Base-Catalyzed Stereospecific Isomerization of Electron-Deficient Allylic Alcohols and Ethers through Ion-Pairing

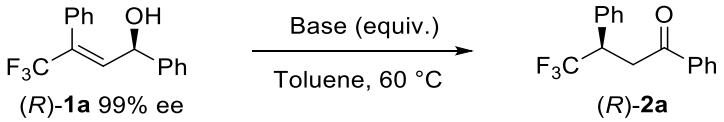
*Samuel Martinez-Erro,‡ Amparo Sanz-Marco,‡ Antonio Bermejo Gómez, Ana Vázquez-Romero, Mårten S. G. Ahlquist, and Belén Martín-Matute**

Supporting Information

Table of contents

Optimization Studies

Table S1. Screening studies of the isomerization of allylic alcohol (*R*)-**1a**.[a]

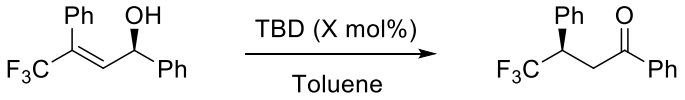


(*R*)-**1a** 99% ee (*R*)-**2a**

Entry	Base	Equiv. of base	t [h]	Conv [%][b]	Yield [%][c]	*ee* [%]
1	Cs_2CO_3	1.2	18	65	45	84
2	NaH	1.2	2	25	20	80
3	*t*-BuOK	1.2	2	>99	33	89
4	*t*-BuOK	0.1	18	12	n.d.[d]	89
5	KHMDS	1.2	18	>99[e]	15	n.d.[d]
6	DMAP	1.2	18	<1	n.d.[d]	n.d.[d]
7	DABCO	1.2	18	<1	n.d.[d]	n.d.[d]
8	Proton Sponge	1.2	18	<1	n.d.[d]	n.d.[d]
9	DBU	1.2	18	80	80	85
10	DBU	0.1	18	18	n.d.[d]	88
11[f]	TBD[g]	1.2	18	>99	>99	54
12	TBD[g,h]	1.2	18	>99	>99	46
13[f]	**TBD**[g]	**0.1**	**18**	**>99**	**>99**	**90**
14	MTBD[i]	1,2	18	42	40	n.d.[d]
15	MTBD[i]	0.1	18	4	n.d.[d]	n.d.[d]
16	TMG[j]	1.2	18	<1	n.d.[d]	n.d.[d]

[a] Unless otherwise noted, the reactions were run using **1a** (0.165 mmol) in toluene (degassed, 1.65 mL) under Ar at 60 °C. [b] Determined by ^{19}F NMR spectroscopy. [c] With an I.S. (trifluorotoluene). [d] Not determined. [e] Decomposition. [f] Reaction under air atmosphere. [g] 1,5,7-Triazabicyclo[4.4.0]dec-5-ene. [h] The reaction was performed in THF. [i] 7-Methyl-1,5,7-Triazabicyclo[4.4.0]dec-5-ene. [j] 1,1,3,3-Tetramethylguanidine.

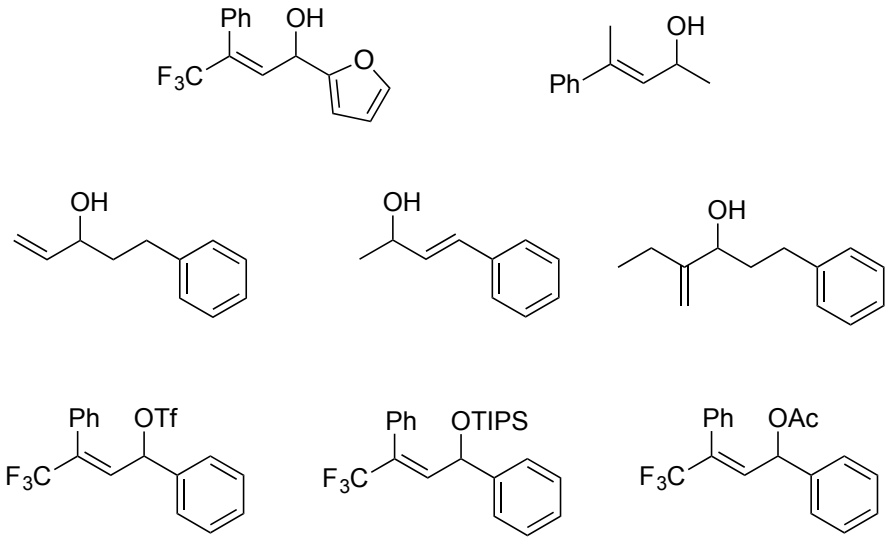
Table S2. Optimization of the enantiospecific TBD-catalyzed isomerization of (*R*)-**1a**.



(*R*)-**1a** 99% *ee* (*R*)-**2a**

Entry	TBD [mol%]	T [°C]	Solvent	t [h]	Yield [%]	*ee* [%][a]
1	10	60	Toluene	6	85	90
2	5	60	Toluene	18	84	93
3[b]	5	60	Toluene	18	76	-
4[c]	5	60	Toluene	18	84	93
5	2.5	60	Toluene	72	84	94
6	1	60	Toluene	96	14	94
7	**2.5**	**80**	**Toluene**	**18**	**82**	**94(99)**
8	2.5	80	Dioxane	18	71	84
9	2.5	80	FC_6H_5	18	90	86
10	2.5	80	THF	18	30	74
11	2.5	80	CH_2Cl_2	18	28	80
12	2.5	80	CH_3CN	18	27	60

[a] In parenthesis *ee* after recrystallization from hexane / CH_2Cl_2.
[b] 0.05 M [c] 0.25 M



Scheme S1. Unsuccessful substrates.

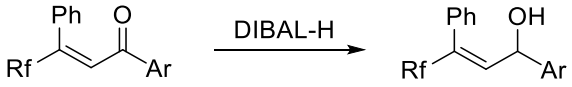
General information:

All reagents were used as obtained from commercial sources without further purification. Flash chromatography was performed with 60 Å (35-70 μm) silica gel (GC 60A 35-70 Micron, DAVISIL) using mixtures pentane/EtOAc as eluent. Analytical TLC was performed on aluminum plates pre-coated (0-25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were detected by exposure to UV light or by revealing the plates in a solution of 5% $KMnO_4$ in water. Melting points were recorded in metal block and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively on a Bruker Advance spectrometer. Chemical shifts (δ) are shown in ppm, using as a reference the residual peaks of $CDCl_3$ (δ_H 7.26 and δ_C 77.00). Coupling constants (J) are given in Hz. NMR yields were calculated using 1 equiv. of 1,3,5-trimethoxybenzene or trifluorotoluene as internal standars. High resolution mass spectra (HRMS) were recorded on Brucker microTOF ESI-TOF mass spectrometer. GC-MS were obtained on Thermo GC Trace + MSQ. Enantiomeric excesses were determined using chiral HPLC Waters 2695 with an autosampler and UV detection. Optical rotations were recorded on a RUDOLPH AUTOPOL IV with an automatic polarimeter and a path length of 100 mm. Substrates **1a**,[1] **1h**,[1] **1i**,[2] **1n**,[1] **1o**,[3] **1r**,[4] **1s**,[5] **1t**,[6] **1u**,[5] **1v**,[7] **3e**,[8] **3f**[9] were synthesized according to methods described in the literature. *N*-d_1-TBD[10] was also synthesized following a protocol from the literature.

Computational details:

All density functional theory calculations were performed with the Jaguar 7.9 program package by Schrödinger LLC. All calculations were performed using the B3LYP-D3 functional with the Grimme dispersion correction. Geometry optimizations and frequency calculations were performed with the 6-31G** basis set. All minima and transition states were verified to have none and one imaginary vibrational frequencies respectively. Solvation free energies were calculated with the SM8 model and the 6-31+G* basis set. Final energy corrections were performed with the larger cc-pVTZ++ basis set (corresponding to aug-cc-pVTZ). The total free energies for every species were calculated as G = E(B3LYP-D3/cc-pVTZ++) + ZPE(B3LYP-D3/6-31G**) + DH_{298}(B3LYP-D3/6-31G**) + G_{solv}(SM8/B3LYP-D3/6-31+G*) – TS_{298}(B3LYP-D3/6-31G**).

General procedure for the synthesis of allylic alcohols 1a-f, 1j-m and 1p-q:[1]



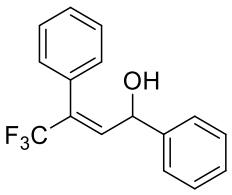
The corresponding enone (1 mmol, 1 equiv.) was dissolved in dry CH_2Cl_2 (2 mL) and DIBAL-H (1 M in hexane, 1.2 mmol, 1.2 mL, 1.2 equiv.) was added at 0 °C under argon atmosphere. The reaction was stirred for 1.5 h and quenched with NH_4Cl saturated aqueous solution and HCl (aq, 0.1 M). The mixture was extracted with CH_2Cl_2 (3 x 15 mL), dried with $MgSO_4$ and the solvent was reduced under vacuum. Silica gel column chromatography was performed using petroleum ether / ethyl acetate as eluent.

General procedure for the synthesis of enantioenriched allylic alcohols (*R*)-1a-f, (*R*)-1j-m, (*R*)-1p-q and (*R*)-3a-c:[1]

The corresponding enone (5.31 mmol) and [RuCl-(*p*-cym){(*R*,*R*)-Tsdpen}] (33.8 mg, 0.05 mmol, 1 mol%) were placed in a pressure tube under an argon atmosphere. Then an azeotropic mixture of NEt_3/HCOOH (5 mol : 2 mol) was injected and the reaction was stirred at room temperature during 24 h. The mixture was quenched with H_2O and extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine and $NaHCO_3$ saturated aqueous solution and then dried over $MgSO_4$. After evaporation of the solvents, the crude was purified by silica gel column chromatography with petroleum ether / ethyl acetate (9:1) as the eluent. The *ee* was determined by HPLC.

The determination of the absolute configuration of the compound **1a** was performed by comparison of the previously reported compound of known stereochemistry.[1] For the rest of compounds **1**, the stereochemistry was assigned upon the assumption of a common stereochemical mechanism.

(*E*)-4,4,4-Trifluoro-1,3-diphenyl-2-buten-1-ol (1a)

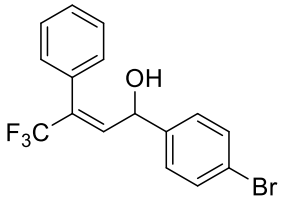


The title compound was prepared from (*E*)-4,4,4-trifluoro-1,3-diphenyl-2-buten-1-one (1 mmol, 278 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1a** as a colorless oil (195 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.43 (m, 3H), 7.39–7.31 (m, 3H), 7.30–7.26 (m, 4H), 6.63 (dq, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{4}J(^{1}H,^{19}F)$ = 1.5 Hz, 1H), 5.15 (d, $^{3}J(^{1}H,^{1}H)$ = 9 Hz, 1H), 1.91 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 136.5 (q, $^{3}J(^{13}C,^{19}F)$ = 5 Hz), 132.1 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 131.3, 129.7, 129.0, 128.9, 128.6, 128.4, 126.2, 123.8 (q, $^{1}J(^{13}C,^{19}F)$ = 274 Hz), 70.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.53 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 11.9 min, t_{minor}(*S*) = 13.3 min, 99% *ee*. $[\alpha]_D^{20}$ –200.3 (*c* 1.0, $CHCl_3$, 99% *ee*).

For complete characterization see: Konno, T.; Takehana, T.; Mishima, M.; Ishihara, T. *J. Org. Chem.* **2006**, *71*, 3545.

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-bromophenyl)-2-buten-1-ol (1b)

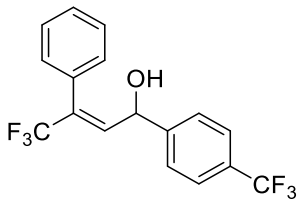


The title compound was prepared from (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-bromophenyl)-2-buten-1-one (1 mmol, 355 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1b** as a white powder (309 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.47 (m, 2H), 7.43–7.48 (m, 3H), 7.27–7.25 (m, 2H), 7.14–7.12 (m, 2H), 6.55 (dq, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{4}J(^{1}H,^{19}F)$ = 1.5 Hz, 1H), 5.14 (dd, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{3}J(^{1}H,^{1}H)$ = 3 Hz, 1H), 2.06 (d, $^{3}J(^{1}H,^{1}H)$ = 3 Hz ,1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 136.1 (q, $^{3}J(^{13}C,^{19}F)$ = 5 Hz), 132.8 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 132.0, 131.2, 129.6, 129.2, 128.7, 127.8, 122.3, 121.6 (q, $^{1}J(^{13}C,^{19}F)$ = 273 Hz), 69.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.63 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 41.2 min, t_{minor}(*S*) = 48.6 min, 98% *ee*. $[\alpha]_D^{20}$ –213.5 (*c* 1.0, $CHCl_3$, 98% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

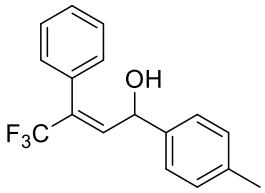
(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-trifluoromethylphenyl)-2-buten-1-ol (1c)



The title compound was prepared from (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-trifluoromethylphenyl)-2-buten-1-one (1 mmol, 344 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1c** as a colorless oil (182 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 2H), 7.48–7.44 (m, 3H), 7.40–7.36 (m, 2H), 7.30–7.26 (m, 2H), 6.57–6.53 (m, 1H), 5.20 (dd, $^3J(^1H,^1H)$ = 9 Hz; $^3J(^1H,^1H)$ = 3 Hz, 1H), 2.02 (d, $^3J(^1H,^1H)$ = 3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 136.3 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 133.4 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.5, 130.0 (q, $^2J(^{13}C,^{19}F)$ = 32 Hz), 130.0, 129.8, 129.3, 126.9, 126.2 (q, $^3J(^{13}C,^{19}F)$ = 3Hz), 124.4 (q, $^1J(^{13}C,^{19}F)$ = 272 Hz), 123.4 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 70.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.65 (s, 3F), –66.72 (s, 3F). HRMS (ESI): m/z calcd for $[C_{17}H_{10}F_6O+Na^+]$: 369.0670; found: 369.0685. HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 27.2 min, t_{minor}(*S*) = 31.7 min, 97% *ee*. $[\alpha]_D^{20}$ –158.8 (*c* 1.0, $CHCl_3$, 97% *ee*).

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-methylphenyl)-2-buten-1-ol (1d)



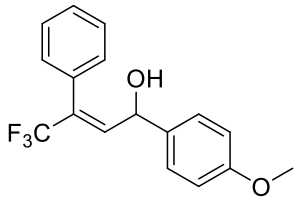
The title compound was prepared from (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-methylphenyl)-2-buten-1-one (1 mmol, 290 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1d** as a white powder (232 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.40 (m, 3H), 7.30–7.26 (m, 2H), 7.20–7.15 (m, 4H), 6.62 (dq, $^3J(^1H,^1H)$ = 9.3 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 5.10 (dd, $^3J(^1H,^1H)$ = 9.3 Hz; $^3J(^1H,^1H)$ = 3.4 Hz, 1H), 2.35 (s, 3H), 1.88 (d, $^3J(^1H,^1H)$ = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 138.4, 136.5 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 131.5 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.3, 129.8, 129.7, 129.1, 128.7, 126.2, 123.1 (q, $^1J(^{13}C,^{19}F)$ = 273 Hz), 70.3, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.47

(s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 27.6 min, t_{minor}(*S*) = 32.3 min, 98% *ee*. $[\alpha]_D^{20}$ –257.4 (*c* 1.0, $CHCl_3$, 98% *ee*).

For complete characterization see: Wu, M.; Kong, L.; Kaiwen, W.; Ronghua, J.; Tanyu, C.; Guohua, L. *Catal. Sci. Technol.* **2015**, *5*, 1750.

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-methoxyphenyl)-2-buten-1-ol (1e)

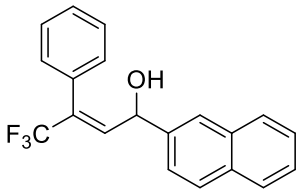


The title compound was prepared from (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-methoxyphenyl)-2-buten-1-one (1 mmol, 306 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1e** as a pink oil (296 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.40 (m, 3H), 7.27–7.25 (m, 2H), 7.20–7.15 (m, 2H), 6.90–6.85 (m, 2H), 6.63–6.60 (m, 1H), 5.10–5.07 (m, 1H), 3.81 (s, 3H), 1.87 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 136.9 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 134.0, 131.9 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.6, 129.8, 129.1, 128.7, 127.7, 121.9 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 114.4, 70.2, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.44 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 53.7 min, t_{minor}(*S*) = 63.0 min, 99% *ee*. $[\alpha]_D^{20}$ –246.0 (*c* 1.0, $CHCl_3$, 99% *ee*).

For complete characterization see: Wu, M.; Kong, L.; Kaiwen, W.; Ronghua, J.; Tanyu, C.; Guohua, L. *Catal. Sci. Technol.* **2015**, *5*, 1750.

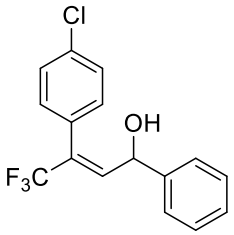
(*E*)-4,4,4-Trifluoro-3-phenyl-1-(naphthalene-2-yl)-2-buten-1-ol (1f)



The title compound was prepared from (*E*)-4,4,4-trifluoro-3-phenyl-1-(naphthalene-2-yl)-2-buten-1-one (1 mmol, 326 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1f** as a colorless oil (244 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.83 (m, 3H), 7.68–7.65 (m, 1H), 7.51–7.49 (m, 2H), 7.46–7.43 (m, 3H), 7.42–7.41 (m, 1H), 7.35–7.30 (m, 2H), 6.70 (dq, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{4}J(^{1}H,^{19}F)$ = 1.5 Hz, 1H), 5.31 (dd, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{3}J(^{1}H,^{1}H)$ = 3 Hz, 1H), 2.05 (d, $^{3}J(^{1}H,^{1}H)$ = 3 Hz ,1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 136.6 (q, $^{3}J(^{13}C,^{19}F)$ = 5 Hz), 133.4, 133.3, 132.5 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 131.5, 129.8, 129.2, 129.0, 128.8, 128.2, 127.9, 126.6, 126.5, 125.3, 124.1, 123.5 (q, $^{1}J(^{13}C,^{19}F)$ = 273 Hz), 70.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.47 (s). HRMS (ESI): m/z calcd for [$C_{20}H_{15}F_3O$+Na^+] : 351.0967; found: 351.0975. HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (97:03) t_{major}(*R*) = 20.9 min, t_{minor}(*S*) = 24.6 min, 98% *ee*. $[\alpha]_D^{20}$ –288.1 (*c* 1.0, $CHCl_3$, 98% *ee*).

(*E*)-3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (1j)

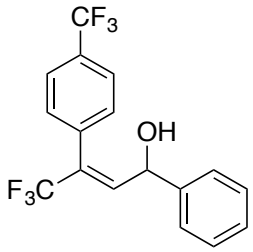


The title compound was prepared from (*E*)-3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (1 mmol, 310 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1j** as a colorless oil (323 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.40 (m, 2H), 7.38–7.31 (m, 3H), 7.25–7.24 (m, 2H), 7.22–7.21 (m, 2H), 6.65 (dq, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{4}J(^{1}H,^{19}F)$ = 1.5 Hz, 1H), 5.12–5.09 (m, 1H), 1.93 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 137.4–137.3 (q, $^{3}J(^{13}C,^{19}F)$ = 5 Hz), 135.5, 131.22 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 131.21, 129.9, 129.15, 129.10, 128.7, 126.4, 123.0 (q, $^{1}J(^{13}C,^{19}F)$ = 273 Hz), 70.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.54 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (95:05) t_{major}(*R*) = 12.0 min, t_{minor}(*S*) = 15.2 min, 97% *ee*. $[\alpha]_D^{20}$ –428.1 (*c* 1.0, $CHCl_3$, 97% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

(*E*)-4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (1k)

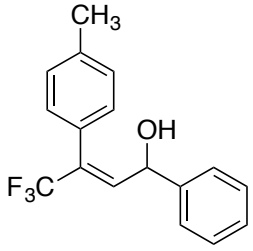


The title compound was prepared from (*E*)-4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-one (1 mmol, 346 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1k** as a white powder (277 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (m, 2H), 7.42–7.40 (m, 2H), 7.39–7.32 (m, 3H), 7.25–7.23 (m, 2H), 6.70 (dq, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 5.07 (dd, $^3J(^1H,^1H)$ = 9 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H), 1.95 (d, $^3J(^1H,^1H)$ = 4 Hz ,1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 137.6 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 135.1, 131.4 (d, $^2J(^{13}C,^{19}F)$ = 33 Hz), 130.9 (d, $^2J(^{13}C,^{19}F)$ = 31 Hz), 130.3, 129.1, 128.7, 126.2, 125.6 (q, $^1J(^{13}C,^{19}F)$ = 4 Hz), 123.9 (q, $^1J(^{13}C,^{19}F)$ = 273 Hz), 122.8 (q, $^1J(^{13}C,^{19}F)$ = 273.5 Hz), 70.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.86 (s), –66.69 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (95:05) t_{major}(*R*) = 12.6 min, t_{minor}(*S*) = 10.4 min, 97% *ee*. $[\alpha]_D^{20}$ –299.1 (*c* 1.0, $CHCl_3$, 97% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

(*E*)-4,4,4-trifluoro-1-phenyl-3-(*p*-tolyl)but-2-en-1-ol (1l)



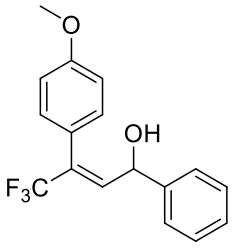
The title compound was prepared from (*E*)-4,4,4-trifluoro-1-phenyl-3-(*p*-tolyl)but-2-en-1-one (1 mmol, 292 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1l** as a white powder (251 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.34 (m, 2H), 7.33–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.18–7.16 (m, 2H), 6.59 (dq, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 5.17–5.15 (m, 1H), 2.40

(s, 3H), 1.91 (d, $^{3}J(^{1}H,^{1}H)$ = 4 Hz ,1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 136.3 (q, $^{3}J(^{13}C,^{19}F)$ = 5 Hz), 132.1 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 129.7, 129.5, 128.8, 128.3, 127.3, 126.2, 123.1 (q, $^{1}J(^{13}C,^{19}F)$ = 274 Hz), 100.0, 70.4, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.69 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (95:05) t_{major}(*R*) = 10.5 min, t_{minor}(*S*) = 13.9 min, 97% *ee*. $[\alpha]_D^{20}$ –377.2 (*c* 1.0, $CHCl_3$, 97% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

(*E*)-3-(4-methoxyphenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (1m)

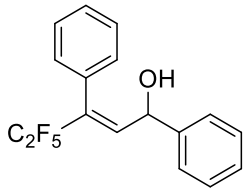


The title compound was prepared from (*E*)-4,4,4-trifluoro-3-(4-methoxyphenyl)-1-phenylbut-2-en-1-one (1 mmol, 308 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1m** as a colorless oil (237 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.27 (m, 5H), 7.22–7.20 (m, 2H), 6.96–6.92 (m, 2H), 6.59 (dq, $^{3}J(^{1}H,^{1}H)$ = 9 Hz; $^{4}J(^{1}H,^{19}F)$ = 1 Hz, 1H), 5.16 (d, $^{3}J(^{1}H,^{1}H)$ = 9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 136.4 (q, $^{3}J(^{13}C,^{19}F)$ = 5 Hz), 131.8 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 130.9, 128.9, 128.8, 128.3, 126.2, 123.4, 123.2 (q, $^{1}J(^{13}C,^{19}F)$ = 273 Hz), 114.0, 70.5, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.54 (s). HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (95:05) t_{major}(*R*) = 14.5 min, t_{minor}(*S*) = 18.9 min, 98% *ee*. $[\alpha]_D^{20}$ –390.6 (*c* 1.0, $CHCl_3$, 98% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

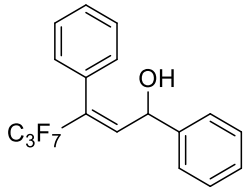
(*E*)-4,4,5,5,5-Pentafluoro-1,3-diphenylpent-2-en-1-ol (1p)



The title compound was prepared from (*E*)-4,4,5,5,5-pentafluoro-1,3-diphenylpent-2-en-1-one (1 mmol, 328 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1p** as a colorless oil (249 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.39 (m, 3H), 7.35–7.28 (m, 3H), 7.24–7.20 (m, 4H), 6.66 (dq, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 5.10 (d, $^3J(^1H,^1H)$ = 9 Hz, 1H), 1.93 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 139.9 (t, $^3J(^{13}C,^{19}F)$ = 8 Hz), 131.6, 131.3 (t, $^2J(^{13}C,^{19}F)$ = 20 Hz), 130.1, 129.1, 129.0, 128.6, 128.5, 126.3, 123.8–109.5 (m, CF_3–CF_2–), 70.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –82.23 (m, 3F), –113.90 (m, 2F). HRMS (ESI): m/z calcd for [$C_{17}H_{13}F_5O$+Na^+]: 351.0787; found: 351.0779. HPLC: CHIRALCEL OK, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 25.9 min, t_{minor}(*S*) = 37.1 min, 99% *ee*. $[\alpha]_D^{20}$ –197.0 (*c* 1.0, $CHCl_3$, 99% *ee*).

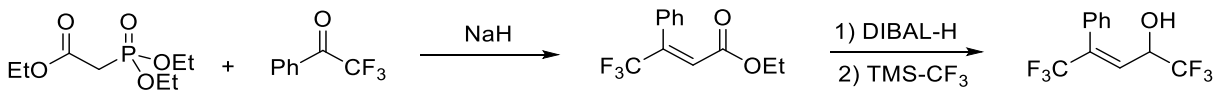
(*E*)-4,4,5,5,6,6,6-Heptafluoro-1,3-diphenylhex-2-en-1-ol (1q)



The title compound was prepared from (*E*)-4,4,5,5,6,6,6-heptafluoro-1,3-diphenylhex-2-en-1-one (1 mmol, 378 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded **1q** as a colorless oil (276 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.40 (m, 3H), 7.38–7.30 (m, 3H), 7.23–7.20 (m, 4H), 6.64 (dq, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1 Hz, 1H), 5.11 (d, $^3J(^1H,^1H)$ = 9 Hz, 1H), 1.91 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 140.5 (q, $^3J(^{13}C,^{19}F)$ = 8 Hz), 131.7, 131.4 (q, $^2J(^{13}C,^{19}F)$ = 22 Hz), 130.21, 129.1, 129.0, 128.52, 128.46, 126.3, 119.8–106.1 (m, CF_3–CF_2–CF_2–), 70.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –80.28 (m, 3F), –110.90 (m, 2F), –124.24 (m, 2F). HRMS (ESI): m/z calcd for [$C_{18}H_{13}F_7O$+Na^+] : 401.0747; found: 401.0762. HPLC: CHIRALCEL IB, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major}(*R*) = 22.0 min, t_{minor}(*S*) = 21.1 min, 98% *ee*. $[\alpha]_D^{20}$ –139.8 (*c* 1.0, $CHCl_3$, 98% *ee*).

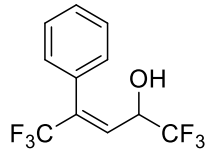
Procedure for the synthesis of allylic alcohols 1g:[2]



NaH 60% dispersion in mineral oil (30 mmol, 1.2 g, 1.5 equiv.) was dissolved in dry THF (40 mL) and the reaction mixture was cooled to 0 °C. Triphenylphosphonoacetate (30 mmol, 6 mL, 1.5 equiv.) was added and the mixture was stirred at 0 °C for 1 h. Then, 2,2,2-trifluoroacetophenone (20 mmol, 2.8 mL, 1 equiv.) was added and the mixture was stirred for another hour at 0 °C and, afterwards, warmed to RT. The reaction was quenched with NH_4Cl saturated aqueous solution and extracted with EtOAc (3 x 15 mL). The solvent was removed under reduced pressure affording a mixture of *E*/*Z* (85/15) products were obtained. Silica gel column chromatography was performed to separate the *E*-enone using petroleum ether / ethyl acetate (30:01) as eluent.

The *E*-enone (1.6 mmol, 400 mg, 1 equiv.) was redissolved in dry Et_2O (5 mL) at –78 °C. DIBAL-H (1 M in hexane, 1.8 mmol, 1.8 mL, 1.1 equiv.) was added dropwise over 2 min and the mixture was stirred 1 h at –78 °C. The reaction was quenched with H_2O, extracted using Et_2O (3 x 15 mL) and purified using silica gel column chromatography (pentane / EtOAc, 90:10). The corresponding aldehyde was then dissolved in dry THF (5 mL) and the mixture was cooled at –78 °C. $TMSCF_3$ (1.8 mmol, 0.3 mL, 1.1 equiv.) and TBAF (1 M in THF, 0.04 mmol, 40 μL, 0.03 equiv.) were added carefully over 2 min and the mixture was warmed to RT. The reaction was quenched with HCl (aq., 5 mL, 0.1 M) and the solvent was removed under reduced pressure. The product is volatile and the removal of the solvent has to be performed very carefully. Silica gel column chromatography was performed to purify **1g** using petroleum ether / ethyl ether (99:1) as eluent (215 mg, 48%).

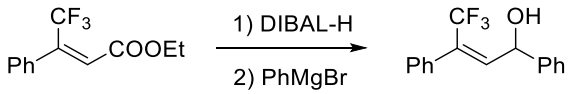
(*E*)-1,1,1,5,5,5-Hexafluoro-4-phenylpent-3-en-2-ol (1g)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.42 (m, 3H), 7.35–7.30 (m, 2H), 6.44–6.41 (m, 1H), 4.43–4.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0 (q, $^2J(^{13}C,^{19}F)$ = 33 Hz), 130.0, 129.6, 129.3, 128.8, 126.9–126.8 (m), 123.88 (q, $^1J(^{13}C,^{19}F)$ = 282 Hz), 122.46 (q, $^1J(^{13}C,^{19}F)$ = 274

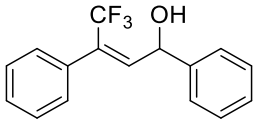
Hz), 67.26 (q, $^{2}J(^{13}C,^{19}F)$ = 33 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −67.60 (s, 3F), −78.45 (s, $^{3}J(^{1}H, ^{19}F)$ = 6 Hz, 3F). GC/MS (m/z): 270.00.

Procedure for the synthesis of allylic alcohol (*Z*)-1a:[3]



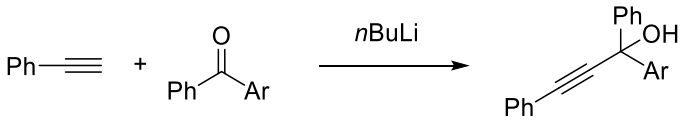
Ethyl (*Z*)-4,4,4-trifluoro-3-phenylbut-2-enoate (0.8 mmol, 200 mg, 1 equiv.) was dissolved in dry Et_2O (2 mL) and the mixture was cooled −78 °C. DIBAL-H (1 M in hexane, 0.9 mmol, 0.9 mL, 1.1 equiv.) was added and the reaction was stirred at −78 °C for 1h. Then PhMgBr (1 M in THF, 0.9 mmol, 0.9 mL, 1.1 equiv.) was added and the reaction was warmed overnight. The reaction was quenched with HCl (aq., 5 mL, 1 M) and the mixture was extracted with Et_2O (3 x 15 mL). The organic phase was dried over $MgSO_4$ and the solvent was reduced under reduced pressure. The product (*Z*)-**1a** was purified by Silica gel column chromatography using petroleum ether / ethyl acetate (90:10) as eluent (135 mg, 59%, colorless oil).

(*Z*)-4,4,4-Trifluoro-1,3-diphenylbut-2-en-1-ol ((*Z*)-1a)



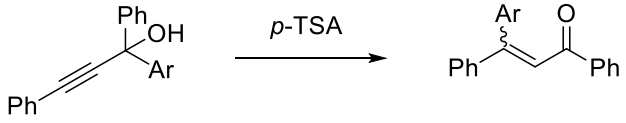
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 2H), 7.42–7.38 (m, 2H), 7.37–7.30 (m, 6H), 6.22 (m, 1H), 5.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8 (q, $^{3}J(^{13}C,^{19}F)$ = 3 Hz), 141.75, 135.5, 131.6 (q, $^{2}J(^{13}C,^{19}F)$ = 30 Hz), 129.0, 128.7, 128.5, 128.4, 128.3, 127.8, 123.7 (q, $^{1}J(^{13}C,^{19}F)$ = 276 Hz), 70.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −56.22 (s). HRMS (ESI): m/z calcd for $[C_{16}H_{13}F_3O+Na^+]$: 301.0811; found: 301.0809.

Procedure for the synthesis of allylic alcohols 1w-y:[11]



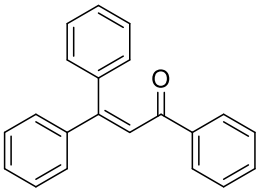
Phenylacetilene (5.5 mmol, 0.6 mL, 2 equiv.) was dissolved in dry THF (14 mL) and *n*BuLi (1.56 M in CH_2Cl_2, 5.5 mmol, 3.5 mL, 2 equiv.) was added dropwise at −78 °C under an argon atmosphere. The mixture was stirred for 30 minutes at −78 °C and the corresponding benzophenone was added (2.7 mmol, 1 equiv.). The mixture was then stirred at RT for 1 h and it was subsequently quenched with NH_4Cl saturated aqueous solution. It was extracted with

EtOAc (3 x 15 mL), dried over $MgSO_4$ and the solvent was reduced under reduced pressure. Silica gel column chromatography was performed to purify the product using petroleum ether / ethyl acetate (80:20) as eluent.



The corresponding propargylic alcohol (2.64 mmol, 750 mg, 1 equiv) and *p*-toluenesulphonic acid (0.79 mmol, 150 mg, 0.3 equiv.) were dissolved in dry DCE (9 mL) under an argon atmosphere. The mixture was stirred at 60 °C for 6 h. The solvent was removed under reduced pressure and the product was purified by silica gel column chromatography (petroleum ether / ethyl acetate, 90:10).

1,3,3-Triphenylprop-2-en-1-one

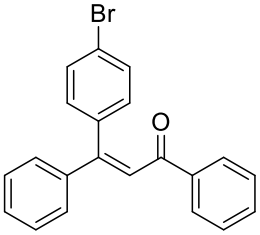


The title compound was prepared from benzophenone (2.7 mmol, 500 mg) according to the above procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded the product (693 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.91 (m, 2H), 7.51–7.46 (m, 1H), 7.42–7.35 (m, 7H), 7.29–7.26 (m, 3H), 7.21–7.18 (m, 2H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 154.8, 141.5, 139.1, 138.4, 132.8, 129.9, 129.5, 128.9, 128.7, 128.6, 128.49, 128.48, 128.2, 124.2.

For complete characterization see: Uyanik, M.; Fukatsu, R.; Ishihara, K. *Org. Lett.*, **2009**, *11*, 3470.

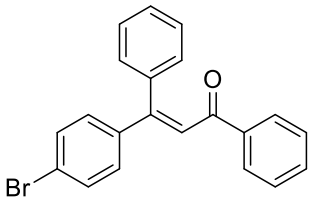
(*Z*)-3-(4-Bromophenyl)-1,3-diphenylprop-2-en-1-one



The title compound was prepared from *p*-bromobenzophenone (2.7 mmol, 700 mg) according to the above procedure. Purification by Combiflash BIOTAGE using cartridges SNAP ultra 25 g (pentane / EtOAc, 99:1) afforded the product (245 mg, 35%, yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.55–7.51 (m, 1H), 7.44–7.35 (m, 9H), 7.17 (s, 1H), 7.09–7.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 153.8, 141.0, 138.3, 138.1, 133.1, 131.45, 131.44, 129.7, 128.80, 128.70, 128.65, 128.64, 124.3, 122.8. HRMS (ESI): m/z calcd for [$C_{21}H_{15}BrO+Na^+$] : 385.0198; found: 385.0219.

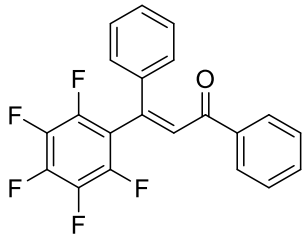
(*E*)-3-(4-Bromophenyl)-1,3-diphenylprop-2-en-1-one



The title compound was prepared from *p*-bromobenzophenone (2.7 mmol, 700 mg) according to the above procedure. Purification by Combiflash BIOTAGE using cartridges SNAP ultra 25 g (pentane / EtOAc, 99:1) afforded the product (200 mg, 29%, yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.88 (m, 2H), 7.52–7.46 (m, 3H), 7.40–7.35 (m, 2H), 7.29–7.24 (m, 5H), 7.16–7.14 (m, 2H), 7.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 153.2, 140.2, 138.4, 138.0, 132.8, 131.6, 130.1, 129.7, 128.7, 128.6, 128.4, 128.1, 124.3, 123.7. HRMS (ESI): m/z calcd for [$C_{21}H_{15}BrO+Na^+$] : 385.0198; found: 385.0233.

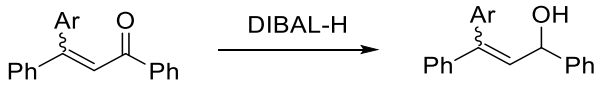
(*E*)-3-(Perfluorophenyl)-1,3-diphenylprop-2-en-1-one



The title compound was prepared from 2,3,4,5,6-pentafluorobenzophenone (2.7 mmol, 735 mg) according to the above procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 95:5) afforded the product (478 mg, 65%, yellow oil).

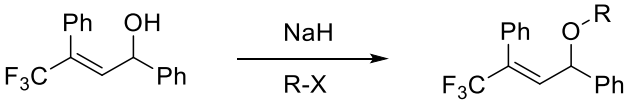
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.90 (m, 2H), 7.50–7.44 (m, 1H), 7.38–7.34 (m, 2H), 7.20–7.19 (m, 5H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 145.3, 136.76–136.74 (m), 136.7, 133.6, 132.7–132.6 (m), 130.25–130.19 (m), 129.7, 129.24, 129.20, 128.9, 128.7,

128.6, 128.5, 126.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −140.2 (m, 2F), −153.4 (m, 1F), −161.2 (m, 2F). HRMS (ESI): m/z calcd for [$C_{21}H_{11}F_5O$+Na^+] : 397.0622; found: 397.0587.



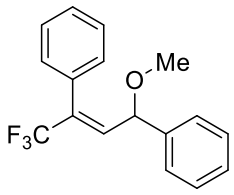
The corresponding enone (3 mmol, 1 equiv.) was dissolved in dry CH_2Cl_2 (10 mL) and DIBAL-H (1 M in hexane, 3.6 mmol, 3.6 mL, 1.2 equiv.) was added at 0 °C under argon atmosphere. The reaction was stirred for 1.5 h and quenched with NH_4Cl saturated aqueous solution and HCl (aq., 5 mL, 0.1 M). The mixture was extracted with CH_2Cl_2 (3 x 15 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. Silica gel column chromatography was performed to purify the product using petroleum ether / ethyl acetate (9:1) as eluent. The allylic alcohols **1w**-**y** were found to be unstable and the isomerization was performed directly after the reduction.

General procedure for the synthesis of allylic ethers 3a-d:



NaH 60% dispersion in mineral oil (1.6 mmol, 65 mg, 1.5 equiv.) was dissolved in dry Et_2O (2 mL) under an argon atmosphere at 0 °C. The allylic alcohol **1a** (1.08 mmol, 300 mg, 1 equiv.) and the corresponding alkylating agent (1.08 mmol, 1 equiv.) were added and the reaction mixture was stirred for 2 h. The reaction was quenched with NH_4Cl saturated aqueous solution and HCl (aq., 5 mL, 0.1 M) and purified using silica gel column chromatography.

(*E*)-(4,4,4-Trifluoro-1-methoxybut-2-ene-1,3-diyl)dibenzene (3a)

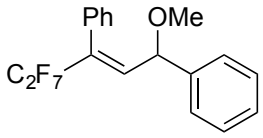


The title compound was prepared according to the general procedure from methyl iodine (1.08 mmol, 68 μL, 1 equiv.). Purification by column chromatography (SiO_2; pentane / EtOAc, 95:5) afforded **3a** as a colorless oil (220 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.43 (m, 3H), 7.37–7.25 (m, 5H), 7.22–7.17 (m, 2H), 6.54 (dq, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 4.57 (d, $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 135.9 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 132.9 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.7, 129.9, 129.1, 128.9, 128.7, 128.5, 127.0, 123.2 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 79.3, 56.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ − 66.53 (s). HRMS (ESI): m/z calcd for $[C_{17}H_{15}F_3O+Na^+]$: 315.0967; found: 315.0968. HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99:01) t_{major} = 8.2 min, t_{minor} = 9.3 min, 98% *ee*. $[\alpha]_D^{20}$ −165.9 (*c* 1.0, $CHCl_3$, 98% *ee*).

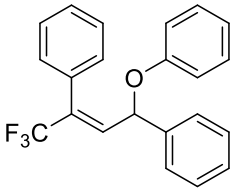
(*E*)-(4,4,5,5,6,6,6-heptafluoro-1-methoxyhex-2-ene-1,3-diyl)dibenzene (3b)



The title compound was prepared according to the general procedure from methyl iodine (1.44 mmol, 90 μL, 1 equiv.). Purification by column chromatography (SiO_2; pentane / EtOAc, 99.5:0.5) afforded **3b** as a colorless oil (368 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.30 (m, 7H), 7.25–7.19 (m, 3H), 6.61 (dt, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 4.60 (d, $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8 (t, $^3J(^{13}C,^{19}F)$ = 8 Hz), 139.5, 132.1 (t, $^2J(^{13}C,^{19}F)$ = 22 Hz), 131.8, 130.2, 128.9, 128.7, 128.4, 128.3, 126.8, 119.4–108.6 (m, CF_3–CF_2–CF_2–), 79.3, 56.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ − 80.30, −110.74, −124.29. HRMS (ESI): m/z calcd for $[C_{19}H_{15}F_7O+Na^+]$: 415.0909; found: 415.0915. HPLC: CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (99.5:0.5) t_{major} = 8.1 min, t_{minor} = 9.2 min, 98% *ee*. $[\alpha]_D^{20}$ −159.7 (*c* 1.0, $CHCl_3$, 98% *ee*).

(*E*)-(4,4,4-trifluoro-1-phenoxybut-2-ene-1,3-diyl)dibenzene (3c)[12]

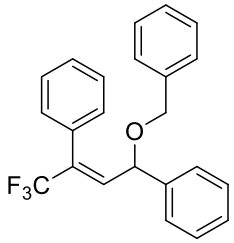


The title compound was prepared according to a modified method from the general procedure. NaH 60% dispersion in mineral oil (0.52 mmol, 25 mg, 1.2 equiv.) was dissolved in dry toluene (2.5 mL) under an argon atmosphere at 0 °C. The allylic alcohol **1a** (0.43 mmol, 120 mg, 1 equiv.) and diphenyliodonium triflate (0.52 mmol, 224 mg, 1.2 equiv.) were added and the reaction mixture was allowed to react overnight at room temperature. The crude was then

diluted with Et_2O (5 mL) and filtered through a silica plug. Purification by column chromatography (SiO_2; pentane / EtOAc, 99:1) afforded **3c** as a colorless oil (86 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.40 (m, 3H), 7.37–7.27 (m, 5H), 7.24–7.21 (m, 2H), 7.20–7.15 (m, 2H), 6.95–6.90 (m, 1H), 6.75–6.70 (m, 2H), 6.69 (dq, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1 Hz, 1H), 5.54 (d, $^3J(^1H,^1H)$ = 9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 139.2, 135.1 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 132.8 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.4, 129.8, 129.5, 129.3, 129.1, 128.8, 128.6, 126.8, 123.2 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 121.7, 116.7, 76.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ – 66.42 (s). HRMS (ESI): m/z calcd for [$C_{22}H_{17}F_3O$+Na^+] : 377.1124; found: 377.1132. CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane / isopropanol (98:02) t_{major} = 13.7 min, t_{minor} = 12.2 min, 98% *ee*. $[\alpha]_D^{20}$ –78.0 (*c* 0.83, $CHCl_3$, 98% *ee*).

(*E*)-(1-(Benzyloxy)-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (3d)



The title compound was prepared according to the general procedure from benzyl bromide (1.08 mmol, 130 μL, 1 equiv.). Purification by column chromatography (SiO_2; pentane / EtOAc, 95:5) afforded **3d** as a colorless oil (302 mg, 76%).

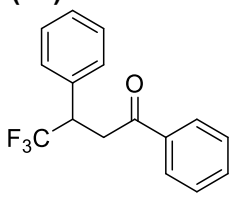
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.28 (m, 10H), 7.26–7.21 (m, 5H), 6.63 (dd, $^3J(^1H,^1H)$ = 9 Hz; $^4J(^1H,^{19}F)$ = 1.5 Hz, 1H), 4.82 (d, $^3J(^1H,^1H)$ = 9 Hz, 1H), 4.36 (d, $^4J(^1H,^1H)$ = 1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 137.7, 135.8 (q, $^3J(^{13}C,^{19}F)$= 4 Hz), 132.5 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.5, 129.6, 128.9, 128.8, 128.5, 128.4, 128.3, 127.8, 127.7, 127.0, 123.1 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 76.8, 70.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.40 (s). HRMS (ESI): m/z calcd for [$C_{23}H_{19}F_3O$+Na^+] : 391.1280; found: 391.1297.

General procedure for the TBD-catalyzed isomerization of allylic substrates:

The corresponding allylic substrate (0.18 mmol, 1 equiv.) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (0.018 mmol, 2.5 mg, 0.1 equiv.) were placed in a pressure tube. Toluene was added (1.8 mL) and the mixture was allowed to react at 60 °C. The reaction was quenched with H_2O (5 mL) and extracted with Et_2O (3 x 5 mL). The solvent was removed under reduced pressure to yield the product.

The determination of the absolute configuration of the compound **2a** was performed by comparison of the previously reported compound of known stereochemistry.[1] For the rest of compounds **2**, the stereochemistry was assigned upon the assumption of a common stereochemical mechanism.

4,4,4-Trifluoro-1,3-diphenylbutanone (2a)

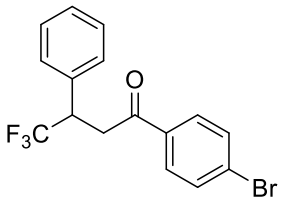


The title compound was prepared from (*E)*-4,4,4-trifluoro-1,3-diphenyl-2-buten-1-ol or from (*Z)*-4,4,4-trifluoro-1,3-diphenyl-2-buten-1-ol (0.18 mmol, 50 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (42 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.60–7.56 (m, 1H), 7.48–7.45 (m, 2H), 7.41–7.39 (m, 2H), 7.36–7.30 (m, 3H), 4.30–4.19 (m, 1H), 3.70 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.62 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 136.4, 134.7–134.6 (m), 133.7, 129.2, 128.9, 128.8, 128.4, 128.2, 125.7 (q, $^1J(^{13}C,^{19}F)$ = 275 Hz), 44.9 (q, $^2J(^{13}C,^{19}F)$ = 27 Hz), 38.4–38.3 (m). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.64 (d, $^3J(^1H,\ ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (99:01), t_{major}(*R*) = 49.9 min, t_{minor}(*S*) = 60.1 min, 94% *ee*. $[\alpha]_D^{20}$ +46.0 (*c* 1.0, $CHCl_3$, 94% *ee*). Recrystallization from CH_2Cl_2 / hexane afforded the product with 99% *ee*.

For complete characterization see: Bizet, V.; Pannecoucke, X.; Renaud, J.-L.; Cahard, D. *Angew. Chem. Int. Ed.* **2012**, *51*, 6467.

4,4,4-Trifluoro-3-phenyl-1-(4'-Bromophenyl)-butanone (2b)

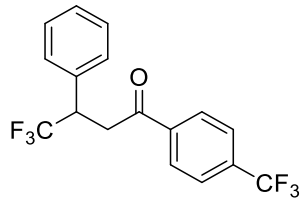


The title compound was prepared from (*E)*-4,4,4-trifluoro-3-phenyl-1-(4'-bromophenyl)-2-buten-1-ol (0.18 mmol, 64 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (58 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.77 (m, 2H), 7.62–7.58 (m, 2H), 7.40–7.30 (m, 5H), 4.23 (m, 1H), 3.65 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.55 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 135.2, 134.4–134.3 (m), 132.2, 129.7, 129.1, 129.0, 128.9, 128.5, 125.6 (q, $^1J(^{13}C,^{19}F)$ = 279 Hz), 44.8 (q, $^1J(^{13}C,^{19}F)$ = 27.5 Hz), 38.25–38.23 (m). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.66 (d, $^3J(^1H, ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (90:10), t_{major}(*R*) = 32.0 min, t_{minor}(*S*) = 26.6 min, 94% *ee*. $[\alpha]_D^{20}$ +23.6 (*c* 1.0, $CHCl_3$, 94% *ee*). Recrystallization from CH_2Cl_2 / hexane afforded the product with 99% *ee*.

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

4,4,4-Trifluoro-3-phenyl-1-(4'-Trifluoromethylphenyl)-butanone (2c)

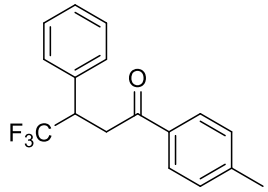


The title compound was prepared from (*E)*-4,4,4-trifluoro-3-phenyl-1-(4'-trifluoromethylphenyl)-2-buten-1-ol (0.18 mmol, 62 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (52 mg, 84%). m.p. 66–67 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, $^3J(^1H,^1H)$ = 8 Hz, 2H), 7.73 (d, $^3J(^1H,^1H)$ = 8 Hz, 2H), 7.40–7.30 (m, 5H), 4.25 (m, 1H), 3.71 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.62 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 139.0, 135.0

($^2J(^{13}C,^{19}F)$ = 33 Hz), 134.19–134.18 (m), 129.1, 128.9, 128.6, 128.5, 126.0 (q, $^3J(^{13}C,^{19}F)$ = 4 Hz), 125.5 (q, $^1J(^{13}C,^{19}F)$ = 280 Hz), 122.7 (q, $^1J(^{13}C,^{19}F)$ = 273 Hz), 44.9 (q, $^2J(^{13}C,^{19}F)$ = 28 Hz), 45.1–44.3 (m). ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.22 (s, 3F), –69.69 (d, $^3J(^1H,^{19}F)$ = 9.5 Hz, 3F). HRMS (ESI): m/z calcd for [$C_{17}H_{12}F_6O$+Na^+] : 369.0685; found: 369.0674. HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (95:5), t_{major}(*R*) = 25.0 min, t_{minor}(*S*) = 20.6 min, 95% *ee*. $[\alpha]_D^{20}$ +32.8 (*c* 1.0, $CHCl_3$, 95% *ee*). Recrystallization from CH_2Cl_2 / hexane afforded the product with 99% *ee*.

