Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Enantiospecific Deoxyfluorination of Cyclic α-OH-β-Ketoesters

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1. General Information:

Spectroscopy: NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer with a broad band observe probe and a sample changer for 16 samples, on a Bruker Avance DRX 500 MHz spectrometer, and on a Bruker Avance III 700 MHz spectrometer with an Ascend magnet and TCI cryoprobe which are property to the Austro Czech NMR Research Center "RERI uasb". Chemical shifts (δ) are given in parts per million (ppm), coupling constants (*J*) are given in Hertz (Hz). All NMR spectra were referenced on the solvent residual peak ($CDCl_3$: δ 7.26 ppm for ^{1}H NMR and δ 77.16 ppm for ^{13}C NMR). ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constants, number of protons, assignment). Peak multiplicities are denoted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublet, etc. ***Mass spectrometry:*** High resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL hybrid FT mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer. ***Polarimetry****:* Optical rotations ($[\alpha]_\lambda^{temp}$) were measured on a Schmidt+Haensch Unipol L 100 polarimeter and data is reported as follows: [α]-values are listed in $deg \cdot cm^3 \cdot g^{-1} \cdot dm^{-1}$, concentration (*c* in g/100 mL), and solvent. ***Melting Points:*** Melting points (MP) are reported in degrees Celsius (°C), using a Büchi M-560 apparatus and are reported uncorrected. ***Chromatography:*** Preparative column chromatography was carried out using Davisil LC 60A 70– 200 MICRON silica gel. Thin layer chromatography was performed on Macherey-Nagel pre-coated TLC plates (silica gel, 60 F_{254}, 0.20 mm, ALUGRAM® Xtra SIL). TLC plates were visualized under 254 nm UV lamp and using permanent staining methods (*p*-anisaldehyde: 2.5 mL *p*-anisaldehyde, 93 mL absolute EtOH, 3.5 mL conc. H_2SO_4 and 1 mL glacial AcOH). The enantiomeric excesses (ee) were determined by HPLC analysis using a Dionex Summit HPLC system with CHIRALCEL OD-H (4.6 × 250 mm, 5 µm), OJ-H (4.6 × 250 mm, 5 µm), CHIRALPAK AD-H (4.6 × 250 mm, 5 µm) and a YMC Chiral ART Amylose SA (4.6 × 250 mm, 5 µm) chiral stationary phase. The enantiospecificity (e.s.) of the reaction is calculated as follows: % e.s. = 100 × [% ee of product]/[% ee of starting material].[1] Determination of the absolute configuration of α-fluorinated product **3a** has been reported by *Sodeoka* et al.[2] and assignment of the herein prepared **3a** was carried out by comparison of our analytical data with those literature values. All other derivatives were assigned in analogy. The starting α-hydroxylated compounds **2** were prepared in enantioenriched forms as reported recently (*vide infra*) and their absolute configuration was assigned in accordance with previous publications.[3] ***Naming of compounds:*** Compound names are those generated by ChemBioDraw® 18.2 software (PerkinElmer), following IUPAC nomenclature. ***Solvents and reagents:*** Anhydrous dichloromethane was provided by the Institute of Catalysis (JKU Linz, Austria) and was dried using a purification column composed of

(1) (a) S. E. Denmark, T. Vogler, *Chem. Eur. J*. **2009**, *15*, 11737. (b) S. E. Denmark, M. T, Burk, A. J. Hoover, *J. Am. Chem. Soc.* **2010**, *132*, 1232.
(2) Y. Hamashima, K. Yagi, H. Takano, L. Tamas; M. Sodeoka, *J. Am. Chem. Soc.* **2002**, *124*, 14530.
(3) (a) F. A. Davis, H. Liu, B.-C. Chen, P. Zhou, *Tetrahedron* **1998**, *54*, 10481. (b) S. F. McCann,G. D. Annis, R. Shapiro, D. W. Piotrowski, D. G. P. Lahm, J. K. Long, K. C. Lee, M. M. Hughes, B. J. Myers, S. M. Griswold, B. M. Reeves, R. W. March, P. L. Sharpe, P. Lowder, W. E. Barnette, K. D. Wing, K, *Pest. Manag. Sci.* **2001**, *57*, 153. (c) M. R. Acocella, O. G. Mancheño, M. Bella, K. A. Jørgensen, *J. Org. Chem.* **2004**, *69*, 8165. (d) T. Ishimaru, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa, *J. Am. Chem. Soc.* **2006**, *128*, 16488.

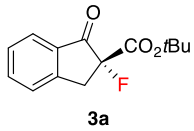
activated alumina and was stored over activated 3 Å molecular sieves. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were carried out under an argon atmosphere using flame-dried glassware. β-Ketoesters were prepared according to literature-known methods.[4] Starting enantioenriched α-hydroxy-β-ketoesters **2** were prepared as reported previously.[5]

CAUTION: Reactions in the presence of *N*,*N*-diethylaminosulfur trifluoride (DAST) should not be conducted at temperatures >50 °C, due to safety issues. DAST is known to be thermally unstable, prone to detonation when heated >90 °C and undergoes catastrophic decomposition at ≈140 °C.[6] Moreover, explosive decomposition of DAST upon contact with water, generating tissue damaging hydrofluoric acid, has also been reported.[7]

(4) (a) T. A. Moss, D. R. Fenwick, D. J. Dixon, *J. Am. Chem. Soc.* **2008**, *130*, 10076. (b) D. Y. Kim, E. J. Park, *Org. Lett.* **2002**, *4*, 545. (c) X. Wang, Q. Lan, S. Shirakawa, K. Maruoka, *Chem. Commun.* **2010**, *46*, 321. (d) E.-M. Tanzer, W. B. Schweizer, M.-O. Ebert, R. Gilmour, *Chem. Eur. J.* **2012**, *18*, 2006. (e) M. Lian, J. Du, Q. Meng, Z. Gao, *Eur. J. Org. Chem*. **2010**, *34*, 6525.
(5) (a) J. Novacek, J. A. Izzo, M. J. Vetticatt and M. Waser, *Chem. Eur. J.* **2016**, *22*, 17339. (b) C. Mairhofer, J. Novacek and M. Waser, *Org. Lett.* **2020**, *22*, 6138.
(6) (a) W. J. Middleton, Explosive hazards with DAST *Chem. Eng. News* **1979**, *57*, 21, 43. (b) P. A. Messina, K. C. Mange, W. J. Middleton, *J. Fluorine Chem.* **1989**, *42*, 137. (c) G. S. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic, H. J. Cheng, *Org. Chem.* **1999**, *64*, 7048. (d) G. S. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic, *Chem. Commun.* **1999**, *2*, 215.
(7) J. Cochran, Laboratory explosions *Chem. Eng. News* **1979**, *57*, 12, 4.

2. Characterization Data of *α*-Deoxyfluorinated Products

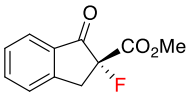
tert-Butyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3a):



3a

Enantiospecificity: 98.0% e.s. Prepared following the general procedure on a 0.1 mmol (24.8 mg of (*S*)-**2a**, 94.6% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (15:1 to 8:1) provided the title compound (*R*)-**3a** as a white crystalline solid (21.0 mg, 84% yield, 92.8% ee). **MP**: 41.6−43.0 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.43 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[8] **[α]$_D^{23.3}$** = +3.8 (*c* 0.81, $CHCl_3$, 91.0% ee). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.82 (d, *J* = 7.7 Hz, 1H, Ar***H***), 7.68 (t, *J* = 7.5 Hz, 1H, Ar***H***), 7.49 (d, *J* = 7.7 Hz, 1H, Ar***H***), 7.45 (t, *J* = 7.5 Hz, 1H, Ar***H***), 3.72 (dd, *J* = 17.4, 10.8 Hz, 1H, C***H***H), 3.39 (dd, *J* = 22.9, 17.5 Hz, 1H, CH***H***), 1.42 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 195.9 (d, *J* = 18.2 Hz, 1C, ***C***=O), 166.4 (d, *J* = 27.8 Hz, 1C, ***C***O_2R), 151.1 (d, *J* = 3.8 Hz, 1C, ***C***$_{Ar}$), 136.6 (1C, ***C***$_{Ar}$), 133.7 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 128.6 (1C, ***C***$_{Ar}$), 126.6 (d, *J* = 1.5 Hz, 1C, ***C***$_{Ar}$), 125.6 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 94.5 (d, *J* = 201.7 Hz, 1C, ***C***qF), 84.3 (1C, ***C***qMe_3), 38.5 (d, *J* = 24.2 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −164.0 (dd, *J* = 22.8, 10.7 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{19}FO_3N$, 268.1343; found, 268.1334. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 200:1, flow rate 0.75 mL/min, 10 °C, λ = 240 nm), retention times t_R(minor) = 25.6 min, t_R(major) = 31.2 min.

Methyl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3b):

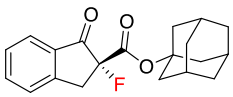


3b

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 70 µmol (14.4 mg of (*S*)-**2b**, 68.0% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (12:1 to 6:1) provided the title compound (*R*)-**3b** as a white crystalline solid (10.6 mg, 51 µmol, 73% yield, 68.3% ee). **MP**: 99.2−101.6 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.29 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[8] **[α]$_D^{22.9}$** = −18.3 (*c* 0.50, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.85 (d, *J* = 7.7 Hz, 1H, Ar***H***), 7.71 (t, *J* = 7.5 Hz, 1H, Ar***H***), 7.53 – 7.44 (m, 2H, Ar***H***), 3.82 (s, 3H, C***H***$_3$), 3.80 (dd, *J* = 17.6, 11.4 Hz, 1H, C***H***H), 3.45 (dd, *J* = 23.3, 17.6 Hz, 1H, CH***H***). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 195.3 (d, *J* = 18.1 Hz, 1C, ***C***=O), 167.9 (d, *J* = 27.8 Hz, 1C, ***C***O_2R), 151.0 (d, *J* = 3.5 Hz, 1C, ***C***$_{Ar}$), 136.9 (1C, ***C***$_{Ar}$), 133.4 (1C, ***C***$_{Ar}$), 128.8 (1C, ***C***$_{Ar}$), 126.7 (d, *J* = 1.5 Hz, (1C, ***C***$_{Ar}$), 125.9 (1C, ***C***$_{Ar}$), 94.8 (d, *J* = 201.8 Hz, 1C, ***C***qF), 53.4 (1C, ***C***H_2), 38.4 (d, *J* = 23.7 Hz, 1C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −164.5 (dd, *J* = 23.3, 11.2 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_{10}FO_3$, 209.0608; found, 209.0604. **HPLC**: Chiralcel OD-H (*n*-hexane:*i*-PrOH = 95:5, flow rate 0.75 mL/min, 10 °C, λ = 270 nm), retention times t_R(major) = 22.6 min, t_R(minor) = 28.1 min.

(8) J. Novacek, M. Waser, *Eur. J. Org. Chem.* **2014**, 802.

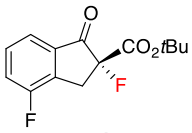
Adamantan-1-yl (*R*)-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3c):



3c

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 80 µmol (26.1 mg of (*S*)-**2c**, 80.4% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 10:1) provided the title compound (*R*)-**3c** as a white crystalline solid (18.9 mg, 58 µmol, 72% yield, 80.6% ee). **MP**: 80.2–81.3 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.51 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[8] **[α]$_D^{23.0}$** = −1.4 (*c* 0.82, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.80 (d, *J* = 7.7 Hz, 1H, Ar***H***), 7.67 (t, *J* = 7.5 Hz, 1H, Ar***H***), 7.48 (d, *J* = 7.8 Hz, 1H, Ar***H***), 7.43 (t, *J* = 7.5 Hz, 1H, Ar***H***), 3.72 (dd, *J* = 17.4, 10.5 Hz, 1H, C***H***H), 3.38 (dd, *J* = 22.8, 17.5 Hz, 1H, CH***H***), 2.12 (s, 3H, C***H***), 2.03 (s, 6H, C$\boldsymbol{H}_2$), 1.60 (s, 6H, C$\boldsymbol{H}_2$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 196.0 (d, *J* = 18.5 Hz, 1C, ***C***=O), 165.9 (d, *J* = 27.8 Hz, 1C, ***C***O_2R), 151.1 (d, *J* = 4.0 Hz, 1C, $\boldsymbol{C}_{Ar}$), 136.5 (1C, $\boldsymbol{C}_{Ar}$), 133.7 (d, *J* = 1.3 Hz, 1C, $\boldsymbol{C}_{Ar}$), 128.5 (1C, $\boldsymbol{C}_{Ar}$), 126.5 (d, *J* = 1.4 Hz, 1C, $\boldsymbol{C}_{Ar}$), 125.5 (d, *J* = 1.3 Hz, 1C, $\boldsymbol{C}_{Ar}$), 94.4 (d, *J* = 201.5 Hz, 1C, ***C***qF), 84.2 (1C, ***C***qAd), 41.1 (3C, $\boldsymbol{C}_{Ad}H_2$), 38.5 (d, *J* = 24.0 Hz, 1C, ***C***H_2), 36.0 (3C, $\boldsymbol{C}_{Ad}$H), 30.9 (3C, $\boldsymbol{C}_{Ad}H_2$). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −164.1 (dd, *J* = 22.8, 10.4 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{20}H_{25}FNO_3N$, 346.1813; found, 346.1801. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 99:1, flow rate 0.7 mL/min, 10 °C, λ = 270 nm), retention times t_R(minor) = 32.7 min, t_R(major) = 46.0 min.

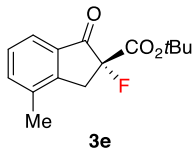
***tert*-Butyl (*R*)-2,4-difluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3d):**



3d

Enantiospecificity: 96.2% e.s. Prepared following the general procedure on a 65 µmol (17.3 mg of (*S*)-**2d**, 85.0% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 9:1) provided the title compound (*R*)-**3d** as a white crystalline solid (14.1 mg, 52 µmol, 81% yield, 81.8% ee). **MP**: 91.2–91.9 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.53 (UV, *p*-anisaldehyde). **[α]$_D^{23.5}$** = +2.5 (*c* 0.69, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.64 (d, *J* = 7.6 Hz, 1H, Ar***H***), 7.51 – 7.43 (m, 1H, Ar***H***), 7.38 (t, *J* = 8.3 Hz, 1H, Ar***H***), 3.75 (dd, *J* = 17.8, 10.9 Hz, 1H, C***H***H), 3.37 (dd, *J* = 22.6, 17.8 Hz, 1H, CH***H***), 1.44 (s, 9H, C$\boldsymbol{H}_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 194.8 (dd, *J* = 18.8, 3.0 Hz, 1C, ***C***=O), 165.9 (d, *J* = 27.4 Hz, 1C, ***C***O_2R), 159.7 (dd, *J* = 251.6, 1.2 Hz, 1C, $\boldsymbol{C}_{Ar}$), 137.0 (dd, *J* = 19.5, 4.0 Hz, 1C, $\boldsymbol{C}_{Ar}$), 136.2 (dd, *J* = 4.8, 1.4 Hz, 1C, $\boldsymbol{C}_{Ar}$), 130.6 (d, *J* = 6.3 Hz, 1C, $\boldsymbol{C}_{Ar}$), 122.7 (d, *J* = 19.8 Hz, 1C, $\boldsymbol{C}_{Ar}$), 121.3 (dd, *J* = 4.2, 1.2 Hz, 1C, $\boldsymbol{C}_{Ar}$), 94.0 (d, *J* = 203.0 Hz, 1C, ***C***qF), 84.7 (1C, ***C***qMe_3), 34.4 (d, *J* = 25.3 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −118.1 (m), −163.3 (dd, *J* = 22.6, 10.6 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}F_2O_3N$, 286.1249; found, 286.1238. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 95:5, flow rate 0.75 mL/min, 10 °C, λ = 240 nm), retention times t_R(minor) = 8.0 min, t_R(major) = 11.7 min.

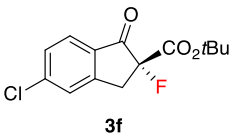
***tert*-Butyl (*R*)-2-fluoro-4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3e):**



3e

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 80 µmol (21.0 mg of (*S*)-**2e**, 78.1% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 10:1) provided the title compound (*R*)-**3e** as a yellow crystalline solid (13,7 mg, 52 µmol, 65% yield, 78.4% ee). **MP**: 63.7−64.6 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.45 (UV, *p*-anisaldehyde). $[\alpha]_D^{23.1}$ = −23.8 (*c* 0.68, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.66 (d, *J* = 7.6 Hz, 1H, Ar***H***), 7.49 (d, *J* = 7.3 Hz, 1H, Ar***H***), 7.36 (t, *J* = 7.5 Hz, 1H, Ar***H***), 3.61 (dd, *J* = 17.5, 11.3 Hz, 1H, C***H***H), 3.26 (dd, *J* = 23.2, 17.5 Hz, 1H, CH***H***), 2.36 (s, 3H, ArC***H***$_3$), 1.44 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 196.2 (d, *J* = 18.2 Hz, 1C, ***C***=O), 166.6 (d, *J* = 27.4 Hz, 1C, ***C***O_2R), 150.2 (d, *J* = 3.4 Hz, 1C, ***C***$_{Ar}$), 137.1 (1C, ***C***$_{Ar}$), 135.9 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 133.5 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 128.8 (1C, ***C***$_{Ar}$), 123.0 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 94.5 (d, *J* = 201.3 Hz, 1C, ***C***qF), 84.3 (1C, ***C***qMe_3), 37.4 (d, *J* = 24.1 Hz, 1C, ***C***H_2), 28.0 (3C, ***C***H_3), 17.9 (1C, Ar***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.3 (dd, *J* = 23.2, 11.4 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_3N$, 282.1500; found, 282.1490. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 99:1, flow rate 1.0 mL/min, 10 °C, λ = 240 nm), retention times t_R(minor) = 10.7 min, t_R(major) = 13.4 min.

***tert*-Butyl (*R*)-5-chloro-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3f):**

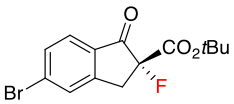


3f

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 80 µmol (22.6 mg of (*S*)-**2f**, 84.6% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 10:1) provided the title compound (*R*)-**3f** as a white crystalline solid (21.9 mg, 77 µmol, 96% yield, 84.9% ee). **MP**: 100.8−101.9 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.56 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[9] $[\alpha]_D^{23.3}$ = −31.4 (*c* 1.00, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.75 (d, *J* = 8.2 Hz, 1H, Ar***H***), 7.49 (s, 1H, Ar***H***), 7.43 (dd, *J* = 8.1, 1.9 Hz, 1H, Ar***H***), 3.70 (dd, *J* = 17.7, 10.6 Hz, 1H, C***H***H), 3.37 (dd, *J* = 22.6, 17.7 Hz, 1H, CH***H***), 1.43 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 194.5 (d, *J* = 18.5 Hz, 1C, ***C***=O), 166.0 (d, *J* = 27.7 Hz, 1C, ***C***O_2R), 152.4 (d, *J* = 3.9 Hz, 1C, ***C***$_{Ar}$), 143.3 (1C, ***C***$_{Ar}$), 132.1 (d, *J* = 1.6 Hz, 1C, ***C***$_{Ar}$), 129.5 (1C, ***C***$_{Ar}$), 126.9 (d, *J* = 1.6 Hz, 1C, ***C***$_{Ar}$), 126.6 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 94.3 (d, *J* = 202.8 Hz, 1C, ***C***qF), 84.6 (1C, ***C***qMe_3), 38.1 (d, *J* = 24.5 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.32 (dd, *J* = 22.6, 10.5 Hz). (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}ClFO_3N$, 302.0954; found, 302.0942. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 99:1, flow rate 1.0 mL/min, 10 °C, λ = 220 nm), retention times t_R(minor) = 13.8 min, t_R(major) = 18.1 min.

(9) X. Gu, Y. Zhang, Z.-J. Xu, C.-M. Che, *Chem. Commun.* **2014**, *50*, 7870.

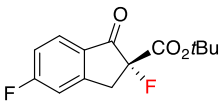
***tert*-Butyl (*R*)-5-bromo-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3g):**



3g

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 70 µmol (22.9 mg of (*S*)-**2g**, 90.6% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 9:1) provided the title compound (*R*)-**3g** as a pale yellow crystalline solid (19.8 mg, 60 µmol, 86% yield, 92.4% ee). **MP**: 121.9–122.5 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.51 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[8] $[\alpha]_D^{23.2}$ = −25.3 (*c* 1.00, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.70 – 7.66 (m, 1H, Ar***H***), 7.60 (d, *J* = 8.1 Hz, 2H, Ar***H***), 3.70 (dd, *J* = 17.7, 10.6 Hz, 1H, C***H***H), 3.38 (dd, *J* = 22.6, 17.6 Hz, 1H, CH***H***), 1.43 (s, 9H, ***C***H_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 194.7 (d, *J* = 18.5 Hz, 1C, ***C***=O), 166.0 (d, *J* = 27.4 Hz, 1C, ***C***O_2R), 152.5 (d, *J* = 4.1 Hz, 1C, ***C***$_{Ar}$), 132.5 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 132.4 (1C, ***C***$_{Ar}$), 132.2 (1C, ***C***$_{Ar}$), 130.0 (d, *J* = 1.5 Hz, 1C, ***C***$_{Ar}$), 126.6 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 94.2 (d, *J* = 202.8 Hz, 1C, ***C***qF), 84.6 (1C, ***C***qMe_3), 38.1 (d, *J* = 24.5 Hz, 1C, ***C***H_2), 28.0 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.4 (dd, *J* = 22.9, 10.5 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}BrFO_3N$, 346.0449; found, 346.0436. **HPLC**: Chiralcel OD-H (*n*-hexane:*i*-PrOH = 95:5, flow rate 0.75 mL/min, 10 °C, λ = 220 nm), retention times t_R(major) = 11.2 min, t_R(minor) = 13.5 min.

