Copper(I)-Catalyzed Diastereoselective Hydroxytrifluoromethylation of Dienes Accelerated by Phosphine Ligands

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Supporting Material

A. General Information

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottom flasks and vials. Stainless steel syringes and cannula were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from Sigma Aldrich.

Materials. Commercial reagents were purchased from Sigma Aldrich, Fluka, EM Science, and Lancaster and used as received. All solvents were used after being freshly distilled unless otherwise noted.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker UltraShield-400 (400 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ($CHCl_3$: δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.0). For those complicated spin-spin splitting patterns, coupling constants were obtained by 2D J-resolve experiments. Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constants in Hertz (Hz), and integration.

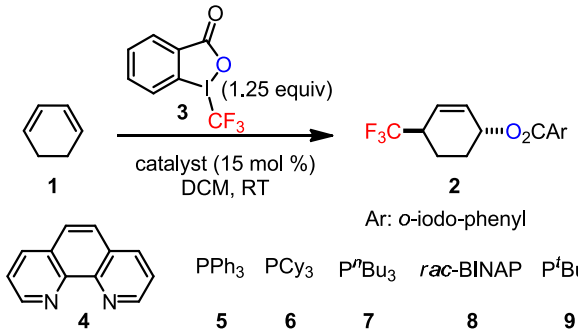
The mass spectroscopic data were obtained at the Georgia State University mass spectrometry facility using a Micromass Platform II single quadrupole instrument. Infrared (IR) spectra were obtained by using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}).

Molecular modeling was carried on some compounds to assist the stereochemistry determination. Optimal geometries of diastereomers were achieved by analytical gradient methods with the Gaussian09 software package. The density functional theory (DFT) calculations were performed at the B3LYP 6-31+G** or M06L 6-31+G** + LANL2DZ level of theories as noted.[1]

Abbreviations used: EtOH – ethanol, EtOAc – ethyl acetate, THF – tetrahydrofuran, MeOH – methanol, Et_2O – diethyl ether, DCM – dichloromethane, TEA – triethylamine, MS – molecular sieves, TLC – thin layer chromatography.

B. Catalyst Discovery for Diastereoselective Hydroxytrifluoromethylation of Dienes

Table S1. Catalyst discovery for hydroxytrifluoromethylation of dienes



entry[a]	Cu $(X)_n$	ligand (15 mol %)	*T* (h)	conversion[b] (%)	yield[b] (%)	*dr*[b]
1	$Cu(MeCN)_4PF_6$	NA	4	90	32	1.2
2	CuCl	NA	4	80	56	2.0
3	CuCN	NA	12	<10	trace	NA
4[c]	CuCN	**4**	12	<10	trace	NA
5[c]	CuCN	**5**	6	>95	53	3.0
6[c]	CuCN	**6**	4	>95	47	5.0
7[c]	CuCN	**7**	4	>95	40	4.2
8[c]	CuCN	**8**	12	50	23	7.0
9[c,d]	CuCN	**9**	6	>95	77	6.7
10[c]	$Cu(MeCN)_4PF_6$	**9**	12	trace	NA	NA
11[c]	CuCl	**9**	12	<20	13	5.5

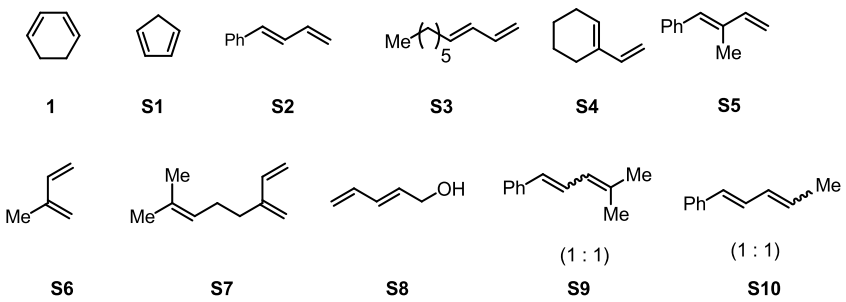
General Procedure

To a flame-dried sealable 2-dram vial equipped with a stir bar were added a copper salt (0.03 mmol) and the corresponding ligand (0.03 mmol). After the vial was evacuated and backfilled three times, dry dichloromethane (2 mL) was added via a syringe and the mixture was stirred for 30 min at room temperature and then cooled to 0 ^{o}C. Diene **1** (0.2 mmol) was added to the vial via a syringe. The Togni's reagent **3** (76 mg, 0.24 mmol) was then dissolved in dichloromethane (2 mL) and added via a syringe. The reaction mixture was degassed again by brief evacuation and backfilling with argon three times, then warmed to room temperature and kept stirring until the starting material was fully consumed (monitored by GC). α,α,α-Trifluorotoluene was then added as an internal standard and the reaction was analyzed by ^{19}F NMR.

C. Procedures for Copper(I)-Catalyzed Diastereoselective Hydroxytrifluoromethylation and Product Relative Stereochemistry Determination

a. Synthesis of Dienes

Table S2. Tested Diene Substrates



1 **S1** **S2** **S3** **S4** **S5** **S6** **S7** **S8** **S9** **S10**

The diene substrates 1,3-cyclohexadiene (**1**), isoprene (**S6**), and 7-methyl-3-methylene-1,6-octadiene (myrcene, **S7**) were purchased from Sigma-Aldrich and redistilled before use. The substrate cyclopentadiene (**S1**) was obtained via retro-Diels–Alder reaction by heating commercially available dicyclopentadiene above 150 ^{o}C.

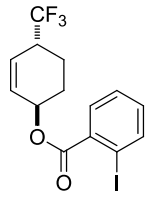
Substrates (*E*)-Buta-1,3-dienylbenzene diene (**S2**),[2] (*E*)-deca-1,3-diene (**S3**),[3] 1-vinylcyclohex-1-ene (**S4**),[4] (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene (**S5**),[5] (*E*)-penta-2,4-dien-1-ol (**S8**),[6] (4-methylpenta-1,3-dien-1-yl)benzene (**S9**),[7] and (1*E*)-penta-1,3-dien-1-ylbenzene (**S10**)[8] were prepared according to literature procedures and their NMR spectra were in accordance with the previously reported data. The Togni's reagent **3** (3,3-Dimethyl-1-(trifluoromethyl)-1,2-benziodoxole) was synthesized according to a literature.[9]

b. General Procedure

To a flame-dried sealable 2-dram vial equipped with a stir bar were added CuCN (13 mg, 0.15 mmol, tri-*tert*-butylphosphonium tetrafluoroborate (44 mg, 0.15 mmol) and *N*,*N*-diisopropylethylamine (26 μL, 0.15 mmol). After the vial was evacuated and backfilled three times, dry dichloromethane (10 mL) was added via a syringe and the mixture was stirred for 30 min at room temperature. The diene substrate (1.0 mmol) was then added to the vial via a syringe. To another flame dried vial was added the Togni's reagent **3** (379 mg, 1.2 mmol) dissolved in dichloromethane (12 mL). Both of the vials were degassed by brief evacuating and backfilling with argon three times and the Togni's reagent was then added to the substrate dropwise by

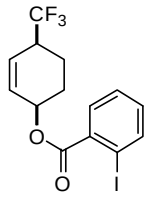
syringe pump over 3 hours. The reaction mixture was stirred until the diene was consumed which was monitored by TLC. After the reaction was quenched by saturated aqueous sodium bicarbonate solution, the aqueous layer was separated and extracted by ether (20 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography to afford the 1,4-hydroxytrifluoromethylation product.

c. Product Characterization and Relative Stereochemistry Determination



2

***trans*-4-(Trifluoromethyl)cyclohex-2-en-1-yl 2-iodobenzoate(2):** by following the general procedure (1.0 mmol scale), product **2** was obtained from **1** and isolated by silica gel flash column (hexanes : ether = 99 : 1 to 9 : 1) as colorless oil (249 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.15 (d, *J* = 10.3 Hz, 1H), 5.92 (d, *J* = 10.3 Hz, 1H), 5.66 – 5.52 (m, 1H), 3.07 – 2.88 (m, 1H), 2.43 – 2.26 (m, 1H), 2.22 – 2.09 (m, 1H), 1.94 – 1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 141.3, 135.3, 132.7, 131.4, 130.9, 127.9, 126.7 (q, *J* = 279.8), 124.9 (q, *J* = 3.0 Hz), 94.0, 69.4, 39.9 (q, *J* = 27.5 Hz), 26.2, 19.6 (q, *J* = 2.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.33 (d, *J* = 9.2 Hz); HRMS (ESI, m/z): calcd for $C_{14}H_{12}F_3INaO_2$+ ($M + Na^+$), 418.9726, found 418.9715; IR ν_{max} (neat)/cm^{-1}: 3043 (w), 2956 (m, sharp), 1719 (s, C=O).



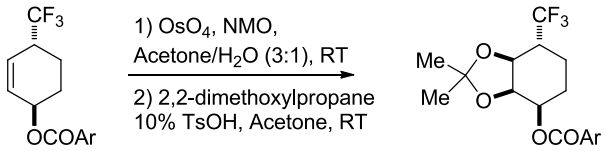
2'

***cis*-4-(Trifluoromethyl)cyclohex-2-en-1-yl 2-iodobenzoate (2′):** by following the general procedure (1.0 mmol scale), product **2′** was obtained from **1** and isolated by silica gel flash

column (hexanes : ether = 99 : 1 to 9 : 1) as colorless oil (37 mg, 9% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 10.0 Hz, 1H), 6.03 (d, *J* = 10.2 Hz, 1H), 5.57 – 5.45 (m, 1H), 3.01 – 2.79 (m, 1H), 2.26 – 2.12 (m, 1H), 2.06 – 1.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 141.3, 135.4, 132.6, 130.9, 129.4, 127.9, 126.7 (q, *J* = 283.8 Hz),126.5 (q, *J* = 3.3 Hz), 93.8, 67.0, 40.4 (q, *J* = 27.5 Hz), 26.1, 17.7 (q, *J* = 2.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.27 (d, *J* = 9.2 Hz); HRMS (ESI, m/z): calcd for $C_{14}H_{12}F_3INaO_2^+$ ($M + Na^+$), 418.9726, found 418.9715; IR ν_{max} (neat)/cm^{-1}: 3045 (w), 2959 (m, sharp), 1717 (s, C=O).

Relative stereochemistry determination: The relative stereochemistry of **2** and **2′** is determined by nuclear overhauser effect (*NOE*) analysis after the derivatization for both of them.

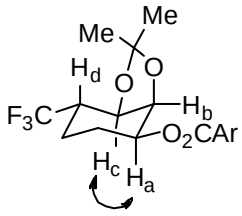
Derivatization of compound **2:**



2 Ar = 2-I-Ph **2a**

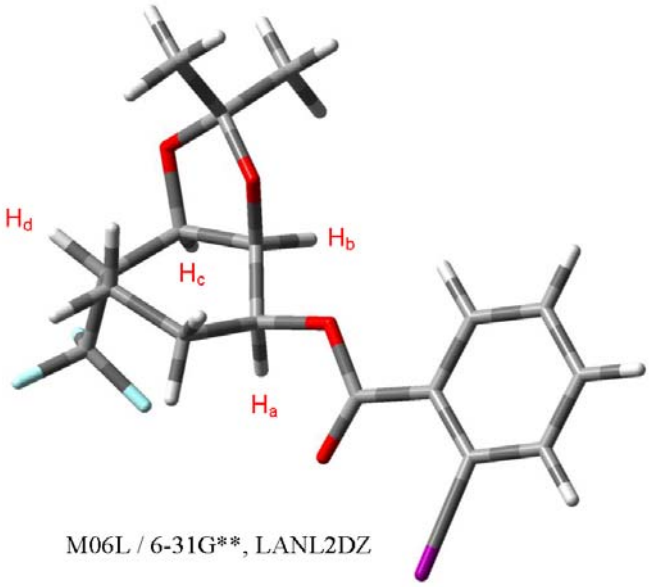
2 (100 mg, 0.25 mmol, 1.0 equiv) and NMO (*N*-Methylmorpholine *N*-oxide) (44.3 mg, 0.38 mmol, 1.5 equiv) were dissolved in acetone/water 3:1 mixture (4 mL). Then OsO_4 dissolved in acetonitrile (*c* = 0.0066 mmol/ml, 1.9 ml, 5 mol%) was slowly added via a syringe at room temperature. The mixture was stirred for 2 days, and then quenched by saturated NaS_2O_3 solution. After evaporation of acetone, the aqueous phase was extracted by ethyl acetate (4 × 5 mL) and then dried over anhydrous Na_2SO_4. The diol was purified by column chromatography to afford colorless oil (60 mg, 56%), which was used without further purification. The colorless oil was dissolved in acetone (3 mL) and 2,2-dimethoxylpropane (0.5 mL) to which *p*-toluenesulfonic acid monohydrate (2.6 mg, 0.013 mmol, ca.10 mol%) was added subsequently. After 3 hours, the reaction was quenched with solid $NaHCO_3$. The mixture was filtered and the filtrate was concentrated under vacuum. The desired compound was isolated as colorless oil after purification by column chromatography (58 mg, 49% two step combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.19

(t, J = 7.7 Hz, 1H), 5.31 – 5.21 (m, 1H), 4.65 – 4.57 (m, 1H), 4.38 – 4.28 (m, 1H), 2.46 – 2.33 (m, 1H), 2.12 – 1.93 (m, 3H), 1.58 (s, 3H), 1.50 – 1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 141.3, 134.9, 132.8, 131.1, 128.0, 127.2 (q, J = 280.1 Hz), 110.4, 94.1, 73.6, 73.4, 71.4, 44.3 (q, J = 25.2 Hz), 28.3, 26.2, 23.4, 19.8 (d, J = 3.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.73 (d, J = 8.1 Hz); HRMS (ESI, m/z): calcd for $C_{17}H_{19}F_3IO_4^+$ ($M + H^+$), 471.0275, found 471.0283. IR ν_{max} (neat)/cm^{-1}: 2977(m), 2936 (m), 1724 (s, C=O).

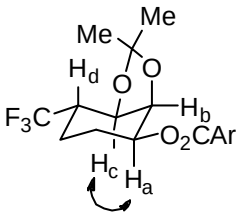


3.060 Å, *NOE* predicted
Ar: *o*-iodo-phenyl

2a



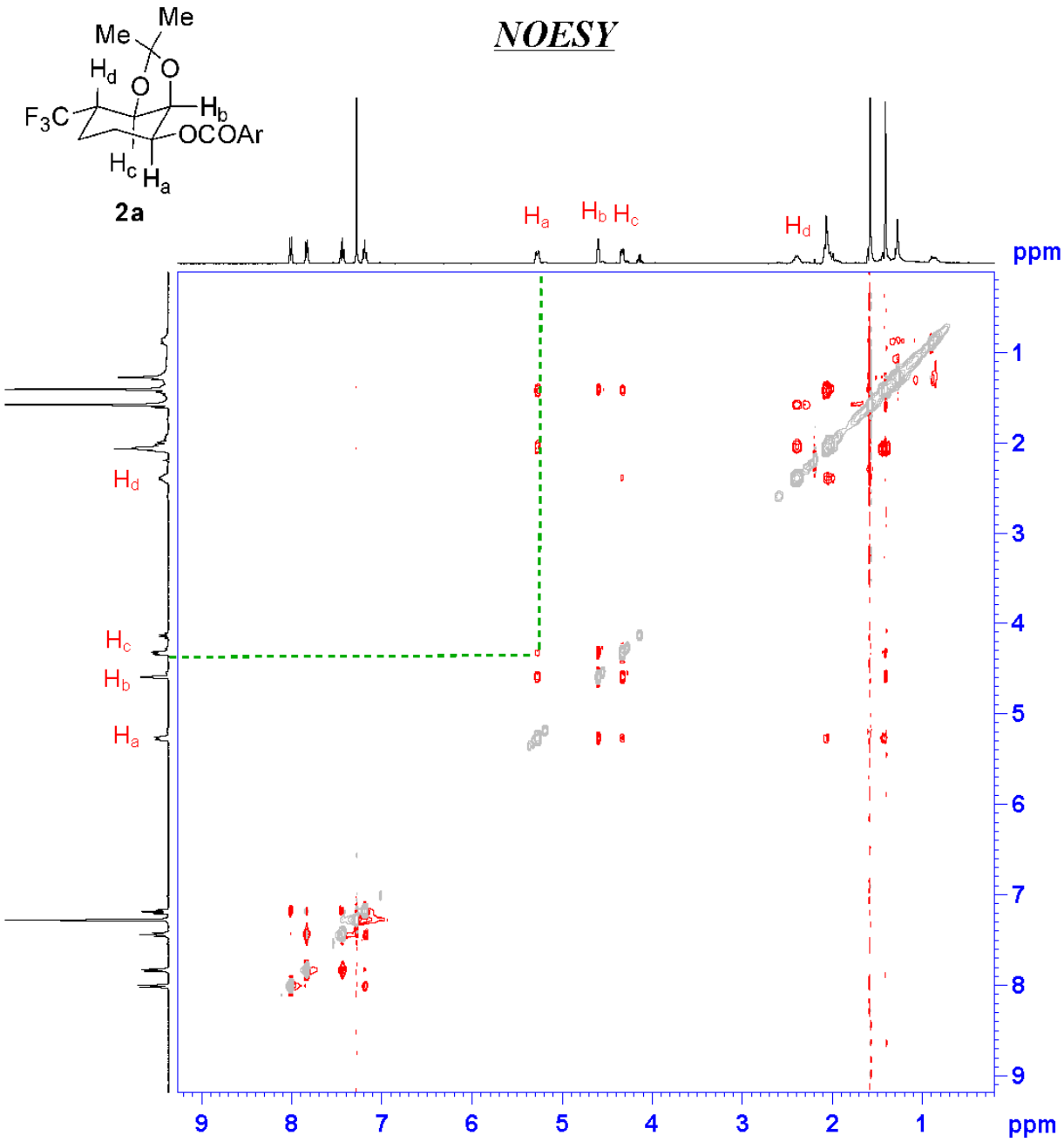
M06L / 6-31G**, LANL2DZ



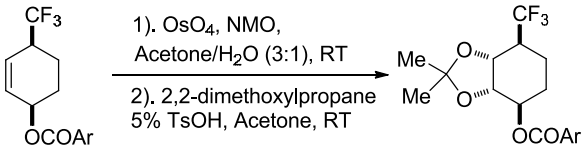
Ar: *o*-iodo-phenyl

NOE observed

2a

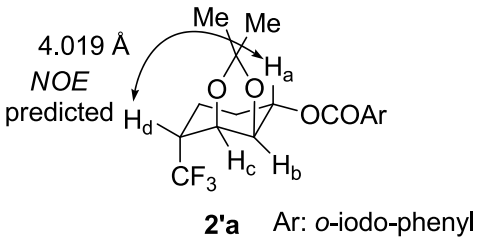


Derivatization of compound **2′:**

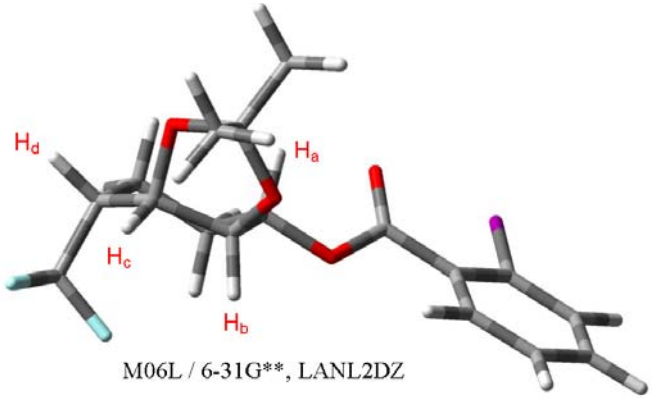


2' Ar = 2-I-Ph **2'a**

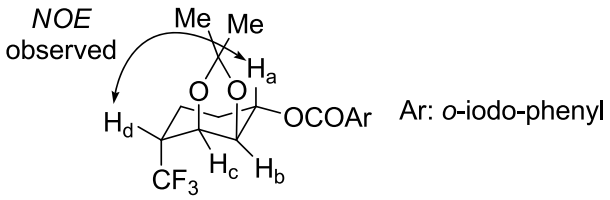
2′ a: **2′** was converted to **2′ a** by following the previously mentioned procedure with 72% overall yield after two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.52 (d, *J* = 3.3 Hz, 1H), 4.43 (t, *J* = 6.3 Hz, 1H), 4.32 (s, 1H), 2.54 – 2.35 (m, 1H), 1.97 (t, *J* = 11.0 Hz, 2H), 1.93 – 1.75 (m, 2H), 1.57 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 141.5, 134.8, 133.0, 131.2, 128.1, 127.2 (q, *J* = 280.0 Hz), 109.5, 93.9, 74.6, 71.8 (d, *J* = 1.8 Hz), 71.2, 43.8 (q, *J* = 25.3 Hz), 28.2, 26.3, 24.2, 17.6 (q, *J* = 2.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.08 (d, *J* = 8.7 Hz); HRMS (ESI, m/z): calcd for $C_{17}H_{19}F_3IO_4^+$ ($M + H^+$), 471.0275, found 471.0273. IR ν_{max} (neat)/cm^{-1}: 3058 (w), 2987 (m, sharp), 1729 (s, C=O).



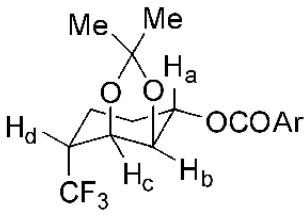
2'a Ar: *o*-iodo-phenyl



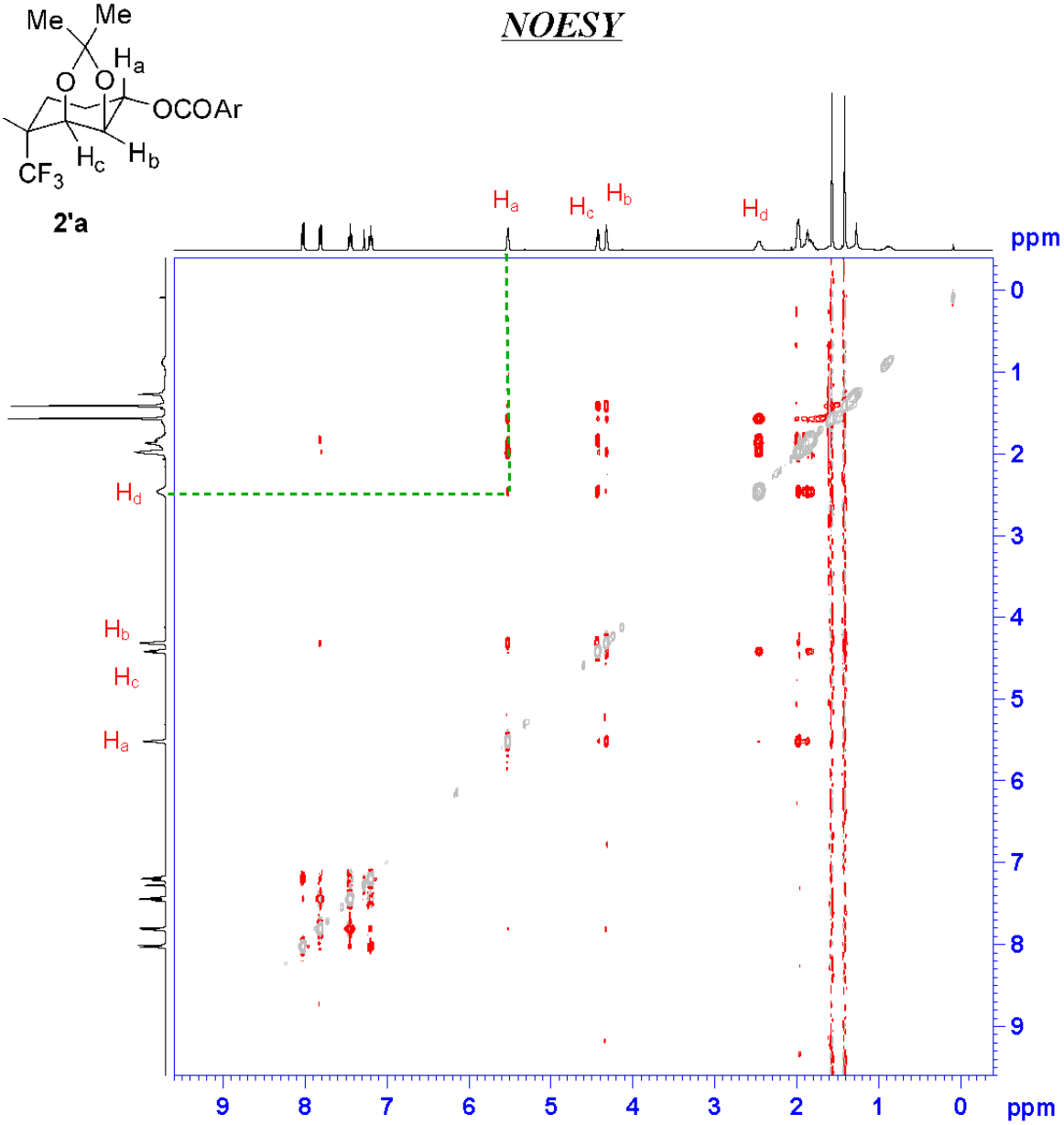
M06L / 6-31G**, LANL2DZ

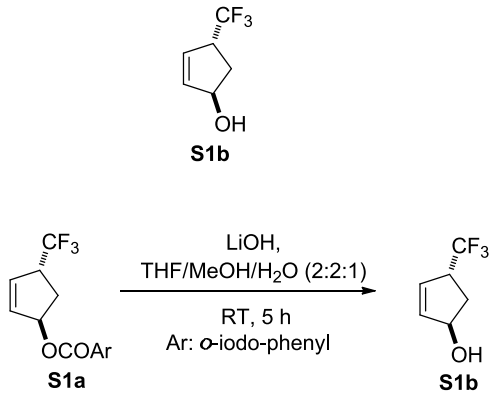


2'a



2'a

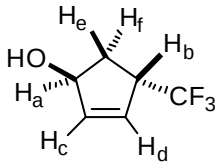




***trans*-4-(Trifluoromethyl)cyclopent-2-enol (S1b)**: by following the general procedure (1.0 mmol scale) with the variation (1.5 eq cyclopentadiene and 1.0 eq Togni's reagent were used).

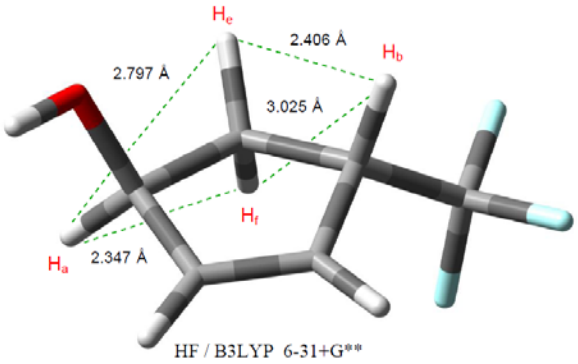
To facilitate the product separation, **S1a** was hydrolyzed to **S1b** according to a literature procedure. To a vial charged with ester (0.2 mmol) and a co-solvent of THF/MeOH/H_2O (2:2:1, 5 mL) was added lithium hydroxide (0.3 mmol). The reaction was stirred at room temperature until the ester was consumed which was indicated by TLC. Then the reaction mixture was concentrated under reduced pressure to remove the organic solvent and the aqueous phase was extracted by ether (2 mL × 4). The combined organic phase was dried over anhydrous sodium sulfate, concentrated and purified by a silica gel flash column (hexanes : EtOAc = 10 : 1 to 4 : 1) **S1b** was obtained as colorless oil (102 mg, 67% yield). (Note: the product is volatile and it should be handled carefully under the vacuum) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 – 6.05 (m, 1H), 5.91 – 5.81 (m, 1H), 5.01 (d, J = 3.4 Hz, 1H), 3.65 – 3.53 (m, 1H), 2.36 (ddd, J = 14.5, 7.2, 4.5 Hz, 1H), 1.95 (ddd, J = 14.4, 8.6, 3.5 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 139.1, 128.8 (q, J = 2.8 Hz), 127.1 (q, J = 277.8 Hz), 76.4, 49.0 (q, J = 28.7 Hz), 33.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.34 (d, J = 9.2 Hz); HRMS (ESI, m/z): calcd for $C_6H_6F_3O^-$ (M – H^+), 151.0376, found 151.0373; IR ν_{max} (neat)/cm^{-1}: 3321 (br, O-H), 3073 (w), 2916 (w, sharp).

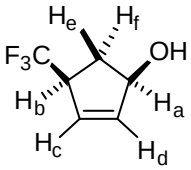
NOE results predicted based on computational studies:



S1b

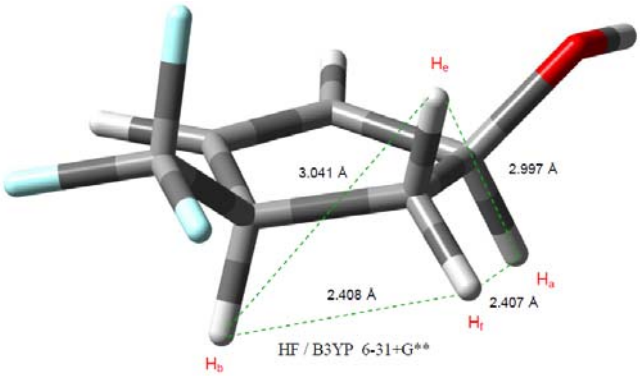
H_a–H_f: 2.347 Å, strong *NOE* predicted
H_a–H_e: 2.797 Å, weak *NOE* predicted
H_b–H_f: 3.025 Å weak *NOE* predicted
H_b–H_e: 2.406 Å strong *NOE* predicted

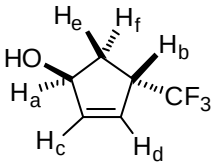




S1'b

H_a–H_f: 2.407 Å, strong *NOE* predicted
H_a–H_e: 2.997 Å, weak *NOE* predicted
H_b–H_f: 2.408 Å, strong *NOE* predicted
H_b–H_e: 3.041 Å, weak *NOE* predicted

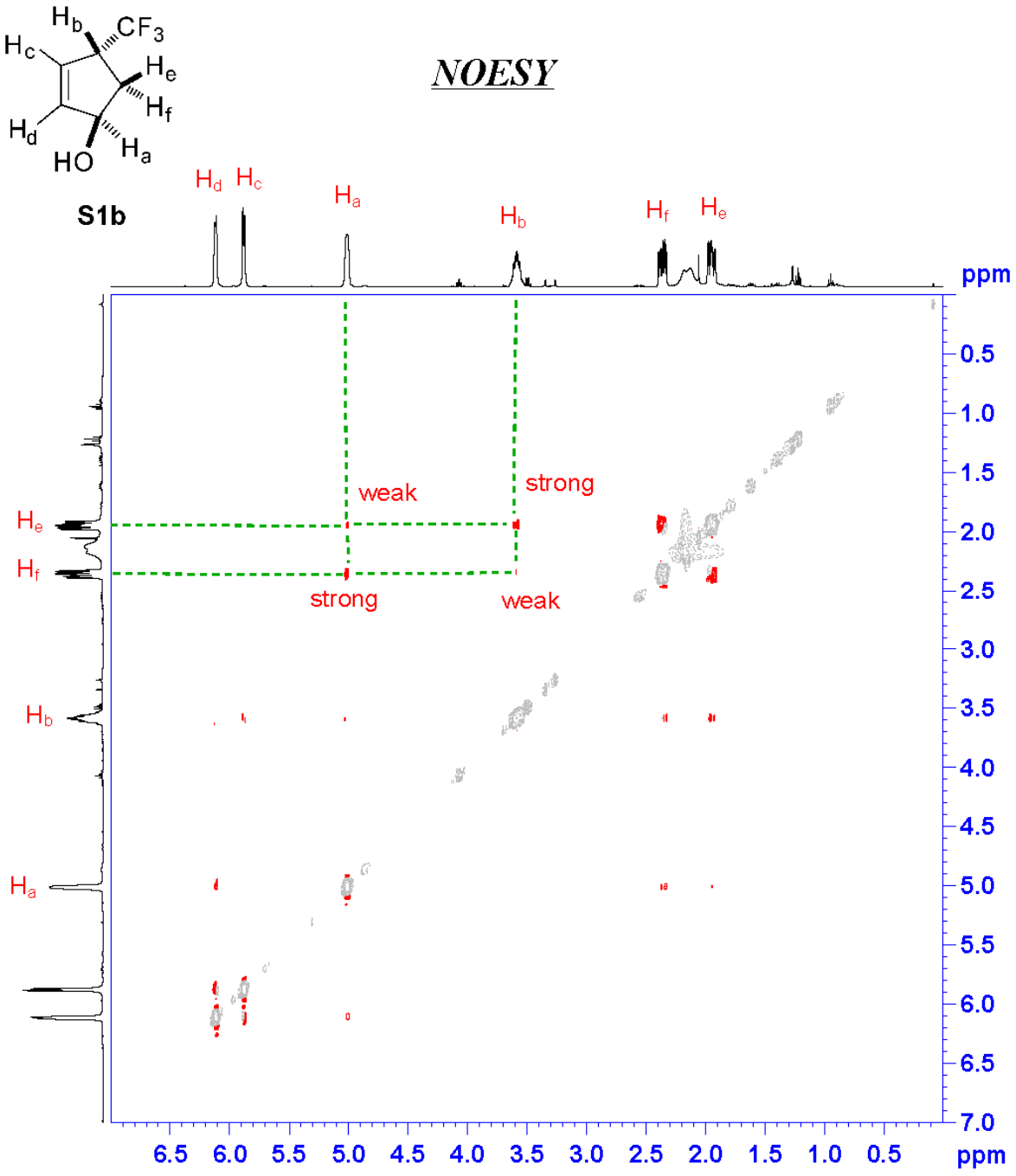


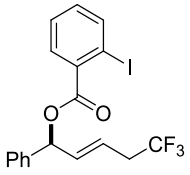


S1b

H_a–H_f: strong *NOE* observed;
H_a–H_e: weak *NOE* observed;
H_b–H_f: weak *NOE* observed;
H_b–H_e: strong *NOE* observed.

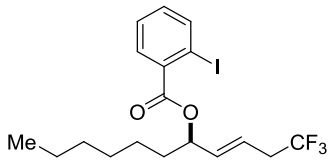
NOE results observed:





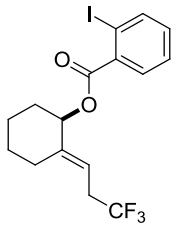
S2a

(*E*)-5,5,5-Trifluoro-1-phenylpent-2-en-1-yl 2-iodobenzoate (S2a): following the general procedure (1.0 mmol scale), the title compound was obtained from **S2** and isolated by a silica gel flash column (deactived by 1% Et_3N, hexanes : ether = 99 : 1 to 20 : 1) as colorless oil (321 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.31 (m, 6H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 6.1 Hz, 1H), 6.08 (dd, *J* = 15.5, 6.1 Hz, 1H), 5.89 – 5.78 (m, 1H), 2.98 – 2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 141.5, 138.1, 135.3, 134.9, 132.8, 131.0, 128.7, 128.6, 128.0, 127.3, 125.6 (q, *J* = 276.7 Hz), 121.6 (q, *J* = 3.6 Hz), 94.2, 76.6, 37.0 (q, *J* = 30.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.08 (t, *J* = 10.6 Hz); HRMS (ESI, m/z): calcd for $C_{18}H_{14}F_3INaO_2^+$ ($M + Na^+$), 468.9883, found 468.9905; IR ν_{max} (neat)/cm^{-1}: 3062 (w), 2926 (m), 1726 (s, C=O).



