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Supporting Information

Iodoarene-catalyzed fluorination and aminofluorination by Ar-I/HF·pyridine/*m*CPBA system

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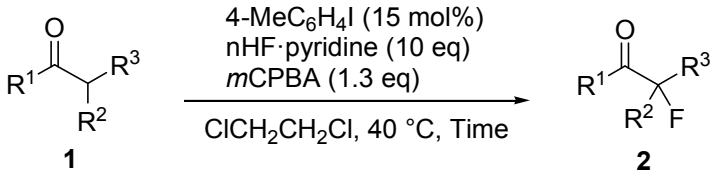
General Methods:

All reactions were performed in EFP test tube under a positive pressure of nitrogen. Solvents were transferred *via* syringe. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid in ethanol/heat or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. The ^{1}H-NMR (600 MHz, 300 MHz), ^{13}C-NMR (150.9 MHz, 75.5 MHz) and ^{19}F-NMR (282 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker Avance 600 and a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS, $CFCl_3$ or $CDCl_3$. Mass spectra were recorded on a SHIMADZU LCMS-2010EV. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer. HPLC analyses were performed on a JASCO PU-2080 plus using 4.6 x 250 mm CHIRALCEL OJ-H, CHIRALPAK IA and CHIRALPAK ID column. Optical rotations were measured on a HORIBA SEPA-300. nHF·pyridine (Sigma-Aldrich) was used by ~70% HF and ~30% pyridine.

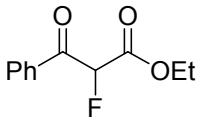
Experimental Section

General procedure for the fluorination of carbonyl compounds 2.



To a stirring mixture of carbonyl compounds **1** (0.2 mmol), 4-methyliodobenzene (0.030 mmol) and nHF·pyridine (HF; ca. 70%, 2.0 mmol) in $ClCH_2CH_2Cl$ (2.0 ml), *m*CPBA (0.13 mmol) was added under nitrogen atmosphere and stirred at 40 °C. After 10 minutes, *m*CPBA (0.13 mmol) was added and stirred at the same temperature. The reaction was monitored by TLC with UV light and $KMnO_4$ in water staining until starting material was consumed. The resulting mixture was quenched with saturated $NaHCO_3$ aqueous solution and extracted with CH_2Cl_2 three times. The organic layer was washed with brine, dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate) to give α-fluoro- carbonyl compounds **2**.

Ethyl 2-fluoro-3-oxo-3-phenylpropanoate (2a)

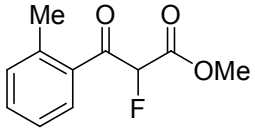


This compound has been previously prepared and characterized.[1]

A reaction of ethyl 3-oxo-3-phenylpropanoate **1a** (38.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 95/5) to give **2a** (41.0 mg, 98%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (t, *J* = 7.2 Hz, 3H), 4.30 (q, *J* = 7.5 Hz, 2H), 5.88 (d, *J* = 48.9 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 6.9 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.9 (d, *J* = 48.5 Hz); MS (ESI, m/z) 233 ($M+Na^+$). These assignments matched with those previously published.[1]

Methyl 2-fluoro-3-(2-methylphenyl)-3-oxopropanoate (2b)

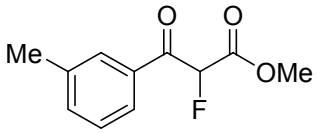


A reaction of methyl 3-(2-methylphenyl)-3-oxopropanoate **1b** (38.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3

eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2b** (27.4 mg, 65%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 2.53 (s, 3H), 3.85 (s, 3H), 5.83 (d, J = 48.9 Hz, 1H), 7.30-7.34 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.6, 53.1, 90.2 (d, J = 199.1 Hz), 125.7, 129.9 (d, J = 5.2 Hz), 132.3, 132.9, 133.0, 140.4, 165.4 (d, J = 24.3 Hz), 192.2 (d, J = 19.9 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −189.2 (d, J = 48.5 Hz); IR (neat) 2959, 1766, 1698, 1601, 1571, 1489, 1457, 1438, 1239, 1137, 1108, 959, 861, 770, 725, 661, 580 cm^{-1}; MS (ESI, m/z) 233 ($M+Na^+$); HRMS (ESI) $C_{11}H_{11}FNaO_3$ ($M+Na^+$) 233.0590 calcd for 233.0588.

Methyl 2-fluoro-3-(3-methylphenyl)-3-oxopropanoate (2c)

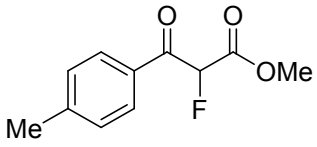


This compound has been previously prepared and characterized.[2]

A reaction of methyl 3-(3-methylphenyl)-3-oxopropanoate **1c** (38.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2c** (27.7 mg, 66%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 3.85 (s, 3H), 5.89 (d, J = 48.9 Hz, 1H), 7.37-7.48 (m, 2H), 7.85 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.8 (d, J = 48.5 Hz); MS (ESI, m/z) 233 ($M+Na^+$).

Methyl 2-fluoro-3-(4-methylphenyl)-3-oxopropanoate (2d)

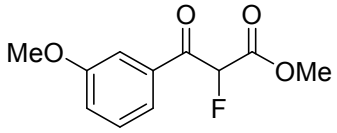


This compound has been previously prepared and characterized.[3]

A reaction of methyl 3-(4-methylphenyl)-3-oxopropanoate **1d** (38.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2d** (22.4 mg, 53%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 3.84 (s, 3H), 5.88 (d, J = 48.6 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.7 (d, J = 48.5 Hz); IR (neat) 2958, 1768, 1692, 1606, 1438, 1288, 1253, 1185, 1111, 961, 822, 719 cm^{-1}; MS (ESI, m/z) 233 (M+Na$^+$).

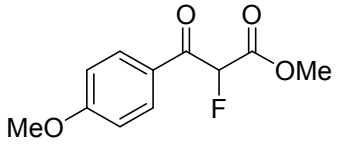
Methyl 2-fluoro-3-(3-methoxyphenyl)-3-oxopropanoate (2e)



A reaction of methyl 3-(3-methoxyphenyl)-3-oxopropanoate **1e** (41.6 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2e** (27.4 mg, 61%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.85 (s, 3H), 3.87 (s, 3H), 5.88 (d, J = 48.6 Hz, 1H), 7.19 (dd, J = 8.1, 2.7 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.55 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 53.2, 55.5, 89.9 (d, J = 198.0 Hz), 113.2 (d, J = 2.7 Hz), 121.4, 122.2 (d, J = 4.5 Hz), 129.8, 134.4, 159.9, 165.3 (d, J = 24.3 Hz), 189.1 (d, J = 20.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.7 (d, J = 48.2 Hz); IR (neat) 2958, 1766, 1695, 1598, 1582, 1489, 1435, 1262, 1111, 1038, 872, 790, 684, 565 cm^{-1}; MS (ESI, m/z) 249 (M+Na$^+$); HRMS (ESI) $C_{11}H_{11}FNaO_4$ (M+Na$^+$) 249.0539 calcd for 249.0543.

Methyl 2-fluoro-3-(4-methoxyphenyl)-3-oxopropanoate (2f)

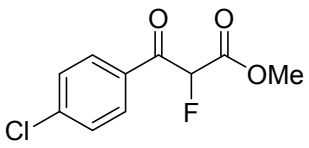


This compound has been previously prepared and characterized.[2]

A reaction of methyl 3-(4-methoxyphenyl)-3-oxopropanoate **1f** (41.6 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2f** (32.5 mg, 72%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.84 (s, 3H), 3.89 (s, 3H), 5.85 (d, J = 48.9 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.1 (d, J = 48.2 Hz); IR (neat) 2958, 1766, 1684, 1600, 1574, 1513, 1457, 1439, 1424, 1314, 1258, 1173, 1115, 1023, 961, 839, 722, 638, 607 cm^{-1}; MS (ESI, m/z) 249 (M+Na$^+$).

Methyl 3-(4-chlorophenyl)-2-fluoro-3-oxopropanoate (2g)

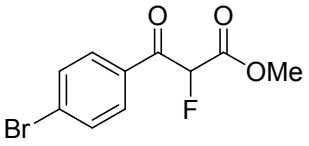


This compound has been previously prepared and characterized.[2]

A reaction of methyl 3-(4-chlorophenyl)-3-oxopropanoate **1g** (42.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2g** (35.8 mg, 78%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 3.85 (t, *J* = 7.2 Hz, 3H), 5.84 (d, *J* = 48.9 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.5 (d, *J* = 48.5 Hz); IR (neat) 2958, 1767, 1697, 1590, 1490, 1439, 1403, 1285, 1249, 1181, 1093, 1013, 963, 835, 765, 727, 672, 595 cm^{-1}; MS (ESI, m/z) 253 ($M+Na^+$).

Methyl 3-(4-bromophenyl)-2-fluoro-3-oxopropanoate (2h)

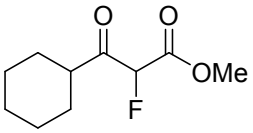


This compound has been previously prepared and characterized.[4]

A reaction of methyl 3-(4-bromophenyl)-3-oxopropanoate **1h** (51.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5/5) to give **2h** (43.0 mg, 78%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 3.85 (s, 3H), 5.84 (d, *J* = 48.9 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 53.4, 90.1 (d, *J* = 198.6 Hz), 130.2, 130.9 (d, *J* = 3.3 Hz), 131.0 (d, *J* = 3.9 Hz), 132.7, 165.1 (d, *J* = 24.3 Hz), 188.5 (d, *J* = 20.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −190.6 (d, *J* = 48.5 Hz); IR (neat) 2957, 1768, 1697, 1585, 1488, 1438, 1399, 1362, 1285, 1250, 1181, 1108, 1071, 1011, 961, 827, 746 cm^{-1}; MS (ESI, m/z) 297 ($M+Na^+$).

Methyl 3-cyclohexyl-2-fluoro-3-oxopropanoate (2i)

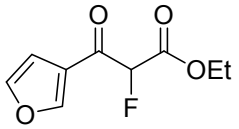


This compound has been previously prepared and characterized.[5]

A reaction of methyl 3-cyclohexyl-3-oxopropanoate **1i** (36.8 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2i** (36.8 mg, 91%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 1.18-1.46 (m, 5H), 1.67-1.89 (m, 5H), 2.87-2.88 (m, 1H), 3.85 (s, 3H), 5.30 (d, J = 49.2 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −196.3 (d, J = 49.6 Hz); MS (ESI, m/z) 255 ($M+Na^+$).

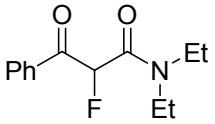
Ethyl 2-fluoro-3-(furan-3-yl)-3-oxopropanoate (2j)



A reaction of ethyl 3-(furan-3-yl)-3-oxopropanoate **1j** (36.4 mg, 0.10 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2j** (29.0 mg, 72%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, J = 6.9 Hz, 3H), 4.30 (dd, J = 6.9, 2.1 Hz, 2H), 5.71 (d, J = 48.6 Hz, 1H), 6.64 (m, 1H), 7.51 (s, 1H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.9, 62.7, 89.2 (d, J = 197.5 Hz), 112.9, 121.9 (d, J = 6.0 Hz), 148.5, 164.4 (d, J = 24.4 Hz), 177.5 (d, J = 21.6 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −193.7 (d, J = 48.5 Hz); IR (neat) 3139, 2984, 1763, 1684, 1568, 1464, 1395, 1261, 1213, 1120, 1085, 1021, 884, 865, 771, 591 cm^{-1}; MS (ESI, m/z) 223 ($M+Na^+$); HRMS (ESI) $C_9H_9FNaO_4$ ($M+Na^+$) 223.0383 calcd for 223.0377.

***N*,*N*-Diethyl-2-fluoro-3-oxo-3-phenylpropanamide (2k)**

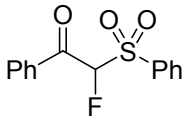


A reaction of *N*,*N*-diethyl-3-oxo-3-phenylpropanamide **1k** (43.8 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 30 min, and a purification by column chromatography on silica gel (*n*-

hexane/CH_2Cl_2 = 5/5) to give **2k** (30.8 mg, 66%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.11 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 3.35-3.57 (m, 4H), 6.12 (d, *J* = 48.9 Hz, 1H), 7.46-7.52 (m, 2H), 7.59-7.64 (m, 1H), 8.15 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 12.4, 14.1, 40.9, 41.6 (d, *J* = 5.5 Hz), 92.6 (d, *J* = 197.5 Hz), 128.4, 128.6, 129.6 (d, *J* = 2.8 Hz), 130.1, 133.6, 134.3, 163.4 (d, *J* = 19.9 Hz), 191.9 (d, *J* = 19.9 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −187.1 (d, *J* = 49.9 Hz); IR (neat) 2975, 2937, 1716, 1698, 1648, 1449, 1385, 1313, 1259, 1215, 1089, 977, 882, 766, 689, 648 cm^{-1}; MS (ESI, m/z) 260 (M+Na$^+$); HRMS (ESI) $C_{13}H_{16}FNNaO_2$ (M+Na$^+$) 260.1063 calcd for 260.1068.

2-Fluoro-1-phenyl-2-(phenylsulfonyl)ethanone (2l)

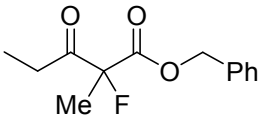


This compound has been previously prepared and characterized.[6]

A reaction of 1-phenyl-2-(phenylsulfonyl)ethanone **1l** (50.4 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 24 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2l** (39.5 mg, 71%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.35 (d, *J* = 48.0 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.66-7.78 (m, 2H), 7.88 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 7.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –180.1 (d, *J* = 48.2 Hz); MS (ESI, m/z) 301 (M+Na$^+$).

Benzyl 2-fluoro-2-methyl-3-oxopentanoate (2m)

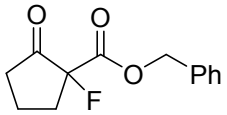


This compound has been previously prepared and characterized.[7]

A reaction of benzyl 2-methyl-3-oxopentanoate **1m** (44.0 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 95/5) to give **2m** (21.9 mg, 46%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.70 (d, *J* = 22.2 Hz, 3H), 2.56-2.76 (m, 2H), 5.23 (s, 2H), 7.34-7.40 (m, 5H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –159.7 (dd, *J* = 44.0, 22.8 Hz); MS (ESI, m/z) 261 (M+Na$^+$).

Benzyl 1-fluoro-2-oxocyclopentanecarboxylate (2n)

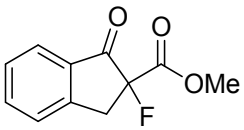


This compound has been previously prepared and characterized.[8]

A reaction of benzyl 2-oxocyclopentanecarboxylate **1n** (22.1 mg, 0.101 mmol), 4-methyliodobenzene (3.3 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 µl, 1.01 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 95/5) to give **2n** (6.0 mg, 25%) as a colorless oil.

