Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Catalytic Photochemical Enantioselective α-Alkylation with Pyridinium Salts

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Contents:

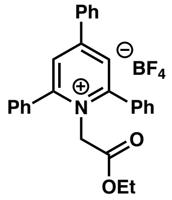
1. General Information

All reactions were carried out in capped reaction vials with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. For irradiation, a 390 Kessil LED lamp (model number: PR-160-390) or a 427 Kessil LED lamp (model number: PR-160-427) was placed 4 cm away from the reaction vials. NMR spectra were recorded on Varian MR400, Bruker AN400, and Bruker AN600 instruments and calibrated using residual undeuterated solvent as an internal reference. Data for ^{1}H NMR spectra are reported relative to chloroform or benzene as an internal standard (7.26 ppm and 7.16 ppm respectively) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform or benzene as an internal standard (77.2 ppm and 128.1 ppm respectively) and are reported in terms of chemical shift (δ ppm). HRMS electrospray (ESI) data was obtained on a Sciex Triple Quad 6500+ System. UV-Vis absorption spectra were recorded on a Cary 60 UV-Vis spectrometer (Agilent Technologies). All measurements were carried out with a 1.0 cm path length quartz cell. Optical rotations were measured on a JAS DIP-360 digital polarimeter. Chiral HPLC analyses were performed on an Agilent 1200 Series system. Low temperature photochemical-reactions were performed using EasyMax 102 Advanced Thermostat system from Mettler-Toledo AutoChem, Inc. (Product ID: 51161711).

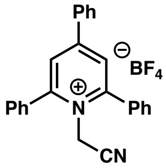
2. Synthesis and Characterization of Pyridinium Substrates

Preparation of Pyridinium Salts

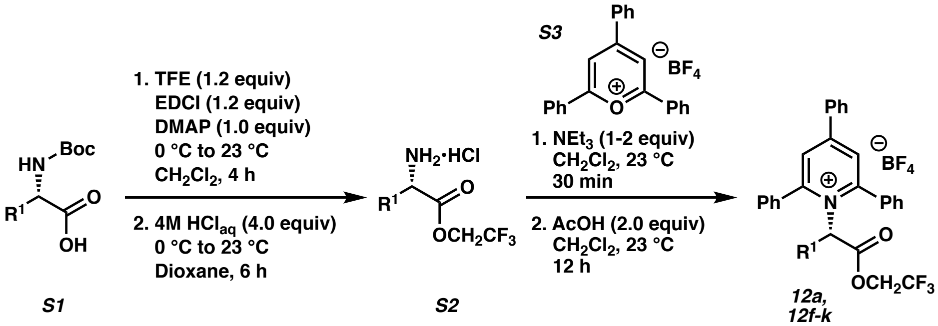
Pyridinium salt **10a** was synthesized as described previously.[1]



Pyridinium salt **14g** was synthesized as described previously.[2]

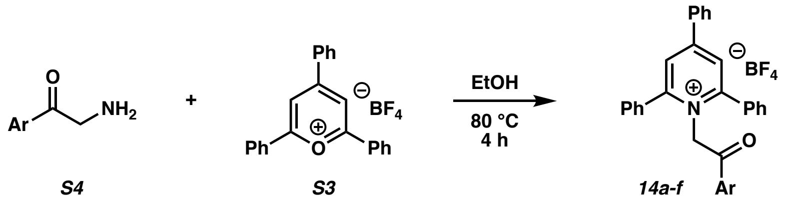


General Procedure A: **Synthesis of Trifluoroethyl Aminoester Pyridinium Salts 12**



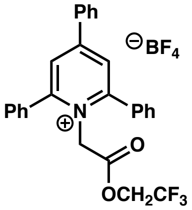
Following the reported method,[3] *N*-Boc-amino acid derivatives **S1** were converted to trifluoroethyl aminoester•HCl salts **S2**. Further following the literature reports,[4] these aminoesters (1.0 equiv) were added to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate **S3** (1.0 equiv), powdered activated 4Å molecular sieves (~500 mg/mmol), and CH_2Cl_2 (0.5 M) in a round-bottomed flask equipped with a stir bar. The flask was fitted with a septum and a vent needle. The mixture was stirred as Et_3N (1.0 equiv for free base amines; 2.0 equiv for amine hydrochloride salts) was added by syringe. The vent needle was removed, and the mixture was stirred at 23 °C for 30 min. The vent needle was reinserted before the addition of acetic acid (2.0 equiv). The needle was again removed, and the mixture was stirred at 23 °C for 12 h. The mixture was then filtered through a short pad of celite using CH_2Cl_2 to rinse the flask and celite pad. The filtrate was washed successively with aqueous HCl (1.0 M, 2 x 30 mL), saturated aqueous $NaHCO_3$ (2 x 30 mL), and saturated aqueous NaCl (2 x 30 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel chromatography with acetone/CH_2Cl_2 as the eluent or recrystallization.

General Procedure B: **Synthesis of Aminoketone Pyridinium Salts 14**



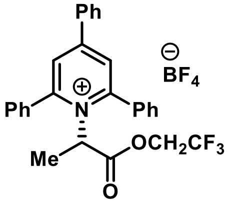
Following the previously described methods[1], aminoketone **S4** (1.2 equiv) was added to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate **S3** (1.0 equiv) and EtOH (1.0 M) in a round-bottomed flask. The flask was fitted with a reflux condenser. The mixture was stirred and heated at reflux in an oil bath at 80 ºC for 4 h. The mixture was then allowed to cool to 23 °C, concentrated under reduced pressure, and purified by silica gel chromatography with acetone/CH_2Cl_2 as the eluent or recrystallization.

1-(2-*oxo*-2-(2,2,2-Trifluoroethoxy)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 12a:



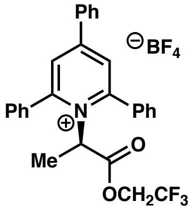
12a was synthesized by following the general procedure A at 5.0 mmol scale from N-Boc glycine and purified by silica gel column chromatography (1→10→20% acetone in CH_2Cl_2). **12a** was obtained as a white solid (2.0 g, 75%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.94 – 7.78 (m, 3H), 7.79 – 7.31 (m, 12H), 5.21 (s, 2H), 4.36 (q, *J* = 8.1 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.00, 157.48, 157.41, 133.69, 132.79, 131.82, 131.69, 129.97, 129.63, 128.87, 128.36, 126.28, 121.99 (q, *J* = 277.7 Hz), 61.42 (d, *J* = 37.6 Hz), 55.82. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -73.68, -153.15. **HRMS (ESI)** calculated for $[C_{27}H_{21}F_3NO_2, M – BF_4]^+$: 448.1519, Found 448.1582.

(*S*)-1-(1-*oxo*-1-(2,2,2-Trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*S*)-12f:



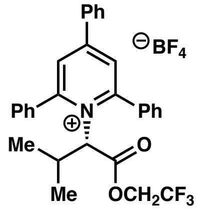
(*S*)-12f was synthesized by following the general procedure A at 5.0 mmol scale from (*S*)-N-Boc alanine and purified by silica gel column chromatography (1→10→20% acetone in CH_2Cl_2). **(*S*)-12f** was obtained as a white solid (2.2 g, 80%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.87 – 7.81 (m, 2H), 7.73 (brs, 3H), 7.65 – 7.45 (m, 10H), 5.68 (q, *J* = 7.2 Hz, 1H), 4.54 – 4.46 (m, 1H), 4.45 – 4.34 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.0, 157.4, 134.0, 132.7, 132.5, 131.7, 129.8, 129.4, 128.6, 62.1 (d, *J* = 32.9 Hz), 17.1. **^{19}F NMR** (565 MHz, C_6D_6) δ -73.4, -153.1. **HRMS (ESI)** calculated for $[C_{28}H_{24}F_3NO_2$, M + H-$BF_4]^+$: 463.1754, Found 463.1807.

(*R*)-1-(1-*oxo*-1-(2,2,2-Trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*R*)-12f:



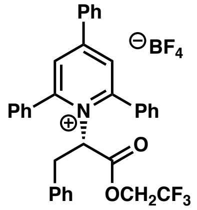
(*R*)-12f was synthesized by following the general procedure A at 5.0 mmol scale from (*R*)-N-Boc alanine and purified by silica gel column chromatography (1→10→20% acetone in CH_2Cl_2). **(*R*)-12f** was obtained as a white solid (2.3 g, 84%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.83 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.77 (brs, 3H), 7.64 – 7.47 (m, 10H), 5.68 (d, *J* = 7.2 Hz, 1H), 4.50 (dq, *J* = 12.6, 8.1 Hz, 1H), 4.40 (dq, *J* = 12.6, 8.1 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl3) 168.0, 157.4, 134.0, 132.7, 132.5, 131.7, 129.8, 129.4, 128.6, 62.1 (d, *J* = 32.9 Hz), 17.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -73.4, -153.1. **HRMS (ESI)** calculated for $[C_{28}H_{24}F_3NO_2$, M + H-$BF_4]^+$: 463.1754, Found 463.1813.

(*S*)-1-(3-Methyl-1-oxo-1-(2,2,2-trifluoroethoxy)butan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*S*)-12g:



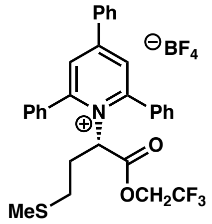
(*S*)-12g was synthesized by following General Procedure B on a 3.05 mmol scale from N-Boc valine and purified by recrystallization (EtOH/Et_2O). **(*S*)-12g** was obtained as a white powder (1.07 g, 61%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.74 – 7.53 (m, 11H), 7.50 (t, *J* = 7.5 Hz, 2H), 5.21 (d, *J* = 10.2 Hz, 1H), 4.62 (q, *J* = 8.2 Hz, 2H), 2.14 (dt, *J* = 10.3, 6.5 Hz, 1H), 0.75 (dd, *J* = 8.2, 6.5 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.31, 157.80, 133.48, 133.29, 132.34, 132.11, 130.20, 129.87, 129.79, 129.38, 129.10, 128.29, 122.76 (q, *J* = 277.8 Hz), 73.47, 61.97 (q, *J* = 37.1 Hz), 30.43, 22.32, 19.43. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -73.19, -153.03. **HRMS (ESI)** calculated for $[C_{30}H_{27}F_3NO_2$, MH – $BF_4]^+$: 491.2061, Found 491.2091.

(*S*)-1-(1-oxo-3-Phenyl-1-(2,2,2-trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium, (*S*)-12h:



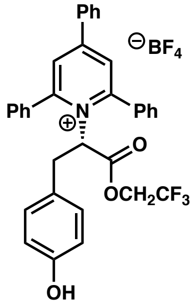
(*S*)-12h was synthesized by following General Procedure B on a 2.54 mmol scale from N-Boc phenylalanine and purified by recrystallization (EtOH/Et_2O). **(*S*)-12h** was obtained as a white powder (1.02 g, 64%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.89 – 7.71 (m, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.49 (m, 11H), 7.11 – 7.06 (m, 3H), 6.77 (d, *J* = 7.3 Hz, 2H), 5.76 (d, *J* = 4.1 Hz, 1H), 4.52 (d, *J* = 5.3 Hz, 1H), 4.40 – 4.35 (m, 1H), 3.55 (dd, *J* = 14.4, 3.9 Hz, 1H), 2.86 (dd, *J* = 14.5, 8.3 Hz, 1H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.54, 157.40, 135.86, 133.69, 132.58, 132.15, 131.78, 129.76, 129.32, 128.97, 128.68, 128.62, 127.40, 122.26 (q, *J* = 277.4 Hz), 70.01, 62.14 (q, *J* = 37.2 Hz), 37.65. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -72.93, -152.70. **HRMS (ESI)** calculated for $[C_{34}H_{27}F_3NO_2$, M – $BF_4]^+$: 538.1988, Found 538.2001.

(*S*)-1-(4-(Methylthio)-1-oxo-1-(2,2,2-trifluoroethoxy)butan-2-yl)-2,4,6-triphenylpyridin-1-ium, (*S*)-12i:



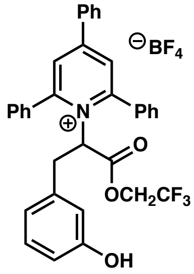
(*S*)-12i was synthesized by following General Procedure B on a 2.76 mmol scale from N-Boc methionine and purified by silica gel column chromatography (1→10→20% acetone in CH_2Cl_2) as eluting solvent. **(*S*)-12i** was obtained as a yellow powder (811.3 mg, 48%): ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.96 (m, 3H), 7.86 – 7.82 (m, 3H), 7.66 – 7.47 (m, 11H), 6.21 (dd, *J* = 9.1, 2.6 Hz, 1H), 4.58 – 4.42 (m, 2H), 2.51 – 2.44 (m, 1H), 2.44 – 2.37 (m, 1H), 2.32 – 2.24 (m, 1H), 1.87 (s, 3H), 1.88 – 1.80 (m, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 167.49, 157.54, 134.14, 133.96, 132.50, 132.36, 132.15, 131.64, 131.35, 129.69, 129.63, 128.61, 122.18 (q, *J* = 277.4 Hz), 66.30, 62.03 (q, *J* = 37.3 Hz), 31.44, 30.54, 14.68. ^{19}**F NMR** (565 MHz, $CDCl_3$) δ -73.22, -152.73. **HRMS (ESI)** calculated for $[C_{30}H_{27}F_3NO_2S, M - BF_4]^+$: 522.1709, Found 522.1705.

(*S*)-1-(3-(4-Hydroxyphenyl)-1-oxo-1-(2,2,2-trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*S*)-12j:



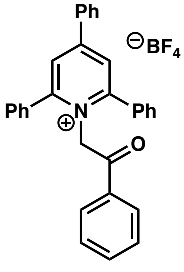
(*S*)-12j was synthesized by following the general procedure A at 5.0 mmol scale from N-Boc tyrosine and purified by silica gel column chromatography (1→10→40% acetone in CH_2Cl_2). **(*S*)-12j** was obtained as a white solid (2.5 g, 78%): ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.83 – 7.76 (m, 2H), 7.67(brs, 2H), 7.61 – 7.35 (m, 9H), 7.26 (s, 2H), 6.88 (brs, 1H), 6.63 – 6.48 (m, 2H), 6.47 – 6.33 (m, 2H), 5.67 (t, *J* = 6.7 Hz, 1H), 4.64 – 4.49 (m, 1H), 4.40 (dq, *J* = 12.6, 8.2 Hz, 1H), 3.15 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.84 (dd, *J* = 14.8, 6.6 Hz, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.24, 157.20, 156.32, 133.27, 132.94, 132.05, 131.88, 129.95, 129.84, 129.43, 128.65, 125.52, 122.42 (q, J = 277.3 Hz), 116.13, , 70.39, 62.16 (q, J = 37.2 Hz), 36.61. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -72.92, -151.32. **HRMS (ESI)** calculated for [$C_{34}H_{27}F_3NO_3$, M + H-BF_4]$^+$: 555.2016, Found 555.2162.

1-(3-(3-Hydroxyphenyl)-1-oxo-1-(2,2,2-trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium, 12k:



12k was synthesized by following General Procedure B on a 2.67 mmol scale from (dl)-N-Boc meta-tyrosine and purified by silica gel column chromatography (1→10→40% acetone in CH_2Cl_2) as eluting solvent. **12k** was obtained as a white powder (891.4 mg, 52%): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.89 (d, J = 6.8 Hz, 2H), 7.71 – 7.31 (m, 10H), 6.95 (dd, J = 8.9, 6.9 Hz, 3H), 6.78 – 6.68 (m, 1H), 6.42 (s, 1H), 6.18 (d, J = 7.6 Hz, 1H), 5.71 (d, J = 4.3 Hz, 1H), 4.62 – 4.37 (m, 2H), 3.27 – 3.14 (m, 1H), 2.99 (dd, J = 14.8, 4.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.99, 157.38, 135.28, 133.22, 132.97, 132.00, 131.75, 130.33, 129.91, 128.76, 122.41 (q, J = 277.4 Hz), 120.25, 115.51, 115.27, 70.07, 62.27 (q, J = 37.2 Hz), 36.81. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -72.98, -150.71. **HRMS (ESI)** calculated for [$C_{34}H_{27}F_3NO_3$, M – BF_4]$^+$: 554.1938, Found 554.1944.

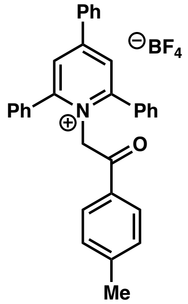
1-(2-*oxo*-2-Phenylethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14a:



14a was synthesized by following the general procedure B at 5.0 mmol scale from α-amino acetophenone and purified by silica gel column chromatography (1→10% acetone in CH_2Cl_2). **14a** was obtained as a white solid (1.8 g, 70%):. **^{1}H NMR** (600 MHz, DMSO) δ 8.64 (s, 2H), 8.41 –

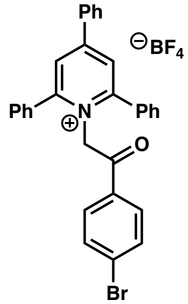
8.33 (m, 2H), 7.80 – 7.54 (m, 15H), 7.44 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.01 (s, 2H). **^{13}C NMR** (151 MHz, DMSO) δ 191.55, 156.62, 155.42, 135.12, 133.12, 132.73, 132.33, 131.12, 129.64, 129.54, 129.13, 129.01, 128.99, 128.97, 128.07, 127.95, 125.84, 61.12. **^{19}F NMR** (565 MHz, DMSO) δ -148.2. **HRMS (ESI)** calculated for [$C_{31}H_{25}NO$, M + H-BF_4]$^+$: 427.1931, Found 427.1940.

1-(2-oxo-2-(*p*-Tolyl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14b:



14b was synthesized by following the general procedure B at 2.5 mmol scale from α-amino 4-methylacetophenone and purified by silica gel column chromatography (1→10% acetone in CH_2Cl_2). **14b** was obtained as a white solid (0.8 g, 60%):. **^{1}H NMR** (400 MHz, DMSO) δ 8.60 (s, 2H), 8.37 – 8.27 (m, 2H), 7.77 – 7.42 (m, 15H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.92 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (151 MHz, DMSO) δ 191.29, 157.04, 155.83, 146.38, 133.57, 132.78, 131.55, 130.65, 130.09, 129.94, 129.55, 129.43, 128.46, 126.27, 61.52, 40.39, 40.25, 40.11, 21.72. **^{19}F NMR** (565 MHz, DMSO) δ -148.2. **HRMS (ESI)** calculated for [$C_{32}H_{27}NO$, M + H-BF_4]$^+$: 441.2087, Found 441.2000.

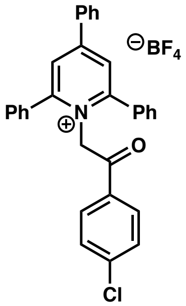
1-(2-(4-Bromophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium, 14c:



14c was synthesized by following General Procedure A on a 2.69 mmol scale from α-amino 4-bromoacetophenone and purified by silica gel column chromatography (1→10% acetone in CH_2Cl_2) as eluting solvent followed by trituration with Et_2O. **14c** was obtained as a white powder

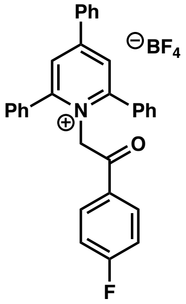
(594.9 mg, 46%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.60 – 7.18 (m, 13H), 5.91 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.09, 157.52, 156.60, 133.73, 132.61, 132.43, 132.04, 131.39, 131.36, 130.61, 129.93, 129.44, 128.16, 125.91, 61.69. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -152.76. **HRMS (ESI)** calculated for [$C_{31}H_{23}BrNO$, M – BF_4]$^+$: 504.0958, Found 504.0951.

1-(2-(4-Chlorophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14d:



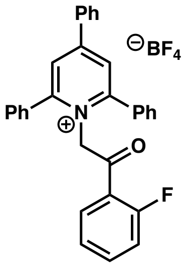
14d was synthesized by following the general procedure B at 2.5 mmol scale from α-amino 4-chloroacetophenone and purified by silica gel column chromatography (1→10% acetone in CH_2Cl_2). **14d** was obtained as a white solid (1.0 g, 73%): **^{1}H NMR** 1H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 3H), 7.91 – 7.83 (m, 2H), 7.70 – 7.56 (m, 6H), 7.56 – 7.29 (m, 8H), 5.94 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 190.76, 156.61, 155.44, 139.84, 132.25, 131.48, 131.07, 129.83, 129.59, 129.16, 129.07, 128.93, 125.79, 60.95. **^{19}F NMR** (565 MHz, DMSO) δ -148.24. **HRMS (ESI)** calculated for [$C_{31}H_{24}ClNO$, M + H-BF_4]$^+$: 461.1541, Found 461.1528.

1-(2-(4-Fluorophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14e:



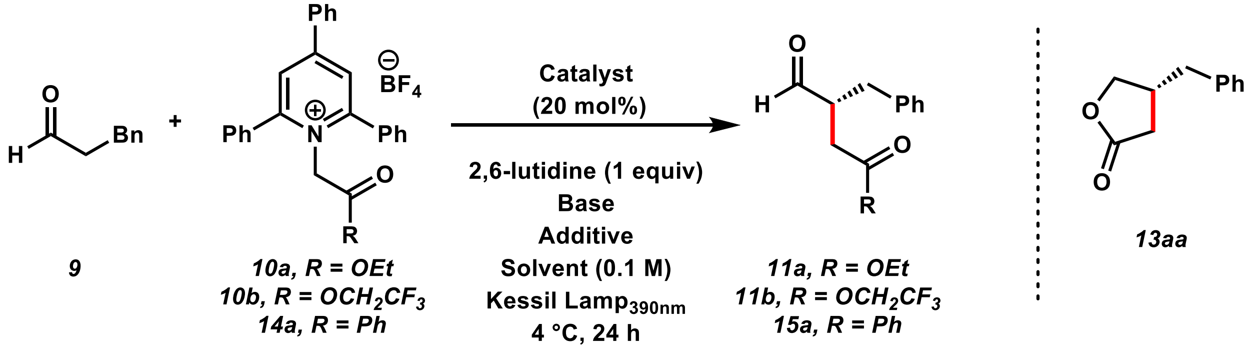
14e was synthesized by following the general procedure B at 2.5 mmol scale from α-amino 4-fluoroacetophenone and purified by silica gel column chromatography (1→20% acetone in CH_2Cl_2). **14e** was obtained as a white solid (0.7 g, 53%): **^{1}H NMR** (400 MHz, DMSO) δ 8.61 (s, 2H), 8.36 – 8.31 (m, 2H), 7.83 – 7.41 (m, 17H), 5.99 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 190.80, 156.63, 155.45, 139.86, 133.09, 132.67, 132.28, 131.50, 131.10, 129.87, 129.62, 129.20, 129.10, 128.96, 125.81, 60.97. **^{19}F NMR** (565 MHz, DMSO) δ -102.57, -148.27. **HRMS (ESI)** calculated for [$C_{31}H_{24}FNO$, M + H-BF_4]$^+$: 444.1836, Found 444.1825.

1-(2-(2-Fluorophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium, 14f:



14f was synthesized by following General Procedure A on a 2.00 mmol scale from α-amino 2-fluoroacetophenone and purified by silica gel column chromatography (1→20% acetone in CH_2Cl_2) followed by trituration with Et_2O. **14f** was obtained as a white powder (478.8 mg, 44%): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.87 – 7.79 (m, 2H), 7.76 – 7.20 (m, 15H), 7.15 (td, *J* = 7.6, 1.0 Hz, 1H), 6.97 (dd, *J* = 11.1, 8.4 Hz, 1H), 5.75 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.73, 162.73, 160.17, 156.92, 156.55, 136.55, 136.45, 133.73, 132.15, 132.06, 131.03, 129.95, 129.57, 128.00, 125.86, 124.67, 116.85, 116.63, 64.02. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -108.09, -153.26. **HRMS (ESI)** calculated for [$C_{31}H_{23}FNO$, M – BF_4]$^+$: 444.1758, Found 444.1784.

3. Optimization Studies



9

10a, R = OEt
10b, R = OCH_2CF_3
14a, R = Ph

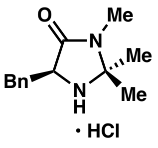
11a, R = OEt
11b, R = OCH_2CF_3
15a, R = Ph

13aa

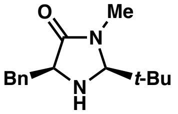
Entry	Pyridinium Salt	Catalyst	Solvent	Base	Additive	Yield[b] (%)	ee[c] (%)
1	*10a*	*A*	CH_2Cl_2	2,6-lutidine	–	5	58
2	*10b*	*A*	CH_2Cl_2	2,6-lutidine	–	36	60
3	*10b*	*A*	DMA	2,6-lutidine	–	40	92
4	*10b*	*B*	DMA	2,6-lutidine	–	22	5
5	*10b*	*C*	DMA	2,6-lutidine	–	55	15
6	*10b*	*D*	DMA	2,6-lutidine	–	52	23
7	*10b*	*A*	DMA	2,6-lutidine	NaI	65	92
8	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	75	92
9[d]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	80	46
10[e]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	58	91
11[f]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	50	91
12[g]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	62	92
13[h]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	18	92
14[j]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	< 5	–
15[k]	*10b*	*A*	DMA	2,6-lutidine	NaI, H_2O	< 5	–

16[d,i]	*14a*	*D*	MTBE	2,6-lutidine	–	40	56
17[d,i]	*14a*	*D*	Et_2O	2,6-lutidine	–	49	60
18[d,i]	*14a*	*D*	DMSO	2,6-lutidine	–	30	57
19[d,i]	*14a*	*D*	$PhCF_3$	2,6-lutidine	–	60	74
20[d,i]	*14a*	*D*	MeCN	2,6-lutidine	–	35	66
21[d,i]	*14a*	*D*	THF	2,6-lutidine	–	22	48
22[d,i]	*14a*	*D*	1,4-dioxane	2,6-lutidine	–	75	67
23[d,i]	*14a*	*D*	1,2-DCE	2,6-lutidine	–	83	55
24[d,i]	*14a*	*D*	DME	2,6-lutidine	–	50	62
25[d,i]	*14a*	*D*	benzene	2,6-lutidine	–	20	4
26[d,i]	*14a*	*D*	$CDCl_3$	2,6-lutidine	–	60	74
27[d,i]	*14a*	*D*	TFE	2,6-lutidine	–	–	–
28[d,i]	*14a*	*D*	Hexane	2,6-lutidine	–	–	–
29[d,i]	*14a*	*D*	EtOAc	2,6-lutidine	–	–	–
30[d,i]	*14a*	*D*	MeOH	2,6-lutidine	–	–	–
31[d,i]	*14a*	*D*	toluene	2,6-lutidine	–	65	70
32[d,i]	*14a*	*D*	CH_2Cl_2	Na_2CO_3	–	80	82
33[d,i]	*14a*	*D*	CH_2Cl_2	LiOAc	–	75	80
34[d,i]	*14a*	*D*	DMSO	iPr_2NEt	–	5	10
35[d,i]	*14a*	*D*	Anisole	iPr_2NEt	–	18	92
36[d,i]	*14a*	*D*	CH_2Cl_2	DABCO	–	30	80
37[d,i]	*14a*	*D*	CH_2Cl_2	Imidazole	–	30	76
38[d,i]	*14a*	*A*	DMSO	iPr_2NEt	–	68	35
39[d,i]	*14a*	*B*	DMSO	iPr_2NEt	–	70	47
40[d,i]	*14a*	*C*	DMSO	iPr_2NEt	–	60	42
41[d,i]	*14a*	*A*	CH_2Cl_2	2,6-lutidine	–	45	92
42[d,h]	*14a*	*A*	CH_2Cl_2	2,6-lutidine	–	70	92

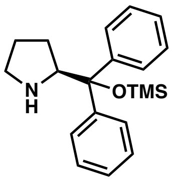
[a]Reaction conditions: **9** (3 equiv, 0.30 mmol), **10** (1 equiv, 0.1 mmol), catalyst (20 mol%, 0.02 mmol), base (1 equiv, 0.1 mmol) NaI (1 equiv, 0.1 mmol), H_2O (1.0 mmol), 4 °C, 24 h. [b]Isolated yield. [c]Enantiomeric excess determined by chiral HPLC analysis of lactone derivative **13aa**. [d]Reaction conducted at 23 °C. [e]50 mol% (0.05 mmol) NaI. [f]No 2,6-lutidine. [g]Irradiation with 370 nm Kessil Lamp. [h]Irradiation with 427 nm Kessil Lamp. [i]Irradiation with 467 nm Kessil Lamp. [j]Irradiation with 525 nm Kessil Lamp. [k]No light.



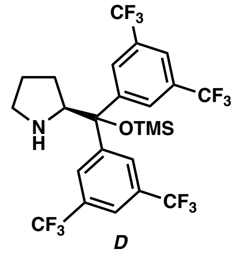
A



B



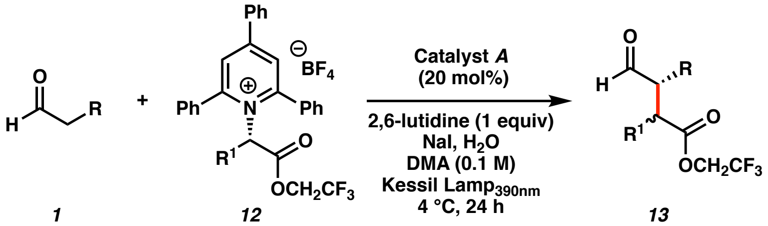
C



D

4. General Procedures for Catalytic Photochemical Enantioselective α-Alkylation with Pyridinium Salts

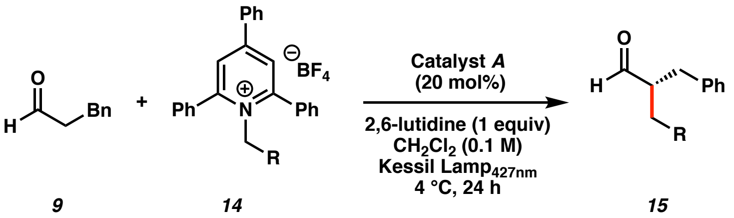
General Procedure C: Enantioselective α-Alkylation with Amino Acid Derived Pyridinium Salts



1 *12* *13*

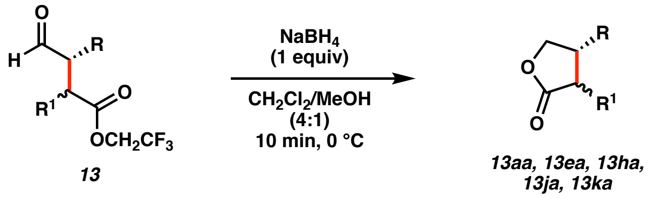
In a flame dried vial under argon, the MacMillan catalyst **A** (5 mg, 20 mol%, 0.02 mmol), pyridinium salt **12** (1.0 equiv, 0.1 mmol), and NaI (15 mg, 1 equiv, 0.1 mmol) were dissolved in 1.0 mL DMA. Aldehyde **1** (3 equiv, 0.3 mmol), 2,6-lutidine (12 µL, 1 equiv, 0.1 mmol), and H_2O (18 µL, 10 equiv, 1.0 mmol) were then added. The reaction mixture was carefully degassed via freeze-pump-thaw (three times), and the vial was refilled with argon. The reaction was stirred and irradiated at 4 °C with a 390 nm Kessil Lamp positioned approximately at 4 cm distance from the reaction vessel using the EasyMax 102 Advanced Thermostat system (Figure S1). After 24 h of irradiation, saturated aqueous NaCl (2 mL) was added, and the mixture was extracted with EtOAc (4 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column flash chromatography on silica gel using hexanes/EtOAc as an eluent to afford the desired product **13**.

General Procedure D: Enantioselective α-Alkylation with Aminoketone Derived Pyridinium Salts



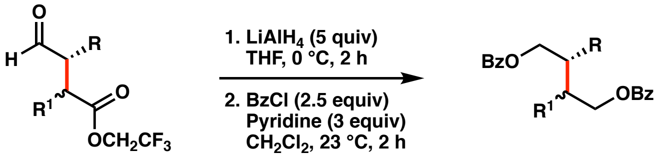
In a flame dried vial under argon, the Macmillan catalyst **A** (5 mg, 20 mol%, 0.02 mmol) and pyridinium salt **14** (1.0 equiv, 0.1 mmol) were dissolved in 1.0 mL CH_2Cl_2. Aldehyde **9** (3 equiv, 0.3 mmol) and 2,6-lutidine (12 µL, 1 equiv, 0.1 mmol) were then added. The reaction mixture was carefully degassed via freeze-pump-thaw (three times), and the vial was refilled with argon. The reaction was stirred and irradiated at 4 °C with a 427 nm Kessil Lamp positioned approximately at 4 cm distance from the reaction vessel using the EasyMax 102 Advanced Thermostat system (Figure S1). After 24 h of irradiation, saturated aqueous NaCl (2 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column flash chromatography on silica gel using hexanes/EtOAc as an eluent to afford the desired products **15**.

General Procedure E: Synthesis of Lactones



To assess the enantiopurity of the products **13** derived from amino acids, a duplicate experiment of the enantioselective α-alkylation (general procedure C) was performed. Upon completion of the reaction, the crude mixture was concentrated under reduced pressure, redissolved in CH_2Cl_2/MeOH (4/1 ratio, 1 mL) under argon, and cooled to 0 °C. $NaBH_4$ (1.0 equiv, 0.1 mmol) was added. After 10 minutes of stirring, the mixture was concentrated under reduced pressure. The reaction mixture was diluted with EtOAc (10 mL) and washed with saturated aqueous NaCl (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexanes/EtOAc as an eluent to afford the desired lactone.

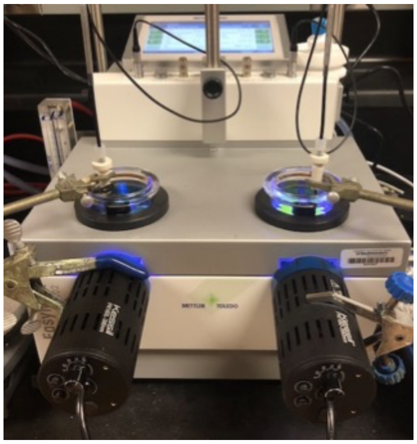
General Procedure F: Synthesis of Diesters



13

13ba, 13ca, 13da, 13fa, 13ga, 13gb, 13ia, 13ib

To assess the enantiopurity of the products **13** derived from amino acids, a duplicate experiment of the enantioselective α-alkylation (general procedure C) was performed. Upon completion of the reaction, the crude mixture was concentrated under reduced pressure, redissolved in THF (1 mL) under argon, and cooled to 0 °C. $LiAH_4$ (5.0 equiv, 0.5 mmol) was added. The reaction mixture was stirred at 0 °C for 2 h and then quenched according to the Fieser workup method by the sequential addition of 10 µL H_2O, 10 µL 15% aqueous NaOH, and 30 µL H_2O. The reaction was dried over $MgSO_4$, passed through a short pad of celite and concentrated under reduced pressure. The crude diol was dissolved in CH_2Cl_2 (1.0 mL) and treated with pyridine (3.0 equiv, 0.3 mmol) and benzoyl chloride (2.5 equiv, 0.25 mmol). After 2 h of stirring at 23 °C, the reaction mixture was concentrated under reduced pressure and purified by preparative TLC using hexanes/EtOAc as the eluent to afford the desired diester.



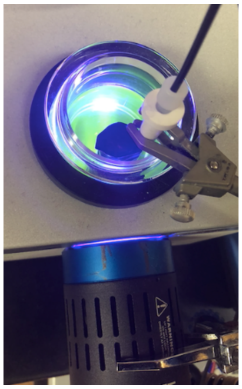
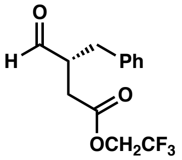


Figure S1. Reaction Setup

The EasyMax 102 Advanced Thermostat system from Mettler-Toledo AutoChem, Inc. (Product ID: 51161711) was used for the first time to perform low temperature photochemical reactions. We chose the EasyMax 102 for reaction setup because of the ease of maintaining low reaction temperatures for long periods of time, while also shining light on the reaction mixture through the clear window display. All photochemical reactions were carried out using Kessil lamps PR160L (https://www.kessil.com/science/PR160L.php) with wavelength of peak intensity of 390 nm or 427 nm. The lamp intensity was set to 100% and positioned at a distance of 4 cm from the reaction vessel, unless otherwise stated.

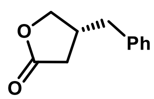
5. Characterization Data for Products

2,2,2-Trifluoroethyl (*R*)-3-benzyl-4-oxobutanoate, 13a:



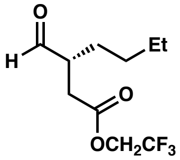
13a was synthesized by following the general procedure C at 0.1 mmol scale from **12a** and purified by silica gel column chromatography using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13a** was obtained as a colorless oil (21 mg, 75%): $[\alpha]_D^{25}$ = 3.33 (c = 0.15, $CHCl_3$). **^{1}H NMR** (600 MHz, C_6D_6) δ 9.26 (s, 1H), 7.05 (t, *J* = 7.3 Hz, 2H), 7.03 – 6.97 (m, 1H), 6.84 – 6.76 (m, 2H), 3.95 – 3.85 (m, 1H), 3.88 – 3.79 (m, 1H), 2.69 – 2.62 (m, 1H), 2.55 (dd, J = 13.8, 6.2 Hz, 1H), 2.30 (dd, *J* = 17.1, 8.2 Hz, 1H), 2.19 (dd, *J* = 13.8, 8.6 Hz, 1H), 1.93 (dd, *J* = 17.2, 5.0 Hz, 1H). **^{13}C NMR** (151 MHz, C_6D_6) δ 200.5, 170.1, 137.8, 128.8, 128.5, 126.6, 123.5 (d, *J* = 277.2 Hz), 60.2 (q , *J* = 36.0 Hz) 49.2, 34.2, 31.6. **^{19}F NMR** (565 MHz, C_6D_6) δ 73.8. **HRMS (ESI)** calculated for $[C_{13}H_{13}F_3O_3$, M + Na$]^+$: 297.0709, Found 297.0712. The enantiomeric excess of product **13a** determined to be 92% after conversion to lactone **13aa.**

(*R*)-4-Benzyldihydrofuran-2(3*H*)-one, 13aa:



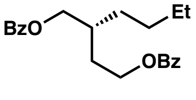
13aa was synthesized by following the general procedure E at 0.1 mmol scale from **13a** and purified by silica gel column chromatography using hexanes/EtOAc (9:1) as eluting solvent. **13aa** was obtained as a colorless oil (10 mg, 57%): 92% ee. HPLC conditions: Chiralpak AD_H column (25 cm × 0.46 cm ID), hexanes/IPA = 95:05, 0.8 mL/min, 210 nm UV detector, tR = 22.68 min (major) and tR= 24.62 min (minor). **[α]$_D$^{25}** = 7.98 (c = 0.05, CHCl$_3$). **^{1}H NMR** (400 MHz, CDCl3) δ 7.31 – 7.22 (m, 2H), 7.21 – 7.14 (m, 1H), 7.13 – 7.04 (m, 2H), 4.27 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.97 (dd, *J* = 9.2, 6.1 Hz, 1H), 2.86 – 2.65 (m, 3H), 2.54 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.23 (dd, *J* = 17.5, 6.9 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 177.0, 138.3, 129.0, 128.8, 127.0, 77.5, 77.2, 76.8, 72.8, 39.1, 37.3, 34.4. **HRMS (ESI)** calculated for [$C_{11}H_{12}O_2$, M + Na]$^+$: 199.0730, Found 199.0745.

2,2,2-Trifluoroethyl (*R*)-3-formylheptanoate, 13b:



13b was synthesized by following the general procedure C at 0.1 mmol scale from **12b** and purified by silica gel column chromatography using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13b** was obtained as a colorless oil (16.5 mg, 69%). **[α]$_D$^{25}** = +5.38 (c = 0.29, CHCl$_3$). **^{1}H NMR** (600 MHz, C_6D_6) δ 9.21 (s, 1H), 4.04 (dq, *J* = 12.8, 8.6 Hz, 1H), 3.83 (dq, *J* = 12.8, 8.6 Hz, 1H), 2.43 – 2.27 (m, 2H), 1.95 – 1.83 (m, 1H), 1.22 – 1.12 (m, 1H), 1.06 – 0.96 (m, 2H), 0.95 – 0.80 (m, 3H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, C_6D_6) δ 201.1, 170.3, 123.5 (d, *J* = 277.2 Hz), 60.2 (q, *J* = 33.8 Hz), 47.5, 32.0, 28.8, 28.0, 22.9, 13.9. **HRMS (ESI)** calculated for [$C_{10}H_{15}F_3O_3$, M + Na]$^+$: 263.0866, Found 263.0868. The enantiomeric excess of product **13b** determined to be 91% after conversion to diester **13ba.**

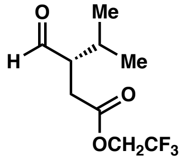
(*R*)-2-Butylbutane-1,4-diyl dibenzoate, 13ba:



13ba was synthesized by following the general procedure F at 0.1 mmol scale from **13b** and purified by preparative TLC using hexanes/EtOAc (9:1) as eluting solvent. **13ba** was obtained as a colorless oil (19 mg, 54%): 91% ee. HPLC conditions: Chiralpak AD_H column (25 cm × 0.46 cm ID), hexanes/IPA = 95:05, 0.7 mL/min, 230 nm UV detector, tR = 12.53 min (major) and tR=

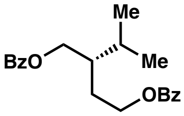
11.74 min (minor). **[α]$_D$^{25}** = -27.99 (c = 0.05, CHCl$_3$). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.03 (ddd, *J* = 8.4, 4.2, 1.4 Hz, 4H), 7.60 – 7.50 (m, 2H), 7.43 (td, *J* = 7.6, 5.8 Hz, 4H), 4.51 – 4.41 (m, 2H), 4.38 (dd, *J* = 11.1, 5.9 Hz, 1H), 4.29 (dd, *J* = 11.1, 5.9 Hz, 1H), 2.04 (qd, *J* = 6.4, 5.1 Hz, 1H), 1.93 (dq, *J* = 10.8, 7.0 Hz, 2H), 1.50 (ddt, *J* = 8.3, 6.2, 2.5 Hz, 2H), 1.37 (ddtd, *J* = 19.7, 9.5, 7.5, 5.9 Hz, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 166.7, 166.7, 133.1, 133.0, 130.4, 129.7, 128.5, 128.5, 67.5, 63.3, 35.1, 31.2, 30.9, 29.1, 23.0, 14.1. **HRMS (ESI)** calculated for [$C_{22}H_{26}O_4$, M + Na]$^+$: 377.1723, Found 377.1713.

2,2,2-Trifluoroethyl (*S*)-3-formyl-4-methylpentanoate, 13c:



13c was synthesized by following the general procedure C at 0.1 mmol scale from **12c** and purified by silica gel column chromatography using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13c** was obtained as a colorless oil (14 mg, 62%). **[α]$_D$^{25}** = +34.26 (c = 0.17, CHCl$_3$). **^{1}H NMR** (600 MHz, C$_6$D$_6$) δ 9.37 (s, 1H), 4.26 – 4.14 (m, 1H), 3.92 (dddd, *J* = 14.7, 8.3, 4.0, 1.9 Hz, 1H), 2.59 (dd, *J* = 16.7, 9.8 Hz, 1H), 2.52 (dt, *J* = 9.7, 4.1 Hz, 1H), 1.93 (ddd, *J* = 16.8, 3.8, 2.0 Hz, 1H), 1.67 – 1.58 (m, 1H), 0.63 (dd, *J* = 6.9, 1.8 Hz, 3H), 0.53 (dd, *J* = 7.0, 1.8 Hz, 3H). **^{13}C NMR** (151 MHz, C$_6$D$_6$) δ 201.5, 170.8, 123.7 (q, *J* = 277.2 Hz), 60.2 (q, *J* = 36.4 Hz), 53.4, 53.3, 28.8, 27.3, 19.8, 18.6. **^{19}F NMR** (565 MHz, CDCl$_3$) δ -73.80 (t, *J* = 8.5 Hz). **HRMS (ESI)** calculated for [$C_9H_{13}F_3O_3$, M + Na]$^+$: 249.0709, Found 249.0710. The enantiomeric excess of product **13c** determined to be 95% after conversion to diester **13ca**.

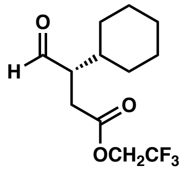
(*S*)-2-Isopropylbutane-1,4-diyl dibenzoate, 13ca:



13ca was synthesized by following the general procedure F at 0.1 mmol scale from **13c** and purified by preparative TLC using hexanes/EtOAc (9:1) as eluting solvent. **13ca** was obtained as a colorless oil (12 mg, 34%): 95% ee. HPLC conditions: Chiralpak AD_H column (25 cm × 0.46 cm ID), hexanes/IPA = 95:05, 0.7 mL/min, 230 nm UV detector, tR = 13.75 min (major) and tR=

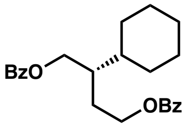
12.80 min (minor). **[α]$_D^{25}$** = +13.99 (c = 0.20, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 8.4, 3.0, 1.4 Hz, 4H), 7.55 (dddd, *J* = 8.7, 5.5, 2.8, 1.4 Hz, 2H), 7.42 (tdd, *J* = 7.4, 4.3, 1.6 Hz, 4H), 4.50 – 4.39 (m, 3H), 4.32 (dd, *J* = 11.2, 5.8 Hz, 1H), 2.03 – 1.81 (m, 4H), 1.01 (dd, *J* = 6.8, 4.5 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.8, 166.7, 133.1, 133.0, 130.4, 130.4, 129.7, 128.5, 128.5, 66.1, 63.8, 40.7, 29.1, 28.1, 19.7, 19.7. **HRMS (ESI)** calculated for [$C_{21}H_{24}O_4$, M + H]$^+$: 341.1747, Found 341.1789.

2,2,2-Trifluoroethyl (*S*)-3-cyclohexyl-4-oxobutanoate, 13d:



13d was synthesized by following the general procedure C at 0.1 mmol scale from **12d** and purified by silica gel column chromatography using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13d** was obtained as a colorless oil (16 mg, 60%). **[α]$_D^{25}$** = +9.59 (c = 0.25, $CHCl_3$). **^{1}H NMR** (600 MHz, C_6D_6) δ 9.32 (s, 1H), 4.12 (dd, *J* = 12.8, 8.6 Hz, 1H), 3.81 (dd, *J* = 12.8, 8.6 Hz, 1H), 2.54 (dd, J = 16.9, 9.8 Hz, *1*H), 2.48 – 2.40 (m, 1H), 1.87 (dd, *J* = 16.8, 3.8 Hz, 1H), 1.53 – 1.40 (m, 3H), 1.23 (dddt, *J* = 13.4, 10.0, 6.5, 3.5 Hz, 2H), 1.10 (ddd, *J* = 13.2, 4.6, 2.2 Hz, 1H), 1.05 – 0.78 (m, 3H), 0.60 (dqd, *J* = 35.3, 12.2, 3.3 Hz, 2H).**^{13}C NMR** (151 MHz, C_6D_6) δ 201.6, 170.8, 124.6 (q, *J* = 275.1 Hz), 60.3 (q, *J* = 33.8 Hz), 53.1, 37.5, 30.6, 29.4, 29.4, 26.6, 26.5, 26.1. **^{19}F NMR** (565 MHz, C_6D_6) δ 73.8. **HRMS (ESI)** calculated for [$C_{12}H_{17}F_3O_3$, M + Na]$^+$: 289.1022, Found 289.1044. The enantiomeric excess of product **13d** determined to be 96% after conversion to diester **13da.**

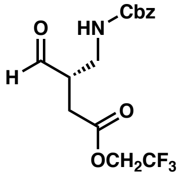
(*S*)-2-Cyclohexylbutane-1,4-diyl dibenzoate, 13da:



13da was synthesized by following the general procedure F at 0.1 mmol scale from **13d** and purified by preparative TLC using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13da** was obtained as a colorless oil (12 mg, 32%): 96% ee. HPLC conditions: Chiralcel OJ_H column (25 cm × 0.46 cm ID), hexanes/IPA = 97:03, 0.6 mL/min, 230 nm UV detector. tR = 24.64 min (major) and tR= 27.51 min (minor). **[α]$_D^{25}$** = -24.20 (c = 0.19, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 – 7.98

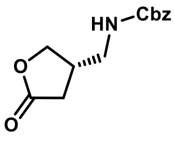
(m, 4H), 7.60 – 7.50 (m, 2H), 7.47 – 7.37 (m, 4H), 4.50 – 4.38 (m, 3H), 4.30 (dd, *J* = 11.2, 5.9 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.94 – 1.85 (m, 2H), 1.77 (tt, *J* = 10.6, 3.4 Hz, 3H), 1.71 – 1.64 (m, 1H), 1.60 – 1.51 (m, 2H), 1.31 – 1.20 (m, 3H), 1.15 (dddd, *J* = 17.3, 13.6, 8.6, 3.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.8, 166.7, 133.1, 133.0, 130.4, 129.7, 129.7, 128.5, 128.5, 66.2, 63.9, 40.3, 39.6, 30.5, 29.9, 28.4, 26.9, 26.8, 26.7. **HRMS (ESI)** calculated for [$C_{24}H_{28}O_4$, M + Na]$^+$: 403.1880, Found 403.1908.

2,2,2-Trifluoroethyl (S)-4-(((benzyloxy)carbonyl)amino)-3-formylbutanoate, 13f:



13f was synthesized by following the general procedure C at 0.1 mmol scale from **12f** and purified by silica gel column chromatography using hexanes/EtOAc (8.5:1.5) as eluting solvent. **13f** was obtained as a colorless oil (27 mg, 78%). **$[\alpha]_D^{25}$** = +3.50 (c = 0.40, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.40 – 7.28 (m, 5H), 5.09 (dd, *J* = 10.3, 5.3 Hz, 3H), 4.47 (q, *J* = 8.4 Hz, 2H), 3.57 (q, *J* = 6.1, 5.6 Hz, 2H), 3.06 (q, *J* = 6.1 Hz, 1H), 2.85 (dd, *J* = 17.3, 6.9 Hz, 1H), 2.64 (dd, *J* = 17.3, 6.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.8, 200.8, 170.2, 156.7, 136.2, 128.7, 128.5, 128.3, 123.8 (q, *J* = 275.1 Hz), 67.2, 60.9 (q, *J* = 32.8 Hz), 48.5, 39.4, 30.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ 73.7. **HRMS (ESI)** calculated for [$C_{15}H_{16}F_3NO_5$, M + Na]$^+$: 370.0873, Found 370.0854. The enantiomeric excess of product **13f** determined to be 90% after conversion to lactone **13fa**

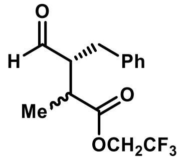
Benzyl (*S*)-((5-oxotetrahydrofuran-3-yl)methyl)carbamate, 13fa:



13fa was synthesized by following the general procedure E at 0.1 mmol scale from **13f** and purified by silica gel column chromatography using hexanes/EtOAc (9:1) as eluting solvent. **13fa** was obtained as a colorless oil (15 mg, 60%): 90% ee. HPLC conditions: Chiralcel OJ_H column (25 cm × 0.46 cm ID), hexanes/IPA = 70:30, 0.8 mL/min, 230 nm UV detector, tR = 38.15 min (major) and tR= 35.58 min (minor). **$[\alpha]_D^{25}$** = -11.99 (c = 0.15, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44

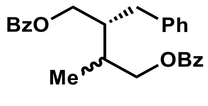
– 7.28 (m, 5H), 5.10 (s, 2H), 4.95 (s, 1H), 4.40 (dd, J = 9.4, 7.3 Hz, 1H), 4.09 (dd, *J* = 9.4, 5.6 Hz, 1H), 3.30 (td, *J* = 6.7, 3.7 Hz, 2H), 2.89 – 2.78 (m, 1H), 2.63 (dd, *J* = 17.7, 8.7 Hz, 1H), 2.31 (dd, *J* = 17.7, 6.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.2, 156.5, 136.0, 128.6, 128.2, 70.8, 67.1, 42.9, 35.9, 31.9. **HRMS (ESI)** calculated for [$C_{13}H_{15}NO_4$, M + Na]$^+$: 272.0893, Found 272.0871.

2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-methyl-4-oxobutanoate, 13g:



13g was synthesized by following the general procedure C at 0.1 mmol scale from **12g** and purified by silica gel column chromatography using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13g** was obtained as a colorless oil (16 mg, 56%): *dr* 2:1, **[α]$_D$^{25}** = +6.82 (c = 0.16, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.66 (s, 1.2H), 9.63 (d, *J* = 1.1 Hz, 1H), 7.23 (td, *J* = 7.4, 4.0 Hz, 5H), 7.19 – 7.14 (m, 2.74 H), 7.14 – 7.07 (m, 4.91H), 4.45 – 4.33 (m, 3.79 H), 4.28 (dq, *J* = 12.6, 8.4 Hz, 1.41 H), 3.10 – 3.01 (m, 2.57H), 3.01 – 2.93 (m, 2.90H), 2.91 – 2.77 (m, 4.12H), 2.76 – 2.66 (m, 1.35H), 1.21 (dd, *J* = 7.2, 5.1 Hz, 7.94H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.23, 202.16, 173.38, 172.97, 137.92, 137.84, 129.16, 129.02, 128.94, 128.88, 126.97, 126.95, 123.93 (q, *J* = 275.1 Hz), 123.89 (q, *J* = 275.1 Hz), 60.73 (q, *J* = 32.8 Hz), 55.21, 54.70, 38.64, 38.04, 32.84, 32.37, 14.23, 13.50. **^{19}F NMR** (565 MHz, $CDCl_3$) δ 73.74, 73.76. **HRMS (ESI)** calculated for [$C_{14}H_{15}F_3O_3$, M + Na]$^+$: 311.0866, Found 311.0872. The enantiomeric excess of product **13g** determined to be 99% and 97% for the major and minor diastereomers, respectively, after conversion to diester **13ga.**

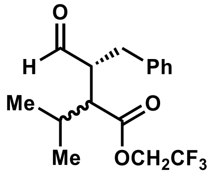
(2*R*)-2-Benzyl-3-methylbutane-1,4-diyl dibenzoate, 13ga:



13ga was synthesized by following the general procedure F at 0.1 mmol scale from **13g** and purified by preparative TLC using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13ga** was obtained as a colorless oil (20 mg, 50%): *dr* 2:1, 99% ee, 97%ee. HPLC conditions: Chiralcel OJ_H column (25 cm × 0.46 cm ID), hexanes/IPA = 70:30, 0.8 mL/min, 230 nm UV detector, *dr*1 tR = 14.76 min (major) and tR= 19.01 min (minor), tR = 16.52 min (major) and tR= 19.94 min (minor). **[α]$_D$^{25}** =

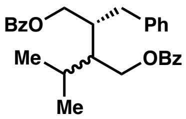
-15.64 (c = 0.11, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 8.02 – 7.98 (m, 2H), 7.98 – 7.94 (m, 2H), 7.60 – 7.51 (m, 4H), 7.46 – 7.39 (m, 8H), 7.27 (dt, *J* = 4.9, 3.3 Hz, 6H), 7.23 – 7.16 (m, 6H), 4.42 (ddd, *J* = 11.2, 6.4, 4.9 Hz, 2H), 4.38 – 4.30 (m, 4H), 4.28 (dd, *J* = 11.3, 4.5 Hz, 2H), 2.92 (dd, *J* = 13.9, 4.6 Hz, 2H), 2.88 – 2.80 (m, 2H), 2.67 (dd, *J* = 13.9, 9.4 Hz, 2H), 2.42 – 2.32 (m, 4H), 1.16 (dd, *J* = 6.9, 5.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) 166.69, 166.65, 166.64, 166.62, 140.12, 140.02, 133.15, 133.12, 130.33, 130.23, 129.70, 129.67, 129.15, 129.14, 128.57, 128.53, 126.40, 68.21, 67.66, 65.07, 64.81, 53.59, 41.96, 41.53, 35.82, 34.23, 33.76, 33.69, 13.91, 13.64. **HRMS (ESI)** calculated for $[C_{26}H_{26}O_4, M + Na]^+$: 425.1723, Found 425.1721.

2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-isopropyl-4-oxobutanoate, 13h:



13h was synthesized by following the general procedure C at 0.1 mmol scale from **12h** and purified by silica gel column chromatography using hexanes/EtOAc (9.5:0.5) as eluting solvent. **13h** was obtained as a colorless oil (16 mg, 51%): *dr* 1:1. **$[\alpha]_D^{25}$** = -8.80 (c = 0.13, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.83 (d, *J* = 1.3 Hz, 1H), 4.61 – 4.39 (m, 2H), 3.07 – 2.97 (m, 2H), 2.90 – 2.80 (m, 1H), 2.53 (dd, *J* = 7.7, 6.1 Hz, 1H), 2.26 – 2.15 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.8, 202.8, 172.3, 137.7, 129.1, 128.9, 127.0, 123.9 (q, *J* = 274.1 Hz), 60.4 (q, *J* = 38.0 Hz), 52.2, 51.9, 33.5, 28.0, 20.9, 19.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ 73.74. **HRMS (ESI)** calculated for $[C_{14}H_{15}F_3O_3, M + Na]^+$: 339.1179, Found 339.1187. The enantiomeric excess of product **13h** determined to be 97% and 98% for the major and minor diastereomers, respectively, after conversion to diester **13ha** and **13hb.**

(2*R*)-2-Benzyl-3-isopropylbutane-1,4-diyl dibenzoate, 13ha and 13hb:

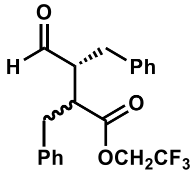


13ha and **13hb** were synthesized by following the general procedure F at 0.2 mmol scale from **13h** and purified by silica gel column chromatography using hexanes/EtOAc (10:1) as eluting solvent to yield separable diastereomers.

13ha (diastereomer 1) was obtained as a colorless oil (6.2 mg, 8% yield, 97% ee): HPLC conditions: Chiralpak AD-H column (25 cm × 0.46 cm ID), hexanes/IPA = 95:5, 0.8 mL/min, 230 nm UV detector, tR = 9.05 min (major) and tR= 11.19 min (minor). **$[\alpha]_D^{25}$** = +37.1 (c = 0.07, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.97 – 7.90 (m, 2H), 7.61 – 7.50 (m, 2H), 7.43 (dt, *J* = 14.0, 7.7 Hz, 4H), 7.31 – 7.22 (m, 7H), 7.19 (d, *J* = 7.3 Hz, 3H), 4.60 – 4.48 (m, 2H), 4.35 – 4.27 (m, 2H), 3.03 (dd, *J* = 13.7, 4.0 Hz, 1H), 2.65 (dd, *J* = 13.7, 10.7 Hz, 1H), 2.52 (dp, *J* = 10.2, 5.0 Hz, 1H), 2.09 (h, *J* = 6.7 Hz, 1H), 1.95 (p, *J* = 5.2 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.73, 166.59, 140.41, 133.15, 133.08, 130.34, 130.27, 129.69, 129.64, 129.10, 128.72, 128.61, 128.52, 126.39, 65.77, 63.86, 44.28, 40.03, 34.77, 27.53, 21.94, 20.19. **HRMS (ESI)** calculated for $[C_{28}H_{30}O_4, M + Na]^+$: 453.2042, Found 453.2020.

13hb (diastereomer 2) was obtained as a colorless oil (4.8 mg, 6% yield, 98% ee): HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 98:2, 0.5 mL/min, 230 nm UV detector, tR = 26.67 min (major) and tR= 28.52 min (minor). **$[\alpha]_D^{25}$** = -5.0 (c = 0.12, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 24.6, 8.3, 1.3 Hz, 4H), 7.59 – 7.51 (m, 2H), 7.45 – 7.37 (m, 4H), 7.31 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 4.57 – 4.47 (m, 3H), 4.30 (dd, *J* = 11.3, 6.6 Hz, 1H), 2.99 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.85 (dd, *J* = 13.9, 7.4 Hz, 1H), 2.53 (qt, *J* = 7.4, 4.5 Hz, 1H), 2.15 – 2.04 (m, *J* = 6.9 Hz, 1H), 1.76 – 1.70 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.62, 166.54, 140.02, 133.00, 132.96, 130.18, 130.15, 129.54, 129.53, 129.09, 128.57, 128.46, 128.40, 126.23, 65.38, 63.37, 44.52, 40.07, 37.00, 27.56, 21.59, 20.22. **HRMS (ESI)** calculated for $[C_{28}H_{30}O_4, M + Na]^+$: 453.2042, Found 453.2024.

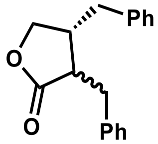
2,2,2-Trifluoroethyl (3*R*)-2,3-dibenzyl-4-oxobutanoate, 13i:



13i was synthesized by following the general procedure C at 0.1 mmol scale by **12i** and purified by silica gel column chromatography using pentane/Et_2O (9.5:0.5) as eluting solvent. **13i** was obtained as a colorless oil (20 mg, 55%): *dr* 1:1, **$[\alpha]_D^{25}$** = -5.50 (c = 0.35, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.78 (s, 0.3H), 9.68 (d, *J* = 1.5 Hz, 1H), 7.29 (td, *J* = 7.4, 4.9 Hz, 5.2H), 7.25 – 7.21 (m, 3.2H), 7.14 (dd, *J* = 9.0, 7.2 Hz, 4.4H), 7.10 – 7.05 (m, 1.4H), 4.54 – 4.36 (m, 1.7H), 4.36

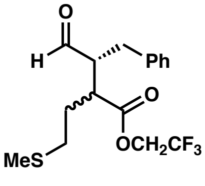
– 4.22 (m, 1.6H), 3.31 (dt, *J* = 8.9, 6.4 Hz, 1.1H), 3.22 – 3.02 (m, 3.7H), 3.00 – 2.87 (m, 4.8H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 202.14, 201.85, 172.20, 171.67, 137.74, 129.16, 129.08, 129.01, 128.92, 128.85, 128.79, 127.14, 127.02, 123.76 (q, *J* = 275.1 Hz), 60.53 (q, *J* = 38.0 Hz), 53.61, 53.35, 46.83, 45.94, 35.39, 35.38, 33.05, 32.84. **^{19}F NMR** (565 MHz, CDCl$_3$) δ 73.52, 73.53. **HRMS (ESI)** calculated for [$C_{20}H_{19}F_3O_3$, M + Na]$^+$: 387.1179, Found 387.1153. The enantiomeric excess of product **13i** determined to be 97% and 97% respectively, after conversion to lactone **13ia.**

(4*R*)-3,4-Dibenzyldihydrofuran-2(3*H*)-one, 13ia:



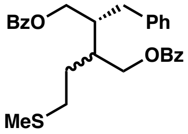
13ia was synthesized by following the general procedure E at 0.2 mmol scale from **13i** and purified by silica gel column chromatography using hexanes/EtOAc (5:1) as eluting solvent. **13ia** was obtained as a colorless oil (10.3 mg, 19% yield, 3:2 dr, 97%/97% ee). HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 0.8 mL/min, 210 nm UV detector: tR = 33.91 min (major), tR = 35.19 min (major) tR= 38.86 min (minor), 46.22 min (minor). **$[\alpha]_D^{25}$** = +14.7 (c = 0.45, CHCl$_3$). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.37 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.19 (m, 13H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 7.0 Hz, 2H), 6.99 (d, *J* = 7.1 Hz, 2H), 4.11 – 3.99 (m, 3H), 3.86 (dd, *J* = 9.2, 7.8 Hz, 1H), 3.35 (dd, *J* = 15.0, 4.7 Hz, 1H), 3.16 – 3.06 (m, 2H), 3.02 – 2.93 (m, 2H), 2.85 (dd, *J* = 15.0, 10.9 Hz, 1H), 2.71 – 2.60 (m, 3H), 2.55 – 2.46 (m, 2H), 2.39 (dd, *J* = 13.7, 12.5 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 178.51, 177.96 138.60, 137.96, 137.71, 129.32, 128.98, 128.84, 128.76, 128.75, 128.61, 128.41, 126.93, 126.80, 126.75, 126.71, 71.18, 69.43, 46.45, 45.29, 41.32, 39.92, 38.53, 35.05, 32.93, 30.88. **HRMS (ESI)** calculated for [$C_{18}H_{18}O_2$, M + Na]$^+$: 289.1199, Found 289.1140.

2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-(2-(methylthio)ethyl)-4-oxobutanoate, 13j:



13j was synthesized by following the general procedure C at 0.1 mmol scale from **12j** and purified by silica gel column chromatography using pentane/Et$_2$O (9.5:0.5) as eluting solvent. **13j** was obtained as a colorless oil (15 mg, 43%): *dr* 1:1.7, **[α]$_D$^{25}** = -23.63 (c = 0.11, $CHCl_3$).**^{1}H NMR** (600 MHz, CDCl3) δ 9.75 (s, 0.6H), 9.68 (d, J = 1.5 Hz, 1H), 7.31 (t, J = 7.9 Hz, 4H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 4H), 4.62 – 4.31 (m, 3.9H), 3.19 – 3.00 (m, 5.7H), 2.88 (dd, J = 13.5, 5.5 Hz, 0.7H), 2.80 (dd, J = 13.3, 5.0 Hz, 1.2H), 2.62 – 2.50 (m, 2.2H), 2.48 – 2.42 (m, 2.2H), 2.20 – 2.07 (m, 2H), 2.06 (d, J = 7.3 Hz, 6H), 1.94 – 1.71 (m, 2H). **^{13}C NMR** (151 MHz, CDCl3) δ 201.86, 201.83, 172.35, 171.97, 137.74, 137.67, 129.14, 129.09, 129.07, 128.95, 128.94, 127.05, 125.67, 123.90 (q, J = 276.0 Hz), 123.84 (q, J = 276.6 Hz), 122.06, 122.00, 120.16, 60.95 (q, J = 35.0 Hz), 60.79 (q, J = 36.0 Hz), 54.34, 54.30, 43.71, 42.94, 33.09, 32.71, 32.01, 31.80, 28.49, 28.36, 15.46, 15.41. **^{19}F NMR** (565 MHz, $CDCl_3$) δ 73.50 (m). **HRMS (ESI)** calculated for [$C_{16}H_{19}F_3O_3S$, M + Na]$^+$: 371.0899, Found 371.0915. The enantiomeric excess of product **13j** determined to be 99% and 97% respectively, after conversion to diesters **13ja** and **13jb.**

(2*R*)-2-Benzyl-3-(2-(methylthio)ethyl)butane-1,4-diyl dibenzoate, 13ja and 13jb:



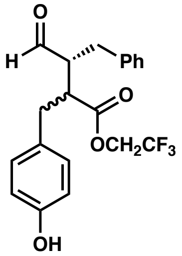
13ja and **13jb** were synthesized by following the general procedure F at 0.25 mmol scale from **13j** and purified by silica gel column chromatography using hexanes/EtOAc (5:1) as eluting solvent to yield separable diastereomers.

13ja (diastereomer 1) was obtained as a colorless oil (12.9 mg, 11% yield, 97% ee): HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 95:5, 0.8 mL/min, 230 nm UV detector, tR = 22.42 min (major) and tR= 25.17 min (minor). **[α]$_D$^{25}** = +13.8 (c = 0.39, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 4H), 7.61 – 7.51 (m, 2H), 7.43 (m, 4H), 7.33 – 7.24 (m, 3H), 7.21 (m, 3H), 4.55 – 4.39 (m, 2H), 4.42 – 4.27 (m, 2H), 2.90 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.83 – 2.72 (m, 1H), 2.74 – 2.63 (m, 1H), 2.65 – 2.53 (m, 1H), 2.53 – 2.39 (m, 1H), 2.37 – 2.25 (m, 1H), 1.99 – 1.76 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.50, 166.45, 139.81, 133.10, 133.05, 130.02, 130.00, 129.57, 128.99, 128.65, 128.51, 128.48, 128.44, 126.39, 65.46, 65.08, 41.26, 37.67, 35.09, 32.47, 28.03, 15.57. **HRMS (ESI)** calculated for [$C_{28}H_{30}O_4S$, M + Na]$^+$: 485.1757, Found 483.1745.

13jb (diastereomer 2) was obtained as a colorless oil (13.5 mg, 12% yield, 99% ee): HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 95:5, 0.8 mL/min, 230 nm

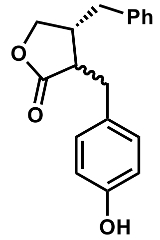
UV detector, tR = 17.97 min (major) and tR= 20.72 min (minor). **[α]$_D$^{25}** = +8.9 (c = 0.38, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 8.01 – 7.93 (m, 2H), 7.61 – 7.51 (m, 2H), 7.48 – 7.36 (m, 4H), 7.32 – 7.24 (m, 2H), 7.24 – 7.16 (m, 3H), 4.51 (dd, *J* = 11.5, 6.1 Hz, 1H), 4.46 – 4.35 (m, 2H), 4.30 (dd, *J* = 11.4, 5.3 Hz, 1H), 2.91 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.80 (dd, *J* = 13.9, 8.9 Hz, 1H), 2.65 – 2.51 (m, 2H), 2.50 – 2.38 (m, 1H), 2.35 – 2.23 (m, 1H), 2.06 (s, 3H), 1.97 – 1.80 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.55, 166.46, 139.75, 133.14, 133.06, 130.02, 130.00, 129.57, 129.55, 129.00, 128.66, 128.51, 128.44, 126.38, 65.10, 64.80, 41.40, 37.99, 35.37, 32.36, 28.57, 15.50. **HRMS (ESI)** calculated for [$C_{28}H_{30}O_4S$, M + Na]$^+$: 485.1757, Found 485.1755.

2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-(4-hydroxybenzyl)-4-oxobutanoate, 13k:



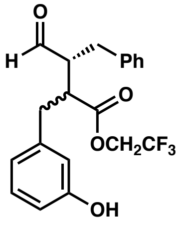
13k was synthesized by following the general procedure C at 0.1 mmol scale from **12k** and purified by silica gel column chromatography using hexanes/EtOAc (8.0:2.0) as eluting solvent. **13k** was obtained as a colorless oil (25 mg, 66%): *dr* 2:1, **[α]$_D$^{25}** = -5.83 (c = 0.26, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.76 (d, J = 1.5 Hz, 0.35H), 9.66 (d, J = 1.5 Hz, 1H), 7.29 (dt, J = 7.7, 6.6 Hz, 4H), 7.25 – 7.20 (m, 3H), 7.17 – 7.12 (m, 3H), 7.10 – 7.07 (m, 1H), 6.99 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.5 Hz, 1H), 6.74 (dd, J = 13.6, 8.5 Hz, 3H), 5.06 (brs, 2H), 4.49 – 4.36 (m, 2H), 4.35 – 4.21 (m, 2H), 3.24 (dt, J = 8.9, 6.5 Hz, 1H), 3.17 – 3.11 (m, 0.74H), 3.06 – 3.01 (m, 2H), 2.98 – 2.93 (m, 2H), 2.86 (ddd, J = 28.1, 14.0, 6.0 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.28, 202.01, 172.26, 171.74, 154.72, 154.65, 137.76, 137.66, 130.23, 130.14, 129.74, 129.15, 129.09, 128.92, 127.02, 126.99, 123.85 (q, J = 276.2 Hz), 123.78 (q, J = 275.6 Hz), 115.69, 115.62, 60.76 (q, J = 36.0 Hz), 60.62 (q, J = 36.0 Hz), 53.57, 53.26, 47.10, 46.24, 34.60, 34.55, 33.04, 32.88. **^{19}F NMR** (565 MHz, $CDCl_3$) δ 73.49 (t, J = 8.7) 73.74 (t, J = 8.9). **HRMS (ESI)** calculated for [$C_{20}H_{19}F_3O_4$, M + Na]$^+$: 403.1128, Found 403.1154. The enantiomeric excess of product **13k**determined to be 97% and 96% for the major and minor diastereomers, respectively, after conversion to lactone **13ka.**

(4*R*)-4-Benzyl-3-(4-hydroxybenzyl)dihydrofuran-2(3*H*)-one, 13ka:



13ka was synthesized by following the general procedure E at 0.1 mmol scale from **13k** and purified by silica gel column chromatography using hexanes/EtOAc (8:2) as eluting solvent. **13ka** was obtained as a colorless oil (10 mg, 35%): *dr* 2:1 97% ee, 96% ee. HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 80:20, 0.9 mL/min, 230 nm UV detector, *dr*1 tR = 19.44 min (major) and tR= 22.273 min (minor), *dr*2 tR = 28.70 min (major) and tR= 28.42 min (minor). **[α]$_D$^{25}** = +16.87 (c = 1.1, CHCl$_3$). **^{1}H NMR** (600 MHz, C$_6$D$_6$) δ 7.08 – 6.97 (m, 4H), 6.86 (d, J = 8.4 Hz, 1.5H), 6.81 (d, *J* = 8.4 Hz, 0.9H), 6.69 – 6.63 (m, 2H), 6.55 (d, *J* = 8.5 Hz, 0.9H), 6.49 (d, *J* = 8.5 Hz, 1.43H), 4.31 (brs, 0.5H), 4.24 (brs, 0.7H), 3.60 (d, *J* = 9.1 Hz, 0.7H), 3.42 (dd, *J* = 8.9, 7.1 Hz, 1H), 3.22 (dd, *J* = 9.2, 4.0 Hz, 0.7H), 3.18 – 3.12 (m, 1H), 2.81 – 2.65 (m, 1.9H), 2.58 – 2.45 (m, 1.3H), 2.43 – 2.37 (m, 0.6H), 2.16 (dd, J = 13.7, 4.7 Hz, 1H), 2.03 – 1.92 (m, 2.7H), 1.81 (dd, J = 13.7, 8.7 Hz, 1H).. **^{13}C NMR** (151 MHz, C$_6$D$_6$) δ 177.96, 177.29, 155.52, 155.26, 139.20, 138.69, 130.88, 130.85, 129.85, 129.81, 129.21, 128.81, 128.33, 128.14, 127.98, 115.72, 115.68, 70.56, 68.68, 46.74, 46.63, 45.30, 38.37, 38.25, 33.97, 30.41, 30.23. **HRMS (ESI)** calculated for [C$_{18}$H$_{18}$O$_3$, M + Na]$^+$: 305.1148, Found 305.1120.

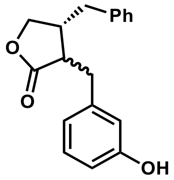
2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-(3-hydroxybenzyl)-4-oxobutanoate, 13l:



13l was synthesized by following the general procedure C at 0.1 mmol scale from **12l** and purified by silica gel column chromatography using hexanes/EtOAc (8:1) as eluting solvent. **13l** was obtained as a colorless oil (18.2 mg, 48% yield, 5:4 dr): **[α]$_D$^{25}** = -4.4 (c = 0.91, CHCl$_3$). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 9.70 (s, 1H), 9.59 (d, *J* = 1.5 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.19 (m, 2H), 7.10 – 6.98 (m, 6H), 6.62 (dd, *J* = 8.4, 2.3 Hz, 3H), 6.56 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 6.41 (t,

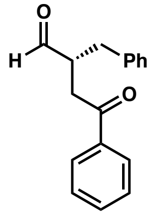
J = 2.1 Hz, 1H), 5.00 – 4.76 (m, 2H), 4.34 (dd, J = 12.9, 8.4 Hz, 2H), 4.30 – 4.19 (m, 2H), 3.25 – 3.18 (m, 1H), 3.13 – 3.05 (m, 1H), 3.02 – 2.76 (m, 10H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.22, 201.91, 172.08, 171.56, 155.81, 155.74, 139.46, 137.63, 137.52, 129.98, 129.94, 129.06, 129.03, 128.82, 126.93, 126.88, 121.33, 121.19, 115.72, 114.01, 113.92, 60.71, 60.46, 53.44, 53.22, 46.55, 45.47, 35.06, 35.05, 32.94, 32.67. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -73.47. **HRMS (ESI)** calculated for [$C_{20}H_{19}F_3O_4$, M + Na]$^+$: 403.1128, Found 403.1158. The enantiomeric excess of product **13l** determined to be 98% and 83% for the major and minor diastereomers, respectively, after conversion to lactone **13la**.

(4*R*)-4-Benzyl-3-(3-hydroxybenzyl)dihydrofuran-2(3*H*)-one, 13la:



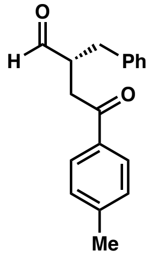
13la was synthesized by following the general procedure E at 0.05 mmol scale from **13l** and purified by silica gel column chromatography using hexanes/EtOAc (3:1) as eluting solvent. **13la** was obtained as a colorless oil (2.8 mg, 20% yield, 5:4 dr, 98%/83% ee). HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), hexanes/IPA = 80:20, 0.8 mL/min, 210 nm UV detector: tR = 28.83 min (minor), tR = 30.43 min (major), tR = 33.90 min (minor) and tR= 38.14 min (major). **$[\alpha]_D^{25}$** = +11.7 (c = 0.12, $CDCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (m, 6H), 7.22 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.07 – 6.99 (m, 3H), 6.88 (d, J = 7.6 Hz, 1H), 6.78 (t, J = 2.1 Hz, 1H), 6.74 (dd, J = 8.0, 2.6 Hz, 1H), 6.73 – 6.68 (m, 2H), 6.58 (t, J = 2.1 Hz, 1H), 4.78 (s, 1H), 4.72 (s, 1H), 4.13 – 4.08 (m, 1H), 4.08 – 3.99 (m, 2H), 3.90 – 3.84 (m, 1H), 3.30 (dd, J = 15.1, 4.7 Hz, 1H), 3.11 (ddd, J = 11.5, 7.2, 4.7 Hz, 1H), 3.00 (td, J = 15.7, 14.9, 4.7 Hz, 2H), 2.92 (dd, J = 14.1, 7.0 Hz, 1H), 2.80 (dd, J = 15.1, 10.9 Hz, 1H), 2.75 – 2.64 (m, 2H), 2.61 (ddd, J = 8.7, 7.0, 5.3 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.38 (dd, J = 13.7, 12.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.58, 177.96, 155.85, 155.78, 140.55, 139.47, 138.45, 138.00, 130.05, 129.93, 128.99, 128.79, 128.70, 126.80, 126.72, 121.81, 120.86, 116.04, 115.33, 113.91, 113.71, 71.26, 69.49, 46.28, 45.14, 41.21, 39.90, 38.55, 34.68, 32.94, 30.74. **HRMS (ESI)** calculated for [$C_{18}H_{18}O_3$, M + Na]$^+$: 305.1148, Found 305.1177.

(*R*)-2-Benzyl-4-oxo-4-phenylbutanal, 15a:



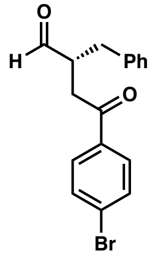
15a was synthesized by following the general procedure D at 0.1 mmol scale from **14a** and purified by silica gel column chromatography using Hexane/EtOAc (9:1) as eluting solvent. **15a** was obtained as a colorless oil (18 mg, 70%): 93% ee. HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 0.8 mL/min, 220 nm UV detector, tR = 30.26 min (maJor) and tR= 23.98 min (minor). **$[\alpha]_D^{25}$** = -7.27 (c = 0.1, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.91 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.45 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 3.52 – 3.32 (m, 2H), 3.17 (dd, *J* = 13.9, 6.1 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.83 (dd, *J* = 13.9, 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.1, 198.0, 138.3, 136.6, 133.5, 129.2, 128.9, 128.8, 128.2, 126.9, 48.5, 37.4, 34.9. **HRMS (ESI)** calculated for $[C_{17}H_{16}O_2$, M + Na$]^+$: 275.1043, Found 275.1048.

