Trifluoromethylation of Allylsilanes under Photoredox Catalysis

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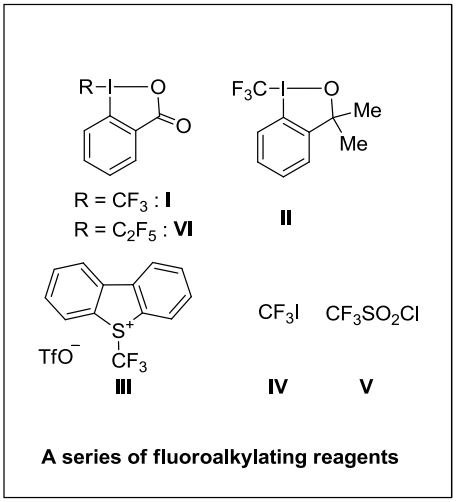
1. General Information

All NMR spectra were recorded on BrukerDPX200, DPX250, AV400, AVC500, AVB500 and DRX500 spectrometers. ^{1}H and ^{13}C NMR spectral data are reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak using the Bruker internal referencing procedure (edlock). ^{19}F NMR spectra are referenced relative to $CFCl_3$ in $CDCl_3$. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (*J*) are measured in hertz (Hz).The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet. NMR spectra were processed in ACD/Spec Manager. High resolution mass spectra (HRMS, *m*/*z*) were recorded on a Bruker MicroTOF spectrometer using positive electrospray ionization (ESI+) or on a Micromass GCT spectrometer using field ionization (FI+) or chemical ionization (CI+). IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Absorptions are measured in wavenumbers and only peaks of interest are reported. High-pressure liquid chromatography (HPLC) was performed on a Waters HPLC using a chiral column (250 mm) as noted for each compound. Optical rotations were measured on a PerkinElmer Polarimeter model 341 and are reported as $[\alpha]_D^{20}$ value; the corresponding concentration (c) is given in g/100 mL. Melting points of solids were measured on a Griffin apparatus and are uncorrected. IUPAC names were obtained using the ACD/ILab service. All reactions were performed in flame-dried apparatuses with magnetic stirring under an inert atmosphere. All solvents were dried on a column of alumina prior to use. Flash column chromatography was performed over Merck silica gel C60 (40−60 μm) using the eluent system described for each experiment. 1-Trifluoromethyl-1,2-benziodoxol-3-(*1H*)-one (Togni reagent **I)** and 1-pentafluoroethyl-1,2-benziodoxol-3-(*1H*)-one **VI** were prepared on multi-gram scale according to literature procedures.[1] $Ru(bpy)_3Cl_2•6H_2O$, CuCl, and trifluoromethylating reagents **II—V** were purchased from Sigma-Aldrich. Unless otherwise specified, other reagents were obtained from commercial suppliers. In a general experiment, a 14 W fluorescent light bulb (OSRAM DULUXSTAR®) was used as a visible light source. The light source was placed at a distance of approximately 5.0 cm from the reaction vial. The *E/Z* stereochemistry for **2a**−**i** is determined by analogy based on coupling constant values of the double. For the assignment of the relative configuration of **2e-i**, 2-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate **3** derived from representative **2f**, was characterized by single crystal X-ray diffraction (See, Section 3-6).

14 W Fluorescent Light Bulb

Reaction Setup



2. Cyclic Voltammetry Measurements

Electrochemical measurements were performed using an EG & G-Princeton Applied Research 263A all-in-one potentiostat and Autolab PGSTAT 128N electrochemical analyzer using a standard three-electrode setup with a glassy carbon electrode (working electrode, diameter = 3 mm), platinum wire auxiliary electrode and a non aqueous Ag/Ag^+ (0.1 M *n*-Bu_4NClO_4 + 0.01 M $AgNO_3$) system in acetonitrile as the reference electrode. The solutions of the compounds under the study were 0.1 M in the supporting electrolyte *n*-Bu_4NPF_6 or *n*-Bu_4NBF_4 with the voltage scan rate of 0.2 $V.s^{-1}$. Solutions were thoroughly bubbled with dry nitrogen for 15 minutes to remove any oxygen before any experiment and kept under positive pressure of nitrogen. Under these experimental conditions the ferrocene/ferricinium couple, used as internal reference for potential measurements, was located at $E_{1/2}$ = + 0.050 V in DMF, $E_{1/2}$ = + 0.046V in CH_3CN and $E_{1/2}$ = + 0.065V in MeOH. Typical 2.0 mL cyclic voltammetry cell used for the cyclic voltammetry experiments and the EG & G-Princeton Applied Research 263A potentiostat-galvanostat. For conversion factors (SCE *vs* Ag/Ag^+), see: a) J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasnic, R. M. Wightman, J. K. Kochi, *J. Am. Chem. Soc*. **1984**, *106*, 3968–3976; b) C. Amatore, C. J. Lefrou, *J. Electroanal. Chem.* **1992**, *325*, 239–246.

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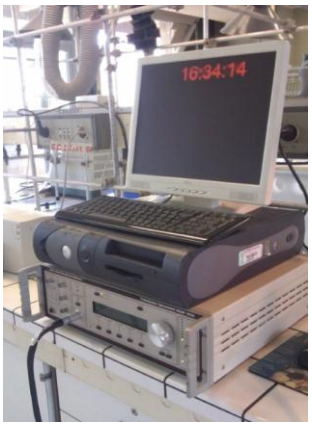
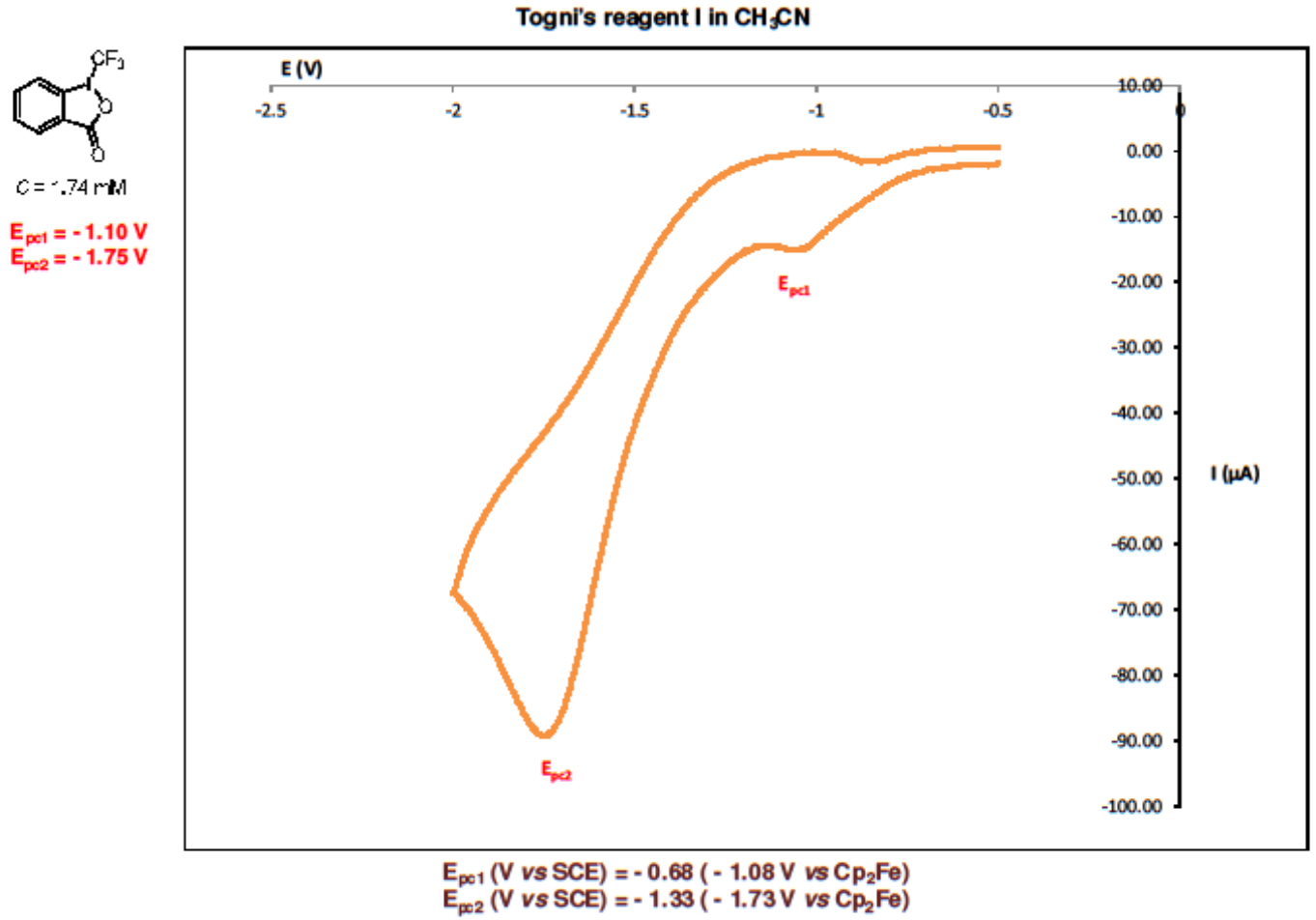
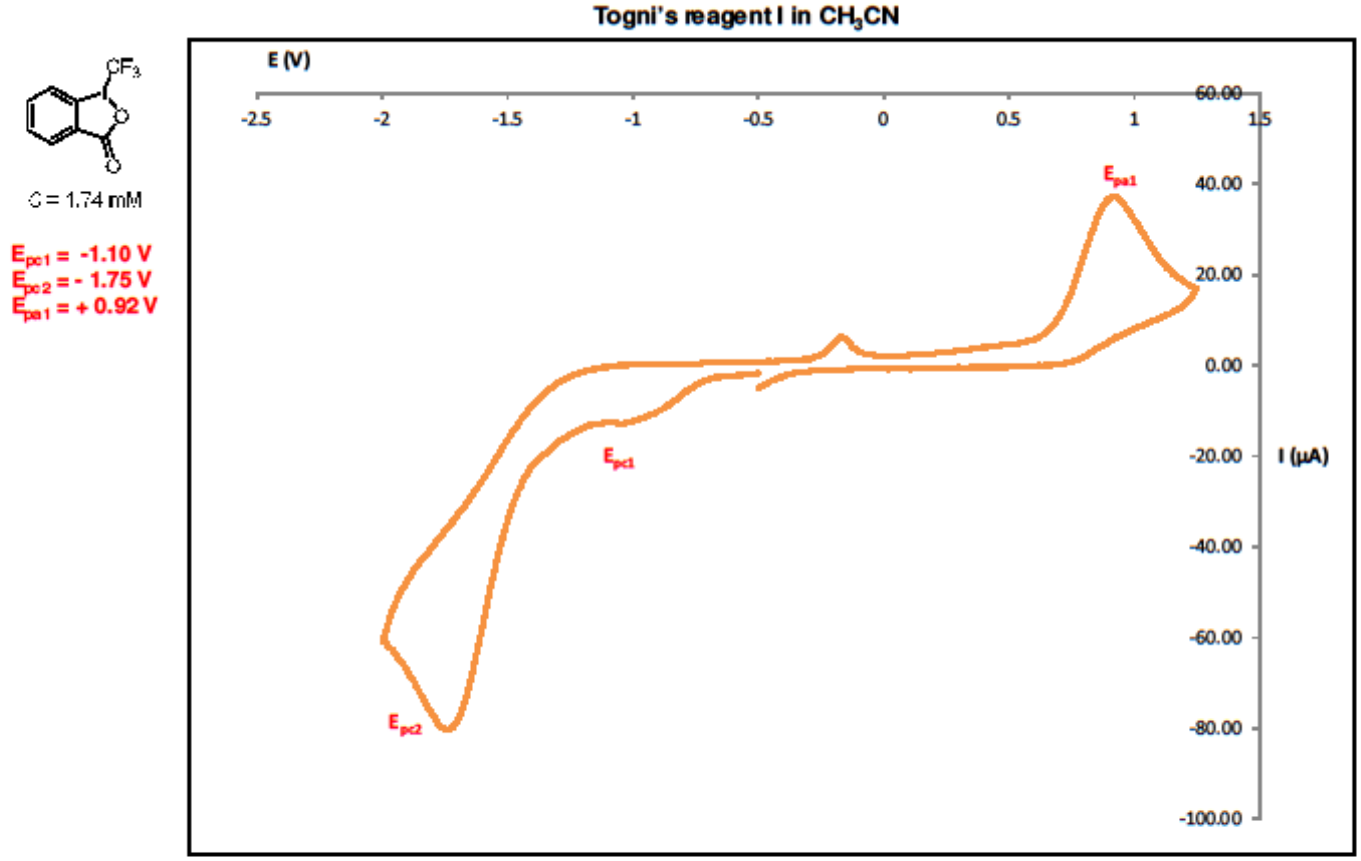




E_{pc1} (V *vs* SCE) = - 0.68 (- 1.08 V *vs* Cp_2Fe)
E_{pc2} (V *vs* SCE) = - 1.33 (- 1.73 V *vs* Cp_2Fe)

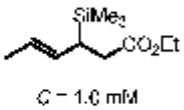
Cyclic voltammetry of Togni's reagent **I** in anhydrous acetonitrile + 0.1 M *n*-Bu_4NPF_6, glassy carbon electrode, scan rate = 0.2 V s^{-1}, T = 293K. Scanning potential from -0.5 V to -2.0 V, then -2.0 V to -0.5 V.



E_{pc1} (V *vs* SCE) = = - 0.68 (- 1.08 V *vs* Cp_2Fe); E_{pc2} (V *vs* SCE) = - 1.33 (- 1.73 V *vs* Cp_2Fe)
E_{pa1} (V *vs* SCE) = + 1.34 (+ 0.94 V *vs* Cp_2Fe); such oxidation is not observed when potential is scanned from 0.0 to + 1.5 V and corresponds to the oxidation of a product obtained at -1.33 V *vs* SCE (iodide oxidation).

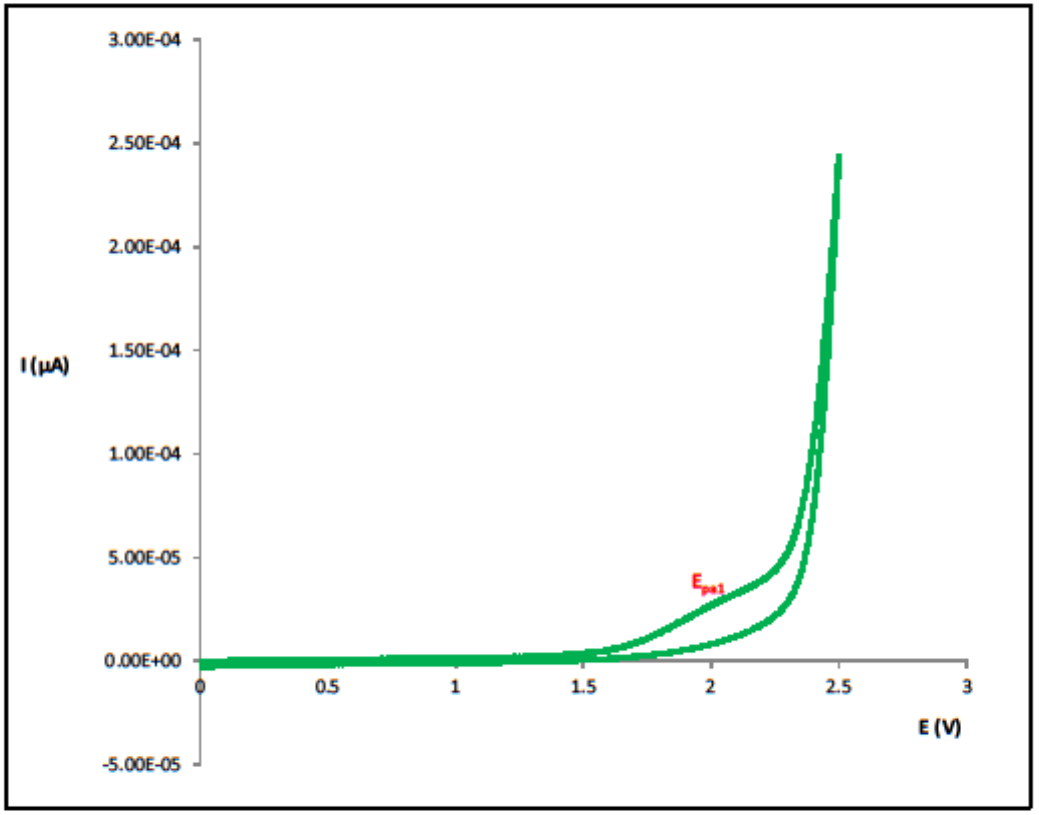
Cyclic voltammetry of Togni's reagent **I** in anhydrous acetonitrile + 0.1 M *n*-Bu_4NPF_6, glassy carbon electrode, scan rate = 0.2 V s^{-1}, T = 293K. Scanning potential from -0.5 V to -2.0 V, then -2.0 V to +1. 25 V and then +1.25V to -0.5V.

Allylsilane 1a in MeCN



C = 1.0 mM

E_{pa1} = > 1.8 V

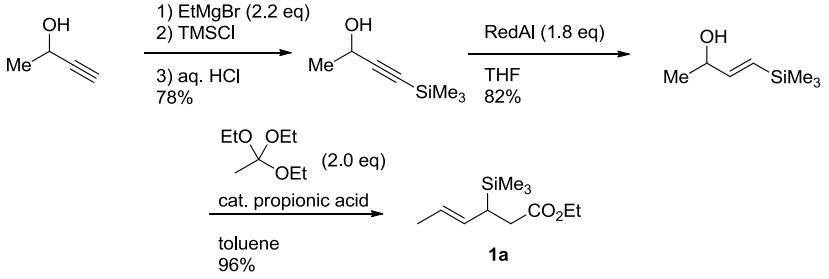


E_{pa1} (V *vs* SCE) = > 2.22

Cyclic voltammetry of allylsilane **1a** in anhydrous acetonitrile + 0.1 M *n*-Bu_4NBF_4, glassy carbon electrode, Ag/AgCl reference electrode, scan rate = 50 mV s^{-1}, T = 293K. Scanning potential from 0.0 V to 2.5 V, then 2.5 V to 0.0 V.

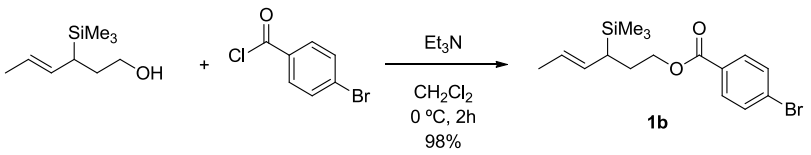
3. Experimental Procedures and Characterization Data

3-1. Synthesis of Allylsilane Starting Materials



Preparation of 3-(trimethylsilyl)hex-4-enoate (1a)[2]

Addition of the anion of but-3-yn-2-ol generated by addition of EtMgBr to excess chloro(trimethyl)silane, followed by selective acid-mediated desilyation of the silyl ether afforded the γ-trimethylsilyl-substituted propargylic alcohol. Subsequent Red-Al reduction gave 4-trimethylsilyl-but-3-en-2-ol. The 3-(trimethylsilyl)hex-4-enoate was prepared by a Johnson–Claisen [3,3]-sigmatropic rearrangement following condensation with triethylorthoacetate. For experimental details, see Ref. [2].

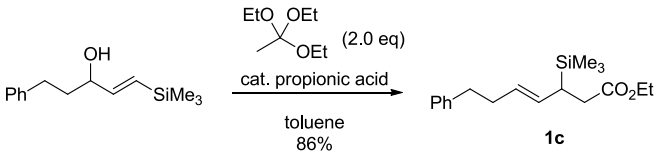


Preparation of (*E*)-3-(trimethylsilyl)hex-4-en-1-yl 4-bromobenzoate (1b)

(*E*)-3-(trimethylsilyl)hex-4-en-1-ol[3] (350 mg, 2.2 mmol) was dissolved in CH_2Cl_2 (5.0 mL). Et_3N (367 μL, 2.7 mmol) and *p*-bromobenzoyl chloride (581 mg, 2.7 mmol) were sequentially added at 0˚C. The mixture was allowed to warm to room temperature and stir for 3 hrs before being quenched with water. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:4) yielded **1b** (726 mg, 98% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 1.51–1.58 (m, 1H), 1.65 (d, *J* = 5.3 Hz, 3H), 1.69–1.77 (m, 1H), 1.87–1.94 (m, 1H), 5.20–5.33 (m, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –3.3, 18.1, 27.9, 29.6, 65.3, 123.6, 127.8, 129.5, 130.8, 131.1, 131.6, 165.9; **IR** (neat) ν 2955, 1720, 1591, 1398, 1269, 1247, 1172, 1101, 1069, 1012, 966, 834, 755 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{16}H_{23}BrO_2NaSi$ $[M+Na]^+$ 377.0541, found 377.0543.

(*E*)-Ethyl 7-phenyl-3-(trimethylsilyl)hept-4-enoate (1c)



(*E*)-5-phenyl-1-trimethylsilyl-penten-3-ol[4] (424 g. 1.8 mmol), triethylorthoacetate (660 μL, 3.6 mmol) and propionic acid (2 drops) were dissolved in toluene (5 mL) and refluxed at 110 ˚C for 12 hrs. The toluene was

removed on a rotary evaporator, and the crude mixture was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:20) to afford **1c** (474 mg, 86% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ –0.05 (s, 9H), 1.23(t, *J* = 7.2 Hz, 3H), 1.94–1.99 (m, 1H), 2.27–2.36 (m, 4H), 2.64 (t, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 5.27–5.38 (m, 2H), 7.15–7.18 (m, 3H), 7.26 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –3.4, 14.3, 29.2, 34.4, 34.5, 36.4, 60.2, 125.7, 127.8, 128.2, 128.4, 130.2, 142.0, 173.7; **IR** (neat) ν 2954, 1734, 1248, 1179, 838 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{18}H_{28}O_2Si$ $[M]^+$ 304.1859, found 304.1903.

Synthesis of 2,3-*anti*-α-substituted-β-silyl-(*E*)-hex-4-enoates

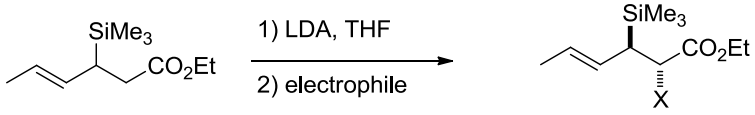


Table 1. Electrophilic Addition Reactions to β-Silyl Ester Enolates

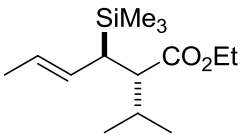
Entry	Electrophile	product			
		X	Yield (%)[a]	compd. no	ref
1	methyl iodide	Me	66	**1e**	3
2	benzyl bromide	$PhCH_2$	81	**1f**	5
3[b]	isopropyl iodide	*i*Pr	78	**1g**	
4	2,4,6-triisopropylbenzenesulfonyl azide	N_3	56		

[a] Yield refers to the quantity of diastereomerically pure 2,3-anti-α-substituted-β-silyl-(*E*)-hex-4-enoates isolated after column chromatography on silica gel. [b] Reaction was carried out with 20 % HMPA/THF (v/v).

Representative procedure for the alkylation of (*E*)-3-(trimethylsilyl)hex-4-enoate[6]

To a solution of diisopropylamine (2.1 mL. 12.0 mmol) in THF (9 mL) at 0 ˚C was added *n*-BuLi (7.5 mL , 12.0 mmol, 1.6M, in hexane) and the reaction was allowed to stir for 30 min. The solution was cooled to −78 ˚C and a solution of (*E*)-3-(trimethylsilyl)hex-4-enoate (2.1 g, 10 mmol) in THF (4.5 mL) was added via a syringe. The light yellow solution was stirred for 30 min. A solution of electrophile (12.0 mmol) in THF (2 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature and stir for 12 hrs. The reaction was quenched by the addition of a saturated solution of NH_4Cl at 0 ˚C. The aqueous phase was extracted with Et_2O (50 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by SiO_2 gel column chromatography afforded diastereomerically pure 2,3-*anti*-α-substituted-β-silyl-(*E*)-hex-4-enoate.

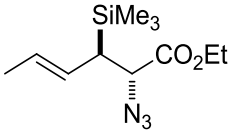
***anti*-(*E*)-Ethyl 2-isopropyl-3-(trimethylsilyl)hex-4-enoate (1g)**



(401 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ–0.07 (s, 9H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz,

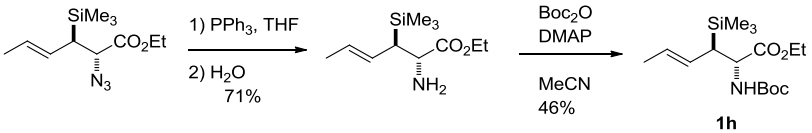
3H),1.26 (t, J = 7.2 Hz, 3H), 1.66 (dd, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 3H),1.90–2.02 (m, 2H), 2.39 (dd, J_1 = 12.0 Hz, J_2 = 4.4 Hz, 1H), 4.13 (m, 2H), 5.08 (ddd, J_1 = 15.2, J_2 = 11.2 Hz, J_3 = 1.6 Hz, 1H), 5.27–5.35 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –2.4, 14.3, 15.8, 18.1, 21.5, 29.0, 32.9, 50.5, 59.7, 124.4, 129.5, 174.3; **IR** (neat) ν 2960, 1730, 1248, 1144, 837 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{14}H_{28}O_2Si$ $[M]^+$ 256.1859, found 256.1861.

***anti*-(*E*)-Ethyl 2-azido-3-(trimethylsilyl)hex-4-enoate**



(288 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ –0.05 (s, 9H),1.28 (t, J = 7.2 Hz, 3H),1.66 (d, J = 5.2 Hz, 3H),2.08 (dd, J_1 = 9.2 Hz, J_2 = 6.0 Hz, 1H),3.96 (d, J = 6.0 Hz, 1H),4.13–4.28 (m, 2H), 5.25–5.43 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –2.6, 14.2, 18.1, 36.6, 61.5, 63.5, 125.6, 127.2, 170.5; **IR** (neat) ν 2959, 2102, 1741, 1248, 1192, 1096, 1030, 838 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{11}H_{21}N_3NaO_2Si$ $[M+Na]^+$ 278.1295, found 278.1292.

***anti*-(*E*)-Ethyl 2-[(*tert*-butoxycarbonyl)amino]-3-(trimethylsilyl)hex-4-enoate (1h)**



1h

To a solution of *anti*-(*E*)-ethyl 2-azido-3-(trimethylsilyl)hex-4-enoate (250 mg, 0.98 mmol) in THF (2.0 mL) was added PPh_3 (308 mg, 1.17 mmol) at room temperature. The reaction mixture was heated to 60 ˚C and stirred for 8 hrs. The reaction mixture was cooled to room temperature, distilled H_2O (1.0 mL) was added, and the solution was allowed to stir for 1 hr. The organic layer was separated, and the aqueous phase was extracted with Et_2O (2 × 10 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:2) afforded diastereomerically pure (*E*)-*anti*-ethyl 2-amino-3-(trimethylsilyl)hex-4-enoate(159 mg, 71 % yield) as a colorless oil.

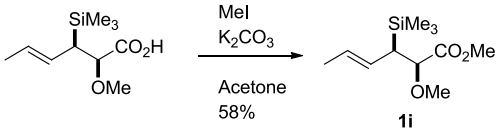
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1.25 (t, J = 7.3 Hz, 3H), 1.58 (br. s, NH_2) 1.66 (d, J = 4.5 Hz, 3H), 1.94 (dd, J_1 = 4.5 Hz, J_2 = 9.8 Hz, 1H), 3.56 (d, J = 4.5 Hz, 1H), 4.09–4.18 (m, 2H), 5.32–5.35 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –2.2, 14.4, 18.2, 38.4, 55.5, 60.6, 125.9, 126.7, 176.0; **IR** (neat) ν 2956, 1731, 1245, 1197, 1027, 959, 862, 836, 750, 691 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{11}H_{23}NO_2Si$ $[M]^+$ 229.1494, found 229.1498.

To a solution of (*E*)-*anti*-ethyl 2-amino-3-(trimethylsilyl)hex-4-enoate (110 mg, 0.48 mmol) in MeCN (3.0 mL) were successively added DMAP (6.1 mg, 0.05 mmol) and Boc_2O (132 μL, 0.58 mmol) at room temperature, and the reaction mixture was stirred for 10 hrs. The solvent was removed *in vacuo*, and the crude mixture was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane=1/10) to afford **1h** (72.8 mg, 46% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.25 (t, J = 7.3 Hz, 3H), 1.45 (s, 9H), 1.66 (dd, J_1 = 1.3 Hz, J_2 = 6.3 Hz, 3H), 2.00 (dd, J_1 = 4.1 Hz, J_2 = 10.4 Hz, 1H), 4.11–4.21 (m, 2H), 4.46 (dd, J_1 = 4.1 Hz, J_2 = 9.5 Hz, 1H), 4.99 (br. d,

J = 9.5 Hz, NH), 5.25 (dd, J_1 = 10.4 Hz, J_2 = 14.9 Hz, 1H), 5.36 (dq, J_1 = 6.3 Hz, J_2 = 14.9 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ –2.6, 14.3, 18.2, 28.3, 37.1, 54.1, 61.0, 79.7, 125.5, 127.5, 155.3, 172.8; **IR** (neat) ν 3400, 2900, 1740, 1687, 1535, 1365, 1348, 1250, 1200, 1167, 1097, 1030, 872, 839 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{16}H_{31}NNaO_4Si$ $[M+Na]^+$ 352.1911, found 352.1915.

***syn*-(*E*)-Methyl 2-methoxy-3-(trimethylsilyl)hex-4-enoate (1i)**

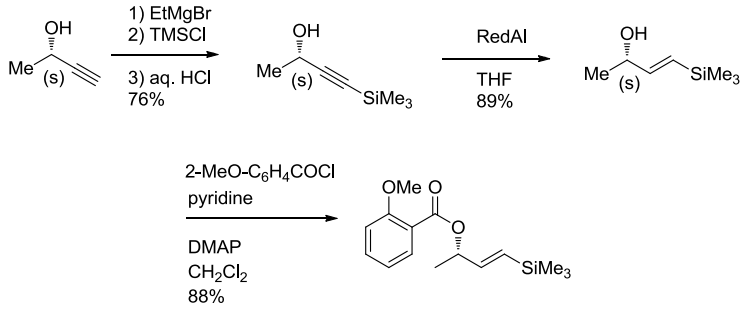


1i

To a solution of *syn*-(*E*)-2-methoxy-3-(trimethylsilyl)-4-hexenoic acid[6] (1.51 g, 7.0 mmol) in acetone (50.0 mL) were successively added K_2CO_3(1.93g, 14.0 mmol) and MeI (868 μL, 14.0 mmol) at room temperature, and the reaction mixture was stirred for 12 hrs. The reaction mixture was quenched with water, and then aqueous phase was extracted with Et_2O (50 mL). The organic phase was washed with water (50 mL) and brine (50 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane=1/10) afforded **1i** (675 mg, 58% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ –0.01 (s, 9H), 1.64 (d, J = 6.0 Hz, 3H), 2.02 (dd, J_1 = 10.0 Hz, J_2 = 8.8 Hz, 1H), 3.33 (s, 3H), 3.71 (s, 3H), 3.77 (d, J = 8.4 Hz, 1H), 5.19–5.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –2.00, 18.1, 38.1, 51.5, 57.9, 83.0, 125.6, 126.8, 173.12; **IR** (neat) ν 2954, 1740, 1436, 1247, 1197, 1114, 1100, 909, 838, 730 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{11}H_{26}NO_3Si$ $[M+NH_4]^+$ 248.1682, found 248.1682.

Preparation of optically active α-arylated allylsilanes



(*S*)-4-trimethylsilyl-but-3-yl-2-ol was prepared according to a literature procedure.[2]

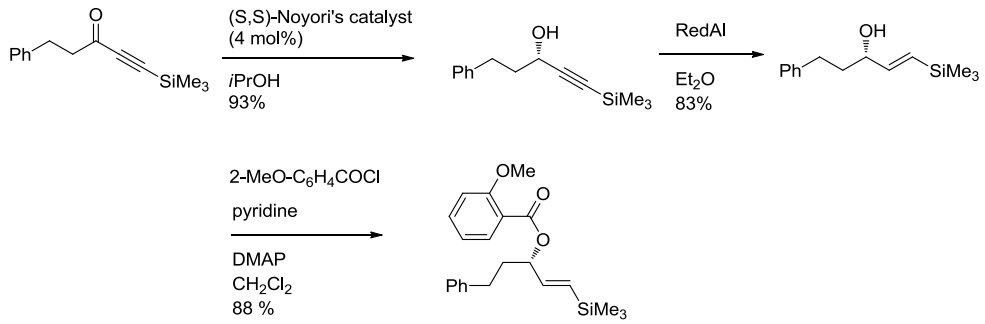
1.2M Grignard reagent in anhydrous Et_2O (70 mL) was first prepared from magnesium (2.1 g, 86 mmol) and ethyl bromide (9.3 g, 86 mmol). The resulting clear brown solution was cooled to 0 ˚C and a solution of (*S*)-but-3-yn-2-ol (3.0 g, 43 mmol) in anhydrous Et_2O (25 mL) was carefully added. A tar-like precipitate formed after approximately half of the alcohol had been added. Following completion of the addition, the reaction mixture was allowed to warm to room temperature and stand for 12 hrs. To the reaction mixture was then added trimethylsilylchloride (9.3 g, 86 mmol) at 0 ˚C. After stirring for 1 hr, a second equivalent of trimethylsilyl chloride (9.3 g, 86 mmol) was added, and the mixture was stirred at reflux for 12 hrs. The reaction mixture was allowed to cool to room temperature. To quench the reaction, the entire contents of reaction vessel were poured onto a beaker containing ice water (100 mL). The aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic

phases were washed with 2 N sulphuric acid (2 × 25 mL), saturated sodium bicarbonate solution (2 × 25 mL), water (25 mL) and brine (25 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford (*S*)-4-trimethylsilyl-but-3-yl-2-ol (4.6 g, 76% yield) as a yellow oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 0.18 (s, 9H), 3.77 (d, *J* = 8.4 Hz, 1H), 1.46 (d, *J* = 6.6 Hz, 3H), 2.46 (br. d, *J* = 2.1 Hz, OH), 4.52 (q, *J* = 6.6 Hz, 1H). Characterization data correspond to the literature.[2]

A solution of RedAl (17.1 mL, 65% solution in toluene, 56.2 mmol) was slowly added to (*S*)-4-trimethylsilyl-but-3-yl-2-ol (4.0 g, 28.1 mmol) in THF (40 mL) at 0˚C. The mixture was stirred at 0 ˚C for 4 hrs, and then quenched with 1 N HCl. The aqueous layer was extracted with Et_2O (2 × 20 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane=1/4) to afford (*S*, *E*)-4-trimethylsilyl-but-3-en-2-ol (3.6 g, 89% yield) as a pale yellow oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.27 (d, *J* = 6.5 Hz, 3H), 2.36 (s, OH), 4.29 (ddq, J_1 = 1.3 Hz, J_2 = 4.9, J_3 = 6.5 Hz, 1H), 4.33 (dd, J_1 = 1.3, J_2 = 18.7 Hz, 1H), 6.09 (dd, J_1 = 4.9, J_2 = 18.7 Hz, 1H). Characterization data correspond to the literature.[2]

(*S*, *E*)-4-trimethylsilyl-but-3-en-2-ol (1.4 g, 9.7 mmol) was dissolved in CH_2Cl_2 (20 mL). Pyridine (0.94 mL, 11.6 mmol), *o*-methoxybenzoyl chloride (1.73 mL, 11.6 mmol) and DMAP (59.2 mg, 0.49 mmol) were sequentially added at 0˚C. The mixture was allowed to warm to room temperature and stir for 3 hrs before being quenched with water. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo.* The crude residue was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:4) to afford (3*S*, 1*E*)-4-(trimethylsilyl)but-3-en-2-yl 2-methoxybenzoate (2.38g, 88% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.42 (d, *J* = 6.6 Hz, 3H), 3.9 (s, 3H), 5.57–5.63 (m, 1H), 5.97 (d, *J* = 18.7 Hz, 1H), 6.11 (dd, J_1 = 4.8 Hz, J_2 =18.7 Hz, 1H), 6.97–7.01 (m, 2H), 7.47 (dd, J_1 = 1.8 Hz, J_2 = 8.3 Hz, 1H), 7.82 (dd, J_1 = 1.8 Hz, J_2 = 8.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –1.4, 19.9, 55.9, 72.5, 112.0, 120.1, 120.6, 130.3, 131.4, 133.3, 144.8, 159.1, 165.3; **IR** (neat) ν 2955, 1725, 1601, 1491, 1464, 1437, 1294, 1246, 1129, 1074, 1025, 988, 835, 753 cm^{-1}; **HRMS** (ESI) *m/z* Calcd for $C_{15}H_{22}O_3NaSi$ $[M+Na]^+$ 301.1236, found 301.1230.

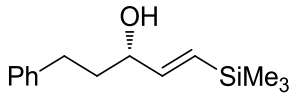


(*S*)-5-Phenyl-1-(trimethylsilyl)pent-1-yn-3-ol

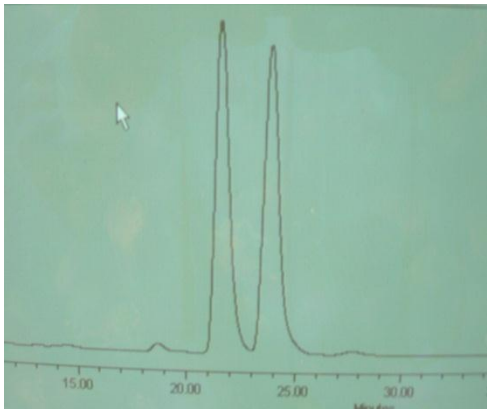
iso-Propanol (21 ml) was degassed for 10 min with argon and added to (*S*, *S*)-Noyori's catalyst (346 mg, 0.57 mmol)[7] giving a brown solution. Upon addition of 5-phenyl-1-(trimethylsilyl)pent-1-yn-3-one (2.25g, 9.77 mmol)

the solution turned a deep purple color that gradually changed to brown over time. The mixture was stirred under argon for 20 hrs at 30 ˚C and concentrated *in vacuo*. The crude residue was purified by SiO_2 gel chromatography (EtOAc/n-hexane = 95/5 to 90/10) to afford (*S*)-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-ol (2.0 g, 88% yield, 99% ee) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 0.20 (s, 9H), 1.84 (br. s, 1H), 1.95–2.11 (m, 2H), 2.81 (t, *J*= 7.8 Hz, 2H), 4.37 (t, *J* = 6.1 Hz, 1H), 7.18–7.25 (m, 3H), 7.28–7.33 (m, 2H). Characterization data correspond to the literature.[8]

(1*S*,2*E*)-5-Phenyl-1-(trimethylsilyl)pent-1-en-3-ol

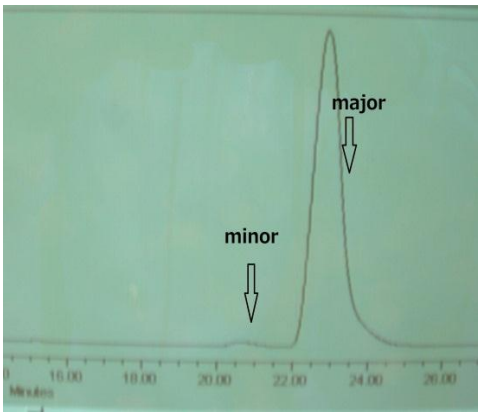


To a solution of RedAl (5.15 mL, 65% solution in toluene, 17.5 mmol) in Et_2O (10 ml) was slowly added a solution of (*S*)-4-trimethylsilyl-but-3-yl-2-ol (4.0 g, 28.1 mmol) in Et_2O (5 mL) at 0 ˚C. The mixture was stirred at 0 ˚C for 10 min and then at room temperature for 2 hrs, after which the mixture was quenched at 0 ˚C with 3.6N H_2SO_4 (40 ml). The aqueous layer was extracted with Et_2O (3 × 30 mL), and the combined organic layers were washed with water (30 mL) and brine (30 mL), then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 95/5 to 90/10) to afford (*S*, *E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-3-ol (1.95 g, 83%, 99% ee) as a pale yellow oil. Characterization were correspond to the literature.[4] The enantiomeric purity of (1*S*,2*E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-3-ol was determined by HPLC analysis: CHIRACEL® OJ-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 97:3, 0.3 min/mL, 25 ˚C, UV detector (220 nm), t_R (minor) = 20.6 min and t_R (major) = 22.7 min. $[\alpha]_D^{20}$ = +9.3 (c = 1.0, $CHCl_3$).



5-phenyl-1-(trimethylsilyl)pent-1-en-3-ol

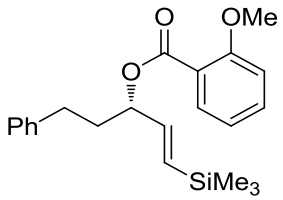
Time (min)	Area	%area
21.528	26221517	49.08
23.701	27209317	50.92



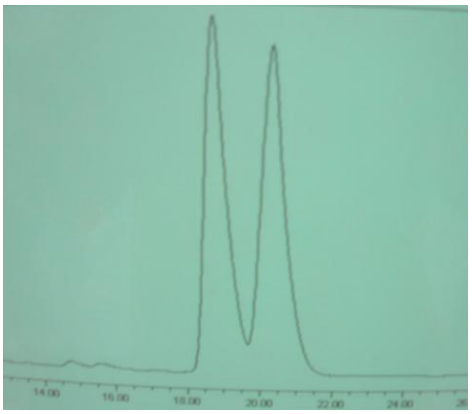
(1*S*,2*E*)- 5-phenyl-1-(trimethylsilyl)pent-1-en-3-ol

Time (min)	Area	%area
20.577	40282	0.44
22.678	9033395	99.56

(3*S*,1*E*)-5-Phenyl-1-(trimethylsilyl)pent-1-en-3-yl 2-methoxybenzoate

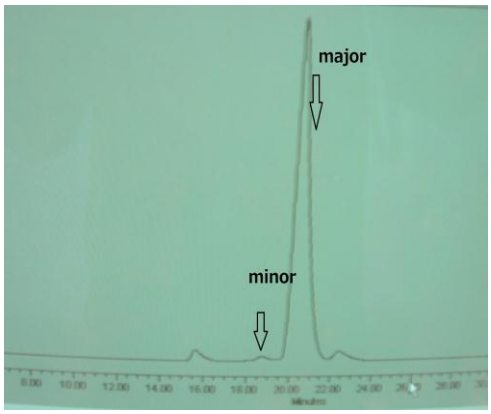


(*S*,*E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-3-ol (1.29 g, 5.5 mmol) was dissolved in CH_2Cl_2 (12 mL). Pyridine (1.31 mL, 16.5 mmol), *o*-methoxybenzoyl chloride (1.63 mL, 11.0 mmol) and DMAP (67.1 mg, 0.55 mmol) were sequentially added at 0 ˚C. The mixture was allowed to warm to room temperature and stir for 4 hrs before being quenched with water. The organic phase was separated, and the aqueous phase was extracted twice with CH_2Cl_2 (20 mL). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:9) to afford (*S*, *E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-3-yl 2-methoxybenzoate (1.78 g, 88% yield, 99% ee) as a colorless oil. Characterization data correspond to the literature.[4] The enantiomeric purity of (*S*,*E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-3-yl 2-methoxybenzoate was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 99:1, 0.4 min/mL, 25 ˚C, UV detector (210 nm), t_R (minor) = 18.72 min and t_R (major) = 20.24 min). $[\alpha]_D^{20}$ = +15.2 (c = 1.0, $CHCl_3$).



***rac*-benzoate derivative**

Time (min)	Area	%area
54.242	**10844960**	**49.86**
60.129	**10908247**	**50.14**

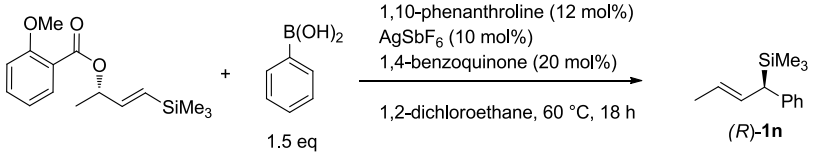


(*S*,*E*)-benzoate derivative

Time (min)	Area	%area
–	–	–
65.614	**13472478**	**>99**

***General Procedure (A) for palladium-catalyzed allyl–aryl coupling*[4]**

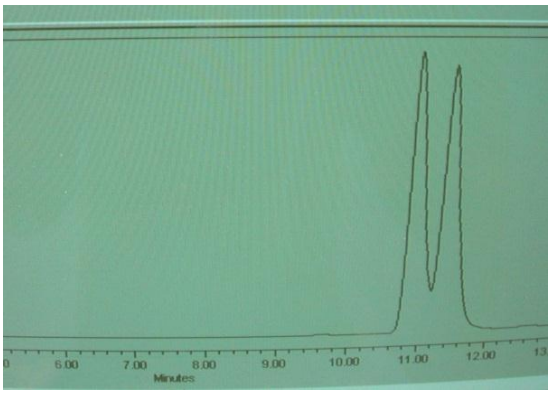
[(1*R*, 2*E*)-1-(trimethylsilyl)-2-buten-1-yl]-benzene (1n)



A 100 mL round bottom flask containing a magnetic stir bar was charged with $Pd(OAc)_2$ (121 mg, 0.54 mmol),

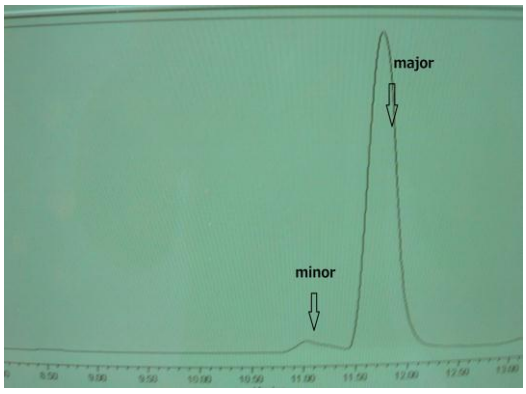
1,10-phenanthroline (117 mg, 0.65 mmol), $AgSbF_6$ (186 mg, 0.54 mmol) and 1,4-benzoquinone (117 mg, 1.08 mmol). 1,2-Dichloroethane (35 mL) was introduced and the mixture was sonicated at 25 ˚C for 1 min, then stirred at 25˚C for 3 min to give a yellow suspension. Phenylboronic acid (988 mg, 8.1 mmol) and (*S*, *E*)-4-(trimethylsilyl)but-3-en-2-yl 2-methoxybenzoate (1.5 g, 5.4 mmol) were sequentially added and the resulting mixture was heated at 60 ˚C for 18 hrs. After cooling to room temperature, the mixture was filtered through a short pad of silica gel then washed with Et_2O, and the filtrate was concentrated *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (*n*-hexane) to afford [(1*R*, 2*E*)-1-(trimethylsilyl)-2-buten-1-yl]-benzene (411 mg, 37% yield, 94% ee) as a colorless oil. The enantiomeric purity of (*R*)-**1n** was determined by HPLC analysis. CHIRACEL® OD-H column, 4.6 mm × 250 mm, *n*-hexane, 0.4 min/mL, 25 ˚C, UV detector (235 nm), t_R (minor) = 10.9 min and t_R (major) = 11.4 min. The absolute configuration at C-2 was assigned as *R* on the basis of the sign of the optical rotation, consistent with the corresponding data for the *R* compound previously reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 1.75 (d, *J* = 6.3 Hz, 3H), 2.92 (d, *J* = 9.8 Hz, 1H), 5.45 (dq, J_1 = 6.3, J_2 = 14.9 Hz, 1H), 5.84 (dd, J_1 = 9.6 Hz, J_1 = 14.9 Hz, 1H), 7.10–7.15 (m, 3H), 7.27–7.31 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –3.0, 18.1, 42.8, 123.5, 124.4, 127.1, 128.2, 130.2, 143.2; **IR** (neat) ν 2958, 1493, 1247, 1084, 964, 861, 833, 762, 741, 698 cm^{-1}; **HRMS** (EI) *m/z* Calcd for $C_{13}H_{20}Si$ $[M]^+$ 204.1329, found 204.1334. $[\alpha]_D^{20}$ = –40.1 (c = 2.0, $CHCl_3$).



rac-1n

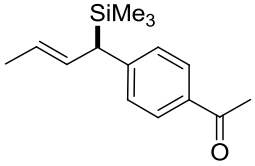
Time (min)	Area	%area
10.918	13041423	49.82
11.386	13136761	50.18



(*R*)-1n

Time (min)	Area	%area
11.029	1744541	3.35
11.672	50289489	96.65

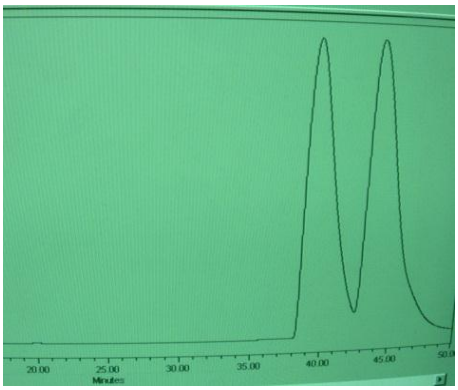
(1*R*,2*E*)-1-[4-(1-(trimethylsilyl)but-2-en-1-yl]phenyl)ethanone (1o)



(1*R*,2*E*)-1-[4-(1-(trimethylsilyl)but-2-en-1-yl]phenyl)ethanone was prepared according to the general procedure (A) using $Pd(OAc)_2$ (80.8 mg, 0.36 mmol), 1,10-phenanthroline (77.6 mg, 0.43 mmol), $AgSbF_6$ (123.4 mg, 0.35 mmol), 1,4-benzoquinone (117 mg, 1.08 mmol), 4-acethylphenylboronic acid (882 mg, 5.39 mmol), (*S*,

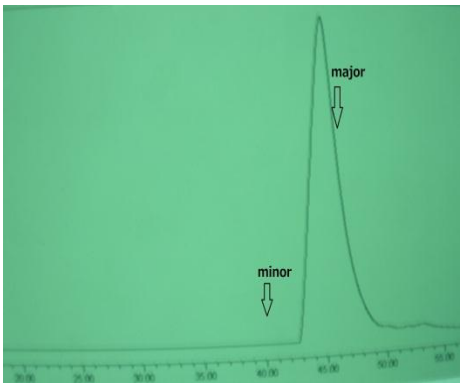
E)-4-(trimethylsilyl)but-3-en-2-yl 2-methoxybenzoate (1.0 g, 3.59 mmol) and 1,2-dichloroethane (24.0 mL). After 24 hrs, the reaction mixture was subjected to the workup described in the general procedure (A) and purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:10) to afford (*R*,*E*)-1-[4-(1-(trimethylsilyl)but-2-en-1-yl)phenyl]ethanone **1o** (369 mg, 41% yield, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 9H), 1.72 (d, J = 6.6 Hz, 3H), 2.57 (s, 3H), 3.00 (d, J = 9.8 Hz, 1H), 5.40–5.48 (m, 1H), 5.81 (dd, J_1 = 10.1, J_2 = 14.6 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –3.1, 18.1, 26.4, 43.6, 124.4, 127.0, 128.5, 128.9, 133.7, 149.6, 197.8; **IR** (neat) ν 2958, 1679, 1601, 1414, 1358, 1269, 1247, 1179, 965, 836, 748, 692 cm^{-1}; **HRMS** (ESI+) *m/z* Calcd for $C_{15}H_{22}OSi$ $[M]^+$ 269.1335, found 269.1332; $[\alpha]_D^{20}$ = –56.0 (c = 1.0, MeOH). The enantiomeric purity of (*R*)-**1o** was determined by HPLC analysis. CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane, 0.5 min/mL, 25 ˚C, UV detector (254 nm), t_R (minor) = 39.3 min and t_R (major) = 43.9 min.



***rac*-1o**

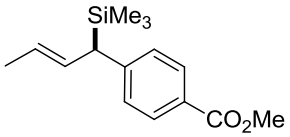
Time (min)	Area	%area
39.317	**44715854**	**48.52**
43.633	**47450135**	**51.48**



(*R*)-1o

Time (min)	Area	%area
–	–	–
43.865	**69504196**	**>99**

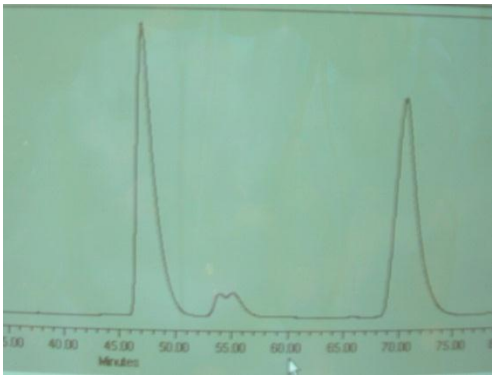
(1*R*,2*E*)-Methyl 4-[1-(trimethylsilyl)but-2-en-1-yl]benzoate (1p)



(1*R*,2*E*)-methyl 4-[1-(trimethylsilyl)but-2-en-1-yl]benzoate was prepared according to the general procedure (A) using $Pd(OAc)_2$ (44.8 mg, 0.20 mmol), 1,10-phenanthroline (43.2 mg, 0.24 mmol), $AgSbF_6$ (68.7 mg, 0.20 mmol), 1,4-benzoquinone (43.2 mg, 0.40 mmol), 4-methoxycarbonylphenylboronic acid (540 mg, 3.0 mmol), (*S*, *E*)-4-(trimethylsilyl)but-3-en-2-yl 2-methoxybenzoate (560 mg, 3.0 mmol) and 1,2-dichloroethane (12.0 mL). After 18 hrs, the reaction mixture was subjected to the workup described in the general procedure (A) and purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1/15) followed by kugelrohr distillation (oven temp. 120 ˚C, < 1.0 mmHg) to afford (*R*, *E*)-methyl 4-(1-(trimethylsilyl)but-2-en-1-yl)benzoate **1p** (200 mg, 38% yield, 99% ee) as a colorless oil.