^1H NMR ($CDCl_3$, 300 MHz) δ 2.10-2.18 (m, 2H), 2.25-2.38 (m, 1H), 2.46-2.60 (m, 3H), 5.26 (dd, *J* = 15.0, 12.3 Hz, 2H), 7.35 (m, 5H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –164.5 (t, *J* = 20.0 Hz); MS (ESI, m/z) 259 ($M+Na^+$).

Methyl 2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2o)



This compound has been previously prepared and characterized.[8]

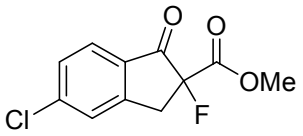
A reaction of methyl 2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate **1o** (38.0 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/dichloromethane = 1/1) to give **2o** (29.7 mg, 71%) as a white solid.

^1H NMR ($CDCl_3$, 300 MHz) δ 3.45 (dd, *J* = 23.1, 18.0 Hz, 1H), 3.76-3.86 (m, 1H), 3.82 (s, 3H), 7.46-7.53 (m, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –165.0 (dd, *J* = 23.1, 11.8 Hz); MS (ESI, m/z) 231 ($M+Na^+$).

Asymmetric reaction of methyl 2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate **1o** (38.0 mg, 0.20 mmol), (*S*)-binaphthyl diiodide **10b** (15.1 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in toluene (2.0 ml) at room temperature for 3 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **2o** (29.6 mg, 71%, 25% ee).

HPLC: (CHIRALCEL OJ-H, *n*-hexane/*i*-PrOH = 90/10, 2.0 mL/min, λ = 254 nm) t_R (major) = 23.2 min, t_R (minor) = 20.2 min; $[\alpha]_D^{25}$ –6.65 (*c* = 0.957, $CHCl_3$), 25% ee.

Methyl 5-chloro-2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2p)

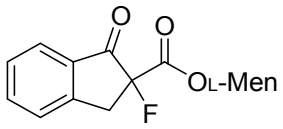


This compound has been previously prepared and characterized.[8]

A reaction of methyl 5-chloro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate **1p** (44.9 mg, 0.20 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/dichloromethane = 1/1) to give **2p** (28.6 mg, 59%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.43 (dd, *J* = 23.1, 18.9 Hz, 1H), 3.74-3.87 (m, 1H), 3.84 (s, 3H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −164.6 (dd, *J* = 22.8, 11.0 Hz); MS (ESI, m/z) 265 ($M+Na^+$).

L-Menthyl 2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2q)



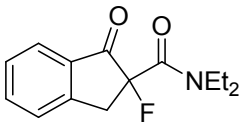
This compound has been previously prepared and characterized.[9]

A reaction of L-menthyl 2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate **1q** (31.1 mg, 0.0989 mmol), 4-methyliodobenzene (3.3 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 µl, 0.989 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 95/5) to give **2q** (19.3 mg, 59%) as a colorless oil. Two diastereomers were not separated.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.70-1.80 (m, 17H), 2.02 (d, *J* = 12.0 Hz, 1H), 3.44 (dd, *J* = 22.8, 17.7 Hz, 1H), 3.76 (dd, *J* = 17.4, 11.4 Hz, 1H), 4.74-4.84 (m, 1H), 7.45-7.52 (m, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) major; δ –164.7 (dd, *J* = 23.5, 13.0 Hz), minor; δ –165.2 (dd, *J* = 22.7, 10.2 Hz) dr = 57:43; MS (ESI, m/z) 355 ($M+Na^+$).

Asymmetric reaction of L-Menthyl 2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate **1q** (18.9 mg, 0.060 mmol), (*S*)-binaphthyl diiodide **10b** (4.6 mg, 0.009 mmol, 0.15 eq), nHF·pyridine (17 µl, 0.6 mmol, 10.0 eq), *m*CPBA (19.7 mg, 0.078 mmol, 1.3 eq) in toluene (1.0 ml) at room temperature for 19 h, and a purification by column chromatography on silica gel (*n*-hexane/dichloromethane = 6/4) to give **2q** (12.5 mg, 63%, 65% de).

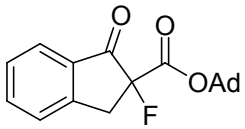
***N*,*N*-Diethyl-2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxamide (2r)**



A reaction of *N*,*N*-diethyl-2,3-dihydro-1-oxo-1*H*-indene-2-carboxamide **1r** (46.3 mg, 0.020 mmol), 4-methyliodobenzene (6.5 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 µl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C for 1 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8/2) to give **2r** (39.2 mg, 79%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.12 (t, *J* = 6.0 Hz, 3H), 1.28 (t, *J* =6.0 Hz, 3H), 3.29-3.44 (m, 4H), 4.02-4.09 (m, 2H), 7.41 (t, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 6.0 Hz, 1H), 7.65 (t, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 12.4, 14.7, 39.3 (d, *J* =24.1 Hz), 42.0, 42.1 (d, *J* =13.6 Hz), 98.9 (d, *J* =209.8 Hz), 125.3, 126.2, 128.2, 133.4, 136.4, 151.2 (d, *J* =4.5 Hz), 165.7 (d, *J* =21.1 Hz), 197.4 (d, *J* =18.1 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –159.0 (dd, *J* = 22.8, 8.5 Hz); IR (neat) 2977, 2936, 1731, 1633, 1464, 1383, 1364, 1292, 1214, 1154, 1095, 919, 753, 731, 658 cm^{-1}; MS (ESI, m/z) 272 ($M+Na^+$); HRMS (ESI) $C_{14}H_{16}FNNaO_2$ ($M+Na^+$) 272.1066 calcd for 272.1063.

1-Adamantyl 2-fluoro-2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate (2s)



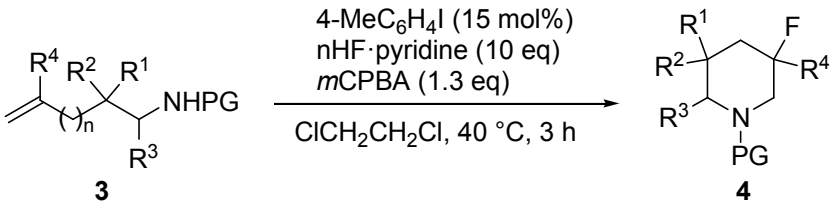
This compound has been previously prepared and characterized.[9]

A reaction of 1-adamantyl 2,3-dihydro-1-oxo-1*H*-indene-2-carboxylate **1s** (31.0 mg, 0.10 mmol), (*R*)-binaphthyl diiodide **10a** (7.6 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 µl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in toluene (1.0 ml) at room temperature for 17 h, and a purification by column chromatography on silica gel (*n*-hexane/dichloromethane = 1/1) to give **2s** (13.6 mg, 41%, 56% ee) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (bs, 6H), 2.05 (bs, 6H), 2.15 (bs, 6H), 3.40 (dd, *J* = 22.8, 18.0 Hz, 1H), 3.74 (dd, *J* = 17.6, 10.5 Hz, 1H), 7.43-7.51 (m, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –164.6 (dd, *J* = 22.8, 11.0 Hz); MS (ESI, m/z) 351 ($M+Na^+$); HPLC: (CHIRALPAK IA, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 254 nm) t_R (major) = 16.0 min, t_R (minor) = 20.6 min; $[\alpha]_D^{25}$ –1.73 (*c* = 0.45, $CHCl_3$), 56% ee.

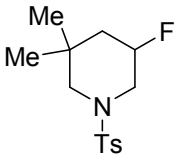
These assignments matched with those previously published.[9]

General procedure for the aminofluorination of alkene compounds.



To a stirring mixture of alkene compounds **3** (0.1 mmol), 4-methyliodobenzene (0.015 mmol) and nHF·pyridine (HF; ca. 70%, 1.0 mmol) in $ClCH_2CH_2Cl$ (1.0 ml), *m*CPBA (0.065 mmol) was added under nitrogen atmosphere and stirred at 40 °C. After 5 minutes, *m*CPBA (0.065 mmol) was added and stirred at the same temperature for 3 h. The resulting mixture was quenched with saturated $NaHCO_3$ aqueous solution and extracted with CH_2Cl_2 three times. The organic layer was washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate) to give cyclic fluoroamine compounds **4**.

5-Fluoro-3,3-dimethyl-1-tosylpiperidine (4a)

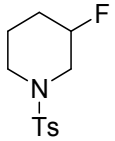


This compound has been previously prepared and characterized.[10]

A reaction of 2,2-dimethyl-*N*-tosylpent-4-en-1-amine **3a** (26.7 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 µl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **4a** (20.9 mg, 73%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (s, 3H), 1.04 (s, 3H), 1.34 (dd, *J* = 21.6, 12.9 Hz, 1H), 1.73 (dd, *J* = 12.3, 12.6 Hz, 1H), 2.37 (d, *J* = 11.4 Hz, 1H), 2.44 (s, 3H), 2.61 (dd, *J* = 18.8, 7.5 Hz, 1H), 2.97 (d, *J* = 11.4 Hz, 1H), 3.62 (dd, *J* = 9.6, 8.1 Hz, 1H), 4.69-4.87 (m, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −183.7 (dm, *J* = 48.5 Hz); MS (ESI, m/z) 339 ($M+Na^+$).

3-Fluoro-1-tosylpiperidine (4b)

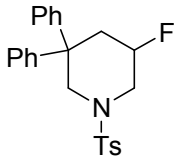


This compound has been previously prepared and characterized.[10]

A reaction of *N*-tosylpent-4-en-1-amine **3b** (47.8 mg, 0.20 mmol), 4-methyliodobenzene (6.54 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 μl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 85/15) to give **4b** (28.2 mg, 55%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60-1.71 (m, 2H), 1.79-1.88 (m, 2H), 2.44 (s, 3H), 2.85-2.91 (m, 1H), 2.98 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.10-3.15 (m, 1H), 3.4 (dd, *J* = 17.2, 12.0 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −183.3 (m); MS (ESI, m/z) 280 ($M+Na^+$).

5-Fluoro-3,3-diphenyl-1-tosylpiperidine (4c)



This compound has been previously prepared and characterized.[11]

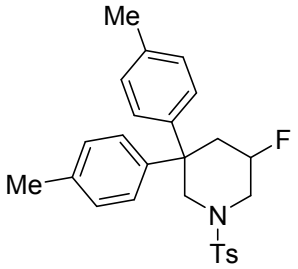
A reaction of 2,2-diphenyl-*N*-tosylpent-4-en-1-amine **3c** (39.1 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 μl, 1.0 mmol, 10.0 eq), *m*CPBA (48.8 mg, 0.195 mmol, 1.95 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **4c** (27.6 mg, 68%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.16 (q, *J* = 11.4 Hz, 1H), 2.29 (dt, *J* = 9.6, 5.7 Hz, 1H), 2.40 (d, *J* = 12.3 Hz, 1H), 2.42 (s, 3H), 2.93-2.99 (m, 1H), 4.02-4.05 (m, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.54 (dm, *J* = 47.4 Hz, 1H), 7.13-7.36 (m, 10H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −186.0 (d, *J* = 48.5 Hz); MS (ESI, m/z) 432 ($M+Na^+$).

Asymmetric reaction of 2,2-diphenyl-*N*-tosylpent-4-en-1-amine **3c** (39.1 mg, 0.10 mmol), (*R*)-binaphthyl diiodide **10a** (7.6 mg, 0.015 mmol, 0.15 eq), 46% HF aq. (43.5 μl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in toluene (1.0 ml) at 0 °C for 24 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give (*R*)-**4c** (18.8 mg, 46%, 70% ee).

HPLC: (CHIRALPAK ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm) t_R (major) = 20.0 min, t_R (minor) = 17.5 min; $[\alpha]_D^{25}$ –143.36 (*c* = 0.28, $CHCl_3$), 69% ee; Lit. (*R*)-**4c**: $[\alpha]_D^{26}$ –167 (*c* = 0.45, CH_2Cl_2), 99% ee.[11]

5-Fluoro-3,3-di-*p*-tolyl-1-tosylpiperidine (4d)

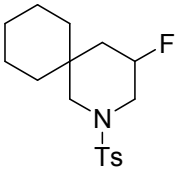


This compound has been previously prepared and characterized.[11]

A reaction of 2,2-di-*p*-tolyl-*N*-tosylpent-4-en-1-amine **3d** (41.9 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 µl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 92/8) to give **4d** (24.6 mg, 56%) as a white solid.

^1H NMR ($CDCl_3$, 300 MHz) δ 2.11 (q, J = 10.8 Hz, 1H), 2.20-2.38 (m, 2H), 2.27 (s, 3H), 2.31 (s, 3H), 2.42 (s, 3H), 2.92 (m, 1H), 4.02 (t, J = 4.8 Hz, 1H), 4.45-4.65 (m, 2H), 7.04 (dd, J = 13.1, 8.1 Hz, 4H), 7.13 (d, J = 7.8 Hz, 2H), 7.29-7.35 (m, 4H), 7.63 (d, J = 7.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −186.1 (dm, J = 48.2 Hz); MS (ESI, m/z) 460 ($M+Na^+$).

4-Fluoro-2-tosyl-2-azaspiro[5,5]undecane (4e)



This compound has been previously prepared and characterized.[10]

A reaction of (1-allylcyclohexyl)-*N*-tosylmethanamine **3e** (30.7 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 µl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8/2) to give **4e** (22.9 mg, 70%) as a white solid.

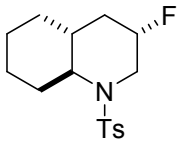
^1H NMR ($CDCl_3$, 300 MHz) δ 1.26-1.48 (m, 11H), 1.78-1.87 (m, 1H), 2.41 (d, J = 12.0 Hz, 1H), 2.44 (s, 3H), 2.60-2.69 (m, 1H), 3.20 (d, J = 10.2 Hz, 1H), 3.59-3.67 (m, 1H), 4.78 (dm, J = 47.7 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −183.1 (dm, J = 45.7 Hz); MS (ESI, m/z) 348 ($M+Na^+$).

3,5-*cis* and *trans*-3-Fluoro-decahydro-1-tosylquinoline (4f)

This compound has been previously prepared and characterized.[10]

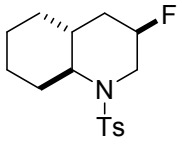
A reaction of *trans*-2-allyl-*N*-tosylcyclohexanamine **3f** (29.3 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 μl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give ***cis*-4f** and ***trans*-4f** (19.2 mg, 62%) as a white solid.