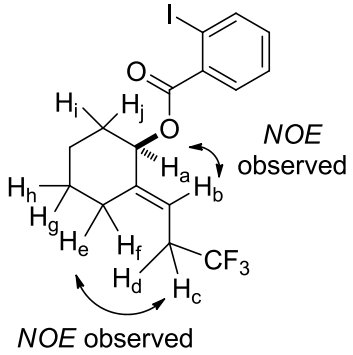
S3a

(*E*)-1,1,1-trifluoroundec-3-en-5-yl 2-iodobenzoate (S3a): by following the general procedure (1.0 mmol scale), **S3a** was obtained from **S3** and isolated by a silica gel flash column (hexanes : ether = 99 : 1 to 20 : 1) as colorless oil (308 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (td, *J* = 7.6, 1.4 Hz, 1H), 5.90 – 5.71 (m, 2H), 5.52 (q, *J* = 6.4 Hz, 1H), 2.97 – 2.77 (m, 2H), 1.92 – 1.79 (m, 1H), 1.79 – 1.68 (m, 1H), 1.46 – 1.23 (m, 8H), 0.90 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 141.3, 135.6, 135.5, 132.6, 130.8, 127.9, 125.7 (d, *J* = 276.5 Hz), 121.4 (q, *J* = 3.5 Hz), 93.9, 75.5, 37.1 (q, *J* = 30.0 Hz), 34.2, 31.7, 29.0, 25.0, 22.6, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.24 (t, *J* = 10.6 Hz); HRMS (ESI, m/z): calcd for $C_{18}H_{22}F_3INaO_2^+$ ($M + Na^+$), 477.0509, found 477.0520; IR ν_{max} (neat)/cm^{-1}: 3062 (*w*), 2926 (*m*, sharp), 1726 (s, C=O).

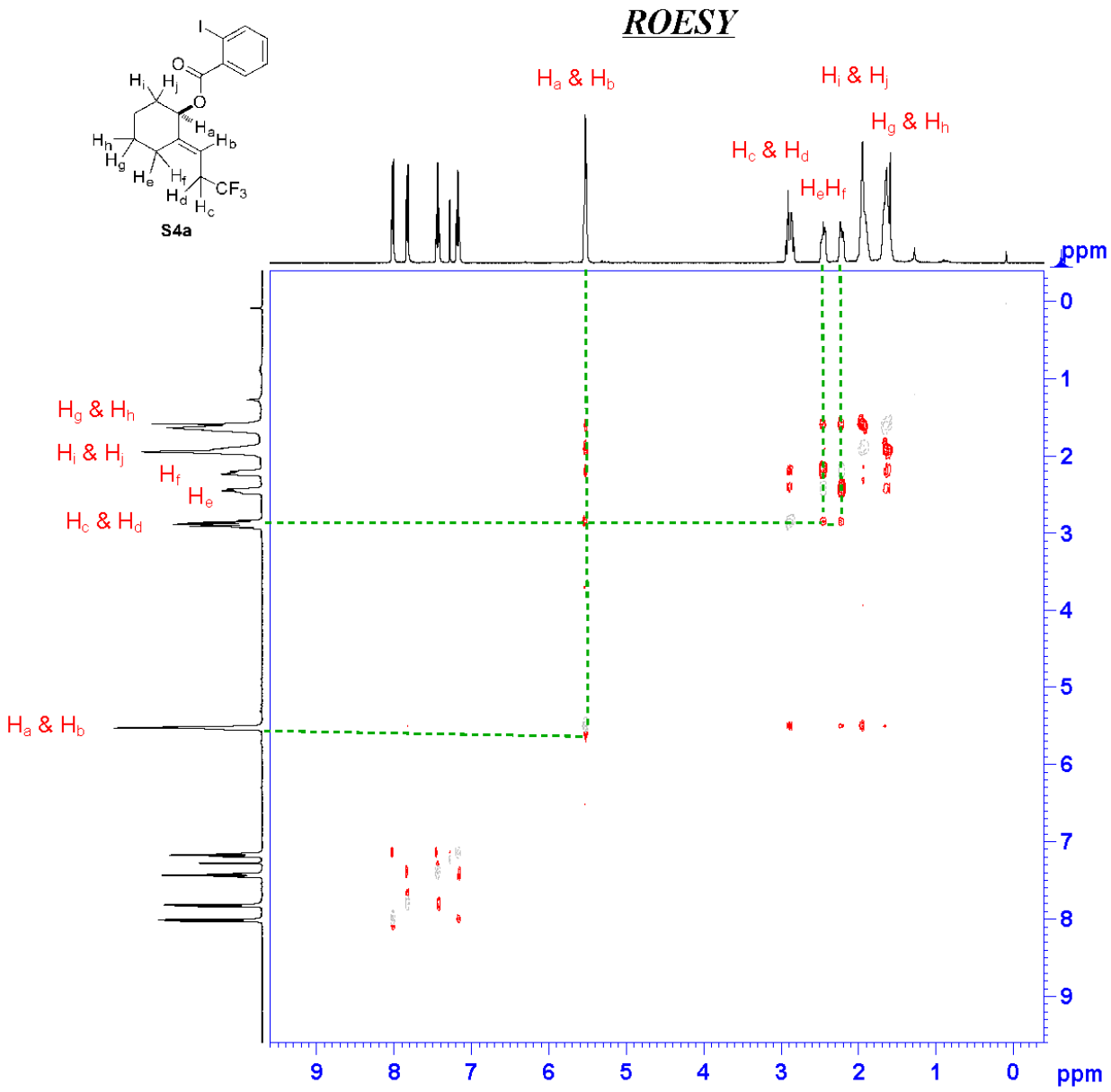


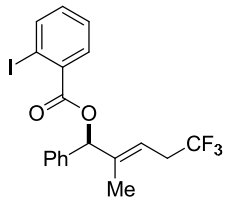
S4a

(*E*)-2-(3,3,3-trifluoropropylidene)cyclohexyl 2-iodobenzoate (S4a): by following the general procedure (1.0 mmol scale), S**4a** was obtained from **S4** and isolated by a silica gel flash column (hexanes : ether = 99 : 1 to 9 : 1) as colorless oil (309 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 10.8, 4.5 Hz, 1H), 5.58 – 5.44 (m, 2H), 2.99 – 2.78 (m, 2H), 2.53 – 2.37 (m, 1H), 2.23 (dd, *J* = 12.4, 6.1 Hz, 1H), 2.02 – 1.81 (m, 3H), 1.80 – 1.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 143.1, 141.3, 135.7, 132.5, 130.8, 127.9, 126.1 (q, *J* = 276.6 Hz), 111.6, 111.5, 93.8, 76.7, 33.1, 32.0 (q, *J* = 29.9 Hz), 26.7 (d, *J* = 2.9 Hz), 22.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.08 (t, *J* = 10.8 Hz); HRMS (ESI, m/z): calcd for $C_{16}H_{17}F_3IO_2^+$ (M + H^+), 425.0220, found 425.0231; IR ν_{max} (neat)/cm^{-1}: 2936 (*m*, sharp), 1724 (*s*, C=O).



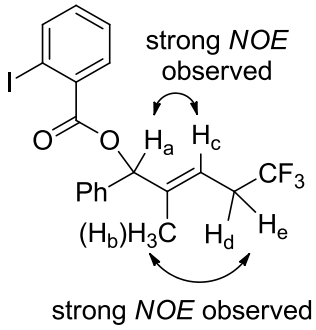
S4a



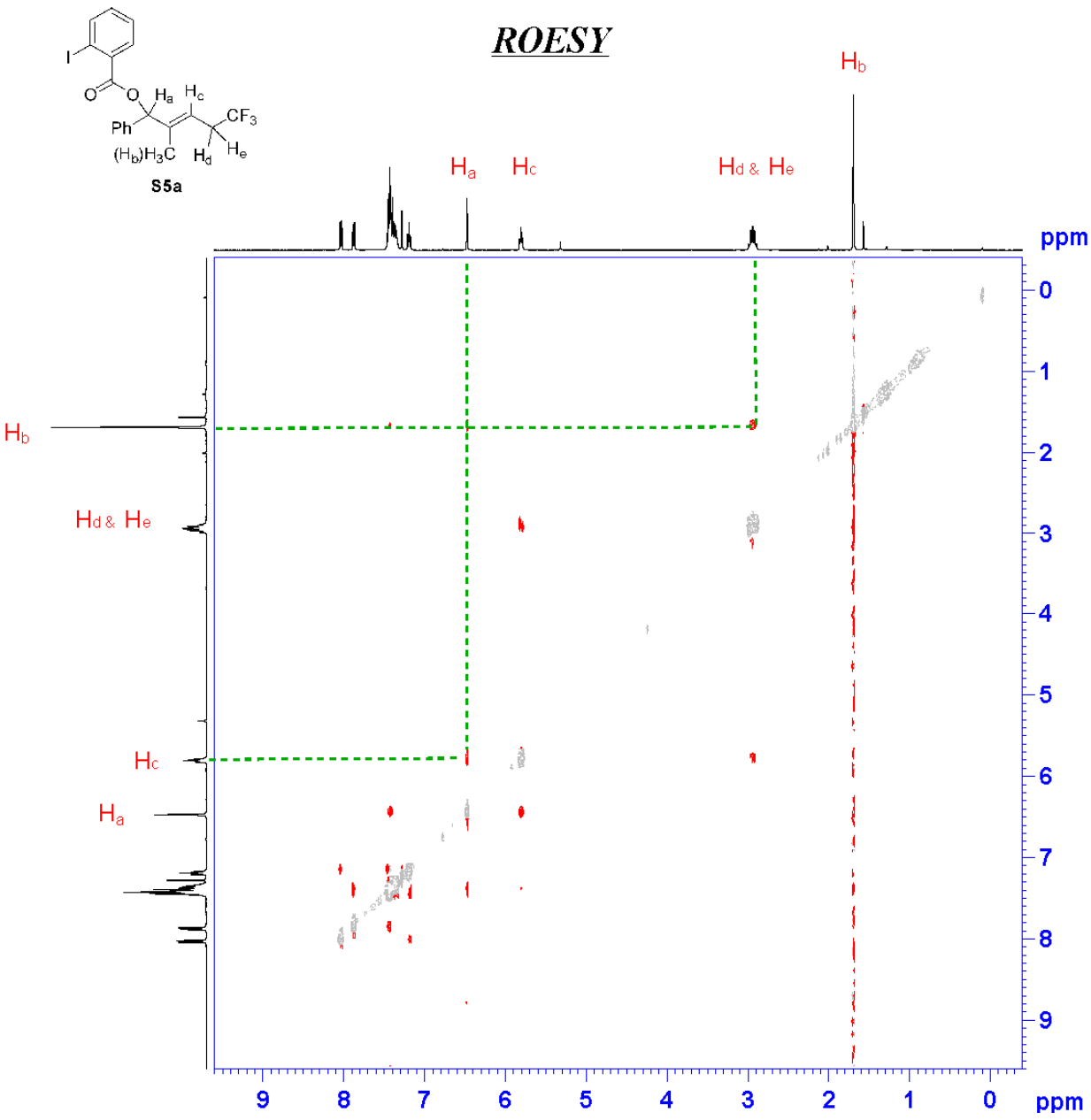


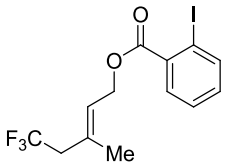
S5a

***(E)*-5,5,5-trifluoro-2-methyl-1-phenylpent-2-en-1-yl 2-iodobenzoate (S5a):** by following the general procedure (1.0 mmol scale), **S5a** was obtained from **S5** and isolated by a silica gel flash column (deactived by 1% Et_3N, hexanes : ether = 99 : 1 to 20 : 1) as colorless oil (340 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.86 (t, *J* = 11.1 Hz, 1H), 7.51 – 7.31 (m, 6H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.47 (s, 1H), 5.81 (t, *J* = 7.3 Hz, 1H), 3.06 – 2.85 (m, 2H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 141.6, 139.8, 137.6, 134.8, 132.8, 131.0, 128.6, 128.3, 128.0, 127.1, 126.2 (q, *J* = 276.9 Hz), 115.6 (q, *J* = 3.4 Hz), 94.2, 80.4, 32.8 (q, *J* = 29.8 Hz), 13.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -65.83 (t, *J* = 10.8 Hz); HRMS (ESI, m/z): calcd for $C_{19}H_{16}F_3INaO_2^+$ ($M + Na^+$), 483.0039, found 483.0056; IR ν_{max} (neat)/cm^{-1}: 3067 (w), 2927 (s, sharp), 1729 (s, C=O).



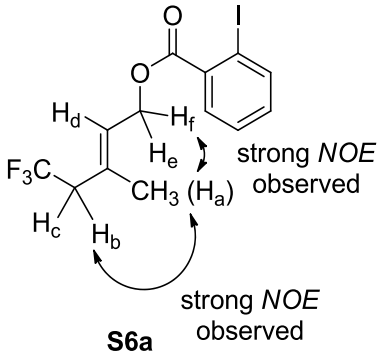
S5a



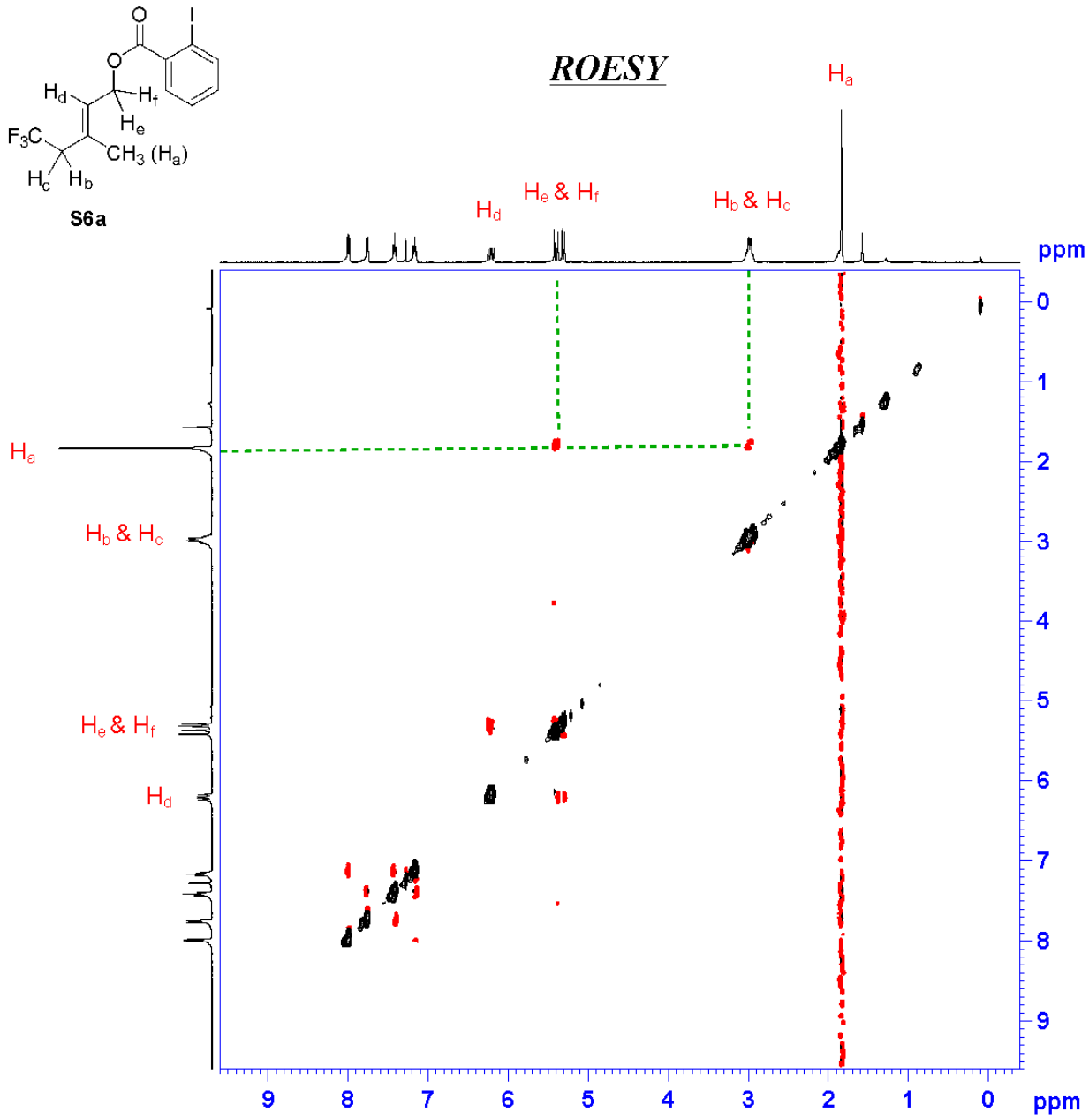


S6a

(*E*)-5,5,5-trifluoro-3-methylpent-2-en-1-yl 2-iodobenzoate (S6a): by following the general procedure (1.0 mmol scale), **S6a** was obtained from **S6** and isolated by a silica gel flash column (deactived by 1% Et_3N, hexanes : ether = 99 : 1 to 9 : 1) as colorless oil (257 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (q, *J* = 7.4 Hz, 1H), 6.21 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.40 (d, *J* = 17.4 Hz, 1H), 5.31 (d, *J* = 11.0 Hz, 1H), 3.08 – 2.88 (m, 2H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 141.2, 139.8, 135.7, 132.6, 130.8, 128.0, 125.4 (q, *J* = 278.2 Hz), 115.0, 93.8, 80.1, 41.9 (q, *J* = 27.4 Hz), 24.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.19 (t, *J* = 10.7 Hz); HRMS (ESI, m/z): calcd for $C_{13}H_{13}F_3IO_2^+$ (M + H^+), 384.9907, found 384.9913; IR ν_{max} (neat)/cm^{-1}: 2977 (m), 2856 (w), 1726 (s, C=O).



S6a


ROESY
S6a
Ha
Hd
He & Hf
Hb & Hc
ppm
0
1
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1
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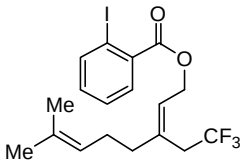
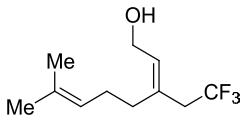


S7a

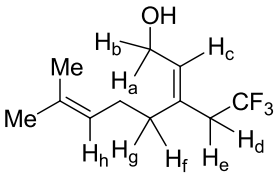
(*Z*)-7-methyl-3-(2,2,2-trifluoroethyl)octa-2,6-dien-1-yl 2-iodobenzoate (S7a): by following the general procedure C (1.0 mmol scale), **S7a** was obtained through the reaction of myrcene **S7** (2.0 equiv) and Togni's reagent (1.0 equiv), and isolated by a silica gel flash column (hexanes : ether = 99 : 1 to 20 : 1) as colorless oil (262 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 5.96 (dd, *J* = 17.3, 11.1 Hz, 1H), 5.42 (d, *J* = 17.3 Hz, 1H), 5.37 (d, *J* = 11.1 Hz, 1H), 5.11 (t, *J* = 6.6 Hz, 1H), 3.37 – 3.19 (m, 1H), 2.99 – 2.82 (m, 1H), 2.51 – 2.38 (m, 1H), 2.12 – 1.97 (m, 2H), 1.93 – 1.81 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 141.4, 138.4, 135.4, 132.6, 130.9, 128.0, 125.4 (q, *J* = 278.1 Hz), 122.8, 115.4, 94.0, 82.4, 39.6 (q, *J* = 27.1 Hz), 37.0, 25.7, 21.7, 17.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.99 (t, *J* = 10.7 Hz); HRMS (ESI, m/z): calcd for $C_{18}H_{21}F_3IO_2^+$ (M + H^+), 453.0533, found 453.0529; IR ν_{max} (neat)/cm^{-1}: 2916 (m, sharp), 1729 (s, C=O). IR ν_{max} (neat)/cm^{-1}: 2916 (m, sharp), 1729 (s, C=O).



S7b

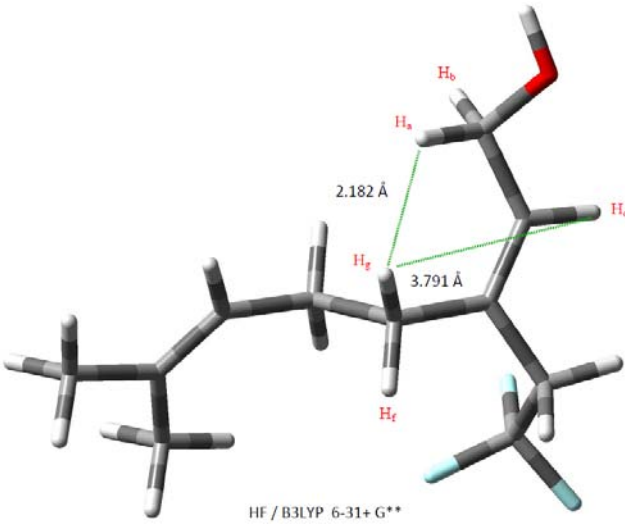
(*E*)-7-methyl-3-(2,2,2-trifluoroethyl)octa-2,6-dien-1-ol (S7b): the configuration of **S7b** was determined by ROESY experiment after hydrolysis by following the typical hydrolysis procedure (at 50 ^{o}C for 5 hours in this case); **S7b** was isolated by silica gel flash column (hexanes : ethyl acetate = 50:1 to 9:1) as colorless oil in 50% yield (note: product is volatile); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.36 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 5.13 (t, *J* = 6.8 Hz, 1H), 2.53 – 2.31 (m, 2H), 2.16 – 1.95 (m, 2H), 1.78 – 1.67 (m, 4H), 1.67 – 1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 132.7, 125.9 (q, *J* = 278.2 Hz), 123.6, 113.8, 73.1, 44.5 (q, *J* = 25.6 Hz), 40.6, 25.7, 22.0, 17.7; ^{19}F NMR (377 MHz, $CDCl_3$)

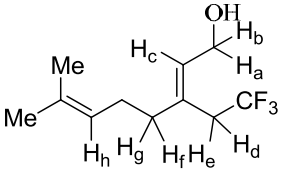
δ -59.82 (t, *J* = 11.1 Hz); HRMS (ESI, m/z): calcd for $C_{11}H_{16}F_3O^-$ (M - H^+), 221.1159, found 221.1152; IR ν_{max} (neat)/cm^{-1}: 3473 (br), 2926 (s), 1259 (s).



S7b

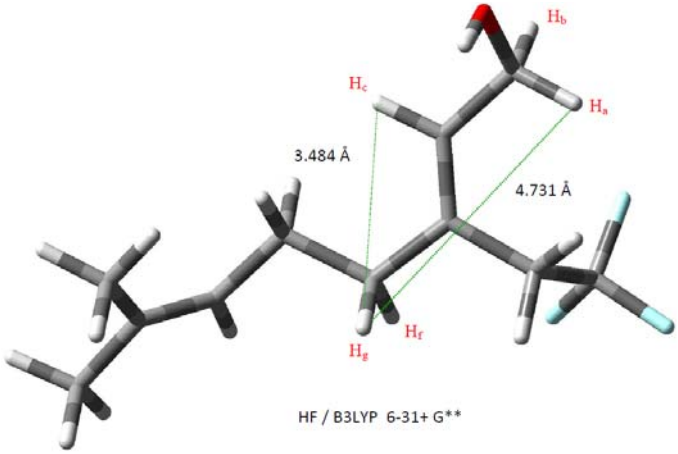
H_a–$H_{g/h}$: 2.182 Å, strong *NOE* predicted;
H_c–$H_{g/h}$: 3.791Å , weak *NOE* predicted.

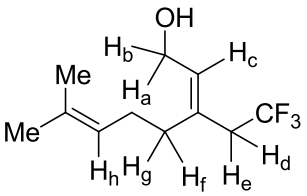




S7'b

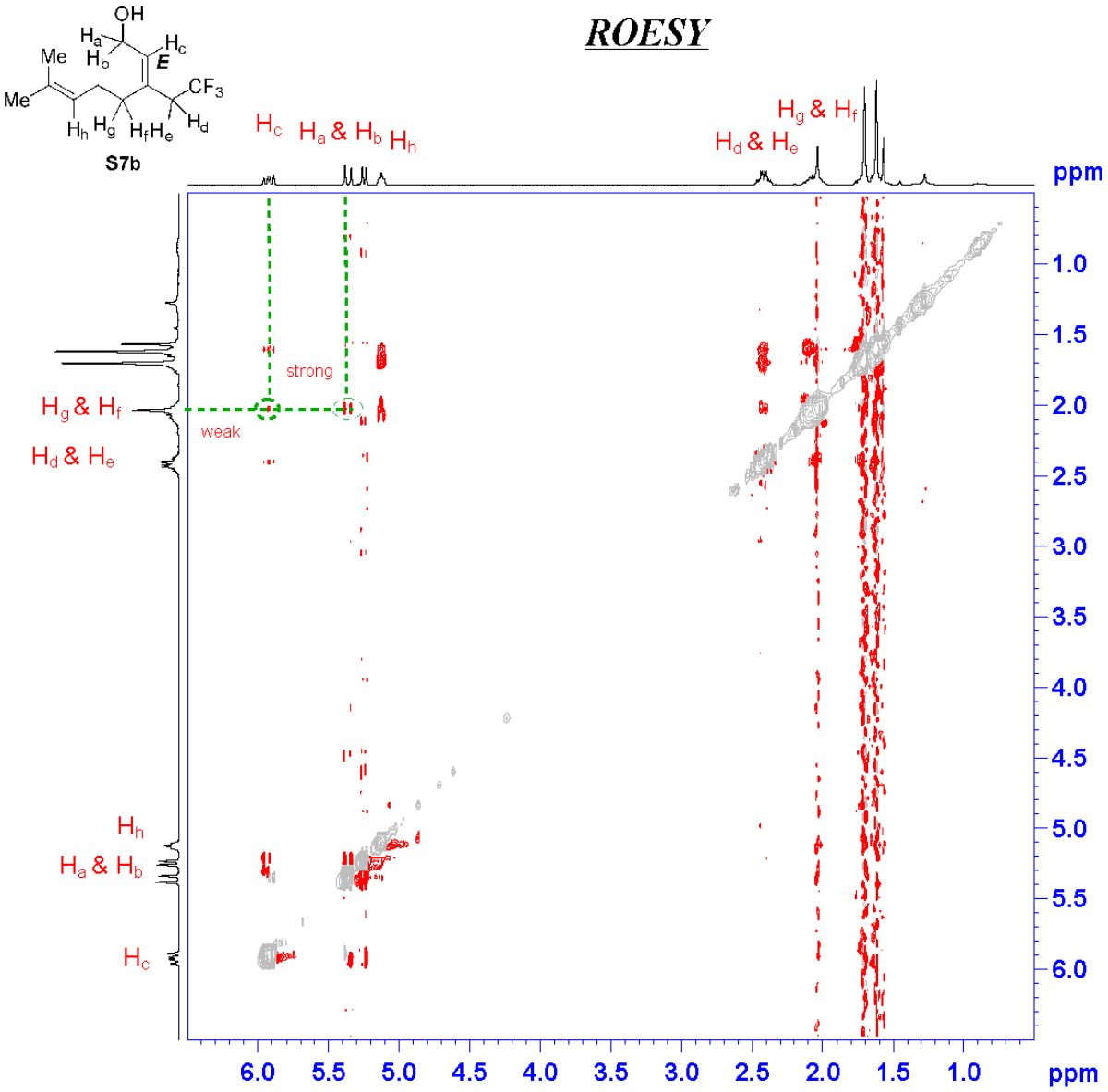
H_a–$H_{g/h}$: 4.731Å, very weak *NOE* predicted;
H_c–$H_{g/h}$: 3.481Å, medium *NOE* predicted.

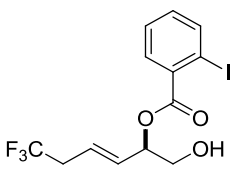




S7b

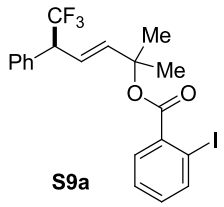
H_a–$H_{g/h}$: strong *NOE* observed;
H_c–$H_{g/h}$: weak *NOE* observed.





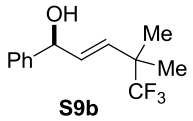
S8a

(*E*)-6,6,6-trifluoro-1-hydroxyhex-3-en-2-yl 2-iodobenzoate (S8a): by following the general procedure C (1.0 mmol scale), **S8a** was obtained from **S8** and isolated by a silica gel flash column (deactived by 1% Et_3N, hexanes : ether = 9 : 1 to 3 : 1) as colorless oil (272 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 5.98 – 5.78 (m, 2H), 5.67 – 5.59 (m, 1H), 3.98 – 3.78 (m, 2H), 2.90 (qd, *J* = 10.6, 4.1 Hz, 2H), 2.03 (br, *J* = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 141.3, 135.4, 132.8, 131.8, 131.1, 128.0, 125.5 (q, *J* = 276.5 Hz), 123.4 (q, *J* = 3.5 Hz), 93.7, 76.1, 64.3, 37.1 (q, *J* = 30.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.21 (t, *J* = 10.6 Hz); HRMS (ESI, m/z): calcd for $C_{13}H_{13}F_3IO_3^+$ (M + H^+), 400.9856, found 400.9856; IR ν_{max} (neat)/cm^{-1}: 3431 (br, O-H), 3058 (w), 2936 (m, sharp), 1721 (s, C=O).



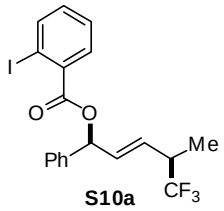
S9a

(*E*)-6,6,6-trifluoro-2-methyl-5-phenylhex-3-en-2-yl 2-iodobenzoate (S9a): by following the general procedure C (1.0 mmol scale), a mixture of two region- isomers were obtained from **S9** and purified by a silica gel flash column (deactived by 1% Et_3N, hexanes : ether = 99 : 1 to 20 : 1) as colorless oil (2:1, 318 mg, 67% overall yield). The mixture was subjected to hydrolysis with LiOH according to the previously mentioned procedure and **S9a** was recovered by a silica gel flash column (hexanes : EtOAc = 99 : 1 to 9 : 1) as colorless oil (166 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.11 – 3.96 (m, 1H), 1.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 139.9, 139.3, 136.0, 133.4, 131.1, 129.4, 128.2, 127.8, 127.2, 126.9, 125.0 (q, *J* = 280.0 Hz), 121.7, 92.4, 80.9, 51.7 (q, *J* = 27.8 Hz), 25.8, 25.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -68.98 (d, *J* = 9.4 Hz); HRMS (ESI, m/z): calcd for $C_{20}H_{18}F_3INaO_2^+$ (M + Na^+), 497.0196, found 497.0188; IR ν_{max} (neat)/cm^{-1}: 2972 (m, sharp), 2865 (m), 1722 (s, C=O).



S9b

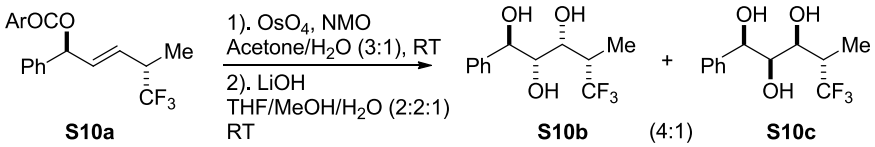
(*E*)-5,5,5-trifluoro-4,4-dimethyl-1-phenylpent-2-en-1-ol (S9b): by following the general procedure C (1.0 mmol scale), two region- isomers (2:1, 318 mg, 67% overall yield) were obtained from **S9** which showed on the TLC plate as one spot. The mixture was subjected to hydrolysis with LiOH according to the previously mentioned procedure. **S9b** was isolated by silica gel flash column (hexanes : EtOAc = 9 : 1 to 5 : 1) as colorless oil (49 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 5H), 5.94 (d, *J* = 15.8 Hz, 1H), 5.87 (dd, *J* = 15.8, 5.5 Hz, 1H), 5.26 (s, 1H), 1.99 (s, 1H), 1.28 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 133.8, 131.2, 131.2, 128.7, 128.3 (q, *J* = 282.4 Hz), 127.9, 126.3, 74.6, 42.3 (q, *J* = 25.4 Hz), 21.1 (q, *J* = 2.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -77.86 (s); HRMS (ESI, m/z): calcd for $C_{13}H_{15}F_3NaO^+$ (M + Na^+), 267.0967, found 267.0973; IR ν_{max} (neat)/cm^{-1}: 3354 (br, O-H), 2980 (s, sharp).



S10a

(*E*)-5,5,5-trifluoro-4-methyl-1-phenylpent-2-en-1-yl 2-iodobenzoate (S10a): by following the general procedure C (1.0 mmol scale), **S10a** was obtained from **S10** and purified by a silica gel flash column (deactived by 1% Et_3N, hexanes : ether = 99 : 1 to 9 : 1) as colorless oil (267 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.30 (m, 6H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 6.1 Hz, 1H), 6.04 (dd, *J* = 15.6, 6.2 Hz, 1H), 5.85 (dd, *J* = 15.6, 7.7 Hz, 1H), 3.03 – 2.88 (m, 1H), 1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 141.4, 138.2, 132.8, 132.6, 131.0, 128.7, 128.5 (q, *J* = 3.6 Hz), 128.0, 127.4, 127.3, 126.1 (q, *J* = 279.7), 100.0, 94.1, 76.8, 41.2 (q, *J* = 27.9 Hz), 13.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.51 (d, *J* = 8.6 Hz); HRMS (ESI, m/z): calcd for $C_{19}H_{16}F_3INaO_2^+$ (M + Na^+), 483.0039, found 483.0056; IR ν_{max} (neat)/cm^{-1}: 3062 (w), 2936 (m, sharp), 1727 (s, C=O).

Derivatization of compound **S10a** for relative stereochemistry determination



Following the similar procedure in the deravatization of compound **2** and **2′**, compound **S10a** (a single diastereomer, 230 mg, 0.5 mmol) was subjected to the *cis*-dihydroxylation condition and then hydrolyzed to afford an inseparable mixture of two diastereomers (85 mg, 65% overall yield after two steps, *dr* = 4:1 based on ^{1}H NMR). A single crystal (**S10b**) was obtained from recrystallization of the major diastereomer by slow diffusion of hexanes vapor to ethyl acetate solvent.

