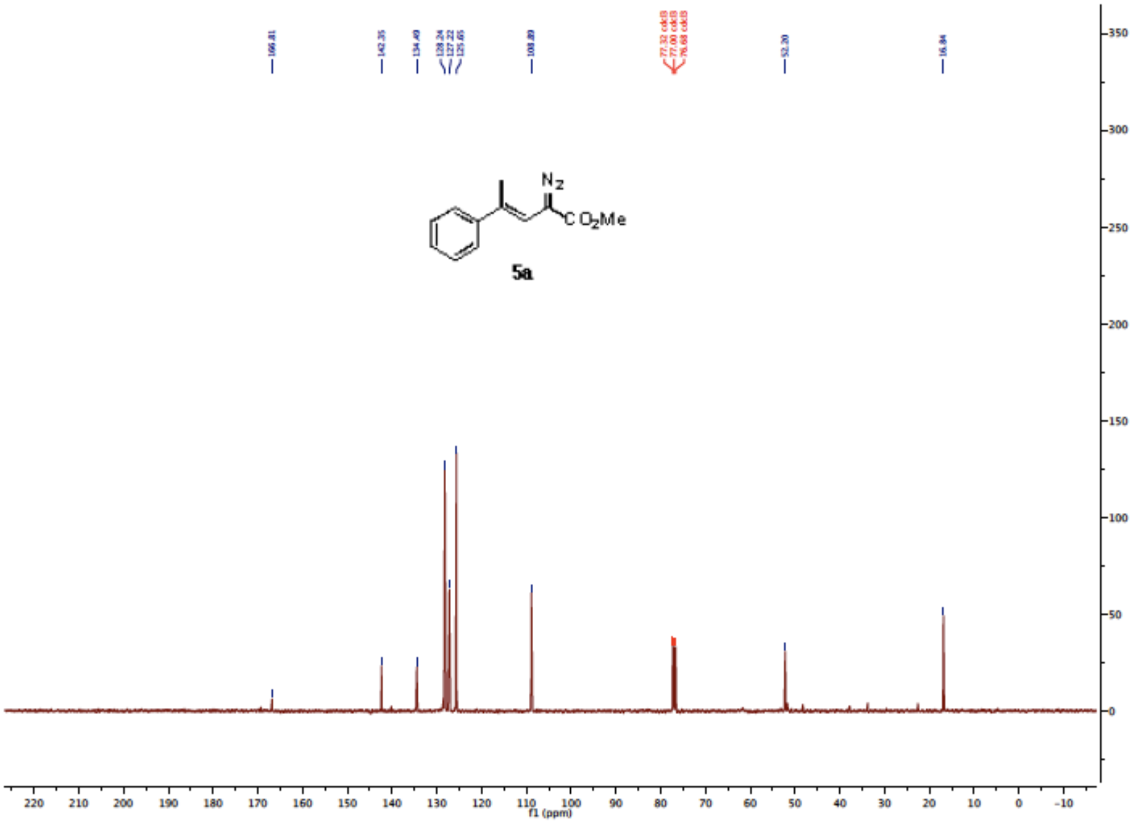
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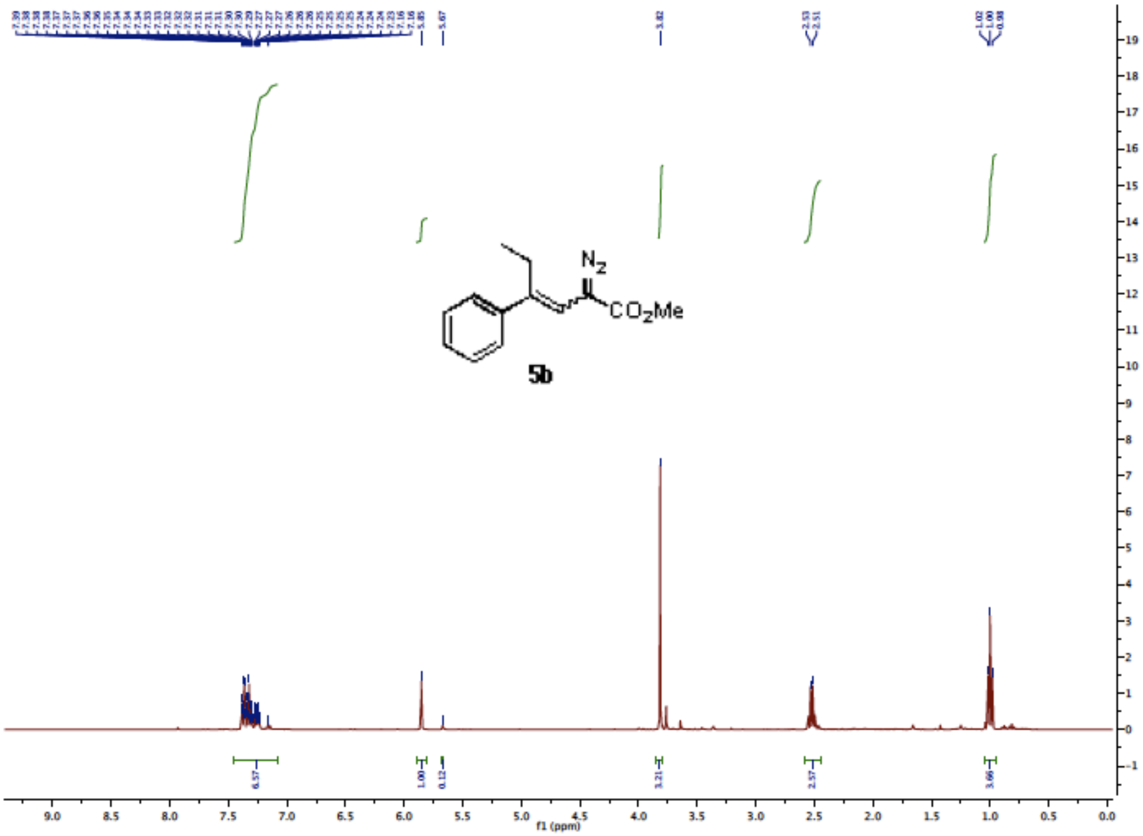
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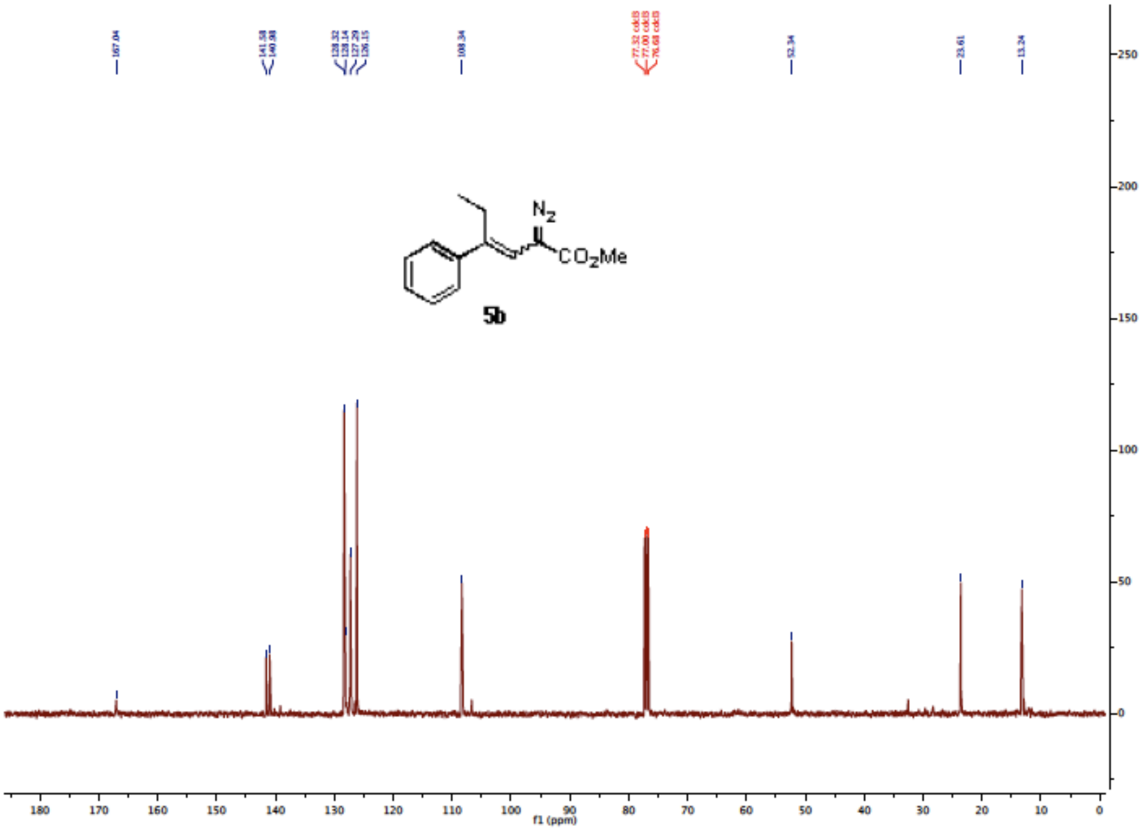
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CO2Me
5b
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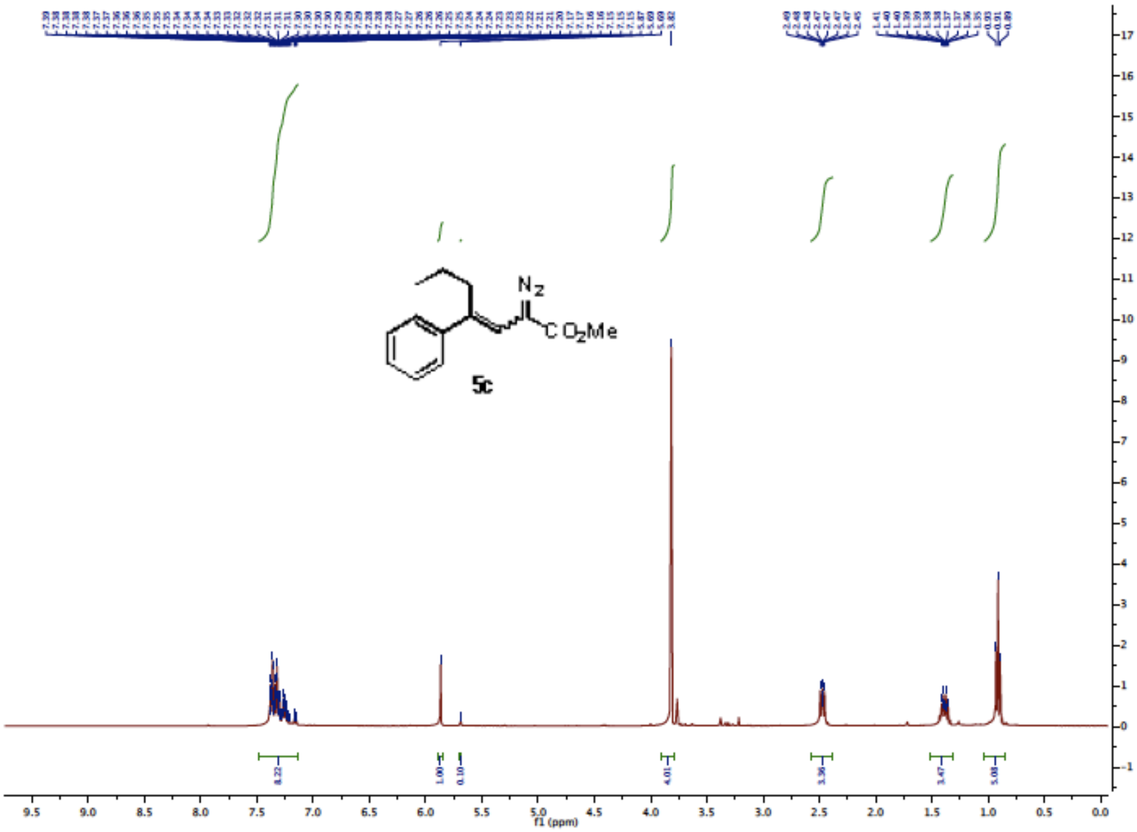
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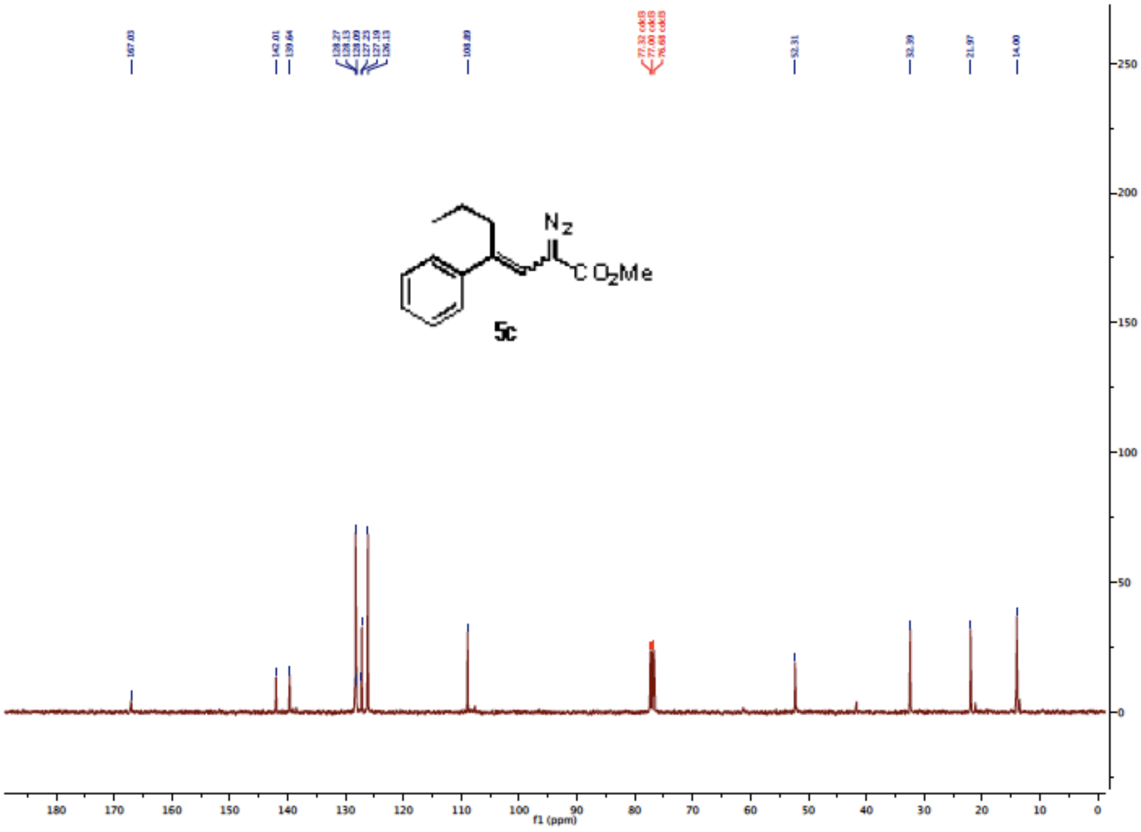
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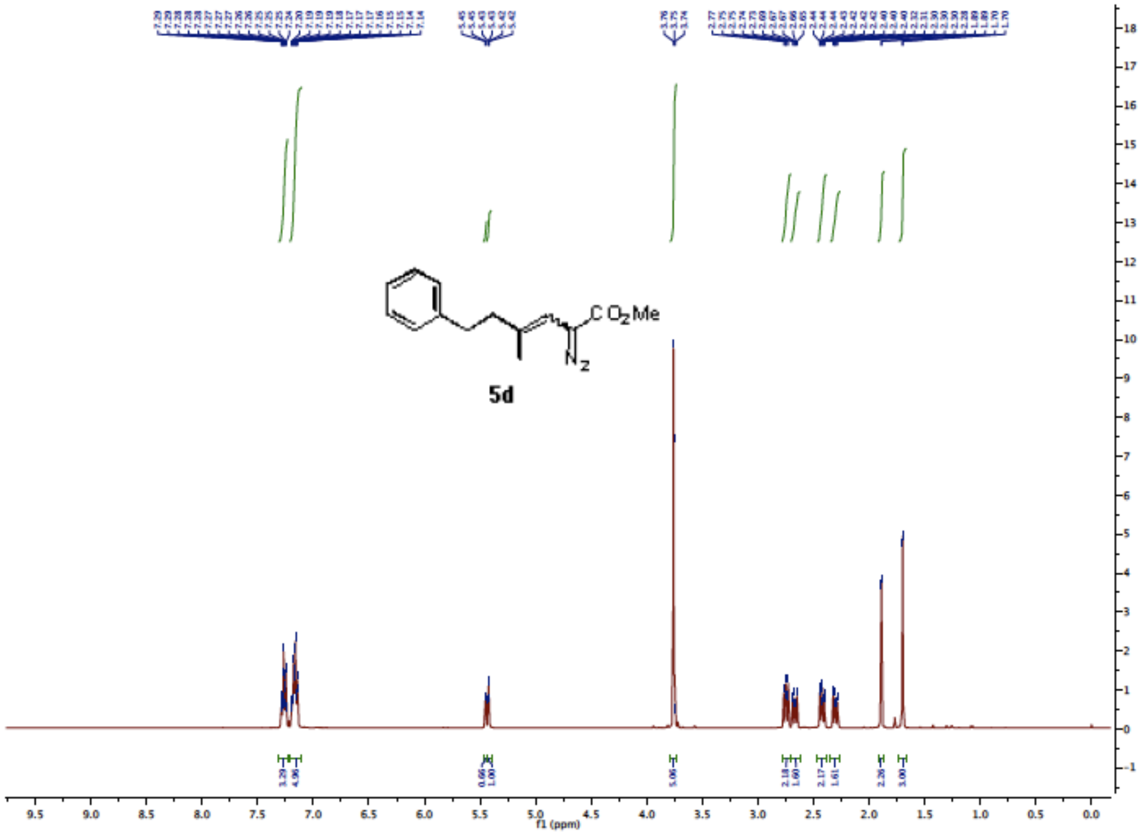
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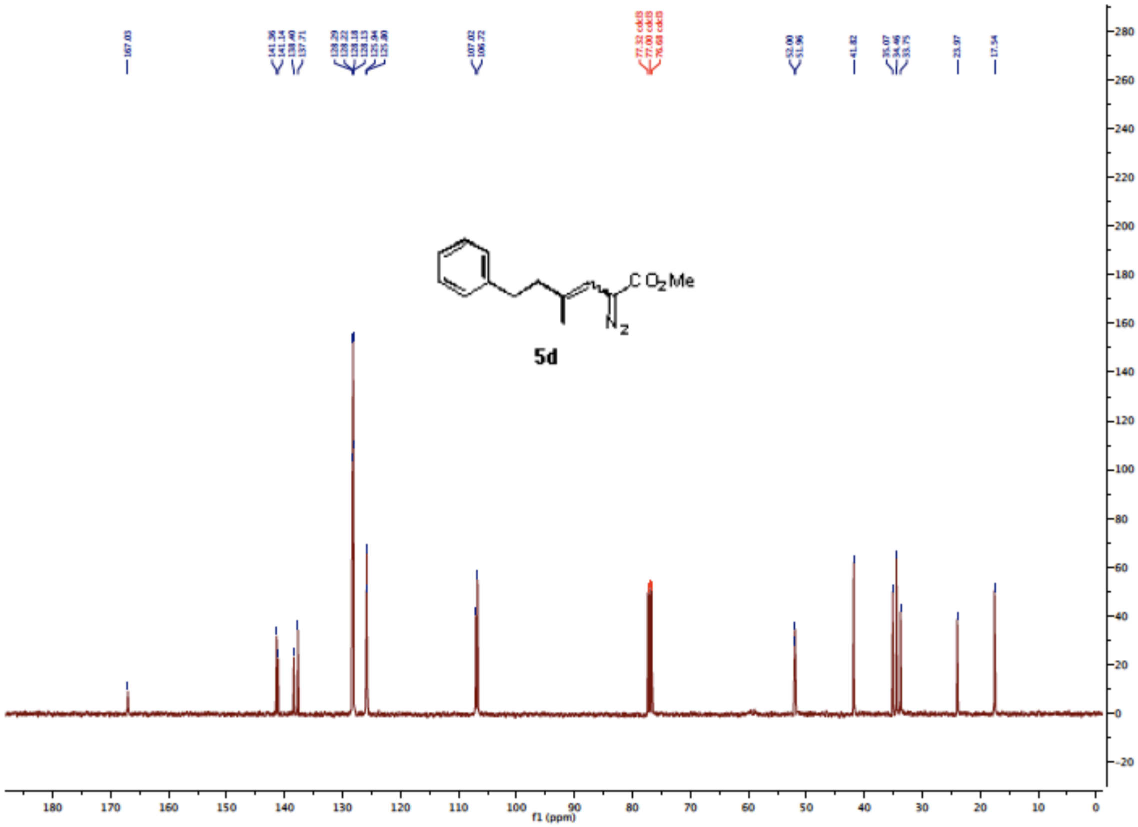
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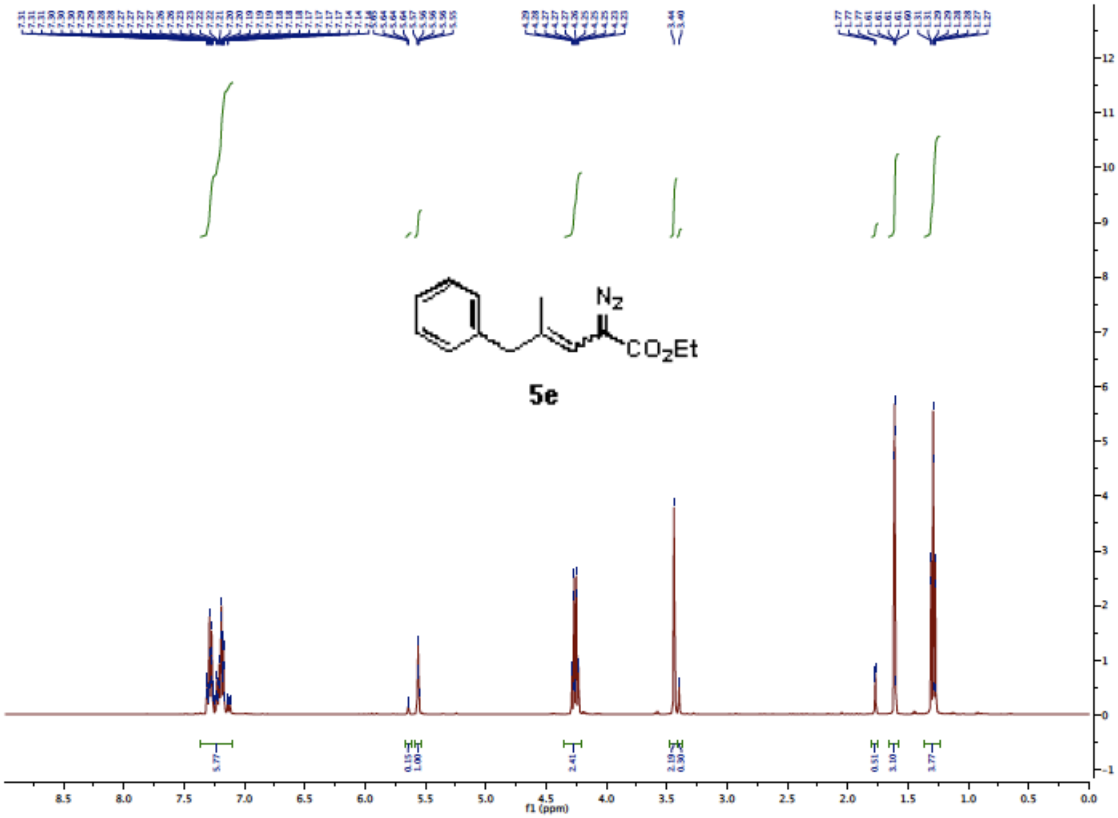
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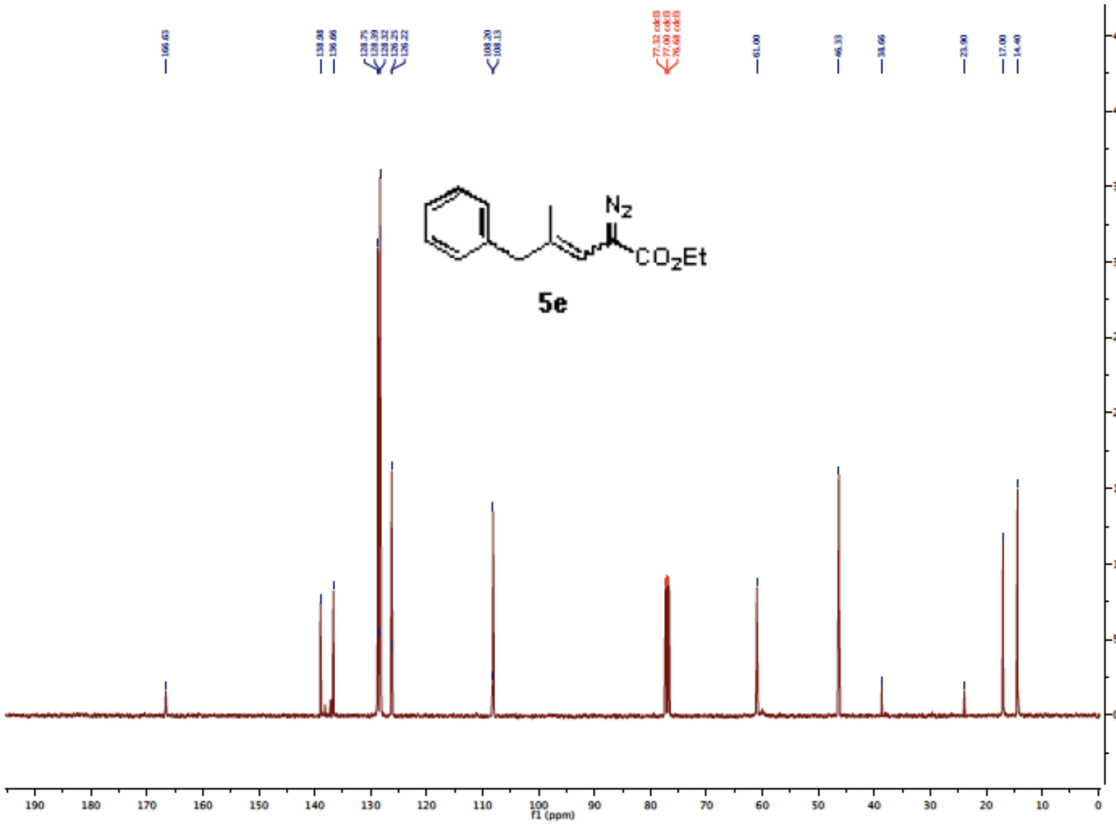
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5e
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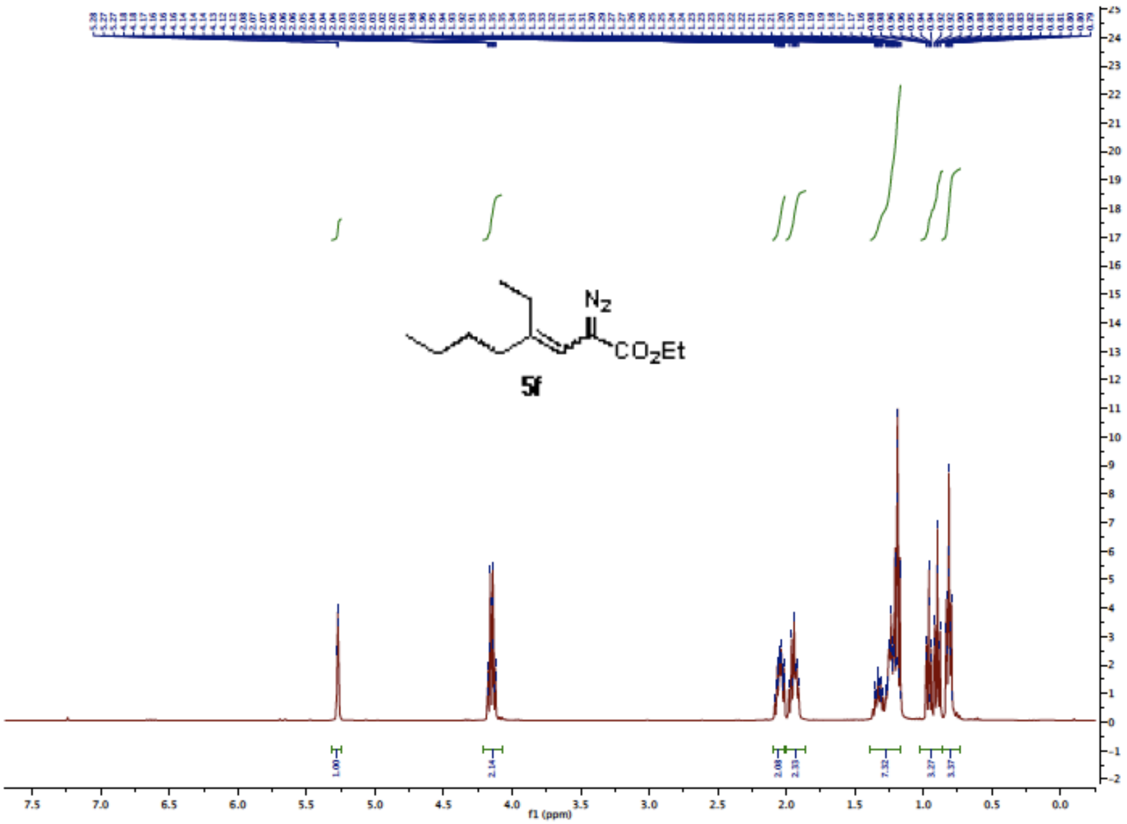
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CO2Et
5f
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2.14
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7.32
3.27
3.37
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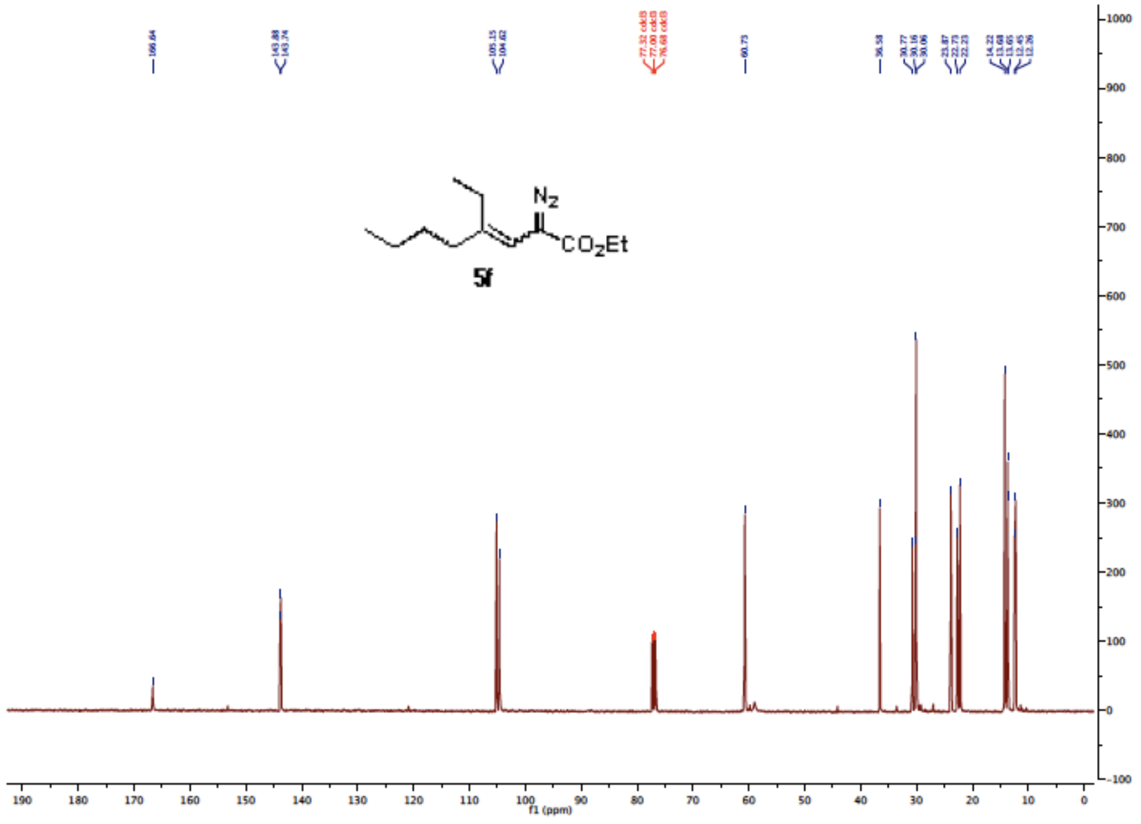
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CO2Et
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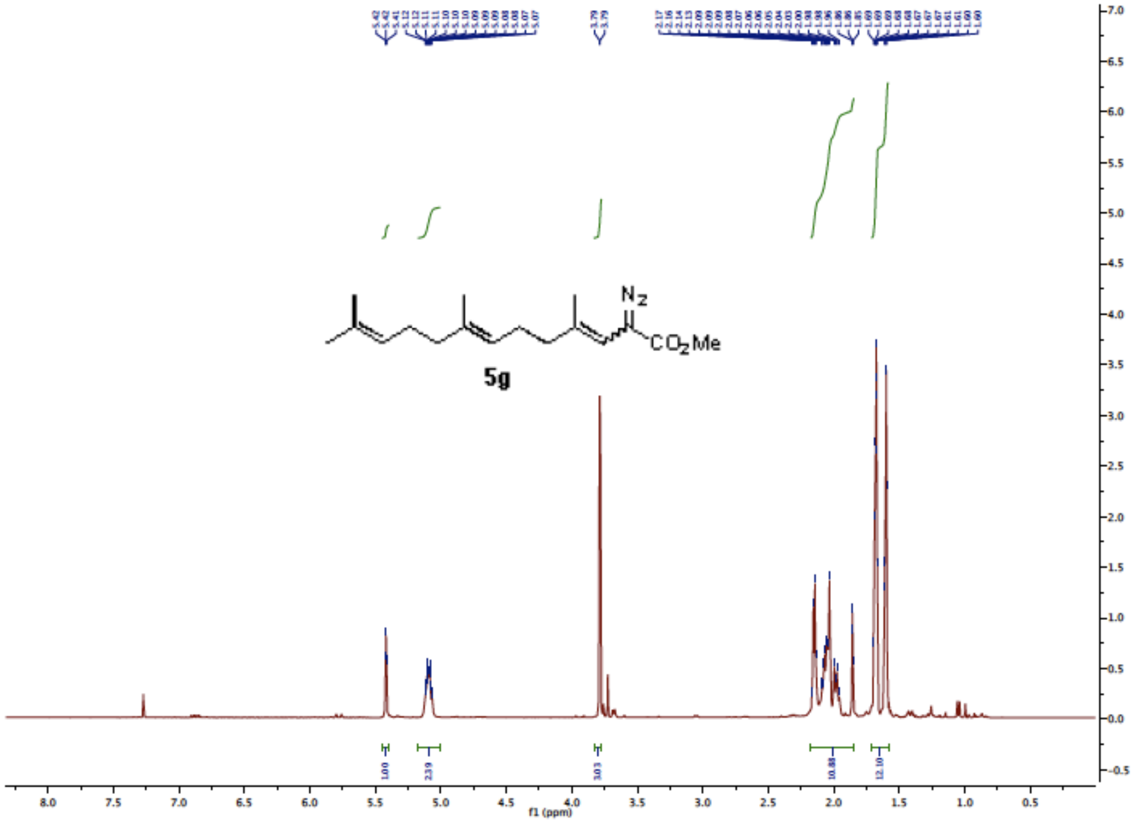
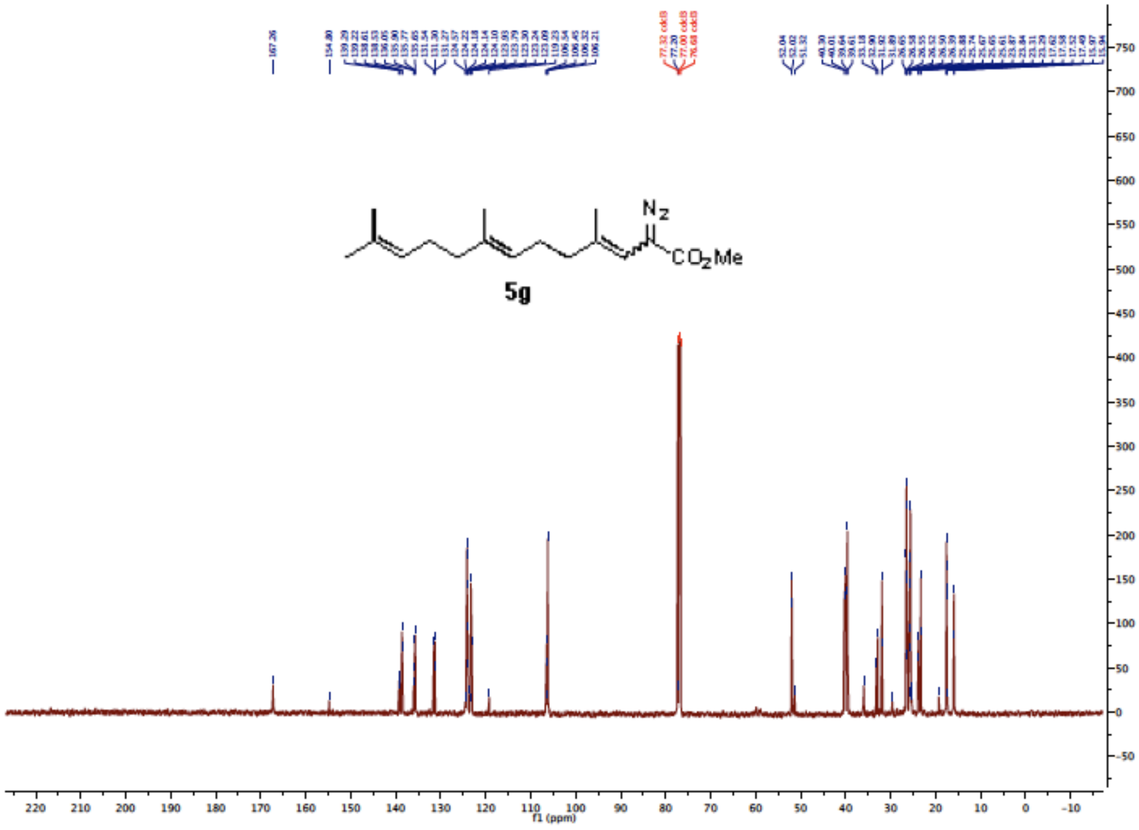
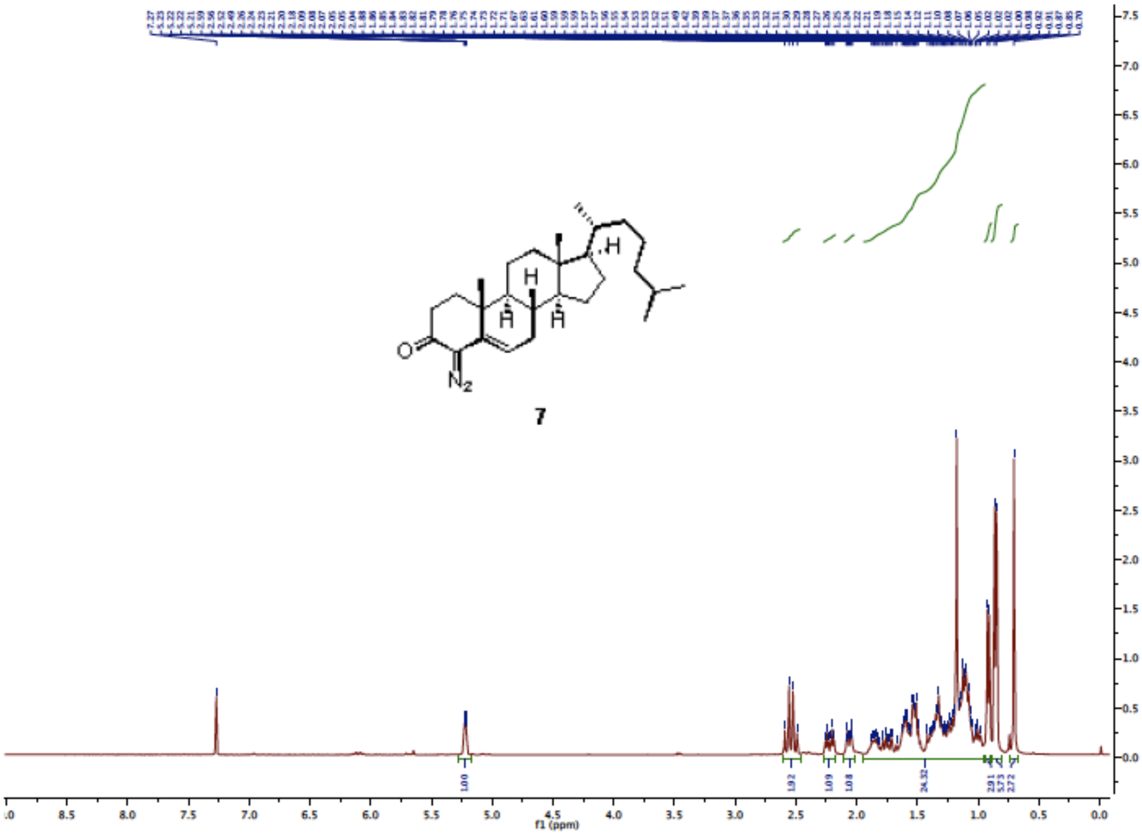
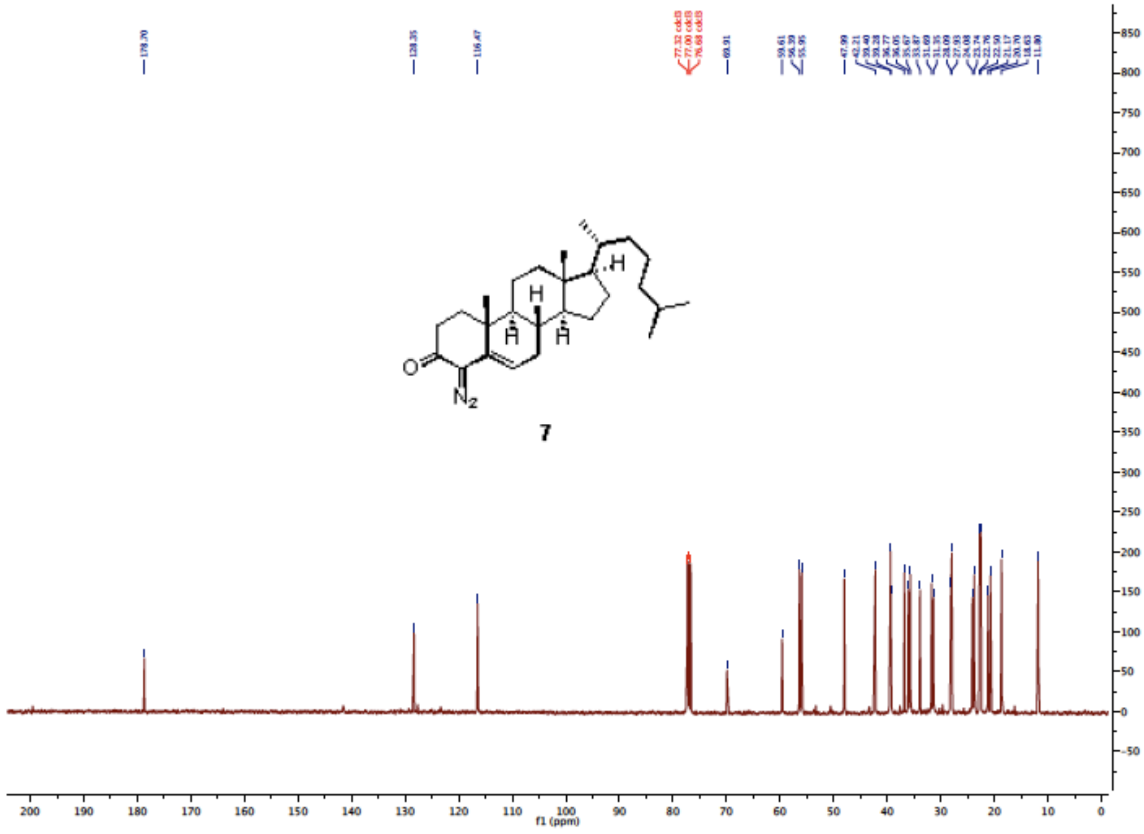
10
0
f1 (ppm)
1000
900
800
700
600
500
400
300
200
100
0
-100