(*R*)-2-Benzyl-4-oxo-4-(*p*-tolyl)butanal, 15b:



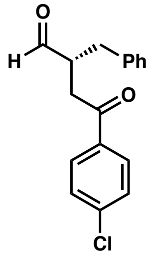
15b was synthesized by following the general procedure D at 0.1 mmol scale from **14b** and purified by silica gel column chromatography using Hexane/EtOAc (9:1) as eluting solvent. **15b** was obtained as a colorless oil (16 mg, 60%): 93% ee. HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 1.0 mL/min, 254 nm UV detector, tR = 39.56 min (maJor) and tR= 32.94 min (minor). **$[\alpha]_D^{25}$** = +7.99 (c = 0.12, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.25 – 7.18 (m, 5H), 3.45 – 3.34 (m, 2H), 3.16 (dd, *J* = 13.9, 6.1 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.82 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 203.3, 197.6, 144.4, 138.3, 134.1, 129.4, 129.2, 128.9, 128.3, 126.8, 48.5, 37.3, 34.9, 21.8. **HRMS (ESI)** calculated for $[C_{18}H_{18}O_2$, M + Na$]^+$: 289.1199, Found 289.1207.

(*R*)-2-Benzyl-4-(4-bromophenyl)-4-oxobutanal, 15c:



15c was synthesized by following the general procedure D at 0.20 mmol scale from **14c** and purified by silica gel column chromatography using hexanes/EtOAc (9:1) as eluting solvent. **15c** was obtained as a colorless oil (27.3 mg, 41% yield, 90% ee): HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 0.8 mL/min, 254 nm UV detector, tR = 20.31 min (minor) and tR= 22.30 min (major). **[α]$_D$^{25}** = +10.5 (c = 1.10, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.15 (m, 3H), 3.47 – 3.31 (m, 2H), 3.23 – 3.12 (m, 1H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.82 (dd, *J* = 14.0, 8.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.84, 196.92, 137.93, 135.16, 131.96, 129.60, 129.03, 128.83, 128.58, 126.86, 48.40, 37.05, 34.67. **HRMS (ESI)** calculated for $[C_{17}H_{15}BrO_2, M + Na]^+$: 353.0148, Found 353.0169, 355.0151.

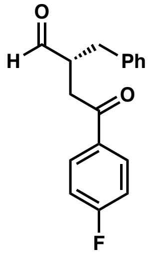
(*R*)-2-Benzyl-4-(4-chlorophenyl)-4-oxobutanal, 15d:



15d was synthesized by following the general procedure D at 0.1 mmol scale from **14d** and purified by silica gel column chromatography using Hexane/EtOAc (9:1) as eluting solvent. **15d** was obtained as a colorless oil (20.5 mg, 72%): 82% ee. HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 1.0 mL/min, 254 nm UV detector, tR = 21.75 min (maJor) and tR= 19.51 min (minor). **[α]$_D$^{25}** = +9.59 (c = 0.25, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.4

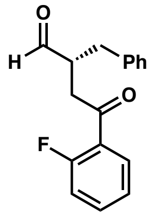
Hz, 1H), 7.21 – 7.17 (m, 2H), 3.44 – 3.32 (m, 2H), 3.17 (dd, *J* = 14.0, 6.1 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.82 (dd, *J* = 13.9, 8.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 203.0, 196.8, 139.9, 138.0, 134.9, 129.6, 129.1, 129.1, 128.9, 127.0, 48.5, 37.2, 34.8. **HRMS (ESI)** calculated for $[C_{17}H_{15}ClO_2, M + Na]^+$: 309.0653, Found 309.0629.

(*R*)-2-Benzyl-4-(4-fluorophenyl)-4-oxobutanal, 15e:



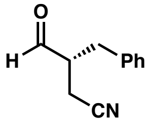
15e was synthesized by following the general procedure D at 0.1 mmol scale from **14e** and purified by silica gel column chromatography using Hexane/EtOAc (9:1) as eluting solvent. **15e** was obtained as a colorless oil (15.8 mg, 58%): 84% ee. HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 1.0 mL/min, 254 nm UV detector, tR = 23.08 (maJor) and tR= 18.92 min (minor). **$[\alpha]_D^{25}$** = -9.83 (c = 0.30, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.93 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 7.11 (t, *J* = 8.6 Hz, 2H), 3.47 – 3.32 (m, 2H), 3.23 – 3.11 (m, 1H), 3.02 – 2.90 (m, 1H), 2.82 (dd, J = 13.9, 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.0, 196.4, 166.0 (d, ^1J = 255.2 Hz, Cq), 138.1, 133.0 (d, ^4J = 2.9 Hz, Cq), 130.8 (d, ^3J = 9.4 Hz, CH), 129.2, 128.9, 126.9, 115.8 (d, ^2J = 21.9 Hz, CH), 48.5, 37.2, 34.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.7. **HRMS (ESI)** calculated for $[C_{17}H_{15}FO_2, M + Na]^+$: 293.0948, Found 293.0971.

(*R*)-2-Benzyl-4-(2-fluorophenyl)-4-oxobutanal, 15f:



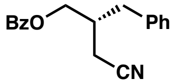
15f was synthesized by following the general procedure D at 0.20 mmol scale from **14f** and purified by silica gel column chromatography using hexanes/EtOAc (9:1) as eluting solvent. **15f** was obtained as a colorless oil (26.9 mg, 50% yield, 90% ee): HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 90:10, 0.8 mL/min, 230 nm UV detector, tR = 20.16 min (minor) and tR= 23.69 min (major). **[α]$_D$^{25}** = -2.1 (c = 1.35, CHCl$_3$). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 9.87 (s, 1H), 7.83 (td, J = 7.6, 1.9 Hz, 1H), 7.51 (tdd, J = 7.4, 5.0, 1.9 Hz, 1H), 7.29 (d, J = 7.4 Hz, 2H), 7.21 (tt, J = 7.5, 4.6 Hz, 4H), 7.11 (dd, J = 11.3, 8.3 Hz, 1H), 3.50 – 3.31 (m, 2H), 3.16 (dd, J = 13.9, 5.9 Hz, 1H), 3.06 (dd, J = 14.4, 3.2 Hz, 1H), 2.78 (dd, J = 13.9, 8.0 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 202.90, 196.07, 163.33, 160.80, 138.15, 134.93, 134.84, 130.63, 129.04, 128.73, 126.72, 124.47, 116.82, 116.58, 48.51, 42.41, 34.77. **^{19}F NMR** (565 MHz, CDCl$_3$) δ -108.63. **HRMS (ESI)** calculated for [$C_{17}H_{15}FO_2$, M + Na]$^+$: 293.0948, Found 293.0971.

(*R*)-3-Benzyl-4-oxobutanenitrile, 15g:



15g was synthesized by following the general procedure D at 0.1 mmol scale from **14g** and purified by silica gel column chromatography using hexanes/EtOAc (4:1) as eluting solvent. **15g** was obtained as a colorless oil (13.7 mg, 39% yield): **[α]$_D$^{26}** = +8.0 (c = 0.50, CHCl$_3$). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 9.78 (s, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 6.9 Hz, 2H), 3.25 – 3.17 (m, 1H), 3.05 – 2.97 (m, 2H), 2.53 (dd, *J* = 17.1, 5.8 Hz, 1H), 2.45 (dd, *J* = 16.9, 5.7 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 199.49, 135.91, 129.15, 128.98, 127.47, 117.62, 49.42, 34.10, 15.60. **HRMS (ESI)** calculated for [$C_{11}H_{11}NO$, M + Na]$^+$: 196.0733, Found 196.0749. The enantiomeric excess of product **15g** determined to be 94% after conversion to ester **15ga**.

(*R*)-2-Benzyl-3-cyanopropyl benzoate, 15ga:

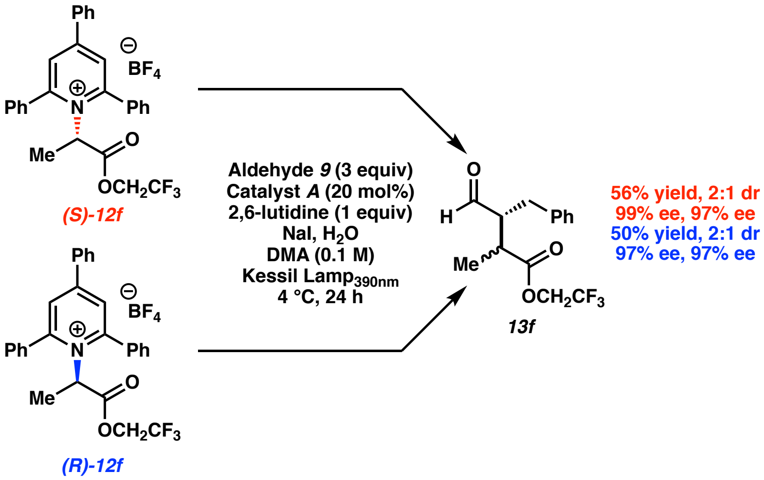


15ga was synthesized by following the general procedure F at 0.1 mmol scale from **15g** and purified by silica gel column chromatography using hexanes/EtOAc (3:1) as eluting solvent. **15ga** was obtained as a colorless oil (2.3 mg, 8% yield, 94% ee). HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 80:20, 0.8 mL/min, 230 nm UV detector, tR = 19.46 min (major) and tR= 22.86 min (minor). **[α]$_D$^{25}** = +8.3 (c = 0.12, CHCl$_3$). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.09 – 8.01 (m, 2H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.34 (t, *J* = 7.2

Hz, 2H), 7.30 – 7.19 (m, 5H), 4.45 (dd, *J* = 11.4, 4.3 Hz, 1H), 4.28 (dd, *J* = 11.4, 6.7 Hz, 1H), 2.93 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.83 (dd, *J* = 13.9, 7.5 Hz, 1H), 2.58 – 2.40 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.20, 137.43, 133.76, 133.38, 130.22, 129.67, 129.60, 129.05, 128.93, 128.56, 128.53, 127.04, 117.90, 65.62, 37.17, 36.66, 19.32. **HRMS (ESI)** calculated for [$C_{18}H_{17}NO_2$, M + Na]$^+$: 302.1151, Found 302.1112.

6. Mechanistic Studies

A. Enantioconvergent Synthesis



Following the general procedure C at 0.1 mmol scale, both enantiomers of alanine-derived Katritzky salt, **(*S*)-12f** and **(*R*)-12f**, were subjected to reaction conditions to test whether the same enantiomer of product would be favored. Alkylation product **13f** was synthesized from **(*S*)-12f** in 56% yield (2:1 dr, 99% ee, 97% ee) and from **(*R*)-12f** in 50% yield (2:1 dr, 97% ee, 97% ee). In both cases, the major enantiomer of both diastereomers of product **13f** was the same, as measured by chiral HPLC analysis of diester **13fa**. HPLC conditions: Chiralcel OJ_H column (25 cm × 0.46 cm ID), hexanes/IPA = 70:30, 0.8 mL/min, 230 nm UV detector.

B. Quantum Yield

The quantum yield of the reaction was determined using procedures reported previously by standard ferrioxalate actinometry.[5]

Determination of the light intensity at 390 nm

The photon flux of the Kessil lamp (390 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (2.21 g) in in 0.05 M H_2SO_4 (30 mL). A buffered solution of phenanthroline was prepared by dissolving phenanthroline (50 mg) and sodium acetate (11.25 g) in 0.5 M H_2SO_4 (50 mL). Both solutions were stored in the dark. To determine the photon flux of the Kessil lamp (390 nm), 2.0 mL of the ferrioxalate solution was placed in a vial and irradiated for 90 s. After irradiation, 0.35 mL of the phenanthroline solution was added to the vial, and the solution was stored in the dark for 1 h. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

$$\text{mol Fe}^{2+} = \frac{\text{V} \bullet \Delta\text{A}}{\text{l} \bullet \varepsilon} \tag{1}$$

V is the total volume (0.00235 L), ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions (0.587), l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The mol Fe^{2+} was calculated to be 1.24×10^{-7}, which was then used to calculate the photon flux with eq 2.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \bullet \text{t} \bullet \text{f}} \tag{2}$$

Φ is the quantum yield for the ferrioxalate actinometer (1.13 for a 0.15 M solution at *405* nm), t is the time (1800.0 s), and f is the fraction of light absorbed at 390 nm (> 0.999, A = 4.77, eq 3). The photon flux was calculated to be 1.22×10^{-9} einstein s^{-1}.

$$\text{f} = 1 - 10^{-\text{A}} \tag{3}$$

Determination of quantum yield

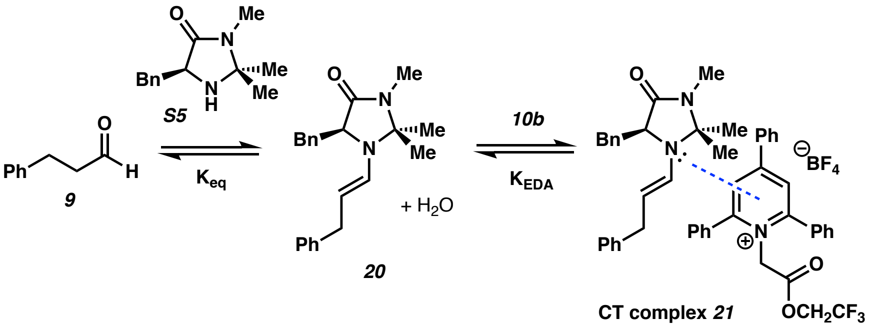
Standard reaction conditions (0.1 mmol scale) with an NMR standard were employed in the same vial size with the same volume of solvent as performed for the photon flux calculation.

Pyridinium salt **10b** (0.1 mmol), aldehyde **9** (0.3 mmol), catalyst **A** (0.02 mmol), 2,6-lutidine (0.1 mmol), NaI (0.1 mmol), H_2O (1.0 mmol) and $PhCF_3$ (0.1 mmol) were dissolved in DMA (2 mL) and were degassed via freeze-pump-thaw (three times) before irradiation at 390 nm for 1800 s (30 min). The yield of product formed was determined by ^{19}F NMR based on the $PhCF_3$ standard for a diluted aliquot of the reaction sample in $CDCl_3$. The quantum yield was determined using eq 4. Essentially all incident light is absorbed by the reaction mixture at 390 nm (f > 0.999, A = 4.57, eq 3).

$$\Phi = \frac{\text{mol product}}{\text{flux} \bullet \text{t} \bullet \text{f}} \tag{4}$$

Based on the observed 9% yield (0.009 mmol product), **Φ(9%) = 4**.

C. CT Complex Effect on Enamine Equilibrium[6]



The equilibrium constants (**K_{eq}**) for the formation of the enamine, generated upon condensation of amine catalyst **A** and aldehyde **9**, were determined by ^{1}H NMR spectroscopy. For these measurements, a 0.16 M stock solution of the *free base* of catalyst **A (S5)** was prepared in dry CD_3CN with $PhSiMe_3$ as an internal standard. Multiple experiments were performed to calculate **K_{eq}** of **9** and **20** in the presence of other reaction components in the same relative proportions. After mixing the components in dry CD_3CN with a total volume of 1 mL, solutions were stirred in the dark for 30 minutes to secure equilibration. The relative amount of enamine **20** in solution with respect to free catalyst **S5** was determined by integration of the following diagnostic peaks: doublet at 6.25 ppm (J = 13.8 Hz, 1H) for enamine **20**; doublet of doublet at 3.70 (J = 8.8, 3.9 Hz, 1H) for catalyst **S5**. The integration of **S5** and **20** compared to the internal standard $PhSiMe_3$ gave their concentrations, which could be used to calculate **K_{eq}** based on eq 5.

$$K_{eq} = \frac{[\mathbf{20}][H_2O]}{[\mathbf{S5}][\mathbf{9}]} = \frac{[\mathbf{20}]^2}{[\mathbf{S5}][0.3\ \text{M} - [\mathbf{S5}]]} \tag{5}$$

<u>Sample 1:</u> amine catalyst **S5** (0.02 mmol) and aldehyde **9** (0.3 mmol). Ratio of **S5**:**20** = 20.7:1. Calculated **K_{eq}** = 1.4 x 10^{-4}.

<u>Sample 2:</u> amine catalyst **S5** (0.02 mmol), aldehyde **9** (0.3 mmol), and Katritzky salt **10b** (0.1 mmol). Ratio of **S5**:**20** = 11.2:1. Calculated **K_{eq}** = 4.8 x 10^{-4}.

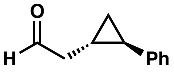
<u>Sample 3:</u> amine catalyst **S5** (0.02 mmol), aldehyde **9** (0.3 mmol), Katritzky salt **10b** (0.1 mmol),

NaI (0.1 mmol), and DMA (50 μL). Ratio of **S5**:**20** = 5.1:1. Calculated $\mathbf{K_{eq}}$ = 2.1 x 10^{-3}.

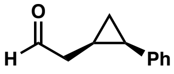
Sample 4: amine catalyst **S5** (0.02 mmol), aldehyde **9** (0.3 mmol), and 2,6-lutidine (0.1 mmol). Ratio of **S5**:**20** = 10.8:1. Calculated $\mathbf{K_{eq}}$ = 5.4 x 10^{-4}.

D. Radical Probe Experiments

***cis*-22 and *trans*-22** aldehyde starting materials were prepared according to literature procedure.[7]

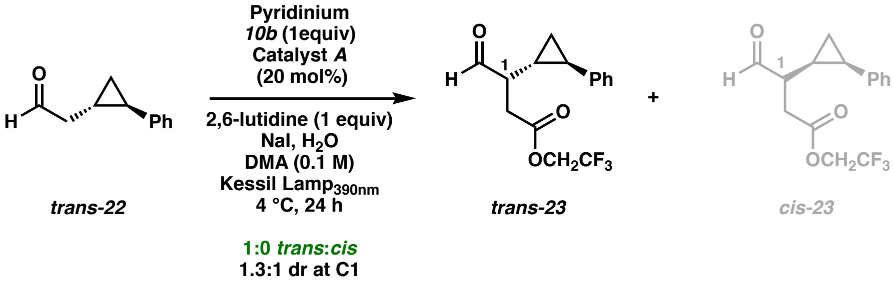


trans-22



cis-22

Photocatalyzed α-alkylation of aldehyde trans-22



trans-23 was synthesized by following the general procedure C using ***trans-22*** at 0.1 mmol scale and purified by silica gel column chromatography using hexanes/EtOAc (9.5:1.5) as eluting solvent. ***trans-23*** was obtained as a colorless oil (15 mg, 40%) as an inseparable 1.3:1 mixture of diastereomers at C1.

trans-23: $[\alpha]_D^{25}$ = -9.99 (c = 0.10, $CHCl_3$). **^{1}H NMR** (600 MHz, C_6D_6) δ 9.37 (s, 0.62H, minor), 9.34 (s, 0.82H, major), 7.13 – 7.08 (m, 3.2H), 7.07 – 7.00 (m, 1.7H), 6.83 – 6.79 (m, 1.3H), 6.79 – 6.74 (m, 1.7H), 4.06 (dd, J = 12.8, 8.6 Hz, 0.8H), 4.00 – 3.94 (m, 1H), 3.89 – 3.79 (m, 1.7H), 2.48 (ddd, J = 21.7, 16.9, 8.2 Hz, 1.8H), 2.08 (ddd, J = 16.8, 5.3, 4.0 Hz, 1.8H), 1.71 (ddt, J = 10.2, 8.3, 5.6 Hz, 1.9H), 1.51 (dt, J = 9.4, 5.0 Hz, 1H), 1.30 (dd, J = 9.1, 4.6 Hz, 2H), 1.18 – 1.06 (m, 0.5H), 0.61 (ddt, J = 10.9, 8.6, 5.2 Hz, 1.7H), 0.58 – 0.45 (m, 2.7H), 0.34 (dt, J = 8.8, 5.0 Hz, 0.8H). **^{13}C NMR** (151 MHz, C_6D_6) δ 199.5, 199.3, 169.8, 141.5, 141.4, 128.0, 127.8, 127.6, 126.0, 125.9, 125.9, 125.8, 59.9, 51.9, 51.8, 32.4, 32.2, 29.9, 22.0, 22.0, 21.1, 21.0, 14.1, 13.6. **^{19}F NMR** (565 MHz, C_6D_6) δ -73.70 – -73.81 (m). **HRMS (ESI)** calculated for [$C_{15}H_{15}F_3O_3$, M + Na]$^+$: 323.0866, Found 323.0862.

nOe experiments on ***trans*-23**

The *trans* stereochemistry of the substituents on the cyclopropane ring was assigned based nOe experiments on pure ***trans*-23** as a mixture of diastereomers at C1. Selective excitation ^{1}H NMR spectra were recorded on a Varian Mercury 400 in C_6D_6 (Figure S2).

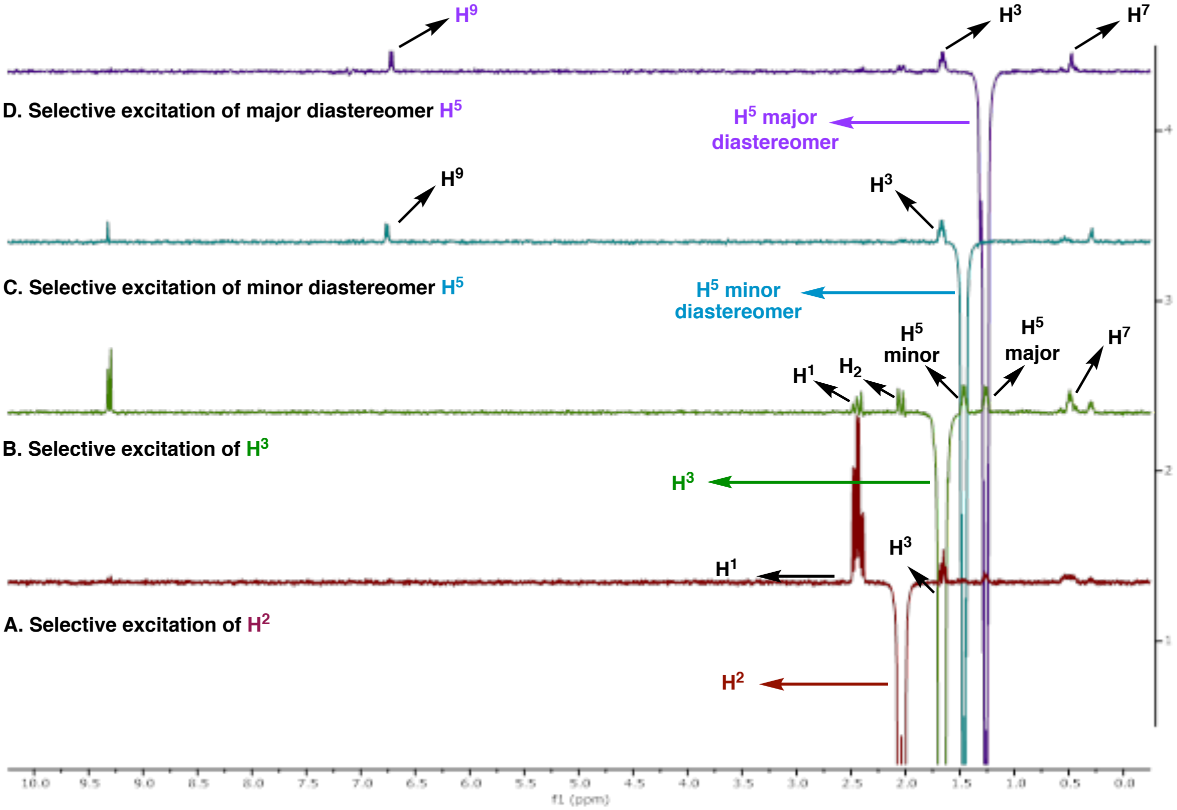


Figure S2. Selective excitation experiments of H^2, H^3, H^5(minor) and H^5 (major) on *trans-23* (inseparable mixture of diastereomers)

A. Selective excitation of H^2 shows a nOe interaction with H^1 and H^3.

B. Selective excitation of H^3 shows a nOe interaction with H^1, H^2, H^5 (major and minor diastereomers) and H^7.

C. Selective excitation of H^5 signal of the *minor* diastereomer shows a nOe interaction with H^3, H^7, and H^9.

D. Selective excitation of H^5 signal of the *major* diastereomer shows a nOe interaction with H^3, H^7, and H^9.

***trans*-23** was assigned the indicated relative stereochemistry based on key nOe interactions between H^3–H^5 and H^5–H^7, as shown in Figure S3.

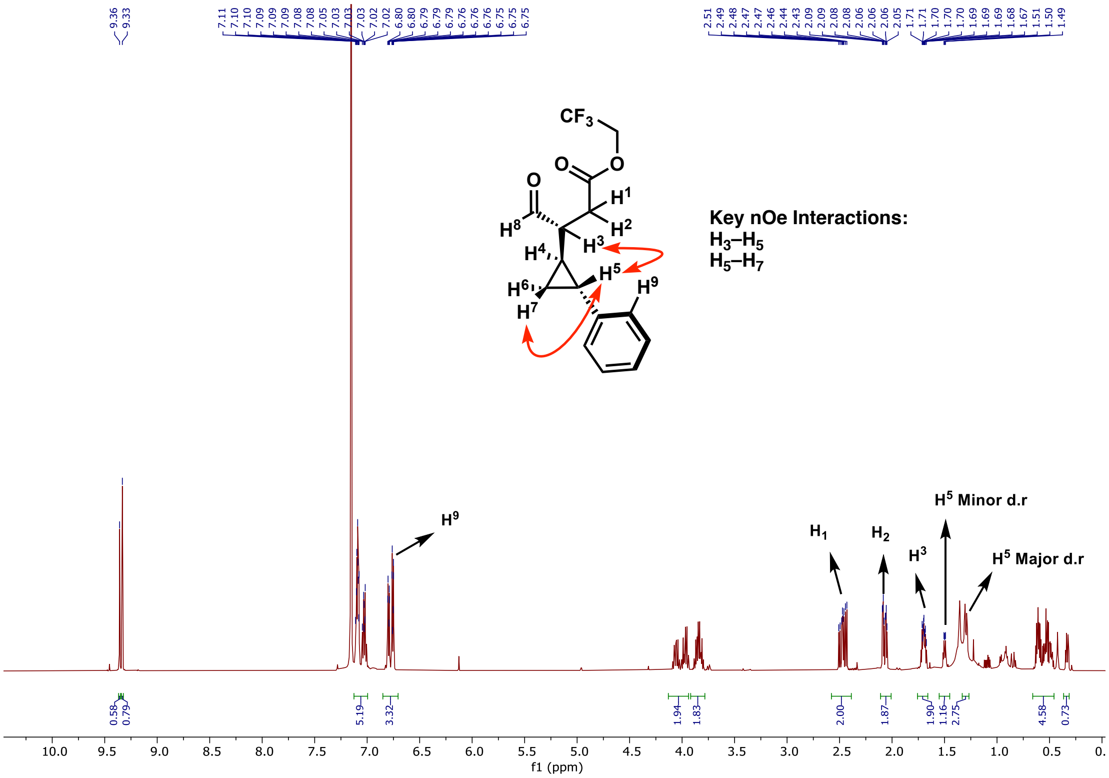
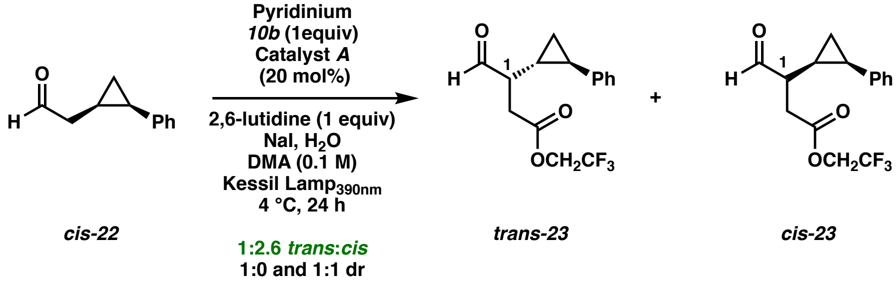


Figure S3. ^{1}**HMNR spectrum of *trans-23* diastereomers (inseparable mixture of diastereomers)**

Photocatalyzed α-alkylation of aldehyde cis-22.



Following the general procedure C using ***cis*-22** aldehyde as starting material at 0.1 mmol scale, both ***cis-23*** and ***trans*-23** alkylation products were formed in 2.6:1 ratio and purified by silica gel column chromatography using hexanes/EtOAc (9.5:1.5) as eluting solvent. ***cis*-23** was obtained as a colorless oil (7.5 mg, 20%) as a single diastereomer. ***trans*-23** was obtained as a colorless oil (3.0 mg, 8%) as an inseparable 1:1 mixture of diastereomers at C1 (see Figure S4).

cis-23: $[\alpha]_D^{25}$ = -10.22 (c = 0.19, $CHCl_3$). ^{1}**H NMR** (600 MHz, C_6D_6) δ (*cis* diastereomer) 9.20 (s, 1H), 7.07 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.94 (m, 2H), 3.97 (dq, *J* = 12.9, 8.6 Hz, 1H), 3.83 (dq, *J* = 12.8, 8.6 Hz, 1H), 2.48 (dd, *J* = 16.8, 7.0 Hz, 1H), 2.16 (dd, *J* = 16.8, 5.9 Hz, 1H), 2.01 – 1.82 (m, 3H), 0.68 (dtd, *J* = 11.1, 8.4, 5.9 Hz, 1H), 0.62 – 0.52 (m, 3H). **^{13}C NMR** (151 MHz, C_6D_6) δ 199.6, 169.8, 137.7, 128.6, 128.3, 128.2, 126.4, 59.5, 46.1, 32.7, 21.2, 18.7, 7.9. **^{19}F NMR** (565 MHz, C_6D_6) δ -73.75 (t, *J* = 8.2 Hz). **ESI-MS** calcd for [$C_{15}H_{15}F_3O_3$, M + Na]$^+$: 323.0866, Found 323.0860.

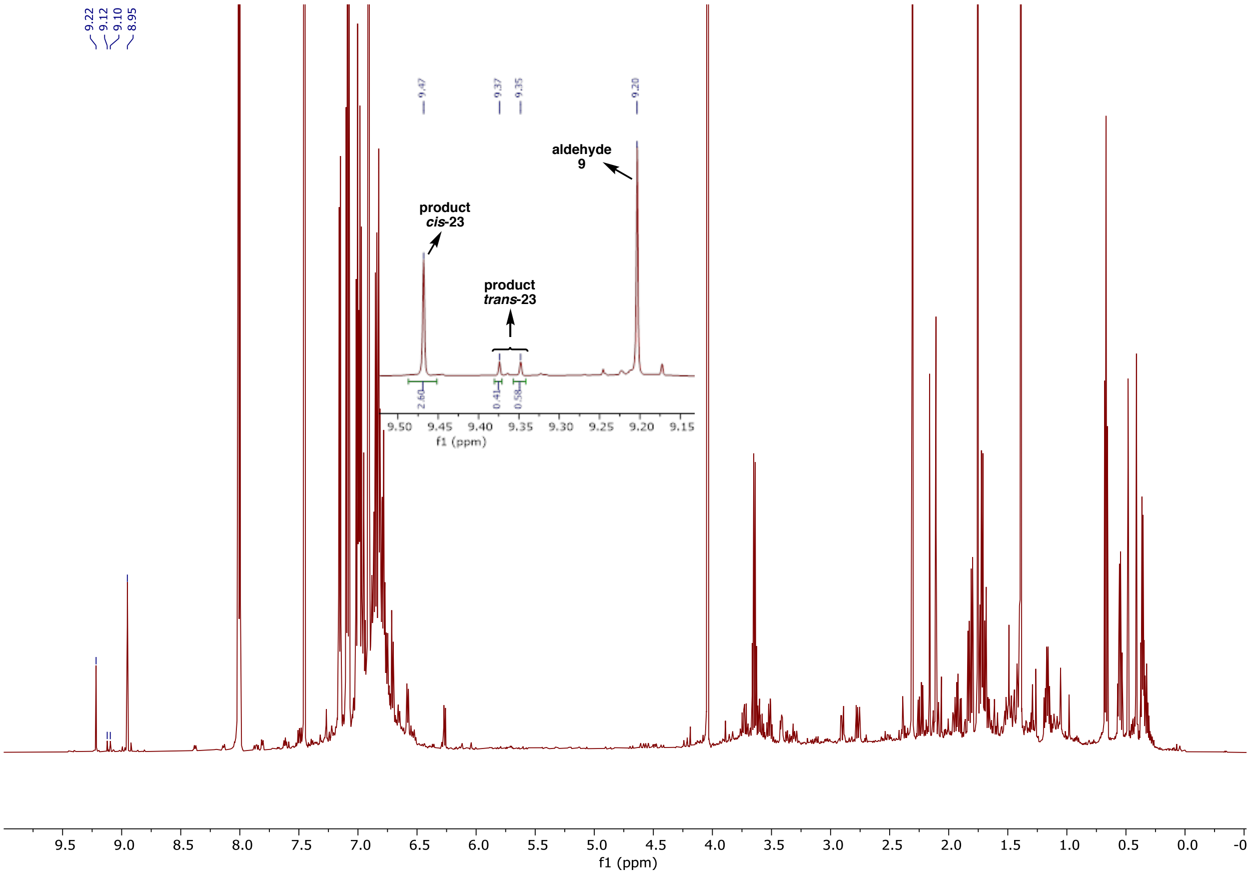


Figure S4. Crude reaction mixture of the photochemical alkylation of aldehyde *cis*-22

nOe experiments on ***cis*-23**

The *cis* stereochemistry of the substituents on the cyclopropane ring was assigned based nOe experiments on pure ***cis*-23**. Selective excitation ^{1}H NMR spectra were recorded on a Varian Mercury 400 in C_6D_6 (Figure S5).

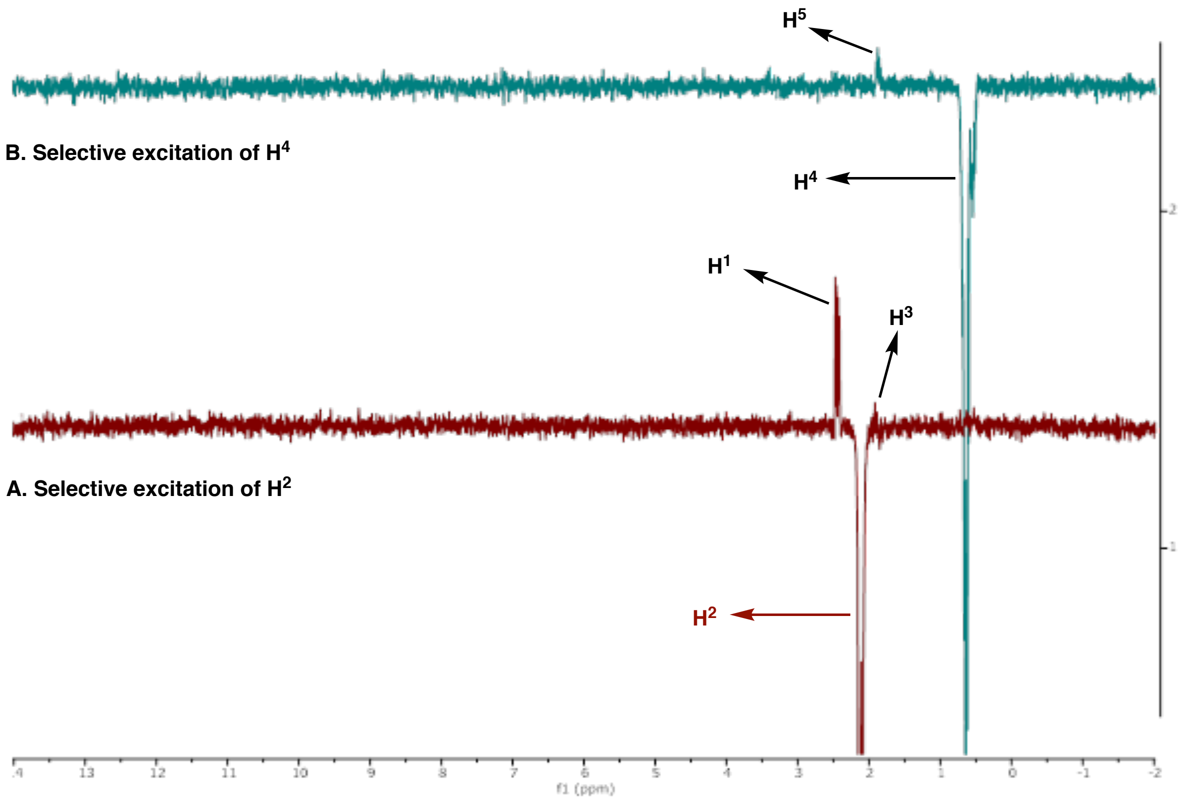


Figure S5. Selective excitation experiments of H^2 and H^4 on *cis-23*

A. Selective excitation of H^2 shows a nOe interaction with H^1 and H^3.

B. Selective excitation of H^4 shows a nOe interaction with H^5.

***cis*-23** was assigned the indicated relative stereochemistry based on the key nOe interaction between H^4–H^5, as shown in Figure S6.

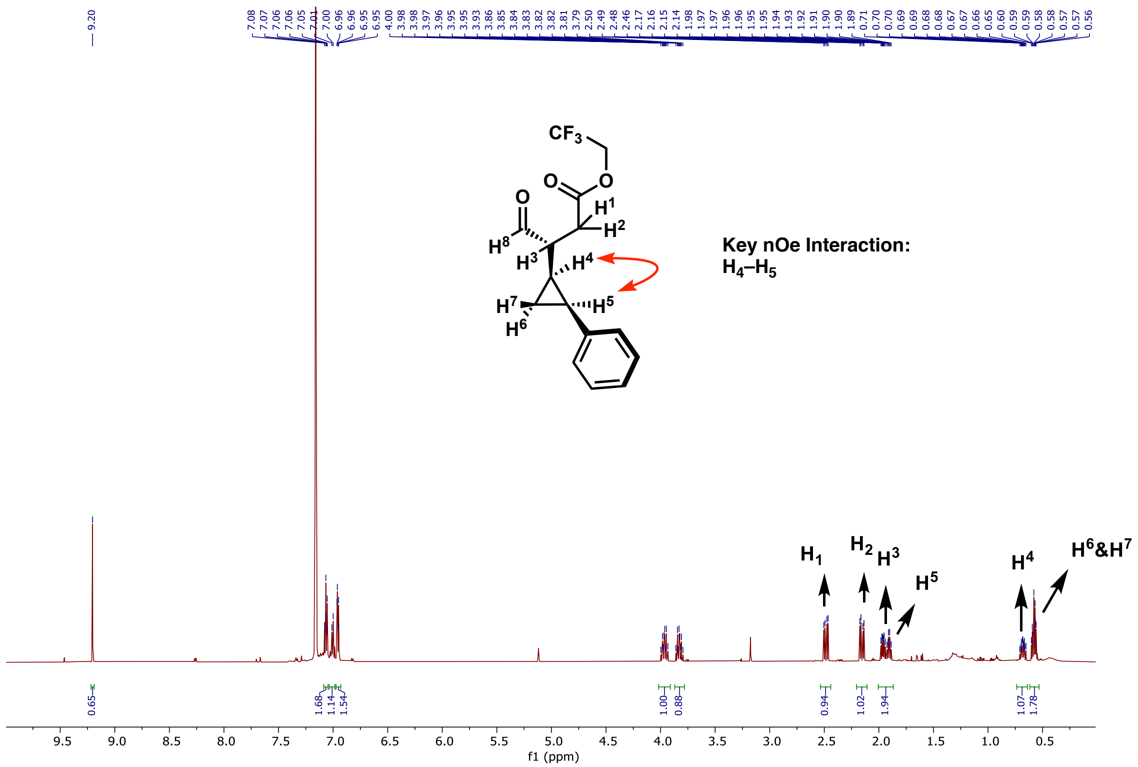


Figure S6. ^{1}HMNR spectrum of ***cis*-*23***

Our interpretation of the radical probe experiments is summarized in Figure S7. Radical probe ***trans*-22** exclusively formed the alkylation product ***trans*-23** as a 1.3:1 mixture of diastereomers at C1, which is consistent with either a radical chain or in-cage radical recombination. With radical probe ***cis*-22**, the expectation was that an in-cage radical process would exclusively furnish the thermodynamically stable alkylation product ***trans*-23** via acyclic intermediate **27**. Alternatively, the alkylation product ***cis*-23** would form exclusively if the reaction proceeded through a radical chain. Surprisingly, starting from radical probe ***cis*-22**, we isolated both *trans* and *cis* isomers of alkylation product **24** in a 1:2.6 ratio. These observations suggest that the catalytic enantioselective reaction may proceed simultaneously through two mechanisms, which are both remarkably highly enantioselective. The existence of two distinct mechanistic pathways is also consistent with the measured quantum yield of 4.

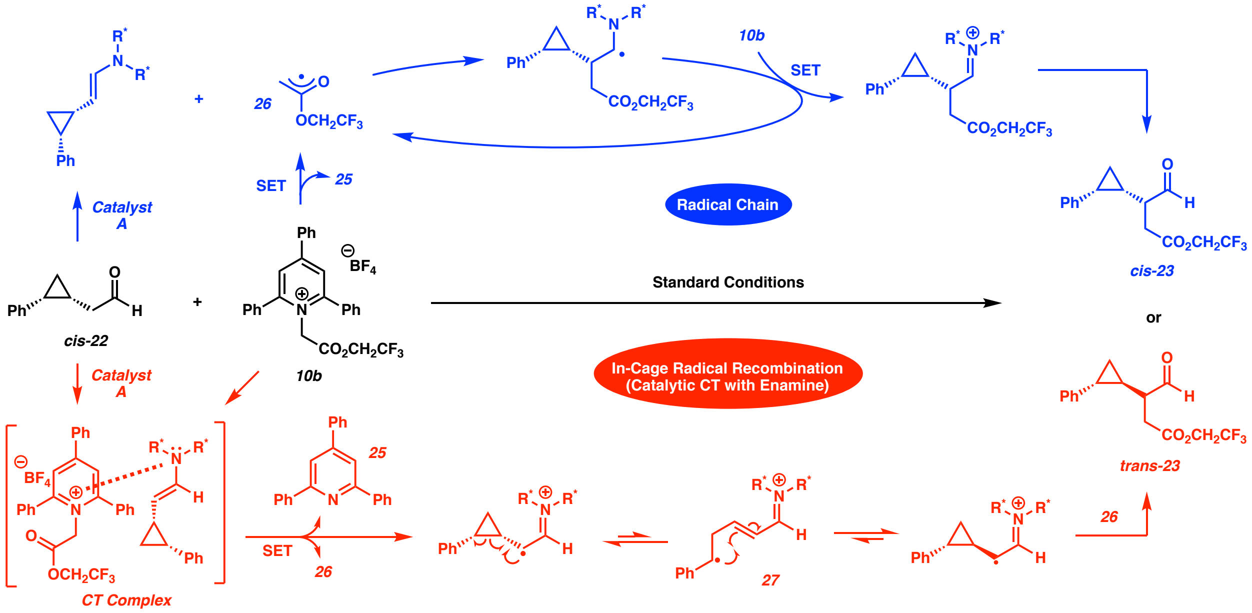
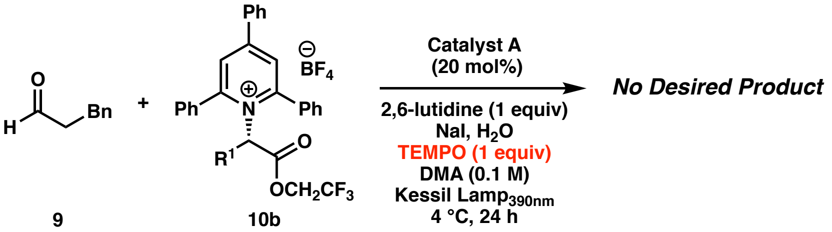


Figure S7. Interpretation of Radical Probe Experiments

E. Stability of Pyridinium Salt with Sodium Iodide

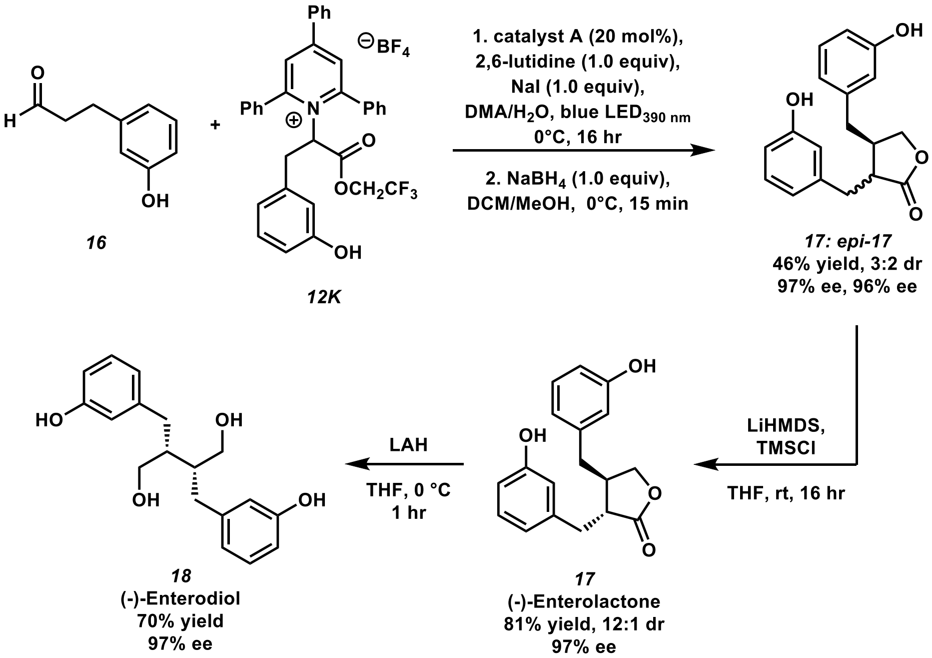
To test for the possibility of *in situ* generation of an α-iodoester species from the starting pyridinium salts, these salts were subjected to NaI conditions in the presence of various amounts of light. The starting pyridinium salt **10b** was dissolved in DMA and treated with NaI and water, according to the proportions found in general procedure C at a 0.05 mmol scale. Me_3SiPh was added as an internal standard. Three separate samples were prepared and stirred for 1 h before an aliquot was taken for ^1H analysis. The three samples were stirred in the presence of different amounts of light as follows: the first was wrapped in aluminum foil (no light), the second was left stirring in a clear vial (ambient fume hood lighting), and the final sample was subjected to 390 nm light at 0 °C, as in the reaction conditions. After 1 h, all three samples showed no decomposition of starting material in reference to the internal standard.

F. Reaction with TEMPO

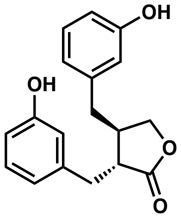


The reaction was performed following the general procedure C with 1 equiv TEMPO.

7. Synthesis of (–)-Enterolactone and (–)-Enterodiol

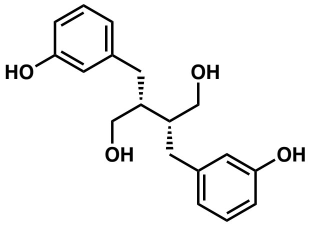


(–)-Enterolactone, 17:



17 was synthesized by a two-reaction sequence. First, the general procedures C and E were carried out at 0.147 mmol scale using 3-(3-hydroxyphenyl)propanal[8] and purified by silica gel column chromatography using hexanes/EtOAc (3:2) as eluent (20.1 mg, 46% yield, 3:2 dr, 97%/96% ee). The inseparable mixture of diastereomers (6.8 mg, 0.0228 mmol) was dissolved in THF (750 μL) before LiHMDS (1.0 M in THF, 228 μL, 0.228 mmol) and TMSCl (15 μL, 0.114 mmol) were added at 0 °C. The reaction was allowed to warm to 23 °C and stirred. After 16 h, 3M aqueous HCl (0.5 mL) was added dropwise, and the reaction was stirred for 30 additional min before adding H_2O and extracting with CH_2Cl_2 (x2). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified by preparatory thin layer chromatography using hexanes/EtOAc (3:2) as eluent. (–)-Enterolactone **17** was obtained as a colorless oil (5.5 mg, 81% yield, 12:1 dr, 97% ee): HPLC conditions: Chiralcel OD-H column (25 cm × 0.46 cm ID), hexanes/IPA = 75:25, 0.5 mL/min, 220 nm UV detector: tR = 22.95 min (major), tR = 28.18 min (minor) tR= 36.52 min (minor), 42.21 min (major). **$[\alpha]_D^{26}$** = -36.4° (c = 0.20, MeOH). **^{1}H NMR** (600 MHz, acetone-d^6) δ 8.33 (s, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.80 – 6.77 (m, 1H), 6.75 – 6.65 (m, 3H), 6.64 (t, *J* = 2.1 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 4.03 (dd, *J* = 8.9, 7.4 Hz, 1H), 3.88 (t, *J* = 8.8 Hz, 1H), 2.96 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.91 – 2.86 (m, 1H), 2.71 – 2.64 (m, 2H), 2.57 – 2.48 (m, 2H). **^{13}C NMR** (600 MHz, acetone-d^6) δ 177.84, 157.57, 157.55, 140.47, 139.95, 129.51, 129.42, 120.57, 119.70, 116.23, 115.54, 113.56, 113.35, 70.60, 45.90, 41.28, 37.79, 34.40. **HRMS (ESI)** calculated for [$C_{18}H_{18}O_4$, M + Na]$^+$: 321.1097, Found 321.1122.

(–)-Enterodiol, 18:



17 (enterolactone) (4.2 mg, 12:1 dr, 0.0141 mmol) was dissolved in THF (1 mL), cooled to 0 °C, and treated with $LiAlH_4$ (3.0 mg, 0.07 mmol). After 1 h, the reaction was quenched according to the Fieser workup method by the sequential addition of 10 μL H_2O, 10 μL 15% aqueous NaOH, and 30 μL H_2O. The mixture was dried over $MgSO_4$ and passed through celite plug and concentrated under reduced pressure. The product was purified by preparatory thin layer chromatography using hexanes/EtOAc (1:3) as eluent to yield a single diastereomer of (–)-enterodiol **18**, which was obtained as a colorless oil (3.0 mg, 70% yield, 97% ee): HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), hexanes/IPA = 75:25, 0.7 mL/min, 280 nm UV detector, tR = 6.31 min (major) and tR= 7.46 min (minor). **$[\alpha]_D^{26}$** = -11.0 (c = 0.10, MeOH). **^{1}H NMR** (600 MHz, CD_3OD) δ 7.08 – 7.05 (m, 2H), 6.65 – 6.58 (m, 6H), 3.63 (dd, *J* = 11.1, 4.0 Hz, 2H), 3.54 (dd, *J* = 11.1, 5.2 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 4H), 2.01 (m, 2H). **^{13}C NMR** (600 MHz, acetone-d_6) δ 157.29, 143.17, 129.02, 120.23, 115.98, 112.59, 60.08, 44.01, 35.28. **HRMS (ESI)** calculated for [$C_{18}H_{22}O_4$, M + Na]$^+$: 325.1410, Found 325.1436.

8. References

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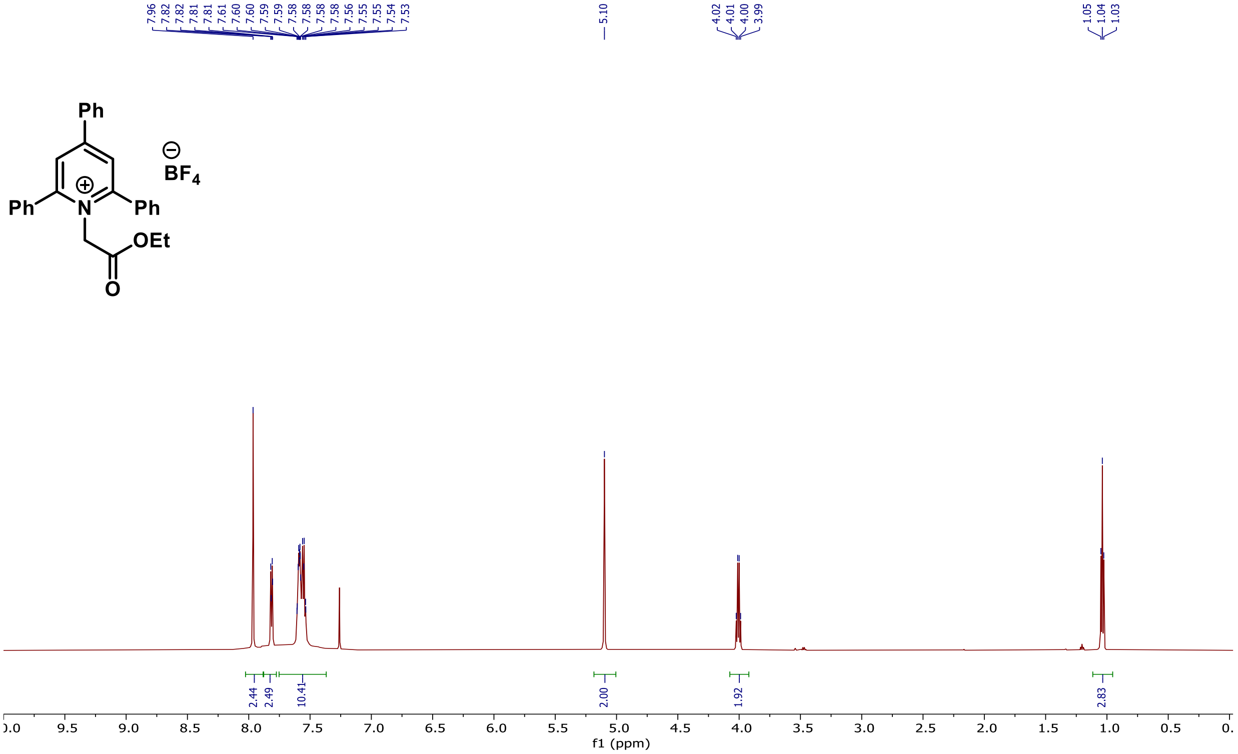
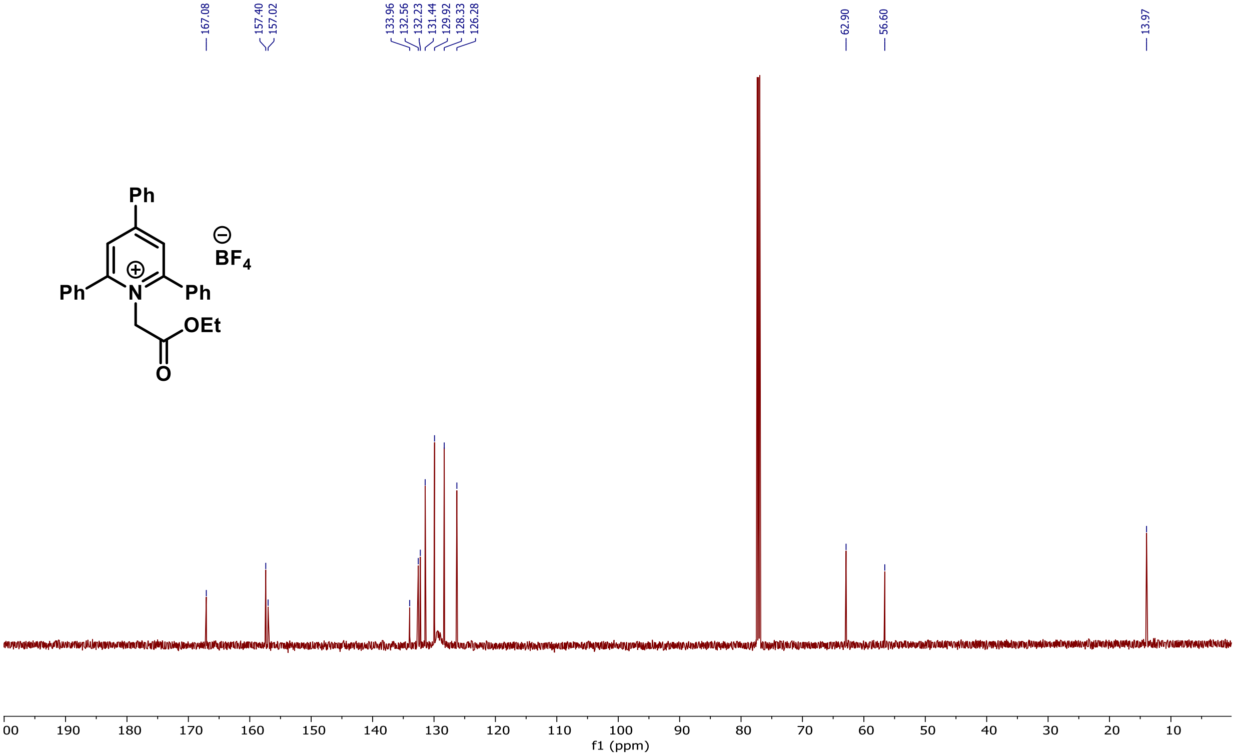
9. NMR Spectra

1-(2-Ethoxy-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 10a:

^{1}H NMR (600 MHz, CDCl$_3$)

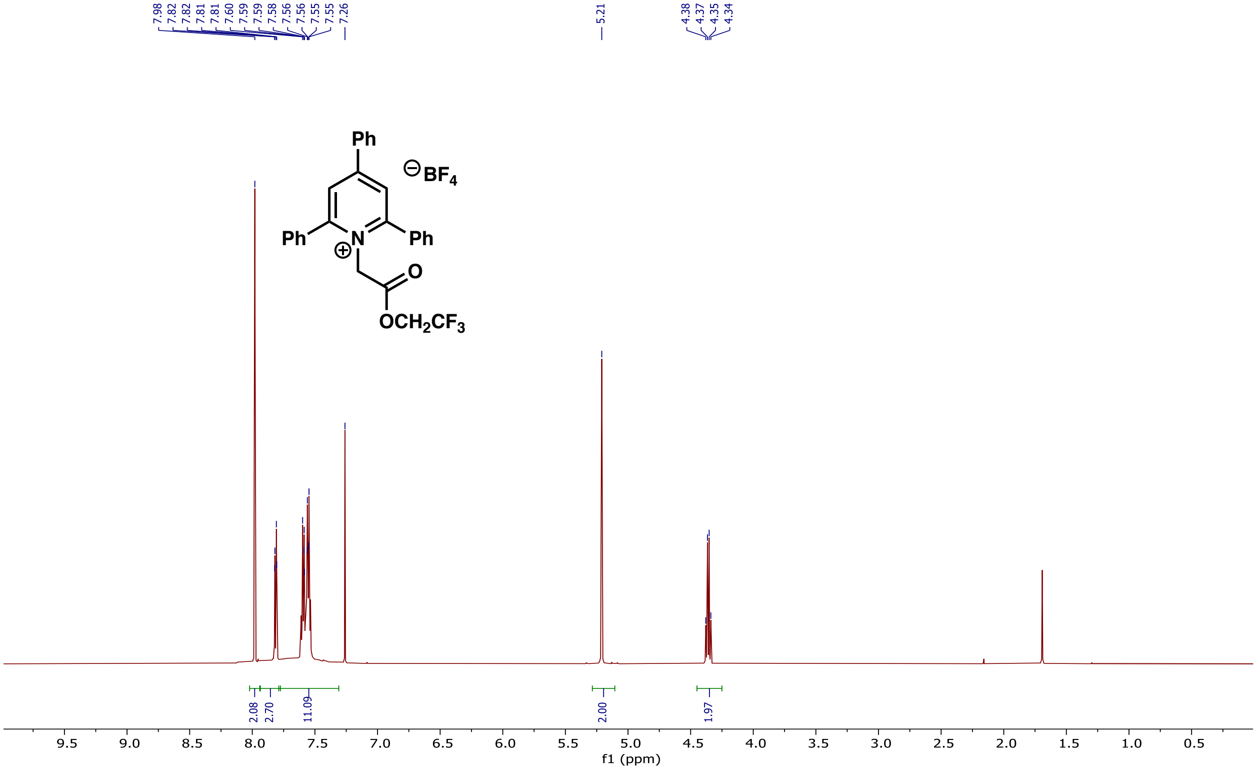


^{13}C NMR (151 MHz, CDCl$_3$)



1-(2-*oxo*-2-(2,2,2-Trifluoroethoxy)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 10b:

^{1}H NMR (600 MHz, CDCl$_3$)



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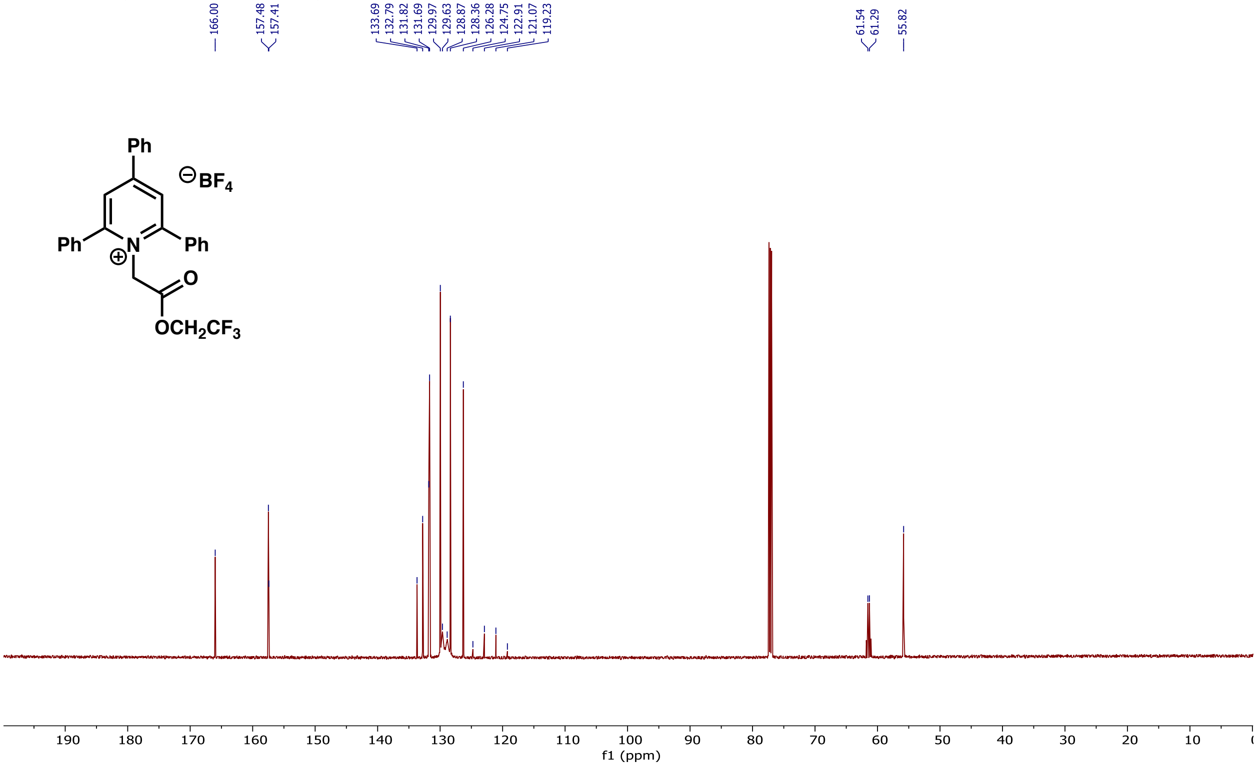
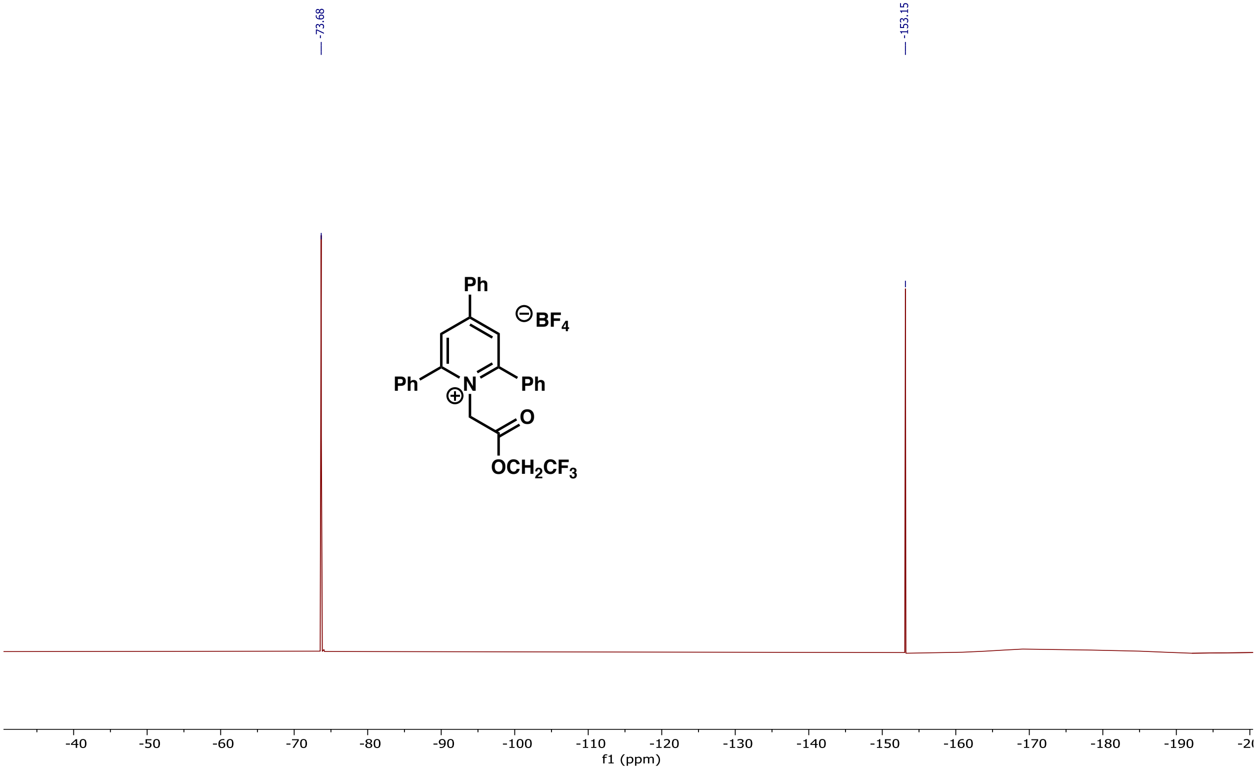
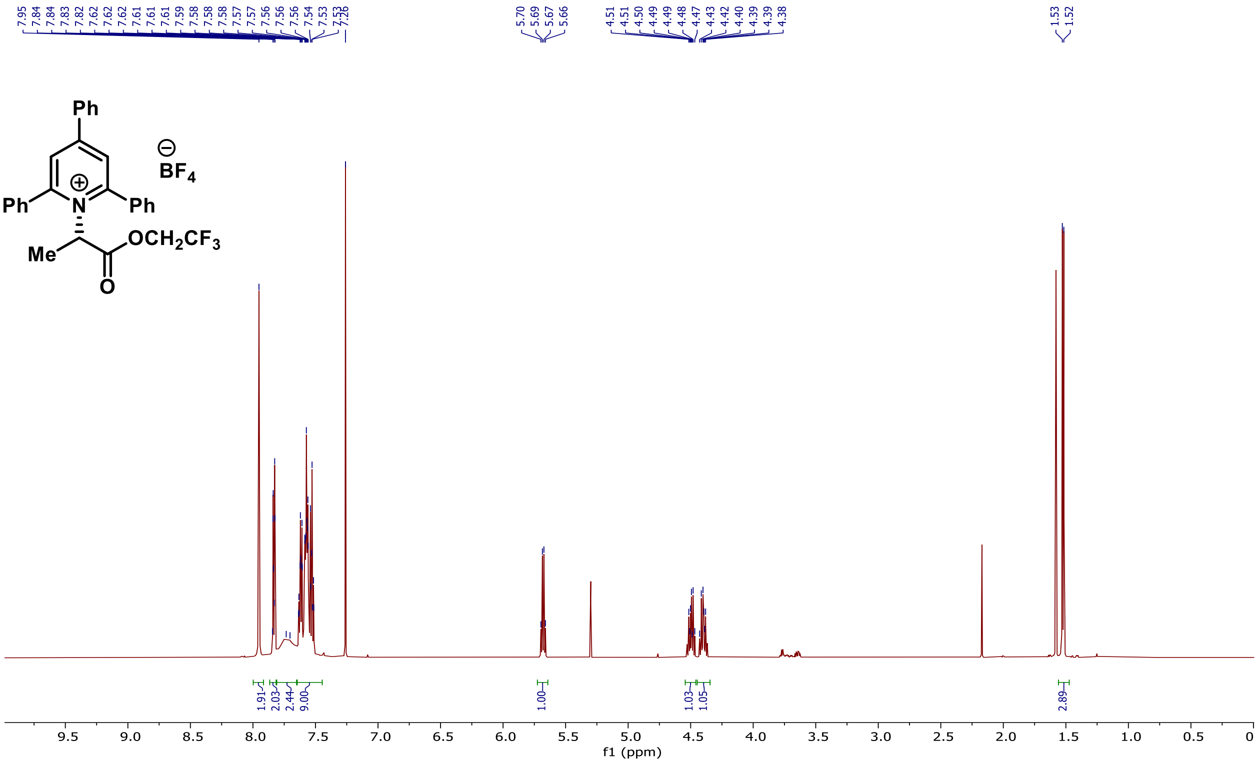


^{19}F NMR (565 MHz, CDCl$_3$)

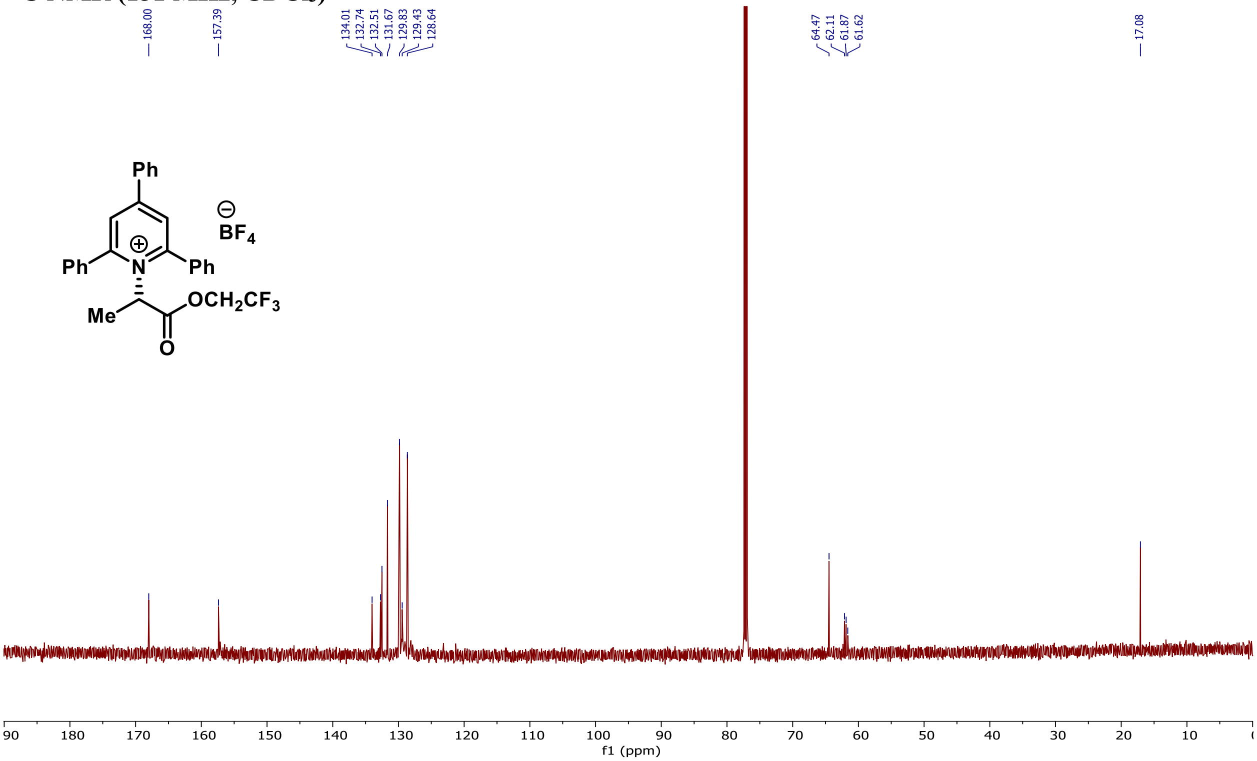


(*S*)-1-(1-*oxo*-1-(2,2,2-Trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*S*)-12f:

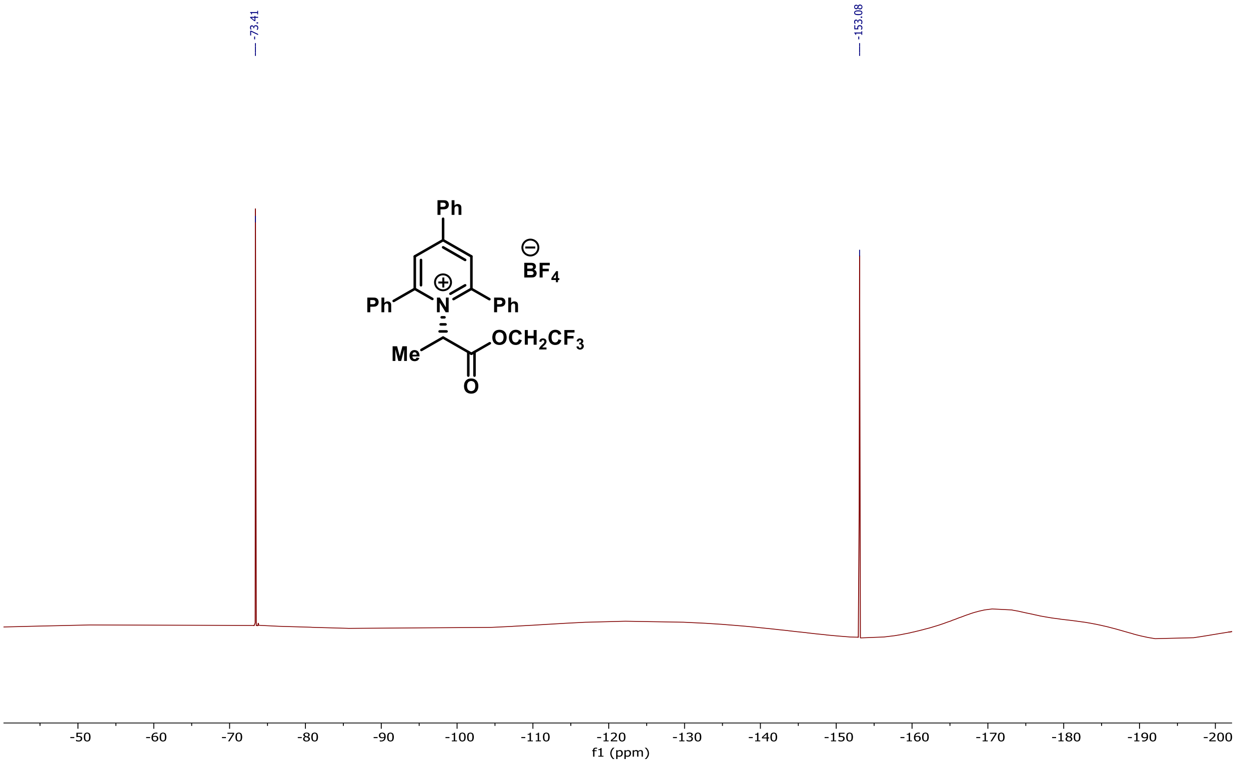
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

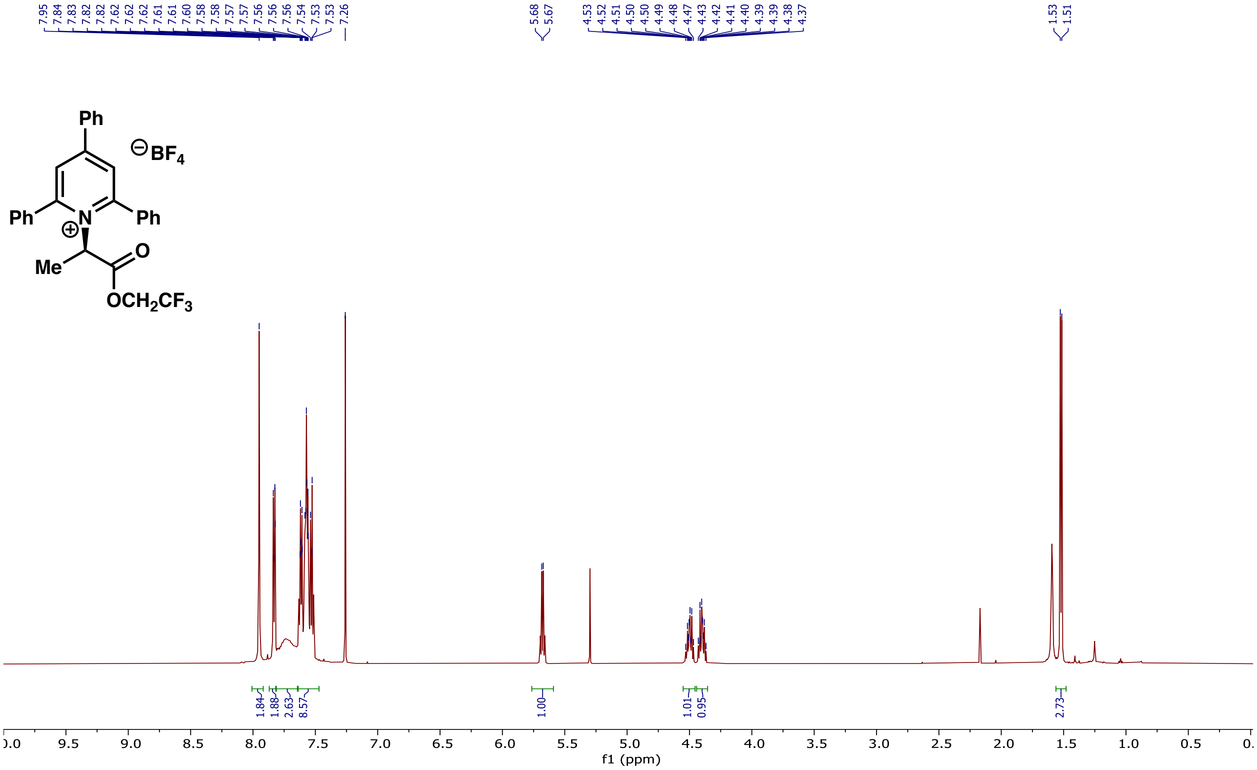


^{19}F NMR (565 MHz, CDCl$_3$)