S10b: ^{1}H NMR (400 MHz, MeOD) δ 7.44 (m, 2H), 7.36 (m, 2H), 7.28 (m, 1H), 4.73 (d, *J* = 8.2 Hz, 1H), 4.11 (d, *J* = 9.0 Hz, 1H), 3.65 (d, *J* = 8.1 Hz, 1H), 2.64 – 2.46 (m, 1H), 1.11 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, MeOD) δ 142.9, 128.5 (q, *J* = 279.7 Hz), 127.7, 127.1, 126.9, 73.6, 73.3, 68.8, 41.1 (q, *J* = 24.0 Hz), 9.2 (q, *J* = 3.5 Hz); ^{19}F NMR (377 MHz, MeOD) δ -69.82 (d, *J* = 9.1 Hz);

S10c: ^{1}H NMR (400 MHz, MeOD) δ 7.44 (m, 2H), 7.36 (m, 2H), 7.28 (m, 1H), 4.68 (d, *J* = 7.8 Hz, 1H), 4.21 (dd, *J* = 4.3, 2.0 Hz, 1H), 3.65 (m, 1H), 2.65 – 2.48 (m, 1H), 1.23 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, MeOD) δ 142.7, 128.1 (q, *J* = 279.6 Hz), 127.7, 127.1, 126.9, 75.8, 74.3, 66.9, 41.2 (q, *J* = 24.3 Hz), 7.6 (q, *J* = 3.1 Hz); ^{19}F NMR (377 MHz, MeOD) δ -71.77 (d, *J* = 9.7 Hz).

HRMS (ESI, m/z): calcd for $C_{12}H_{14}F_3O_3^-$ (M – H^+), 263.0901, found 263.0895; IR ν_{max} (neat)/cm^{-1}: 3326 (s, broad), 2921 (m, sharp), 1456 (m, sharp), 1251 (s), 1170 (s).

X-ray crystallographic analysis of **S10b**

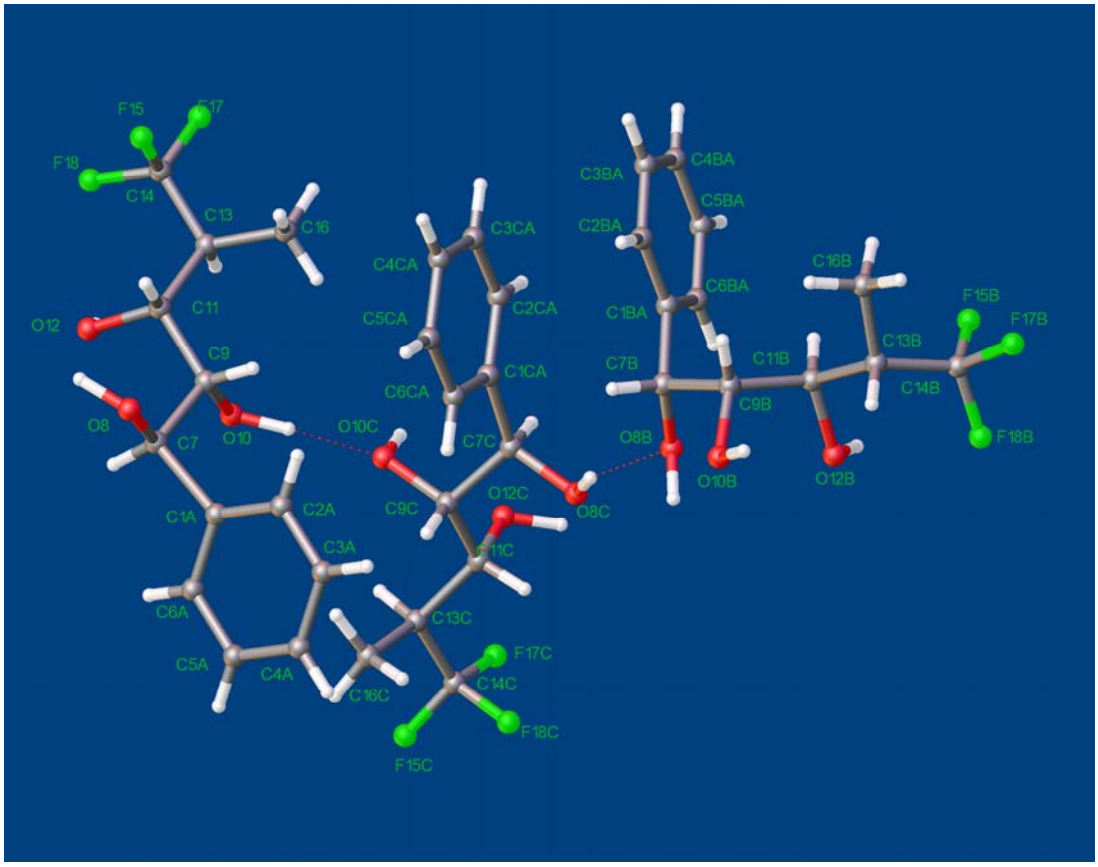


Table 1. Crystal data and structure refinement for twin4.

Identification code	twin4	
Empirical formula	C12 H15 F3 O3	
Formula weight	264.24	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.4133(3) Å	α= 111.700(2)°.
	b = 12.3601(4) Å	β= 102.333(2)°.
	c = 16.6001(6) Å	γ = 93.499(2)°.
Volume	1916.15(11) $Å^3$	
Z	6	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	1.094 mm^{-1}	
F(000)	828	

Crystal size	0.584 x 0.341 x 0.232 mm^3
Theta range for data collection	2.963 to 69.439°.
Index ranges	-12<=h<=12, -14<=k<=14, -19<=l<=20
Reflections collected	17421
Independent reflections	6701 [R(int) = 0.0164]
Completeness to theta = 67.679°	94.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.6562
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6701 / 133 / 508
Goodness-of-fit on F^2	2.099
Final R indices [I>2sigma(I)]	R1 = 0.1206, wR2 = 0.4204
R indices (all data)	R1 = 0.1287, wR2 = 0.4381
Extinction coefficient	n/a
Largest diff. peak and hole	1.337 and -0.887 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for twin4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

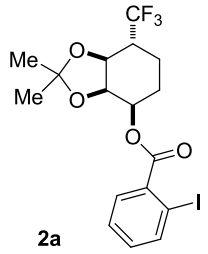
	x	y	z	U(eq)
O(12C)	1269(2)	4603(3)	390(2)	47(1)
O(10C)	-931(2)	4807(3)	1105(2)	47(1)
O(8C)	2283(2)	4988(3)	2570(2)	50(1)
O(10)	-3578(3)	4755(3)	839(2)	60(1)
O(12)	-6166(2)	5350(3)	824(2)	62(1)
O(8B)	3671(3)	5869(2)	4359(2)	49(1)
O(8)	-5436(3)	4141(3)	2282(2)	61(1)
F(17B)	8986(3)	8575(3)	7754(3)	101(1)
O(10B)	4358(3)	5725(2)	6057(2)	58(1)
F(18B)	8723(4)	7218(6)	6463(5)	198(4)
O(12B)	6357(3)	6394(3)	5431(3)	82(1)
F(15B)	8287(4)	8878(7)	6582(4)	147(2)
C(9C)	204(3)	4387(3)	1470(2)	39(1)
F(18C)	1802(6)	1665(5)	-260(4)	161(2)
C(7C)	1117(3)	5416(4)	2260(2)	49(1)
C(11C)	914(3)	3782(3)	751(2)	39(1)
C(11)	-5059(3)	5904(4)	1574(3)	47(1)
F(15)	-5769(7)	8229(5)	2378(4)	144(2)
C(9)	-4134(3)	5014(4)	1606(2)	49(1)
C(7B)	3354(3)	6671(3)	5134(2)	42(1)
F(15C)	161(6)	1125(4)	-1339(4)	141(2)
C(9B)	4407(4)	6845(3)	5988(2)	44(1)
F(18)	-6442(6)	7548(5)	979(5)	152(2)
C(1BB)	3013(12)	7779(7)	4956(8)	39(1)
C(2BB)	2268(11)	8463(9)	5494(7)	52(2)
C(3BB)	1903(10)	9477(8)	5392(6)	71(2)
C(4BB)	2282(11)	9808(7)	4752(7)	76(2)
C(5BB)	3027(10)	9124(8)	4214(6)	73(2)
C(6BB)	3393(10)	8110(8)	4316(7)	52(2)
C(1CB)	385(5)	5749(5)	3027(3)	48(2)
C(2CB)	-136(7)	6797(6)	3207(4)	77(3)

C(3CB)	-796(8)	7174(7)	3883(5)	103(3)
C(4CB)	-936(8)	6502(8)	4379(4)	105(4)
C(5CB)	-415(7)	5454(7)	4200(4)	92(3)
C(6CB)	246(6)	5077(5)	3524(4)	62(2)
C(13B)	6776(4)	7748(3)	6931(3)	58(1)
F(17C)	1505(7)	2696(5)	-965(4)	165(2)
C(11B)	5797(4)	7323(4)	6005(3)	54(1)
C(7)	-4856(3)	3883(4)	1548(3)	50(1)
C(1B)	-3923(4)	2971(3)	1536(5)	49(1)
C(2B)	-2853(4)	3233(3)	2276(5)	47(1)
C(3B)	-2095(4)	2368(4)	2343(5)	58(2)
C(4B)	-2408(5)	1241(4)	1671(6)	82(3)
C(5B)	-3478(6)	979(3)	932(6)	103(3)
C(6B)	-4236(5)	1844(4)	864(5)	76(2)
F(17)	-4769(7)	8918(4)	1626(4)	143(2)
C(13C)	30(4)	2704(4)	-30(3)	64(1)
C(14B)	8166(5)	8087(6)	6941(5)	93(2)
C(13)	-4394(5)	7046(5)	1578(4)	69(1)
C(16B)	6353(6)	8752(5)	7609(4)	86(2)
C(14)	-5313(9)	7923(6)	1647(5)	98(2)
C(14C)	851(8)	2057(7)	-652(6)	114(2)
C(16C)	-747(7)	1923(5)	225(5)	92(2)
C(1CA)	529(6)	6264(5)	2970(4)	48(2)
C(2CA)	525(7)	7460(5)	3171(4)	65(2)
C(3CA)	-56(8)	8117(6)	3838(5)	92(3)
C(4CA)	-633(8)	7579(8)	4303(5)	103(3)
C(5CA)	-629(8)	6383(8)	4102(5)	91(3)
C(6CA)	-48(6)	5726(6)	3436(4)	63(2)
C(1BA)	3262(9)	7864(5)	5102(6)	39(1)
C(2BA)	2654(8)	8662(7)	5681(6)	52(2)
C(3BA)	2585(8)	9774(6)	5666(5)	71(2)
C(4BA)	3124(9)	10088(5)	5072(5)	76(2)
C(5BA)	3732(8)	9291(7)	4493(5)	73(2)
C(6BA)	3801(8)	8179(6)	4508(5)	52(2)
C(16)	-3127(8)	7540(7)	2309(5)	110(3)
C(1A)	-3700(20)	3080(20)	1900(20)	49(1)

C(2A)	-2680(20)	3412(19)	2670(20)	47(1)
C(3A)	-1860(20)	2610(20)	2790(30)	58(2)
C(4A)	-2060(30)	1470(20)	2140(30)	82(3)
C(5A)	-3090(40)	1140(20)	1360(30)	103(3)
C(6A)	-3900(30)	1950(20)	1240(30)	76(2)

D. Optimized Geometric Details of Conformations by Computational Studies

Optimized coordinates of the compounds **2a**, **2'a**, **S1b**, **S1'b**, **S7b** and **S7'b** are given below.

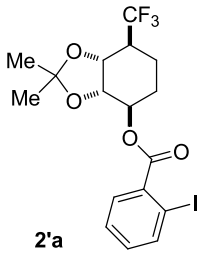


2a

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.297328	0.810202	-0.563975
2	6	0	-3.649860	0.077365	-0.640397
3	6	0	-3.780699	-1.108357	0.331340
4	6	0	-2.890612	-0.917752	1.558499
5	6	0	-1.401878	-0.745849	1.233545
6	6	0	-1.154651	-0.062329	-0.111612
7	8	0	-2.543733	1.830926	0.390115
8	8	0	-4.584881	1.074032	-0.245925
9	6	0	-3.878561	2.253716	0.165829
10	6	0	-3.951213	3.295678	-0.938361
11	6	0	-4.452216	2.743846	1.473477
12	6	0	-3.592831	-2.450672	-0.334206
13	9	0	-3.806546	-3.455135	0.537245
14	9	0	-4.454710	-2.617775	-1.360443
15	9	0	-2.350842	-2.628970	-0.841500
16	8	0	0.009581	0.787649	-0.057218
17	6	0	1.196529	0.142595	-0.182960
18	6	0	2.328494	1.106357	-0.166776
19	8	0	1.283153	-1.059772	-0.307576
20	6	0	2.043521	2.480529	-0.254995
21	6	0	3.048305	3.433288	-0.289839
22	6	0	4.377726	3.028227	-0.233397
23	6	0	4.688408	1.677264	-0.131907
24	6	0	3.676796	0.717968	-0.096595
25	53	0	4.361663	-1.297849	0.131647
26	1	0	-2.048235	1.253356	-1.541578
27	1	0	-3.874758	-0.242722	-1.665991
28	1	0	-4.828463	-1.110539	0.649771
29	1	0	-3.035906	-1.744589	2.259043
30	1	0	-3.251392	-0.013298	2.058184
31	1	0	-0.878643	-1.705619	1.229692
32	1	0	-0.937607	-0.134486	2.012710
33	1	0	-0.972812	-0.815106	-0.883789
34	1	0	-4.992445	3.555439	-1.143082

35	1	0	-3.513637	2.914898	-1.864572
36	1	0	-3.414327	4.202248	-0.647181
37	1	0	-5.499516	3.025545	1.344498
38	1	0	-3.897588	3.615583	1.828196
39	1	0	-4.390771	1.956426	2.227622
40	1	0	1.003328	2.781626	-0.298017
41	1	0	2.794593	4.486485	-0.361039
42	1	0	5.180956	3.759277	-0.263165
43	1	0	5.725421	1.363268	-0.077483

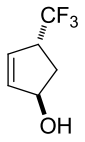


2'a

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.292492	0.753128	0.417335
2	6	0	-3.654369	0.328181	-0.123176
3	6	0	-3.886484	-1.162751	-0.342517
4	6	0	-2.656016	-1.870325	-0.911946
5	6	0	-1.385094	-1.551060	-0.134217
6	6	0	-1.148677	-0.054734	-0.179894
7	8	0	-2.222674	2.111510	0.011075
8	8	0	-3.662230	0.993268	-1.379028
9	6	0	-3.067981	2.271904	-1.145425
10	6	0	-2.247406	2.642016	-2.360135
11	6	0	-4.126392	3.305243	-0.810621
12	6	0	-4.373338	-1.790338	0.947063
13	9	0	-4.450349	-3.129712	0.856406
14	9	0	-5.599507	-1.338871	1.280761
15	9	0	-3.558118	-1.508144	1.994583
16	8	0	0.028526	0.321549	0.560055
17	6	0	1.201016	0.220223	-0.111855
18	6	0	2.313579	0.785417	0.696892
19	8	0	1.295216	-0.244981	-1.227250
20	6	0	2.009568	1.788138	1.632421
21	6	0	2.998094	2.408105	2.380516
22	6	0	4.323782	2.020194	2.217900
23	6	0	4.650302	1.020699	1.308179
24	6	0	3.657197	0.411360	0.543483
25	53	0	4.332569	-1.136016	-0.771730
26	1	0	-2.238524	0.719558	1.510625
27	1	0	-4.444348	0.735875	0.529982

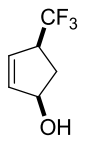
28	1	0	-4.723392	-1.263004	-1.042807
29	1	0	-2.534354	-1.537328	-1.948904
30	1	0	-2.835573	-2.947569	-0.947455
31	1	0	-0.525419	-2.056645	-0.582455
32	1	0	-1.459086	-1.888885	0.905268
33	1	0	-1.002953	0.245291	-1.223944
34	1	0	-2.888841	2.726429	-3.241003
35	1	0	-1.484609	1.885516	-2.555835
36	1	0	-1.751654	3.601869	-2.199080
37	1	0	-4.777727	3.481290	-1.670547
38	1	0	-3.654302	4.249925	-0.529545
39	1	0	-4.737649	2.970619	0.031012
40	1	0	0.970788	2.080755	1.742422
41	1	0	2.734315	3.189254	3.086872
42	1	0	5.112670	2.491193	2.797600
43	1	0	5.683819	0.712086	1.190886



S1b

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.511737	1.353183	-0.238603
2	6	0	0.128177	0.005791	-0.504333
3	6	0	-0.813313	-0.992424	0.220931
4	6	0	-2.129732	-0.226118	0.459320
5	6	0	-1.728524	1.224068	0.296899
6	8	0	-3.072149	-0.642121	-0.548326
7	6	0	1.570653	-0.080468	-0.038278
8	9	0	2.098275	-1.309910	-0.273032
9	9	0	2.358309	0.817245	-0.688842
10	9	0	1.715101	0.162346	1.288886
11	1	0	-0.028368	2.288577	-0.501274
12	1	0	0.168184	-0.187360	-1.584643
13	1	0	-0.378565	-1.283184	1.181136
14	1	0	-0.996019	-1.898945	-0.359047
15	1	0	-2.552213	-0.440833	1.450455
16	1	0	-2.392471	2.048550	0.541827
17	1	0	-3.881659	-0.121161	-0.460574



S1'b

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.438065	1.460837	-0.096207
2	6	0	-0.251370	0.227057	-0.645956
3	6	0	0.829786	-0.877331	-0.515877
4	6	0	2.171146	-0.126836	-0.375608
5	6	0	1.751568	1.265691	0.042553
6	8	0	2.978814	-0.815726	0.585165
7	6	0	-1.558306	-0.104755	0.053665
8	9	0	-1.412116	-0.311530	1.383845
9	9	0	-2.127511	-1.225847	-0.461832
10	9	0	-2.465067	0.899370	-0.091911
11	1	0	-0.094914	2.383832	0.107206
12	1	0	-0.531027	0.384120	-1.696903
13	1	0	0.818053	-1.580370	-1.350975
14	1	0	0.682572	-1.444644	0.407916
15	1	0	2.709653	-0.091952	-1.336308
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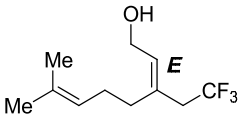
17	1	0	3.877985	-0.463561	0.560219



S7b

Standard orientation:

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3	6	0	-2.204027	1.351649	0.052956
4	6	0	-1.867912	2.757833	0.447073
5	6	0	0.075803	0.731362	-0.838065
6	6	0	1.039036	0.710663	0.379179
7	6	0	2.446160	1.080795	-0.008347
8	6	0	3.560033	0.330491	0.063515
9	6	0	4.894868	0.885771	-0.377536
10	6	0	3.614890	-1.088949	0.575541
11	8	0	-2.963910	3.592371	0.050398
12	6	0	-1.454797	-2.080855	-0.010492
13	9	0	-1.675209	-1.891604	1.312955
14	9	0	-0.123946	-2.323827	-0.156721
15	9	0	-2.095573	-3.228531	-0.357864
16	1	0	-1.696318	-1.177587	-1.895298
17	1	0	-3.029712	-0.915297	-0.767137

18	1	0	-3.237648	1.076929	0.259210
19	1	0	-0.933805	3.094233	-0.022488
20	1	0	-1.731315	2.809914	1.539394
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23	1	0	0.999036	-0.270309	0.857131
24	1	0	0.670139	1.430407	1.123197
25	1	0	2.554979	2.092868	-0.404307
26	1	0	5.618905	0.870544	0.448274
27	1	0	4.810975	1.915495	-0.737089
28	1	0	5.327172	0.276490	-1.182619
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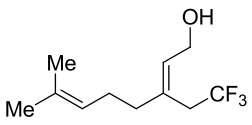

S7'b

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5	6	0	-1.770956	0.327288	-0.543332
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7	6	0	-4.221980	-0.248451	-0.025715
8	6	0	-5.367399	-1.224162	-0.169858
9	6	0	-4.562442	0.997950	0.756249
10	6	0	2.648370	-1.349714	0.097325
11	9	0	3.365302	-0.652804	-0.819225
12	9	0	1.908393	-2.257559	-0.589337
13	9	0	3.541600	-2.053814	0.841833
14	6	0	2.211046	2.327057	-0.323482
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19	1	0	-0.943818	-0.576712	1.234262
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21	1	0	-1.454464	0.525560	-1.577209
22	1	0	-1.959810	1.302391	-0.084103

23	1	0	-2.918705	-1.455113	-1.112416
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25	1	0	-5.730611	-1.553173	0.813052
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27	1	0	-4.914331	0.735012	1.762624
28	1	0	-5.384082	1.542926	0.272777
29	1	0	-3.722369	1.686553	0.864076
30	1	0	2.616947	2.373392	-1.339818
31	1	0	2.989543	1.884129	0.310133
32	1	0	1.578704	3.714111	0.919115

E. References

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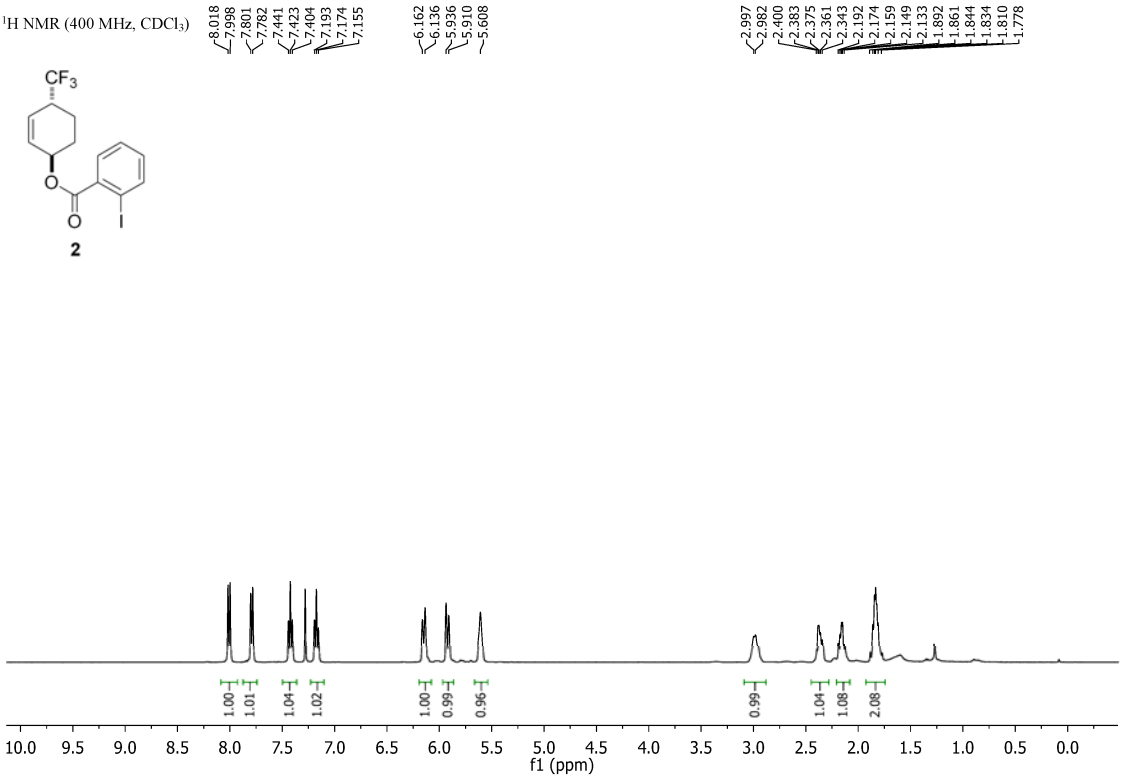
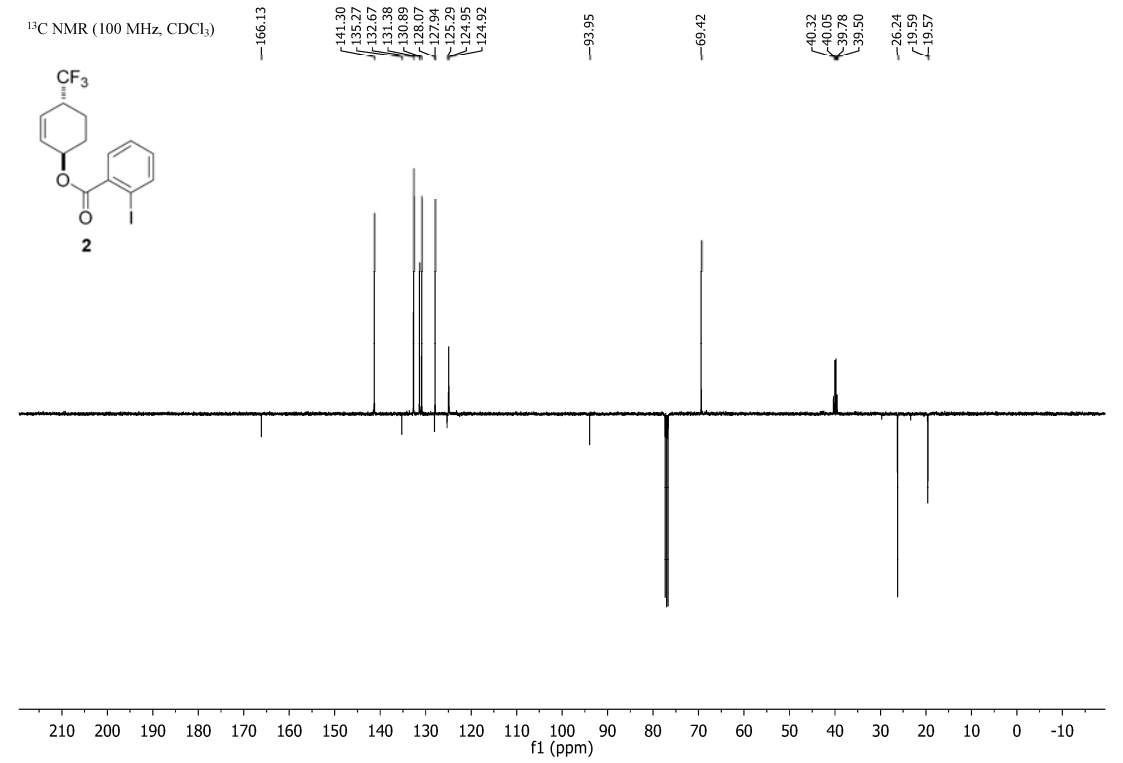
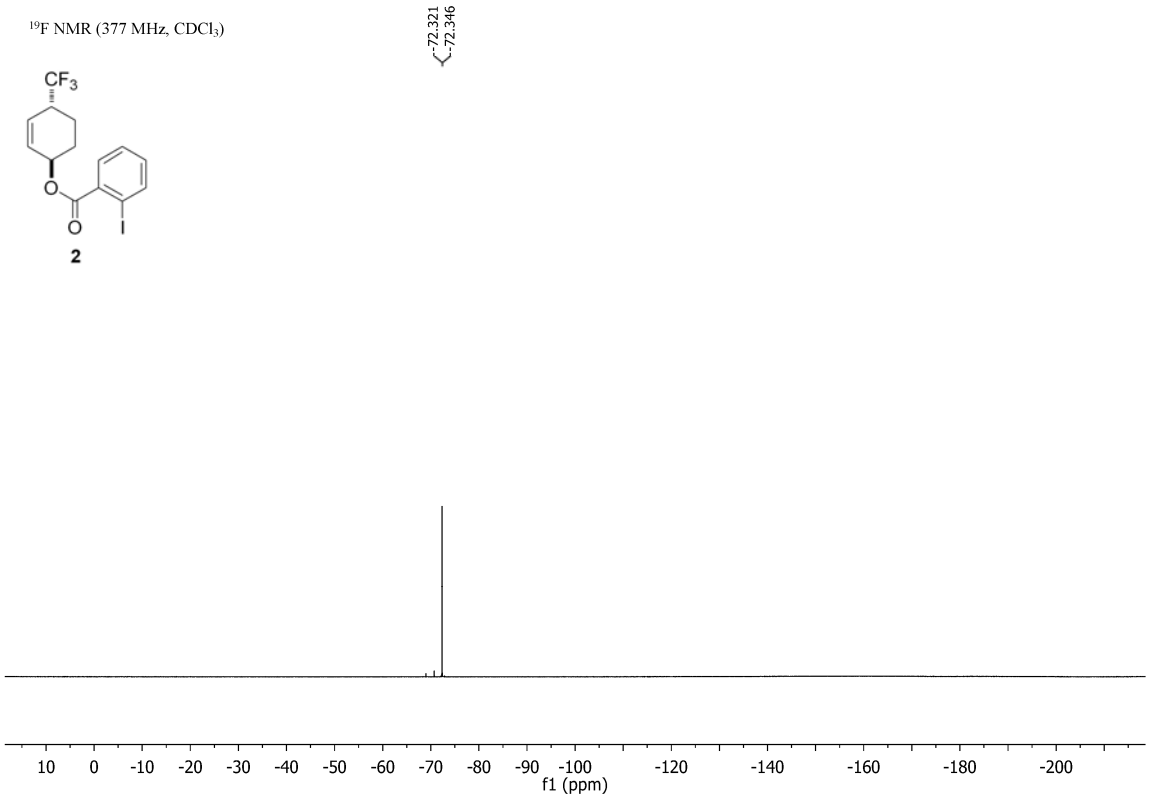
F. NMR Spectra





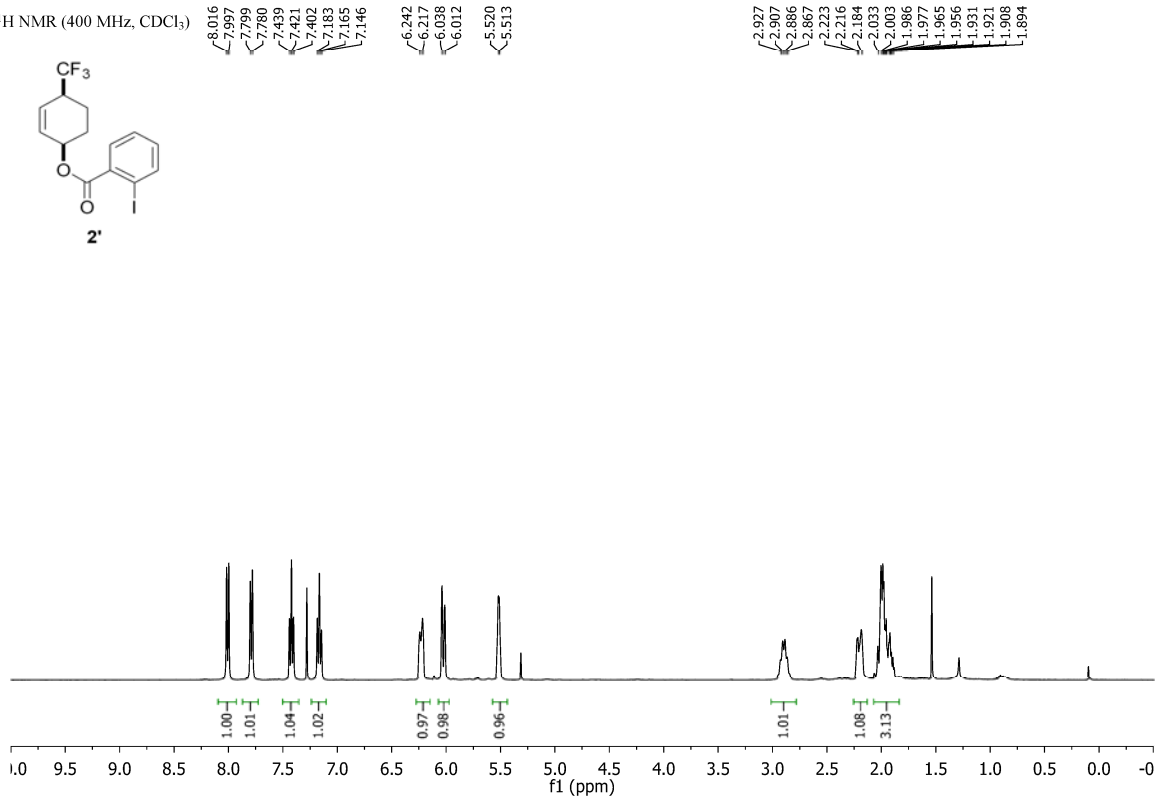
^{19}F NMR (377 MHz, $CDCl_3$)

2



^{1}H NMR (400 MHz, $CDCl_3$)

2'



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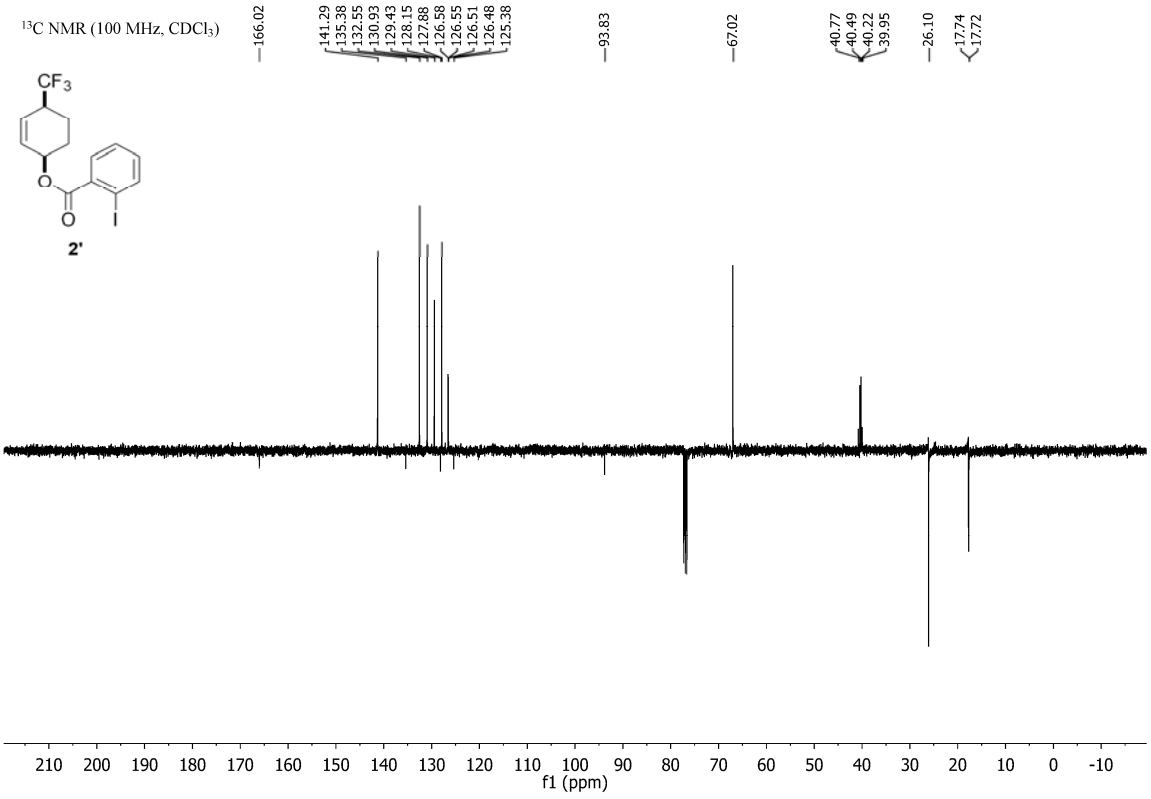