4,4,4-Trifluoro-3-phenyl-1-(4'-Methylphenyl)-butanone (2d)

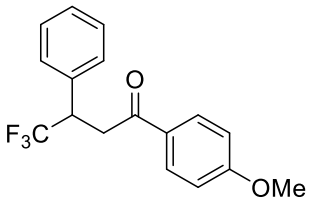


The title compound was prepared from (*E)*-4,4,4-trifluoro-3-phenyl-1-(4'-methylphenyl)-2-buten-1-ol (0.18 mmol, 53 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (50 mg, 95%).

^1H NMR (400 MHz, $CDCl_3$): δ 7.84–7.81 (m, 2H), 7.45–7.40 (m, 2H), 7.40–7.30 (m, 3H), 7.30–7.27 (m, 2H), 4.30–4.19 (m, 1H), 3.70 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.60 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 144.6, 134.82–134.79 (m), 134.0, 129.5, 129.1, 128.8, 128.4, 128.3, 125.8 (q, $^1J(^{13}C,^{19}F)$ = 280 Hz), 45.0 (q, $^2J(^{13}C,^{19}F)$ = 27 Hz), 38.25–38.24 (m), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.61 (d, $^3J(^1H,\ ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (95:5), t_{major}(*R*) = 19.2 min, t_{minor}(*S*) = 22.6 min, 92% *ee*. $[\alpha]_D^{20}$ +54.0 (*c* 1.0, $CHCl_3$, 92% *ee*). Recrystallization from CH_2Cl_2 / hexane afforded the product with 99% *ee*.

For complete characterization see: Okusu, S.; Sugita, Y.; Tokunaga, E.; Shibata, N. *Beilstein J. Org. Chem.* **2013**, *9*, 2189.

4,4,4-Trifluoro-3-phenyl-1-(4'-Methoxyphenyl)-butanone (2e)

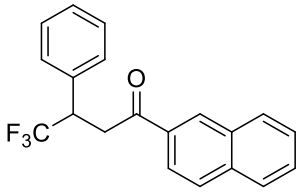


The title compound was prepared from (*E)*-4,4,4-trifluoro-3-phenyl-1-(4'-methoxyphenyl)-2-buten-1-ol (0.18 mmol, 55 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (49 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.89 (m, 2H), 7.40–7.38 (m, 2H), 7.35–7.27 (m, 3H), 6.94–6.90 (m, 2H), 4.30–4.19 (m, 1H), 3.86 (s, 3H), 3.64 (dd, $^2J(^1H,^1H)$ = 17.5 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.53 (dd, $^2J(^1H,^1H)$ = 17.5 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 164.0, 134.9, 130.5, 129.6, 129.2, 128.8, 128.4, 125.8 (q, $^1J(^{13}C,^{19}F)$ = 278 Hz), 114.0, 55.6, 44.9 (q, $^1J(^{13}C,^{19}F)$ = 27.5 Hz), 37.83–37.82 (m). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.61 (d, $^3J(^1H,\ ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (90:10), t_{major}(*R*) = 30.1 min, t_{minor}(*S*) = 38.2 min, 88% *ee*. $[\alpha]_D^{20}$ +65.9 (*c* 1.0, $CHCl_3$, 88% *ee*). Recrystallization from CH_2Cl_2 / hexane afforded the product with 99% *ee*.

For complete characterization see: Okusu, S.; Sugita, Y.; Tokunaga, E.; Shibata, N. *Beilstein J. Org. Chem.* **2013**, *9*, 2189.

4,4,4-Trifluoro-1-(naphthalen-2-yl)-3-phenylbutan-1-one (2f)

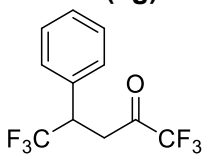


The title compound was prepared from (*E*)-4,4,4-trifluoro-3-phenyl-1-(naphthalene-2-yl)-2-buten-1-ol (0.18 mmol, 59 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (50 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.98–7.96 (m, 2H), 7.90–7.85 (m, 2H), 7.65–7.55 (m, 2H), 7.46–7.42 (m, 2H), 7.38–7.30 (m, 3H), 4.37–4.26 (m, 1H), 3.85 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.73 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.3, 135.9, 134.81–134.76 (m), 133.8, 132.5, 130.0, 129.7, 129.2, 128.90, 128.85, 128.80, 128.4, 127.9, 127.1 (q, $^1J(^{13}C,^{19}F)$ = 279 Hz), 127.0, 123.7, 45.0 (q,

$^{2}J(^{13}C,^{19}F)$ = 27.5 Hz), 38.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −69.56 (d, $^{3}J(^{1}H, ^{19}F)$ = 10 Hz). HRMS (ESI): m/z calcd for $[C_{20}H_{15}F_3O+Na^+]$: 351.0967; found: 351.0989. HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (70:30), $t_{major}(R)$ = 36.2 min, $t_{minor}(S)$ = 25.9 min, 87% *ee*. $[\alpha]_D^{20}$ +103.3 (*c* 1.0, $CHCl_3$, 87% *ee*).

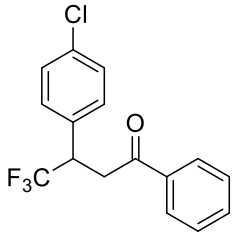
1,1,1,5,5,5-Hexafluoro-4-phenylpentan-2-one (2g)



The title compound was prepared from (*E*)-1,1,1,5,5,5-hexafluoro-4-phenylpent-3-en-2-ol (0.18 mmol, 49 mg) according to the general procedure. The crude of **2g** was obtained in 50% yield as determined by ^{1}H NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.36 (m, 5H), 4.20–4.18 (m, 1H), 3.45–3.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5 (q, $^{2}J(^{13}C,^{19}F)$ = 37 Hz), 132.9, 129.2, 129.1, 128.9, 126.2 (q, $^{1}J(^{13}C,^{19}F)$ = 280 Hz), 115.4 (q, $^{1}J(^{13}C,^{19}F)$ = 291 Hz), 44.1 (q, $^{2}J(^{13}C,^{19}F)$ = 28.4 Hz), 36.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.28 (d, $^{3}J(^{1}H, ^{19}F)$ = 9.1 Hz, 3F), −79.62 (s, 3F). GC/MS (m/z): 269.98.

3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbutan-1-one (2j)



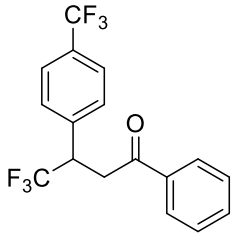
The title compound was prepared from (*E*)-3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (0.18 mmol, 56 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (48 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.91 (m, 2H), 7.60–7.57 (m, 1H), 7.48–7.45 (m, 2H), 7.34–7.30 (m, 4H), 7.36–7.30 (m, 3H), 4.26–4.18 (m, 1H), 3.67 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 9 Hz, 1H), 3.59 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 136.3, 134.5, 133.9, 133.2–133.1 (m), 130.5, 129.1, 128.2, 127.9, 126.8 (q, $^{1}J(^{13}C,^{19}F)$ = 280 Hz), 44.5 (q, $^{2}J(^{13}C,^{19}F)$ = 27 Hz), 38.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −69.54 (d, $^{3}J(^{1}H, ^{19}F)$

= 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (90:10), t_{major}(*R*) = 10.8 min, t_{minor}(*S*) = 9.5 min, 86% *ee*. $[\alpha]_D^{20}$ +98.1 (*c* 0.95, $CHCl_3$, 86% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)butan-1-one (2k)

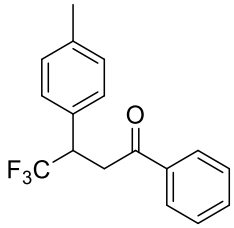


The title compound was prepared from (*E*)-3-(4-trifluoromethylphenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (0.18 mmol, 62 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (55 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.91 (m, 2H), 7.61–7.58 (m, 3H), 7.54–7.58 (m, 2H), 7.49–7.45 (m, 2H), 4.36–4.27 (m, 1H), 3.73 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 9 Hz, 1H), 3.63 (dd, $^2J(^1H,^1H)$ = 18 Hz; $^3J(^1H,^1H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 138.7, 136.1, 133.9, 130.7 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 129.6, 129.0, 128.2, 126.7 (q, $^1J(^{13}C,^{19}F)$ = 280 Hz), 125.8 (q, $^3J(^{13}C,^{19}F)$ = 4 Hz), 124.2 (q, $^1J(^{13}C,^{19}F)$ = 278 Hz), 44.8 (q, $^2J(^{13}C,^{19}F)$ = 27 Hz), 38.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.80 (s), –69.40 (d, $^3J(^1H, ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (90:10), t_{major}(*R*) = 10.7 min, t_{minor}(*S*) = 9.1 min, 59% *ee*. $[\alpha]_D^{20}$ +62.3 (*c* 0.73, $CHCl_3$, 59% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

4,4,4-trifluoro-1-phenyl-3-(p-tolyl)butan-1-one (2l)

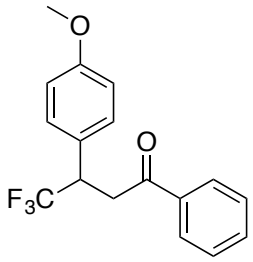


The title compound was prepared from (*E*)-3-(4-methylphenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (0.18 mmol, 53 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (42 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 2H), 7.60–7.57 (m, 1H), 7.49–7.46 (m, 2H), 7.31–7.29 (m, 2H), 7.17–7.15 (m, 2H), 4.27–4.19 (m, 1H), 3.70 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 9 Hz, 1H), 3.60 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 138.2, 136.5, 133.6, 131.7–131.6 (m), 129.5, 129.0, 128.8, 128.3, 127.2 (q, $^{1}J(^{13}C,^{19}F)$ = 280 Hz), 44.5 (q, $^{2}J(^{13}C,^{19}F)$ = 27 Hz), 38.4, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.79 (d, $^{3}J(^{1}H, ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (95:05), t_{major}(*R*) = 10.5 min, t_{minor}(*S*) = 14.2 min, 95% *ee*. $[\alpha]_D^{20}$ +80.8 (*c* 0.95, $CHCl_3$, 95% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

4,4,4-trifluoro-3-(4-methoxyphenyl)-1-phenylbutan-1-one (2m)

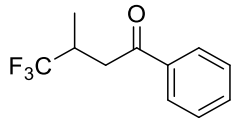


The title compound was prepared from (*E*)-3-(4-methoxyphenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (0.18 mmol, 56 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (49 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.58–7.55 (m, 1H), 7.48–7.43 (m, 2H), 7.32–7.29 (m, 2H), 6.88–6.84 (m, 2H), 4.23–4.14 (m, 1H), 3.78 (s, 3H), 3.66 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 9 Hz, 1H), 3.56 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 159.4, 136.4, 133.5, 130.1, 128.8, 128.7, 128.0, 127.2 (q, $^{1}J(^{13}C,^{19}F)$ = 280 Hz), 114.1, 55.2, 44.5–43.8 (m), 38.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.87 (d, $^{3}J(^{1}H, ^{19}F)$ = 10 Hz). HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (90:10), t_{major}(*R*) = 11.6 min, t_{minor}(*S*) = 11.2 min, 98% *ee*. $[\alpha]_D^{20}$ +75.6 (*c* 0.80, $CHCl_3$, 98% *ee*).

For complete characterization see: Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.

4,4,4-Trifluoro-1-phenylbutanone (2n)

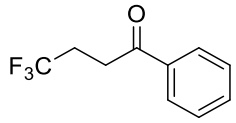


The title compound was prepared from (*E*)-4,4,4-trifluoro-3-methyl-1-phenylbut-2-en-1-ol (0.18 mmol, 39 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (29 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.96 (m, 2H), 7.62–7.58 (m, 1H), 7.51–7.47 (m, 2H), 3.34–3.27 (m, 1H), 3.09–2.99 (m, 2H), 1.18 (d, $^3J(^1H,^1H)$ = 6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 136.7, 133.7, 128.9, 128.2, 127.0 (q, $^1J(^{13}C,^{19}F)$ = 278 Hz), 38.5–38.4 (m), 34.1 (q, $^2J(^{13}C,^{19}F)$ = 27 Hz), 13.3–13.2 (m). ^{19}F NMR (376 MHz, $CDCl_3$): δ –73.37 (d, $^3J(^1H, ^{19}F)$ = 9 Hz).

For complete characterization see: Bizet, V.; Pannecoucke, X.; Renaud , J.-L.; Cahard, D. *Angew. Chem. Int. Ed.* **2012**, *51*, 6467.

4,4,4-Trifluoro-1-phenylbutanone (2o)

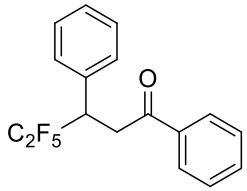


The title compound was prepared from (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (0.18 mmol, 36 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (24 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.96 (m, 2H), 7.63–7.58 (m, 1H), 7.52–7.47 (m, 2H), 3.29–3.25 (m, 2H), 2.66–2.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 136.2, 133.6, 129.0, 128.2, 125.9 (q, $^1J(^{13}C,^{19}F)$ = 272 Hz), 31.3–31.2 (m), 28.5 (q, $^2J(^{13}C,^{19}F)$ = 27 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.44 (t, $^3J(^1H, ^{19}F)$ = 11 Hz).

For complete characterization see: Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn*. **1987**, *60,* 3823.

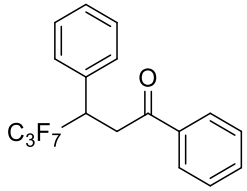
4,4,5,5,5-Pentafluoro-1,3-diphenylpentan-1-one (2p)



The title compound was prepared from (*E*)-4,4,5,5,5-pentafluoro-1,3-diphenylpent-2-en-1-ol (0.18 mmol, 59 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 95:5) afforded the product as a white powder (37 mg, 62%). m.p. 81–82 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.90 (m, 2H), 7.59–7.54 (m, 1H), 7.47–7.43 (m, 2H), 7.40–7.38 (m, 2H), 7.32–7.28 (m, 3H), 4.36–4.24 (m, 1H), 3.69–3.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 136.5, 134.43–134.37 (m), 133.7, 129.5, 128.85, 128.80, 128.5, 128.2, 121.0–113.4 (m, CF_3–CF_2–), 42.7–42.3 (m), 38.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –81.29 (s, 3F), –116.54 (m, 2F). HRMS (ESI): m/z calcd for [$C_{17}H_{13}F_5O$+Na^+] : 351.0779; found: 351.0784. HPLC: CHIRALCEL AD, flow rate 0.5 mL/min, iso-hexane / iso-propanol (99:1), t_{major}(*R*) = 14.8 min, t_{minor}(*S*) = 12.3 min, 92% *ee*. $[\alpha]_D^{20}$ +17.6 (*c* 1.0, $CHCl_3$, 92% *ee*).

4,4,5,5,6,6,6-Heptafluoro-1,3-diphenylhexan-1-one (2q)

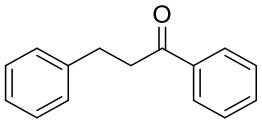


The title compound was prepared from (*E*)-4,4,5,5,6,6,6-heptafluoro-1,3-diphenylhex-2-en-1-ol (0.18 mmol, 68 mg) according to the general procedure. Purification by column chromatography (SiO_2; pentane / EtOAc, 95:5) afforded the product as a white powder (48 mg, 74%). M.p. 89–90 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.90 (m, 2H), 7.59–7.54 (m, 1H), 7.47–7.39 (m, 4H), 7.34–7.27 (m, 3H), 4.41 (m, 1H), 3.68 (d, ^3J(^{1}H,^{1}H) = 7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 136.5, 134.44–134.38 (m), 133.7, 129.6, 128.9, 128.8, 128.4, 128.2, 120.1–106.4 (m, CF_3–CF_2–CF_2–), 42.9–42.5 (m), 38.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –80.63 (m, 3F), –113.93 (m, 2F), –123.36 (m, 2F). HRMS (ESI): m/z calcd for [$C_{18}H_{13}F_7O$+Na^+] : 401.0747; found:

401.0758. HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (99:1), t_{major}(*R*) = 19.4 min, t_{minor}(*S*) = 16.1 min, 95% *ee*. $[\alpha]_D^{20}$ +12.2 (*c* 1.0, $CHCl_3$, 95% *ee*).

1,3-Diphenylpropan-1-one (2r)

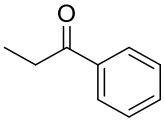


The title compound was prepared from (*E*)-1,3-diphenylprop-2-en-1-ol (0.18 mmol, 38 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (30 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H), 7.58–7.54 (m, 1H), 7.47–7.43 (m, 2H), 7.32–7.19 (m, 5H), 3.33–3.29 (m, 2H), 3.10–3.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 141.4, 137.0, 133.2, 128.74, 128.70, 128.6, 128.2, 126.3, 40.6, 30.3.

For complete characterization see: Li, X.; Zou, G. *J. Organomet. Chem.* **2015**, *794*, 136.

Propiophenone (2s)

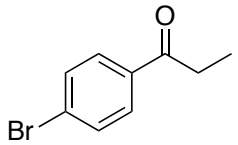


The title compound was prepared from 1-phenylprop-2-en-1-ol (0.18 mmol, 24 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (22 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H), 7.56–7.52 (m, 1H), 7.47–7.43 (m, 2H), 3.00 (q, $^3J(^1H,^1H)$ = 7 Hz, 2H), 1.22 (t, $^3J(^1H,^1H)$ = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 136.9,132.9, 128.5, 128.0, 31.8, 8.2.

For complete characterization see: Iinuma, M; Moriyama, K.; Togo, Hideo *Tetrahedron*, **2013**, *69*, 2961.

1-(4-bromophenyl)propan-1-one (2t)

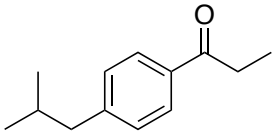


The title compound was prepared from 1-(4-bromophenyl)prop-2-en-1-ol (0.18 mmol, 38 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (28 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.80 (m, 2H), 7.60–7.57 (m, 2H), 2.96 (q, $^1J(^1H,^1H)$ = 7 Hz, 2H), 1.21 (t, $^1J(^1H,^1H)$ = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 135.6, 131.8, 129.5, 128.0, 31.7, 8.1.

For complete characterization see: Chen, T.; Jiang, J.-J.; Xu, Q.; Shi, M. *Org. Lett.* **2007**, *9*, 865.

1-(4-isobutylphenyl)propan-1-one (2u)

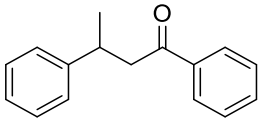


The title compound was prepared from 1-(4-isobutylphenyl)prop-2-en-1-ol (0.18 mmol, 34 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a white powder (14 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, $^1J(^1H,^1H)$ = 8 Hz, 2H), 7.23 (d, $^1J(^1H,^1H)$ = 8 Hz, 2H), 2.53 (d, $^1J(^1H,^1H)$ = 7 Hz, 2H), 1.93–1.83 (m, 1H), 1.22 (t, $^1J(^1H,^1H)$ = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 147.2, 134.7, 129.2, 127.9, 45.4, 31.6, 30.1, 22.3, 8.3.

For complete characterization see: Bogdan, A. R.; Poe, S. L.; Kubis, D. C.; Broadwater, S. J.; McQuade, D. T. *Angew. Chem. Int. Ed.* **2009**, *48*, 8547.

1,3-diphenylbutan-1-one (2v)



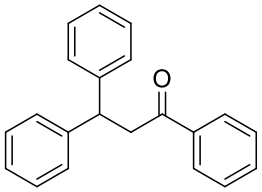
The title compound was prepared from (*E*)-1,3-diphenylbut-2-en-1-ol or from (*Z*)-1,3-diphenylbut-2-en-1-ol (0.18 mmol, 40 mg) according to the general procedure. From **1q**,

purification by column chromatography (SiO_2; pentane / EtOAc, 90:10) afforded the product as a colorless oil (20 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.90 (m, 2H), 7.57–7.52 (m, 1H), 7.47–7.42 (m, 2H), 7.35–7.25 (m, 5H), 3.55–3.50 (m, 1H), 3.30 (dd, $^2J(^1H,^1H)$ = 16.5 Hz; $^3J(^1H,^1H)$ = 8 Hz, 1H), 3.19 (dd, $^2J(^1H,^1H)$ = 16.5 Hz; $^3J(^1H,^1H)$ = 8 Hz, 1H), 1.34 (d, $^3J(^1H,^1H)$ = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 146.7, 128.71, 128.68, 128.5, 128.2, 128.0, 127.0, 126.2, 47.2, 35.7, 22.0.

For complete characterization see: Yang, C.; Wang, J.; Tian, S. *Chem. Comm.* **2011**, *47*, 8343.

1,3,3-Triphenylpropan-1-one (2w)

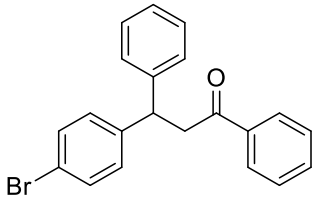


The title compound was prepared from 1,3,3-triphenylprop-2-en-1-ol (0.18 mmol, 51 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (33 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H), 7.58–7.55 (m, 1H), 7.48–7.44 (m, 2H), 7.32–7.27 (m, 10H), 7.22–7.18 (m, 2H), 4.87 (t, $^3J(^1H,^1H)$ = 7 Hz, 1H), 3.73 (d, $^3J(^1H,^1H)$ = 7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 144.1, 137.0, 133.0, 128.54, 128.52, 128.51, 128.50, 128.49, 128.0, 127.80, 127.79, 126.3, 46.1, 44.9.

For complete characterization see: Bedford, R. B.; Betham, M.; Chamart, J. P. H.; Haddow, M. F.; Orpen, A. G.; Pilarski, L. T. *Organometallics*, **2007**, *26*, 6346.

3-(4-Bromophenyl)-1,3-diphenylpropan-1-one (2x)



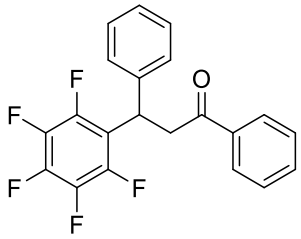
The title compound was prepared from (*E*)-3-(4-bromophenyl)-1,3-diphenylprop-2-en-1-ol or from (*Z*)-3-(4-bromophenyl)-1,3-diphenylprop-2-en-1-ol (0.18 mmol, 66 mg) according to

the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (48 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.96 (m, 2H), 7.54–7.59 (m, 1H), 7.43–7.47 (m, 2H), 7.37–7.42 (m, 2H), 7.25–7.32 (m, 5H), 7.13–7.17 (m, 2H), 4.80 (t, $^{3}J(^{1}H,^{1}H)$ = 7 Hz, 1H), 3.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 143.6, 143.1, 136.9, 133.2, 131.6, 129.6, 128.7, 128.6, 128.0, 127.7, 126.6, 120.0, 45.3, 44.5.

For complete characterization see: Dong, L.; Xu, Y.-J.; Gong, L.-Z.; Mi, A.-Q.; Jiang, Y.-Z. *Synthesis*, **2004**, *7*, 1057.

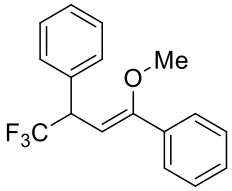
3-(Perfluorophenyl)-1,3-diphenylpropan-1-one (2y)



The title compound was prepared from (*E*)-3-(perfluorophenyl)-1,3-diphenylprop-2-en-1-ol (0.18 mmol, 68 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (46 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.97 (m, 2H), 7.61–7.57 (m, 1H), 7.50–7.46 (m, 2H), 7.39–7.32 (m, 4H), 7.29–7.25 (m, 1H), 5.18–5.15 (m, 1H), 4.10 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 9, 1H), 3.82 (dd, $^{2}J(^{1}H,^{1}H)$ = 18 Hz; $^{3}J(^{1}H,^{1}H)$ = 6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 140.6, 138.0, 136.2, 133.5, 128.9, 128.7, 128.0, 127.4, 127.3, 124.9, 124.7, 117.3, 41.7 (t, $^{4}J(^{13}C, ^{19}F)$ = 3.5 Hz), 36.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −141.8 (m, 2F), −156.8 (m, 1F), −162.0 (m, 2F). HRMS (ESI): m/z calcd for $[C_{21}H_{13}F_5O+Na^+]$: 399.0779; found: 399.0771.

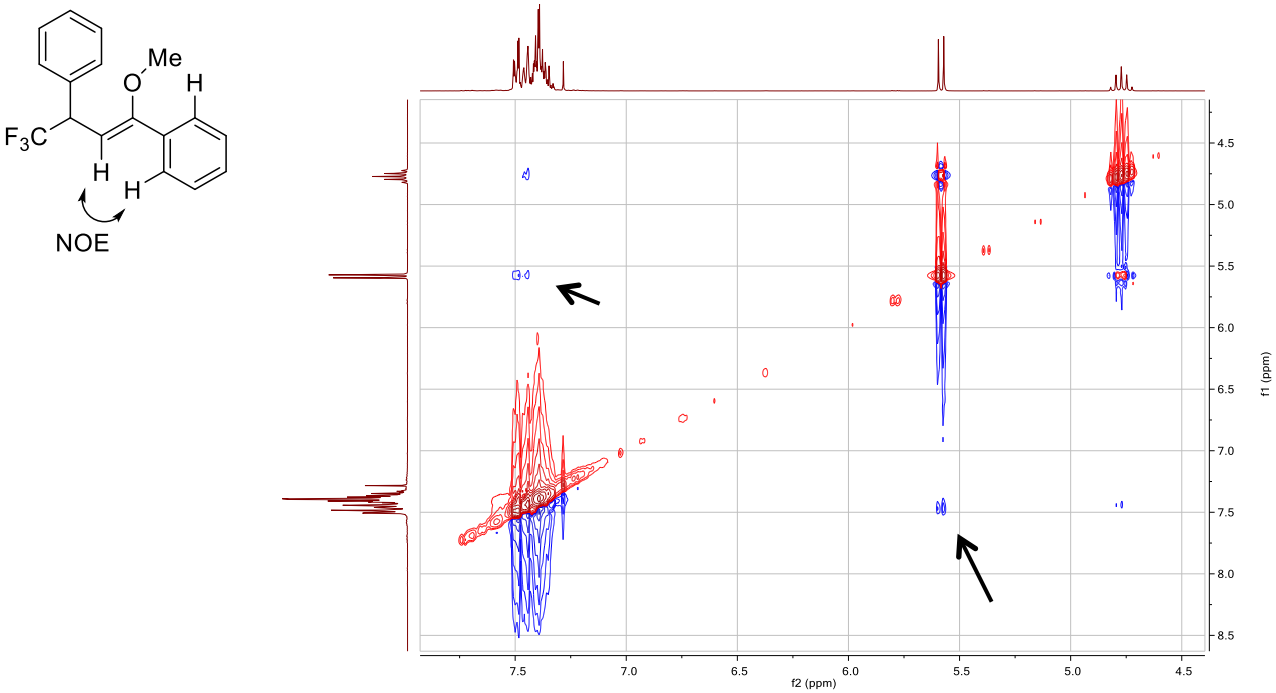
(*Z*)-(4,4,4-Trifluoro-1-methoxybut-1-ene-1,3-diyl)dibenzene (4a)



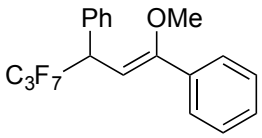
The title compound was prepared from (*E*)-(4,4,4-trifluoro-1-methoxybut-2-ene-1,3-diyl)dibenzene (0.18 mmol, 53 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (45 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.32 (m, 10H), 5.57 (d, $^{3}J(^{1}H,^{1}H)$ = 9.6 Hz, 1H), 4.76 (m, 1H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 136.0 (q, $^{3}J(^{13}C, ^{19}F)$ = 1.5 Hz), 134.7, 129.1, 129.0, 128.8, 128.6, 128.0, 127.0, 126.4 (q, $^{1}J(^{13}C,^{19}F)$ = 280 Hz), 106.7 (q, $^{3}J(^{13}C, ^{19}F)$ = 2 Hz), 58.5, 46.5 (q, $^{2}J(^{13}C, ^{19}F)$ = 27 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.38 (d, $^{3}J(^{1}H, ^{19}F)$ = 10 Hz). HRMS (ESI): m/z calcd for $[C_{17}H_{15}F_3O+Na^+]$: 315.0967; found: 315.0976. HPLC: CHIRALCEL OB, flow rate 0.5 mL/min, isohexane / isopropanol (99:1), t_{major} = 21.1 min, t_{minor} = 13.9 min, 97% *ee*. $[\alpha]_D^{20}$ +25.2 (*c* 1.0, $CHCl_3$, 97% *ee*).

NOE analysis of **4a**



(*Z*)-(4,4,5,5,6,6,6-heptafluoro-1-methoxyhex-1-ene-1,3-diyl)dibenzene (4b)

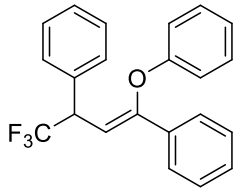


The title compound was prepared from (*E*)-(4,4,5,5,6,6,6-heptafluoro-1-methoxyhex-2-ene-1,3-diyl)dibenzene (0.18 mmol, 71 mg) according to the general procedure. After

quenching, evaporation of the solvent afforded the product as a white powder (49 mg, 69%). The product descomposed upon time.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.30 (m, 10H), 5.52 (d, $^3J(^1H,^1H)$ = 10 Hz, 1H), 4.88–4.79 (m, 1H), 3.44 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –83.30 (m, 3F), –113.30 (m, 2F), –124.43 (m, 2F). HRMS (ESI): m/z calcd for $[C_{19}H_{15}F_7O+Na^+]$: 415.0909; found: 415.0909. HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (99.5:0.5) t_{major} = 14.6 min, t_{minor} = 12.8 min, 95% *ee*. $[\alpha]_D^{20}$ 35.2 (*c* 0.66, $CHCl_3$, 95% *ee*).

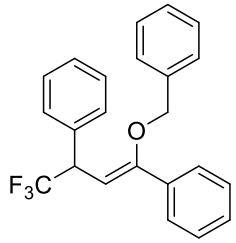
(*Z*)-(4,4,4-trifluoro-1-phenoxybut-1-ene-1,3-diyl)dibenzene (4c)



The title compound was prepared from (*E*)-(4,4,4-trifluoro-1-phenoxybut-2-ene-1,3-diyl)dibenzene (0.18 mmol, 64 mg) according to the general procedure. After quenching, evaporation of the solvent afforded the product as a colorless oil (52 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.50 (m, 2H), 7.37–7.28 (m, 8H), 7.22–7.13 (m, 2H), 6.97–6.93 (m, 1H), 6.90–6.87 (m, 2H), 6.15 (d, $^3J(^1H,^1H)$ = 10 Hz, 1H), 4.67–4.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 153.0, 135.0, 134.3, 129.7, 129.2, 129.0, 128.9, 128.7, 128.2, 126.4, 126.3 (q, $^1J(^{13}C,^{19}F)$ = 280 Hz), 122.3, 116.4, 110.4 (q, $^3J(^{13}C, ^{19}F)$ = 3 Hz), 47.9 (q, $^2J(^{13}C, ^{19}F)$ = 28 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.00 (d, $^3J(^1H, ^{19}F)$ = 9 Hz). HRMS (ESI): m/z calcd for $[C_{22}H_{17}F_3O+Na^+]$: 377.1124; found: 377.1122. HPLC: CHIRALCEL OJ, flow rate 0.5 mL/min, isohexane / isopropanol (99:1), t_{major} = 17.4 min, t_{minor} = 19.6 min, 97% *ee*. $[\alpha]_D^{20}$ -19.5 (*c* 0.66, $CHCl_3$, 97% *ee*).

(*Z*)-(1-(Benzyloxy)-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (4d)

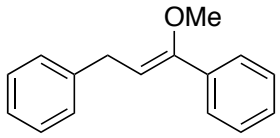


The title compound was prepared from (*E*)-(1-(benzyloxy)-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (0.18 mmol, 66 mg) according to the general procedure. Purification by column

chromatography (SiO_2; pentane / EtOAc, 90:10) afforded the product as a colorless oil (50 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 2H), 7.44–7.39 (m, 3H), 7.38–7.27 (m, 10H), 5.60 (d, $^3J(^1H,^1H)$ = 10 Hz, 1H), 4.71–4.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 136.9, 135.7 (q, $^3J(^{13}C, ^{19}F)$ = 2 Hz), 134.9, 129.0, 128.9, 128.59, 128.56, 128.5, 128.11, 128.06, 127.8, 127.0, 126.2 (q, $^1J(^{13}C,^{19}F)$ = 278 Hz), 107.6 (q, $^3J(^{13}C, ^{19}F)$ = 3 Hz), 72.2, 46.4 (q, $^2J(^{13}C, ^{19}F)$ = 28 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.30 (d, $^3J(^1H, ^{19}F)$ = 10 Hz). HRMS (ESI): m/z calcd for $[C_{23}H_{19}F_3O+Na^+]$: 391.1280; found: 391.1278.

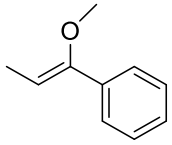
(*Z*)-(1-methoxyprop-1-ene-1,3-diyl)dibenzene (4e)



The title compound was prepared from (*E*)-(3-methoxyprop-1-ene-1,3-diyl)dibenzene (0.18 mmol, 40 mg) according to the general procedure. After the reaction time, 1,3,5-trimethoxybenzene (0.18 mmol, 30 mg) was added and the yield was measured using ^{1}H NMR (53% yield). He analysis of the ^{1}H NMR spectrum showed a mixture 92:08 of both regioisomers *Z* and *E*.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.50 (m, 2H), 7.39–7.30 (m, 8H), 5.52 (t, $^1J(^1H,^1H)$ = 7.5 Hz, 2H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 141.2, 130.1, 129.4, 128.6, 128.3, 127.9, 125.8, 84.3, 58.8, 31.7.

(*Z*)-(1-Methoxyprop-1-en-1-yl)benzene (4f)



The title compound was prepared from (1-methoxyallyl)benzene (2.34 mmol, 300 mg) according to the general procedure. After the reaction time, 1,3,5-trimethoxybenzene (2.34 mmol, 57 mg) was added and the yield was measured using ^{1}H NMR (45% yield). He analysis of the ^{1}H NMR spectrum showed a mixture 97:3 of both regioisomers *Z* and *E*.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 2H), 7.29–7.26 (m, 3H), 5.40 (q, $^3J(^1H,^1H)$ = 7 Hz, 1H, *Z*), 5.40 (q, $^3J(^1H,^1H)$ = 7 Hz, 1H, *Z*), 4.82 (q, $^3J(^1H,^1H)$ = 7 Hz, 1H, *E*), 3.65 (s, 3H, *E*),

3.56 (s, 3H, *Z*), 1.81 (d, $^{3}J(^{1}H,^{1}H)$ = 7 Hz, 3H, *Z*), 1.70 (d, $^{3}J(^{1}H,^{1}H)$ = 7 Hz, 3H, *E*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 136.2, 128.5, 127.7, 125.8, 109.0, 58.5, 11.0.

For complete characterization see: Basdevant, B.; Legault, C. Y. *J. Org. Chem.* **2015**, *80*, 6897.

Kinetic studies

The effect of the substitution of the phenyl ring on the reaction rate of the reaction was studied by applying the general procedure to **1a**, **1b**, **1c**, **1d** and **1e** and taking aliquots every 10–15 min. The samples were quenched with water and extracted with Et_2O. Plotting the conversion versus time afforded the kinetic profile for each substrate.

Reaction rates for each compound were determined and Hammett plot was constructed by representing log k / k_o versus the Hammett sigma (σ_p) values for each substituents in *para* position. A good linear fitting of 0.95 was obtained and the slope was found to be 1.87 (Figure S1).

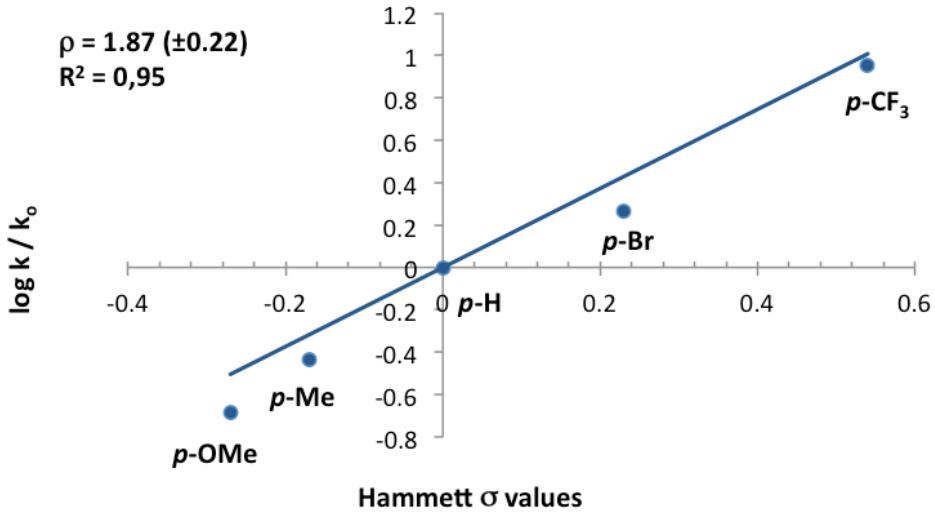


Figure S1. Hammett plot of TBD-catalyzed isomerization of **1a**-**e**.

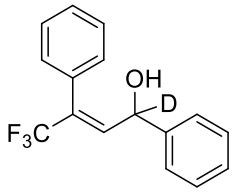
Deuterium labelling studies:

Procedure for the synthesis of the deuterated allylic alcohol 1a-d_1

(*E*)-4,4,4-Trifluoro-1,3-diphenyl-2-buten-1-one (3.62 mmol, 1 g, 1 equiv.) and $CeCl_3{\cdot}7H_2O$ (3.62 mmol, 1.35g, 1 equiv.) were placed in a flask and dissolved in methanol (9 mL). $NaBD_4$ (3.62 mmol, 151.5 mg, 1equiv.) was added with stirring over a period of 2 min. The mixture was allowed to react for adittional 5 min. After hydrolysis, extraction with Et_2O (3 x 30

mL) and evaporation of the solvent the product was isolated in 75% yield as a colorless oil. 96% D.

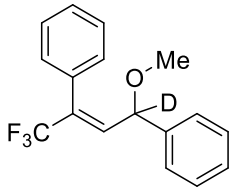
(*E*)-4,4,4-Trifluoro-1,3-diphenyl-2-buten-1-*d*-1-ol (1a-d_1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.42 (m, 3H), 7.39–7.32 (m, 3H), 7.31–7.26 (m, 4H), 6.61 (s, 1H), 1.93 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 136.5 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 131.8 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.3, 129.7, 129.0, 128.9, 128.6, 128.4, 126.2, 123.1 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 70.1 (t, $^1J(^{13}C,^{2}H)$ = 23 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.51 (s).

For complete characterization see: Bizet, V.; Pannecoucke, X.; Renaud, J.-L.; Cahard, D. *Angew. Chem. Int. Ed.* **2012**, *51*, 6467.

(*E*)-(4,4,4-Trifluoro-1-methoxybut-2-ene-1,3-diyl-1-d)dibenzene (3a-d_1)

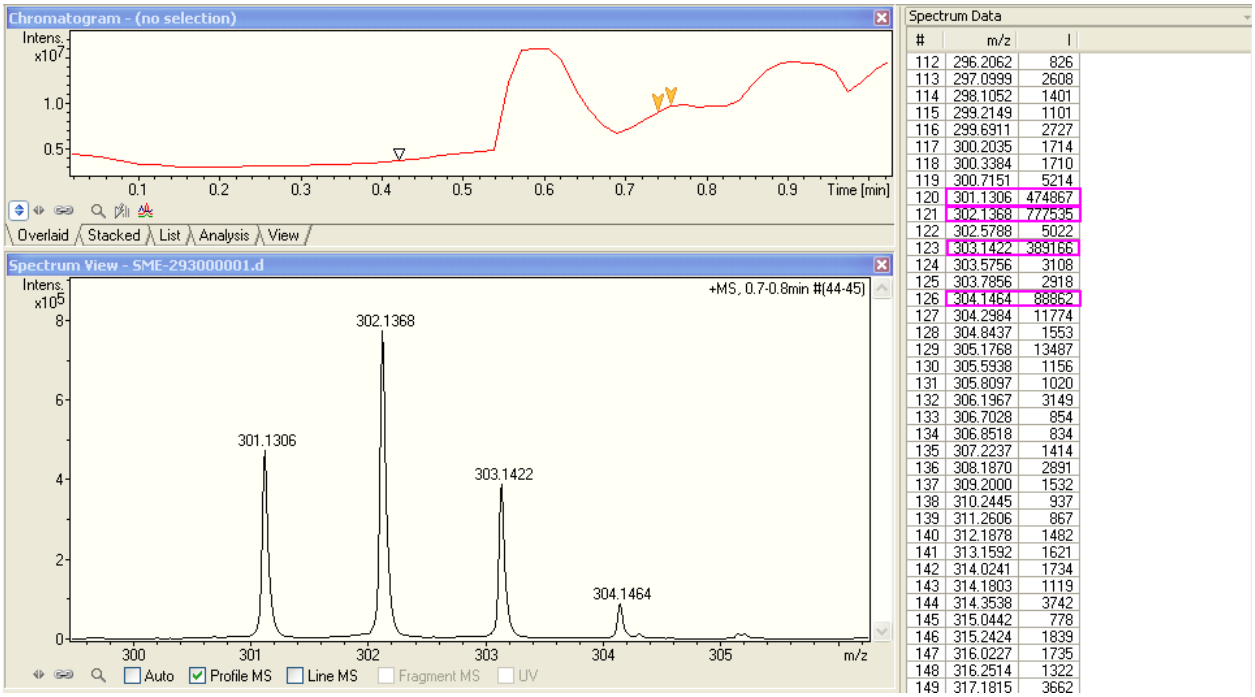


The title compound was synthesized was synthezised from (*E*)-4,4,4-Trifluoro-1,3-diphenyl-2-buten-1-*d*-1-ol (**1a**-d_1) (1.08 mmol, 300 mg) following the general procedure for the synthesis of allylic ethers (See S14). After purification using column chromatography (SiO_2; pentane / EtOAc, 90:10), the product was isolated with 68% yield (215 mg) and 96% D.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.44 (m, 3H), 7.38–7.32 (m, 3H), 7.29–7.27 (m, 2H), 7.23–7.21 (m, 2H), 6.56 (s, 1H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 135.9 (q, $^3J(^{13}C,^{19}F)$ = 5 Hz), 132.9 (q, $^2J(^{13}C,^{19}F)$ = 30 Hz), 131.7, 129.8, 129.1, 128.9, 128.7, 128.5, 127.0, 123.2 (q, $^1J(^{13}C,^{19}F)$ = 274 Hz), 78.9 (m), 56.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.53 (s). HRMS (ESI): m/z calcd for [$C_{17}H_{14}DF_3O$+Na^+] : 316.1030; found: 316.1040.

HRMS analysis of **2a**-d_x

The deuterium distribution in **2a**-*d* was analyzed using the relative intensities of **2a**-d_0, **2a**-d_1, **2a**-d_2 and **2a**-d_3, and the corresponding isotopic distribution for each peak (100% $[M+Na]^+$, 17.5% $[M^{+1}+Na]^+$, 6.5% $[M^{+2}+Na]^+$).

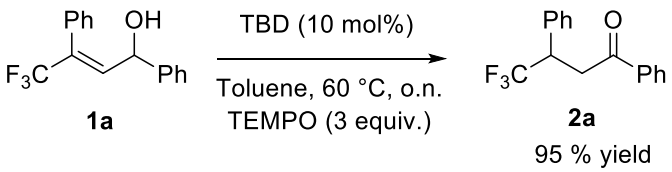


#	m/z	I
112	296.2062	826
113	297.0999	2608
114	298.1052	1401
115	299.2149	1101
116	299.6911	2727
117	300.2035	1714
118	300.3384	1710
119	300.7151	5214
120	301.1306	474867
121	302.1368	777535
122	302.5788	5022
123	303.1422	389166
124	303.5756	3108
125	303.7856	2918
126	304.1464	88862
127	304.2984	11774
128	304.8437	1553
129	305.1768	13487
130	305.5938	1156
131	305.8097	1020
132	306.1967	3149
133	306.7028	854
134	306.8518	834
135	307.2237	1414
136	308.1870	2891
137	309.2000	1532
138	310.2445	937
139	311.2606	867
140	312.1878	1482
141	313.1592	1621
142	314.0241	1734
143	314.1803	1119
144	314.3538	3742
145	315.0442	778
146	315.2424	1839
147	316.0227	1735
148	316.2514	1322
149	317.1815	3662

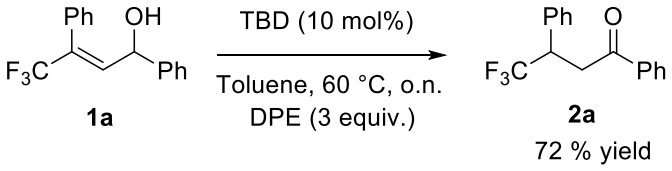
Kinetic isotopic effect

The kinetic isotopic effect was measured by performing two parallel reactions with **1a** and **1a**-d_1 following the general procedure. Different aliquots from each reaction were taken at 30, 45, 60 and 75 minutes and the samples were quenched with water and extracted with Et_2O. The initial rate of the reaction was obtained from the slope of the kinetic profile constructed by plotting the product versus time. The division of the corresponding initial rates yielded a KIE of 5.0 ± 0.6.

Radical trapping experiments



Allylic alcohol **1a** (0.18 mmol, 50 mg, 1 equiv.), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (0.018 mmol, 2.5 mg, 0.1 equiv.) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (0.54 mmol, 84.6 mg, 3 equiv.) were placed in a pressure tube. Toluene was added (1.8 mL) and the mixture was allowed to react overnight at 60 °C. After the reaction time, 1,3,5-trimethoxybencene (2.34 mmol, 57 mg) was added and the yield was measured using ^{1}H NMR (95% yield).



Allylic alcohol **1a** (0.18 mmol, 50 mg, 1 equiv.), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (0.018 mmol, 2.5 mg, 0.1 equiv.) and 1,1-diphenylethylene (DPE) (0.54 mmol, 95 μL, 3 equiv.) were placed in a pressure tube. Toluene was added (1.8 mL) and the mixture was allowed to react overnight at 60 °C. After the reaction time, 1,3,5-trimethoxybencene (2.34 mmol, 57 mg) was added and the yield was measured using ^{1}H NMR (72% yield).

This outcome suggests that a radical pathway may not be involved in this transformation.

Tatton, M. R.; Simpson, I.; Donohoe, T. J. *Org. Lett.* **2014**, 16, 1920.

