Supporting Information for

Iron-Catalyzed Cross-Coupling Reactions Between Arylzinc Reagents with Alkyl Halides Bearing β-fluorines

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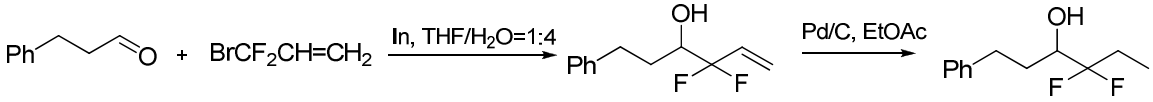
1) General

General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer or Bruker AM-400. ^{19}F NMR was recorded on a Bruker AM-300 spectrometer ($CFCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. THF, ether and toluene were distilled from sodium and benzophenone immediately before use. Dichloromethane were distilled from CaH_2. All reagents were weighed and handled in the glove box, and refilled with an inert atmosphere of argon at room temperature. Ethyl 2,2-difluoro-3-hydroxy-5-phenylpentanoate,[1] ethyl 2,2-difluoro-3-hydroxytridec-12-enoate, [1] ethyl 2,2-difluoro-3-hydroxy-5-methylhexanoate,[2] ethyl 2,2-difluoro-3-hydroxydecanoate,[3] ethyl 3-cyclohexyl-2,2-difluoro-3-hydroxypropanoate,[4] ethyl 2,2-difluoro-3-hydroxy-4,4-dimethylpentanoate,[4] ethyl 2,2-difluoro-3-hydroxyoct-7-enoate,[5] ethyl 2,2-difluoro-3-iodooct-7-enoate (**1o**) ,[5] and 3-(benzyloxy)-3-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-difluoropropan-1-ol [6] were prepared according to the published procedures.

2) Preparation of α-hydroxy-β,β-difluoroethylene-containing compounds

a) Preparation of 4,4-difluoro-1-phenylhexan-3-ol



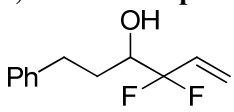
A heterogeneous solution of Indium powder (1.38 g, 12 mmol), 3-phenylpropanal (1.34 g, 10 mmol), tetrahydrofuran (5 mL) and water (20 mL) was cooled to 0 ^{O}C in an ice water bath, and 3-bromo-3,3-difluoropropene (1.88 g, 12 mmol) was slowly added via an additional funnel. After the addition was completed, the reaction mixture was warmed to room temperature and then stirred at room temperature overnight. Then, a solution of 10% aqueous hydrochloric acid (15 mL) was added to the reaction mixture. Excess Indium was removed by suction filtration and washed with ether (30 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 x 50 mL). The combined organic layer was washed with brine (50 mL), and then dried over anhydrous sodium

(1) Watanabe, S.; Fujita, T.; Sakamoto, M.; Takeda, H.; Kitazume, T.; Yamazaki, T. *J. Fluorine Chem.* **1997,** *82,* 1.
(2) Kaneda, T.; Komura, S.; Kitazume, T. *J. Fluorine Chem.* **2005,** *126,* 17.
(3) Yoshida, M.; Suzuki, D.; Iyoda, M. *Synth. Commun.* **1996,** *26,* 2523.
(4) Linderman, R. J.; Graves, D. M. *J. Org. Chem.* **1989,** *54,* 661.
(5) Morikawa, T.; Uejima, M.; Kobayashi, Y.; Taguchi, T. *J. Fluorine Chem.***1993,** *65,* 79.
(6) Zheng, F.; Fu, L.; Wang, R.; Qing, F.-L. *Org. Biomol. Chem.* **2010**, *8*, 163.

sulfate. The organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography to give 4,4-difluoro-1-phenylhex-5-en-3-ol (1.71 g, 80% yield).

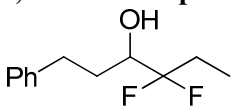
A solution of 4,4-difluoro-1-phenylhex-5-en-3-ol (1.07 g, 5 mmol), Pd/C (100 mg) in EtOAc (50 mL) was stirred at an atmosphere of H_2 (1 atm) at room temperature for 12 h. The solid was removed by suction filtration and washed with ether (30 mL). The solvent was concentrated *in vacuo*, and the residue was purified by column chromatography to give 4,4-difluoro-1-phenylhexan-3-ol (1.01 g, 94% yield).

4,4-Difluoro-1-phenylhex-5-en-3-ol



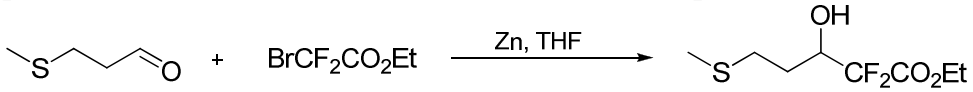
Colorless oil, yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.30-7.18 (m, 5H), 6.02-5.89 (m, 1H), 5.69 (d, J = 13.2 Hz, 1H), 5.52 (d, J = 8.4Hz, 1H), 3.76 (m, 1H), 2.94-2.87 (m, 1H), 2.74-2.66 (m, 1H), 2.09 (s, 1H), 1.97-1.88 (m. 1H), 1.82-1.72 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -108.5 (AB, J_{AB} = 248.4 Hz, $^3J_{HF}$ = 10.2 Hz, 1F), -111.8.4(AB, J_{AB} = 248.4 Hz, $^3J_{HF}$ = 9.9 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 141.2, 129.7 (t, J = 26.3 Hz), 128.5, 126.1, 121.4 (t, J = 10.1 Hz), 120.3 (t, J = 243.1 Hz), 72.7 (t, J = 28.5 Hz), 31.7, 31.5. IR (ATR): υ_{max} 3436, 3028, 2957, 2930, 1610, 1505, 1496, 1455, 1421, 1305, 1205, 1162, 1082, 987, 954, 750, 700 cm^{-1}. MS (EI): *m/z*（%）212 (M^+), 194, 135, 117, 105, 91(100), 77, 65, 51, 39, 27. HRMS: Calculated for $C_{12}H_{14}F_2O$: 212.1013. Found: 212.1013.

4,4-Difluoro-1-phenylhexan-3-ol



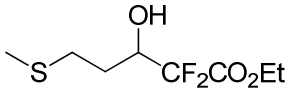
Colorless oil, yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.31-7.17 (m, 5H), 3.76-3.63 (m, 1H), 2.96-2.87 (m, 1H), 2.75-2.65 (m, 1H), 2.06-1.72 (m, 5H), 1.01 (t, J = 7.5 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -112.3 (AB, J_{AB} = 247.0 Hz, $^3J_{HF}$ = 22.6 Hz, 1F), -114.3 (AB, J_{AB} = 247.0 Hz, $^3J_{HF}$ = 35.3 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 141.3, 128.6, 128.5, 126.2, 124.4 (t, J = 244.5 Hz), 72.1 (t, J = 29.3 Hz), 31.8, 31.7, 25.5 (t, J = 25.0 Hz), 5.6 (t, J = 5.9 Hz). IR (ATR): υ_{max} 3447, 2986, 2947, 1497, 1466, 1455, 1373, 1300, 1217, 1177, 1151, 1085, 977, 739, 700 cm^{-1}. MS (EI): *m/z*（%）214 (M^+), 196, 117, 91(100), 65, 28. HRMS: Calculated for $C_{12}H_{16}F_2O$: 214.1169. Found: 214.1169.

b) Preparation of ethyl 2,2-difluoro-3-hydroxy-5-(methylthio)pentanoate



A solution of 3-(methylthio)propanal (1.04 g, 10 mmol), zinc dust (0.85 g, 13 mmol) and ethyl bromodifluoroacetate (2.64 g, 13 mmol) in tetrahydrofuran (40 mL) was stirred at 60 ^{o}C for 7 h. A solution of 10 % aqueous hydrochloric acid (15 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with ether (2 x 50 mL). The combined organic layer was washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography to give ethyl 2,2-difluoro-3-hydroxy-5-(methylthio)pentanoate (1.60g, 70% yield).

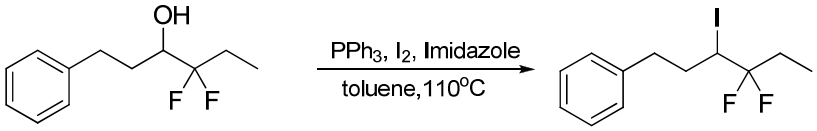
Ethyl 2,2-difluoro-3-hydroxy-5-(methylthio)pentanoate



Colorless oil, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 4.37 (q, J = 7.2 Hz, 2H), 4.32-4.23 (m, 1H), 2.78-2.56 (m, 3H), 2.12 (s, 3H), 2.01-1.86 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -114.3 (AB, J_{AB} = 264.7 Hz, $^{3}J_{HF}$ = 7.3 Hz, 1F), -122.3 (AB, J_{AB} = 264.7 Hz, $^{3}J_{HF}$ = 15.5 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 163.3 (dd, J = 32.7 Hz, J = 30.9 Hz), 114.3 (dd, J = 257.8 Hz, J = 254.6 Hz), 70.4 (dd, J = 28.2 Hz, J = 25.5 Hz), 62.9, 29.7, 27.6 (dd, J = 2.7 Hz, J = 1.8 Hz), 14.9, 13.7. IR (ATR): υ_{max} 3479, 2919, 1759, 1436, 1374, 1305, 1201, 1094 cm^{-1}. MS (ESI): *m/z*（%）228.9 ($M+H^+$), 251.0 ($M+Na^+$), 267.0 ($M+K^+$). HRMS: Calculated for $C_8H_{14}F_2O_3S$: 228.0632. Found: 251.0523 ($M+Na^+$).

3) Preparation of α-halo-β,β-difluoroethylene-containing compounds

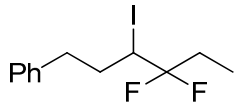
a) General procedures for preparation of α-iodo-β,β-difluoroethylene-containing compounds: 1a-1i



A dry 250 mL flask, equipped with a mechanical stirrer and a septum, was charged with 4,4-difluoro-1-phenylhexan-3-ol (2.14 g, 10 mmol), PPh_3 (10.49 g, 40 mmol), imidazole (1.84 g, 27 mmol), iodine (6.85 g, 27 mmol) in toluene (100 mL) and the resulting mixture was stirred at 110^{o}C for 3 h. The reaction was quenched with water (50 mL). The aqueous phase was extracted with hexane (2 x 50 mL). The combined organic layer was washed with brine (50 mL), and dried over anhydrous

sodium sulfate. The organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography to give (4,4-difluoro-3-iodohexyl)benzene (2.10 g, 65% yield).

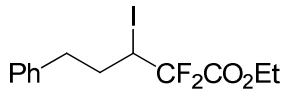
(4,4-Difluoro-3-iodohexyl)benzene (1a):



(1a)

Colorless oil, yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.32-7.22 (m, 5H), 4.04-3.91 (m, 1H), 3.03-2.95 (m, 1H), 2.72-2.62 (m, 1H), 2.25-2.01 (m, 4H), 0.97 (t, J = 7.5 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -99.60 - 101.55 (AB, 2F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 140.1, 128.7, 128.6, 126.5, 122.9 (t, J = 245.5 Hz), 35.3, 34.8 (t, J = 2.9 Hz), 32.9 (t, J = 27.7 Hz), 28.4 (t, J = 25.9 Hz), 6.1 (t, J = 5.5 Hz). IR (ATR): υ_{max} 3027, 2984, 2945, 2888, 1496, 1465, 1454, 1366, 1206, 1188, 1100, 966, 784, 749, 699 cm^{-1}. MS (EI): *m/z*（%）323 (M^+), 197, 91(100), 77, 65, 51, 41. HRMS: Calculated for $C_{12}H_{15}F_2I$: 324.0186. Found: 324.0187.

Ethyl 2,2-difluoro-3-iodo-5-phenylpentanoate (1b):

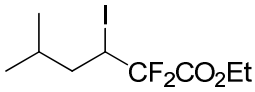


(1b)

1b was prepared from ethyl 2,2-difluoro-3-hydroxy-5-phenylpentanoate according to the general procedure.

Colorless oil, yield: 62%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.19 (m, 5H), 4.29 (q, J = 6.6 Hz, 2H), 4.24-4.15 (m, 1H), 3.05-2.96 (m, 1H), 2.74-2.64 (m, 1H), 2.18-2.11 (m, 2H), 1.32 (t, J = 6.6 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.2 (AB, J_{AB} = 252.1 Hz, $^{3}J_{HF}$ = 12.9 Hz, 1F), -105.4 (AB, J_{AB} = 252.1 Hz, $^{3}J_{HF}$ = 15.2 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 161.9 (t, J = 33.1 Hz), 139.6, 128.7, 128.5, 126.6, 114.2 (t, J = 204.9 Hz), 63.4, 34.7, 33.4, 27.9 (t, J = 24.9 Hz), 13.9. IR (ATR): υ_{max} 3063, 3027, 2983, 2940, 1774, 1496, 1454, 1373, 1306, 1213, 1089, 1048, 855, 781, 751, 699 cm^{-1}. MS (EI): *m/z*（%）368 (M^+), 241, 147, 91 (100), 77, 65, 51, 41. HRMS: Calculated for $C_{13}H_{15}F_2IO_2$: 368.0085. Found: 368.0085.

Ethyl 2,2-difluoro-3-iodo-5-methylhexanoate (1c):

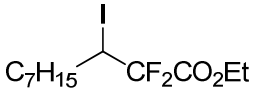


(1c)

1c was prepared from ethyl 2,2-difluoro-3-hydroxy-5-methylhexanoate according to the general procedure.

Colorless oil, yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 4.39 (q, J = 6.9 Hz, 2H), 4.36-4.27 (m, 1H), 1.95-1.81 (m, 2H), 1.39 (t, J = 6.9Hz, 3H), 1.43-1.35 (m, 1H), 1.02 (d, J = 6.3Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -99.6 (AB, J_{AB} = 250.4 Hz, $^{3}J_{HF}$ = 11.9 Hz, 1F), -102.5 (AB, J_{AB} = 250.4 Hz, $^{3}J_{HF}$ = 14.4 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 162.1 (t, J = 32.9 Hz), 114.3 (t, J = 255.2 Hz), 63.4, 40.1, 27.6, 27.4 (t, J = 25.1 Hz), 23.1, 20.2, 13.9. IR (ATR): υ_{max} 2961, 2872, 1770, 1759, 1469, 1371, 1308, 1266, 1211, 1097, 1049, 727 cm^{-1}. MS (EI): *m/z*（%）320 (M^+), 193, 145, 77, 43 (100). HRMS: Calculated for $C_9H_{15}F_2IO_2$: 320.0085. Found: 320.0085.

Ethyl 2,2-difluoro-3-iododecanoate (1d):

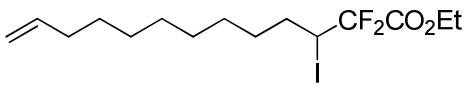


(1d)

1d was prepared from ethyl 2,2-difluoro-3-hydroxydecanoate according to the general procedure.

Colorless oil, yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 4.38 (q, J = 6.9 Hz, 2H), 4.33-4.24 (m, 1H), 1.90-1.61 (m, 3H), 1.38 (t, J = 6.9 Hz, 3H), 1.41-1.29 (m, 9H), 0.89 (t, J = 6.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.5 (AB, J_{AB} = 251.5 Hz, 1F), -107.2 (AB, J_{AB} = 251.5 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 162.2 (t, J = 32.1 Hz), 114.2 (t, J = 253.5 Hz), 63.4, 31.7, 31.6, 29.1, 28.9, 28.9 (t, J = 25.1 Hz), 28.47, 22.58, 14.03, 13.92. IR (ATR): υ_{max} 2956, 2928, 2857, 1777, 1760, 1456, 1373, 1305, 1208, 1095, 1048 cm^{-1}. MS (EI): *m/z*（%）362 (M^+), 235,189, 151, 99, 77, 57, 43(100). HRMS: Calculated for $C_{12}H_{21}F_2IO_2$: 362.0554. Found: 362.0554

Ethyl 2,2-difluoro-3-iodotridec-12-enoate (1e):



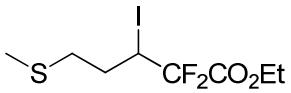
(1e)

1e was prepared from ethyl 2,2-difluoro-3-hydroxytridec-12-enoate according to the general procedure.

Colorless oil, yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 5.88-5.75 (m, 1H),

5.03-4.92 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 4.33-4.23 (m, 1H), 2.08-2.01 (m, 2H), 1.85-1.76 (m, 2H), 1.65-1.61 (m, 1H), 1.38 (t, J = 7.2 Hz, 3H), 1.42-1.30 (m, 11H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.3 (AB, J_{AB} = 251.3 Hz, $^3J_{HF}$ = 10.4 Hz, 1F), -107.2 (AB, J_{AB} = 251.3 Hz, $^3J_{HF}$ = 12.9 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 162.2 (t, J = 33.0 Hz), 139.2, 114.2, 114.2 (t, J = 256.3 Hz), 63.4, 33.8, 31.6, 29.3, 29.3, 29.1, 29.0, 28.9, 28.9 (t, J = 25.7 Hz), 28.5, 13.9. IR (ATR): υ_{max} 2927, 2855, 1777, 1759, 1641, 1382, 1305, 1209, 1069, 1048, 910 cm^{-1}. MS (EI): *m/z*（%）402 (M^+), 275, 97, 83, 69, 55 (100), 41. HRMS: Calculated for $C_{15}H_{25}F_2IO_2$: 402.0867. Found: 402.0867.

Ethyl 2,2-difluoro-3-iodo-5-(methylthio)pentanoate (1f):

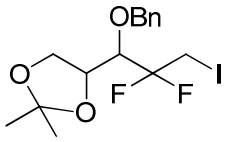


(1f)

1f was prepared from ethyl 2,2-difluoro-3-hydroxy-5-(methylthio)pentanoate according to the general procedure.

Colorless oil, yield: 55%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 4.66-4.52 (m, 1H), 4.39 (q, J = 7.5 Hz, 2H), 2.87-2.76 (m, 1H), 2.65-2.55 (m, 1H), 2.18-2.04 (m, 5H), 1.39 (t, J = 7.5 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -102.9 (AB, J_{AB} = 250.4 Hz, $^3J_{HF}$ = 11.8 Hz, 1F), -106.9 (AB, J_{AB} = 250.4 Hz, $^3J_{HF}$ = 14.9 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 161.9 (t, J = 32.7 Hz), 114.2 (t, J = 255.8 Hz), 63.5, 33.3, 30.8, 26.7 (t, J = 24.7 Hz), 15.1, 13.9. IR (ATR): υ_{max} 2982, 2918, 1775, 1762, 1437, 1372, 1298, 1277, 1214, 1096, 1049 cm^{-1}. MS (EI): *m/z*（%） 338 (M^+), 211 (100), 61. HRMS: Calculated for $C_8H_{13}IO_2S$: 337.9649. Found: 337.9649.

4-(1-(Benzyloxy)-2,2-difluoro-3-iodopropyl)-2,2-dimethyl-1,3-dioxolane (1g):



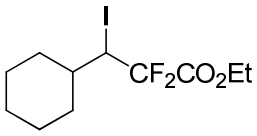
(1g)

1g was prepared from 3-(benzyloxy)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-difluoropropan-1-ol according to the general procedure.

Colorless oil, yield: 45%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.36-7.30 (m, 5H), 4.89 -4.80 (AB, J_{AB} = 11.1 Hz, 2H), 4.42-4.37 (m, 1H), 4.24-4.14 (m, 1H), 4.08-3.92 (m, 2H), 3.57-3.46 (m. 2H), 1.45 (s, 3H), 1.36 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -101.7 (AB, J_{AB} = 251.0 Hz, 1F), -102.6 (AB, J_{AB} = 251.0 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 137.2, 128.6, 128.3, 128.3, 120.1 (t, J = 248.0 Hz), 109.0, 77.6, 75.8, 74.6, 65.2 (t, J = 4.7 Hz), 26.4, 24.9, 1.9 (t, J = 29.4 Hz). IR (ATR): υ_{max} 3029, 2986, 1934, 2898, 1500, 1455, 1410, 1381, 1372, 1210, 1156, 1138,

1062, 1027, 997, 844, 753, 698 cm^{-1}. MS (ESI): *m/z* 413 ($M+H^+$), 434 ($M+Na^+$). HRMS: Calculated for $C_{15}H_{19}F_2IO_3$: 412.0347. Found: 435.0239 ($M+Na^+$).

Ethyl 3-cyclohexyl-2,2-difluoro-3-iodopropanoate (1h):

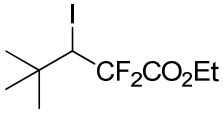


(1h)

1h was prepared from ethyl 3-cyclohexyl-2,2-difluoro-3-hydroxypropanoate according to the general procedure.

Colorless oil, yield: 58%. ^1H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 4.45-4.34 (m, 3H), 1.91-1.55 (m, 5H), 1.41-1.05 (m, 6H), 1.38 (t, J = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -99.7 (AB, J_{AB} = 250.1 Hz, $^3J_{HF}$ = 13.5 Hz, 1F), -102.1 (AB, J_{AB} = 250.1 Hz, $^3J_{HF}$ = 16.6 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 162.4 (t, J = 32.1Hz), 114.7 (t, J = 256.8 Hz), 63.4, 38,6 (t, J = 23.6 Hz), 37.9, 33.4, 31.6, 25.9, 25.7, 25.6, 13.9. IR (ATR): υ_{max} 2929, 2855, 1774, 1761, 1454, 1372, 1303, 1278, 1211, 1187, 1043, 853 cm^{-1}. MS (EI): *m/z*（%）346 (M^+), 219,173(100). HRMS: Calculated for $C_{11}H_{17}F_2IO_2$: 346.0241. Found: 346.0249.

Ethyl 2,2-difluoro-3-iodo-4,4-dimethylpentanoate (1i):

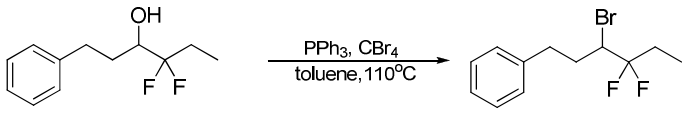


(1i)

1i was prepared from ethyl 2,2-difluoro-3-hydroxy-4,4-dimethylpentanoate according to the general procedure.

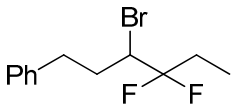
Colorless oil, yield: 43%. ^1H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 4.46 (q, J = 10.2 Hz, J = 22.1 Hz, 1H), 4.36 (q, J = 7.5 Hz, 2H), 1.39 (t, J = 7.5 Hz, 3H), 1.26 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -94.9 (AB, J_{AB} = 253.2 Hz, 1F), -104.2 (AB, J_{AB} = 253.2 Hz, $^3J_{HF}$ = 22.6 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 162.9 (t, J = 32.6 Hz), 115.7 (t, J = 258.3 Hz), 63.3, 43.9 (t, J = 22.5 Hz), 35.5, 29.9 (t, J = 2.0 Hz), 13.8. IR (ATR): υ_{max} 2969, 2913, 1776, 1759, 1467, 1371, 1217, 1190, 1081, 1046, 1024, 784 cm^{-1}. MS (EI): *m/z*（%） 320 (M^+), 277, 205, 193, 165 (100), 145, 127, 105, 99, 77, 57, 41. HRMS: Calculated for $C_9H_{15}F_2IO_2$: 320.0085. Found: 320.0085.

b) General procedures for preparation of α-bromo-β,β-difluoroethylene-containing compounds: 1a′, 1e′



A dry 250 mL flask, equipped with a mechanical stirrer and a septum, was charged with 4,4-difluoro-1-phenylhexan-3-ol (2.14 g, 10 mmol), PPh_3 (5.25 g, 20 mmol), CBr_4 (6.63 g, 20 mmol) in toluene (100 mL) and the resulting mixture was stirred at 110°C for 3 h. The reaction was quenched with water (50 mL). The organic layer was separated and the aqueous phase was extracted with hexane (2 x 50 mL). The combined organic layer was washed with brine (50 mL), and dried over anhydrous sodium sulfate. The organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography to give (3-bromo-4,4-difluorohexyl)benzene (2.16 g, 78% yield).

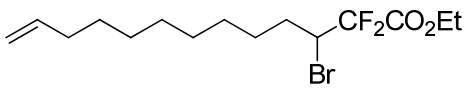
(3-Bromo-4,4-difluorohexyl)benzene (1a′):



(1a′)

Colorless oil, yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.21 (m, 5H), 3.95-3.83 (m, 1H), 3.01 (m, 1H), 2.72 (m, 1H), 2.38-1.98 (m, 4H), 0.99 (t, J = 7.8 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -104.3 (AB, J_{AB} = 243.4 Hz, $^3J_{HF}$ = 6.2 Hz, $^3J_{HF}$ = 14.2 Hz, $^3J_{HF}$ = 22.6 Hz, 1F), -107.5 (AB, J_{AB} = 243.4 Hz, $^3J_{HF}$ = 11.3 Hz, $^3J_{HF}$ = 16.8 Hz, $^3J_{HF}$ = 23.1 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 140.1, 128.6, 128.5, 126.4, 122.9 (t, J = 246.6 Hz), 52.7 (t, J = 30.9 Hz), 33.3, 33.2 (t, J = 2.9 Hz), 27.6 (t, J = 25.5 Hz), 5.9 (t, J = 6.1 Hz). IR (ATR): υ_{max} 3028, 2986, 2947, 1496, 1465, 1455, 1370, 1204, 1108, 971, 791, 749, 699 cm^{-1}. MS (EI): *m/z* (%) 278 (M^+), 276, 91(100), 77, 65, 51, 41. HRMS: Calculated for $C_{12}H_{15}F_2Br$: 276.0325. Found: 276.0325.

Ethyl 3-bromo-2,2-difluorotridec-12-enoate (1e′):



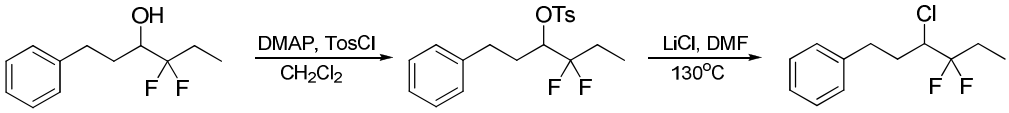
(1e′)

1e′ was prepared from ethyl 2,2-difluoro-3-hydroxytridec-12-enoate according to the general procedure.

Colorless oil, yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 5.88-5.74 (m, 1H), 5.03-4.92 (m, 2H), 4.38 (q, J = 19.2 Hz, J = 9.1 Hz, 2H), 4.31-4.18 (m, 1H), 2.08-1.95 (m, 3H),

1.91-1.78 (m, 1H), 1.67-1.59 (m, 1H), 1.37 (t, J = 9.6 Hz, 3H), 1.40-1.31 (m, 11H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -104.6 (AB, J_{AB} = 255.5 Hz, $^3J_{HF}$ = 8.5Hz, 1F), -115.1 (AB, J_{AB} = 255.5 Hz, $^3J_{HF}$ = 16.4 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 162.5 (t, J = 32.4 Hz), 149.1, 114.2, 113.6 (q, J =252.7 Hz, J = 257.8 Hz), 63.3, 50.2 (q, J = 25.9 Hz, J = 27.8 Hz), 33.8, 30.2, 29.3, 29.2, 29.0, 28.9, 28.7, 28.9, 13.9. IR (ATR): υ_{max} 2928, 2856, 1779, 1762, 1640, 1465, 1310, 1216, 1085, 1059, 910 cm^{-1}. MS (EI)：*m/z*（%）335, 295, 147, 231 (100), 213, 199, 188, 172, 128, 57, 41. HRMS: Calculated for $C_{15}H_{25}BrF_2O_2$: 354.1006. Found: 354.1006.