3,5-*cis*-3-Fluoro-decahydro-1-tosylquinoline (*cis*-4f)



^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01-1.23 (m, 4H), 1.41-1.80 (m, 5H), 2.09-2.12 (m, 1H), 2.20-2.24 (m, 1H), 2.37-2.49 (m, 1H), 2.43 (s, 3H), 2.81-2.88 (m, 1H), 4.25-4.29 (m, 1H), 4.47-4.79 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −175.7 (d, J = 45.7 Hz); MS (ESI, m/z) 334 ($M+Na^+$).

3,5-*trans*-3-Fluoro-decahydro-1-tosylquinoline (*trans*-4f)



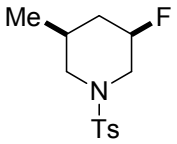
^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96-1.04 (m, 1H), 1.10-1.28 (m, 3H), 1.36-1.47 (m, 1H), 1.64-1.92 (m, 5H), 2.24-2.28 (m, 1H), 2.43 (s, 3H), 2.76 (dt, J = 10.8, 3.6 Hz, 1H), 3.30 (ddd, J = 24.3, 14.4, 3.6 Hz, 1H), 4.03 (dt, J = 13.2, 5.4 Hz, 1H), 4.74 (dm, J = 48.6 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −181.3 (m); MS (ESI, m/z) 334 ($M+Na^+$).

***cis* and *trans*-3-Fluoro-5-methyl-1-tosylpiperidine (4g)**

This compound has been previously prepared and characterized.[10]

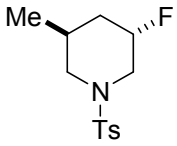
A reaction of 2-methyl-*N*-tosylpent-4-en-1-amine **3g** (25.3 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 μl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give ***cis*-4g** and ***trans*-4g** (20.8 mg, 77%) as a white solid.

***cis*-3-Fluoro-5-methyl-1-tosylpiperidine (*cis*-4g)**



^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (d, *J* = 4.8 Hz, 3H), 0.97-1.10 (m, 1H), 1.78-1.83 (m, 2H), 2.11-2.19 (m, 2H), 2.45 (s, 3H), 3.64-3.70 (m, 1H), 4.02-4.05 (m, 1H), 4.50-4.74 (m, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −181.3 (dm, *J* = 46.8 Hz); MS (ESI, m/z) 294 ($M+Na^+$).

***trans*-3-Fluoro-5-methyl-1-tosylpiperidine (*trans*-4g)**



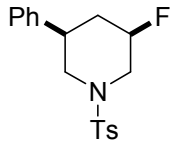
^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (d, *J* = 5.7 Hz, 3H), 1.00-1.21 (m, 1H), 1.97-2.18 (m, 3H), 2.44 (s, 3H), 2.56 (dd, *J* = 36.0, 13.8 Hz, 1H), 3.66 (d, *J* = 9.0 Hz, 1H), 3.89 (t, *J* = 11.4 Hz, 1H), 4.78 (d, *J* = 46.2 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −184.5 (m); MS (ESI, m/z) 294 ($M+Na^+$).

***cis* and *trans*-3-Fluoro-5-phenyl-1-tosylpiperidine (4h)**

This compound has been previously prepared and characterized.[10]

A reaction of 2-phenyl-*N*-tosylpent-4-en-1-amine **3h** (63.1mg, 0.20 mmol), 4-methyliodobenzene (6.54 mg, 0.030 mmol, 0.15 eq), nHF·pyridine (56 μl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give ***cis*-4h** and ***trans*-4h** (51.6 mg, 60%) as a white solid.

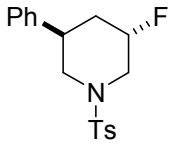
***cis*-3-Fluoro-5-phenyl-1-tosylpiperidine (*cis*-4h)**



^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52-1.71 (m, 1H), 2.15 (t, *J* = 11.4 Hz, 1H), 2.25 (dt, *J* = 10.2, 3.9 Hz, 1H), 2.41-2.48 (m, 1H), 2.44 (s, 3H), 2.97 (m, 1H), 3.86-3.90 (m, 1H), 4.19 (m, 1H), 4.78 (dm, *J* = 48.0 Hz, 1H),

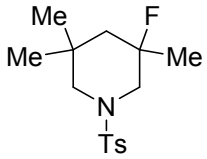
7.18 (d, J = 8.1 Hz, 2H), 7.23-7.35 (m, 5H), 7.64 (d, J = 7.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −181.7 (dm, J = 47.1 Hz); MS (ESI, m/z) 356 ($M+Na^+$).

trans-3-Fluoro-5-phenyl-1-tosylpiperidine (_trans_-4h)



^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60-1.78 (m, 1H), 2.23-2.31 (m, 1H), 2.39-2.46 (m, 1H), 2.44 (s, 3H), 2.62 (dd, J = 37.7, 13.2 Hz, 1H), 3.21-3.29 (m, 1H), 3.90-3.94 (m, 1H), 4.09-4.17 (m, 1H), 4.90 (dm, J = 46.2 Hz, 1H), 7.16 (d, J = 7.8 Hz, 2H), 7.23-7.34 (m, 5H), 7.67 (d, J = 8.1 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −185.0 (m); MS (ESI, m/z) 356 ($M+Na^+$).

3-Fluoro-3,5,5-trimethyl-1-tosylpiperidine (4i)

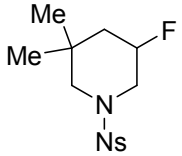


This compound has been previously prepared and characterized.[10]

A reaction of 2,2,4-trimethyl-_N_-tosylpent-4-en-1-amine **3i** (28.1 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 μl, 1.0 mmol, 10.0 eq), _m_CPBA (48.8 mg, 0.195 mmol, 1.95 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (_n_-hexane/ethyl acetate = 9/1) to give **4i** (9.1 mg, 31%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (s, 3H), 1.14 (s, 3H), 1.23 (dd, J = 16.5, 15.0 Hz, 1H), 1.31 (d, J = 20.4 Hz, 3H), 1.70-1.78 (m, 1H), 2.13 (d, J = 11.7 Hz, 1H), 2.33 (dd, J = 31.4, 12.6 Hz, 1H), 2.44 (s, 3H), 3.32 (d, J = 11.4 Hz, 1H), 3.72 (t, J = 12.3 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −145.6 (s); MS (ESI, m/z) 322 ($M+Na^+$).

5-Fluoro-3,3-dimethyl-1-nosylpiperidine (4j)

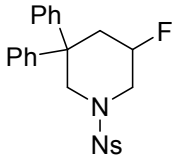


This compound has been previously prepared and characterized.[10]

A reaction of 2,2-dimethyl-*N*-nosylpent-4-en-1-amine **3j** (29.8 mg, 0.10 mmol), 4-methyliodobenzene (3.27 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 μl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (1.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8/2) to give **4j** (24.0 mg, 75%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 3H), 1.07 (s, 3H), 1.51 (dt, *J* = 12.9, 8.7 Hz, 1H), 1.79 (ddd, *J* = 17.1, 14.4, 3.3 Hz, 1H), 2.87 (d, *J* = 12.3 Hz, 1H), 3.03-3.18 (m, 2H), 3.75 (dt, *J* = 12.6, 3.3 Hz, 1H), 4.81 (dm, *J* = 47.4 Hz, 1H), 7.62-7.75 (m, 3H), 7.97-8.01 (m, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −183.6 (dm, *J* = 36.9 Hz); MS (ESI, m/z) 339 ($M+Na^+$).

5-Fluoro-3,3-diphenyl-1-nosylpiperidine (4k)



Asymmetric reaction of 2,2-diphenyl-*N*-nosylpent-4-en-1-amine **3k** (42.3 mg, 0.10 mmol), (*R*)-binaphthyl diiodide **10a** (7.6 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (28 μl, 1.0 mmol, 10.0 eq), *m*CPBA (32.5 mg, 0.13 mmol, 1.30 eq) in toluene (1.0 ml) at room temperature for 24 h, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8/2) to give **4k** (26.4 mg, 60%, 45% ee) as a white solid.

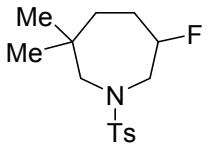
^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.26 (dd, *J* = 21.6, 10.8 Hz, 1H), 2.73 (dd, *J* = 15.3, 10.2 Hz, 1H), 2.98 (d, *J* = 12.6 Hz, 1H), 3.07 (bt, 1H), 4.13-4.17 (m, 1H), 4.55-4.73 (m, 2H), 7.20-7.30 (m, 8H), 7.40-7.42 (m, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 40.9 (d, *J* = 18.6 Hz), 46.7 (d, *J* = 10.8 Hz), 49.6 (d, *J* = 31.7 Hz), 53.8, 85.2 (d, *J* = 174.8 Hz), 124.1, 126.2, 126.6, 127.0, 127.3, 128.7, 128.8, 129.7, 131.0, 131.5, 134.1, 142.6, 145.1; ^{19}F NMR ($CDCl_3$, 282 MHz) δ −185.5 (d, *J* = 47.4 Hz); IR (neat) 3088, 3060, 3025, 2958, 2917, 2853, 1546, 1497, 1471, 1448, 1373, 1294, 1173, 1126, 1043, 1029, 998, 923, 851, 701, 653, 583 cm^{-1}; MS (ESI, m/z) 463 ($M+Na^+$); HRMS (ESI) $C_{23}H_{21}FN_2NaO_4S$ ($M+Na^+$) 463.1105 calcd for 463.1104; mp 63-67 °C ($CHCl_3$); HPLC: (CHIRALPAK ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm) t_R (major) = 39.1 min, t_R (minor) = 44.1 min; $[\alpha]_D^{25}$ –62.67 (*c* = 0.47, $CHCl_3$), 42% ee.

6-Fluoro-3,3-dimethyl-1-tosylazepane (4l) and 2-(fluoromethyl)-5,5-dimethyl-1-tosylpiperidine (5)

This compound has been previously prepared and characterized.[10]

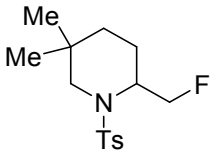
A reaction of 2,2-dimethyl-*N*-tosylhex-5-en-1-amine **3l** (56.3 mg, 0.20 mmol), 4-methyliodobenzene (6.54 mg, 0.015 mmol, 0.15 eq), nHF·pyridine (56 μl, 2.0 mmol, 10.0 eq), *m*CPBA (65.0 mg, 0.26 mmol, 1.3 eq) in $ClCH_2CH_2Cl$ (2.0 ml) at 40 °C, and a purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1) to give **4l** and **5** (28.5 mg, 48%). These compounds can't be separated column chromatography on silica gel.

6-Fluoro-3,3-dimethyl-1-tosylazepane (4l)



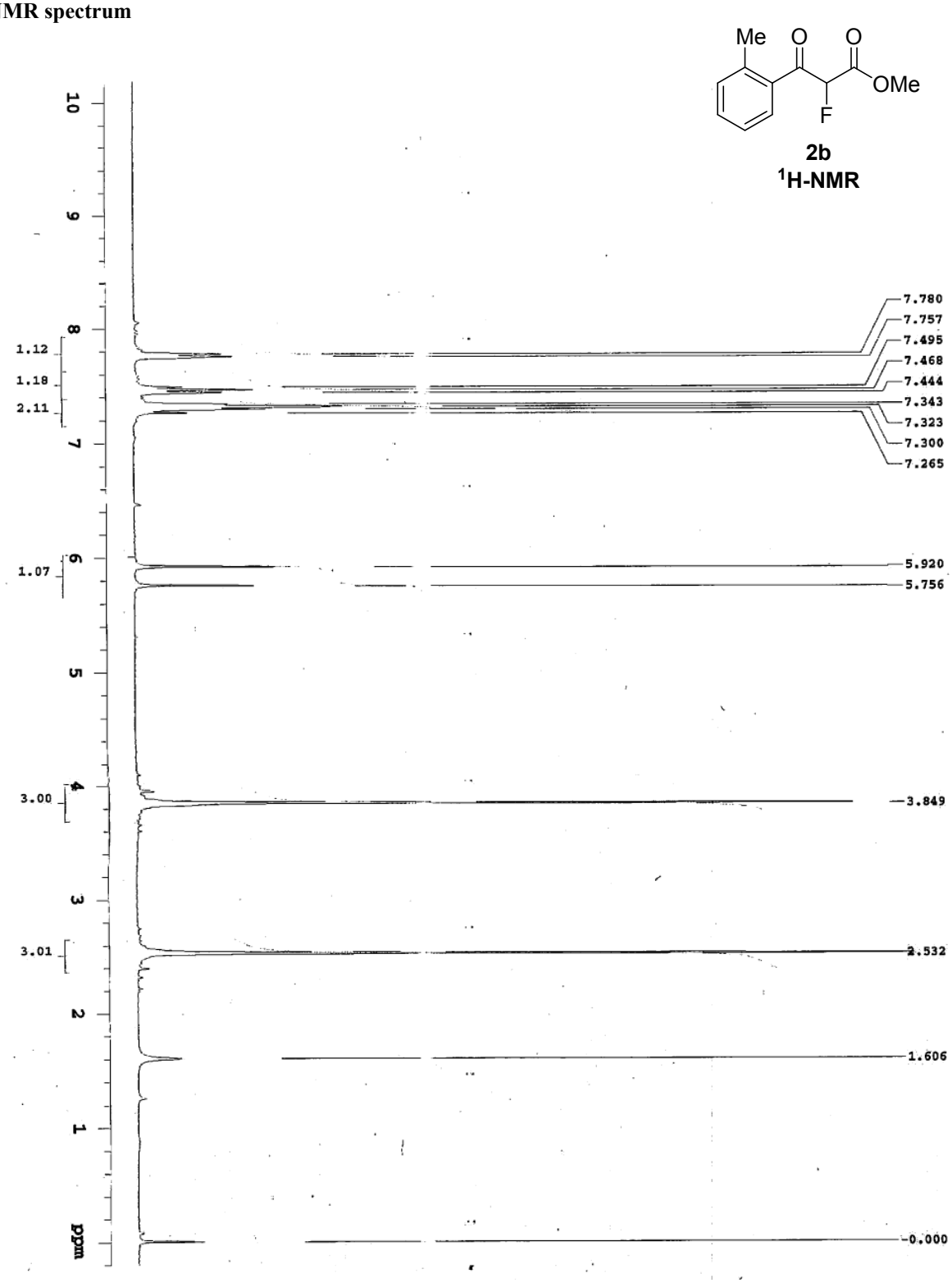
^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 3H), 1.04 (s, 3H), 1.25-1.33 (m, 2H), 1.87-1.98 (m, 2H), 2.43 (s, 3H), 2.71 (d, *J* = 13.8 Hz, 1H), 2.96-3.06 (m, 1H), 3.11 (d, *J* = 14.4 Hz, 1H), 3.63 (ddd, *J* = 19.2, 14.1, 5.7 Hz, 1H), 4.85 (dm, *J* = 48.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −174.7 (m); MS (ESI, m/z) 322 ($M+Na^+$).