Computacional studies:

DFT Calculations for the TBD-catalyzed isomerization of allylic alcohols

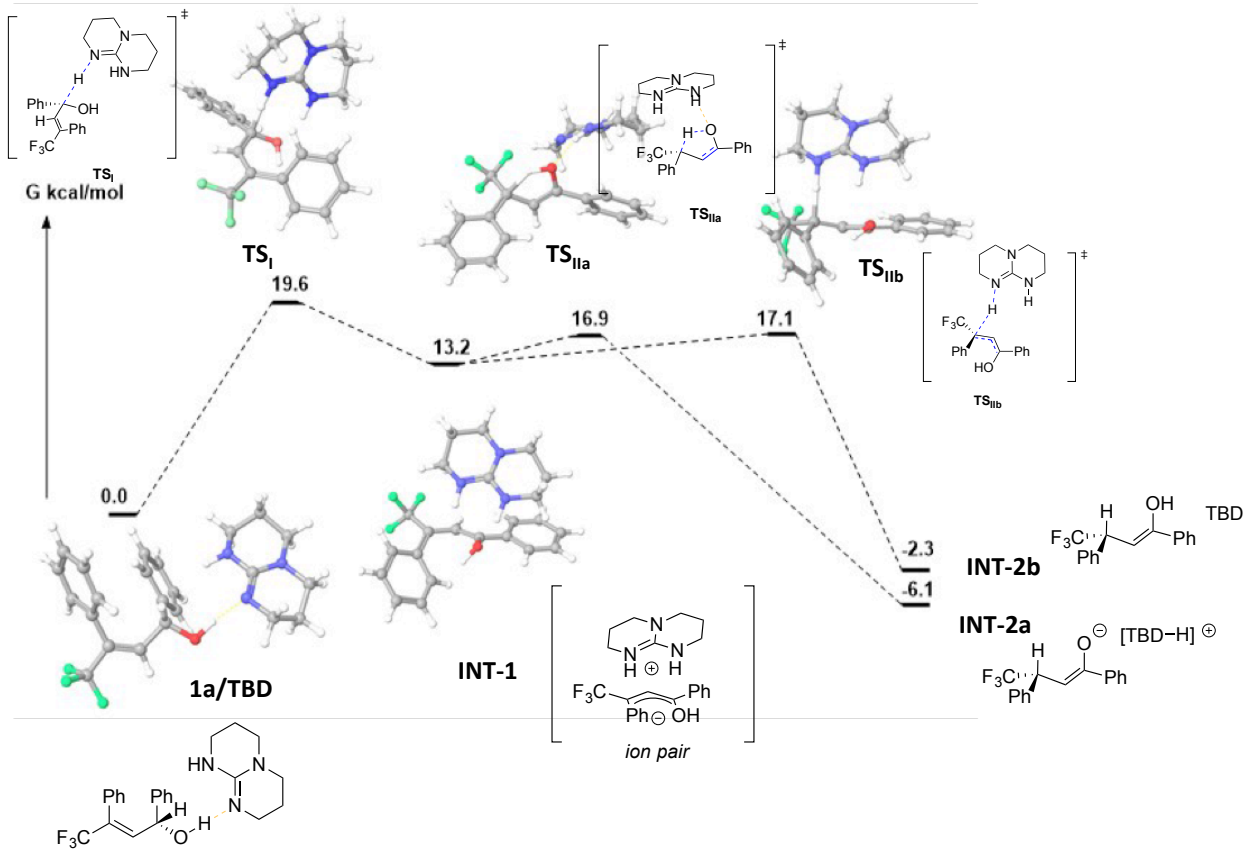


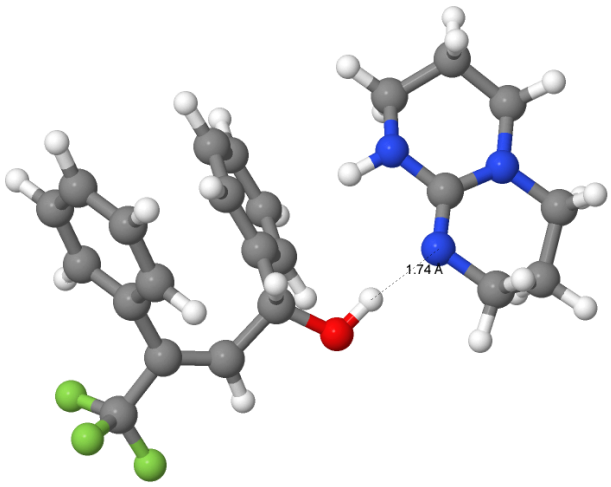
Figure S2: Reaction profile for the TBD-catalyzed isomerization of allylic alcohols

Table with absolute energies and energy corrections

	E(B3LYP-D3/cc-pVTZ++)	G_{solv}(SM8/B3LYP-D3/6-31+G*)	ZPE(B3LYP-D3/6-31G**)	DH_{298}(B3LYP-D3/6-31G**)	TS_{298}(B3LYP-D3/6-31G**)	G
1a + TBD	-1431,701831	-29,489	289,564	17,164	184,018	-898168,625
TS_I	-1431,659557	-32,797	286,219	17,591	186,274	-898148,997
INT-1	-1431,684751	-29,634	290,37	17,239	178,092	-898155,404
TS_{IIa}	-1431,663885	-35,292	287,771	17,224	181,818	-898151,694
TS_{IIb}	-1431,675394	-27,61	286,91	17,24	180,064	-898151,556
INT-2a	-1431,71461	-26,584	289,855	16,334	172,838	-898170,944
INT-2b	-1431,71318	-30,576	289,6	16,719	175,411	-898174,676

Optimized structures and Cartesian coordinates

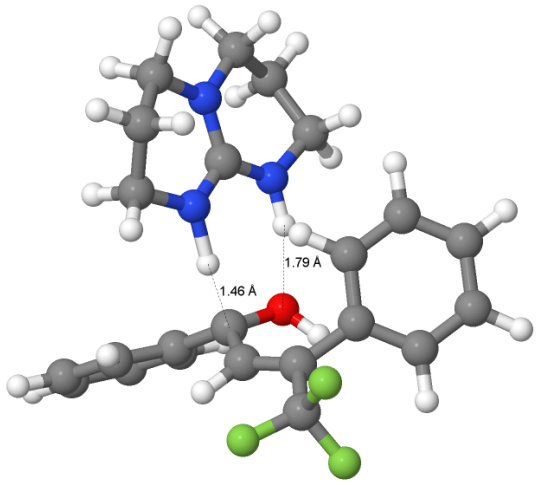
1a and TBD (hydrogen bonded)



C	2.88816	2.20382	3.39553
C	3.54632	2.30931	4.55623
H	3.43727	2.29214	2.46275
C	1.41579	1.89880	3.19499
H	0.81414	2.50301	3.89175
C	0.70547	-2.29532	4.04879
C	0.44727	-1.33611	5.02994
C	0.66956	0.01822	4.76530
C	1.15294	0.42381	3.51482
C	1.40037	-0.54308	2.53198
C	1.18049	-1.89362	2.79671
H	0.53120	-3.34798	4.25509
H	0.07213	-1.63877	6.00404
H	0.46813	0.76016	5.53274
H	1.73793	-0.20966	1.55612
H	1.37384	-2.63473	2.02563
C	1.59768	1.87478	8.35996
C	1.28661	2.95565	7.53212
C	1.94285	3.11349	6.31155
C	2.91288	2.18871	5.89941
C	3.23297	1.11777	6.74637
C	2.57697	0.96143	7.96632
H	1.08326	1.74862	9.30854
H	0.53462	3.67766	7.83767
H	1.70579	3.95522	5.66849
H	3.98212	0.39941	6.43354
H	2.82595	0.11974	8.60649
C	5.03632	2.52903	4.54991
F	5.69848	1.45758	5.06795
F	5.54223	2.73810	3.31567
F	5.37773	3.59434	5.31167
O	1.12743	2.20991	1.85425
H	0.17482	1.96644	1.67500
C	-1.65743	2.43343	-0.07505
C	-2.10768	1.57484	-1.25919

C	-3.36703	0.80966	-0.85856
N	-1.43262	1.62571	1.11502
H	-2.41326	3.21242	0.12137
H	-0.72505	2.95858	-0.31040
H	-1.30934	0.86611	-1.50929
H	-2.30964	2.18069	-2.14894
H	-4.23854	1.48218	-0.84974
H	-3.58239	0.01706	-1.58769
N	-3.21483	0.18809	0.45847
C	-4.06605	-0.97673	0.69791
C	-4.04428	-1.42469	2.15795
C	-2.59756	-1.45098	2.64292
N	-2.06112	-0.11176	2.48390
C	-2.20959	0.59990	1.31212
H	-3.73898	-1.80715	0.04992
H	-5.09032	-0.72327	0.39278
H	-4.61285	-0.72215	2.77687
H	-4.51143	-2.41101	2.24321
H	-2.53298	-1.71916	3.70100
H	-2.01885	-2.20418	2.08184
H	-1.20549	0.10668	2.97600

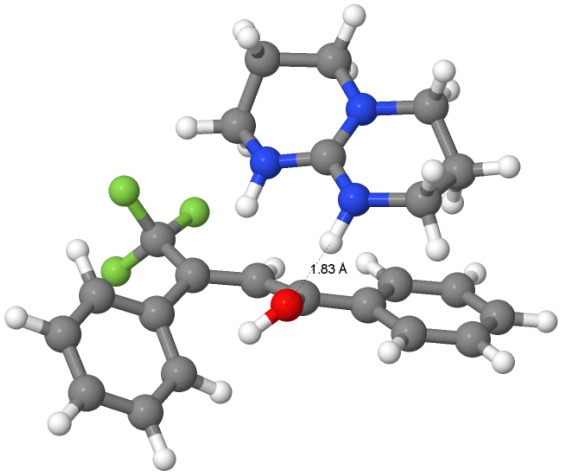
TS_I



C	0.00000	0.00000	0.00000
H	0.00000	0.00000	1.46263
N	0.16586	0.00000	2.69723
C	-1.07776	-0.87173	-0.39713
C	-1.09926	-2.22868	-0.56228
H	-2.01081	-0.35669	-0.60730
C	-0.35623	4.24861	-0.67318
C	-1.42784	3.51469	-0.15853
C	-1.31077	2.14272	0.04577
C	-0.12507	1.45345	-0.28187
C	0.95004	2.20721	-0.78369
C	0.83160	3.58307	-0.97828
H	-0.44496	5.32038	-0.82608
H	-2.35884	4.01608	0.09485

H	-2.14787	1.59570	0.47421
H	1.87554	1.69655	-1.02546
H	1.67637	4.13961	-1.37751
C	2.09751	-4.90726	0.52226
C	1.64196	-3.93840	1.41861
C	0.59937	-3.08704	1.06209
C	-0.00368	-3.16704	-0.20684
C	0.45381	-4.15933	-1.09311
C	1.49167	-5.01733	-0.73052
H	2.90922	-5.57429	0.79903
H	2.09054	-3.85294	2.40565
H	0.23165	-2.35004	1.76705
H	-0.00558	-4.24771	-2.07129
H	1.83366	-5.77081	-1.43490
C	-2.33532	-2.86375	-1.11622
F	-2.73312	-3.93708	-0.38357
F	-3.39583	-2.02223	-1.18410
F	-2.15581	-3.34164	-2.38900
O	1.33639	-0.49105	-0.22487
H	1.30276	-1.19500	-0.88698
C	-0.92740	0.46234	3.53316
C	-0.81199	-0.16141	4.92365
C	0.55889	0.17696	5.50802
H	-0.92760	1.56084	3.60440
H	-1.86475	0.17294	3.04694
H	-0.92147	-1.24832	4.83858
H	-1.59603	0.20521	5.59314
H	0.59370	1.22999	5.82322
H	0.75711	-0.43416	6.39703
N	1.63339	-0.07373	4.54133
C	2.97557	-0.25022	5.10165
C	4.05747	-0.06662	4.04015
C	3.70319	-0.90727	2.81578
N	2.37268	-0.54304	2.36625
C	1.37069	-0.19848	3.20628
H	3.05429	-1.24874	5.55834
H	3.10364	0.48345	5.90657
H	4.11727	0.98754	3.74876
H	5.02776	-0.36162	4.45036
H	4.40161	-0.72203	1.99508
H	3.76198	-1.97985	3.05842
H	2.12245	-0.63775	1.37298

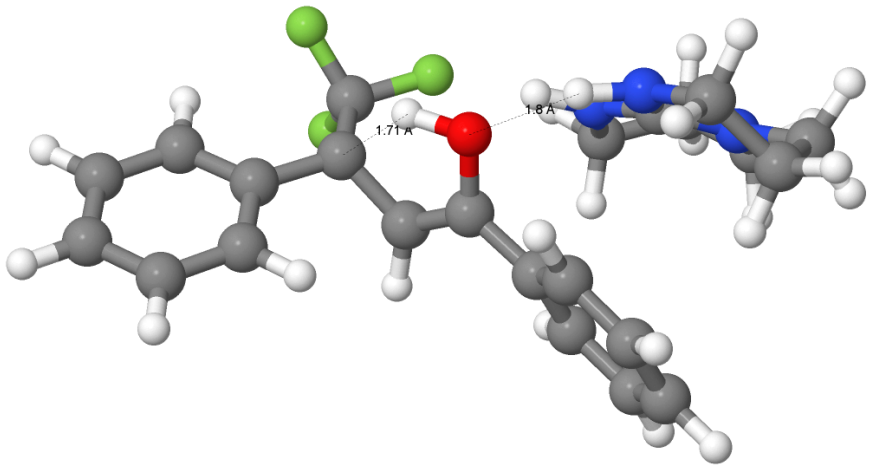
Intermediate Ion-Pair INT-1



C	2.77475	2.61604	2.80044
C	3.28389	2.77349	4.11456
H	3.39783	2.98655	1.99270
C	1.60082	2.00938	2.40628
C	0.02895	1.62401	-1.58084
C	1.33519	2.08583	-1.37604
C	1.85196	2.23311	-0.09443
C	1.08096	1.91947	1.05485
C	-0.24219	1.46512	0.82527
C	-0.75216	1.32315	-0.46286
H	-0.36947	1.51370	-2.58486
H	1.96036	2.33542	-2.23022
H	2.86975	2.59296	0.02114
H	-0.86850	1.24381	1.68278
H	-1.77687	0.98197	-0.59323
C	0.75492	3.20023	7.59201
C	0.28959	3.53122	6.32217
C	1.11833	3.40445	5.20373
C	2.45107	2.91696	5.30596
C	2.90840	2.62054	6.61643
C	2.08046	2.76267	7.72240
H	0.11258	3.29393	8.46238
H	-0.72011	3.91391	6.19139
H	0.77671	3.78719	4.24399
H	3.92308	2.26673	6.75506
H	2.47035	2.51665	8.70746
C	4.72191	3.08585	4.25915
F	5.41992	2.17094	5.05015
F	5.39326	3.08169	3.06886
F	4.99484	4.28208	4.84791
O	0.83440	1.29691	3.35401
H	0.66913	1.84297	4.15385
C	4.74043	-0.22196	3.25957
C	5.44374	-1.45532	2.70738
C	4.88357	-1.77018	1.32301
N	3.30647	-0.50469	3.29543
H	4.94241	0.66344	2.64559

H	5.05756	0.01993	4.27259
H	5.28237	-2.30366	3.38141
H	6.52088	-1.28442	2.63207
H	5.25431	-1.04464	0.58602
H	5.19617	-2.76685	0.99057
N	3.41332	-1.73710	1.30709
C	2.77444	-2.26862	0.09235
C	1.39165	-1.66127	-0.11892
C	0.59458	-1.78991	1.17494
N	1.35092	-1.19644	2.27817
C	2.69390	-1.13290	2.27646
H	2.72048	-3.36375	0.16499
H	3.43118	-2.02674	-0.75024
H	1.47695	-0.60333	-0.38331
H	0.88494	-2.17809	-0.93855
H	-0.34998	-1.25046	1.09852
H	0.37835	-2.84308	1.39867
H	0.90190	-0.45130	2.82102
H	2.73001	0.14611	3.82675

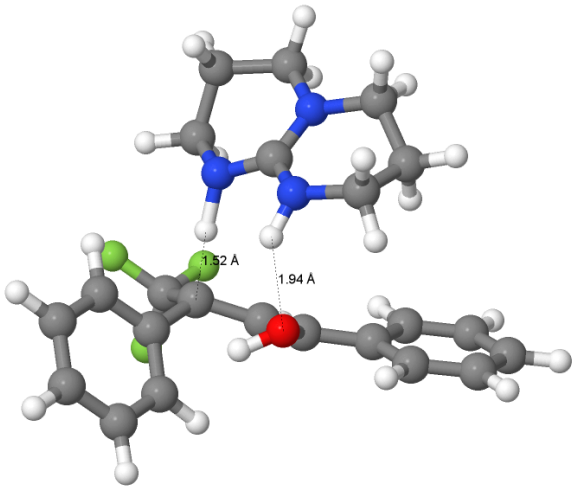
TS_{IIa}



O	0.00000	0.00000	0.00000
H	0.00000	0.00000	1.08620
C	1.24535	0.00000	2.25957
C	2.07060	0.13832	1.02229
H	3.12510	0.41409	1.02700
C	1.35991	0.18307	-0.12757
C	2.81940	1.13929	-4.03822
C	3.59743	0.37409	-3.16640
C	3.12120	0.05097	-1.89642
C	1.85550	0.48953	-1.47108
C	1.07567	1.25237	-2.36004
C	1.55787	1.58240	-3.62433
H	3.19174	1.39149	-5.02703
H	4.57902	0.02618	-3.47746
H	3.72506	-0.54464	-1.21847

H	0.10141	1.59836	-2.02852
H	0.95073	2.18867	-4.29163
C	1.55765	3.46728	4.83727
C	1.64616	3.57305	3.44825
C	1.54486	2.44305	2.64314
C	1.35373	1.14930	3.18518
C	1.27101	1.06587	4.59413
C	1.36784	2.20188	5.39528
H	1.63469	4.34846	5.46836
H	1.79103	4.54619	2.98347
H	1.60301	2.55466	1.56429
H	1.13512	0.10300	5.07138
H	1.30202	2.09277	6.47563
C	1.23319	-1.34558	2.84800
F	0.24323	-1.55085	3.75812
F	1.03758	-2.34062	1.88106
F	2.38300	-1.75947	3.48681
C	2.21326	-3.57868	-0.58392
C	2.19870	-4.76514	-1.54242
C	2.03665	-4.25773	-2.97489
N	0.99560	-2.80990	-0.80241
H	3.09573	-2.94644	-0.75274
H	2.22024	-3.88529	0.46205
H	1.36667	-5.42866	-1.28392
H	3.12526	-5.34050	-1.46581
H	2.96899	-3.79488	-3.32716
H	1.80291	-5.08645	-3.65222
N	0.95440	-3.26897	-3.09043
C	0.47972	-2.96638	-4.44693
C	-0.04377	-1.53630	-4.53601
C	-1.06615	-1.29625	-3.42744
N	-0.51044	-1.69968	-2.13770
C	0.49036	-2.58609	-2.02149
H	-0.29547	-3.69184	-4.73082
H	1.32527	-3.10418	-5.12857
H	0.78627	-0.83335	-4.42119
H	-0.49919	-1.37161	-5.51671
H	-1.31720	-0.23530	-3.35863
H	-1.99300	-1.85033	-3.62565
H	-0.58567	-1.04716	-1.34051
H	0.66940	-2.22985	-0.03516

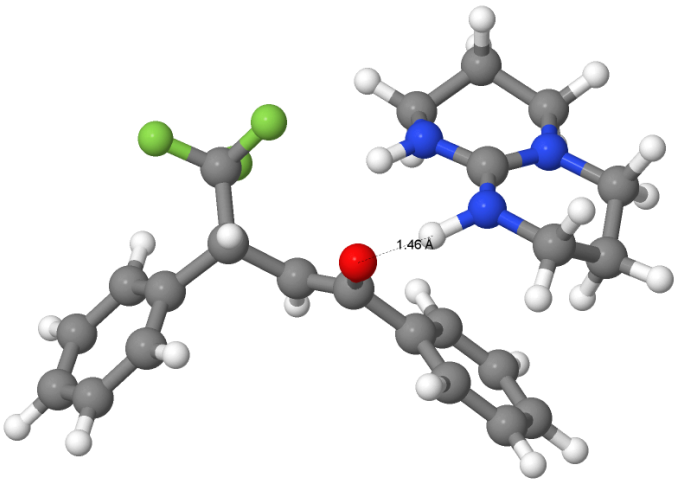
TS_{IIb}



N	0.00000	0.00000	0.00000
H	0.00000	0.00000	1.22000
C	0.24946	0.00000	2.72084
C	0.37452	2.52157	2.79053
H	-1.12231	2.01447	0.85915
N	-0.79199	2.16195	-0.09211
C	0.93398	1.28923	2.86967
H	2.01625	1.25846	2.93033
C	2.43094	6.27227	2.37014
C	3.12534	5.06910	2.20978
C	2.47174	3.84876	2.34830
C	1.09943	3.79173	2.67365
C	0.41311	5.01318	2.82865
C	1.07076	6.23269	2.67727
H	2.94311	7.22295	2.25302
H	4.18367	5.08223	1.96261
H	3.02843	2.93050	2.19046
H	-0.64293	4.98965	3.07267
H	0.51498	7.15820	2.80504
C	-3.60985	-0.57266	4.60236
C	-2.67263	0.28421	5.17712
C	-1.41625	0.44995	4.58734
C	-1.07416	-0.21690	3.39296
C	-2.03084	-1.08643	2.83628
C	-3.27556	-1.26503	3.43443
H	-4.58832	-0.70129	5.05646
H	-2.91088	0.81968	6.09262
H	-0.67187	1.08393	5.06407
H	-1.78865	-1.61226	1.91887
H	-3.99790	-1.93775	2.97916
C	1.15763	-1.17172	2.89243
F	0.62778	-2.31515	2.35905
F	2.36264	-0.98592	2.26566
F	1.46819	-1.48442	4.18346
O	-1.01210	2.68390	2.67702

H	-1.45701	2.02212	3.23624
C	-0.69824	3.56569	-0.48779
C	0.65755	3.83775	-1.12976
C	0.88791	2.81477	-2.23855
H	-1.50679	3.81285	-1.19023
H	-0.83362	4.16999	0.41195
H	1.44193	3.75662	-0.36916
H	0.69165	4.85010	-1.54262
H	0.20296	2.99403	-3.08104
H	1.90961	2.89378	-2.62818
N	0.71534	1.44966	-1.73230
C	1.42225	0.38946	-2.45420
C	0.89627	-0.98612	-2.05326
C	0.84675	-1.06684	-0.53179
C	-0.00426	1.18397	-0.60312
H	2.50031	0.46276	-2.24726
H	1.28436	0.56222	-3.52896
H	-0.11033	-1.13293	-2.46115
H	1.54466	-1.76330	-2.46904
H	0.43507	-2.01964	-0.18957
H	1.85976	-0.99698	-0.11265

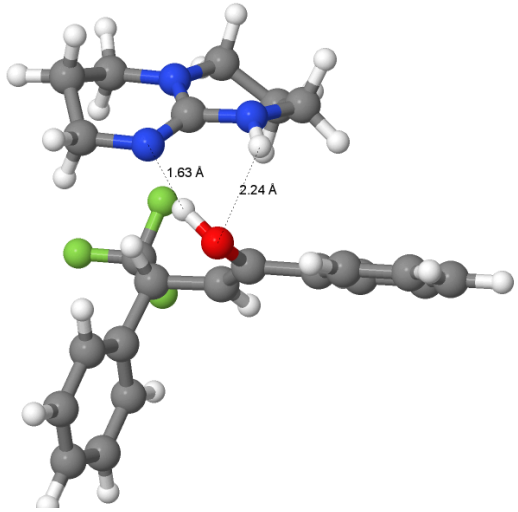
Enolate Product INT-2a



N	0.00000	0.00000	0.00000
H	0.00000	0.00000	2.41221
C	0.61536	0.00000	3.30974
C	1.94313	1.75090	2.09240
H	1.98091	1.24305	-0.48760
N	2.17363	0.27160	-0.69075
C	1.86964	0.78490	3.03093
H	2.70984	0.61560	3.69353
C	5.45945	4.12748	1.36148
C	5.57070	2.91803	2.05207
C	4.44093	2.14161	2.29767

C	3.17066	2.55921	1.86154
C	3.07487	3.76969	1.15508
C	4.20685	4.54731	0.91397
H	6.34205	4.73111	1.16903
H	6.54350	2.57321	2.39208
H	4.55223	1.19234	2.81243
H	2.10124	4.09197	0.80405
H	4.10851	5.48488	0.37316
C	-1.66471	1.97333	6.41626
C	-0.53327	1.23170	6.76053
C	0.19916	0.56545	5.77844
C	-0.19810	0.62560	4.43680
C	-1.33234	1.37342	4.09925
C	-2.06170	2.04357	5.08075
H	-2.22977	2.49642	7.18281
H	-0.21530	1.17577	7.79824
H	1.08128	-0.00102	6.05574
H	-1.63102	1.44780	3.05699
H	-2.93692	2.62323	4.80020
C	0.92951	-1.46843	3.52843
F	-0.19016	-2.19800	3.72409
F	1.55329	-2.00088	2.43862
F	1.75351	-1.69286	4.58139
O	0.91204	2.11075	1.28197
H	0.40570	1.31512	0.87993
C	3.57104	-0.14757	-0.69796
C	3.69561	-1.50945	-0.02098
C	2.67443	-2.46834	-0.63214
H	3.94751	-0.20506	-1.72996
H	4.16473	0.60538	-0.16953
H	3.49000	-1.40397	1.04893
H	4.70727	-1.90781	-0.14415
H	2.93752	-2.69683	-1.67625
H	2.67218	-3.41514	-0.08054
N	1.32514	-1.90576	-0.55490
C	0.21979	-2.83185	-0.31603
C	-1.10660	-2.13805	-0.61427
C	-1.17611	-0.83995	0.19373
C	1.12275	-0.55933	-0.38673
H	0.24400	-3.18634	0.72449
H	0.35946	-3.70048	-0.97021
H	-1.16525	-1.90983	-1.68501
H	-1.94157	-2.80092	-0.36519
H	-2.06412	-0.26166	-0.08905
H	-1.30363	-1.09560	1.25916

Enol Product INT-2b



O	0.00000	0.00000	0.00000
H	0.00000	0.00000	2.44203
C	1.06163	0.00000	2.71494
C	1.84688	0.29357	1.46128
H	2.85920	0.65805	1.58978
C	1.24807	0.34598	0.23541
C	3.47849	1.80869	-3.16588
C	4.10032	0.96563	-2.24161
C	3.39343	0.48768	-1.13629
C	2.05012	0.83786	-0.93526
C	1.43097	1.67104	-1.88024
C	2.13861	2.16343	-2.97556
H	4.02952	2.18407	-4.02374
H	5.13920	0.67774	-2.38290
H	3.87945	-0.16953	-0.42051
H	0.38704	1.92881	-1.72797
H	1.64594	2.82254	-3.68606
C	1.81903	3.25518	5.47126
C	0.82056	3.34722	4.49909
C	0.57290	2.27246	3.64866
C	1.31337	1.08726	3.75105
C	2.31573	1.00481	4.72482
C	2.56275	2.08103	5.57993
H	2.01680	4.09281	6.13452
H	0.23719	4.25893	4.40083
H	-0.19008	2.35174	2.87830
H	2.91099	0.10300	4.81682
H	3.34403	2.00045	6.33125
C	1.30832	-1.40561	3.24131
F	0.75986	-1.62356	4.45565
F	0.75644	-2.33721	2.40295
F	2.62583	-1.72534	3.33796

C	2.35400	-3.32426	0.05499
C	2.66744	-4.47488	-0.89623
C	2.86389	-3.92693	-2.30870
N	1.17468	-2.63807	-0.45300
H	3.20435	-2.63110	0.13409
H	2.12876	-3.67677	1.06075
H	1.83545	-5.18693	-0.88190
H	3.57198	-5.00590	-0.58582
H	3.84136	-3.42892	-2.38977
H	2.85135	-4.74120	-3.04290
N	1.81958	-2.96515	-2.68192
C	1.78160	-2.56868	-4.09536
C	1.25588	-1.14488	-4.25389
C	-0.05291	-1.00192	-3.47830
N	0.12411	-1.43252	-2.09795
C	1.04516	-2.33359	-1.76363
H	1.16302	-3.28338	-4.65672
H	2.80249	-2.64251	-4.48612
H	1.98744	-0.43589	-3.85685
H	1.10731	-0.92361	-5.31521
H	-0.37531	0.04195	-3.45586
H	-0.85071	-1.58626	-3.95815
H	-0.08607	-0.73441	-1.26119
H	0.66629	-2.01822	0.17537

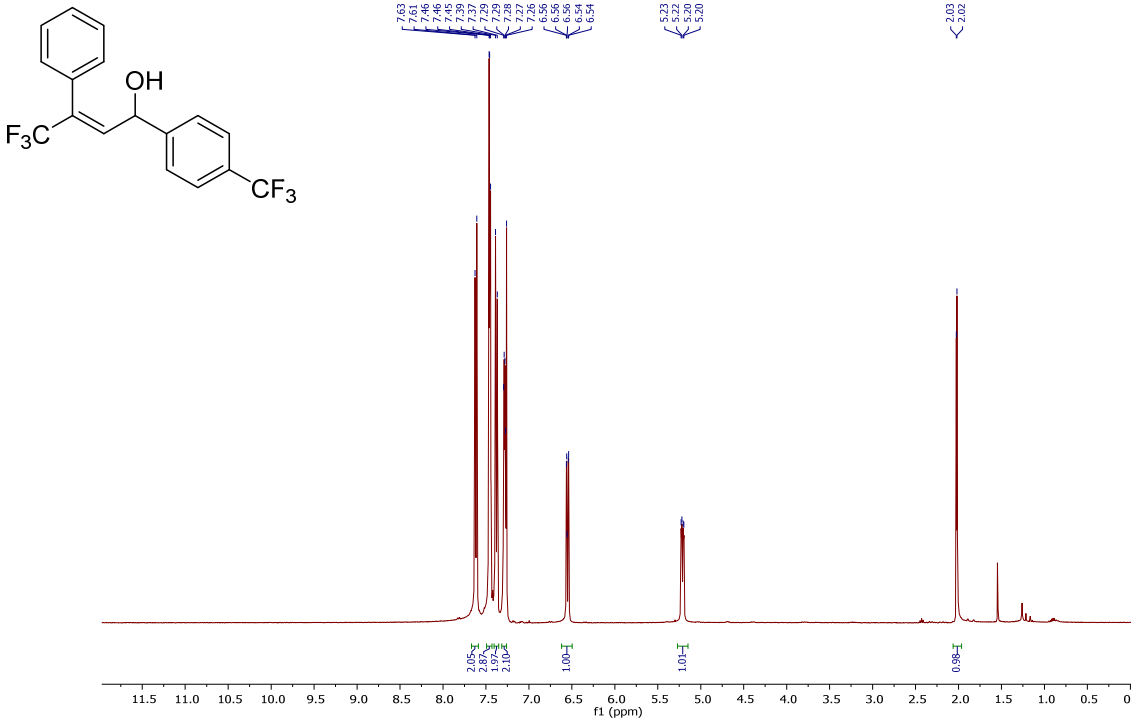
References

[1] Bizet, V.; Pannecoucke, X.; Renaud , J.-L.; Cahard, D. *Angew. Chem. Int. Ed.* **2012**, *51*, 6467.
[2] Cahard, D.; Bizet, V.; Dai, X.; Gaillard, S.; Renaud, J.-L. *J. Fluorine Chem.* **2013**, *155*, 78.
[3] Yamazaki, T.; Ichikawa, M.; Kawasaki-Takasuka, T.; Yamada, S. *J. Fluorine Chem.* **2013**, *155*, 151.
[4] Chen, S.-J.; Lu, G.-P.; Cai, C. *Synthesis* **2015**, *47*, 976.
[5] Ahlsten, N.; Bermejo Gómez, A.; Martín-Matute, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 6273.
[6] Bouziane, A.; Hélou, M.; Carboni, B.; Carreaux, F.; Demerseman, B.; Bruneau, C.; Renaud, J.-L. *Chem. Eur. J.* **2008**, *14*, 5630.
[7] Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065.
[8] Yang, H.; Fang, L.; Zhang, M.; Zhu, C. *Eur. J. Org. Chem.* **2009**, 666.
[9] Tao, J.-L.; Yang, B.; Wang, Z.-X. *J. Org. Chem*. **2015**, *80*, 12627.
[10] Kämphen U.; Eschenmoser, A. *Helvetica Chimica Acta* **1989**, *72*, 185.
[11] Park, J.; Yun, J.; Kim, J.; Jang, D.-J.; Park, C. H.; Lee, K. *Synthetic Communications* **2014**, *44*, 1924.
[12] Ghosh, R.; Lindstedt, E.; Jalalian, N.; Olofsson, B. *ChemistryOpen* **2014**, *3*, 54.

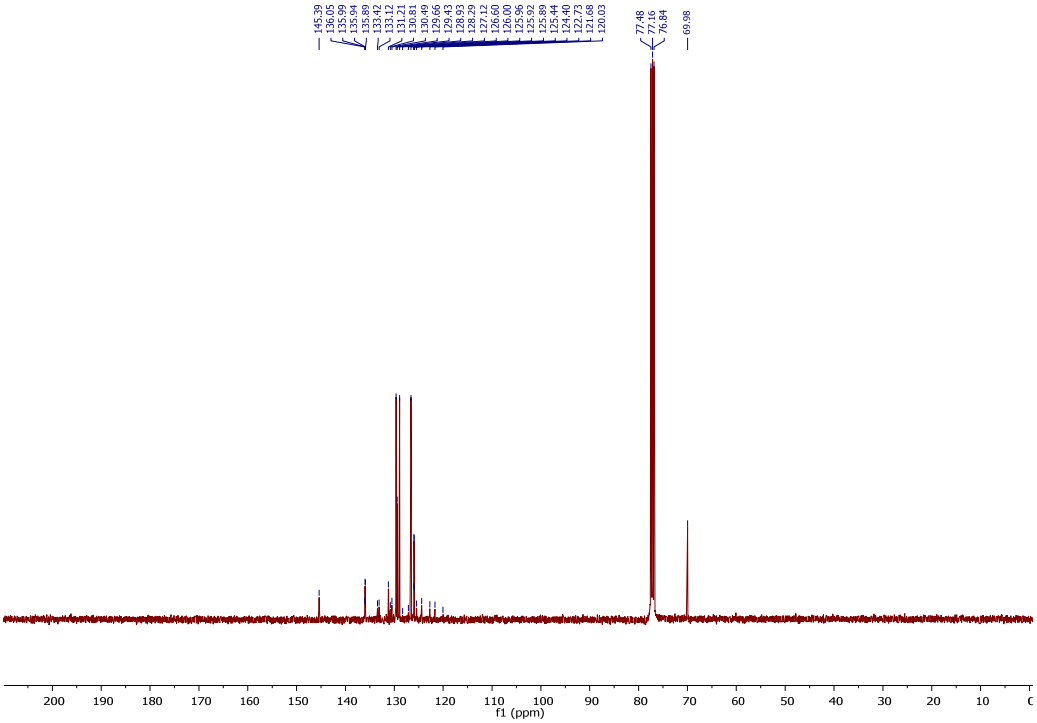
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of starting materials not reported previously

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-Trifluoromethylphenyl)-2-buten-1-ol (1c)

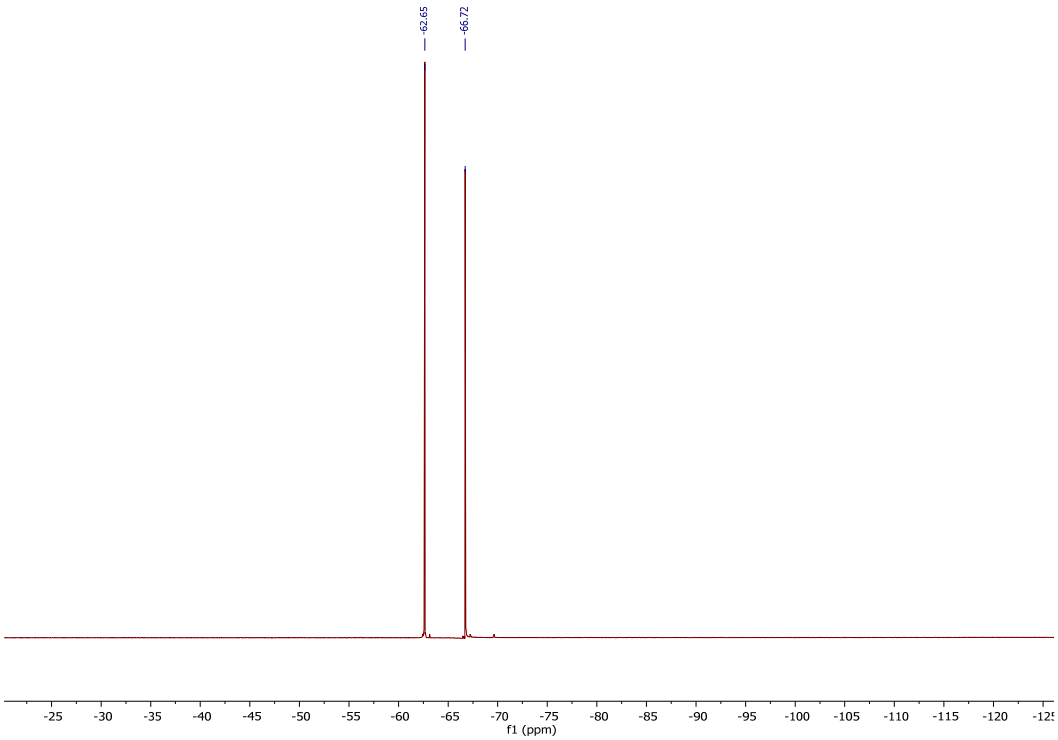
^{1}H NMR (400 Hz, $CDCl_3$)



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

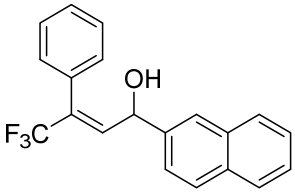


^{19}F NMR (376 Hz, $CDCl_3$)

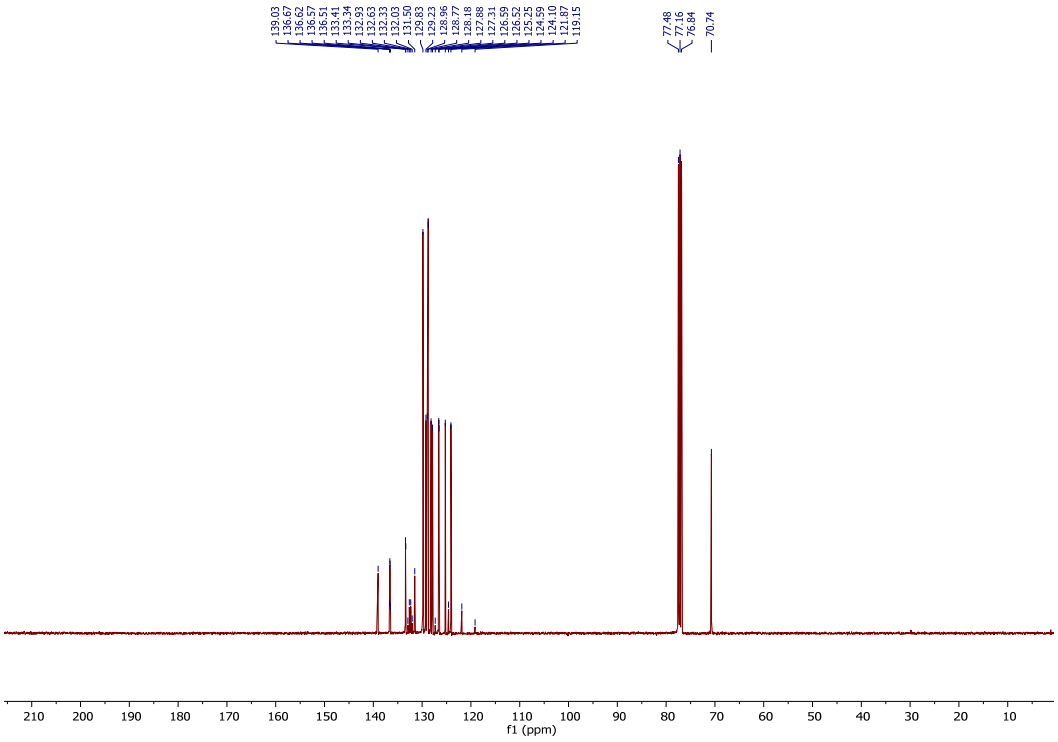


(*E*)-4,4,4-Trifluoro-3-phenyl-1-(naphthalene-2-yl)-2-buten-1-ol (1f)

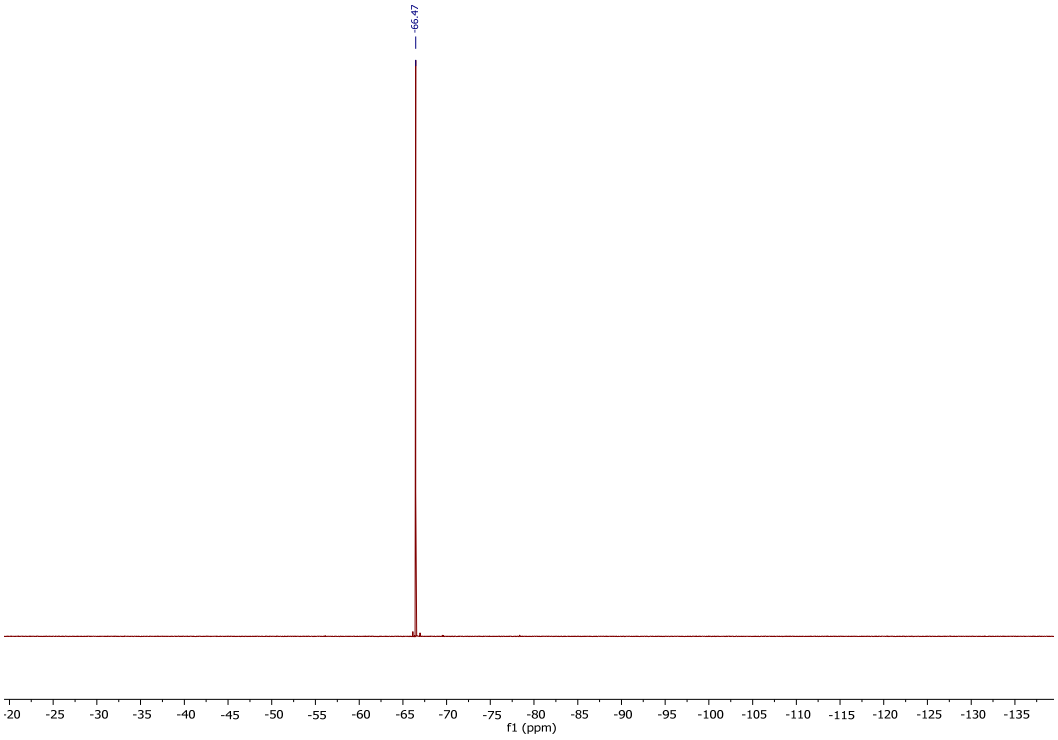
^{1}H NMR (400 Hz, $CDCl_3$)



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

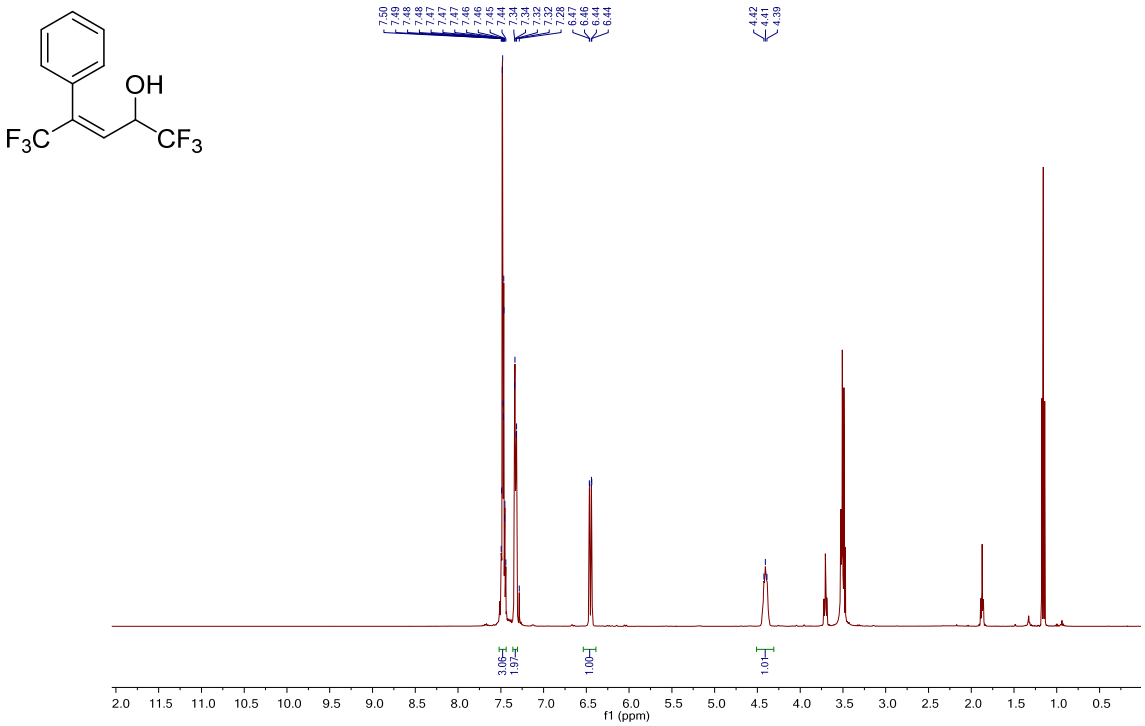


^{19}F NMR (376 Hz, $CDCl_3$)

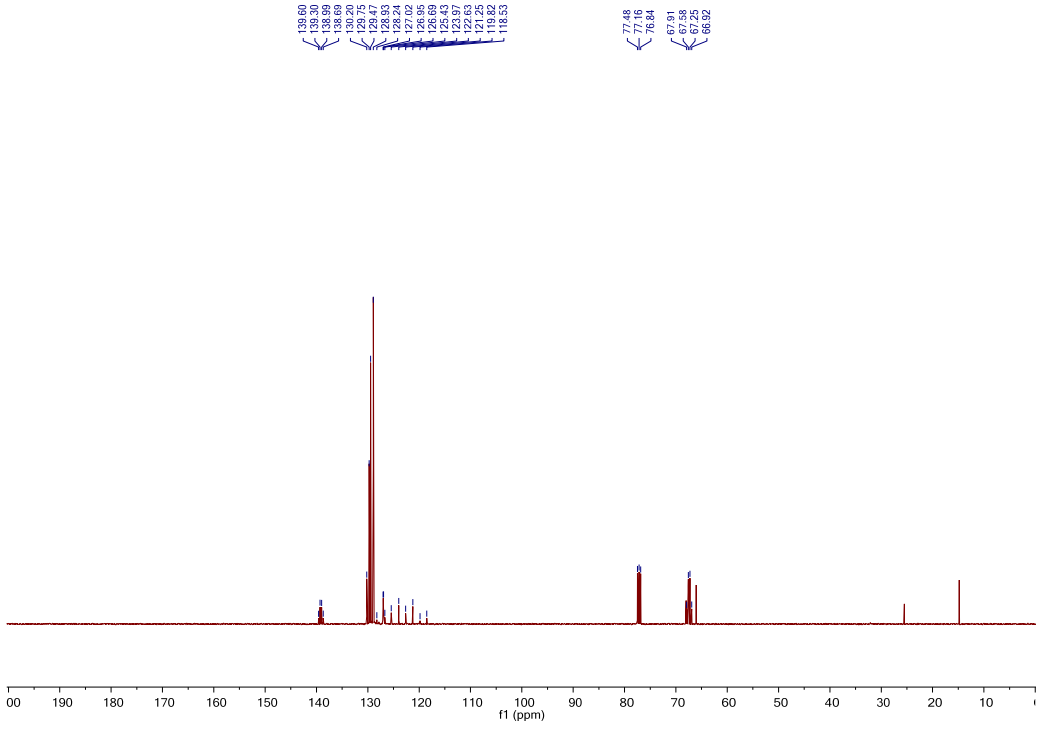


(*E*)-1,1,1,5,5,5-Hexafluoro-4-phenylpent-3-en-2-ol (1g): [i]

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

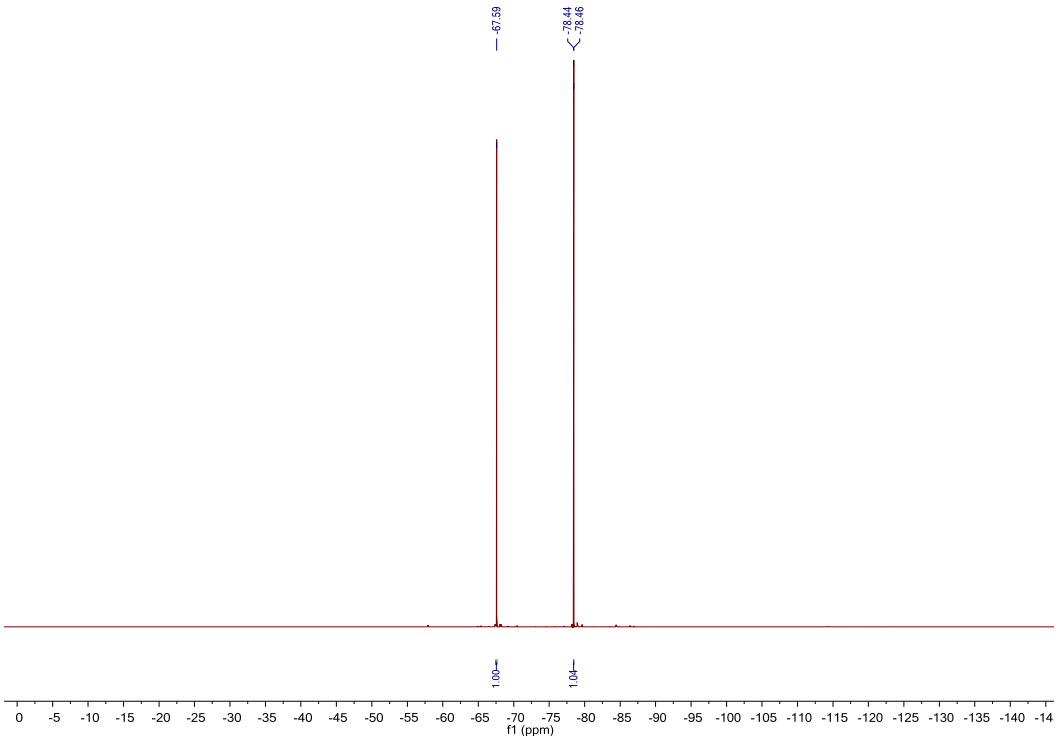


^{13}C NMR (100 Hz, $CDCl_3$)



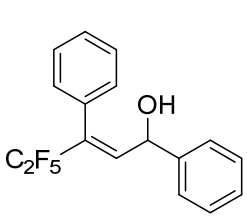
[i] The product is very volatile; spectra shows the corresponding peaks of THF and Et_2O.

