Gold(I)-Catalyzed [2+4] Cycloaddition of 1,1-Difluoroallenes with Conjugated Enones: Syntheses of Ring-Difluorinated Dihydro-2*H*-Pyrans

Daisuke Miyazaki,[1] Reo Eto,[1] Junji Ichikawa,[2] and Kohei Fuchibe[1]*

kfuchibe@chem.tsukuba.ac.jp,[1] jichikawa@sagami.or.jp[2]

Division of Chemistry, Faculty of Pure and Applied Sciences
University of Tsukuba, Tsukuba, Ibaraki 305–8571, Japan[1]

Sagami Chemical Research Institute, 2743-1 Hayakawa
Ayase, Kanagawa 252–1193, Japan[2]

— Supporting Information —

Table of Contents

1. General Statements

1–1. Solvents and Reagents

Superdry THF, dichloromethane and DMF were purchased from Kanto Chemical Co., Inc. and used as received. 1,2-Dichloroethane was distilled from P_4O_{10} and from CaH_2 sequently, and then stored over MS 4A.

AuCl, $AuCl_3$ and AuCl(IPr) were purchased from Merck KGaA and used as received. $AuCl(PPh_3)$ was purchased from FUJIFILM Wako Pure Chemical Co., Ltd. and used as received. $AgSbF_6$ was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Molecular sieves 4A was purchased from Merck KGaA, dried under microwave irradiation (3 min), and further flame-dried in a reaction vessel just before use.

α,α,α-Trifluorotoluene (an internal standard for ^{19}F NMR quantitative analysis) was purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

1,1-Difluoroallenes **1a**–**c** were prepared by our reported method.[1] The spectral data of 1,1-difluoroallenes **1a**–**c** were provided in our previous publication.[1b]

1–2. Purification

Column chromatography was conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc.). Preparative thin-layer chromatography was conducted on silica gel (Wakogel B-5F, FUJIFILM Wako Pure Chemical Corporation).

1–3. Analyses

IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. NMR spectra were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$ at 500 MHz (^1H NMR), at 126 MHz (^{13}C NMR) and at 471 MHz (^{19}F NMR). Chemical shifts were given in ppm relative to internal Me_4Si (for ^1H NMR: $\delta = 0.00$), $CDCl_3$ (for ^{13}C NMR: $\delta = 77.0$) and C_6F_6 (for ^{19}F NMR: $\delta = 0.0$; C_6F_6 exhibits a ^{19}F NMR signal at –162.9 ppm vs. $CFCl_3$). Elemental analyses (EA) were performed with a Yanako MT-3 CHN Corder apparatus. High-resolution mass spectroscopy (HRMS) was conducted with a Jeol JMS-T100GCV (EI, TOF) spectrometer.

---

[1] a) Fuchibe, K.; Abe, M.; Oh, K.; Ichikawa, J. *Org. Synth.* **2016**, *93*, 352–366; b) Oh, K.; Fuchibe, K.; Ichikawa, J. *Synthesis* **2011**, *2011*, 881–886.

2. Typical Procedures

2–1. Synthesis of (*E*)-3-Alkylidene-2,2-Difluorodihydro-2*H*-Pyrans

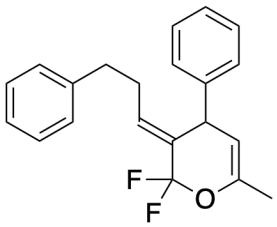
To a flame-dried molecular sieves 4A (401 mg) were added *trans*-chalcone **2d** (218 mg, 1.05 mmol), AuCl(IPr) (12 mg, 0.020 mmol), $AgSbF_6$ (0.007 mg, 0.019 mmol), and 1,2-dichloroethane (4 mL). After stirring for 10 min at room temperature, white precipitates were observed. To the resulting suspension was added a 1,2-dichloroethane solution (1 mL) of 1,1-difluoroallene **1a** (186 mg, 1.03 mmol) at room temperature. After stirring for 1 h at room temperature, the reaction mixutre was passed through a small pad of silica gel using dichlromethane as an eluent. After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 30:1) to give difluorodihydropyran **3f** (399 mg, quantitative) as a colorless liquid.

3. Spectral Data of Products

3–1. (*E*)-2,2-Difluoro-6-methyl-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3a**

Synthesized from 1,1-difluoroallene **1a** (54 mg, 0.30 mmol), *trans*-benzalacetone **2a** (45 mg, 0.31 mmol), AuCl(IPr) (3.4 mg, 0.006 mmol), $AgSbF_6$ (2.0 mg, 0.006 mmol) and MS 4A (119 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 20:1).



3a

A colorless liquid, 88 mg, 90% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31–7.23 (m, 6H), 7.23–7.16 (m, 2H), 7.08 (d, J = 7.3 Hz, 2H), 6.29 (td, J = 7.3, 2.5 Hz, 1H), 4.89 (br d, J = 4.3 Hz, 1H), 4.31 (br s, 1H), 2.69–2.57 (m, 2H), 2.53–2.34 (m, 2H), 1.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.6 (d, J_{CF} = 4 Hz), 141.5, 140.9, 131.3 (dd, J_{CF} = 6, 6 Hz), 128.5, 128.4, 128.3, 128.2 (dd, J_{CF} = 31, 21 Hz), 127.47, 127.45, 126.7, 126.1, 119.8 (dd, J_{CF} = 258, 249 Hz), 101.9, 39.4 (d, J_{CF} = 3 Hz), 34.6 (d, J_{CF} = 1 Hz), 30.0, 19.0.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 103.1 (d, J = 159 Hz, 1F), 79.4 (d, J = 159 Hz, 1F).