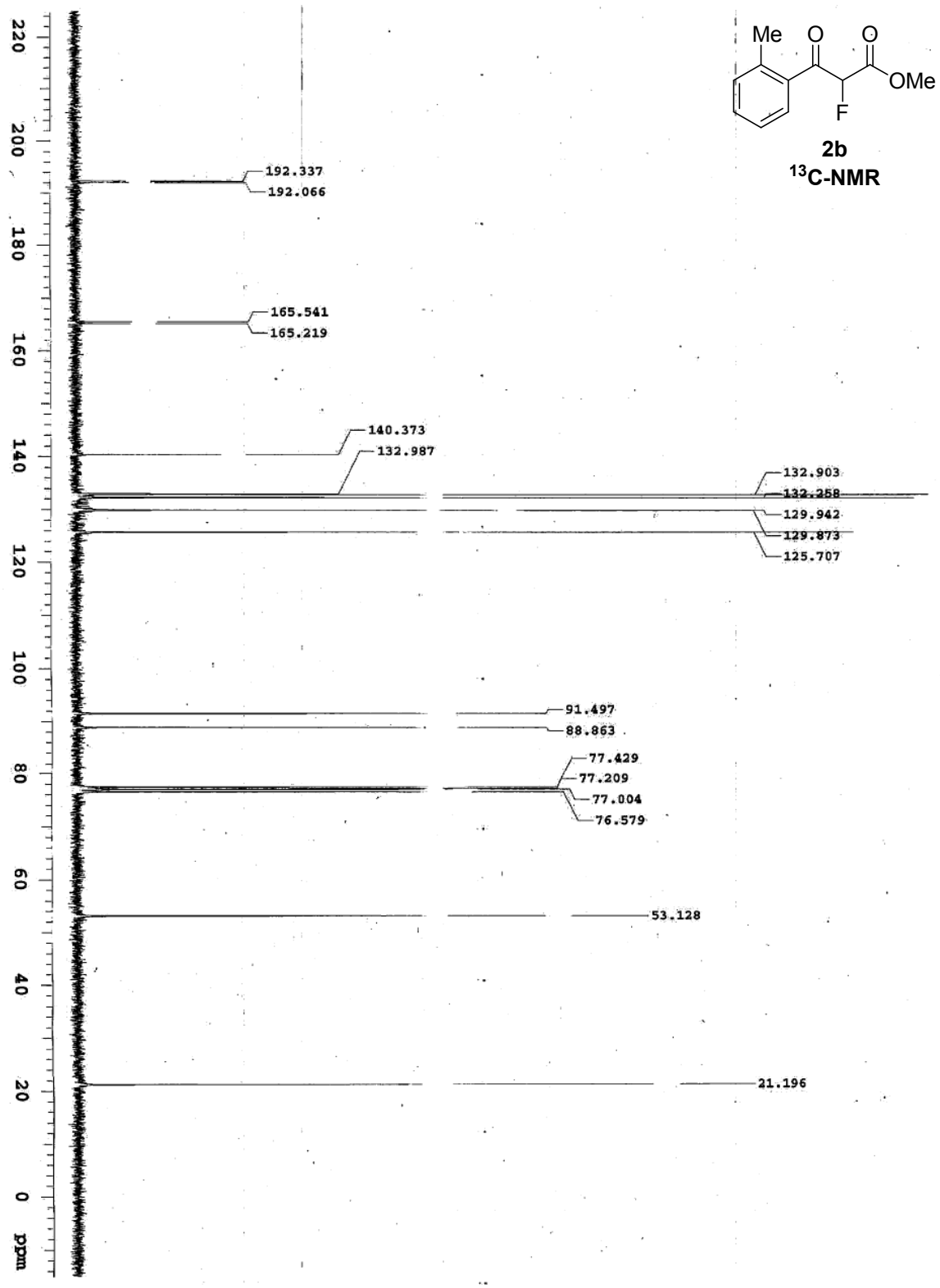
2-(Fluoromethyl)-5,5-dimethyl-1-tosylpiperidine (5)

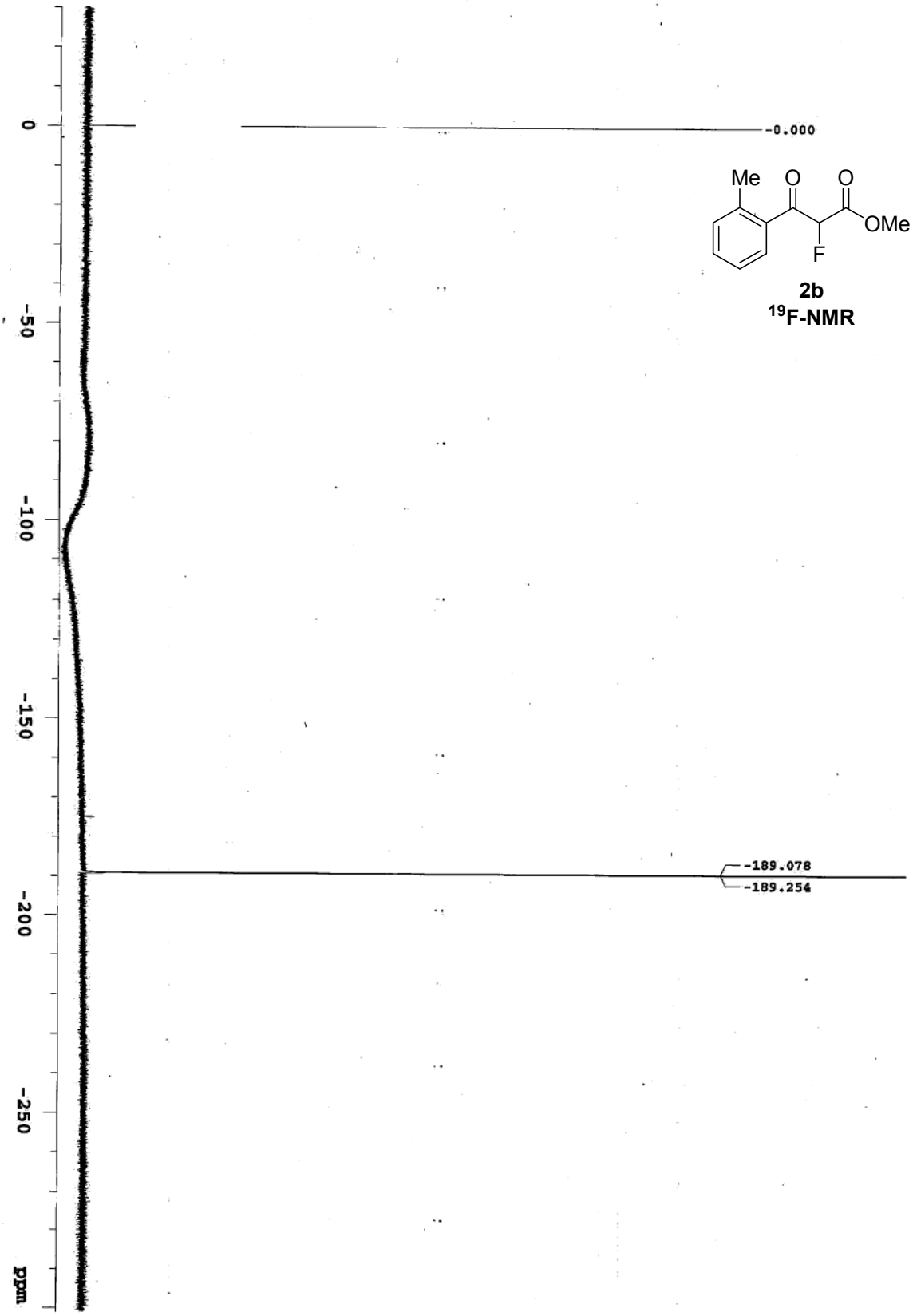


^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (s, 3H), 0.93 (s, 3H), 1.10-1.40 (m, 4H), 3.19-3.36 (m, 2H), 4.22-4.31 (m, 2H), 4.46 (d, *J* = 6.3 Hz, 1H) The tosyl peaks were not found because overlapped with **4l** ; ^{19}F NMR ($CDCl_3$, 282 MHz) δ −224 (m).

NMR spectrum

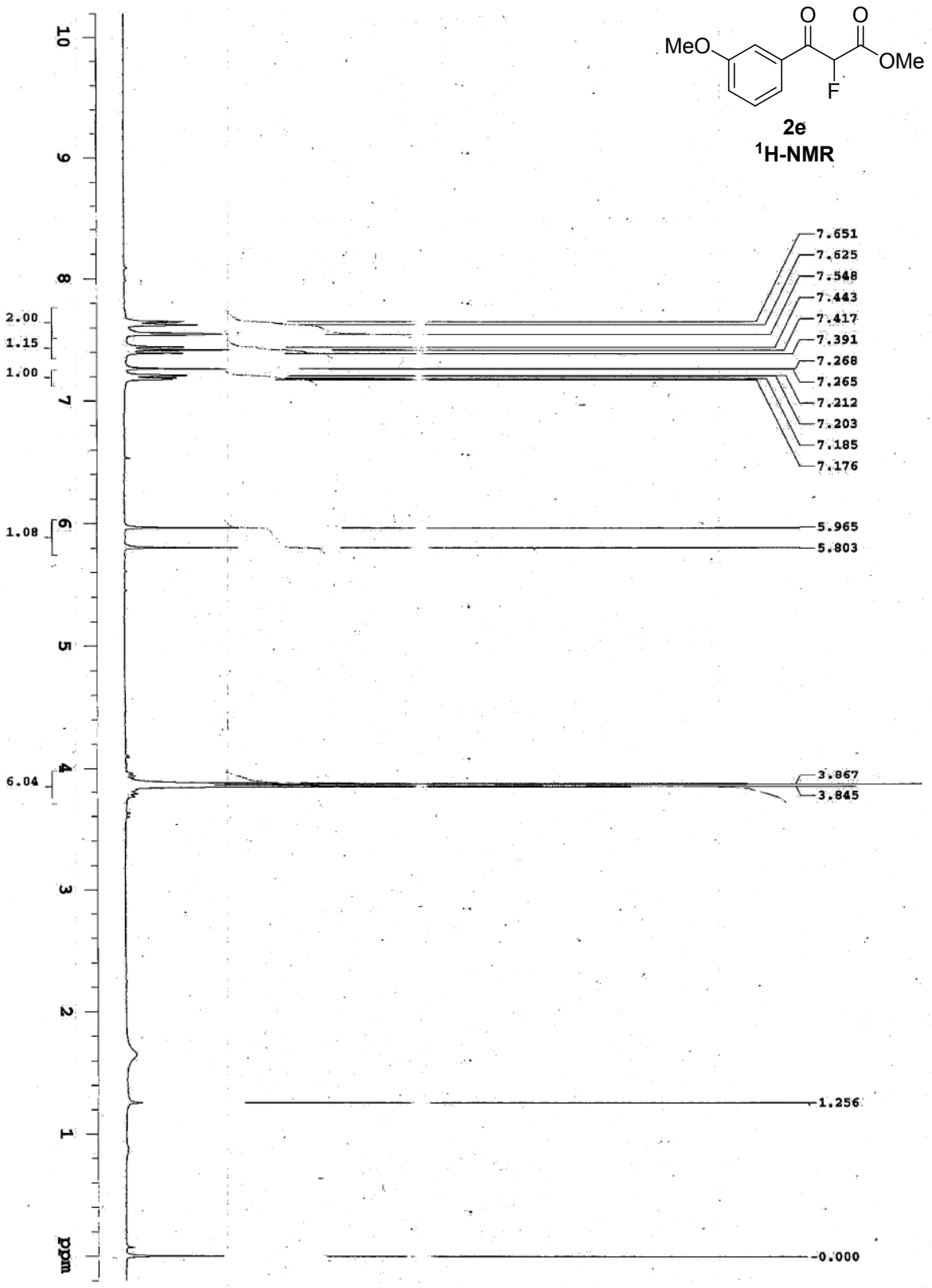



Me
O
O
OMe
F
2b
13C-NMR
192.337
192.066
165.541
165.219
140.373
132.987
132.903
132.258
129.942
129.873
125.707
91.497
88.863
77.429
77.209
77.004
76.579
53.128
21.196
220
200
180
160
140
120
100
80
60
40
20
0
ppm



2b

^{19}F-NMR


MeO
O
O
OMe
F
2e
1H-NMR
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7.548
7.443
7.417
7.391
7.268
7.265
7.212
7.203
7.185
7.176
5.965
5.803
3.867
3.845
1.256
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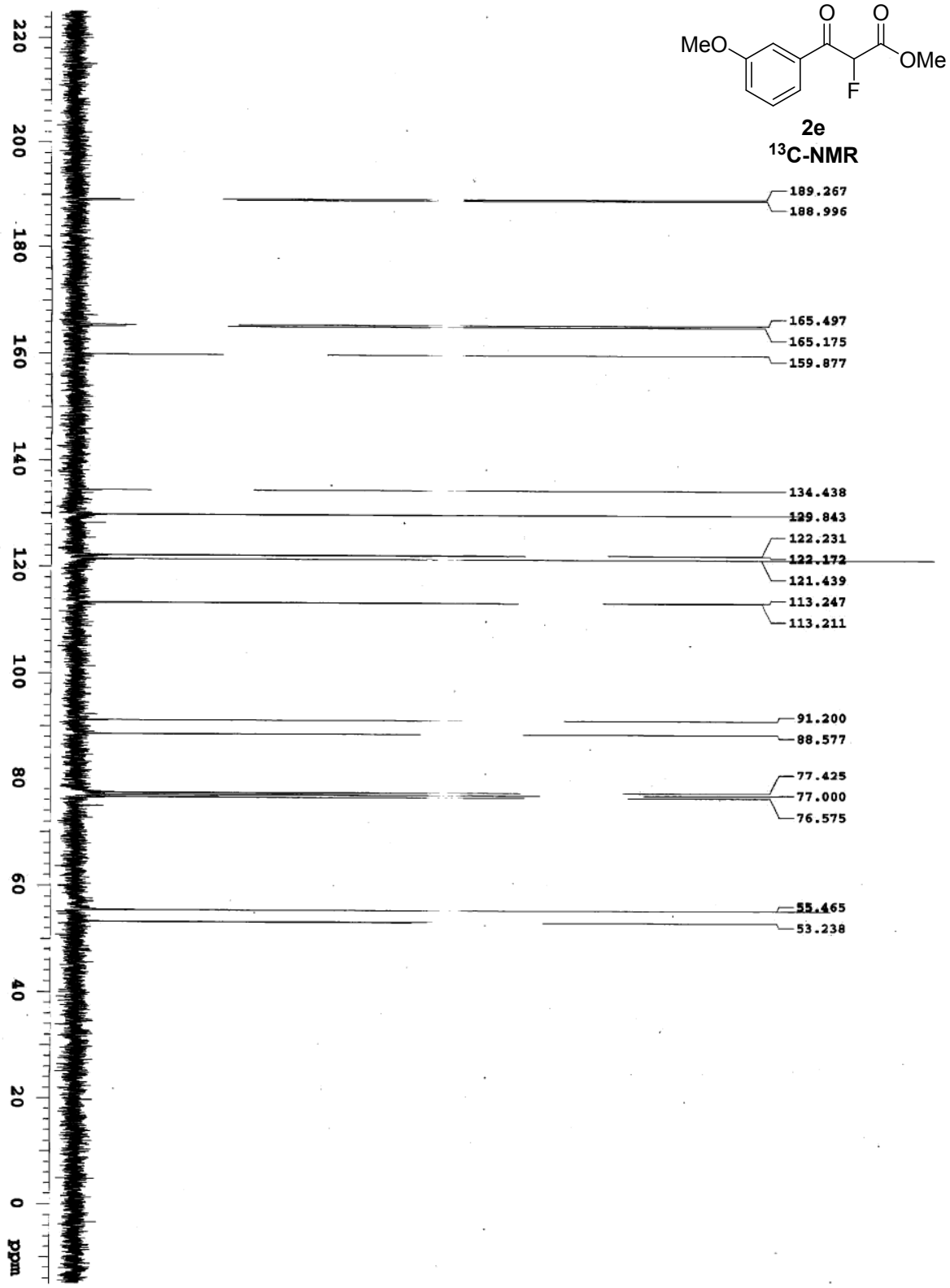
1.15
1.00
1.08
6.04
ppm


