Enantioselective Fluorination of Homoallylic Alcohols Enabled by the Tuning of Non-Covalent Interactions

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Supporting Information

General Information

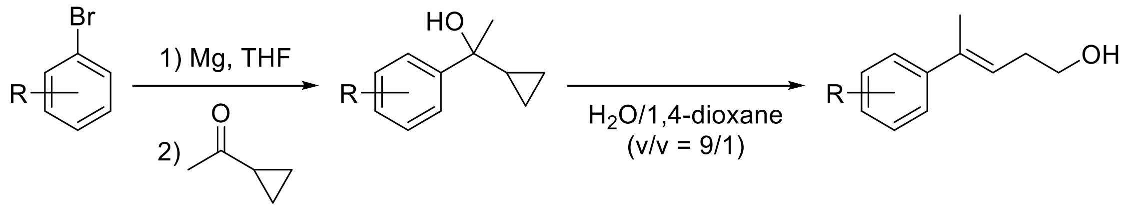
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Catalysts **5**[1], **6**[2] and **7**[3] were synthesized according to reported procedures. Tetrahydrofuran (THF), dichloromethane (DCM), toluene and triethylamine (Et_3N) were purified by passage through an activated alumina column under argon.

Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV or by staining with phosphomolybdic acid or $KMNO_4$ stains. Column chromatography was performed on Merck Silica Gel 60 Å, 230 X 400 mesh.

Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-600 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, app t = apparent triplet, m = multiplet, br = broad resonance. Mass spectral data were obtained from the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. Enantiomeric excesses were measured on a Shimadzu VP Series Chiral HPLC using Chiralpak AD-H column.

Synthesis of Substrates

General procedure for the synthesis of (*E*)-homoallylic alcohols

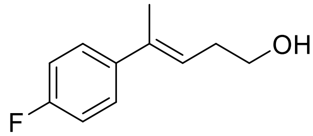


To a mixture of Mg (1.15 equiv, 0.28 g, 11.5 mmol) and I_2 (ca. 10 mg) in dry THF (10 mL) was added a solution of aryl bromide (10 mmol) in dry THF (10 mL) dropwise at room temperature and the resulting mixture was stirred for 30 min. The reaction mixture was then cooled to 0°C and cyclopropylmethylketone (1.0 equiv, 0.85 mL, 10 mmol) was added dropwise. After the mixture was stirred for 2 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL). The mixture was extracted with EtOAc (3 × 20 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (Hexanes/EtOAc = 5:1) to give the corresponding cyclopropylcarbinol.

To a mixture of water/1,4-dioxane (v/v = 9/1, 125 mL) was added cyclopropylcarbinol (5.0 mmol) and the resulting solution was refluxed overnight. The mixture was cooled to room temperature and extracted with EtOAc (3 × 50 mL), dried over Na_2SO_4 and concentrated in *vacuo*. The obtained crude product was purified by column chromatography on silica gel (hexane-EtOAc = 10/1-5:1) to give the desired (*E*)-homoallylic alcohols as a major product.

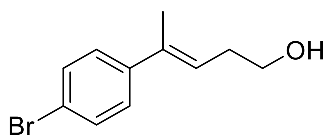
(*E*)-4-Phenylpent-3-en-1-ol (*E*-2a)[4] and **(*E*)-4-(*p*-tolyl)pent-3-en-1-ol (*E*-2d)**[5] are known compounds and the NMR spectral data are in accordance with the literature.

(*E*)-4-(4-Fluorophenyl)pent-3-en-1-ol (*E*-2b)



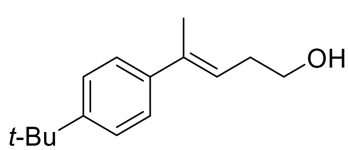
The title compound was prepared according to the general procedure and obtained as a colorless oil (0.252 g, 28%). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.34–7.31 (m, 2H), 7.00–6.94 (m, 2H), 5.72 (t, *J* = 10.8 Hz, 1H), 3.71 (t, *J* = 10.2 Hz, 2H), 2.91 (br s, 1H), 2.46 (dt, *J* = 10.8, 10.2 Hz, 2H) 2.02 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 161.9 (d, *J* = 243.8 Hz), 139.6 (d, *J* = 4.7 Hz), 136.2, 128.1 (d, *J* = 11.8 Hz), 123.8, 114.9 (d, *J* = 32.0 Hz), 62.1, 32.3, 16.0. **^{19}F NMR (376 MHz, CDCl$_3$) δ** -115.41 – -115.48 (m). **HRMS (EI) m/z** Calcd. for $C_{11}H_{13}FO$ [M]$^+$: 180.0950. Found: 180.0953.

(*E*)-4-(4-Bromophenyl)pent-3-en-1-ol (*E*-2c)



The title compound was prepared according to the general procedure and obtained as a colorless oil (0.109 g, 9% yield). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.43–7.41 (m, 2H), 7.26–7.24 (m, 2H), 5.79 (td, *J* = 7.2, 1.8 Hz, 1H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.49 (td, *J* = 7.2, 6.0 Hz, 2H), 2.05 (s, 3H), 1.50 (br s, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 142.5, 137.7, 131.4, 127.4, 124.6, 120.8, 62.4, 32.5, 16.1. **HRMS (EI)** Calcd for $C_{11}H_{13}O^{81}Br$ [M]$^+$: 242.0129. Found: 242.0126.

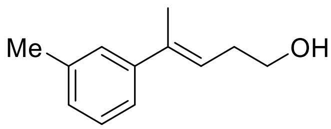
(*E*)-4-(4-(*tert*-Butyl)phenyl)pent-3-en-1-ol (*E*-2e)



The title compound was prepared according to the general procedure and obtained as a white solid (0.197 g, 18% yield). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.384–7.379 (m, 4H), 5.81 (td, *J* = 7.2, 1.8 Hz, 1H), 3.76 (t,

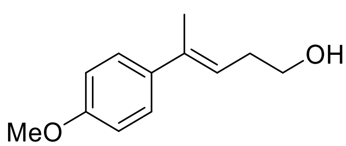
J = 6.6 Hz, 2H), 2.52 (td, J = 7.2, 6.6 Hz, 2H), 2.11 (s, 3H), 1.95 (br s, 1H), 1.36 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 149.9, 140.6, 137.4, 125.3, 125.2, 123.1, 62.4, 34.5, 32.5, 31.4, 16.0. **HRMS (EI)** Calcd for $C_{15}H_{22}O$: $[M]^+$: 218.1671. Found: 218.1665.

(*E*)-4-(*m*-Tolyl)pent-3-en-1-ol (*E*-2f)



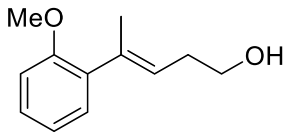
The title compound was prepared according to the general procedure and obtained as a colorless oil (0.273 g, 31% yield). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.25–7.21 (m, 3H), 7.08 (m, 1H), 5.79 (td, J = 7.2, 1.2 Hz, 1H), 3.76 (t, J = 6.6 Hz, 2H), 2.51 (td, J = 7.2, 6.6 Hz, 2H), 2.38 (s, 3H), 2.09 (s, 3H), 1.84 (br s, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 143.7, 137.9, 137.8, 128.2, 127.7, 126.5, 123.6, 122.9, 62.4, 32.4, 21.6, 16.2. **HRMS (EI)** Calcd for $C_{12}H_{16}O$: $[M]^+$: 176.1201. Found: 176.1201.

(*E*)-4-(4-Methoxyphenyl)pent-3-en-1-ol (*E*-2g)



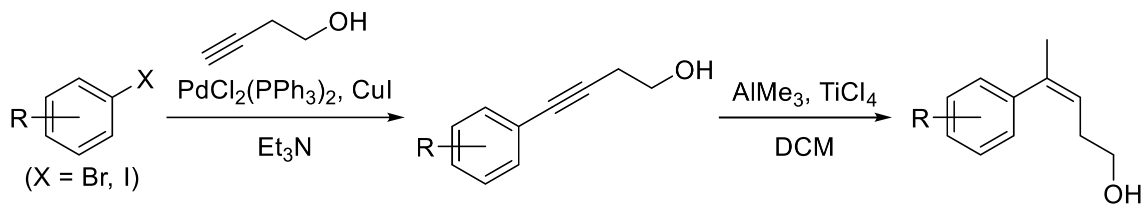
The title compound was prepared according to the general procedure and obtained as a white solid (0.288 g, 30% yield). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.35–7.33 (m, 2H), 6.87–6.85 (m, 2H) 5.71 (t, J = 9.0 Hz, 1H), 3.82 (s, 3H), 3.74 (t, J = 6.6 Hz, 2H), 2.49 (m, 2H), 2.06 (s, 3H), 1.51 (br s, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 158.8, 137.3, 136.2, 126.8, 122.2, 113.7, 62.6, 55.4, 32.5, 16.2. **HRMS (EI)** Calcd for $C_{12}H_{16}O_2$: $[M]^+$: 192.1150. Found: 192.1152.

(*E*)-4-(2-Methoxyphenyl)pent-3-en-1-ol (*E*-2i)



The title compound was prepared according to the general procedure and obtained as a colorless oil (0.337 g, 35% yield). The crude product was a *E*/*Z* mixture of 7:1. **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.24 (m, 1H), 7.13 (m, 1H), 6.92 (m, 1H), 6.87 (m, 1H), 5.44 (td, *J* = 7.2, 1.8 Hz, 1H), 3.82 (s, 3H), 3.73 (t, *J* = 6.6 Hz, 2H), 2.48 (td, *J* = 7.2, 6.6 Hz, 2H), 2.02 (s, 3H), 1.91 (br s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 156.5, 138.1, 134.7, 129.5, 128.1, 125.3, 120.6 110.8, 62.3, 55.5, 32.0, 17.5. **HRMS (EI)** Calcd for $C_{12}H_{16}O_2$: $[M]^+$: 192.1150. Found: 192.1154.

General procedure for the synthesis of (*Z*)-homoallylic alcohols

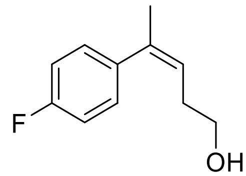


To a solution of aryl bromide or aryl iodide (10 mmol) in Et_3N (40 mL) were added $PdCl_2(PPh_3)_2$ (2 mol%, 0.140 g, 0.2 mmol), and CuI (1 mol%, 0.019 g, 0.1 mmol) under N_2 atmosphere. After the reaction mixture was stirred for 5 min. at room temperature, but-3-yn-1-ol (1.2 equiv, 0.91 mL, 12 mmol) was added by a syringe. The reaction mixture was then heated to 60°C and stirred overnight. The resulting mixture was filtered through a short column of silica gel and concentrated in *vacuo*. The obtained crude product was purified by column chromatography on silica (Hexanes/EtOAc = 5:1) to give the corresponding 4-arylbut-3-yn-1-ol.

To a cooled (0°C) solution of $AlMe_3$ (2 equiv, 5.0 mL, 2.0 M solution in toluene, 10 mmol) in DCM (10 mL) was added 4-arylbut-3-yn-1-ol (5.0 mmol) dropwise at 0°C and the mixture was stirred at the same temperature for 20 min. The reaction mixture was then cooled to –45 °C followed by the slow addition of a cooled (0 °C) solution of $TiCl_4$ (1 equiv, 0.55 mL, 5.0 mmol) in DCM (15 mL). The resulting mixture was allowed to stir for 4 h at –45 °C and then quenched by the slow addition of cooled (0°C) MeOH (4.0 mL). 3 M HCl *aq.* saturated with NaCl (10 mL) was then added and the mixture was stirred at room temperature for 30 min. The resulting solution was extracted with Et_2O (3 × 25 mL), dried over Na_2SO_4 and concentrated in *vacuo*. The obtained crude product was purified by column chromatography on silica gel (hexanes/EtOAc = 10/1-5:1) to give the desired (*Z*)-homoallylic alcohols.

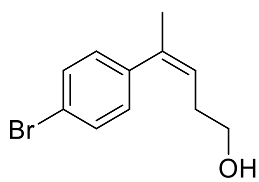
(*Z*)-4-Phenylpent-3-en-1-ol (*Z*-2a)[6] is a known compound and the NMR spectral data are in accordance with the literature.

(*Z*)-4-(4-Fluorophenyl)pent-3-en-1-ol (*Z*-2b)



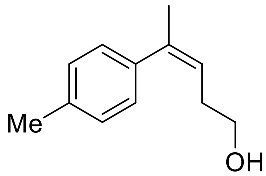
The title compound was prepared according to the general procedure using 1-bromo-4-fluorobenzene (X= Br) and obtained as a colorless oil (0.360 g, 40% yield). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.17–7.13 (m, 2H), 7.03–6.98 (m, 2H), 6.02 (td, *J* = 10.8, 1.8 Hz, 1H), 3.58 (t, *J* = 9.6 Hz, 2H), 2.22 (td, *J* = 10.8, 9.6 Hz, 2H), 2.03 (d, *J* = 2.4 Hz, 3H), 1.95 (br s, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 161.6 (d, *J* = 246.1 Hz), 138.1, 137.6, 129.5 (d, *J* = 7.6 Hz), 123.6, 114.5 (d, *J* = 21.1 Hz), 62.5, 32.6, 25.8. **^{19}F NMR (376 MHz, CDCl$_3$) δ** -115.11 – -115.19 (m). **HRMS (EI)** Calcd. for $C_{11}H_{13}FO$ [M]$^+$: 180.0950. Found: 180.0952.

(*Z*)-4-(4-Bromophenyl)pent-3-en-1-ol (*Z*-2c)



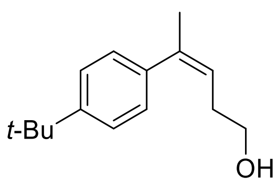
The title compound was prepared according to the general procedure using 1-bromo-4-iodobenzene (X= I) and obtained as a pale yellow oil (0.639 g, 53%). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.46–7.43 (m, 2H), 7.07–7.05 (m, 2H), 5.49 (td, *J* = 7.2, 1.8 Hz, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.21 (td, *J* = 7.2, 6.6 Hz, 2H), 2.02 (s, 3H), 1.68 (br s, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 140.7, 138.2, 131.4, 129.8, 124.0, 120.6, 62.6, 32.6, 25.7. **HRMS (EI)** Calcd for $C_{11}H_{13}O^{81}Br$ [M]$^+$: 242.0129. Found: 242.0133.

(*Z*)-4-(*p*-Tolyl)pent-3-en-1-ol (*Z*-2d)



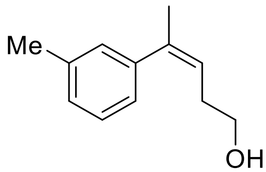
The title compound was prepared according to the general procedure using 1-iodo-4-methylbenzene (X= I) and obtained as a pale yellow oil (0.344 g, 39% yield). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.19 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.50 (td, *J* = 7.2, 1.8 Hz, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 2.33 (br s, 1H), 2.29 (td, *J* = 7.2, 6.6 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 138.9, 138.8, 136.2, 128.8, 127.8, 122.9, 62.6, 32.6, 25.8, 21.1. **HRMS (EI)** Calcd. for $C_{12}H_{16}O$ $[M]^+$: 176.1201. Found: 176.1198.

(*Z*)-4-(4-(*tert*-Butyl)phenyl)pent-3-en-1-ol (*Z*-2e)



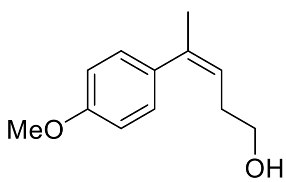
The title compound was prepared according to the general procedure using 1-bromo-4-(*tert*-butyl)benzene (X= Br) and obtained as a pale yellow oil (0.207 g, 19%). **^{1}H NMR (600 MHz, CDCl$_3$) δ** 7.38–7.36 (m, 2H), 7.16–7.14 (m, 2H), 5.47 (td, *J* = 7.8, 1.2 Hz, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.30 (td, *J* = 7.8, 6.6 Hz, 2H), 2.07 (s, 3H), 1.75 (br s, 1H), z1.35 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 149.5, 139.2, 138.7, 127.6, 125.1, 122.9, 62.8, 34.6, 32.8, 31.5, 25.9. **HRMS (EI)** Calcd for $C_{15}H_{22}O$: $[M]^+$: 218.1671. Found: 218.1668.

(*Z*)-4-(*m*-Tolyl)pent-3-en-1-ol (*Z*-2f)



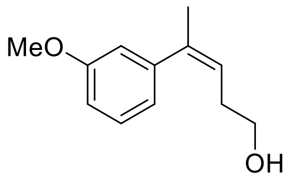
The title compound was prepared according to the general procedure using 1-iodo-3-methylbenzene (X= I) and obtained as a pale yellow oil (0.238 g, 27%). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.26 (m, 1H), 7.09 (m, 1H), 7.05–7.02 (m, 2H), 5.50 (td, *J* = 7.2, 1.8 Hz, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 2.34 (br s, 1H), 2.28 (td, *J* = 7.2, 6.6 Hz, 2H), 2.09 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 141.7, 139.2, 137.6, 128.5, 128.0, 127.4, 125.0, 123.0, 62.5, 32.6, 25.8, 21.5. **HRMS (EI)** Calcd for $C_{12}H_{16}O$: $[M]^+$: 176.1201. Found: 176.1201.

(*Z*)-4-(4-Methoxyphenyl)pent-3-en-1-ol (*Z*-2g)



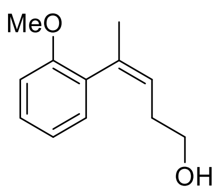
The title compound was prepared according to the general procedure using 1-bromo-4-methoxybenzene (X= Br) and obtained as a colorless oil (0.452 g, 47%). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.14–7.13 (m, 2H), 6.88–6.87 (m, 2H), 5.44 (td, *J* = 7.2, 1.8 Hz, 1H), 3.80 (s, 3H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.28 (td, *J* = 7.2, 6.6 Hz, 2H), 2.04 (s, 3H), 1.46 (br s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 158.4, 139.1, 134.1, 129.1, 122.8, 113.7, 62.9, 55.4, 32.8, 26.0. **HRMS (EI)** Calcd for $C_{12}H_{16}O_2$: $[M]^+$: 192.1150. Found: 192.1154.

(*Z*)-4-(3-Methoxyphenyl)pent-3-en-1-ol (*Z*-2h)



The title compound was prepared according to the general procedure using 1-bromo-3-methoxybenzene (X= Br) and obtained as a colorless oil (0.528 g, 55%). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.25 (m, 1H), 6.80–6.77 (m, 2H), 6.75 (m, 1H), 5.47 (td, J = 7.8, 1.2 Hz, 1H), 3.80 (s, 3H), 3.58 (t, J = 6.6 Hz, 2H), 2.25 (td, J = 7.8, 6.6 Hz, 2H), 2.05 (d, J = 1.2 Hz, 3H), 1.94 (br s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 159.4, 143.3, 139.2, 129.2, 123.3, 120.4, 113.8, 111.9, 62.6, 55.2, 32.7, 25.8. **HRMS (EI)** Calcd for $C_{12}H_{16}O_2$: $[M]^+$: 192.1150. Found: 192.1154.

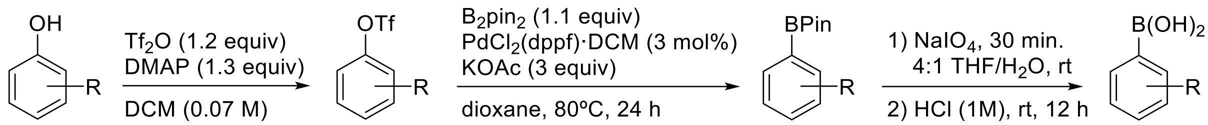
(*Z*)-4-(2-Methoxyphenyl)pent-3-en-1-ol (*Z*-2i)



The title compound was prepared according to the general procedure using 1-bromo-2-methoxybenzene (X= I) and obtained as a colorless oil and a crude *E*/*Z* mixture of 1:9 (0.240 g, 25%). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.27–7.24 (m, 1H), 7.03–7.02 (m, 1H), 6.95 (m, 1H), 6.91 (m, 1H), 5.52 (td, J = 7.2, 1.2 Hz, 1H), 3.82 (s, 3H), 3.55 (t, J = 6.0 Hz, 2H), 2.08 (td, J = 7.2, 6.0 Hz, 2H), 2.00 (s, 3H), 1.87 (br s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 156.0, 137.8, 130.9, 129.8, 128.3, 124.2, 120.9, 111.0, 62.2, 55.5, 32.9, 25.2. **HRMS (EI)** Calcd for $C_{12}H_{16}O_2$: $[M]^+$: 192.1150. Found: 192.1152.

Synthesis of Boronic Acids

General Procedure for preparation of boronic acids from the corresponding phenol

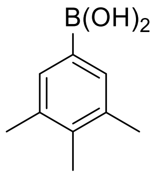


To a magnetically-stirred solution of phenol derivative (2 mmol) in DCM (30 mL) were added 4-dimethylaminopyridine (0.317 g, 2.6 mmol) and trifluoromethanesulfonic anhydride (0.4 mL, 2.4 mmol) at 0ºC. The reaction mixture was allowed to warm to ambient temperature and was then stirred for 5 h. The reaction mixture was diluted with a sat. aq. sol. of NH_4Cl (30 mL) and extracted with EtOAc (2 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was suspended in hexanes/EtOAc 1:1 and passed through a short plug of silica gel. The filtrate was concentrated under reduced pressure.

To a solution of the triflate derivative in dioxane (12.5 mL) were added bis(pinacolato)diboron (1.1 equiv), potassium acetate (3 equiv), and Pd(dppf)Cl_2·DCM (3 mol%). The mixture was heated at 80ºC with stirring under an atmosphere of nitrogen. After 24 h, the mixture was filtered through a pad of celite, and the filtrate diluted with sat. aq. sol. of NH_4Cl and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexanes/EtOAc as eluent (9:1 to 1:1).

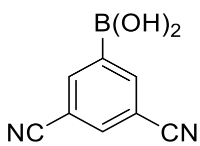
The resulting purified pinacolboronic ester was dissolved in THF/H_2O (4:1, 0.15 M), and $NaIO_4$ (3.0 equiv) was added. After stirring 15 min, 1 M HCl (2 mL) was added, and the reaction mixture was stirred at ambient temperature overnight. The reaction mixture was then extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated in vacuum. The crude residue was triturated with hexanes, and the resulting solid was collected *via* vacuum filtration.

(3,4,5-trimethylphenyl)boronic acid



The corresponding pinacolboronic ester (^{1}H NMR data match those reported in the literature[7]) was subjected to cleavage according to the general procedure to yield the title compound (0.100 g, 30% yield over three steps) as a white solid. **^{1}H NMR (600 MHz, DMSO-d$_6$) δ** 7.81 (s, 2H), 7.40 (s, 2H), 2.22 (s, 6H), 2.12 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d$_6$) δ** 136.5, 134.5, 133.5, 130.4, 20.2, 15.2. **HRMS (ESI)** calcd. for $C_{10}H_{14}BO_2$ $[M+13]^-$ $(M+MeOH-H_2O)^-$: 177.1092; found 177.1092.

(3,5-dicyanophenyl)boronic acid



The corresponding pinacolboronic ester (^{1}H NMR data match those reported in the literature[8]) was subjected to cleavage according to the general procedure to yield the title compound (0.220 g, 64% yield over three steps) as a light yellow solid. **^{1}H NMR (600 MHz, acetone-d$_6$) δ** 8.42 (m, 2H), 8.33 (m, 1H), 7.86 (s, 1H). **^{13}C NMR (151 MHz, acetone-d$_6$) δ** 142.4, 137.9, 118.1, 114.3. **HRMS (ESI)** calcd. for $C_9H_6BN_2O_2$ $[M+13]^-$ $(M+MeOH-H_2O)^-$: 185.0528; found 185.0543.

Enantioselective Fluorination Reactions

General Procedure for Enantioselective Fluorination Reactions (Note 1):

A stock solution of homoallylic alcohol ***E*-2** or ***Z*-2** (0.1 M in toluene) was prepared immediately prior to use. A 1-dram vial was charged with the appropriate catalyst (0.005 mmol), boronic acid (0.065 mmol), Na_2HPO_4 (0.20 mmol, Note 2), MS 4Å (40 mg, Note 3) and an 8 mm Teflon magnetic stir bar. To this vial was added 0.5 mL of the substrate stock solution, and the resulting mixture was placed directly onto the surface of a stirring plate to allow stirring at 500-600 rpm. After 30 min, Selectfluor (23 mg, 0.065 mmol, Note 4) was added to the vial, and the mixture was again placed directly on the surface of the stirring plate to stir at 500-600 rpm for 42-48h. After the designated time, the reaction mixture was filtered through a plug of silica gel using DCM (5 mL) as eluent. The filtrate was concentrated in *vacuo*, and the residue was dissolved in 10 % IPA/hexanes for direct analysis of enantiomeric excess by HPLC using a chiral stationary phase (Chiralpak AD-H column, 99:01 hexanes:isopropanol, 1 mL/min); tr = 44, 46 min). In some of the reactions 1-fluoro-nitrobenzene was used as internal standard to determine the conversion of the homoallylic alcohols.

Note 1: Enantioselective fluorination reactions were run in 1 dram vials equipped with a screw cap and stirred using a magnetic Teflon stir bar, placed on the surface of a magnetic stir plate. Due to the heterogeneous nature of these reactions, it was important that fast and efficient stirring be maintained over the course of the reaction in order to obtain optimal results.

Note 2: Na_2HPO_4 was ground with a mortar and pestle and dried at 140 ºC overnight prior to use.

Note 3: Powdered MS 4Å were dried at 140ºC overnight prior to use.

Note 4: Selectfluor was ground with a mortar and pestle and dried under high vacuum at 80ºC for 30 min. The resulting powder was stored in a desiccator when not in use.

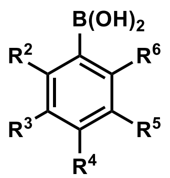
Enantioselectivity for All Boronic Acid/Phosphoric Acid Combinations

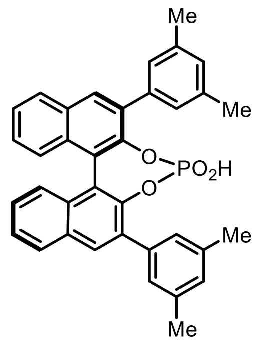
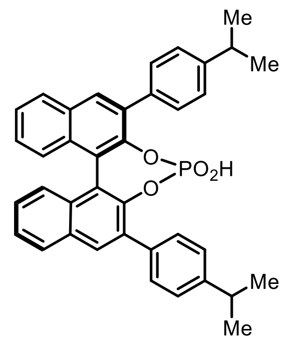
Alkene	PA	BA	ee (%)[a]
E-	**5** (6,6'-Mes-PA)	2-Br-Ph	-28, -32
E-	**5** (6,6'-Mes-PA)	3,5-(CF3)$_2$-Ph	-2, -1
E-	**5** (6,6'-Mes-PA)	3,5-Me$_2$-Ph	-9, -4
E-	**5** (6,6'-Mes-PA)	3,5-(OMe)$_2$-Ph	-28, -29
E-	**5** (6,6'-Mes-PA)	Ph	11, 9
E-	**5** (6,6'-Mes-PA)	4-NO$_2$-Ph	0, 2
E-	**5** (6,6'-Mes-PA)	4-Me-Ph	16, 14
E-	**5** (6,6'-Mes-PA)	2-Me-Ph	10, 7
E-	**5** (6,6'-Mes-PA)	2,4,6-Me$_3$-Ph	-2, -5 (low yield)
E-	**6** (*R*-TRIP)	3,5-(CF$_3$)$_2$-Ph	35, 41
E-	**6** (*R*-TRIP)	3,4,5-(OMe)$_3$-Ph	54, 54
E-	**6** (*R*-TRIP)	3,4,5-F$_3$-Ph	31, 32
E-	**6** (*R*-TRIP)	3,5-Br$_2$-Ph	69, 70
E-	**6** (*R*-TRIP)	3,5-Me$_2$-Ph	68, 73, 69, 72
E-	**6** (*R*-TRIP)	3,4,5-Cl$_3$-Ph	76, 77
E-	**6** (*R*-TRIP)	3,4,5-Me$_3$-Ph	63, 63
E-	**6** (*R*-TRIP)	2,6-Cl$_2$-Ph	31, 24 (low conversion)
E-	**6** (*R*-TRIP)	4-Me-Ph	35, 38
E-	**6** (*R*-TRIP)	4-NO$_2$-Ph	24, 24
E-	**6** (*R*-TRIP)	2-Me-Ph	20, 21
E-	**6** (*R*-TRIP)	4-*t*-Bu-Ph	51, 55
E-	**6** (*R*-TRIP)	4-OMe-Ph	49, 52
E-	**6** (*R*-TRIP)	2-Br-Ph	15, 13
E-	**6** (*R*-TRIP)	2-OMe-Ph	1, -3 (low yield)
E-	**6** (*R*-TRIP)	4-Py	-4, -9
E-	**6** (*R*-TRIP)	4-CF$_3$-Ph	33, 34
E-	**6** (*R*-TRIP)	Ph	30, 32
E-	**6** (*R*-TRIP)	3,5-Cl$_2$-Ph	73, 74
E-	**6** (*R*-TRIP)	2-Napht	63, 62
E-	**6** (*R*-TRIP)	3,5-(OMe)$_2$-Ph	61, 62
E-	**7** (*R*-TCYP)	3,5-(CN)$_2$-Ph	-12, -14
E-	**7** (*R*-TCYP)	3,5-(OMe)$_2$-Ph	-63, -60
E-	**7** (*R*-TCYP)	3,4,5-(OMe)$_3$-Ph	-77, -74, -69, -70
E-	**7** (*R*-TCYP)	3,5-Br$_2$-Ph	-25, -25
E-	**7** (*R*-TCYP)	3,5-Cl$_2$-Ph	-20, -21
E-	**7** (*R*-TCYP)	3,5-(CF$_3$)$_2$-Ph	-7, -6
E-	**7** (*R*-TCYP)	Ph	16, 21
E-	**7** (*R*-TCYP)	4-Me-Ph	22, 28
E-	**7** (*R*-TCYP)	4-NO$_2$-Ph	16, 21
E-	**7** (*R*-TCYP)	2-Me-Ph	18, 16
E-	**7** (*R*-TCYP)	2,4,6-Me$_3$-Ph	5, 1
E-	**7** (*R*-TCYP)	2-OMe-Ph	-3, -5
E-	**7** (*R*-TCYP)	2-Br-Ph	1, 1
Z-	**7** (*R*-TCYP)	3,4,5-(OMe)$_3$-Ph	89, 90
Z-	**7** (*R*-TCYP)	3,5-(OMe)$_2$-Ph	88, 88
Z-	**7** (*R*-TCYP)	3,5-Me$_2$-Ph	72, 74
Z-	**7** (*R*-TCYP)	3,5-(CF$_3$)$_2$-Ph	64, 56, 58
Z-	**7** (*R*-TCYP)	3,5-Br$_2$-Ph	72, 78
Z-	**7** (*R*-TCYP)	3,5-Cl$_2$-Ph	76, 79
Z-	**7** (*R*-TCYP)	3,4,5-Cl$_3$-Ph	85, 86
Z-	**7** (*R*-TCYP)	3,4,5-F$_3$-Ph	43, 45
Z-	**7** (*R*-TCYP)	3-Cl-5-Me-Ph	73, 74

[a] Each enantioselectivity value was obtained in duplicate.

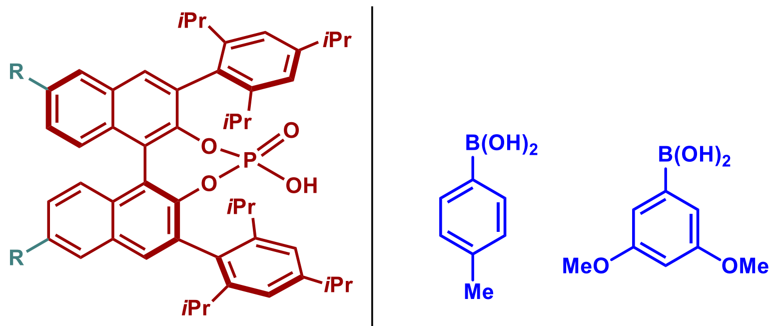
Additional Enantioselectivity data

The data obtained with phosphoric acid catalysts bearing Ar=3,5-Me_2 or Ar=4-*i*Pr is summarized in the following table. This data was not included in the model because these phosphoric acid catalysts provided a nonlinear effect between product and catalyst enantioselectivities, which is tentatively attributed to the reduced steric profile proximal to the phosphate moiety resulting in dimeric salts with Selectfluor, as previously reported by us.[9]



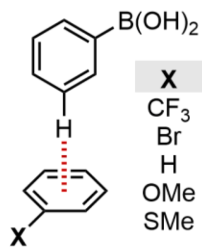
R^2	R^3	R^4	R^5	R^6		
H	H	H	H	H	-61	-70
Me					-36	-62
Br					-11	10
OMe					-19	-28
OPh					-62	-47
Me				Me	25	-14
Cl				Cl	10	10
CF_3				CF_3	-11	-13
F		OMe		F		0
Me		Me		Me	31	-9
Me		OMe		Me		-1
	Me		Me		-78	-78
	CF_3		CF_3		-24	-15
	OMe		OMe		-71	-66
	Ph		Ph			-66
	Br		Br		-64	-47
	Cl		Cl		-62	-35
	F					-9
	Ph					-57
	Me				-10	-1
	F	OMe				-71
	Me	OMe			-60	-74
	OMe	OMe			-33	-65
	Me	F			-75	-78
		Me			-71	-74
		i-Bu			-60	-70
		t-Bu			-50	-8
		CF_3			-31	-12
		NO_2			-47	-52
		OMe			-64	-71
		OBn			-57	-68
		F			-64	-71

Enantioselective data obtained with modified catalysts bearing R=Ph, Bn and Br was not significantly different from R=H (TRIP catalyst).



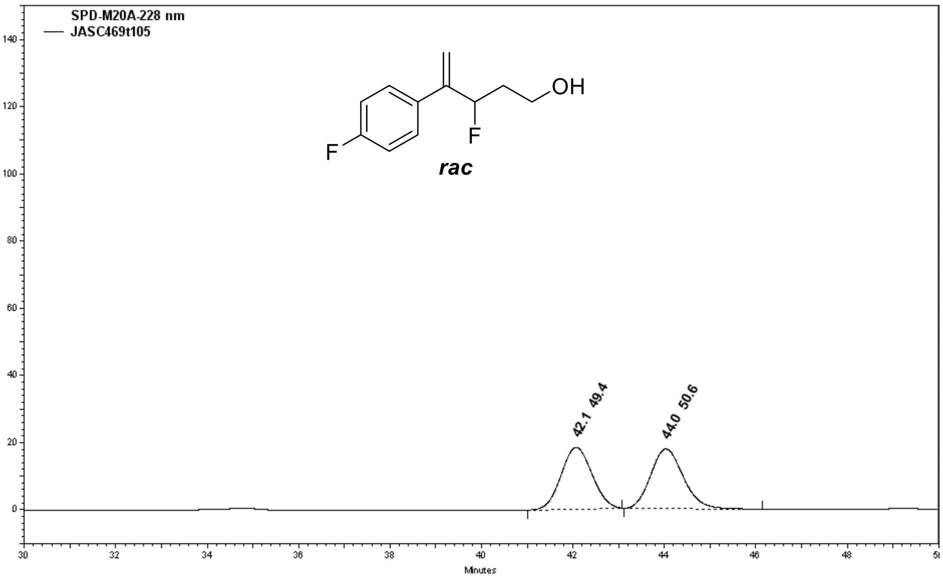
R= H, (*R*)-TRIP	+36	+62	*E*-homoallylic
	+45	+62	*Z*-homoallylic
R= Ph, (*S*)-6,6'-Ph_2-TRIP	-30	-58	*E*-homoallylic
	-45	-59	*Z*-homoallylic
R = Bn, (*S*)-6,6'-Bn_2-TRIP	-39	-63	*E*-homoallylic
	-47	-63	*Z*-homoallylic
R = Br, (*S*)-6,6'-Br_2-TRIP	-31	-61	*E*-homoallylic

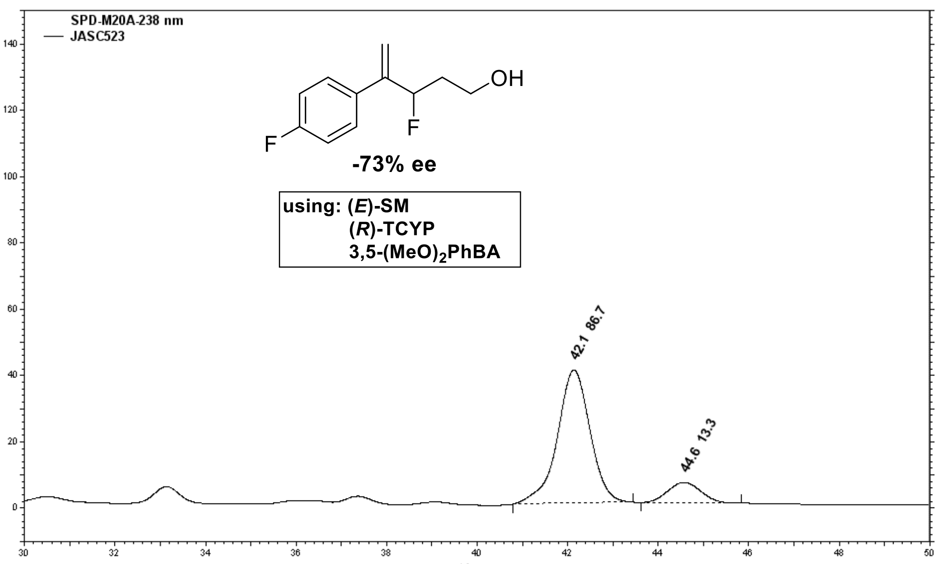
In fact, the calculated parameters ${}^{T}E\pi$ and ${}^{T}D\pi$ for different X-substituents were all very similar:

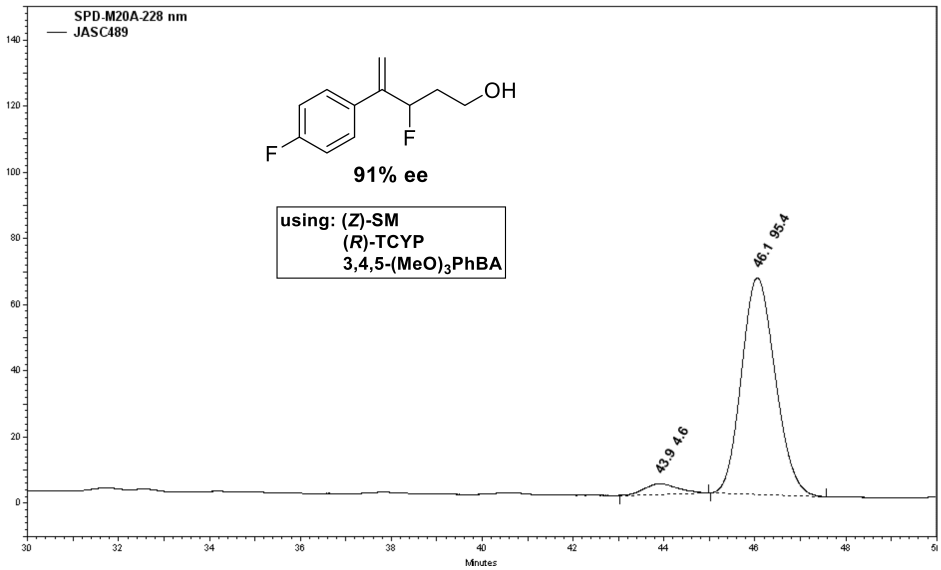


X	${}^{T}E\pi$	${}^{T}D\pi$
CF_3	-3.11	2.43
Br	-3.01	2.43
H	-2.95	2.44
OMe	-3.37	2.41
SMe	-3.37	2.40

Representative HPLC Traces



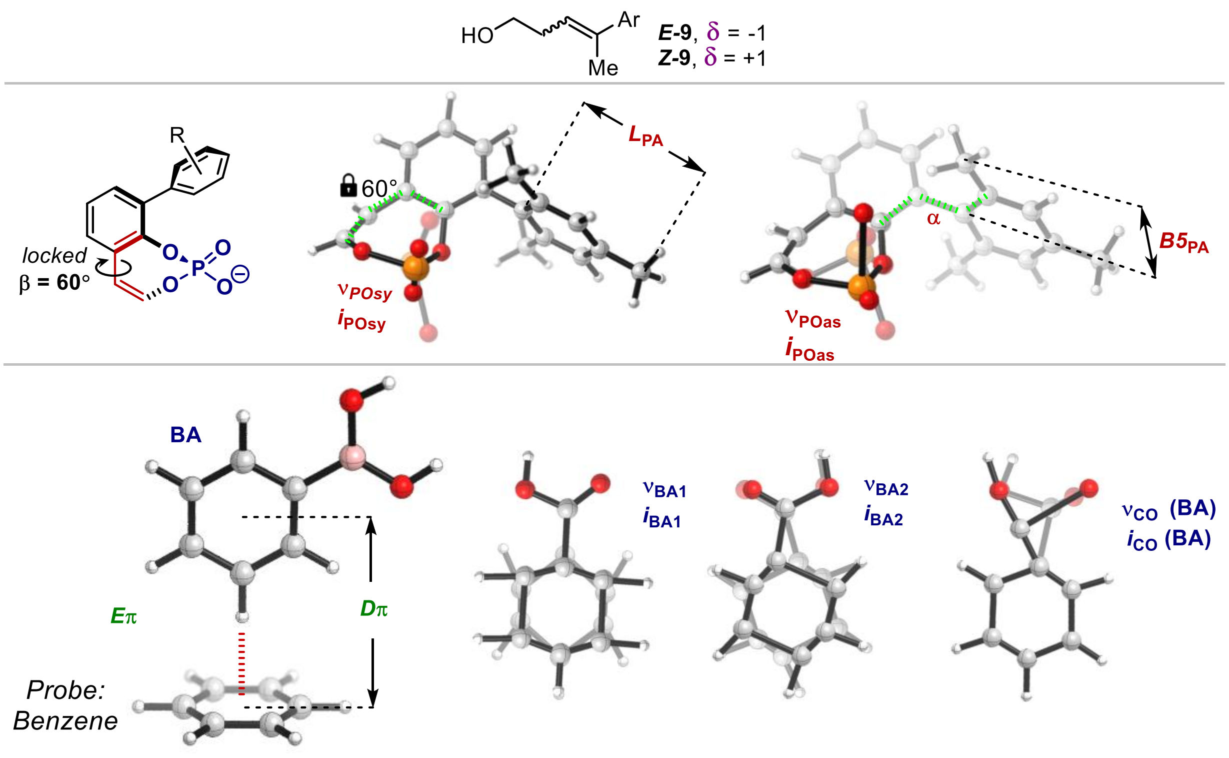



SPD-M20A-228 nm
JASC489
OH
F
F
91% ee
using: (Z)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
43.9 4.6
46.1 95.4
Minutes

Model development

Parameters collected

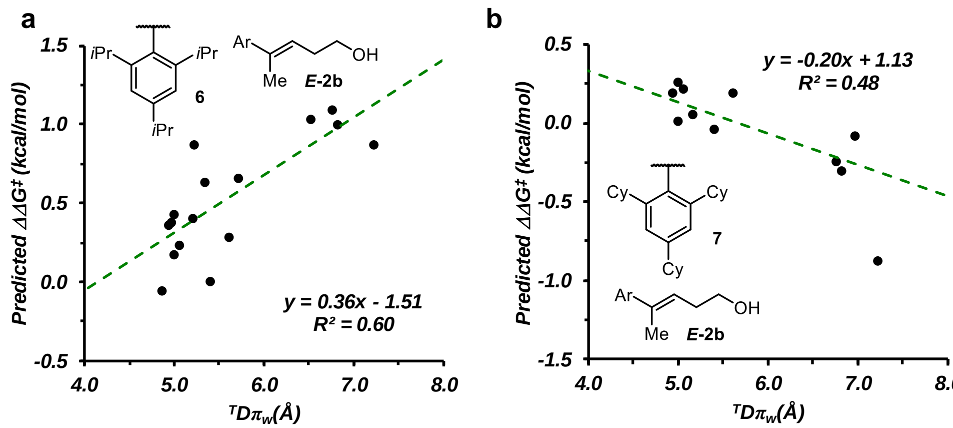
The calculated parameters are summarized in the following table. Sterimol parameters **L**, **B1** and **B5**, represent the length, the minimum and the maximum widths of the substituent, respectively. The calculation of the **π-parameters**, BAs' frequencies and intensities of the carbonyl stretching ($\boldsymbol{\nu_{CO}}$ and $\boldsymbol{i_{CO}}$) and of the arene compressions ($\boldsymbol{\nu_{BA1}}$, $\boldsymbol{i_{BA1}}$, $\boldsymbol{\nu_{BA2}}$ and $\boldsymbol{i_{BA2}}$) and the parameters relative to chiral phosphoric acids **5**, **6** and **7** have been previously reported by us[10].



Alkene	PA	BA	δ	BA Parameters															PA Parameters							
				$^{T}E\pi_{d}$	$^{T}E\pi_{D}$	$^{T}E\pi_{w}$	$^{T}D\pi_{d}$	$^{T}D\pi_{D}$	$^{T}D\pi_{w}$	$B1_{BA}$	$B5_{BA}$	L_{BA}	ν_{CO} (BA)	i_{CO} (BA)	ν_1 (BA)	i_1 (BA)	ν_2 (BA)	i_2 (BA)	α	ν_{POsy} (PA)	i_{POsy} (PA)	ν_{POas} (PA)	i_{POas} (PA)	L_{PA}	$B1_{PA}$	$B5_{PA}$
E-2b	5	2-Br-Ph	-1	-3.23	-3.32	-3.28	4.91	5.05	4.99	1.79	4.81	6.45	1865.04	325.60	1664.65	40.49	1518.78	18.77	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	3,5-(CF$_3$)$_2$-Ph	-1	-1.62	-1.62	-1.62	6.96	6.96	6.96	2.50	4.99	7.00	1864.49	364.46	1686.29	42.32	1520.14	1.98	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	3,5-Me$_2$-Ph	-1	-1.77	-1.77	-1.77	6.51	6.51	6.51	1.95	4.58	6.32	1849.43	380.00	1674.41	9.52	1524.82	0.17	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	3,5-(OMe)$_2$-Ph	-1	-2.04	-2.04	-2.04	7.21	7.21	7.21	2.08	4.83	7.21	1854.36	363.21	1676.22	23.43	1529.14	0.89	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	Ph	-1	-2.95	-2.95	-2.95	4.93	4.93	4.93	1.77	3.19	6.36	1852.13	385.46	1677.45	24.81	1542.51	8.34	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	4-NO$_2$-Ph	-1	-2.12	-2.12	-2.12	5.60	5.60	5.60	1.77	3.23	7.81	1861.50	366.86	1675.29	11.35	1543.90	3.95	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	4-Me-Ph	-1	-3.30	-3.30	-3.30	4.99	4.99	4.99	1.88	3.23	7.39	1848.99	413.29	1685.76	65.69	1564.49	4.64	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	2-Me-Ph	-1	-2.91	-3.08	-3.01	4.93	5.12	5.04	1.86	4.51	6.34	1840.76	374.94	1673.56	34.23	1535.63	17.43	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	5	2,4,6-Me$_3$-Ph	-1	-3.52	-3.52	-3.52	5.16	5.16	5.16	2.04	4.52	7.47	1842.70	387.25	1680.62	75.01	1533.12	2.78	98.4	1152.15	184.09	1388.05	288.79	7.36	1.87	4.57
E-2b	6	3,5-(CF$_3$)$_2$-Ph	-1	-1.62	-1.62	-1.62	6.96	6.96	6.96	2.50	4.99	7.00	1864.49	364.46	1686.29	42.32	1520.14	1.98	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,5-Br$_2$-Ph	-1	-2.12	-2.12	-2.12	6.80	6.80	6.80	1.92	4.75	6.45	1859.92	358.12	1653.75	0.60	1482.47	27.39	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,5-Me$_2$-Ph	-1	-1.77	-1.77	-1.77	6.51	6.51	6.51	1.95	4.58	6.32	1849.43	380.00	1674.41	9.52	1524.82	0.17	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	2,6-Cl$_2$-Ph	-1	-3.61	-3.61	-3.61	4.95	4.95	4.95	2.03	4.53	6.62	1883.36	333.93	1663.27	55.46	1496.48	11.93	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	4-Me-Ph	-1	-3.30	-3.30	-3.30	4.99	4.99	4.99	1.88	3.23	7.39	1848.99	413.29	1685.76	65.69	1564.49	4.64	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	4-NO$_2$-Ph	-1	-2.12	-2.12	-2.12	5.60	5.60	5.60	1.77	3.23	7.81	1861.50	366.86	1675.29	11.35	1543.90	3.95	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	2-Me-Ph	-1	-2.91	-3.08	-3.01	4.93	5.12	5.04	1.86	4.51	6.34	1840.76	374.94	1673.56	34.23	1535.63	17.43	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	4-*t*Bu-Ph	-1	-3.35	-3.35	-3.35	5.70	5.70	5.70	2.90	3.39	8.80	1849.26	428.65	1684.13	73.31	1563.26	29.30	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	4-OMe-Ph	-1	-2.98	-2.81	-2.91	4.94	5.84	5.32	1.89	3.25	8.54	1844.14	419.14	1680.06	209.51	1569.38	32.33	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	2-Br-Ph	-1	-3.23	-3.32	-3.28	4.91	5.05	4.99	1.79	4.81	6.45	1865.04	325.60	1664.65	40.49	1518.78	18.77	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	2-OMe-Ph	-1	-2.79	-2.71	-2.75	4.94	5.91	5.39	1.86	5.52	6.45	1857.41	432.62	1672.21	118.53	1541.84	108.22	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	4-Py	-1	-2.86	-2.86	-2.86	4.86	4.86	4.86	1.77	3.15	5.93	1863.23	341.23	1676.95	0.22	1546.42	15.16	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	4-CF$_3$-Ph	-1	-3.51	-3.51	-3.51	5.19	5.19	5.19	2.19	3.14	7.86	1858.73	372.04	1694.57	2.29	1567.85	42.80	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	Ph	-1	-2.95	-2.95	-2.95	4.93	4.93	4.93	1.77	3.19	6.36	1852.13	385.46	1677.45	24.81	1542.51	8.34	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,5-Cl$_2$-Ph	-1	-1.35	-1.35	-1.35	6.75	6.75	6.75	1.77	4.46	6.45	1860.26	357.83	1659.22	0.11	1487.19	27.60	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	2-Napht	-1	-3.58	-2.28	-3.45	4.97	7.26	5.21	1.77	4.24	8.54	1848.65	380.71	1707.23	20.95	1560.04	9.17	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,5-(OMe)$_2$-Ph	-1	-2.04	-2.04	-2.04	7.21	7.21	7.21	2.08	4.83	7.21	1854.36	363.21	1676.22	23.43	1529.14	0.89	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	7	3,5-(CN)$_2$-Ph	-1	0.29	0.29	0.29	8.12	8.12	8.12	1.78	5.04	6.46	1868.10	355.46	1662.97	16.40	1484.76	9.62	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	3,5-(OMe)$_2$-Ph	-1	-2.04	-2.04	-2.04	7.21	7.21	7.21	2.08	4.83	7.21	1854.36	363.21	1676.22	23.43	1529.14	0.89	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	3,5-Br$_2$-Ph	-1	-2.12	-2.12	-2.12	6.80	6.80	6.80	1.92	4.75	6.45	1859.92	358.12	1653.75	0.60	1482.47	27.39	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	3,5-Cl$_2$-Ph	-1	-1.35	-1.35	-1.35	6.75	6.75	6.75	1.77	4.46	6.45	1860.26	357.83	1659.22	0.11	1487.19	27.60	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	3,5-(CF$_3$)$_2$-Ph	-1	-1.62	-1.62	-1.62	6.96	6.96	6.96	2.50	4.99	7.00	1864.49	364.46	1686.29	42.32	1520.14	1.98	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	Ph	-1	-2.95	-2.95	-2.95	4.93	4.93	4.93	1.77	3.19	6.36	1852.13	385.46	1677.45	24.81	1542.51	8.34	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	4-Me-Ph	-1	-3.30	-3.30	-3.30	4.99	4.99	4.99	1.88	3.23	7.39	1848.99	413.29	1685.76	65.69	1564.49	4.64	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	4-NO$_2$-Ph	-1	-2.12	-2.12	-2.12	5.60	5.60	5.60	1.77	3.23	7.81	1861.50	366.86	1675.29	11.35	1543.90	3.95	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	2-Me-Ph	-1	-2.91	-3.08	-3.01	4.93	5.12	5.04	1.86	4.51	6.34	1840.76	374.94	1673.56	34.23	1535.63	17.43	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	2,4,6-Me$_3$-Ph	-1	-3.52	-3.52	-3.52	5.16	5.16	5.16	2.04	4.52	7.47	1842.70	387.25	1680.62	75.01	1533.12	2.78	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	2-OMe-Ph	-1	-2.79	-2.71	-2.75	4.94	5.91	5.39	1.86	5.52	6.45	1857.41	432.62	1672.21	118.53	1541.84	108.22	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	7	2-Br-Ph	-1	-3.23	-3.32	-3.28	4.91	5.05	4.99	1.79	4.81	6.45	1865.04	325.60	1664.65	40.49	1518.78	18.77	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,5-(OMe)$_2$-Ph	1	-2.04	-2.04	-2.04	7.21	7.21	7.21	2.08	4.83	7.21	1854.36	363.21	1676.22	23.43	1529.14	0.89	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,5-Me$_2$-Ph	1	-1.77	-1.77	-1.77	6.51	6.51	6.51	1.95	4.58	6.32	1849.43	380.00	1674.41	9.52	1524.82	0.17	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,5-(CF$_3$)$_2$-Ph	1	-1.62	-1.62	-1.62	6.96	6.96	6.96	2.50	4.99	7.00	1864.49	364.46	1686.29	42.32	1520.14	1.98	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,5-Br$_2$-Ph	1	-2.12	-2.12	-2.12	6.80	6.80	6.80	1.92	4.75	6.45	1859.92	358.12	1653.75	0.60	1482.47	27.39	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,5-Cl$_2$-Ph	1	-1.35	-1.35	-1.35	6.75	6.75	6.75	1.77	4.46	6.45	1860.26	357.83	1659.22	0.11	1487.19	27.60	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3-Cl-5-Me-Ph	1	-1.96	-1.15	-1.79	6.46	6.77	6.53	1.91	4.54	6.43	1855.10	368.00	1673.11	6.05	1514.69	11.30	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
E-2b	6	3,4,5-(OMe)$_3$-Ph	-1	-2.33	-2.33	-2.33	7.20	7.20	7.20	2.07	5.50	8.57	1845.53	386.66	1660.67	7.60	1573.98	53.52	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,4,5-F$_3$-Ph	-1	-1.00	-1.00	-1.00	5.95	5.95	5.95	1.77	3.80	7.15	1859.67	362.16	1696.43	13.94	1597.64	129.53	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,4,5-Cl$_3$-Ph	-1	-1.63	-1.63	-1.63	6.72	6.72	6.72	1.77	4.48	7.86	1860.02	381.62	1651.90	29.07	1484.05	1.48	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	6	3,4,5-Me$_3$-Ph	-1	-2.04	-2.04	-2.04	6.46	6.46	6.46	2.08	4.53	7.48	1846.70	409.69	1679.41	29.34	1537.88	1.32	84.4	1151.38	157.41	1386.72	174.16	8.66	3.29	5.73
E-2b	7	3,4,5-(OMe)$_3$-Ph	-1	-2.33	-2.33	-2.33	7.20	7.20	7.20	2.07	5.50	8.57	1845.53	386.66	1660.67	7.60	1573.98	53.52	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,4,5-(OMe)$_3$-Ph	1	-2.33	-2.33	-2.33	7.20	7.20	7.20	2.07	5.50	8.57	1845.53	386.66	1660.67	7.60	1573.98	53.52	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,4,5-Cl$_3$-Ph	1	-1.63	-1.63	-1.63	6.72	6.72	6.72	1.77	4.48	7.86	1860.02	381.62	1651.90	29.07	1484.05	1.48	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57
Z-2b	7	3,4,5-F$_3$-Ph	1	-1.00	-1.00	-1.00	5.95	5.95	5.95	1.77	3.80	7.15	1859.67	362.16	1696.43	13.94	1597.64	129.53	86.5	1149.17	161.84	1389.83	68.11	10.73	3.47	7.57

Single parameter correlations

Single parameter correlations for the fluorination of homoallylic alcohols are reported in the following graphs. In **a**, the datapoints relative to catalyst *R*-TRIP **6** show a trend with $^{T}\mathbf{D\pi_w}$ (R^2 = 0.60); **b** shows the correlation between the datapoints of **PA 7** (*R*-TCYP) and $^{T}\mathbf{D\pi_w}$ with substrates ***E*-2b** (R^2 = 0.48). Notably, even though these graphs only show a trend between the reaction selectivity and $^{T}\mathbf{D\pi_w}$, no other trend/correlation was found with any other parameter.