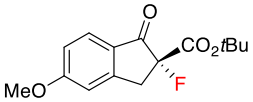
***tert*-Butyl (*R*)-2,5-difluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3h):**



3h

Enantiospecificity: 95.5% e.s. Prepared following the general procedure on a 75 µmol (20.0 mg of (*S*)-**2h**, 85.5% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 9:1) provided the title compound (*R*)-**3h** as a white crystalline solid (12.9 mg, 48 µmol, 64% yield, 81.7% ee). **MP**: 96.7−97.6 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.46 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[8] $[\alpha]_D^{23.4}$ = −3.9 (*c* 0.57, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.88 – 7.80 (m, 1H, Ar***H***), 7.21 – 7.10 (m, 2H, Ar***H***), 3.71 (dd, *J* = 17.7, 10.5 Hz, 1H, C***H***H), 3.38 (dd, *J* = 22.5, 17.7 Hz, 1H, CH***H***), 1.43 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 194.0 (d, *J* = 18.5 Hz, 1C, ***C***=O), 168.1 (d, *J* = 259.8 Hz, 1C, ***C***$_{Ar}$F), 166.1 (d, *J* = 27.7 Hz, 1C, ***C***O_2R), 154.1 (dd, *J* = 10.6, 4.1 Hz, 1C, ***C***$_{Ar}$), 130.1 (t, *J* = 1.7 Hz, 1C, ***C***$_{Ar}$), 128.1 (dd, *J* = 10.7, 1.2 Hz, 1C, ***C***$_{Ar}$), 117.1 (d, *J* = 24.0 Hz, 1C, ***C***$_{Ar}$), 113.5 (dd, *J* = 23.0, 1.4 Hz, 1C, ***C***$_{Ar}$), 94.5 (d, *J* = 202.7 Hz, 1C, ***C***qF), 84.5 (1C, ***C***qMe_3), 38.3 (dd, *J* = 24.7, 2.1 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −98.8 (m), −163.2 (dd, *J* = 22.5, 10.5 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}F_2O_3N$, 286.1249; found, 286.1239. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 95:5, flow rate 0.75 mL/min, 10 °C, λ = 240 nm), retention times t_R(minor) = 10.9 min, t_R(major) = 12.6 min.

***tert*-Butyl (*R*)-2-fluoro-5-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3i):**

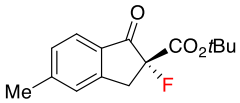


3i

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 80 µmol (22.3 mg of (*S*)-**2i**, 88.6% ee) scale. Purification by silica gel column

chromatography using heptanes/EtOAc (12:1 to 8:1) provided the title compound (*R*)-**3i** as a white crystalline solid (5.4 mg, 19 µmol, 24% yield, 88.7% ee). **MP**: 151.9−153.4 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.32 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[10] **[α]$_D^{23.4}$** = +34.1 (*c* 0.27, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.74 (d, *J* = 8.6 Hz, 1H, Ar***H***), 6.95 (d, *J* = 8.6 Hz, 1H, Ar***H***), 6.89 (s, 1H, Ar***H***), 3.90 (s, 3H, ArOC***H***$_3$), 3.66 (dd, *J* = 17.5, 10.8 Hz, 1H, C***H***H), 3.31 (dd, *J* = 22.7, 17.5 Hz, 1H, CH***H***), 1.42 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 193.8 (d, *J* = 18.5 Hz, 1C, ***C***=O), 166.7 (1C, ***C***O_2R), 166.5 (1C, ***C***$_{Ar}$), 154.3 (d, *J* = 3.8 Hz, 1C, ***C***$_{Ar}$), 127.4 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 126.7 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 116.6 (1C, ***C***$_{Ar}$), 109.8 (d, *J* = 1.5 Hz, 1C, ***C***$_{Ar}$), 94.9 (d, *J* = 201.1 Hz, 1C, ***C***qF), 84.0 (1C, ***C***qMe_3), 56.0 (1C, O***C***H_3), 38.4 (d, *J* = 24.4 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$) δ −162.9 (dd, *J* = 22.9, 11.4 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_4N$, 298.1449; found, 298.1437. **HPLC**: Chiralcel OJ-H (*n*-hexane:*i*-PrOH = 80:20, flow rate 0.9 mL/min, 10 °C, λ = 270 nm), retention times t_R(major) = 17.0 min, t_R(minor) = 18.7 min.

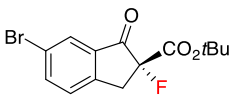
***tert*-Butyl (*R*)-2-fluoro-5-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3j):**



3j

Enantiospecificity: 99.1% e.s. Prepared following the general procedure on a 80 µmol (21.0 mg of (*S*)-**2j**, 89.3% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (15:1 to 9:1) provided the title compound (*R*)-**3j** as a yellow crystalline solid (16.7 mg, 63 µmol, 79% yield, 88.5% ee). **MP**: 81.9−82.8 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.41 (UV, *p*-anisaldehyde). **[α]$_D^{22.1}$** = −11.7 (*c* 0.92, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.70 (d, *J* = 7.9 Hz, 1H, Ar***H***), 7.27 (s, 1H, Ar***H***), 7.24 (d, *J* = 7.9 Hz, 1H, Ar***H***), 3.66 (dd, *J* = 17.5, 10.8 Hz, 1H, C***H***H), 3.32 (dd, *J* = 22.9, 17.5 Hz, 1H, CH***H***), 2.46 (s, 3H, ArC***H***$_3$), 1.42 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 195.3 (d, *J* = 18.2 Hz, 1C, ***C***=O), 166.5 (d, *J* = 27.5 Hz, 1C, ***C***O_2R), 151.6 (d, *J* = 3.8 Hz, 1C, ***C***$_{Ar}$), 148.3 (1C, ***C***$_{Ar}$), 131.4 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 129.9 (1C, ***C***$_{Ar}$), 126.9 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 125.4 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 94.8 (d, *J* = 201.5 Hz, 1C, ***C***qF), 84.1 (1C, ***C***qMe_3), 38.3 (d, *J* = 24.3 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3), 22.4 (1C, Ar***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.6 (dd, *J* = 22.9, 10.8 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_3N$, 282.1500; found, 282.1492. **HPLC**: Chiralcel OD-H (*n*-hexane:*i*-PrOH = 99:1, flow rate 1.0 mL/min, 10 °C, λ = 240 nm), retention times t_R(major) = 12.3 min, t_R(minor) = 13.2 min.

***tert*-Butyl (*R*)-6-bromo-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3k):**



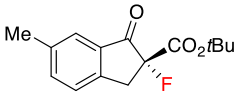
3k

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 70 µmol (22.9 mg of (*S*)-**2k**, 84.5% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 9:1) provided the title compound (*R*)-**3k** as a white crystalline solid (21.0 mg, 64 µmol, 91% yield, 85.1% ee). **MP**: 87.4−88.4 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.48 (UV, *p*-anisaldehyde).

(10) X. Wang, Q. Lan, S. Shirakawa, K. Maruoka, *Chem. Commun.* **2010**, *46*, 321.

[α]$_D^{23.6}$ = +12.0 (*c* 0.88, CH_2Cl_2, 81.3% ee). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.94 (s, 1H, Ar***H***), 7.78 (dd, *J* = 8.1, 2.0 Hz, 1H, Ar***H***), 7.38 (d, *J* = 8.1 Hz, 1H, Ar***H***), 3.67 (dd, *J* = 17.6, 10.4 Hz, 1H, C***H***H), 3.33 (dd, *J* = 22.5, 17.6 Hz, 1H, CH***H***), 1.43 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 194.6 (d, *J* = 18.6 Hz, 1C, ***C***=O), 165.9 (d, *J* = 27.6 Hz, 1C, ***C***O_2R), 149.6 (d, *J* = 3.8 Hz, 1C, ***C***$_{Ar}$), 139.3 (1C, ***C***$_{Ar}$), 135.4 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 128.3 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 128.1 (d, *J* = 1.4 Hz, 1C, ***C***$_{Ar}$), 122.7 (1C, ***C***$_{Ar}$), 94.5 (d, *J* = 203.2 Hz, 1C, ***C***qF), 84.6 (1C, ***C***qMe_3), 38.1 (d, *J* = 24.4 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.4 (dd, *J* = 22.5, 10.5 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{14}H_{18}BrFO_3N$, 346.0449; found, 346.0453. **HPLC**: Chiralcel OD-H (*n*-hexane:*i*-PrOH = 95:5, flow rate 0.75 mL/min, 10 °C, λ = 220 nm), retention times t_R(minor) = 11.1 min, t_R(major) = 12.4 min.

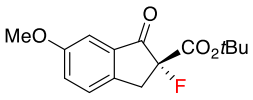
***tert*-Butyl (*R*)-2-fluoro-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3l):**



3l

Enantiospecificity: 98.5% e.s. Prepared following the general procedure on a 75 µmol (19.7 mg of (*S*)-**2l**, 93.4% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 9:1) provided the title compound (*R*)-**3l** as a white crystalline solid (15.5 mg, 59 µmol, 78% yield, 91.9% ee). **MP**: 60.3−61.6 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.49 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[9] **[α]$_D^{23.2}$** = +3.4 (*c* 1.00, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.60 (s, 1H, Ar***H***), 7.48 (d, *J* = 7.8 Hz, 1H, Ar***H***), 7.36 (d, *J* = 7.9 Hz, 1H, Ar***H***), 3.66 (dd, *J* = 17.3, 10.7 Hz, 1H, C***H***H), 3.32 (dd, *J* = 22.9, 17.4 Hz, 1H, CH***H***), 2.40 (s, 3H, ArC***H***$_3$), 1.41 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 195.9 (d, *J* = 18.5 Hz, 1C, ***C***=O), 166.5 (d, *J* = 27.7 Hz, 1C, ***C***O_2R), 148.5 (d, *J* = 3.9 Hz, 1C, ***C***$_{Ar}$), 138.7 (1C, ***C***$_{Ar}$), 137.9 (1C, ***C***$_{Ar}$), 133.8 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 126.2 (d, *J* = 1.5 Hz, 1C, ***C***$_{Ar}$), 125.3 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 94.8 (d, *J* = 201.5 Hz, 1C, ***C***qF), 84.1 (1C, ***C***qMe_3), 38.1 (d, *J* = 24.1 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3), 21.2 (1C, Ar***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.7 (dd, *J* = 23.4, 11.2 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{15}H_{21}FO_3N$, 282.1500; found, 282.1491. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 99:1, flow rate 1.0 mL/min, 10 °C, λ = 240 nm), retention times t_R(minor) = 12.9 min, t_R(major) = 21.4 min.

***tert*-Butyl (*R*)-2-fluoro-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3m):**

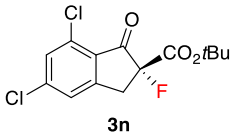


3m

Enantiospecificity: 99.3% e.s. Prepared following the general procedure on a 70 µmol (19.5 mg of (*S*)-**2m**, 91.1% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (15:1 to 8:1) provided the title compound (*R*)-**3m** as a white crystalline solid (16.1 mg, 57 µmol, 82% yield, 90.5% ee). **MP**: 62.4−63.2 °C (EtOAc/heptane). **TLC** (30% EtOAc/heptane): R_f = 0.39 (UV, *p*-anisaldehyde). Analytical data are in accordance with those reported in the literature.[9] **[α]$_D^{23.6}$** = +11.0 (*c* 1.00, CH_2Cl_2). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K) δ 7.38 (d, *J* = 8.4 Hz, 1H, Ar***H***), 7.31 – 7.25 (m, 1H, Ar***H***), 7.24 (s, 1H, Ar***H***), 3.86 (s, 3H, OC***H***$_3$), 3.65 (dd, *J* = 17.1, 10.3 Hz, 1H, C***H***H), 3.32 (dd, *J* =

22.6, 17.1 Hz, 1H, CH***H***), 1.44 (s, 9H, ***C***H_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 195.9 (d, *J* = 18.5 Hz, 1C, ***C***=O), 166.4 (d, *J* = 27.8 Hz, 1C, ***C***O_2R), 160.1 (1C, ***C***$_{Ar}$), 144.1 (d, *J* = 3.9 Hz, 1C, ***C***$_{Ar}$), 134.8 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 127.3 (d, *J* = 1.3 Hz, 1C, ***C***$_{Ar}$), 126.0 (1C, ***C***$_{Ar}$), 106.4 (d, *J* = 1.2 Hz, 1C, ***C***$_{Ar}$), 95.1 (d, *J* = 201.9 Hz, 1C, ***C***qF), 84.2 (1C, ***C***qMe_3), 55.8 (1C, O***C***H_3), 37.8 (d, *J* = 24.0 Hz, 1C, ***C***H_2), 27.9 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −163.5 (dd, *J* = 22.6, 10.3 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_4N$, 298.1449; found, 298.1439. **HPLC**: Chiralpak AD-H (*n*-hexane:*i*-PrOH = 99:1, flow rate 1.0 mL/min, 10 °C, λ = 250 nm), retention times t_R(minor) = 17.8 min, t_R(major) = 19.4 min.

***tert*-Butyl (*R*)-5,7-dichloro-2-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3n):**

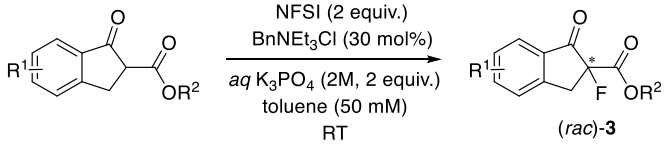


3n

Enantiospecificity: >99.8% e.s. Prepared following the general procedure on a 40 µmol (12.7 mg of (*S*)-**2n**, 75.5% ee) scale. Purification by silica gel column chromatography using heptanes/EtOAc (20:1 to 10:1) provided the title compound (*R*)-**3n** as a white amorphous solid (6.3 mg, 20 µmol, 49% yield, 75.5% ee). **TLC** (30% EtOAc/heptane): R_f = 0.50 (UV, *p*-anisaldehyde). **$[\alpha]_D^{23.7}$** = +2.0 (*c* 0.55, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.42 (s, 1H, Ar***H***), 7.39 (s, 1H, Ar***H***), 3.67 (dd, *J* = 17.7, 11.1 Hz, 1H, C***H***H), 3.34 (dd, *J* = 22.5, 17.8 Hz, 1H, CH***H***), 1.46 (s, 9H, C***H***$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K) δ 191.6 (d, *J* = 19.0 Hz, 1C, ***C***=O), 165.7 (d, *J* = 27.3 Hz, 1C, ***C***O_2R), 153.9 (d, *J* = 3.8 Hz, 1C, ***C***$_{Ar}$), 143.0 (1C, ***C***$_{Ar}$), 134.6 (1C, ***C***$_{Ar}$), 130.5 (1C, ***C***$_{Ar}$), 128.7 (1C, ***C***$_{Ar}$), 125.3 (1C, ***C***$_{Ar}$), 94.4 (d, *J* = 203.7 Hz, 1C, ***C***qF), 84.9 (1C, ***C***qMe_3), 37.5 (d, *J* = 24.4 Hz, 1C, ***C***H_2), 28.0 (3C, ***C***H_3). **^{19}F NMR** (471 MHz, $CDCl_3$, 298 K) δ −161.8 (dd, *J* = 22.5, 11.2 Hz). **HRMS** (ESI-Orbitrap, MeOH) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{17}Cl_2FO_3N$, 336.0564; found, 336.0575. **HPLC**: YMC Chiral ART Amylose SA (*n*-hexane:*i*-PrOH = 99:1, flow rate 1.0 mL/min, 10 °C, λ = 220 nm), retention times t_R(major) = 10.4 min, t_R(minor) = 24.1 min.

3. Synthesis of Racemic Fluorinated Products:

General Procedure



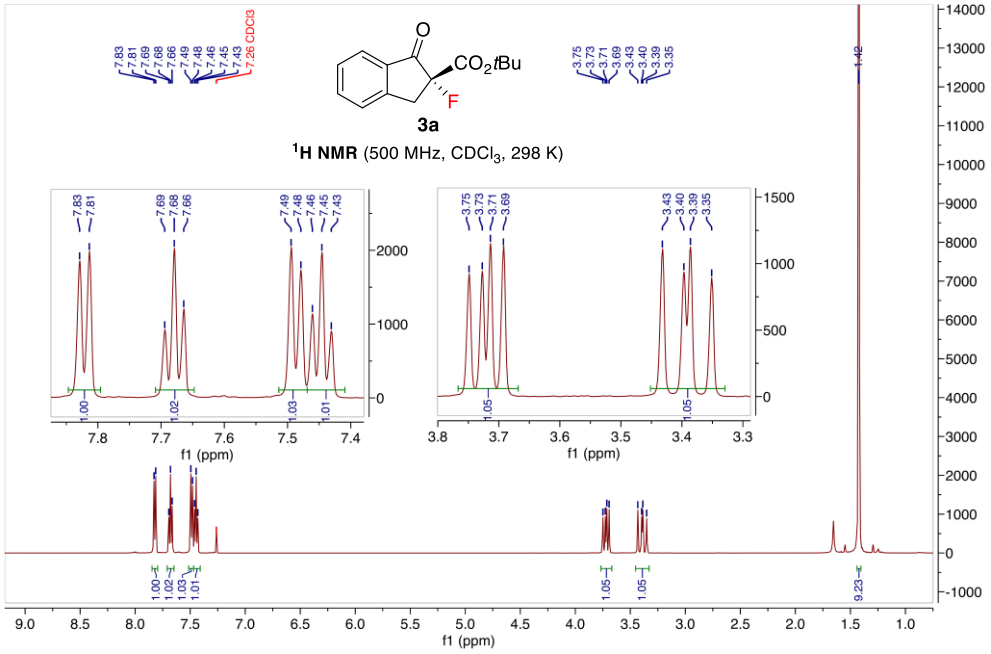
(*rac*)-**3**

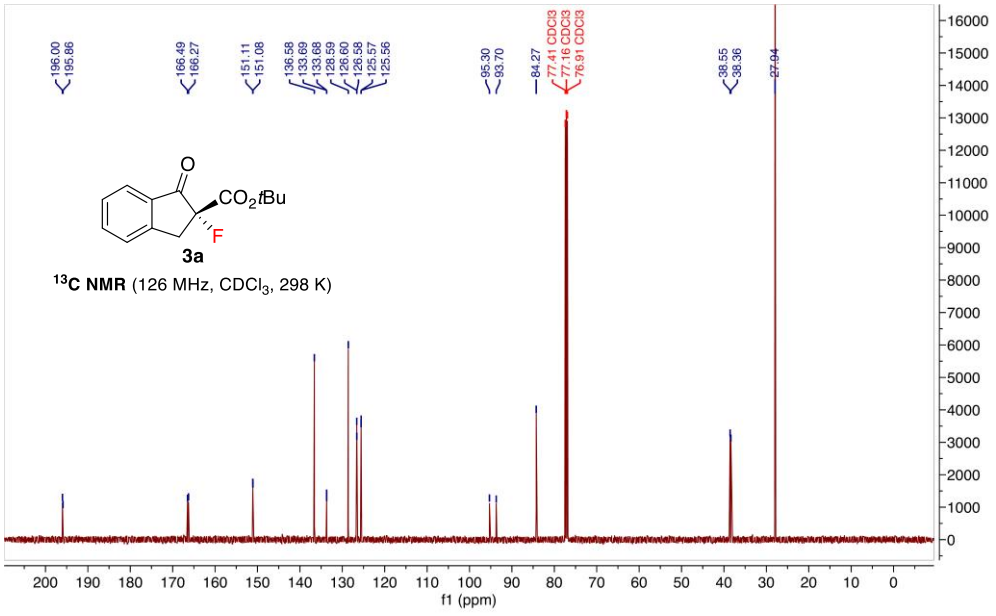
Racemic fluorinated products (**3**) were prepared according to a modified literature procedure[8]: Aqueous K_3PO_4 (2M, 2 equiv.) was added to a mixture of β-ketoester and benzyltriethylammonium chloride (BTEAC, 30 mol%) in toluene (50 mM concerning substrate) at room temperature under an atmosphere of argon. Then, *N*-fluorobenzene sulfonimide (NFSI, 2 equiv.) was added portionwise over 5 min under heavy stirring. The reaction was monitored by TLC using heptanes/EtOAc (7:3) as mobile phase. After stirring for 18 h, the resulting mixture was quenched by addition of *aq.* sat. NH_4Cl (25 mL per mmol substrate), the organic phase was separated and the aqueous phase was extracted

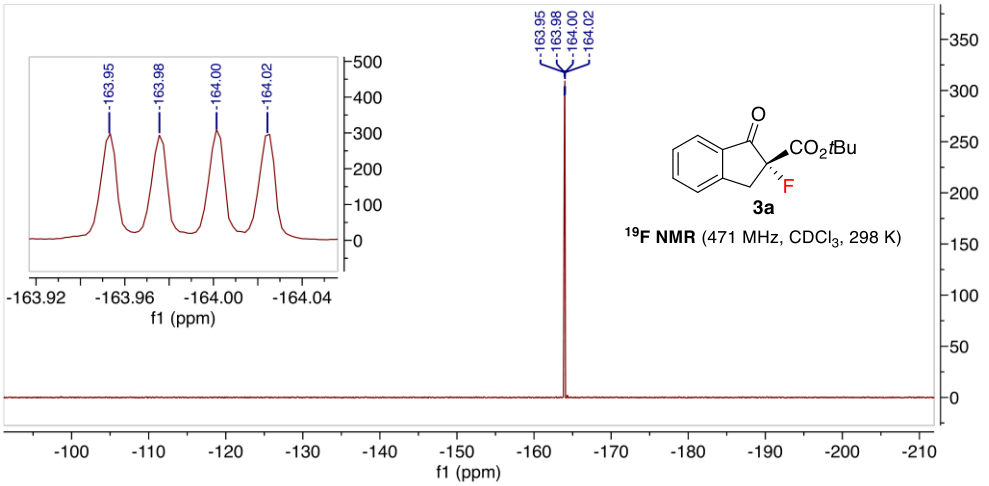
with dichloromethane (3 × 50 mL per mmol substrate). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The residue was purified by silica gel column chromatography (eluent: heptanes/EtOAc).

