# Supplementary Information

# Palladium-catalyzed Asymmetric Carbofluorination of *gem*-Difluorostyrenes with Cesium Fluoride and Allylic Acetates

Eryn Nelson, Rajesh K. Bisoyi, and Christian Wolf *

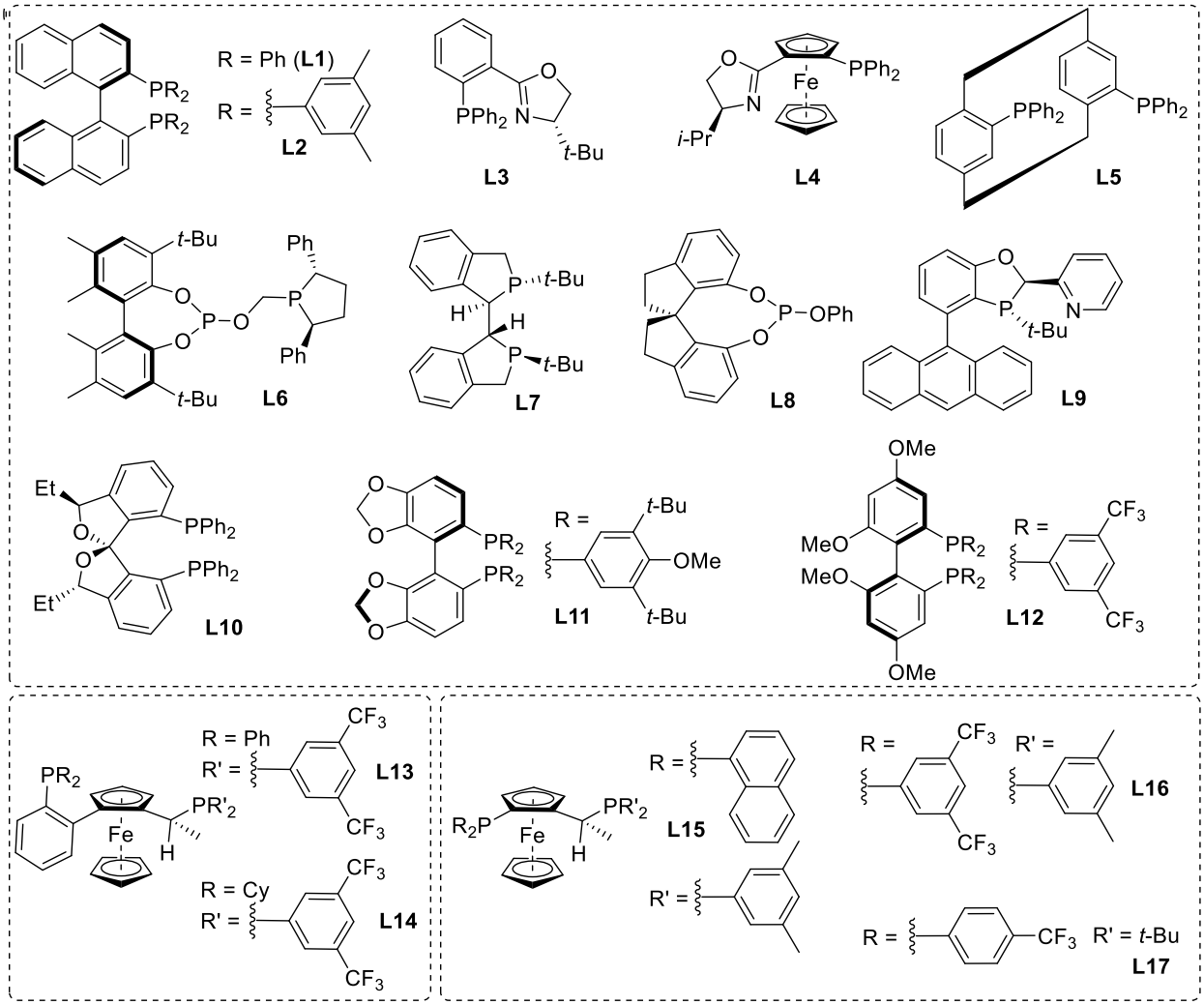
Department of Chemistry, Georgetown University, 37th and O St., Washington DC 20057, USA.
Email: cw27@georgetown.edu

**Contents** **Page**

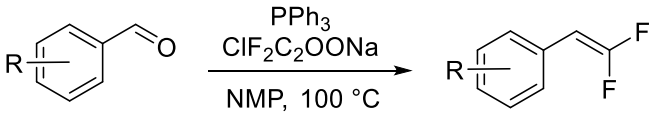
## 1. General information

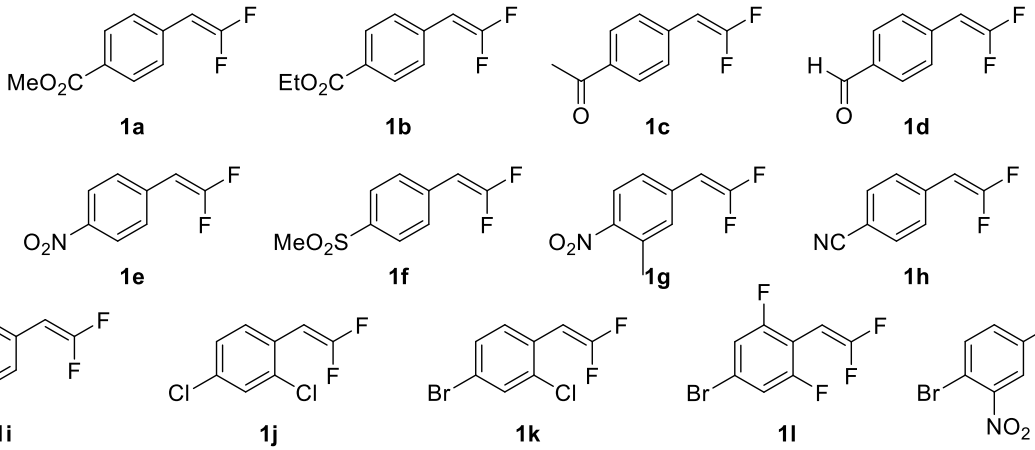
Commercially available ligands, catalysts, (*E*)-1,3-diphenylallyl acetate, cesium fluoride, 18-crown-6, reagents and solvents were used as purchased without further purification. *Gem*-difluoroalkenes[1,2] and (*E*)-1,3-diarylallyl acetates[3,4] were synthesized by following literature procedures. NMR spectra were obtained at 400 MHz ($^{1}$H NMR), 376 MHz ($^{19}$F NMR), and 100 MHz ($^{13}$C NMR) in deuterated chloroform. Reaction products were purified by column chromatography on silica gel as described below. All reactions were carried out under nitrogen atmosphere unless otherwise noted. HPLC enantioseparations using Chiralpak AD-H were performed at room temperature with a flow rate of 1.0 mL/min using hexanes:IPA mixtures.

Ligands used in this study (**L1**-**L17**):



## 2. Synthesis of *gem*-difluoroalkenes

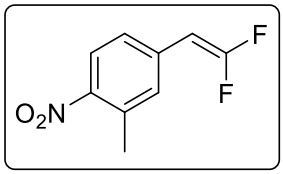


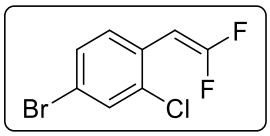

**Method I (1a-d, 1i-l):** The aldehyde (2.5 mmol) and $PPh_3$ (5.0 mmol) were dissolved in 4 mL NMP and heated to 100 °C. Sodium chlorodifluoroacetate (5.0 mmol) was added and the reaction was stirred for 15 minutes at 100 °C. The solution was cooled to room temperature, quenched with water, and extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with 1.5 mL 30% $H_2O_2$ followed by brine, then dried over $Na_2SO_4$ and purified by silica gel chromatography using EtOAc:hexanes as the eluent.

**Method II (1e-g, 1m):** The aldehyde (2.5 mmol) and $PPh_3$ (2.5 mmol) were dissolved in 4 mL NMP and heated to 100 °C. Sodium chlorodifluoroacetate (2.5 mmol) was added and the reaction was stirred for 15 minutes at 100 °C. The solution was cooled to room temperature, quenched with water, and extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with 1.5 mL 30% $H_2O_2$ followed by brine, then dried over $Na_2SO_4$ and purified by silica gel chromatography using EtOAc:hexanes as the eluent.

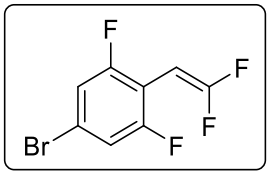
NMR spectra of **1a-f** and **1h-j** were in agreement with literature reports.[1,2]



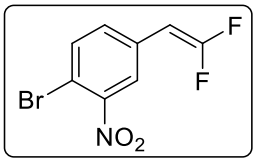

**4-(2,2-Difluorovinyl)-2-methyl-1-nitrobenzene (1g).** Compound **1g** was obtained as a colorless oil in 25% yield (125 mg, 0.63 mmol) using Method II. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.21 (m, 2H), 5.30 (dd, *J* = 25.6, 3.4 Hz, 1H), 2.58 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.0 (dd, $J_{C-F}$ = 301.3, 292.2 Hz), 147.3, 135.7 (dd, $J_{C-F}$ = 7.6, 6.4 Hz), 134.3, 131.6 (dd, $J_{C-F}$ = 6.5, 3.8 Hz), 125.7 (dd, $J_{C-F}$ = 7.3, 3.4 Hz), 125.3, 81.4 (dd, $J_{C-F}$ = 30.5, 12.9 Hz), 20.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -78.05 (dd, *J* = 25.5, 20.3 Hz), -79.48 (dd, *J* = 20.5, 3.7 Hz). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_9H_7F_2NO2$ 200.0518, found 200.0517.




**4-Bromo-2-chloro-1-(2,2-difluorovinyl)benzene (1k)**. Compound **1k** was obtained as a colorless oil in 61% yield (390 mg, 1.5 mmol) using Method I. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 0.7 Hz, 1H), 7.40 – 7.30 (m, 2H), 5.61 (dd, *J* = 21.8, 3.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.7 (dd, $J_{C-F}$ = 299.4, 289.9 Hz), 133.5 (dd, $J_{C-F}$ = 5.5, 2.1 Hz), 132.2, 130.2, 129.7 (dd, $J_{C-F}$ = 10.2, 1.6 Hz), 127.6 (dd, $J_{C-F}$ = 7.8, 6.2 Hz), 121.0 (dd, $J_{C-F}$ = 2.1, 2.1 Hz), 78.4 (dd, $J_{C-F}$ = 33.5, 12.2 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -80.33 (dd, *J* = 23.8, 3.5 Hz), -81.19 (dd, *J* = 24.6, 24.6 Hz). Attempts to obtain elemental analysis and HRMS data were unsuccessful due to the high volatility of this compound.



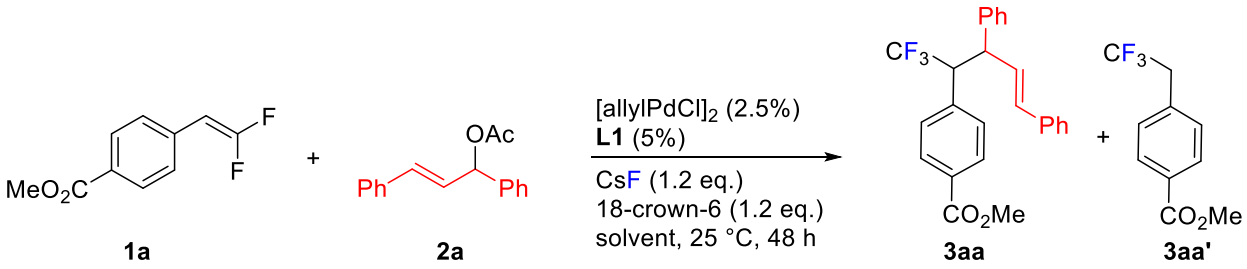

**5-Bromo-2-(2,2-difluorovinyl)-1,3-difluorobenzene (1l).** Compound **1l** was obtained as a colorless oil in 56% yield (363 mg, 1.4 mmol) using Method I. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.03 (m, 2H), 5.14 (dd, $J$ = 25.9, 2.1 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 161.1 (ddt, $J_{C\text{-}F}$ = 254.9, 8.6, 1.6 Hz), 157.8 (ddt, $J_{C\text{-}F}$ = 290.0, 289.4, 1.6 Hz), 121.2 (dd, $J_{C\text{-}F}$ = 12.3 Hz), 115.3 (td, $J_{C\text{-}F}$ = 29.4, 25.1, 12.9 Hz), 106.9 (tdd, $J_{C\text{-}F}$ = 19.3, 8.1, 4.1 Hz), 68.9 (ddt, $J_{C\text{-}F}$ = 37.5, 18.3, 2.4 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -75.78 (dddd, $J$ = 24.7, 24.7, 16.2, 16.2 Hz), -80.48 (dddd, $J$ = 16.2, 16.2, 3.3, 3.3 Hz), -109.15 (ddd, $J$ = 24.2, 10.8, 2.9 Hz). Attempts to obtain elemental analysis and HRMS data were unsuccessful due to the high volatility of this compound.




**1-Bromo-4-(2,2-difluorovinyl)-2-nitrobenzene (1m)**. Compound **1m** was obtained as a yellow solid in 24% yield (311 mg, 1.18 mmol) using Method II. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, $J$ = 2.2 Hz, 1H), 7.68 (d, $J$ = 8.4 Hz, 1H), 7.36 (dd, $J$ = 8.4, 2.2 Hz, 1H), 5.30 (dd, $J$ = 25.0, 3.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.0 (dd, $J$ = 300.4, 292.5 Hz), 150.1, 135.3, 131.7 (dd, $J$ = 6.8, 3.5 Hz), 131.3 (dd, $J$ = 7.7, 6.1 Hz), 124.2 (dd, $J$ = 6.9, 3.8 Hz), 112.4 (dd, $J$ = 2.6, 2.6 Hz), 80.6 (dd, $J$ = 31.5, 13.2 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -77.91 (dd, $J$ = 25.1, 21.7 Hz), -79.58 (dd, $J$ = 21.5, 3.0 Hz). EA Found: C, 36.8; H, 1.7; N, 5.2. $C_8H_4BrF_2NO_2$ requires C, 36.4; H, 1.5; N, 5.3%.

## 3. Reaction optimization

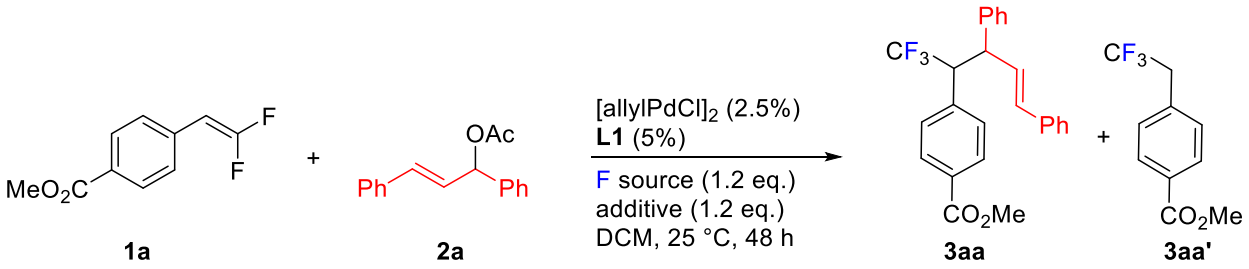
### 3.1. Solvent screening[a]




| Entry | Solvent | Conversion[b] | 3aa : 3aa'[c] | *dr*[d] | *ee* (major)[e] |
|---|---|---|---|---|---|
| 1 | DCM | 83% | 11 : 1 | 1 : 3.6 | 87% |
| 2 | ACN | 100% | 5 : 1 | 1 : 2.6 | 92% |
| 3 | acetone | 100% | 2 : 1 | 1 : 2.8 | 87% |
| 4 | TBME | 55% | 4 : 1 | 1 : 3.0 | 87% |
| 5 | EtOAc | 100% | 6 : 1 | 1 : 2.8 | 85% |
| 6 | PhCN | 100% | 1 : 1 | 1: 2.9 | n.d. |
| 7 | dioxane | 83% | 3 : 1 | 1 : 1.7 | n.d. |
| 8 | toluene | 85% | 3 : 1 | 1 : 2.9 | n.d. |
| 9 | DMF | 100% | 4 : 1 | 1 : 2.3 | n.d. |

[a] Reaction conditions: **L1** (5 mol%), $[allylPdCl]_2$ (2.5 mol%), **1a** (0.15 mmol), **2a** (0.3 mmol), CsF (0.18 mmol), and 18-crown-6 (0.18 mmol) in 1.0 mL of solvent at 25 °C. [b] Conversion of **1a** determined by $^{19}F$ NMR spectroscopy of the crude reaction mixture. [c] Determined by $^{19}F$ NMR spectroscopy of the crude reaction mixture. [d] Determined by $^{19}F$ NMR spectroscopy of the crude reaction mixture. [e] Determined by Chiral HPLC using Chiralpak AD-H. n.d. = not determined.

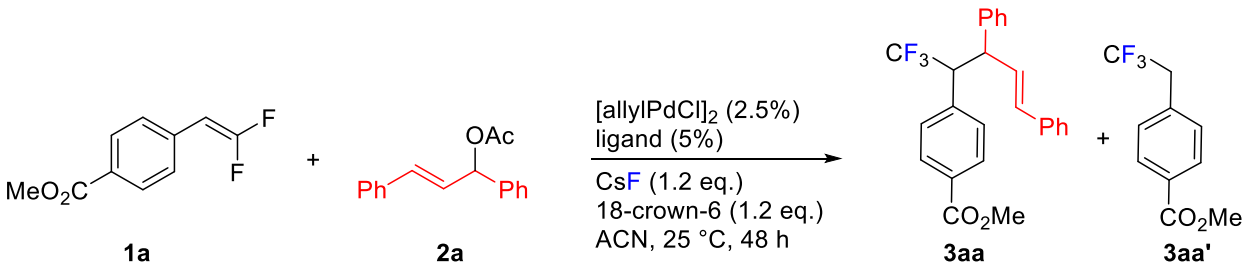
### 3.2. Fluoride source and additives screening[a]




| Entry | Fluoride source | additive | Conversion[b] | 3aa : 3aa'[c] | *dr*[d] | *ee* (major)[e] |
|---|---|---|---|---|---|---|
| 1 | CsF | none | 20% | 21 : 1 | 1 : 3.5 | 83% |
| 2 | CsF | 18-crown-6 | 83% | 11 : 1 | 1 : 3.6 | 87% |
| 3[f] | CsF | 18-crown-6 | n.r. | - | - | - |
| 4 | AgF | 18-crown-6 | n.r. | - | - | - |
| 5 | KF | 18-crown-6 | 64% | 1 : 3.5 | 1 : 3.6 | n.d. |
| 6 | $TBAF_2Ph_3Sn$ | none | n.r. | - | - | - |

[a] Reaction conditions: **L1** (5 mol%), $[allylPdCl]_2$ (2.5 mol%), **1a** (0.15 mmol), **2a** (0.3 mmol), fluoride source (0.18 mmol), and aditive (0.18 mmol) in 1.0 mL of $CH_2Cl_2$ at 25 °C. [b] Conversion of **1a** determined by $^{19}F$ NMR spectroscopy of the crude reaction mixture. [c] Determined by $^{19}F$ NMR spectroscopy of the crude reaction mixture. [d] Determined by $^{19}F$ NMR spectroscopy of the crude reaction mixture. [e] Determined by Chiral HPLC using Chiralpak AD-H. [f] Reaciton was run without $[allylPdCl]_2$. n.r. = no reaction. n.d. = not determined.

### 3.3. Ligand screening[a]

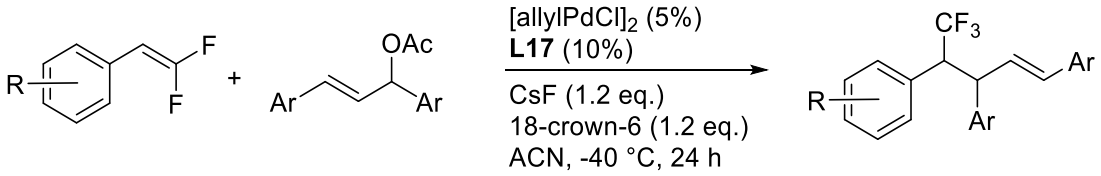



**1a** **2a** **3aa** **3aa'**

| Entry | Ligand | Conversion[b] | 3aa : 3aa'[c] | *dr*[d] | *ee* (major)[e] |
|---|---|---|---|---|---|
| 1 | **L1** | 100% | 5 : 1 | 1 : 2.6 | 92% |
| 2 | **L2** | 100% | 2 : 1 | 1 : 4.9 | n.d. |
| 3[f] | **L3** | 67% | 2 : 1 | 1 : 1.8 | >99% |
| 4[f] | **L4** | 66% | 3 : 1 | 1 : 2.2 | 95% |
| 5 | **L5** | 100% | 3 : 1 | 1 : 2.0 | n.d. |
| 6 | **L6** | 100% | 1 : 1 | 1 : 2.9 | n.d. |
| 7 | **L7** | 77% | 1 : 1 | 1 : 1.5 | n.d. |
| 8 | **L8** | 89% | 1 : 3 | 1 : 2.7 | n.d. |
| 9 | **L9** | 89% | 1 : 1 | 1 : 2.6 | n.d. |
| 10 | **L10** | 100% | 3 : 1 | 1:3.4 | n.d. |
| 11[g] | **L11** | 100% | 10 : 1 | 1 : 3 | n.d. |
| 12 | **L12** | 100% | 5 : 1 | 1 : 2.7 | n.d. |
| 13[h] | **L13** | 100% | 12 : 1 | 1 : 4.4 | 80% |
| 14[h] | **L14** | 100% | 6 : 1 | 1 : 1.5 | n.d. |
| 15[h] | **L15** | 79% | 1 : 1 | 1 : 3.0 | n.d. |
| 16[h] | **L16** | 100% | 1 : 7 | 1 : 3.7 | n.d. |
| 17[h] | **L17** | 100% | 24:1 | 1 : 3.5 | n.d. |
| 18[g,h] | **L17** | 100% | 16:1 | 1:4.3 | 91% |

[a] Reaction conditions: ligand (5 mol%), [allylPdCl]$_2$ (2.5 mol%), **1a** (0.15 mmol), **2a** (0.3 mmol), CsF (0.18 mmol), and 18-crown-6 (0.18 mmol) in 1.0 mL of acetonitrile at 25 °C. [b] Conversion of **1a** determined by $^{19}$F NMR spectroscopy of the crude reaction mixture. [c] Determined by $^{19}$F NMR spectroscopy of the crude reaction mixture. [d] Determined by $^{19}$F NMR spectroscopy of the crude reaction mixture. [e] Determined by Chiral HPLC using Chiralpak AD-H. [f] Reaction was run in 1.0 mL dichloromethane. [g] Reaction was run at -40 °C. [h] Reaction was run for 24 h. n.d. = not determined.

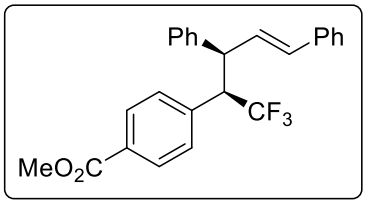
## 4. Product synthesis and characterization



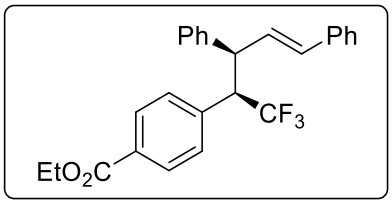

**Method A:** In an 8 mL vial under nitrogen atmosphere, [allylPdCl]$_2$ (5 mol%, 1.4 mg), ligand (10 mol%, 5.1 mg), CsF (0.09 mmol, 14 mg), and 18-crown-6 (0.09 mmol, 24 mg) were dissolved in 300.0 µL ACN and stirred for 5 minutes. Allylic acetate (0.09 mmol) was dissolved in 50.0 µL ACN then added to the reaction mixture. The solution was stirred for 5 minutes and then cooled to -40 °C. A solution of difluoroalkene (0.075 mmol) in 150.0 µL ACN was added at -40 °C and the reaction was stirred overnight. After 24 hours, the crude reaction mixture was purified via flash chromatography on silica gel using EtOAc:hexanes as the eluent.

**Method B:** In an 8 mL vial under nitrogen atmosphere, [allylPdCl]$_2$ (5 mol%, 1.4 mg), ligand (10 mol%, 5.1 mg), CsF (0.09 mmol, 14 mg), and 18-crown-6 (0.09 mmol, 24 mg) were dissolved in 300.0 µL ACN and stirred for 5 minutes. Allylic acetate (0.188 mmol) was dissolved in 50.0 µL ACN and then added to the reaction mixture. The solution was stirred for 5 minutes then cooled

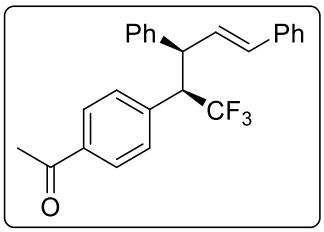
to -40 °C. A solution of difluoroalkene (0.075 mmol) in 150.0 µL ACN was added slowly at -40 °C (10.0 µL every 30 min.) and the reaction was stirred overnight. After 24 hours the crude reaction mixture was purified via flash chromatography on silica gel using EtOAc:hexanes as the eluent.




**Methyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3aa).** Compound **3aa** was obtained as a colorless oil in 79% yield (57.8 mg, 0.14 mmol) using Method A. The *dr* was determined to be 1:4 by $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer 91% *ee*, $t_R$ (major) = 10.2 min., $t_R$ (minor) = 12.2 min.; minor diastereomer 94% *ee*, $t_R$ (major) = 18.1 min., $t_R$ (minor) = 20.2 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J$ = 8.3 Hz, 2H), 7.39 – 7.28 (m, 5H), 7.24 – 7.19 (m, 5H), 7.14 – 7.11 (m, 2H), 6.28 (d, $J$ = 15.7 Hz, 1H), 6.08 (dd, $J$ = 15.7, 9.0 Hz, 1H), 4.19 (dd, $J$ = 8.5, 8.5 Hz, 1H), 3.90 (s, 3H), 3.82 (dq, $J$ = 8.8 Hz, 8.8 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.3, 143.9, 141.3, 139.5, 135.3, 132.5, 132.4, 131.5 (q, $J_{C-F}$ = 282.8 Hz), 131.4, 131.2, 131.1, 130.5, 130.2, 129.8, 128.9, 58.8 (q, $J_{C-F}$ = 25.1 Hz), 54.8, 52.0. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.29 (d, $J$ = 8.9 Hz, minor diastereomer), -64.42 (d, $J$ = 9.2 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{21}F_3O_2$ 411.1566, found 411.1571.

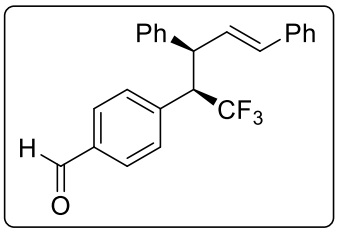



**Ethyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3ba).** Compound **3ba** was obtained as a colorless oil in 75% yield (24.6 mg, 0.058 mmol) using Method A. The *dr* was determined to be 1:5 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 92% *ee*, $t_R$ (major) = 8.5 min., $t_R$ (minor) = 11.5 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 15.1 min., $t_R$ (minor) = 16.1 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.38 – 7.25 (m, 5H), 7.23 – 7.18 (m, 4H), 7.16 – 7.10 (m, 3H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.08 (dd, *J* = 15.7, 8.9 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.18 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.82 (dq,, *J* = 9.0, 9.0 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.9, 141.1, 139.5, 135.3, 133.1, 132.5, 132.4, 131.4, 131.2, 131.1, 131.1 (q, $J_{C-F}$ = 280.5 Hz), 130.5, 130.2, 129.8, 128.9, 63.8, 58.8 (q, $J_{C-F}$ = 24.6 Hz), 52.0, 17.0. $^{19}$F NMR (376 MHz,CDCl) δ -63.34 (d, *J* = 9.0 Hz, minor diastereomer), -64.49 (d, *J* = 9.0 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{26}H_{23}F_3O_2$ 425.1723, found 425.1726.



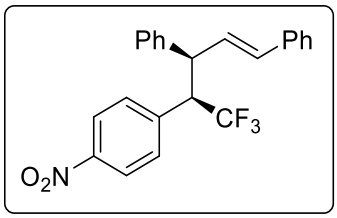

**(*E*)-1-(4-(1,1,1-Trifluoro-3,5-diphenylpent-4-en-2-yl)phenyl)ethan-1-one (3ca).** Compound **3ca** was obtained as a colorless oil in 64% yield (34 mg, 0.087 mmol) using Method A. The *dr* was determined to be 1:6 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC

(CHIRALPAK AD-H, Hexanes/IPA 98:2, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 93 % *ee*, $t_R$ (major) = 12.6 min., $t_R$ (minor) = 16.5 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 39.4 min., $t_R$ (minor) = 37.3 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.25 (m, 5H), 7.23 – 7.09 (m, 7H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.07 (dd, *J* = 15.7, 9.0 Hz, 1H), 4.18 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.83 (dq, *J* = 8.9, 8.9 Hz, 1H), 2.58 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.2, 143.9, 141.4, 139.5, 139.4, 135.4, 132.7, 131.4, 131.1, 130.7 (q, $J_{C-F}$ = 261.7 Hz), 130.5, 130.2, 128.9, 58.7 (q, $J_{C-F}$ = 24.9 Hz), 52.0, 29.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -64.44 (d, *J* = 9.1 Hz). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{21}F_3O$ 395.1617, found 395.1622.

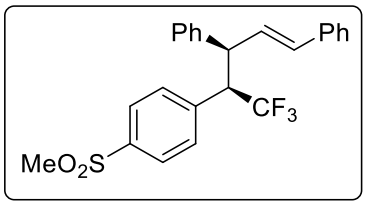



**(*E*)-4-(1,1,1-Trifluoro-3,5-diphenylpent-4-en-2-yl)benzaldehyde (3da).** Compound **3da** was obtained as a colorless oil in 53% yield (17 mg, 0.044 mmol) using Method B. The *dr* was determined to be 1:4 by $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1 to 98:2, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 94% *ee*, $t_R$ (major) = 21.5 min., $t_R$ (minor) = 26.6 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 115.3 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.25 – 7.17 (m, 5H), 7.13 – 7.08 (m, 2H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.06 (dd, *J* = 15.7, 9.0 Hz, 1H), 4.18 (dd, *J* = 8.6, 8.6 Hz, 1H), 3.85 (dq, *J* = 8.6, 8.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.3, 143.7, 143.0, 139.3, 138.8, 135.5, 133.1, 132.4, 131.5, 131.2, 131.1 (q, $J_{C-F}$ = 280.7 Hz), 131.0, 130.5, 130.3, 129.9, 128.8, 58.9 (q, $J_{C-F}$ = 25.6 Hz), 52.1. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.20 (d, *J* = 8.9 Hz, minor diastereomer), -64.31 (d, *J*

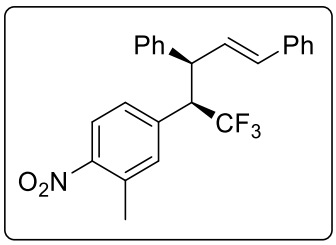
= 8.9 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{19}F_3O$ 381.1461, found 381.1462.




**(*E*)-(5,5,5-Trifluoro-4-(4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ea).** Compound **3ea** was obtained as a colorless oil in 67% yield (20 mg, 0.050 mmol) using Method B. The *dr* was determined to be 1:4 by crude $^{19}F$ NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 94% *ee*, $t_R$ (major) = 12.0 min., $t_R$ (minor) = 14.1 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 33.3 min., $t_R$ (minor) = 54.2 min. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.23 – 7.19 (m, 3H), 7.15 – 7.10 (m, 5H), 6.30 (d, *J* = 15.7 Hz, 1H), 6.04 (dd, *J* = 15.6, 9.2 Hz, 1H), 4.19 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.90 (dq, *J* = 8.5, 8.5 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 150.5, 143.5, 143.4, 139.1, 135.8, 133.4, 131.6, 131.2, 130.6 (q, $J_{C-F}$ = 280.9 Hz), 130.5, 130.4, 130.1, 129.1, 128.9, 126.3, 58.6 (q, $J_{C-F}$ = 25.1 Hz), 52.1. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.24 (d, *J* = 8.8 Hz, minor diastereomer), -64.35 (d, *J* = 8.8 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M-H]^-$ calcd for $C_{23}H_{18}F_{3N}O_2$ 396.1217, found 396.1207.

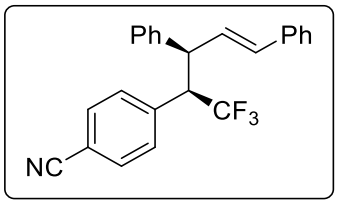



**(*E*)-(5,5,5-Trifluoro-4-(4-(methylsulfonyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3fa).** Compound **3fa** was obtained as a pale yellow oil in 74% yield (51 mg, 0.12 mmol) using Method B. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 95:5, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, >99% *ee*, $t_R$ (major) = 23.4 min., $t_R$ (minor) = 24.7 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 46.4 min., $t_R$ (minor) = 57.9 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J$ = 8.4 Hz, 2H), 7.47 (d, $J$ = 8.2 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.23 – 7.18 (m, 4H), 7.14 – 7.10 (m, 2H), 6.29 (d, $J$ = 15.7 Hz, 1H), 6.04 (dd, $J$ = 15.7, 9.1 Hz, 1H), 4.19 (dd, $J$ = 8.6, 8.6 Hz, 1H), 3.89 (dq, $J$ = 8.7, 8.7 Hz, 1H), 3.01 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.1, 142.5, 139.2, 135.8, 133.5, 131.5, 131.2, 130.9 (q, $J_{C\text{-}F}$ = 283.5 Hz), 130.5, 130.4, 130.2, 130.1, 130.0, 128.9, 58.8 (q, $J_{C\text{-}F}$ = 25.3 Hz), 52.0, 47.1. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.17 (d, $J$ = 8.8 Hz, minor diastereomer), -64.32 (d, $J$ = 9.0 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{21}F_3O_2S$ 431.1287, found 431.1290.



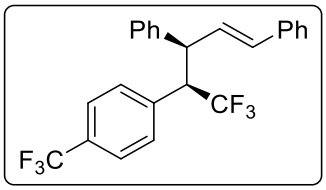

**(*E*)-(5,5,5-Trifluoro-4-(3-methyl-4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ga).** Compound **3ga** was obtained as a pale yellow oil in 71% yield (44 mg, 0.11 mmol) using Method B. The *dr* was determined to be 1:4 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by

HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 89% *ee*, $t_R$ (major) = 9.5 min., $t_R$ (minor) = 10.5 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 21.2 min., $t_R$ (minor) = 23.1 min. $^1$H NMR (400 MHz, CDCl3$_3$) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.17 (m, 7H), 7.17 – 7.12 (m, 2H), 6.31 (m, 1H), 6.06 (dd, *J* = 15.7, 9.0 Hz, 1H), 4.18 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.83 (dq, *J* = 8.9, 8.9 Hz, 1H), 2.59 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 143.6, 141.7, 139.3, 137.0, 136.6, 136.4, 135.7, 131.5, 131.2, 130.8, 130.7, 130.4, 130.3 (q, $J_{C\text{-}F}$ = 281.8 Hz), 130.0, 128.9, 127.6, 58.4 (q, $J_{C\text{-}F}$ = 25.2 Hz), 51.9, 23.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.22 (d, *J* = 8.9 Hz, minor diastereomer), -64.34 (d, *J* = 8.9 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{20}F_3NO_2$ 412.1519, found 412.1522.

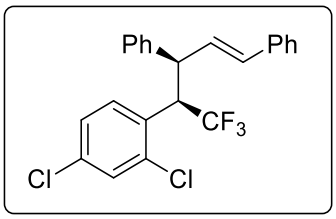



**(*E*)-4-(1,1,1-Trifluoro-3,5-diphenylpent-4-en-2-yl)benzonitrile (3ha).** Compound **3ha** (1414) was obtained as a colorless oil in 79% yield (32.5 mg, 0.086 mmol) using Method A. The *dr* was determined to be 1:4 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 88% *ee*, $t_R$ (major) = 18.5min., $t_R$ (minor) = 20.0 min.; minor diastereomer, > 99% *ee*, $t_R$ (major) = 55.7 min., $t_R$ (minor) = 57.5 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.25 (m, 6H), 7.23 – 7.09 (m, 6H), 6.28 (d, *J* = 15.7 Hz, 1H), 6.03 (dd, *J* = 15.7, 9.1 Hz, 1H), 4.16 (dd, *J* = 8.7, 8.7 Hz 1H), 3.83 (dq, *J* = 8.6, 8.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.6, 139.2, 135.7, 134.9, 133.2, 131.5, 131.2, 130.9 (q, $J_{C\text{-}F}$ = 281.7 Hz), 130.6, 130.4, 130.0,

128.9, 121.0, 115.1, 58.9 (q, $J_{C\text{-}F}$ = 25.2 Hz), 52.0. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.24 (d, $J$ = 8.7 Hz, minor diastereomer), -64.35 (d, $J$ = 8.9 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M]^+$ calcd for $C_{24}H_{18}F_3N$ 376.1308, found 376.1311.