MeO
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O
OMe
F
2e
13C-NMR
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159.877
134.438
129.843
122.231
122.172
121.439
113.247
113.211
91.200
88.577
77.425
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55.465
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220
200
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140
120
100
80
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20
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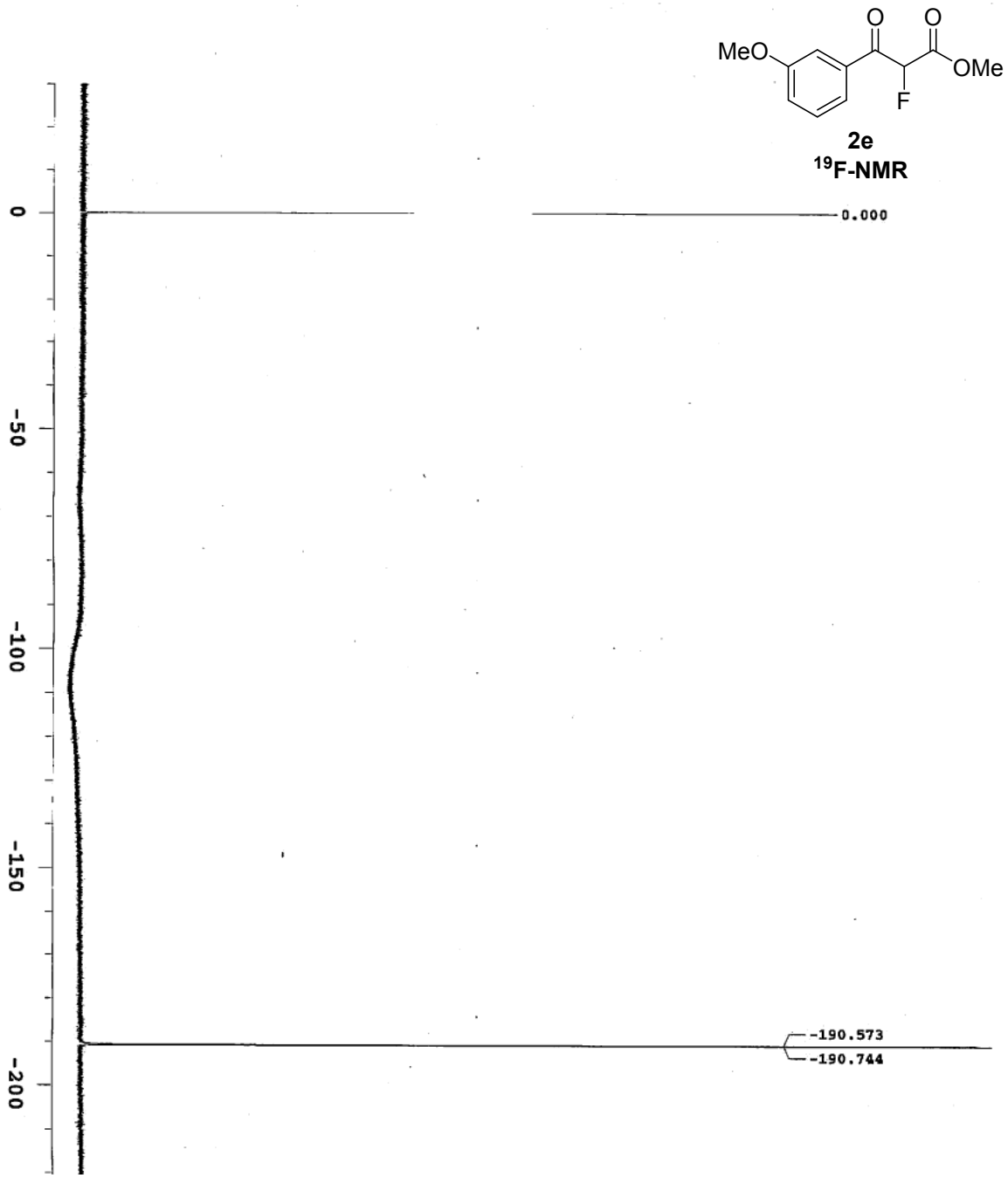
ppm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O
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OMe
F
2e
19F-NMR
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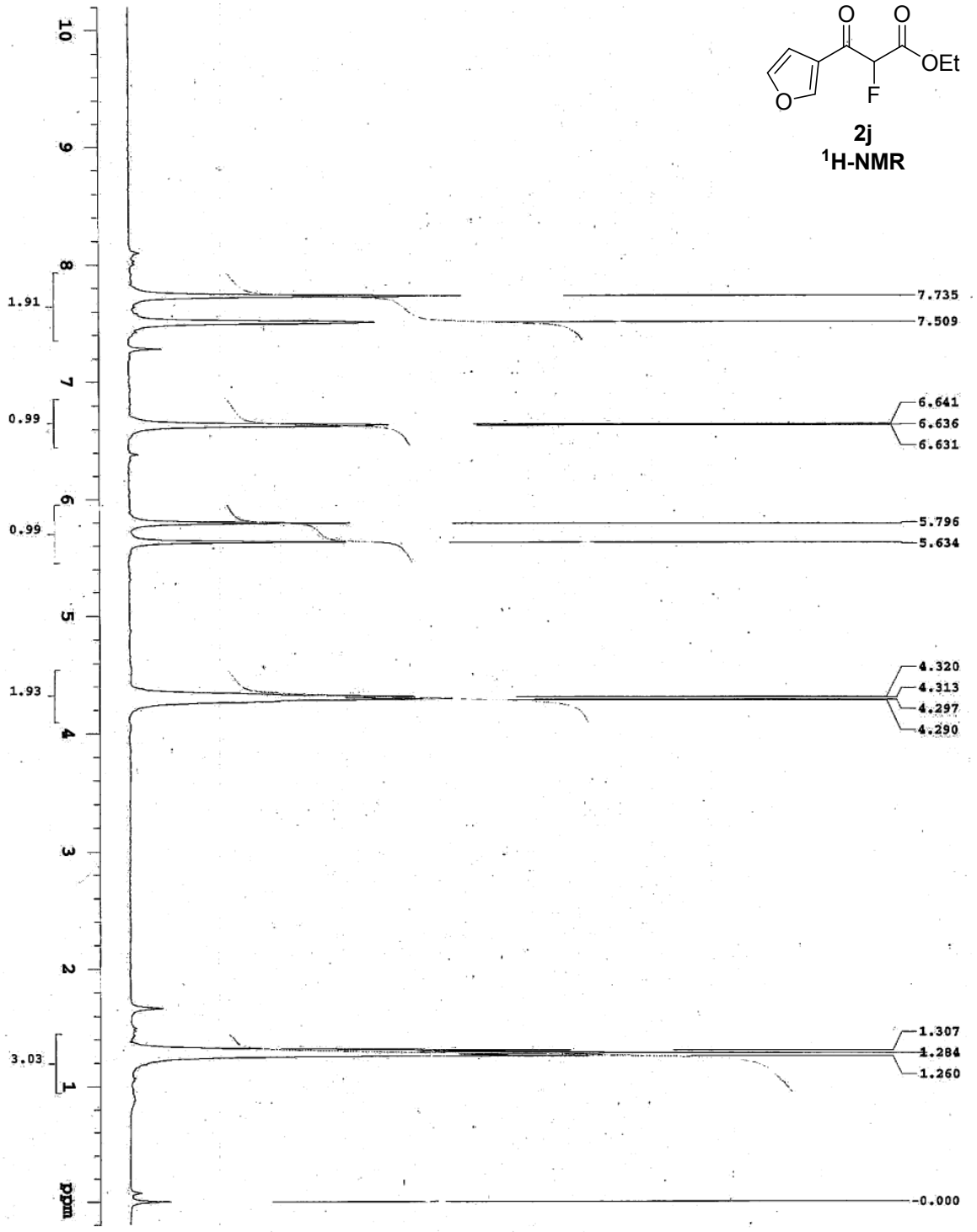
-190.744
0
-50
-100
-150
-200


O
O
OEt
F
O
2j
1H-NMR
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6.641
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6.631
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5.634
4.320
4.313
4.297
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1.307
1.284
1.260
0.000
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0.99
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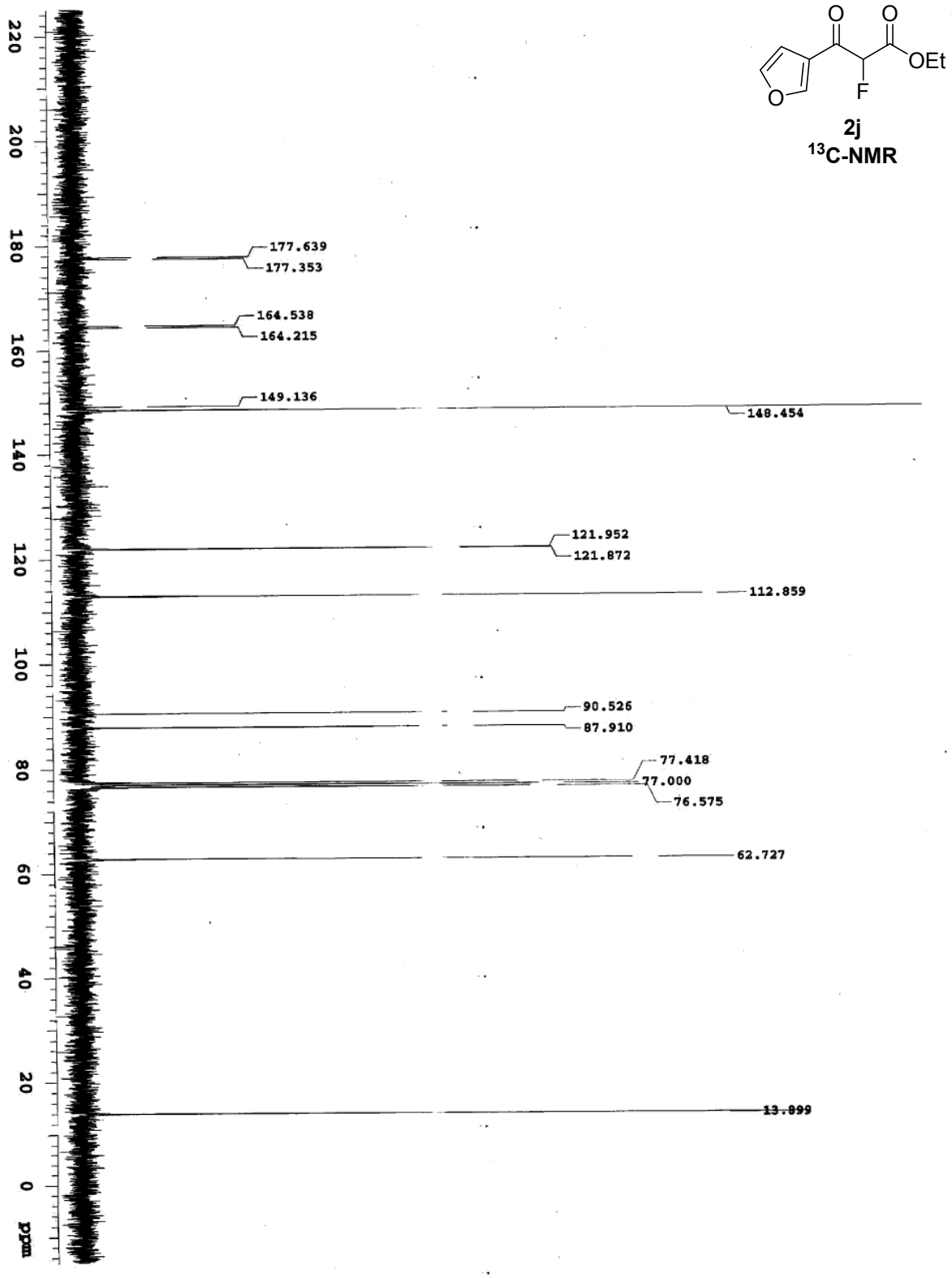
ppm