N2
CO2Me
5g
1.00
2.99
3.03
10.88
12.10
f1 (ppm)

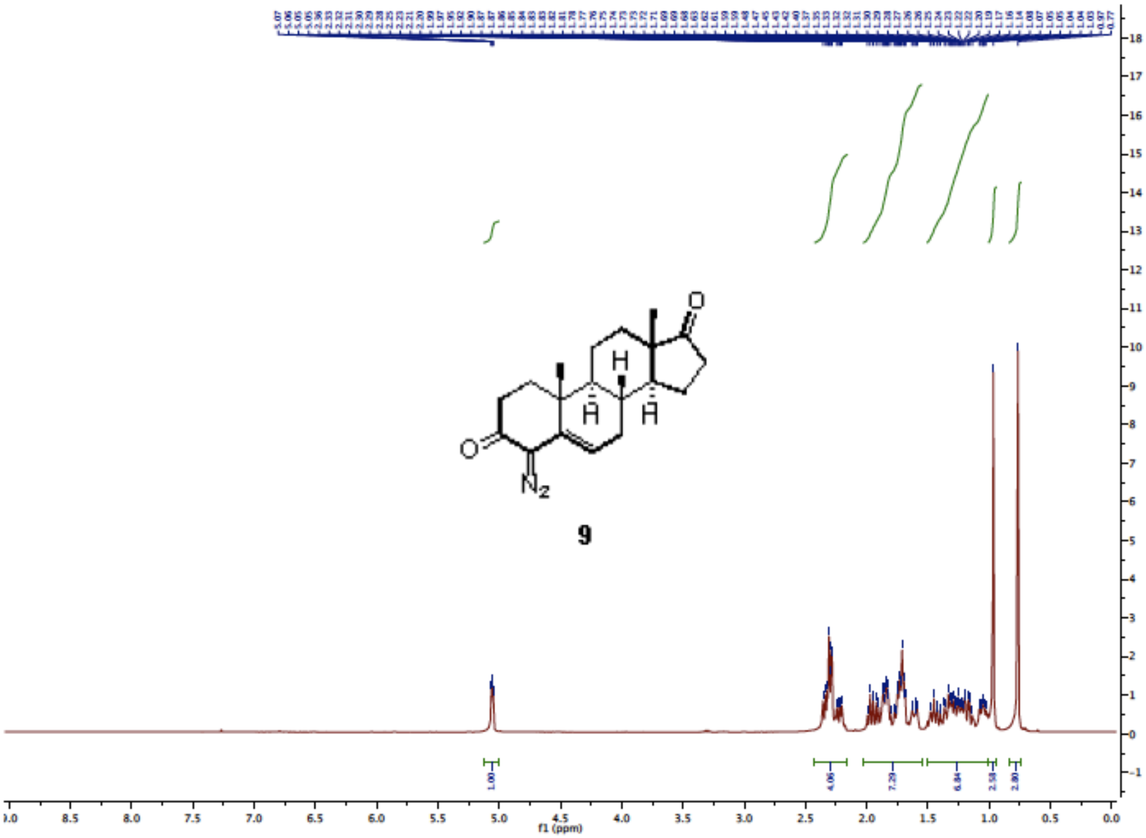

N2
CO2Me
5g
f1 (ppm)



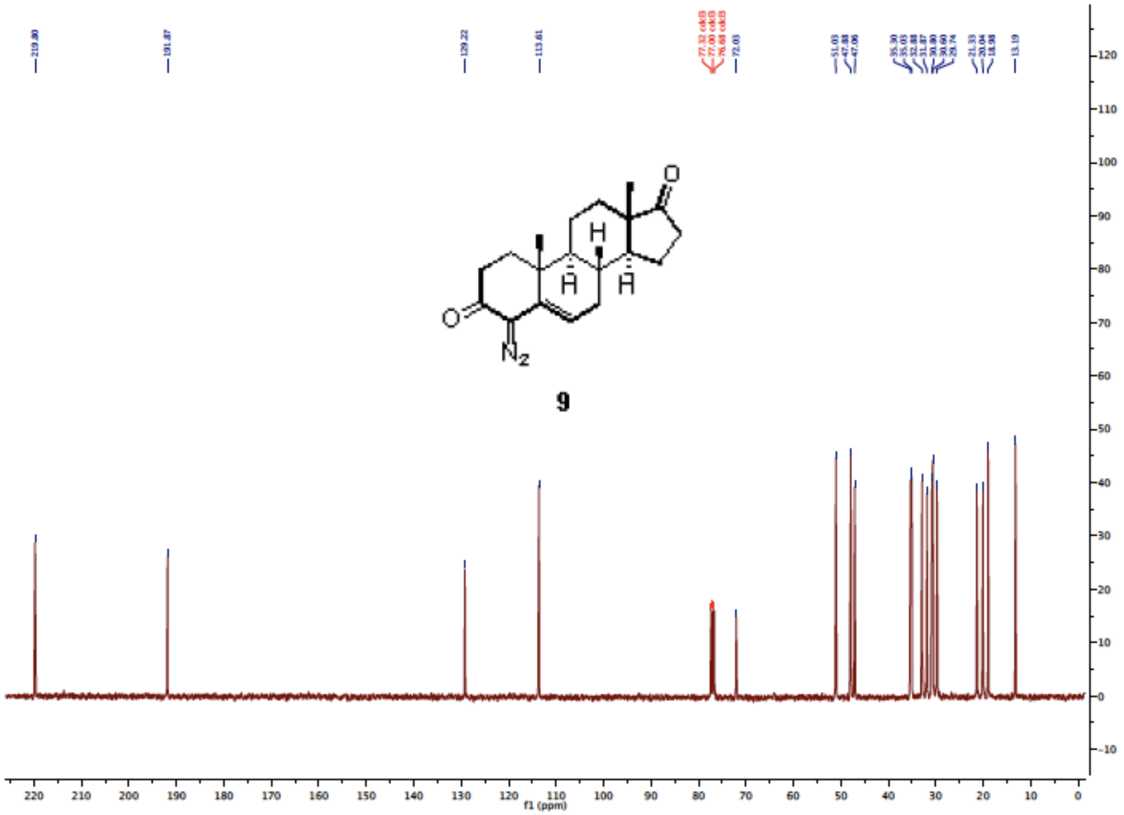
7
1.00
1.92
1.09
1.08
24.32
2.91
5.73
2.72
f1 (ppm)



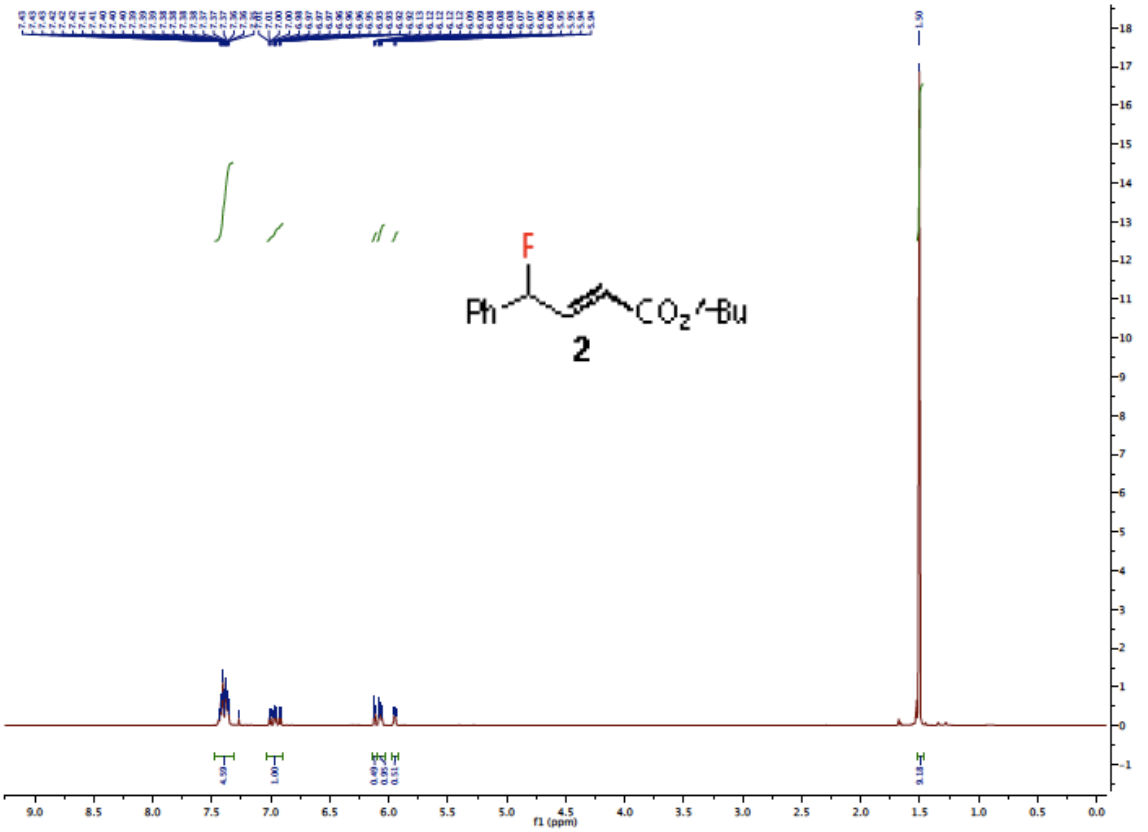
7
178.70
128.35
116.47
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
69.91
59.61
56.39
55.95
47.99
42.21
39.40
39.28
36.77
36.05
35.67
33.87
31.69
31.35
28.09
27.93
24.08
23.74
22.76
22.50
21.17
20.70
18.63
11.80
f1 (ppm)

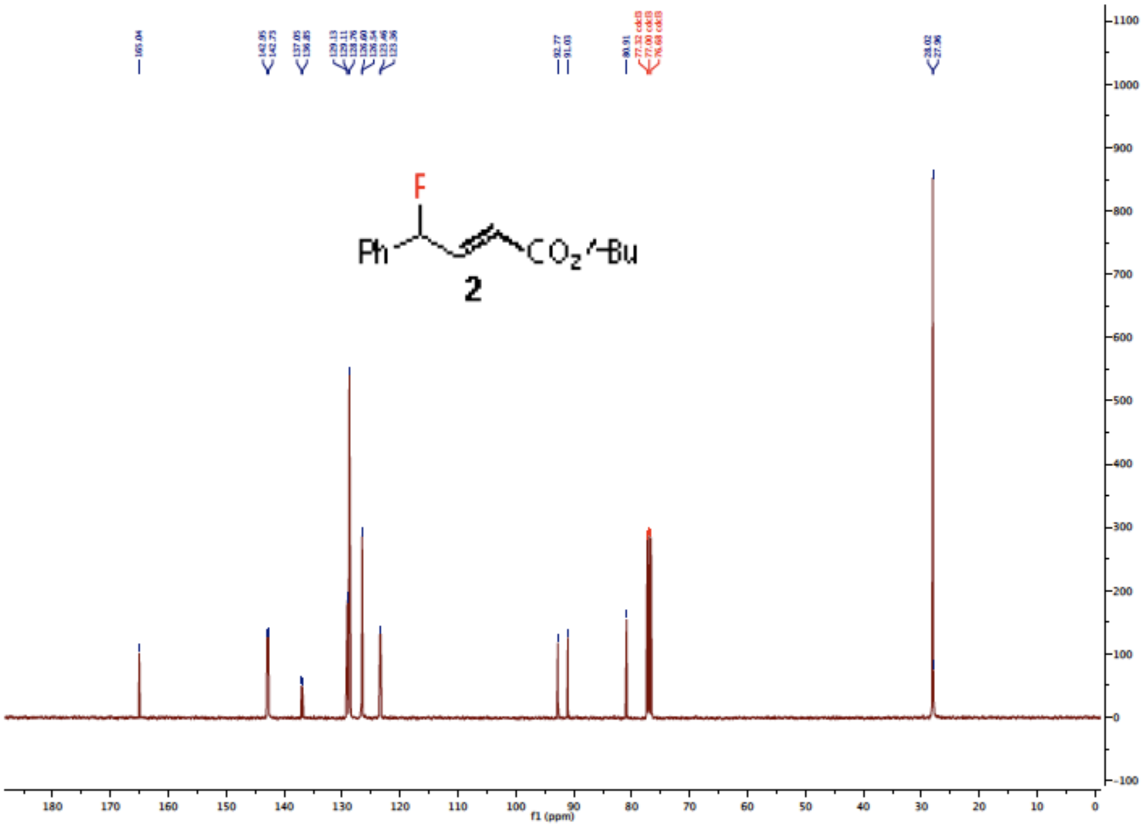

1.00
4.08
7.29
6.84
2.58
2.80
f1 (ppm)