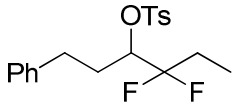
c) General procedure for preparation of α-chloro-β,β-difluoroethylene-containing compound: 1a″



To a solution of 4,4-difluoro-1-phenylhexan-3-ol (642 mg, 3 mmol) in CH_2Cl_2 (40 mL) was added DMAP (1.10 g, 9 mmol), followed by *p*-toluenesulfonyl chloride (1.71 g, 9 mmol) at 0°C. The reaction mixture was allowed to warm to room tempareture and stirred for 16 h. The solvent was concentrated *in vacuo*, and the residue was purified by column chromatography to give 4,4-difluoro-1-phenylhexan-3-yl 4-methylbenzenesulfonate (550 mg, 50% yield).

A dry 25 mL flask, equipped with a mechanical stirrer and a septum, was charged with the sulfonate (550 mg, 1.5 mmol), LiCl (252 mg, 6 mmol) in DMF (10 mL) and the resulting mixture was stirred at 130°C for 24 h. The reaction was quenched with water (10 mL). The organic layer was separated and the aqueous phase was extracted with hexane (2 x 20 mL). The combined organic layer was washed with brine (10 mL), and dried over anhydrous sodium sulfate. The organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography to give (3-chloro-4,4-difluorohexyl)benzene (244 mg, 70% yield).

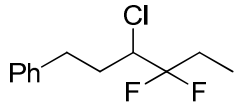
4,4-Difluoro-1-phenylhexan-3-yl 4-methylbenzenesulfonate



Colorless oil, yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.81-7.11 (m, 9H), 4.80-4.72 (m, 1H), 2.79-2.61 (m, 2H), 2.45 (s, 3H), 2.11-1.78 (m, 4H), 0.97 (t, J = 5.4 Hz, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -108.9 (AB, J_{AB} = 248.4 Hz, 1F), -110.7 (AB, J_{AB} = 245.1 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δppm 145.1, 140.6, 134.1, 129.8, 128.5, 128.4, 127.9, 126.3, 122.1 (t, J = 247.7 Hz), 80.2 (t, J = 32.0 Hz), 31.24, 30.9, 26.2 (t, J = 24.9 Hz), 21.7, 5.3 (t, J =

5.6 Hz). IR (ATR): υ_{max} 3208, 2927, 2855, 1497, 1466, 1455, 1370, 1110, 976, 807, 748, 700 cm^{-1}. MS (ESI): *m/z*（%）386 ($M+NH_4^+$), 391 ($M+Na^+$). HRMS: Calculated for $C_{19}H_{22}F_2O_2S$: 368.1258. Found: 368.1258.

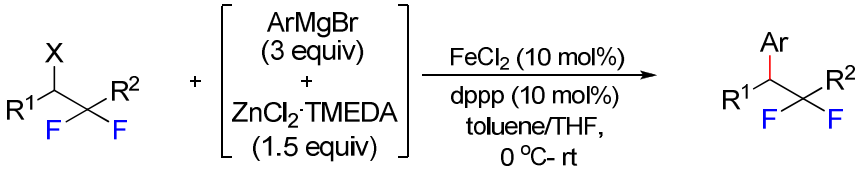
(3-Chloro-4,4-difluorohexyl)benzene (1a″):



(1a″)

Colorless oil, yield: 70%. ^1H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.32-7.20 (m, 5H), 3.89-3.81 (m, 1H), 3.02-2.96 (m, 1H), 2.77-2.70 (m, 1H), 2.33-2.24 (m, 1H), 2.12-1.96 (m, 3H), 1.01 (t, J = 7.2 Hz, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -105.9 (AB, J_{AB} = 245.1 Hz, $^3J_{HF}$ = 6.5 Hz, $^3J_{HF}$ = 15.2 Hz, $^3J_{HF}$ = 22.6 Hz, 1F), -110.2 (AB, J_{AB} = 245.1 Hz, $^3J_{HF}$ = 10.2 Hz, $^3J_{HF}$ = 14.9 Hz, $^3J_{HF}$ = 21.3 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δppm 140.3, 128.67, 128.6, 126.4, 123.3 (dd, J = 244.9 Hz, J = 247.7 Hz), 60.5 (dd, J = 30.1 Hz, J = 32.7 Hz), 32.6 (t, J = 2.5 Hz), 32.3, 26.9 (t, J = 24.4 Hz), 5.8 (dd, J = 5.1 Hz, J = 6.3 Hz). IR (ATR): υ_{max} 3208, 2927, 2855, 1497, 1466, 1455, 1370, 1110, 976, 807, 748, 700 cm^{-1}. MS (EI): *m/z*（%）232 (M^+), 105, 91 (100), 77, 65, 51, 41. HRMS: Calculated for $C_{12}H_{15}ClF_2$: 232.0830. Found: 232.0830.

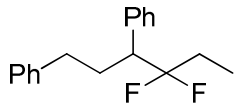
4) **Iron-catalyzed cross coupling reactions**



1 **2** **3**

In a dry reaction vessel, a mixture of PhMgBr (0.6 mL of a 1.0-M THF solution, 0.6 mmol) and $ZnCl_2$·TMEDA (75.8 mg, 0.3 mmol) was stirred for 1h. Then the resulting suspension was added to a mixture of (4,4-difluoro-3-iodohexyl)benzene (**1a**) (65.0 mg, 0.2 mmol), $FeCl_2$ (2.8 mg, 10 mol%) and 1,3-bis(diphenylphosphino)propane (8.8 mg, 10 mol%) in toluene (1.2 mL) at 0 °C in one port. The reaction mixture was stirred at that temperature for 15 min after completion of the addition of phenylzinc reagent and stirred at room temperature for 12 h. A saturated aqueous solution of NH_4Cl (1.0 mL) was added to quench the reaction. The organic layer was separated and the aqueous phase was extracted with ether (2 x 2 mL). The combined organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography to give (4,4-difluorohexane-1,3-diyl)dibenzene (42.8 mg, 78 % yield).

(4,4-Difluorohexane-1,3-diyl)dibenzene (3a):

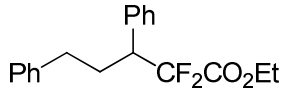


(3a)

3a was prepared from (4,4-difluoro-3-iodohexyl)benzene (**1a**) according to the general procedure.

Colorless oil, yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.07 (m, 10H), 3.01-2.87 (m, 1H), 2.55-2.29 (m, 3H), 2.16-2.10 (m, 1H), 1.71-1.52 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.3 (AB, J_{AB} = 239.4 Hz, 1F), -107.5 (AB, J_{AB} = 239.4 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 141.7, 138.1, 138.0, 129.4, 128.7, 128.5, 128.4, 127.5, 126.0, 125.6 (t, J = 246.4 Hz), 51.4 (t, J = 23.7 Hz), 33.3, 30.1 (t, J = 3.5 Hz), 28.7 (t, J = 26.8 Hz), 6.1 (t, J = 5.7 Hz). IR (ATR): υ_{max} 3028, 2984, 2946, 2887, 1496, 1454, 1367, 1202, 1187, 971, 946, 762, 734, 700 cm^{-1}. MS (EI): *m/z*（%）274 (M^+), 117, 105, 117, 91 (100), 65, 51, 41. HRMS: Calculated for $C_{18}H_{20}F_2$: 274.1533. Found: 274.1533.

Ethyl 2,2-difluoro-3,5-diphenylpentanoate (3b):

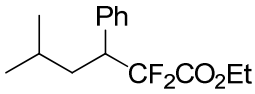


(3b)

3b was prepared from ethyl 2,2-difluoro-3-iodo-5-phenylpentanoate (**1b**) according to the general procedure.

Colorless oil, yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.06 (m, 10H), 4.08 (q, J = 6.9 Hz, 2H), 3.39-3.24 (m, 1H), 2.60-2.51 (m, 1H), 2.44-2.18 (m, 3H), 1.08 (t, J = 6.9 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -107.0 (AB, J_{AB} = 250.9 Hz, $^{3}J_{HF}$ = 11.6 Hz, 1F), -113.9 (AB, J_{AB} = 250.9 Hz, $^{3}J_{HF}$ = 20.3 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 163.9 (t, J = 32.6 Hz), 141.0, 134.9, 134.8, 129.6, 128.7, 128.5, 128.4, 128.2, 126.2, 116.6 (q, J = 254.0 Hz, J = 256.9 Hz), 62.6, 49.6 (t, J = 22.5 Hz), 32. 8, 29.3, 13.7. IR (ATR): υ_{max} 3029, 2983, 2956, 1774, 1759, 1496, 1455, 1373, 1304, 1190, 1101, 1063, 1016, 722, 699 cm^{-1}. MS (EI): *m/z*（%）318 (M^+), 117, 105, 91 (100), 77, 65, 51, 43. HRMS: Calculated for $C_{19}H_{20}F_2O_2$: 318.1431. Found: 318.1431.

Ethyl 2,2-difluoro-5-methyl-3-phenylhexanoate (3c):

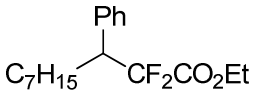


(3c)

3c was prepared from ethyl 2,2-difluoro-3-iodo-5-methylhexanoate (**1c**) according to the general procedure.

Colorless oil, yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.30-7.25 (m, 5H), 4.19-4.08 (qm, *J* = 7.2 Hz, 2H), 3.49-3.33 (m, 1H), 1.97-1.87 (m, 1H), 1.66-1.56 (m, 1H), 1.38-1.27 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.87 (d, *J* = 3.3 Hz, 3H), 0.85 (d, *J* = 2.7 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -108.3 (AB, J_{AB} = 250.1 Hz, $^{3}J_{HF}$ = 12.1 Hz, 1F), -114.5 (AB, J_{AB} = 250.1 Hz, $^{3}J_{HF}$ = 18.9 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 164.1 (t, *J* = 32.2 Hz), 135.4 (d, *J* = 6.0 Hz), 129.5, 128.5, 127.9, 116.8 (t, *J* = 253.8 Hz), 62.5, 48.2 (t, *J* = 22.2 Hz), 36.4, 24.8, 23.7, 20.9, 13.7. IR (ATR): υ_{max} 3012, 2959, 2871, 1774, 1759, 1500, 1468, 1455, 1371, 1267, 1189, 1131, 1093, 1060, 713, 700 cm^{-1}. MS (EI): *m/z*（%）270 (M^+), 250, 194, 147, 105, 91 (100), 77, 51, 43. HRMS: Calculated for $C_{15}H_{20}F_2O_2$: 270.1431. Found: 270.1431.

Ethyl 2,2-difluoro-3-phenyldecanoate (3d):

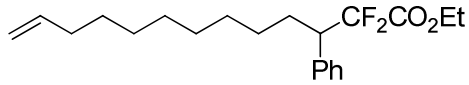


(3d)

3d was prepared from ethyl 2,2-difluoro-3-iododecanoate (**1d**) according to the general procedure.

Colorless oil, yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.31-7.26 (m, 5H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.37-3.22 (m, 1H), 1.95-1.80 (m, 2H), 1.26-1.20 (m, 10H), 1.12 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 5.7 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -106.9 (AB, J_{AB} = 251.3 Hz, $^{3}J_{HF}$ = 12.9 Hz, 1F), -113.6 (AB, J_{AB} = 251.3 Hz, $^{3}J_{HF}$ = 20.3 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 164.1 (t, *J* = 32.5 Hz), 135.4 (d, *J* = 6.9 Hz), 129.5, 128.5, 127.9, 116.7 (t, *J* = 256.8 Hz), 62.5, 50.3 (t, *J* = 21.8 Hz), 31.7, 29.3, 28.9, 27.5, 26.9, 22.6, 14.0, 13.7. IR (ATR): υ_{max} 3013, 2928, 2857, 1773, 1759, 1500, 1466, 1455, 1311, 1130, 1095, 1063, 721, 699 cm^{-1}. MS (EI): *m/z*（%）312 (M^+), 292, 208, 189, 91 (100), 77, 51, 41. HRMS: Calculated for $C_{18}H_{26}F_2O_2$: 312.1901. Found: 312.1901.

Ethyl 2,2-difluoro-3-phenyltridec-12-enoate (3e):

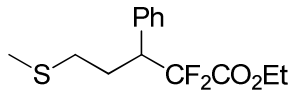


(3e)

3e was prepared from ethyl 2,2-difluoro-3-iodotridec-12-enoate (**1e**) according to the general procedure.

Colorless oil, yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.31-7.25 (m, 5H), 5.86-5.73 (m, 1H), 5.00-4.90 (m, 2H), 4.12 (q, J = 6.9 Hz, 2H), 3.37-3.21 (m, 1H), 2.04-1.98 (m, 2H), 1.95-1.80 (m, 2H), 1.33-1.21 (m, 12H), 1.12 (t, J = 6.9 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -107.2 (AB, J_{AB} = 251.3 Hz, $^{3}J_{HF}$ = 14.1 Hz, 1F), -114.1 (AB, J_{AB} = 251.3 Hz, $^{3}J_{HF}$ = 19.7 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 164.1 (t, J = 32.8 Hz), 139.2, 135.4 (d, J = 6.2 Hz), 129.5, 128.5, 127.9, 116.7 (t, J = 256.6 Hz), 114.1, 62.5, 50.3 (t, J = 22.6 Hz), 33.8, 29.4, 29.3, 29.2, 29.0, 28.9, 27.6 (d, J = 2.0 Hz), 26.9, 13.7. IR (ATR): υ_{max} 3030, 3011, 2927, 2855, 1773, 1759, 1640, 1500, 1455, 1310, 1188, 1069, 1062, 910, 721, 699 cm^{-1}. MS (EI): *m/z*（%）352 (M^+), 332, 253, 226, 131, 117,105, 91 (100), 41. HRMS: Calculated for $C_{21}H_{30}F_2O_2$: 352.2214. Found: 352.2214.

Ethyl 2,2-difluoro-5-(methylthio)-3-phenylpentanoate (3f):

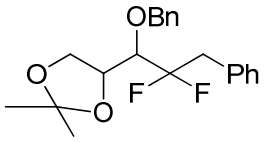


(3f)

3f was prepared from ethyl 2,2-difluoro-3-iodo-5-(methylthio)pentanoate (**1f**) according to the general procedure.

Colorless oil, yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.26 (m, 5H), 4.12 (q, J = 7.2 Hz, 2H), 3.65-3.53 (m, 1H), 2.47-2.40 (m, 1H), 2.29-2.08 (m, 3H), 2.04 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -106.1 (AB, J_{AB} = 266.2 Hz, $^{3}J_{HF}$ = 11.8 Hz, 1F), -114.1 (AB, J_{AB} = 266.2 Hz, $^{3}J_{HF}$ = 20.3 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 163.8 (t, J = 32.8 Hz), 134.4 (d, J = 6.7 Hz), 129.5, 128.7, 128.2, 116.6 (dd, J = 254.1 Hz, J = 256.8 Hz), 62.6, 48.7 (t, J = 22.8 Hz), 31.2, 26.9, 15.0, 13.7. IR (ATR): υ_{max} 3015, 2982, 2918, 1773, 1759, 1496, 1455, 1301, 1282, 1196, 1100, 1063, 720, 700 cm^{-1}. MS (EI): *m/z*（%）288 (M^+) (100), 220, 191, 167, 147, 117, 91, 77, 61, 51. HRMS: Calculated for $C_{14}H_{18}F_2O_2S$: 288.0996. Found: 288.0996.

4-(1-(Benzyloxy)-2,2-difluoro-3-phenylpropyl)-2,2-dimethyl-1,3-dioxolane (3g):

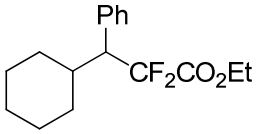


(3g)

3g was prepared from 4-(1-(benzyloxy)-2,2-difluoro-3-iodopropyl)-2,2-dimethyl-1,3-dioxolane (**1g**) according to the general procedure.

Colorless oil, yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.36-7.24 (m, 10H), 4.89-4.58 (AB, J_{AB} = 11.1 Hz, 2H), 4.45 (m, 1H), 4.12-4.02 (m, 2H), 3.90-3.82 (m, 1H), 3.28-3.15 (m, 2H), 1.43 (s, 3H), 1.35 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.9 (AB, J_{AB} = 254.4 Hz, 1F), -105.7 (AB, J_{AB} = 254.4 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 137.7, 132.6 (d, J = 5.1 Hz), 130.6, 128.5, 128.4, 128.0, 127.8, 127.4, 122.8 (q, J = 246.9 Hz, J = 249.3 Hz), 108.6, 77.9 (t, J = 27.3 Hz), 75.2, 74.8 (d, J = 27.3 Hz), 64.9 (d, J = 5.3 Hz), 40.0 (t, J = 23.5 Hz), 26.3, 24.9. IR (ATR): υ_{max} 3030, 2987, 2932, 1497, 1455, 1380, 1371, 1209, 1159, 1130, 1062, 1016, 846, 699 cm^{-1}. MS (ESI): *m/z*（%）363 ($M+H^+$), 385 ($M+Na^+$). HRMS: Calculated for $C_{21}H_{24}F_2O_3$: 362.1694. Found: 385.1585 ($M+Na^+$).

Ethyl 3-cyclohexyl-2,2-difluoro-3-phenylpropanoate (3h):

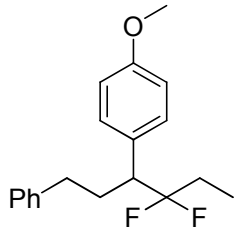


(3h)

3h was prepared from ethyl 3-cyclohexyl-2,2-difluoro-3-iodopropanoate (**1h**) according to the general procedure.

Colorless oil, yield: 49%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.29-7.21 (m, 5H), 4.02 (q, J = 7.2 Hz, 2H). 3.23-3.08 (m, 1H), 2.04-2.01 (m, 2H), 1.78-1.45 (m, 4H), 1.37-1.10 (m, 4H), 1.04 (t, J = 7.2 Hz, 3H), 0.87-0.79 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -99.9 (AB, J_{AB} = 253.2 Hz, $^{3}J_{HF}$ = 14.4 Hz, 1F), -112.4 (AB, J_{AB} = 253.2 Hz, $^{3}J_{HF}$ = 23.1 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 164.0 (t, J = 33.0 Hz), 135.5 (d, J = 7.7 Hz), 129.9 , 128.3, 127.6, 117.7 (dd, J = 255.8 Hz, J = 258.6 Hz), 62.4, 55.8 (t, J = 22.5 Hz), 38.2 (d, J = 2.8 Hz), 31.9 (d, J = 3.8 Hz), 31.1, 26.3, 26.2, 26.1, 13.6. IR (ATR): υ_{max} 3010, 2926, 2854, 1773, 1759, 1490, 1451, 1309, 1282, 1205, 1174, 1102, 1046, 701 cm^{-1}. MS (EI): *m/z*（%）296 (M^+), 276, 214, 194 (100), 140, 91, 83, 77, 51, 41. HRMS: Calculated for $C_{17}H_{22}F_2O_2$: 296.1588. Found: 296.1588.

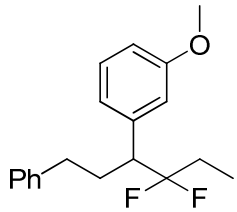
1-(4,4-Difluoro-1-phenylhexan-3-yl)-4-methoxybenzene (3j):



(3j)

3j was prepared from (4,4-difluoro-3-iodohexyl)benzene (**1a**) according to the general procedure. Colorless oil, yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.27-6.87 (m, 9H), 3.81 (s, 3H), 2.92 (m, 1H), 2.53-2.46 (m, 1H), 2.38-2.29 (m, 2H), 2.12-2.04 (m, 1H), 1.69-1.52 (m, 2H), 0.89 (t, J = 7.2, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.6 (AB, J_{AB} = 240.3 Hz, 1F), -107.9 (AB, J_{AB} = 240.3 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 158.9, 141.7, 130.3, 129.9 (d, J = 7.4 Hz), 128.5, 128.4, 125.9, 125.7 (t, J = 245.6 Hz), 114.0, 55.2, 50.5 (t, J = 24.2 Hz), 33.2, 30.2 (t, J = 3.8 Hz), 28.6 (t, J = 26.1 Hz), 6.0 (t, J = 6.1 Hz). IR (ATR): υ_{max} 3026, 2984, 1946, 1612, 1515, 1496, 1464, 1303, 1250, 1179, 1036, 970, 824, 699 cm^{-1}. MS (EI): *m/z*（%）304 (M^+), 225, 121, 91 (100), 77, 65, 43. HRMS: Calculated for $C_{19}H_{22}F_2O$: 304.1639. Found: 304.1639.

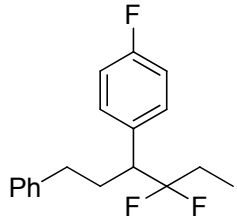
1-(4,4-Difluoro-1-phenylhexan-3-yl)-3-methoxybenzene (3k):



(3k)

3k was prepared from (4,4-difluoro-3-iodohexyl)benzene (**1a**) according to the general procedure. Colorless oil, yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.29-6.83 (m, 9H), 3.79 (s, 3H), 2.95 (m, 1H), 2.56-2.29 (m, 3H), 2.19-2.06 (m, 1H), 1.73-1.54 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.0 (AB, J_{AB} = 239.7 Hz, 1F), -107.5 (AB, J_{AB} = 239.7 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 159.8, 141.7, 139.7 (d, J = 7.4 Hz), 129.5, 128.5, 128.2, 125.9, 125.5 (t, J = 246.7 Hz), 121.8, 115.2, 112.5, 55.2, 51.4 (t, J = 24.0 Hz), 33.2, 30.0 (t, J = 4.7 Hz), 28.7 (t, J = 25.8 Hz), 6.0 (t, J = 4.8 Hz). IR (ATR): υ_{max} 3026, 2984, 2945, 1601, 1584, 1490, 1465, 1454, 1290, 1263, 1164, 1049, 971, 777, 699 cm^{-1}. MS (EI): *m/z*（%） 304 (M^+), 200 (100), 121, 91, 77, 65, 51, 41. HRMS: Calculated for $C_{19}H_{22}F_2O$: 304.1639. Found: 304.1639.

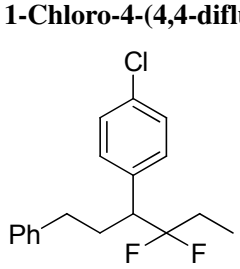
1-(4,4-Difluoro-1-phenylhexan-3-yl)-4-fluorobenzene (3l):



(3l)

3l was prepared from (4,4-difluoro-3-iodohexyl)benzene (**1a**) according to the general procedure. Colorless oil, yield: 58%. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.28-7.01 (m, 9H), 2.94 (dt, *J* = 27.6 Hz, *J* = 11.1 Hz, 1H), 2.55-2.29 (m, 3H), 2.16-2.05 (m, 1H), 1.69-1.52 (m, 2H), 0.90 (td, *J* = 7.4 Hz, *J* = 2.4 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.9 (AB, J_{AB} = 242.0 Hz, 1F), -107.7 (AB, J_{AB} = 242.0 Hz, 1F), -115.09 (q, *J* = 4.8 Hz, *J* = 8.5 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 163.5, 161.0, 141.4, 133.7 (dd, *J* = 3.3 Hz, *J* = 6.8 Hz), 130.8 (d, *J* = 8.1 Hz), 128.4, 126.1, 125.4 (t , *J* = 246.3 Hz), 115.5 (d, *J* = 21.4 Hz), 50.5 (t, *J* = 24.9 Hz), 33.1, 30.1 (t, *J* = 3.9 Hz), 28.6 (t, *J* = 26.08 Hz), 6.0 (t, *J* = 4.8 Hz). IR (ATR): υ_{max} 3085, 3027, 2946, 2857, 1606, 1510, 1497, 1545, 1365, 1220, 1187, 1162, 972, 826, 748, 699 cm^{-1}. MS (EI): *m/z*（%）292 (M^+), 213, 200, 117, 109, 105, 91 (100), 77, 65, 44. HRMS: Calculated for $C_{18}H_{19}F_3$: 292.1439. Found: 292.1439.

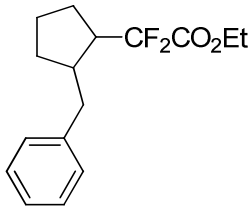
1-Chloro-4-(4,4-difluoro-1-phenylhexan-3-yl)benzene (3m):



(3m)

3m was prepared from (4,4-difluoro-3-iodohexyl)benzene (**1a**) according to the general procedure. Colorless oil, yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.34-7.06 (m, 9H), 2.98-2.87 (m, 1H), 2.52-2.47 (m, 1H), 2.40-2.30 (m, 2H), 2.13-2.03 (m, 1H), 1.70-1.53 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -103.8(AB, J_{AB} = 240.8 Hz, 1F), -107.6 (AB, J_{AB} = 240.8 Hz, 1F). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 141.3, 136.5 (d, *J* = 6.3 Hz), 133.4, 130.7, 128.8, 128.4, 128.4, 127.5 (t, *J* = 226.9 Hz), 126.1, 50.7 (t, *J* = 23.8 Hz), 33.0, 29.9 (t, *J* = 4.5 Hz), 28.6 (t, *J* = 25.6 Hz), 5.9 (t, *J* = 6.3 Hz). IR (ATR): υ_{max} 3027, 2983, 2929, 2855, 1500, 1494, 1464, 1454, 1180, 1101, 1093, 972, 820, 730, 699 cm^{-1}. MS (EI): *m/z* (%) 308 (M^+), 288, 217, 197, 184, 151, 125, 105, 91 (100), 77, 65, 51, 39. HRMS: Calculated for $C_{18}H_{19}ClF_2$: 308.1143. Found: 308.1143.