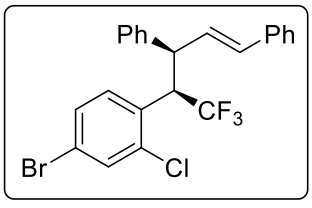



**(*E*)-(5,5,5-Trifluoro-4-(4-(trifluoromethyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3ia).** Compound **3ia** was obtained as a colorless oil in 60% yield (37.5 mg, 0.089 mmol) using Method A. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 96% *ee*, $t_R$ (major) = 7.7 min., $t_R$ (minor) = 7.3 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 14.3 min., $t_R$ (minor) = 12.9 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J$ = 8.1 Hz, 2H), 7.40 – 7.32 (m, 6H), 7.25 – 7.18 (m, 3H), 7.16 – 7.11 (m, 3H), 6.30 (d, $J$ = 15.7 Hz, 1H), 6.07 (dd, $J$ = 15.7, 9.0 Hz, 1H), 4.19 (dd, $J$ = 8.5, 8.5 Hz, 1H), 3.83 (dq, $J$ = 9.03, 8.78 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.1, 136.7, 132.9, 130.2, 128.8, 128.7, 128.5, 127.8, 127.8, 127.6, 127.4 (q, $J_{C\text{-}F}$ = 281.4 Hz), 127.4 (q, $J_{C\text{-}F}$ = 272.9 Hz), 127.2, 126.4, 126.2, 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 55.9 (q, $J_{C\text{-}F}$ = 25.3 Hz), 49.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.70 (major diastereomer), -62.75 (minor diastereomer), -63.36 (d, $J$ = 8.9 Hz, minor diastereomer), -64.55 (d, $J$ = 9.1 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M]^+$ calcd for $C_{24}H_{18}F_6$ 419.1229, found 419.1228.




**(*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja).**

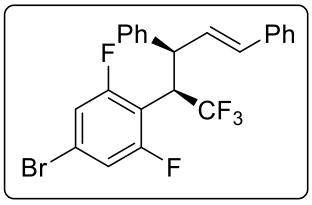
Compound **3ja** was obtained as a pale yellow oil in 71% yield (33.6 mg, 0.080 mmol) using Method A. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 0.8 mL/min, λ = 254 nm): major diastereomer, 93% *ee*, $t_R$ (major) = 6.0 min., $t_R$ (minor) = 6.4 min.; minor diastereomer, 93% *ee*, $t_R$ (major) = 7.0 min., $t_R$ (minor) = 13.1 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.37 – 7.32 (m, 4H), 7.32 – 7.26 (m, 2H), 7.23 – 7.19 (m, 2H), 7.14 – 7.05 (m, 3H), 6.19 (d, *J* = 15.7 Hz, 1H), 6.09 (dd, *J* = 15.7, 8.7 Hz, 1H), 4.63 (dq, *J* = 9.5, 9.5 Hz, 1H), 4.05 (dd, *J* = 9.5, 9.5 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.9, 136.7, 136.2, 134.5, 132.4, 130.1, 129.9, 129.6, 128.9, 128.7, 128.6 (q, $J_{C-F}$ = 281.6 Hz), 128.4, 127.8, 127.6, 127.6, 127.3, 126.2, 50.6, 49.9 (q, $J_{C-F}$ = 25.2 Hz).$^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.85 (d, *J* = 8.9 Hz, major diastereomer), -64.09 (d, *J* = 8.9 Hz, minor diastereomer). HRMS (ESI-TOF) *m/z*: $[M]^+$ calcd for $C_{23}H_{17}Cl_2F_3$ 419.0576, found 419.0574.




**(*E*)-(4-(4-Bromo-2-chlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ka).**

Compound **3ka** was obtained as a colorless solid in 79% yield (109.8 mg, 0.24 mmol) using Method A. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were

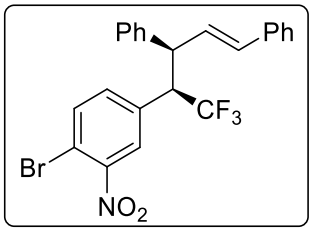
determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 0.8 mL/min, λ = 254 nm): major diastereomer, 93% *ee*, $t_R$ (major) = 6.3 min., $t_R$ (minor) = 6.9 min.; minor diastereomer, >99% *ee*, $t_R$ (major) = 7.4 min., $t_R$ (minor) = 12.7 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.2 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.38 – 7.25 (m, 5H), 7.23 – 7.09 (m, 5H), 6.18 (d, *J* = 15.7 Hz, 1H), 6.08 (dd, *J* = 15.7, 8.8 Hz, 1H), 4.60 (dq, *J* = 9.9, 8.7 Hz, 1H), 4.04 (dd, *J* = 9.9, 8.8 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.7, 136.4, 132.5, 132.3, 131.5 (q, $J_{C-F}$ = 1.9 Hz), 130.5, 130.4 (q, $J_{C-F}$ = 1.8 Hz), 128.8, 128.6, 128.4, 127.7, 127.5, 127.2, 127.0 (q, $J_{C-F}$ = 281.8 Hz), 126.2, 122.3, 50.5, 49.9 (q, $J_{C-F}$ = 25.3 Hz). $^{19}$F NMR (376 MHz, $cdcl_3$) δ -63.86 (d, *J* = 8.8 Hz, major diastereomer), -64.08 (d, *J* = 8.4 Hz, minor diastereomer). EA Found: C, 59.6; H, 3.9. $C_{23}H_{17}BrClF_3$ requires C, 59.3; H, 3.7%.




**(*E*)-(4-(4-Bromo-2,6-difluorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3la).**

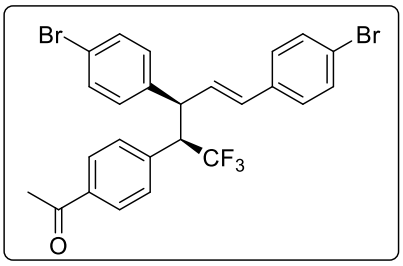
Compound **3la** was obtained as a colorless solid in 87% yield (30.4 mg, 0.065 mmol) after 48 hours using Method A. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK IB, Hexanes/DCM 99:1, flow rate 0.3 mL/min, λ = 254 nm): major diastereomer, 90.4% *ee*, $t_R$ (major) = 25.3 min., $t_R$ (minor) = 24.5 min.; minor diastereomer, 97% *ee*, $t_R$ (major) = 23.0 min., $t_R$ (minor) = 22.4 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.28 (m, 1H), 7.22 – 7.14 (m, 3H), 7.11 – 7.05 (m, 4H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.01 (dd, *J* = 15.7, 8.5 Hz, 1H), 4.37 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.36 (dq, *J* = 9.7, 9.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, $J_{C-F}$ = 255.6 Hz), 161.2 (d, $J_{C-F}$ = 253.4 Hz), 141.1, 136.6, 131.7, 129.1, 128.9, 128.4, 127.6, 127.3, 126.9, 126.3 (q, $J_{C-F}$ = 281.9 Hz), 126.2, 122.5

(dd, $J_{C\text{-}F}$ = 12.9 Hz), 116.3 (d, $J_{C\text{-}F}$ = 27.7 Hz), 115.4 (d, $J_{C\text{-}F}$ = 28.7 Hz), 110.3 (dd, $J_{C\text{-}F}$ = 17.8 Hz), 47.4, 45.7 (q, $J_{C\text{-}F}$ = 27.0 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.31 (dd, *J* = 16.4, 8.5 Hz, minor diastereomer), -63.60 (dd, *J* = 17.0, 7.5 Hz, major diastereomer), -105.90 (dq, *J* = 15.9, 15.9 Hz, major diastereomer), -106.27 (dq, *J* = 11.23, 11.23 Hz, minor diastereomer), -111.77 (d, *J* = 7.4 Hz, minor diastereomer), -111.93 (d, *J* = 8.7 Hz, major diastereomer). EA Found: C, 59.4; H, 3.6. $C_{23}H_{16}BrF_5$ requires C, 59.1; H, 3.45%.

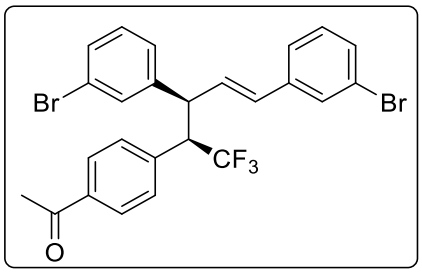



**(*E*)-(4-(4-Bromo-3-nitrophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ma).**

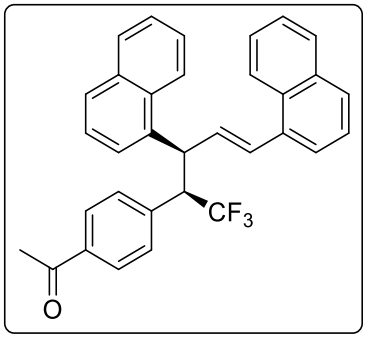
Compound **3ma** was obtained as a colorless oil in 72% yield (25.8 mg, 0.054 mmol) after 48 hours using Method B. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 87% *ee*, $t_R$ (major) = 14.8 min., $t_R$ (minor) = 18.6 min.; minor diastereomer, 94% *ee*, $t_R$ (major) = 39.9 min., $t_R$ (minor) = 24.4 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.25 (m, 5H), 7.24 – 7.14 (m, 6H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.04 (dd, *J* = 15.7, 9.3 Hz, 1H), 4.16 (dd, *J* = 8.6, 8.6 Hz, 1H), 3.82 (dq, *J* = 8.7, 8.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.3, 135.2, 134.6, 134.3, 133.6, 129.0, 128.6, 127.9, 127.6 (q, $J_{C\text{-}F}$ = 281.2 Hz), 127.6, 127.5, 127.3, 126.9, 126.3, 114.6, 55.2 (q, $J_{C\text{-}F}$ = 24.7 Hz), 49.10. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.58 (d, *J* = 8.7 Hz, minor diastereomer), -64.74 (d, *J* = 8.8 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+HCOO]^-$ calcd for $C_{23}H_{17}BrF_3NO_2$ 520.0377, found 520.0368.




**(*E*)-1-(4-(3,5-Bis(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cb).** Compound **3cb** was obtained as a pale yellow oil in 79% yield (41 mg, 0.074 mmol) using Method A. The *dr* was determined to be 1:5 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 98:2, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, 91% *ee*, $t_R$ (major) = 40.4 min., $t_R$ (minor) = 60.4 min.; minor diastereomer, > 99 *ee*, $t_R$ (major) = 71.7 min., $t_R$ (minor) = 81.1 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.08 (dd, *J* = 8.5, 5.8 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.17 (d, *J* = 15.7 Hz, 1H), 6.00 (dd, *J* = 15.7, 8.7 Hz, 1H), 4.12 (dd, *J* = 8.6, 8.6 Hz, 1H), 3.77 (dq, *J* = 8.8, 8.8 Hz, 1H), 2.58 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.1, 142.5, 141.0, 139.7, 138.0, 134.6, 134.3, 132.6, 132.2, 132.2, 131.7 (q, $J_{C-F}$ = 282.0 Hz), 131.3, 131.3, 130.4, 124.3, 123.9, 58.5 (q, $J_{C-F}$ = 25.0 Hz), 51.5, 29.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.43 (d, *J* = 8.9 Hz, minor diastereomer), -64.31 (d, *J* = 8.9 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{19}Br_2F_3O$ 552.9809, found 552.9783.

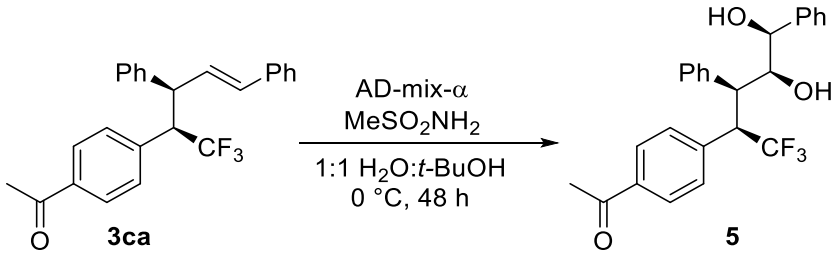



**(*E*)-1-(4-(3,5-Bis(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cc).** Compound **3cc** was obtained as a pale yellow oil in 88% yield (37 mg, 0.067 mmol) after 48 hours using Method A. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, > 99% *ee*, $t_R$ (major) = 16.3 min., $t_R$ (minor) = 19.8 min.; minor diastereomer, > 99% *ee*, $t_R$ (major) = 22.1 min., $t_R$ (minor) = 38.0 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J$ = 8.4 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.25 – 7.23 (m, 2H), 7.19 (m, 1H), 7.13 (m, 1H), 7.07 (m, 1H), 7.01 (m, 1H), 6.18 (d, $J$ = 15.6 Hz, 1H), 5.99 (dd, $J$ = 15.7, 9.0 Hz, 1H), 4.11 (dd, $J$ = 8.8, 8.8 Hz, 1H), 3.79 (dq, $J$ = 8.8, 8.8 Hz, 1H), 2.59 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.1, 145.8, 141.2, 140.9, 139.8, 134.5, 133.5, 133.3, 133.2, 133.1, 132.7, 132.6, 132.0, 131.7, 131.3, 129.1, 129.0 (q, $J_{C\text{-}F}$ = 281.0 Hz), 127.6, 125.5, 125.4, 58.4 (q, $J_{C\text{-}F}$ = 25.4 Hz), 51.8, 29.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.43 (d, $J$ = 8.9 Hz, minor diastereomer), -64.35 (d, $J$ = 8.8 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{19}Br_2F_3O$ 552.9809, found 552.9808.

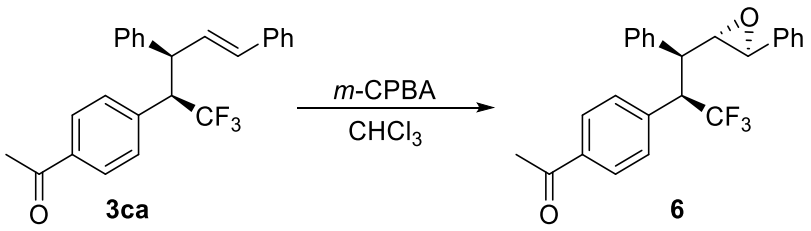



**(*E*)-1-(4-(1,1,1-Trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd).** Compound **3cd** was obtained as a white paste in 76% yield (34 mg, 0.068 mmol) using Method A. The *dr* was determined to be 1:3 by crude $^{19}$F NMR spectroscopy. The *ee*'s were determined by HPLC (CHIRALPAK AD-H, Hexanes/IPA 99:1, flow rate 1.0 mL/min, λ = 254 nm): major diastereomer, > 99% *ee*, $t_R$ (major) = 16.9 min., $t_R$ (minor) = 21.6 min.; minor diastereomer, > 99% *ee*, $t_R$ (major) = 20.2 min., $t_R$ (minor) = 33.2 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, $J$ = 8.7 Hz, 1H), 7.97 – 7.88 (m, 3H), 7.83 – 7.74 (m, 2H), 7.74 – 7.63 (m, 3H), 7.57 (m, 1H), 7.47 – 7.26 (m, 7H), 7.22 – 7.13 (m, 2H), 6.30 (dd, $J$ = 15.4, 9.2 Hz, 1H), 5.26 (dd, $J$ = 7.7, 7.7 Hz, 1H), 4.10 (dq, $J$ = 9.6, 6.9 Hz, 1H), 2.57 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$δ 200.2, 141.1, 139.6, 139.5, 137.6, 137.0, 136.1, 133.8, 133.7, 133.5, 133.3, 133.0, 132.2, 131.0, 130.7, 130.6, 130.3 (q, $J_{C\text{-}F}$ = 282.1 Hz), 129.4, 128.6, 128.6, 128.5, 128.2, 127.9, 126.7, 126.5, 125.1, 57.9 (q, $J_{C\text{-}F}$ = 25.2 Hz), 46.7, 29.3. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.94 (d, $J$ = 8.8 Hz, minor diastereomer), -64.45 (d, $J$ = 9.4 Hz, major diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{33}H_{25}F_3O$ 495.1930, found 495.1923.

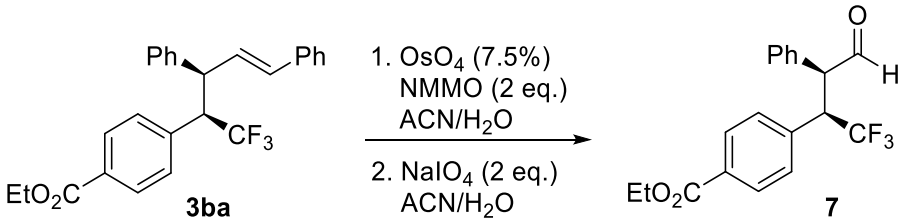
**5. Product derivatizations**



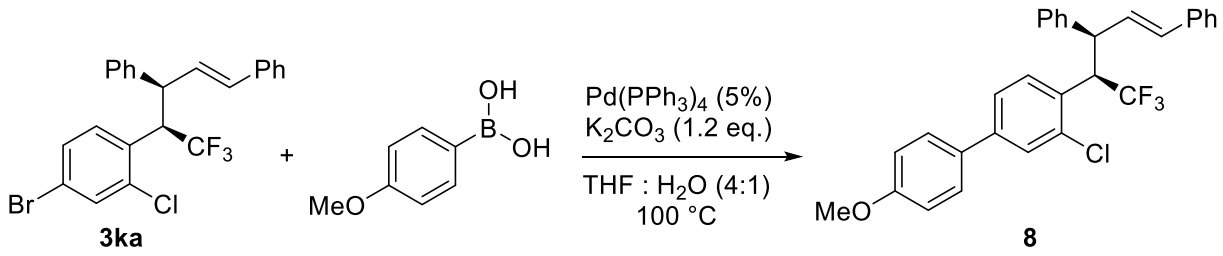

A solution of AD-mix-α (180.0 mg), methanesulfonamide (13.3 mg, 0.14 mmol), and **3ca** (56 mg, 0.14 mmol, *dr* = 1:10) was stirred in 4 mL of a 1:1 water/*t*-BuOH mixture at 0 °C. After 48 hours, excess $Na_2SO_3$ was added and the reaction was stirred for another hour. To the mixture was added $CH_2Cl_2$ and the organic layer was washed with water and dried over $Na_2SO_4$. The crude product was purified by flash chromatography on silica gel using EtOAc:hexanes (1:5) as the mobile phase to obtain **5** as a colorless oil in 78% yield (47.0 mg, 0.11 mmol). The *dr* was determined to be 1:12 by $^{19}F$ NMR spectroscopy. The *ee* was determined to be 94% by $^{19}F$ NMR spectroscopy integration of the resulting diastereomers. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J$ = 8.0 Hz, 2H), 7.41 – 7.26 (m, 10H), 6.94 – 6.88 (m, 2H), 4.14 (dq, $J$ = 11.8, 8.9 Hz, 1H), 3.92 (d, $J$ = 9.0 Hz, 1H), 3.53 (dd, $J$ = 9.0, 2.4 Hz, 1H), 2.85 (dd, $J$ = 11.8, 2.4 Hz, 1H), 2.62 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 200.4, 142.9, 142.1, 139.6, 139.5, 133.1, 132.2, 131.6, 131.4, 131.4, 131.2 (q, $J_{C-F}$ = 281.4 Hz), 130.7, 130.2, 78.5, 77.1, 55.7 (q, $J_{C-F}$ = 24.8 Hz), 49.2, 29.3. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -61.13 (d, $J$ = 9.8 Hz, minor diastereomer), δ -63.07 (d, $J$ = 8.7 Hz, major diastereomer), -63.49 (d, $J$ = 9.2 Hz, minor diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{23}F_3O_3$ 429.1672, found 429.1665.




A solution of **3ca** (39.0 mg, 0.1 mmol, *dr* = 1:10) in 1.5 mL $CHCl_3$ was cooled to 0 °C followed by dropwise addition of a solution of 3-chloroperbenzoic acid (≤ 77%, 34.0 mg, 0.15 mmol) in 1.5 mL $CHCl_3$. The reaction mixture was left to warm to room temperature overnight and quenched with 5% aq. $Na_2CO_3$. The solution was extracted with EtOAc (3 x 5 mL) and the organic layers were combined and washed with $Na_2CO_3$ solution and brine. The organic solution was dried over $Na_2SO_4$ and purified by silica gel chromatography using EtOAc:hexanes (1:25) as the mobile phase to obtain **6** as a white solid in 77% yield (31.0 mg, 0.076 mmol). The *dr* was determined to be 1:4 by $^{19}F$ NMR spectroscopy. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.90 (d, $J$ = 8.3 Hz, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.30 (m, 3H), 7.18 – 7.12 (m, 3H), 6.77 – 6.69 (m, 2H), 3.89 (dq, $J$ = 9.6, 9.0 Hz, 1H), 3.28 (dd, $J$ = 10.1, 7.6 Hz, 1H), 3.22 (d, $J$ = 2.0 Hz, 1H), 2.87 (dd, $J$ = 7.7, 1.9 Hz, 1H), 2.58 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 199.9, 141.4, 140.3, 139.9, 138.7, 132.8, 132.1, 131.6, 131.4, 131.1 (q, $J_{C-F}$ = 290.7 Hz), 130.9, 130.8, 130.5, 127.8, 66.8, 62.8, 56.7 (q, $J_{C-F}$ = 26.0 Hz), 51.4, 29.3. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.74 (d, $J$ = 8.5 Hz, major diastereomer), -64.50 (d, $J$ = 9.3 Hz, minor diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{21}F_3O_2$ 411.1566, found 411.1571.



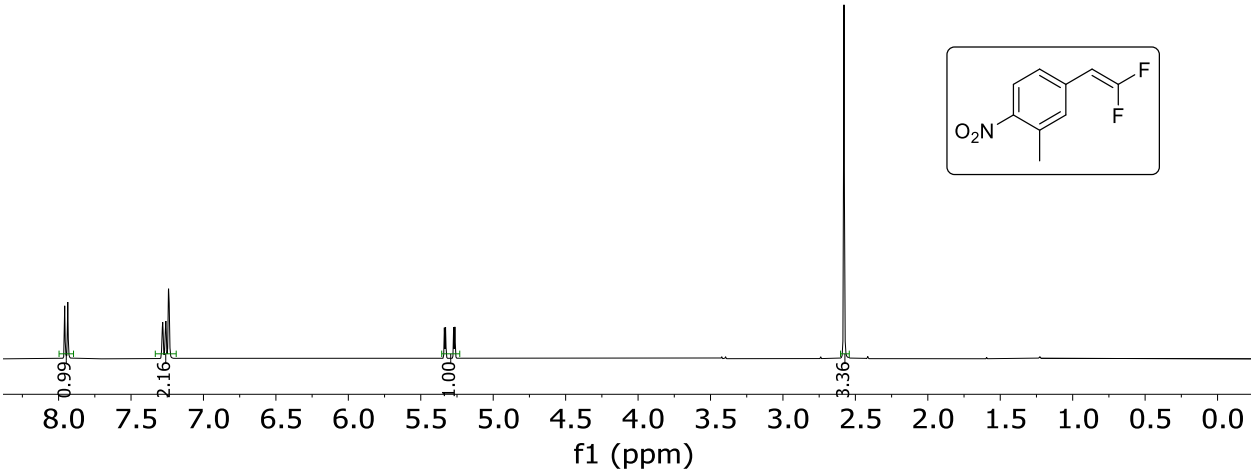

Compound **3ba** (85.0 mg, 0.2 mmol, *dr* = 1:10) and *N*-methylmorpholine *N*-oxide (54.0 mg, 0.4 mmol) were stirred in 6.0 mL of ACN/$H_2O$ (4:1) followed by addition of $OsO_4$ (188.0 µL, 2.5 wt% in *t*-BuOH). The reaction was stirred at room temperature for 24 hours followed by dilution with EtOAc. The organic layer was washed with brine and dried over $Na_2SO_4$ then purified by silica gel chromatography using EtOAc:hexanes (1:5) as the mobile phase to obtain the dihydroxylated product as a colorless oil in 58% yield (53.0 mg, 0.12 mmol). The diol was dissolved in 1 mL ACN and a solution of $NaIO_4$ (50.0 mg, 0.24 mmol) in 1 mL $H_2O$ was added to the reaction and left to stir overnight. The reaction mixture was diluted with $H_2O$ and extracted with EtOAc (3 x 5 mL). The organic solution was dried over $Na_2SO_4$ and purified by silica gel chromatography using EtOAc:hexanes (1:50) as the mobile phase to obtain **7** as a white solid in 58% yield (24.1 mg, 0.069 mmol).The *dr* was determined to be 1:10 by $^{19}F$ NMR spectroscopy. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 1.8 Hz, 1H), 8.09 – 8.01 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.33 – 7.27 (m, 2H), 4.43 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.21 (dq, *J* = 11.2, 8.8 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 197.3, 168.6, 141.2, 134.3, 133.5, 132.7, 132.4, 132.0, 131.4, 128.5 (q, $J_{C\text{-}F}$ = 282.2 Hz), 63.8, 62.2, 53.3 (q, $J_{C\text{-}F}$ = 26.2 Hz), 17.0. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -64.21 (d, *J* = 8.7 Hz, major diastereomer), -66.57 (d, *J* = 9.0 Hz, minor diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{17}F_3O_3$ 351.1203, found 351.1204.



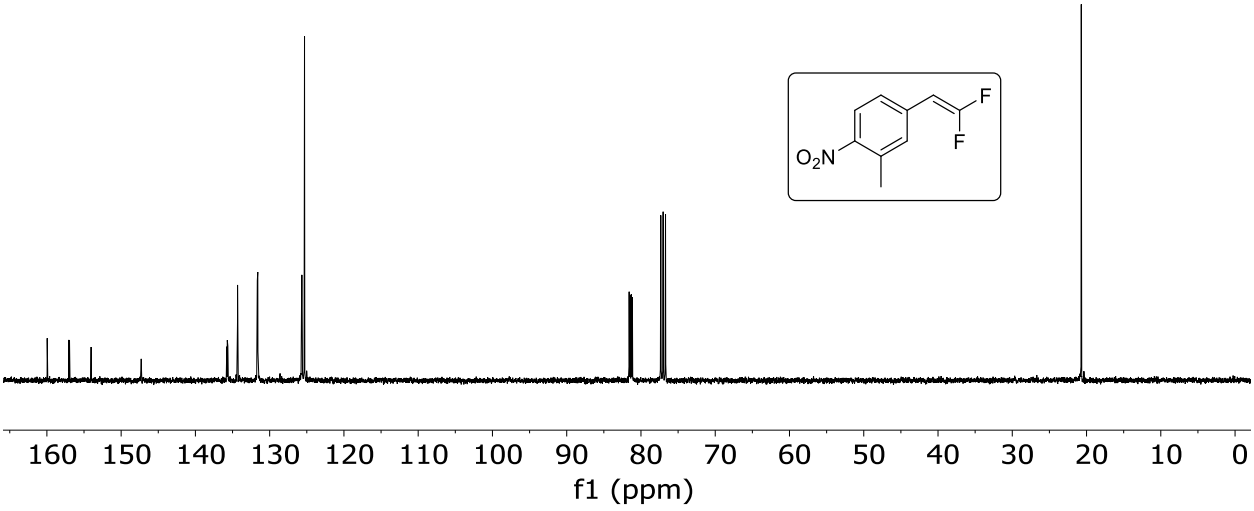

Compound **3ka** (44.0 mg, 0.1 mmol, *dr* = 1:2), boronic acid (23.0 mg, 0.15 mmol), $K_2CO_3$ (21.0 mg, 0.12 mmol), and $Pd(PPh_3)_4$ (6.0 mg, 5 mol%) were combined in 2.0 mL THF/$H_2O$ (4:1) under nitrogen atmosphere. The solution was heated to reflux for 48 hours then cooled to room temperature, extracted with EtOAc (3 x 5 mL) and washed with brine. The organic solution was dried over $Na_2SO_4$ and purified by silica gel chromatography using EtOAc:hexanes as the mobile phase to obtain **8** as a white solid in 89% yield (41.5 mg, 0.084 mmol).The *dr* was determined to be 1:2 by $^{19}F$ NMR spectroscopy. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $J$ = 1.6 Hz, 2H), 7.48 (dd, $J$ = 8.6, 1.5 Hz, 3H), 7.39 – 7.32 (m, 5H), 7.23 – 7.08 (m, 5H), 6.98 – 6.93 (m, 2H), 6.19 (d, $J$ = 15.8 Hz, 1H), 6.16 (dd, $J$ = 15.4, 7.8 Hz, 1H), 4.69 (dq, $J$ = 9.2, 9.2 Hz, 1H), 4.10 (dd, $J$ = 8.8, 8.8 Hz, 1H), 3.83 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.7, 141.9, 141.3, 137.0, 135.9, 132.2, 131.4, 130.2, 129.3, 128.8, 128.4, 128.1, 127.9, 127.9 (q, $J_{C-F}$ = 282.1 Hz), 127.8, 127.5, 127.3, 127.1, 126.2, 125.3, 114.3, 55.3, 50.6, 49.9 (q, $J_{C-F}$ = 25.8 Hz). $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -63.78 (d, $J$ = 8.8 Hz, major diastereomer), -63.95 (d, $J$ = 8.8 Hz, minor diastereomer). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{30}H_{24}ClF_3O$ 493.1541, found 493.1534.

## 6. $^{1}H$, $^{13}C$, and $^{19}F$ NMR Spectra

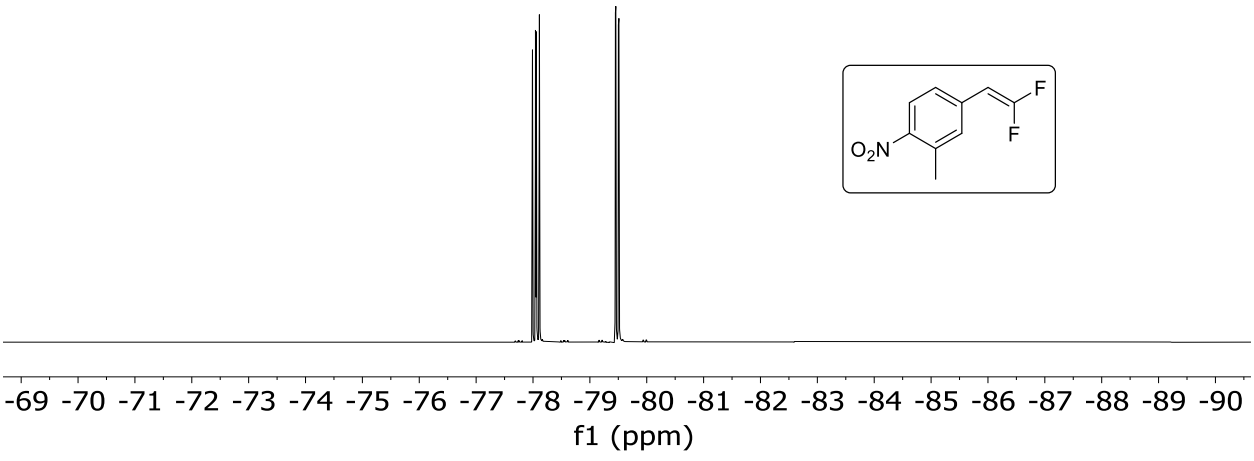
**$^{1}H$ NMR spectrum of 4-(2,2-difluorovinyl)-2-methyl-1-nitrobenzene (1g)**



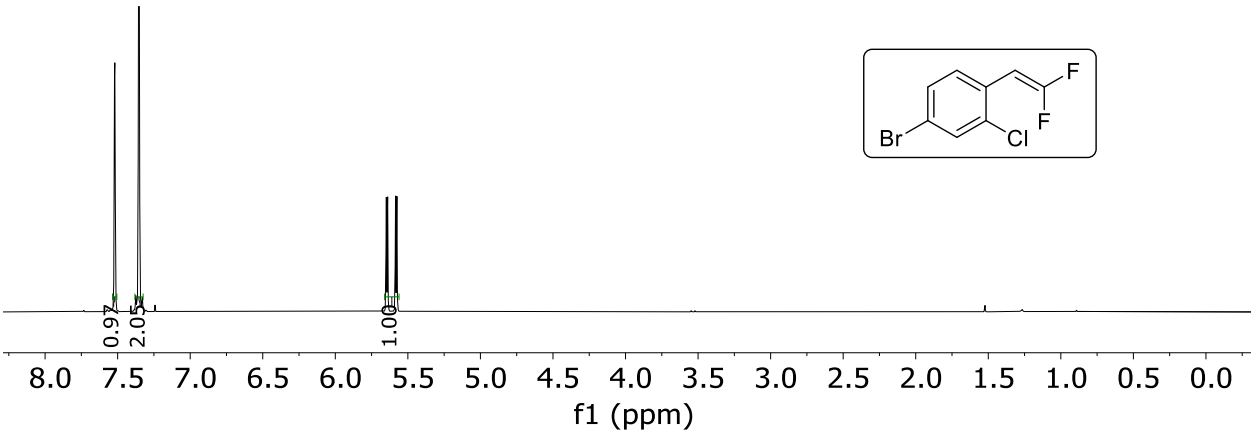

**$^{13}C$ NMR spectrum of 4-(2,2-difluorovinyl)-2-methyl-1-nitrobenzene (1g)**



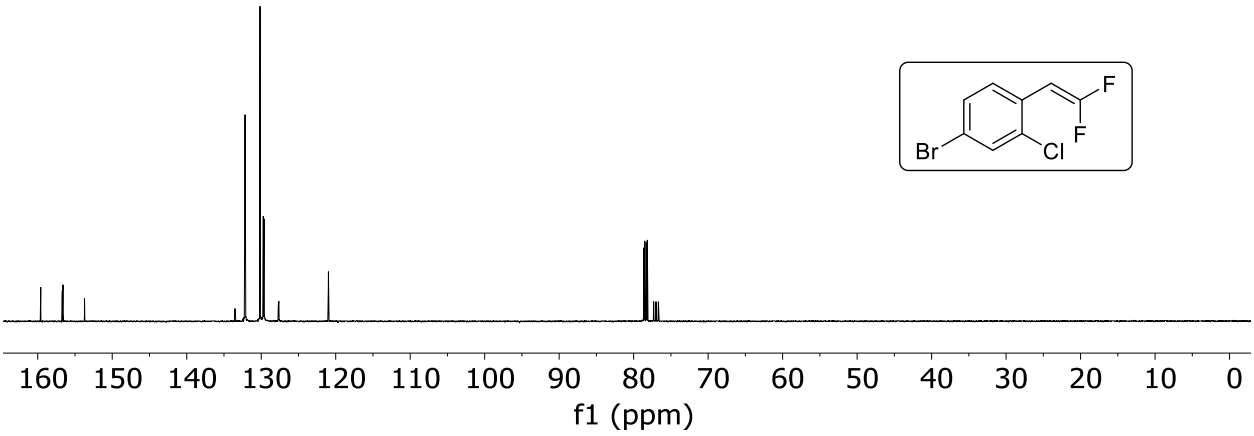

**$^{19}F$ NMR spectrum of 4-(2,2-difluorovinyl)-2-methyl-1-nitrobenzene (1g)**



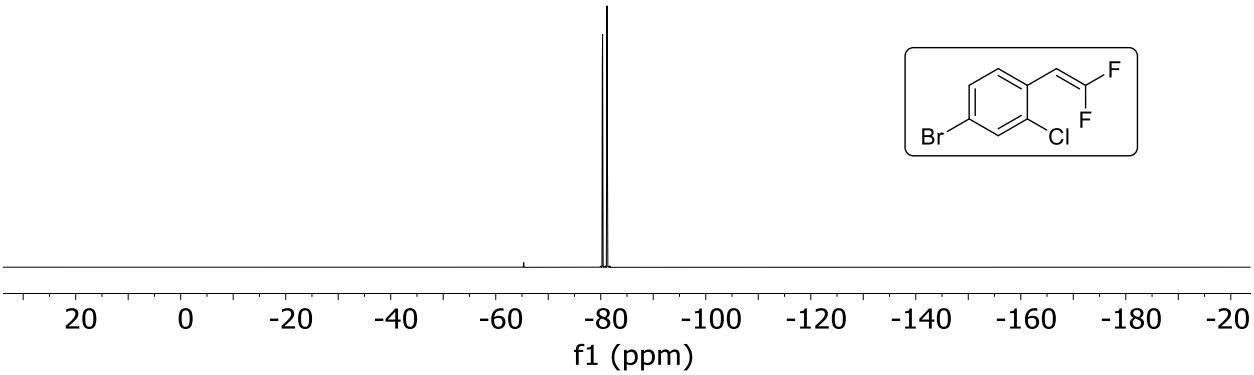
**$^{1}$H NMR spectrum of 4-Bromo-2-chloro-1-(2,2-difluorovinyl)benzene (1k)**