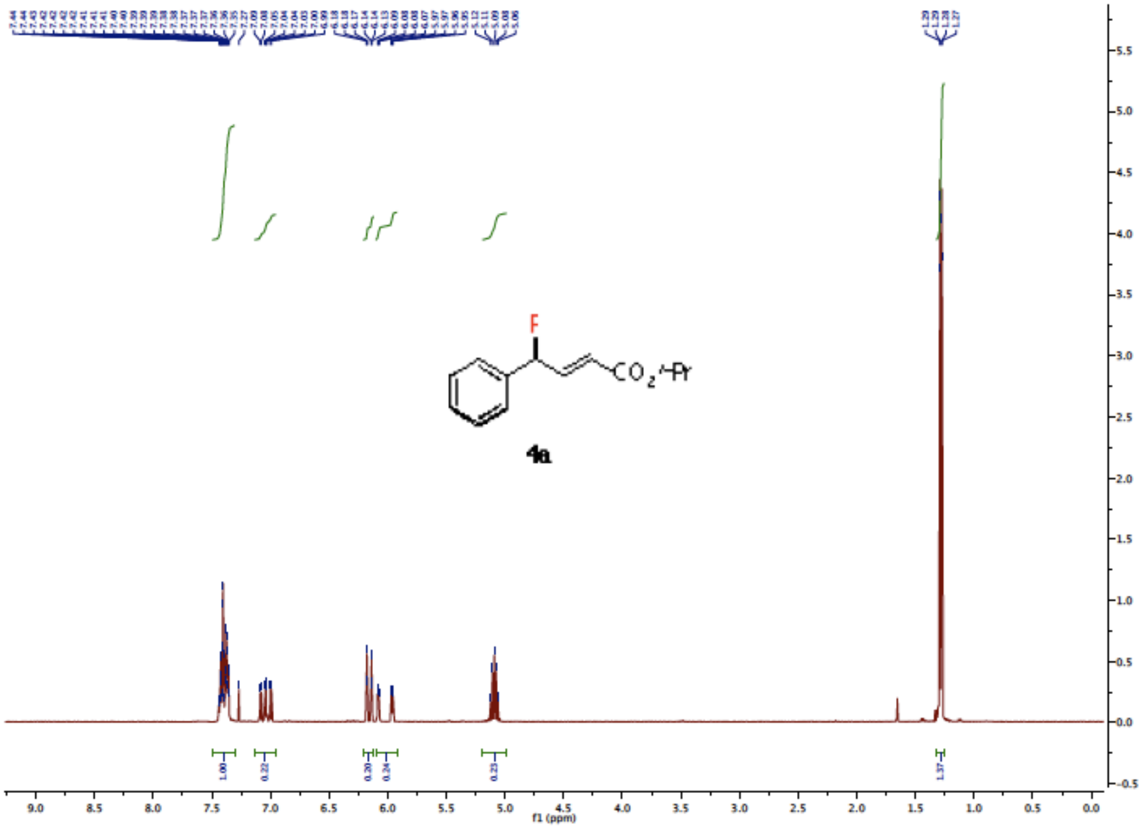
9

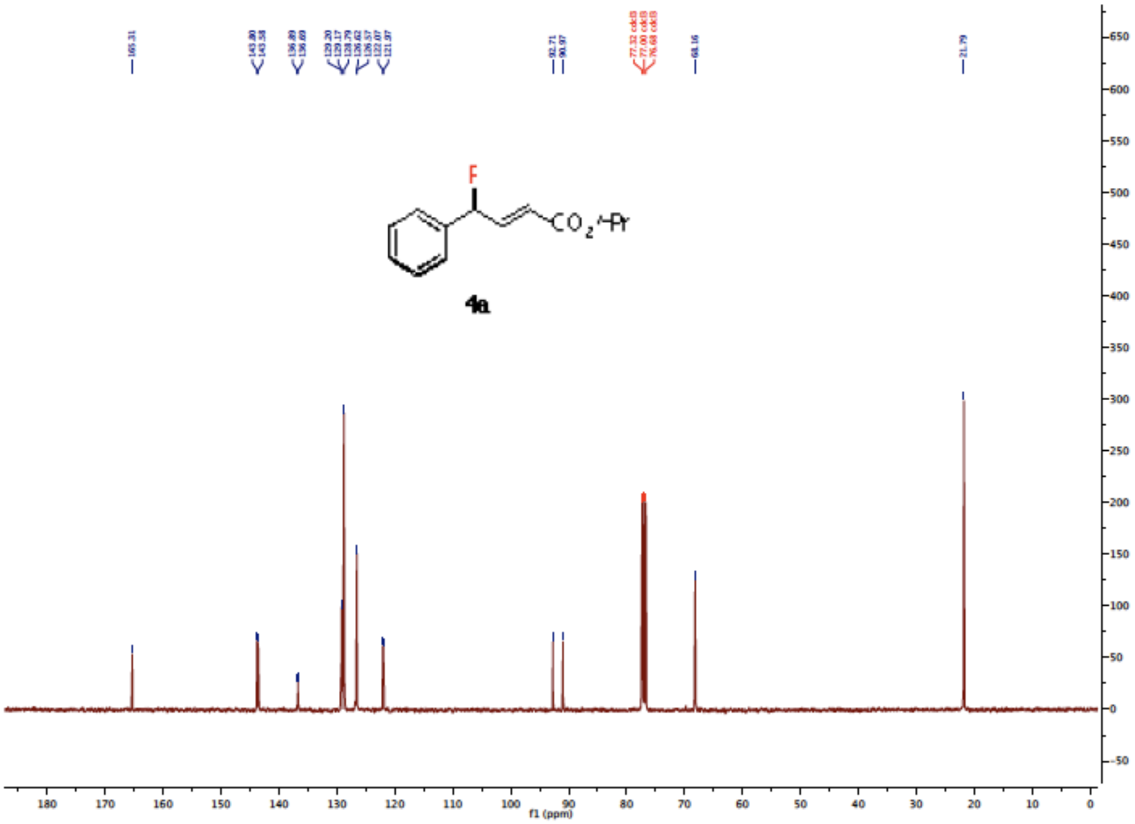

219.80
191.47
129.22
113.61
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
72.03
51.03
47.88
47.06
35.30
35.03
32.88
31.87
30.80
30.60
29.74
21.33
20.04
18.98
13.19
f1 (ppm)

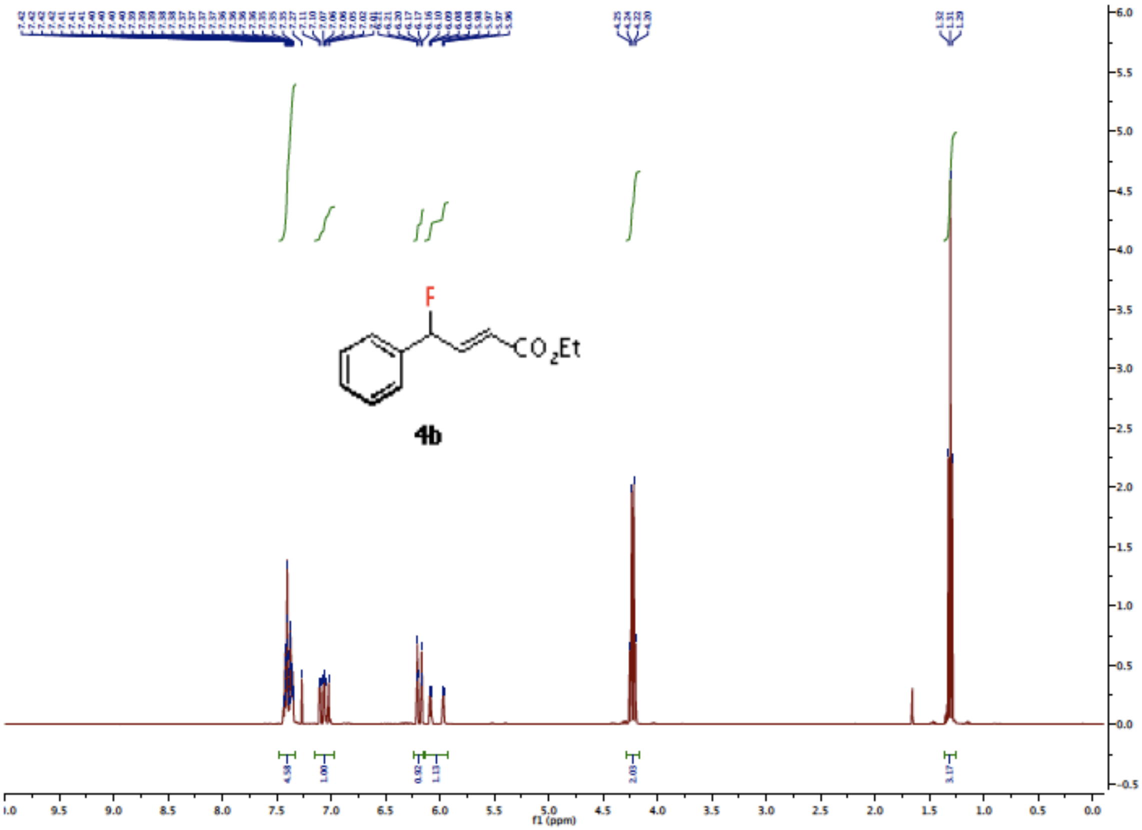
9

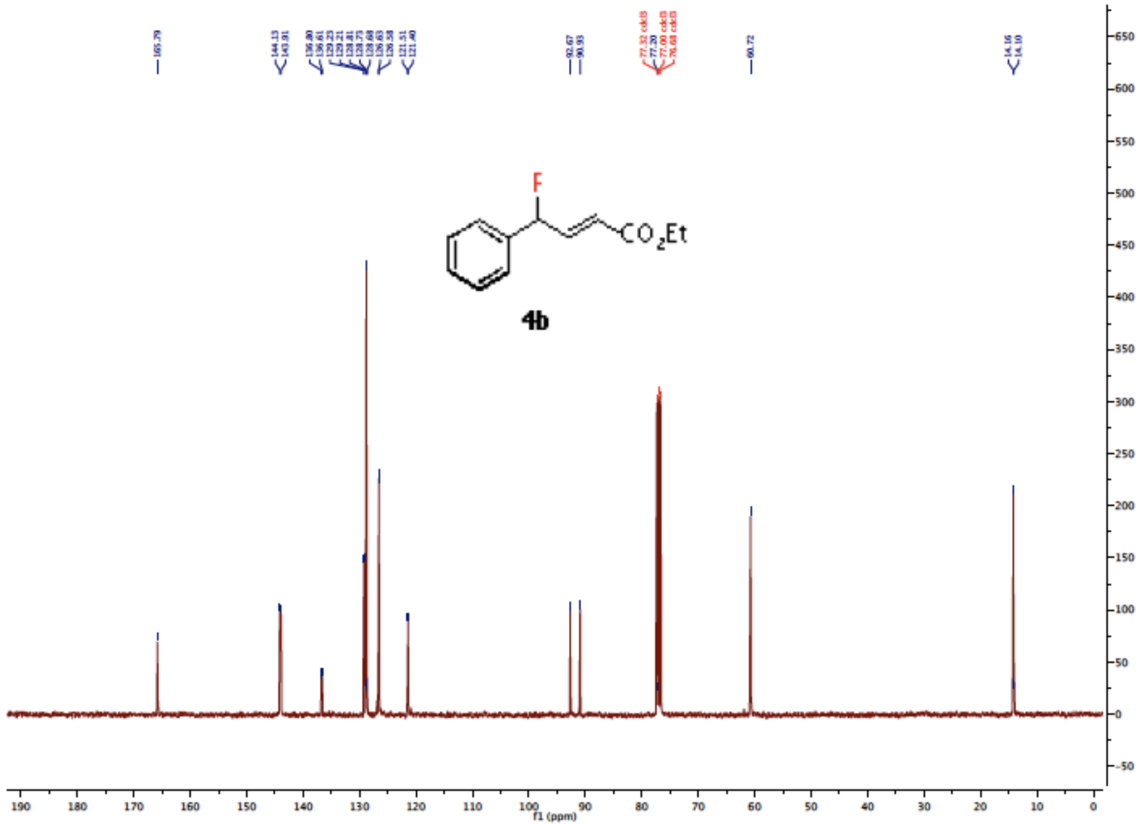

1.50
F
Ph
CO2t-Bu
2
4.59
1.00
0.49
0.95
0.51
9.18
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

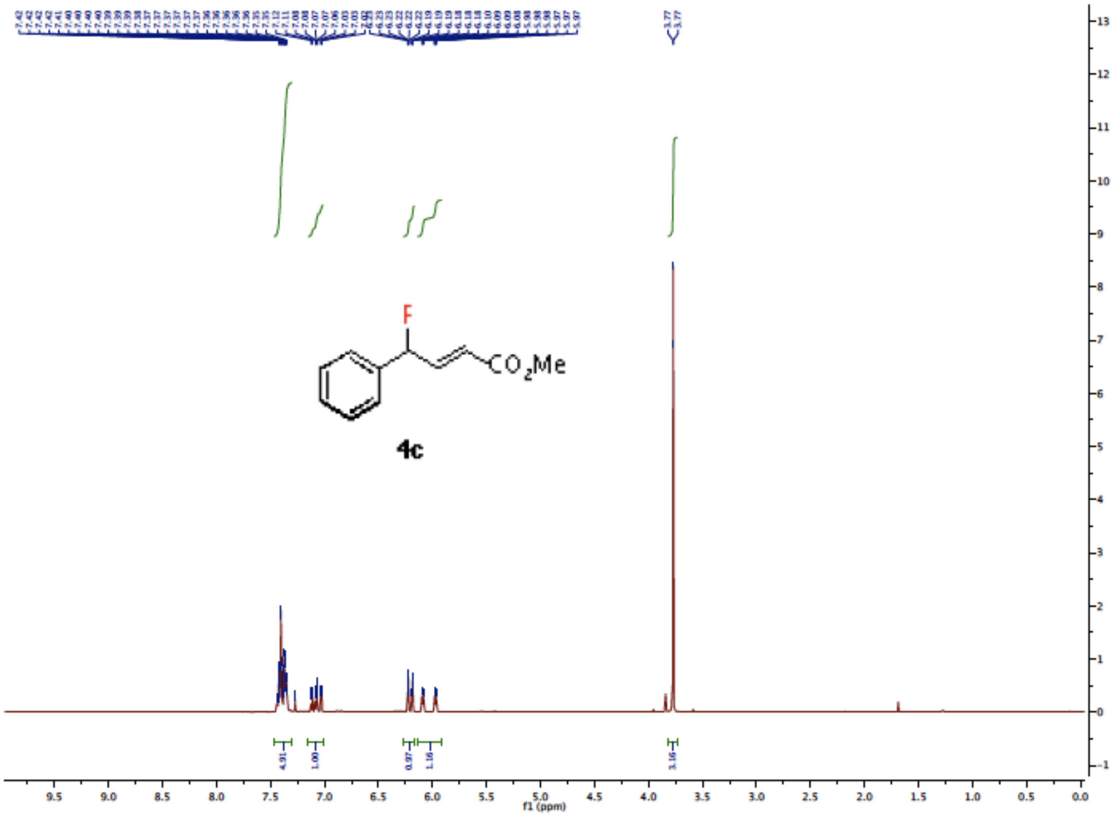

165.04
142.95
142.73
137.05
136.85
129.13
129.11
128.76
126.60
126.54
123.46
123.36
92.77
91.03
80.91
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
28.02
27.96
F
Ph
CO2t-Bu
2
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.44
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.27
7.09
7.08
7.05
7.04
7.04
7.03
7.00
6.99
6.99
6.18
6.18
6.17
6.14
6.14
6.13
6.09
6.08
6.08
6.07
5.97
5.97
5.96
5.95
5.12
5.11
5.09
5.08
5.06
1.29
1.29
1.28
1.27
F
CO2i-Pr
4a
1.00
0.22
0.20
0.24
0.23
1.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

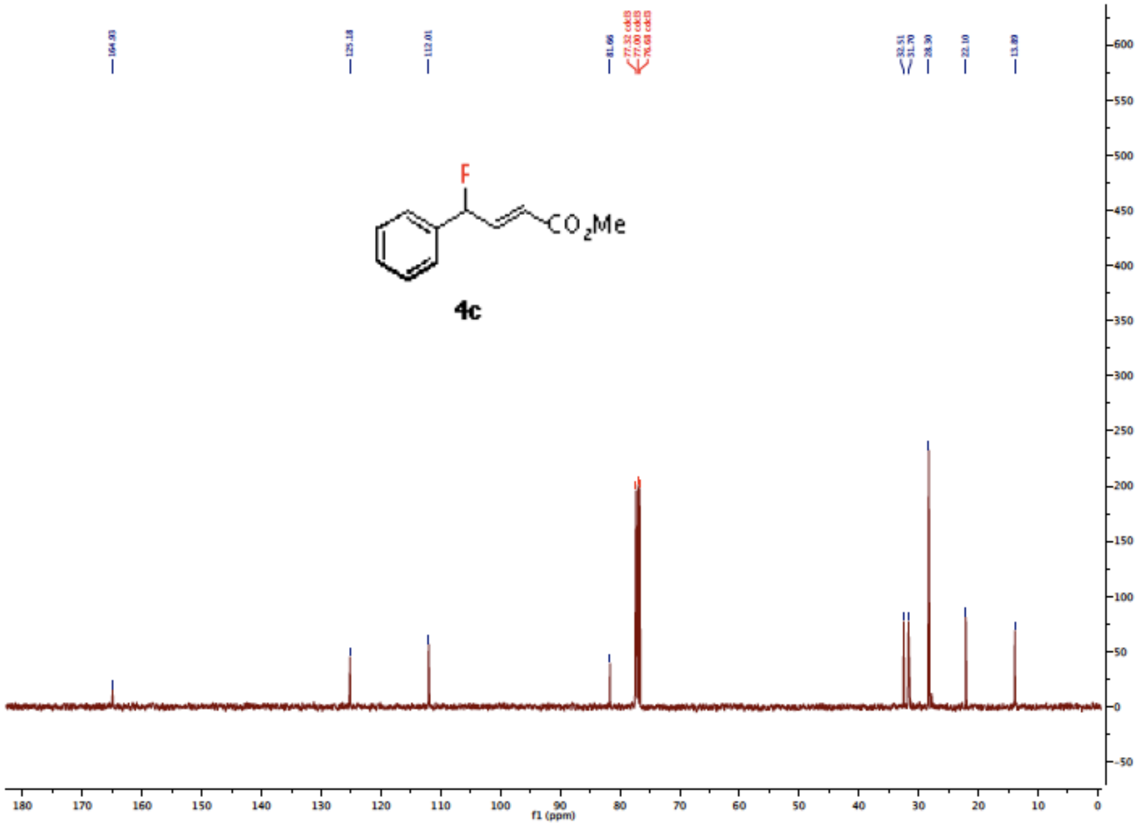

165.31
143.80
143.58
136.89
136.69
129.20
129.17
128.79
126.62
126.57
122.07
121.97
92.71
90.97
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
68.16
21.79
F
CO2i-Pr
4a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50


7.42
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.35
7.27
7.11
7.10
7.07
7.06
7.06
7.05
7.02
6.21
6.21
6.20
6.17
6.17
6.16
6.10
6.09
6.08
6.08
5.98
5.97
5.97
5.96
4.25
4.24
4.22
4.20
1.32
1.31
1.29
F
CO2Et
4b
4.58
1.00
0.92
1.13
2.03
3.17
f1 (ppm)

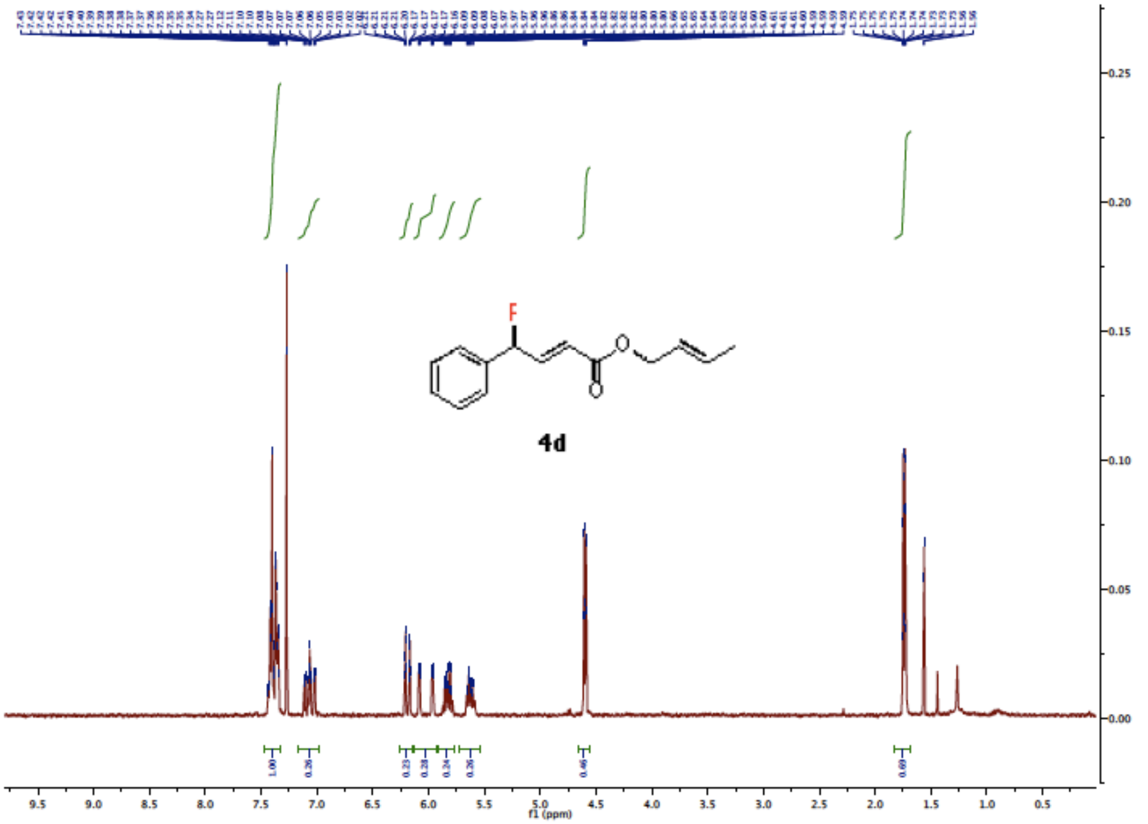

165.79
144.13
143.91
136.80
136.61
129.23
129.21
128.81
128.75
128.68
126.63
126.58
121.51
121.40
92.67
90.93
77.32 cdcl3
77.20
77.00 cdcl3
76.68 cdcl3
60.72
14.16
14.10
F
CO2Et
4b
f1 (ppm)

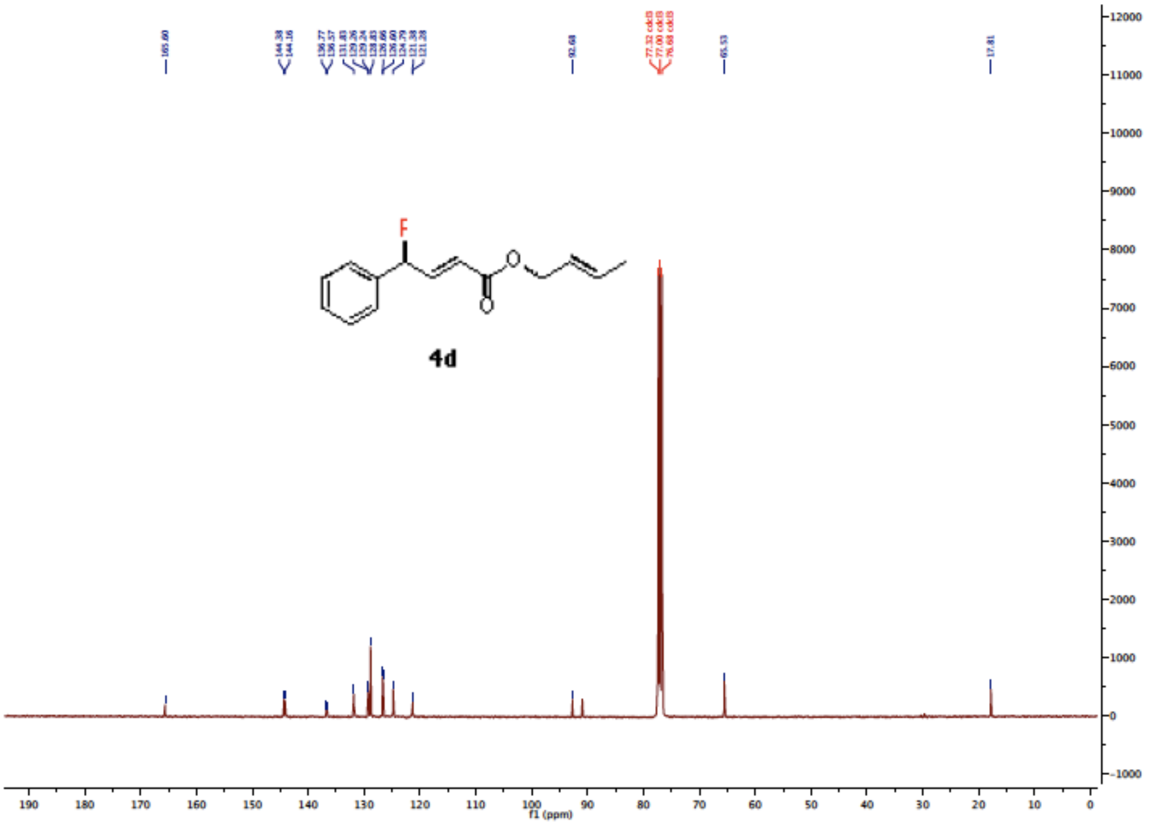


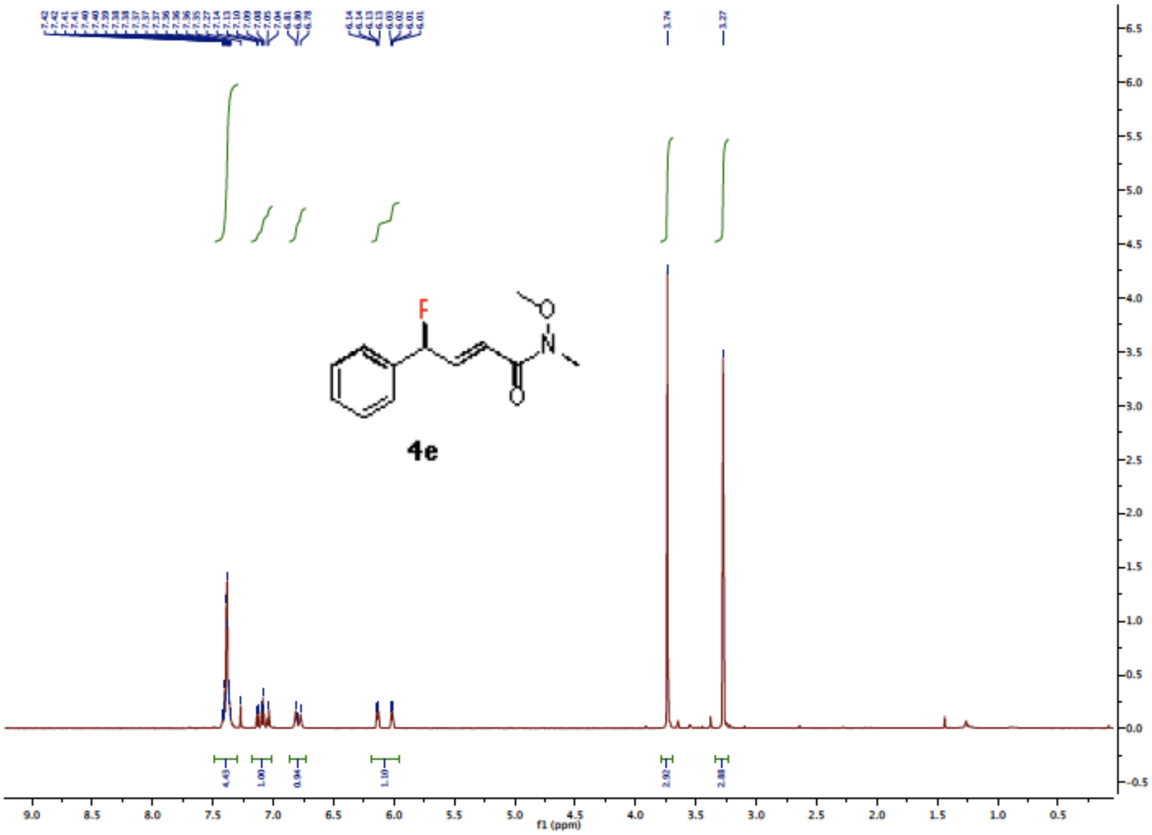
3.77
3.77
F
CO2Me
4c
4.91
1.00
0.97
1.16
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