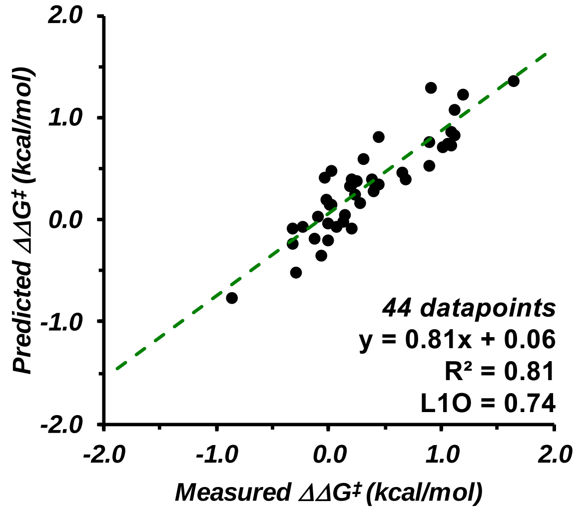


Model development

Measured ΔΔG‡ values were calculated using the formula ΔΔG‡ = -RTln(*er*) where R is the gas constant, T is temperature, and *er* is the enantiomeric ratio (*er* is the average enantiomeric ratio of two experimental results and the temperature is set at 298 K). Multiple linear regression models were developed using the functions *LinearModel.stepwise* and *LinearModel.fit* implemented in MATLAB® R2014a software in order to obtain the predicted ΔΔG‡. A good linear correlation (R^2 close to 1.0 and intercept close to 0.0) between the **Predicted ΔΔG‡** and the **Measured ΔΔG‡** indicates that the obtained model adequately approximates the system under study. Leave-K-Out (LKO) values were also generated using MATLAB and are always reported below the R^2 value in the plots.

The model presents $R^2 = 0.81$ and intercept = 0.06.

$$\Delta\Delta G^{\ddagger} = 0.21 + 0.29\ {}^{T}E\pi_{D} + 0.63\ \delta\ {}^{T}D\pi_{w} + 0.20\ B5_{PA} + \nu_{POas}\,(0.14\ {}^{T}E\pi_{D} - 0.34\ {}^{T}D\pi_{w} - 0.46)$$



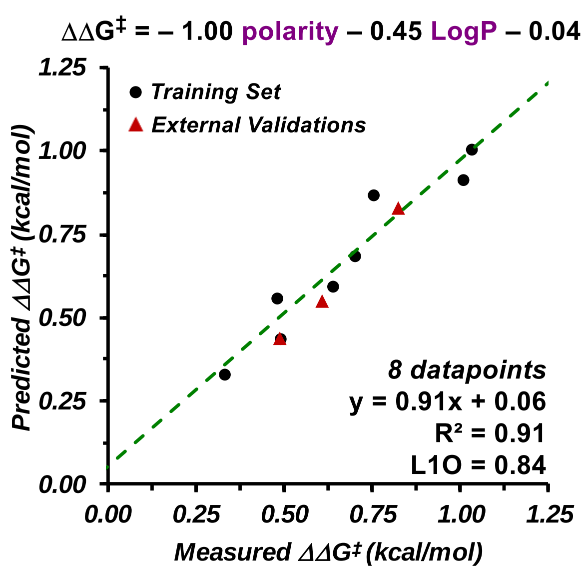
Alkene	PA	BA	Measured ΔΔG‡ (kcal/mol)	Predicted ΔΔG‡ (kcal/mol)
***E*-9**	**5**	**2-Br-Ph**	-0.34	-0.08
***E*-9**	**5**	**3,5-$(CF_3)_2$-Ph**	-0.02	-0.03
***E*-9**	**5**	**3,5-Me_2-Ph**	-0.11	0.03
***E*-9**	**5**	**3,5-$(OMe)_2$-Ph**	-0.34	-0.23
***E*-9**	**5**	**Ph**	0.13	0.05
***E*-9**	**5**	**4-NO_2-Ph**	0.00	0.15
***E*-9**	**5**	**4-Me-Ph**	0.19	-0.07
***E*-9**	**5**	**2-Me-Ph**	0.12	-0.02
***E*-9**	**5**	**2,4,6-Me_3-Ph**	-0.02	-0.19
***E*-9**	**6**	**3,5-$(CF_3)_2$-Ph**	0.43	0.81
***E*-9**	**6**	**3,5-Br_2-Ph**	1.00	0.71
***E*-9**	**6**	**3,5-Me_2-Ph**	1.04	0.75
***E*-9**	**6**	**2,6-Cl_2-Ph**	0.38	0.29
***E*-9**	**6**	**4-Me-Ph**	0.43	0.35
***E*-9**	**6**	**4-NO_2-Ph**	0.29	0.60
***E*-9**	**6**	**2-Me-Ph**	0.24	0.39
***E*-9**	**6**	**4-*t*Bu-Ph**	0.67	0.40
***E*-9**	**6**	**4-OMe-Ph**	0.63	0.46
***E*-9**	**6**	**2-Br-Ph**	0.18	0.34
***E*-9**	**6**	**2-OMe-Ph**	0.01	0.49
***E*-9**	**6**	**4-Py**	-0.05	0.41
***E*-9**	**6**	**4-CF_3-Ph**	0.41	0.33
***E*-9**	**6**	**Ph**	0.37	0.40
***E*-9**	**6**	**3,5-Cl_2-Ph**	1.10	0.84
***E*-9**	**6**	**2-Napht**	0.88	0.54
***E*-9**	**6**	**3,5-$(OMe)_2$-Ph**	0.88	0.76
***E*-9**	**7**	**3,5-$(CN)_2$-Ph**	-0.14	-0.17
***E*-9**	**7**	**3,5-$(OMe)_2$-Ph**	-0.88	-0.76
***E*-9**	**7**	**3,5-Br_2-Ph**	-0.30	-0.51
***E*-9**	**7**	**3,5-Cl_2-Ph**	-0.24	-0.06
***E*-9**	**7**	**3,5-$(CF_3)_2$-Ph**	-0.08	-0.35
***E*-9**	**7**	**Ph**	0.19	0.40
***E*-9**	**7**	**4-Me-Ph**	0.26	0.17
***E*-9**	**7**	**4-NO_2-Ph**	0.19	0.36
***E*-9**	**7**	**2-Me-Ph**	0.22	0.25
***E*-9**	**7**	**2,4,6-Me_3-Ph**	0.06	-0.07
***E*-9**	**7**	**2-OMe-Ph**	-0.04	0.20
***E*-9**	**7**	**2-Br-Ph**	0.01	0.16
***Z*-9**	**7**	**3,5-$(OMe)_2$-Ph**	1.63	1.36
***Z*-9**	**7**	**3,5-Me_2-Ph**	1.07	0.74
***Z*-9**	**7**	**3,5-$(CF_3)_2$-Ph**	0.90	1.30
***Z*-9**	**7**	**3,5-Br_2-Ph**	1.07	0.87
***Z*-9**	**7**	**3,5-Cl_2-Ph**	1.18	1.23
***Z*-9**	**7**	**3-Cl-5-Me-Ph**	1.10	1.09
***E*-9**	**6**	**3,4,5-$(OMe)_3$-Ph**	0.72	0.71
***E*-9**	**6**	**3,4,5-F_3-Ph**	0.38	0.83
***E*-9**	**6**	**3,4,5-Cl_3-Ph**	1.18	0.79
***E*-9**	**6**	**3,4,5-Me_3-Ph**	0.88	0.70
***E*-9**	**7**	**3,4,5-$(OMe)_3$-Ph**	-1.09	-0.91
***Z*-9**	**7**	**3,4,5-$(OMe)_3$-Ph**	1.68	1.19
***Z*-9**	**7**	**3,4,5-Cl_3-Ph**	1.51	1.04
***Z*-9**	**7**	**3,4,5-F_3-Ph**	0.54	0.54

Solvent Parameters/Data

All parameters were calculated using Molecular Modeling, Version 6.3.6. Fragment addition LogP and van Krevelen and Hoftyzer type 3-D solubility parameters ($J^{1/2}$ $cm^{-3/2}$) for polarity were used in the model.

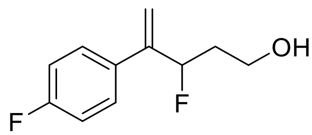
Solvent	Polarity	Log P	Measured ΔΔG‡ (kcal/mol)	Predicted ΔΔG‡ (kcal/mol)
Toluene (Me-Ph)	0.42802	2.791	1.00	0.92
Benzene (H-Ph)	0.49667	2.142	1.03	1.01
1,3,5-F_3-Ph	9.13052	2.571	0.49	0.44
1,4-F_2-Ph	7.37654	2.428	0.47	0.56
CF_3-Ph	0.64882	3.025	0.75	0.87
1,4-Et_2-Ph	0.29512	4.498	0.70	0.69
1,3-$(CF_3)_2$-Ph	7.72369	3.908	0.33	0.33
Cl-Ph	5.78438	2.855	0.63	0.59
1,3-Me_2-Ph	0.37604	3.440	0.82	0.83
1-Me,4-Cl-Ph	5.02120	3.504	0.60	0.55
1,2,3-F_3-Ph	9.13052	2.571	0.49	0.44

The model presents R^2 = 0.91 and intercept = 0.06.



Characterization Data of Fluorination Products

3-Fluoro-4-(4-fluorophenyl)pent-4-en-1-ol (4b)



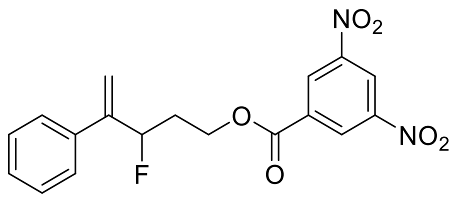
Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.372–7.337 (m, 2H), 7.06–7.01 (m, 2H), 5.55 (m, 1H), 5.42 (d, J = 1.8 Hz, 1H), 5.39 (d, J = 1.8 Hz, 1H), 3.86–3.74 (m, 2H), 1.98–1.84 (m, 2H), 1.58 (br s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 162.7 (d, J = 247.6 Hz), 146.4 (d, J = 16.6 Hz), 134.4 (d, J = 3.0 Hz), 128.8 (d, J = 7.6 Hz), 115.6 (d, J = 21.1 Hz), 115.0 (d, J = 10.6 Hz), 91.8 (d, J = 21.1 Hz), 59.1 (d, J = 4.5 Hz), 37.2 (d, J = 22.3 Hz). **^{19}F NMR (376 MHz, $CDCl_3$) δ** -113.27 – -113.35 (m), -179.16 – -179.42 (m). **HRMS (EI)** Calcd. for $C_{11}H_{12}OF_2$ $[M]^+$: 198.0856. Found: 198.0854.

General Protocol for the Benzoylation reaction

The resulting reaction mixture of fluorination (0.1 mmol scale with respect to homoallylic alcohol) was filtered through a plug of silica gel using DCM (10 mL) as eluent, and the crude product concentrated in *vacuo*. Then, to a solution of the fluorinated crude product in DCM (1 mL) were added 3,5-dinitrobenzoyl chloride (1.5 equiv, 35 mg, 0.15 mmol), DMAP (1.5 equiv, 18 mg, 0.15 mmol), Et_3N (1.5 equiv, 20 μL), and the resulting mixture stirred at rt. After complete consumption of the starting material, as judged by TLC analysis (up to 20 minutes), the crude product was purified by column chromatography on silica gel to give the desired 3,5-dinitrobenzoylesters.

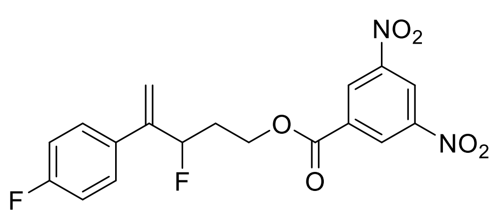
Characterization data of Benzoylation Products

3-Fluoro-4-phenylpent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9a)



The title compound was obtained according to the general procedure and obtained as a colorless oil (18.4 mg, 49% yield) from ***Z*-2a** (18.0 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.23 (t, *J* = 1.8 Hz, 1H), 9.12 (d, *J* = 1.8 Hz, 2H), 7.40–7.32 (m, 5H), 5.61 (m, 1H), 5.49 (m, 2H), 4.62–4.55 (m, 2H), 2.26 (m, 1H), 2.22 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.5, 148.8, 146.5 (d, *J* = 15.1 Hz), 138.0, 133.9, 129.5, 128.9, 128.5, 126.9, 122.6, 115.1 (d, *J* = 12.0 Hz), 92.3 (d, *J* = 176.7 Hz), 63.2 (d, *J* = 3.0 Hz), 33.6 (d, *J* = 24.2 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -179.95 – -180.21 (m). **HRMS (EI)** Calcd. for $C_{18}H_{15}N_2O_6F$ $[M]^+$: 374.0920. Found: 374.0915. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (17.1 min), t_{minor} (19.5 min); 88% ee from ***Z*-2a** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

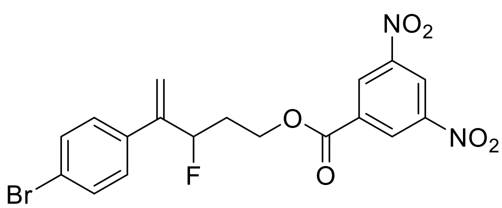
3-Fluoro-4-(4-fluorophenyl)pent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9b)



The title compound was obtained according to the general procedure and obtained as a colorless oil (14.5 mg, 37% yield) from ***Z*-2b** (19.8 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.23 (t, *J* = 1.8 Hz, 1H), 9,13 (d, *J* = 1.8 Hz, 2H), 7.38–7.36 (m, 2H), 7.08–7.05 (m, 2H), 5.54 (m, 1H), 5.48 (s, *J* = 1H), 5.45 (d, *J* = 2.4 Hz, 1H), 4.62–4.56 (m, 2H), 2.24 (m, 1H), 2.20 (m, 1H).

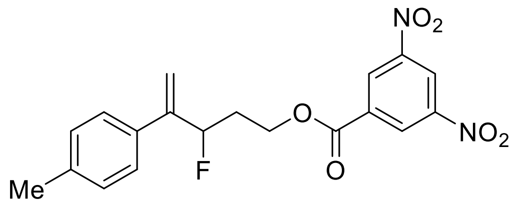
^{13}C NMR (151 MHz, CDCl$_3$) δ 162.9 (d, *J* = 247.6 Hz), 162.5, 148.9, 145.5 (d, *J* = 16.6 Hz), 134.0, 133.8, 129.5, 128.7 (d, *J* = 9.1 Hz), 122.6, 115.8 (d, *J* = 22.7 Hz), 115.6 (d, *J* = 10.6 Hz), 90.9 (d, *J* = 24.2 Hz), 63.1 (d, *J* = 4.5 Hz), 33.5 (d, *J* = 2.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -112.58 – -112.66 (m), -179.07 – -179.33 (m). **HRMS (EI)** Calcd. for $C_{18}H_{14}N_2O_6F_2$ $[M]^+$: 392.0825. Found: 392.0820. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (22.7 min), t_{minor} (24.2 min); 91% ee from ***Z*-2b** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

4-(4-Bromophenyl)-3-fluoropent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9c)



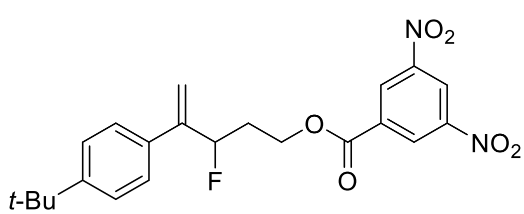
The title compound was obtained according to the general procedure and obtained as a colorless oil (16.8 mg, 37%) yield from ***E*-2c** (25.9 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.24 (t, *J* = 1.8 Hz, 1H), 9.12 (d, *J* = 1.8 Hz, 2H), 7.50–7.49 (m, 2H), 7.28–7.25 (m, 2H), 5.54 (m, 1H), 5.51 (s, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 4.61–4.54 (m, 2H), 2.24 (m, 1H), 2.20 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.4, 148.9, 145.6, 145.5, 136.9 (d, *J* = 1.5 Hz), 133.8, 132.0, 129.5, 128.6, 122.6, 116.1 (d, *J* = 10.6 Hz), 91.2 (d, *J* = 176.7 Hz), 63.1 (d, *J* = 4.5 Hz), 33.5 (d, *J* = 24.2 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -179.16 – -179.41 (m). **HRMS (EI)** Calcd. for $C_{18}H_{14}N_2O_6F^{79}Br$ $[M]^+$: 452.0025. Found: 452.0018. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (26.1 min), t_{minor} (28.2 min); 95% ee from ***Z*-2c** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

3-Fluoro-4-(*p*-tolyl)pent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9d)



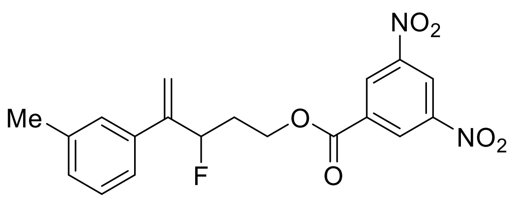
The title compound was obtained according to the general procedure and obtained as a colorless oil (27.2 mg, 70% yield) from ***Z*-2d** (19.4 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, $CDCl_3$) δ** 9.23 (d, *J* = 2.4 Hz, 1H), 9.12 (d, *J* = 2.4 Hz, 2H), 7.28–7.27 (m, 2H), 7.18–7.16 (m, 2H), 5.60 (m, 1H), 5.45 (d, *J* = 3.0 Hz, 1H), 5.44 (s, 1H), 4.61–4.54 (m, 2H), 2.34 (s, 3H), 2.26 (m, 1H), 2.22 (m, 1H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 162.5, 148.8, 146.4, 146.2, 138.4, 135.1 (d, *J* = 3.0 Hz), 133.9, 129.5 (d, *J* = 4.5 Hz), 126.7, 122.6, 114.2 (d, *J* = 10.6 Hz), 90.8 (d, *J* = 24.2 Hz), 63.2 (d, *J* = 3.0 Hz), 33.6 (d, *J* = 22.7 Hz), 21.3. **^{19}F NMR (376 MHz, $CDCl_3$) δ** -180.15 – -180.40 (m). **HRMS (EI)** Calcd. for $C_{19}H_{17}N_2O_6F$ $[M]^+$: 388.1076. Found: 388.1072. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (15.4 min), t_{minor} (17.5 min); 96% ee from ***Z*-2d** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

4-(4-(*tert*-Butyl)phenyl)-3-fluoropent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9e)



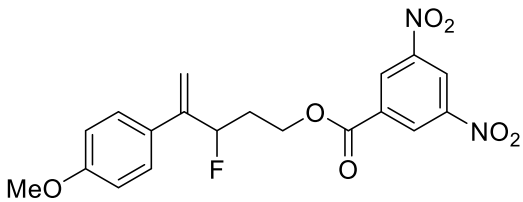
The title compound was obtained according to the general procedure and obtained as a yellow solid (26.2 mg, 61% yield) from ***E*-2e** (23.6 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, $CDCl_3$) δ** 9.23 (t, *J* = 1.8 Hz, 1H), 9.14 (d, *J* = 1.8 Hz, 2H), 7.40–7.38 (m, 2H), 7.33–7.32 (m, 2H), 5.61 (m, 1H), 5.47 (d, *J* = 2.4 Hz, 1H), 5.45 (s, 1H), 4.63–4.56 (m, 2H), 2.30–2.26 (m, 1H), 2.26–2.22 (m, 1H), 1.32 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.5, 159.81, 148.8, 145.9, 145.8, 133.9, 130.3, 129.5, 128.0, 122.6, 114.2, 113.7 (d, *J* = 10.6 Hz), 91.4 (d, *J* = 175.2 Hz), 63.2 (d, *J* = 3.0 Hz), 55.4, 33.6 (d, *J* = 22.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -179.67 – -179.93 (m). **HRMS (EI)** Calcd. for $C_{22}H_{23}N_2O_6F$ $[M]^+$: 430.1546. Found: 430.1541. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (11.1 min), t_{minor} (11.9 min); 89% ee from ***Z*-2e** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

3-Fluoro-4-(*m*-tolyl)pent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9f)



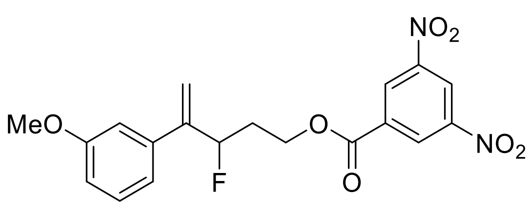
The title compound was obtained according to the general procedure and obtained as a white solid (17.9 mg, 46% yield) from ***Z*-2f** (19.4 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.23(t, *J* = 2.4 Hz, 1H), 9.12 (d, *J* = 2.4 Hz, 2H), 7.25 (m, 1H), 7.19–7.14 (m, 3H), 5.69 (m, 1H), 5.463 (s, 1H), 5.458 (s, 1H), 4.62–4.55 (m, 2H), 2.35 (s, 3H), 2.26 (m, 1H), 2.22 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.5, 148.8, 146.6 (d, *J* = 16.6 Hz), 138.5, 138.0 (d, *J* = 3.0 Hz), 133.9, 129.5, 129.2, 128.7, 127.6, 123.9, 122.6, 114.8 (d, *J* = 10.6 Hz), 91.3 (d, *J* = 176.7 Hz), 63.2 (d, *J* = 4.5 Hz), 33.6 (d, *J* = 22.7 Hz), 21.6. **^{19}F NMR (376 MHz, CDCl$_3$) δ** -179.91 – -180.16 (m). **HRMS (EI)** Calcd. for $C_{19}H_{17}N_2O_6F$ $[M]^+$: 388.1076. Found: 388.1072. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (13.1 min), t_{minor} (15.2 min); 85% ee from ***Z*-2f** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

3-Fluoro-4-(4-methoxyphenyl)pent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9g)



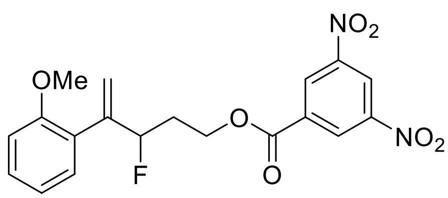
The title compound was obtained according to the general procedure and obtained as a pale yellow oil (17.0 mg, 42% yield) from ***Z*-2g** (21.0 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.23 (m, 1H), 9.120–9.115 (m, 2H), 7.33–7.31 (m, 2H), 6.90–6.87 (m, 2H), 5.57 (m ,1H), 5.41 (d, *J* = 3.0 Hz, 1H), 5.40 (s, 1H), 4.61–4.54 (m, 2H), 3.81 (s, 3H), 2.26 (m, 1H), 2.22 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.5, 159.8, 148.8, 145.8 (d, *J* = 16.6 Hz), 133.9, 130.3, 129.5, 128.0, 122.6, 114.2, 113.7 (d, *J* = 10.6 Hz), 91.4 (d, *J* = 175.2 Hz), 63.2 (d, *J* = 3.0 Hz), 55.4, 33.6 (d, *J* = 22.3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -179.67 – -179.93 (m). **HRMS (EI)** Calcd. for $C_{19}H_{17}N_2O_7F$ $[M]^+$: 404.1025. Found: 404.1019. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (27.4 min), t_{minor} (30.0 min); 81% ee from ***Z*-2g** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

3-Fluoro-4-(3-methoxyphenyl)pent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9h)



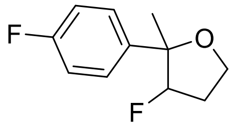
The title compound was obtained according to the general procedure and obtained as a white solid (13.0 mg, 32% yield) from ***Z*-2h** (21.0 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.23 (t, *J* = 1.8 Hz, 1H), 9.11–9.10 (m, 2H), 7.28 (m, 1H), 6.95 (m, 1H), 6.88–6.85 (m, 2H), 5.58 (m,1H), 5.480 (s, 1H), 5.478 (s, 1H), 4.58 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 2.27 (m, 1H), 2.22 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.5, 159.9, 148.8, 146.3 (d, *J* = 16.6 Hz), 139.4 (d, *J* = 3.0 Hz), 133.9, 129.9, 129.5, 122.5, 119.2, 115.1 (*J* = 10.6 Hz), 113.4, 113.1, 91.3 (d, *J* = 175.2 Hz), 63.1 (d, *J* = 3.0 Hz), 55.4, 33.6 (d, *J* = 227 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -179.86 – -180.12 (m). **HRMS (EI)** Calcd. for $C_{19}H_{17}N_2O_7F$ $[M]^+$: 404.1025. Found: 404.1020. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1 mL/min; t_{major} (23.0 min), t_{minor} (25.2 min); 94% ee from ***Z*-2h** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

3-Fluoro-4-(2-methoxyphenyl)pent-4-en-1-yl 2-(3,5-dinitrophenyl)acetate (9i)



The title compound was obtained according to the general procedure and obtained as a yellow solid (15.0 mg, 37% yield) from ***Z*-2i** (21.0 mg, 0.1 mmol) using (*R*)-TRIP and *p*-tolylboronic acid. **^{1}H NMR (600 MHz, CDCl$_3$) δ** 9.22 (t, *J* = 1.8 Hz, 1H), 9.12 (d, *J* = 1.8 Hz, 2H), 7.31 (m, 1H), 7.21 (m, 1H), 6.95 (m, 1H), 6.90 (m, 1H), 5.74 (m, 1H), 5.58 (m, 1H), 5.28 (d, *J* = 3.6 Hz, 1H), 4.59–4.57 (m, 2H), 3.84 (s, 3H), 2.19 (m, 1H), 2.08 (m, 1H). **^{13}C NMR (151 MHz, CDCl$_3$) δ** 162.5, 156.6, 148.8, 146.4 (d, *J* = 18.1 Hz), 134.1, 130.7, 129.7, 129.5, 128.1, 122.5, 121.2, 115.2 (d, *J* = 12.1 Hz), 111.1, 90.4 (d, *J* = 176.7 Hz), 63.4 (d, *J* = 3.0 Hz), 55.7, 33.5 (d, *J* = 21.1 Hz). **^{19}F NMR (376 MHz, CDCl$_3$) δ** -182.32 – -182.58 (m). **HRMS (EI)** Calcd. for $C_{19}H_{17}N_2O_7F$ $[M]^+$: 404.1025. Found: 404.1020. **HPLC** (CHIRALPAK AD-H column) 95:5 (hexane/*i*PrOH) 1mL/min; t_{major} (14.0 min), t_{minor} (17.7 min); 64% ee from ***Z*-2i** using (*R*)-TCYP and 3,5-(dimethoxyphenyl)boronic acid.

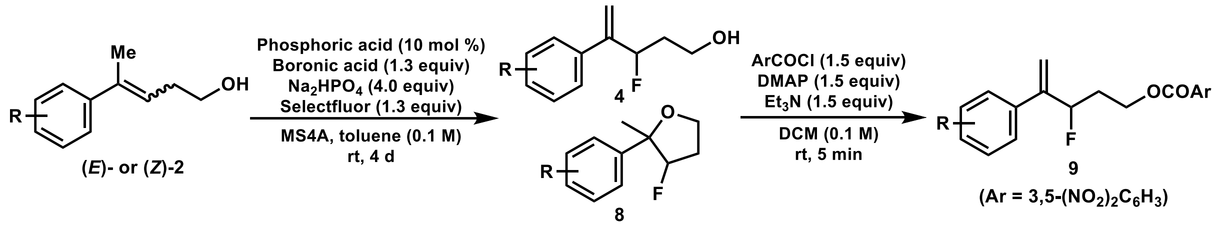
3-Fluoro-2-(4-fluorophenyl)-2-methyltetrahydrofuran (8b, major diastereomer)



Major diastereomer: Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.35–7.33 (m, 2H), 7.05–7.01 (m, 2H), 5.10 (dd, $J_{H–F}$ = 54.1 Hz, *J* = 4.2 Hz, 1H), 4.18 (m, 1H), 4.03 (td, *J* = 9.0, 3.0 Hz, 1H), 2.15 (m, 1H), 1.98 (m, 1H), 1.55 (d, *J* = 3.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 162.1 (d, *J* = 246.1 Hz), 140.4, 126.6 (d, *J* = 7.6 Hz), 115.4 (d, *J* = 21.1 Hz), 98.9 (d, *J* = 187.2 Hz), 87.0 (d, *J* = 16.9 Hz), 65.8, 32.1 (d, *J* = 21.1 Hz), 23.4 (d, *J* = 9.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$) δ** -115.06 – -115.13 (m), -182.97 – -183.28 (m). **HRMS (EI)** Calcd for $C_{11}H_{12}OF$ $[M]^+$: 198.0856. Found: 198.0854.

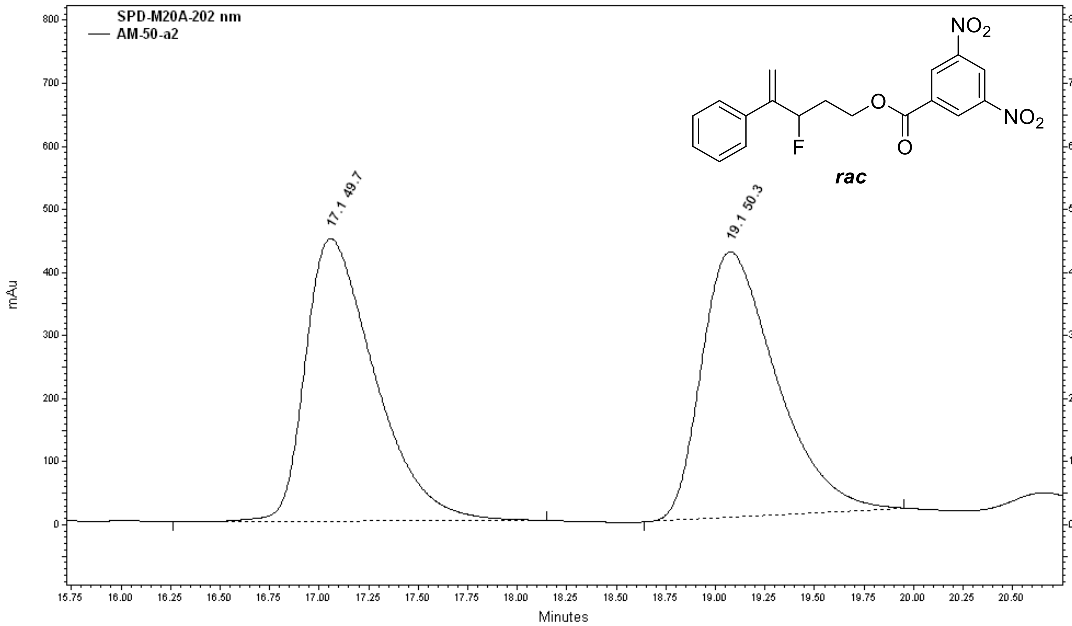
Minor diastereomer: Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.43–7.38 (m, 2H), 7.07–7.01 (m, 2H), 5.10 (ddd, $J_{H–F}$ = 53.6.6 Hz, *J* = 4.5, 1.4 Hz, 1H), 4.23–4.13 (m, 2H), 2.51–2.23 (m, 2H), 1.44 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 162.0 (d, *J* = 244.9 Hz), 137.7, 127.6 (d, *J* = 8.1 Hz), 114.9 (d, *J* = 21.1 Hz), 97.5 (d, *J* = 185.0 Hz), 86.7 (d, *J* = 19.3 Hz), 65.9, 32.9 (d, *J* = 22.4 Hz), 26.8 (d, *J* = 4.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$) δ** -115.55 – -115.61 (m), -175.50 – -175.80 (m).

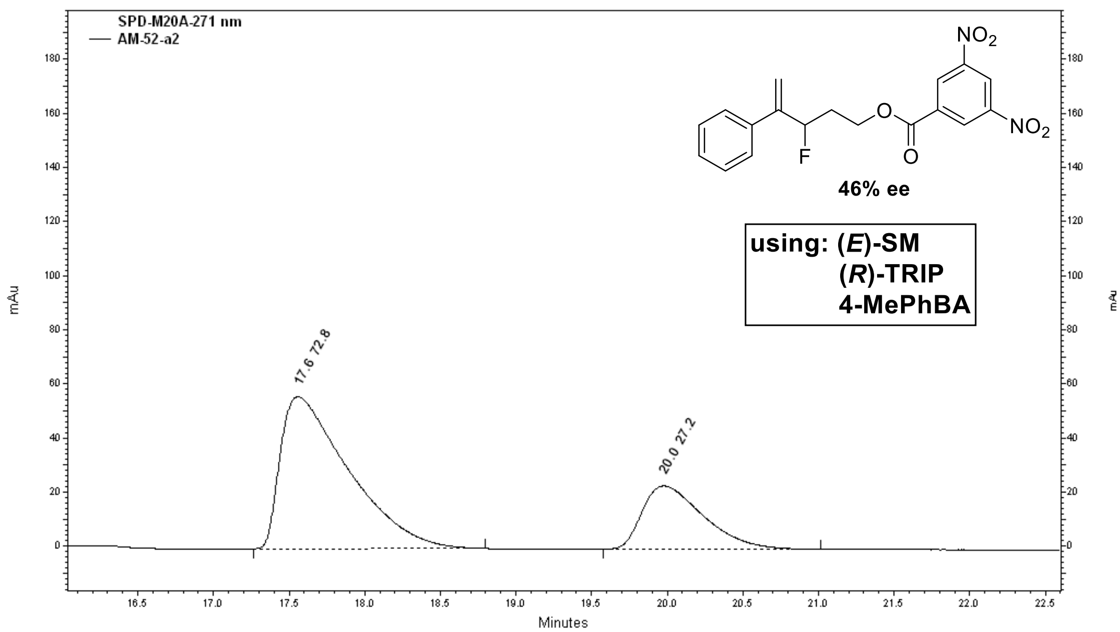
Scope data

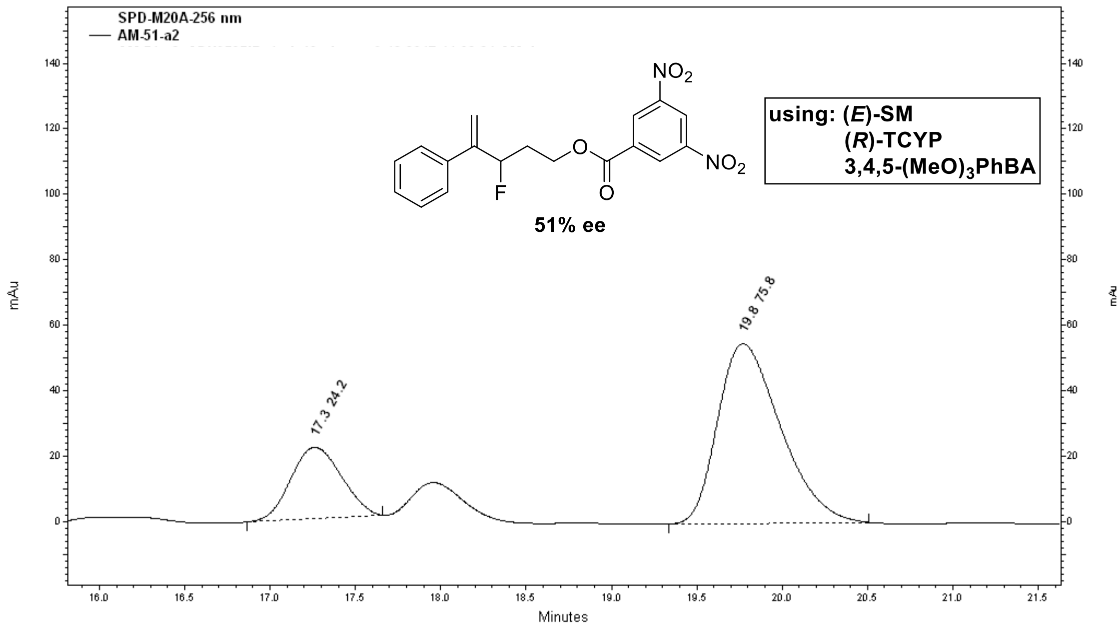


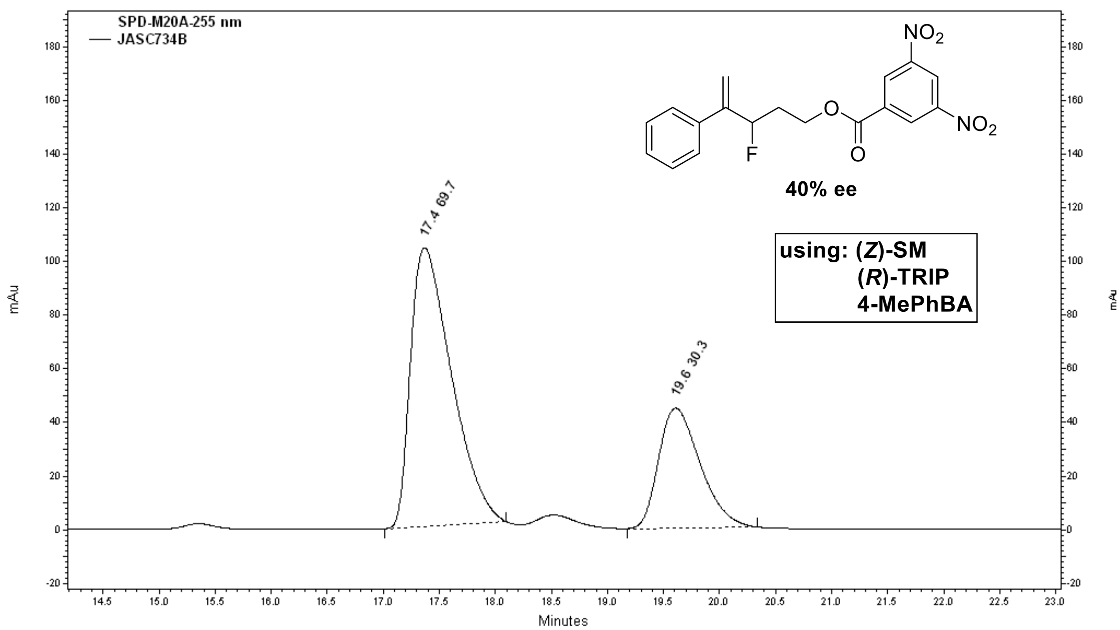
E/Z	R	PA	BA	NMR Yield 4	Isolated Yield 9	ee 9
Z	4-F	(*R*)-TRIP (**6**)	4-Me-PhB$(OH)_2$	40% (20% **2**, 6% **8**)	37%	41%
	H			60% (8% **2**, 18% **8**)	49%	40%
	4-Me			65% (10% **8**)	70%	42%
	4-*t*-Bu			50% (20% **8**)	44%	28%
	3-Me			45% (15% **2**, 5% **8**)	46%	45%
	4-Br			40% (15% **2**, 6% **8**)	30%	46%
	2-MeO			42% (19% **2**)	37%	33%
	3-MeO			32% (12% **2**, 14% **8**)	32%	43%
	4-MeO			46% (4% **8**)	42%	17%
Z	4-F	(*R*)-TCYP (**7**)	3,5-$(MeO)_2$-PhB$(OH)_2$	40% (24% **2**, 10% **8**) *10d:* 45% (25% **2**, 8% **8**)	ND	**91%**
	H			40% (30% **2**, 10% **8**)	ND	**88%**
	4-Me			50% (25% **2**, 8% **8**)	ND	**96%**
	4-*t*-Bu			50% (20% **2**, 4% **8**)	ND	**89%**
	3-Me			30% (35% **2**, 2% **8**)	ND	**85%**
	4-Br			32% (35% **2**, 4% **8**)	ND	**95%**
	2-MeO			20% (59% **2**)	ND	**64%**
	3-MeO			24% (66% **2**)	ND	**94%**
	4-MeO			26% (51% **2**, 1% **8**)	ND	**81%**
E	4-F	(*R*)-TRIP (**5**)	4-Me-PhB$(OH)_2$	32% (17% **8**)	34%	38%
	H			26% (5% **8**)	31%	46%
	4-Me			22% (17% **8**)	22%	38%
	4-*t*-Bu			60% (27% **8**)	61%	28%
	3-Me			37% (7% **2**, 24% **8**)	39%	40%
	4-Br			36% (30% **2**, 19% **8**)	37%	23%
	2-MeO			8% (3% **8**)	7%	32%
	3-MeO			29% (5% **2**, 17% **8**)	36%	82%
	4-MeO			31% (9% **8**)	31%	32%
E	4-F	(*R*)-TCYP (**7**)	3,4,5-$(MeO)_3$-PhB$(OH)_2$	7% (44% **2**, 1% **8**)	ND	-73%
	H			11% (59% **2**, 2% **8**)	ND	-51%
	4-Me			11% (55% **2**, 2% **8**)	ND	-65%
	4-*t*-Bu			10% (48% **2**, 2% **8**)	ND	-75%
	3-Me			8% (66% **2**, 3% **8**)	ND	-28%
	4-Br			7% (68% **2**, 2% **8**)	ND	-87%
	2-MeO			15% (49% **2**)	ND	-21%
	4-MeO			18% (36% **2**, 2% **8**)	ND	-41%

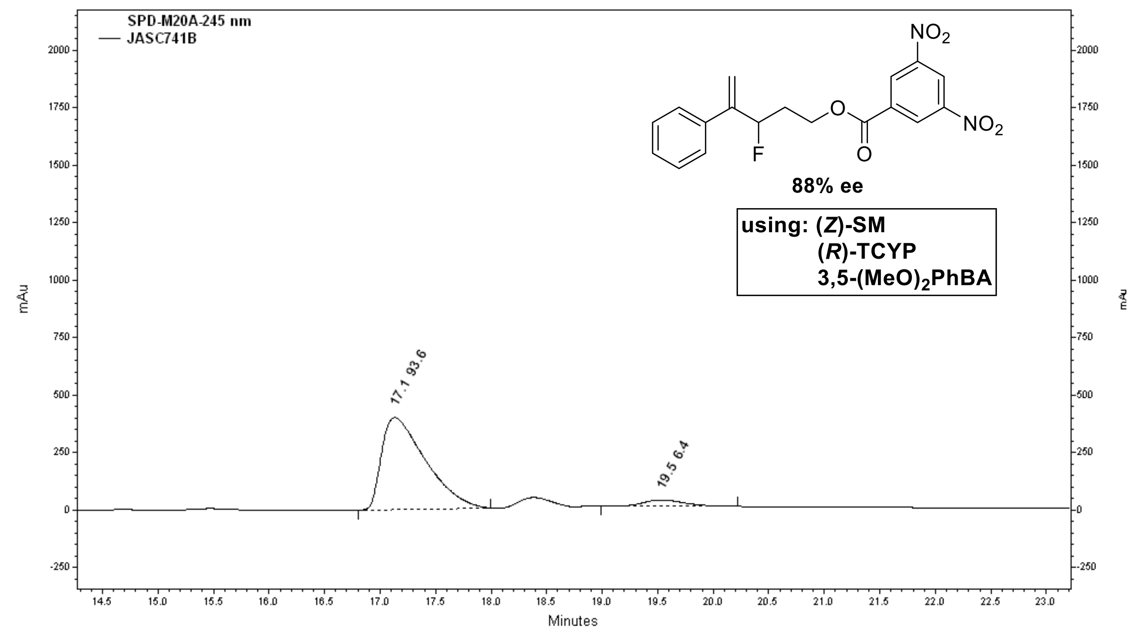
HPLC Chromatograms

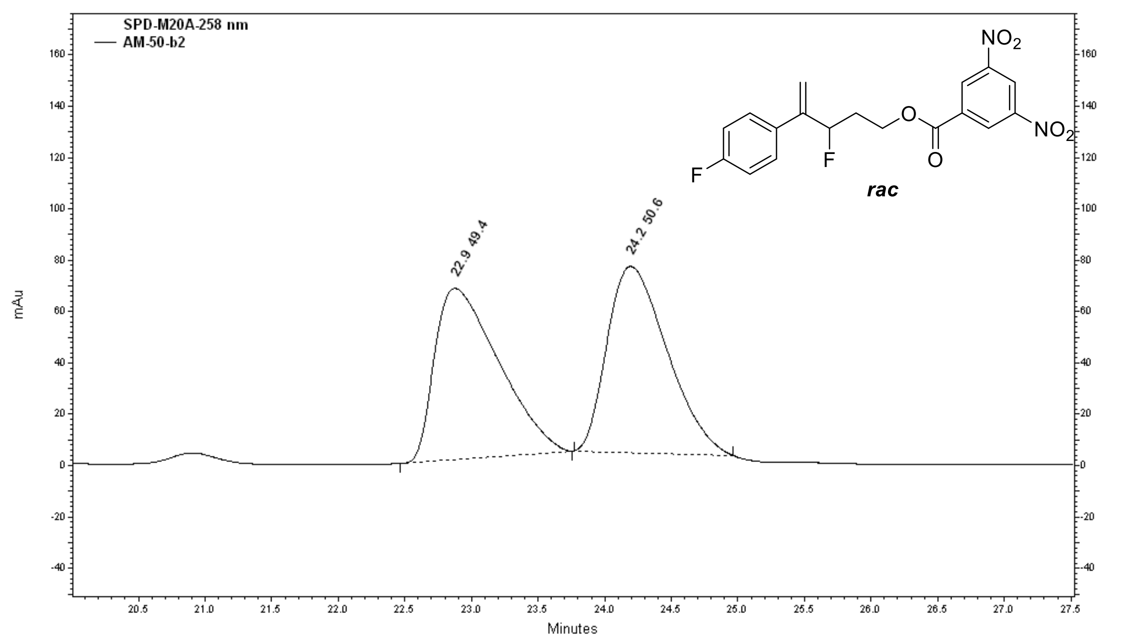


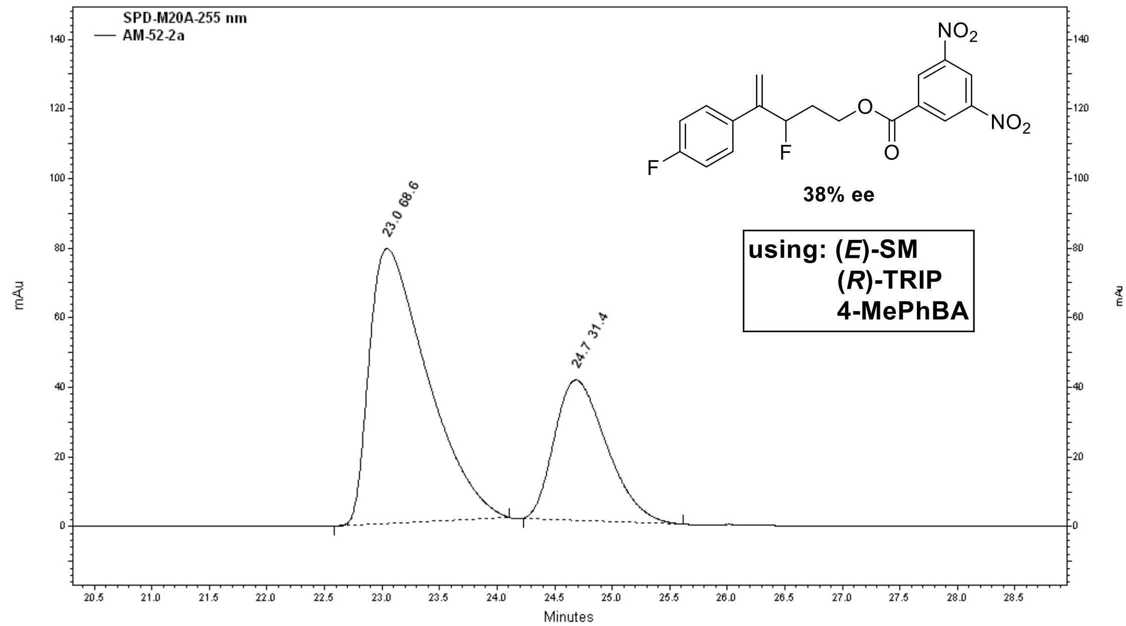


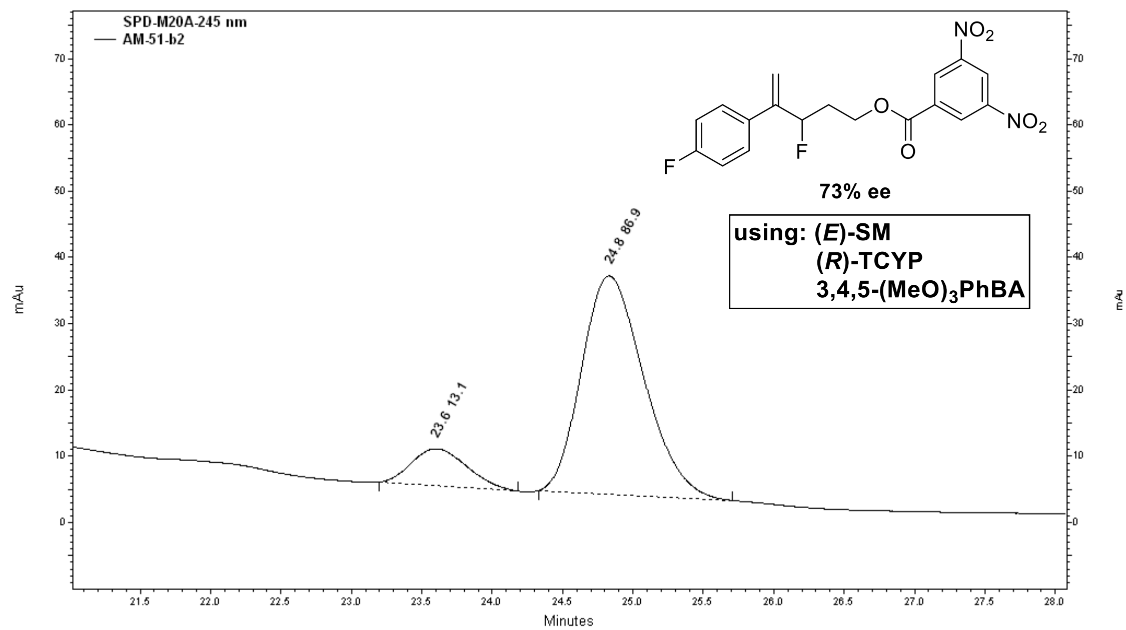

SPD-M20A-256 nm
AM-51-a2
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
51% ee
17.3 24.2
19.8 75.8
mAu
Minutes