4. Copies of NMR Spectra of Deoxyfluorination Products:

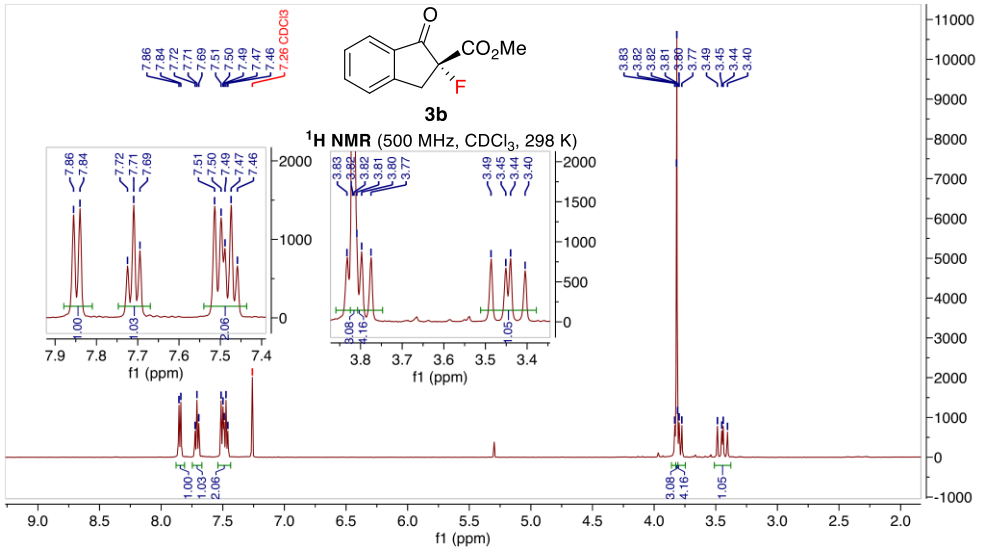
NMR spectra of compound **3a**

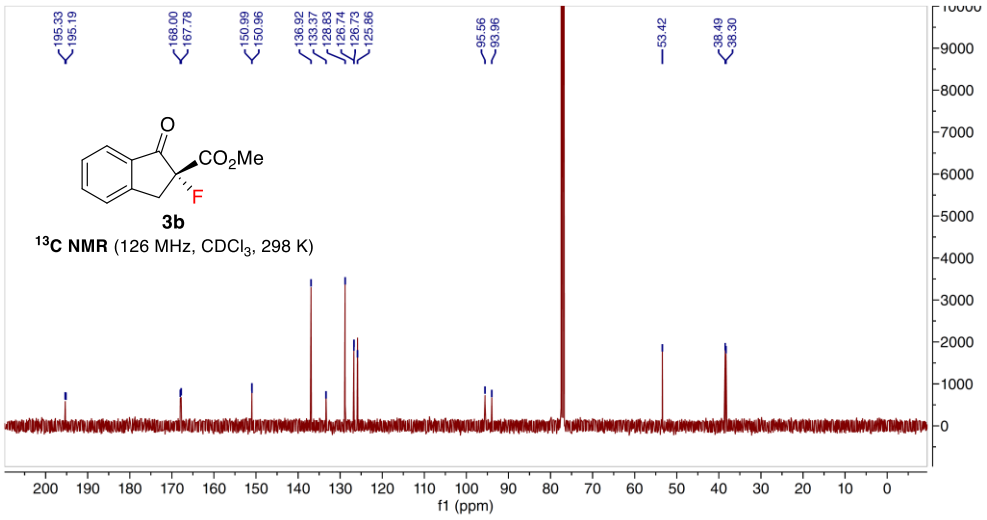


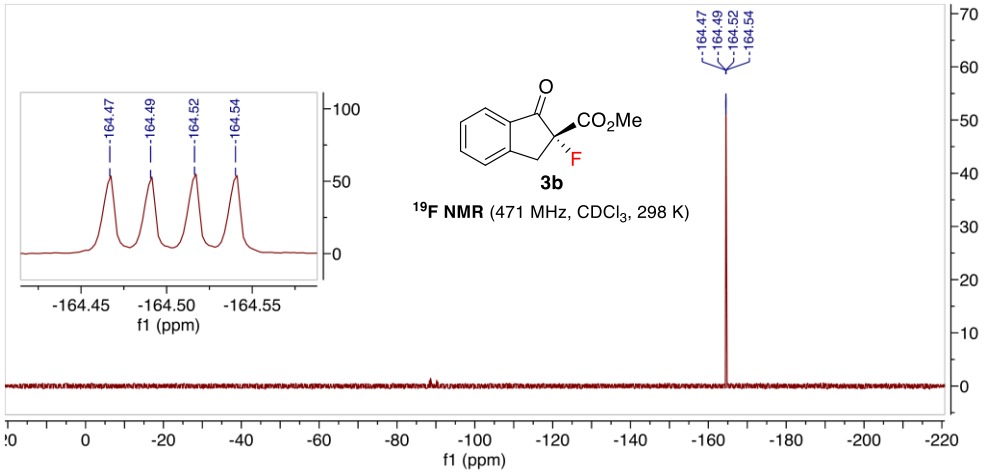




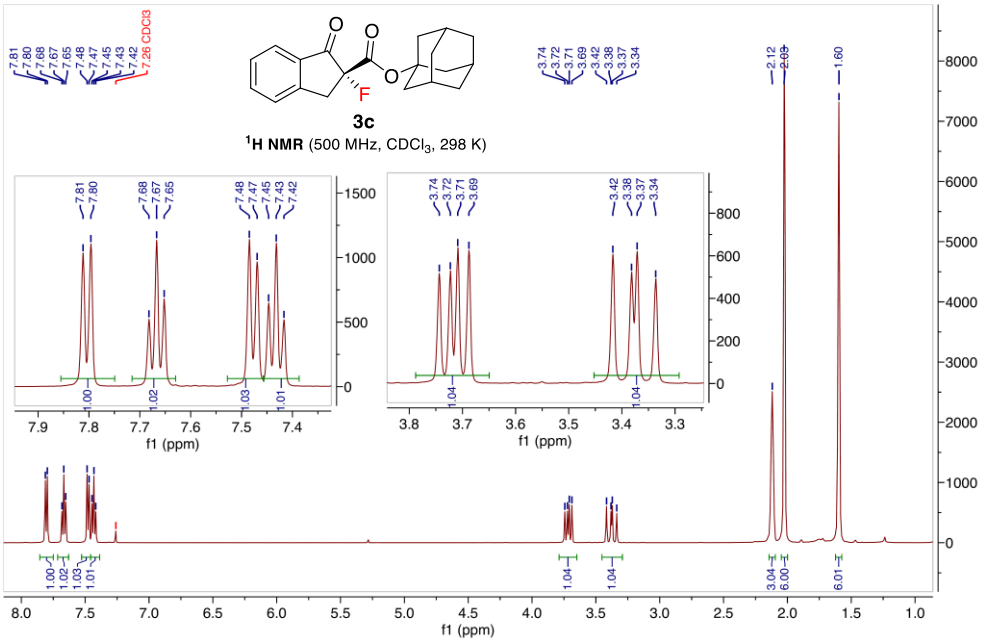
NMR spectra of compound **3b**

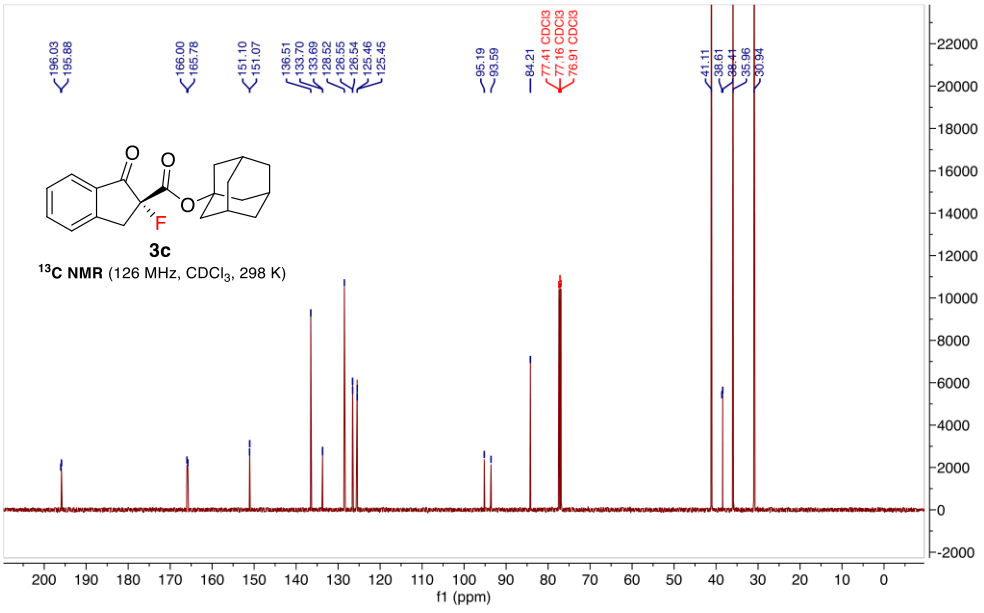


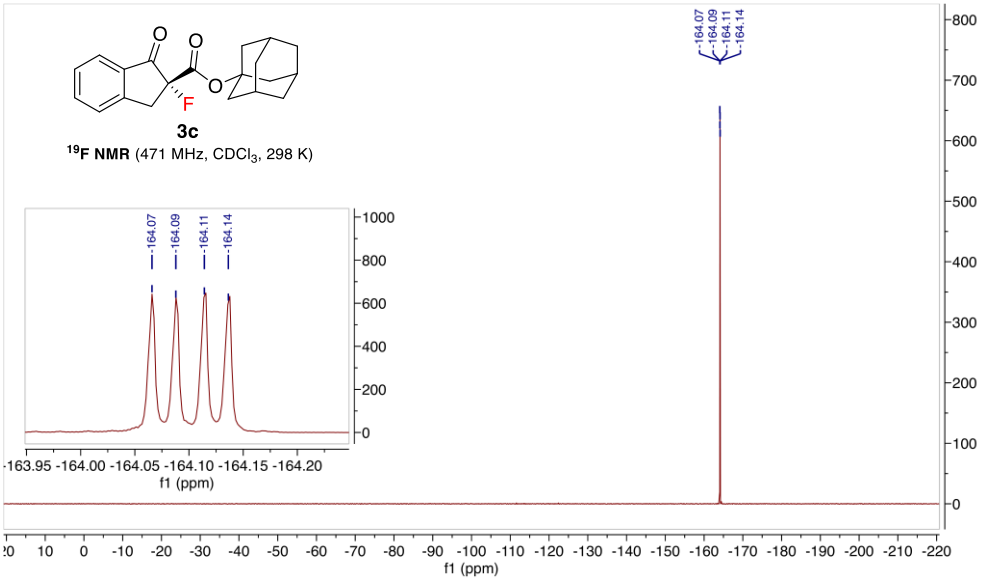




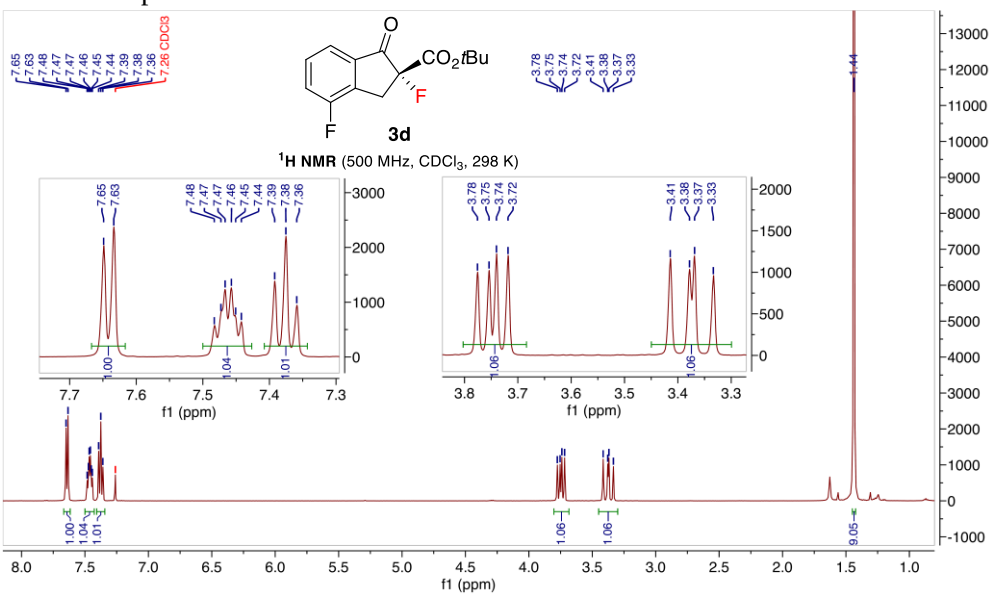
NMR spectra of compound **3c**

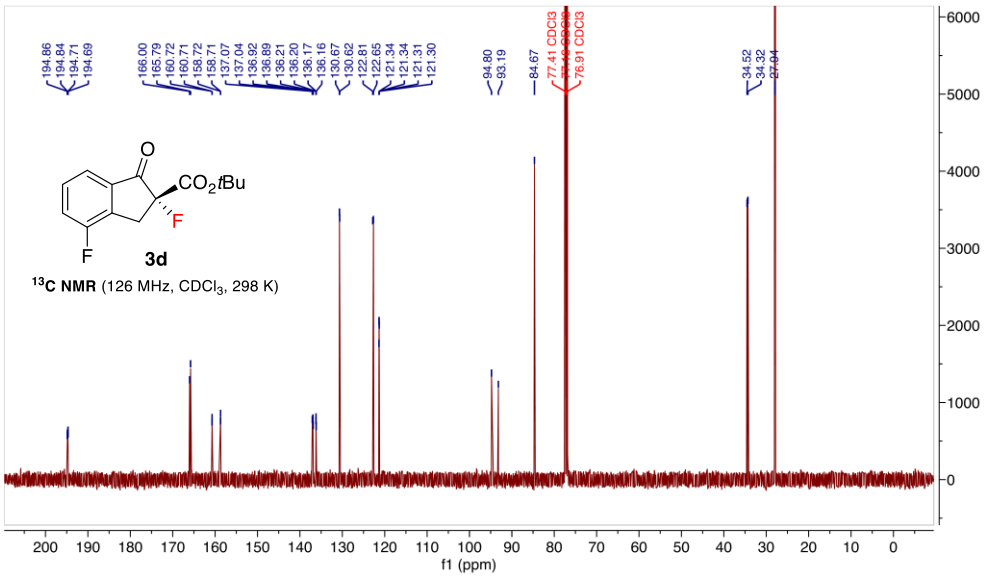


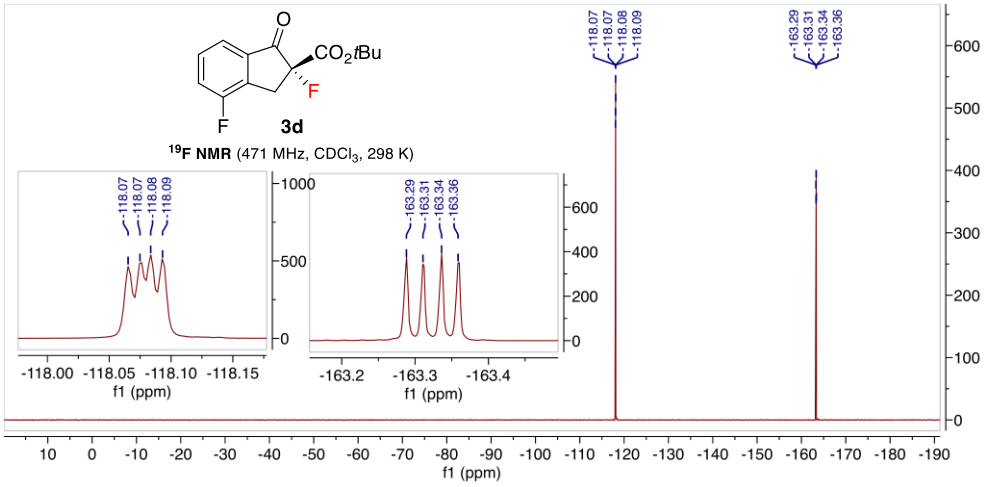




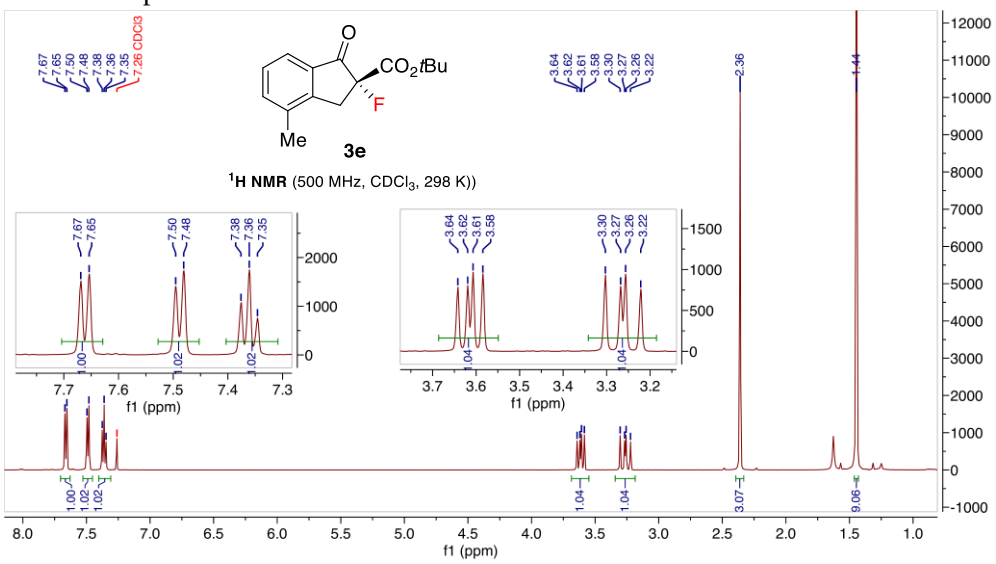
NMR spectra of compound **3d**

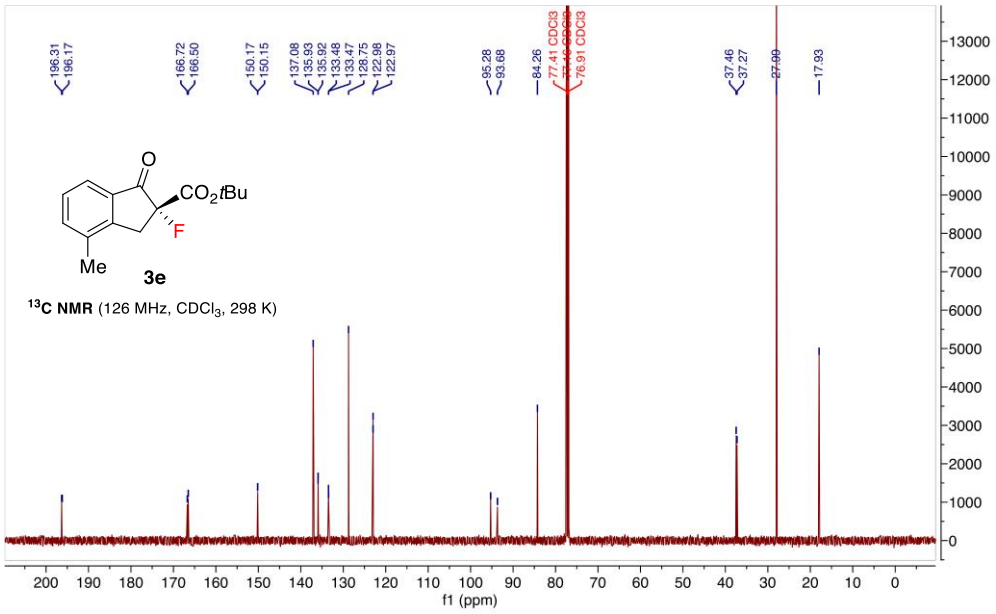


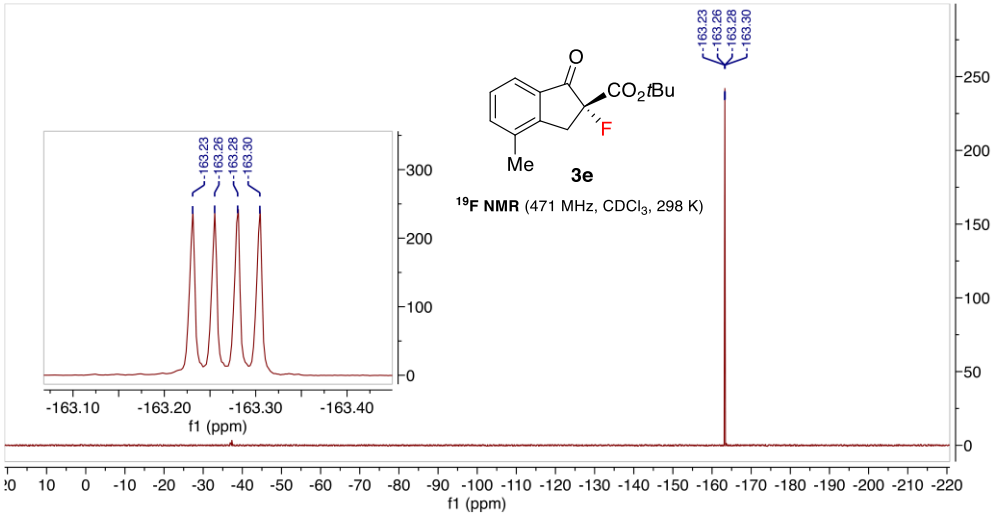




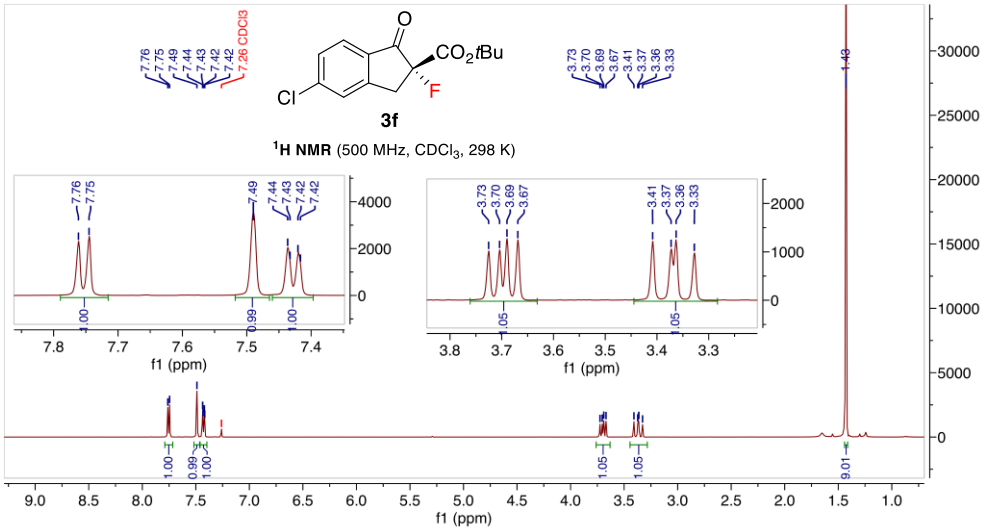
NMR spectra of compound **3e**