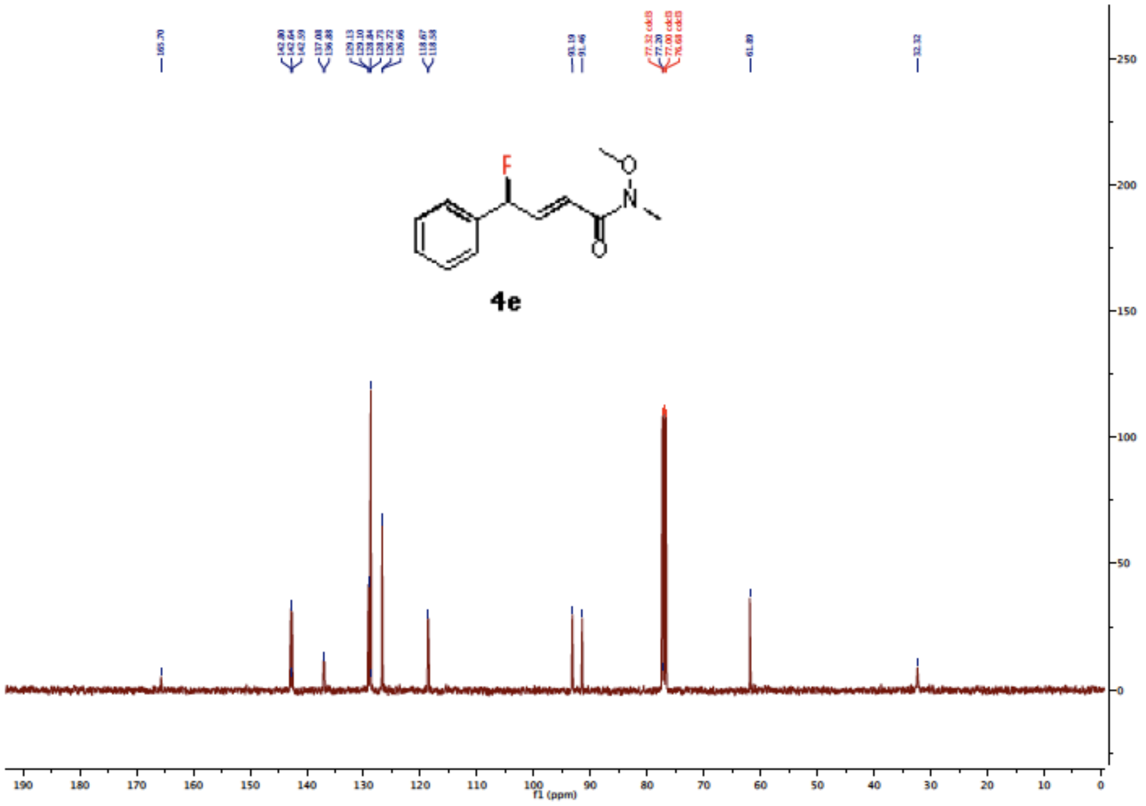


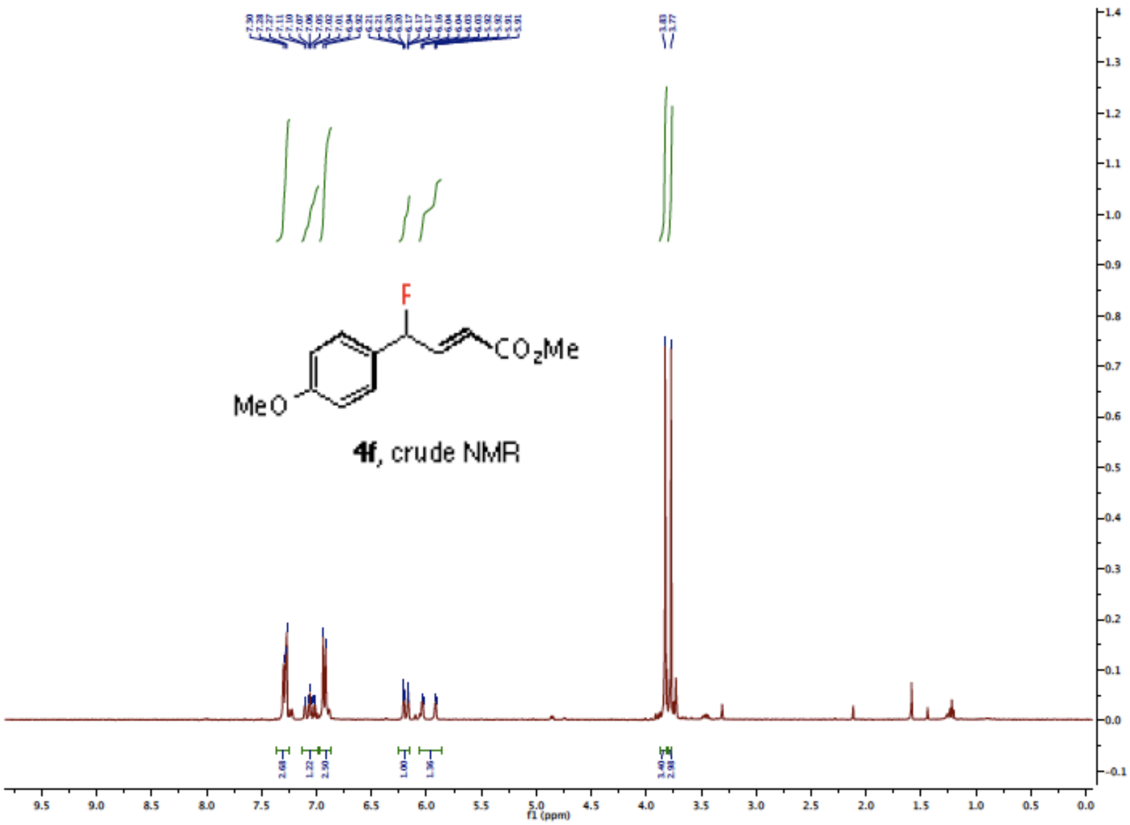
164.93
125.18
112.01
81.66
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
32.51
31.70
28.30
22.10
13.89
F
CO2Me
4c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50


F
O
O
4d
1.00
0.26
0.23
0.28
0.24
0.26
0.49
0.69
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
0.25
0.20
0.15
0.10
0.05
0.00

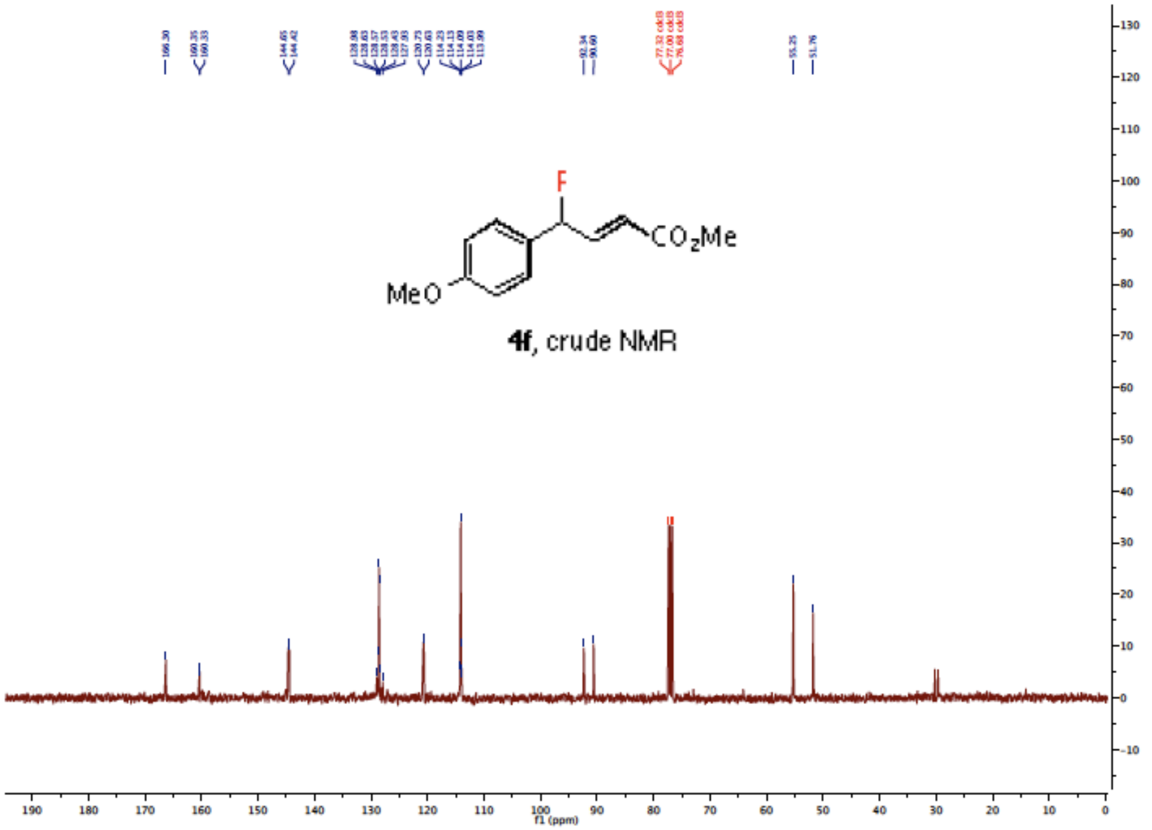

165.60
144.38
144.16
136.77
136.57
131.83
129.26
129.24
128.83
126.66
126.60
124.79
121.38
121.28
92.68
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
65.53
17.81
F
O
O
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.27
7.14
7.13
7.10
7.09
7.08
7.05
7.04
6.81
6.80
6.78
6.14
6.14
6.13
6.13
6.03
6.02
6.01
6.01
3.74
3.27
F
O
N
O
4e
4.43
1.00
0.94
1.10
2.92
2.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

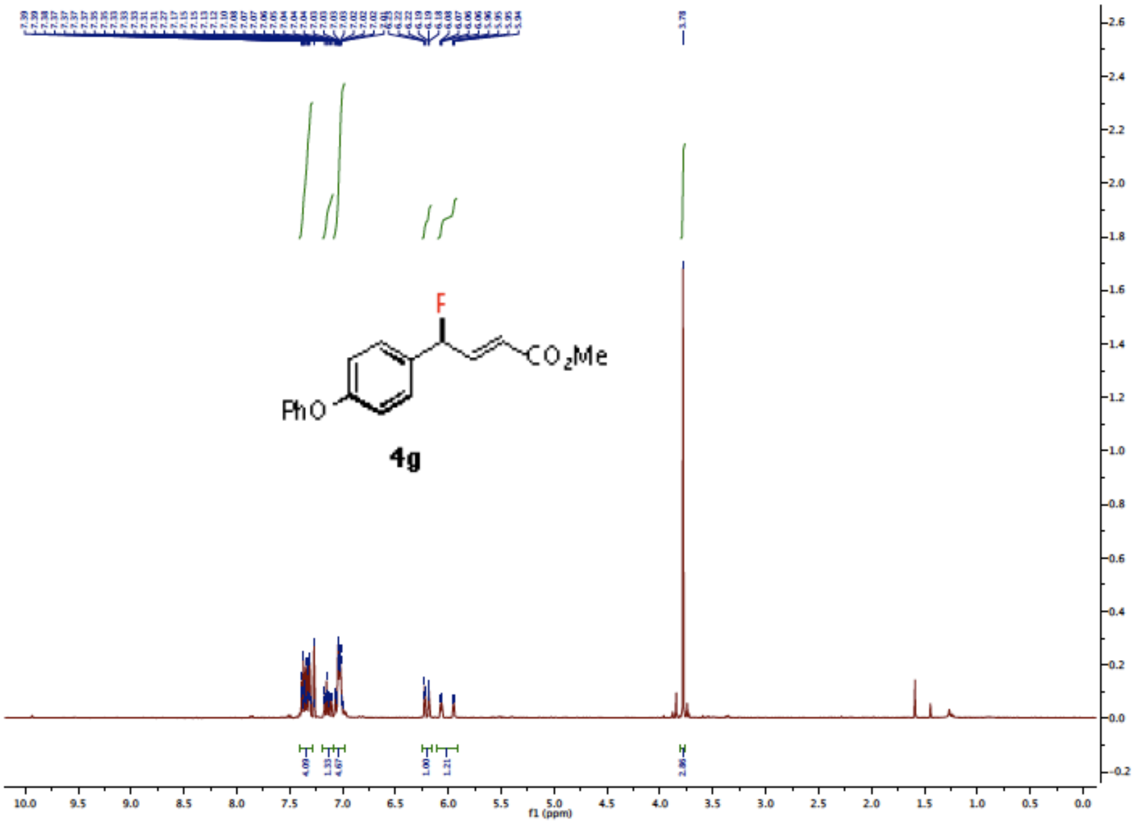

165.70
142.80
142.64
142.59
137.08
136.88
129.13
129.10
128.84
128.73
126.72
126.66
118.67
118.58
93.19
91.46
77.32 cdcl3
77.20
77.00 cdcl3
76.68 cdcl3
61.89
32.32
F
O
N
O
4e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
250
200
150
100
50
0

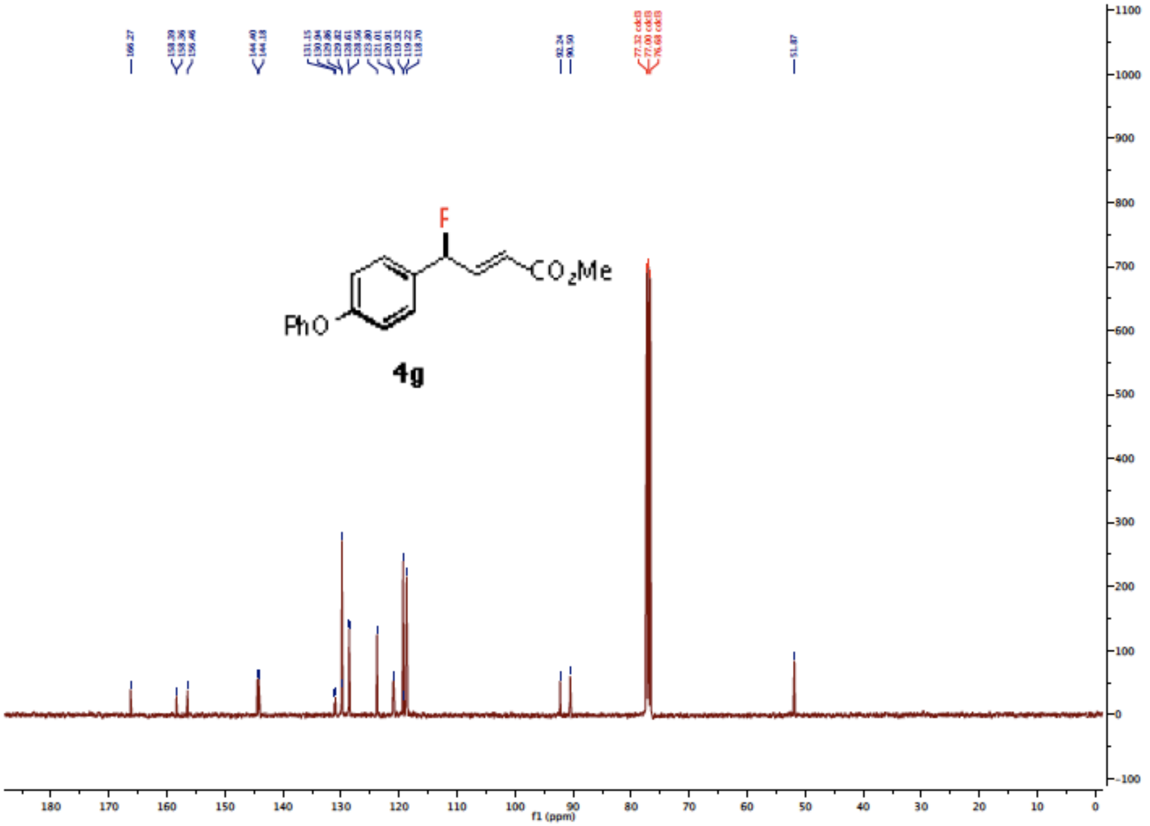


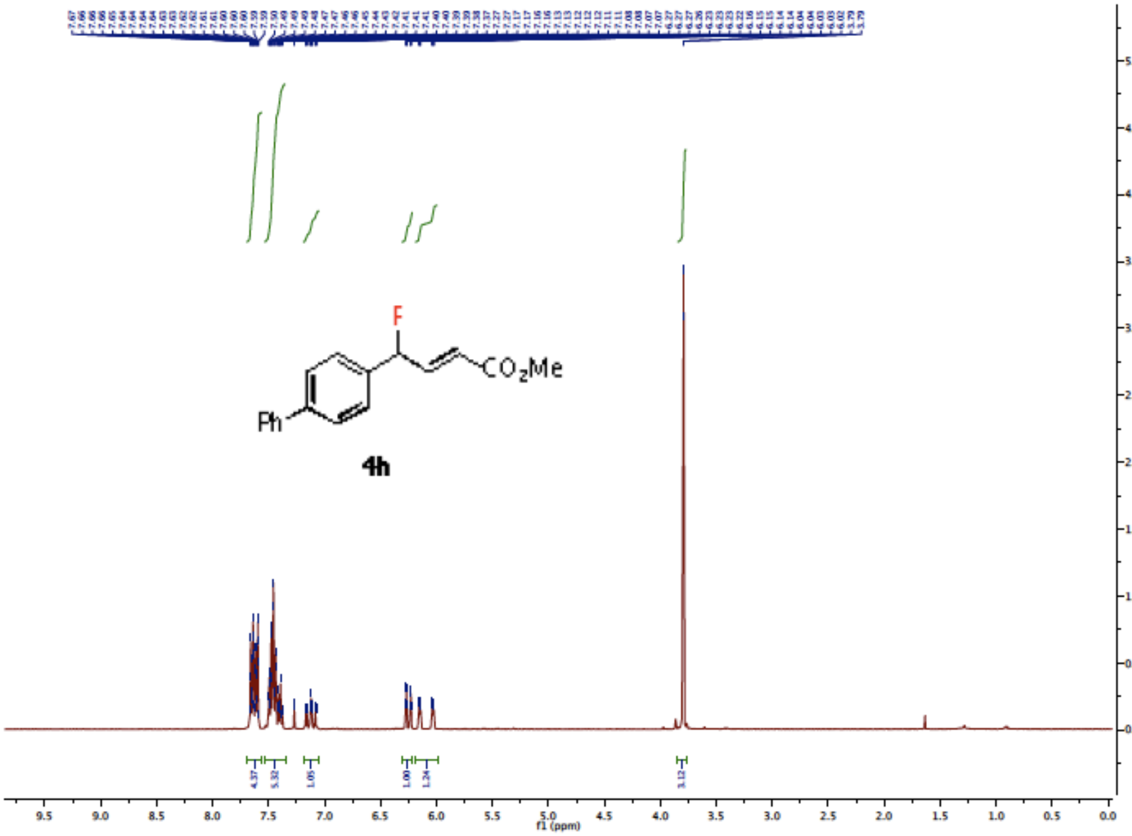
4f, crude NMR



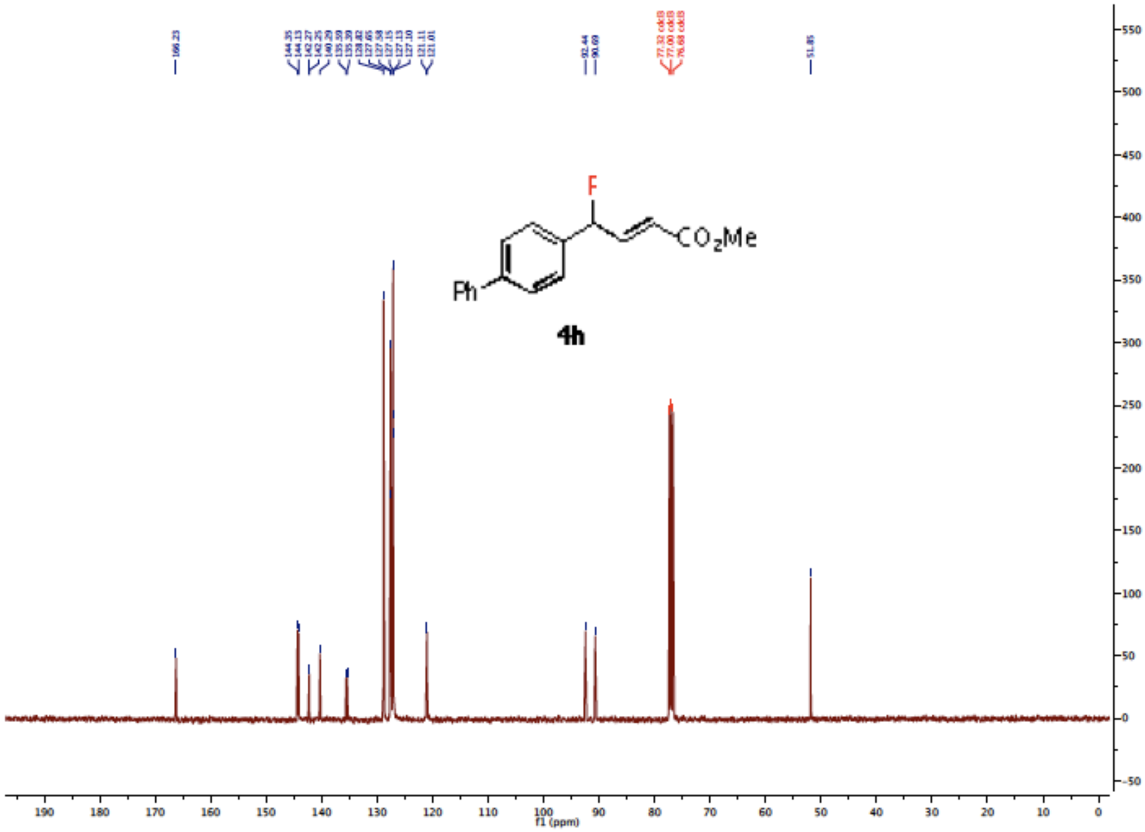
4f, crude NMR


7.39 7.39 7.38 7.37 7.37 7.37 7.37 7.35 7.33 7.33 7.33 7.31 7.31 7.27 7.17 7.15 7.15 7.13 7.12 7.10 7.08 7.07 7.07 7.06 7.05 7.04 7.04 7.04 7.03 7.03 7.03 7.03 7.02 7.02 7.02 6.23 6.22 6.22 6.19 6.19 6.18 6.08 6.07 6.06 6.06 5.96 5.95 5.95 5.94
3.78
F
CO2Me
PhO
4g
4.09
1.33
4.07
1.00
1.21
2.86
f1 (ppm)

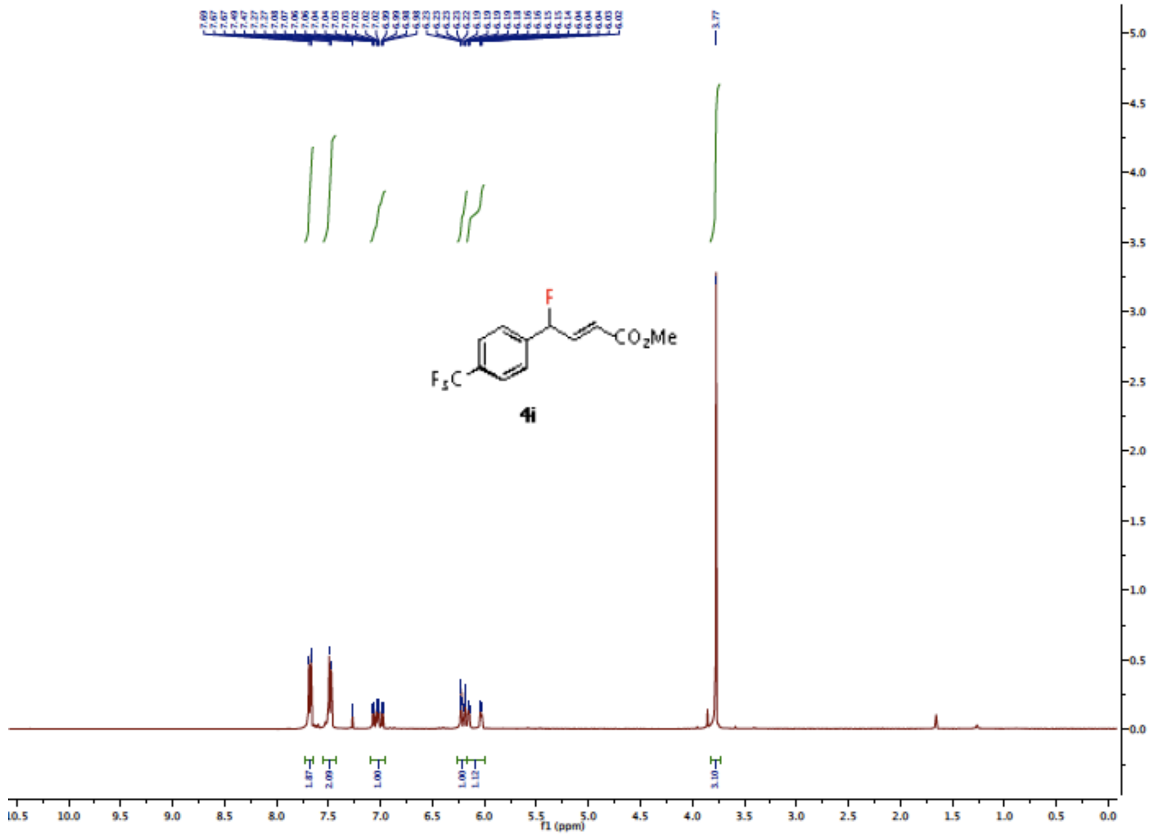

166.27
158.39
158.36
156.46
144.40
144.18
131.15
130.94
129.86
129.82
128.61
128.56
123.80
121.01
120.91
119.32
119.22
118.70
92.24
90.50
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.87
F
CO2Me
PhO
4g
f1 (ppm)

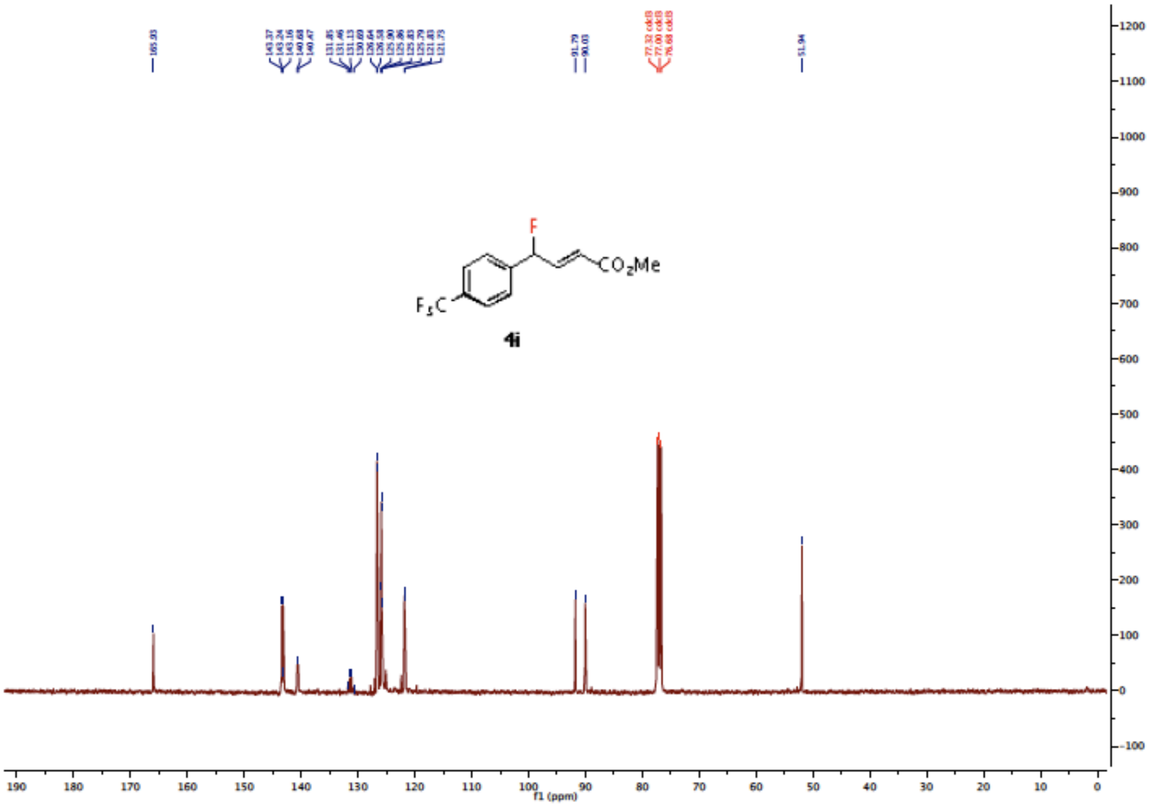

F
CO2Me
Ph
4.37
5.32
1.05
1.00
1.24
3.12
f1 (ppm)