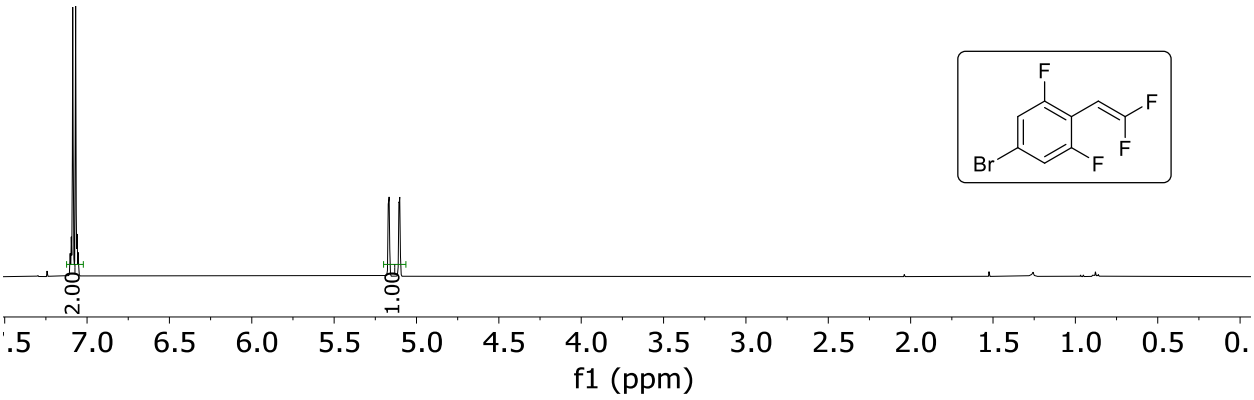

**$^{13}$C NMR spectrum of 4-Bromo-2-chloro-1-(2,2-difluorovinyl)benzene (1k)**



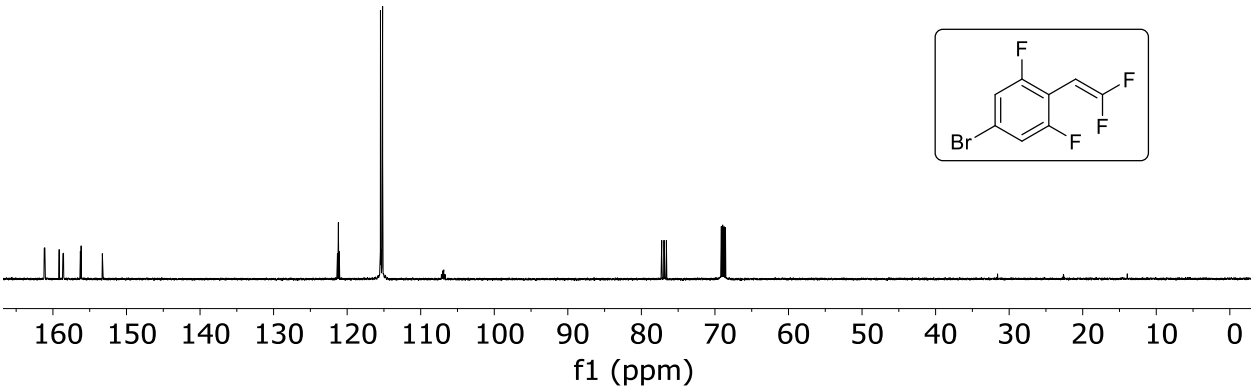

**$^{19}$F NMR spectrum of 4-Bromo-2-chloro-1-(2,2-difluorovinyl)benzene (1k)**



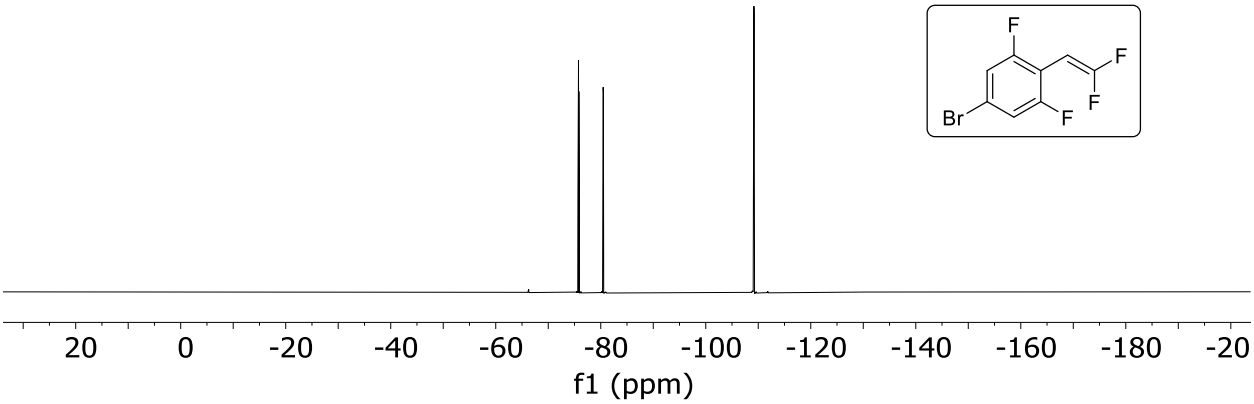
**$^{1}$H NMR spectrum of 5-Bromo-2-(2,2-difluorovinyl)-1,3-difluorobenzene (1l).**



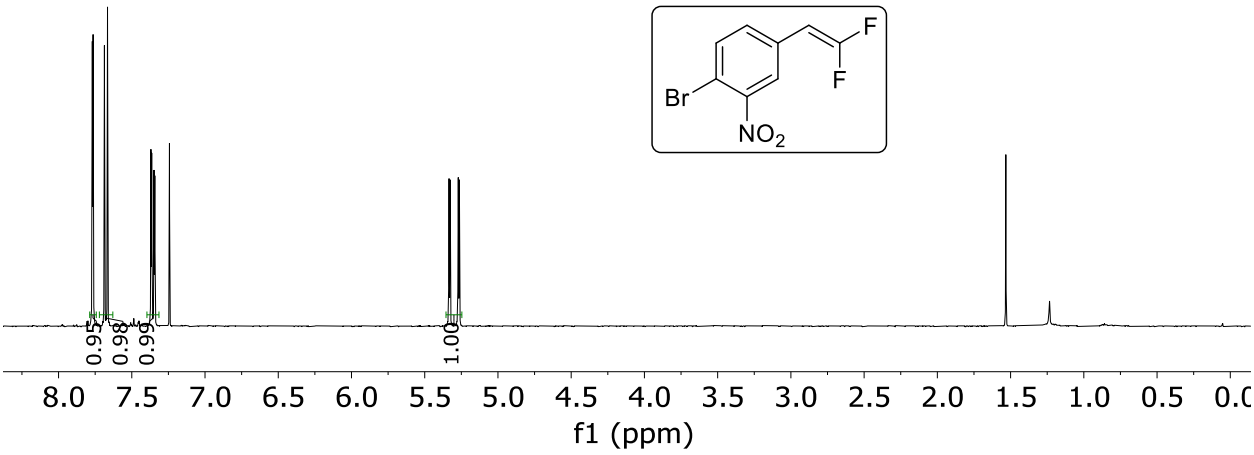

**$^{13}$C NMR spectrum of 5-Bromo-2-(2,2-difluorovinyl)-1,3-difluorobenzene (1l).**



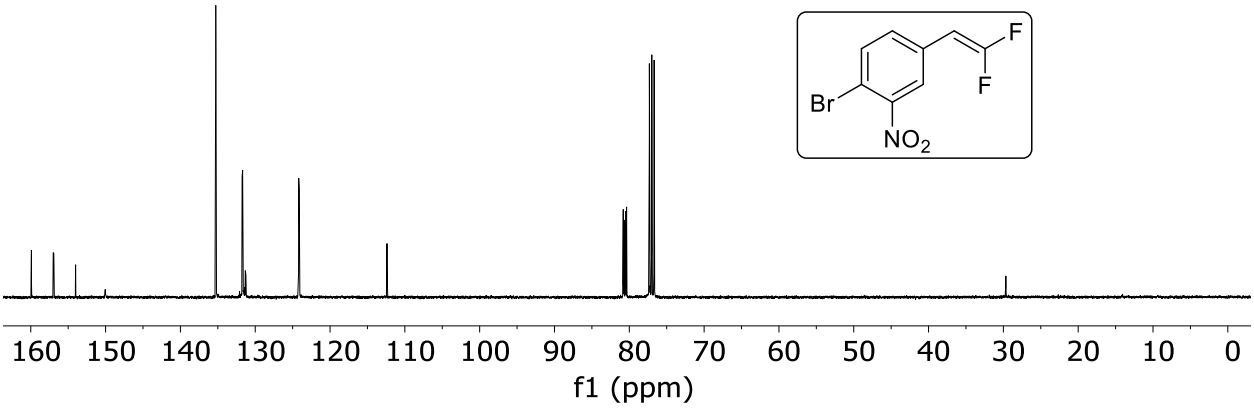

**$^{19}$F NMR spectrum of 5-Bromo-2-(2,2-difluorovinyl)-1,3-difluorobenzene (1l).**



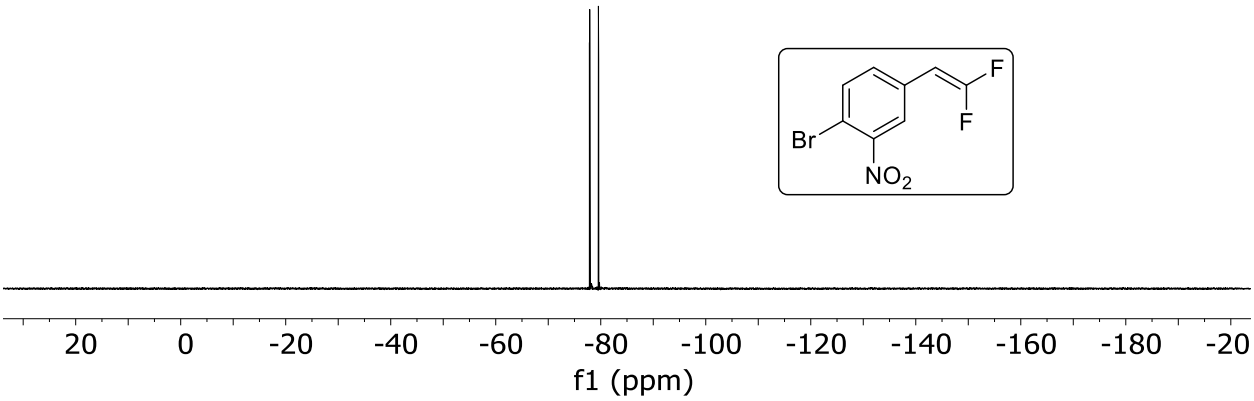
**$^{1}$H NMR spectrum of 1-Bromo-4-(2,2-difluorovinyl)-2-nitrobenzene (1m).**



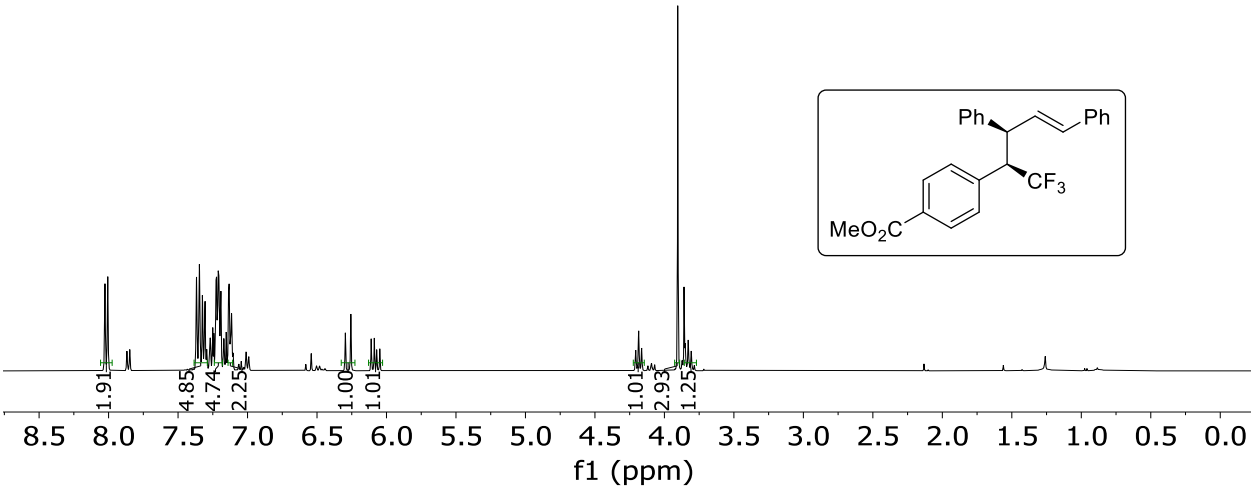

**$^{13}$C NMR spectrum of 1-Bromo-4-(2,2-difluorovinyl)-2-nitrobenzene (1m).**



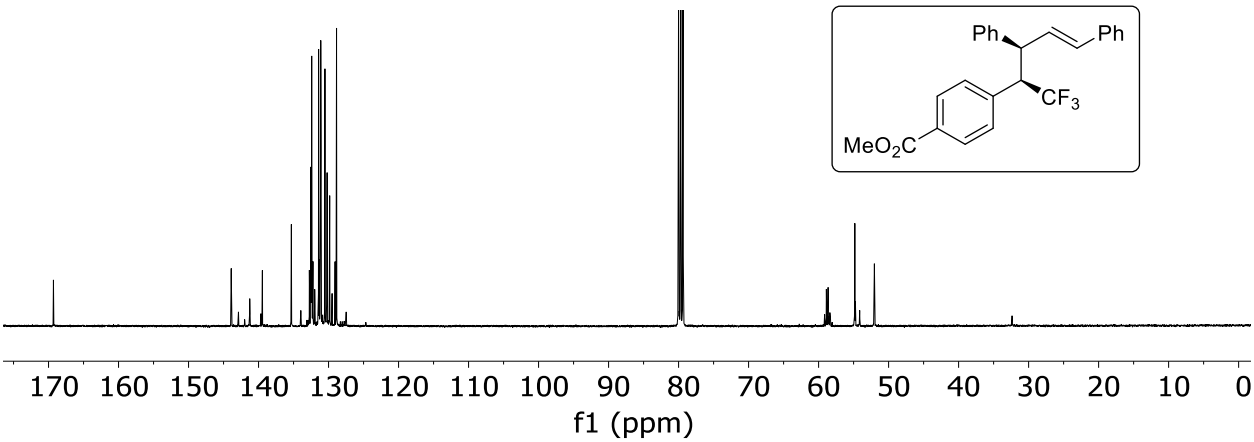

**$^{19}$F NMR spectrum of 1-Bromo-4-(2,2-difluorovinyl)-2-nitrobenzene (1m).**



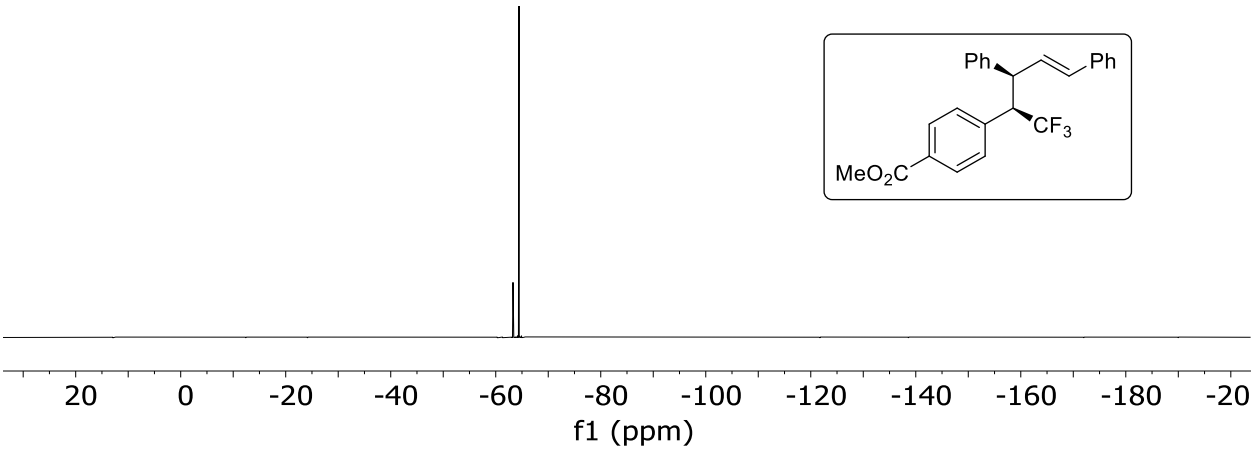
**$^{1}$H NMR spectrum of methyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3aa)**



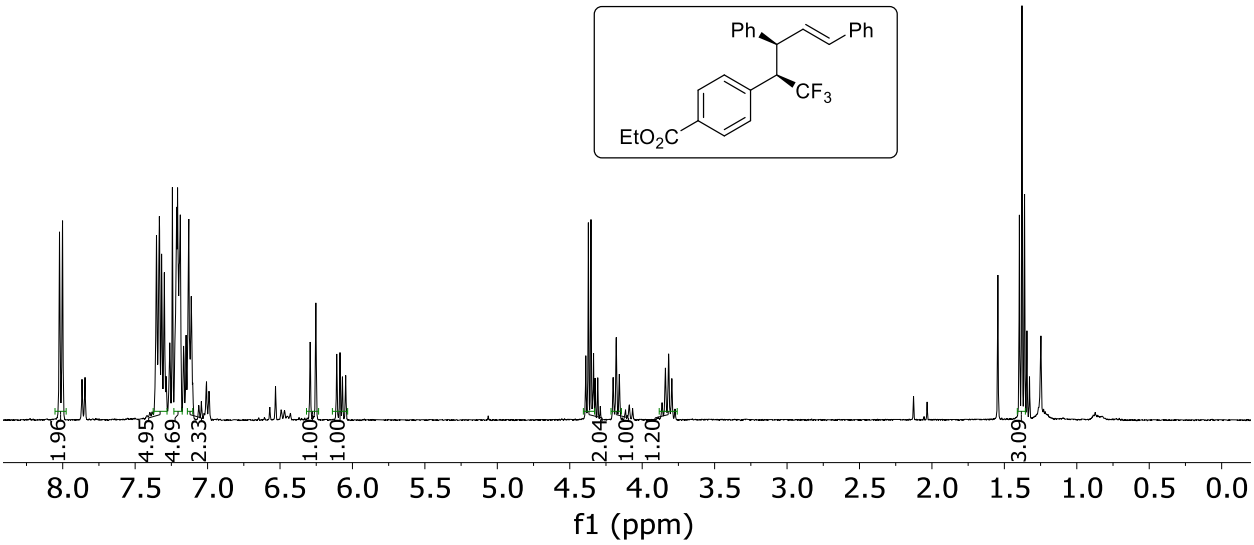

**$^{13}$C NMR spectrum of methyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3aa)**



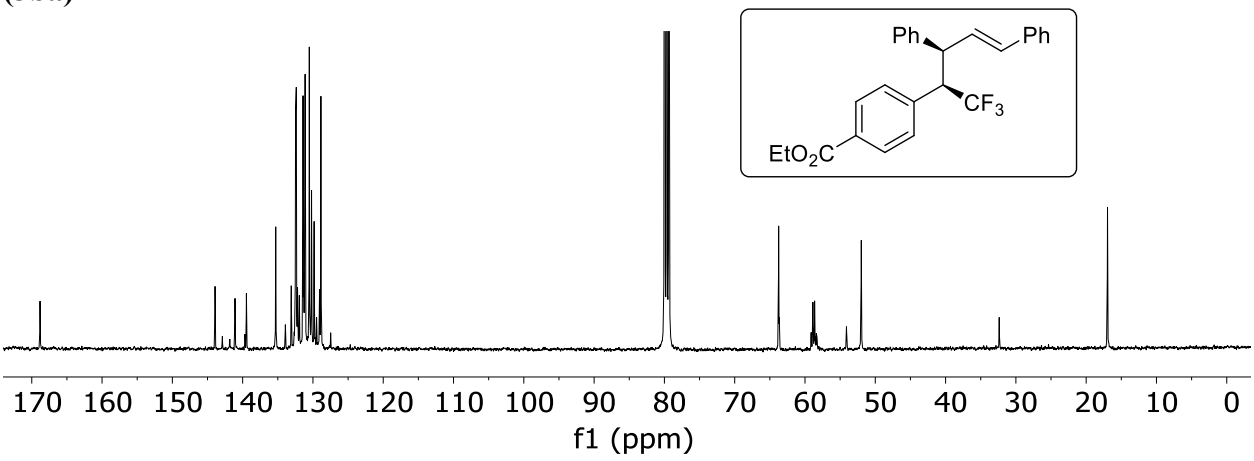

**$^{19}$F NMR spectrum of methyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3aa)**



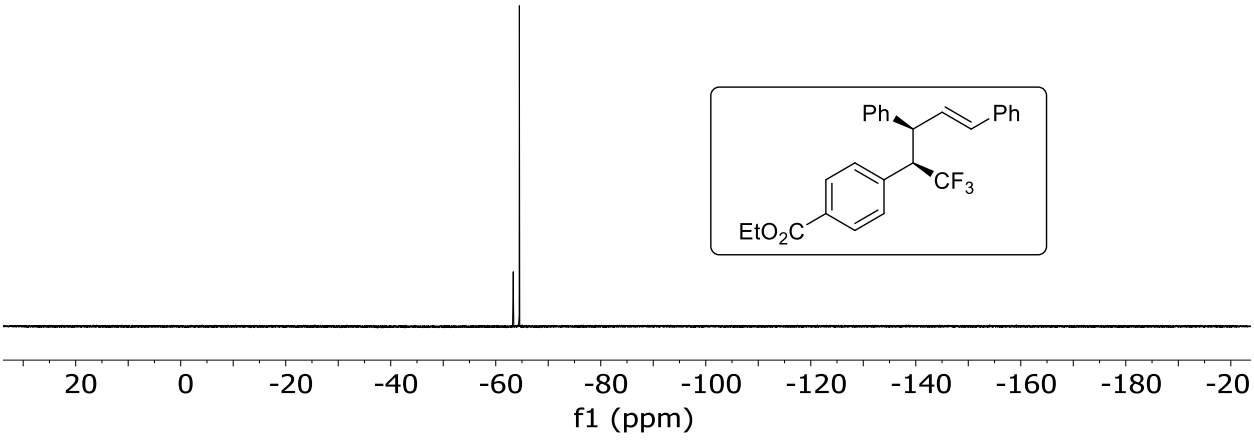
**$^{1}$H NMR spectrum of ethyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3ba)**



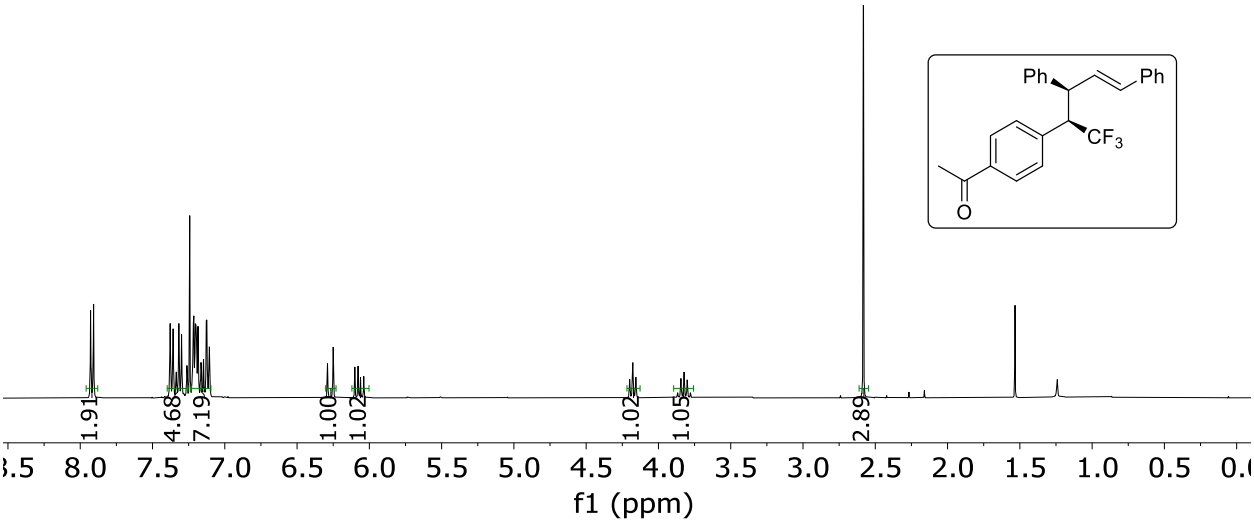

**$^{13}$C NMR spectrum of ethyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3ba)**



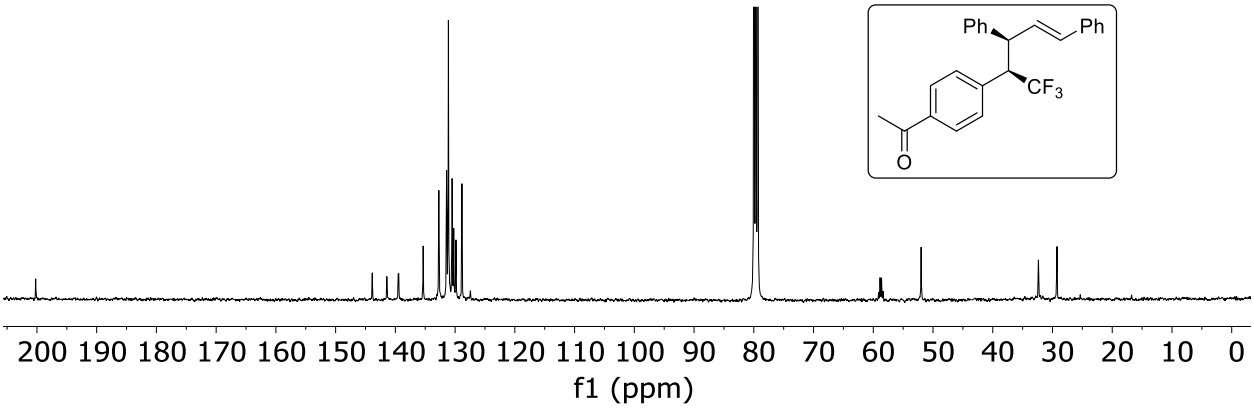

**$^{19}$F NMR spectrum of ethyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3ba)**



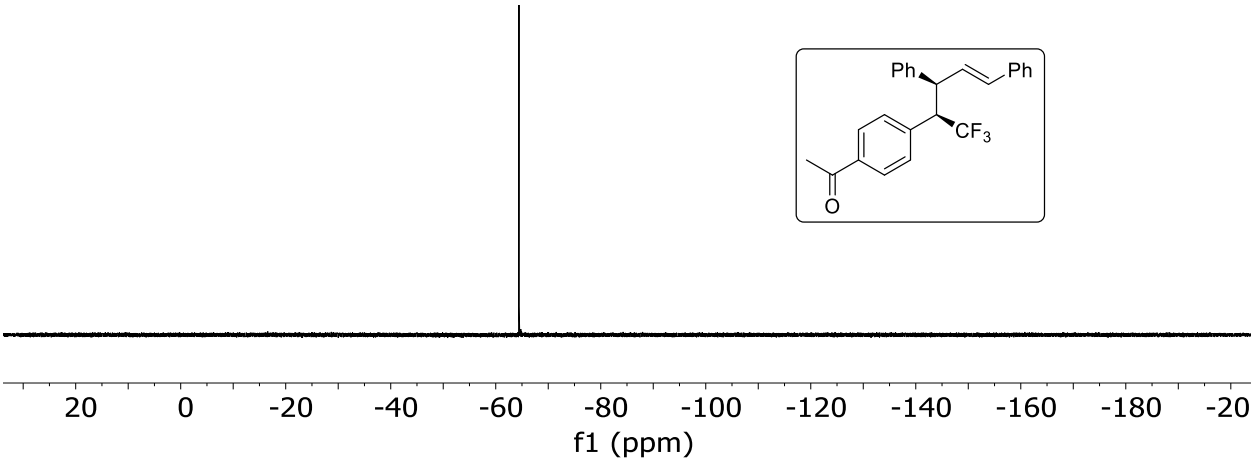
**$^{1}$H NMR spectrum of (*E*)-1-(4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)phenyl)ethan-1-one (3ca)**



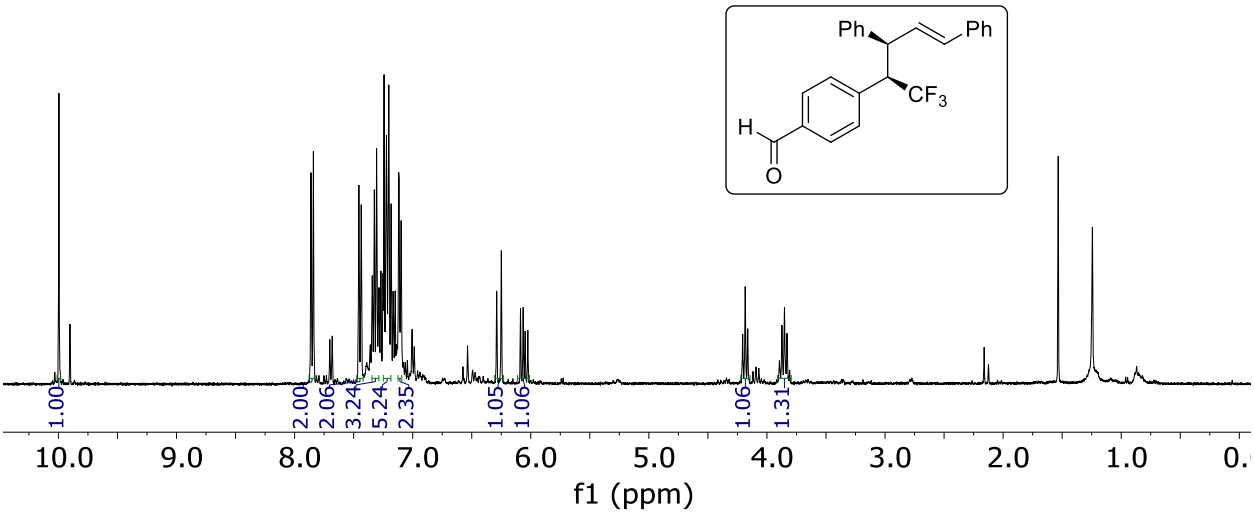

**$^{13}$C NMR spectrum of (*E*)-1-(4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)phenyl)ethan-1-one (3ca)**



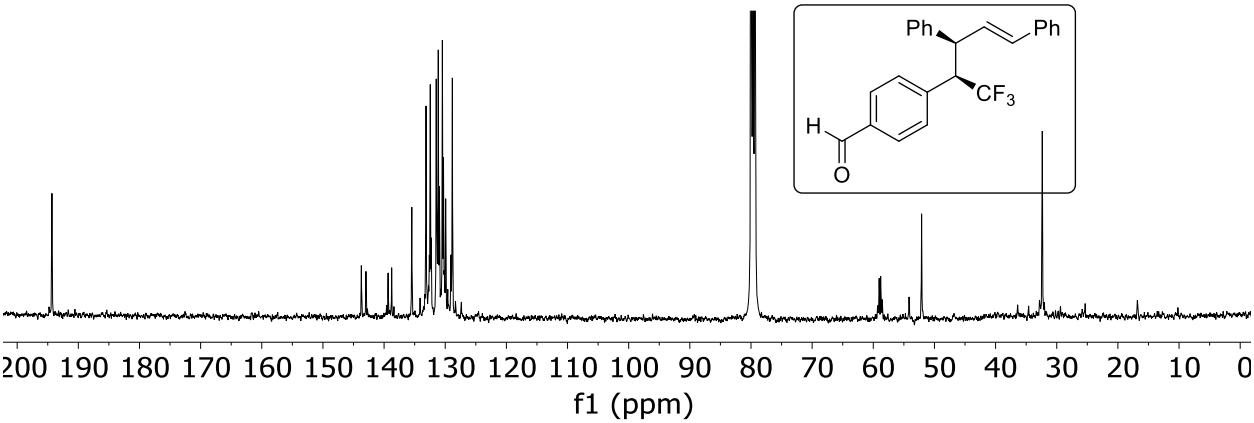

**$^{19}$F NMR spectrum of (*E*)-1-(4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)phenyl)ethan-1-one (3ca)**



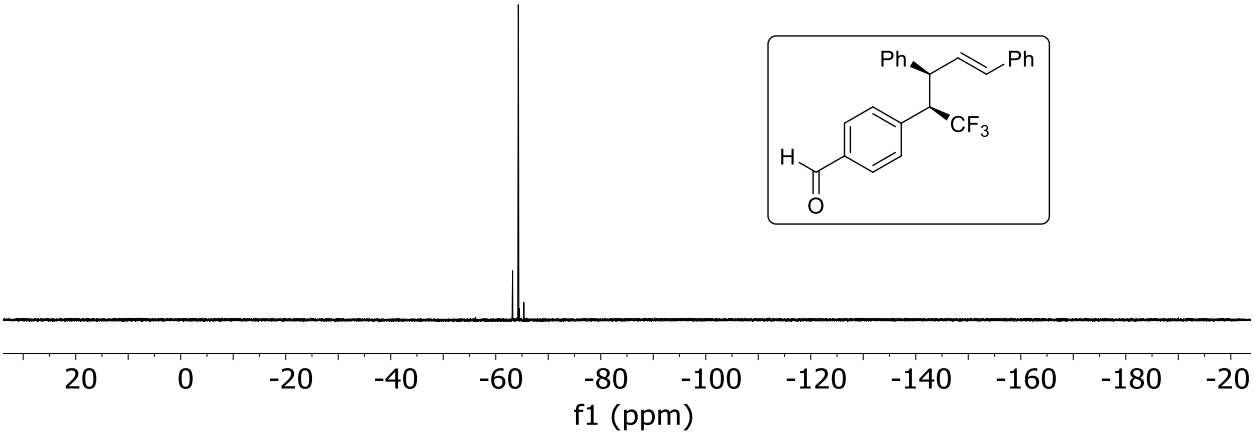
**$^{1}$H NMR spectrum of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzaldehyde (3da)**