Ethyl 2-(2-benzylcyclopentyl)-2,2-difluoroacetate (3o):



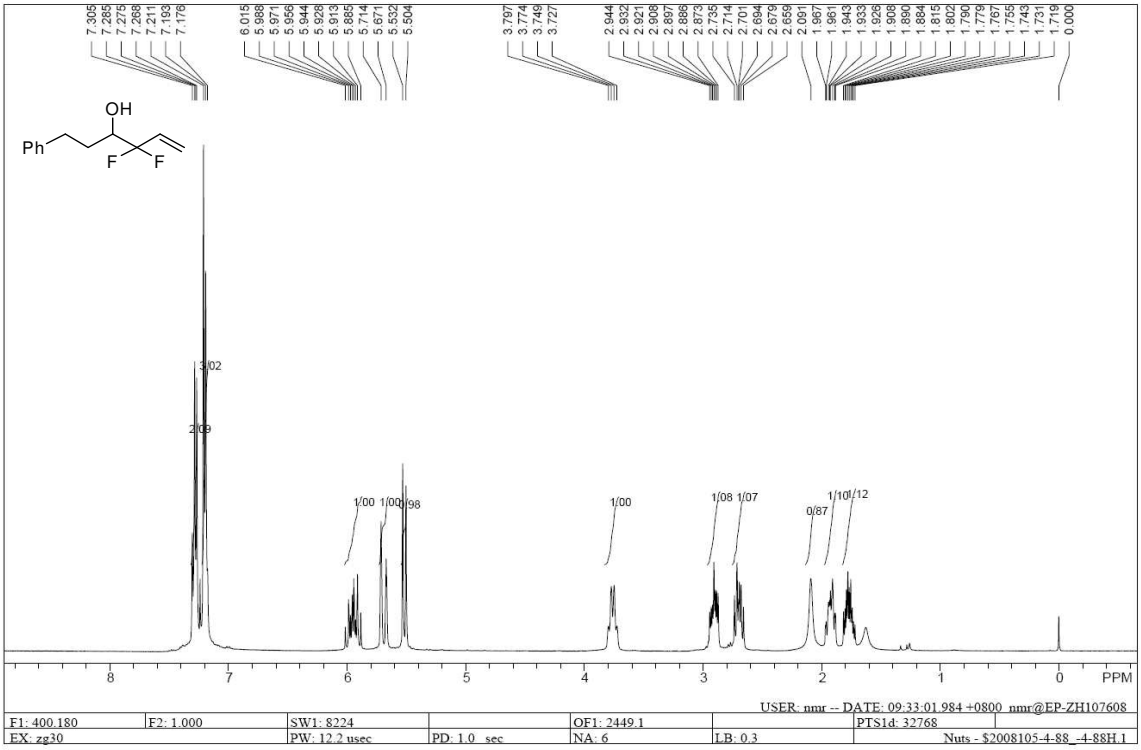
(3o)

3o was prepared from 2,2-difluoro-3-iodooct-7-enoate (**1o**) according to the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$, 293K, TMS): δ ppm 7.29-7.13 (m, 5H), 4.37-4.24 (m, 2H), 2.95 (dd, *J* = 7.2 Hz, *J* = 32.1 Hz, 1H), 2.81-2.80 (m, 0.5H), 2.47-2.35 (m, 2.5 H), 1.89-1.43 (m, 6H), 1.38-1.32 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ ppm -105.79 (AB, J_{AB} = 260.0 Hz, $^{3}J_{HF}$ = 20.3 Hz), -106.85 (AB, J_{AB} = 260.0 Hz, $^{3}J_{HF}$ = 17.5Hz). -109.54 (AB, J_{AB} = 252.7 Hz, $^{3}J_{HF}$ = 16.4 Hz), -111.4 (AB, J_{AB} = 252.7 Hz, $^{3}J_{HF}$ = 17.8 Hz). ^{13}C NMR (100.7 MHz, $CDCl_3$, 293K, TMS): δ ppm 164.7 (t, *J* = 33.5 Hz), 164.6 (t, *J* = 32.6 Hz), 141.5, 140.8, 129.0, 128.9, 128.3, 128.3, 126.0, 125.9, 117.8 (t, *J* = 253.7 Hz)，117.7 (t, *J* = 251.5 hz）, 62.7, 62.7, 48.3 (t, *J* = 21.4 Hz), 46.1 (t, *J* = 20.8 Hz), 42.6 (d, *J* = 2.4 Hz), 47. 8, 41.1 (d, *J* = 2.2 Hz), 35.4 (d, *J* = 1.7 Hz), 32.4, 30.4, 26.4 (dd, *J* = 5.3 Hz, *J* = 2.9 Hz), 24.8, 24.3 (dd, *J* = 4.9 Hz, *J* = 2.4 Hz), 22.3, 14.0. IR (ATR): υ_{max} 3027, 2961, 2876, 1773, 1500, 1496, 1453, 1371, 1303, 1221, 1120, 1065, 740, 700 cm^{-1}. MS (EI): *m/z* (%) 282 (M^+), 262, 236, 191, 188, 163, 143, 117, 91 (100), 77, 65, 51, 41. HRMS: Calculated for $C_{16}H_{20}F_2O_2$: 282.1431. Found: 282.1431.

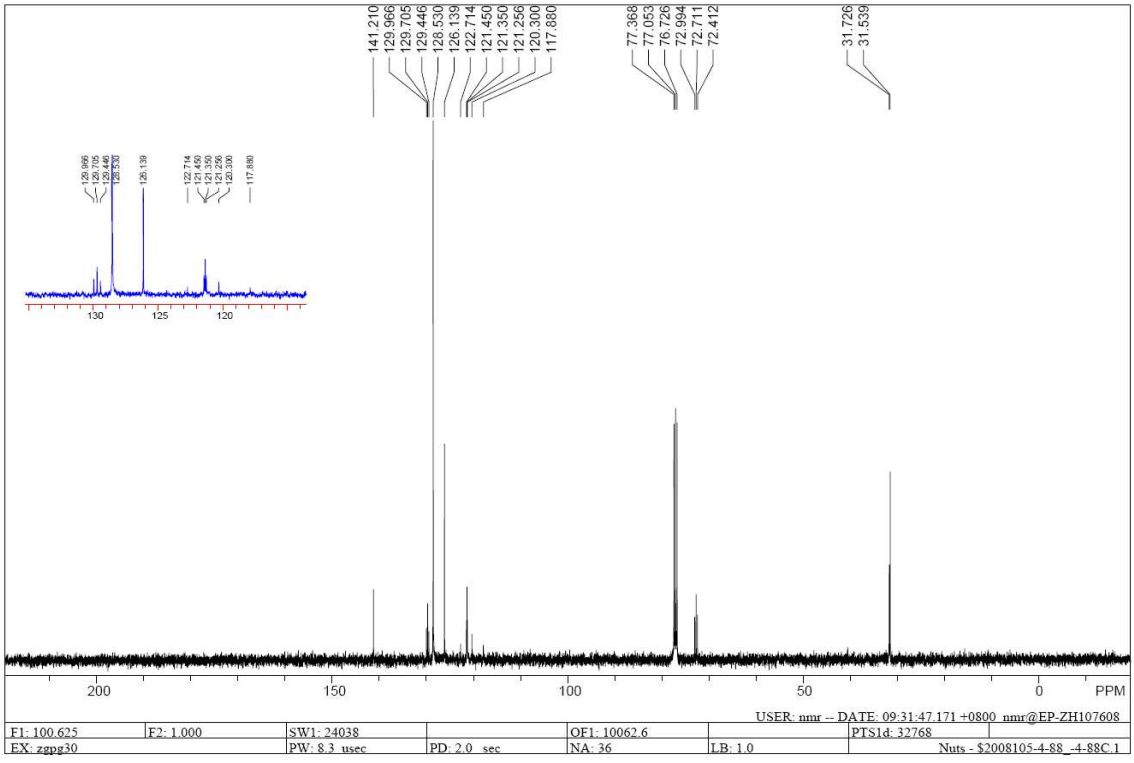
5) ^{1}H NMR and ^{13}C NMR spectra

4,4-difluoro-1-phenylhex-5-en-3-ol

^{1}H NMR

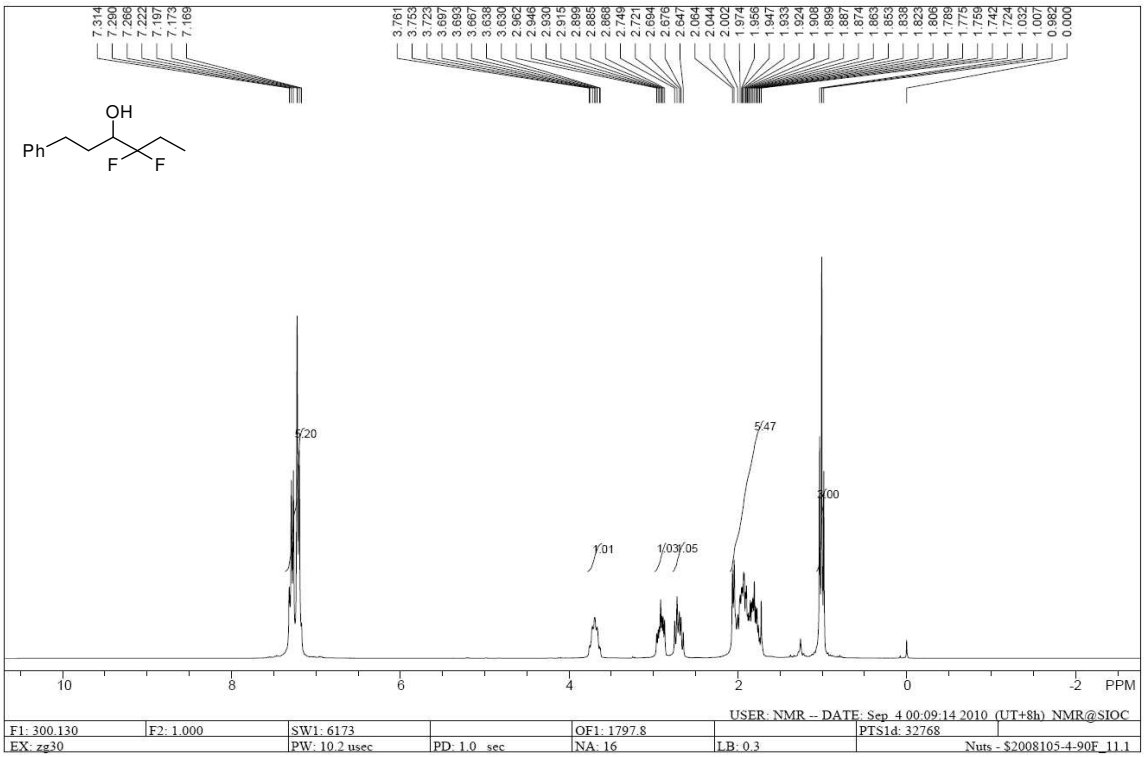


^{13}C NMR

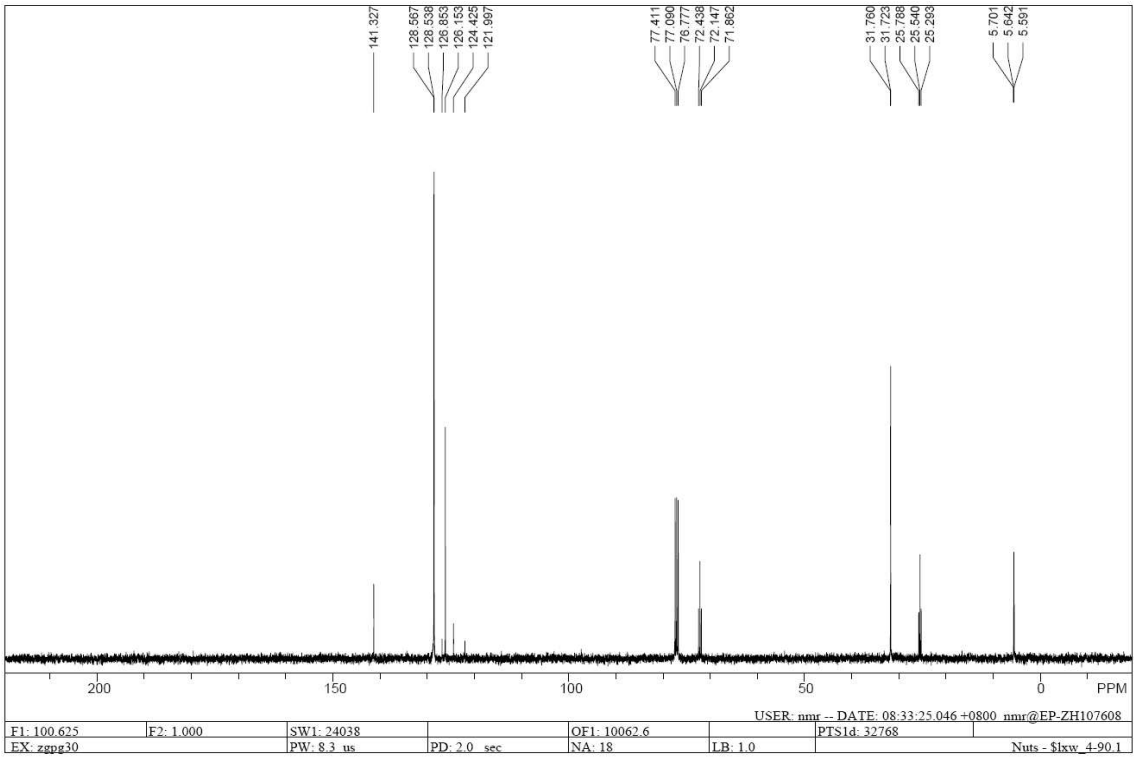


4,4-difluoro-1-phenylhexan-3-ol

^{1}H NMR

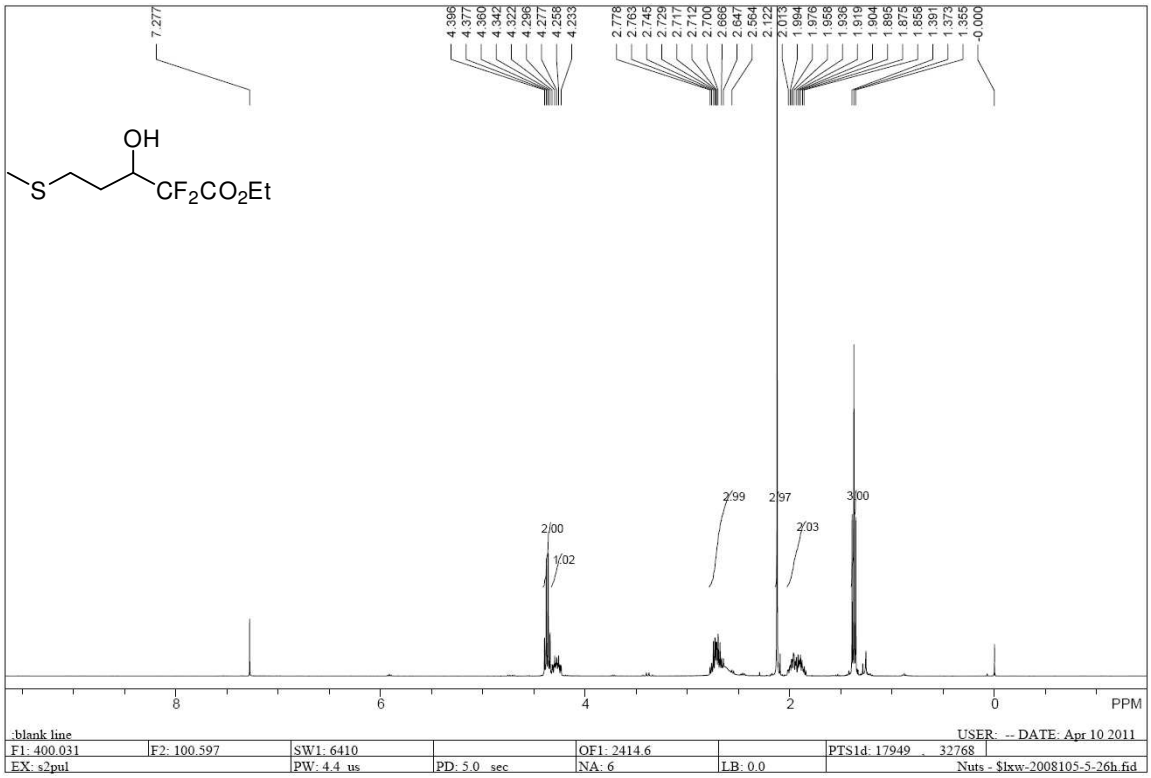


^{13}C NMR

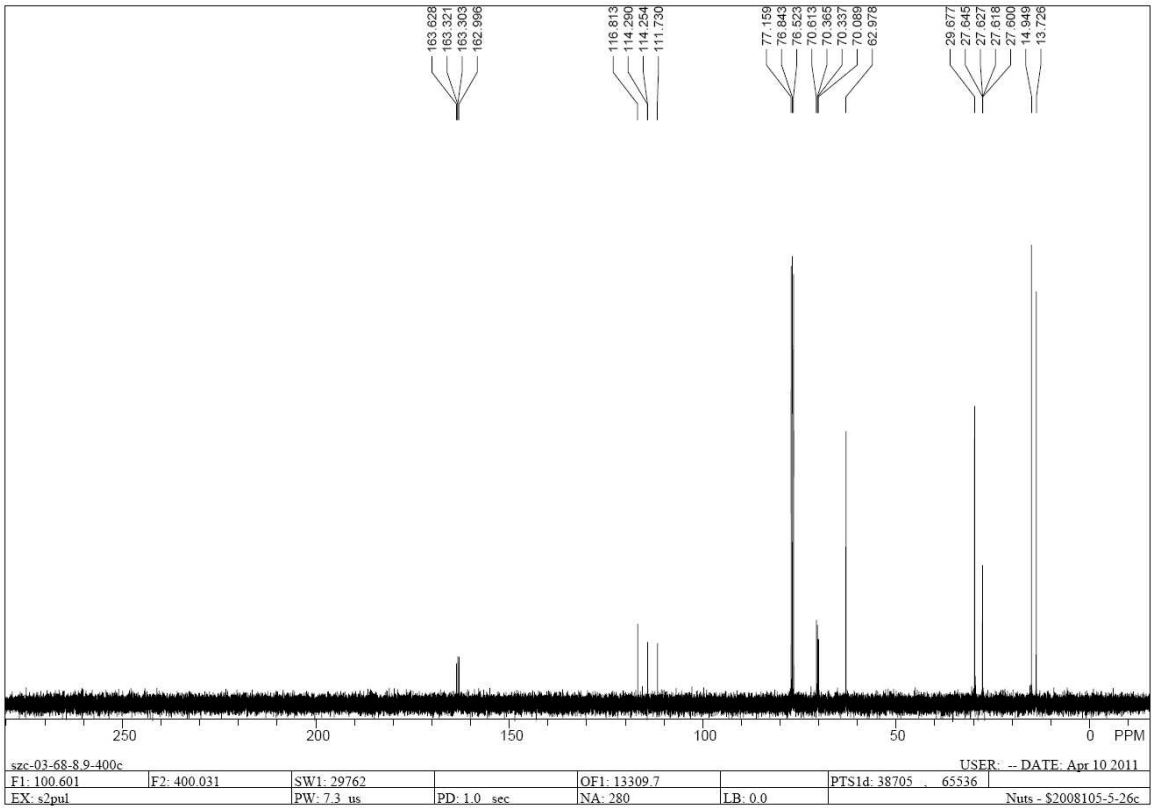


Ethyl 2,2-difluoro-3-hydroxy-5-(methylthio)pentanoate

^{1}H NMR

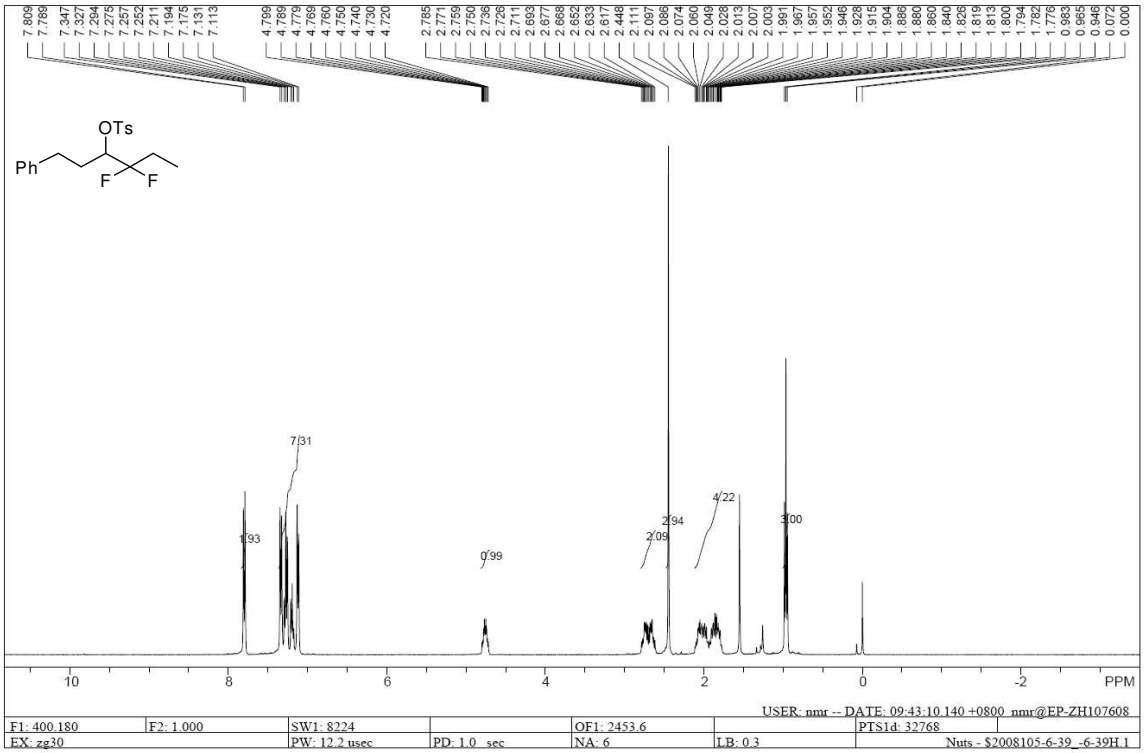


^{13}C NMR

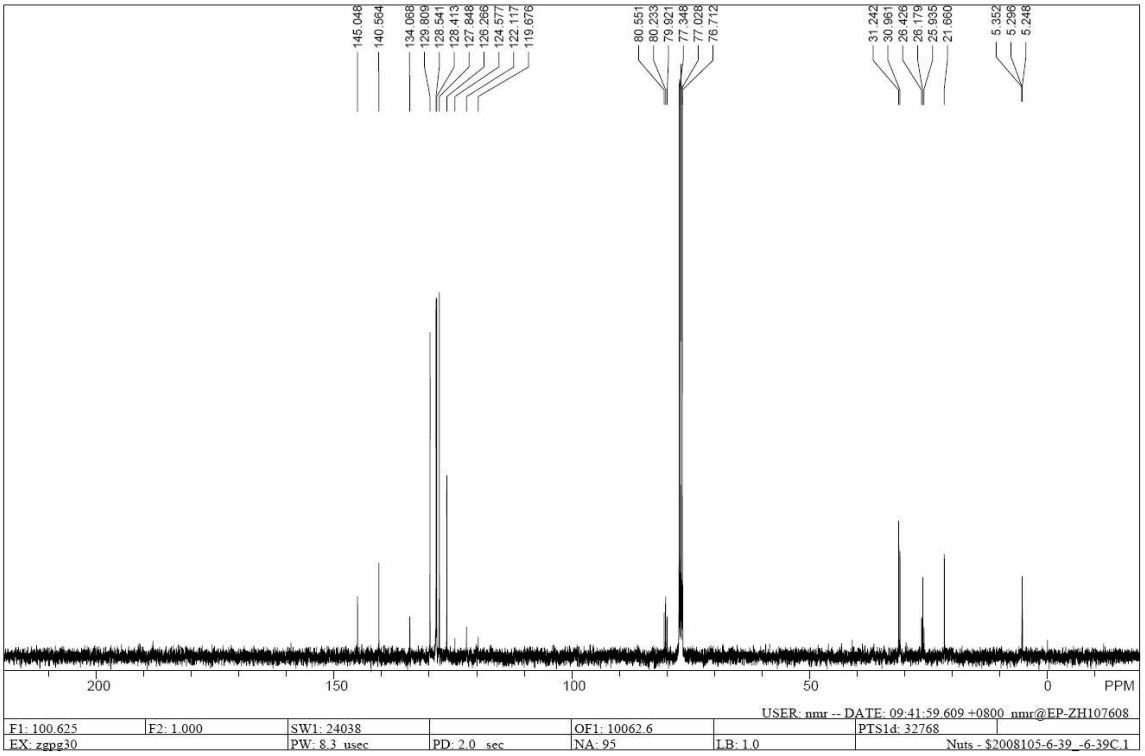


4,4-difluoro-1-phenylhexan-3-yl 4-methylbenzenesulfonate

^{1}H NMR

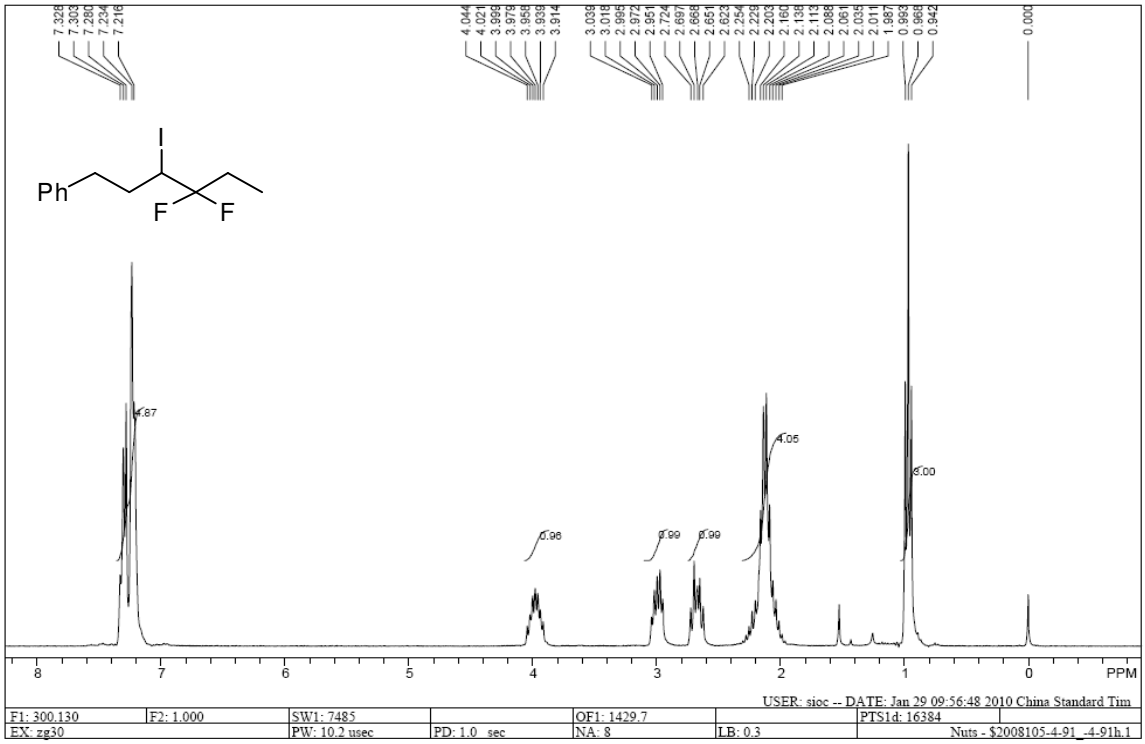


^{13}C NMR

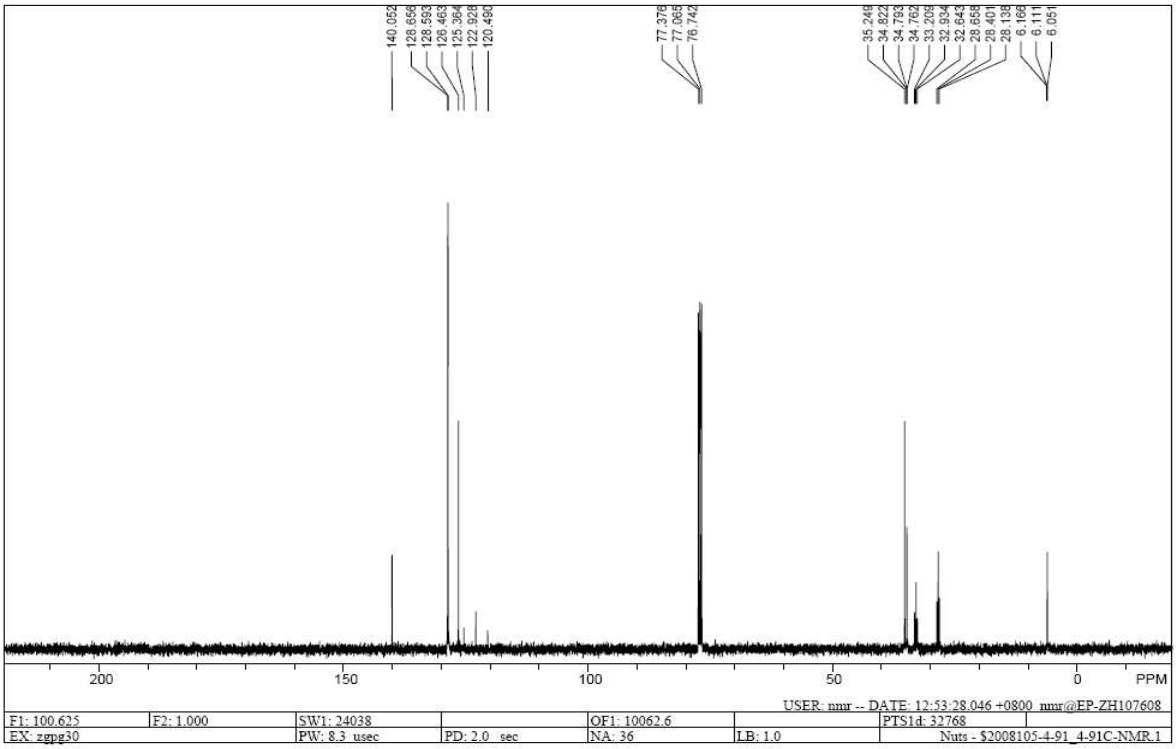


(4,4-difluoro-3-iodohexyl)benzene (1a):

