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Electronic Supplementary Information

General and selective *syn*-carboxylation-trifluoromethylation of terminal alkynes: Application to the late-stage modification of dehydrocholic acid

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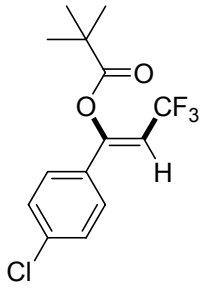
1. General experimental details

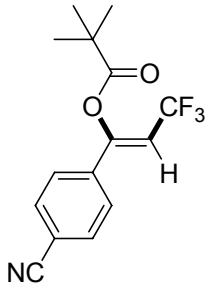
All chemicals were purchased commercially, except for Cu(III)-CF_3 complexes (py)$Cu^{III}(CF_3)_3$ and (phen) $Cu^{III}(CF_3)_3$ which were prepared according to our previous reports (please refer to: S.-L. Zhang and W.-F. Bie, *RSC Adv.* **2016**, *6*, 70902; S.-L. Zhang, C. Xiao and H.-X. Wan, *Dalton Trans.* **2018**, 47, 4779). DMF, toluene, NMP and CH_2Cl_2 solvents were simply dried over Na_2SO_4 before use to extrude adventitious water. Other reactants were used as received without further purification. All of the reactions were performed in a sealed Schlenk tube under N_2 atmosphere which was realized through evacuation/backfill techniques after three times. NMR yields were determined using ^{19}F NMR analyses of the crude mixture with 4,4-difluorobiphenyl as the internal standard. Column chromatography on silica gel was used to obtain purified products that are suitable for NMR spectroscopic characterization. NMR spectra were recorded on a 400 MHz spectrometer and processed with MestReNova program. Chemical shifts are reported in ppm and referenced to residual solvent peaks. NMR signals are reported as follows to delineate possible splitting: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. Coupling constants are reported in Hertz where present. All the ^{13}C and ^{19}F NMR spectra were obtained with complete proton decoupling. Elemental analyses were performed by the Analytic Laboratory of Jiangnan University. High resolution mass spectra (HRMS) were determined on Thermo Scientific LTQ Orbitrap XL with ESI ionization mode. FT-IR spectra were recorded on an IRTracer-100 spectrometer.

2. General reaction procedure and characterization data for the products

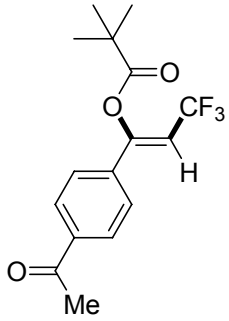
In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added carboxylic acid (**3**, 0.4 mmol) and NaO*t*Bu (0.4 mmol). The tube was then sealed, evacuated and refilled with dry nitrogen. Anhydrous DMF (2 mL) was then added via syringe. The contents in the tube were stirred vigorously at 100 °C for 45 min (seated in an oil bath). Then, a solution of (py)$Cu^{III}(CF_3)_3$ (**1**, 0.1 mmol) and alkynes (**2**, 0.1 mmol) in DMF (1 mL) was slowly injected into the tube by a syringe. The mixture was stirred for 12 hours until the reaction is complete (as monitored by TLC analysis of the crude mixture) and then cooled to room temperature. The crude mixture was extracted with excess dichloromethane. The combined organic layers were washed sequentially with large amounts of water (3 times) and with brine (once), and then dried over magnesium sulphate. After filtration, the solvent in the filtrate was removed by rotary evaporation in vacuum. The resulting residue is purified by column chromatography on silica gel to give the final products **4**.



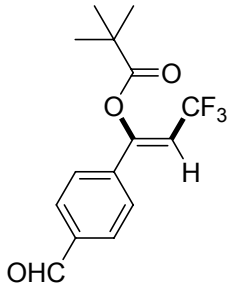
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (**4a**, 18 mg, 59%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 4H), 5.93 (q, *J* = 7.5 Hz, 1H), 1.37 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.38 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.22 (s), 154.80 (q, *J* = 5.8 Hz), 136.86 (s), 131.74 (s), 129.23 (s), 126.85 (s), 122.24 (q, *J* = 269.9 Hz), 106.51 (q, *J* = 35.3 Hz), 39.21 (s), 26.95 (s). IR (KBr) 3101, 2991, 1751 ($\nu_{C=O}$), 1637 ($\nu_{C=C}$), 1489, 1332, 1269, 1097, 839, 796 cm^{-1}. Anal. Calcd. for $C_{14}H_{14}ClF_3O_2$: C, 54.82; H, 4.60. Found: C, 54.98; H, 4.52. HRMS (ESI) m/z calcd for $C_{14}H_{15}ClF_3O_2^+$ $(M+H)^+$ 307.0713, found 307.0710.



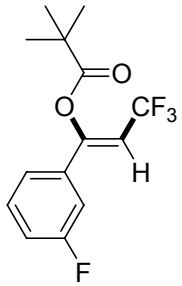
(Z)-1-(4-cyanophenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (**4b**, 20 mg, 67%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 6.03 (q, *J* = 7.3 Hz, 1H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.66 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.17 (s), 153.98 (q, *J* = 5.7 Hz), 137.54 (s), 132.70 (s), 126.16 (s), 121.88 (q, *J* = 270.3 Hz), 117.87 (s), 114.32 (s), 108.82 (q, *J* = 35.6 Hz), 39.23 (s), 26.90 (s). IR (KBr) 3093, 2980, 2232, 1759, 1673, 1481, 1336, 1266, 1133, 804, 663 cm^{-1}. Anal. Calcd for $C_{15}H_{14}F_3NO_2$: C, 60.60; H, 4.75; N, 4.71. Found: C, 60.72; H, 4.82; N, 4.60.



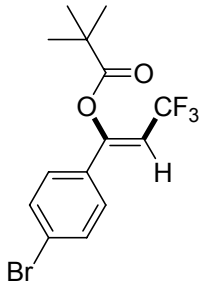
(Z)-1-(4-acetylphenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (**4c**, 17 mg, 54%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.03 (q, *J* = 7.4 Hz, 1H), 2.63 (s, 3H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.49 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.02 (s), 175.25 (s), 154.77 (q, *J* = 5.8 Hz), 138.51 (s), 137.38 (s), 128.85 (s), 125.77 (s), 122.12 (q, *J* = 270.1 Hz), 107.88 (q, *J* = 35.4 Hz), 39.22 (s), 26.94 (s), 26.67 (s). IR (KBr) 3081, 2995, 1755, 1680, 1606, 1481, 1336, 1266, 1125, 808, 659 cm^{-1}. Anal. Calcd for $C_{16}H_{17}F_3O_3$: C, 61.14; H, 5.45. Found: C, 61.40; H, 5.62. Anal. Calcd for $C_{16}H_{17}F_3O_3$: C, 61.14; H, 5.45. Found: C, 61.01; H, 5.32.



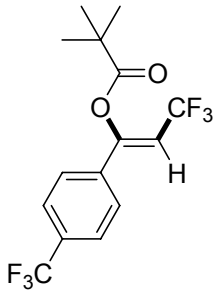
(Z)-3,3,3-trifluoro-1-(4-formylphenyl)prop-1-en-1-yl pivalate (**4d**, 16 mg, 53%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 6.06 (q, *J* = 7.4 Hz, 1H), 1.39 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.57 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.13 (s), 175.24 (s), 154.60 (q, *J* = 6.0 Hz), 138.71 (s), 137.60 (s), 130.13 (s), 126.18 (s), 122.03 (d, *J* = 270.1 Hz), 108.44 (q, *J* = 35.5 Hz), 39.24 (s), 26.94 (s). IR (KBr) 3093, 2917, 1751, 1704, 1606, 1481, 1340, 1258, 1101, 804, 690 cm^{-1}. Anal. Calcd for $C_{15}H_{15}F_3O_3$: C, 60.00; H, 5.04. Found: C, 60.11; H, 5.12.



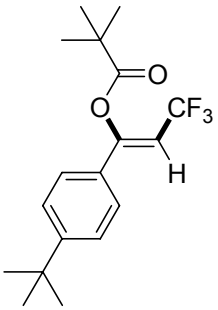
(Z)-3,3,3-trifluoro-1-(3-fluorophenyl)prop-1-en-1-yl pivalate (**4e**, 13 mg, 45%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H), 7.31 – 7.27 (m, 1H), 7.20 – 7.12 (m, 2H), 5.96 (q, *J* = 7.5 Hz, 1H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.49 (s, 3F), -111.58 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.23 (s), 162.87 (d, *J* = 247.6 Hz), 154.51 (q, *J* = 5.8 Hz), 135.43 (d, *J* = 7.7 Hz), 130.64 (d, *J* = 8.3 Hz), 122.17 (q, *J* = 270.0 Hz), 121.27 (d, *J* = 2.9 Hz), 117.67 (d, *J* = 21.3 Hz), 112.70 (d, *J* = 23.6 Hz), 107.11 (q, *J* = 35.4 Hz), 39.21 (s), 26.94 (s). IR (KBr) 3093, 2984, 1763, 1673, 1590, 1481, 1226, 1089, 780, 686 cm^{-1}. Anal. Calcd for $C_{14}H_{14}F_4O_2$: C, 57.93; H, 4.86. Found: C, 58.11; H, 4.95.



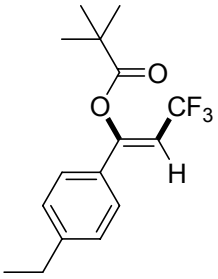
(Z)-1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (**4f**, 22 mg, 63%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 5.94 (q, *J* = 7.5 Hz, 1H), 1.37 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.41 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.22 (s), 154.89 (q, *J* = 5.8 Hz), 132.20 (s), 127.05 (s), 125.16 (s), 122.23 (q, *J* = 270.0 Hz), 106.57 (q, *J* = 35.4 Hz), 39.20 (s), 26.95 (s). IR (KBr) 3101, 2987, 1751, 1673, 1485, 1332, 1097, 839, 702 cm^{-1}. Anal. Calcd for $C_{14}H_{14}BrF_3O_2$: C, 47.88; H, 4.02. Found: C, 47.91; H, 4.15.



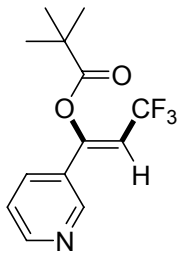
(Z)-3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl pivalate (**4g**, 22 mg, 65%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 6.01 (q, *J* = 7.4 Hz, 1H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.60 (s, 3F), -63.02 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.23 (s), 154.49 (q, *J* = 5.8 Hz), 136.73 (s), 132.48 (q, *J* = 32.9 Hz), 125.98 (q, *J* = 3.7 Hz), 125.95 (s), 123.60 (q, *J* = 272.4 Hz), 122.04 (q, *J* = 270.1 Hz), 108.04 (q, *J* = 35.5 Hz), 39.22 (s), 26.91 (s). IR (KBr) 3117, 2987, 1759, 1676, 1414, 1320, 1133, 800, 698 cm^{-1}. Anal. Calcd for $C_{15}H_{14}F_6O_2$: C, 52.95; H, 4.15. Found: C, 53.12; H, 4.26.



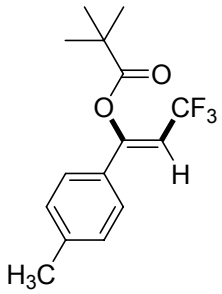
(Z)-1-(4-(tert-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (**4h**, 20 mg, 61%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 4H), 5.93 (q, *J* = 7.6 Hz, 1H), 1.39 (s, 9H), 1.34 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.07 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.36 (s), 155.77 (q, *J* = 5.9 Hz), 154.16 (s), 130.11 (s), 125.89 (s), 125.25 (s), 122.58 (q, *J* = 269.7 Hz), 105.12 (q, *J* = 35.1 Hz), 39.21 (s), 34.85 (s), 31.13 (s), 27.03 (s). IR (KBr) 3097, 2972, 1763, 1673, 1481, 1332, 1273, 1093, 804, 655 cm^{-1}. Anal. Calcd for $C_{18}H_{23}F_3O_2$: C, 65.84; H, 7.06. Found: C, 66.03; H, 7.21.



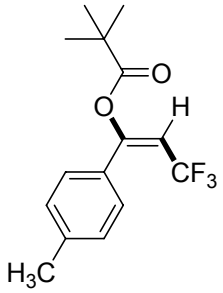
(Z)-1-(4-ethylphenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (**4i**, 16 mg, 53%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.91 (q, *J* = 7.6 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.38 (s, 9H), 1.26 (t, *J* = 7.7 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.09 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.33 (s), 155.87 (q, *J* = 5.9 Hz), 147.30 (s), 130.48 (s), 128.43 (s), 125.51 (s), 122.56 (q, *J* = 269.7 Hz), 105.10 (q, *J* = 35.0 Hz), 39.20 (s), 28.69 (s), 27.02 (s), 15.20 (s). IR (KBr) 3093, 2972, 1763, 1673, 1481, 1269, 1097, 839, 667 cm^{-1}. Anal. Calcd for $C_{16}H_{19}F_3O_2$: C, 63.99; H, 6.38. Found: C, 64.11; H, 6.57. HRMS (ESI) m/z calcd for $C_{16}H_{20}F_3O_2^+$ $(M+H)^+$ 301.1415, found 301.1412.



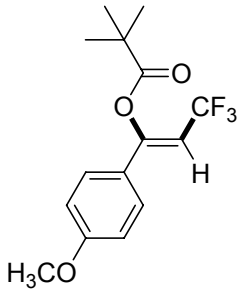
(Z)-3,3,3-trifluoro-1-(pyridin-3-yl)prop-1-en-1-yl pivalate (**4j**, 14 mg, 51%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (br s, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.44 (br s, 1H), 6.00 (q, *J* = 7.4 Hz, 1H), 1.37 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.54 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.21 (s), 153.47 (s), 151.11 (q, *J* = 4.2 Hz), 146.57 (s), 133.01 (s), 130.58 (s), 128.89 (s), 121.97 (q, *J* = 270.1 Hz), 107.88 (q, *J* = 35.5 Hz), 39.25 (s), 26.92 (s). IR (KBr) 3085, 2980, 1763, 1680, 1590, 1481, 1273, 1093, 792, 702, 636 cm^{-1}. Anal. Calcd for $C_{13}H_{14}F_3NO_2$: C, 57.14; H, 5.16; N, 5.13. Found: C, 57.28; H, 5.25; N, 4.99. HRMS (ESI) m/z calcd for $C_{13}H_{15}F_3NO_2^+$ $(M+H)^+$ 274.1055, found 274.1049.



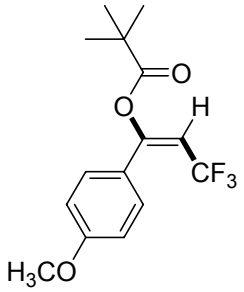
(Z)-3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl pivalate (**4m**, 18 mg, 63%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.91 (q, *J* = 7.6 Hz, 1H), 2.40 (s, 3H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.10 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.28 (s), 155.86 (q, *J* = 5.9 Hz), 141.05 (s), 130.32 (s), 129.60 (s), 125.42 (s), 122.55 (q, *J* = 269.6 Hz), 105.06 (q, *J* = 35.1 Hz), 39.19 (s), 27.00 (s), 21.34 (s). IR (KBr) 3097, 2990, 1763, 1669, 1481, 1332, 1273, 1125, 1019, 796, 671 cm^{-1}. Anal. Calcd for $C_{15}H_{17}F_3O_2$: C, 62.93; H, 5.99. Found: C, 63.04; H, 6.08.



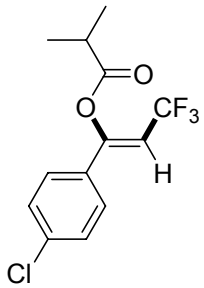
(E)-3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl pivalate (**4m'**, 6 mg, 14%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.70 (q, *J* = 8.0 Hz, 1H), 2.40 (s, 3H), 1.27 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.56 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.70 (s), 157.36 (q, *J* = 6.3 Hz), 140.55 (s), 129.70 (s), 128.89 (s), 128.11 (q, *J* = 1.6 Hz, through-space C-F coupling), 122.68 (d, *J* = 268.8 Hz), 108.64 (q, *J* = 35.9 Hz), 39.01 (s), 26.85 (s), 21.44 (s). IR (KBr) 3097, 2968, 1759, 1680, 1481, 1367, 1207, 1097, 823, 800 cm^{-1}. Anal. Calcd for $C_{15}H_{17}F_3O_2$: C, 62.93; H, 5.99. Found: C, 63.11; H, 6.12.



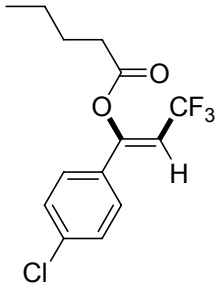
(Z)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl pivalate (**4n**, 15 mg, 50%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.85 (q, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.91 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.33 (s), 161.55 (s), 155.54 (q, *J* = 5.9 Hz), 127.08 (s), 125.46 (s), 122.65 (q, *J* = 269.6 Hz), 114.33 (s), 104.05 (q, *J* = 35.0 Hz), 55.40 (s), 39.22 (s), 27.03 (s). IR (KBr) 3093, 2968, 2921, 1759, 1669, 1516, 1461, 1250, 1097, 835, 671, 542 cm^{-1}. Anal. Calcd for $C_{15}H_{17}F_3O_3$: C, 59.60; H, 5.67. Found: C, 59.71; H, 5.58.



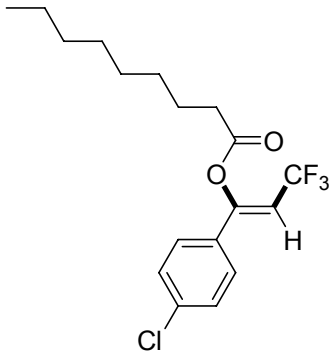
(E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl pivalate (**4n'**, 4 mg, 13%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.66 (q, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 1.27 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.56 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.77 (s), 161.10 (s), 157.07 (q, *J* = 6.6 Hz), 129.78 (q, *J* = 1.9 Hz, through-space C-F coupling), 124.87 (s), 122.78 (q, *J* = 268.8 Hz), 113.64 (s), 108.12 (q, *J* = 35.9 Hz), 55.28 (s), 39.03 (s), 26.87 (s). IR (KBr) 3085, 2964, 1759, 1676, 1610, 1512, 1367, 1101, 839, 714 cm^{-1}. Anal. Calcd for $C_{15}H_{17}F_3O_3$: C, 59.60; H, 5.67. Found: C, 59.78; H, 5.77.



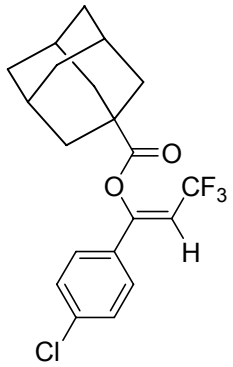
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl isobutyrate (**4o**, 15 mg, 51%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 5.94 (q, *J* = 7.5 Hz, 1H), 2.85 (septet, *J* = 7.0 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.51 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.74 (s), 154.46 (q, *J* = 5.8 Hz), 136.91 (s), 131.57 (s), 129.23 (s), 126.90 (s), 122.24 (q, *J* = 269.9 Hz), 106.43 (q, *J* = 35.3 Hz), 34.06 (s), 18.64 (s). IR (KBr) 3105, 2984, 1759, 1673, 1489, 1273, 1133, 835, 796 cm^{-1}. Anal. Calcd for $C_{13}H_{12}ClF_3O_2$: C, 53.35; H, 4.13. Found: C, 53.24; H, 4.25.



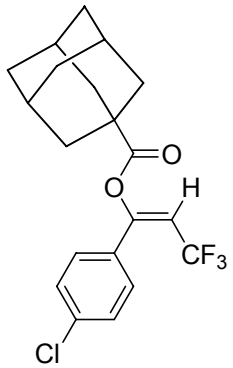
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl pentanoate (**4p**, 15 mg, 50%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 4H), 5.93 (q, *J* = 7.4 Hz, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.73 (quintet, *J* =7.5 Hz, 2H), 1.49 – 1.38 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.64 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.57 (s), 154.32 (q, *J* = 5.7 Hz), 136.93 (s), 131.53 (s), 129.22 (s), 126.97 (s), 122.22 (q, *J* = 269.8 Hz), 106.39 (q, *J* = 35.2 Hz), 33.59 (s), 26.56 (s), 22.13 (s), 13.61 (s). IR (KBr) 3101, 2968, 1774, 1673, 1493, 1328, 1266, 1133, 800, 651 cm^{-1}. Anal. Calcd for $C_{14}H_{14}ClF_3O_2$: C, 54.83; H, 4.60. Found: C, 54.72; H, 4.51.



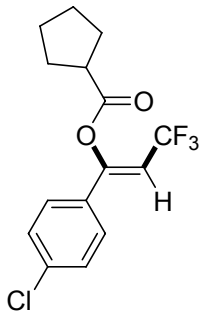
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl nonanoate (**4q**, 12 mg, 32%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 4H), 5.93 (q, *J* = 7.4 Hz, 1H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.68 (m, 2H), 1.42 – 1.25 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.64 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.60 (s), 154.32 (q, *J* = 5.7 Hz), 136.93 (s), 131.54 (s), 129.22 (s), 126.98 (s), 122.22 (q, *J* = 269.9 Hz), 106.40 (q, *J* = 35.2 Hz), 33.88 (s), 31.78 (s), 29.14 (s), 29.07 (s), 28.99 (s), 24.54 (s), 22.63 (s), 14.07 (s). IR (KBr) 3101, 2929, 1774, 1673, 1493, 1328, 1266, 1133, 800, 651 cm^{-1}. Anal. Calcd for $C_{18}H_{22}ClF_3O_2$: C, 59.59; H, 6.11. Found: C, 59.65; H, 6.23.



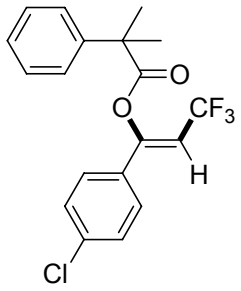
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl adamantane-1-carboxylate (**4s**, 24 mg, 62%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 4H), 5.93 (q, *J* = 7.5 Hz, 1H), 2.12 (br s, 3H), 2.06 (d, *J* = 2.5 Hz, 6H), 1.85 – 1.74 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.19 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.29 (s), 154.81 (q, *J* = 5.8 Hz), 136.81 (s), 131.73 (s), 129.21 (s), 126.86 (s), 122.29 (q, *J* = 270.0 Hz), 106.36 (q, *J* = 35.3 Hz), 41.16 (s), 38.59 (s), 36.31 (s), 27.80 (s). IR (KBr) 3105, 2911, 2855, 1759, 1673, 1595, 1491, 1266, 1133, 1047, 836, 720, 649 cm^{-1}. Anal. Calcd for $C_{20}H_{20}ClF_3O_2$: C, 62.42; H, 5.24. Found: C, 62.28; H, 5.32.



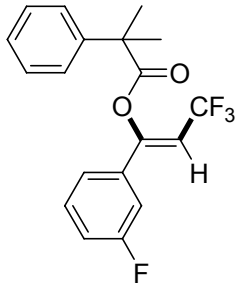
(E)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl adamantane-1-carboxylate (**4s'**, 5 mg, 13%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 5.75 (q, *J* = 7.9 Hz, 1H), 2.07 (br s, 3H), 1.93 (d, *J* = 2.5 Hz, 6H), 1.77 – 1.67 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.64 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.71 (s), 156.15 (q, *J* = 6.2 Hz), 136.44 (s), 131.16 (s), 129.63 (q, *J* = 1.8 Hz, through-space C-F coupling), 128.56 (s), 122.44 (q, *J* = 269.0 Hz), 109.67 (q, *J* = 35.9 Hz), 40.98 (s), 38.48 (s), 36.27 (s), 27.72 (s). IR (KBr) 3085, 2913, 2858, 1755, 1680, 1598, 1493, 1363, 1199, 1133, 1058, 835, 772, 702, 565 cm^{-1}. Anal. Calcd for $C_{20}H_{20}ClF_3O_2$: C, 62.42; H, 5.24. Found: C, 62.56; H, 5.40.



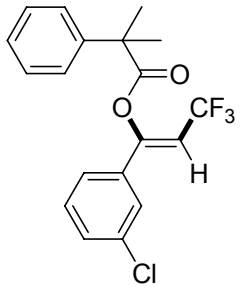
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl cyclopentanecarboxylate (**4t**, 16 mg, 50%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.36 (m, 4H), 5.93 (q, *J* = 7.5 Hz, 1H), 3.02 (quintet, *J* = 8.0 Hz, 1H), 2.12 – 1.89 (m, 4H), 1.85 – 1.63 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.48 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.41 (s), 154.51 (q, *J* = 5.7 Hz), 136.88 (s), 131.66 (s), 129.23 (s), 126.94 (s), 122.26 (q, *J* = 270.0 Hz), 106.42 (q, *J* = 35.2 Hz), 43.65 (s), 29.80 (s), 25.67 (s). IR (KBr) 3098, 2962, 1765, 1673, 1595, 1492, 1331, 1115, 800, 651 cm^{-1}. Anal. Calcd for $C_{15}H_{14}ClF_3O_2$: C, 56.53; H, 4.43. Found: C, 56.62; H, 4.55.



(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 2-methyl-2-phenylpropanoate (**4u**, 23 mg, 62%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.35 (m, 5H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.86 (q, *J* = 7.5 Hz, 1H), 1.75 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.33 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.04 (s), 154.56 (q, *J* = 5.8 Hz), 142.43 (s), 136.75 (s), 131.28 (s), 128.92 (s), 128.66 (s), 127.45 (s), 126.90 (s), 126.25 (s), 122.19 (q, *J* = 270.0 Hz), 106.48 (q, *J* = 35.4 Hz), 46.42 (s), 25.58 (s). IR (KBr) 3085, 2987, 1755, 1669, 1594, 1489, 1254, 1086, 835, 698, 592 cm^{-1}. Anal. Calcd for $C_{19}H_{16}ClF_3O_2$: C, 61.88; H, 4.37. Found: C, 62.02; H, 4.51.

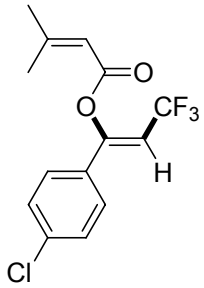


(Z)-3,3,3-trifluoro-1-(3-fluorophenyl)prop-1-en-1-yl 2-methyl-2-phenylpropanoate (19 mg, 54%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.23 (td, *J* = 8.0, 5.8 Hz, 1H), 7.07 (td, *J* = 8.2, 2.3 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.70 – 6.62 (m, 1H), 5.89 (q, *J* = 7.5 Hz, 1H), 1.75 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.44 (s, 3F), -111.78 (s, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.11 (s), 162.66 (d, *J* = 247.5 Hz), 154.34 (qd, *J* = 5.8, 2.8 Hz), 142.34 (s), 134.96 (d, *J* = 7.9 Hz), 130.31 (d, *J* = 8.2 Hz), 128.70 (s), 127.51 (s), 126.17 (s), 122.11 (q, *J* = 270.0 Hz), 121.33 (d, *J* = 3.0 Hz), 117.58 (d, *J* = 21.2 Hz), 112.74 (d, *J* = 23.8 Hz), 107.09 (q, *J* = 35.4 Hz), 46.44 (s), 25.61 (s). IR (KBr) 3089, 2980, 1763, 1673, 1590, 1446, 1332, 1262, 1191, 1086, 784, 698 cm^{-1}. Anal. Calcd for $C_{19}H_{16}F_4O_2$: C, 64.77; H, 4.58. Found: C, 64.89; H, 3.67.

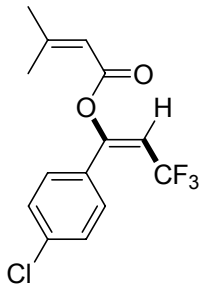


(Z)-1-(3-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 2-methyl-2-phenylpropanoate (**4v**, 22 mg, 60%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 4.2 Hz, 4H), 7.39 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 6.99 (m, 2H), 5.89 (q, *J* = 7.4 Hz, 1H), 1.75 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.41 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.12 (s), 154.31 (q, *J* = 5.8 Hz), 142.35 (s), 134.86 (s), 134.60 (s), 130.67 (s), 129.91 (s), 128.79 (s), 127.53 (s), 126.08 (s), 125.71 (s), 123.76 (s), 122.09 (q, *J* = 270.1 Hz), 107.18 (q, *J* =

35.4 Hz), 46.44 (s), 25.65 (s). IR (KBr) 3062, 2980, 1763, 1676, 1571, 1477, 1328, 1086, 780, 698 cm^{-1}.

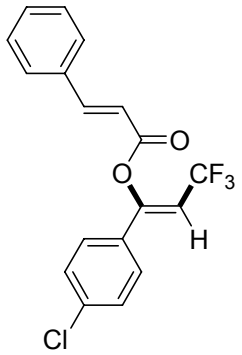


(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 3-methylbut-2-enoate (**4w**, 15 mg, 49%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 5.99 – 5.96 (m, 1H), 5.94 (q, *J* = 7.5 Hz, 1H), 2.20 (d, *J* = 0.8 Hz, 3H), 2.03 (d, *J* = 1.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.56 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.92 (s), 162.77 (s), 154.30 (q, *J* = 5.8 Hz), 136.73 (s), 131.79 (s), 129.17 (s), 126.99 (s), 122.33 (q, *J* = 269.8 Hz), 113.67 (s), 106.26 (q, *J* = 35.2 Hz), 27.77 (s), 20.63 (s). IR (KBr) 3101, 2925, 1747, 1673, 1493, 1332, 1109, 839, 651 cm^{-1}. Anal. Calcd for $C_{14}H_{12}ClF_3O_2$: C, 55.19; H, 3.97. Found: C, 55.32; H, 4.08.

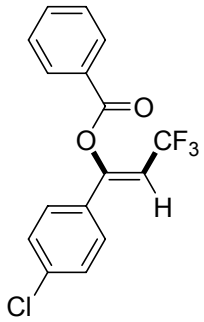


(E)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 3-methylbut-2-enoate (**4w'**, 5 mg, 16%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 5.84 – 5.77 (m, 2H), 2.17 (d, *J* = 0.9 Hz, 3H), 1.97 (d, *J* = 0.9 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.51 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23 (s), 162.31 (s), 155.80 (q, *J* = 6.4 Hz), 136.32 (s), 131.42 (s), 129.75 (q, *J* = 1.8 Hz, through-space coupling), 128.53 (s), 122.56 (q, *J* = 269.1 Hz), 114.09 (s), 109.69 (q, *J* = 36.0 Hz), 27.70 (s), 20.59 (s). IR (KBr) 3089, 2925, 1743, 1645,

1493, 1207, 1133, 1066, 941, 835 cm^{-1}. Anal. Calcd for $C_{14}H_{12}ClF_3O_2$: C, 55.19; H, 3.97. Found: C, 55.41; H, 4.16.

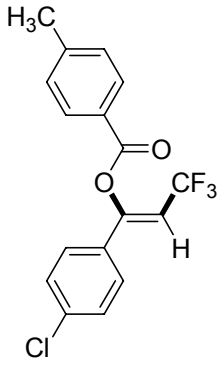


(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl cinnamate (**4x**, 15 mg, 43%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.0 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.52 – 7.43 (m, 5H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.02 (q, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.53 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.70 (s), 154.29 (q, *J* = 5.8 Hz), 148.36 (s), 136.97 (s), 133.74 (s), 131.34 (s), 131.22 (s), 129.25 (s), 129.08 (s), 128.54 (s), 127.03 (s), 122.27 (q, *J* = 269.9 Hz), 115.45 (s), 106.50 (q, *J* = 35.4 Hz). IR (KBr) 3066, 2960, 1743, 1633, 1489, 1266, 1117, 800, 761, 679 cm^{-1}. Anal. Calcd for $C_{18}H_{12}ClF_3O_2$: C, 61.29; H, 3.43. Found: C, 61.41; H, 3.55.

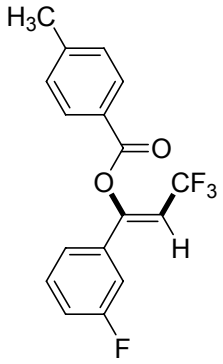


(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl benzoate (**4aa**, 14 mg, 43%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.2 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 6.07 (q, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.51 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63 (s), 154.55 (q, *J* = 5.7 Hz), 137.05 (s), 134.29 (s), 131.29 (s),

130.42 (s), 129.29 (s), 128.85 (s), 128.06 (s), 127.02 (s), 122.28 (q, J = 270.0 Hz), 106.67 (q, J = 35.3 Hz). IR (KBr) 3077, 2925, 1747, 1669, 1594, 1489, 1266, 1136, 804, 706 cm^{-1}. Anal. Calcd for $C_{16}H_{10}ClF_3O_2$: C, 58.82; H, 3.09. Found: C, 59.01; H, 3.23.

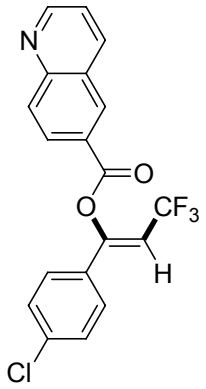


(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 4-methylbenzoate (**4ae**, 19 mg, 56%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.43-7.33 (m, 4H), 6.06 (q, J = 7.4 Hz, 1H), 2.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.49 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.66 (s), 154.60 (q, J = 5.7 Hz), 145.34 (s), 136.97 (s), 131.41 (s), 130.49 (s), 129.56 (s), 129.25 (s), 127.00 (s), 125.29 (s), 122.30 (q, J = 269.9 Hz), 106.57 (q, J = 35.3 Hz), 21.81 (s). IR (KBr) 3042, 2925, 1747, 1610, 1493, 1262, 1136, 831, 745 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{16}ClF_3NO_2^+$ $(M+NH_4)^+$ 358.0822, found 358.0812.

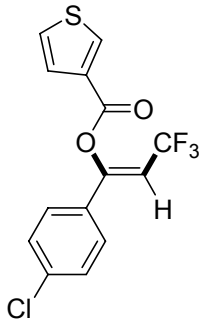


(Z)-3,3,3-trifluoro-1-(3-fluorophenyl)prop-1-en-1-yl 4-methylbenzoate (**4af**, 15 mg, 46%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.2 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.28 – 7.23 (m, 1H), 7.19 – 7.12 (m, 1H), 6.09 (q, J = 7.4 Hz, 1H), 2.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.61 (s, 3F), -111.56 (s, 1F). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 163.65 (s), 162.91 (d, *J* = 247.5 Hz), 154.33 (qd, *J* = 5.7, 2.8 Hz), 145.36 (s), 135.14 (d, *J* = 7.7 Hz), 130.67 (d, *J* = 8.3 Hz), 130.50 (s), 129.57 (s), 125.25 (s), 122.23 (q, *J* = 270.0 Hz), 121.42 (d, *J* = 2.9 Hz), 117.78 (d, *J* = 21.3 Hz), 112.86 (d, *J* = 23.7 Hz), 107.23 (q, *J* = 35.4 Hz), 21.81 (s). IR (KBr) 3105, 2921, 1739, 1673, 1590, 1449, 1269, 1118, 786, 743, 680 cm^{-1}. Anal. Calcd for $C_{17}H_{12}F_4O_2$: C, 62.97; H, 3.73. Found: C, 63.15; H, 3.92.



(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl quinoline-6-carboxylate (**4ah**, 6 mg, 16%). Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 9.11 (br s, 1H), 8.78 (s, 1H), 8.41 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.37 (d, *J* = 8.3 Hz,1H), 8.28 (d, *J* = 8.8 Hz, 1H), 7.58 (dd, *J* = 8.1 Hz, 3.9 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.12 (q, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.47 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.17 (s), 154.46 (q, *J* = 5.7 Hz), 153.13 (s), 150.45 (s), 137.69 (s), 137.21 (s), 132.41 (s), 131.09 (s), 130.42 (s), 129.37 (s), 129.11 (s), 127.03 (s), 126.03 (s), 122.28 (s), 122.25 (s), 122.25 (d, *J* = 269.9 Hz), 106.85 (q, *J* = 35.4 Hz). IR (KBr) 3093, 2964, 1747, 1673, 1590, 1493, 1266, 1121, 800, 726, 651 cm^{-1}. Anal. Calcd for $C_{19}H_{11}ClF_3NO_2$: C, 60.41; H, 2.94; N, 3.71. Found: C, 60.55; H, 3.15; N, 3.78. HRMS (ESI) m/z calcd for $C_{19}H_{12}ClF_3NO_2$ $(M+H)^+$ 378.0509; found 137.0505.



(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl thiophene-3-carboxylate (**4ai**, 14 mg, 42%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.65 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.43 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 6.05 (q, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.51 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.27 (s), 154.21 (q, *J* = 6.0 Hz), 137.04 (s), 135.13 (s), 131.27 (s), 131.19 (s), 129.28 (s), 128.17 (s), 127.02 (s), 126.85 (s), 122.25 (q, *J* = 270.0 Hz), 106.69 (q, *J* = 35.4 Hz). IR (KBr) 3113, 2917, 1743, 1673, 1594, 1493, 1328, 1262, 1136, 816, 741, 651 cm^{-1}. Anal. Calcd for $C_{14}H_8ClF_3O_2S$: C, 50.54; H, 2.42. Found: C, 50.62; H, 2.55.

3. Stereochemistry determination of the products

The *Z*-carboxylate-trifluoromethylation products **4** are generally new products that are unknown in the literature. The assignments of the *Z*- and *E*-stereochemistry is based on the comparison of the isomeric pairs of **4m/4m'**, **4n/4n'**, **4s/4s'** and **4w/4w'**, the previous report of similar *E*-isomeric products[1-4] and the observation of through-space C-F coupling of the CF_3 and the phenyl *ortho*-carbon (relative to the vinyl group) in the *E*-isomers that is absent in the *Z*-isomers. Figure S1 summarizes the major NMR differences between *Z*- and *E*-isomeric products, taking **4n/4n'** as example.

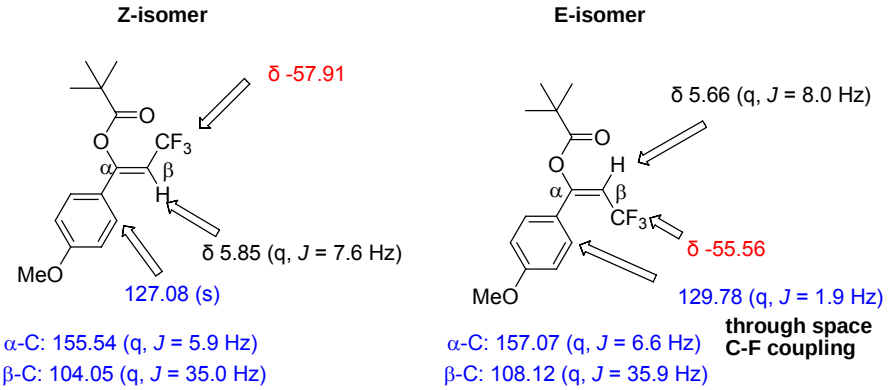


Figure S1. Summary of the NMR differences of Z- and E-isomers. Characteristic ^{1}H, ^{19}F and ^{13}C NMR resonances are marked in black, red and blue in the structures.