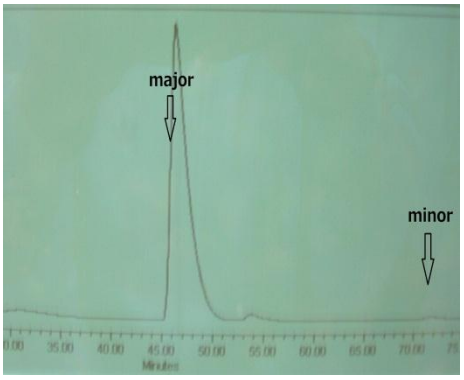
^{1}H NMR (500 MHz, $CDCl_3$) δ –0.08 (s, 9H), 1.72 (dd, J_1 = 1.1 Hz, J_2 = 6.5 Hz, 3H), 2.98 (d, J = 10.1 Hz, 1H),

3.90 (s, 3H), 5.44 (ddq, J_1 = 0.7 Hz, J_2 = 6.5 Hz, J_3 = 15.0 Hz, 1H), 5.81 (ddq, J_1 = 1.4 Hz, J_2 = 10.1 Hz, J_3 = 15.0 Hz, 1H), 7.12 (m, 2H), 7.93 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ –3.1, 18.9, 45.5, 51.9, 124.4, 126.3, 126.9, 129.0, 129.6, 149.2, 167.3; **IR** (neat) ν 2953, 1721, 1278, 838 cm^{-1}; **HRMS** (CI+) *m/z* Calcd for $C_{15}H_{23}O_2Si$ $[M+H]^+$ 263.1467, found 263.1475. $[\alpha]_D^{20}$ = –36.5 (c = 1.0, $CHCl_3$). The enantiomeric purity of (*R*)-**1p** was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane, 0.5 min/mL, 25 ˚C, UV detector (254 nm), t_R (major) = 45.9 min and t_R (minor) = 53.7 min.



rac-1p

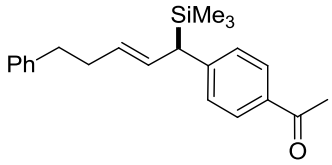
Time (min)	Area	%area
46.816	53475496	50.04
69.521	53396720	49.96



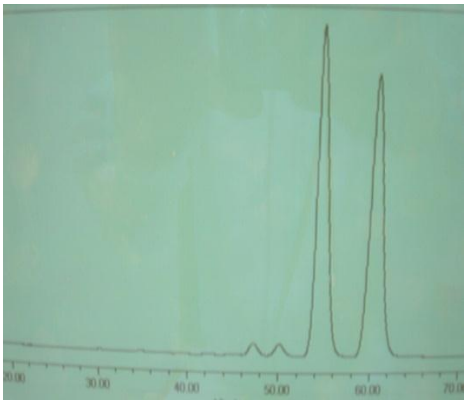
(*R*)-1p

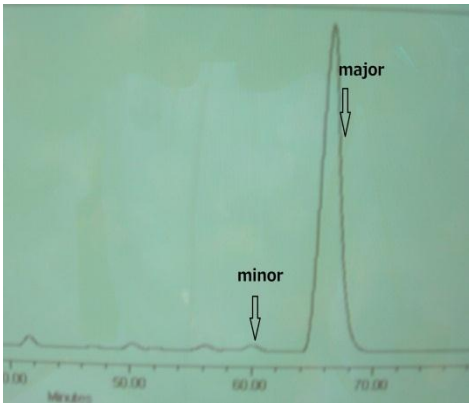
Time (min)	Area	%area
45.942	27257018	99.25
70.681	205629	0.75

(1*R*,2*E*)-1-[4-[5-phenyl-1-(trimethylsily)pent-2-en-1yl]phenyl]ethanone (1q)



(1*R*,2*E*)-**1q** was prepared according to the general procedure (A) using $Pd(OAc)_2$ (67.4 mg, 0.30 mmol), 1,10-phenanthroline (64.9 mg, 0.36 mmol), $AgSbF_6$ (103 mg, 0.30 mmol), 1,4-benzoquinone (64.8 mg, 0.60 mmol), 4-acethylphenylboronic acid (738 mg, 4.5 mmol), (*S*,*E*)-5-phenyl-1-(trimethylsilyl)pent-1-en-3-yl 2-methoxybenzoate (1.11 g, 3.0 mmol) and 1,2-Dichloroethane (20.0 mL). After 24 hrs, the reaction mixture was subjected to the workup described in the general procedure (A) and purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:10) to afford **1q** (500 mg, 50% yield) as a colorless oil. Characterization data correspond to the literature.[4] $[\alpha]_D^{20}$ = –24.2 (c = 0.50, MeOH). The enantiomeric purity of (*R*,*E*)-**1q** was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane/ *i*-PrOH = 99:1, 0.5 min/mL, 25 ˚C, UV detector (254 nm), t_R (minor) = 54.2 min and t_R (major) = 65.6 min.





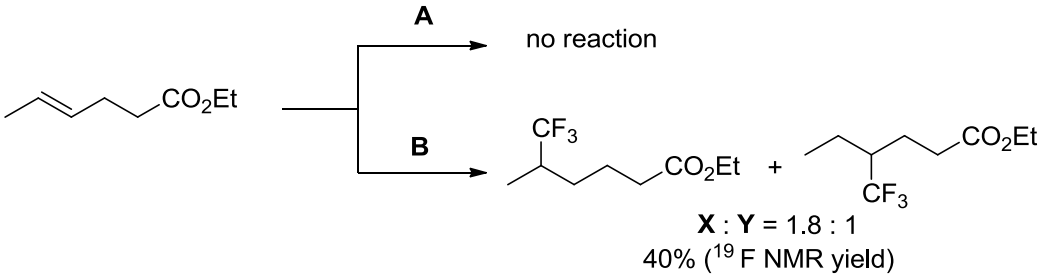
rac-1q

Time (min)	Area	%area
54.242	**10844960**	**49.86**
60.129	**10908247**	**50.14**

(*R*)-1q

Time (min)	Area	%area
–	–	–
65.614	**13472478**	**>99**

3-2. Control Experiments: Trifluoromethylation of (*E*)-Ethyl hex-4-enoate



A : 20 mol% CuCl, 1.2 equiv **I**, MeOH, 70 ºC, 2 h
B : 5 mol%, $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 14W light bulb, 1.8 equiv **I**, MeOH, RT, 24 h

(*E*)-Ethyl hex-4-enoate (21.3 mg, 0.15 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (5.6 mg, 0.0075 mmol), Togni reagent (85.3 mg, 0.27 mmol) and MeOH (0.5 mL) were placed in a vial which was equipped with a magnetic stir bar, and sealed with a cap. The vial was exposed to visible light at room temperature while stirring for 24 hrs. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with Et_2O (× 2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. Products, ethyl 6,6,6-trifluoro-5-methylhexanoate **X** and ethyl 4-(trifluoromethyl)hexanoate **Y** were identified by GC/MS. The yield and ratio were determined by ^{19}F NMR spectroscopy of the crude mixture using benzotrifluoride as an internal standard (40%, ratio **X**:**Y** = 1.8:1).

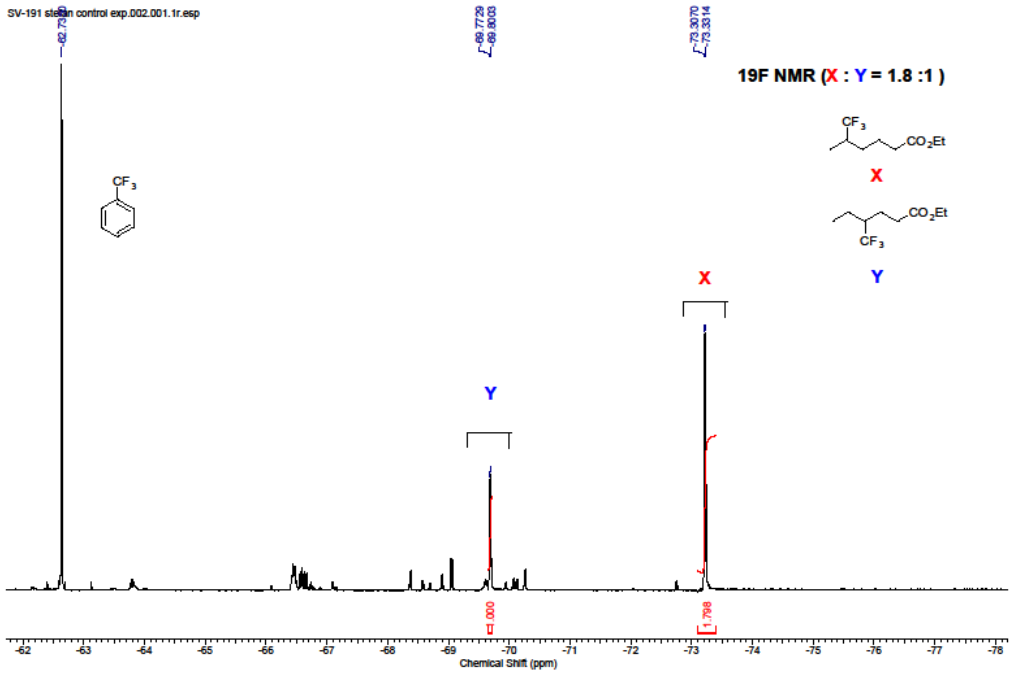
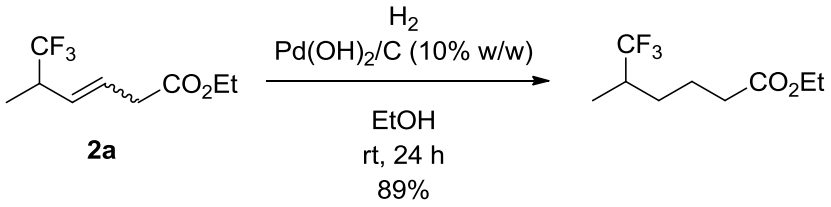


Figure 1. ^{19}F NMR spectra of the crude mixture when using conditions B (377 MHz, $CDCl_3$, ratio **X**:**Y** = 1.8:1)

Ethyl 6,6,6-trifluoro-5-methylhexanoate was prepared by an alternative method shown in the scheme below.

Ethyl 6,6,6-trifluoro-5-methylhexanoate



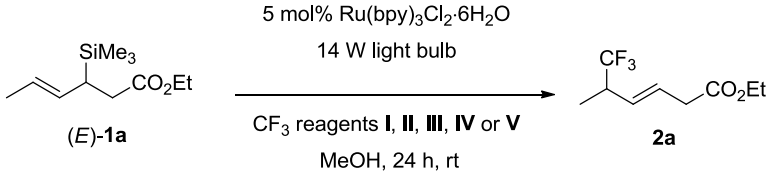
Ethyl 6,6,6-trifluoro-5-methylhex-3-enoate **2a** (30.0 mg, 0.14 mmol), 10% w/w $Pd(OH)_2/C$ (10.0 mg) and EtOH (1.0 mL) were added to a reaction flask. The flask was sealed, and the air was substituted with H_2 using two vacuum/H_2 balloon cycles, and the mixture was stirred for 20 hrs. The reaction mixture was filtered through a Celite pad and washed with EtOH (5.0 mL). The filtrate was concentrated *in vacuo* to afford the title compoud (27.0 mg, 89% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (d, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.32–1.39 (m, 1H), 1.59–1.82 (m, 3H), 2.10–2.20 (m, 1H), 2.31–2.34 (m, 2H), 4.14 (q, *J* = 7.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 12.6 (q, *J* = 2.9 Hz), 14.2, 22.0, 28.8 (q, *J* = 2.9 Hz), 34.0, 37.7 (q, *J* = 26.5 Hz), 60.4, 128.3 (q, *J* = 277.7 Hz), 173.1; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.28 (d, *J* = 9.2 Hz, 3F); **IR** (neat) ν 2986, 1734, 1469, 1374, 1264, 1164, 1127, 1025, 847 cm^{-1}; **HRMS** (FI/EI) *m/z* Calcd for $C_9H_{15}F_3O_2$ $[M]^+$ 212.1026, found 212.1024.

Characterization data for **Y**: **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –69.78 (d, *J* = 9.2 Hz, 3F)

3-3. Optimization of Reaction Conditions

Optimization for the photocatalyzed trifluoromethylation of (*E*)-ethyl 3-(trimethylsilyl)hex-4-enoate[a]



Entry	"CF_3" (equiv)	Cond.	Solvent	Time (h)	Conv. (%)[b]	Yield (%)[b](*E : Z*)
1	I (1.2)	CuCl (20 mol%), 70 ˚C	MeOH	2 h	91	5 (1.4 : 1)
2	I (1.2)	no catalyst	MeOH	24	<5	NR
	I (1.2)	no light	MeOH	24	<5	NR
3	I (1.2)		MeOH	24	45	27 (2.5 : 1)
4	**I (1.8)**		**MeOH**	**48**	**90**	**55 (1.7 : 1)**
5	I (1.8)	2 mol% of Ru	MeOH	48	86	47 (1.7 : 1)
6	I (1.2)	*i*Pr_2NEt (2.0 eq)	MeOH	24	30	ND
7	I (1.2)		EtOH	24	55	30 (2.0 : 1)
8	I (1.2)		MeCN	24	18	17 (2.2 : 1)
9	I (1.2)		CH_2Cl_2	24	42	22 (1.7 : 1)
10	I (1.2)		DMF	24	89	37 (1.8 : 1)
11	II (1.2)		MeOH	24	<5	3 (3.8 : 1)
12	II (1.2)		MeCN	24	<5	NR
13	II (1.2)		DMF	24	<5	NR
14	III (1.2) OTf		MeOH	24	82*	30[c]*(5.3: 1)
15	III (1.2) OTf	*i*Pr_2NEt (2.0 eq)	MeOH	24	<5	NR
16	III (1.2) OTf		EtOH	24	53	34[c] (4.3 : 1)
17	III (1.2) OTf		MeCN	24	>99	7 (8.0 : 1)
18	III (1.2) OTf		DMF	24	76	33 (5.4 : 1)
19	**III (1.8) OTf**		**EtOH**	**48**	**43**	**38[c] (3.4 : 1)**
20	III (1.2) BF4		MeOH	24	75*	34* (4 : 1)
21[d]	IV (10)		MeOH	24	<5	NR
22[d]	IV (10)	*i*Pr_2NEt (2.0 eq)	MeOH	24	48	44 (1 : 1.5)
23[d]	IV (10)	*i*Pr_2NEt (2.0 eq)	DMF	24	49	41 (1 : 1.1)
24	IV (10)	*i*Pr_2NEt (2.0 eq)	MeCN	24	51	42 (1 : 1.2)
25	V (1.2)		MeOH	24	48*	17* (4.2 : 1)
26	V (1.2)		DMF	24	66	10 (3.0 : 1)
27	V (1.2)		MeCN	24	<5	2 (3.2 : 1)
28	I (1.2)	CuCl (20 mol%)+Ru	MeOH	24	64	34 (1.7 :1)

[a] **1a** (0.15mmol, 1.0 equiv), **I** (0.18 mmol, 1.2 equiv), $Ru(bpy)_3Cl_2$ $6H_2O$ (0.0075 mmol, 5 mol%), in MeOH(0.3mL) at

rt for 24 h. [b] Determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c] Isolated yield.[d] **1a** (0.3 mmol, 1 eq), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.015 mmol, 5 mol%), in MeOH (0.6mL) at rt for 24 h. *transesterification of **1a** and **2a**.

3-4. General Procedure: Trifluoromethylation of Allylsilanes

General procedure for trifluoromethylation of allylsilanes under copper catalysis: Conditions A

A 5 mL vial containing a magnetic stir bar was charged with allylsilane (0.25 mmol) and CuCl (5.0 mg, 20 mol%). MeOH (0.5 mL), additive (0.5 mmol) and Togni reagent (0.3–0.5 mmol) were added under Ar atmosphere. The reaction mixture was stirred for 2 hrs at 70 ˚C. Upon completion of the reaction, sat. aq. $NaHCO_3$ was added at room temperature. The resulting mixture was extracted with Et_2O (× 2) and the combined organic phases were washed sequentially with distilled water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography on SiO_2 gel using the indicated solvent system gave the desired CF_3 allylic product.

General procedure for trifluoromethylation of allylsilanes with Togni trifluoromethylating reagent under photocatalysis: Conditions B

Allylsilane (0.25 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (9.4 mg, 0.0125 mmol, 5.0 mol%), Togni reagent **I** (0.45 mmol, 1.8 eq) and MeOH (0.5 mL) were placed in a vial which was equipped with a magnetic stir bar. The vial was exposed to a 14 W fluorescent light bulb at room temperature while stirring for 48 hrs. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with Et_2O (× 2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture. Purification by column chromatography on SiO_2 gel using the indicated solvent system gave the desired CF_3 allylic product.

General procedure for trifluoromethylation of allylsilane with Umemoto's trifluoromethylating reagent under photocatalysis: Conditions C

Allylsilane (0.25 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (9.4 mg, 0.0125 mmol, 5.0 mol%), Umemoto reagent **III** (0.45 mmol, 1.8 eq) and EtOH (0.5 mL) were placed in a vial which was equipped with a magnetic stir bar. The vial was exposed to a 14 W fluorescent light bulb at room temperature while stirring for 24 hrs. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with Et_2O (× 2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture. Purification by column chromatography on SiO_2 gel using the indicated solvent system gave the desired CF_3 allylic product.

Methyl 6,6,6-trifluoro-5-methylhex-3-enoate

Prepared following conditions C using allylsilane (**1a**) (32.2 mg, 0.15 mmol), the Umemoto reagent **III** (108.6 mg, 0.27 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (5.6 mg, 0.0075 mmol,) and MeOH (0.3 mL). The isomeric ratio was determined

by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 5.3). Purification by column chromatography on silica gel (EtOAc/*n*-hexane = 1/15) provided the title compound (8.9 mg, 30% yield, *E/Z* ratio 5.6) as a colorless oil.

Characterization data for the *E/Z* mixtures of methyl 6,6,6-trifluoro-5-methylhex-3-enoate (*E/Z* ratio 5.6)

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.3 Hz, 0.5H), 1.23 (d, *J* = 7.3 Hz, 2.5H), 2.81–2.93 (m, 1H), 3.09–3.16 (m, 2H), 3.71 (s, 2.5H), 3.71 (s, 0.5H), 5.48 (d, *J* = 10.7 Hz, 0.17H), 5.53 (dd, J_1 = 7.6 Hz, J_2 = 15.6 Hz, 0.83H), 5.81 (dt, J_1 = 7.3 Hz, J_2 = 15.6 Hz, 0.83H), 5.85 (dt, J_1 = 7.3 Hz, J_2 = 10.7 Hz, 0.17H); **^{13}C NMR** (125 MHz, $CDCl_3$) for (*E*)-isomer δ 13.3 (q, *J* = 2.8 Hz), 26.9, 37.6, 41.4 (q, *J* = 27.5 Hz), 51.9, 126.8, 127.0 (q, *J* = 277.7 Hz), 128.6 (q, *J* = 2.9 Hz), 171.7; For (*Z*)-isomer δ 13.9 (q, *J* = 2.9 Hz), 29.7, 32.9, 37.0 (q, *J* = 27.4 Hz), 52.0, 125.7, 127.1 (q, *J* = 277.7 Hz), 127.9 (q, *J* =2.8 Hz), 171.3; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.8 (d, *J* = 9.2 Hz, 2.5F), –72.6 (d, *J* = 8.1 Hz, 0.5F).

Note: This compound is volatile, complete evaporation *in vacuo* (<10 mmHg) after 10 min.

Ethyl 6,6,6-trifluoro-5-methylhex-3-enoate (2a)

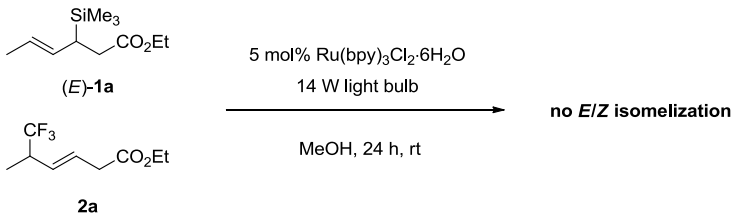
Conditions B: Allylsilane (**1a**) (53.4 mg, 0.25 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 1.7). Purification by column chromatography on SiO_2 gel (EtOAc/*n*-hexane = 1/15) provided **2a** (28.9 mg, 55% yield, *E/Z* ratio 2.3) as a colorless oil.

Conditions C: Allylsilane (**1a**) (53.4 mg, 0.25 mmol), Umemoto reagent **III** (181.0 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and EtOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 3.4). Purification by SiO_2 gel column chromatography provided **2a** (18.0 mg, 34% yield, *E/Z* = 5.2)

Characterization data for the *E/Z* mixtures of ethyl 6,6,6-trifluoro-5-methylhex-3-enoate (*E/Z* ratio 2.3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.1 Hz, 0.9H), 1.27 (t, *J* = 7.1 Hz, 2.1 H), 2.82–2.96 (m, 1H), 3.08–3.14 (m, 2H), 4.16 (q, *J*= 7.1 Hz, 1.4 H), 4.16 (q, *J* = 7.1 Hz, 0.6H), 5.47 (d, *J* = 10.8 Hz, 0.3H), 5.53 (dd, J_1 = 7.6 Hz, J_2 = 15.6 Hz, 0.7H), 5.82 (dt, J_1 = 7.1 Hz, J_2 = 15.6 Hz, 0.7H), 5.85 (dt, J_1 = 7.3 Hz, J_2 = 10.7 Hz, 0.17H); **^{13}C NMR** (125MHz, $CDCl_3$) for (*E*)-isomer, *δ* 13.5 (q, *J* = 2.8), 14.1, 17.2, 41.4 (q, *J* = 27.5 Hz), 42.8, 60.7, 126.2 (q, *J* = 2.9 Hz), 127.0 (q, *J* = 277.7 Hz), 134.0, 174.2; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.8 (d, *J* = 9.2 Hz, 2.1F), –72.6 (d, *J* = 8.0 Hz, 0.9F); **IR** (neat) ν 2989, 1726, 1464, 1260, 1169, 1124, 1018, 972cm^{-1}; **HRMS** (FI/EI) *m/z* Calcd for $C_9H_{13}F_3O_2$ $[M]^+$ 210.0862, found 210.0868.

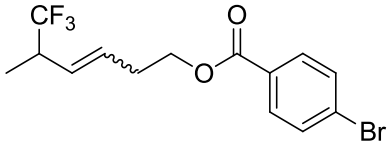
Note: This compound is volatile, complete evaporation *in vacuo* (<10 mmHg) after 10 min.



No *E/Z* isomerization of allylsilane (*E*)-**1a** or **2a** (*E/Z* ratio =1.7) with visible light irradiation in the presence of

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ (5 mol%) was observed.

(*E*)-6,6,6-Trifluoro-5-methylhex-3-en-1-yl-4-bromobenzoate (2b)

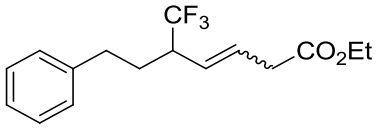


Conditions B: Allylsilane (**1b**) (83.3 mg, 0.25 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 5.8). Purification by column chromatography on SiO_2 gel (EtOAc/*n*-hexane=1/40) provided the title compound (**2b**) (40.6 mg, 46% yield, *E/Z* ratio 7.0) as a colorless oil.

Conditions C: Allylsilane (**1a**) (83.3 mg, 0.25 mmol), Umemoto reagent **III** (181.0 mg, 0.45 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (9.4 mg, 0.0125 mmol) and EtOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 11). Purification by SiO_2 gel column chromatography provided **2b** (22% yield, *E/Z* ratio 12)

Characterization data for (*E*)-isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.20 (d, J = 7.0 Hz, 3H), 2.53 (q, J = 6.6 Hz, 2H), 2.80–2.91 (m, 1H), 4.33–4.40 (m, 2H), 5.54 (dd, J_1 = 7.9 Hz, J_2 = 15.6 Hz, 1H), 5.72 (dt, J_1 = 6.6 Hz, J_2 = 15.6 Hz, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.5 (q, J =1.9 Hz), 32.0, 41.5 (q, J = 27.5 Hz), 63.8, 127.1 (q, J = 277.7 Hz), 127.9 (q, J = 1.9 Hz),128.1, 129.1, 130.5, 131.1, 131.7, 165.8; **^{19}F NMR** (377 MHz, $CDCl_3$) for (*E*)-isomer, δ –72.64 (d, J = 9.2 Hz, 3F); **IR** (neat) ν 2990, 1720, 1591, 1461, 1398, 1266, 1172, 1116, 1101, 1068, 1102, 968, 847, 756 cm^{-1}; **HRMS** (FI/EI) *m/z* Calcd for $C_{14}H_{14}BrF_3O_2$ $[M]^+$ 350.0122, found 350.0129.

Ethyl 7-phenyl-5-(trifluoromethyl)hept-3-enoate (2c)



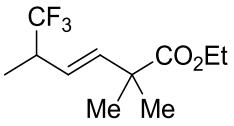
Allylsilane(**1c**) (76.2 mg, 0.25 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (9.4 mg, 0.0125mmol), Togni reagent **I** (118.5 mg, 0.375 mmol, 1.5 eq) and MeOH (0.5 mL) were placed in a vial, which was equipped with a magnetic stir bar. The vial was placed approximately 5cm from a 14 W fluorescent light bulb and exposed to visible light at room temperature. After stirring for 1.5 days, another portion of Togni reagent **I** (118.5 mg, 0.375 mmol, 1.5 eq) was added and the reaction was stirred for an additional 1.5 days. The reaction mixture was quenched with sat. aq. $NaHCO_3$, the aqueous phase was extracted with Et_2O (×2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 1.4). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1:20) gave **2c** (47.2 mg, 63% yield, *E/Z* ratio 1.5) as a colorless oil.

Conditions C: Allylsilane (**1c**) (76.2 mg, 0.25 mmol), Umemoto reagent **III** (181.0 mg, 0.45 mmol), $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (9.4 mg, 0.0125 mmol) and EtOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR

analysis of the crude mixture (*E/Z* ratio 3.3). Purification by SiO_2 gel column chromatography provided **2c** (32.6 mg, 43% yield, *E/Z* ratio 2.5).

Characterization data for the *E/Z* mixture of **2c** (*E/Z* ratio 1.5): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.3 Hz, 1.2H), 1.29 (t, *J* = 7.0 Hz, 1.8H), 1.76–1.83 (m, 1H), 2.05–2.17 (m, 1H), 2.50–2.59 (m, 1H), 2.69–2.80 (m, 1.6H), 2.92–2.99 (m, 0.4H), 3.02 (dd, J_1= 1.9 Hz, J_2 = 7.6 Hz, 0.8H), 3.15 (d, *J* = 6.6 Hz, 1.2H), 4.15–4.21 (m, 2H), 5.41–5.47 (m, 1H), 5.83 (dd, J_1 = 7.3 Hz, J_2 = 14.8 Hz, 0.6H), 6.02 (dd, J_1 = 7.2 Hz, J_2 = 11.1 Hz, 0.4H), 7.15–7.23 (m, 3H), 7.28–7.32 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.1, 14.2, 29.1 (q, *J* = 1.9 Hz), 29.5 (q, *J* = 1.9 Hz), 32.2, 33.3, 37.9, 41.5 (q, *J* = 26.5 Hz), 46.6 (q, *J* = 26.5 Hz), 60.8, 60.9, 126.0 (q, *J* = 1.9 Hz), 126.2, 126.3, 126.7 (q, *J* =278.6 Hz), 127.1 (q, *J* = 1.9 Hz), 128.3, 128.4, 128.4, 128.5, 128.5, 129.4, 140.5, 140.7, 170.8, 171.1; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.65 (d, *J* = 9.2 Hz, 1.8F), –70.95 (d, *J* = 9.2 Hz, 1.2F); **IR** (neat) ν 2936, 1737, 1255, 1161, 1115, 974 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{16}H_{19}F_3NaO_2$ $[M+Na]^+$ 323.1221, found 323.1229.

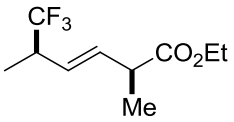
(*E*)-Ethyl 6,6,6-trifluoro-2,2,5-trimethylhex-3-enoate (2d)



Conditions B: Allylsilane (**1d**) (121.2 mg, 0.50 mmol), Togni reagent **I** (284.4 mg, 0.90 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (18.8 mg, 0.025 mmol) and MeOH (1.0 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 14). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1/50) provided **2d** (59.2 mg, 69% yield, *E/Z* ratio >20) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (d, *J* = 6.9 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.30 (s, 6H), 2.79–2.91 (m, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 5.43 (dd, J_1 = 7.9 Hz, J_2 =15.8 Hz, 1H), 5.89 (d, *J* = 15.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.5 (q, *J* = 1.9 Hz), 14.1, 24.7, 24.9, 41.5 (q, *J* = 27.2 Hz), 44.1, 60.8, 123.1 (q, *J* = 2.9 Hz), 127.2 (q, *J* = 277.7 Hz), 139.5, 176.0; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.87 (d, *J* = 8.0 Hz, 3F); **IR** (neat) ν 2985, 1731, 1464, 1386, 1258, 1127, 1019, 972, 864 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{11}H_{17}F_3NaO_2$ $[M+Na]^+$ 261.1083, found 261.1073.

***syn*-(*E*)-Ethyl 6,6,6-trifluoro-2,5-dimethylhex-3-enoate (2e)**



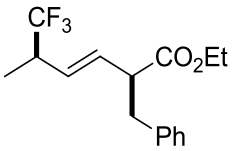
Conditions B: Allylsilane (**1e**) (57.1 mg, 0.25 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 7.0, *syn*:*anti*(*E*) = 15). Purification by column chromatography on SiO_2 gel (EtOAc/*n*-hexane = 1/20 to 1/10) provided **2e** (36.2 mg, 65% yield, *E/Z* ratio 15, *syn*:*anti*(*E*) = 7.4) as a colorless oil.

Conditions C: Allylsilane (**1e**) (57.1 mg, 0.25 mmol), Umemoto reagent **III** (181.0 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and EtOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*:*anti* (*E*) = 6.1, *E/Z* ratio >20). Purification by SiO_2 gel column chromatography

provided **2e** (18.5 mg, 33% yield, *syn*:*anti* (*E*) = 6.4, *E/Z* ratio >20)

Characterization data for *syn*-(*E*)-**2e**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.3 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.28 (d, *J* = 7.0 Hz, 3H), 2.80–2.91 (m, 1H), 3.11–3.17 (m, 1H), 4.14 (q, *J* = 7.3 Hz, 1H), 4.15 (q, *J* = 7.3 Hz, 1H), 5.49 (dd, J_1 = 7.9 Hz, J_2 =15.5 Hz, 1H), 5.78 (dd, J_1 = 7.9 Hz, J_2 =15.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.4 (q, *J* = 2.8 Hz), 14.1, 17.2, 41.4 (q, *J* = 27.5 Hz), 42.8, 60.7, 126.2 (q, *J* = 2.8 Hz), 127.0 (q, *J* = 277.7 Hz), 134.0, 173.2; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.90 (d, *J* = 9.2 Hz, 3F); **IR** (neat) ν 2985, 1734 1462, 1260, 1174, 1129, 1073, 1015, 970 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{10}H_{15}F_3O_2$ $[M]^+$ 224.1027, found 224.1024.

syn-(_E_)-Ethyl 2-benzyl-6,6,6-trifluoro-5-methylhex-3-enoate (2f)

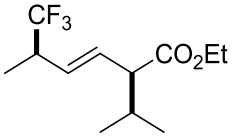


Conditions B: Allylsilane (**1f**) (76.1 mg, 0.25 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*:*anti*(*E*) = 10, *E/Z* ratio 15). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane=1/20) provided the title compound (**2f**) (62.6 mg, 83% yield, *syn*:*anti*(*E*) = 9.0, *E/Z* ratio 19) as a colorless oil.

Conditions C: Allylsilane (**1f**) (76.1 mg, 0.25 mmol), Umemoto reagent **III** (181.0 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and EtOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*:*anti*(*E*) = 8.6, *E/Z* ratio >20). Purification by SiO_2 gel column chromatography provided **2f** (18.3 mg, 24% yield, *syn*:*anti*(*E*) = 9.3, *E/Z* ratio >20)

Characterization data for *syn*-(*E*)-**2f**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.18 (m, 6H), 2.78–2.85 (m, 1H), 2.84 (dd, J_1 = 7.6 Hz, J_2 = 13.6 Hz, 1H), 3.08 (dd, J_1 = 7.6 Hz, J_2 = 13.6 Hz, 1H), 3.29 (q, *J* = 7.6 Hz, 1H), 4.104 (q, *J* = 7.0 Hz, 1H), 4.106 (q, *J* = 7.3 Hz, 1H), 5.38 (dd, J_1 = 7.9 Hz, J_2 = 15.8 Hz, 1H), 5.79 (dd, J_1 = 8.8 Hz, J_2 =15.8 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.4 (q, *J* = 1.9 Hz), 14.0, 38.8, 41.4 (q, *J* = 27.5 Hz), 51.0, 60.7, 126.5, 126.9 (q, *J* = 277.7 Hz), 127.9 (q, *J* = 2.8 Hz), 128.3, 129.1, 132.1, 173.1; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.72 (d, *J* = 9.2 Hz, 3F); **IR** (neat) ν 2986, 1731, 1258, 1171, 1125, 1017, 971, 911, 857 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{16}H_{19}F_3NaO_2$ $[M+Na]^+$ 323.1221, found 323.1229.

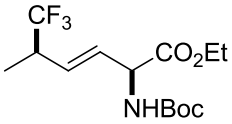
syn-(_E_)-Ethyl 6,6,6-trifluoro-2-isopropyl-5-methylhex-3-enoate (2g)



Conditions B: Allylsilane **(1g)** (64.0 mg, 0.25 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*:*anti*(*E*) = 3.5, *E/Z* ratio >20). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1/20) provided the title compound (**2g**) (34.6 mg, 55% yield, *syn*:*anti*(*E*) = 6.6, *E/Z* ratio >20) as a colorless oil.

Characterization data for *syn*-(*E*)-**2g**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.3 Hz, 3H), 1.96–2.05 (m, 1H), 2.70 (dd, J_1 = 8.5 Hz, J_2 = 9.5 Hz, 1H), 2.82–2.93 (m, 1H), 4.15 (q, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.3 Hz, 1H), 5.43 (dd, J_1 = 8.2 Hz, J_2 = 15.8 Hz, 1H), 5.71 (dd, J_1 = 9.5 Hz, J_2 =15.8Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.5 (q, *J* = 2.9 Hz), 14.2, 19.5, 20.6, 30.9, 41.7 (q, *J* = 27.5 Hz), 56.8, 60.4, 127.1 (q, *J* = 277.7 Hz), 128.2 (q, *J* = 1.9 Hz), 132.1, 173.6; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.84 (d, *J* = 8.1 Hz, 3F); **IR** (neat) ν 2964, 1732, 1258, 1175, 1123, 1017, 975, 840 cm^{-1}; **HRMS** (FI/EI) *m/z* Calcd for $C_{12}H_{19}F_3O_2$ $[M]^+$ 252.1337, found 252.1337.

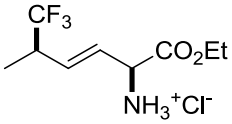
***syn*-(*E*)-Ethyl 2-[(*tert*-butoxycarbonyl)amino]-6,6,6-trifluoro-5-methylhex-3-enoate**



Conditions B: Allylsilane **1h** (50.0 mg, 0.15 mmol), Togni reagent **I** (86.2 mg, 0.27 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (5.6 mg, 0.0075 mmol) and MeOH (0.3 mL). Purification by column chromatography on SiO_2 gel (EtOAc/*n*-hexane=1/10) provided the title compound (25.6 mg, 52% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, *J* =7.1 Hz, 3H), 1.28 (t, *J* = 7.3 Hz, 3H), 1.46 (s, 9H), 2.86–2.95 (m 1H), 4.17–4.29 (m, 2H), 4.84 (br. s, 1H), 5.19 (br. s, 1H), 5.68–5.80 (m, 2H).The presence of rotamers was confirmed by NMR analysis. **IR** (neat) ν 2982, 1715, 1499, 1368, 1258, 1164, 1126, 1019, 970, 863 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_{14}H_{22}F_3NNaO_2$ $[M+Na]^+$ 348.1386, found 348.1393.

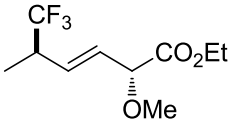
***syn*-(*E*)-Ethyl 2-amino-6,6,6-trifluoro-5-methylhex-3-enoate hydrogenchloride salt (2h)**



syn-(*E*)-Ethyl 2-[(*tert*-butoxycarbonyl)amino]-6,6,6-trifluoro-5-methylhex-3-enoate (21.2 mg, 0.65 mmol) was treated with HCl (1.0 mL, 1.25 M, in EtOH) and stirred for 24 hrs. The mixture was evaporated to yield the desired product (**2h**) (17.1 mg, quant.) as a yellow oil. The isomeric ratio was determined by ^{19}F NMR analysis (*syn*:*anti*(*E*) = 4.5, *E/Z* ratio >20).

Characterization data for *syn*-(*E*)-**2h**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.25 (d, *J* = 6.9 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 2.94–3.05 (m, 1H), 4.20–4.33 (m, 2H), 4.73 (br. s, 1H), 5.98 (dd, J_1 = 5.4 Hz, J_2 = 15.8 Hz, 1H), 6.08 (dd, J_1 = 6.9 Hz, J_2 = 15.8 Hz, 1H), 8.96 (br. s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.5 (q, *J* = 2.8 Hz), 13.8, 41.0 (q, *J* = 28.4 Hz), 54.6, 62.9, 124.5, 126.6 (q, *J* = 277.7 Hz), 134.0 (q, *J* = 2.8 Hz), 167.7; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.33 (d, *J* = 9.2 Hz, 3F); **IR** (neat) ν 2917, 1745, 1508, 1258, 1222, 1176, 1129, 1017, 972, 859 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_9H_{15}ClF_3NO_2$ $[M]^+$ 226.1055, found 226.1049.

***anti*-(*E*)-Ethyl 6,6,6-trifluoro-2-methoxy-5-methylhex-3-enoate (2i)**

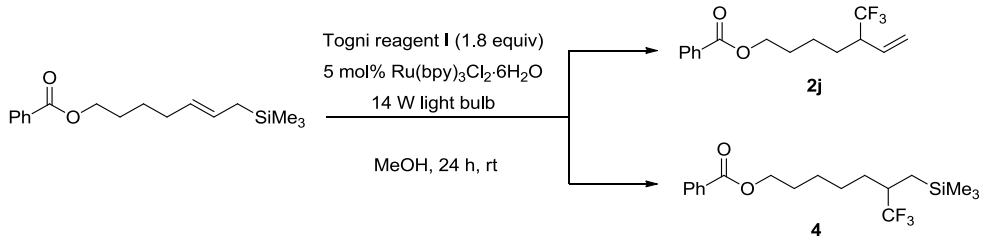


Conditions B: Allylsilane **(1i)** (57.6 mg, 0.25 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2•6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*:*anti*(*E*) = 4.6, *E/Z* ratio >20). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 1/10) provided **2i** (41.4 mg, 73% yield, *syn*:*anti*(*E*) = 9.8, *E/Z* ratio >20) as a colorless oil.

Conditions C: Allylsilane (**1i**) (57.6 mg, 0.25 mmol), Umemoto reagent **III** (181.0 mg, 0.45 mmol), $Ru(bpy)_3Cl_2•6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*:*anti*(*E*) = 9.6, *E/Z* ratio >20). Purification by SiO_2 gel column chromatography provided **2i** (42.7 mg, 76% yield, *syn*:*anti* (*E*) = 4.6, *E/Z* ratio >20)

Characterization data for *anti*-(*E*)-**2i**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.25 (d, *J* = 7.2 Hz, 3H), 2.86–2.97 (m, 1H), 3.42 (s, 3H), 3.78 (s, 3H), 4.29 (d, *J* = 6.3 Hz, 1H), 5.74 (dd, J_1 = 6.0 Hz, J_2 = 15.8 Hz, 1H), 5.87 (ddd, J_1 = 1.3 Hz, J_2 = 7.6Hz, J_3 = 15.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.1 (q, *J* = 2.8 Hz), 41.2 (q, *J* = 28.4 Hz), 52.4, 57.5, 80.4, 126.8 (q, *J* = 277.7 Hz), 129.1, 129.6 (q, *J* = 2.8 Hz), 170.7; **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –72.64(d, *J* = 8.1 Hz, 3F); **IR** (neat) ν 1750, 1260, 1177, 1133, 1014, 907, 802, 728 cm^{-1}; **HRMS** (TOF-ESI) *m/z* Calcd for $C_9H_{13}F_3NaO_3$ $[M+Na]^+$ 249.0704, found 249.0709.

5-(Trifluoromethyl)hept-6-en-1-yl benzoate (2j) and 7,7,7-Trifluoro-6-[(trimethylsilyl)methyl]heptyl benzoate (4)



Conditions B: (*E*)-7-(trimethylsilyl)hept-5-en-1-yl benzoate **1j** (72.5 mg, 0.25 mmol), Togni reagent **I** (94.8 mg, 0.30 mmol), $Ru(bpy)_3Cl_2•6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The ratio of **2j/4** was determined by ^{19}F NMR analysis of the crude mixture (**2j/4** ratio 1.6). Purification by preparative TLC (*n*-hexane/EtOAc = 10/1) provided **2j** (20.5 mg, 44% yield) as a colorless oil and **4** (29.4 mg, 33% yield) as a colorless oil, respectively.

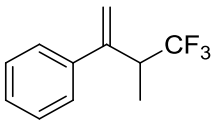
5-(Trifluoromethyl)hept-6-en-1-yl benzoate (2j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32–1.42 (m, 1H), 1.47–1.55 (m, 2H), 1.64–1.80 (m, 3H), 2.57–2.70 (m, 1H), 4.24–4.29 (m, 2H), 5.21 (dd, *J* = 19.4 Hz, 1H), 5.25 (d, *J* = 15.4 Hz, 1H), 5.56 (dt, J_1 = 9.8 Hz, J_2 = 19.4 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 23.0. 27.1 (q, *J* = 2.9 Hz), 28.4, 48.5 (q, *J* = 26.5 Hz), 64.6, 121.3, 126.7 (q, *J* = 277.7 Hz), 128.3, 129.5, 130.3, 131.5 (q, *J* = 2.8 Hz), 132.9, 166.6; **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* –71.63 (d, *J* = 9.2 Hz, 3F); **IR** (neat) ν 2954, 1718, 1272, 1253, 1173, 1110, 1070, 1027, 933, 845, 710 cm^{-1}; **HRMS** (ESI) *m/z* Calcd for $C_{15}H_{17}F_3O_2Na$ $[M]^+$ 286.1181, found 286.1183.

7,7,7-Trifluoro-6-[(trimethylsilyl)methyl]heptyl benzoate (4)

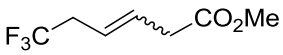
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 9H), 0.67 (ddd, J_1 = 5.1 Hz, J_2 = 8.2 Hz, J_3 = 15.1 Hz, 1H), 0.84 (ddd, J_1 = 5.7 Hz, J_2 = 8.2 Hz, J_3 = 15.1 Hz, 1H), 1.42–1.90 (m, 8H), 2.12–2.21 (m, 1H), 4.32–4.35 (m, 2H), 7.45 (t, J = 7.9 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 8.05 (d, J = 7.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ –1.1, 15.3, 26.3, 26.5, 28.6, 30.8 (q, J = 1.9 Hz), 64.9, 127.7, 128.8 (q, J = 278.6 Hz), 129.5, 130.4, 132.9, 166.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –71.44 (d, J = 9.1 Hz, 3F); **IR** (neat) ν 2954, 1720, 1452, 1271, 1151, 1110, 1070, 1027, 839, 710 cm^{-1}; **HRMS** (ESI) *m/z* Calcd for $C_{18}H_{27}F_3O_2NaSi$ $[M+Na]^+$ 383.1630, found 383.1625.

(4,4,4-trifluoro-3-methylbut-1-en-2-yl)benzene (2k)



Conditions B: (Z)-trimethyl(2-phenylbut-2-en-1-yl)silane[10] (36.7 mg, 0.25 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (5.6 mg, 0.0075 mmol), Togni reagent **I** (56.9 mg, 0.18 mmol) and MeOH (0.5 mL). The crude residue was purified by SiO_2 gel column chromatography (*n*-hexane) to afford **2k** (16.5 mg, 55% yield) as a colorless oil. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 1.40 (d, J = 7.2 Hz, 3H), 3.29–3.53 (m, 1H), 5.42 (s, 1H), 5.51 (s, 1H), 7.33–7.37 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.7, 42.6 (q, J = 27.0 Hz), 116.8, 126.4, 127.1 (q, J = 277.9 Hz), 127.7, 128.4, 141.7, 144.9; **^{19}F NMR** (236 MHz, $CDCl_3$) δ –70.6 (d, J = 8.6 Hz, 3F); **HRMS** (EI/FI) m/z Anal. Calcd for $C_{11}H_{12}F_3$ 200.0813, found $[M]^+$ 200.0820. Characterisation data correspond to the literature.[10]

(*E*)-Methyl 6,6,6-trifluorohex-3-enoate (2l)

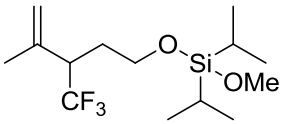


Conditions C: Methyl 3-(trimethylsilyl)-4-pentenoate **1l** (46.6 mg, 0.25 mmol), Umemoto's trifluoromethylating reagent **III** (120.7 mg, 0.30 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The ratio of *E/Z* isomers was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 2.7). Fluorobenzene (23.4 μL, 0.25 mmol) was added as an internal standard and the yield was calculated to be 55% by ^{19}F NMR spectroscopy. Purification by SiO_2 gel column chromatography (*n*-hexane/EtOAc = 20/1) provided **2l** (15.0 mg, 33% yield, *E/Z* ratio 3.3) as a colorless oil.

Note: This compound is volatile, complete evaporation *in vacuo* (<10 mmHg) after 10 min.

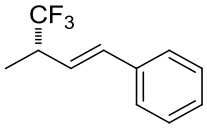
Characterization data for the *E/Z* mixtures of **2l** (*E/Z* ratio 3:3): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.78–2.92 (m.2H), 3.13 (d, J = 6.9 Hz, 2H), 3.71 (s, 2.25H), 3.71 (s, 0.75H), 5.54 (dtt, J_1 = 1.6 Hz, J_2 = 6.9 Hz, J_3 = 1.6 Hz, 15.5 Hz, 0.75 H), 5.62 (dtt, J_1 = 1.9 Hz, J_2 = 7.3 Hz, J_3 = 10.1 Hz, 0.75 H), 5.85 (dt, J_1 = 6.9 Hz, J_2 = 15.5 Hz, 0.75 H), 5.95 (dt, J_1 = 7.9 Hz, J_2 = 10.1 Hz, 0.25 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 32.4 (q, J = 29.4 Hz), 32.8, 37.3 (q, J = 29.4 Hz), 37.5, 120.5 (q, J = 3.8 Hz), 121.9 (q, J = 3.8 Hz), 125.7 (q, J = 274.8 Hz), 127.7, 129.5, 171.2, 171.5; **^{19}F NMR** (236 MHz, $CDCl_3$) δ –66.45 (t, J = 10.8 Hz, 0.75F), –66.84 (t, J = 10.6 Hz, 2.25F); **IR** (neat) ν 1494, 1449, 1344, 1259, 1173, 1123, 1086, 1060, 1016, 974, 884, 747, 697 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_7H_9F_3O_2$ $[M]^+$ 182.0555, found 182.0555.

Diisopropyl(methoxy){[4-methyl-3-(trifluoromethyl)pent-4-en-1-yl]oxy}-silane (2m)



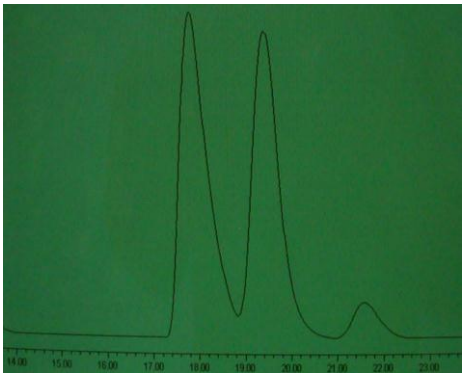
Conditions B: 2,2-diisopropyl-4-methyl-2,3,6,7-tetrahydro-1,2-oxasilepine **1m**[11] (53.0 mg, 0.25 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol), Togni reagent **I** (94.8 mg, 0.3 mmol) and MeOH (0.5 mL). The crude residue was purified by SiO_2 gel column chromatography (Et_2O/*n*-hexane = 1/99) to afford **2m** (31.0 mg, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.04–1.05 (d, 12H), 1.44–1.52 (m, 1H), 1.53–1.65 (m, 1H), 1.67–1.74 (m, 1H), 1.77 (s, 3H), 1.81–1.87 (m, 1H), 3.08 (d quintet, J_1 = 4.0 Hz, J_2 = 9.5 Hz, 1H), 3.57 (s, 3H), 3.67 (dt, J_1 = 6.0 Hz, J_2 = 11.4 Hz, 1H), 4.96 (s, 1H), 5.07 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 11.9, 17.3, 17.3, 19.7, 22.8 (q, J = 2.8 Hz), 29.7, 50.9, 50.9 (q, J = 25.7 Hz), 62.1, 117.7, 127.0 (q, J = 279.0 Hz), 138.6 (q, J = 1.8 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –69.1 (d , J = 10.4 Hz, 3F); **HRMS** (ESI) m/z Anal. Calcd for $C_{14}H_{27}F_3NaSi$ 335.1630, found $[M+Na]^+$ 335.1628. Characterization data correspond to the literature.[10]

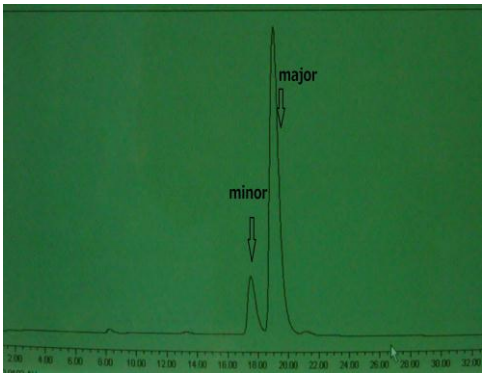
(+)-(*E*)-(4,4,4-Trifluoro-3-methylbut-1-3n-1yl)benzene (2n)



Conditions B: (*R, E*)-allylsilane **1n** (51.1 mg, 0.25 mmol, 94% ee), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 5.0). Purification by SiO_2 gel column chromatography (*n*-hexane) provided **2n** (28.1 mg, 56% yield, *E/Z* ratio 5.0, 71% ee) as a colorless oil. The enantiomeric purity of **2n** was determined by HPLC analysis: CHIRACEL® OJ-H column, 4.6 mm × 250 nm, *n*-hexane, 0.5 min/mL, 25 ˚C, UV detector, t_R (minor) = 17.5 min and t_R (major) = 19.0 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (d, J = 7.0 Hz, 3H), 2.99–3.09 (m, 1H), 6.12 (dd, J_1 = 8.1 Hz, J_2 = 15.9 Hz, 1H), 6.58 (d, J = 16.9 Hz, 1H), 7.26–7.29 (m, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.6 (q, J = 1.9 Hz), 41.9 (q, J = 27.5 Hz), 124.2 (q, J = 2.8 Hz), 126.4, 127.2 (q, J = 277.7 Hz), 128.0, 128.6, 134.1. 136.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –72.53 (d, J = 9.2 Hz, 3F); **IR** (neat) ν 1258, 1172, 1123, 1070, 1016, 965, 839, 747, 693 cm^{-1}; **HRMS** (EI/SI) *m/z* Calcd for $C_{11}H_{11}F_3$ $[M]^+$ 200.0808, found 200.0813. $[\alpha]_D^{20}$ = +6.4 (c = 0.5, MeOH).





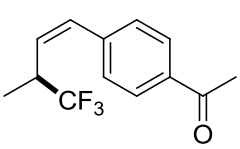
***rac*-(*E*)-2n**

Time (min)	Area	%area
17.796	3908447	52.54
19.355	3531036	47.46

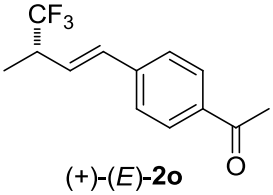
(+)-(*E*)-2n

Time (min)	Area	%area
17.551	2079346	14.34
19.043	12424533	85.66

1-[4-(4,4,4-Trifluoro-3-methylbut-1-3-en-1-yl)phenyl]ethanone (2o)



(-)-(*Z*)-**2o**

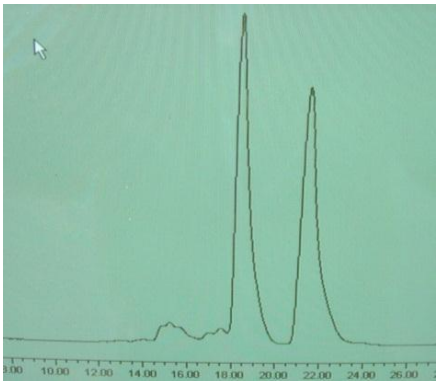


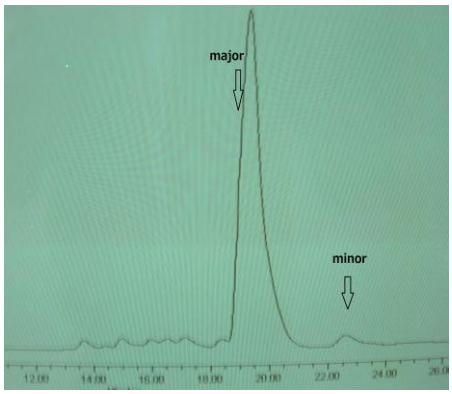
(+)-(*E*)-**2o**

Conditions B: (*R,E*)-allylsilane **1o** (123.1 mg, 0.50 mmol, 99% ee), Togni reagent **I** (284.4 mg, 0.90 mmol), $Ru(bpy)_3Cl_2•6H_2O$ (18.8 mg, 0.025 mmol) and MeOH (1.0 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E*/*Z* = 7.0). Purification by SiO_2 gel column chromatography (*n*-hexane) enabled to isolate *Z*-isomer (11.4 mg, 9% yield, 96% ee) as a colorless oil and the *E*-isomer (71.2 mg, 59% yield, 76% ee) as a colorless oil, respectively.