^{19}F NMR (376 Hz, $CDCl_3$)

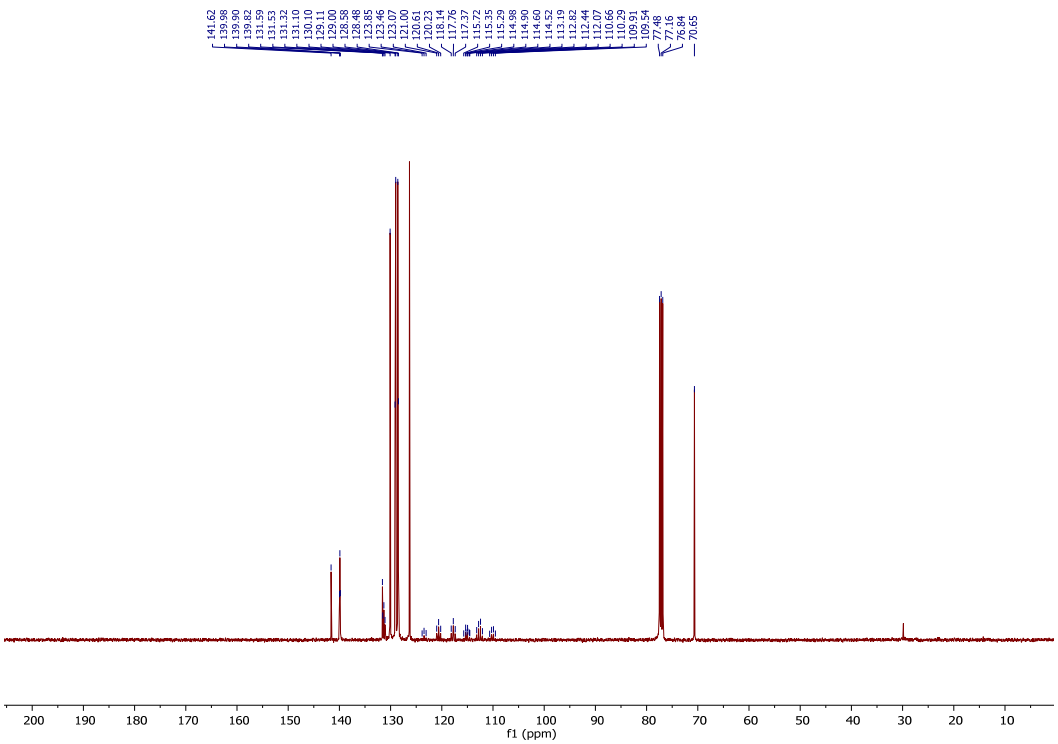


(*E*)-4,4,5,5,5-Pentafluoro-1,3-diphenylpent-2-en-1-ol (1p)

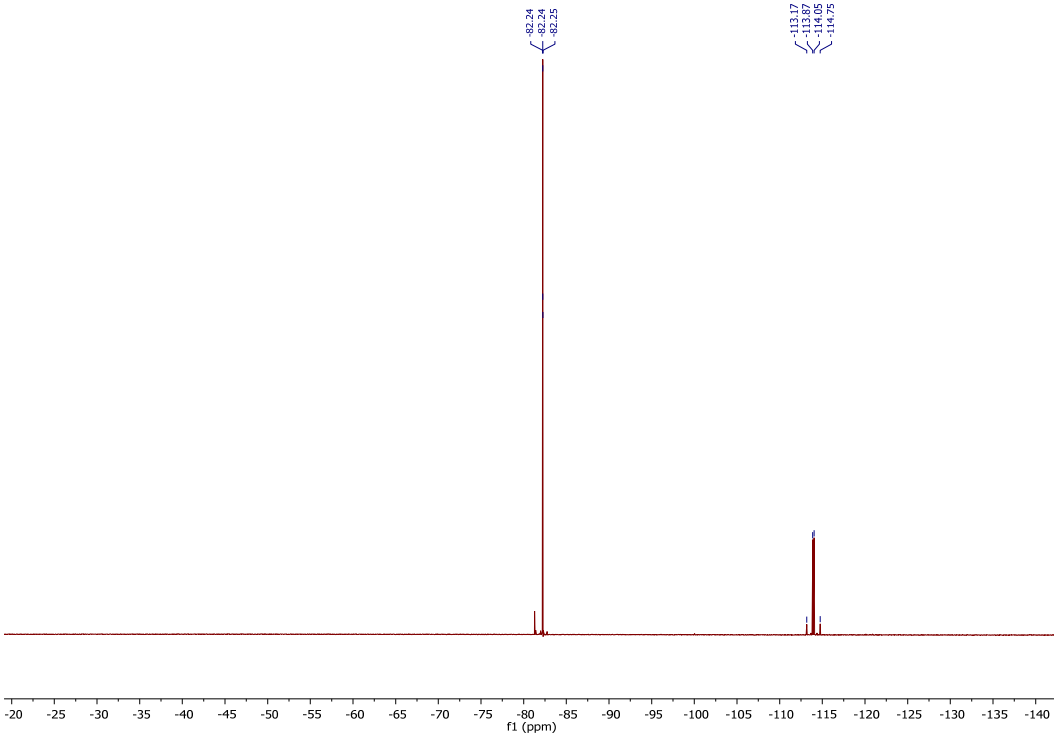
^{1}H NMR (400 Hz, $CDCl_3$)



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

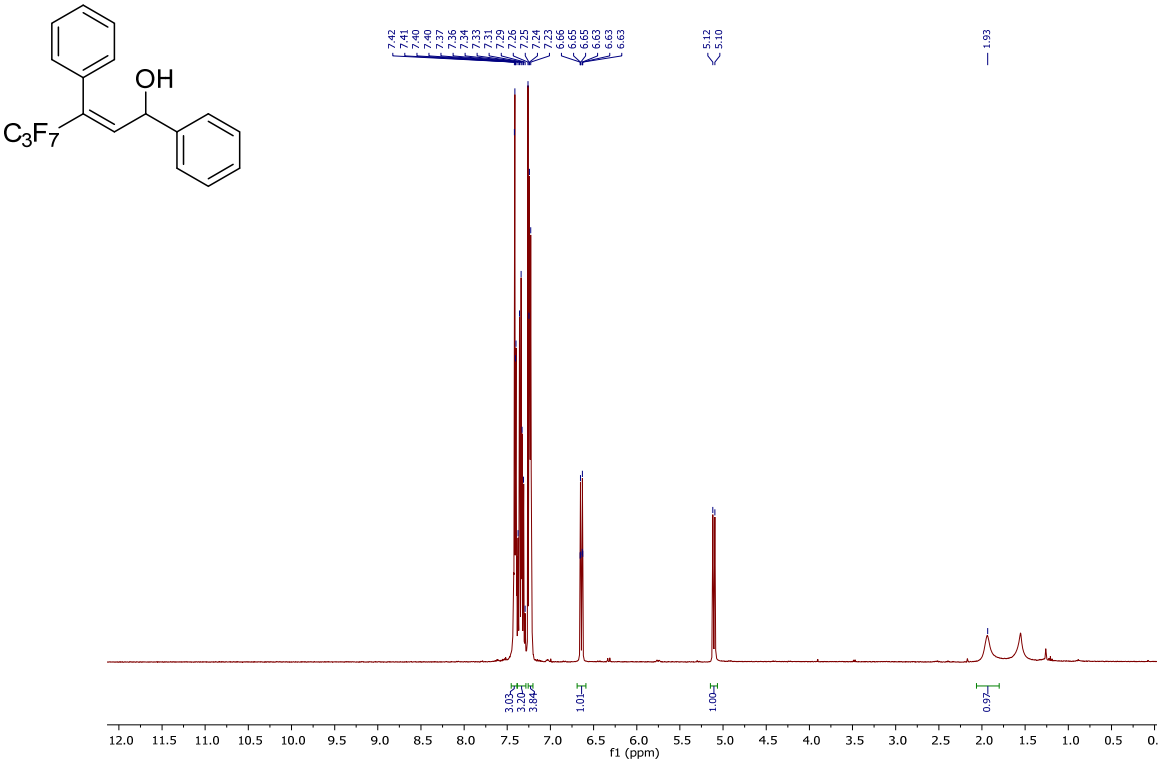


^{19}F NMR (376 Hz, $CDCl_3$)

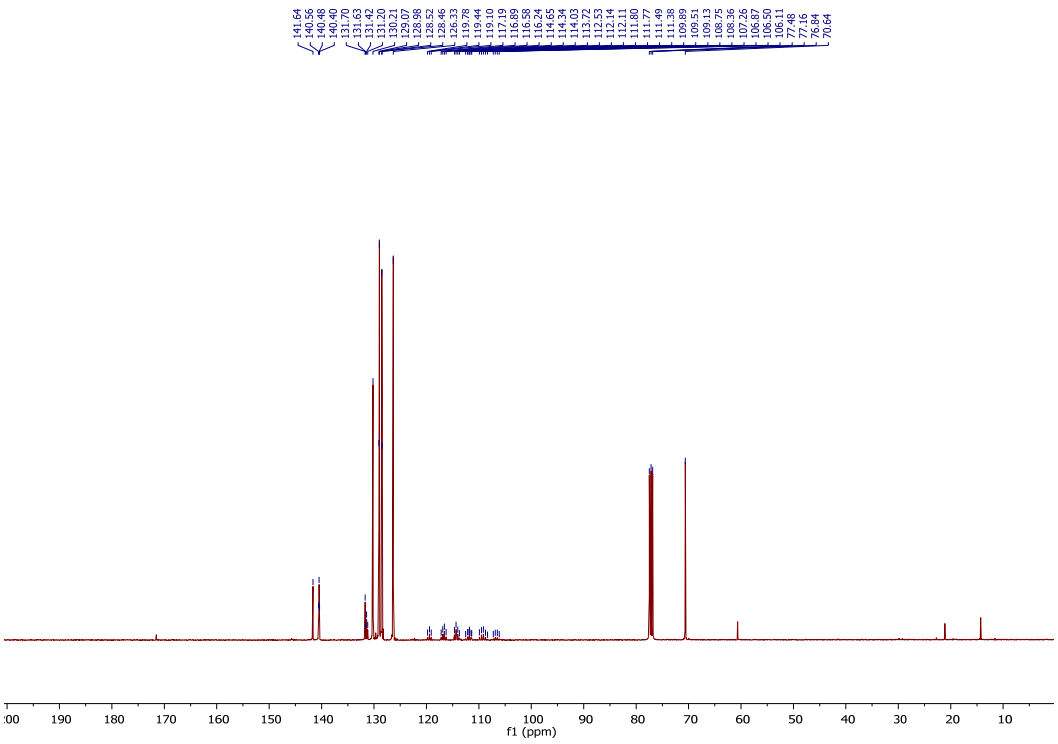


(*E*)-4,4,5,5,6,6,6-Heptafluoro-1,3-diphenylhex-2-en-1-ol (1q)

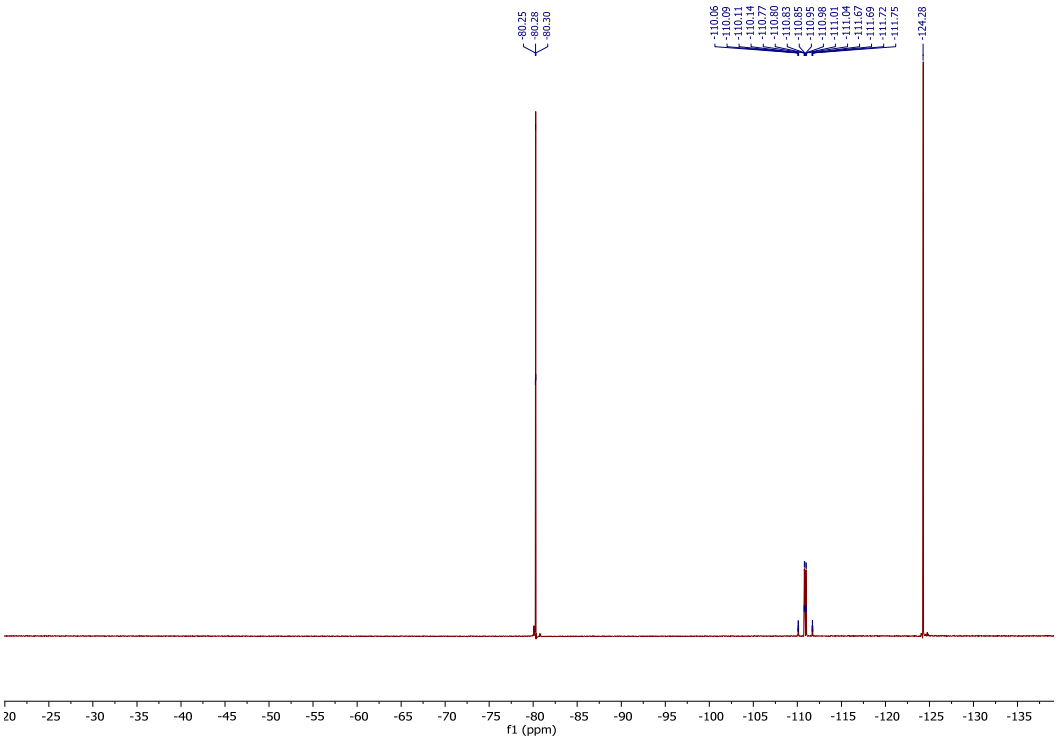
^{1}H NMR (400 Hz, $CDCl_3$)



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

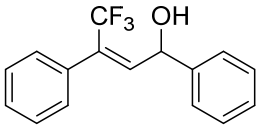


^{19}F NMR (376 Hz, $CDCl_3$)

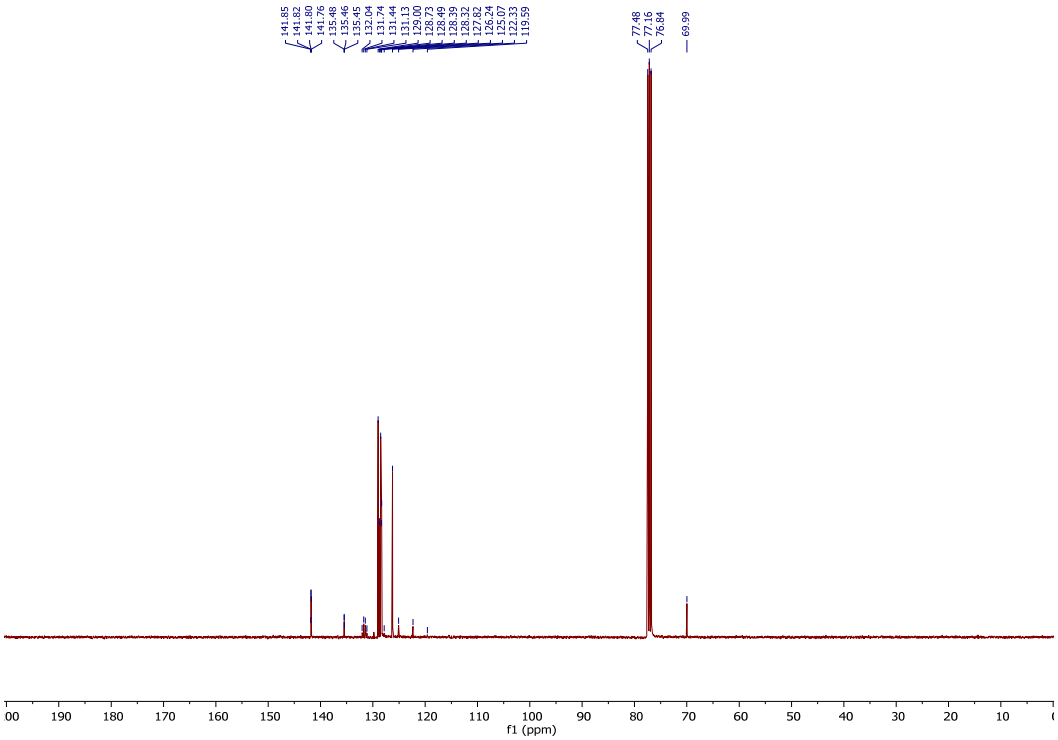


(*Z*)-4,4,4-Trifluoro-1,3-diphenylbut-2-en-1-ol ((*Z*)-1a)

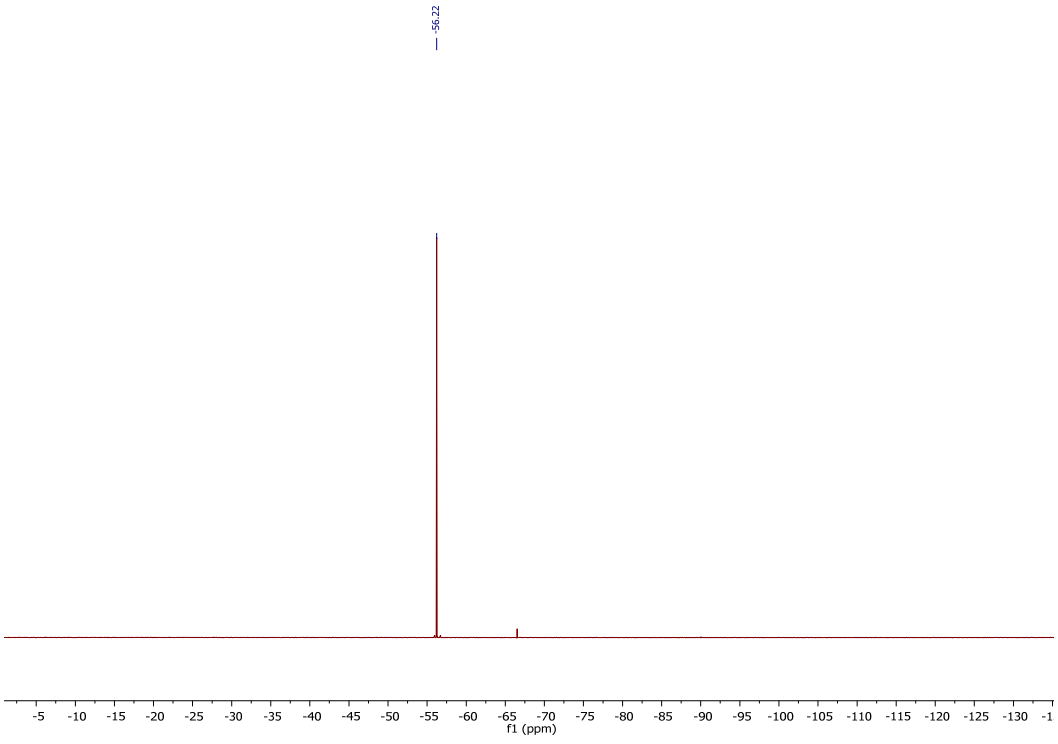
^{1}H NMR (400 Hz, $CDCl_3$)



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

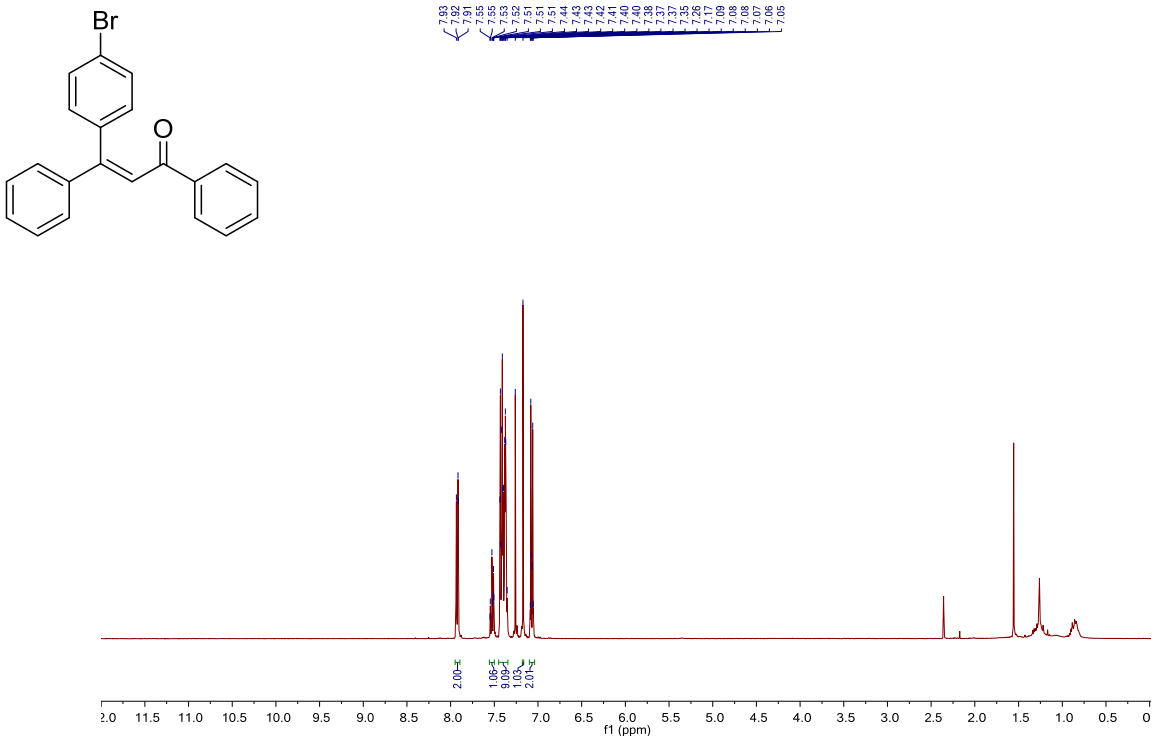


^{19}F NMR (376 Hz, $CDCl_3$)

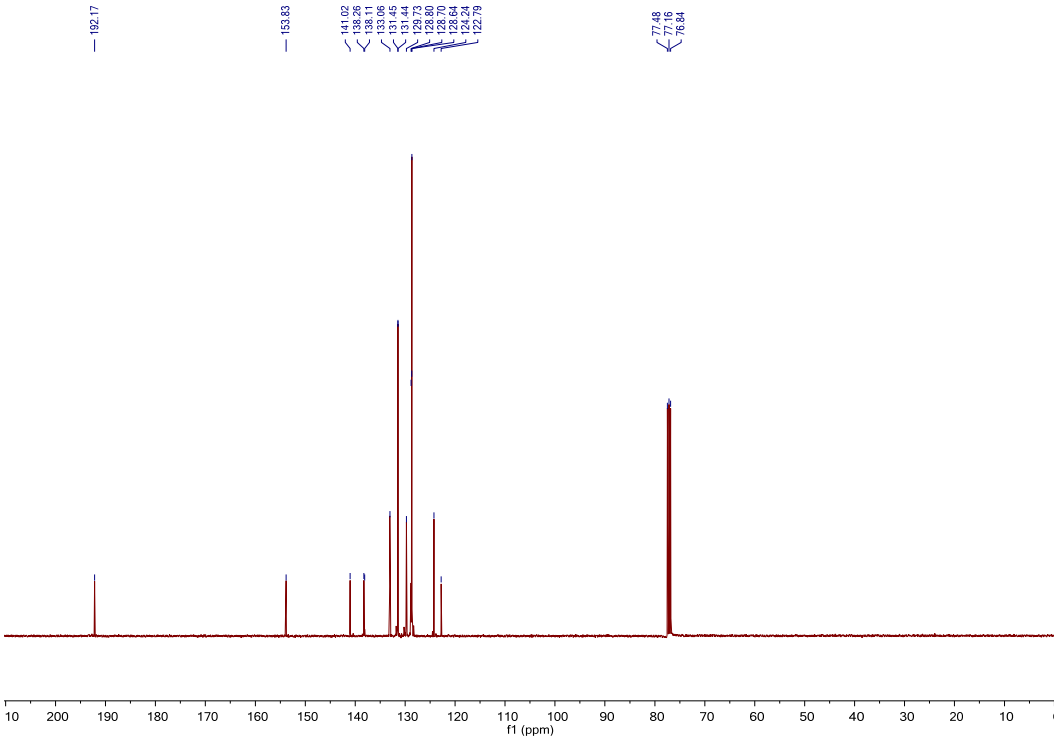


(*Z*)-3-(4-Bromophenyl)-1,3-diphenylprop-2-en-1-one

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

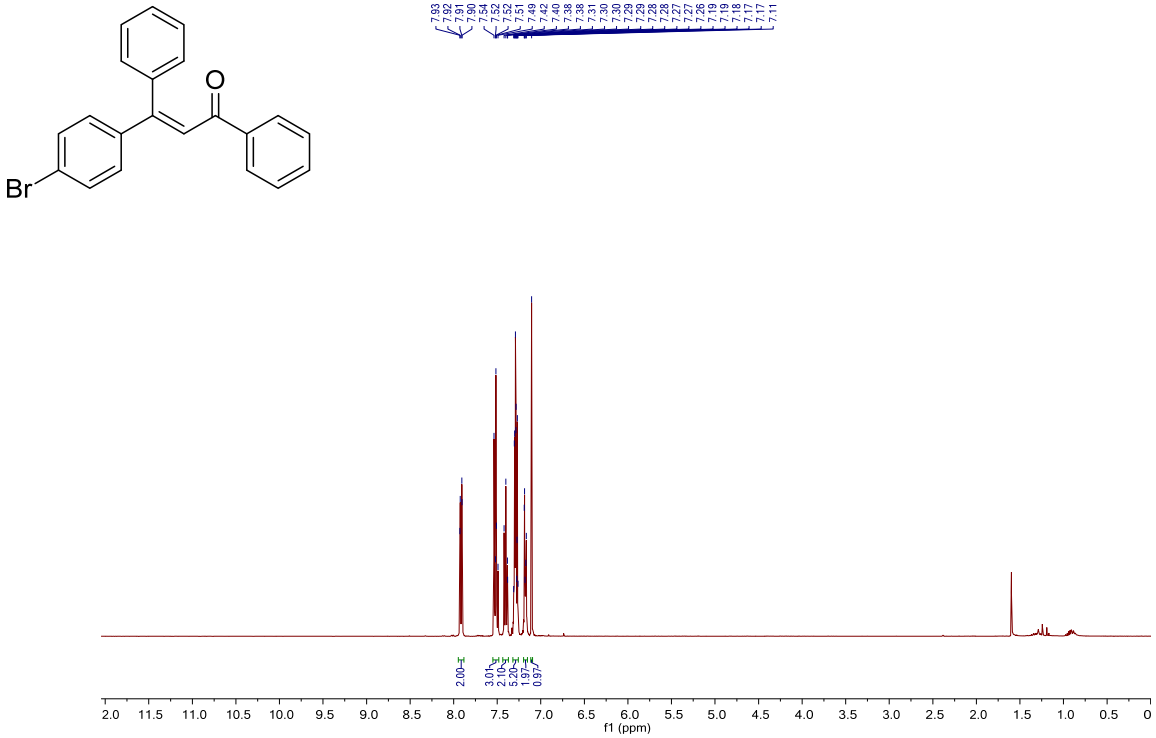


^{13}C NMR (100 Hz, $CDCl_3$)

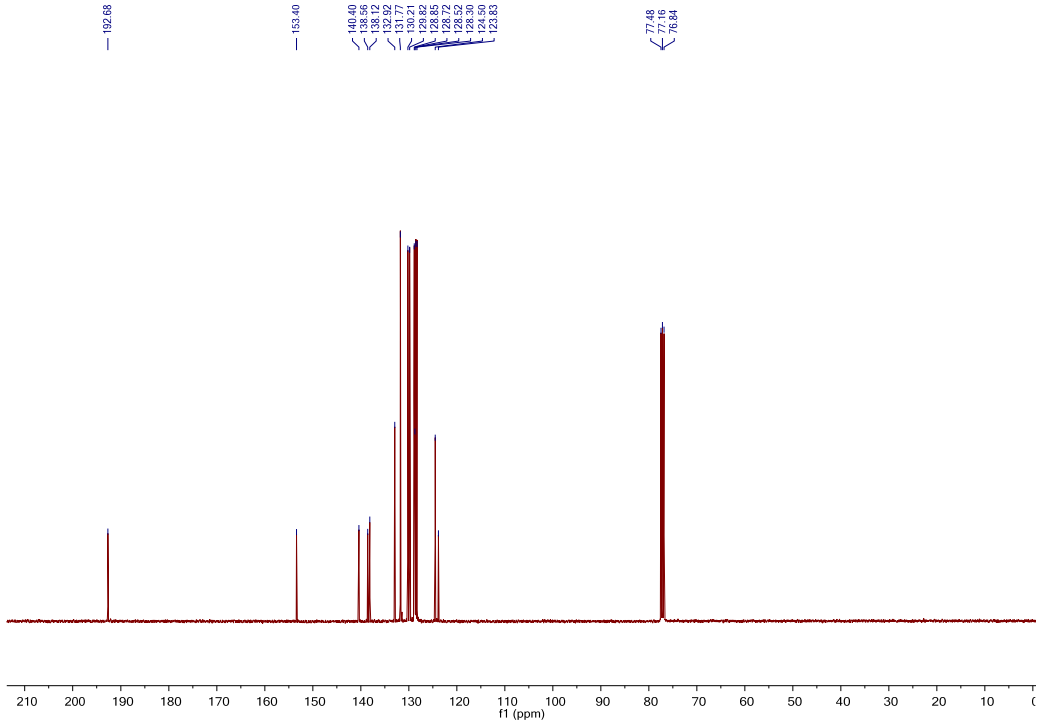


(*E*)-3-(4-Bromophenyl)-1,3-diphenylprop-2-en-1-one

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

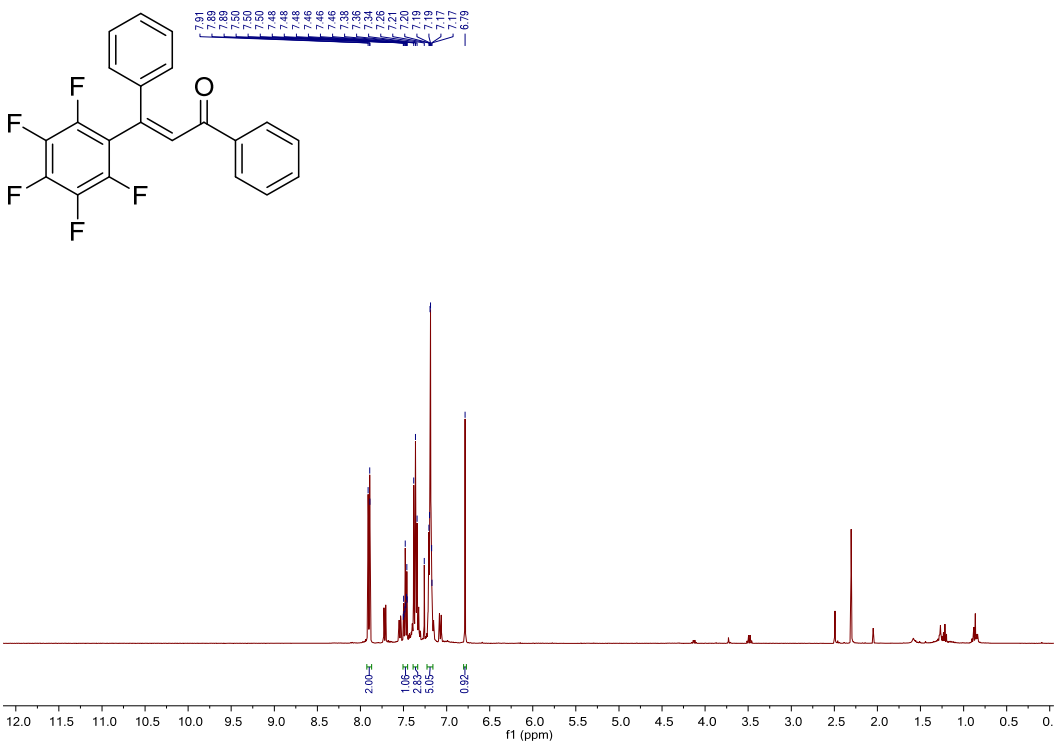


^{13}C NMR (100 Hz, $CDCl_3$)

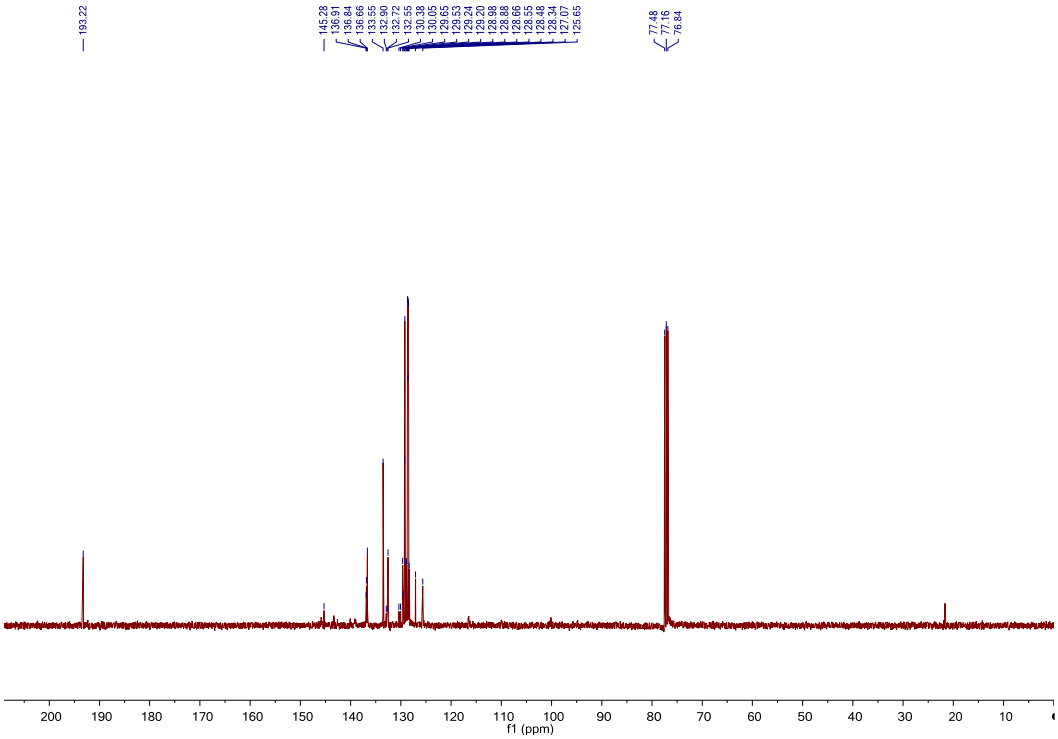


(*E*)-3-(Perfluorophenyl)-1,3-diphenylprop-2-en-1-one

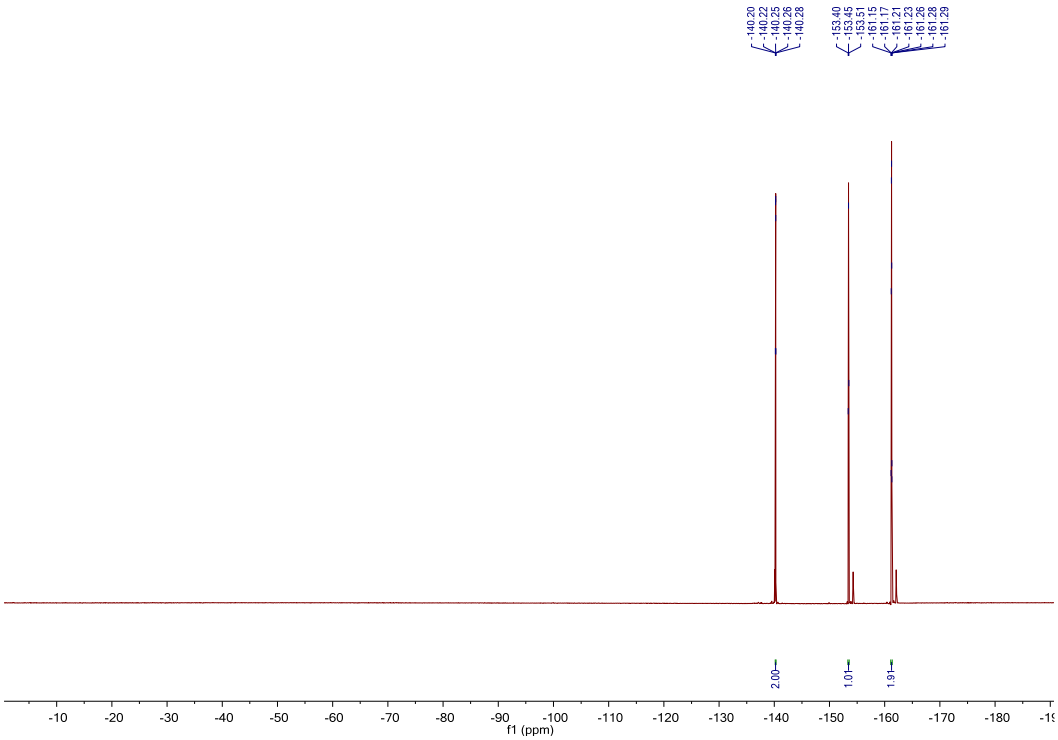
^{1}H NMR (400 Hz, $CDCl_3$)



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

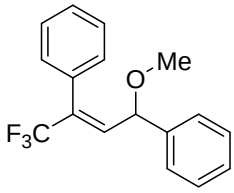


^{19}F NMR (376 Hz, $CDCl_3$)

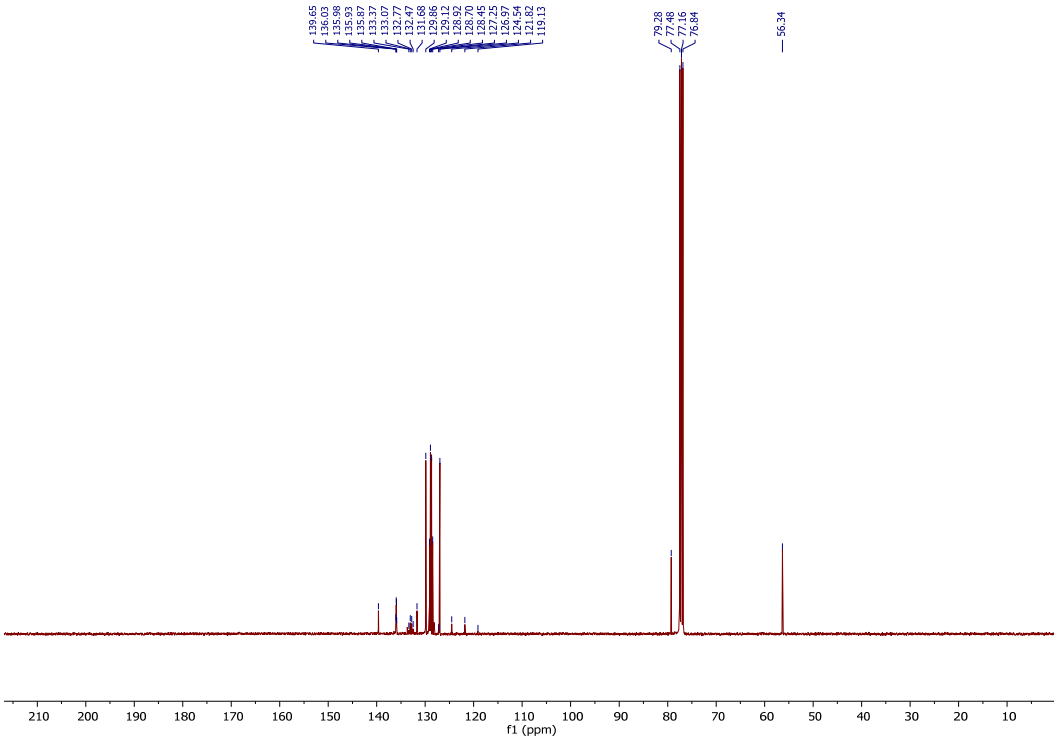


(*E*)-(4,4,4-Trifluoro-1-methoxybut-2-ene-1,3-diyl)dibenzene (3a):

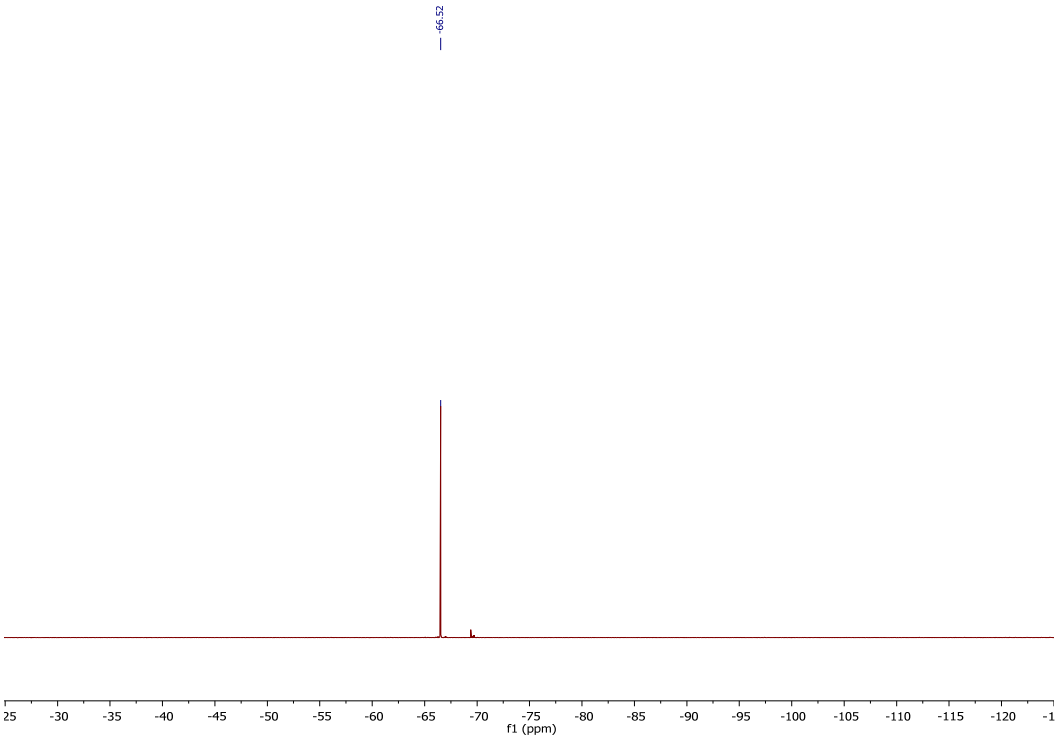
^{1}H NMR (400 Hz, $CDCl_3$)



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

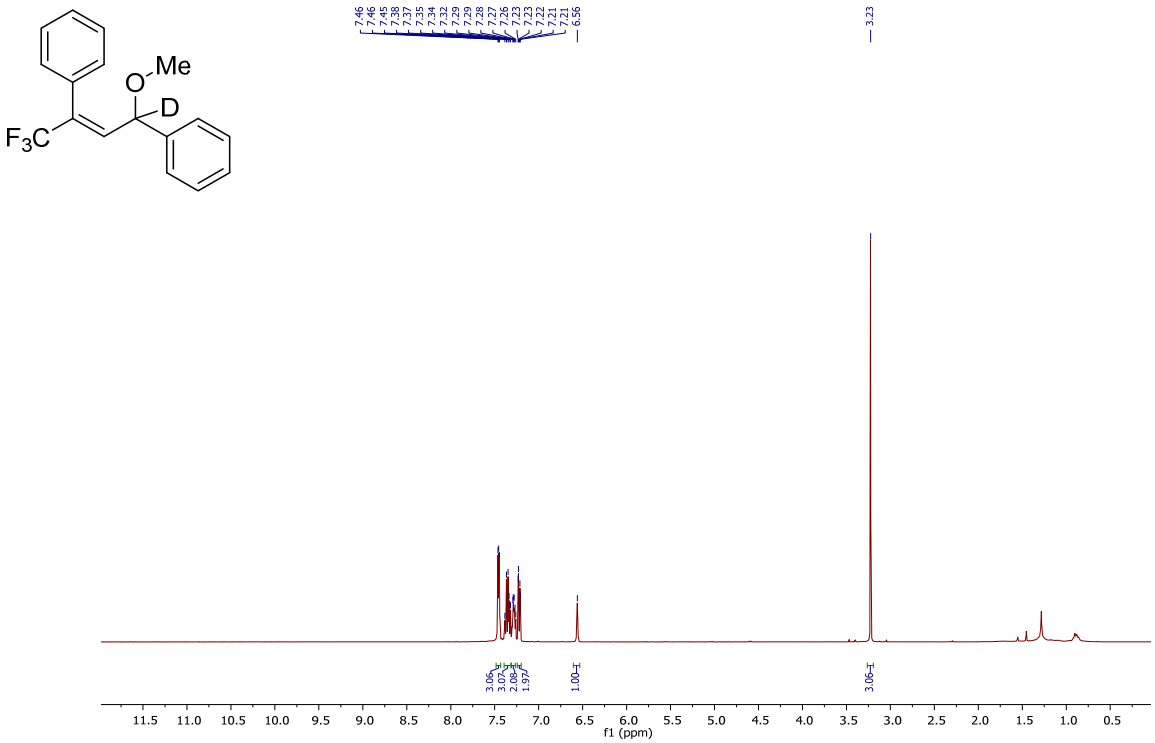


^{19}F NMR (376 Hz, $CDCl_3$)

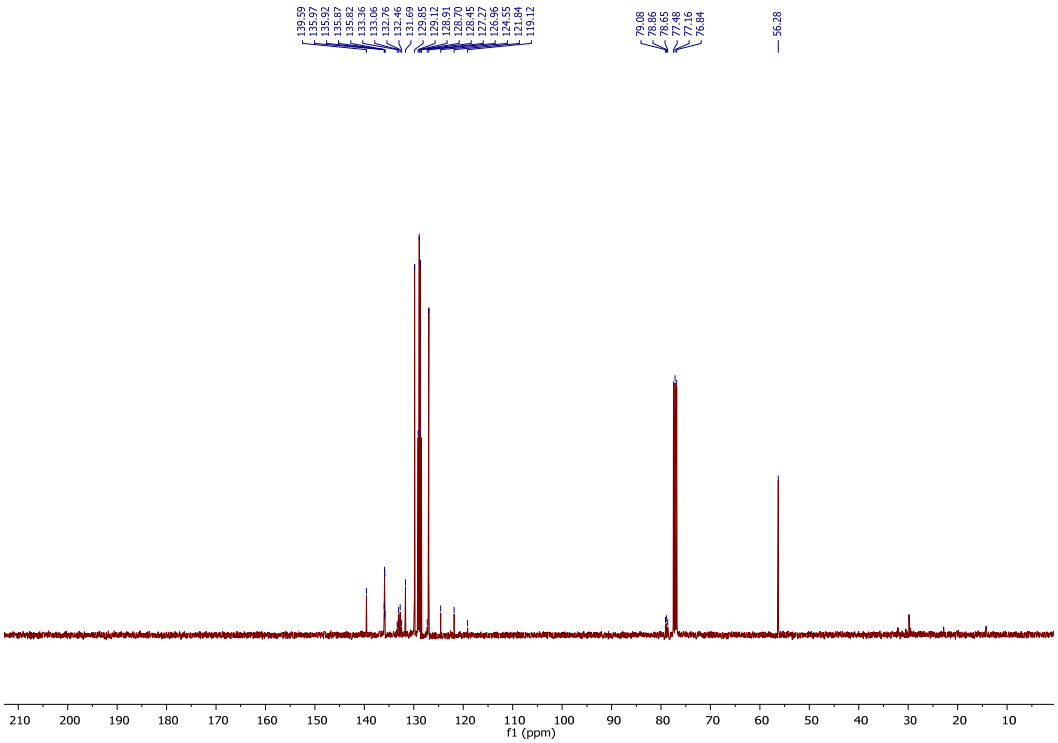


(E)-(4,4,4-Trifluoro-1-methoxybut-2-ene-1,3-diyl-1-d)dibenzene (3a-d_1)

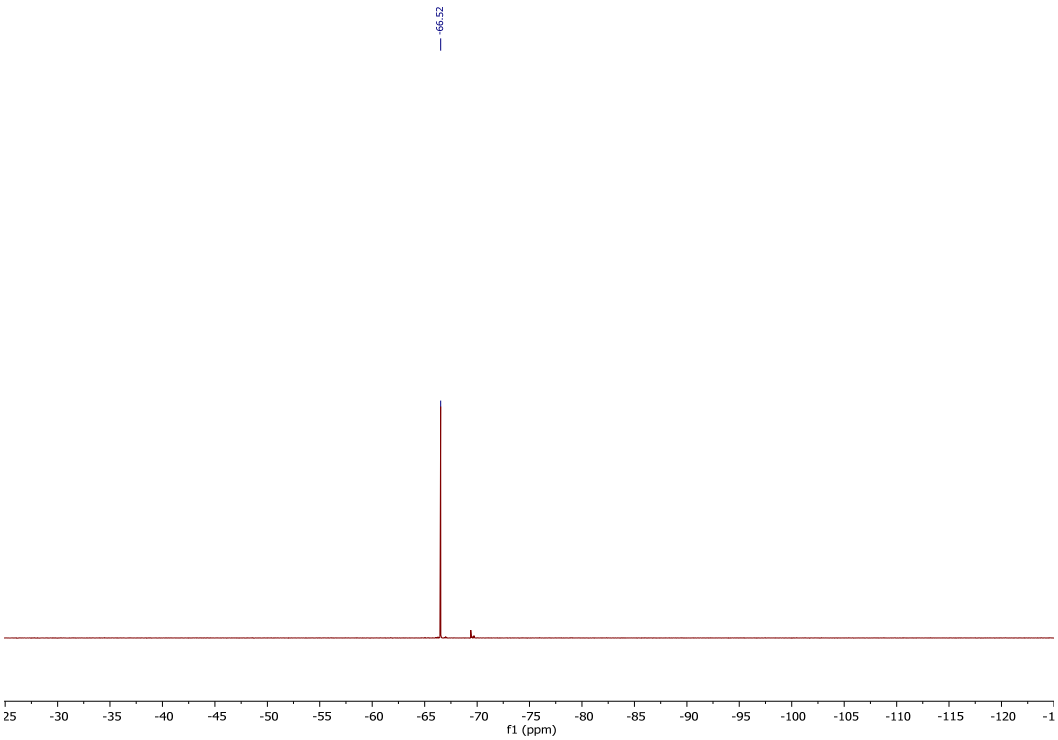
^{1}H NMR (400 Hz, $CDCl_3$)



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

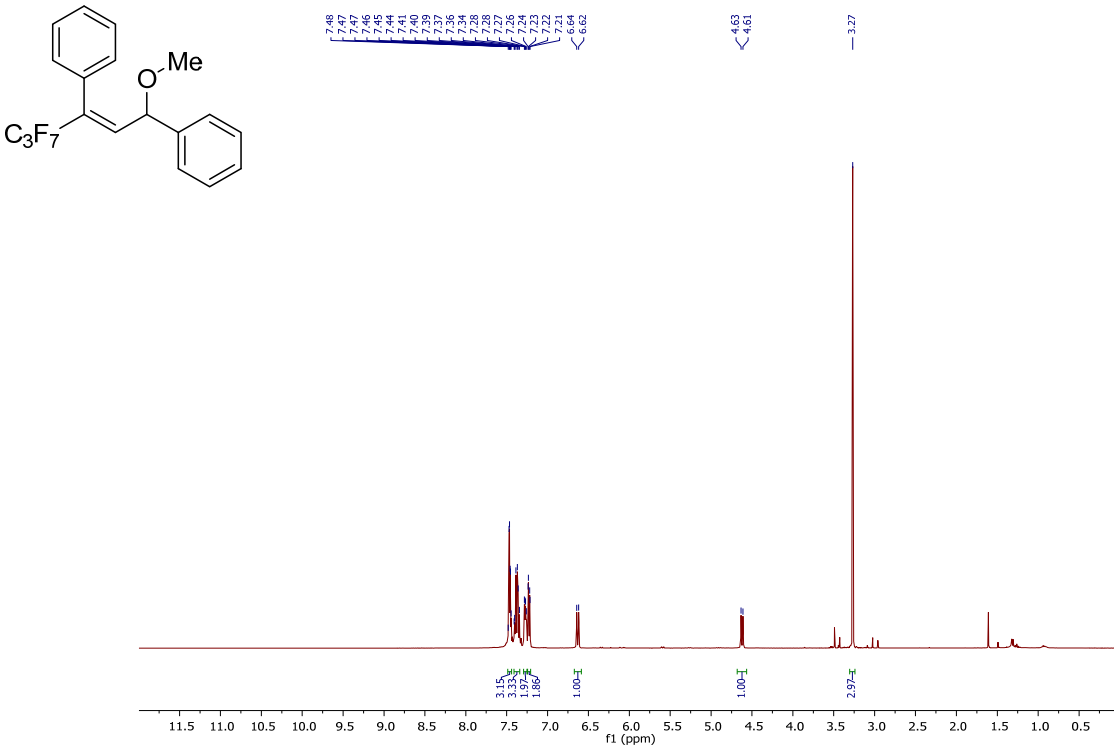


^{19}F NMR (376 Hz, $CDCl_3$)