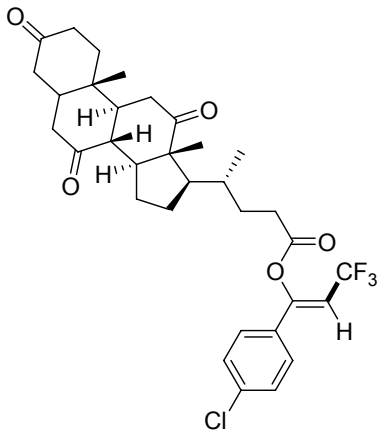
Generally, the *E*-isomer possesses significantly upfield shifted vinylic H and downfield shifted CF_3, and slightly larger coupling constant of $^{3}J_{H\text{-}F}$ coupling between H and CF_3 group. Moreover, for the vinyl C_α and C_β atoms, the *Z*-isomer has smaller ^{13}C chemical shifts and C-F coupling constants than those of the *E*-isomer. Finally, there is significant through-space C-F coupling between *ortho*-carbon of phenyl and the CF_3 group that are spatially approaching to each other in the *E*-isomer, as reflected by ^{13}C NMR spectra of the *E*-isomer.[5] A significant coupling constant of 1.9 Hz is observed (Similar values of 1.6, 1.8 and 1.8 Hz are observed for **4m'**, **4s'** and **4w'**). This effect is expectedly absent in the *Z*-isomer where the phenyl ring and the CF_3 are distal to each other.

References:

1. M. Kawatsura, J. Namioka, K. Kajita, M. Yamamoto, H. Tsuji, T. Itoh, *Org. Lett.* **2011**, *13*, 3285.
2. P. G. Janson, I. Gaoneim, N. O. Ilchenko, K. J. Szabó, *Org. Lett.* **2012**, *14*, 2882.
3. H. Egami, R. Shimizu, S. Kawamura, M. Sodeoka, *Tetrahedron Lett.* **2012**, *53*, 5503.
4. R. Tomita, T. Koike, M. Akita, *Angew. Chem. Int. Ed.* **2015**, *54*, 12923.
5. For a similar observation of such through-space C-F coupling of CF_2 with phenyl carbon in *cis*-configuration on the double bond, see: S. Domanski, O. Staszewska-Krajewska, W. Chaladaj, *J. Org. Chem.* **2017**, *78*, 7998.

4. Late-stage modification of dehydrocholic acid

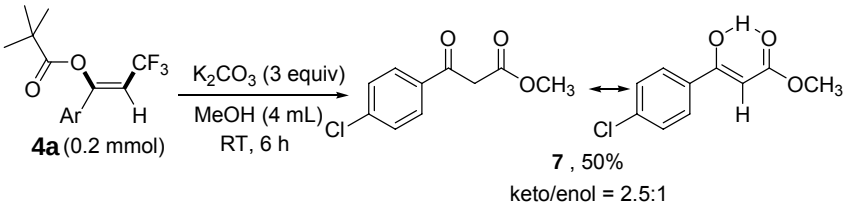
Following the general procedure described in section 2, the desired dehydrocholic trifluoromethylenol ester **6** was obtained in a yield of 20 mg, 33%. As shown by both ^{1}H and ^{19}F NMR, there is very minor amount of the *E*-isomer in a ratio of 1:12 to the major *Z*-isomer.

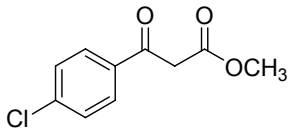


(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl (4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (**6**; 20 mg, 33%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 4H), 5.93 (q, *J* = 7.4 Hz, 1H), 3.15 – 2.81 (m, 4H), 2.74 – 2.49 (m, 2H), 2.42 – 1.89 (m, 13H), 1.64 (td, *J* = 14.3, 5.0 Hz, 1H), 1.42 (s, 3H), 1.40 – 1.23 (m, 4H), 1.09 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.58 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.93 (s), 209.03 (s), 208.65 (s), 170.89 (s), 154.31 (q, *J* = 5.8 Hz), 136.96 (s), 131.45 (s), 129.24 (s), 126.98 (s), 122.21 (q, *J* = 269.9 Hz), 106.40 (q, *J* = 35.2 Hz), 56.92 (s), 51.78 (s), 48.99 (s), 46.85 (s), 45.58 (s), 45.57 (s), 44.98 (s), 42.80 (s), 38.64 (s), 36.50 (s), 36.03 (s), 35.29 (s), 35.25 (s), 30.99 (s), 29.99 (s), 27.55 (s), 25.12 (s), 21.91 (s), 18.52 (s), 11.81 (s). IR (KBr) 2963, 1768, 1711, 1673, 1465, 1267, 1122, 816, 914, 729 cm^{-1}. Anal. Calcd for $C_{33}H_{38}ClF_3O_5$: C, 65.29; H, 6.31. Found: C, 65.38; H, 6.42. HRMS (ESI) m/z calcd for $C_{33}H_{39}ClF_3O_5^+$ $(M+H)^+$ 607.2438, found 607.2443.

Minor *E*-isomer: ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.76 (s). ^{1}H NMR: 5.80 (q, *J* = 7.8 Hz, 1H, vinylic H). The other resonances are overlapping with the major *Z*-isomer.

5. Alcolysis of the product 4a





Methyl 3-(4-chlorophenyl)-3-oxopropanoate (**7**; 21 mg, 50%). Yellow oil; A mixture of keto and enol forms in a ratio of 1: 0.4.

Keto form: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 4.01 (s, 2H), 3.78 (s, 3H). Enol form: ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.52 (s, 0.4 H, enol O*H*), 7.73 (d, *J* = 8.6 Hz, 0.8H), 7.42 (d, *J* = 8.6 Hz, 0.8H), 5.67 (s, 0.4H, C*H*=), 3.83 (s, 1.2 H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2 (s), 173.4 (s), 170.2 (s), 167.7 (s), 140.4 (s), 137.4 (s), 134.3 (s), 131.8 (s), 130.0 (s), 129.2 (s), 128.9 (s), 127.4 (s), 87.3 (s), 52.6 (s), 51.6 (s), 45.7 (s).

These data were in accordance with previous literature report (Wahl, B.; Bonin, H.; Mortreux, A.; Giboulot, S.; Liron, F.; Poli, G.; Sauthier, M. *Adv Synth Catal* **2012,** *354* (16), 3105-3114.)

6. ^{19}F NMR monitoring of the reaction course

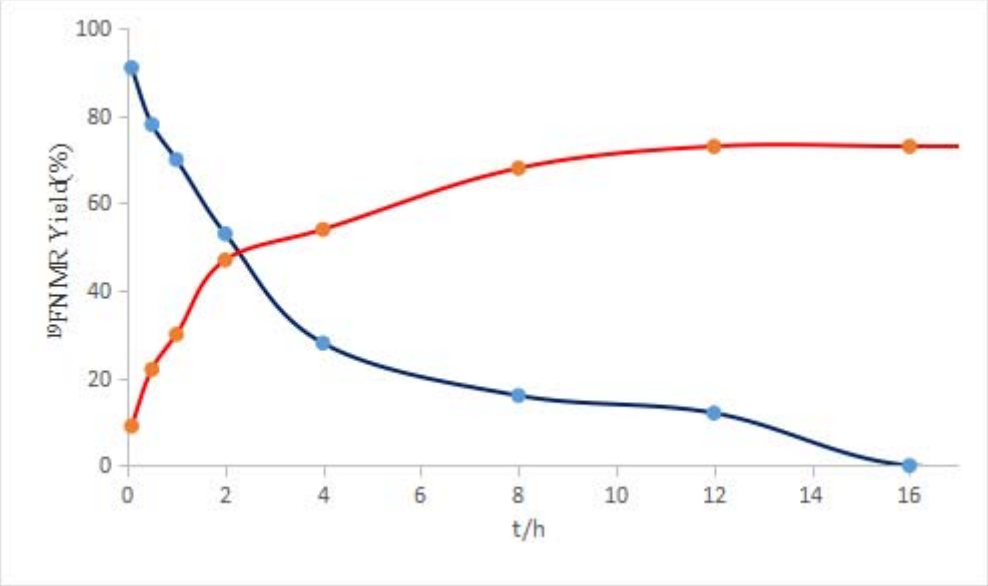
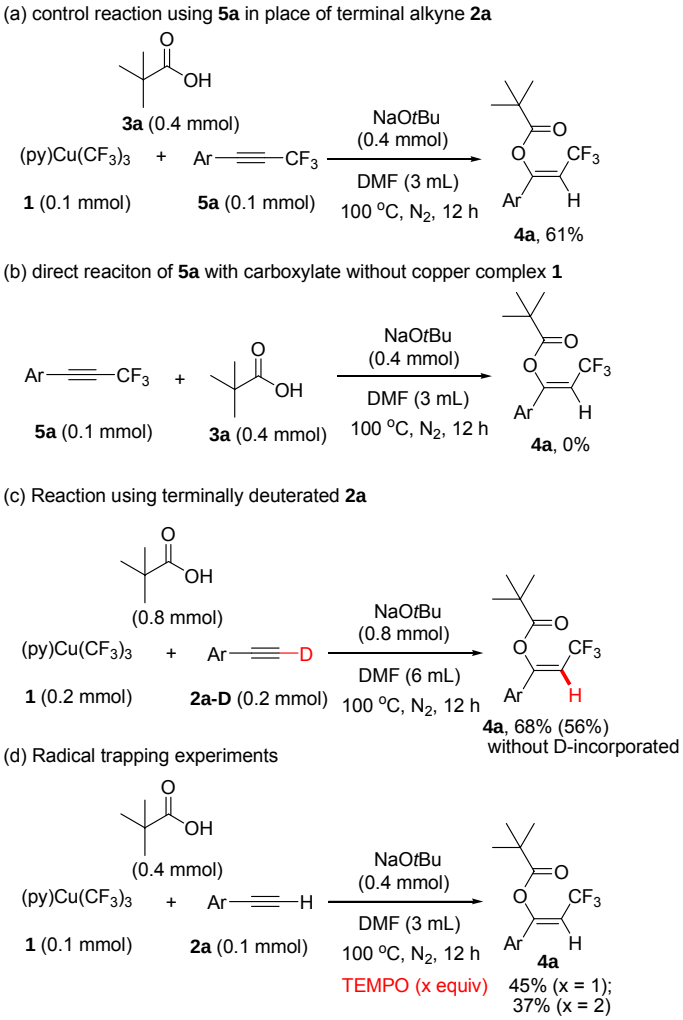


Figure S2. ^{19}F NMR monitoring of the reaction solution in Table 1 in from 5 mins to 0.5, 1, 2, 4, 8, 12, 16 hours respectively. Blue curve: **5a**; red curve: **4a**.

The formation of **5a** is kinetically facile and can reach a yield of ca 90% in only 5 minutes. Then **5a** is gradually consumed with the concurrent accumulation of the desired **4a**. At about 12 hours, the reaction reaches completion, as evidenced by TLC analysis of the crude mixture showing the complete conversion of the alkyne substrate. At this time, **5a** is almost completely consumed and a maximum yield of 72% was achieved for **4a**.

7. Mechanistic studies

Scheme S1. Control reactions, deuterium labeling and radical trapping studies



(1) control experiments using **5a** in place of terminal alkyne **2a** under the optimized reaction conditions showed that the desired product **4a** was indeed generated in 61% yield (Scheme S1a). It should be emphasized that in the carboxylate addition step, copper is required to promote this reaction; without copper salt, the desired **4a** could not be obtained (Scheme S1b). Possibly the triple bond is activated toward carboxylate attack via coordination by the Lewis acidic copper intermediate.

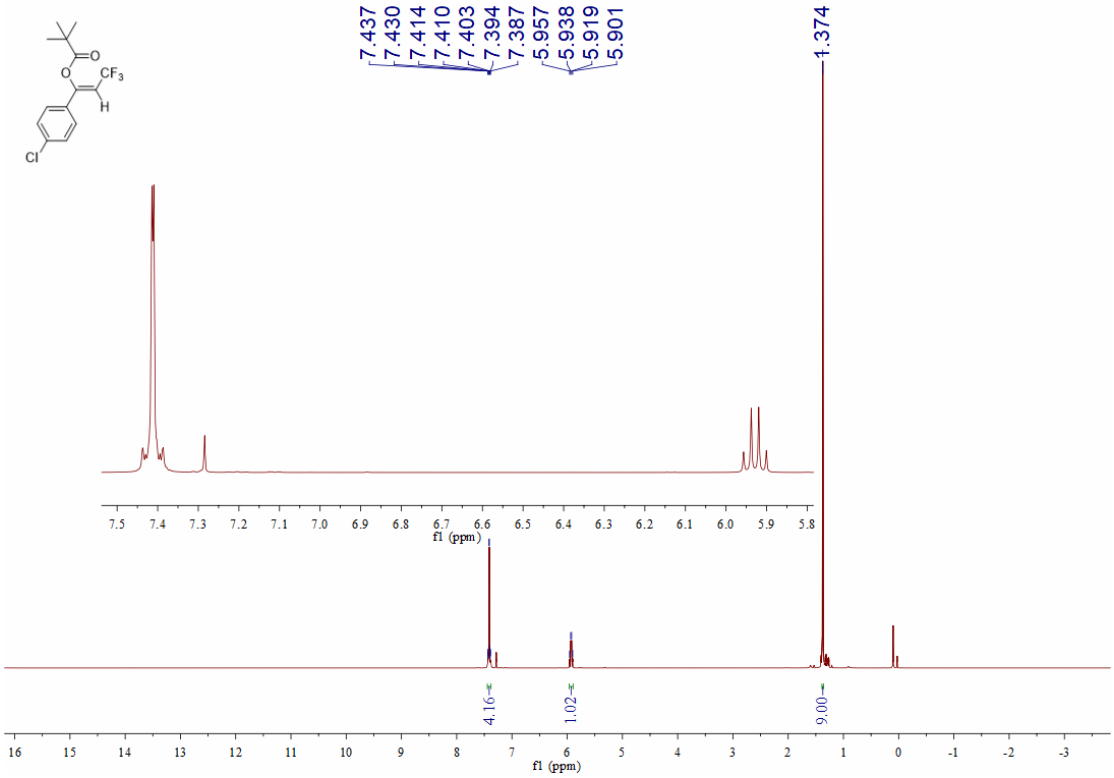
(2) Deuterium labeling experiment using terminally deuterated **2a-D** replacing **2a** showed that the product is still **4a** in a comparable yield of 68% (isolated in 56%) without deuterium incorporation (Scheme S1c). This result and the result in

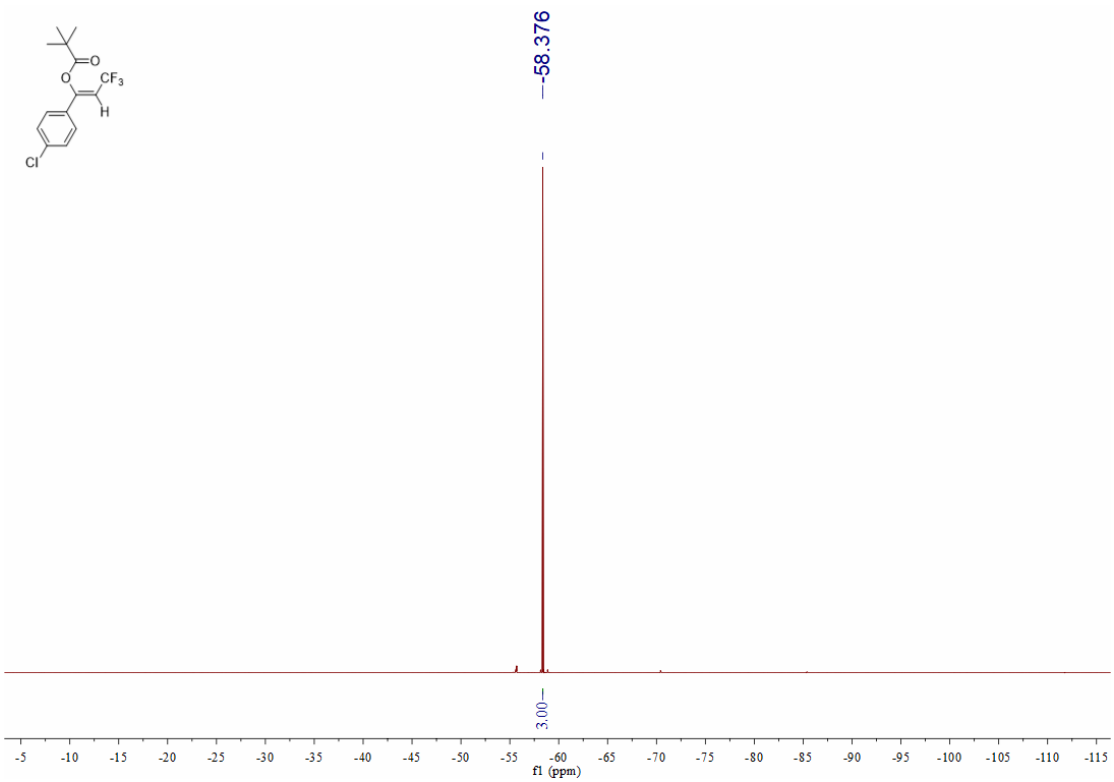
Scheme 4a indicate that the vinylic proton in product **4a** may probably come from carboxylic acid **3a**, rather than the terminal alkyne.

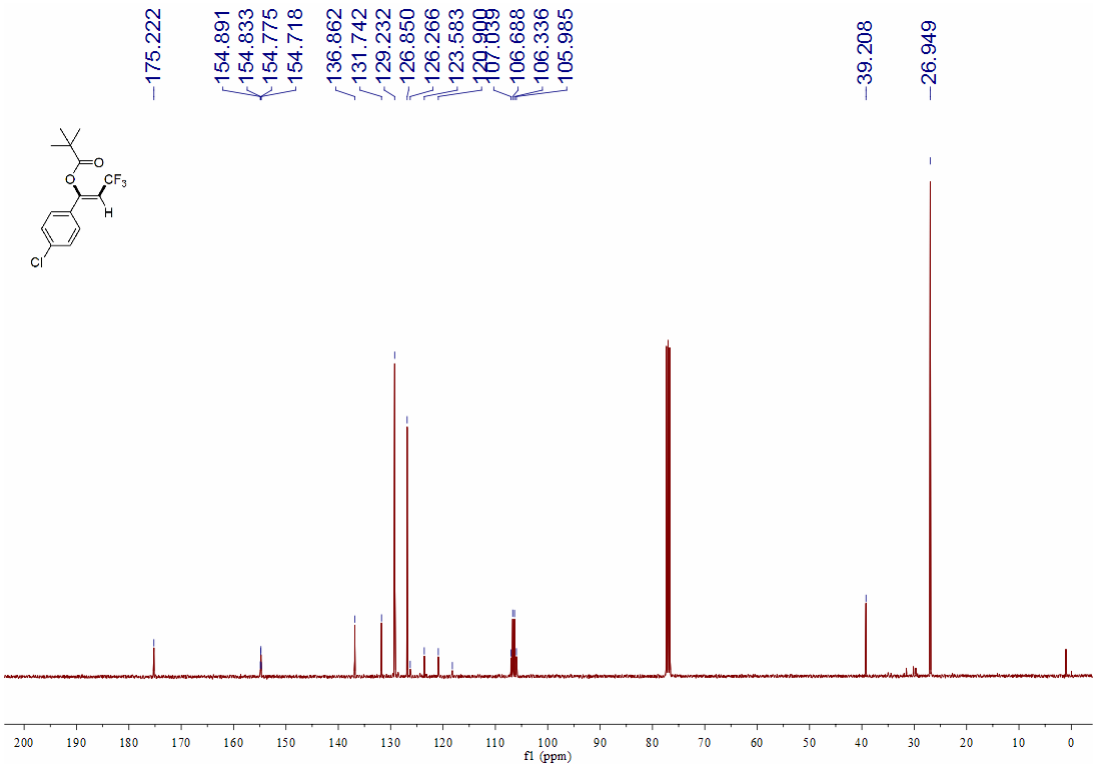
(3) Radical trapping experiments showed that the reaction yield of **4a** greatly reduced to 45% and 37% in the presence of one and two equivalents of radical scavenger TEMPO (Scheme S1d), suggesting that radical species be involved in the reaction course.

8. Copies of ^{1}H, ^{19}F and ^{13}C NMR spectra for all the products

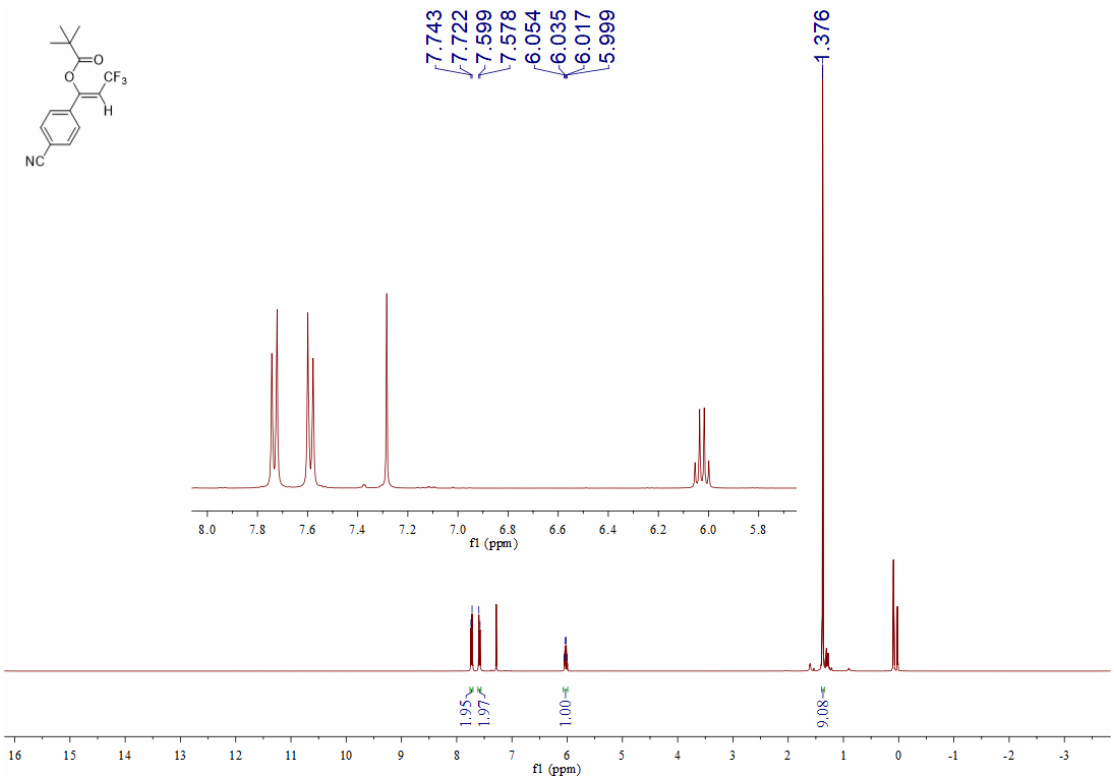
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (4a) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

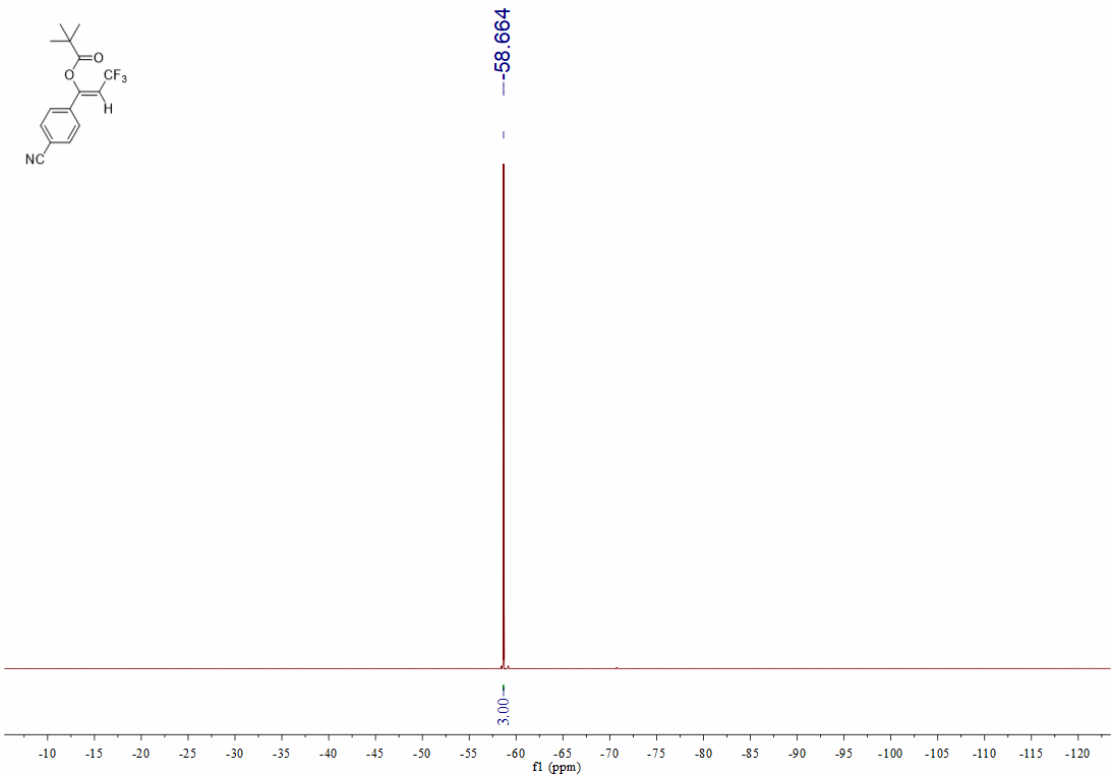






(Z)-1-(4-cyanophenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (4b) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

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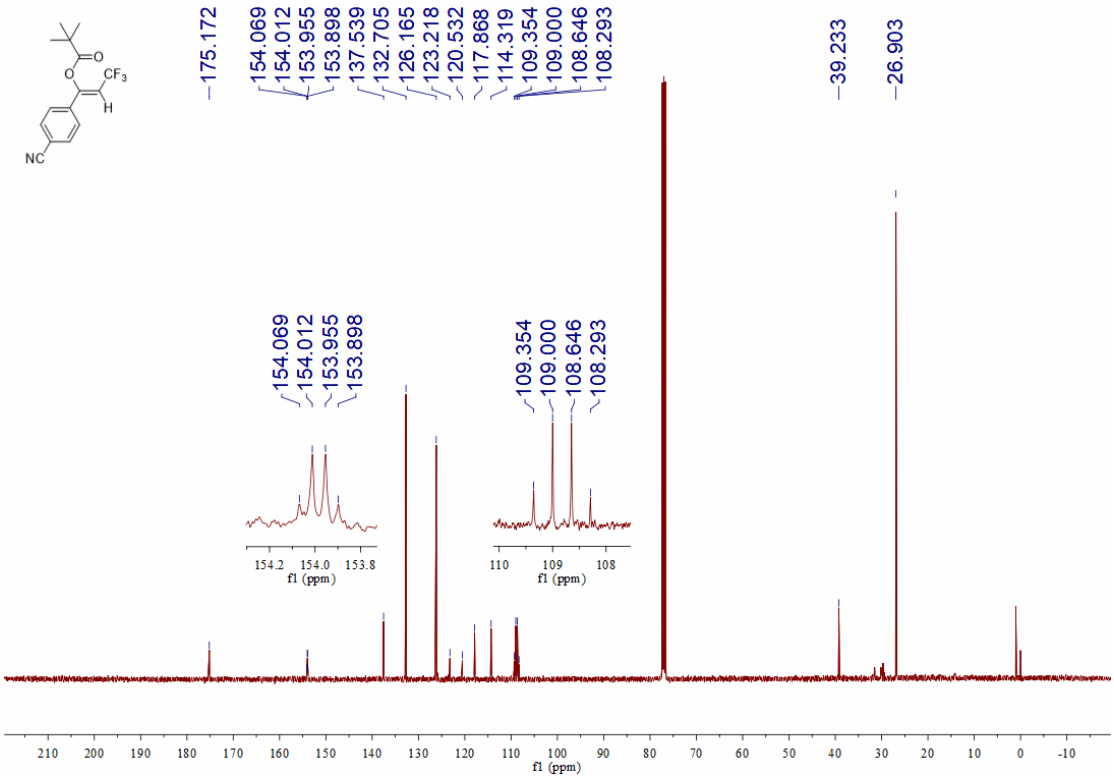
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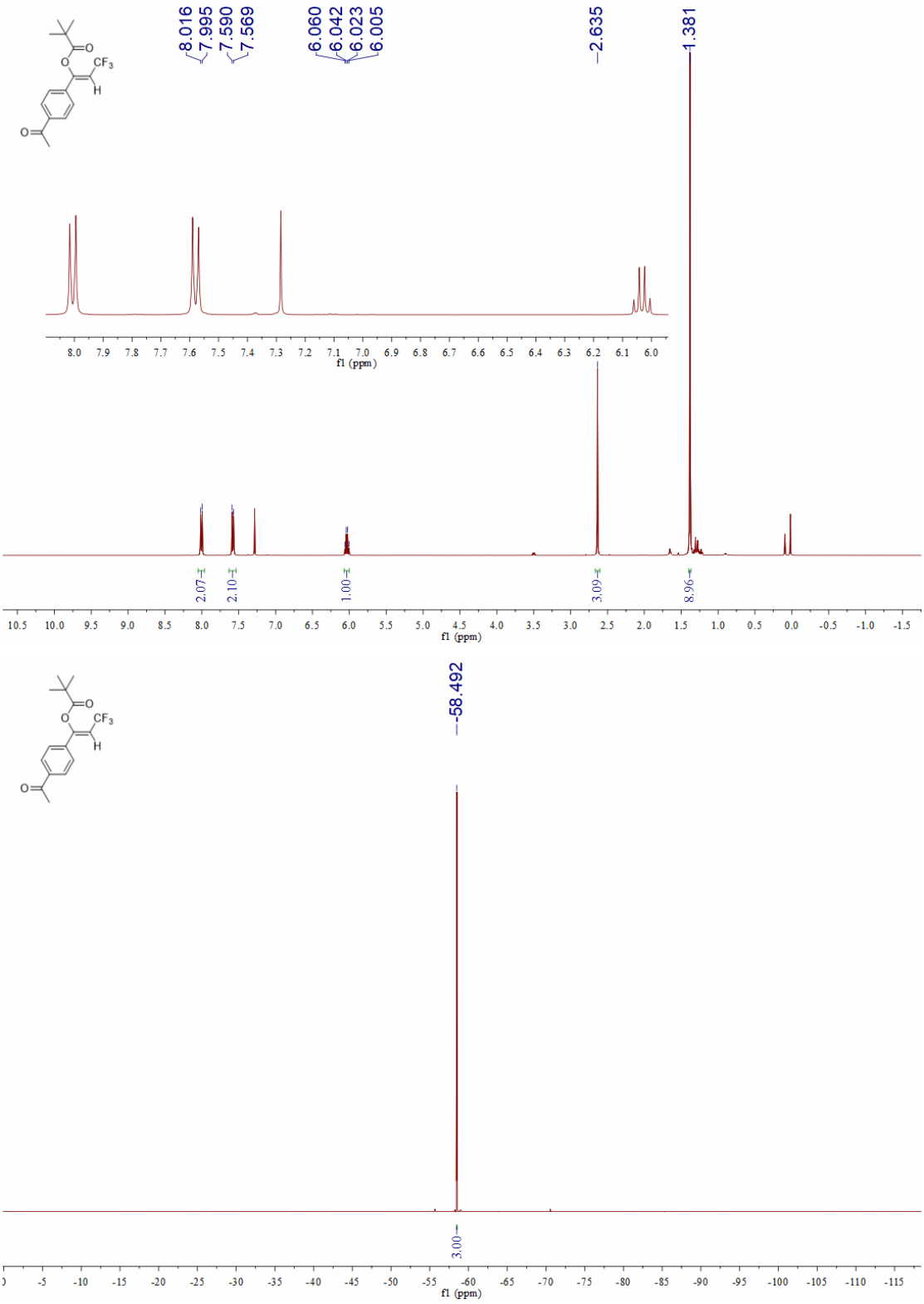
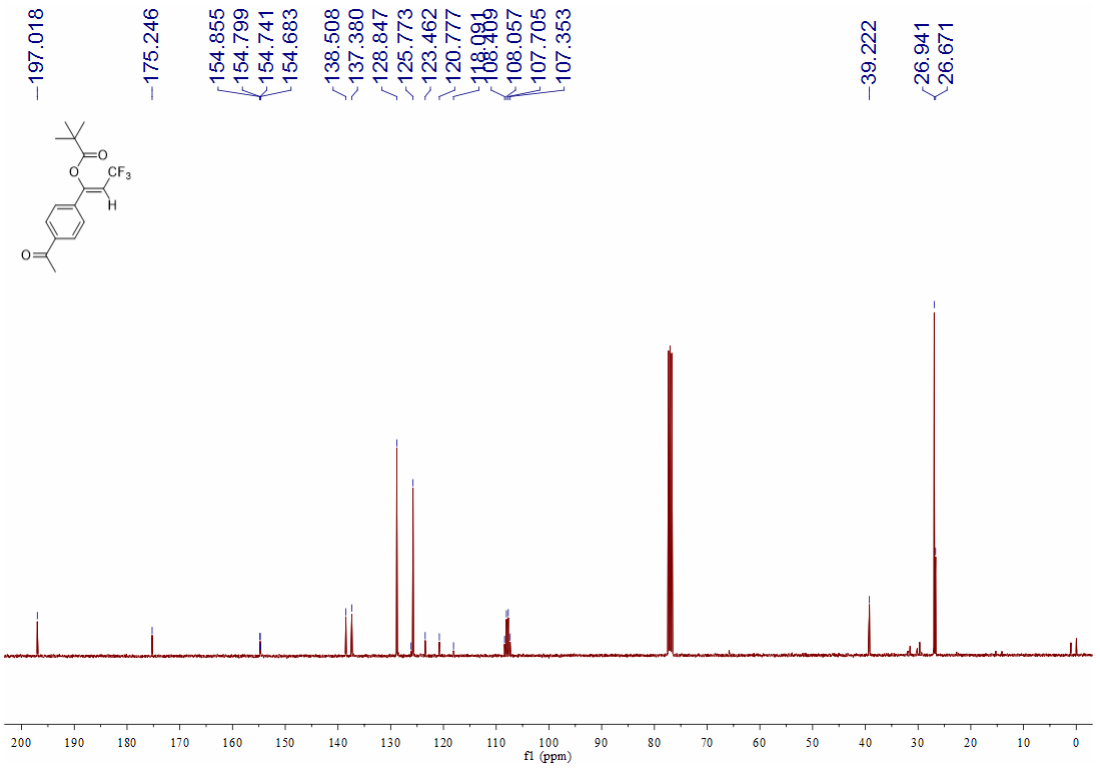
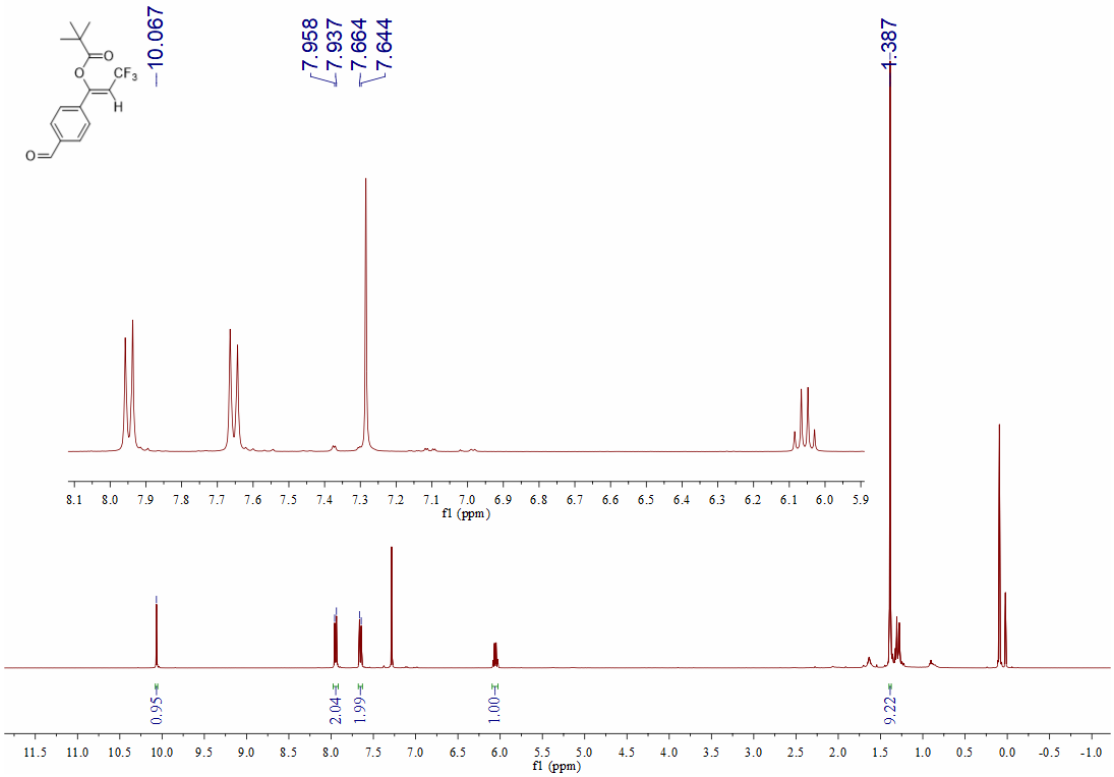
39.233
26.903
f1 (ppm)

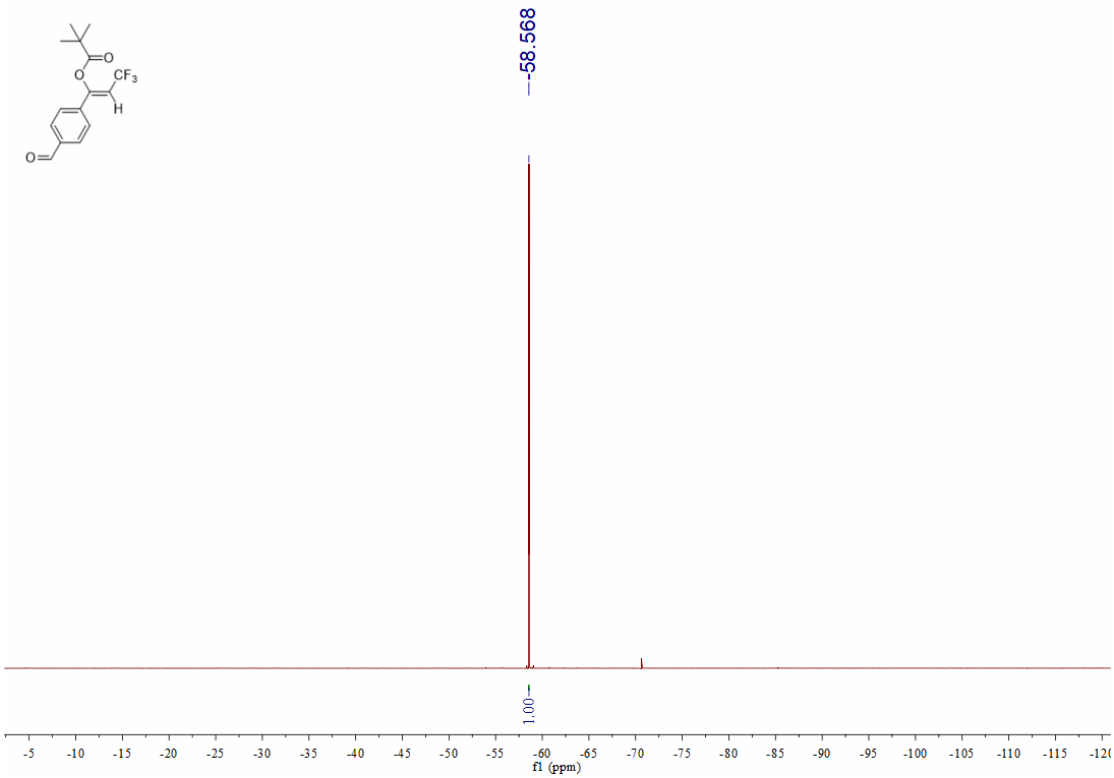
(Z)-1-(4-acetylphenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (4c) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).