O
O
OEt
F
O
2j
13C-NMR
177.639
177.353
164.538
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149.136
148.454
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121.872
112.859
90.526
87.910
77.418
77.000
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220
200
180
160
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120
100
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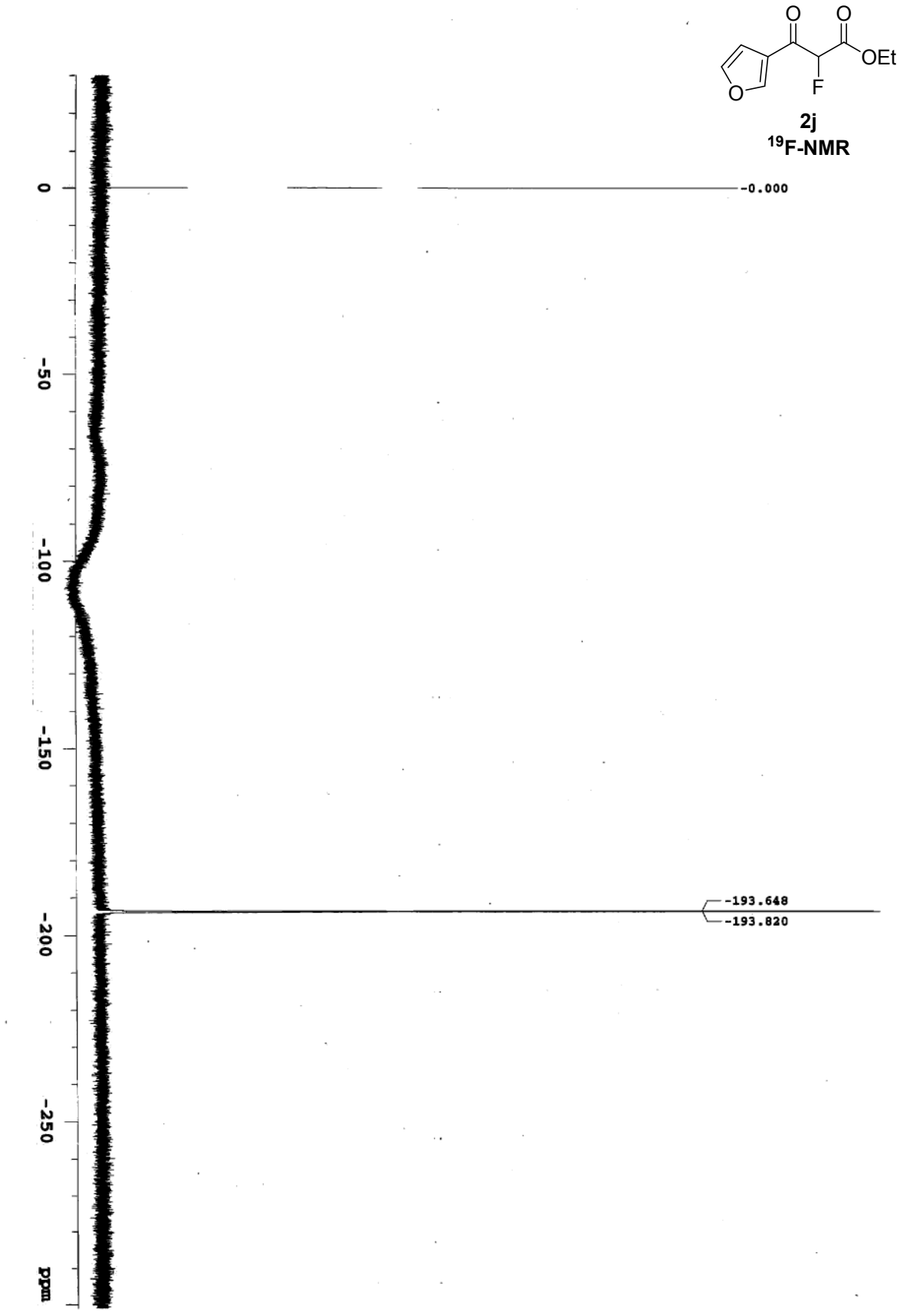
40
20
0
ppm


O
O
OEt
F
O
2j
19F-NMR
0
-50
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-150
-200
-250
ppm
-0.000
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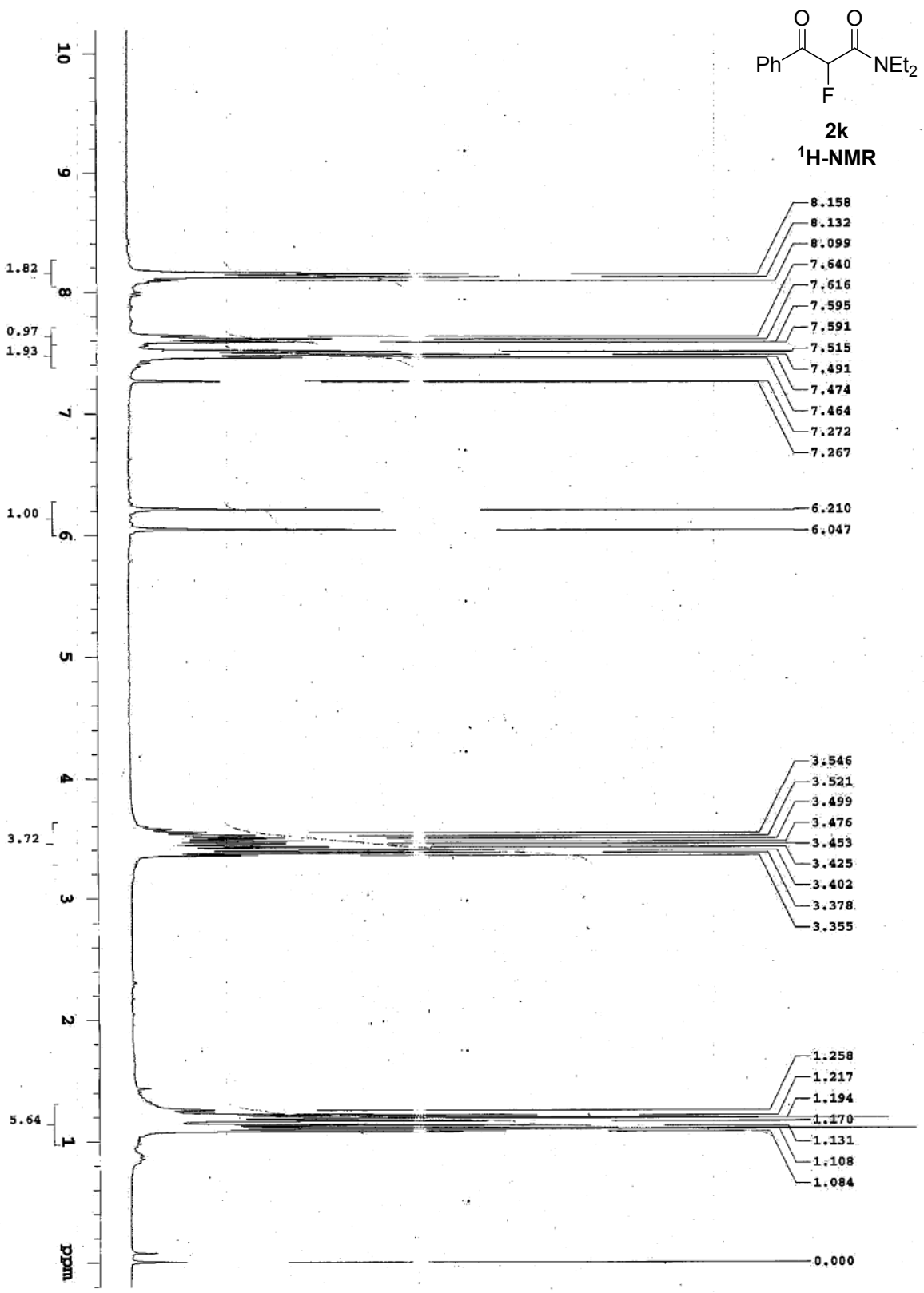
-193.820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O
Ph
NEt2
F
2k
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8.099
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7.616
7.595
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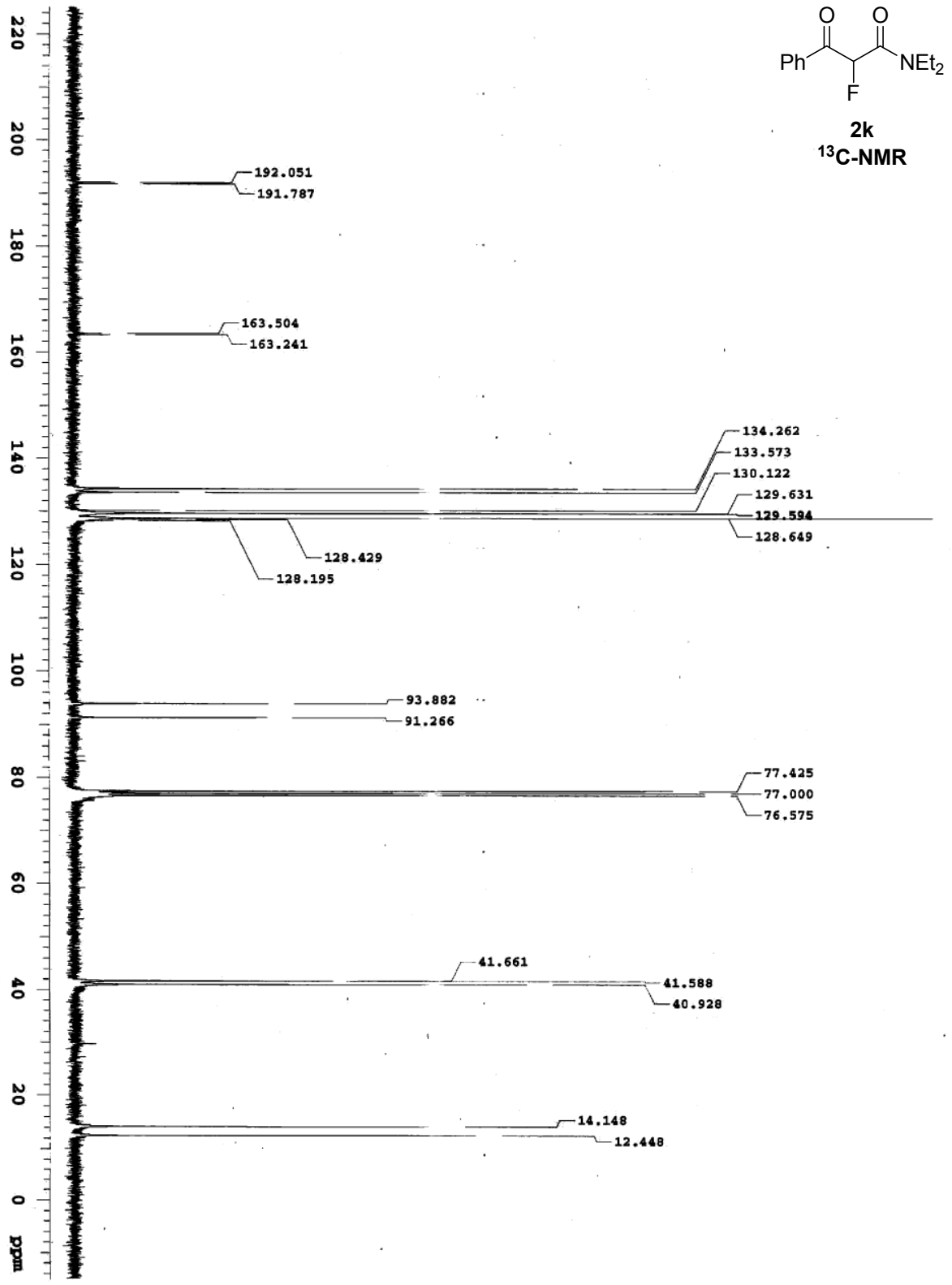
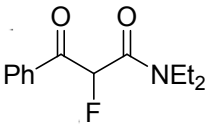
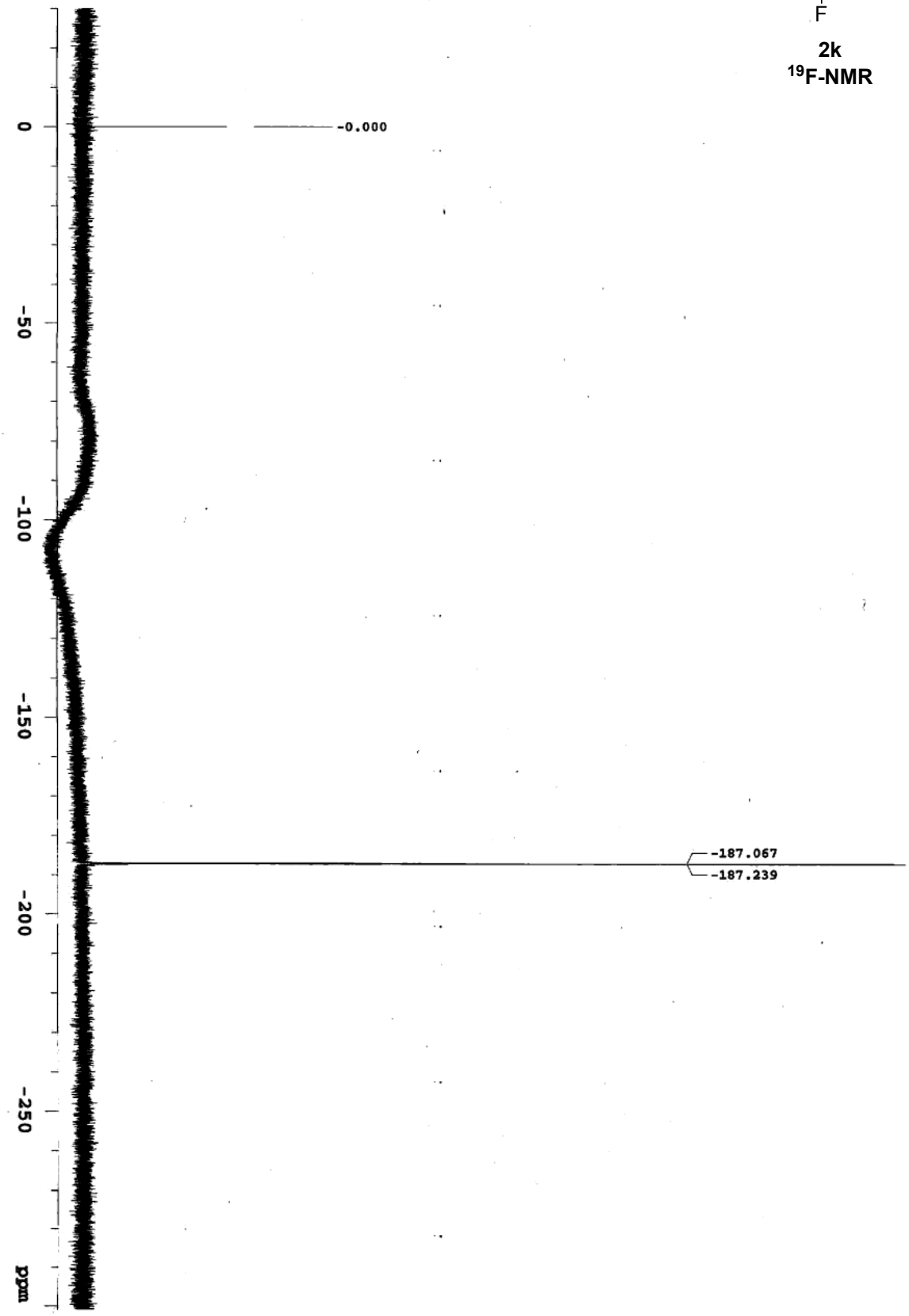
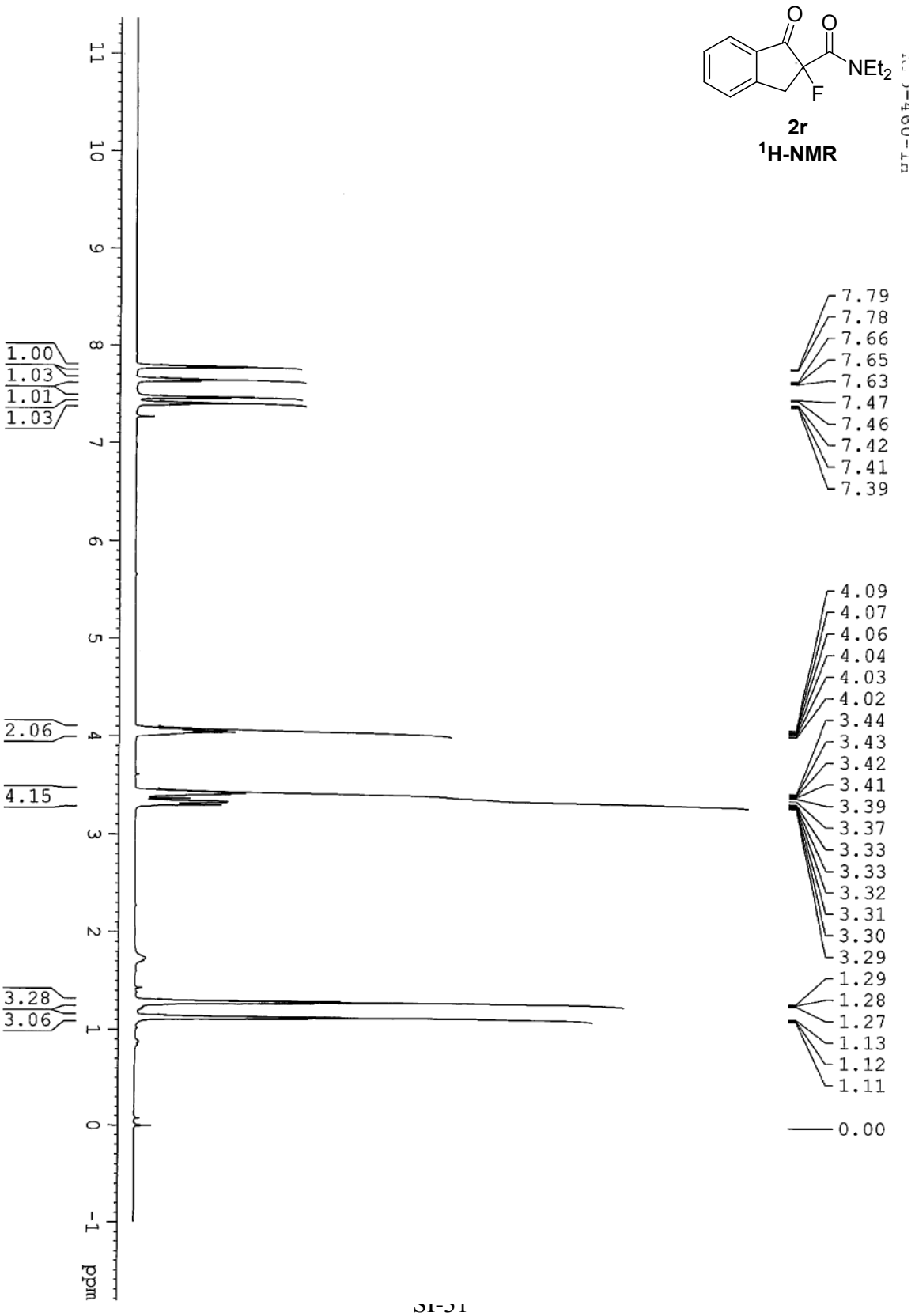
7.515
7.491
7.474
7.464
7.272
7.267
6.210
6.047
3.546
3.521
3.499
3.476
3.453
3.425
3.402
3.378
3.355
1.258
1.217
1.194
1.170
1.131
1.108
1.084
0.000
1.82
0.97
1.93
1.00
3.72
5.64
ppm