^{1}H NMR

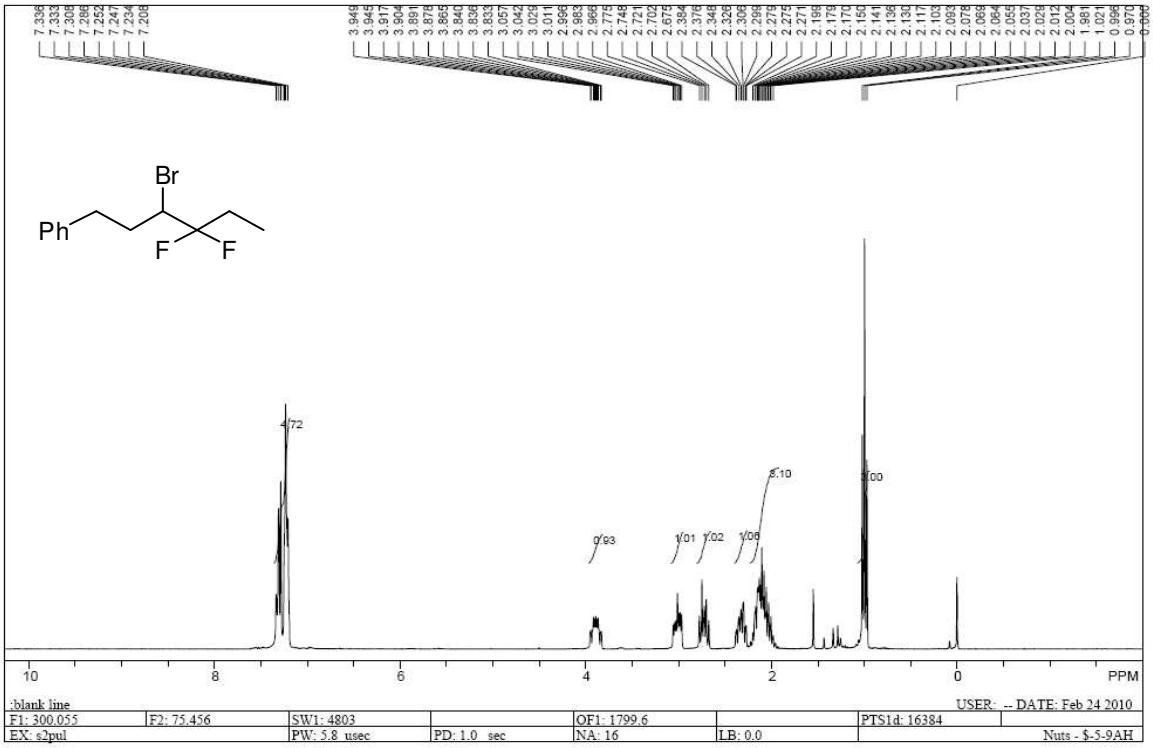


^{13}C NMR

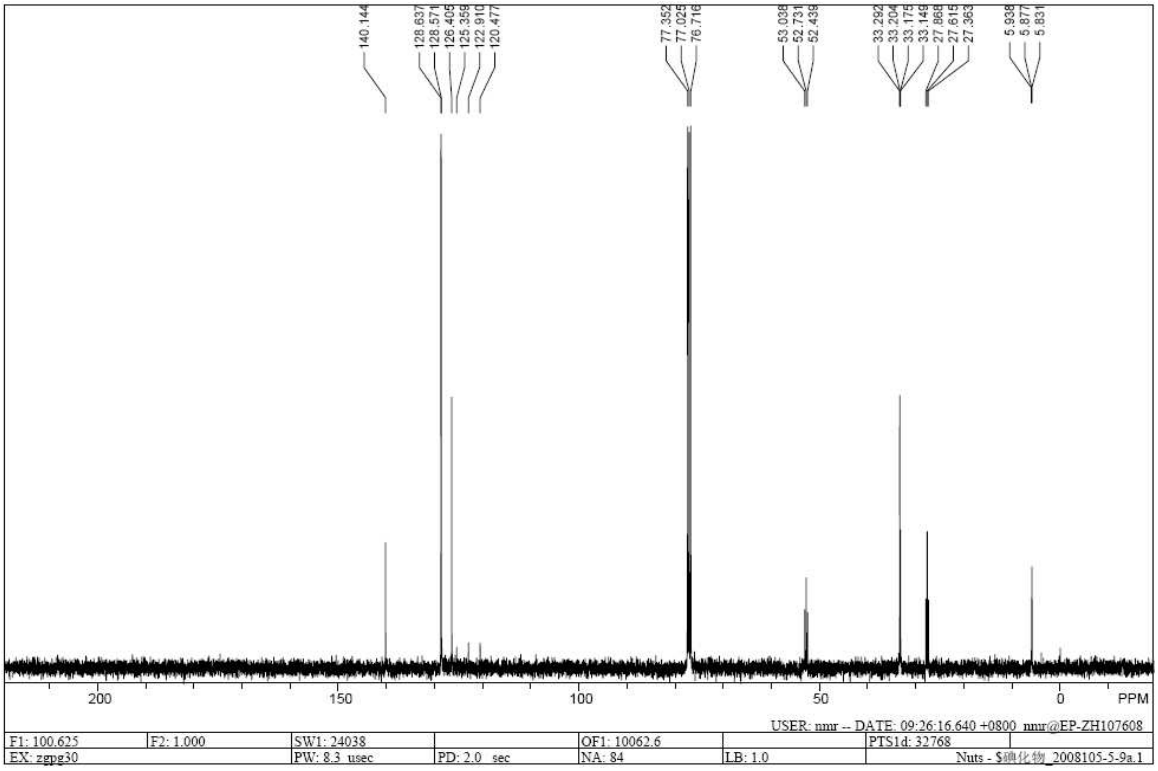


(3-bromo-4,4-difluorohexyl)benzene (1a′):

^{1}H NMR

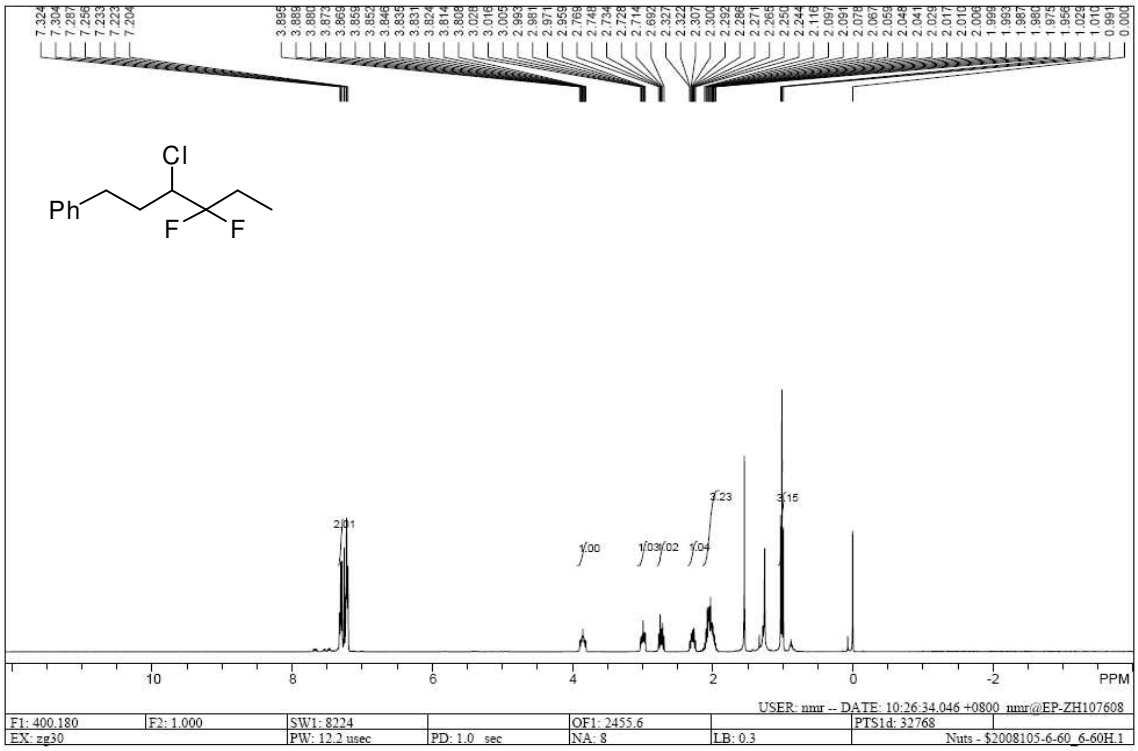


^{13}C NMR

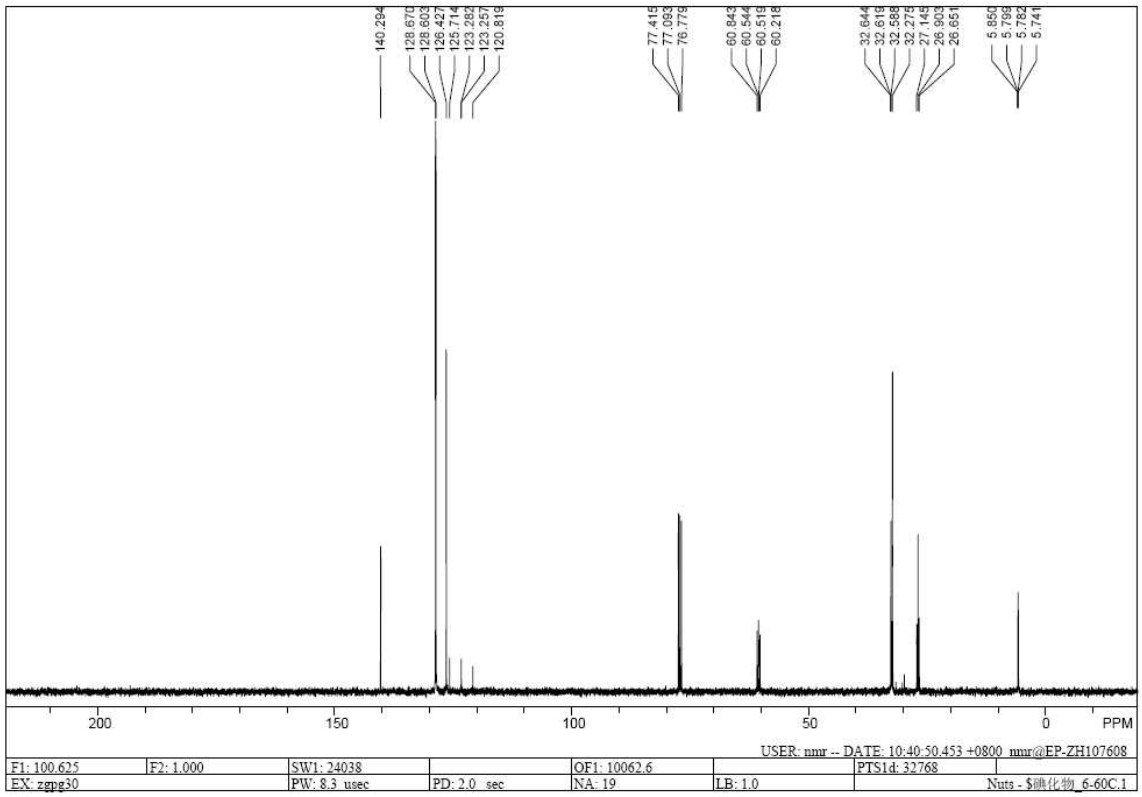


(3-chloro-4,4-difluorohexyl)benzene (1a″):

^{1}H NMR

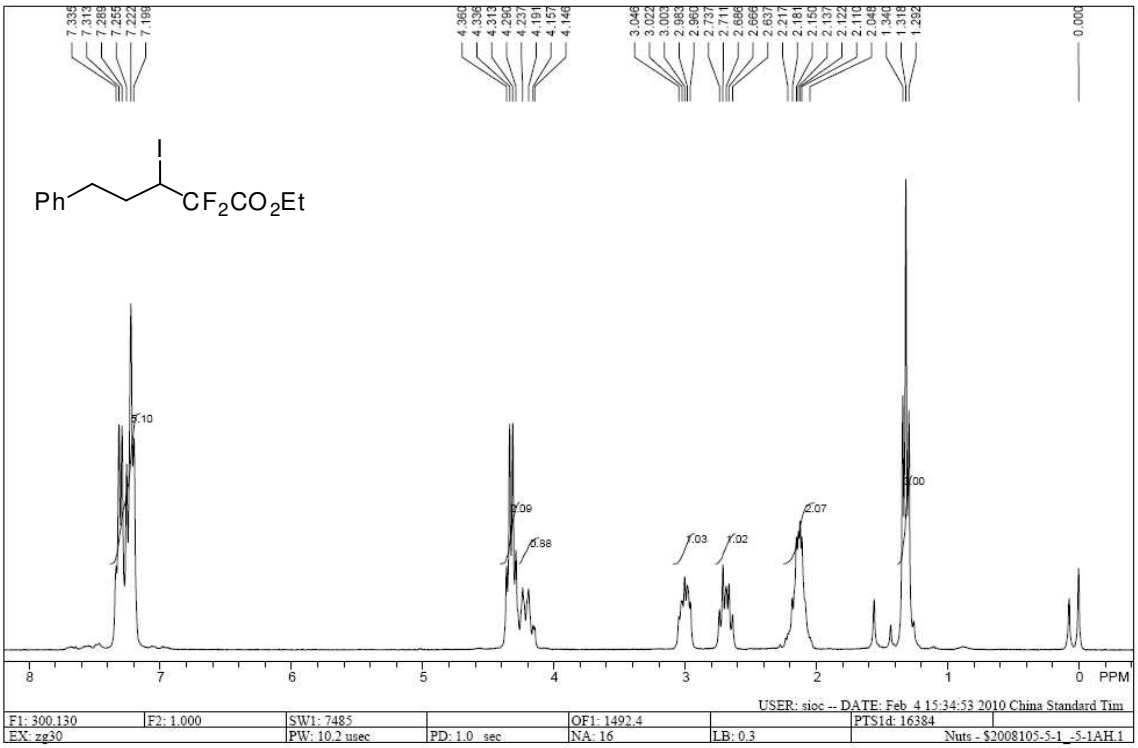


^{13}C NMR

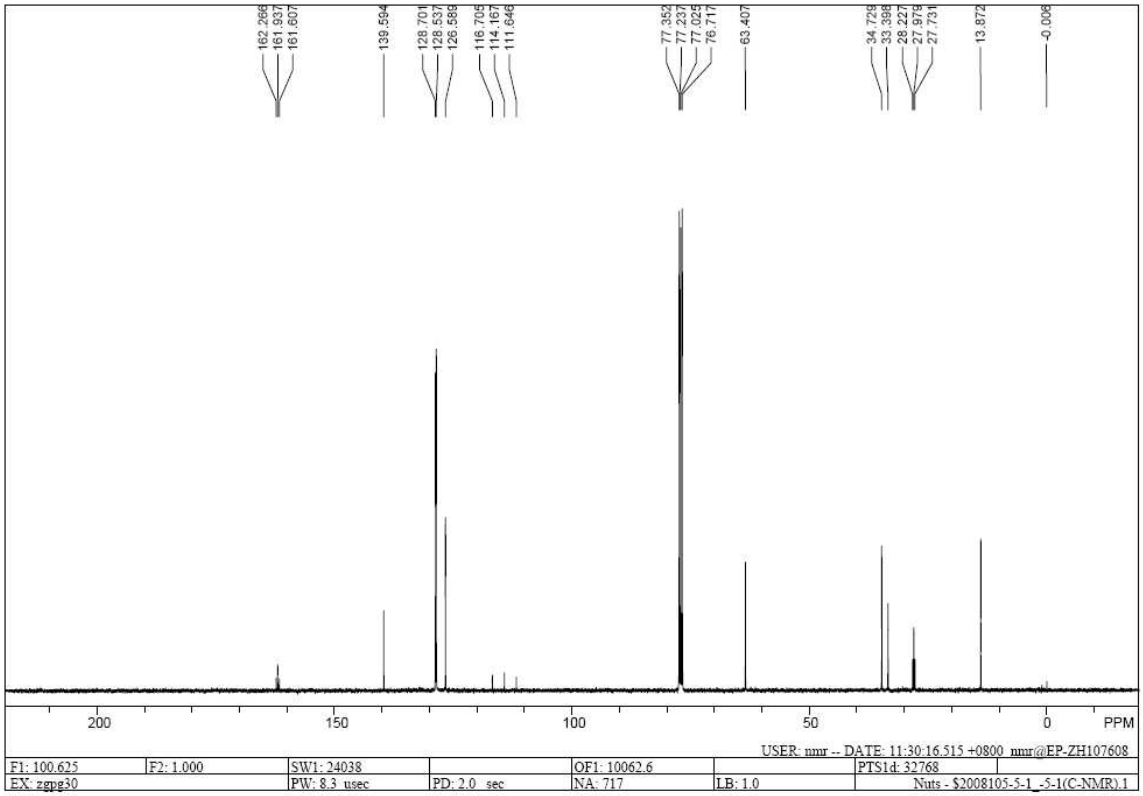


Ethyl 2,2-difluoro-3-iodo-5-phenylpentanoate (1b):

^{1}H NMR

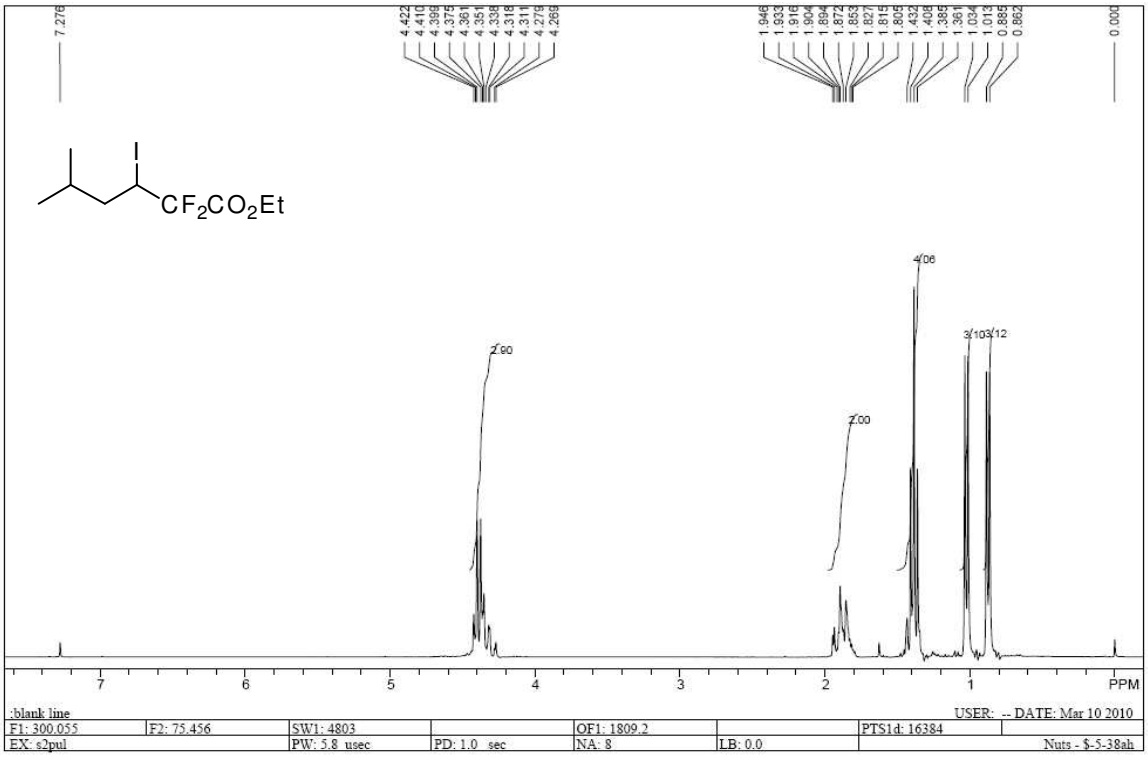


^{13}C NMR

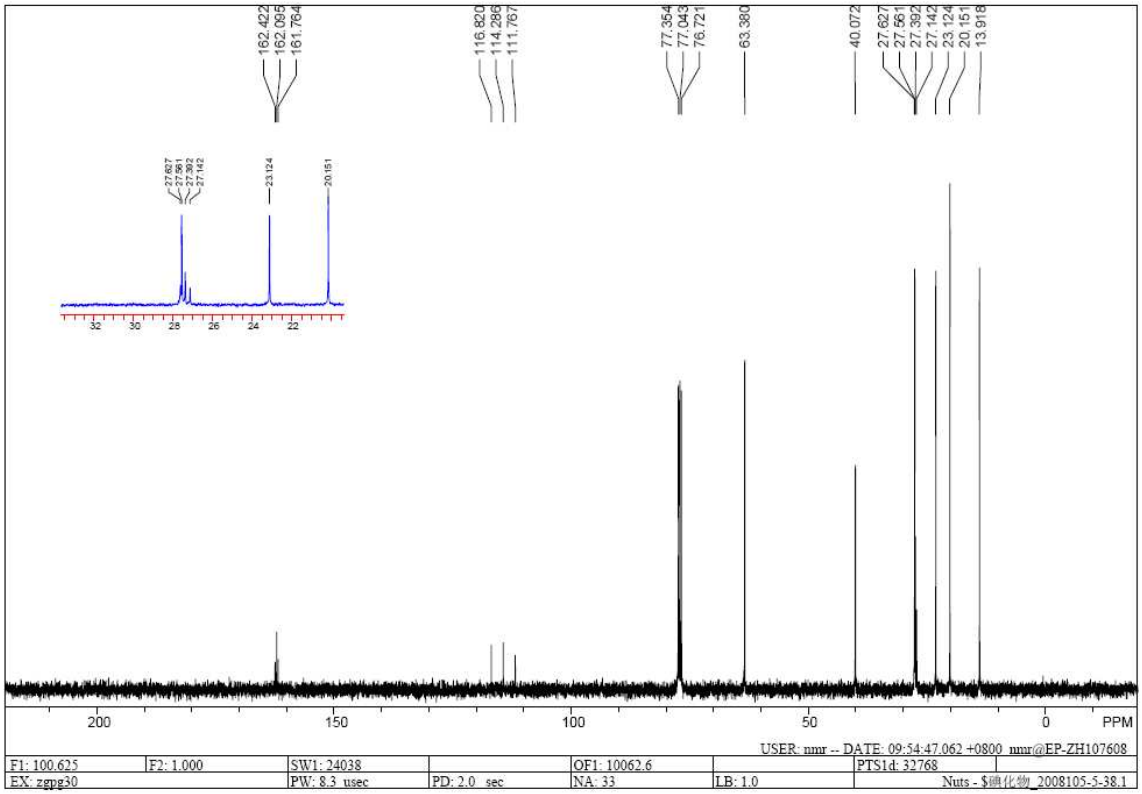


Ethyl 2,2-difluoro-3-iodo-5-methylhexanoate (1c):

^{1}H NMR

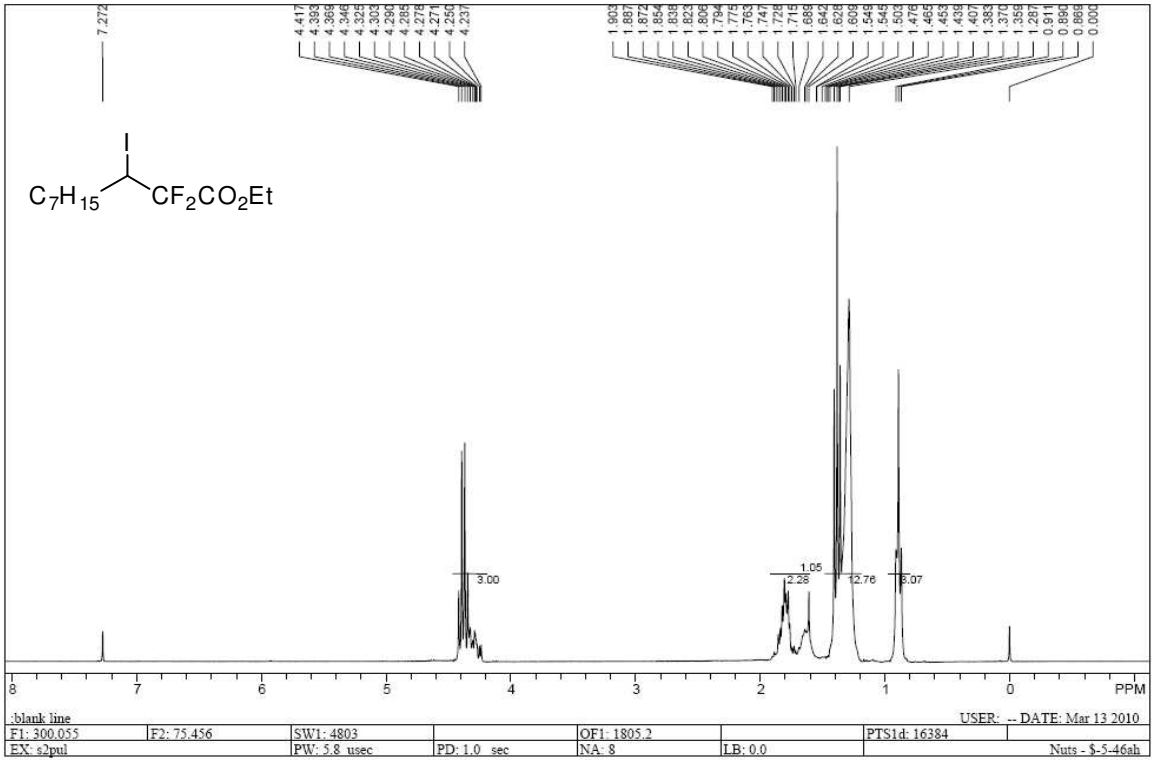


^{13}C NMR

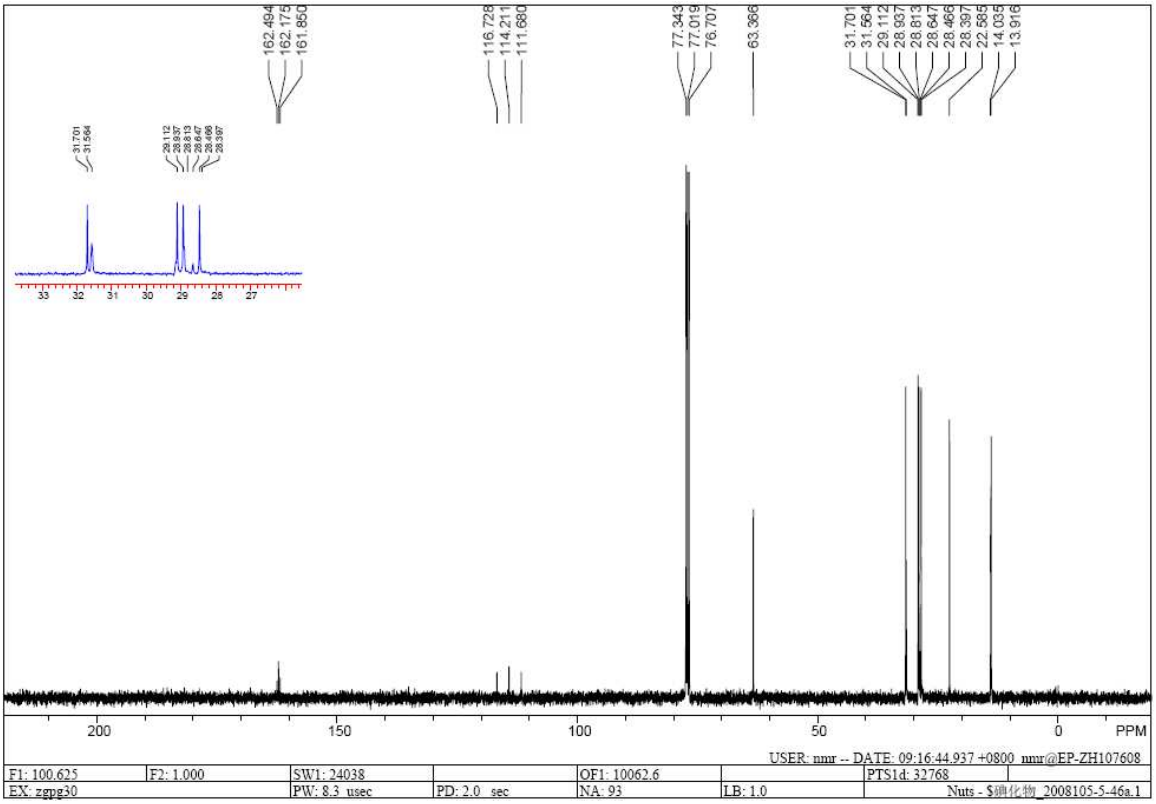


Ethyl 2,2-difluoro-3-iododecanoate (1d):