(Z)-3,3,3-trifluoro-1-(4-formylphenyl)prop-1-en-1-yl pivalate (4d) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

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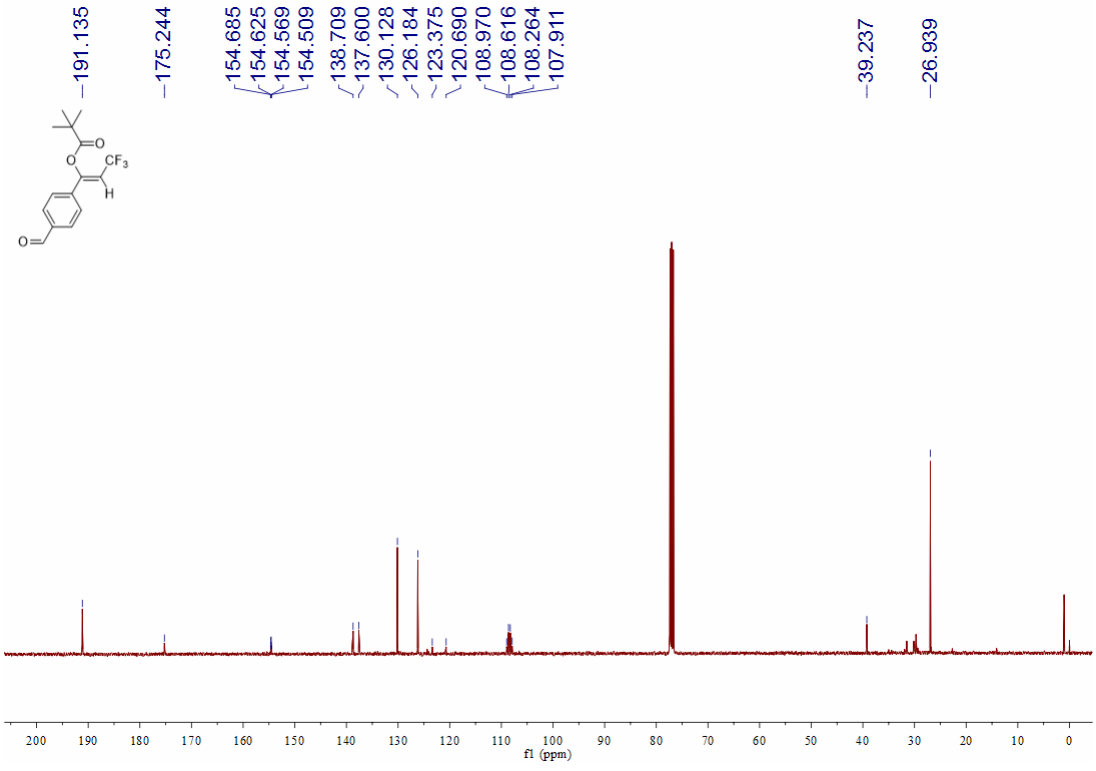
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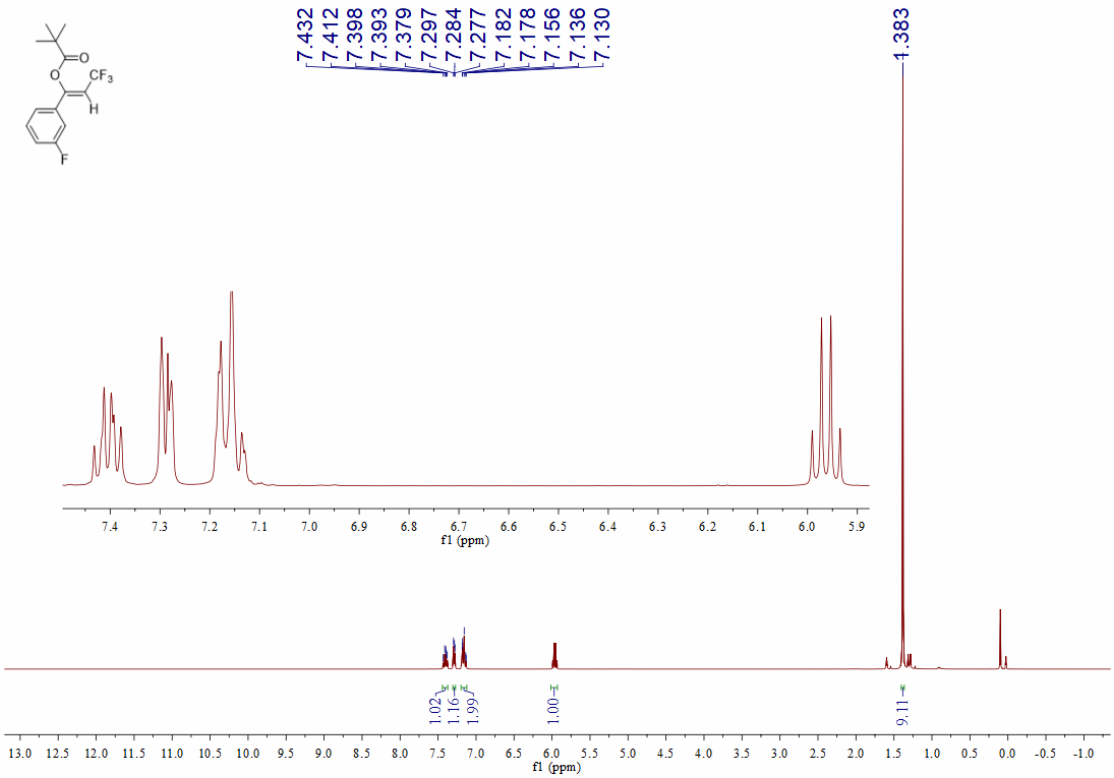
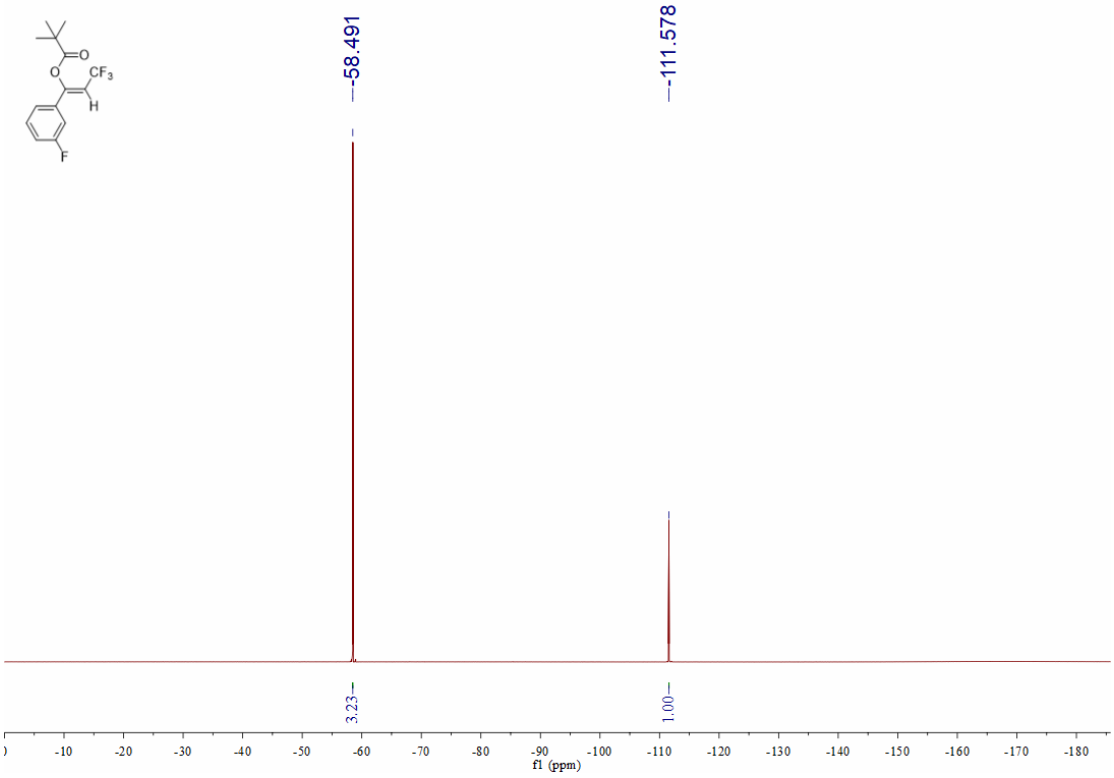
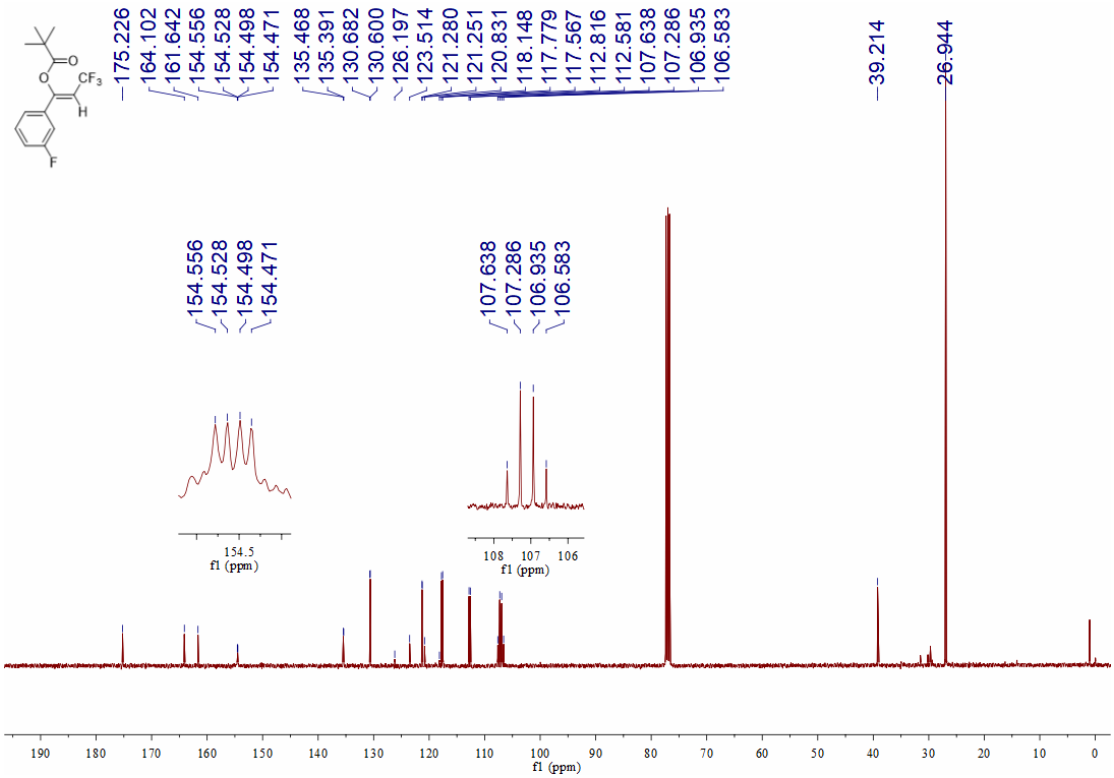
108.616
108.264
107.911
39.237
26.939
f1 (ppm)

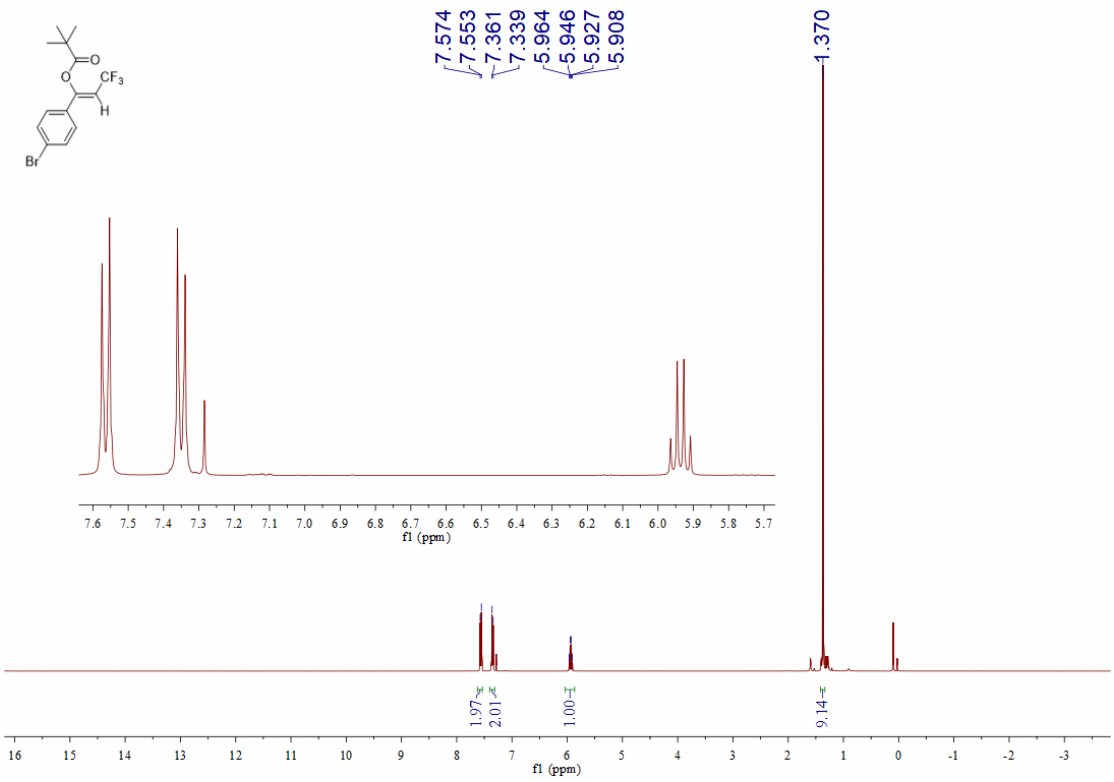
(Z)-3,3,3-trifluoro-1-(3-fluorophenyl)prop-1-en-1-yl pivalate (4e) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

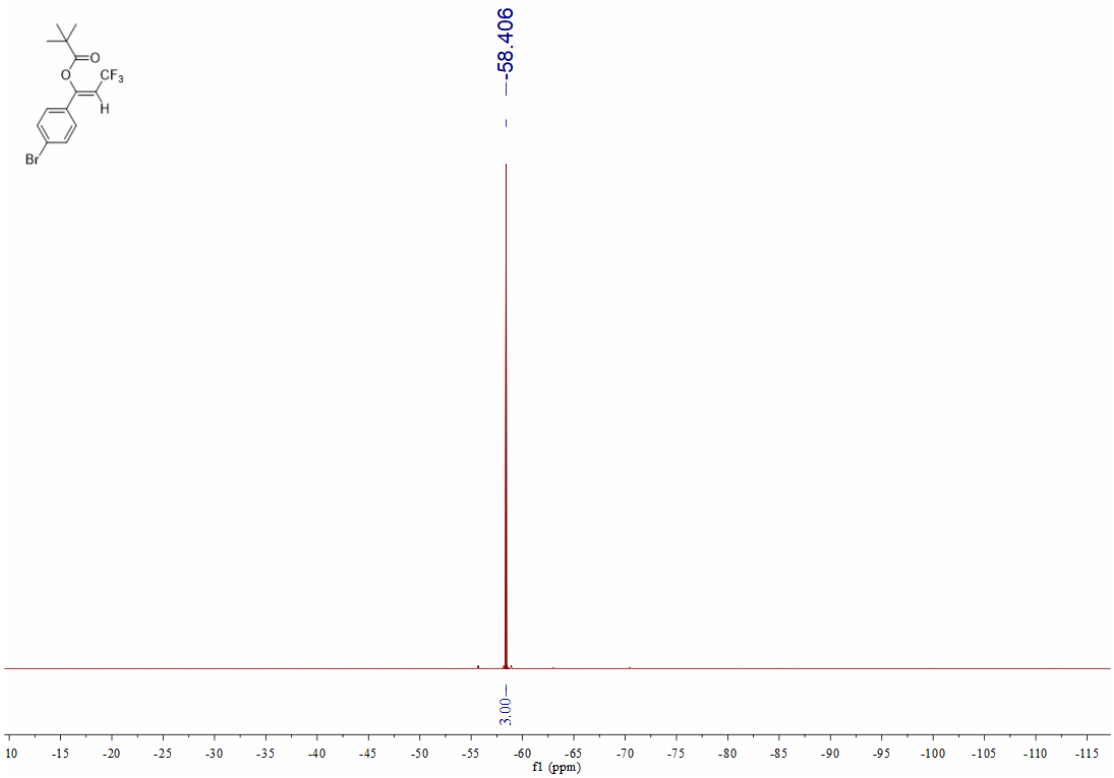






(Z)-1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (4f) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

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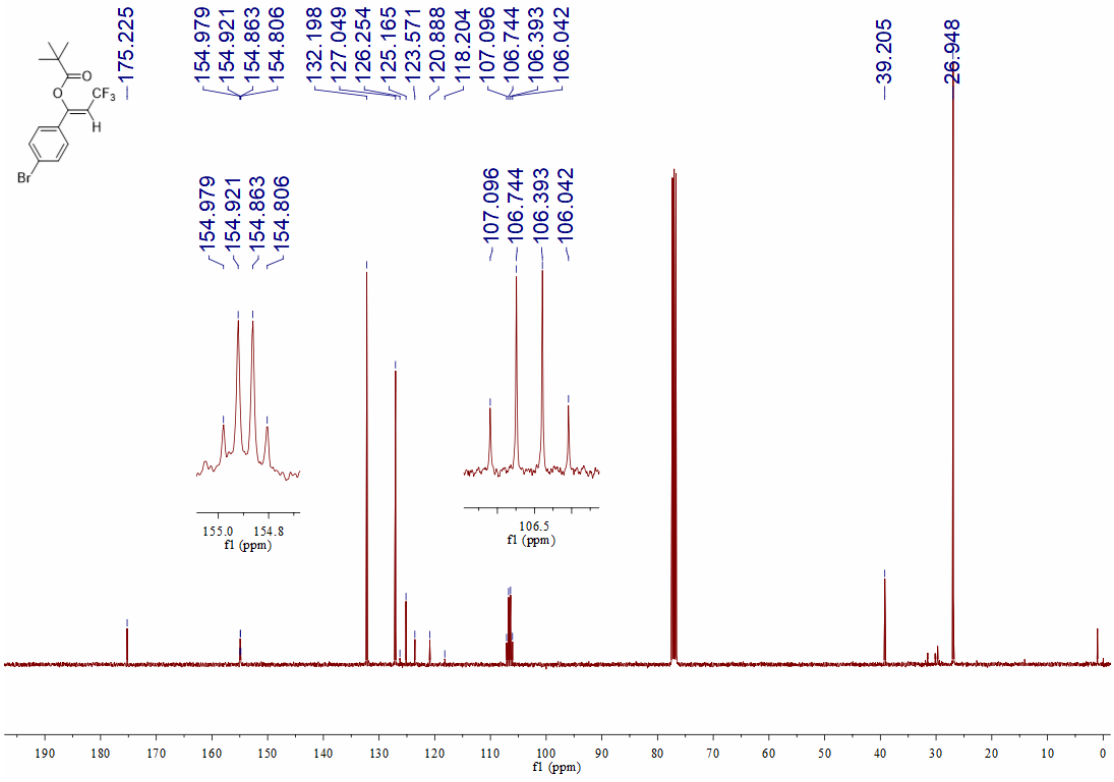
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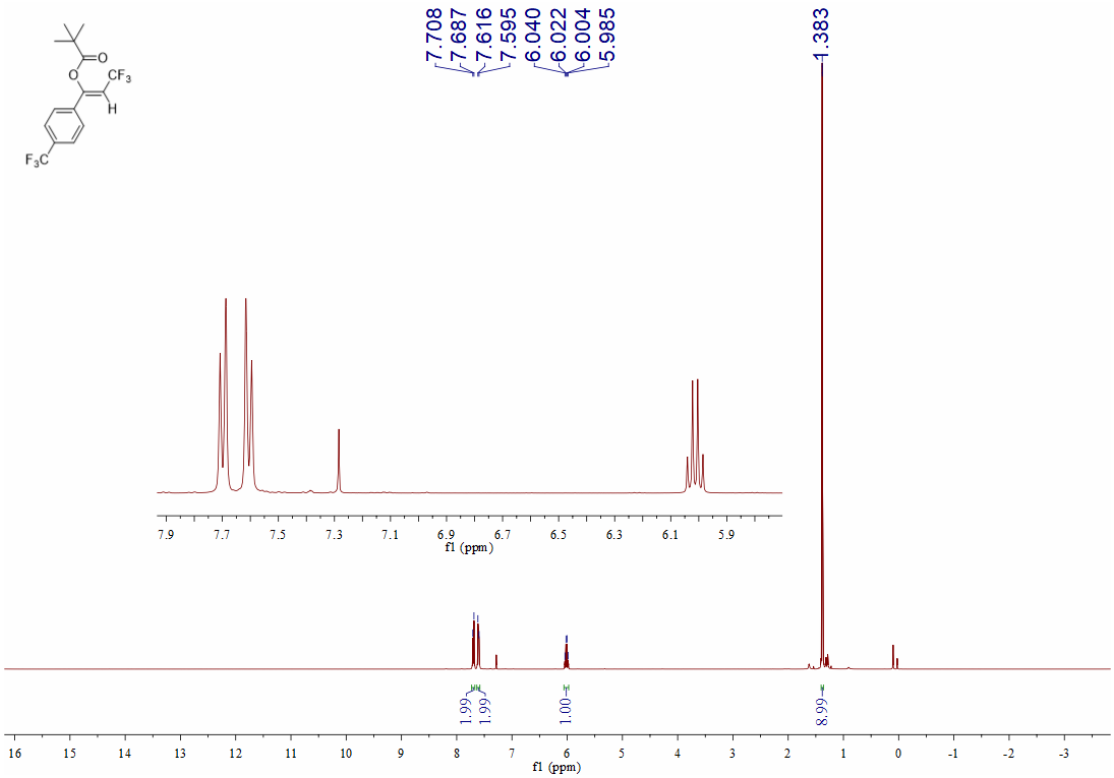
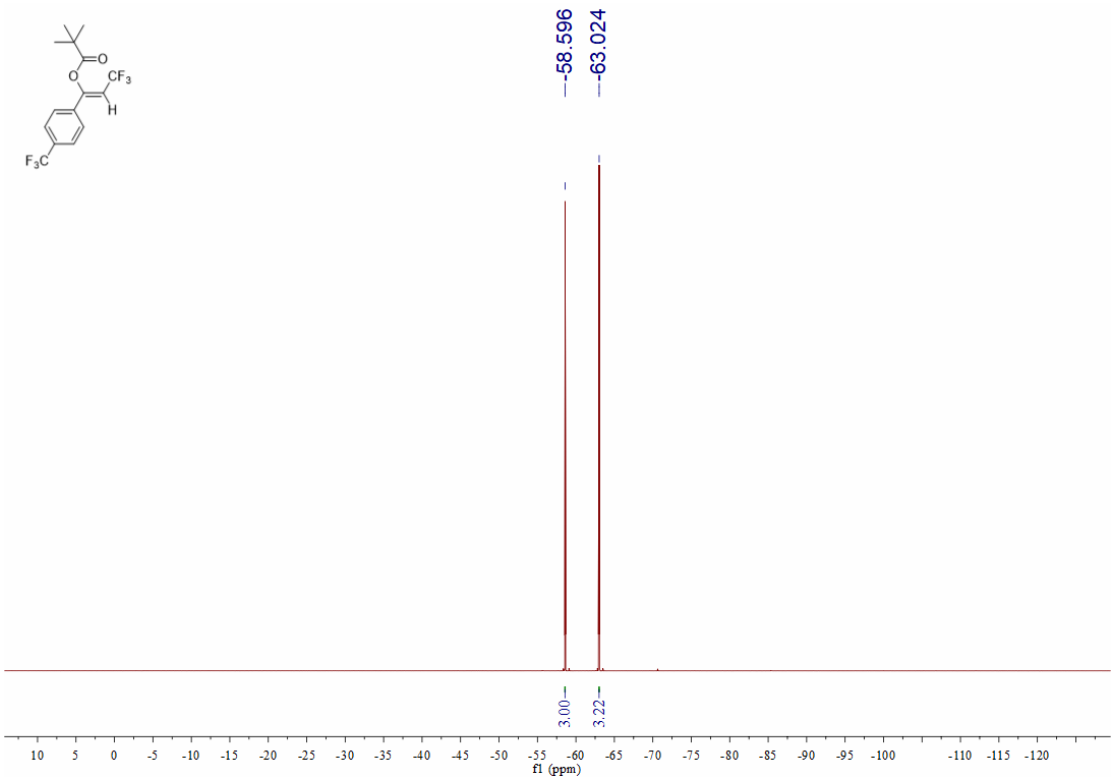
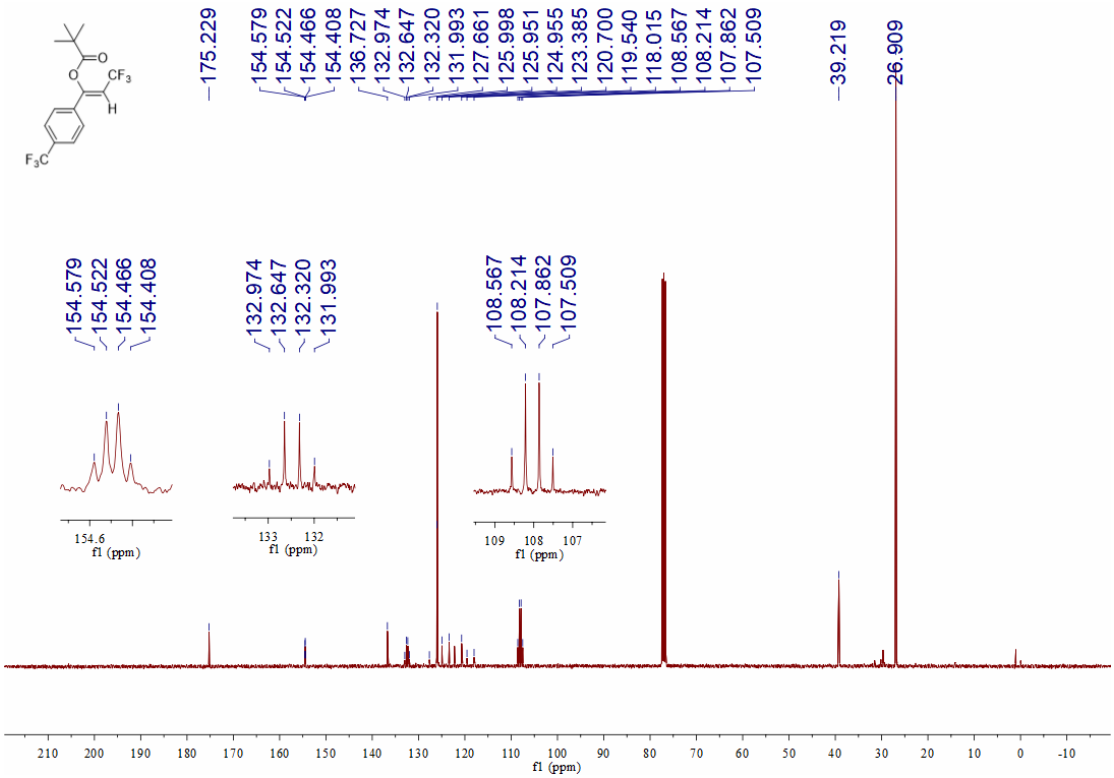
106.744
106.393
106.042
39.205
26.948
f1 (ppm)

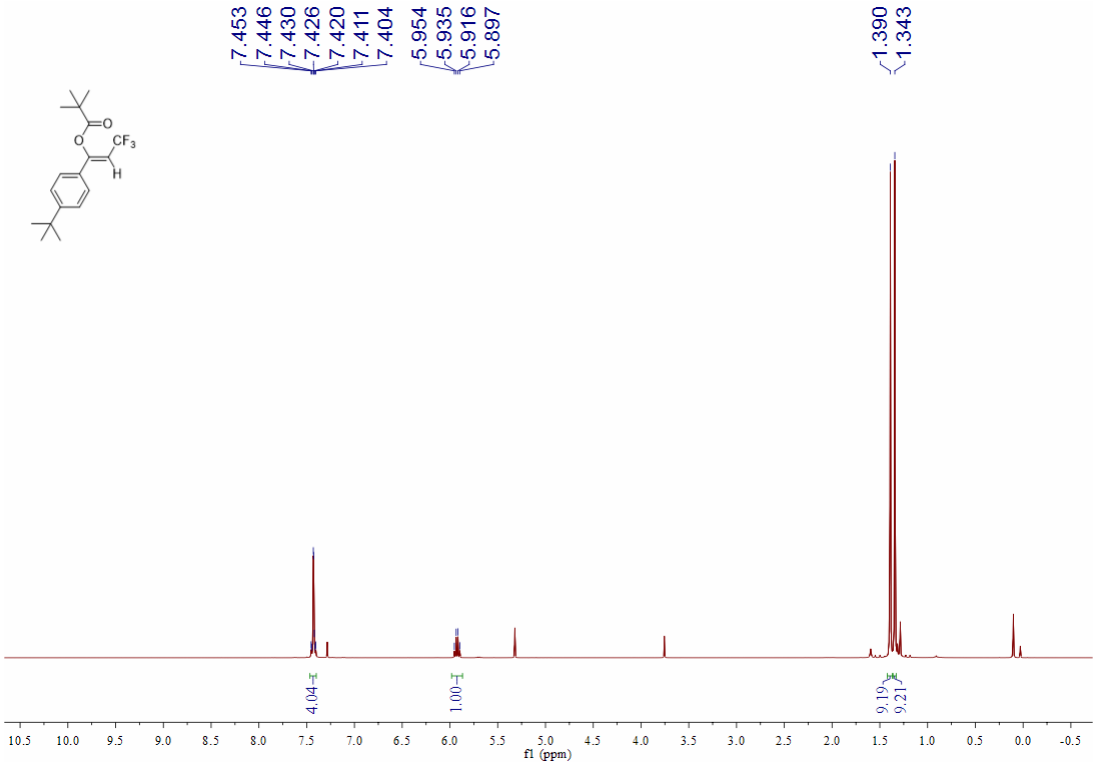
(Z)-3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl pivalate (4g) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

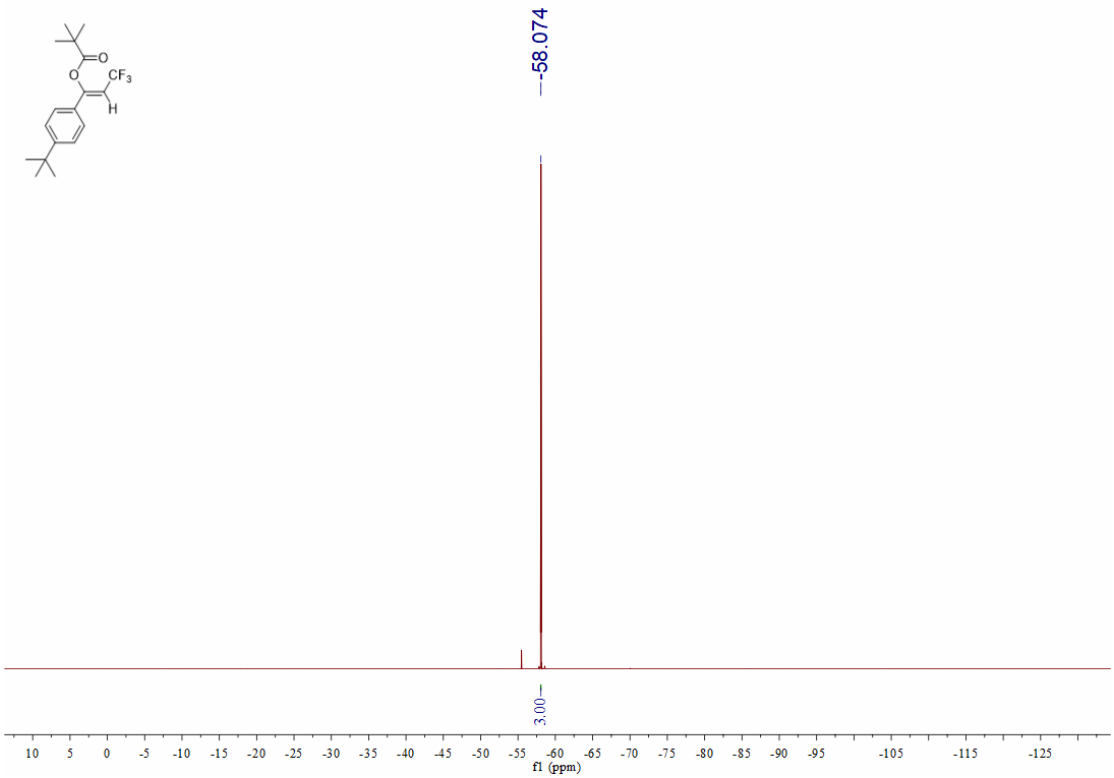


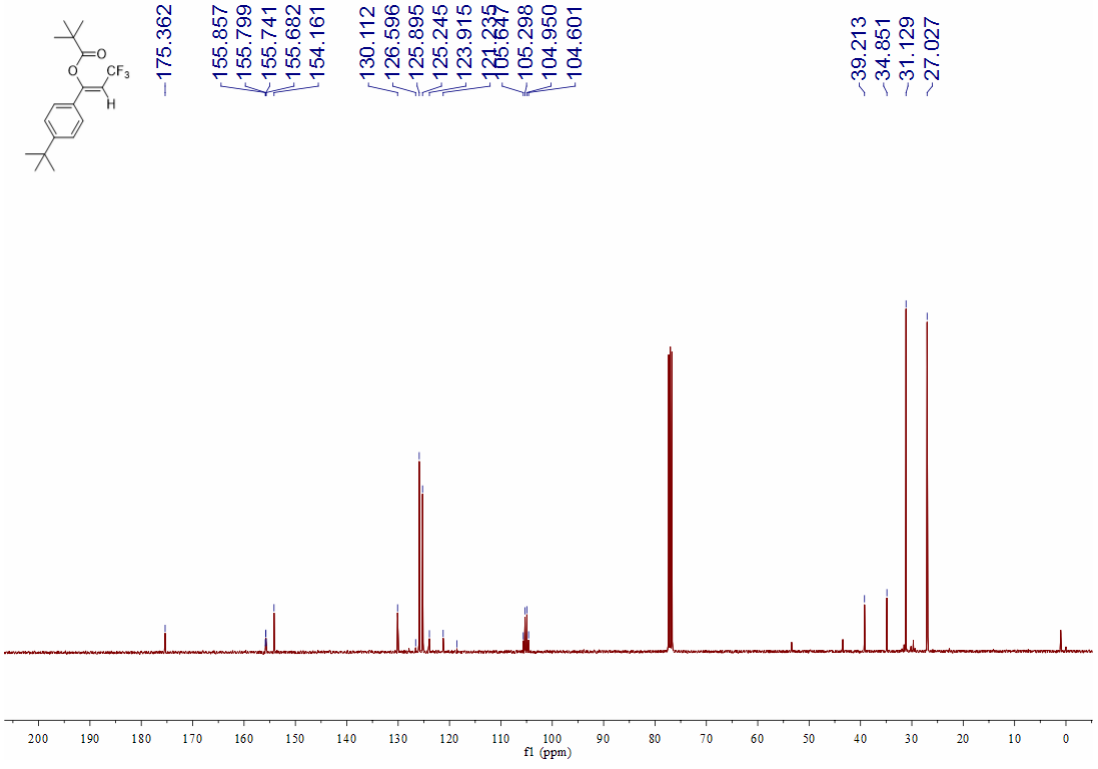




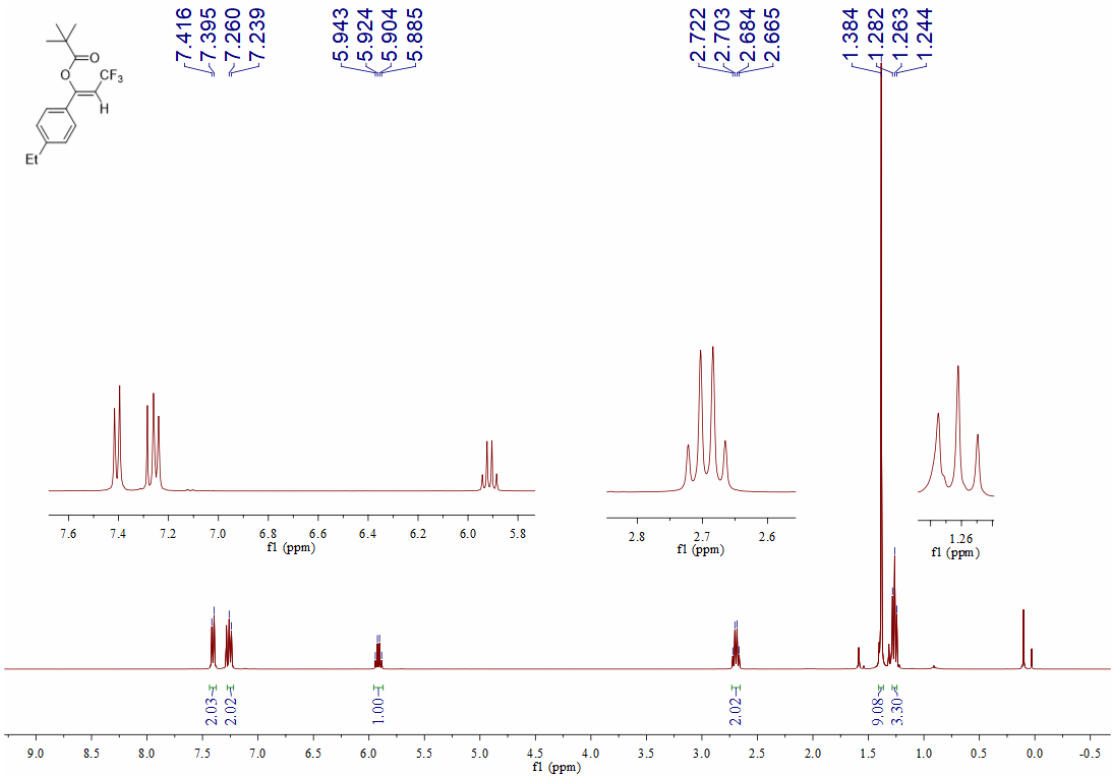
(Z)-1-(4-(tert-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (4h) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