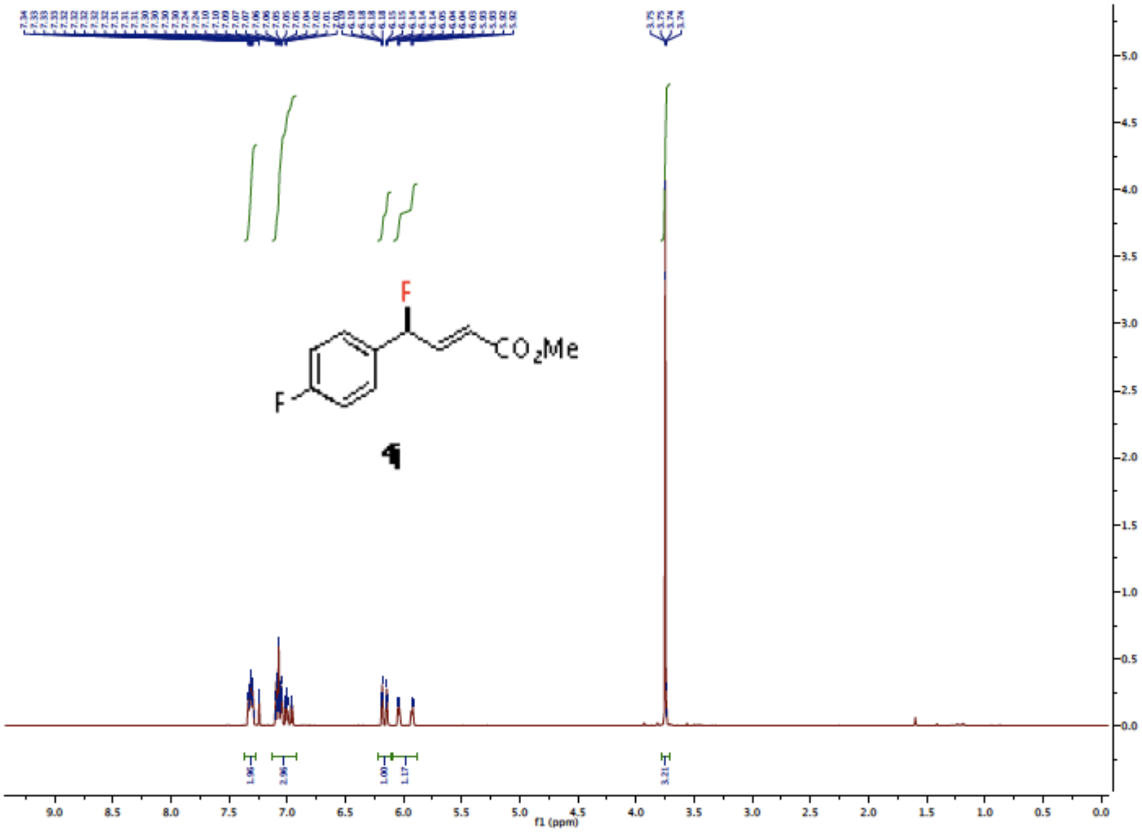
4h

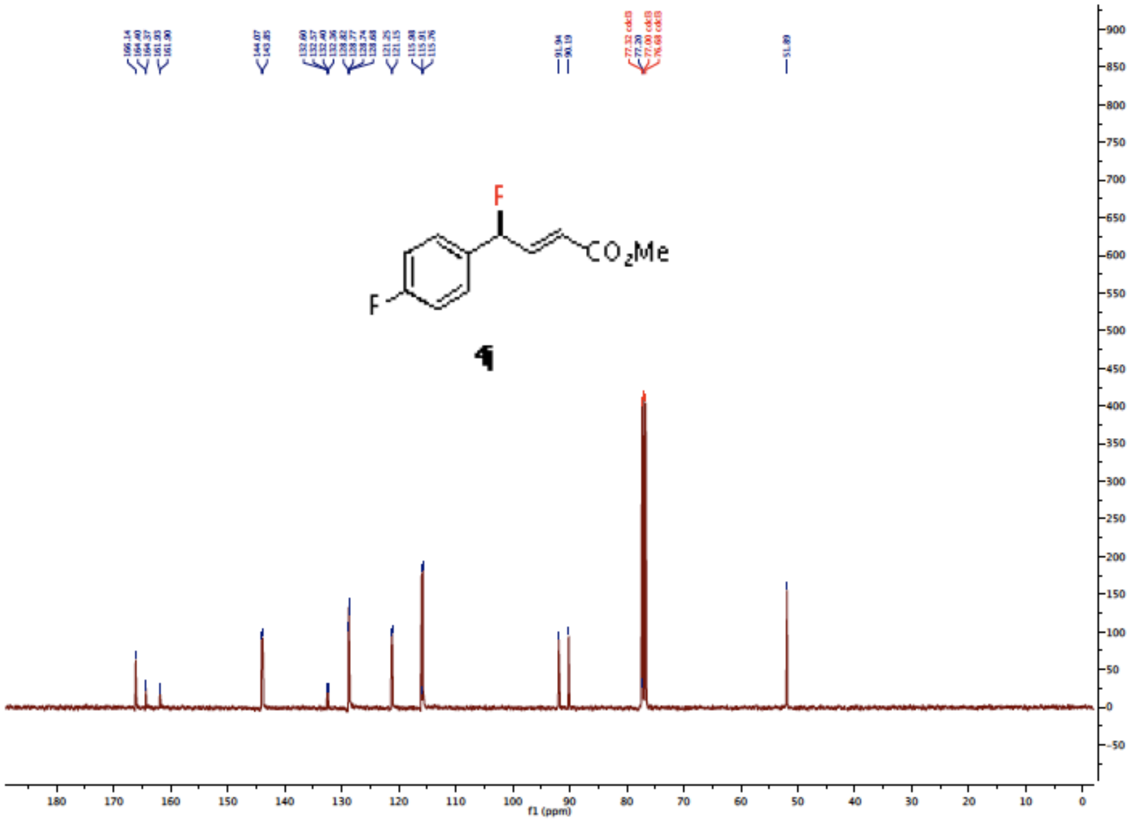

166.23
144.35
144.13
142.27
142.25
140.29
135.59
135.39
128.82
127.65
127.58
127.15
127.13
127.10
121.11
121.01
92.44
90.69
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.85
F
CO2Me
Ph
f1 (ppm)

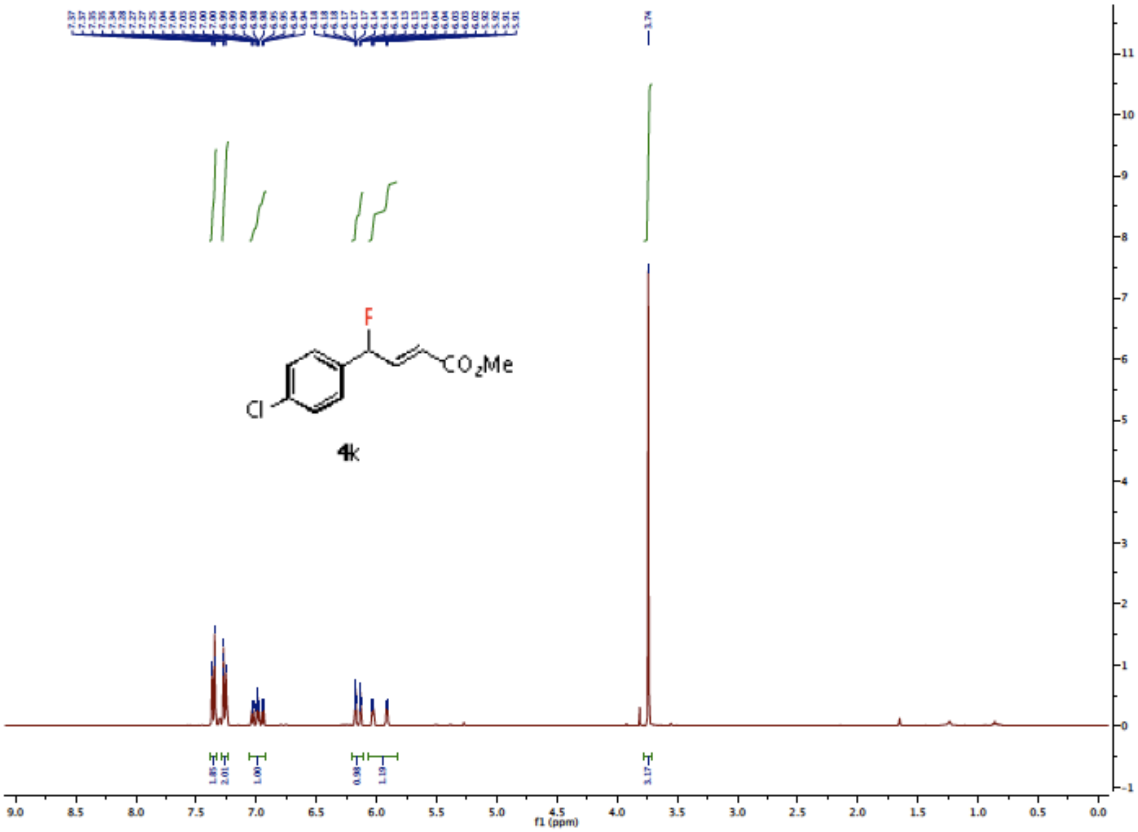
4h


7.69
7.67
7.49
7.47
7.27
7.08
7.07
7.06
7.04
7.04
7.03
7.03
7.02
7.02
6.99
6.99
6.98
6.98
6.23
6.23
6.23
6.22
6.19
6.19
6.19
6.18
6.16
6.16
6.15
6.15
6.14
6.04
6.04
6.04
6.03
6.02
3.77
F
CO2Me
F3C
4i
1.87
2.09
1.00
1.00
1.12
3.10
f1 (ppm)
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

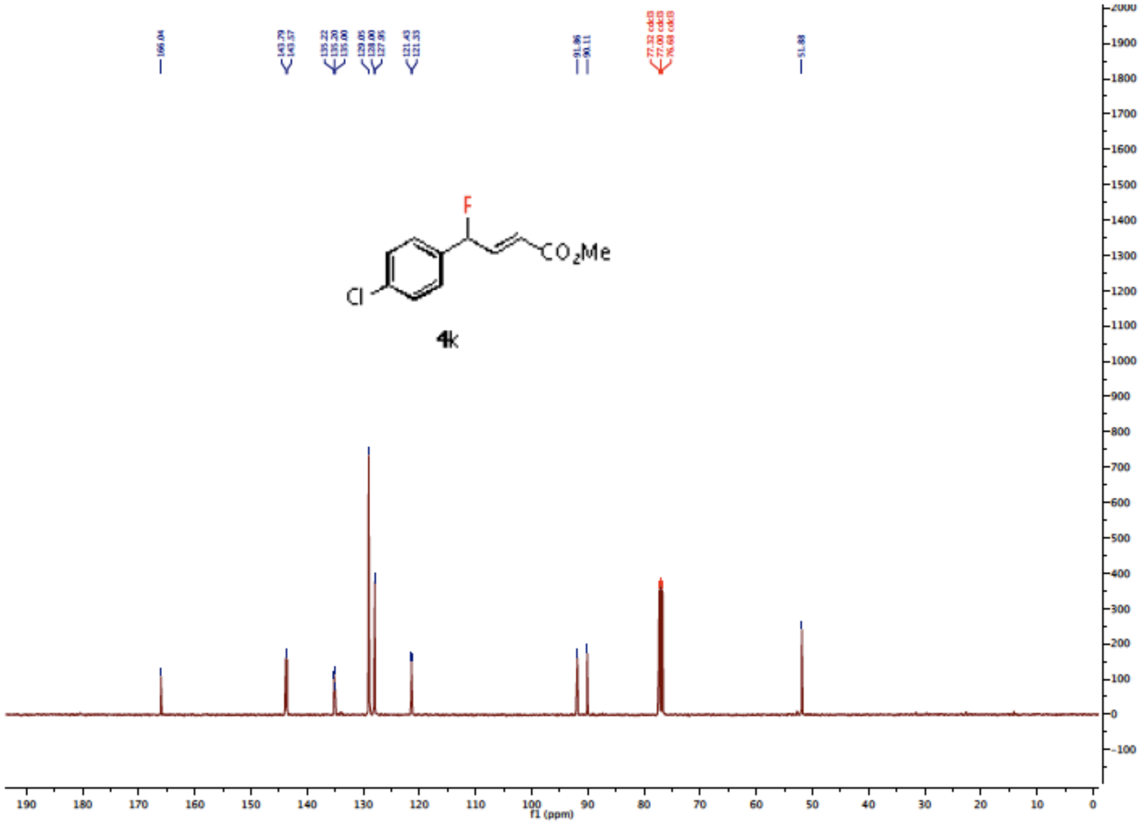

165.93
143.37
143.24
143.16
140.68
140.47
131.85
131.46
131.13
130.69
126.64
126.58
125.90
125.86
125.83
125.79
121.83
121.73
91.79
90.03
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.94
F
CO2Me
F3C
4i
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


7.34 7.33 7.33 7.32 7.32 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.30 7.24 7.24 7.10 7.10 7.09 7.07 7.07 7.06 7.06 7.05 7.05 7.05 7.04 7.02 7.01 7.01 6.19 6.19 6.18 6.18 6.18 6.15 6.15 6.14 6.14 6.14 6.05 6.04 6.04 6.03 5.93 5.93 5.92 5.92
3.75 3.75 3.74 3.74
F
CO$_2$Me
F
4l
1.96
2.96
1.00
1.17
3.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


166.14 164.40 164.37 161.93 161.90
144.07 143.85
132.60 132.57 132.40 132.36 128.82 128.77 128.74 128.68
121.25 121.15
115.98 115.91 115.76
91.94 90.19
77.32 cdcl3 77.20 77.00 cdcl3 76.68 cdcl3
51.89
F
CO$_2$Me
F
4l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50


7.37
7.37
7.35
7.35
7.34
7.28
7.27
7.27
7.25
7.04
7.04
7.03
7.03
7.00
6.99
6.99
6.98
6.98
6.95
6.95
6.94
6.94
6.18
6.18
6.17
6.17
6.14
6.14
6.13
6.13
6.04
6.04
6.03
6.02
5.92
5.92
5.91
5.91
3.74
F
CO2Me
Cl
1.85
2.01
1.00
0.98
1.19
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
11
10
9
8
7
6
5
4
3
2
1
0
-1

4k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143.79
143.57
135.22
135.20
135.00
129.05
128.00
127.95
121.43
121.33
91.86
90.11
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.88
F
CO2Me
Cl
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
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500
400
300
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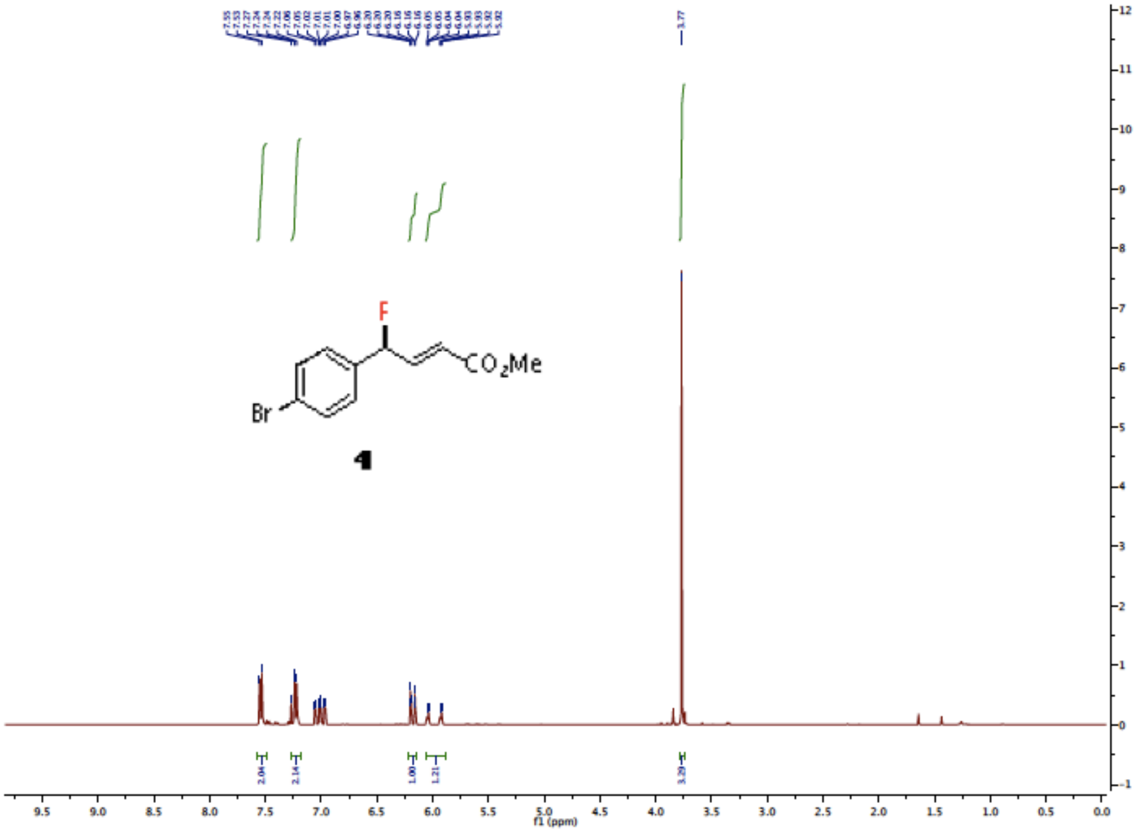
100
0
-100

4k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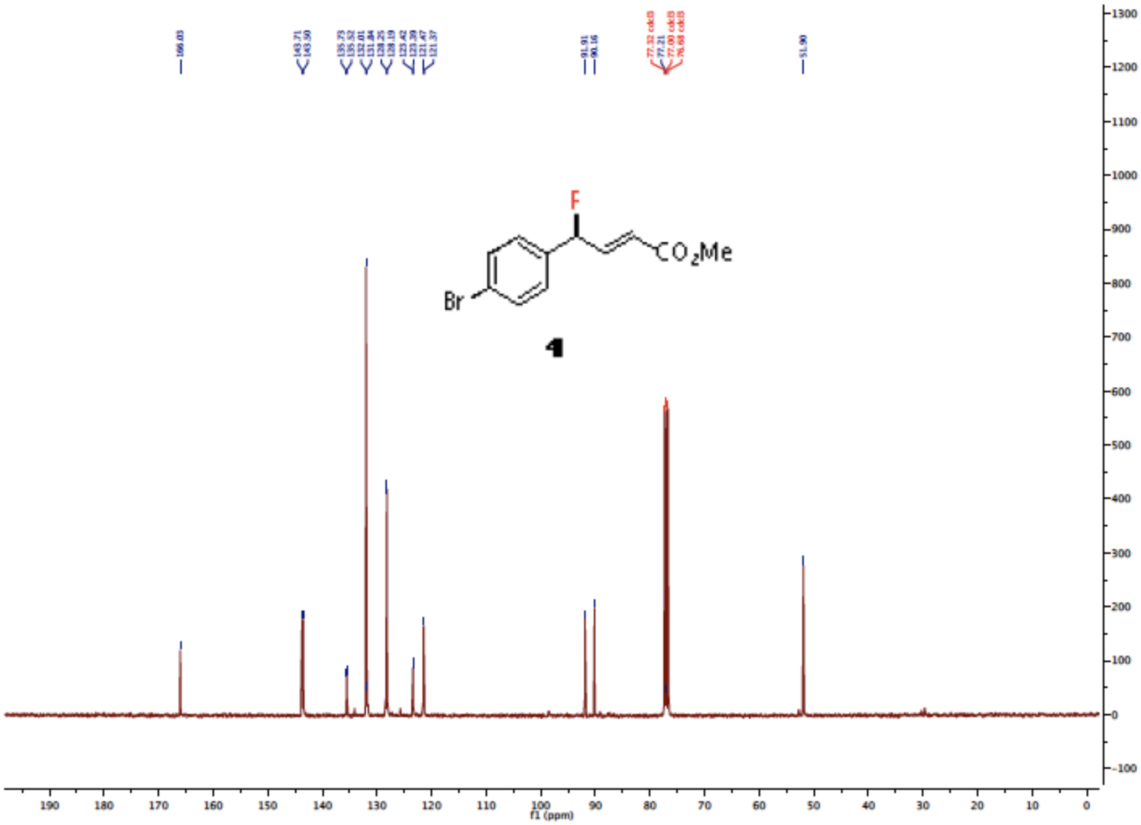
7.22
7.06
7.05
7.02
7.01
7.01
7.00
6.97
6.96
6.20
6.20
6.20
6.16
6.16
6.16
6.05
6.05
6.04
6.04
5.93
5.93
5.92
5.92
3.77
F
Br
CO2Me
4
2.04
2.14
1.00
1.21
3.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
-1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143.71
143.50
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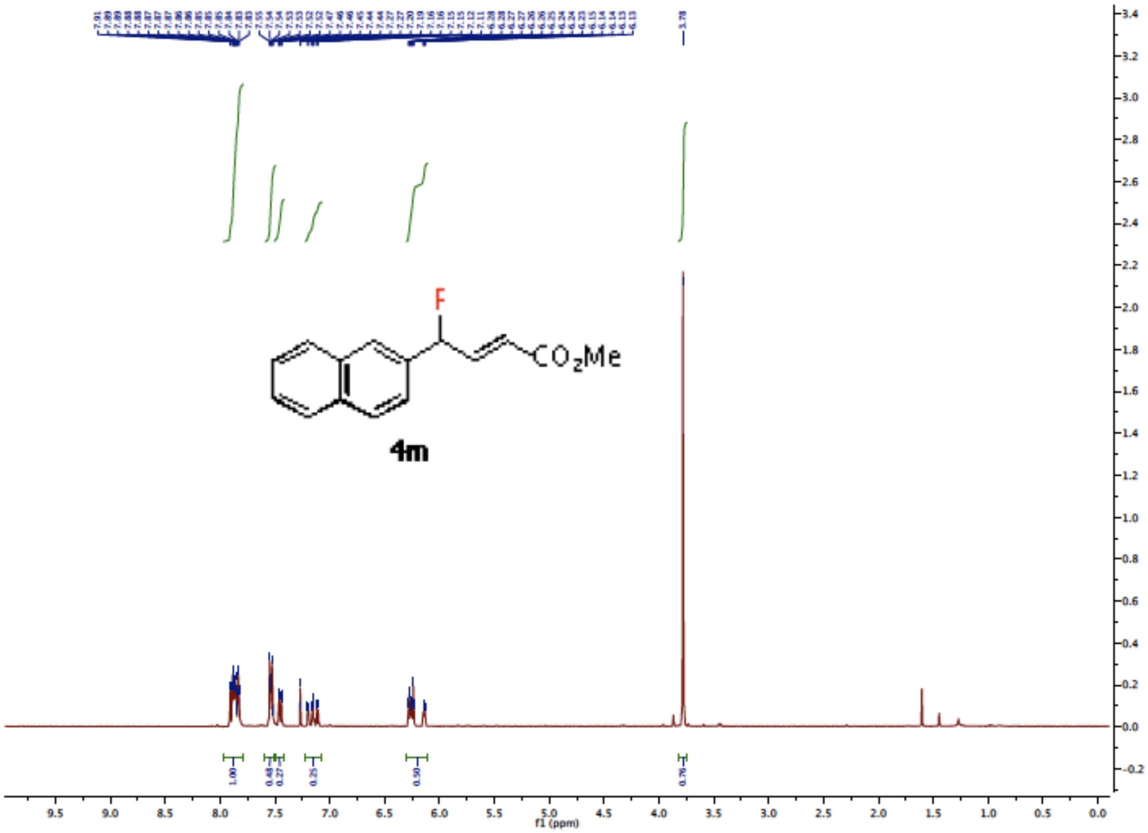
132.01
131.84
128.25
128.19
123.42
123.39
121.47
121.37
91.91
90.16
77.32 cdcl3
77.21
77.00 cdcl3
76.68 cdcl3
51.90
F
Br
CO2Me
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


7.91
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7.89
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7.87
7.87
7.86
7.86
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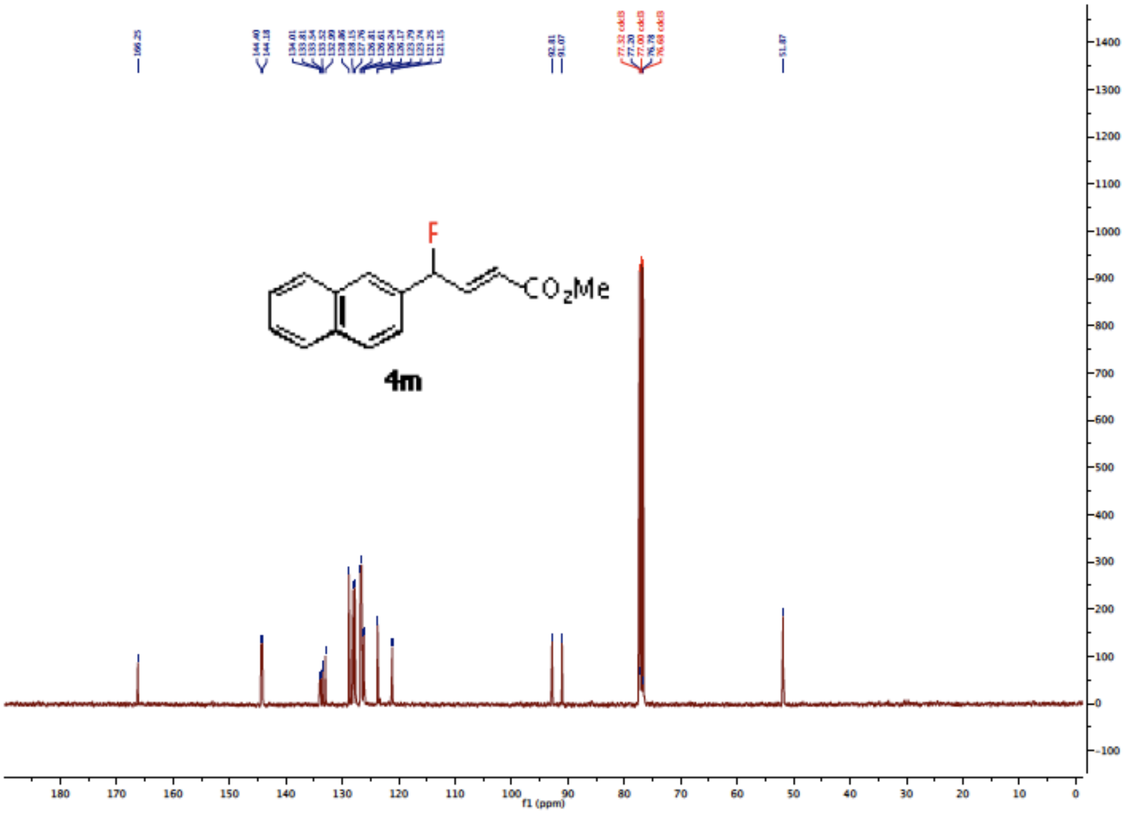
7.85
7.85
7.84
7.83
7.83
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.47
7.46
7.46
7.45
7.44
7.44
7.27
7.27
7.20
7.19
7.16
7.16
7.15
7.15
7.12
7.11
6.28
6.28
6.27
6.27
6.26
6.26
6.25
6.24
6.24
6.23
6.15
6.14
6.14
6.13
6.13
3.78
F
CO2Me
4m
1.00
0.48
0.27
0.25
0.50
0.76
f1 (ppm)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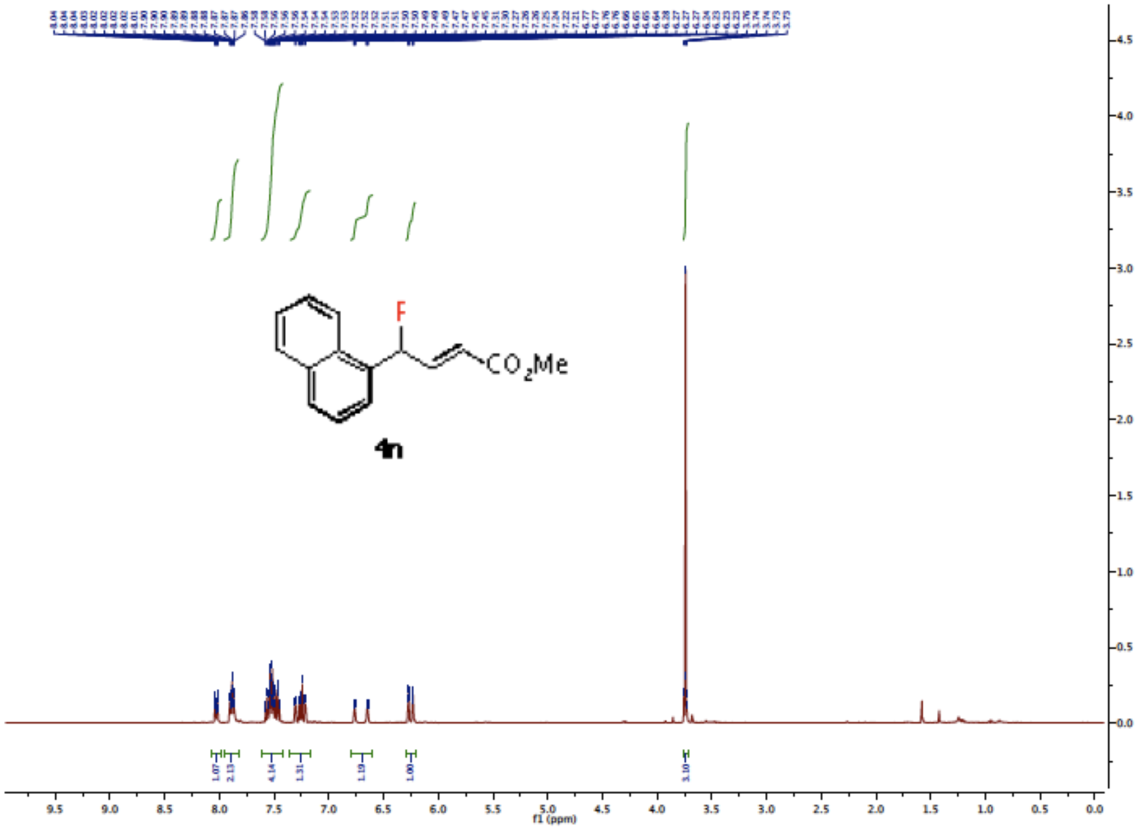
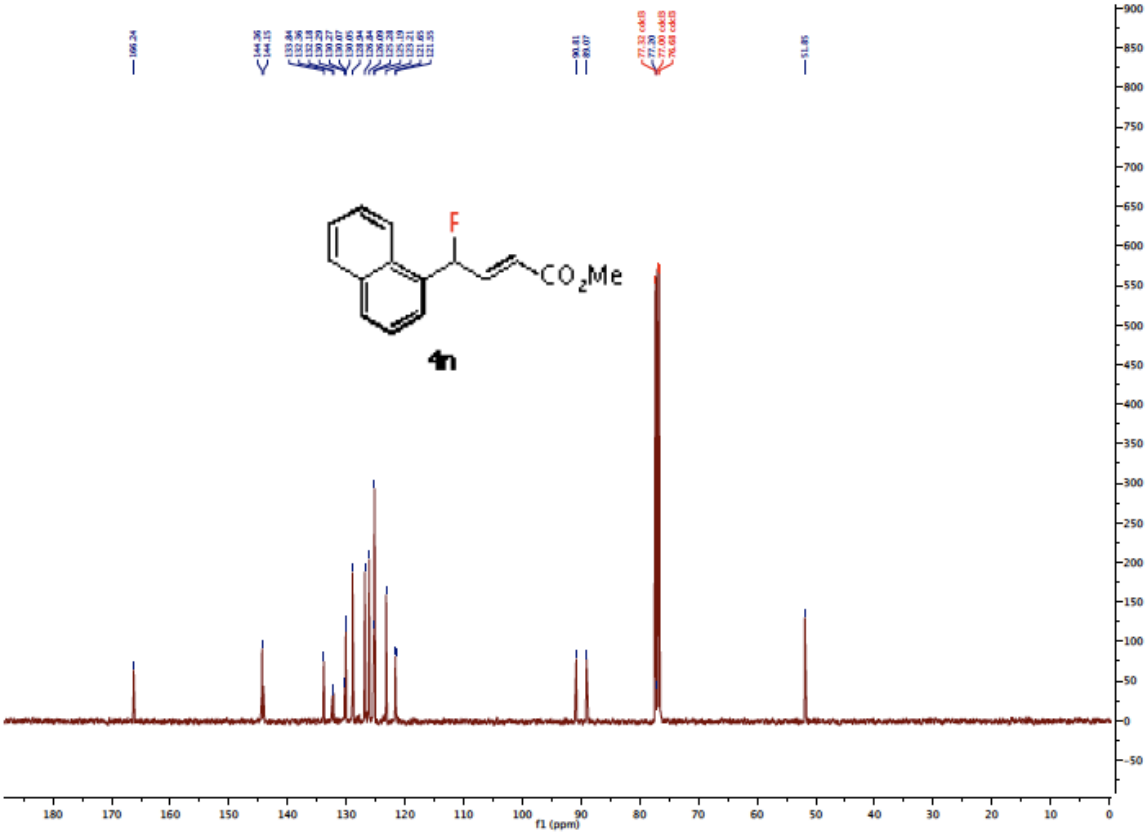
133.54
133.52
132.99
128.86
128.15
127.76
126.81
126.61
126.24
126.17
123.79
123.74
121.25
121.15
92.81
91.07
77.32 cdcl3
77.20
77.00 cdcl3
76.78
76.68 cdcl3
51.87
F
CO2Me
4m
f1 (ppm)