(-)-(*Z*)-1-[4-(4,4,4-Trifluoro-3-methylbut-1-3en-1-yl)phenyl]ethanone

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.9 Hz, 3H), 2.62 (s, 3H), 3.31–3.41 (m, 1H), 5.69 (t, *J* = 11.0 Hz, 1H), 6.72 (d, *J* = 11.0 Hz, 1H), 7.33 (d, *J* = 8.2 H, 2H), 7.96 (d, *J* = 8.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 14.3 (q, *J* = 2.8 Hz), 26.6, 37.5 (q, *J* = 27.4 Hz), 127.2 (q, *J* = 277.7 Hz), 128.4 (q, *J* = 2.8 Hz), 128.5, 128.6, 132.3, 136.0, 141.0, 197.5; **^{19}F NMR** (236 MHz, $CDCl_3$) *δ* –72.51(d, *J* = 8.4 Hz, 3F); **IR** (neat) ν 1683, 1605, 1357, 1259, 1168, 1129, 1104, 1069, 1013, 857, 739, 696 cm^{-1}; **HRMS** (ESI) *m/z* Calcd for $C_{13}H_{13}F_3ONa$ $[M+Na]^+$ 265.0813, found 265.0811; $[\alpha]_D^{20}$ = –24.0 (c = 0.3, MeOH). The enantiomeric purity of (*Z*)-**2o** was determined by HPLC analysis: CHIRACEL® OJ-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 99:1, 0.5 min/mL, 25 ˚C, UV detector (270 nm), t_R (minor) = 19.1 min and t_R (major) = 22.2 min.





rac-(*Z*)-2o

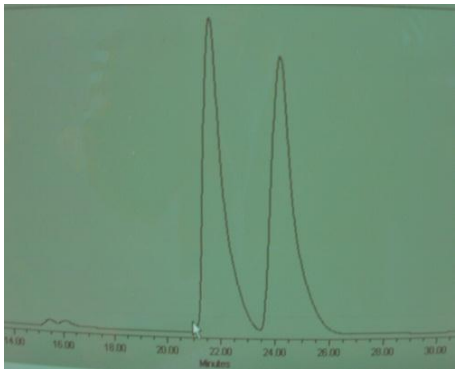
Time (min)	Area	%area
18.390	4080200	49.13
21.258	4172594	50.87

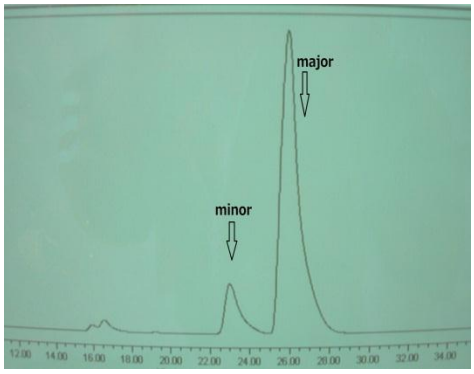
(-)-(*Z*)-2o

Time (min)	Area	%area
19.114	25950110	98.02
22.230	525539	1.98

(+)-(*E*)-1-[4-(4,4,4-Trifluoro-3-methylbut-1-3n-1yl)phenyl]ethanone

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (d, *J* = 7.3 Hz, 3H), 2.61 (s, 3H), 3.02–3.13 (m, 1H), 6.25 (dd, J_1 = 7.9 Hz, J_2 = 16.1 Hz, 1H), 6.63 (d, *J* = 16.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.5 (q, *J* = 2.8 Hz), 26.6, 41.4 (q, *J* = 27.5 Hz), 126.5, 126.9 (q, *J* = 277.7 Hz), 127.1 (q, *J* = 2.8 Hz), 128.8, 133.1, 136.4, 140.8, 197.5; **^{19}F NMR** (236 MHz, $CDCl_3$) *δ* –72.81 (d, *J* = 8.7 Hz, 3F); **IR** (neat) ν 1681, 1604, 1359, 1226, 1171, 1123, 1070, 969, 817 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{13}H_{13}F_3O$ $[M]^+$ 242.0914, found 242.0918. $[\alpha]_D^{20}$ = +11.0 (c = 0.5, MeOH). The enantiomeric purity of (*E*)-**2o** was determined by HPLC analysis: CHIRACEL® OJ-H column, 4.6 mm x 250 mm, *n*-hexane, 0.5 min/mL, 25 ˚C, UV detector (270 nm), t_R (minor) = 23.0 min and t_R (major) = 25.7 min.





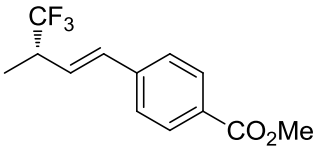
rac-(*E*)-2o

Time (min)	Area	%area
21.665	30651524	50.33
24.057	30246626	49.67

(+)-(*E*)-2o

Time (min)	Area	%area
23.005	8329315	12.2
25.685	59871798	87.8

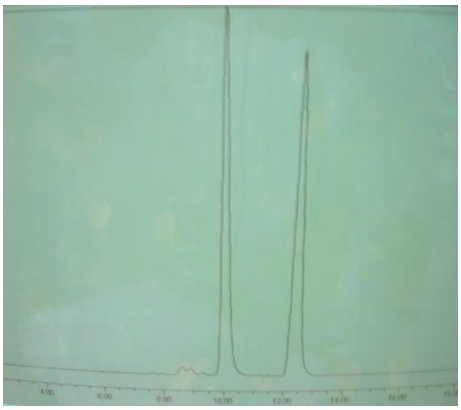
(+)-(*E*)-Methyl 4-(4,4,4-trifluoro-3-methyl-but-1-en-1yl)benzozate (2p)

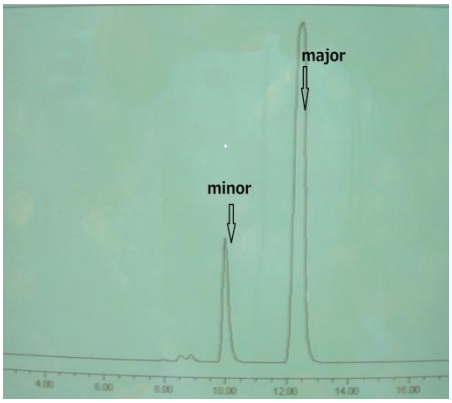


Conditions B: (*R*, *E*)-allylsilane **1p** (65.6 mg, 0.25 mmol, 99% ee), Togni reagent **I** (142.2 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 7.2). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane gradient 99.5/0.5 to 98/2) provided (*E*)-**2p** (27.0 mg, 41% yield, 72% ee) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.35 (d, *J* = 7.1 Hz, 3H), 2.92–3.06 (m, 1H), 3.92 (s, 3H), 6.24 (dd, J_1= 8.0 Hz, J_2 =15.7 Hz, 1H), 6.62 (d, *J* = 15.7 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.5 (q, *J* = 1.9 Hz), 41.9 (q, *J* = 27.5 Hz), 52.1, 126.3, 126.8 (q, *J* = 2.9 Hz), 126.9 (q, *J* = 277.7 Hz), 129.4, 130.0, 133.2, 140.7, 166.8; **^{19}F NMR** (236 MHz, $CDCl_3$) δ –72.8 (d, *J* = 8.7 Hz, 3F); **IR** (neat) ν 2992, 2954, 1722, 1281, 1258, 1177, 1127 cm^{-1}; **HRMS** (CI+) *m/z* Calcd for $C_{13}H_{14}O_2F_3$ $[M+H]^+$ 259.0946, found 259.0951; $[\alpha]_D^{20}$ = +13.0 (c = 1.0, $CHCl_3$). The enantiomeric purity of (*E*)-**2p** was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 97:3, 0.5 min/mL, 25 ˚C, UV detector (270

nm), t_R (minor) = 10.0 min and t_R (major) = 12.3 min.





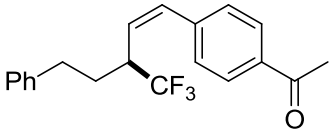
rac-(*E*)-2p

Time (min)	Area	%area
10.016	39889062	49.06
12.287	41411488	50.94

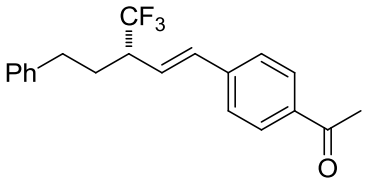
(+)-(*E*)-2p

Time (min)	Area	%area
10.001	7588683	14.04
12.264	46470119	85.96

1-[4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)phenyl]ethanone (2q)



(+)-(*Z*)-**2q**

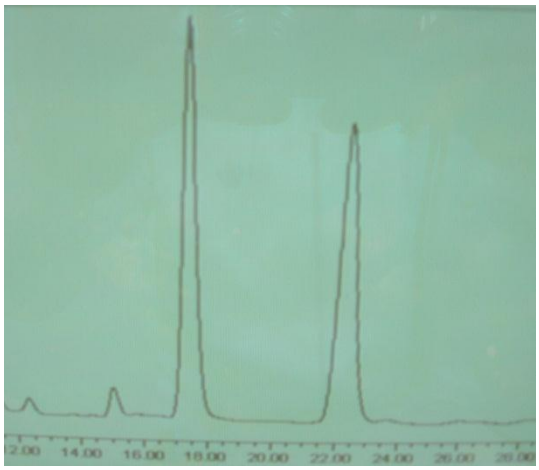


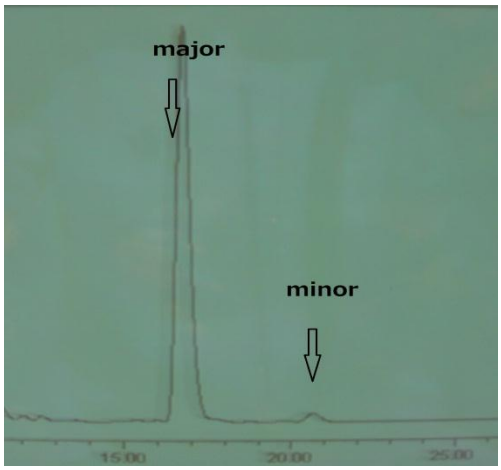
(+)-(*E*)-**2q**

Conditions B: (*R, E*)-allylsilane **1q** (84.0 mg, 0.25 mmol, 99% ee), Togni reagent **I** (142.3 mg, 0.45 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol) and MeOH (0.5 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 3.2). Purification by SiO_2 gel column chromatography (EtOAc/*n*-hexane = 97/3) enabled to isolate the *Z*-isomer (14.2 mg, 17% yield, 96% ee) as a colorless oil and the *E*-isomer (34.6 mg, 42% yield, 69% ee) as a colorless oil, respectively.

(+)-(*Z*)-1-[4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)phenyl]ethanone

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81–1.89 (m, 1H), 2.11–2.18 (m, 1H), 2.43 (dt, J_1 = 7.9 Hz, J_2 = 16.7 Hz, 1H), 2.68 (s,3H), 2.74 (dd, J_1= 5.4 Hz, J_2 = 9.2 Hz, 1H), 3.28–3.37 (m, 1H), 6.71 (t, *J* = 11.7 Hz, 1H), 6.94 (d, *J* = 11.7 Hz, 1H), 7.01–7.03 (m, 2H), 7.19–7.21 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 26.6, 30.2 (q, *J* = 1.9 Hz), 32.2, 44.6 (q, *J* = 26.5 Hz), 126.1, 126.9 (q, *J* = 277.7 Hz), 127.0 (q, *J* = 2.8 Hz), 128.3, 128.4, 128.6, 128.6, 134.4, 136.0, 140.3, 141.0, 197.6; **^{19}F NMR** (236 MHz, $CDCl_3$) *δ* –72.87 (d, *J* = 8.7 Hz, 3F); **IR** (neat) ν 1683, 1604, 1455, 1358, 1252, 1155, 1113, 956, 855, 747, 700 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{20}H_{19}F_3O$ $[M]^+$ 333.1388, found 333.1382; $[\alpha]_D^{20}$ = +10.0 (c = 0.25, MeOH). The enantiomeric purity of (*Z*)-**2q** was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 97:3, 0.5 min/mL, 25 ˚C, UV detector (270 nm), t_R (major) = 16.7 min and t_R (minor) = 20.6 min.





rac-(*Z*)-2q

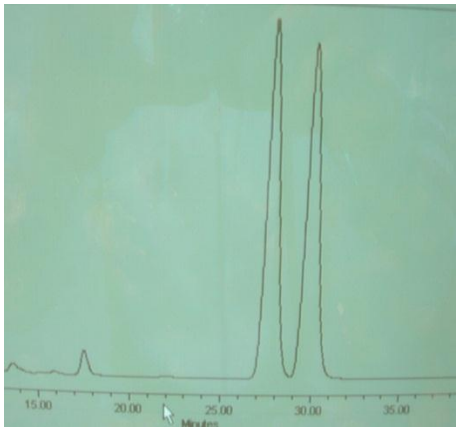
Time (min)	Area	%area
17.410	9450711	50.62
22.155	9218568	49.38

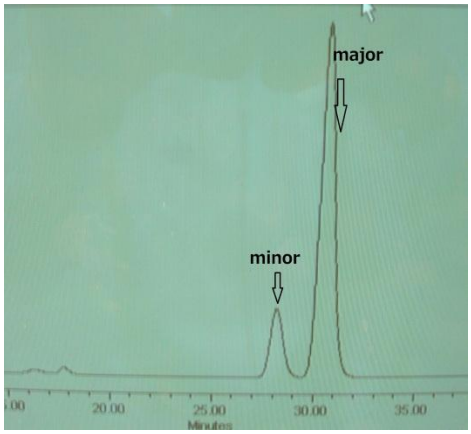
(+)-(*Z*)-2q

Time (min)	Area	%area
16.669	65400952	98.10
20.606	1267420	1.90

(+)-(*E*)-1-[4-(5-phenyl-3-(trifluoromethyl)pent-1-en-1-yl)phenyl]ethanone

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90–1.97 (m, 1H), 2.17–2.24 (m, 1H), 2.57–2.64 (m, 1H), 2.62 (s, 3H), 2.80 (dt, J_1 = 5.1 Hz, J_2 = 9.5 Hz, 1H), 2.68 (ddq, J_1 = 3.5 Hz, J_2 = 7.3 Hz, J_3 = 18.6 Hz, 1H), 6.15 (dd, J_1 = 9.5 Hz, J_2 = 16.0 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.3 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 26.6, 29.2 (q, J = 1.9 Hz), 32.4, 47.2 (q, J = 26.5 Hz), 125.6 (q, J = 1.9 Hz), 126.3, 126.6, 126.7 (q, J = 277.7 Hz), 128.4, 128.6, 128.8, 135.3, 136.5, 140.4, 140.6, 197.5; **^{19}F NMR** (236 MHz, $CDCl_3$) δ –70.17 (d, J = 8.5 Hz, 3F); **IR** (neat) ν 1677, 1601, 1360, 1261, 1160, 1113, 1072, 972, 957, 902, 859, 770, 689, 676 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{20}H_{19}F_3O$ $[M]^+$ 332.1388, found 332.1376; $[\alpha]_D^{20}$ = +105.2 (c = 0.25, MeOH). The ee value of (*E*)-**2q** was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 97/3, 0.5 min/mL, 25 ˚C, UV detector (270 nm), t_R (minor) = 28.1 min and t_R (major) = 30.4 min.



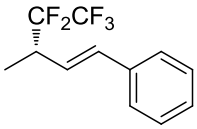


rac-(*E*)-2q **(+)-(*E*)-2q**

Time (min)	Area	%area
27.604	9450711	50.62
29.693	9218568	49.38

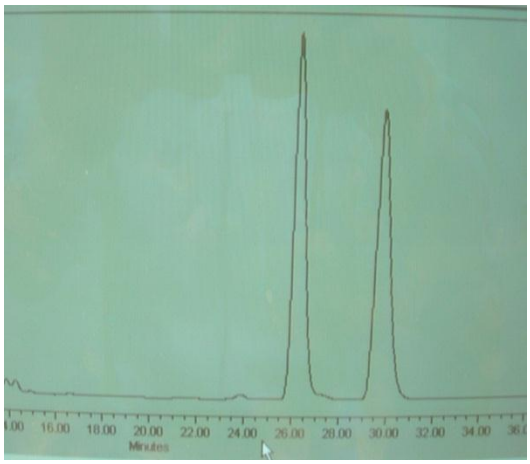
Time (min)	Area	%area
28.146	1698300	14.96
30.430	9654929	85.04

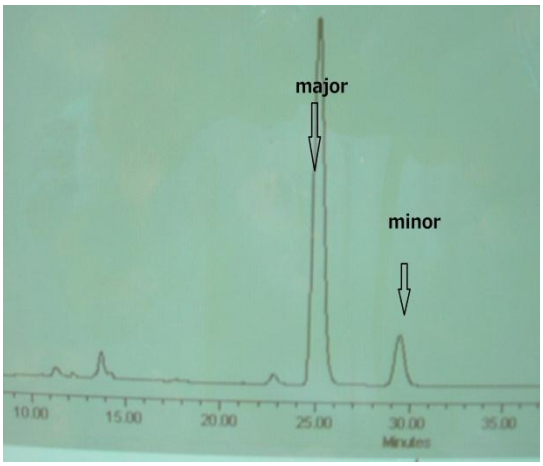
(+)-(*E*)-(4,4,5,5,5-Pentafluoro-3-methylbut-1-en-1yl)benzene (5)



Conditions B: (*R*,*E*)-allylsilane **1m** (40.9 mg, 0.20 mmol, 94% ee), Togni reagent **I** (131.8 mg, 0.40 mmol), $Ru(bpy)_3Cl_2•6H_2O$ (7.5 mg, 0.010 mmol) and MeOH (0.4 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 5.6). Purification by SiO_2 gel column chromatography (*n*-hexane) provided **5** (26.3 mg, 53% yield, 78% ee) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (d, J = 7.3 Hz, 3H), 3.03–3.12 (m, 1H), 6.09 (dd, J_1 = 8.8 Hz, J_2 = 15.8. Hz, 1H), 6.56 (d, J = 15.8 Hz, 1H), 7.26–7.29 (m, 1H), 7.34 (m, J = 7.9 Hz, 2H), 7.38 (d, 6.9 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.4, 40.2 (t, J = 21.8 Hz), 115.8 (tq, J_1 = 36.0 Hz, J_2 = 254.0 Hz), 119.4 (tq, J_1 = 37.0 Hz, J_2 = 285.2 Hz), 124.0 (dd, J_1 = 3.8 Hz, J_2 =5.7 Hz), 126.5, 128.0, 133.9, 136.3; **^{19}F NMR** (236 MHz, $CDCl_3$) δ –122.71 (dd, J_1 = 17.7 Hz, J_2 = 271.0 Hz, 1F), –119.22 (dd, J_1 = 12.2 Hz, J_2 = 270.7 Hz, 1F), –82.01 (s, 3F); **IR** (neat) ν 1189, 1123, 1010, 967, 747, 691 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{12}H_{12}F_5$ $[M]^+$ 250.0781, found 250.0773; $[\alpha]_D^{20}$ = +7.6 (c = 0.25, MeOH). The enantiomeric purity of (*E*)-**7** was determined by HPLC analysis: CHIRACEL® OJ-H column, 4.6 mm x 250 mm, *n*-hexane, 0.5 min/mL, 25 ˚C, UV detector (254 nm), t_R (major) = 24.8 min and t_R (minor) = 29.3 min.





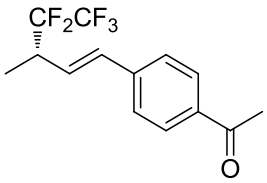
rac-(*E*)-5

Time (min)	Area	%area
26.124	5438804	50.09
29.522	53952029	49.91

(+)-(*E*)-5

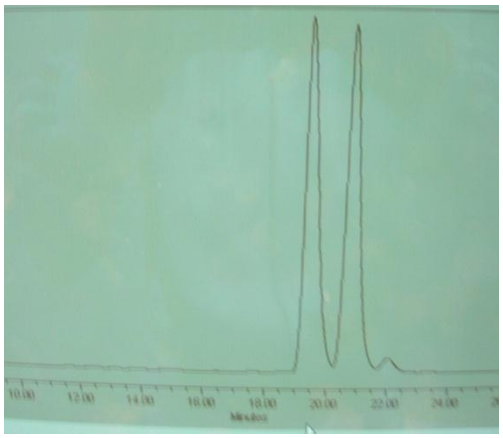
Time (min)	Area	%area
24.845	34005614	89.10
29.318	4158897	10.90

(+)-(*E*)-1-[4-(4,4,5,5,5-Pentafluoro-3-methylpent-1-en-1yl)phenyl]ethanone (6)



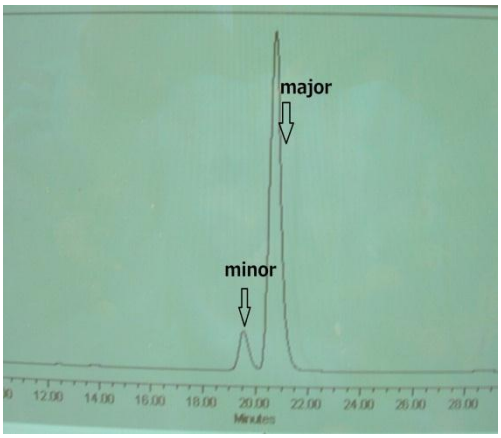
Conditions B: (*R, E*)-allylsilane **1j** (25.8 mg, 0.11 mmol, 99% ee), Togni reagent **I** (60.0 mg, 0.17 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (4.1 mg, 0.0055 mmol) and MeOH (0.3 mL). The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*E/Z* ratio 7.4). Purification by preparative TLC (*n*-hexane/EtOAc = 10/1) provided **6** (19.7 mg, 63% yield, 81% ee) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (d, J = 7.0 Hz, 3H), 2.61 (s, 3H), 3.05–3.17 (m, 1H), 6.22 (dd, J_1 = 8.9 Hz, J_2 = 15.8. Hz, 1H), 6.56 (d, J = 15.8 Hz, 1H), 7.46 (d, 8.5 Hz, 2H), 7.93 (d, J = 8.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.2 (t, J = 4.5 Hz), 26.6, 40.3 (t, J = 21.8 Hz), 115.6 (tq, J_1 = 36.0 Hz, J_2 = 254.0 Hz), 119.3 (tq, J_1 = 36.0 Hz, J_2 = 290.0 Hz), 126.6, 126.9 (dd, J_1 = 2.8 Hz, J_2 = 4.7 Hz), 128.8, 133.0, 136.4, 140.8, 197.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ –122.44 (dd, J_1 = 17.2 Hz, J_2 = 270.3 Hz, 1F), –118.96 (dd, J_1 = 10.4 Hz, J_2 = 270.3 Hz, 1F) ,–81.62 (s, 3F); **IR** (neat) ν 1683, 1604, 1360, 1267, 1191, 1113, 1011, 971, 815 cm^{-1}; **HRMS** (EI/FI) *m/z* Calcd for $C_{14}H_{13}F_5O$ $[M]^+$ 292.0887, found 292.0886; $[\alpha]_D^{20}$ = +10.5 (c = 0.20, MeOH). The enantiomeric purity of (*E*)-**8** was determined by HPLC analysis: CHIRACEL® OD-H column, 4.6 mm x 250 mm, *n*-hexane/*i*-PrOH = 99:1, 0.5 min/mL, 25 ˚C, UV detector (270 nm), t_R (minor) = 19.5 min and t_R (major) = 20.6 min.



rac-(*E*)-6

Time (min)	Area	%area
19.374	44644624	49.39
20.662	45745787	50.61



(+)-(*E*)-6

Time (min)	Area	%area
19.554	5539167	8.91
20.653	56621867	91.09

3-5. Reaction in the presence of TEMPO

Allylsilane (**1a**) (32.1 mg, 0.15 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (5.6 mg, 0.0075 mmol), Togni reagent **I** (142.2 mg, 0.45 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (46.9 mg, 0.3 mmol) and MeOH (0.3 mL) were placed in a vial, which was equipped with a magnetic stir bar. The vial was exposed to visible light at room temperature while stirring for 24 hrs. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with Et_2O (× 2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered

and concentrated *in vacuo*. Analysis of the crude mixture with ^{19}F NMR showed the formation of the TEMPO−CF_3 adduct[12] in 19% yield (diagnostic signal at –56.9 ppm). The yield was determined using benzotrifluoride as an internal standard. No other fluorinated products were formed.

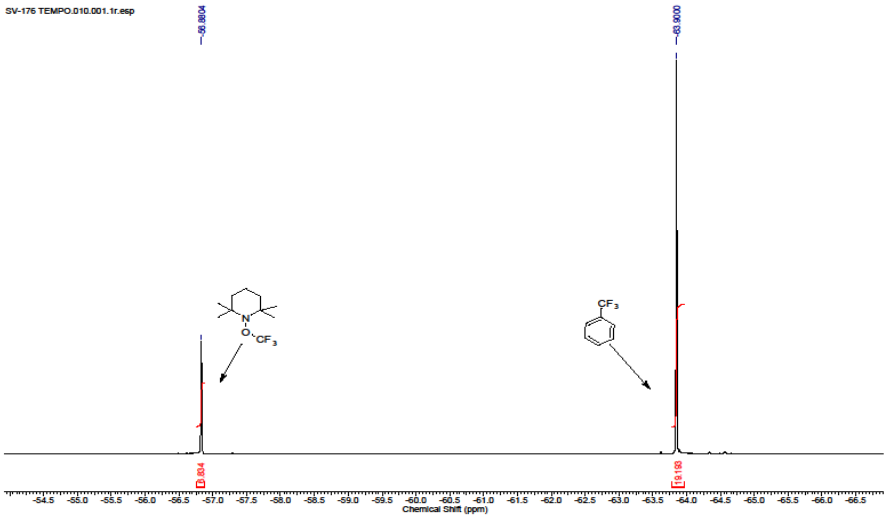
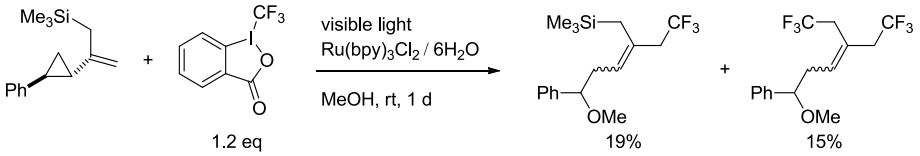


Figure 2. ^{19}F NMR spectra of TEMPO−CF_3 adduct

3-6. Trifluoromethylation of Radical Clock



Trimethyl[2-(*trans*-2-phenylcyclopropyl)allyl]silane[10] (57.6 mg, 0.25 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125mmol, 5mol%), Togni reagent **I** (94.8 mg, 0.3 mmol, 1.2 eq) and MeOH (0.5 mL) were placed in a vial which was equipped with a magnetic stir bar. The vial was exposed to a 14 W fluorescent light bulb at room temperature while stirring for 48 hrs. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with Et_2O (× 2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was filtered through a short pad of silica gel then washed with a mixture solvent (Et_2O/*n*-hexane = 1/10). The filtate evaporated to remove solvents. Preparative T.L.C. on SiO_2 gel using (Et_2O/*n*-hexane = 1/20) as the eluent to obtain [5-methoxy-5-phenyl-2-(2,2,2-trifluoroethyl)-2-pentenyl]trimethylsilane (16.1 mg, 19%, R_f = 0.47) as a colourless oil and [6,6,6-trifluoro-1-methoxyl-4-(2,2,2-trifluoroethyl)hex-3-en-1-yl]benzene(12.3 mg, 15%, R_f = 0.45) as a colourless oil. [5-methoxy-5-phenyl-2-(2,2,2-trifluoroethyl)-2-pentenyl]trimethylsilane (16.1 mg, 19%, R_f = 0.47) as a colourless oil and [6,6,6-trifluoro-1-methoxyl-4-(2,2,2-trifluoroethyl)hex-3-en-1-yl]benzene (12.3 mg, 15%, R_f = 0.45) as a colourless oil.

Allylsilane (0.25 mmol), $Ru(bpy)_3Cl_2$•$6H_2O$ (9.4 mg, 0.0125 mmol, 5.0 mol%), Togni reagent **I** (0.45 mmol, 1.8 eq) and MeOH (0.5 mL) were placed in a vial which was equipped with a magnetic stir bar. The vial was exposed

to a 14 W fluorescent light bulb at room temperature while stirring for 48 hrs. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with Et_2O (× 2). The combined organic phases were washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture. Purification by column chromatography on SiO_2 gel using the indicated solvent system gave the desired CF_3 allylic product.

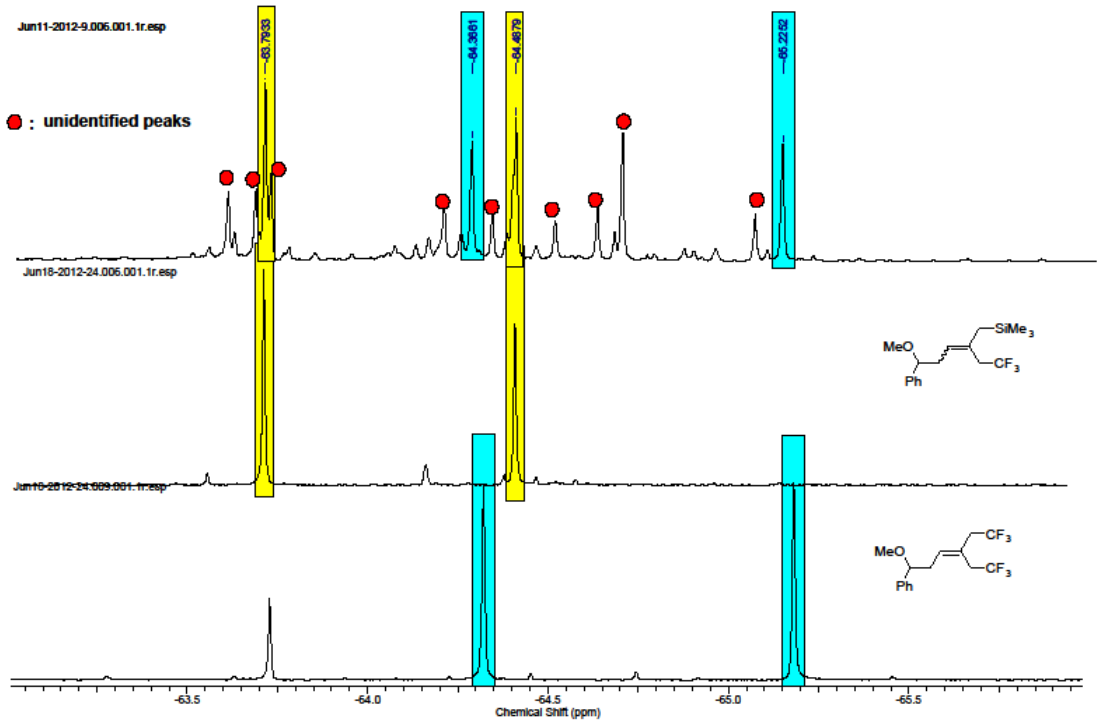
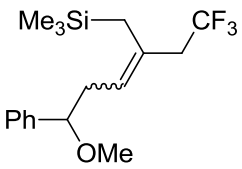
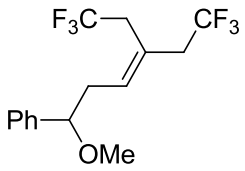


Figure 3. (top) ^{19}F NMR spectrum of the crude reaction mixture with $^{19}F/^{1}H$ decoupling. (middle) ^{19}F NMR spectrum of [5-methoxy-5-phenyl-2-(2,2,2-trifluoroethyl)-2-pentenyl]trimethylsilane. (bottom) ^{19}F NMR spectrum of [6,6,6-trifluoro-1-metoxyl-4-(2,2,2-trifluoroethyl)hex-3-en-1-yl]benzene.



Characterization data for *E, Z* mixture of [5-methoxy-5-phenyl-2-(2,2,2-trifluoroethyl)-2-pente-nyl]trimethyl silane: ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.03 (s, 4.5 H), 0.01 (s, 4.5 H), 1.54–1.59 (m, 2H), 2.28–2.78 (m, 4H), 3.21 (s, 1.5 H), 3.23 (s, 1.5 H), 4.08 (t, J = 7.6 Hz, 0.5 H), 4.10 (t, J = 7.1 Hz, 0.5 H), 5.26 (t, J = 7.1 Hz, 0.5 H), 5.30 (t, J = 7.1 H, 0.5 H), 7.28–7.30 (m, 3H), 7.34–7.38 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –64.5 (t, J = 12.4 Hz, 1.5F), –63.8 (t, J = 11.5 Hz, 1.5F); **HRMS** (EI/FI) m/z Anal. Calcd for $C_{17}H_{25}F_3OSi$ 330.1627, found $[M]^+$ 330.1627.

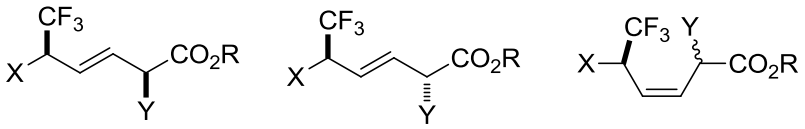


[6,6,6-trifluoro-1-metoxyl-4-(2,2,2-trifluoroethyl)hex-3-en-1-yl]benzene:

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (dt, J_1 = 6.6 Hz, J_2 = 14.9 Hz, 2H), 2.59 (dt, J_1 = 7.4 Hz, J_2 = 14.9 Hz, 2H), 2.87 (q, J = 10.9 Hz, 2H), 3.23 (s, 3H), 4.15 (t, J = 6.6 Hz, 1H), 5.84 (t, J = 7.4 Hz, 1H), 7.27–7.39 (m, 5H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –65.2 (t, J = 10.3 Hz, 3F), –64.4 (t, J = 10.3 Hz, 3F). **HRMS** (EI/FI) m/z Anal. Calcd for $C_{15}H_{16}F_3O$ 326.1105, found $[M]^+$ 330.1150.

3-7. Stereochemistry and X-ray data

Table. 2. $^{3}J_{3,4}$ and Chemical Shift Values for CF_3 Products (**2a–i**)



syn(*E*) *anti*(*E*) (*Z*)

Entry	Compd	R	X	Y	$^{3}J_{3,4}$, Hz (δ ppm)
1	**2a**	Et	Me	H	$J_{3,4}$ (*E*) = 15.6 (5.53, 5.82)
					$J_{3,4}$ (*Z*) = 10.8 (5.47, 5.85)
2	**2b**	Et	Me	H	$J_{3,4}$ (*E*) = 15.6 (5.54, 5.72)
					$J_{3,4}$ (*Z*) = 9.8 (5.45, −)
3	**2c**	Et	CH_2CH_2Ph	H	$J_{3,4}$ (*E*) = 14.8 (5.83, −)
					$J_{3,4}$ (*Z*) = 11.1 (6.02, −)
4	**2d**	Et	Me	H	$J_{3,4}$ (*E*) = 15.8 (5.43, 5.99)
5	**2e**	Et	Me	Me	$J_{3,4syn}$ (*E*) = 15.5 (5.49, 5.78)
					$J_{3,4anti}$ (*E*) = 15.4 (5.80, −)
					$J_{3,4}$ (*Z*) = 10.4 (5.41, 5.67)
6	**2f**	Et	Me	Bn	$J_{3,4syn}$ (*E*) = 15.8 (5.38, 5.79)
					$J_{3,4anti}$ (*E*) = 15.8 (5.56, −)
7	**2g**	Et	Me	*i-Pr*	$J_{3,4syn}$ (*E*) = 15.8 (5.43, 5.71)
					$J_{3,4anti}$ (*E*) = 15.8 (5.53, 5.78)
8	**2h**	Et	Me	$NH_3^+Cl^-$	$J_{3,4syn}$ (*E*) = 15.8 (5.98, 6.08)
9	**2i**	Me	Me	OMe	$J_{3,4syn}$ (*E*) = 15.8 (5.73, 5.87)
					$J_{3,4anti}$ (*E*) = 15.8 (5.74, 5.87)

[a] ^{1}H NMR data were recorded on a Bruker AVC500.

The assignment of *E/Z* stereochemistry for **2a–i** is based on the coupling constant values ($^{3}J_{3,4}$) of the double bond as shown in Table 2. In every case, the coupling constant values for the 3,4-*syn* (*E*) and 3,4-*anti* (*E*) are 15.4−15.8

Hz while coupling constant values for the 3,4-(*Z*) are 9.8−11.1 Hz. It is also notable that the chemical shift of C4 proton of the *Z* isomer appeared at a higher field (Δδ 0.06 to 0.09 Hz) than the corresponding (*E*) isomer. These tendencies are supportive to the assignment of *E/Z* stereochemistry for allylic CF_3compounds (**2a**−**i**).

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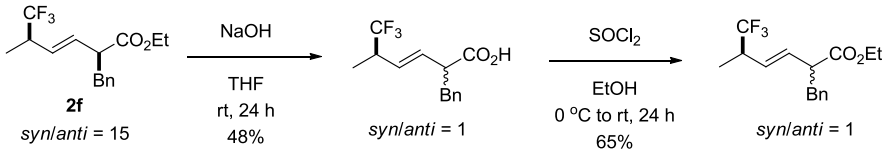


Scheme 1

In order to unequivocally assign the relative stereochemistry of the minor *anti*-(*E*) isomer, the epimerization at C-2 of *syn*-(E)-**2f** was carried out *via* hydrolysis with NaOH affording the corresponding carboxylic acid as a mixture of *syn*/anti (*E*) isomers (*syn*/anti (*E*) ratio = 1:1). Following esterification with thionyl chloride and EtOH, (*E*)-**2f** was successfully obtained as a mixture of *syn*/*anti* isomers (ratio = 1:1). This reference sample allows for unambiguous assignment of *anti* (*E*)-**2f**.

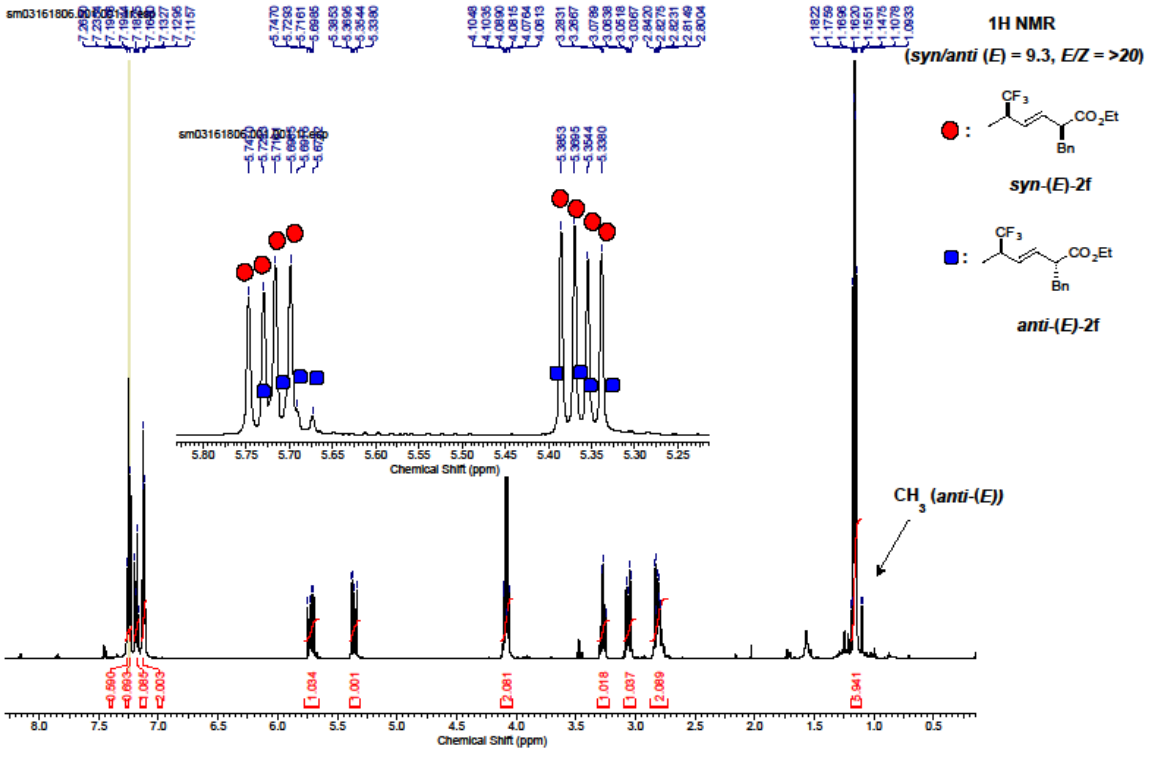


Figure 4. ^{1}H NMR spectra of **2f** (*syn:anti*(*E*) = 9.3, *E*/Z ratio >20)

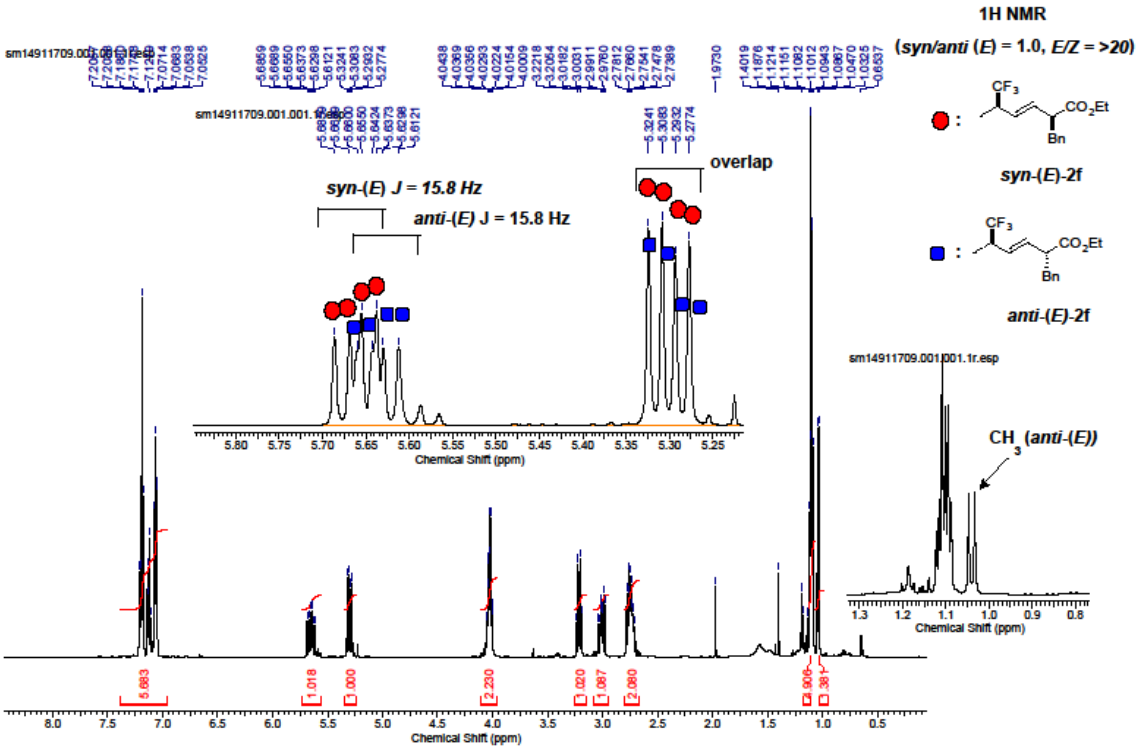
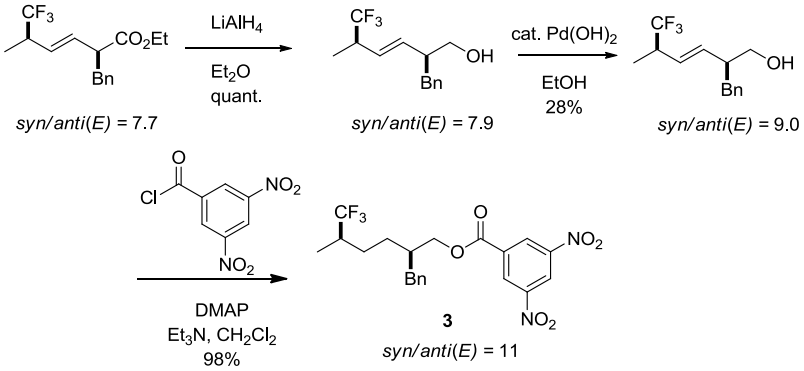


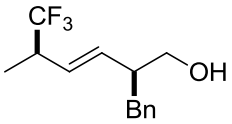
Figure 5. ^{1}H NMR spectra of **2f** (*syn:anti*(*E*) = 1.0, *E*/Z ratio >20)

For the assignment of the relative configuration of **2f** (*syn*-(*E*) as a major product), a representative sample (*syn*/*anti* (*E*) = 7.7) was subjected to sequential alkene then ester reduction with LAH, followed by esterification with 3,5-dinitrobenzoyl chloride (Scheme 2) . The resulting saturated ester, 2-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate **3**, was characterized by single crystal X-ray diffraction. The X-ray data indicate that the trifluoromethylation reaction of *anti*-(*E*) allylsilane **(1f)** leads predominantly to *syn*-(*E*) **2f** ($J_{3,4}$ = 15.8 Hz). *Anti*-(*E*) was assigned as the second major product ($J_{3,4}$ = 15.8 Hz).



Scheme 2. Synthesis of *syn*-2-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate (3)

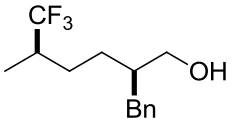
2-benzyl-6,6,6-trifluoro-5-methylhex-3-en-1ol



A solution of a *syn/anti-(E,Z)* mixture of **2f** (83.0 mg, 0.27 mmol, *syn*/*anti* (*E*) = 7.7, *E*/*Z* = > 20) in Et_2O (3.0 mL) was added dropwise to a slurry of $LiAlH_4$ (20.2 mg, 0.53 mmol) in Et_2O (3.0 mL) and allowed to stir at room temperature for 4 hrs. The reaction was quenched with sat. aq. NH_4Cl at 0 ˚C, and the aqueous phase was extracted with Et_2O. The organic phase was washed with distilled water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo* to give 2-benzyl-6,6,6-trifluoro-5-methylhex-3-en-1-ol (75.5 mg, quant.) as a colorless oil which was used without further purification. The isomeric ratio was determined by ^{19}F NMR analysis of the crude mixture (*syn*/*anti* (*E*) = 7.9, *E*/*Z* = > 15).

Characterization data for the *syn*-(*E*)-isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.19 (d, J = 6.8 Hz, 3H), 2.50–2.58 (m, 1H), 2.65 (dd, J_1 = 7.6 Hz, J_2 = 13.4 Hz, 1H), 2.71–2.87 (m, 2H), 3.51 (dd, J_1 = 7.1 Hz, J_2 = 10.6 Hz, 1H), 3.62 (dd, J_1 = 5.0 Hz, J_2 = 10.6 Hz, 1H), 5.41 (dd, J_1 = 7.6 Hz, J_2 = 15.4 Hz, 1H), 5.78 (dd, J_1 = 8.1 Hz, J_2 = 15.4 Hz, 1H), 7.14 (d, J = 7.3 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.26–7.30 (m, 2H); **^{19}F NMR** (377 MHz, $CDCl_3$) δ –72.2 (d, J = 9.2 Hz, 3F); **HRMS** (EI/FI) m/z Anal. Calcd for $C_{14}H_{17}F_3O$ $[M]^+$ 258.1224, found 258.1232.

syn-2-Phenyl-6,6,6-trifluoro-5-methylhexanol

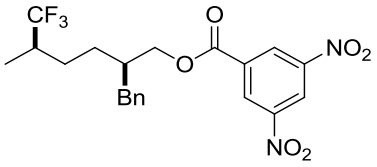


2-Benzyl-6,6,6-trifluoro-5-methylhex-3-en-1ol (35.7 mg, 0.14 mmol), 10% w/w $Pd(OH)_2/C$ (10.0 mg), and EtOH (1.0 mL) were subjected to a reaction flask. The flask was sealed, and the air was substituted with H_2 using two vacuum/H_2 balloon cycles, and the mixture was stirred for 20 hrs. The reaction mixture was filtered through a Celite pad and washed with EtOH (5.0 mL). The filtrate was concentrated *in vacuo* to afford *syn*-2-benzyl-6,6,6-trifluoro-5-methylhexanol (10.2 mg, 28% yield) as a colorless oil. The isomeric ratio was determined by ^{19}F NMR analysis (*syn*/*anti* = 9.0).

Characterization data for the *syn*-isomer

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (d, J = 7.0 Hz, 3H), 1.26–1.40 (m, 2H), 1.51–1.57 (m, 1H), 1.71–1.84 (m, 2H), 2.04–2.13 (m, 1H), 2.62 (dd, J_1 = 7.0 Hz, J_2 = 13.6 Hz, 1H), 2.71 (dd, J_1 = 7.6 Hz, J_2 = 13.6 Hz, 1H), 3.53–3.59 (m, 2H), 7.18 (d, J = 6.7 Hz, 2H), 7.21 (d, J = 7.3 Hz, 1H), 7.30 (t, J = 7.6 Hz, 2H); **^{13}C NMR** (125MHz, $CDCl_3$) δ 12.5 (q, J = 2.8 Hz), 26.7 (q, J = 1.9 Hz), 27.6, 37.6, 38.1 (q, J = 26.5 Hz), 42.4, 64.3, 126.0, 128.4, 128.4 (q, J = 277.7 Hz), 129.1, 140.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –73.29 (d, J = 9.2 H, 3F).

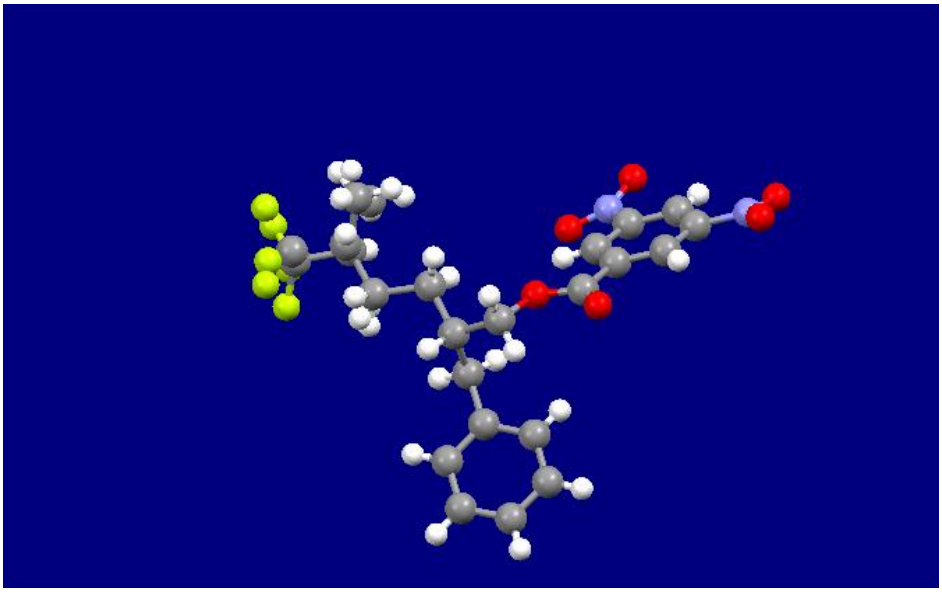
syn-2-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate (3)



2-benzyl-6,6,6-trifluoro-5-methylhexanol (10.0 mg, 0.028mmol, *syn*/*anti* = 9.0) was dissolved in CH_2Cl_2 (1.0 mL). Pyridine (2.5 μL, 0.031mmol), 3,5-dinitrobenzoyl chloride (7.0 mg, 0.031 mmol) and DMAP (1.0 mg, 0.008 mmol) were added at room temperature. After 2 hrs of stirring, water was added to the reaction mixture, and the aqueous phase was extracted with CH_2Cl_2. The organic phase was washed with water and brine, then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by SiO_2 gel column chromatography (EtOAc/*n*-hexane=1/4) to afford **5** (12.5 mg, 98% yield) as a yellow solid. The isomeric ratio was determined by ^{19}F NMR analysis (*syn/anti* = 11.0)

Characterization data for *syn*-2-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate (**3**): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.10 (d, J = 7.1 Hz, 3H), 1.47–1.64 (m, 3H), 1.76–1.89 (m, 1H), 2.11–2.28 (m, 2H), 2.72 (dd, J_1 = 8.1 Hz, J_2 = 13.9 Hz, 1H), 2.82 (dd, J_1 = 6.3 Hz, J_2 = 13.9 Hz, 1H), 4.38 (d, J = 5.6 Hz, 2H), 7.13–7.29 (m, 5H), 9.03 (s, 2H), 9.23 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 13.6 (q, J = 2.9 Hz), 26.8, 28.3, 38.0 (q, J = 26.5 Hz), 38.4, 39.4, 68.8, 122.4, 126.3, 128.2 (q, J =277.7 Hz), 128.6, 128.9, 129.3, 133.7, 139.2, 148.6, 162.4; **^{19}F NMR** (377 MHz, $CDCl_3$) δ –72.10 (d, J = 9.2 Hz, 3F); **HRMS** (TOF-ESI) *m/z* Calcd for $C_{21}H_{21}F_3N_2NaO_6$ $[M+Na]^+$ 477.1246, found 477.1244.

Single-crystal X-ray diffraction report for *syn-2*-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate (3)



Crystals suitable for X-ray diffraction analysis were obtained by recrystallizing *syn*-2-benzyl-6,6,6-trifluoro-5-methylhexyl 3,5-dinitrobenzoate **3** from *n*-hexane and dichloromethane. Single-crystal X-ray diffraction data were collected at 100 K using EH1 on I19 at Diamond Light Source. Raw frame data were reduced using CrysAlisPro, and the structure was solved with SuperFlip and refined with CRYSTALS. On refinement, the structure was found to be disordered, containing ca. 8% of *anti*-**3**, consistent with NMR results.

3-8. "Light/Dark" Experiment of Trifluoromethylation of 1a under photoredox Catalysis

To verify the necessity of light to maintain the trifluoromethylation of **1a** with Togni reagent **I**, an experiment with "light/dark" was performed. Allylsilane **1a** (0.15mmol, 1.0 equiv), **I** (0.18 mmol, 1.2 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.0075 mmol, 5 mol%), in CD_3OD (0.6 mL) was stirred for 36 hrs with continuous irradiation of visible light (Figure **6a**), and with alternating 3 or 6 hrs periods of visible light irradiation and 3 or 6 hrs periods of no light irradiation over 36 hrs (Figure **6b**). Since the reaction progressed steadily with visible light irradiation, it is supportive that the propagation isn't a mechanistic component.