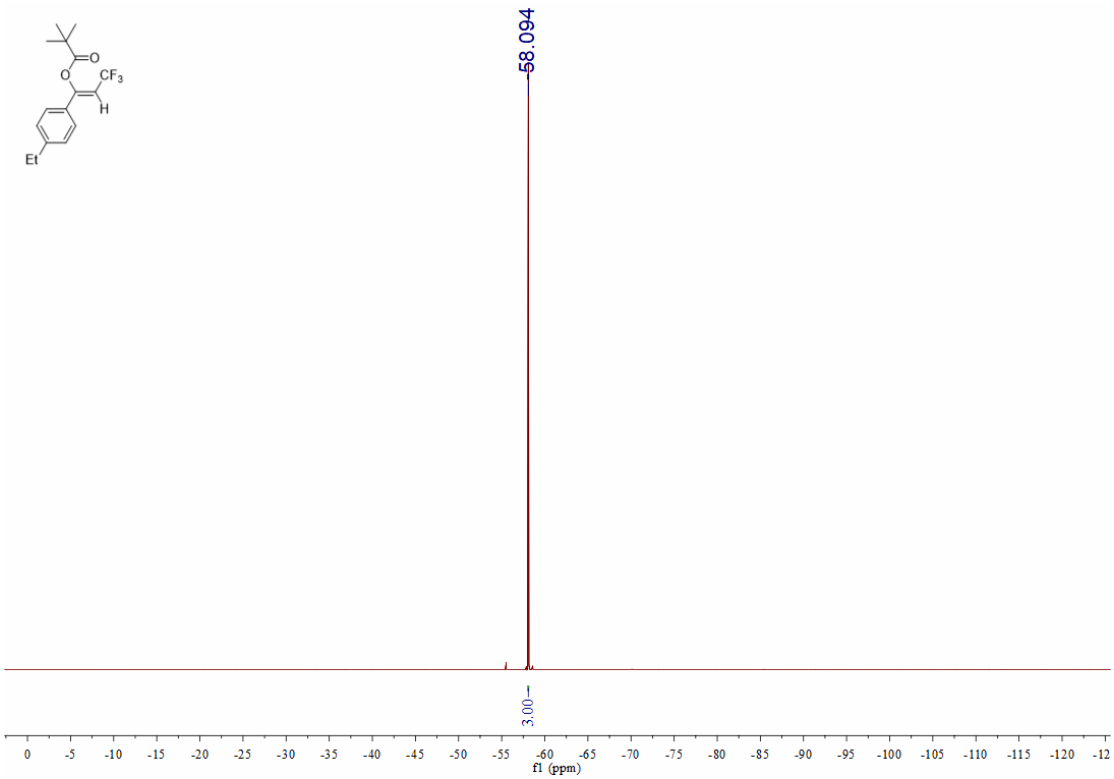


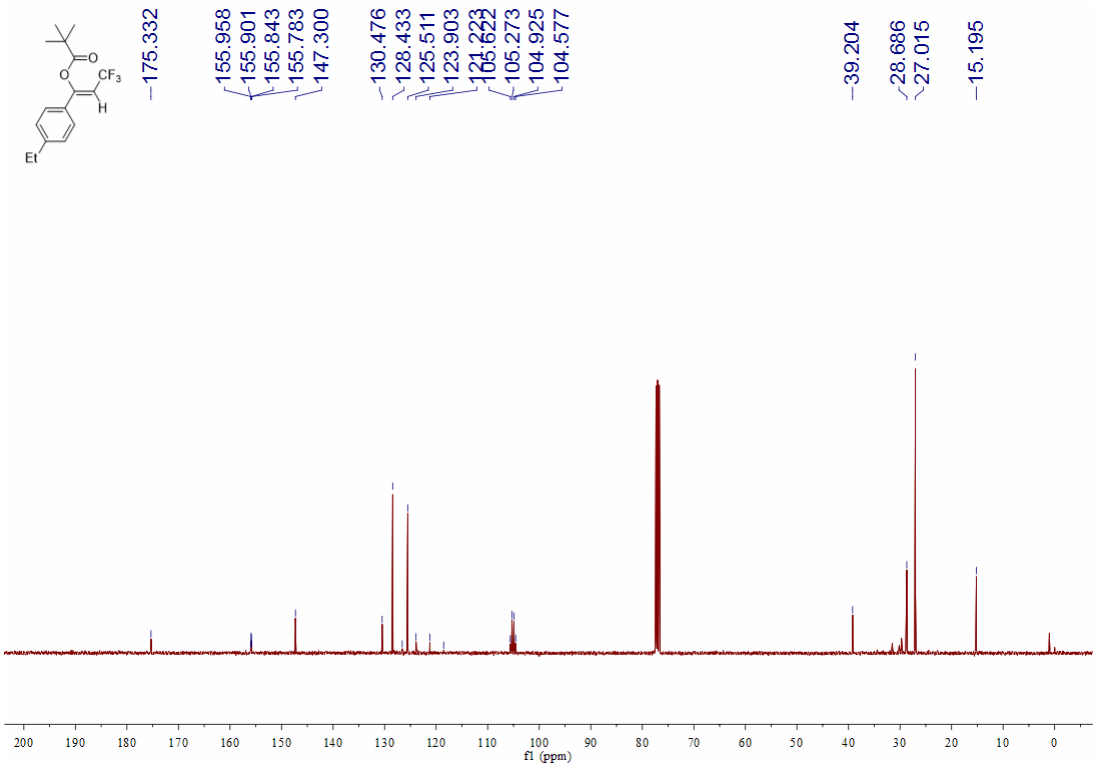

-58.074
3.00
f1 (ppm)


175.362
155.857
155.799
155.741
155.682
154.161
130.112
126.596
125.895
125.245
123.915
121.235
105.298
104.950
104.601
39.213
34.851
31.129
27.027
f1 (ppm)

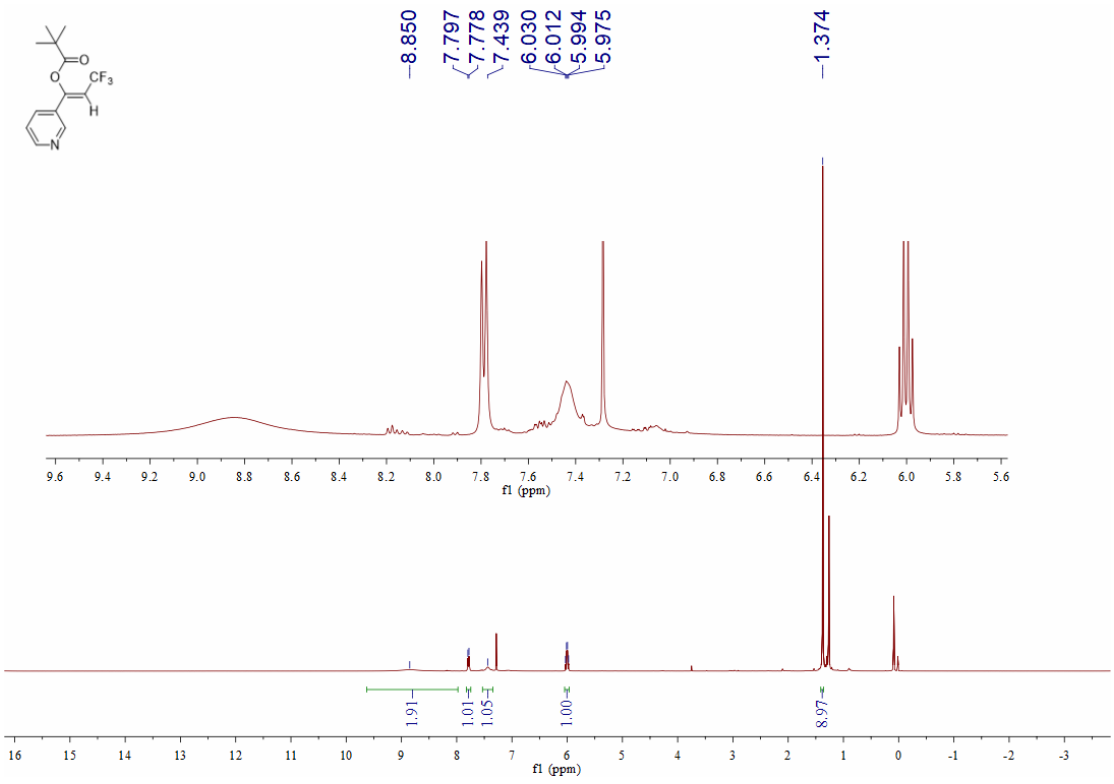
(Z)-1-(4-ethylphenyl)-3,3,3-trifluoroprop-1-en-1-yl pivalate (4i) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

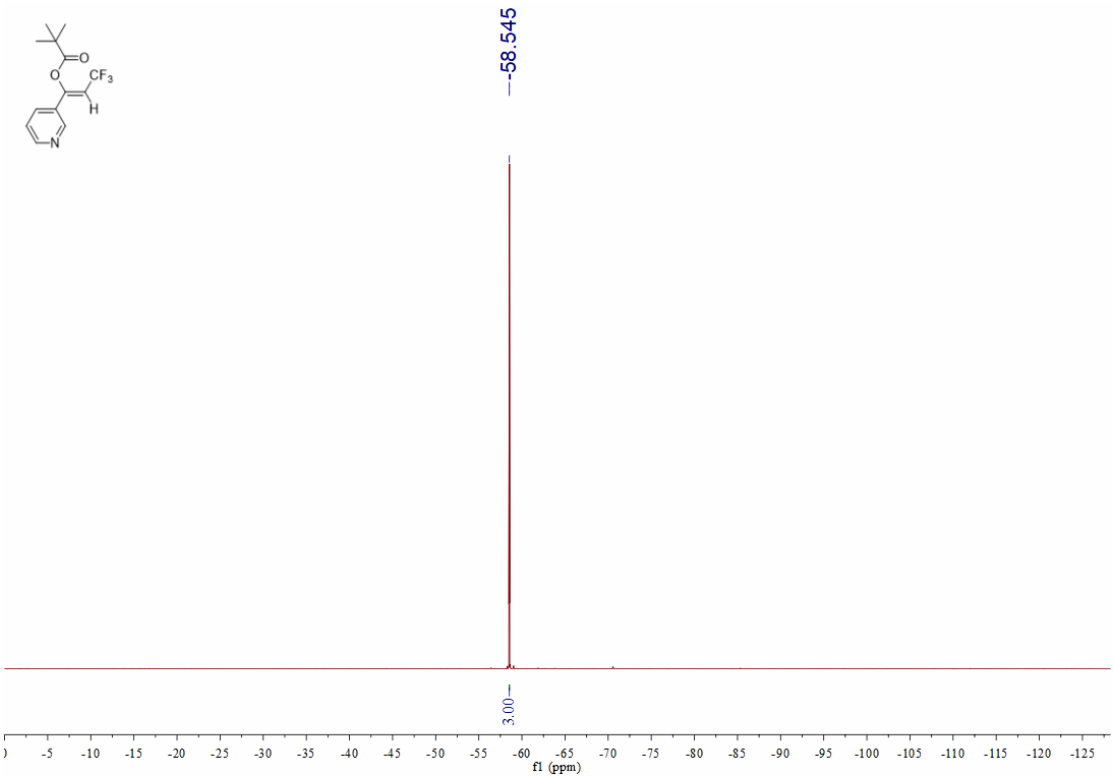


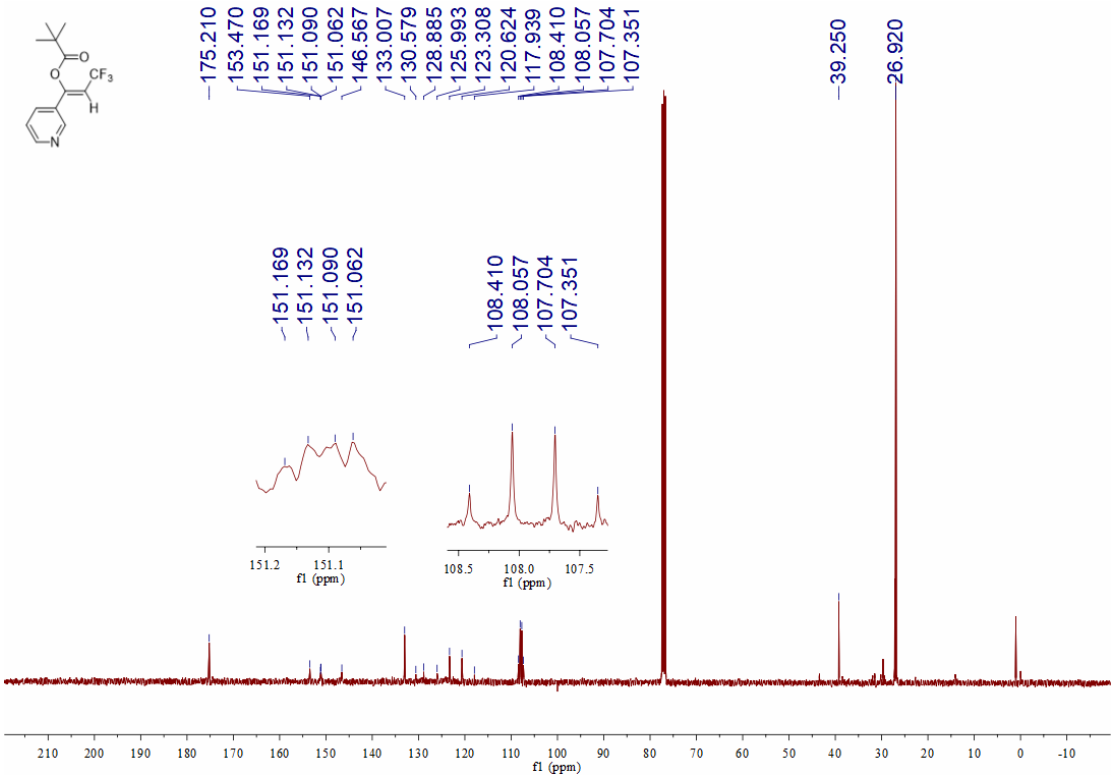




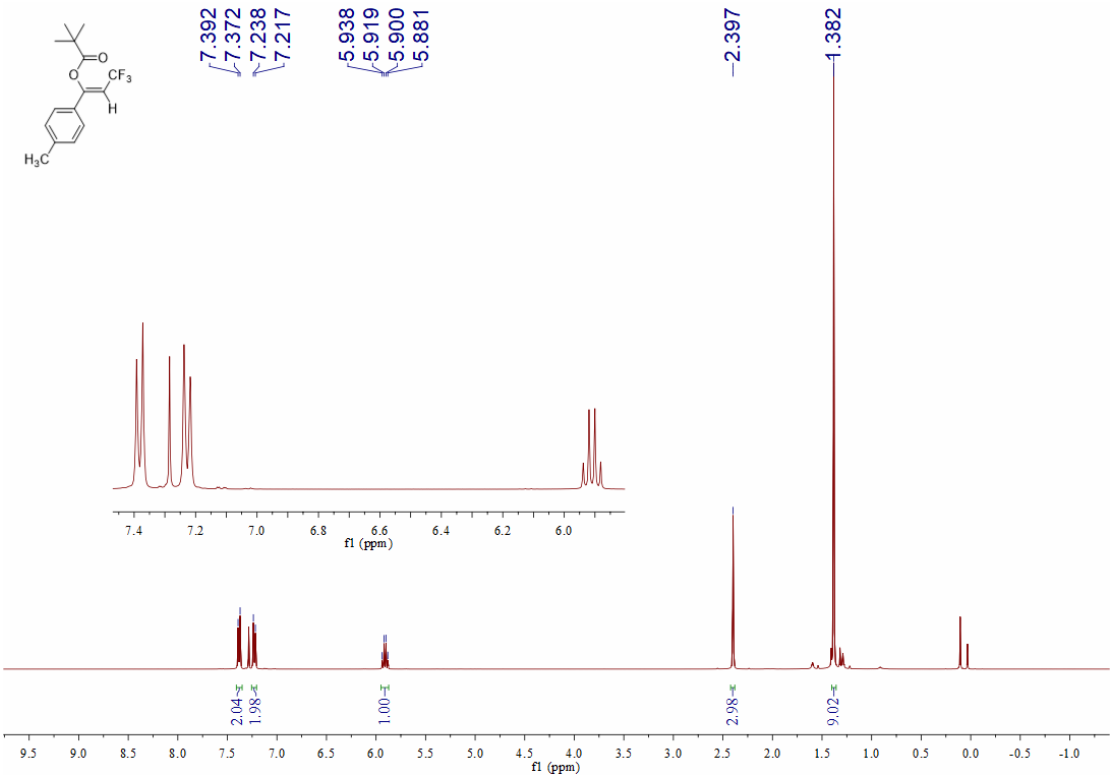
(Z)-3,3,3-trifluoro-1-(pyridin-3-yl)prop-1-en-1-yl pivalate (4j) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

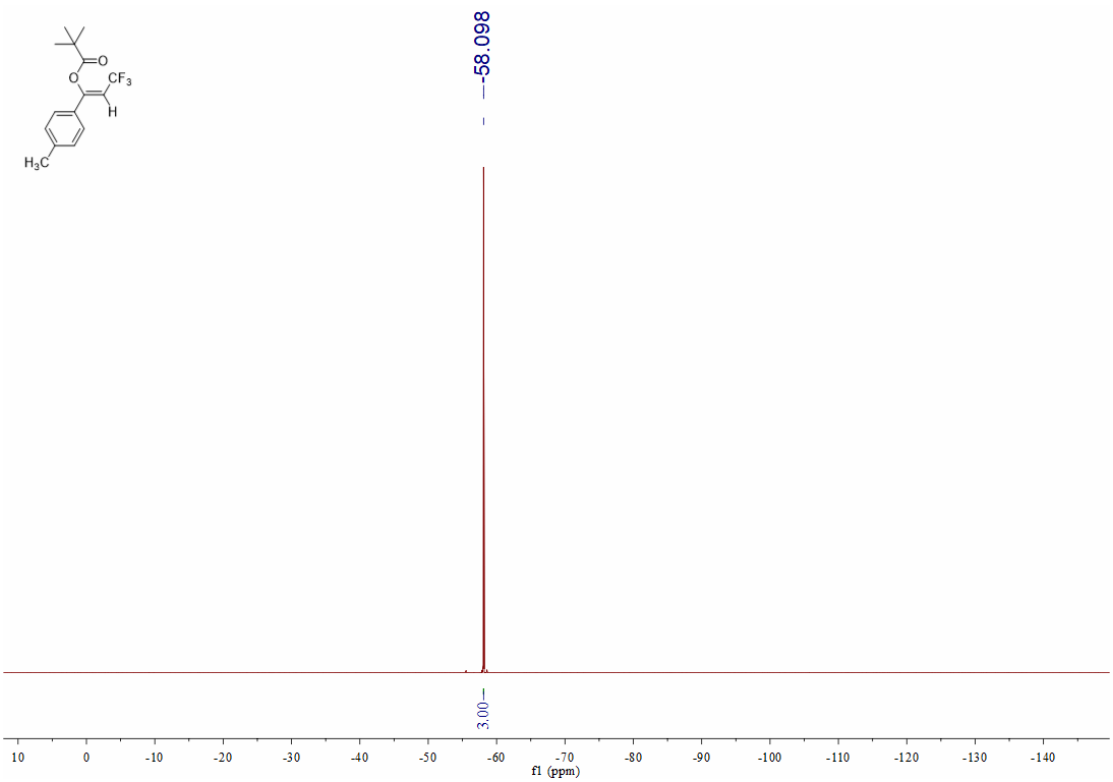


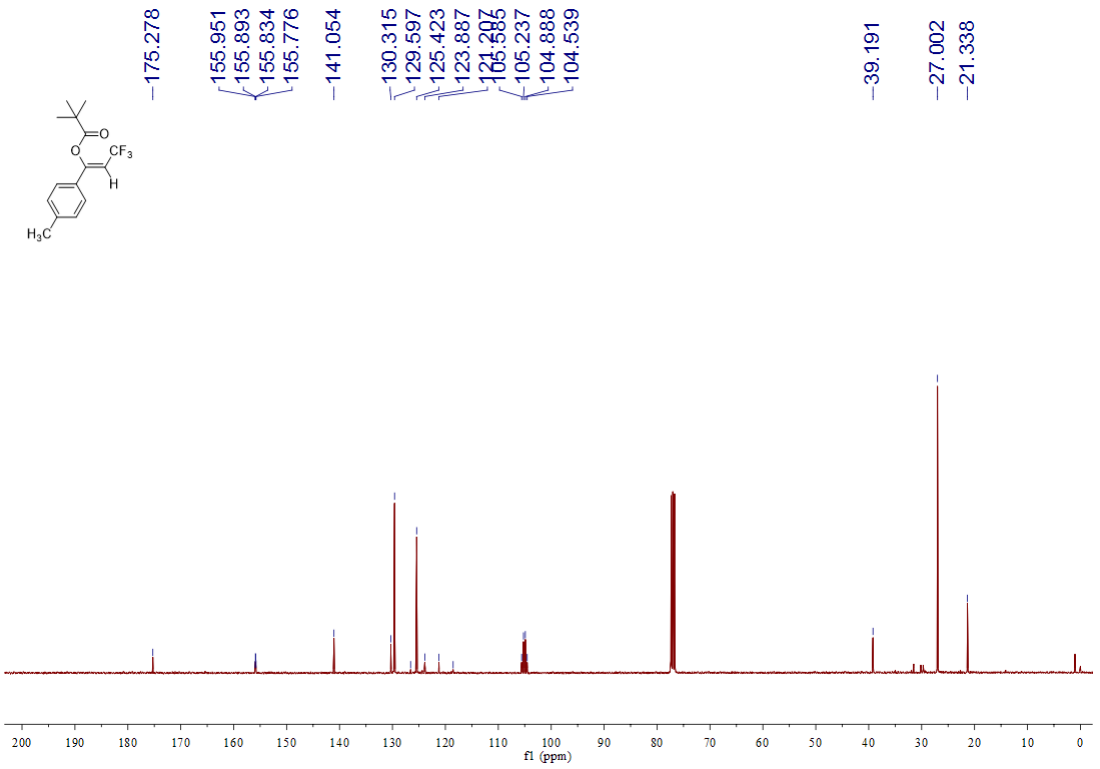

-58.545
3.00
f1 (ppm)


175.210
153.470
151.169
151.132
151.090
151.062
146.567
133.007
130.579
128.885
125.993
123.308
120.624
117.939
108.410
108.057
107.704
107.351
39.250
26.920
151.169
151.132
151.090
151.062
108.410
108.057
107.704
107.351
f1 (ppm)
f1 (ppm)
f1 (ppm)

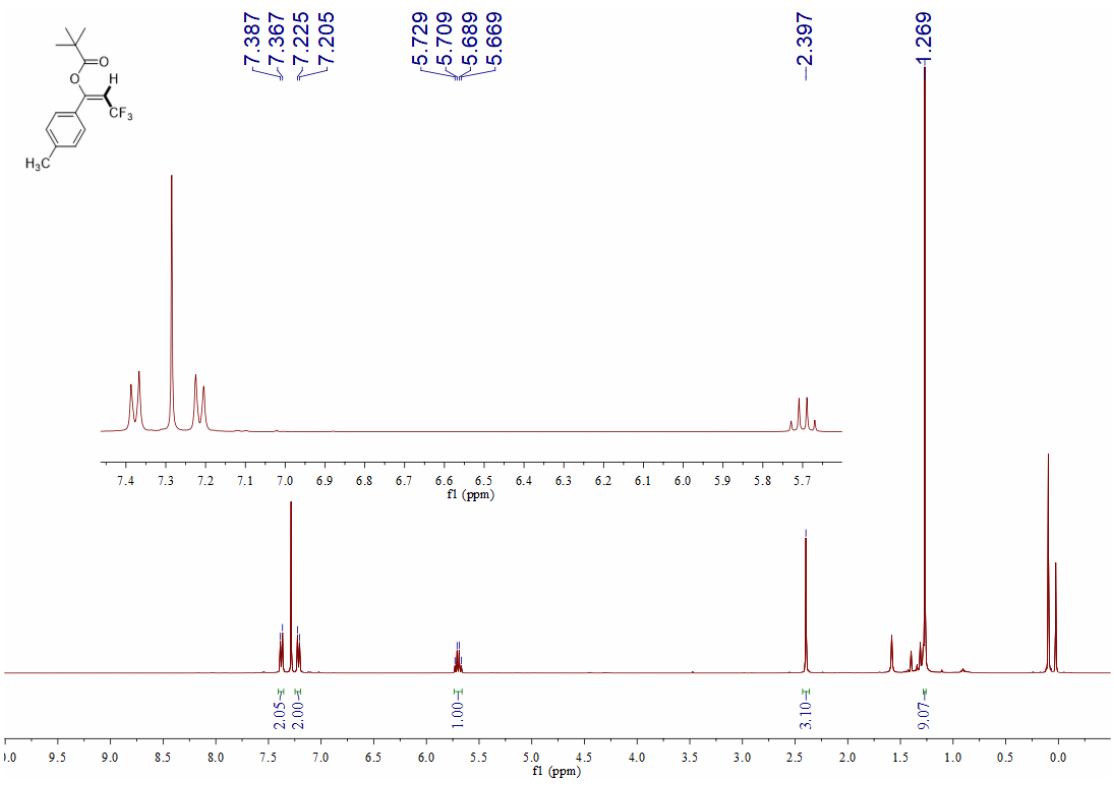
(Z)-3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl pivalate (4m) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

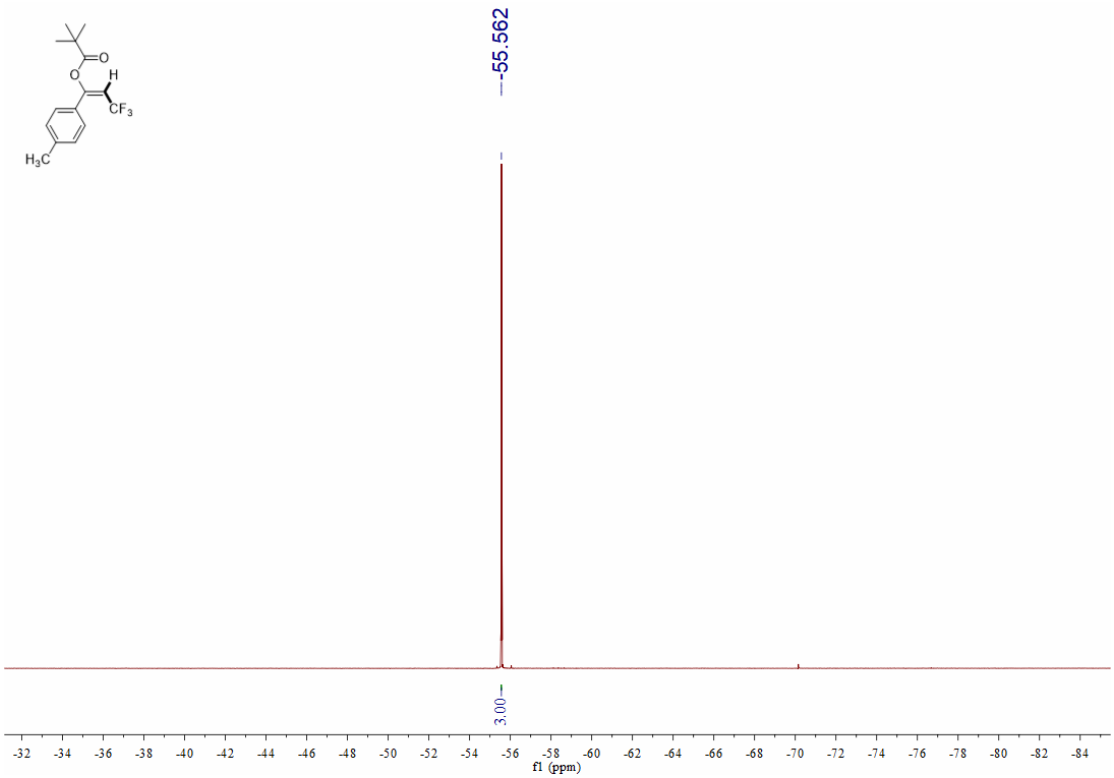


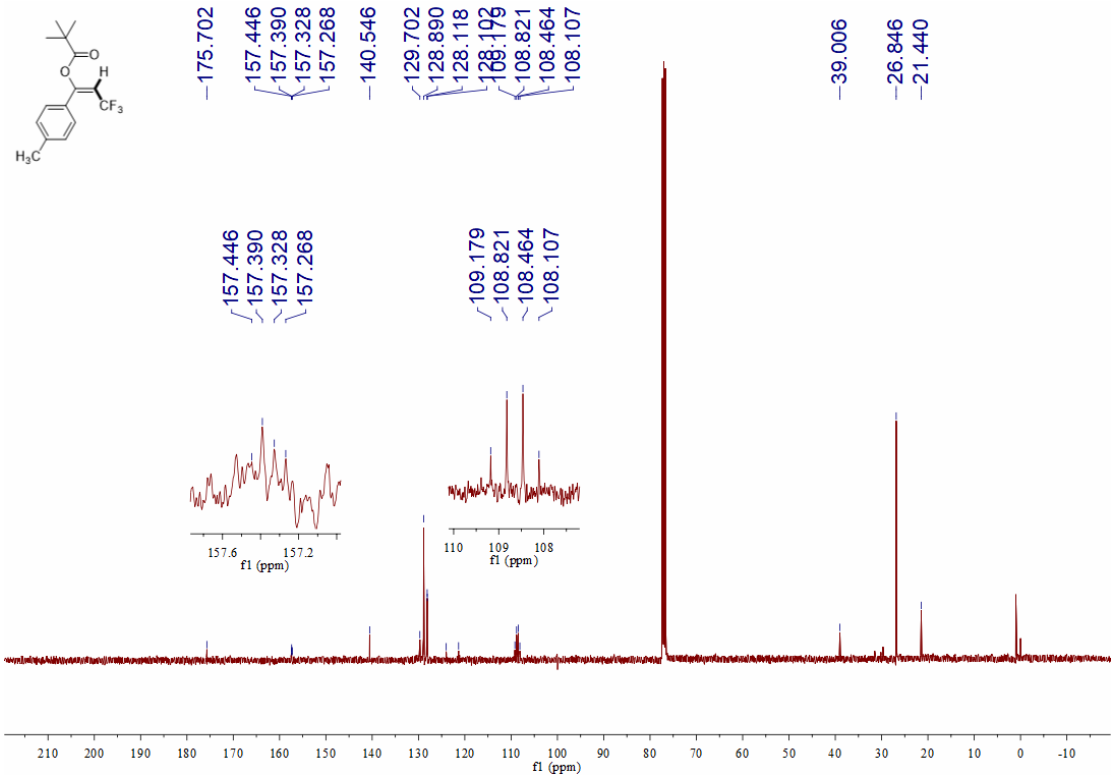




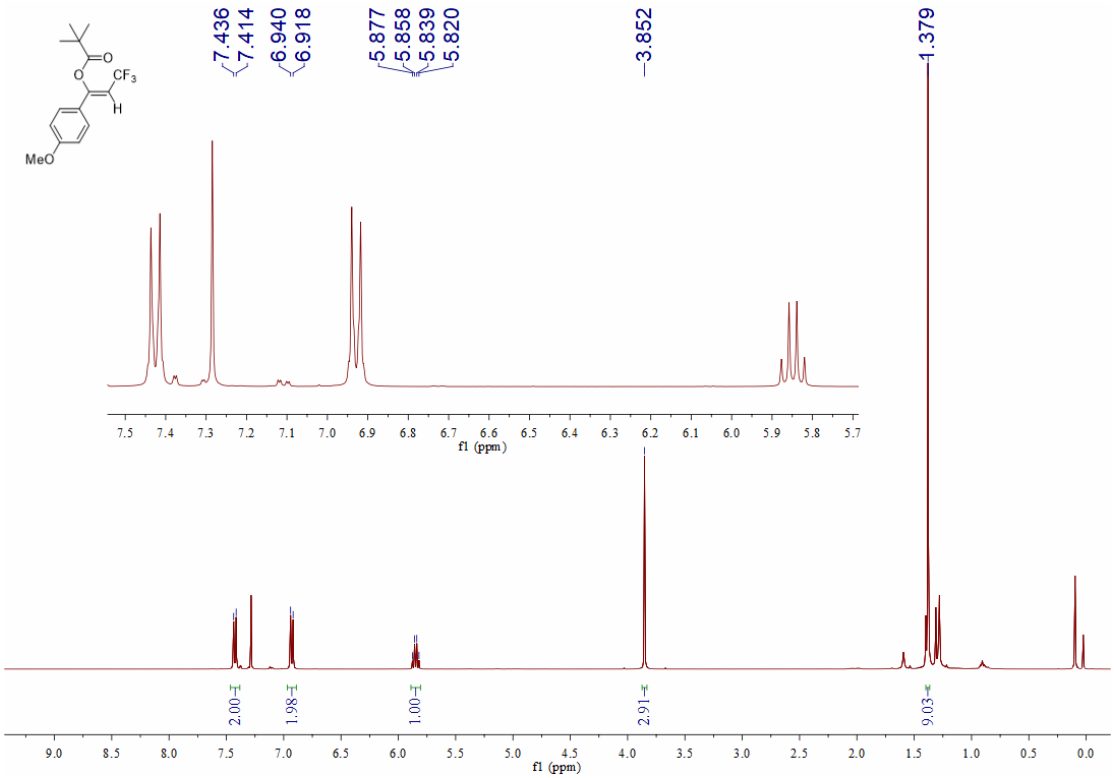
(E)-3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl pivalate (4m') (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

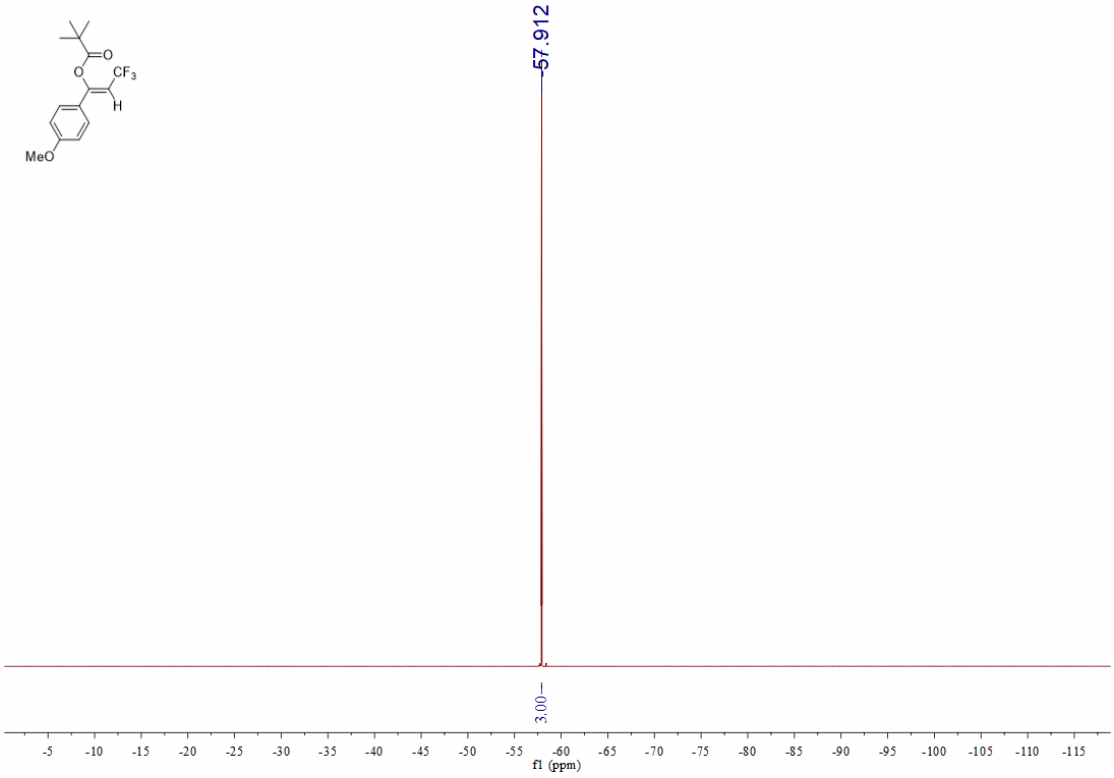


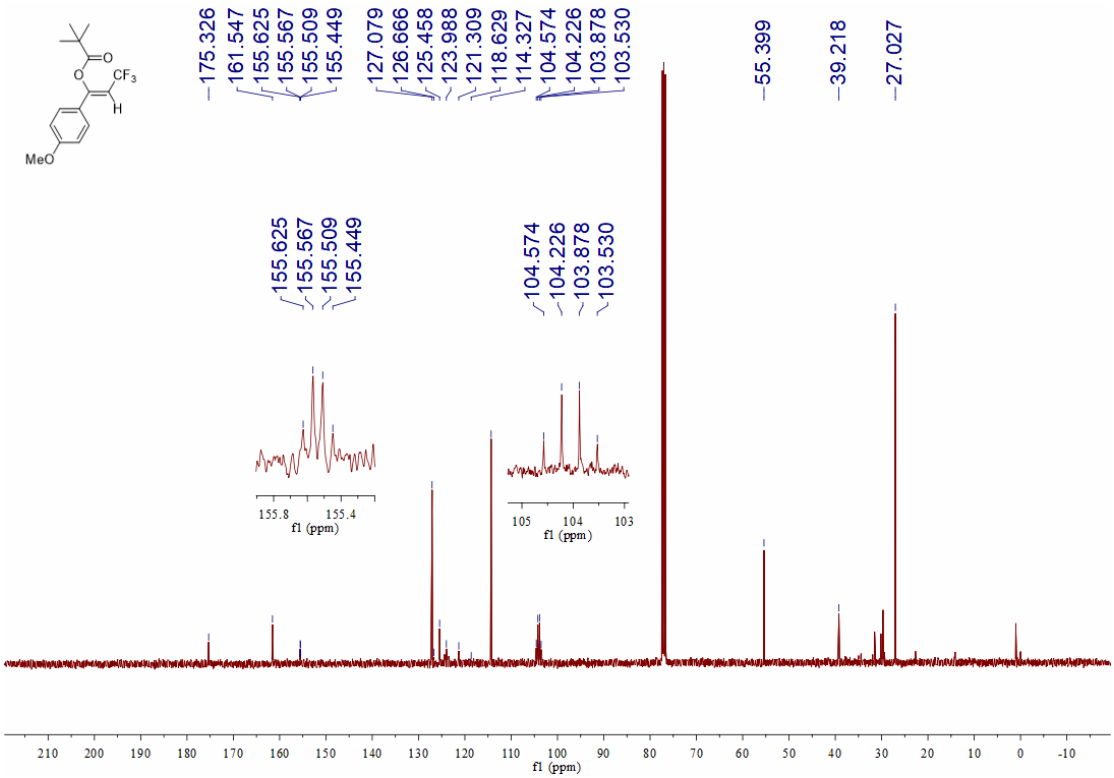

-55.562
3.00
f1 (ppm)


175.702
157.446
157.390
157.328
157.268
140.546
129.702
128.890
128.118
108.821
108.464
108.107
39.006
26.846
21.440
109.179
f1 (ppm)