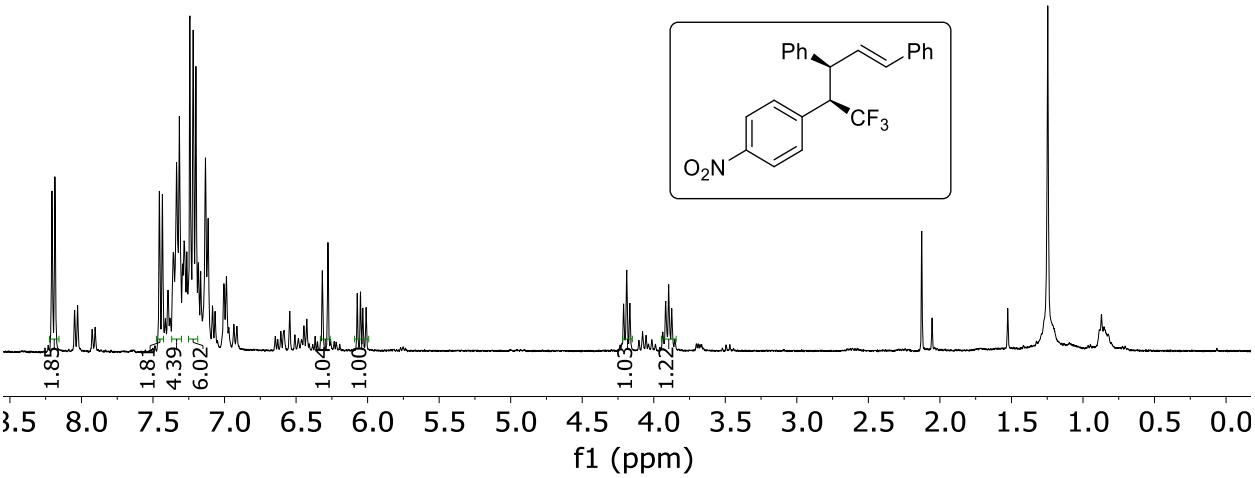

**$^{13}$C NMR spectrum of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzaldehyde (3da)**



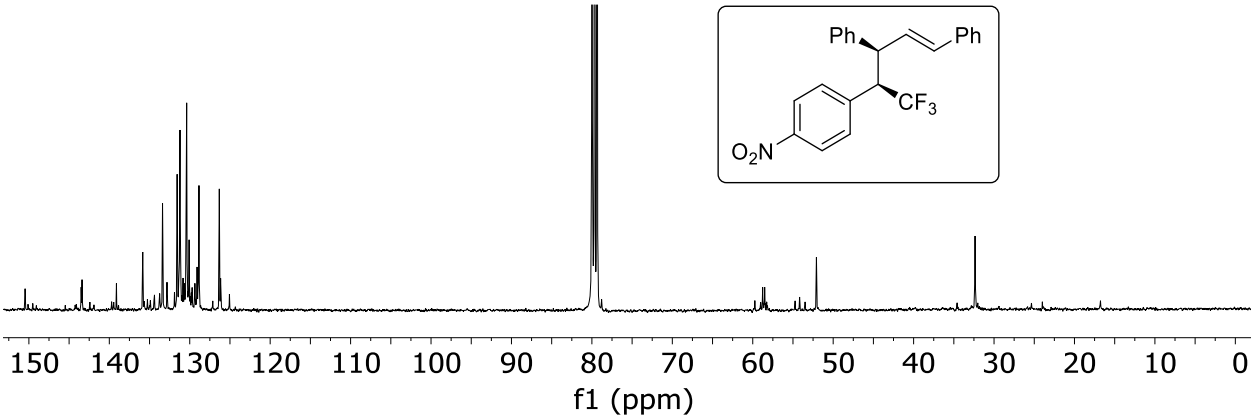

**$^{19}$F NMR spectrum of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzaldehyde (3da)**



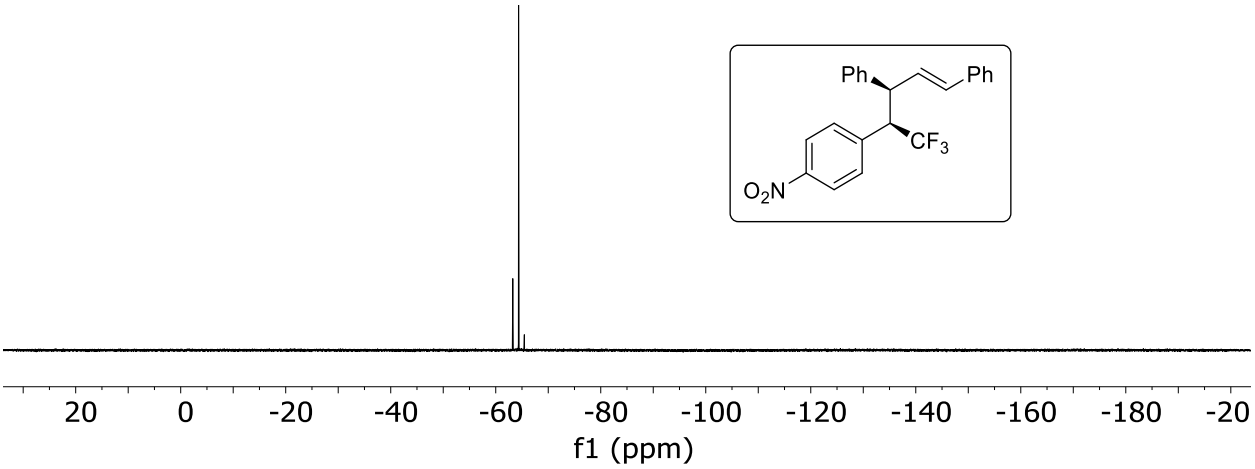
**$^{1}$H NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ea)**



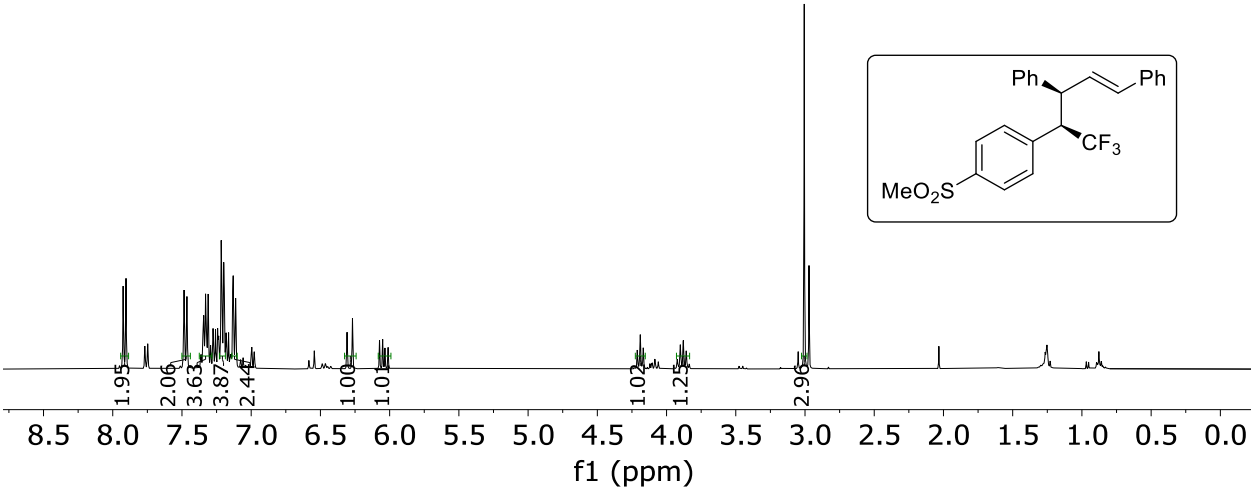

**$^{13}$C NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ea)**



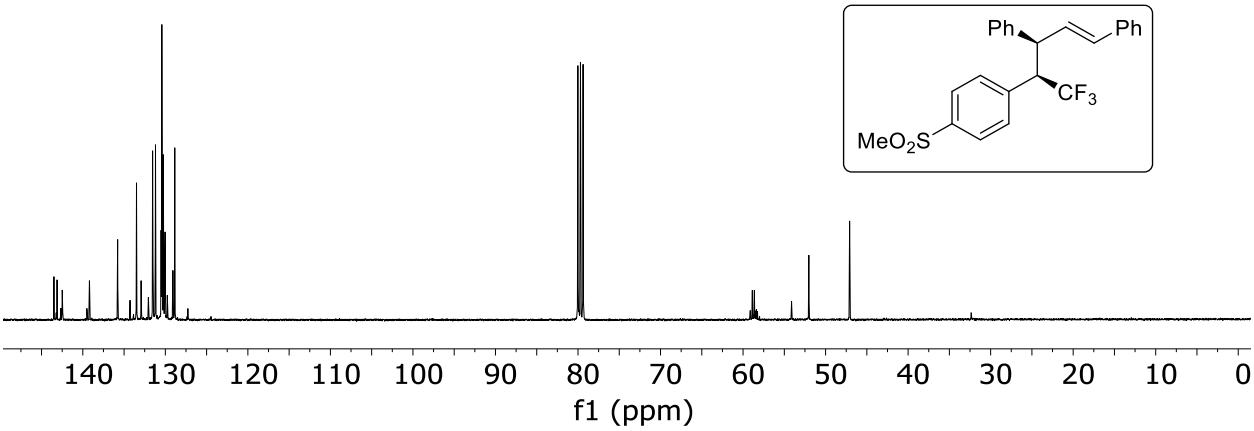

**$^{19}$F NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ea)**



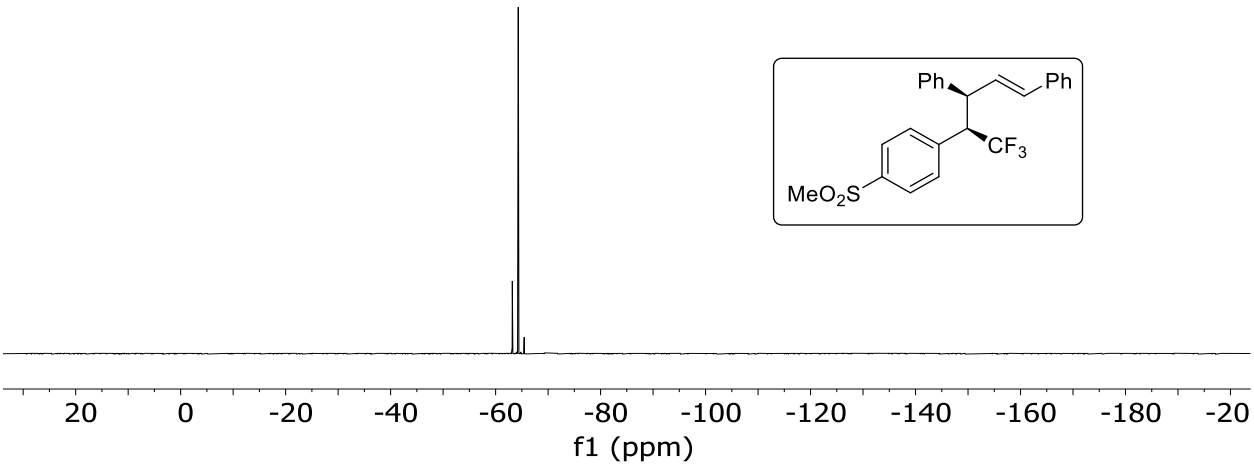
**$^{1}$H NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(4-(methylsulfonyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3fa)**



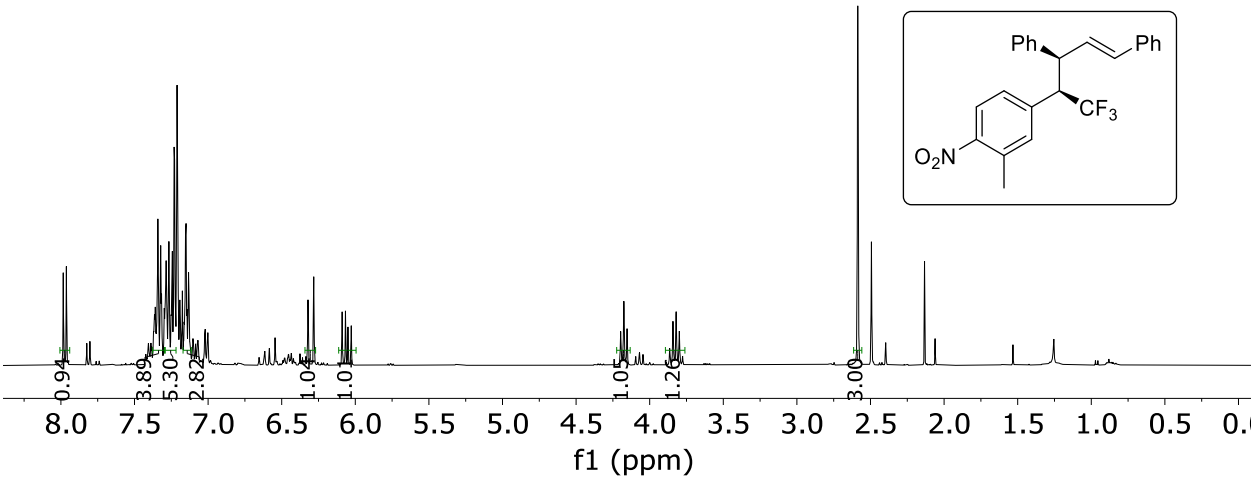

**$^{13}$C NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(4-(methylsulfonyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3fa)**



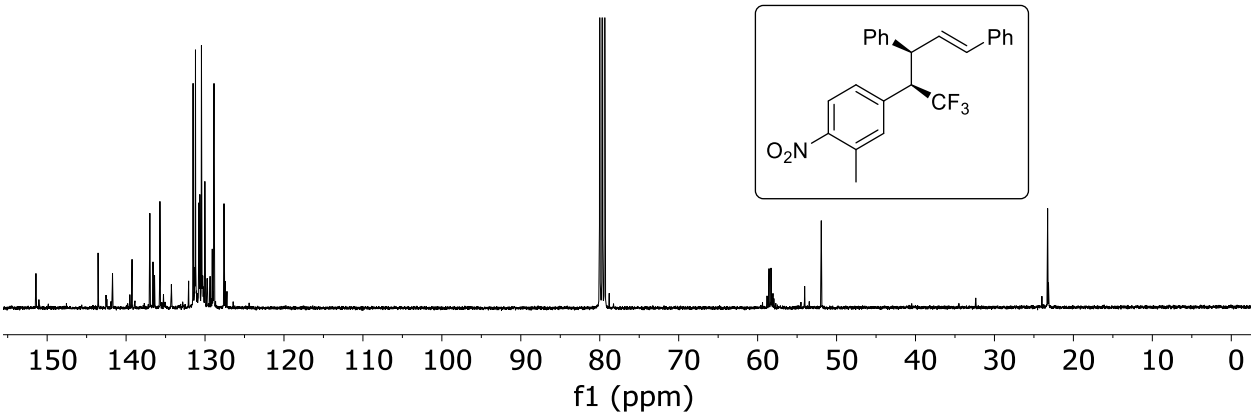

**$^{19}$F NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(4-(methylsulfonyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3fa)**



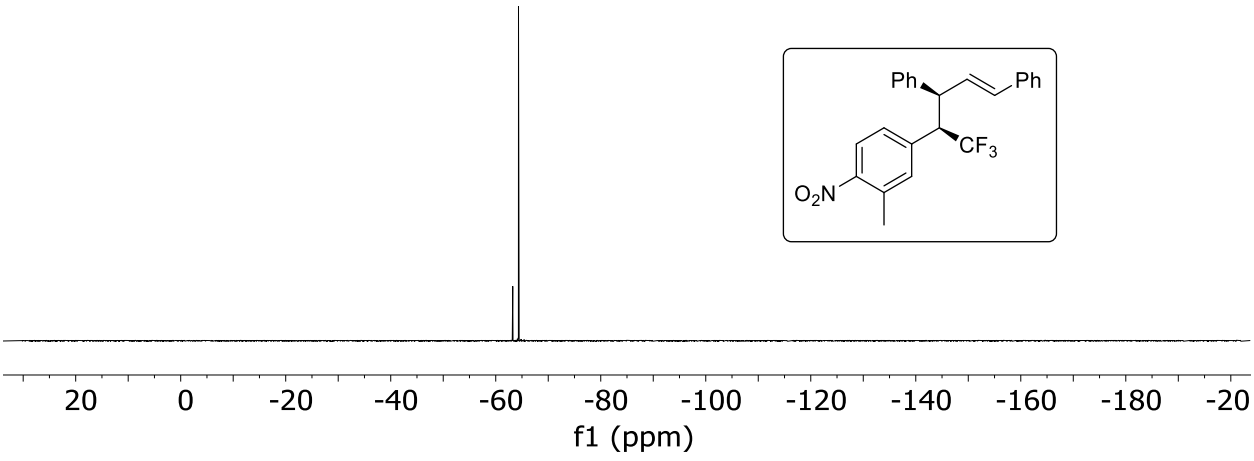
**$^{1}$H NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(3-methyl-4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ga)**



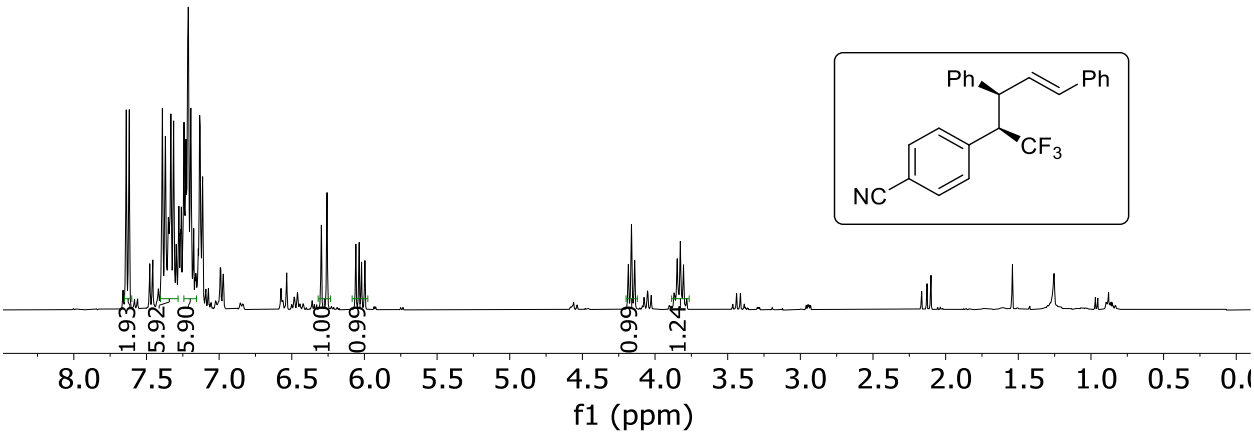

**$^{13}$C NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(3-methyl-4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ga)**



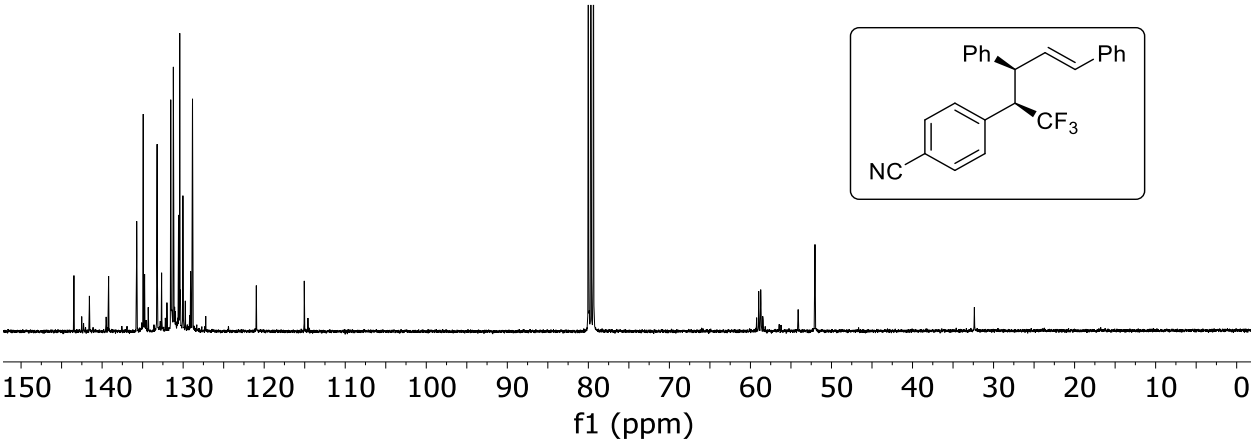

**$^{19}$F NMR spectrum of (*E*)-(5,5,5-trifluoro-4-(3-methyl-4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ga)**



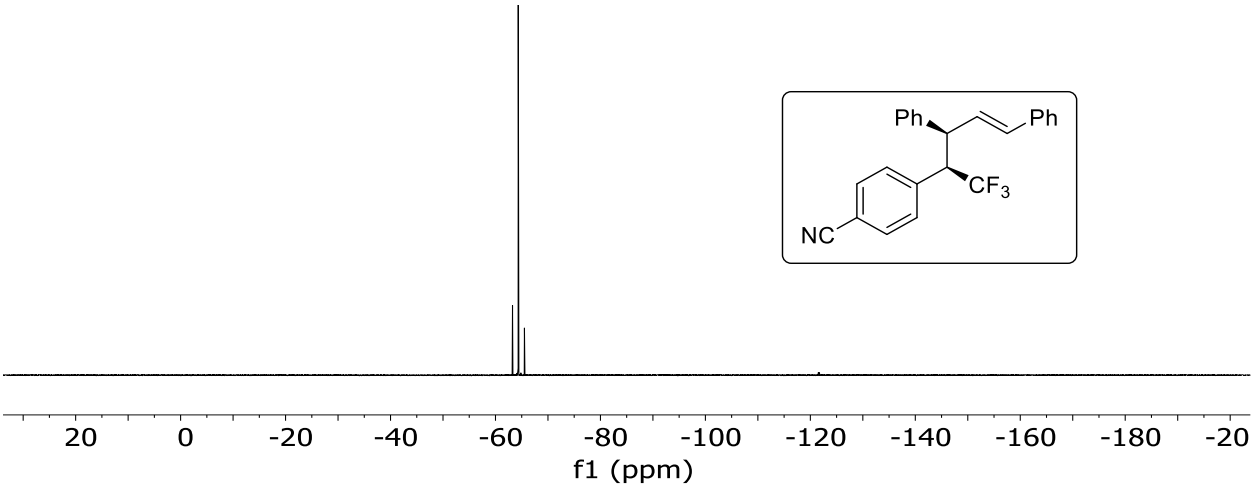
**$^{1}$H NMR spectrum of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzonitrile (3ha)**



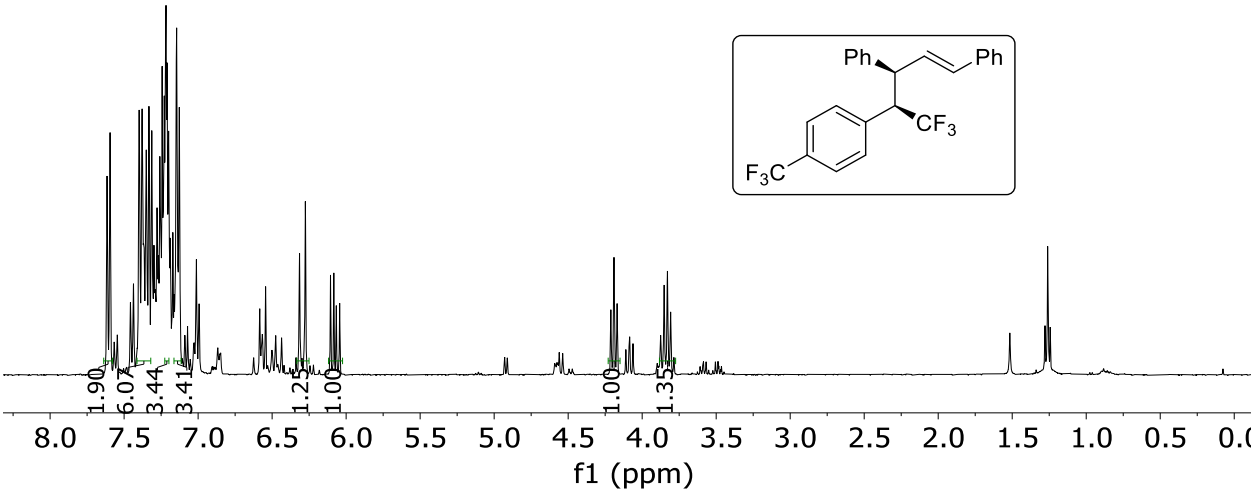

**$^{13}$C NMR spectrum of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzonitrile (3ha)**



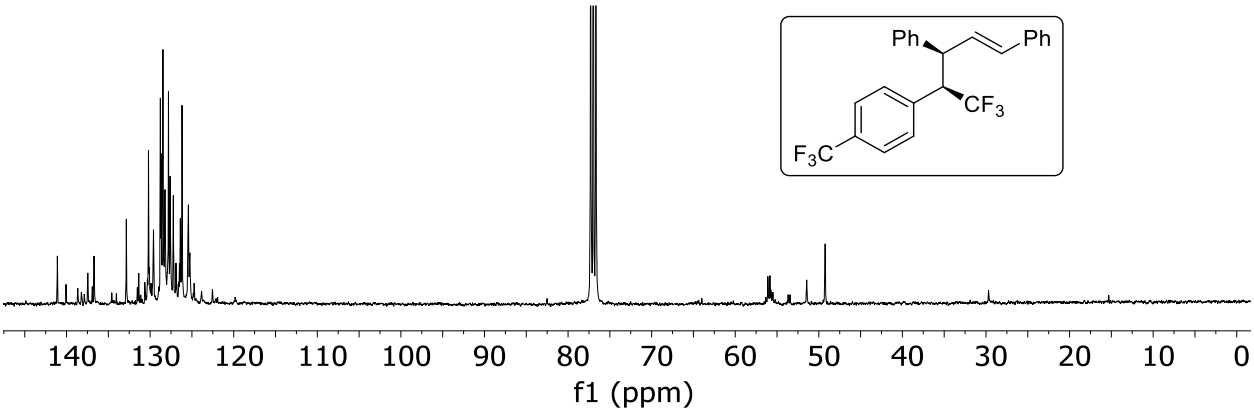

**$^{19}$F NMR spectrum of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzonitrile (3ha)**



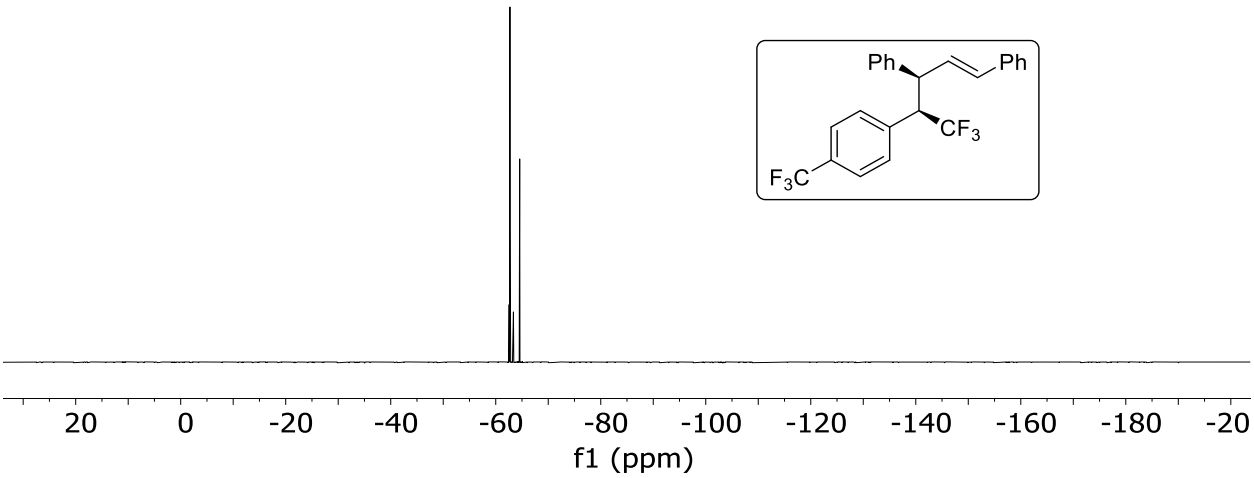
**$^{1}$H NMR spectrum of (*E*)-(5,5,5-Trifluoro-4-(4-(trifluoromethyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3ia)**



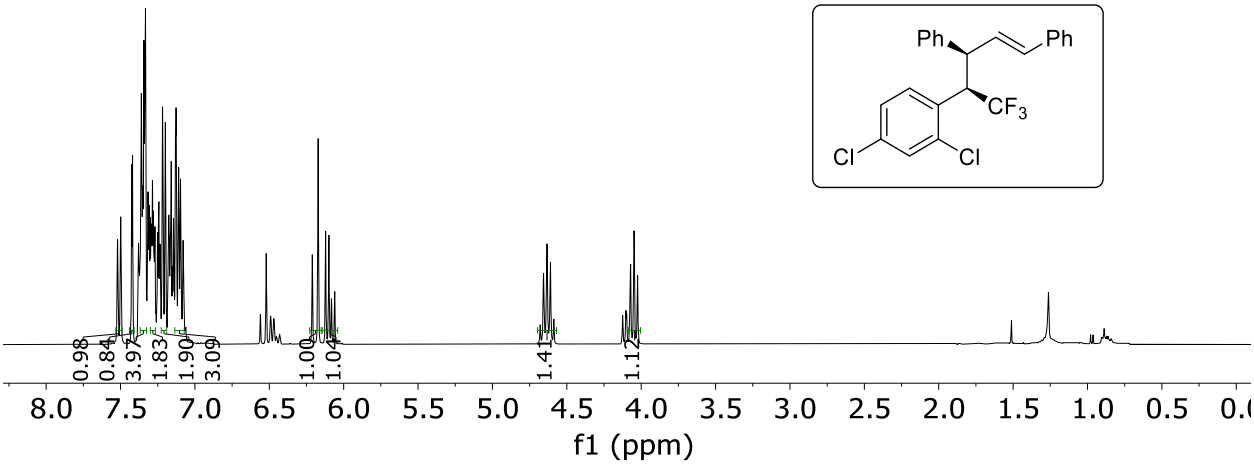

**$^{13}$C NMR spectrum of (*E*)-(5,5,5-Trifluoro-4-(4-(trifluoromethyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3ia)**



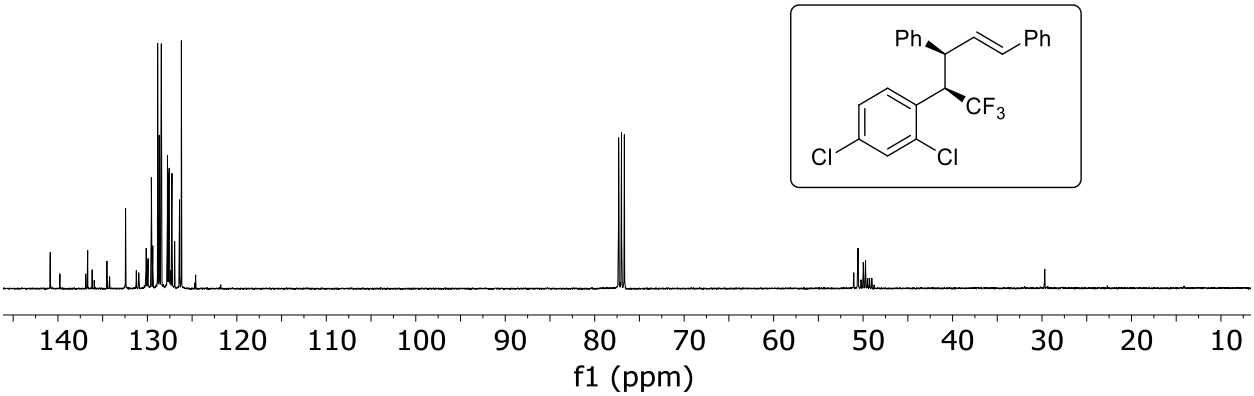

**$^{19}$F NMR spectrum of (*E*)-(5,5,5-Trifluoro-4-(4-(trifluoromethyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3ia)**



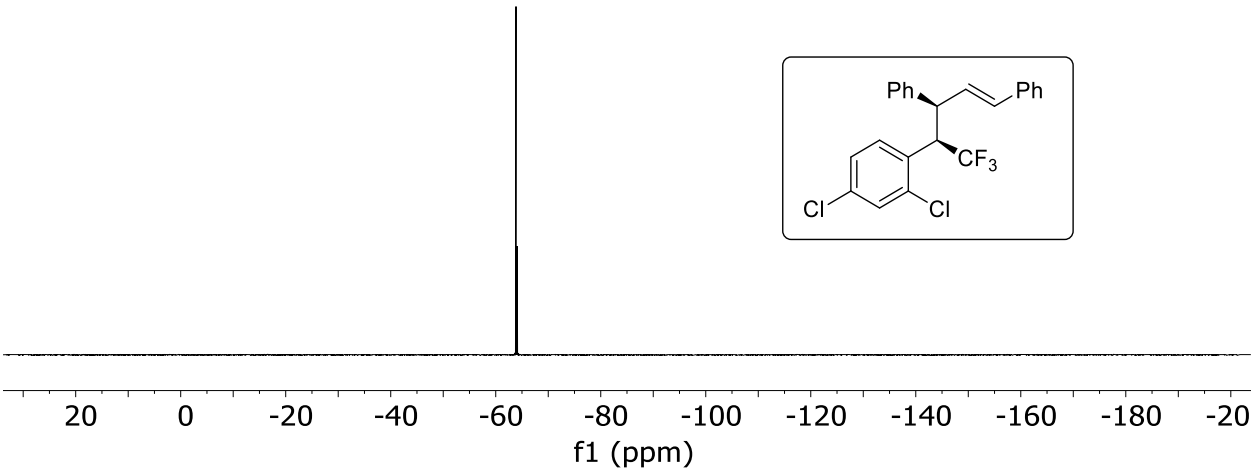
**$^{1}$H NMR spectrum of (*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja)**



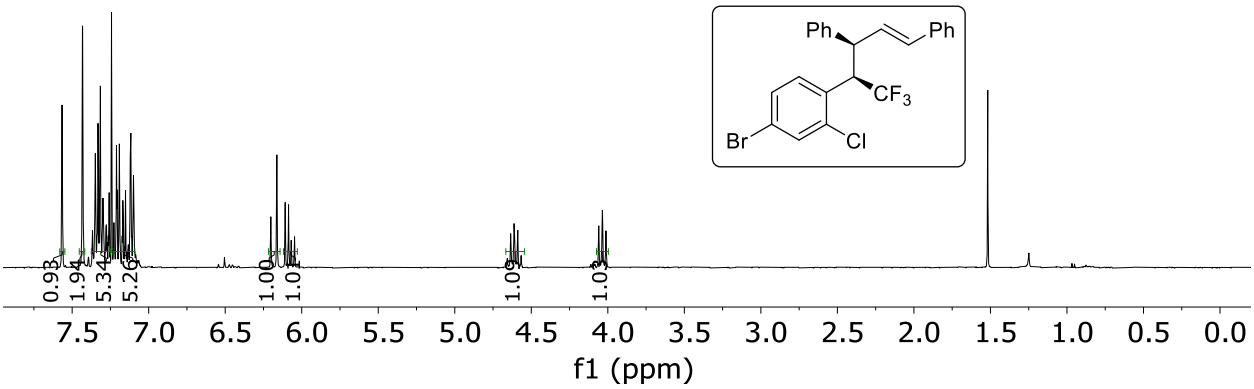

**$^{13}$C NMR spectrum of (*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja)**



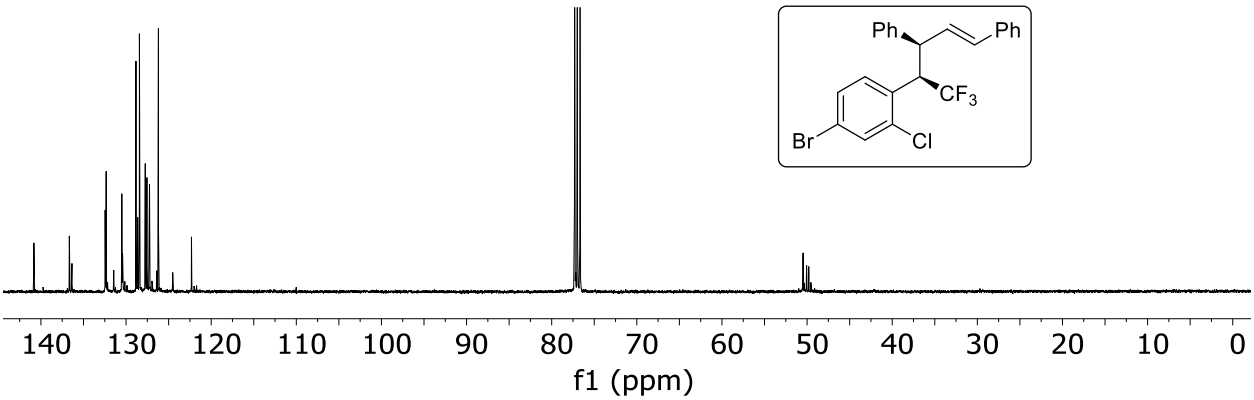

**$^{19}$F NMR spectrum of (*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja)**



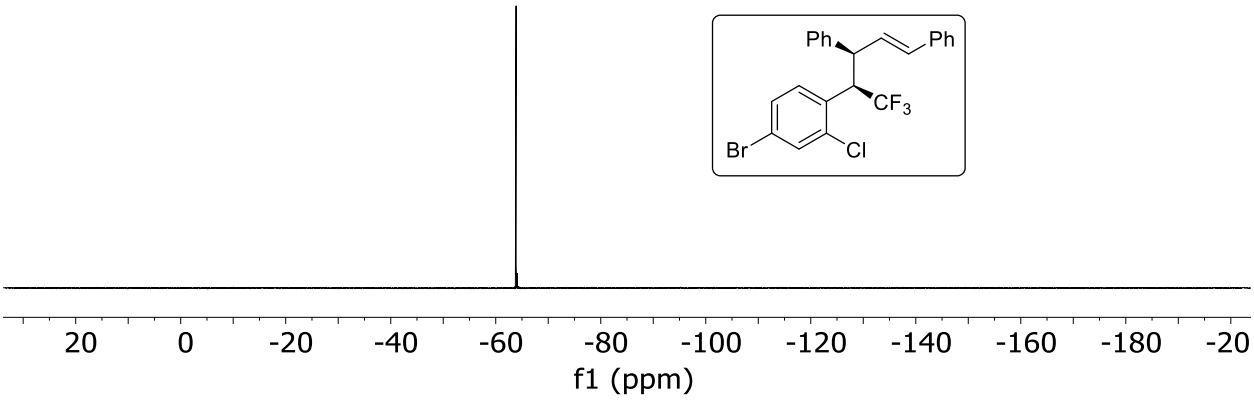
**$^{1}$H NMR spectrum of (*E*)-(4-(4-Bromo-2-chlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ka)**