8.04
8.04
8.04
8.03
8.02
8.02
8.02
8.01
7.90
7.90
7.90
7.89
7.89
7.88
7.88
7.87
7.87
7.87
7.86
7.58
7.58
7.56
7.56
7.56
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.47
7.47
7.45
7.31
7.30
7.27
7.26
7.26
7.25
7.24
7.22
7.21
6.77
6.77
6.76
6.76
6.69
6.65
6.65
6.64
6.28
6.27
6.27
6.24
6.23
6.23
3.76
3.74
3.74
3.73
F
CO2Me
4n
1.07
2.13
4.14
1.31
1.19
1.00
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



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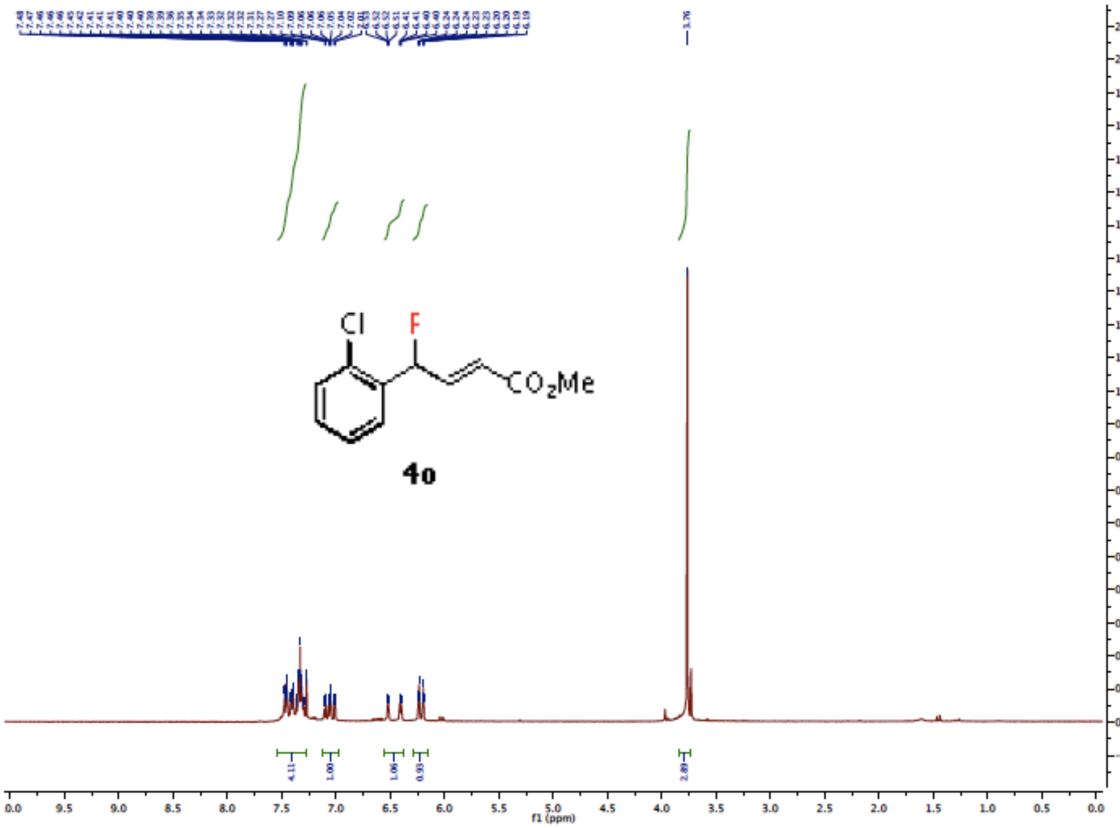
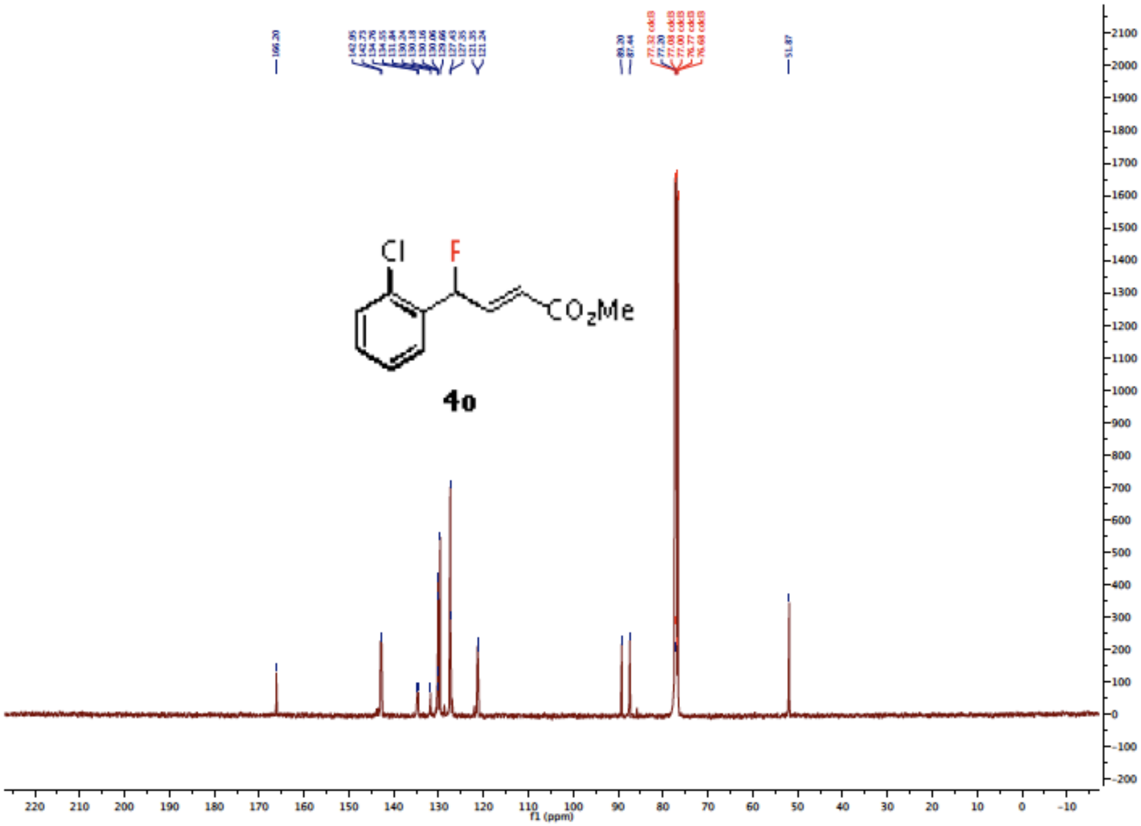
144.36
144.15
133.84
132.36
132.18
130.29
130.27
130.07
130.05
128.94
126.84
126.09
125.28
125.19
123.21
121.65
121.55
90.81
89.07
77.32 cdcl3
77.20
77.00 cdcl3
76.68 cdcl3
51.85
F
CO2Me
4n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50



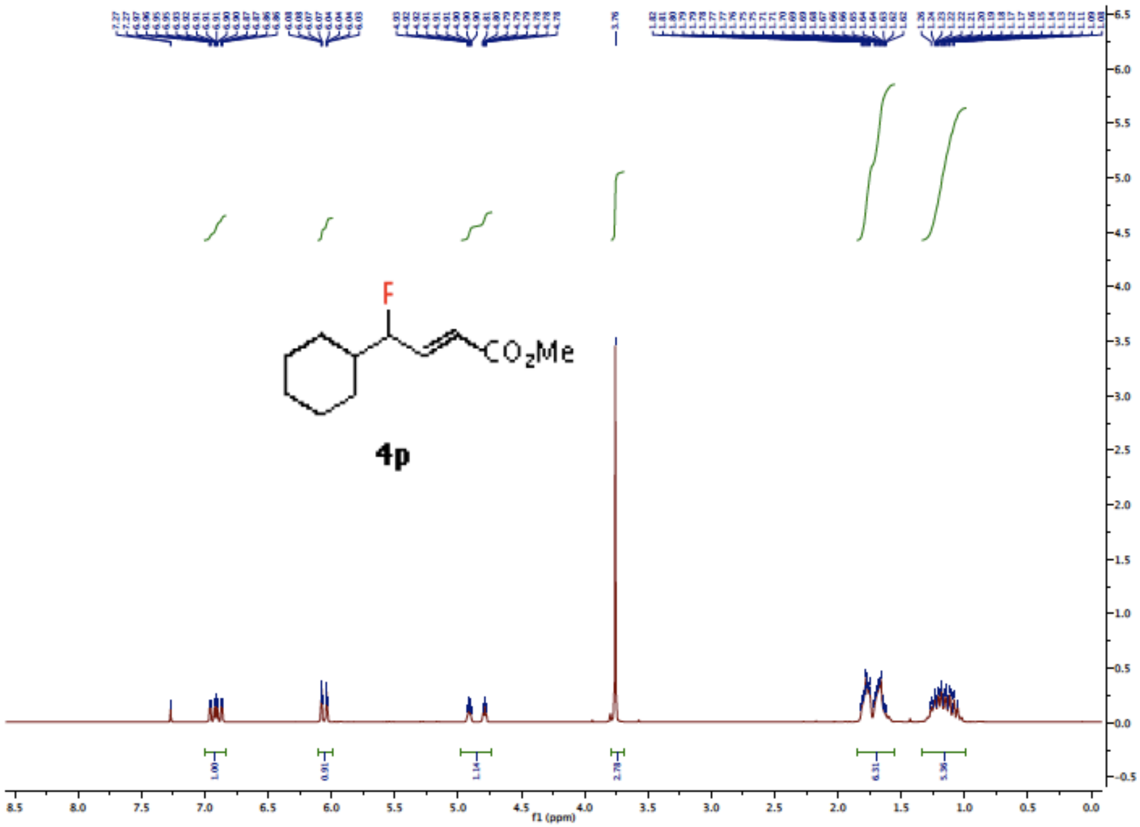
7.48
7.47
7.46
7.46
7.45
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.27
7.10
7.09
7.06
7.06
7.05
7.04
7.02
7.01
6.53
6.52
6.51
6.41
6.41
6.40
6.40
6.24
6.24
6.23
6.20
6.19
6.19
3.76
Cl
F
CO2Me
4.11
1.00
1.06
0.93
2.89
f1 (ppm)

4o

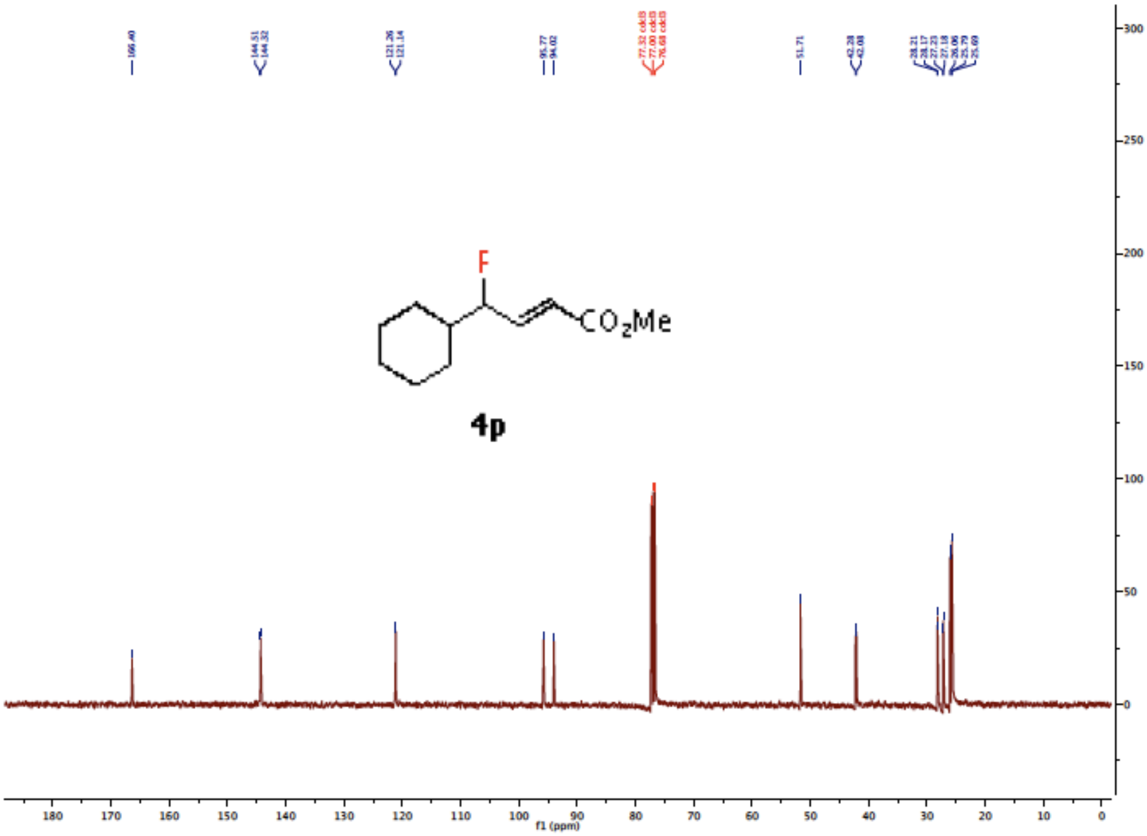


166.20
142.95
142.75
134.76
134.55
131.44
130.24
130.18
130.16
130.06
129.66
127.43
127.35
121.35
121.24
89.20
87.44
77.32 cdcl3
77.20
77.08 cdcl3
77.00 cdcl3
76.77 cdcl3
76.68 cdcl3
51.87
Cl
F
CO2Me
f1 (ppm)

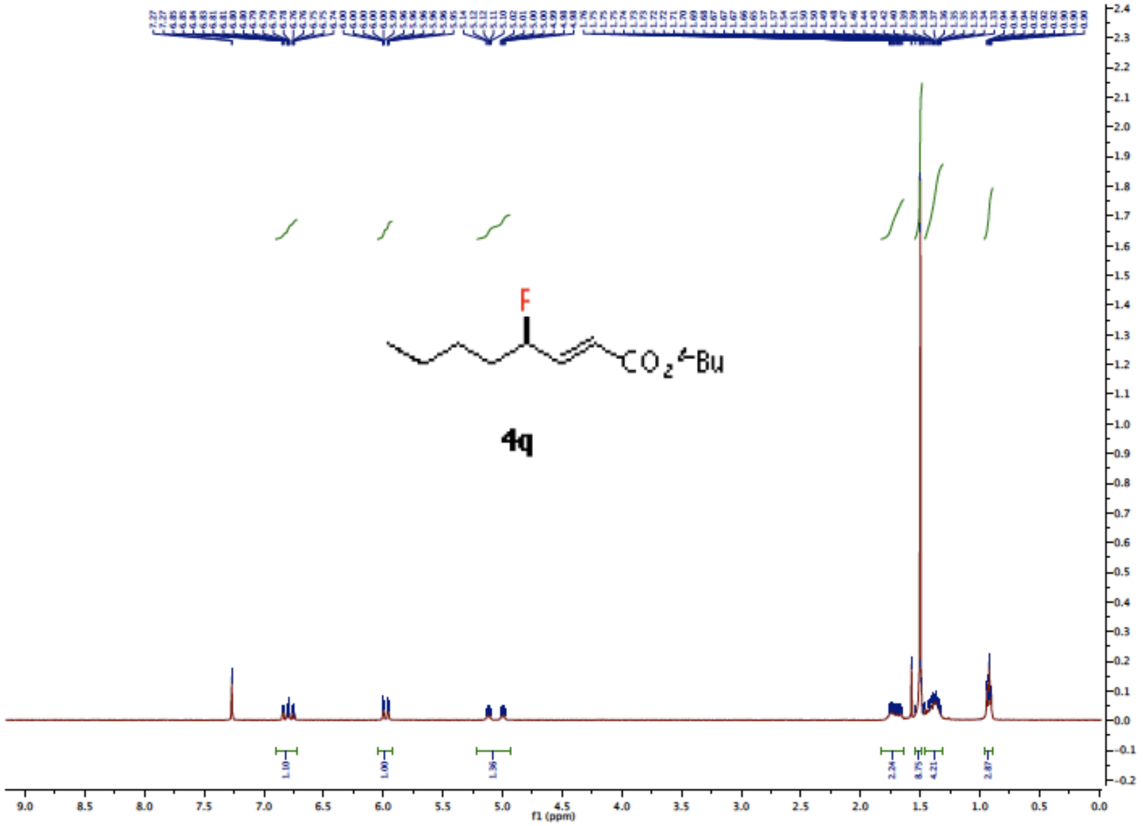
4o

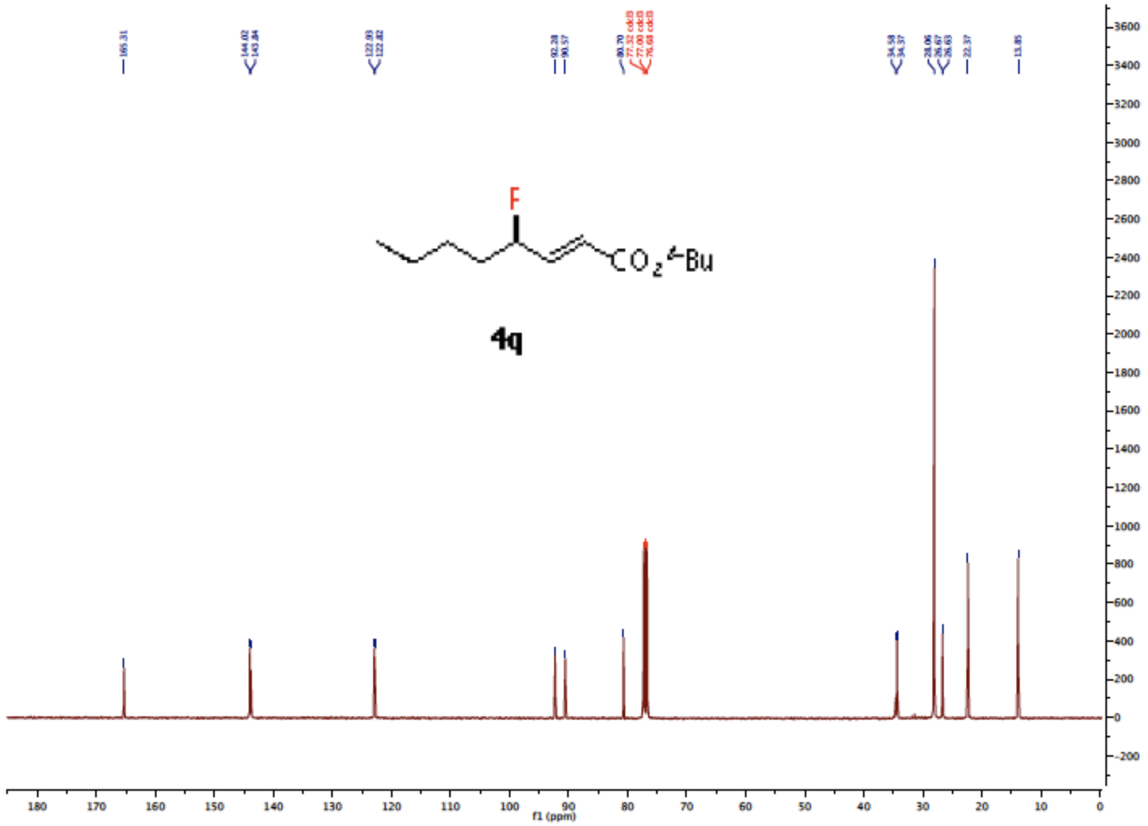

3.76
F
CO2Me
1.00
0.91
1.14
2.78
6.31
5.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

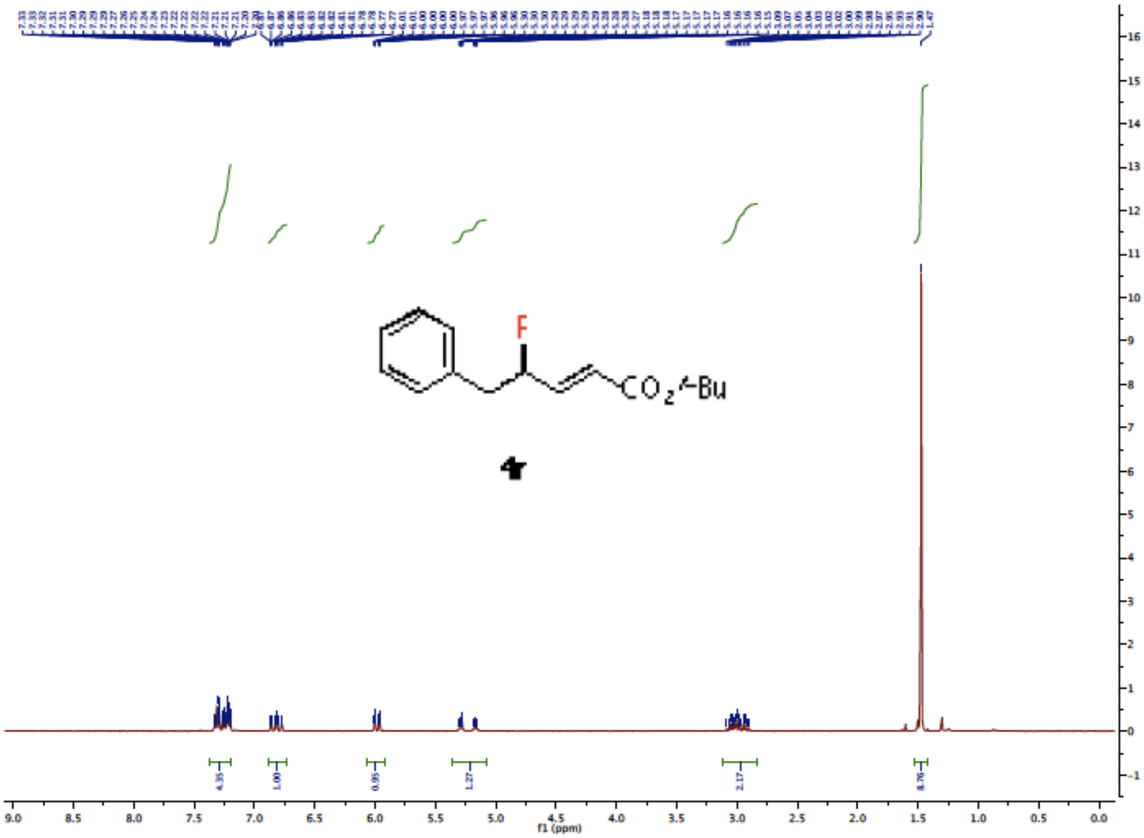
4p


166.40
144.51
144.32
121.26
121.14
95.77
94.02
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.71
42.28
42.08
28.21
28.17
27.23
27.18
26.06
25.79
25.69
F
CO2Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
300
250
200
150
100
50
0

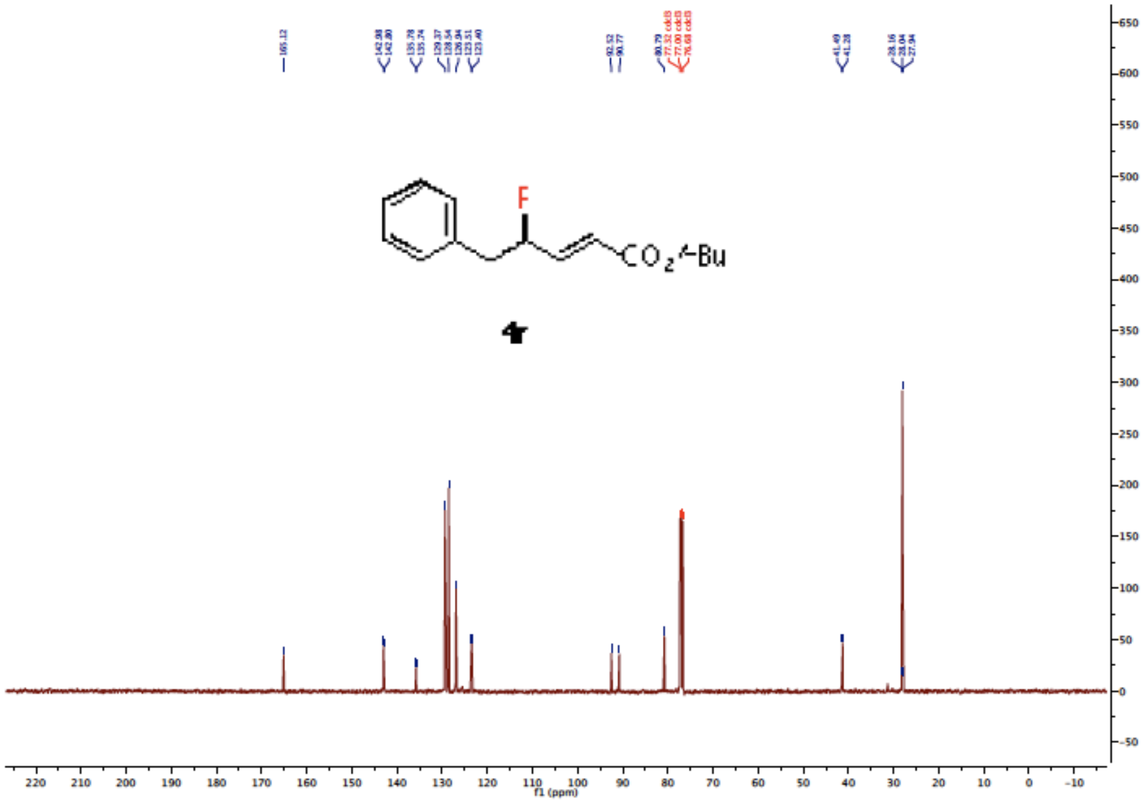
4p


4q
CO2tBu
F
1.10
1.00
1.98
2.24
8.75
4.21
2.87
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


4q
165.31
144.02
143.84
122.93
122.82
92.28
90.57
80.70
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
34.58
34.37
28.06
26.67
26.63
22.37
13.85
CO2tBu
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



7.33
1.47
F
CO2t-Bu
4r
4.35
1.00
0.95
1.27
2.17
8.76
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1



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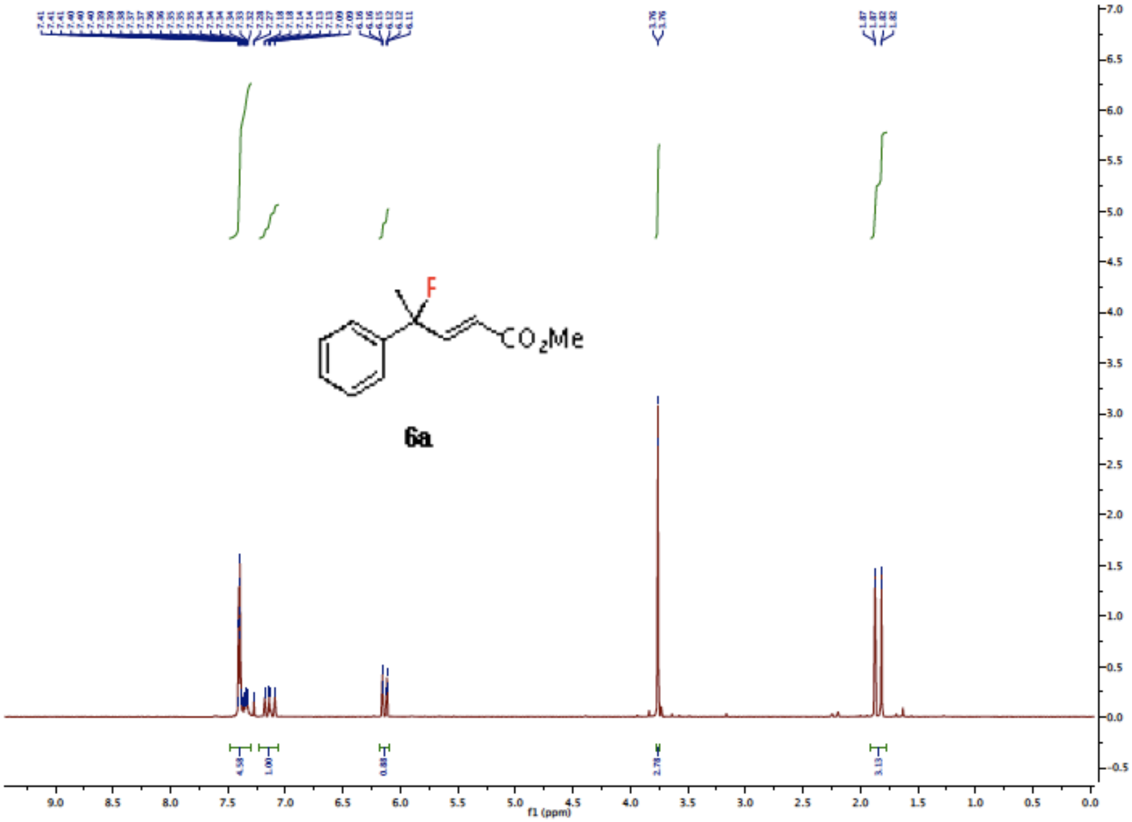
142.98
142.80
135.78
135.74
129.37
128.34
126.94
123.51
123.40
92.52
90.77
80.79
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
41.49
41.28
28.16
28.04
27.94
F
CO2t-Bu
4r
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50