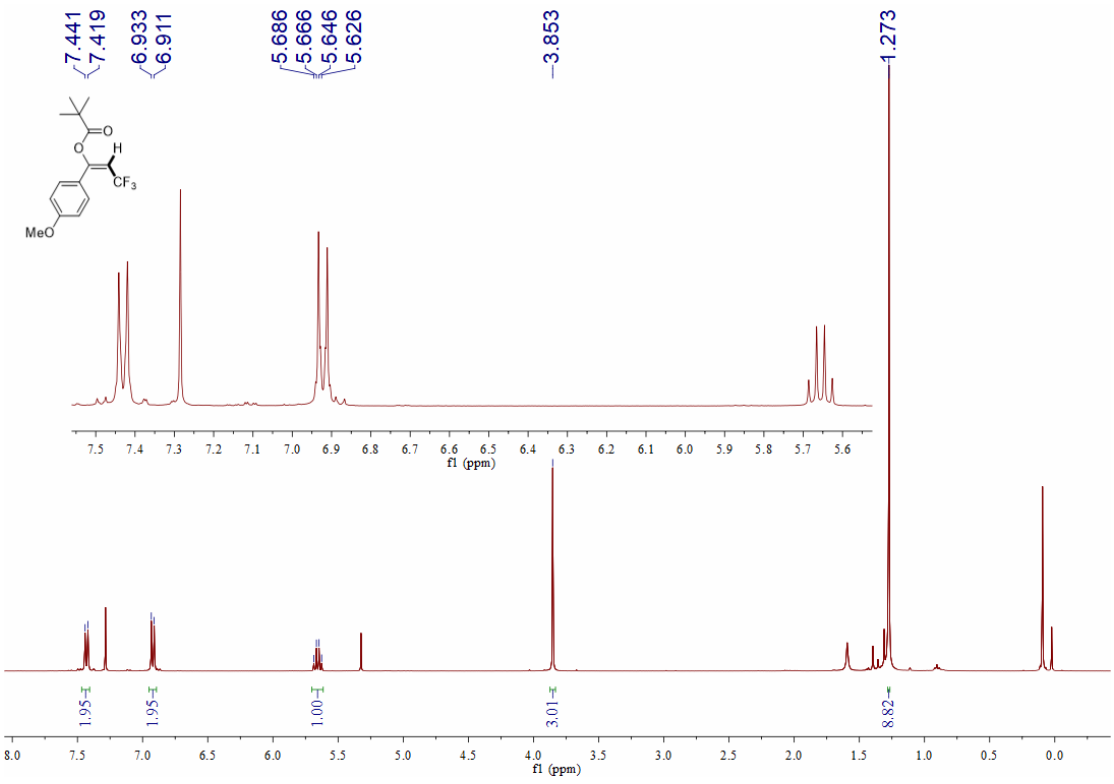
(Z)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl pivalate (4n) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

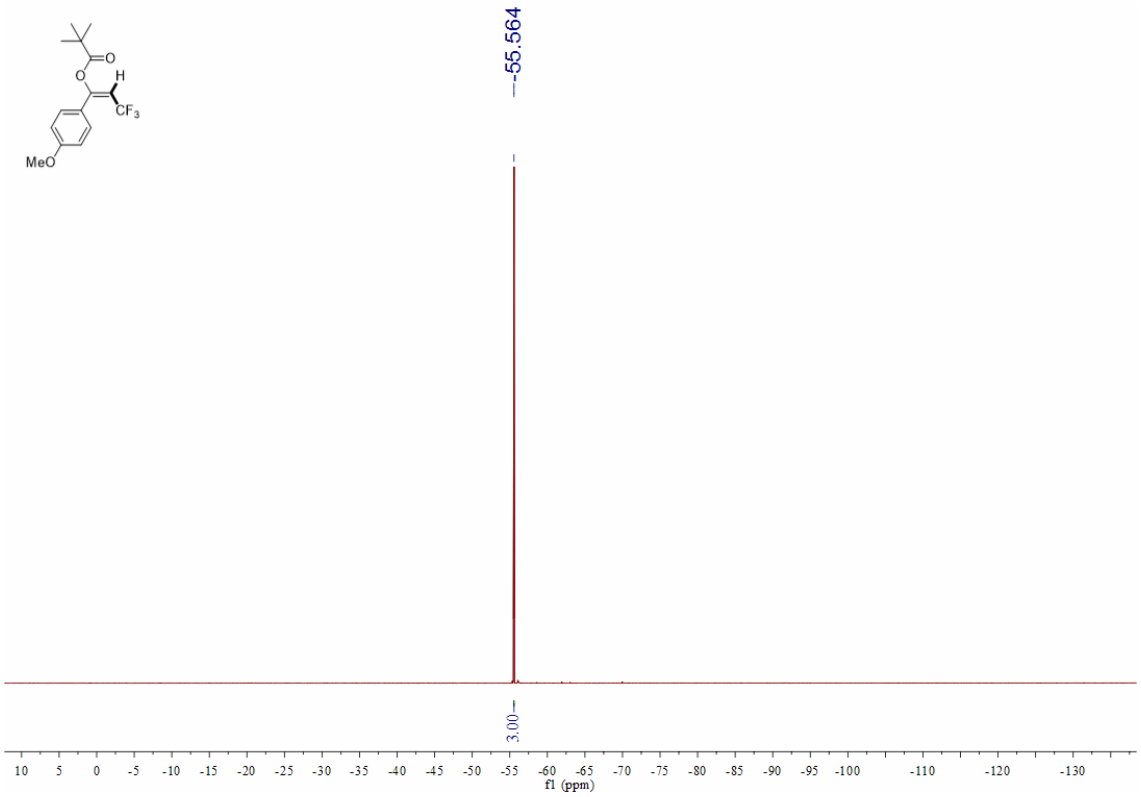


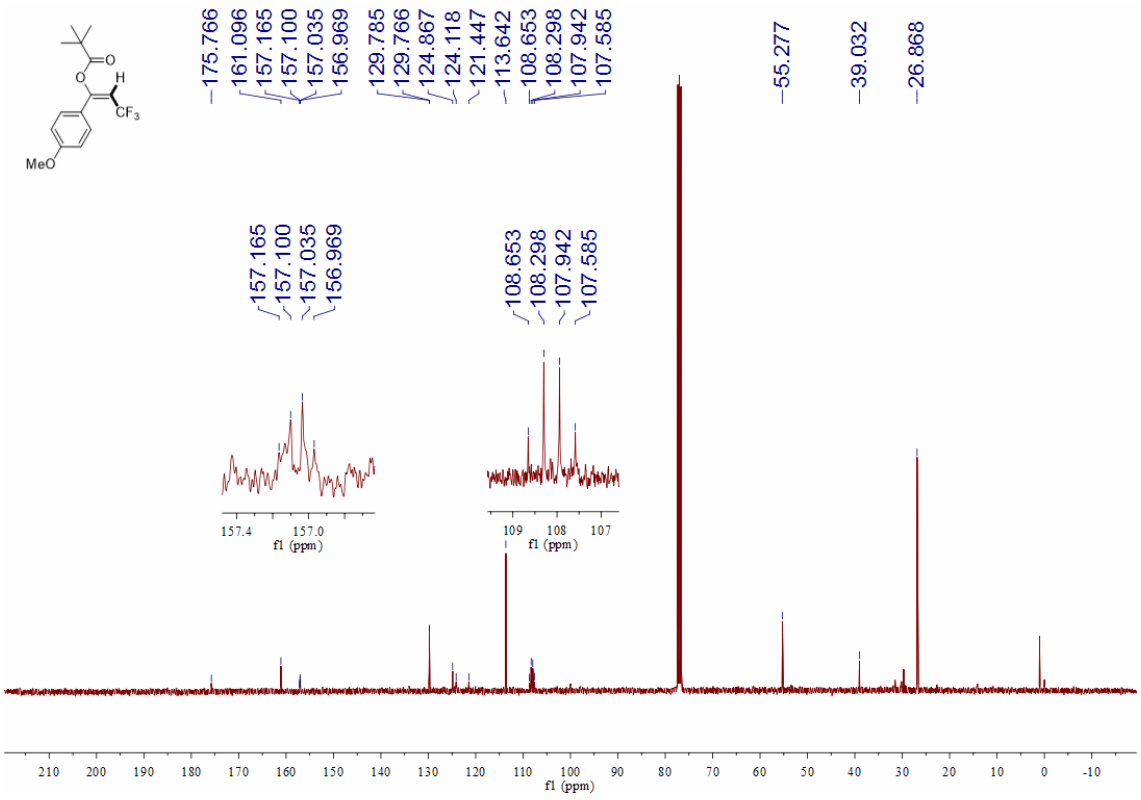




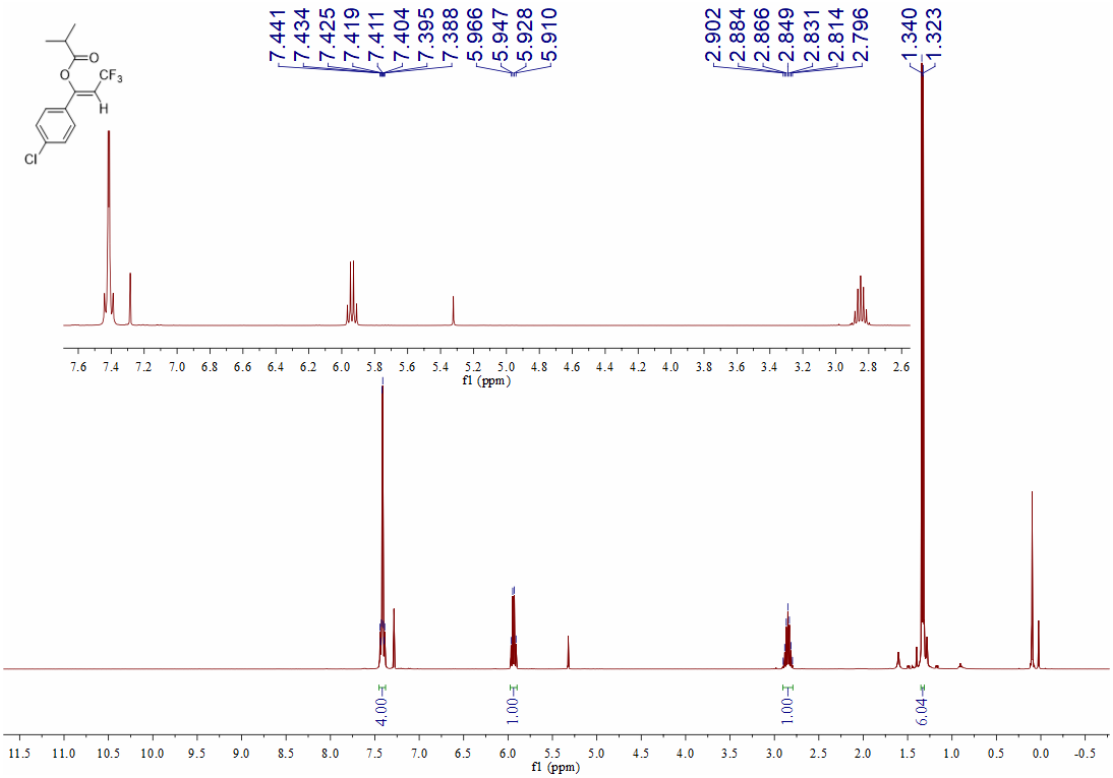
(E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl pivalate (4n') (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

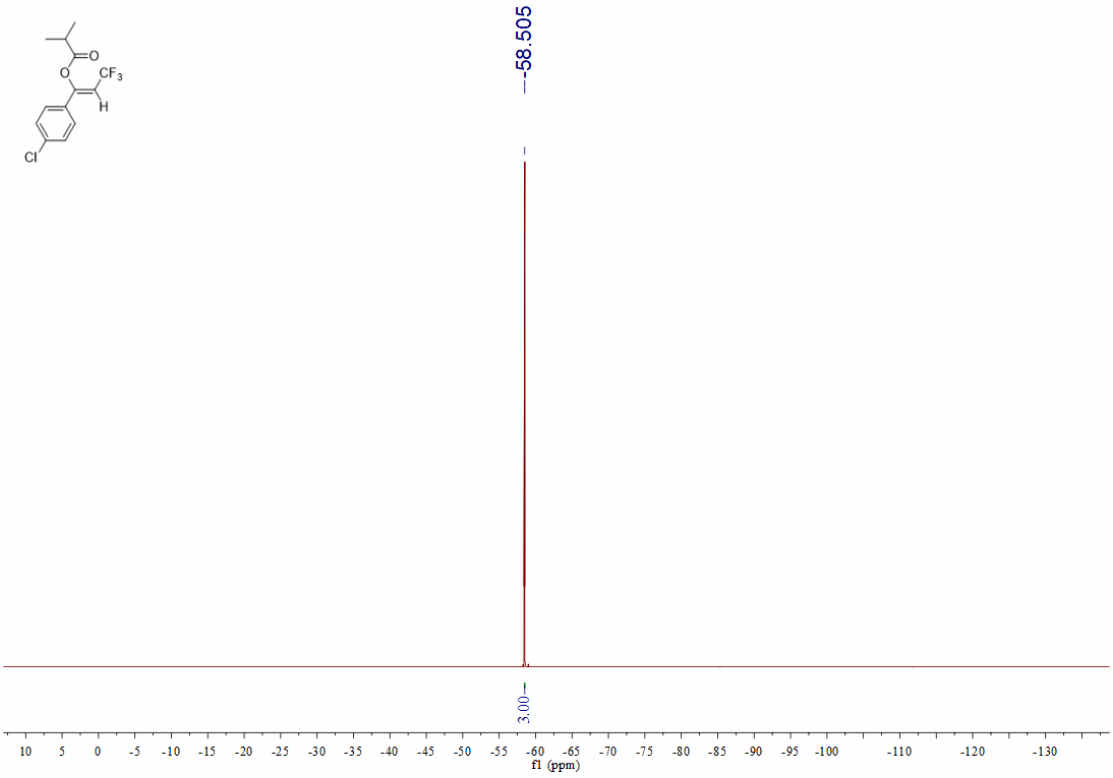


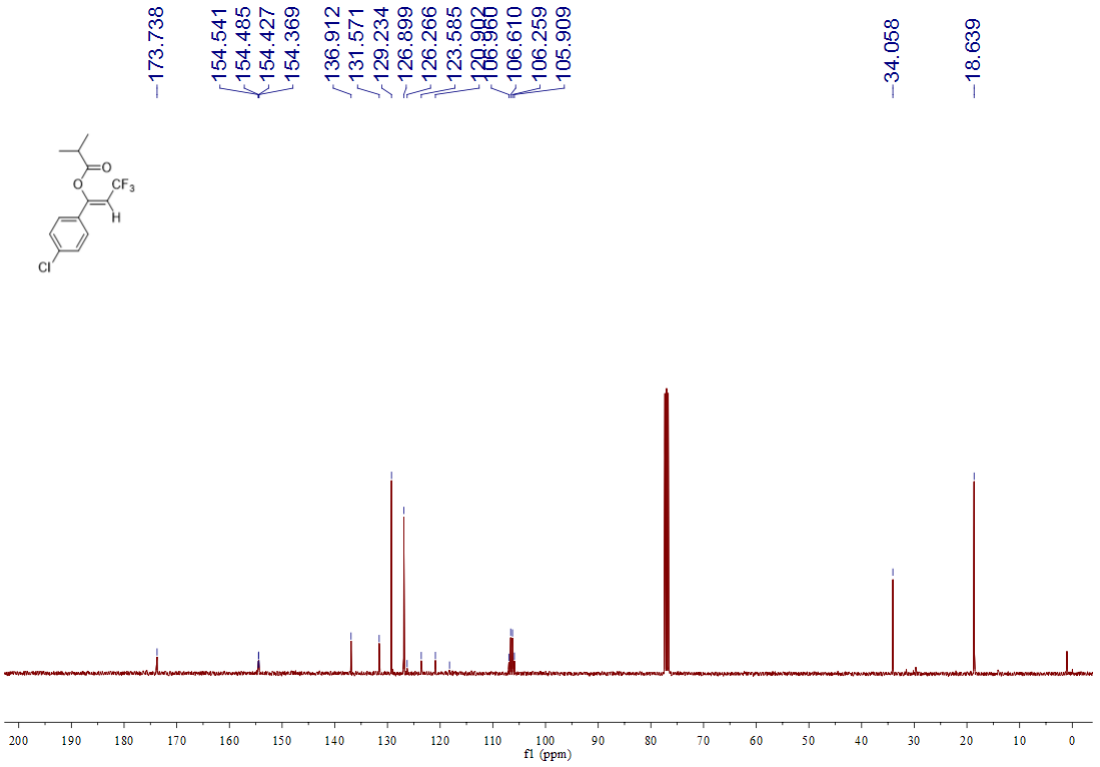

55.564
3.00
f1 (ppm)


175.766
161.096
157.165
157.100
157.035
156.969
129.785
129.766
124.867
124.118
121.447
113.642
108.653
108.298
107.942
107.585
55.277
39.032
26.868
f1 (ppm)

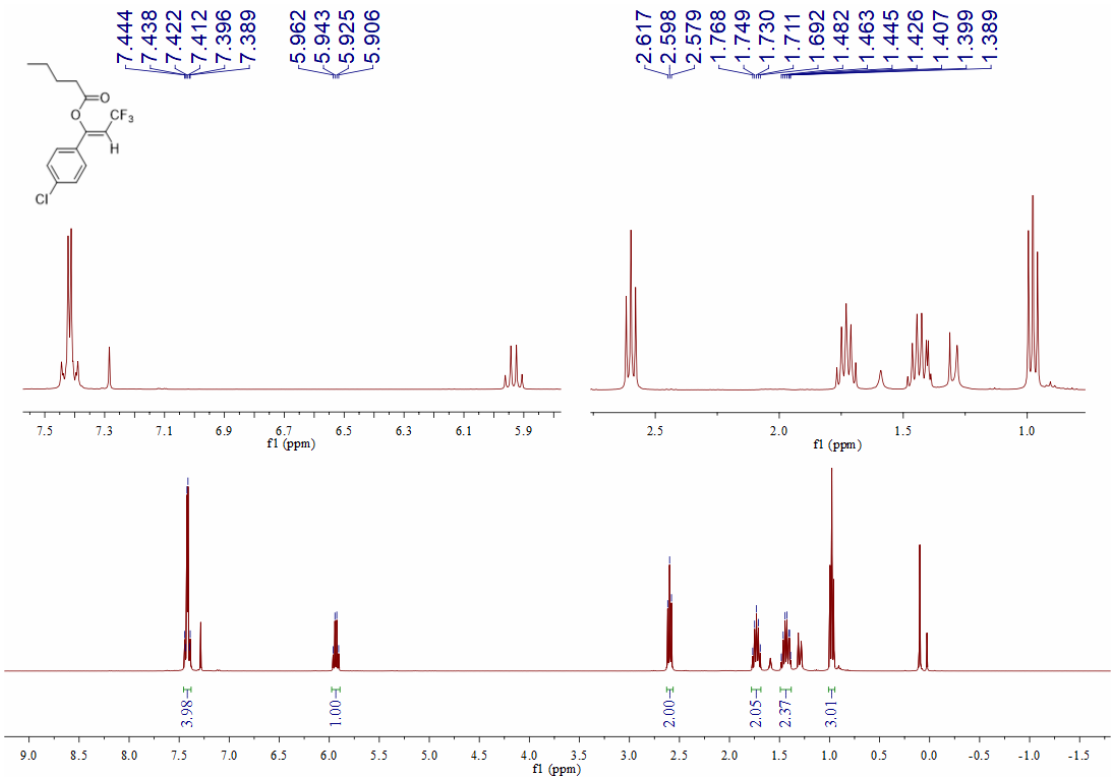
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl isobutyrate (4o) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

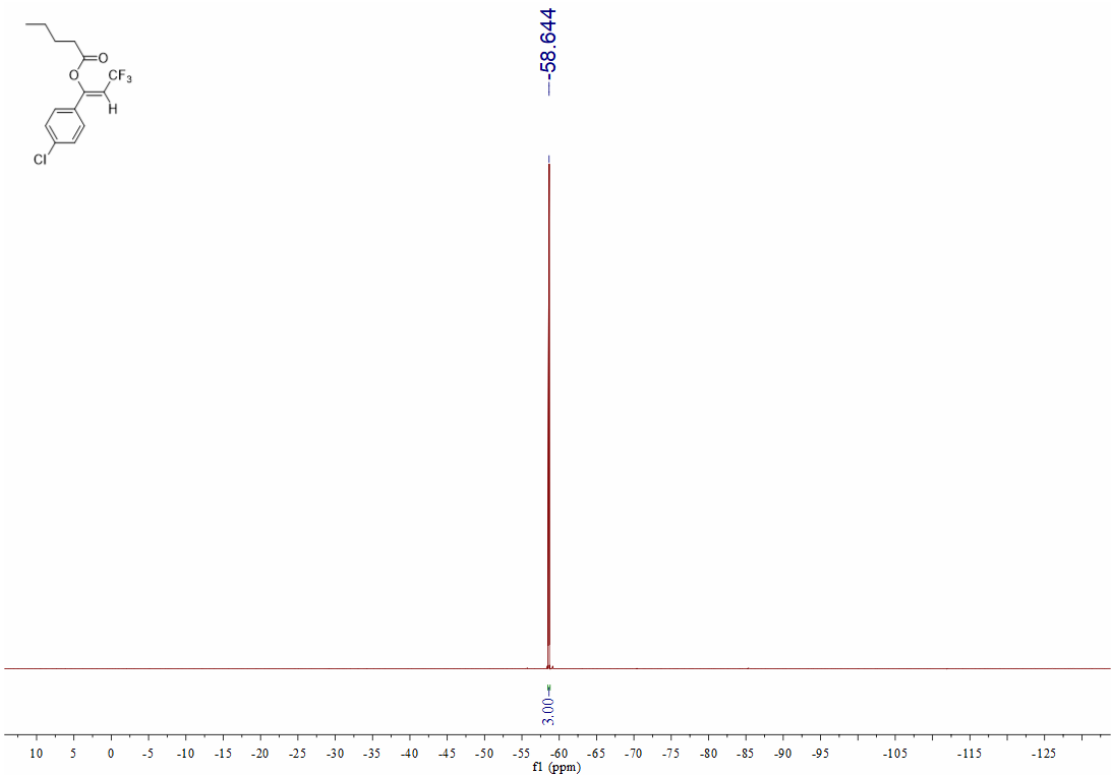


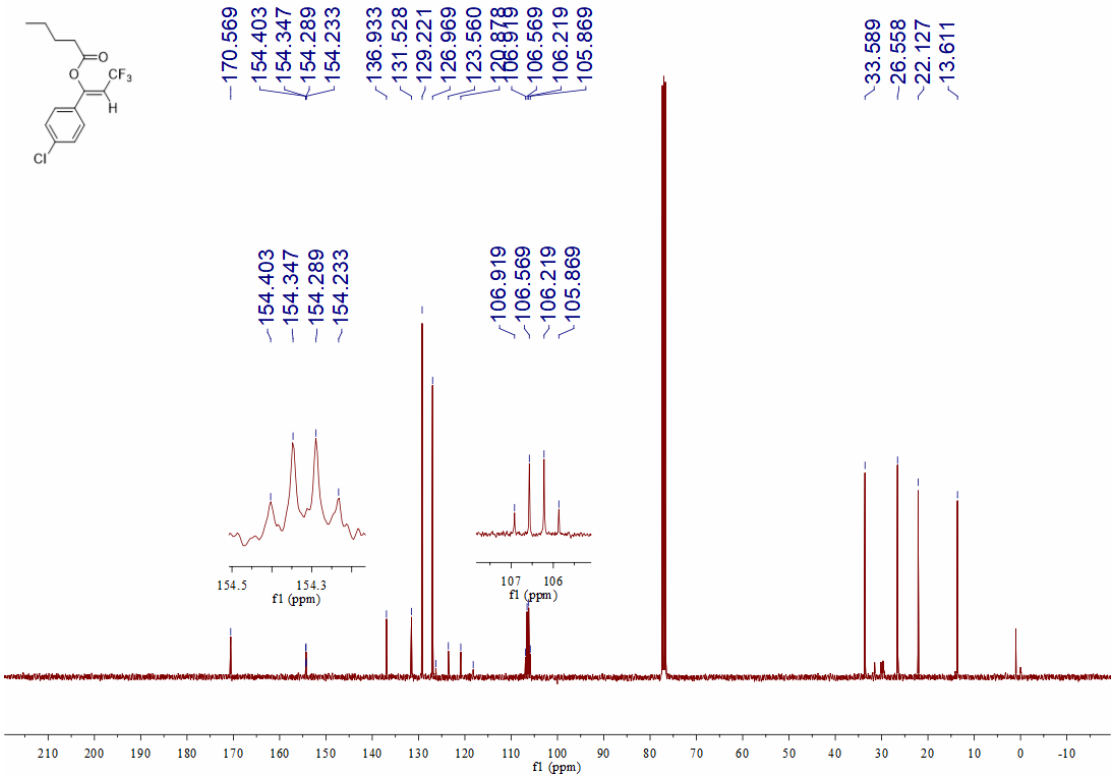




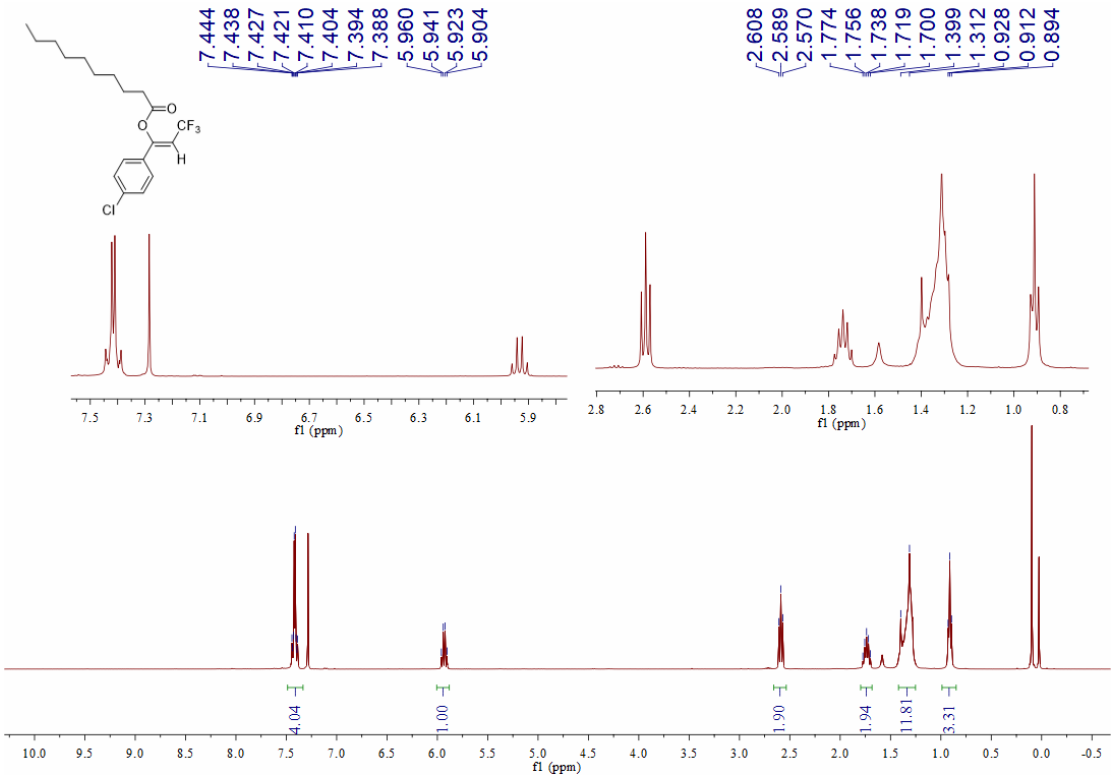
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl pentanoate (4p) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

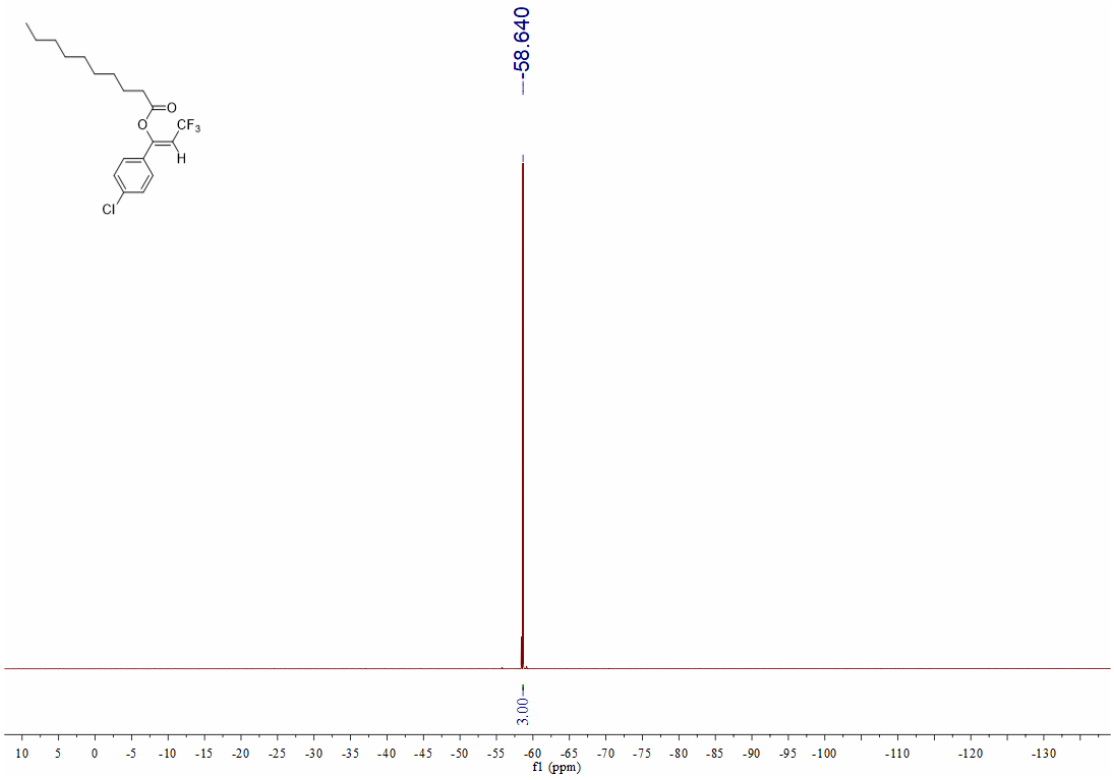


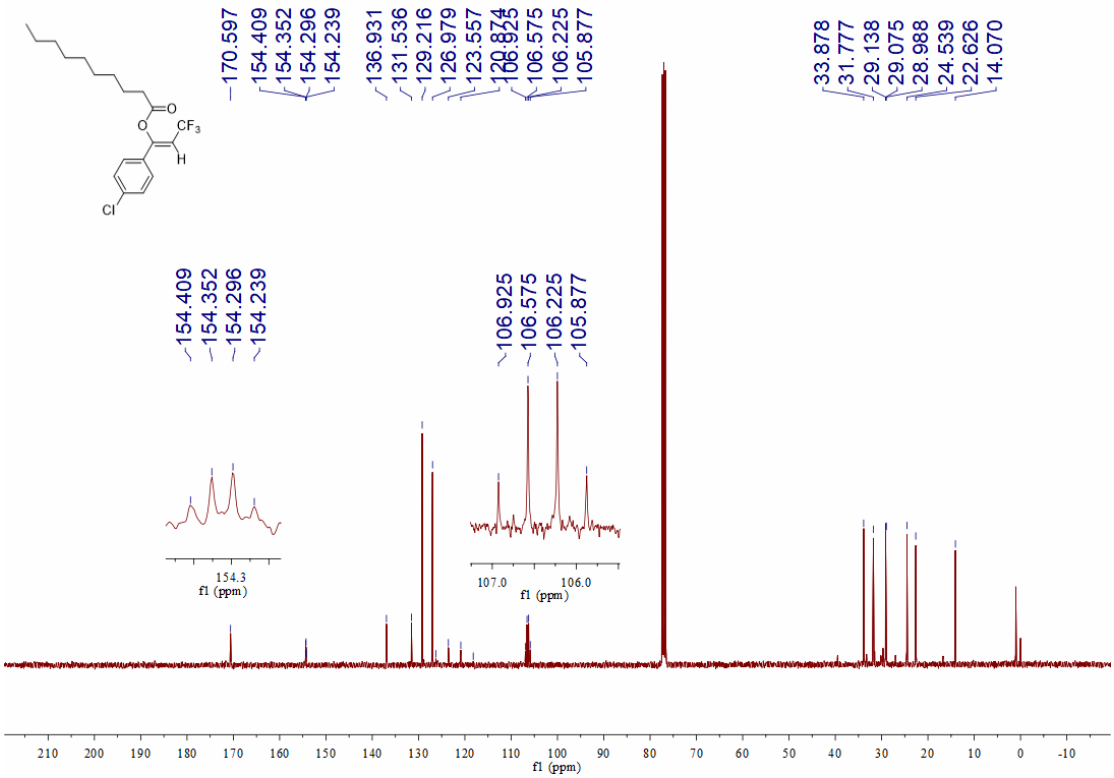

-58.644
3.00
f1 (ppm)


170.569
154.403
154.347
154.289
154.233
136.933
131.528
129.221
126.969
123.560
106.919
106.569
106.219
105.869
33.589
26.558
22.127
13.611
f1 (ppm)

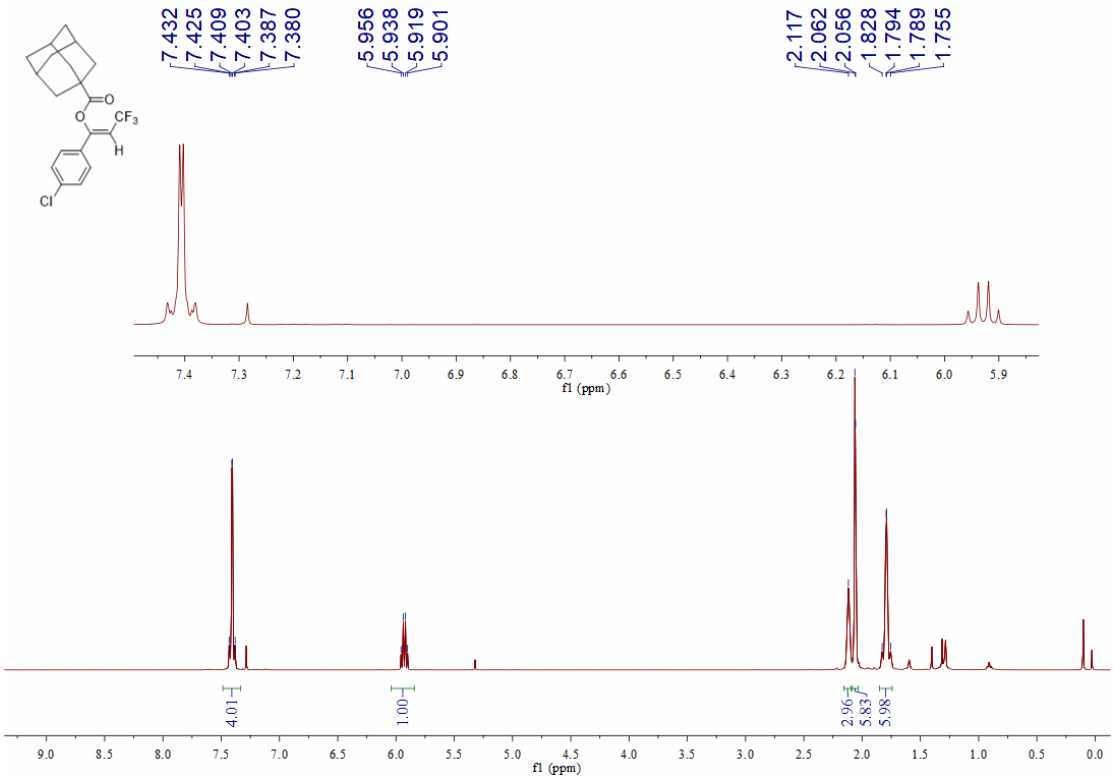
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl decanoate (4q) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

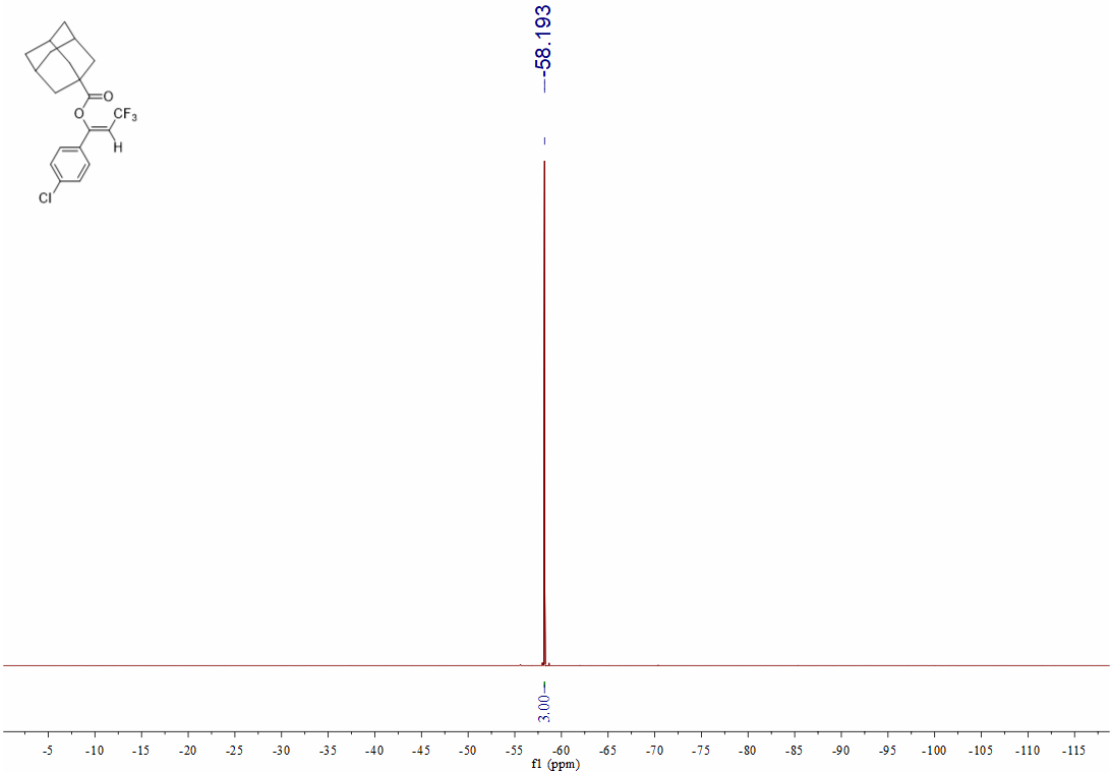


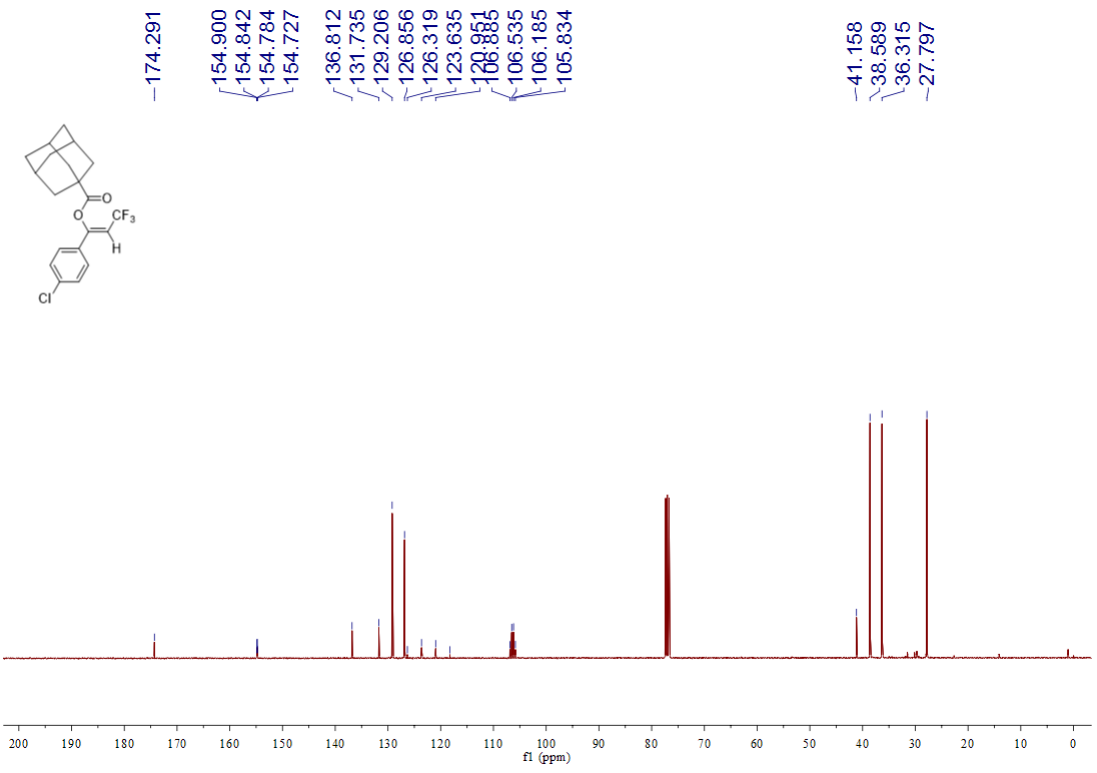




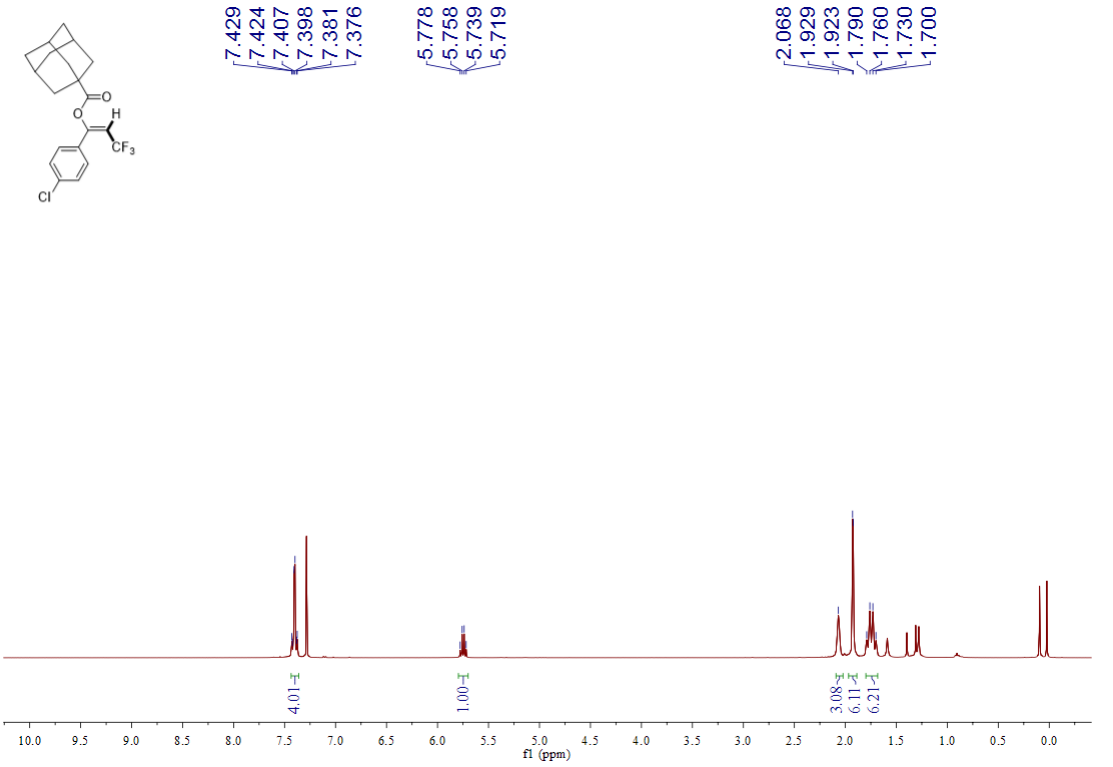
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl (1S,3s)-adamantane-1-carboxylate (4s) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