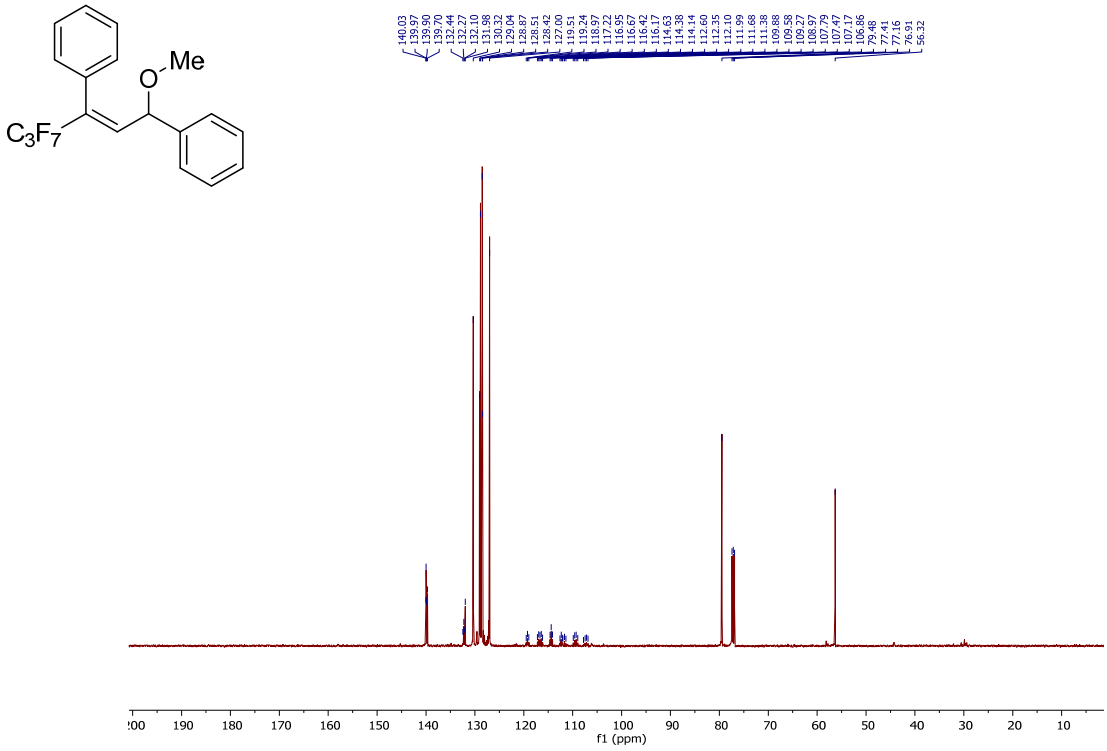


(*E*)-(4,4,5,5,6,6,6-heptafluoro-1-methoxyhex-2-ene-1,3-diyl)dibenzene (3b)

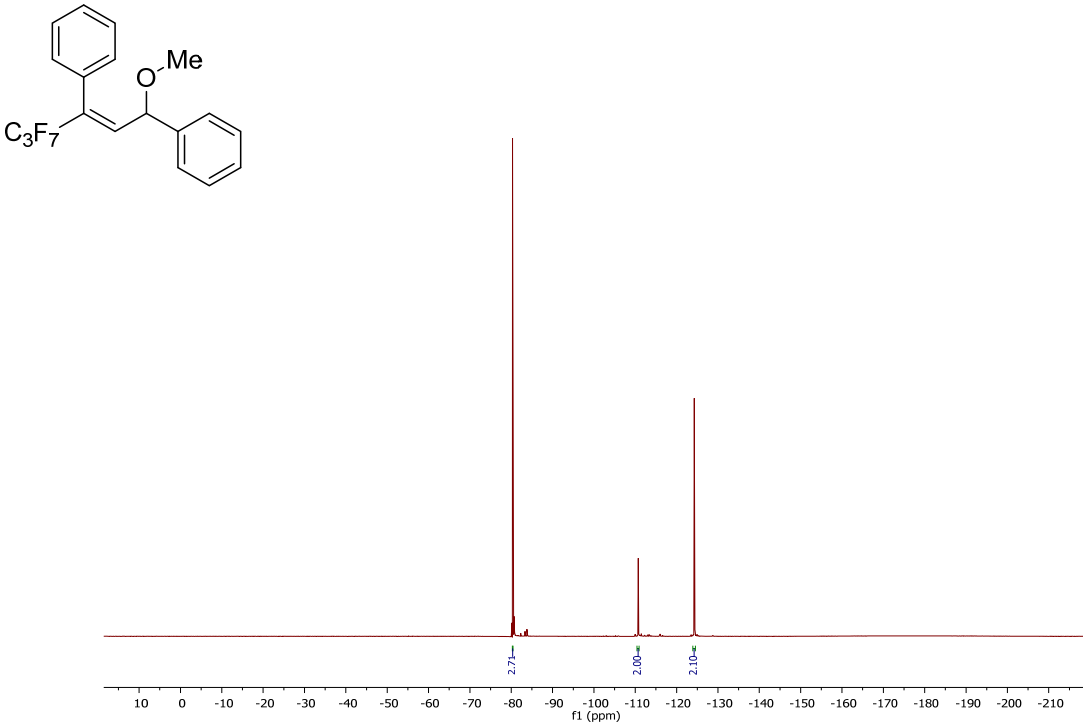
^{1}H NMR (400 Hz, $CDCl_3$)



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

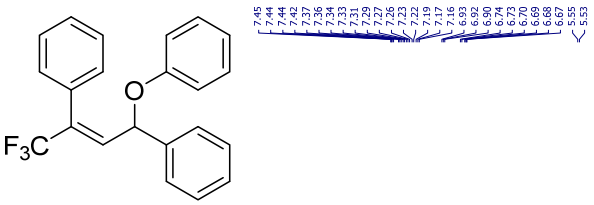


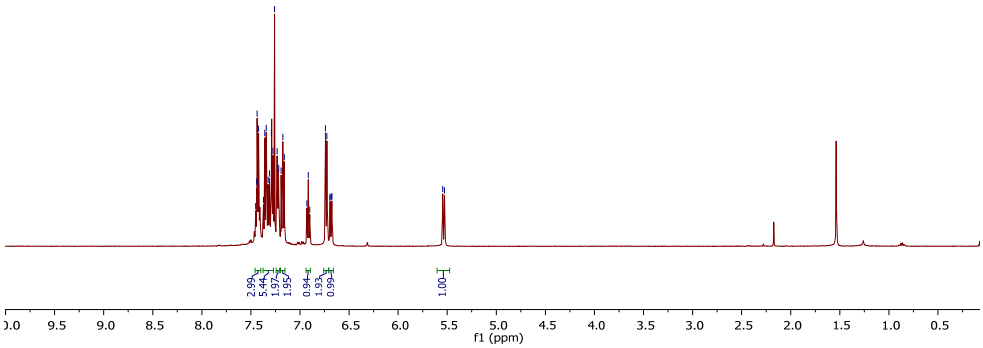
^{19}F NMR (376 Hz, $CDCl_3$)



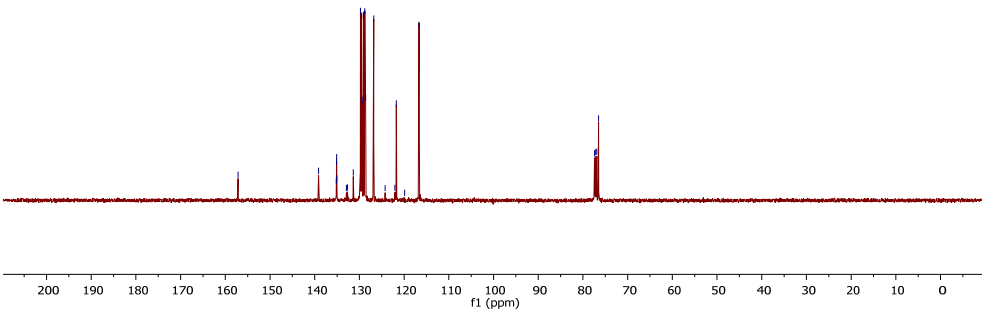
(*E*)-(4,4,4-trifluoro-1-phenoxybut-2-ene-1,3-diyl)dibenzene (3c):

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

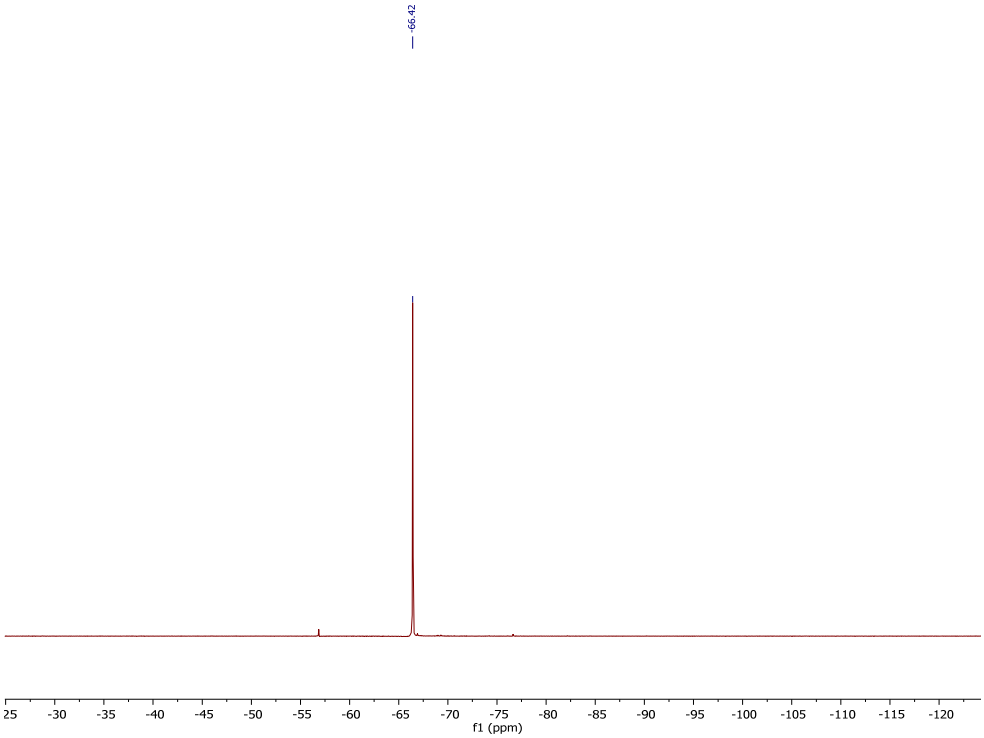




^{13}C NMR (100 Hz, $CDCl_3$)

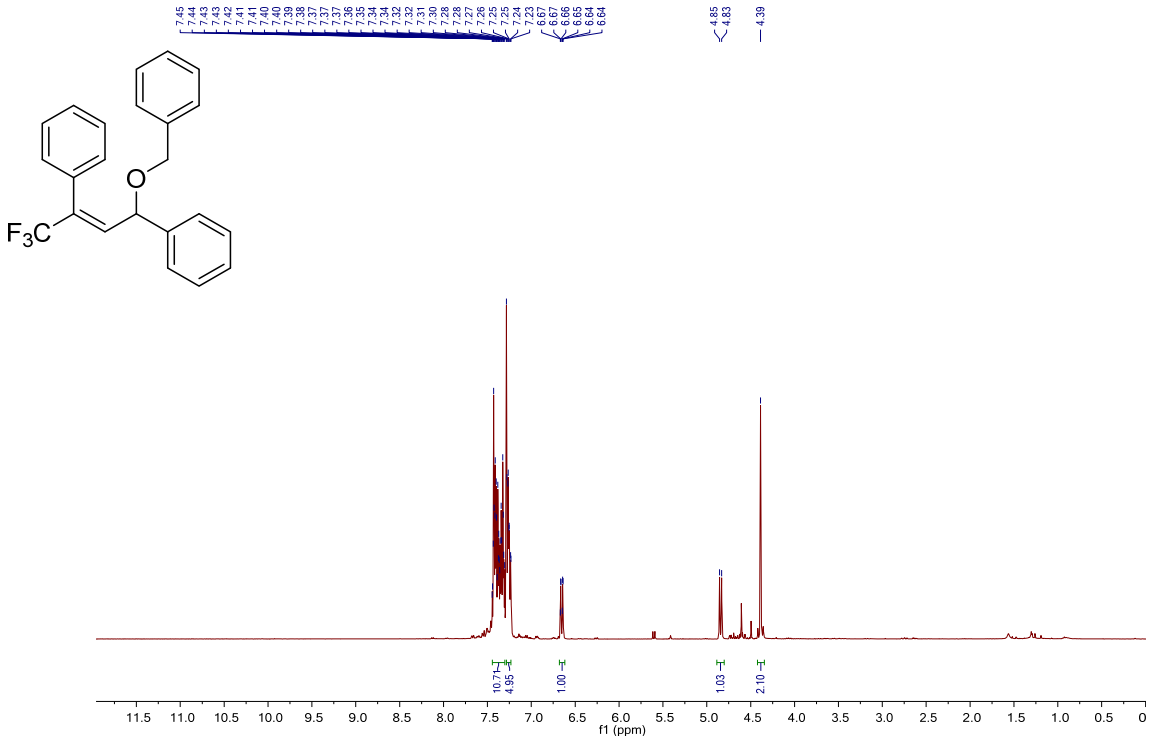


^{19}F NMR (376 Hz, $CDCl_3$)

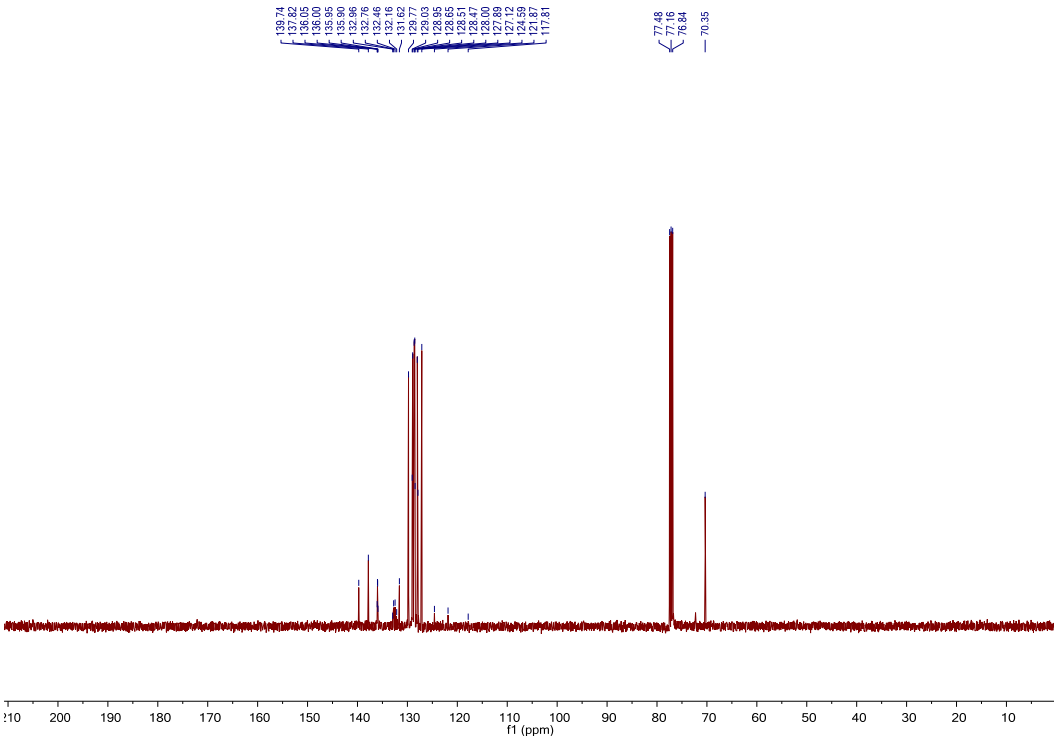


(*E*)-(1-(Benzyloxy)-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (3d):

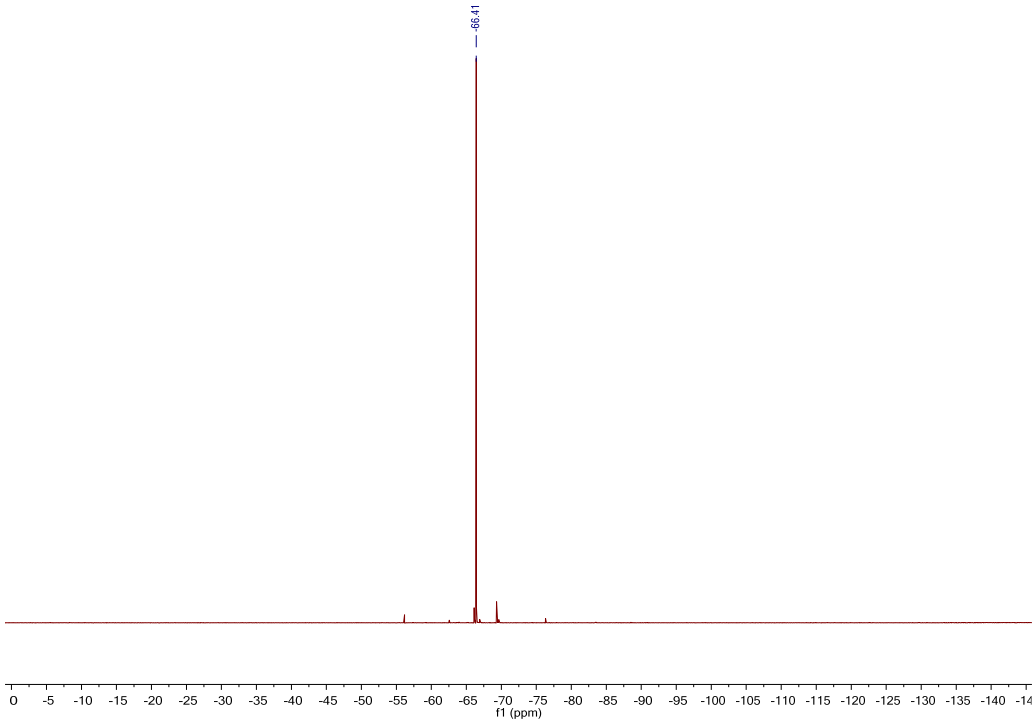
^{1}H NMR (400 Hz, $CDCl_3$)



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



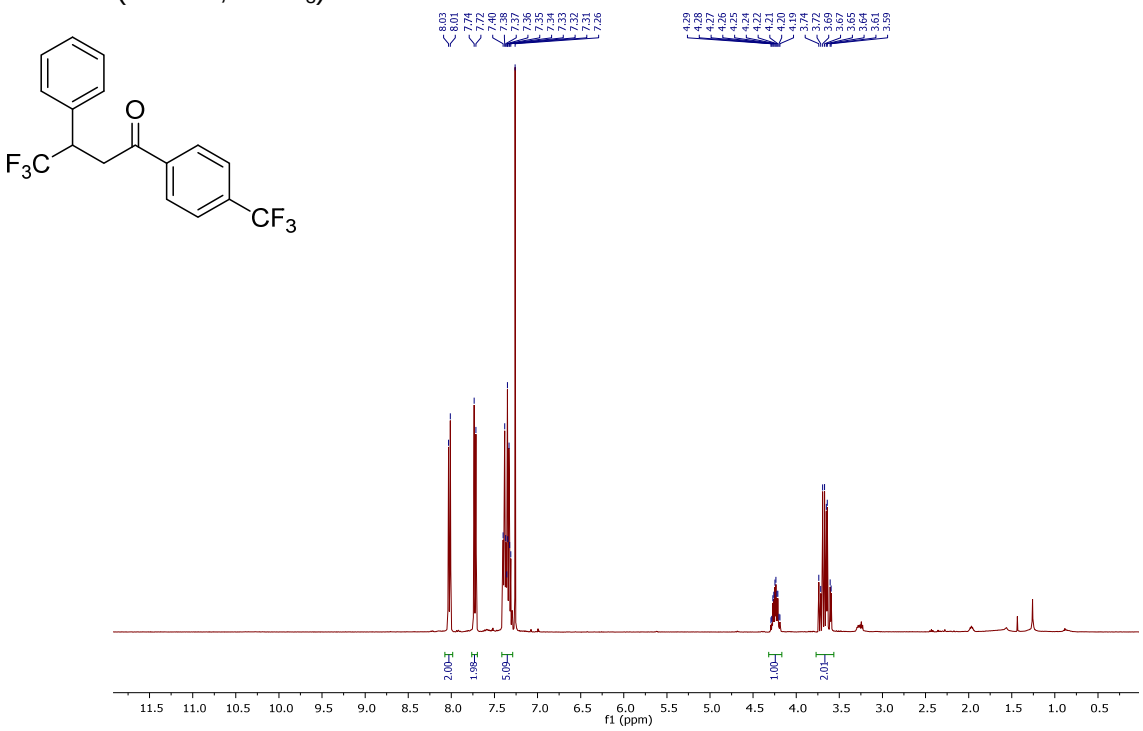
^{19}F NMR (376 Hz, $CDCl_3$)



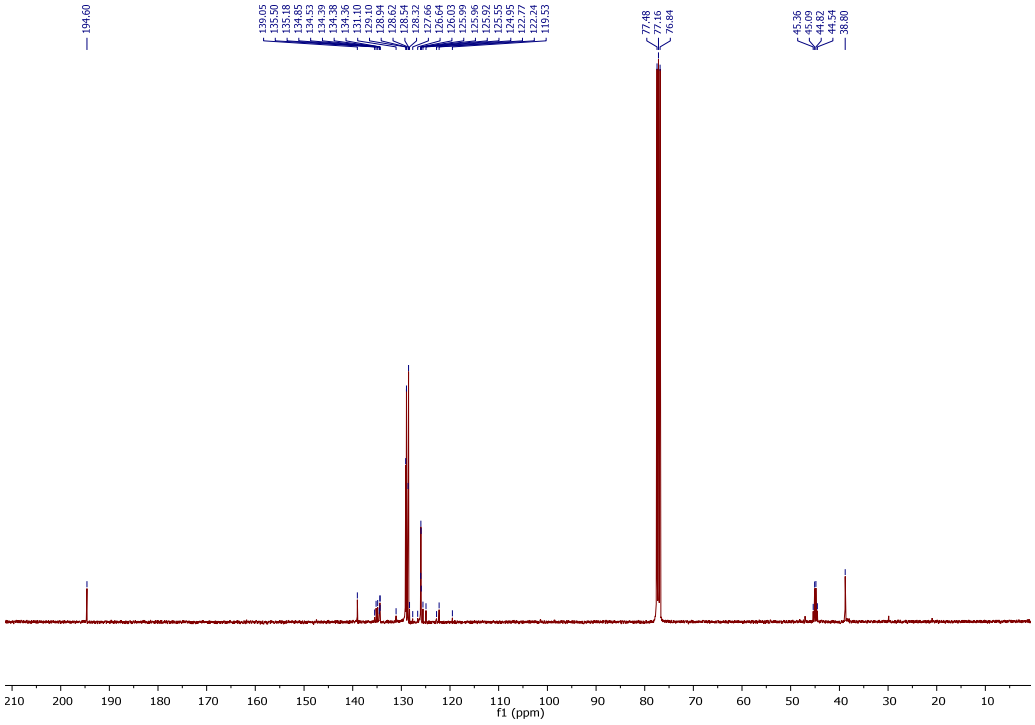
^{1}H NMR, ^{13}C NMR and ^{19}F NMR of isomerization products not previously reported

4,4,4-Trifluoro-3-phenyl-1-(4'-trifluoromethylphenyl)-butanone (2c)

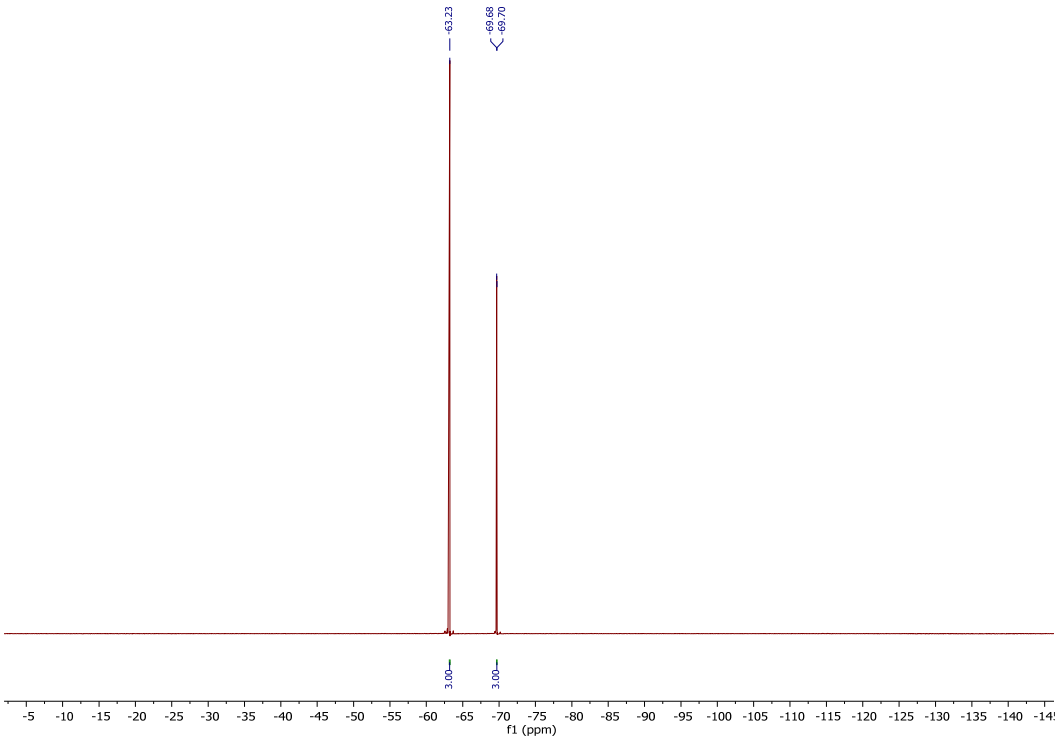
^{1}H NMR (400 Hz, $CDCl_3$)



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

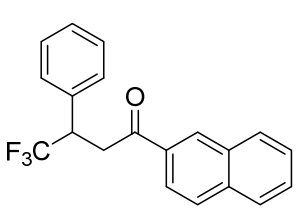


^{19}F NMR (376 Hz, $CDCl_3$)

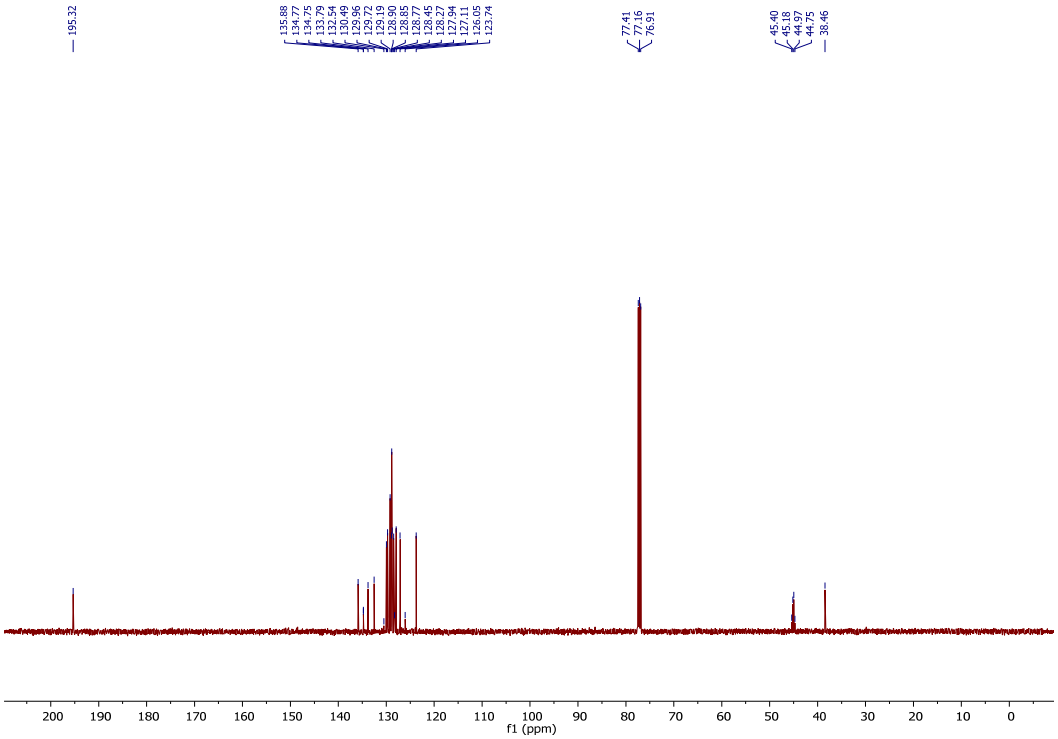


4,4,4-Trifluoro-1-(naphthalen-2-yl)-3-phenylbutan-1-one (2f)

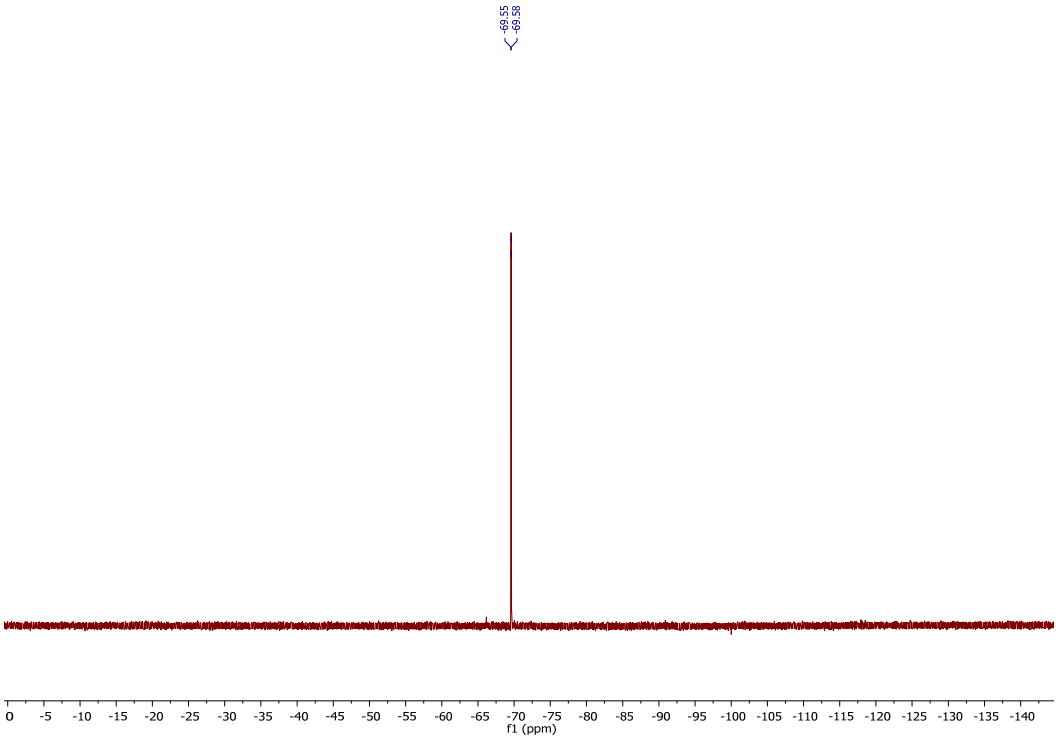
^{1}H NMR (400 Hz, $CDCl_3$)



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

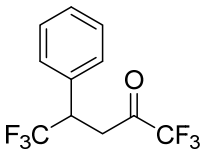


^{19}F NMR (376 Hz, $CDCl_3$)

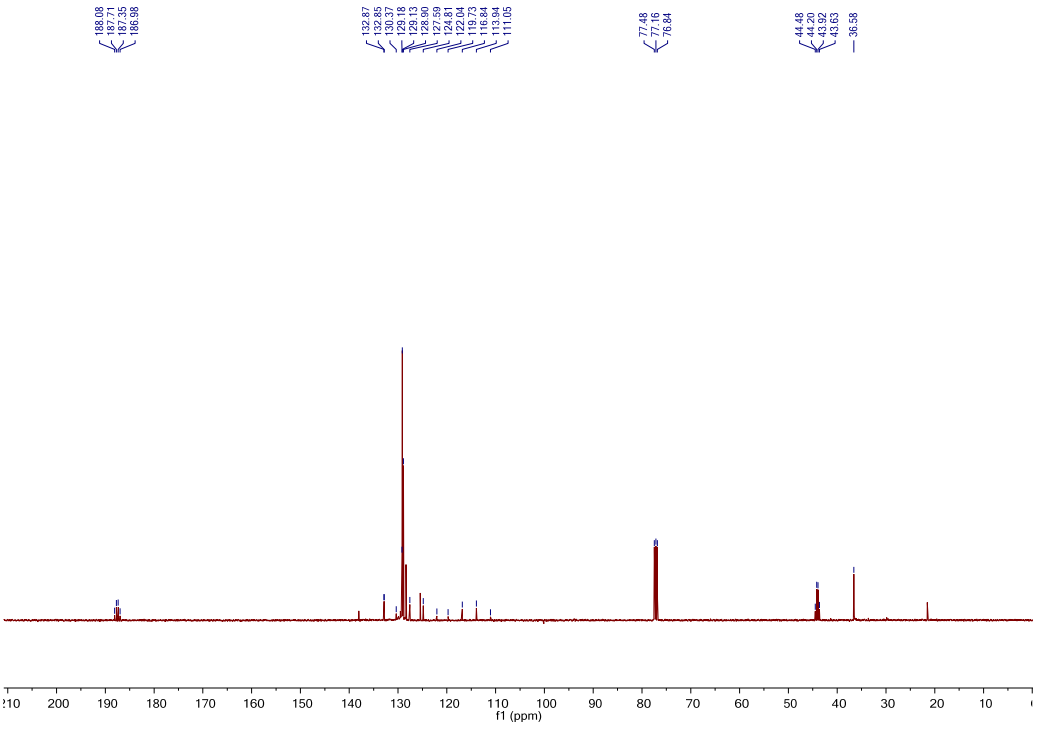


1,1,1,5,5,5-Hexafluoro-4-phenylpentan-2-one (2g)[ii]

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

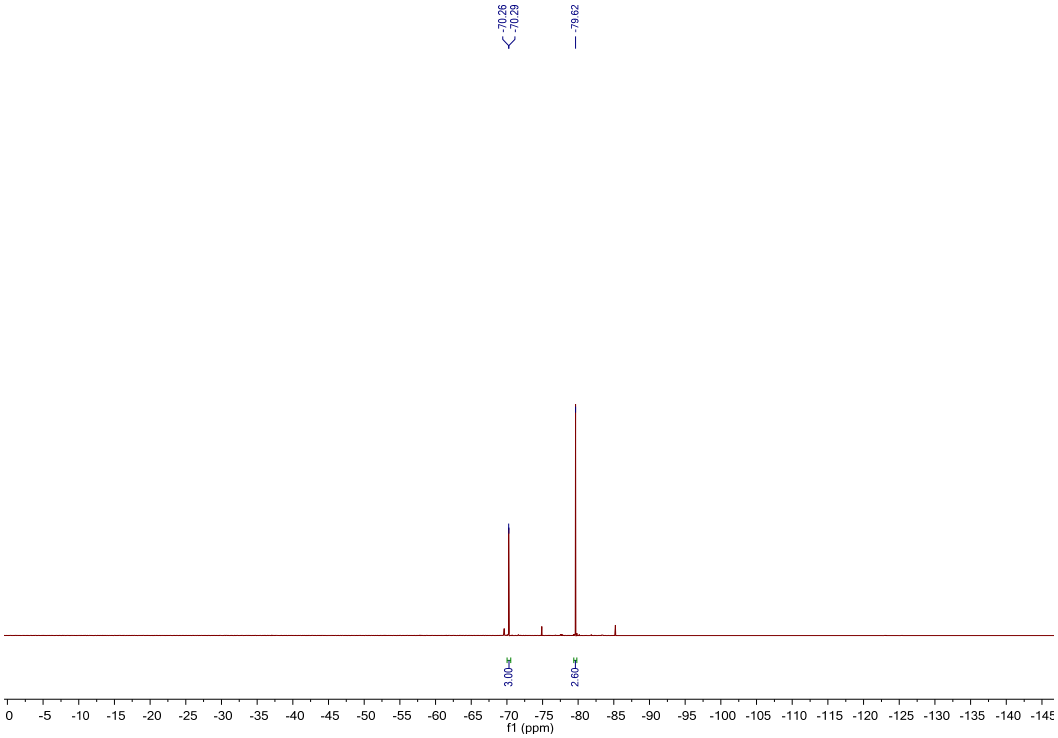


^{13}C NMR (100 Hz, $CDCl_3$)



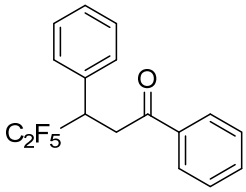
[ii] The product is very volatile, the product shows the corresponding peaks of the solvent (toluene).

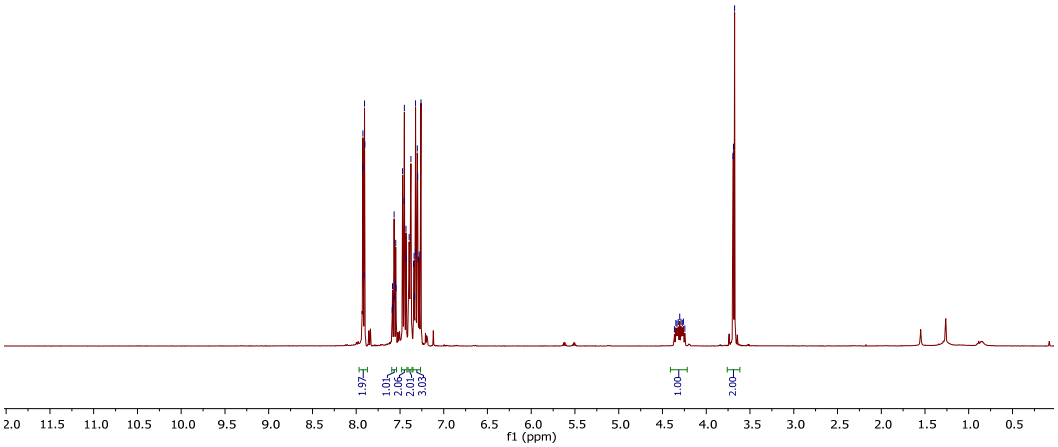
^{19}F NMR (376 Hz, $CDCl_3$)



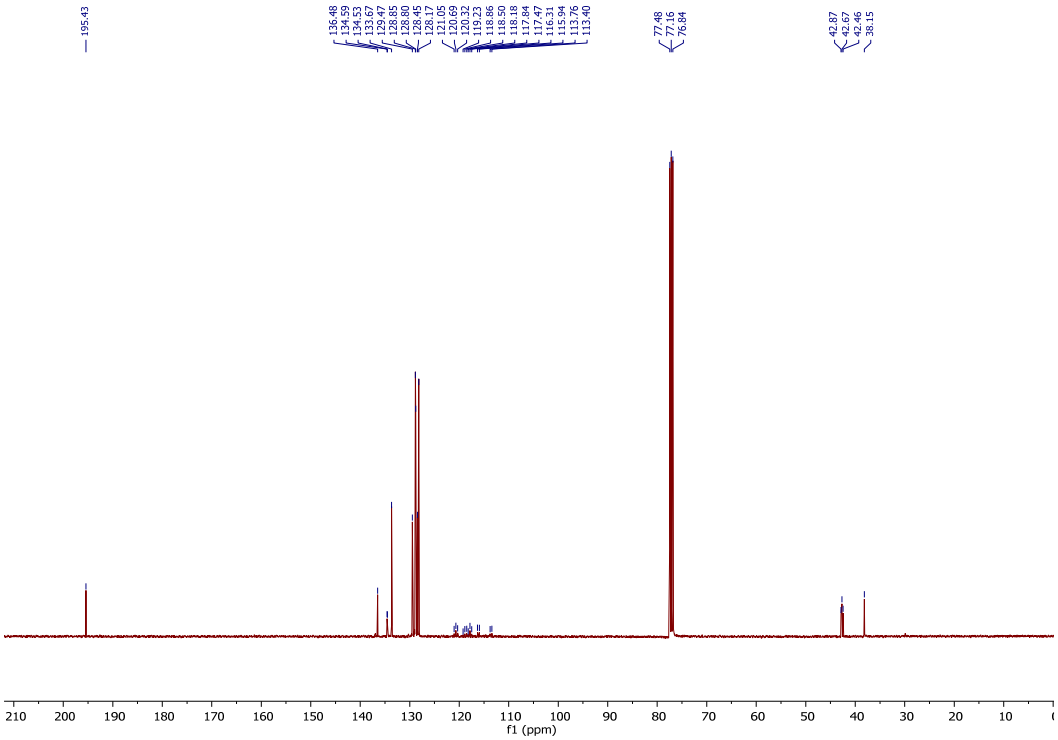
4,4,5,5,5-Pentafluoro-1,3-diphenylpentan-1-one (2p)

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

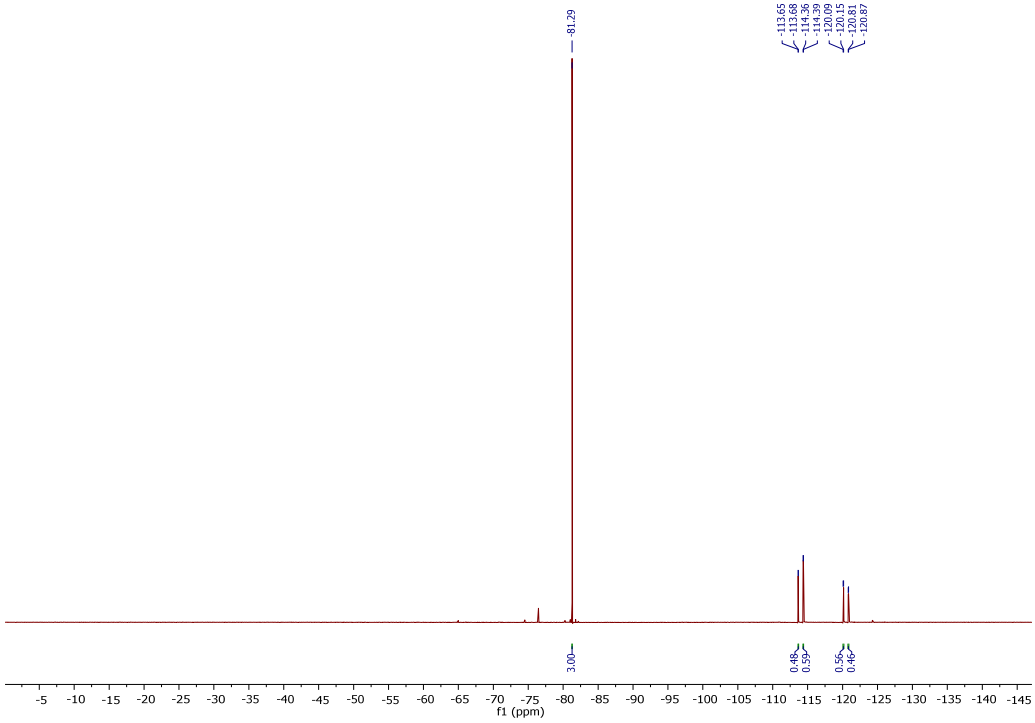




^{13}C NMR (100 Hz, $CDCl_3$)

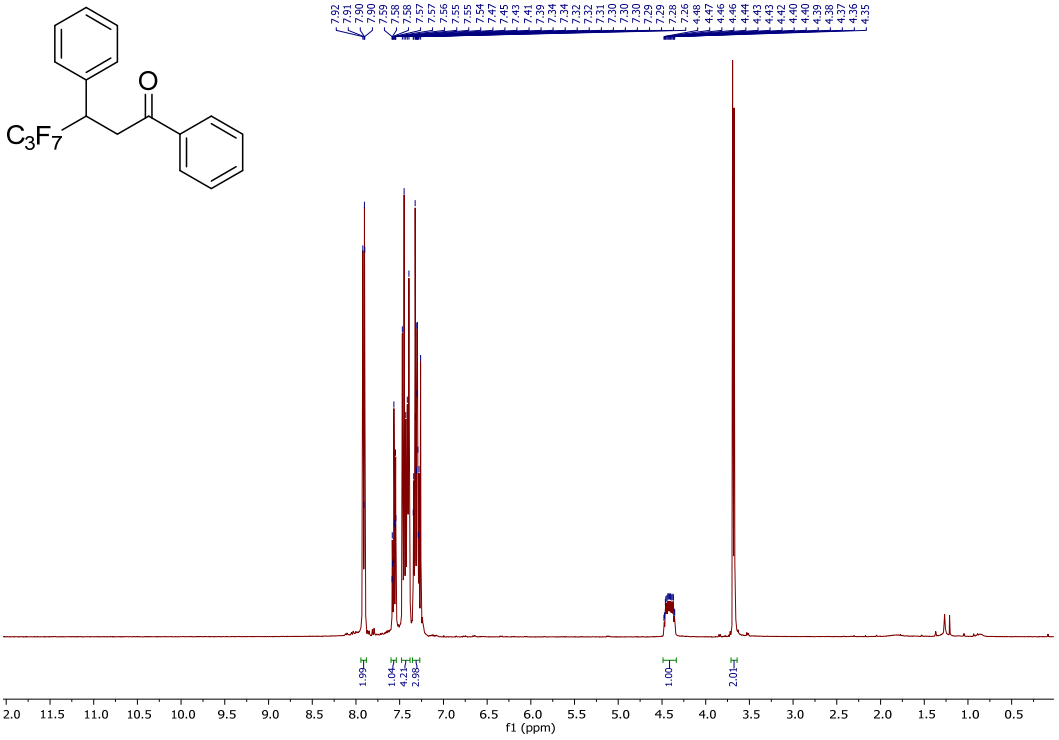


^{19}F NMR (376 Hz, $CDCl_3$)

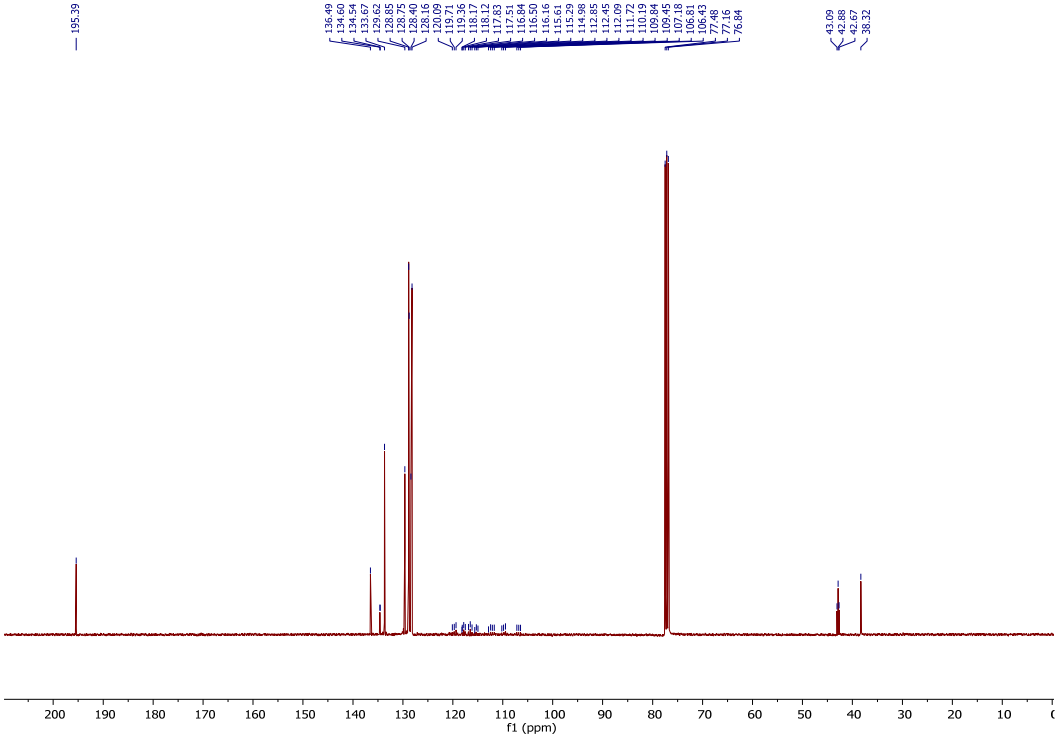


4,4,5,5,6,6,6-Heptafluoro-1,3-diphenylhexan-1-one (2q)

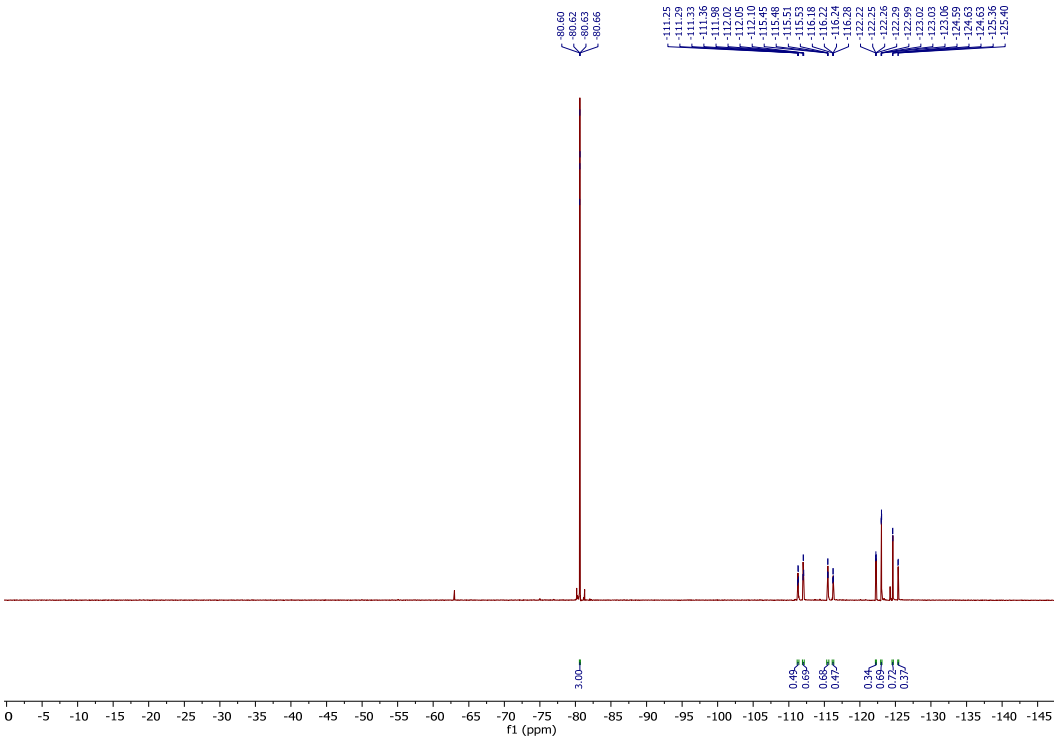
^{1}H NMR (400 Hz, $CDCl_3$)



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

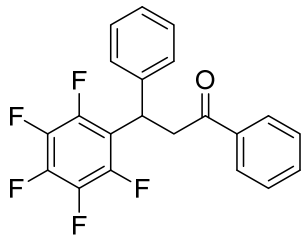


^{19}F NMR (376 Hz, $CDCl_3$)