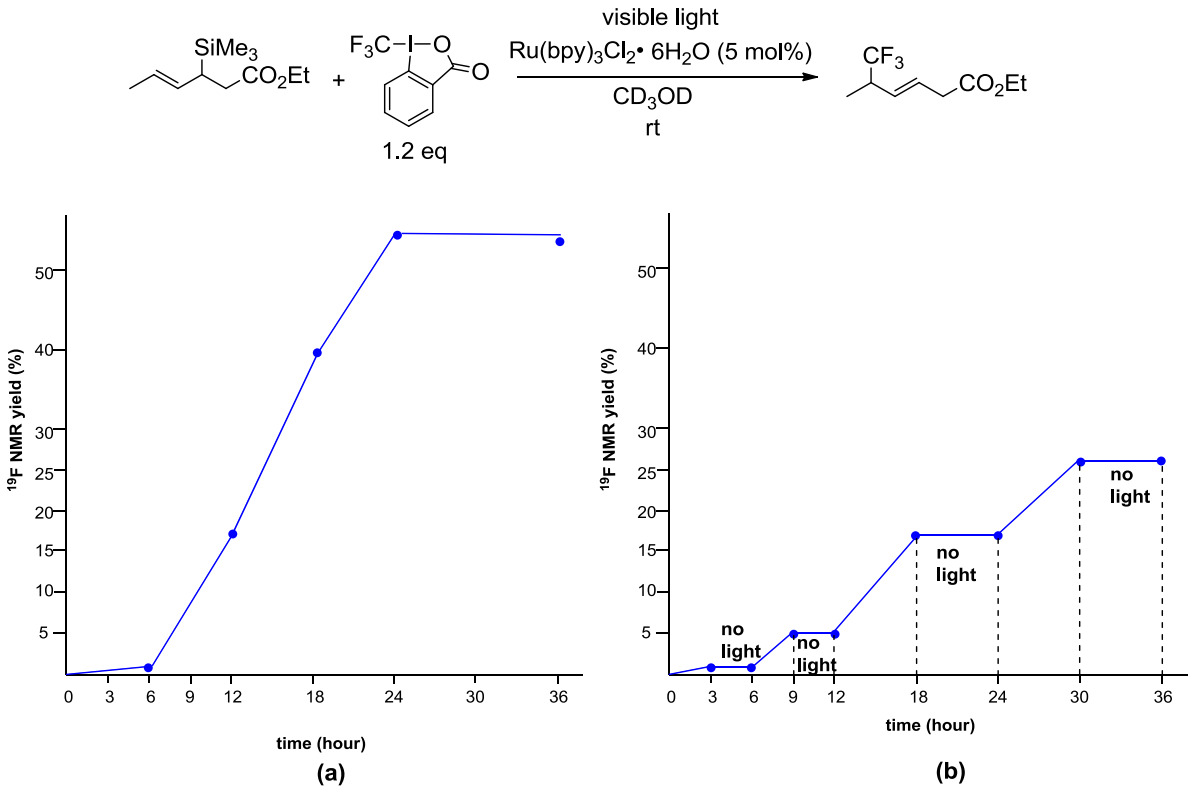


Figure 6.

Reactions with Umemoto reagent **III** (0.18 mmol, 1.2 equiv) instead of Togni reagent **I** were performed: the reaction was stirred for 180 min with continuous irradiation of visible light (Figure **7a**), and with alternating 30 or 60 mins periods of visible light irradiation and 30 or 60 mins periods of no light irradiation (Figure **7b**). These results imply that a visible light irradiation is likely to be a necessary component of the reaction.

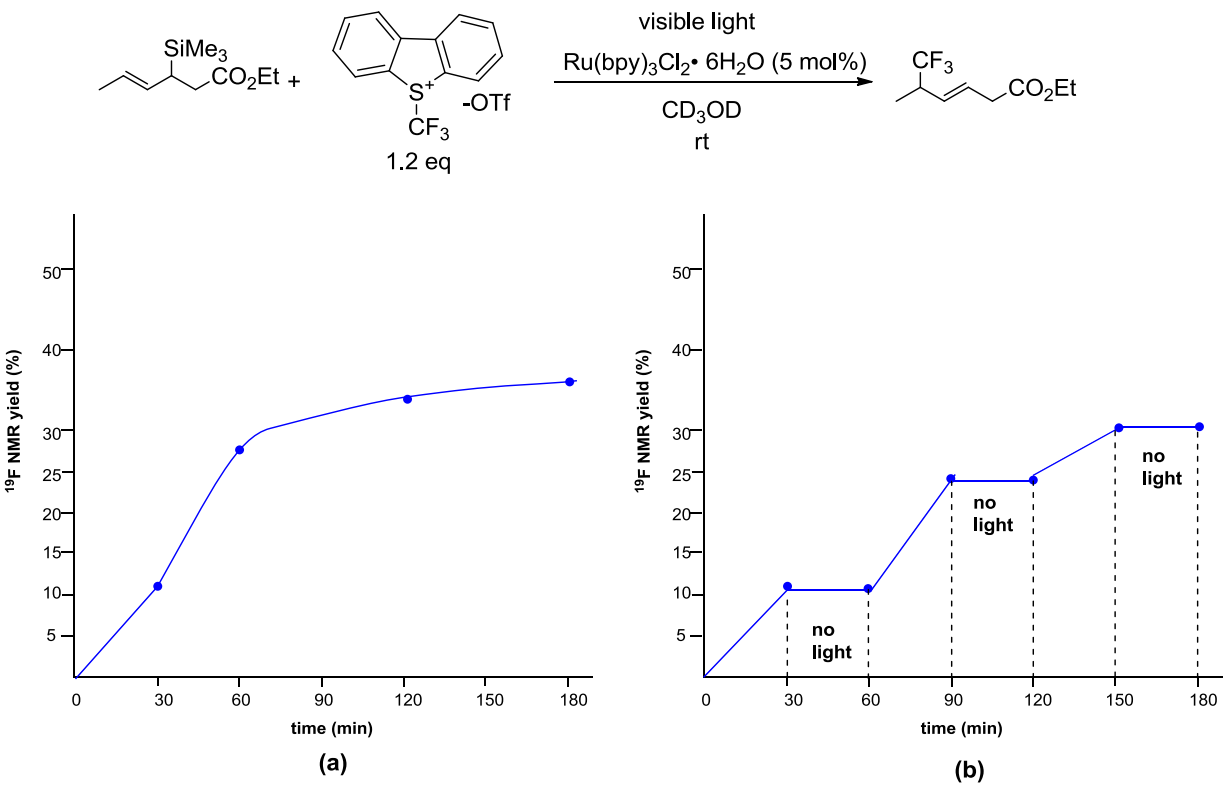


Figure 7.

4. References

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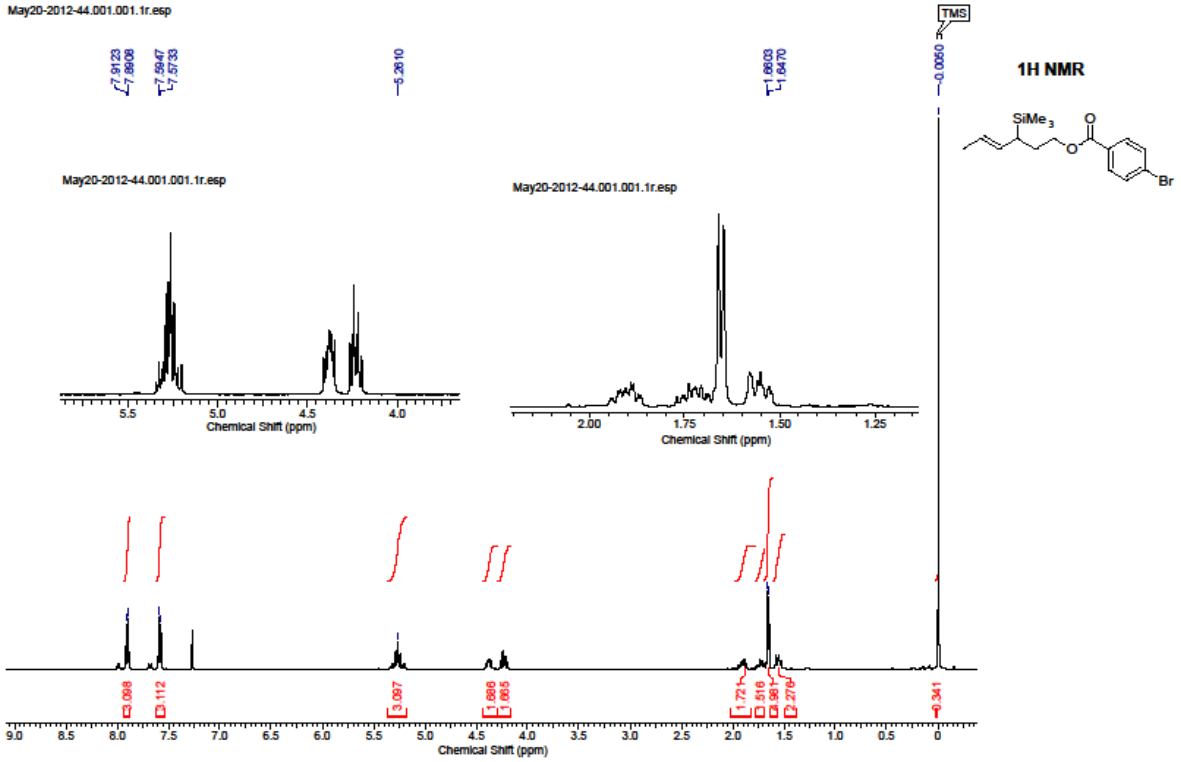
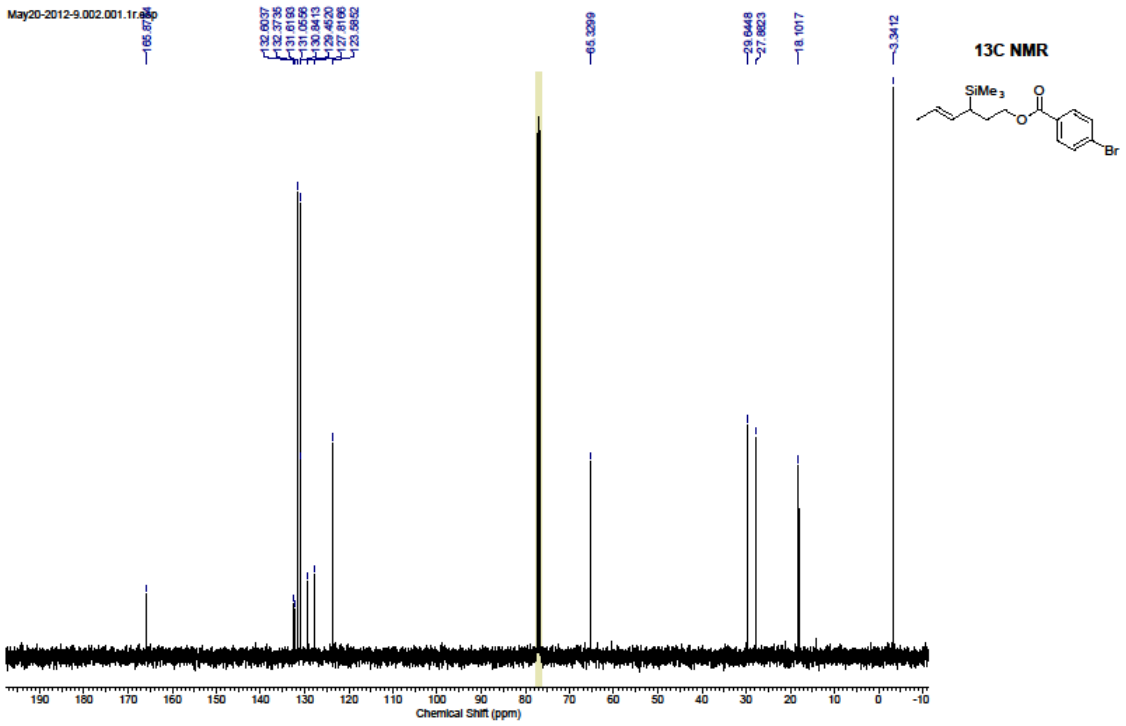
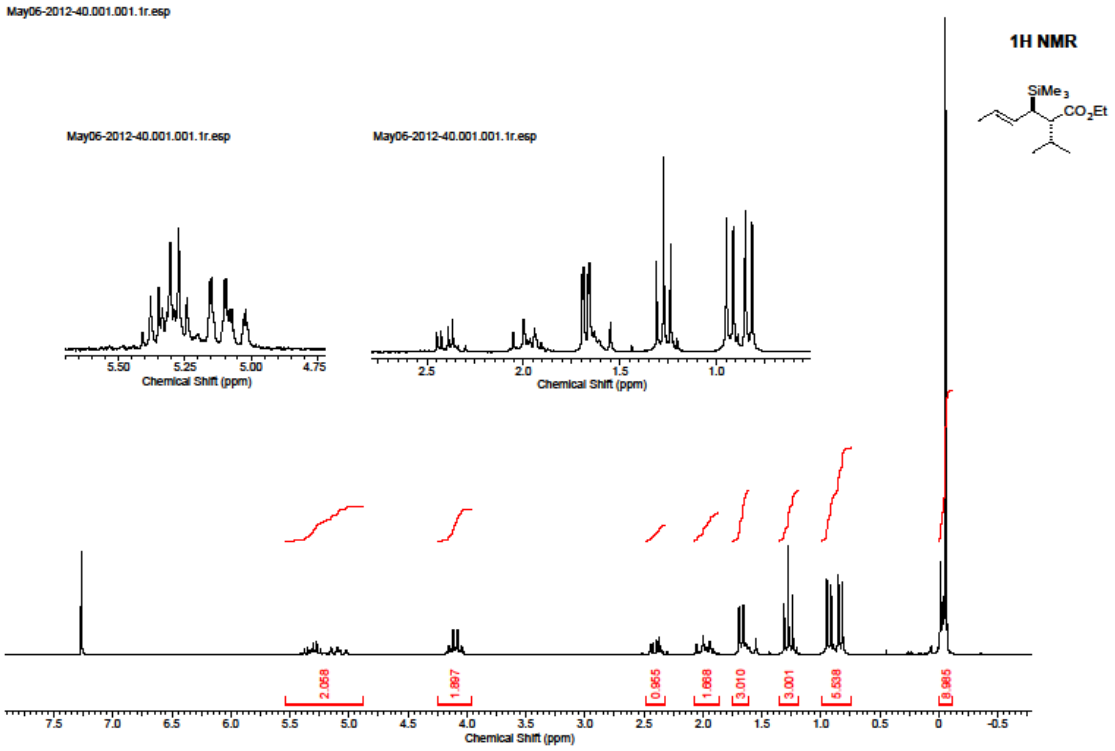
5. NMR Spectra



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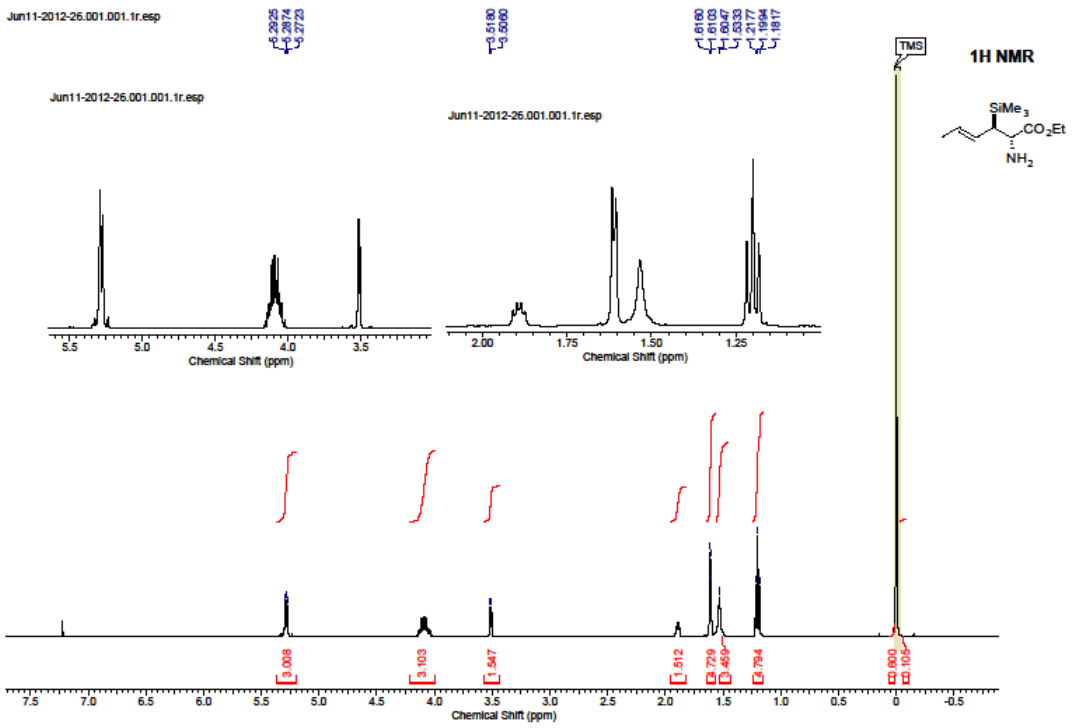
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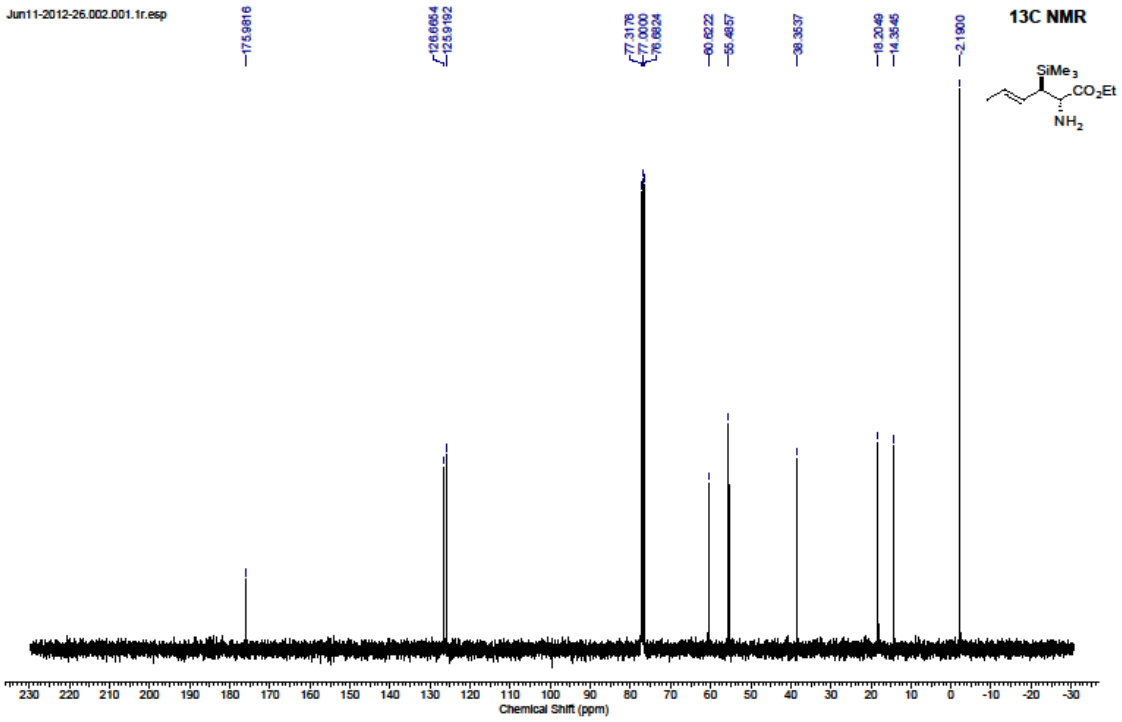
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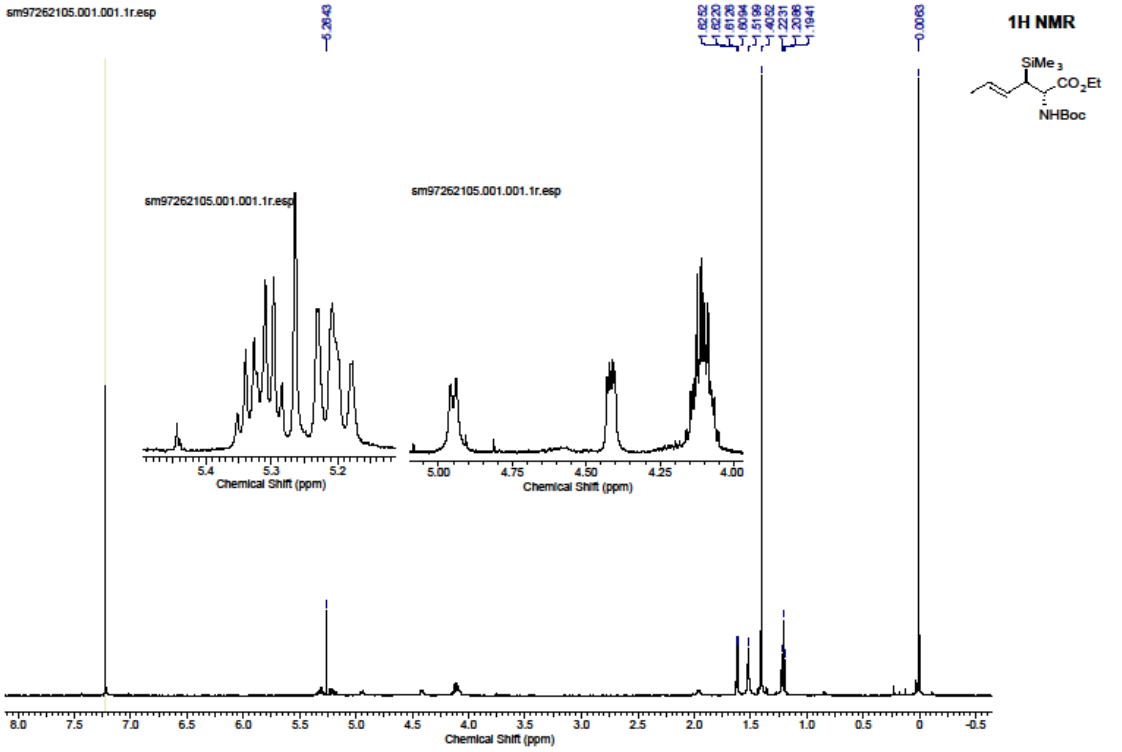
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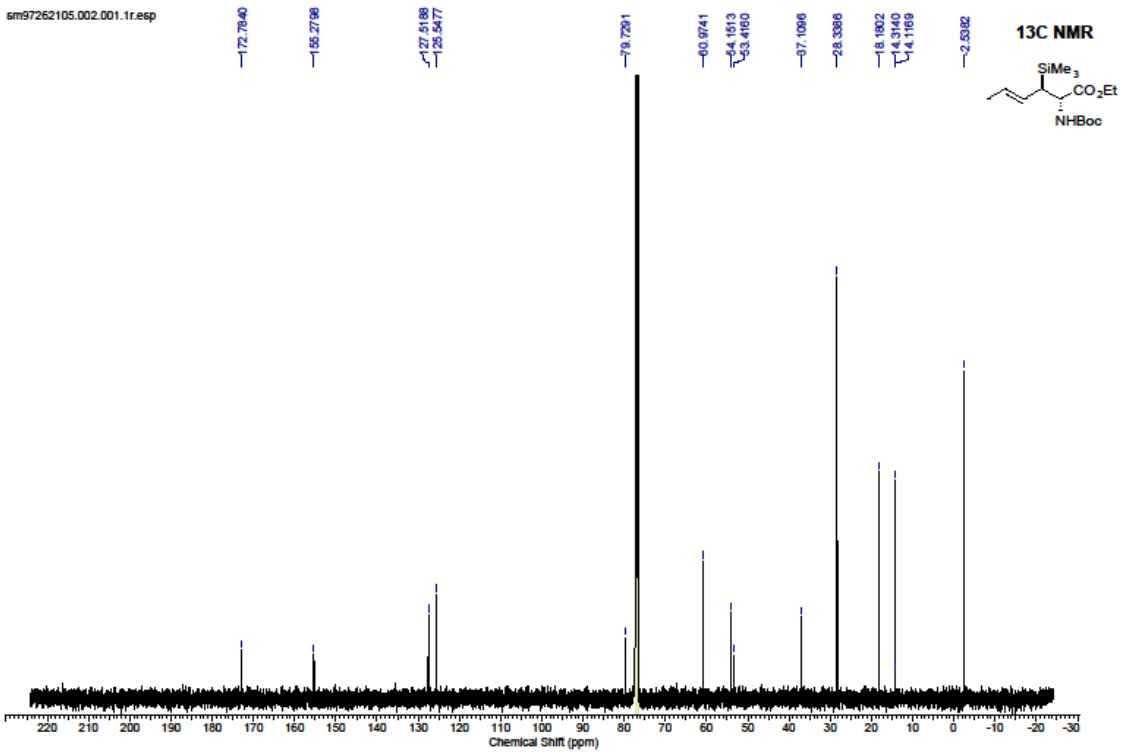
Chemical Shift (ppm)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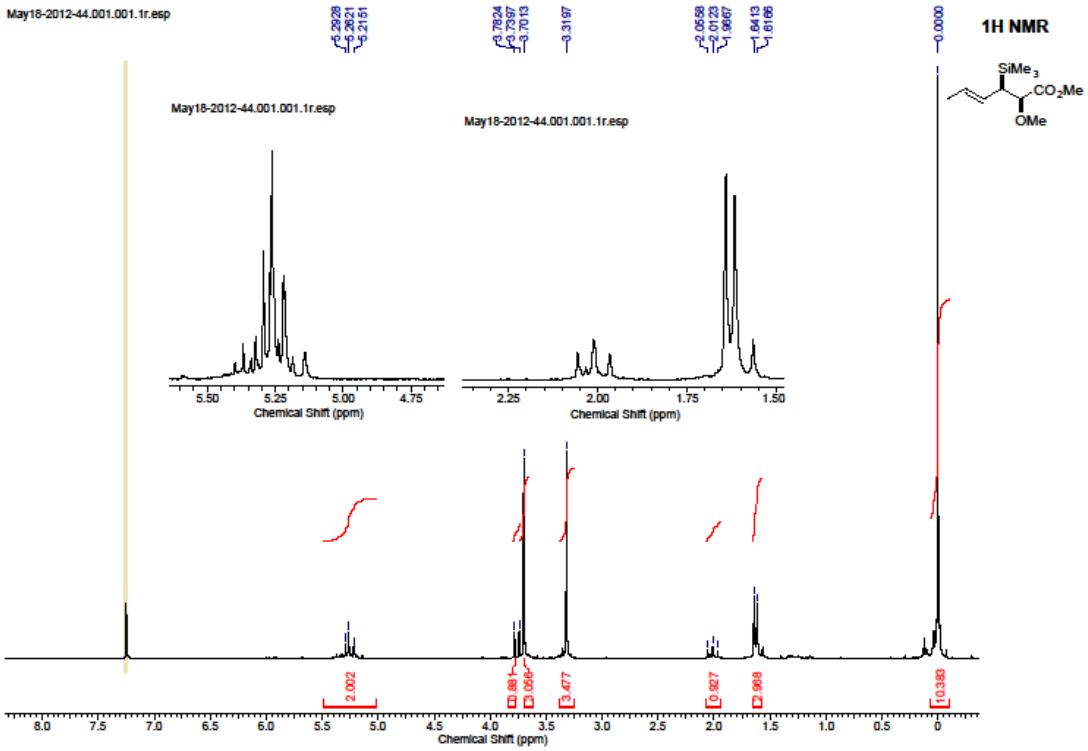
Chemical Shift (ppm)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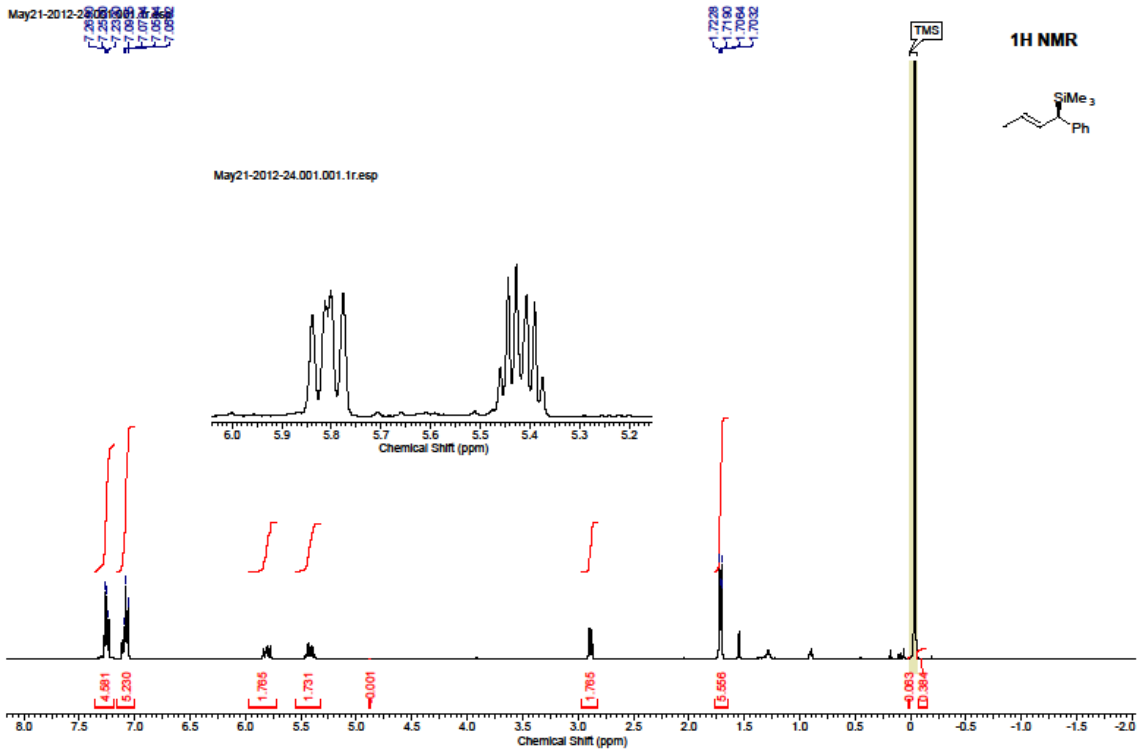
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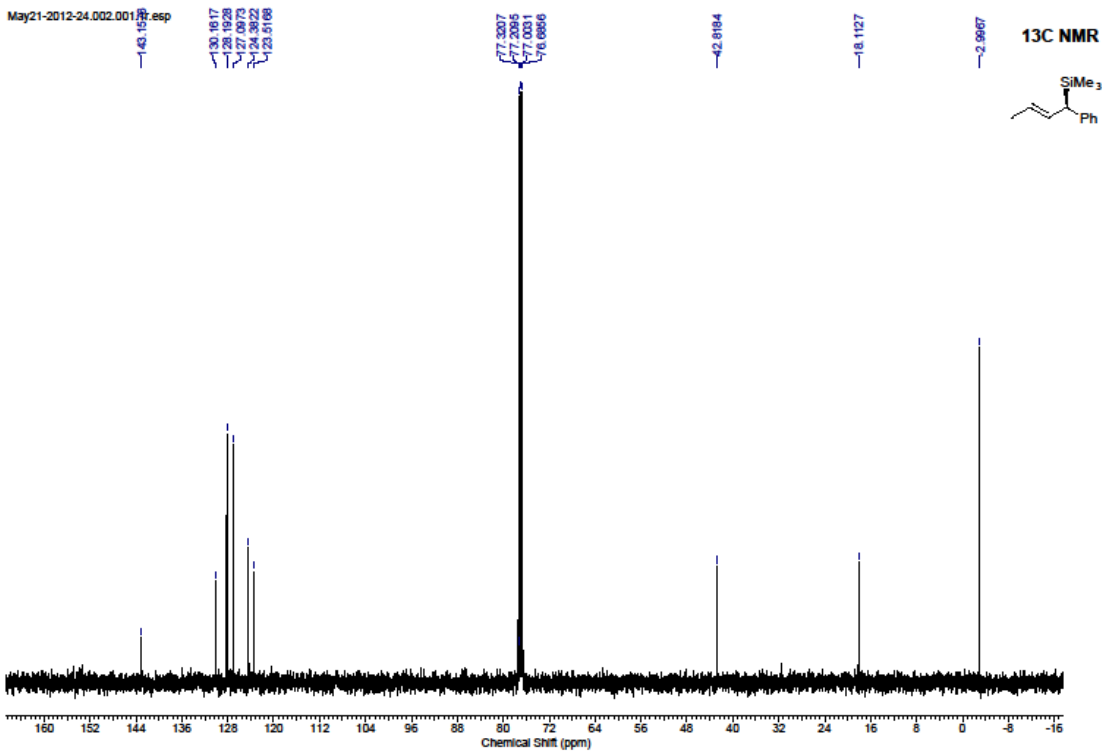
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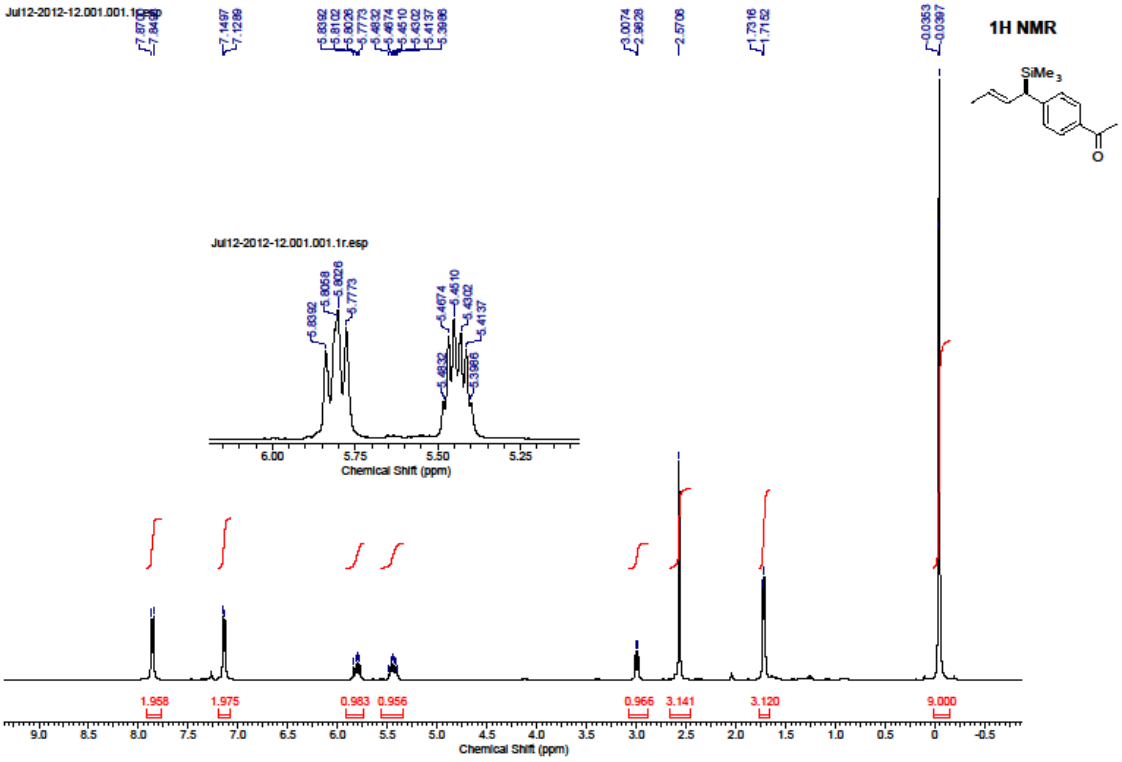
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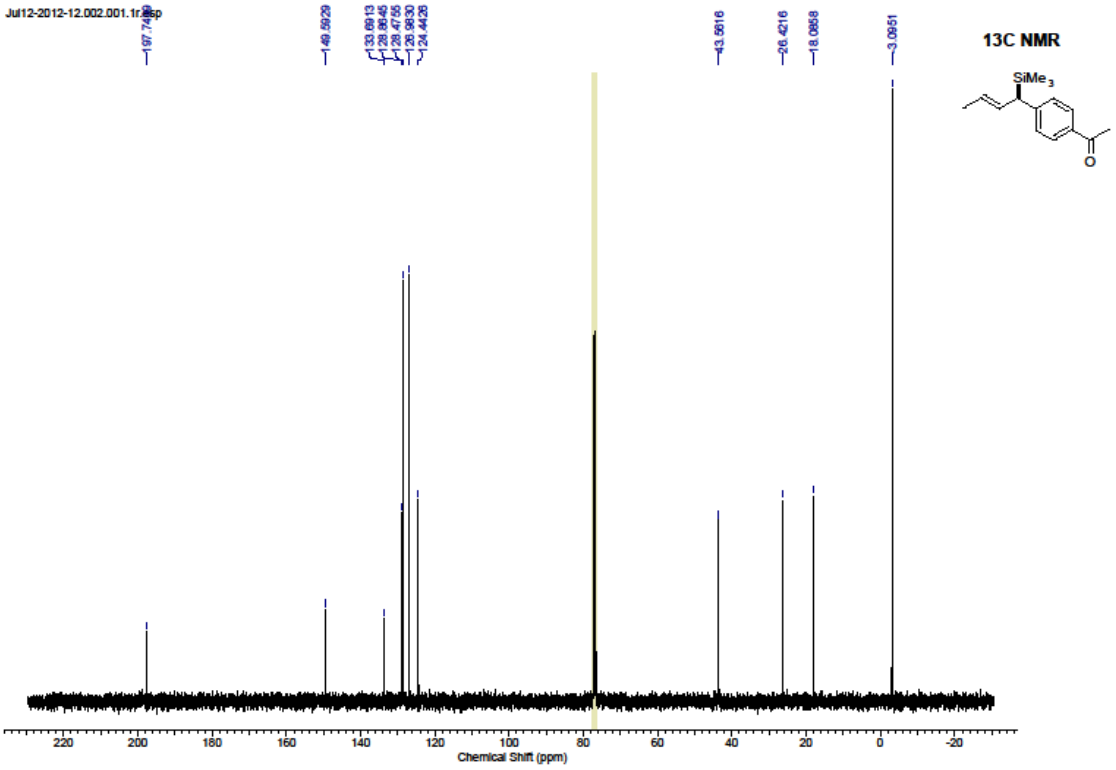
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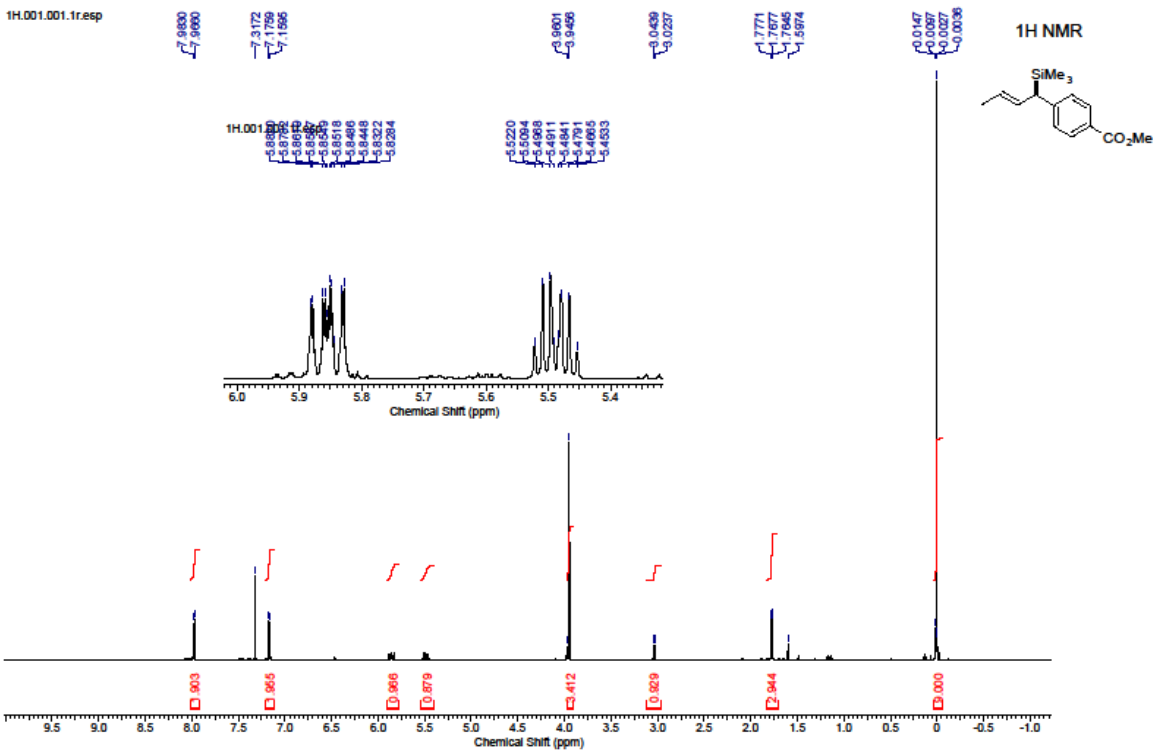
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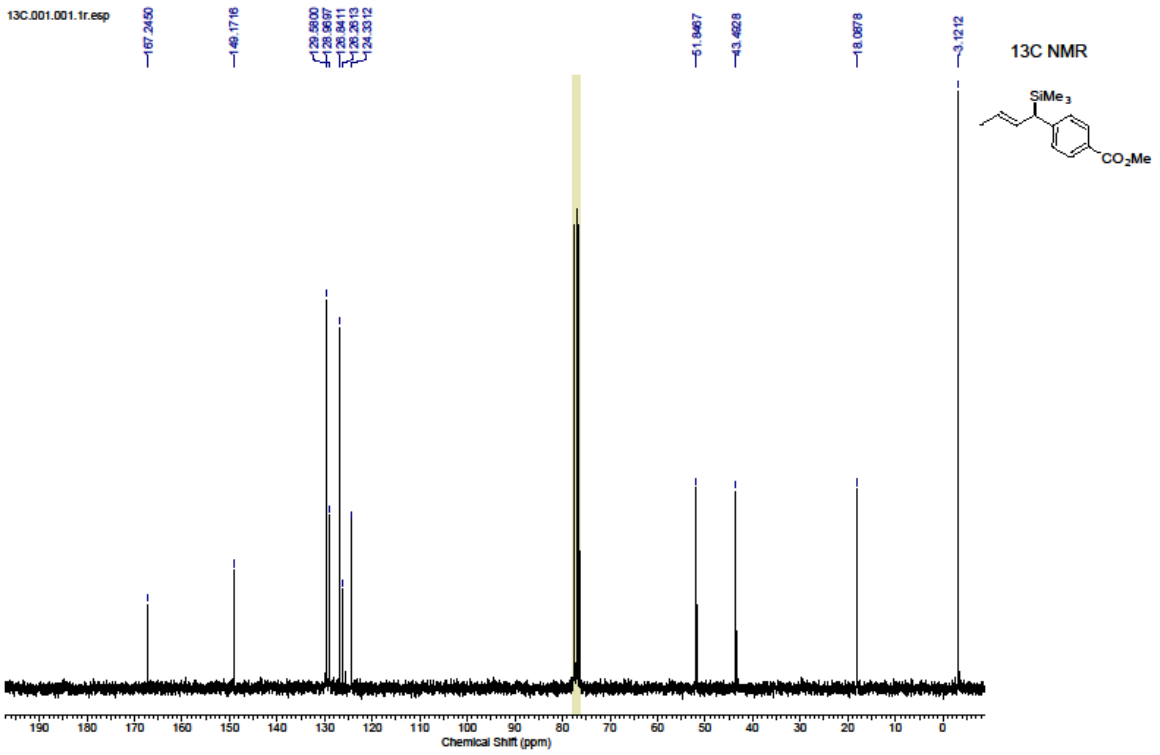
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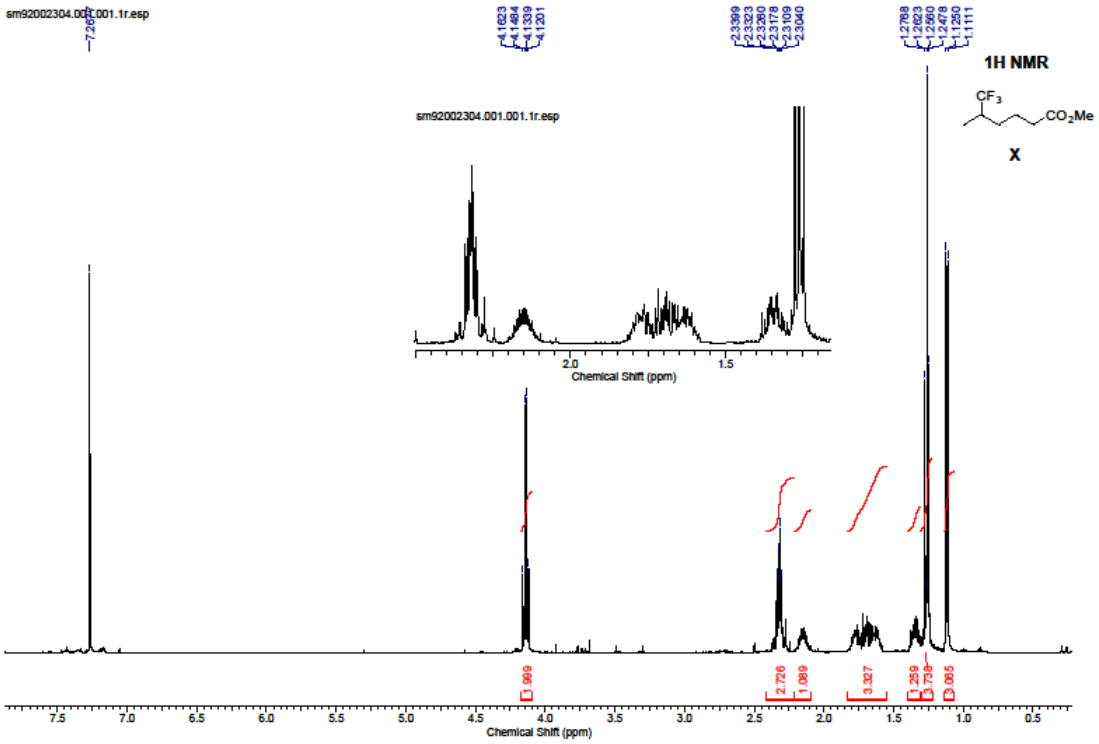
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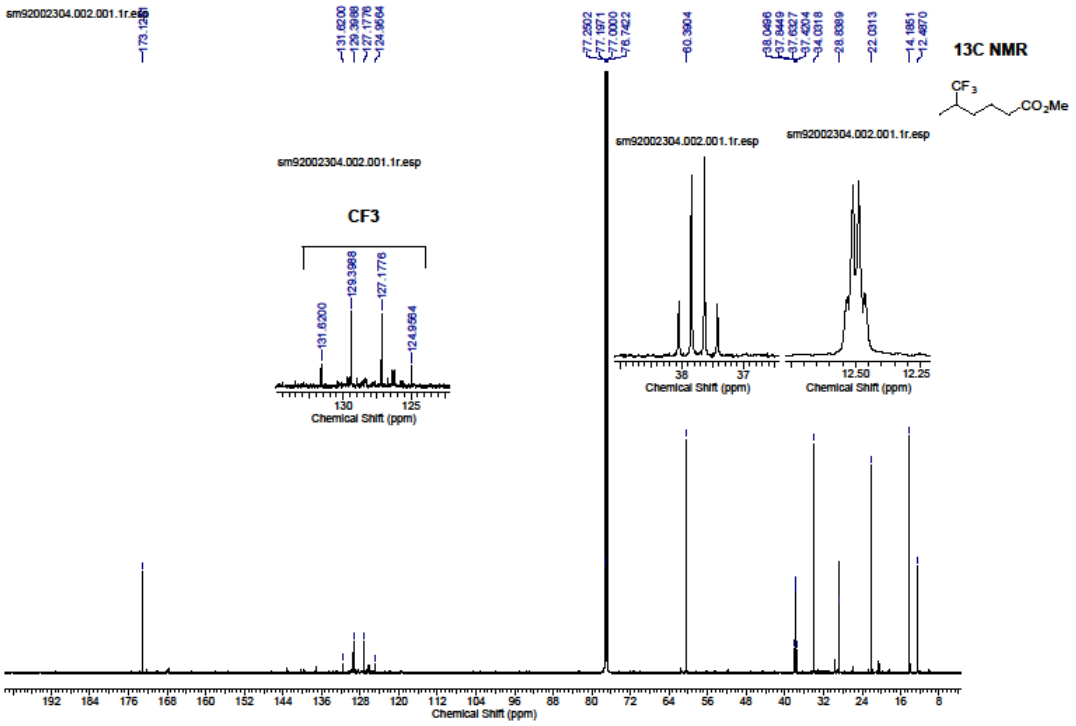
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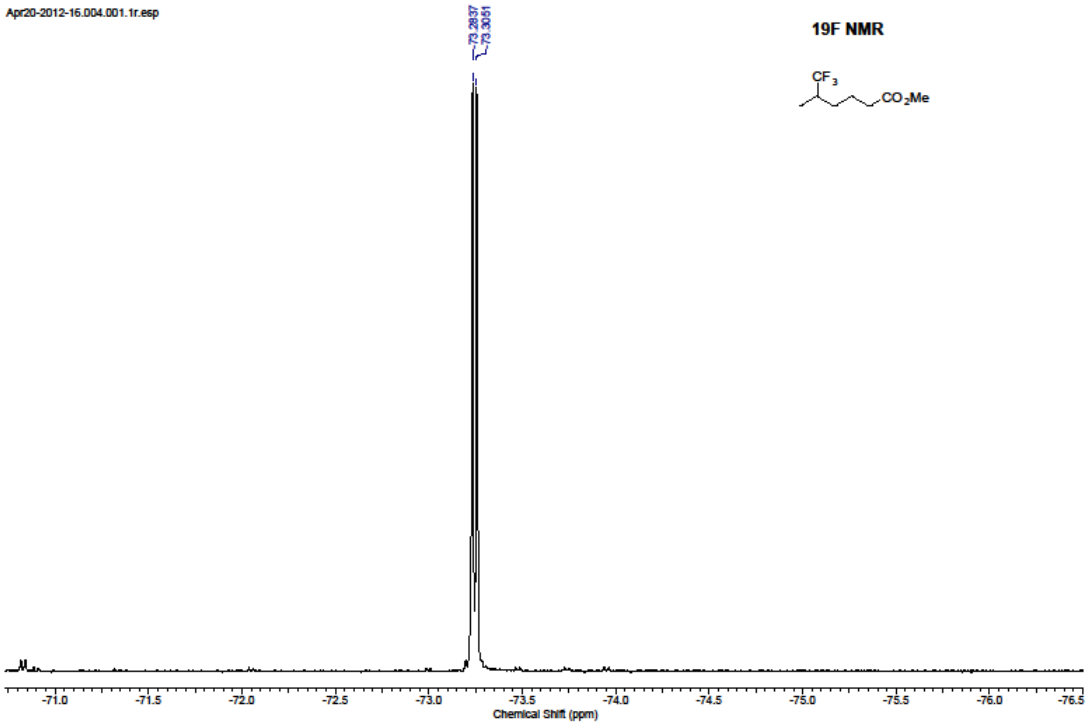
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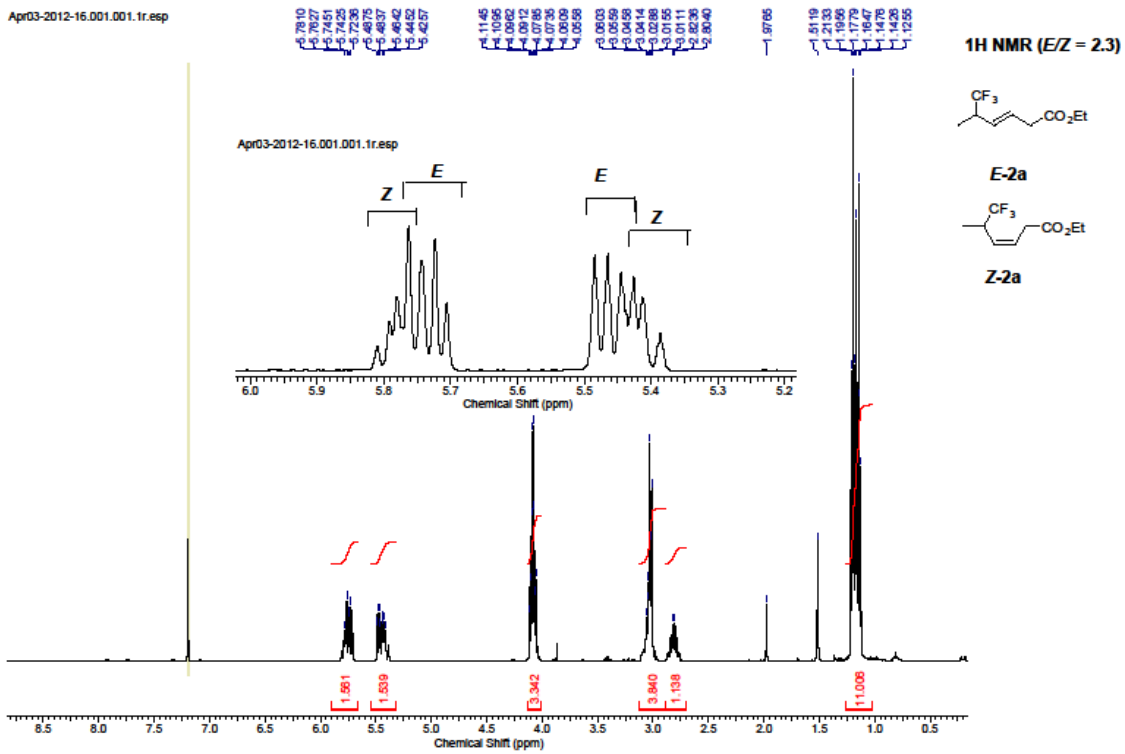
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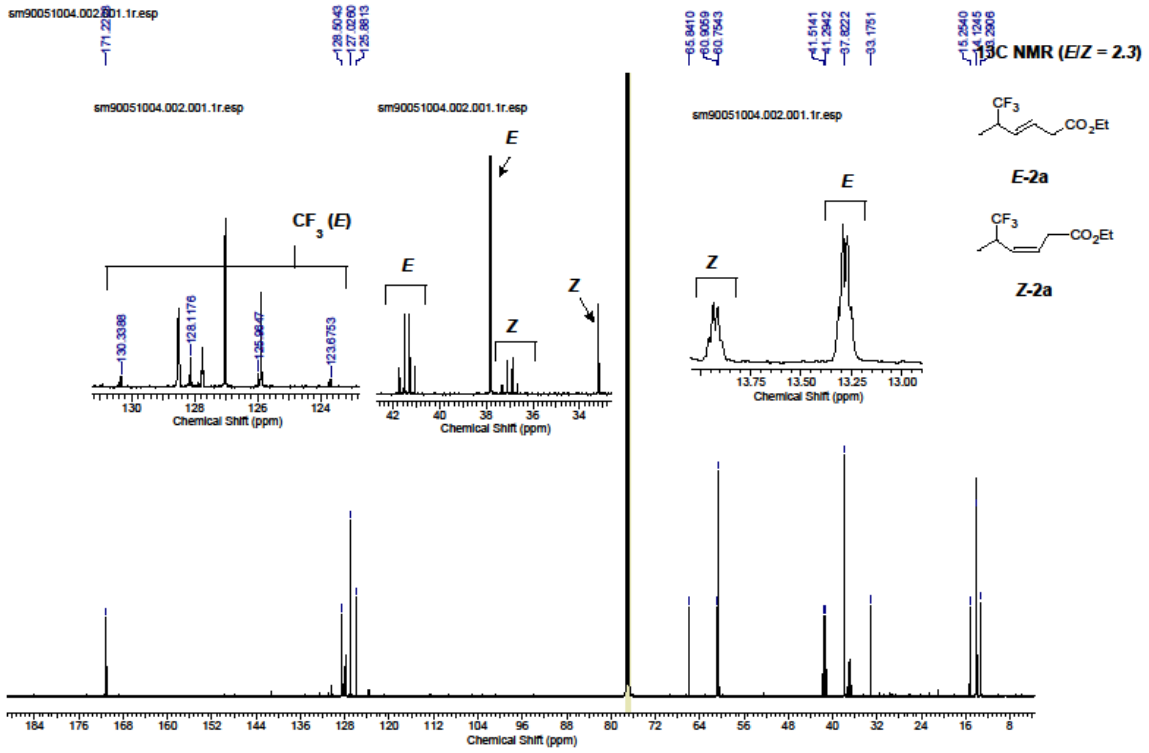
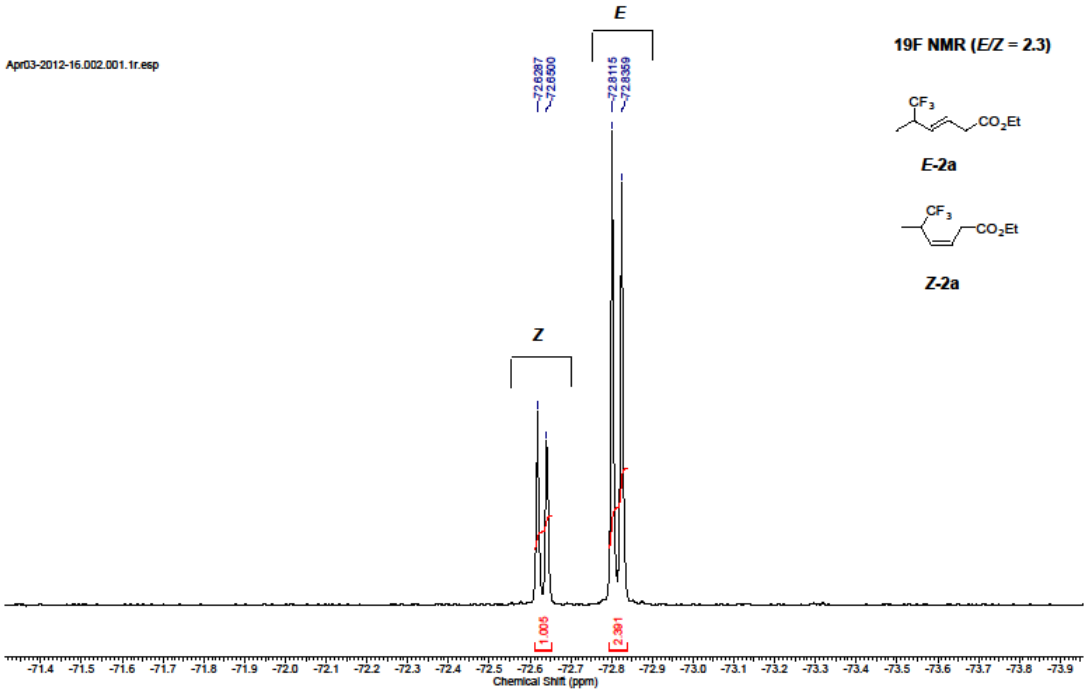
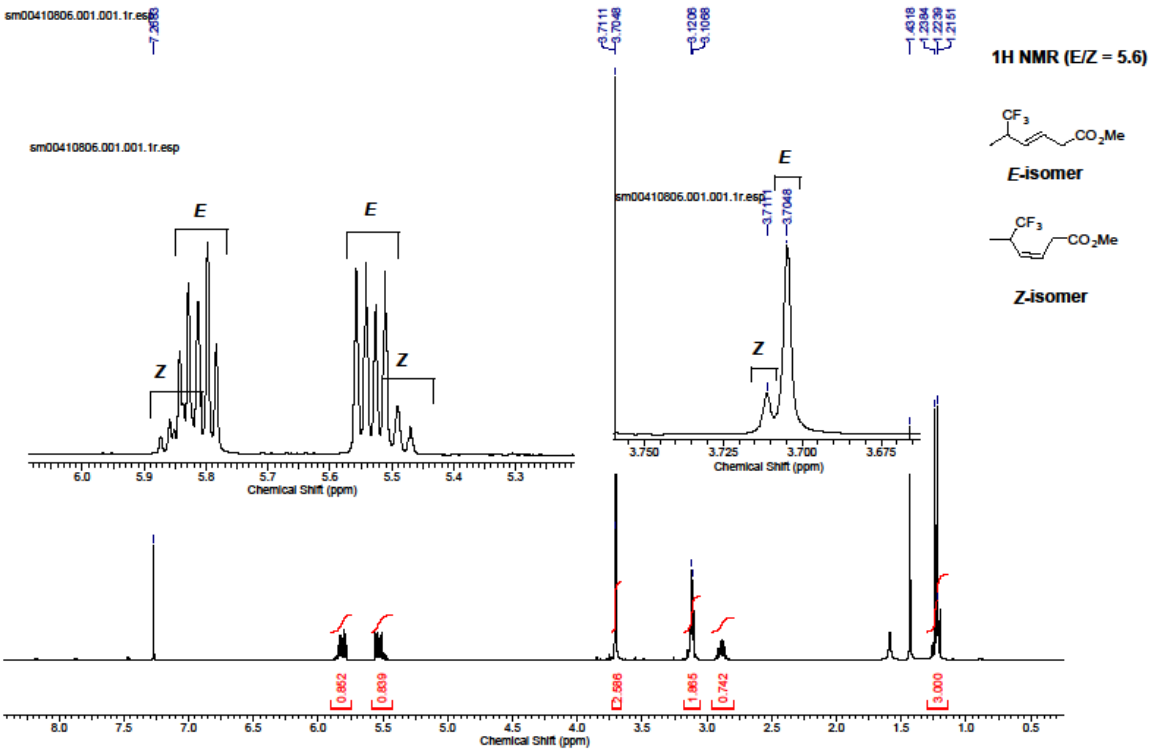
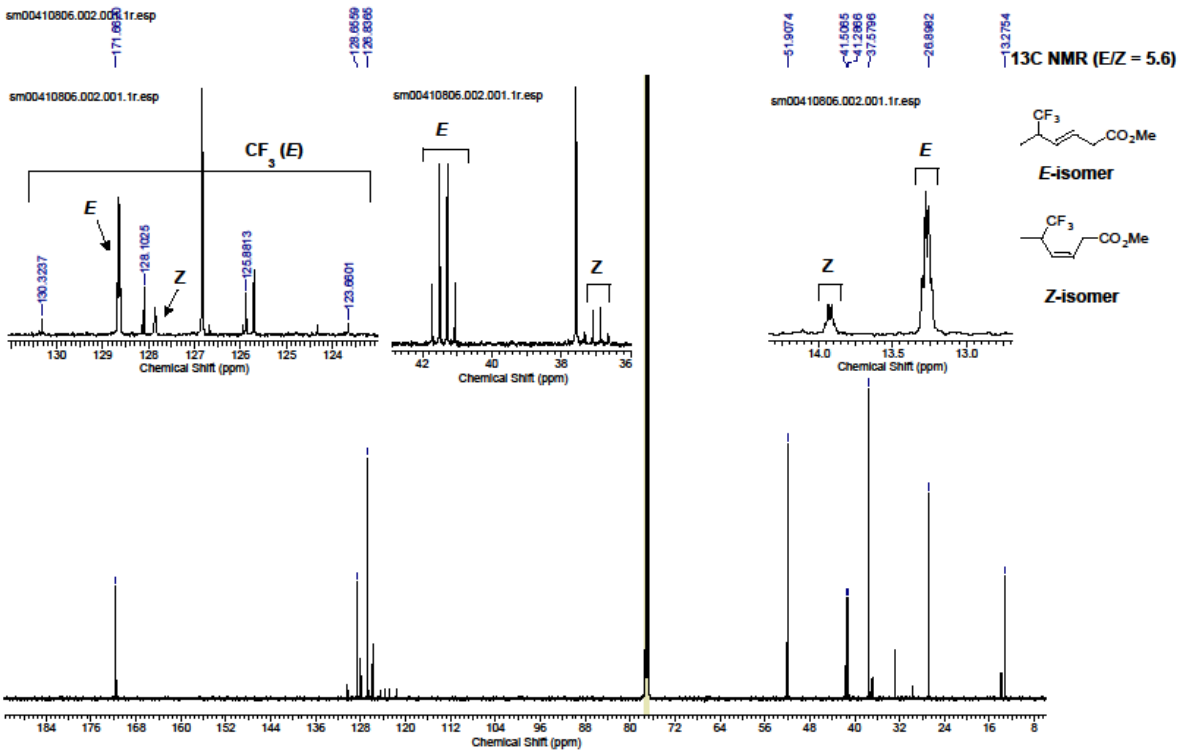
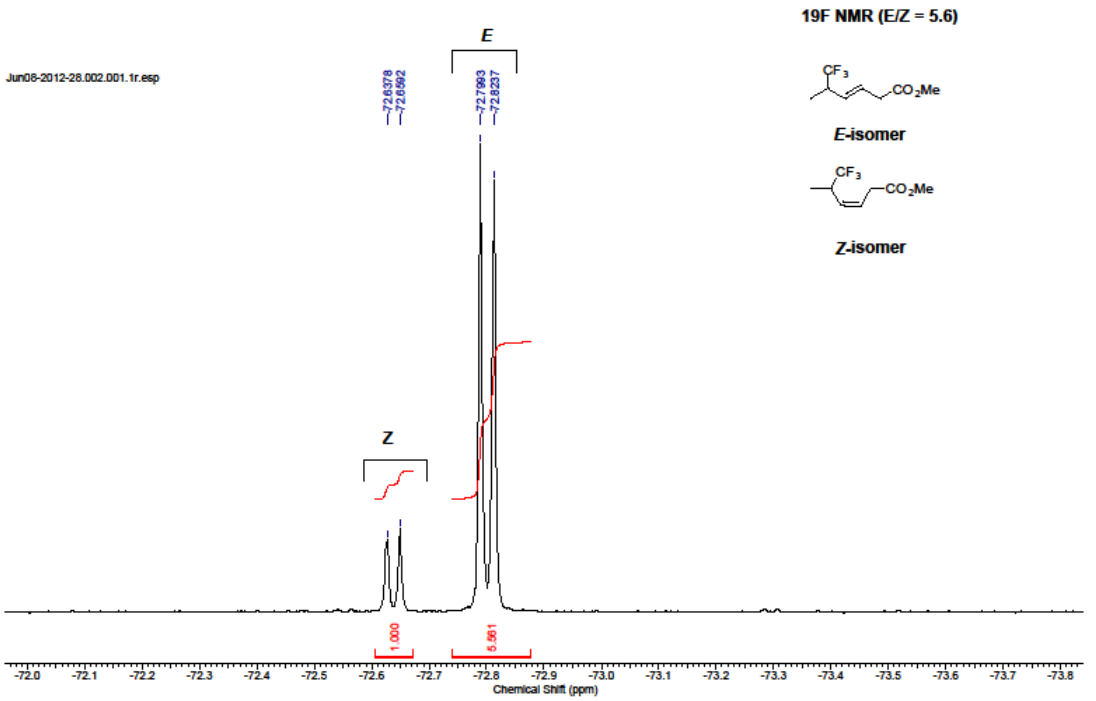
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