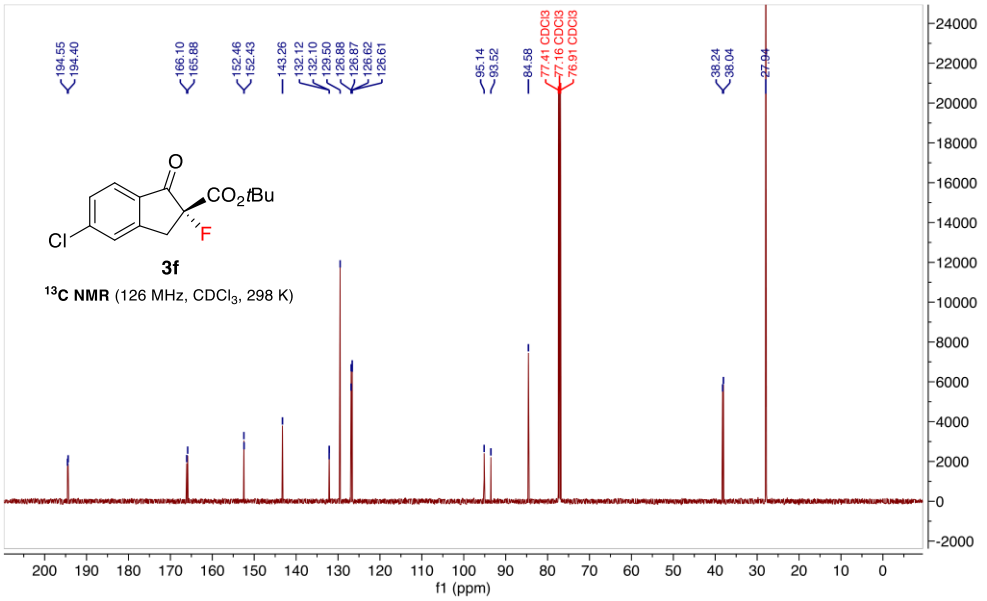


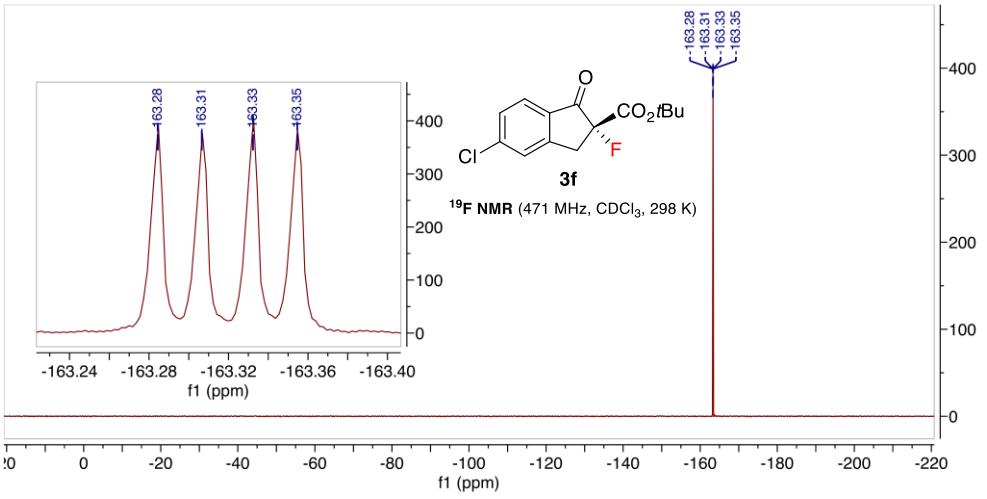




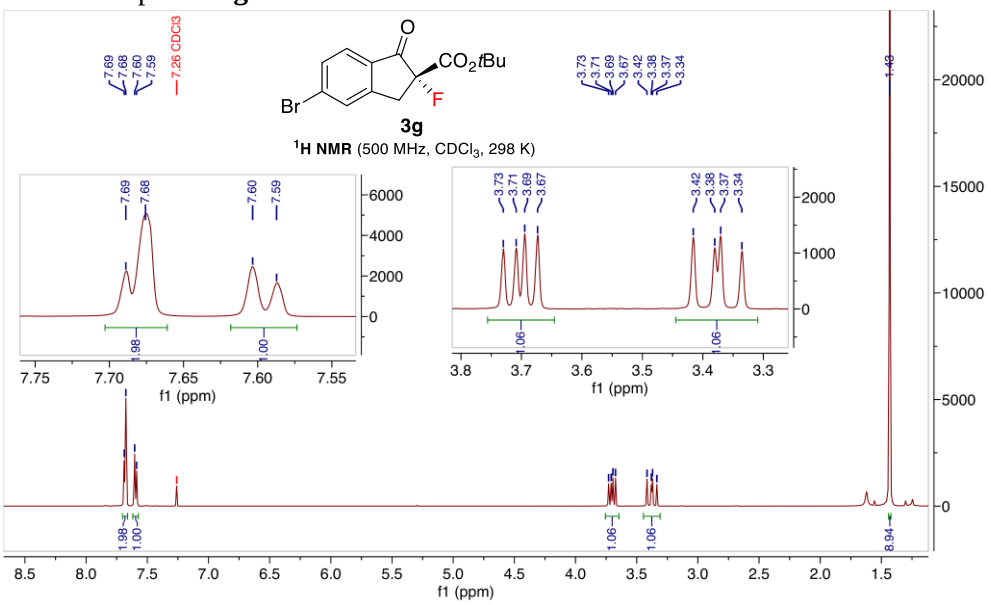
NMR spectra of compound **3f**

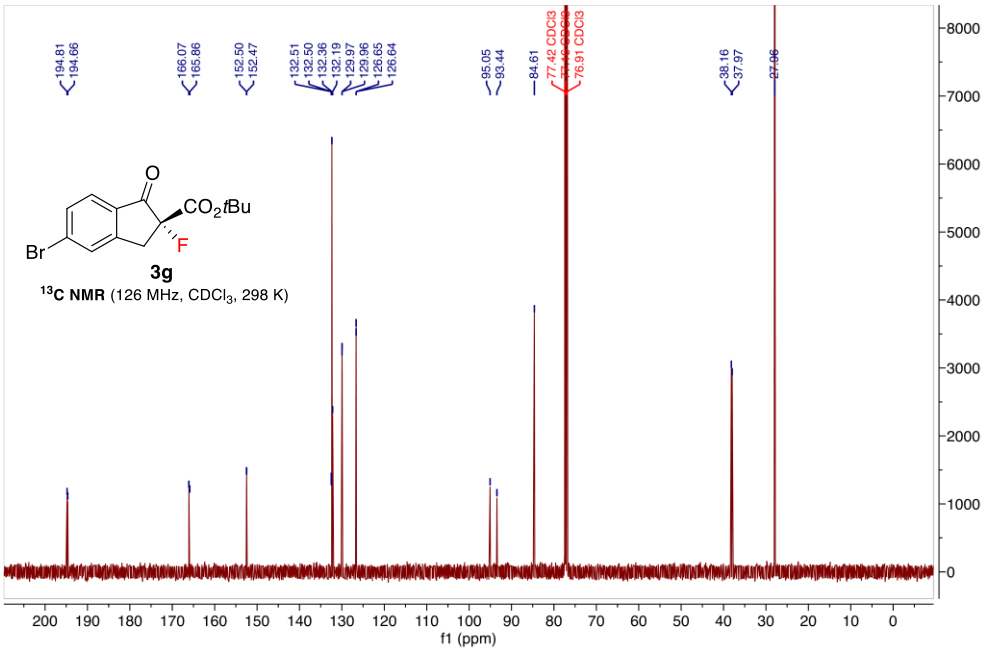


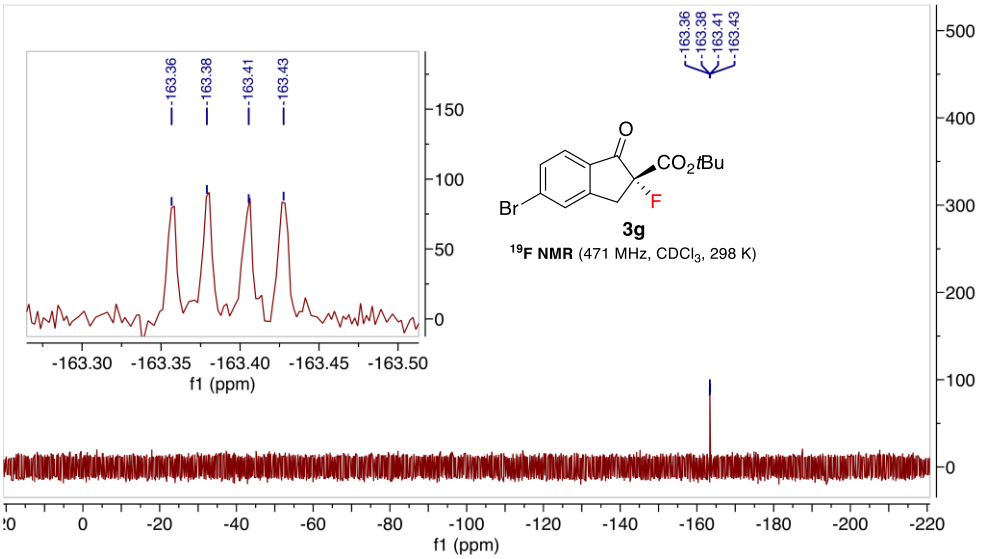




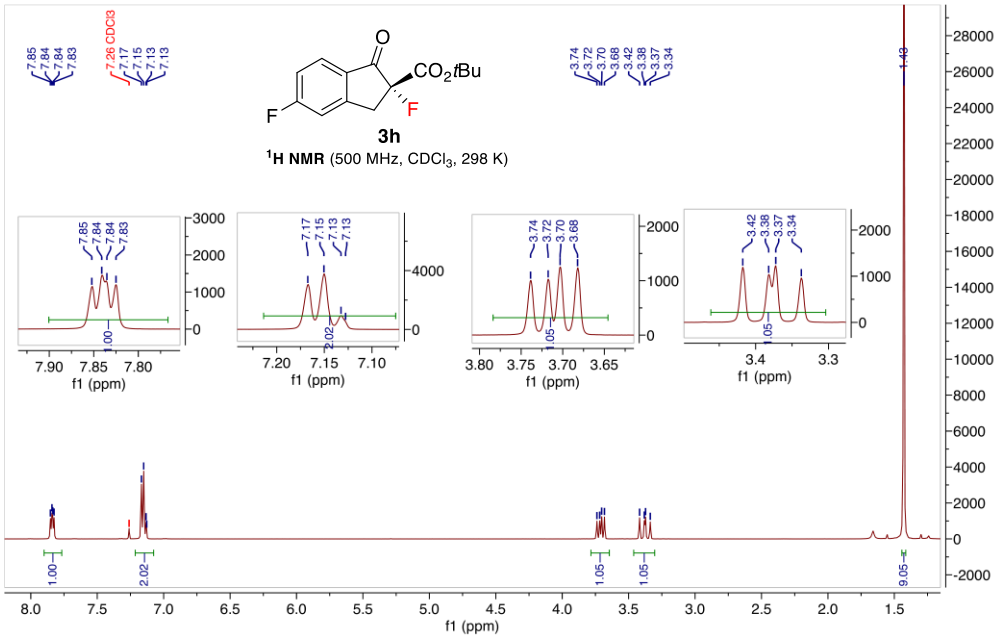
NMR spectra of compound **3g**

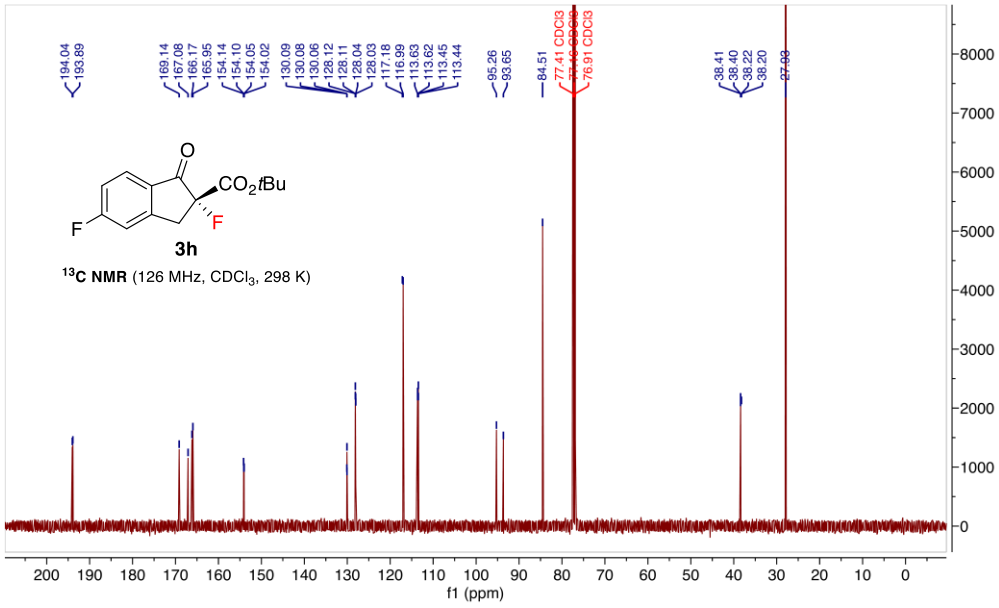


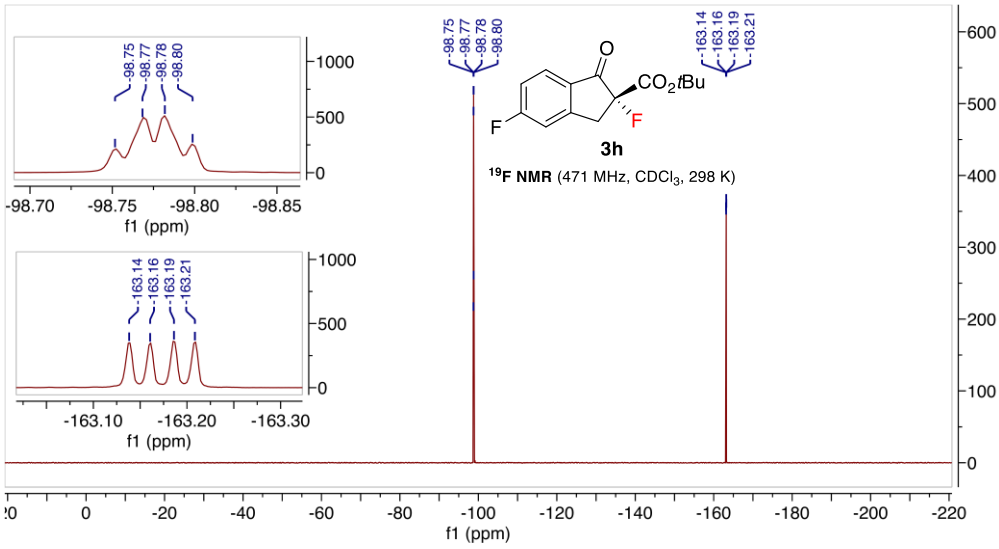




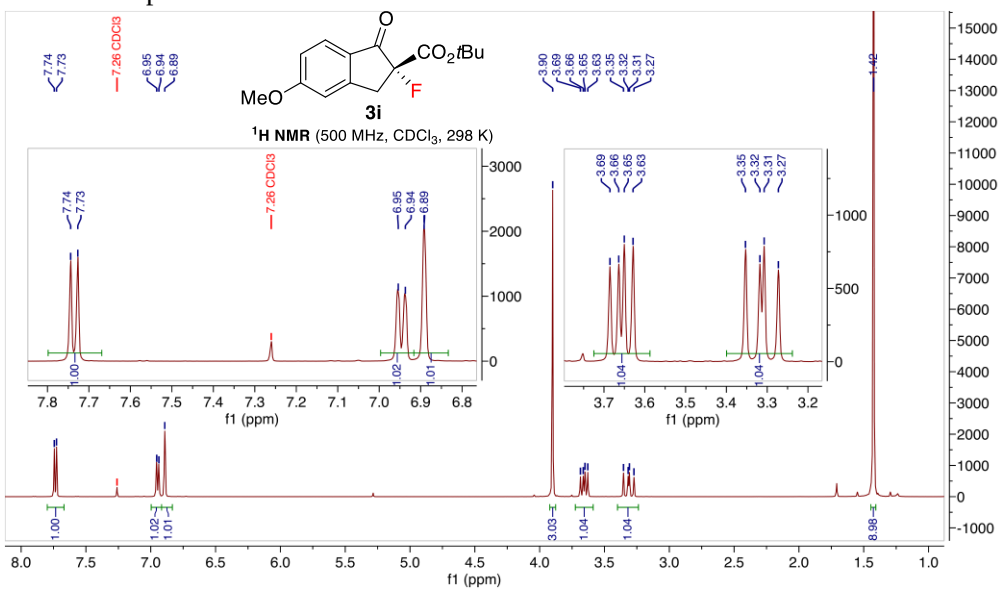
NMR spectra of compound **3h**

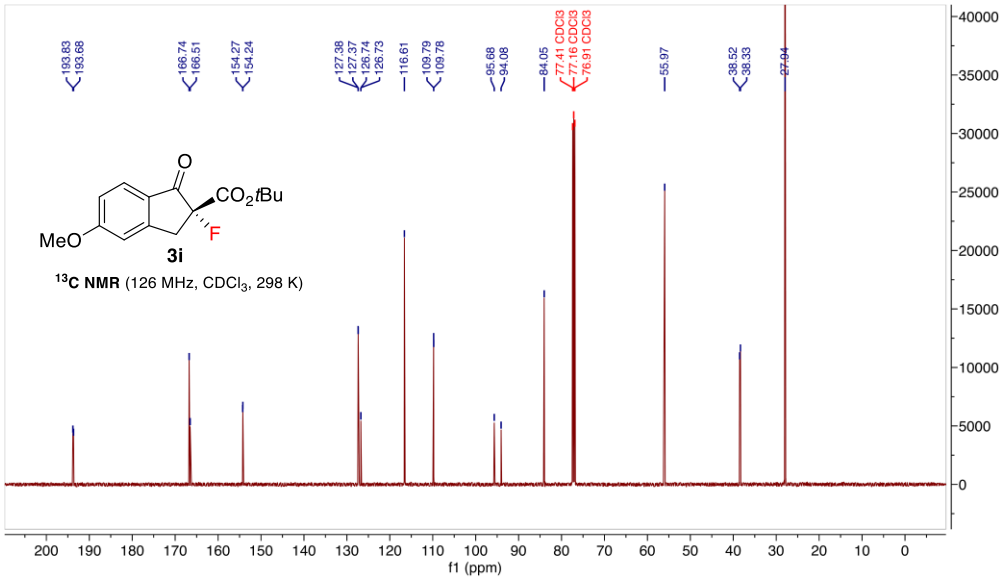


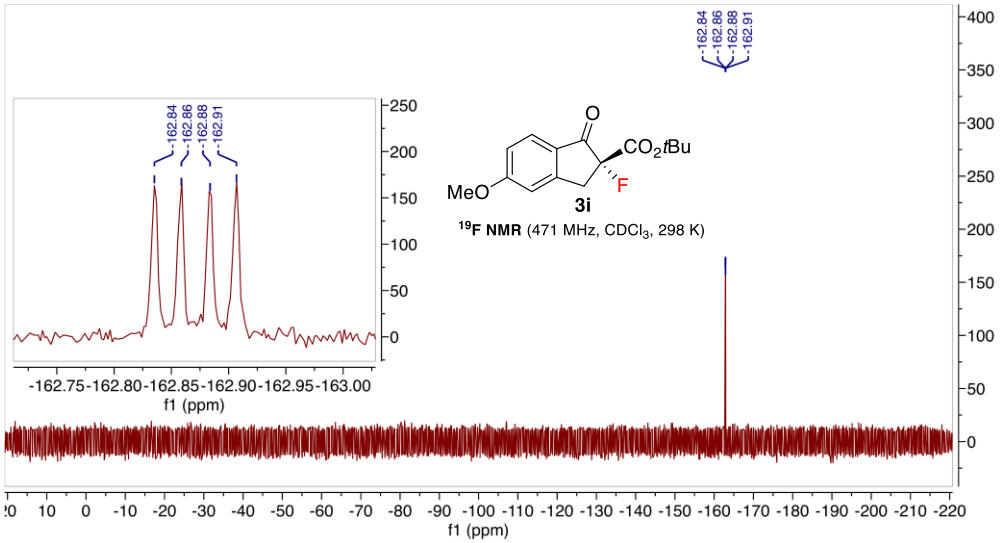




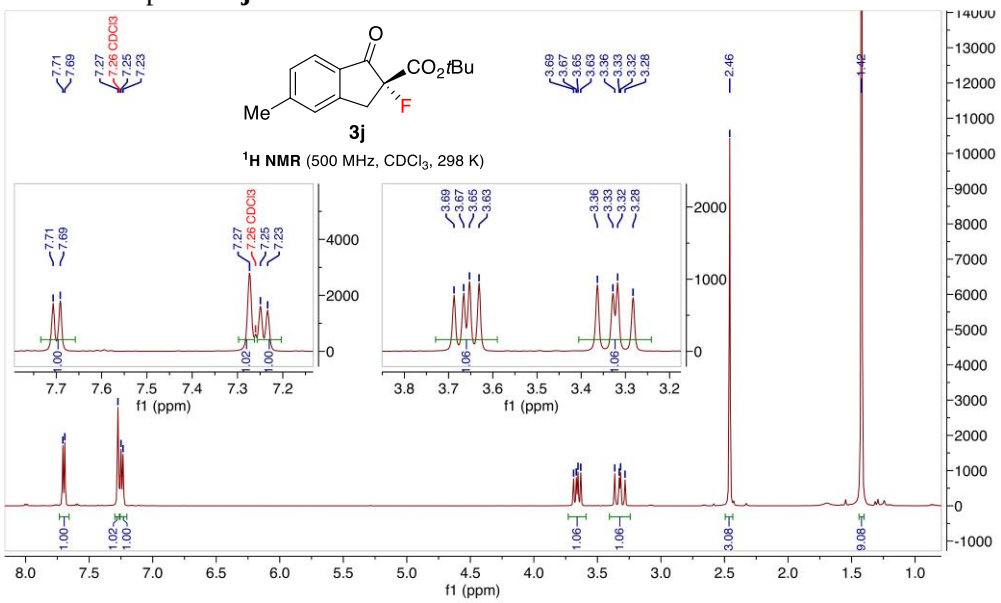
NMR spectra of compound **3i**

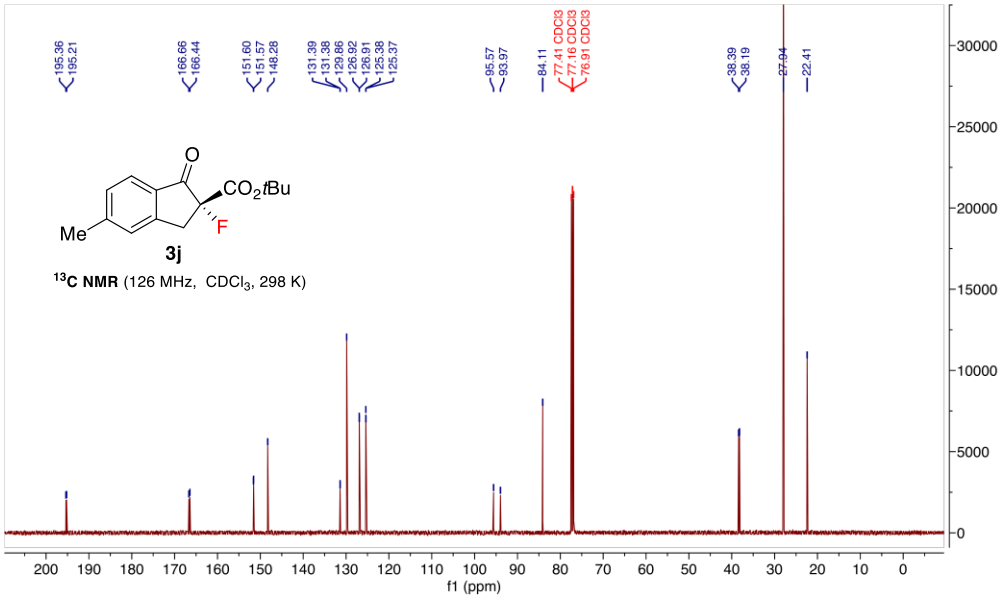


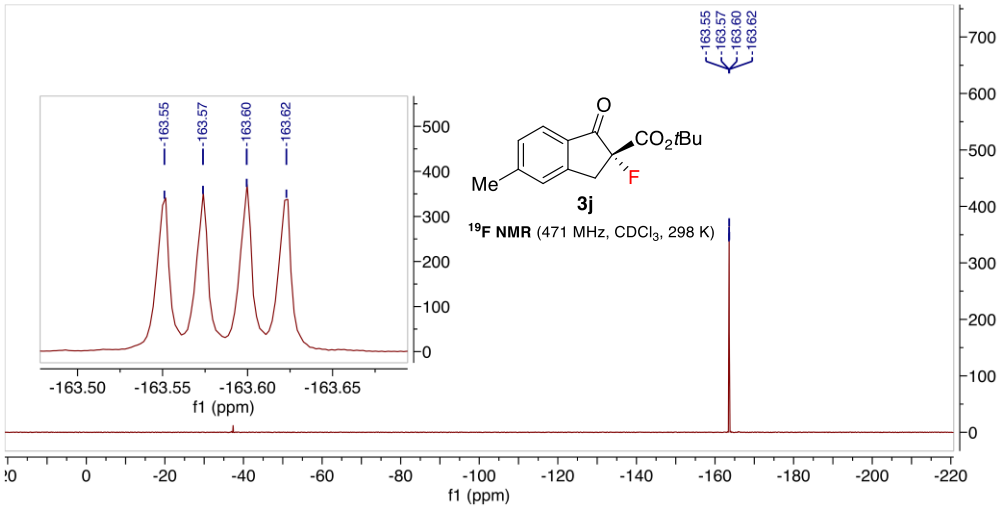