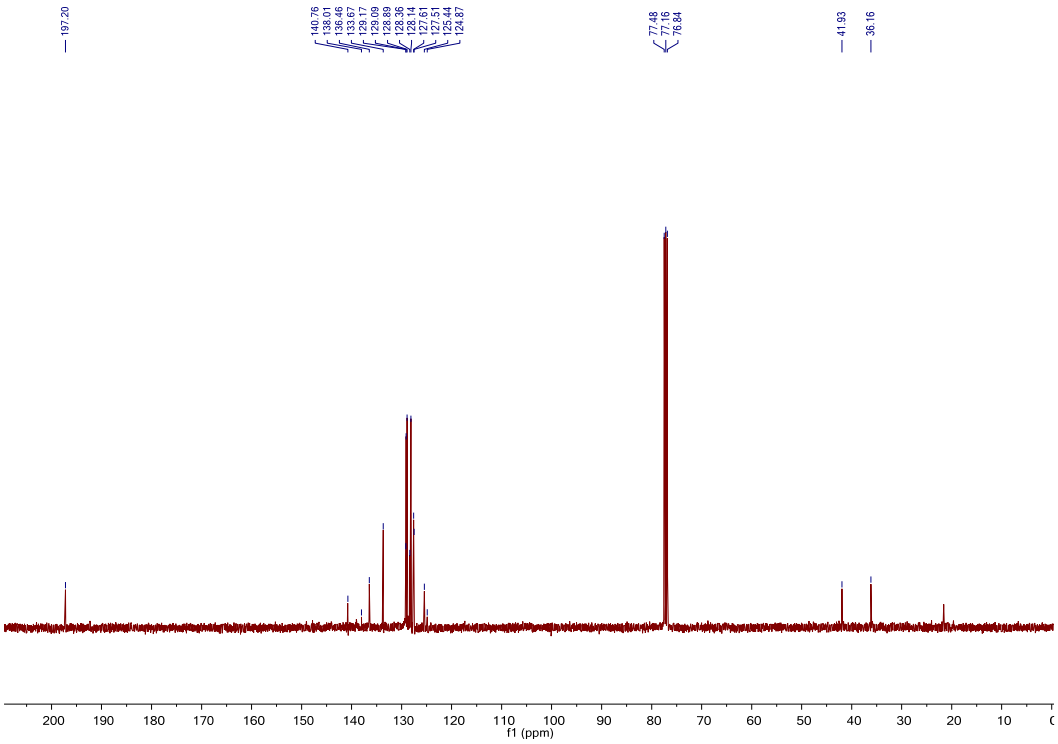


3-(Perfluorophenyl)-1,3-diphenylpropan-1-one (2y)

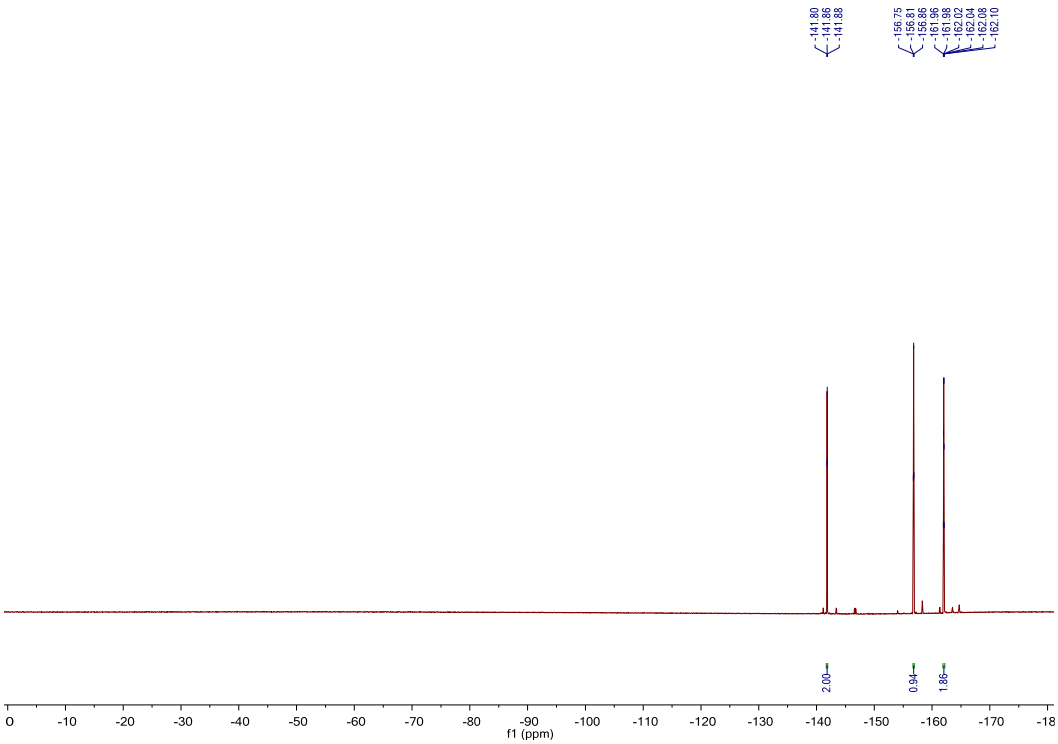
^{1}H NMR (400 Hz, $CDCl_3$)



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

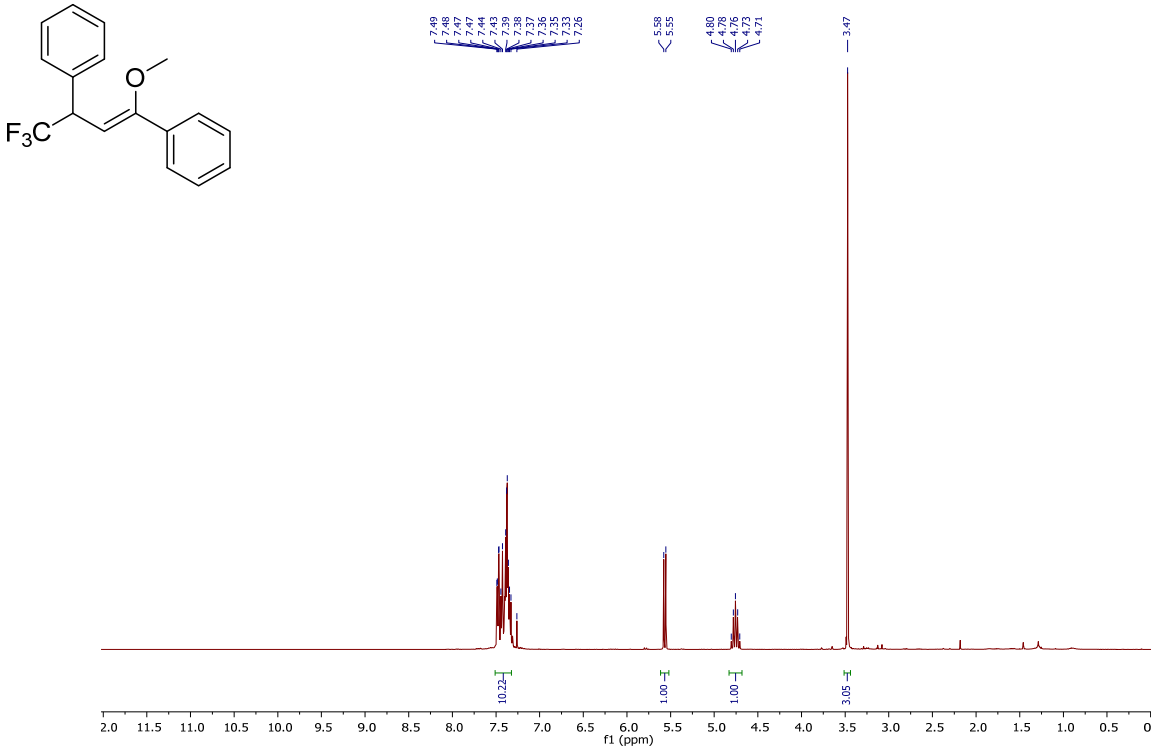


^{19}F NMR (376 Hz, $CDCl_3$)

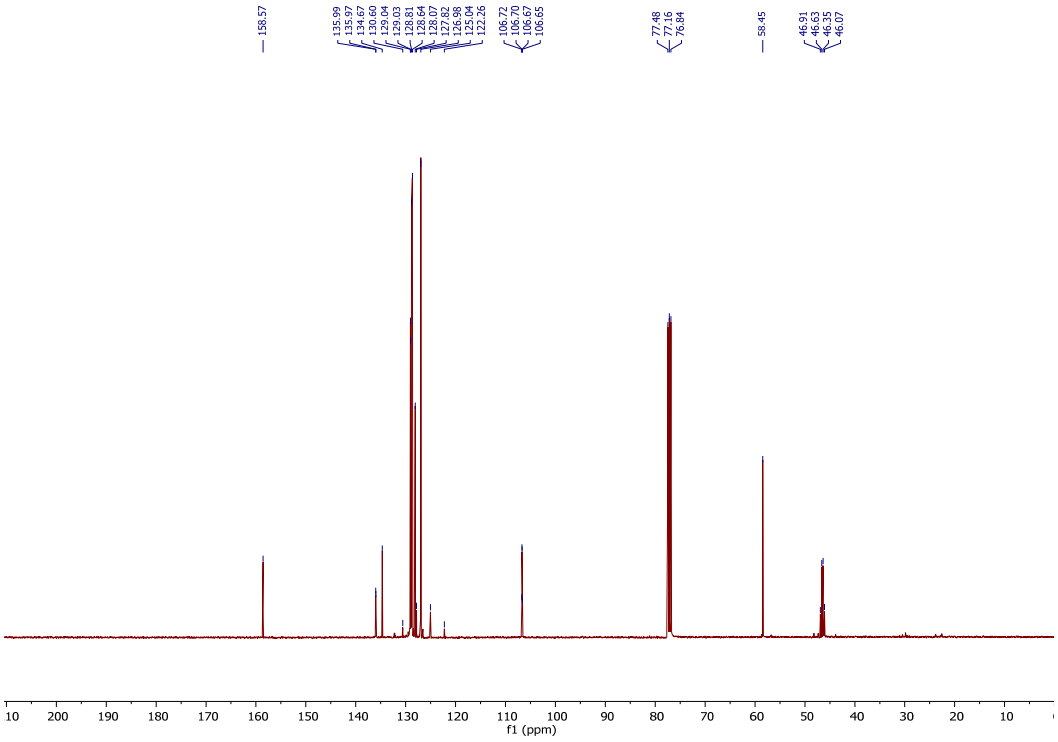


(*Z*)-(4,4,4-Trifluoro-1-methoxybut-1-ene-1,3-diyl)dibenzene (4a)

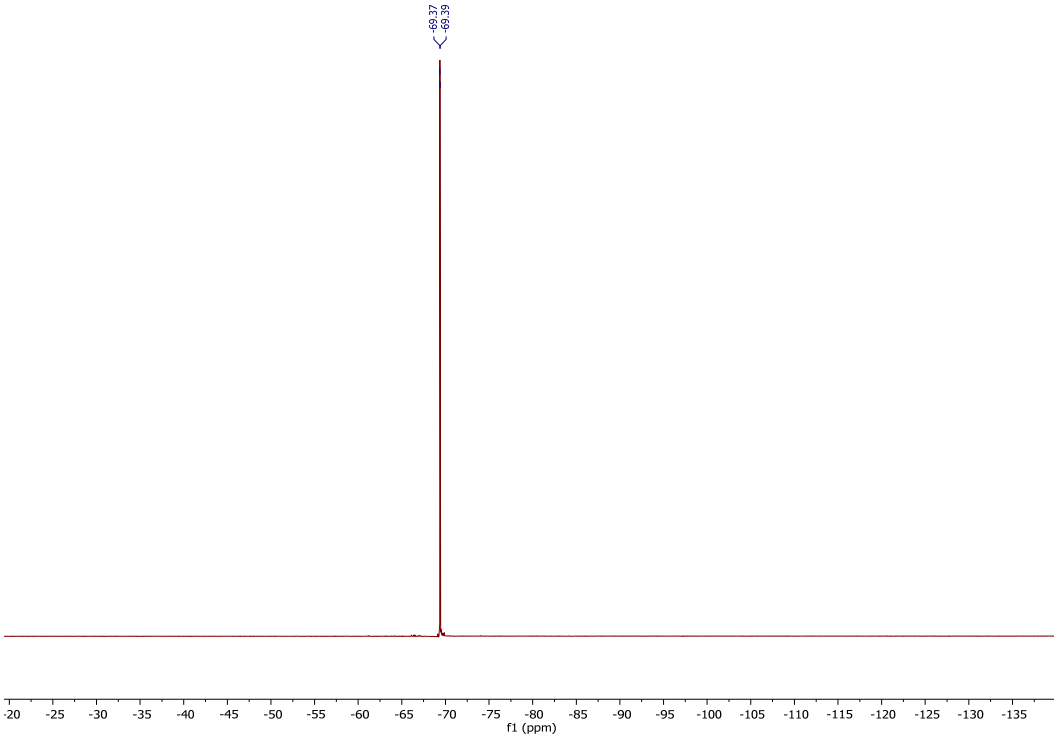
^{1}H NMR (400 Hz, $CDCl_3$)



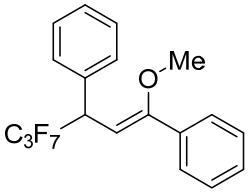
^{13}C NMR (100 Hz, $CDCl_3$)

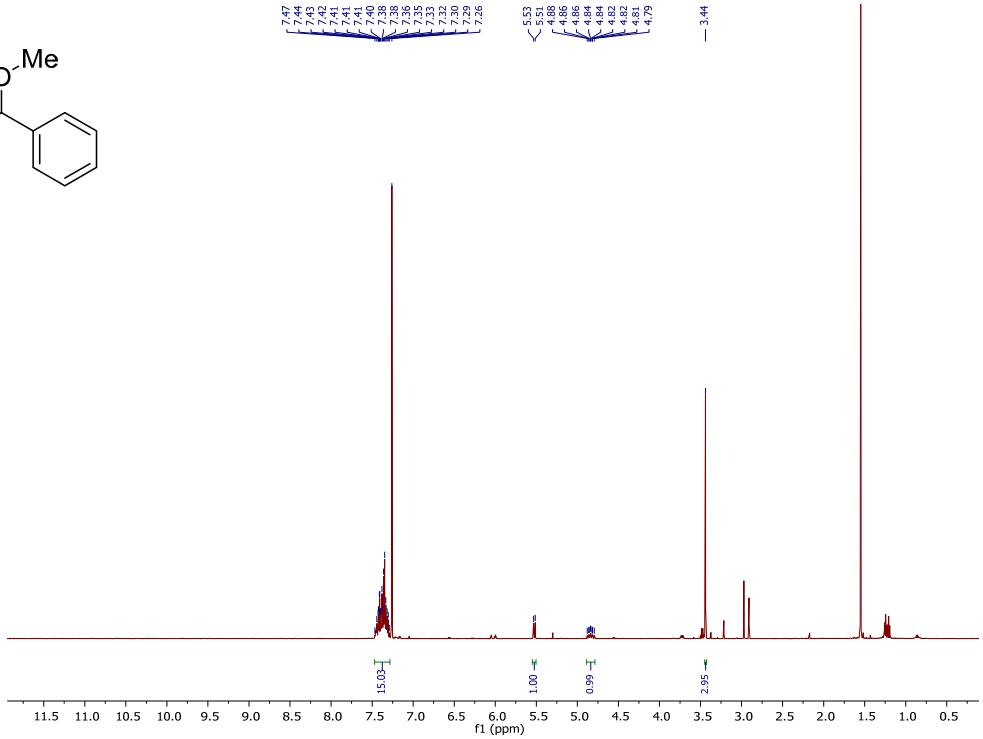


^{19}F NMR (376 Hz, $CDCl_3$)

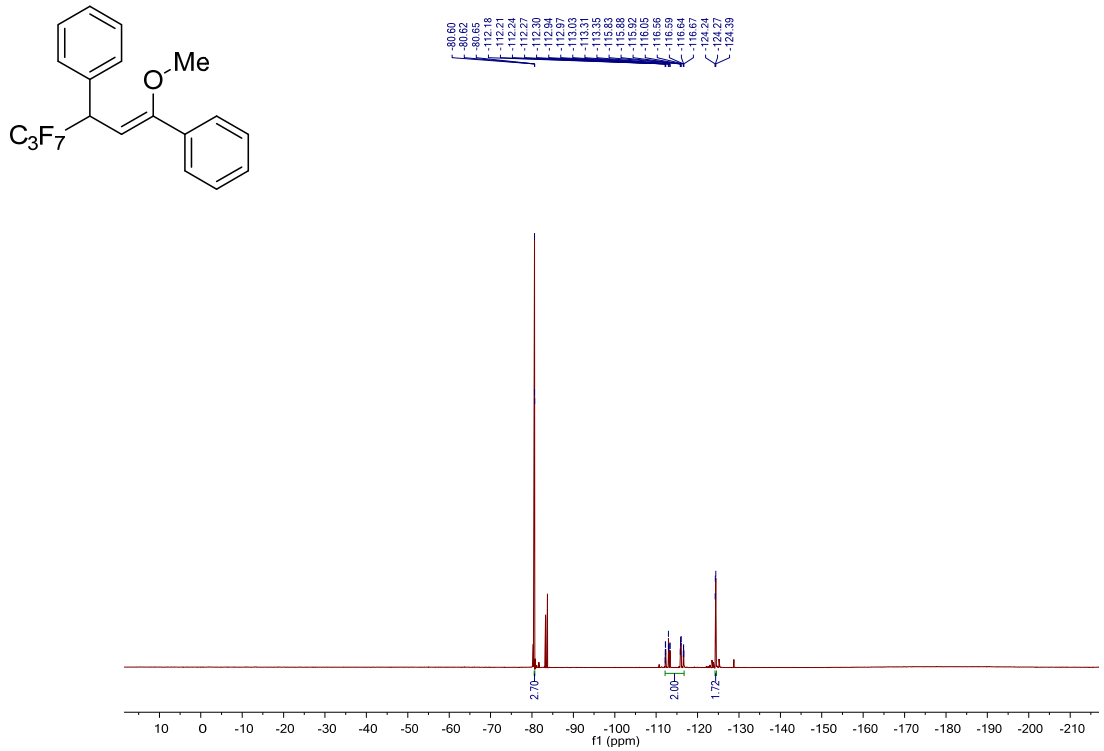


(*Z*)-(4,4,4-trifluoro-1-phenoxybut-1-ene-1,3-diyl)dibenzene (4b)



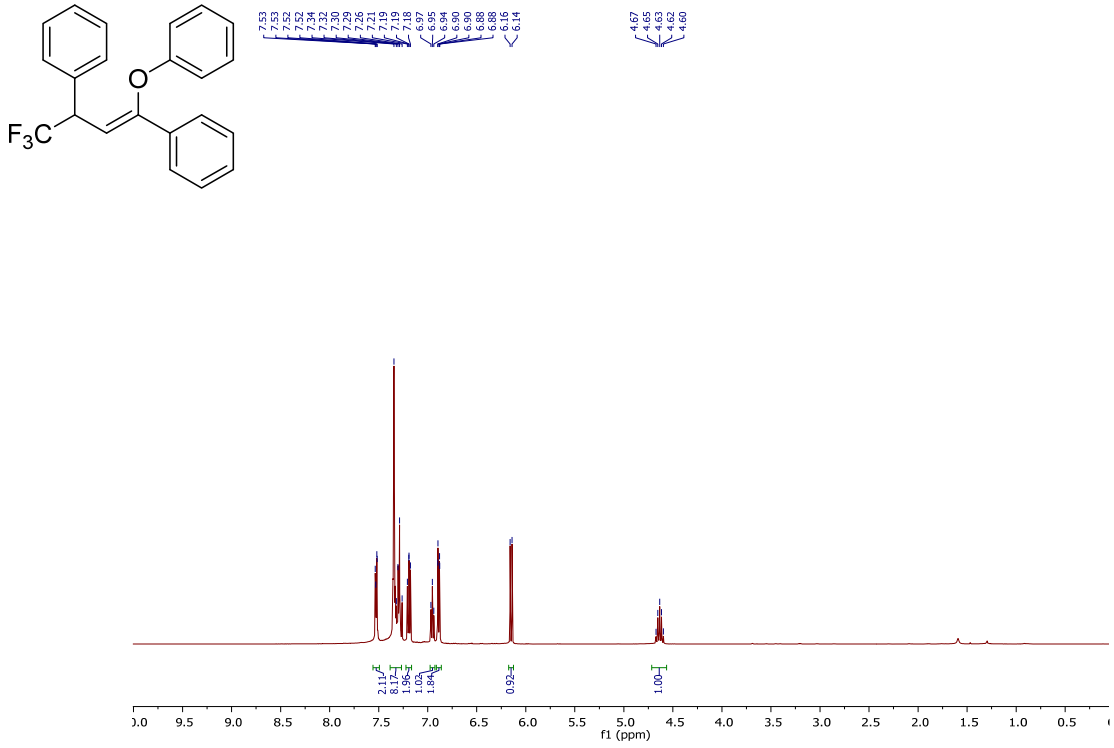


^{19}F NMR (376 Hz, $CDCl_3$)

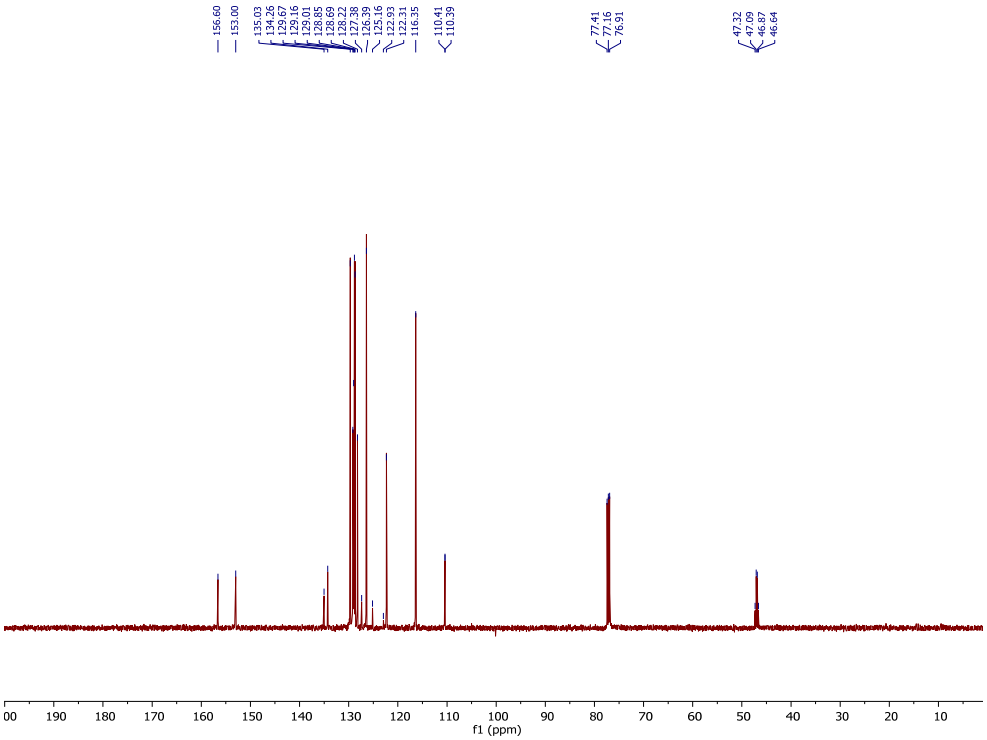


(*Z*)-(4,4,4-trifluoro-1-phenoxybut-1-ene-1,3-diyl)dibenzene (4c)

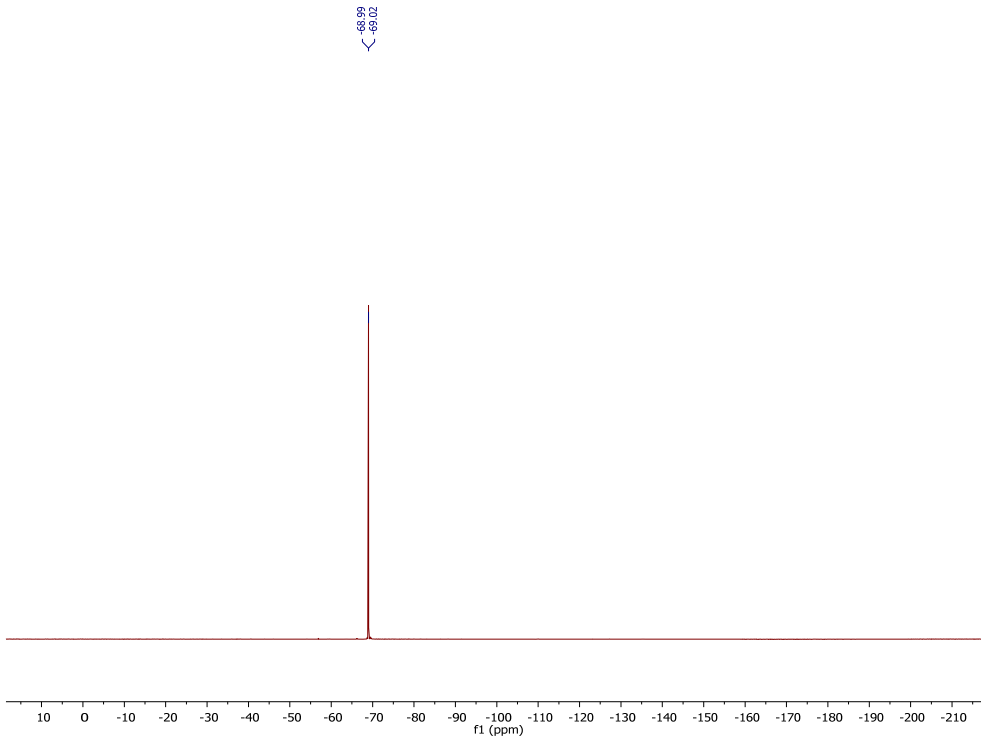
^{1}H NMR (400 Hz, $CDCl_3$)



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

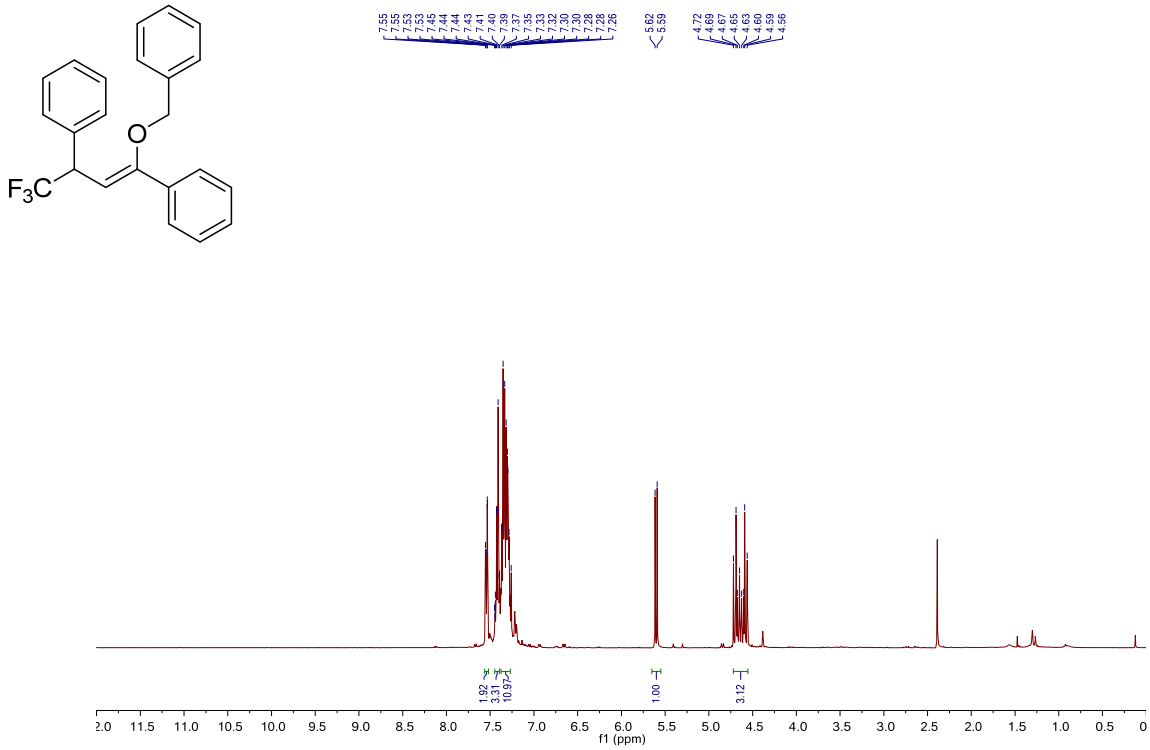


^{19}F NMR (376 Hz, $CDCl_3$)

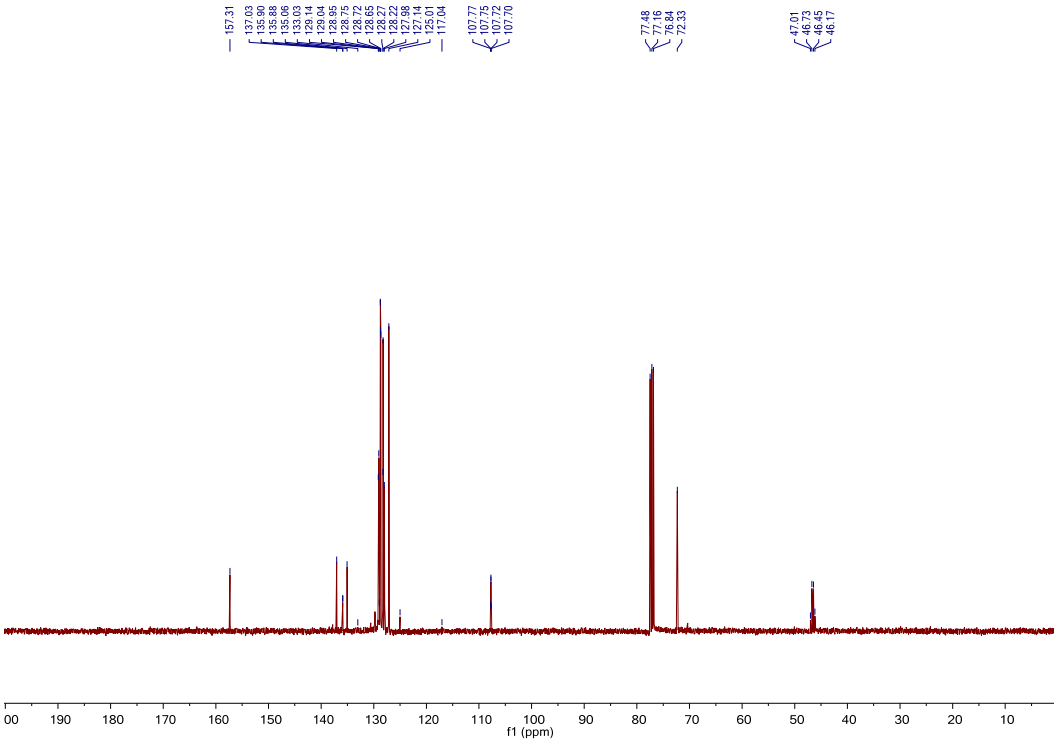


(*Z*)-(1-(Benzyloxy)-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (4d)

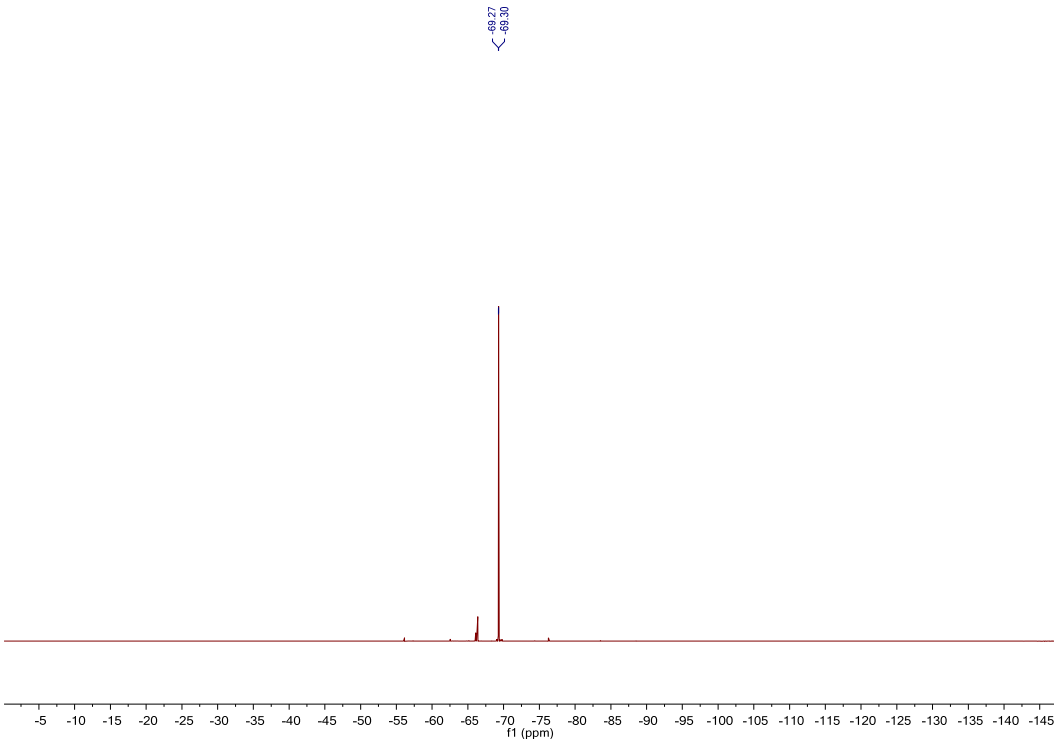
^{1}H NMR (400 Hz, $CDCl_3$)



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

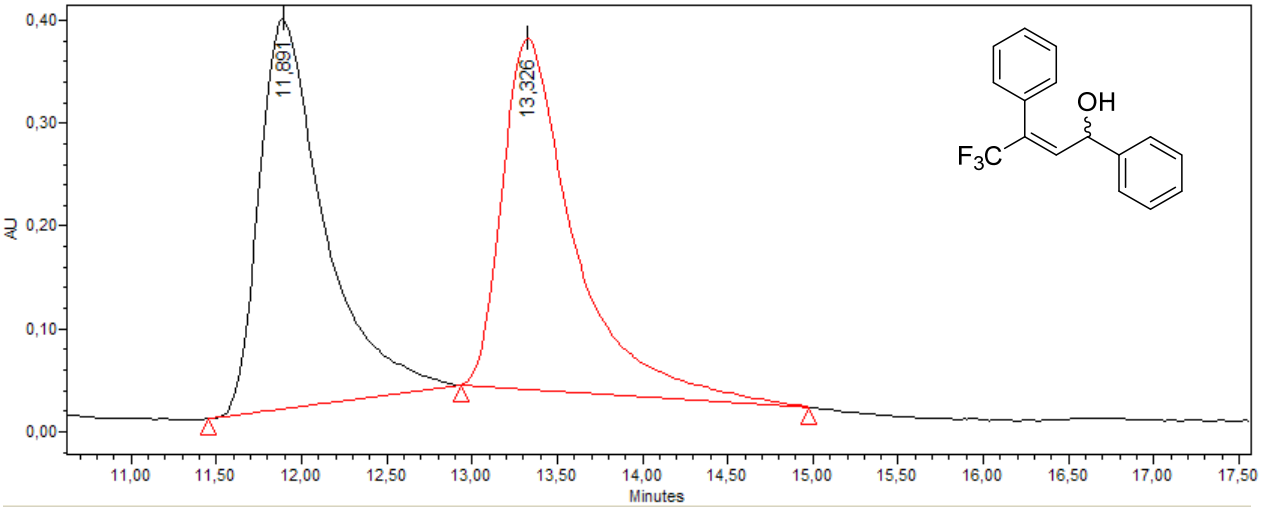


^{19}F NMR (376 Hz, $CDCl_3$)

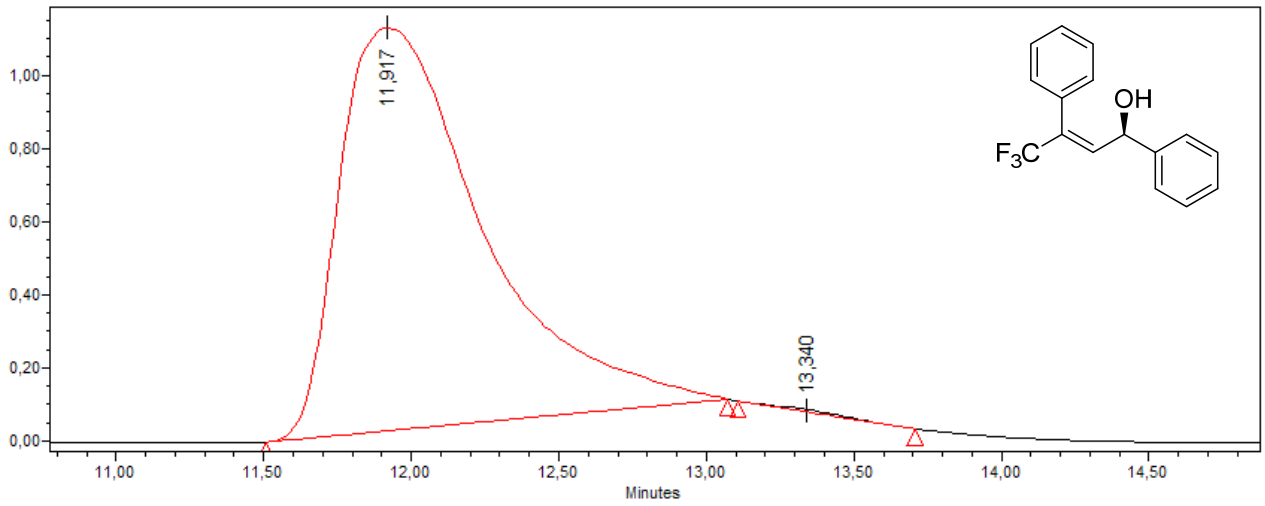


HPLC Chromatograms of allylic substrates 1a-f, 1j-m and 3a-c

(*E*)-4,4,4-Trifluoro-1,3-diphenyl-2-buten-1-ol (1a)

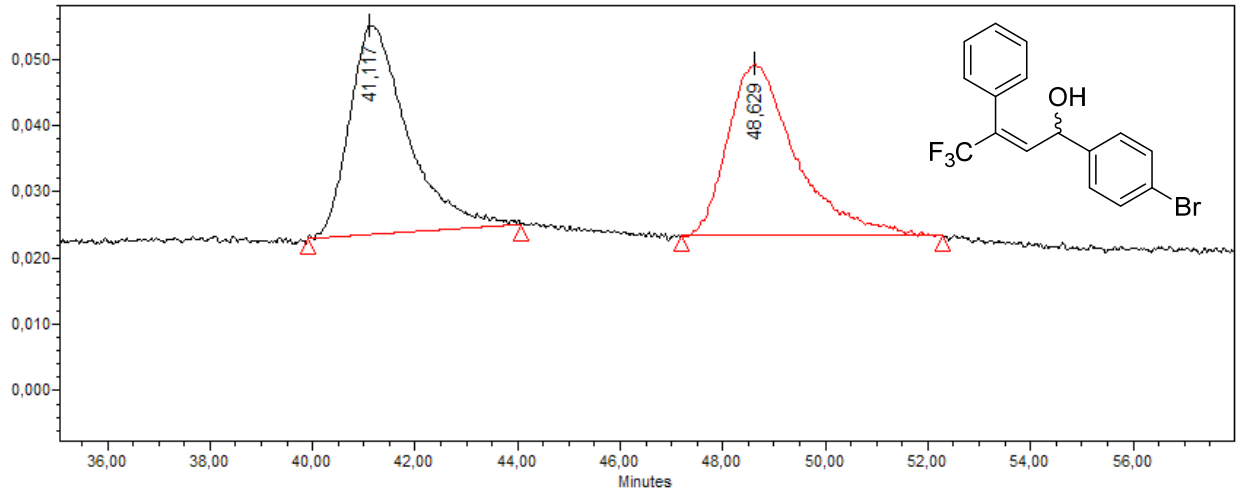


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		11,891							10017567	50,01	378738
2		13,326							10012716	49,99	341141

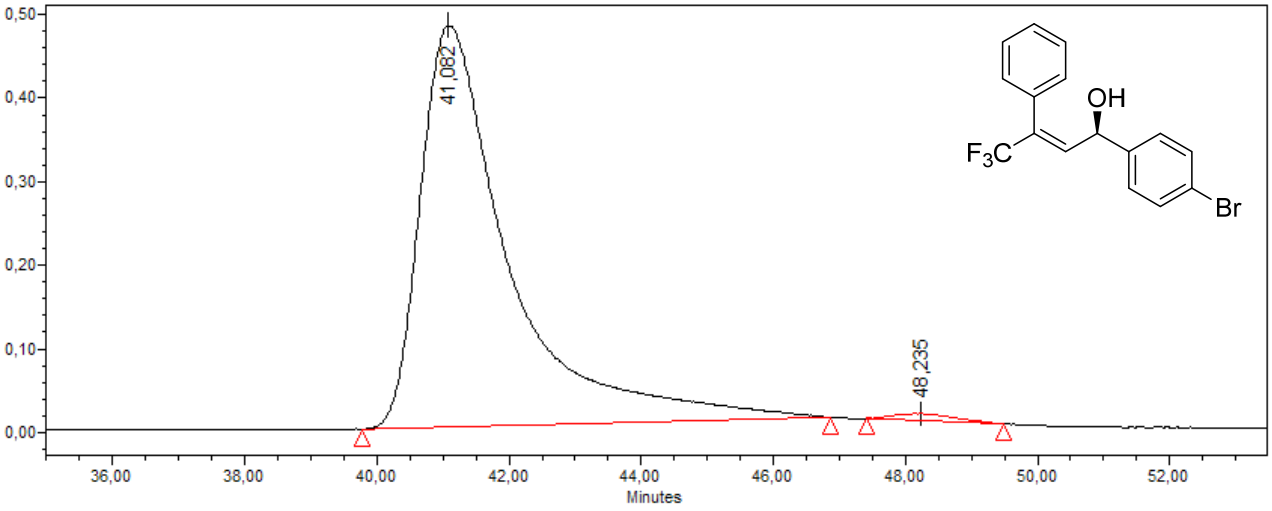


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		11,917							37395687	99,72	1101853
2		13,340							105565	0,28	6904

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-bromophenyl)-2-buten-1-ol (1b)

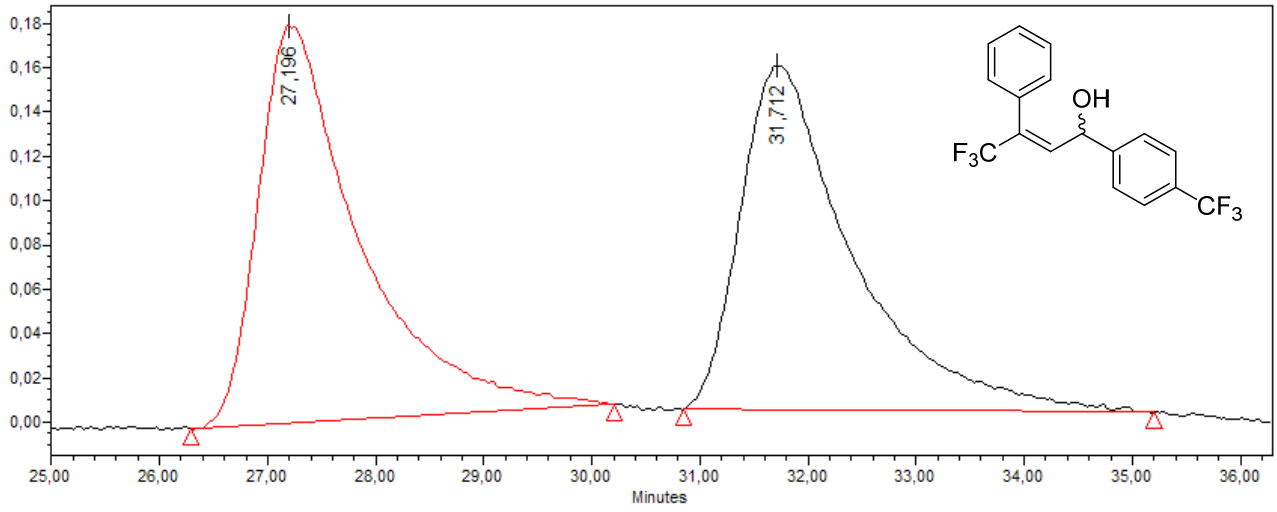


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		41,117							2470724	50,86	31517
2		48,629							2387325	49,14	25928

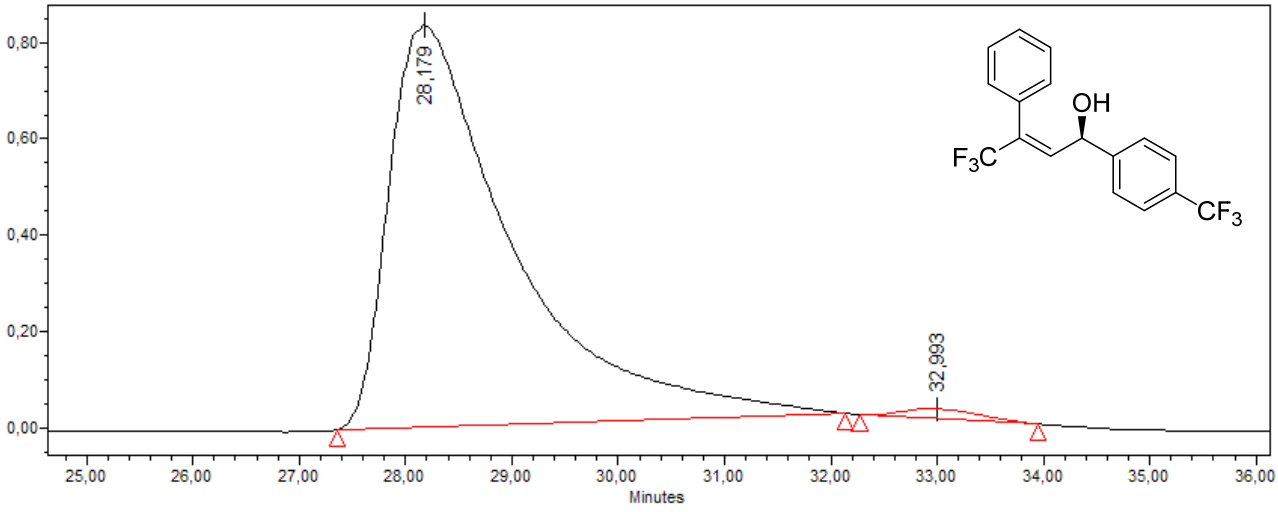


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area
1		41,082							44995158	98,88
2		48,235							509203	1,12

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-trifluoromethylphenyl)-2-buten-1-ol (1c)

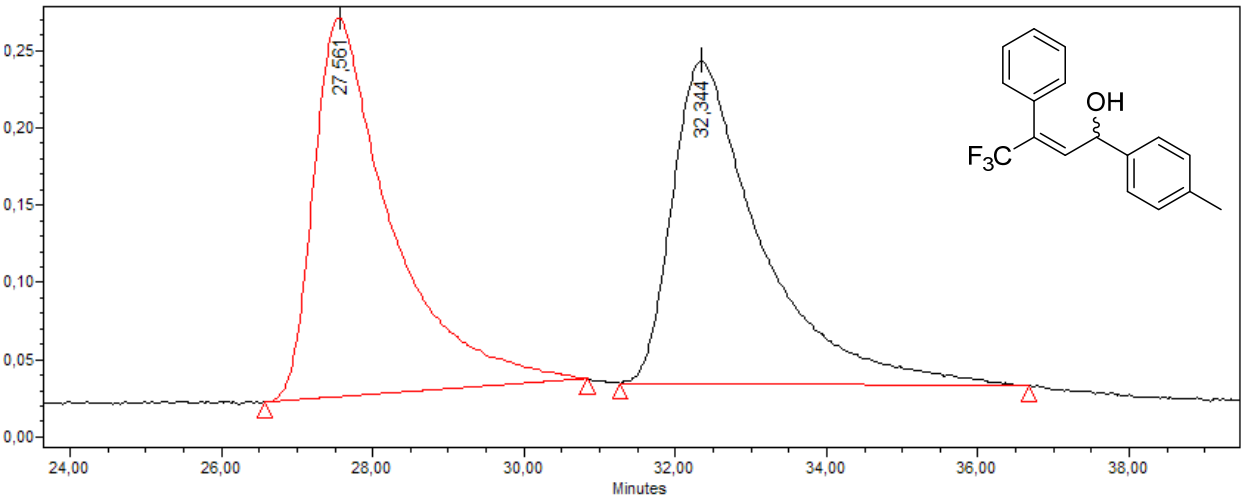


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		27,196							11764660	51,23	179094
2		31,712							11199207	48,77	155165

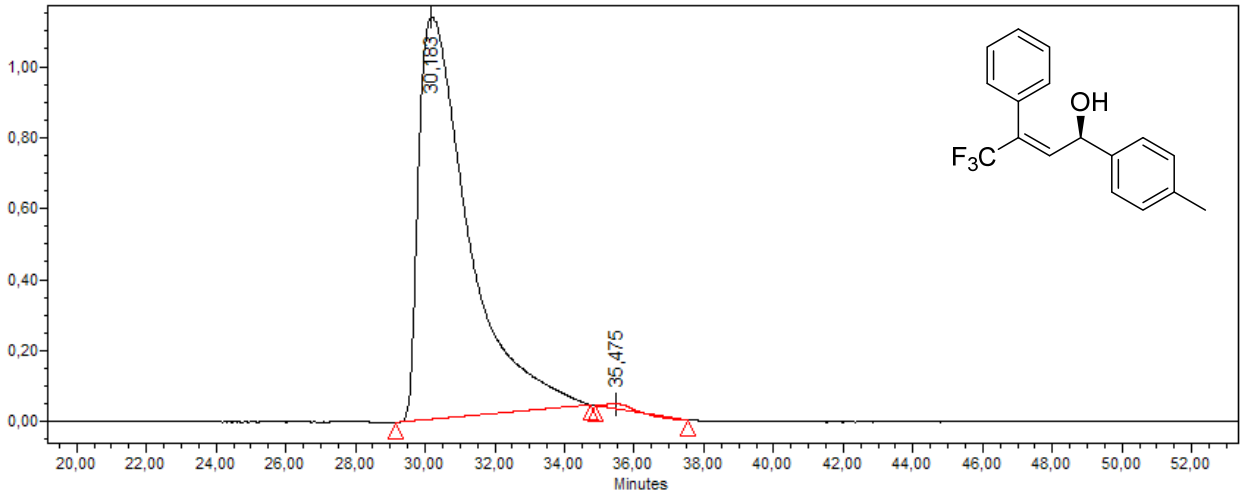


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		28,179							67749383	98,56	834077
2		32,993							987387	1,44	20829

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-methylphenyl)-2-buten-1-ol (1d)