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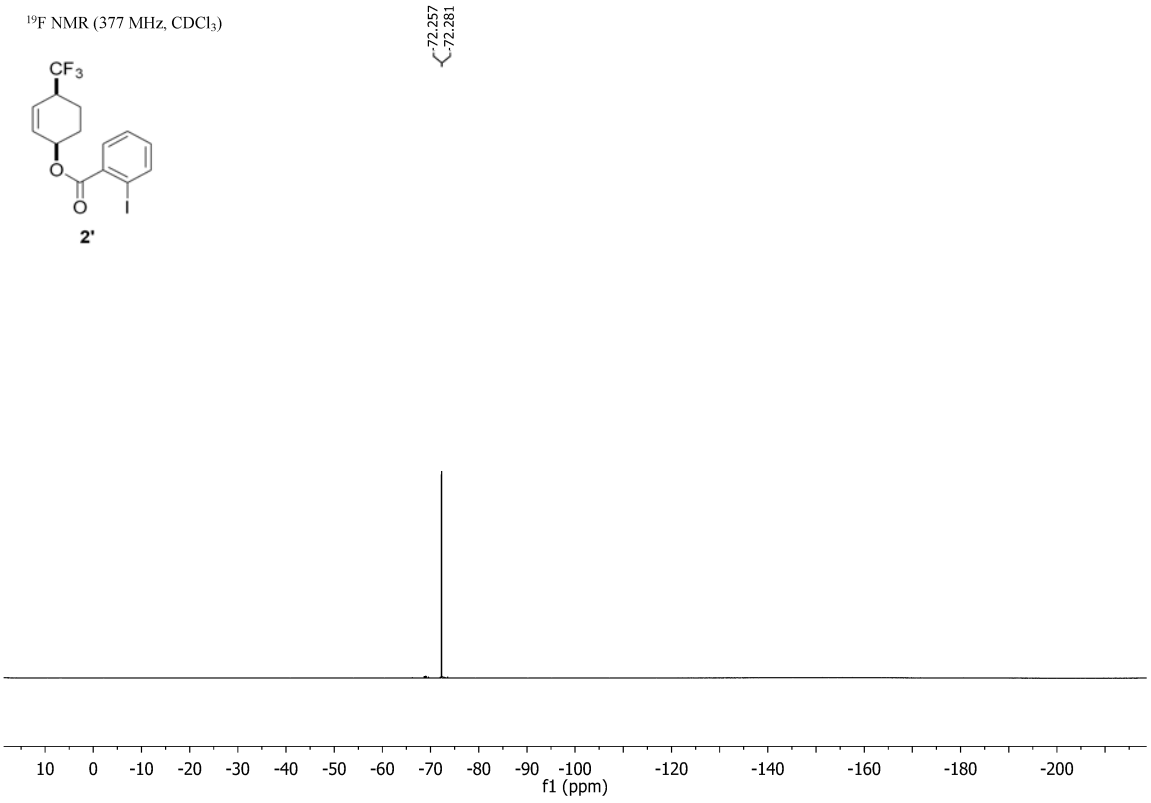

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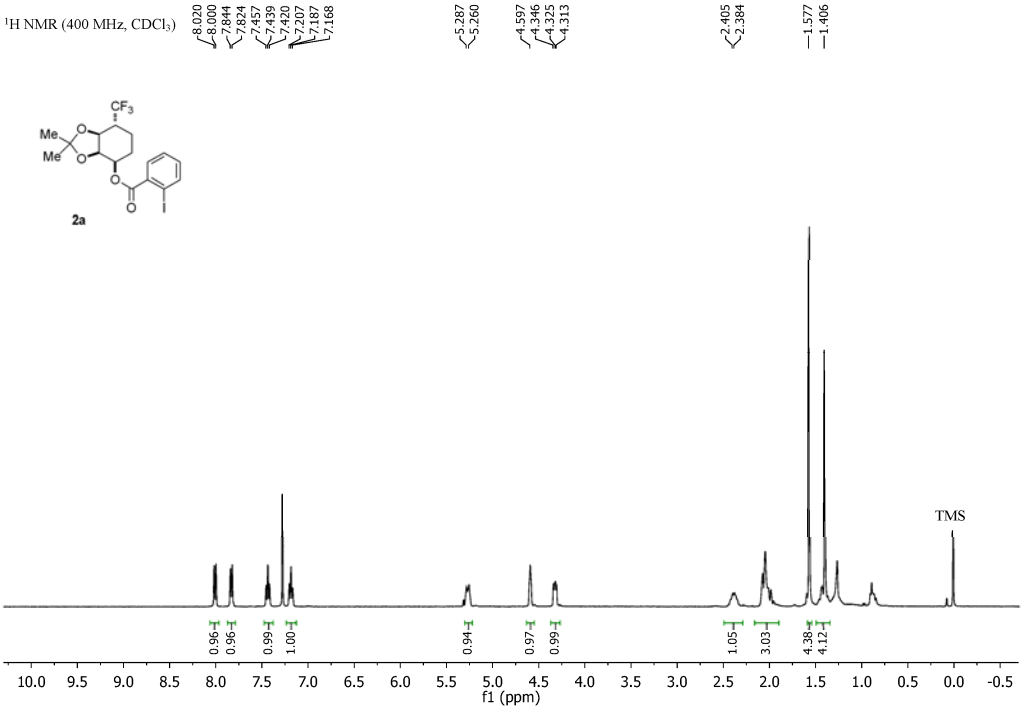

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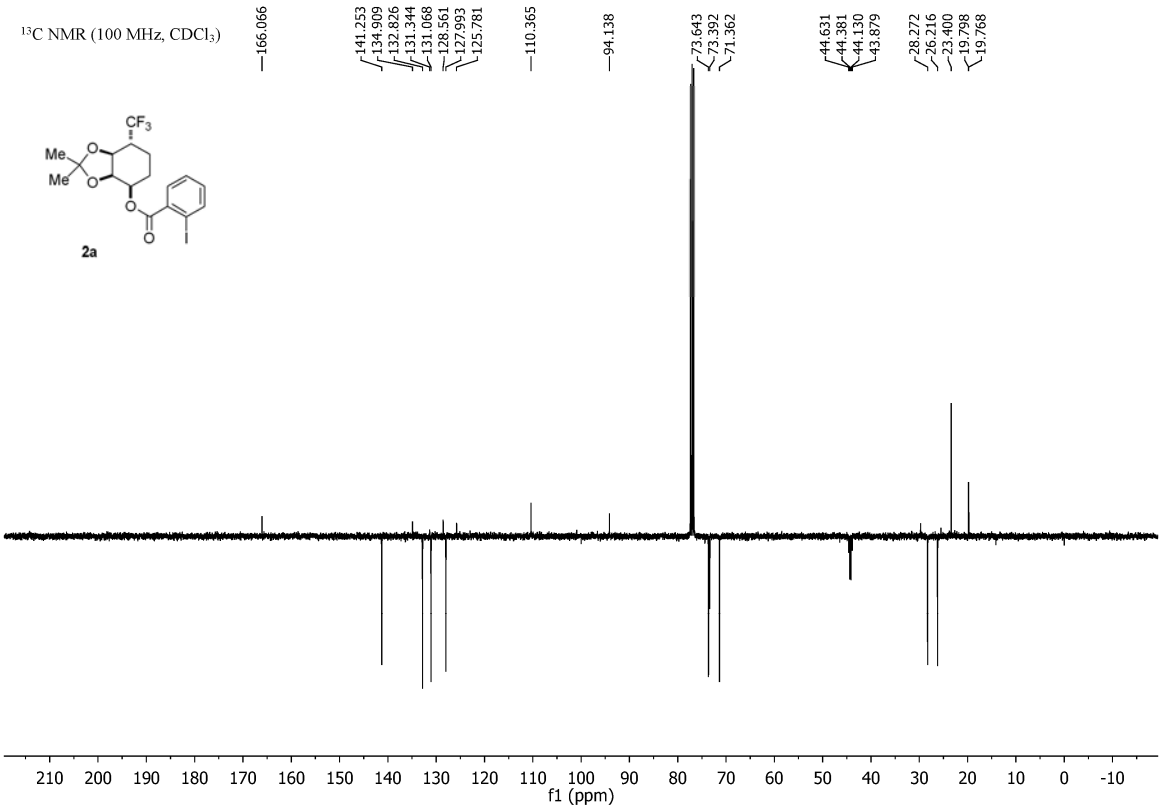

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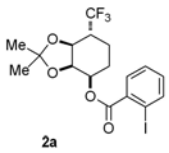

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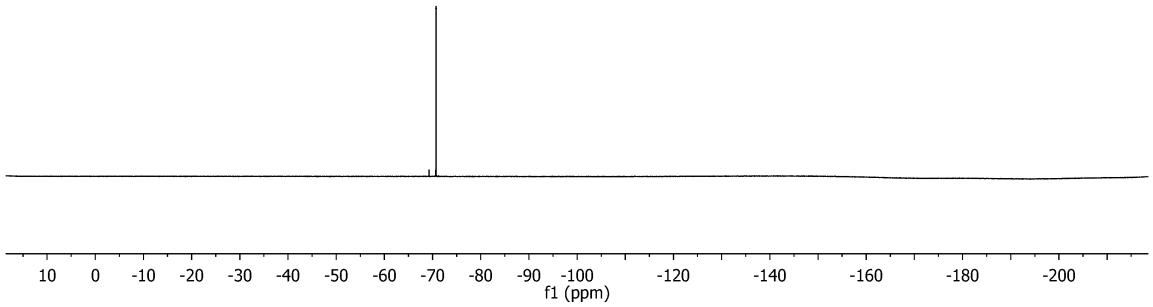

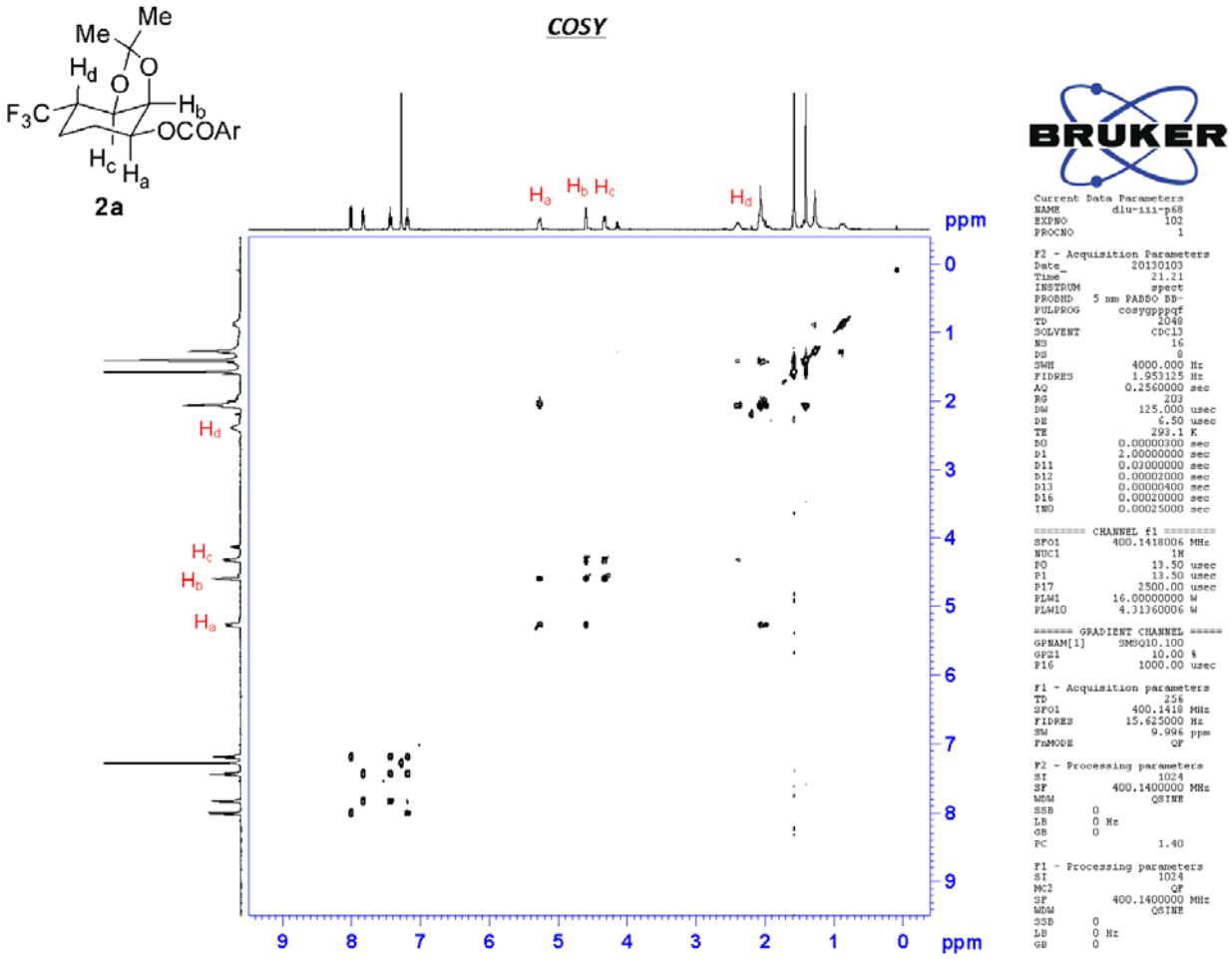

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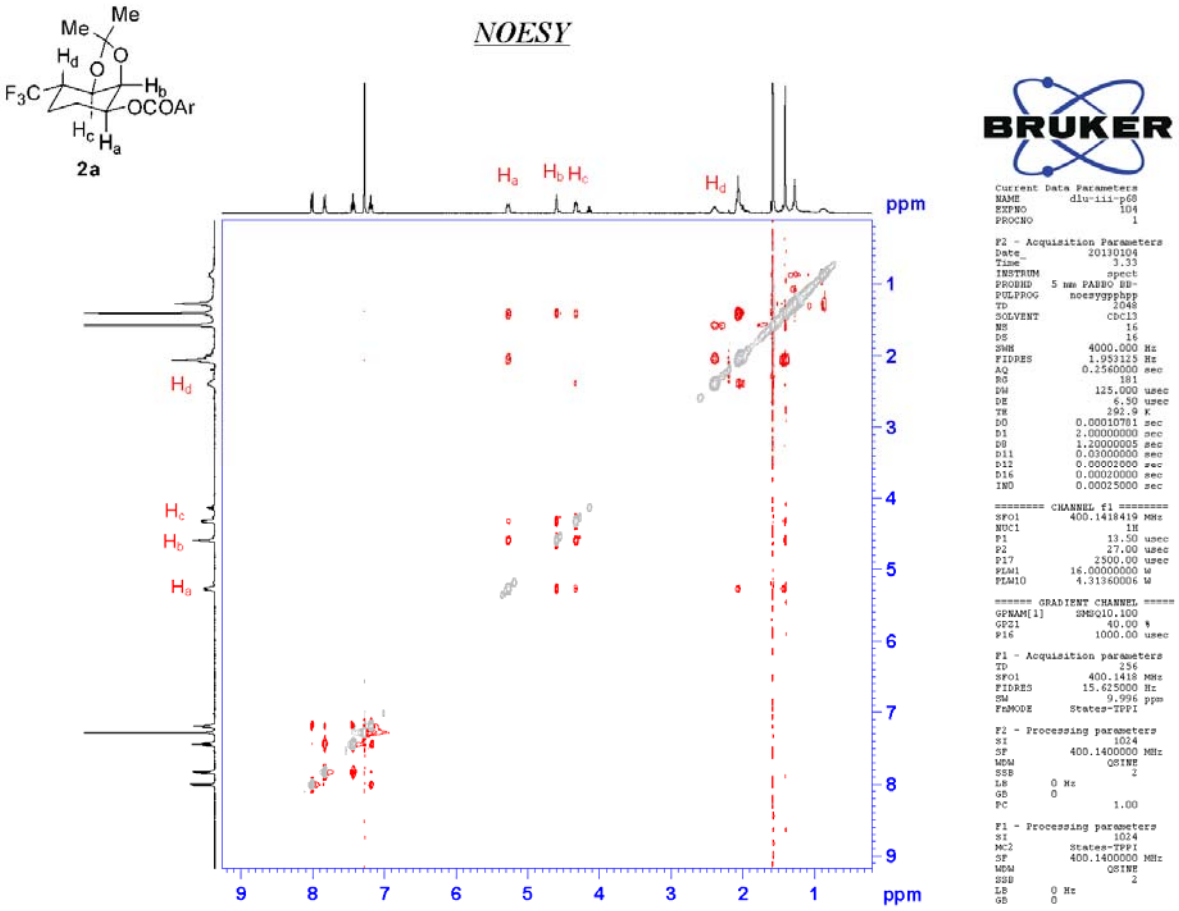
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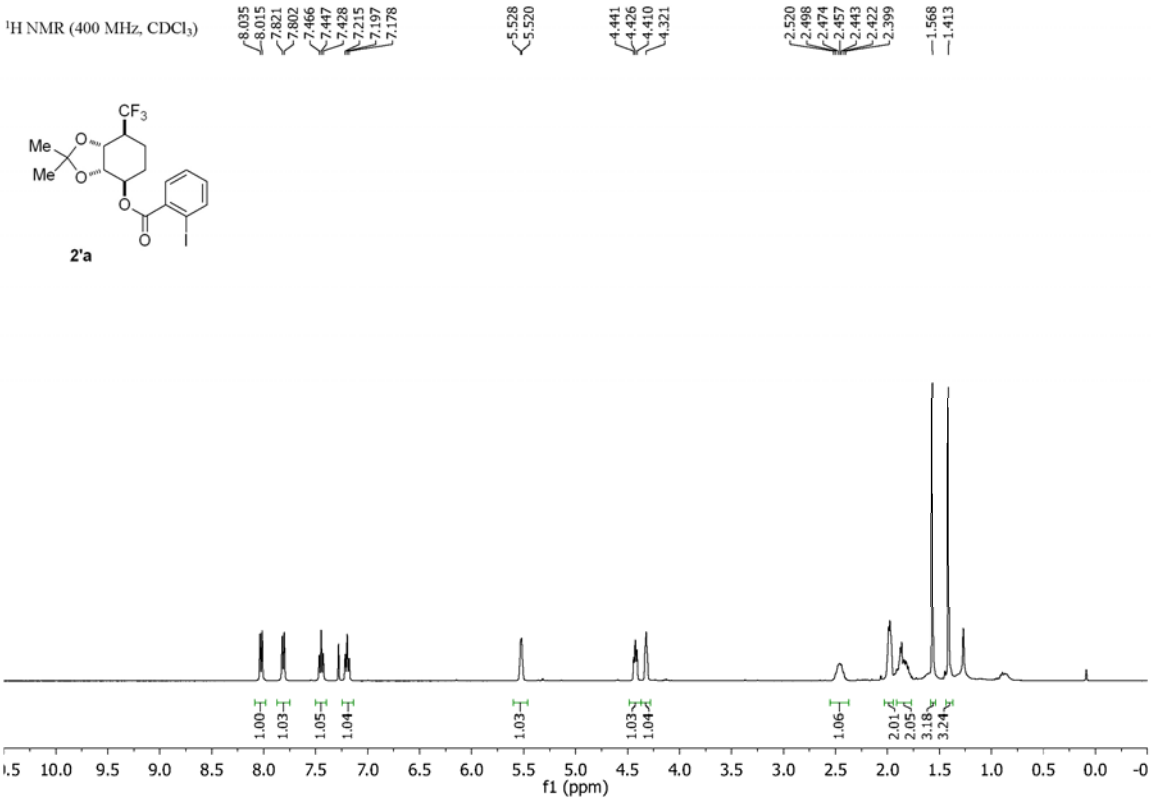
^{1}H NMR (400 MHz, $CDCl_3$)



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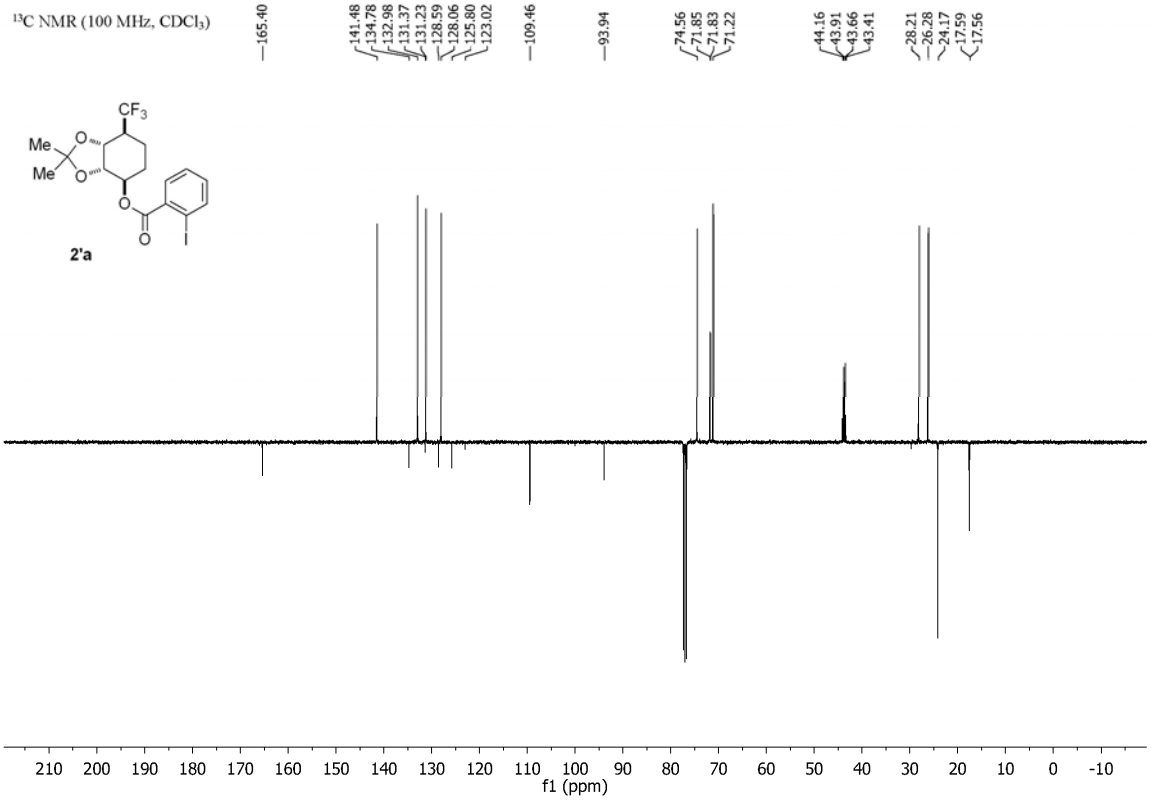

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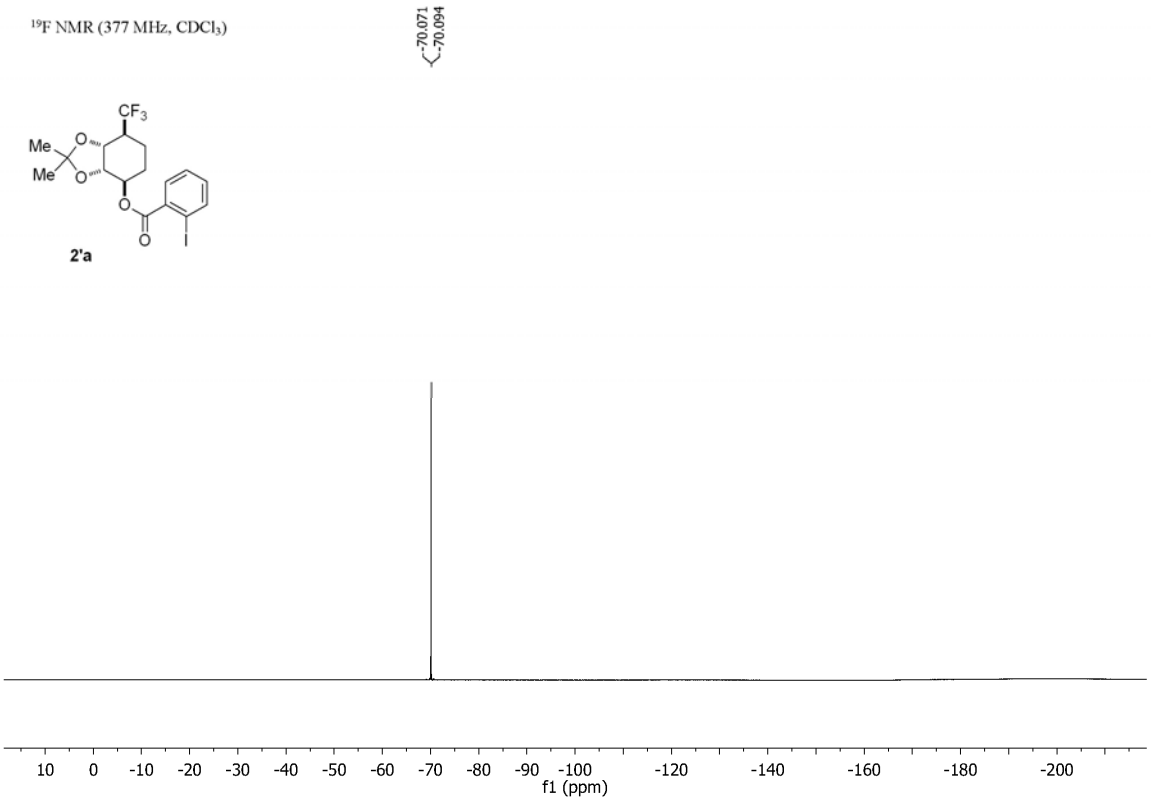
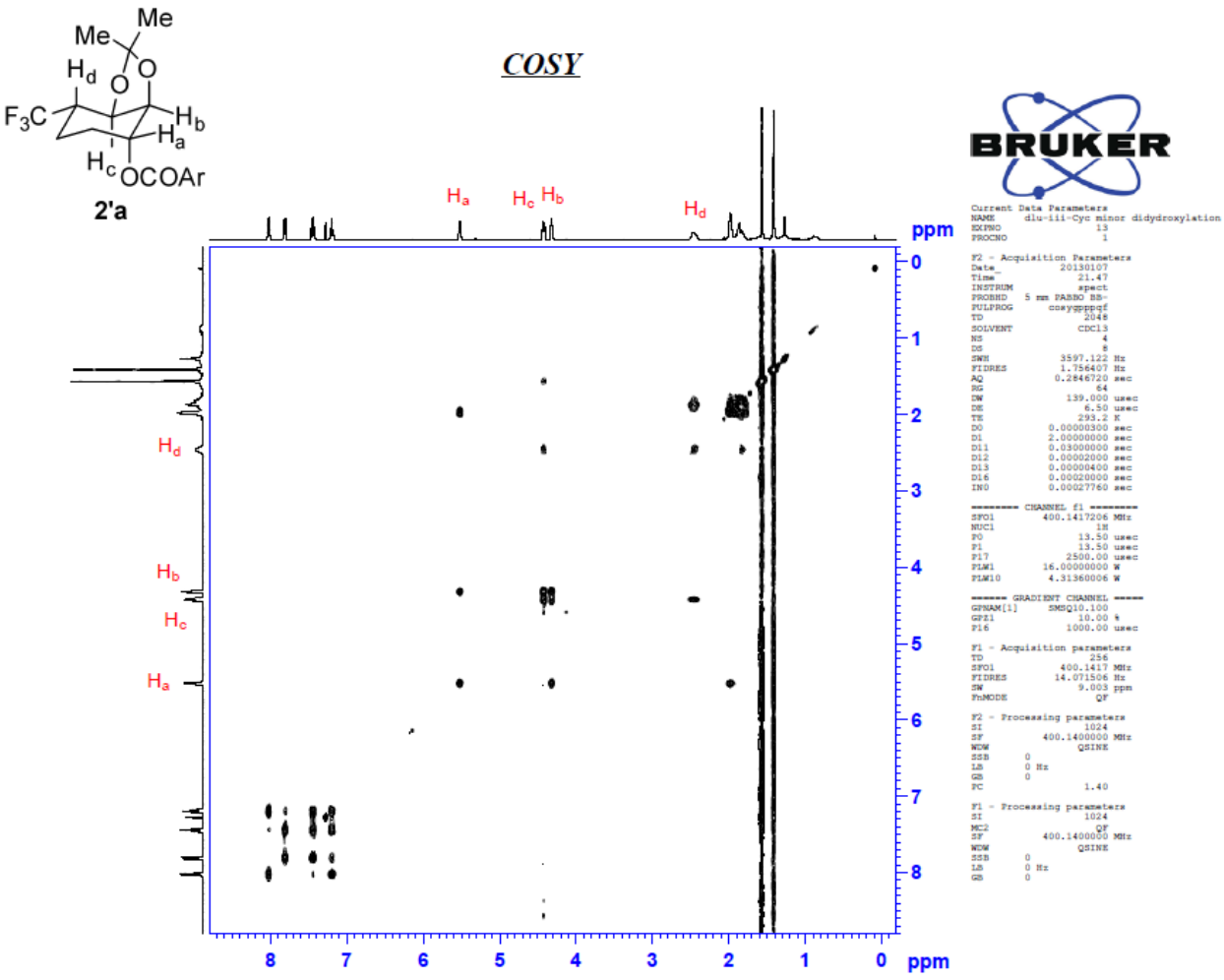


2'a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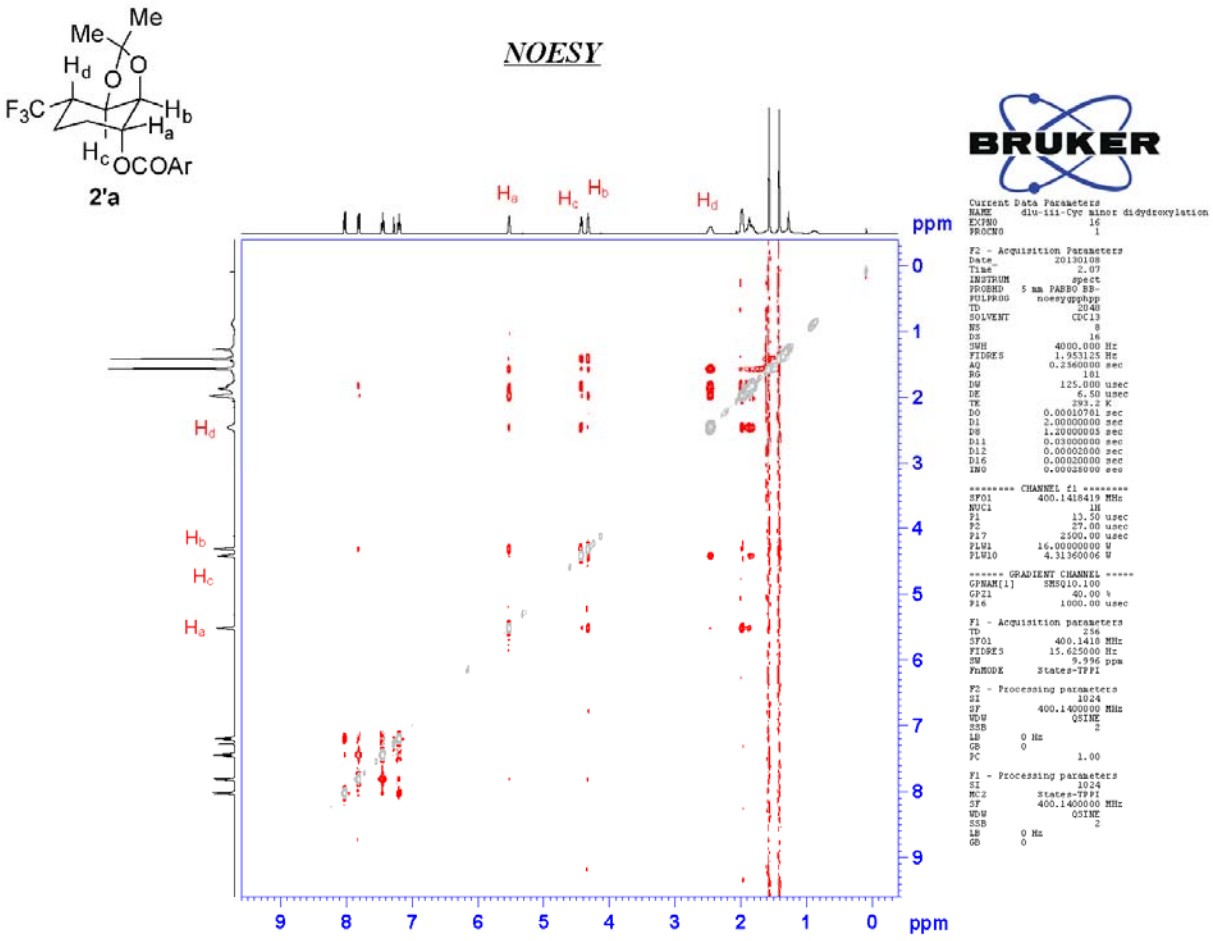
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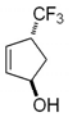
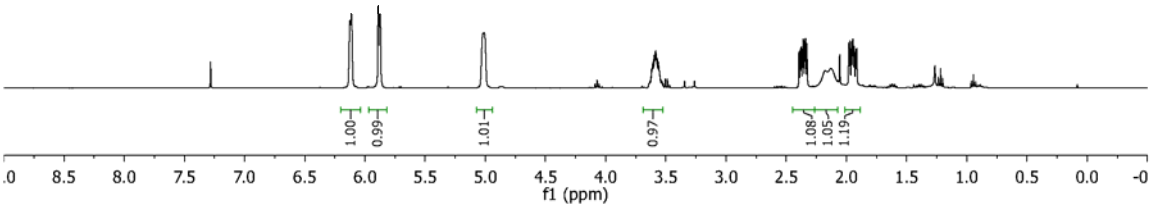
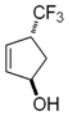
^{1}H NMR (400 MHz, $CDCl_3$)