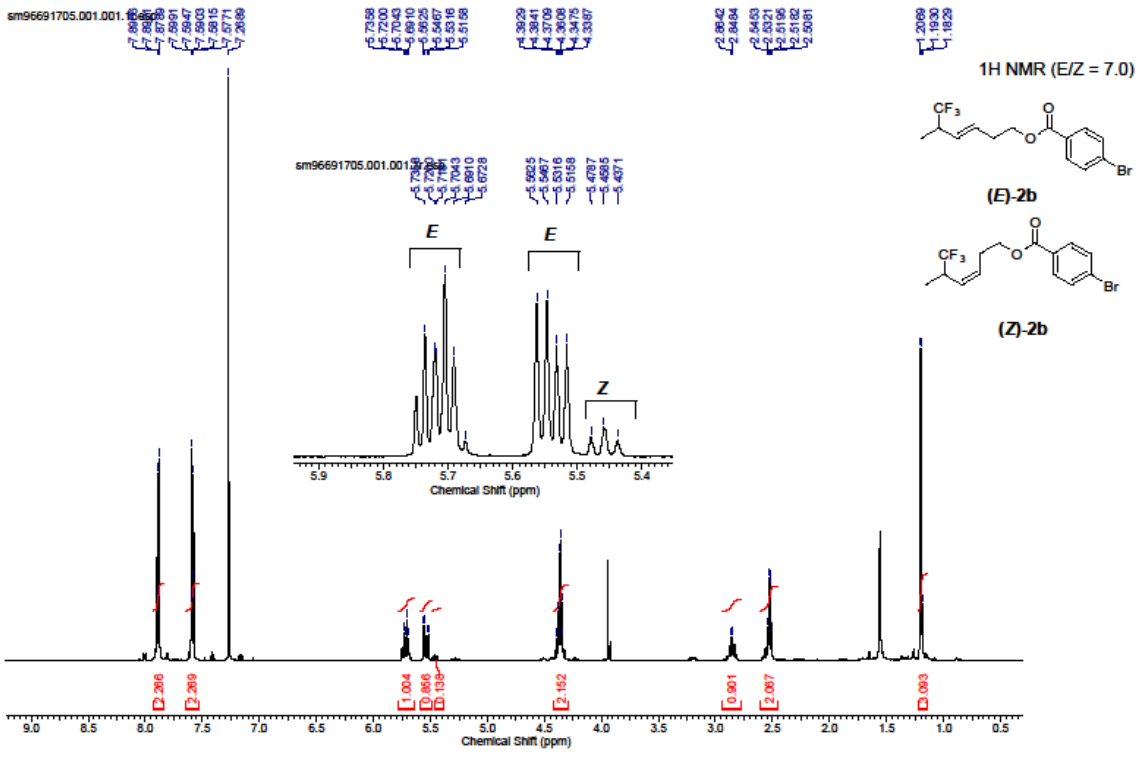

13C NMR (E/Z = 2.3)
E-2a
Z-2a
CF3 (E)
E
Z
Chemical Shift (ppm)

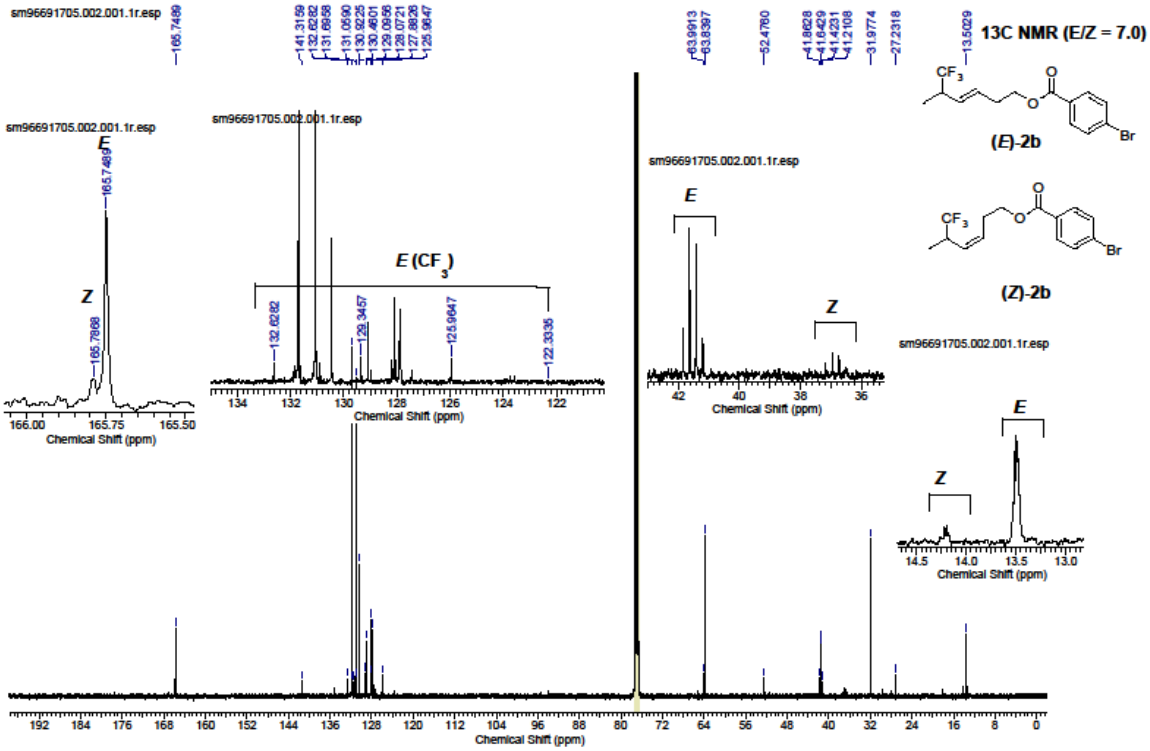

Apr03-2012-16.002.001.1r.esp
19F NMR (E/Z = 2.3)
E-2a
Z-2a
E
Z
1.005
2.391
Chemical Shift (ppm)

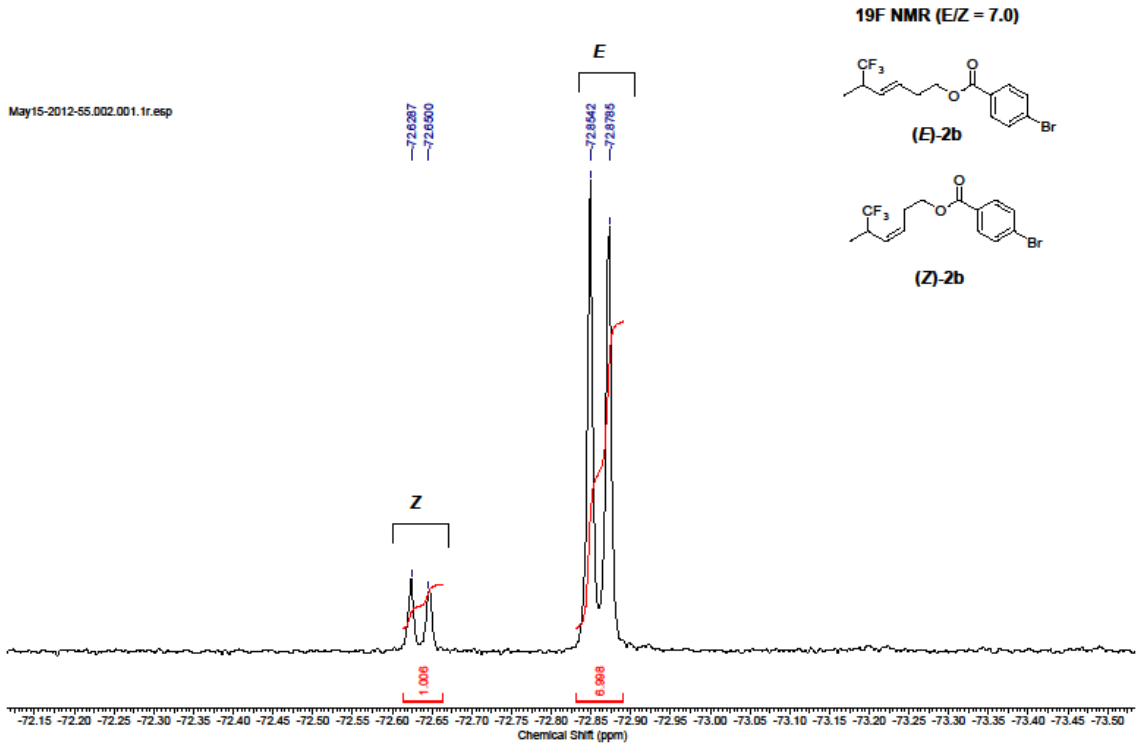

1H NMR (E/Z = 5.6)
E-isomer
Z-isomer
Chemical Shift (ppm)

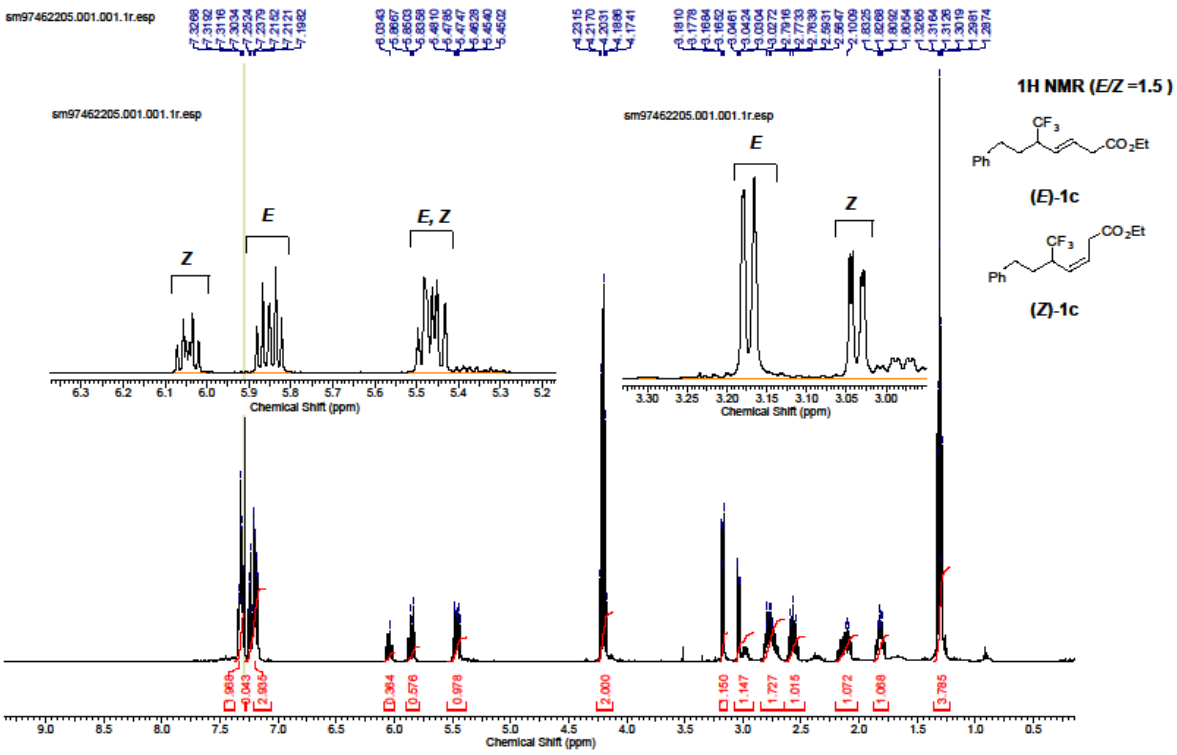

13C NMR (E/Z = 5.6)
E-isomer
Z-isomer
Chemical Shift (ppm)

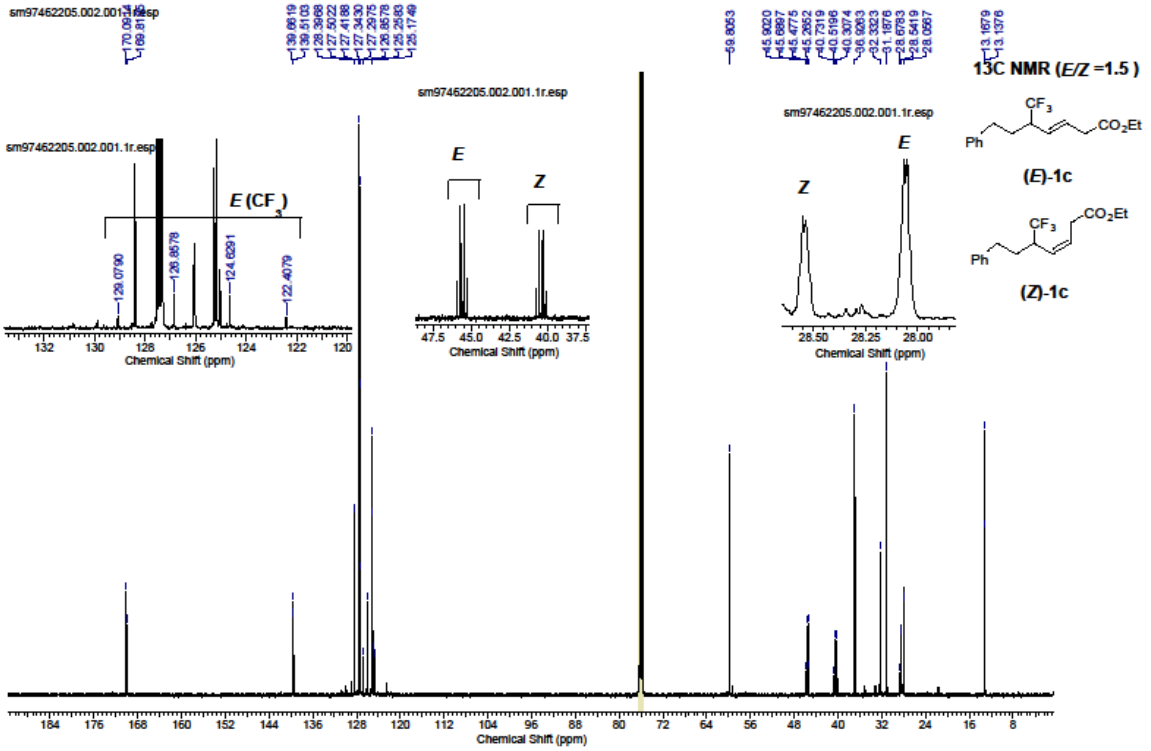

19F NMR (E/Z = 5.6)
Jun08-2012-28.002.001.1r.esp
E
Z
-72.6378
-72.6892
-72.7993
-72.8237
1.000
5.561
Chemical Shift (ppm)
E-isomer
Z-isomer

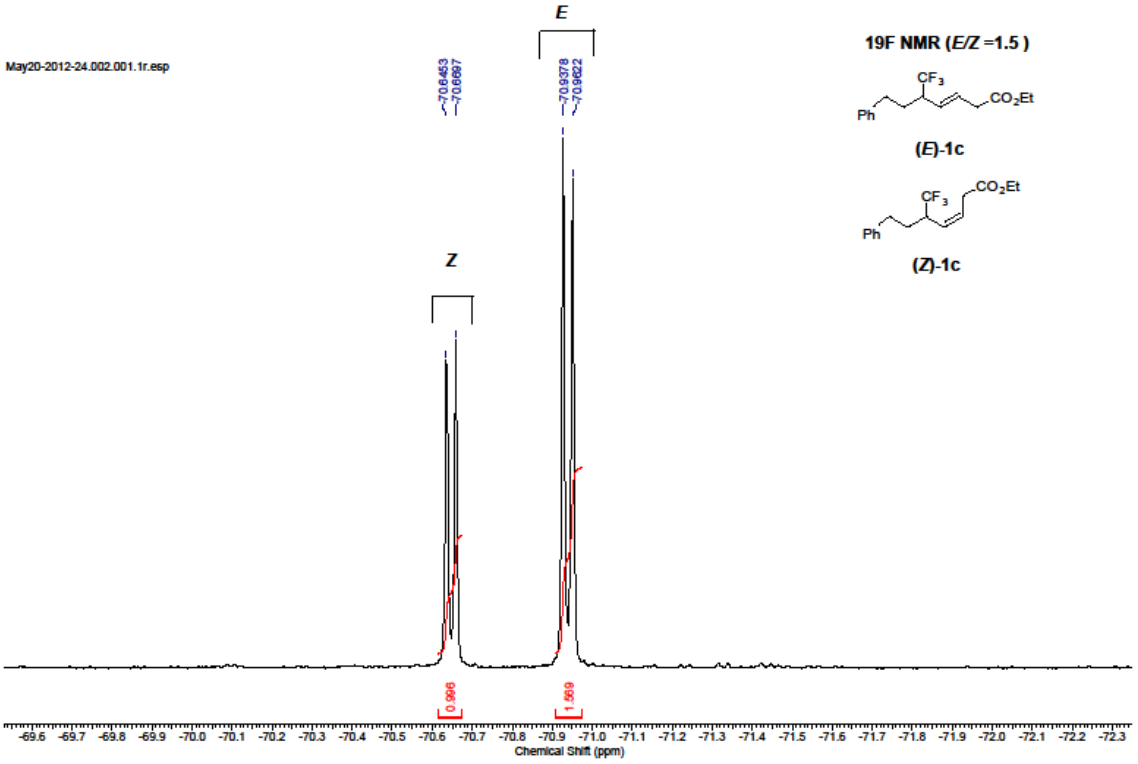

1H NMR (E/Z = 7.0)
sm96691705.001.001
E
E
Z
Chemical Shift (ppm)
(E)-2b
(Z)-2b

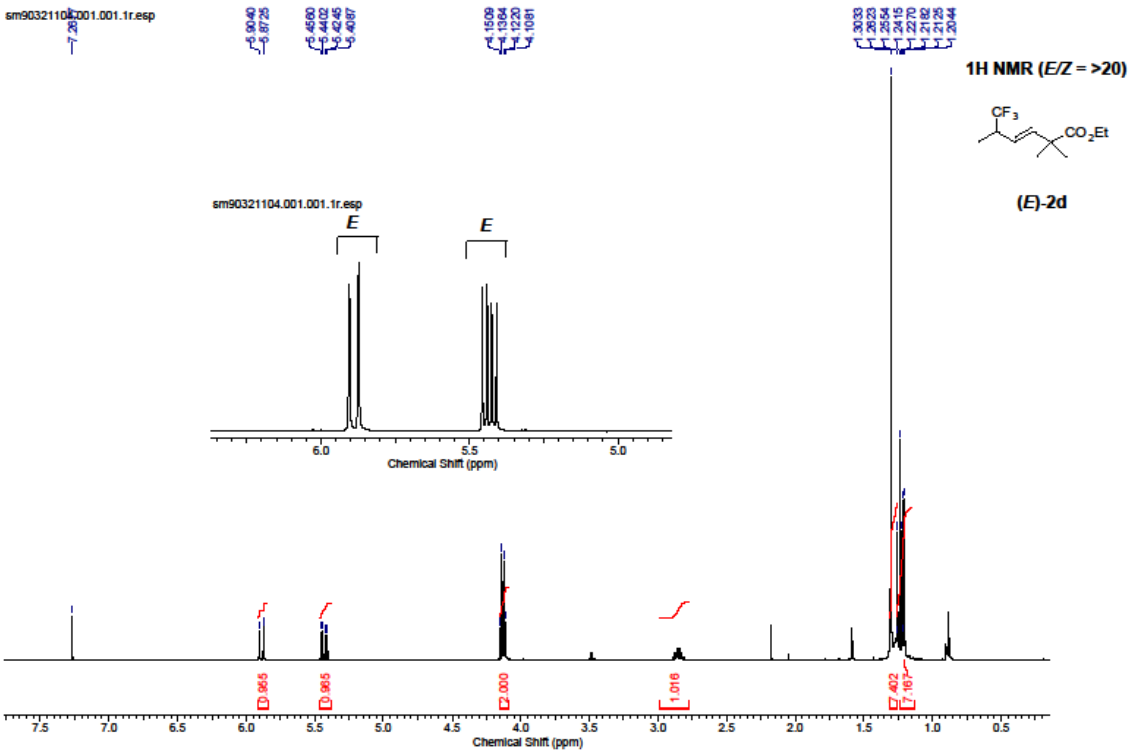

13C NMR (E/Z = 7.0)
(E)-2b
(Z)-2b
Chemical Shift (ppm)

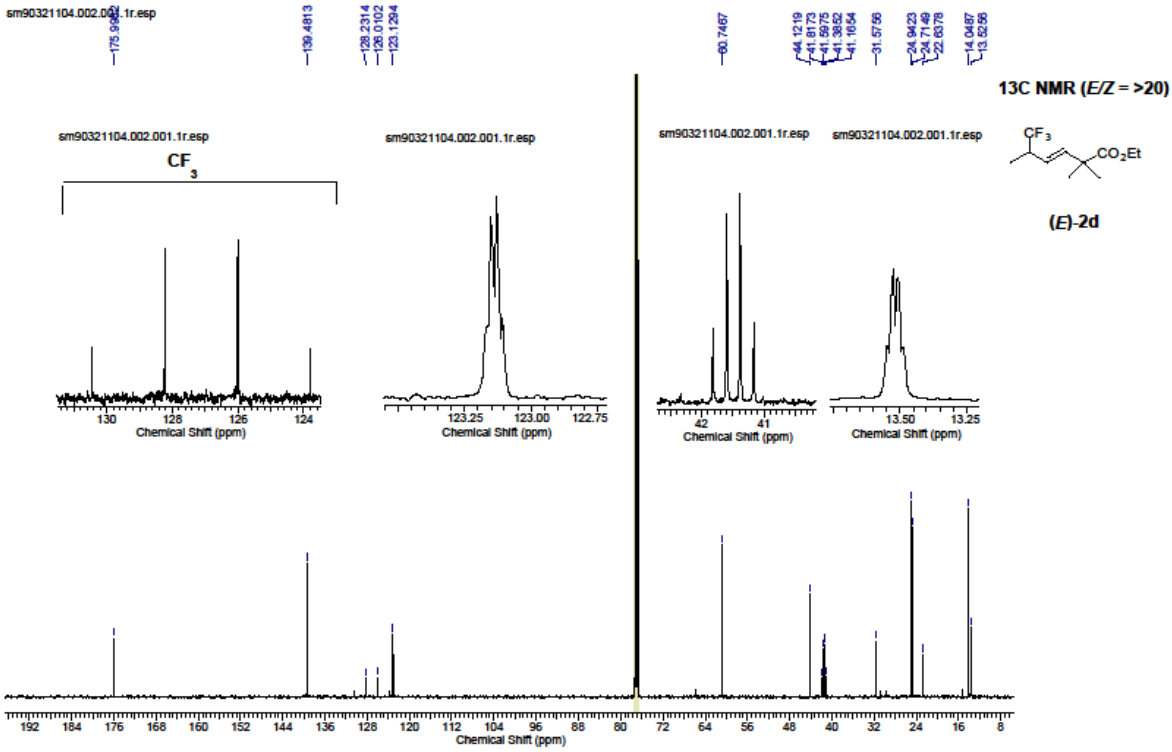

19F NMR (E/Z = 7.0)
(E)-2b
(Z)-2b
Chemical Shift (ppm)

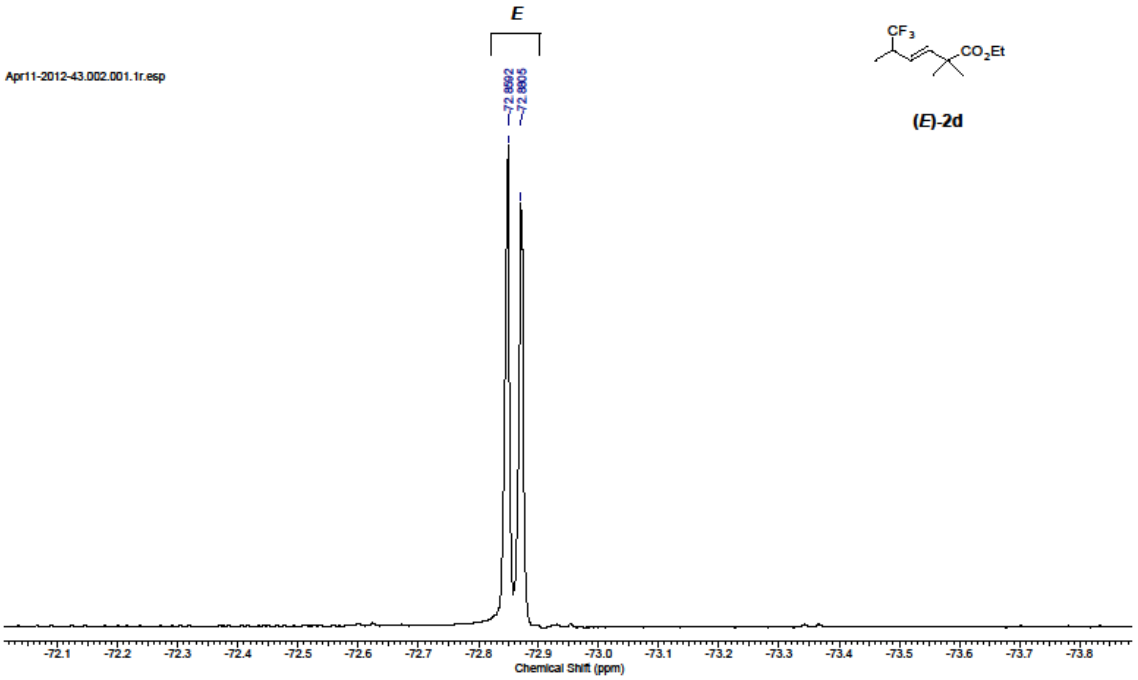

1H NMR (E/Z =1.5)
(E)-1c
(Z)-1c
Chemical Shift (ppm)

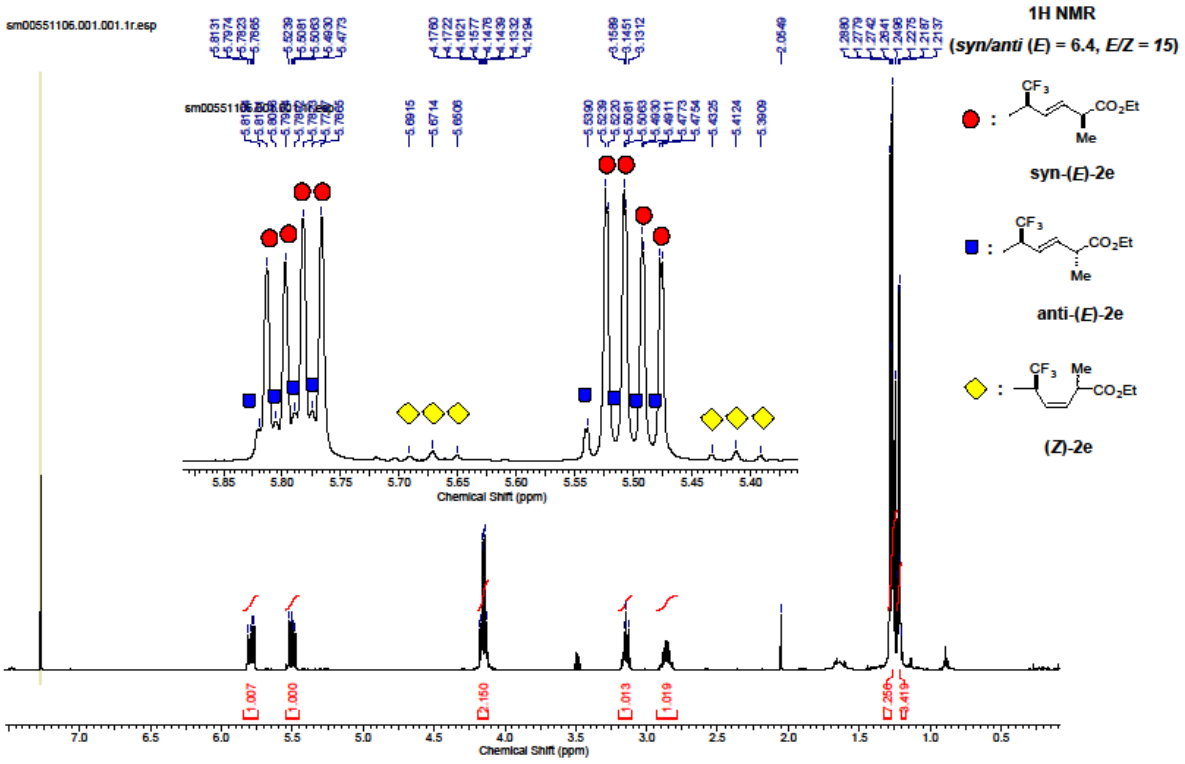

13C NMR (E/Z =1.5)
(E)-1c
(Z)-1c
Chemical Shift (ppm)

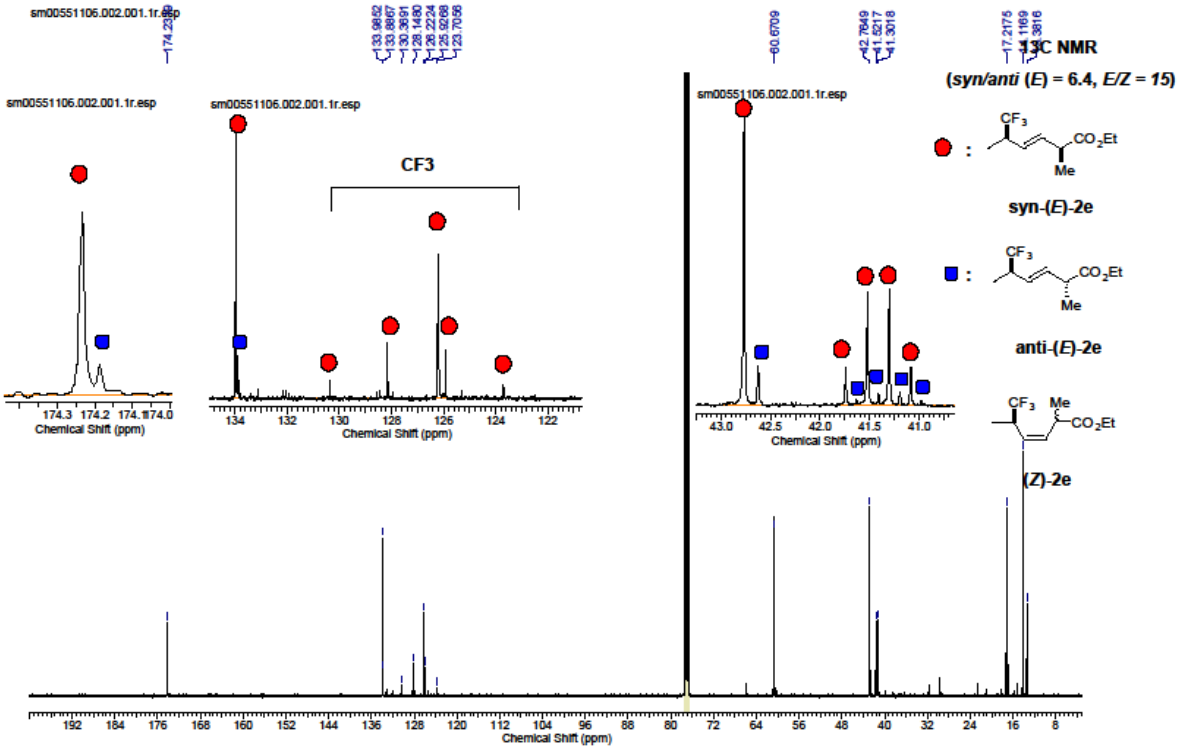

May20-2012-24.002.001.1r.esp
E
Z
-70.6453
-70.6697
-70.9378
-70.9622
0.996
1.999
19F NMR (E/Z =1.5)
CF3
CO2Et
Ph
(E)-1c
(Z)-1c
Chemical Shift (ppm)

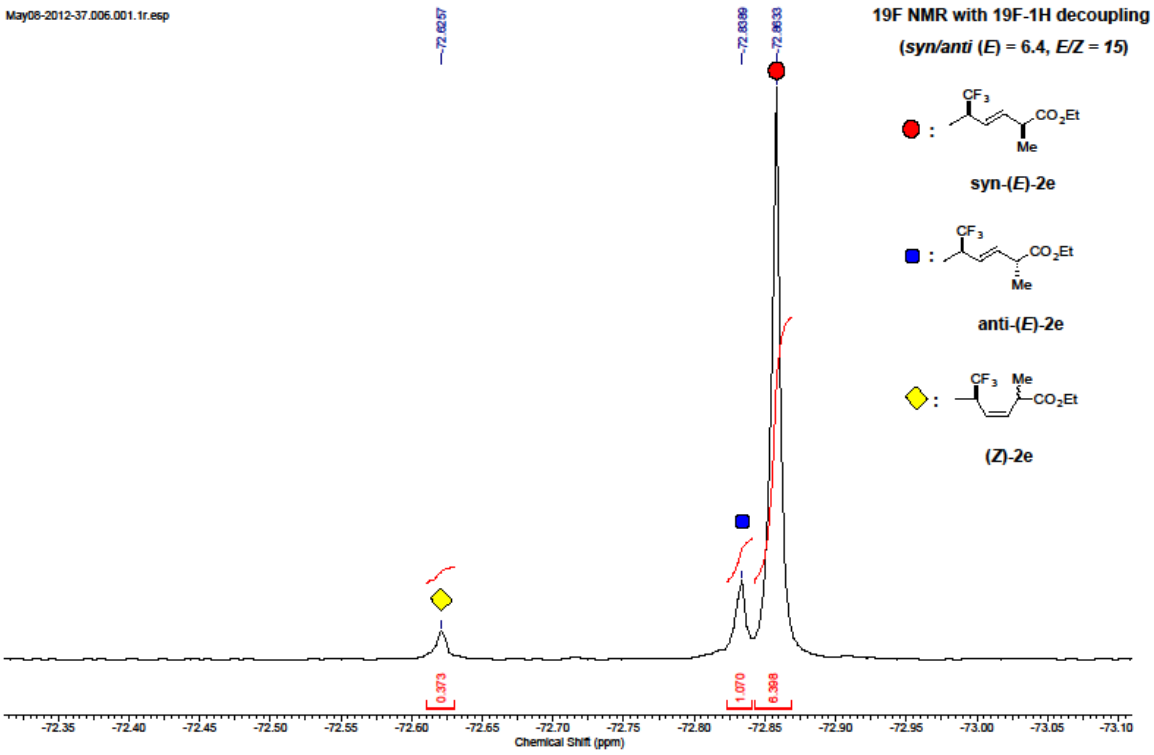

sm90321104.001.001.1r.esp
1H NMR (E/Z = >20)
CF3
CO2Et
(E)-2d
sm90321104.001.001.1r.esp
E
E
Chemical Shift (ppm)
0.965
0.965
2.000
1.016
2.402
7.167
Chemical Shift (ppm)

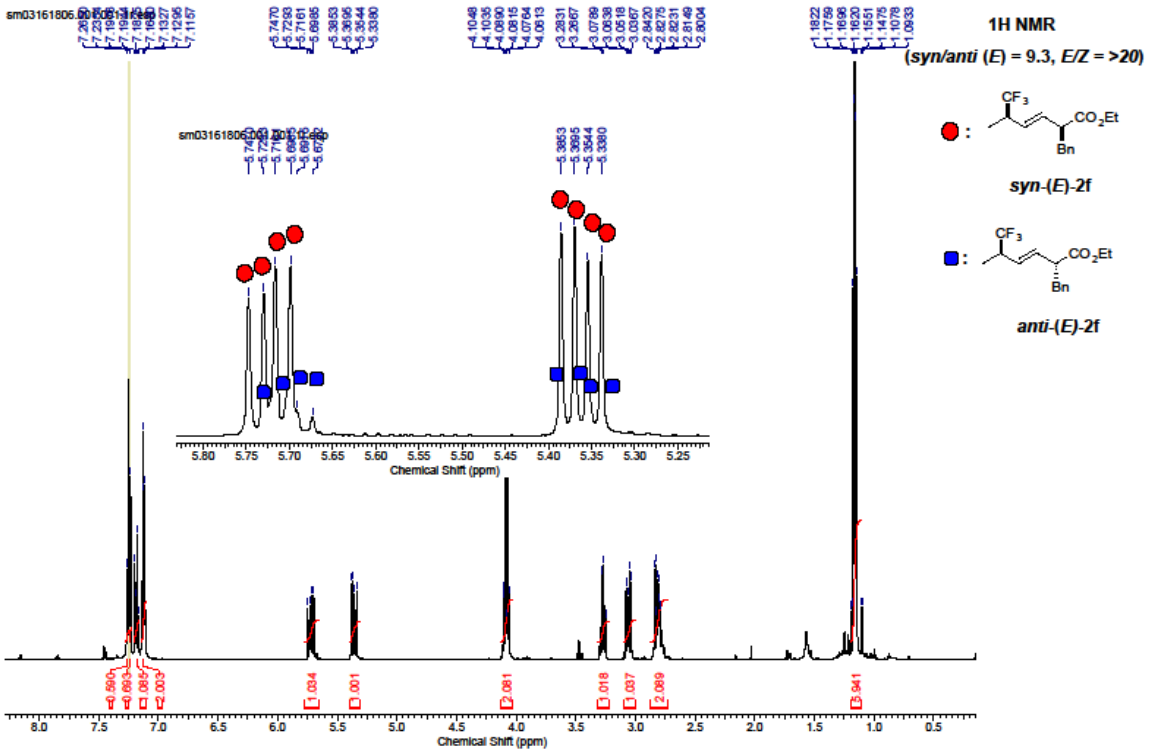

sm90321104.002.001.1r.esp
175.9882
139.4813
128.2314
126.0102
123.1294
60.7467
44.1219
41.8173
41.5975
41.3852
41.1654
31.5756
24.9423
24.7148
22.6378
14.0487
13.5266
13C NMR (E/Z = >20)
CF3
CO2Et
(E)-2d
Chemical Shift (ppm)

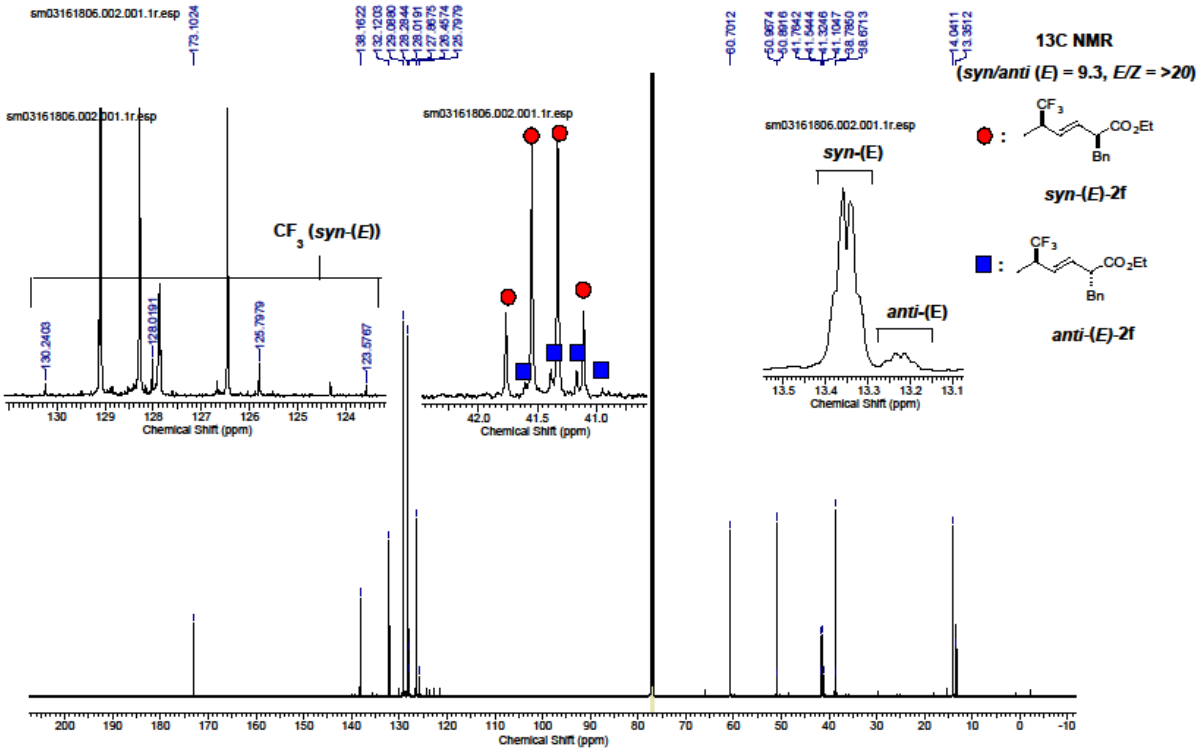

E
Apr11-2012-43.002.001.1r.esp
72.8992
72.8805
13C NMR (E/Z = >20)
CF3
CO2Et
(E)-2d
Chemical Shift (ppm)

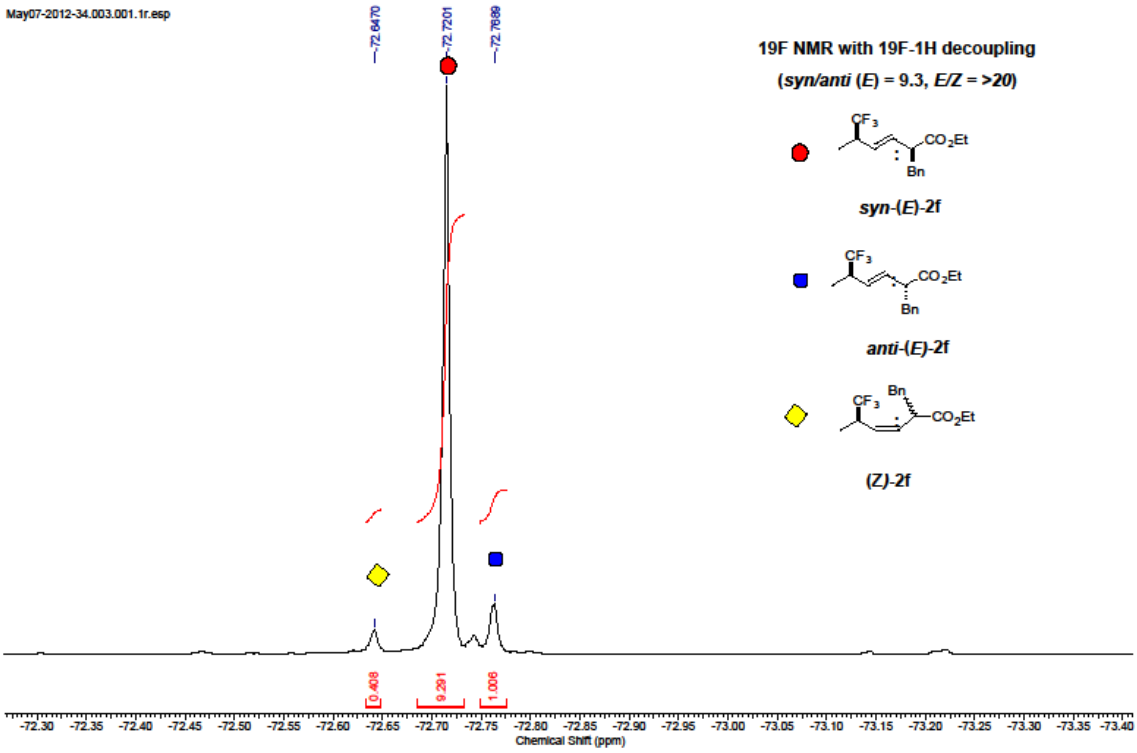

sm00551106.001.001.1r.esp
1H NMR
(syn/anti (E) = 6.4, E/Z = 15)
syn-(E)-2e
anti-(E)-2e
(Z)-2e
Chemical Shift (ppm)