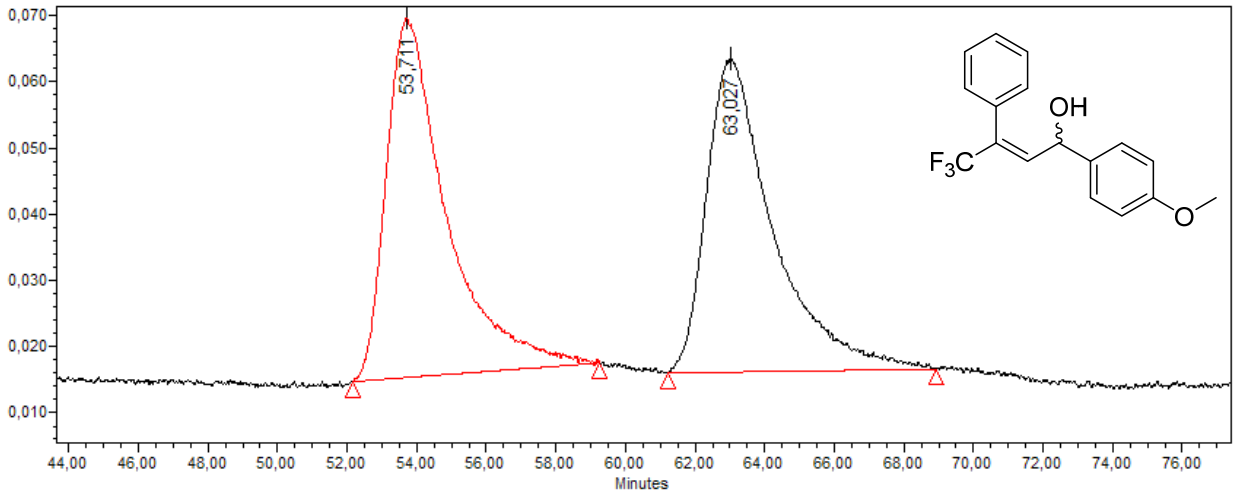


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		27,561							17564714	50,66	244740
2		32,344							17110164	49,34	208910

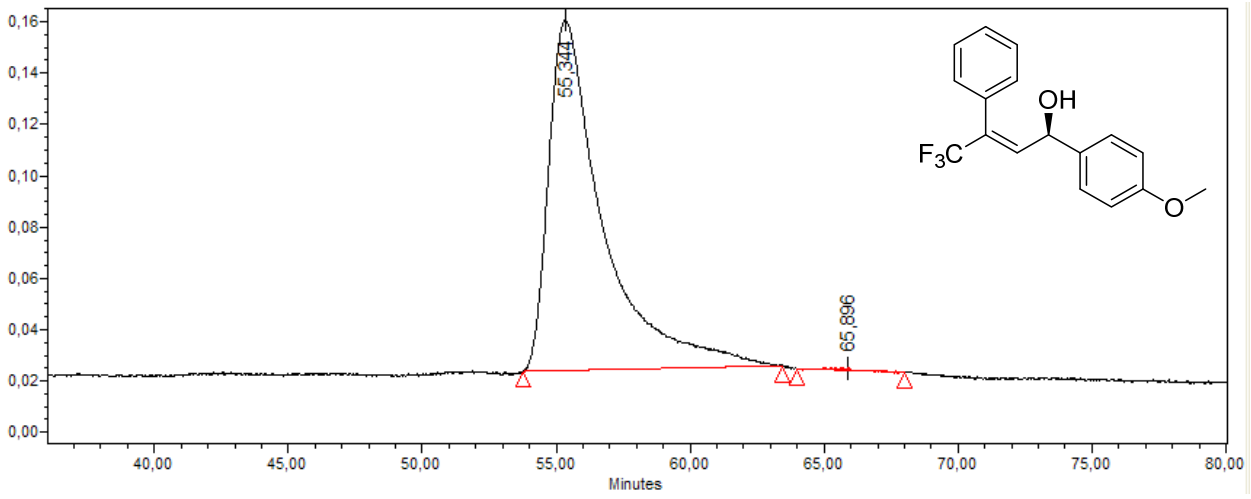


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		30,183							112614825	99,23	1133134
2		35,475							869519	0,77	15535

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(4'-methoxyphenyl)-2-buten-1-ol (1e)

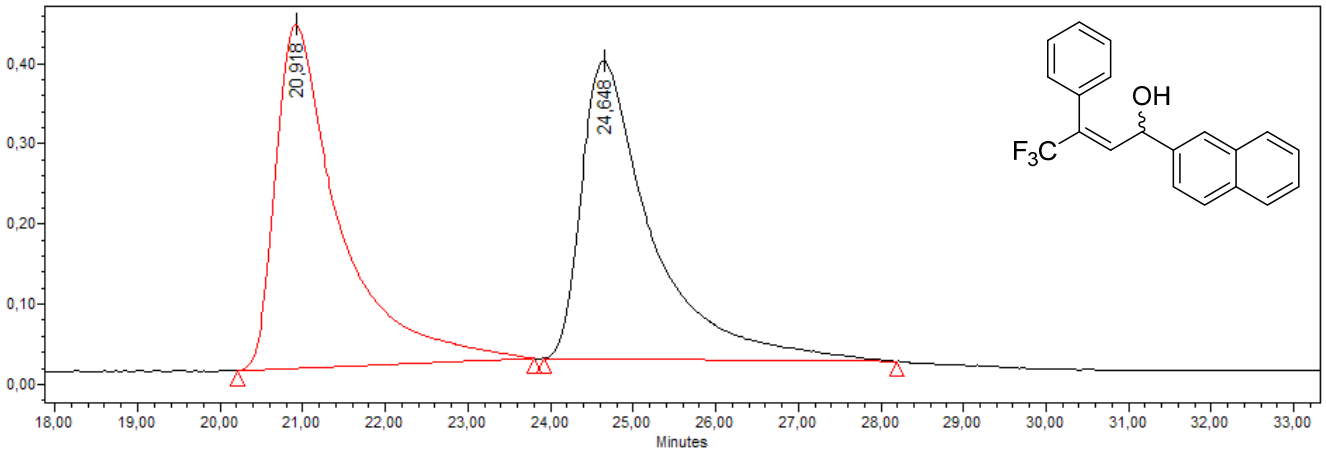


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		53,711							6534293	50,88	54286
2		63,027							6307349	49,12	47323

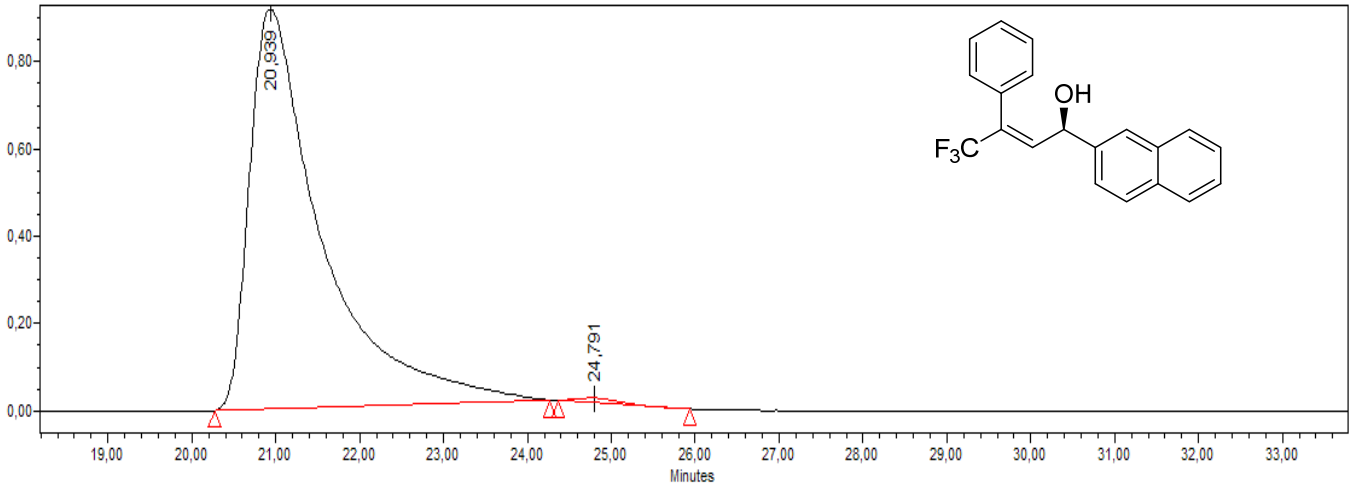


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		55,344							19312337	99,69	136592
2		65,896							60664	0,31	941

(*E*)-4,4,4-Trifluoro-3-phenyl-1-(naphthalene-2-yl)-2-buten-1-ol (1f)

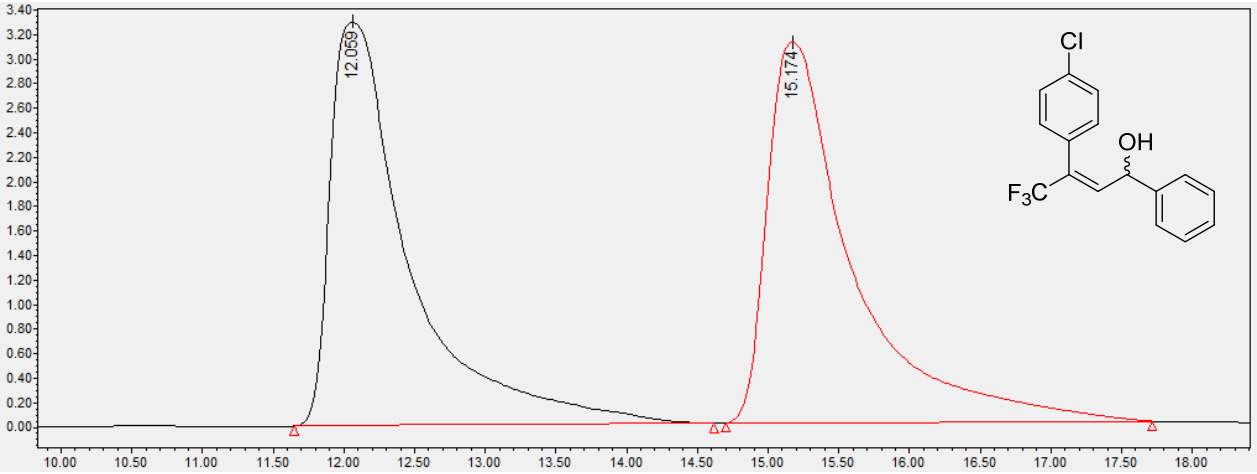


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		20,918							23071261	51,07	429204
2		24,648							22103697	48,93	371791

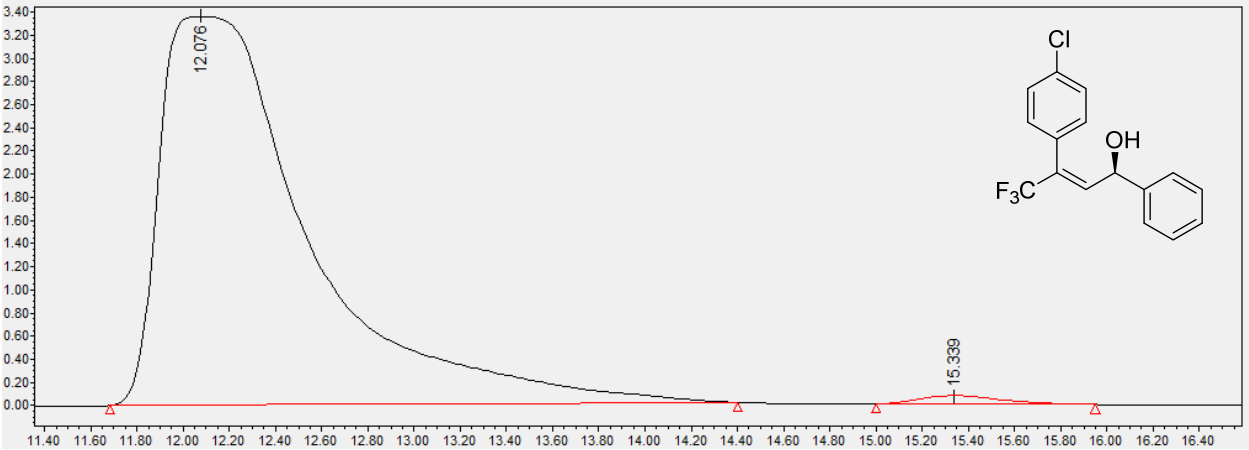


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		20,939							55000047	99,36	915794
2		24,791							351846	0,64	10108

(*E*)-3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (1j)

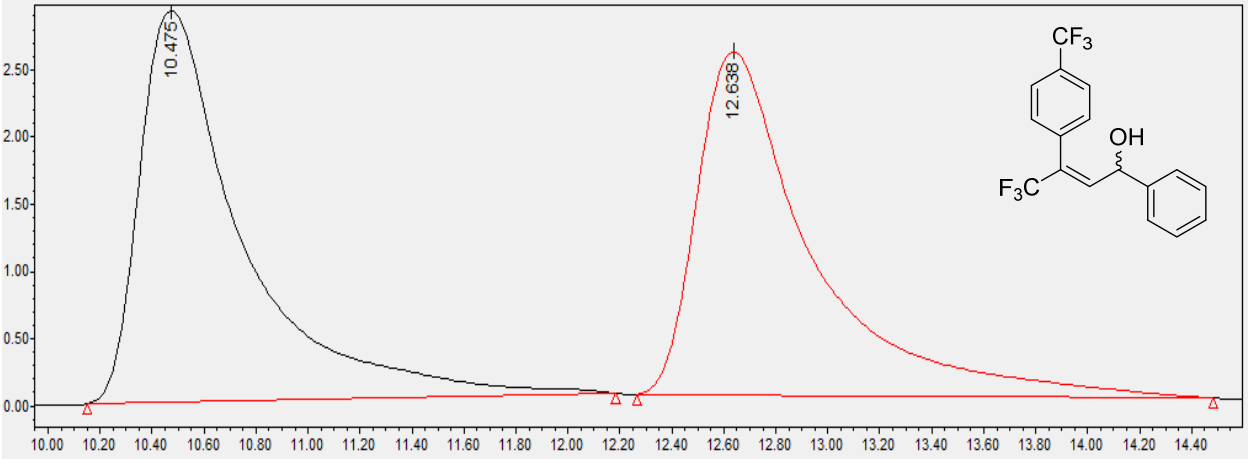


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		12.059	128110167	49.55	3287579	bb			Unknown
2		15.174	130412248	50.45	3098939	bb			Unknown

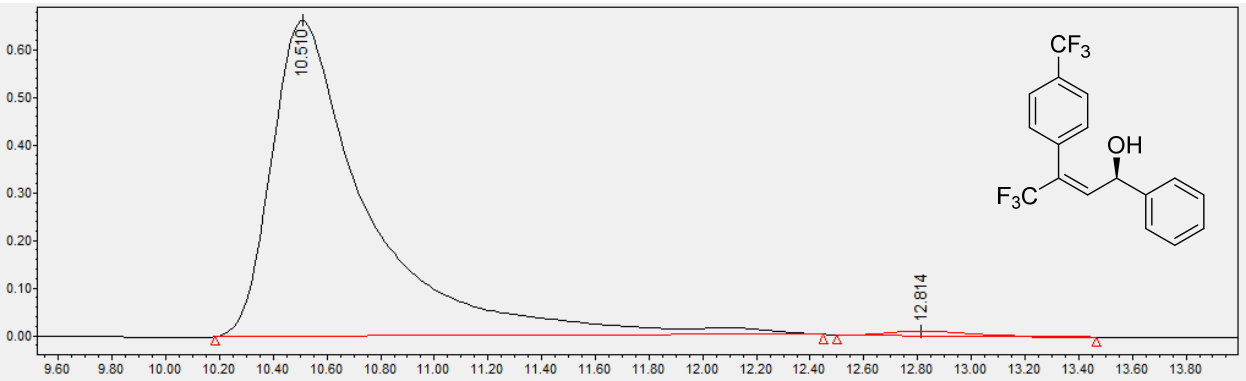


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		12.076	150058421	98.80	3356894	bb			Unknown
2		15.339	1829457	1.20	74639	bb			Unknown

(*E*)-4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (1k)

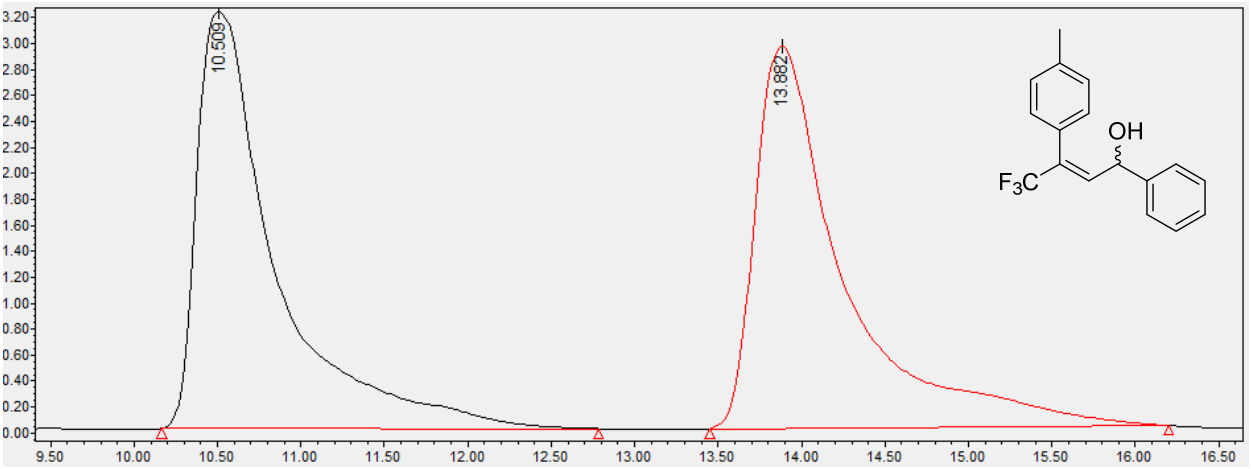


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		10.475	80424694	50.56	2912901	bb			Unknown
2		12.638	78646923	49.44	2551819	bb			Unknown

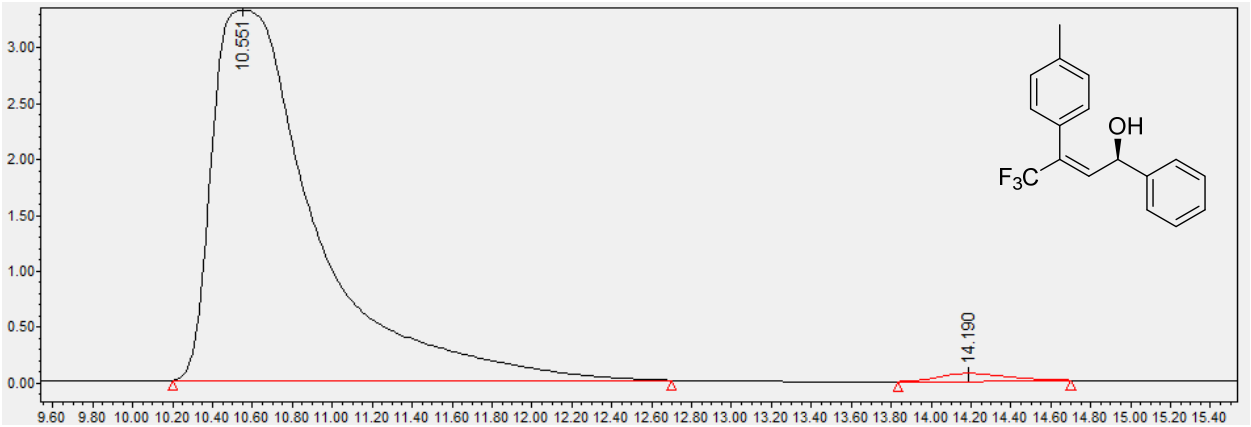


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		10.510	16753525	98.86	663338	bb			Unknown
2		12.814	193109	1.14	9734	bb			Unknown

(*E*)-4,4,4-trifluoro-1-phenyl-3-(p-tolyl)but-2-en-1-ol (1l)

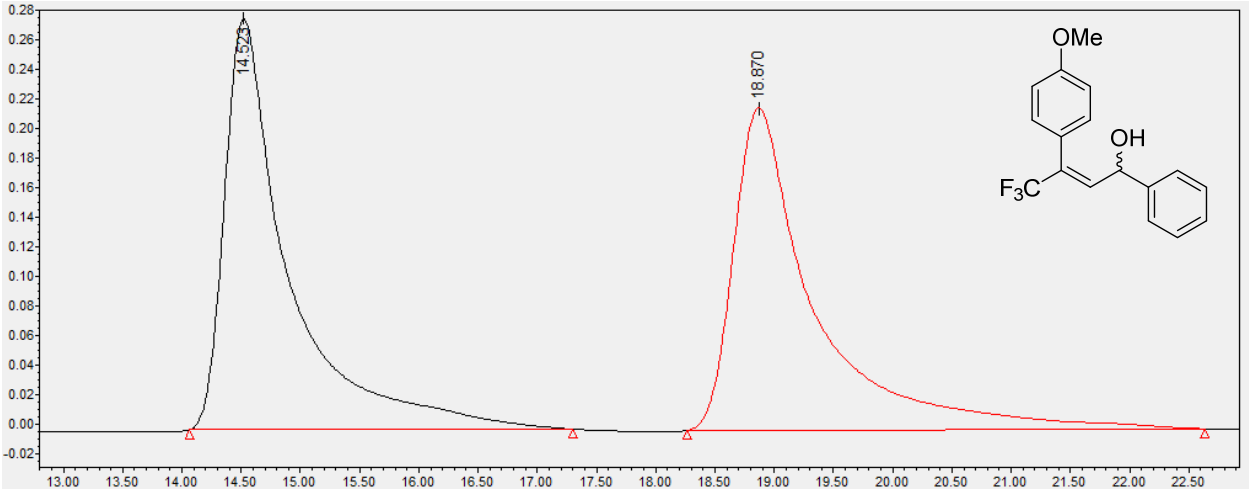


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		10.509	104995356	49.09	3207209	bb			Unknown
2		13.882	108884708	50.91	2940799	bb			Unknown

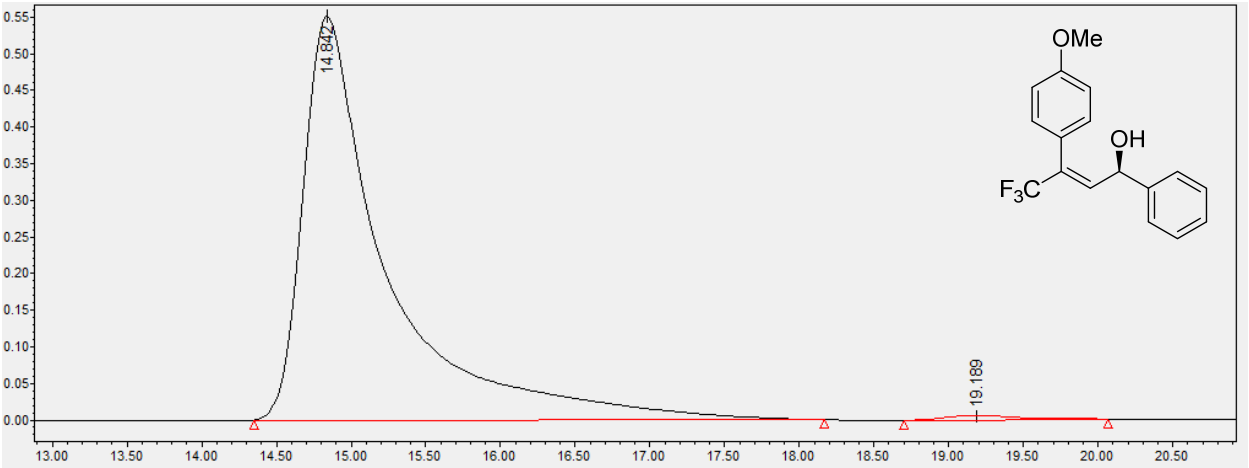


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		10.551	119774038	98.70	3315595	bb			Unknown
2		14.190	1578987	1.30	68413	bb			Unknown

(*E*)-4,4,4-trifluoro-3-(4-methoxyphenyl)-1-phenylbut-2-en-1-ol (1m)

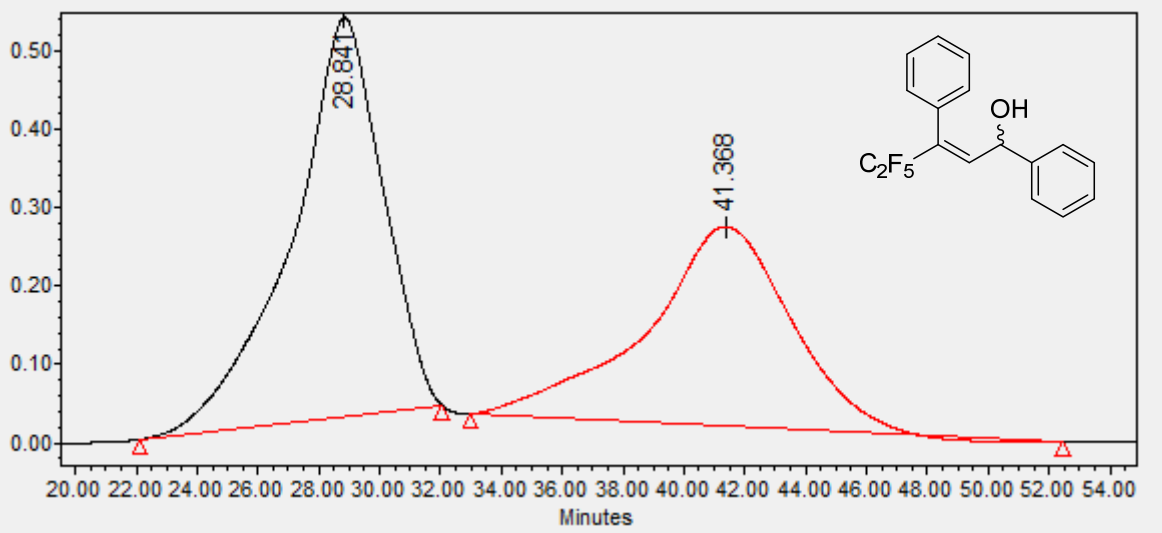


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		14.523	10491887	50.18	278519	bb			Unknown
2		18.870	10416708	49.82	218129	bb			Unknown

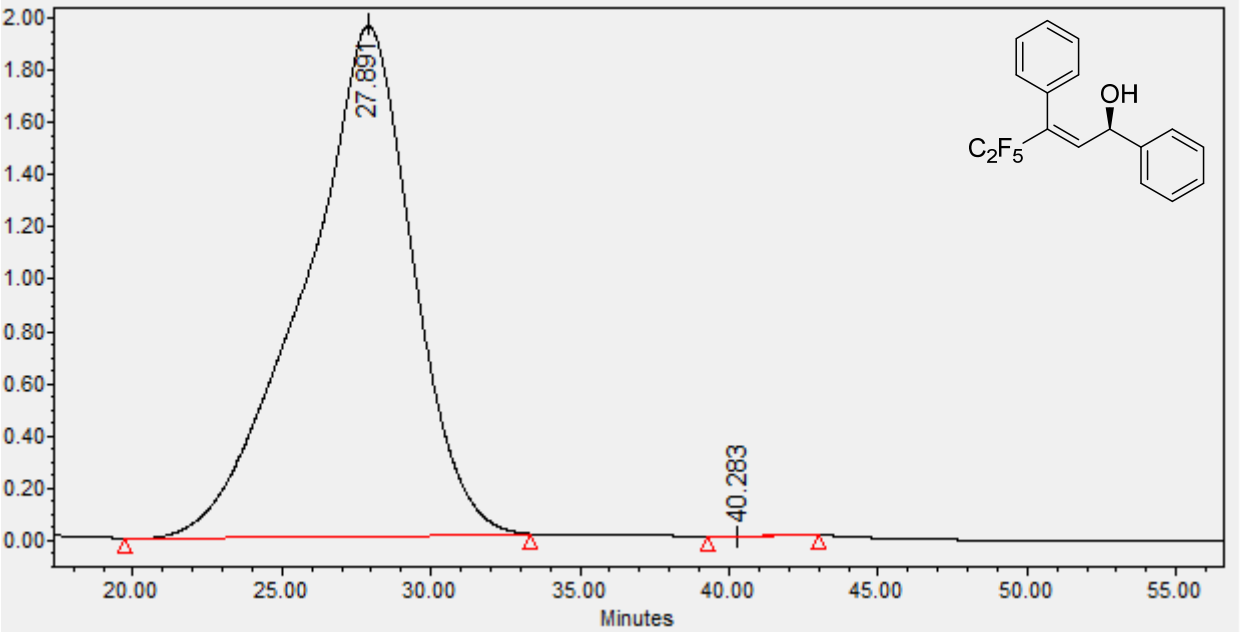


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		14.842	21487867	99.11	551387	bb			Unknown
2		19.189	192389	0.89	5745	bb			Unknown

(*E*)-4,4,5,5,5-Pentafluoro-1,3-diphenylpent-2-en-1-ol (1p)

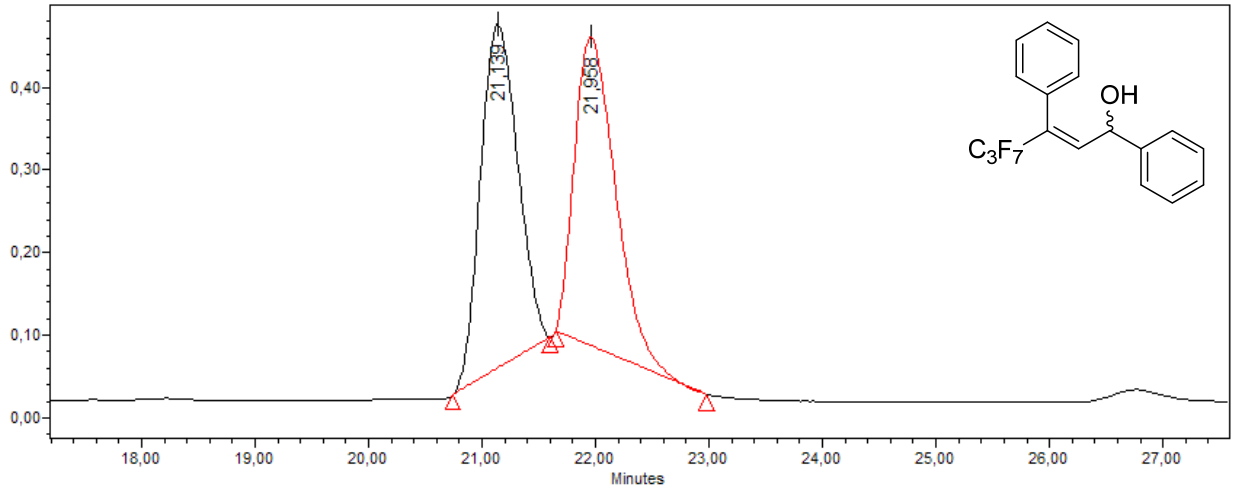


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		28.841	105471907	55.35	508652	bb			Unknown
2		41.368	85097864	44.65	254364	bb			Unknown

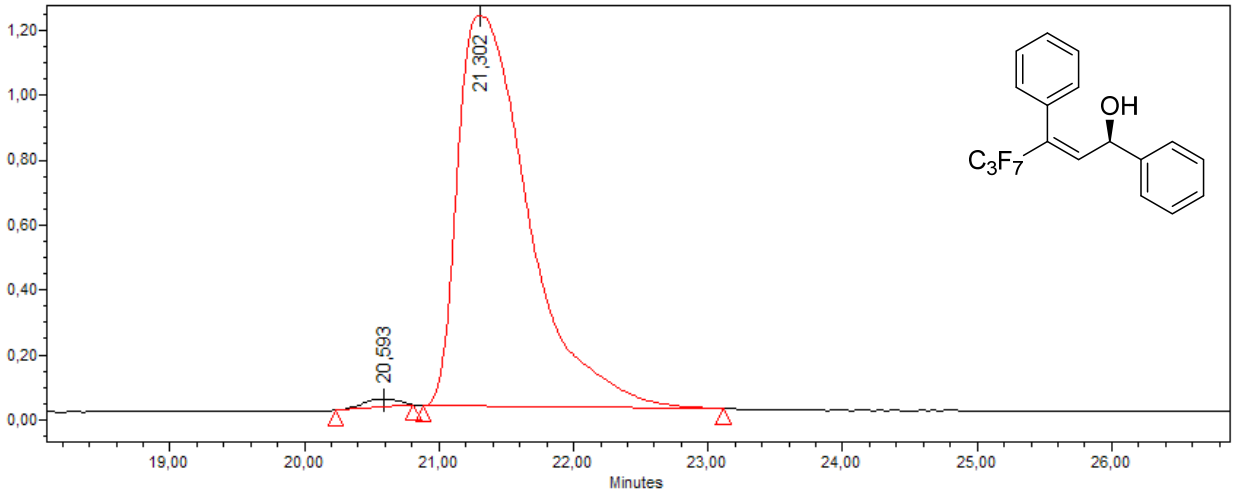


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		27.891	491067214	99.96	1953241	bb			Unknown
2		40.283	208098	0.04	-1683	bb			Unknown

(*E*)-4,4,5,5,6,6,6-Heptafluoro-1,3-diphenylhex-2-en-1-ol (1q)

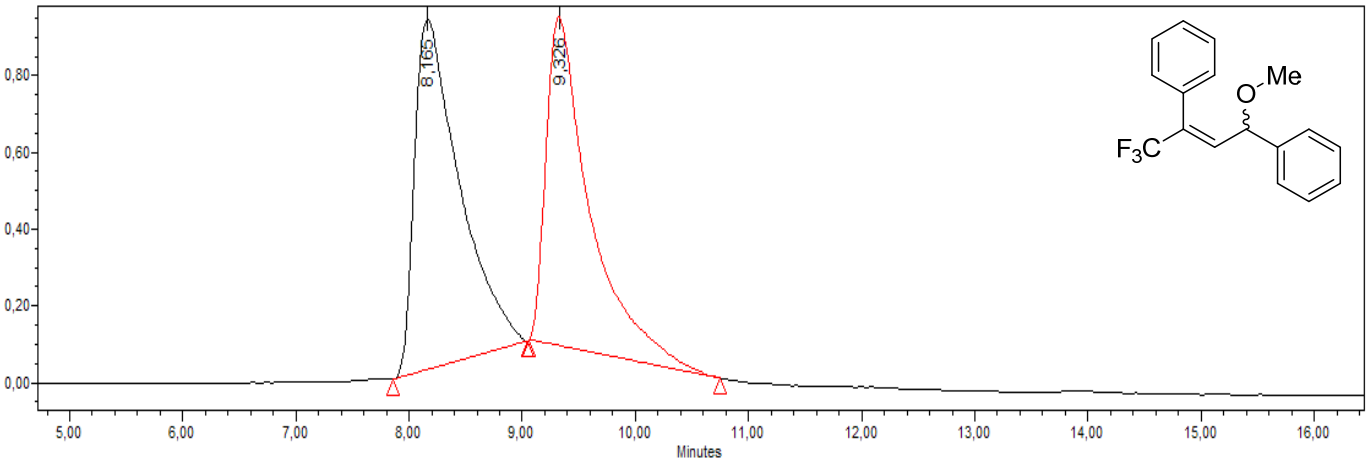


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		21,139							9483030	50,10	416166
2		21,958							9445915	49,90	373618

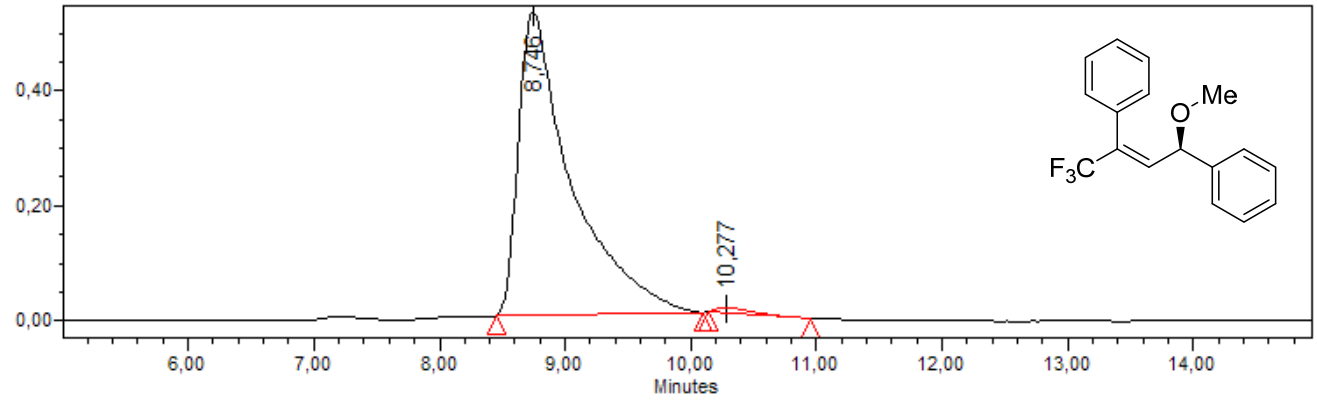


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		20,593							430963	0,97	23486
2		21,302							44034217	99,03	1203402

(*E*)-(4,4,4-Trifluoro-1-methoxybut-2-ene-1,3-diyl)dibenzene (3a):

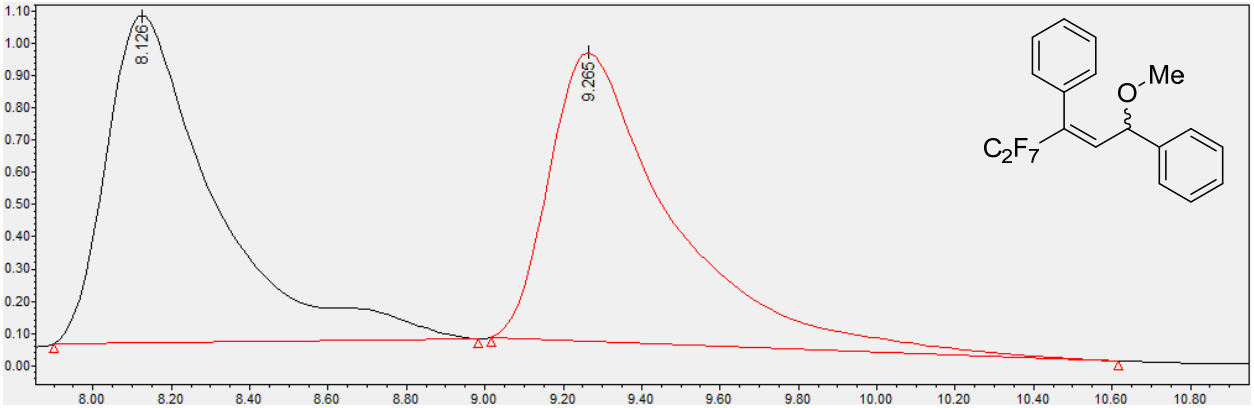


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		8,165							25185306	52,34	912370
2		9,326							22932225	47,66	854467

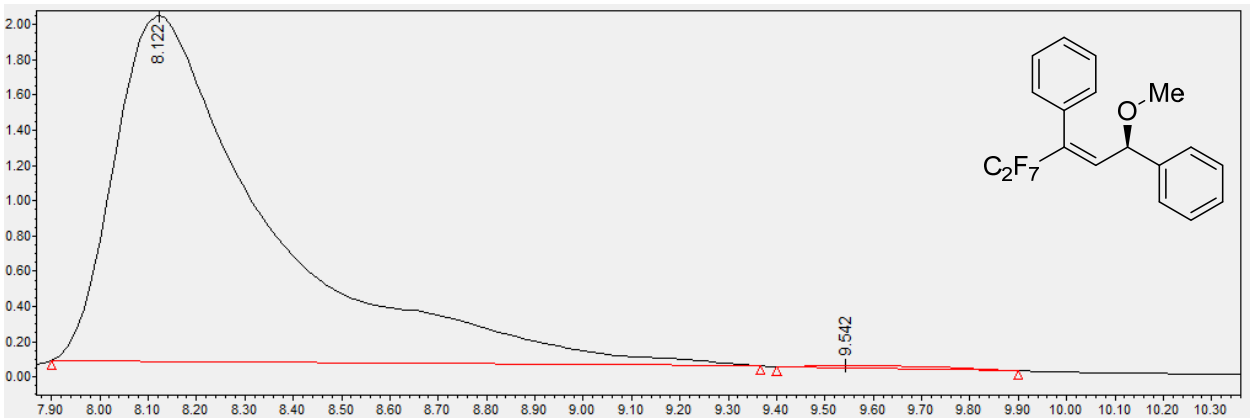


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		8,746							15342483	98,87	528218
2		10,277							175838	1,13	9171

(*E*)-(4,4,5,5,6,6,6-heptafluoro-1-methoxyhex-2-ene-1,3-diyl)dibenzene (3b)

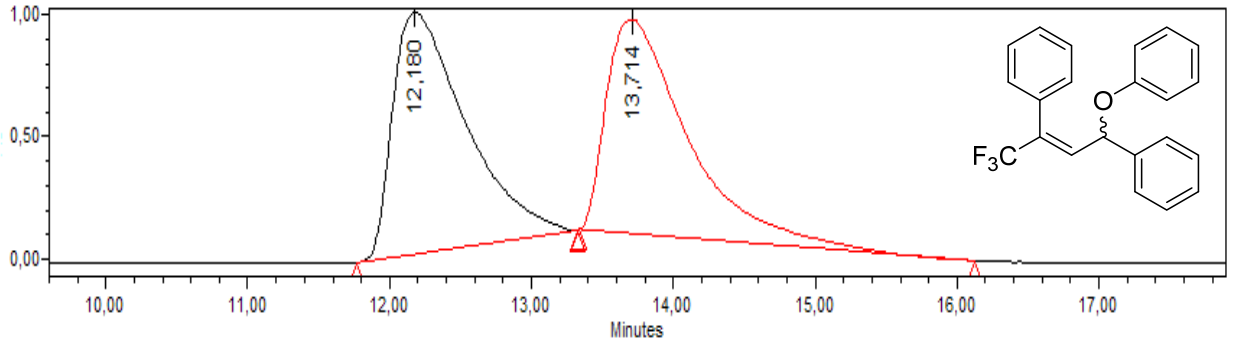


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		8.126	19525306	49.98	1018777	bb			Unknown
2		9.265	19540774	50.02	895985	bb			Unknown

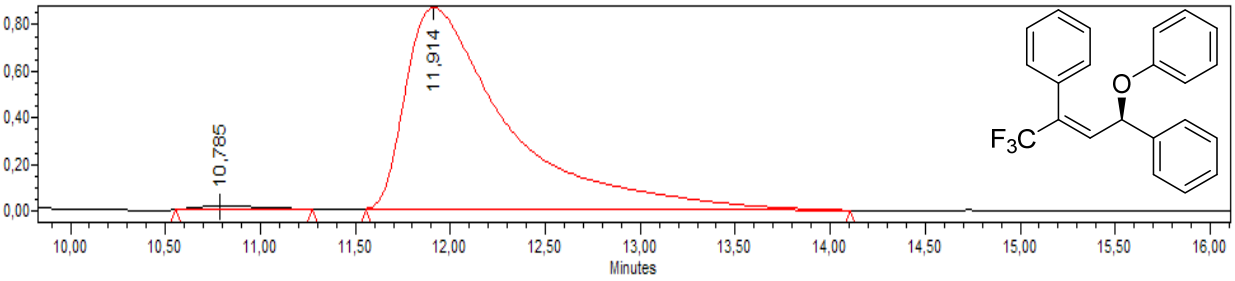


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		8.122	43699937	99.37	1969280	bb			Unknown
2		9.542	275639	0.63	13933	bb			Unknown

(*E*)-(4,4,4-trifluoro-1-phenoxybut-2-ene-1,3-diyl)dibenzene (3c)



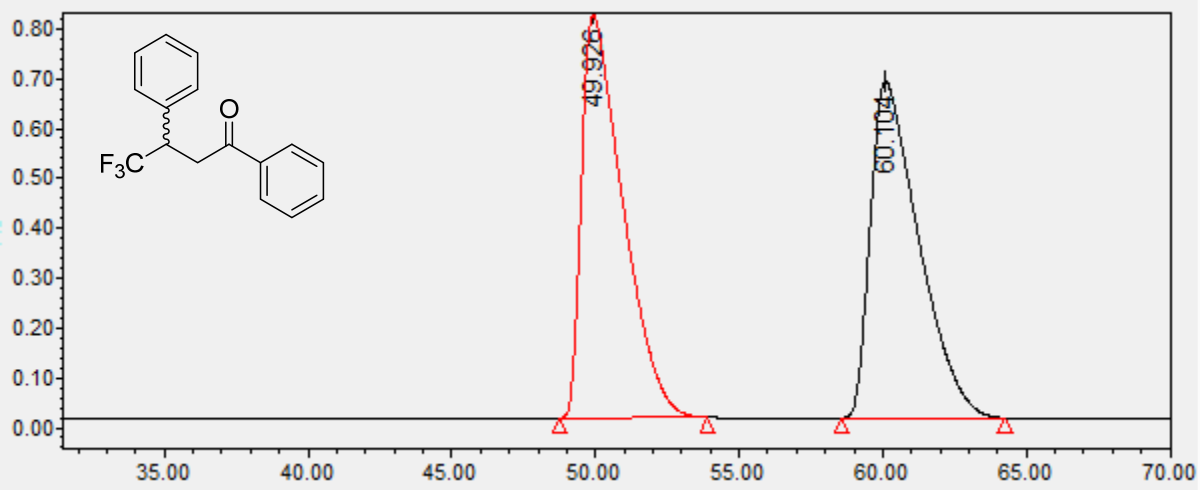
	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		12,180							35368403	50,26	987760
2		13,714							35009320	49,74	876098



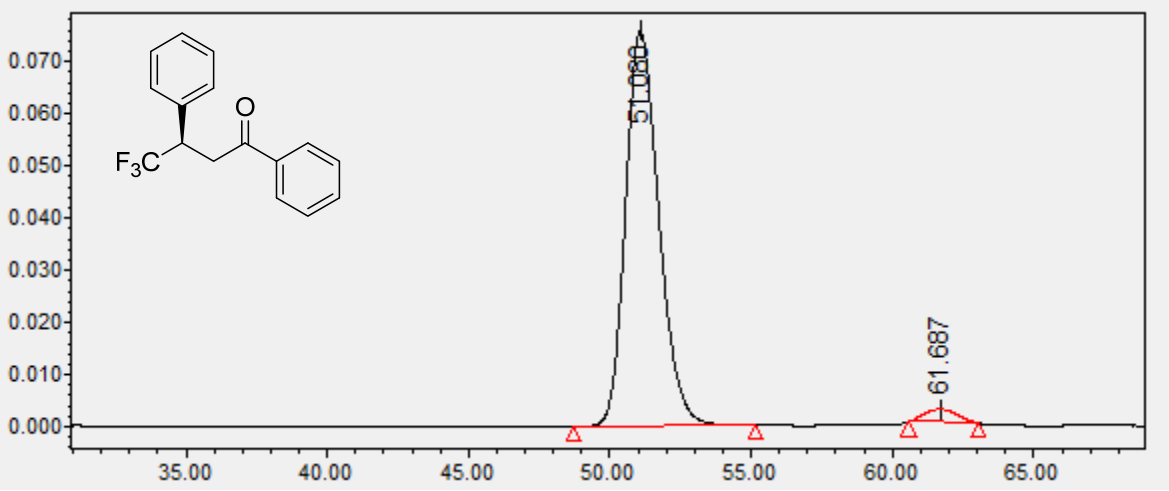
	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		10,785							361874	1,10	15695
2		11,914							32503024	98,90	866668

HPLC Chromatograms of products 2a-f, 2j-m and 4a-c

4,4,4-Trifluoro-1,3-diphenylbutanone (2a)

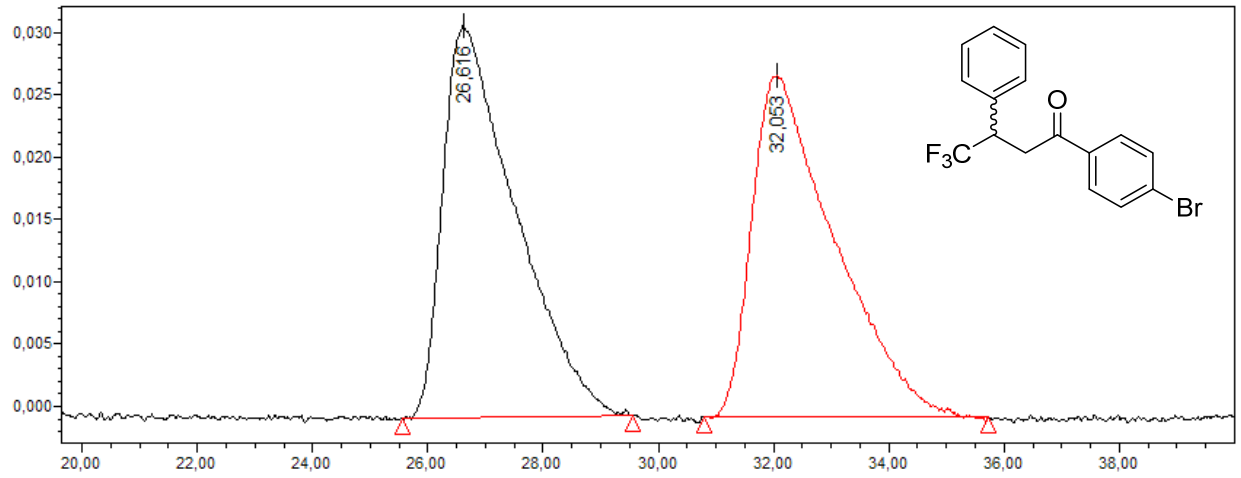


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		49.926	81003980	50.59	808962	bb			Unknown	
2		60.104	79116995	49.41	675104	bb			Unknown	