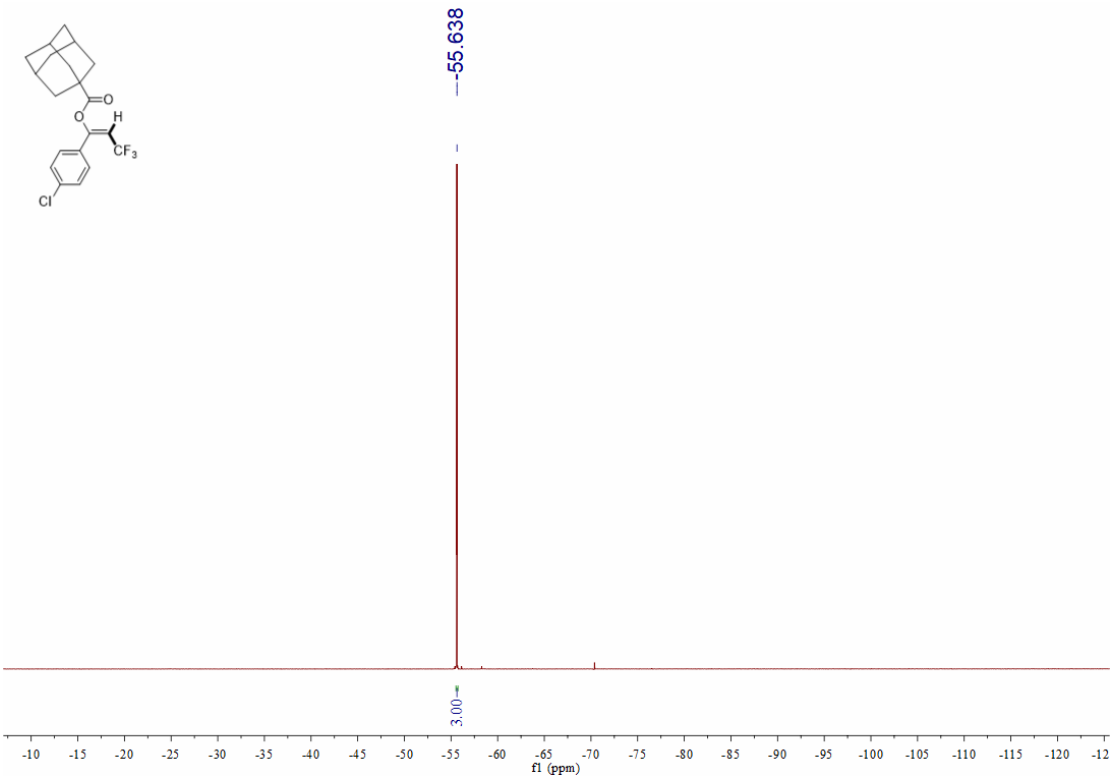


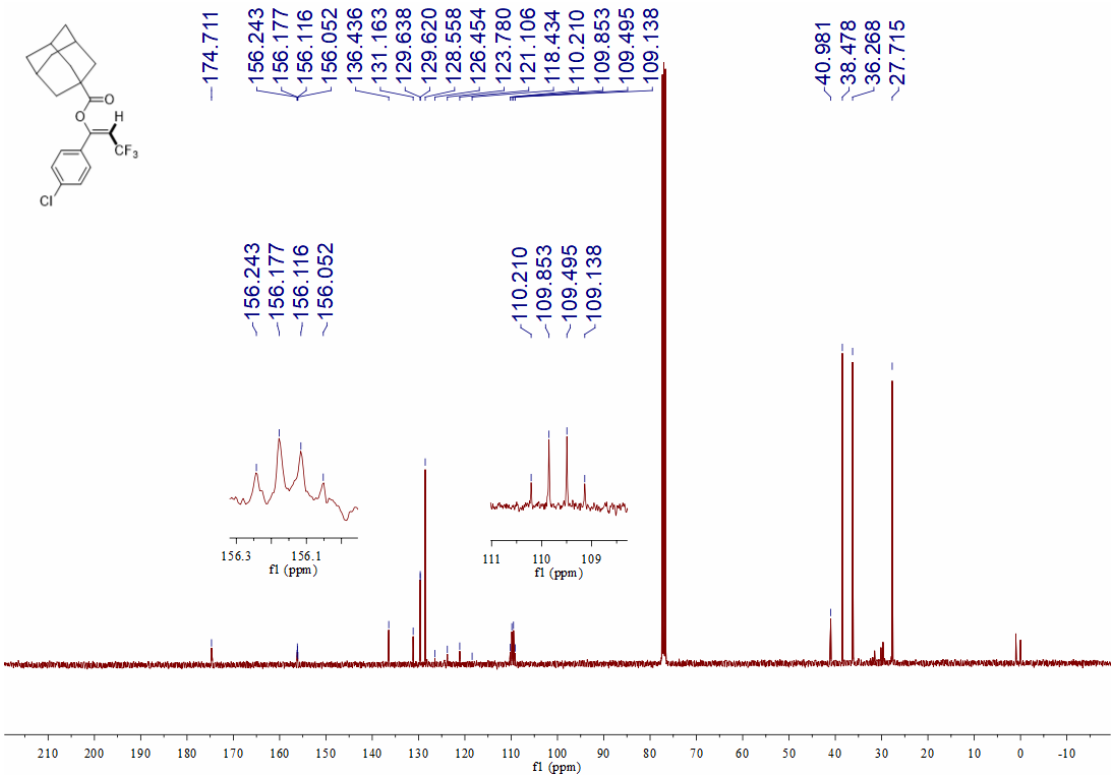

-58.193
3.00
f1 (ppm)


174.291
154.900
154.842
154.784
154.727
136.812
131.735
129.206
126.856
126.319
123.635
106.535
106.185
105.834
41.158
38.589
36.315
27.797
f1 (ppm)

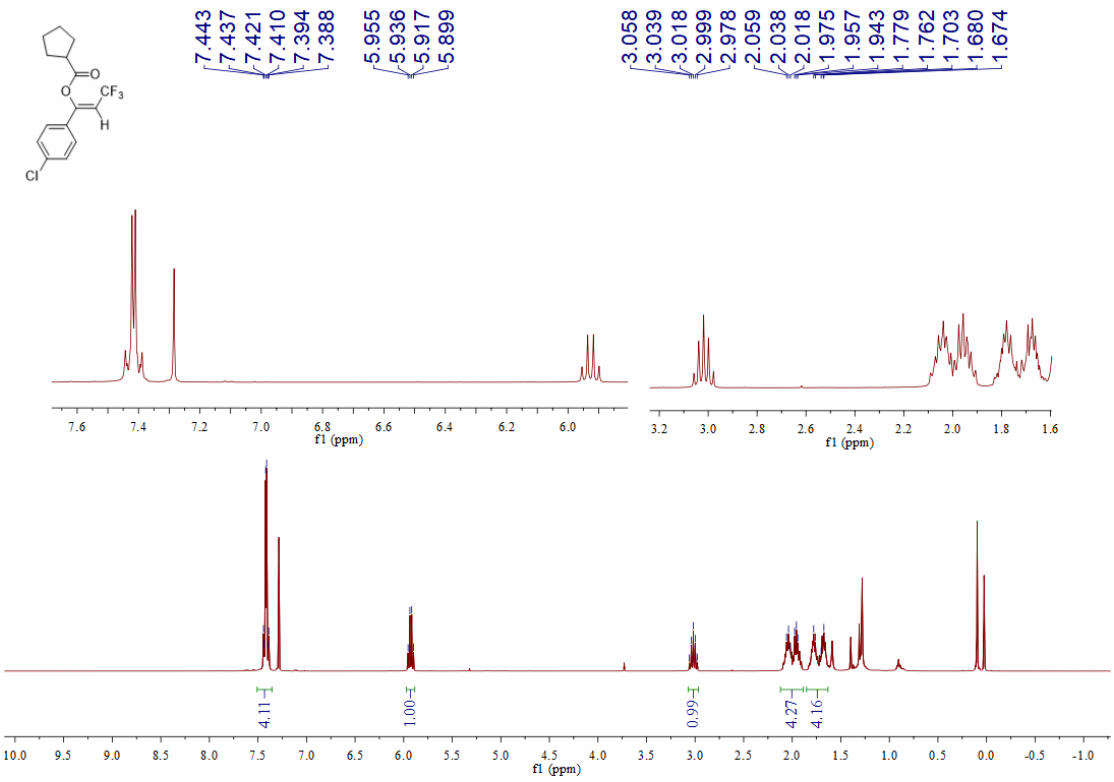
(E)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl adamantane-1-carboxylate (4s') (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

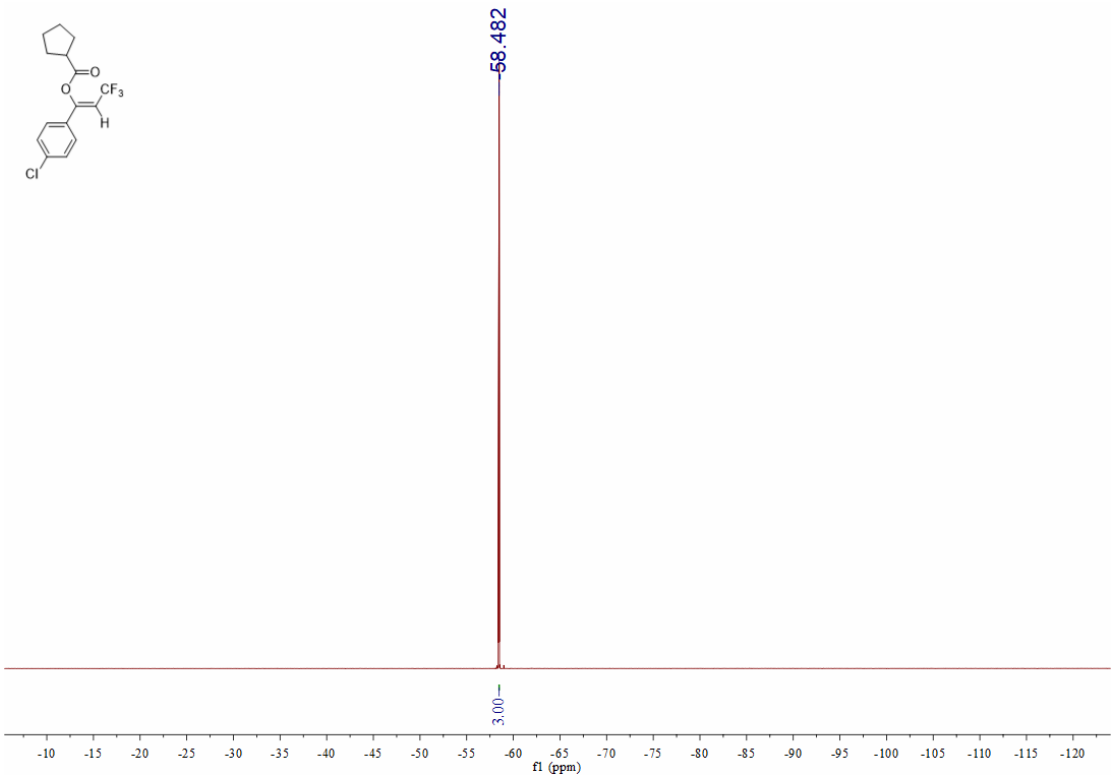


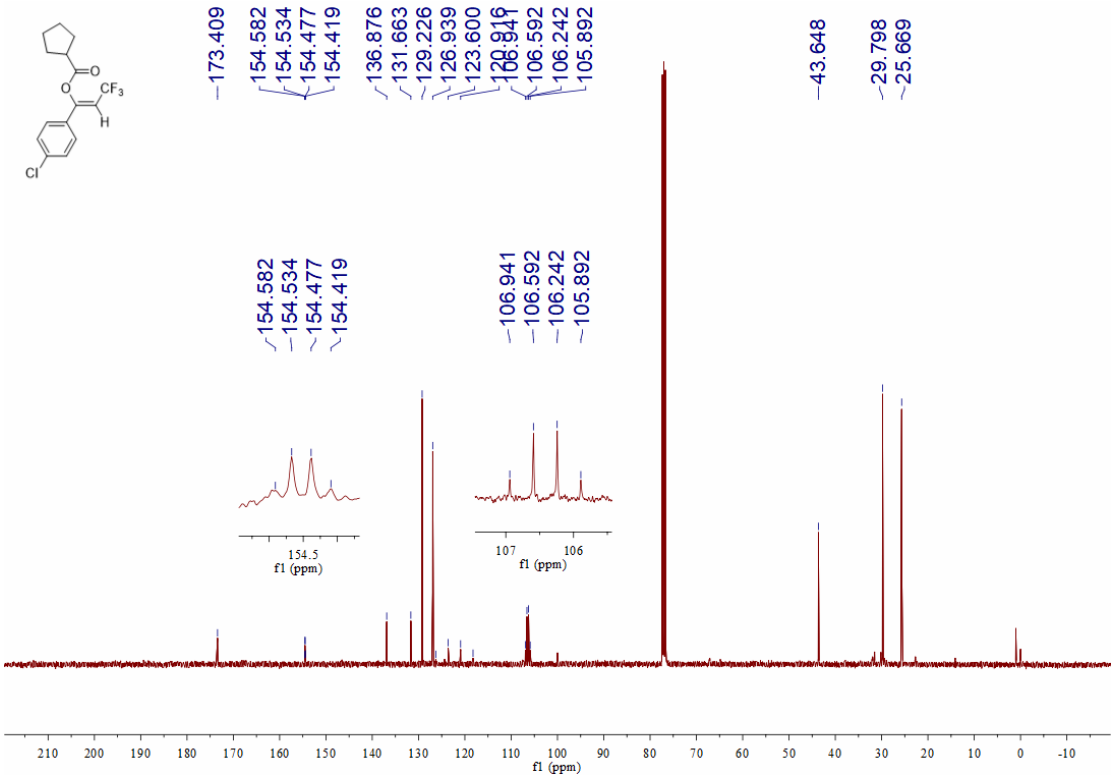




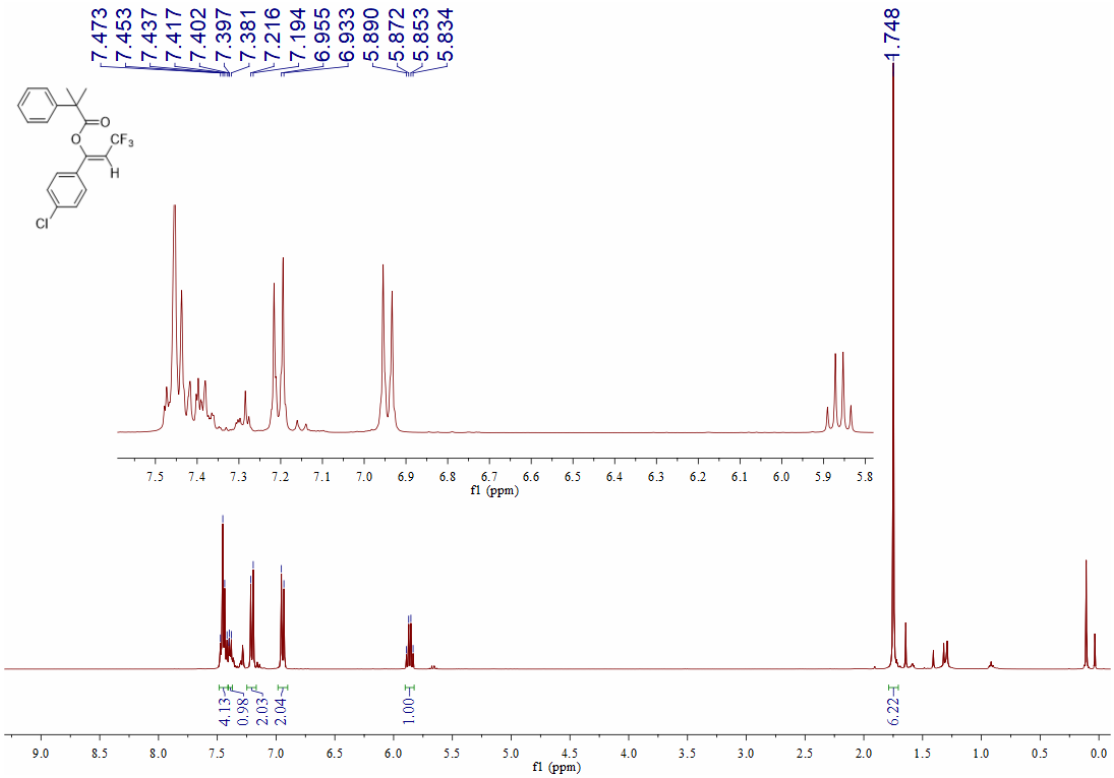
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl cyclopentanecarboxylate (4t) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

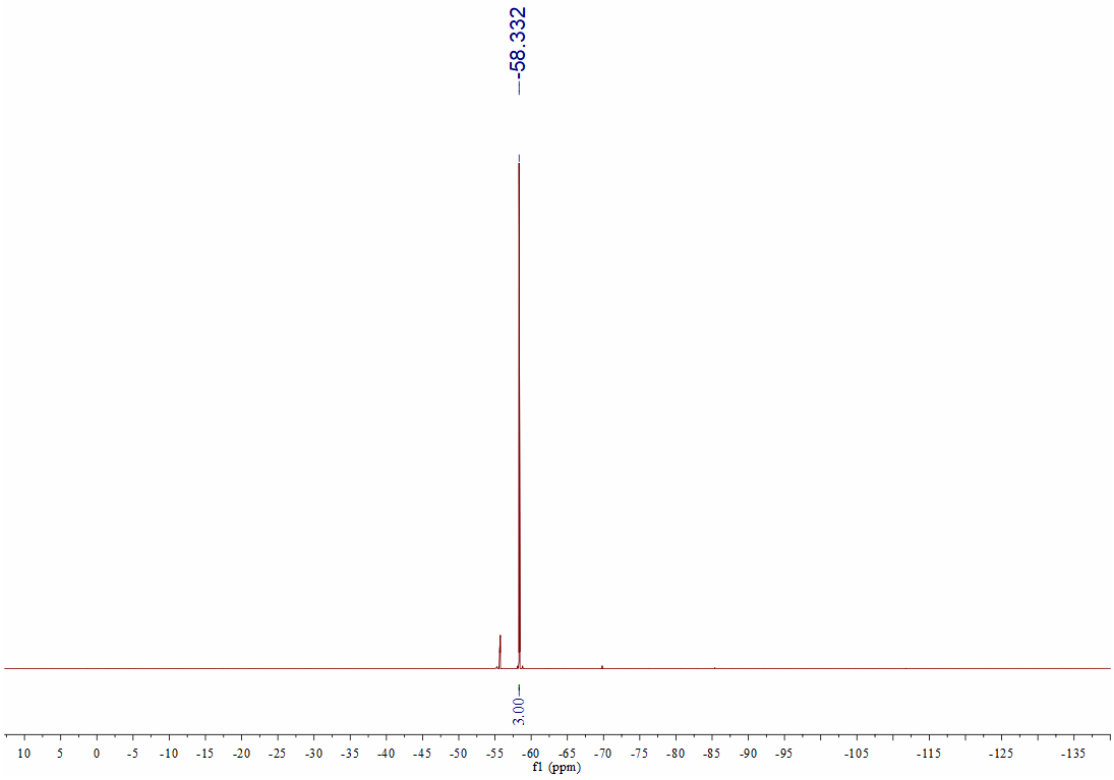


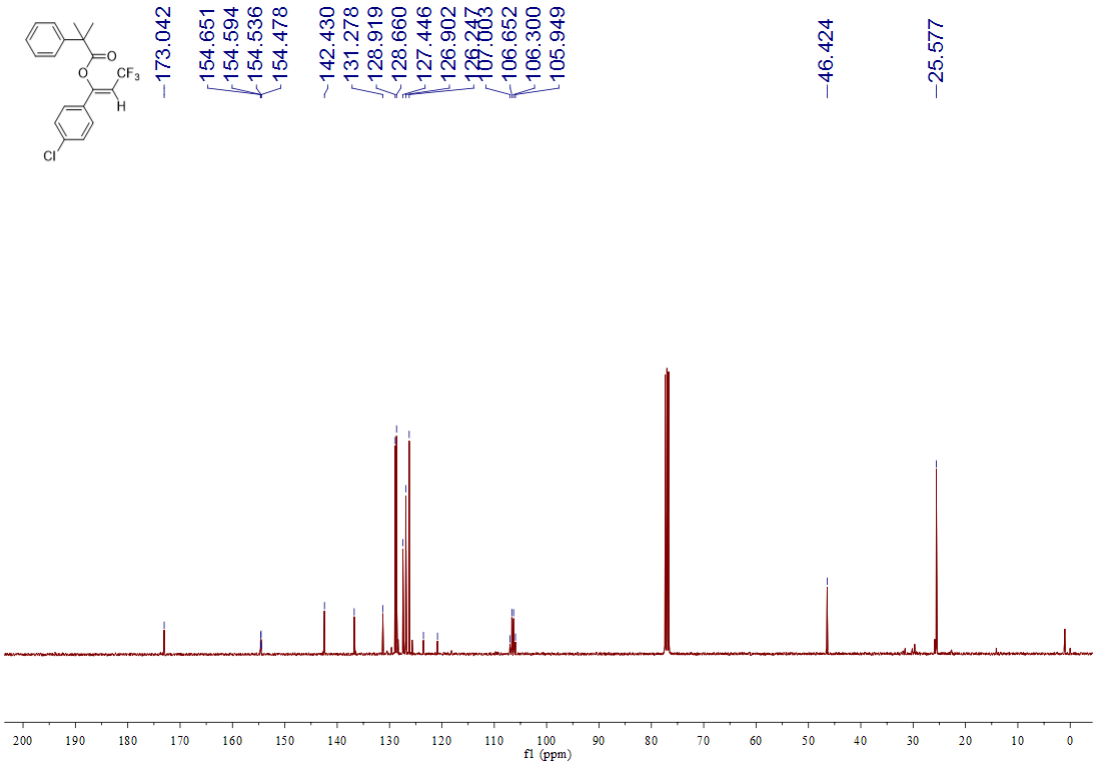

58.482
3.00
f1 (ppm)


173.409
154.582
154.534
154.477
154.419
136.876
131.663
129.226
126.939
123.600
106.941
106.592
106.242
105.892
43.648
29.798
25.669
154.5
f1 (ppm)
107
106
f1 (ppm)
f1 (ppm)

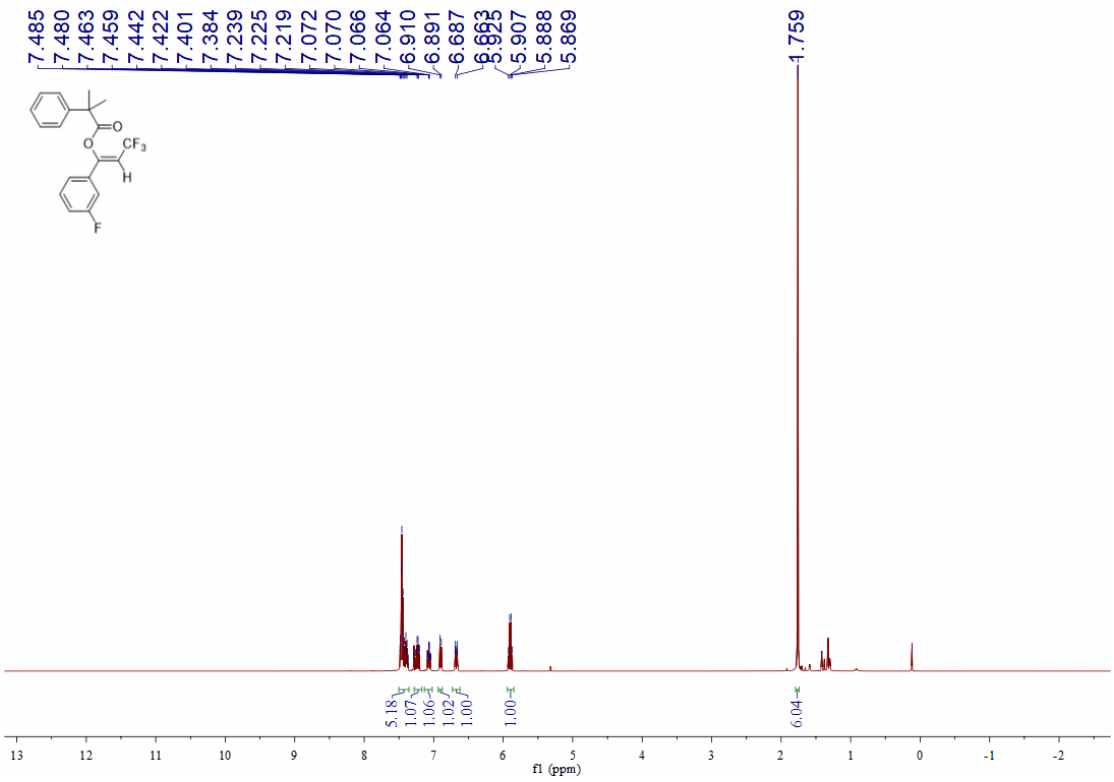
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 2-methyl-2-phenylpropanoate (4u)
(^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

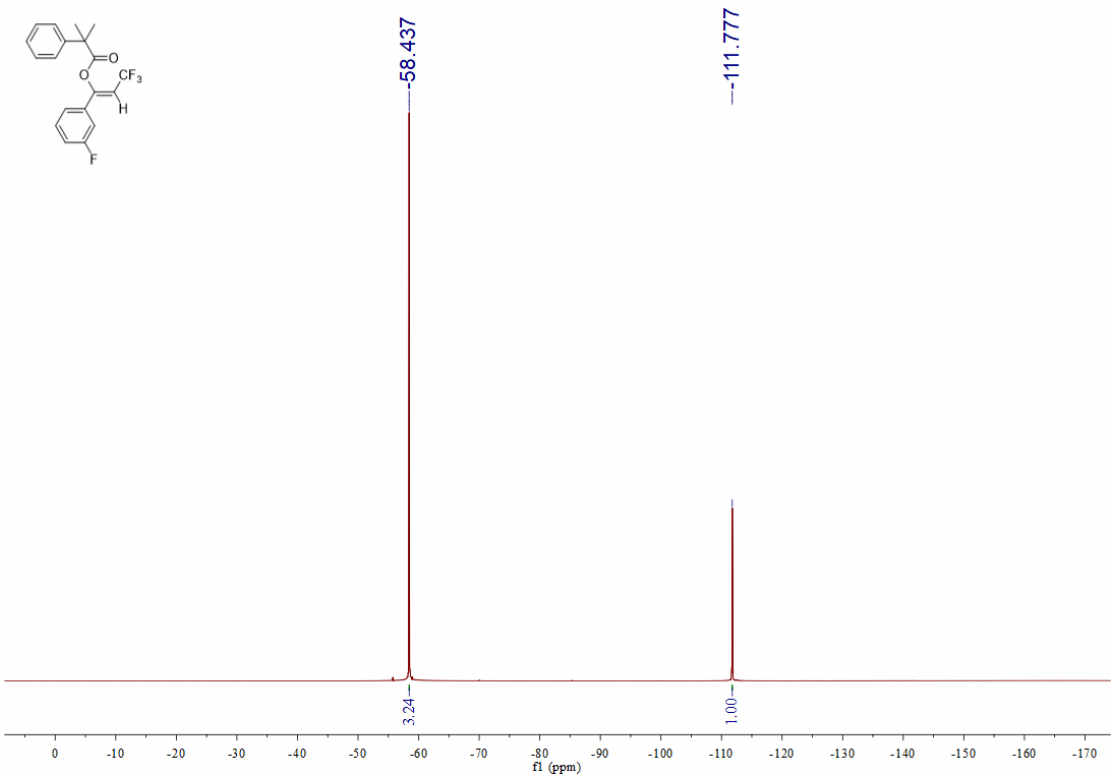


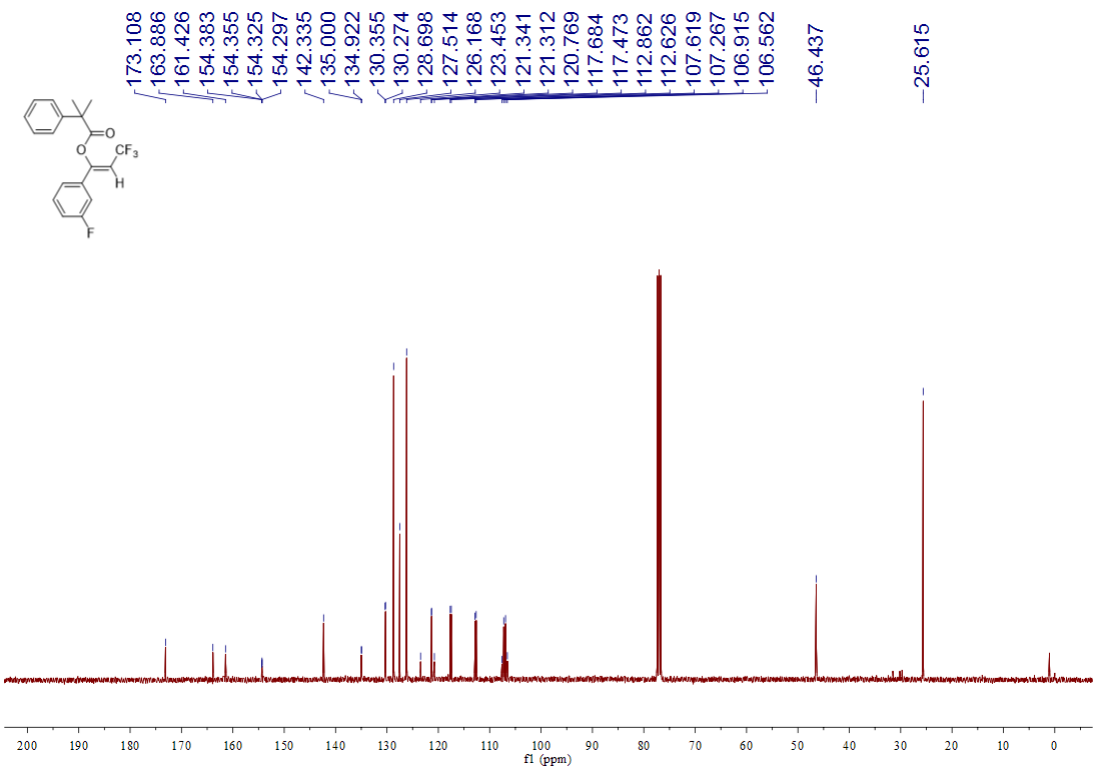




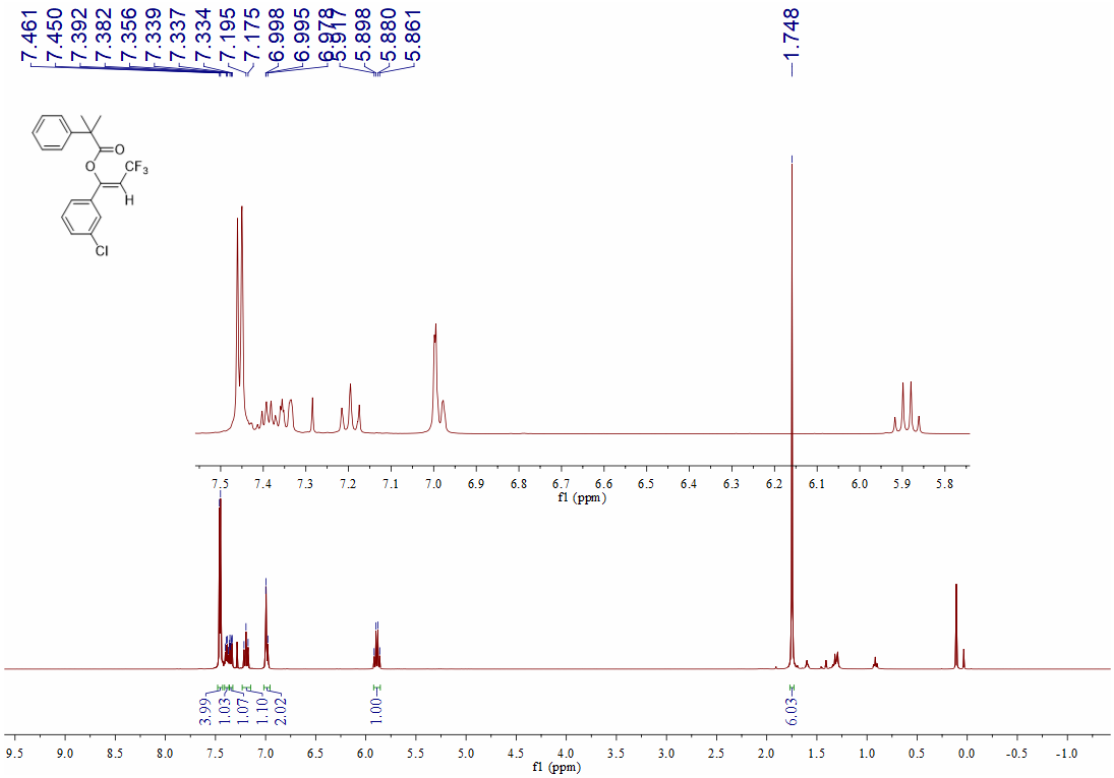
(Z)-3,3,3-trifluoro-1-(3-fluorophenyl)prop-1-en-1-yl 2-methyl-2-phenylpropanoate (4v, X = F) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