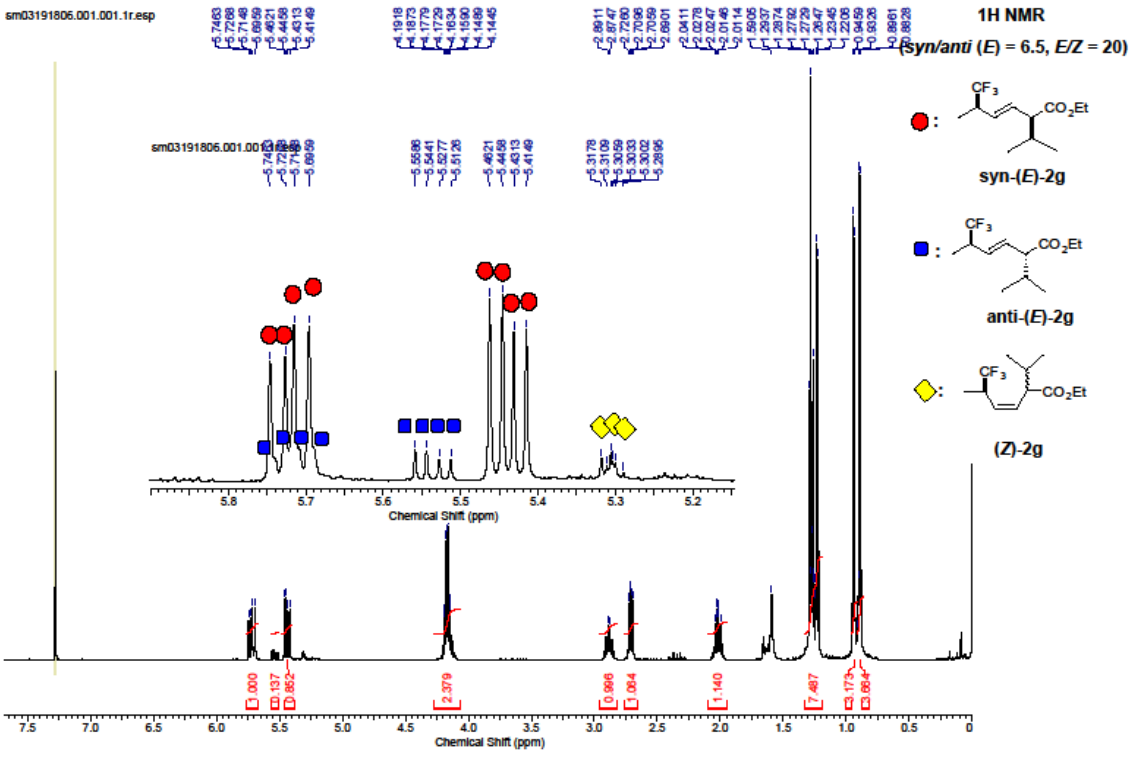

sm00551106.002.001.1r.esp
13C NMR
(syn/anti (E) = 6.4, E/Z = 15)
CF3
syn-(E)-2e
anti-(E)-2e
(Z)-2e
Chemical Shift (ppm)

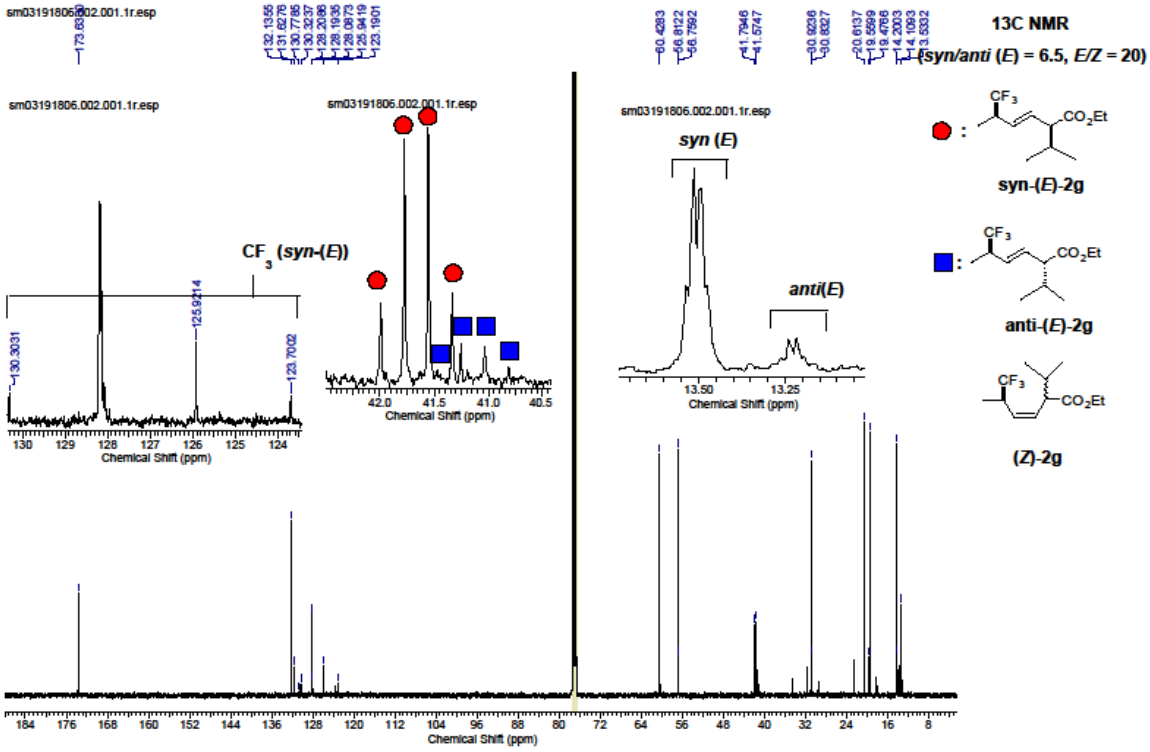

May08-2012-37.006.001.1r.esp
19F NMR with 19F-1H decoupling
(syn/anti (E) = 6.4, E/Z = 15)
syn-(E)-2e
anti-(E)-2e
(Z)-2e
Chemical Shift (ppm)

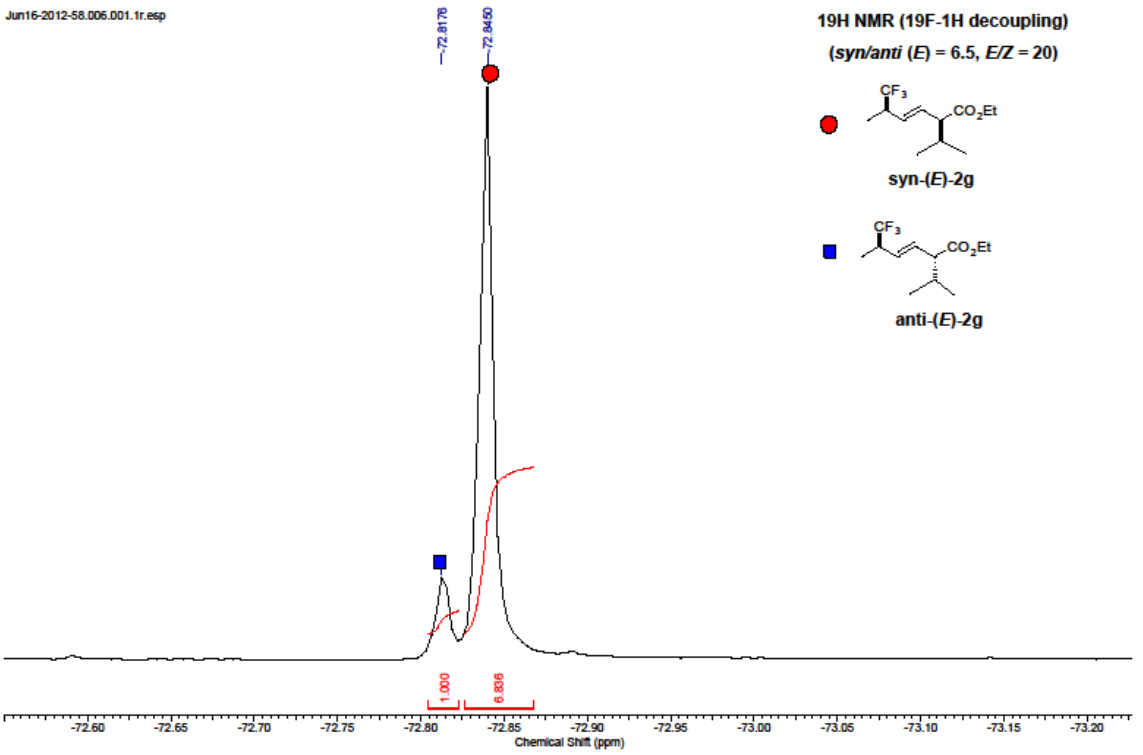

1H NMR
(syn/anti (E) = 9.3, E/Z = >20)
syn-(E)-2f
anti-(E)-2f
Chemical Shift (ppm)

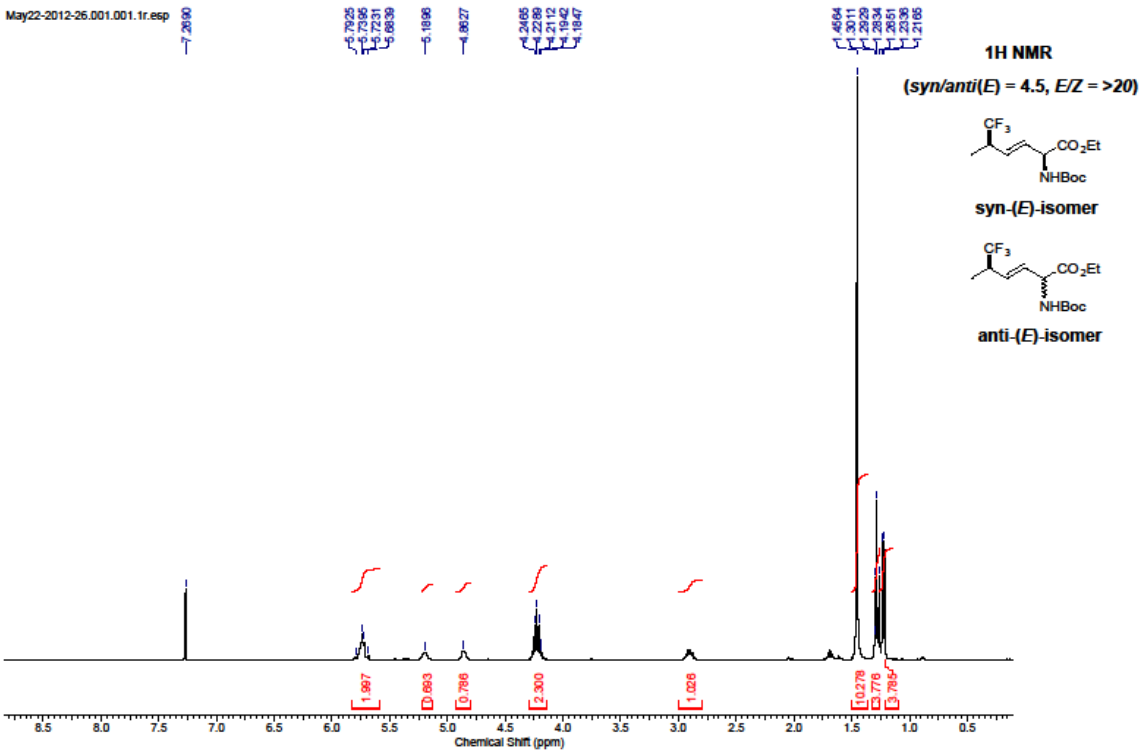

sm03161806.002.001.1r.esp
13C NMR
(syn/anti (E) = 9.3, E/Z = >20)
CF3 (syn-(E))
syn-(E)
anti-(E)
syn-(E)-2f
anti-(E)-2f
Chemical Shift (ppm)

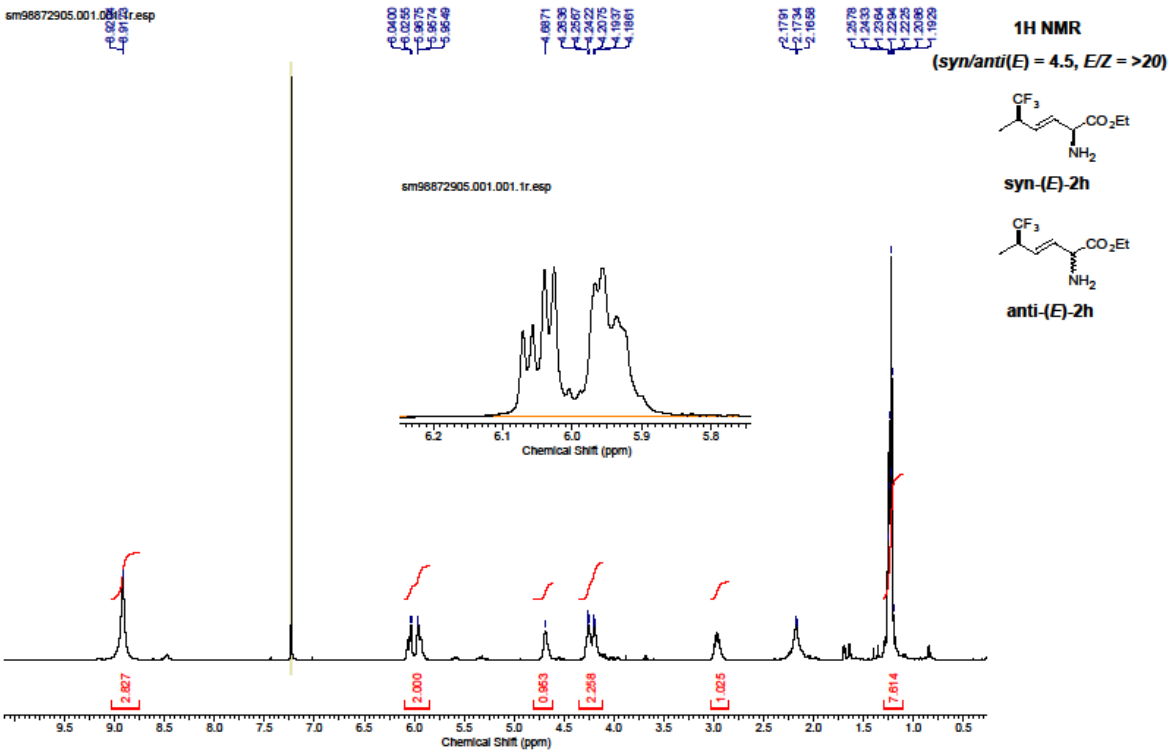

May07-2012-34.003.001.1r.esp
19F NMR with 19F-1H decoupling
(syn/anti (E) = 9.3, E/Z = >20)
syn-(E)-2f
anti-(E)-2f
(Z)-2f
0.409
9.291
1.000
Chemical Shift (ppm)

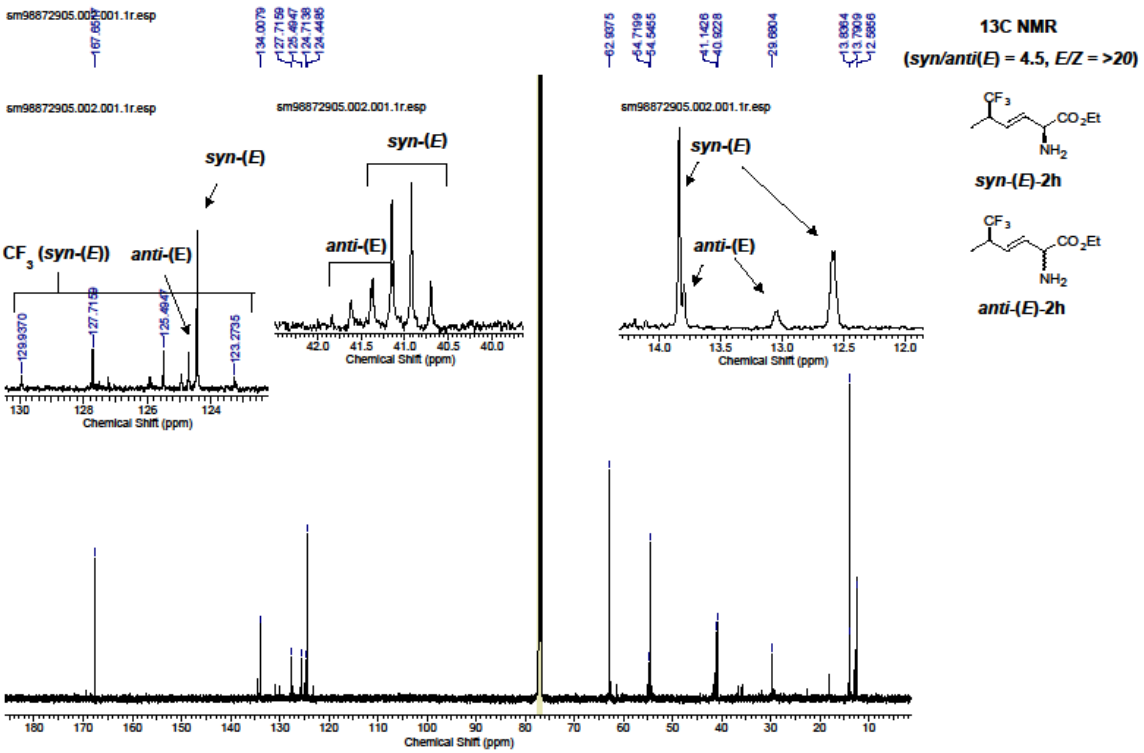

sm03191806.001.001.1r.esp
1H NMR
(syn/anti (E) = 6.5, E/Z = 20)
syn-(E)-2g
anti-(E)-2g
(Z)-2g
Chemical Shift (ppm)

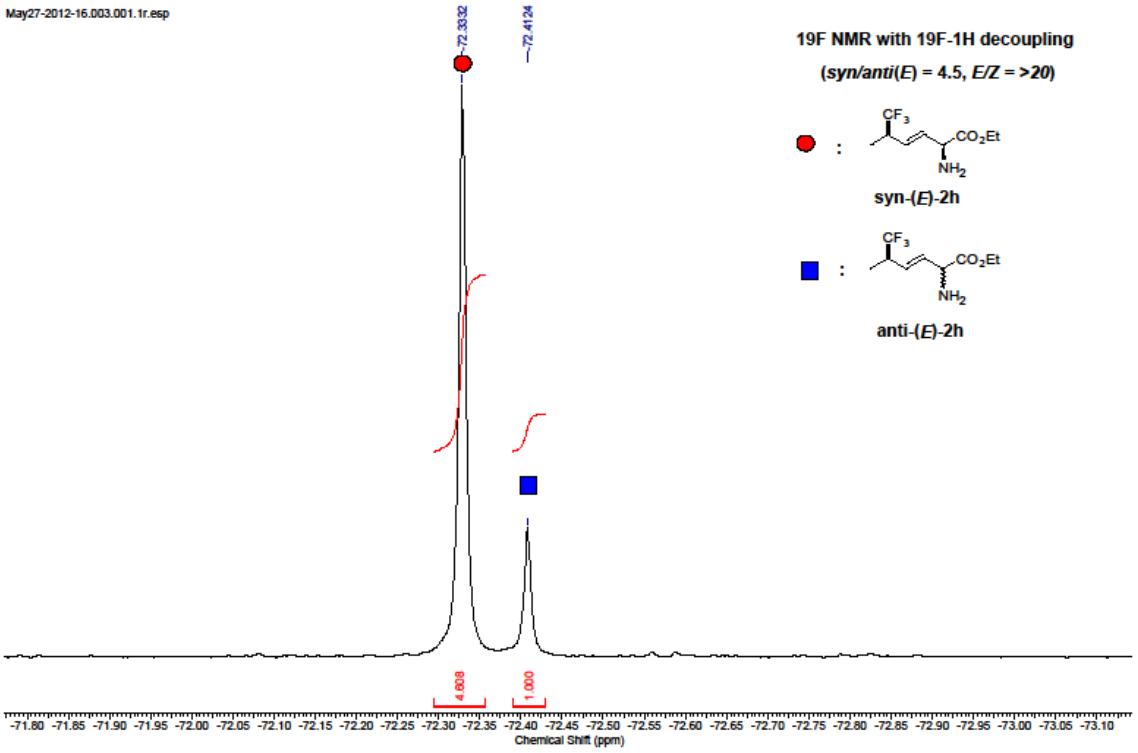

sm03191806.002.001.1r.esp
13C NMR
(syn/anti (E) = 6.5, E/Z = 20)
CF3 (syn-(E))
syn (E)
anti(E)
syn-(E)-2g
anti-(E)-2g
(Z)-2g
Chemical Shift (ppm)

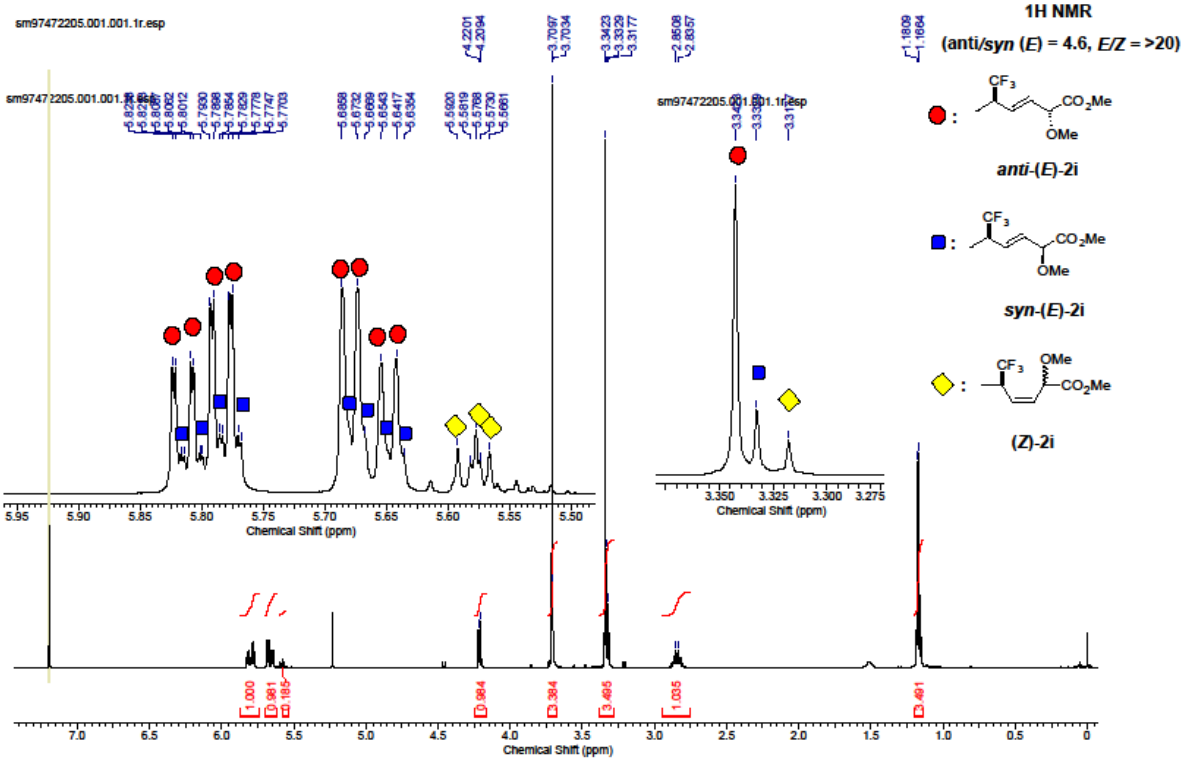

Jun16-2012-58.006.001.1r.esp
-72.8176
-72.8450
19H NMR (19F-1H decoupling)
(syn/anti (E) = 6.5, E/Z = 20)
CF3
CO2Et
syn-(E)-2g
anti-(E)-2g
1.000
6.836
-72.60
-72.65
-72.70
-72.75
-72.80
-72.85
-72.90
-72.95
-73.00
-73.05
-73.10
-73.15
-73.20
Chemical Shift (ppm)

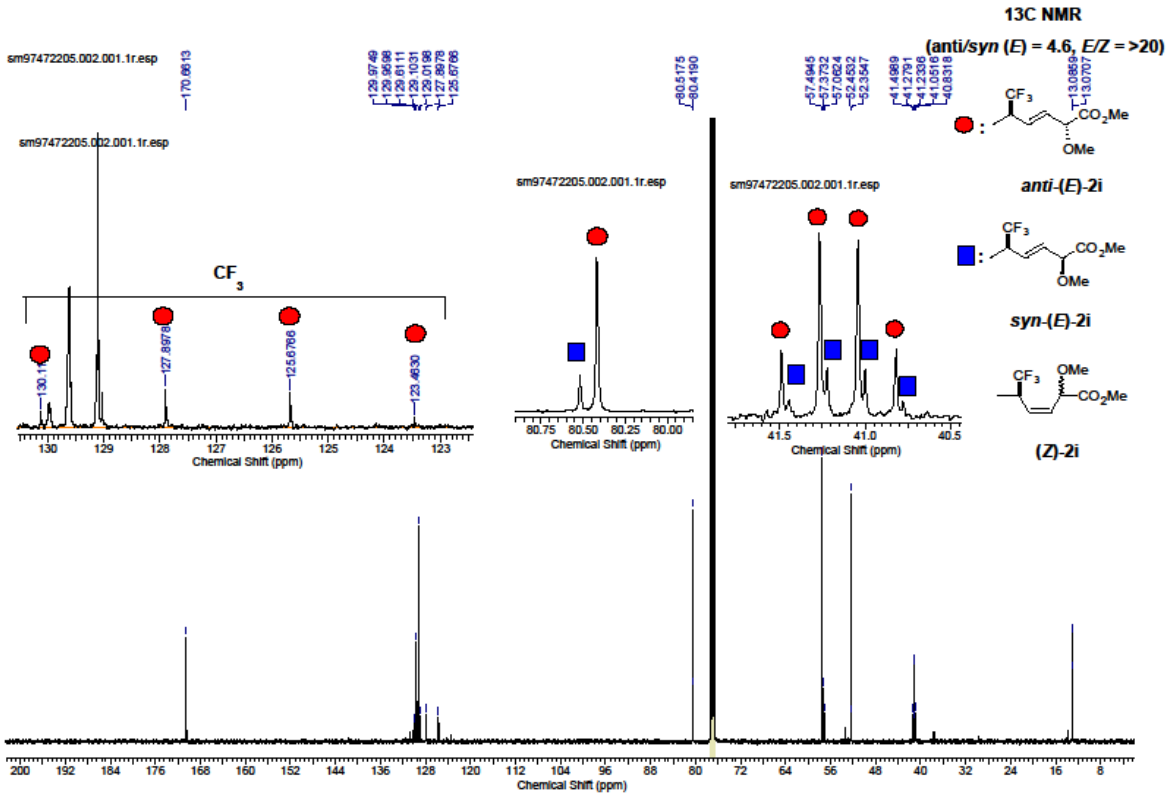

May22-2012-26.001.001.1r.esp
7.2690
5.7925
5.7395
5.7231
5.6839
5.1896
4.8827
4.2465
4.2289
4.2112
4.1942
4.1847
1.4564
1.3011
1.2929
1.2834
1.2651
1.2336
1.2166
1H NMR
(syn/anti(E) = 4.5, E/Z = >20)
CF3
CO2Et
NHBoc
syn-(E)-isomer
anti-(E)-isomer
1.997
0.693
0.786
2.300
1.026
10.278
3.776
3.785
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

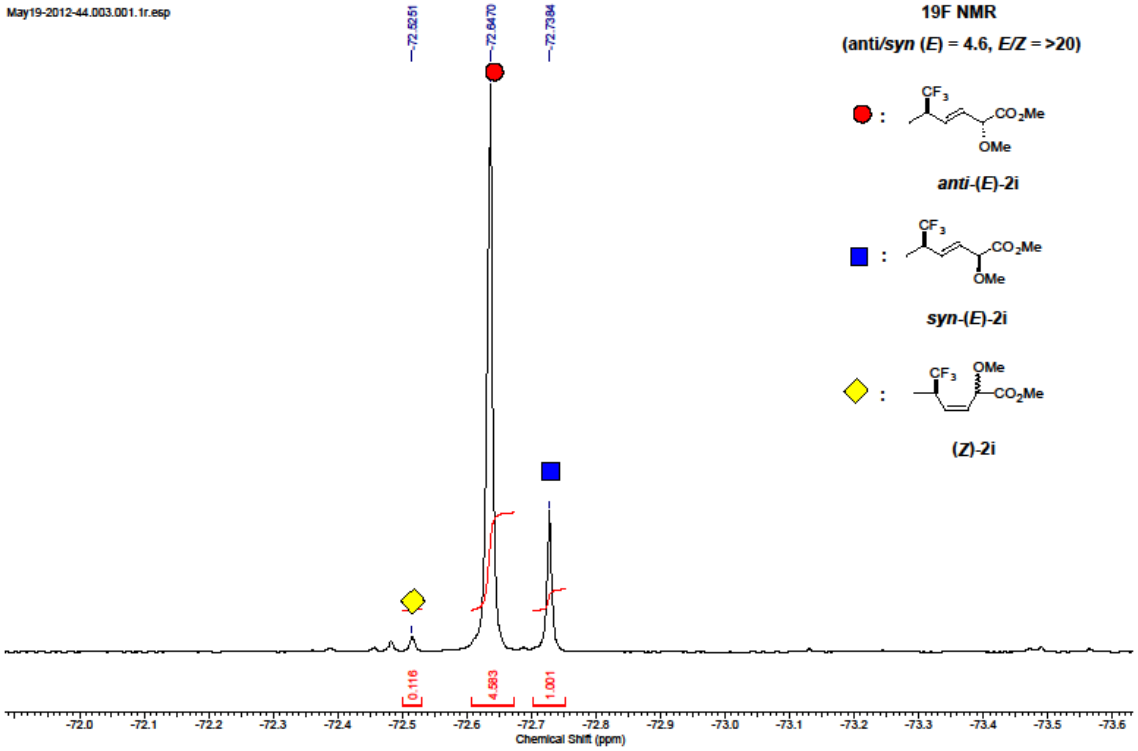

1H NMR
(syn/anti(E) = 4.5, E/Z = >20)
syn-(E)-2h
anti-(E)-2h
Chemical Shift (ppm)

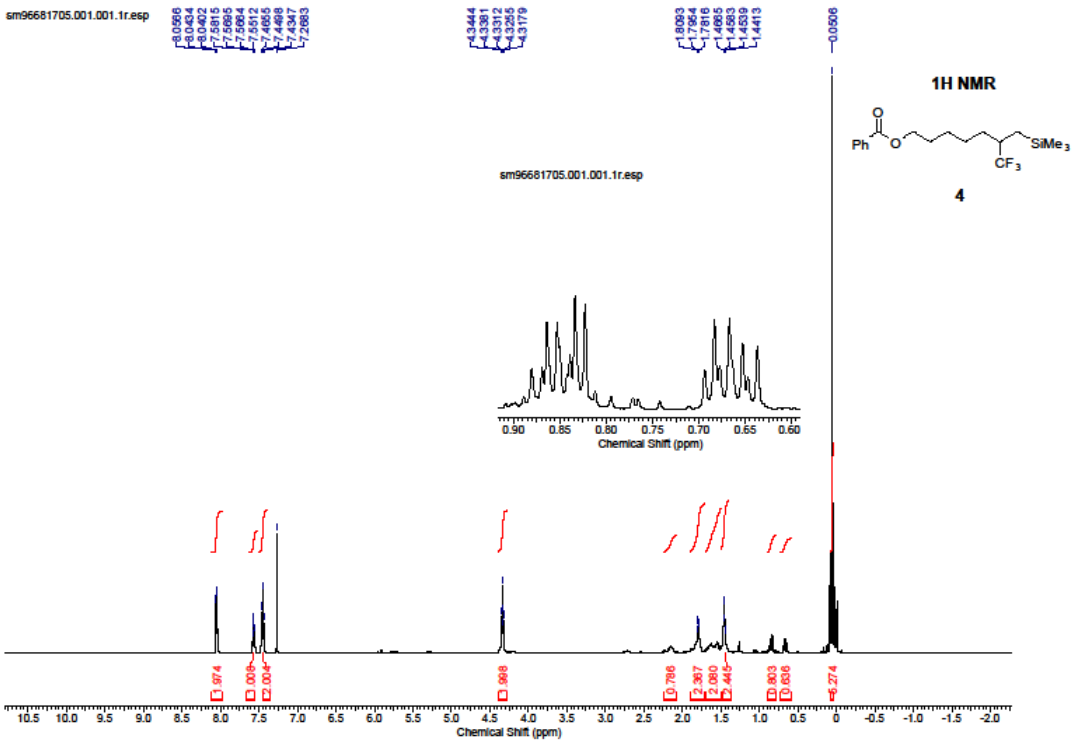

13C NMR
(syn/anti(E) = 4.5, E/Z = >20)
syn-(E)-2h
anti-(E)-2h
syn-(E)
anti-(E)
CF3 (syn-(E))
Chemical Shift (ppm)

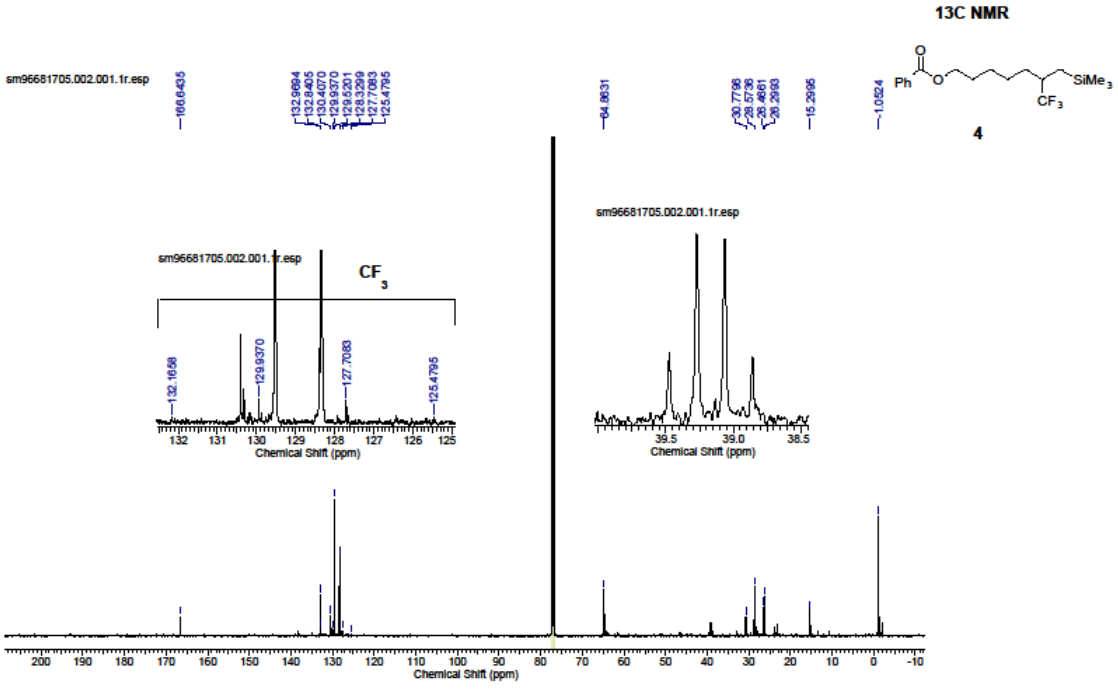

May27-2012-16.003.001.1r.esp
-72.3332
-72.4124
19F NMR with 19F-1H decoupling
(syn/anti(E) = 4.5, E/Z = >20)
CF3
CO2Et
NH2
syn-(E)-2h
anti-(E)-2h
4.608
1.000
Chemical Shift (ppm)


sm97472205.001.001.1r.esp
1H NMR
(anti/syn (E) = 4.6, E/Z = >20)
CF3
CO2Me
OMe
anti-(E)-2i
syn-(E)-2i
(Z)-2i
Chemical Shift (ppm)

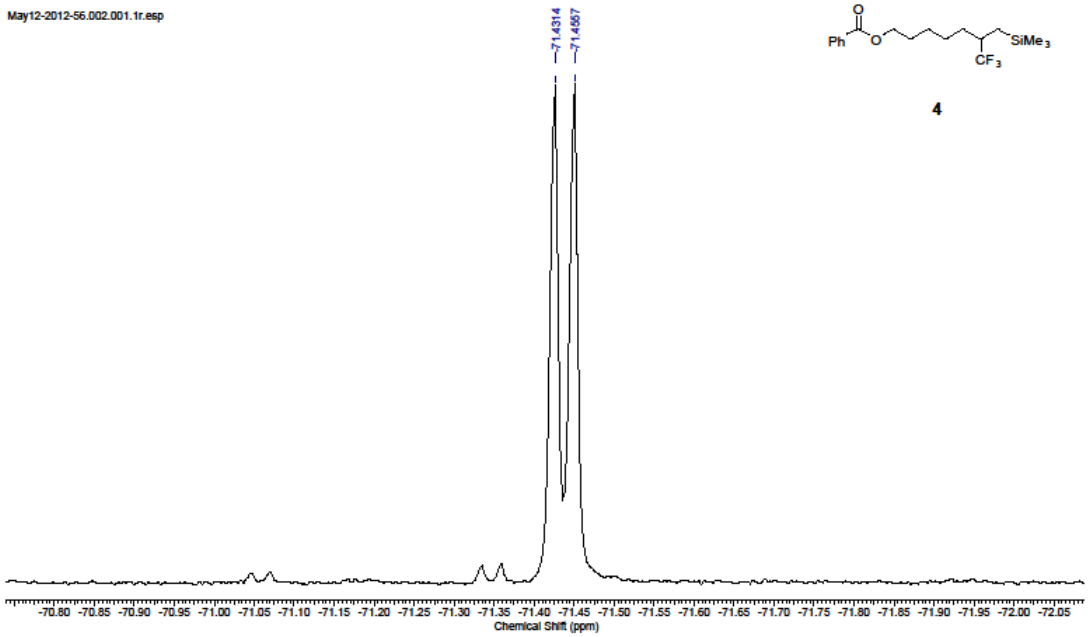

13C NMR
(anti/syn (E) = 4.6, E/Z = >20)
anti-(E)-2i
syn-(E)-2i
(Z)-2i
Chemical Shift (ppm)


19F NMR
(anti/syn (E) = 4.6, E/Z = >20)
anti-(E)-2i
syn-(E)-2i
(Z)-2i
Chemical Shift (ppm)

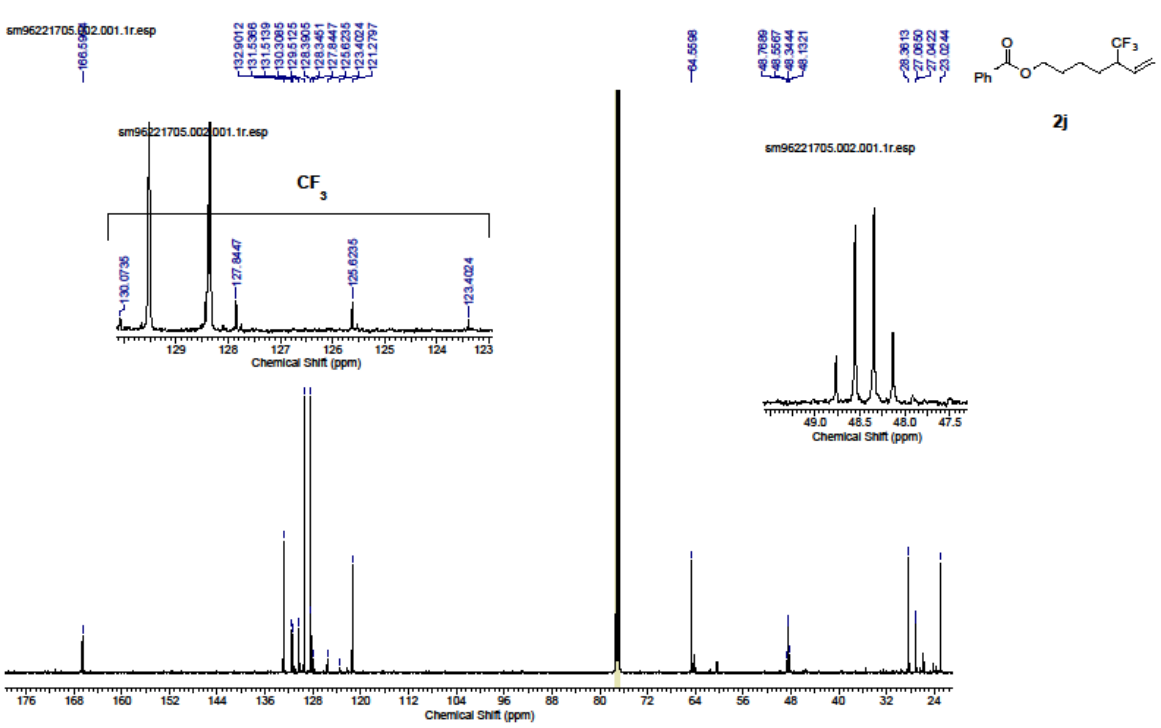

sm96681705.001.001.1r.esp
1H NMR
4
Chemical Shift (ppm)


13C NMR
4
sm96681705.002.001.1r.esp
CF3
Chemical Shift (ppm)

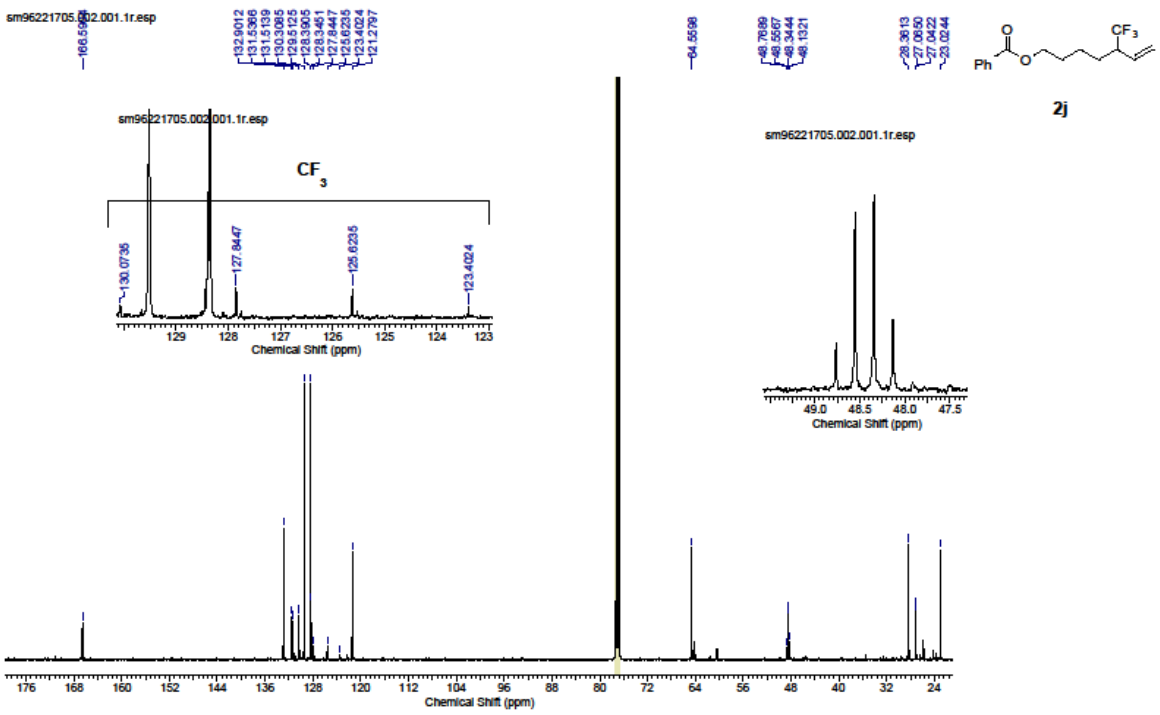
19F NMR



13C NMR

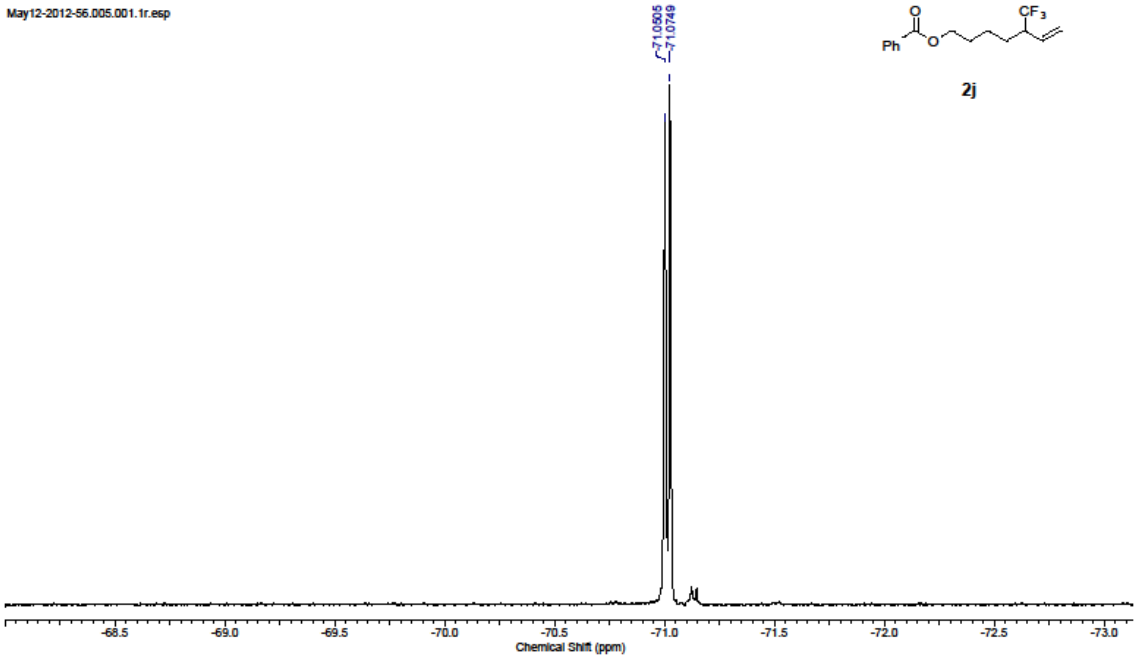


13C NMR

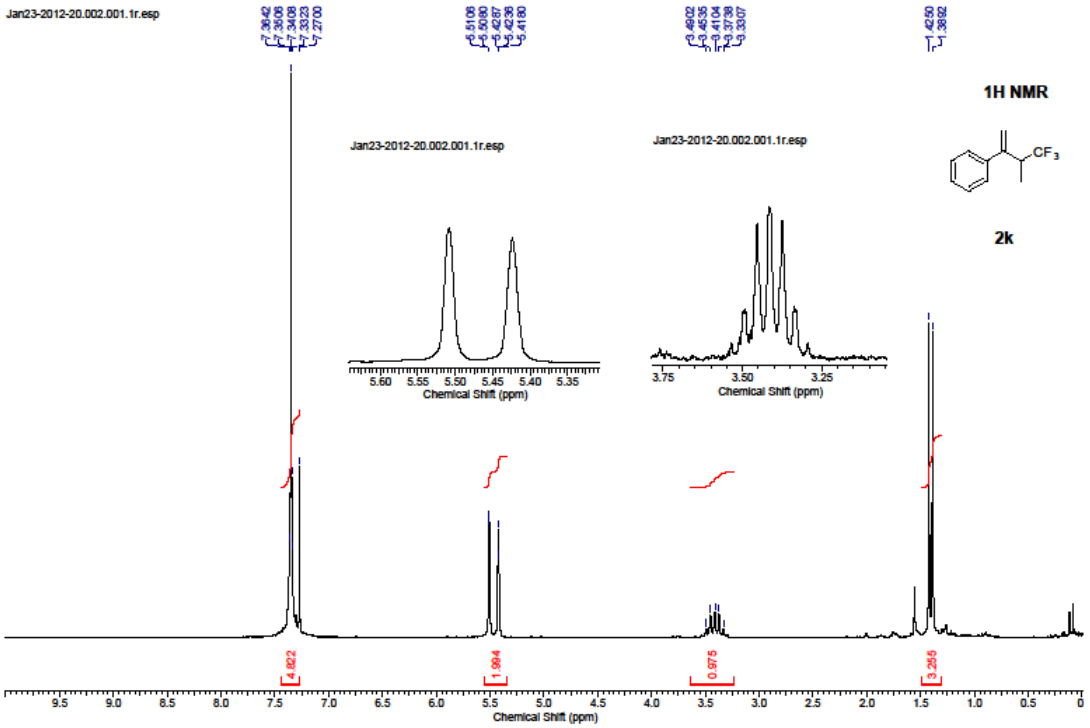


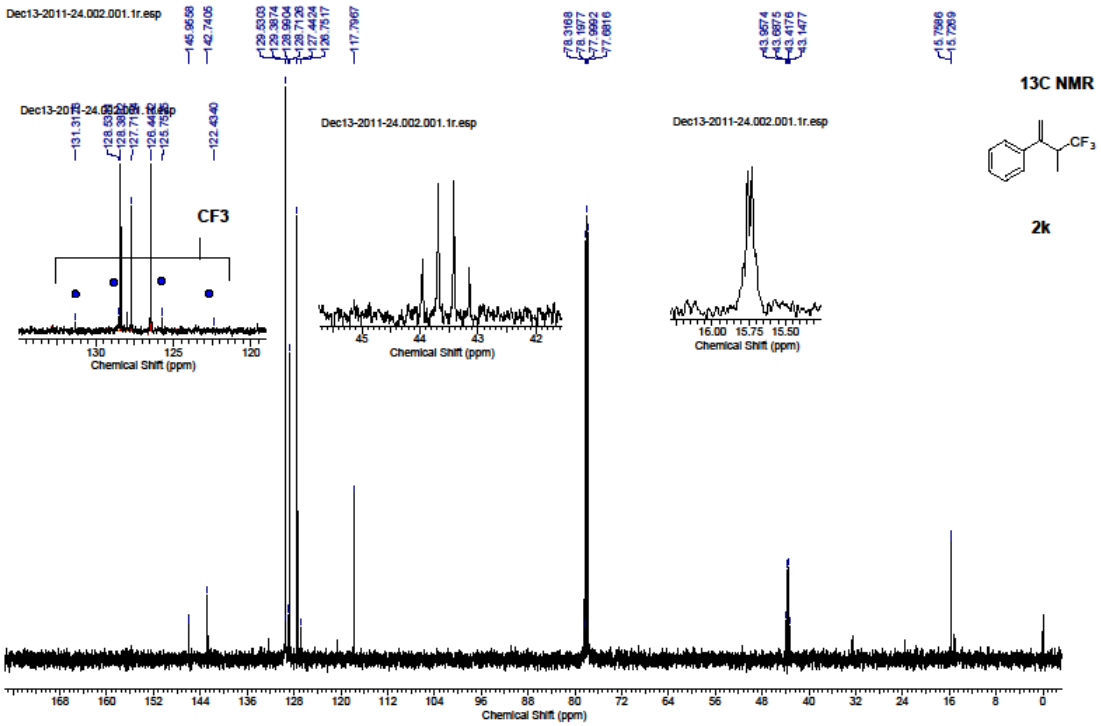
2j

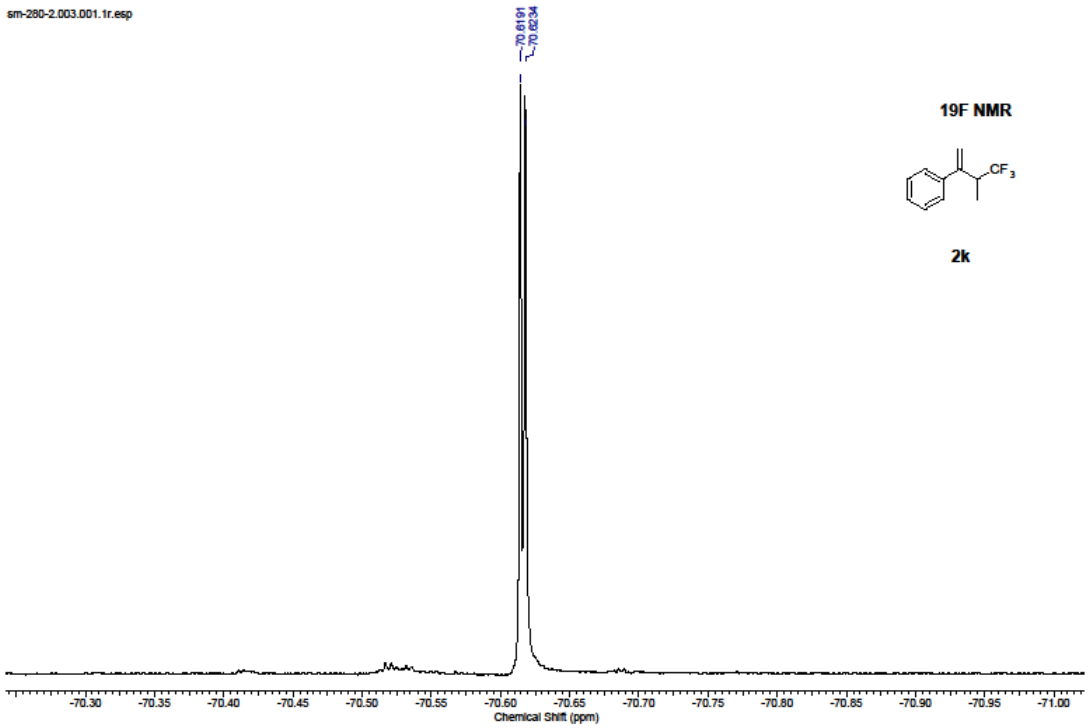
19F NMR

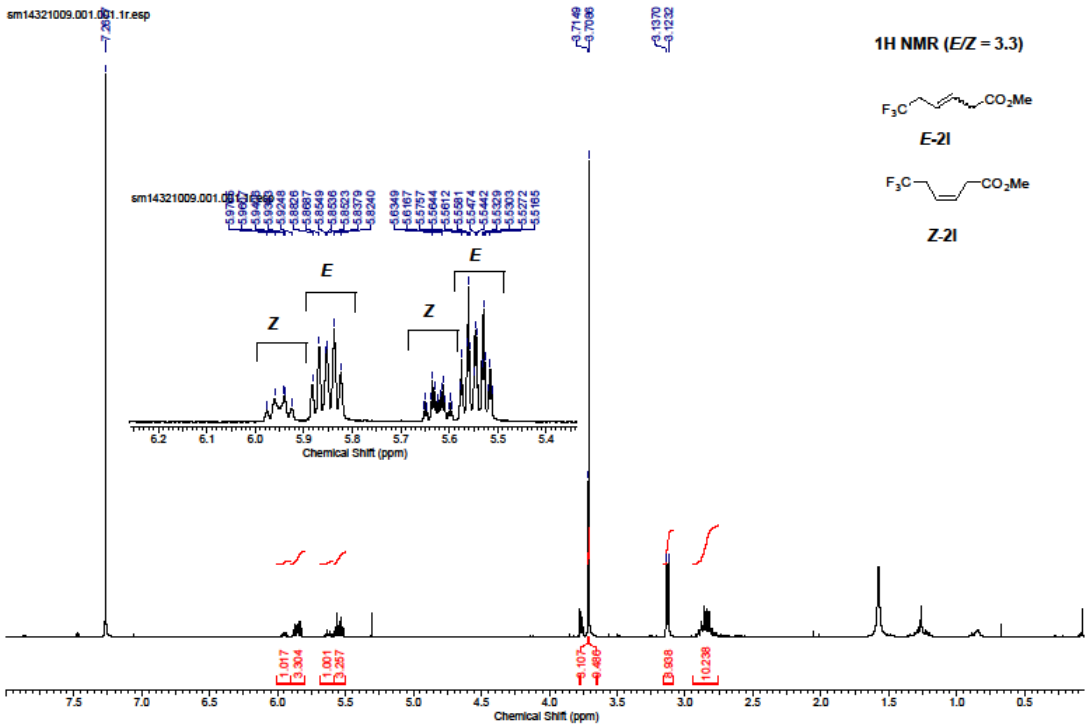


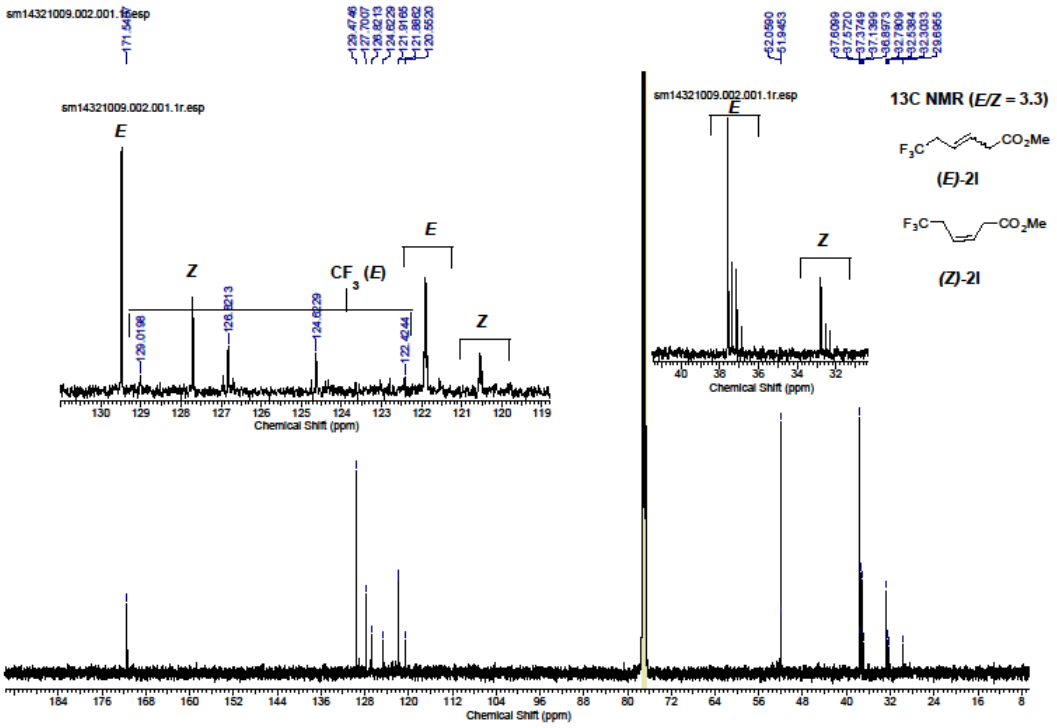
2j

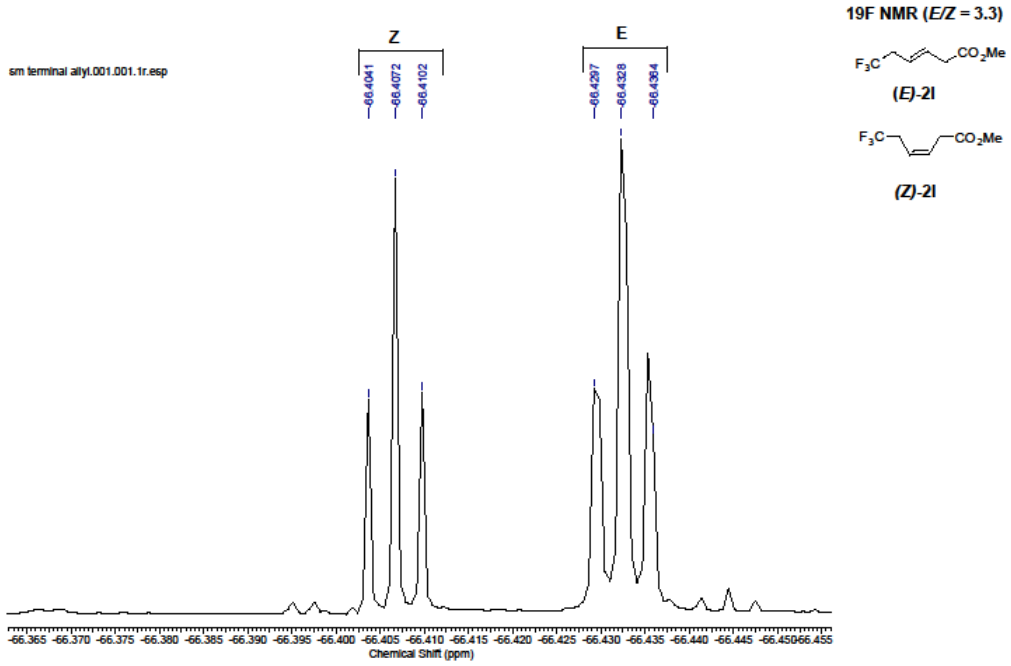

Jan23-2012-20.002.001.1r.esp
1H NMR
2k
Chemical Shift (ppm)