6a

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7.41
7.41
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7.40
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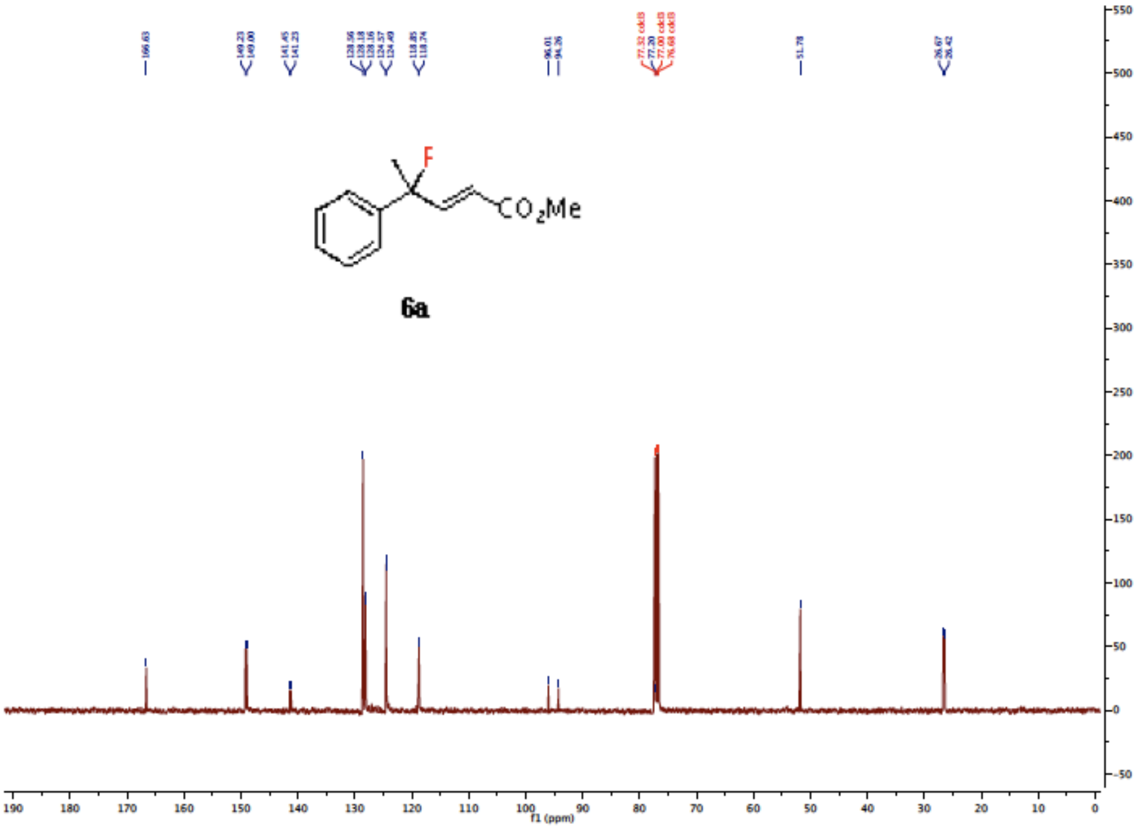
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.28
7.27
7.18
7.18
7.14
7.13
7.13
7.09
6.16
6.16
6.15
6.12
6.12
6.11
3.76
3.76
1.87
1.87
1.82
1.82
F
CO2Me
4.58
1.00
0.88
2.78
3.13
f1 (ppm)


6a

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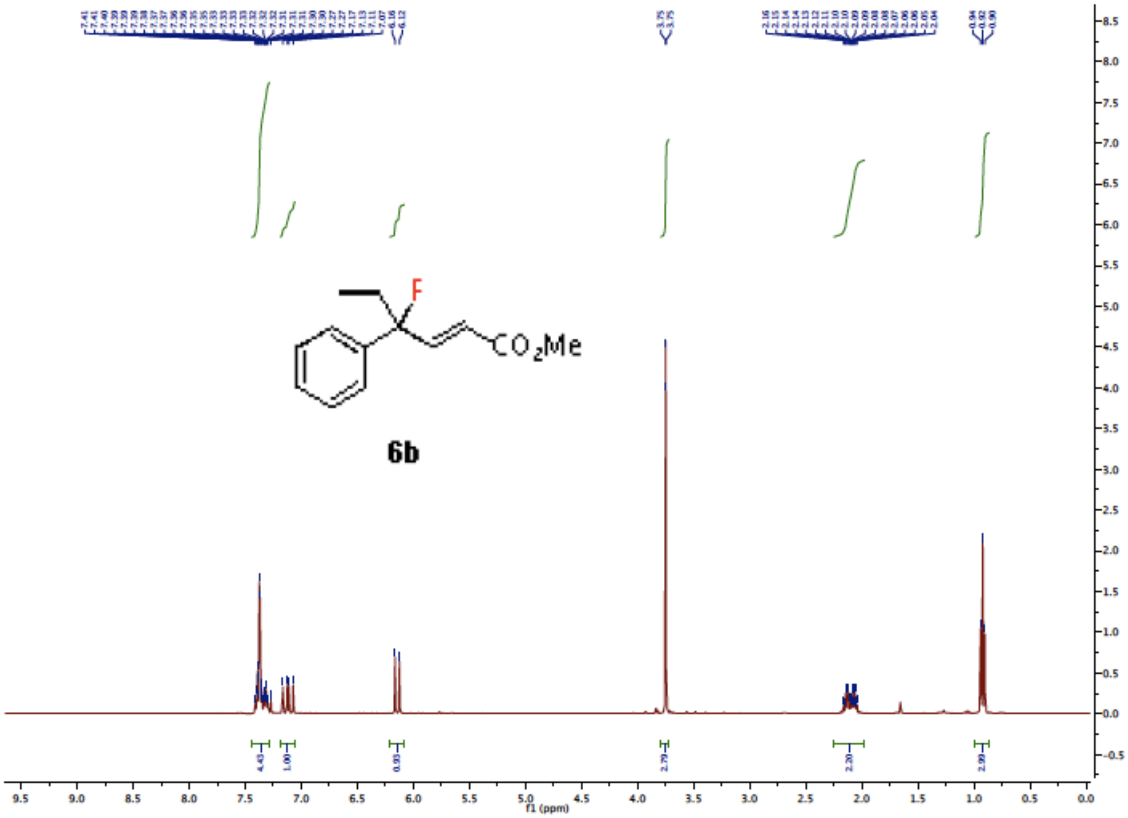
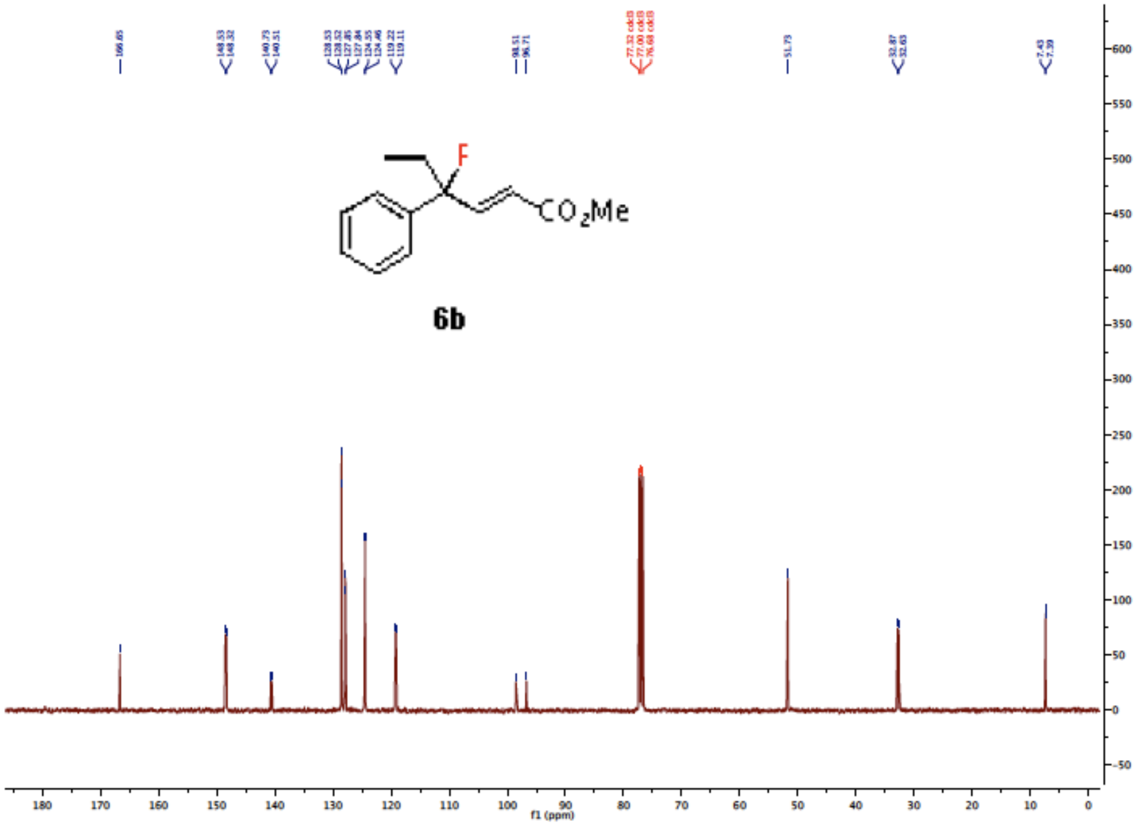
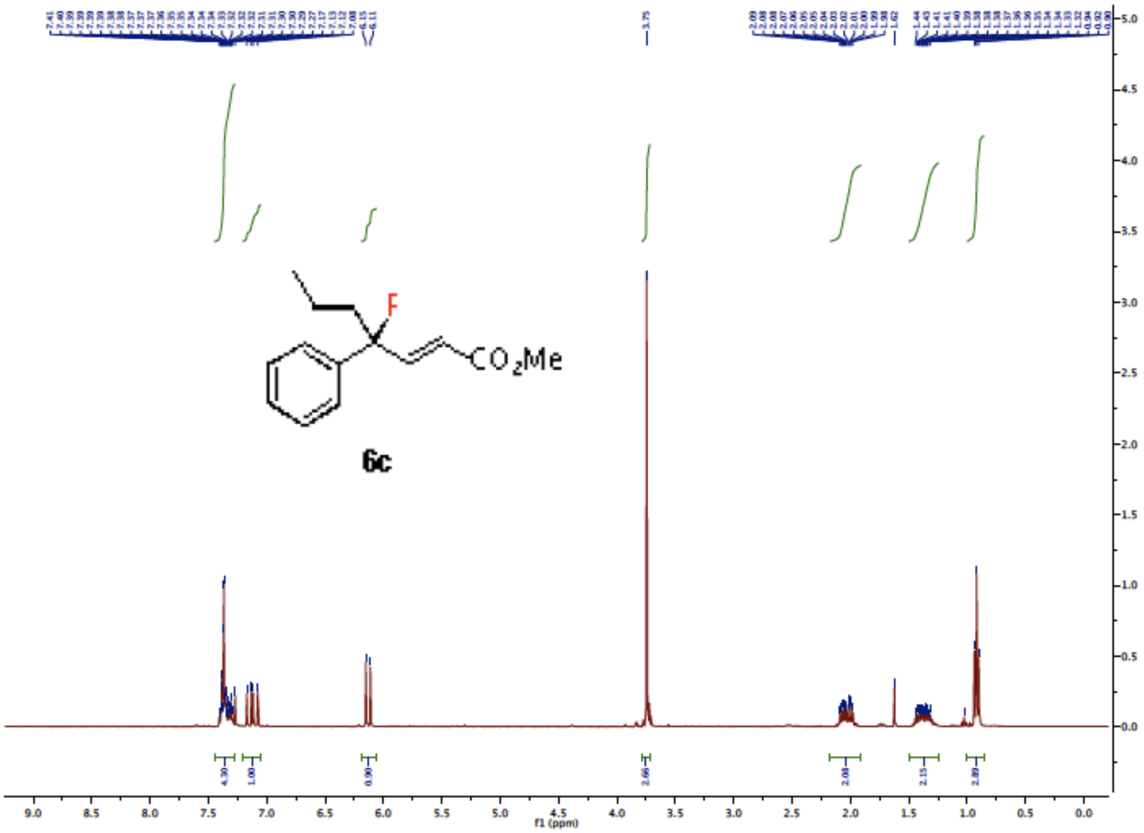
149.00
141.45
141.23
128.56
128.18
128.16
124.57
124.49
118.85
118.74
96.01
94.26
77.32 cdcl3
77.20
77.00 cdcl3
76.68 cdcl3
51.78
26.67
26.42
F
CO2Me
f1 (ppm)



7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.27 7.17 7.13 7.11 7.07 6.16 6.12
3.75 3.75
2.16 2.15 2.14 2.13 2.12 2.11 2.10 2.09 2.09 2.08 2.08 2.07 2.06 2.05 2.04
0.94 0.92 0.90
F
CO2Me
6b
4.43
1.00
0.93
2.79
2.20
2.99
f1 (ppm)



166.65
148.53 148.32
140.73 140.51
128.53 128.52 127.86 127.84 124.55 124.46 119.22 119.11
98.51 96.71
77.32 cdcl3 77.00 cdcl3 76.68 cdcl3
51.73
32.87 32.63
7.43 7.39
F
CO2Me
6b
f1 (ppm)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7.32
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7.17
7.13
7.12
7.08
6.15
6.11
3.75
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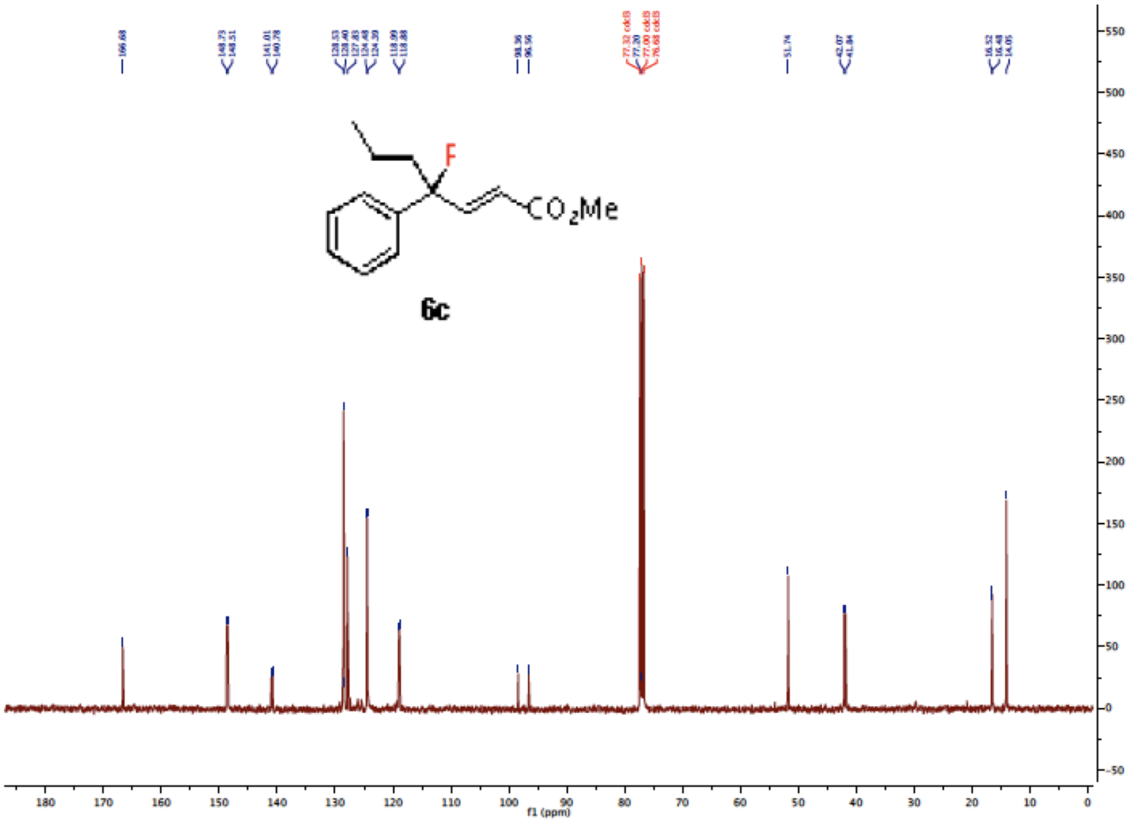
2.07
2.06
2.05
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.62
1.44
1.43
1.41
1.41
1.40
1.39
1.38
1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.04
0.92
0.90
F
CO2Me
6c
4.30
1.00
0.90
2.66
2.08
2.15
2.89
f1 (ppm)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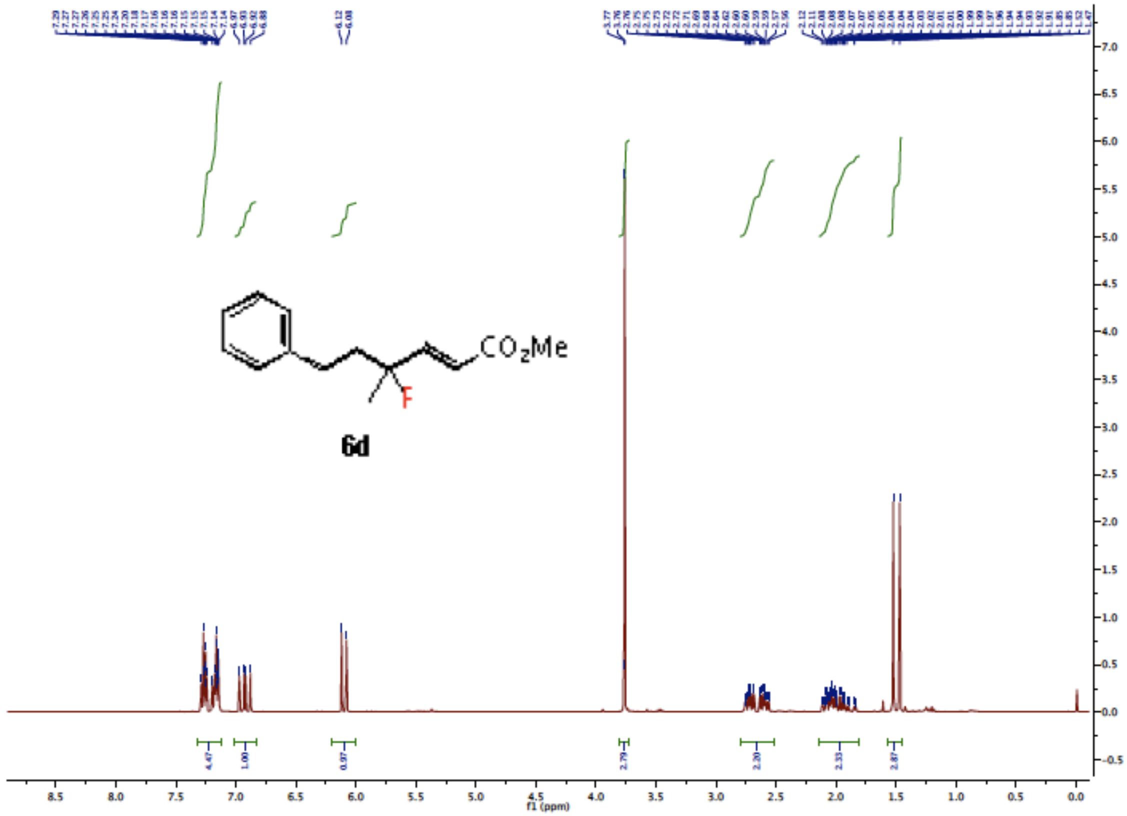
127.83
124.48
124.39
118.99
118.88
98.36
96.56
77.32 cdcl3
77.20
77.00 cdcl3
76.68 cdcl3
51.74
42.07
41.84
16.52
16.48
14.05
F
CO2Me
6c
f1 (ppm)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7.18
7.17
7.16
7.16
7.16
7.15
7.15
7.15
7.14
7.14
6.97
6.93
6.92
6.88
6.12
6.08
3.77
3.76
3.76
2.75
2.75
2.73
2.72
2.72
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2.69
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2.60
2.59
2.59
2.57
2.56
2.12
2.11
2.08
2.08
2.08
2.07
2.07
2.05
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2.04
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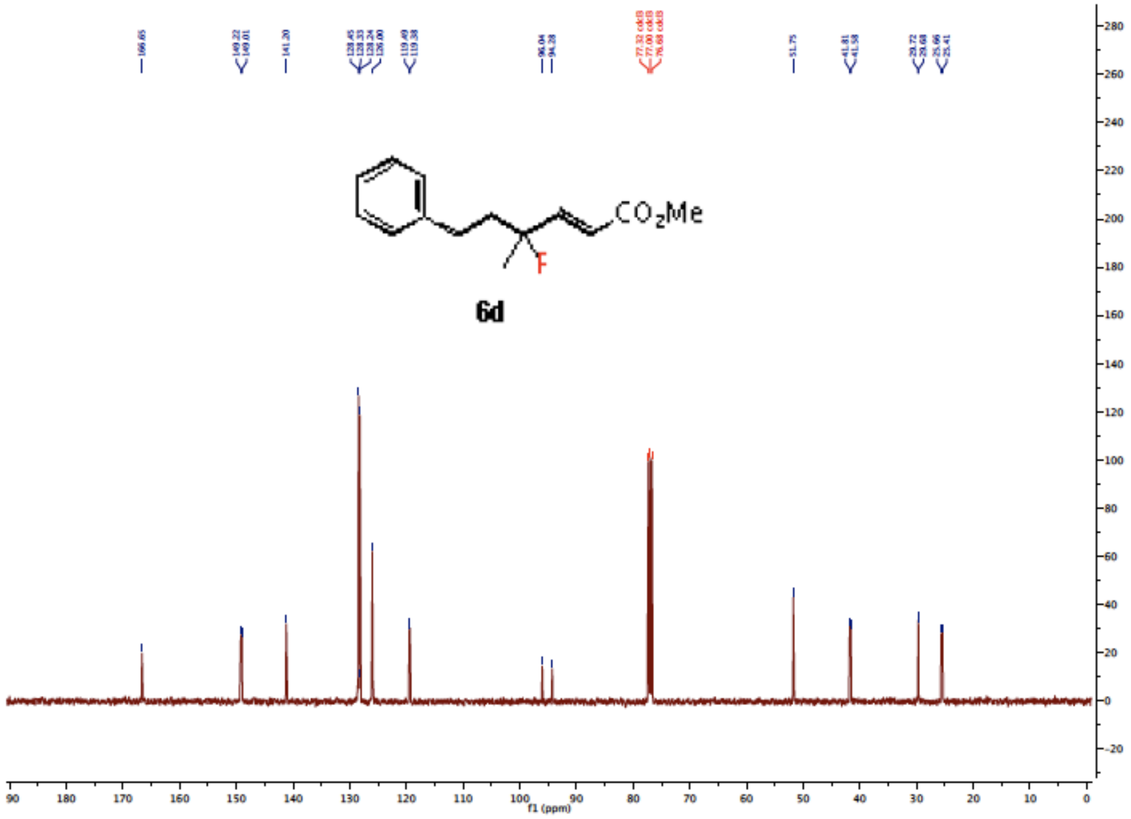
1.99
1.97
1.96
1.94
1.94
1.93
1.92
1.91
1.85
1.85
1.52
1.47
CO2Me
F
6d
4.47
1.00
0.97
2.79
2.20
2.33
2.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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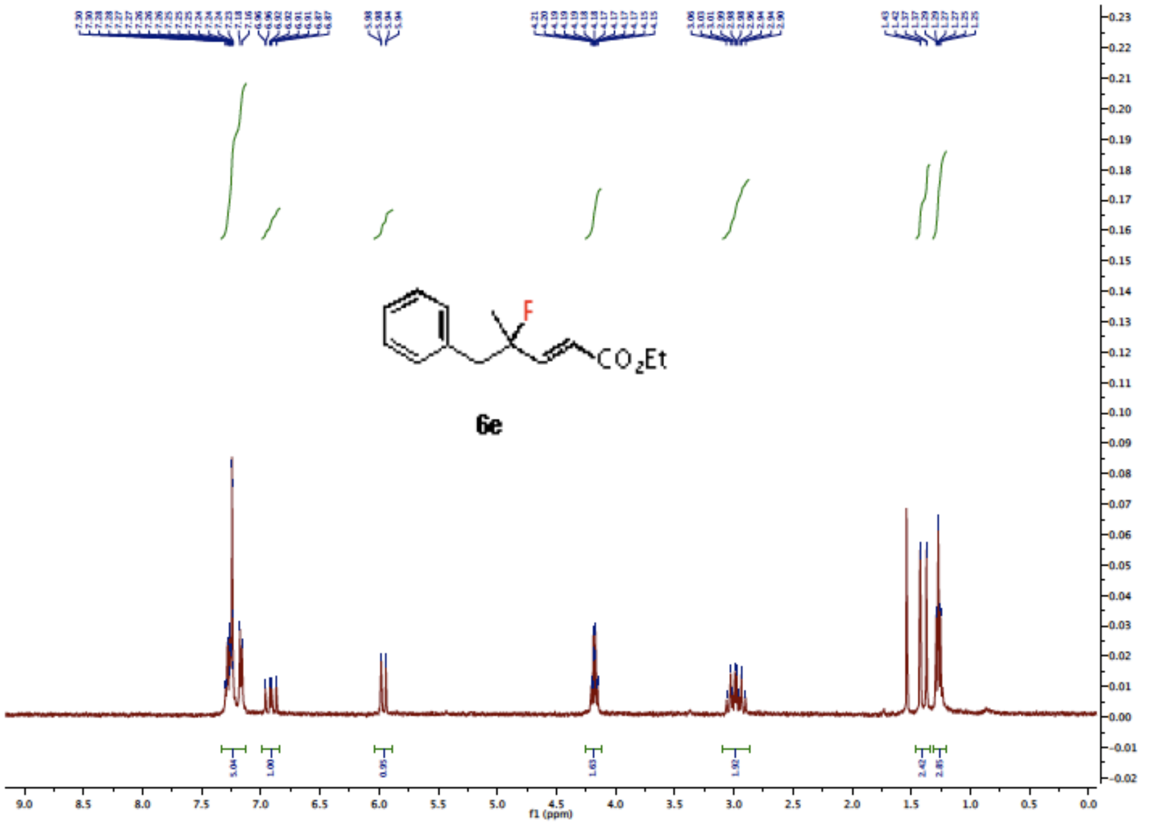
149.22
149.01
141.20
128.45
128.33
128.24
126.00
119.49
119.38
96.04
94.28
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.75
41.81
41.58
29.72
29.68
25.66
25.41
CO2Me
F
6d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20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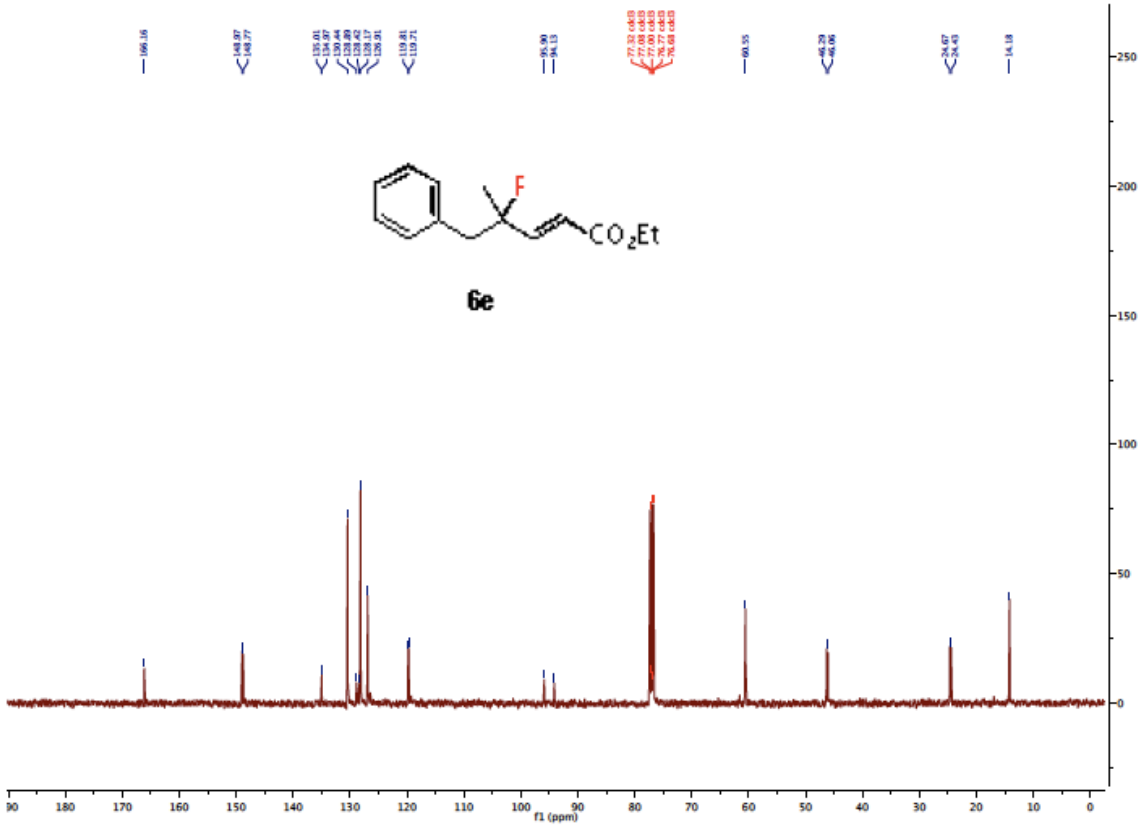
5.98 5.98 5.94 5.94
4.21 4.20 4.19 4.19 4.18 4.18 4.17 4.17 4.17 4.17 4.15 4.15
3.06 3.03 3.01 2.99 2.98 2.98 2.96 2.94 2.94 2.90
1.43 1.42 1.37 1.37 1.29 1.29 1.27 1.27 1.25 1.25
F
CO2Et
5.04
1.00
0.95
1.63
1.92
2.42
2.85
f1 (ppm)