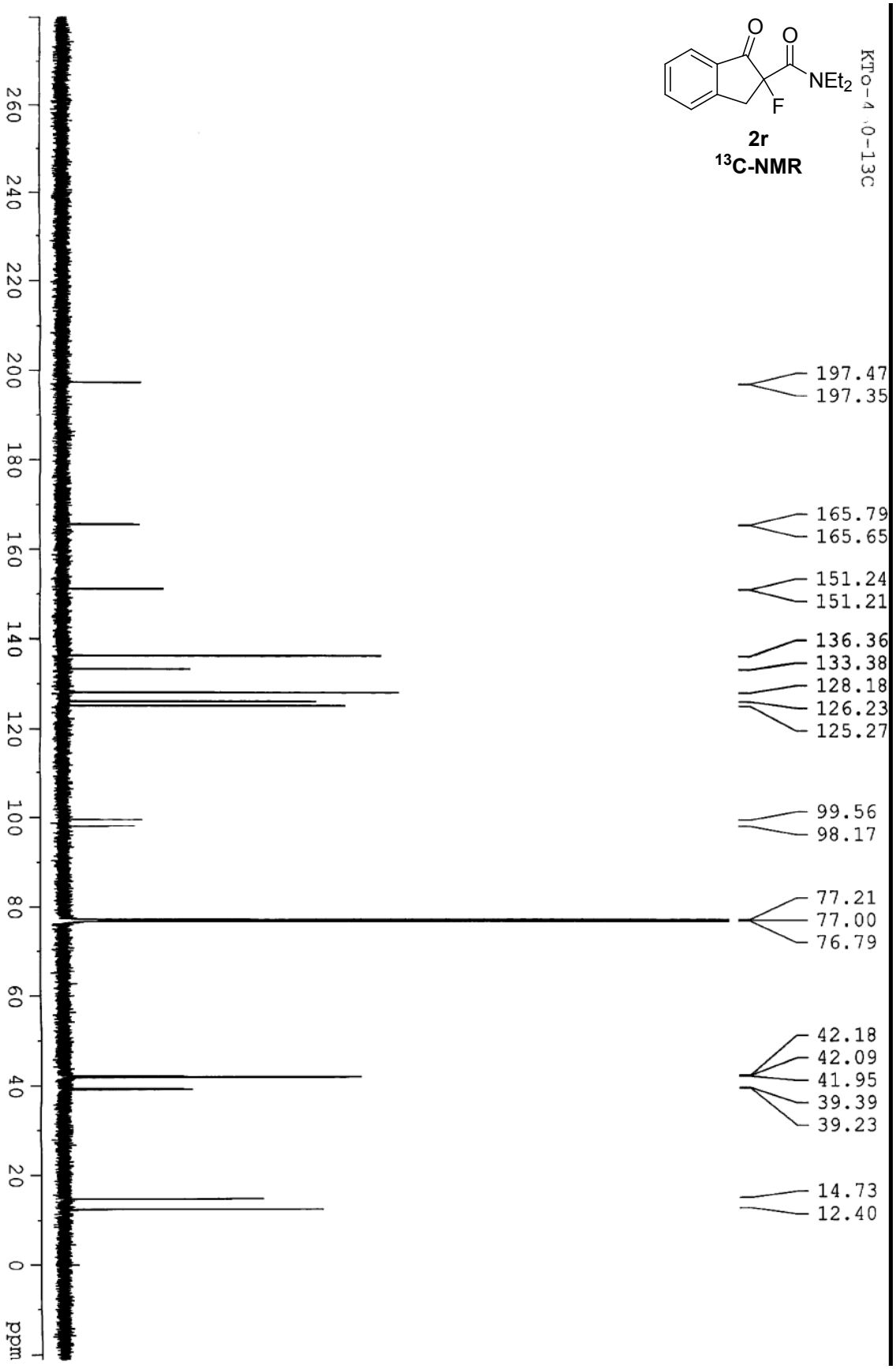

O
O
Ph
NEt2
F
2k
13C-NMR
192.051
191.787
163.504
163.241
134.262
133.573
130.122
129.631
129.594
128.649
128.429
128.195
93.882
91.266
77.425
77.000
76.575
41.661
41.588
40.928
14.148
12.448
220
200
180
160
140
120
100
80
60
40
20
0
ppm

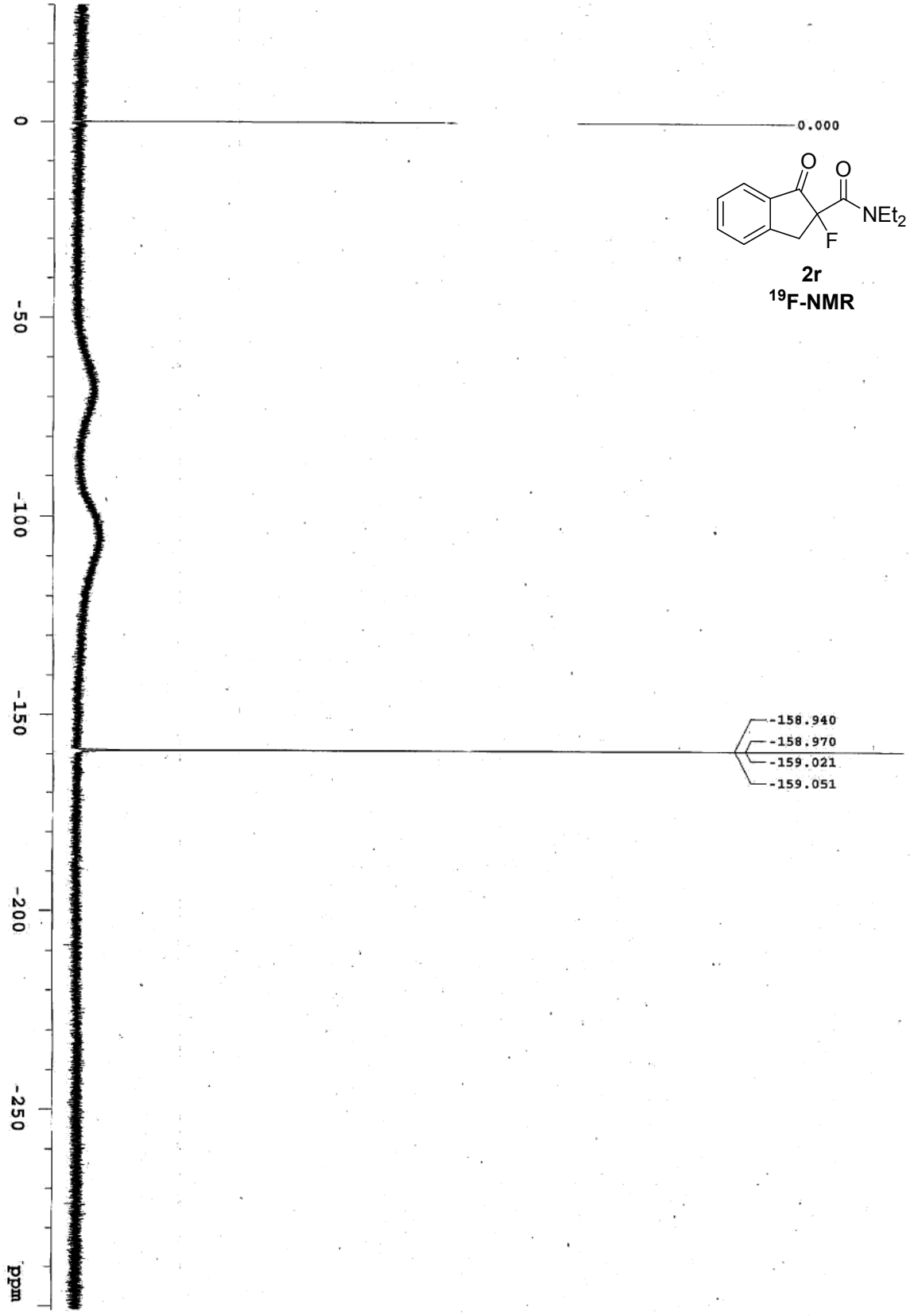


2k
^{19}F-NMR



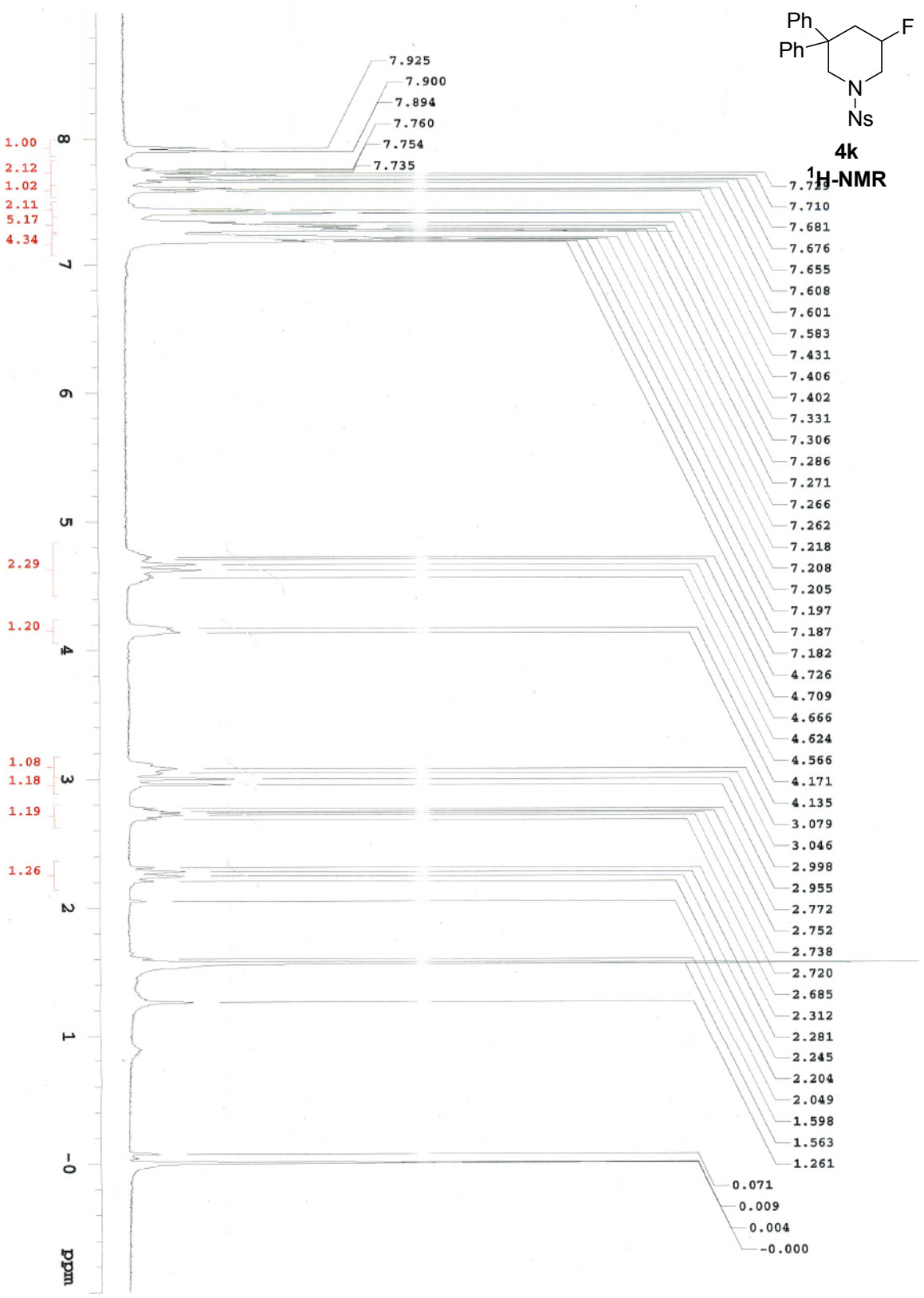

O
O
NEt2
F
2r
1H-NMR
7.79
7.78
7.66
7.65
7.63
7.47
7.46
7.42
7.41
7.39
4.09
4.07
4.06
4.04
4.03
4.02
3.44
3.43
3.42
3.41
3.39
3.37
3.33
3.33
3.32
3.31
3.30
3.29
1.29
1.28
1.27
1.13
1.12
1.11
0.00
1.00
1.03
1.01
1.03
2.06
4.15
3.28
3.06
ppm