Dec13-2011-24.002.001.1r.esp
13C NMR
2k
CF3
Chemical Shift (ppm)


sm-280-2.003.001.1r.esp
-70.6191
-70.6234
19F NMR
CF3
2k
Chemical Shift (ppm)


sm14321009.001.001.1r.esp
7.2607
3.7149
3.7096
3.1370
3.1232
1H NMR (E/Z = 3.3)
F3C
CO2Me
E-2l
F3C
CO2Me
Z-2l
E
Z
E
Z
Chemical Shift (ppm)
1.017
3.304
1.001
3.257
6.107
9.486
3.938
10.238


sm14321009.002.001.1r.esp
E
Z
CF3 (E)
Chemical Shift (ppm)
13C NMR (E/Z = 3.3)
(E)-2l
(Z)-2l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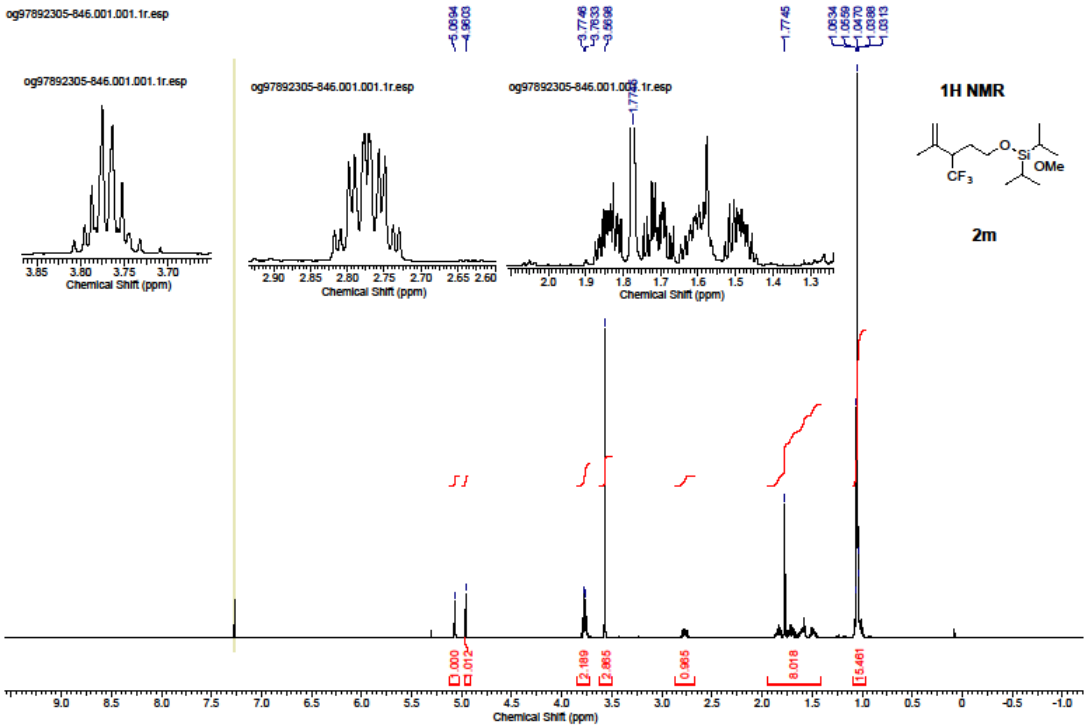
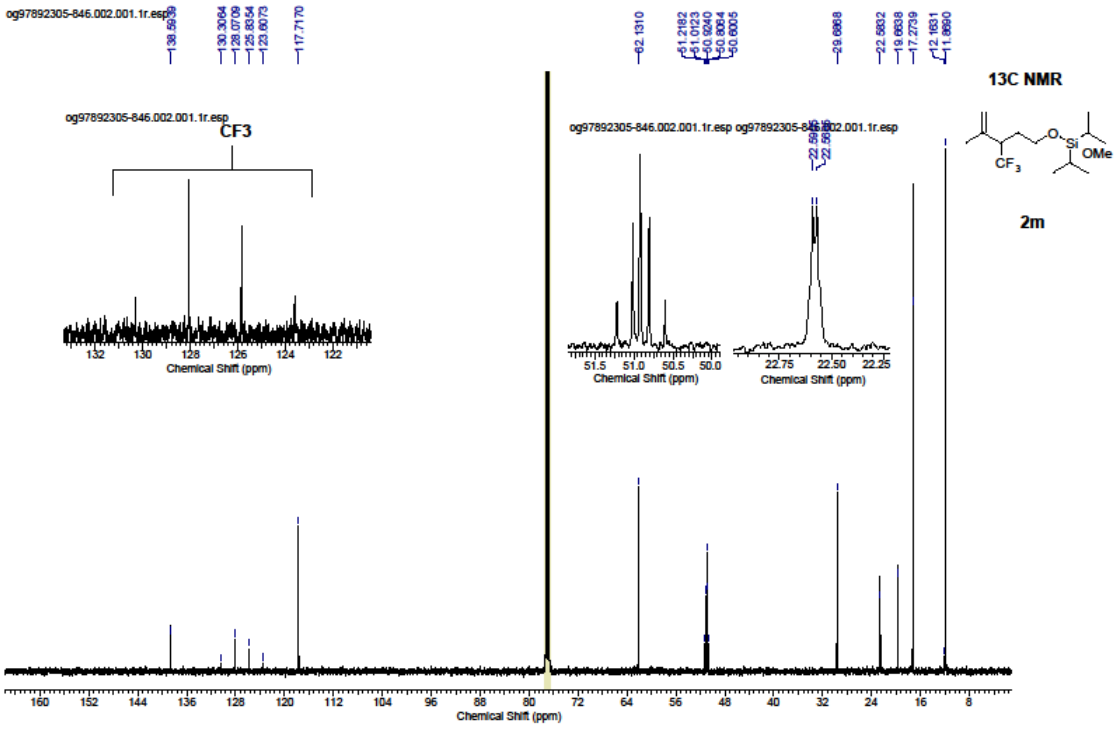
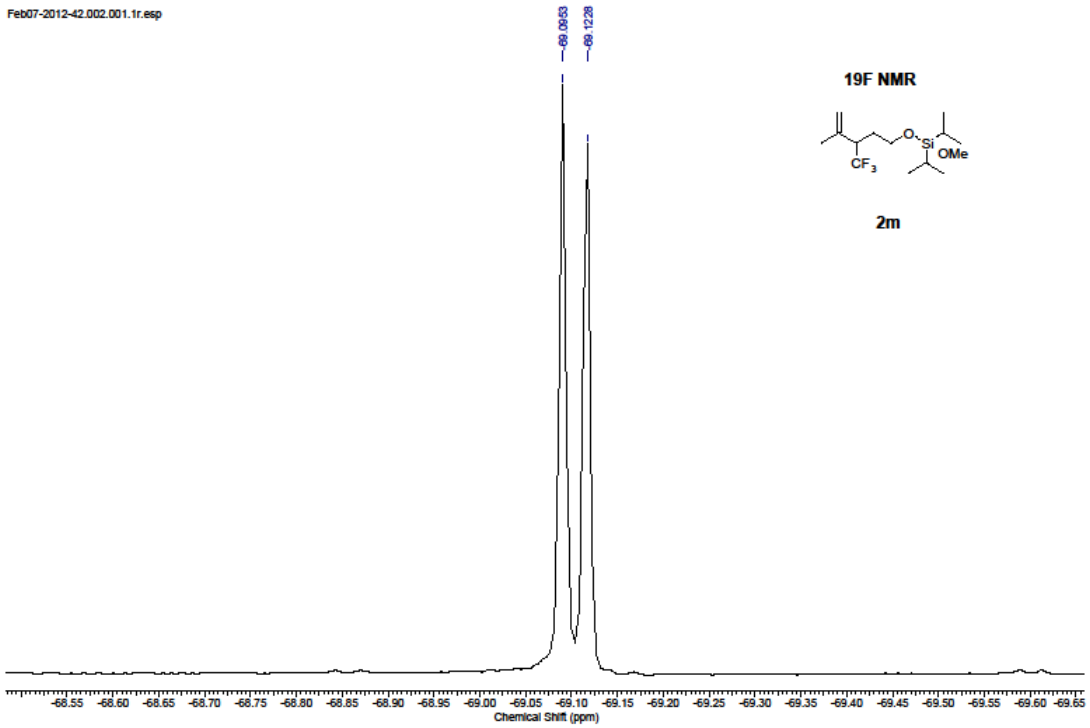
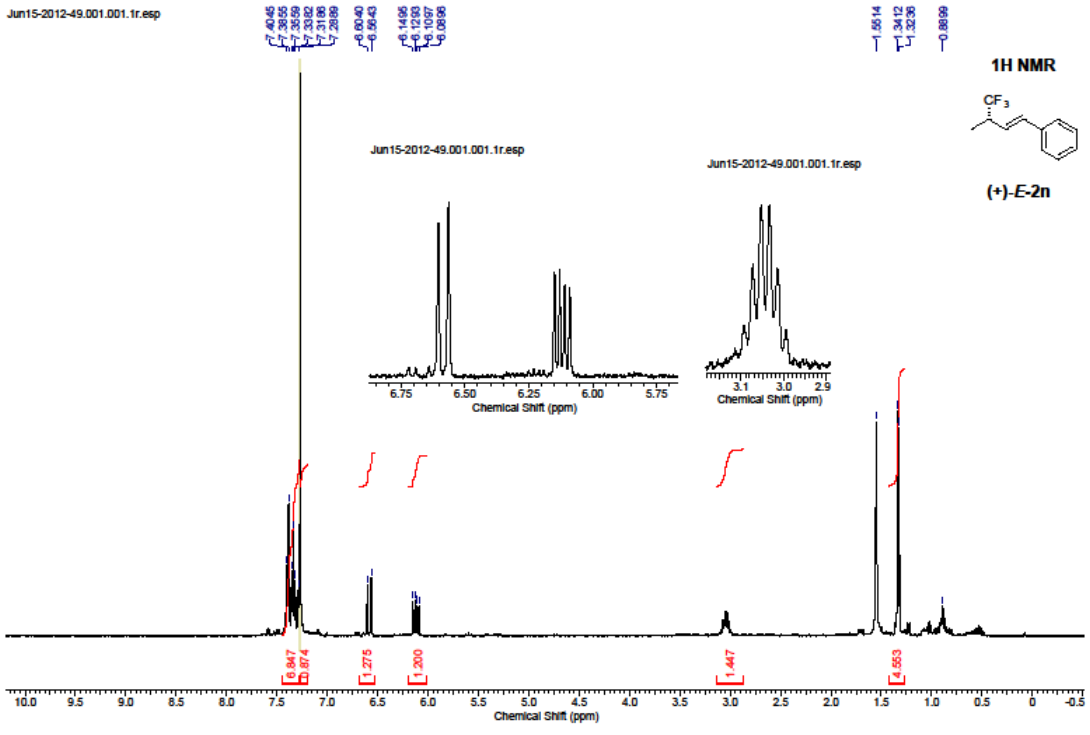
Z
E
Chemical Shift (ppm)
19F NMR (E/Z = 3.3)
(E)-2l
(Z)-2l


1H NMR
2m
Chemical Shift (ppm)


13C NMR
CF3
2m
Chemical Shift (ppm)


Feb07-2012-42.002.001.1r.esp
-69.0953
-69.1228
19F NMR
O
Si
OMe
CF3
2m
-68.55 -68.60 -68.65 -68.70 -68.75 -68.80 -68.85 -68.90 -68.95 -69.00 -69.05 -69.10 -69.15 -69.20 -69.25 -69.30 -69.35 -69.40 -69.45 -69.50 -69.55 -69.60 -69.65
Chemical Shift (ppm)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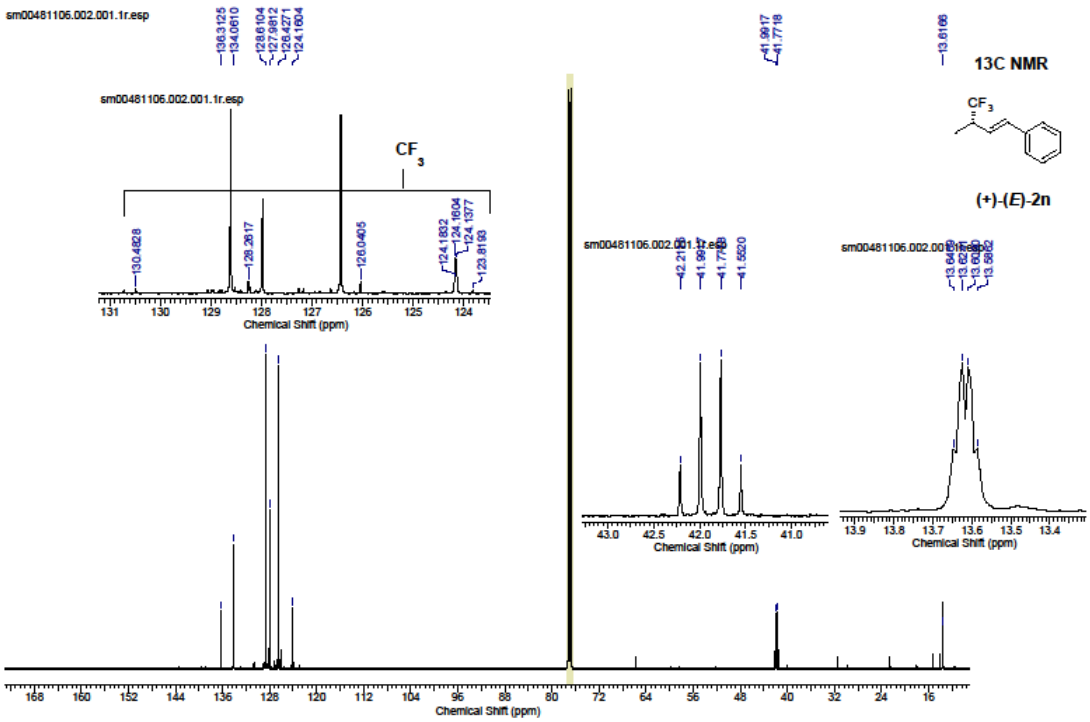
7.3659
7.3392
7.3186
7.2889
6.6040
6.5643
6.1495
6.1293
6.1097
6.0896
1.5514
1.3412
1.3236
0.8699
1H NMR
CF3
(+)-E-2n
Jun15-2012-49.001.001.1r.esp
6.75 6.50 6.25 6.00 5.75
Chemical Shift (ppm)
Jun15-2012-49.001.001.1r.esp
3.1 3.0 2.9
Chemical Shift (ppm)
6.847
6.874
1.275
1.200
1.447
4.553
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)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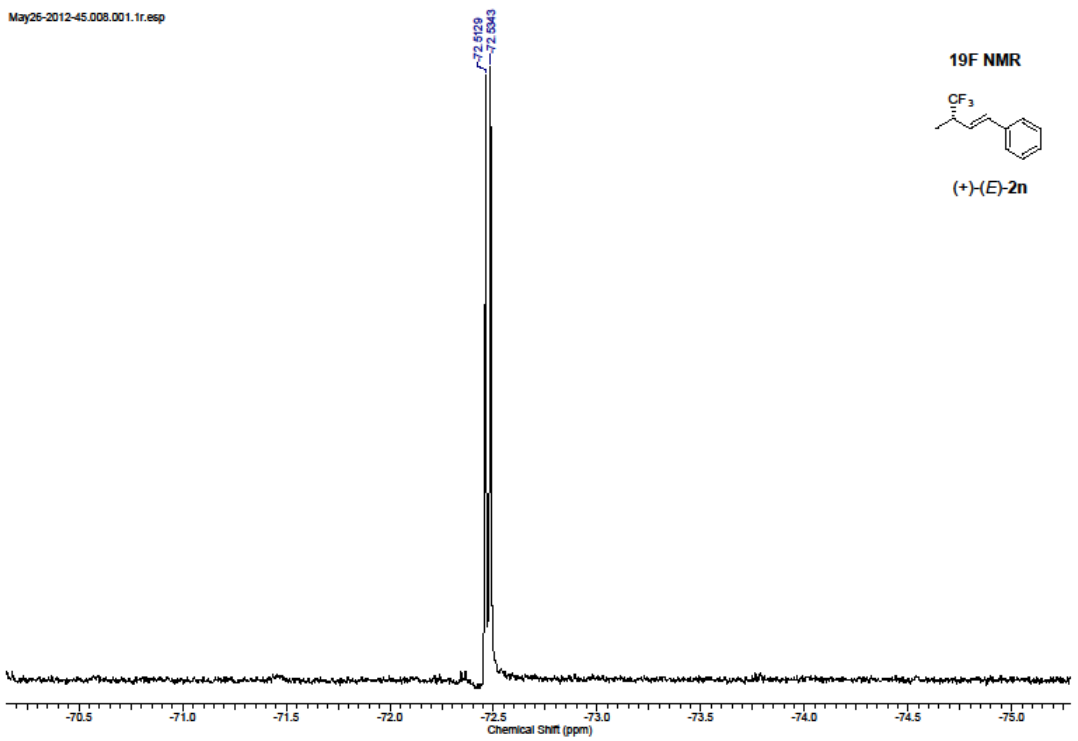
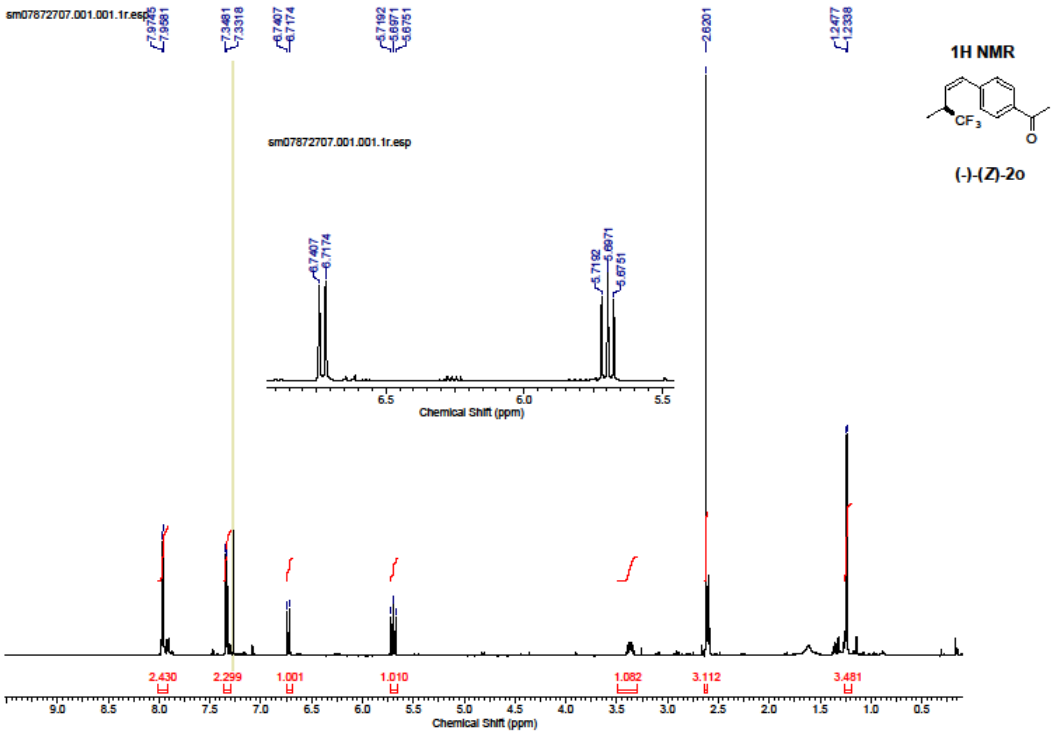
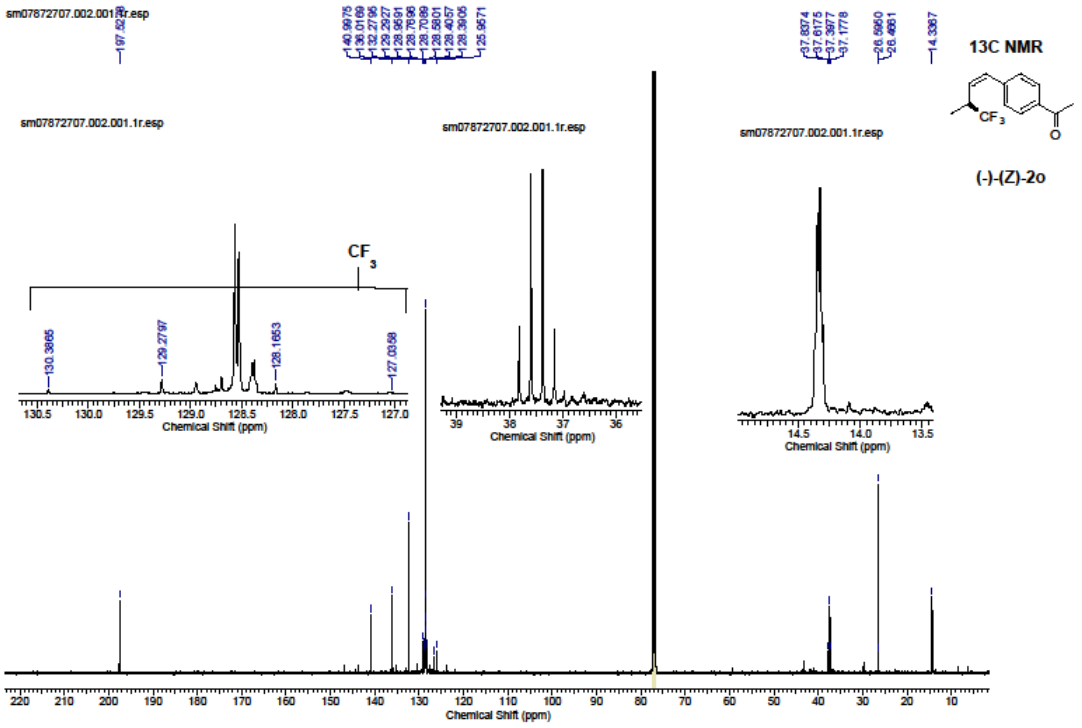
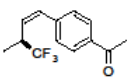
136.3125
134.0610
128.6104
127.9812
126.4271
124.1604
41.9917
41.7718
13.6166
13C NMR
CF3
(+)-(E)-2n
130.4828
129.2617
126.0405
124.1832
124.1604
124.1377
123.8193
Chemical Shift (ppm)


May26-2012-45.008.001.1r.esp
-72.5129
-72.5343
19F NMR
CF3
(+)-(E)-2n
Chemical Shift (ppm)


1H NMR
(-)-(Z)-2o
Chemical Shift (ppm)

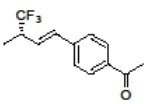

13C NMR
(-)-(Z)-2o
CF3
Chemical Shift (ppm)

19F NMR

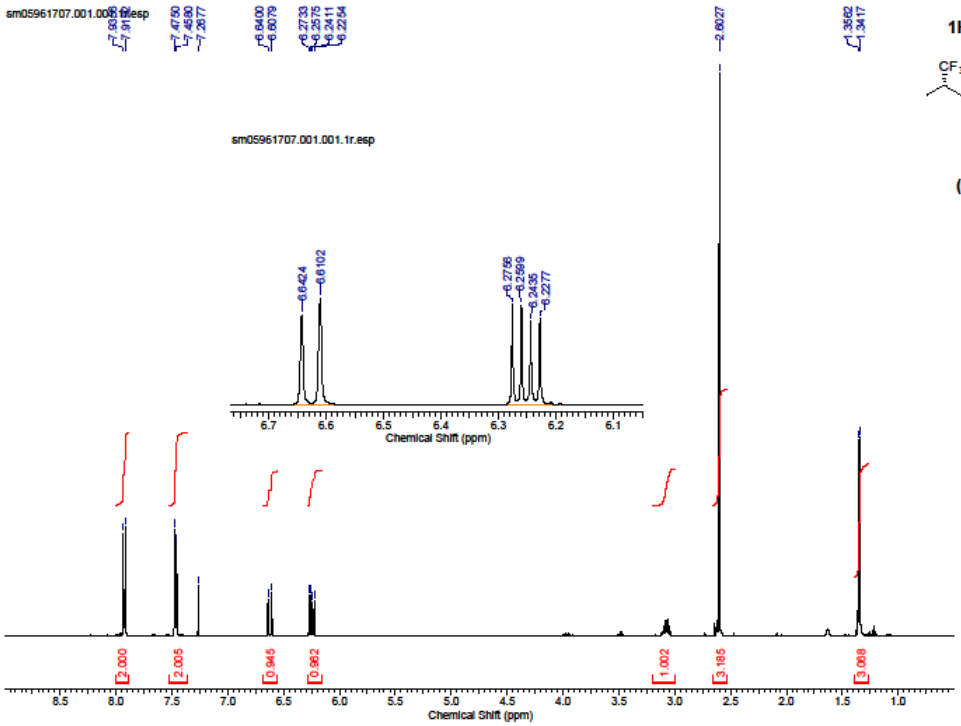


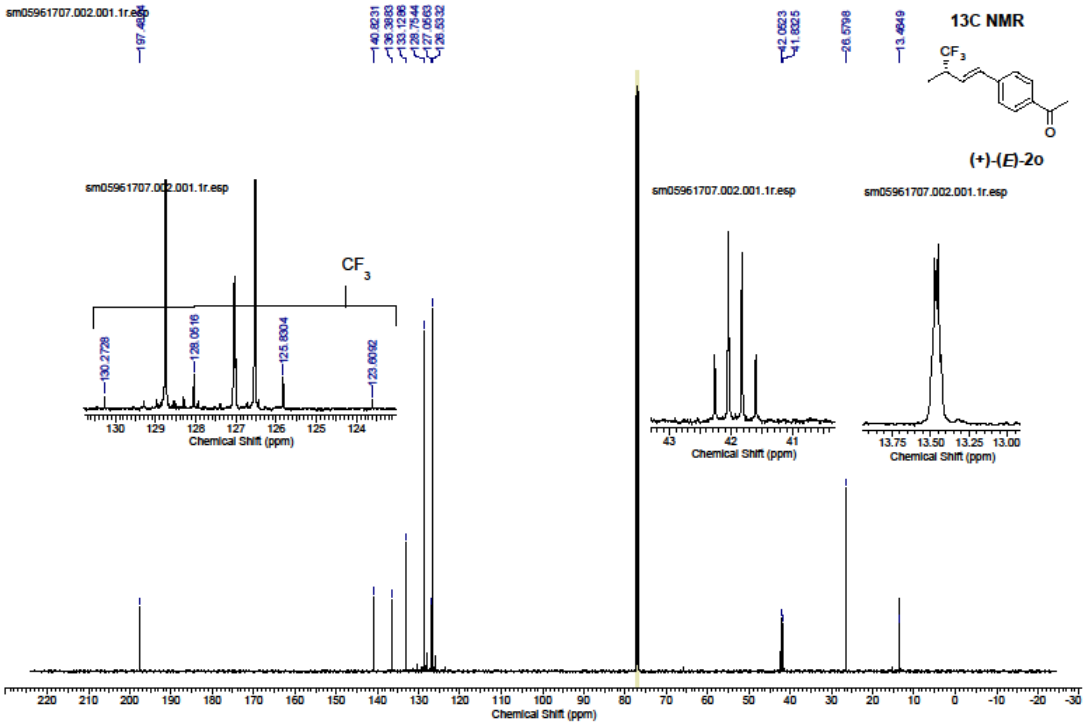
(-)-(Z)-2o

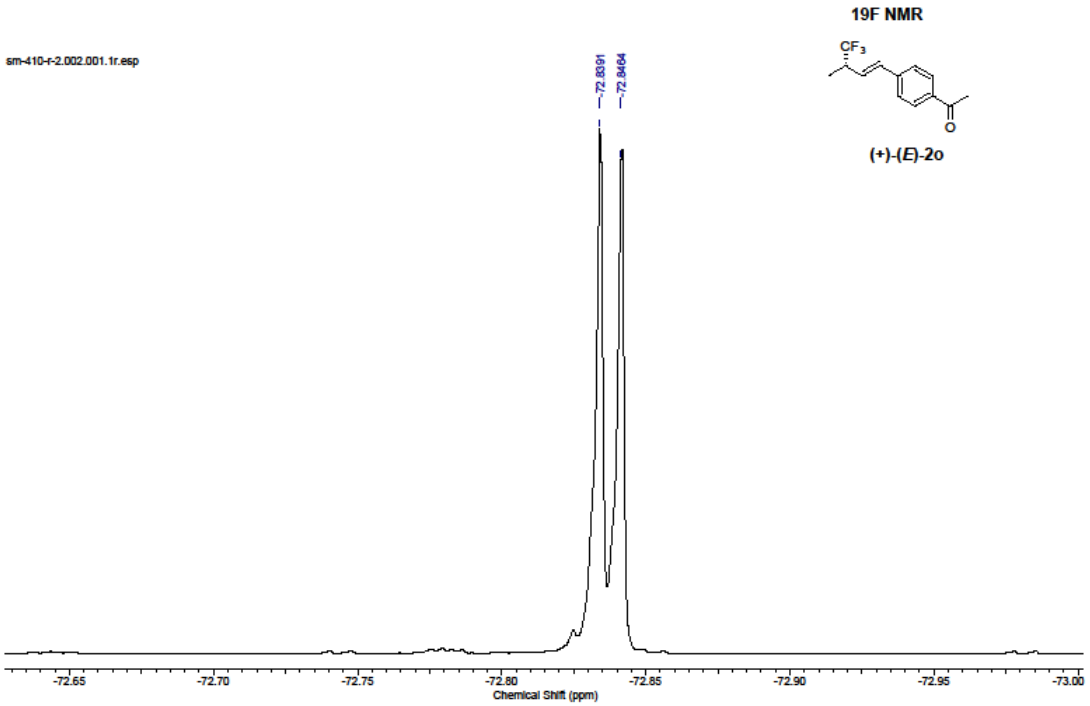
1H NMR

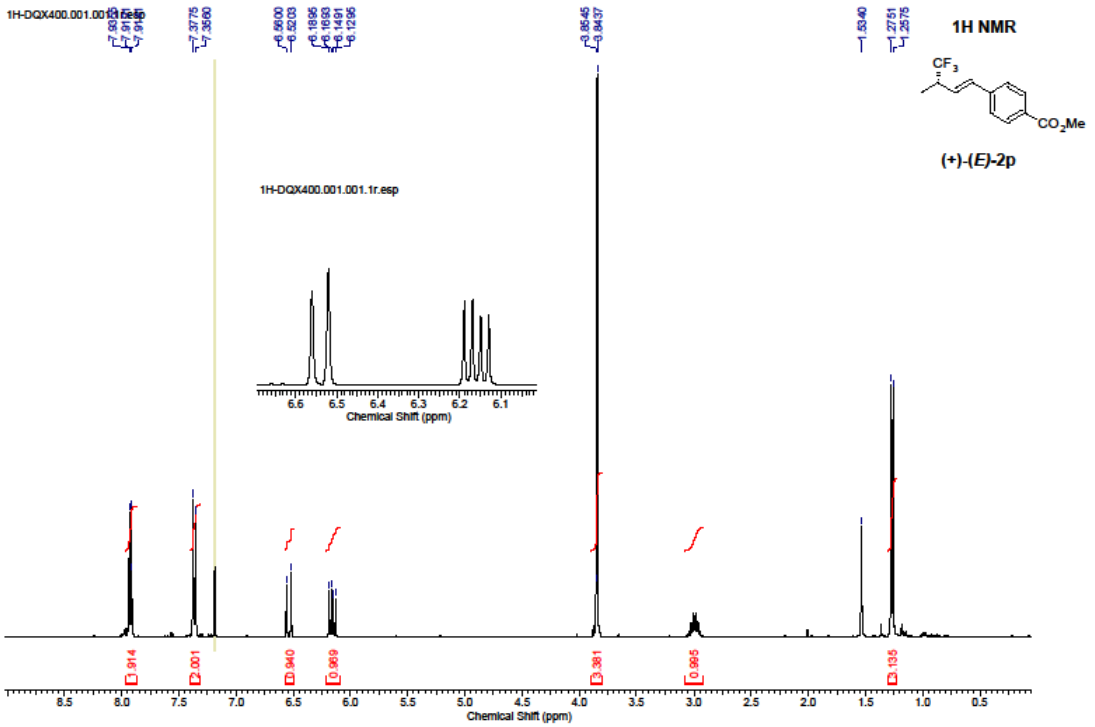


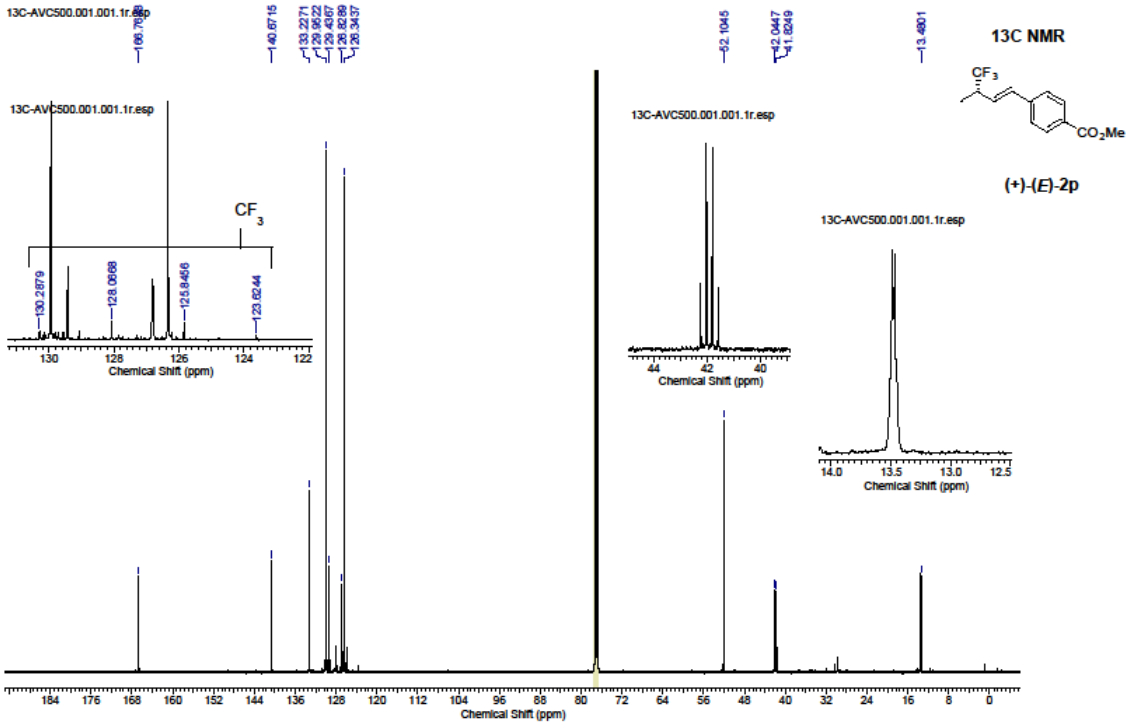
(+)-(*E*)-2o

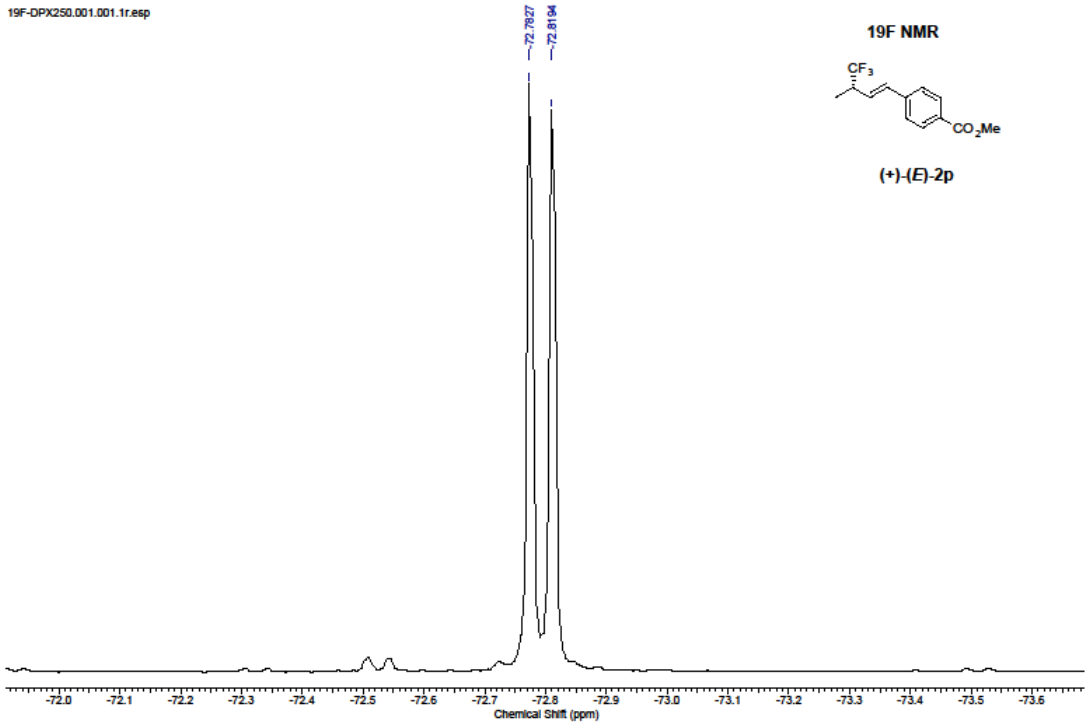



13C NMR
(+)-(E)-2o
Chemical Shift (ppm)


19F NMR
(+)-(E)-2o
Chemical Shift (ppm)


1H NMR
(+)-(E)-2p
1H-DQX400.001.001.1r.esp
Chemical Shift (ppm)


13C NMR
(+)-(E)-2p
13C-AVC500.001.001.1r.esp
Chemical Shift (ppm)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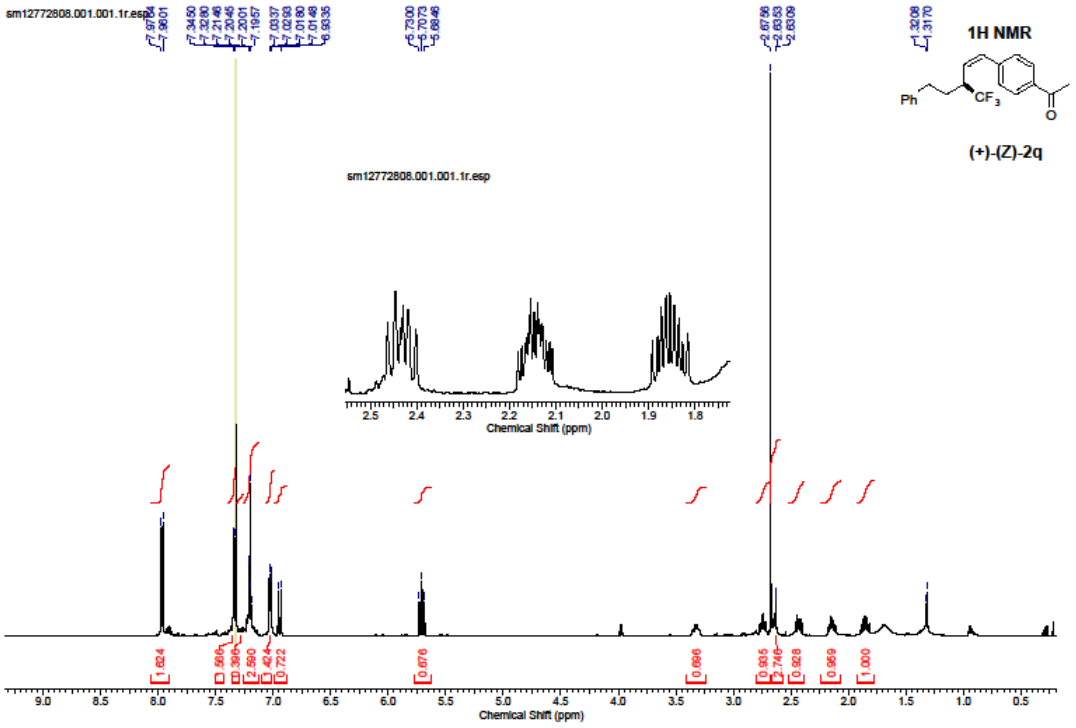
-72.7827
-72.8194
19F NMR
CF3
CO2Me
(+)-(E)-2p
Chemical Shift (ppm)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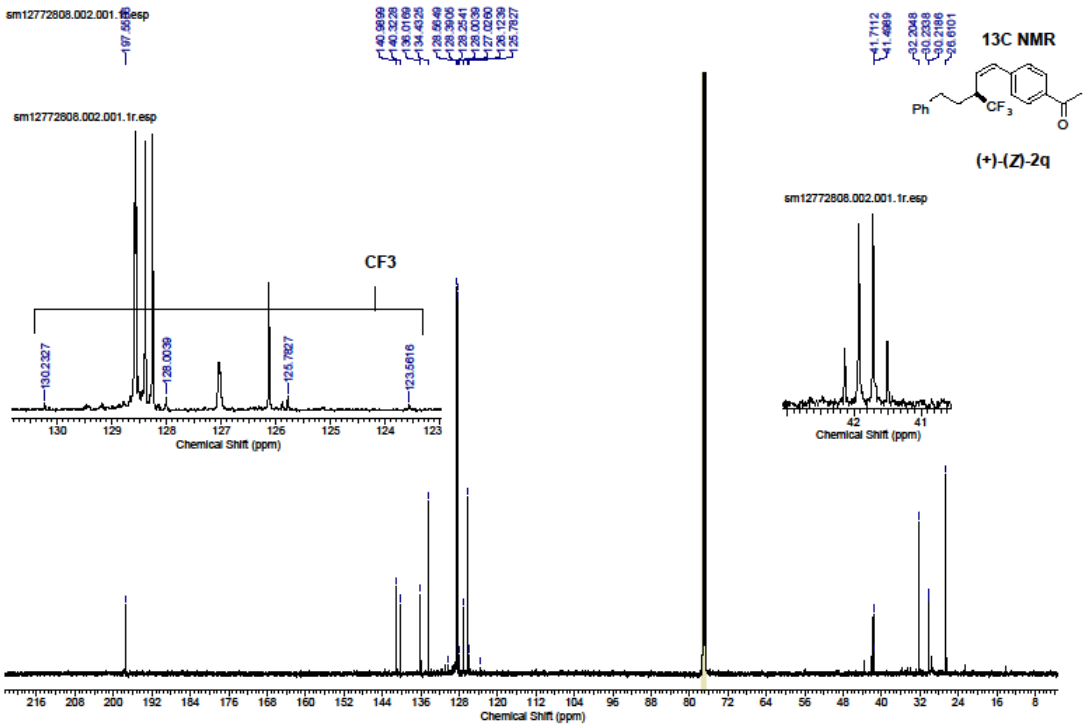
1H NMR
Ph
CF3
O
(+)-(Z)-2q
Chemical Shift (ppm)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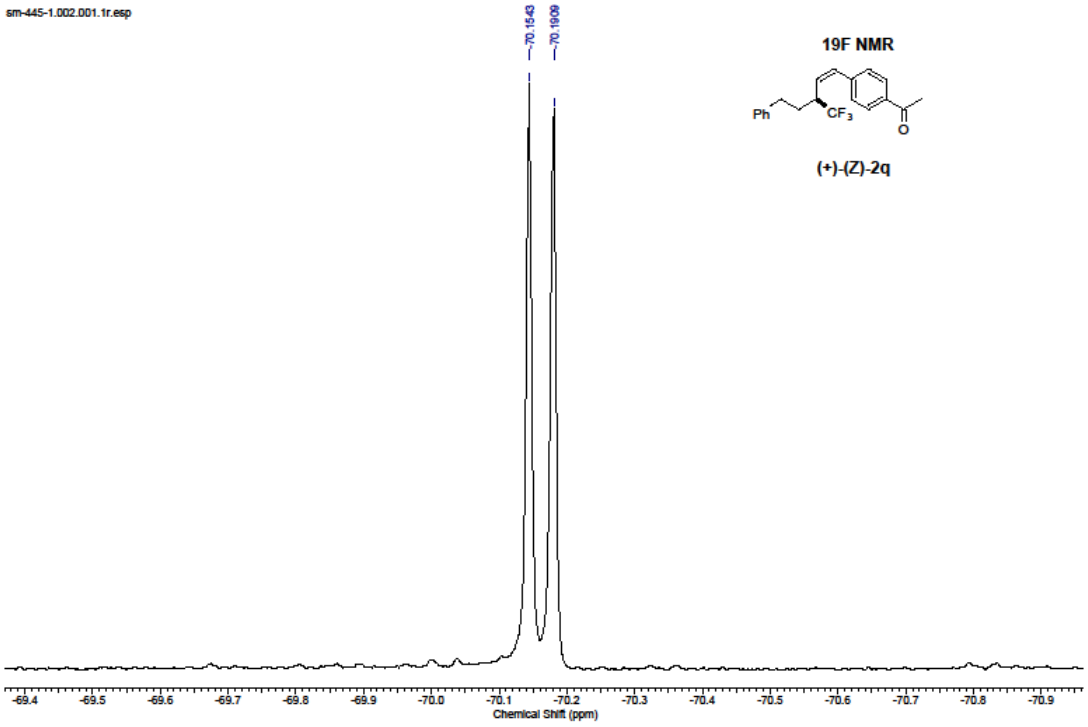
13C NMR
(+)-(Z)-2q
CF3
Chemical Shift (ppm)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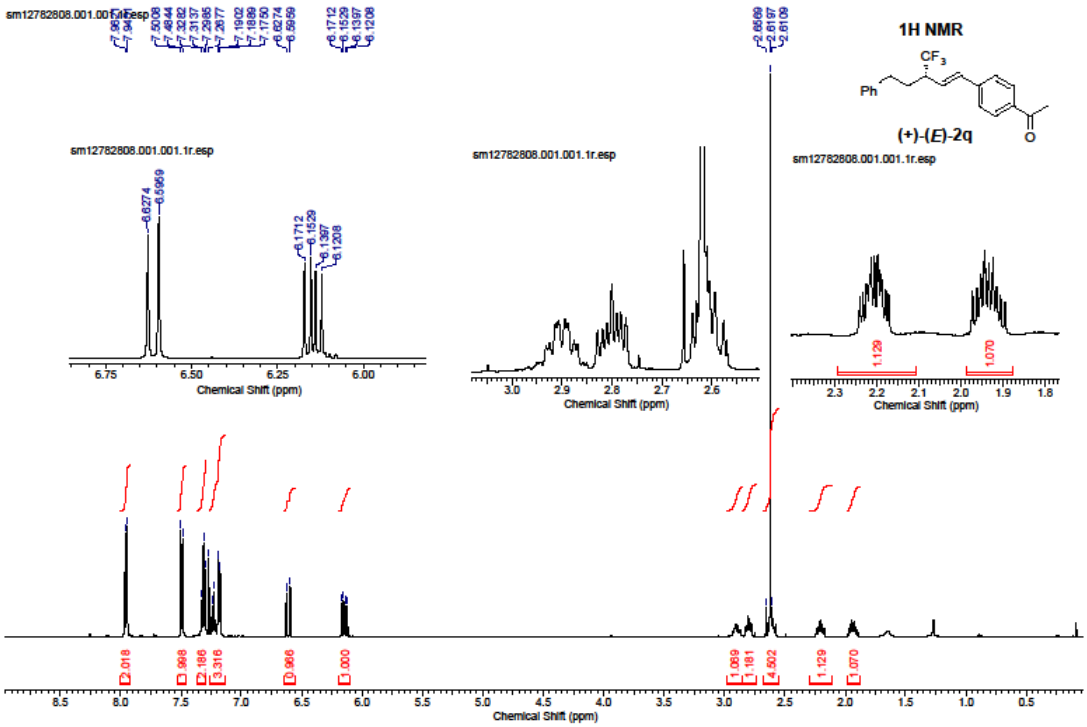
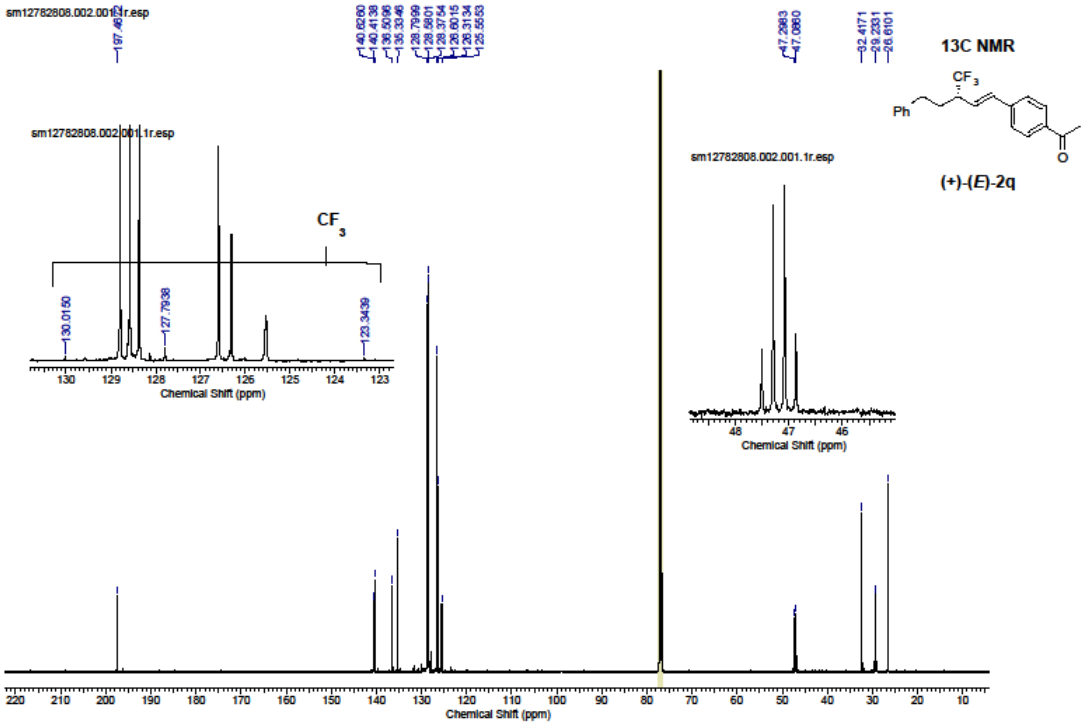
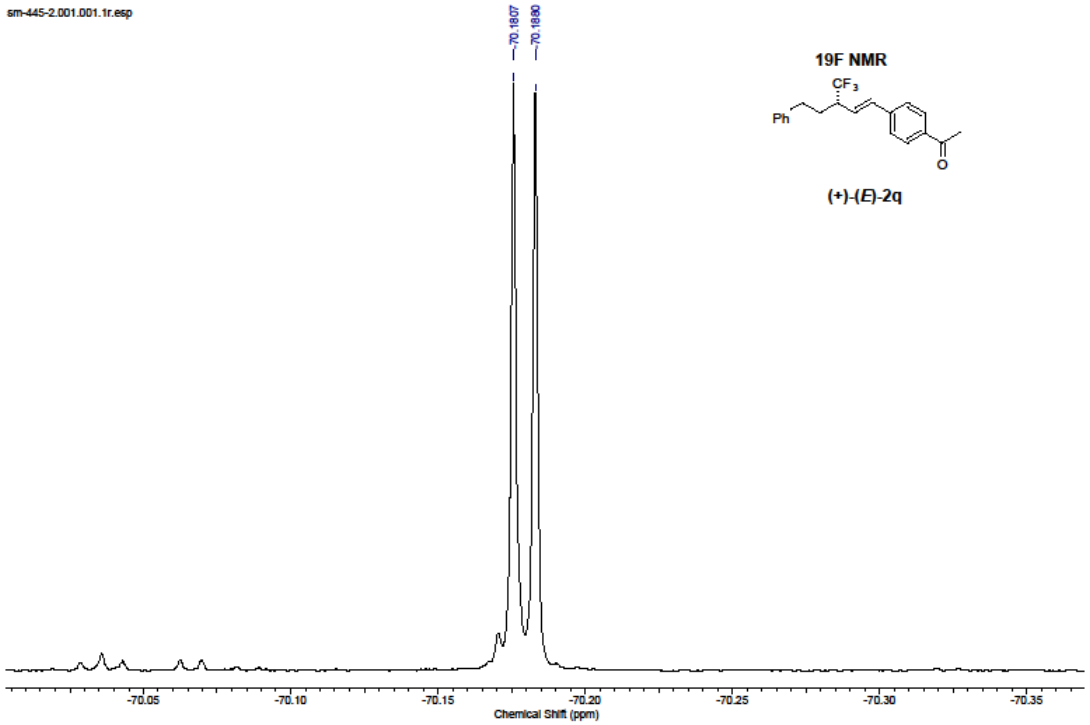
19F NMR
(+)-(Z)-2q
Chemical Shift (ppm)