6e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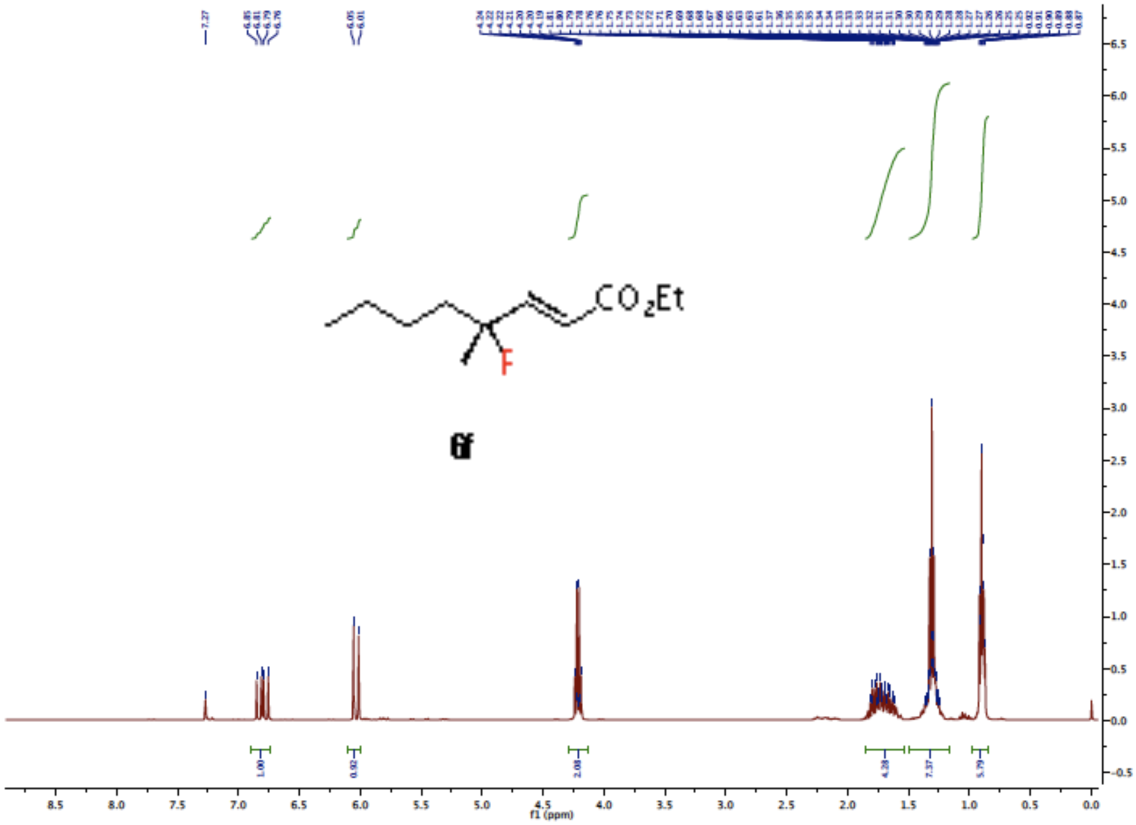
148.97 148.77
135.01 134.97 130.44 128.89 128.42 128.17 126.91
119.81 119.71
95.90 94.13
77.32 cdcl3 77.08 cdcl3 77.00 cdcl3 76.77 cdcl3 76.68 cdcl3
60.55
46.29 46.06
24.67 24.43
14.18
F
CO2Et
f1 (ppm)

6e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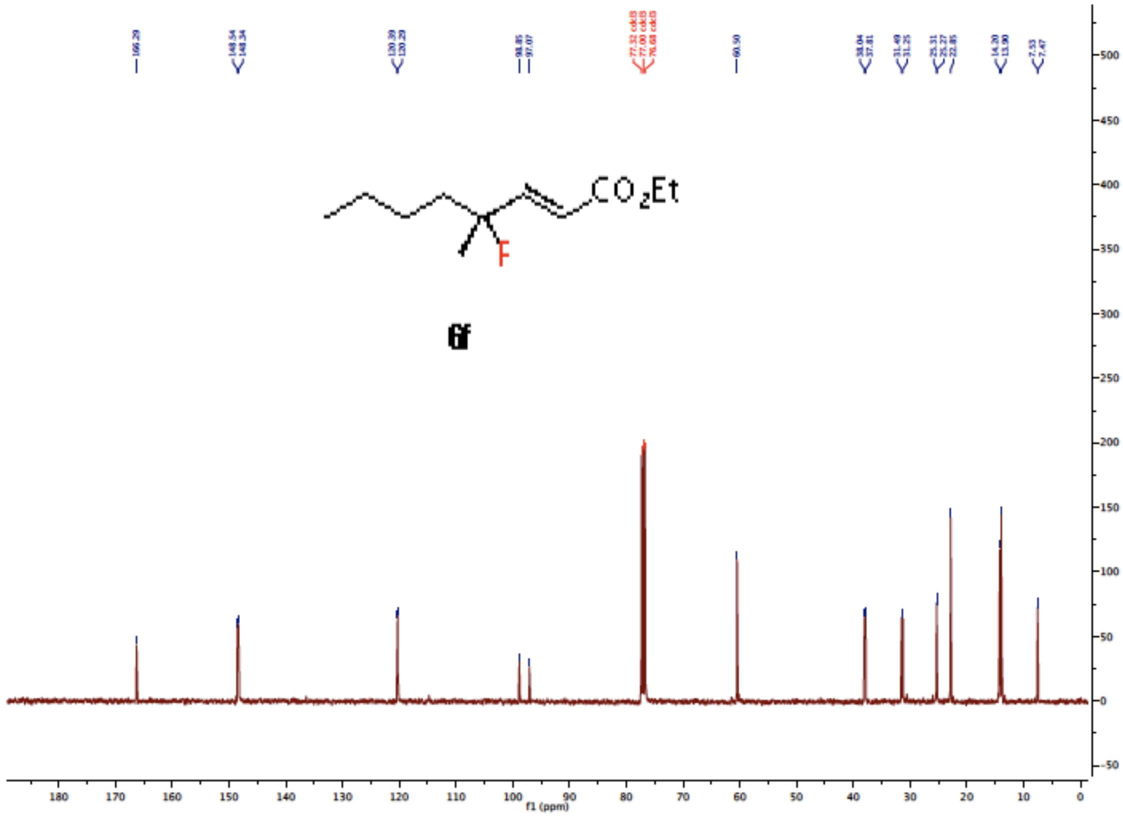
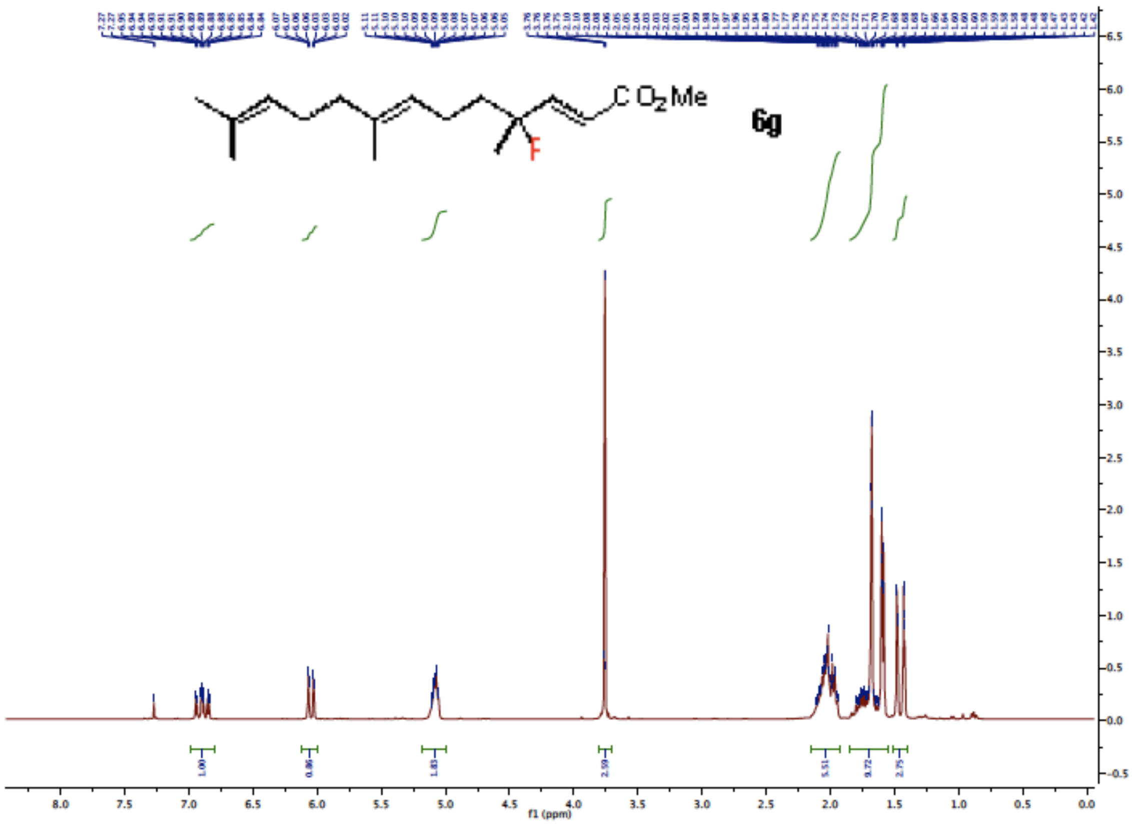
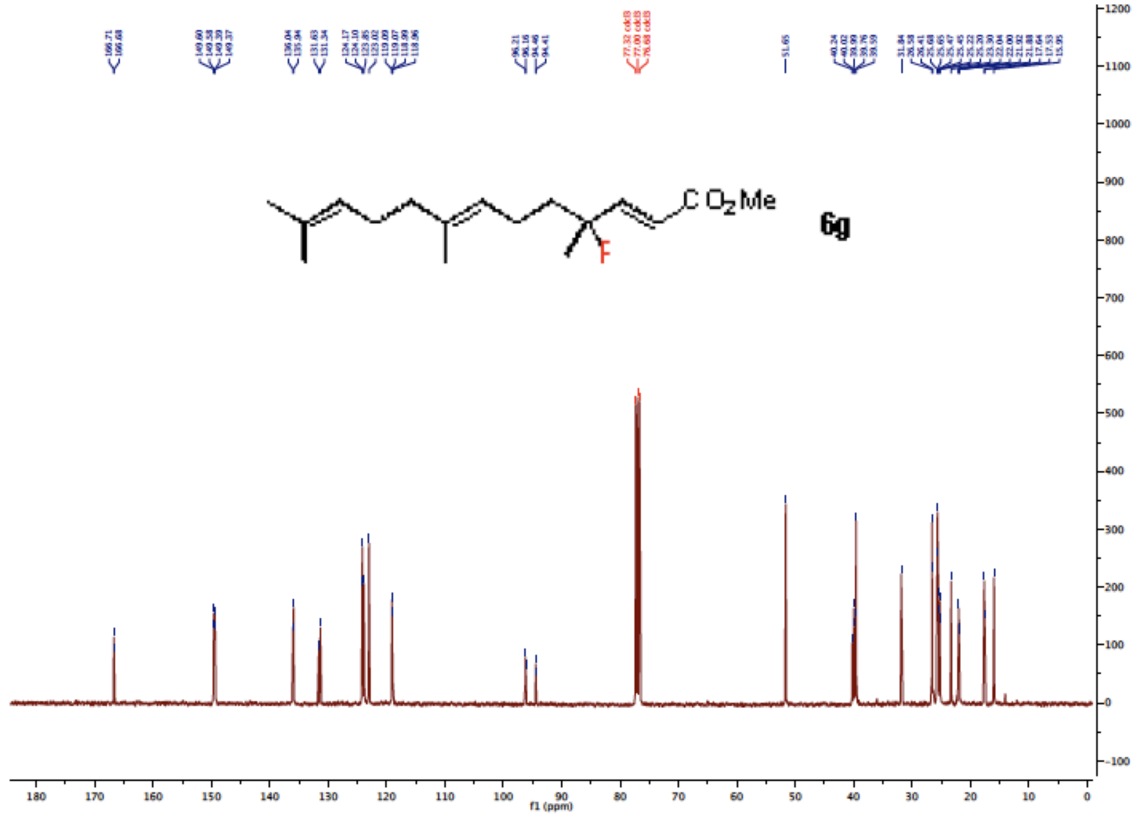
6.85
6.81
6.79
6.76
6.05
6.01
4.24
4.22
4.21
4.20
4.20
4.19
1.81
1.80
1.79
1.78
1.76
1.76
1.75
1.74
1.73
1.72
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.63
1.63
1.61
1.57
1.36
1.35
1.35
1.35
1.34
1.33
1.33
1.33
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.28
1.28
1.27
1.27
1.26
1.26
1.25
1.25
0.92
0.91
0.90
0.89
0.88
0.87
CO2Et
F
6f
1.00
0.92
2.08
4.28
7.37
5.79
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

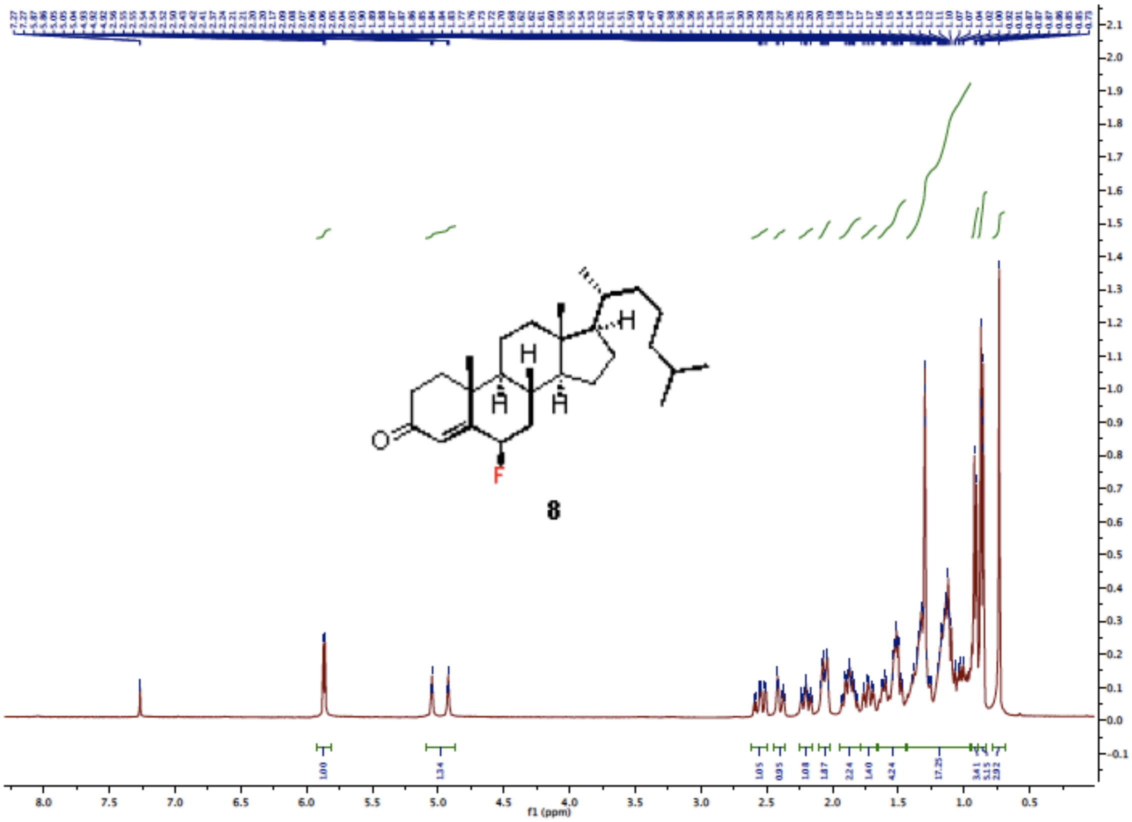

166.29
148.54
148.34
120.39
120.29
98.85
97.07
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
60.50
38.04
37.81
31.49
31.25
25.31
25.27
22.85
14.20
13.90
7.53
7.47
CO2Et
F
6f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
-50

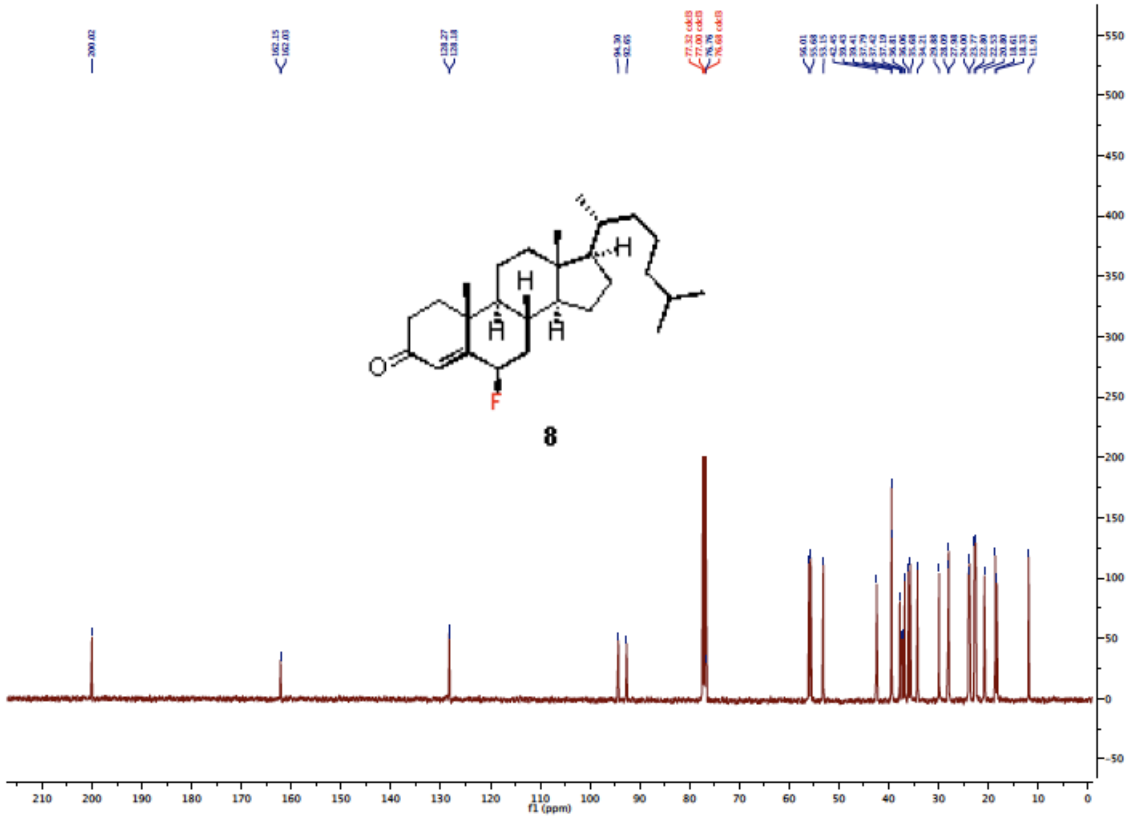

6g

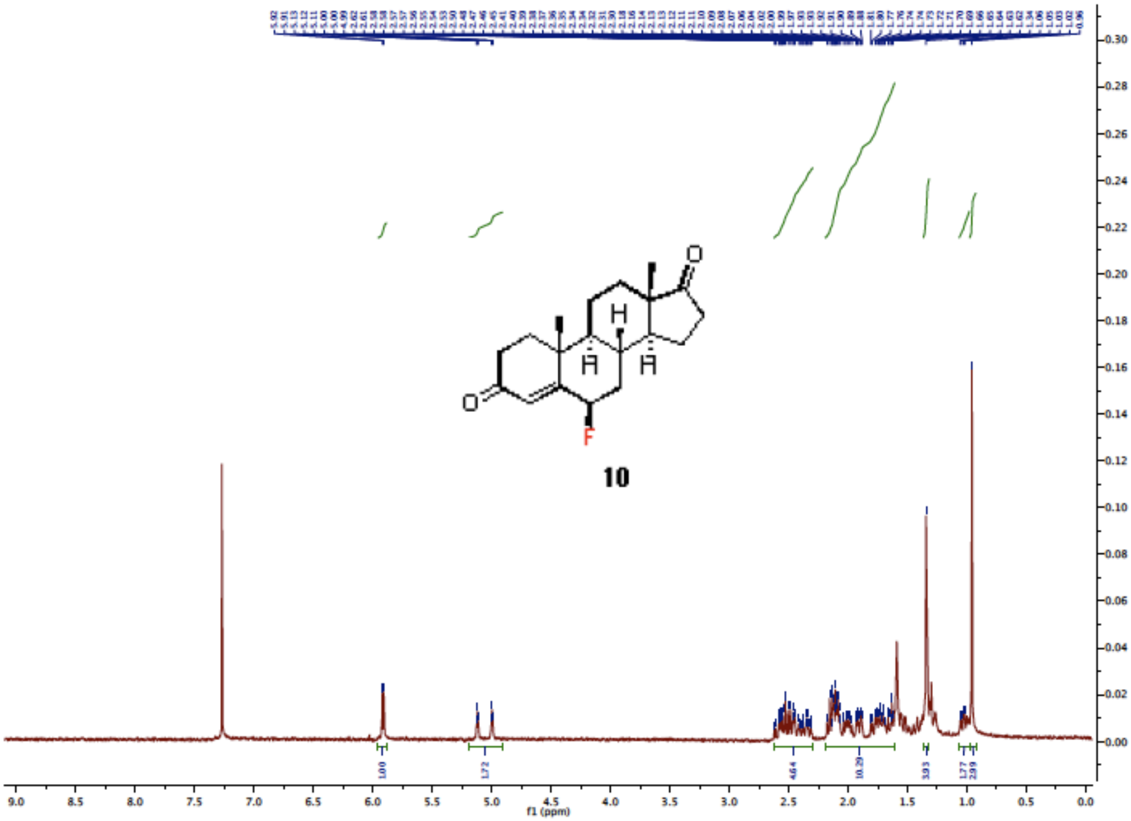
7.27
7.27
6.95
6.94
6.94
6.93
6.91
6.91
6.90
6.89
6.89
6.88
6.88
6.85
6.85
6.84
6.84
6.07
6.07
6.06
6.06
6.03
6.03
6.03
6.02
5.11
5.11
5.10
5.10
5.10
5.09
5.09
5.09
5.08
5.08
5.07
5.07
5.06
5.06
5.05
3.78
3.76
3.76
3.75
2.10
2.10
2.08
2.08
2.06
2.05
2.05
2.04
2.03
2.03
2.02
2.01
2.00
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.80
1.77
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.71
1.70
1.70
1.68
1.68
1.67
1.66
1.64
1.60
1.60
1.59
1.59
1.58
1.58
1.48
1.48
1.47
1.43
1.43
1.42
CO2Me
F
1.00
0.86
1.83
2.59
5.51
9.72
2.75
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


6g

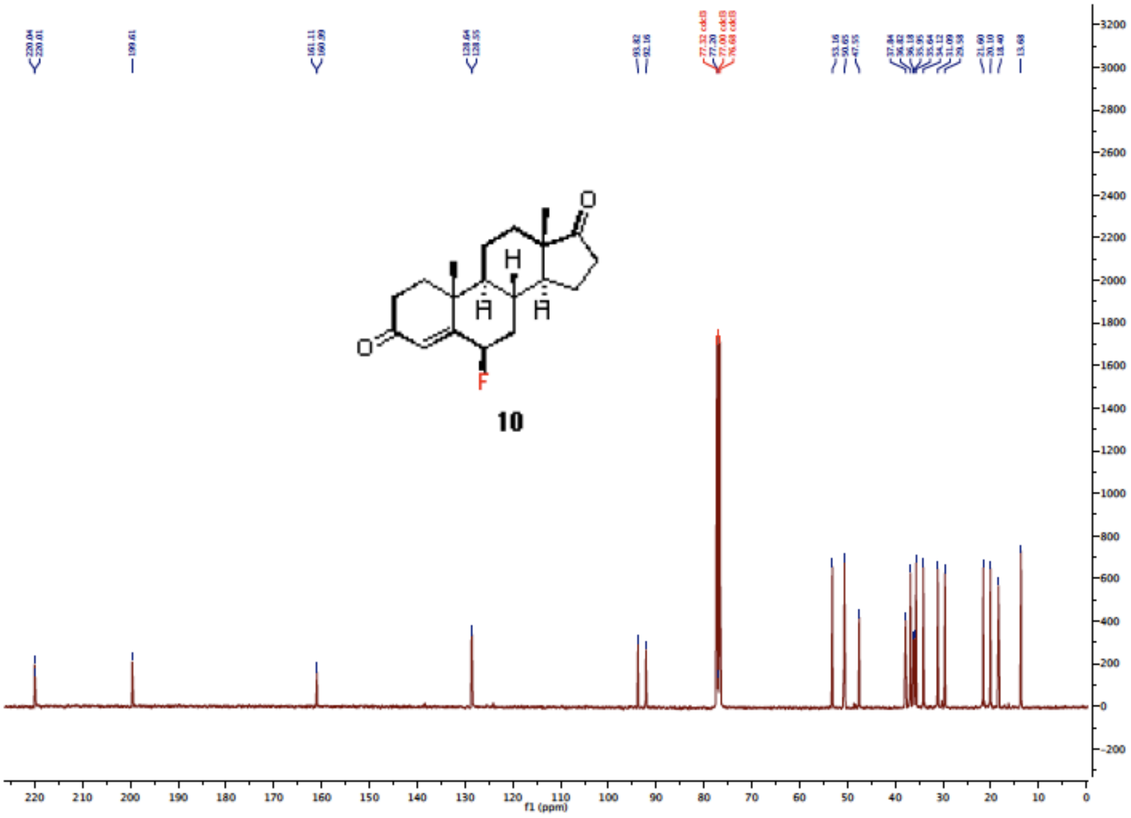
166.71
166.68
149.60
149.58
149.39
149.37
136.04
135.94
131.63
131.54
124.17
124.10
123.85
123.02
119.09
119.07
118.99
118.96
96.21
96.16
94.46
94.41
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.65
40.24
40.02
39.99
39.76
39.59
31.84
26.58
26.41
25.68
25.65
25.47
25.45
25.22
25.20
23.30
22.04
22.00
21.92
21.88
17.64
17.53
15.95
CO2Me
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


8
F
H
O
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
1.34
1.05
0.95
1.08
1.87
2.24
1.40
4.24
17.25
3.41
5.15
2.92
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1


200.02
162.15
162.03
128.27
128.18
94.30
92.65
77.32 cdcl3
77.00 cdcl3
76.76
76.68 cdcl3
56.01
55.68
53.15
42.45
39.43
39.41
37.79
37.42
37.19
36.81
36.06
35.68
34.21
29.88
28.09
27.98
24.00
23.77
22.80
22.53
20.80
18.61
18.33
11.91
8
F
H
O
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
550
500
450
400
350
300
250
200
150
100
50
0
-50


5.92 5.91 5.13 5.12 5.11 5.00 5.00 4.99 2.62 2.61 2.58 2.58 2.57 2.57 2.56 2.55 2.55 2.54 2.53 2.50 2.48 2.47 2.46 2.45 2.41 2.40 2.39 2.38 2.37 2.36 2.35 2.34 2.34 2.32 2.31 2.30 2.18 2.16 2.14 2.13 2.13 2.12 2.11 2.11 2.10 2.09 2.08 2.07 2.06 2.04 2.02 2.00 1.99 1.97 1.95 1.93 1.92 1.91 1.90 1.89 1.88 1.81 1.80 1.77 1.76 1.74 1.74 1.73 1.72 1.71 1.70 1.69 1.66 1.65 1.64 1.63 1.62 1.34 1.06 1.05 1.03 1.02 0.96
O
H
H
H
O
F
1.00
1.72
4.64
10.29
3.93
1.77
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
0.30 0.28 0.26 0.24 0.22 0.20 0.18 0.16 0.14 0.12 0.10 0.08 0.06 0.04 0.02 0.00

10


220.04 220.01
199.61
161.11 160.99
128.64 128.55
93.82 92.16
77.32 cdcl3 77.20 77.00 cdcl3 76.68 cdcl3
53.16 50.65 47.55
37.84 36.82 36.18 35.95 35.64 34.12 31.09 29.58
21.60 20.10 18.40
13.68
O
H
H
H
O
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

10