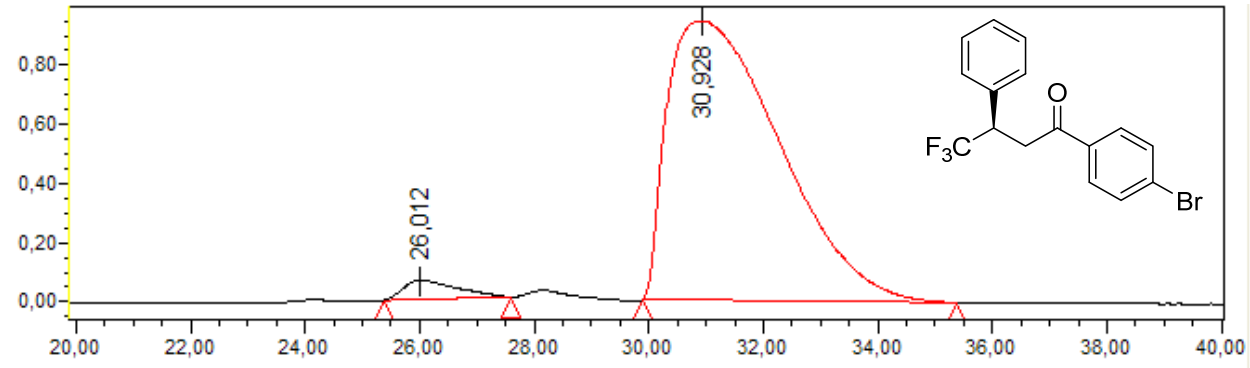


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		51.080	6188915	96.81	75705	bb			Unknown	
2		61.687	203854	3.19	2512	bb			Unknown	

4,4,4-Trifluoro-3-phenyl-1-(4'-Bromophenyl)-butanone (2b)

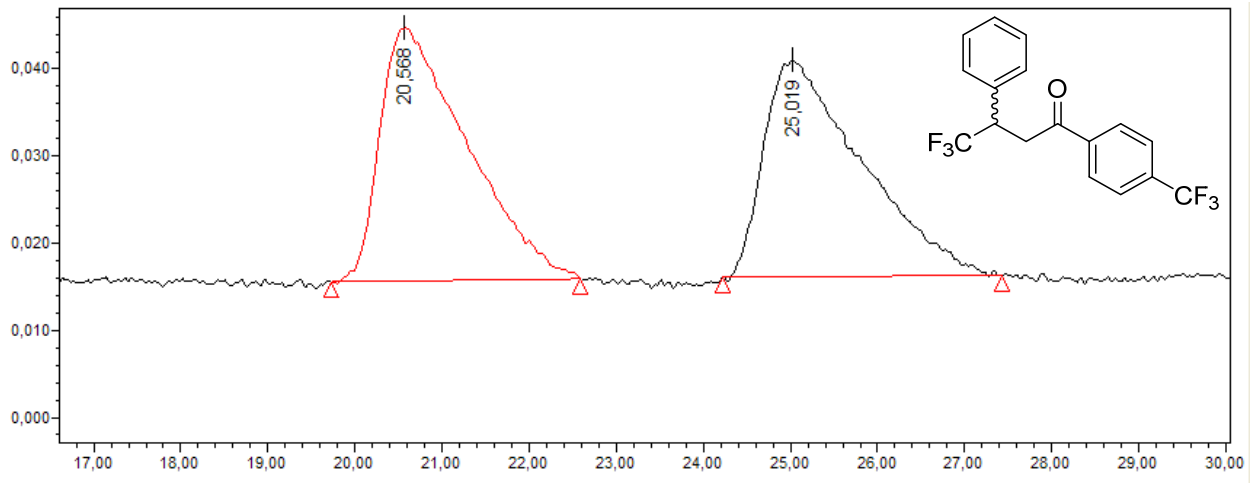


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		26,616							2760831	50,35	31394
2		32,053							2722423	49,65	27346

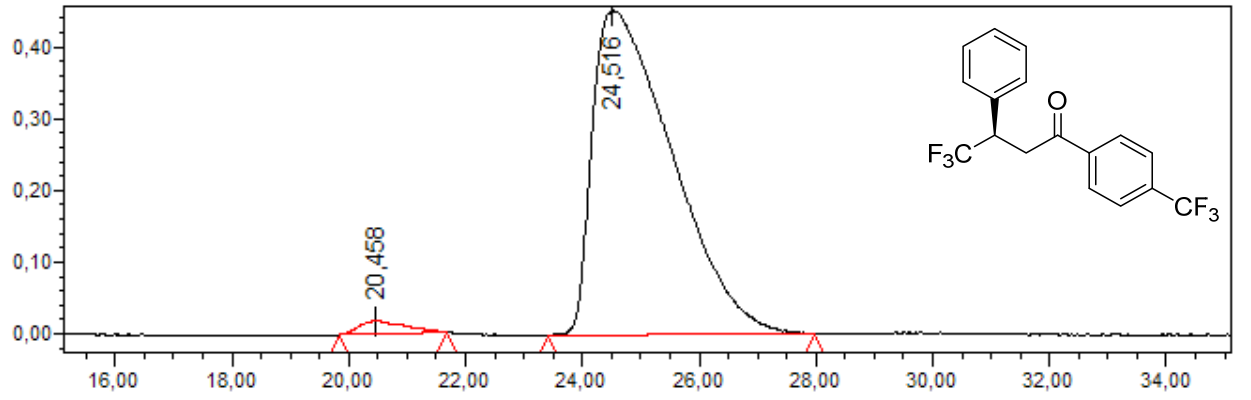


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		26,012							4148610	3,12	64905
2		30,928							128667601	96,88	942721

4,4,4-Trifluoro-3-phenyl-1-(4'-Trifluoromethylphenyl)-butanone (2c)

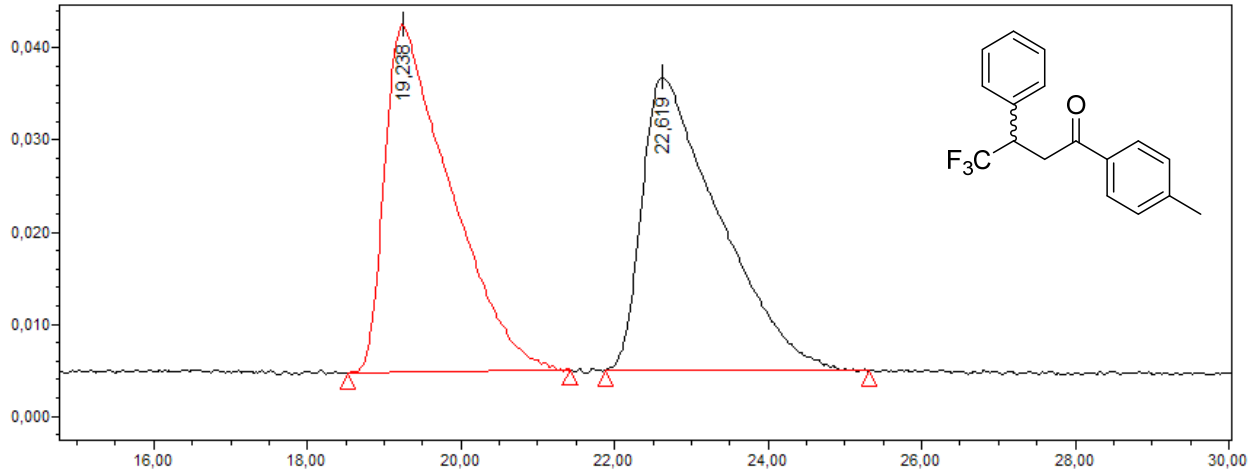


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		20,568							2015928	50,83	29010
2		25,019							1949801	49,17	24819

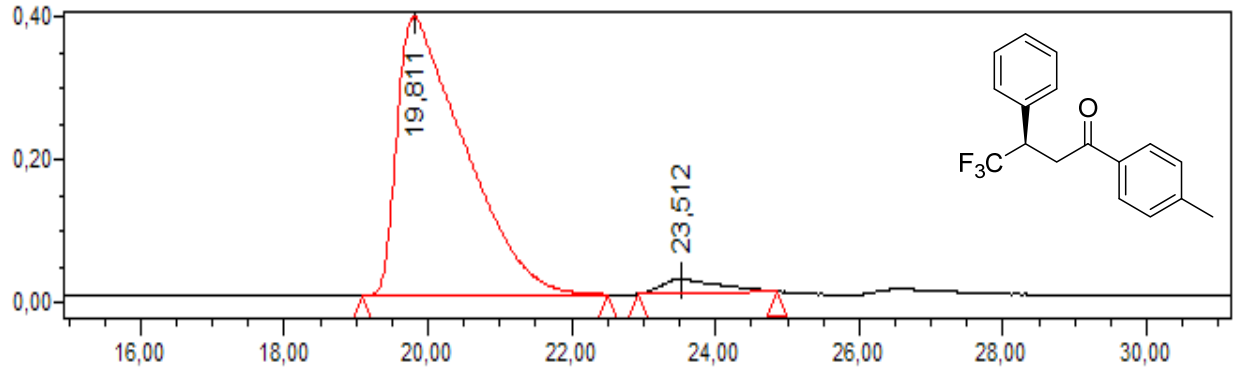


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		20,458							1000908	2,27	18450
2		24,516							43059532	97,73	452614

4,4,4-Trifluoro-3-phenyl-1-(4'-Methylphenyl)-butanone (2d)

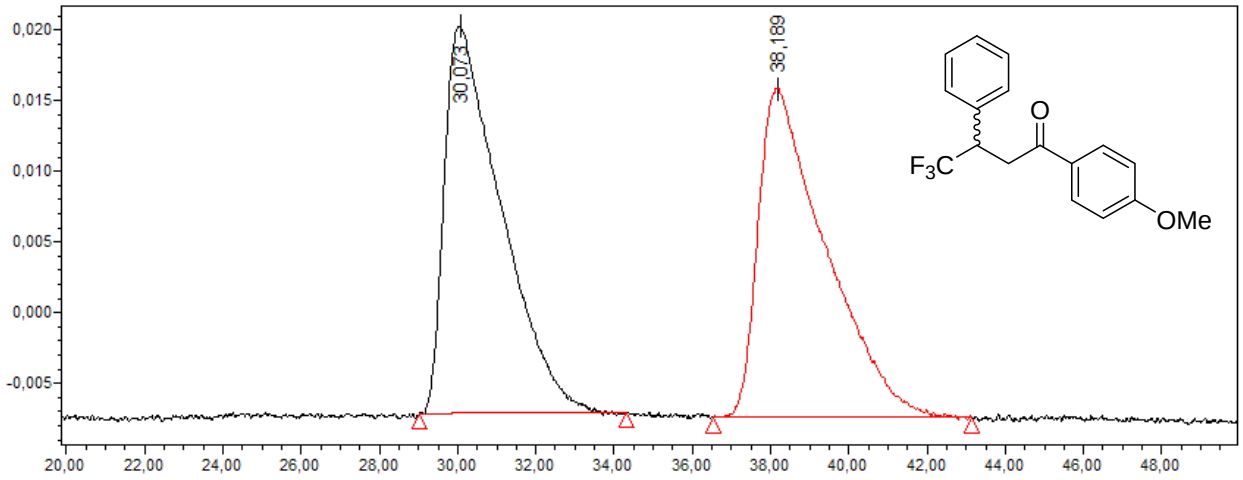


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		19,238							2246691	50,21	37723
2		22,619							2227672	49,79	31790

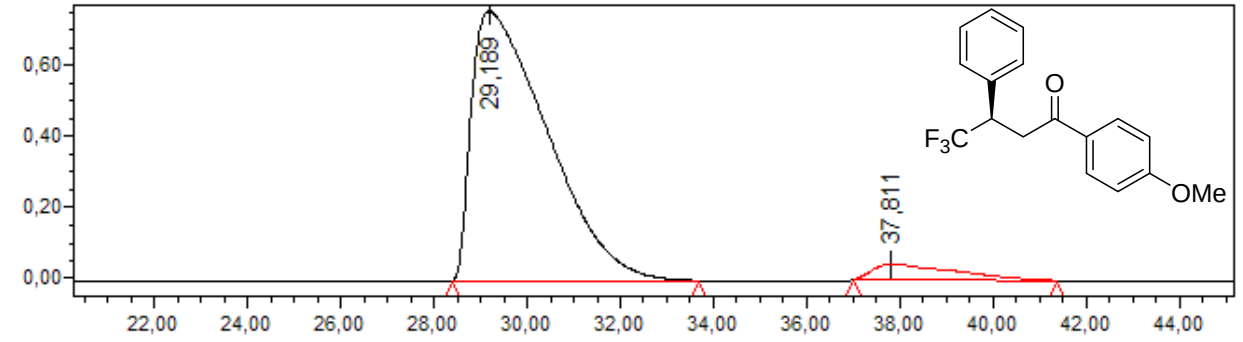


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		19,811							25495604	95,90	390483
2		23,512							1089693	4,10	19052

4,4,4-Trifluoro-3-phenyl-1-(4'-Methoxyphenyl)-butanone (2e)

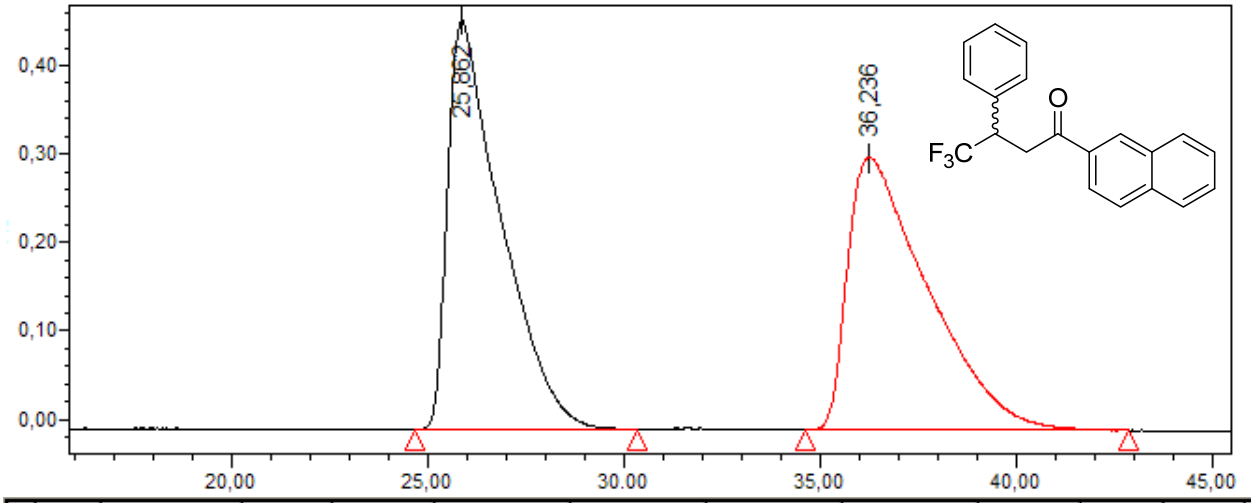


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		30,073							2764878	49,84	27374
2		38,189							2782618	50,16	23240

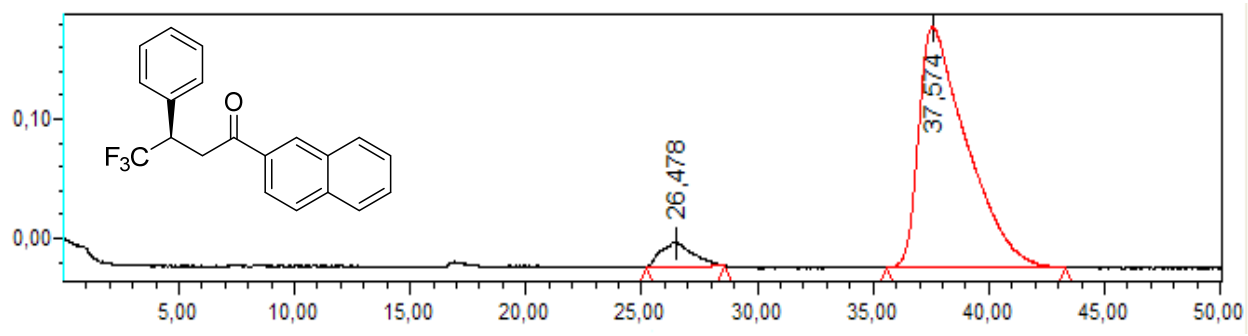


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		29,189							86011391	93,98	759426
2		37,811							5512429	6,02	45279

4,4,4-Trifluoro-1-(naphthalen-2-yl)-3-phenylbutan-1-one (2f)

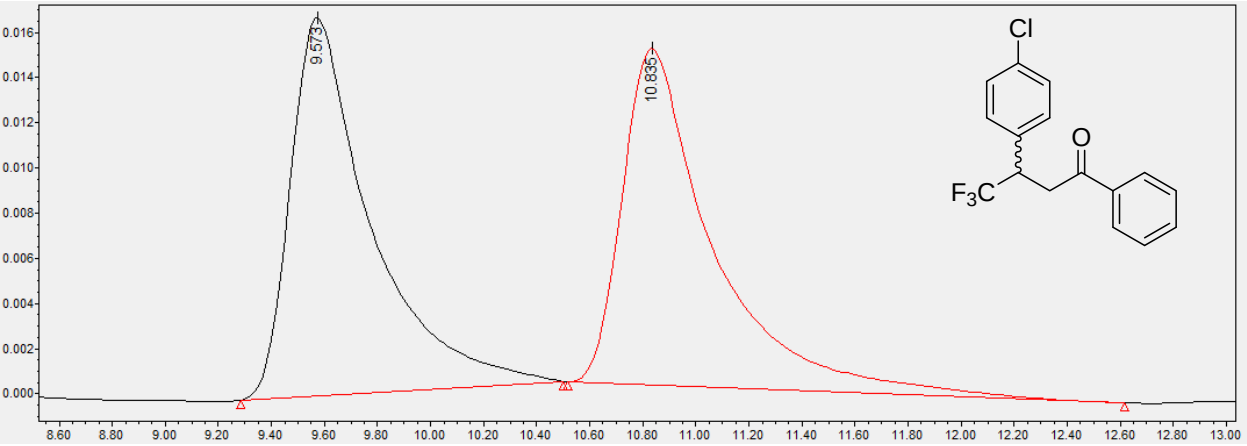


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		25,862							43727265	49,91	462574
2		36,236							43883741	50,09	308081

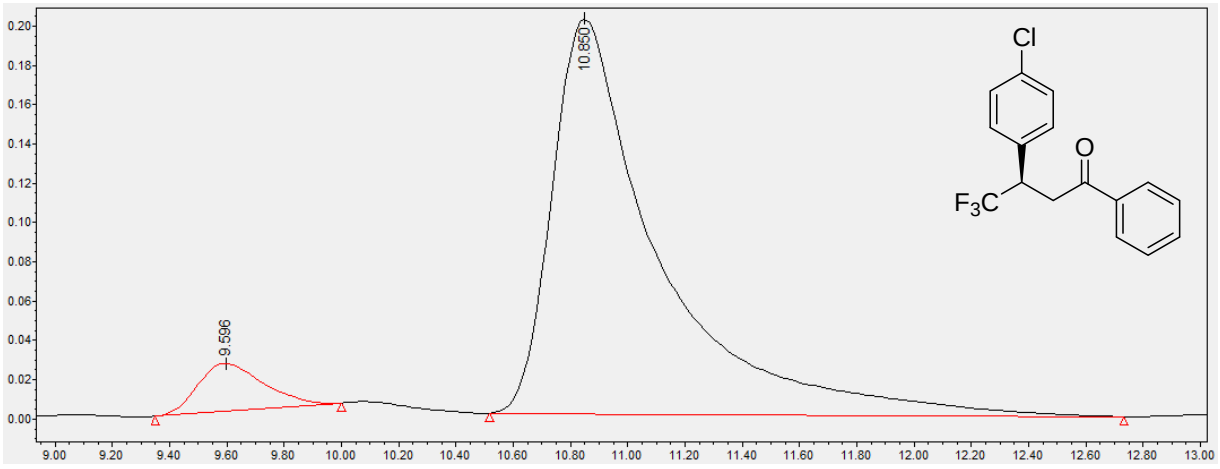


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		26,478							1966660	6,31	20287
2		37,574							29217943	93,69	202635

3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbutan-1-one (2j)

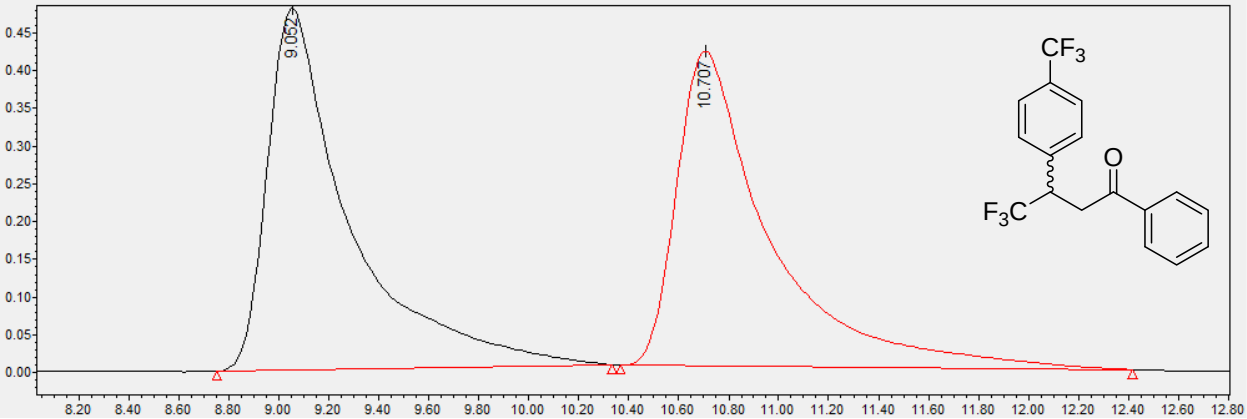


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		9.573	352100	50.04	16734	bb			Unknown
2		10.835	351564	49.96	14891	bb			Unknown

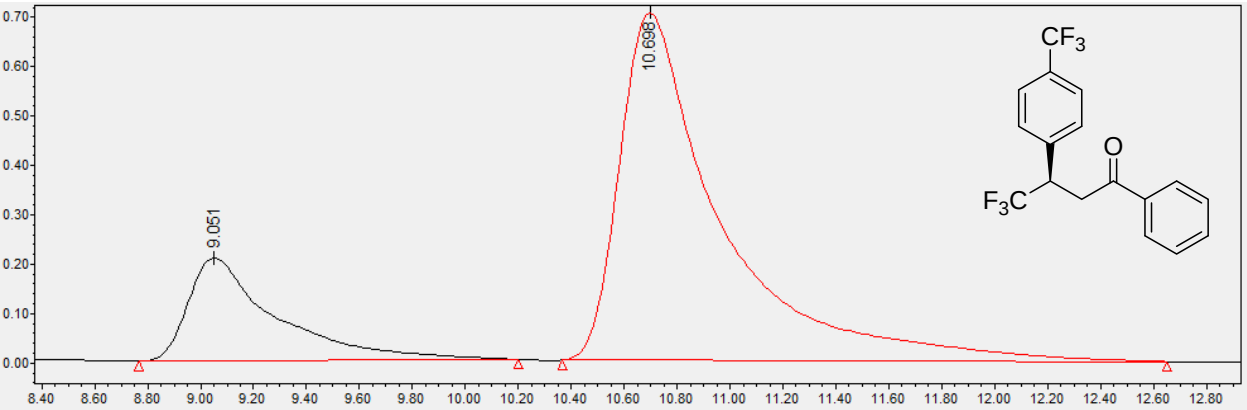


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		9.596	384908	6.91	24382	bb			Unknown
2		10.850	5187172	93.09	200977	bb			Unknown

4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)butan-1-one (2k)

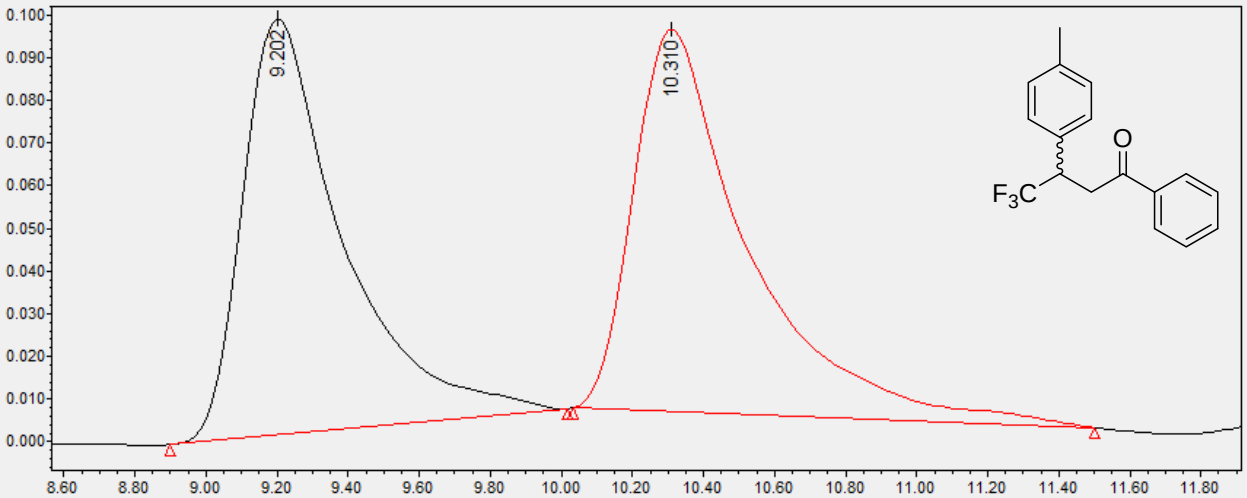


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		9.052	10944738	50.37	479169	bb			Unknown
2		10.707	10785772	49.63	417439	bb			Unknown

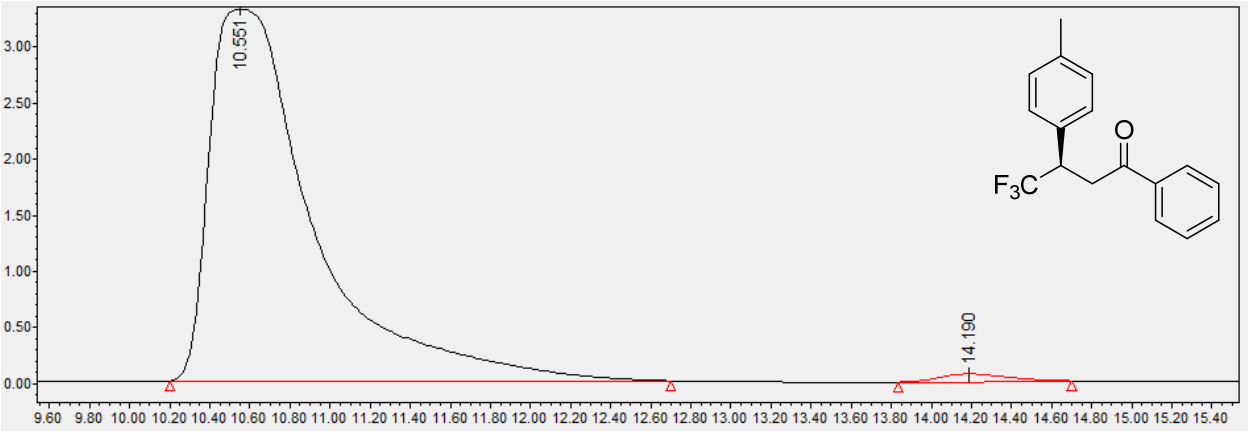


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		9.051	4799907	20.45	209272	bb			Unknown
2		10.698	18675448	79.55	703623	bb			Unknown

4,4,4-trifluoro-1-phenyl-3-(p-tolyl)butan-1-one (2l)

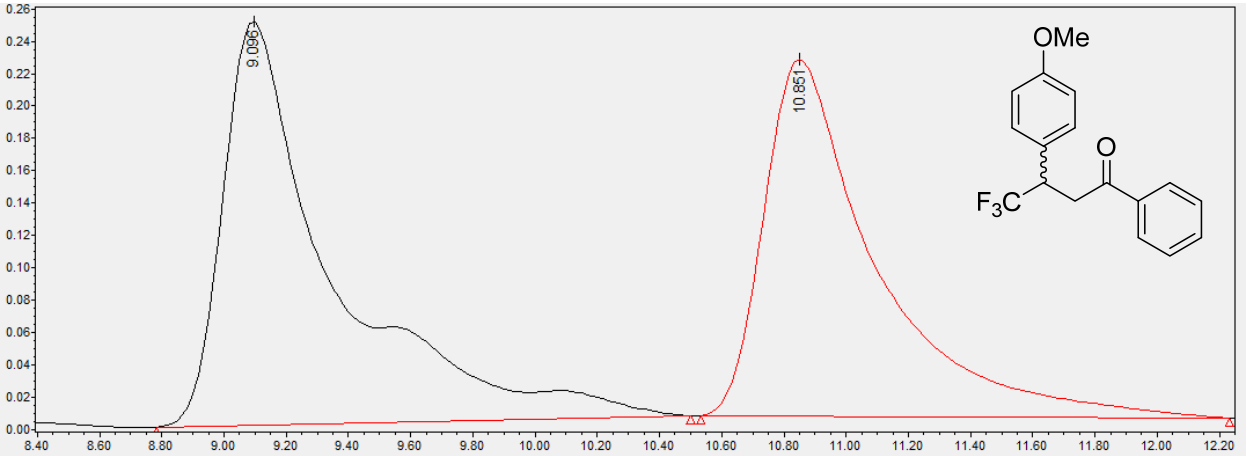


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		9.202	1915264	48.74	97712	bb			Unknown
2		10.310	2013934	51.26	89660	bb			Unknown

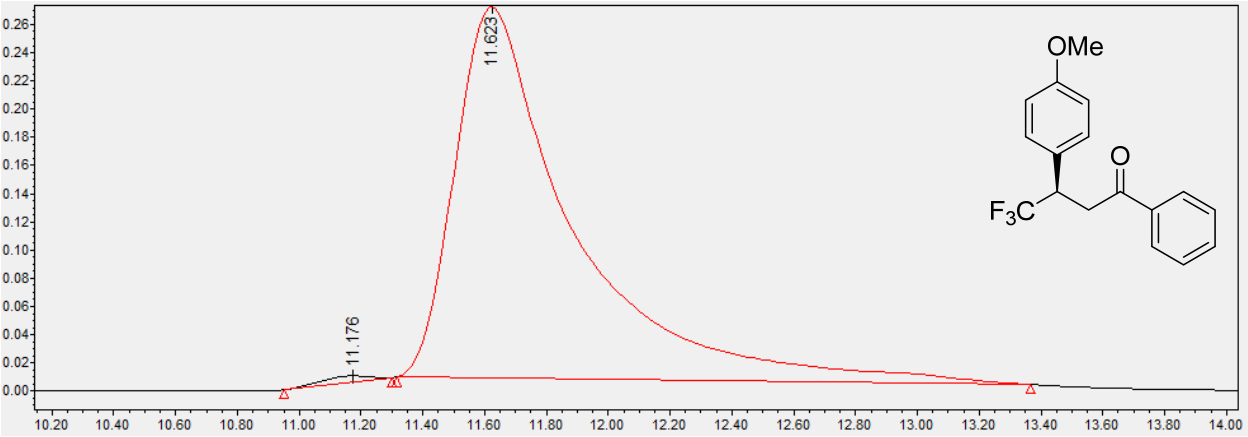


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		10.551	119774038	98.70	3315595	bb			Unknown
2		14.190	1578987	1.30	68413	bb			Unknown

4,4,4-trifluoro-3-(4-methoxyphenyl)-1-phenylbutan-1-one (2m)

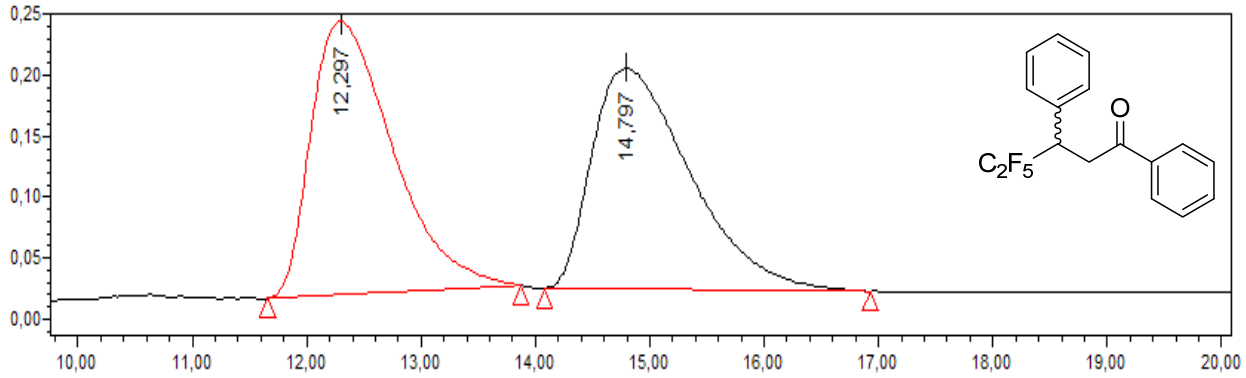


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		9.096	6140148	52.70	249546	bb			Unknown
2		10.851	5511968	47.30	220597	bb			Unknown

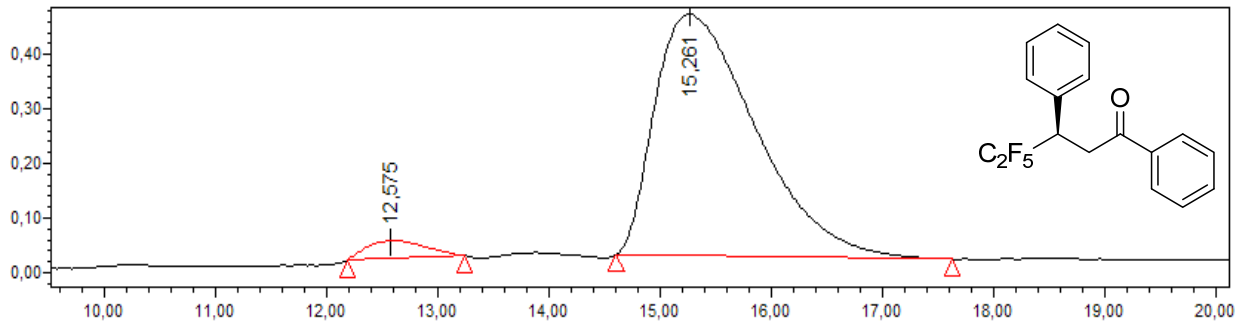


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		11.176	50807	0.72	4498	bb			Unknown
2		11.623	6995684	99.28	263336	bb			Unknown

4,4,5,5,5-Pentafluoro-1,3-diphenylpentan-1-one (2p)

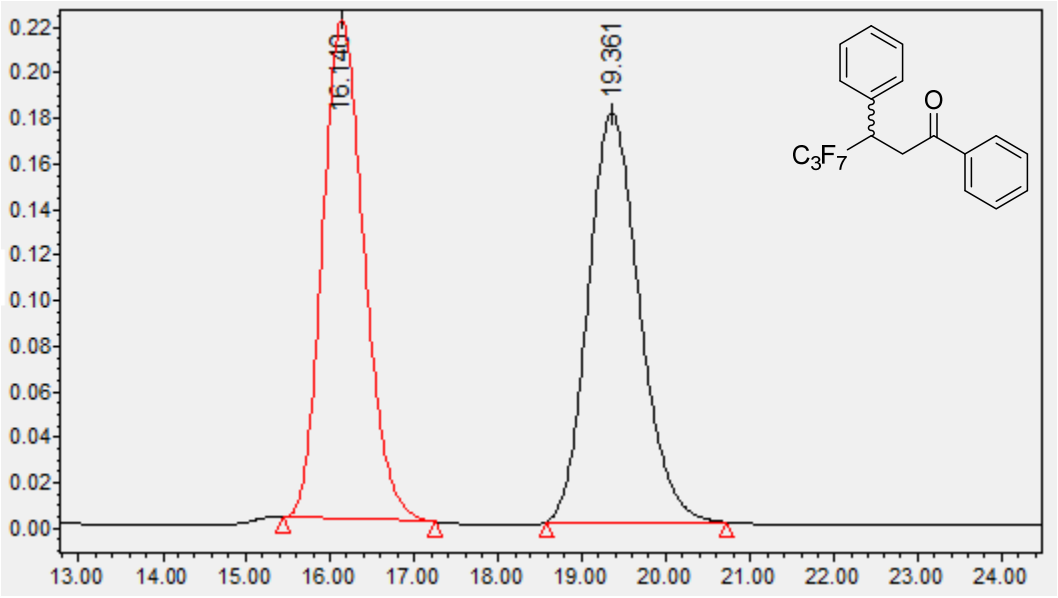


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		12,297							11157215	50,87	224049
2		14,797							10777147	49,13	181082

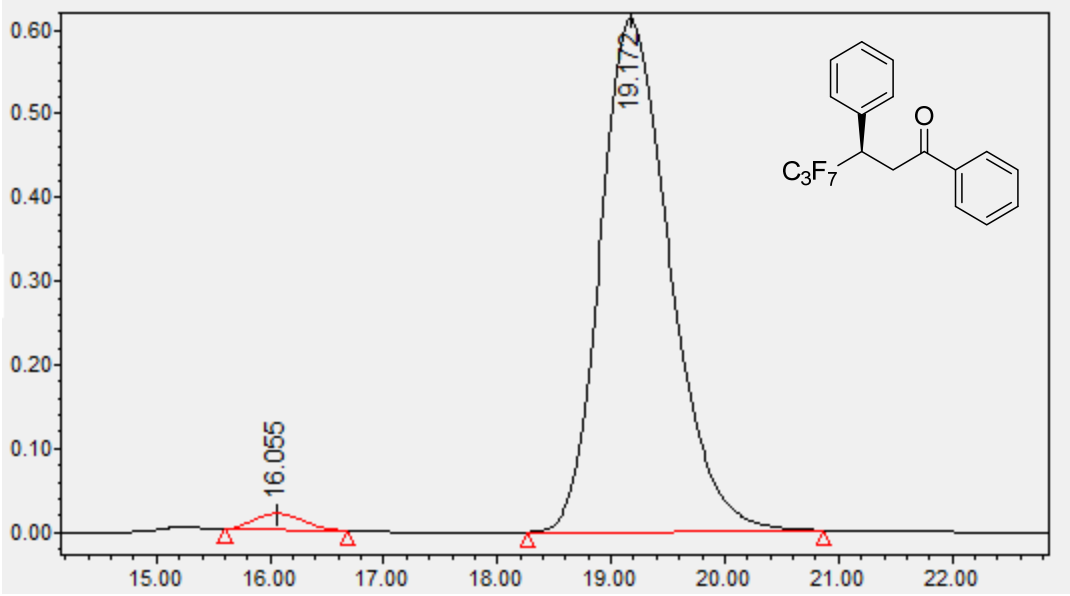


	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		12,575							1152106	3,97	31242
2		15,261							27898773	96,03	443430

4,4,5,5,6,6,6-Heptafluoro-1,3-diphenylhexan-1-one (2q)

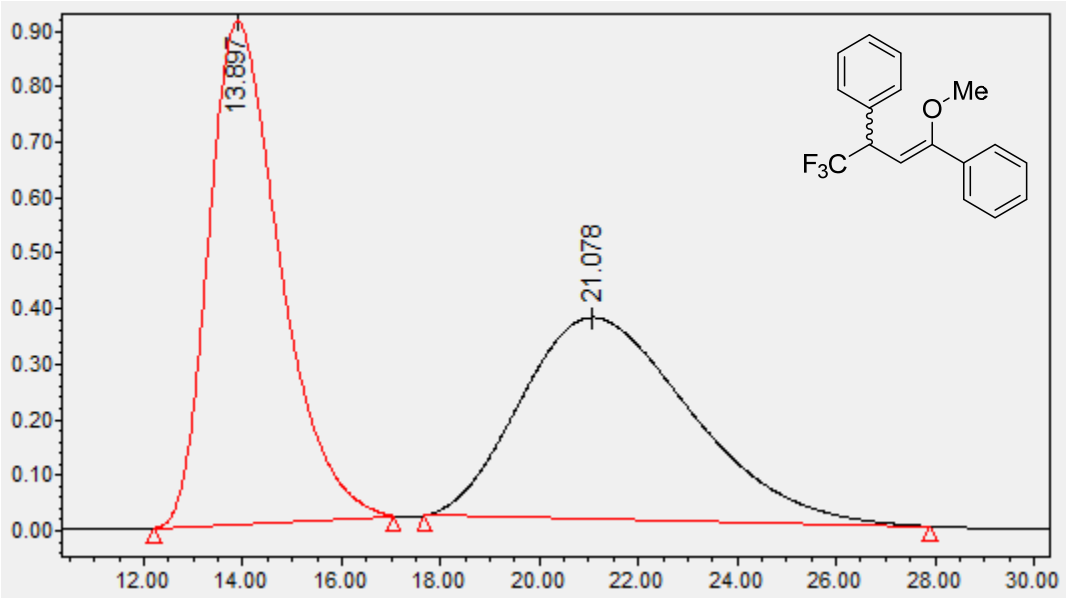


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.140	7541797	49.90	219653	bb			Unknown	
2		19.361	7570574	50.10	179601	bb			Unknown	

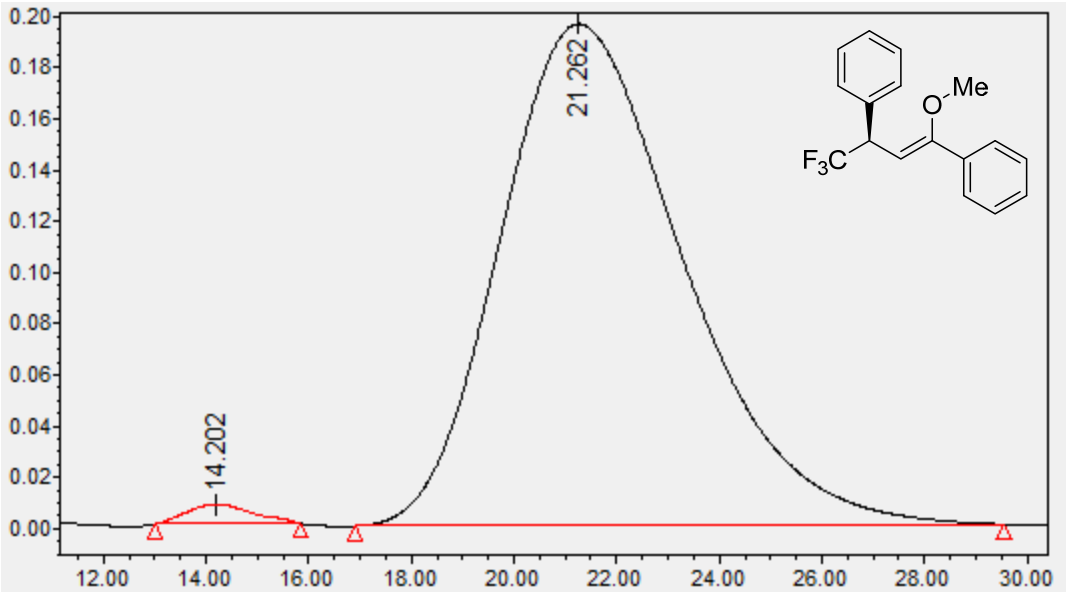


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.055	593620	2.23	19541	bb			Unknown	
2		19.172	26048149	97.77	613926	bb			Unknown	

(*Z*)-(4,4,4-Trifluoro-1-methoxybut-1-ene-1,3-diyl)dibenzene (4a)

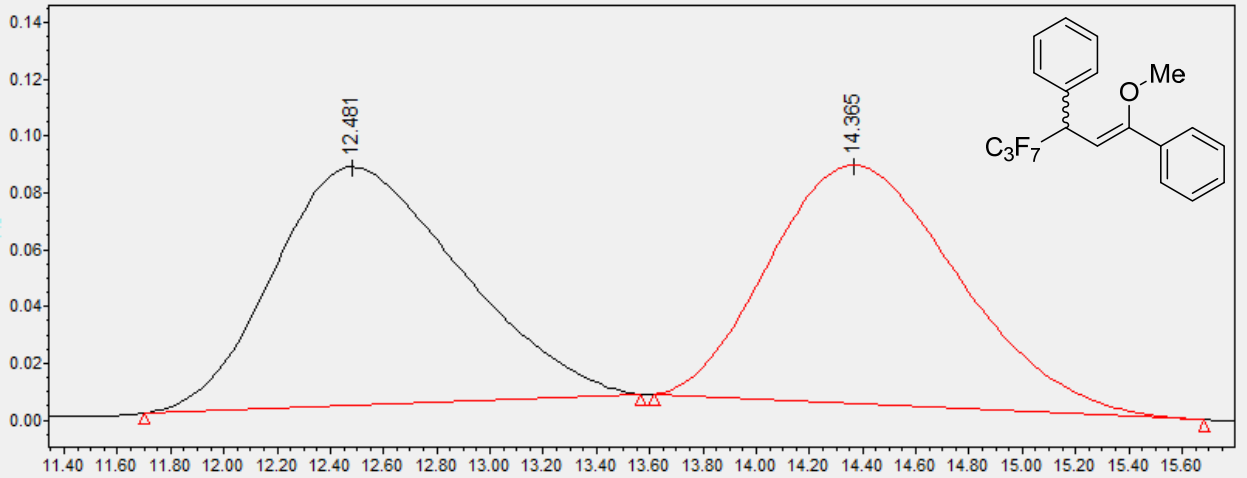


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		13.897	90937823	51.10	905731	bb			Unknown	
2		21.078	87019410	48.90	363531	bb			Unknown	

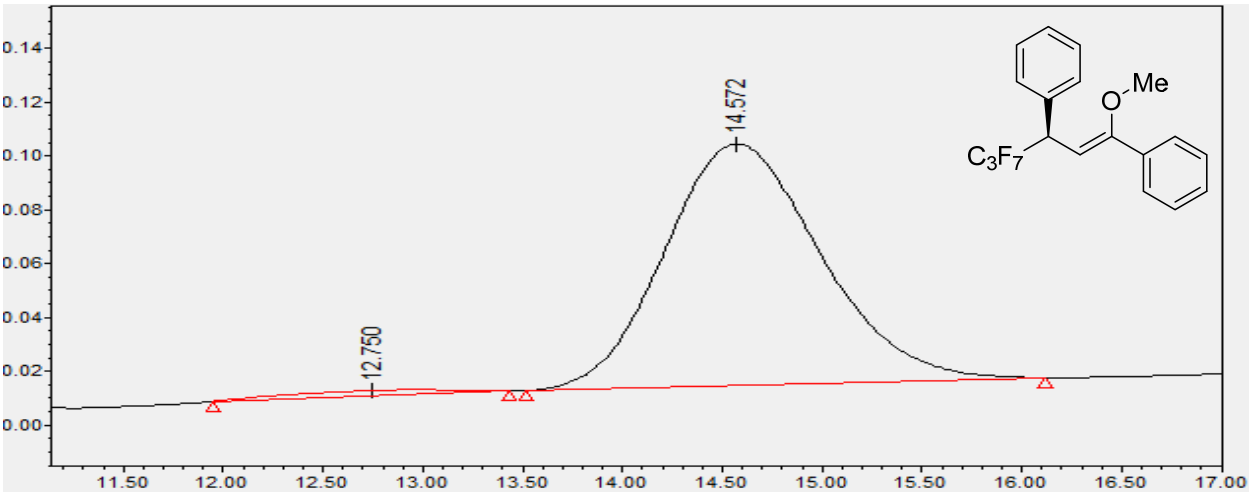


E	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		14.202	675595	1.37	7543	bb			Unknown	
2		21.262	48568763	98.63	195910	bb			Unknown	

(*Z*)-(4,4,5,5,6,6,6-heptafluoro-1-methoxyhex-1-ene-1,3-diyl)dibenzene (4b)

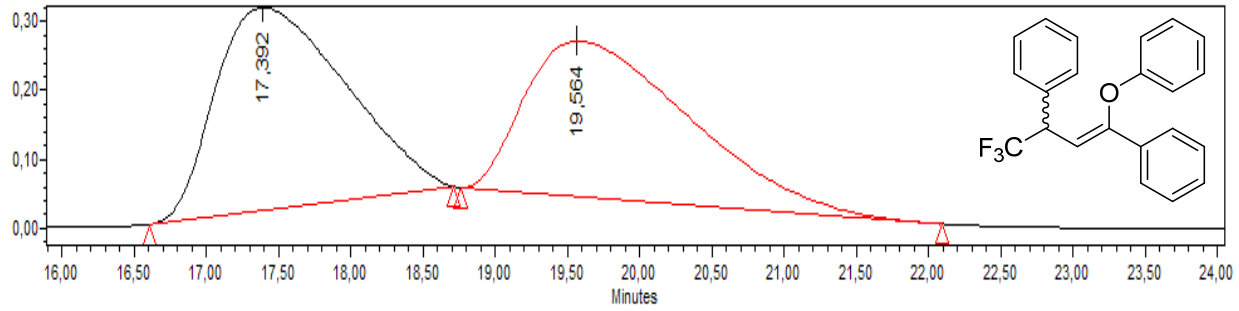


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		12.481	4082250	49.75	83816	bb			Unknown
2		14.365	4123049	50.25	83681	bb			Unknown

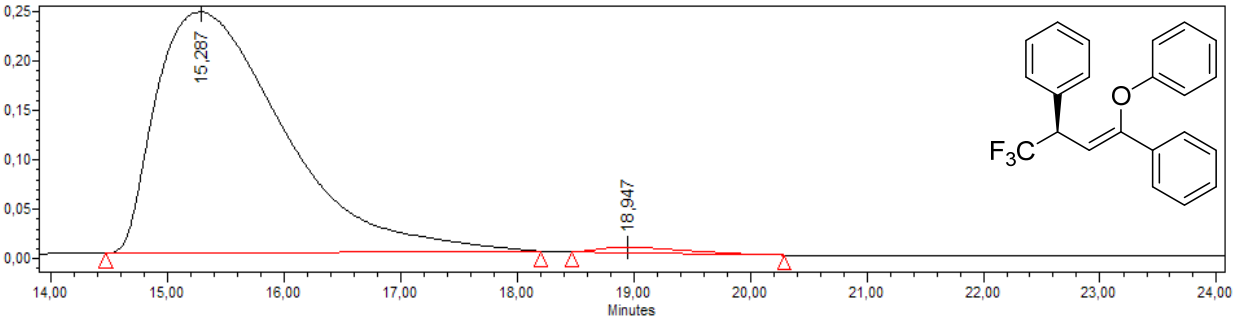


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type
1		12.750	111451	2.24	1956	bb			Unknown
2		14.572	4858689	97.76	89665	bb			Unknown

(*Z*)-(4,4,4-trifluoro-1-phenoxybut-1-ene-1,3-diyl)dibenzene (4c)



	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		17,392							18232629	50,54	293709
2		19,564							17842097	49,46	225076



	Name	Retention Time (min)	Purity1 Angle	Purity1 Threshold	PDA Match1 Spect. Name	PDA Match1 Angle	PDA Match1 Threshold	PDA Match1 Lib. Name	Area (µV*sec)	% Area	Height (µV)
1		15,287							18579654	98,45	243755
2		18,947							293027	1,55	5996