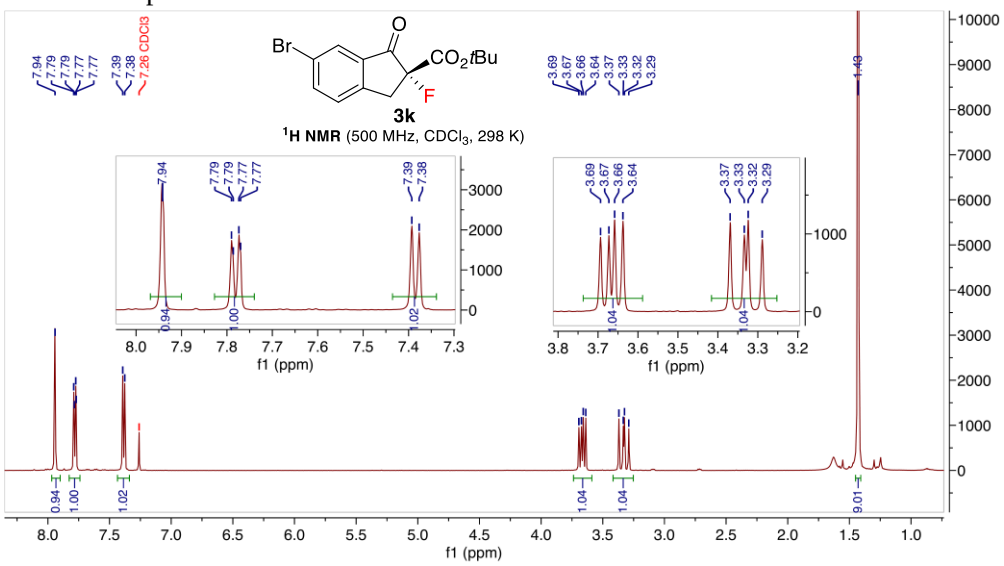
NMR spectra of compound **3j**

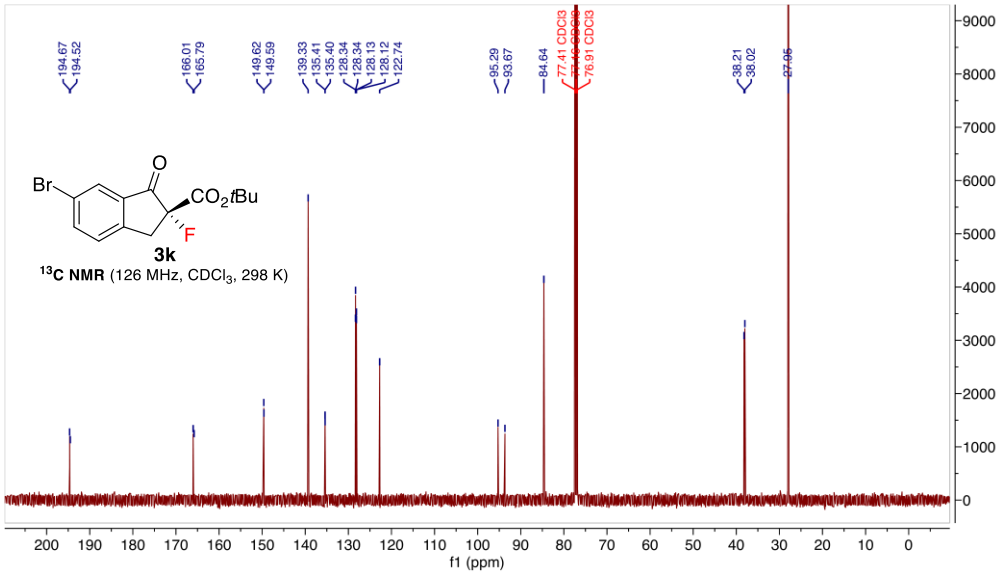


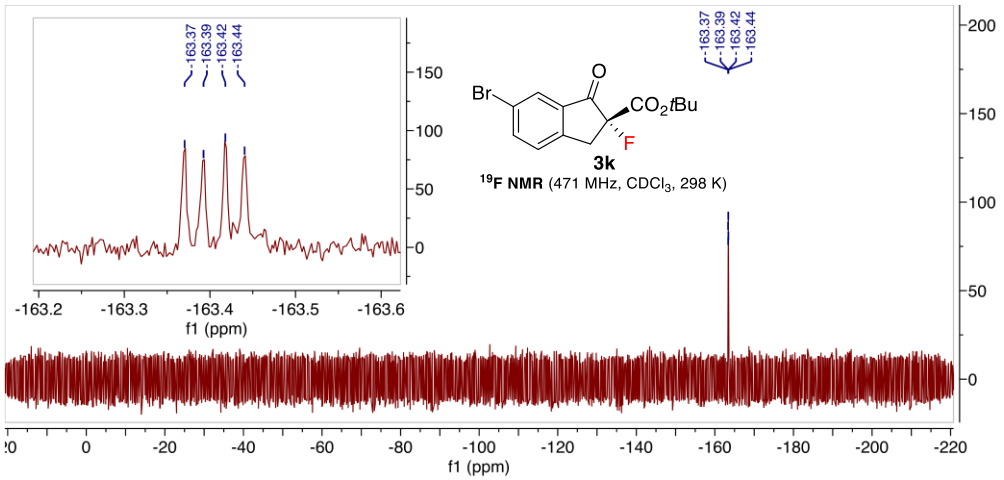




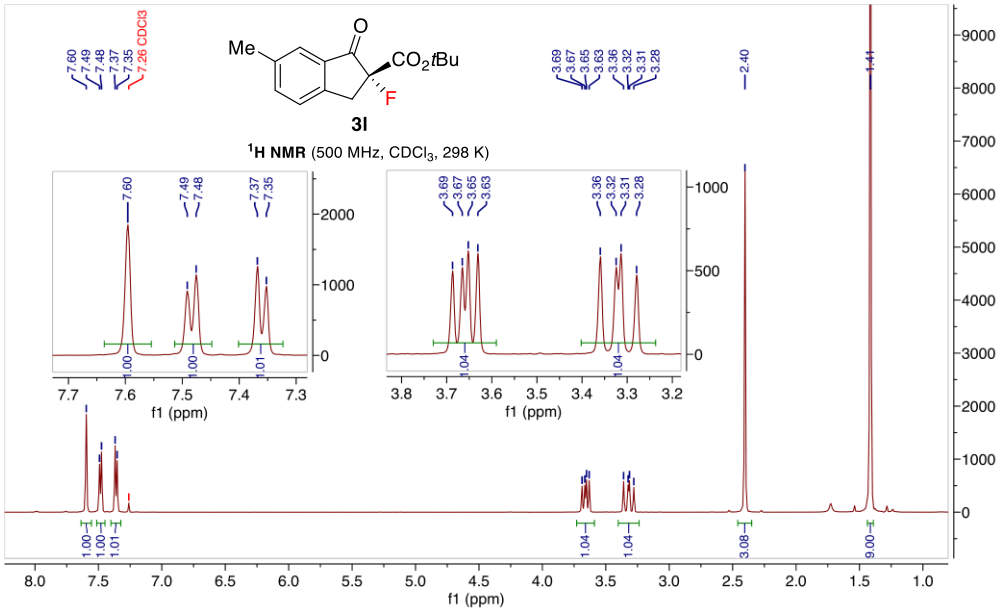
NMR spectra of compound **3k**

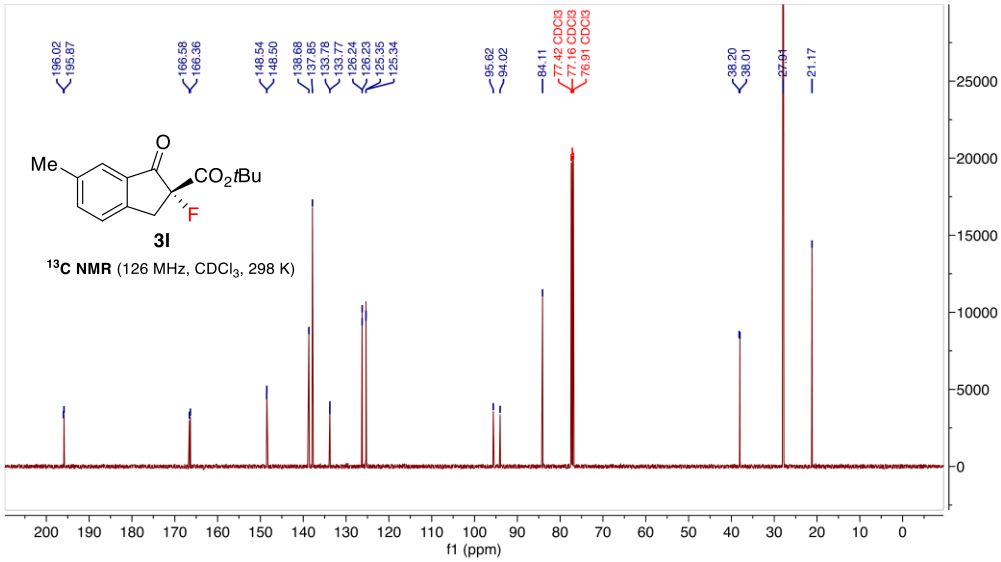


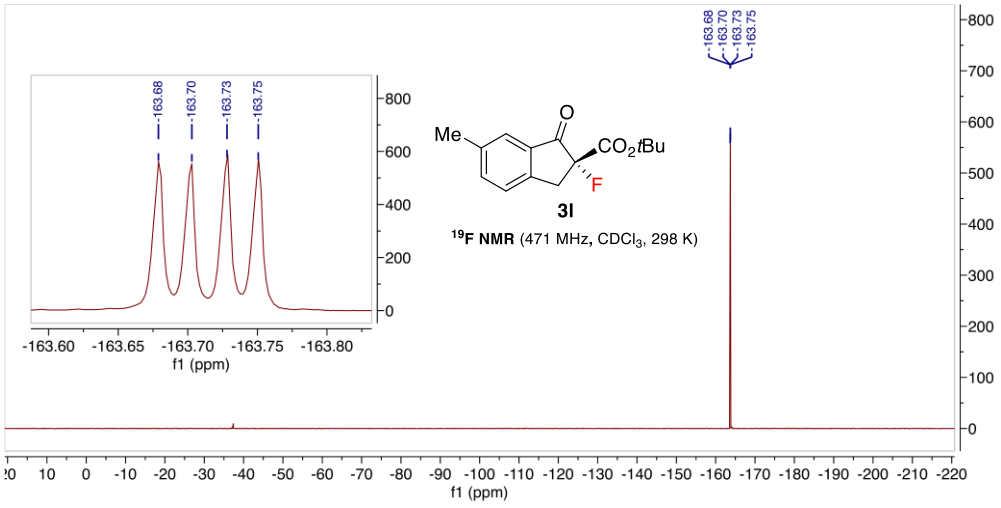




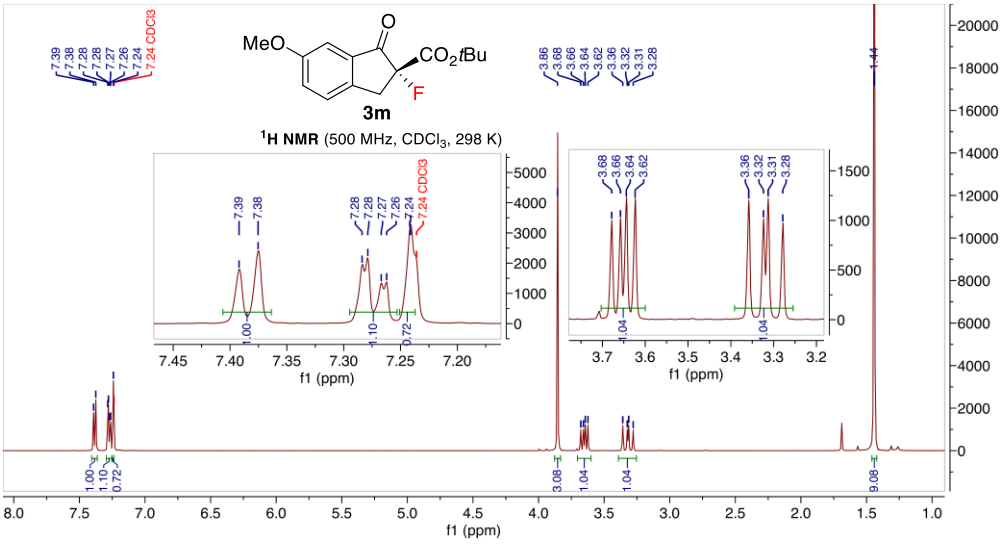
NMR spectra of compound **3l**

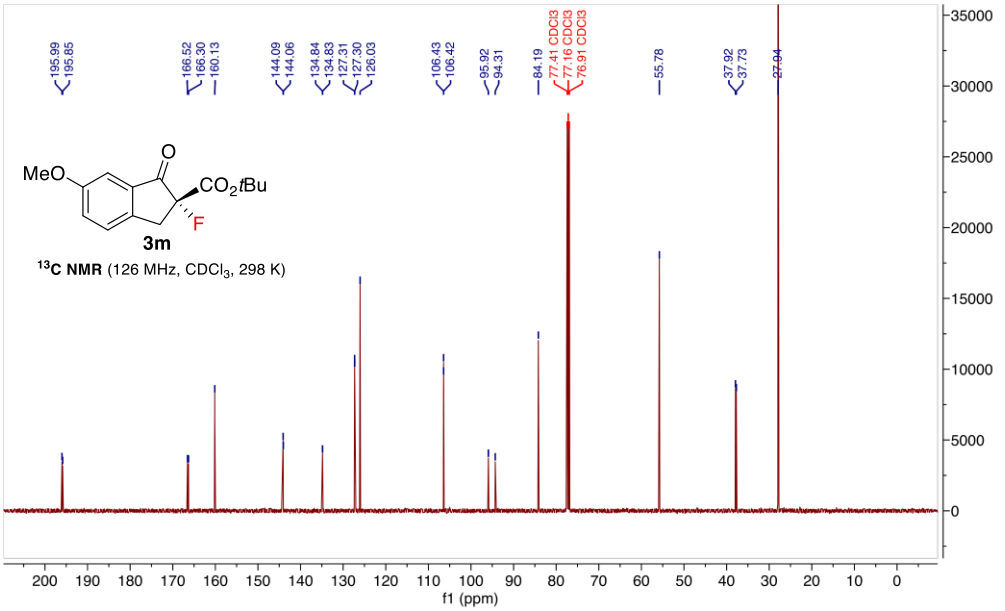


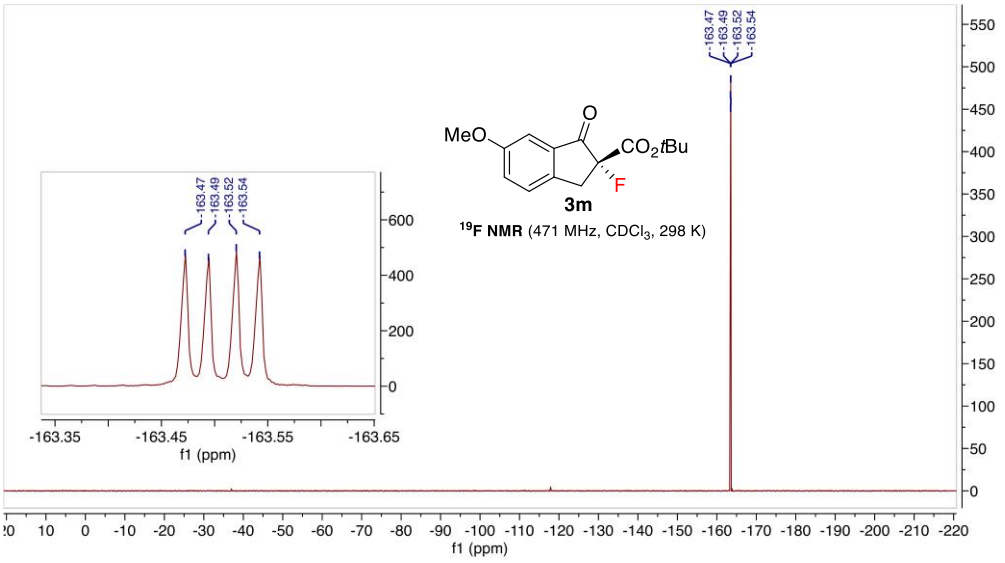




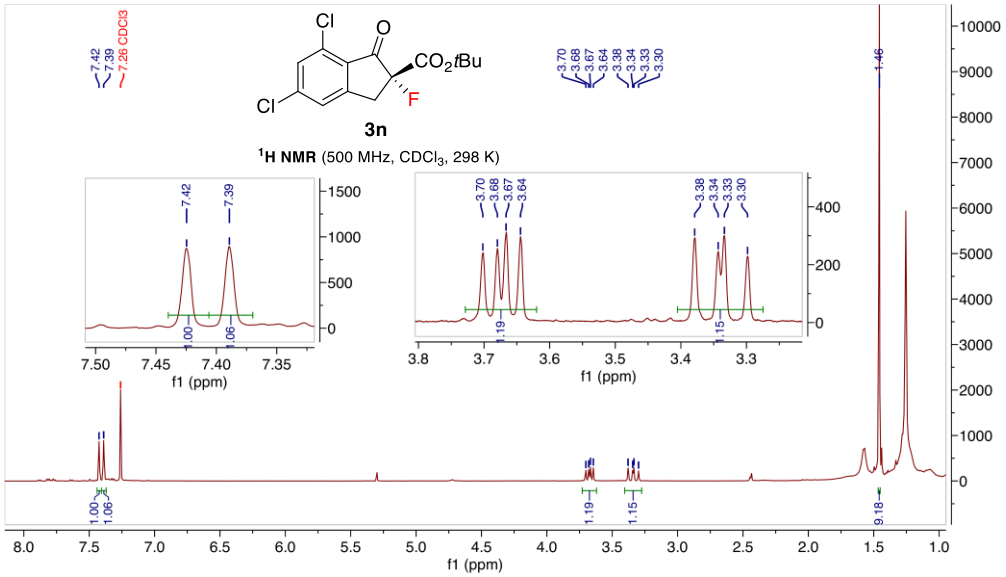
NMR spectra of compound **3m**

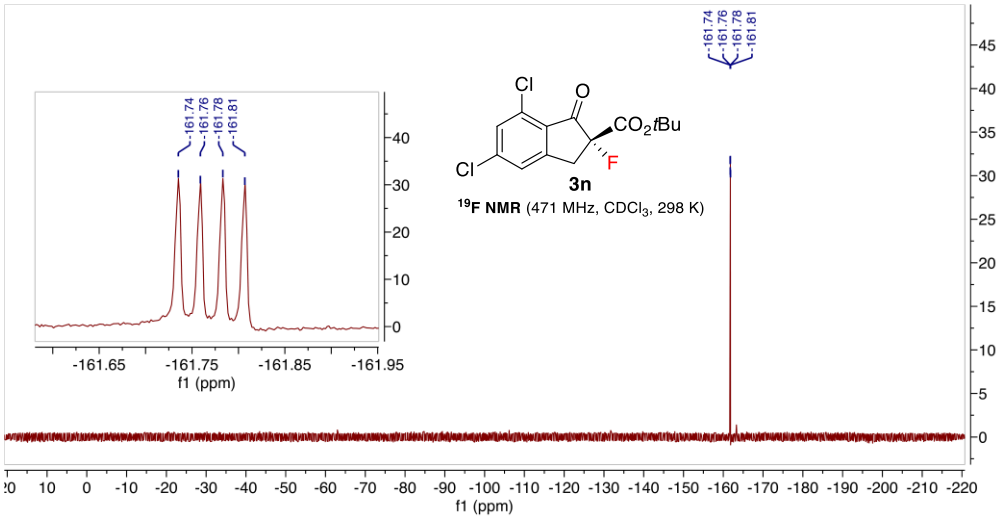






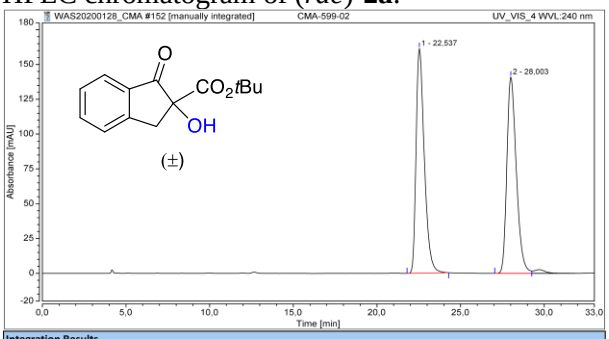
NMR spectra of compound **3n**





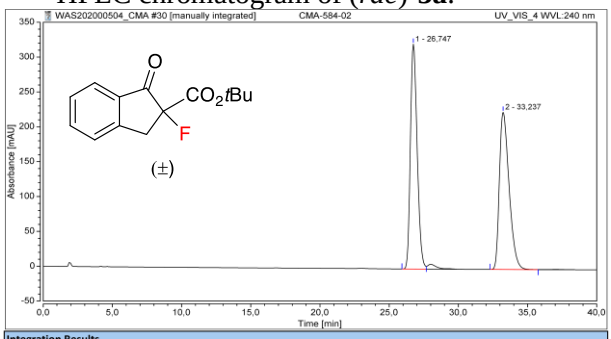
5. HPLC Traces of Hydroxylation/Deoxyfluorination Products:

HPLC chromatogram of (*rac*)-**2a**:



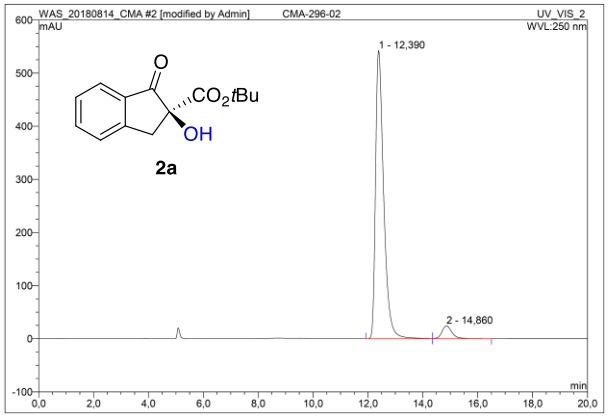
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22,537	91,945	161,562	49,90	53,37	n.a.
2		28,003	92,312	141,184	50,10	46,63	n.a.
Total:			184,256	302,746	100,00	100,00	

HPLC chromatogram of (*rac*)-**3a**:



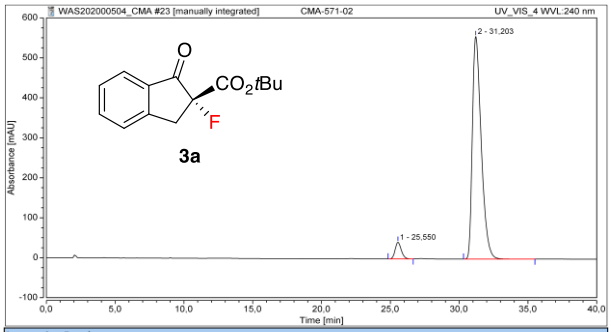
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26,747	182,353	322,737	49,88	58,84	n.a.
2		33,237	183,238	225,749	50,12	41,16	n.a.
Total:			365,591	548,486	100,00	100,00	

HPLC chromatogram of enantioenriched **2a**:



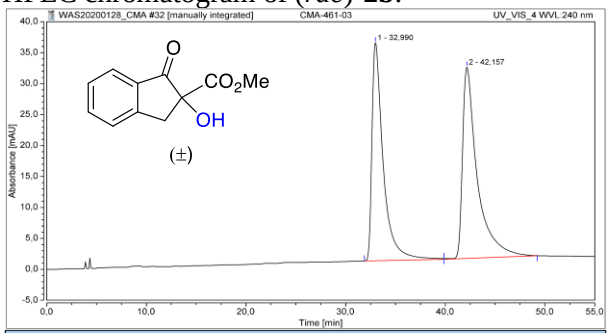
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,39	n.a.	542,205	186,382	94,83	n.a.	BM *
2	14,86	n.a.	24,208	10,151	5,17	n.a.	MB*
Total:			566,413	196,533	100,00	0,000	

HPLC chromatogram of enantioenriched **3a:**



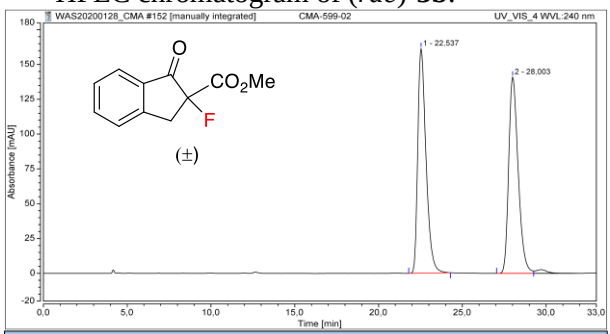
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25,550	21,634	41,719	4,95	6,97	n.a.
2		31,203	415,828	556,534	95,05	93,03	n.a.
Total:			437,461	598,254	100,00	100,00	

HPLC chromatogram of (*rac*)-**2b**:



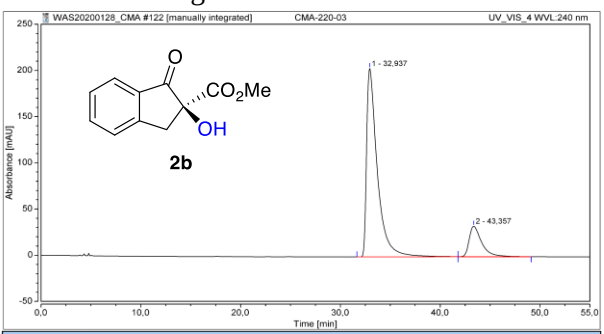
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32,990	46,202	35,227	46,62	53,27	n.a.
2		42,157	52,912	30,904	53,38	46,73	n.a.
Total:			99,114	66,131	100,00	100,00	

HPLC chromatogram of (*rac*)-**3b**:



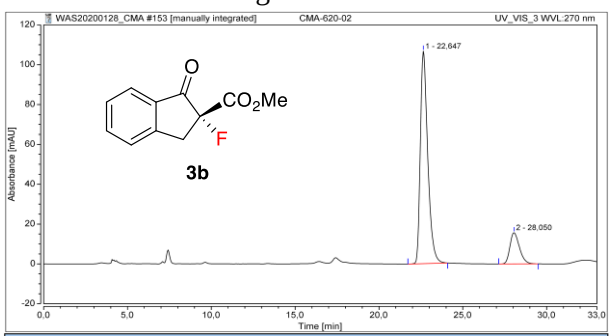
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22,537	91,945	161,562	49,90	53,37	n.a.
2		28,003	92,312	141,184	50,10	46,63	n.a.
Total:			184,256	302,746	100,00	100,00	

HPLC chromatogram of enantioenriched **2b**:



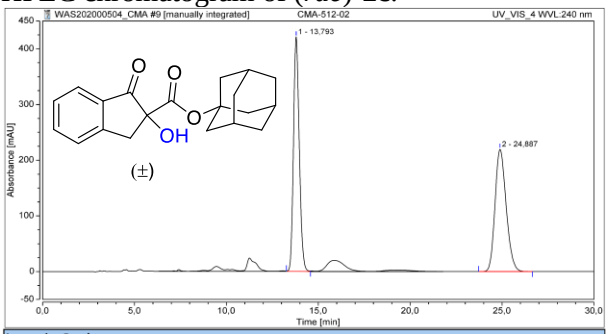
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32,937	254,356	203,877	84,01	86,06	n.a.
2		43,357	48,408	33,021	15,99	13,94	n.a.
Total:			302,764	236,898	100,00	100,00	

HPLC chromatogram of enantioenriched **3b:**



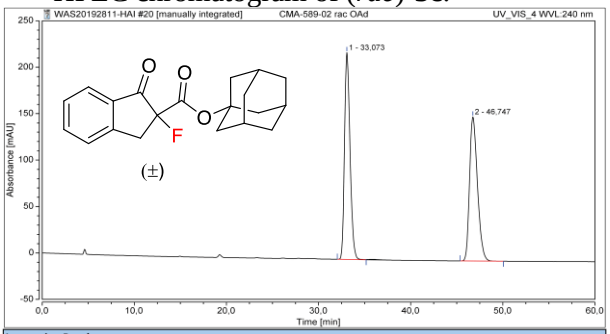
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22,647	54,698	106,683	84,15	87,18	n.a.
2		28,050	10,301	15,694	15,85	12,82	n.a.
Total:			64,999	122,377	100,00	100,00	

HPLC chromatogram of (*rac*)-**2c**:



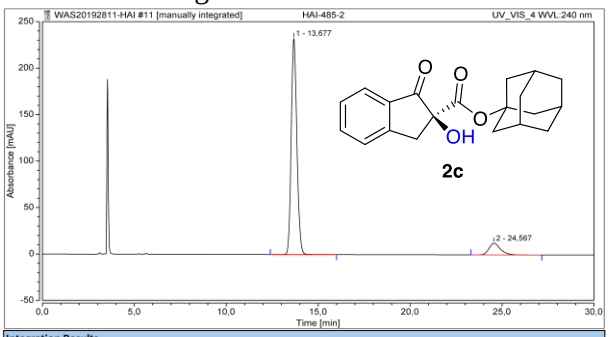
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,793	153,585	421,390	49,99	65,73	n.a.
2		24,887	153,631	219,675	50,01	34,27	n.a.
Total:			307,217	641,065	100,00	100,00	

HPLC chromatogram of (*rac*)-**3c**:



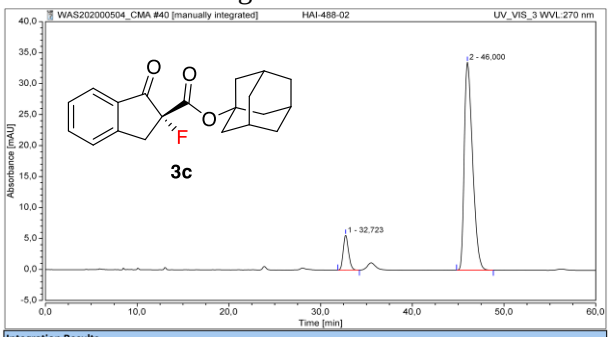
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33,073	154,415	222,720	49,98	58,93	n.a.
2		46,747	154,517	155,192	50,02	41,07	n.a.
Total:			308,932	377,913	100,00	100,00	

HPLC chromatogram of enantioenriched **2c**:



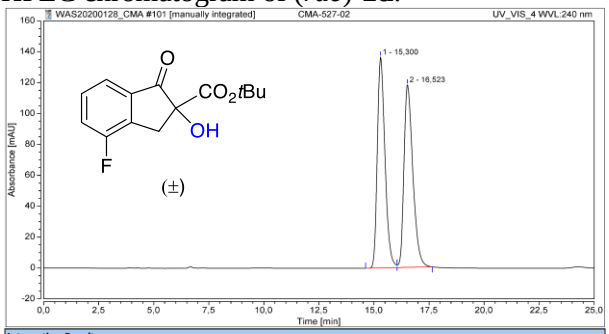
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,677	82,426	232,563	90,19	94,88	n.a.
2		24,567	8,969	12,547	9,81	5,12	n.a.
Total:			91,395	245,111	100,00	100,00	

HPLC chromatogram of enantioenriched **3c**:



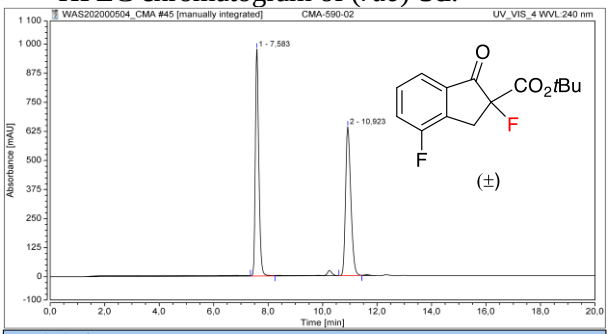
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32,723	3,788	5,644	9,71	14,39	n.a.
2		46,000	35,228	33,567	90,29	85,61	n.a.
Total:			39,016	39,211	100,00	100,00	

HPLC chromatogram of (*rac*)-**2d**:



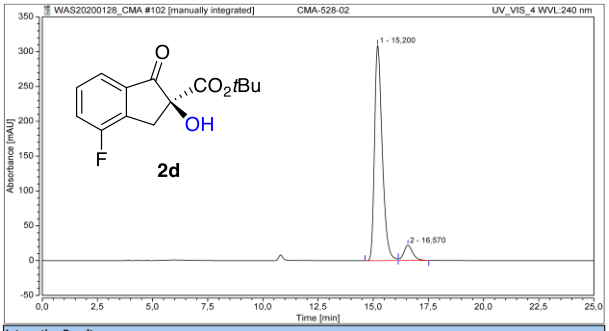
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,300	55,024	136,547	49,90	53,60	n.a.
2		16,523	55,255	118,189	50,10	46,40	n.a.
Total:			110,279	254,735	100,00	100,00	

HPLC chromatogram of (*rac*)-**3d**:



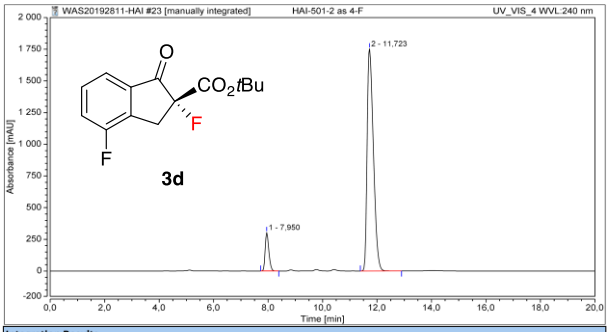
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7,583	143,921	975,960	50,03	60,38	n.a.
2		10,923	143,732	640,460	49,97	39,62	n.a.
Total:			287,654	1616,420	100,00	100,00	

HPLC chromatogram of enantioenriched **2d**:



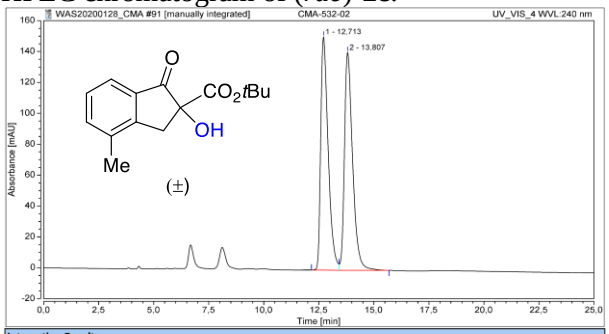
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,200	125,625	308,996	92,49	93,45	n.a.
2		16,570	10,203	21,660	7,51	6,55	n.a.
Total:			135,828	330,656	100,00	100,00	

HPLC chromatogram of enantioenriched **3d**:



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7,950	46,892	303,785	9,12	14,77	n.a.
2		11,723	467,503	1752,719	90,88	85,23	n.a.
Total:			514,395	2056,504	100,00	100,00	

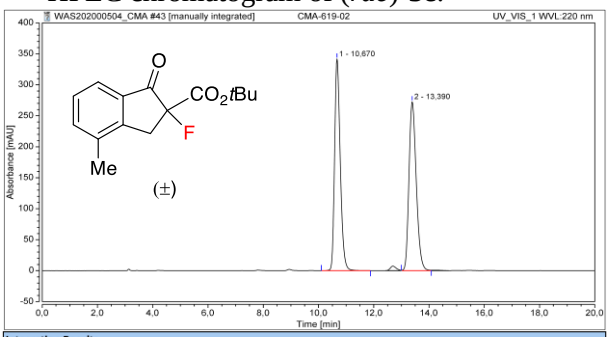
HPLC chromatogram of (*rac*)-**2e**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,713	59,116	151,082	49,37	51,72	n.a.
2		13,807	60,623	141,022	50,63	48,28	n.a.
Total:			119,740	292,103	100,00	100,00	

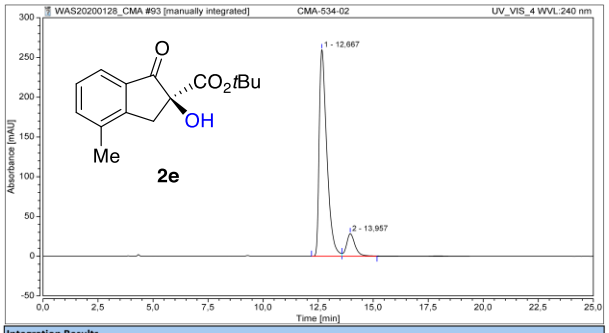
HPLC chromatogram of (*rac*)-**3e**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10,670	82,074	341,767	49,73	55,62	n.a.
2		13,390	82,979	272,699	50,27	44,38	n.a.
Total:			165,053	614,466	100,00	100,00	

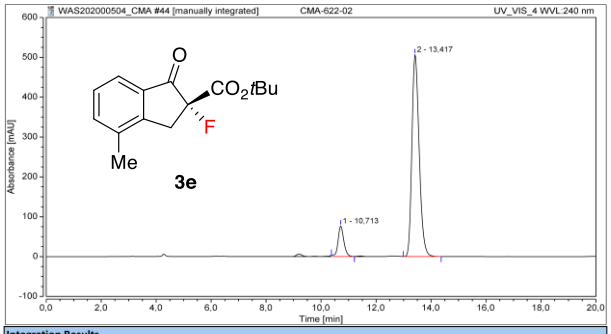
HPLC chromatogram of enantioenriched **2e**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,667	104,600	260,073	89,06	90,10	n.a.
2		13,957	12,844	28,592	10,94	9,90	n.a.

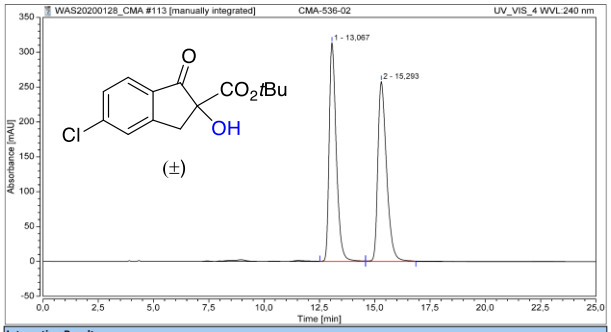
HPLC chromatogram of enantioenriched **3e**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10,713	18,625	76,891	10,79	13,18	n.a.
2		13,417	154,011	506,706	89,21	86,82	n.a.

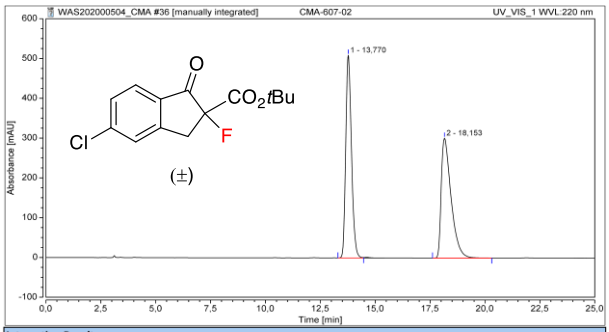
HPLC chromatogram of (*rac*)-**2f**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,067	117,588	313,742	49,89	54,83	n.a.
2		15,293	118,123	258,434	50,11	45,17	n.a.
Total:			235,711	572,176	100,00	100,00	

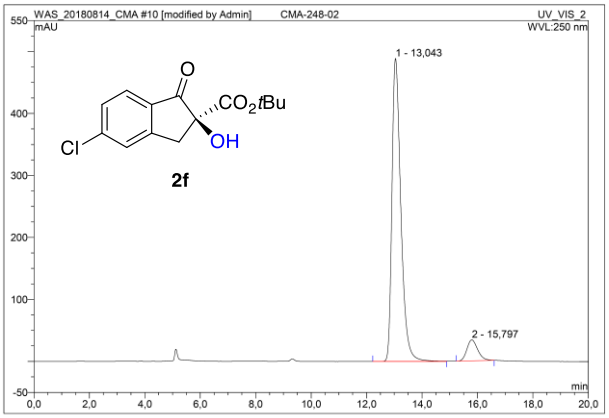
HPLC chromatogram of (*rac*)-**3f**



Integration Results

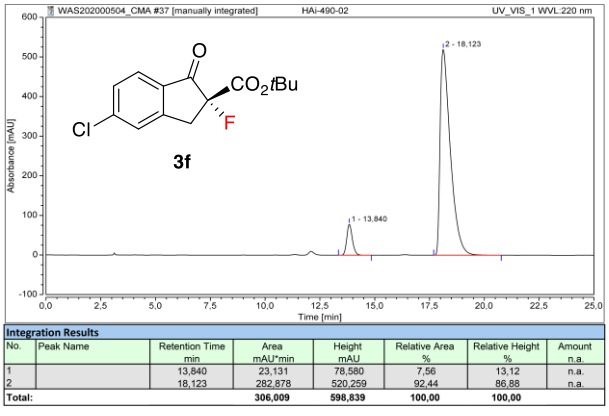
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,770	153,382	509,591	49,58	62,84	n.a.
2		18,153	155,955	301,321	50,42	37,16	n.a.
Total:			309,337	810,912	100,00	100,00	

HPLC chromatogram of enantioenriched **2f**:



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13,04	n.a.	488,885	181,909	92,29	n.a.	BM *
2	15,80	n.a.	33,769	15,207	7,71	n.a.	BMB*
Total:			522,654	197,116	100,00	0,000	

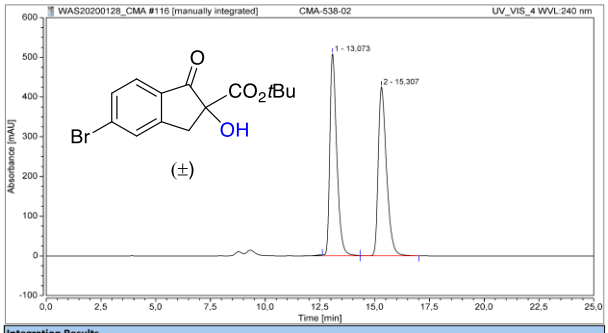
HPLC chromatogram of enantioenriched **3f**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,840	23,131	78,580	7,56	13,12	n.a.
2		18,123	282,878	520,259	92,44	86,88	n.a.
Total:			306,009	598,839	100,00	100,00	