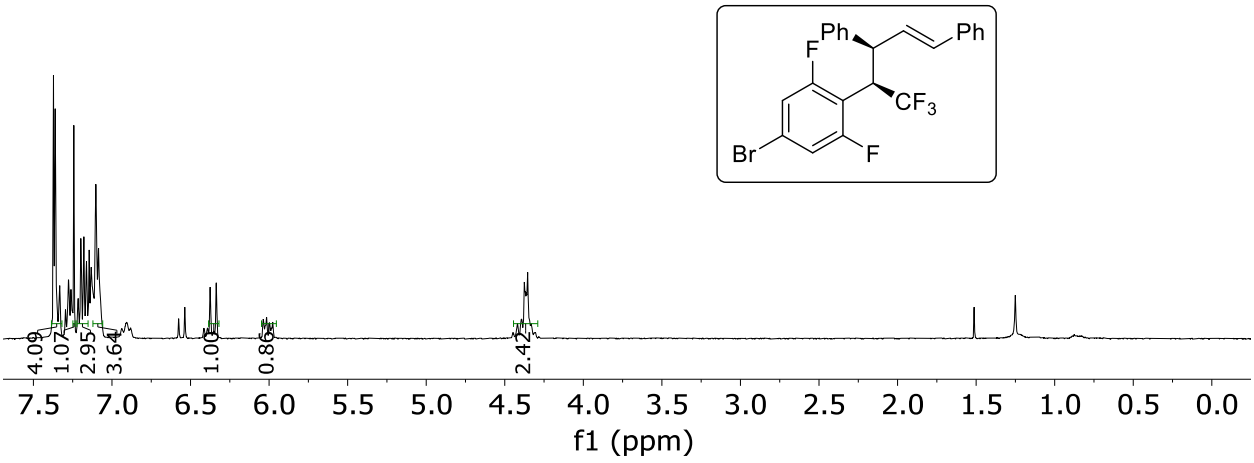

**$^{13}$C NMR spectrum of (*E*)-(4-(4-Bromo-2-chlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ka)**



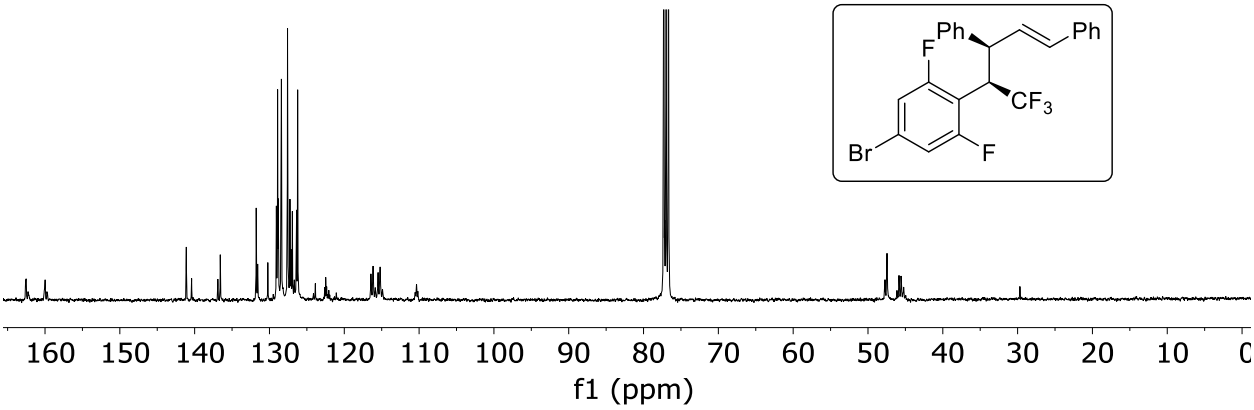

**$^{19}$F NMR spectrum of (*E*)-(4-(4-Bromo-2-chlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ka)**



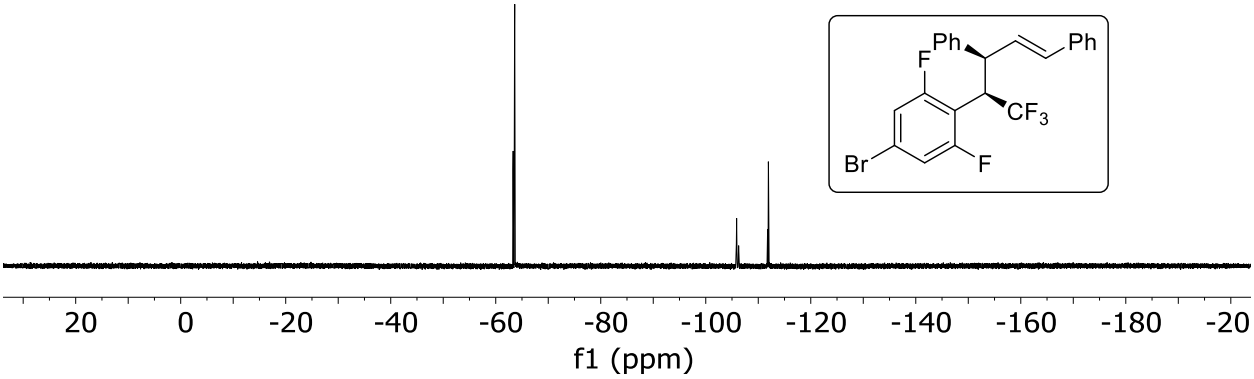
**$^{1}$H NMR spectrum of (*E*)-(4-(4-Bromo-2,6-difluorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3la)**



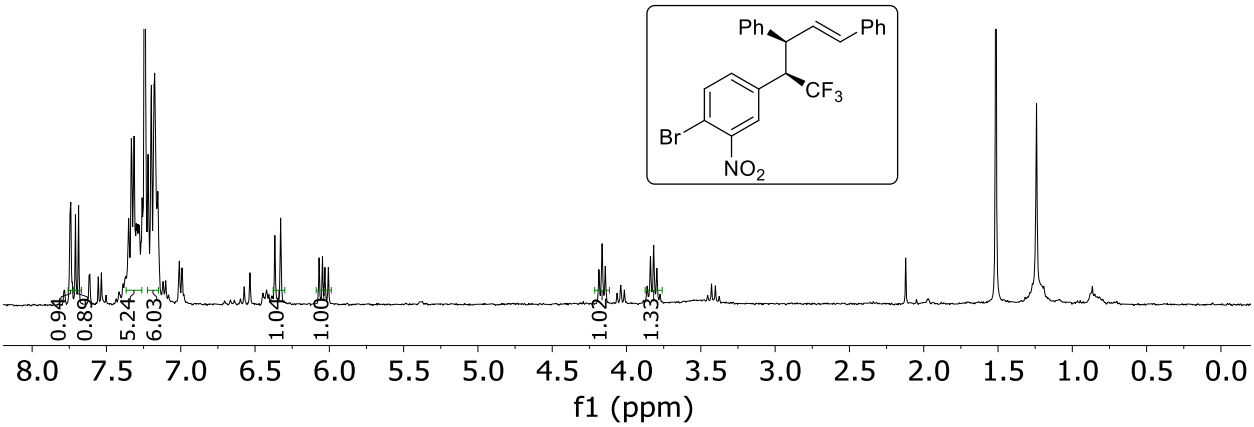

**$^{13}$C NMR spectrum of (*E*)-(4-(4-Bromo-2,6-difluorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3la)**



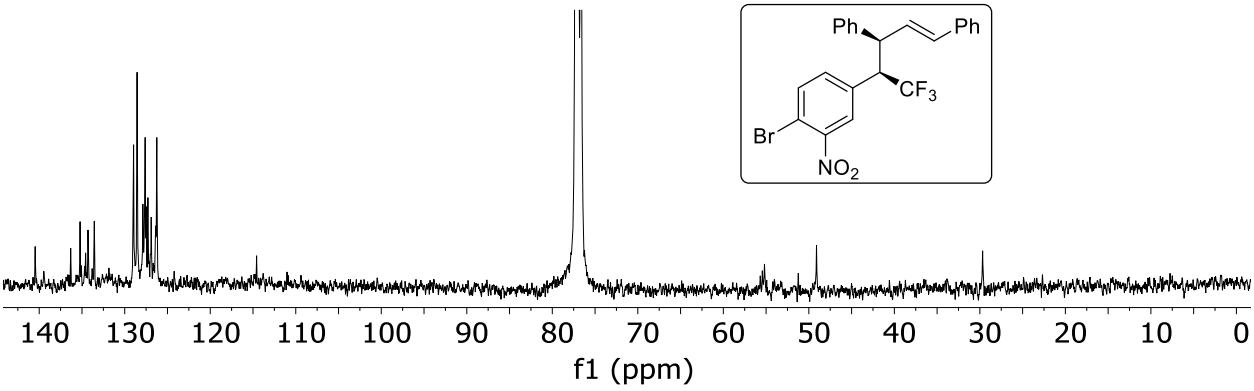

**$^{19}$F NMR spectrum of (*E*)-(4-(4-Bromo-2,6-difluorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3la)**



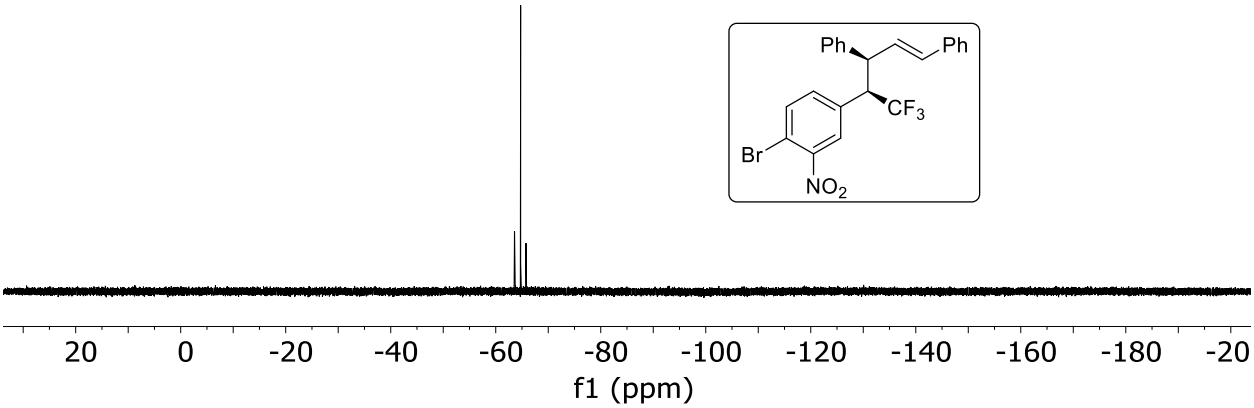
**$^{1}$H NMR spectrum of (*E*)-(4-(4-Bromo-3-nitrophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ma)**



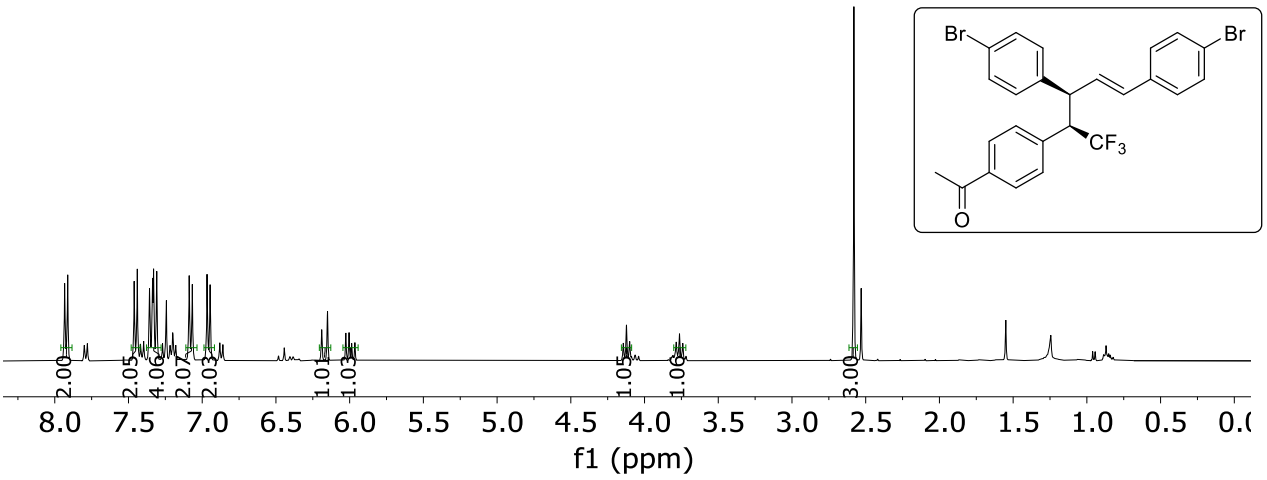

**$^{13}$C NMR spectrum of (*E*)-(4-(4-Bromo-3-nitrophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ma)**



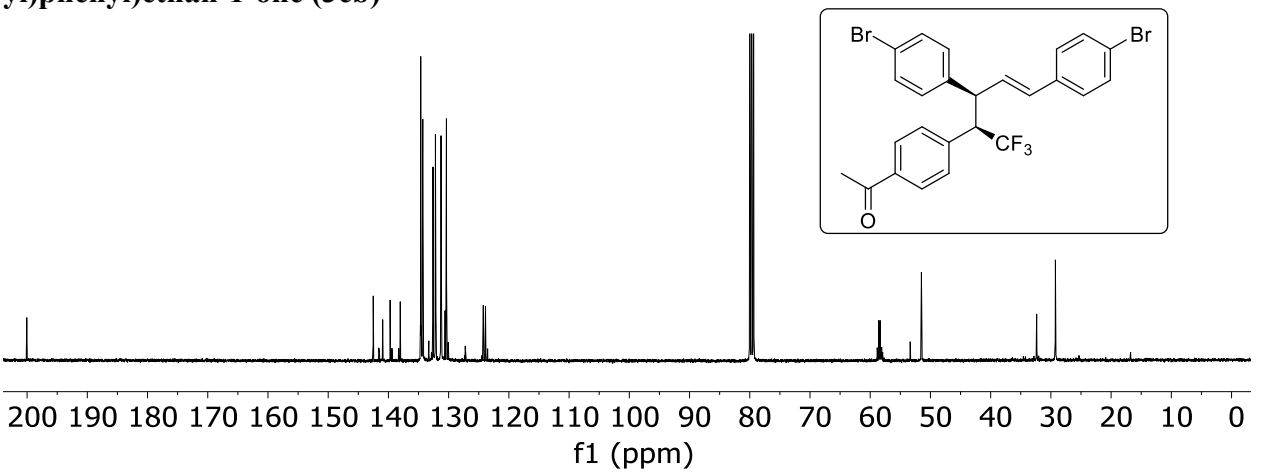

**$^{19}$F NMR spectrum of (*E*)-(4-(4-Bromo-3-nitrophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ma)**



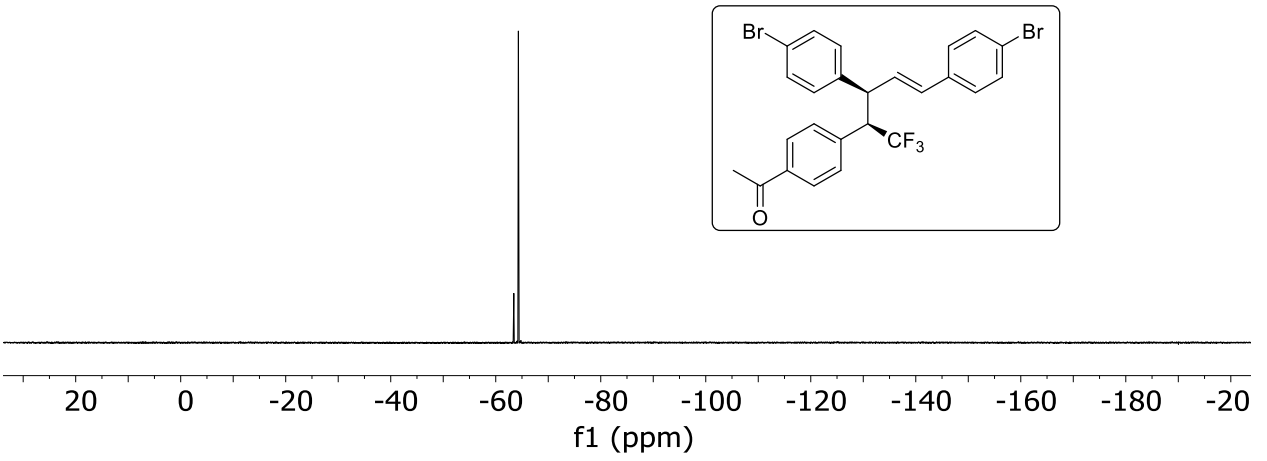
**$^{1}$H NMR spectrum of (*E*)-1-(4-(3,5-bis(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cb)**



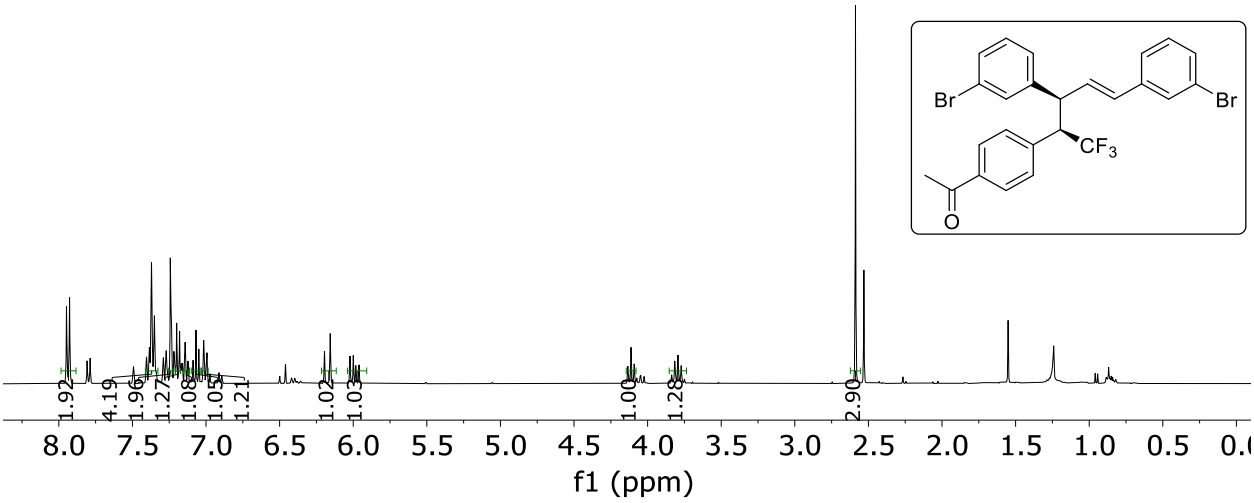

**$^{13}$C NMR spectrum of (*E*)-1-(4-(3,5-bis(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cb)**



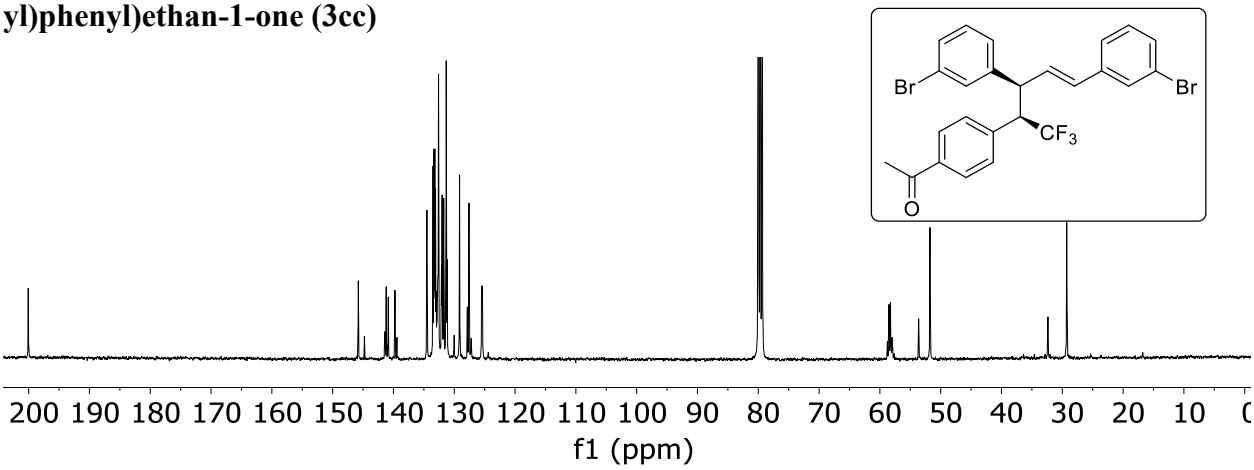

**$^{19}$F NMR spectrum of (*E*)-1-(4-(3,5-bis(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cb)**



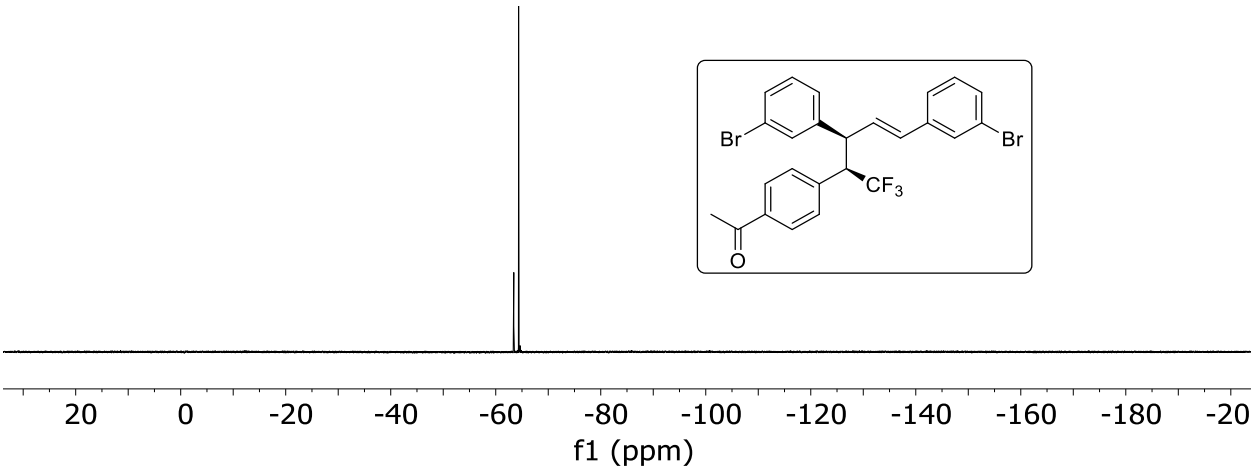
**$^{1}$H NMR spectrum of (*E*)-1-(4-(3,5-bis(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cc)**



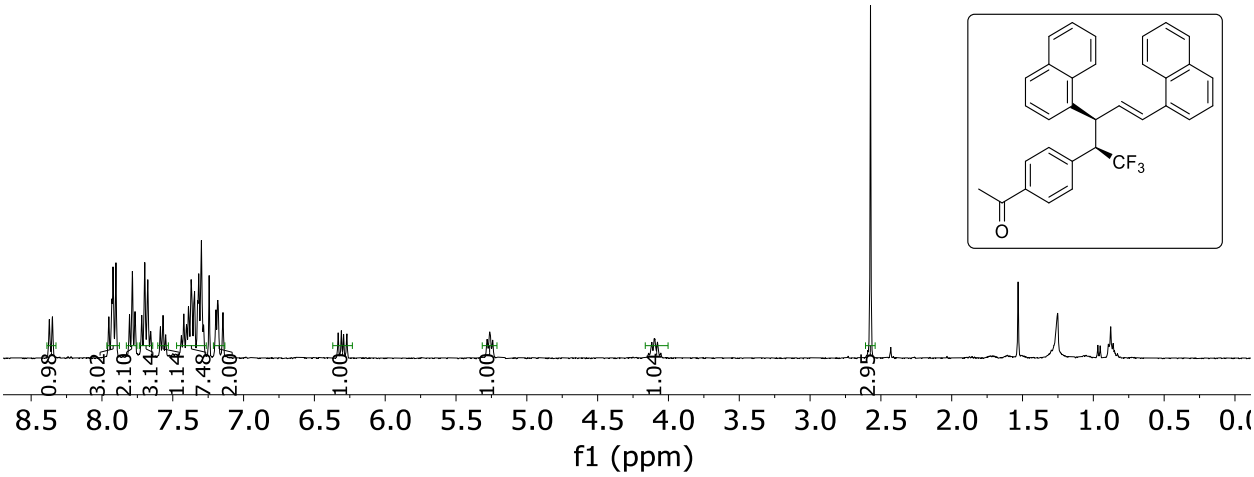

**$^{13}$C NMR spectrum of (*E*)-1-(4-(3,5-bis(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cc)**



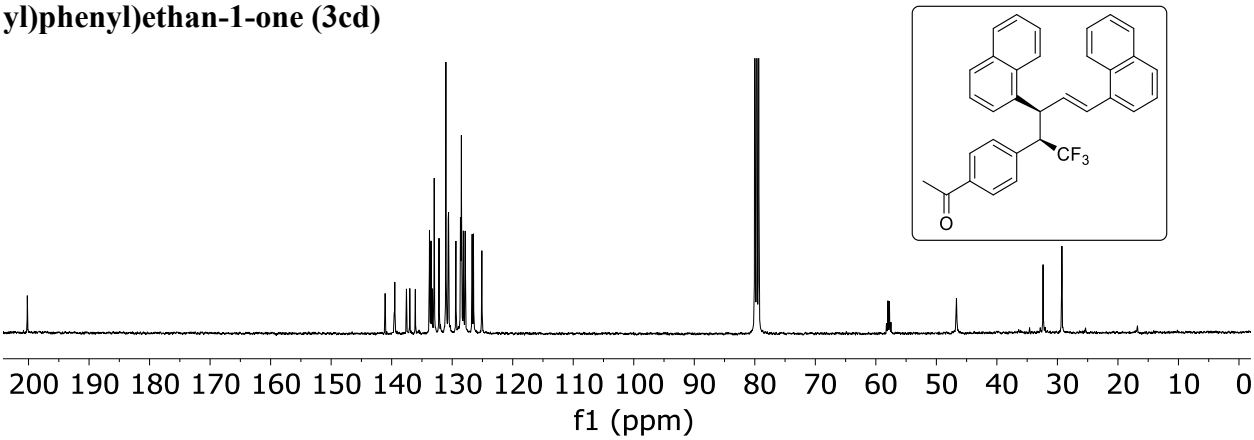

**$^{19}$F NMR spectrum of (*E*)-1-(4-(3,5-bis(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cc)**



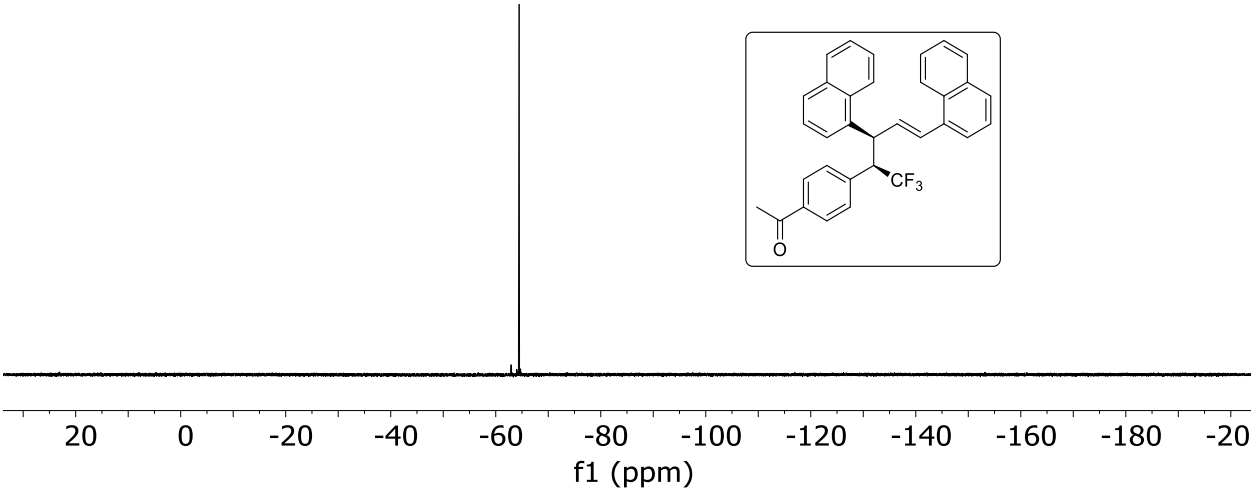
**$^{1}$H NMR spectrum of (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**



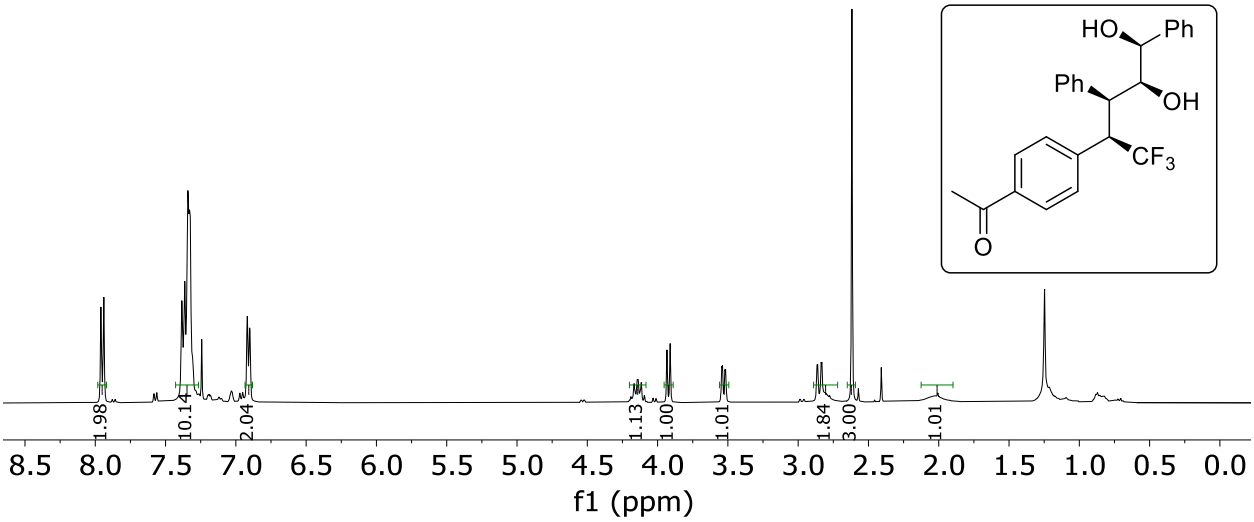

**$^{13}$C NMR spectrum of (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**



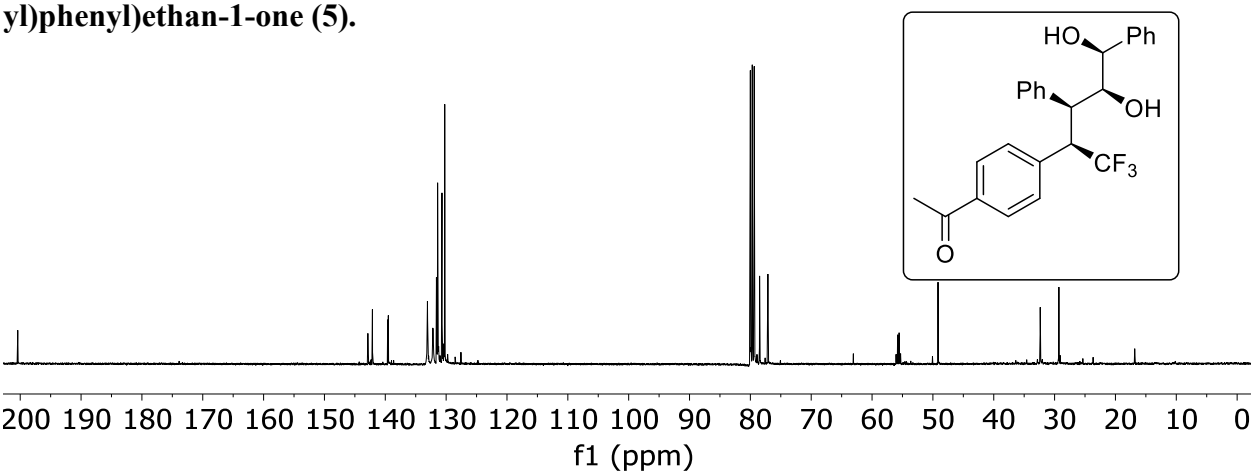

**$^{19}$F NMR spectrum of (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**



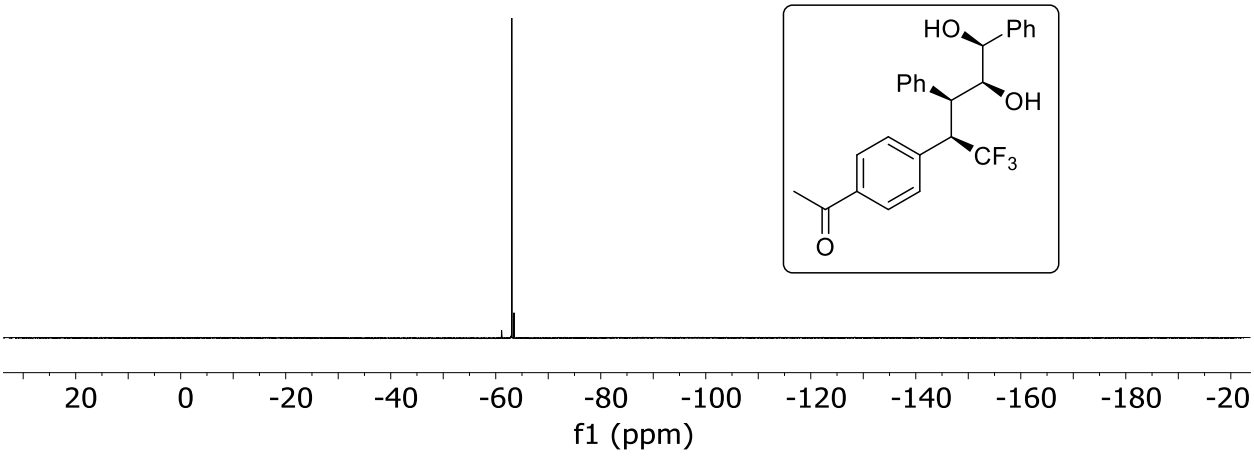
**$^{1}$H NMR spectrum of 1-(4-(1,1,1-trifluoro-4,5-dihydroxy-3,5-diphenylpentan-2-yl)phenyl)ethan-1-one (5).**