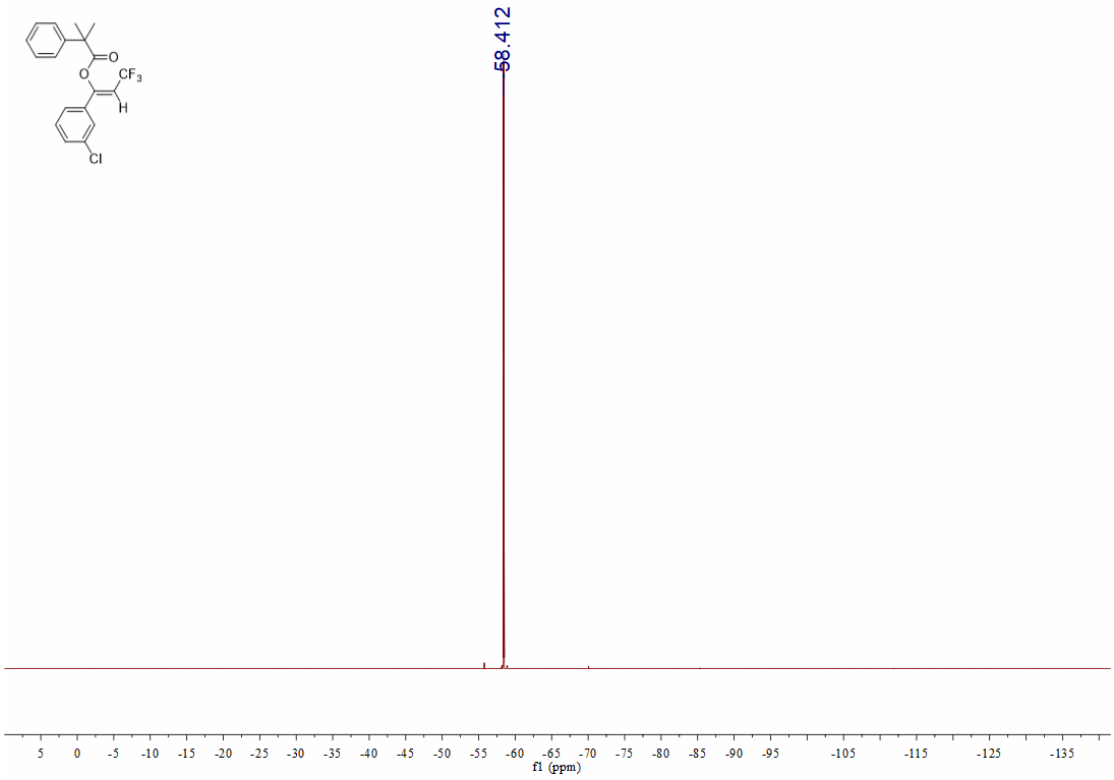


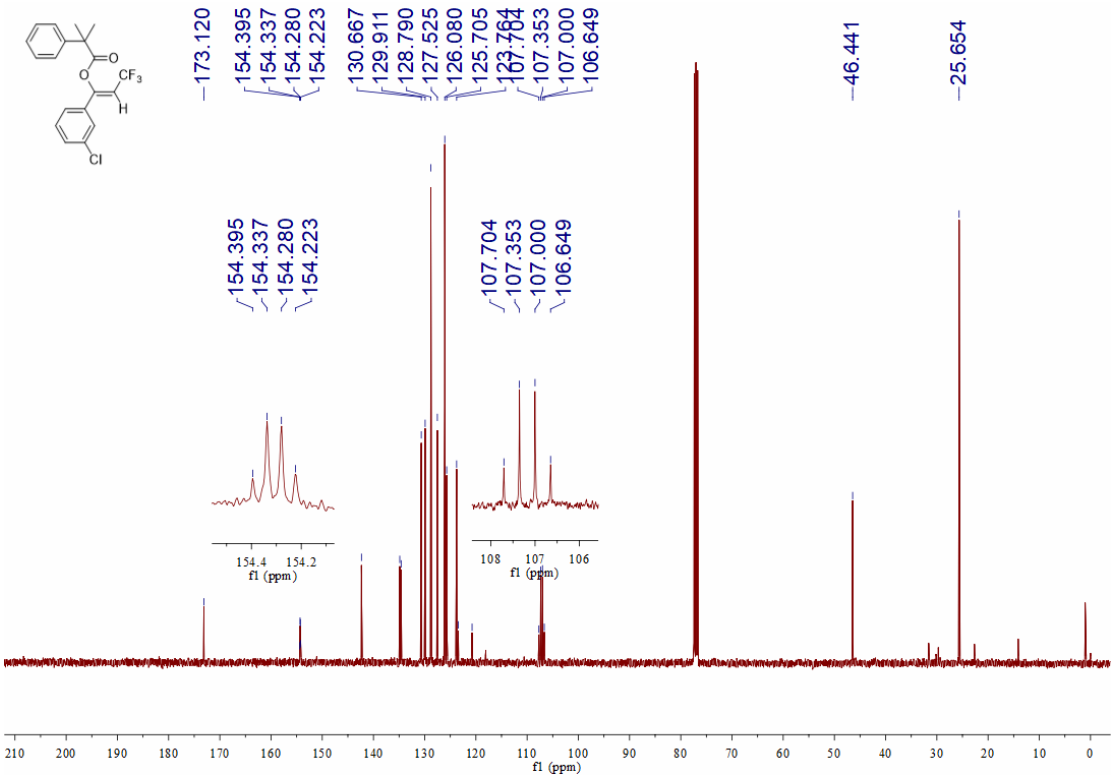

-58.437
--111.777
3.24
1.00
f1 (ppm)


173.108
163.886
161.426
154.383
154.355
154.325
154.297
142.335
135.000
134.922
130.355
130.274
128.698
127.514
126.168
123.453
121.341
121.312
120.769
117.684
117.473
112.862
112.626
107.619
107.267
106.915
106.562
46.437
25.615
f1 (ppm)

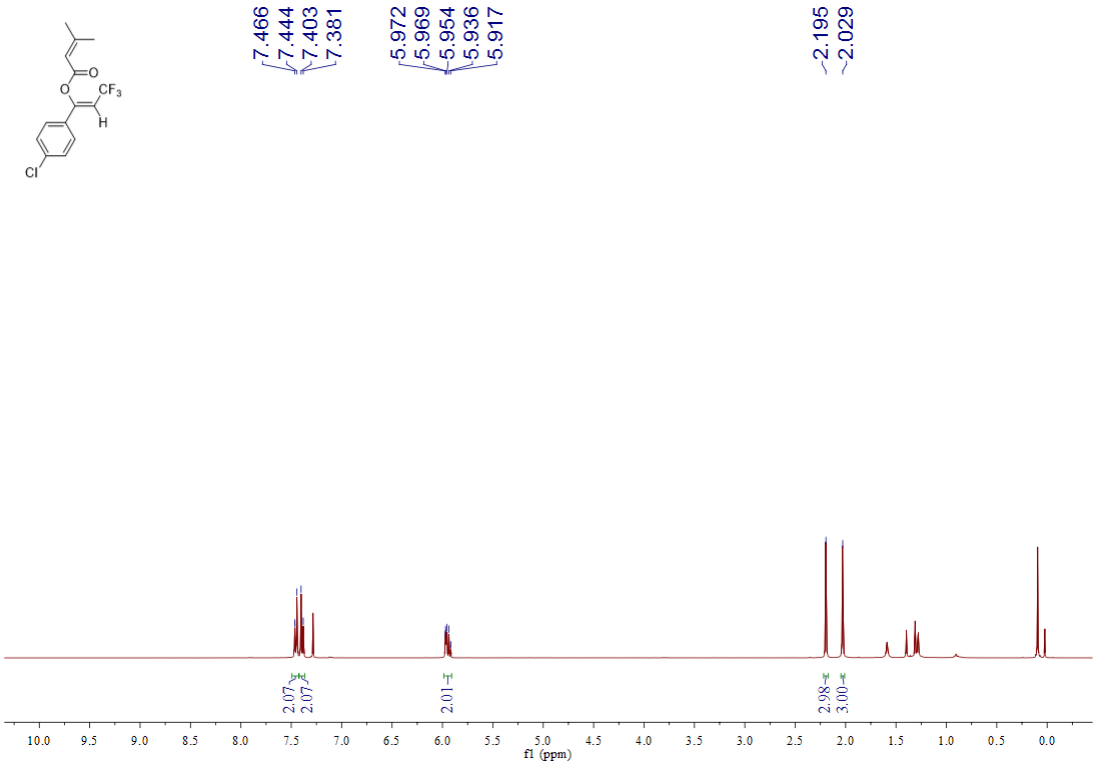
(Z)-1-(3-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 2-methyl-2-phenylpropanoate (4v, X = Cl) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

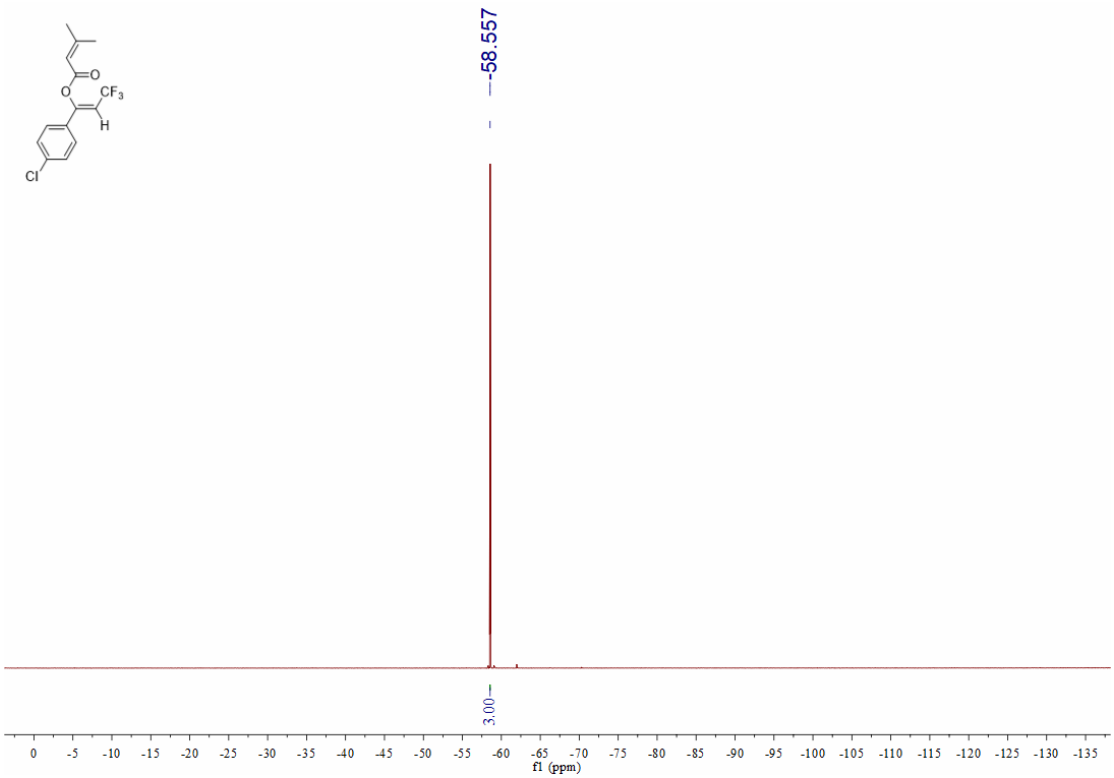


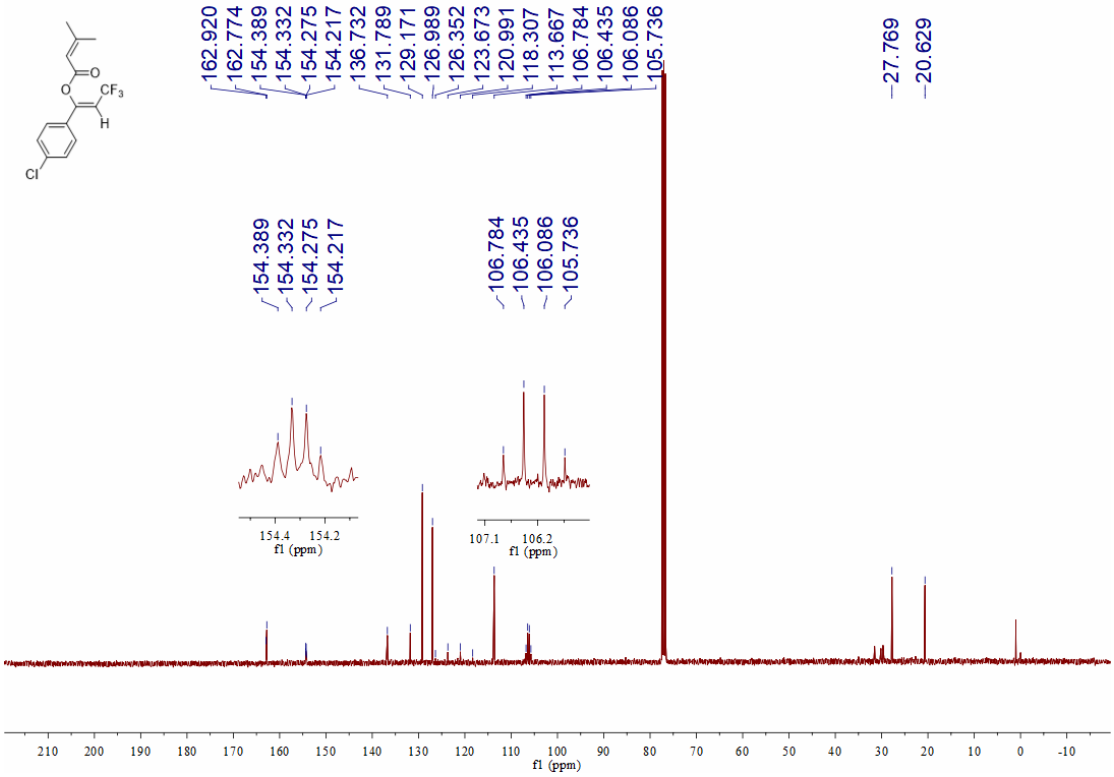




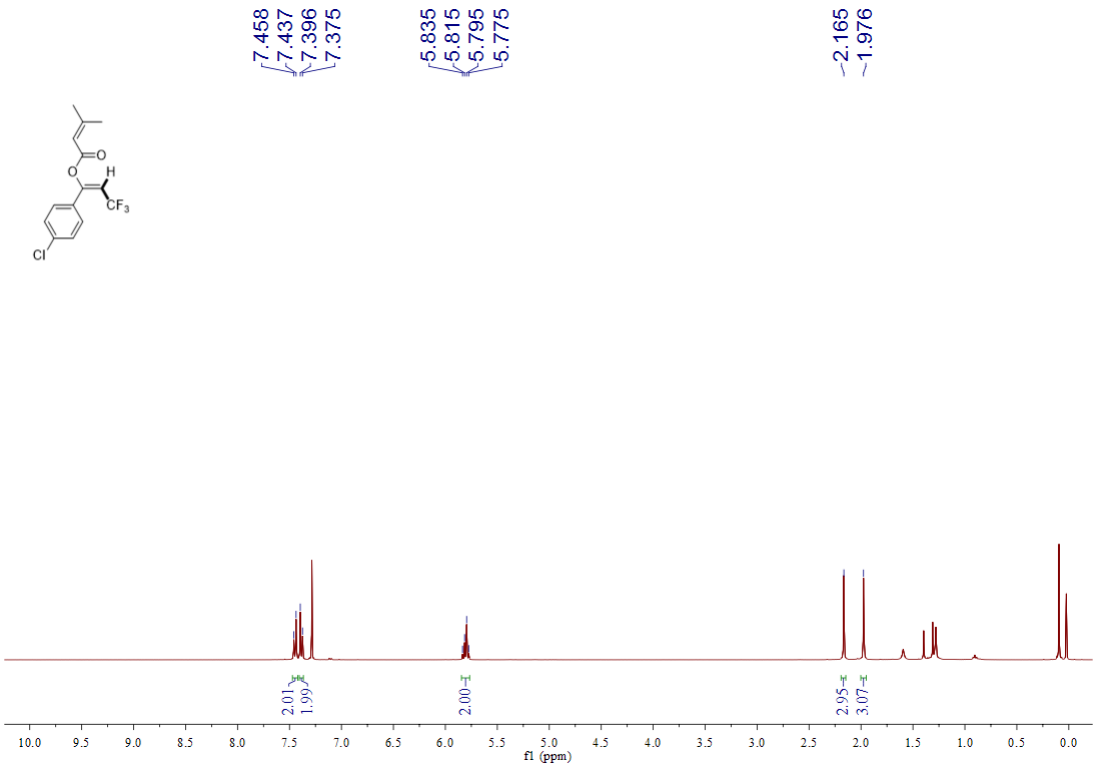
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 3-methylbut-2-enoate (4w) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

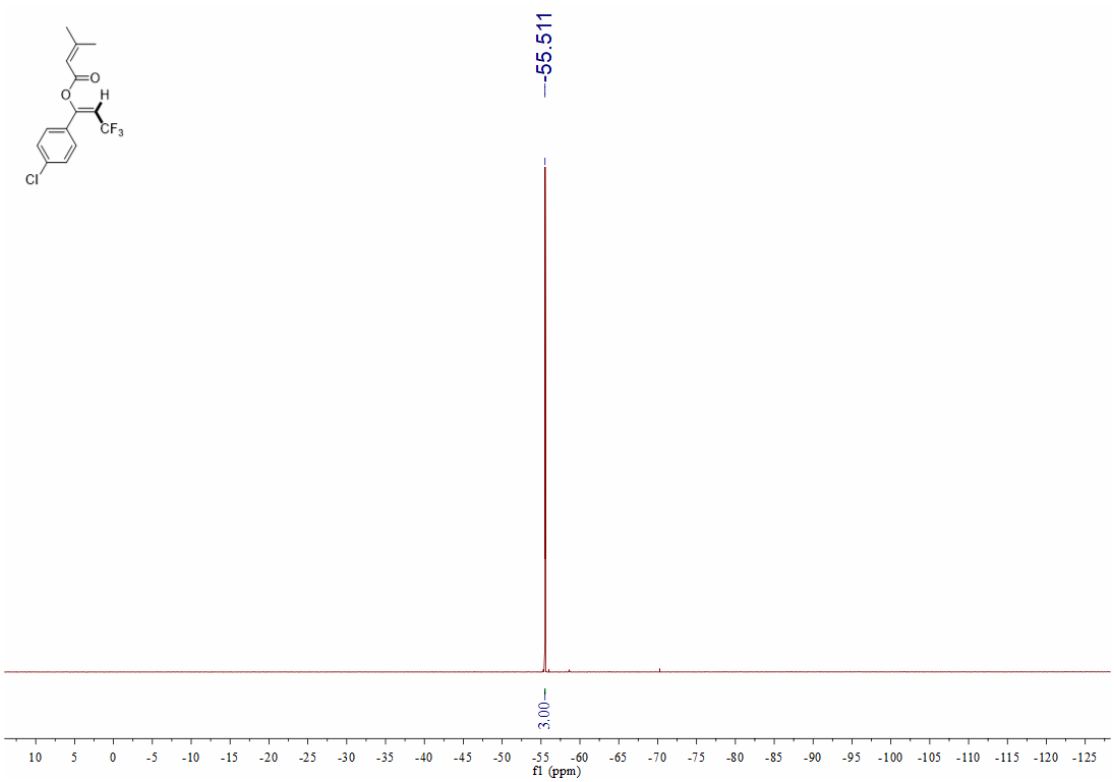


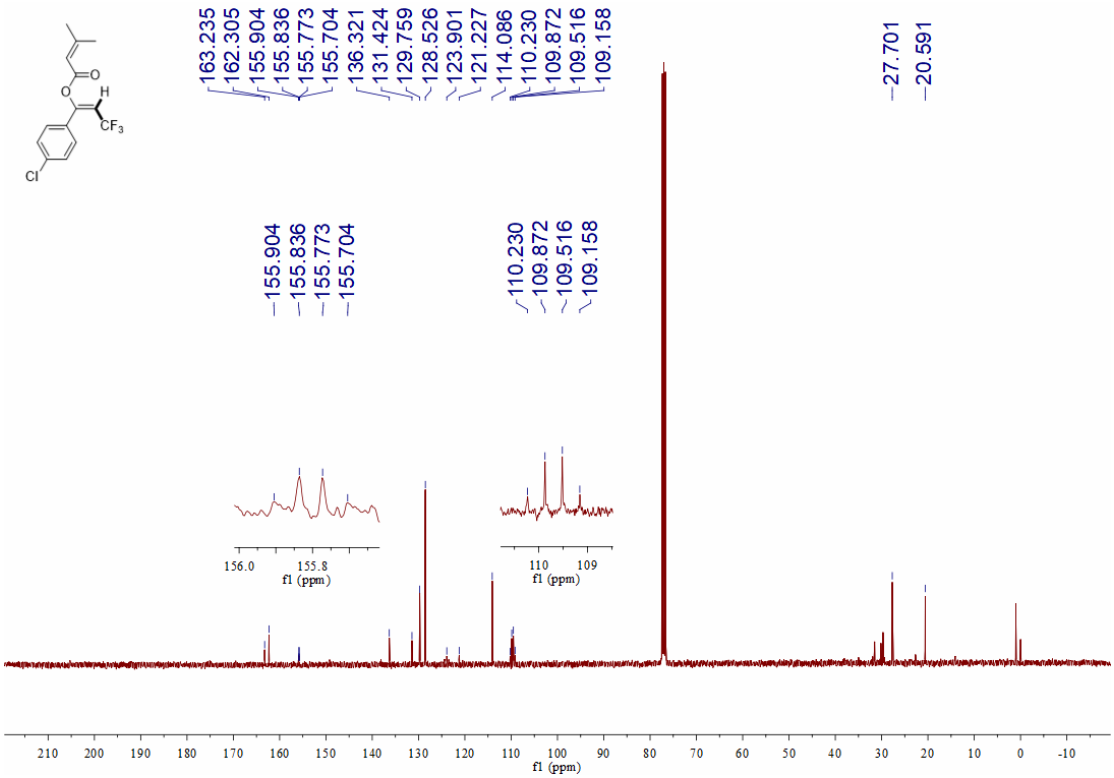

-58.557
3.00
f1 (ppm)


162.920
162.774
154.389
154.332
154.275
154.217
136.732
131.789
129.171
126.989
126.352
123.673
120.991
118.307
113.667
106.784
106.435
106.086
105.736
27.769
20.629
154.4
154.2
f1 (ppm)
107.1
106.2
f1 (ppm)
f1 (ppm)

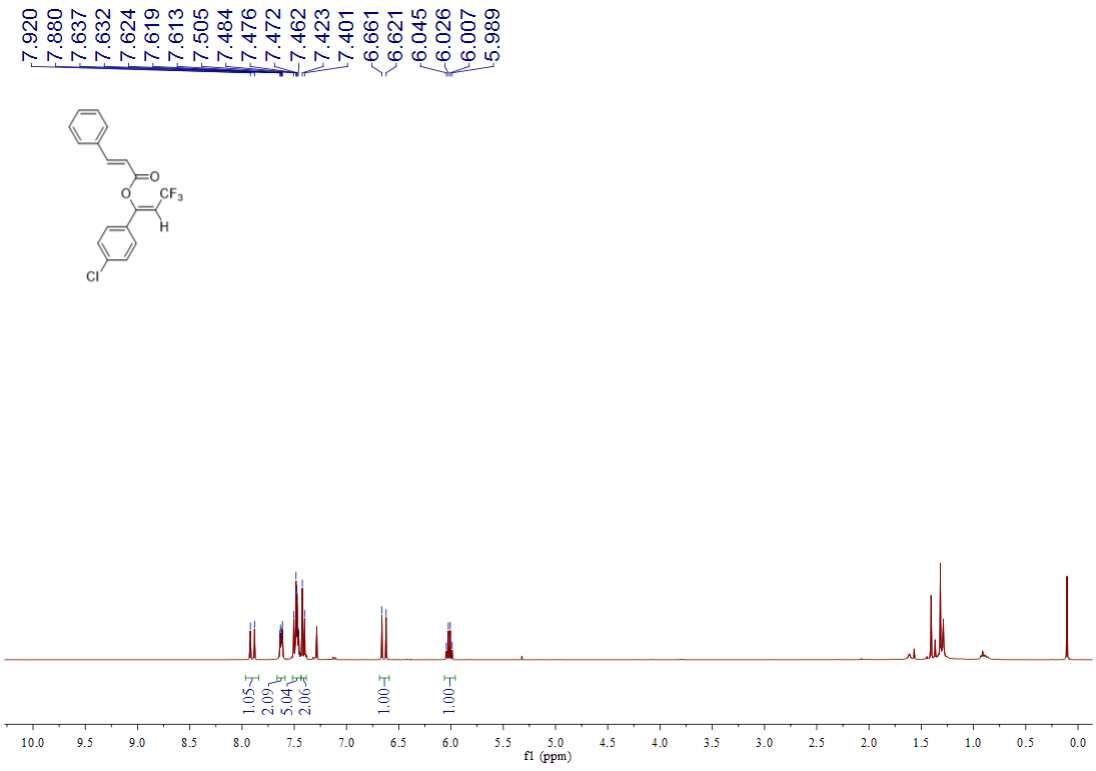
(E)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 3-methylbut-2-enoate (4w') (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

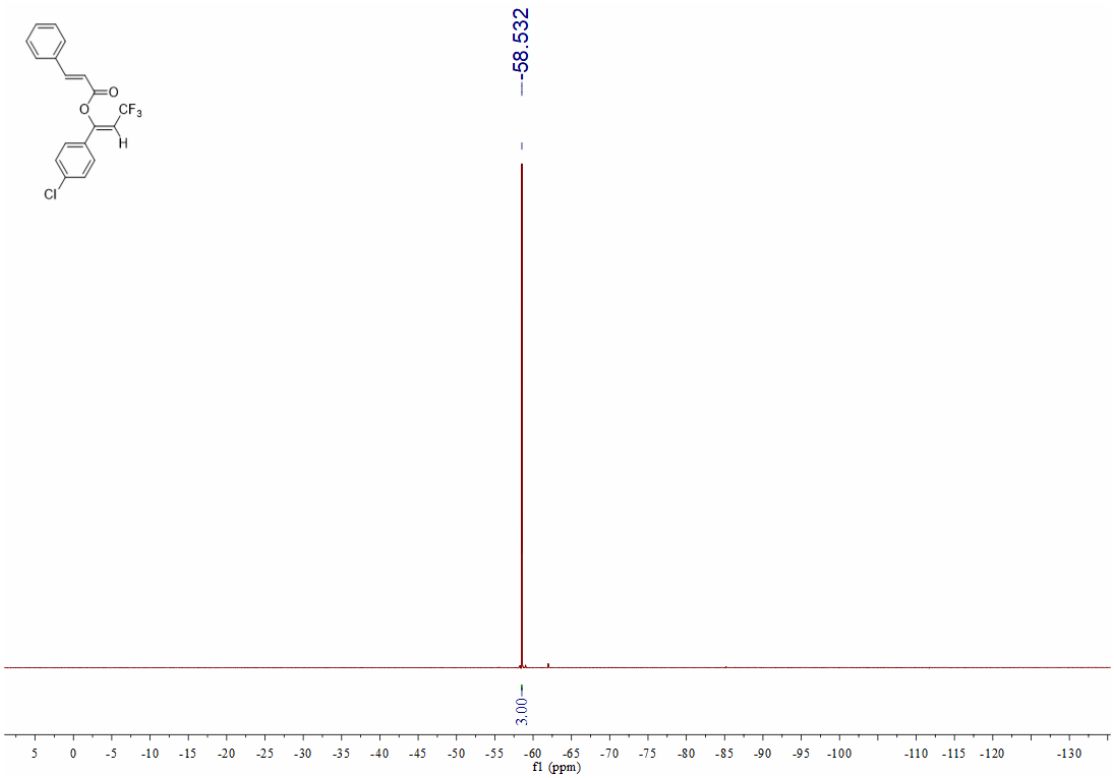


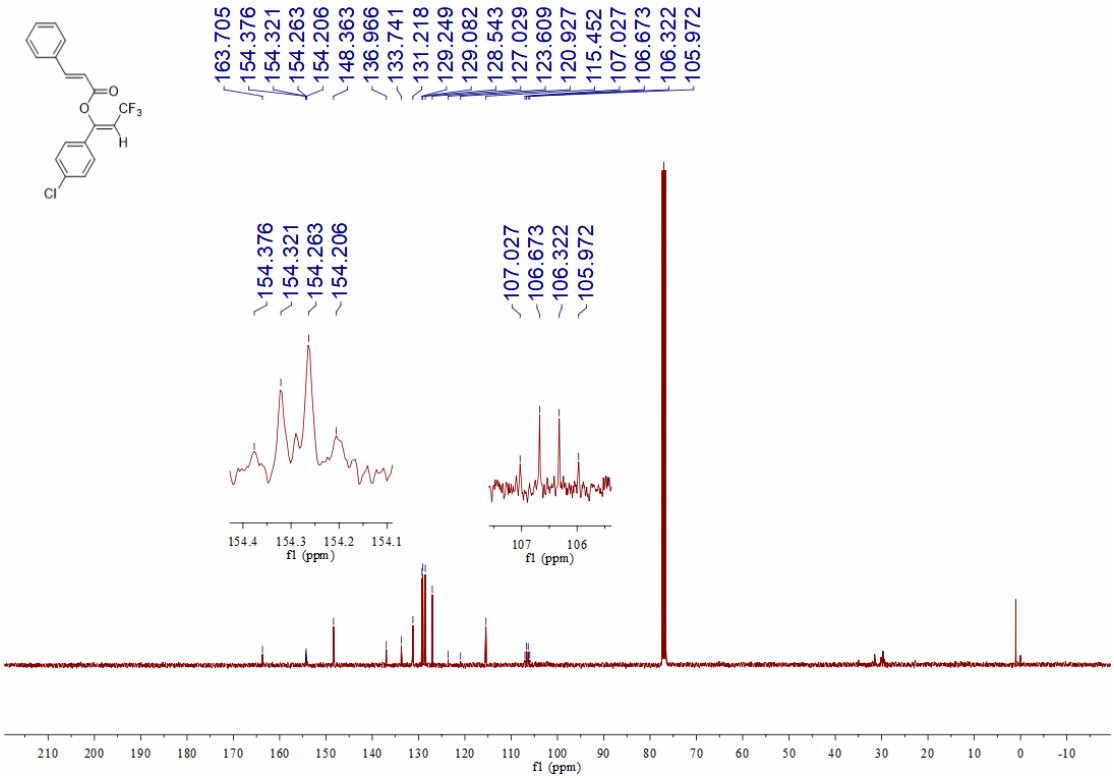




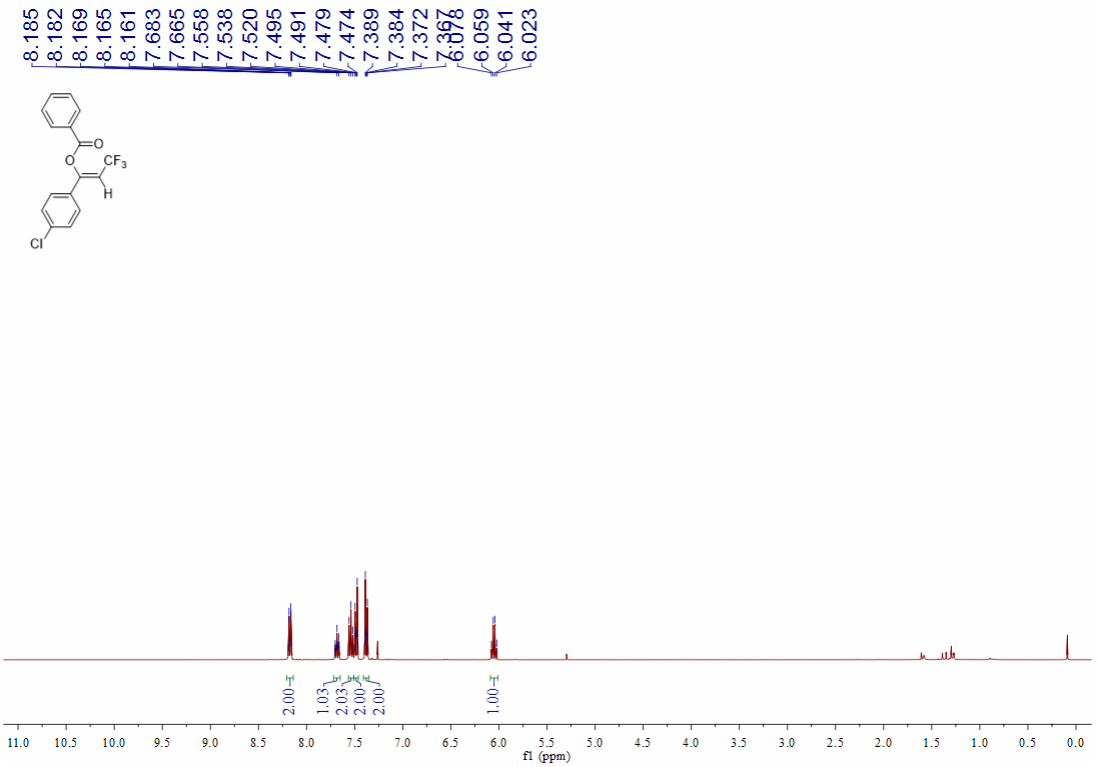
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl cinnamate (4x) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

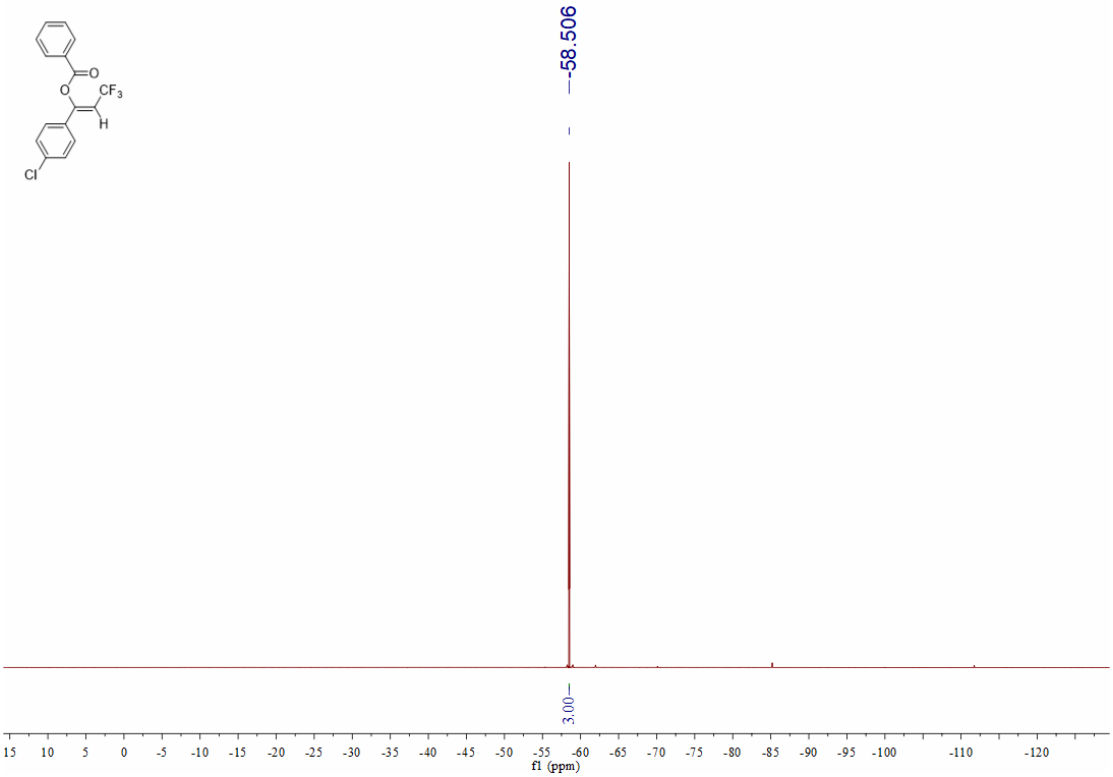


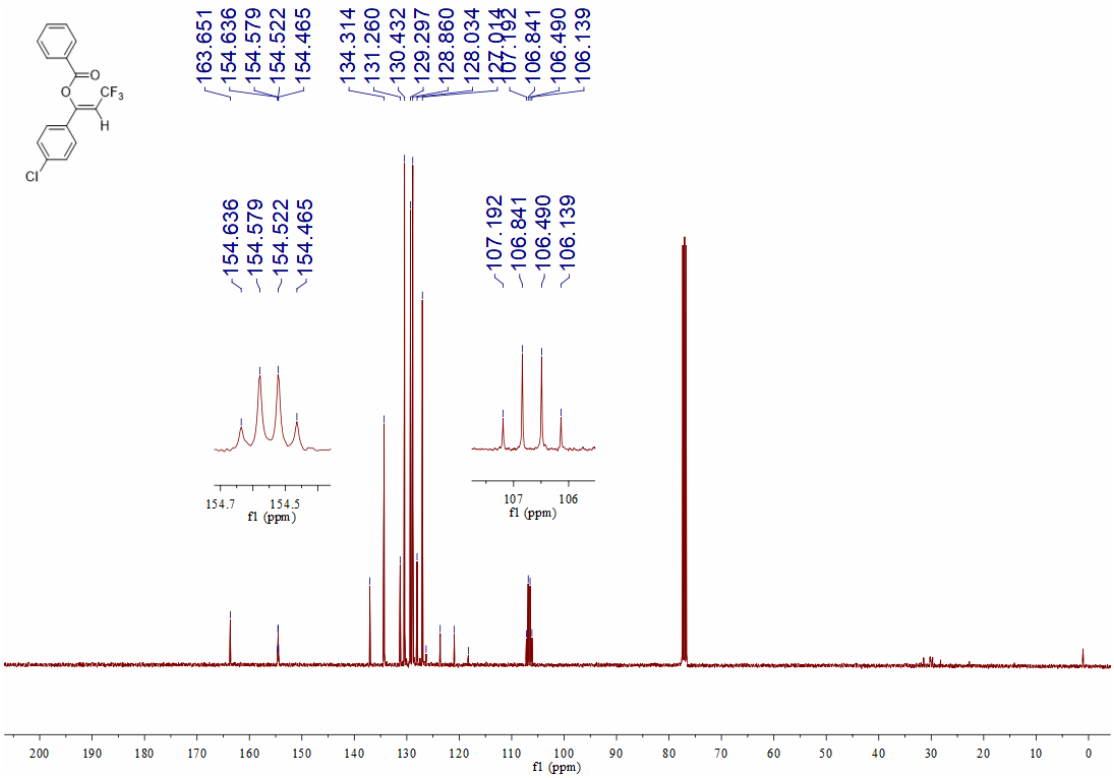

-58.532
3.00
f1 (ppm)


163.705
154.376
154.321
154.263
154.206
148.363
136.966
133.741
131.218
129.249
129.082
128.543
127.029
123.609
120.927
115.452
107.027
106.673
106.322
105.972
f1 (ppm)

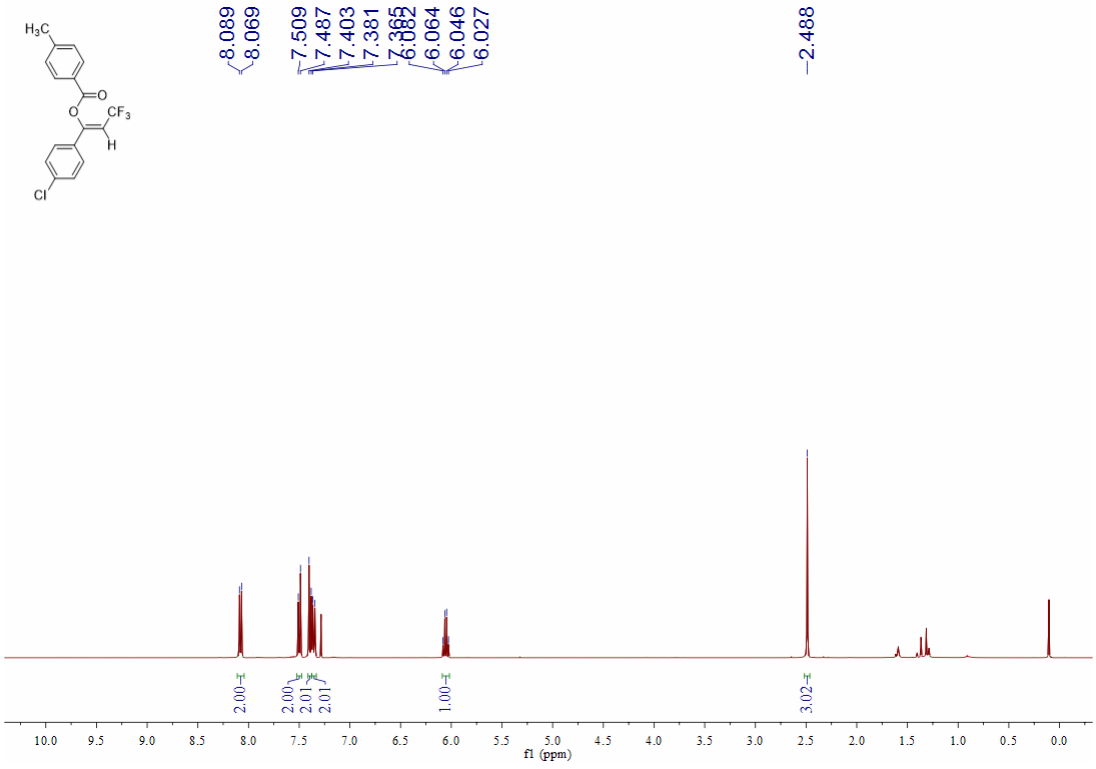
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl benzoate (4aa) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