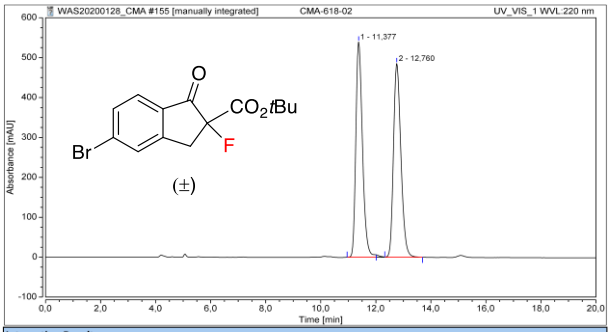
HPLC chromatogram of (*rac*)-**2g**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,073	187,292	509,107	50,08	54,46	n.a.
2		15,307	186,697	425,768	49,92	45,54	n.a.
Total:			**373,989**	**934,876**	**100,00**	**100,00**	

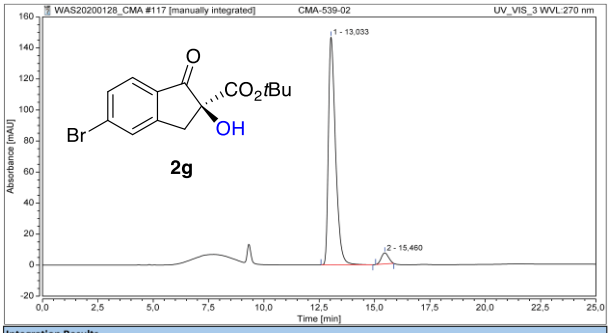
HPLC chromatogram of (*rac*)-**3g**



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11,377	150,355	539,411	49,89	52,63	n.a.
2		12,760	151,033	485,428	50,11	47,37	n.a.
Total:			**301,389**	**1024,839**	**100,00**	**100,00**	

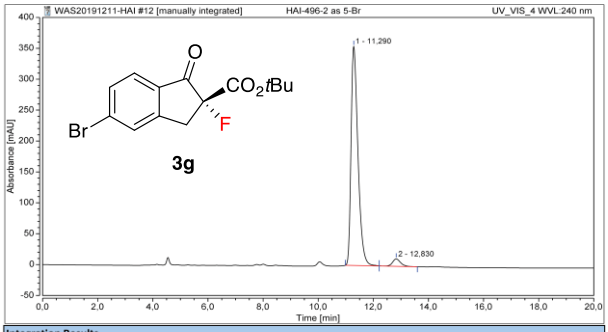
HPLC chromatogram of enantioenriched **2g**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,033	54,881	146,837	95,30	95,37	n.a.
2		15,460	2,709	7,125	4,70	4,63	n.a.
Total:			**57,590**	**153,962**	**100,00**	**100,00**	

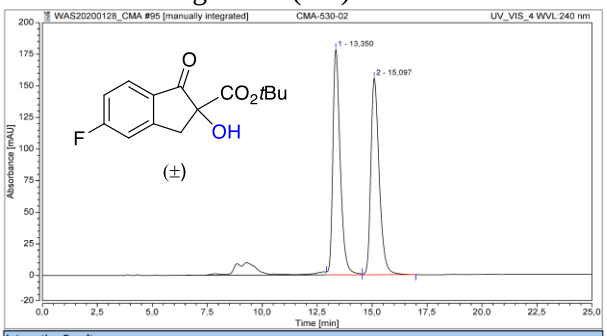
HPLC chromatogram of enantioenriched **3g**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11,290	102,179	354,780	96,18	96,74	n.a.
2		12,830	4,053	11,960	3,82	3,26	n.a.
Total:			**106,232**	**366,740**	**100,00**	**100,00**	

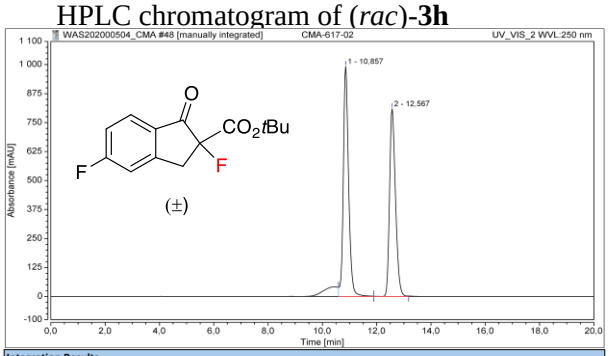
HPLC chromatogram of (*rac*)-**2h**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,350	69,566	178,840	50,23	53,41	n.a.
2		15,097	68,938	156,002	49,77	46,59	n.a.
Total:			**138,504**	**334,841**	**100,00**	**100,00**	

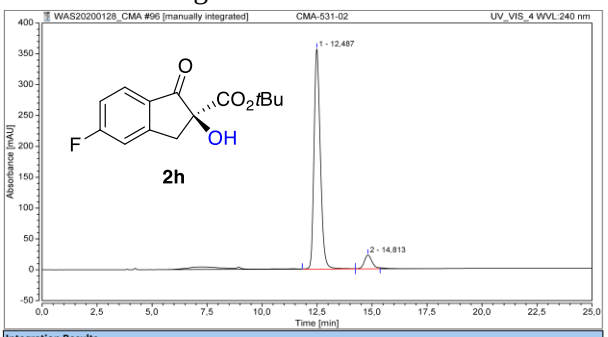
HPLC chromatogram of (*rac*)-**3h**



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10,857	223,344	991,753	52,10	55,07	n.a.
2		12,567	205,345	809,052	47,90	44,93	n.a.
Total:			**428,688**	**1800,806**	**100,00**	**100,00**	

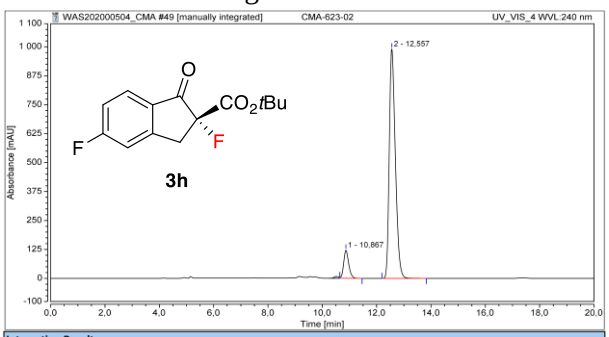
HPLC chromatogram of enantioenriched **2h**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,487	118,709	356,773	92,76	94,05	n.a.
2		14,813	9,263	22,560	7,24	5,95	n.a.
Total:			**127,972**	**379,333**	**100,00**	**100,00**	

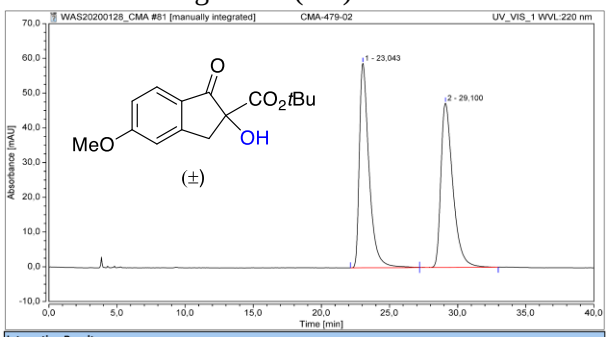
HPLC chromatogram of enantioenriched **3h**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10,867	25,966	122,260	9,16	10,98	n.a.
2		12,557	257,653	991,455	90,84	89,02	n.a.
Total:			**283,619**	**1113,714**	**100,00**	**100,00**	

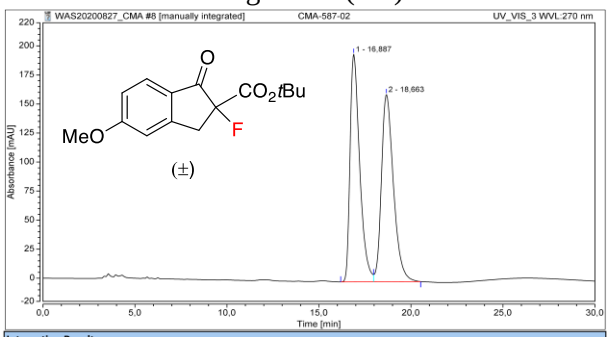
HPLC chromatogram of (*rac*)-**2i**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23,043	48,491	58,877	50,25	55,45	n.a.
2		29,100	48,014	47,297	49,75	44,55	n.a.
Total:			**96,505**	**106,174**	**100,00**	**100,00**	

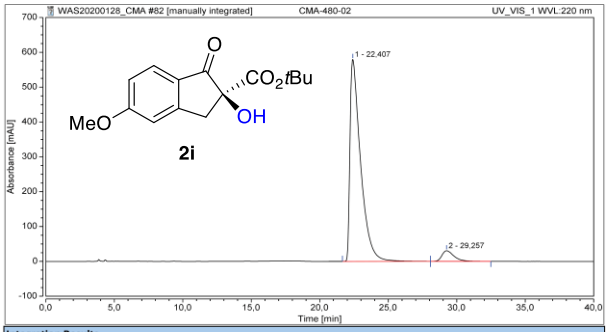
HPLC chromatogram of (*rac*)-**3i**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16,887	119,414	195,968	49,42	54,86	n.a.
2		18,663	122,230	161,244	50,58	45,14	n.a.
Total:			**241,643**	**357,213**	**100,00**	**100,00**	

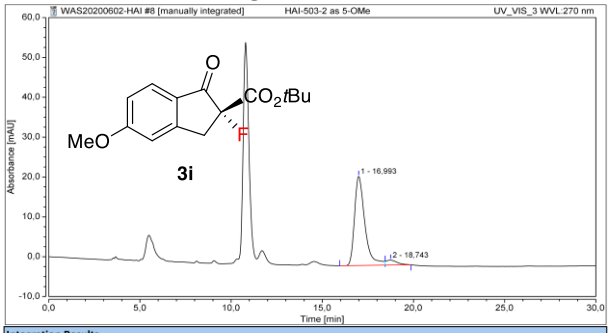
HPLC chromatogram of enantioenriched **2i**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22,407	519,786	579,835	94,31	94,99	n.a.
2		29,257	31,352	30,566	5,69	5,01	n.a.
Total:			**551,139**	**610,400**	**100,00**	**100,00**	

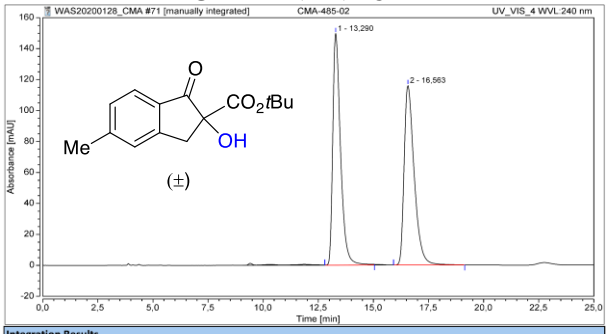
HPLC chromatogram of enantioenriched **3i**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16,993	14,648	22,364	94,34	94,77	n.a.
2		18,743	0,879	1,235	5,66	5,23	n.a.
Total:			**15,527**	**23,599**	**100,00**	**100,00**	

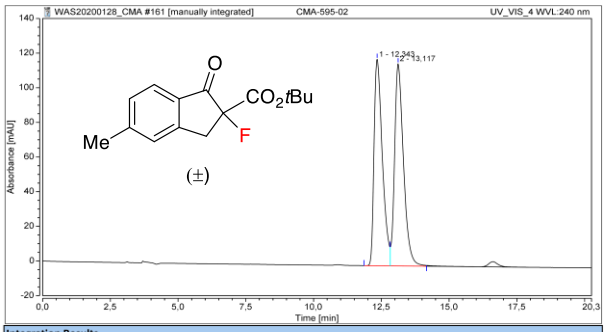
HPLC chromatogram of (*rac*)-**2j**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,290	61,156	149,691	50,00	56,33	n.a.
2		16,563	61,155	116,039	50,00	43,67	n.a.
Total:			**122,311**	**265,729**	**100,00**	**100,00**	

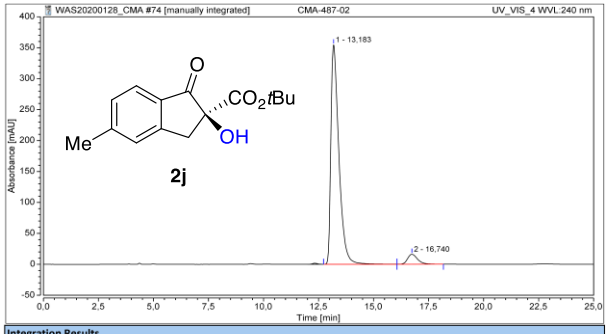
HPLC chromatogram of (*rac*)-**3j**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,343	42,137	119,209	48,65	50,52	n.a.
2		13,117	44,482	116,746	51,35	49,48	n.a.
Total:			**86,619**	**235,955**	**100,00**	**100,00**	

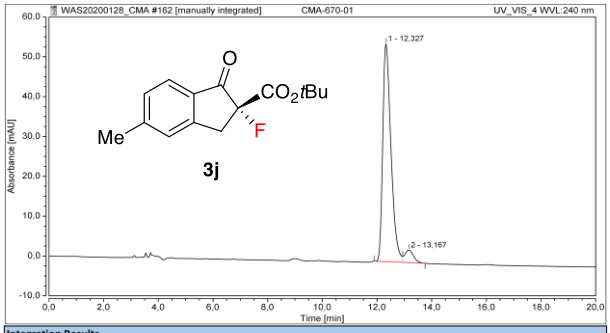
HPLC chromatogram of enantioenriched **2j**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13,183	149,290	354,739	94,64	95,64	n.a.
2		16,740	8,458	16,172	5,36	4,36	n.a.
Total:			**157,748**	**370,911**	**100,00**	**100,00**	

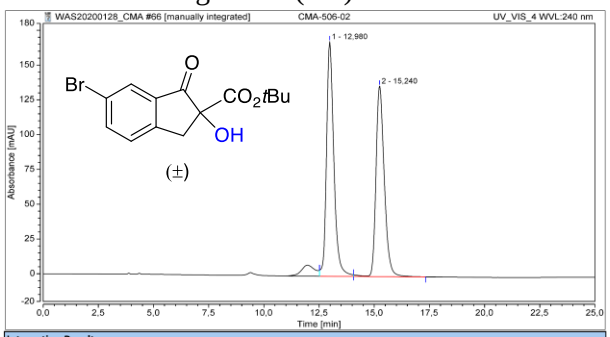
HPLC chromatogram of enantioenriched **3j**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,327	19,040	54,740	94,26	94,55	n.a.
2		13,167	1,159	3,156	5,74	5,45	n.a.
Total:			**20,199**	**57,896**	**100,00**	**100,00**	

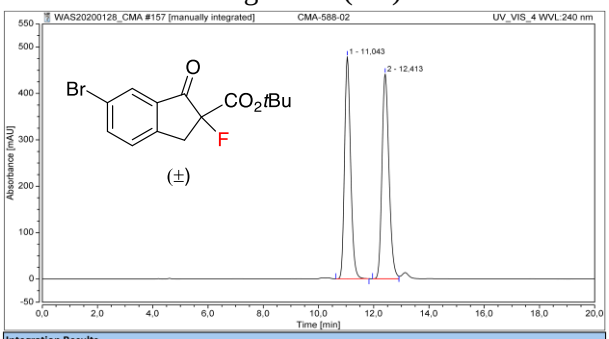
HPLC chromatogram of (*rac*)-**2k**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,980	64,779	168,772	51,97	55,19	n.a.
2		15,240	59,876	137,054	48,03	44,81	n.a.
Total:			**124,655**	**305,826**	**100,00**	**100,00**	

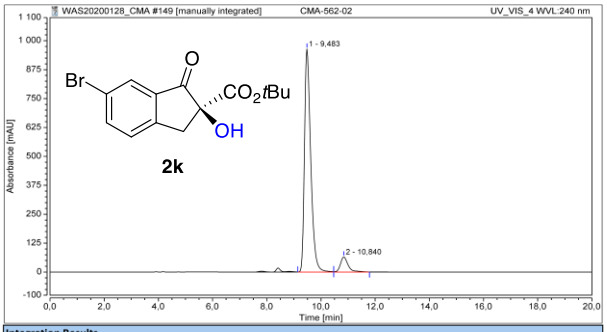
HPLC chromatogram of (*rac*)-**3k**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11,043	121,505	478,674	48,48	52,03	n.a.
2		12,413	129,110	441,359	51,52	47,97	n.a.
Total:			**250,614**	**920,033**	**100,00**	**100,00**	

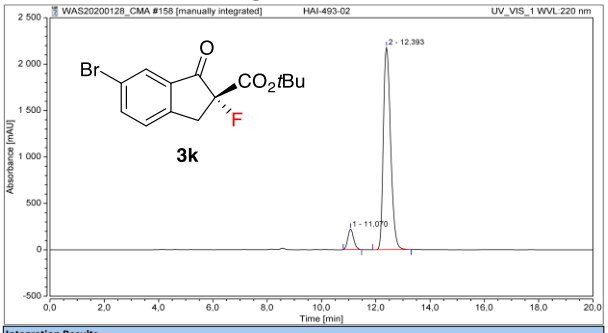
HPLC chromatogram of enantioenriched **2k**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9,483	258,713	964,302	92,24	93,64	n.a.
2		10,840	21,751	65,477	7,76	6,36	n.a.
Total:			**280,465**	**1029,779**	**100,00**	**100,00**	

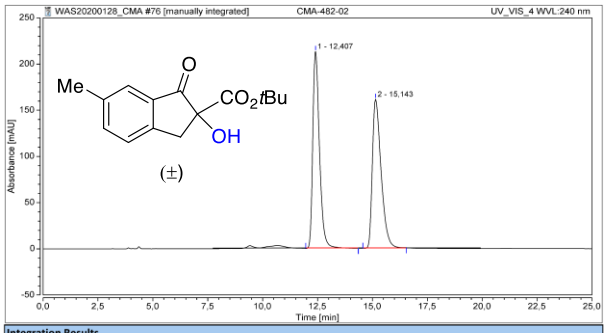
HPLC chromatogram of enantioenriched **3k**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11,070	54,503	220,467	7,47	9,18	n.a.
2		12,393	675,221	2180,545	92,53	90,82	n.a.
Total:			**729,724**	**2401,012**	**100,00**	**100,00**	

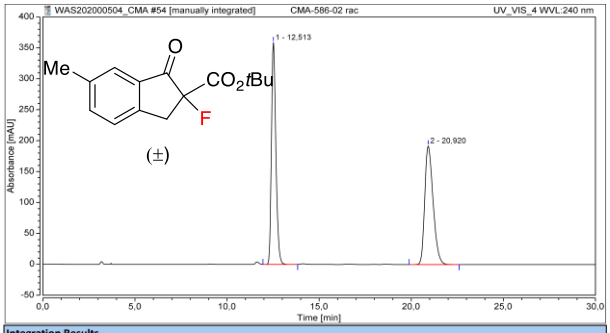
HPLC chromatogram of (*rac*)-**2l**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,407	74,069	212,777	50,01	56,92	n.a.
2		15,143	74,045	161,025	49,99	43,08	n.a.
Total:			**148,114**	**373,802**	**100,00**	**100,00**	

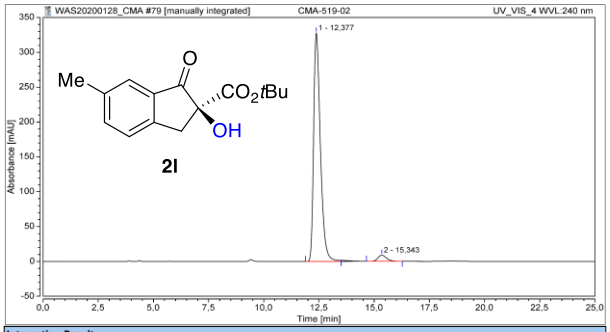
HPLC chromatogram of (*rac*)-**3l**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,513	99,784	358,905	49,79	65,15	n.a.
2		20,920	100,617	191,966	50,21	34,85	n.a.
Total:			**200,401**	**550,872**	**100,00**	**100,00**	

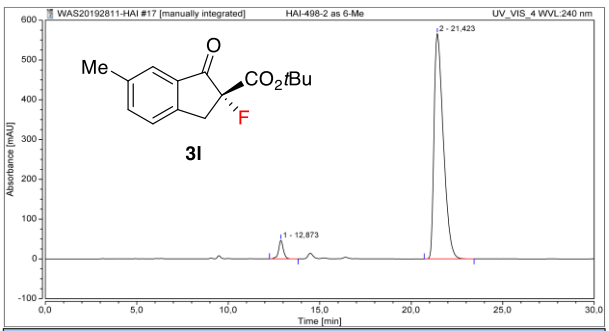
HPLC chromatogram of enantioenriched **2l**:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,377	115,841	327,890	96,68	97,37	n.a.
2		15,343	3,977	8,862	3,32	2,63	n.a.
Total:			**119,819**	**336,751**	**100,00**	**100,00**	

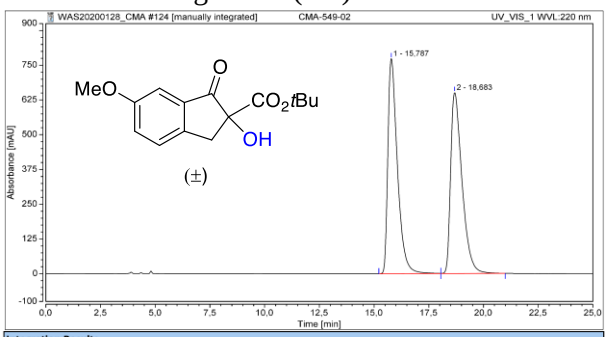
HPLC chromatogram of enantioenriched **3l**:



Integration Results

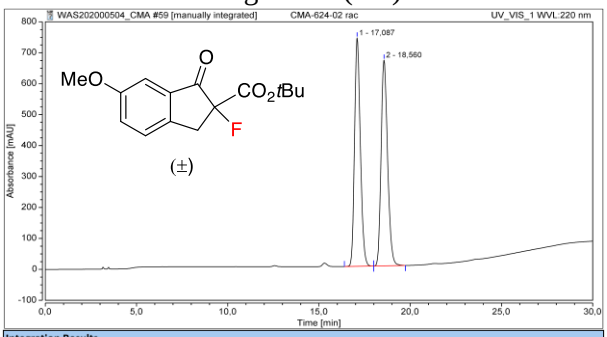
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12,873	13,993	46,778	4,03	7,63	n.a.
2		21,423	332,922	565,967	95,97	92,37	n.a.
Total:			**346,915**	**612,744**	**100,00**	**100,00**	