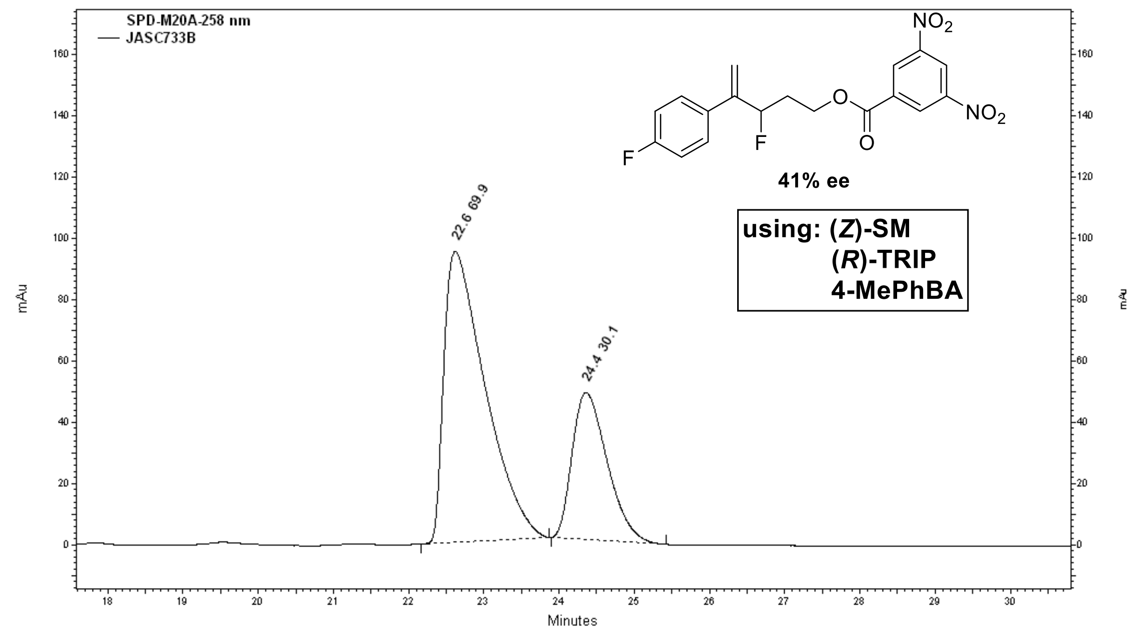

SPD-M20A-255 nm
JASC734B
40% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
17.4 69.7
19.6 30.3
mAu
Minutes

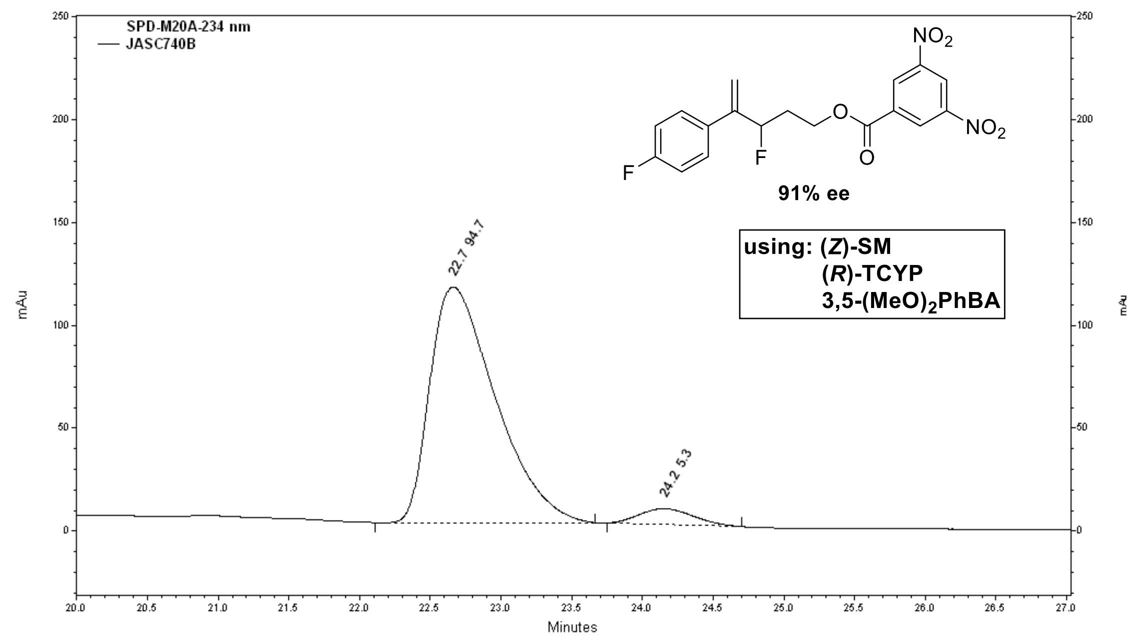

SPD-M20A-245 nm
JASC741B
88% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
17.1 93.6
19.5 6.4
Minutes
mAu

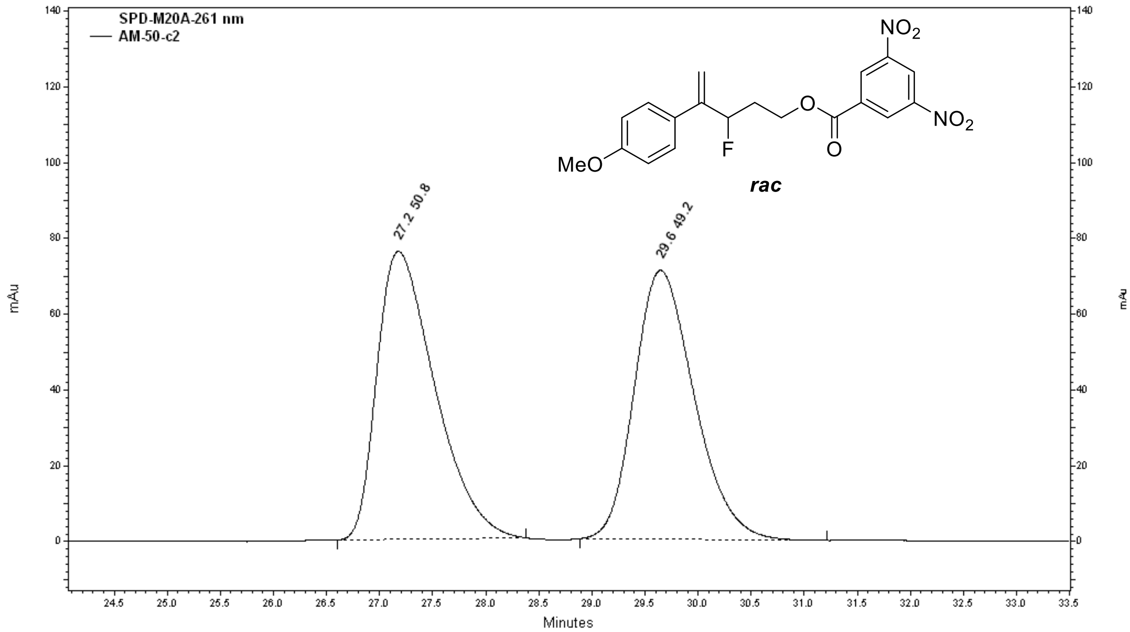

SPD-M20A-258 nm
AM-50-b2
rac
22.9 49.4
24.2 50.6
Minutes
mAu


SPD-M20A-255 nm
AM-52-2a
23.0 68.6
24.7 31.4
NO2
NO2
F
F
O
O
38% ee
using: (E)-SM
(R)-TRIP
4-MePhBA
mAu
Minutes

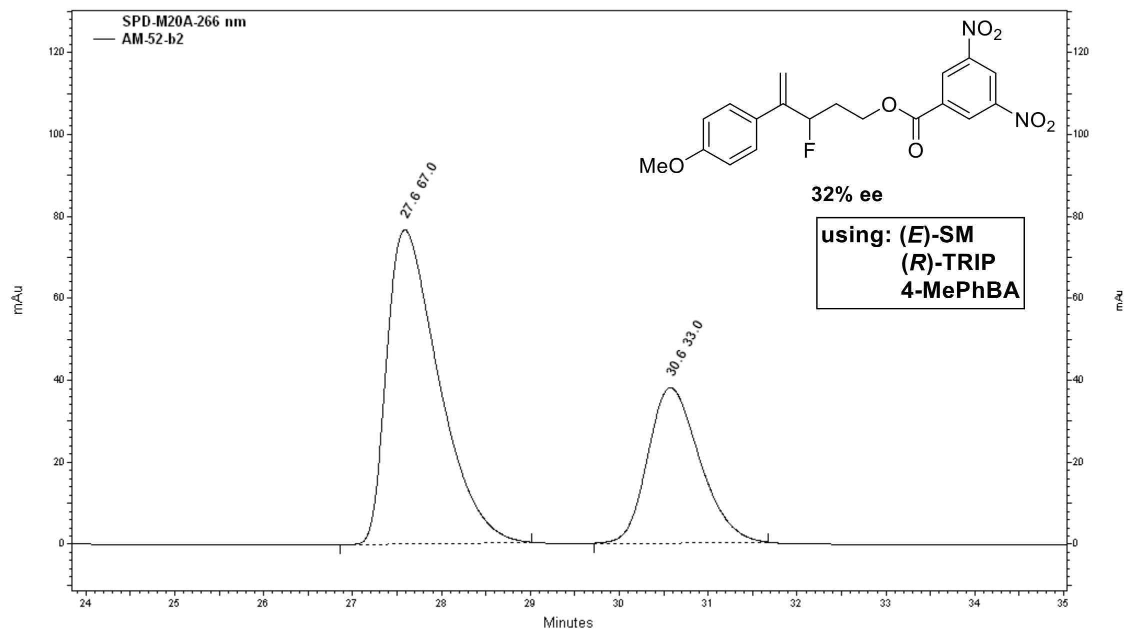

SPD-M20A-245 nm
AM-51-b2
23.6 13.1
24.8 86.9
NO2
NO2
F
F
O
O
73% ee
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
mAu
Minutes


SPD-M20A-258 nm
JASC733B
22.6 69.9
24.4 30.1
41% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
mAu
Minutes

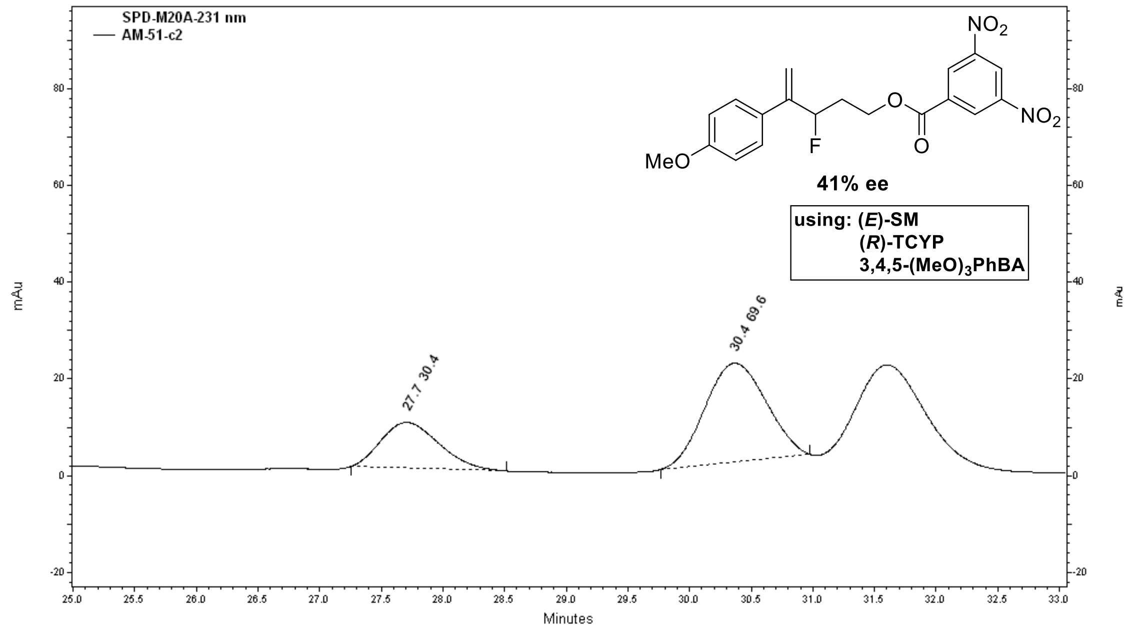

SPD-M20A-234 nm
JASC740B
22.7 94.7
24.2 5.3
91% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
mAu
Minutes

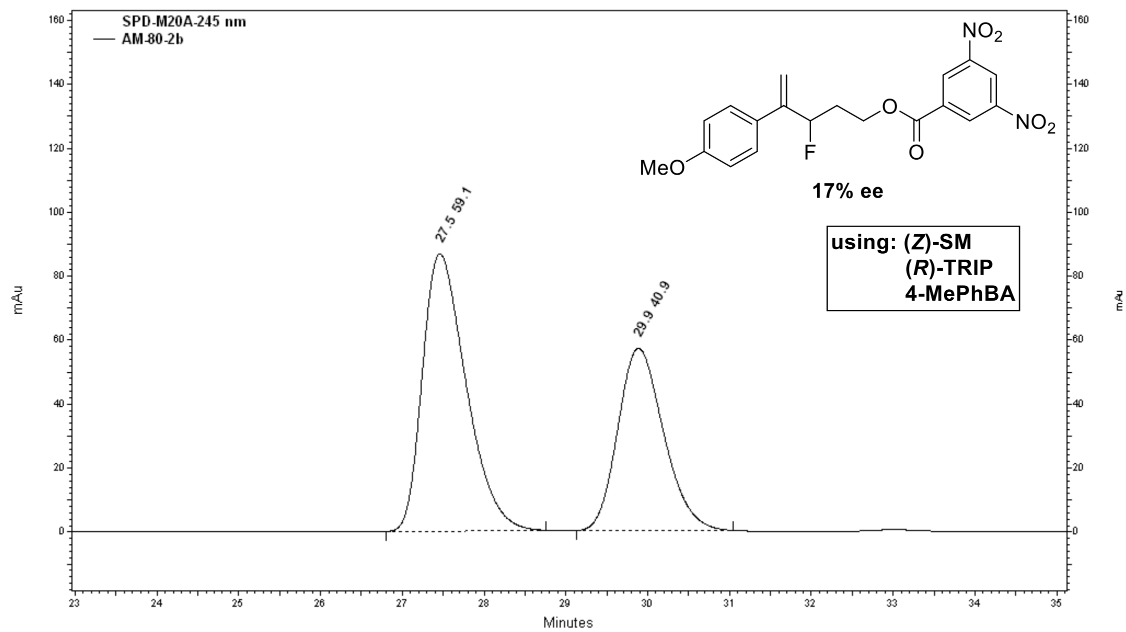


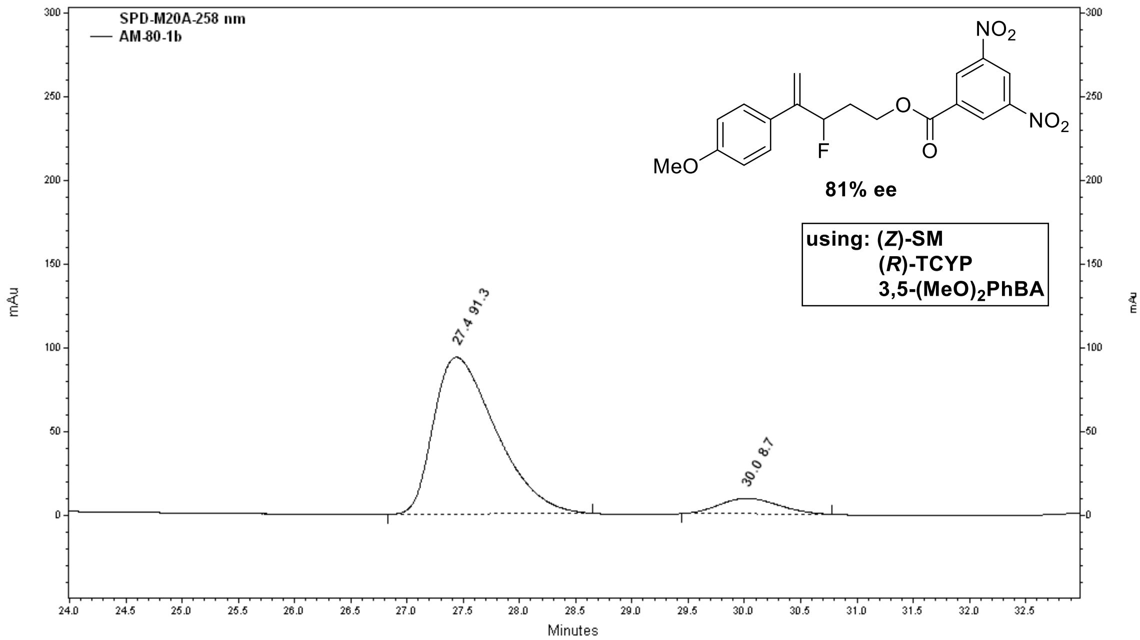
SPD-M20A-261 nm
AM-50-c2
NO2
NO2
MeO
F
O
O
rac
27.2 50.8
29.6 49.2
mAu
Minutes

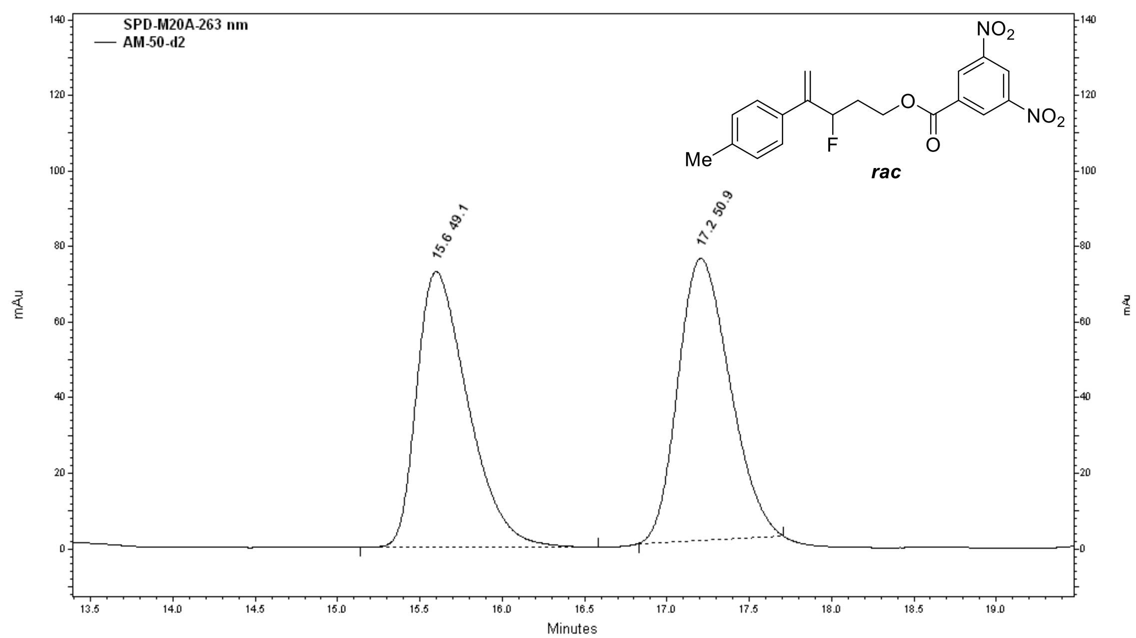


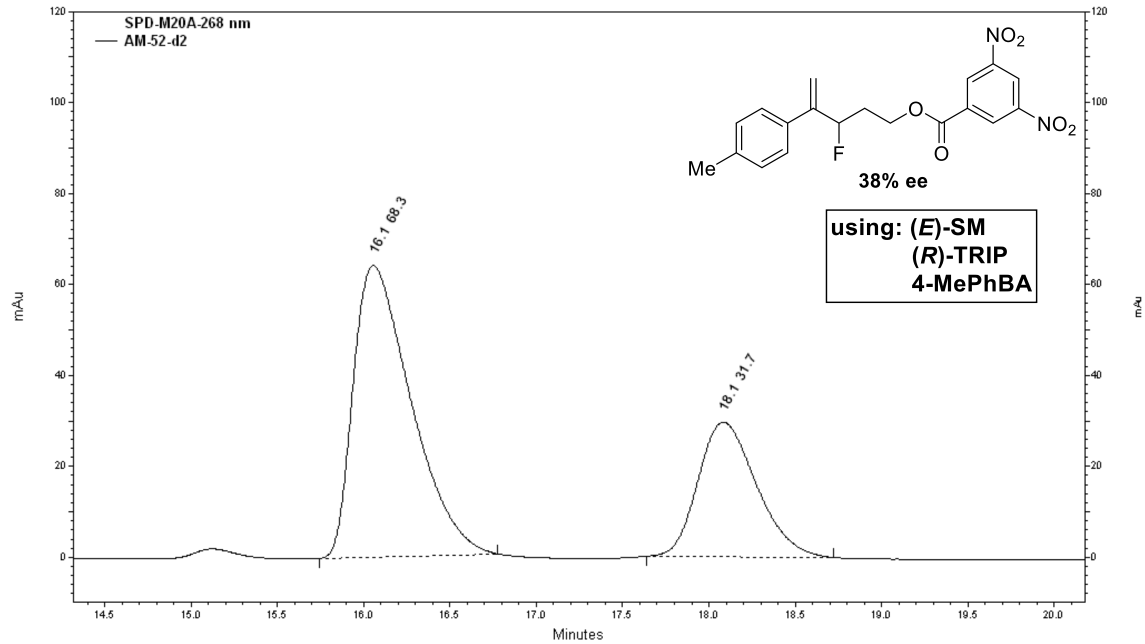
SPD-M20A-266 nm
AM-52-b2
NO2
NO2
MeO
F
O
O
32% ee
using: (E)-SM
(R)-TRIP
4-MePhBA
27.6 67.0
30.6 33.0
mAu
Minutes

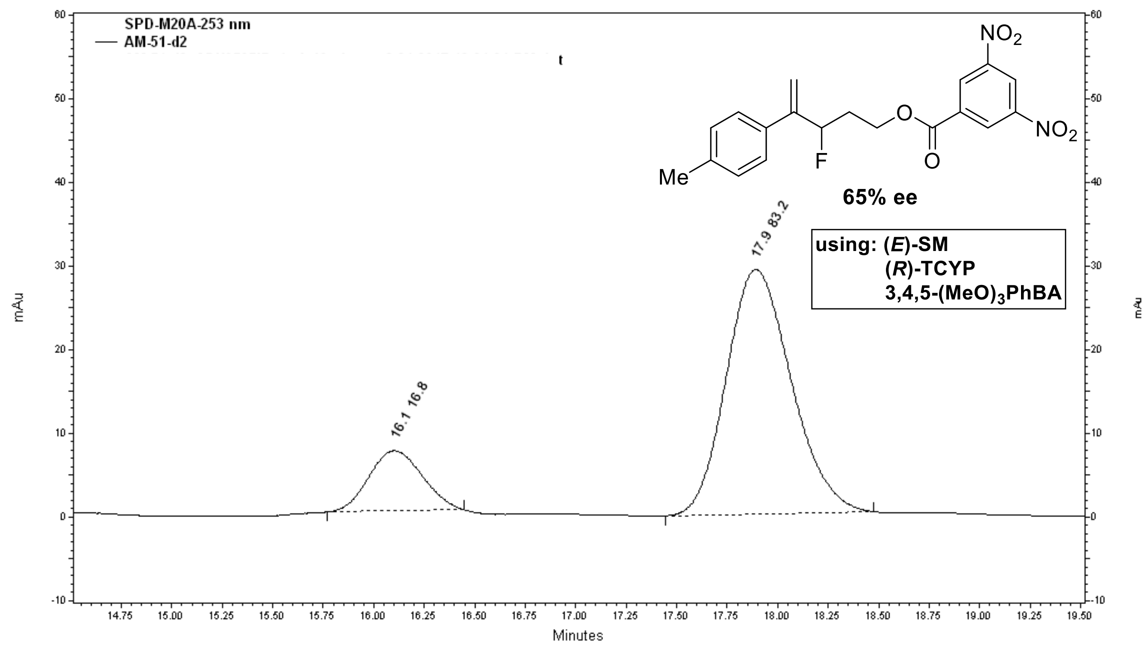

SPD-M20A-231 nm
AM-51-c2
NO2
MeO
F
O
O
NO2
41% ee
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
27.7 30.4
30.4 69.6
mAu
Minutes

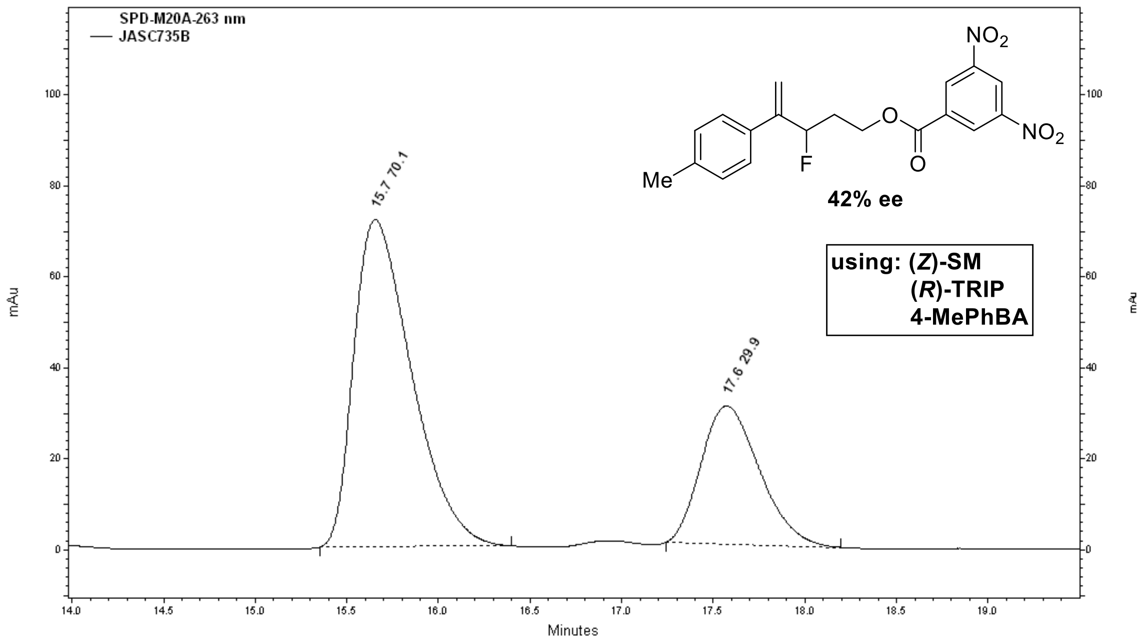

SPD-M20A-245 nm
AM-80-2b
NO2
MeO
F
O
O
NO2
17% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
27.5 59.1
29.9 40.9
mAu
Minutes

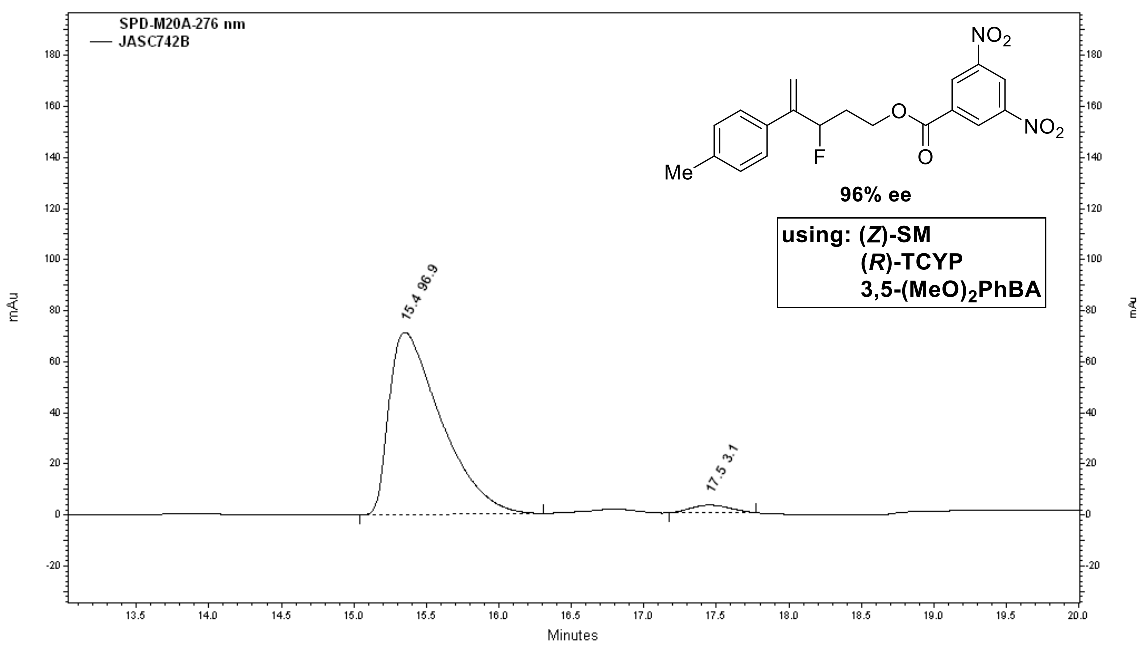

SPD-M20A-258 nm
AM-80-1b
27.4 91.3
30.0 8.7
MeO
F
O
NO2
NO2
81% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
mAu
Minutes

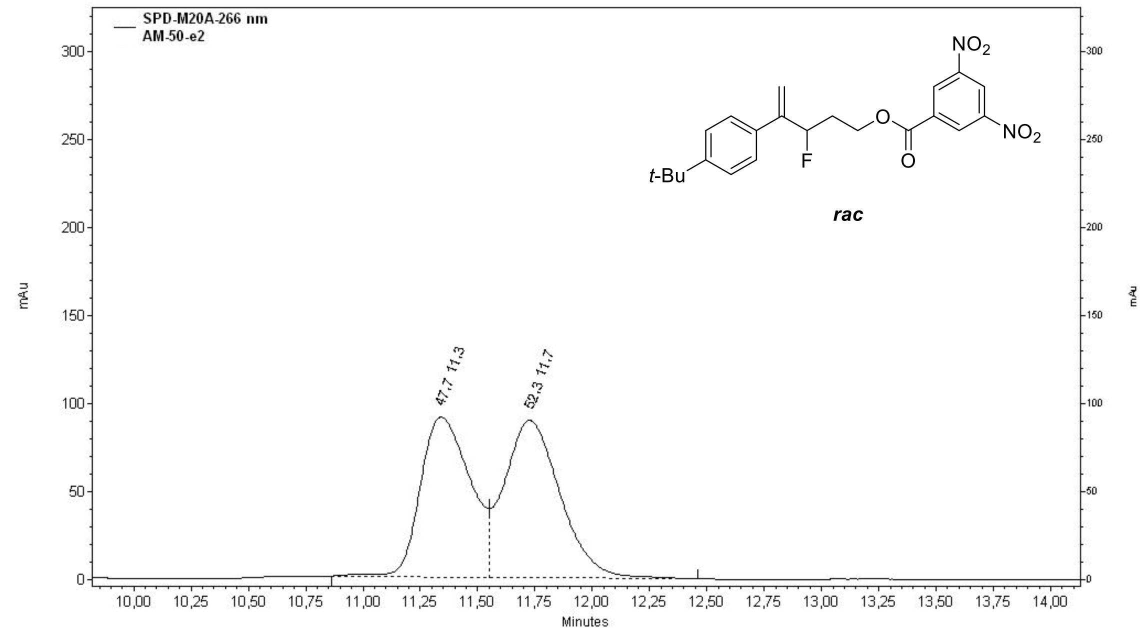

SPD-M20A-263 nm
AM-50-d2
15.6 49.1
17.2 50.9
Me
F
O
NO2
NO2
rac
mAu
Minutes

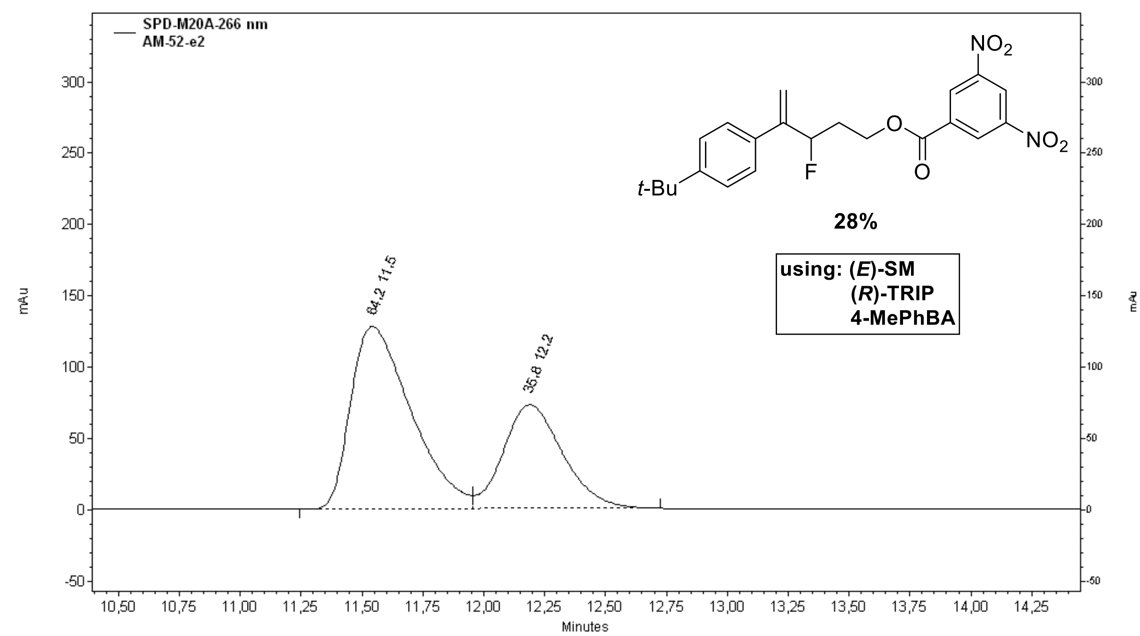

SPD-M20A-268 nm
AM-52-d2
NO2
NO2
Me
F
O
O
38% ee
using: (E)-SM
(R)-TRIP
4-MePhBA
16.1 68.3
18.1 31.7
mAu
Minutes

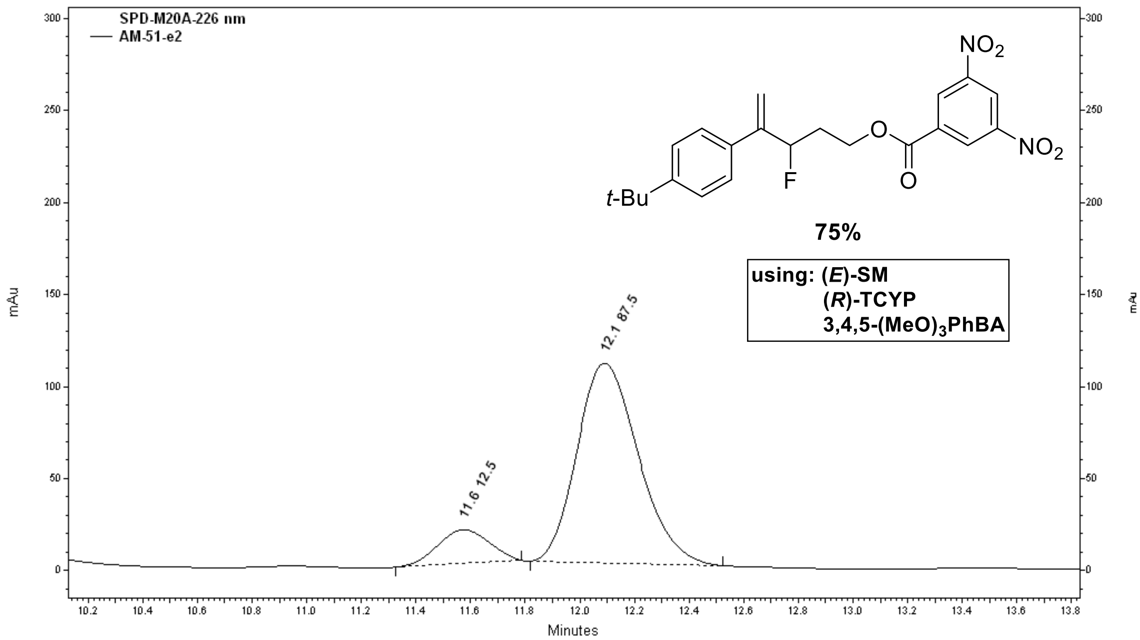

SPD-M20A-253 nm
AM-51-d2
NO2
NO2
Me
F
O
O
65% ee
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
16.1 16.8
17.9 83.2
mAu
Minutes

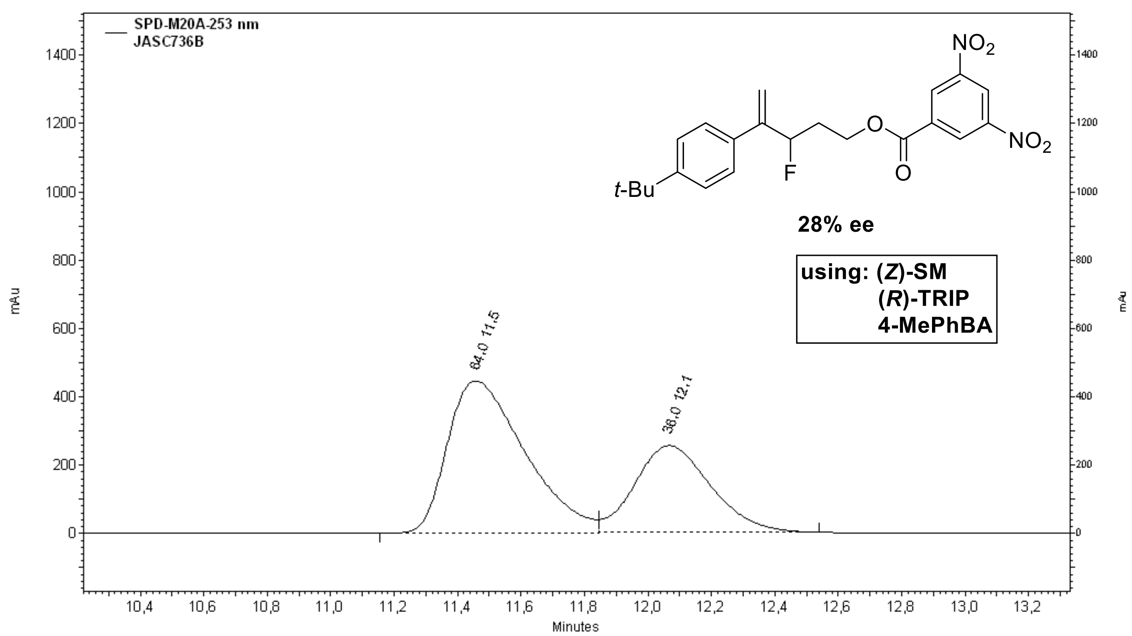

SPD-M20A-263 nm
JASC735B
42% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
15.7 70.1
17.6 29.9
mAu
Minutes

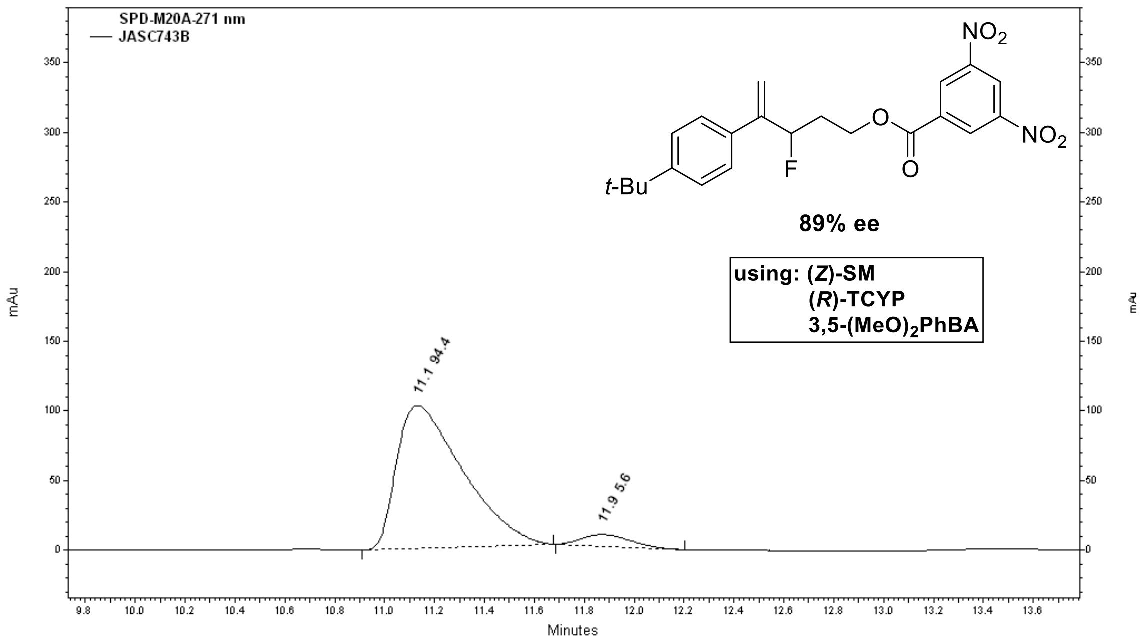

SPD-M20A-276 nm
JASC742B
96% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
15.4 96.9
17.5 3.1
mAu
Minutes

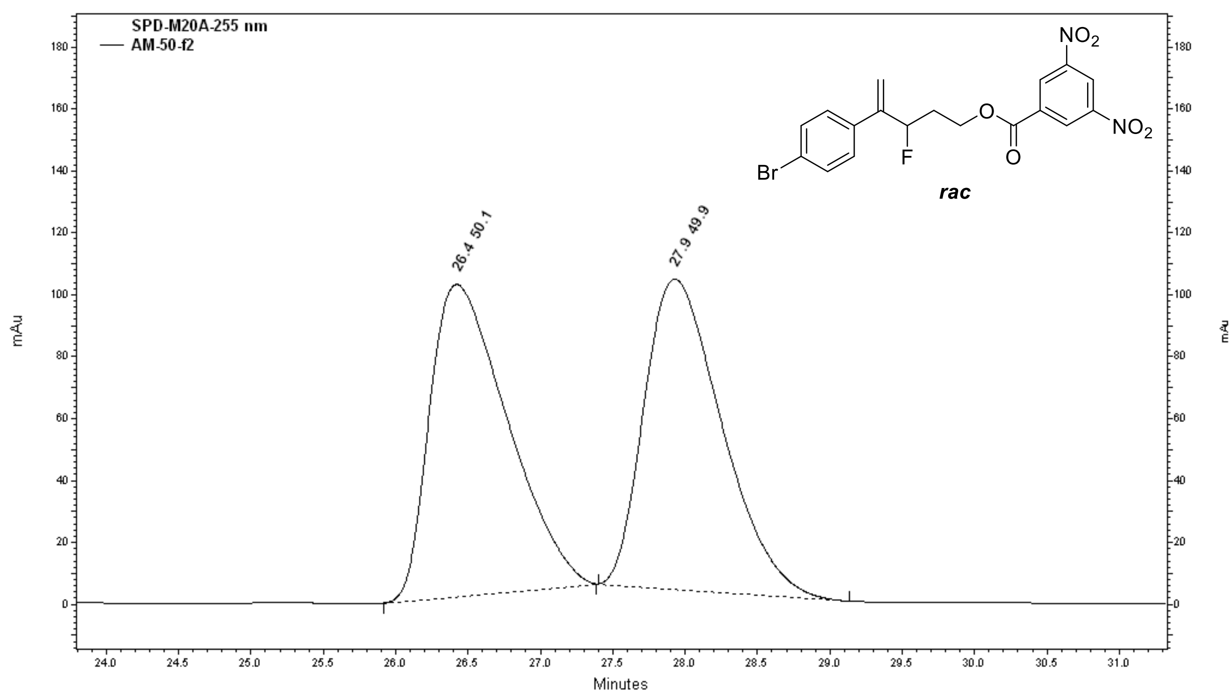

SPD-M20A-266 nm
AM-50-e2
mAu
Minutes
47,7 11,3
52,3 11,7
NO2
NO2
O
O
F
t-Bu
rac

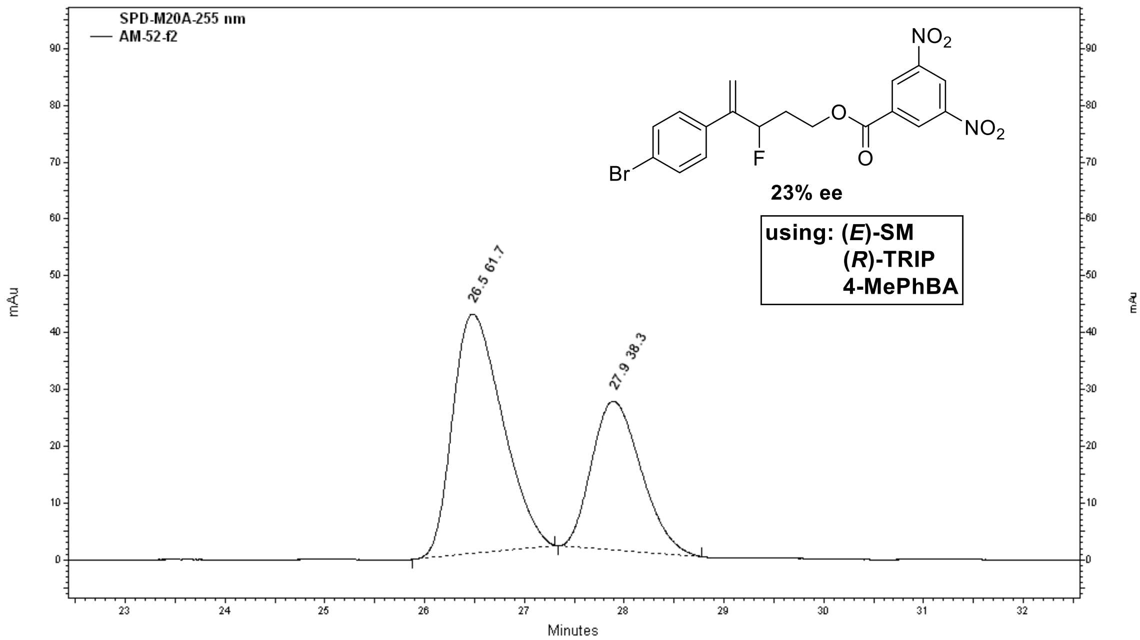

SPD-M20A-266 nm
AM-52-e2
mAu
Minutes
64,2 11,5
35,8 12,2
NO2
NO2
O
O
F
t-Bu
28%
using: (E)-SM
(R)-TRIP
4-MePhBA


SPD-M20A-226 nm
AM-51-e2
NO2
NO2
t-Bu
F
O
75%
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
12.1 87.5
11.6 12.5
mAu
Minutes