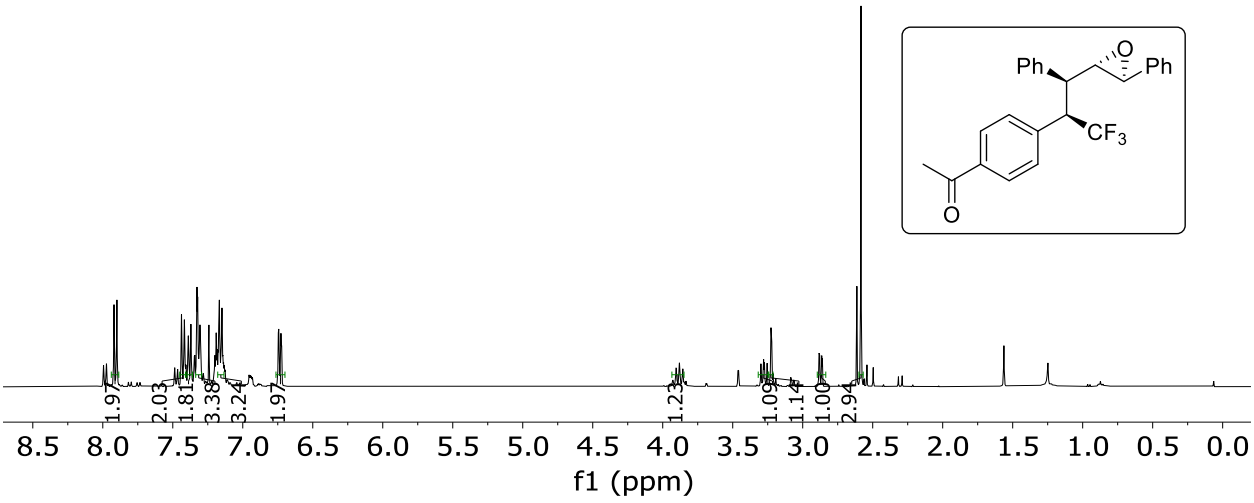

**$^{13}$C NMR spectrum of 1-(4-(1,1,1-trifluoro-4,5-dihydroxy-3,5-diphenylpentan-2-yl)phenyl)ethan-1-one (5).**



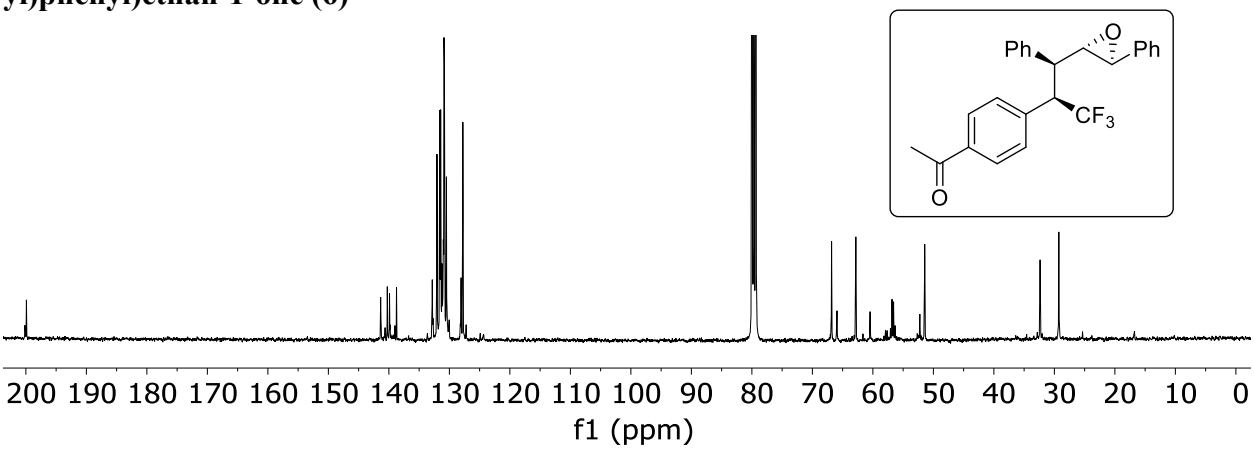

**$^{19}$F NMR spectrum of 1-(4-(1,1,1-trifluoro-4,5-dihydroxy-3,5-diphenylpentan-2-yl)phenyl)ethan-1-one (5).**



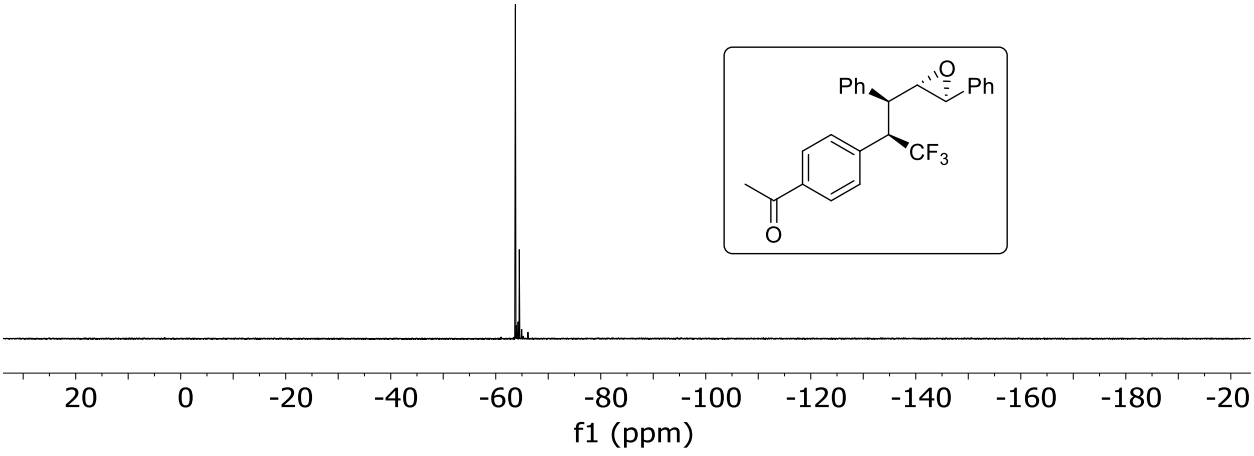
**$^{1}$H NMR spectrum of 1-(4-(1,1,1-trifluoro-3-phenyl-3-(3-phenyloxiran-2-yl)propan-2-yl)phenyl)ethan-1-one (6)**



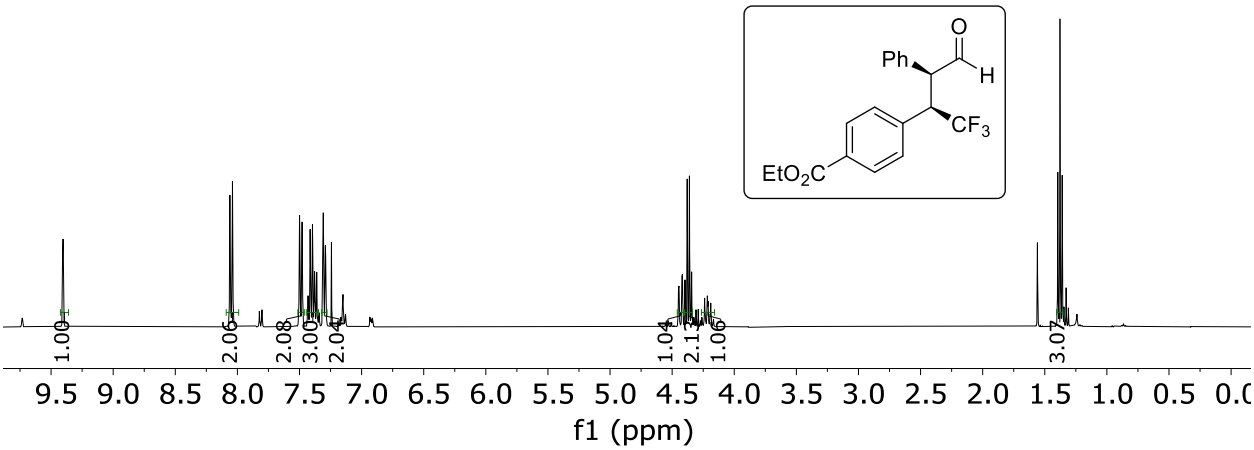

**$^{13}$C NMR spectrum of 1-(4-(1,1,1-trifluoro-3-phenyl-3-(3-phenyloxiran-2-yl)propan-2-yl)phenyl)ethan-1-one (6)**



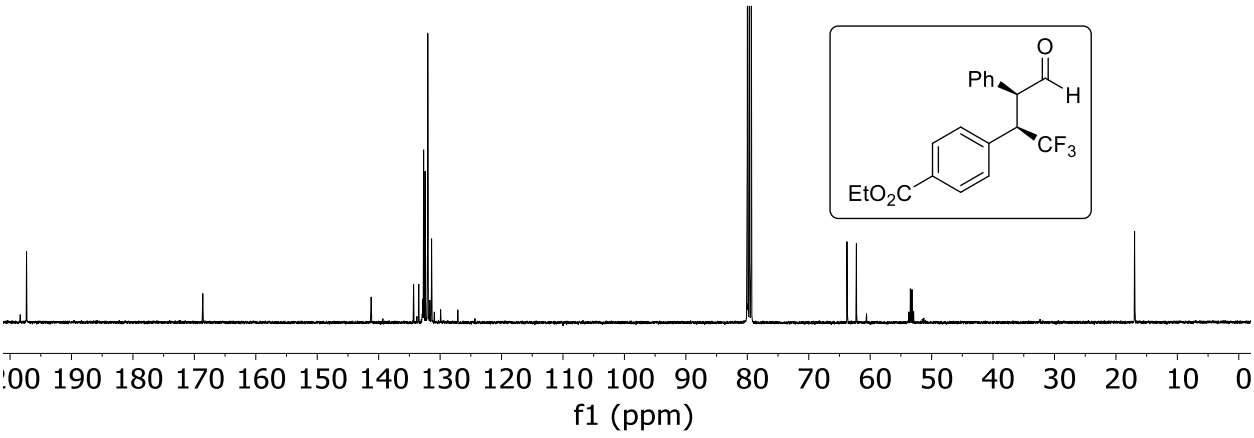

**$^{19}$F NMR spectrum of 1-(4-(1,1,1-trifluoro-3-phenyl-3-(3-phenyloxiran-2-yl)propan-2-yl)phenyl)ethan-1-one (6)**



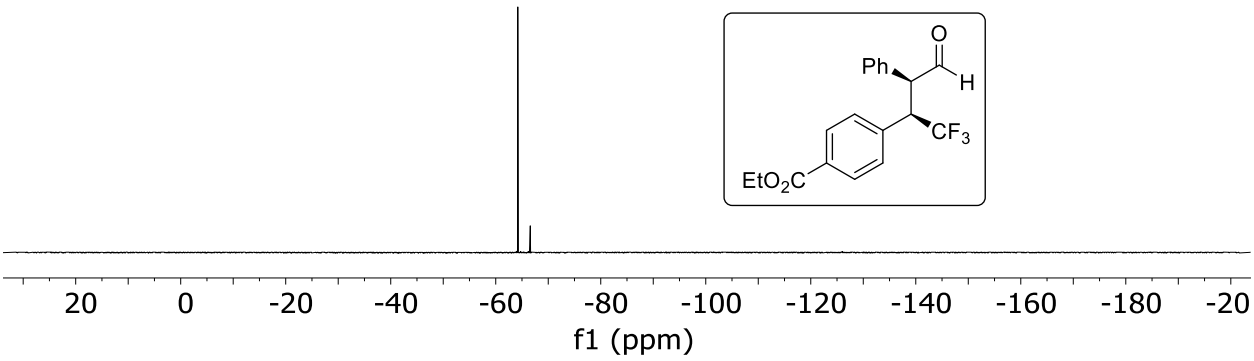
**$^{1}$H NMR spectrum of ethyl 4-(1,1,1-trifluoro-4-oxo-3-phenylbutan-2-yl)benzoate (7)**



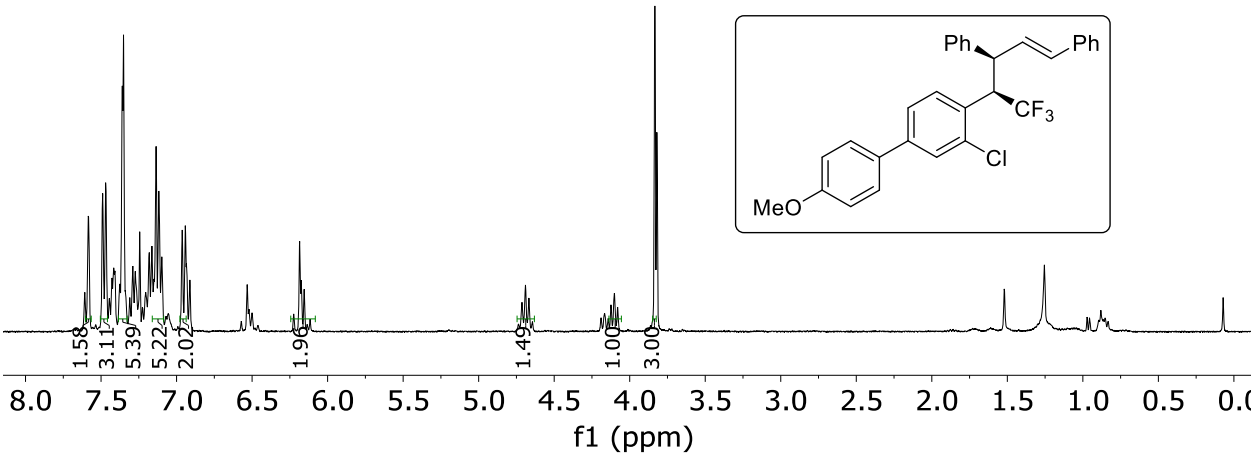

**$^{13}$C NMR spectrum of ethyl 4-(1,1,1-trifluoro-4-oxo-3-phenylbutan-2-yl)benzoate (7)**



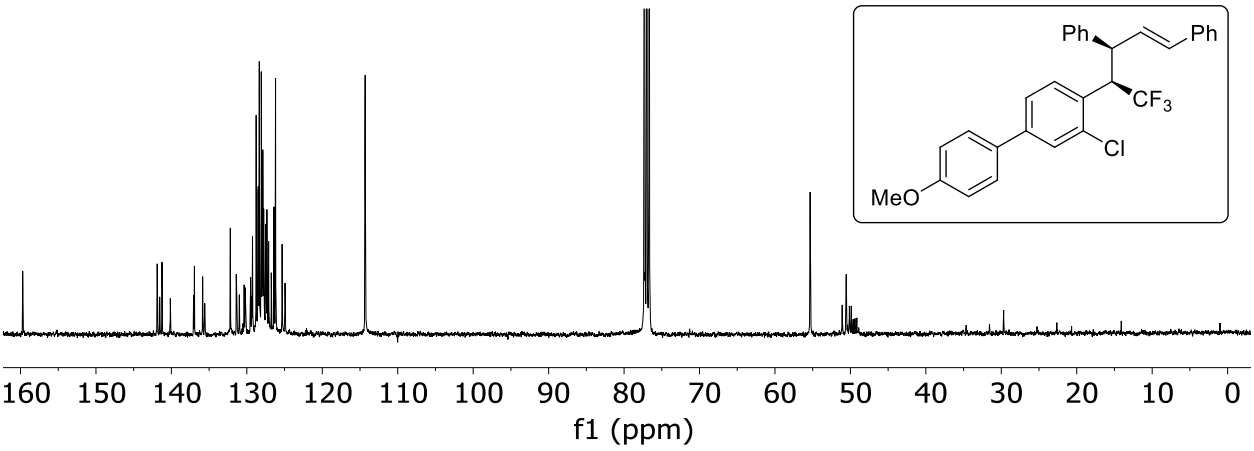

**$^{19}$F NMR spectrum of ethyl 4-(1,1,1-trifluoro-4-oxo-3-phenylbutan-2-yl)benzoate (7)**



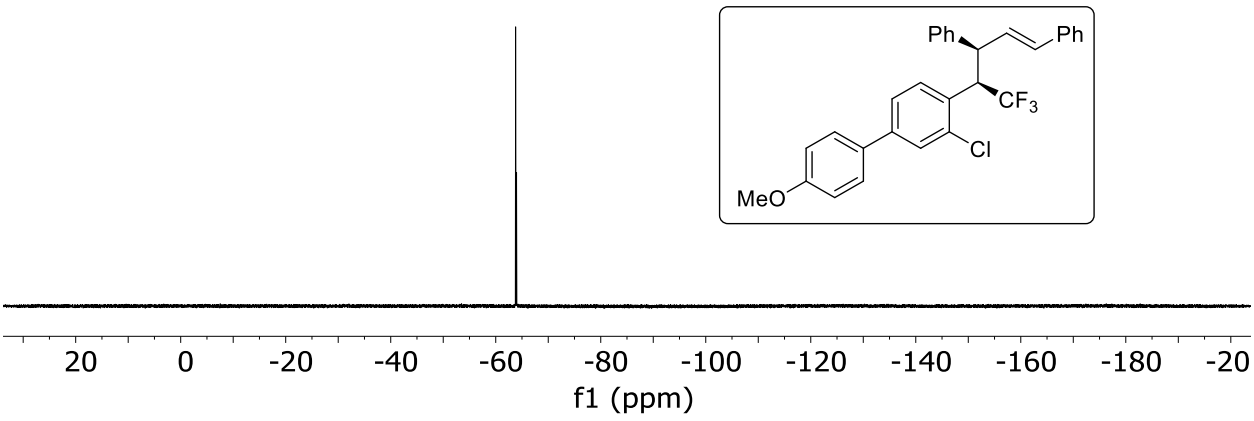
**$^{1}$H NMR spectrum of (*E*)-3-chloro-4'-methoxy-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)-1,1'-biphenyl (8)**




**$^{13}$C NMR spectrum of (*E*)-3-chloro-4'-methoxy-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)-1,1'-biphenyl (8)**

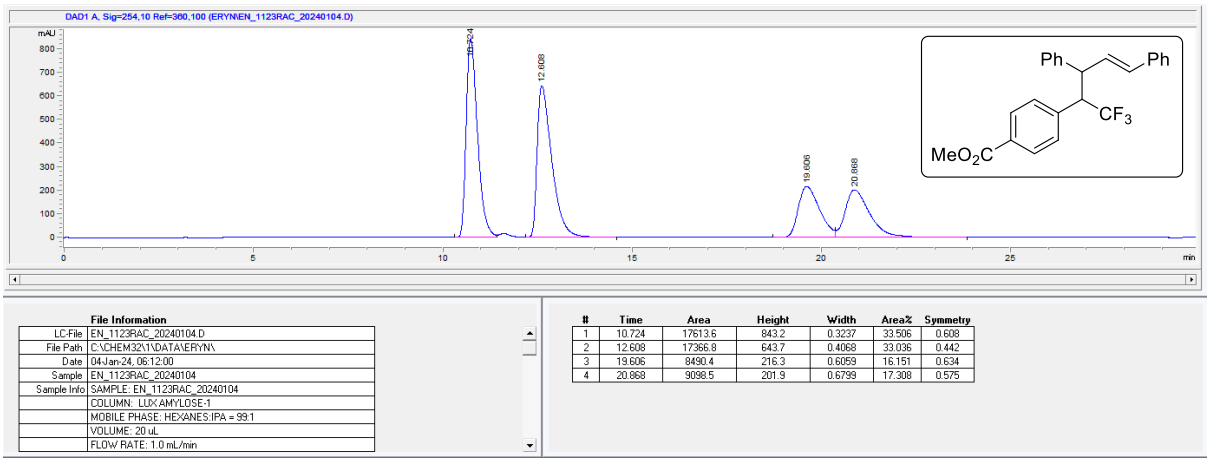



**$^{19}$F NMR spectrum of (*E*)-3-chloro-4'-methoxy-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)-1,1'-biphenyl (8)**



## 7. HPLC chromatograms

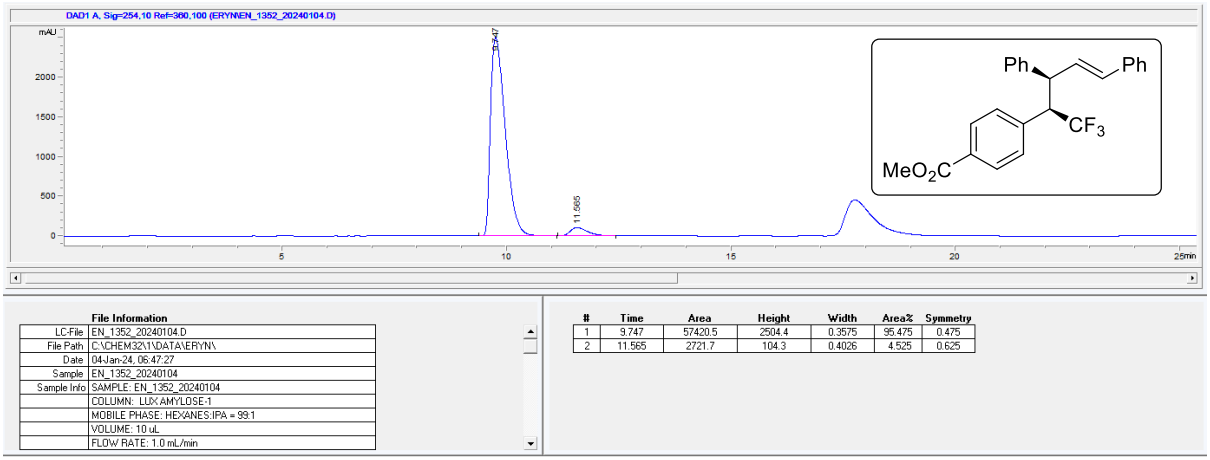
### HPLC of *racemic* methyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3aa)




| File Information | |
|---|---|
| LC-File | EN_1123RAC_20240104.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 04-Jan-24, 06:12:00 |
| Sample | EN_1123RAC_20240104 |
| Sample Info | SAMPLE: EN_1123RAC_20240104 |
| | COLUMN: LUX AMYLOSE-1 |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 10.724 | 17613.6 | 843.2 | 0.3237 | 33.506 | 0.608 |
| 2 | 12.608 | 17366.8 | 643.7 | 0.4068 | 33.036 | 0.442 |
| 3 | 19.606 | 8490.4 | 216.3 | 0.6059 | 16.151 | 0.634 |
| 4 | 20.868 | 9098.5 | 201.9 | 0.6799 | 17.308 | 0.575 |

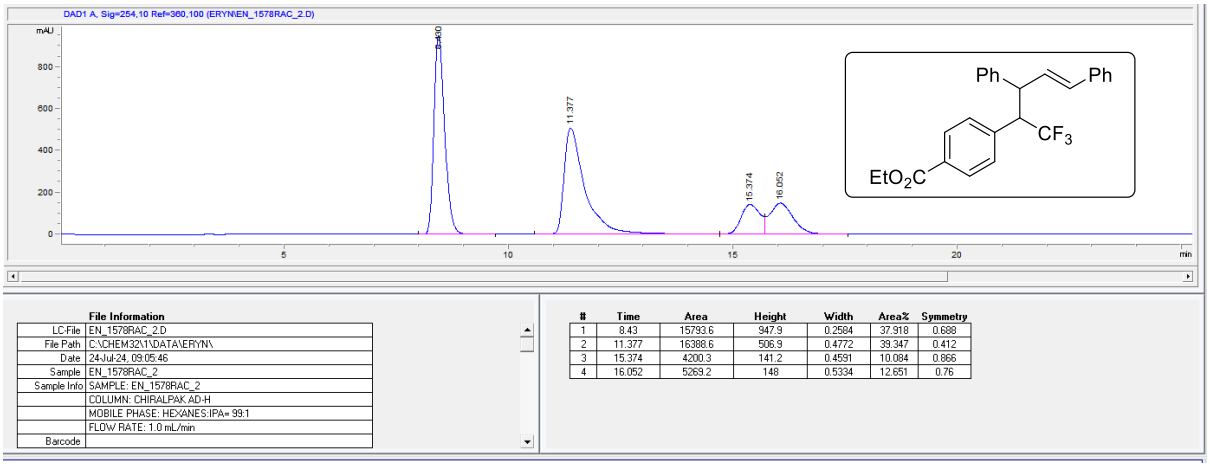
### HPLC of methyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3aa)




| File Information | |
|---|---|
| LC-File | EN_1352_20240104.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 04-Jan-24, 06:47:27 |
| Sample | EN_1352_20240104 |
| Sample Info | SAMPLE: EN_1352_20240104 |
| | COLUMN: LUX AMYLOSE-1 |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | VOLUME: 10 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.747 | 57420.5 | 2504.4 | 0.3575 | 95.475 | 0.475 |
| 2 | 11.565 | 2721.7 | 104.3 | 0.4026 | 4.525 | 0.625 |

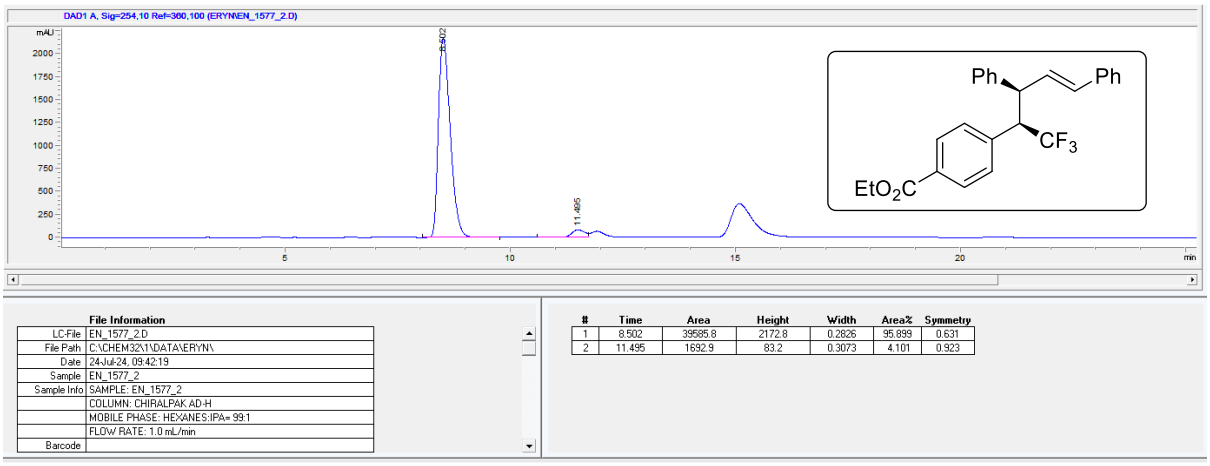
## HPLC of *racemic* ethyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3ba)




| File Information | |
|---|---|
| LC-File | EN_1578RAC_2.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 24-Jul-24, 09:05:46 |
| Sample | EN_1578RAC_2 |
| Sample Info | SAMPLE: EN_1578RAC_2 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 8.43 | 15793.6 | 947.9 | 0.2584 | 37.918 | 0.688 |
| 2 | 11.377 | 16388.6 | 506.9 | 0.4772 | 39.347 | 0.412 |
| 3 | 15.374 | 4200.3 | 141.2 | 0.4591 | 10.084 | 0.866 |
| 4 | 16.052 | 5269.2 | 148 | 0.5334 | 12.651 | 0.76 |

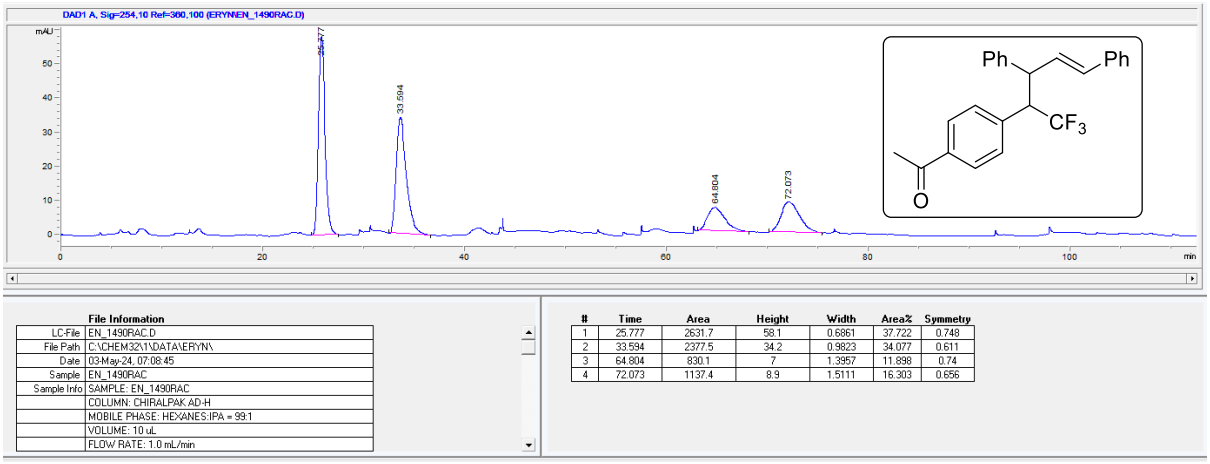
## HPLC of ethyl (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzoate (3ba)




| File Information | |
|---|---|
| LC-File | EN_1577_2.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 24-Jul-24, 09:42:19 |
| Sample | EN_1577_2 |
| Sample Info | SAMPLE: EN_1577_2 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 8.502 | 39585.8 | 2172.8 | 0.2826 | 95.899 | 0.631 |
| 2 | 11.495 | 1692.9 | 83.2 | 0.3073 | 4.101 | 0.923 |

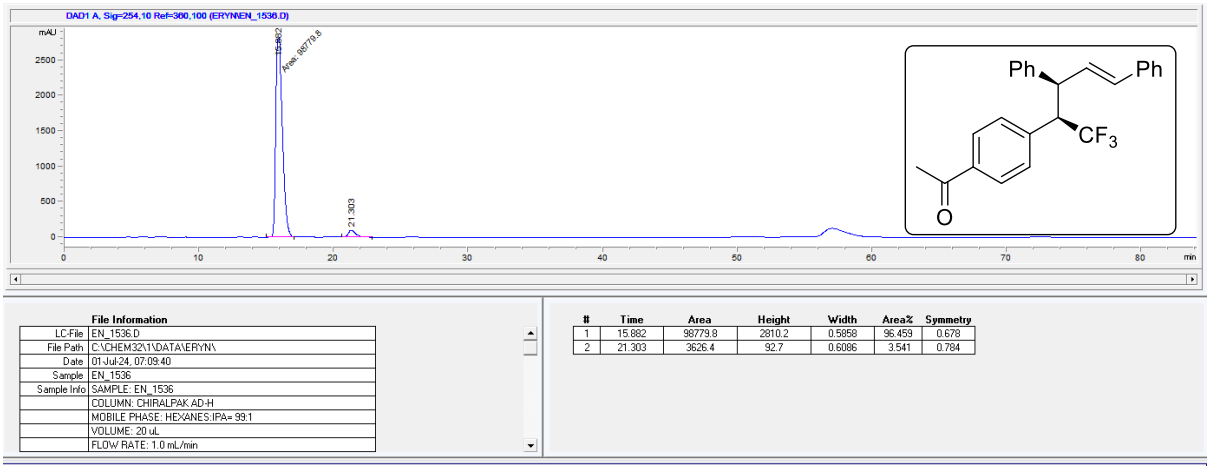
**HPLC of *racemic* (*E*)-1-(4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)phenyl)ethan-1-one (3ca)**




| File Information | |
|---|---|
| LC-File | EN_1490RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 03-May-24, 07:08:45 |
| Sample | EN_1490RAC |
| Sample Info | SAMPLE: EN_1490RAC |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | VOLUME: 10 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 25.777 | 2631.7 | 58.1 | 0.6861 | 37.722 | 0.748 |
| 2 | 33.594 | 2377.5 | 34.2 | 0.9823 | 34.077 | 0.611 |
| 3 | 64.804 | 830.1 | 7 | 1.3957 | 11.898 | 0.74 |
| 4 | 72.073 | 1137.4 | 8.9 | 1.5111 | 16.303 | 0.656 |

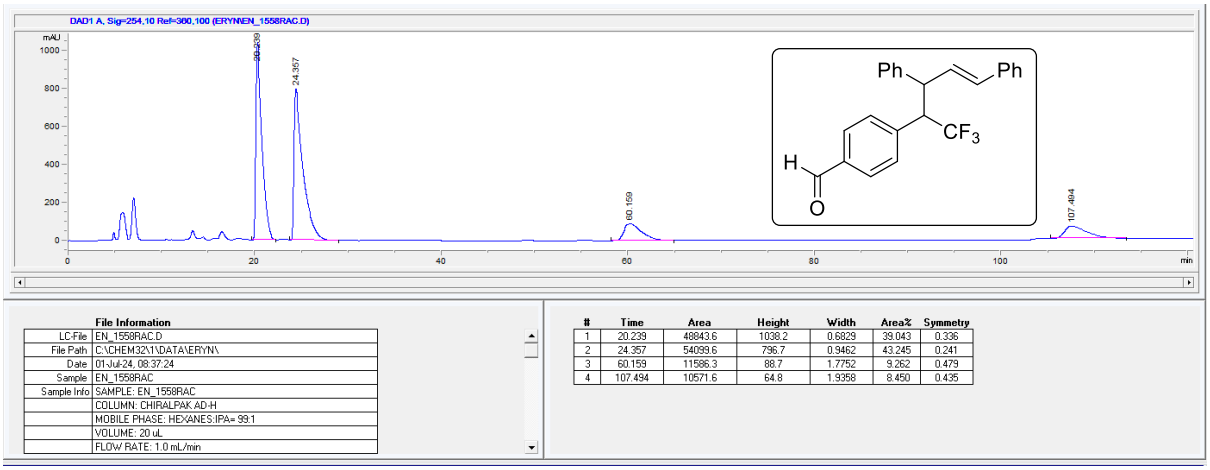
**HPLC of (*E*)-1-(4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)phenyl)ethan-1-one (3ca)**




| File Information | |
|---|---|
| LC-File | EN_1536.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 01-Jul-24, 07:09:40 |
| Sample | EN_1536 |
| Sample Info | SAMPLE: EN_1536 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 15.882 | 98779.8 | 2810.2 | 0.5858 | 96.459 | 0.678 |
| 2 | 21.303 | 3626.4 | 92.7 | 0.6086 | 3.541 | 0.784 |

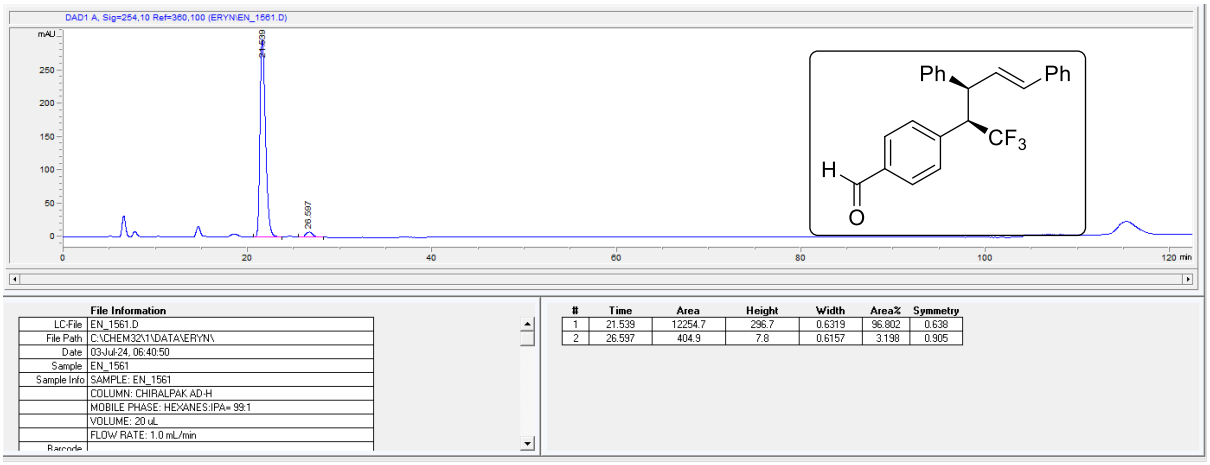
## HPLC of *racemic* (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzaldehyde (3da)




| File Information | |
|---|---|
| LC-File | EN_1558RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 01-Jul-24, 08:37:24 |
| Sample | EN_1558RAC |
| Sample Info | SAMPLE: EN_1558RAC |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 20.239 | 48843.6 | 1038.2 | 0.6829 | 39.043 | 0.336 |
| 2 | 24.357 | 54099.6 | 796.7 | 0.9462 | 43.245 | 0.241 |
| 3 | 60.159 | 11586.3 | 88.7 | 1.7752 | 9.262 | 0.479 |
| 4 | 107.494 | 10571.6 | 64.8 | 1.9358 | 8.450 | 0.435 |