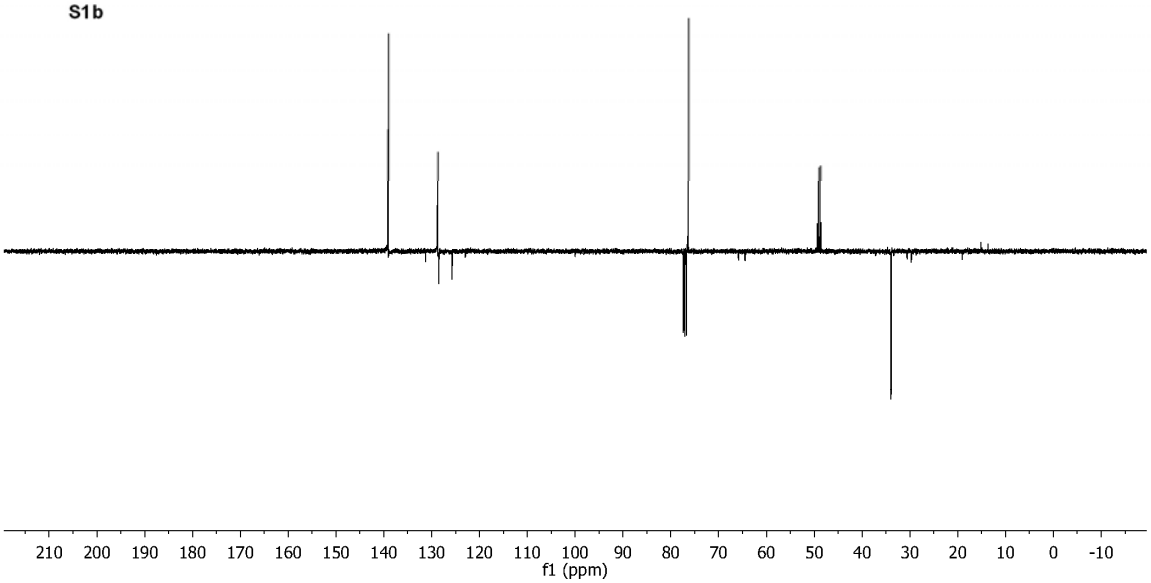
S1b



^{13}C NMR (100 MHz, $CDCl_3$)

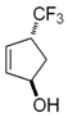


S1b

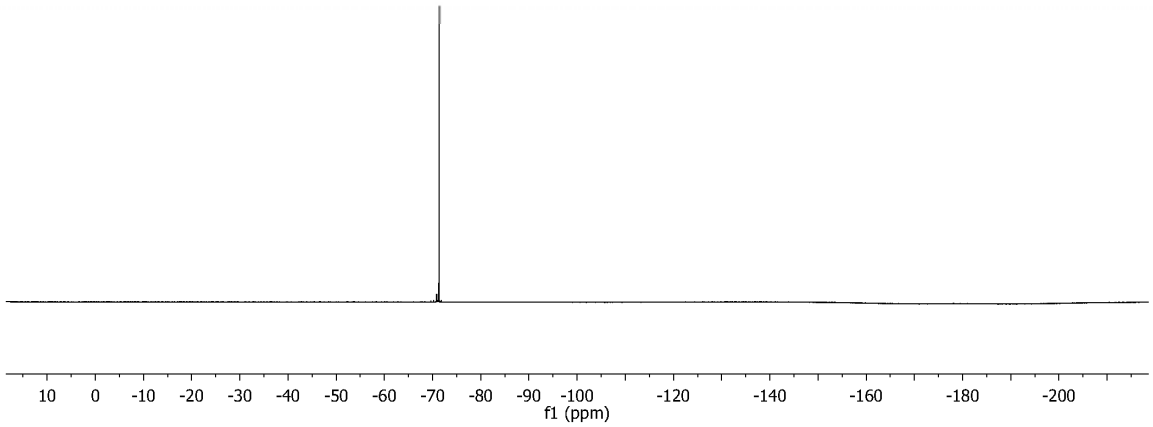


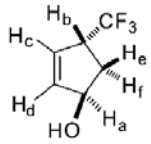
^{19}F NMR (377 MHz, $CDCl_3$)

-71.329
-71.353



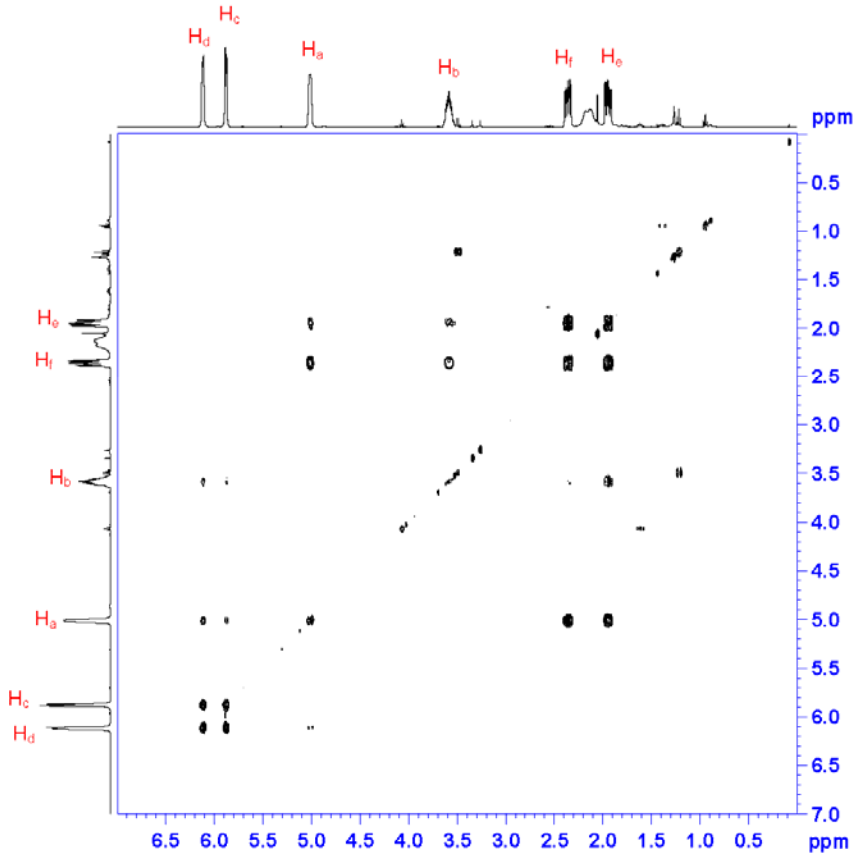
S1b





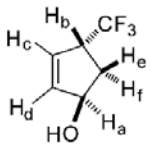
S1b

COSY

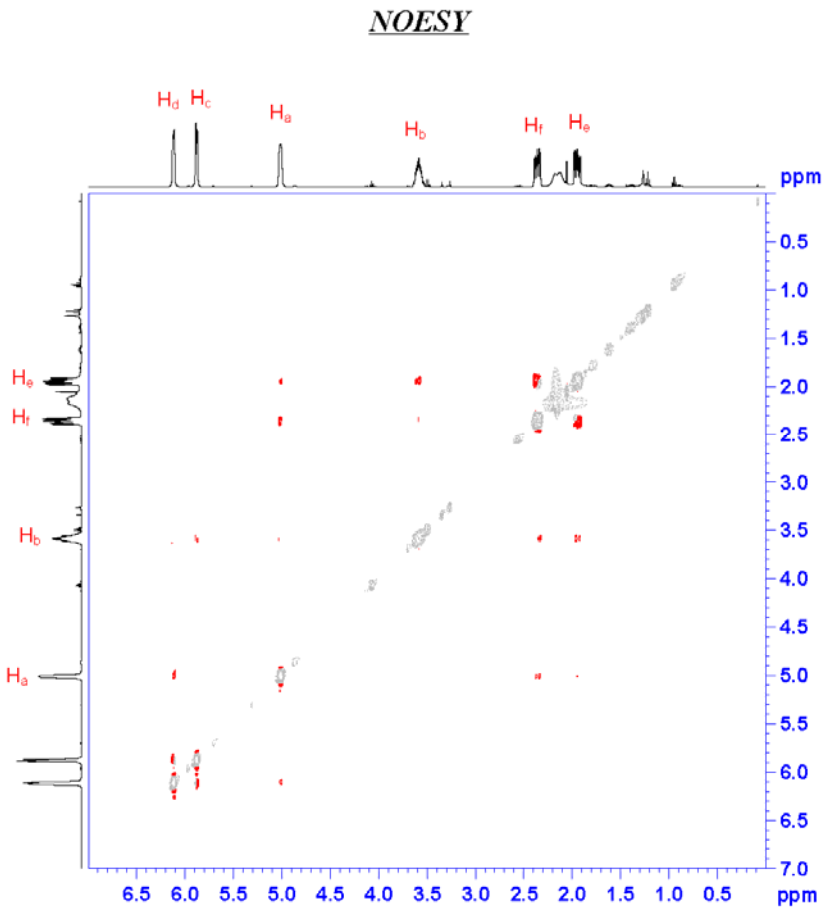


BRUKER

```
Current Data Parameters
NAME                  dlu-iii-p84
EXPNO                         102
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20130110
Time                        15.32
INSTRUM                      spect
PROBHD    5 mm PABBO BB-
PULPROG              cosygpppqf
TD                            2048
SOLVENT                     CDCl3
NS                              2
DS                              8
SWH                      2799.552 Hz
FIDRES                   1.366969 Hz
AQ                       0.3657728 sec
RG                            203
DW                         178.600 usec
DE                           6.50 usec
TE                          294.9 K
D0                       0.00000300 sec
D1                       2.00000000 sec
D11                      0.03000000 sec
D12                      0.00002000 sec
D13                      0.00000400 sec
D16                      0.00020000 sec
IN0                      0.00035700 sec

======== CHANNEL f1 ========
SFO1                   400.1414005 MHz
NUC1                           1H
P0                           13.50 usec
P1                           13.50 usec
P17                        2500.00 usec
PLW1                   16.00000000 W
PLW10                   4.31360006 W

====== GRADIENT CHANNEL =====
GPNAM[1]            SMSQ10.100
GPZ1                        10.00 %
P16                       1000.00 usec

F1 - Acquisition parameters
TD                             162
SFO1                   400.1414 MHz
FIDRES                 17.290867 Hz
SW                          7.000 ppm
FnMODE                         QF

F2 - Processing parameters
SI                            1024
SF                   400.1400000 MHz
WDW                         QSINE
SSB                 0
LB                  0 Hz
GB                  0
PC                          1.40

F1 - Processing parameters
SI                            1024
MC2                            QF
SF                   400.1400000 MHz
WDW                         QSINE
SSB                 0
LB                  0 Hz
GB                  0
```



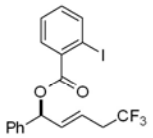
S1b



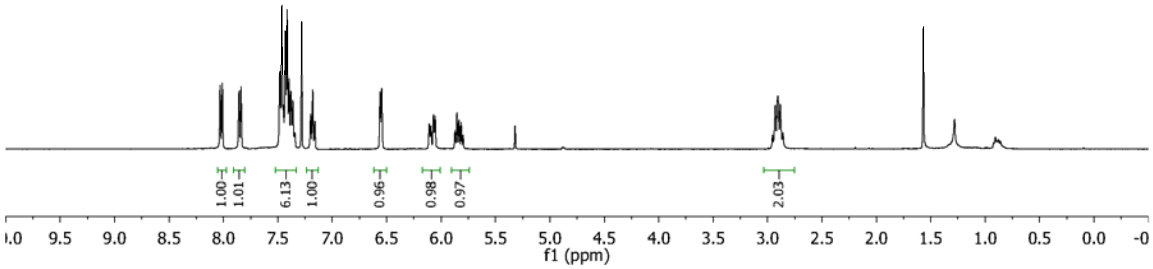
BRUKER

```
Current Data Parameters
NAME          dlu-iii-p84
EXPNO                 104
PROCNO                  1

F2 - Acquisition Parameters
Date_           20130110
Time              20.48
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG     noesygpphpp
TD                 2048
SOLVENT           CDCl3
NS                    8
DS                   16
SWH           2799.552 Hz
FIDRES        1.366969 Hz
AQ            0.3657728 sec
RG                  114
DW              178.600 usec
DE                6.50 usec
TE              295.1 K
D0            0.00016131 sec
D1            2.00000000 sec
D8            1.29999995 sec
D11           0.03000000 sec
D12           0.00002000 sec
D16           0.00020000 sec
IN0           0.00035700 sec

======== CHANNEL f1 ========
SFO1        400.1414005 MHz
NUC1                   1H
P1                 13.50 usec
P2                 27.00 usec
P17              2500.00 usec
PLW1        16.00000000 W
PLW10        4.31360006 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1              40.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   205
SFO1          400.1414 MHz
FIDRES        13.664002 Hz
SW             7.000 ppm
FnMODE       States-TPPI

F2 - Processing parameters
SI                  1024
SF            400.1400000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2          States-TPPI
SF            400.1400000 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```

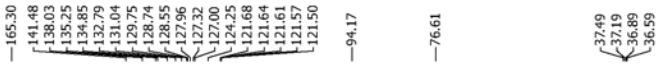
^{1}H NMR (400 MHz, $CDCl_3$)

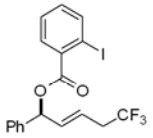


S2a

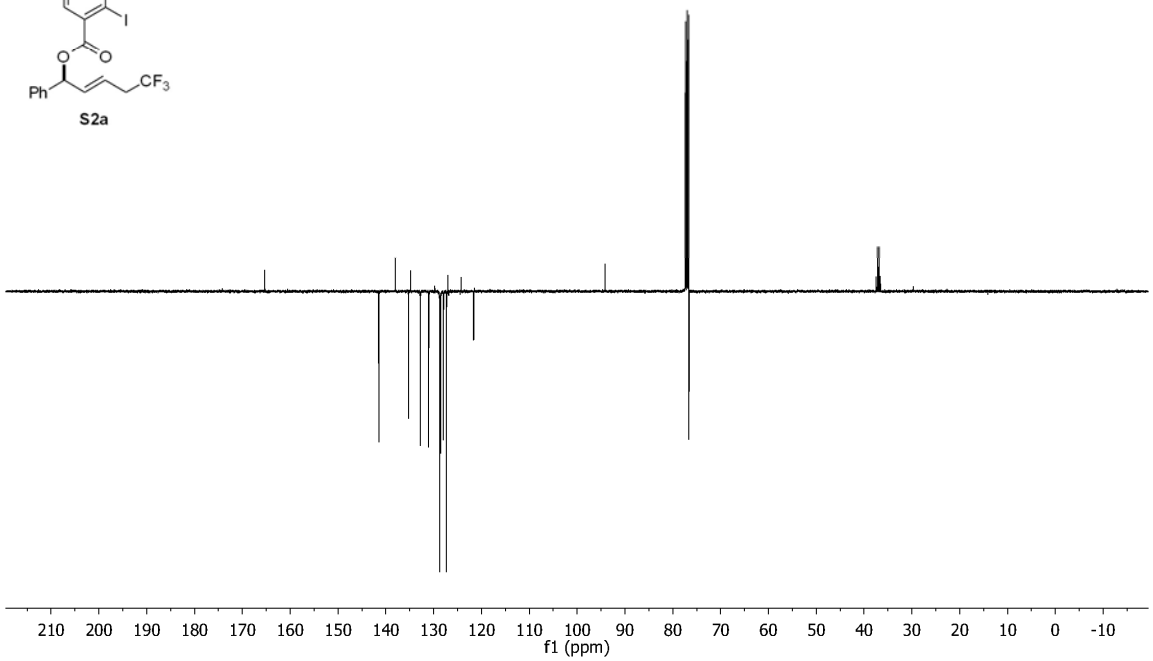


^{13}C NMR (100 MHz, $CDCl_3$)

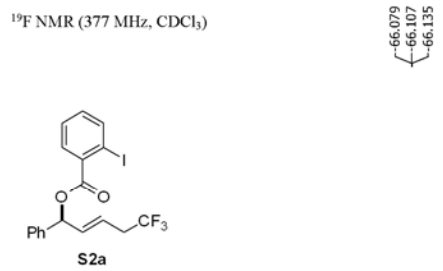




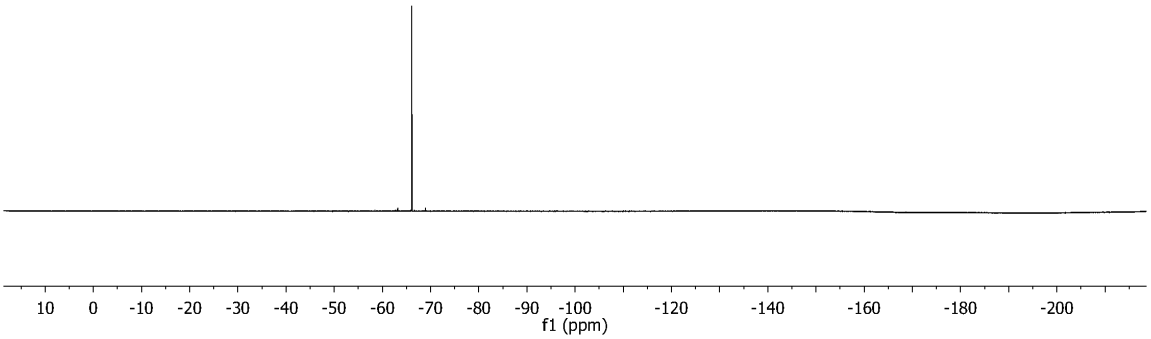
S2a



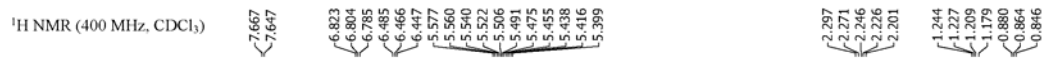
^{19}F NMR (377 MHz, $CDCl_3$)

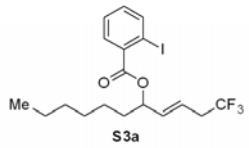


S2a

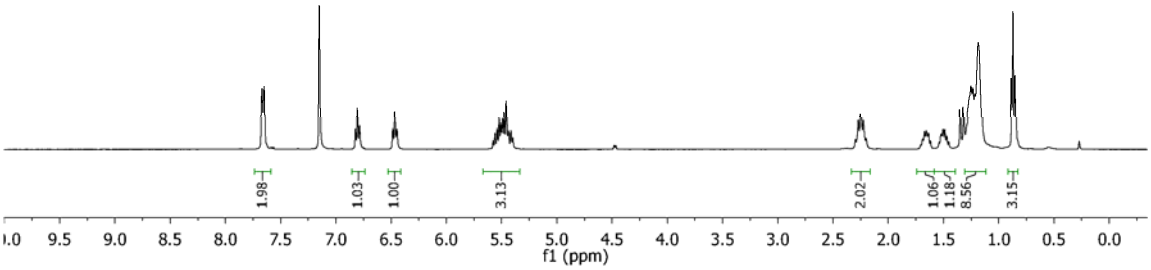


^{1}H NMR (400 MHz, $CDCl_3$)

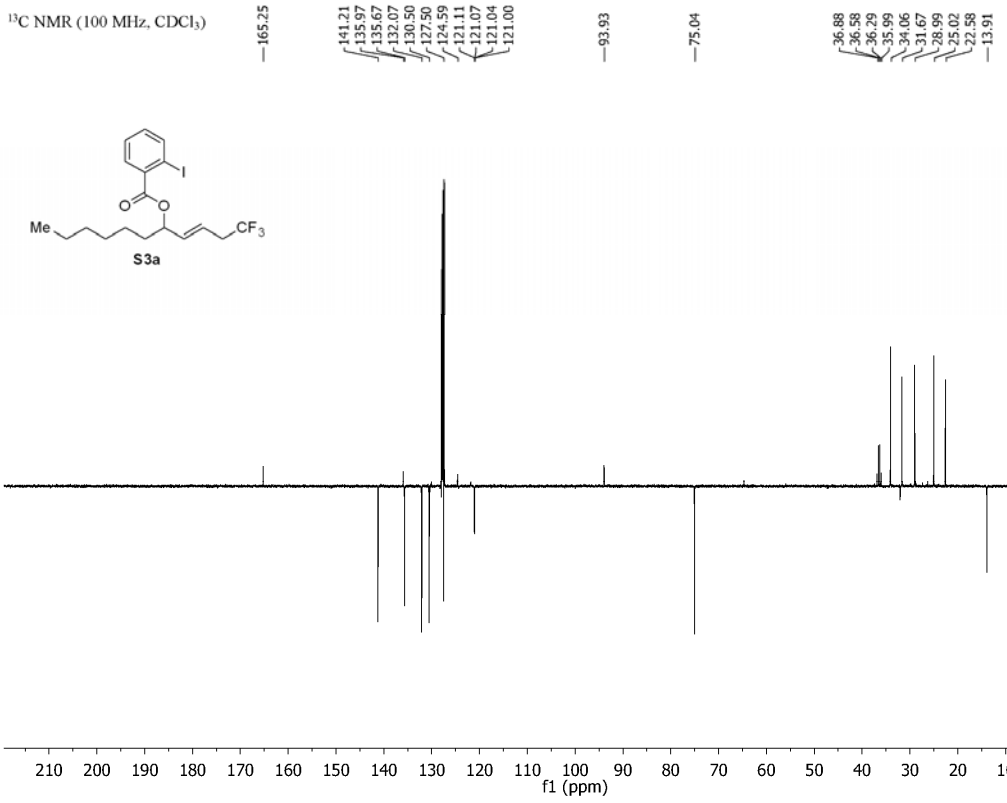




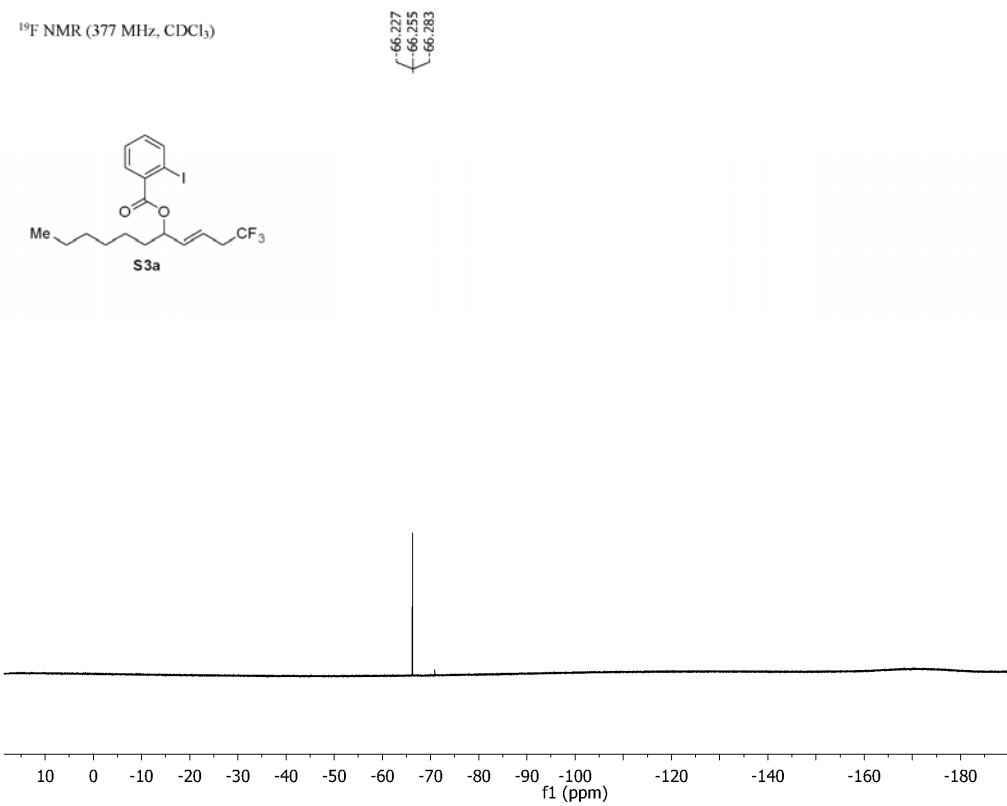
S3a



^{13}C NMR (100 MHz, $CDCl_3$)

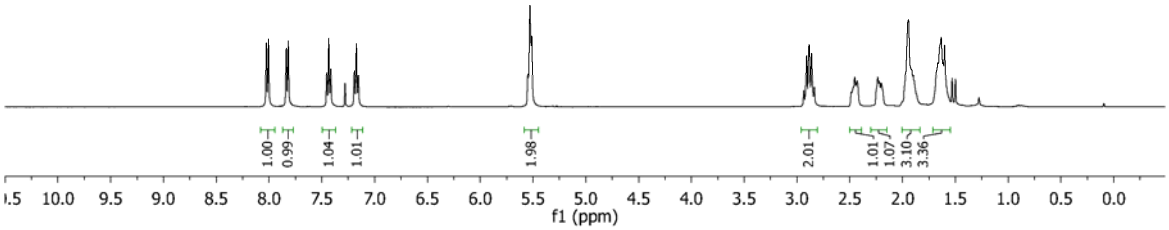


^{19}F NMR (377 MHz, $CDCl_3$)

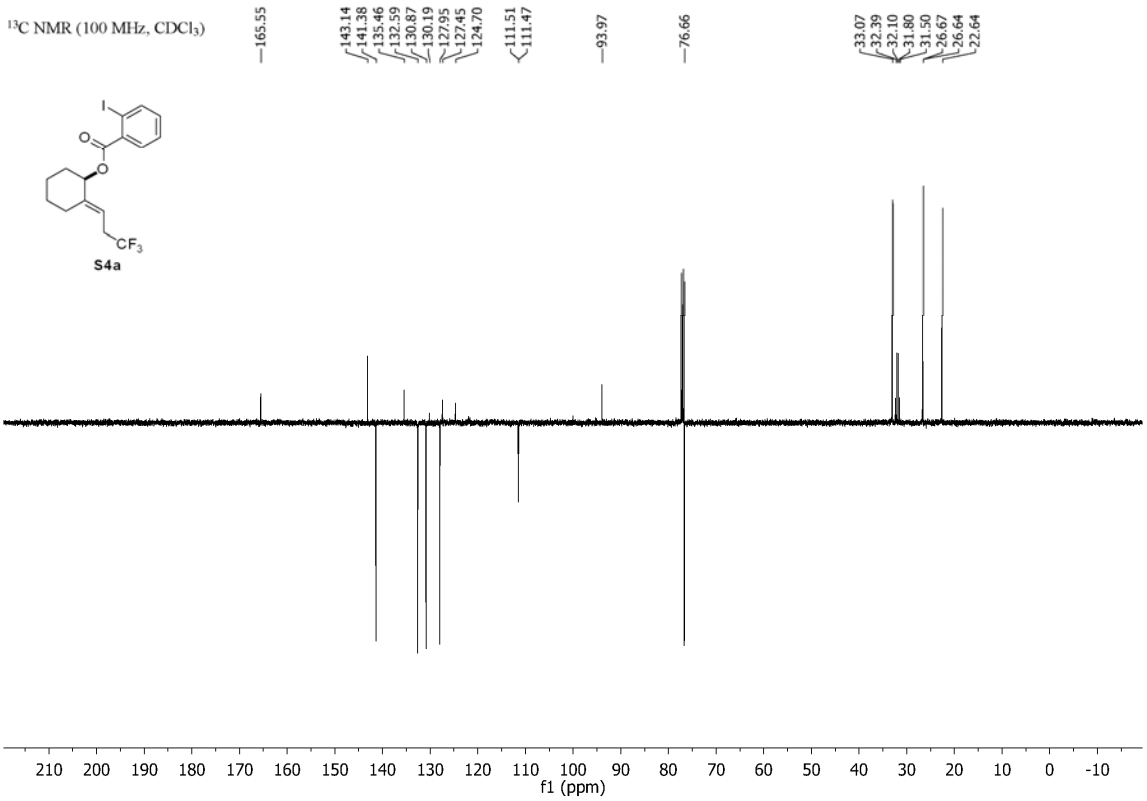


^{1}H NMR (400 MHz, $CDCl_3$)

S4a



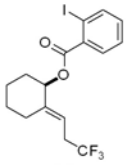
^{13}C NMR (100 MHz, $CDCl_3$)



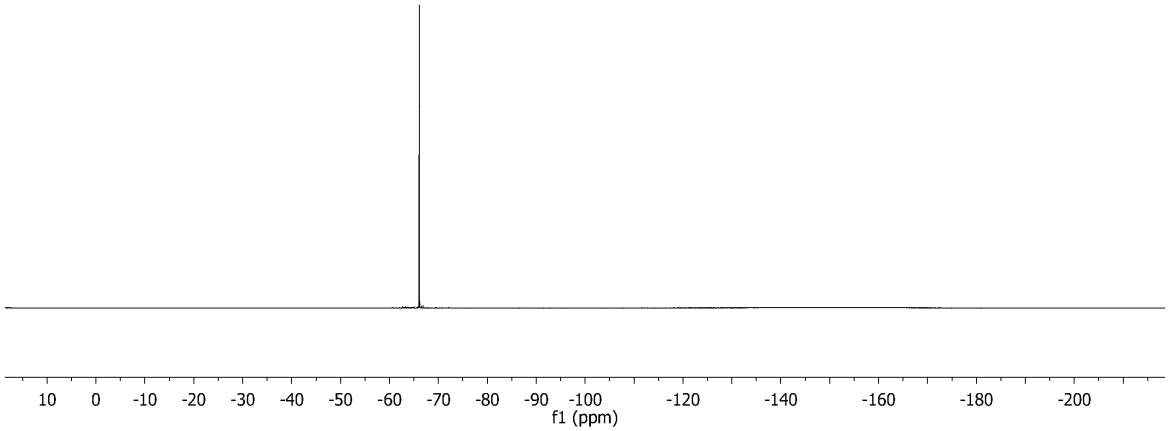
S4a

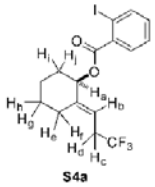
^{19}F NMR (377 MHz, $CDCl_3$)

-66.053
-66.082
-66.111

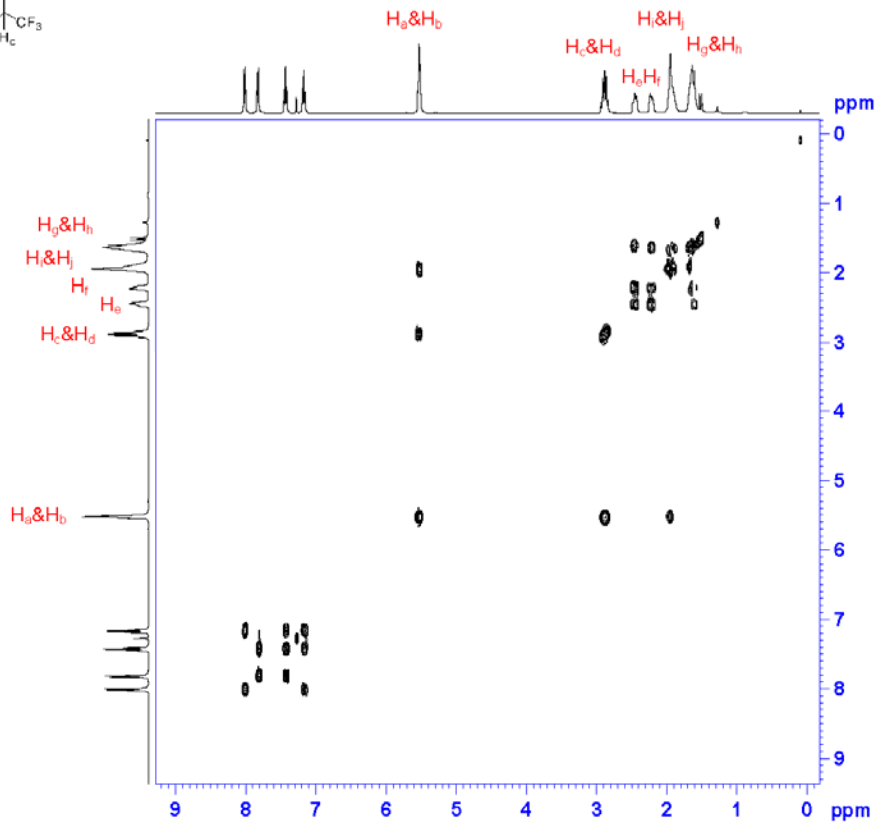


S4a

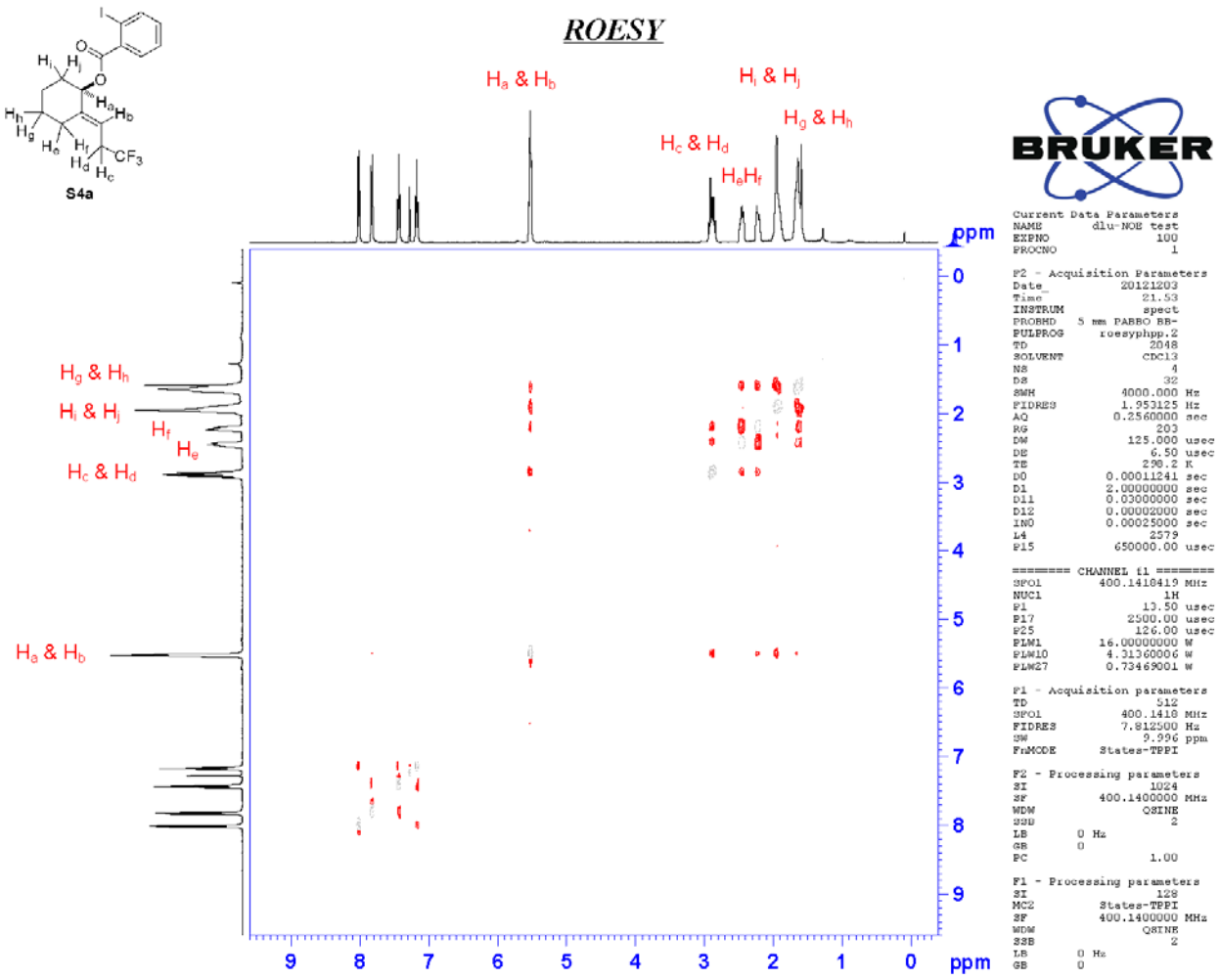




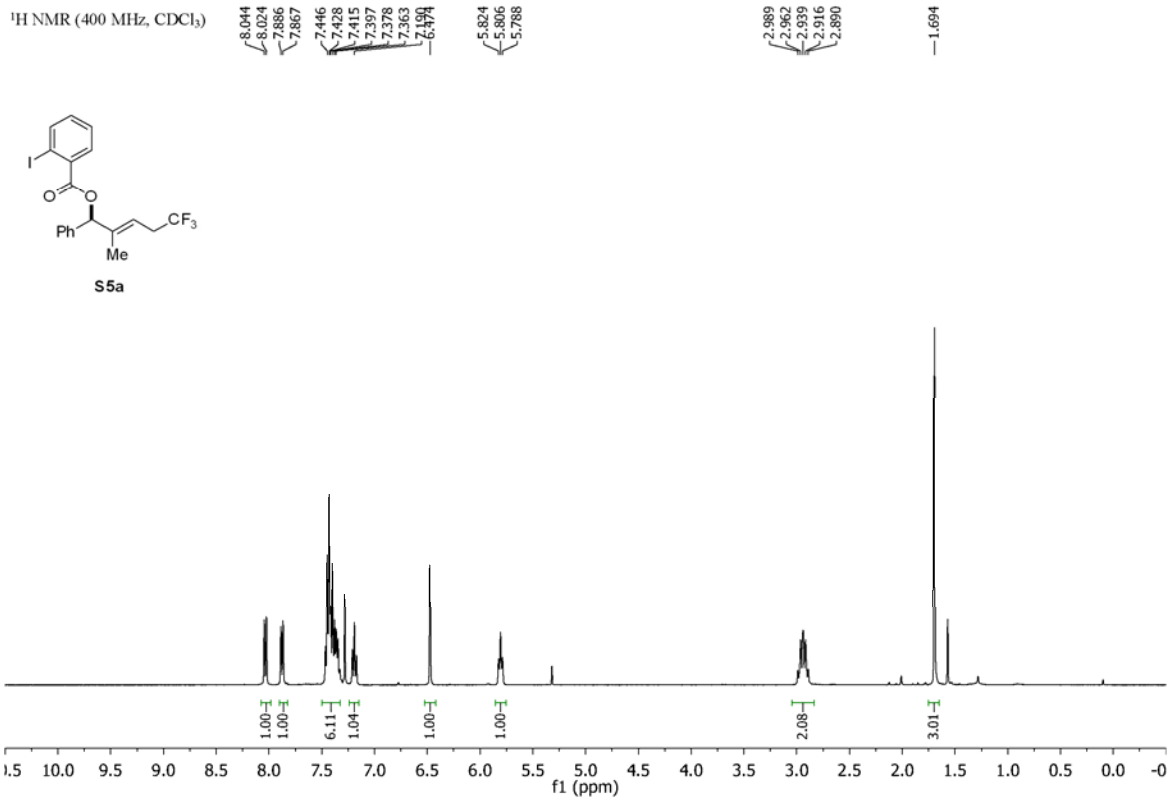
COSY