^{1}H NMR

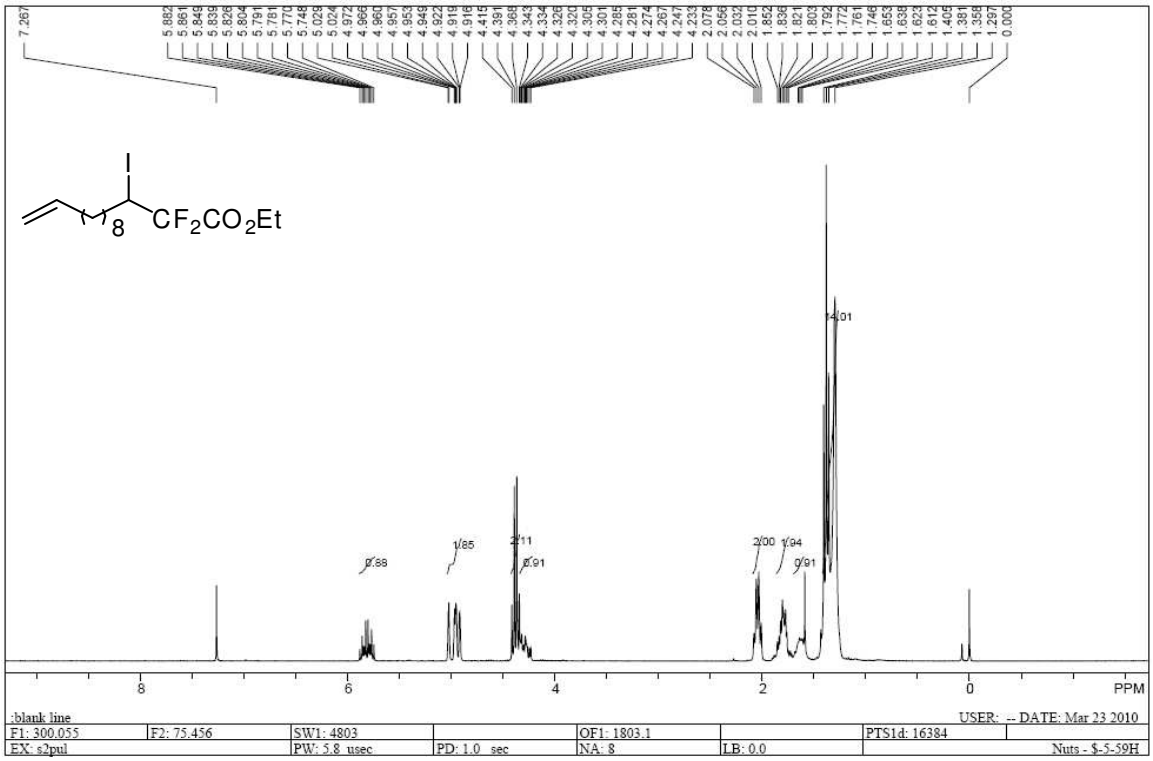


^{13}C NMR

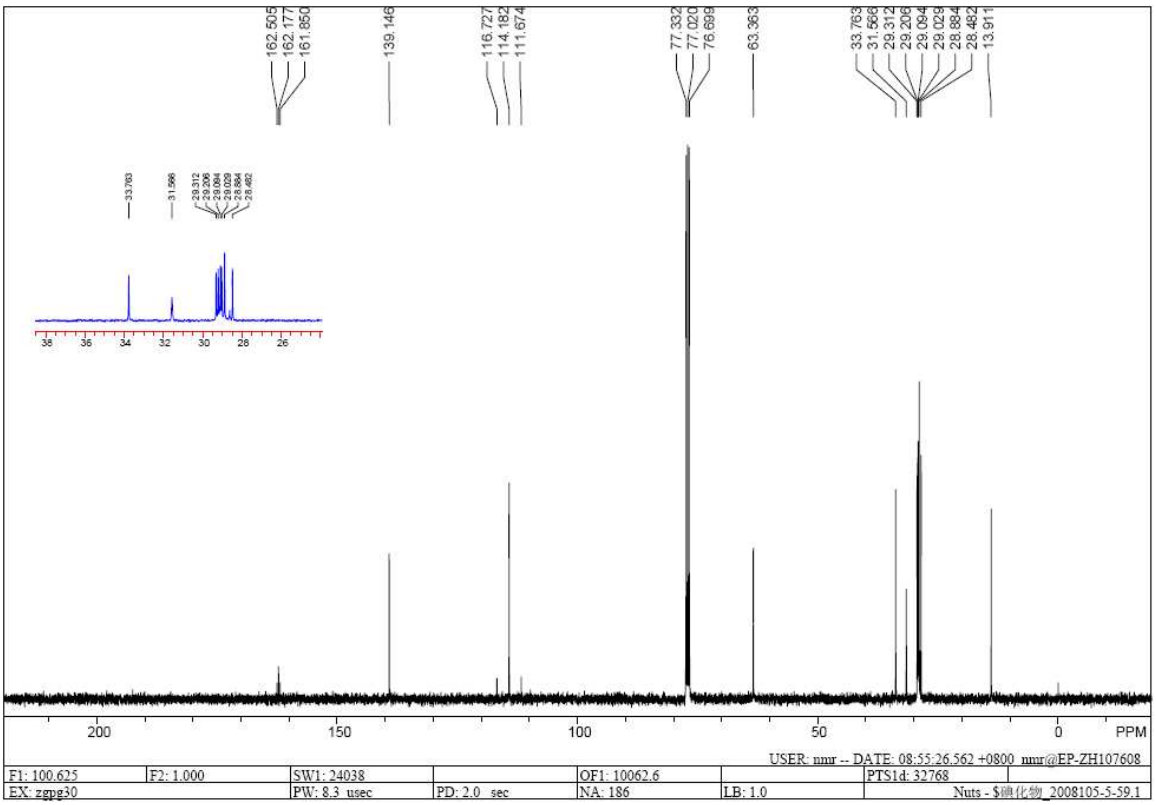


Ethyl 2,2-difluoro-3-iodotridec-12-enoate (1e):

^{1}H NMR

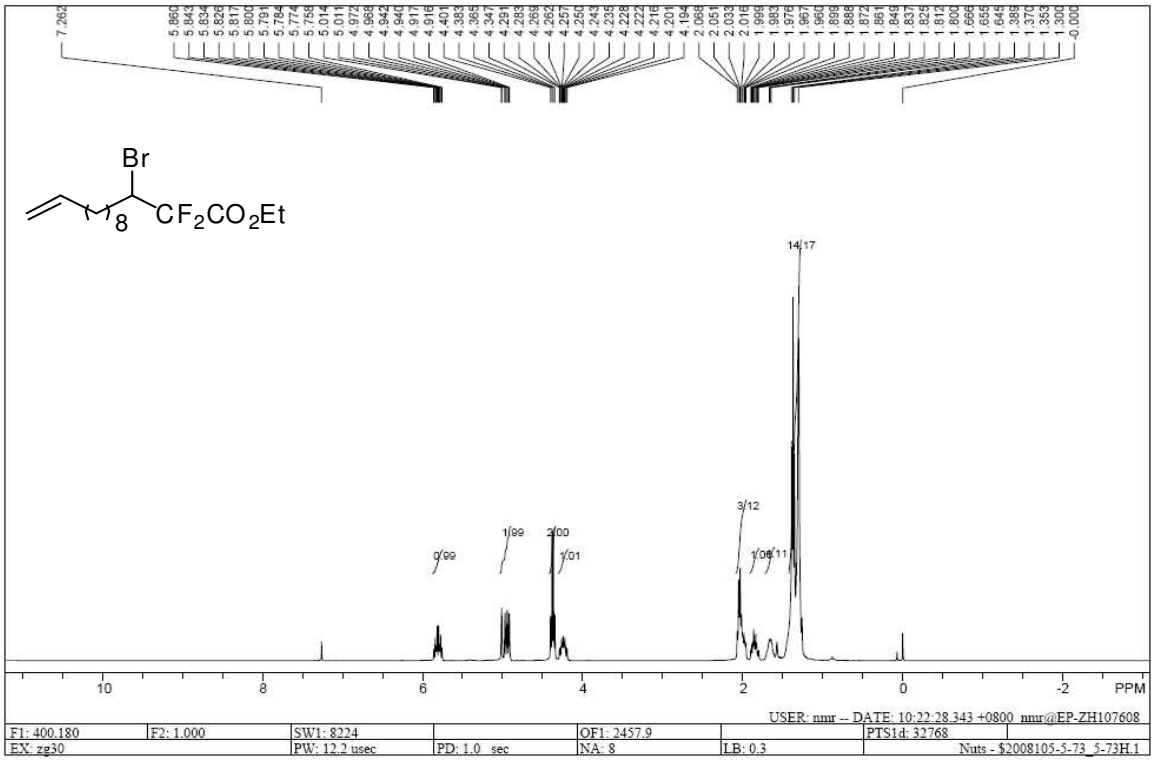


^{13}C NMR

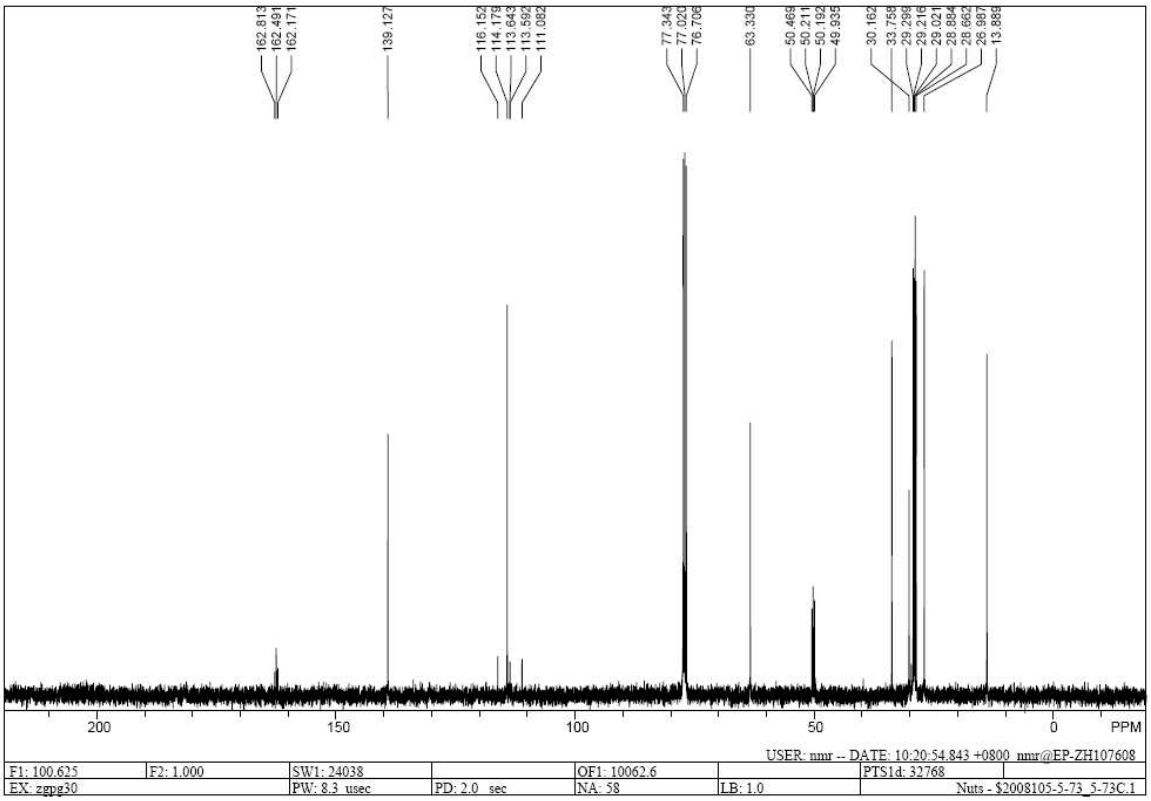


Ethyl 3-bromo-2,2-difluorotridec-12-enoate (1e′):

^{1}H NMR

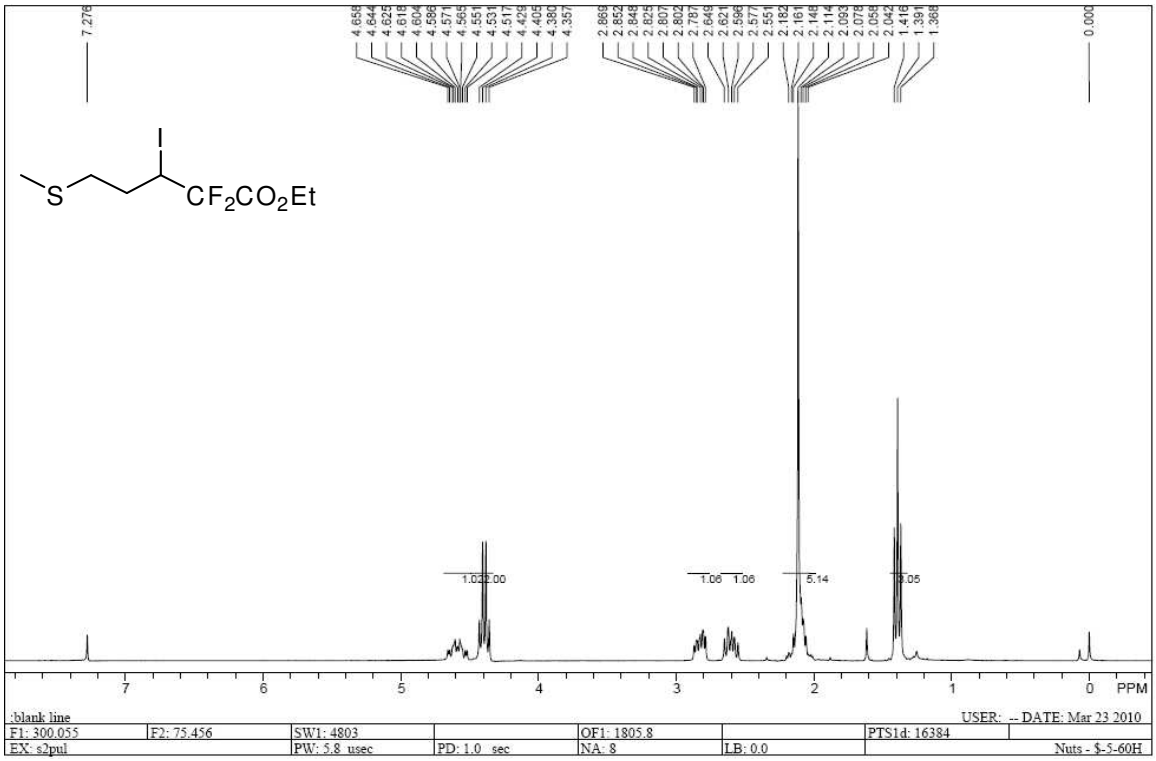


^{13}C NMR

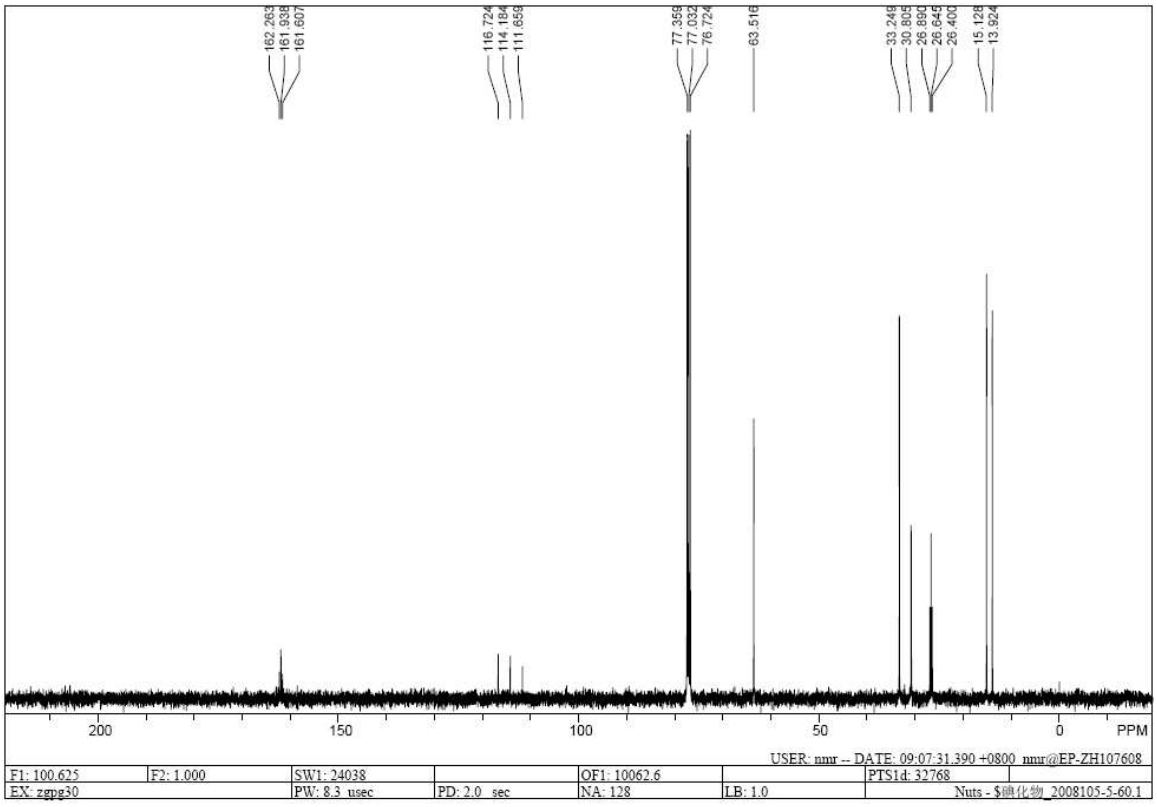


Ethyl 2,2-difluoro-3-iodo-5-(methylthio)pentanoate (1f):

^{1}H NMR

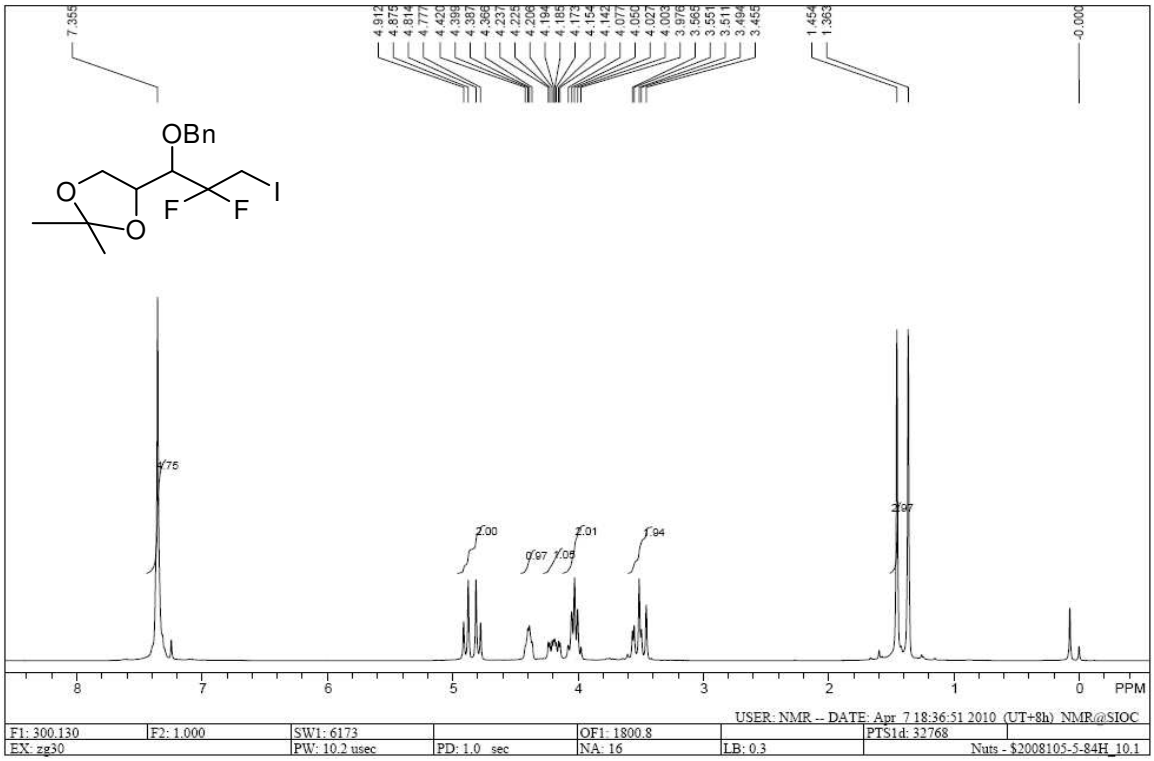


^{13}C NMR

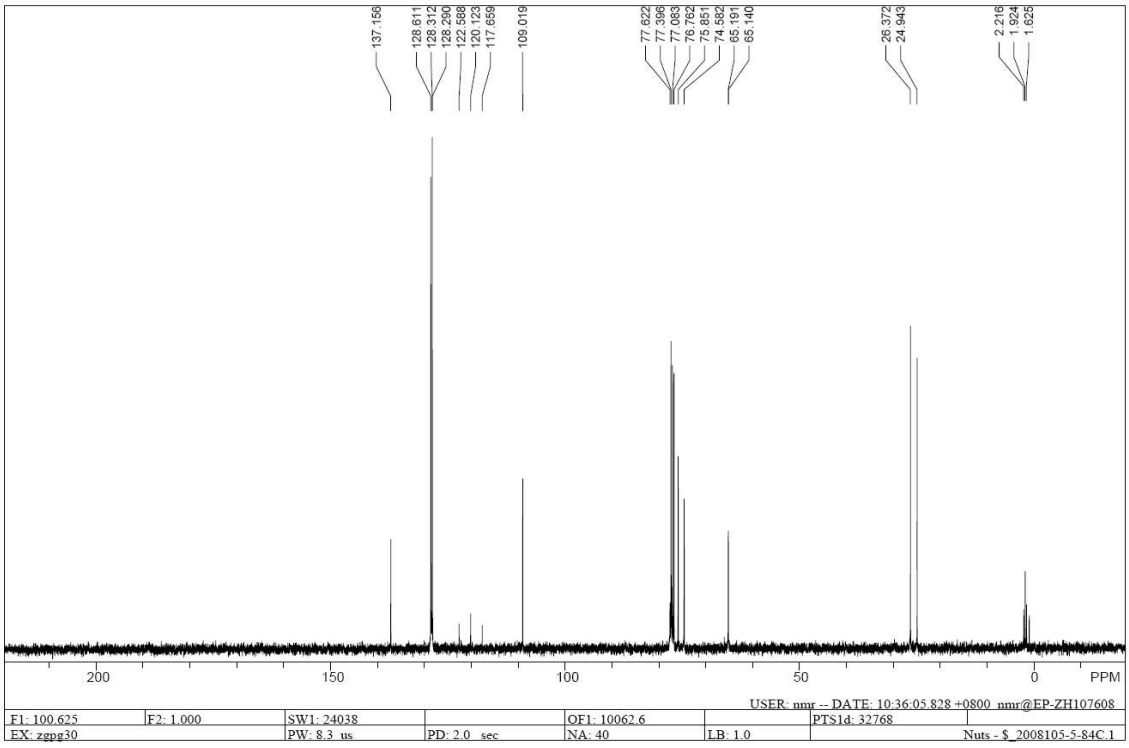


4-(1-(benzyloxy)-2,2-difluoro-3-iodopropyl)-2,2-dimethyl-1,3-dioxolane (1g):