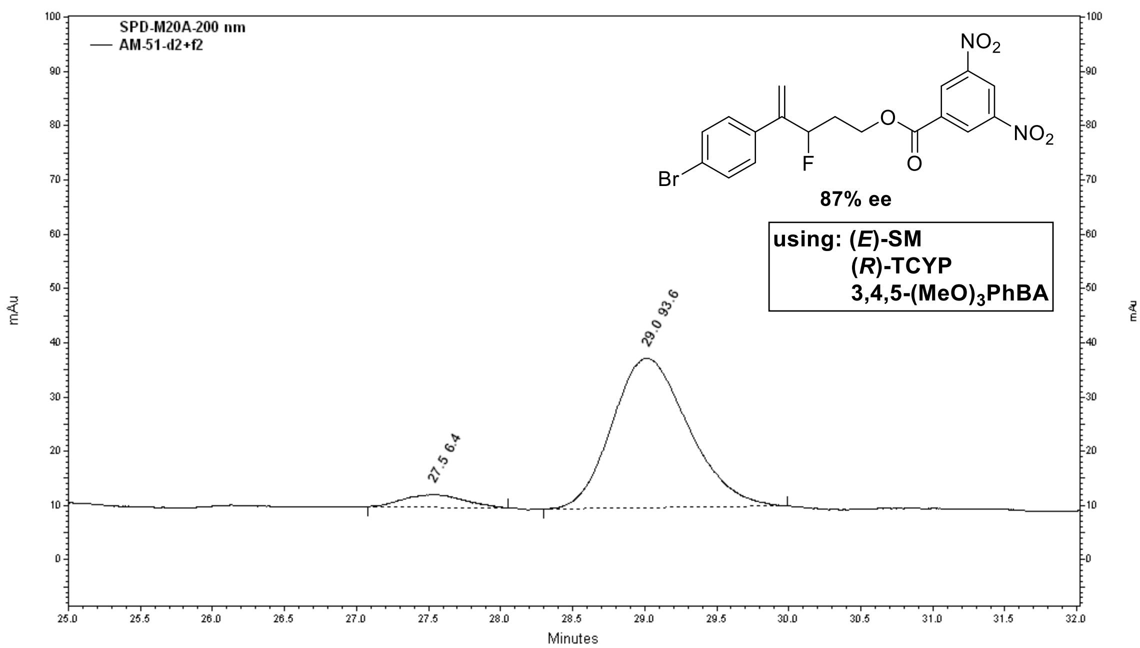

SPD-M20A-253 nm
JASC736B
NO2
NO2
t-Bu
F
O
28% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
64.0 11.5
36.0 12.1
mAu
Minutes


SPD-M20A-271 nm
JASC743B
89% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
11.1 94.4
11.9 5.6
mAu
Minutes

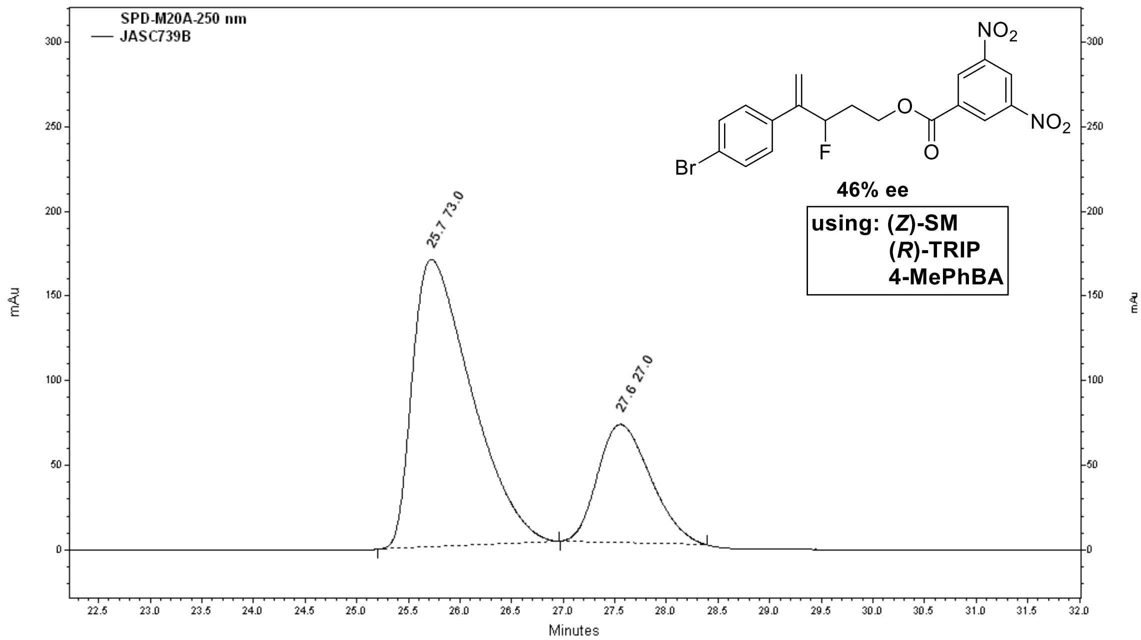

SPD-M20A-255 nm
AM-50-f2
rac
26.4 50.1
27.9 49.9
mAu
Minutes

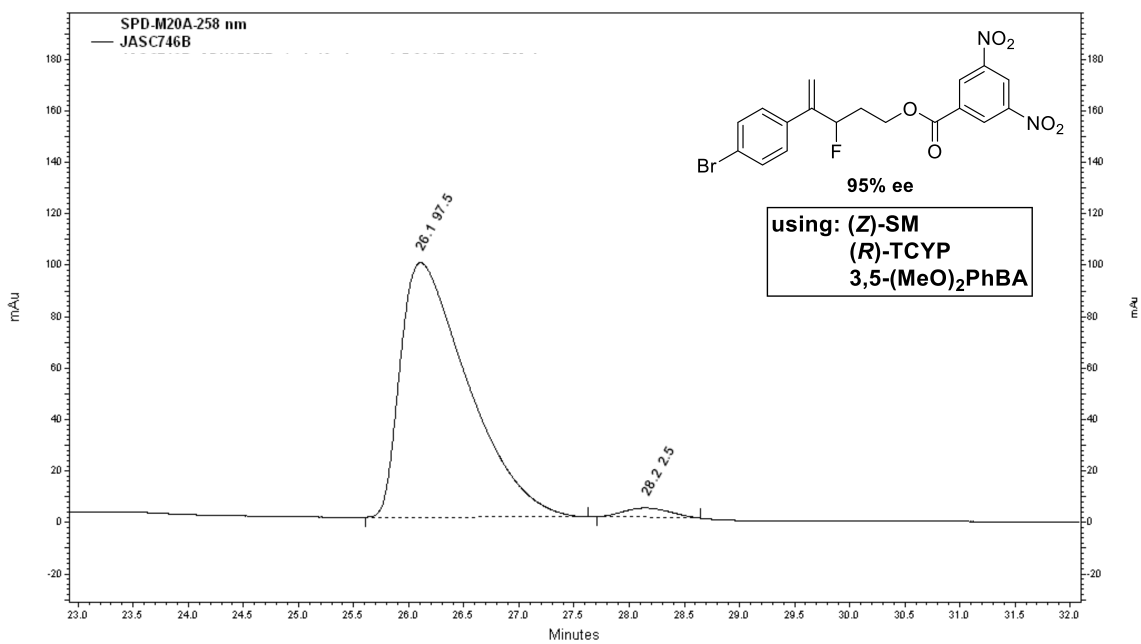


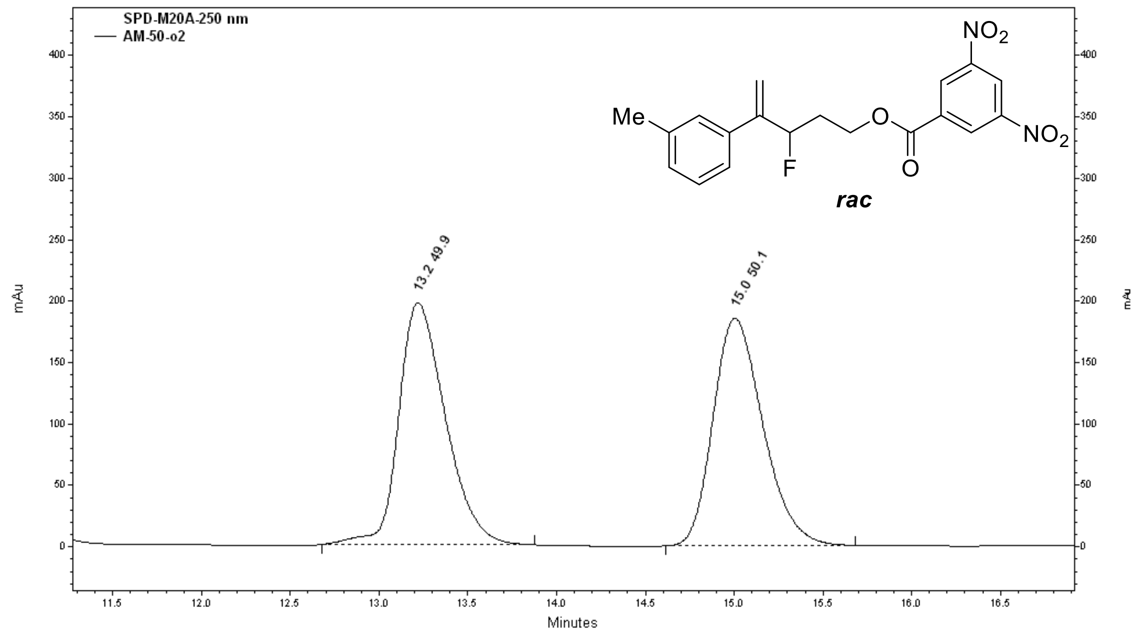
SPD-M20A-255 nm
AM-52-f2
23% ee
using: (E)-SM
(R)-TRIP
4-MePhBA
26.5 61.7
27.9 38.3
mAu
Minutes



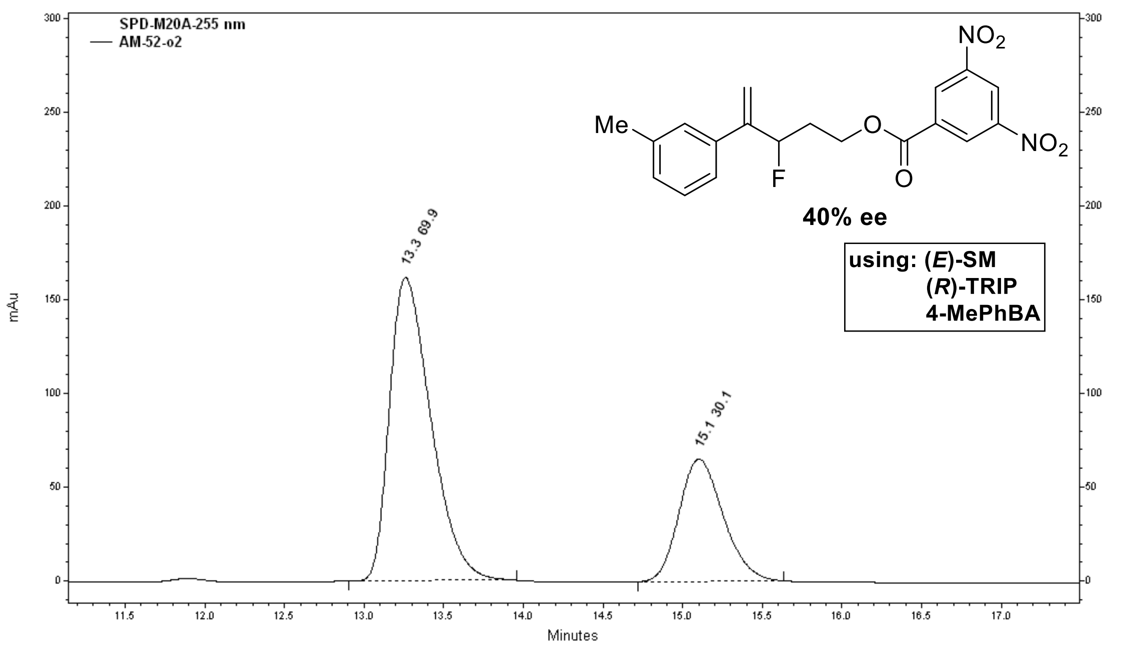
SPD-M20A-200 nm
AM-51-d2+f2
87% ee
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
27.5 6.4
29.0 93.6
mAu
Minutes


SPD-M20A-250 nm
JASC739B
46% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
25.7 73.0
27.6 27.0
mAu
Minutes

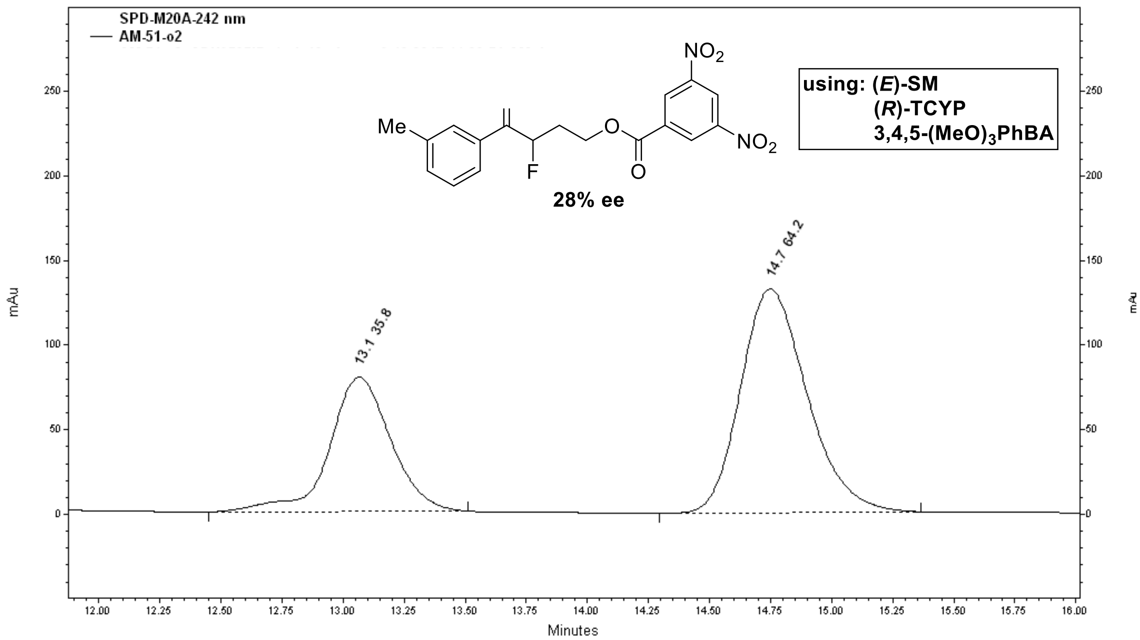

SPD-M20A-258 nm
JASC746B
95% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
26.1 97.5
28.2 2.5
mAu
Minutes

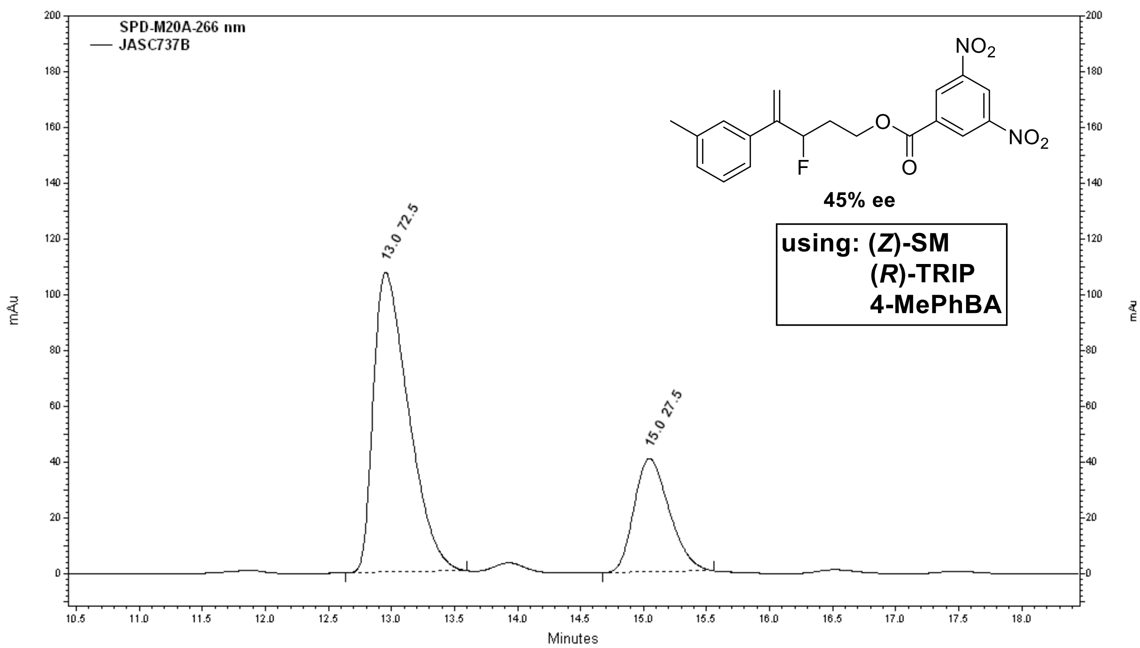


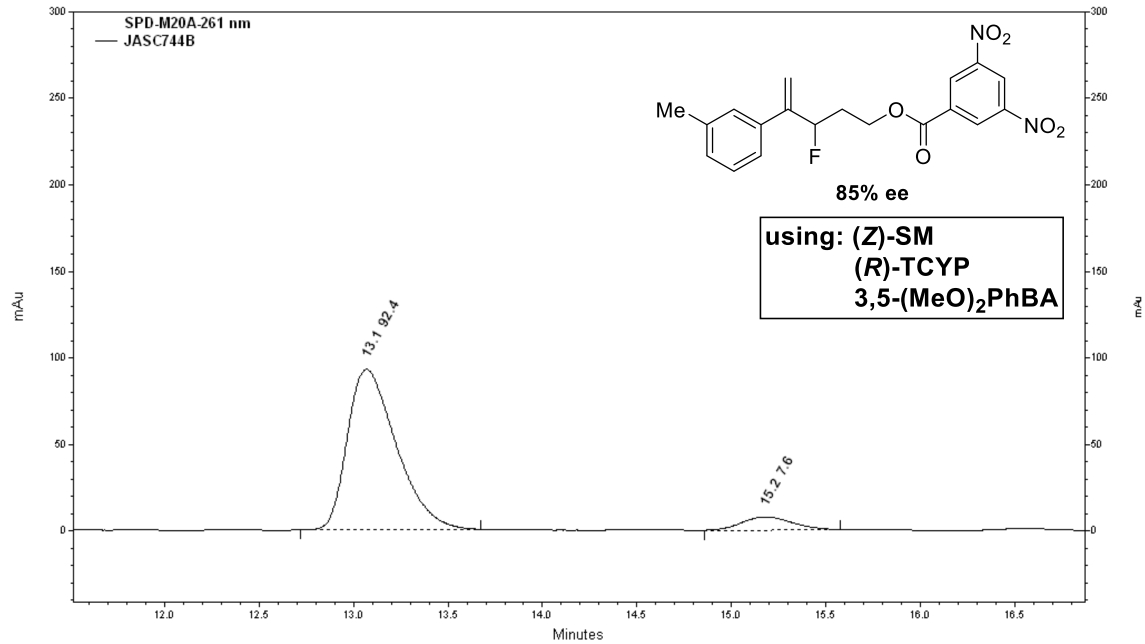
SPD-M20A-250 nm
AM-50-o2
Me
F
O
O
NO2
NO2
rac
13.2 49.9
15.0 50.1
mAu
Minutes

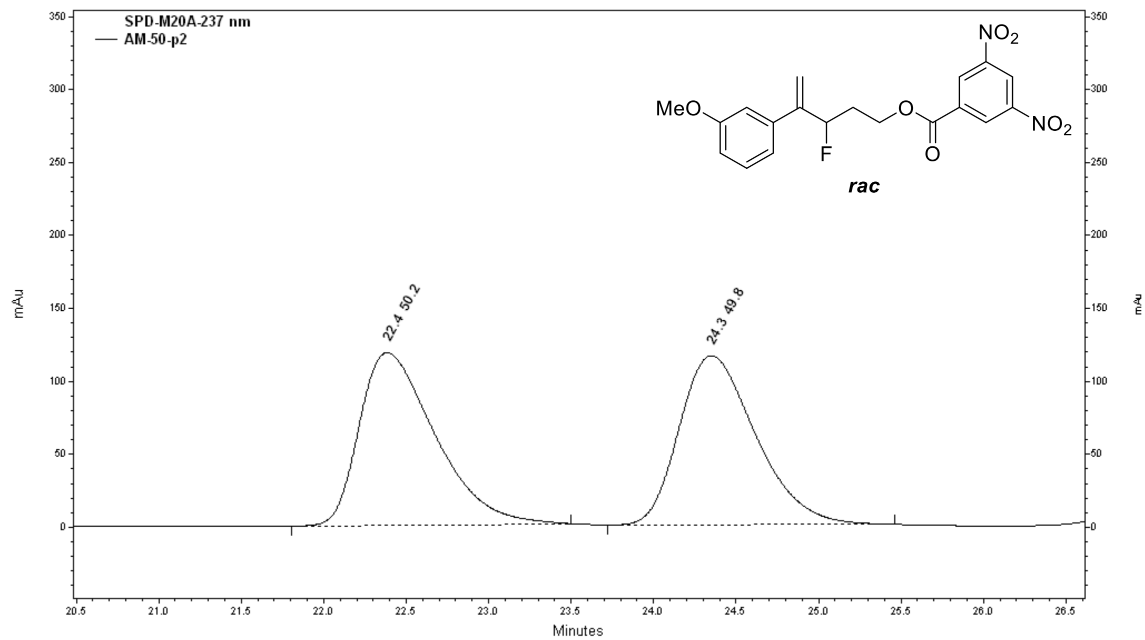


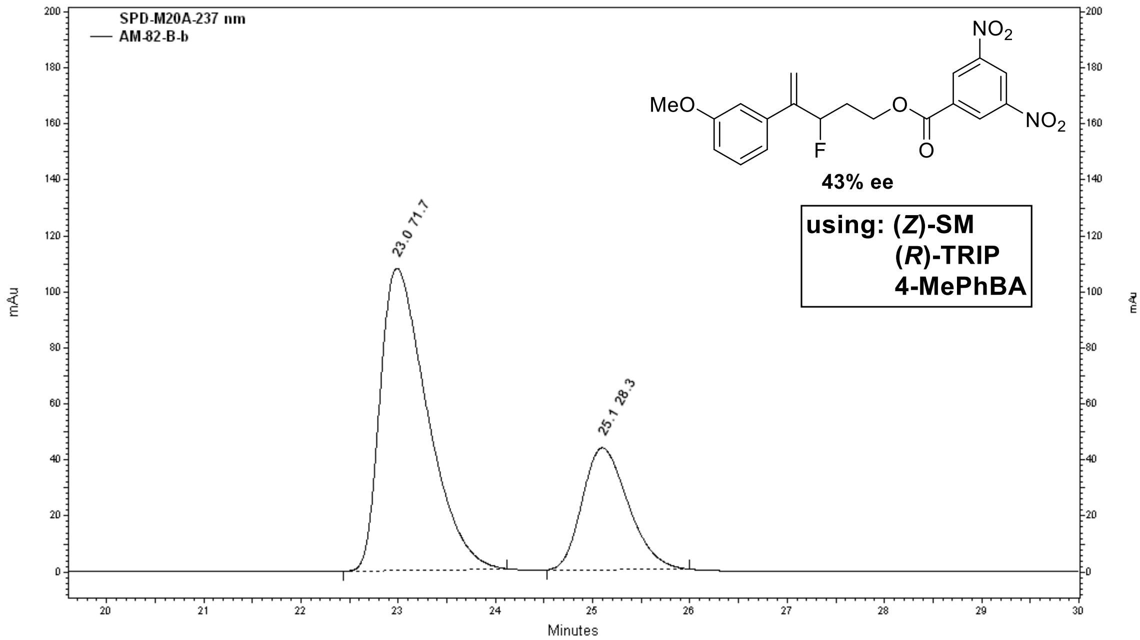
SPD-M20A-255 nm
AM-52-o2
Me
F
O
O
NO2
NO2
40% ee
using: (E)-SM
(R)-TRIP
4-MePhBA
13.3 69.9
15.1 30.1
mAu
Minutes

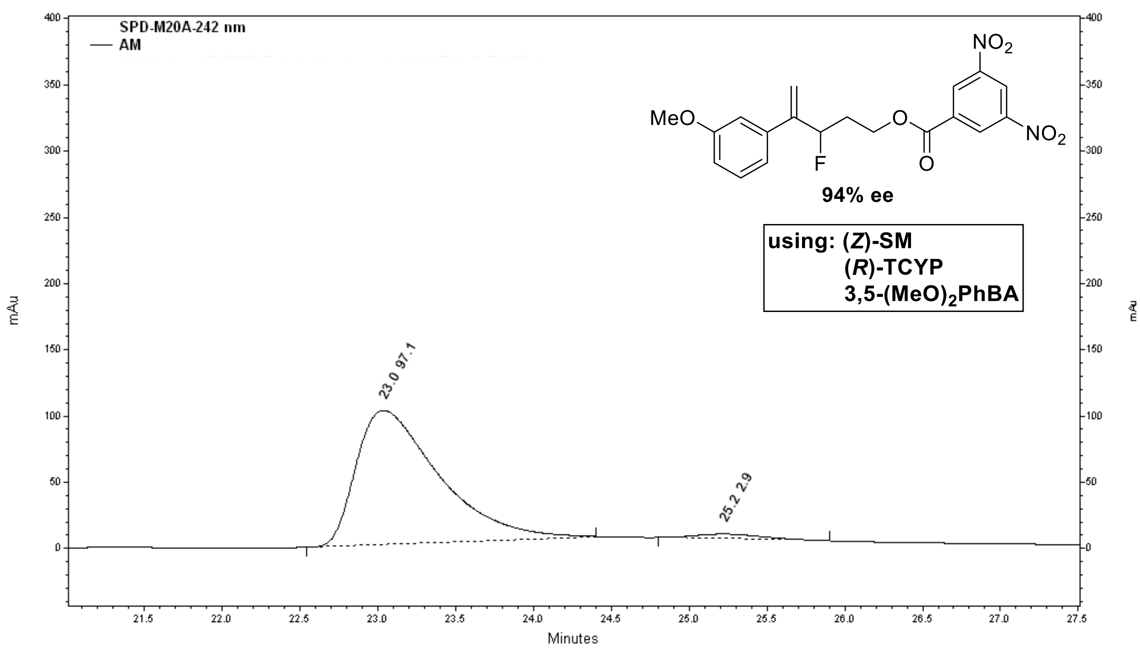

SPD-M20A-242 nm
AM-51-o2
28% ee
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
13.1 35.8
14.7 64.2
mAu
Minutes

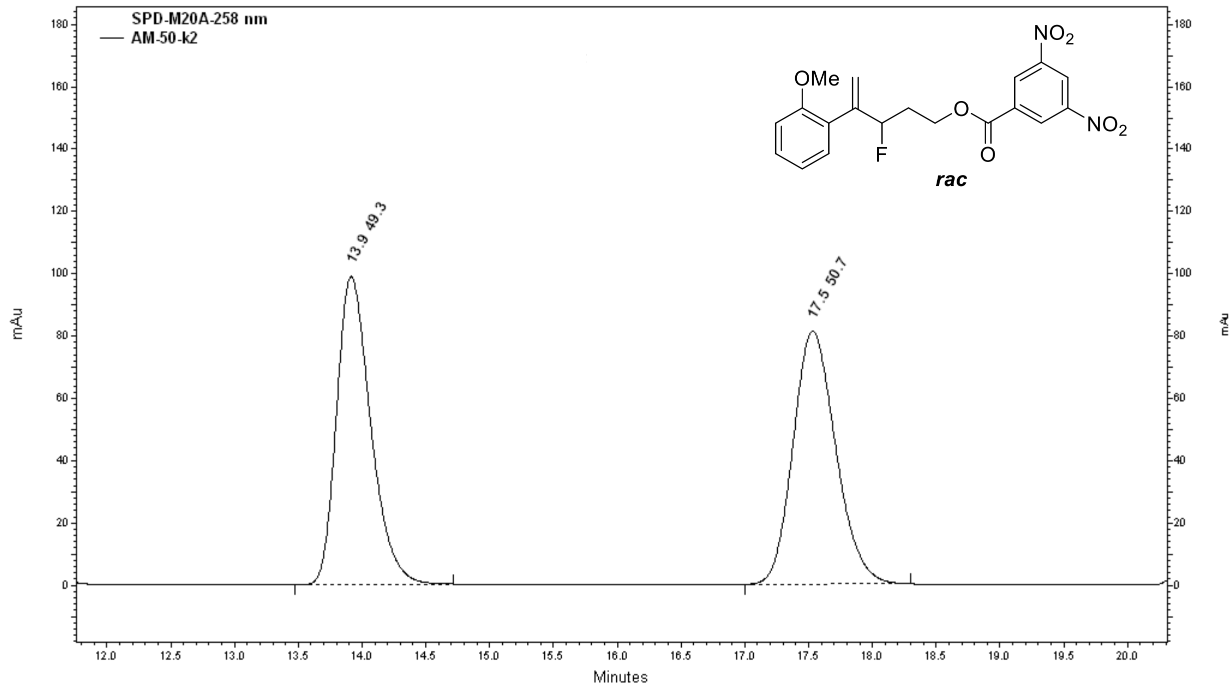

SPD-M20A-266 nm
JASC737B
45% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
13.0 72.5
15.0 27.5
mAu
Minutes

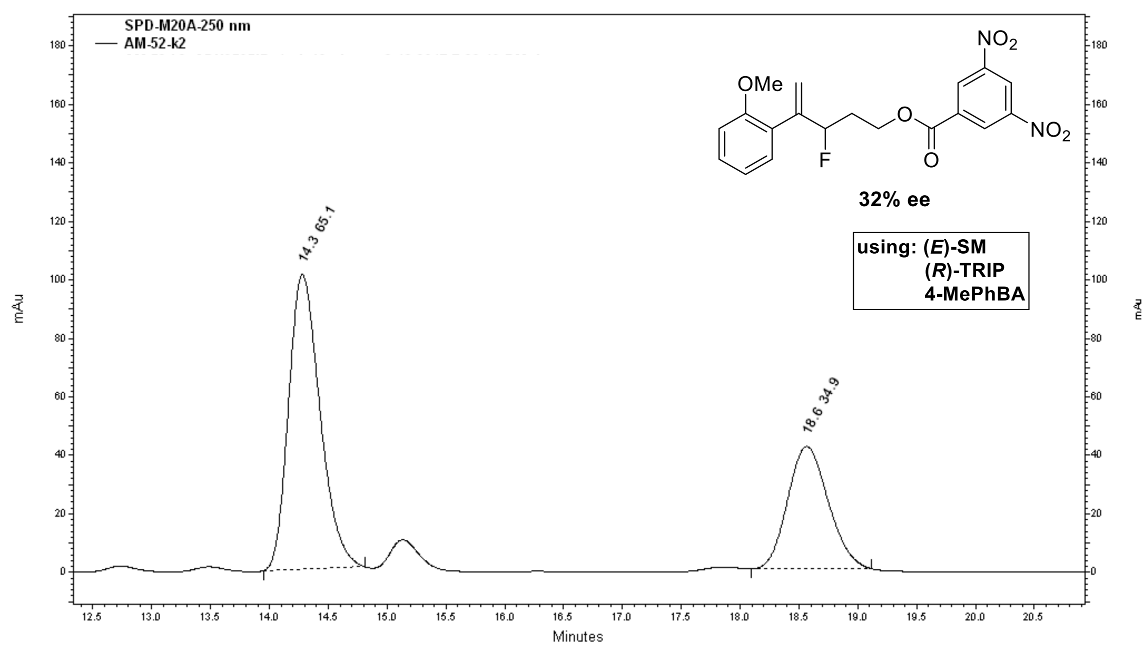

SPD-M20A-261 nm
JASC744B
85% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
13.1 92.4
15.2 7.6
mAu
Minutes

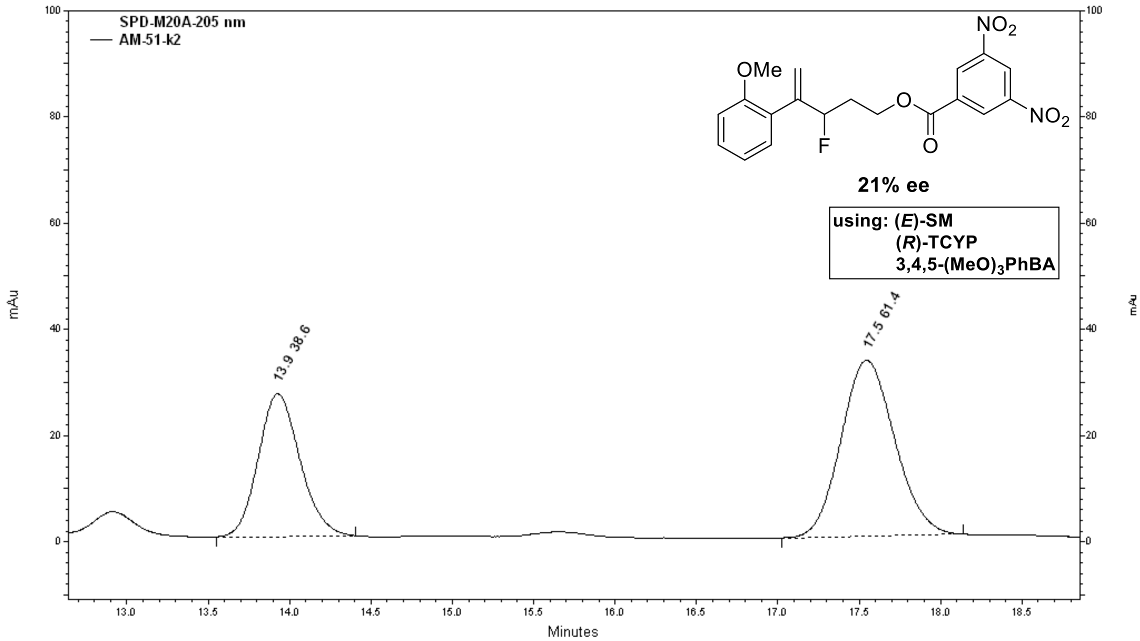

SPD-M20A-237 nm
AM-50-p2
rac
22.4 50.2
24.3 49.8
mAu
Minutes

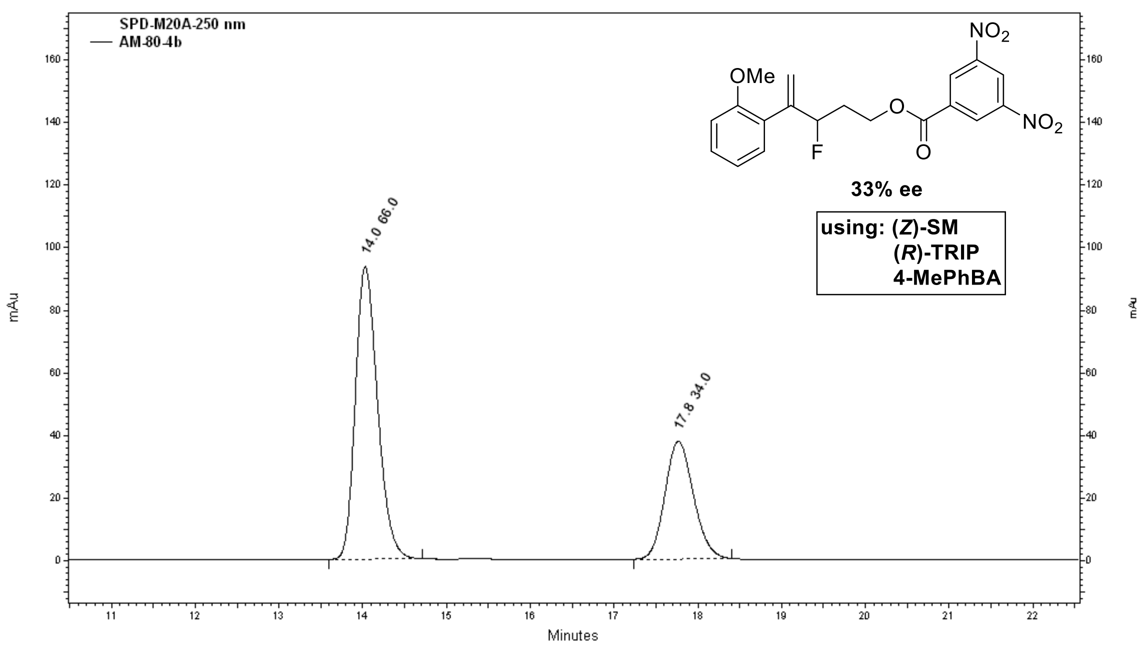

SPD-M20A-237 nm
AM-82-B-b
MeO
NO2
NO2
F
O
43% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
23.0 71.7
25.1 28.3
mAu
Minutes

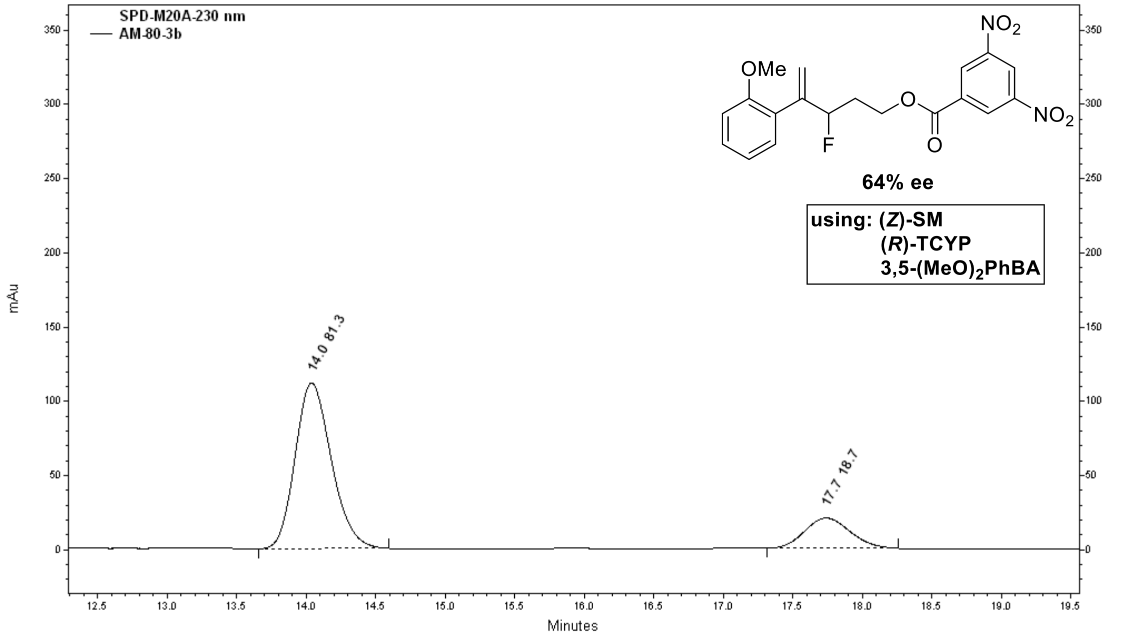

SPD-M20A-242 nm
AM
MeO
NO2
NO2
F
O
94% ee
using: (Z)-SM
(R)-TCYP
3,5-(MeO)2PhBA
23.0 97.1
25.2 2.9
mAu
Minutes


SPD-M20A-258 nm
AM-50-k2
OMe
F
NO2
NO2
O
O
rac
13.9 49.3
17.5 50.7
mAu
Minutes

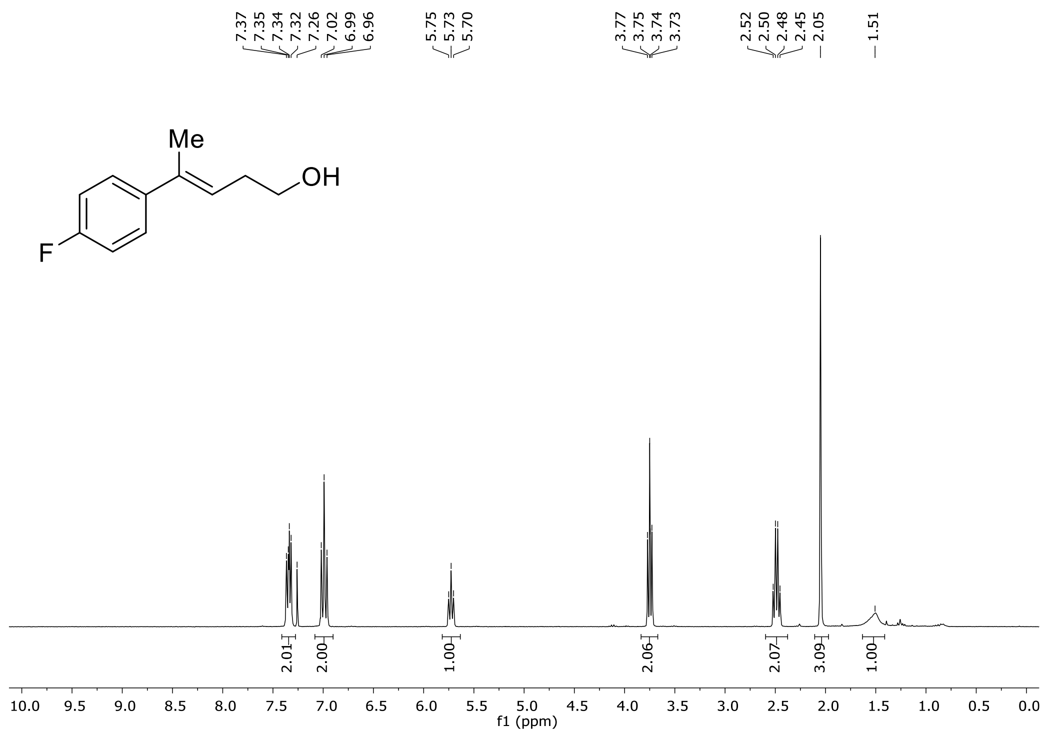

SPD-M20A-250 nm
AM-52-k2
OMe
F
NO2
NO2
O
O
32% ee
using: (E)-SM
(R)-TRIP
4-MePhBA
14.3 65.1
18.6 34.9
mAu
Minutes


SPD-M20A-205 nm
AM-51-k2
OMe
F
O
NO2
NO2
21% ee
using: (E)-SM
(R)-TCYP
3,4,5-(MeO)3PhBA
13.9 38.6
17.5 61.4
mAu
Minutes

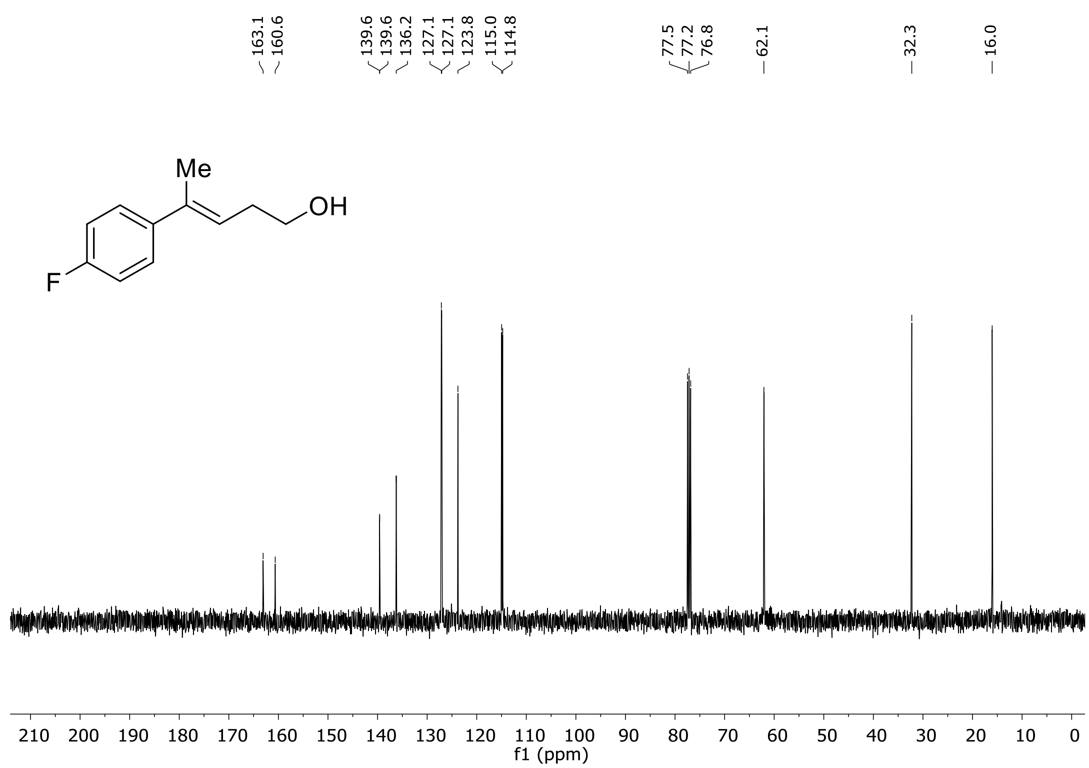

SPD-M20A-250 nm
AM-80-4b
OMe
F
O
NO2
NO2
33% ee
using: (Z)-SM
(R)-TRIP
4-MePhBA
14.0 66.0
17.8 34.0
mAu
Minutes


SPD-M20A-230 nm
AM-80-3b
OMe
F
O
O
NO_2
NO_2
64% ee
using: (*Z*)-SM
(*R*)-TCYP
3,5-$(MeO)_2$PhBA
14.0 81.3
17.7 18.7
mAu
Minutes

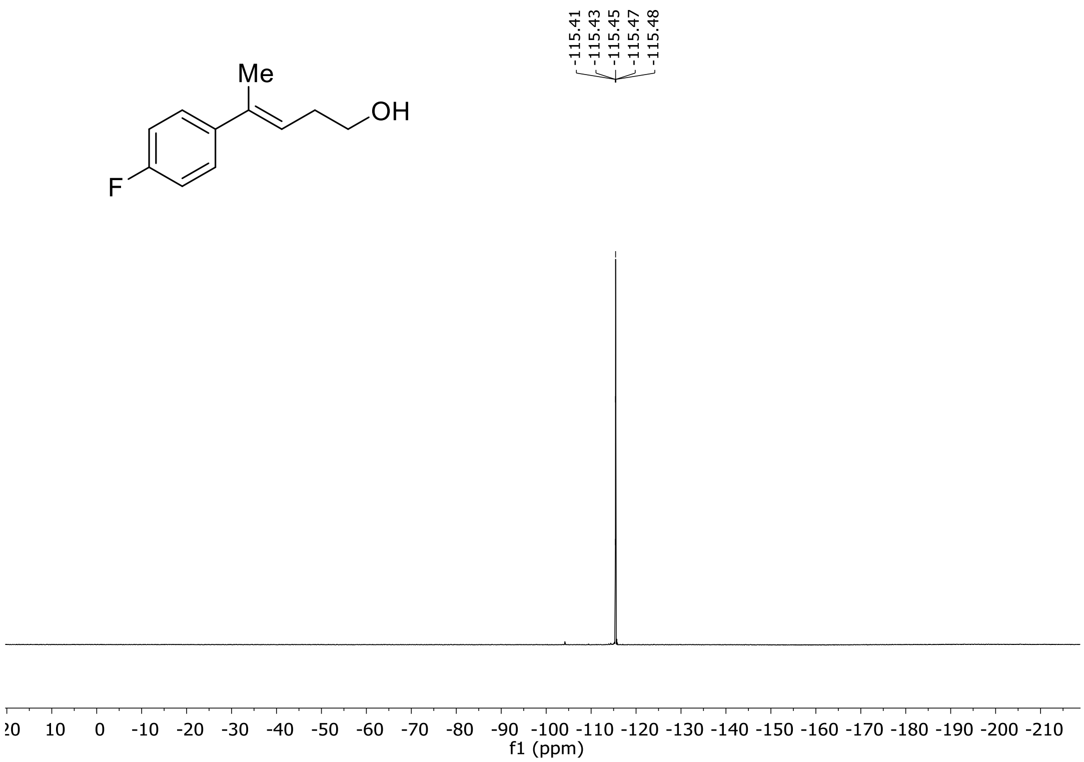
NMR Spectra



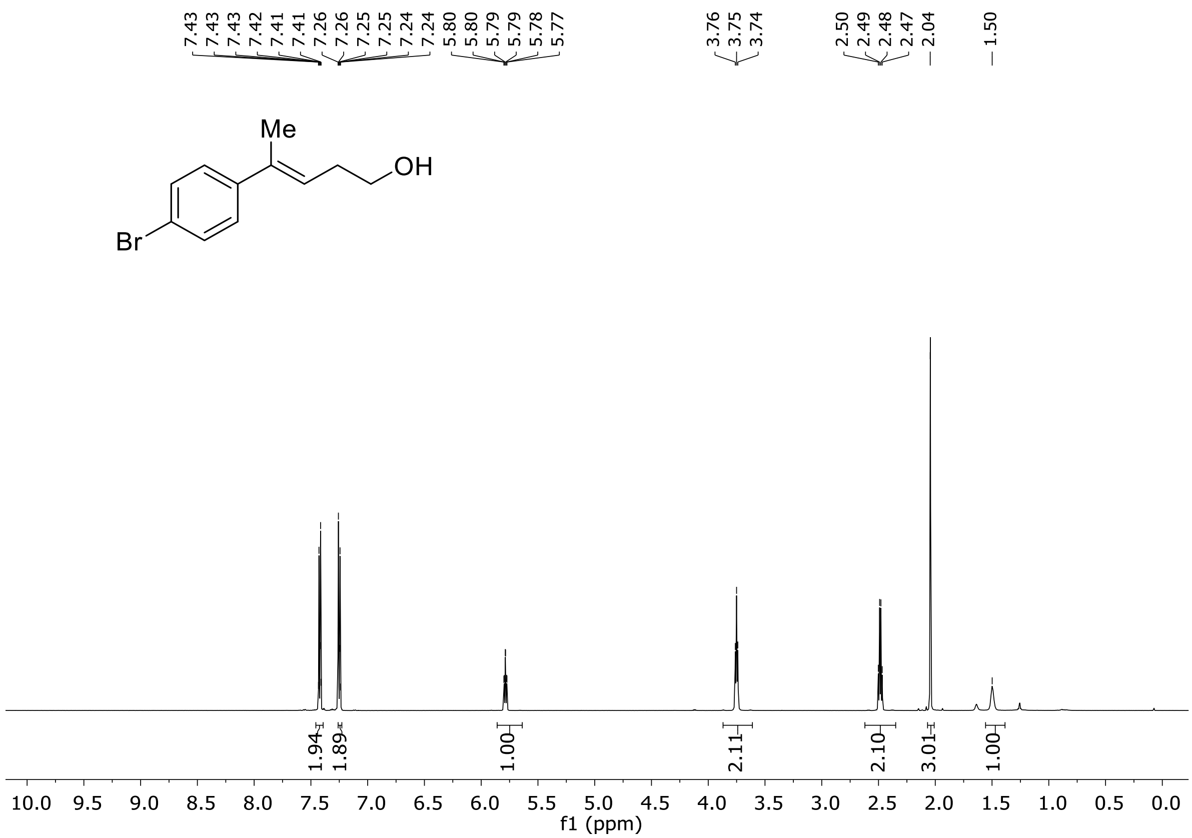
7.37
7.35
7.34
7.32
7.26
7.02
6.99
6.96
5.75
5.73
5.70
3.77
3.75
3.74
3.73
2.52
2.50
2.48
2.45
2.05
1.51
Me
OH
F
2.01
2.00
1.00
2.06
2.07
3.09
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