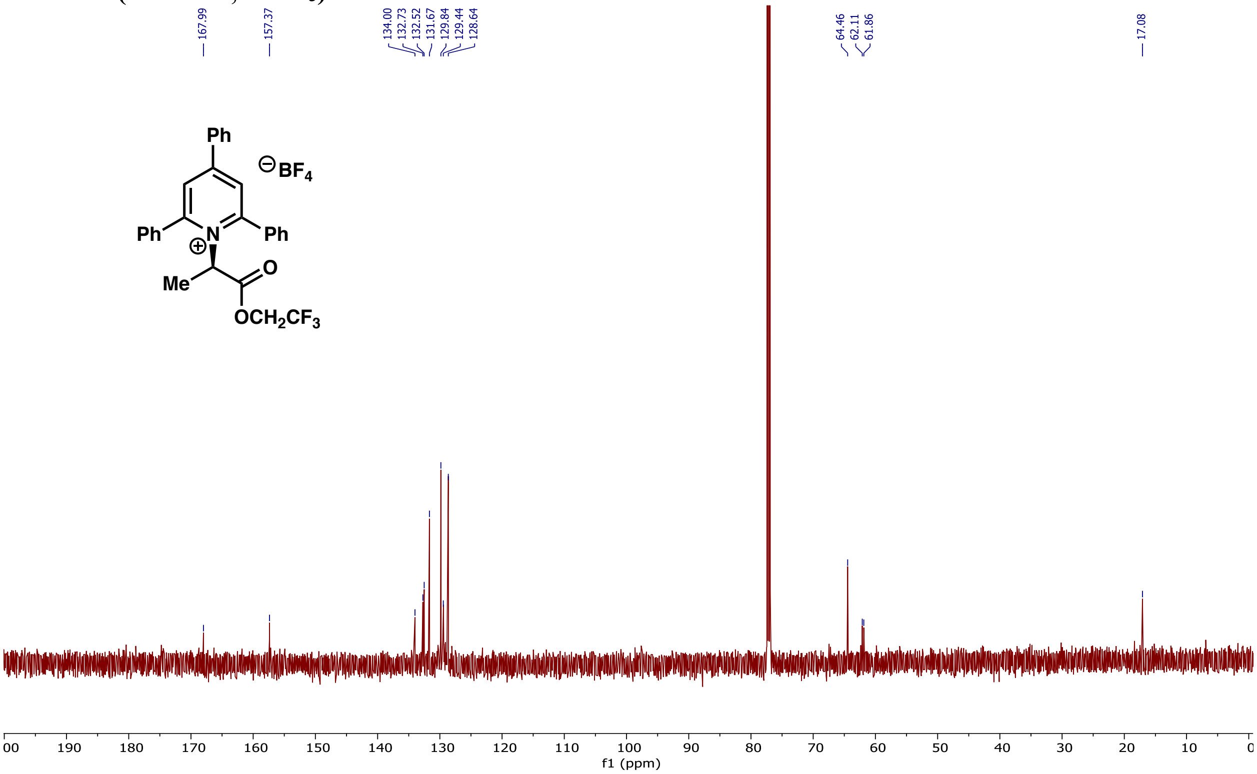


(*R*)-1-(1-*oxo*-1-(2,2,2-Trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*R*)-12f:

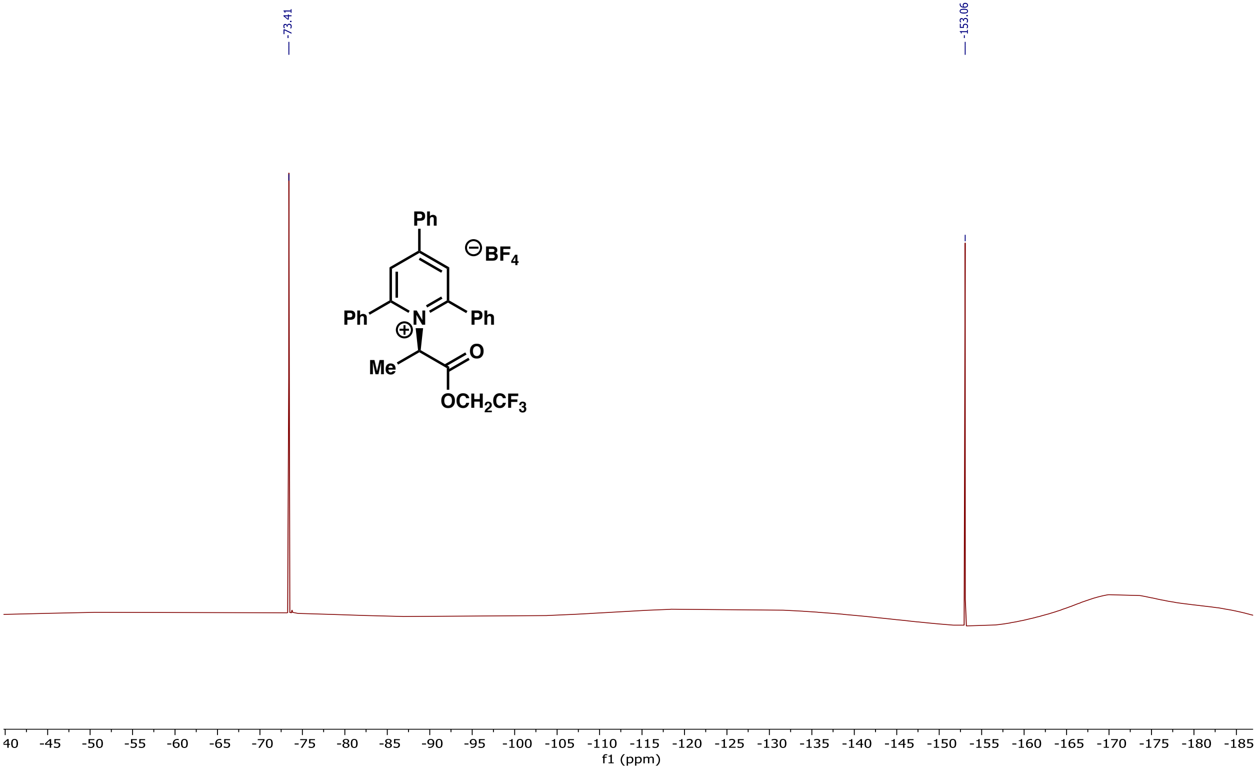
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

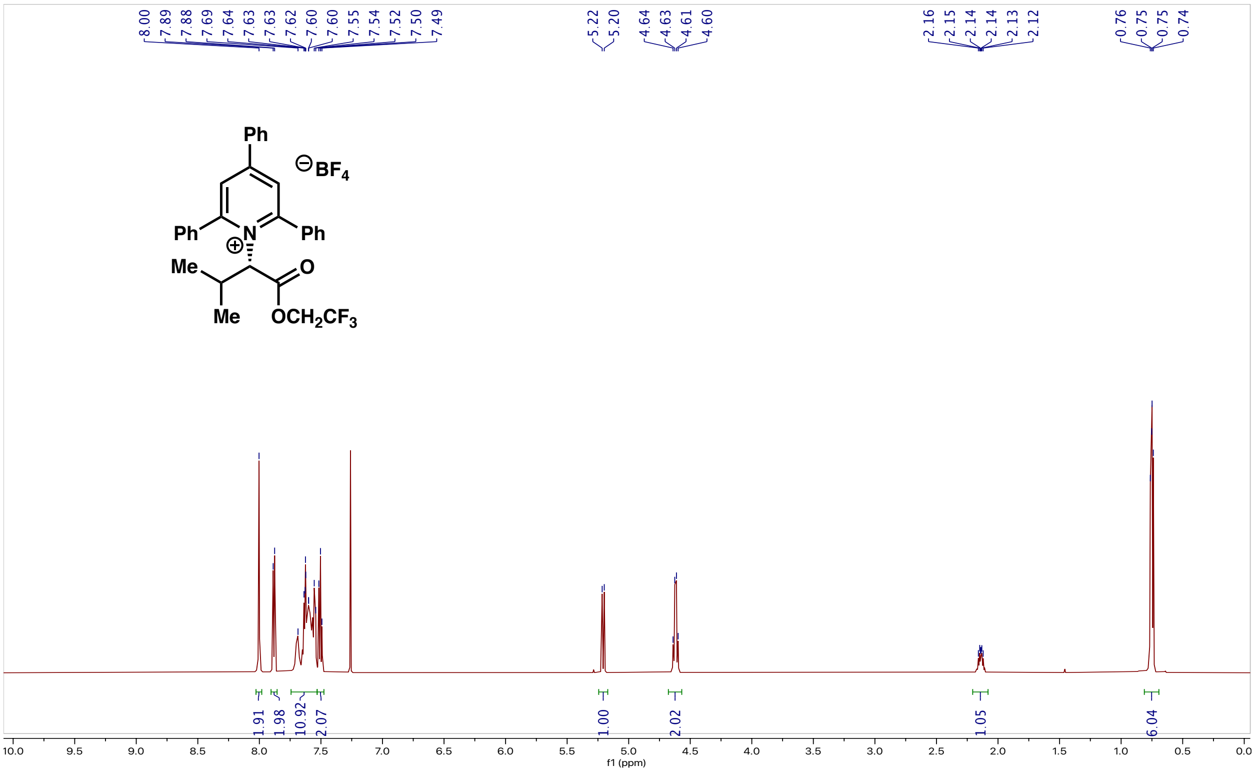


^{19}F NMR (565 MHz, CDCl$_3$)

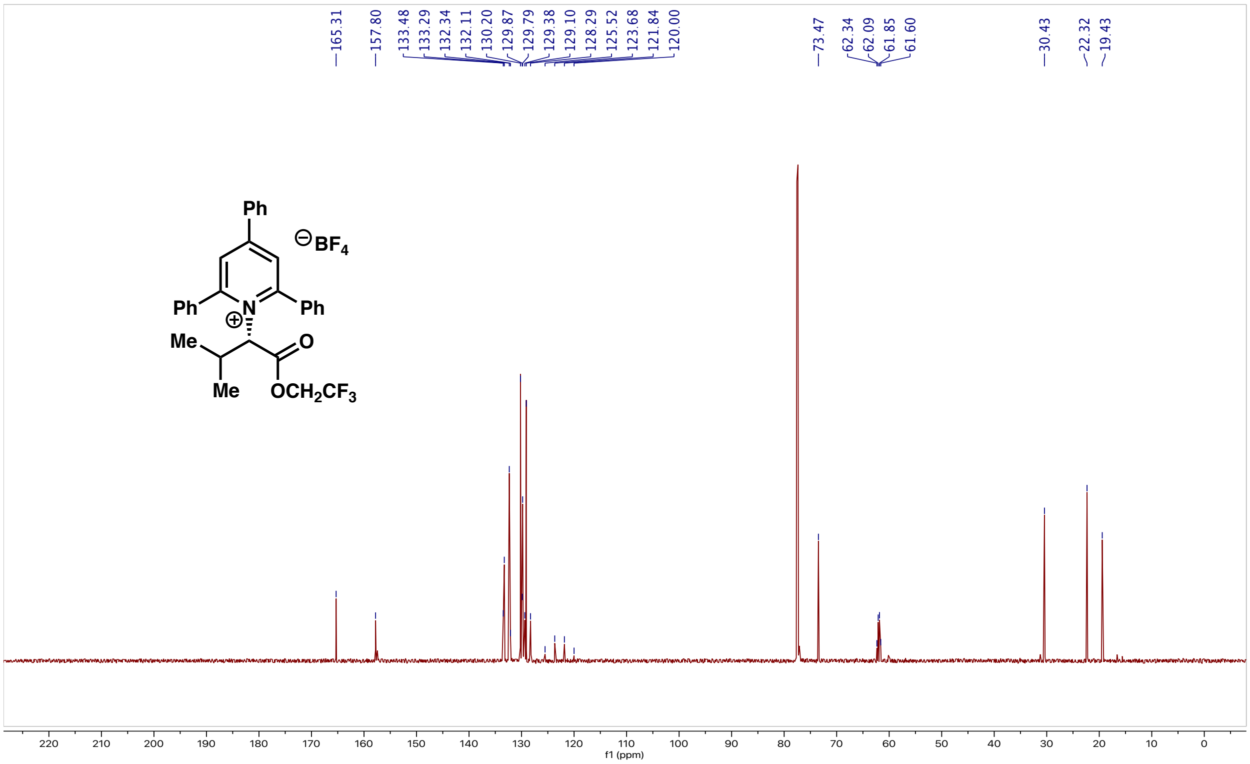


(*S*)-1-(3-Methyl-1-oxo-1-(2,2,2-trifluoroethoxy)butan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*S*)-12g:

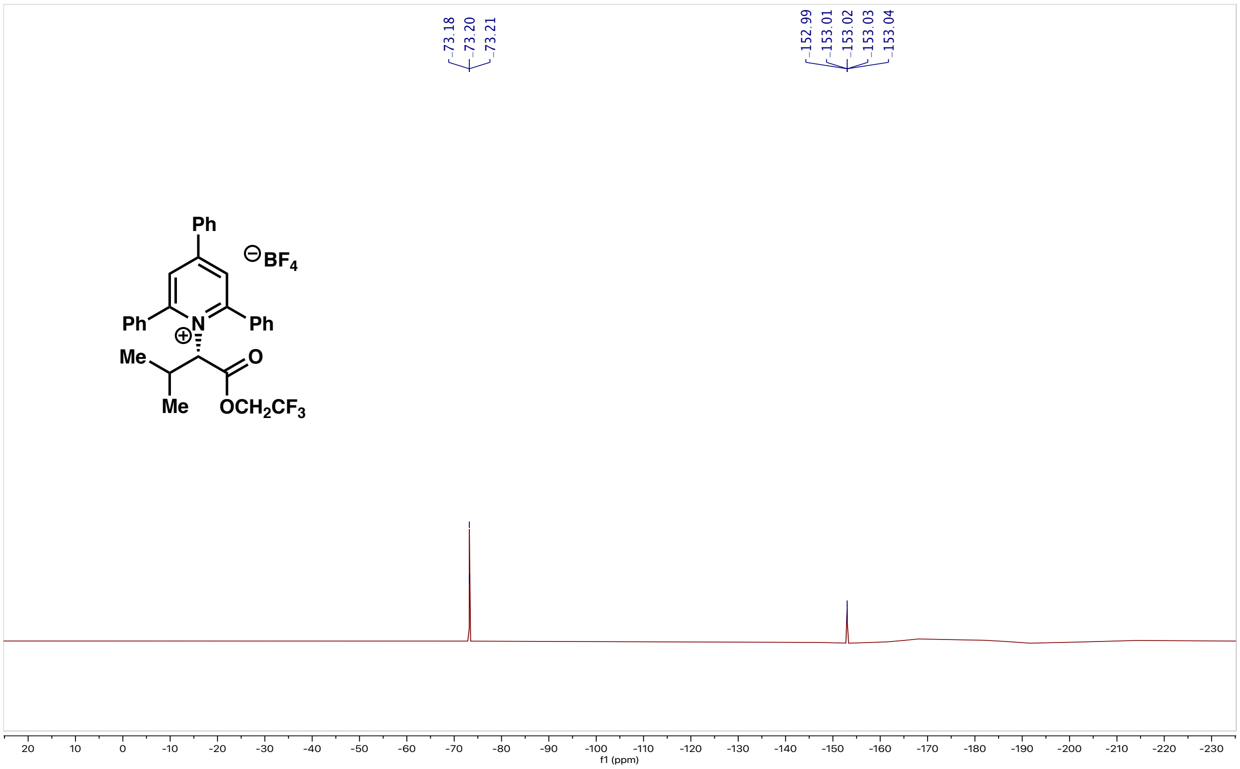
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

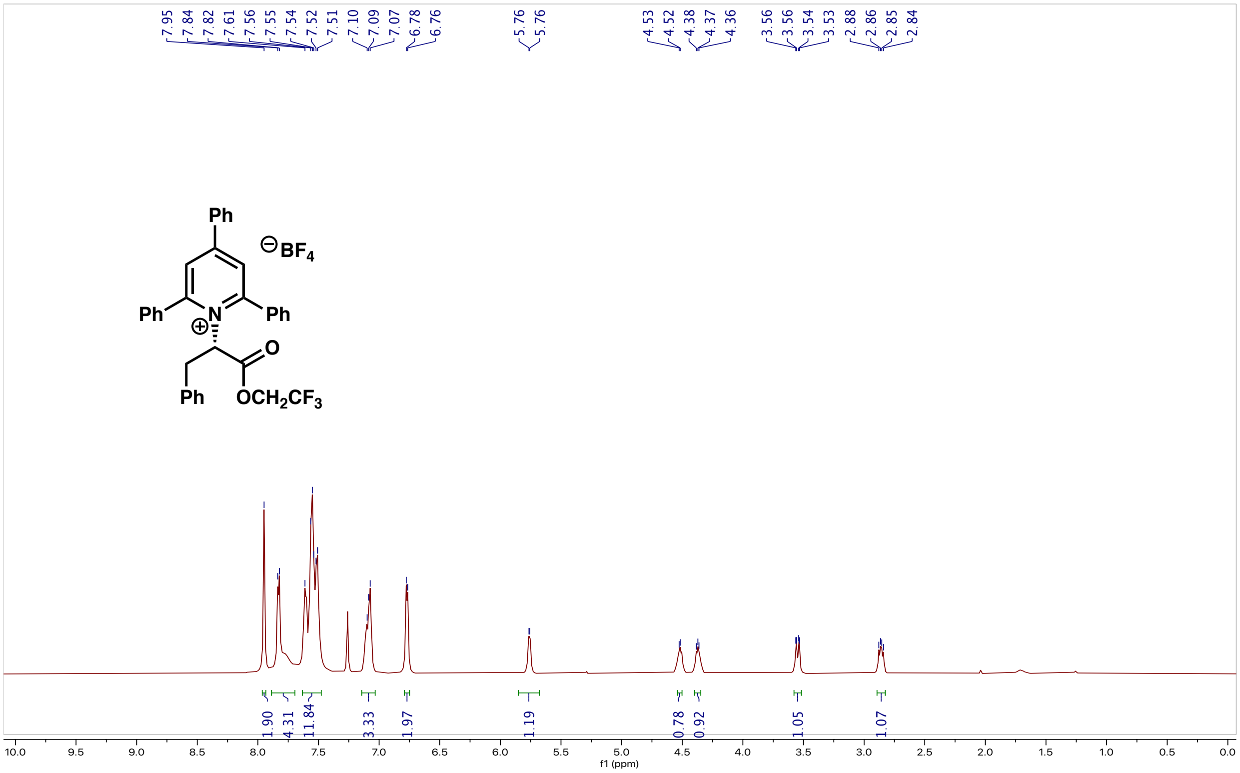


^{19}F NMR (565 MHz, CDCl$_3$)

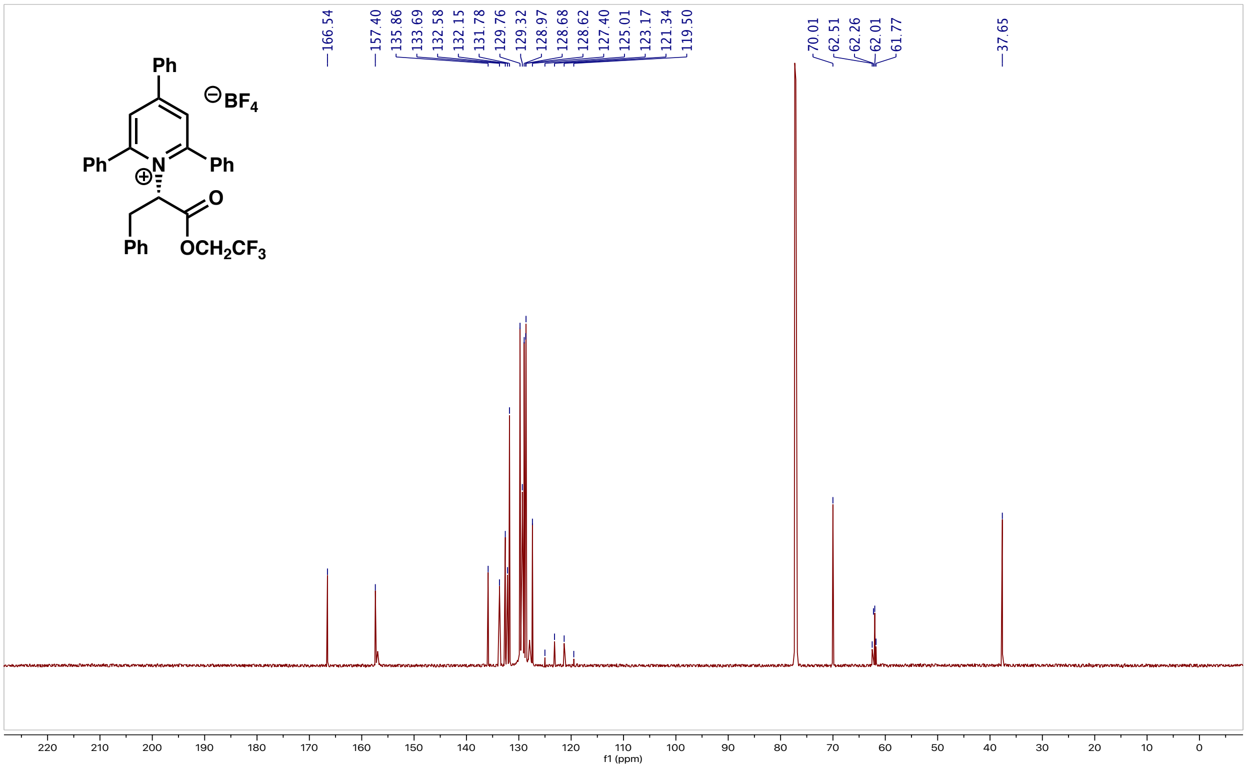


(*S*)-1-(1-*oxo*-3-Phenyl-1-(2,2,2-trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium, (*S*)-12h:

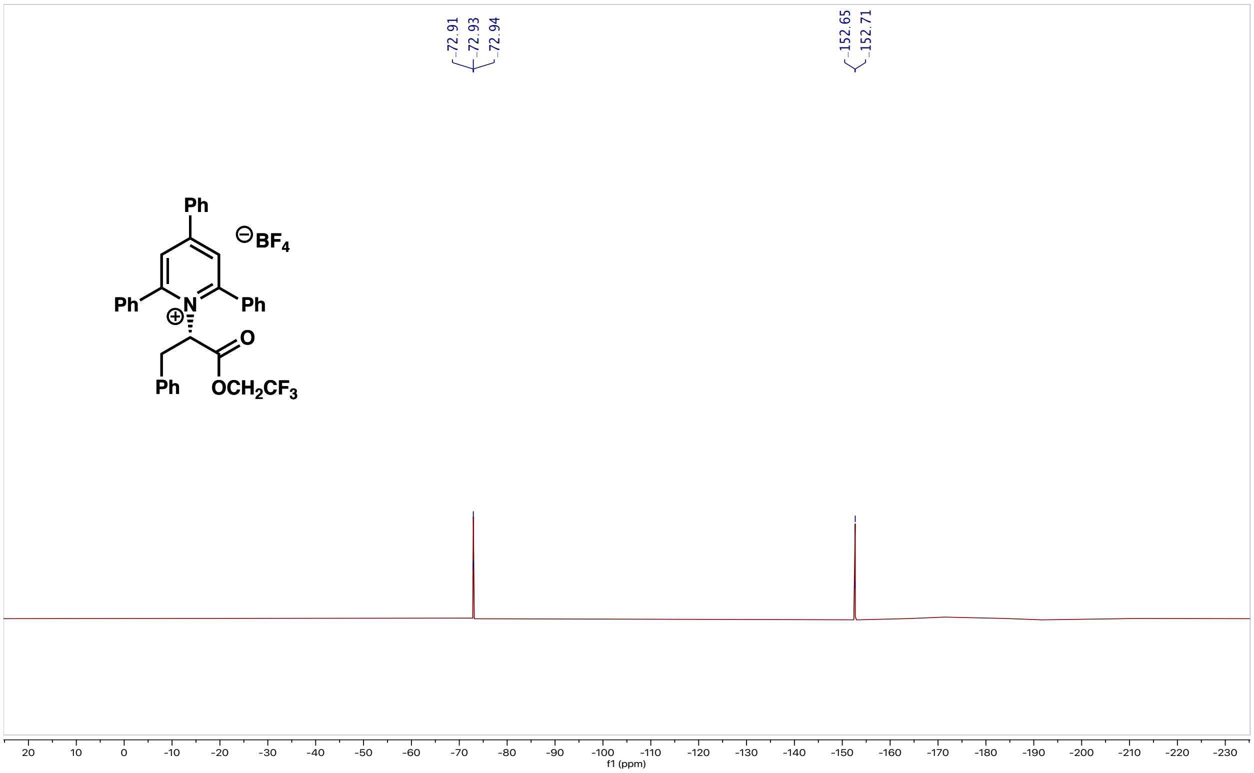
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

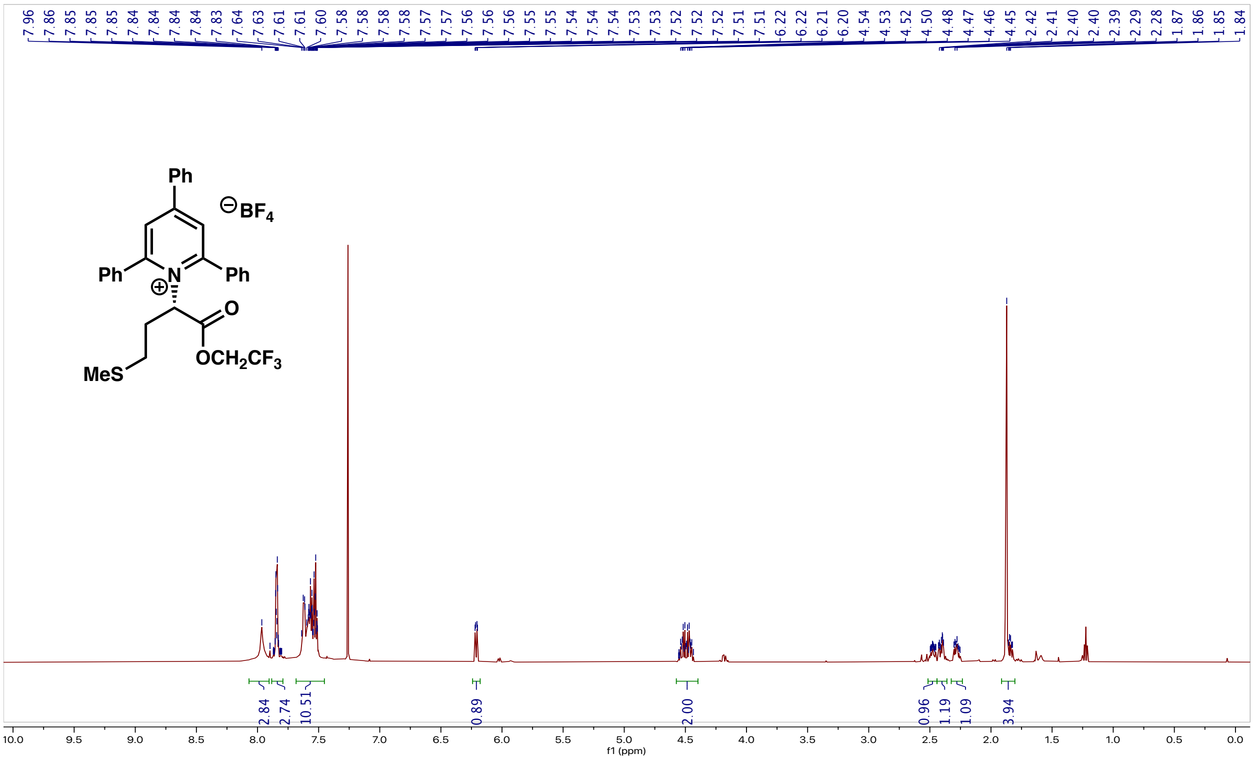


^{19}F NMR (565 MHz, CDCl$_3$)

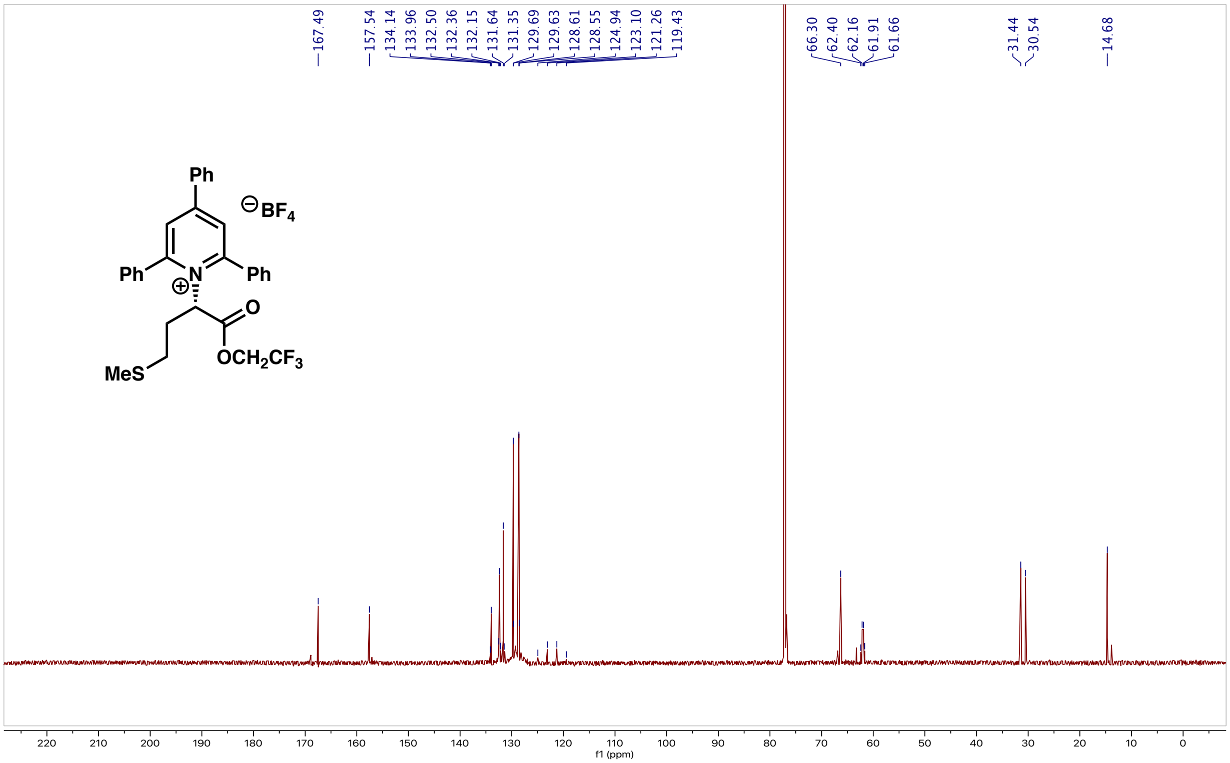


(*S*)-1-(4-(Methylthio)-1-oxo-1-(2,2,2-trifluoroethoxy)butan-2-yl)-2,4,6-triphenylpyridin-1-ium, (*S*)-12i:

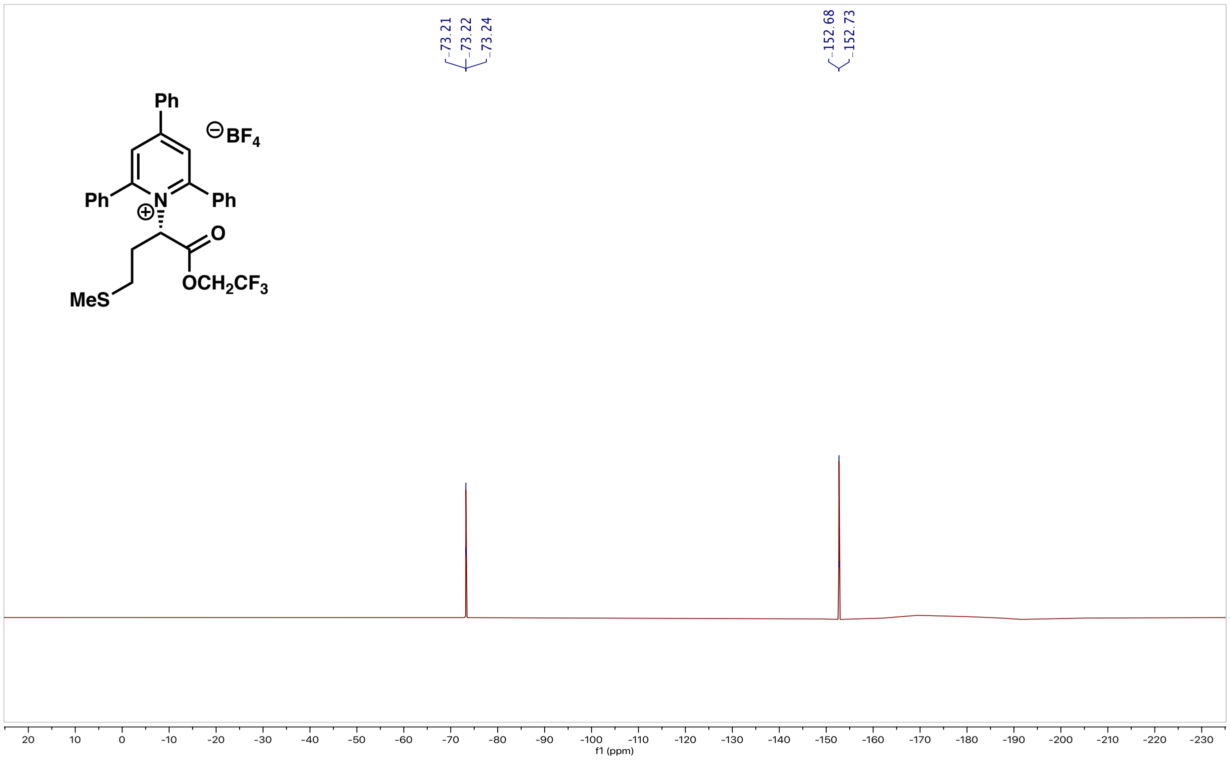
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

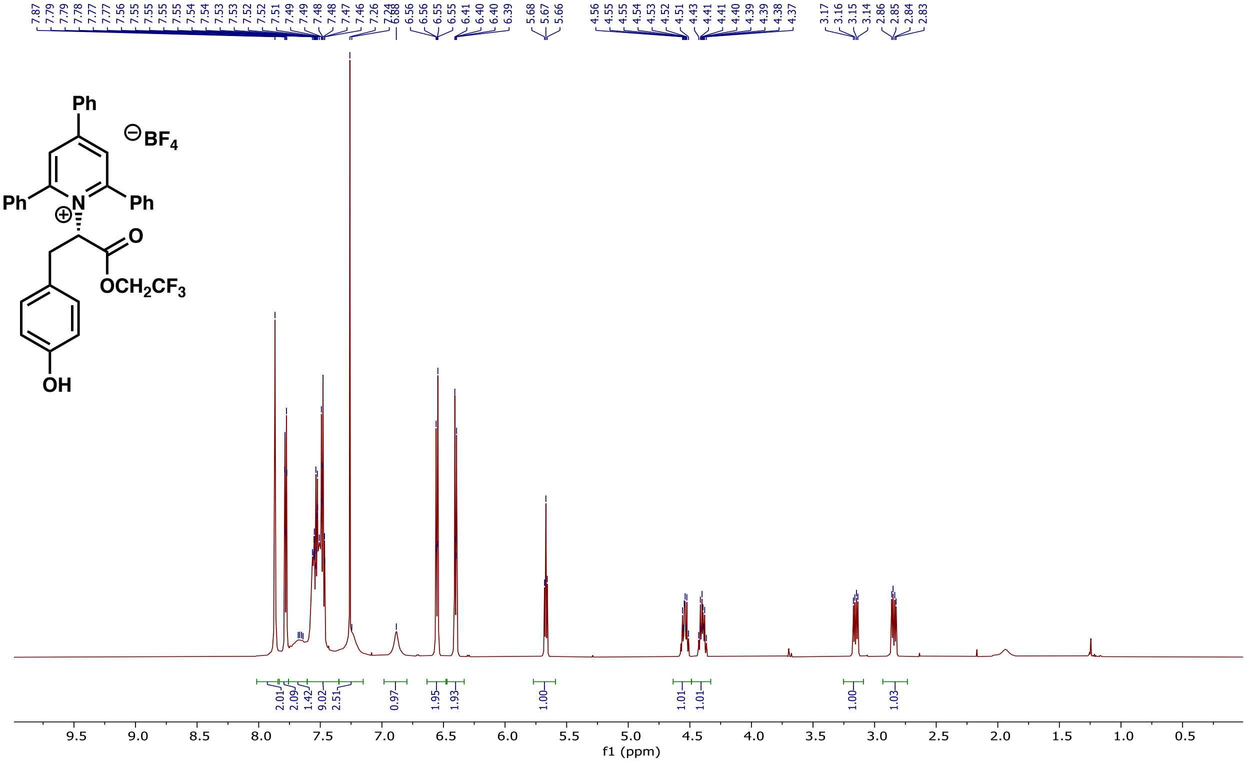


^{19}F NMR (565 MHz, CDCl$_3$)

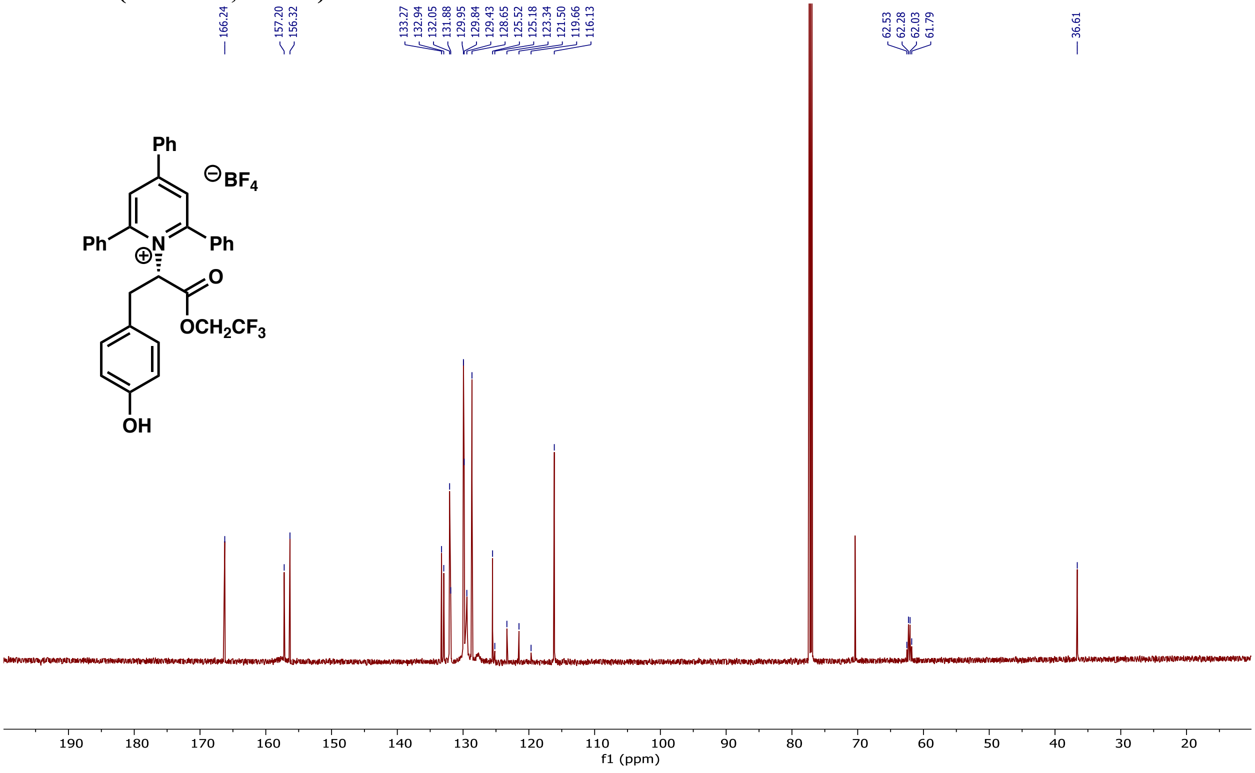


(*S*)-1-(3-(4-Hydroxyphenyl)-1-oxo-1-(2,2,2-trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, (*S*)-12j:

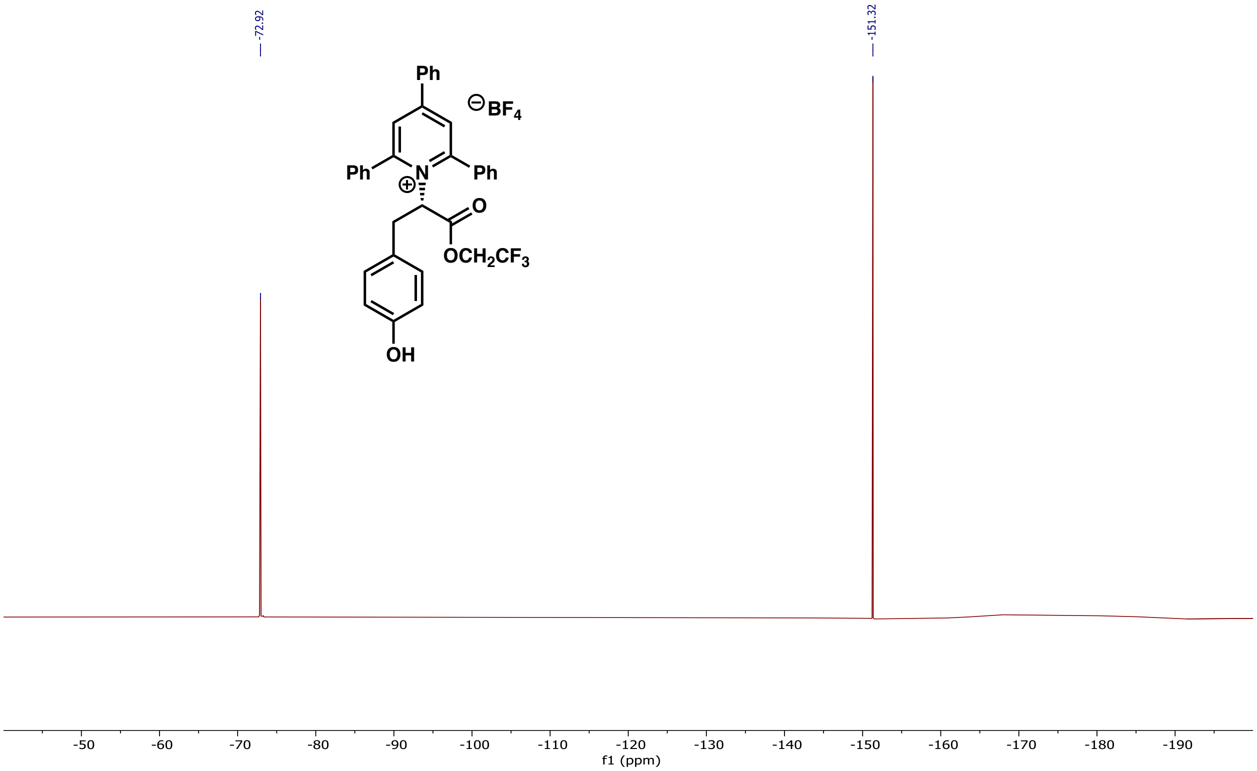
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

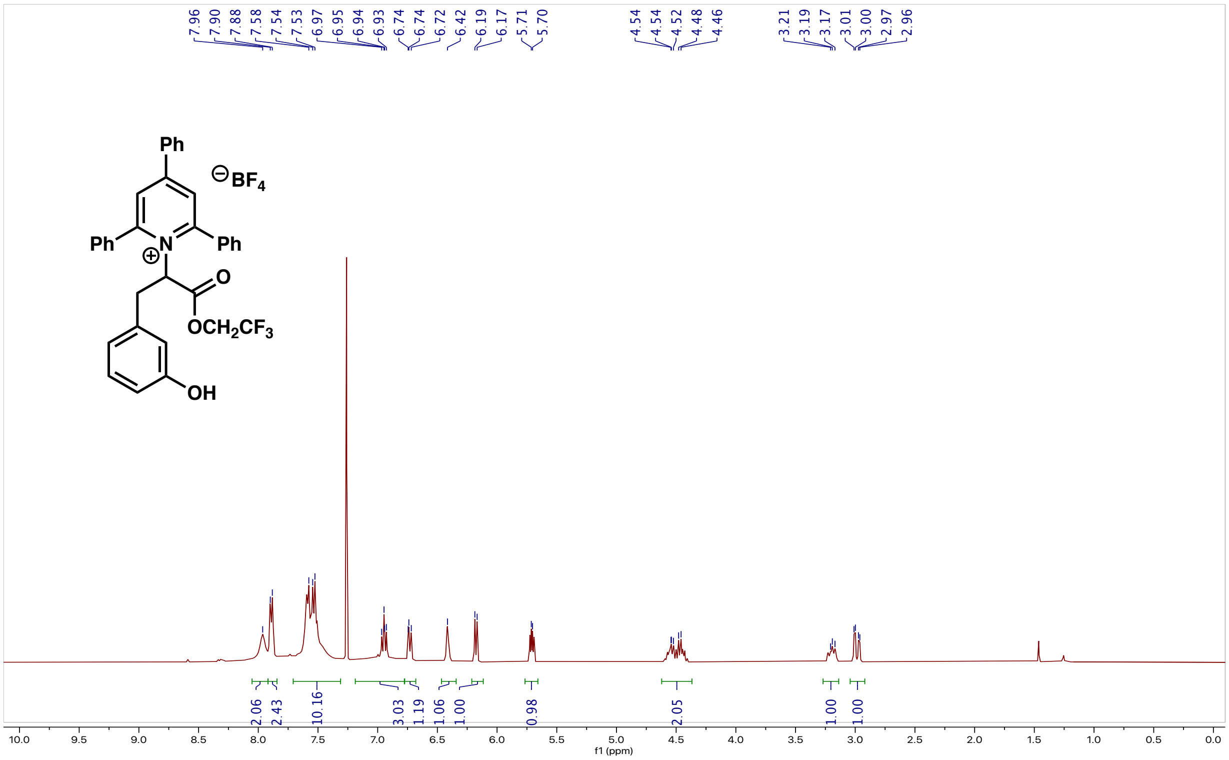


^{19}F NMR (565 MHz, CDCl$_3$)

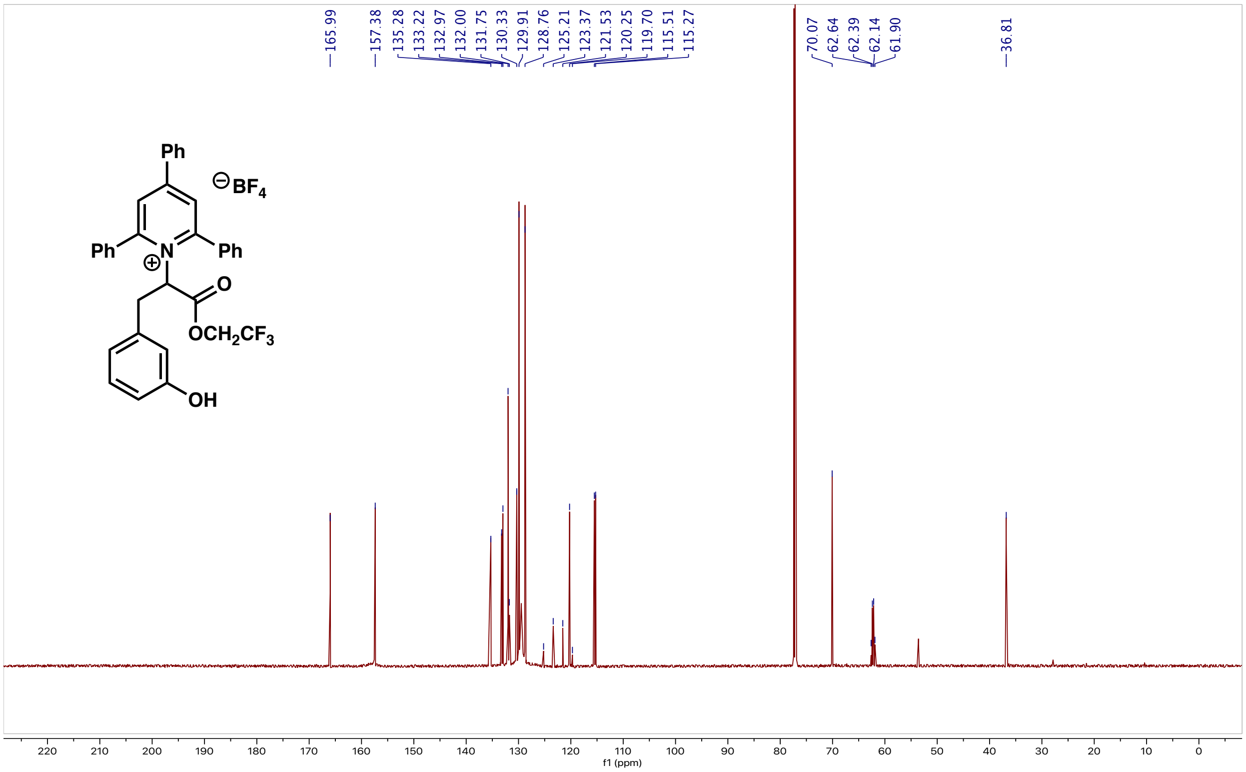


1-(3-(3-Hydroxyphenyl)-1-oxo-1-(2,2,2-trifluoroethoxy)propan-2-yl)-2,4,6-triphenylpyridin-1-ium, 12k:

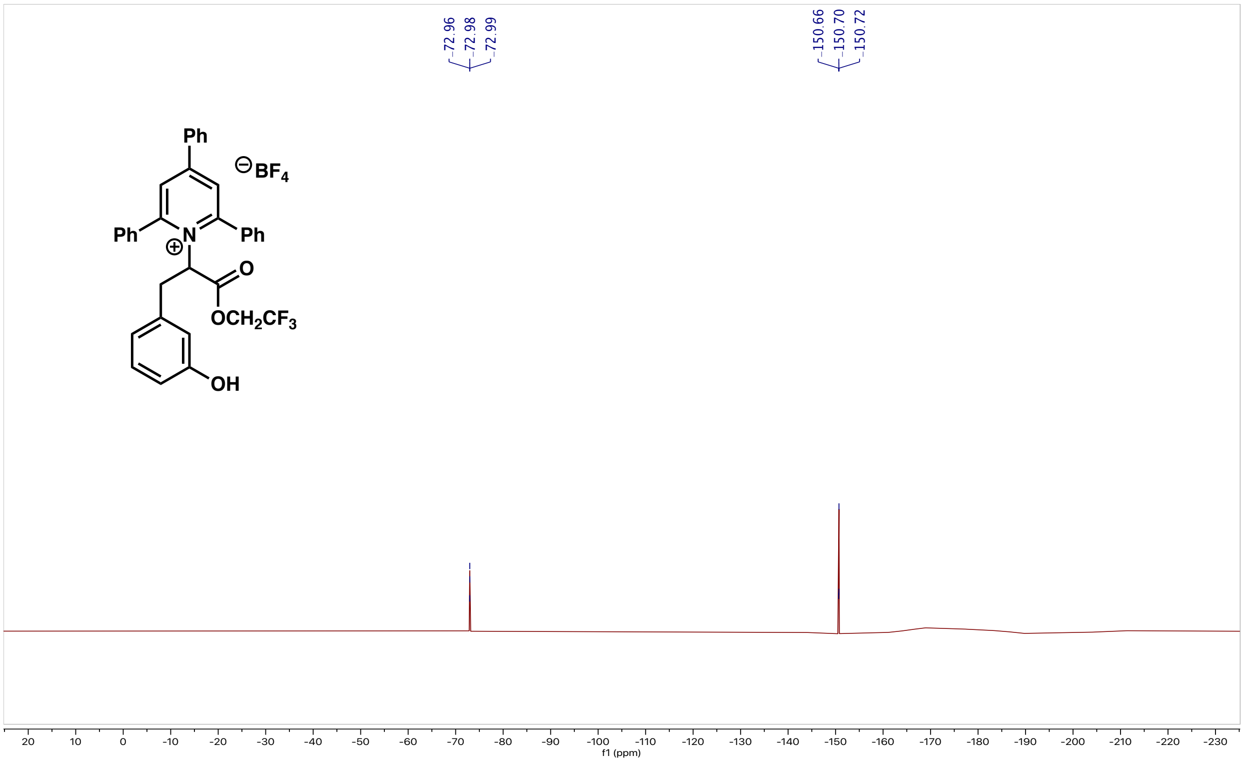
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

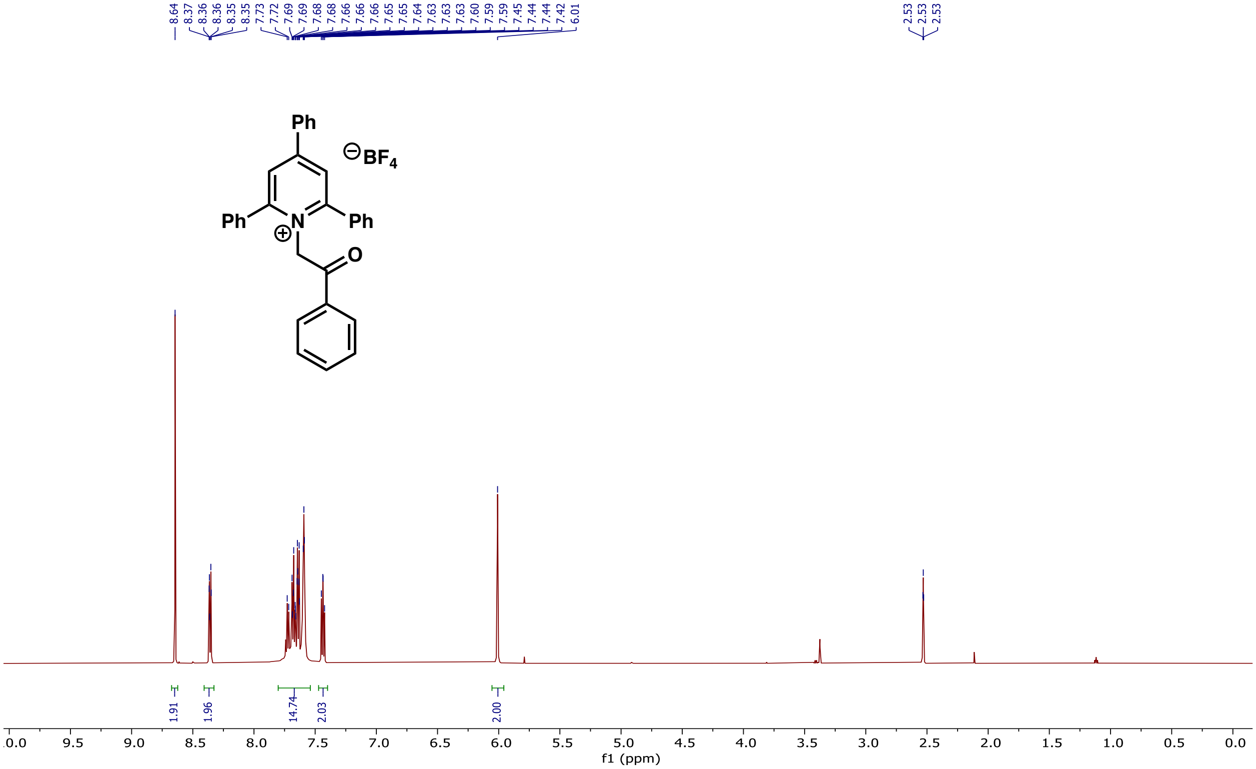


^{19}F NMR (565 MHz, CDCl$_3$)

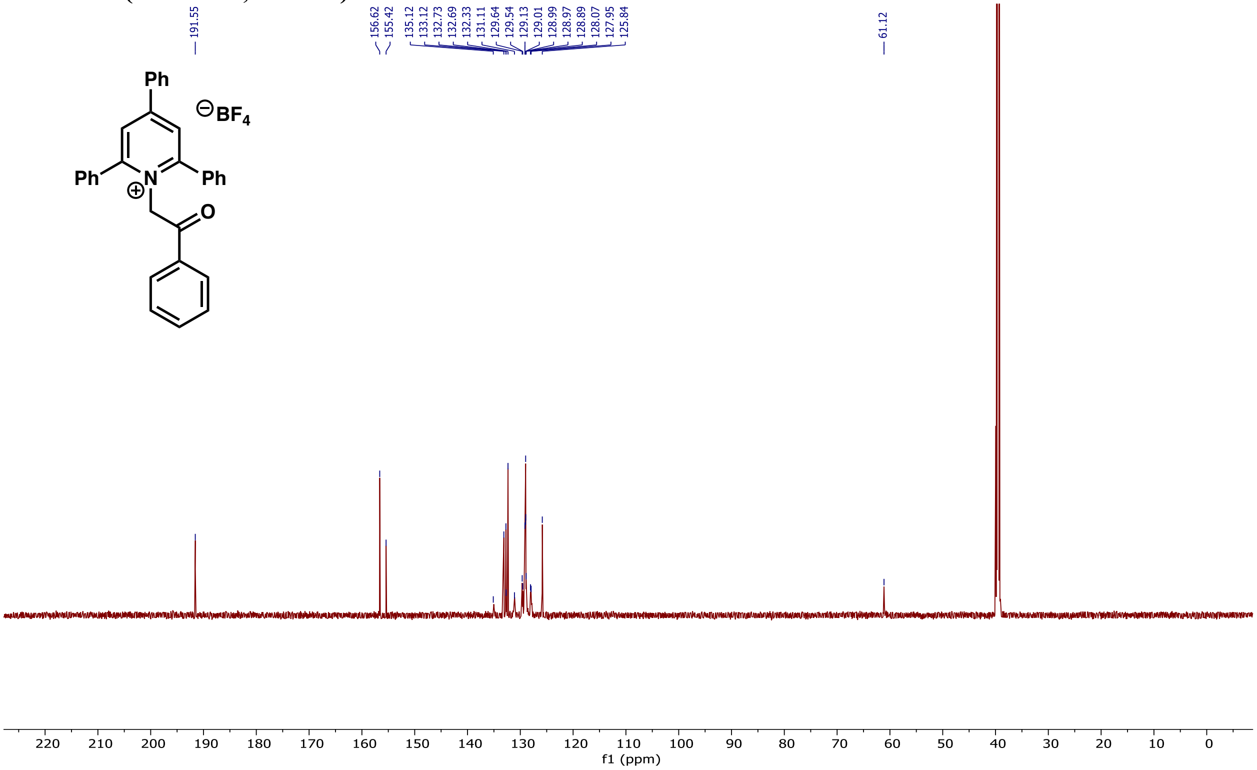


1-(2-*oxo*-2-Phenylethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14a:

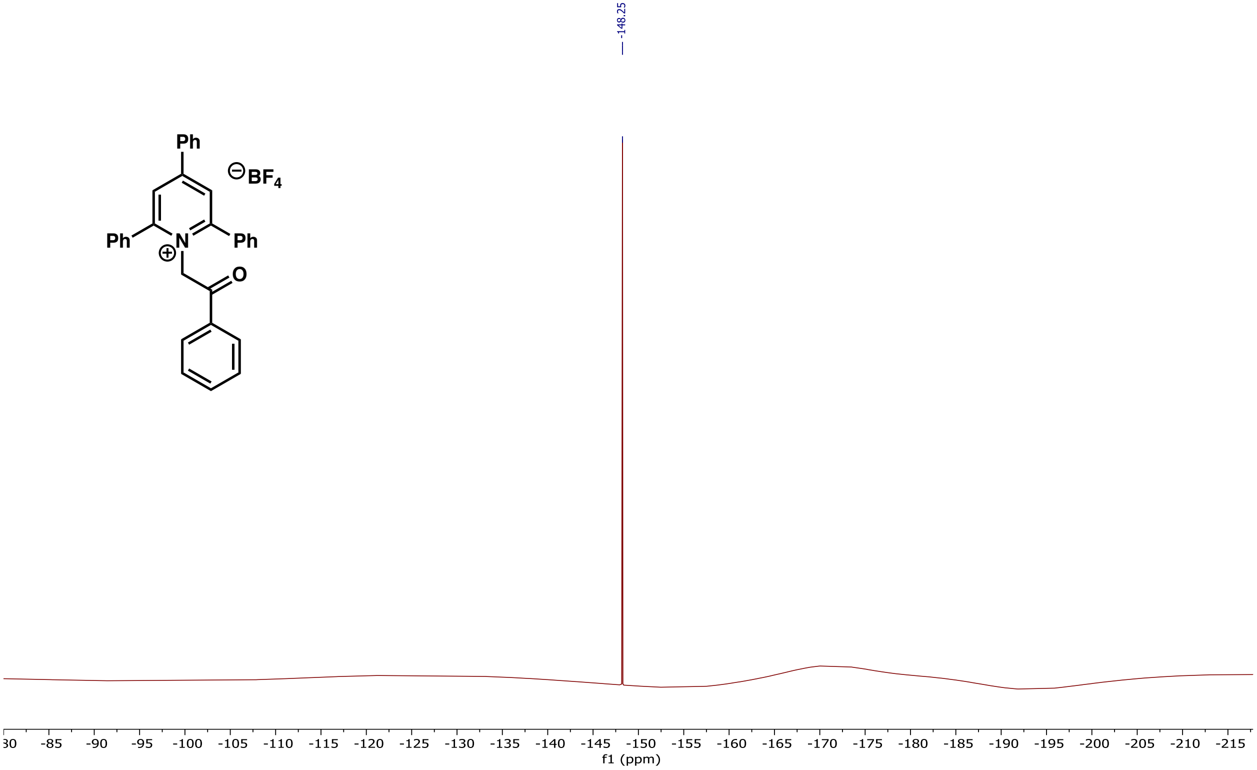
^{1}H NMR (600 MHz, DMSO)



^{13}C NMR (151 MHz, DMSO)

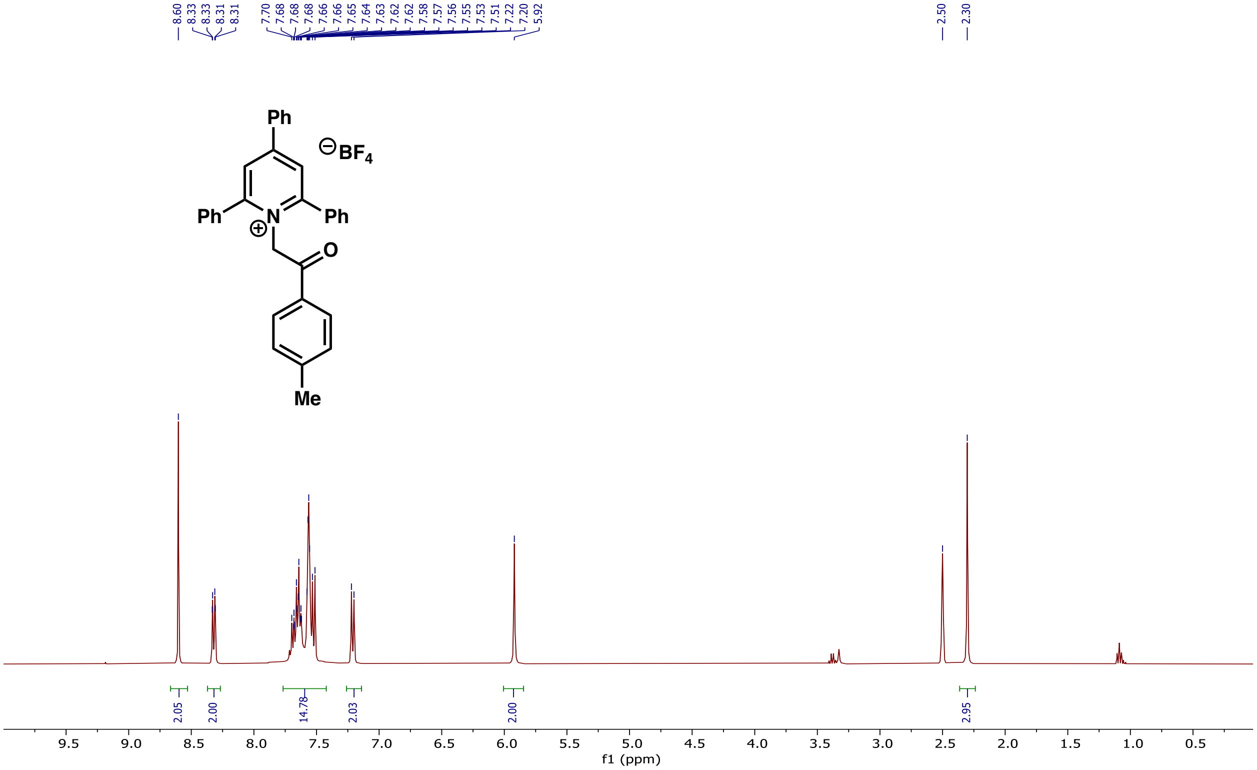


^{19}F NMR (565 MHz, DMSO)

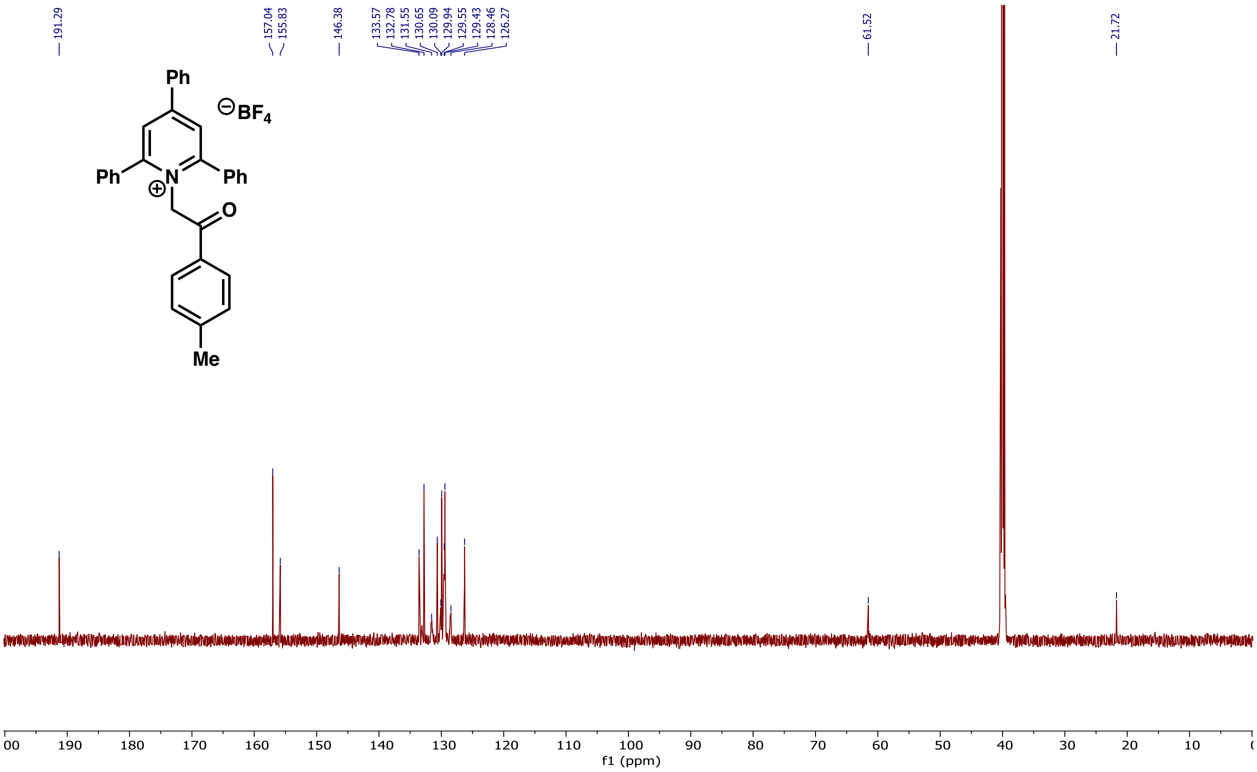


1-(2-oxo-2-(*p*-Tolyl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14b:

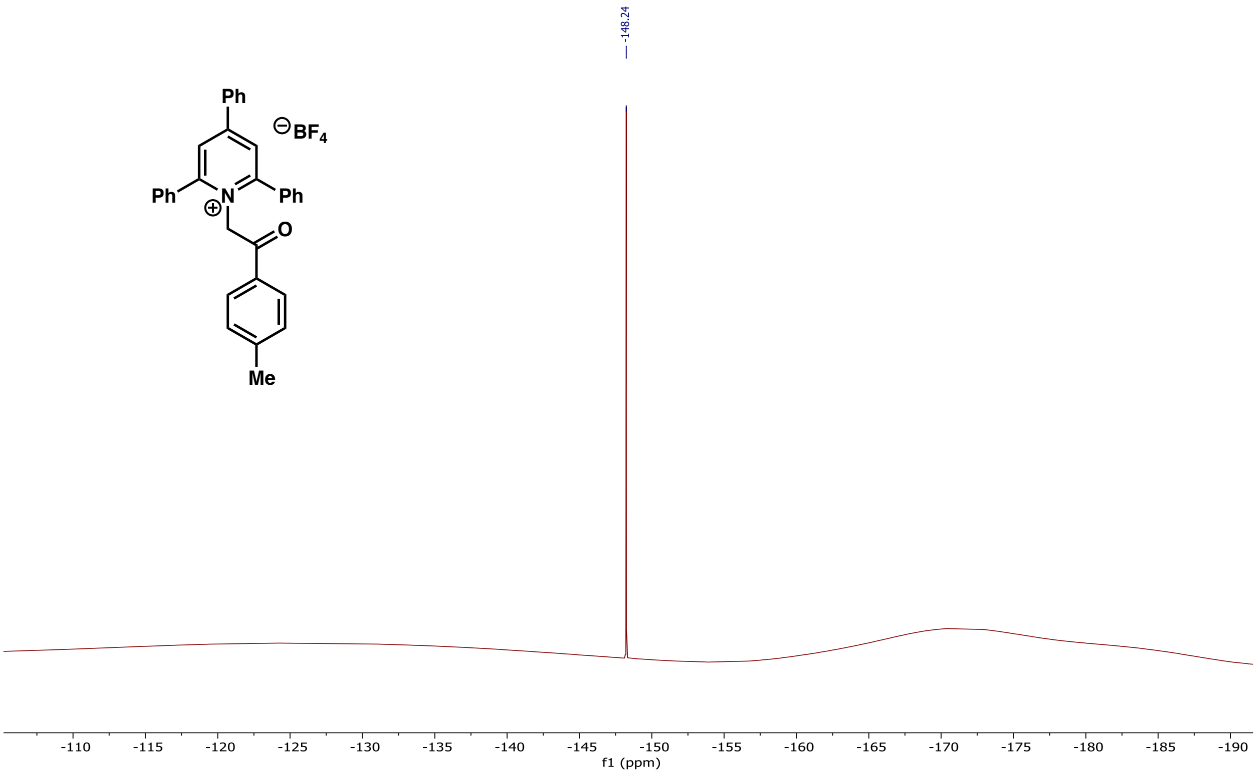
^{1}H NMR (600 MHz, DMSO)



^{13}C NMR (151 MHz, DMSO)

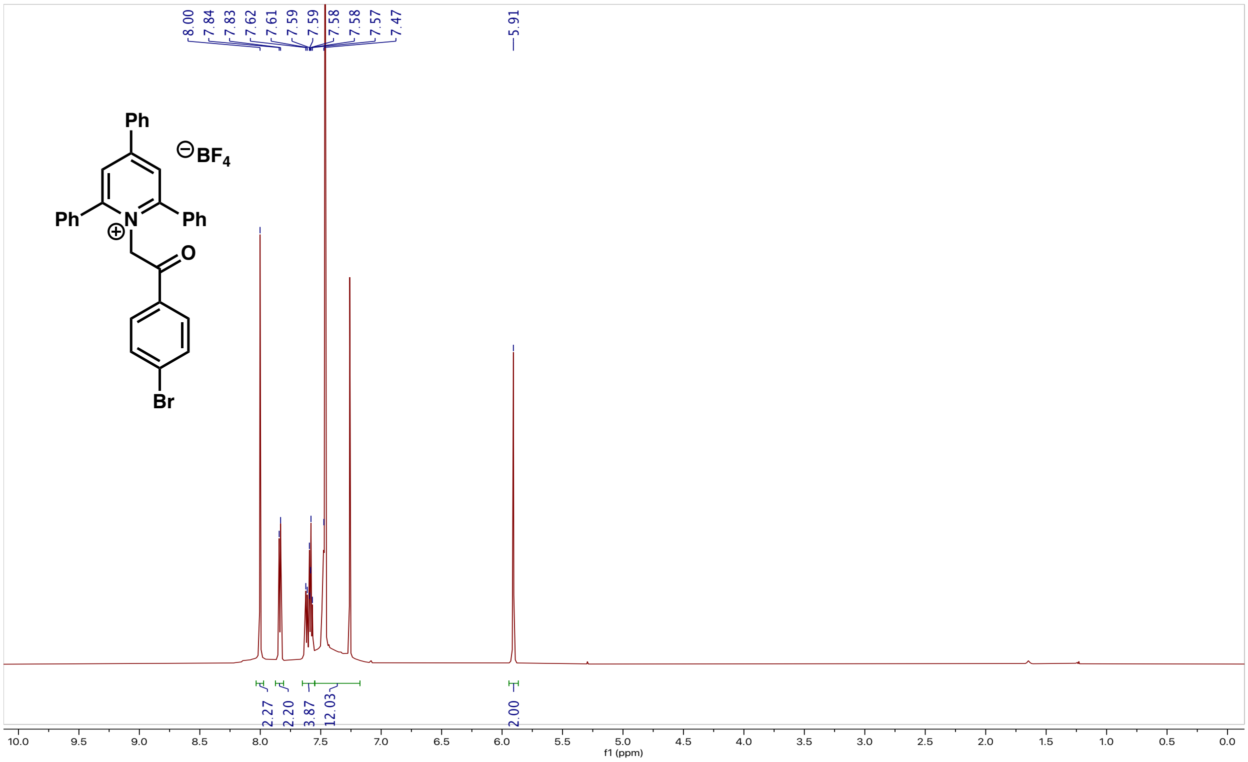


^{19}F NMR (565 MHz, DMSO)

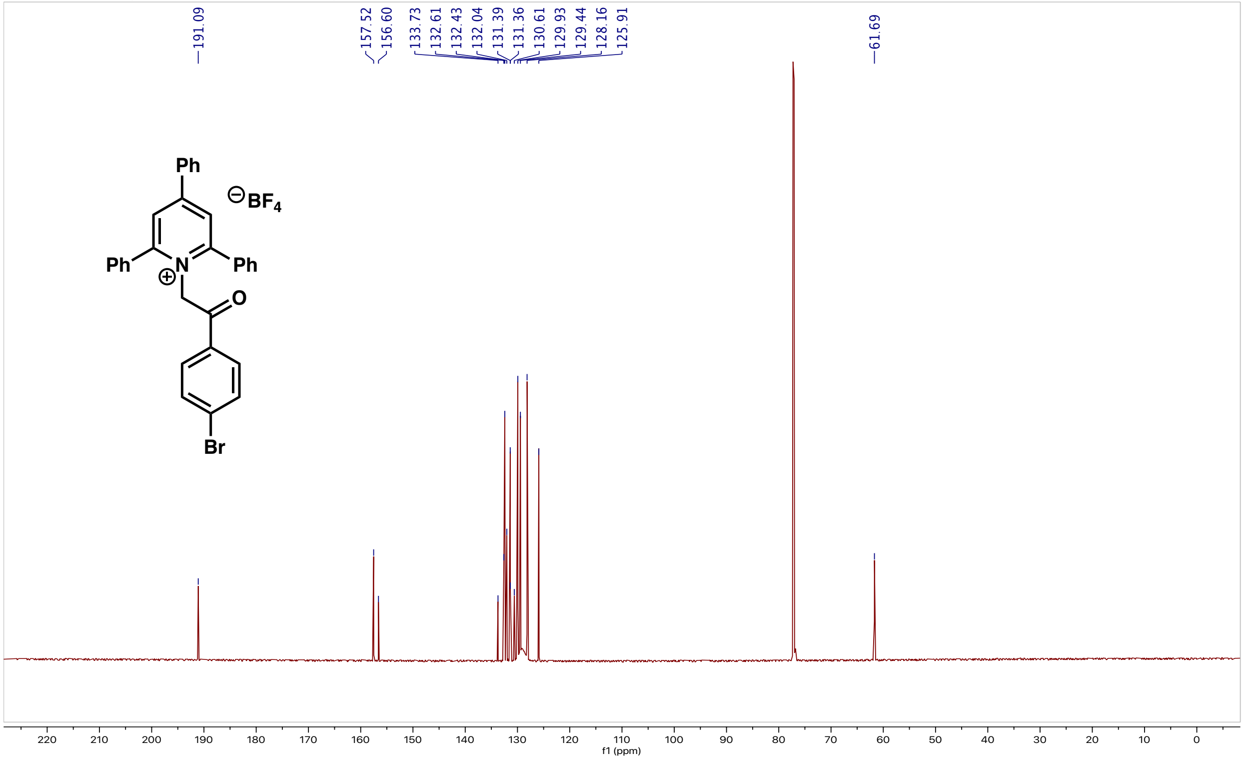


1-(2-(4-Bromophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium, 14c :

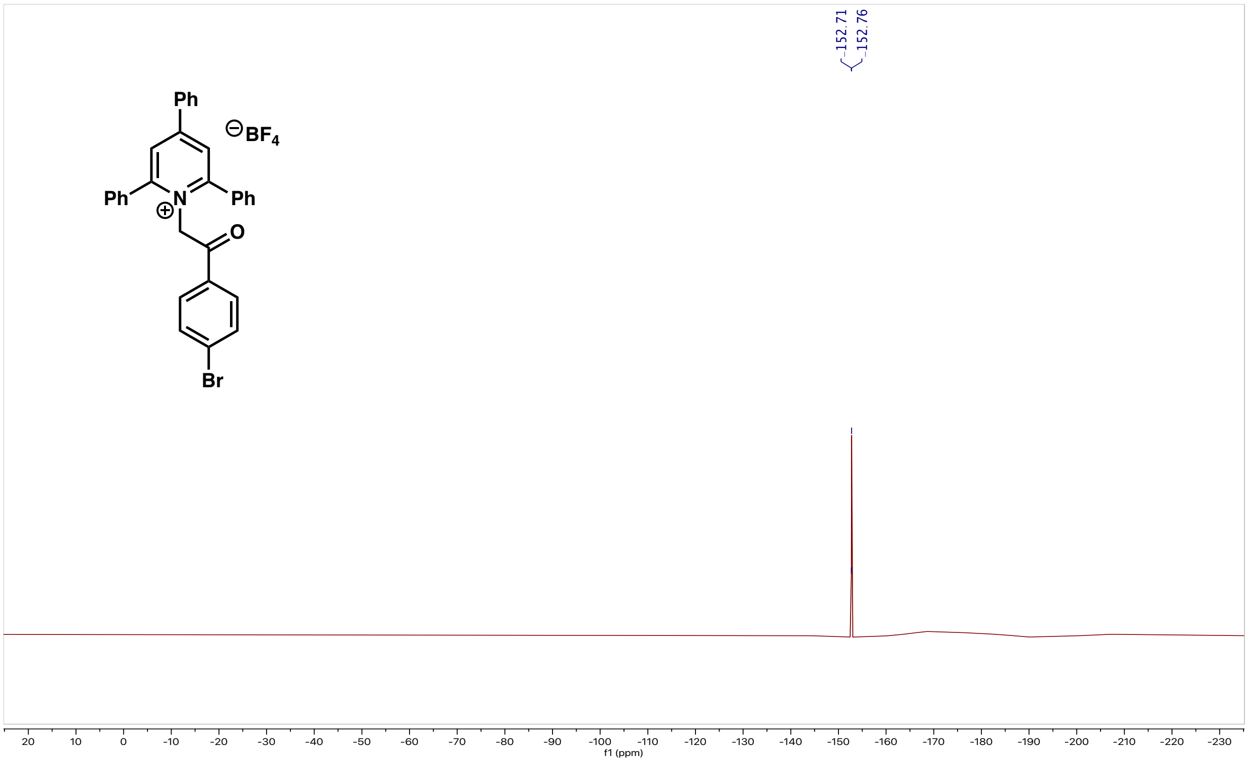
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