HPLC chromatogram of (*rac*)-**2m**:



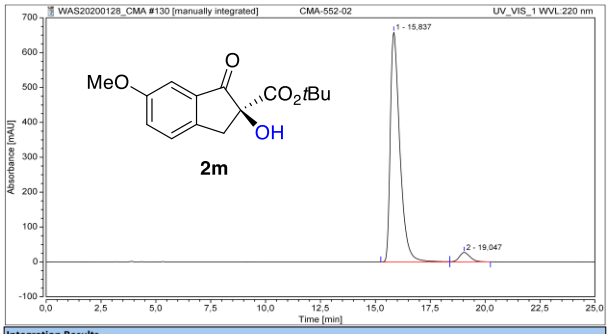
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,787	390,722	773,912	50,00	54,29	n.a.
2		18,683	390,754	651,506	50,00	45,71	n.a.
Total:			781,476	1425,419	100,00	100,00	

HPLC chromatogram of (*rac*)-**3m**:



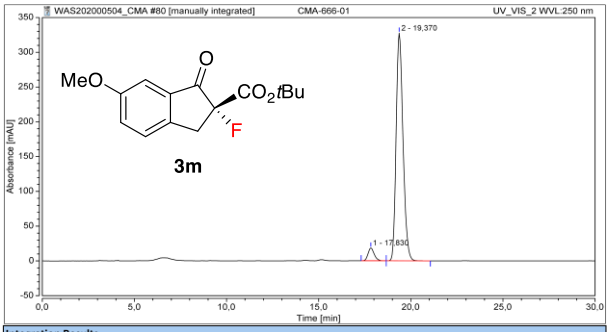
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,087	273,181	738,052	49,94	52,61	n.a.
2		18,560	273,868	664,940	50,06	47,39	n.a.
Total:			547,049	1402,992	100,00	100,00	

HPLC chromatogram of enantioenriched **2m**:



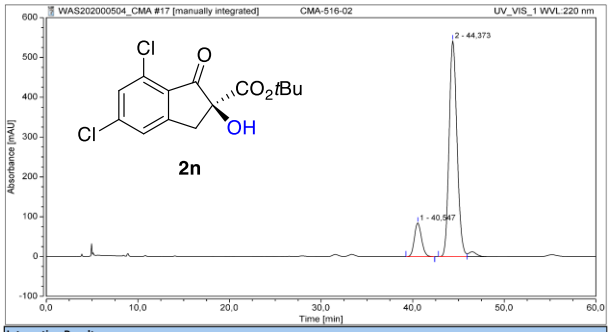
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15,837	331,718	658,813	95,57	96,09	n.a.
2		19,047	15,379	26,803	4,43	3,91	n.a.
Total:			347,097	685,617	100,00	100,00	

HPLC chromatogram of enantioenriched **3m**:



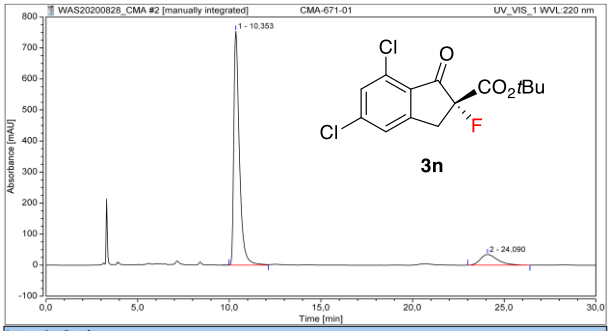
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17,830	7,091	18,385	4,77	5,32	n.a.
2		19,370	141,601	327,399	95,23	94,68	n.a.
Total:			148,692	345,784	100,00	100,00	

HPLC chromatogram of enantioenriched **2n**:



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		40,547	75,826	84,574	12,24	13,49	n.a.
2		44,373	543,531	542,194	87,76	86,51	n.a.
Total:			619,357	626,768	100,00	100,00	

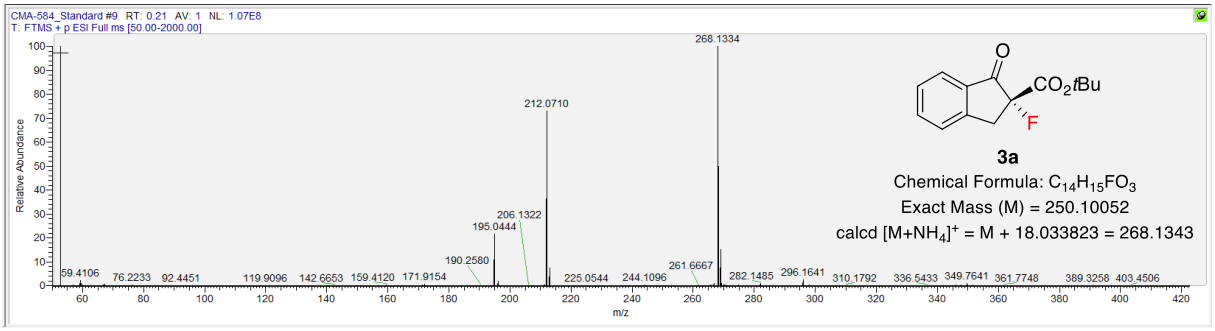
HPLC chromatogram of enantioenriched **3n**:



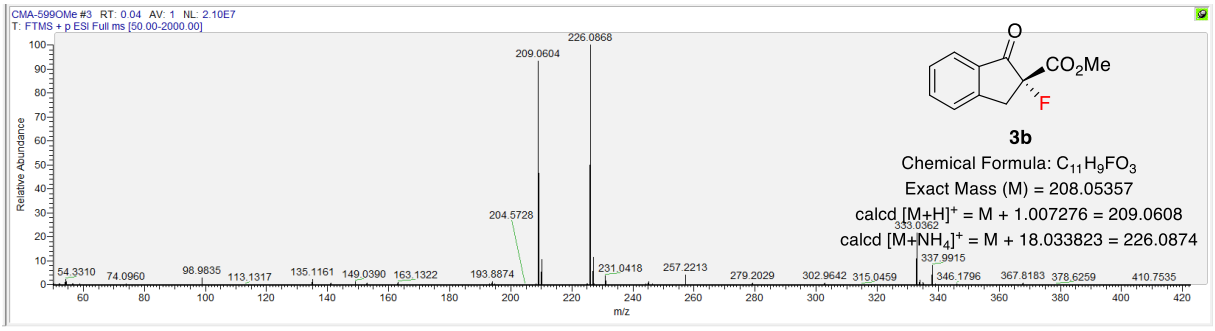
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10,353	267,161	753,922	87,74	95,67	n.a.
2		24,090	37,331	34,129	12,26	4,33	n.a.
Total:			304,492	788,052	100,00	100,00	

6. HRMS Data Report

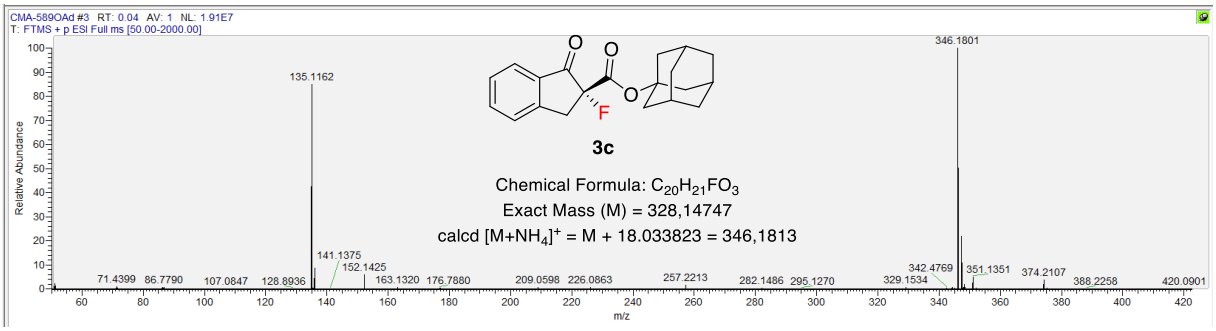
(*R*)-**3a**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{19}FO_3N$, 268.1343; found, 268.1334.



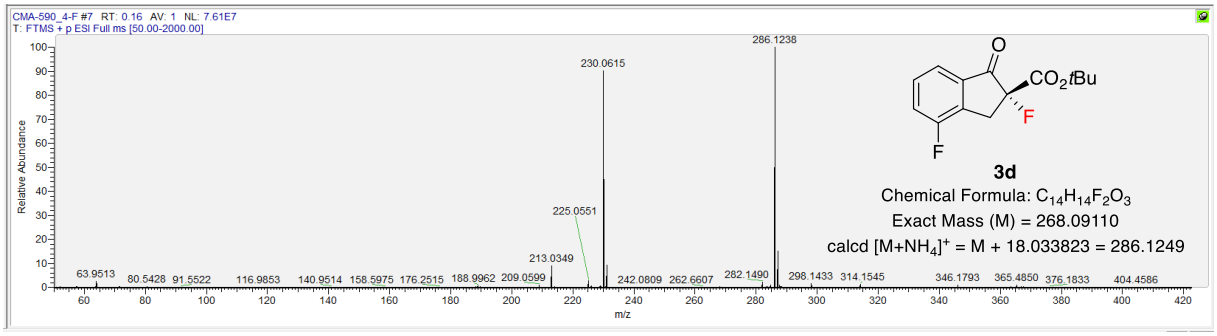
(*R*)-**3b**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{10}FO_3$, 209.0608; found, 209.0604. $[M + NH_4]^+$ calcd for $C_{11}H_{14}FO_3N$, 226.0874; found, 226.0868.



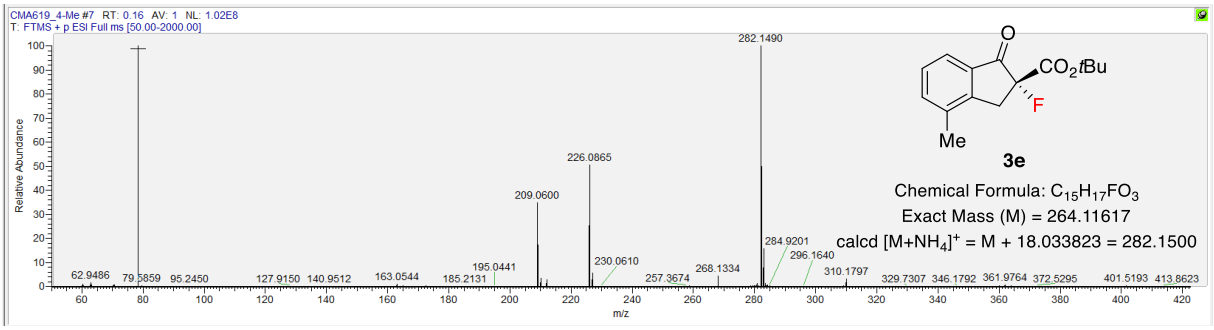
(*R*)-**3c**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{20}H_{25}FNO_3N$, 346.1813; found, 346.1801.



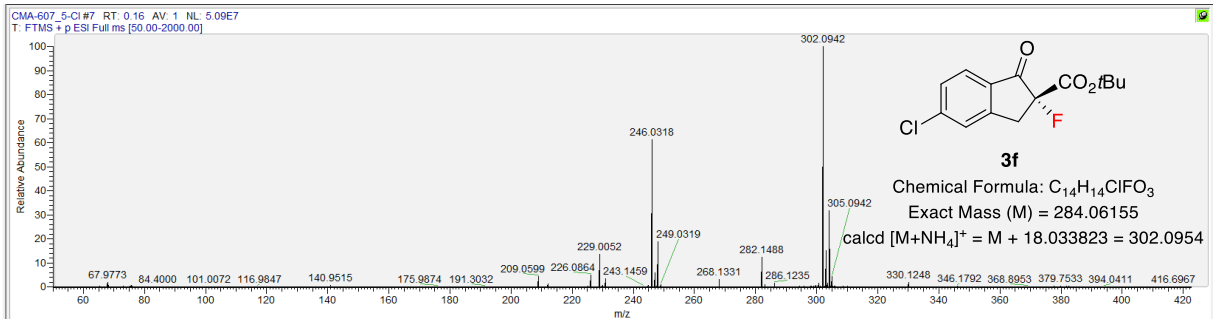
(*R*)-**3d**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}F_2O_3N$, 286.1249; found, 286.1238.



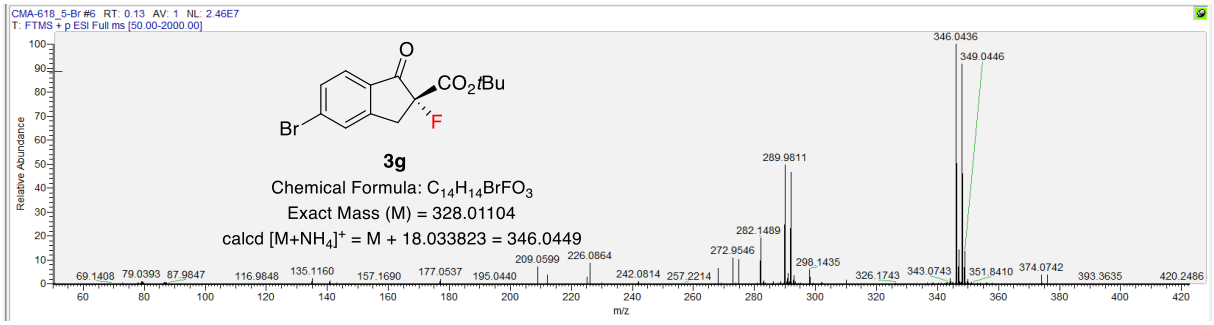
(*R*)-**3e**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_3N$, 282.1500; found, 282.1490.



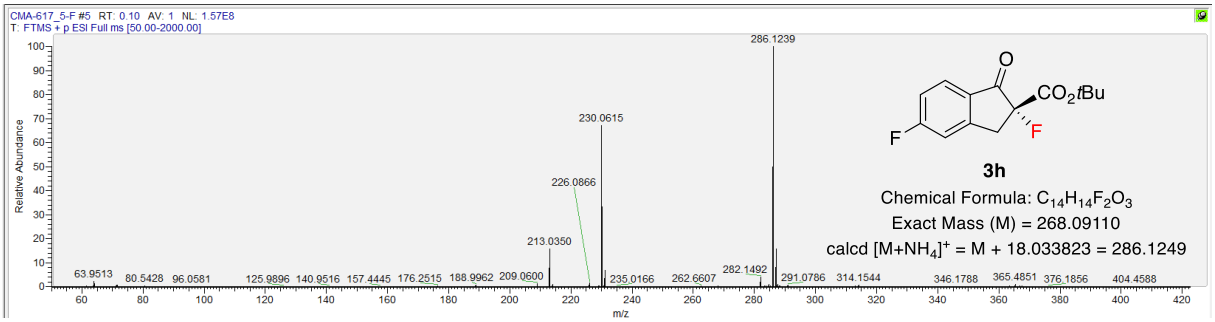
(*R*)-**3f**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}ClFO_3N$, 302.0954; found, 302.0942.



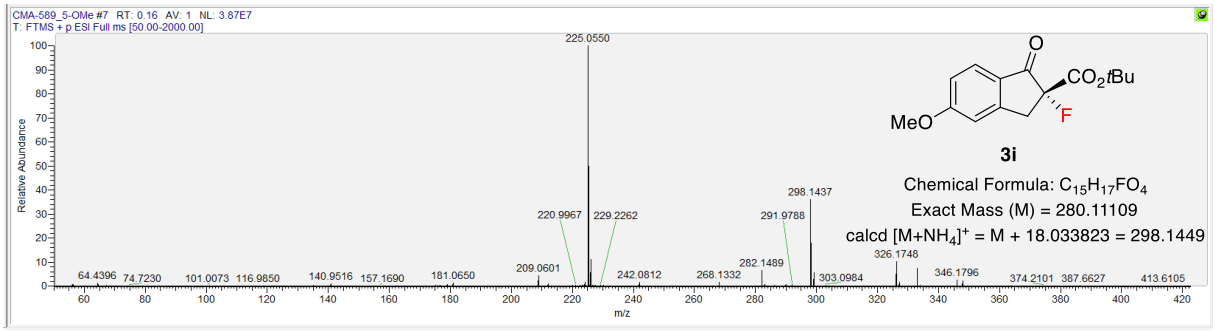
(*R*)-**3g**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}BrFO_3N$, 346.0449; found, 346.0436.



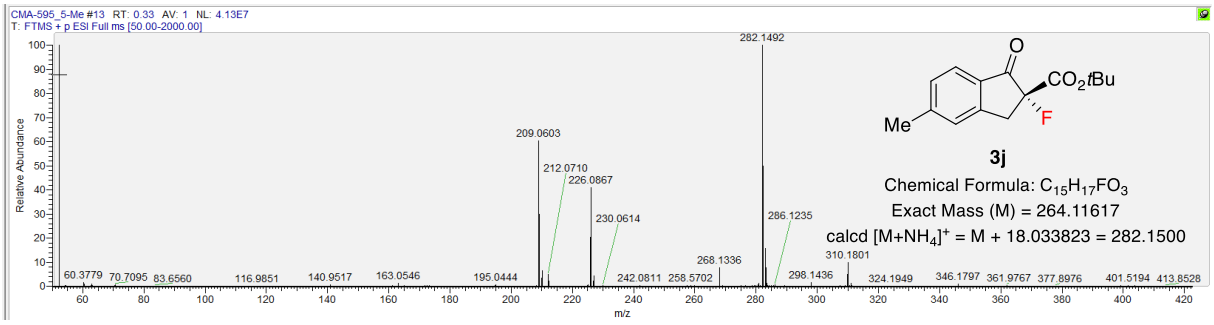
(*R*)-**3h**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}F_2O_3N$, 286.1249; found, 286.1239.



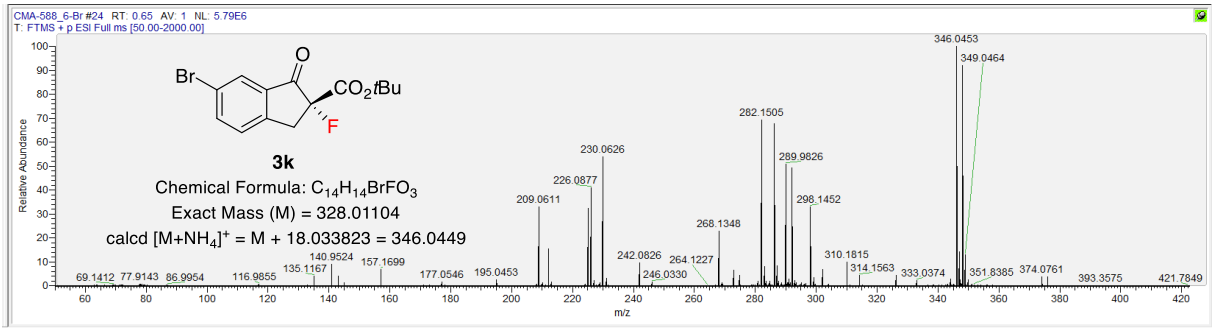
(*R*)-**3i**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_4N$, 298.1449; found, 298.1437.



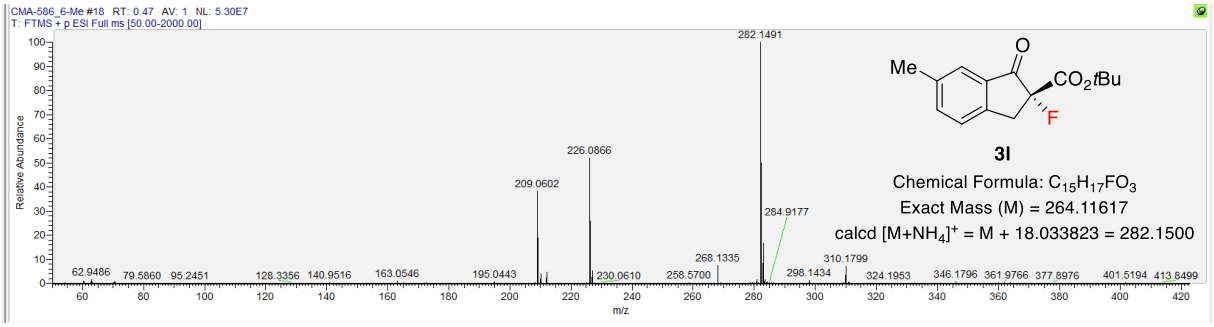
(*R*)-**3j**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_3N$, 282.1500; found, 282.1492.



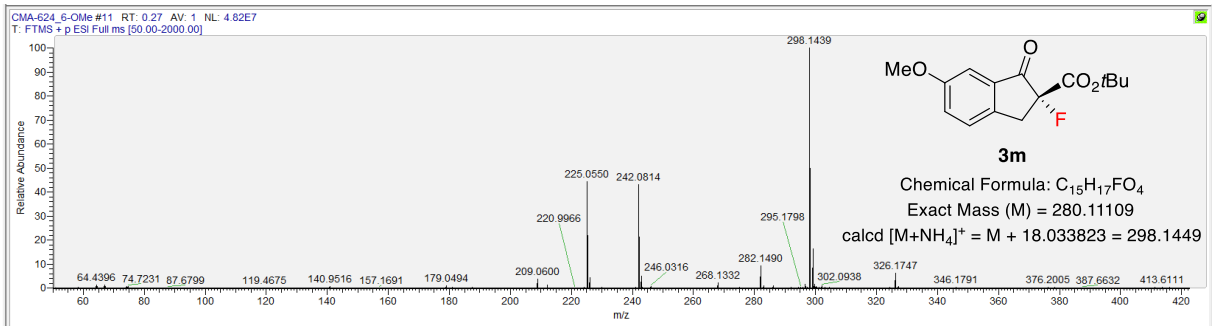
(*R*)-**3k**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{18}BrFO_3N$, 346.0449; found, 346.0453.



(*R*)-**3l**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_3N$, 282.1500; found, 282.1491.



(*R*)-**3m**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{15}H_{21}FO_4N$, 298.1449; found, 298.1439.



(*R*)-**3n**. **HRMS** (ESI-Orbitrap, MeOH) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{17}Cl_2FO_3N$, 336.0564; found, 336.0575.