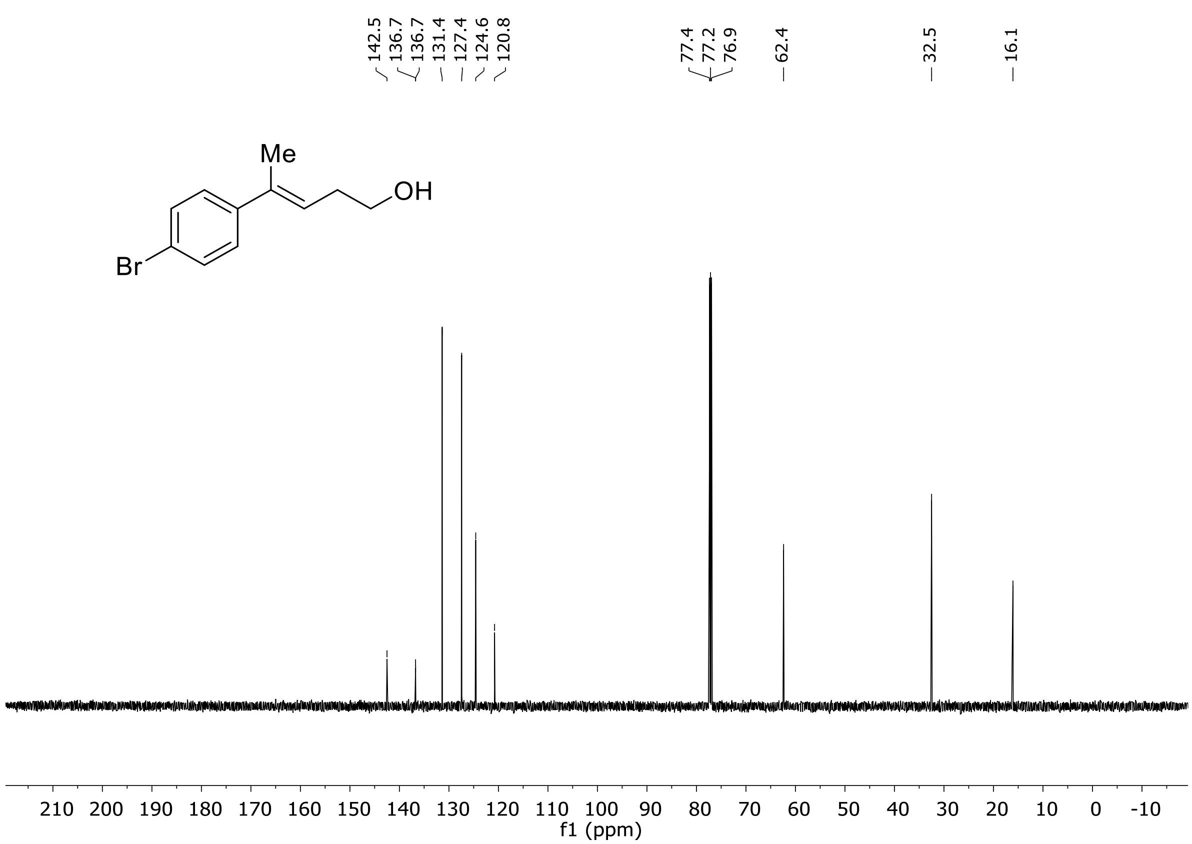


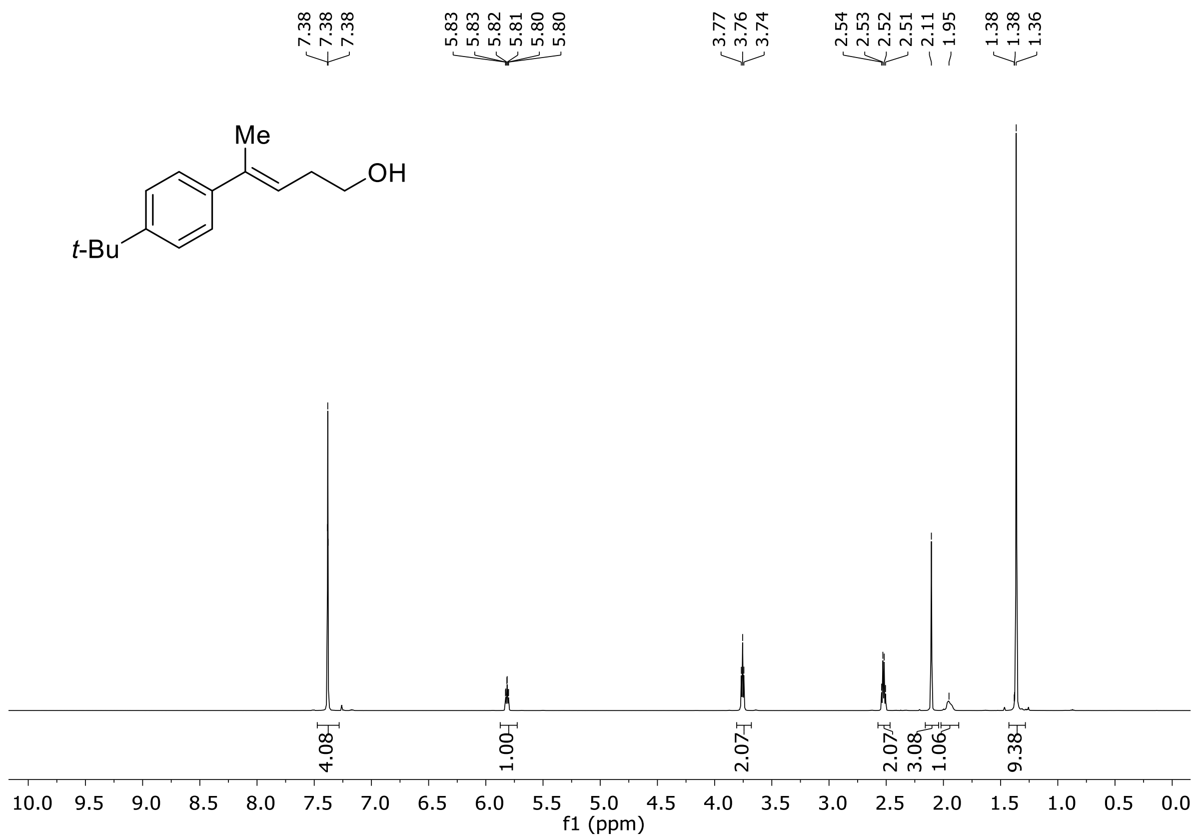
163.1
160.6
139.6
139.6
136.2
127.1
127.1
123.8
115.0
114.8
77.5
77.2
76.8
62.1
32.3
16.0
Me
OH
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



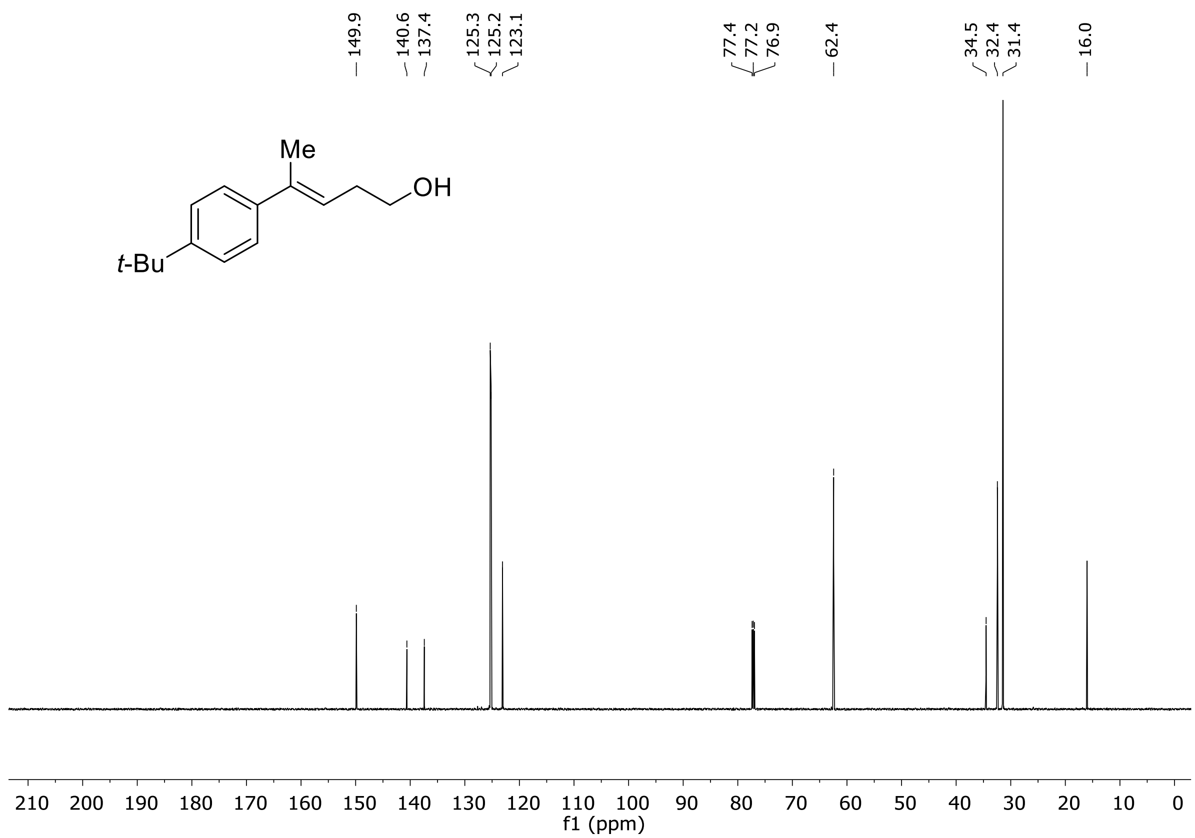
Me
OH
F
-115.41
-115.43
-115.45
-115.47
-115.48
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.43 7.43 7.43 7.42 7.41 7.41 7.26 7.26 7.25 7.25 7.24 7.24 5.80 5.80 5.79 5.79 5.78 5.77 3.76 3.75 3.74 2.50 2.49 2.48 2.47 2.04 1.50
Me
OH
Br
1.94 1.89 1.00 2.11 2.10 3.01 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.5 136.7 136.7 131.4 127.4 124.6 120.8 77.4 77.2 76.9 62.4 32.5 16.1
Me
OH
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



7.38
7.38
7.38
5.83
5.83
5.82
5.81
5.80
5.80
3.77
3.76
3.74
2.54
2.53
2.52
2.51
2.11
1.95
1.38
1.38
1.36
Me
OH
t-Bu
4.08
1.00
2.07
2.07
3.08
1.06
9.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



149.9
140.6
137.4
125.3
125.2
123.1
77.4
77.2
76.9
62.4
34.5
32.4
31.4
16.0
Me
OH
t-Bu
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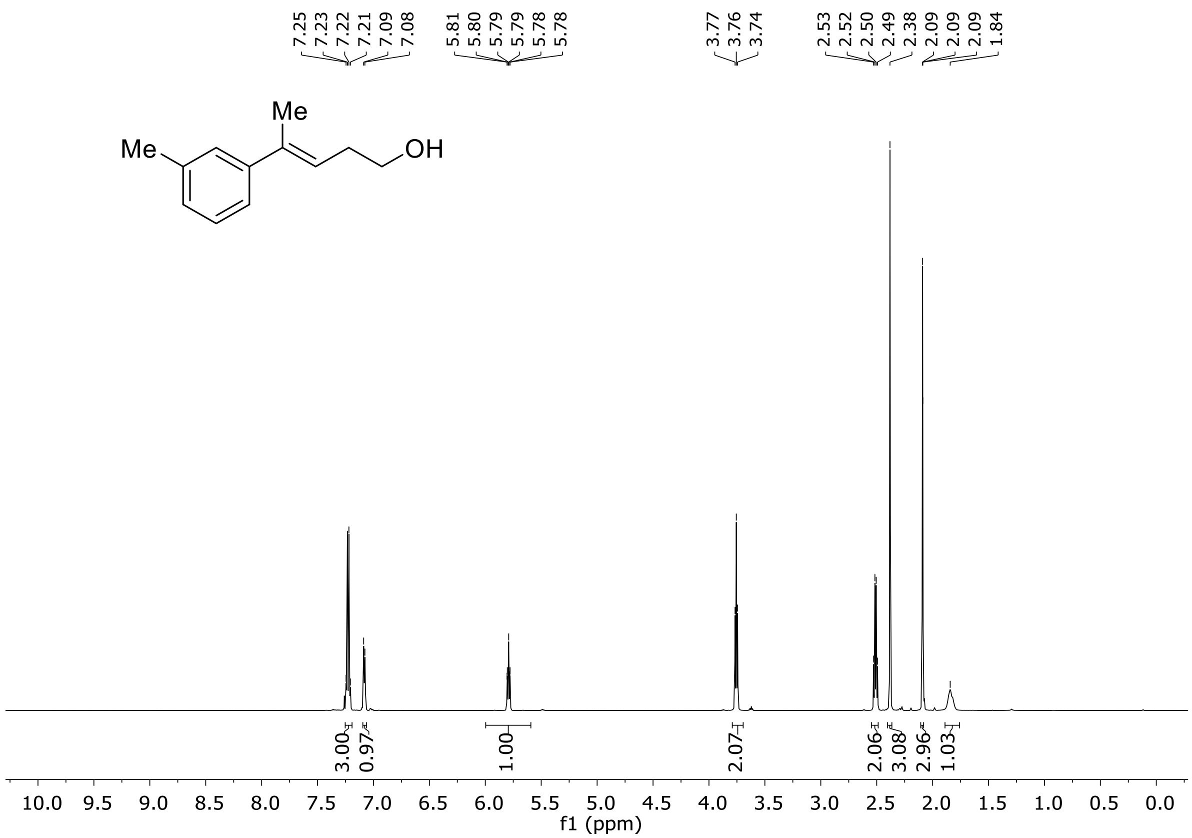
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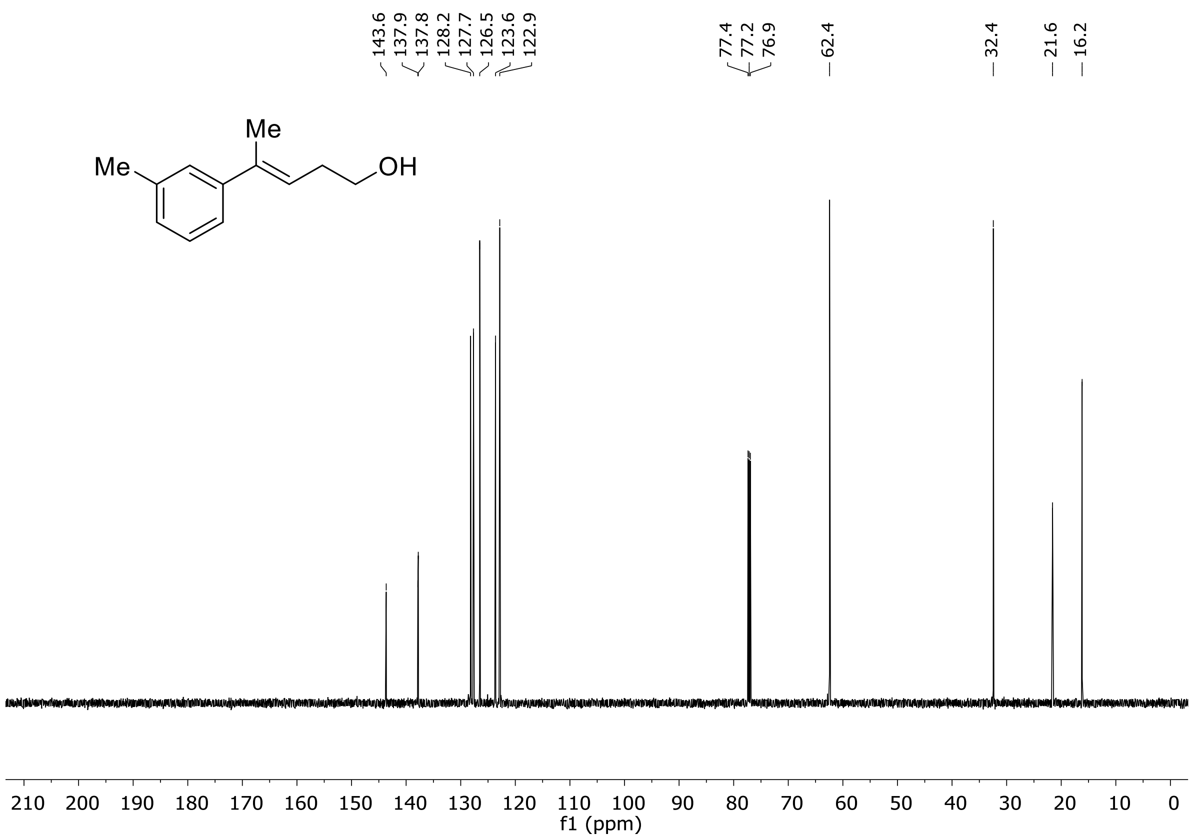
3.76
3.74
2.53
2.52
2.50
2.49
2.38
2.09
2.09
2.09
1.84
Me
Me
OH
3.00
0.97
1.00
2.07
2.06
3.08
2.96
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.9
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16.2
Me
Me
OH
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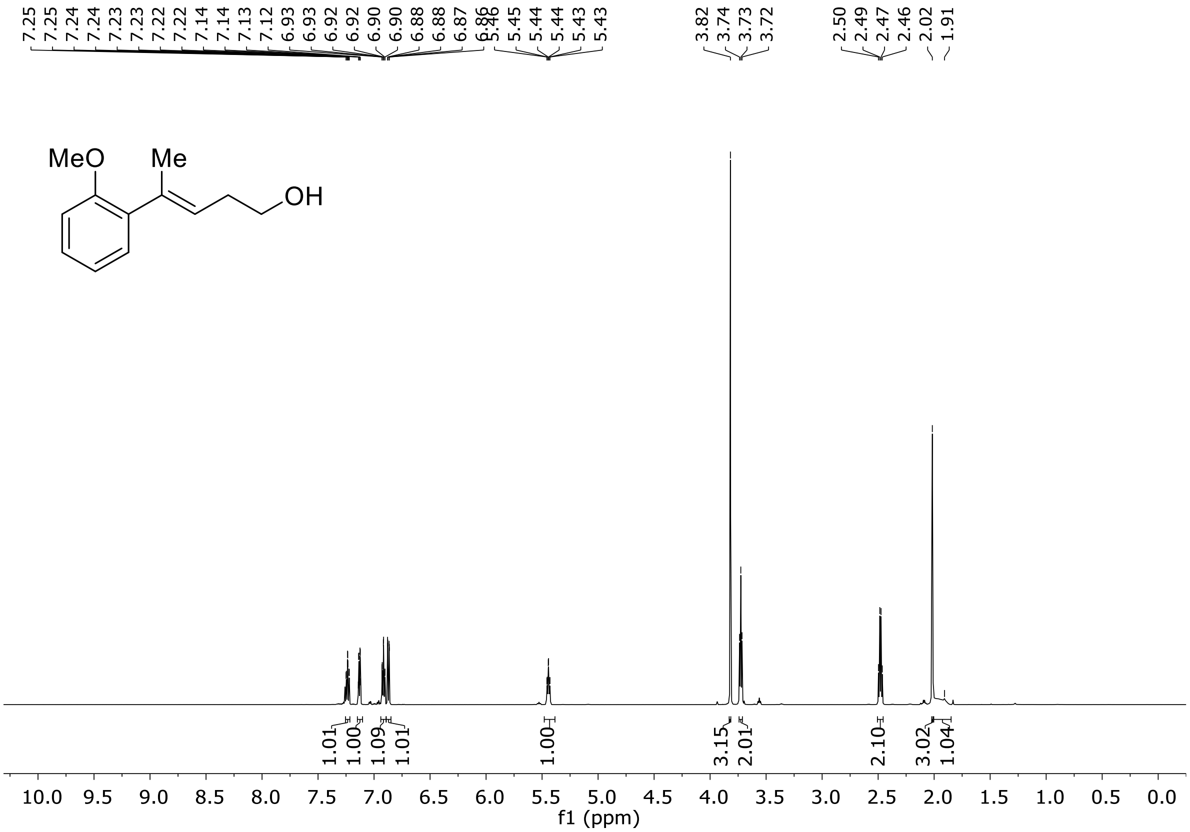
f1 (ppm)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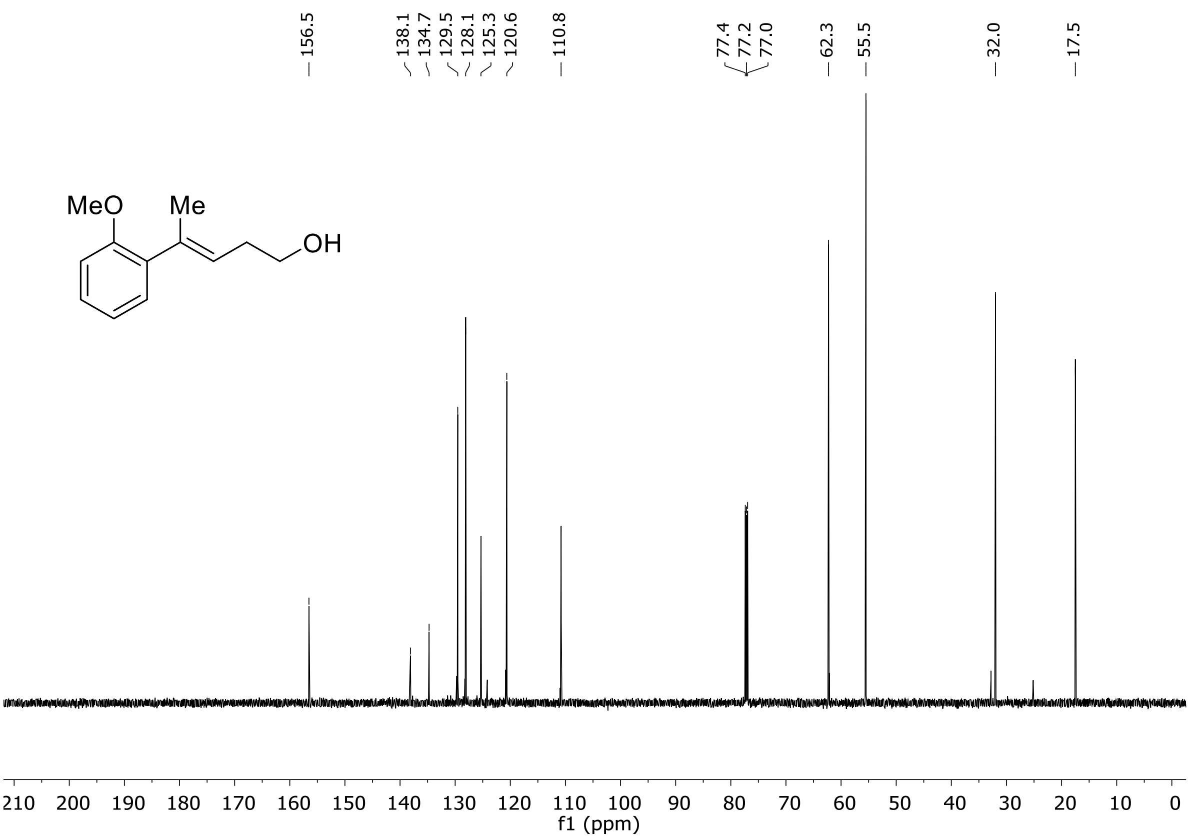
3.82 3.74 3.73 3.72
2.50 2.49 2.47 2.46 2.02 1.91
MeO
Me
OH
1.01 1.00 1.09 1.01 1.00 3.15 2.01 2.10 3.02 1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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Me
OH
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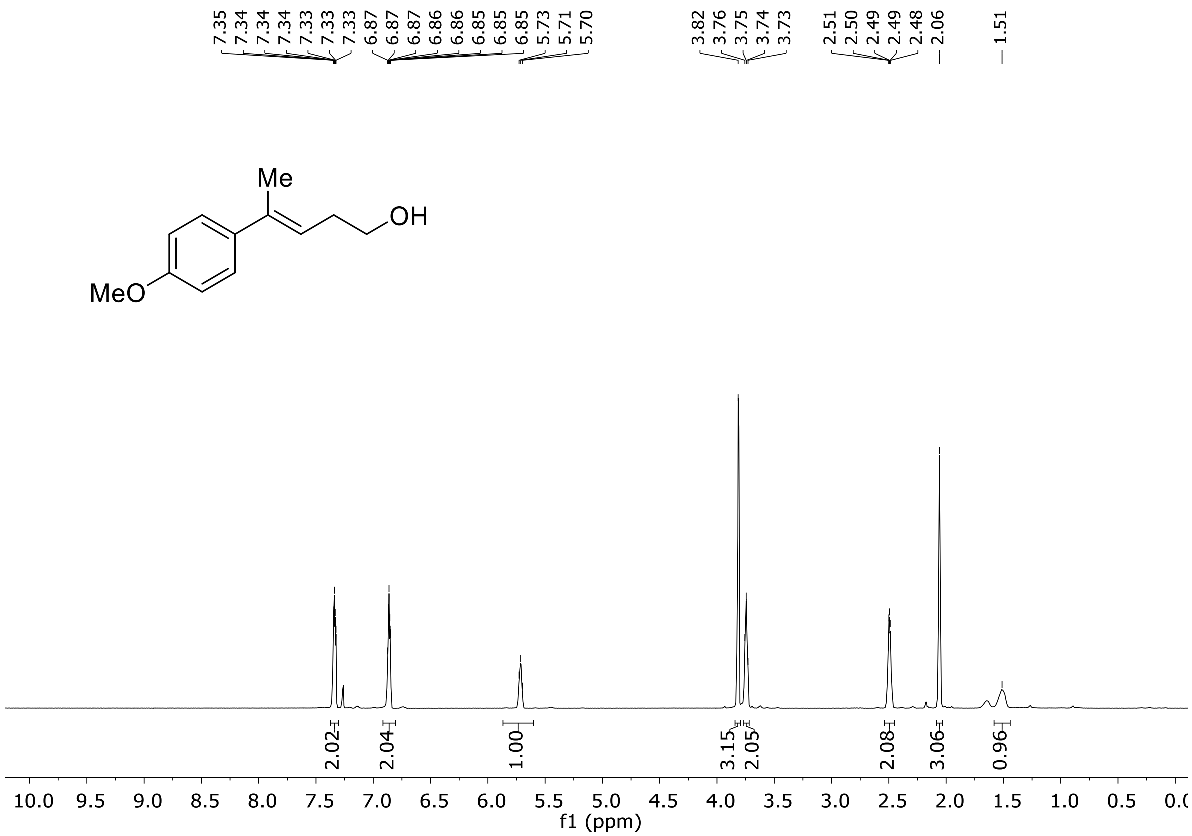
f1 (ppm)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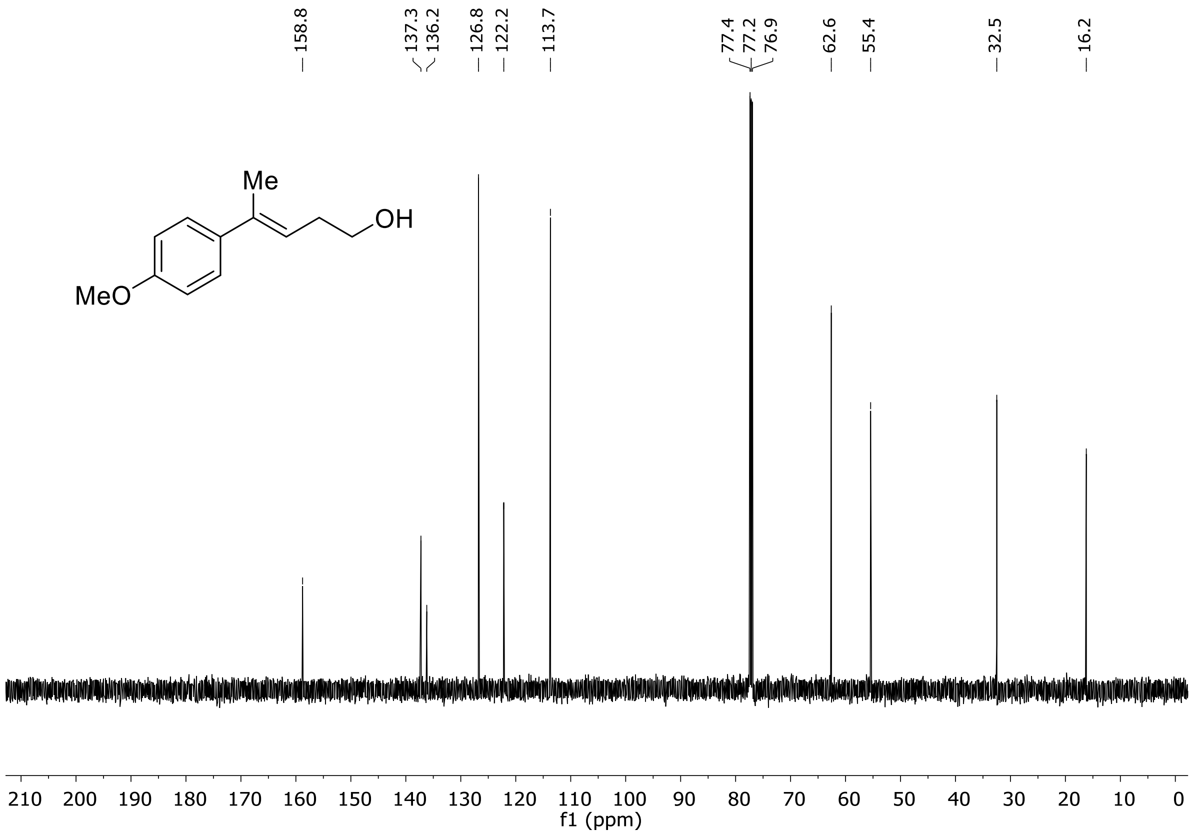
3.82 3.76 3.75 3.74 3.73
2.51 2.50 2.49 2.49 2.48 2.06
1.51
Me
OH
MeO
2.02 2.04 1.00 3.15 2.05 2.08 3.06 0.96
f1 (ppm)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55.4
32.5
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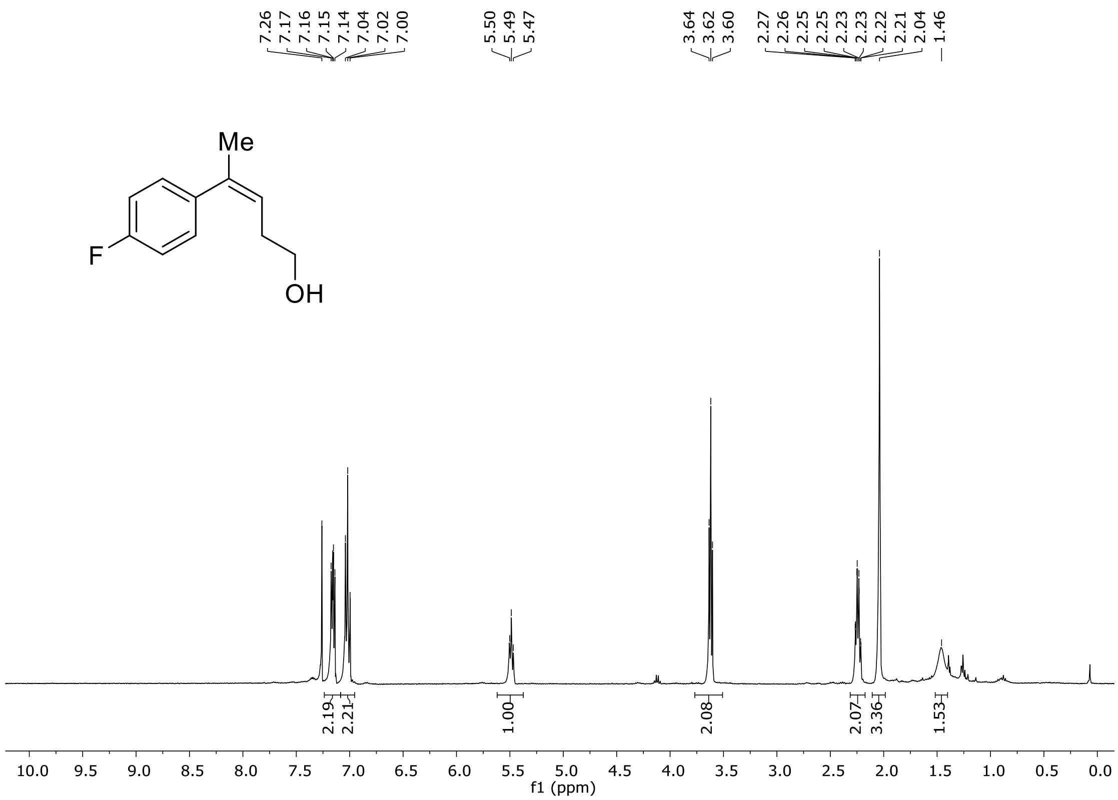
OH
MeO
f1 (ppm)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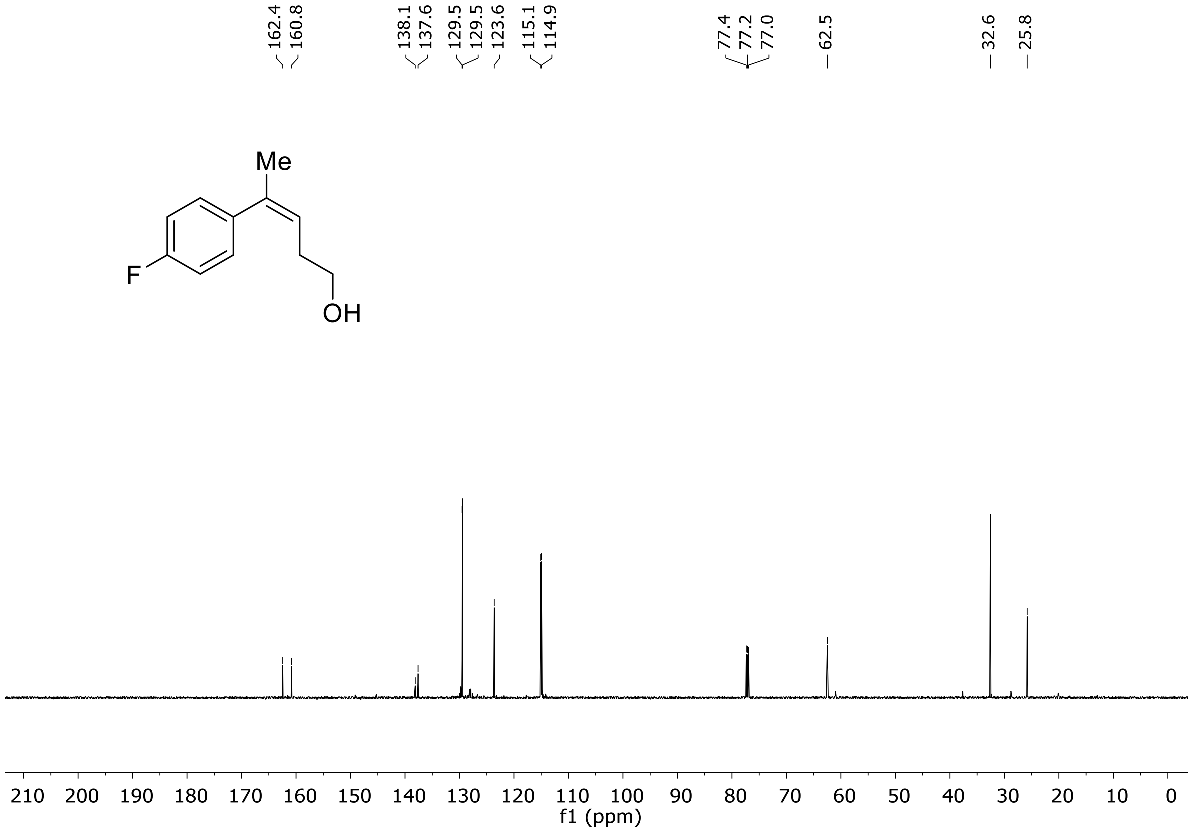
3.60
2.27
2.26
2.25
2.25
2.23
2.23
2.22
2.21
2.04
1.46
Me
F
OH
2.19
2.21
1.00
2.08
2.07
3.36
1.53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.5
123.6
115.1
114.9
77.4
77.2
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32.6
25.8
Me
F
OH
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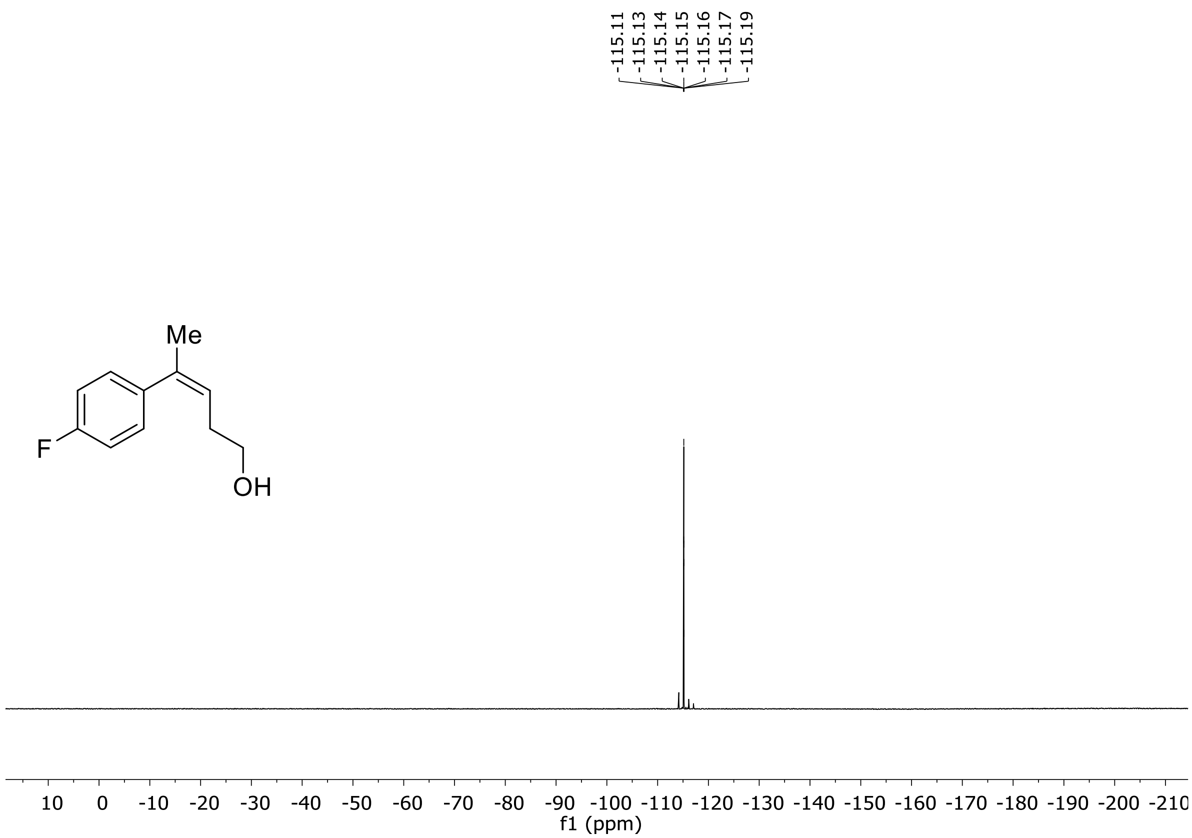
f1 (ppm)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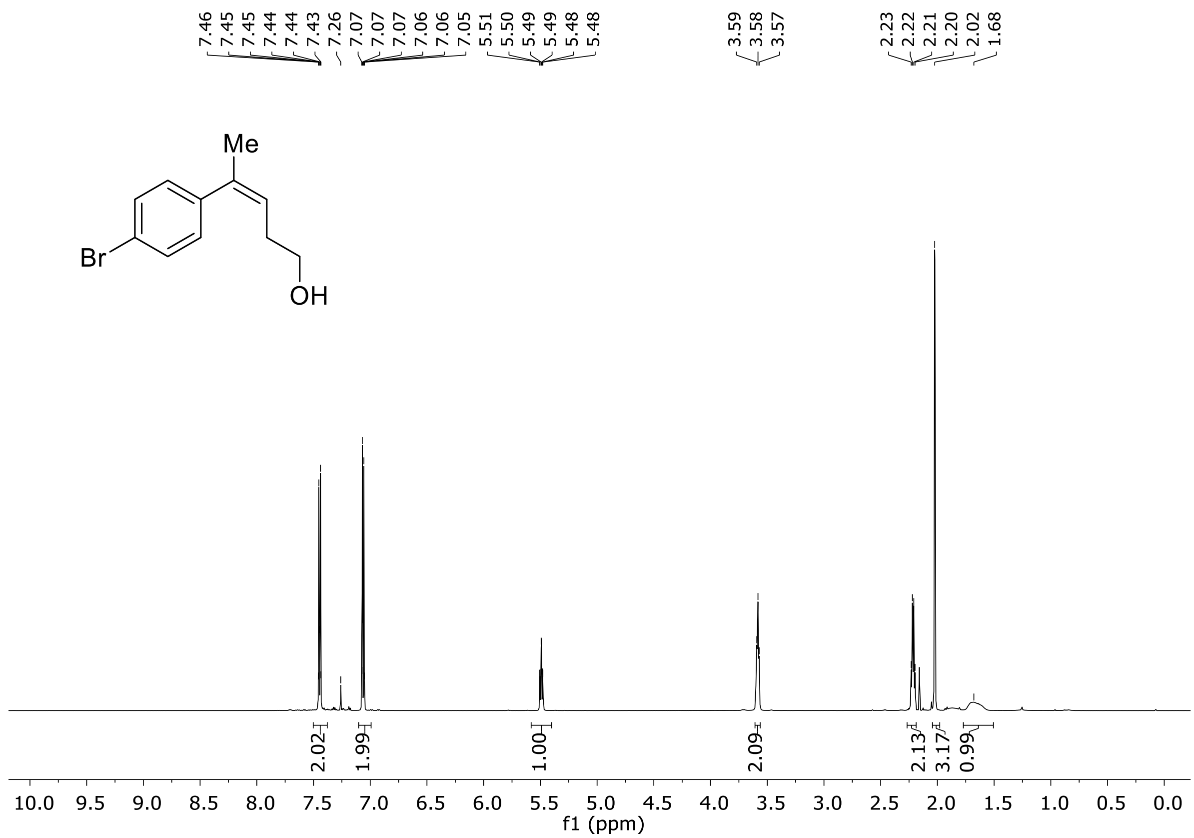
-115.13
-115.14
-115.15
-115.16
-115.17
-115.19
Me
F
OH
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.45
7.44
7.44
7.43
7.26
7.07
7.07
7.07
7.06
7.06
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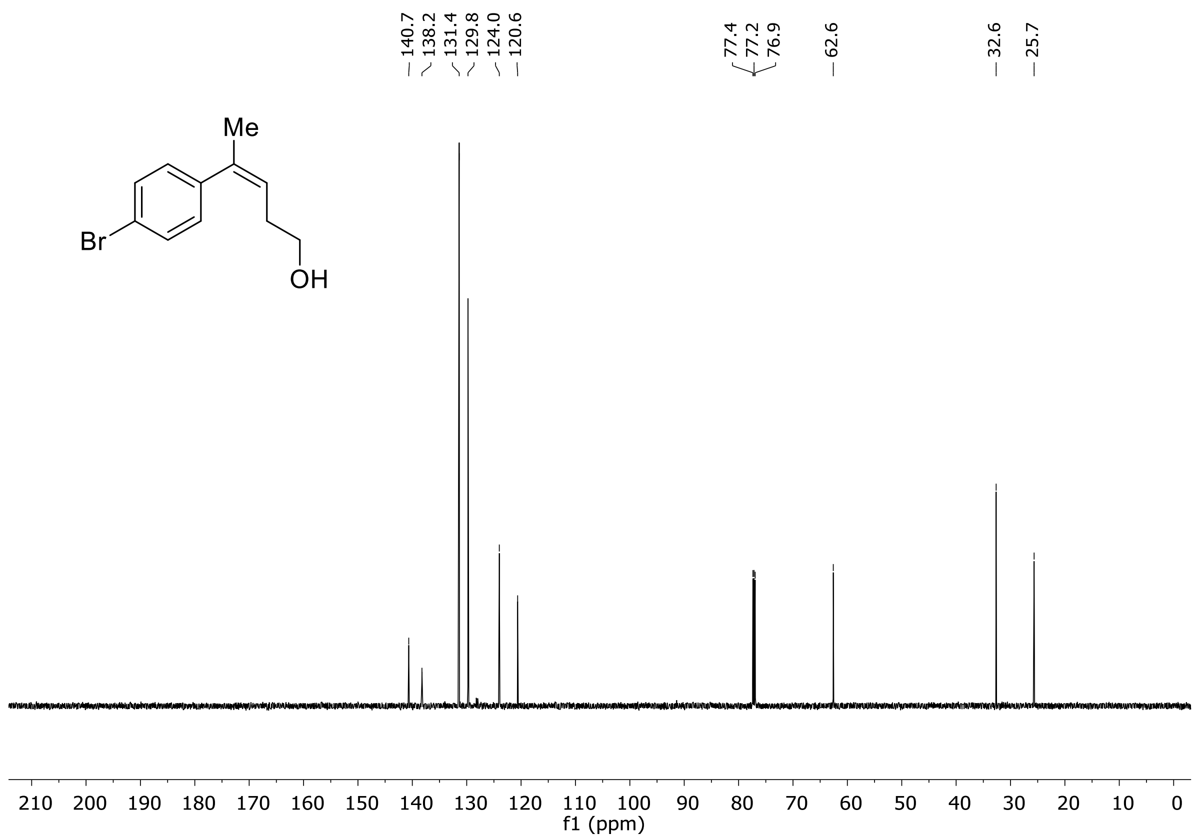
5.51
5.50
5.49
5.49
5.48
5.48
3.59
3.58
3.57
2.23
2.22
2.21
2.20
2.02
1.68
Me
Br
OH
2.02
1.99
1.00
2.09
2.13
3.17
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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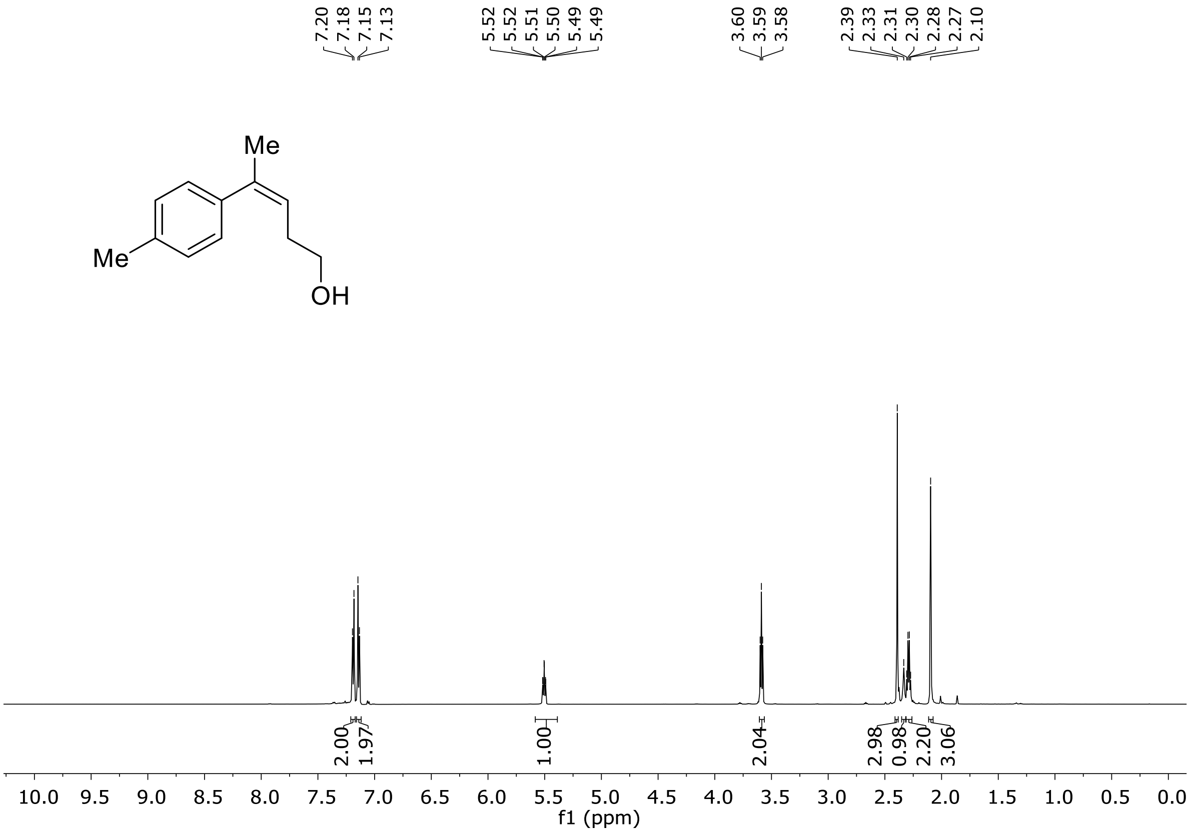
138.2
131.4
129.8
124.0
120.6
77.4
77.2
76.9
62.6
32.6
25.7
Me
Br
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.15
7.13
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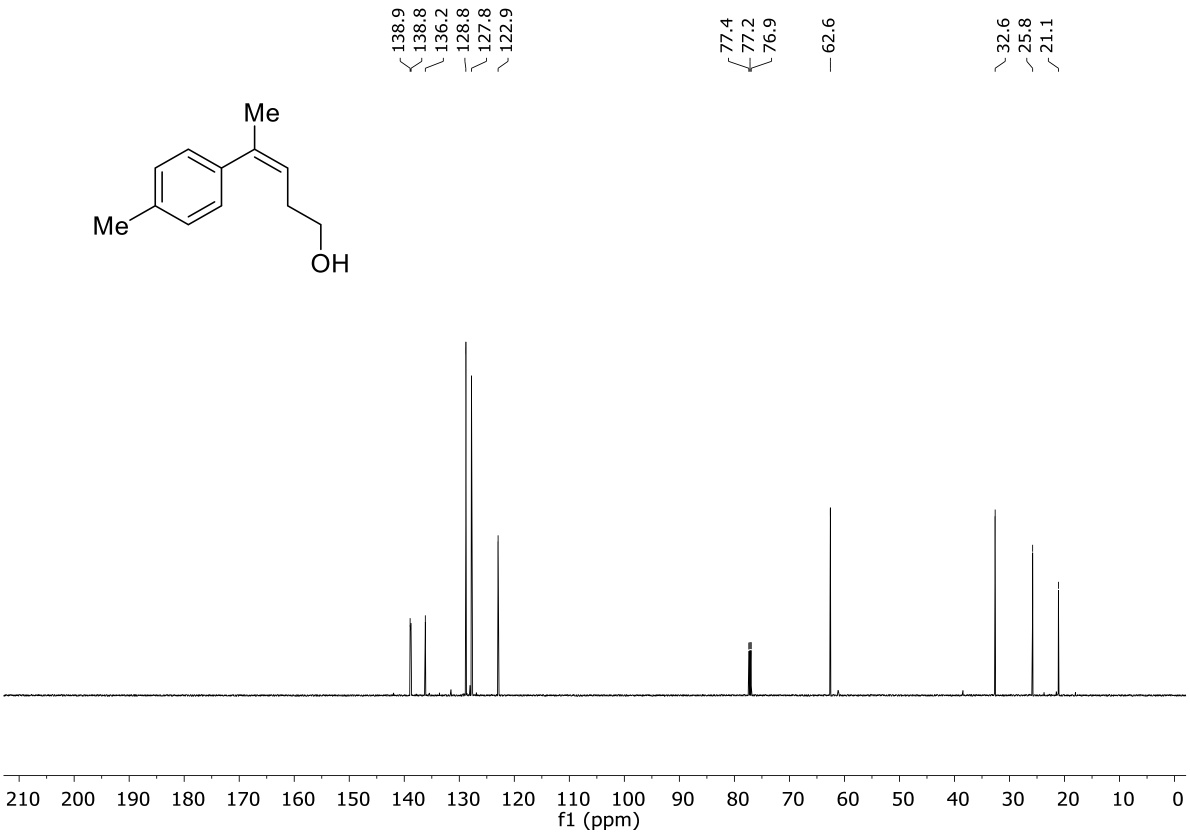
5.52
5.51
5.50
5.49
5.49
3.60
3.59
3.58
2.39
2.33
2.31
2.30
2.28
2.27
2.10
Me
Me
OH
2.00
1.97
1.00
2.04
2.98
0.98
2.20
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.8
127.8
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77.4
77.2
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32.6
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21.1
Me
Me
OH
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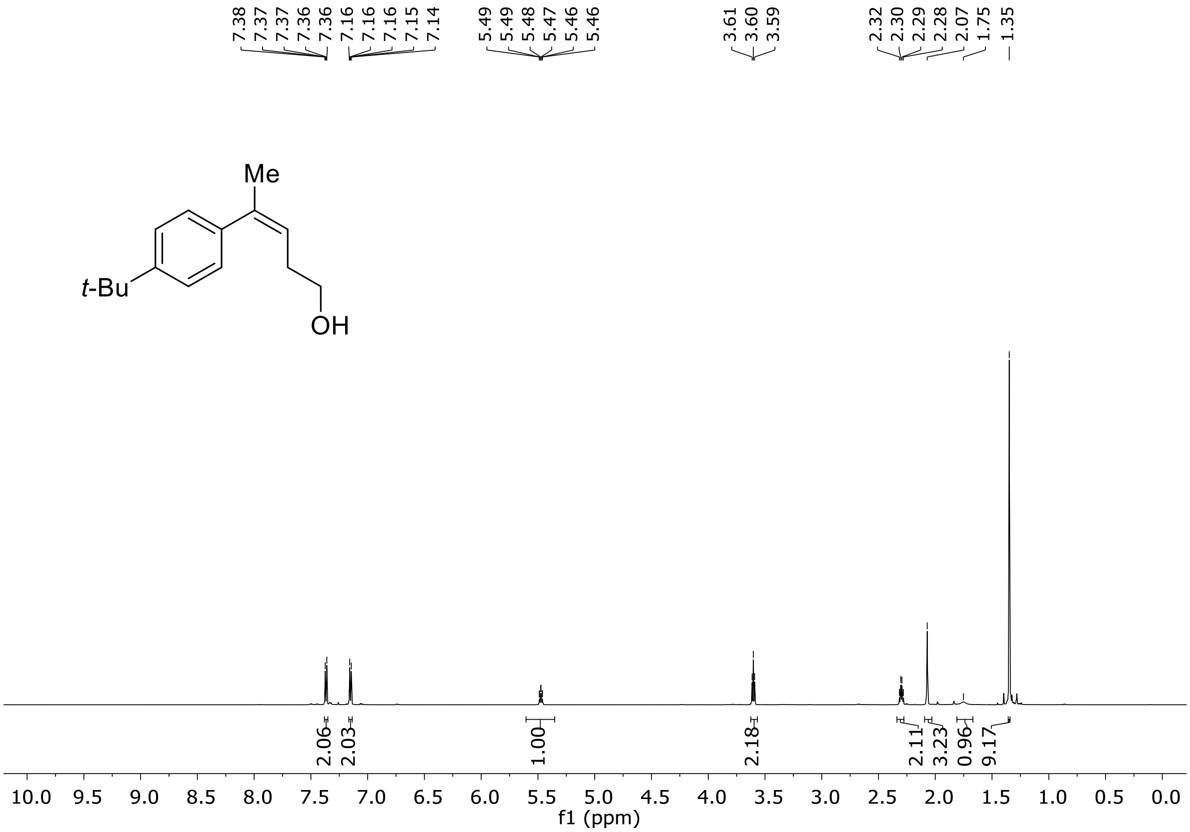
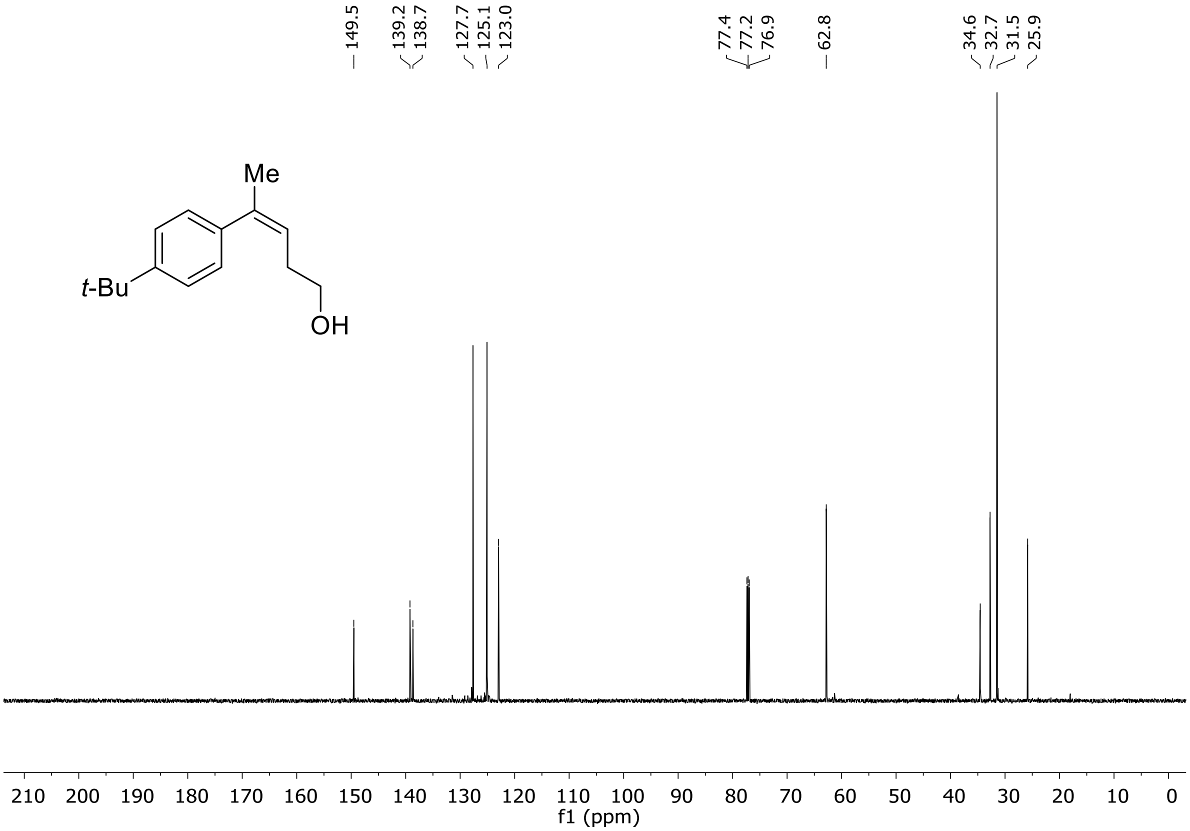
f1 (ppm)