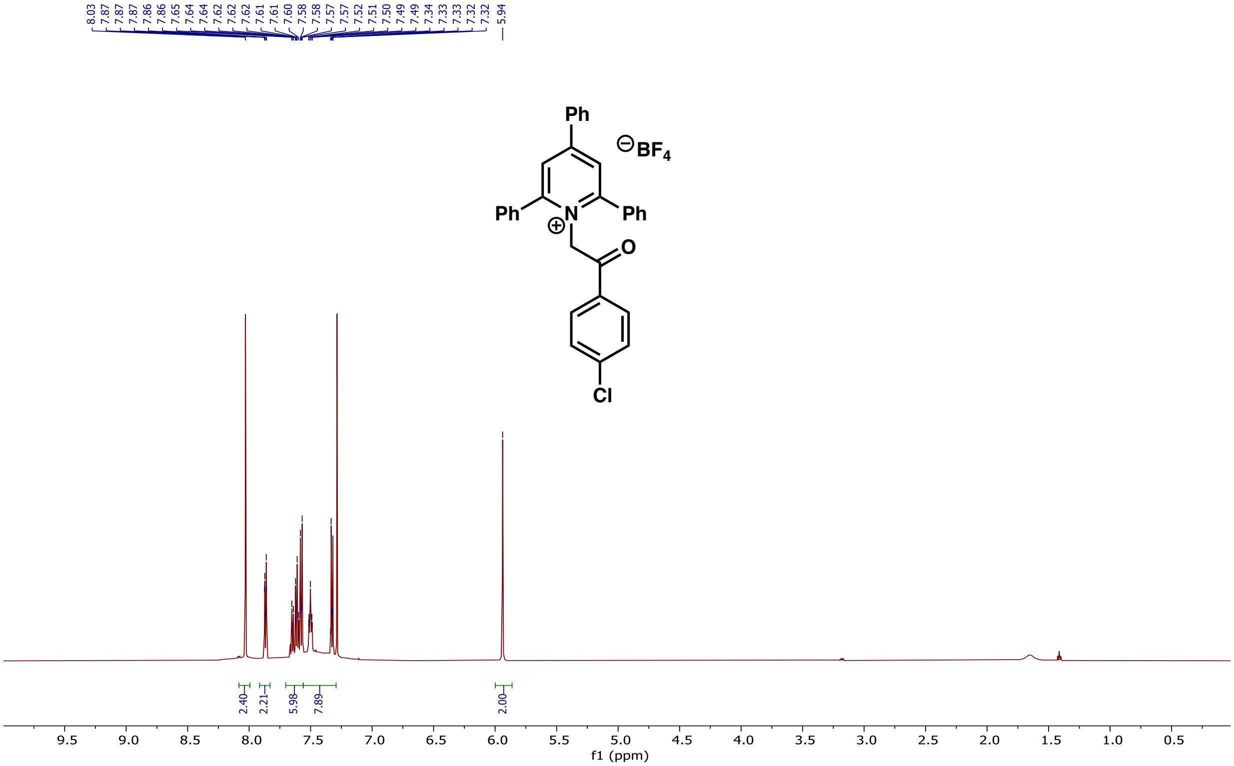


^{19}F NMR (565 MHz, CDCl$_3$)

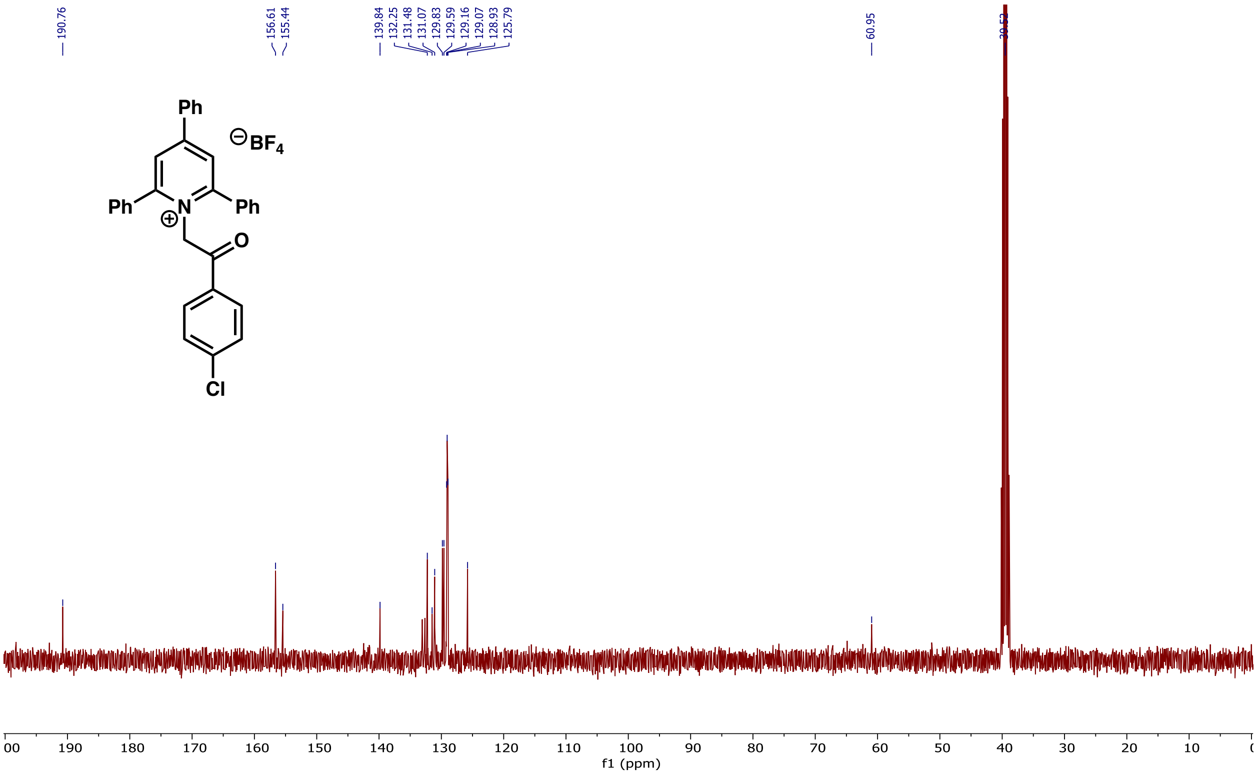


1-(2-(4-Chlorophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14d:

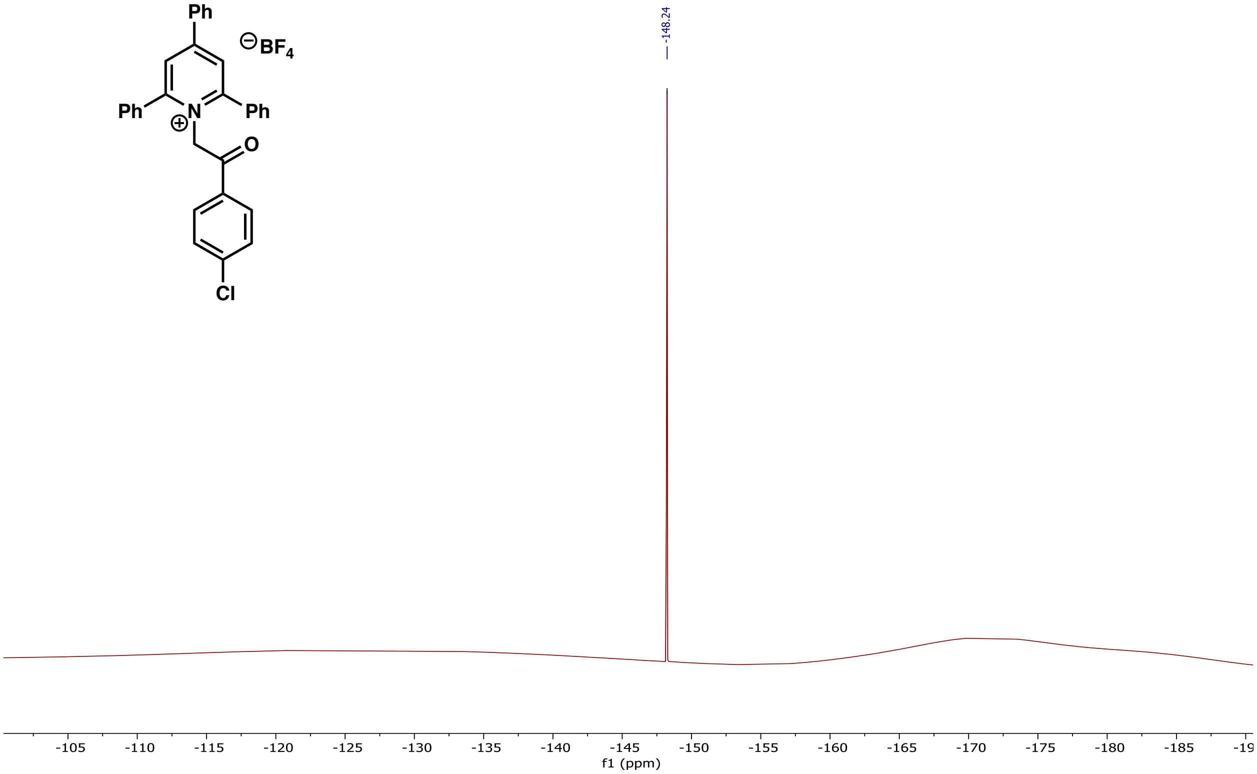
^{1}H NMR (600 MHz, CDCl3)



^{13}C NMR (101 MHz, DMSO)

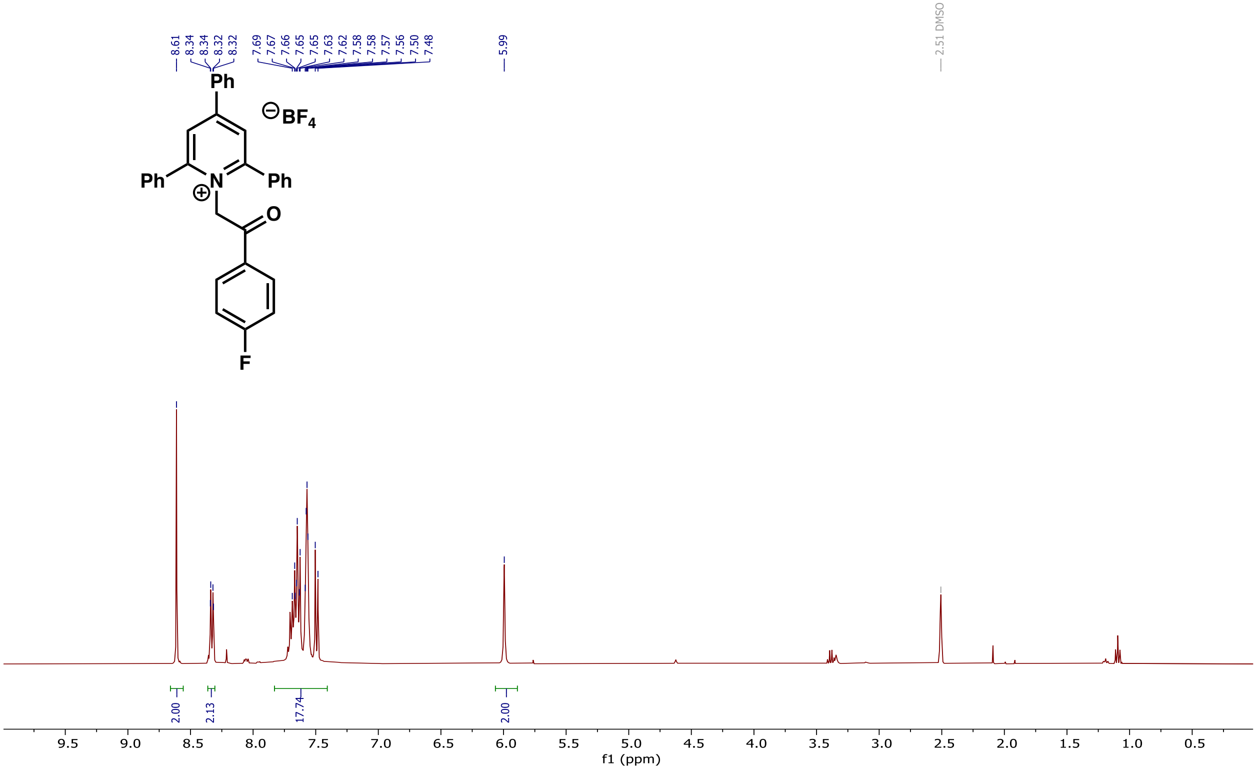


^{19}F NMR (565 MHz, DMSO)

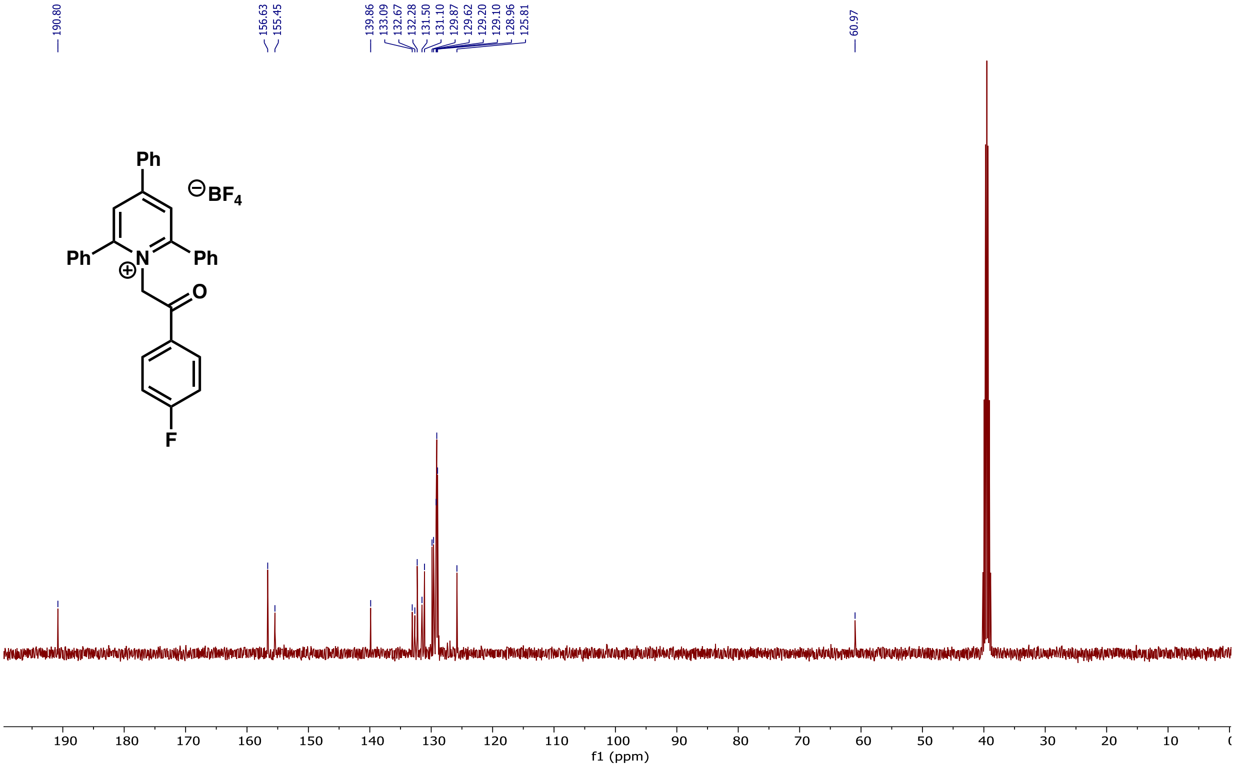


1-(2-(4-Fluorophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 14e:

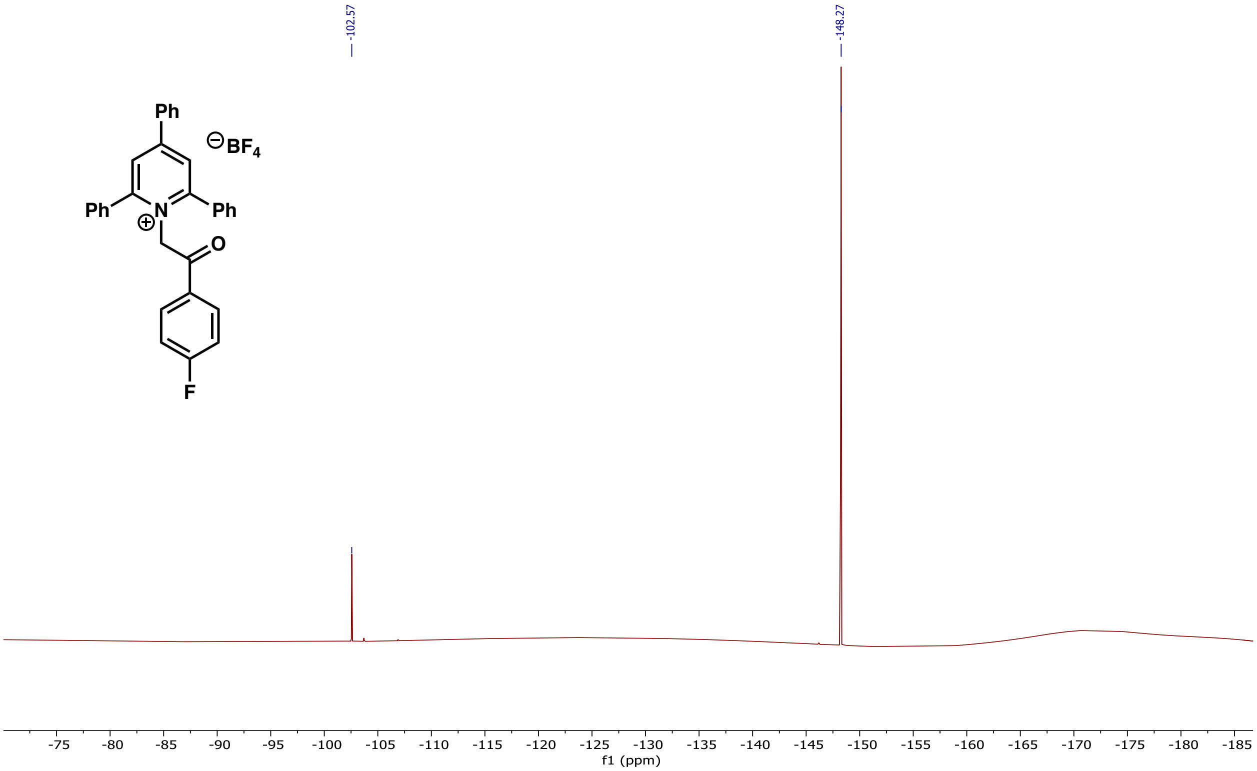
^{1}H NMR (400 MHz, DMSO)



^{13}C NMR (101 MHz, DMSO)

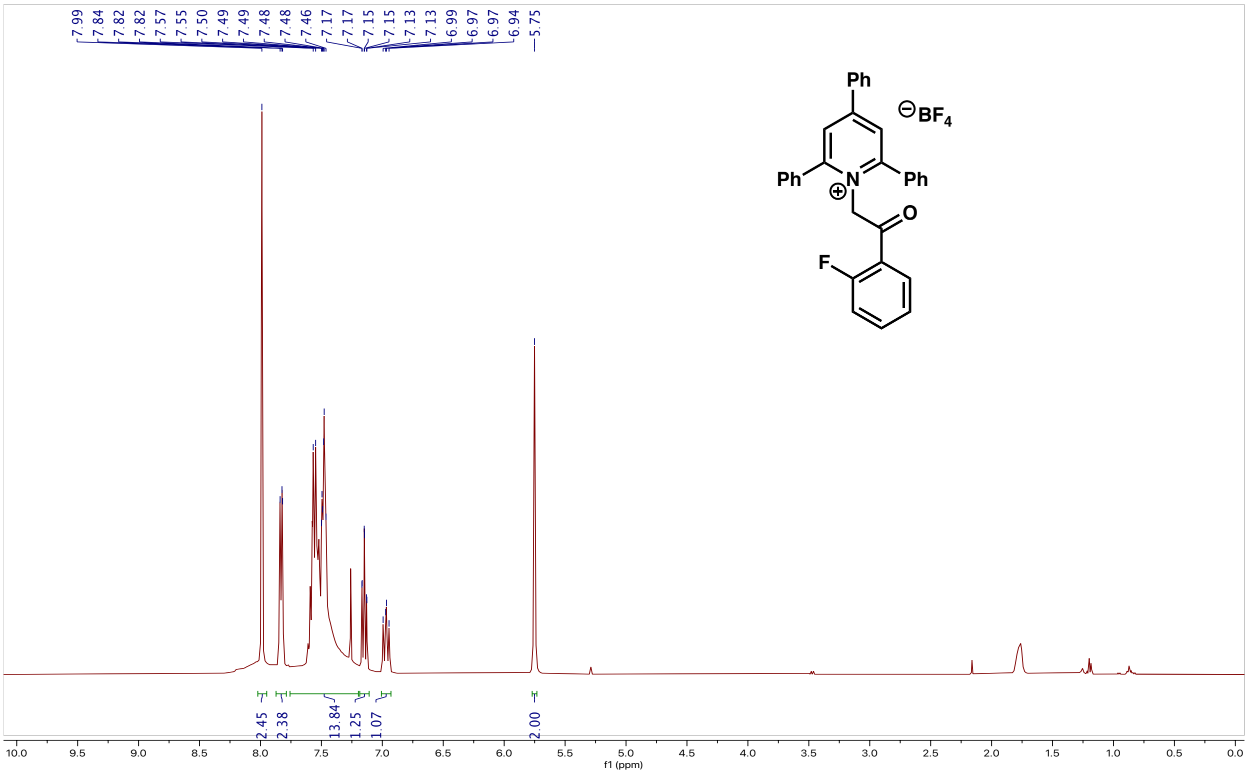


^{19}F NMR (565 MHz, DMSO)

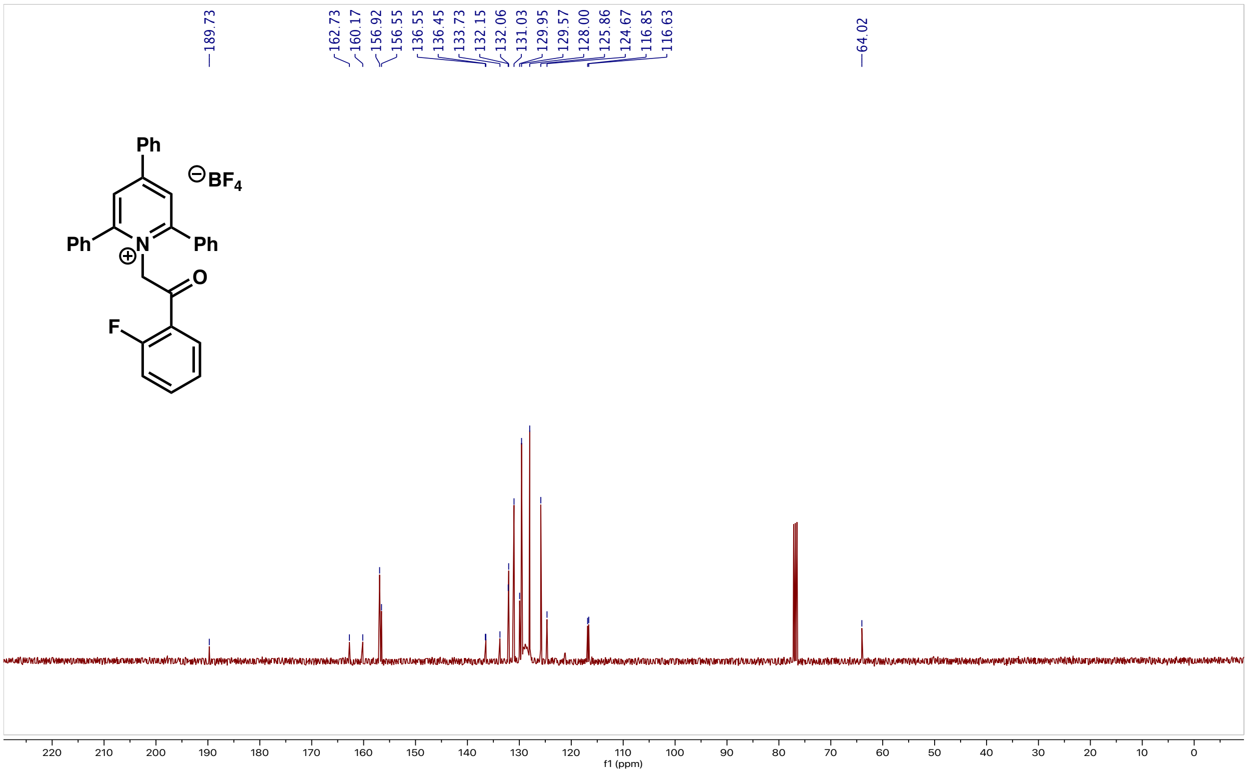


1-(2-(2-Fluorophenyl)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium, 14f :

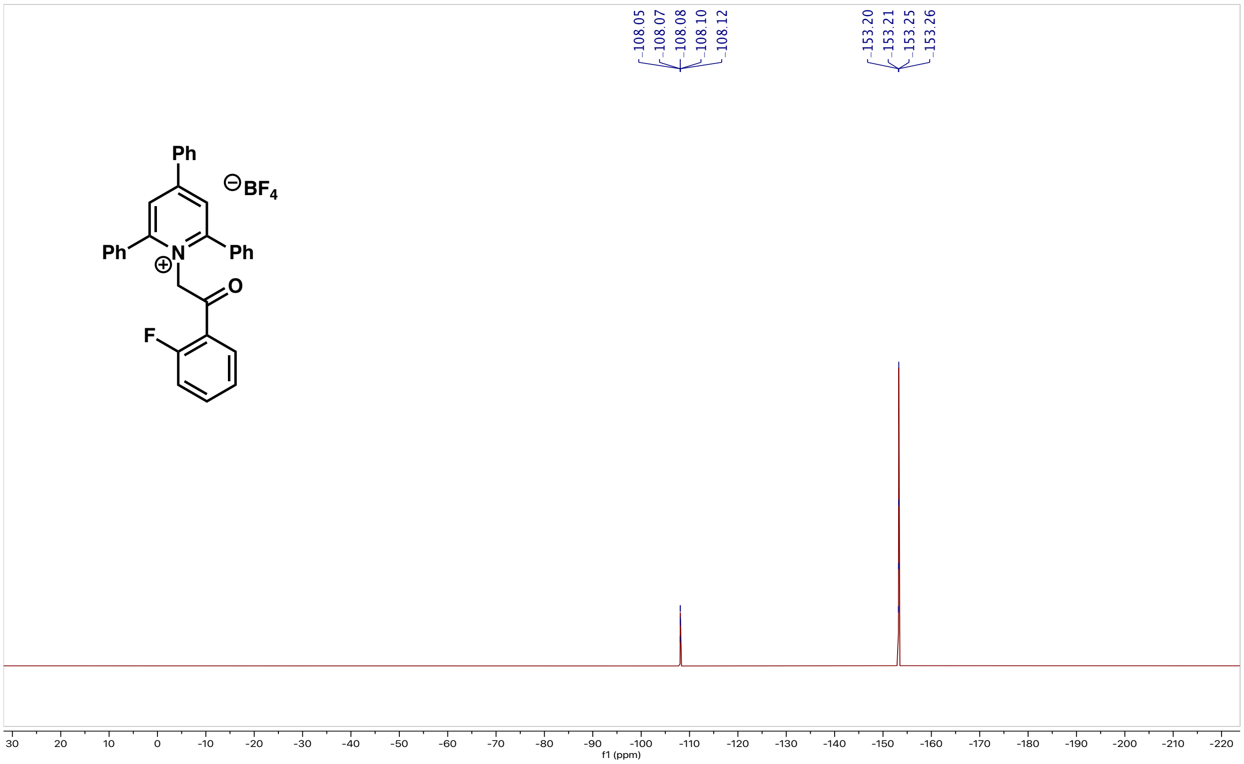
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

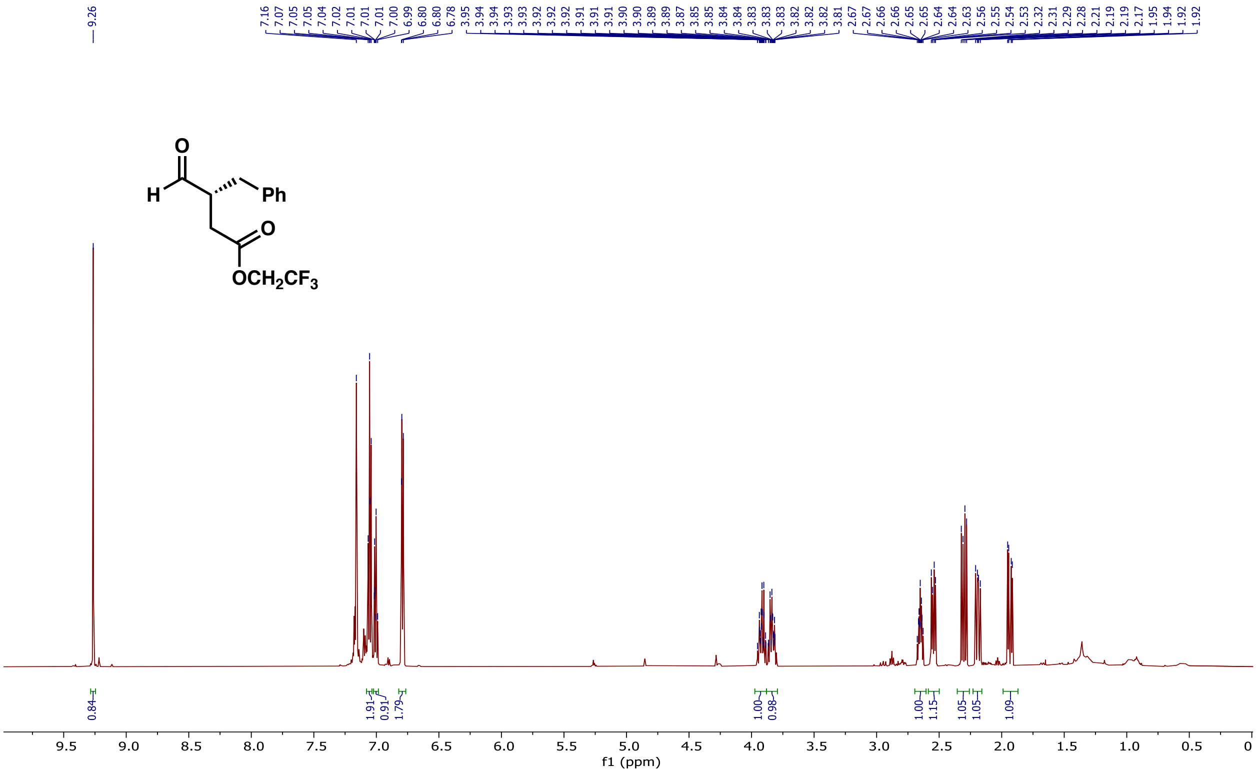


^{19}F NMR (565 MHz, CDCl$_3$)

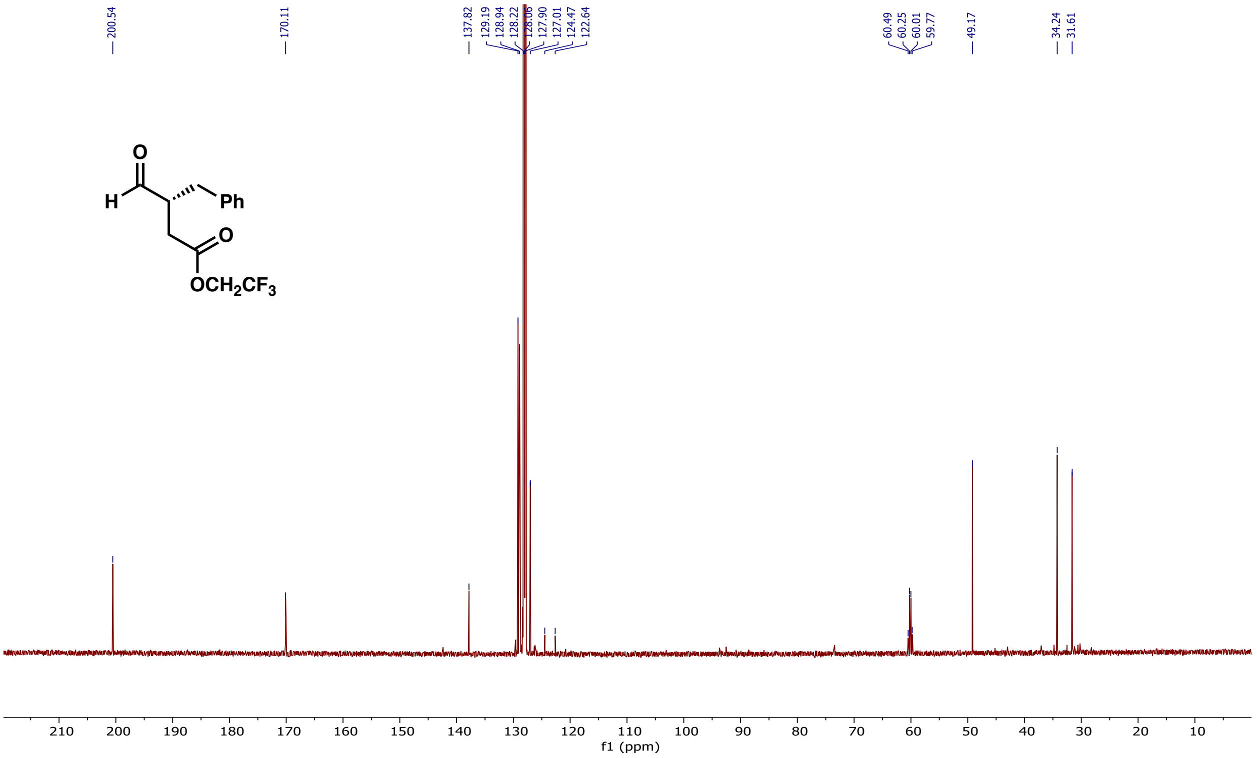


2,2,2-Trifluoroethyl (*R*)-3-benzyl-4-oxobutanoate, 13a:

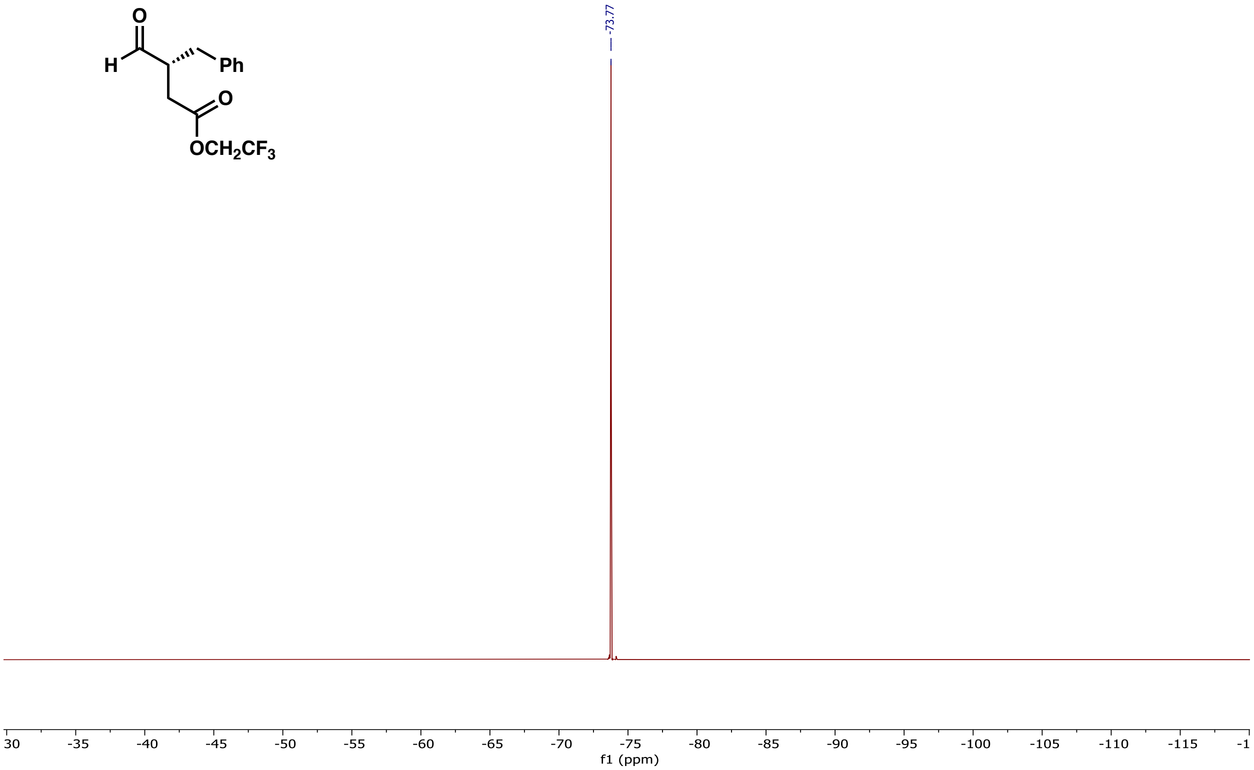
^{1}H NMR (500 MHz, C_6D_6)



^{13}C NMR (151 MHz, C_6D_6)

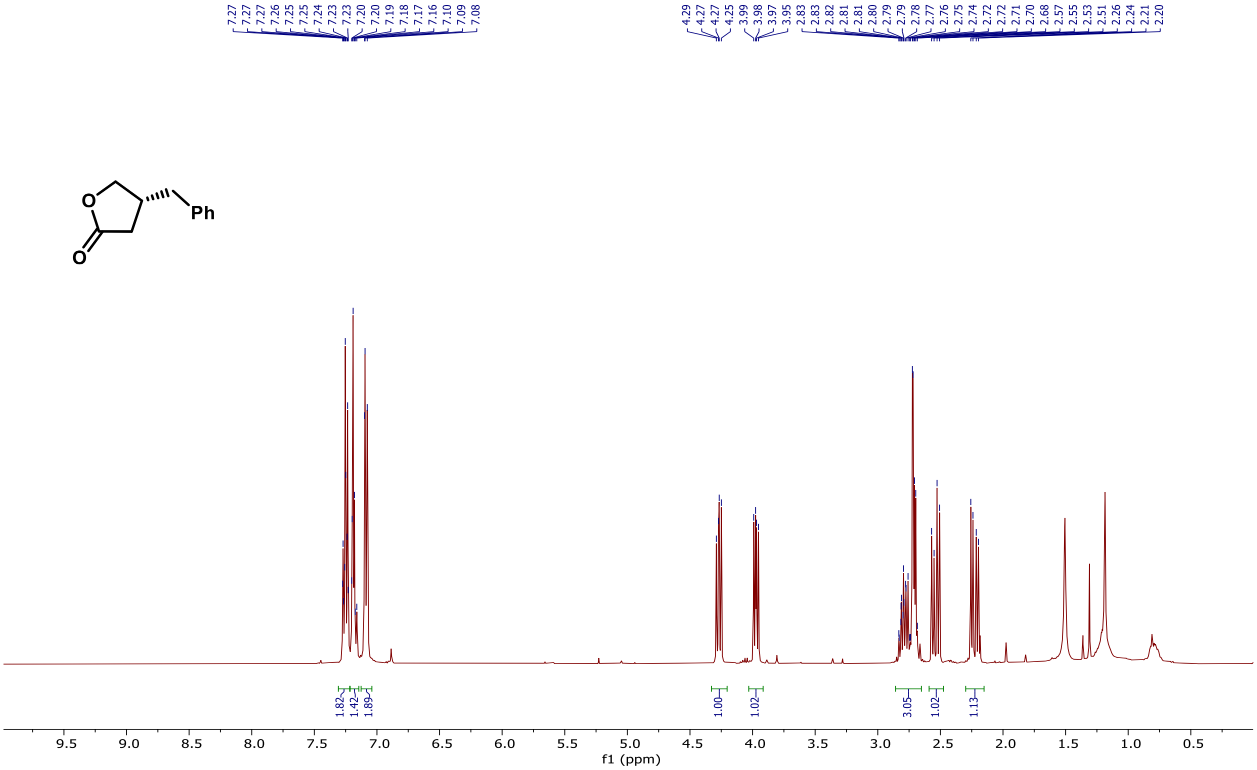


^{19}F NMR (565 MHz, C_6D_6)

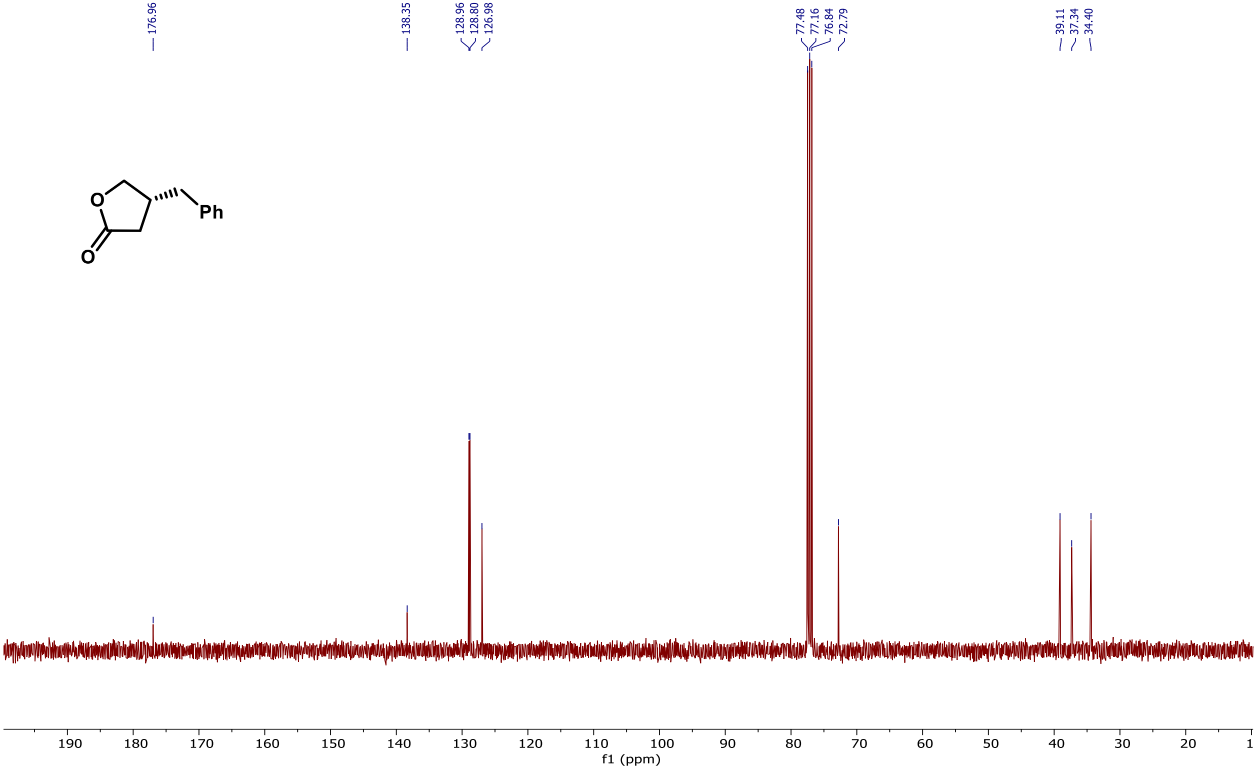


(*R*)-4-Benzyldihydrofuran-2(3*H*)-one, 13aa:

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

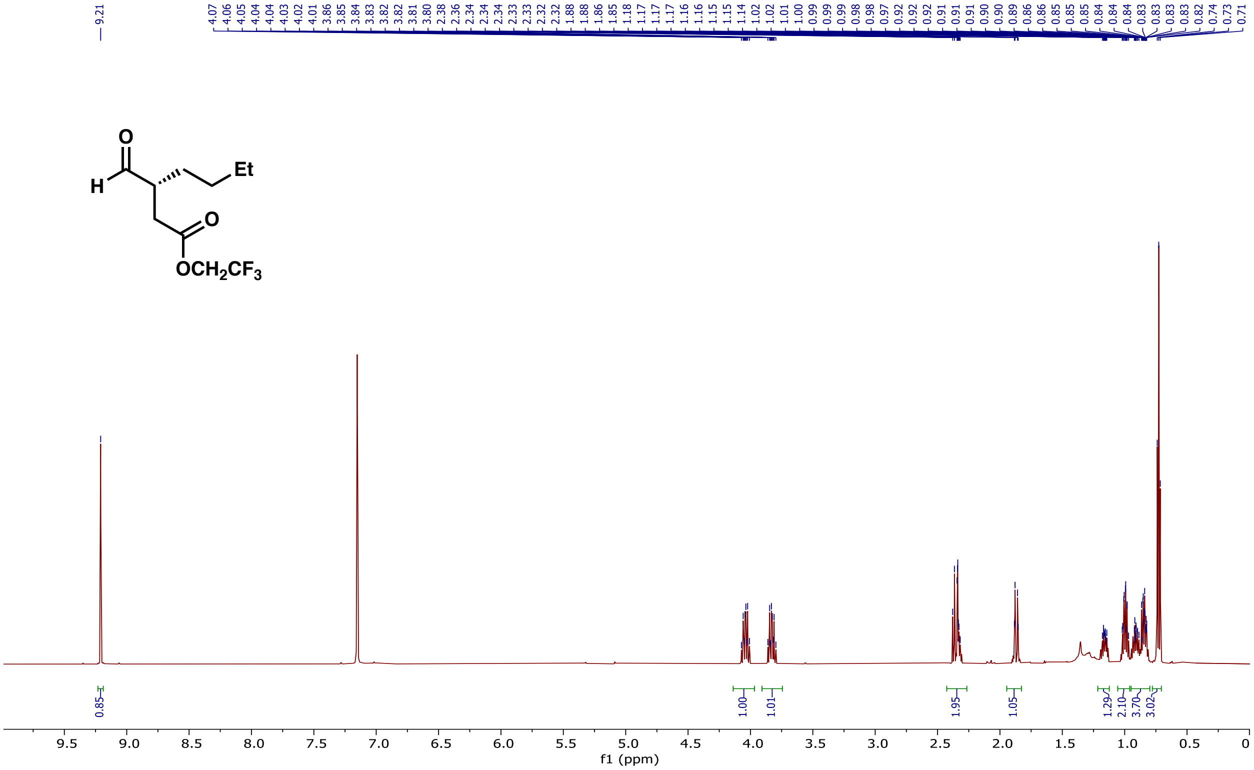


^{13}C NMR (101 MHz, CDCl$_3$)

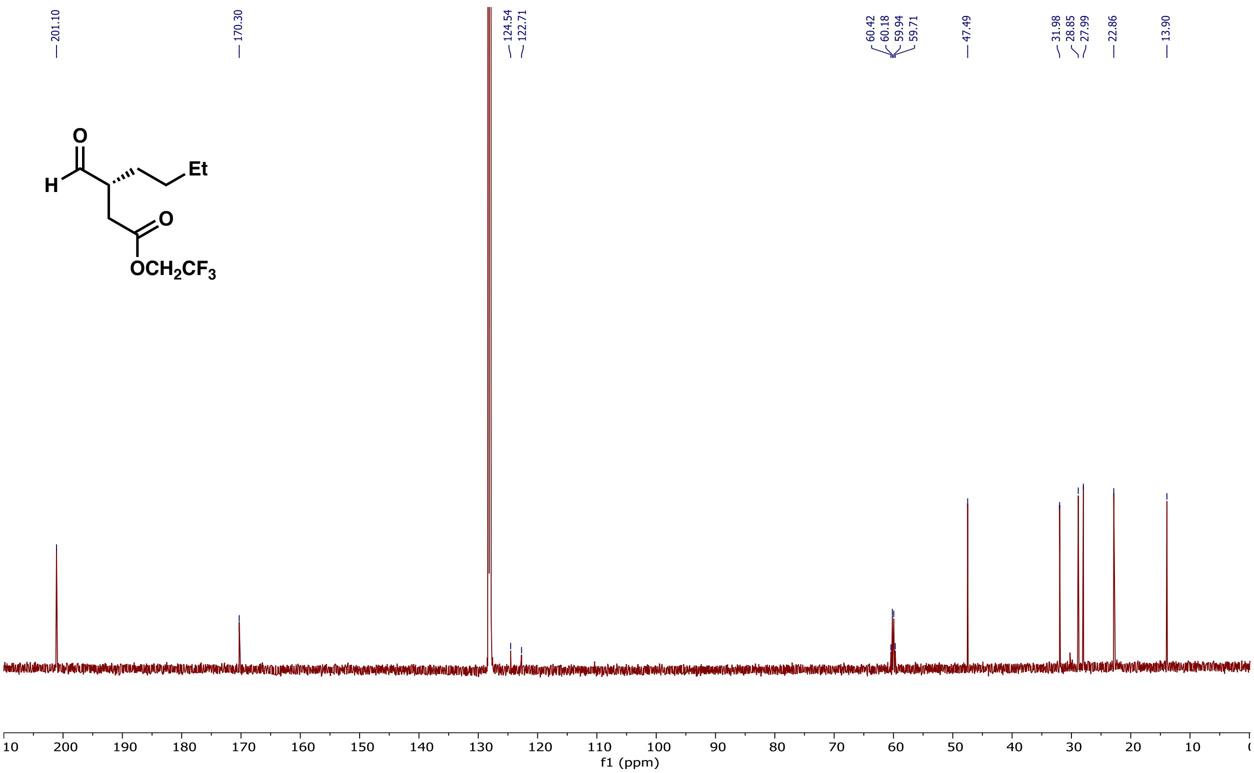


2,2,2-Trifluoroethyl (*R*)-3-formylheptanoate, 13b:

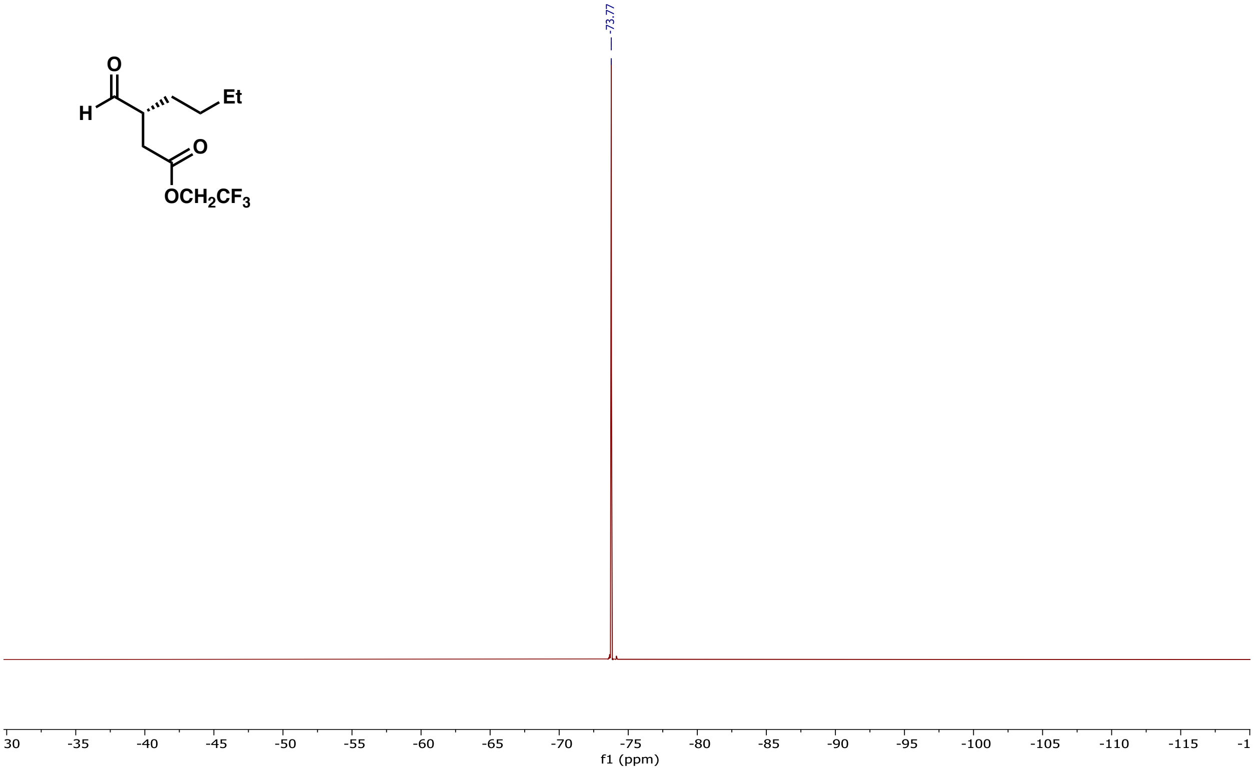
^{1}H NMR (600 MHz, C$_6$D$_6$)



^{13}C NMR (151 MHz, C_6D_6)

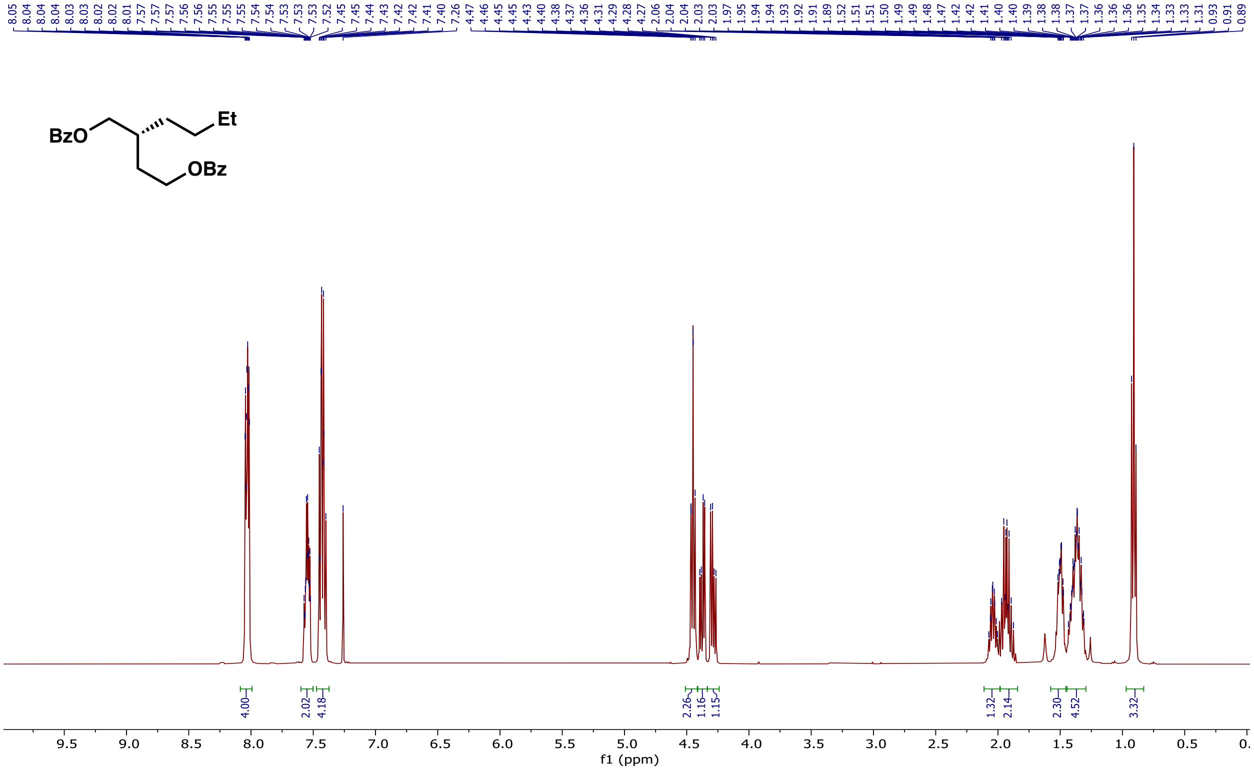


^{19}F NMR (600 MHz, C_6D_6)

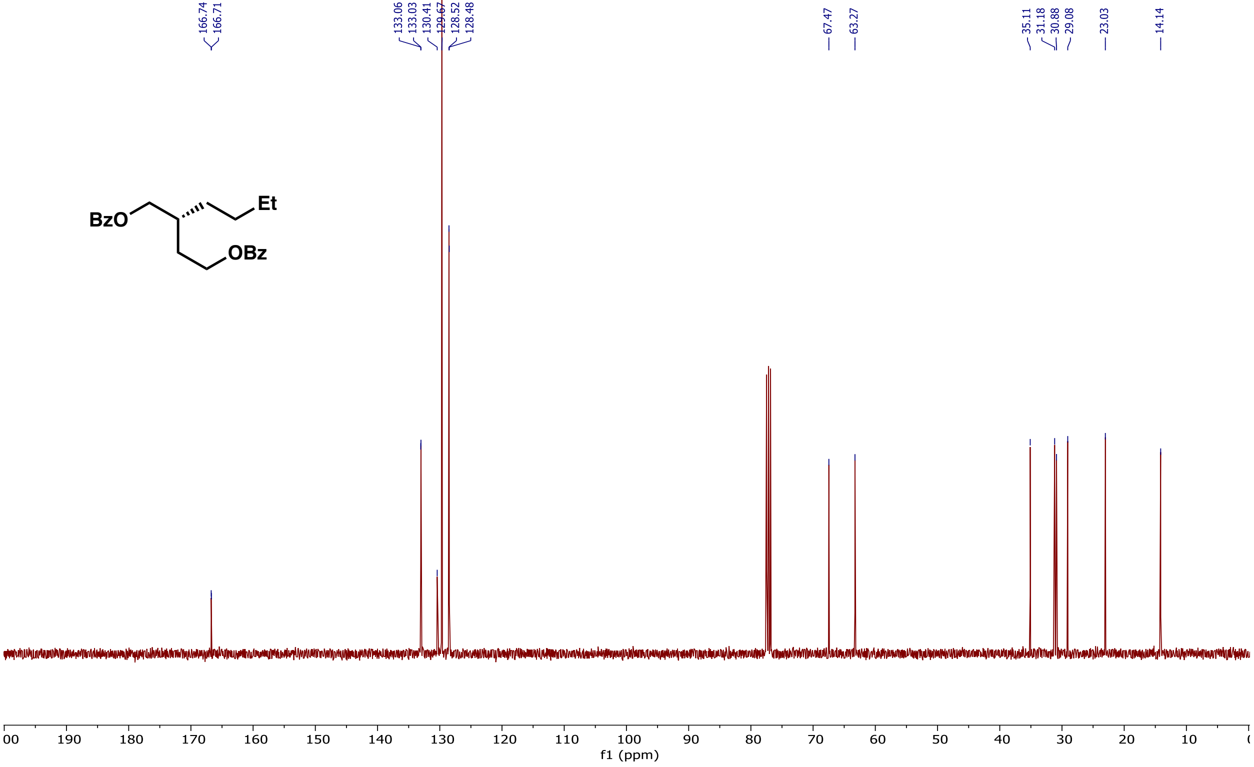


(*R*)-2-Butylbutane-1,4-diyl dibenzoate, 13ba:

^{1}H NMR (400 MHz, CDCl$_3$)

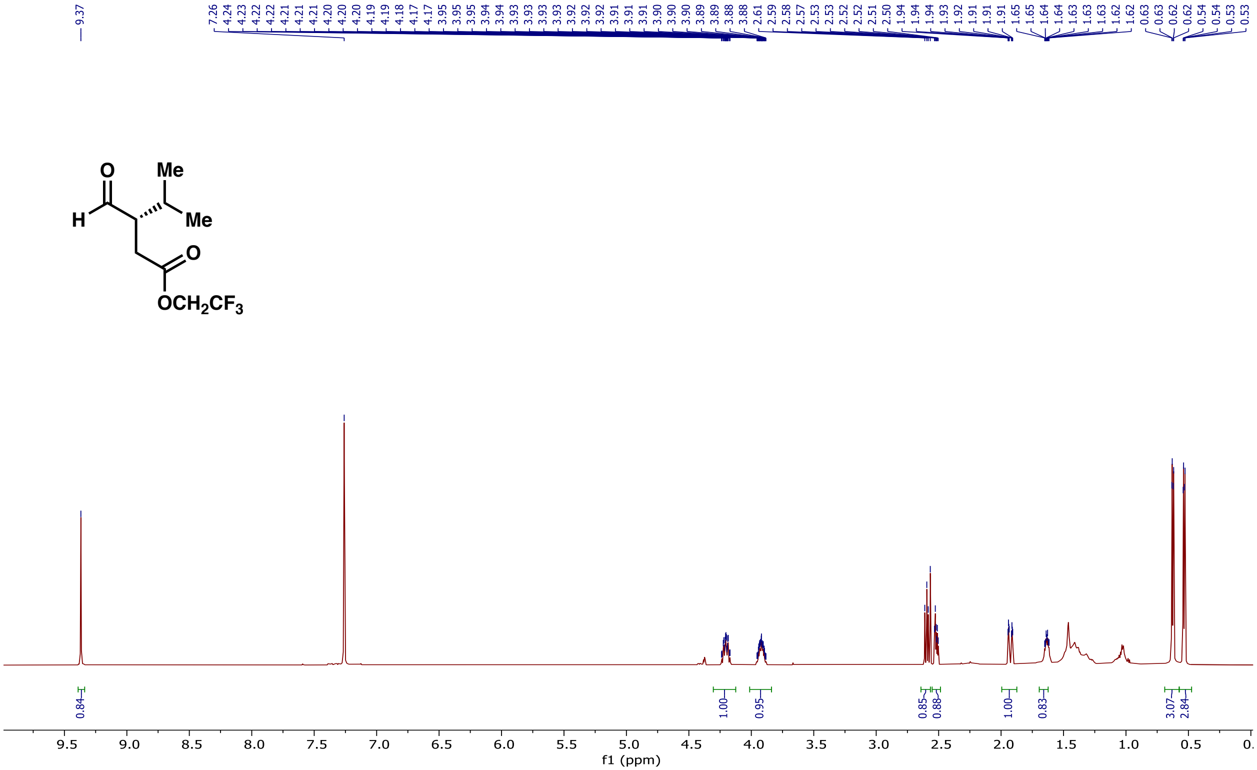


^{13}C NMR (101 MHz, CDCl$_3$)

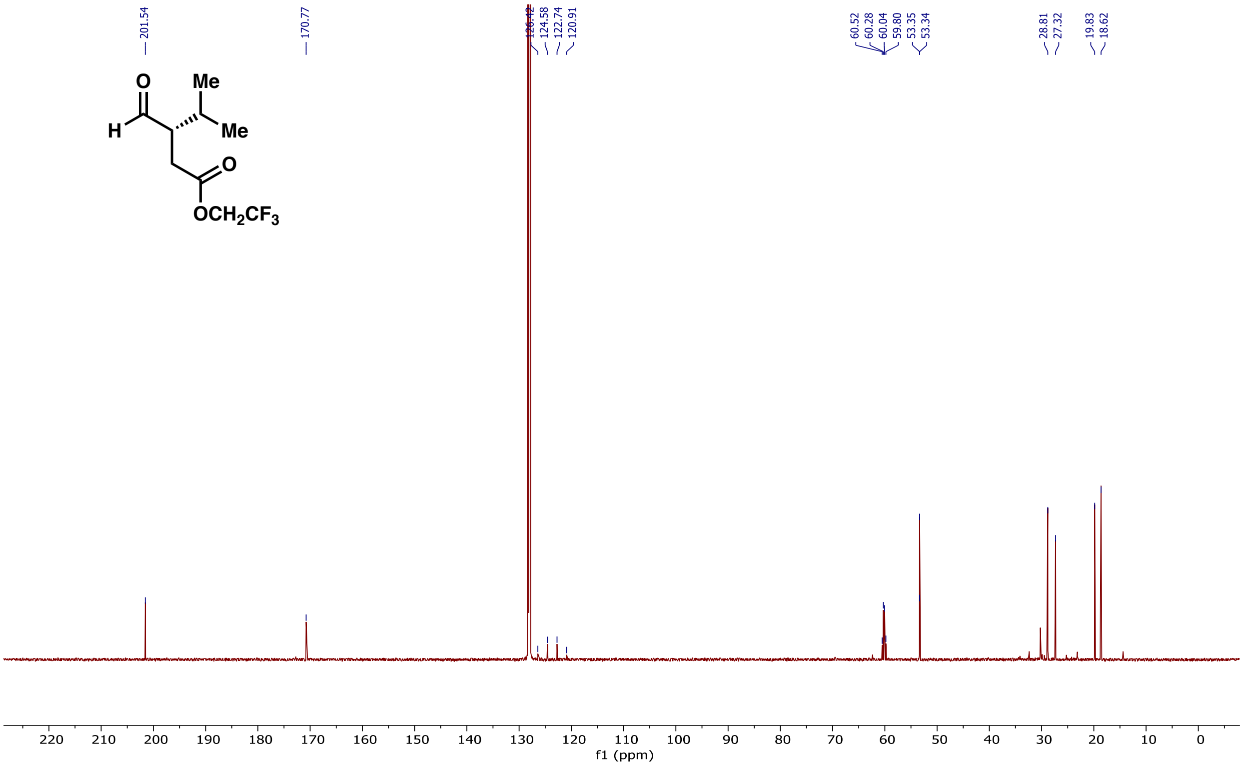


2,2,2-Trifluoroethyl (*S*)-3-formyl-4-methylpentanoate, 13c:

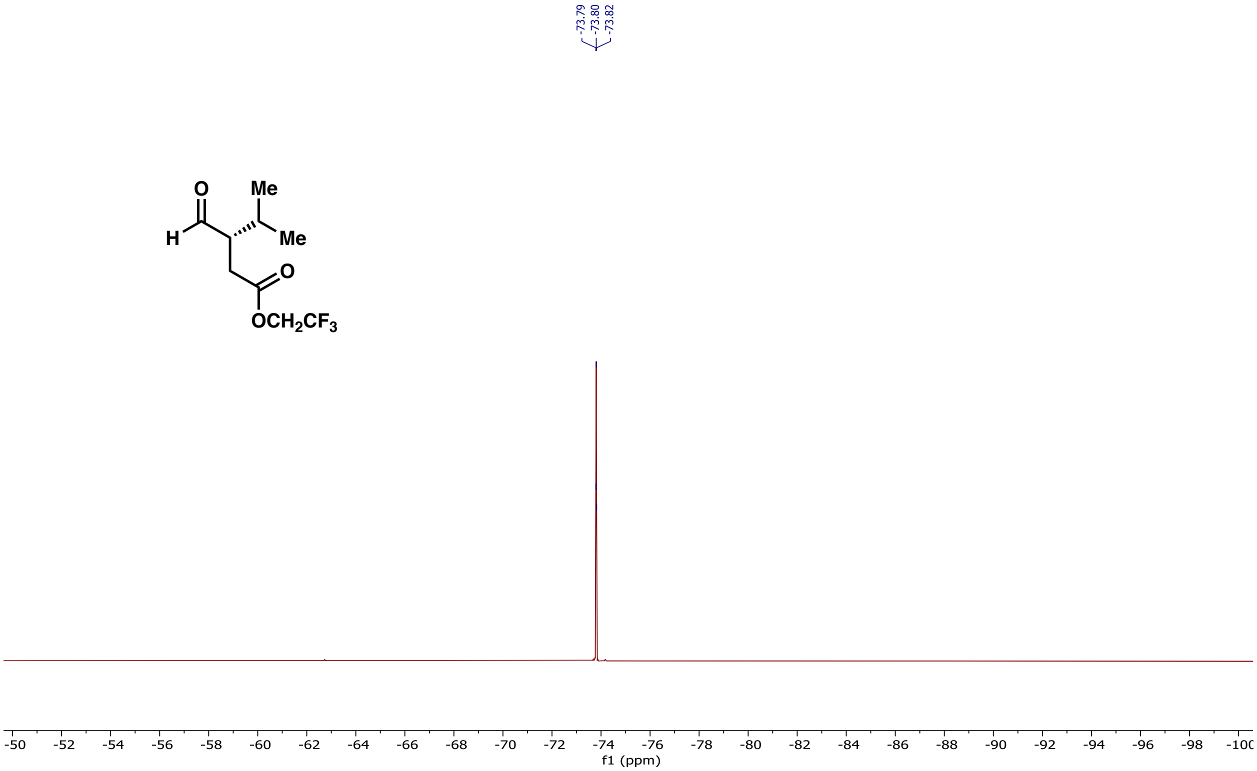
^{1}H NMR (600 MHz, C_6D_6)



^{13}C NMR (151 MHz, C_6D_6)

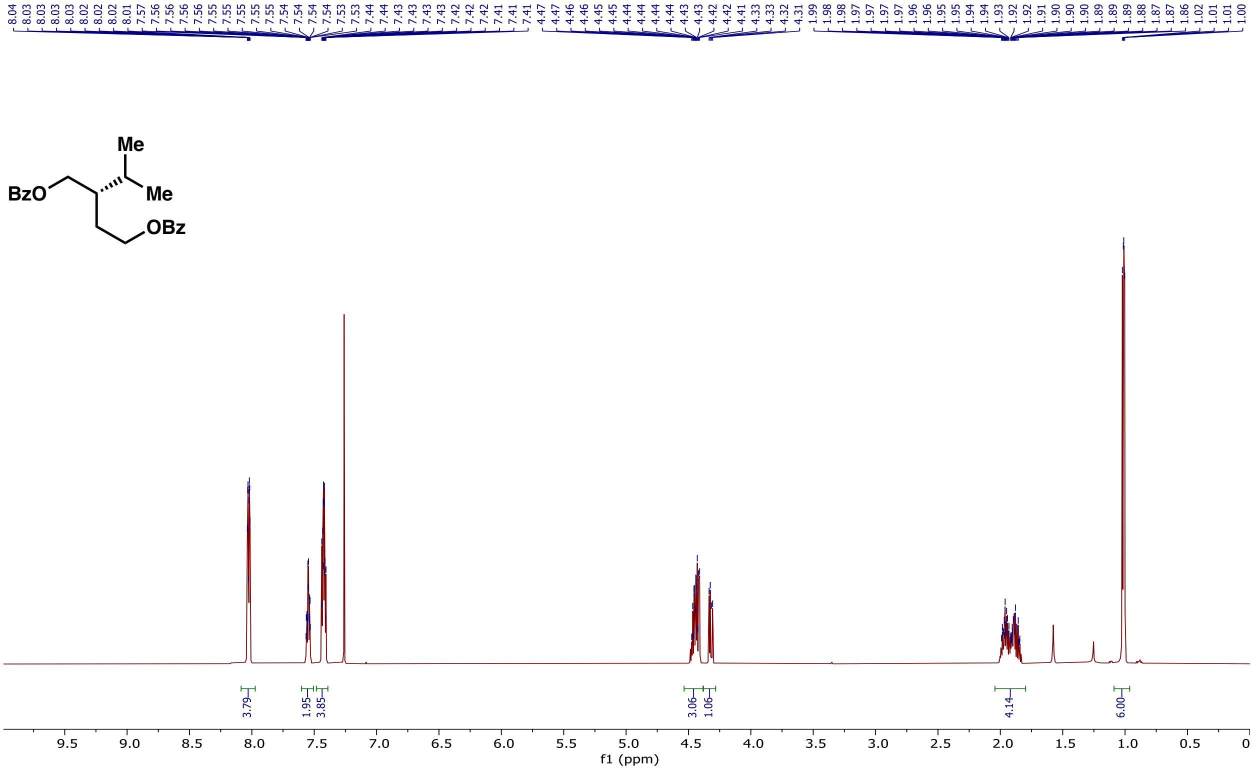


^{19}F NMR (600 MHz, C_6D_6)

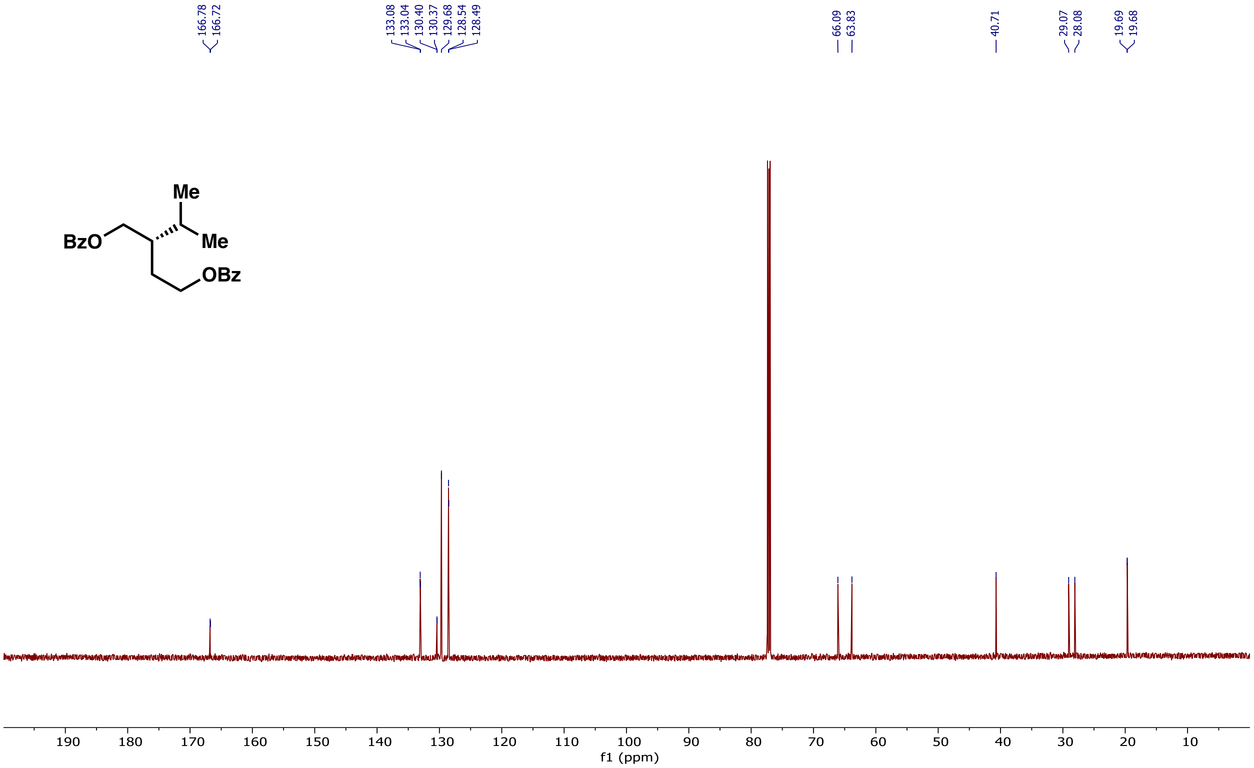


(*S*)-2-Isopropylbutane-1,4-diyl dibenzoate, 13ca:

^{1}H NMR (600 MHz, $CDCl_3$)

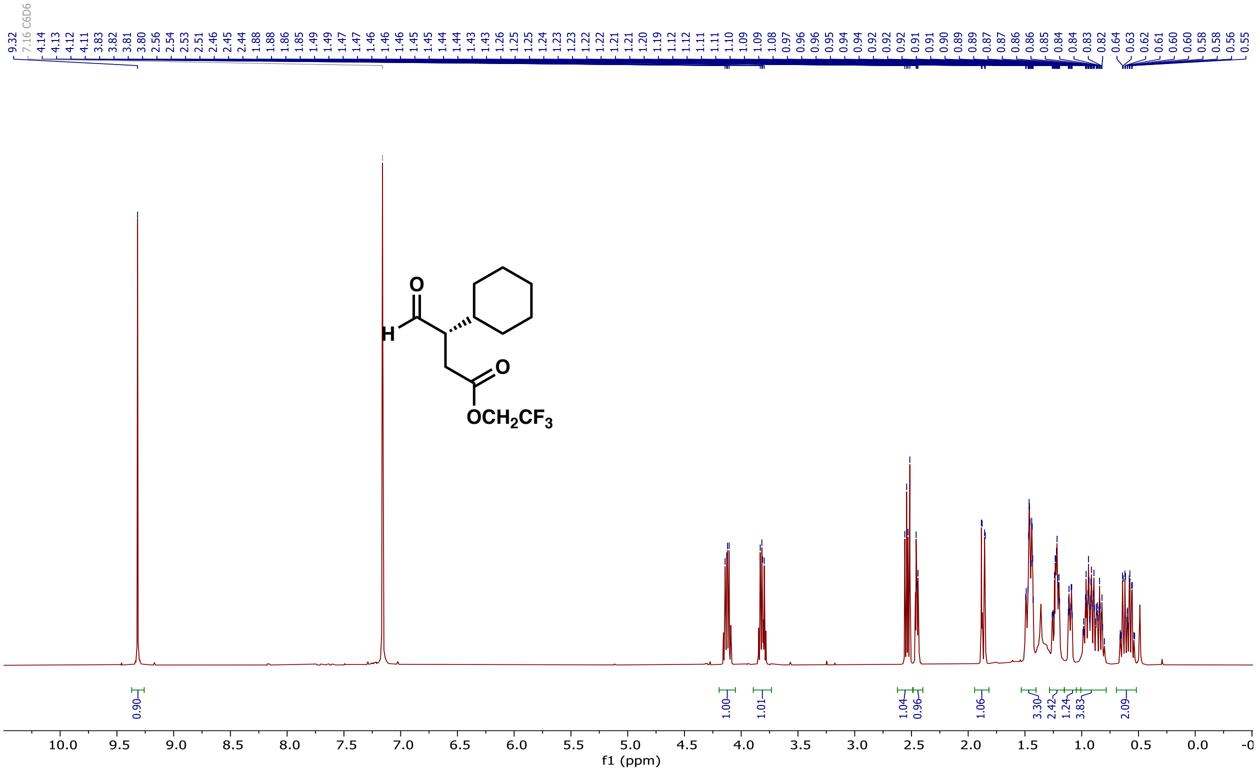


^{13}C NMR (151 MHz, CDCl$_3$)

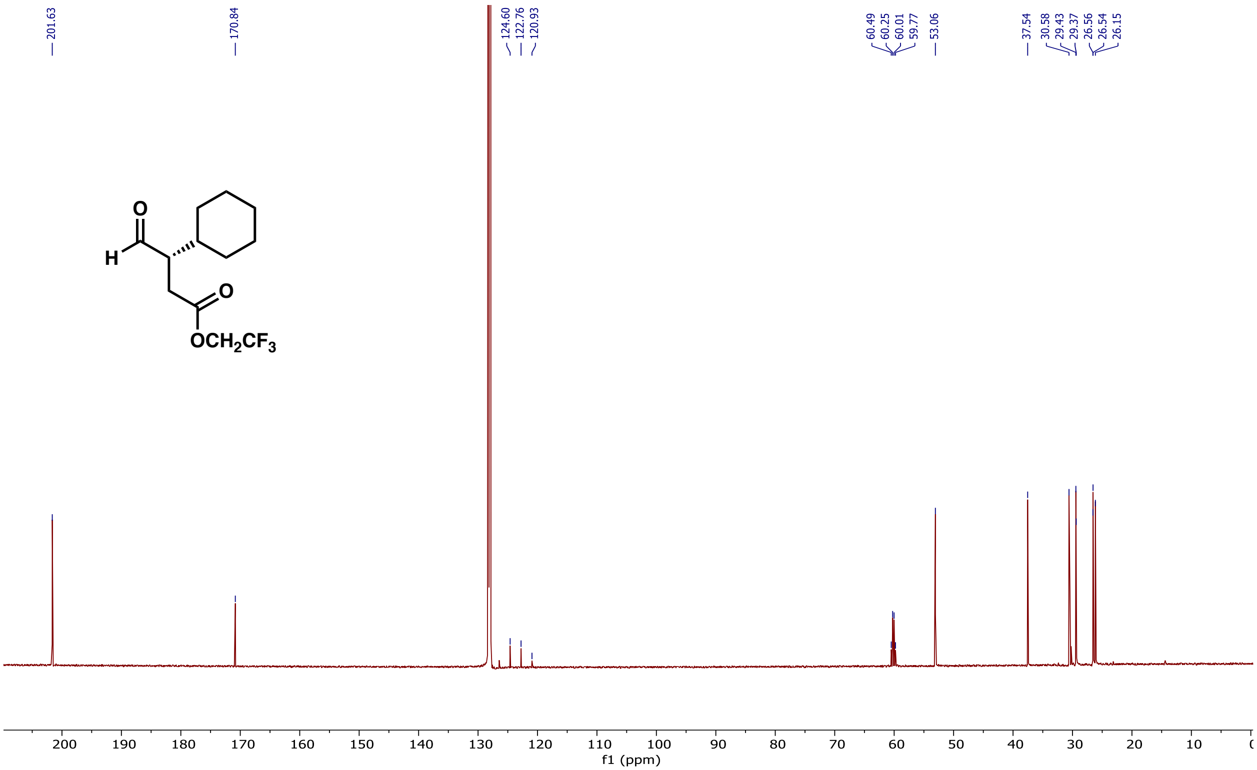


2,2,2-Trifluoroethyl (*S*)-3-cyclohexyl-4-oxobutanoate, 13d:

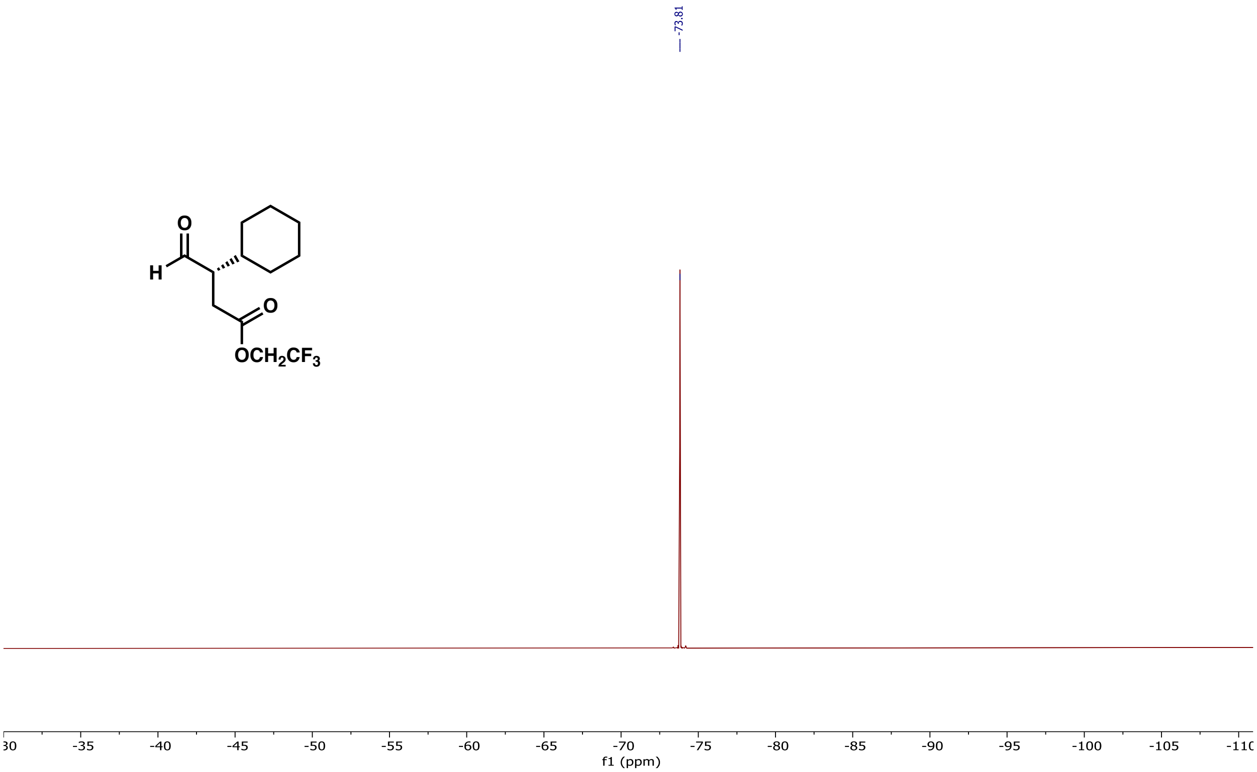
^{1}H NMR (600 MHz, C$_6$D$_6$)



^{13}C NMR (151 MHz, C_6D_6)

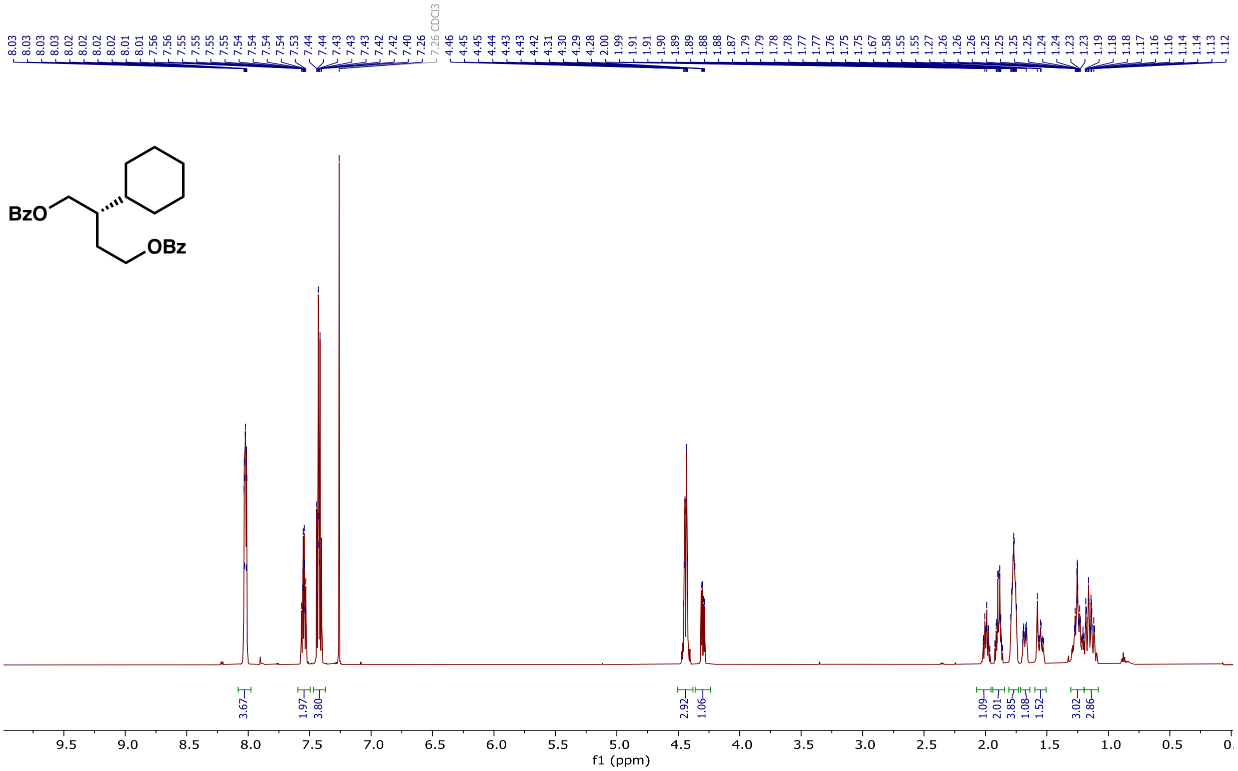


^{19}F NMR (565 MHz, C_6D_6)

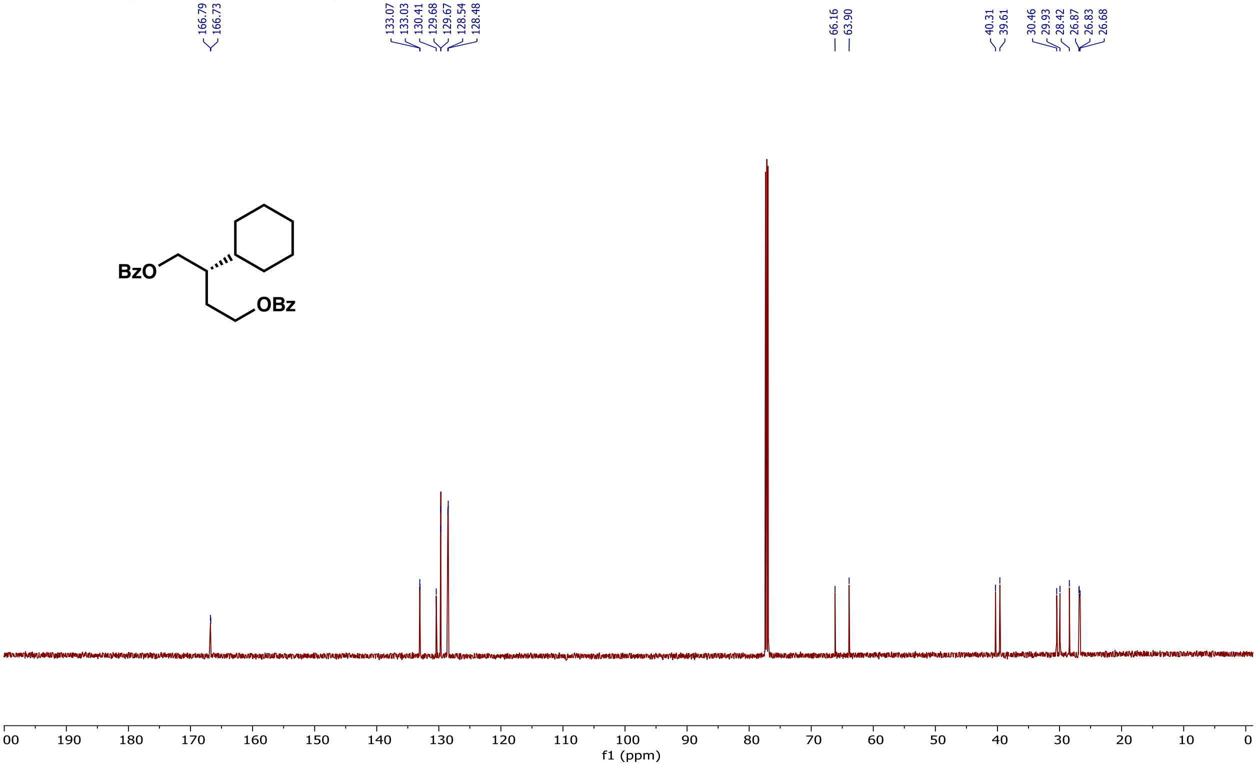


(*S*)-2-Cyclohexylbutane-1,4-diyl dibenzoate, 13da:

^{1}H NMR (600 MHz, CDCl$_3$)

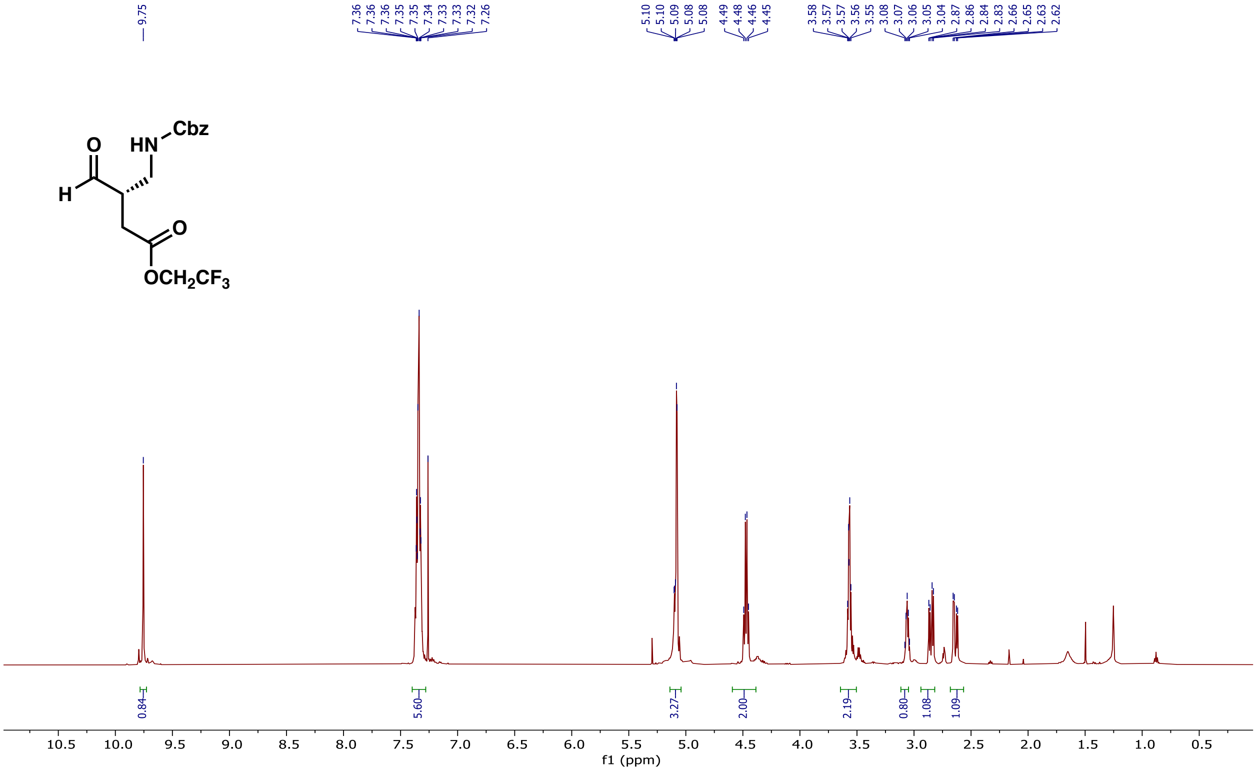


^{13}C NMR (151 MHz, CDCl$_3$)

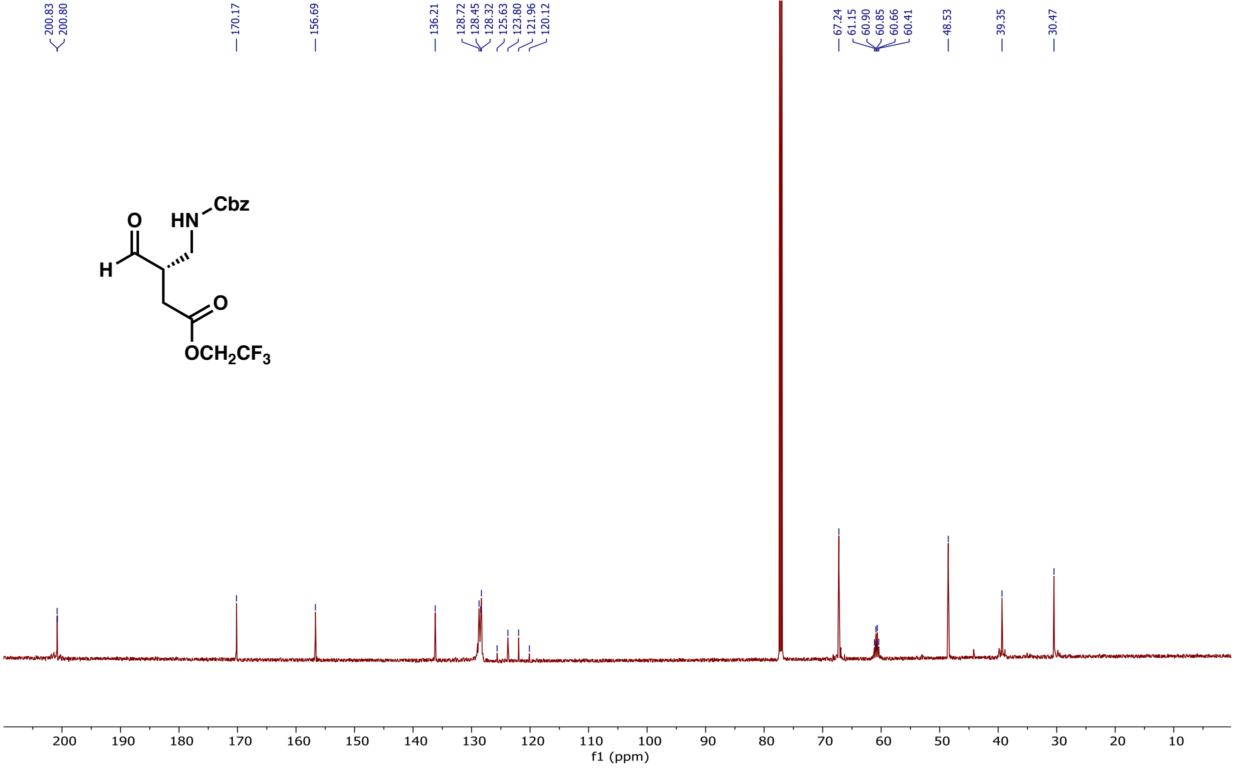


2,2,2-Trifluoroethyl (S)-4-(((benzyloxy)carbonyl)amino)-3-formylbutanoate, 13f:

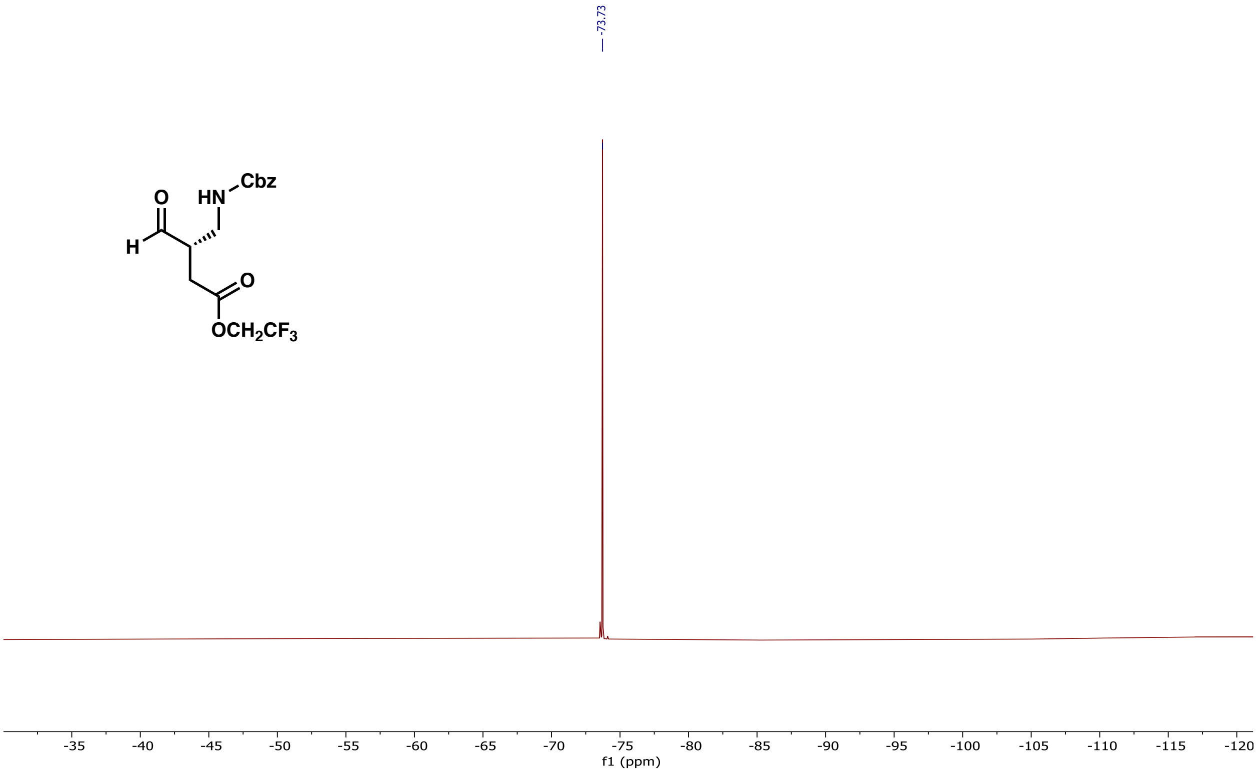
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

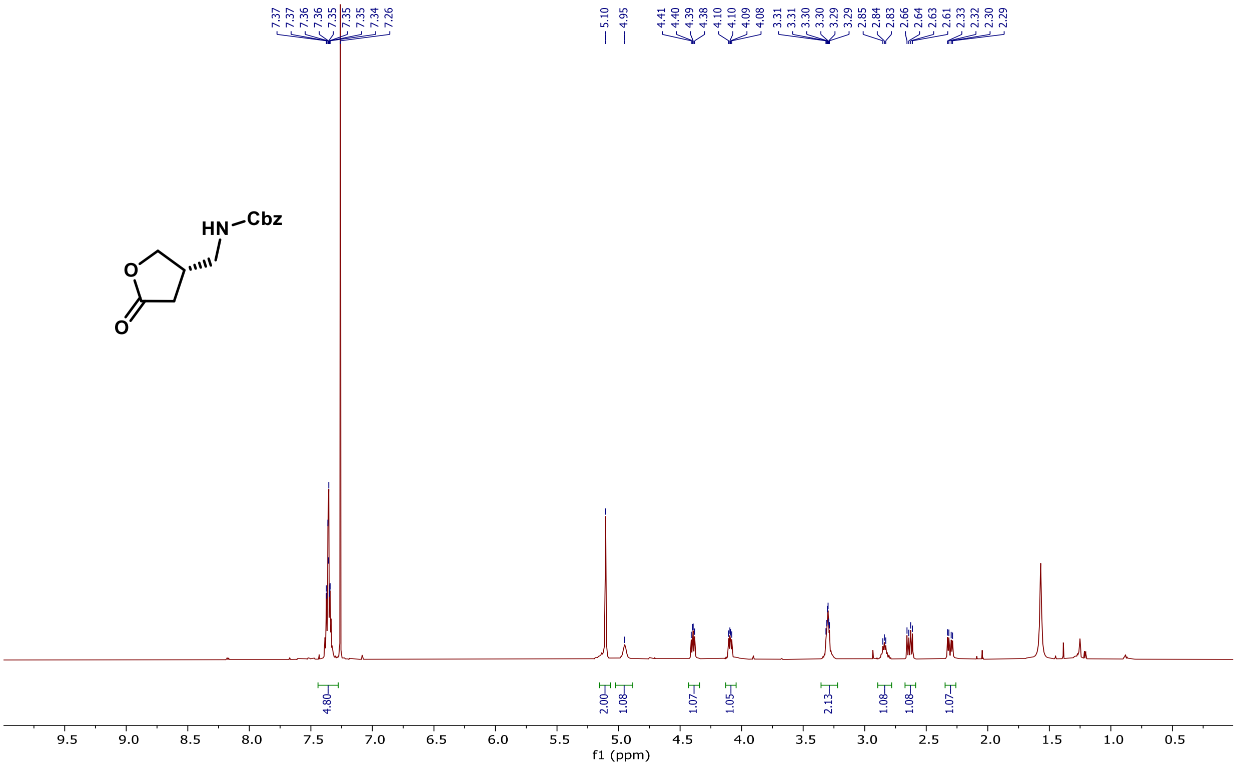


^{19}F NMR (565 MHz, CDCl$_3$)

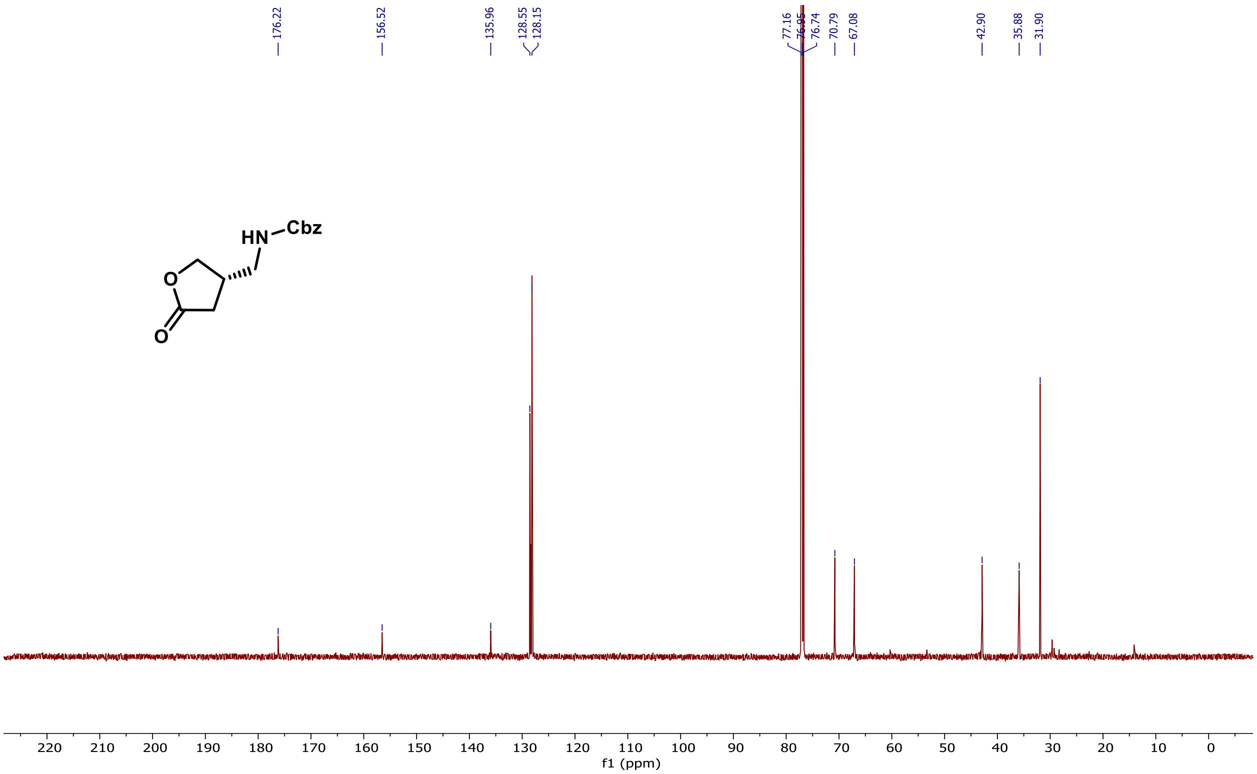


Benzyl (*S*)-((5-oxotetrahydrofuran-3-yl)methyl)carbamate, 13fa:

^{1}H NMR (600 MHz, CDCl$_3$)

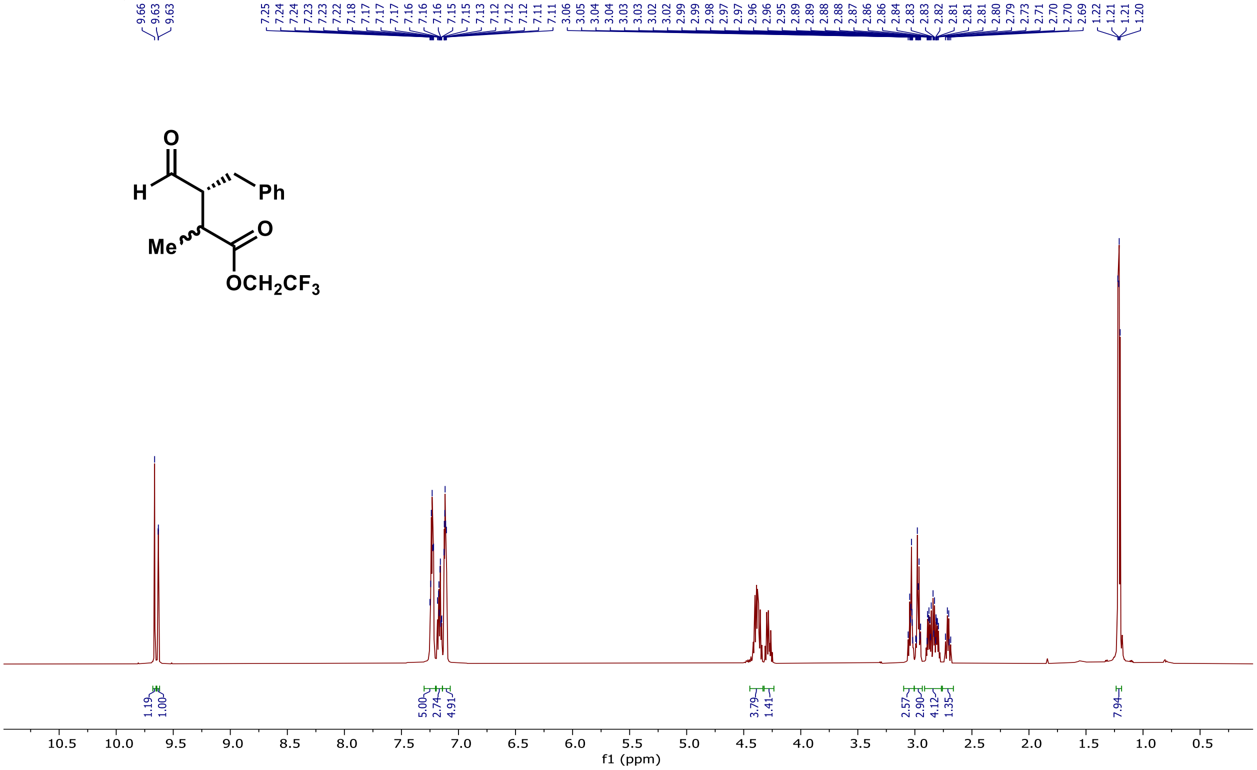


^{13}C NMR (151 MHz, CDCl$_3$)

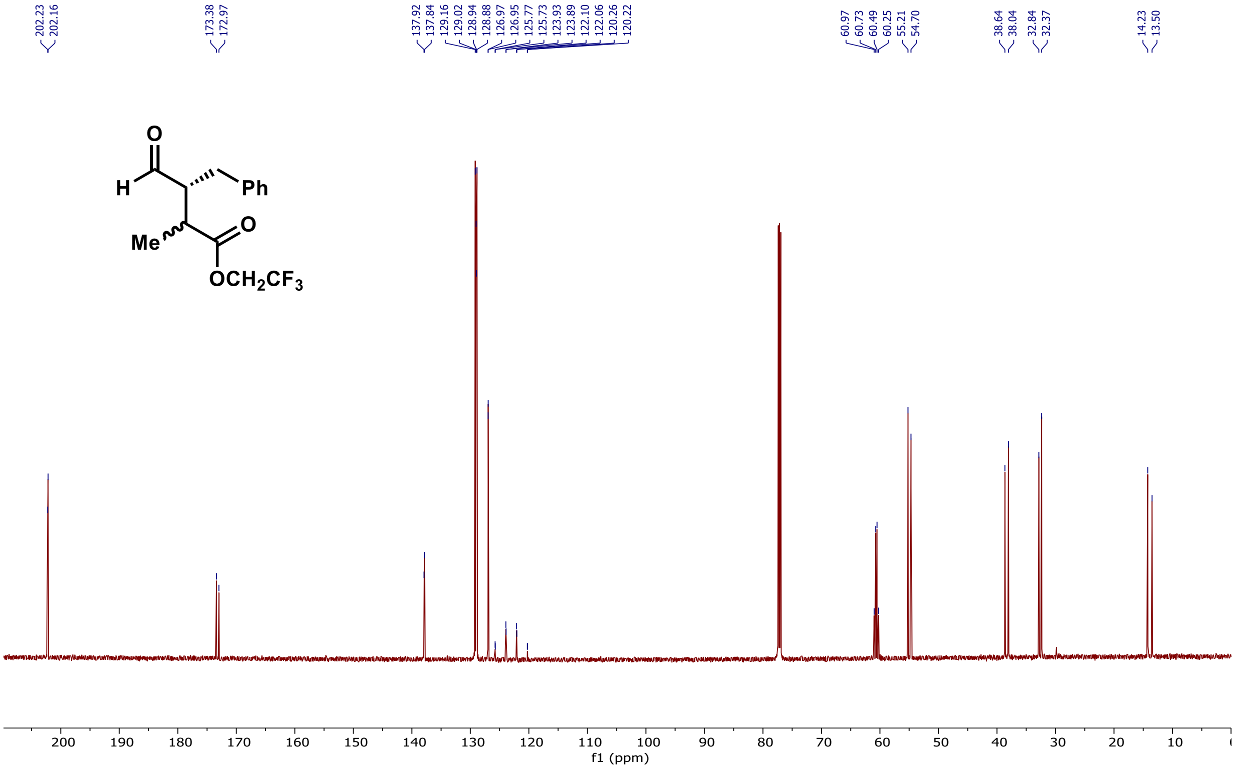


2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-methyl-4-oxobutanoate, 13g:

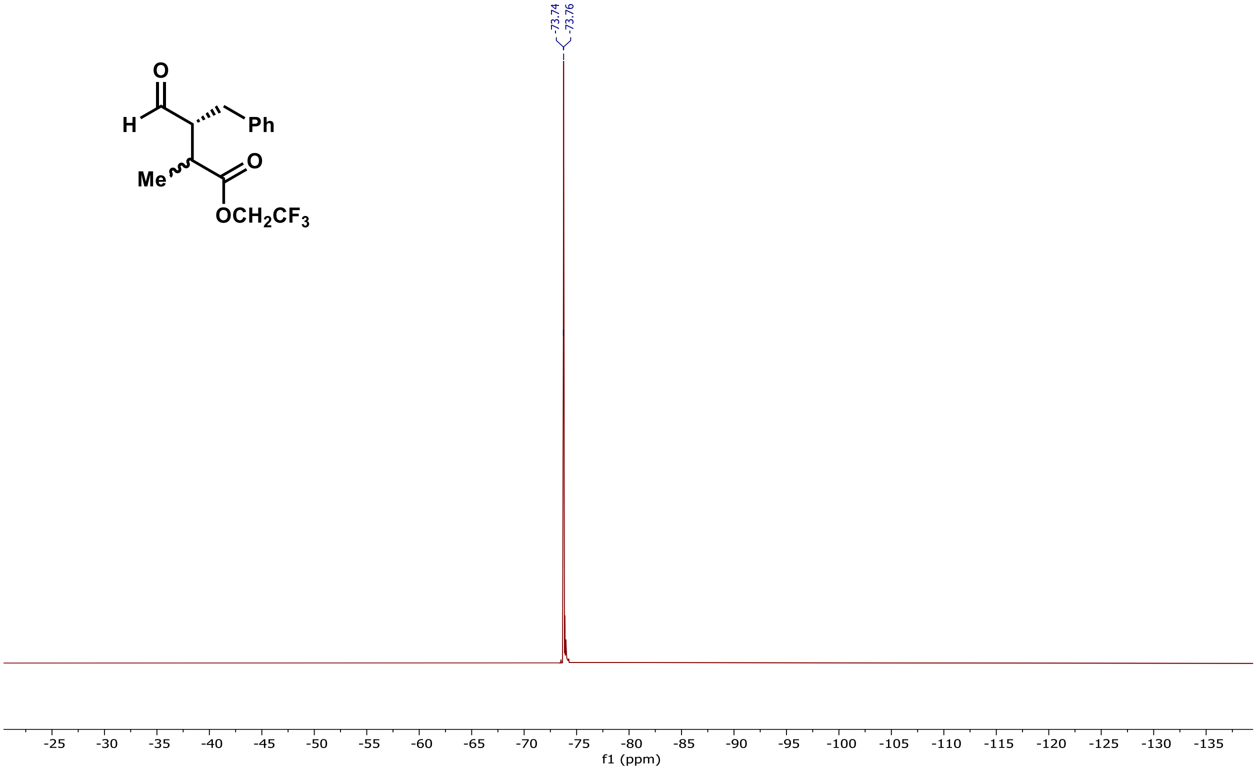
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

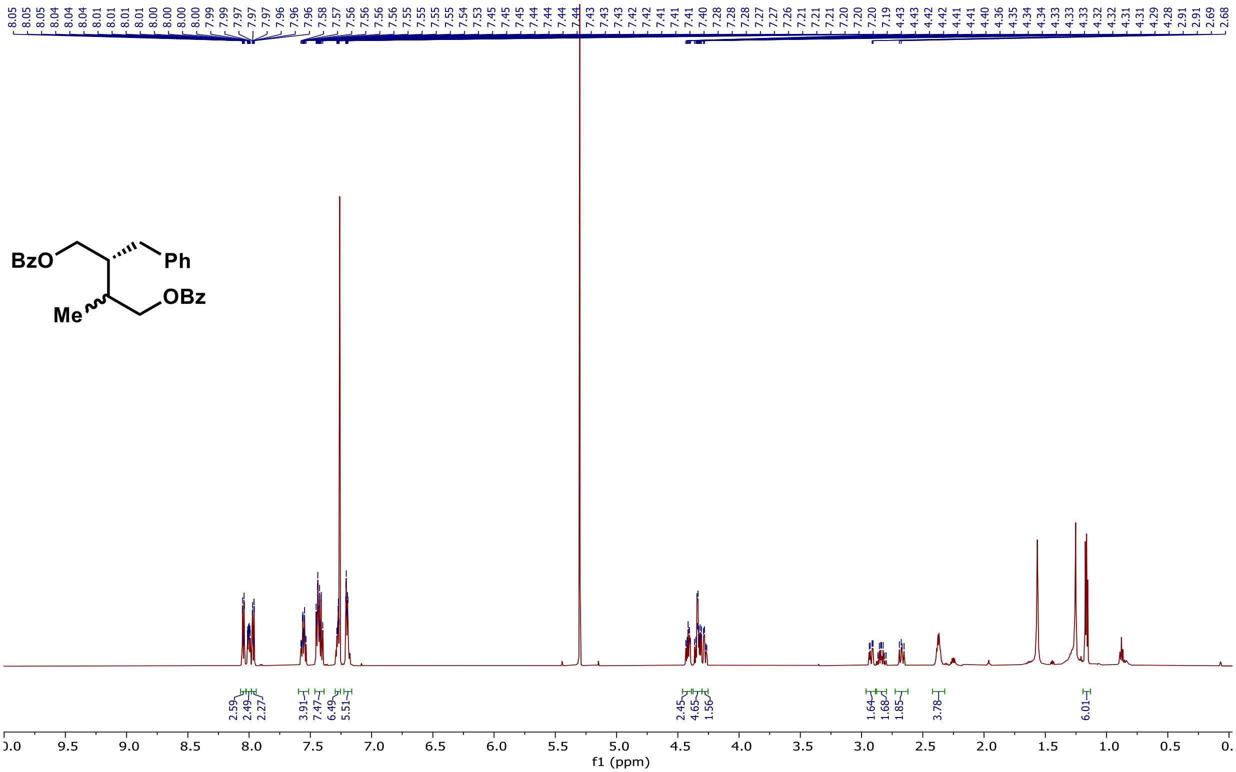


^{19}F NMR (565 MHz, CDCl$_3$)

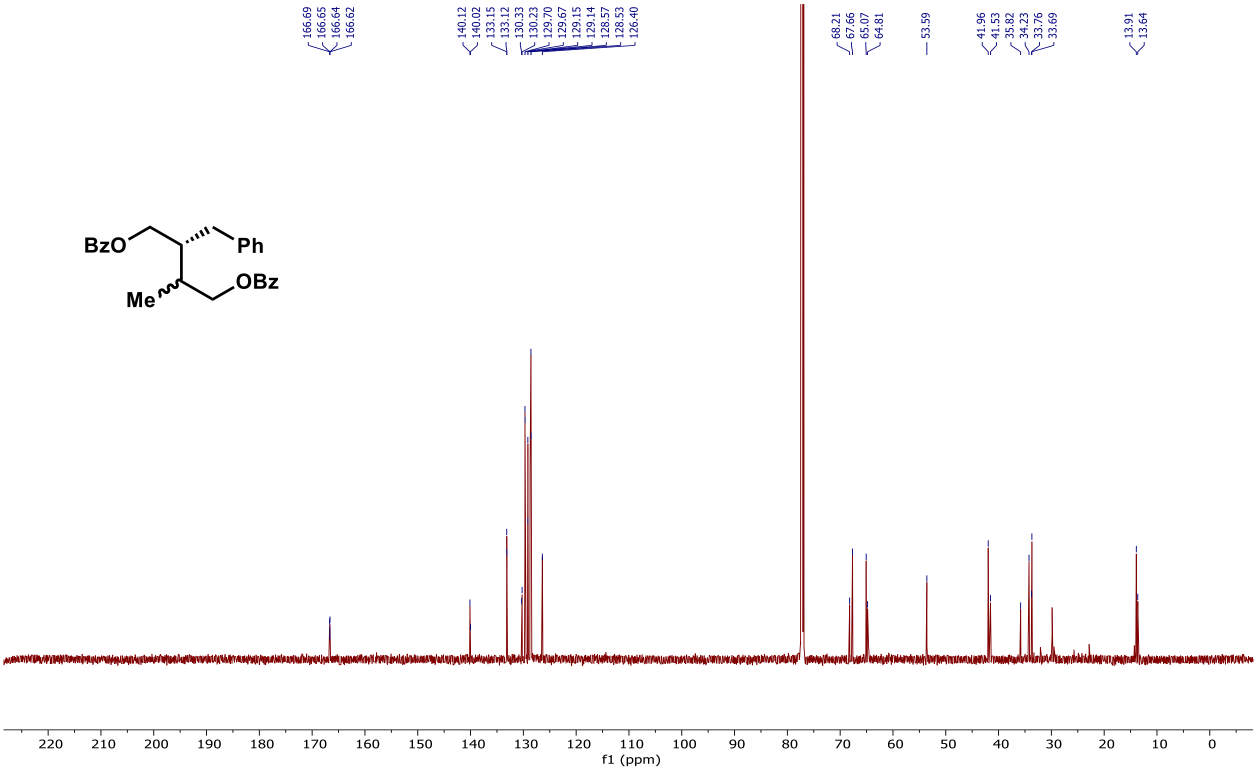


(2*R*)-2-Benzyl-3-methylbutane-1,4-diyl dibenzoate, 13ga:

^{1}H NMR (600 MHz, CDCl$_3$)

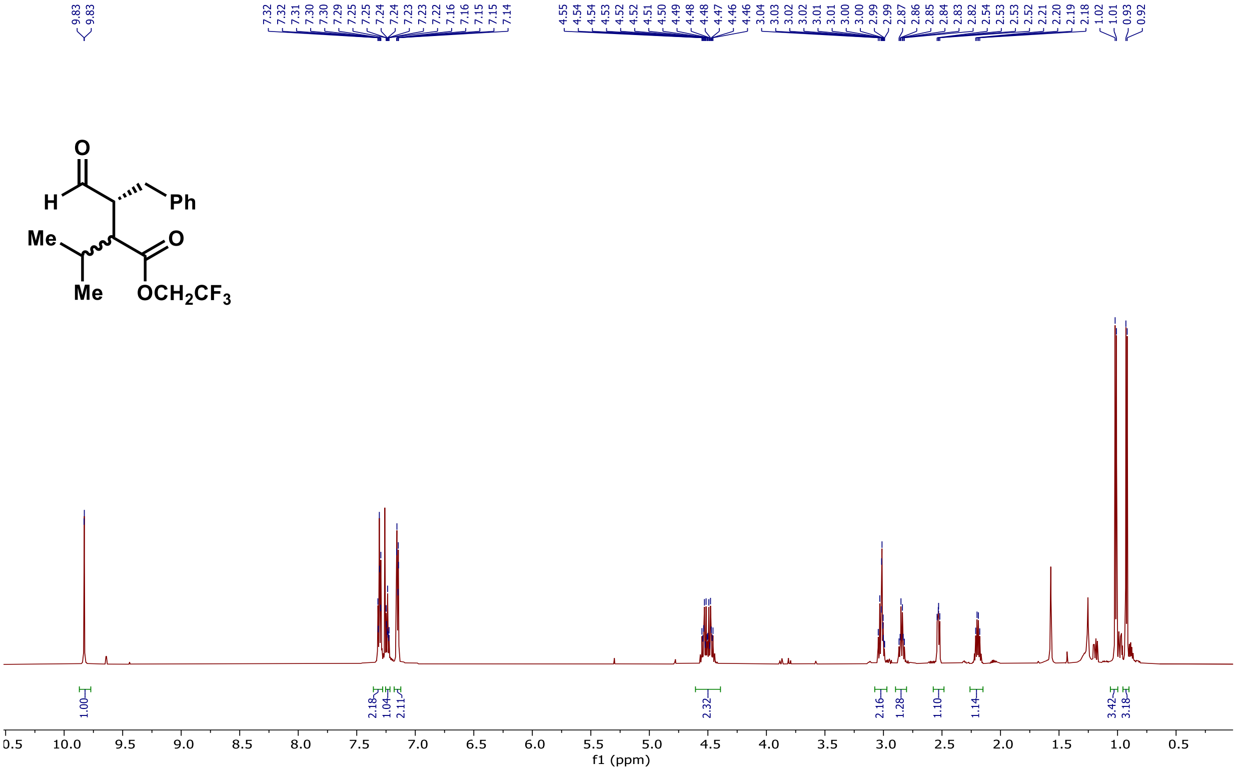


^{13}C NMR (151 MHz, CDCl$_3$)

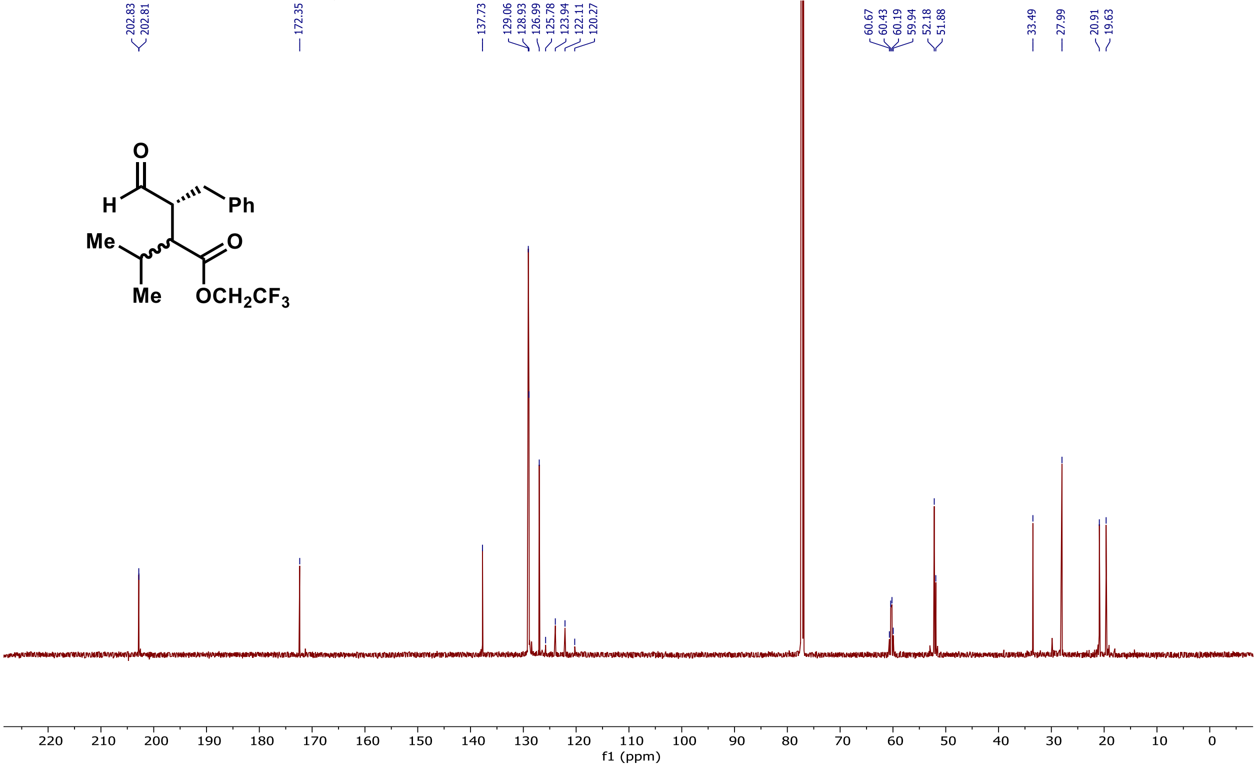


2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-isopropyl-4-oxobutanoate, 13h:

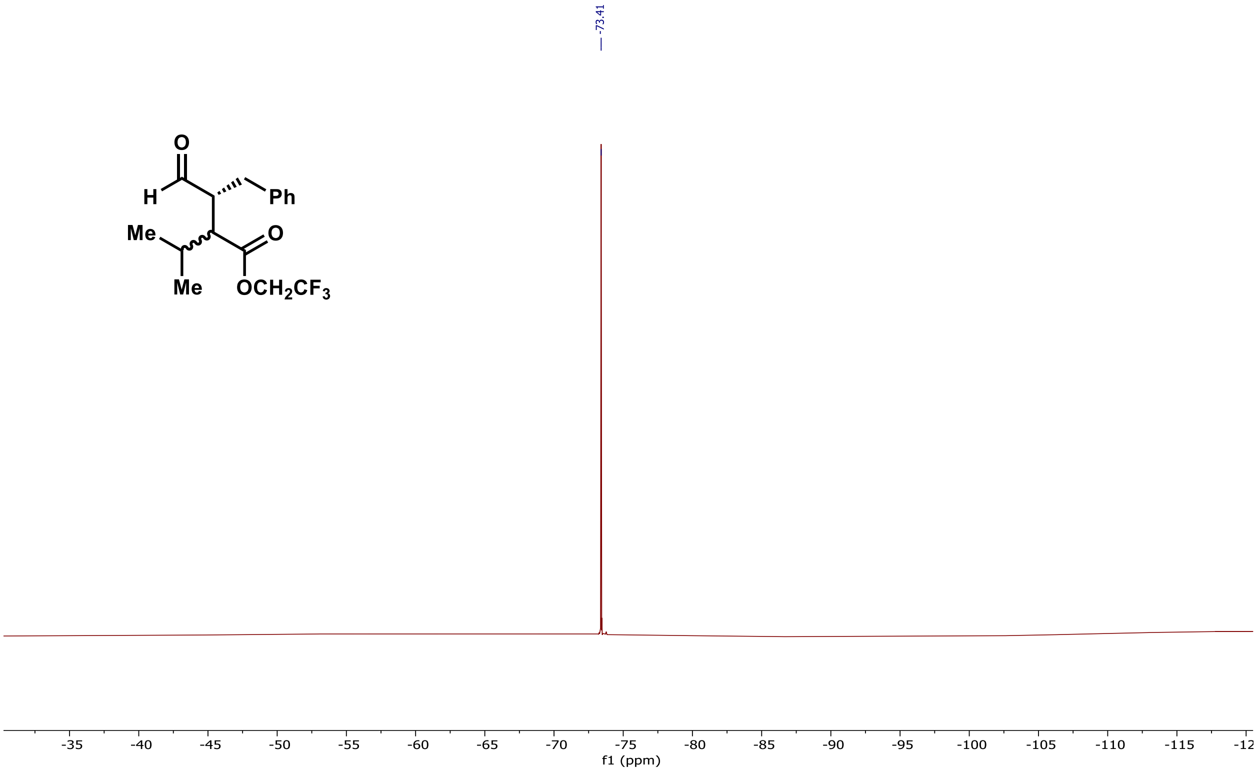
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

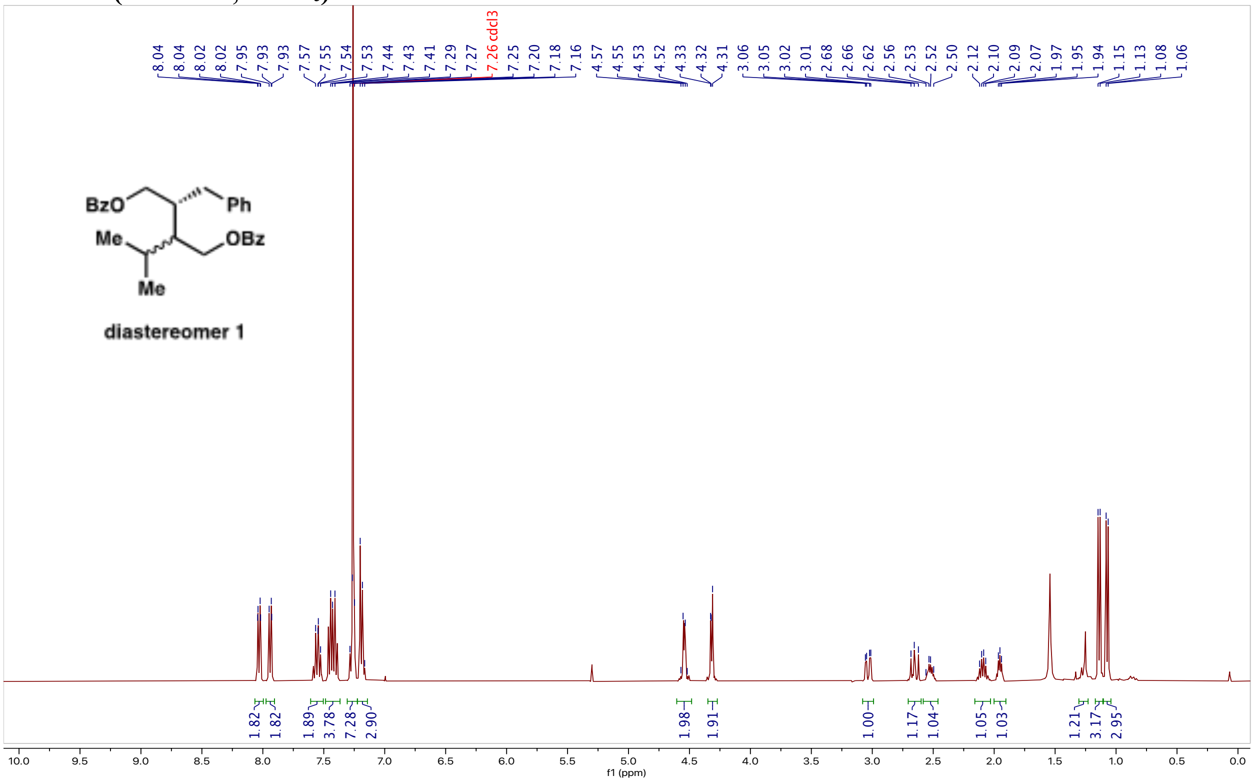


^{19}F NMR (565 MHz, CDCl$_3$)

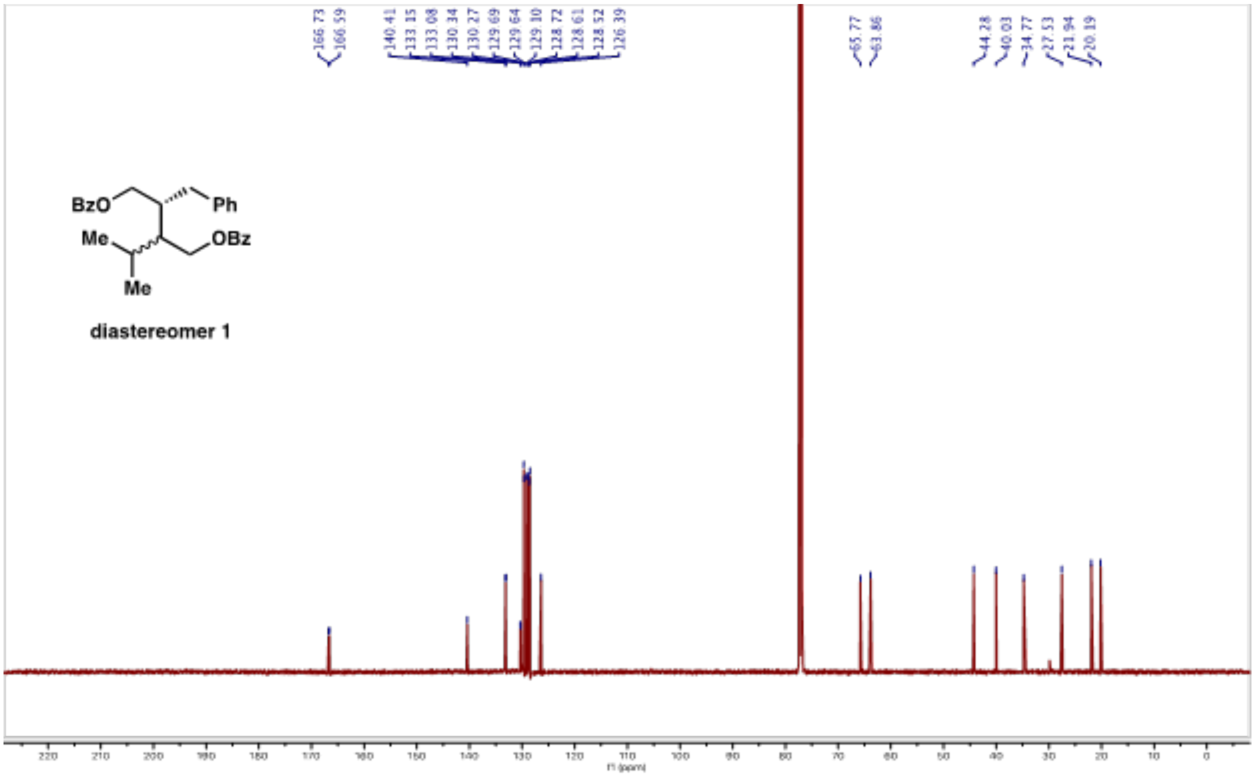


(2R)-2-Benzyl-3-isopropylbutane-1,4-diyl dibenzoate, 13ha

^{1}H NMR (400 MHz, CDCl$_3$)

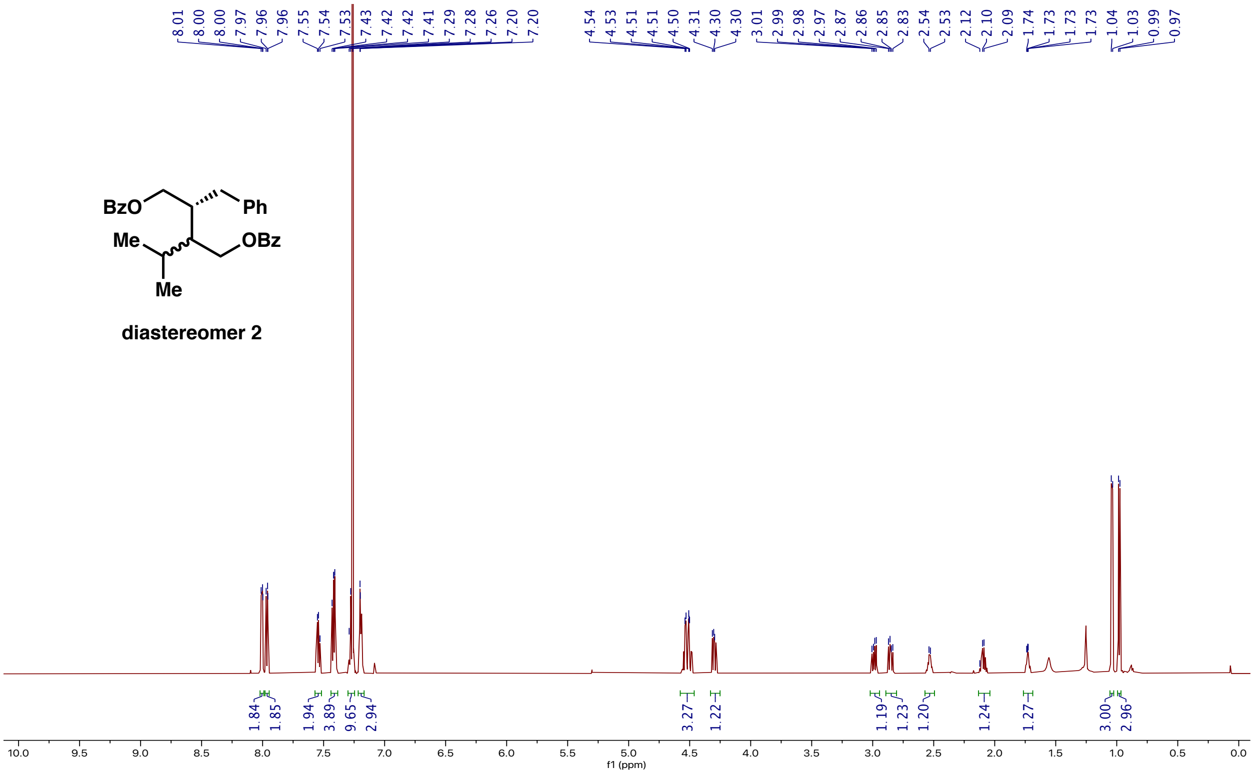


^{13}C NMR (151 MHz, CDCl$_3$)

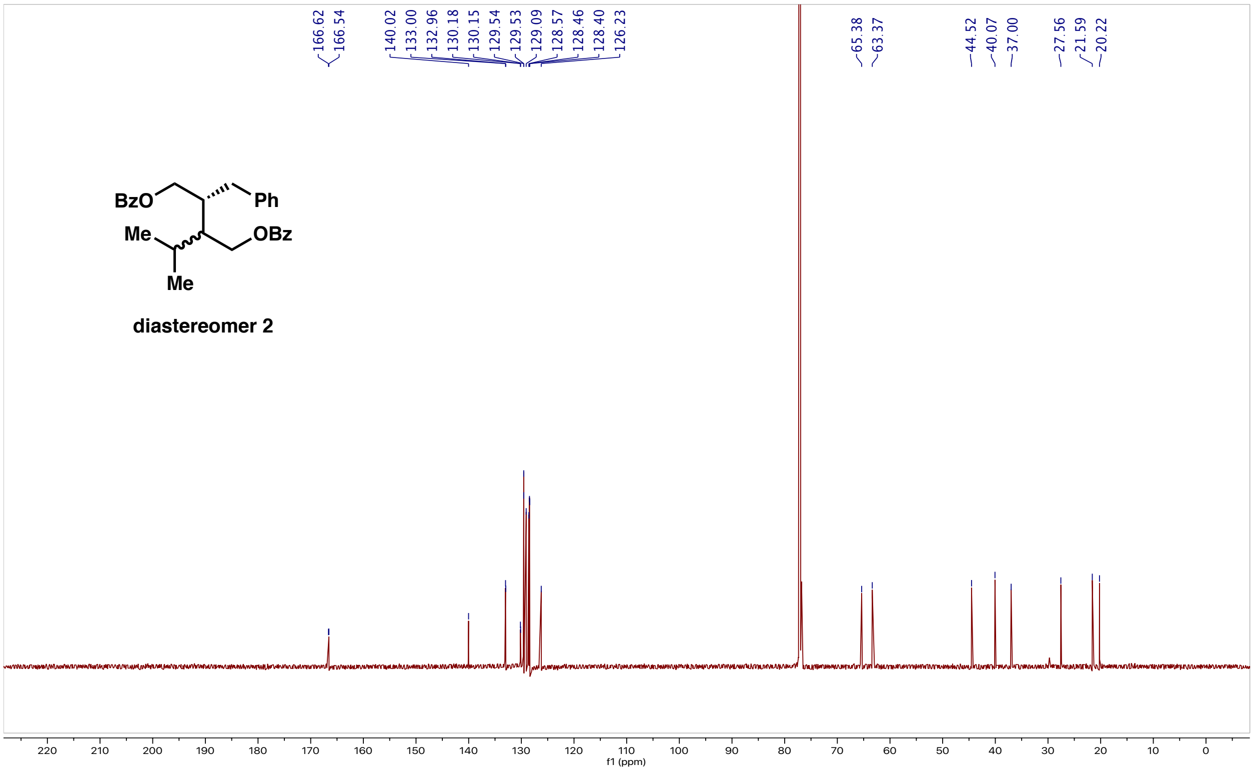


(2*R*)-2-Benzyl-3-isopropylbutane-1,4-diyl dibenzoate, 13hb

^{1}H NMR (400 MHz, CDCl$_3$)

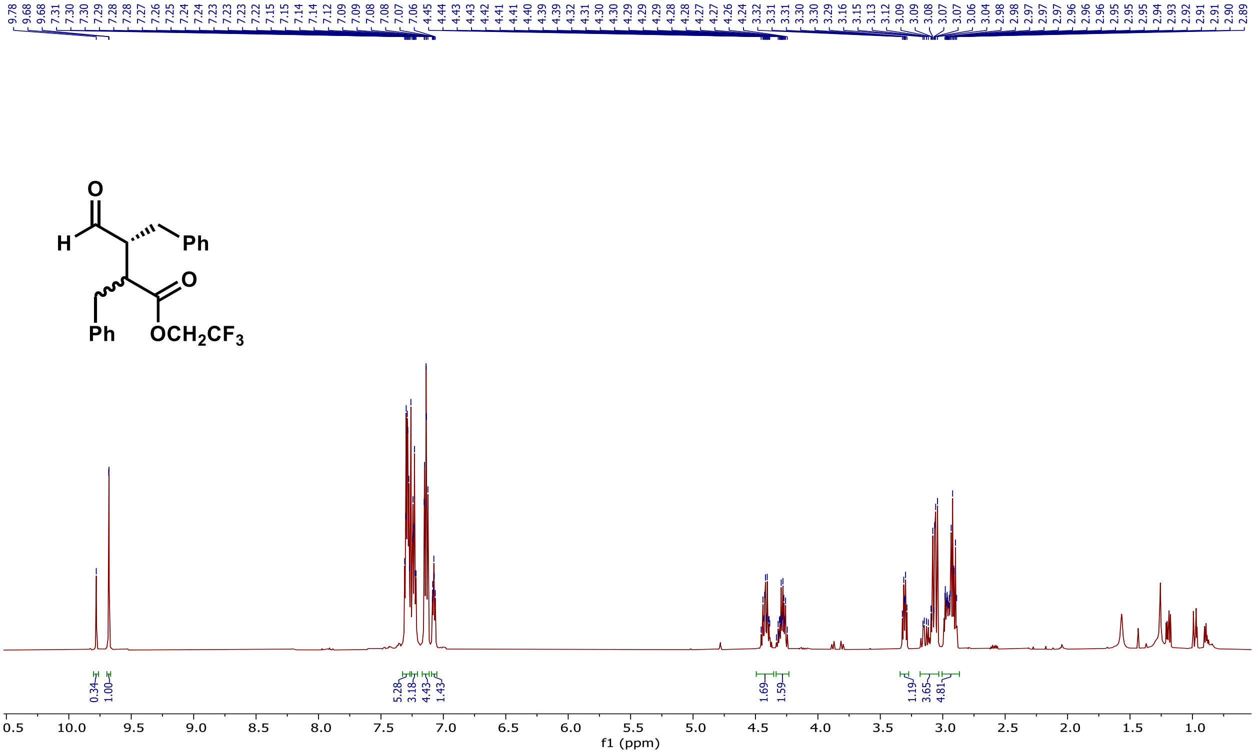


^{13}C NMR (151 MHz, CDCl$_3$)

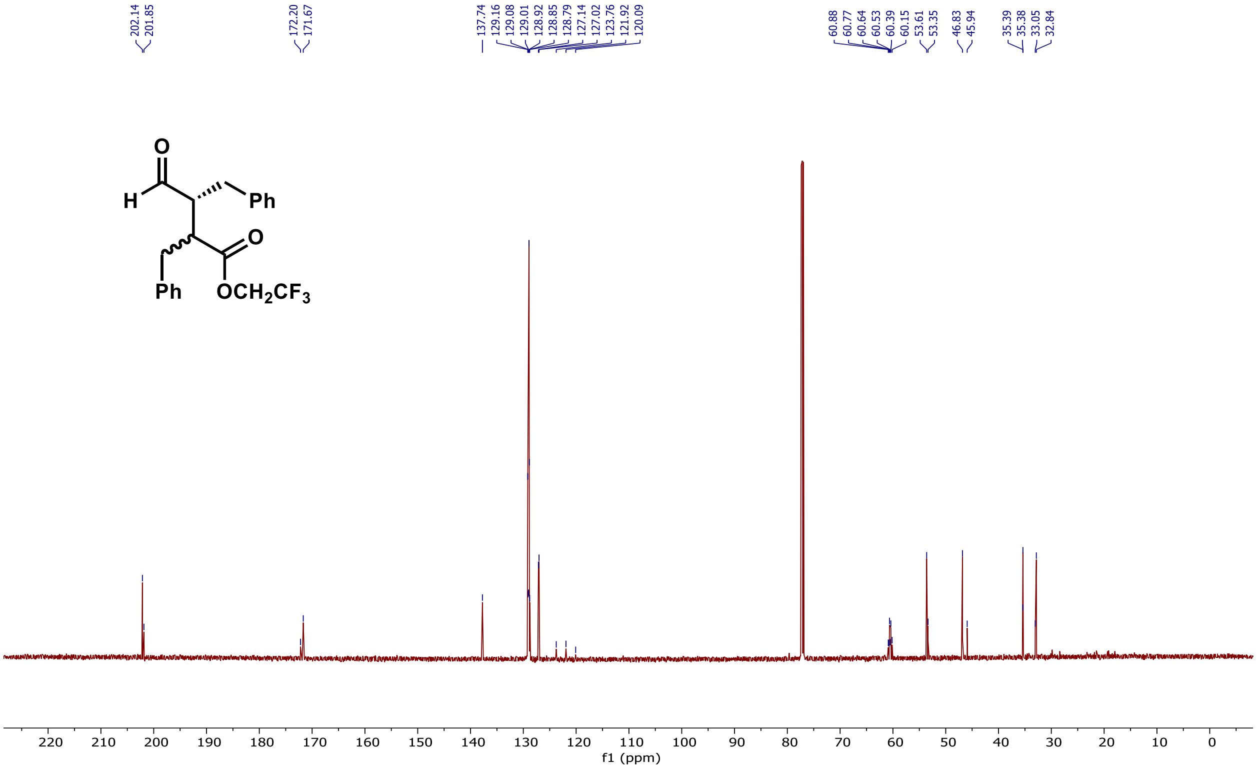


2,2,2-Trifluoroethyl (3*R*)-2,3-dibenzyl-4-oxobutanoate, 13i:

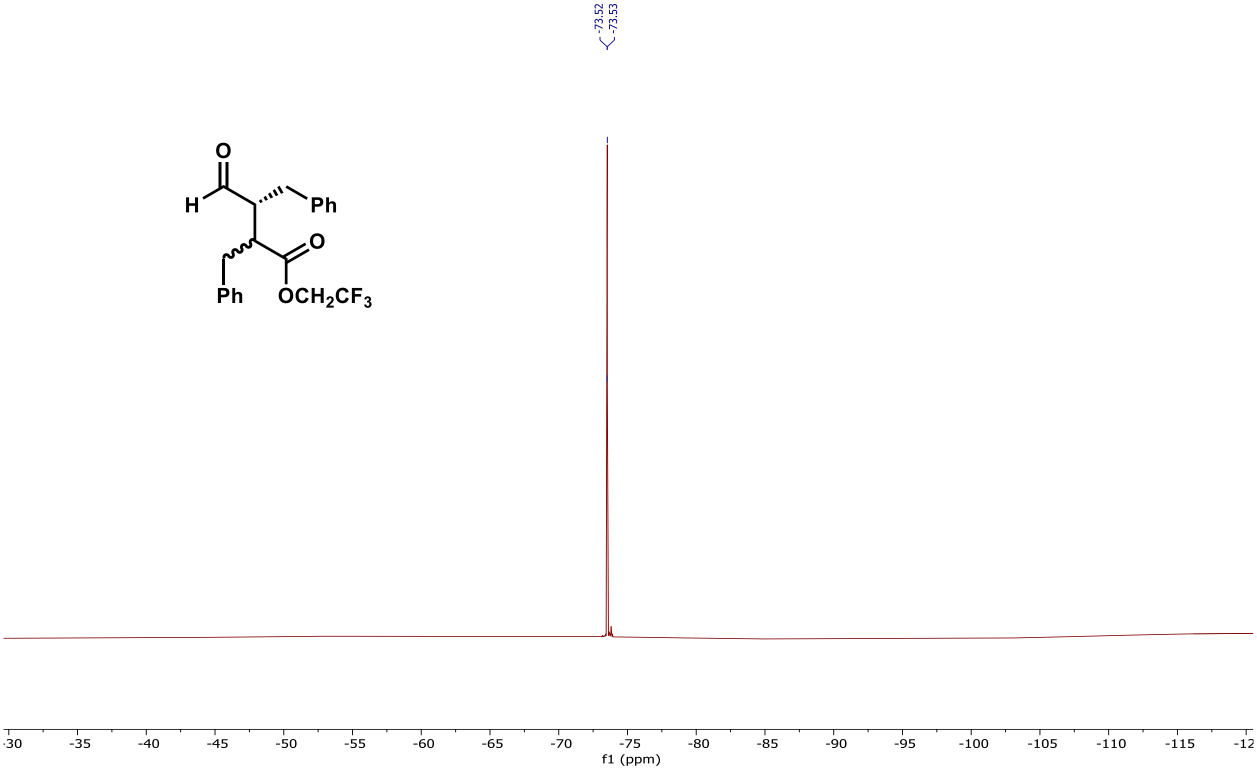
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

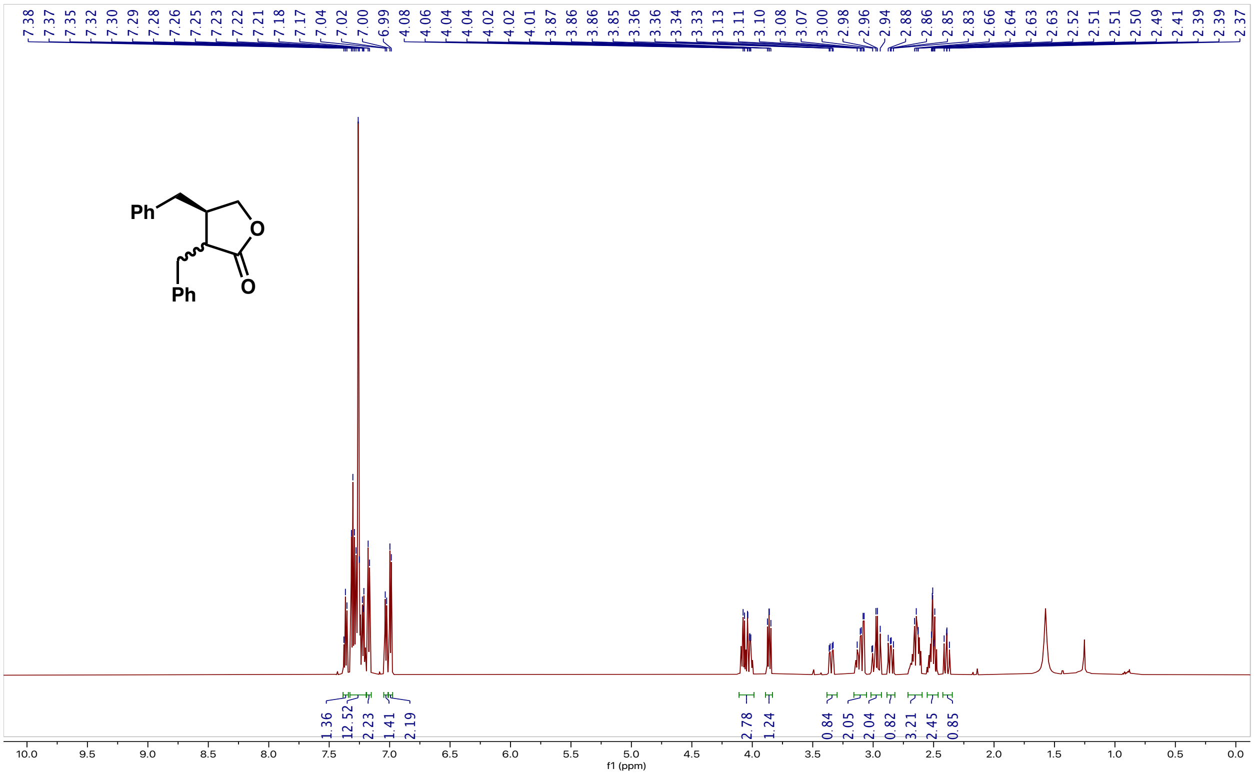


^{19}F NMR (565 MHz, CDCl$_3$)

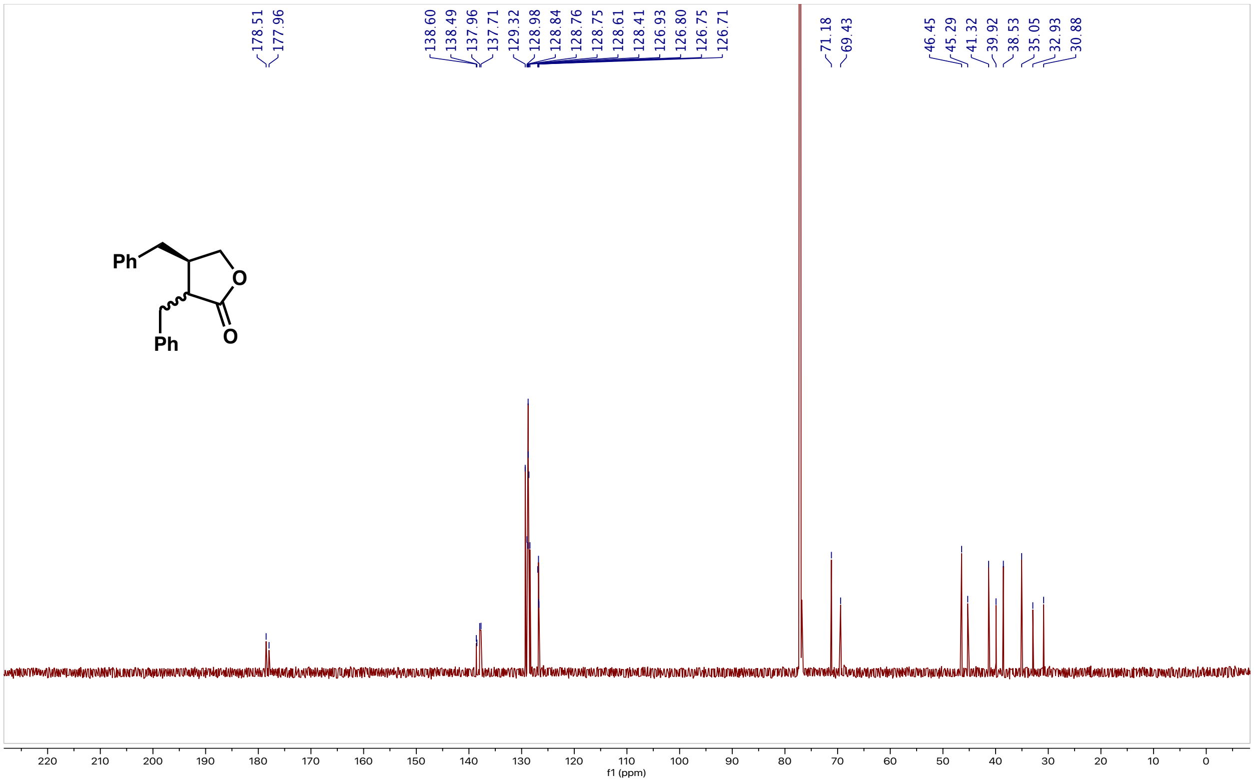


(4*R*)-3,4-Dibenzyldihydrofuran-2(3*H*)-one, 13ia:

^{1}H NMR (600 MHz, CDCl$_3$)