```
Current Data Parameters
NAME          dlu-ii-P142
EXPNO                 101
PROCNO                  1

F2 - Acquisition Parameters
Date_           20121122
Time              10.35
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpppqf
TD                 2048
SOLVENT            CDCl3
NS                    4
DS                    8
SWH             5341.880 Hz
FIDRES          2.608340 Hz
AQ              0.1916928 sec
RG                  161
DW                93.600 usec
DE                 6.50 usec
TE                313.0 K
D0              0.00000300 sec
D1              2.00000000 sec
D11             0.03000000 sec
D12             0.00001000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00018720 sec

======== CHANNEL f1 ========
SFO1          400.1424057 MHz
NUC1                   1H
P0                  13.50 usec
P1                  13.50 usec
P17               2500.00 usec
PLW1         16.00000000 W
PLW10         4.31260006 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            400.1424 MHz
FIDRES          41.733440 Hz
SW                13.350 ppm
FnMODE                QF

F2 - Processing parameters
SI                   1024
SF          400.1400000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   1024
MC2                   QF
SF          400.1400000 MHz
WDW                 QSINE
SSB       0
LB        0 Hz
GB        0
```

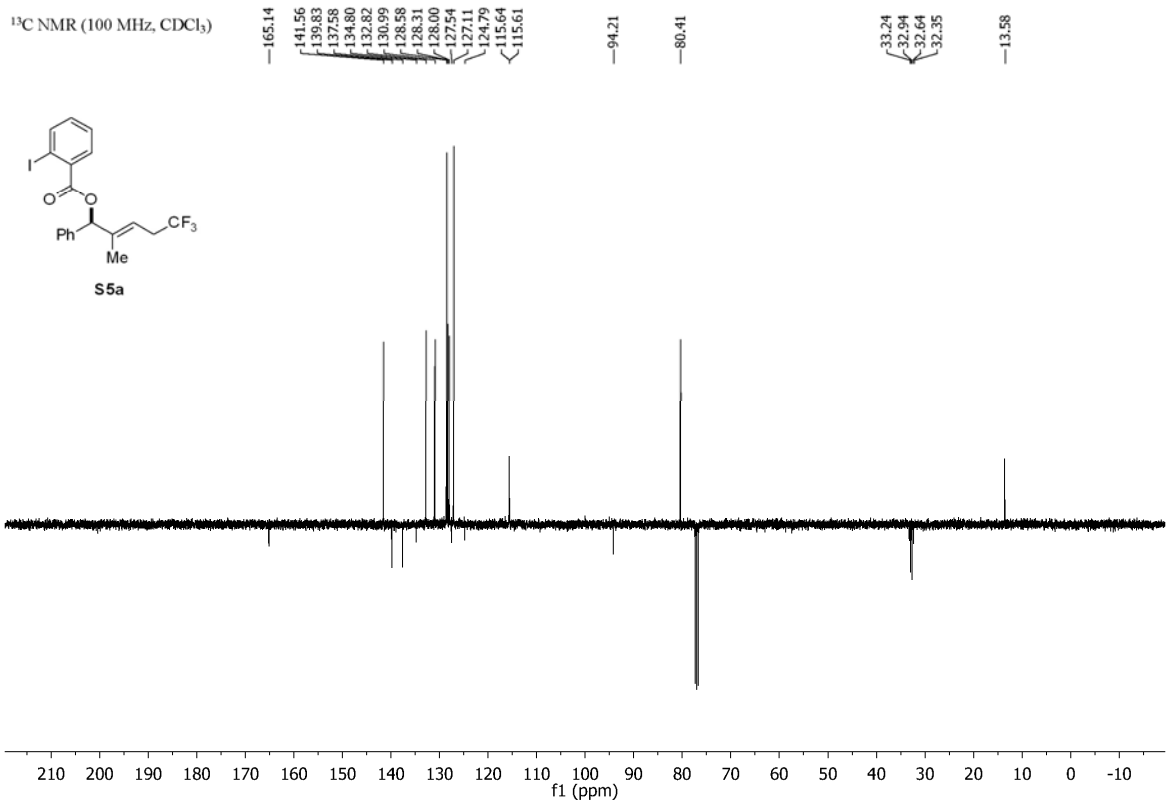

ROESY
S4a
Ha & Hb
Hi & Hj
Hg & Hh
Hc & Hd
HeHf
ppm
Hg & Hh
Hi & Hj
Hf
He
Hc & Hd
Ha & Hb
9 8 7 6 5 4 3 2 1 0 ppm
BRUKER
Current Data Parameters
NAME dlu-NOE test
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121203
Time 21.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG roesyphpp.2
TD 2048
SOLVENT CDCl3
NS 4
DS 32
SWH 4000.000 Hz
FIDRES 1.953125 Hz
AQ 0.2560000 sec
RG 203
DW 125.000 usec
DE 6.50 usec
TE 290.2 K
D0 0.00011241 sec
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
IN0 0.00025000 sec
L4 2579
P15 650000.00 usec
======== CHANNEL f1 ========
SFO1 400.1418419 MHz
NUC1 1H
P1 13.50 usec
P17 2500.00 usec
P25 126.00 usec
PLW1 16.00000000 W
PLW10 4.31360006 W
PLW27 0.73469001 W
F1 - Acquisition parameters
TD 512
SFO1 400.1418 MHz
FIDRES 7.812500 Hz
SW 9.996 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 1024
SF 400.1400000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 128
MC2 States-TPPI
SF 400.1400000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NMR (400 MHz, $CDCl_3$)



S5a

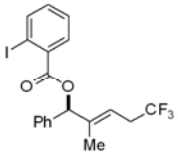
^{13}C NMR (100 MHz, $CDCl_3$)



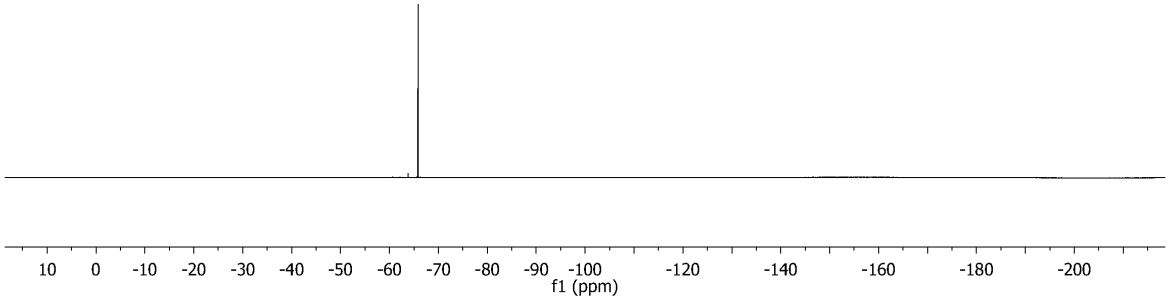
S5a

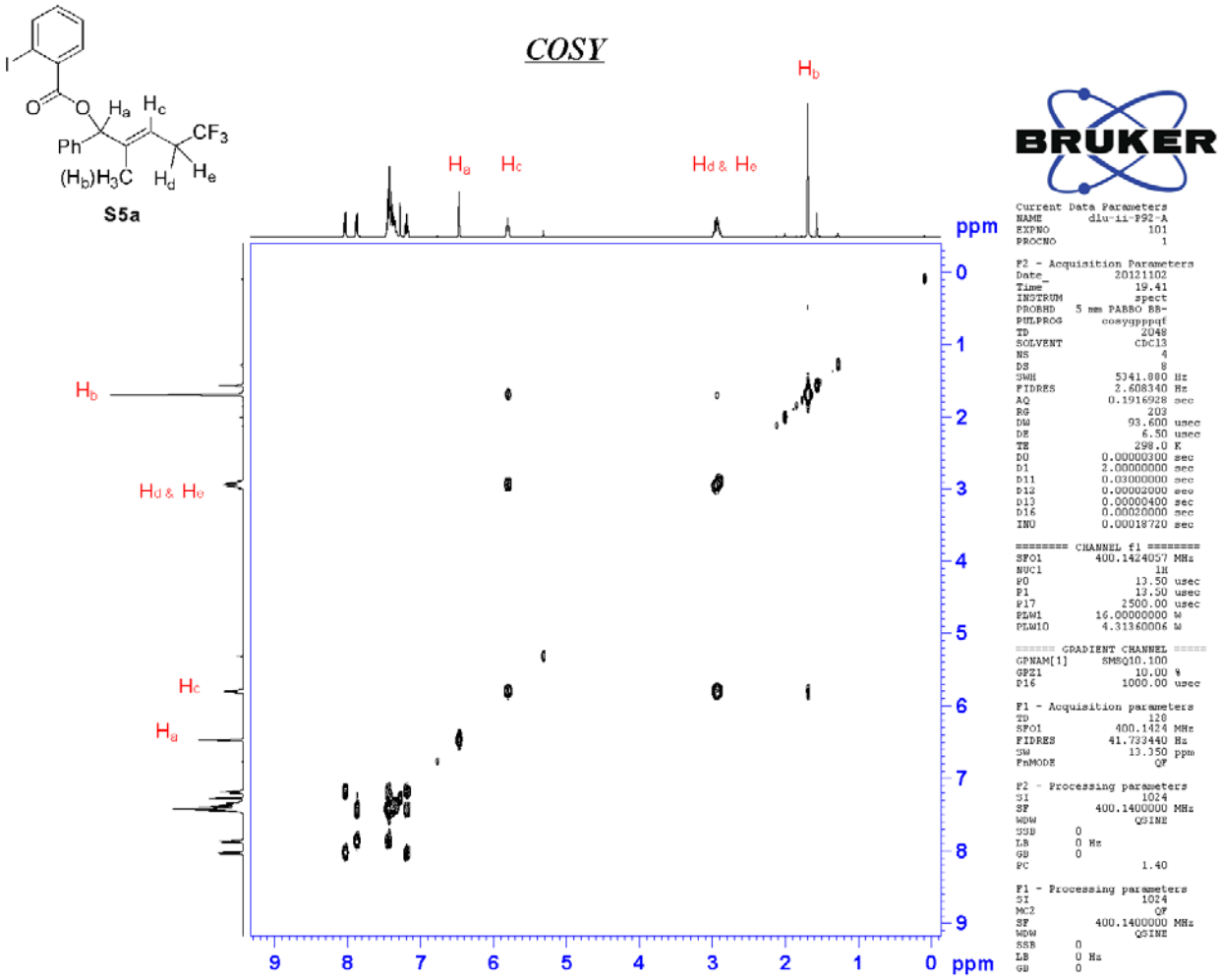
^{19}F NMR (377 MHz, $CDCl_3$)

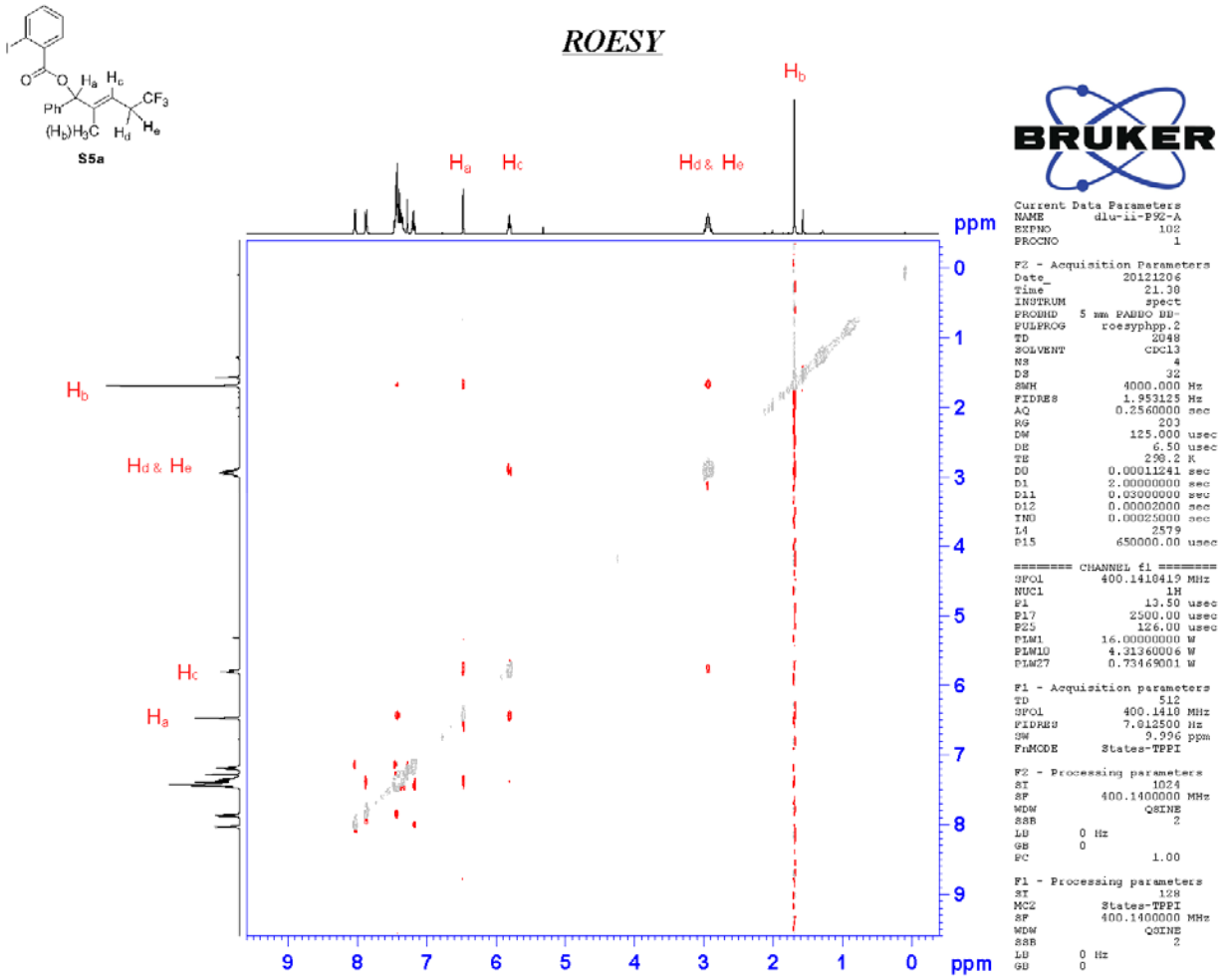
-65.806
-65.834
-65.863



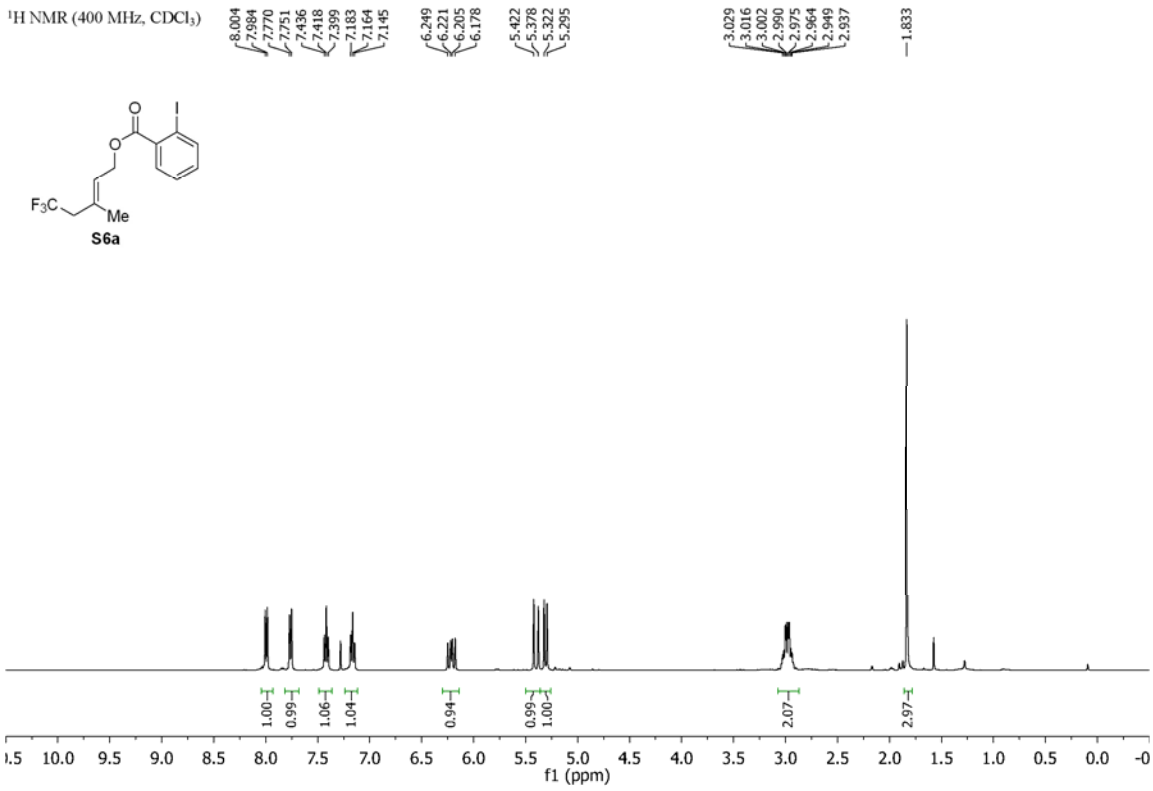
S5a




COSY
S5a
Ha
Hc
Hb
Hd & He
ppm
0
1
2
3
4
5
6
7
8
9
BRUKER
Current Data Parameters
NAME dlu-ii-P92-A
EXPNO 101
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121102
Time 19.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpppqf
TD 2048
SOLVENT CDCl3
NS 4
DS 8
SWH 5341.880 Hz
FIDRES 2.608340 Hz
AQ 0.1916928 sec
RG 203
DW 93.600 usec
DE 6.50 usec
TE 298.0 K
D0 0.00000300 sec
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D13 0.00000400 sec
D16 0.00020000 sec
INU 0.00018720 sec
======== CHANNEL f1 ========
SFO1 400.1424057 MHz
NUC1 1H
P0 13.50 usec
P1 12.50 usec
P17 2500.00 usec
PLW1 16.00000000 W
PLW10 4.31360006 W
====== GRADIENT CHANNEL =====
GPNAM[1] SMSQ10.100
GPZ1 10.00 %
P16 1000.00 usec
F1 - Acquisition parameters
TD 128
SFO1 400.1424 MHz
FIDRES 41.733440 Hz
SW 13.350 ppm
FnMODE QF
F2 - Processing parameters
SI 1024
SF 400.1400000 MHz
WDW QSINE
SSB 0
LB 0 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1400000 MHz
WDW QSINE
SSB 0
LB 0 Hz
GB 0

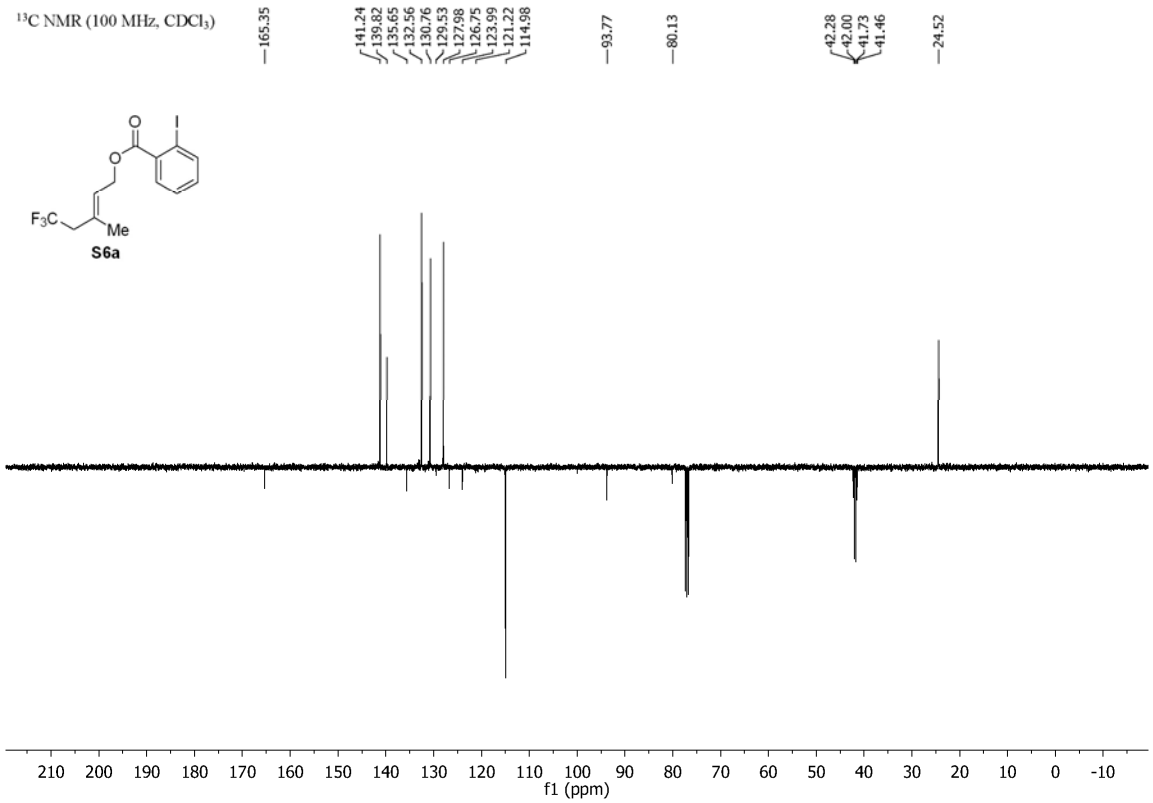

ROESY
S5a
Ha
Hc
Hd & He
Hb
ppm
BRUKER
Current Data Parameters
NAME dlu-ii-P92-A
EXPNO 102
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121206
Time 21.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG roesyphpp.2
TD 2048
SOLVENT CDCl3
NS 4
DS 32
SWH 4000.000 Hz
FIDRES 1.953125 Hz
AQ 0.2560000 sec
RG 203
DW 125.000 usec
DE 6.50 usec
TE 298.2 K
D0 0.00011241 sec
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TN0 0.00025000 sec
L4 2579
P15 650000.00 usec
======== CHANNEL f1 ========
SFO1 400.1410419 MHz
NUC1 1H
P1 13.50 usec
PL7 2500.00 usec
PL25 126.00 usec
PLW1 16.00000000 W
PLW10 4.31360006 W
PLW27 0.73469001 W
F1 - Acquisition parameters
TD 512
SFO1 400.1410 MHz
FIDRES 7.812500 Hz
SW 9.996 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 1024
SF 400.1400000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 128
MC2 States-TPPI
SF 400.1400000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NMR (400 MHz, $CDCl_3$)



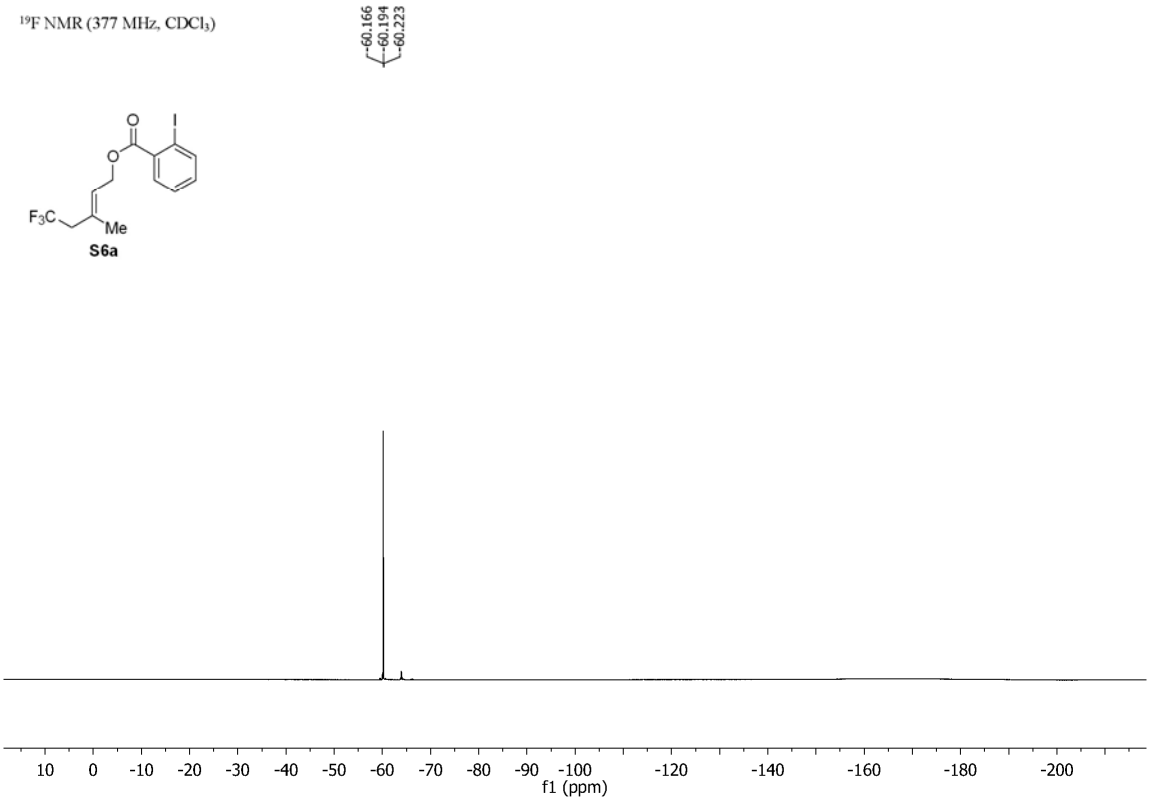
S6a

^{13}C NMR (100 MHz, $CDCl_3$)

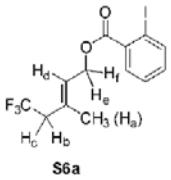


S6a

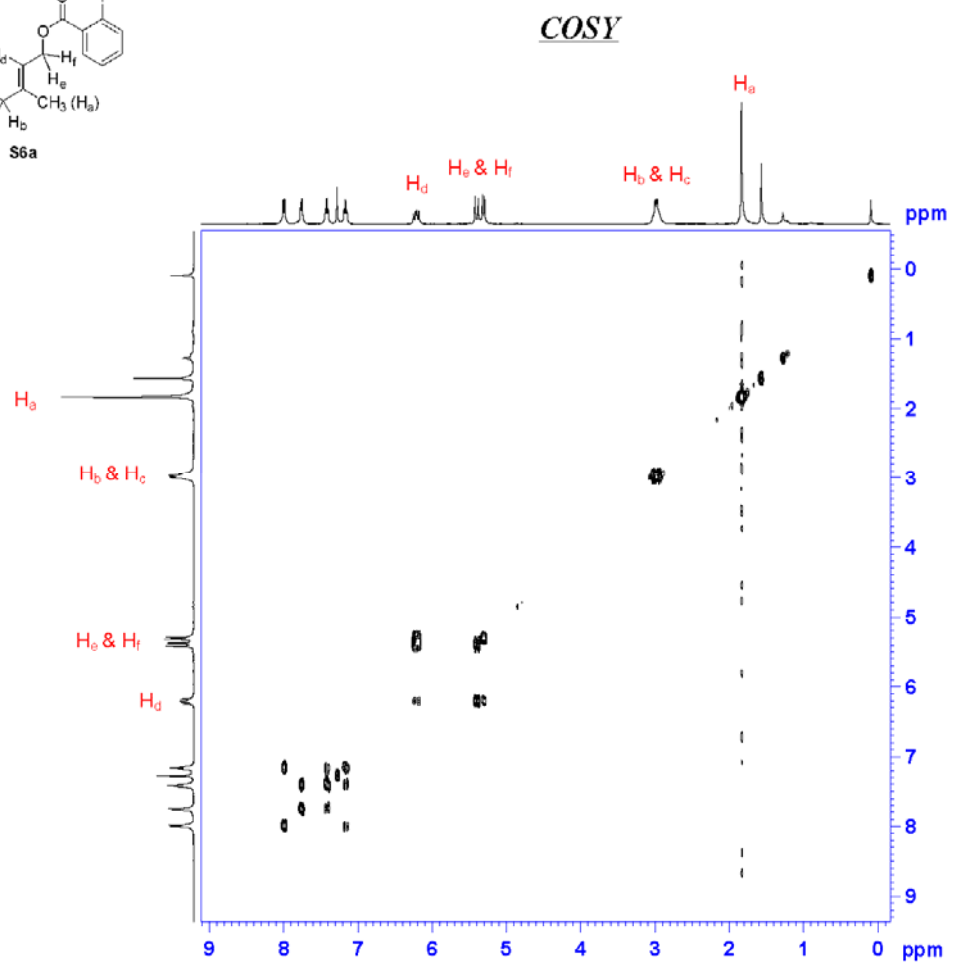
^{19}F NMR (377 MHz, $CDCl_3$)



S6a



S6a

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Current Data Parameters
NAME      dlu-101712-ii-p60
EXPNO              101
PROCNO               1

F2 - Acquisition Parameters
Date_          20121010
Time              12.19
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpppqf
TD                2048
SOLVENT           CDCl3
NS                   2
DS                   8
SWH            5341.880 Hz
FIDRES         2.608340 Hz
AQ             0.1916928 sec
RG                 203
DW              93.600 usec
DE               6.50 usec
TE              298.8 K
D0           0.00000300 sec
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00018720 sec