7.38 7.37 7.37 7.36 7.36 7.16 7.16 7.16 7.15 7.14
5.49 5.49 5.48 5.47 5.46 5.46
3.61 3.60 3.59
2.32 2.30 2.29 2.28 2.07 1.75 1.35
Me
t-Bu
OH
2.06 2.03 1.00 2.18 2.11 3.23 0.96 9.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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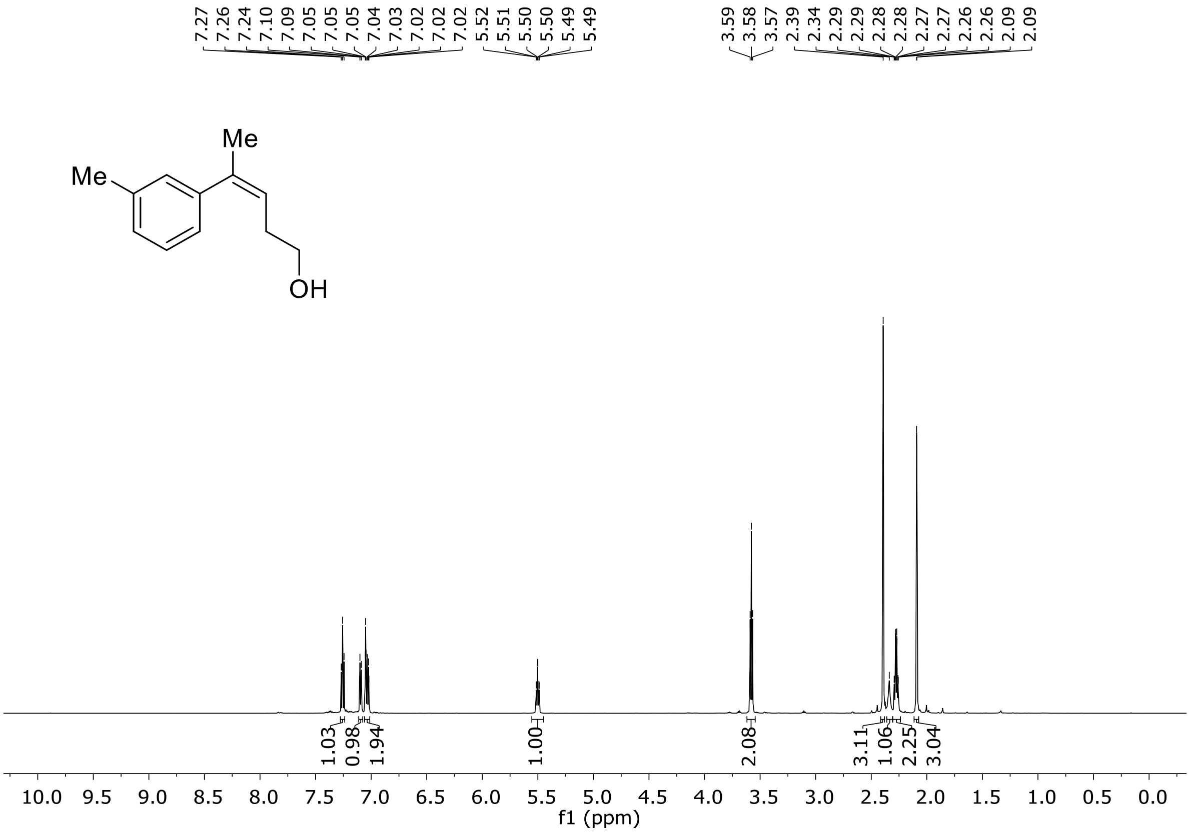
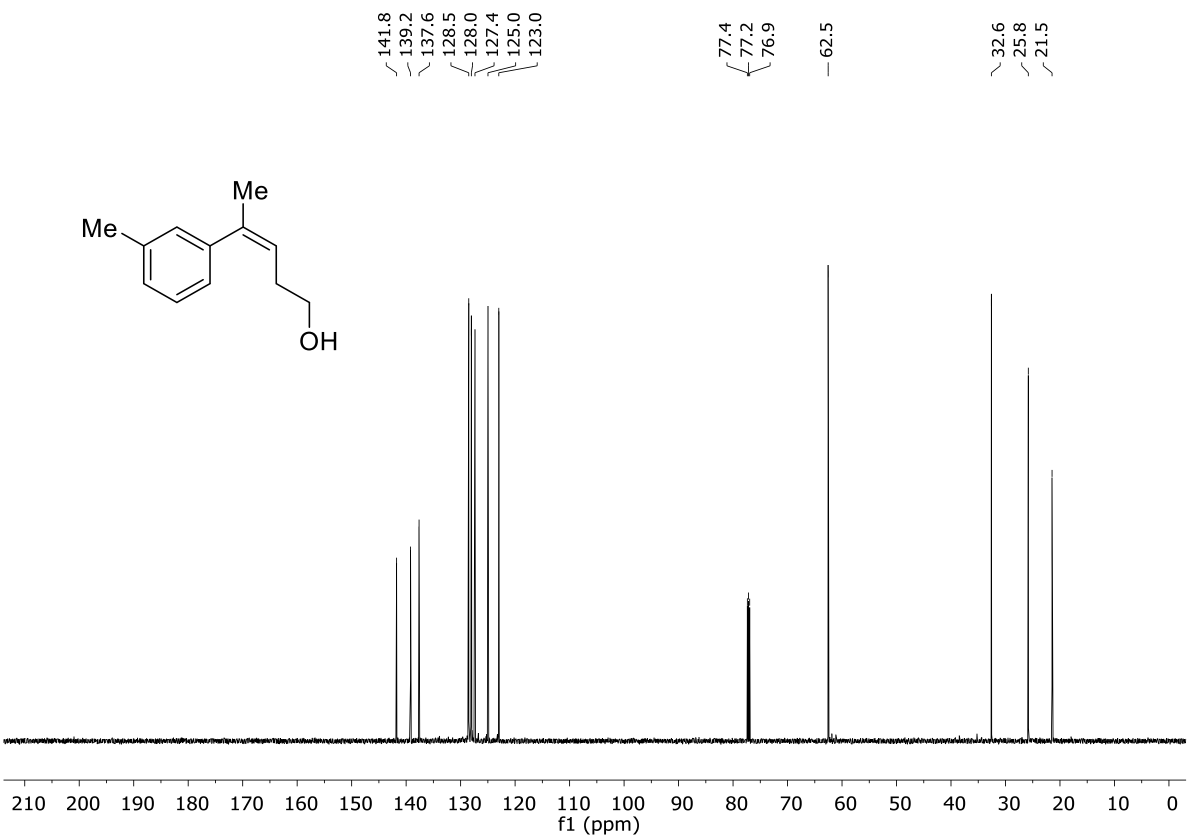
139.2 138.7
127.7 125.1 123.0
77.4 77.2 76.9
62.8
34.6 32.7 31.5 25.9
Me
t-Bu
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.27 7.26 7.24 7.10 7.09 7.05 7.05 7.05 7.04 7.03 7.02 7.02 7.02 5.52 5.51 5.50 5.50 5.49 5.49
3.59 3.58 3.57 2.39 2.34 2.29 2.29 2.28 2.28 2.27 2.27 2.26 2.09 2.09
Me
Me
OH
1.03 0.98 1.94 1.00 2.08 3.11 1.06 2.25 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.4 77.2 76.9
62.5
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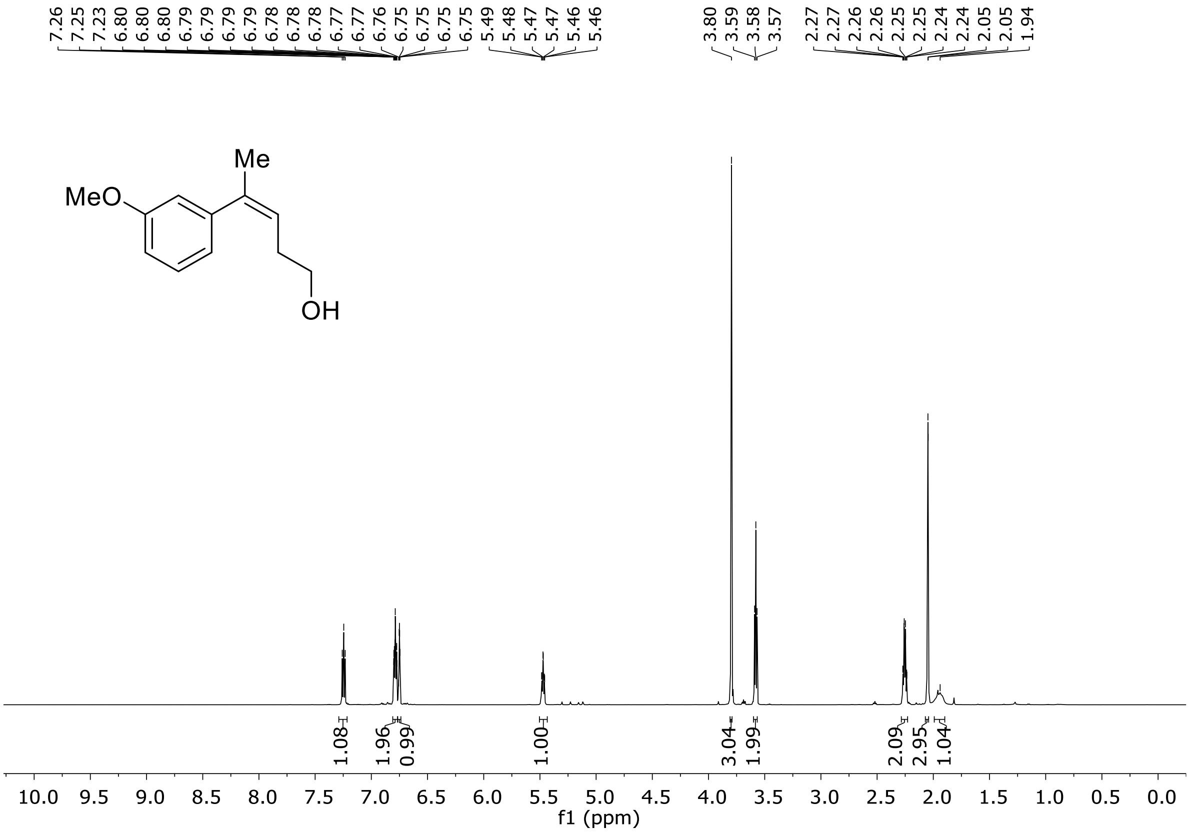
Me
Me
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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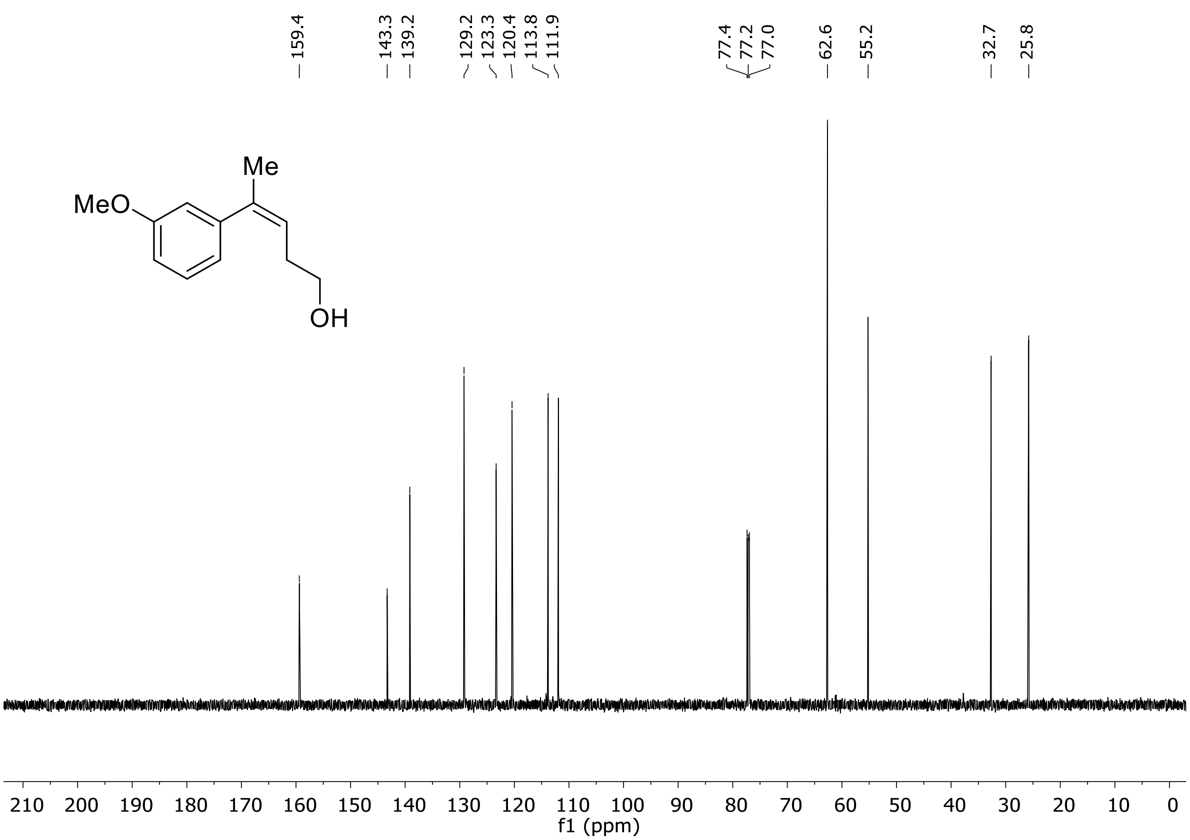
6.77
6.77
6.76
6.75
6.75
6.75
6.75
5.49
5.48
5.47
5.47
5.46
5.46
3.80
3.59
3.58
3.57
2.27
2.27
2.26
2.26
2.25
2.25
2.24
2.24
2.05
2.05
1.94
Me
MeO
OH
1.08
1.96
0.99
1.00
3.04
1.99
2.09
2.95
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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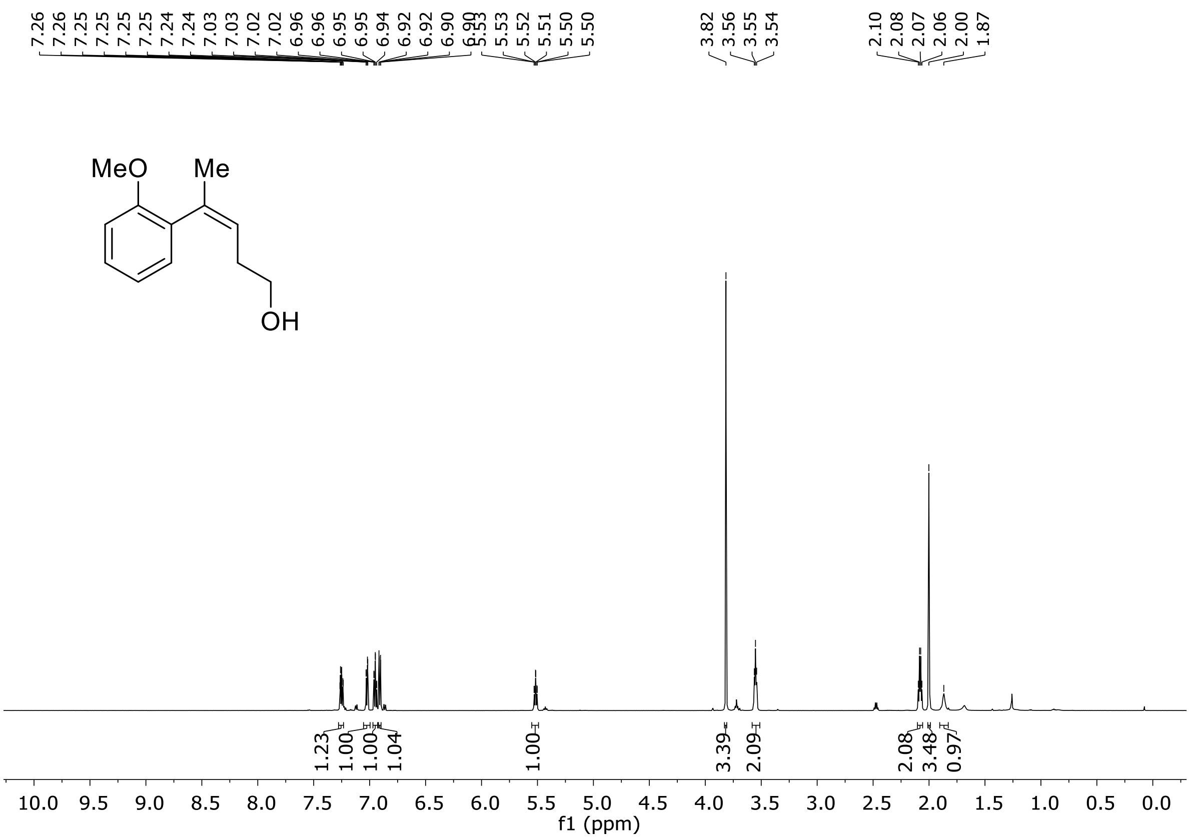
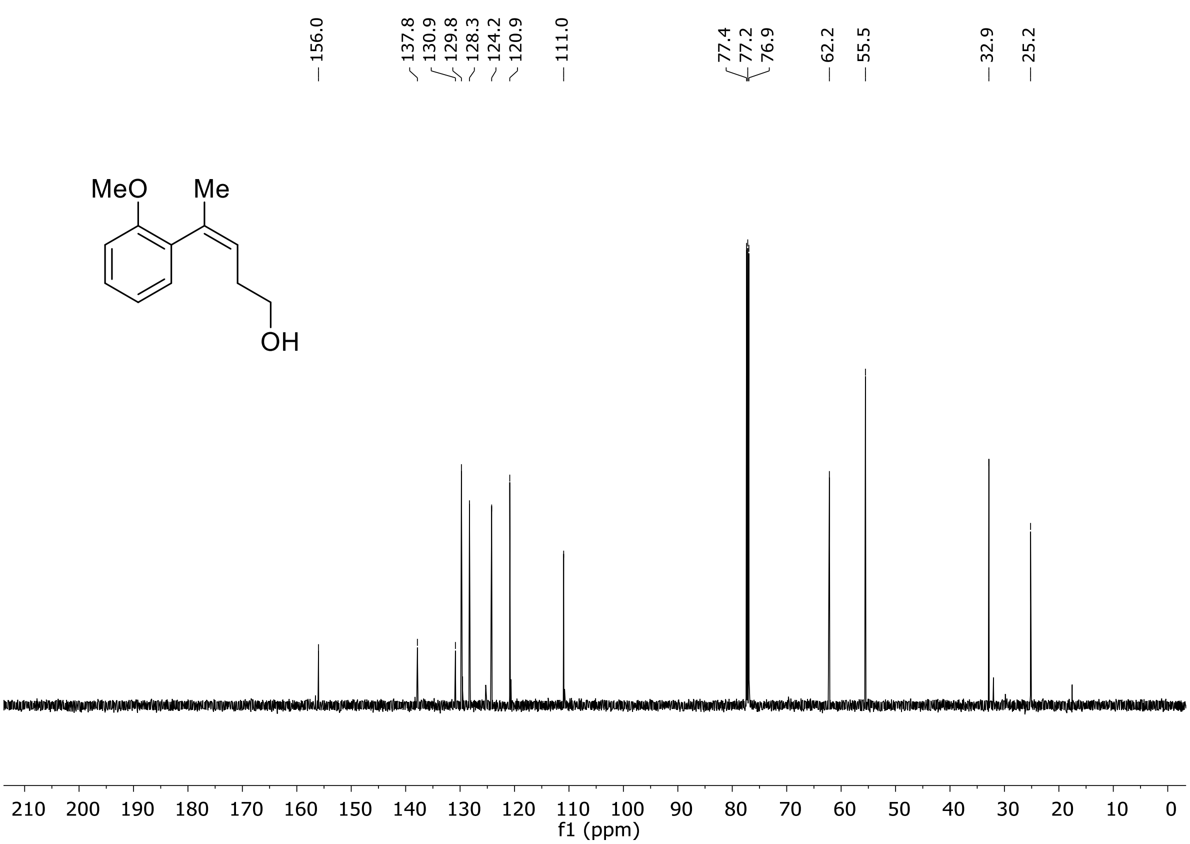
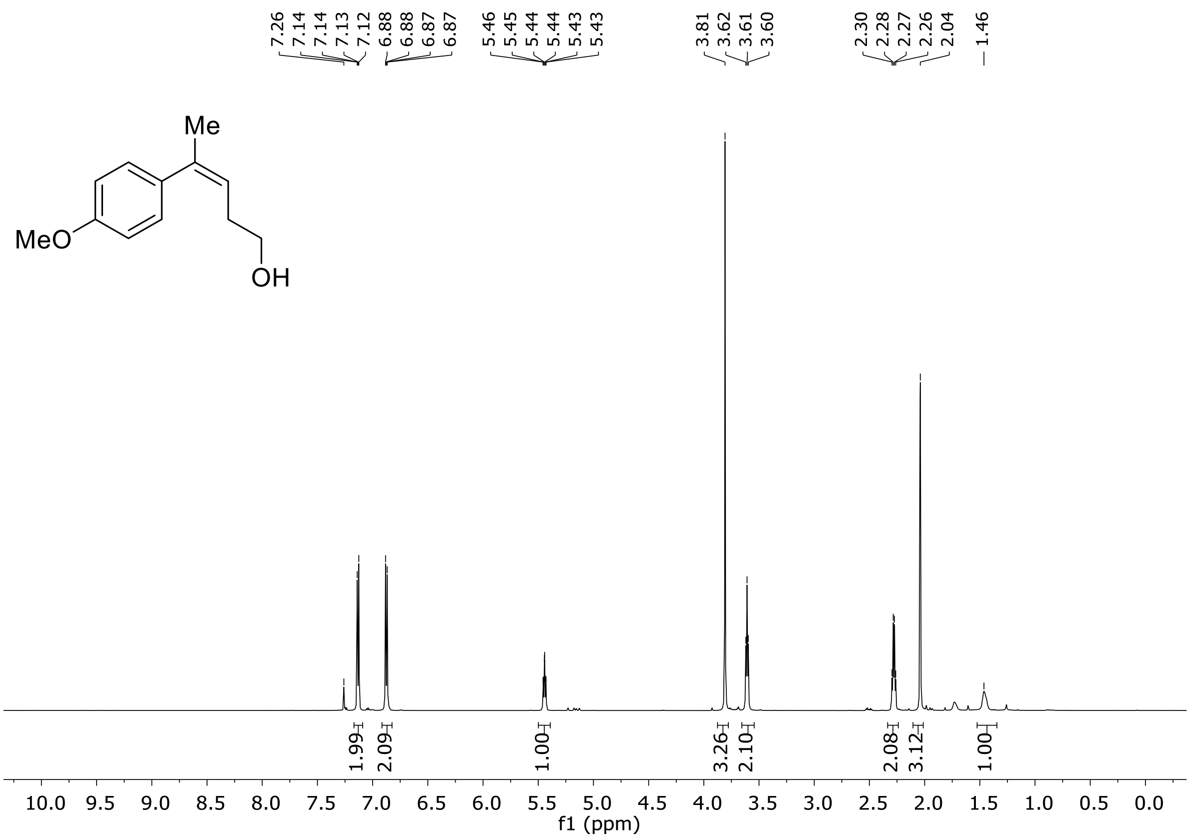
120.4
113.8
111.9
77.4
77.2
77.0
62.6
55.2
32.7
25.8
Me
MeO
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.03 7.03 7.02 7.02 6.96 6.96 6.95 6.95 6.94 6.92 6.92 6.90 6.90 5.53 5.53 5.52 5.51 5.50 5.50
3.82 3.56 3.55 3.54
2.10 2.08 2.07 2.06 2.00 1.87
MeO
Me
OH
1.23 1.00 1.00 1.04
1.00
3.39 2.09
2.08 3.48 0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



156.0
137.8 130.9 129.8 128.3 124.2 120.9
111.0
77.4 77.2 76.9
62.2
55.5
32.9
25.2
MeO
Me
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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6.88
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6.87
6.87
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5.45
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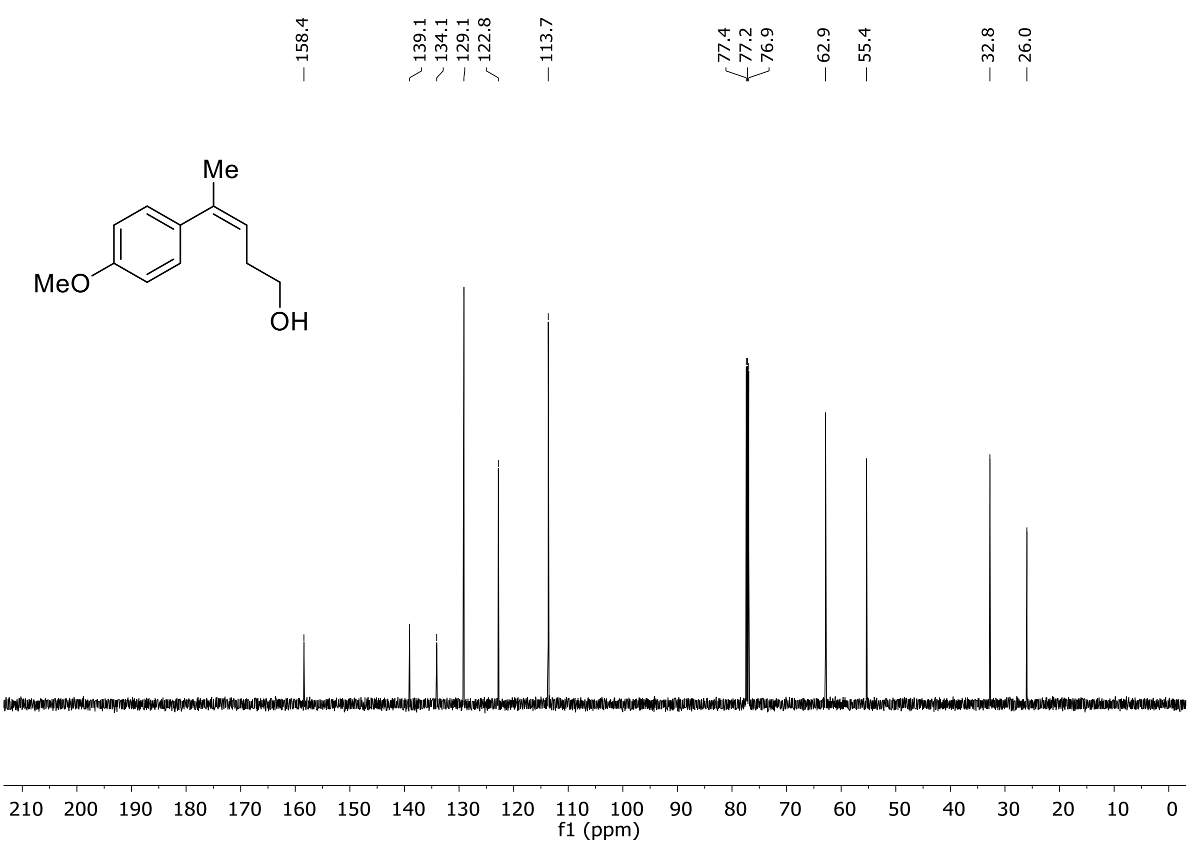
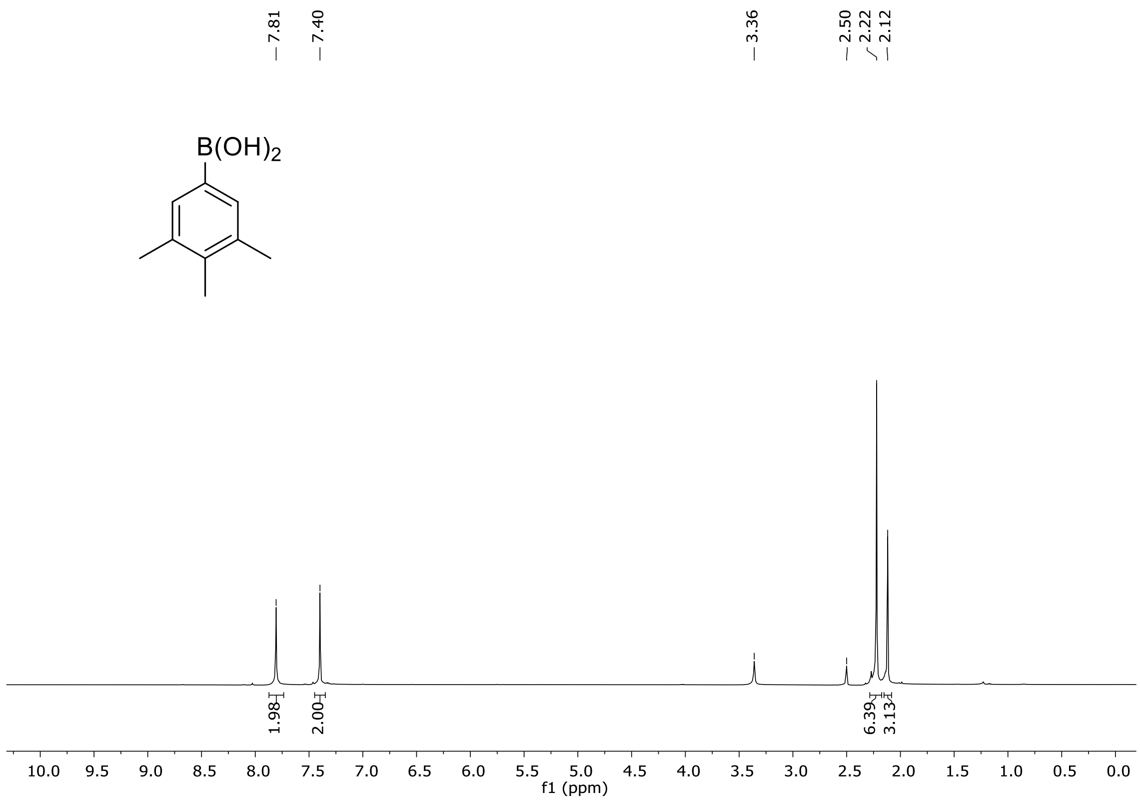
5.44
5.43
5.43
3.81
3.62
3.61
3.60
2.30
2.28
2.27
2.26
2.04
1.46
Me
MeO
OH
1.99
2.09
1.00
3.26
2.10
2.08
3.12
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