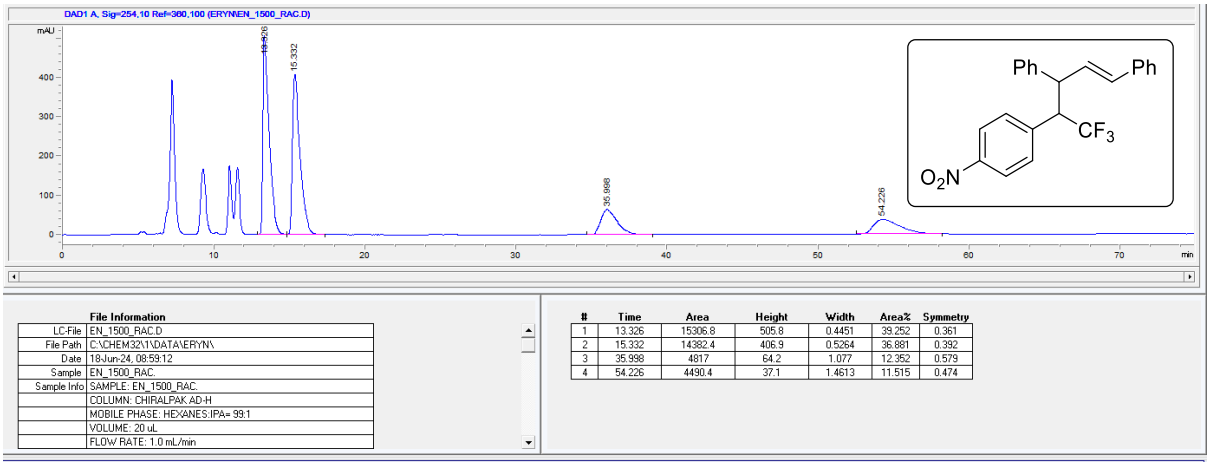
## HPLC of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzaldehyde (3da)




| File Information | |
|---|---|
| LC-File | EN_1561.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 03-Jul-24, 06:40:50 |
| Sample | EN_1561 |
| Sample Info | SAMPLE: EN_1561 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 21.539 | 12254.7 | 296.7 | 0.6319 | 96.802 | 0.638 |
| 2 | 26.597 | 404.9 | 7.8 | 0.6157 | 3.198 | 0.905 |

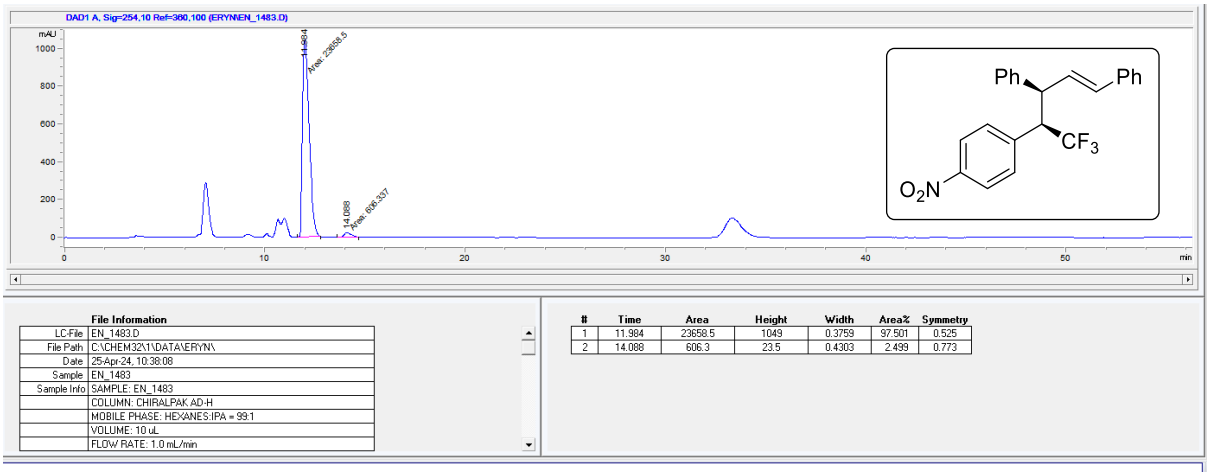
## HPLC of *racemic* (*E*)-(5,5,5-trifluoro-4-(4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ea)




| File Information | |
|---|---|
| LC-File | EN_1500_RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 18-Jun-24, 08:59:12 |
| Sample | EN_1500_RAC. |
| Sample Info | SAMPLE: EN_1500_RAC. |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 13.326 | 15306.8 | 505.8 | 0.4451 | 39.252 | 0.361 |
| 2 | 15.332 | 14382.4 | 406.9 | 0.5264 | 36.881 | 0.392 |
| 3 | 35.998 | 4817 | 64.2 | 1.077 | 12.352 | 0.579 |
| 4 | 54.226 | 4490.4 | 37.1 | 1.4613 | 11.515 | 0.474 |

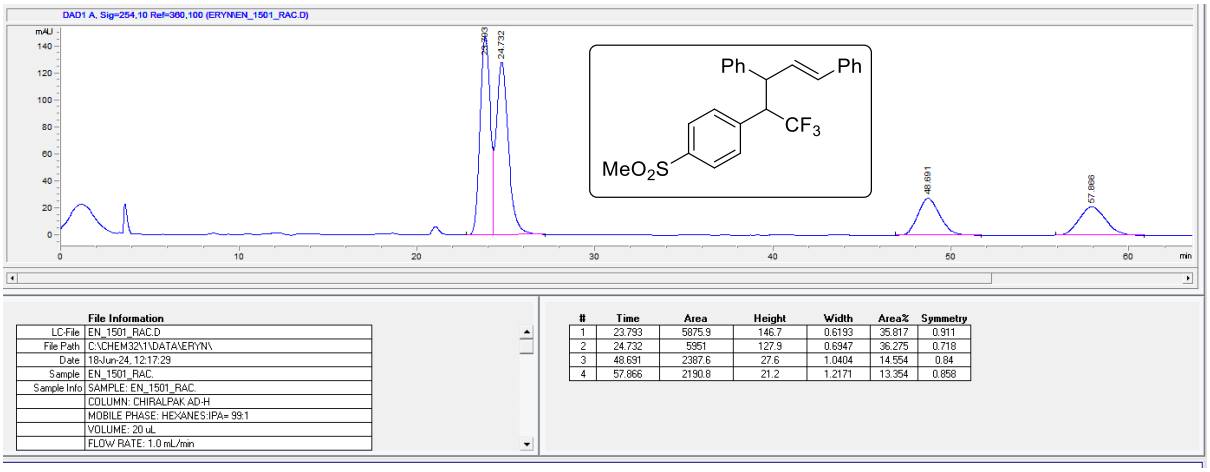
## HPLC of (*E*)-(5,5,5-trifluoro-4-(4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ea)




| File Information | |
|---|---|
| LC-File | EN_1483.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 25-Apr-24, 10:38:08 |
| Sample | EN_1483 |
| Sample Info | SAMPLE: EN_1483 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | VOLUME: 10 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 11.984 | 23658.5 | 1049 | 0.3759 | 97.501 | 0.525 |
| 2 | 14.088 | 606.3 | 23.5 | 0.4303 | 2.499 | 0.773 |

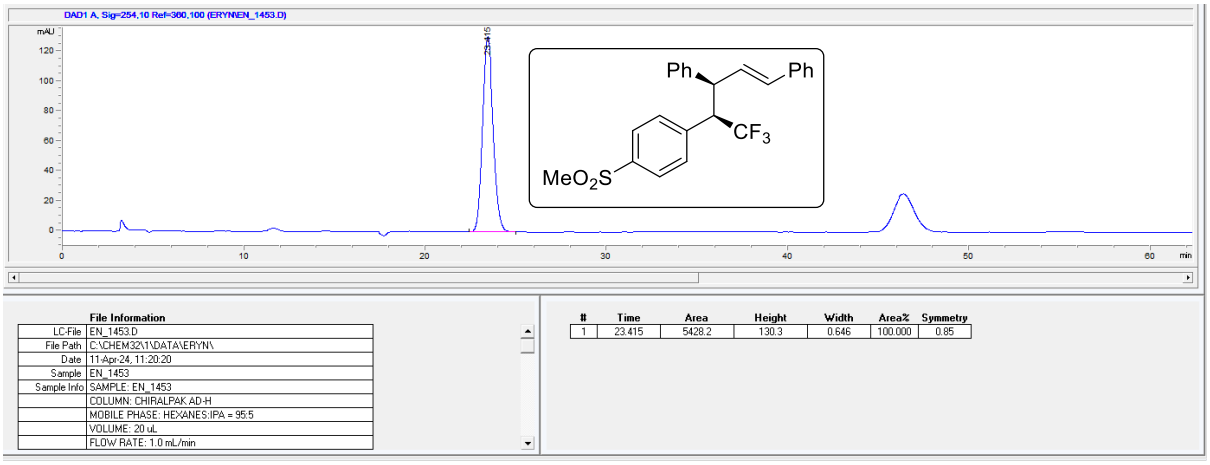
**HPLC of *racemic* (*E*)-(5,5,5-trifluoro-4-(4-(methylsulfonyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3fa)**




| File Information | |
|---|---|
| LC-File | EN_1501_RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 18-Jun-24, 12:17:29 |
| Sample | EN_1501_RAC. |
| Sample Info | SAMPLE: EN_1501_RAC. |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 23.793 | 5875.9 | 146.7 | 0.6193 | 35.817 | 0.911 |
| 2 | 24.732 | 5951 | 127.9 | 0.6947 | 36.275 | 0.718 |
| 3 | 48.691 | 2387.6 | 27.6 | 1.0404 | 14.554 | 0.84 |
| 4 | 57.866 | 2190.8 | 21.2 | 1.2171 | 13.354 | 0.858 |

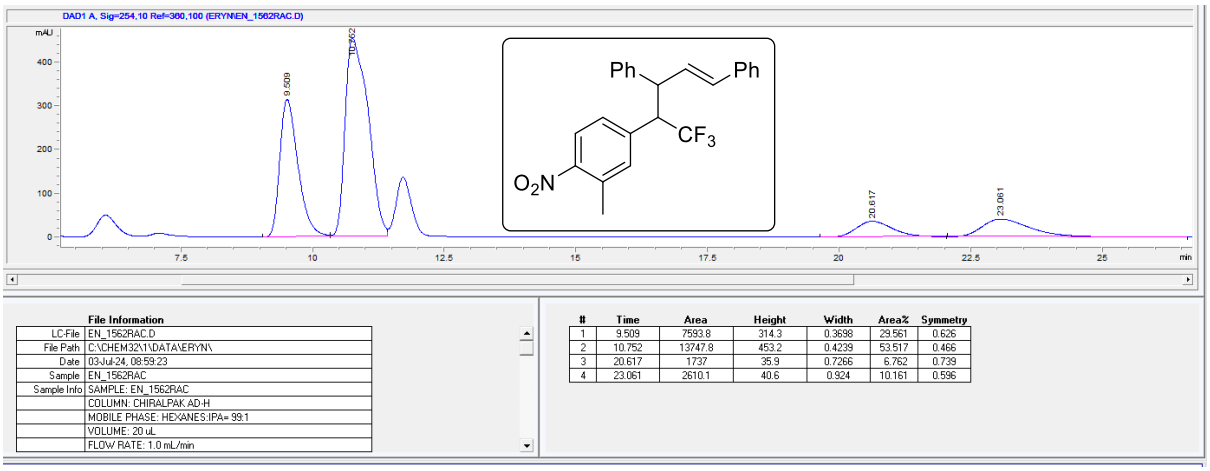
**HPLC of (*E*)-(5,5,5-trifluoro-4-(4-(methylsulfonyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3fa)**




| File Information | |
|---|---|
| LC-File | EN_1453.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 11-Apr-24, 11:20:20 |
| Sample | EN_1453 |
| Sample Info | SAMPLE: EN_1453 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 95:5 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 23.415 | 5428.2 | 130.3 | 0.646 | 100.000 | 0.85 |

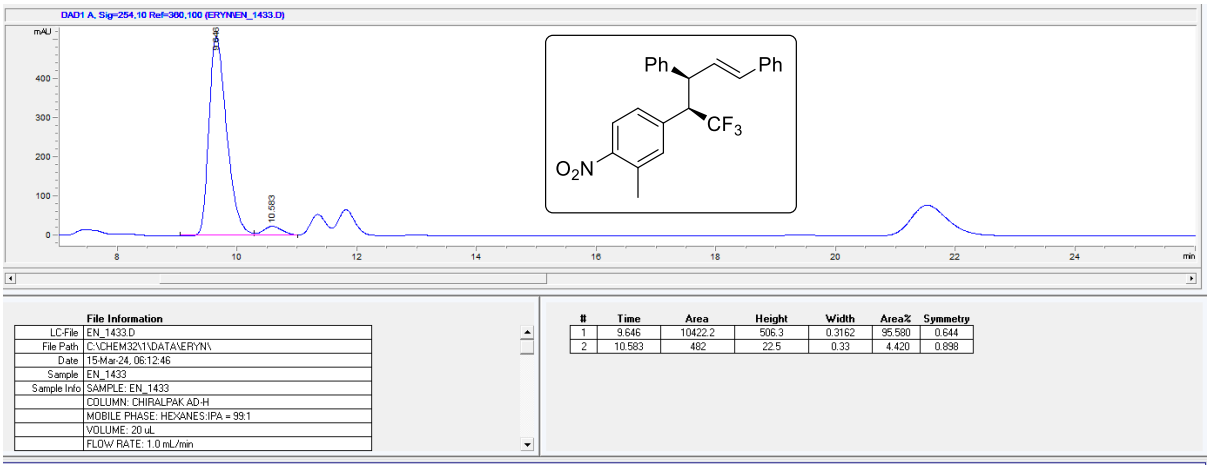
**HPLC of *racemic* (*E*)-(5,5,5-trifluoro-4-(3-methyl-4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ga)**




| File Information | |
|---|---|
| LC-File | EN_1562RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 03-Jul-24, 08:59:23 |
| Sample | EN_1562RAC |
| Sample Info | SAMPLE: EN_1562RAC |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.509 | 7593.8 | 314.3 | 0.3698 | 29.561 | 0.626 |
| 2 | 10.752 | 13747.8 | 453.2 | 0.4239 | 53.517 | 0.466 |
| 3 | 20.617 | 1737 | 35.9 | 0.7266 | 6.762 | 0.739 |
| 4 | 23.061 | 2610.1 | 40.6 | 0.924 | 10.161 | 0.596 |

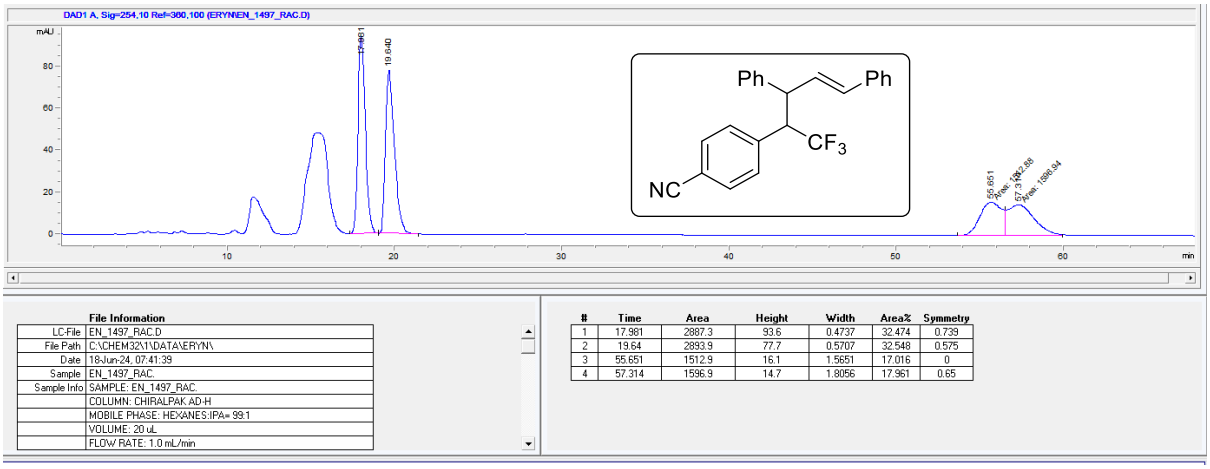
**HPLC of (*E*)-(5,5,5-trifluoro-4-(3-methyl-4-nitrophenyl)pent-1-ene-1,3-diyl)dibenzene (3ga)**




| File Information | |
|---|---|
| LC-File | EN_1433.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 15-Mar-24, 06:12:46 |
| Sample | EN_1433 |
| Sample Info | SAMPLE: EN_1433 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.646 | 10422.2 | 506.3 | 0.3162 | 95.580 | 0.644 |
| 2 | 10.583 | 482 | 22.5 | 0.33 | 4.420 | 0.898 |

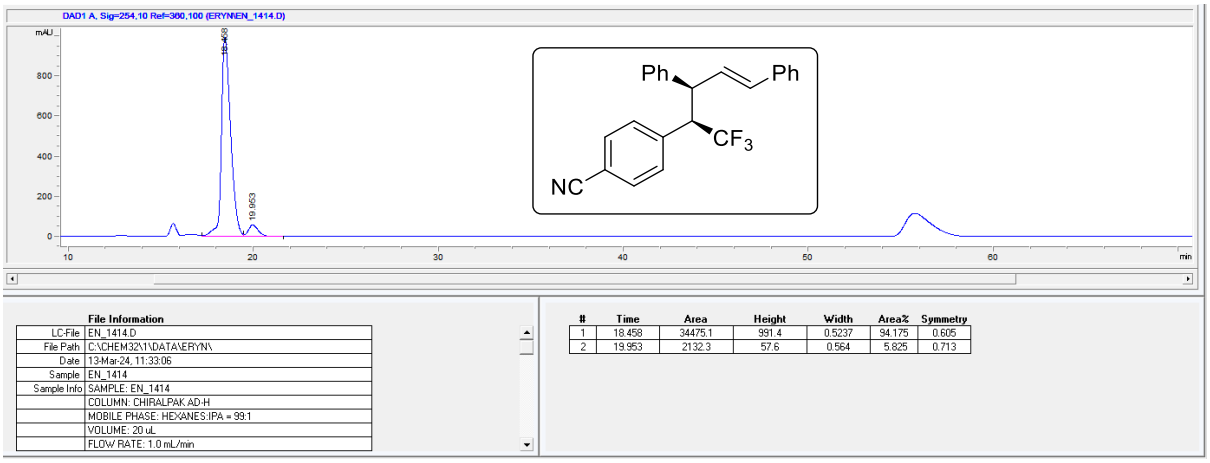
## HPLC of *racemic* (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzonitrile (3ha)




| File Information | |
|---|---|
| LC-File | EN_1497_RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 18-Jun-24, 07:41:39 |
| Sample | EN_1497_RAC. |
| Sample Info | SAMPLE: EN_1497_RAC. |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 17.981 | 2887.3 | 93.6 | 0.4737 | 32.474 | 0.739 |
| 2 | 19.64 | 2893.9 | 77.7 | 0.5707 | 32.548 | 0.575 |
| 3 | 55.651 | 1512.9 | 16.1 | 1.5651 | 17.016 | 0 |
| 4 | 57.314 | 1596.9 | 14.7 | 1.8056 | 17.961 | 0.65 |

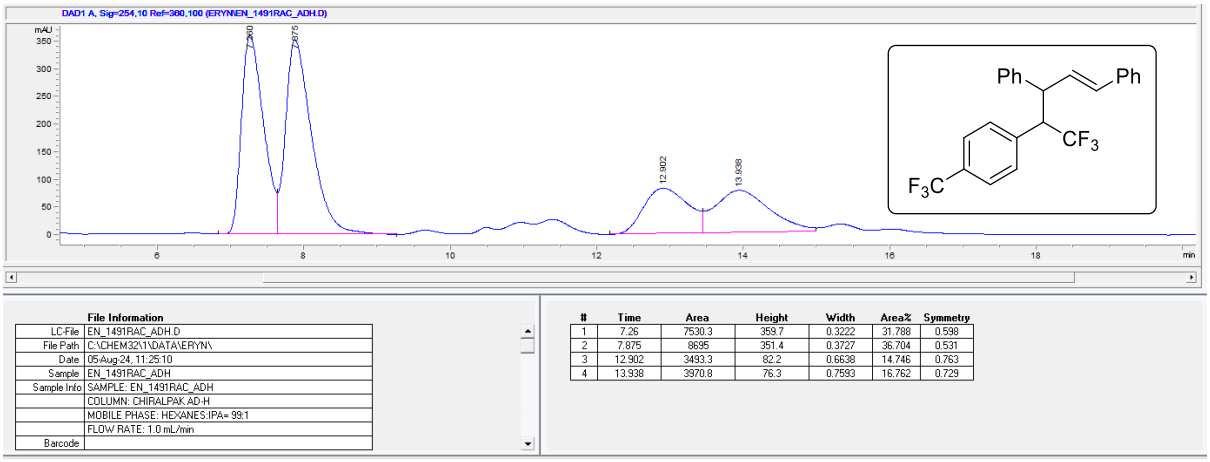
## HPLC of (*E*)-4-(1,1,1-trifluoro-3,5-diphenylpent-4-en-2-yl)benzonitrile (3ha)




| File Information | |
|---|---|
| LC-File | EN_1414.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 13-Mar-24, 11:33:06 |
| Sample | EN_1414 |
| Sample Info | SAMPLE: EN_1414 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | VOLUME: 20 uL |
| | FLOW RATE: 1.0 mL/min |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 18.458 | 34475.1 | 991.4 | 0.5237 | 94.175 | 0.605 |
| 2 | 19.953 | 2132.3 | 57.6 | 0.564 | 5.825 | 0.713 |

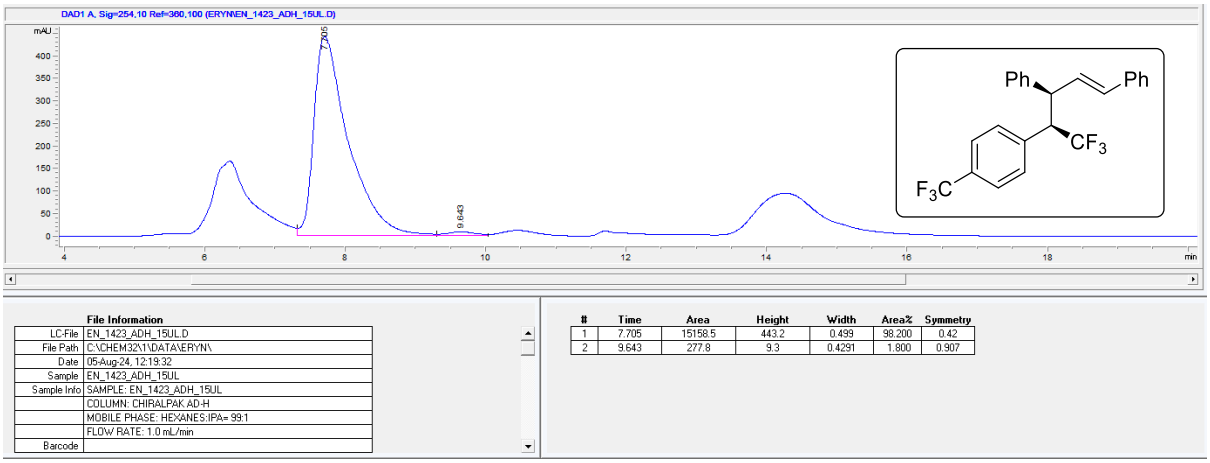
**HPLC of *racemic* (*E*)-(5,5,5-Trifluoro-4-(4-(trifluoromethyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3ia)**




| File Information | |
|---|---|
| LC-File | EN_1491RAC_ADH.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 05-Aug-24, 11:25:10 |
| Sample | EN_1491RAC_ADH |
| Sample Info | SAMPLE: EN_1491RAC_ADH |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 7.26 | 7530.3 | 359.7 | 0.3222 | 31.788 | 0.598 |
| 2 | 7.675 | 8695 | 351.4 | 0.3727 | 36.704 | 0.531 |
| 3 | 12.902 | 3493.3 | 82.2 | 0.6638 | 14.746 | 0.763 |
| 4 | 13.938 | 3970.8 | 76.3 | 0.7593 | 16.762 | 0.729 |

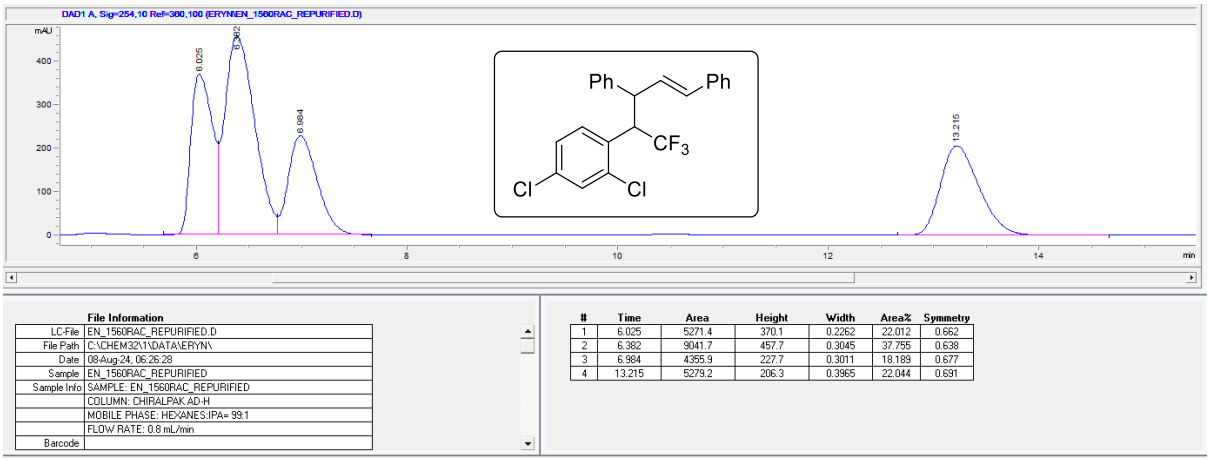
**HPLC of (*E*)-(5,5,5-Trifluoro-4-(4-(trifluoromethyl)phenyl)pent-1-ene-1,3-diyl)dibenzene (3ia)**




| File Information | |
|---|---|
| LC-File | EN_1423_ADH_15UL.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 05-Aug-24, 12:19:32 |
| Sample | EN_1423_ADH_15UL |
| Sample Info | SAMPLE: EN_1423_ADH_15UL |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 7.705 | 15158.5 | 443.2 | 0.499 | 98.200 | 0.42 |
| 2 | 9.643 | 277.8 | 9.3 | 0.4291 | 1.800 | 0.907 |

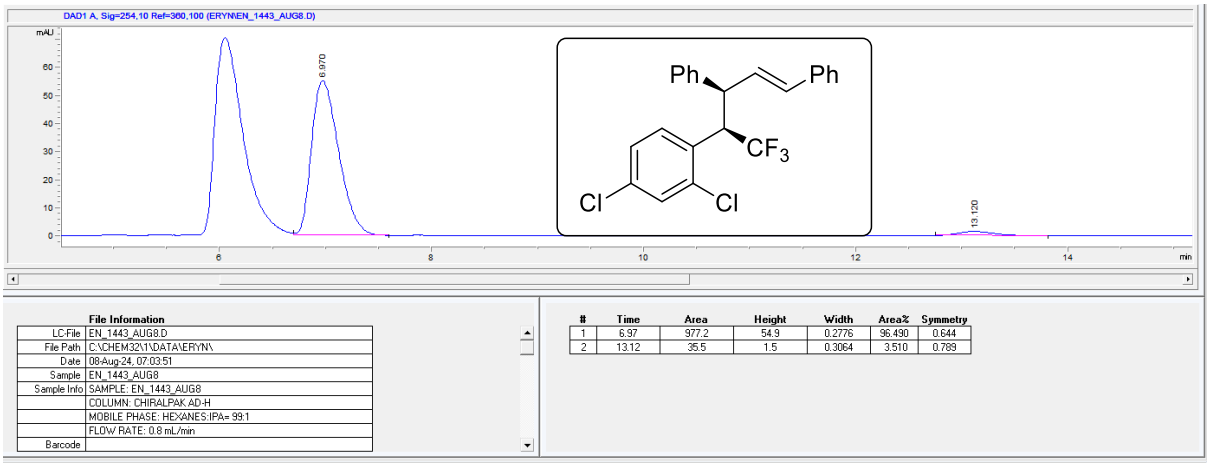
## HPLC of *racemic* (*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja)




| File Information | |
|---|---|
| LC-File | EN_1560RAC_REPURIFIED.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 08-Aug-24, 06:26:28 |
| Sample | EN_1560RAC_REPURIFIED |
| Sample Info | SAMPLE: EN_1560RAC_REPURIFIED |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 0.8 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 6.025 | 5271.4 | 370.1 | 0.2262 | 22.012 | 0.662 |
| 2 | 6.382 | 9041.7 | 457.7 | 0.3045 | 37.755 | 0.638 |
| 3 | 6.984 | 4355.9 | 227.7 | 0.3011 | 18.189 | 0.677 |
| 4 | 13.215 | 5279.2 | 206.3 | 0.3965 | 22.044 | 0.691 |

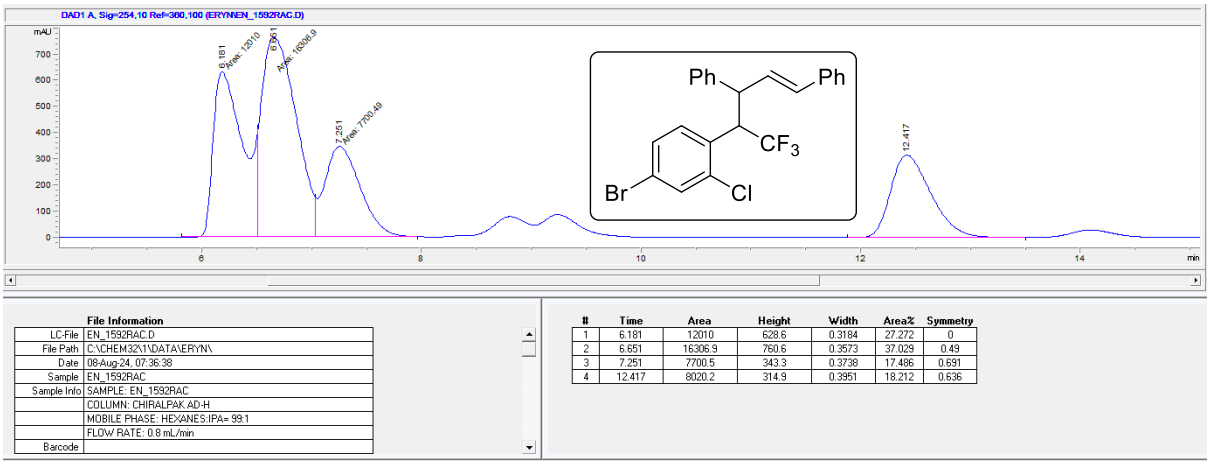
## HPLC of (*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja)




| File Information | |
|---|---|
| LC-File | EN_1443_AUG8.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 08-Aug-24, 07:03:51 |
| Sample | EN_1443_AUG8 |
| Sample Info | SAMPLE: EN_1443_AUG8 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 0.8 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 6.97 | 977.2 | 54.9 | 0.2776 | 96.490 | 0.644 |
| 2 | 13.12 | 35.5 | 1.5 | 0.3064 | 3.510 | 0.789 |

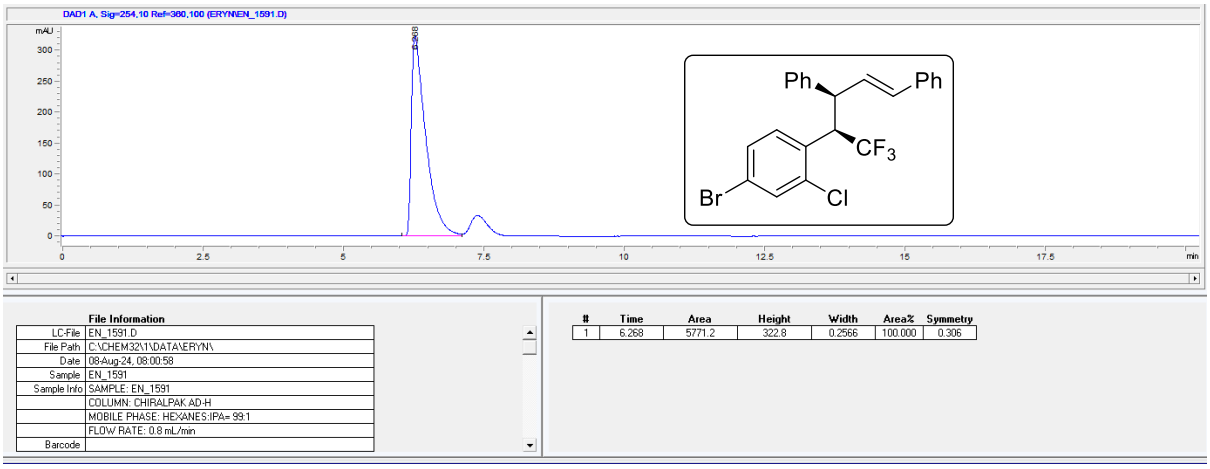
## HPLC of *racemic* (*E*)-(4-(4-Bromo-2-chlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ka)




| File Information | |
|---|---|
| LC-File | EN_1592RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 08-Aug-24, 07:36:38 |
| Sample | EN_1592RAC |
| Sample Info | SAMPLE: EN_1592RAC |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 0.8 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 6.181 | 12010 | 628.6 | 0.3184 | 27.272 | 0 |
| 2 | 6.651 | 16306.9 | 760.6 | 0.3573 | 37.029 | 0.49 |
| 3 | 7.251 | 7700.5 | 343.3 | 0.3738 | 17.486 | 0.691 |
| 4 | 12.417 | 8020.2 | 314.9 | 0.3951 | 18.212 | 0.636 |

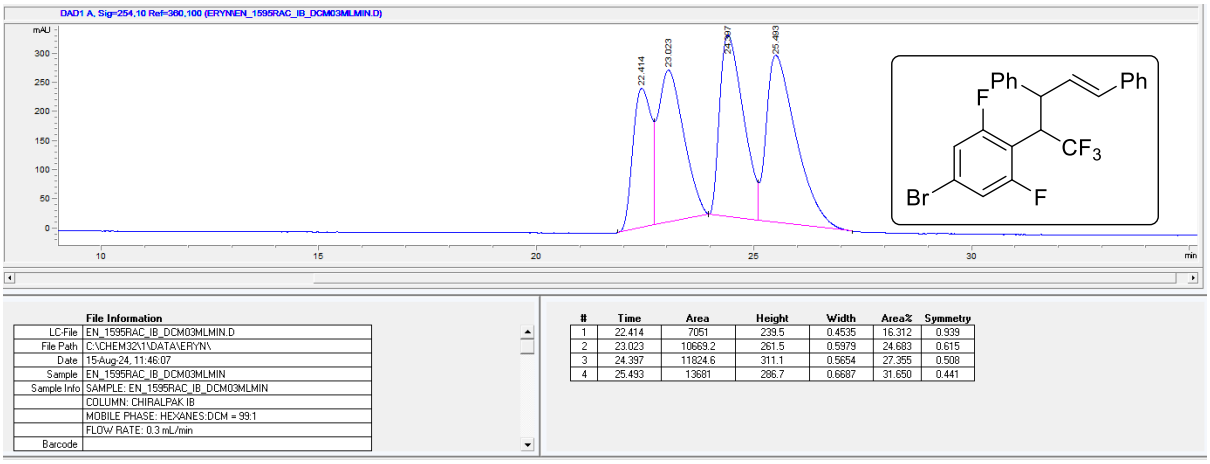
## HPLC of (*E*)-(4-(4-Bromo-2-chlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ka)




| File Information | |
|---|---|
| LC-File | EN_1591.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 08-Aug-24, 08:00:58 |
| Sample | EN_1591 |
| Sample Info | SAMPLE: EN_1591 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 0.8 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 6.268 | 5771.2 | 322.8 | 0.2566 | 100.000 | 0.306 |

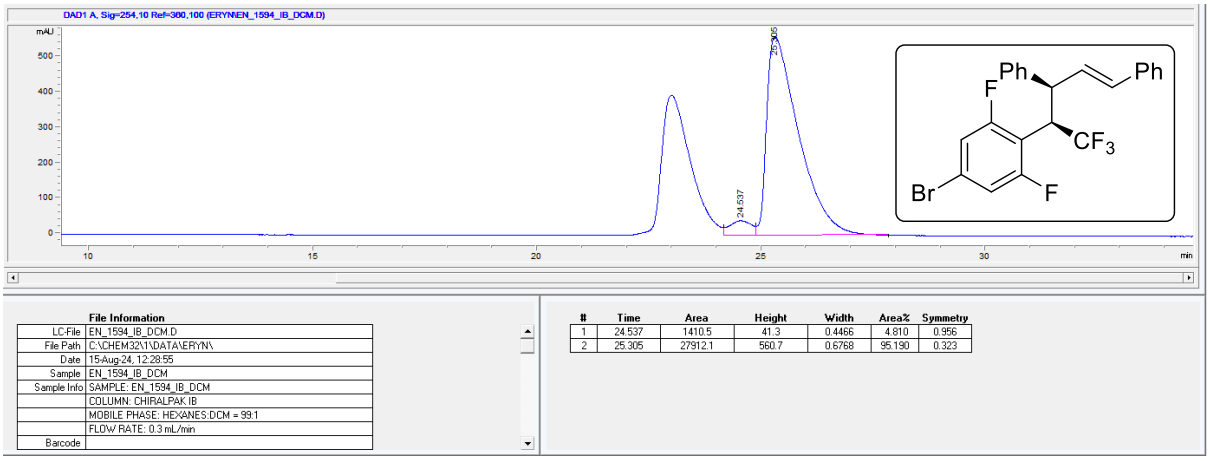
**HPLC of *racemic* (*E*)-(4-(4-Bromo-2,6-difluorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3la)**




| File Information | |
|---|---|
| LC-File | EN_1595RAC_IB_DCM03MLMIN.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 15-Aug-24, 11:46:07 |
| Sample | EN_1595RAC_IB_DCM03MLMIN |
| Sample Info | SAMPLE: EN_1595RAC_IB_DCM03MLMIN |
| | COLUMN: CHIRALPAK IB |
| | MOBILE PHASE: HEXANES:DCM = 99:1 |
| | FLOW RATE: 0.3 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 22.414 | 7051 | 239.5 | 0.4535 | 16.312 | 0.939 |
| 2 | 23.023 | 10669.2 | 261.5 | 0.5979 | 24.683 | 0.615 |
| 3 | 24.397 | 11824.6 | 311.1 | 0.5654 | 27.355 | 0.508 |
| 4 | 25.493 | 13681 | 286.7 | 0.6687 | 31.650 | 0.441 |