^{1}H NMR

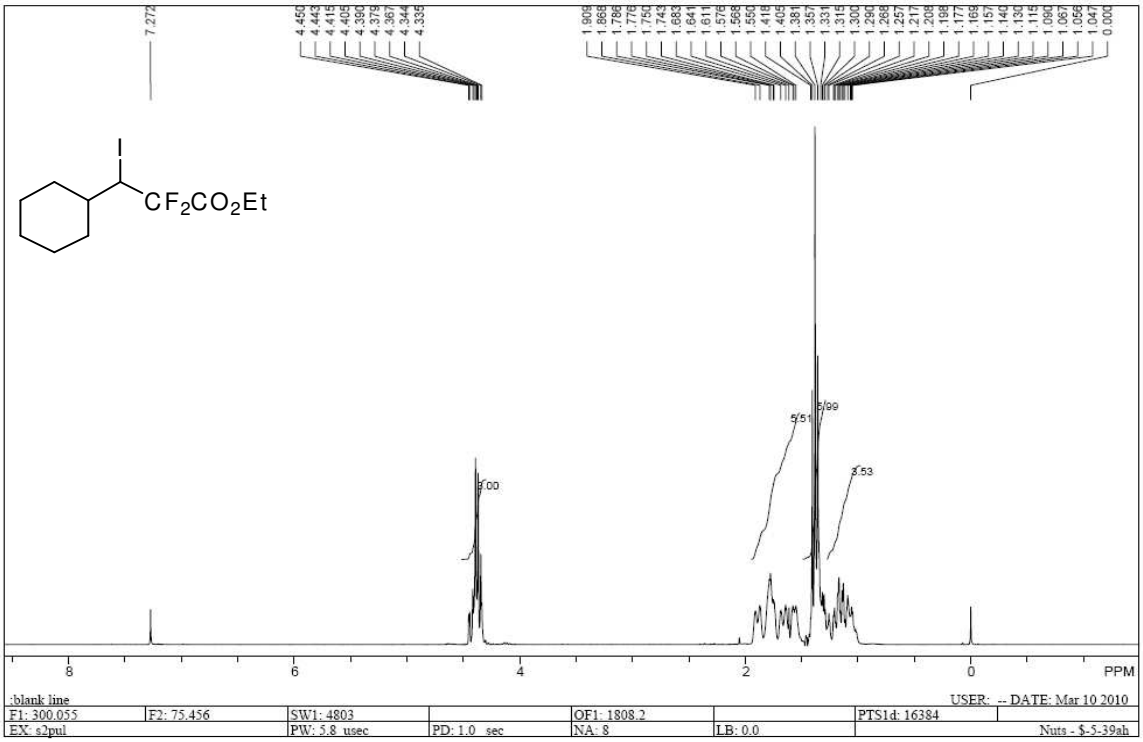


^{13}C NMR

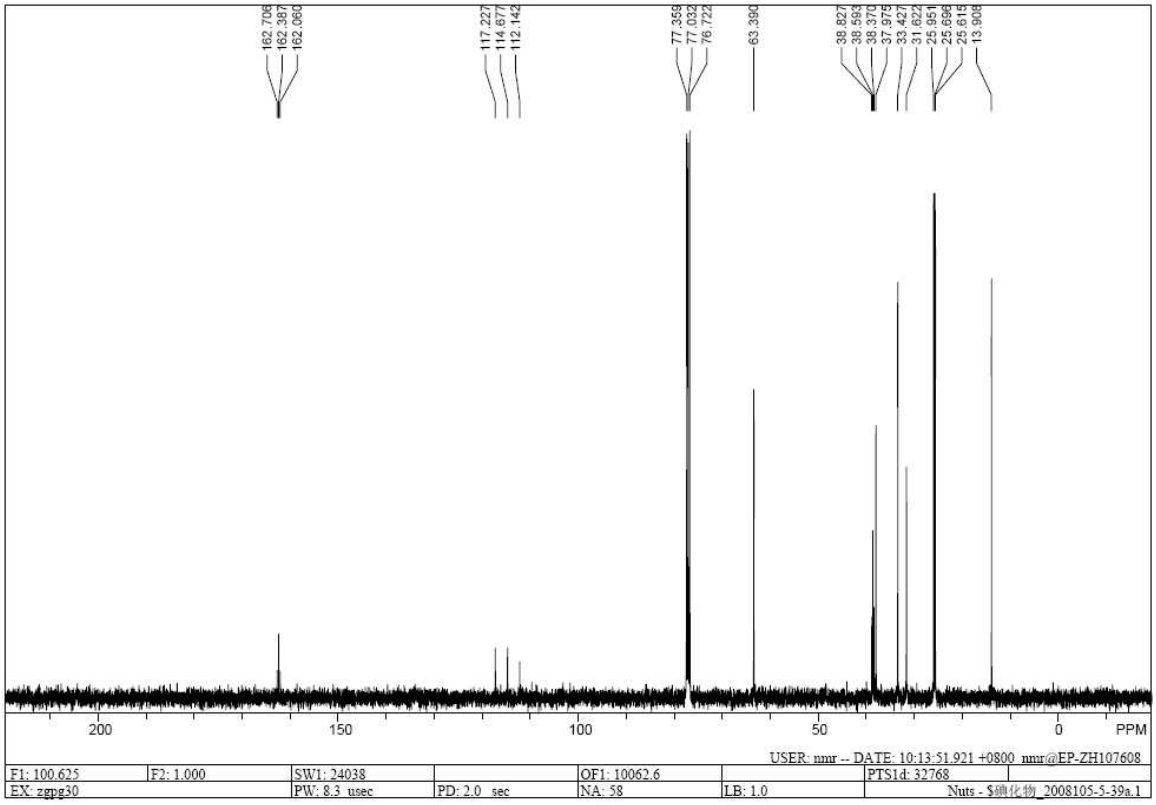


Ethyl 3-cyclohexyl-2,2-difluoro-3-iodopropanoate (1h):

^{1}H NMR

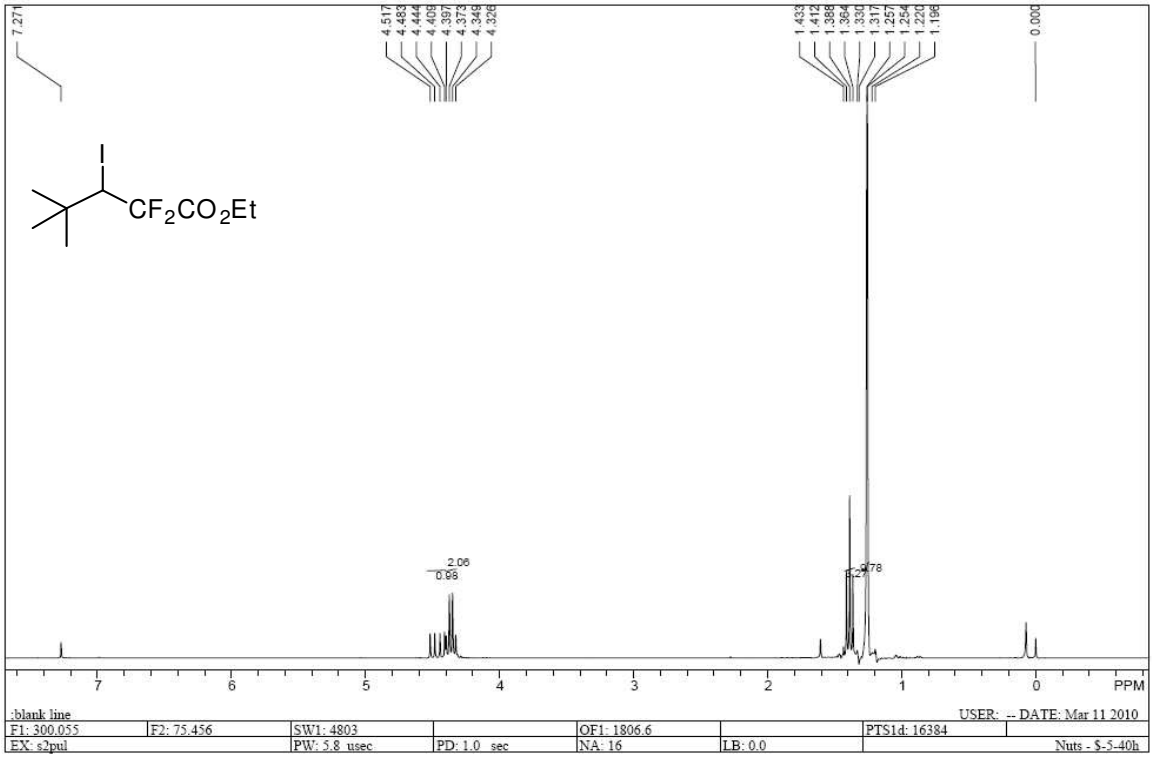


^{13}C NMR

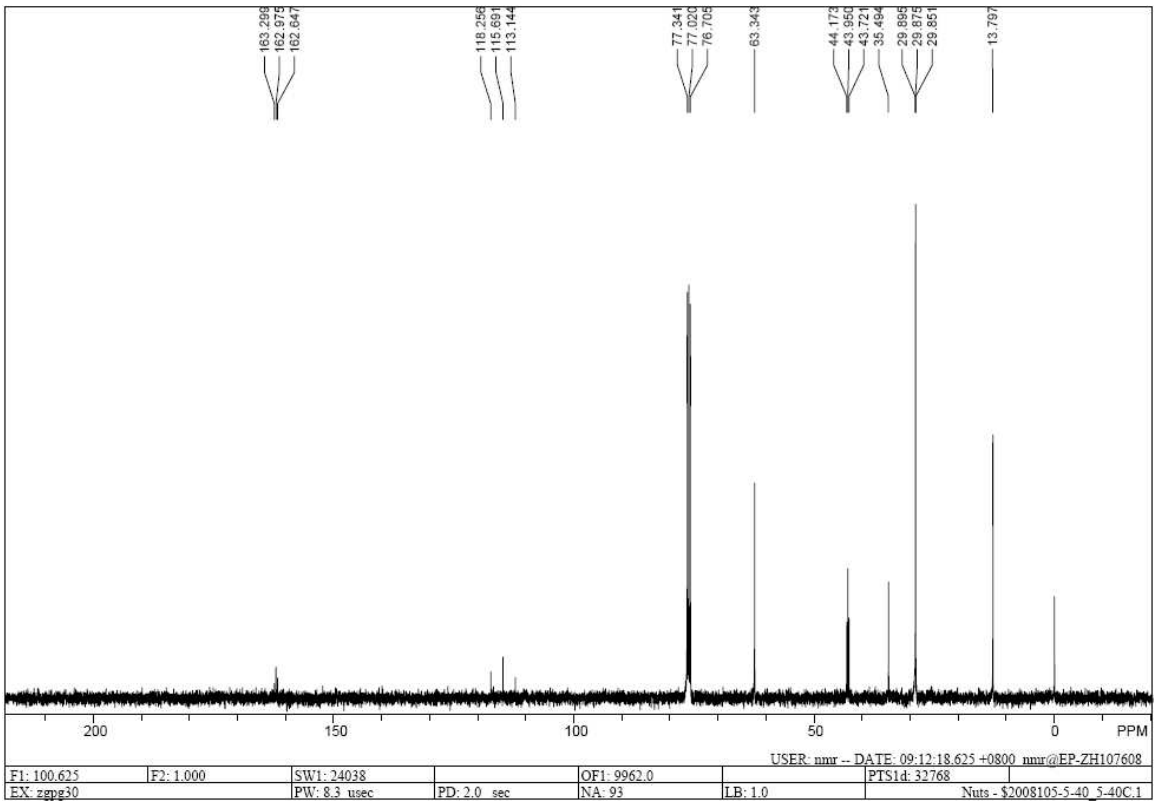


Ethyl 2,2-difluoro-3-iodo-4,4-dimethylpentanoate (1i):

^{1}H NMR

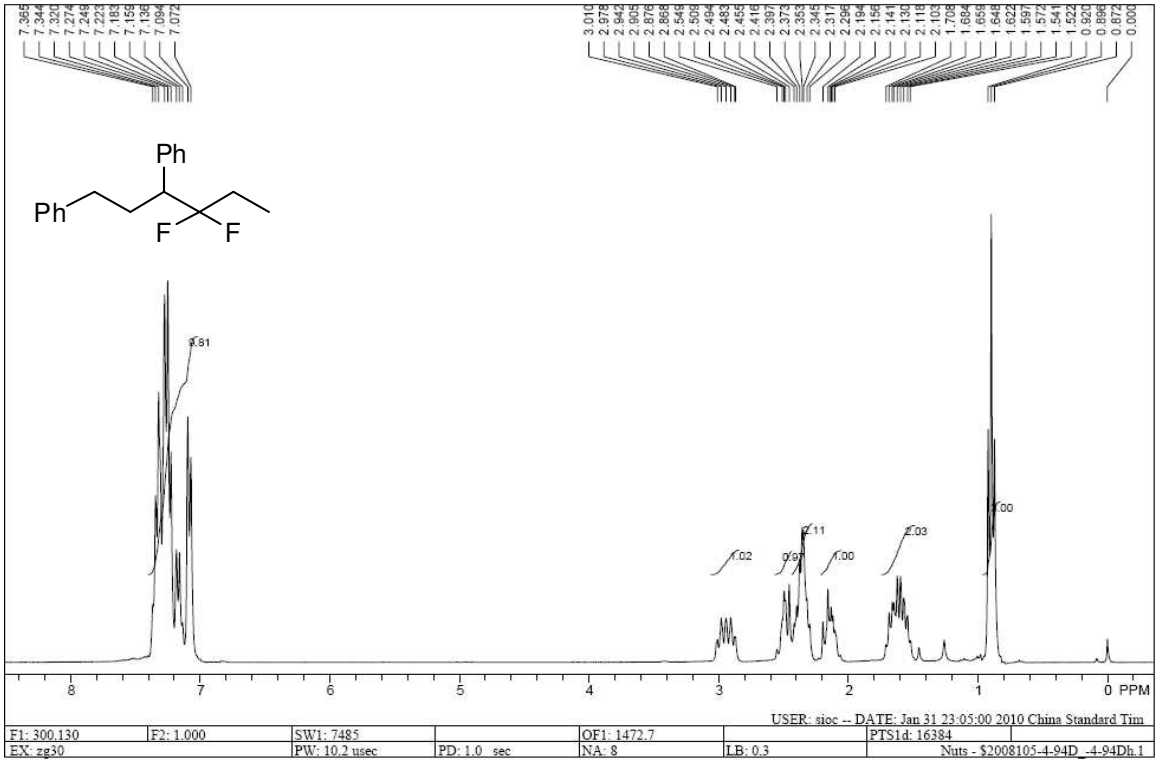


^{13}C NMR

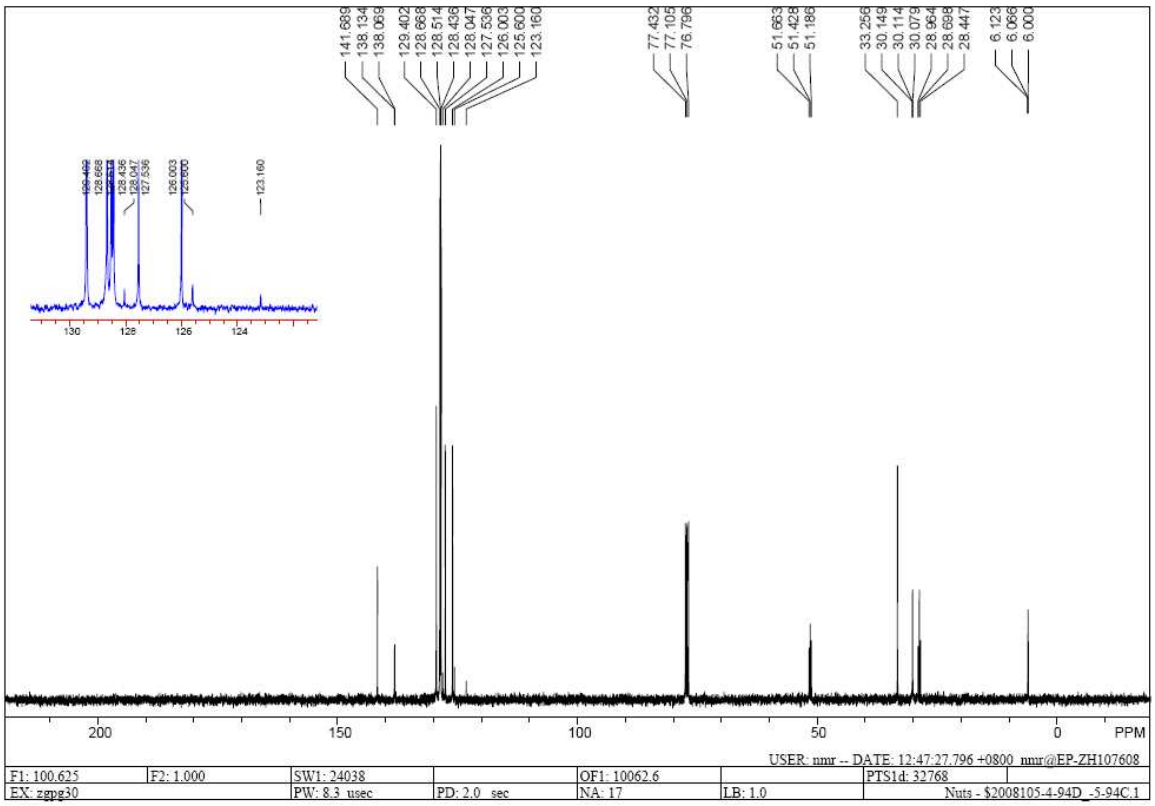


(4,4-difluorohexane-1,3-diyl)dibenzene (3a):

^{1}H NMR

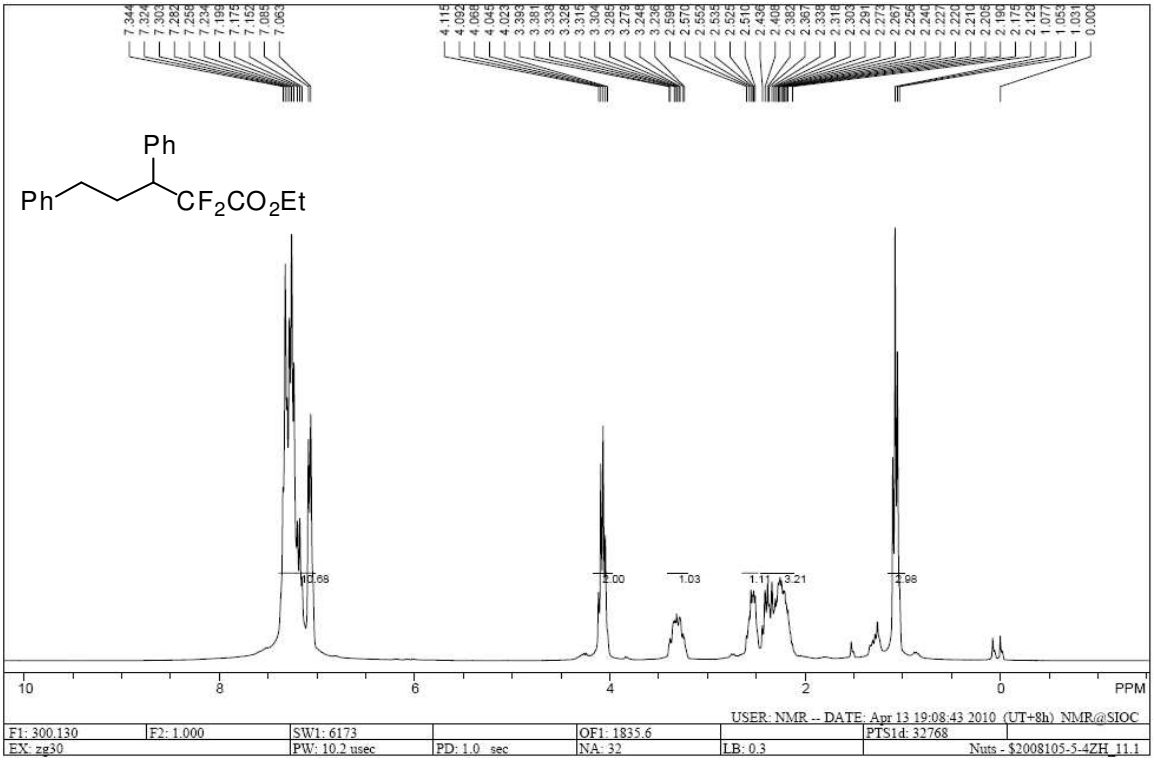


^{13}C NMR

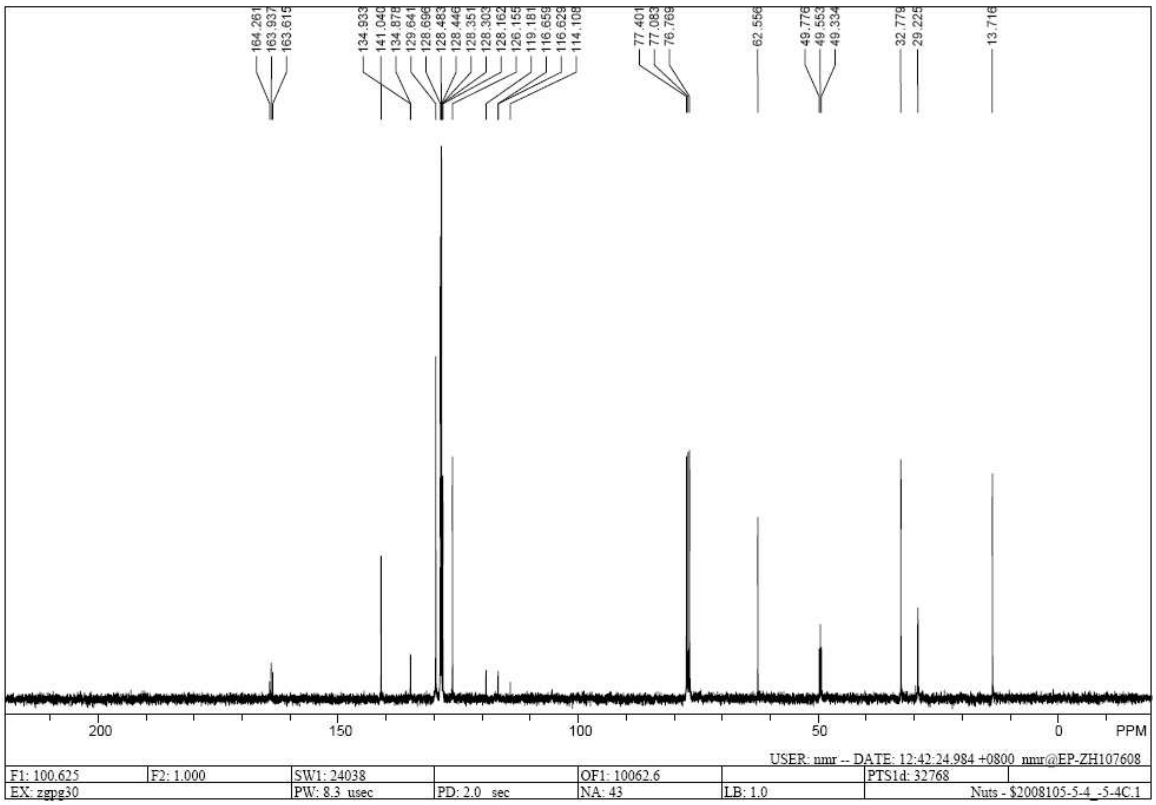


Ethyl 2,2-difluoro-3,5-diphenylpentanoate (3b):

^{1}H NMR

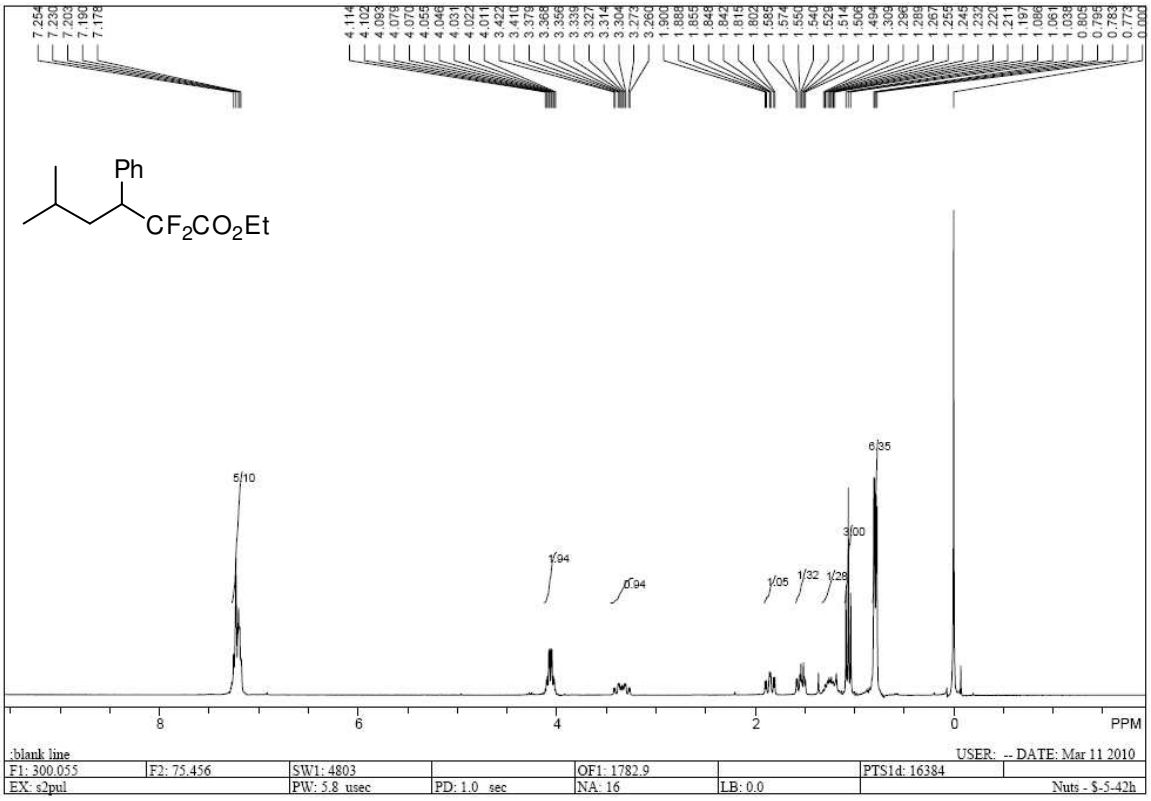


^{13}C NMR

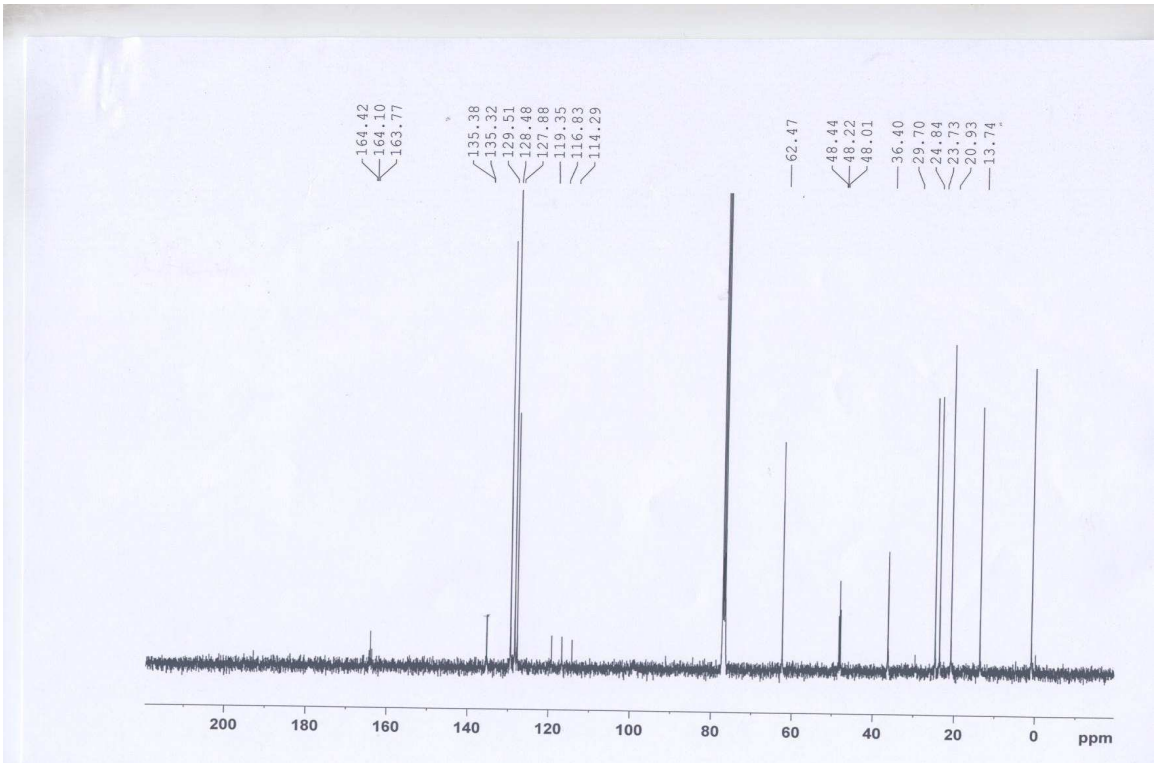


Ethyl 2,2-difluoro-5-methyl-3-phenylhexanoate (3c):