======== CHANNEL f1 ========
SFO1        400.1424057 MHz
NUC1              1H
P0               13.50 usec
P1               13.50 usec
P17            2500.00 usec
PLW1        16.00000000 W
PLW10        4.31360006 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1             10.00 %
P16            1000.00 usec

F1 - Acquisition parameters
TD                128
SFO1        400.1424 MHz
FIDRES       41.733440 Hz
SW           13.350 ppm
FnMODE            QF

F2 - Processing parameters
SI               1024
SF          400.1400000 MHz
WDW              QSINE
SSB       0
LB        0 Hz
GB        0
PC                1.00

F1 - Processing parameters
SI               1024
MC2               QF
SF          400.1400000 MHz
WDW              QSINE
SSB       0
LB        0 Hz
GB        0
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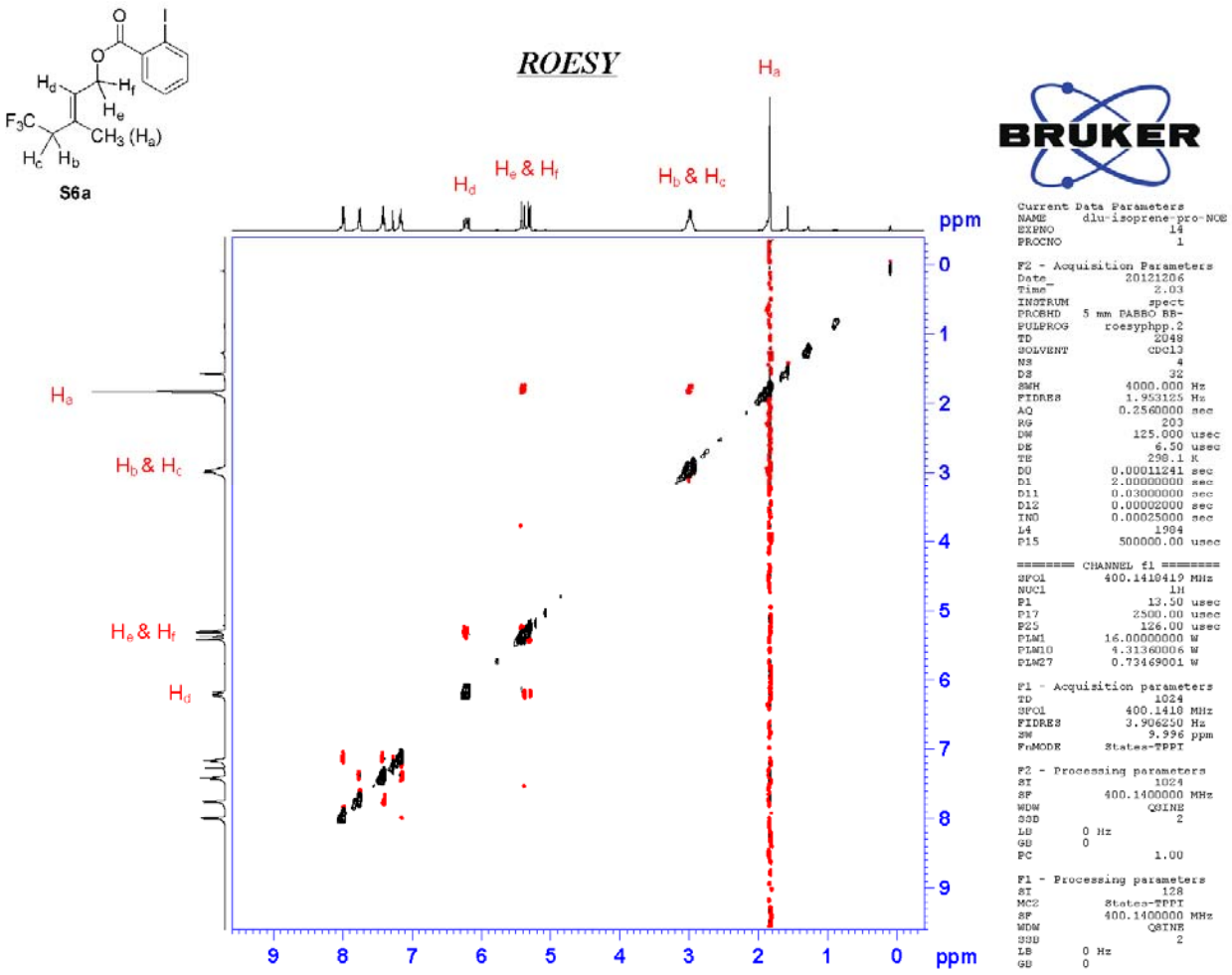
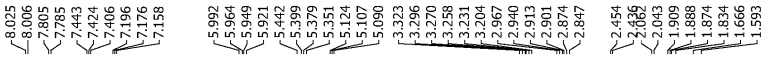
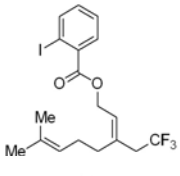
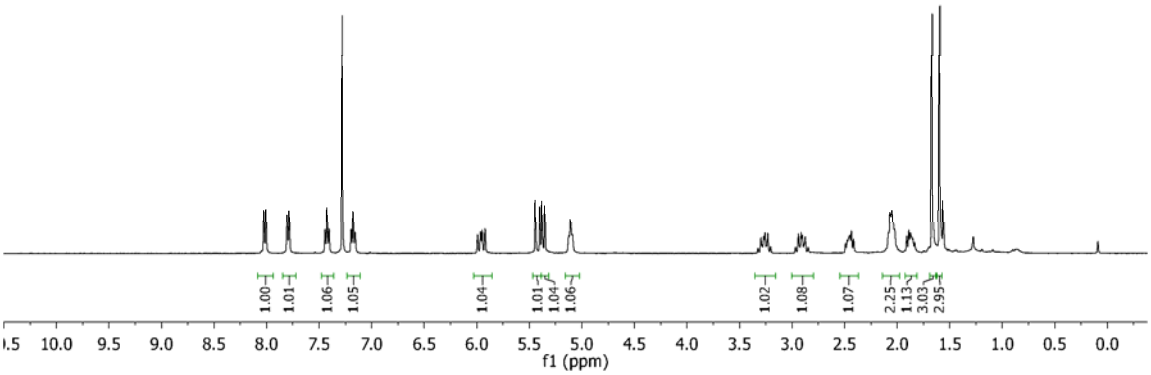

S6a
ROESY
Hd
He & Hf
Hb & Hc
Ha
ppm
Ha
Hb & Hc
He & Hf
Hd
BRUKER
Current Data Parameters
NAME dlu-isoprene-pro-NOE
EXPNO 14
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121206
Time 2.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG roesyphpp.2
TD 2048
SOLVENT CDCl3
NS 4
DS 32
SWH 4000.000 Hz
FIDRES 1.953125 Hz
AQ 0.2560000 sec
RG 203
DW 125.000 usec
DE 6.50 usec
TE 298.1 K
D0 0.00011241 sec
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
IN0 0.00025000 sec
L4 1984
P15 500000.00 usec
======== CHANNEL f1 ========
SFO1 400.1410419 MHz
NUC1 1H
P1 13.50 usec
P17 2500.00 usec
P25 126.00 usec
PLW1 16.00000000 W
PLW10 4.31360006 W
PLW27 0.73469001 W
F1 - Acquisition parameters
TD 1024
SFO1 400.1410 MHz
FIDRES 3.906250 Hz
SW 9.996 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 1024
SF 400.1400000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 128
MC2 States-TPPI
SF 400.1400000 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

^{1}H NMR (400 MHz, $CDCl_3$)

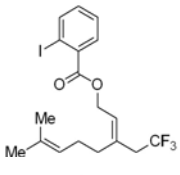




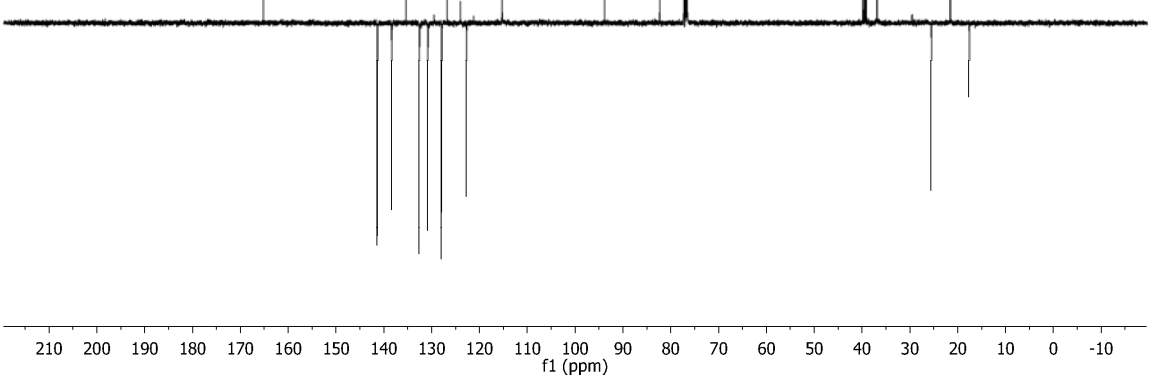
S7a



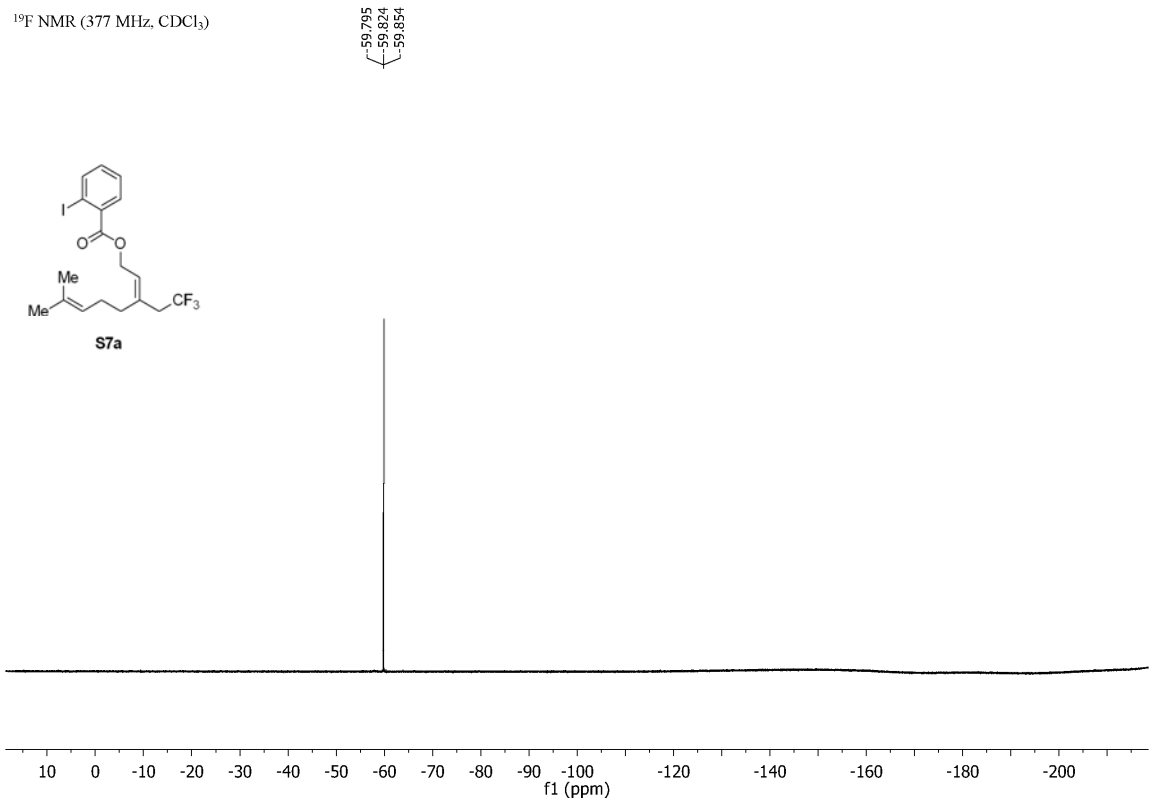
^{13}C NMR (100 MHz, $CDCl_3$)



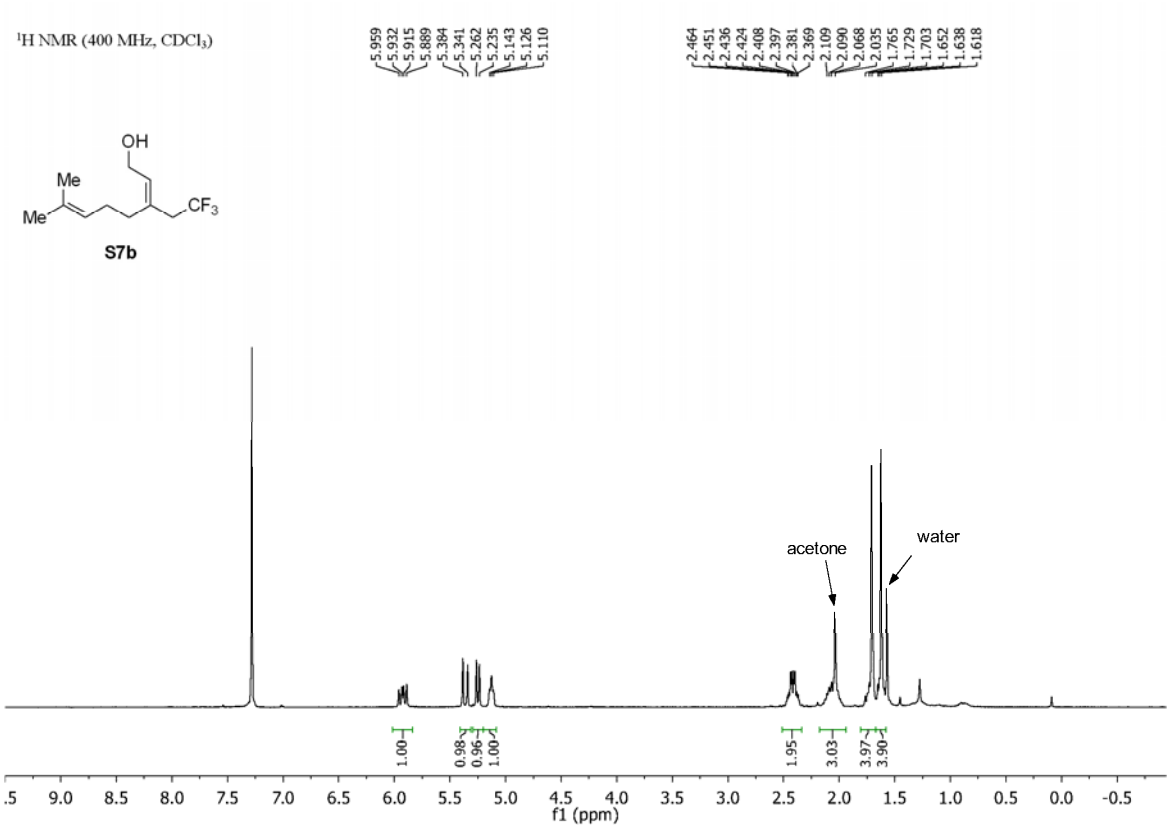
S7a

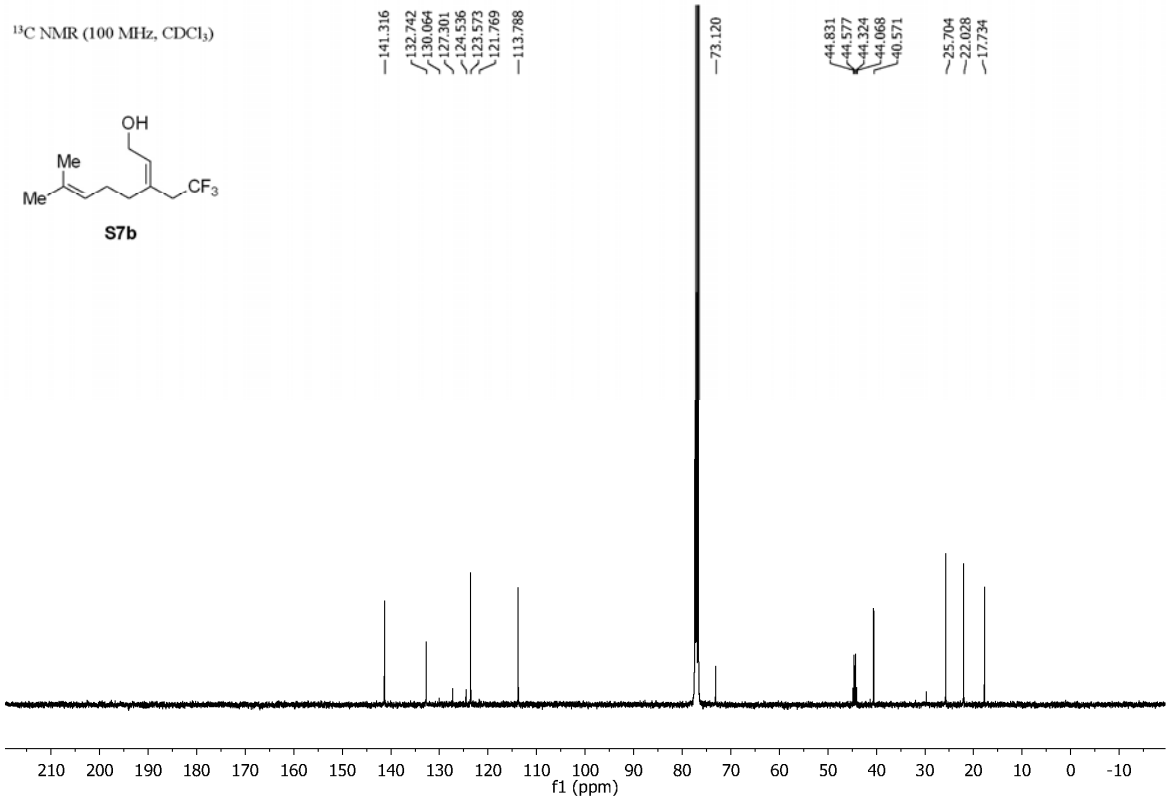


^{19}F NMR (377 MHz, $CDCl_3$)



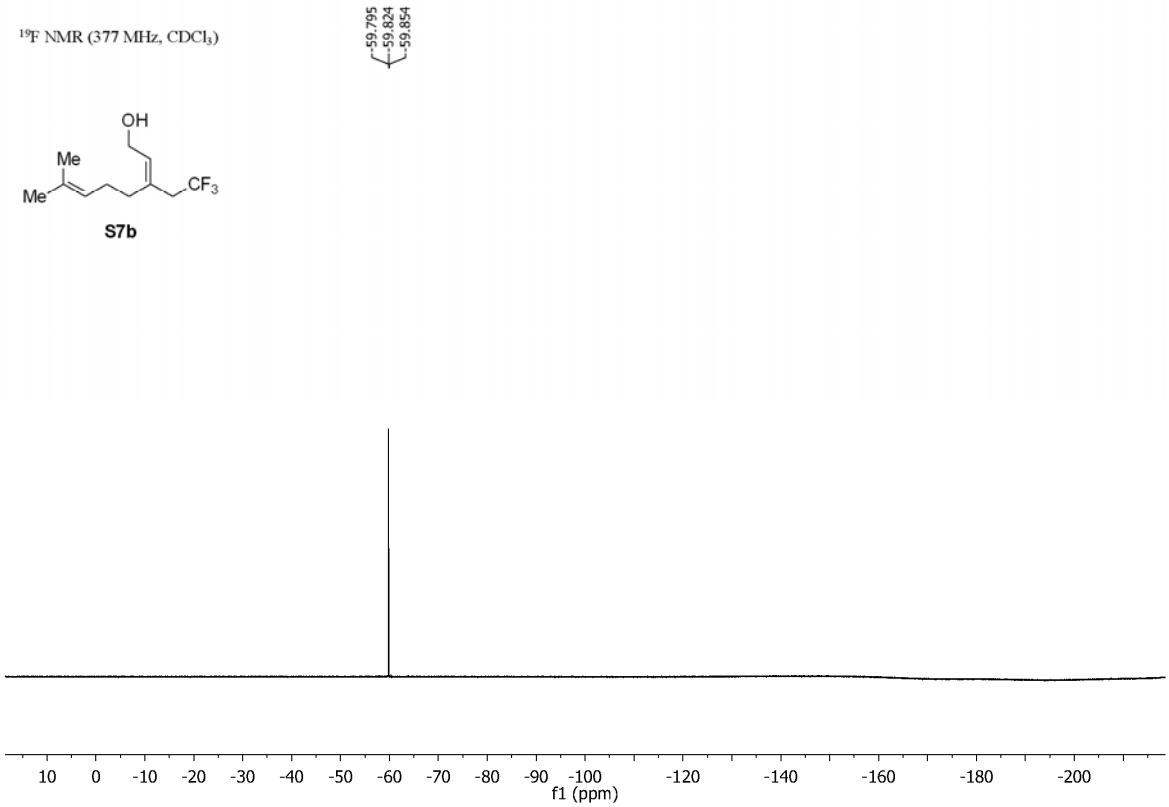
S7a

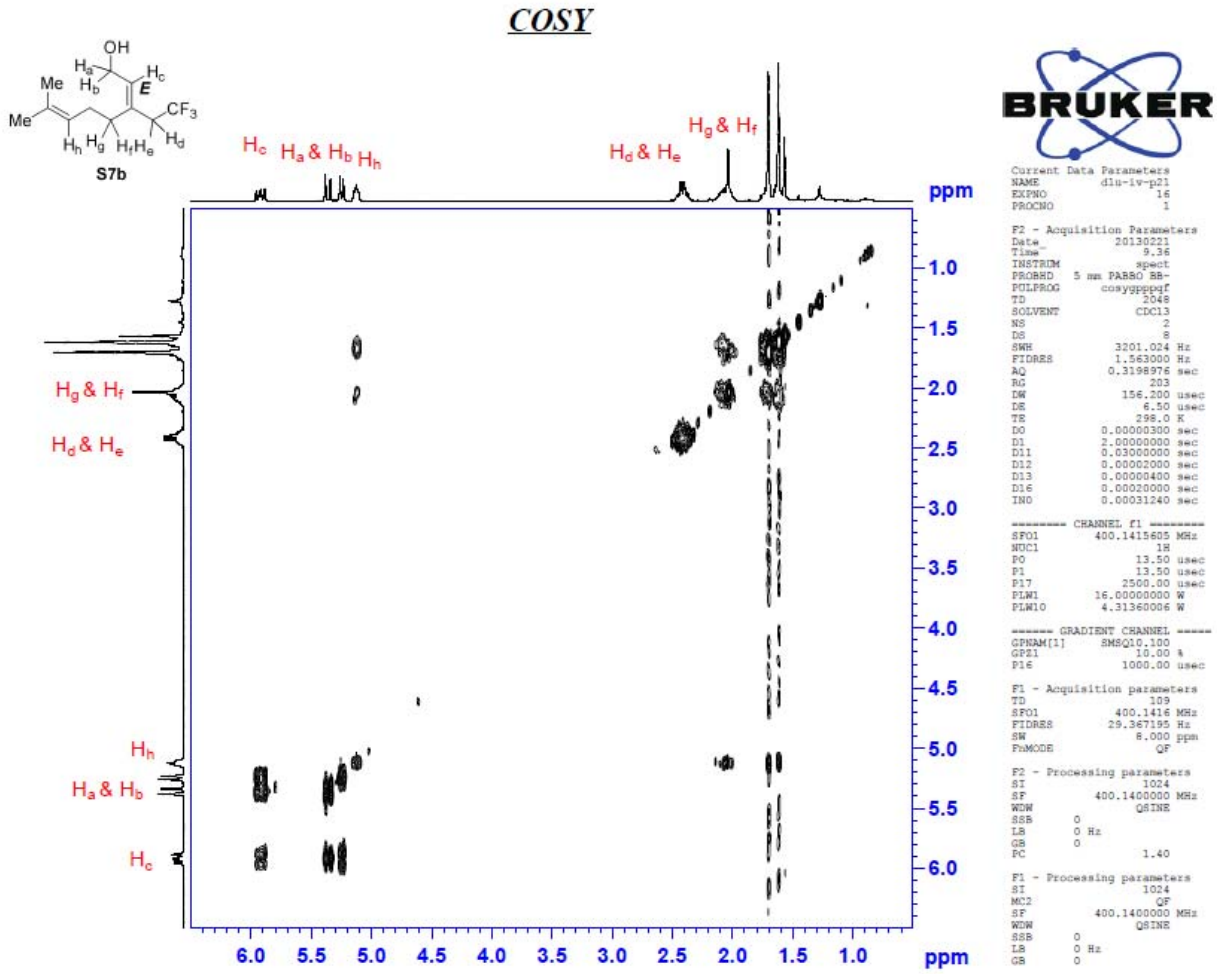

^{1}H NMR (400 MHz, CDCl$_3$)
5.959
5.932
5.915
5.889
5.384
5.341
5.262
5.235
5.143
5.126
5.110
2.464
2.451
2.436
2.424
2.408
2.397
2.381
2.369
2.109
2.090
2.068
2.035
1.765
1.729
1.703
1.652
1.638
1.618
OH
Me
Me
CF3
S7b
acetone
water
1.00
0.98
0.96
1.00
1.95
3.03
3.97
3.90
f1 (ppm)

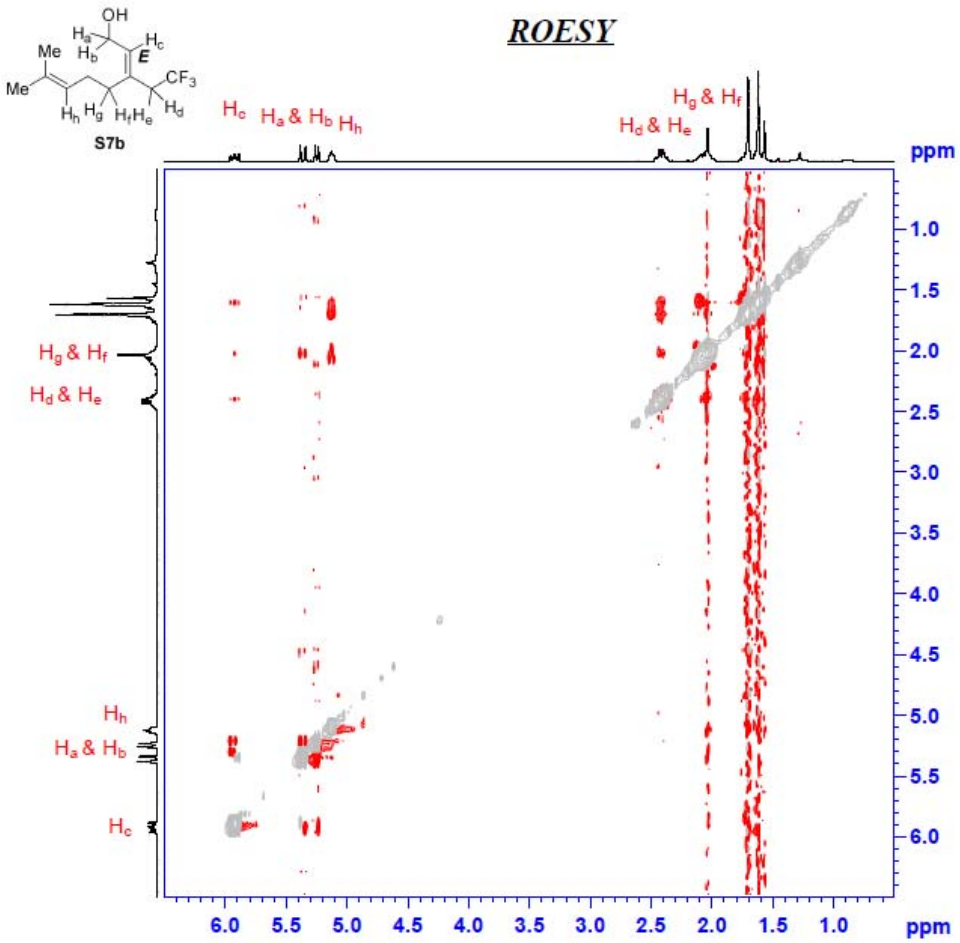

^{13}C NMR (100 MHz, CDCl$_3$)
141.316
132.742
130.064
127.301
124.536
123.573
121.769
113.788
73.120
44.831
44.577
44.324
44.068
40.571
25.704
22.028
17.734
OH
Me
Me
CF3
S7b
f1 (ppm)

^{19}F NMR (377 MHz, $CDCl_3$)

S7b




COSY
S7b
Hc
Ha & Hb
Hh
Hd & He
Hg & Hf
Hg & Hf
Hd & He
Hh
Ha & Hb
Hc
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
BRUKER
Current Data Parameters
NAME dlu-1v-p21
EXPNO 16
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130221
Time 9.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpppqf
TD 2048
SOLVENT CDCl3
NS 2
DS 8
SWH 3201.024 Hz
FIDRES 1.563000 Hz
AQ 0.3198976 sec
RG 203
DW 156.200 usec
DE 6.50 usec
TE 298.0 K
D0 0.00000300 sec
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00031240 sec
======== CHANNEL f1 ========
SFO1 400.1415605 MHz
NUC1 1H
P0 13.50 usec
P1 13.50 usec
P17 2500.00 usec
PLW1 16.00000000 W
PLW10 4.31360006 W
====== GRADIENT CHANNEL =====
GPNAM[1] SMSQ10.100
GPZ1 10.00 %
P16 1000.00 usec
F1 - Acquisition parameters
TD 109
SFO1 400.1416 MHz
FIDRES 29.367195 Hz
SW 6.000 ppm
FnMODE QF
F2 - Processing parameters
SI 1024
SF 400.1400000 MHz
WDW QSINE
SSB 0
LB 0 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1400000 MHz
WDW QSINE
SSB 0
LB 0 Hz
GB 0

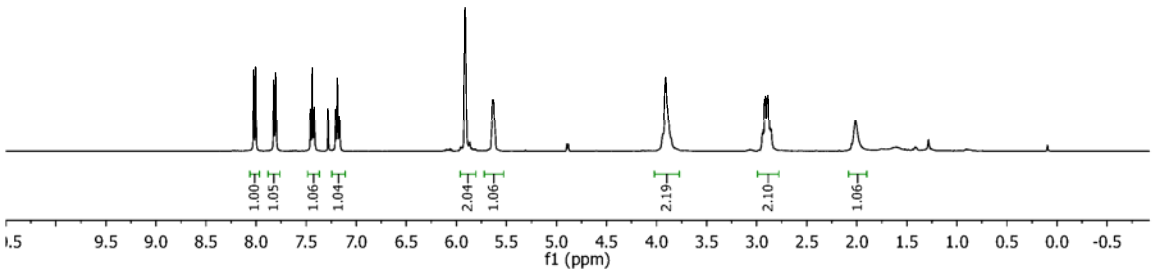


BRUKER

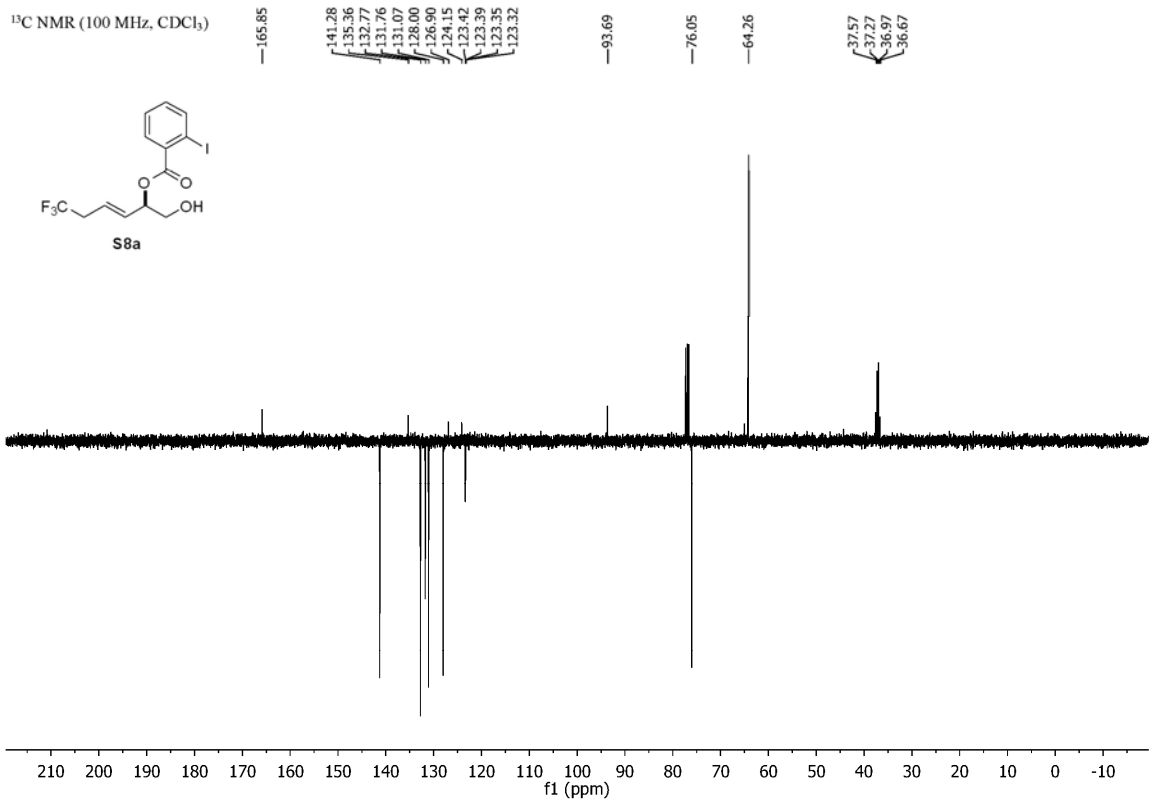
```
Current Data Parameters
NAME                 dlu-iv-p21
EXPNO                        19
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20130223
Time                       1.37
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG          roesyphpp.2
TD                         2048
SOLVENT                  CDCl3
NS                            8
DS                            8
SWH                  2400.768 Hz
FIDRES               1.172250 Hz
AQ                   0.4265301 sec
RG                          203
DW                   208.267 usec
DE                     6.50 usec
TE                     298.2 K
D0                   0.00019571 sec
D1                   2.00000000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec
IN0                  0.00041660 sec
L4                         3175
P15                800000.00 usec

======== CHANNEL f1 ========
SFO1                400.1414005 MHz
NUC1                        1H
P1                       13.50 usec
P17                    2500.00 usec
P25                     126.00 usec
PLW1                16.00000000 W
PLW10                4.31360006 W
PLW27                0.73469001 W

F1 - Acquisition parameters
TD                          512
SFO1                400.1414 MHz
FIDRES               4.688250 Hz
SW                       5.999 ppm
FnMODE           States-TPPI

F2 - Processing parameters
SI                         1024
SF                  400.1400000 MHz
WDW                       QSINE
SSB                           2
LB          0 Hz
GB          0
PC                        1.00