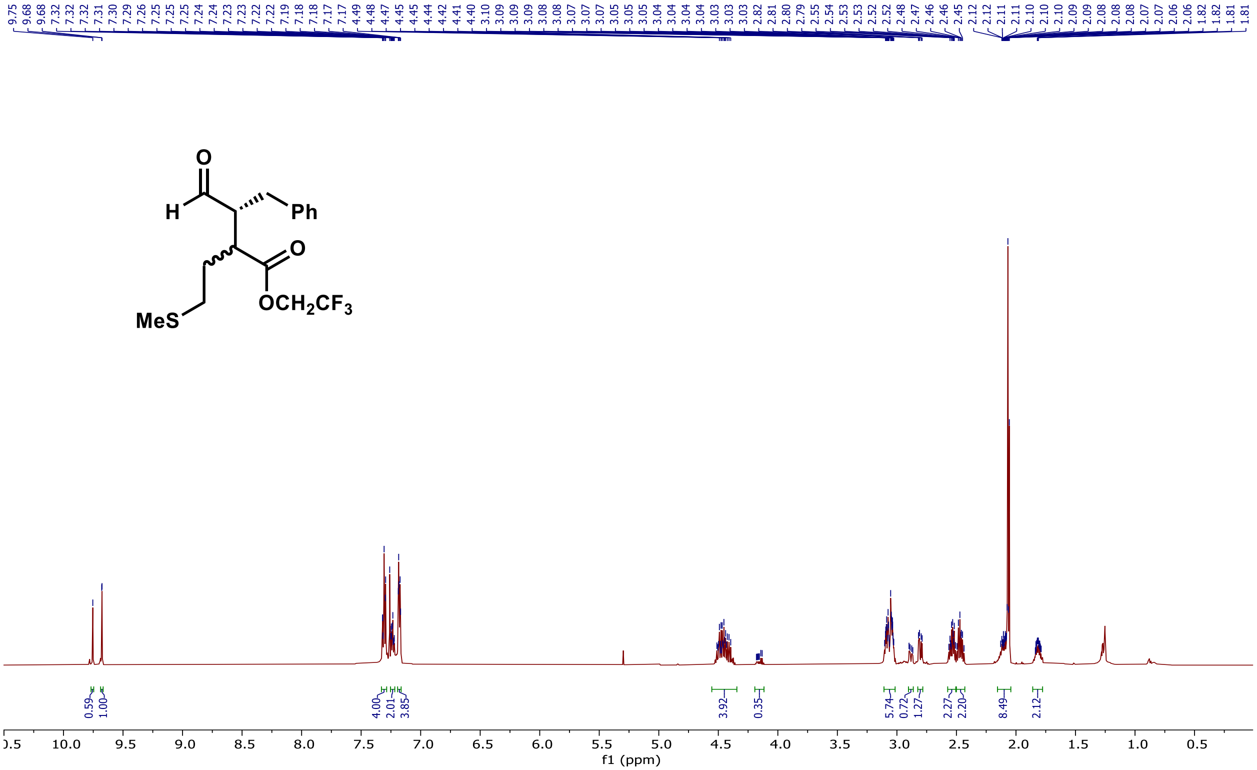


^{13}C NMR (151 MHz, CDCl$_3$)

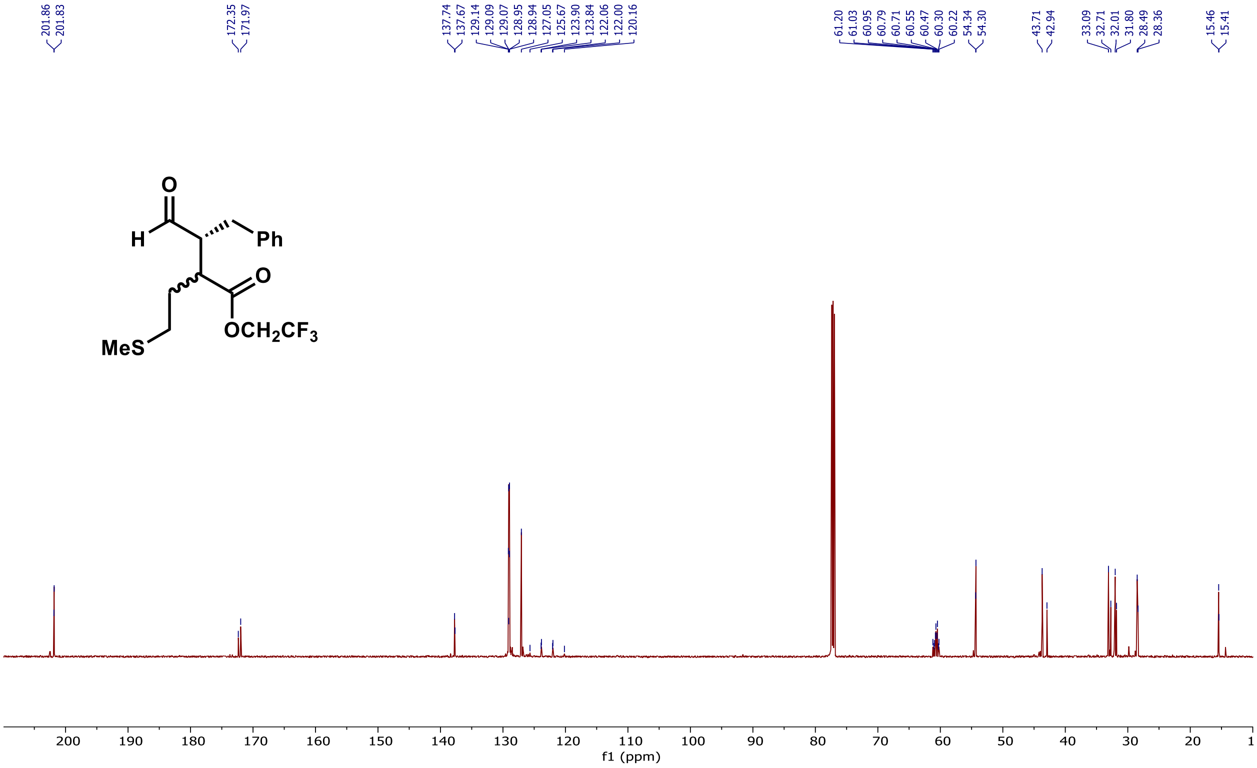


2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-(2-(methylthio)ethyl)-4-oxobutanoate, 13j:

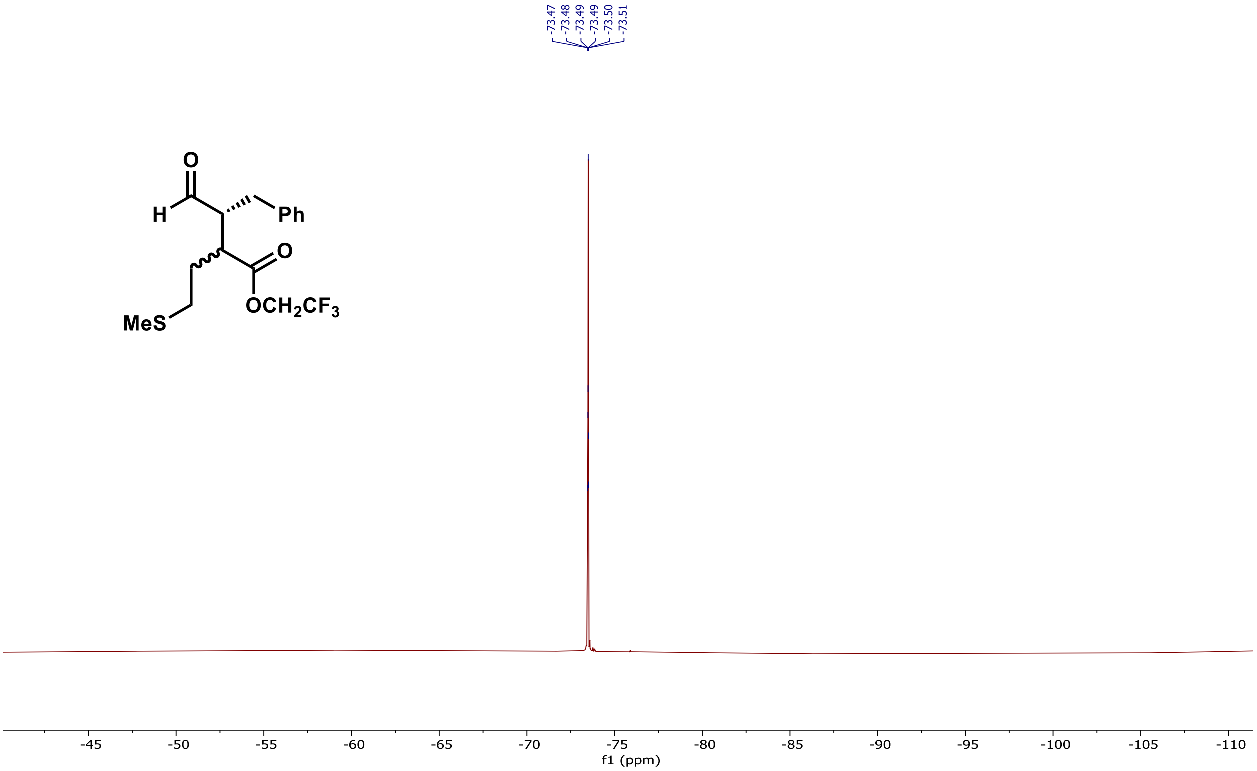
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

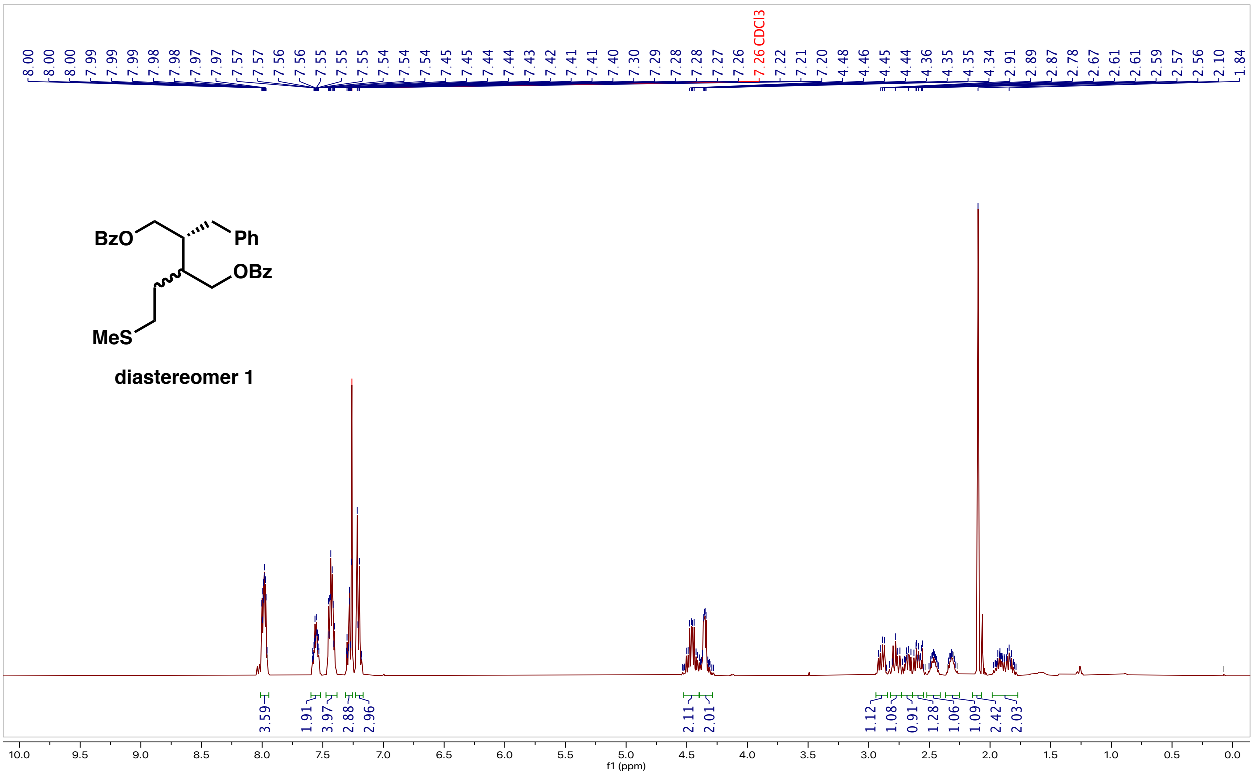


^{19}F NMR (565 MHz, CDCl$_3$)

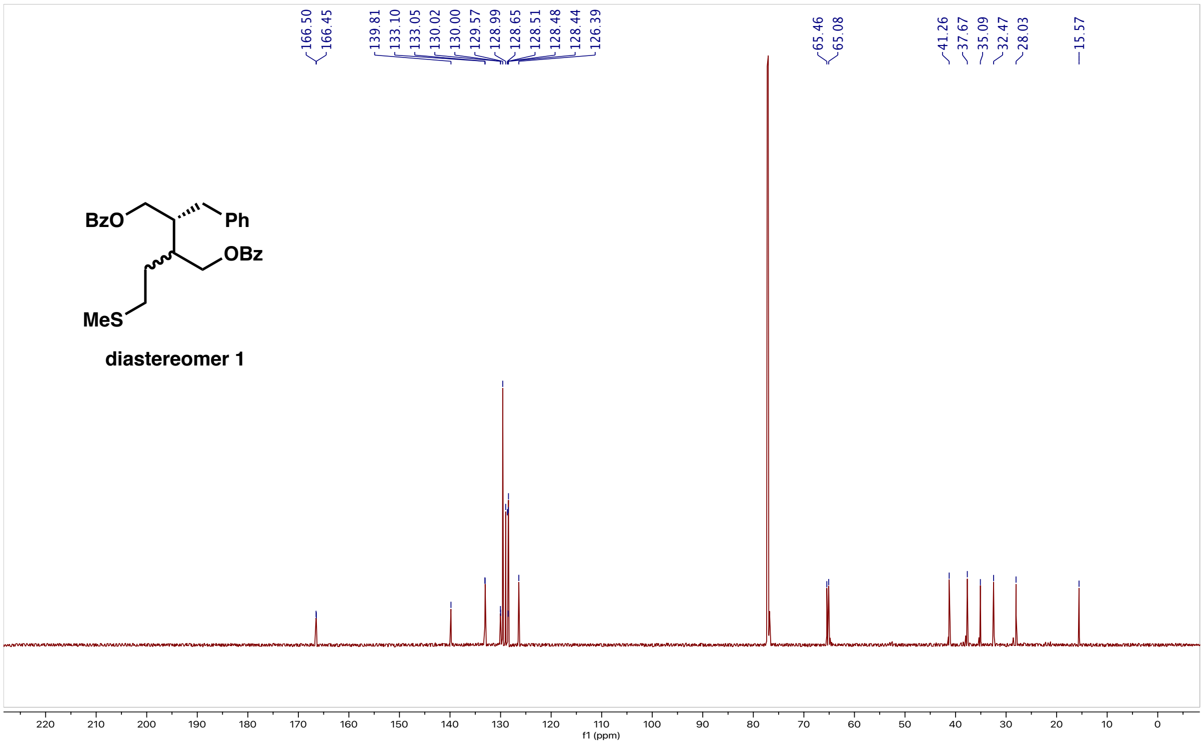


(2*R*)-2-Benzyl-3-(2-(methylthio)ethyl)butane-1,4-diyl dibenzoate, 13ja

^{1}H NMR (600 MHz, CDCl$_3$)

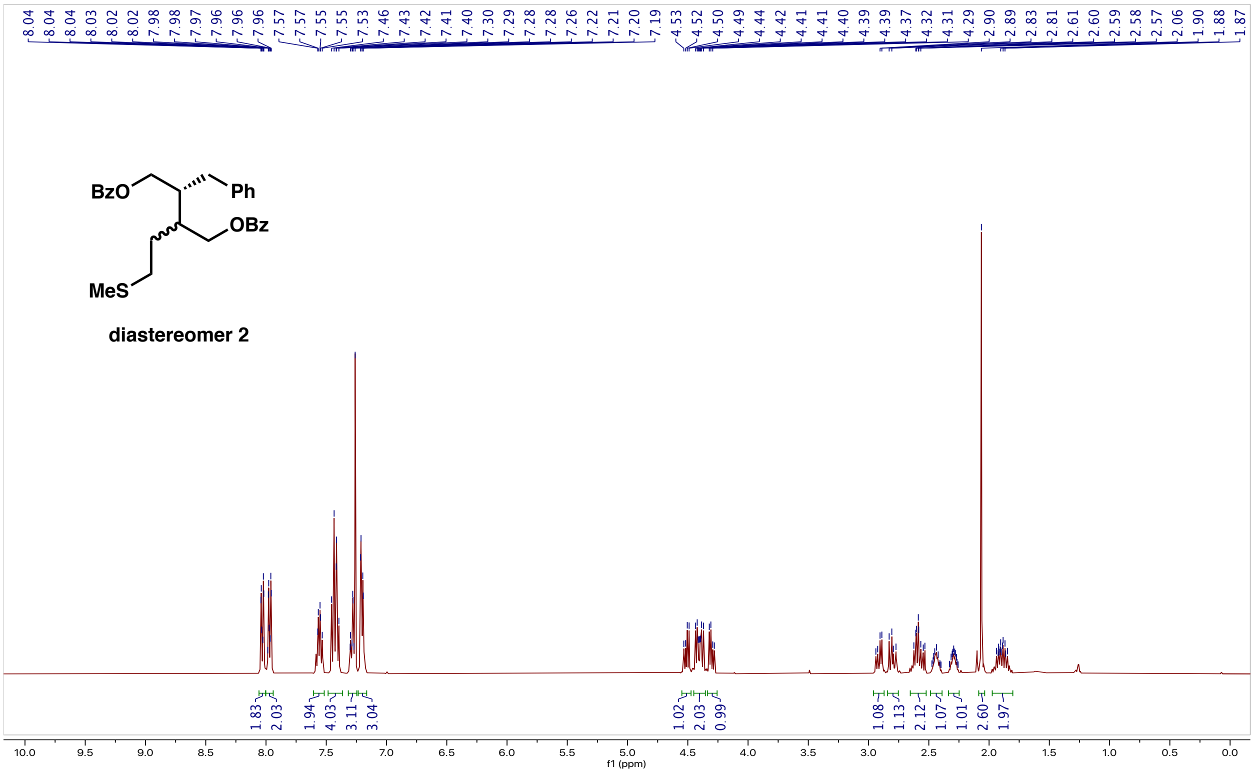


^{13}C NMR (151 MHz, CDCl$_3$)

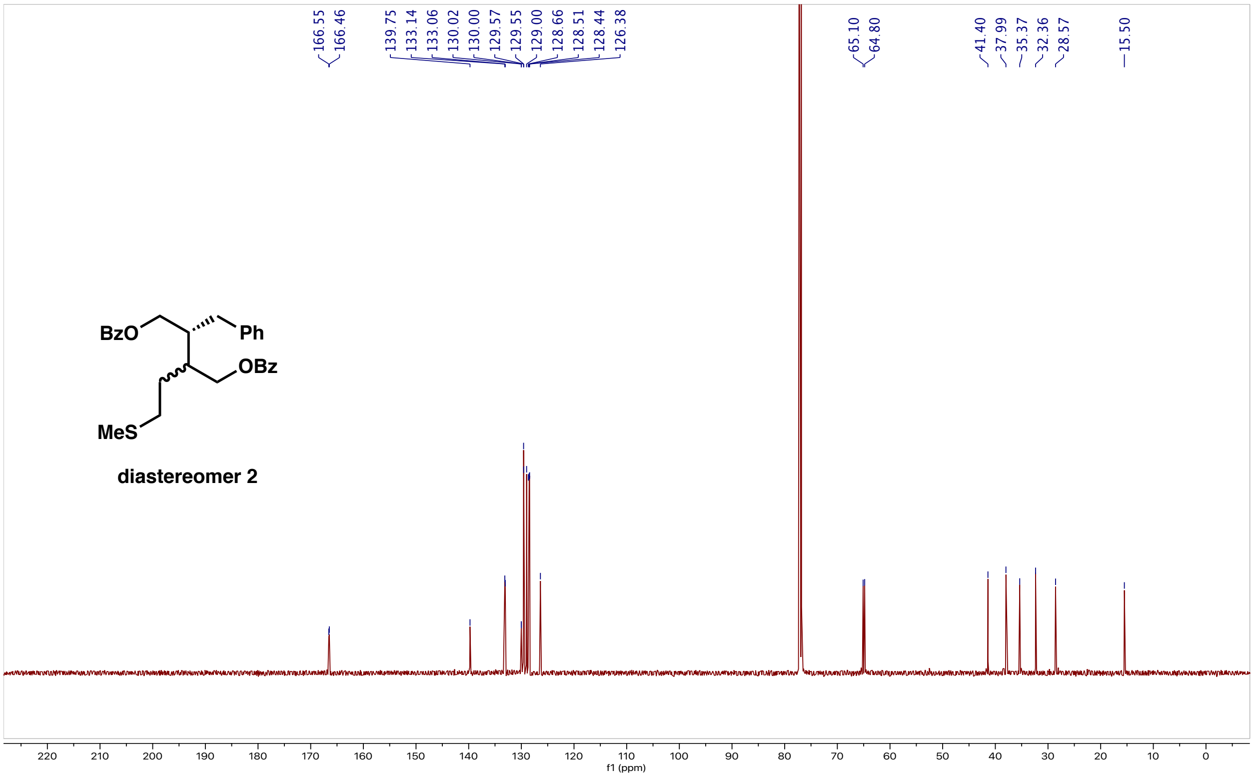


(2*R*)-2-Benzyl-3-(2-(methylthio)ethyl)butane-1,4-diyl dibenzoate, 13jb:

^{1}H NMR (600 MHz, CDCl$_3$)

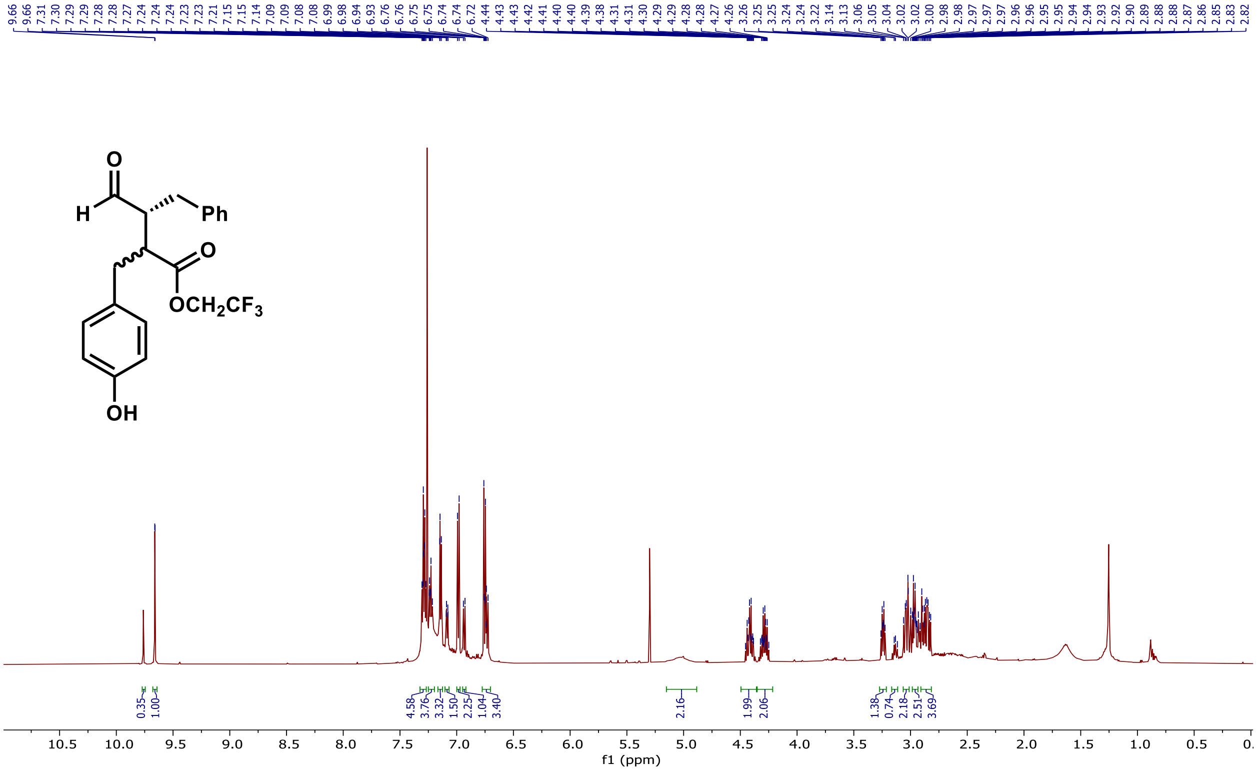


^{13}C NMR (151 MHz, CDCl$_3$)

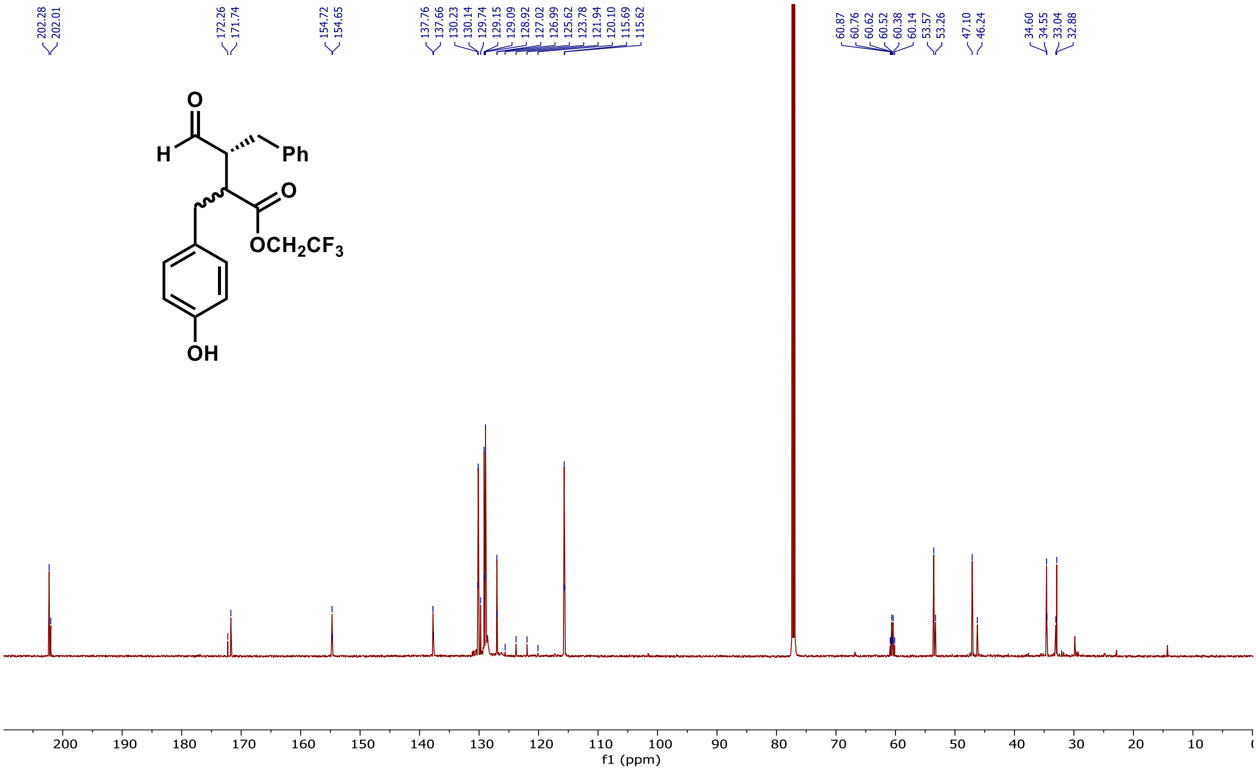


2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-(4-hydroxybenzyl)-4-oxobutanoate, 13k:

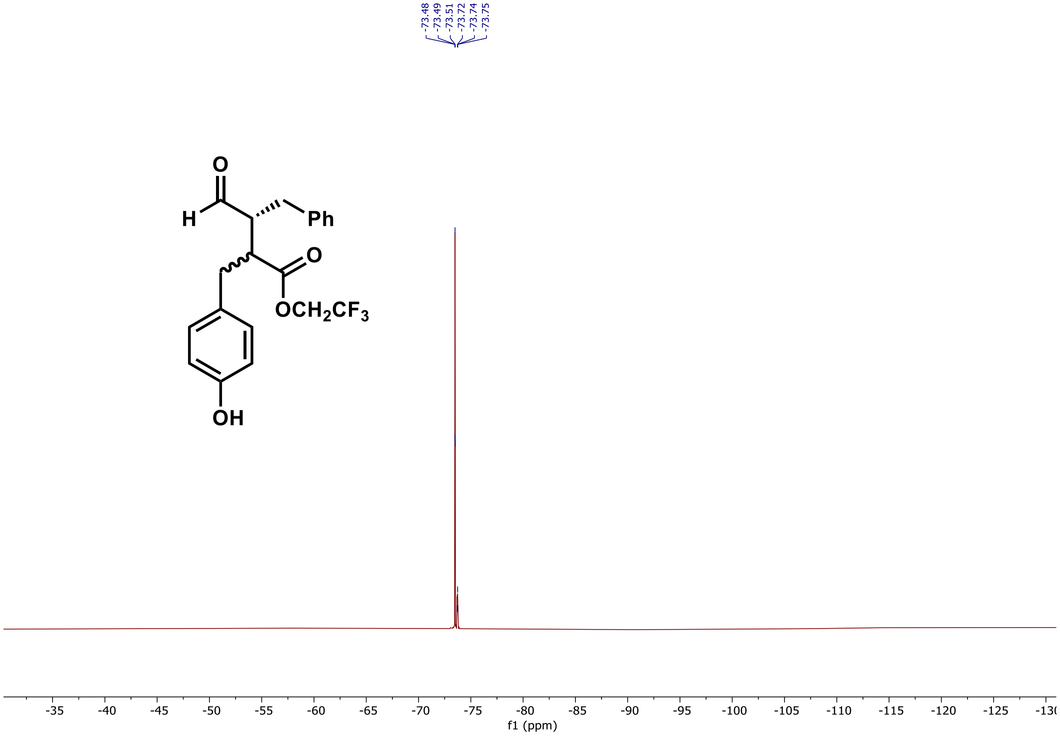
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

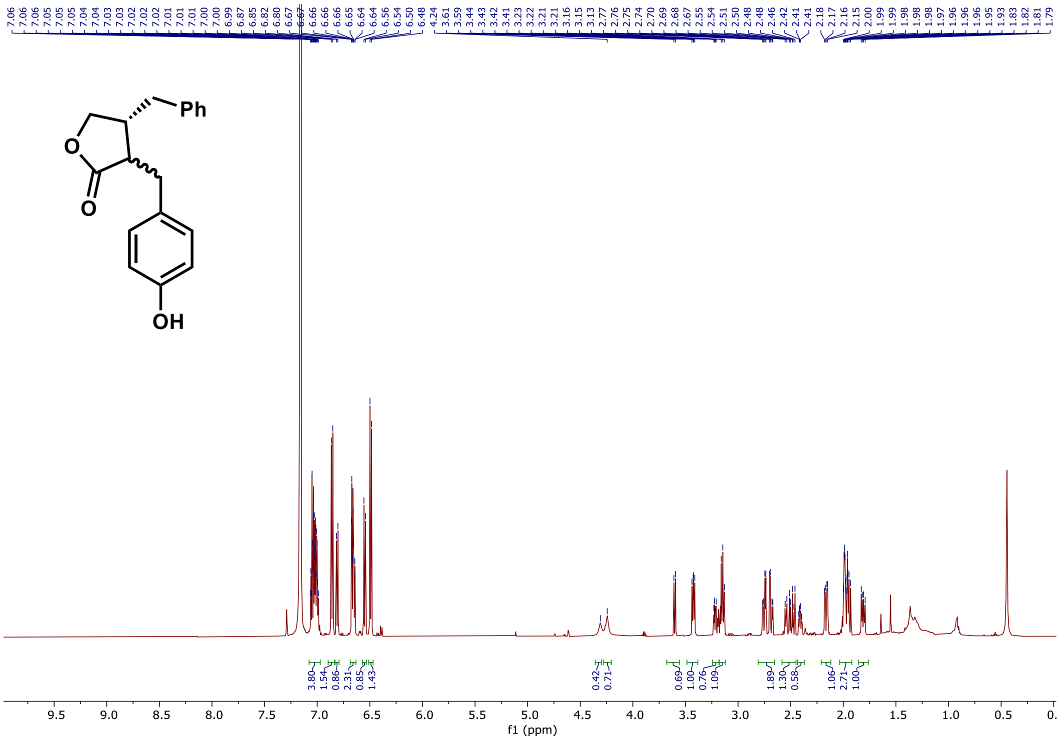


^{19}F NMR (565 MHz, CDCl$_3$)

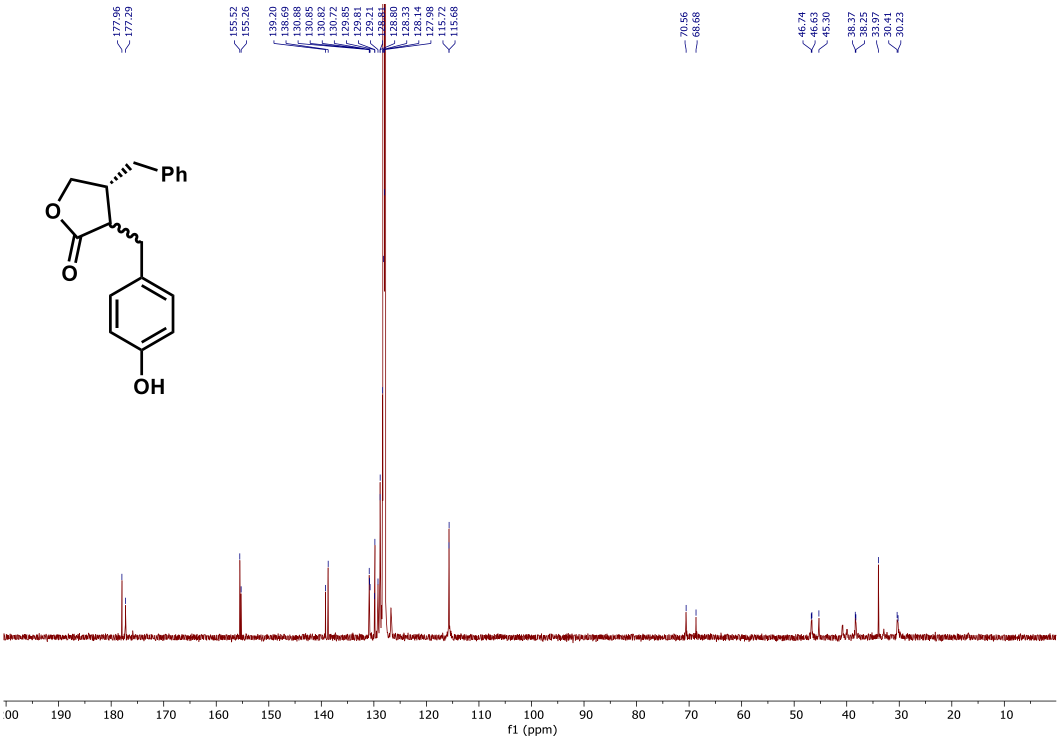


(4*R*)-4-Benzyl-3-(4-hydroxybenzyl)dihydrofuran-2(3*H*)-one, 13ka:

^{1}H NMR (600 MHz, CDCl$_3$)

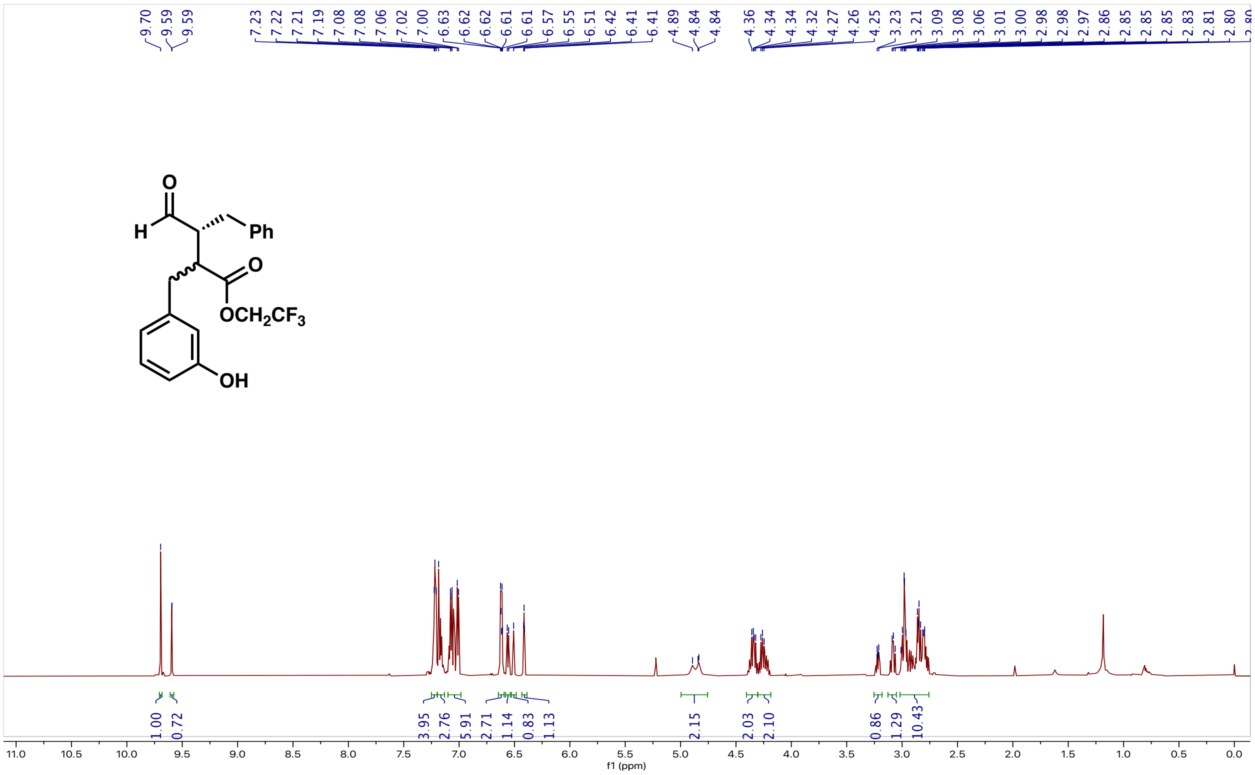


^{13}C NMR (151 MHz, $CDCl_3$)

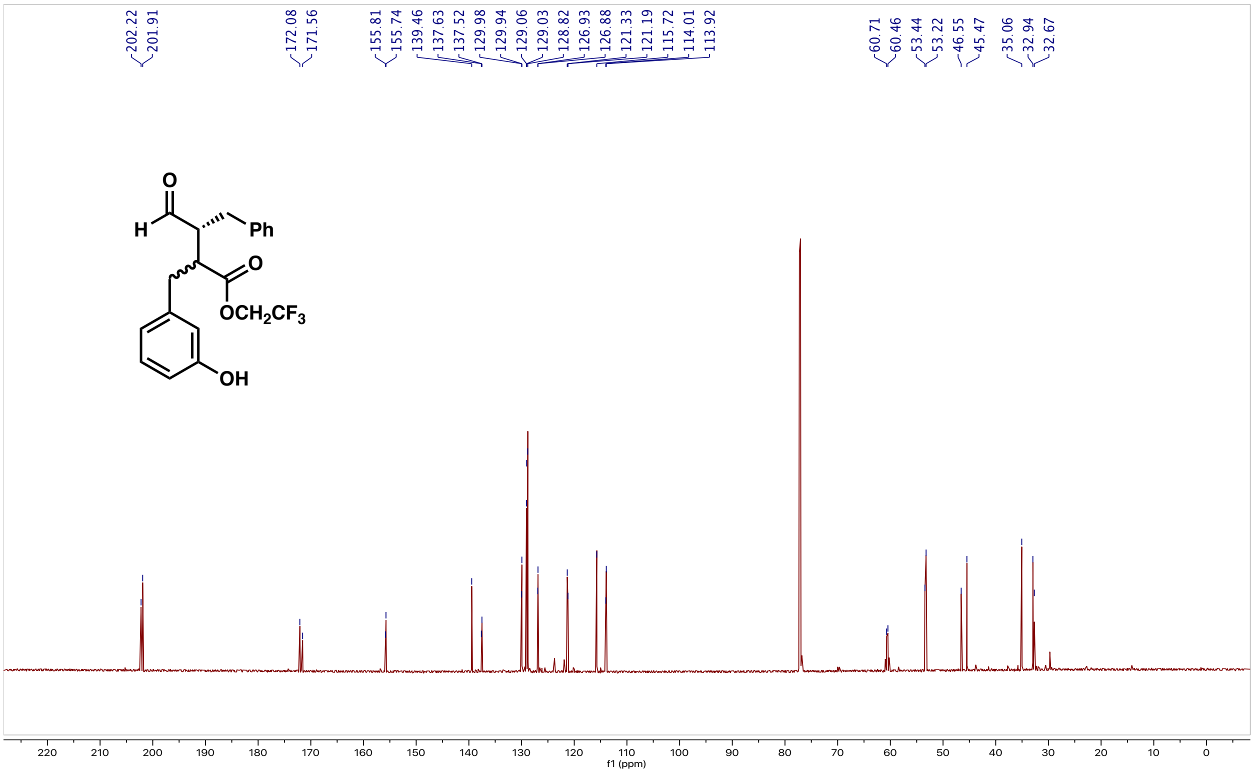


2,2,2-Trifluoroethyl (3*R*)-3-benzyl-2-(3-hydroxybenzyl)-4-oxobutanoate, 13l :

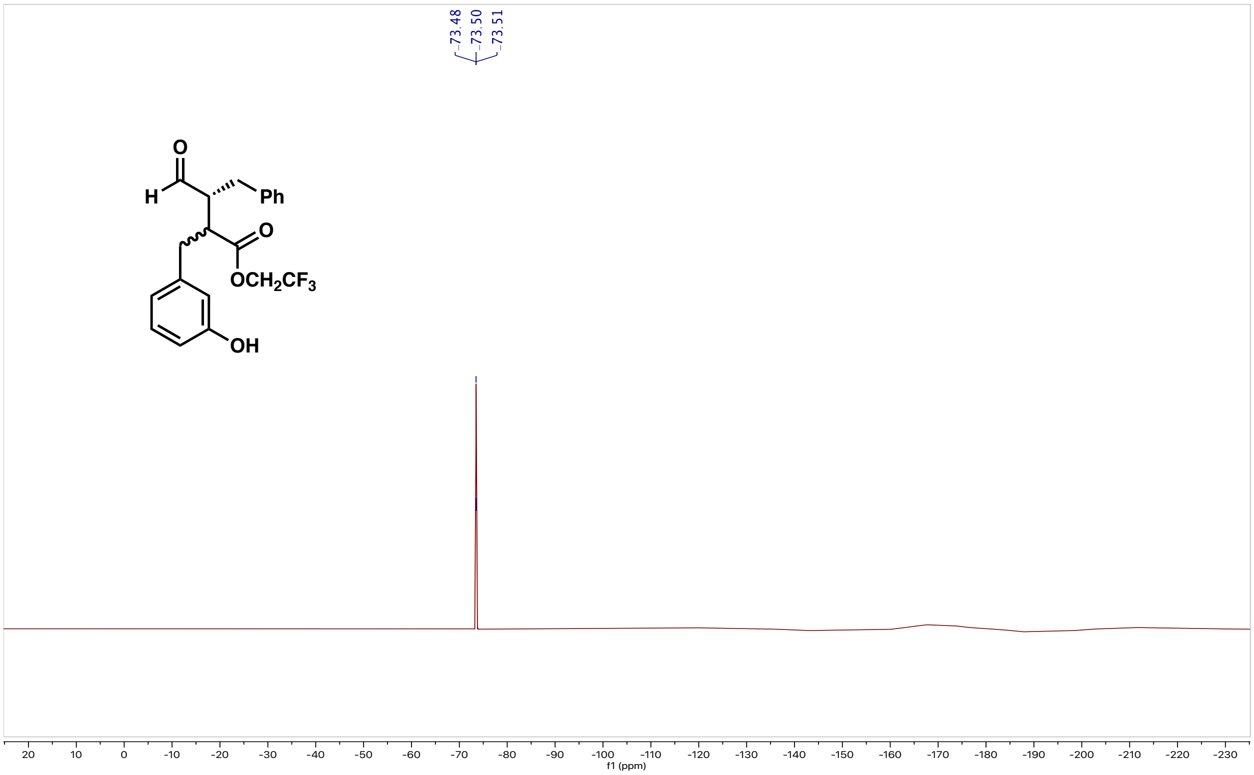
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

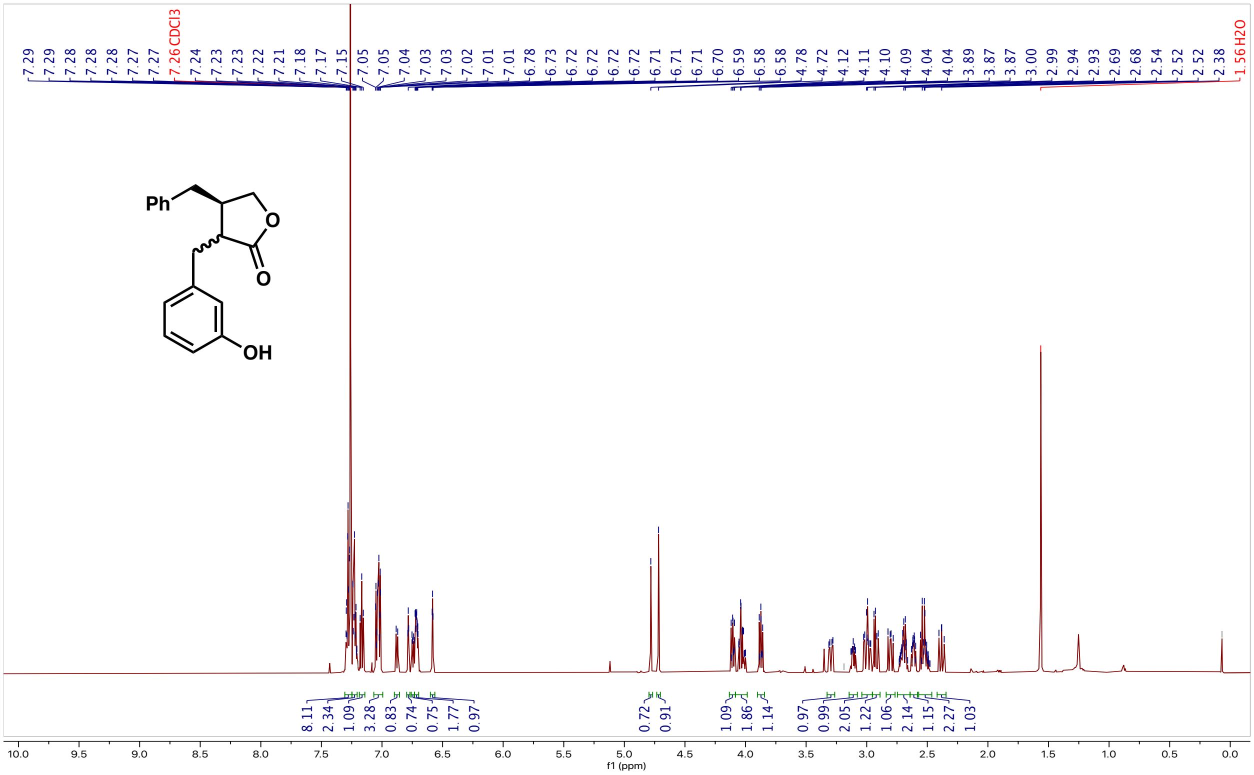


^{19}F NMR (565 MHz, $CDCl_3$)

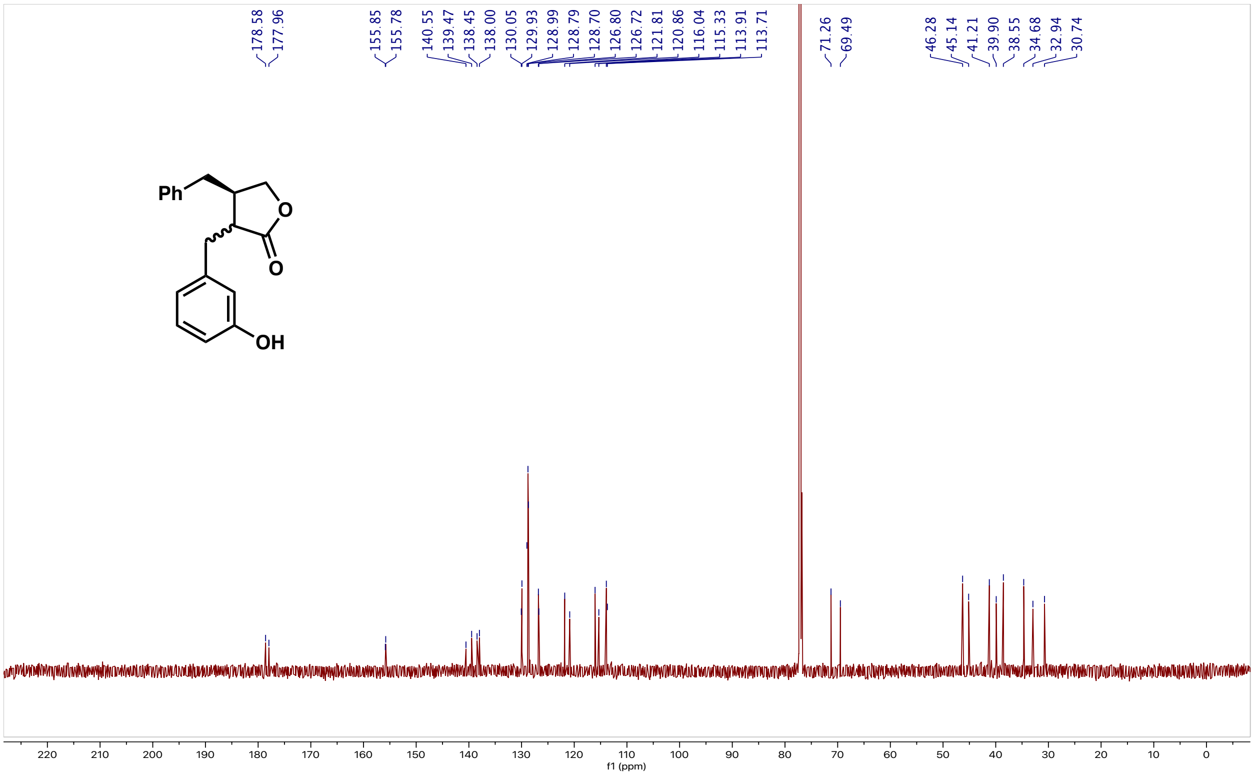


(4*R*)-4-Benzyl-3-(3-hydroxybenzyl)dihydrofuran-2(3*H*)-one, 13la :

^{1}H NMR (600 MHz, CDCl$_3$)

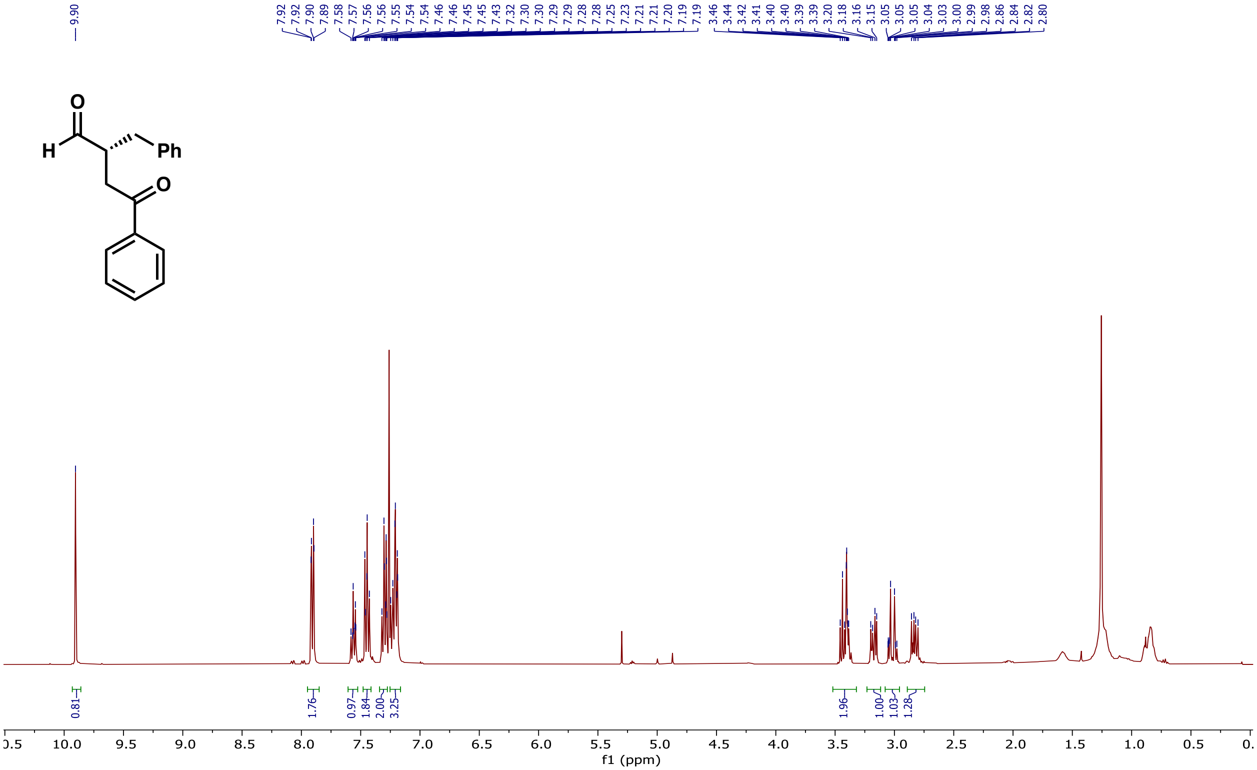


^{13}C NMR (151 MHz, CDCl$_3$)

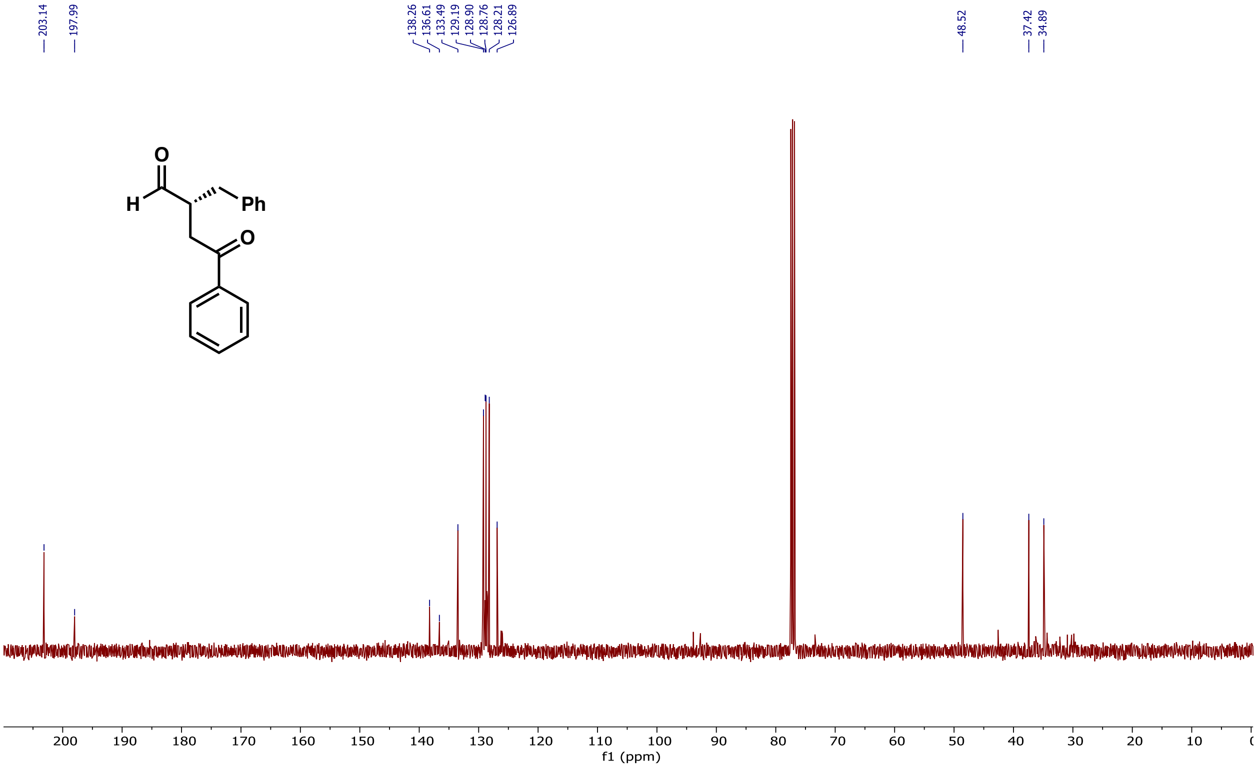


(*R*)-2-Benzyl-4-oxo-4-phenylbutanal, 15a:

^{1}H NMR (400 MHz, CDCl$_3$)

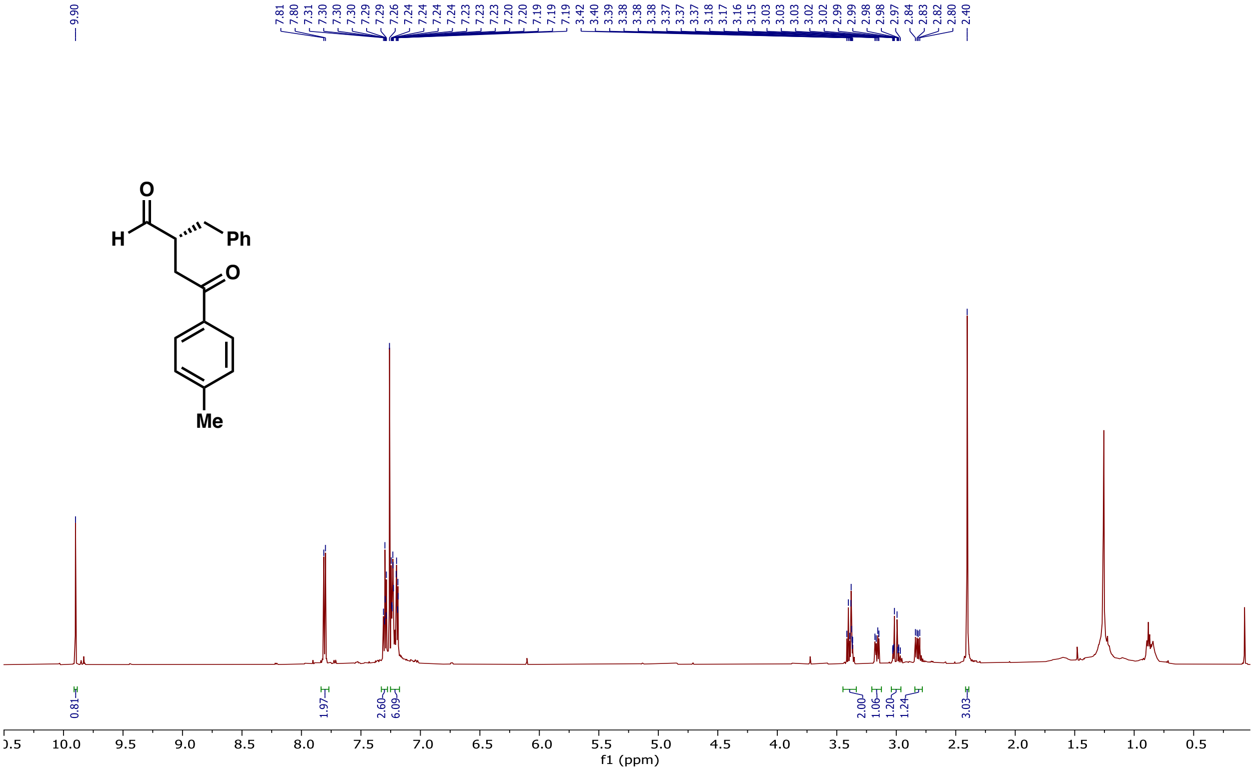


^{13}C NMR (101 MHz, CDCl$_3$)

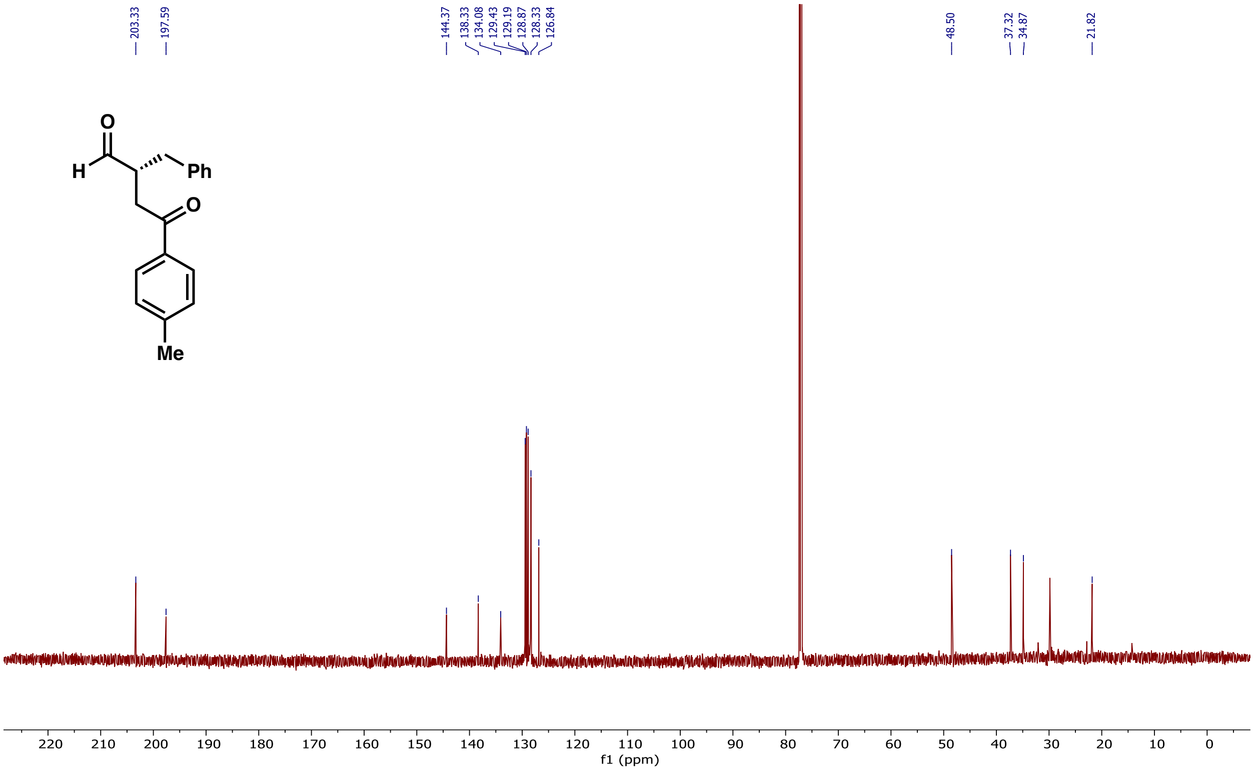


(*R*)-2-Benzyl-4-oxo-4-(*p*-tolyl)butanal, 15b:

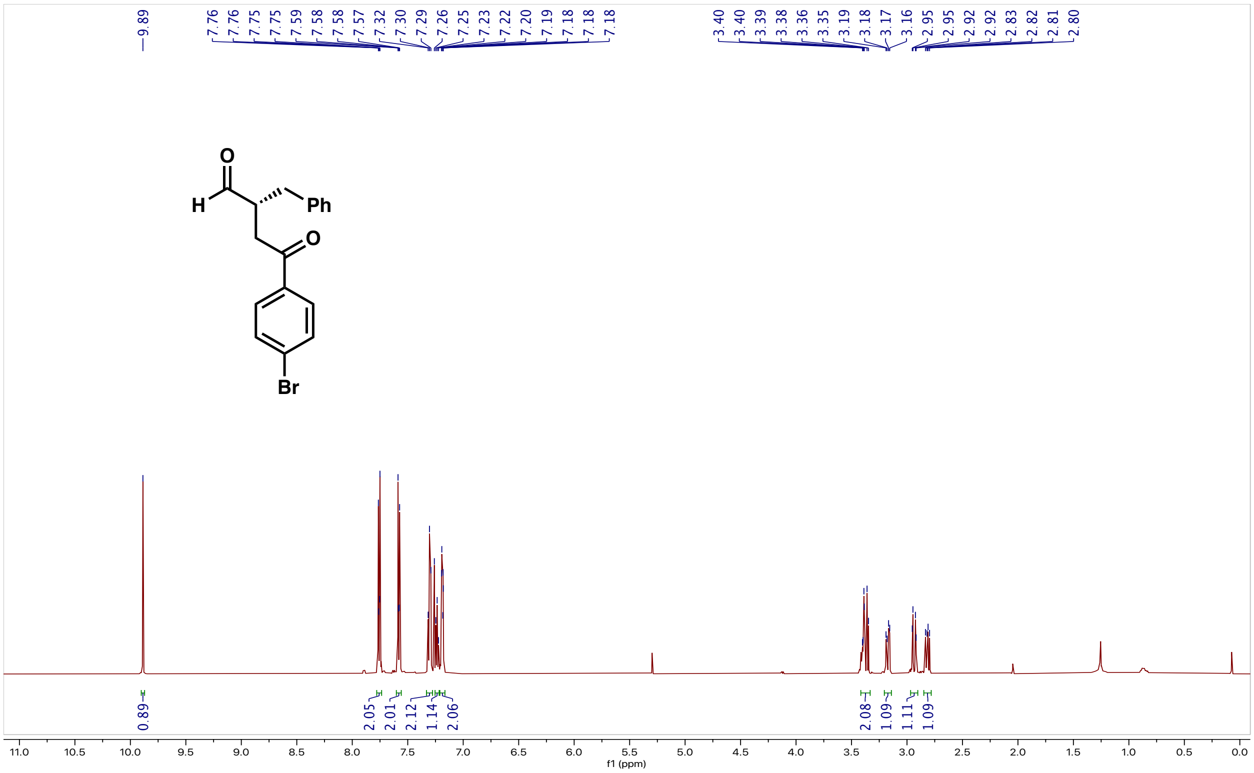
^{1}H NMR (600 MHz, CDCl$_3$)



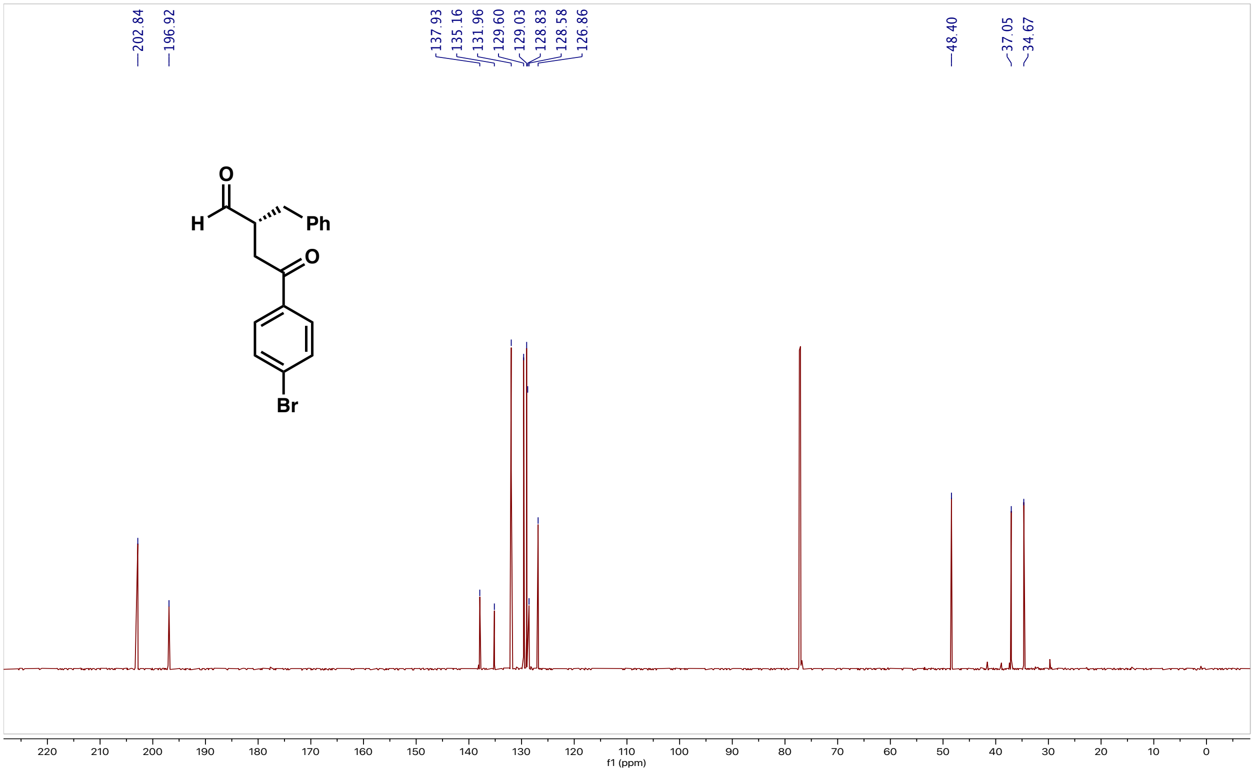
^{13}C NMR (151 MHz, CDCl$_3$)



(*R*)-2-Benzyl-4-(4-bromophenyl)-4-oxobutanal, 15c :
^{1}H NMR (400 MHz, CDCl$_3$)

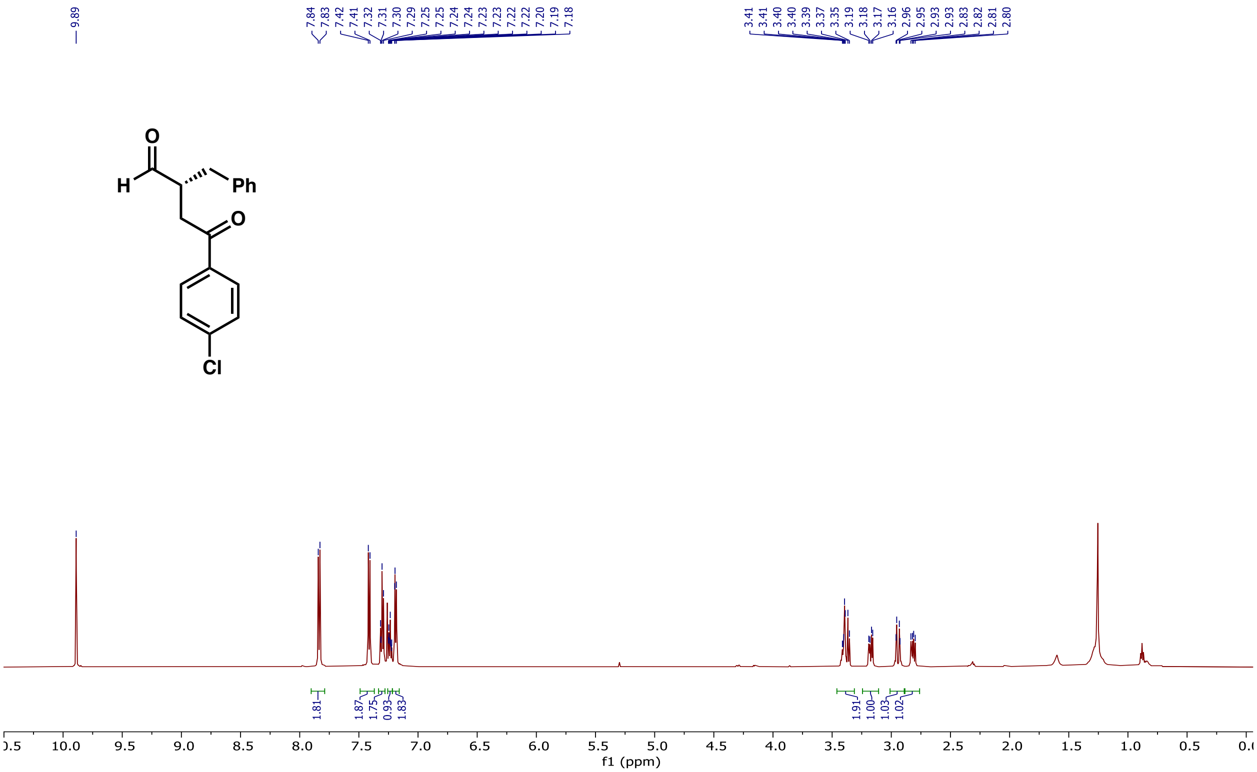


^{13}C NMR (151 MHz, CDCl$_3$)

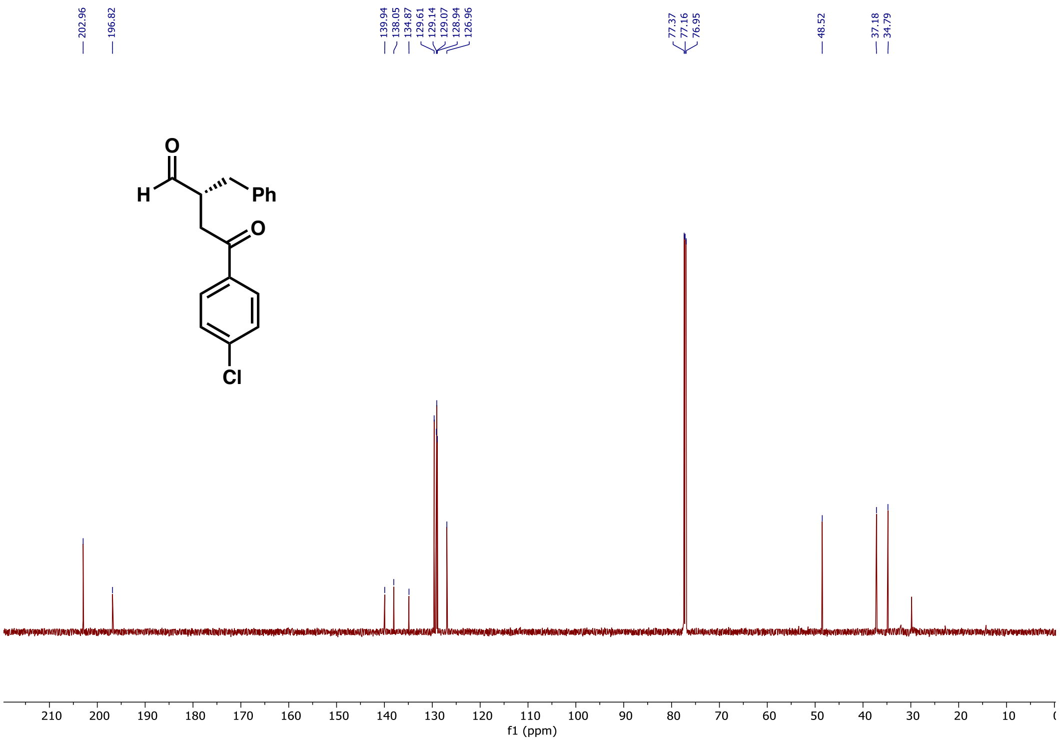


(*R*)-2-Benzyl-4-(4-chlorophenyl)-4-oxobutanal, 15d:

^{1}H NMR (600 MHz, CDCl$_3$)

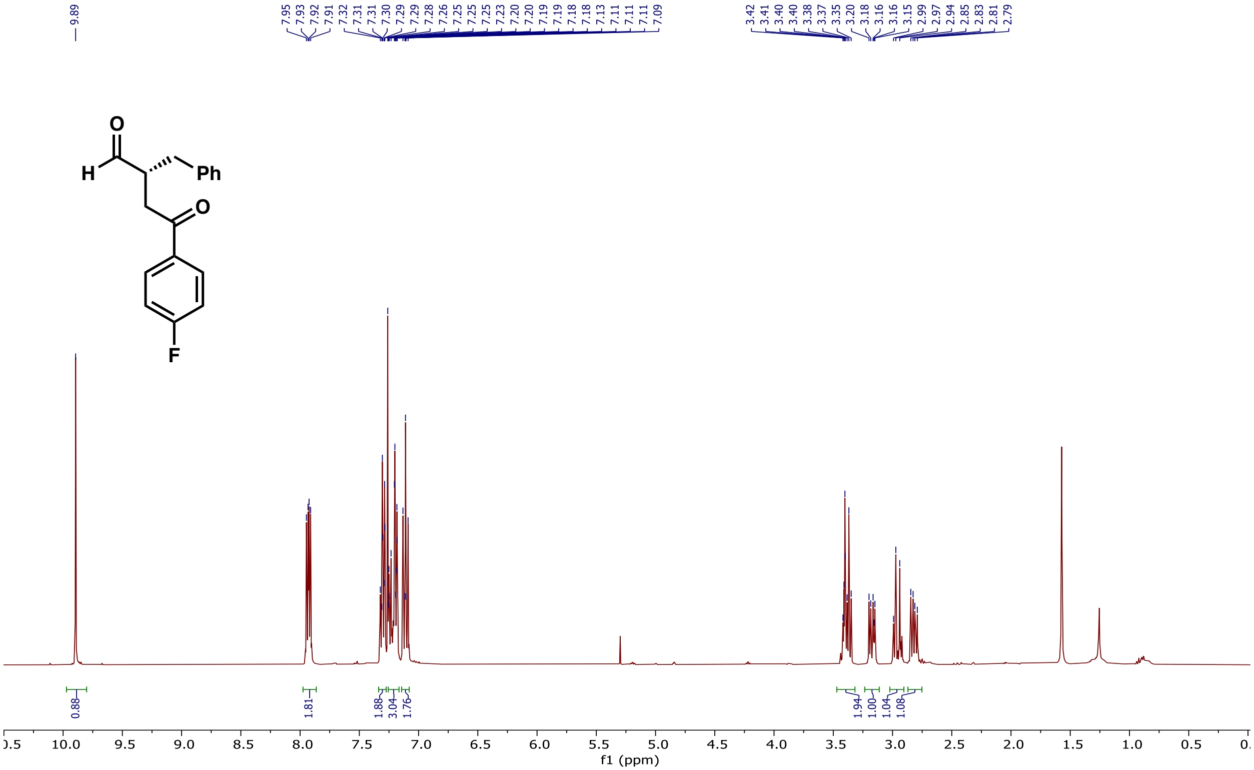


^{13}C NMR (151 MHz, CDCl$_3$)

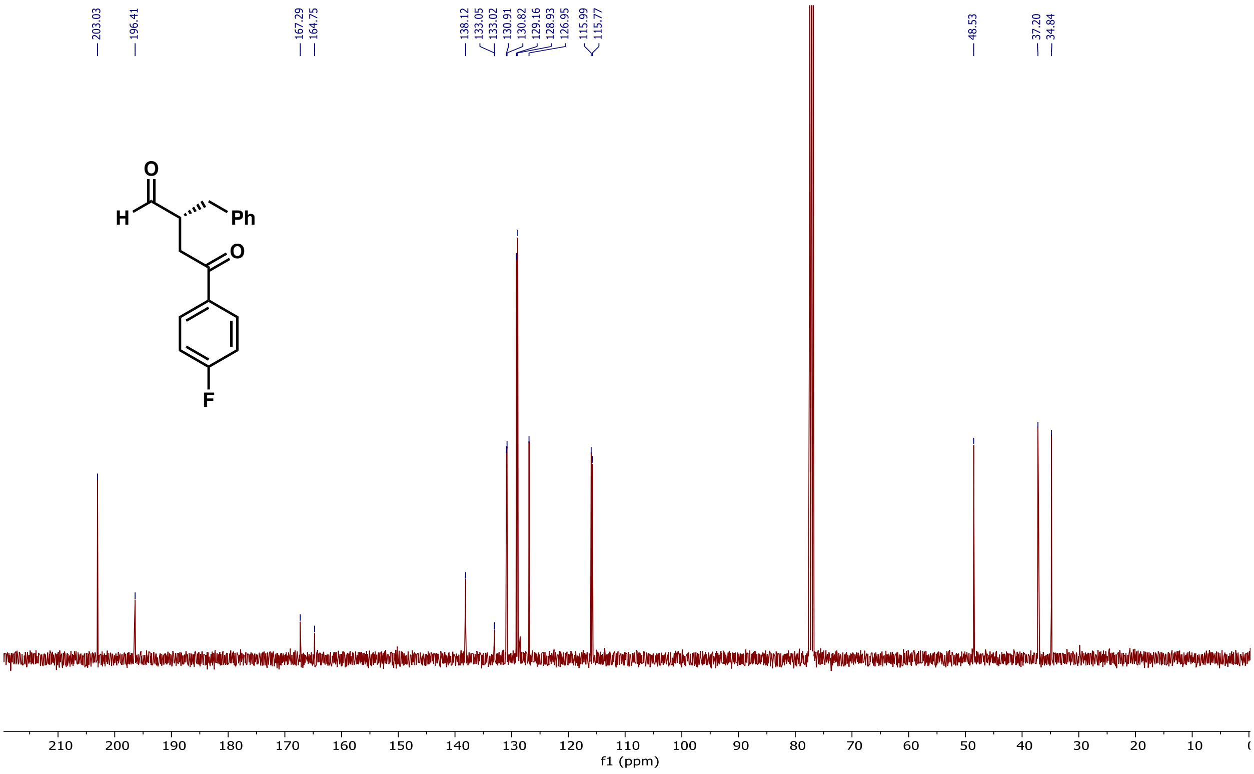


(*R*)-2-Benzyl-4-(4-fluorophenyl)-4-oxobutanal, 15e:

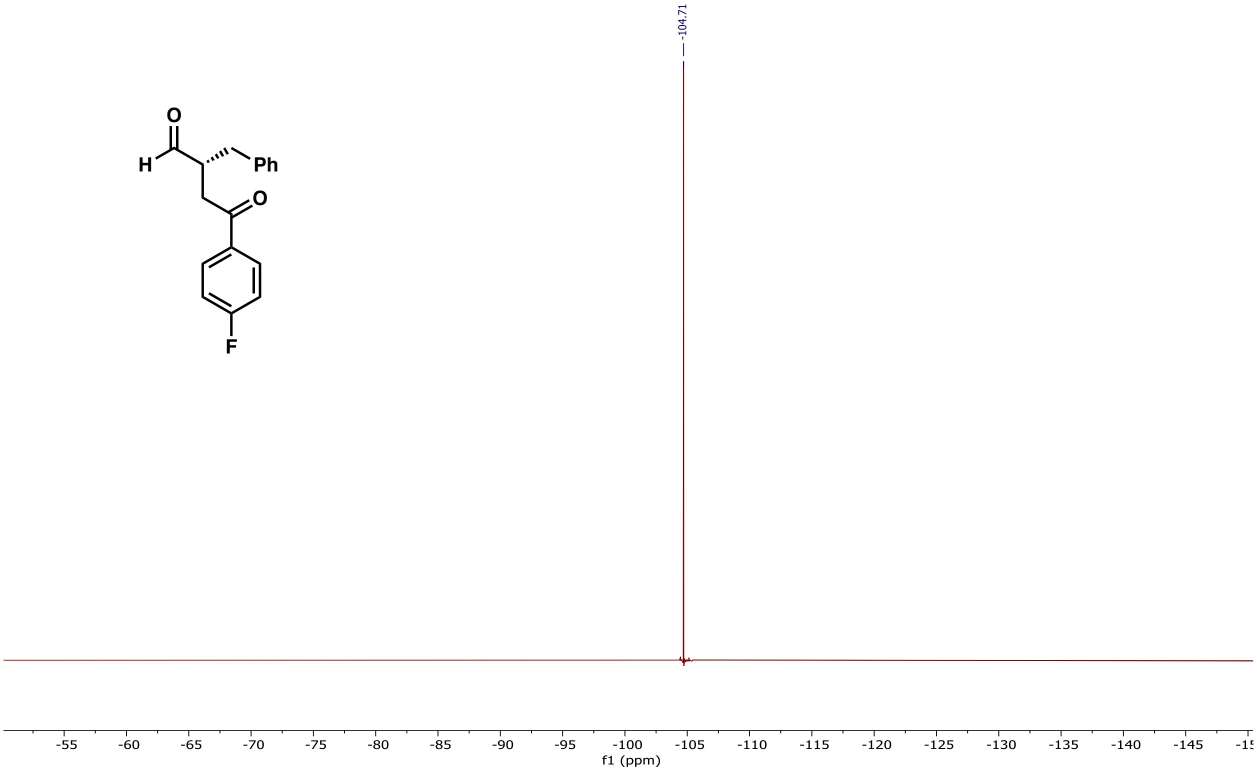
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

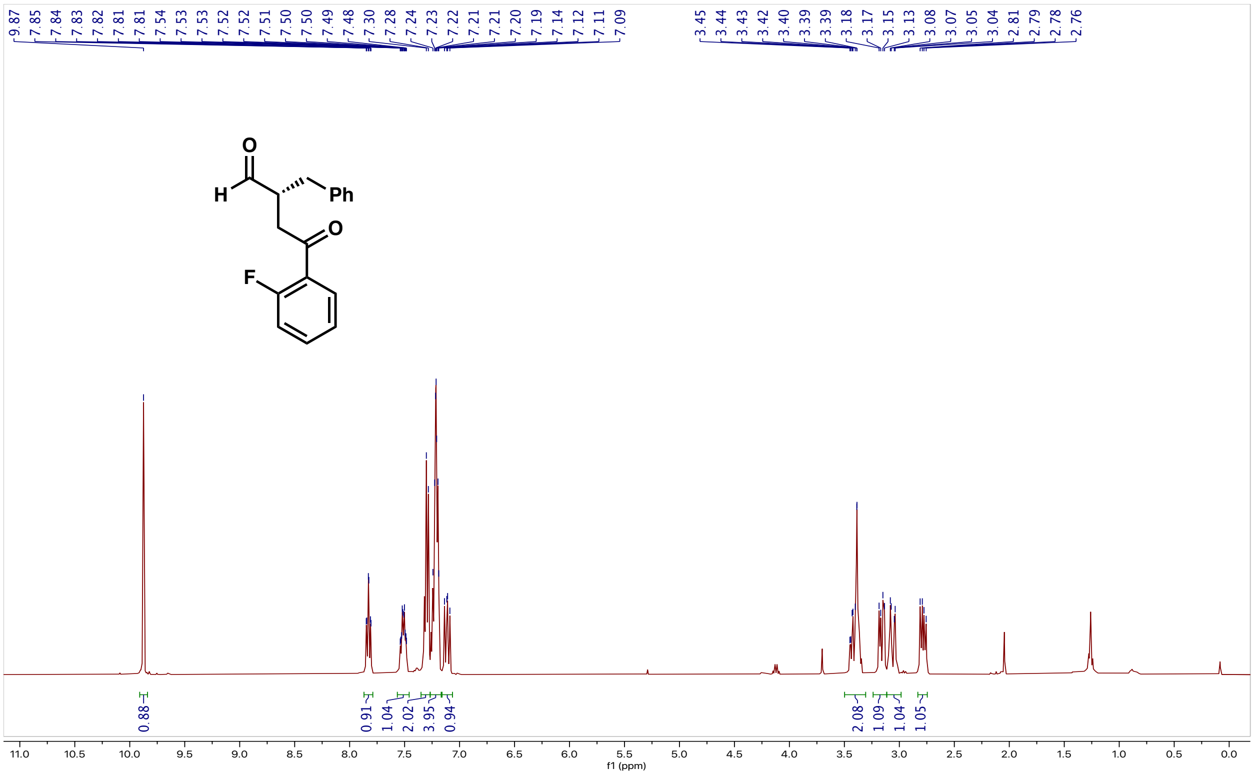


^{19}F NMR (376 MHz, CDCl$_3$)

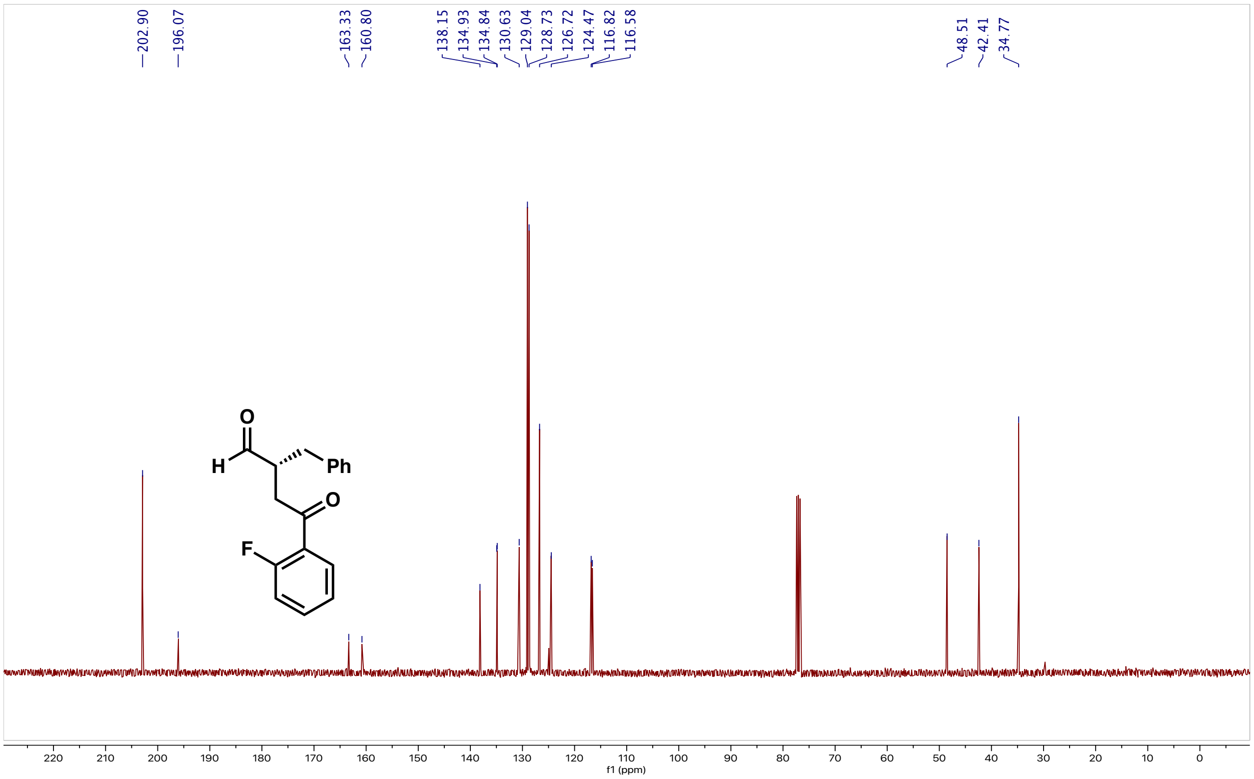


(*R*)-2-Benzyl-4-(2-fluorophenyl)-4-oxobutanal, 15f :

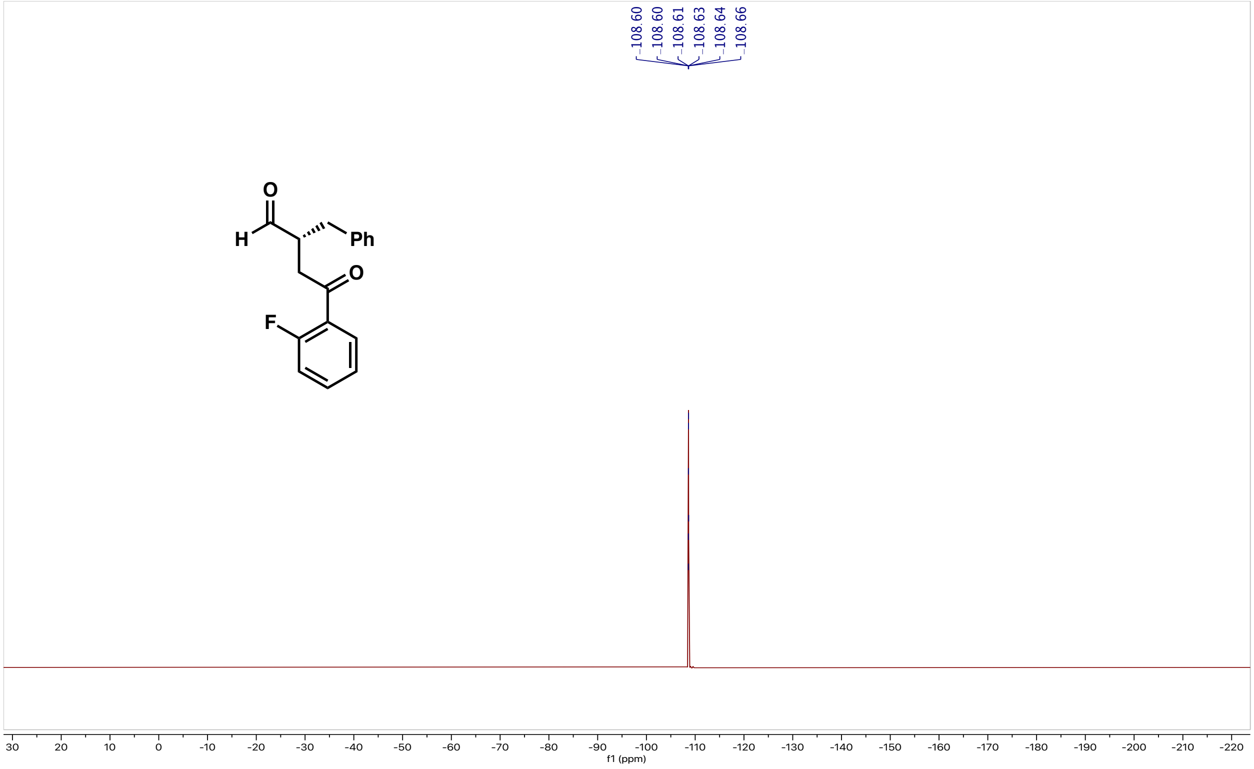
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

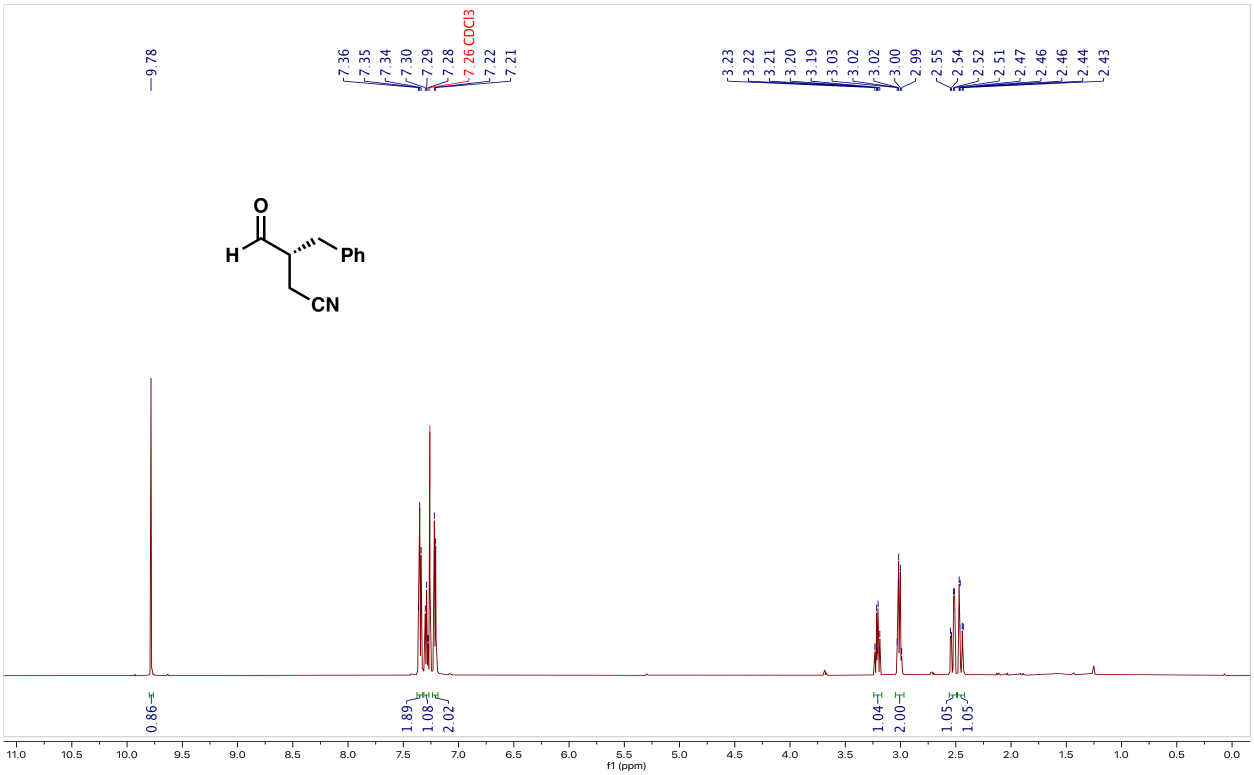


^{19}F NMR (565 MHz, CDCl$_3$)

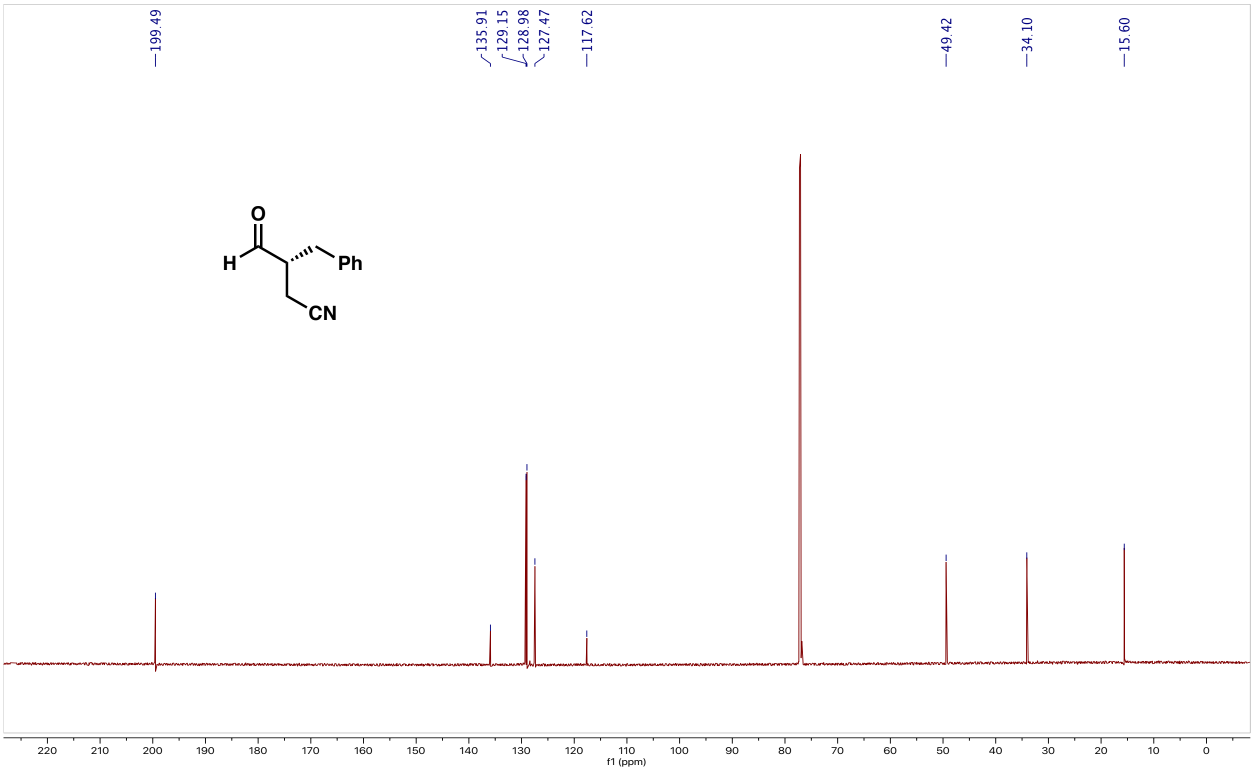


(*R*)-3-Benzyl-4-oxobutanenitrile, 15g :

^{1}H NMR (600 MHz, CDCl$_3$)

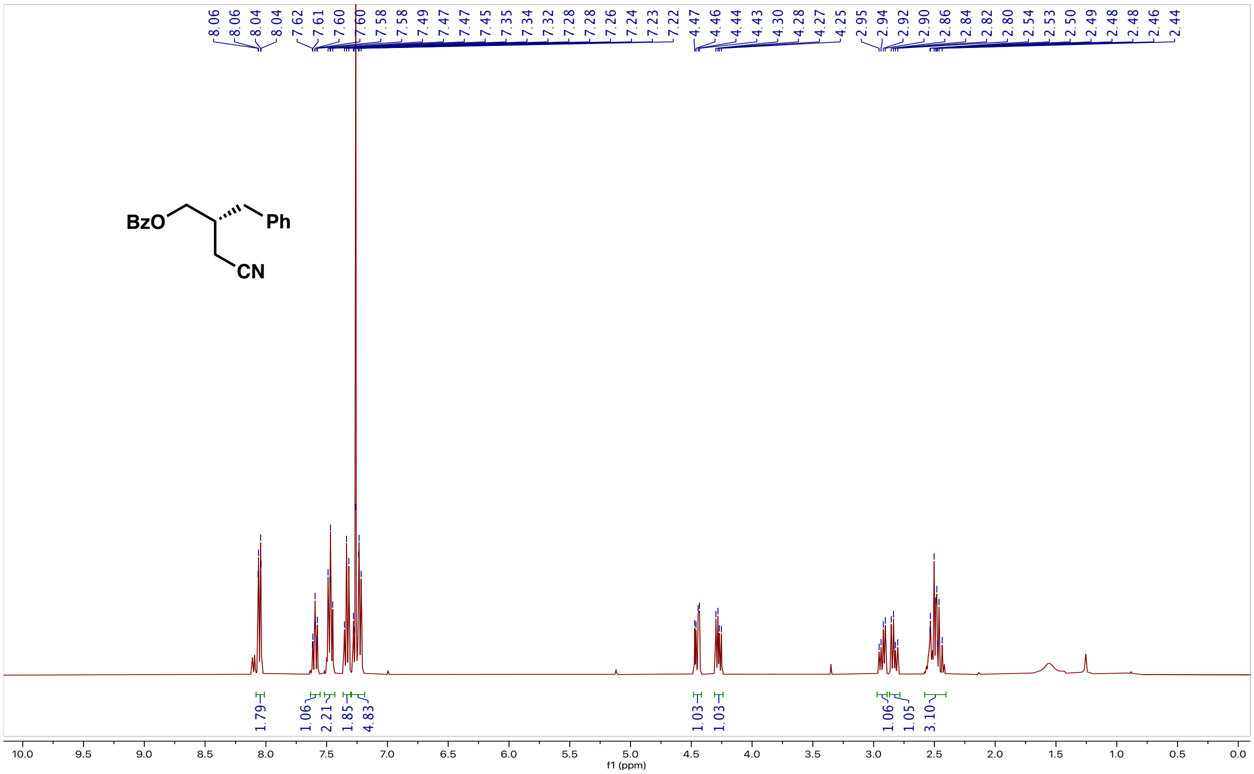


^{13}C NMR (151 MHz, CDCl$_3$)

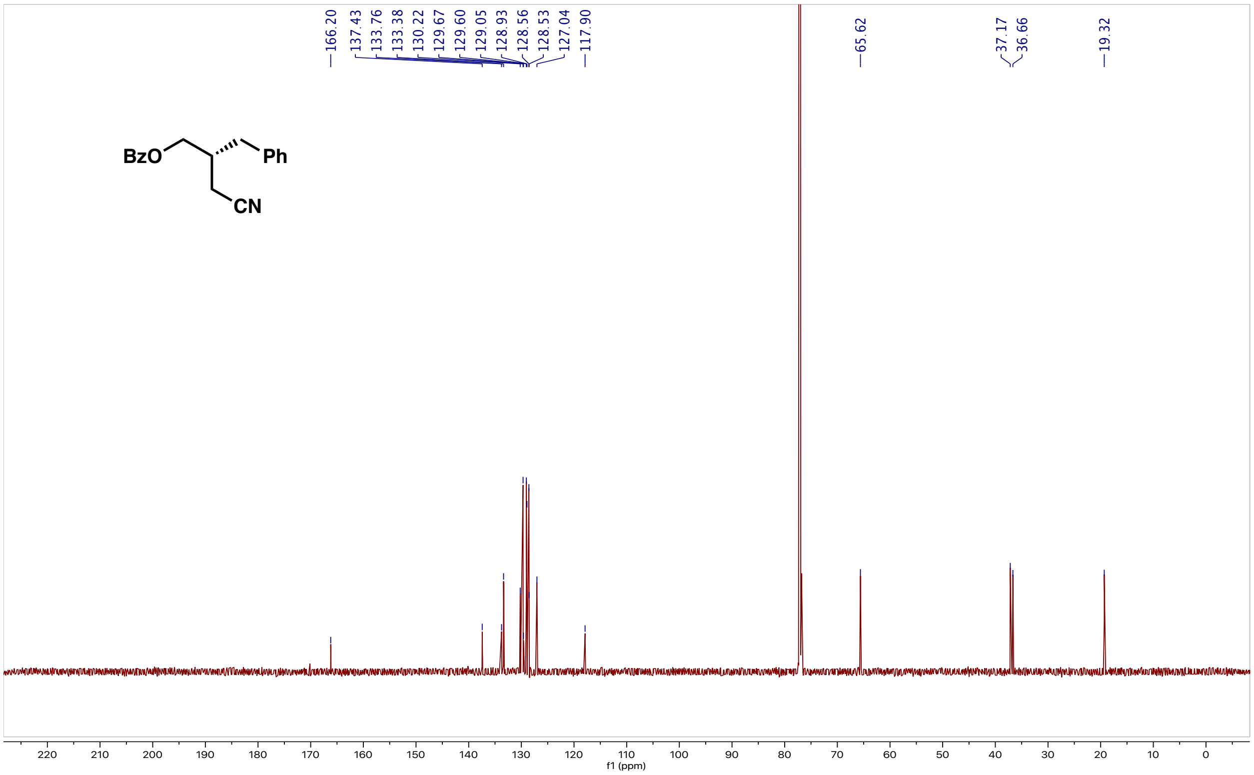


(*R*)-2-Benzyl-3-cyanopropyl benzoate, 15ga :

^{1}H NMR (400 MHz, CDCl$_3$)

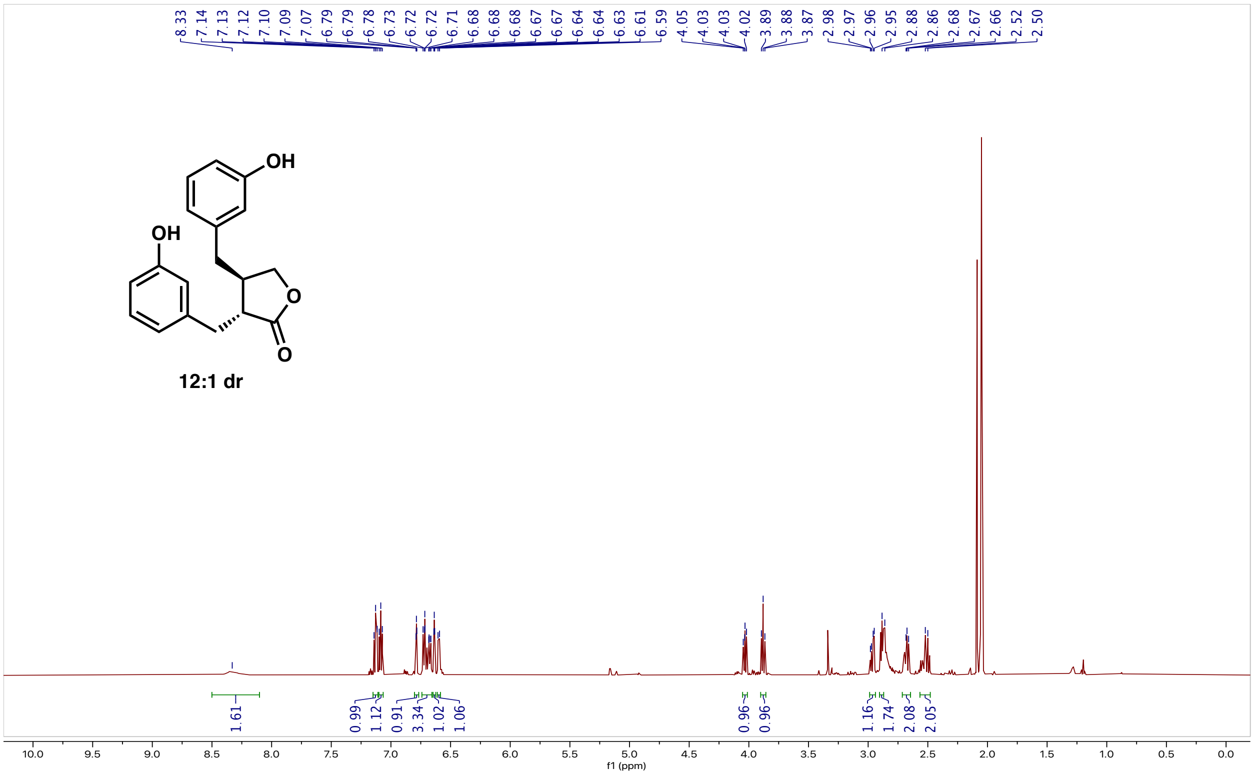


^{13}C NMR (151 MHz, CDCl$_3$)

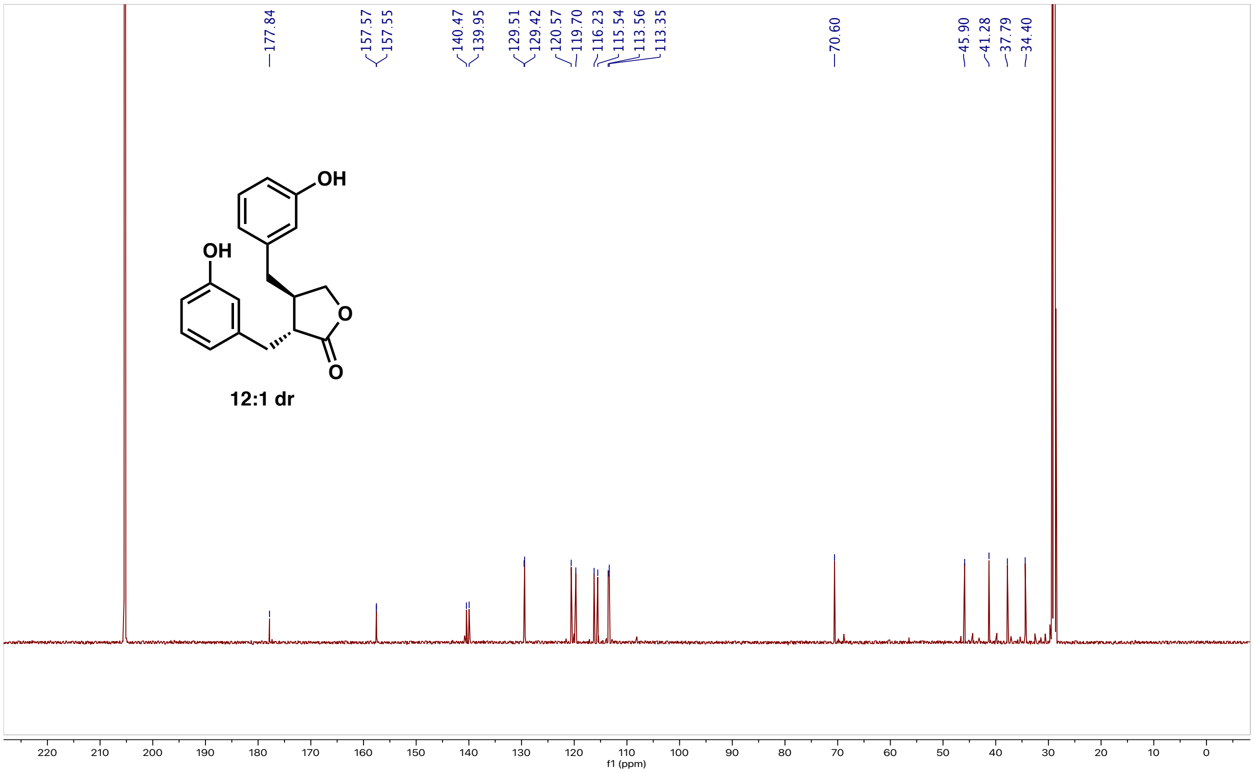


(-)-Enterolactone, 17 :

^{1}H NMR (600 MHz, acetone-d^6)

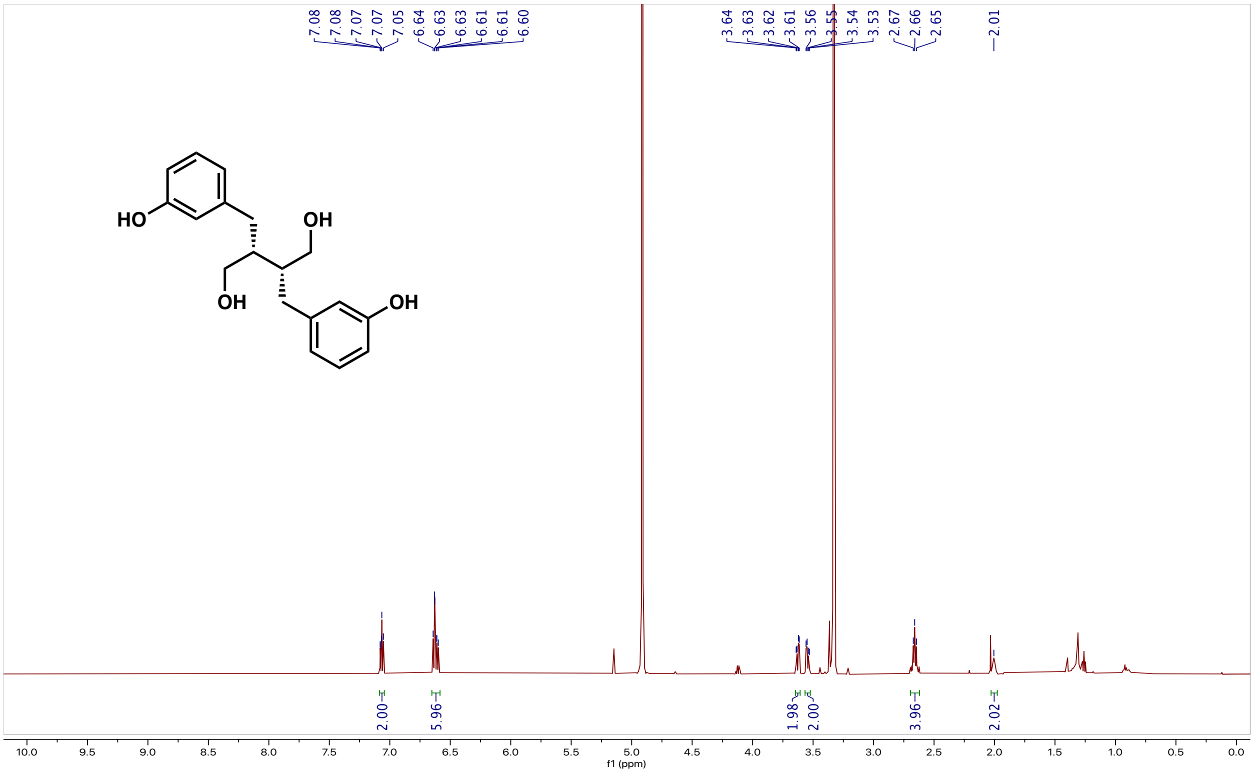


^{13}C NMR (151 MHz, acetone-d^6)

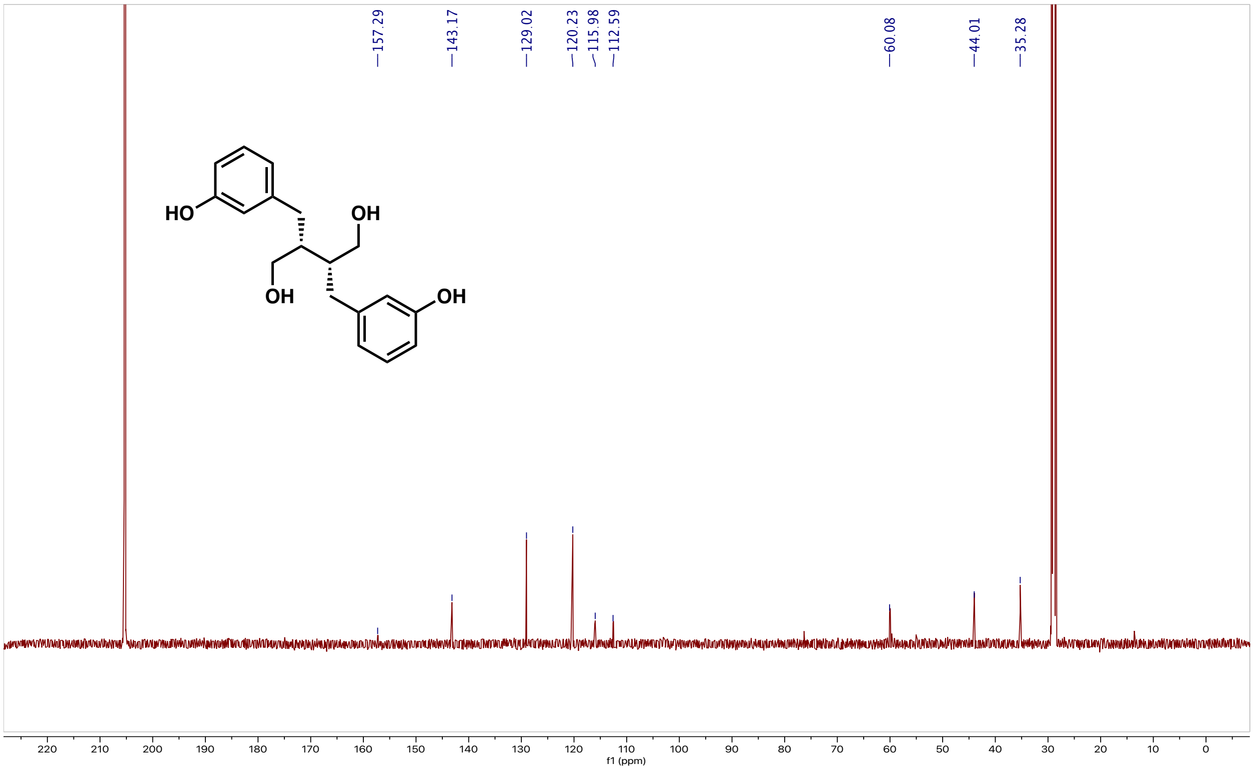


(-)-Enterodiol, 18

^{1}H NMR (600 MHz, CD_3OD)

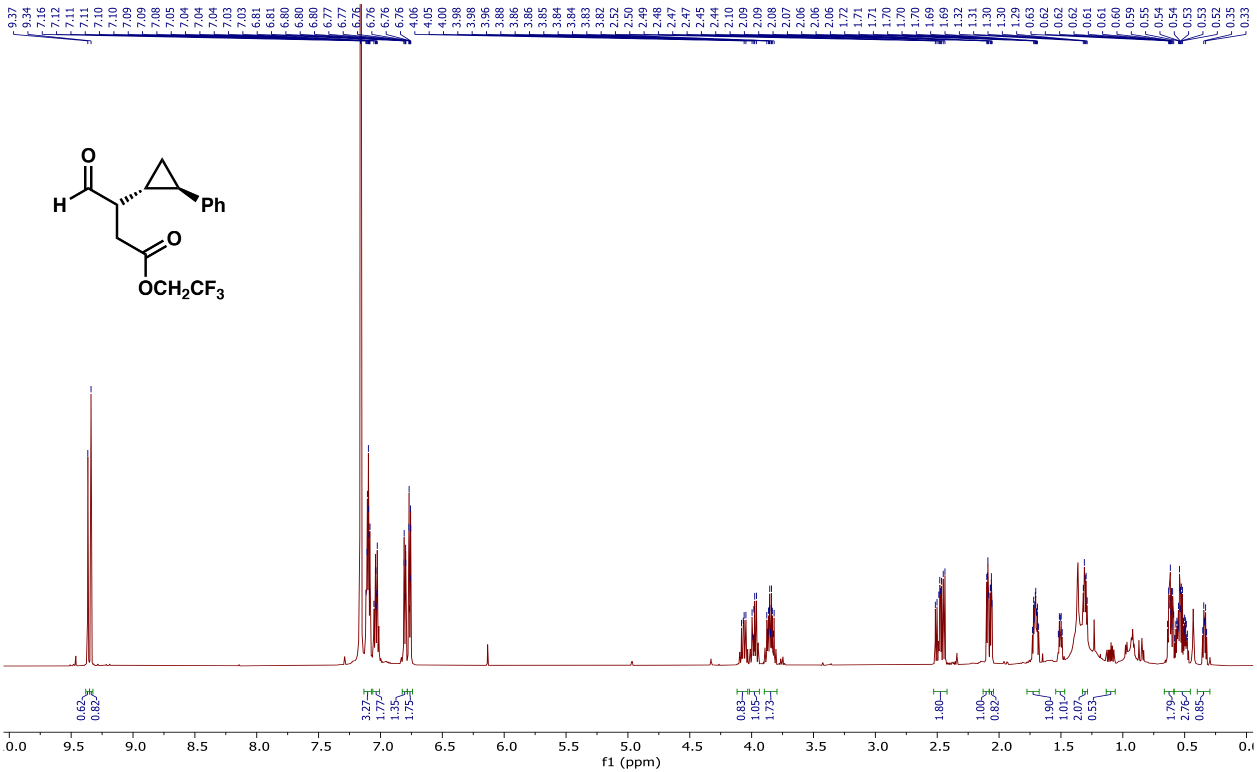


^{13}C NMR (151 MHz, acetone-d^6)

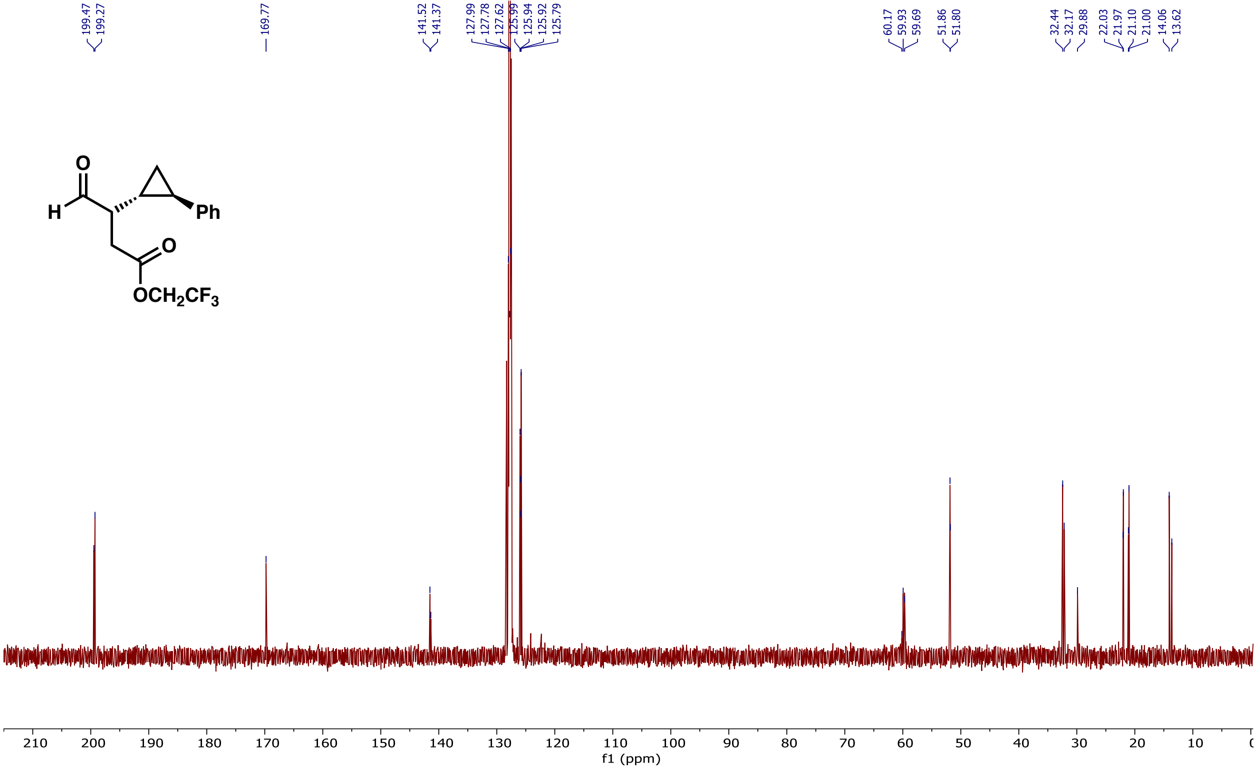


2,2,2-Trifluoroethyl (*R*)-4-oxo-3-((1*R*,2*R*)-2-phenylcyclopropyl)butanoate, *trans*-23:

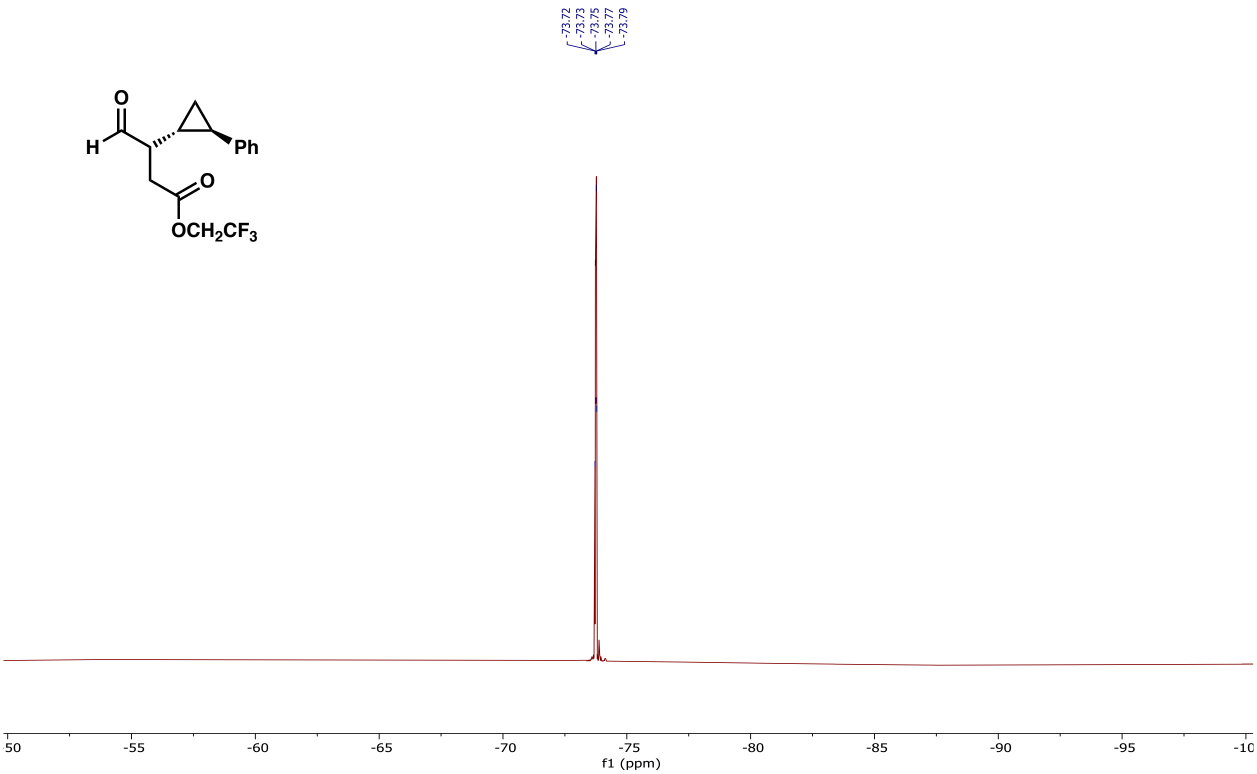
^{1}H NMR (600 MHz, C_6D_6)



^{13}C NMR (151 MHz, C_6D_6)

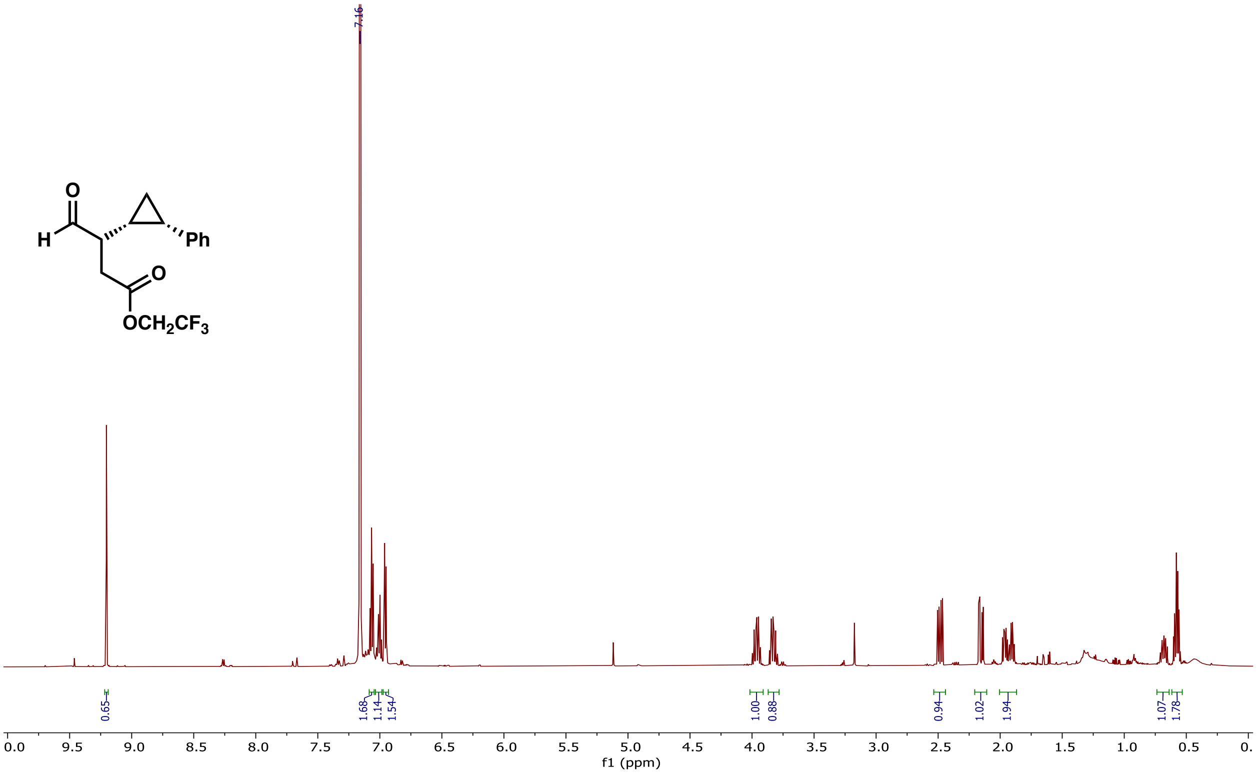


^{19}F NMR (565 MHz, C_6D_6)

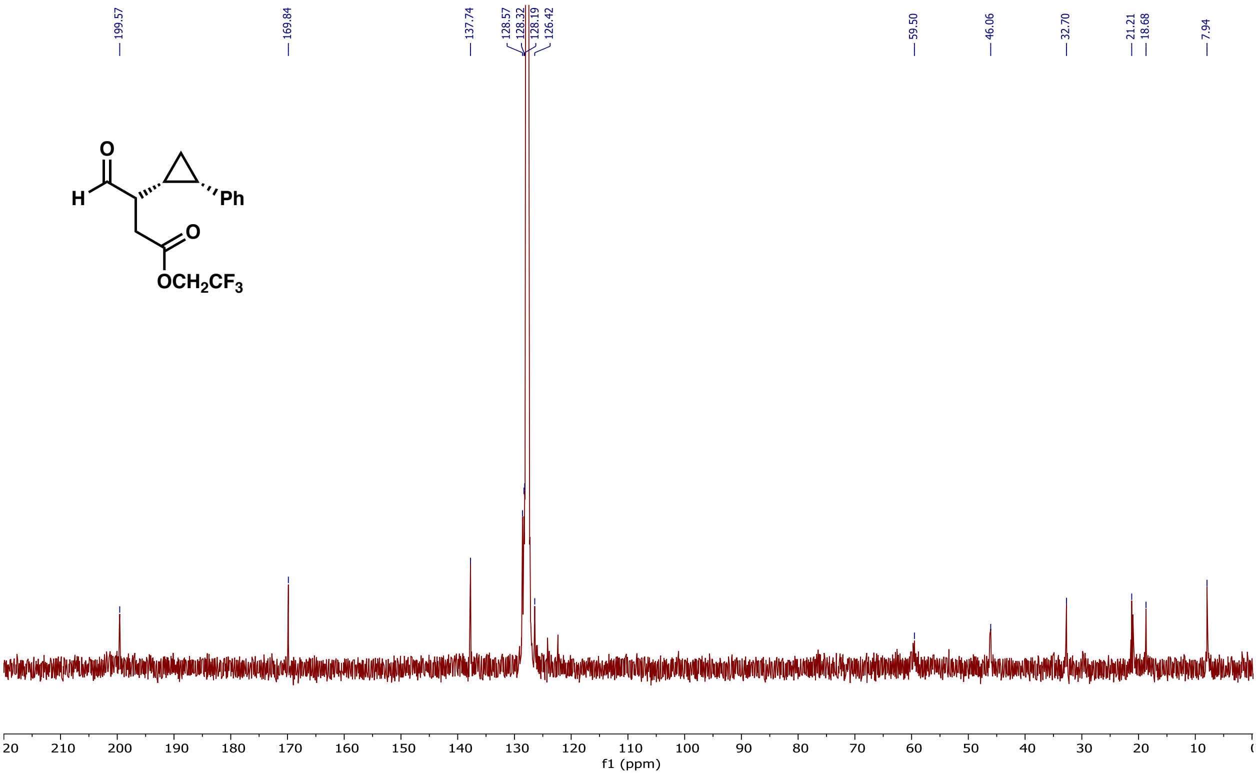


2,2,2-Trifluoroethyl (*R*)-4-oxo-3-((1*R*,2*S*)-2-phenylcyclopropyl)butanoate, *cis*-23:

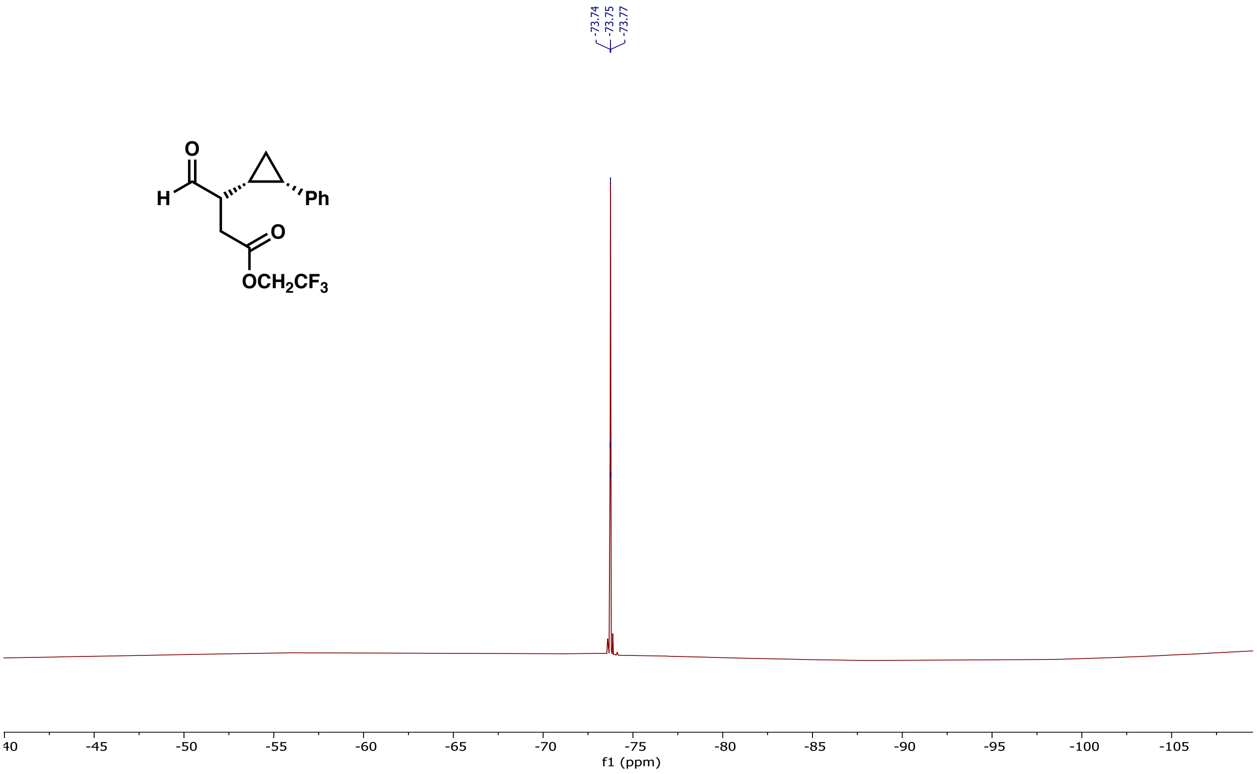
^{1}H NMR (600 MHz, C_6D_6)



^{13}C NMR (151 MHz, C_6D_6)



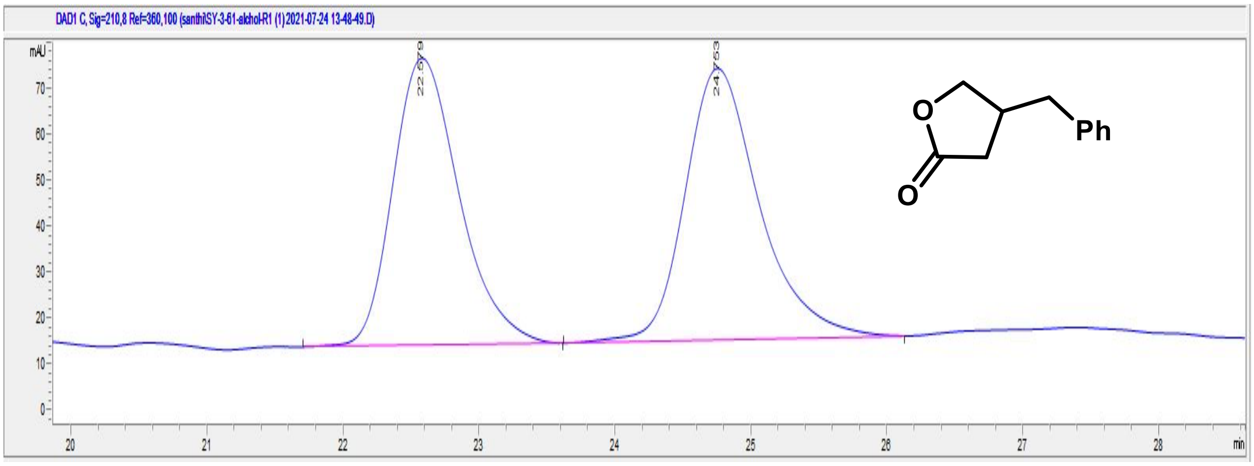
^{19}F NMR (565 MHz, C_6D_6)



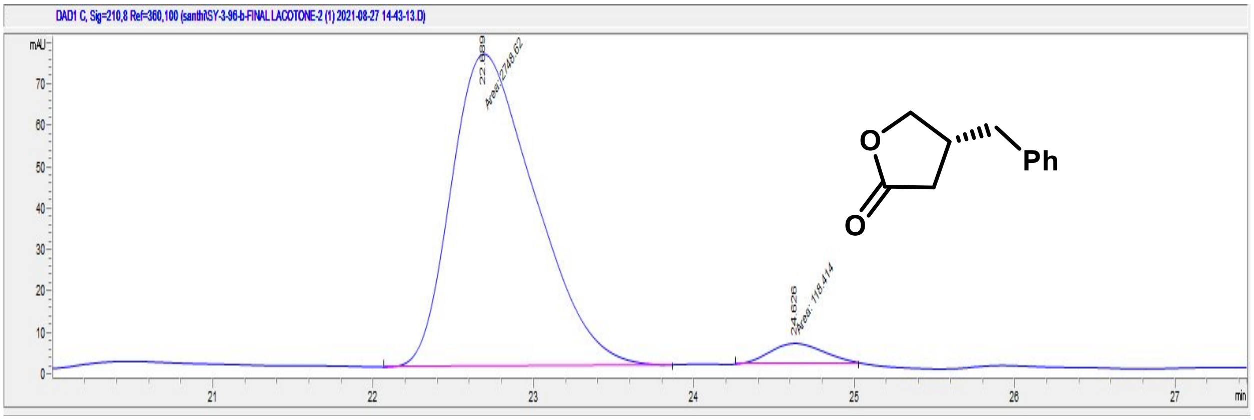
10. HPLC Charts

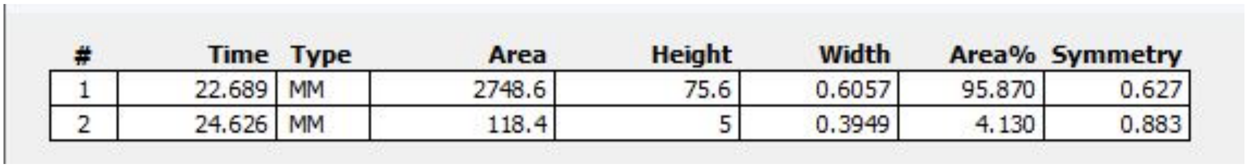
(*R*)-4Benzyldihydrofuran-2(3*H*)-one, 13aa

HPLC conditions: Chiralpak AD_H column (25 cm × 0.46 cm ID), Hex/IPA = 95:05, 0.8 mL/min, 210 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.579	BB	2103.5	62.1	0.515	48.500	0.745
2	24.753	BB	2233.6	58.8	0.5655	51.500	0.75

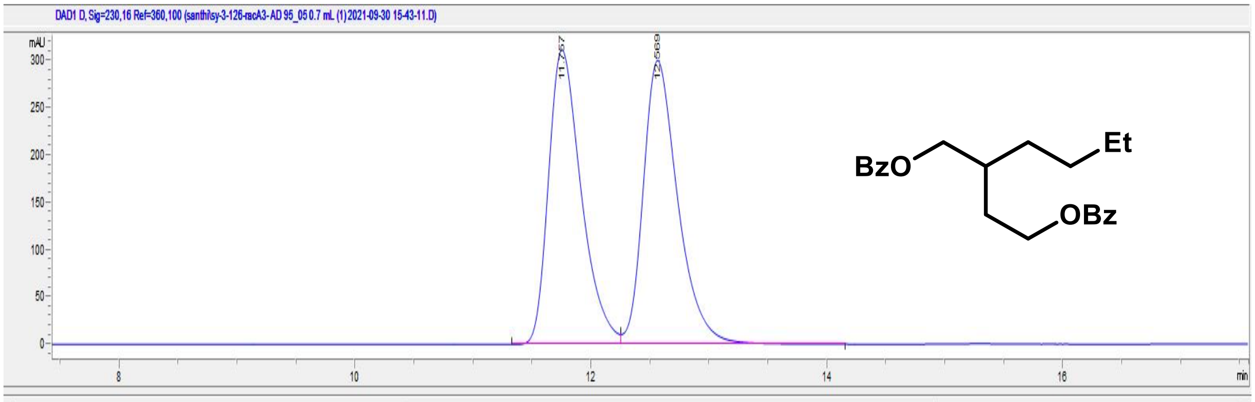


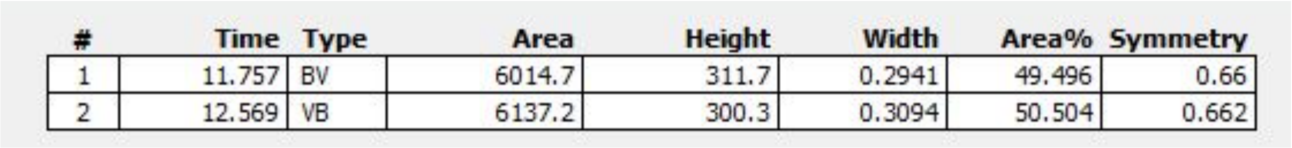


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.689	MM	2748.6	75.6	0.6057	95.870	0.627
2	24.626	MM	118.4	5	0.3949	4.130	0.883

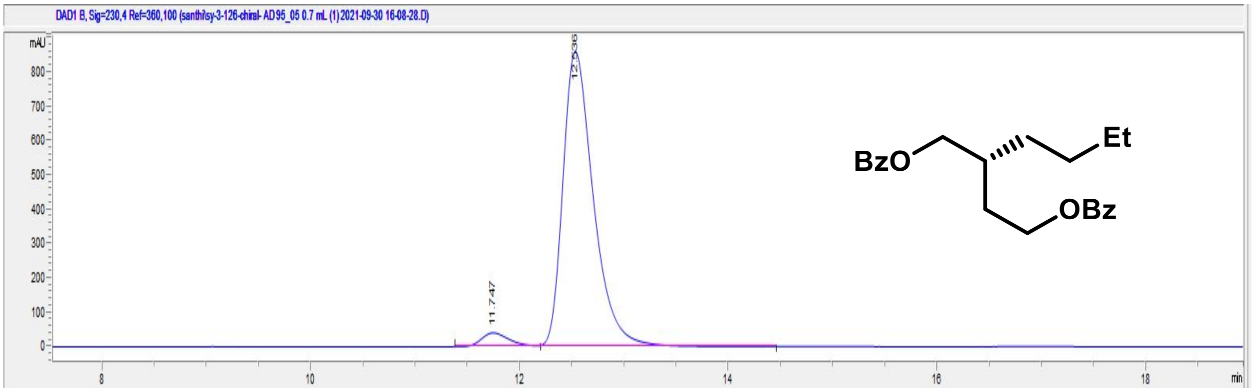
(*R*)-2-Butylbutane-1,4-diyl dibenzoate, 13ba:

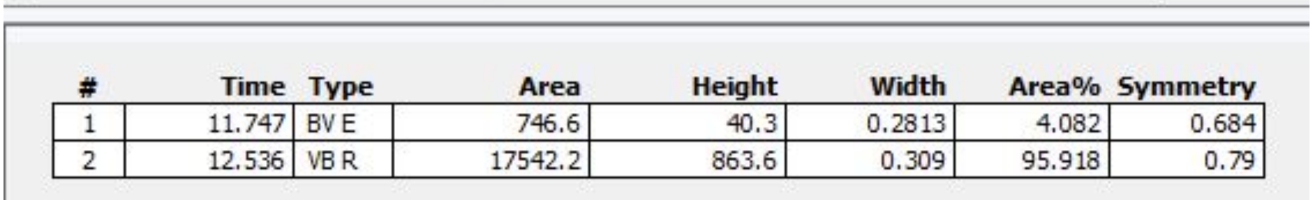
HPLC conditions: Chiralpak AD_H column (25 cm × 0.46 cm ID), Hex/IPA = 95:05, 0.7 mL/min, 230 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.757	BV	6014.7	311.7	0.2941	49.496	0.66
2	12.569	VB	6137.2	300.3	0.3094	50.504	0.662

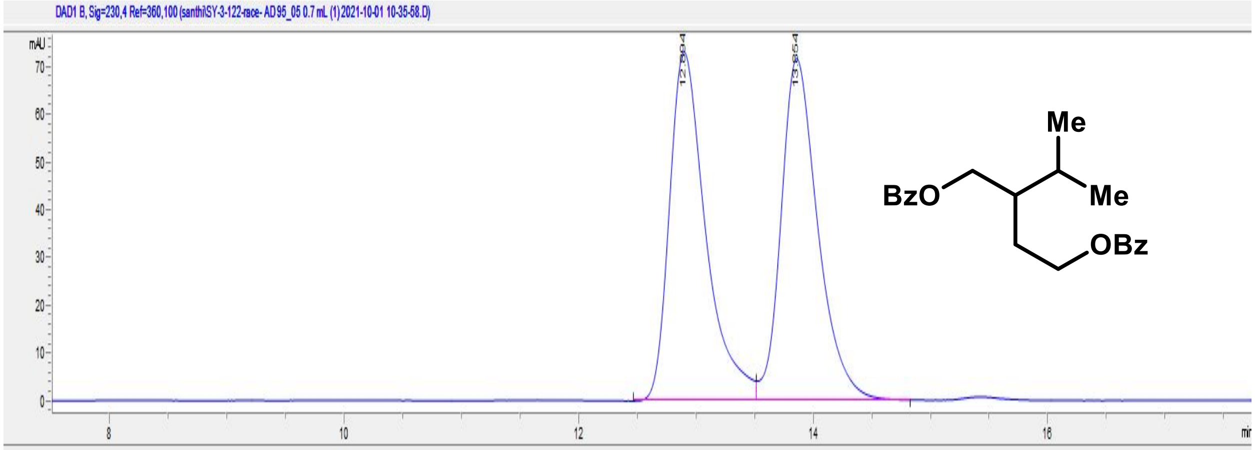


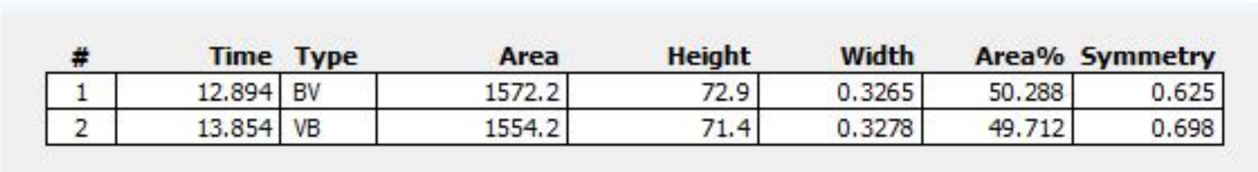


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.747	BV E	746.6	40.3	0.2813	4.082	0.684
2	12.536	VB R	17542.2	863.6	0.309	95.918	0.79

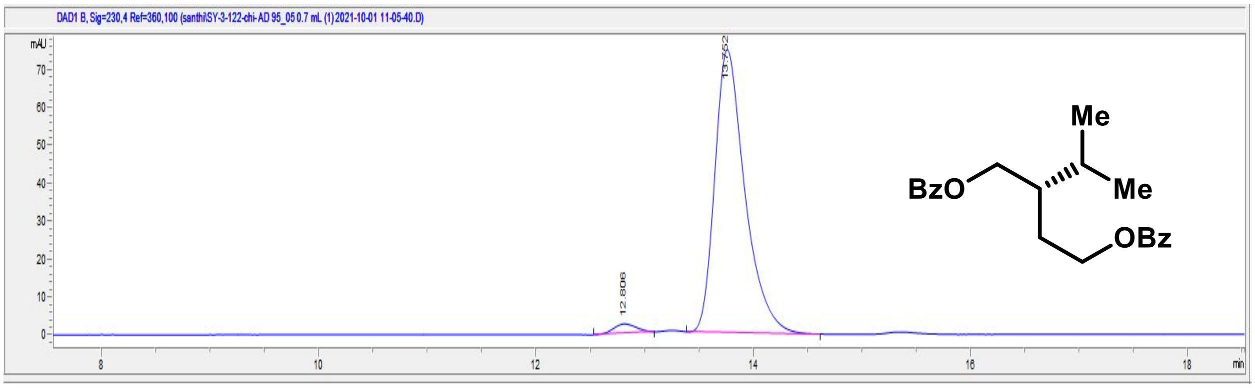
(*S*)-2-Isopropylbutane-1,4-diyl dibenzoate, 13ca:

HPLC conditions: Chiralpak AD_H column (25 cm × 0.46 cm ID), Hex/IPA = 95:05, 0.7 mL/min, 230 nm UV detector.





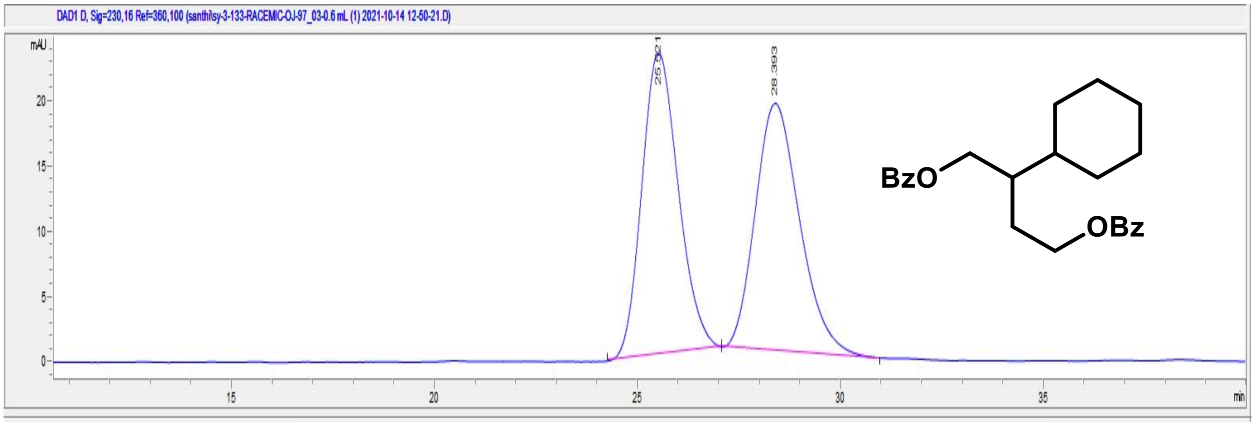
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.894	BV	1572.2	72.9	0.3265	50.288	0.625
2	13.854	VB	1554.2	71.4	0.3278	49.712	0.698

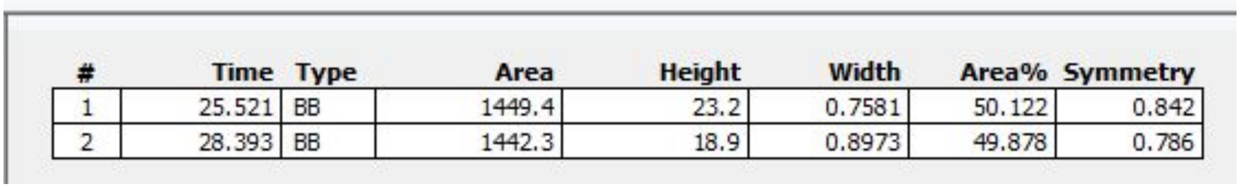


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	12.806	BB	35.8	2.4	0.1845	2.443	0.865
2	13.752	BB	1429.5	74.3	0.2865	97.557	0.663

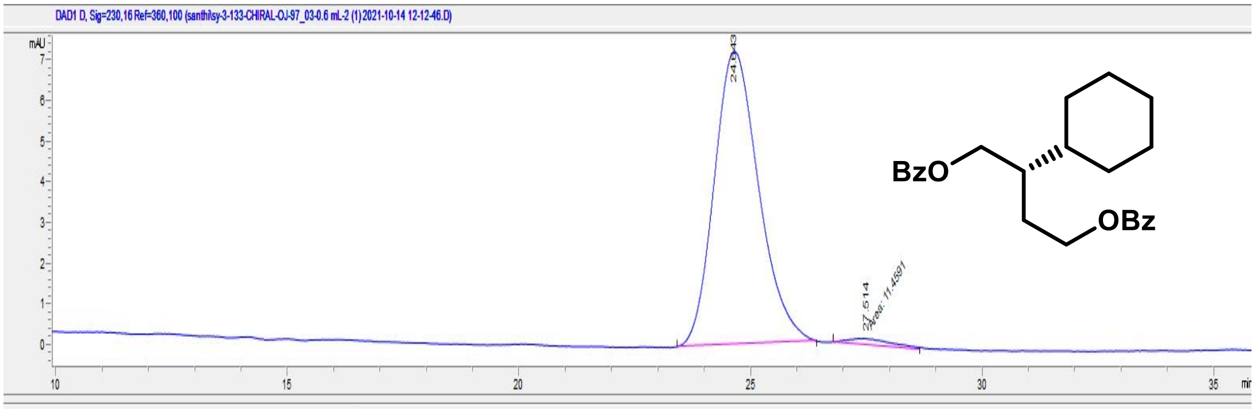
(*S*)-2-Cyclohexylbutane-1,4-diyl dibenzoate, 13da:

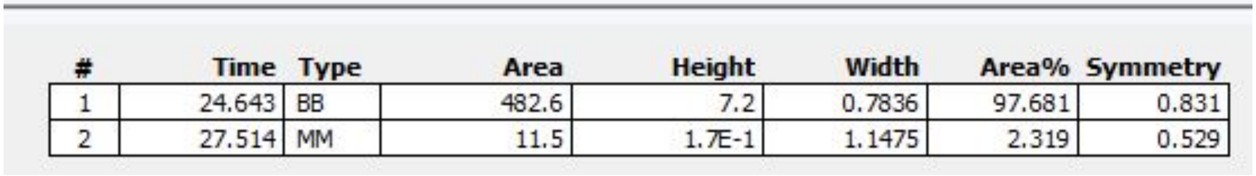
HPLC conditions: Chiralcel OJ_H column (25 cm × 0.46 cm ID), Hex/IPA = 97:03, 0.6 mL/min, 230 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	25.521	BB	1449.4	23.2	0.7581	50.122	0.842
2	28.393	BB	1442.3	18.9	0.8973	49.878	0.786

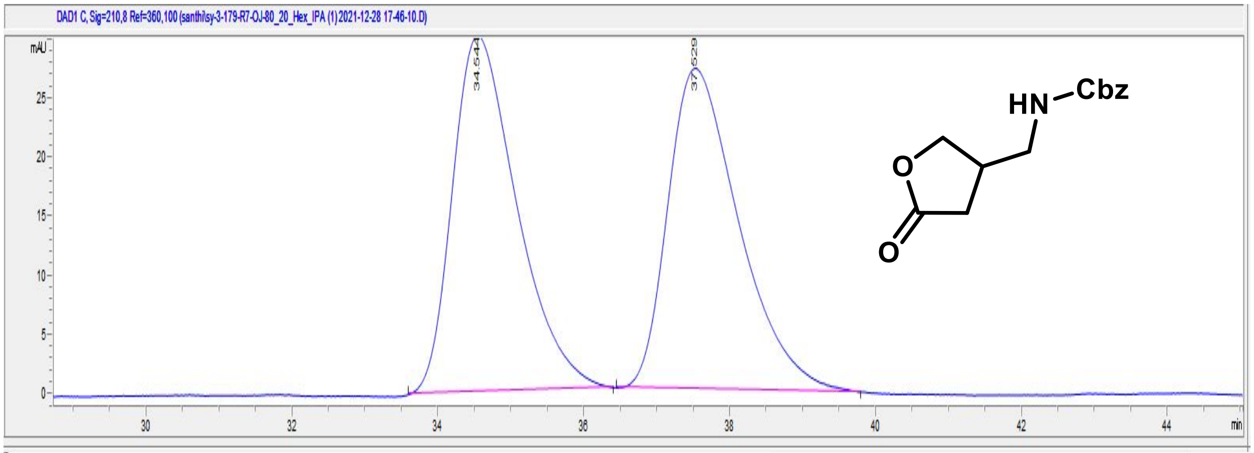




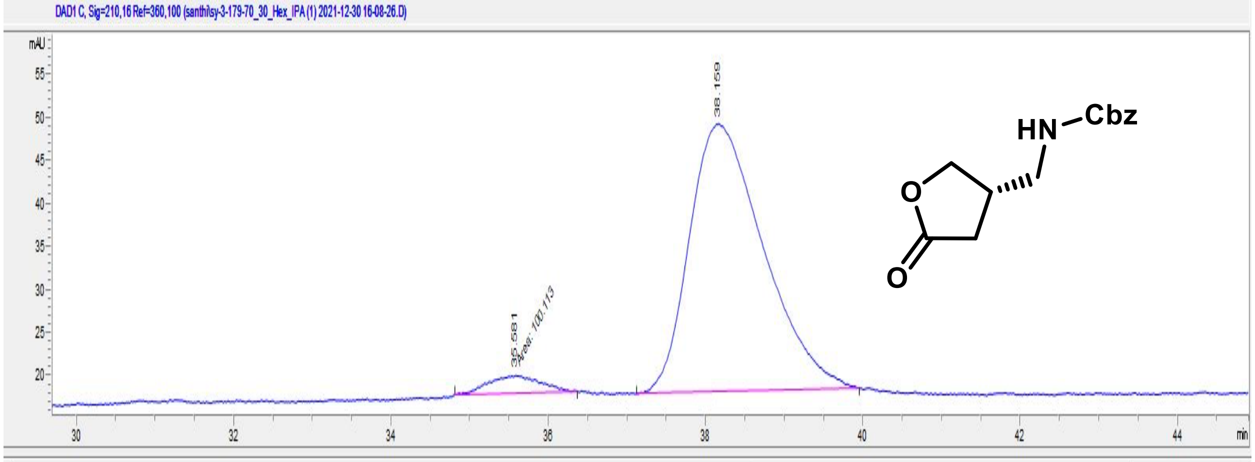
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	24.643	BB	482.6	7.2	0.7836	97.681	0.831
2	27.514	MM	11.5	1.7E-1	1.1475	2.319	0.529

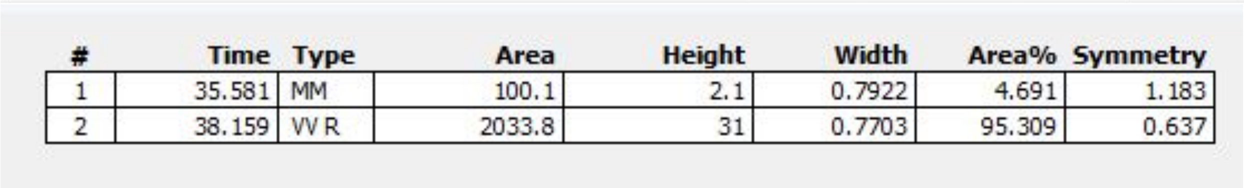
Benzyl (*S*)-((5-oxotetrahydrofuran-3-yl)methyl)carbamate, 13fa:

HPLC conditions: Chiralcel OJ_H column (25 cm × 0.46 cm ID), Hex/IPA = 70:30, 0.8 mL/min, 230 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	34.544	BB	1855	30.2	0.7256	50.141	0.632
2	37.529	BB	1844.6	27.2	0.8059	49.859	0.602

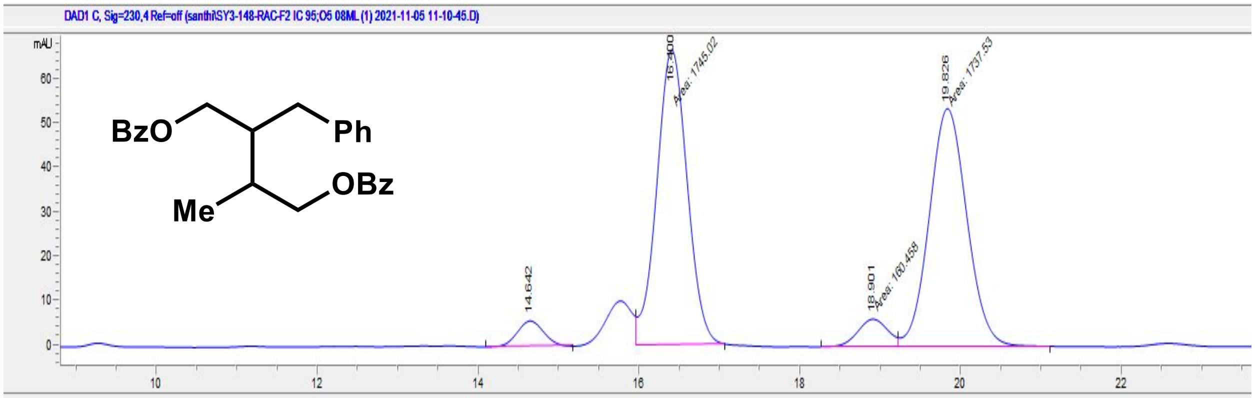




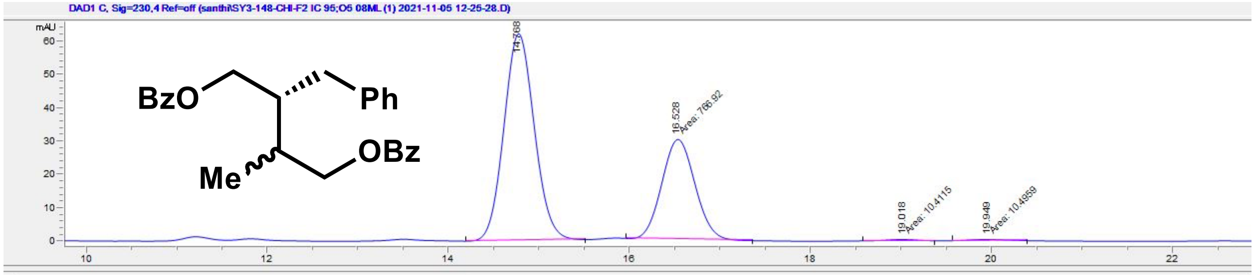
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	35.581	MM	100.1	2.1	0.7922	4.691	1.183
2	38.159	VV R	2033.8	31	0.7703	95.309	0.637

(2*R*)-2-Benzyl-3-methylbutane-1,4-diyl dibenzoate, 13ga:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 95:05, 0.8 mL/min, 230 nm UV detector.