^{1}H NMR

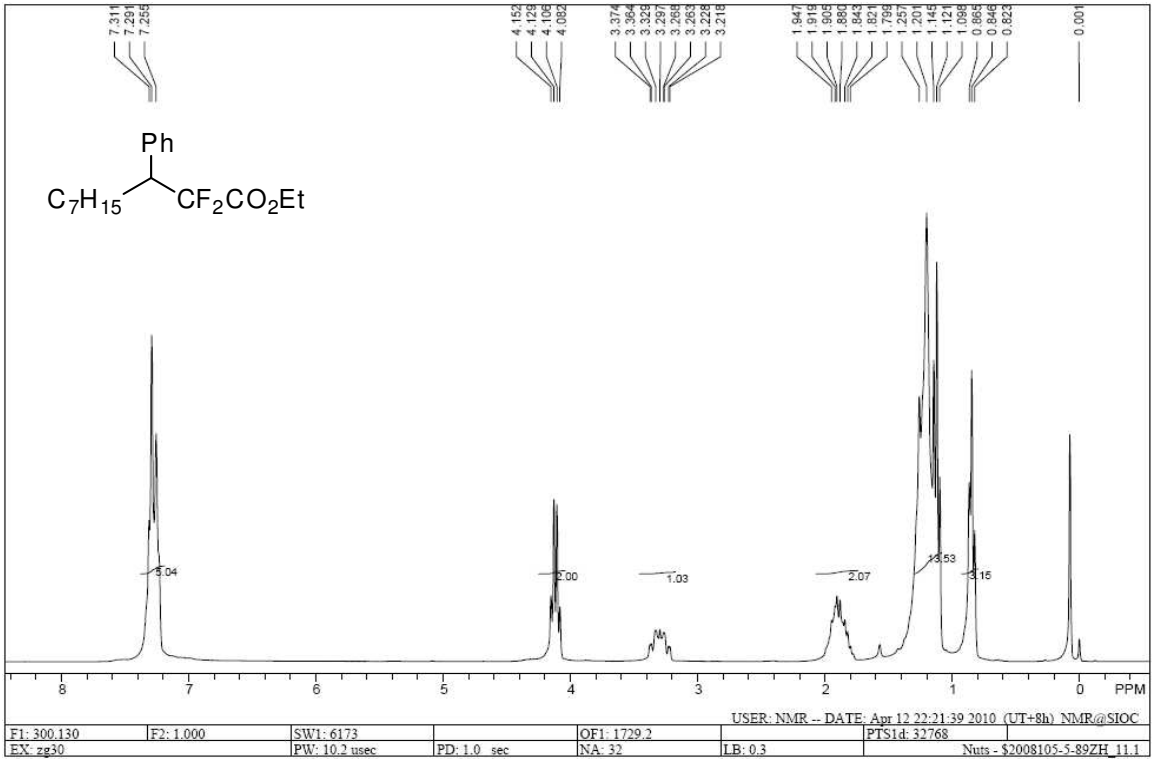


^{13}C NMR

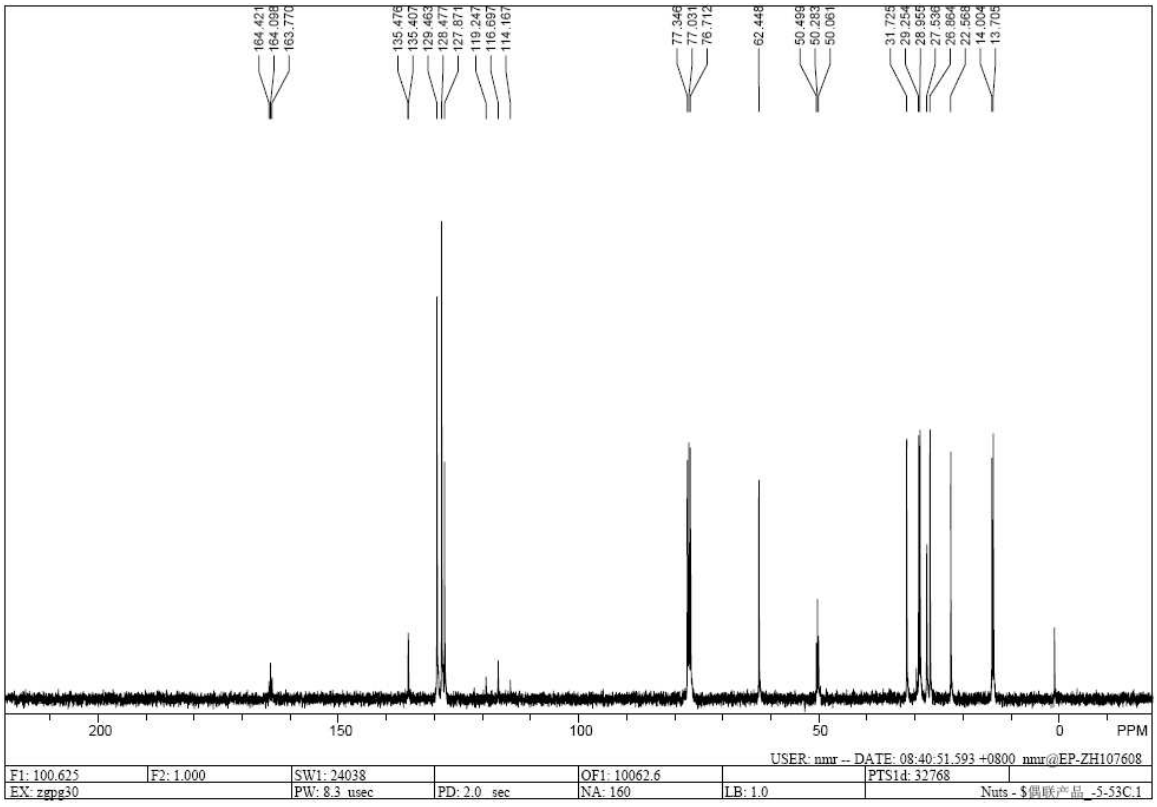


Ethyl 2,2-difluoro-3-phenyldecanoate (3d):

^{1}H NMR

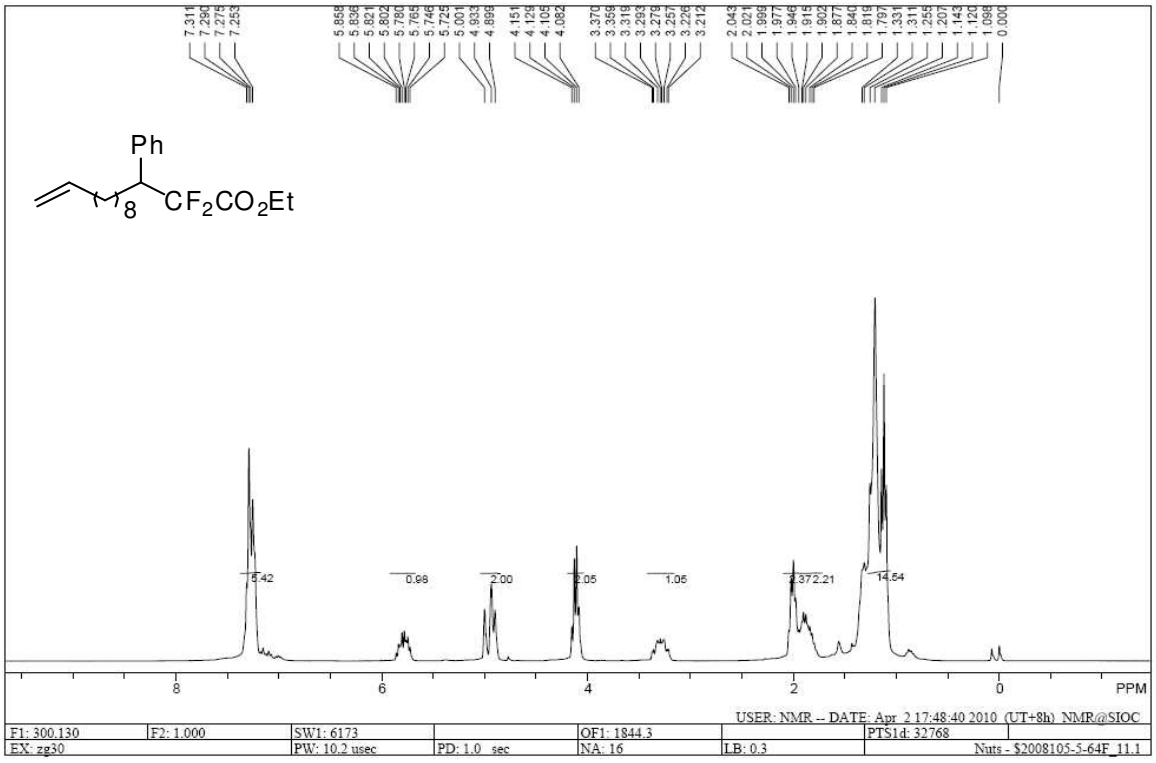


^{13}C NMR

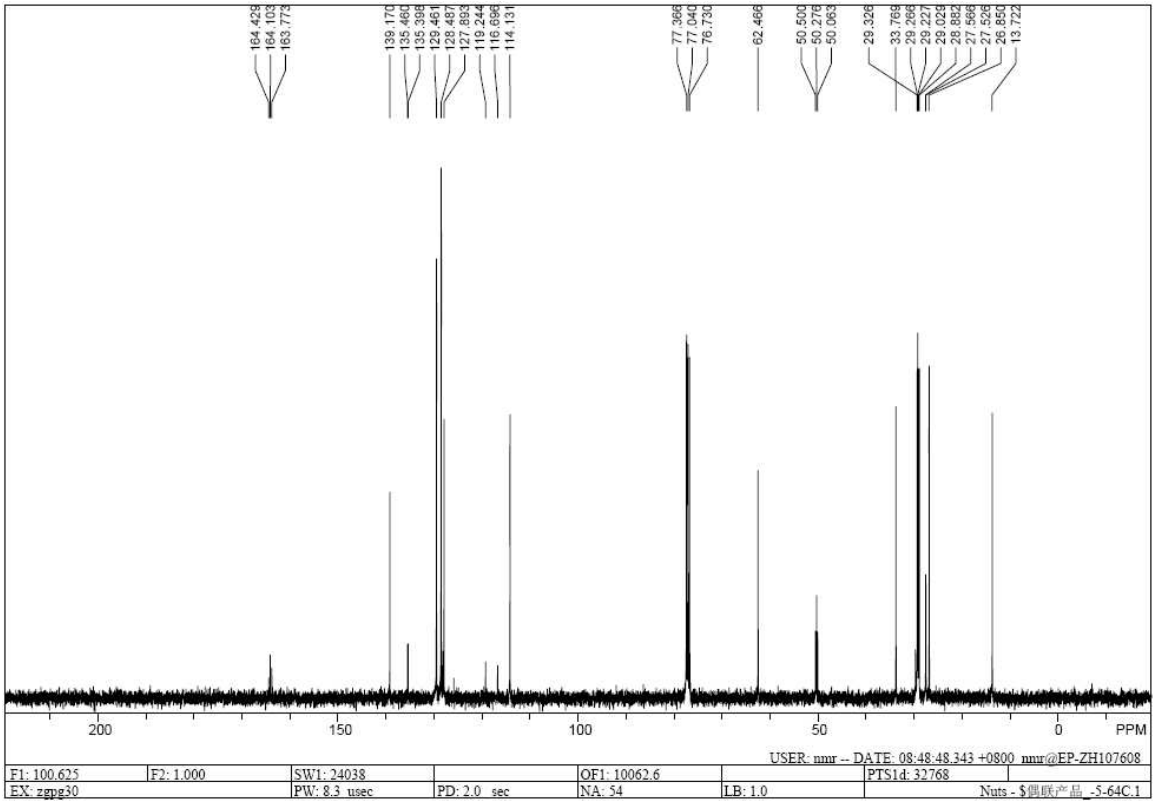


Ethyl 2,2-difluoro-3-phenyltridec-12-enoate (3e):

^{1}H NMR

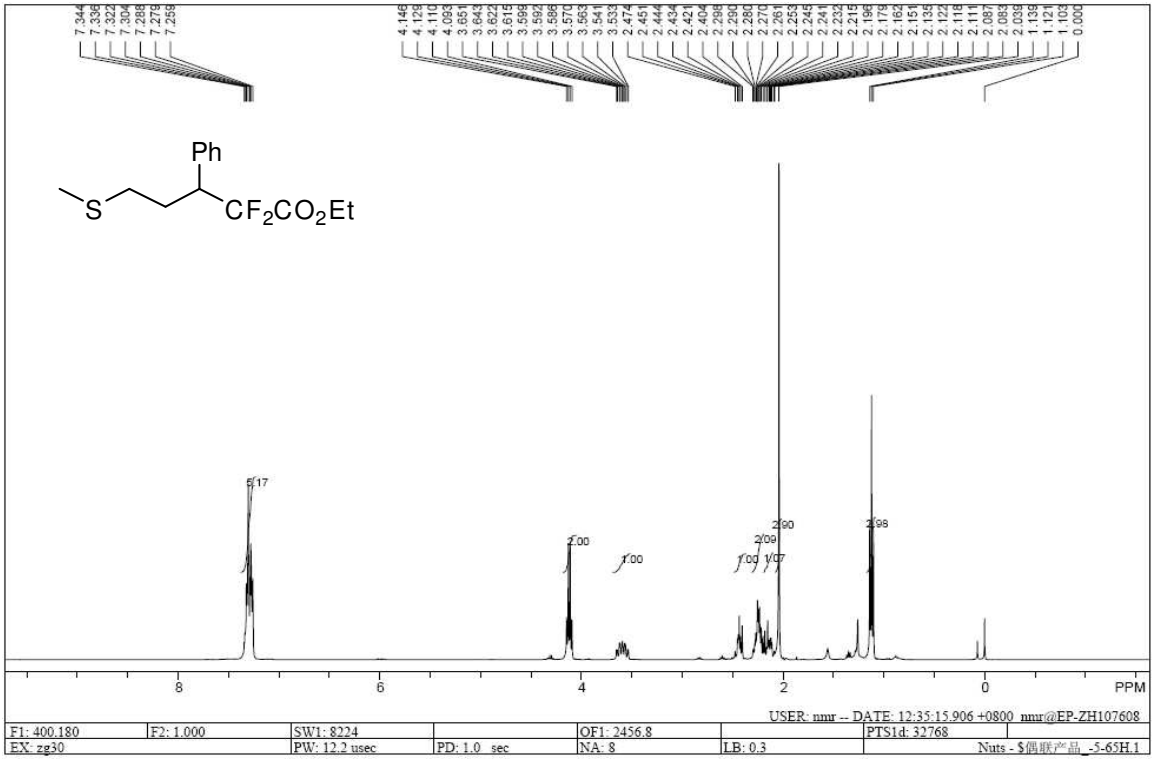


^{13}C NMR

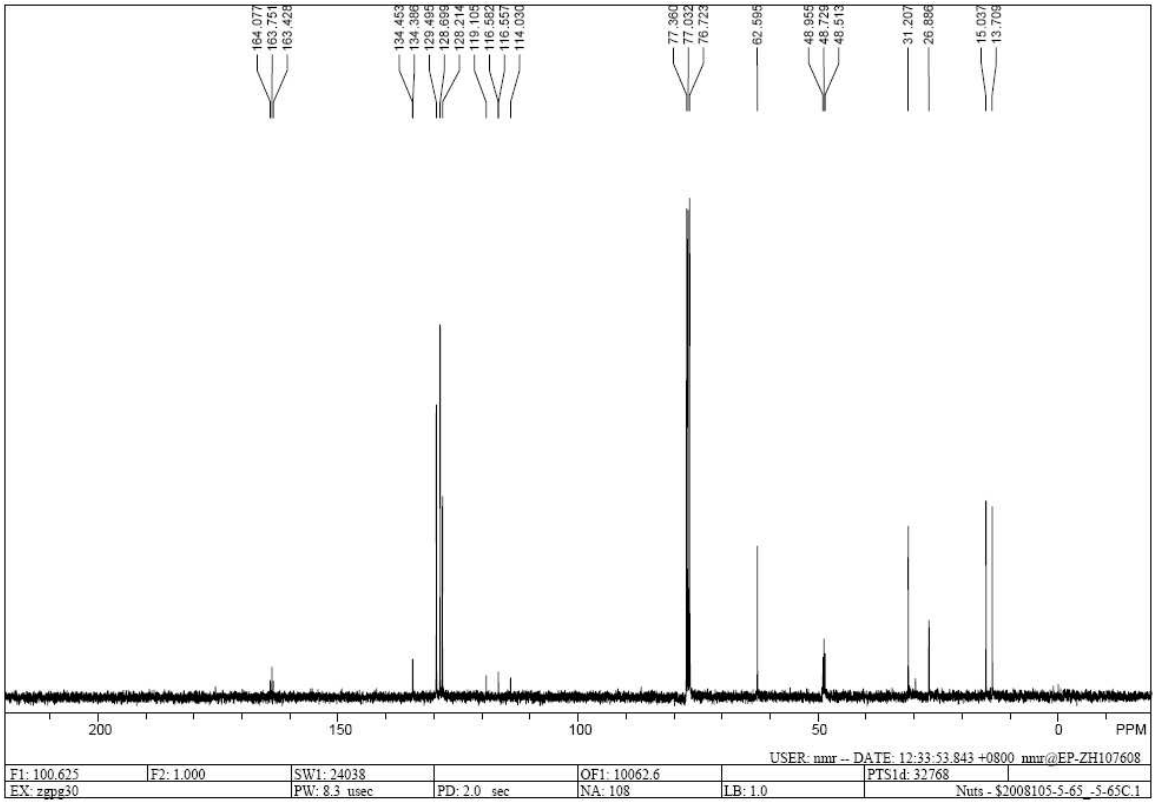


Ethyl 2,2-difluoro-5-(methylthio)-3-phenylpentanoate (3f):

^{1}H NMR

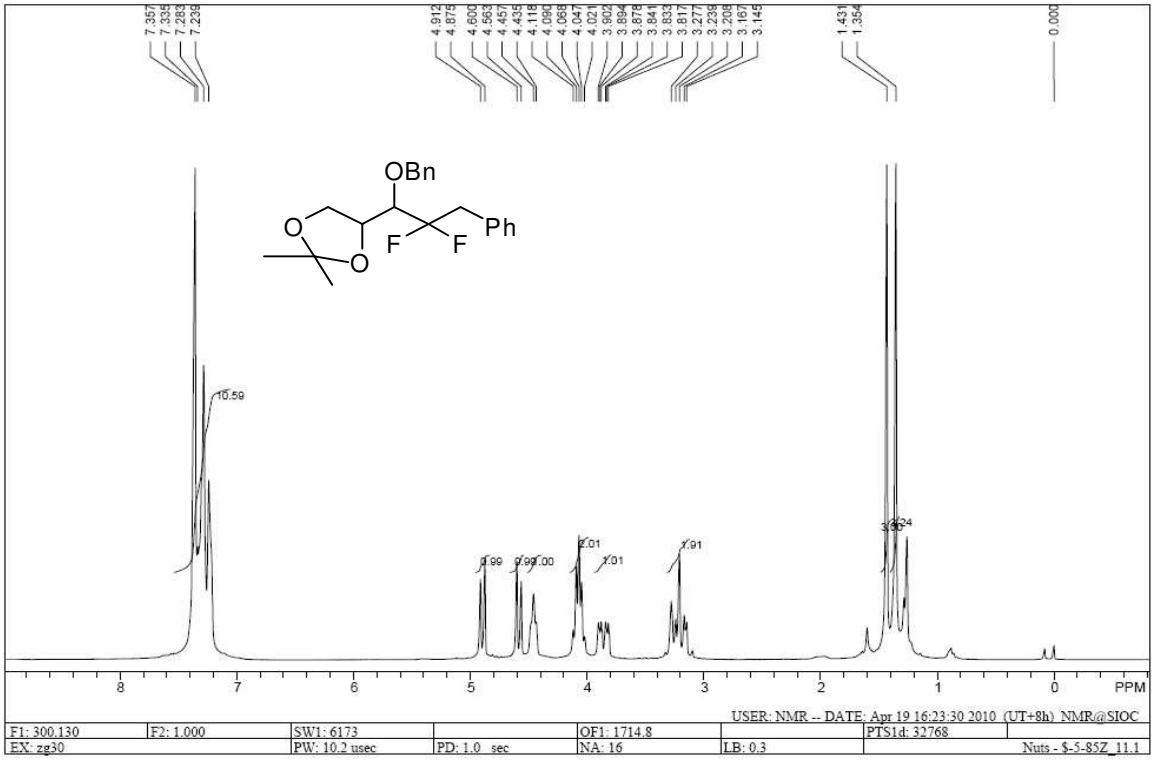


^{13}C NMR

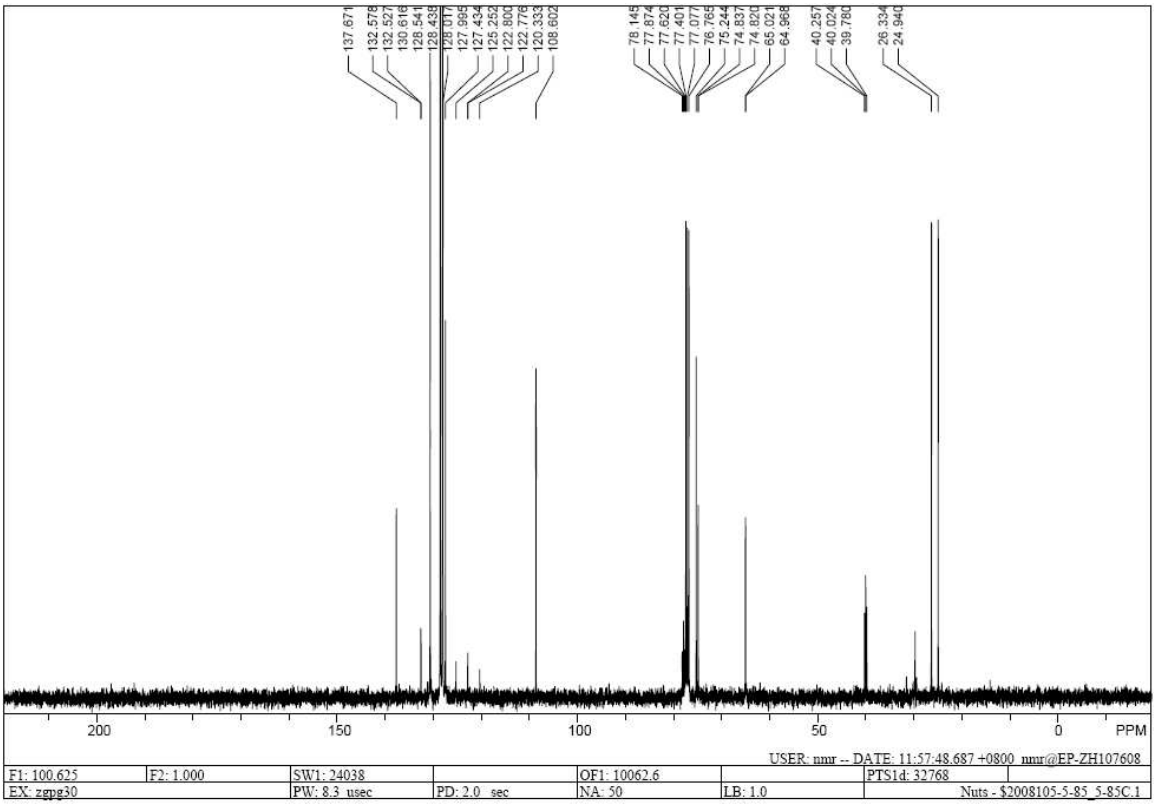


4-(1-(benzyloxy)-2,2-difluoro-3-phenylpropyl)-2,2-dimethyl-1,3-dioxolane (3g):

^{1}H NMR

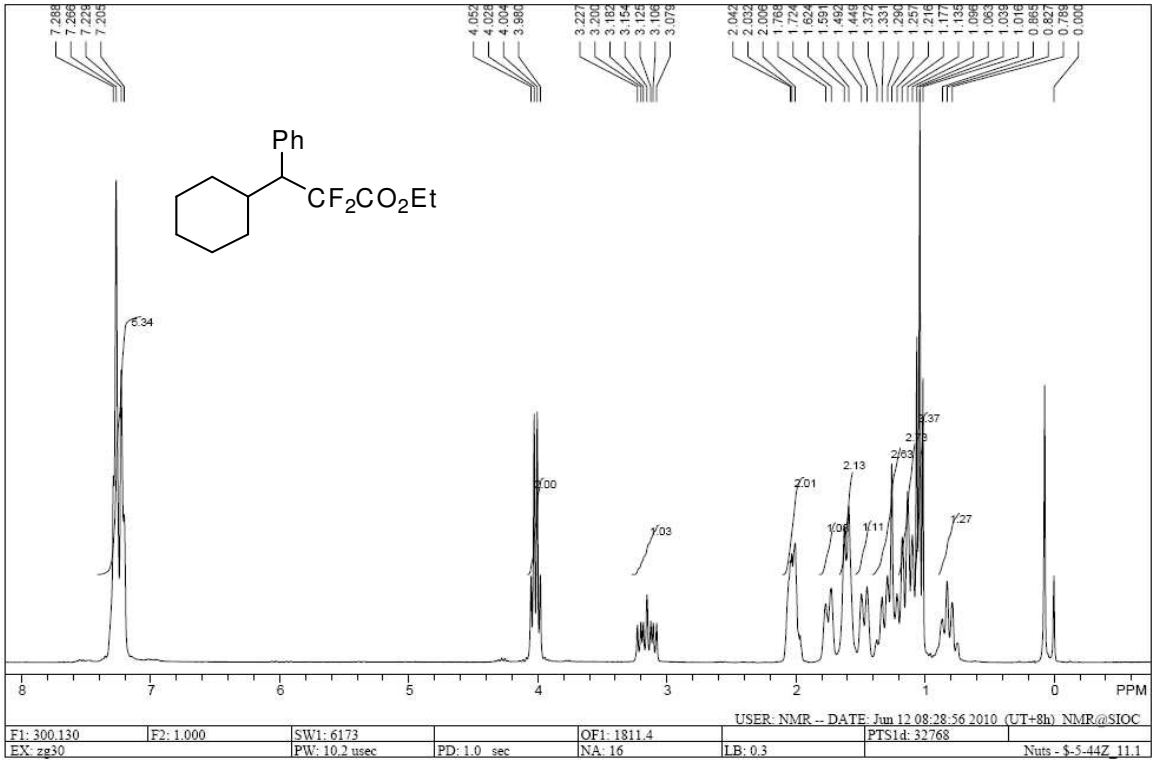


^{13}C NMR

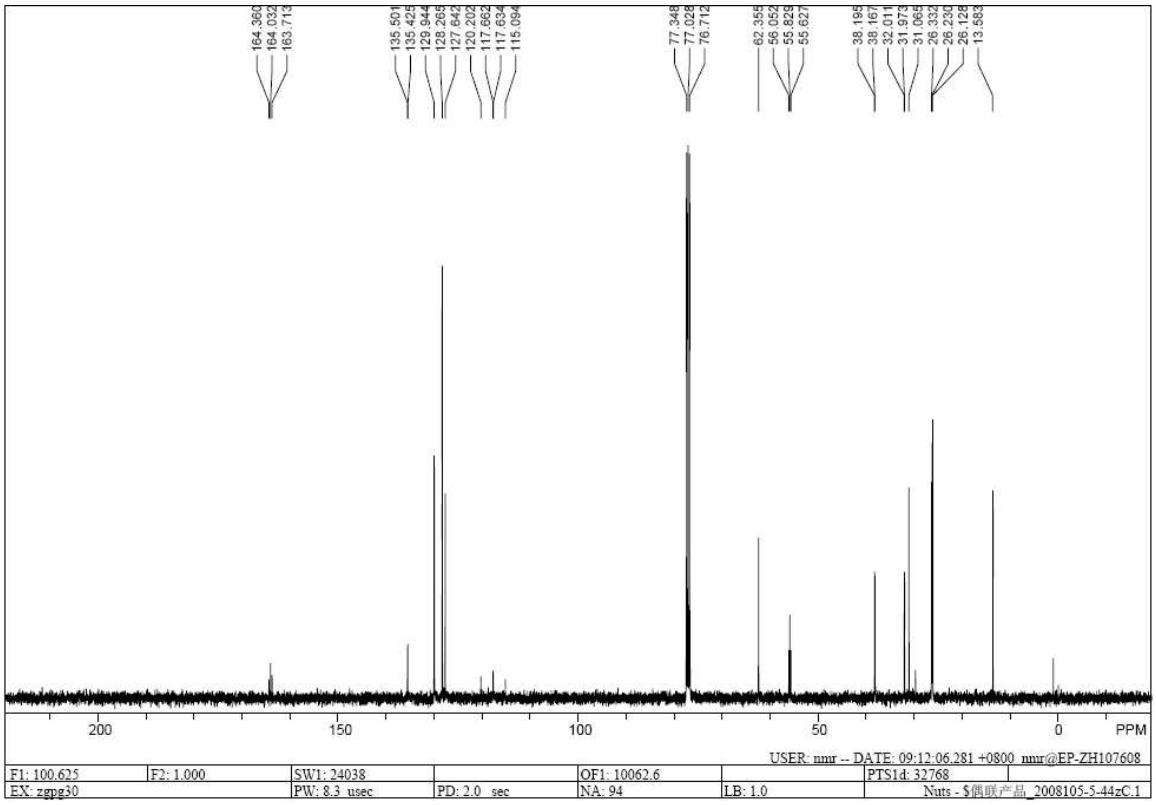


Ethyl 3-cyclohexyl-2,2-difluoro-3-phenylpropanoate (3h):