1H NMR
(+)-(E)-2q
Chemical Shift (ppm)


13C NMR
(+)-(E)-2q
CF3
Chemical Shift (ppm)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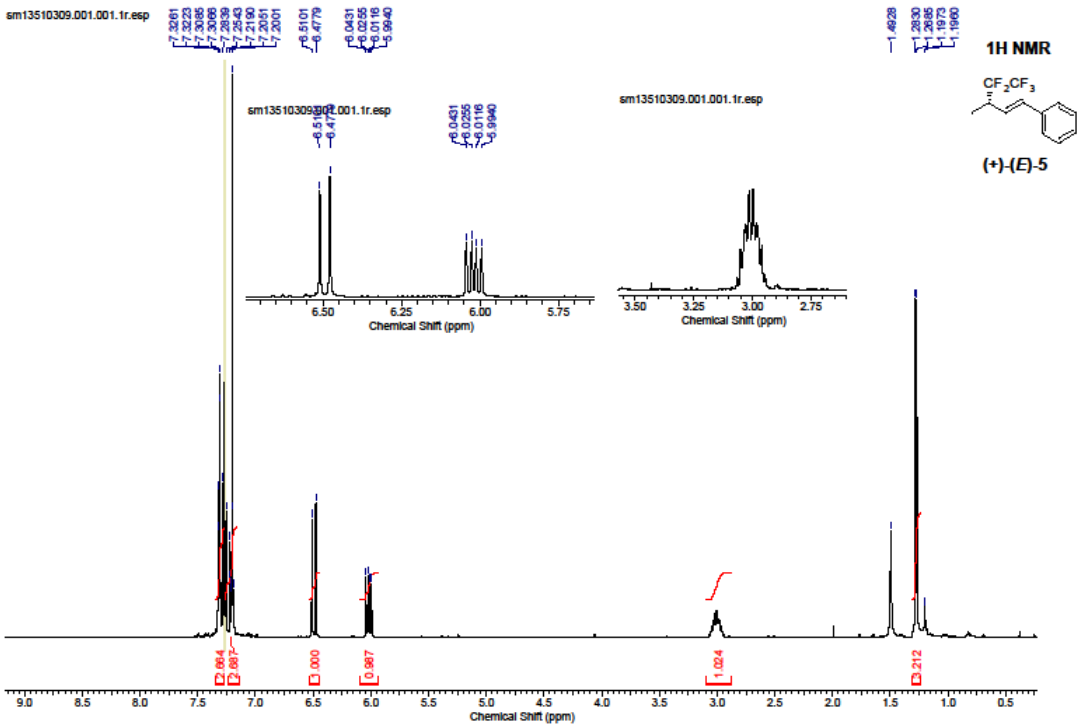
-70.1807
-70.1880
19F NMR
CF3
Ph
O
(+)-(E)-2q
-70.05
-70.10
-70.15
-70.20
-70.25
-70.30
-70.35
Chemical Shift (ppm)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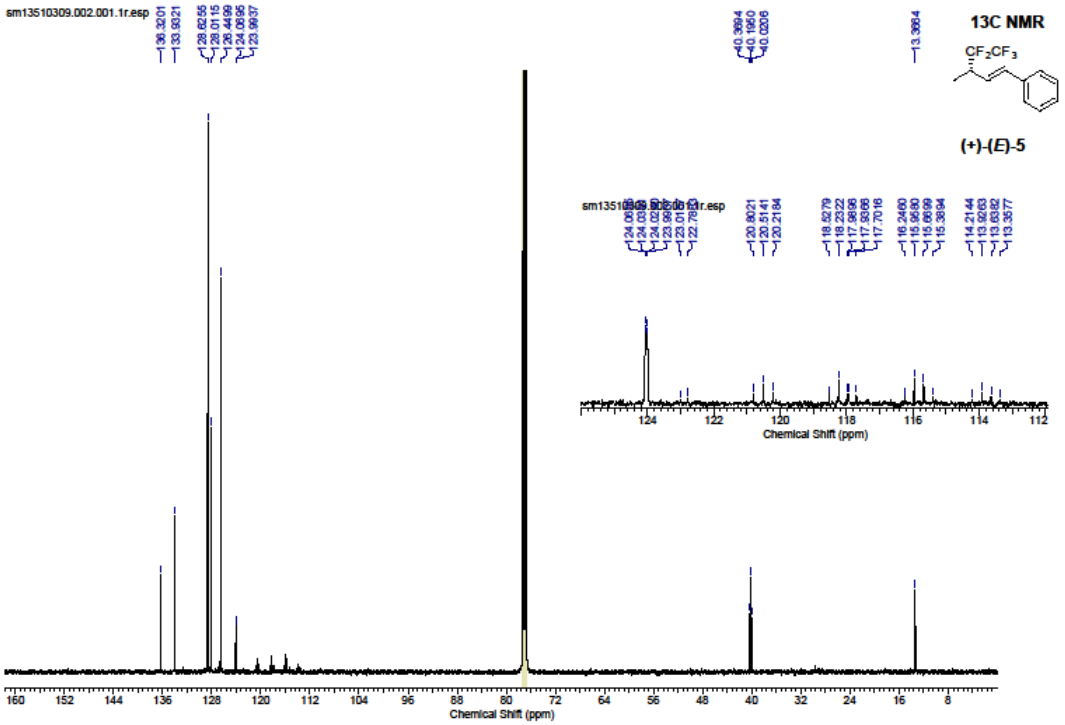
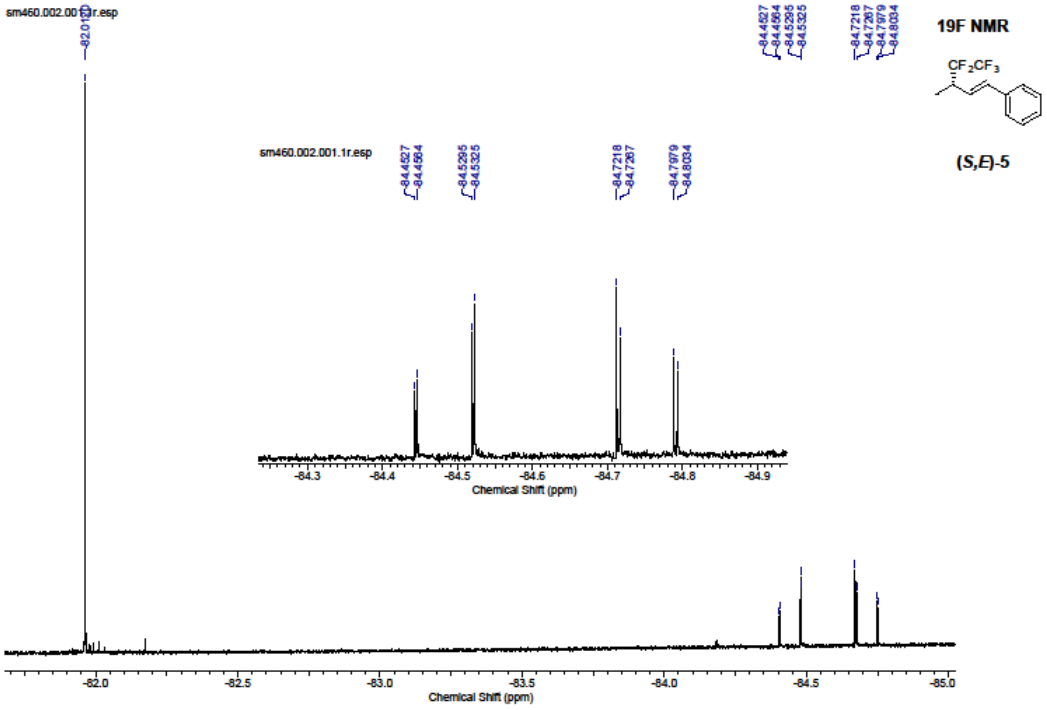
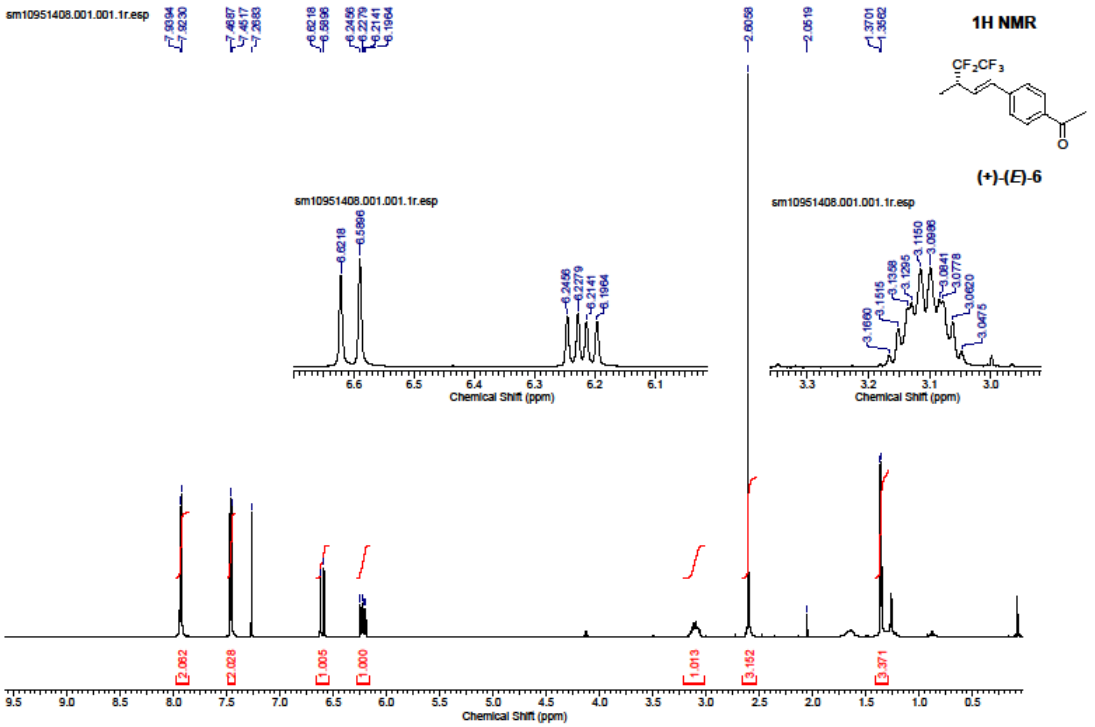
7.3261
7.3223
7.3085
7.3066
7.2839
7.2543
7.2190
7.2061
7.2001
6.5101
6.4779
6.0431
6.0255
6.0116
5.9940
1.4928
1.2930
1.2685
1.1973
1.1960
1H NMR
CF2CF3
(+)-(E)-5
sm13510309.001.001.1r.esp
sm13510309.001.001.1r.esp
6.50
6.25
6.00
5.75
Chemical Shift (ppm)
3.50
3.25
3.00
2.75
Chemical Shift (ppm)
2.864
2.887
3.000
0.987
1.024
3.212
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


13C NMR
(+)-(E)-5
Chemical Shift (ppm)


19F NMR
(S,E)-5
Chemical Shift (ppm)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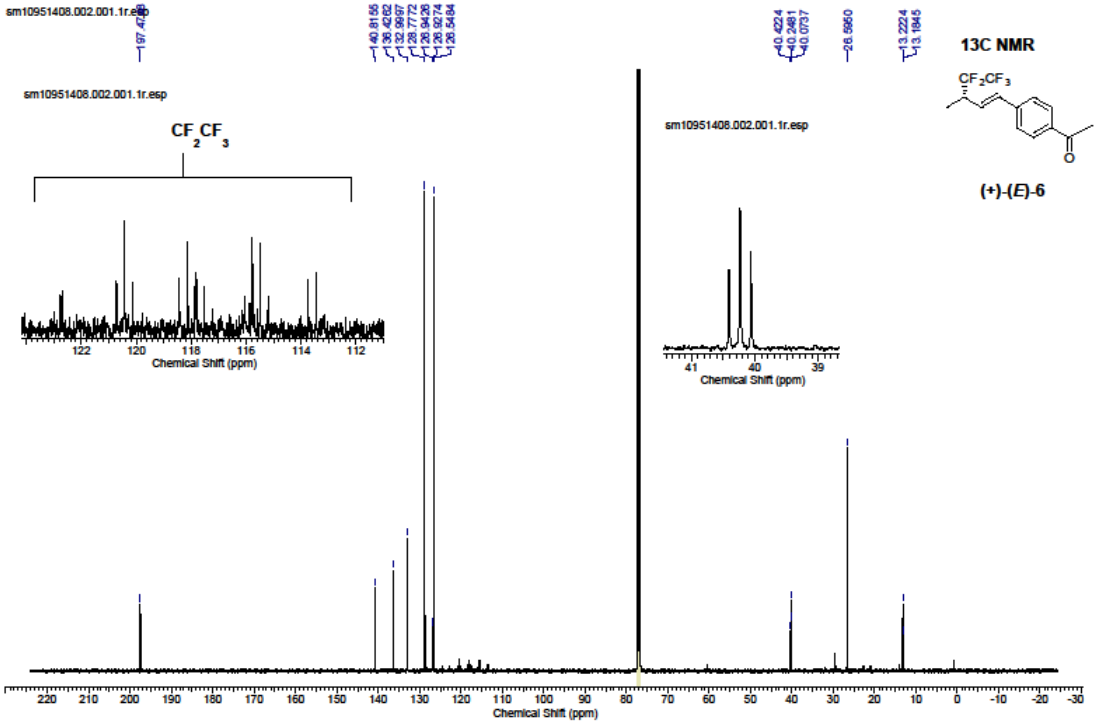
1H NMR
(+)-(E)-6
Chemical Shift (ppm)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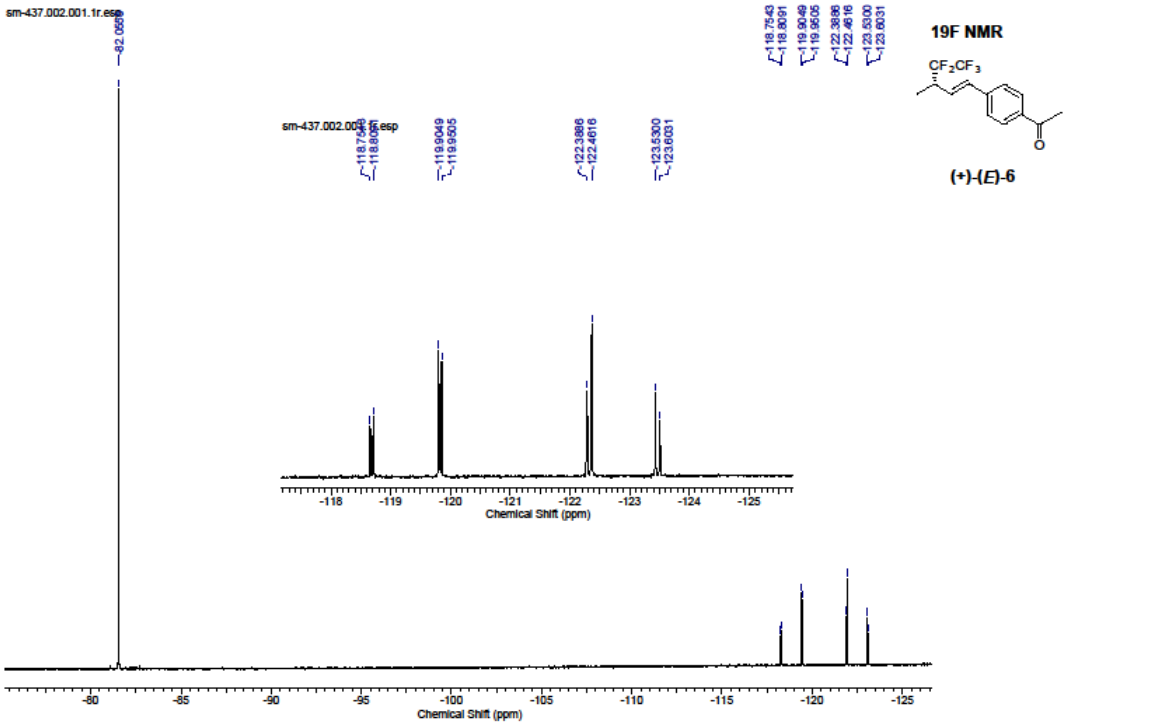
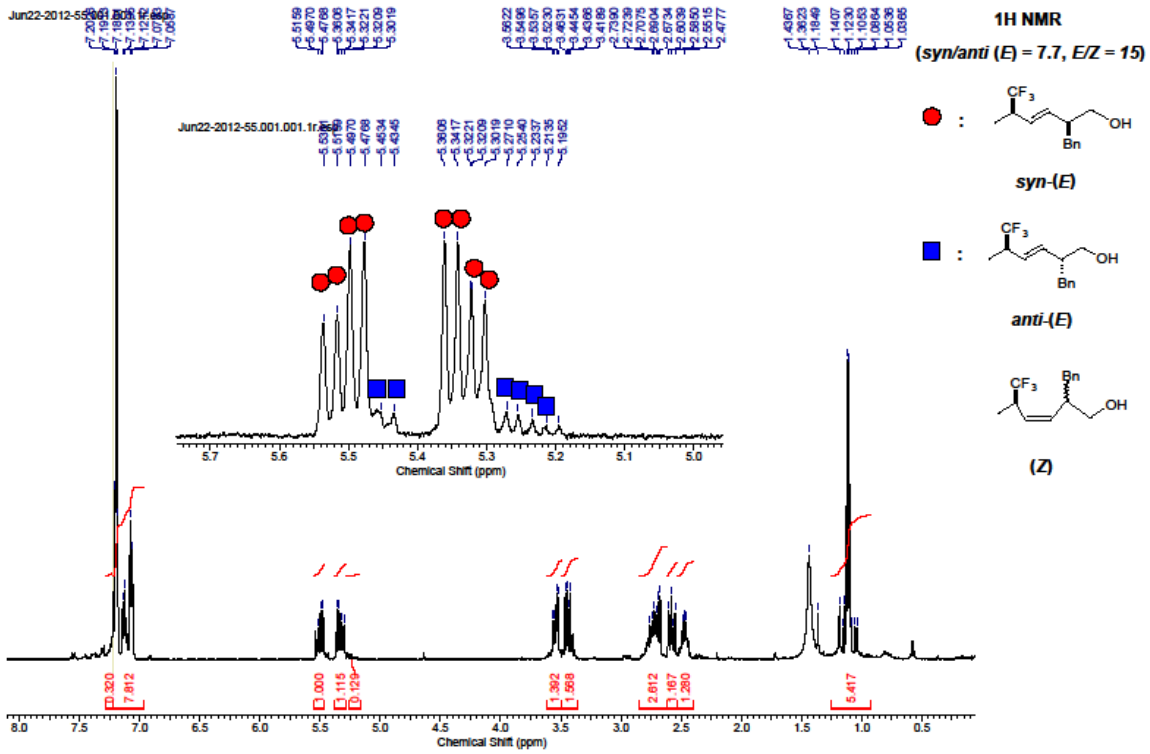
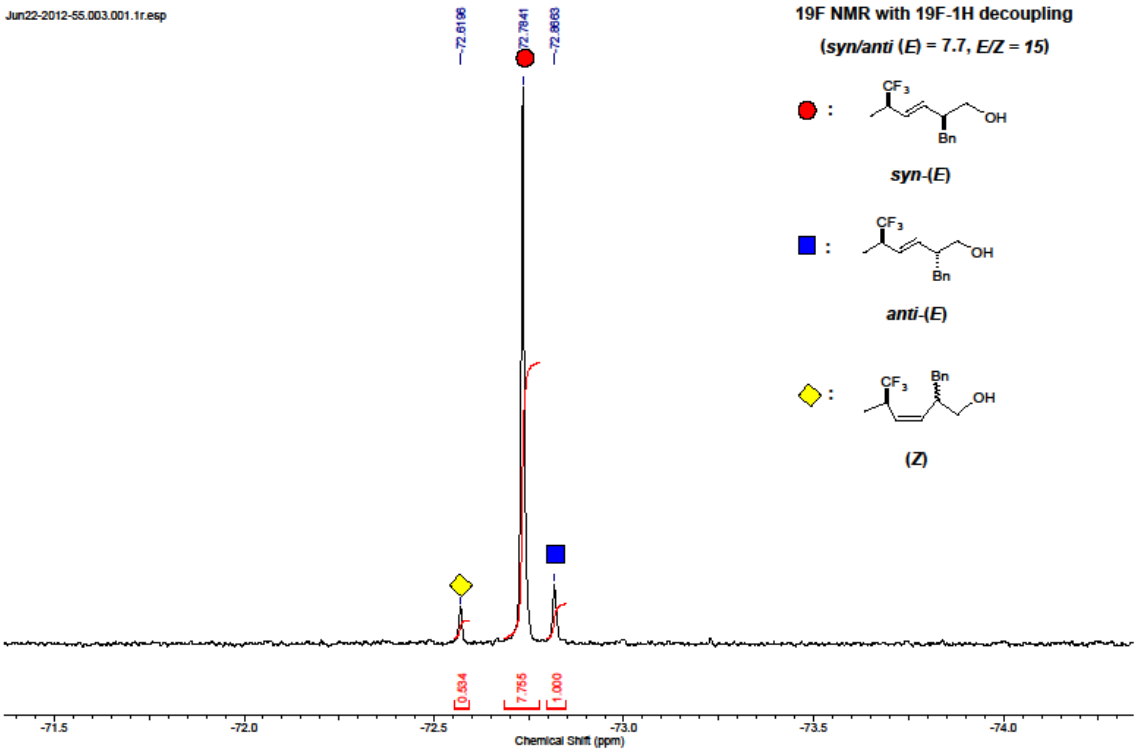
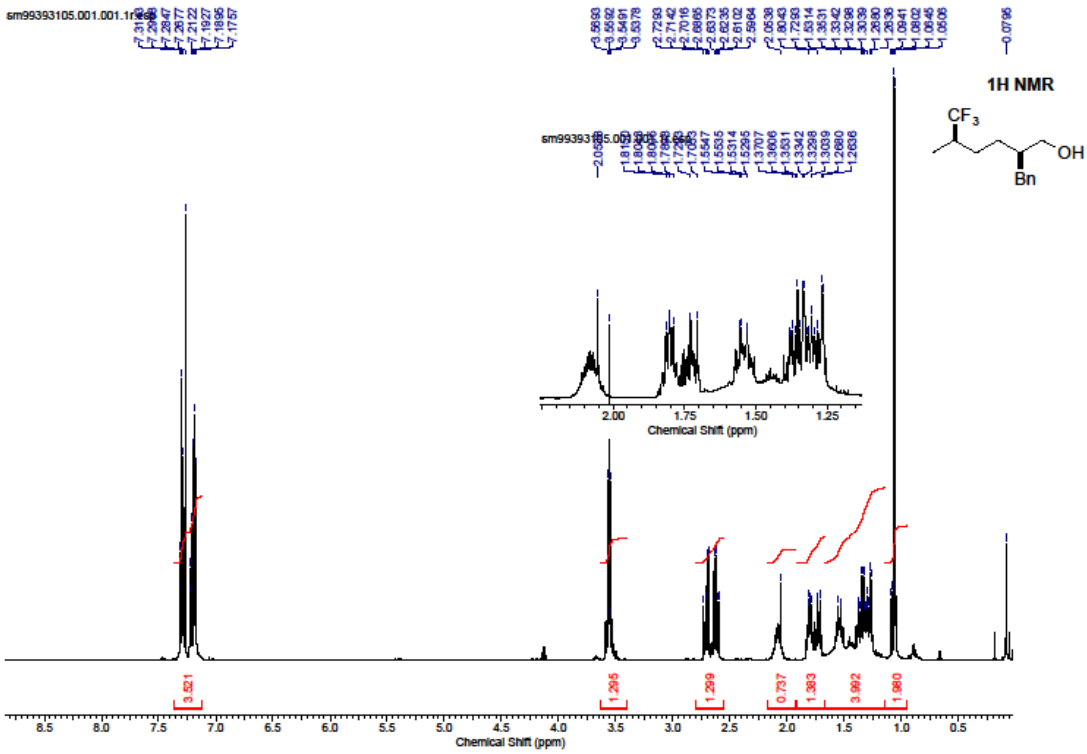
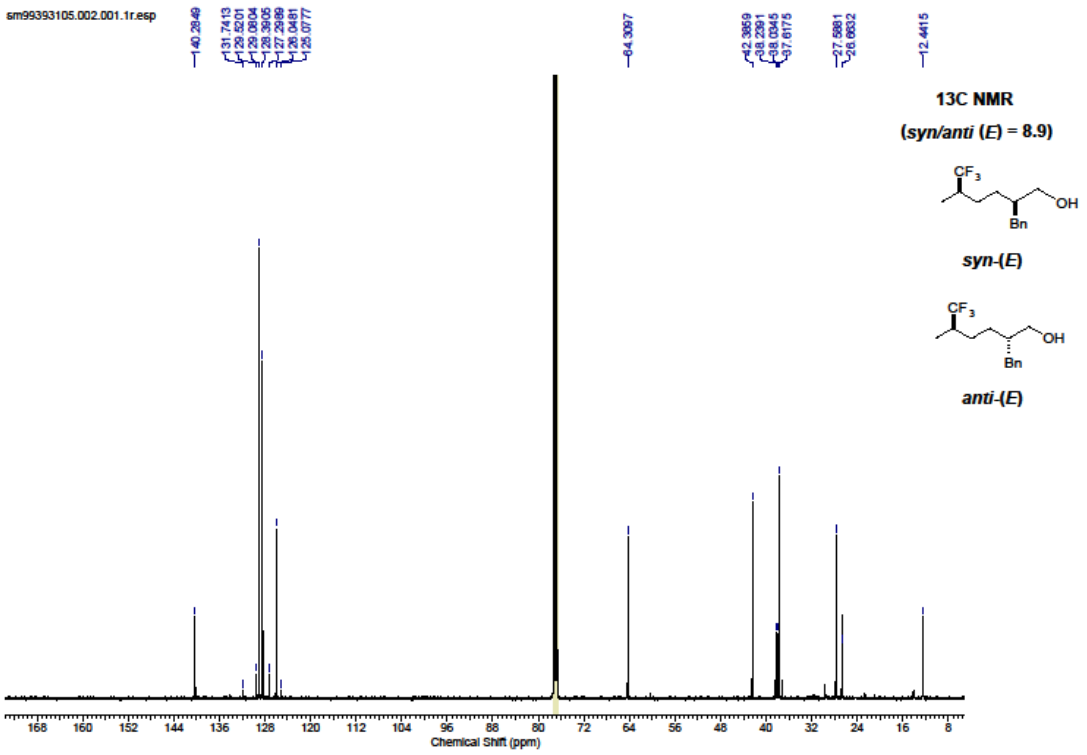
13C NMR
(+)-(E)-6
Chemical Shift (ppm)


19F NMR
(+)-(E)-6
Chemical Shift (ppm)


1H NMR
(syn/anti (E) = 7.7, E/Z = 15)
syn-(E)
anti-(E)
(Z)
Chemical Shift (ppm)


Jun22-2012-55.003.001.1r.esp
19F NMR with 19F-1H decoupling
(syn/anti (E) = 7.7, E/Z = 15)
syn-(E)
anti-(E)
(Z)
Chemical Shift (ppm)


1H NMR
Chemical Shift (ppm)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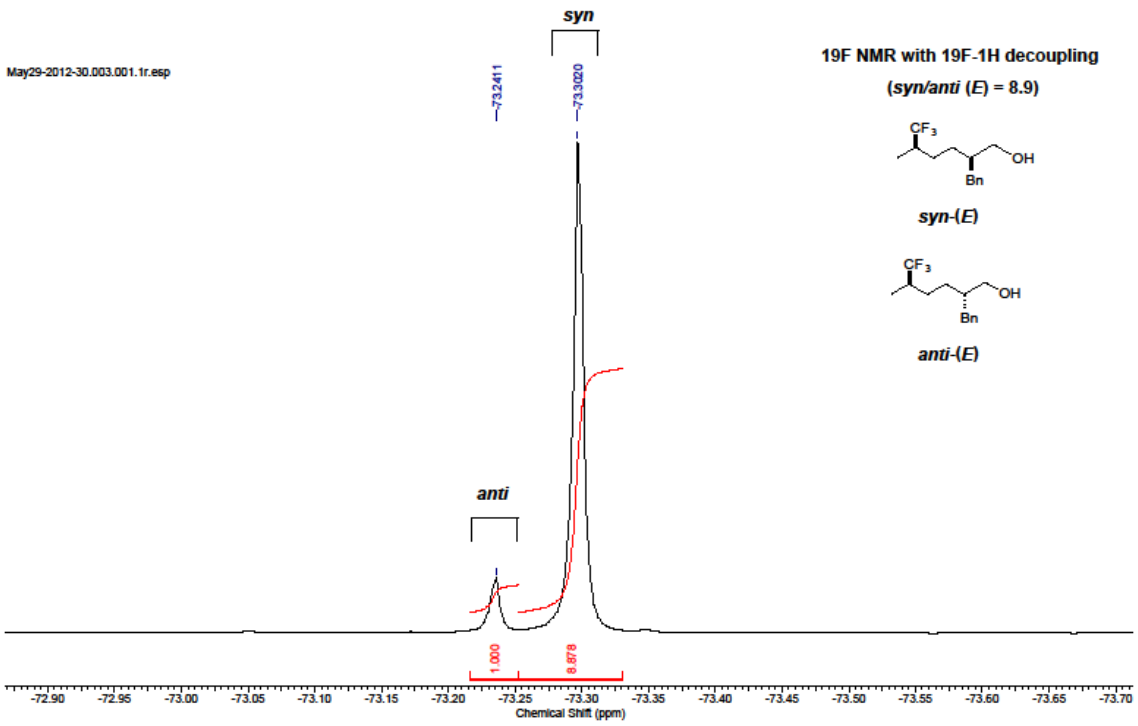
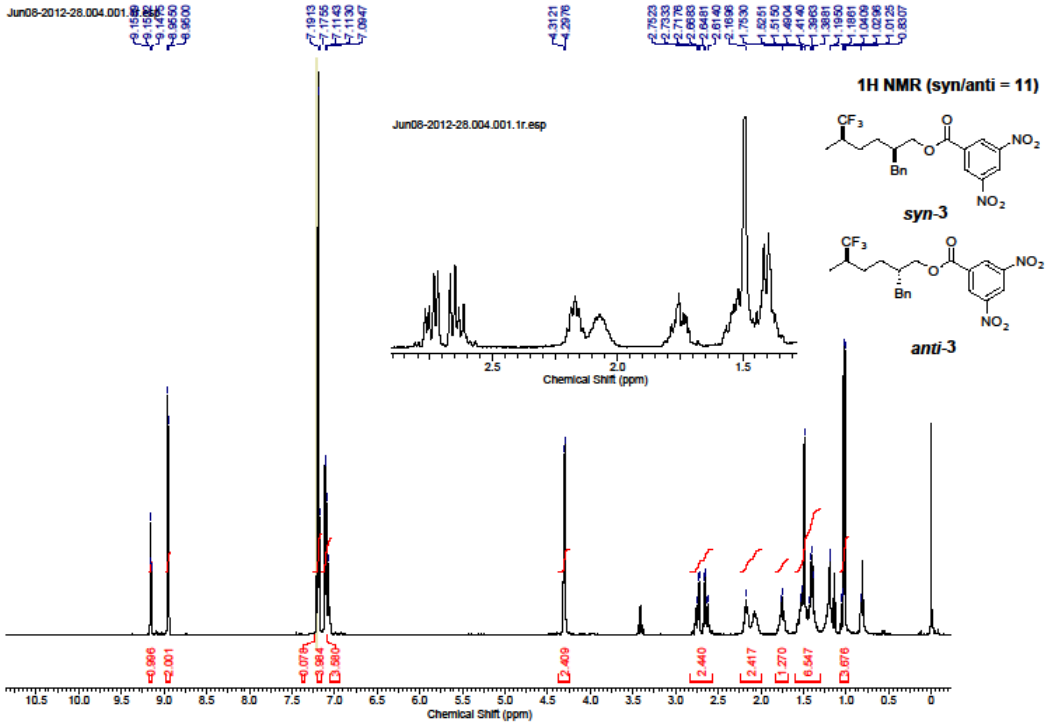
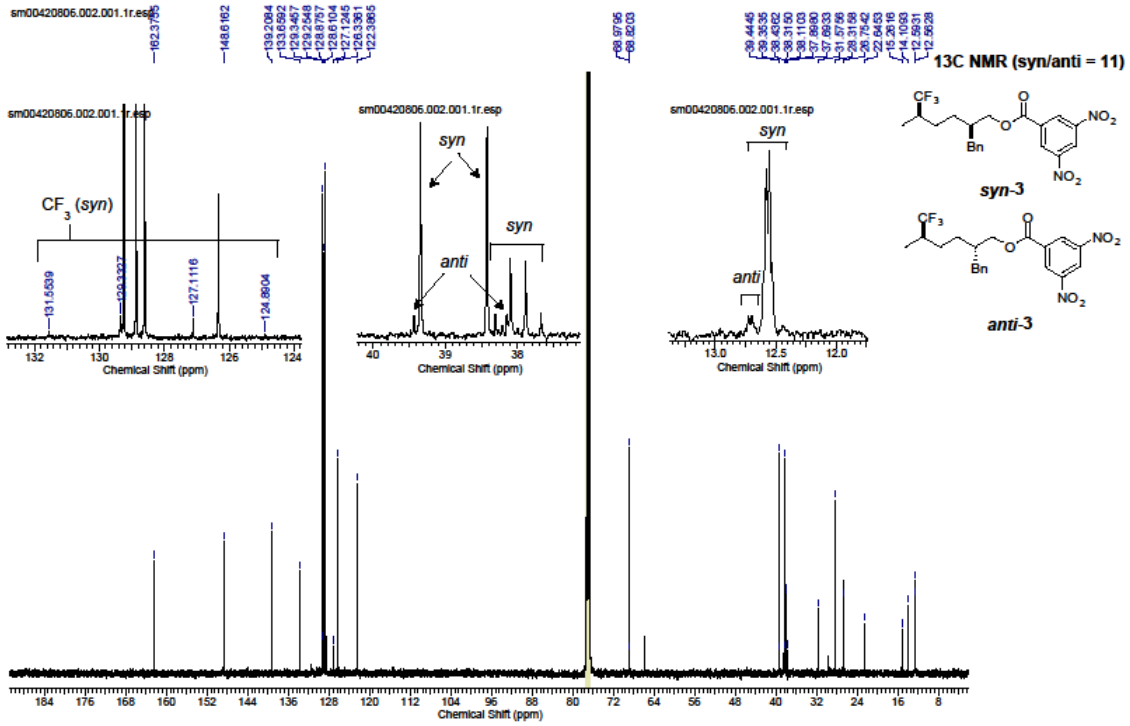
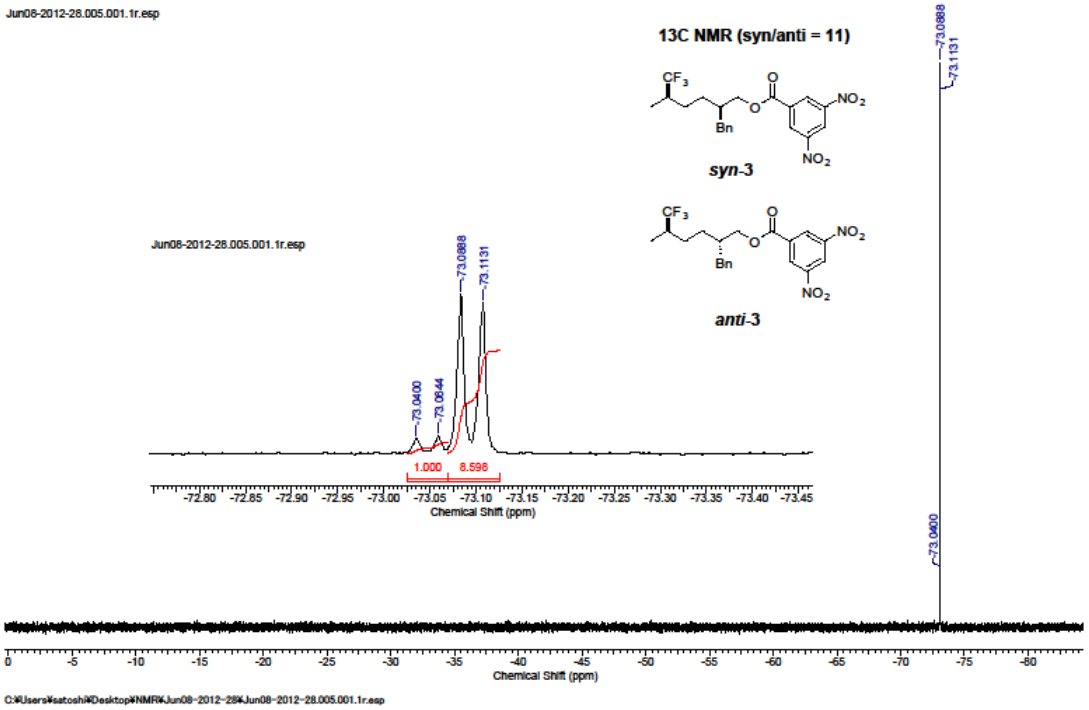
129.0604
128.3906
127.2989
126.0491
125.0777
64.3097
42.3859
38.2391
38.0345
37.6175
27.5881
26.6632
12.4415
13C NMR
(syn/anti (E) = 8.9)
CF3
OH
Bn
syn-(E)
anti-(E)
Chemical Shift (ppm)


May29-2012-30.003.001.1r.esp
syn
anti
-73.2411
-73.3020
1.000
8.878
19F NMR with 19F-1H decoupling
(syn/anti (E) = 8.9)
CF3
OH
Bn
syn-(E)
anti-(E)
Chemical Shift (ppm)


1H NMR (syn/anti = 11)
syn-3
anti-3
Chemical Shift (ppm)


13C NMR (syn/anti = 11)
CF3 (syn)
syn
anti
syn-3
anti-3
Chemical Shift (ppm)


Jun08-2012-28.005.001.1r.esp
13C NMR (syn/anti = 11)
syn-3
anti-3
Chemical Shift (ppm)
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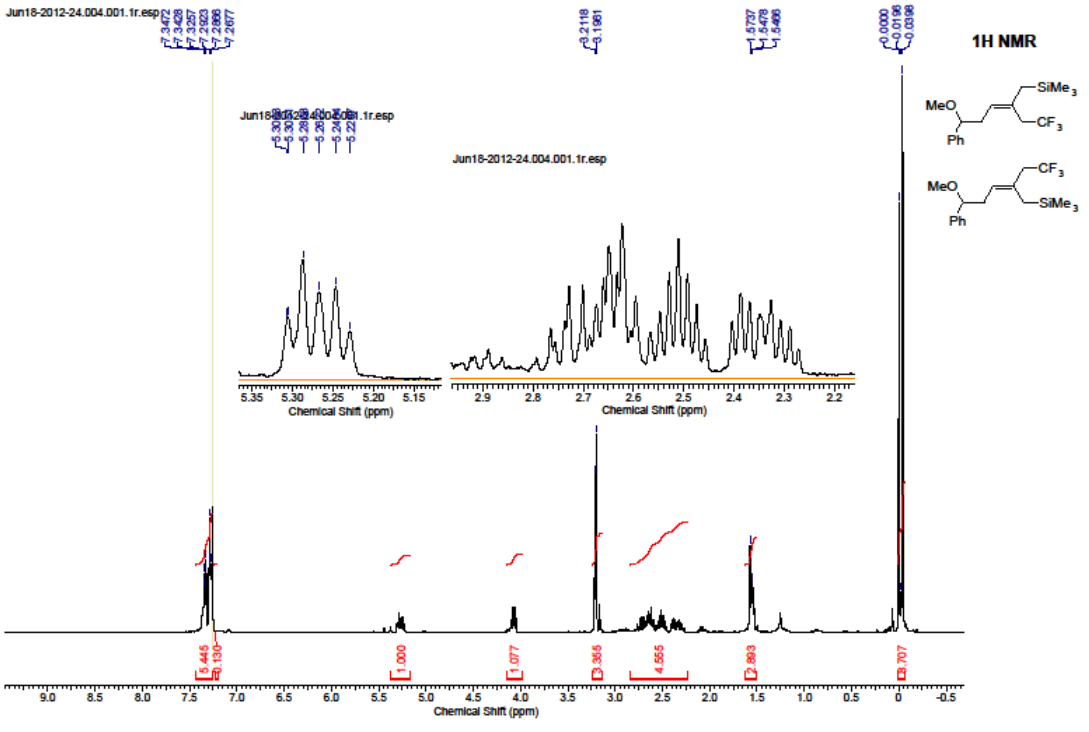
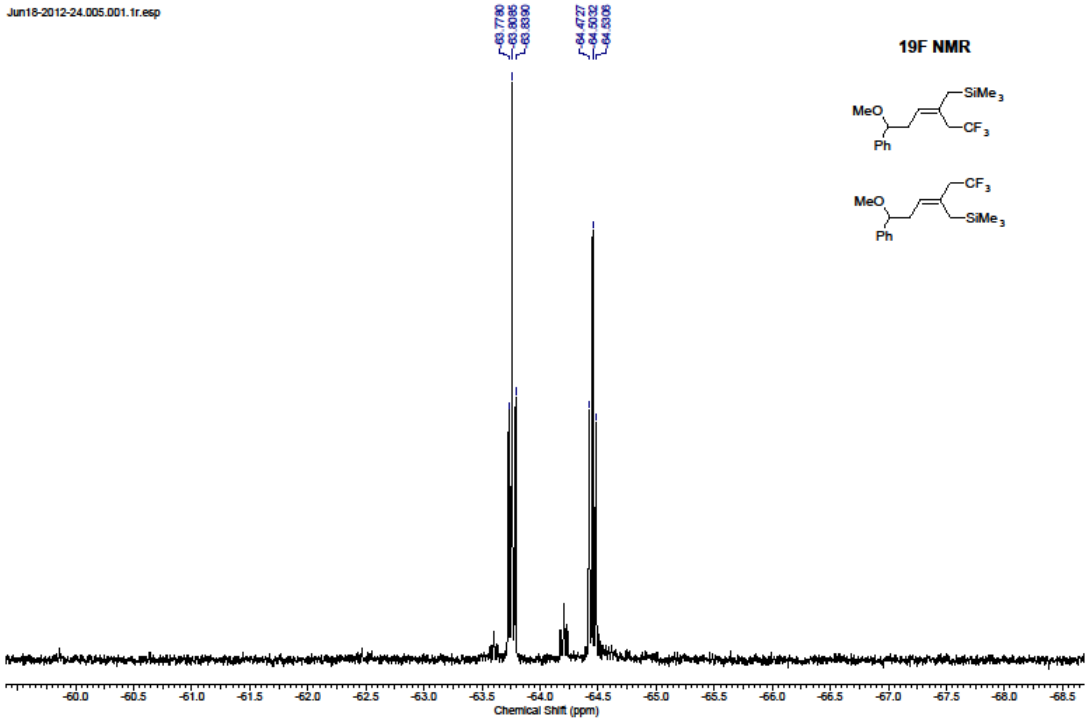

Jun18-2012-24.004.001.1r.esp
1H NMR
Chemical Shift (ppm)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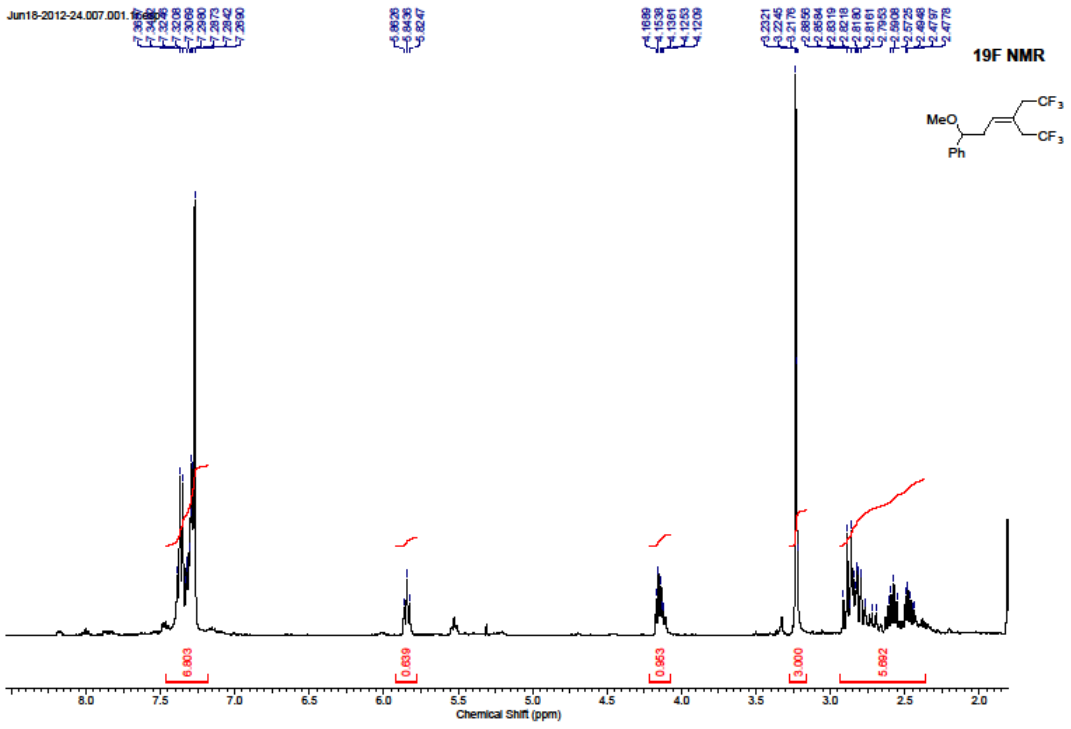
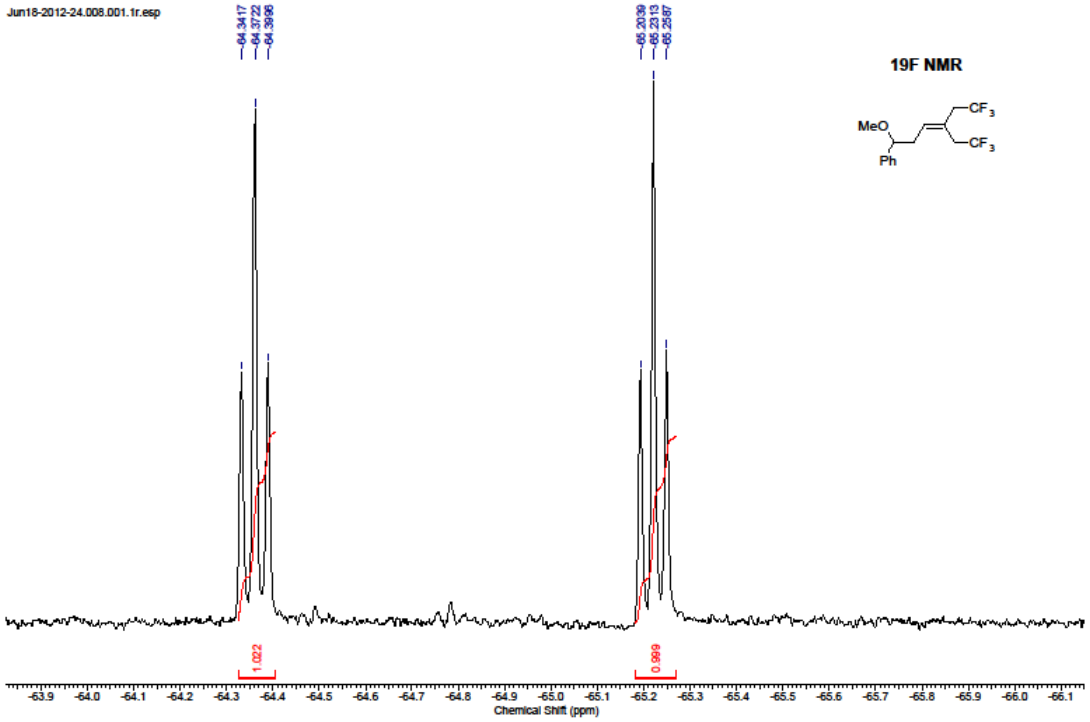
19F NMR
MeO
Ph
SiMe3
CF3
Chemical Shift (ppm)


19F NMR
MeO
Ph
CF3
CF3
6.803
0.639
0.953
3.000
5.892
Chemical Shift (ppm)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-64.3417
-64.3722
-64.3986
-65.2039
-65.2313
-65.2587
19F NMR
MeO
Ph
CF3
CF3
1.022
0.999
-63.9 -64.0 -64.1 -64.2 -64.3 -64.4 -64.5 -64.6 -64.7 -64.8 -64.9 -65.0 -65.1 -65.2 -65.3 -65.4 -65.5 -65.6 -65.7 -65.8 -65.9 -66.0 -66.1
Chemical Shift (ppm)