F1 - Processing parameters
SI                          128
MC2              States-TPPI
SF                  400.1400000 MHz
WDW                       QSINE
SSB                           2
LB          0 Hz
GB          0
```

^{1}H NMR (400 MHz, $CDCl_3$)

S8a



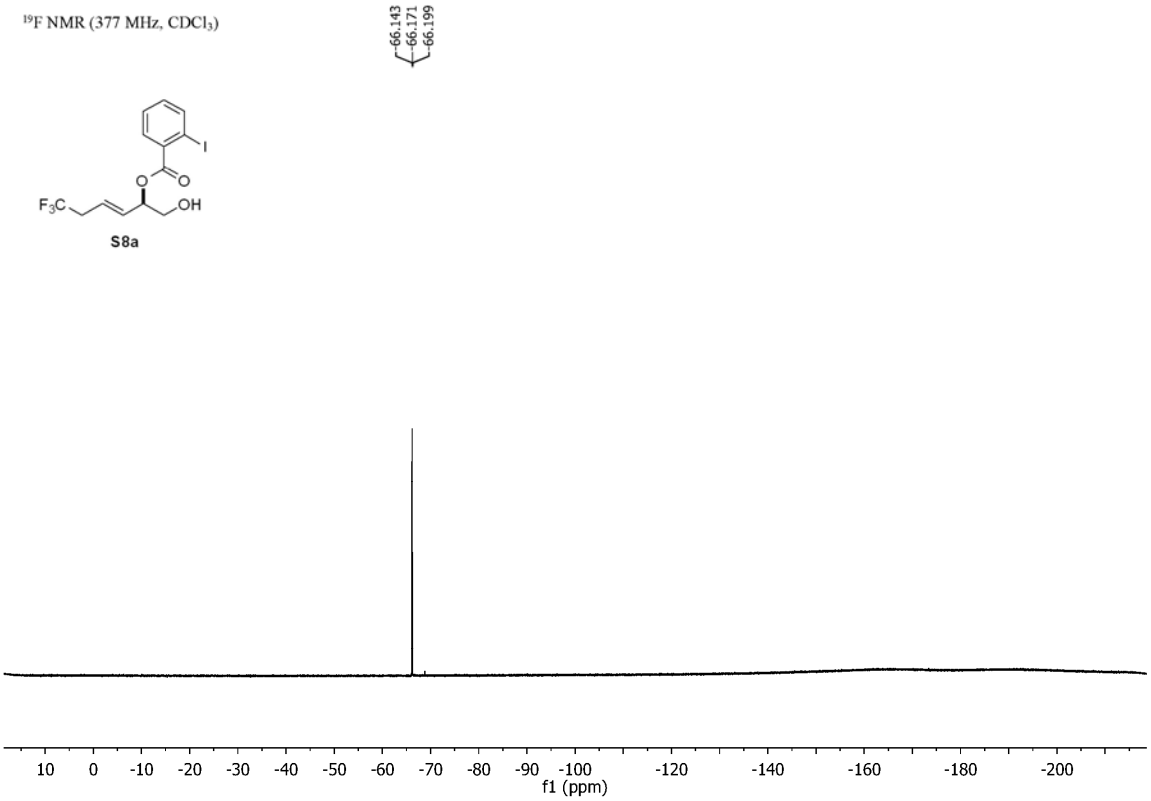
^{13}C NMR (100 MHz, $CDCl_3$)



S8a

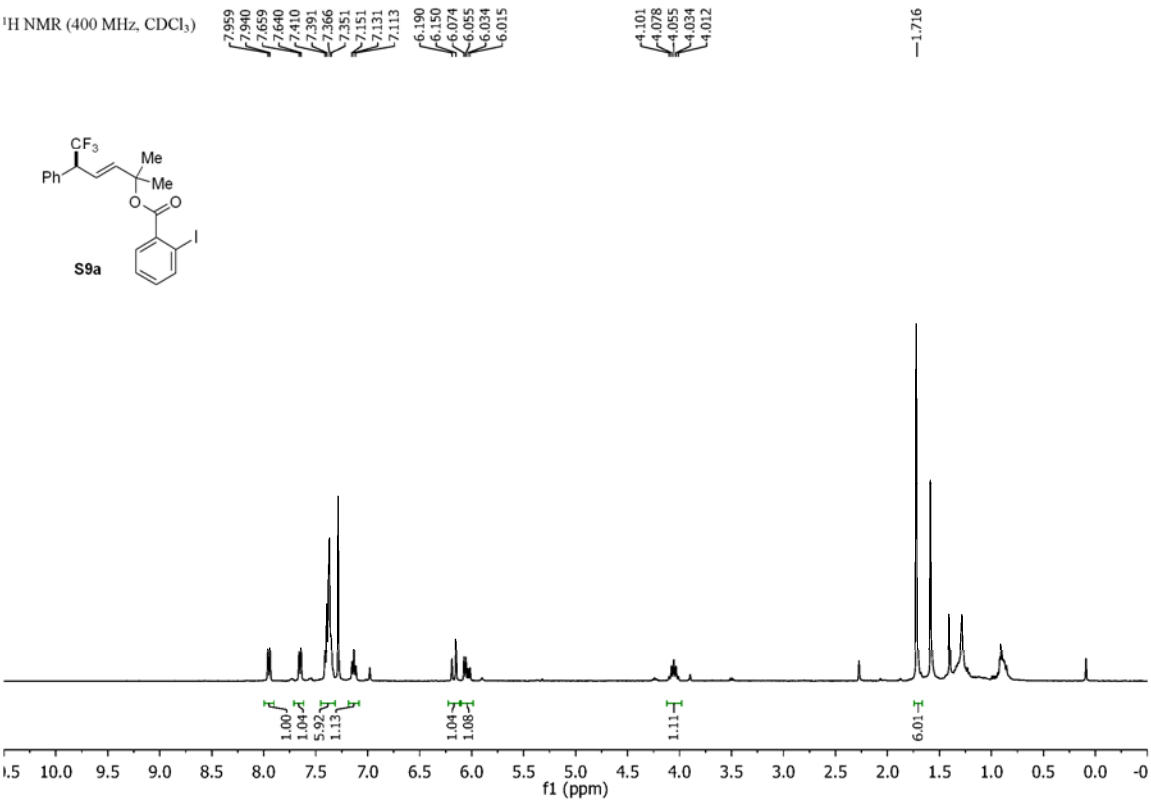
^{19}F NMR (377 MHz, $CDCl_3$)

S8a

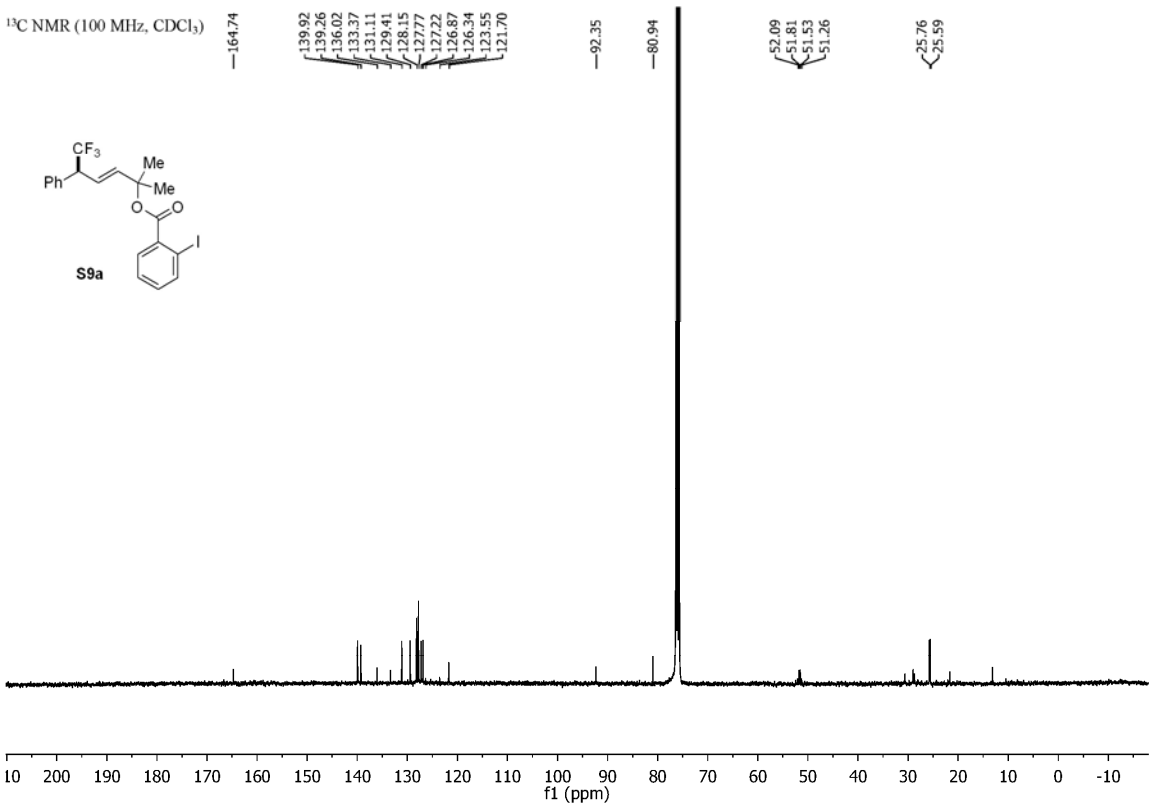


^{1}H NMR (400 MHz, $CDCl_3$)

S9a

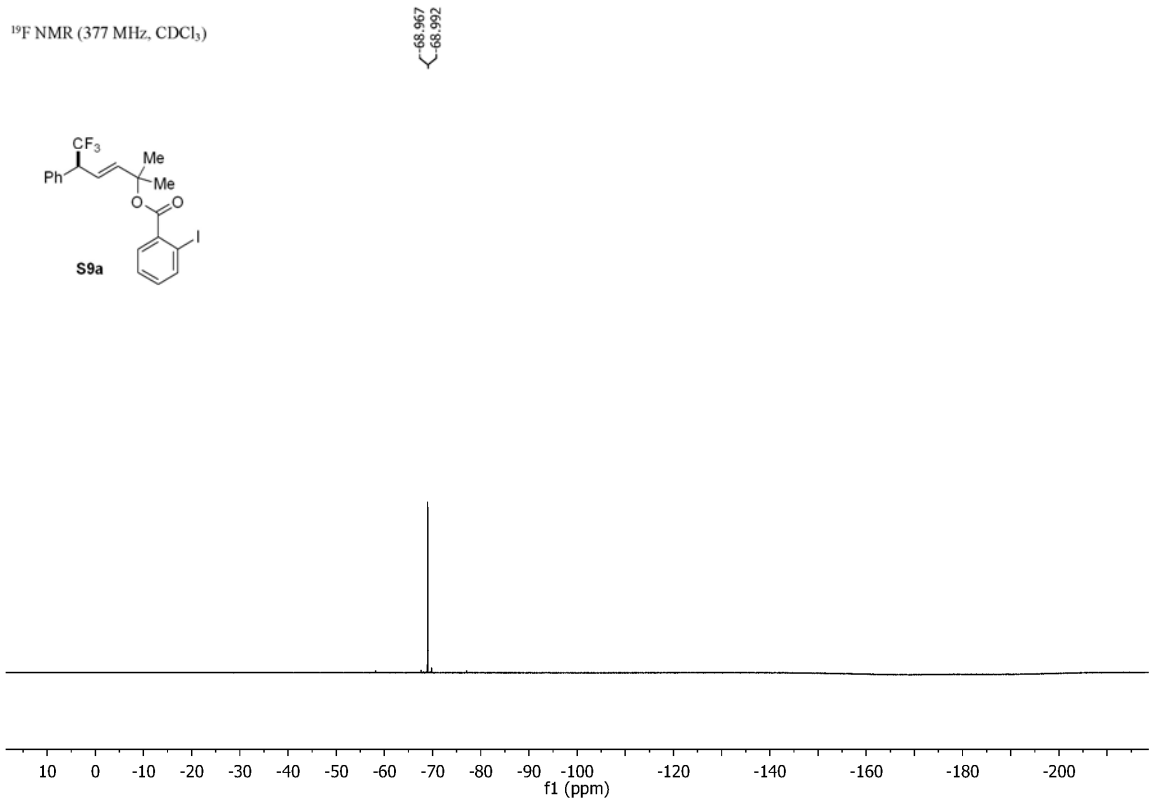


^{13}C NMR (100 MHz, $CDCl_3$)



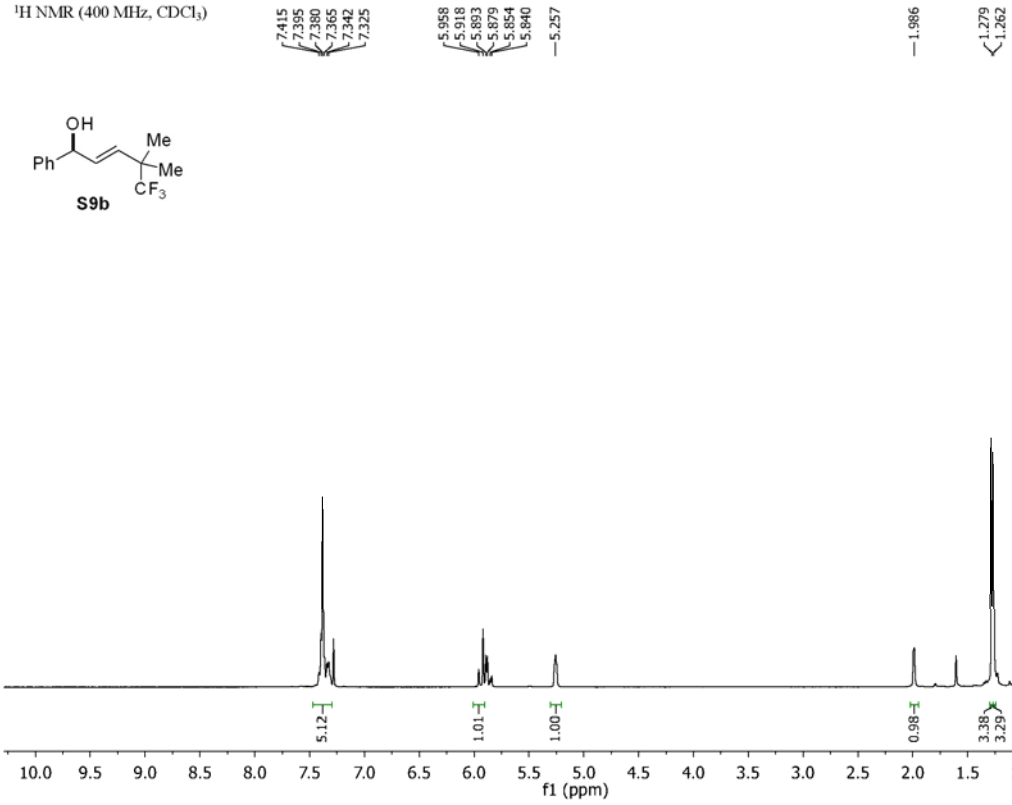
S9a

^{19}F NMR (377 MHz, $CDCl_3$)

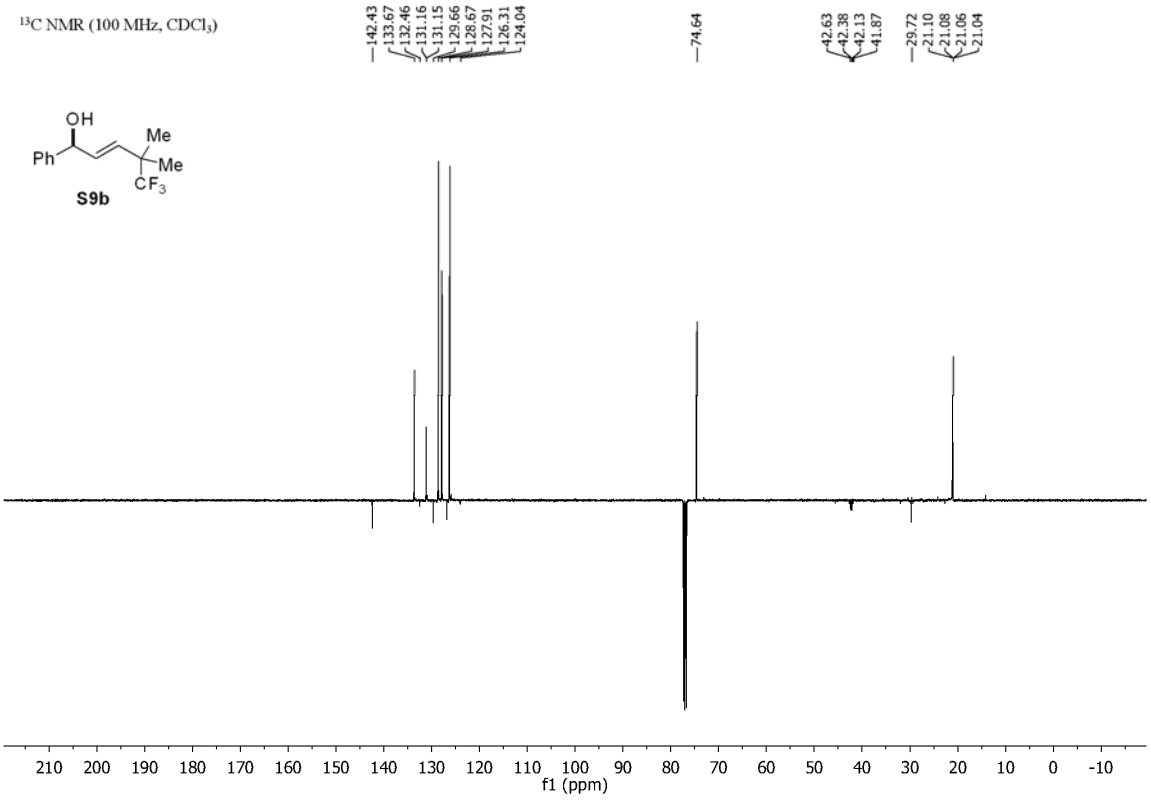


S9a

^{1}H NMR (400 MHz, $CDCl_3$)

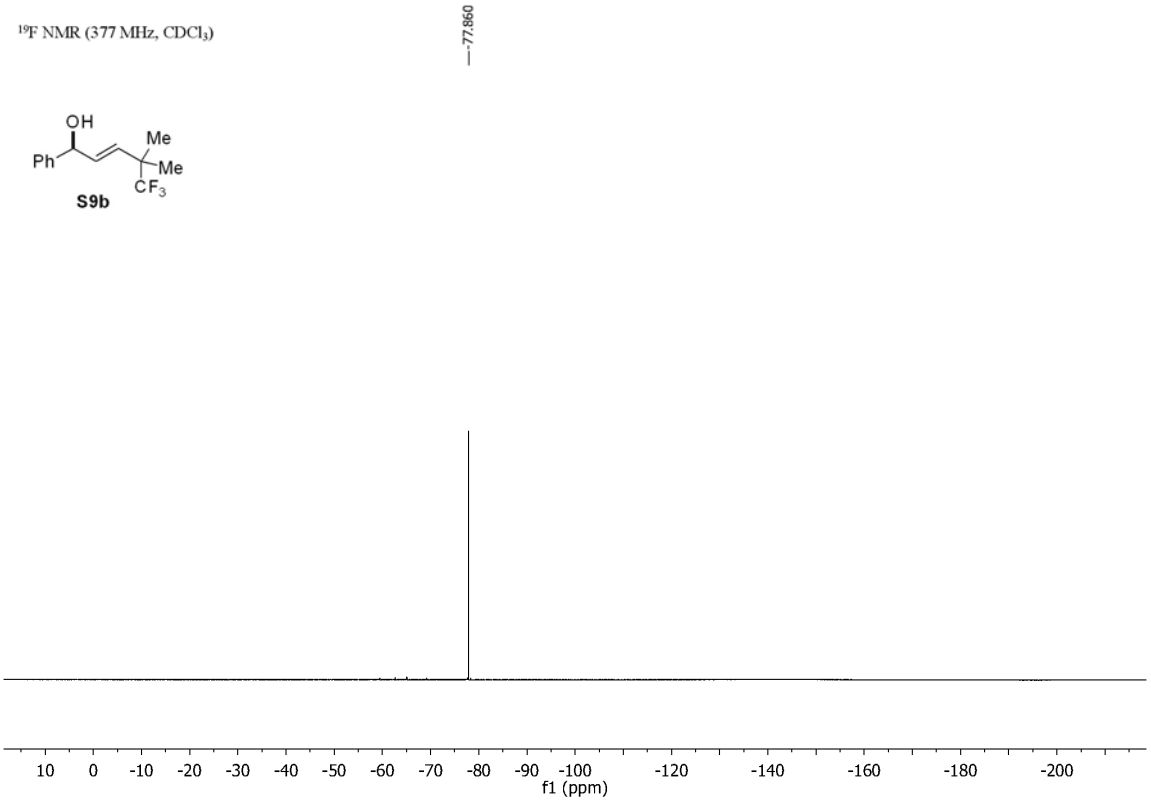


^{13}C NMR (100 MHz, $CDCl_3$)

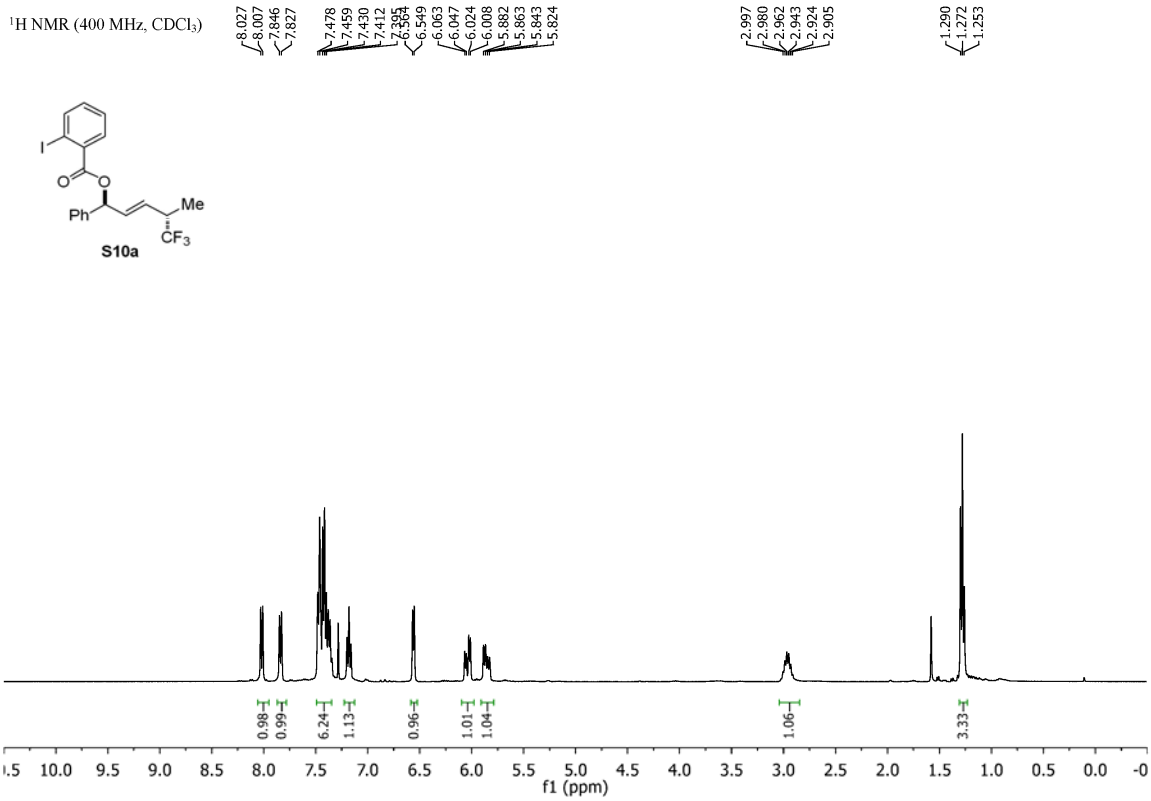


^{19}F NMR (377 MHz, $CDCl_3$)

S9b

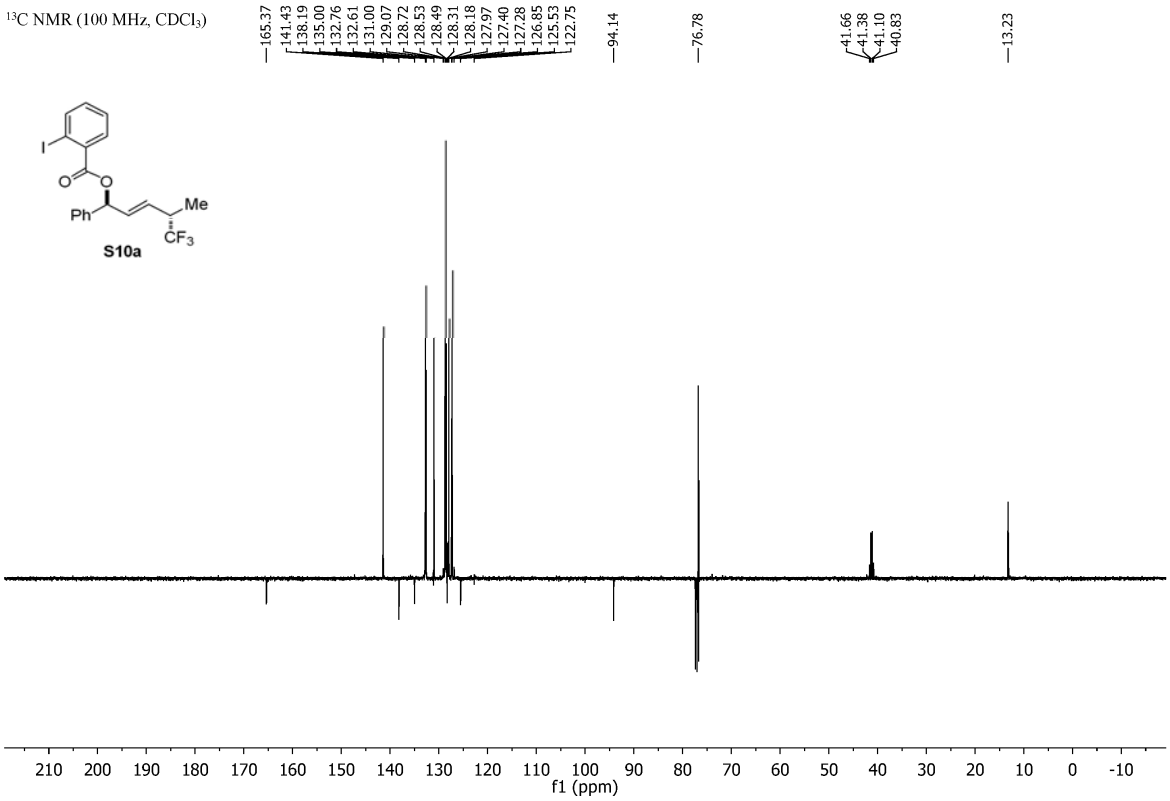


^{1}H NMR (400 MHz, $CDCl_3$)

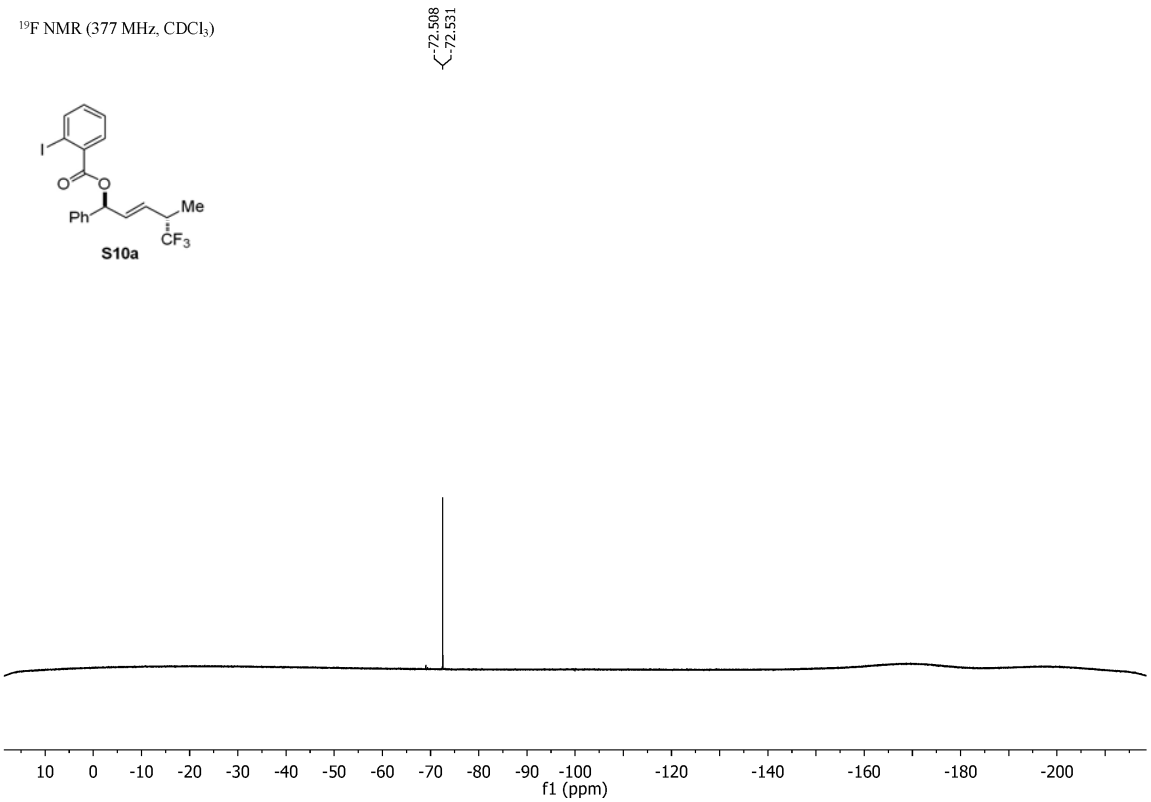


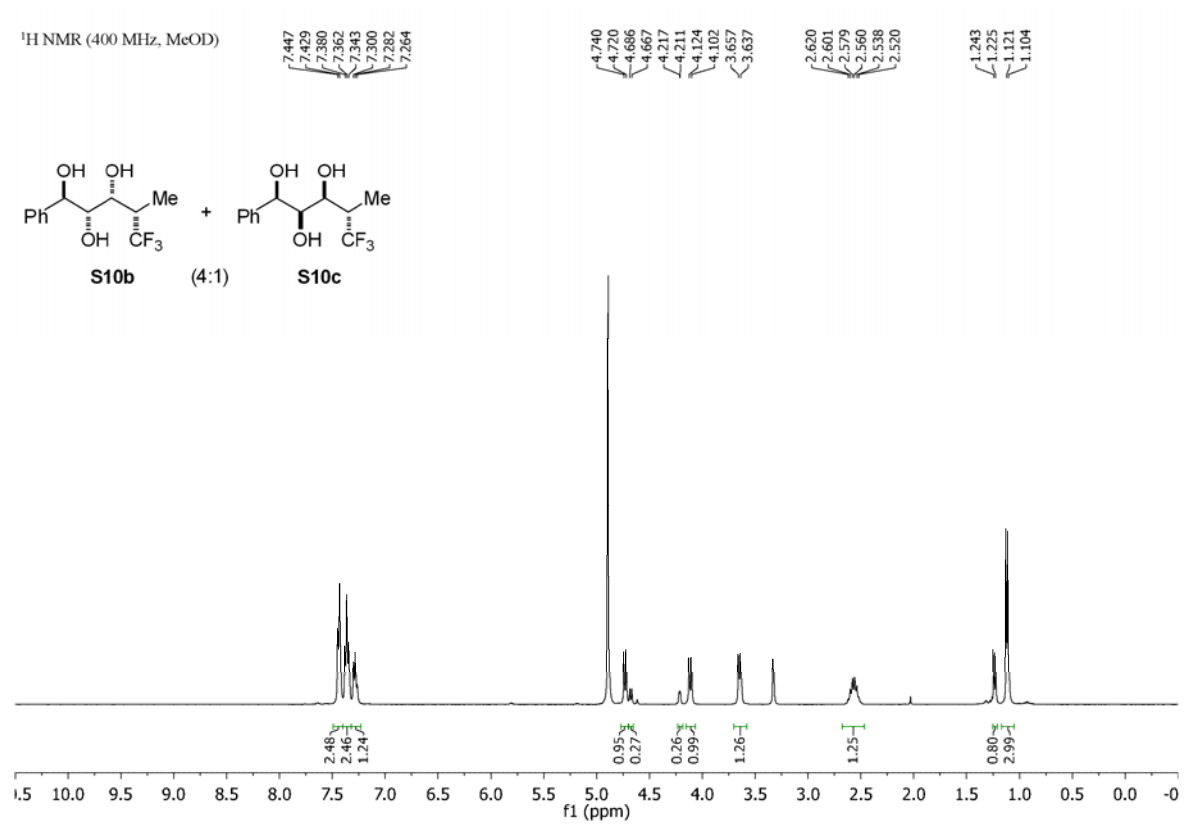
S10a

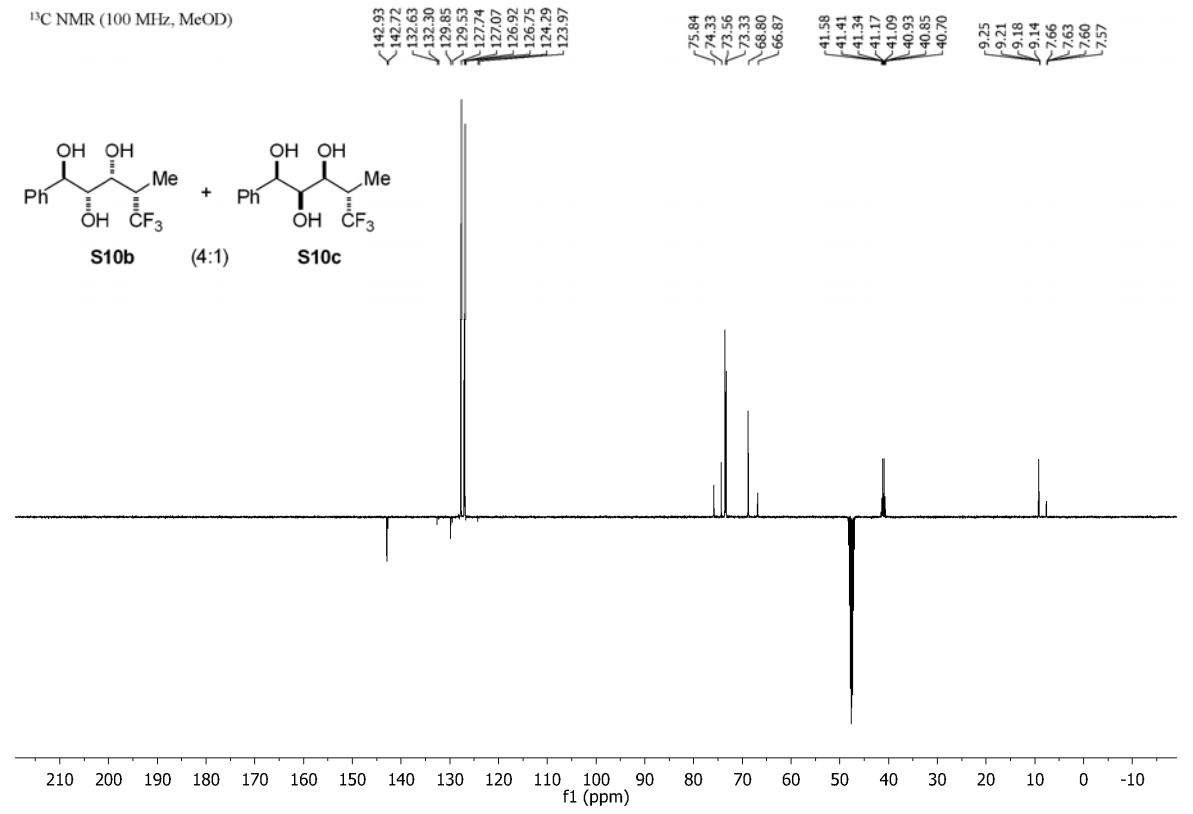
^{13}C NMR (100 MHz, $CDCl_3$)



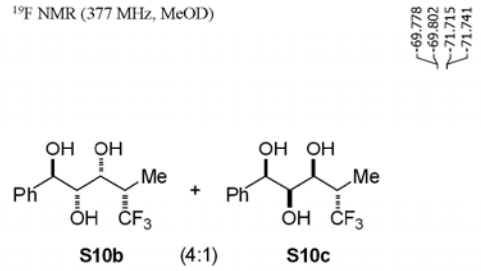
^{19}F NMR (377 MHz, $CDCl_3$)




¹H NMR (400 MHz, MeOD)
7.447
7.429
7.380
7.362
7.343
7.300
7.282
7.264
4.740
4.720
4.686
4.667
4.217
4.211
4.124
4.102
3.657
3.637
2.620
2.601
2.579
2.560
2.538
2.520
1.243
1.225
1.121
1.104
OH OH Me
Ph
OH CF3
+
S10b (4:1) S10c
2.48
2.46
1.24
0.95
0.27
0.26
0.99
1.26
1.25
0.80
2.99
f1 (ppm)


¹³C NMR (100 MHz, MeOD)
142.93
142.72
132.63
132.30
129.85
129.53
127.74
127.07
126.92
126.75
124.29
123.97
75.84
74.33
73.56
73.33
68.80
66.87
41.58
41.41
41.34
41.17
41.09
40.93
40.85
40.70
9.25
9.21
9.18
9.14
7.66
7.63
7.60
7.57
OH OH Me
Ph
OH CF3
+
S10b (4:1) S10c
f1 (ppm)

^{19}F NMR (377 MHz, MeOD)



S10b (4:1) **S10c**