158.4
139.1
134.1
129.1
122.8
113.7
77.4
77.2
76.9
62.9
55.4
32.8
26.0
Me
MeO
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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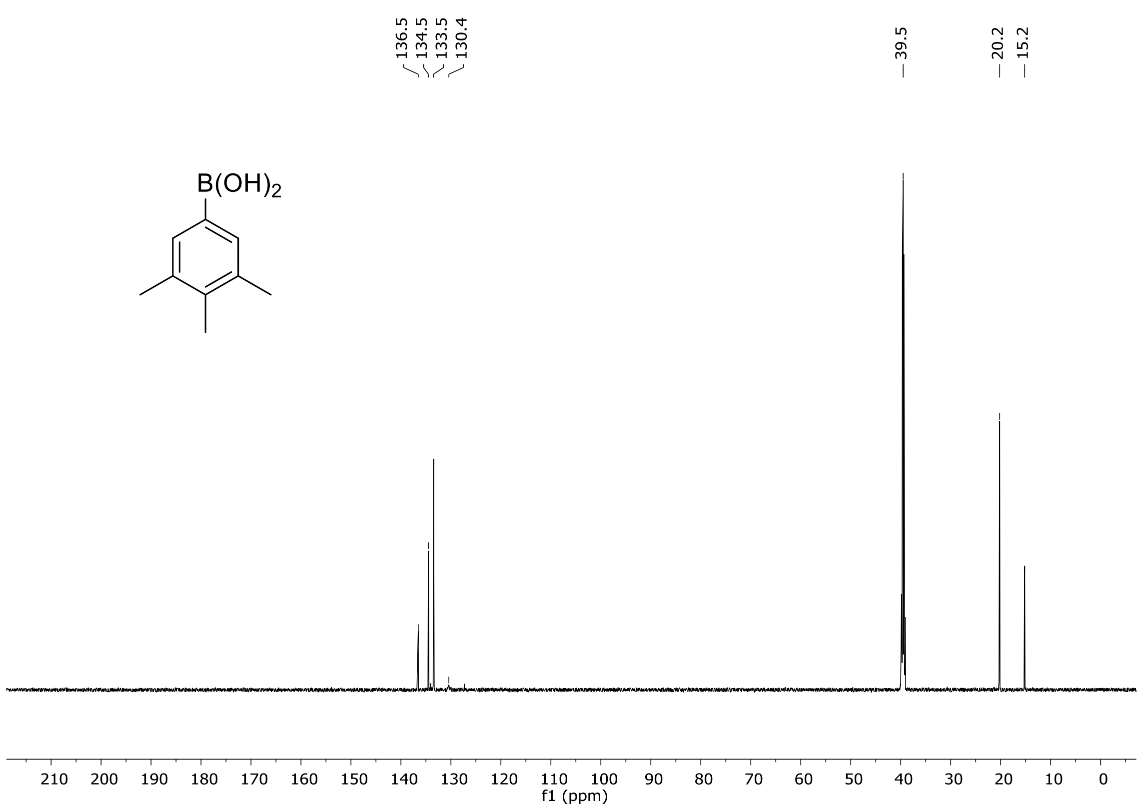
2.50
2.22
2.12
B(OH)2
1.98
2.00
6.39
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.5
130.4
39.5
20.2
15.2
B(OH)2
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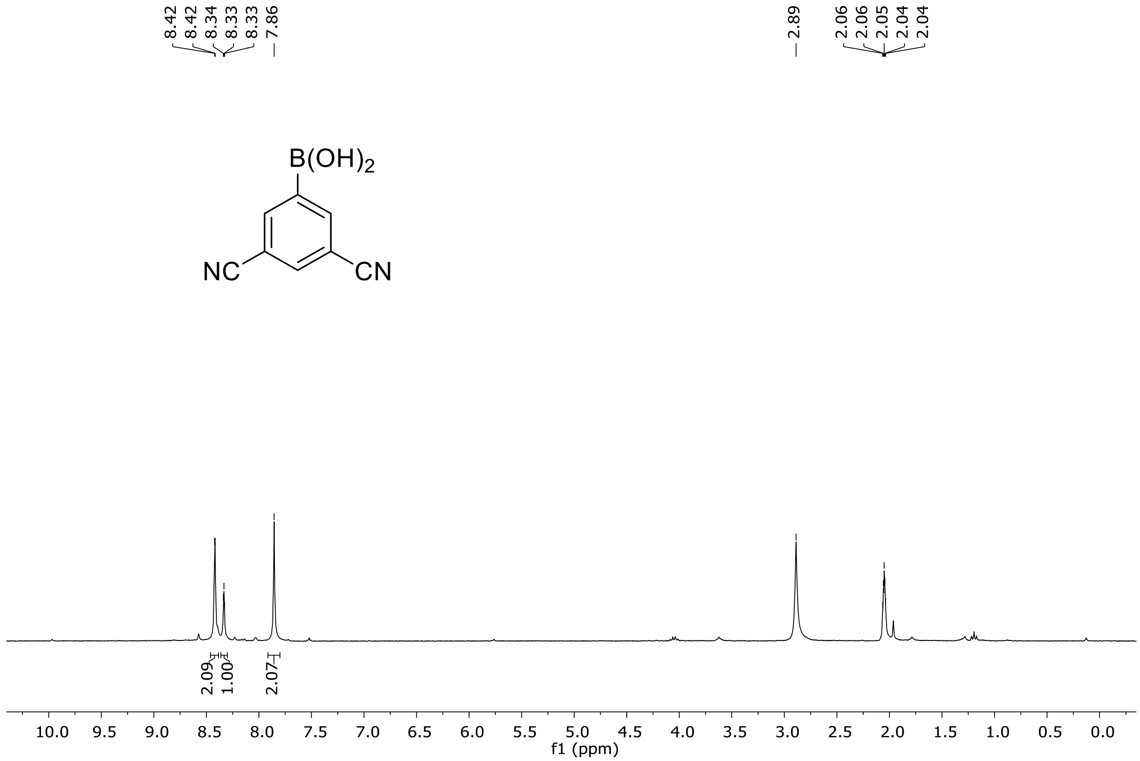
f1 (ppm)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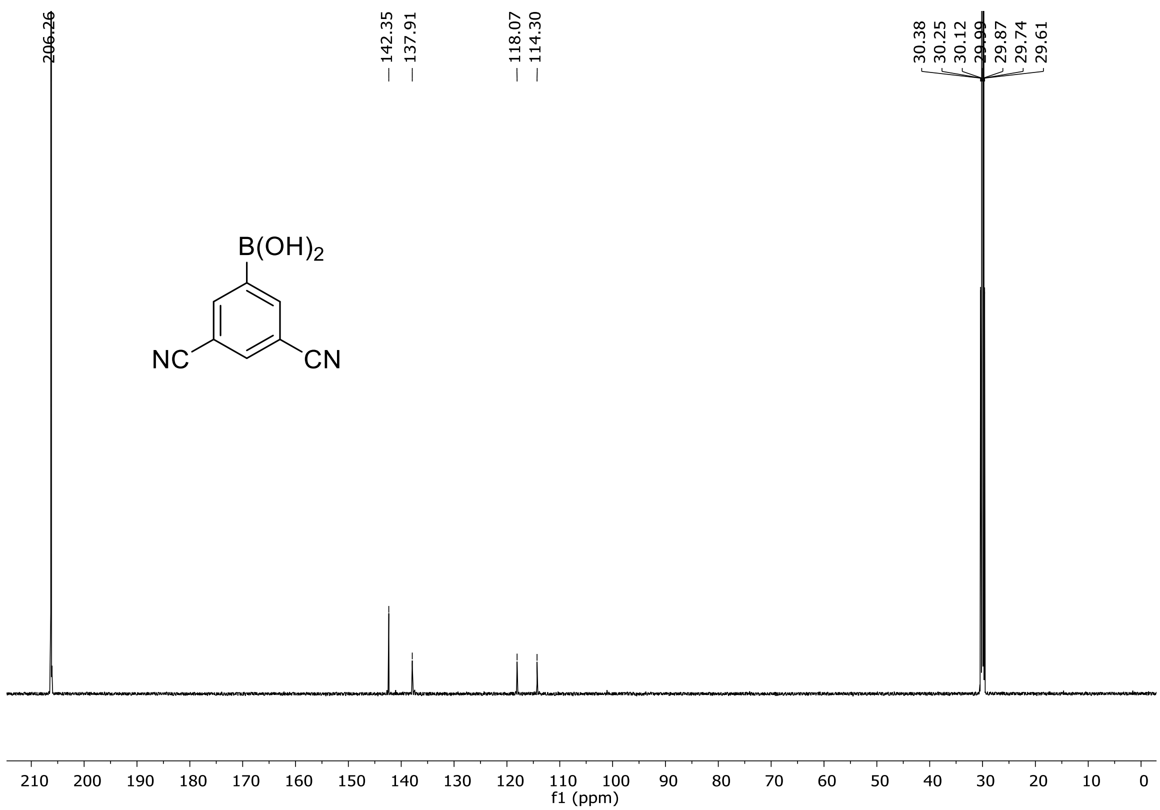
7.86
2.89
2.06
2.06
2.05
2.04
2.04
B(OH)2
NC
CN
2.09
1.00
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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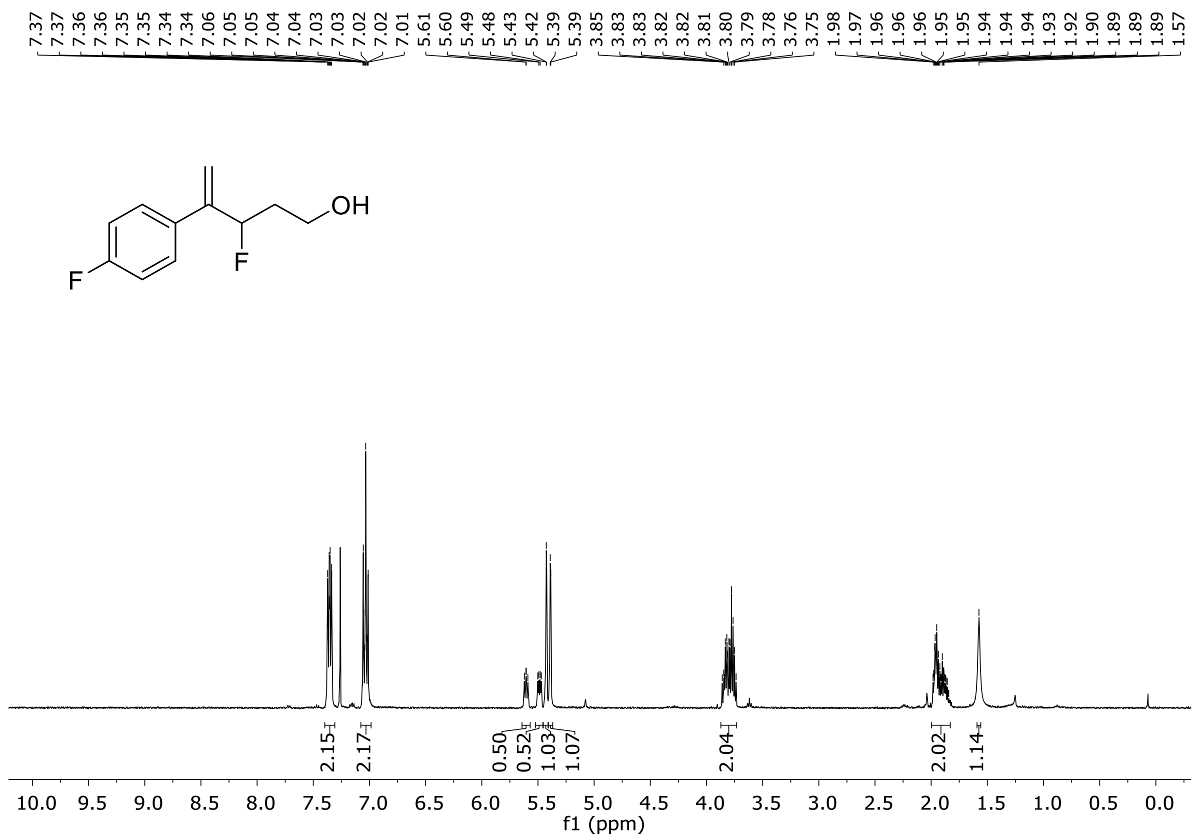
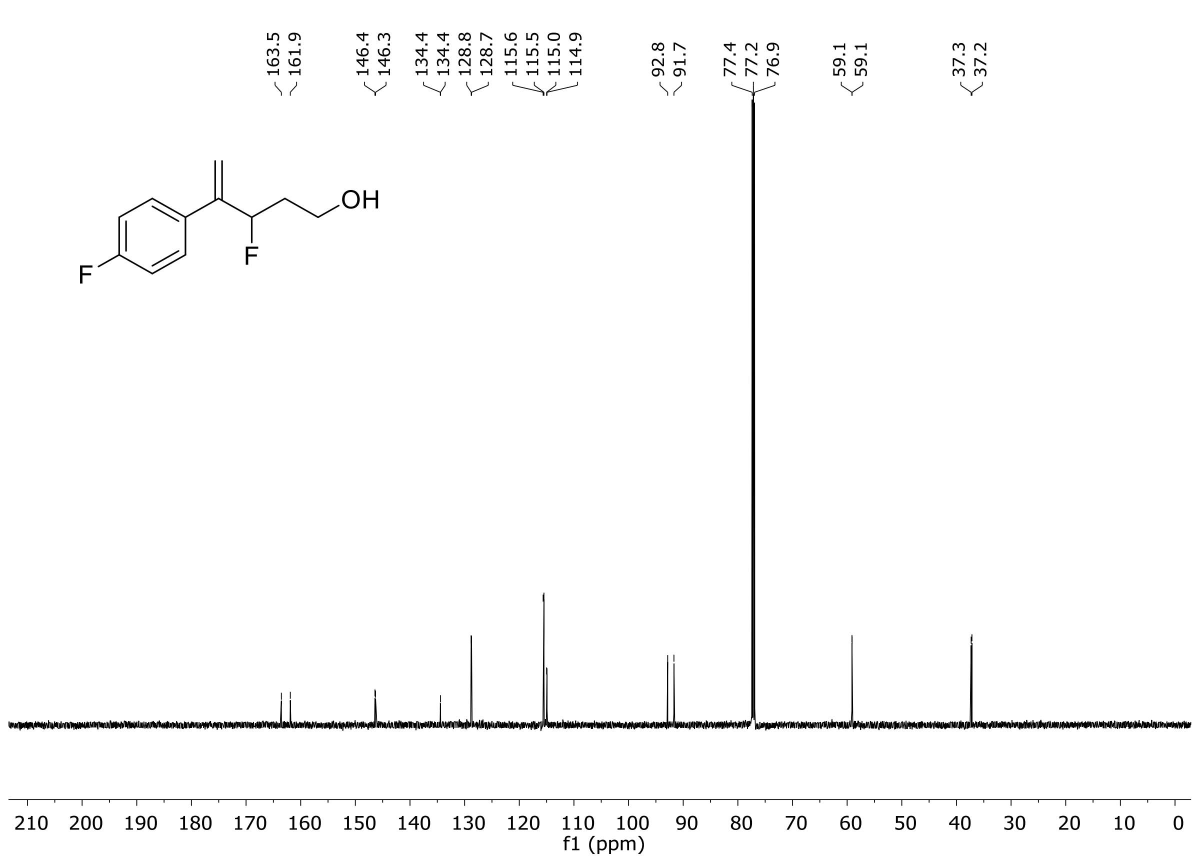
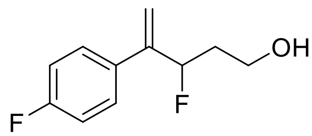
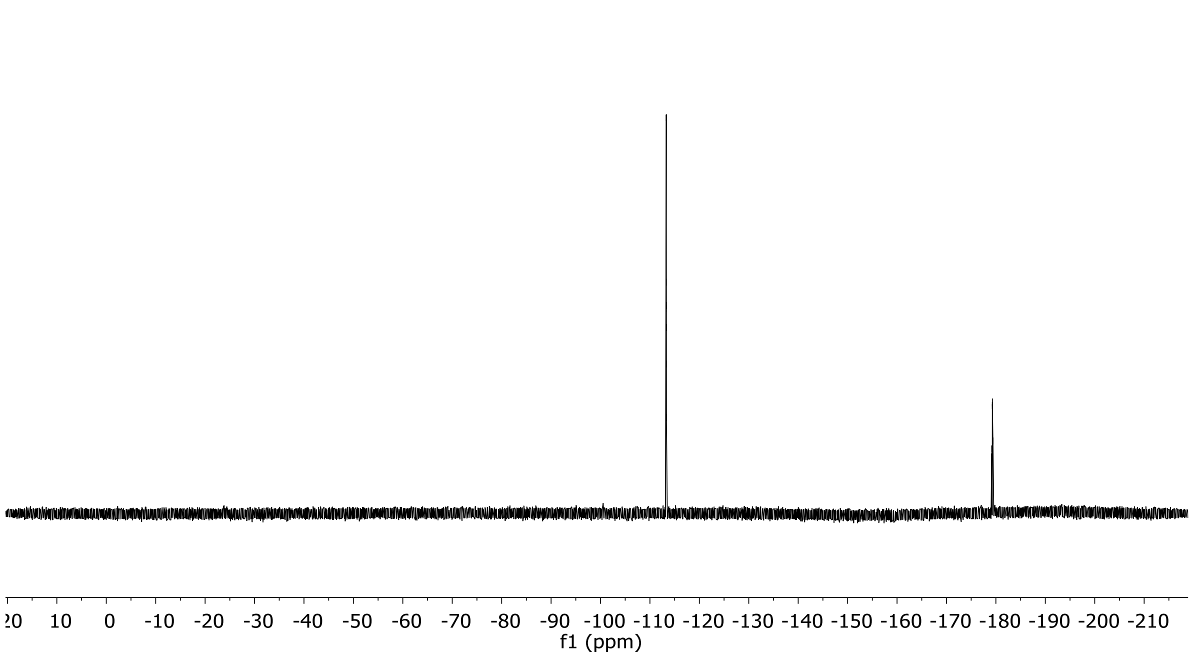
114.30
30.38
30.25
30.12
29.99
29.87
29.74
29.61
B(OH)2
NC
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.06 7.05 7.05 7.04 7.04 7.03 7.03 7.02 7.02 7.01 5.61 5.60 5.49 5.48 5.43 5.42 5.39 5.39 3.85 3.83 3.82 3.82 3.81 3.80 3.79 3.78 3.76 3.75 1.98 1.97 1.96 1.96 1.96 1.95 1.95 1.94 1.94 1.94 1.93 1.92 1.90 1.89 1.89 1.89 1.57
OH
F
F
2.15
2.17
0.50
0.52
1.03
1.07
2.04
2.02
1.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.5 161.9 146.4 146.3 134.4 134.4 128.8 128.7 115.6 115.5 115.0 114.9 92.8 91.7 77.4 77.2 76.9 59.1 59.1 37.3 37.2
OH
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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-113.33
-113.35
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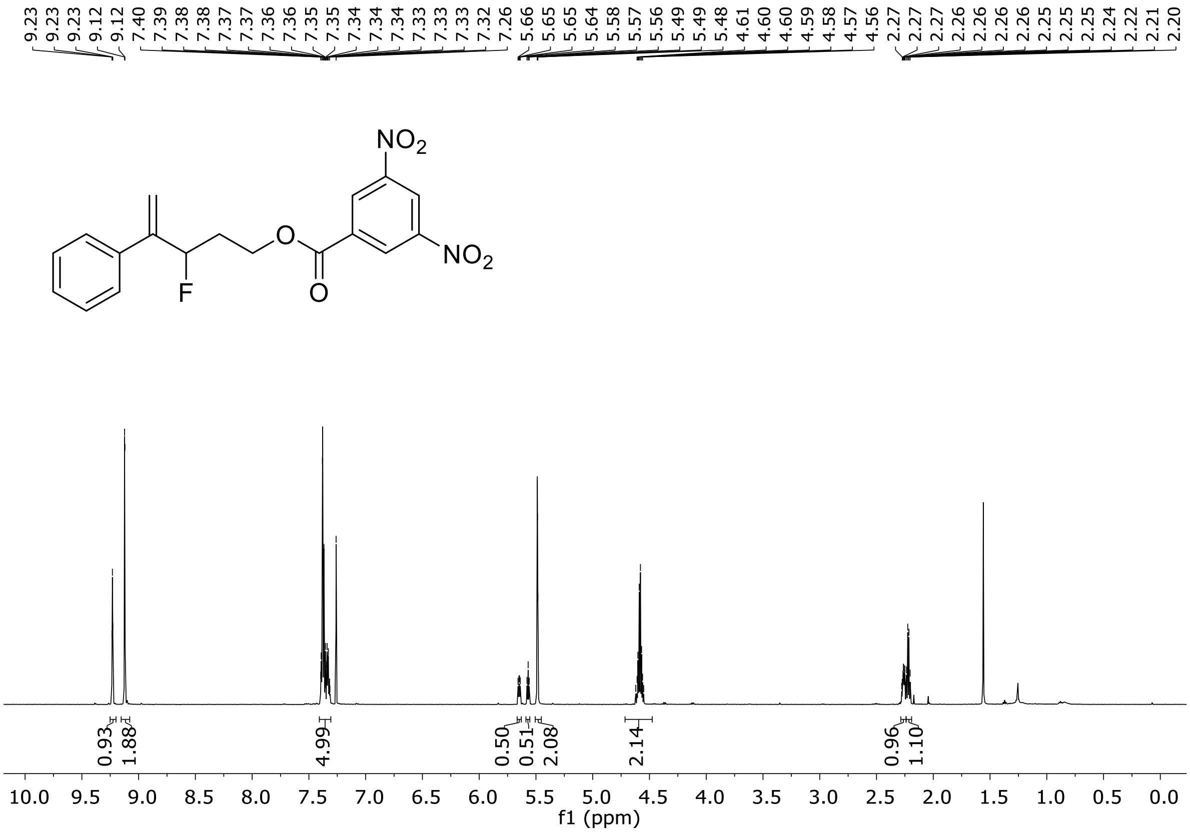
-179.24
-179.28
-179.29
-179.34
-179.36
-179.42
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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9.23
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7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.33
7.32
7.26
5.66
5.65
5.65
5.64
5.58
5.57
5.56
5.49
5.49
5.48
4.61
4.60
4.60
4.59
4.58
4.57
4.56
2.27
2.27
2.27
2.26
2.26
2.26
2.25
2.25
2.25
2.24
2.22
2.21
2.20
NO2
NO2
O
O
F
0.93
1.88
4.99
0.50
0.51
2.08
2.14
0.96
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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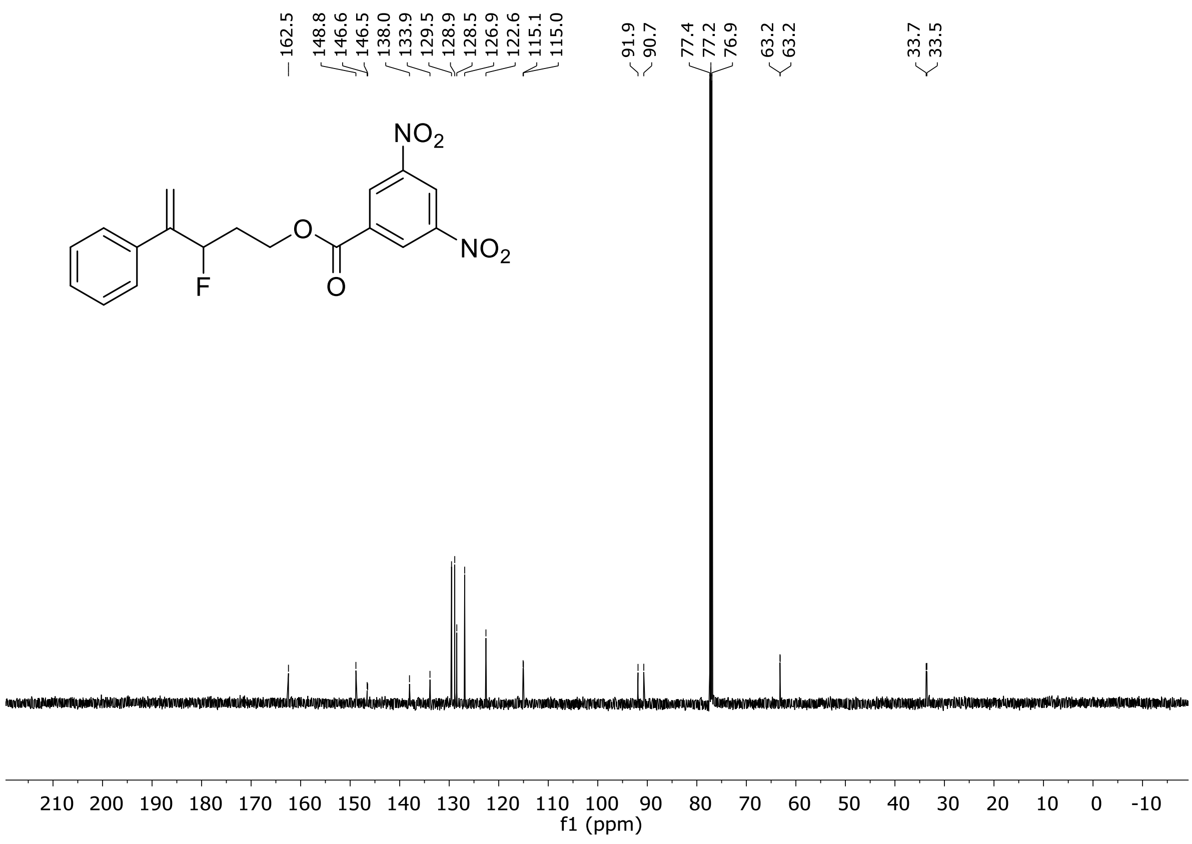
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128.9
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122.6
115.1
115.0
91.9
90.7
77.4
77.2
76.9
63.2
63.2
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33.5
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NO2
O
O
F
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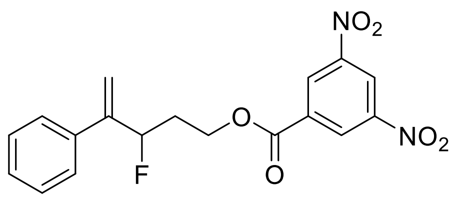
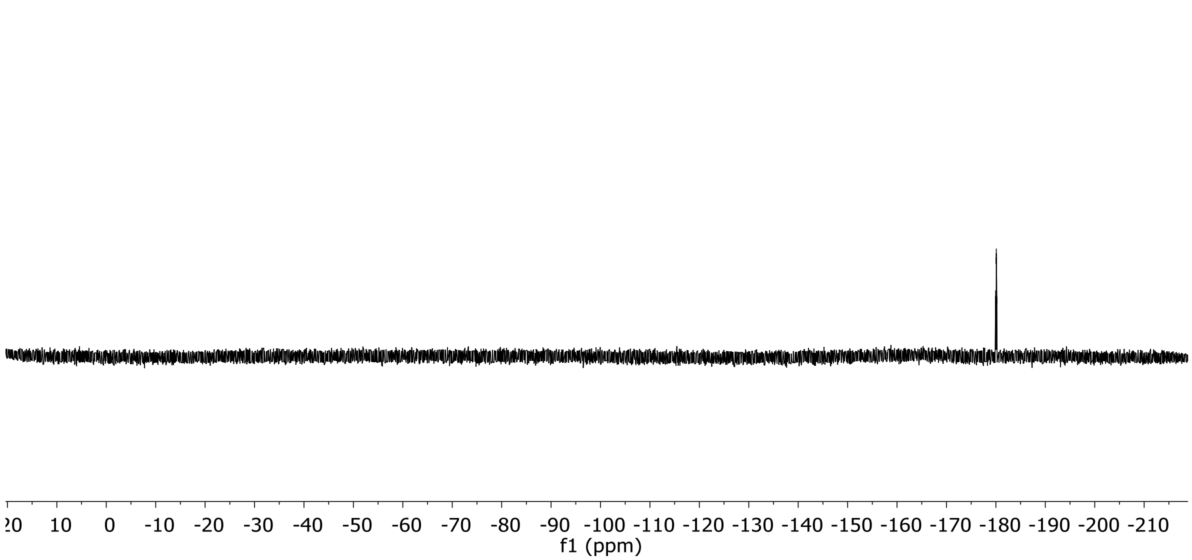
f1 (ppm)

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-180.15
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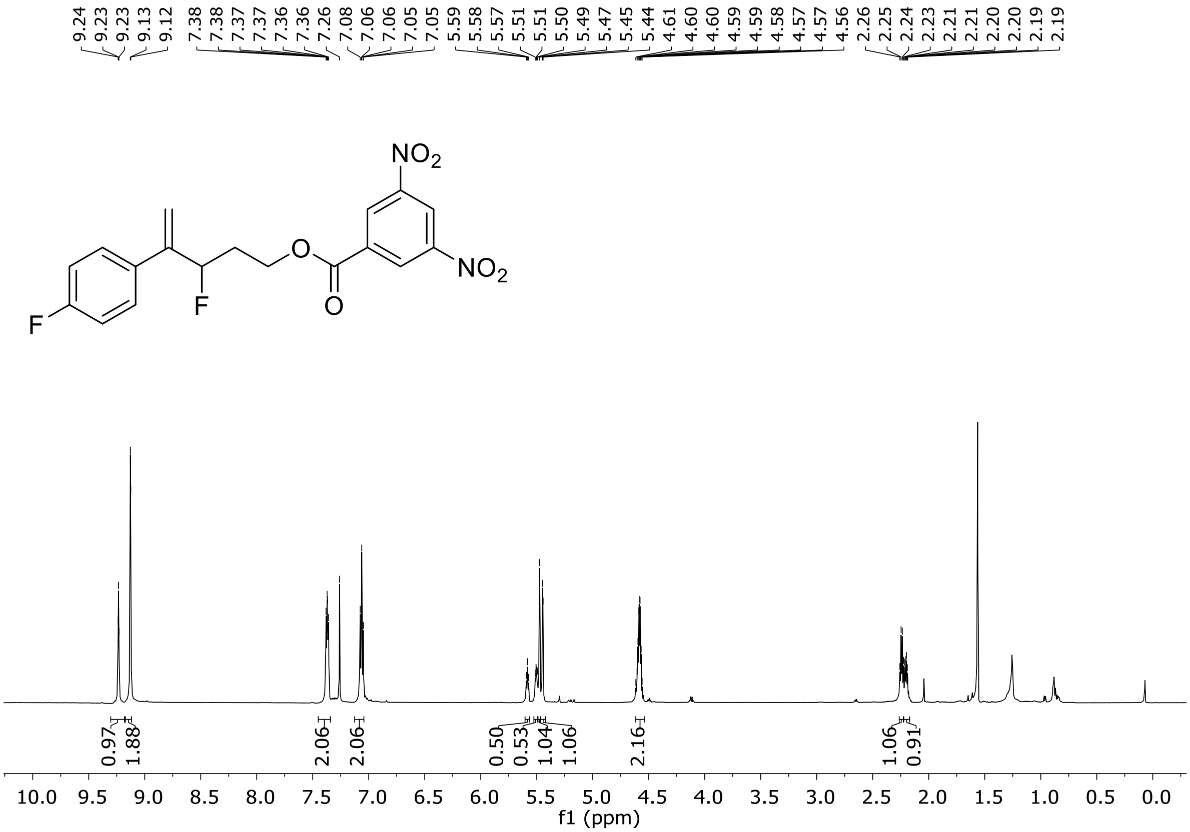
f1 (ppm)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NO2
NO2
O
O
F
F
0.97 1.88 2.06 2.06 0.50 0.53 1.04 1.06 2.16 1.06 0.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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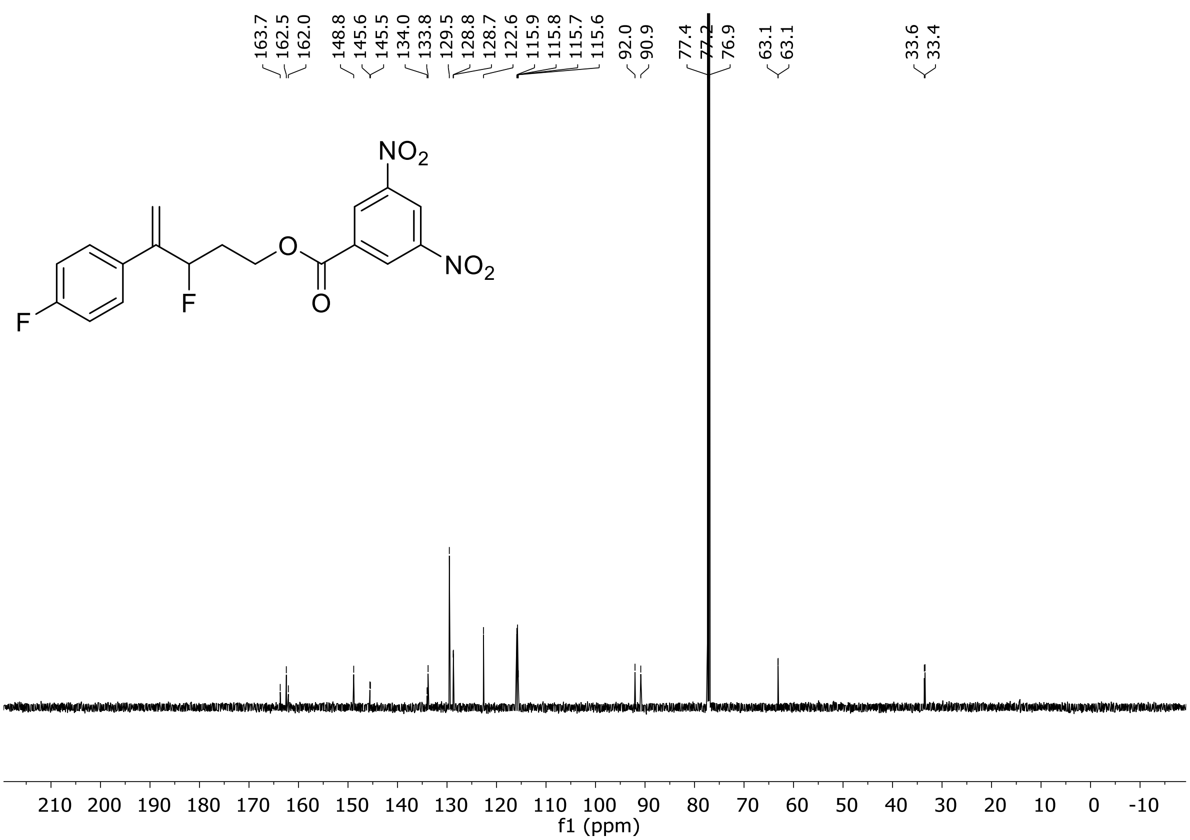
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NO2
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O
F
F
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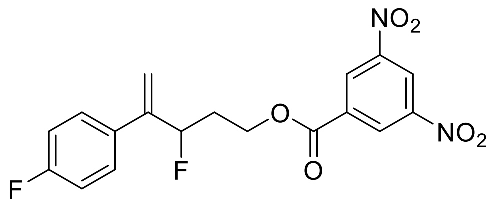
f1 (ppm)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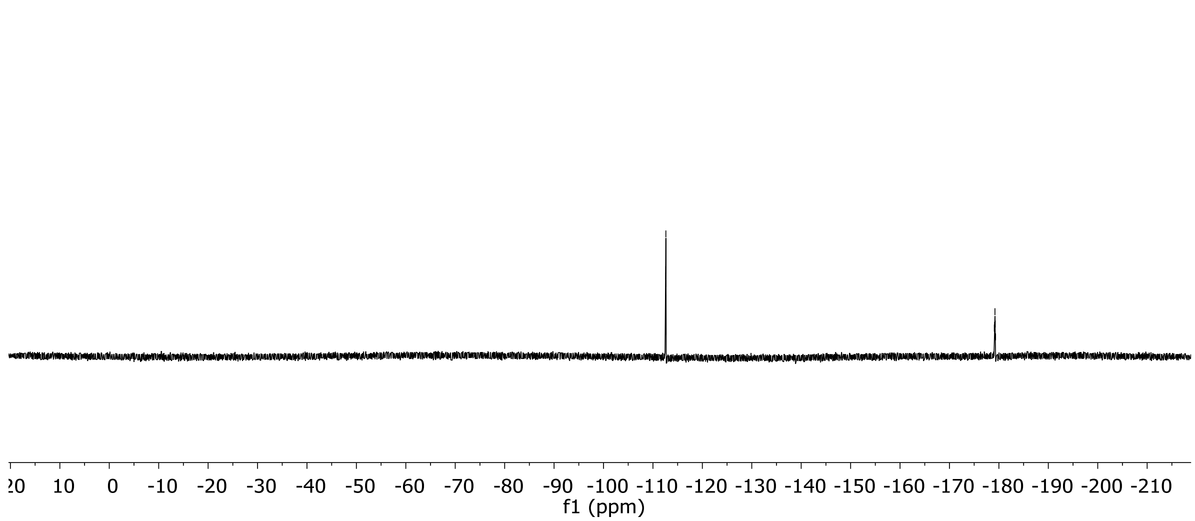
F
O
O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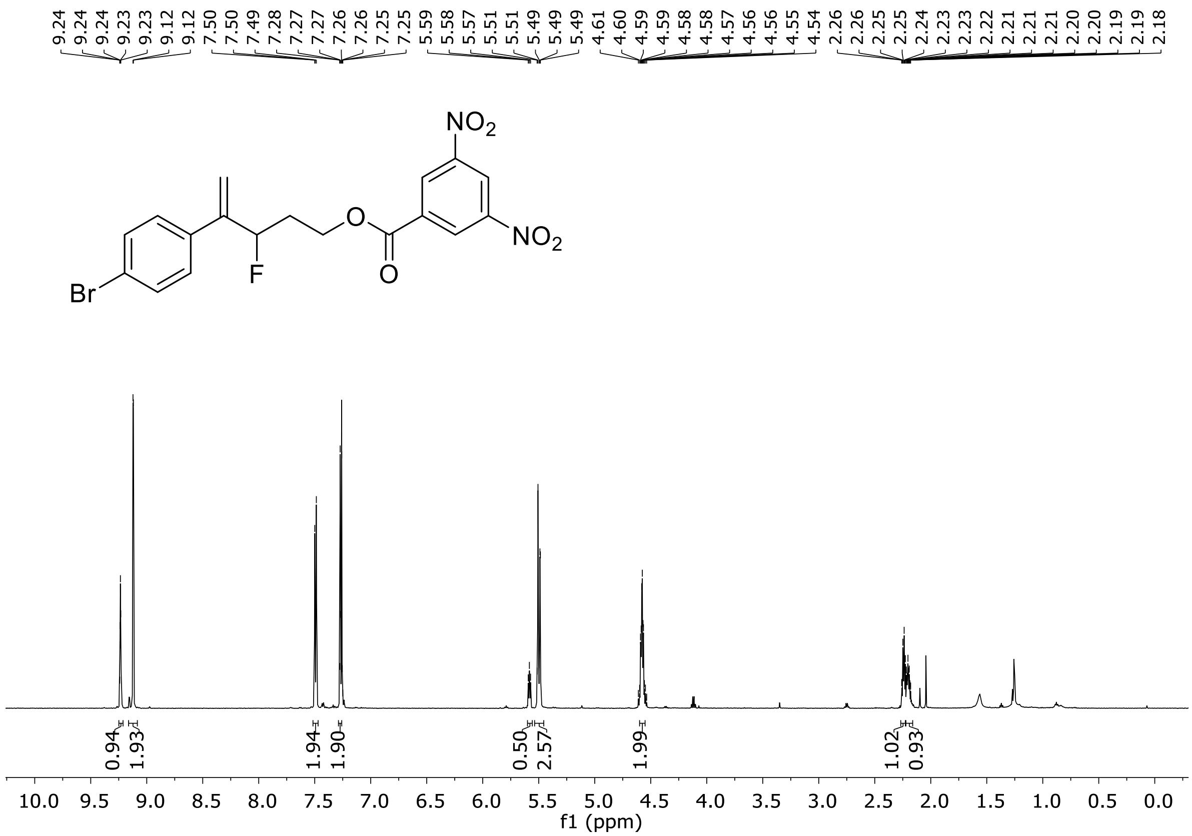
f1 (ppm)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NO2
NO2
O
O
Br
F
0.94
1.93
1.94
1.90
0.50
2.57
1.99
1.02
0.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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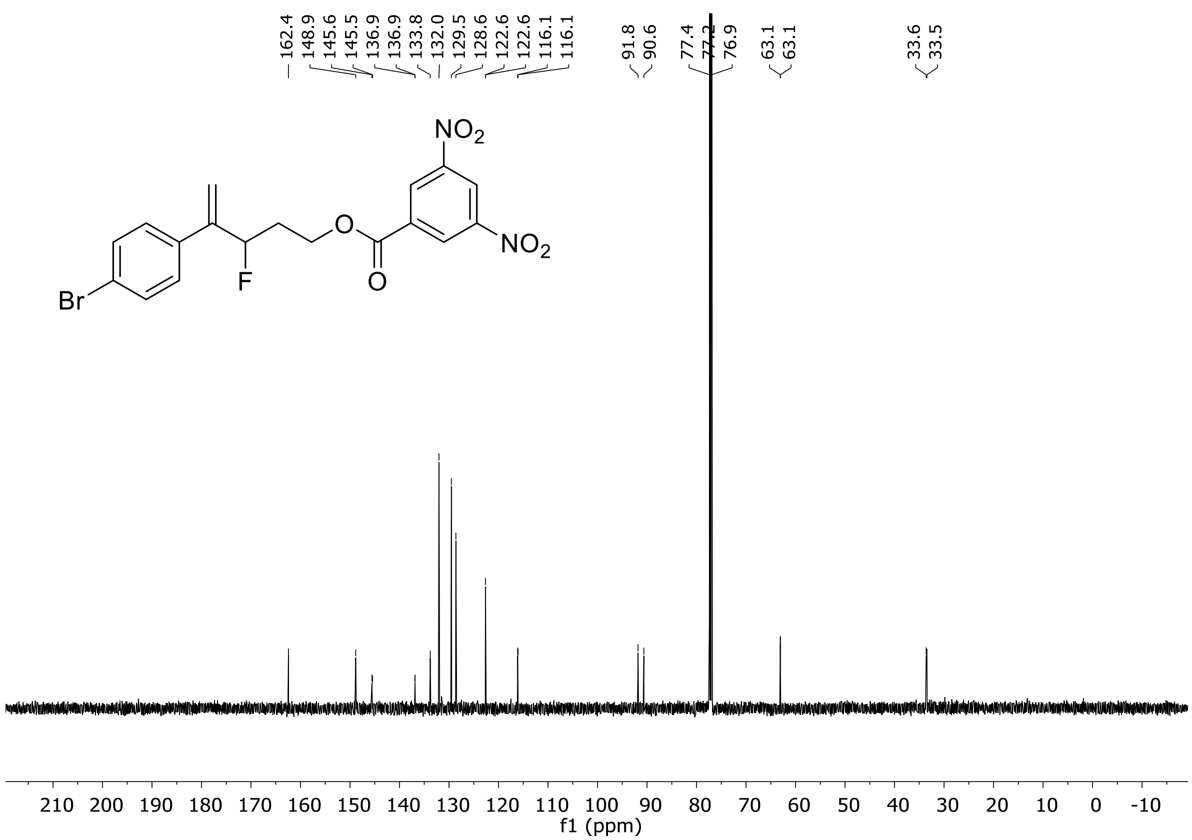
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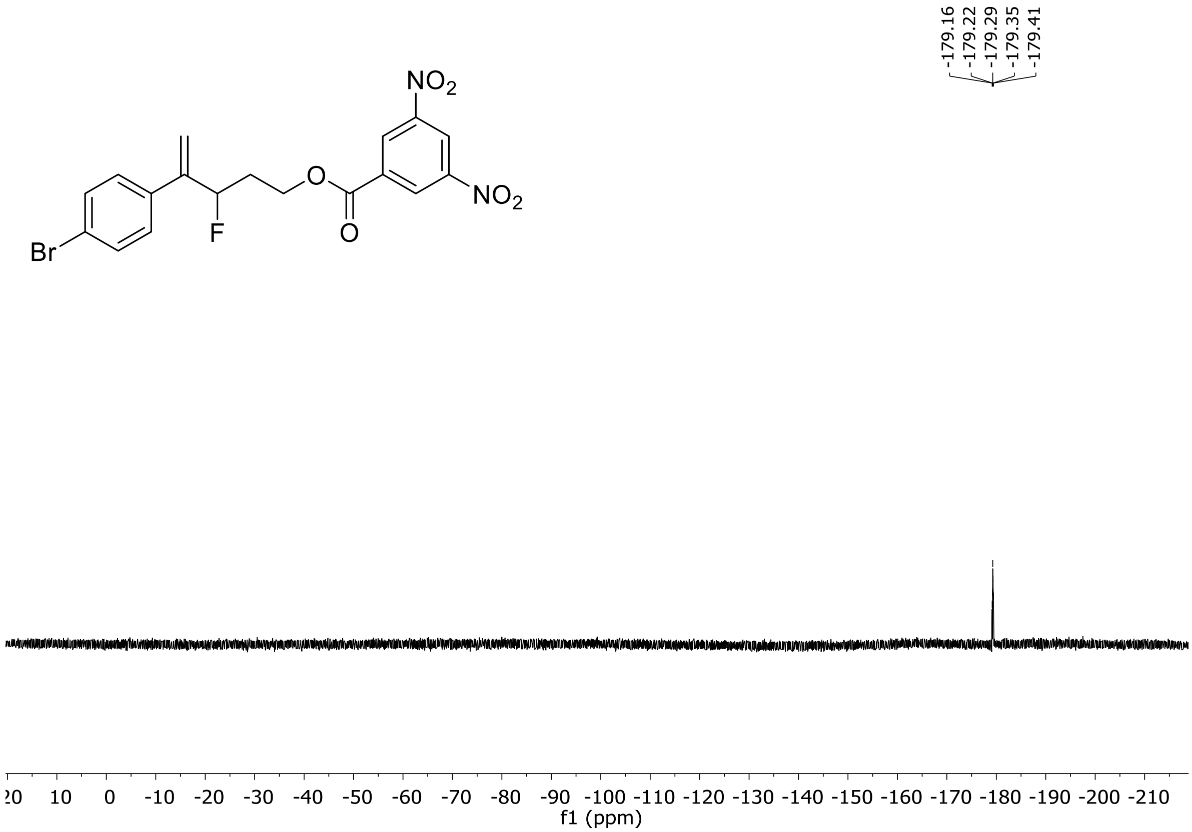
NO2
O
O
Br
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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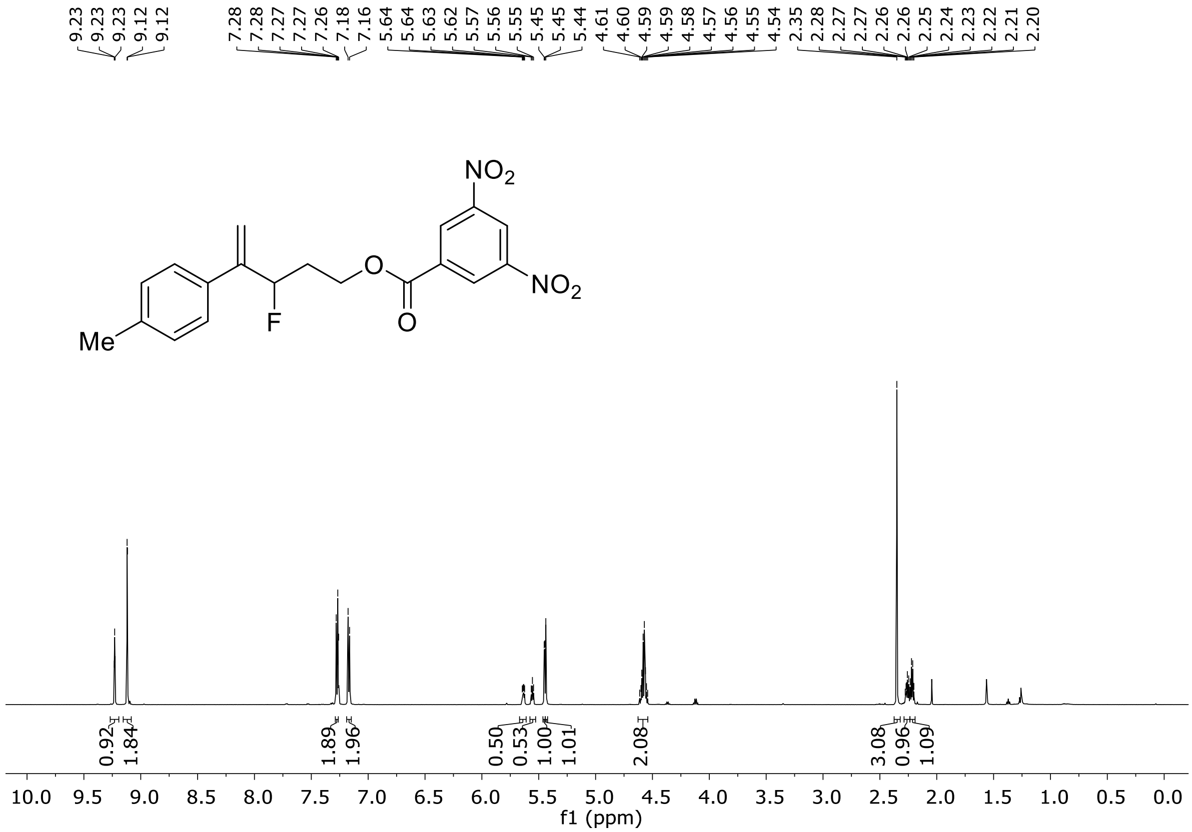
f1 (ppm)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7.26
7.18
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5.64
5.63
5.62
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2.27
2.26
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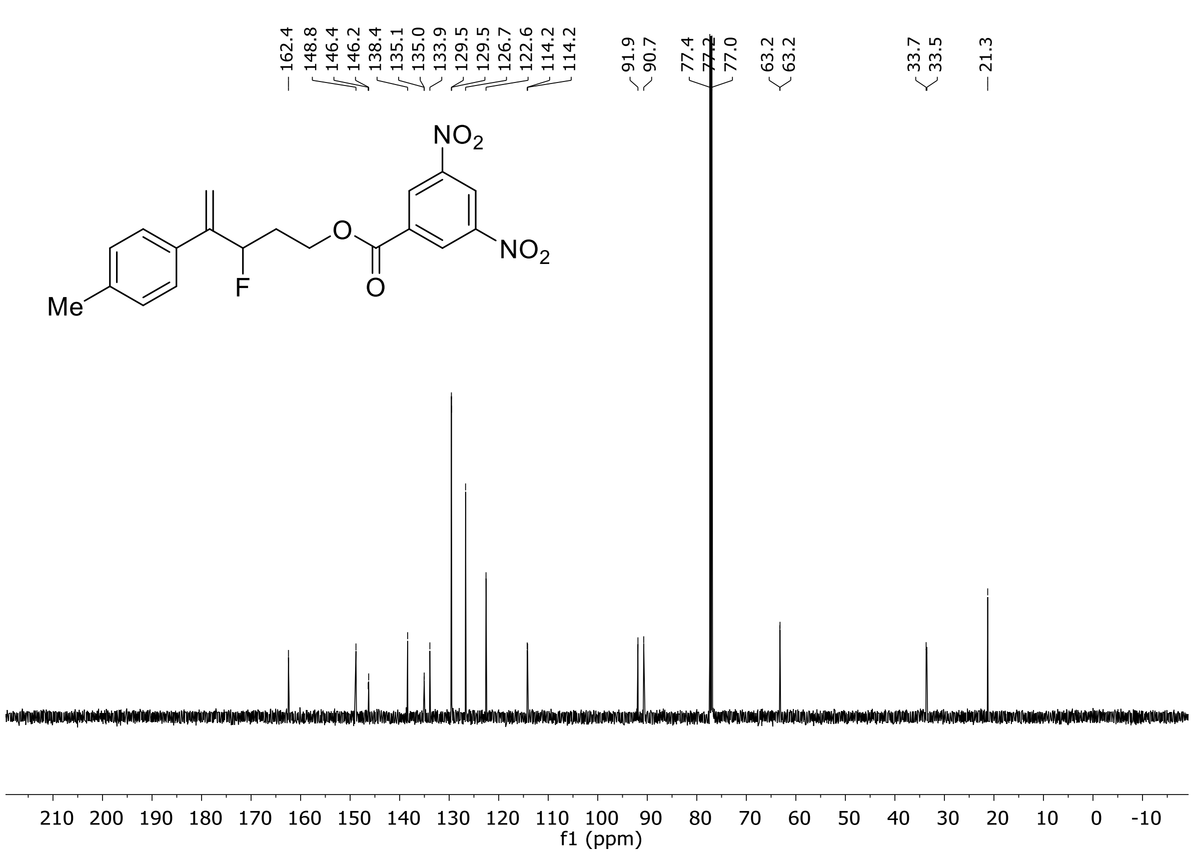
2.25
2.24
2.23
2.22
2.21
2.20
NO2
NO2
O
O
F
Me
0.92
1.84
1.89
1.96
0.50
0.53
1.00
1.01
2.08
3.08
0.96
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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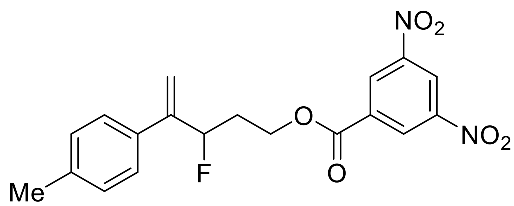
135.0
133.9
129.5
129.5
126.7
122.6
114.2
114.2
91.9
90.7
77.4
77.2
77.0
63.2
63.2
33.7
33.5
21.3
NO2
NO2
O
O
F
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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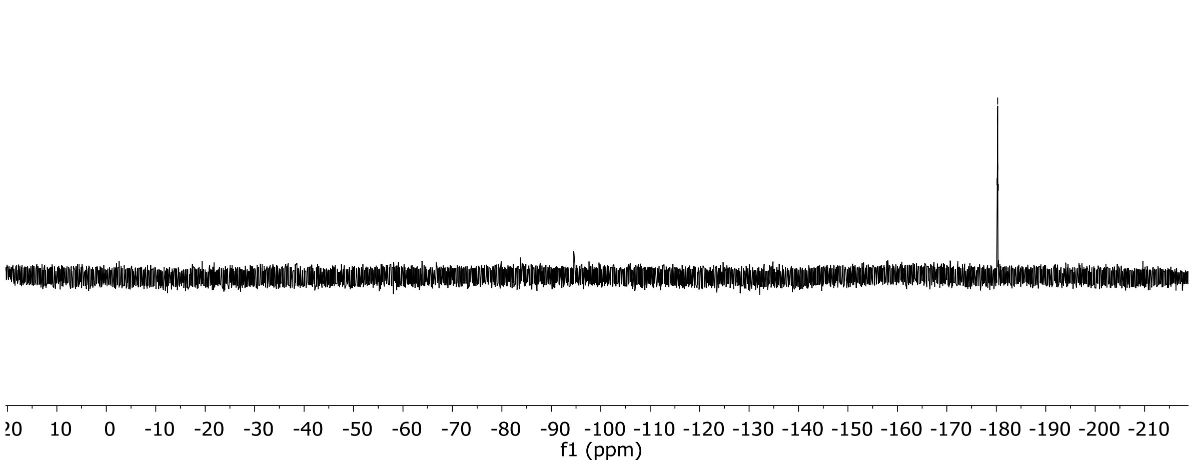
NO2
O
O
F
Me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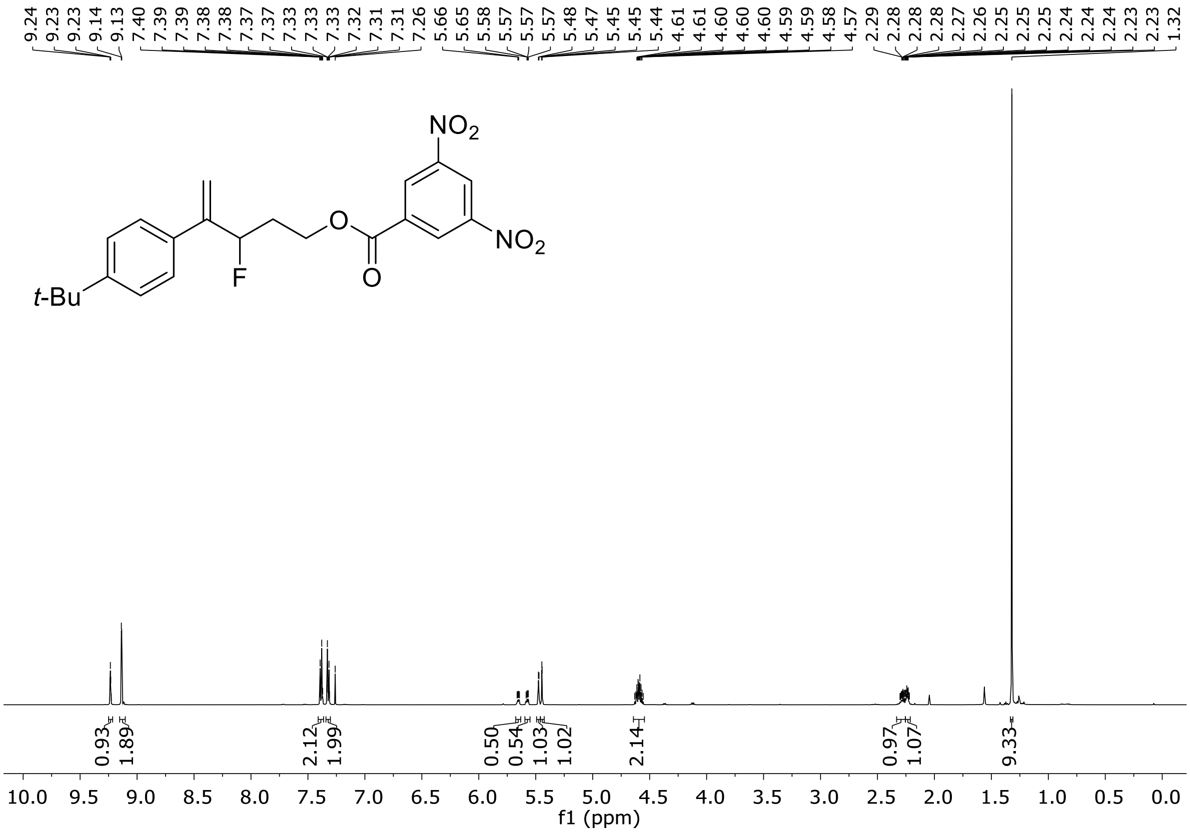
f1 (ppm)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2.25
2.25
2.24
2.24
2.24
2.23
2.23
1.32
NO2
NO2
O
O
F
t-Bu
0.93
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0.54
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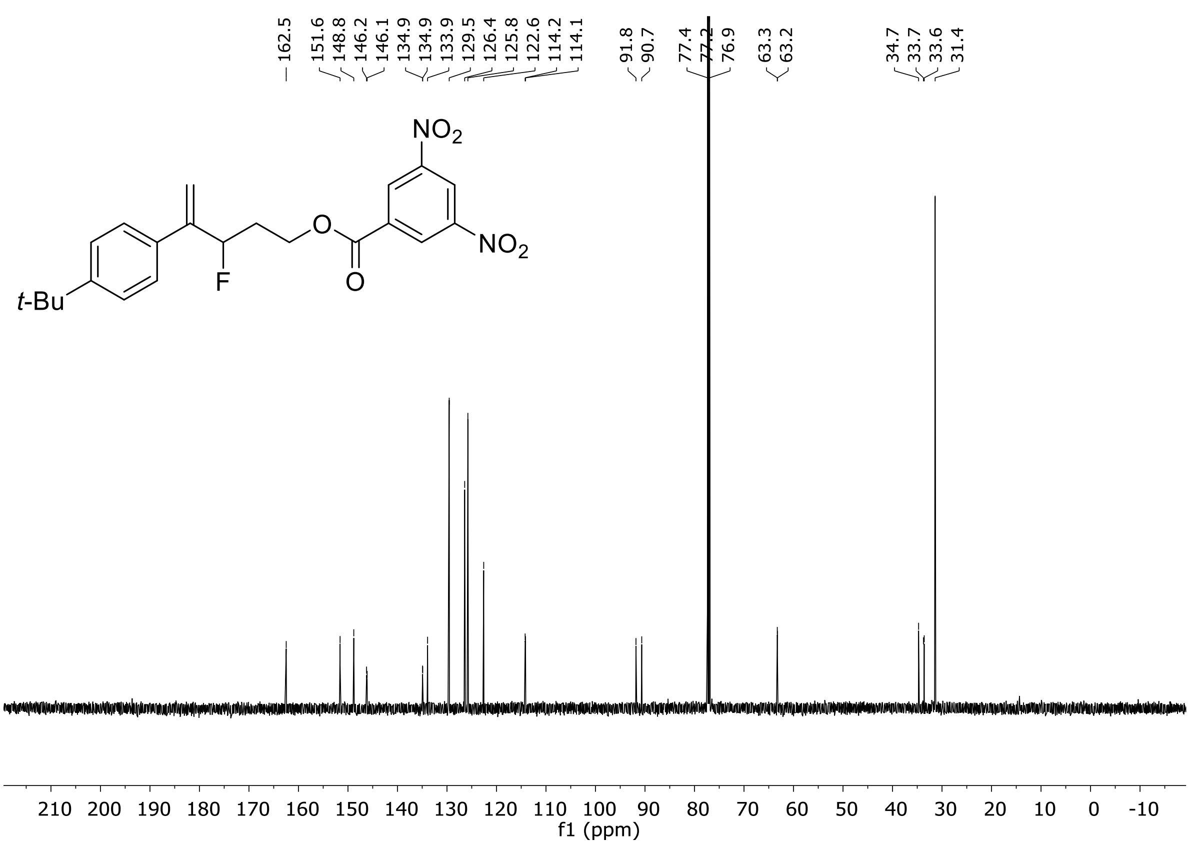
1.02
2.14
0.97
1.07
9.33
f1 (ppm)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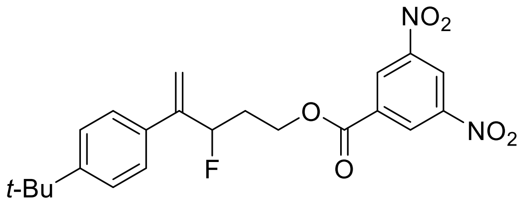
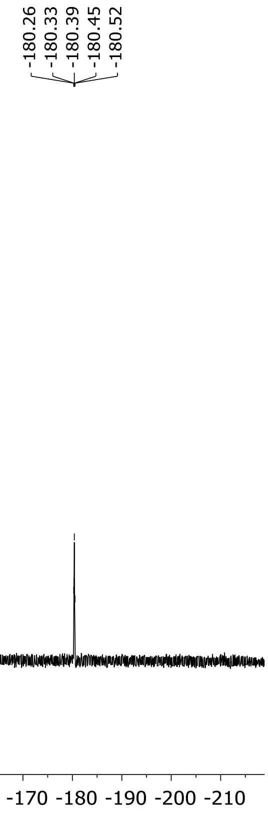
133.9
129.5
126.4
125.8
122.6
114.2
114.1
91.8
90.7
77.4
77.2
76.9
63.3
63.2
34.7
33.7
33.6
31.4
NO2
NO2
O
O
F
t-Bu
f1 (ppm)