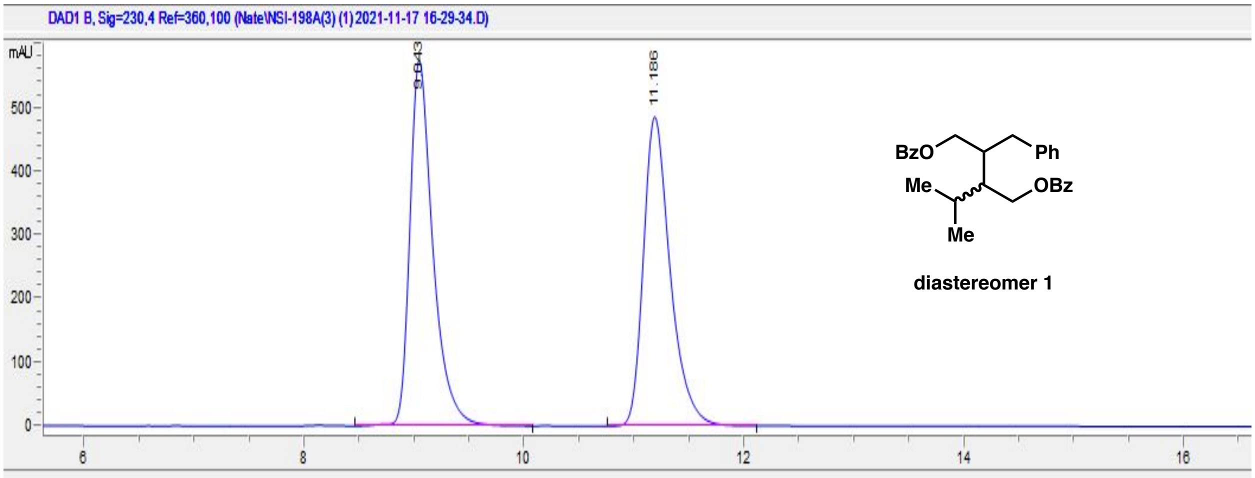
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.642	BB	131.8	5.7	0.3563	3.492	0.937
2	16.4	FM T	1745	66.4	0.4378	46.228	0.946
3	18.901	MF	160.5	6.2	0.4331	4.251	1.005
4	19.826	FM	1737.5	53.5	0.5418	46.029	0.918



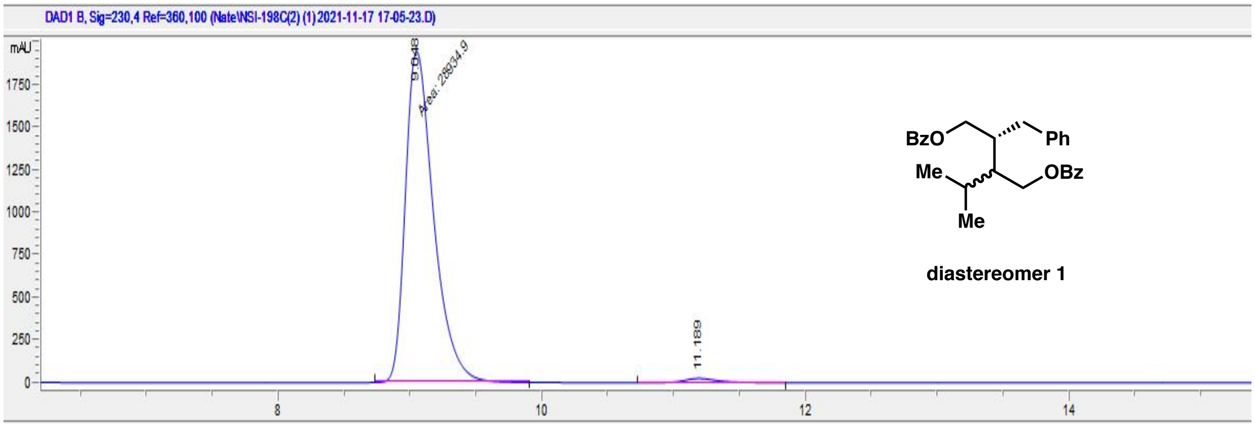
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	14.768	BB	1451.8	62.2	0.3622	64.823	0.904
2	16.528	MM	766.9	30.1	0.4251	34.243	0.917
3	19.018	MM	10.4	4.1E-1	0.4267	0.465	1.243
4	19.949	MM	10.5	3.6E-1	0.4798	0.469	1.002

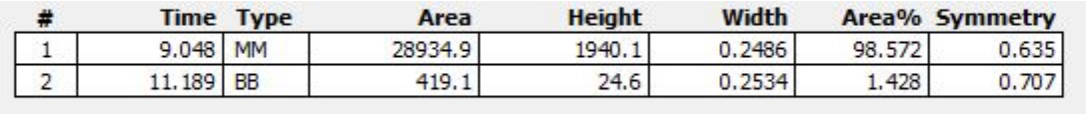
(2*R*)-2-Benzyl-3-isopropylbutane-1,4-diyl dibenzoate, 13ha:

HPLC conditions: Chiralpak AD-H column (25 cm × 0.46 cm ID), Hex/IPA = 95:5, 0.8 mL/min, 230 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.043	BB	8395.8	576.4	0.2169	50.418	0.639
2	11.186	BB	8256.6	487.1	0.2568	49.582	0.683

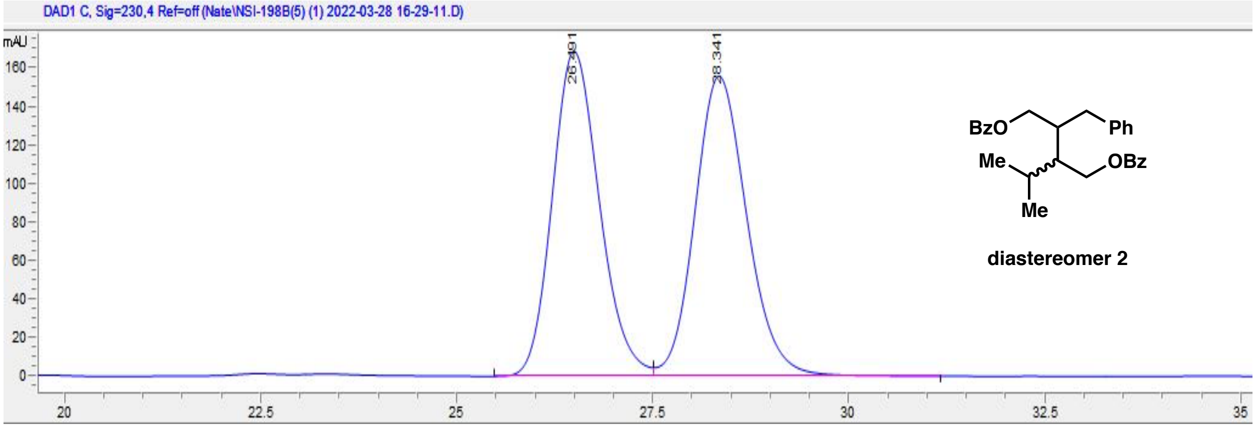




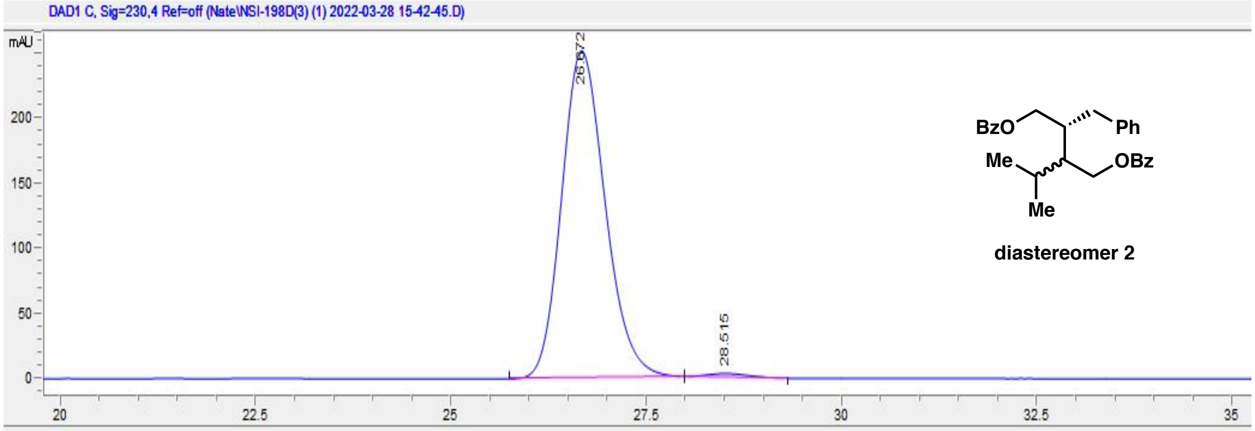
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.048	MM	28934.9	1940.1	0.2486	98.572	0.635
2	11.189	BB	419.1	24.6	0.2534	1.428	0.707

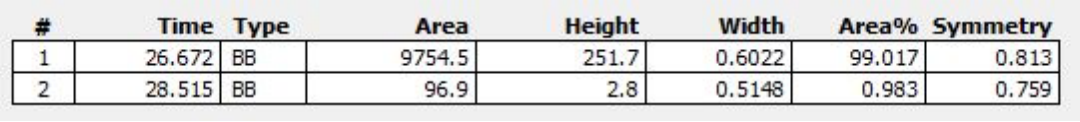
(2*R*)-2-Benzyl-3-isopropylbutane-1,4-diyl dibenzoate, 13hb:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 98:2, 0.5 mL/min, 230 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	26.491	BV	7070.8	169.4	0.6469	49.552	0.816
2	28.341	VB	7198.6	156.5	0.7127	50.448	0.825

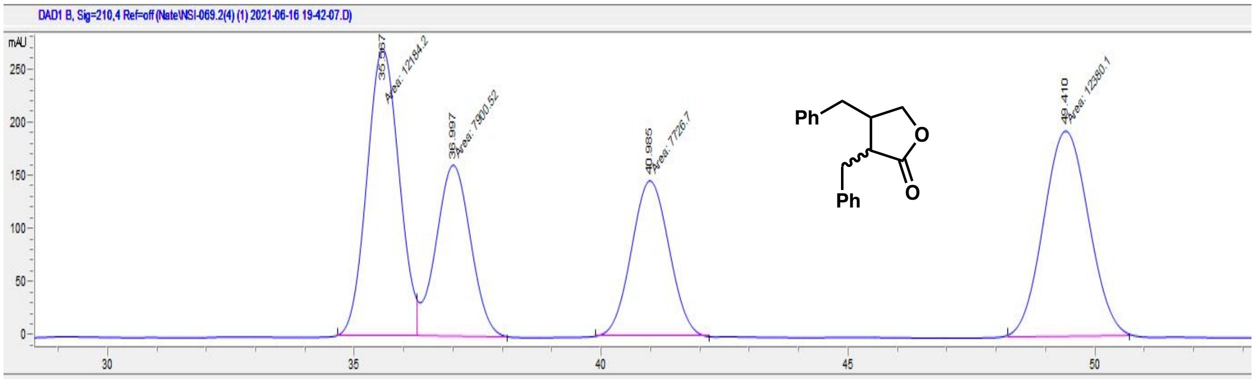




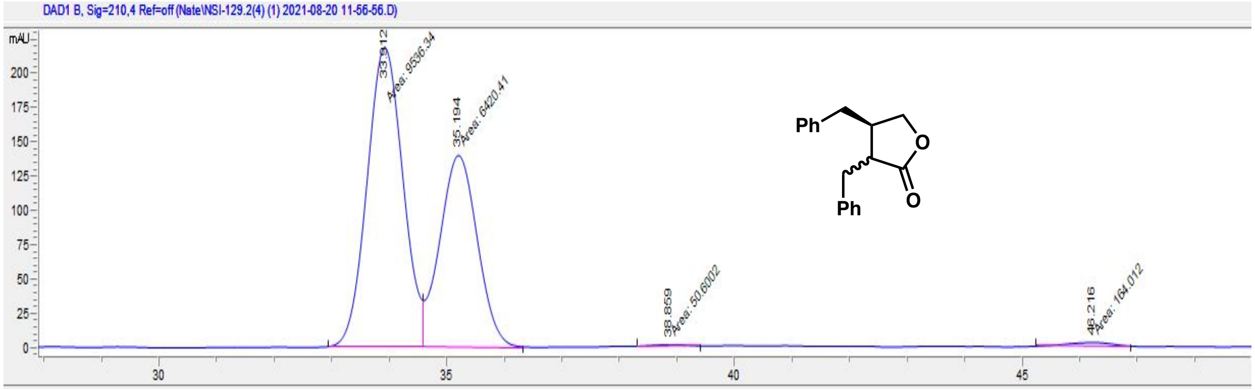
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	26.672	BB	9754.5	251.7	0.6022	99.017	0.813
2	28.515	BB	96.9	2.8	0.5148	0.983	0.759

(4*R*)-3,4-Dibenzyldihydrofuran-2(3H)-one, 13ia:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 0.8 mL/min, 210 nm UV detector.



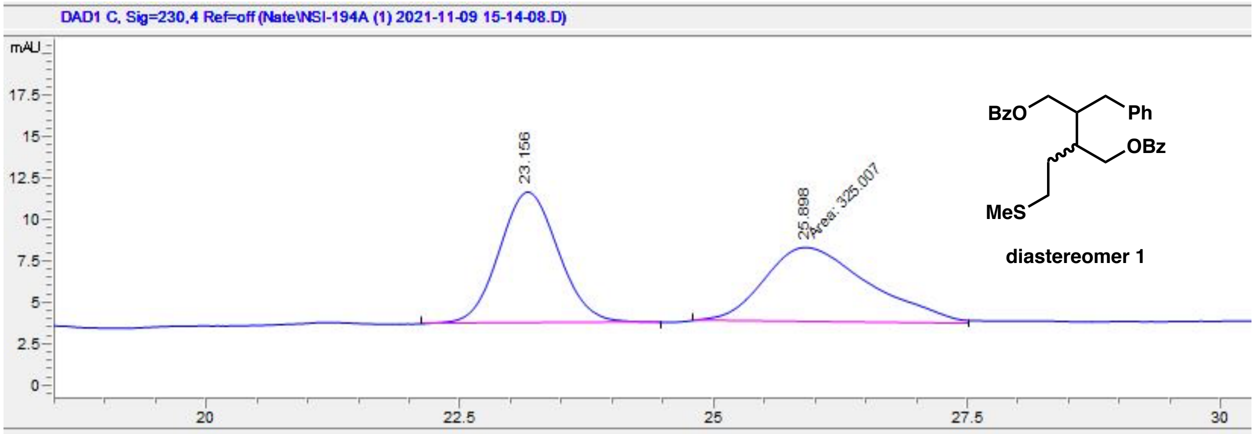
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	35.567	MM	12184.2	269.7	0.753	30.315	0.947
2	36.997	MM	7900.5	160.8	0.8187	19.657	0.967
3	40.985	MM	7726.7	145.8	0.8835	19.225	0.944
4	49.41	MM	12380.1	193.5	1.0662	30.803	0.94



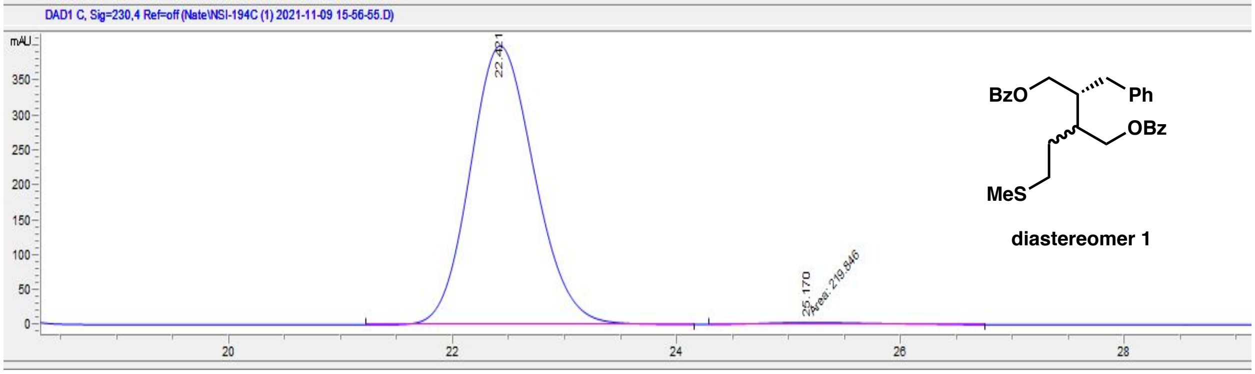
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	33.912	MM	9536.3	219.6	0.7237	58.971	0.947
2	35.194	MM	6420.4	140.8	0.7599	39.702	0.951
3	38.859	MM	50.6	1.2	0.7092	0.313	1.127
4	46.216	MM	164	2.9	0.9364	1.014	1.345

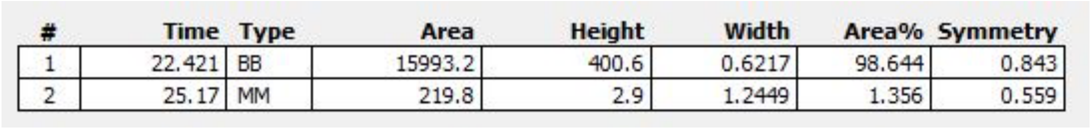
(2*R*)-2-Benzyl-3-(2-(methylthio)ethyl)butane-1,4-diyl dibenzoate , 13ja:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 95:5, 0.8 mL/min, 230 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.156	BB	322	7.9	0.6225	49.769	0.913
2	25.898	MM	325	4.5	1.2059	50.231	0.644

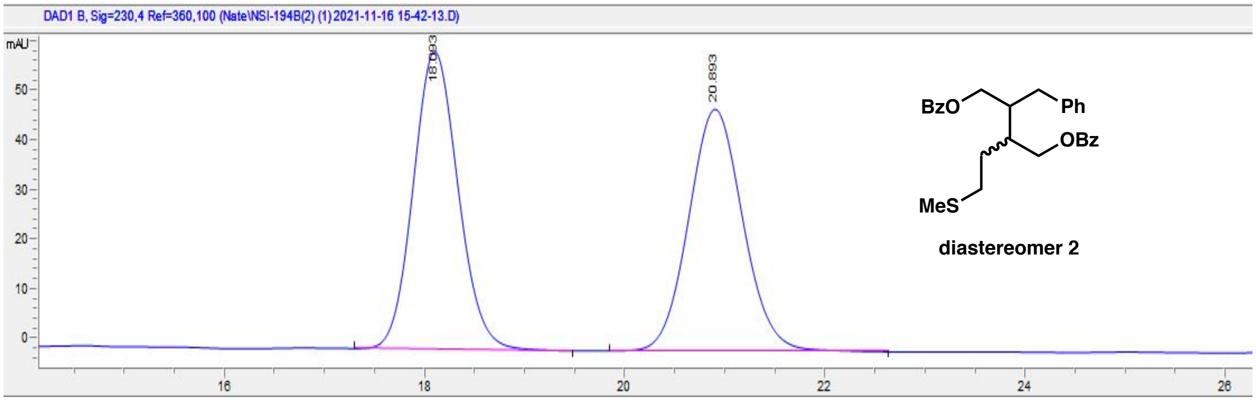




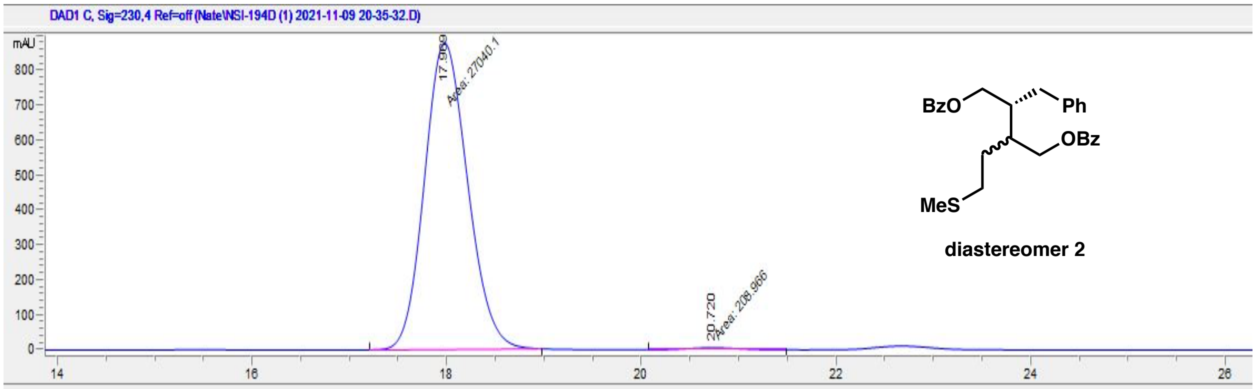
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.421	BB	15993.2	400.6	0.6217	98.644	0.843
2	25.17	MM	219.8	2.9	1.2449	1.356	0.559

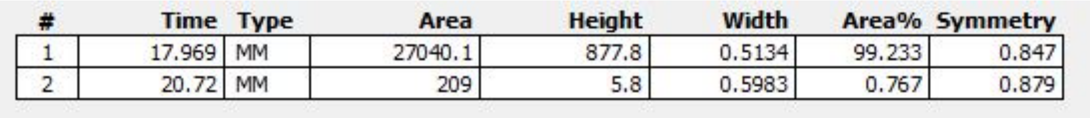
(2*R*)-2-Benzyl-3-(2-(methylthio)ethyl)butane-1,4-diyl dibenzoate , 13jb:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 95:5, 0.8 mL/min, 230 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.093	BB	1871.8	60.1	0.4853	50.432	0.876
2	20.893	BB	1839.7	48.8	0.5839	49.568	0.913

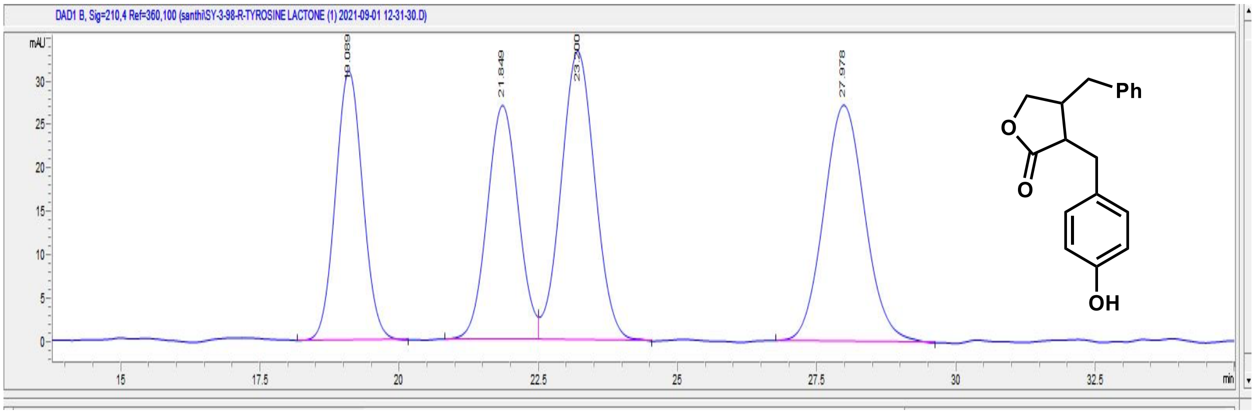


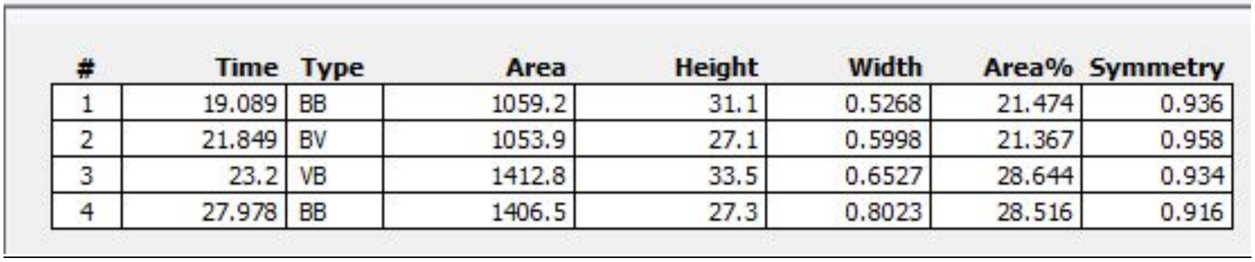


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	17.969	MM	27040.1	877.8	0.5134	99.233	0.847
2	20.72	MM	209	5.8	0.5983	0.767	0.879

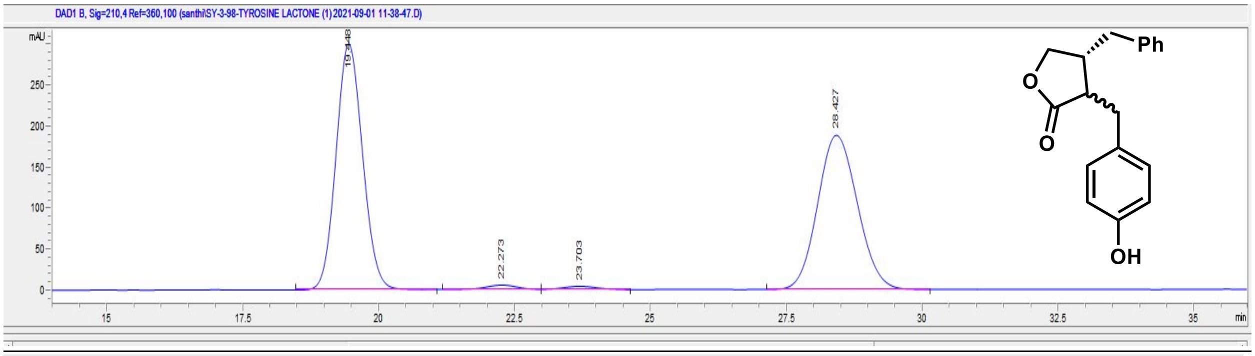
(4*R*)-4-Benzyl-3-(4-hydroxybenzyl)dihydrofuran-2(3*H*)-one, 13ka:

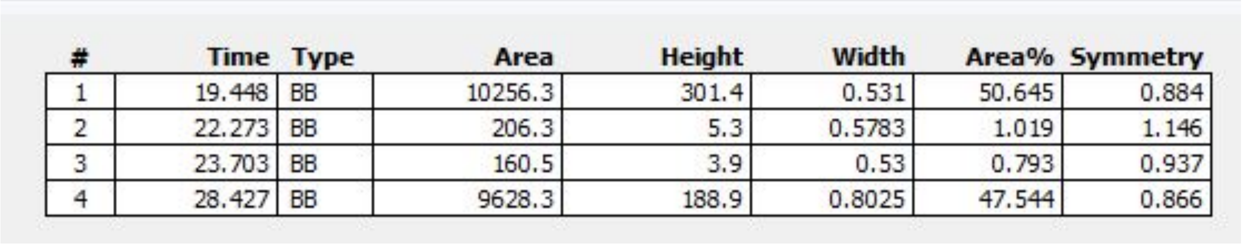
HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 80:20, 0.9 mL/min, 230 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.089	BB	1059.2	31.1	0.5268	21.474	0.936
2	21.849	BV	1053.9	27.1	0.5998	21.367	0.958
3	23.2	VB	1412.8	33.5	0.6527	28.644	0.934
4	27.978	BB	1406.5	27.3	0.8023	28.516	0.916

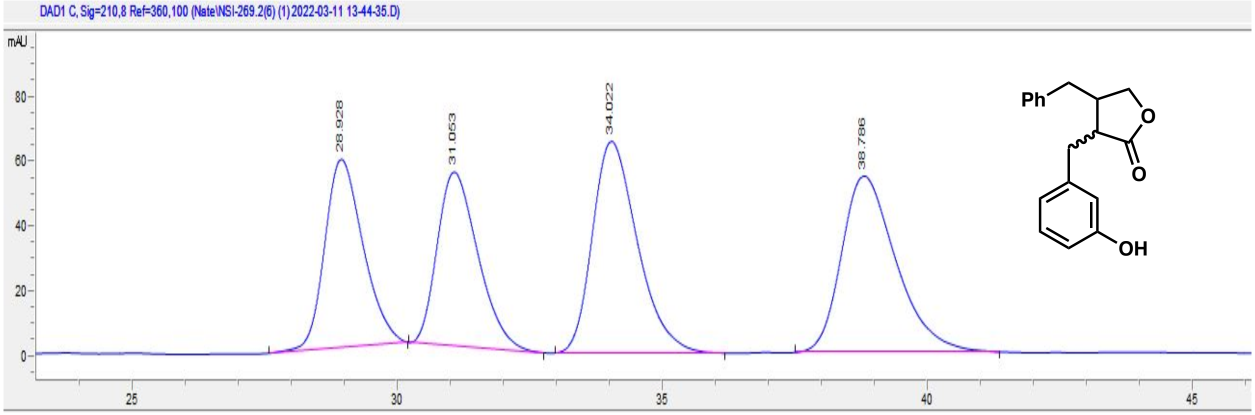


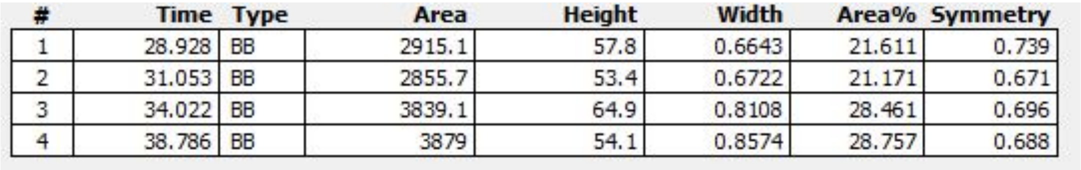


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.448	BB	10256.3	301.4	0.531	50.645	0.884
2	22.273	BB	206.3	5.3	0.5783	1.019	1.146
3	23.703	BB	160.5	3.9	0.53	0.793	0.937
4	28.427	BB	9628.3	188.9	0.8025	47.544	0.866

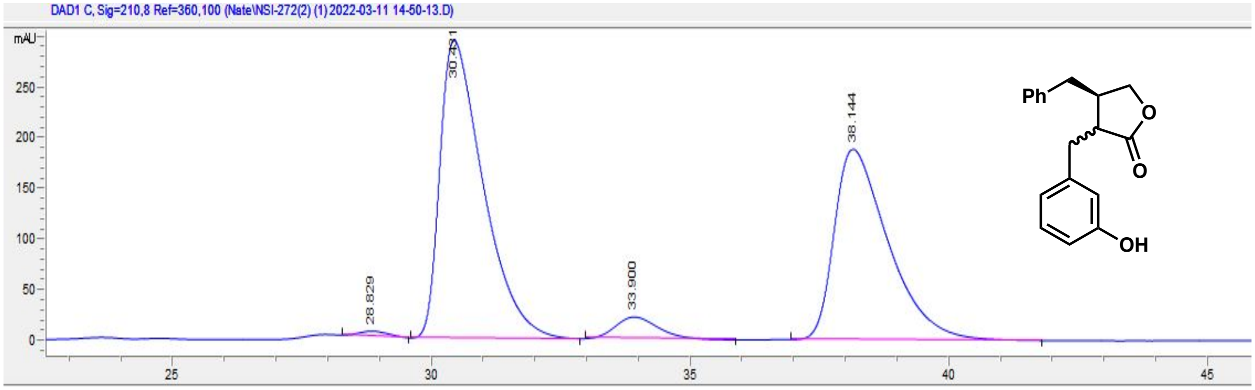
(4*R*)-4-Benzyl-3-(3-hydroxybenzyl)dihydrofuran-2(3H)-one, 13la:

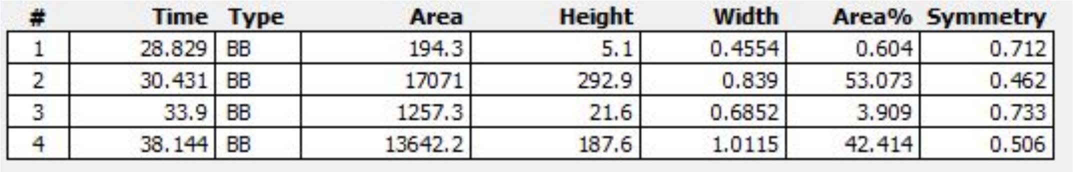
HPLC conditions: Chiralcel OJ-H column (25 cm × 0.46 cm ID), Hex/IPA = 80:20, 0.8 mL/min, 210 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	28.928	BB	2915.1	57.8	0.6643	21.611	0.739
2	31.053	BB	2855.7	53.4	0.6722	21.171	0.671
3	34.022	BB	3839.1	64.9	0.8108	28.461	0.696
4	38.786	BB	3879	54.1	0.8574	28.757	0.688

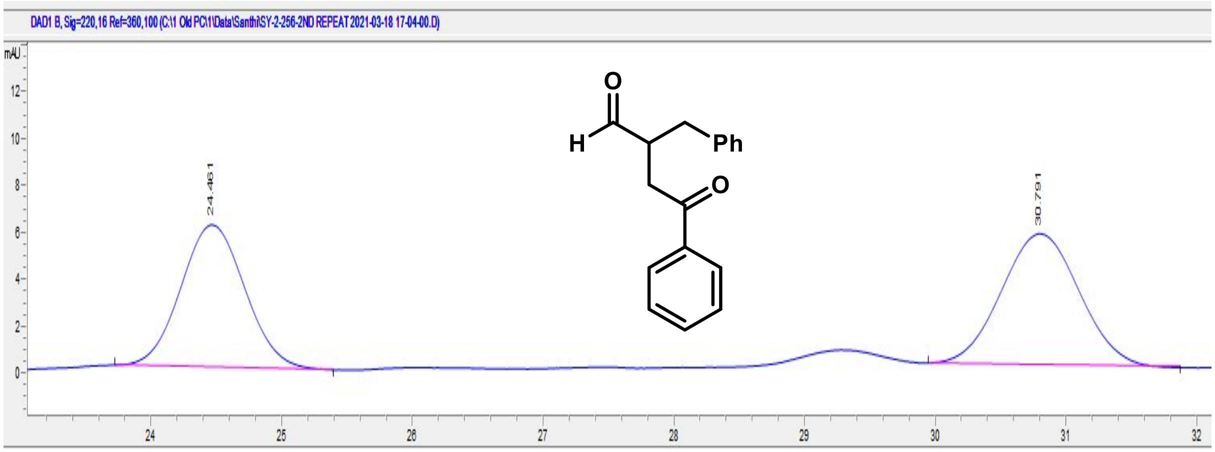


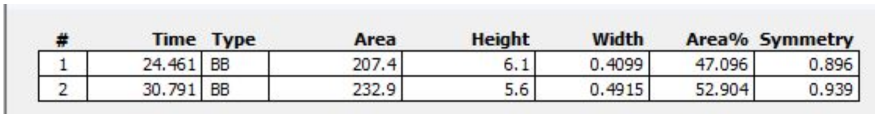


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	28.829	BB	194.3	5.1	0.4554	0.604	0.712
2	30.431	BB	17071	292.9	0.839	53.073	0.462
3	33.9	BB	1257.3	21.6	0.6852	3.909	0.733
4	38.144	BB	13642.2	187.6	1.0115	42.414	0.506

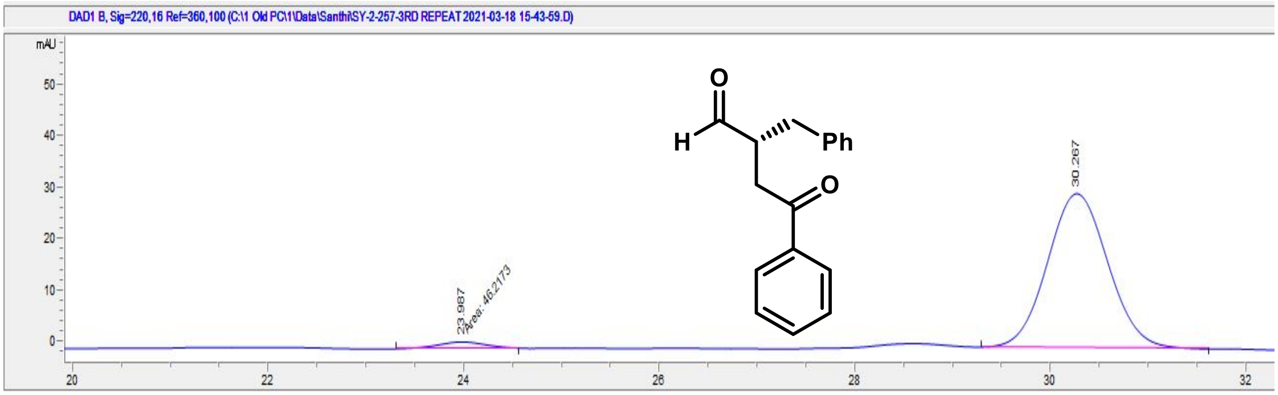
(*R*)-2-Benzyl-4-oxo-4-phenylbutanal, 15a

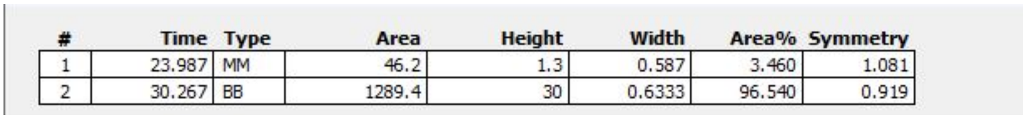
HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 0.8 mL/min, 220 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	24.461	BB	207.4	6.1	0.4099	47.096	0.896
2	30.791	BB	232.9	5.6	0.4915	52.904	0.939

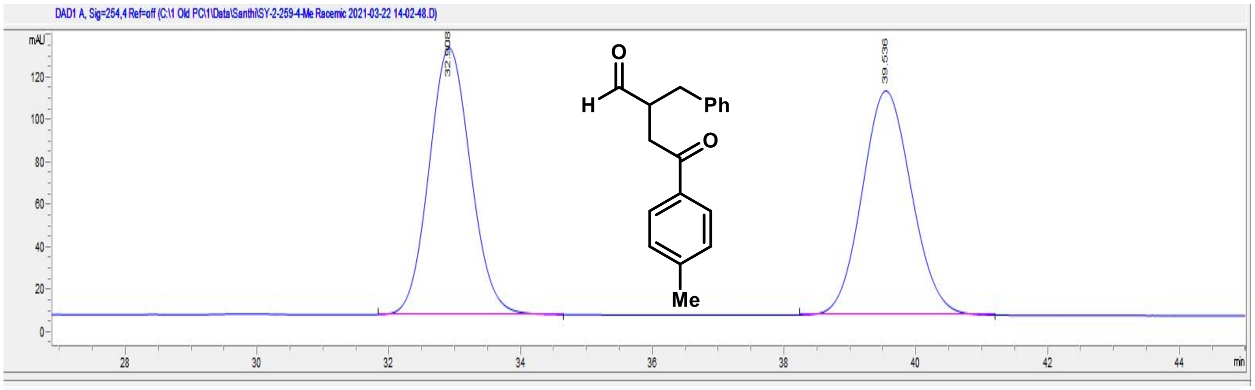


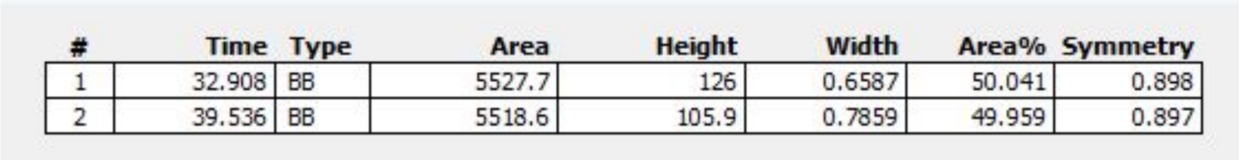


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.987	MM	46.2	1.3	0.587	3.460	1.081
2	30.267	BB	1289.4	30	0.6333	96.540	0.919

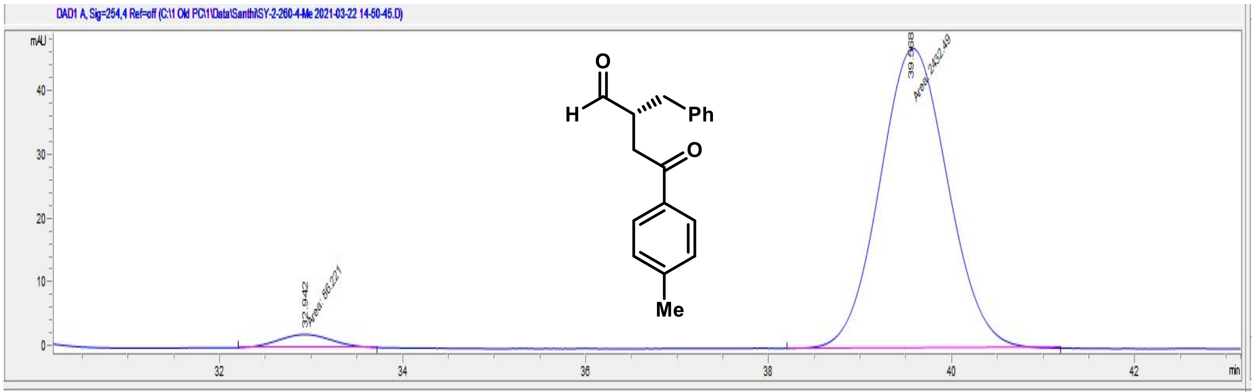
(*R*)-2-Benzyl-4-oxo-4-(*p*-tolyl)butanal, 15b

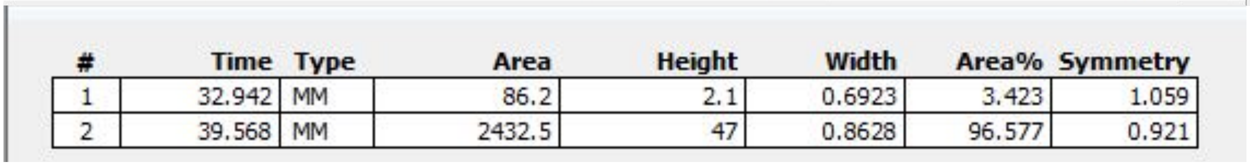
HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 1.0 mL/min, 254 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	32.908	BB	5527.7	126	0.6587	50.041	0.898
2	39.536	BB	5518.6	105.9	0.7859	49.959	0.897

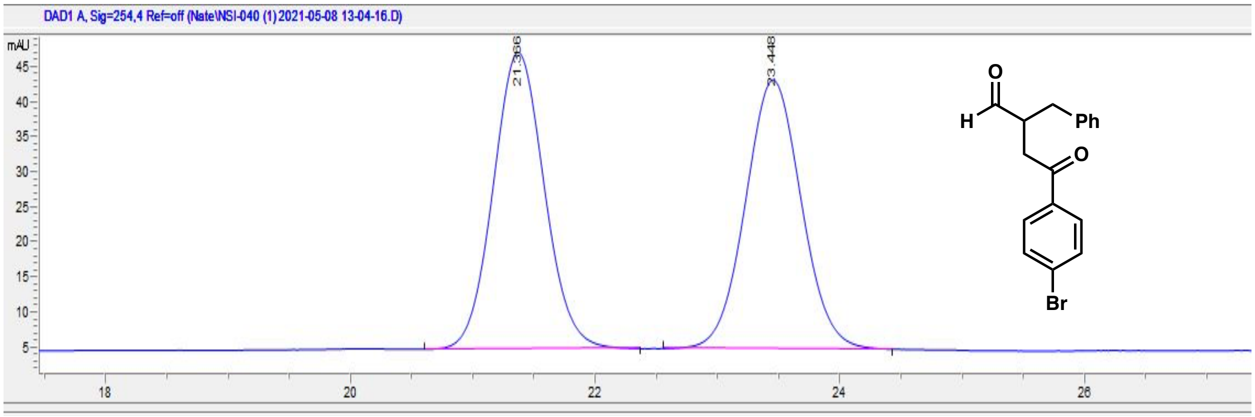




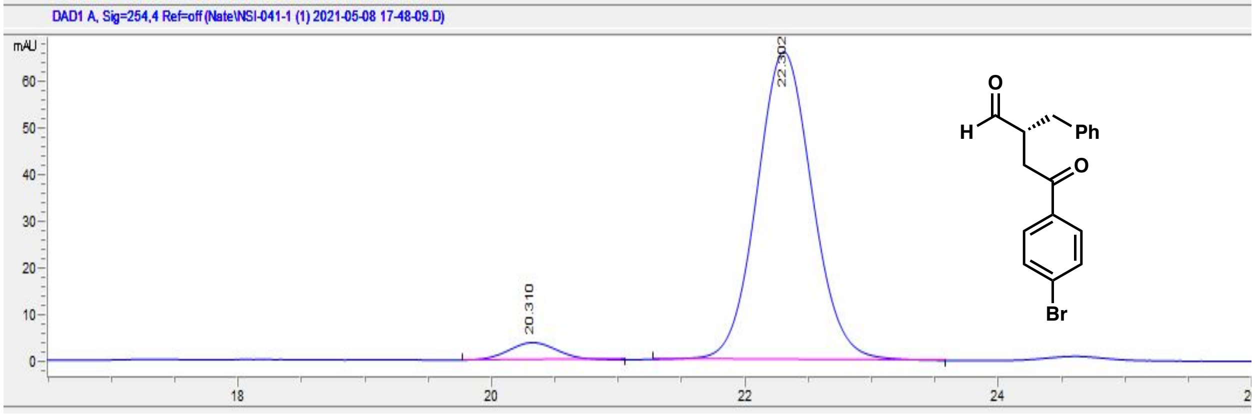
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	32.942	MM	86.2	2.1	0.6923	3.423	1.059
2	39.568	MM	2432.5	47	0.8628	96.577	0.921

(*R*)-2-Benzyl-4-(4-bromophenyl)-4-oxobutanal, 15c:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 0.8 mL/min, 254 nm UV detector.



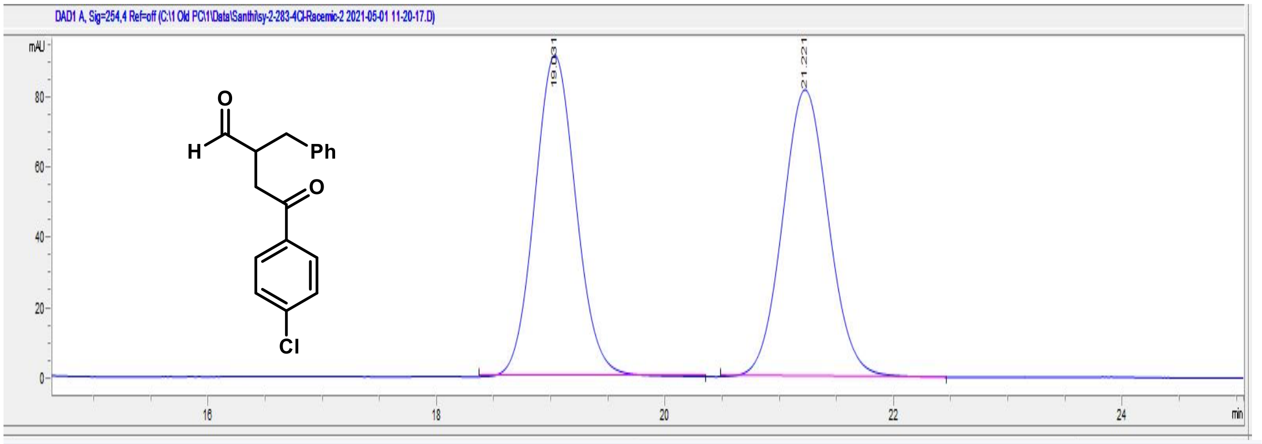
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	21.366	BB	1230.2	42.3	0.4442	50.215	0.921
2	23.448	BB	1219.6	38.4	0.4768	49.785	0.946

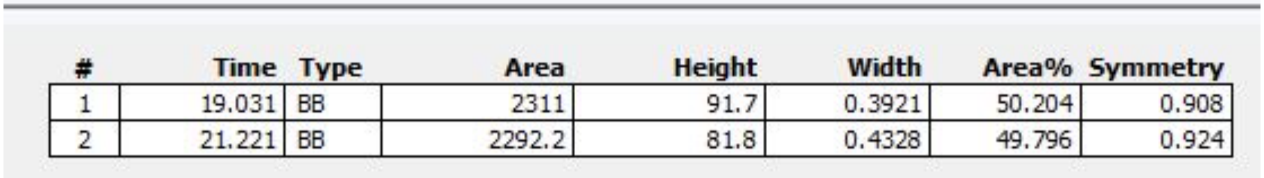


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.31	BB	100.3	3.7	0.3212	4.769	0.851
2	22.302	BB	2003.3	65.8	0.4712	95.231	0.922

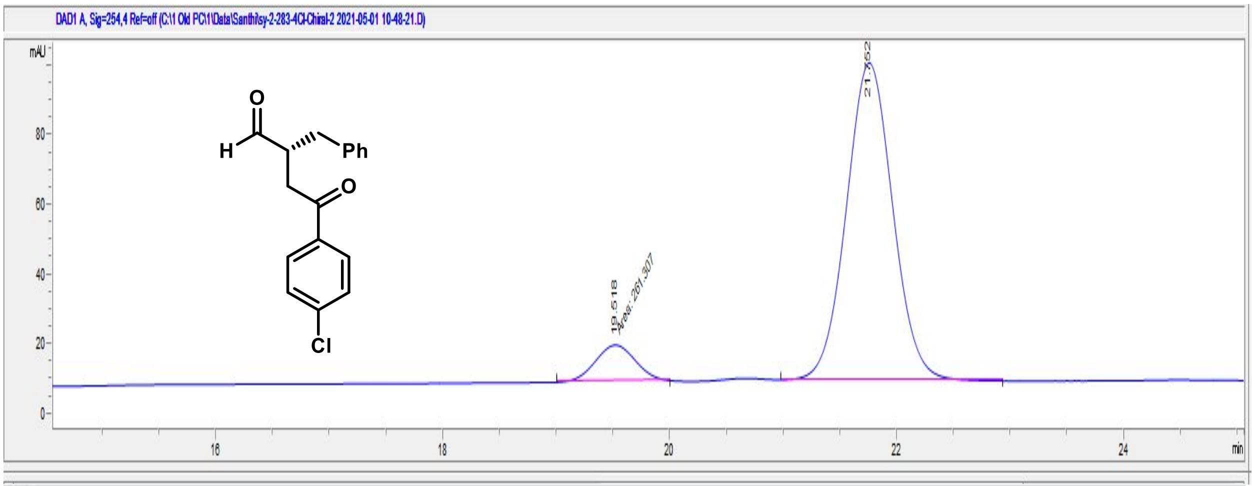
(*R*)-2-Benzyl-4-(4-chlorophenyl)-4-oxobutanal, 15d:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 1.0 mL/min, 254 nm UV detector.





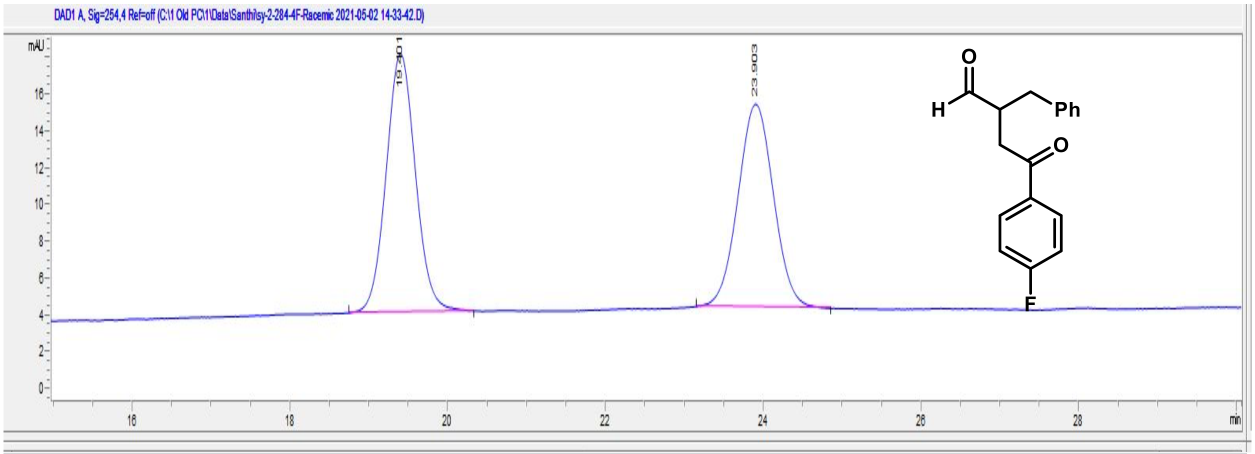
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.031	BB	2311	91.7	0.3921	50.204	0.908
2	21.221	BB	2292.2	81.8	0.4328	49.796	0.924



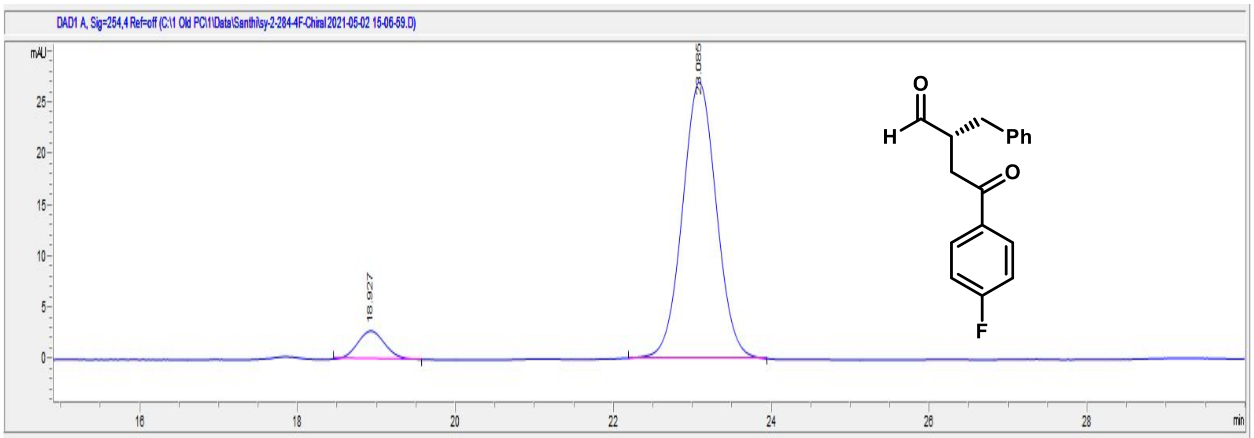
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.518	MM	261.3	10.5	0.4132	9.114	1.004
2	21.752	BB	2605.8	91.7	0.4414	90.886	0.948

(*R*)-2-Benzyl-4-(4-fluorophenyl)-4-oxobutanal, 15e:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 1.0 mL/min, 254 nm UV detector.



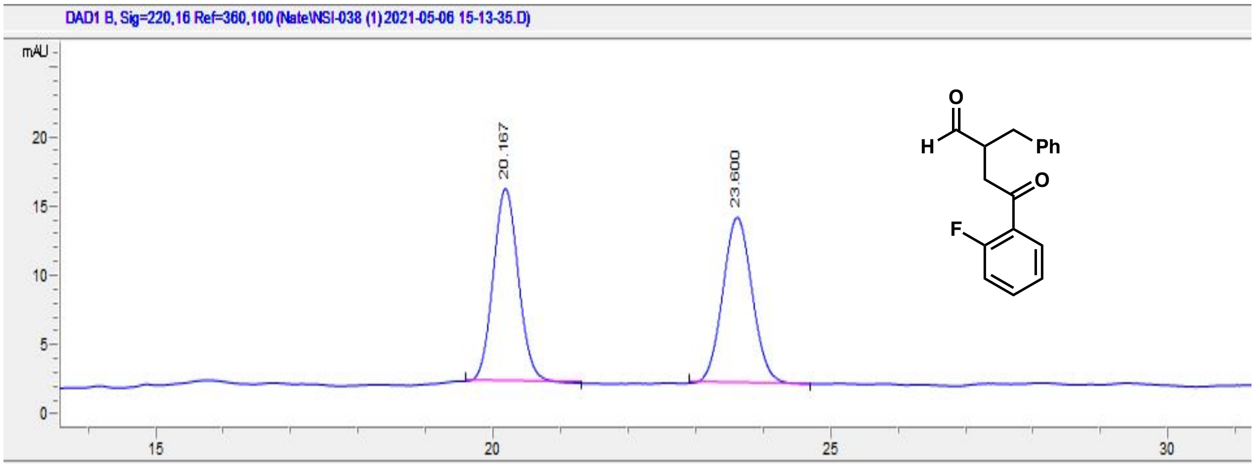
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.401	BB	362.9	14	0.3755	51.145	0.929
2	23.903	BB	346.7	11	0.4046	48.855	0.977



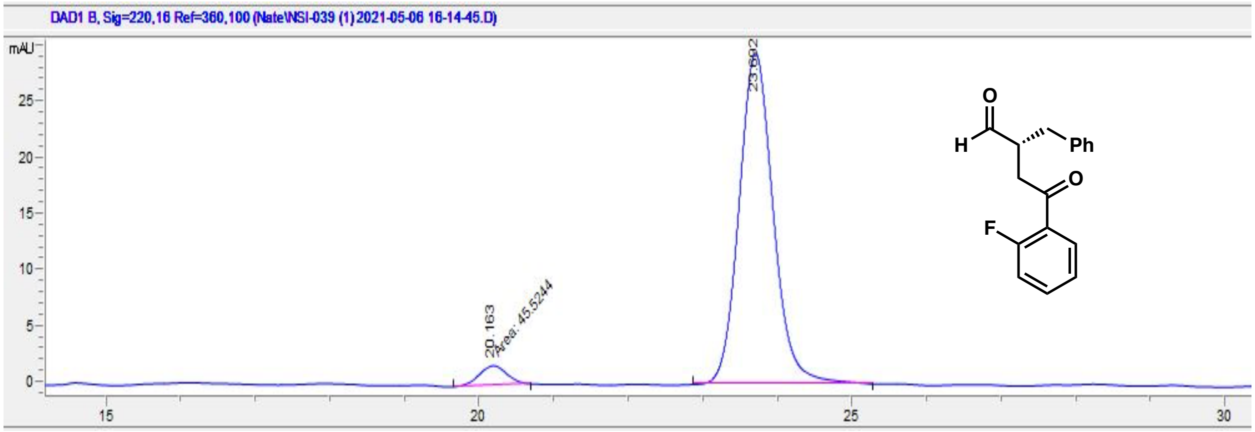
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	18.927	BB	67.1	2.8	0.299	7.685	0.978
2	23.085	BB	805.6	26.9	0.4534	92.315	0.953

(*R*)-2-Benzyl-4-(2-fluorophenyl)-4-oxobutanal, 15f:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 90:10, 0.8 mL/min, 230 nm UV detector.



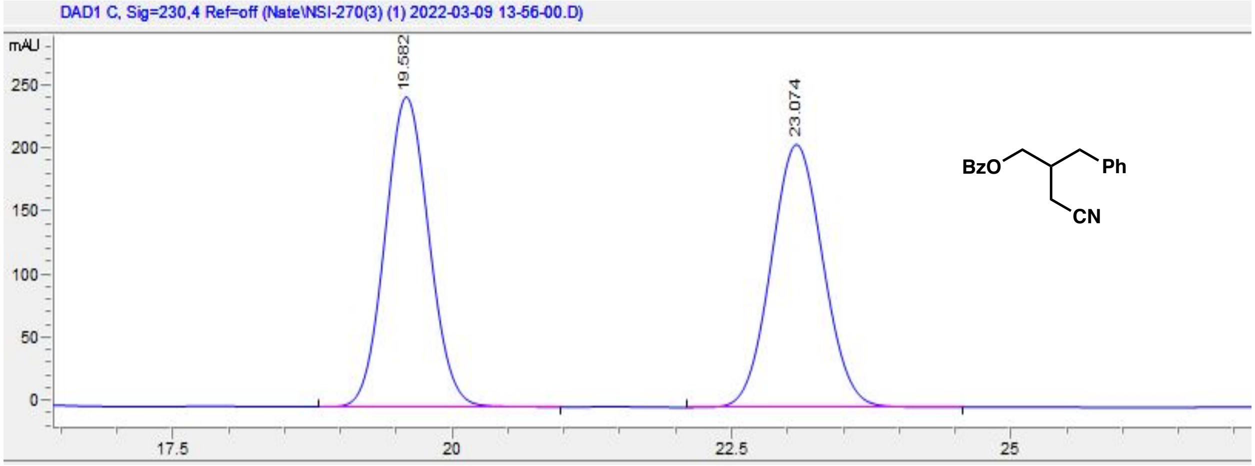
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.167	BB	364.9	14	0.3974	49.879	0.908
2	23.6	BB	366.6	12	0.4423	50.121	0.934

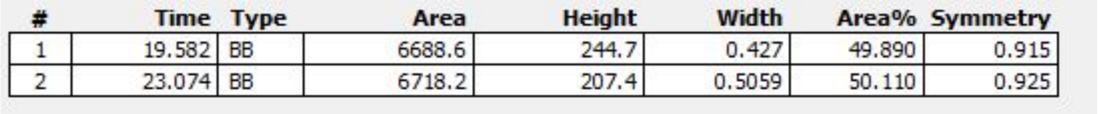


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	20.163	MM	45.5	1.7	0.4336	4.586	0.937
2	23.692	BB	947.2	29.6	0.4821	95.414	0.862

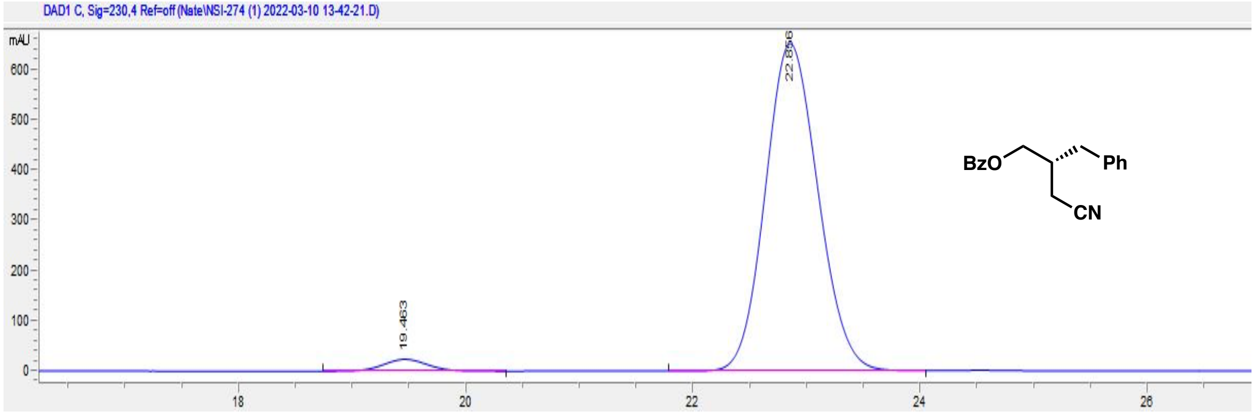
(*R*)-2-Benzyl-3-cyanopropyl benzoate, 15g:

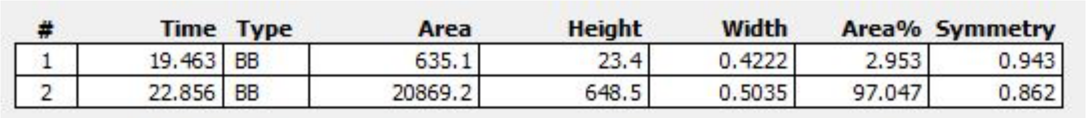
HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 80:20, 0.8 mL/min, 230 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.582	BB	6688.6	244.7	0.427	49.890	0.915
2	23.074	BB	6718.2	207.4	0.5059	50.110	0.925

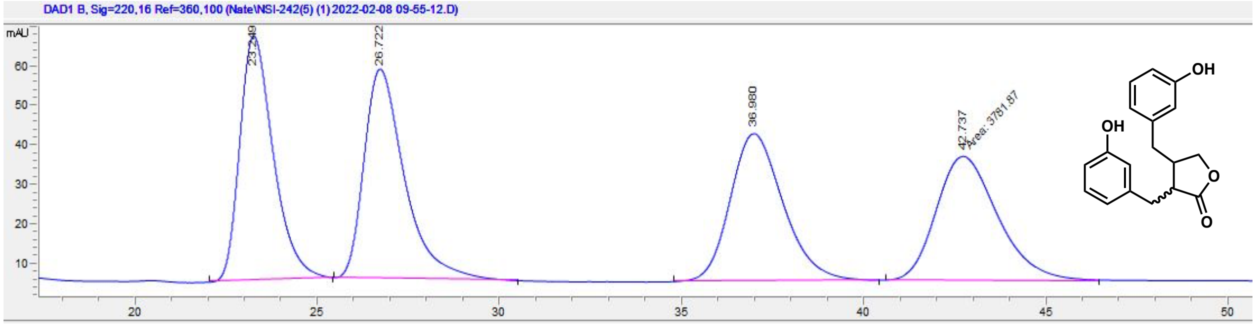




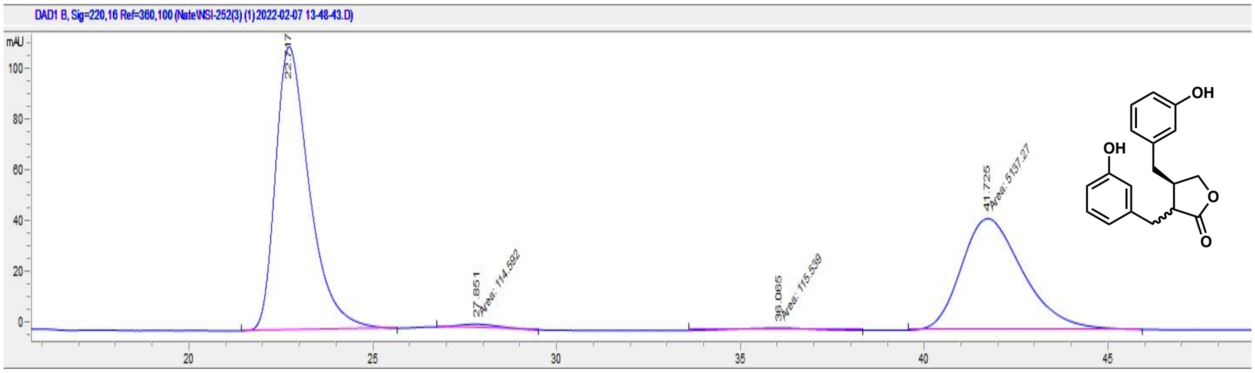
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	19.463	BB	635.1	23.4	0.4222	2.953	0.943
2	22.856	BB	20869.2	648.5	0.5035	97.047	0.862

(-)-Enterolactone, 17:

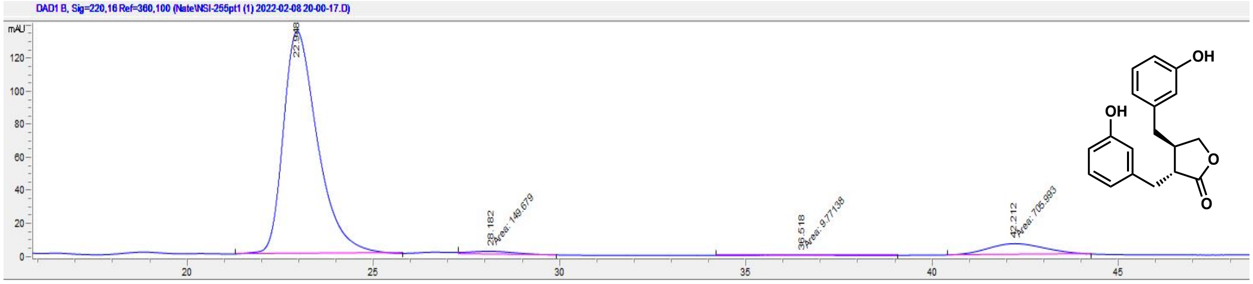
HPLC conditions: Chiralcel OD-H column (25 cm × 0.46 cm ID), Hex/IPA = 75:25, 0.5 mL/min, 220 nm UV detector.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	23.249	BB	3980.8	62.3	0.886	25.386	0.672
2	26.722	BB	4123.4	53.3	1.0201	26.295	0.606
3	36.98	BB	3795	37.5	1.1892	24.201	0.767
4	42.737	MM	3781.9	31.7	1.9869	24.117	0.742



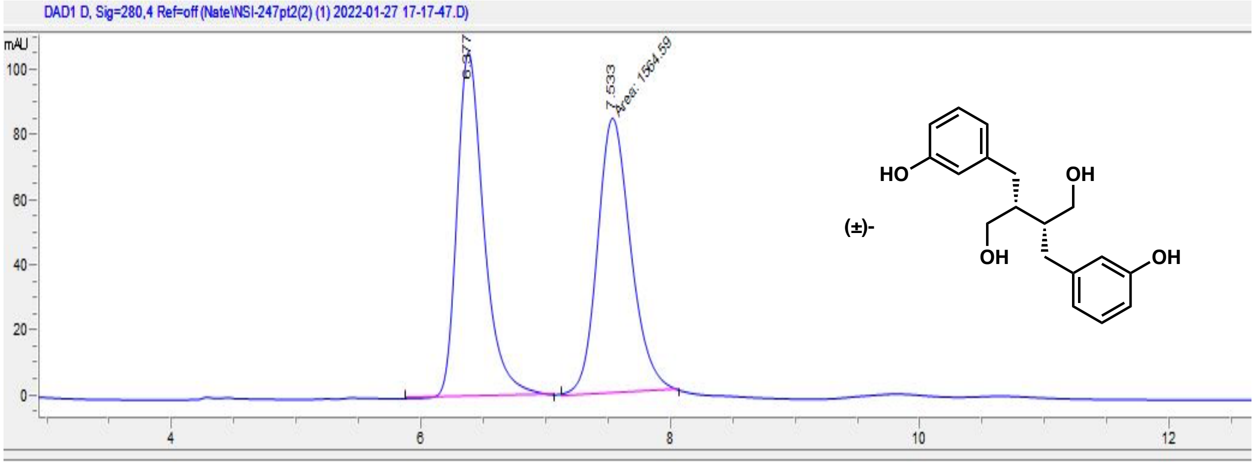
#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.717	BB	7187.1	112.2	0.9416	57.247	0.633
2	27.851	MM	114.6	1.5	1.2931	0.913	0.841
3	36.065	MM	115.5	8.7E-1	2.218	0.920	1.31
4	41.725	MM	5137.3	44	1.9444	40.920	0.725

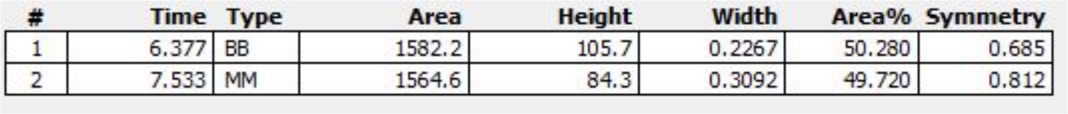


#	Time	Type	Area	Height	Width	Area%	Symmetry
1	22.948	BB	8659.8	135.4	0.9252	90.914	0.635
2	28.182	MM	149.7	1.7	1.4446	1.571	0.697
3	36.518	MM	9.8	9.9E-2	1.638	0.103	1.097
4	42.212	MM	706	6.6	1.7786	7.412	0.874

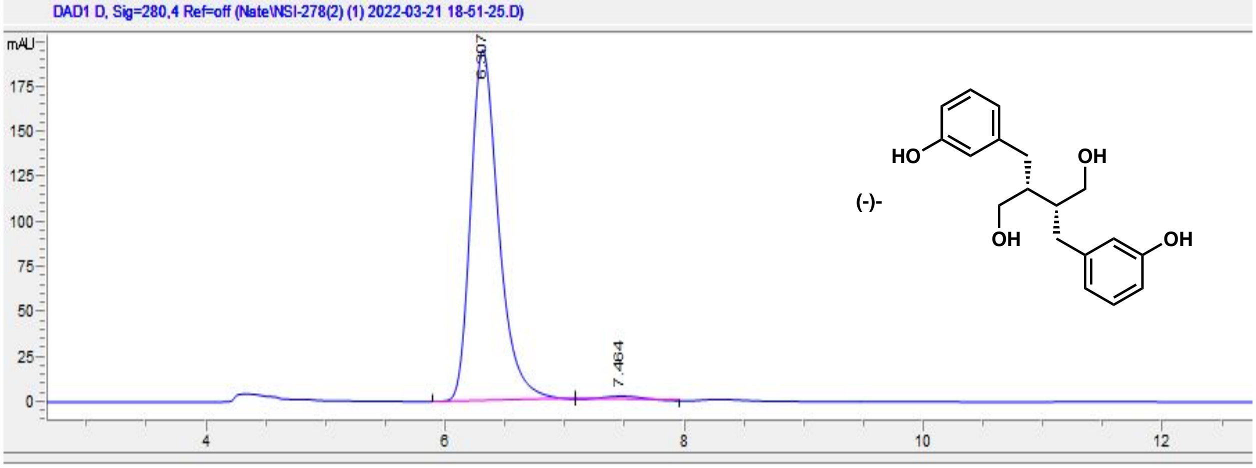
(-)-Enterodiol, 18:

HPLC conditions: Chiralpak IC column (25 cm × 0.46 cm ID), Hex/IPA = 75:25, 0.7 mL/min, 280 nm UV detector.





#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.377	BB	1582.2	105.7	0.2267	50.280	0.685
2	7.533	MM	1564.6	84.3	0.3092	49.720	0.812



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.307	BB	3157.8	194.2	0.2477	98.558	0.708
2	7.464	BB	46.2	2	0.367	1.442	0.783