^{1}H NMR

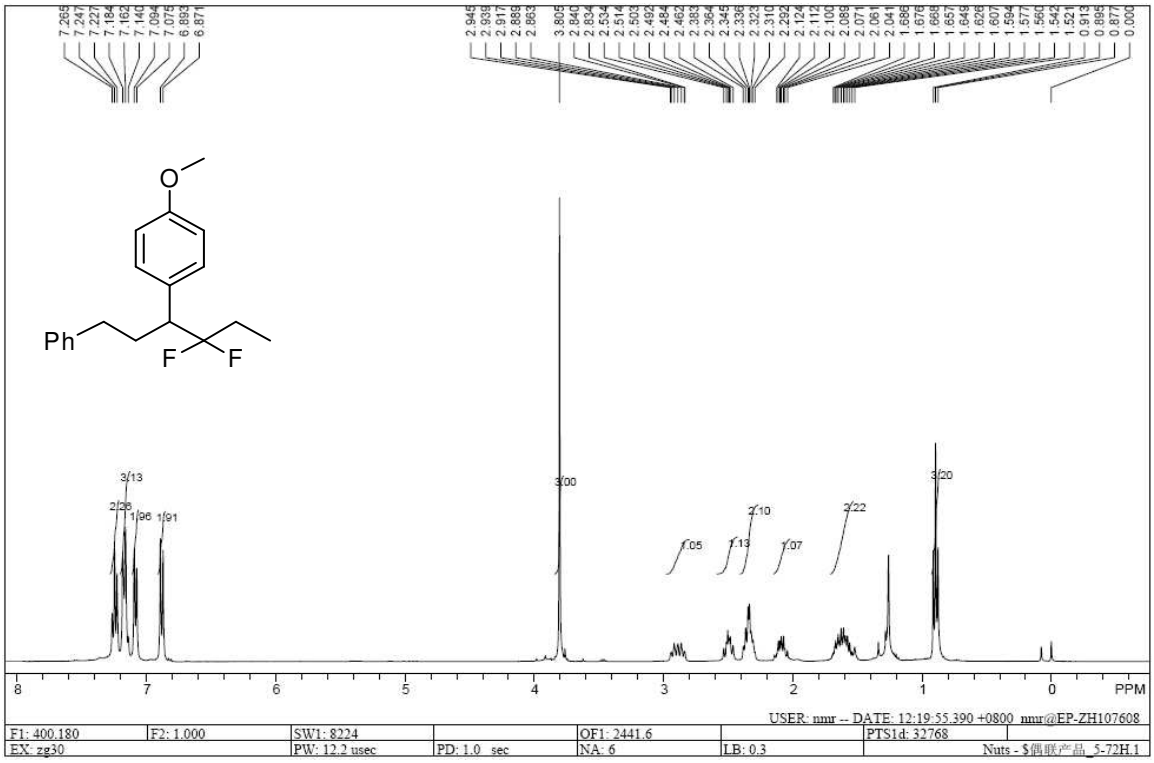


^{13}C NMR

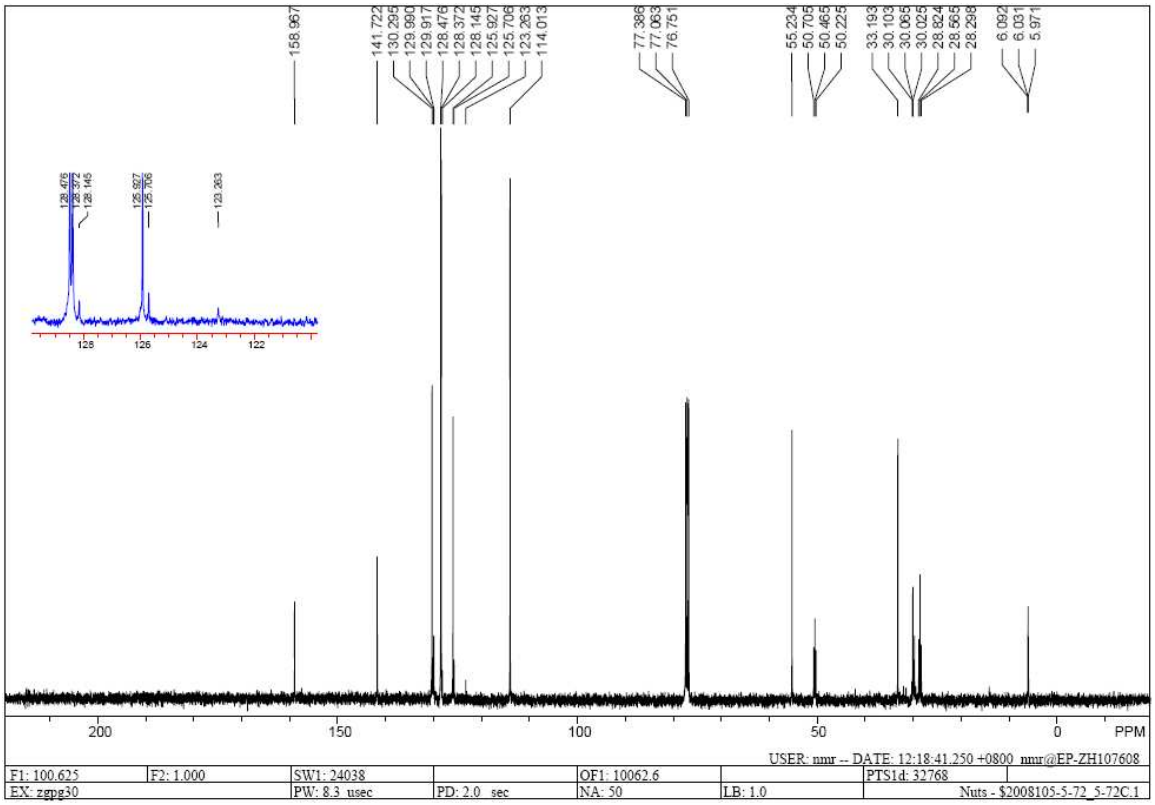


(4,4-difluoro-1-phenylhexan-3-yl)-4-methoxybenzene (3j):

^{1}H NMR

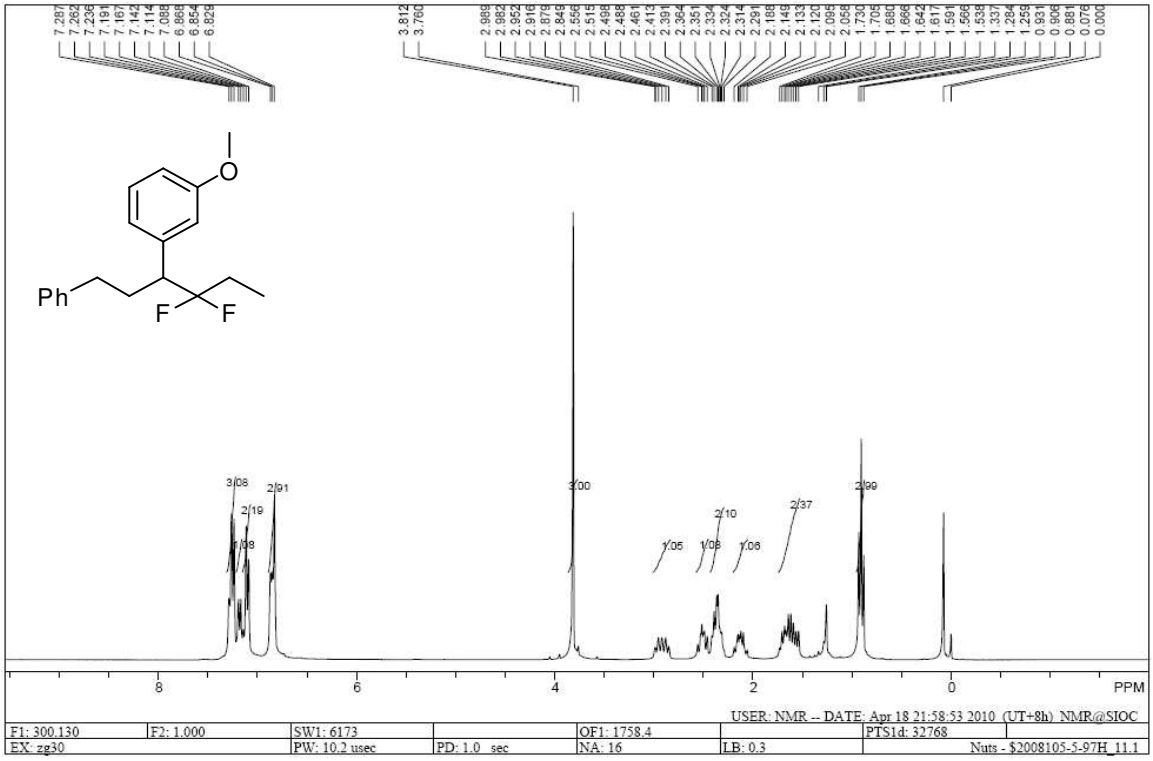


^{13}C NMR

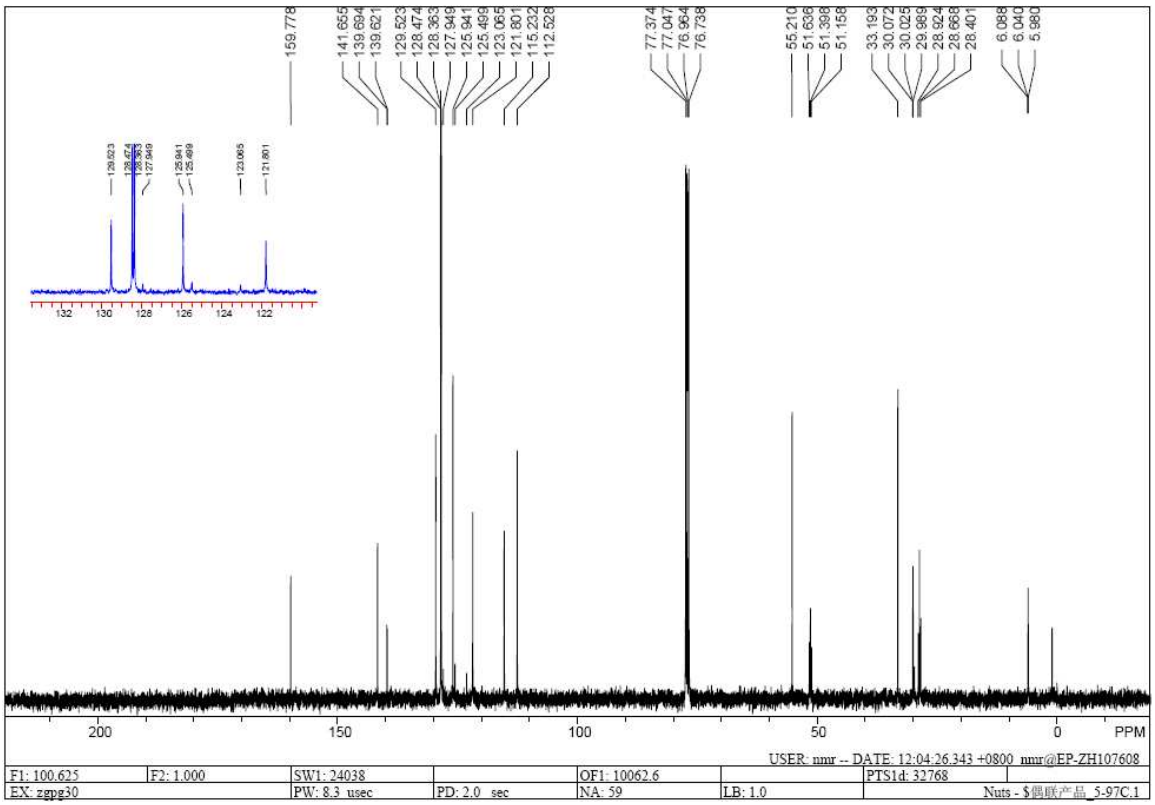


1-(4,4-difluoro-1-phenylhexan-3-yl)-3-methoxybenzene (3k):

^{1}H NMR

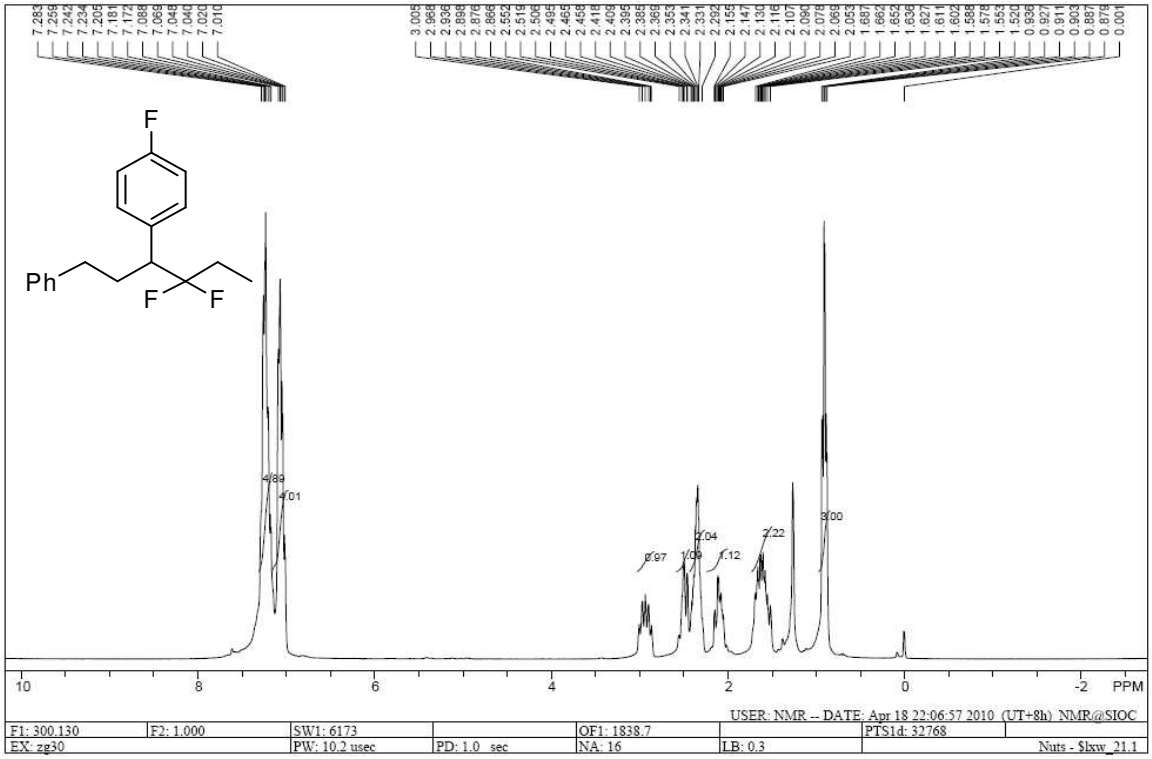


^{13}C NMR

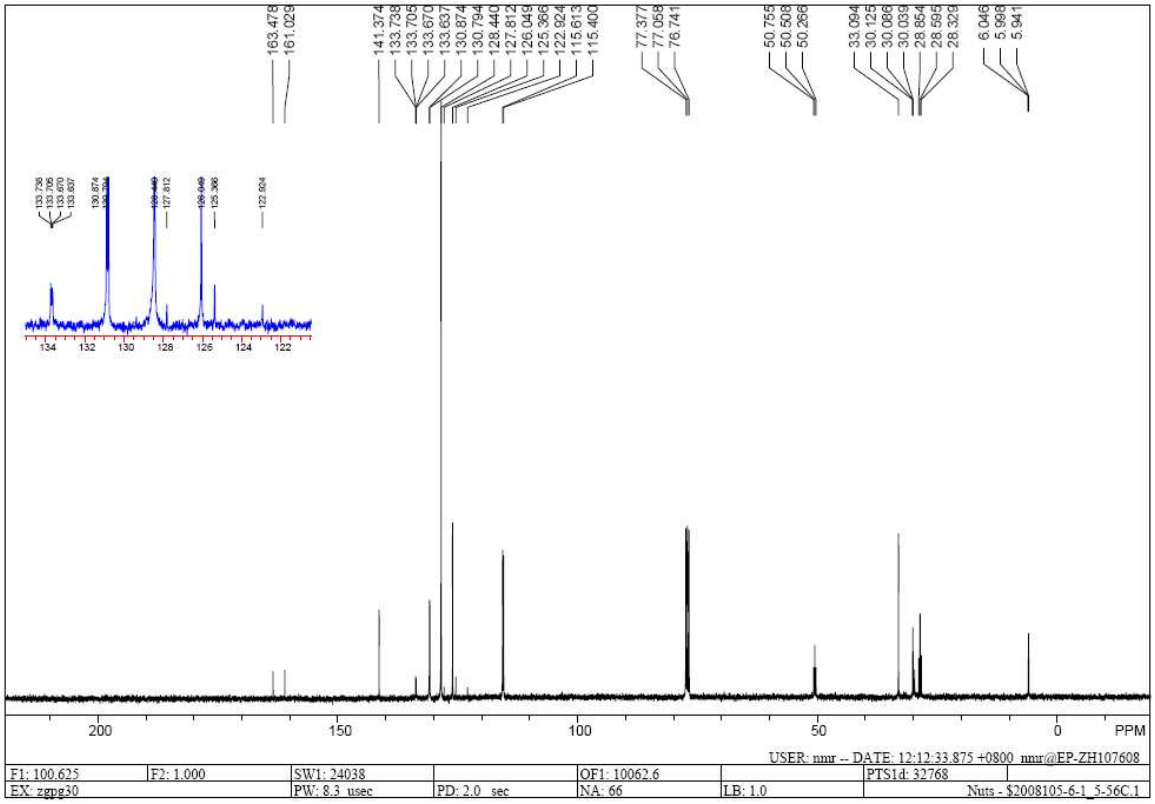


1-(4,4-difluoro-1-phenylhexan-3-yl)-4-fluorobenzene (3l):

^{1}H NMR

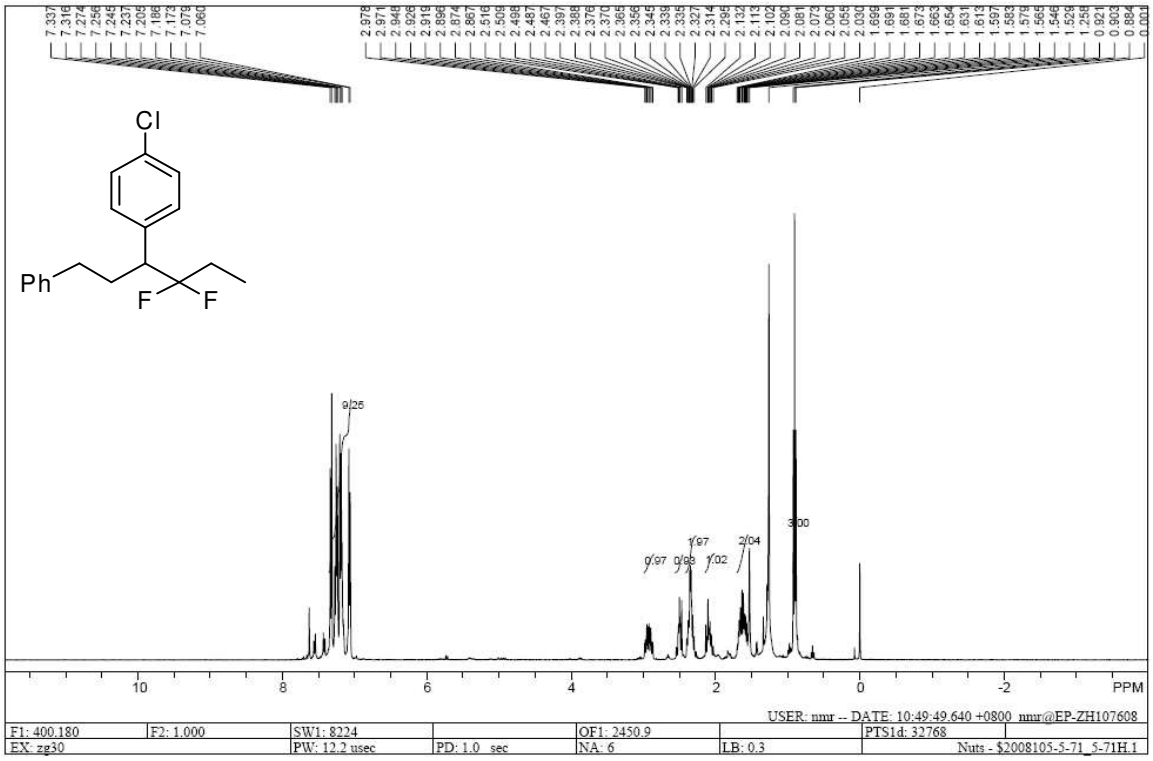


^{13}C NMR

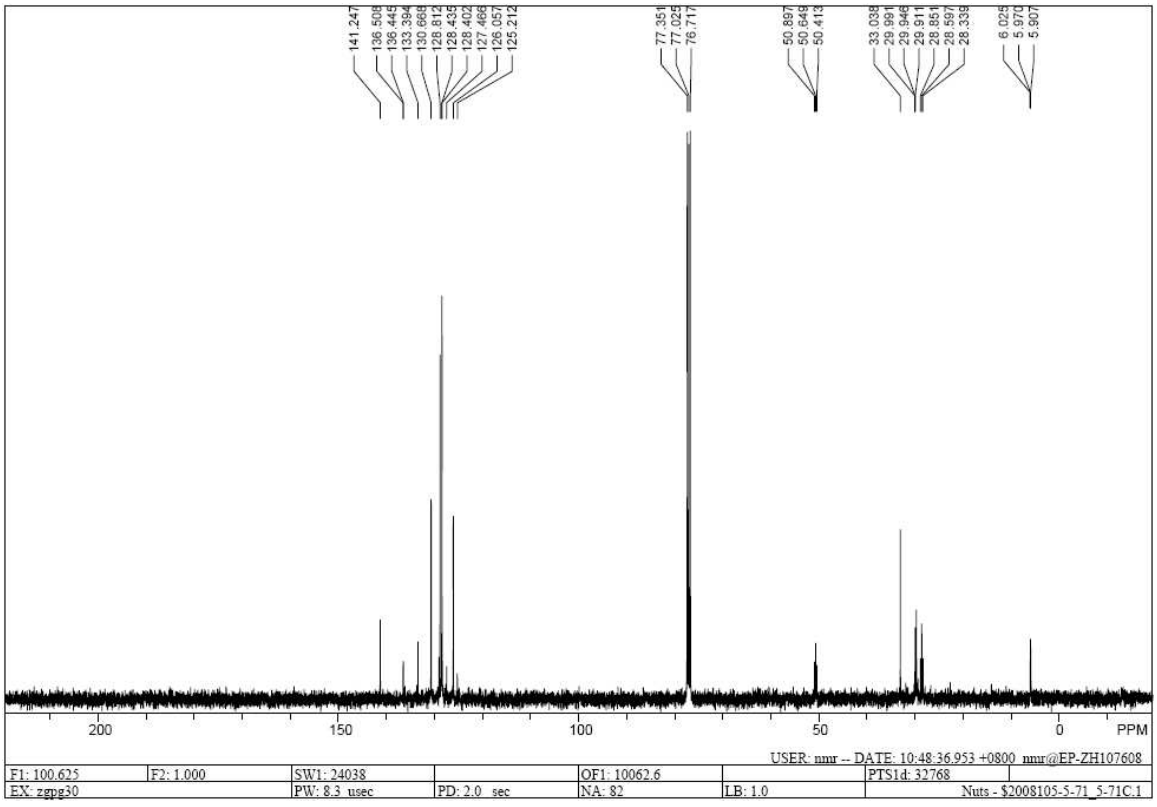


1-chloro-4-(4,4-difluoro-1-phenylhexan-3-yl)benzene (3m):

^{1}H NMR

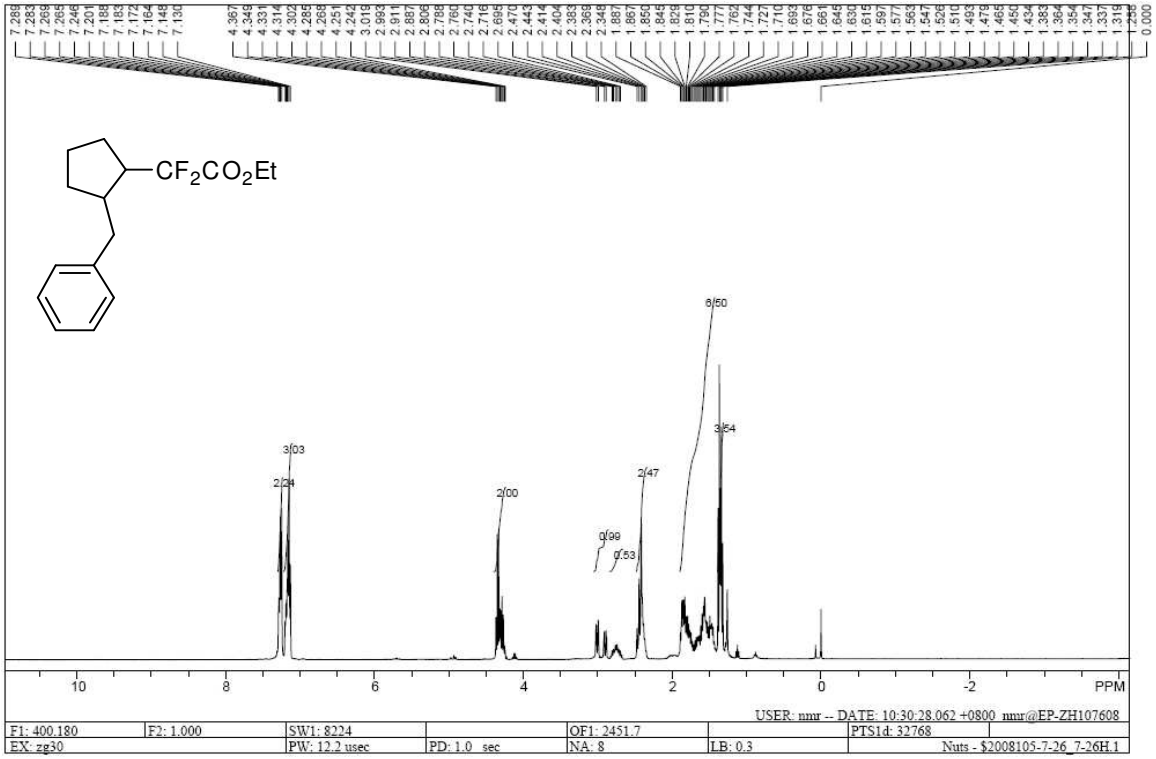


^{13}C NMR



Ethyl 2-(2-benzylcyclopentyl)-2,2-difluoroacetate (3o):

^{1}H NMR



^{13}C NMR