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-180.45
-180.52
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-30
-40
-50
-60
-70
-80
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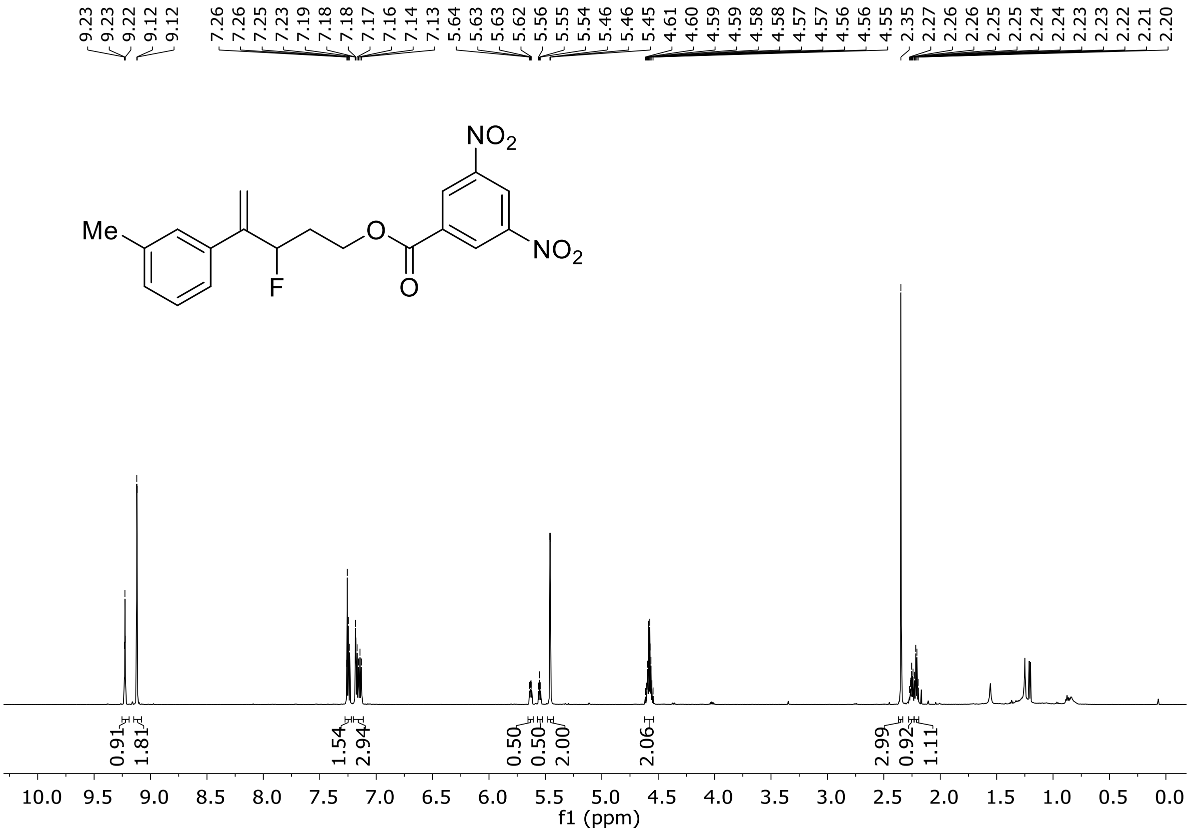
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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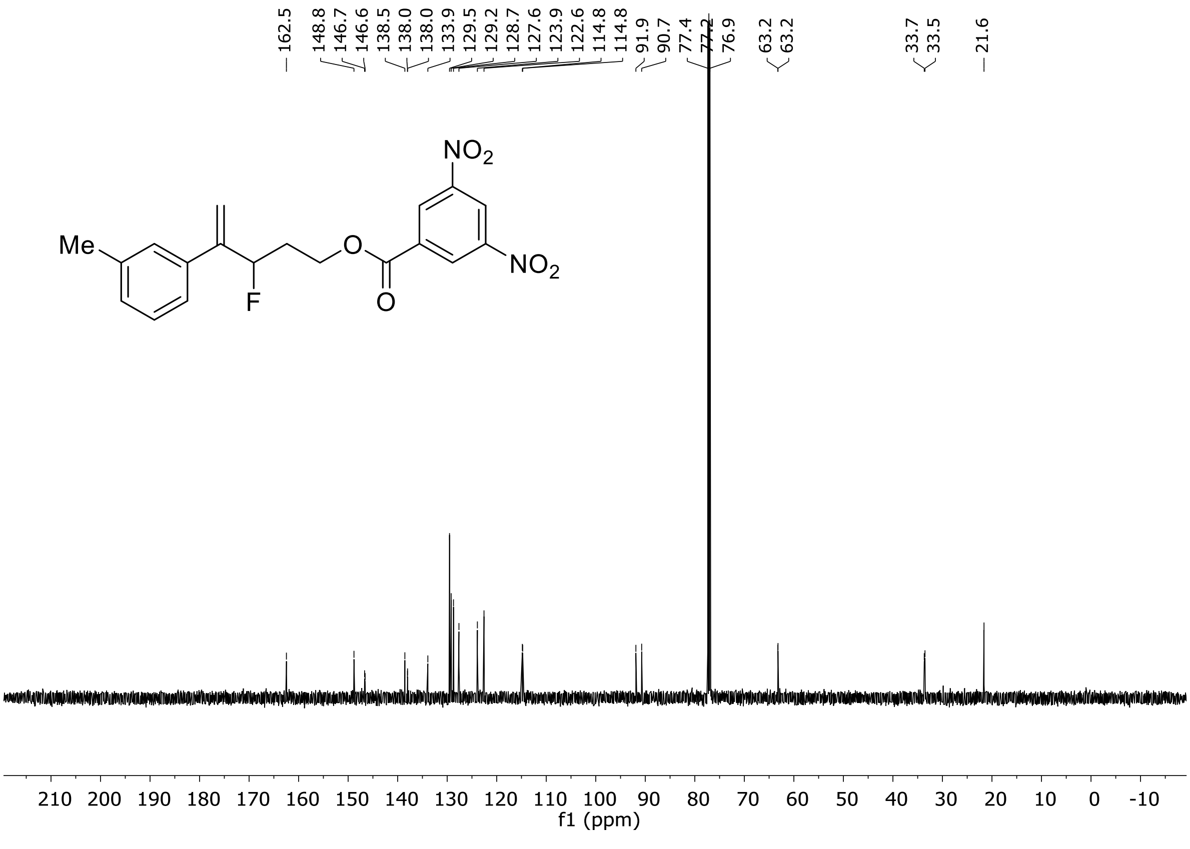
NO_2
Me
F
O
O
NO_2
0.91 1.81 1.54 2.94 0.50 0.50 2.00 2.06 2.99 0.92 1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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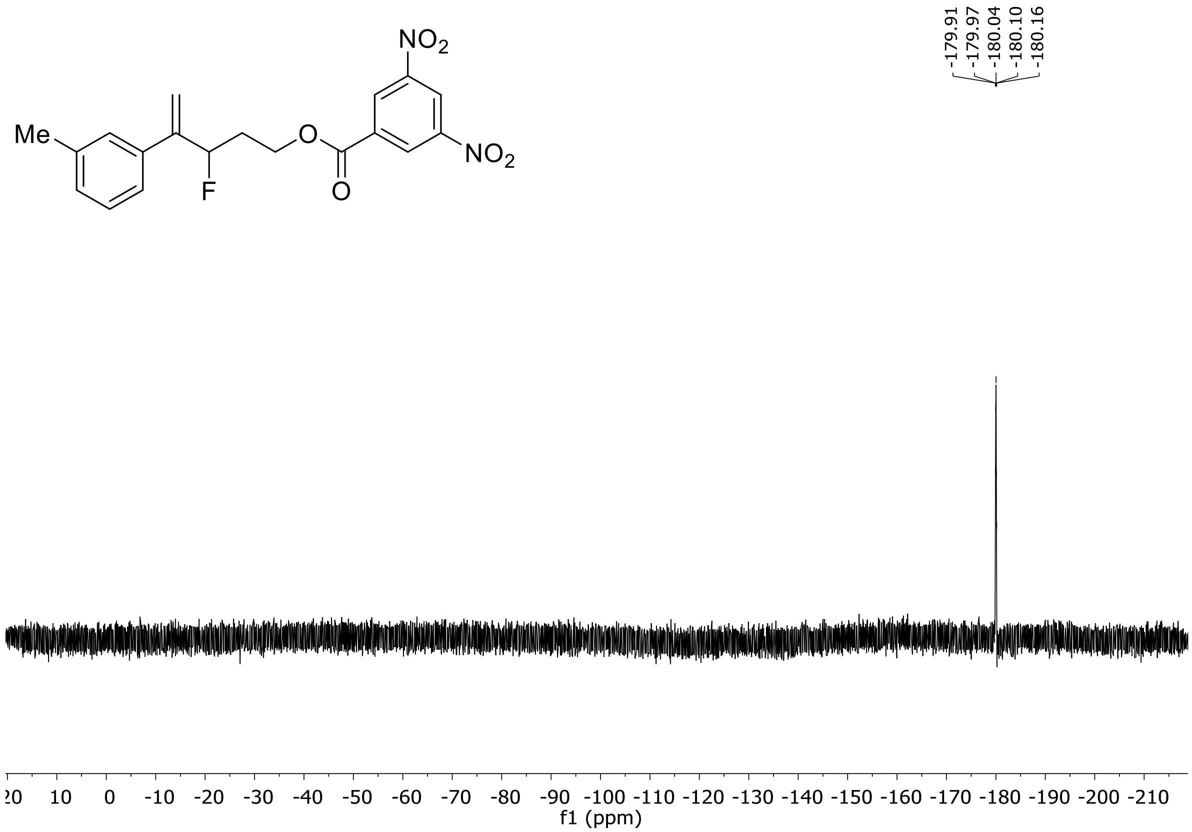
NO_2
Me
F
O
O
NO_2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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F
O
O
NO2
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-180.04
-180.10
-180.16
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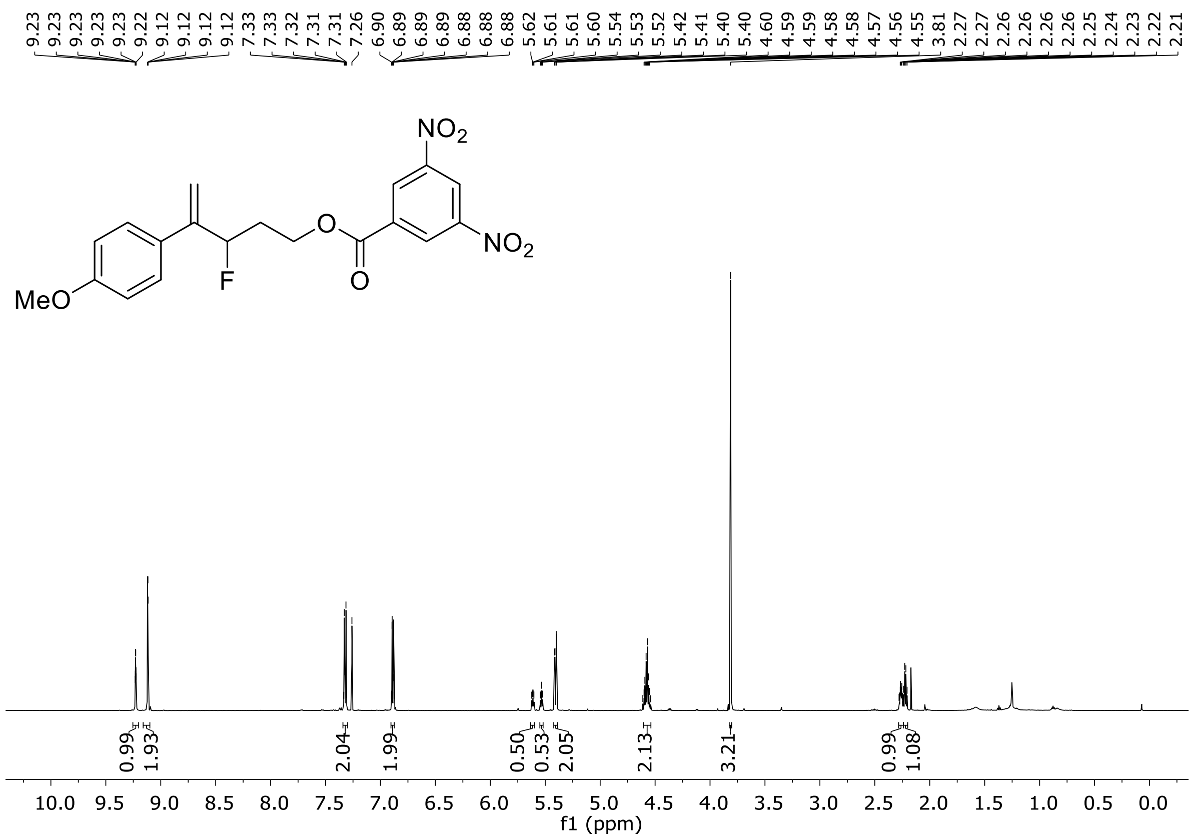
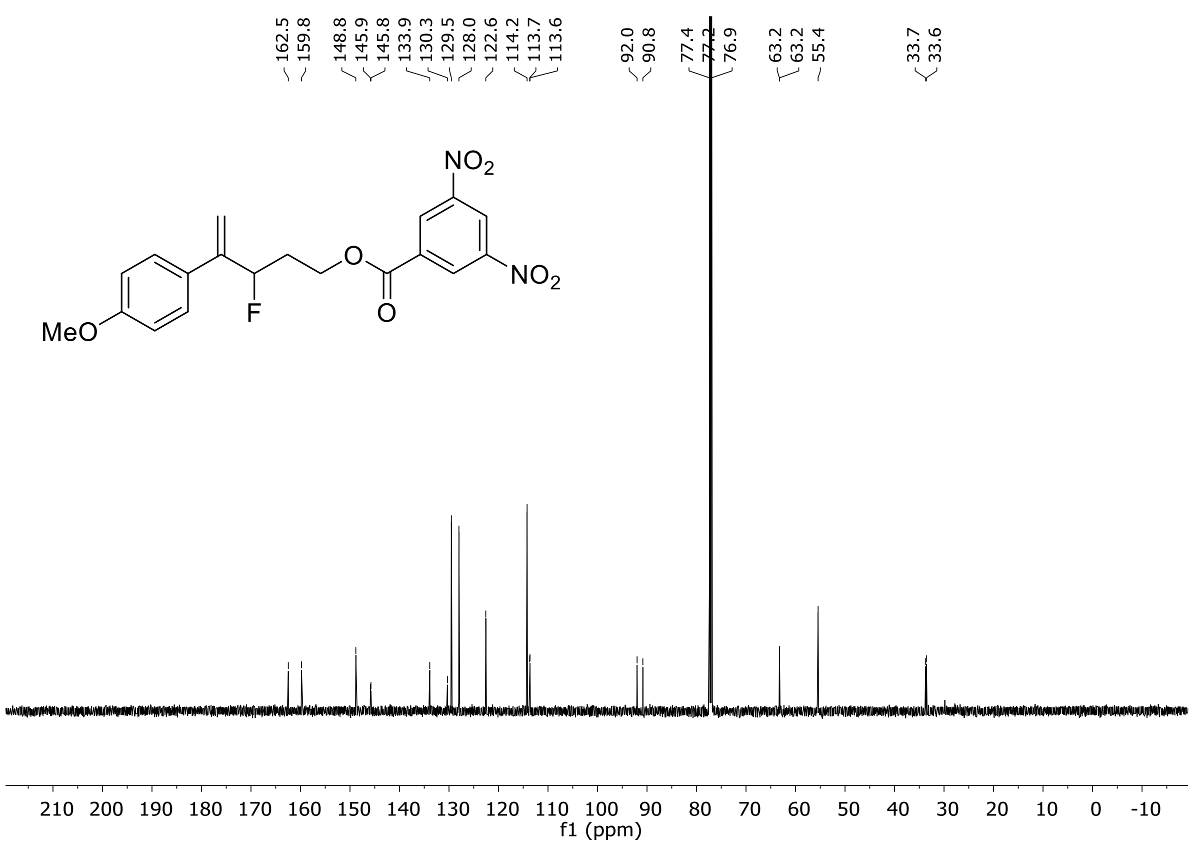
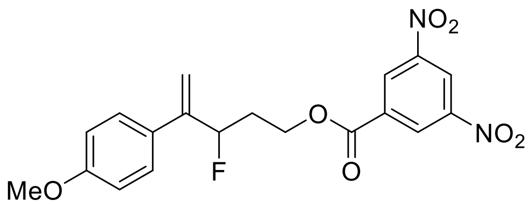
f1 (ppm)



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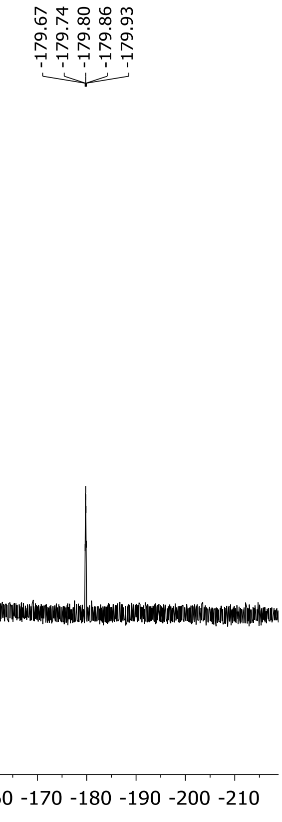
NO2
MeO
F
O
O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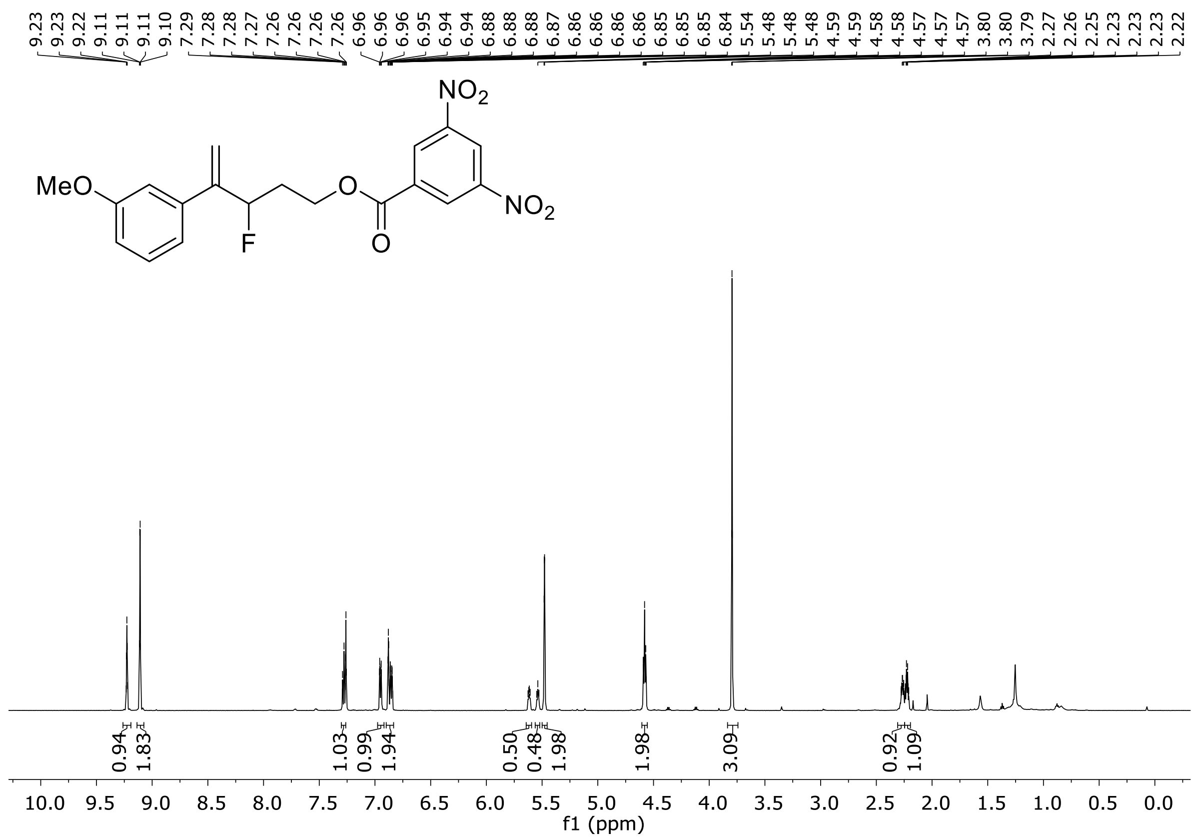
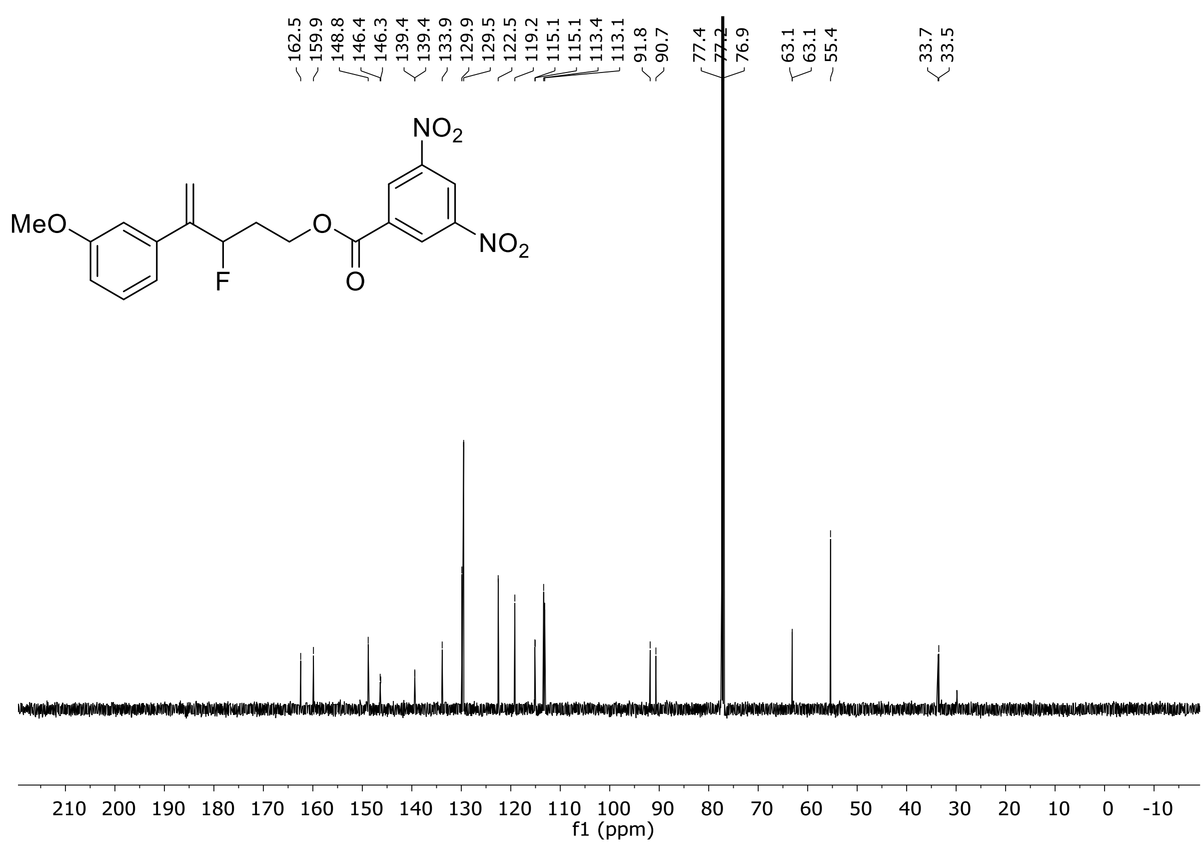
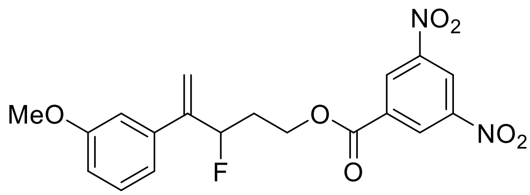
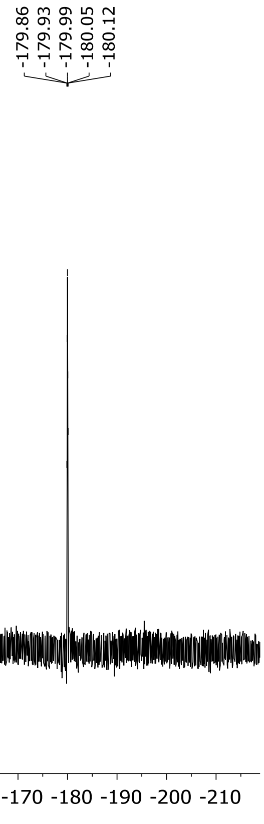
f1 (ppm)





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0
-10
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-40
-50
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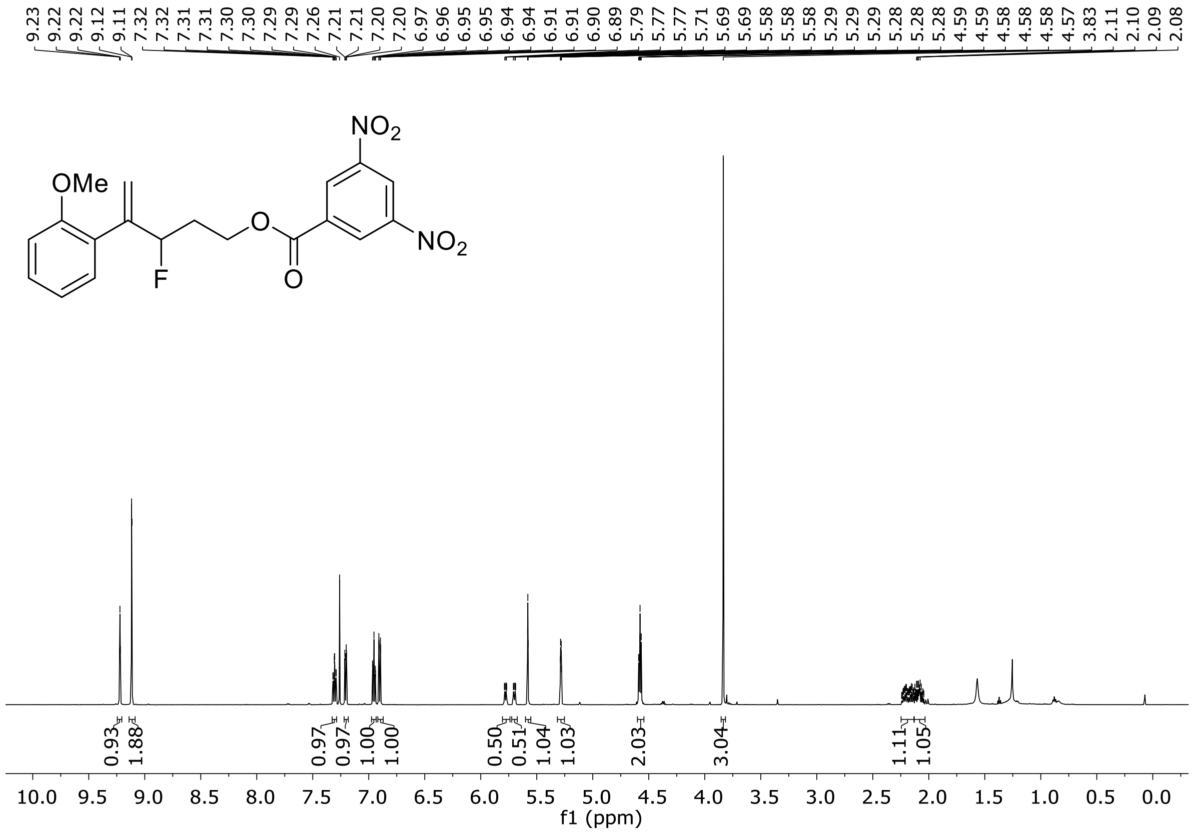
-200
-210
f1 (ppm)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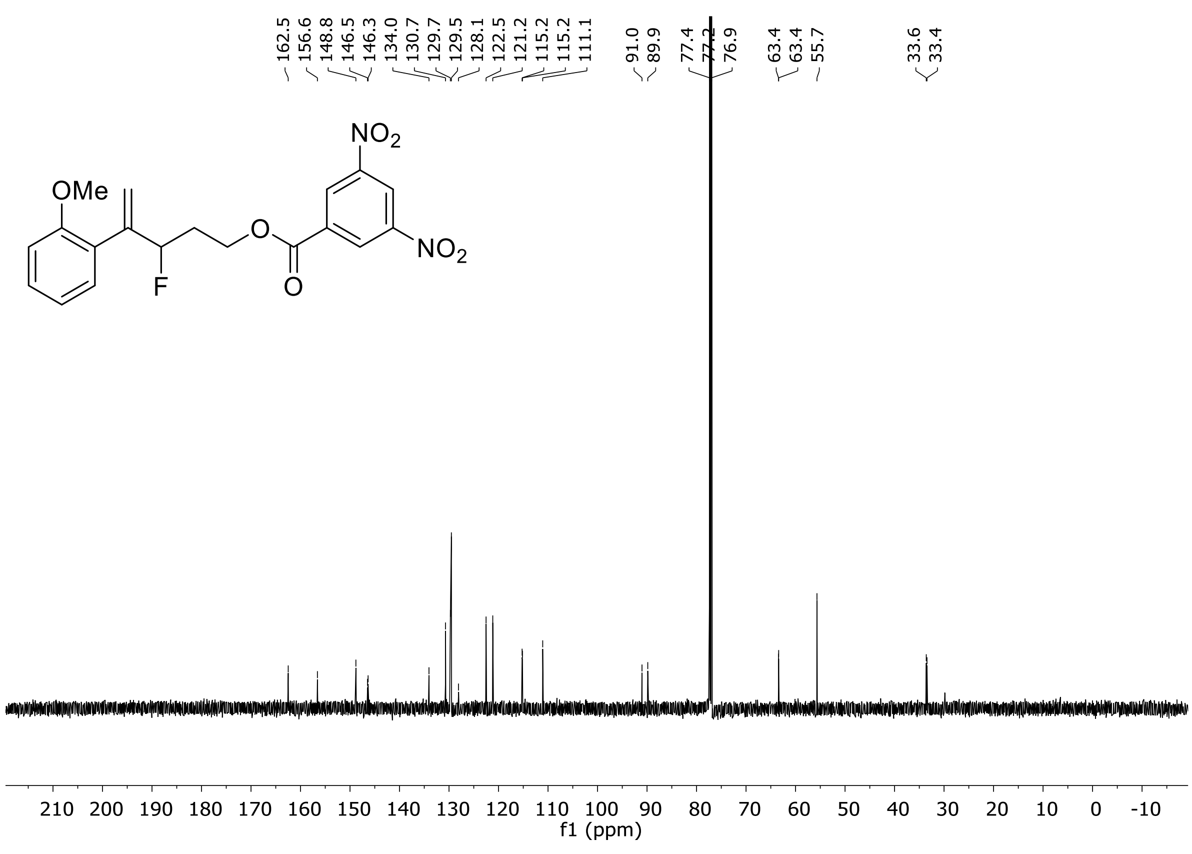
NO2
OMe
F
O
NO2
0.93
1.88
0.97
0.97
1.00
1.00
0.50
0.51
1.04
1.03
2.03
3.04
1.11
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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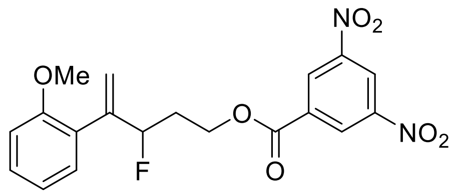
NO2
OMe
F
O
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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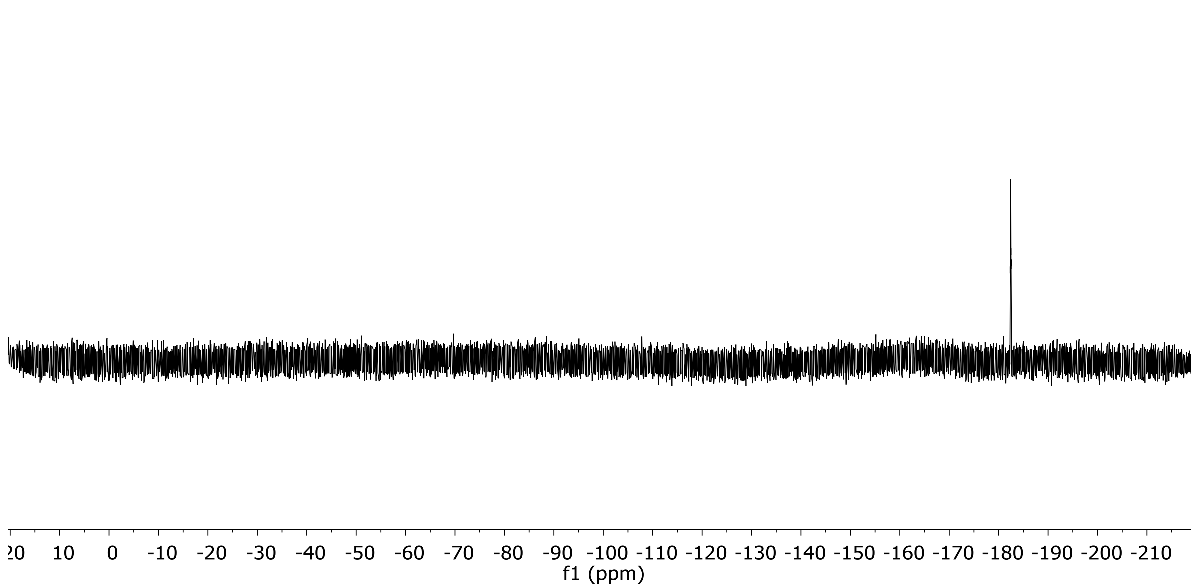
F
O
O
NO2
NO2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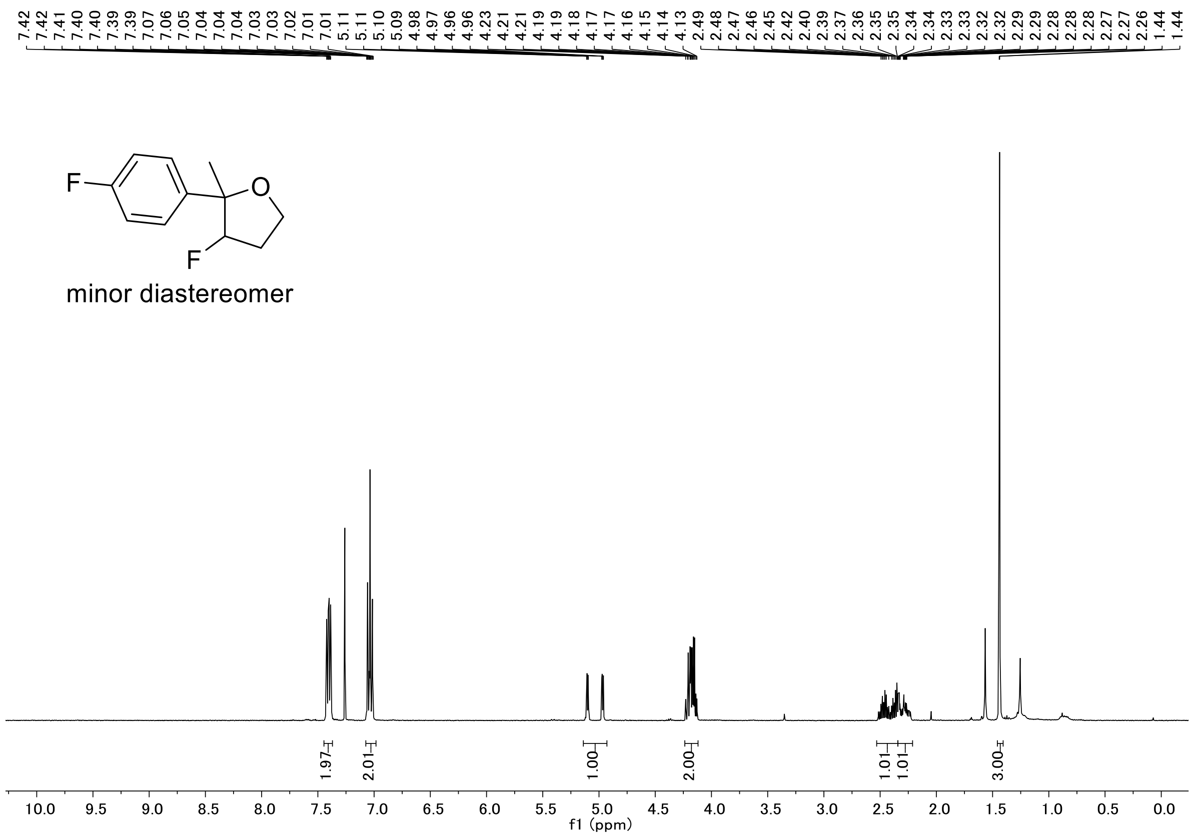
f1 (ppm)



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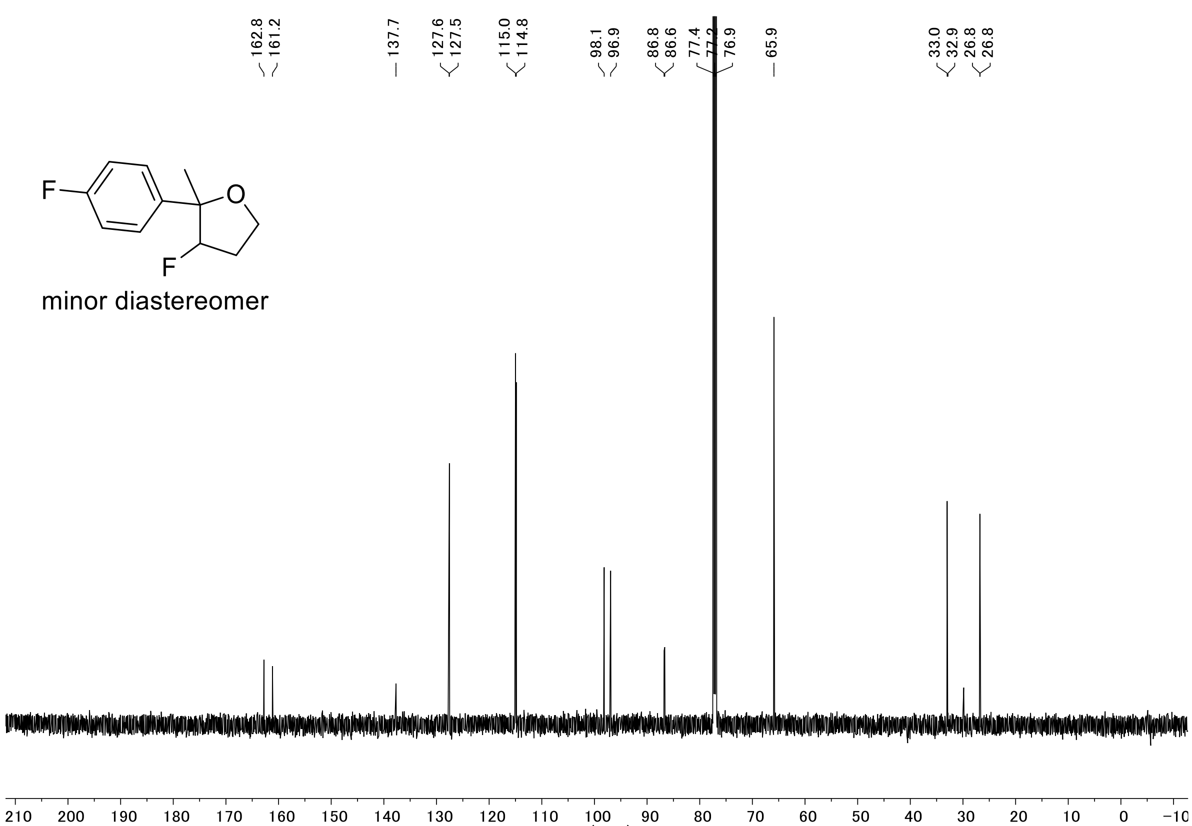
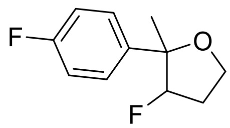
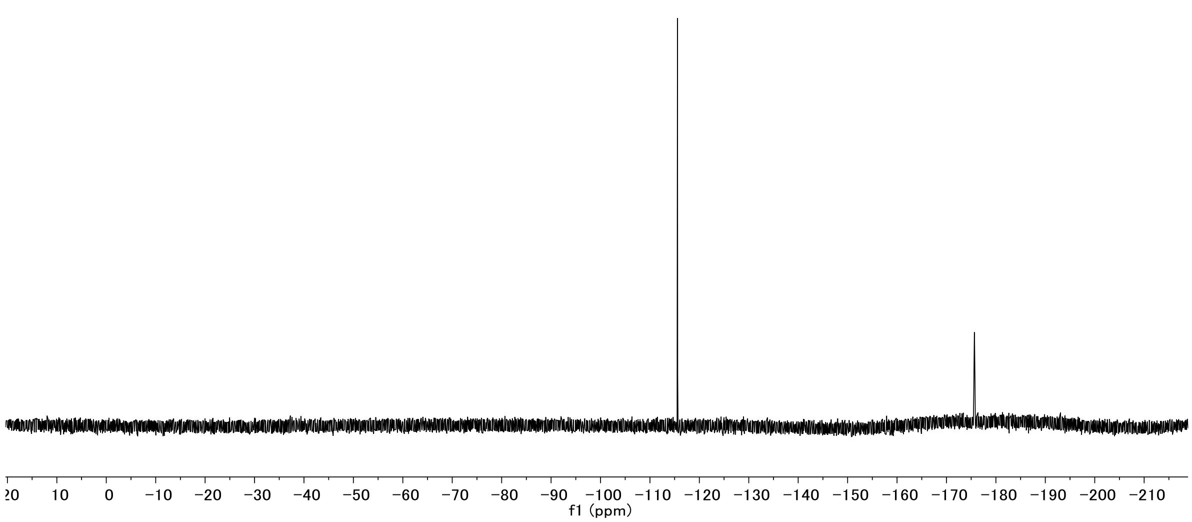
F
O
F
minor diastereomer
1.97
2.01
1.00
2.00
1.01
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

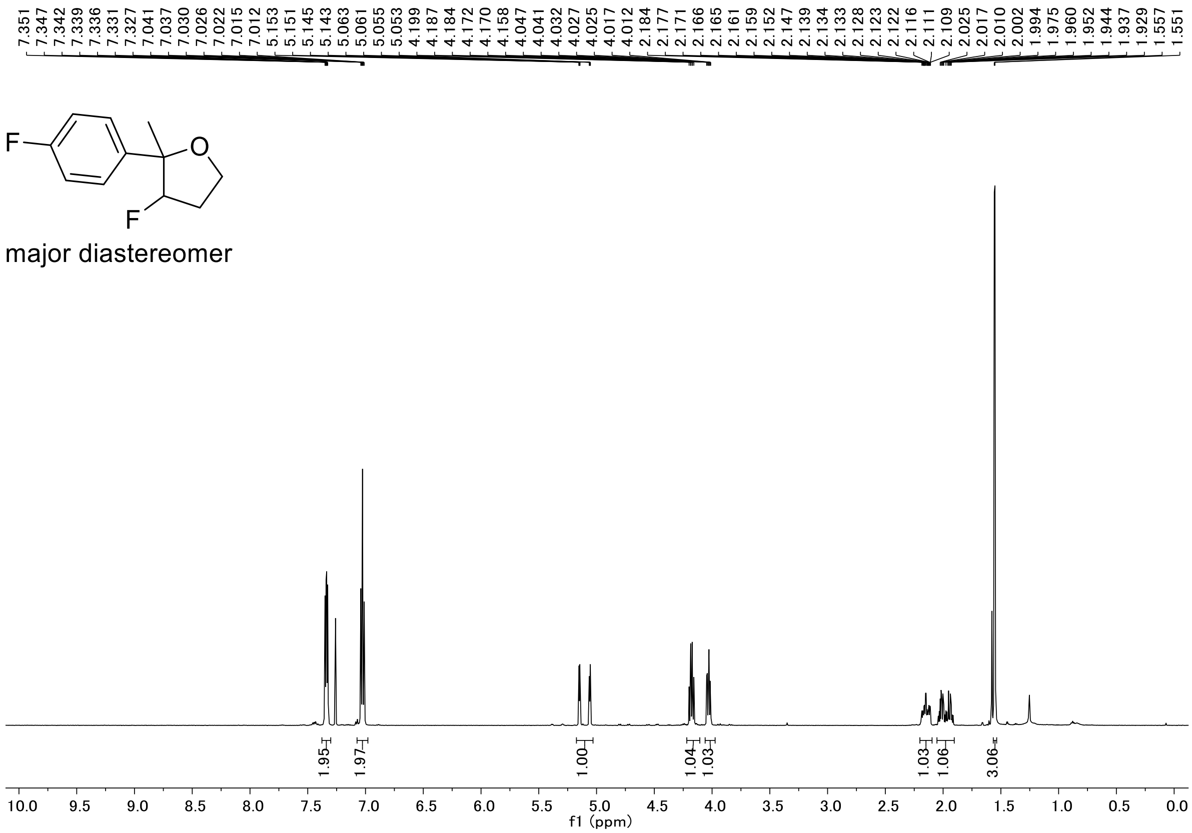


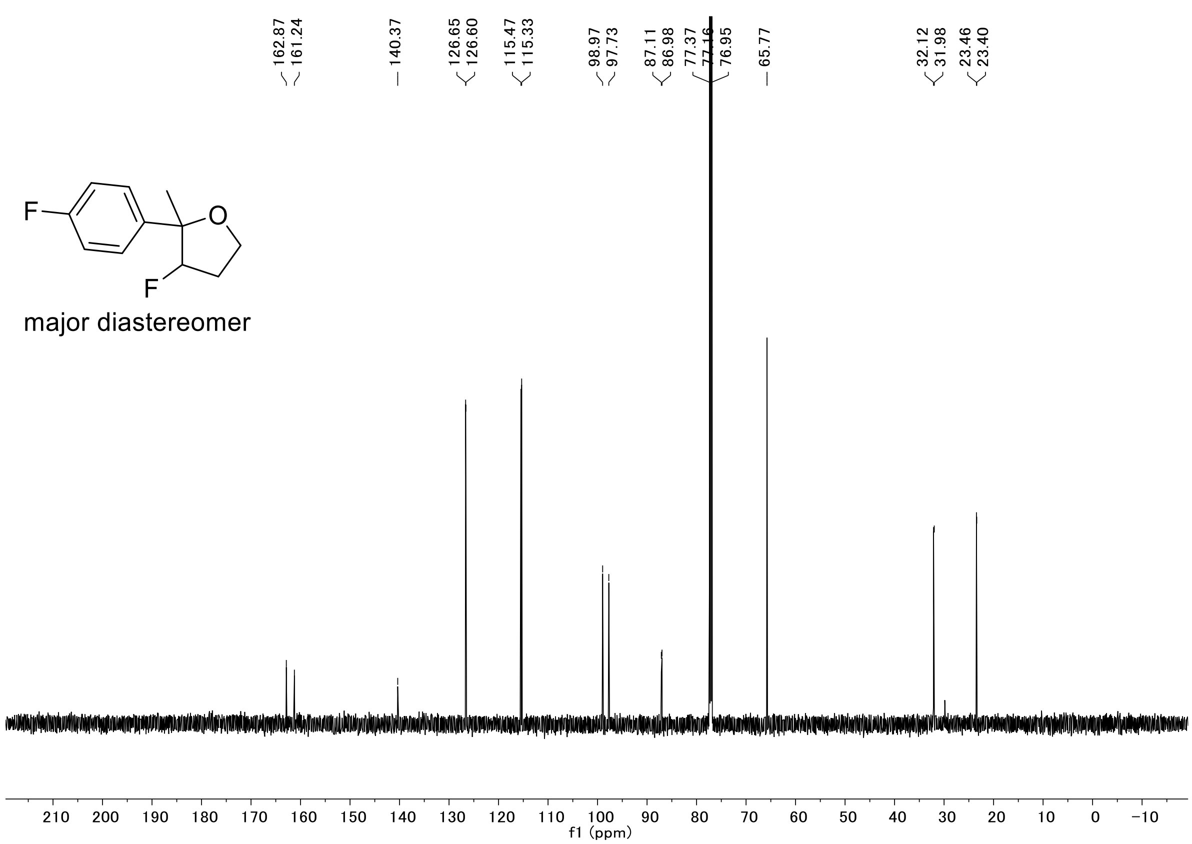
162.8 161.2 137.7 127.6 127.5 115.0 114.8 98.1 96.9 86.8 86.6 77.4 77.2 76.9 65.9 33.0 32.9 26.8 26.8
F
O
F
minor diastereomer
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

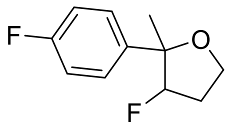


minor diastereomer

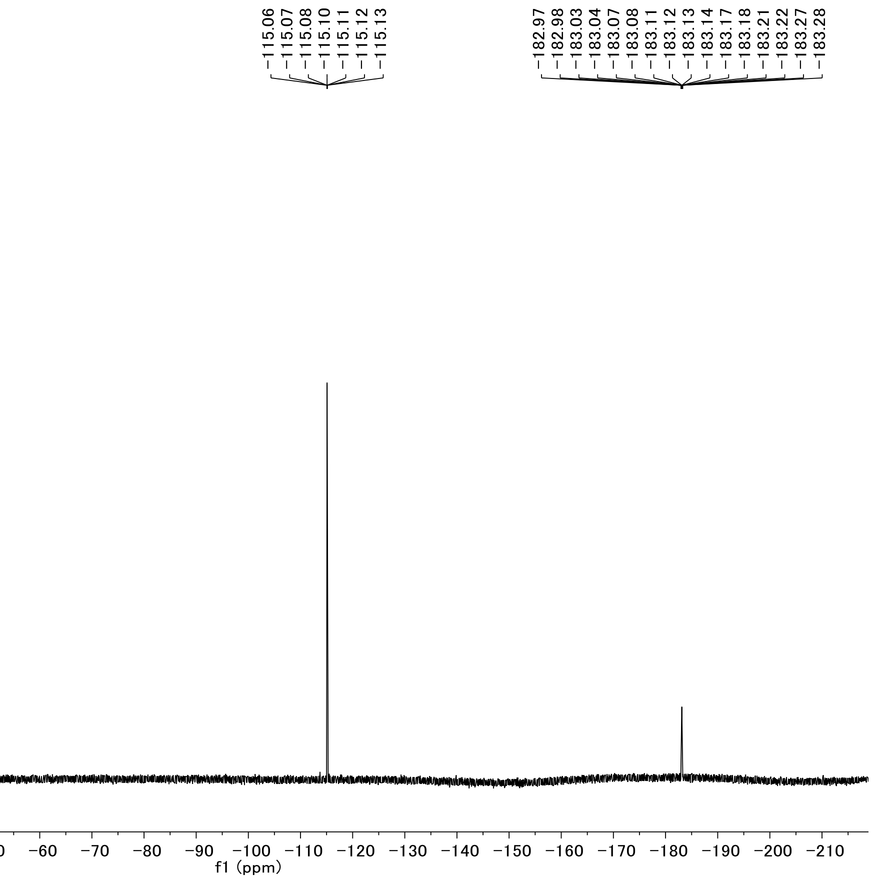



7.351 7.347 7.342 7.339 7.336 7.331 7.327 7.041 7.037 7.030 7.026 7.022 7.015 7.012 5.153 5.151 5.145 5.143 5.063 5.061 5.055 5.053 4.199 4.187 4.184 4.172 4.170 4.158 4.047 4.041 4.032 4.027 4.025 4.017 4.012 2.184 2.177 2.171 2.166 2.165 2.161 2.159 2.152 2.147 2.139 2.134 2.133 2.128 2.123 2.122 2.116 2.111 2.109 2.025 2.017 2.010 2.002 1.994 1.975 1.960 1.952 1.944 1.937 1.929 1.557 1.551
F
O
F
major diastereomer
1.95
1.97
1.00
1.04
1.03
1.03
1.06
3.06
f1 (ppm)


162.87 161.24
140.37
126.65 126.60
115.47 115.33
98.97 97.73
87.11 86.98
77.37 77.16 76.95
65.77
32.12 31.98
23.46 23.40
F
O
F
major diastereomer
f1 (ppm)



major diastereomer



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