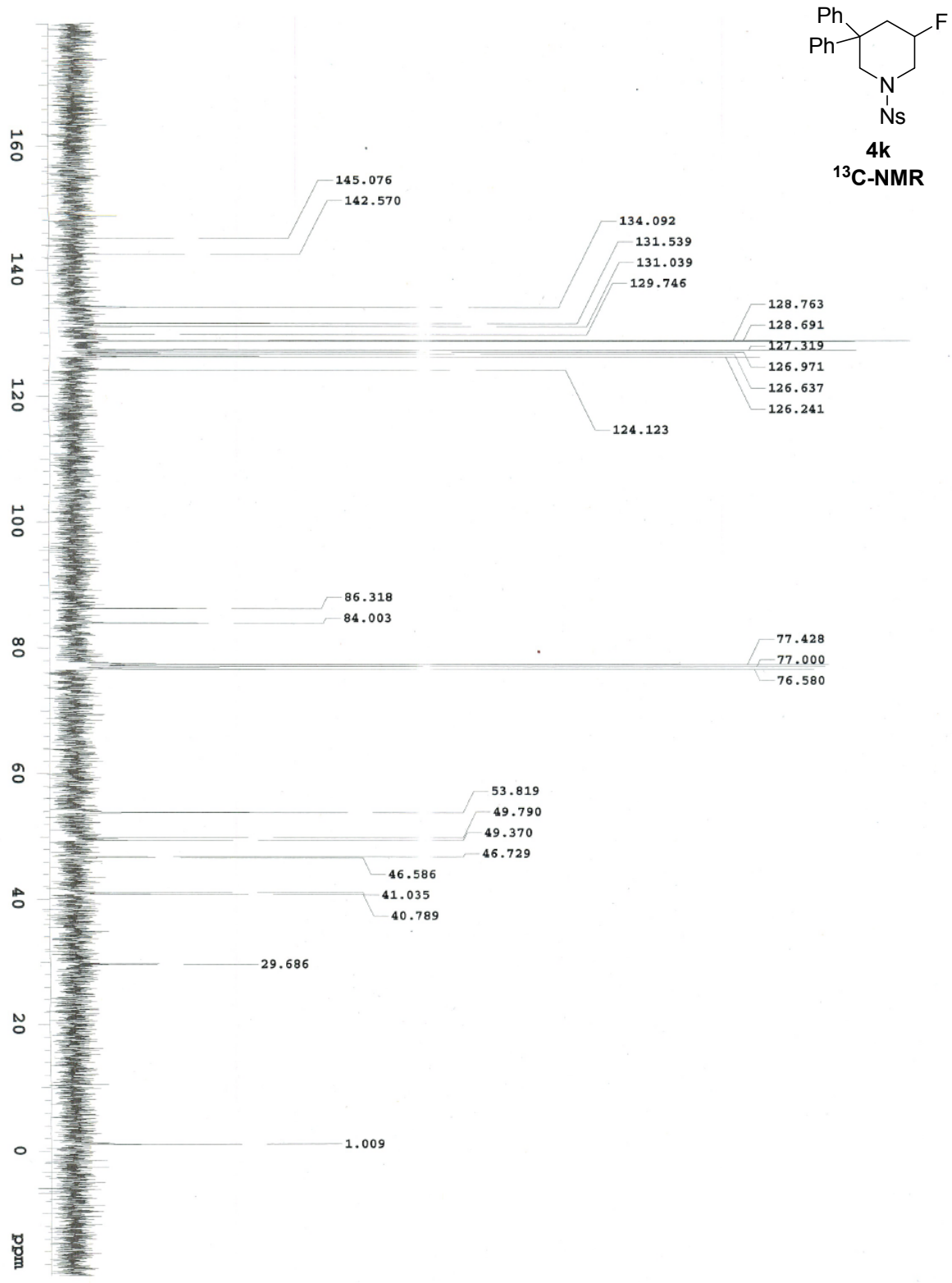

O
O
NEt2
F
2r
13C-NMR
KTo-4 0-13C
197.47
197.35
165.79
165.65
151.24
151.21
136.36
133.38
128.18
126.23
125.27
99.56
98.17
77.21
77.00
76.79
42.18
42.09
41.95
39.39
39.23
14.73
12.40
260
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

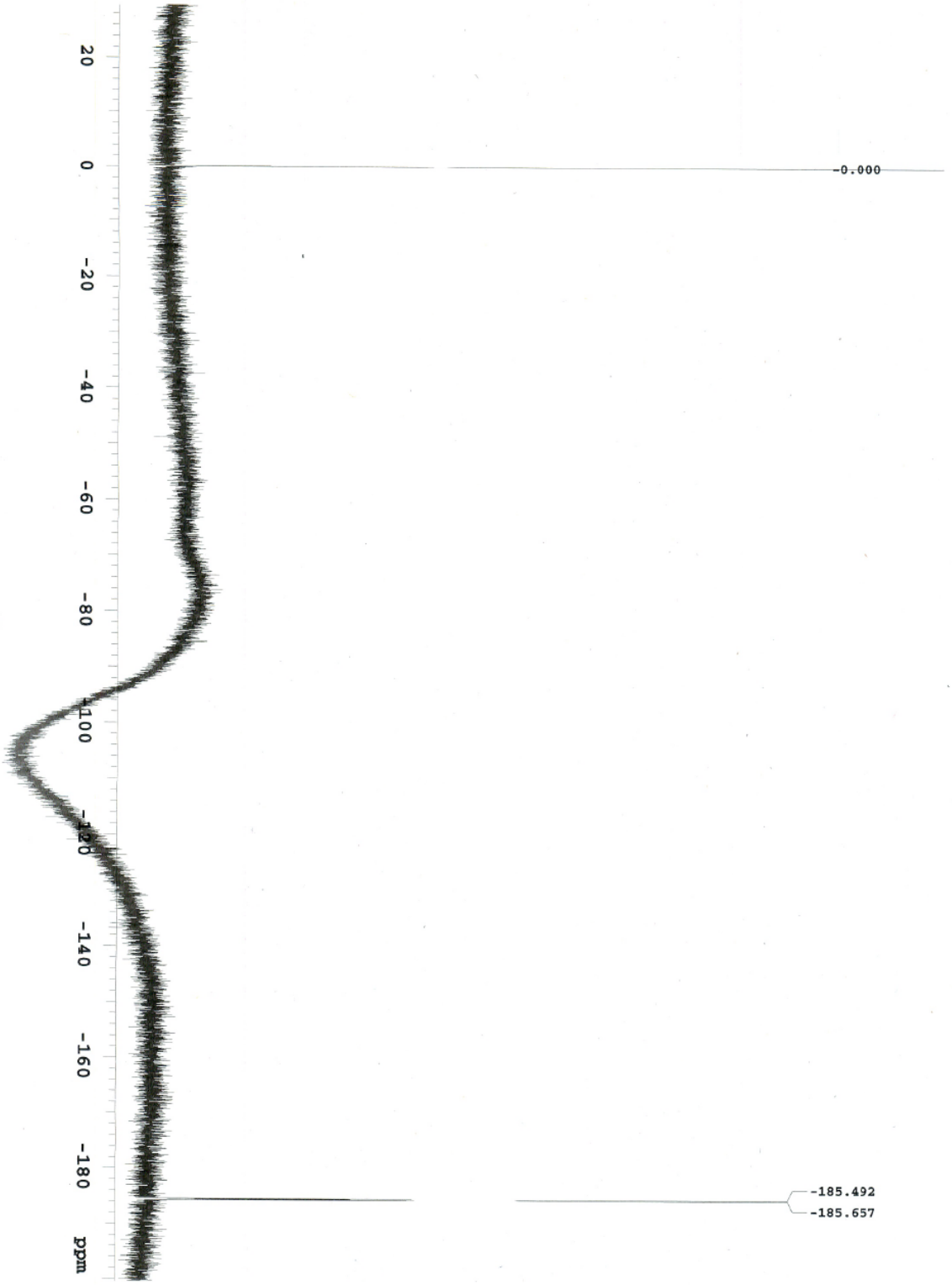

0
-50
-100
-150
-200
-250
ppm
0.000
-158.940
-158.970
-159.021
-159.051
O
O
NEt2
F

2r

^{19}F-NMR


Ph
Ph
F
N
Ns
4k
1H-NMR
7.925
7.900
7.894
7.760
7.754
7.735
7.710
7.681
7.676
7.655
7.608
7.601
7.583
7.431
7.406
7.402
7.331
7.306
7.286
7.271
7.266
7.262
7.218
7.208
7.205
7.197
7.187
7.182
4.726
4.709
4.666
4.624
4.566
4.171
4.135
3.079
3.046
2.998
2.955
2.772
2.752
2.738
2.720
2.685
2.312
2.281
2.245
2.204
2.049
1.598
1.563
1.261
0.071
0.009
0.004
-0.000
1.00
2.12
1.02
2.11
5.17
4.34
2.29
1.20
1.08
1.18
1.19
1.26
8
7
6
5
4
3
2
1
-0
ppm

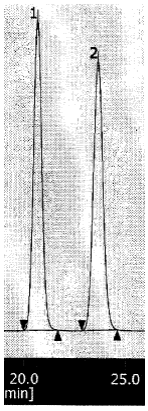

Ph
Ph
F
N
Ns
4k
13C-NMR
145.076
142.570
134.092
131.539
131.039
129.746
128.763
128.691
127.319
126.971
126.637
126.241
124.123
86.318
84.003
77.428
77.000
76.580
53.819
49.790
49.370
46.729
46.586
41.035
40.789
29.686
1.009
160
140
120
100
80
60
40
20
0
ppm

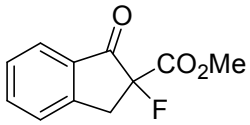

20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
-0.000
-185.492
-185.657

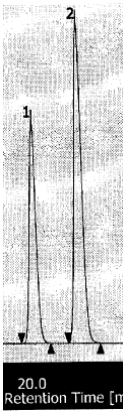
HPLC charts

HPLC using an OJ-H column

2o, 25% ee (Hex/*i*-PrOH=90/10, flow rate 2.0 mL/ min, λ=254 nm)





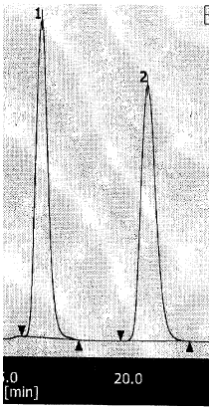


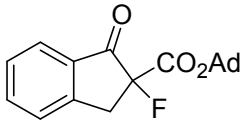
No	Time [min]	Area [%]	Height [%]
1	20.6	50.327	53.631
2	23.6	49.673	46.369

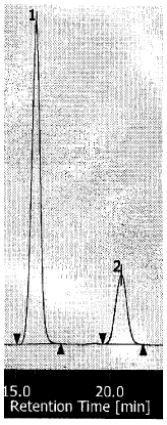
No	Time [min]	Area [%]	Height [%]
1	20.2	37.421	40.818
2	23.2	62.579	59.182

HPLC using an IA column

2s, 56% ee (Hex/*i*-PrOH=99/1, flow rate 1.0 mL/ min, λ=254 nm)





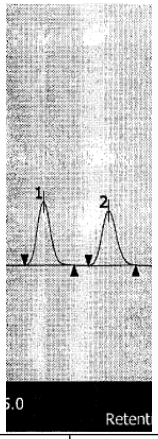


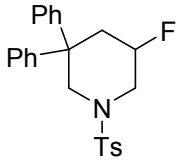
No	Time [min]	Area [%]	Height [%]
1	16.4	50.088	55.356
2	20.7	49.912	44.644

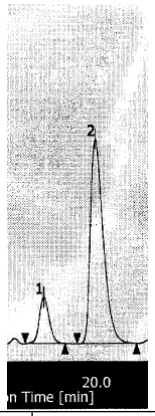
No	Time [min]	Area [%]	Height [%]
1	16.0	77.842	82.129
2	20.6	22.158	17.781

HPLC using an ID column

4c, 70% ee (Hex/*i*-PrOH=90/10, flow rate 1.0 mL/ min, λ=254 nm)





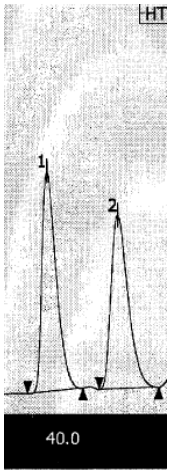


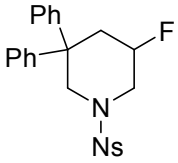
No	Time [min]	Area [%]	Height [%]
1	16.1	50.626	53.799
2	18.0	49.374	46.201

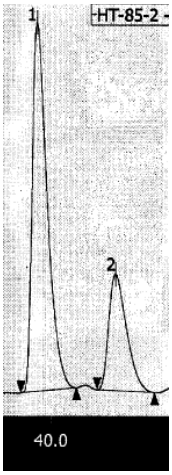
No	Time [min]	Area [%]	Height [%]
1	17.5	15.123	18.617
2	20.0	84.877	81.383

HPLC using an ID column

4k, 45% ee (Hex/*i*-PrOH=90/10, flow rate 1.0 mL/ min, λ=254 nm)







No	Time [min]	Area [%]	Height [%]
1	39.0	51.266	55.960
2	43.6	48.734	44.040

No	Time [min]	Area [%]	Height [%]
1	39.1	72.397	76.057
2	44.1	27.603	23.943

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