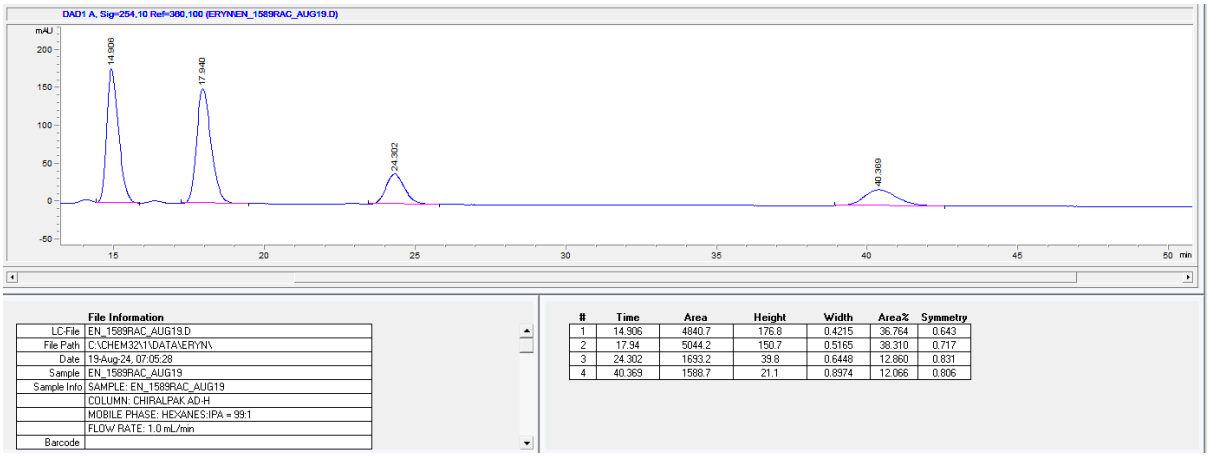
**HPLC of (*E*)-(4-(4-Bromo-2,6-difluorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3la)**




| File Information | |
|---|---|
| LC-File | EN_1594_IB_DCM.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 15-Aug-24, 12:28:55 |
| Sample | EN_1594_IB_DCM |
| Sample Info | SAMPLE: EN_1594_IB_DCM |
| | COLUMN: CHIRALPAK IB |
| | MOBILE PHASE: HEXANES:DCM = 99:1 |
| | FLOW RATE: 0.3 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 24.537 | 1410.5 | 41.3 | 0.4466 | 4.810 | 0.956 |
| 2 | 25.305 | 27912.1 | 560.7 | 0.6768 | 95.190 | 0.323 |

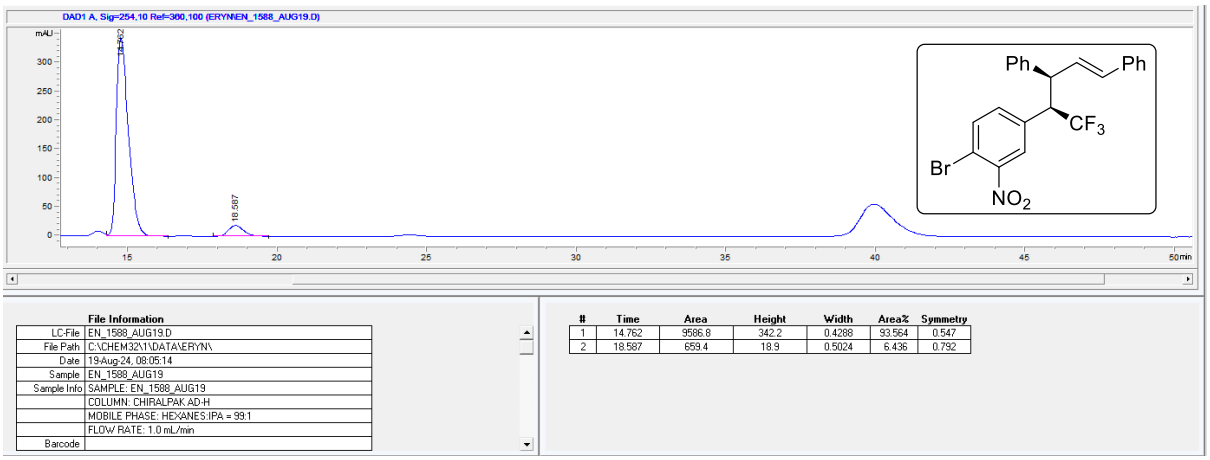
**HPLC of *racemic* (*E*)-(4-(4-Bromo-3-nitrophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ma).**




| File Information | |
|---|---|
| LC-File | EN_1589RAC_AUG19.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Aug-24, 07:05:28 |
| Sample | EN_1589RAC_AUG19 |
| Sample Info | SAMPLE: EN_1589RAC_AUG19 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 14.906 | 4840.7 | 176.8 | 0.4215 | 36.764 | 0.643 |
| 2 | 17.94 | 5044.2 | 150.7 | 0.5165 | 38.310 | 0.717 |
| 3 | 24.302 | 1693.2 | 39.8 | 0.6448 | 12.860 | 0.831 |
| 4 | 40.369 | 1588.7 | 21.1 | 0.8974 | 12.066 | 0.806 |

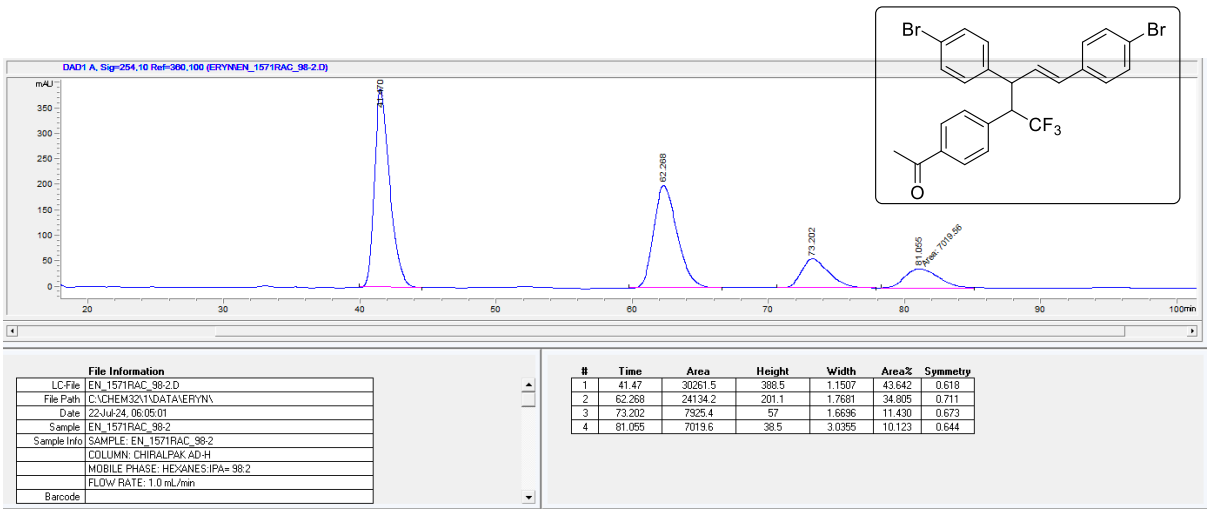
**HPLC of (*E*)-(4-(4-Bromo-3-nitrophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ma).**




| File Information | |
|---|---|
| LC-File | EN_1588_AUG19.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Aug-24, 08:05:14 |
| Sample | EN_1588_AUG19 |
| Sample Info | SAMPLE: EN_1588_AUG19 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA = 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 14.762 | 9586.8 | 342.2 | 0.4288 | 93.564 | 0.547 |
| 2 | 18.587 | 659.4 | 18.9 | 0.5024 | 6.436 | 0.792 |

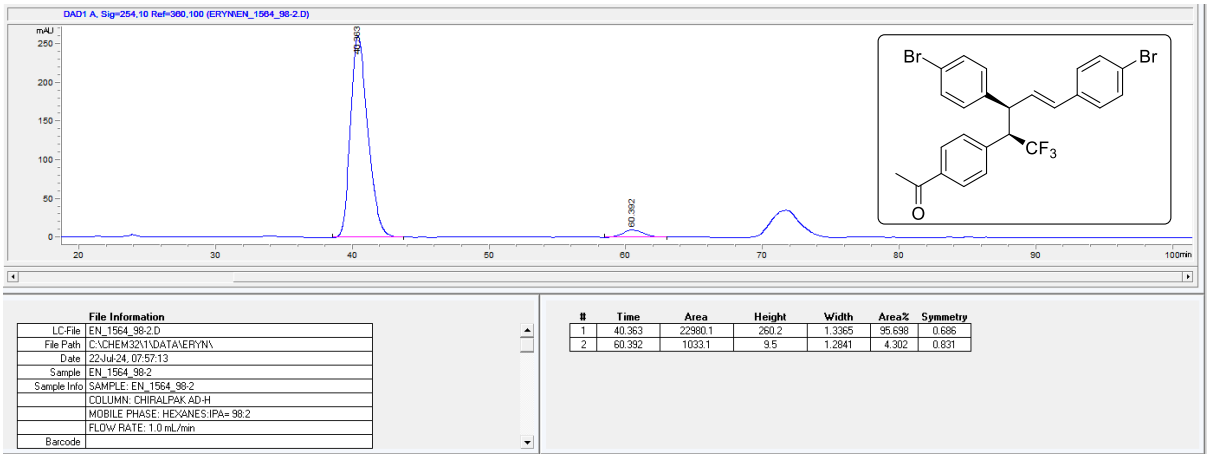
## HPLC of *racemic* (*E*)-1-(4-(3,5-bis(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cb)




| File Information | |
|---|---|
| LC-File | EN_1571RAC_98-2.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 22-Jul-24, 06:05:01 |
| Sample | EN_1571RAC_98-2 |
| Sample Info | SAMPLE: EN_1571RAC_98-2 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 98:2 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 41.47 | 30261.5 | 388.5 | 1.1507 | 43.642 | 0.618 |
| 2 | 62.268 | 24134.2 | 201.1 | 1.7681 | 34.805 | 0.711 |
| 3 | 73.202 | 7925.4 | 57 | 1.6696 | 11.430 | 0.673 |
| 4 | 81.055 | 7019.6 | 38.5 | 3.0355 | 10.123 | 0.644 |

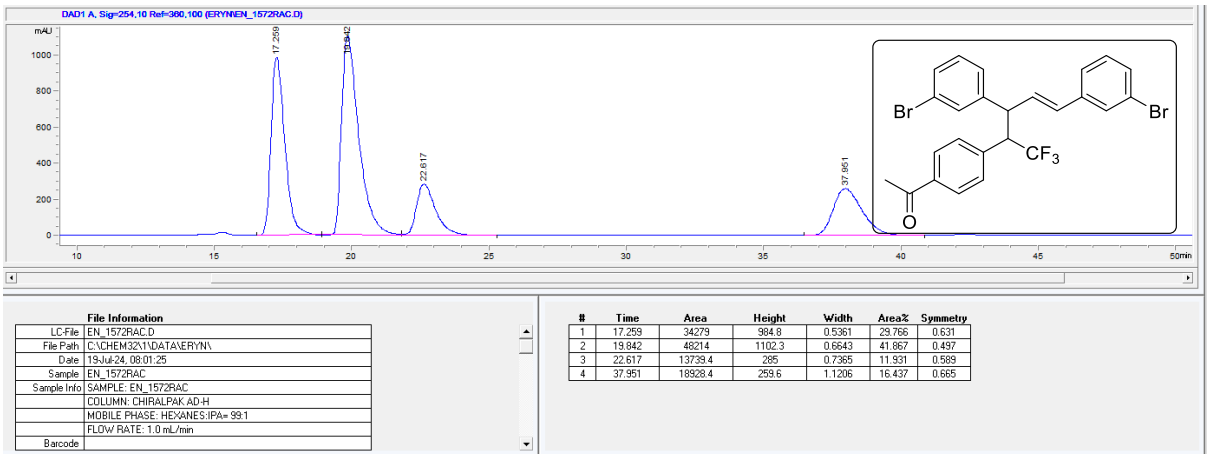
## HPLC of (*E*)-1-(4-(3,5-bis(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cb)




| File Information | |
|---|---|
| LC-File | EN_1564_98-2.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 22-Jul-24, 07:57:13 |
| Sample | EN_1564_98-2 |
| Sample Info | SAMPLE: EN_1564_98-2 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 98:2 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 40.363 | 22980.1 | 260.2 | 1.3365 | 95.698 | 0.686 |
| 2 | 60.392 | 1033.1 | 9.5 | 1.2841 | 4.302 | 0.831 |

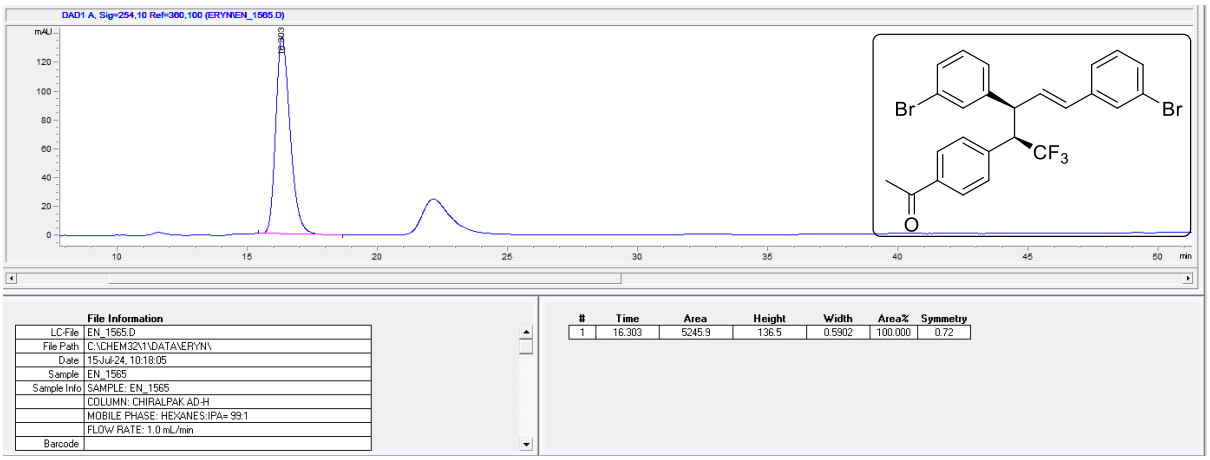
**HPLC of *racemic* (*E*)-1-(4-(3,5-bis(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cc)**




| File Information | |
|---|---|
| LC-File | EN_1572RAC.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Jul-24, 08:01:25 |
| Sample | EN_1572RAC |
| Sample Info | SAMPLE: EN_1572RAC |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 17.259 | 34279 | 984.8 | 0.5361 | 29.766 | 0.631 |
| 2 | 19.842 | 48214 | 1102.3 | 0.6643 | 41.867 | 0.497 |
| 3 | 22.617 | 13739.4 | 285 | 0.7365 | 11.931 | 0.589 |
| 4 | 37.951 | 18928.4 | 259.6 | 1.1206 | 16.437 | 0.665 |

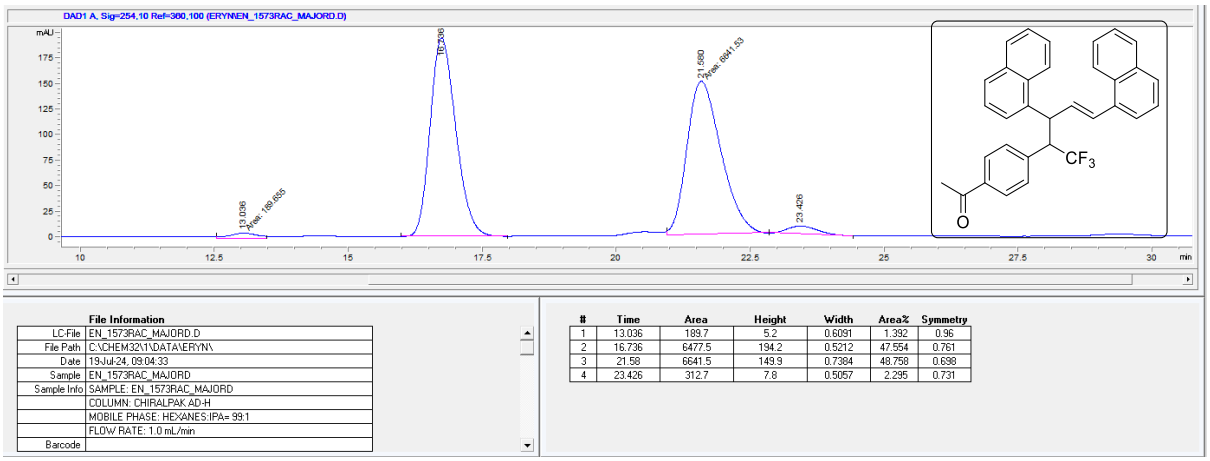
**HPLC of (*E*)-1-(4-(3,5-bis(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)phenyl)ethan-1-one (3cc)**




| File Information | |
|---|---|
| LC-File | EN_1565.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 15-Jul-24, 10:18:05 |
| Sample | EN_1565 |
| Sample Info | SAMPLE: EN_1565 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 16.303 | 5245.9 | 136.5 | 0.5902 | 100.000 | 0.72 |

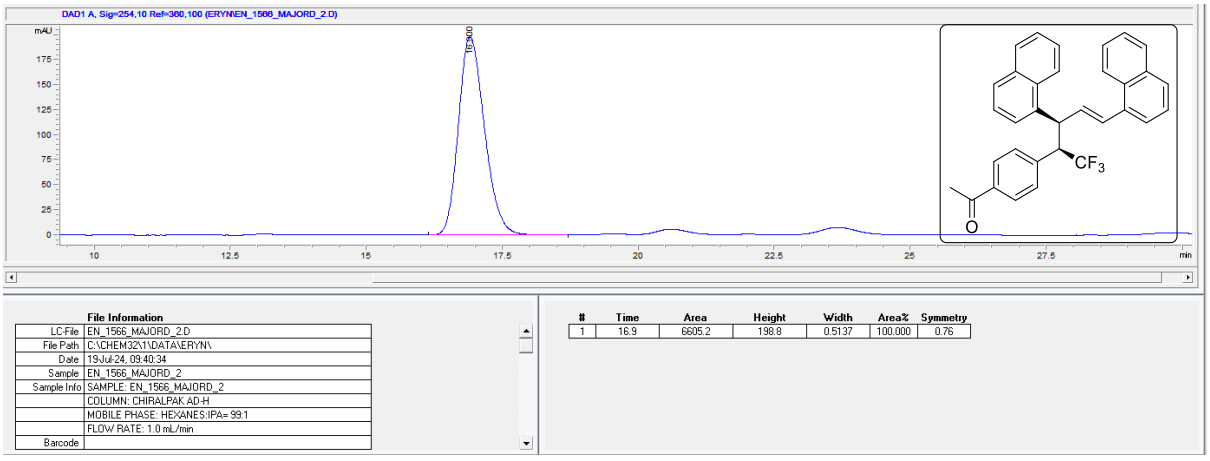
**HPLC of the major diastereomer of *racemic* (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**




| File Information | |
|---|---|
| LC-File | EN_1573RAC_MAJORD.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Jul-24, 09:04:33 |
| Sample | EN_1573RAC_MAJORD |
| Sample Info | SAMPLE: EN_1573RAC_MAJORD |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 13.036 | 189.7 | 5.2 | 0.6091 | 1.392 | 0.96 |
| 2 | 16.736 | 6477.5 | 194.2 | 0.5212 | 47.554 | 0.761 |
| 3 | 21.58 | 6641.5 | 149.9 | 0.7384 | 48.758 | 0.698 |
| 4 | 23.426 | 312.7 | 7.8 | 0.5057 | 2.295 | 0.731 |

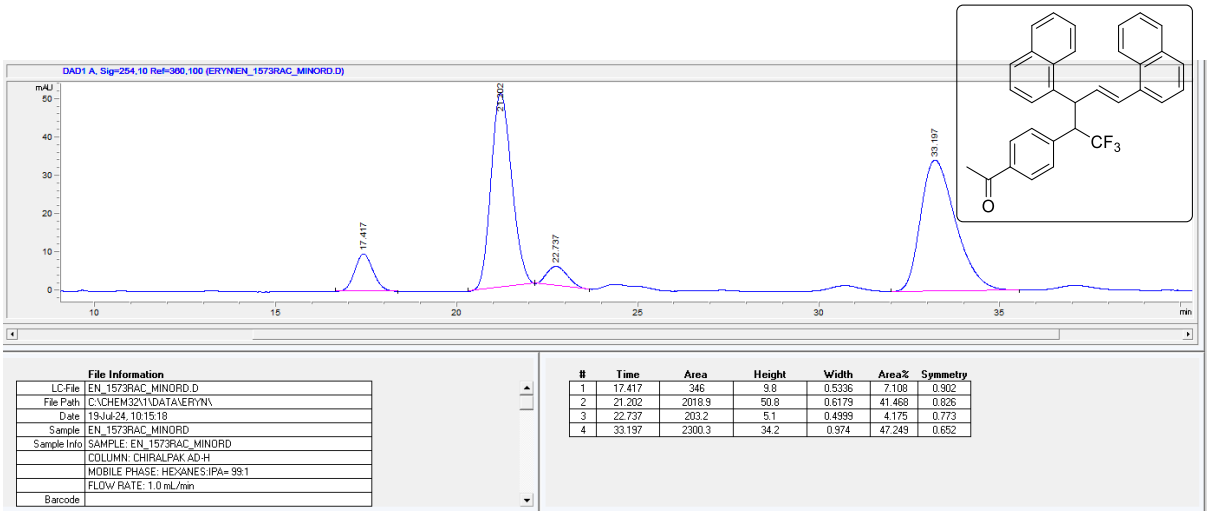
**HPLC of the major diastereomer of (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**




| File Information | |
|---|---|
| LC-File | EN_1566_MAJORD_2.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Jul-24, 09:40:34 |
| Sample | EN_1566_MAJORD_2 |
| Sample Info | SAMPLE: EN_1566_MAJORD_2 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 16.9 | 6605.2 | 198.8 | 0.5137 | 100.000 | 0.76 |

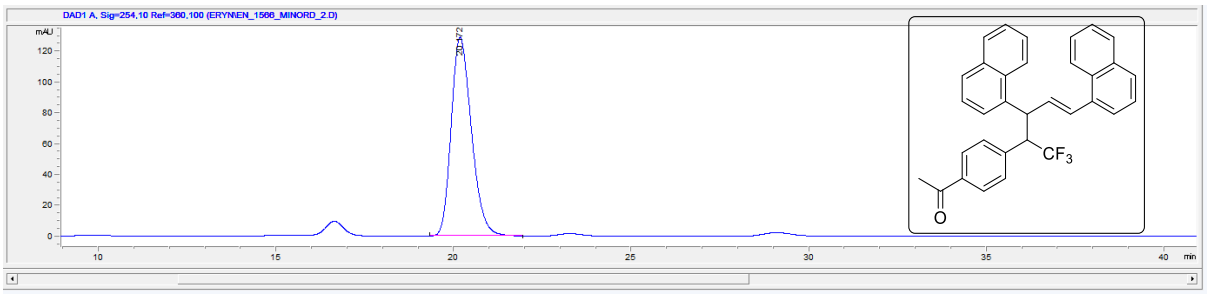
**HPLC of the minor diastereomer of *racemic* (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**




| File Information | |
|---|---|
| LC-File | EN_1573RAC_MINORD.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Jul-24, 10:15:18 |
| Sample | EN_1573RAC_MINORD |
| Sample Info | SAMPLE: EN_1573RAC_MINORD |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 17.417 | 346 | 9.8 | 0.5336 | 7.108 | 0.902 |
| 2 | 21.202 | 2018.9 | 50.8 | 0.6179 | 41.468 | 0.826 |
| 3 | 22.737 | 203.2 | 5.1 | 0.4999 | 4.175 | 0.773 |
| 4 | 33.197 | 2300.3 | 34.2 | 0.974 | 47.249 | 0.652 |

**HPLC of the minor diastereomer of (*E*)-1-(4-(1,1,1-trifluoro-3,5-di(naphthalen-1-yl)pent-4-en-2-yl)phenyl)ethan-1-one (3cd)**

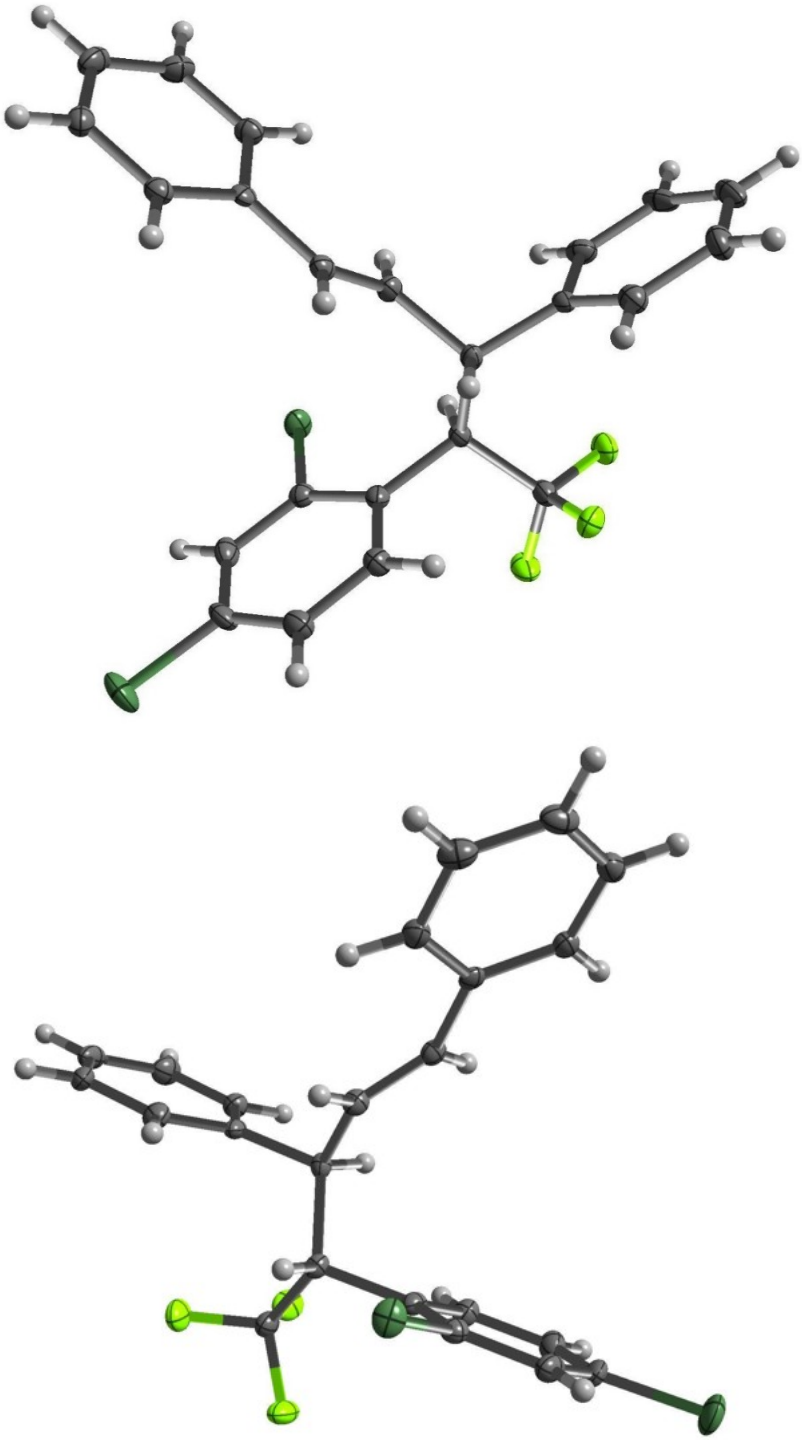



| File Information | |
|---|---|
| LC-File | EN_1566_MINORD_2.D |
| File Path | C:\CHEM32\1\DATA\ERYN\ |
| Date | 19-Jul-24, 11:04:09 |
| Sample | EN_1566_MINORD_2 |
| Sample Info | SAMPLE: EN_1566_MINORD_2 |
| | COLUMN: CHIRALPAK AD-H |
| | MOBILE PHASE: HEXANES:IPA= 99:1 |
| | FLOW RATE: 1.0 mL/min |
| Barcode | |

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 20.172 | 5118.6 | 129 | 0.6191 | 100.000 | 0.74 |

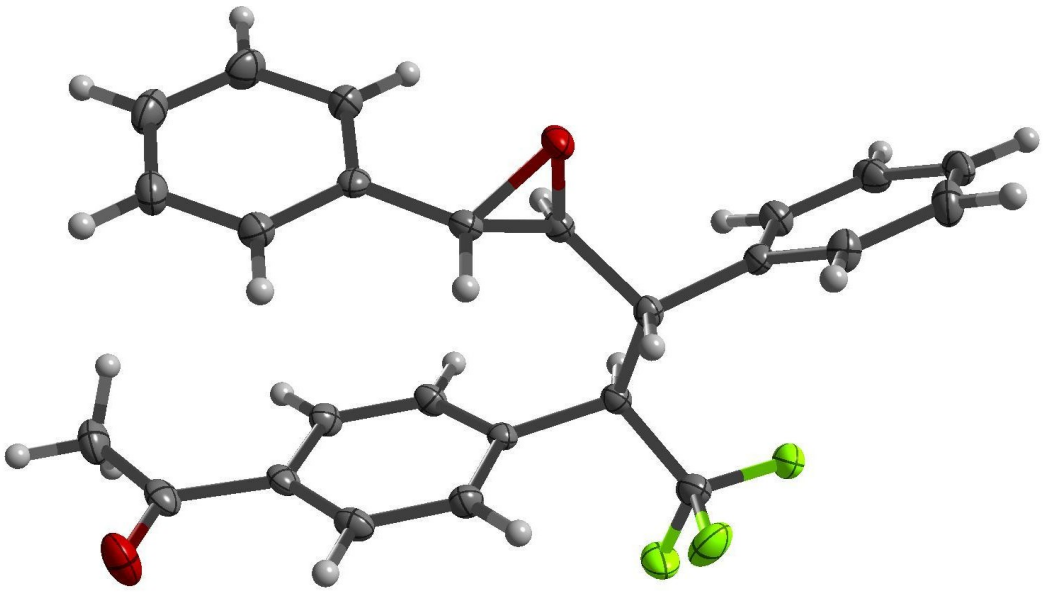
## 8. Crystallographic data

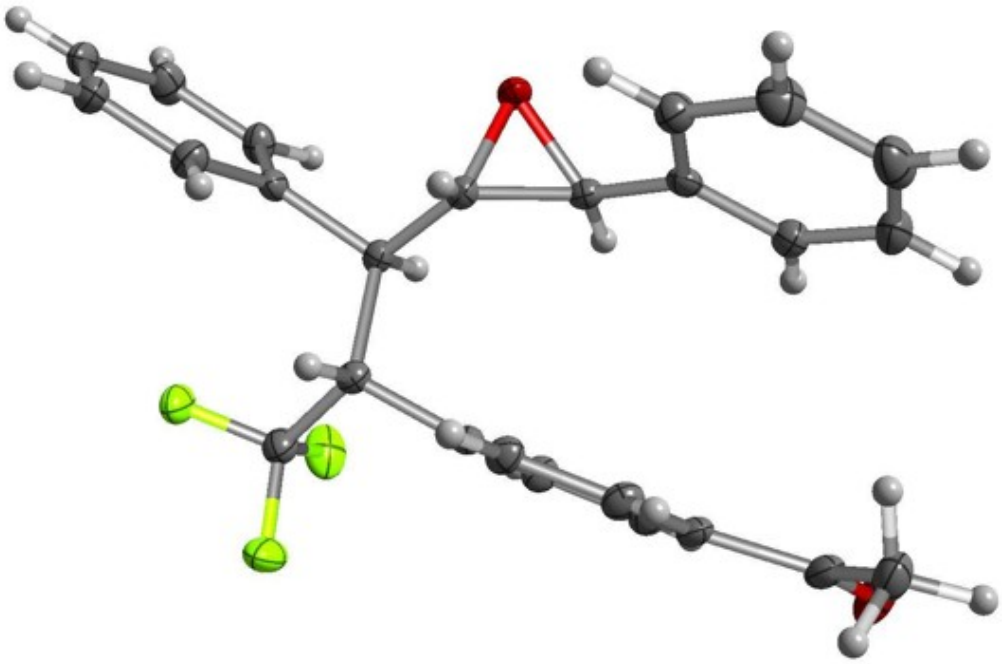
**(3*S*,4*R*,*E*)-(4-(2,4-Dichlorophenyl)-5,5,5-trifluoropent-1-ene-1,3-diyl)dibenzene (3ja, major diastereomer)**



A single crystal was obtained by slow evaporation of a solution containing **3ja** in dichloromethane. Single crystal X-ray analysis was performed at 100 K using a Bruker APEX DUO equipped with a Cu-Kα (λ = 1.54178 Å) micro-focus source, an ApexII detector, and an Oxford 700 Cryostream. Data were integrated using the Bruker SAINT program. Structure solution and refinement was performed using the SHELXTL/PC suite and ShelXle. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABs. Non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data: $C_{23}H_{17}C_{12}F_3$, *M* = 421.26, colorless rod, 0.044 x 0.121 x 0.418 $mm^3$, orthorhombic, space group P21212, a = 16.9540(3), b = 20.1285(3), c = 5.70930(10) Å, V = 1948.35(6) $Å^3$, Z = 4. Absolute structure parameter = 0.011(4) (Flack, H. D. Acta Cryst. 1983, A39, 876-881). CCDC 2383108

**1-(4-((2*R*,3*S*)-1,1,1-Trifluoro-3-phenyl-3-((2*S*,3*S*)-3-phenyloxiran-2-yl)propan-2-yl)phenyl)ethan-1-one (6, major diastereomer)**





A single crystal was obtained by slow evaporation of a solution containing **6** in dichloromethane. Single crystal X-ray analysis was performed at 100 K using a Bruker APEX DUO equipped with a Cu-Kα (λ = 1.54178 Å) micro-focus source, an ApexII detector, and an Oxford 700 Cryostream. Data were integrated using the Bruker SAINT program. Structure solution and refinement was performed using the SHELXTL/PC suite and ShelXle. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABs. Non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data: $C_{25}H_{21}F_3O_2$, *M* = 410.42, colorless plate, 0.074 x 0.31 x 0.482 $mm^3$, orthorhombic, space group $P2_12_12_1$, a = 8.9675(2), b = 9.7971(2), c = 22.7498(5) Å, V = 1998.70(7) $Å^3$, Z = 4. Absolute structure parameter = 0.01(3) (Flack, H. D. Acta Cryst. 1983, A39, 876-881). CCDC 2383107

## 9. References

1 P. Tian, C.-Q. Wang, S.-H. Cai, S. Song, L. Ye, C. Feng, T.-P. Loh. *J. Am. Chem. Soc.* **2016**, *138*, 15869–15872.

2 T.-Y. Lin, Z. Pan, Y. Tu, S. Zhu, H.-H. Wu, Y. Liu, Z. Li, J. Zhang. *Angew. Chem. Int. Ed*. **2020**, *59*, 22957–22962.

3 Yuan, F-Q.; Gao, L-Z.; Han, F-S. *Chem. Commun*, **2011**, *47*, 5289–5291.

4 S. Jayakumar, N. Kumarswamyreddy, M. Prakash, V. Kesavan, *Org. Lett*. **2015**, *17*, 1066–1069.