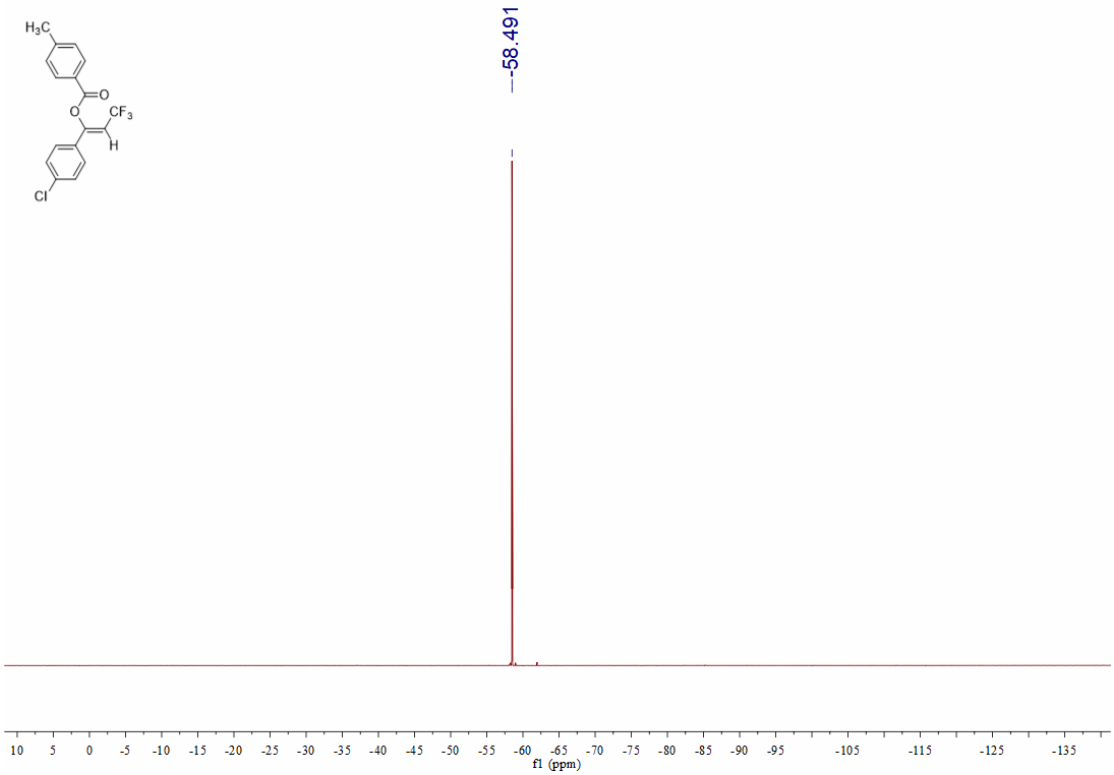


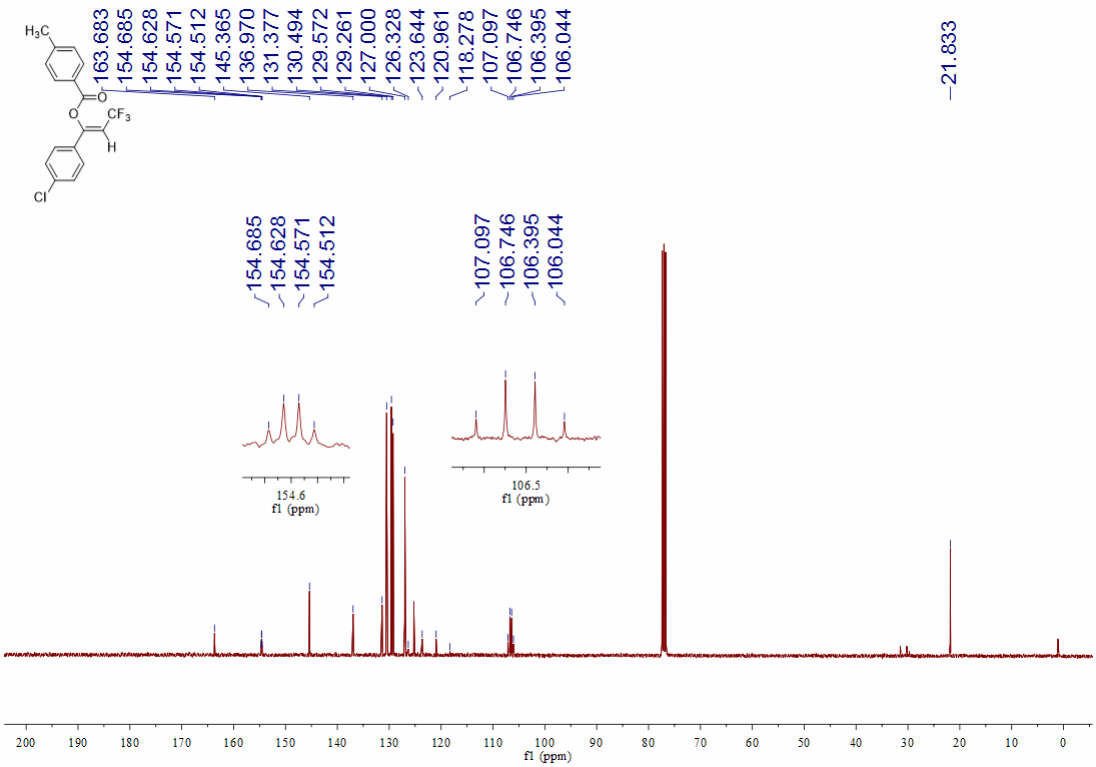




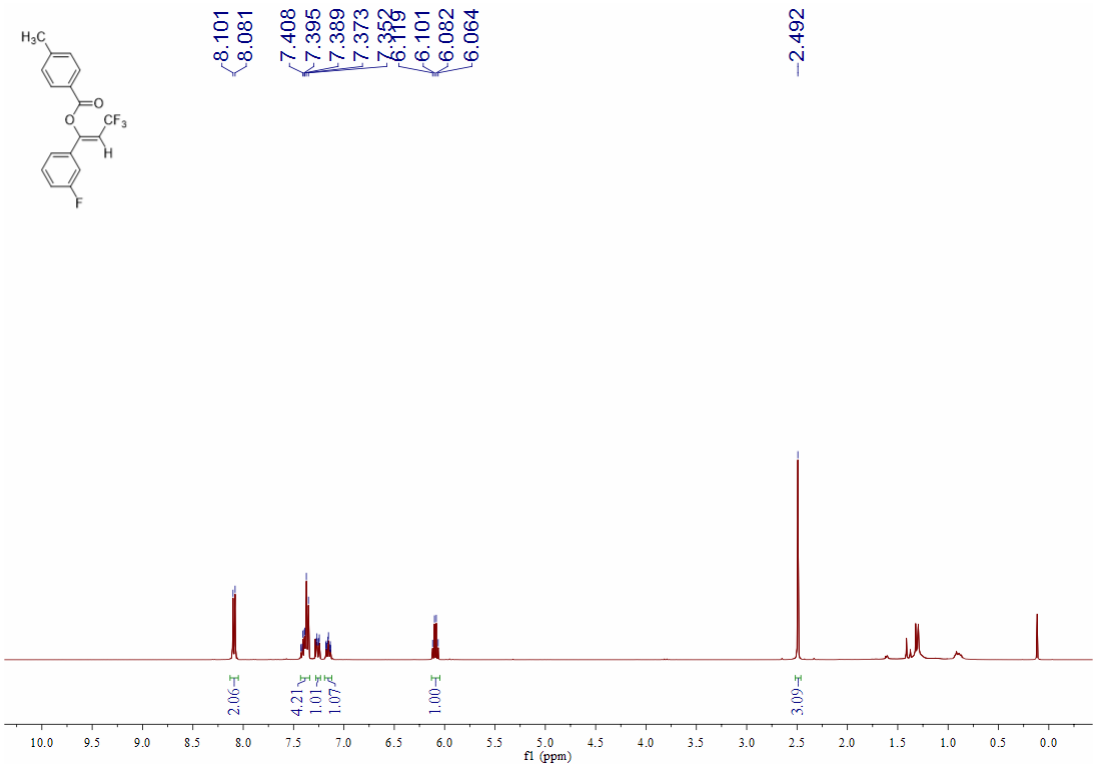
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl 4-methylbenzoate (4ae) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

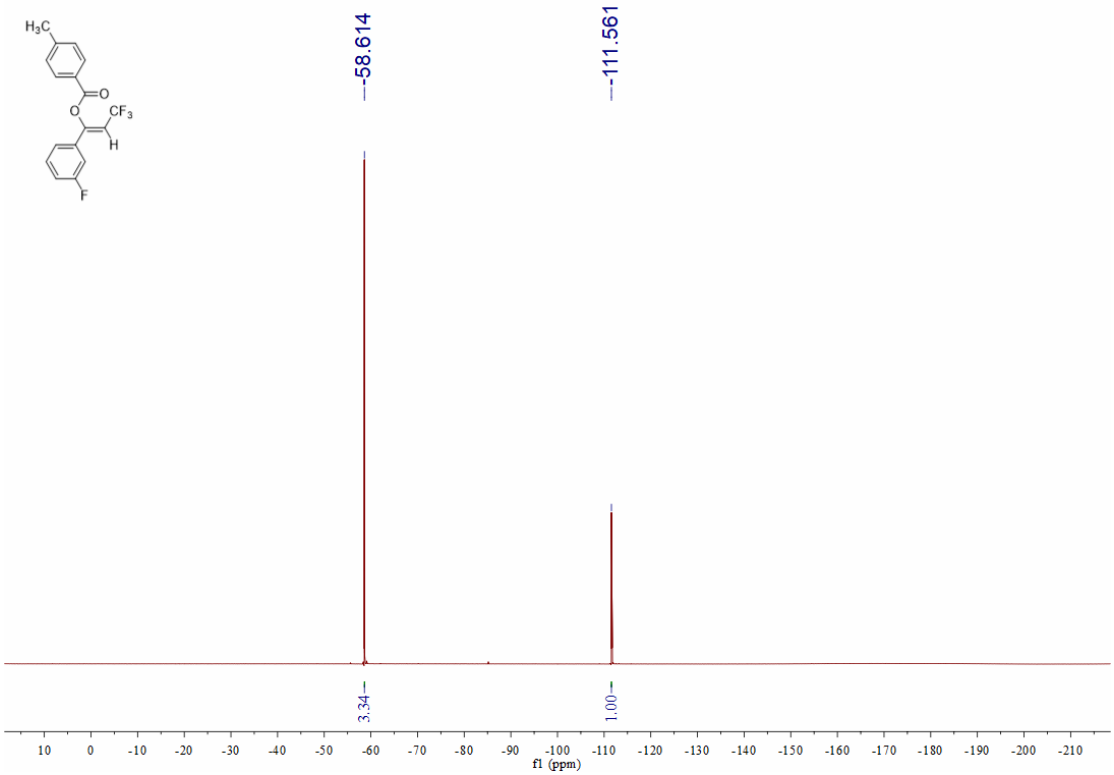


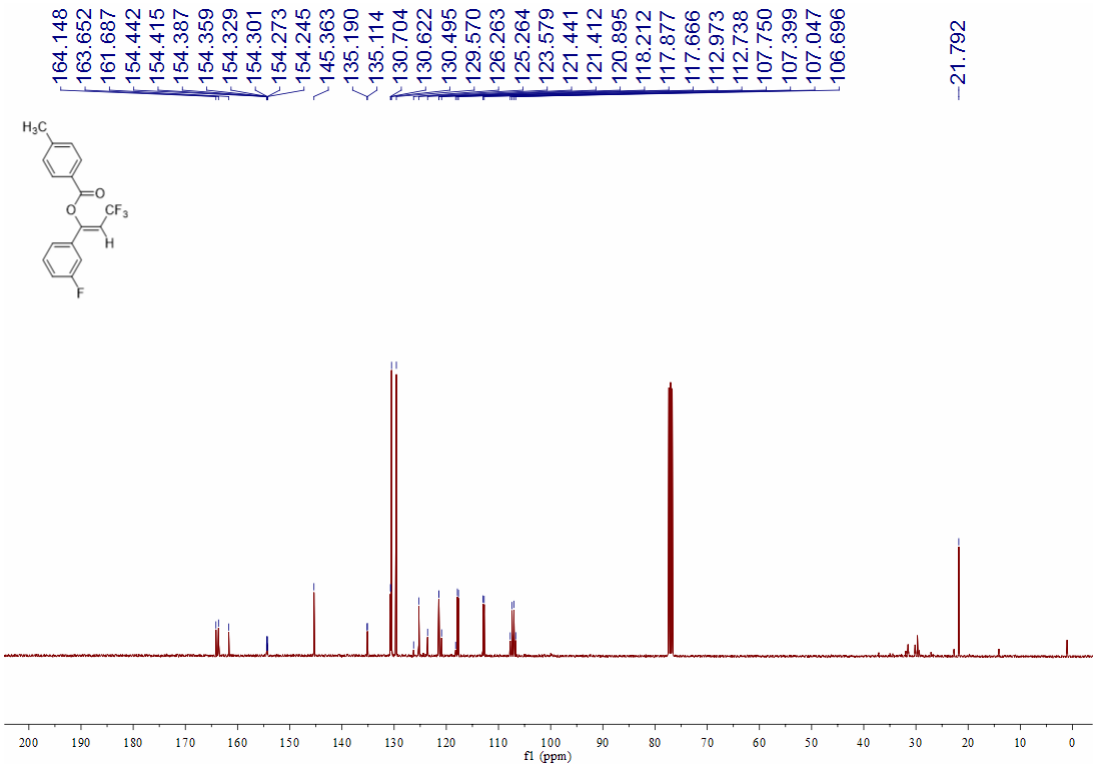

H3C
O
O
CF3
H
Cl
-58.491
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135
f1 (ppm)


H3C
O
O
CF3
H
Cl
163.683
154.685
154.628
154.571
154.512
145.365
136.970
131.377
130.494
129.572
129.261
127.000
126.328
123.644
120.961
118.278
107.097
106.746
106.395
106.044
-21.833
154.685
154.628
154.571
154.512
107.097
106.746
106.395
106.044
154.6
f1 (ppm)
106.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

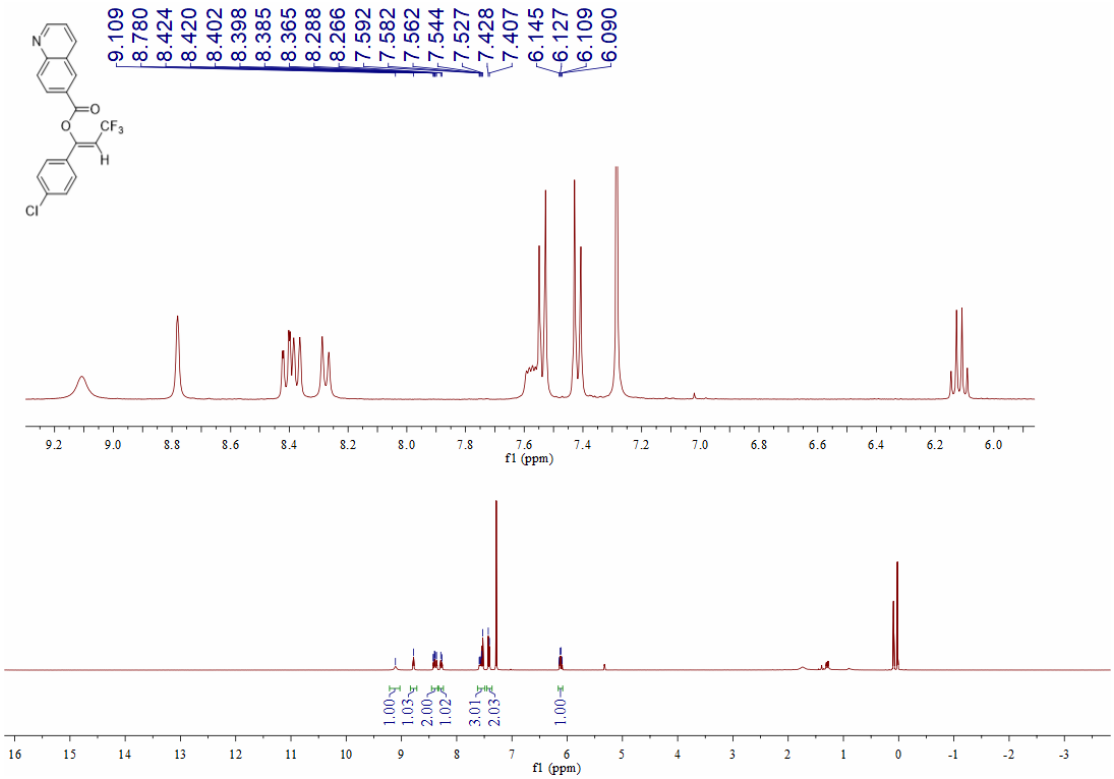
(Z)-3,3,3-trifluoro-1-(3-fluorophenyl)prop-1-en-1-yl 4-methylbenzoate (4af) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

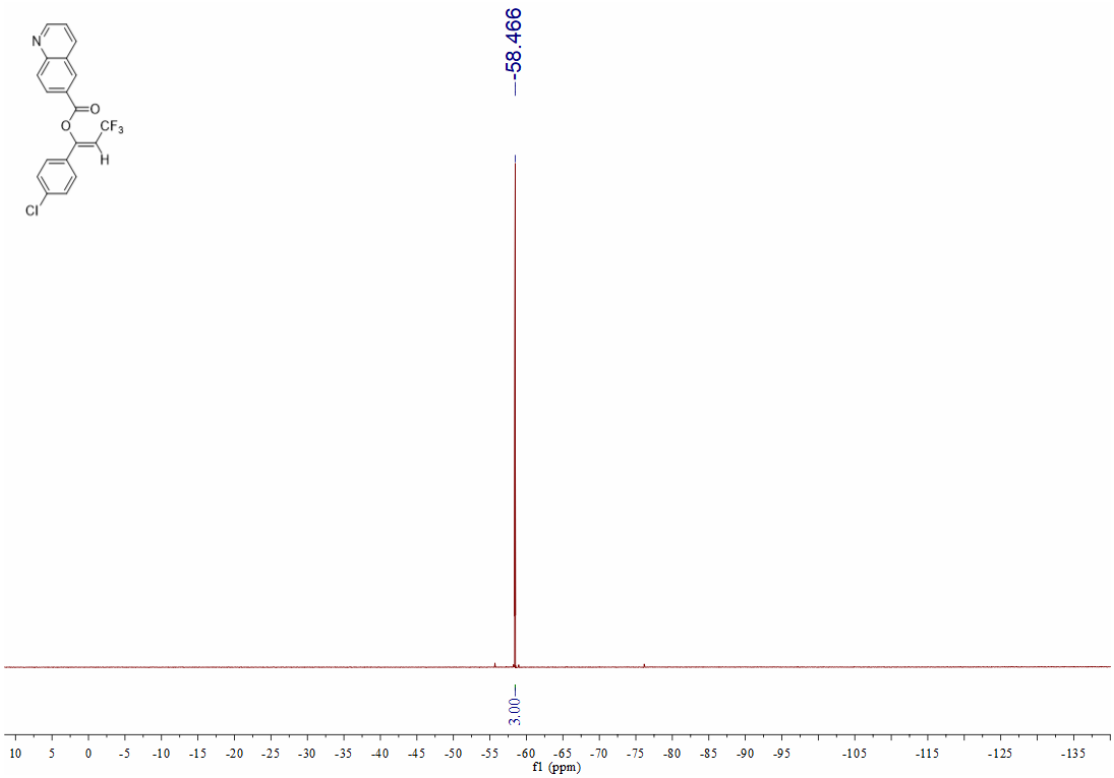


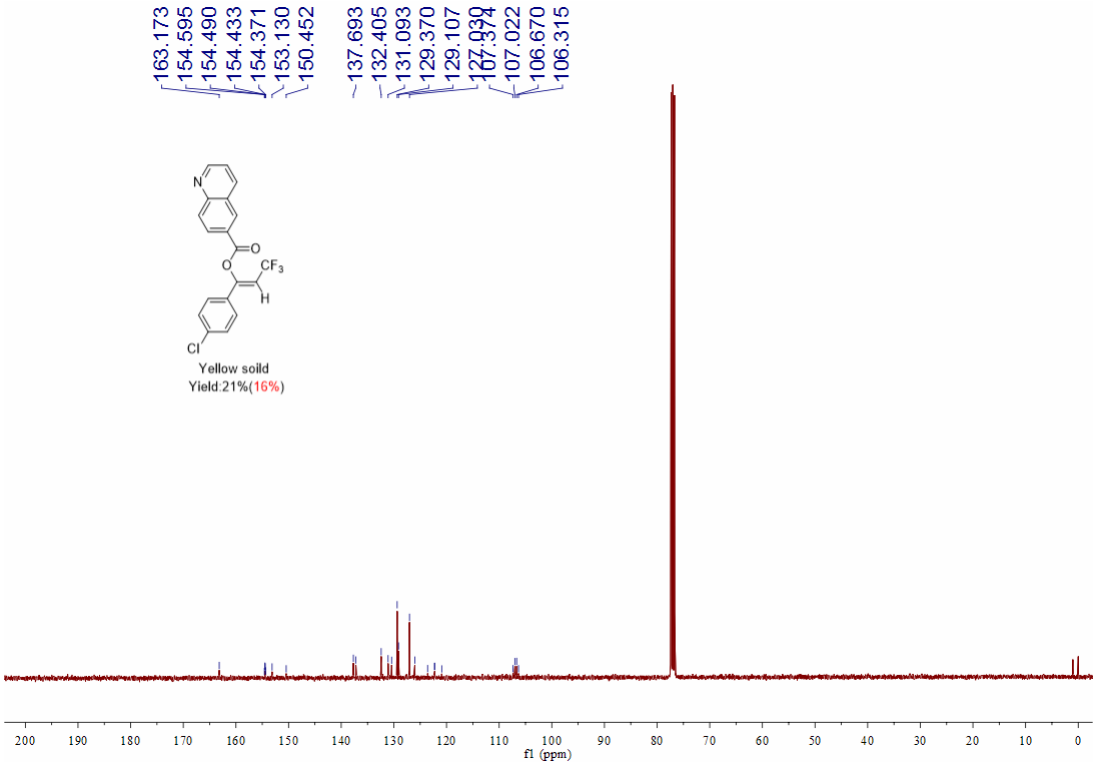




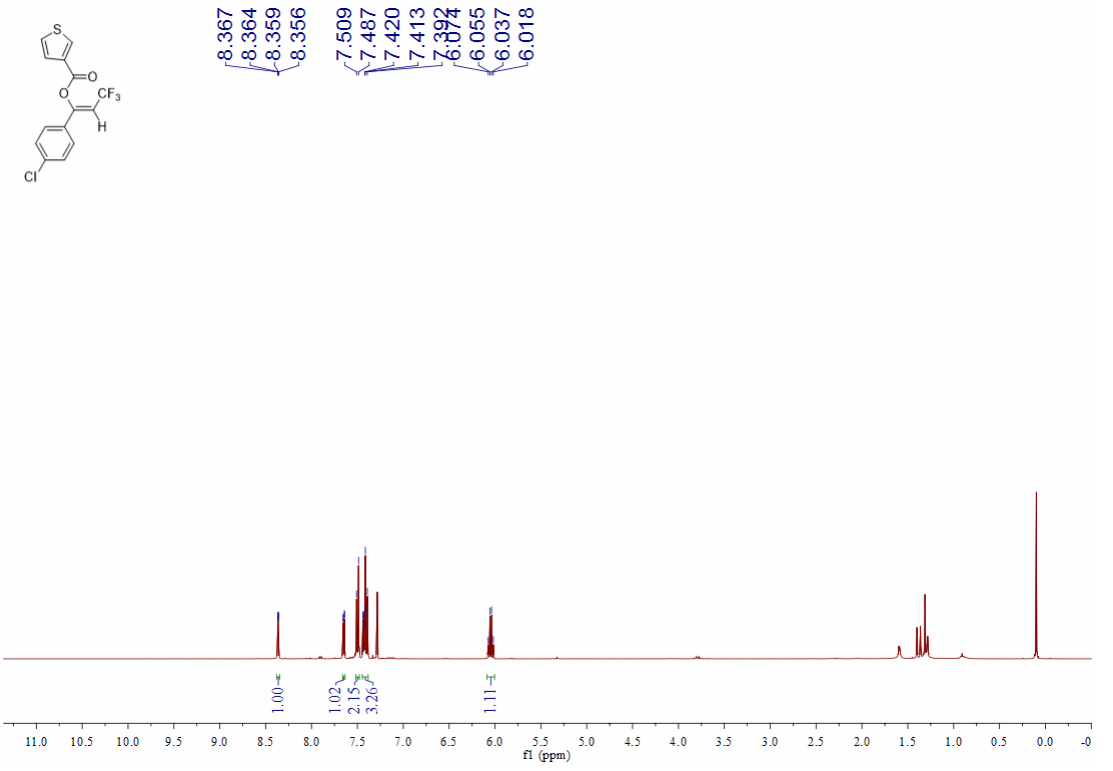
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl quinoline-6-carboxylate (4ah) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

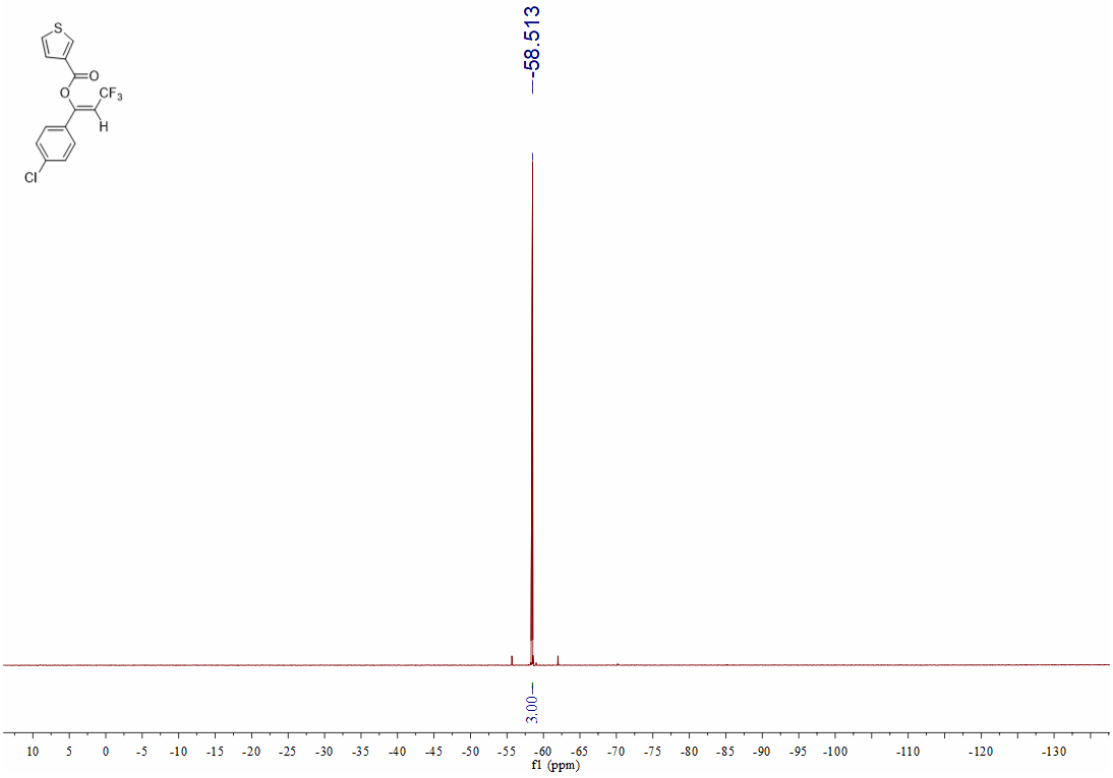


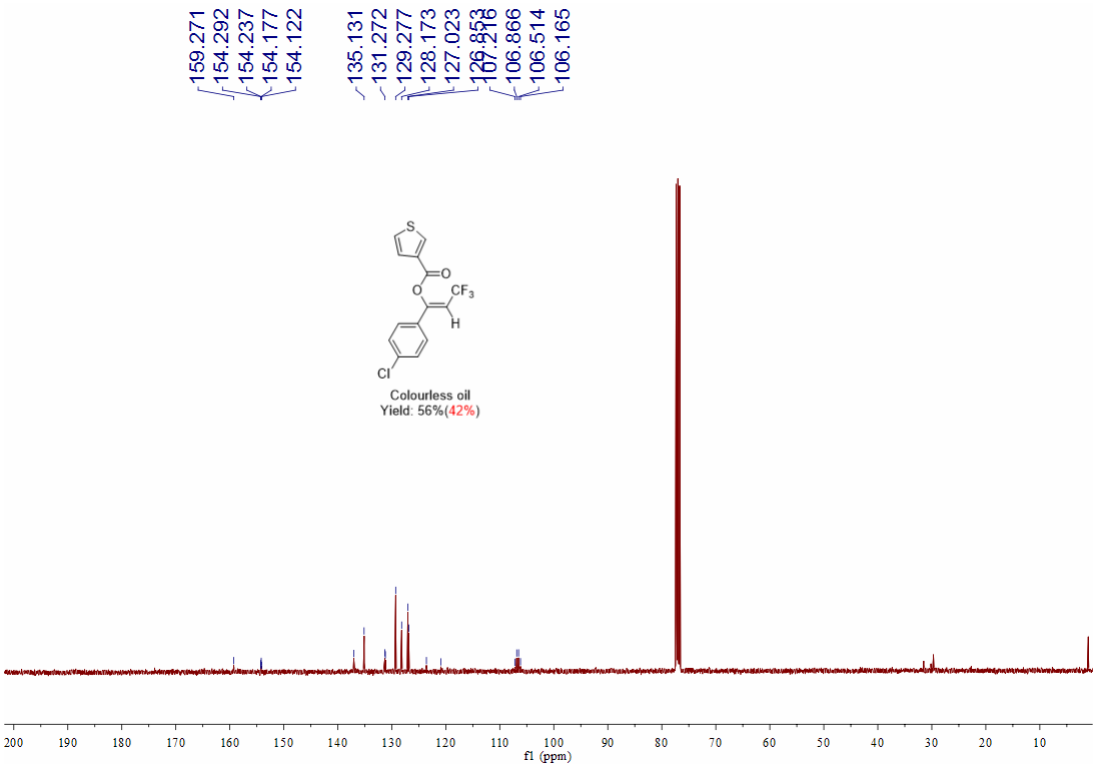

-58.466
3.00
f1 (ppm)


163.173
154.595
154.490
154.433
154.371
153.130
150.452
137.693
132.405
131.093
129.370
129.107
127.030
107.374
107.022
106.670
106.315
Yellow soild
Yield:21%(16%)
f1 (ppm)

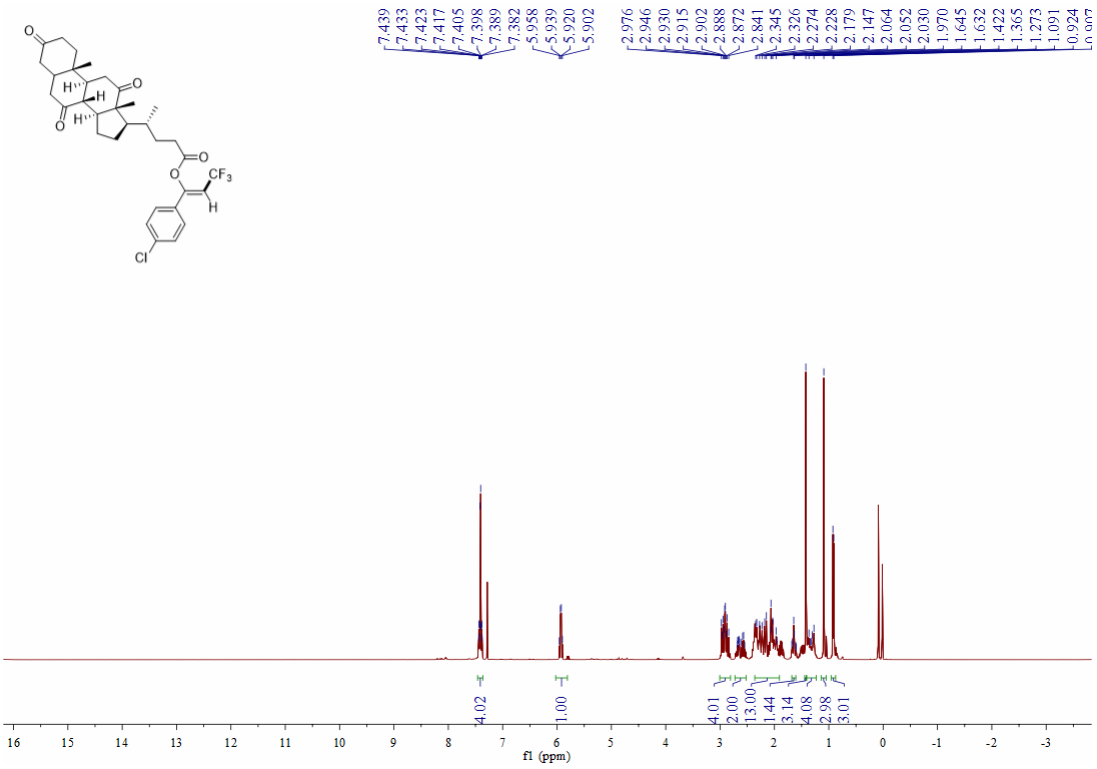
(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl thiophene-3-carboxylate (4ai) (^{1}NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).

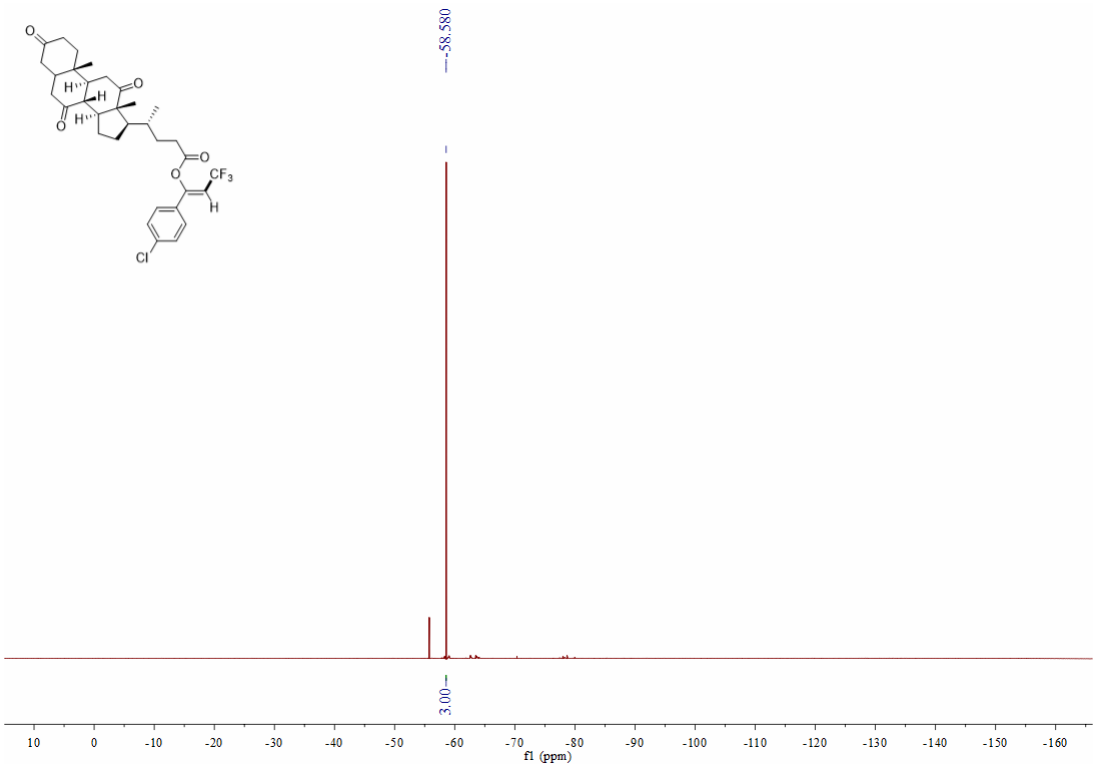


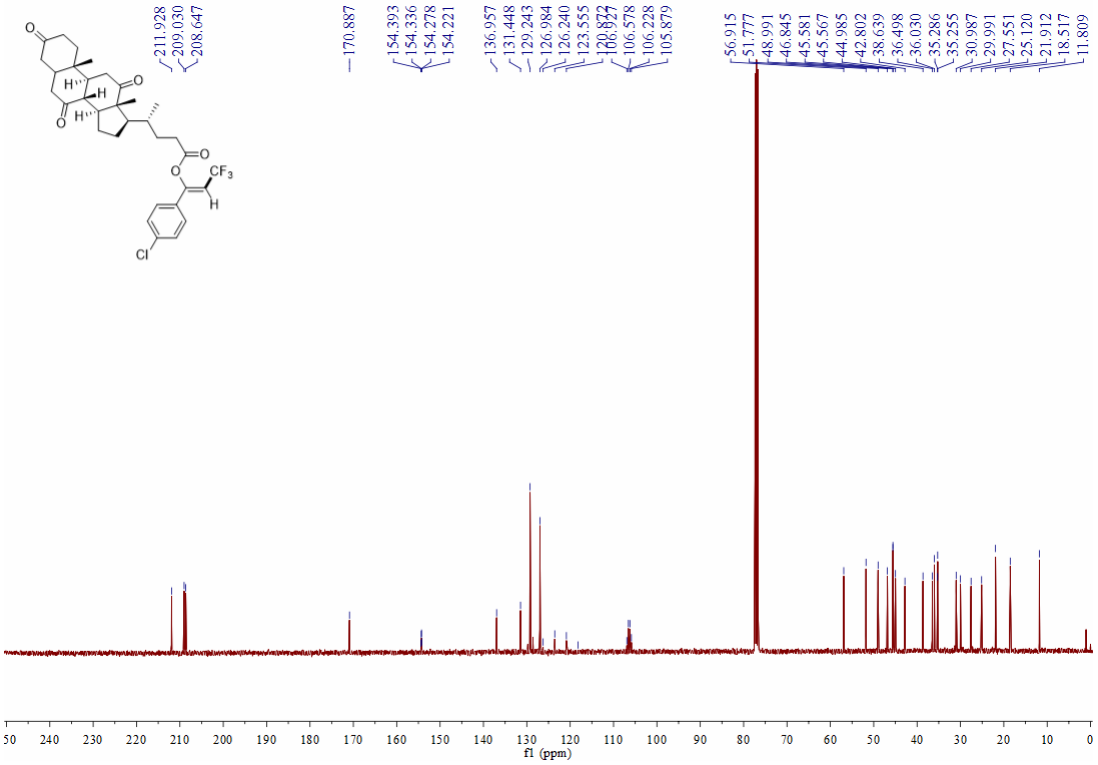



159.271
154.292
154.237
154.177
154.122
135.131
131.272
129.277
128.173
127.023
126.853
107.216
106.866
106.514
106.165
S
O
O
CF3
H
Cl
Colourless oil
Yield: 56%(42%)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

(Z)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl (4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta [a]phenanthren-17-yl)pentanoate (^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$).—contains very minor amount of *E*-isomer as indicated by ^{19}F NMR in a ratio of ca 12:1 of Z/E.




-58.580
3.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


211.928
209.030
208.647
170.887
154.393
154.336
154.278
154.221
136.957
131.448
129.243
126.984
126.240
123.555
120.872
106.578
106.228
105.879
56.915
51.777
48.991
46.845
45.581
45.567
44.985
42.802
38.639
36.498
36.030
35.286
35.255
30.987
29.991
27.551
25.120
21.912
18.517
11.809
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)