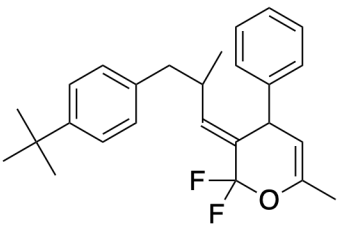
IR (neat): $\tilde{\nu}$ = 2927, 1703, 1450, 1319, 1154, 1069, 909 cm^{-1}.

HRMS (EI): *m*/*z* calcd. for $C_{21}H_{20}F_2O$ $[M]^+$: 326.1472; found: 326.1474.

3–2. (*E*)-3-[3-(4-*tert*-Butylphenyl)-2-methylpropan-1-ylidene]-2,2-difluoro-6-methyl-4-phenyl-3,4-dihydro-2*H*-pyran **3b**

Synthesized from 1,1-difluoroallene **1b** (75 mg, 0.30 mmol), *trans*-benzalacetone **2a** (44 mg, 0.30 mmol), AuCl(IPr) (3.8 mg, 0.006 mmol), $AgSbF_6$ (2.1 mg, 0.006 mmol) and MS 4A (120 mg).

Purified by preparative thin-layer chromatography (SiO_2, hexane/ethyl acetate = 30:1).



3b

A colorless liquid, 99 mg, 83% yield (dr = 83:17).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30–7.23 (m, 4H), 7.22–7.15 (m, 3H), 7.03 (d, J = 8.2 Hz, 1.66H), 6.75 (d, J = 8.2 Hz, 0.34H), 6.16 (br d, J = 11.2 Hz, 0.17H), 6.02 (br dd, J = 10.5, 2.5 Hz, 0.83H), 4.93 (br d, J = 4.3 Hz, 0.17H), 4.61 (br d, J = 4.6 Hz, 0.83H), 4.40 (br s, 0.17H), 3.80 (br s, 0.83H), 2.74–2.65 (m, 1H), 2.64 (dd, J = 13.2, 5.7 Hz, 0.83H), 2.50 (dd, J = 13.2, 8.5 Hz, 0.83H), 2.45 (dd, J = 13.3, 6.0 Hz, 0.17H), 2.26 (dd, J = 13.3, 8.8 Hz, 0.17H), 1.87 (s, 0.51H), 1.81 (s, 2.49H), 1.30 (s, 7.47H), 1.29 (s, 1.53H), 0.97 (d, J = 6.5 Hz, 2.49H), 0.93 (d, J = 6.6 Hz, 0.51H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 148.8, 148.7, 146.2 (d, J_{CF} = 4 Hz), 146.1 (d, J_{CF} = 4 Hz), 142.0, 141.6, 137.9 (dd, J_{CF} = 6, 6 Hz), 136.6, 136.4 (dd, J_{CF} = 6, 6 Hz), 136.2, 128.83, 128.82, 128.6,

128.4, 127.50, 127.48, 127.24, 127.22, 126.8 (dd, J_{CF} = 34, 23 Hz), 126.7, 126.5, 125.9 (dd, J_{CF} = 34, 23 Hz), 125.04, 125.00, 119.9 (dd, J_{CF} = 258, 249 Hz), 119.8 (dd, J_{CF} = 258, 249 Hz), 102.5, 101.5, 42.7, 41.4 (d, J_{CF} = 2 Hz), 39.6 (d, J_{CF} = 3 Hz), 38.9 (d, J_{CF} = 3 Hz), 35.4, 34.6, 34.35, 34.34, 31.4, 19.7 (d, J_{CF} = 2 Hz), 19.1, 19.0.

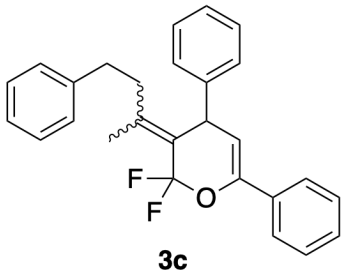
^{19}F NMR ($CDCl_3$, 471 MHz) δ 103.0 (d, J = 159 Hz, 0.17F), 102.6 (d, J = 158 Hz, 0.83F), 79.6 (d, J = 159 Hz, 0.17F), 79.2 (d, J = 158 Hz, 0.83F).

IR (neat): $\tilde{\nu}$ = 2930, 1705, 1462, 1312, 1153, 1069, 902 cm^{-1}.

HRMS (EI): *m*/*z* calcd. for $C_{26}H_{30}F_2O$ $[M]^+$: 396.2260; found: 396.2253.

3–3. 2,2-Difluoro-4,6-diphenyl-3-(4-phenylbutan-2-ylidene)-3,4-dihydro-2*H*-pyran **3c**

Synthesized from 1,1-difluoroallene **1c** (75 mg, 0.39 mmol), *trans*-chalcone **2d** (81 mg, 0.39 mmol), AuCl(IPr) (11.0 mg, 0.018 mmol), $AgSbF_6$ (6.2 mg, 0.018 mmol) and MS 4A (156 mg).



3c

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 20:1).

A colorless liquid, 151 mg, 97% yield (*E*/*Z* = 53:47).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61–7.54 (m, 2H), 7.33–7.12 (m, 12H), 6.98–6.94 (m, 1H), 5.94 (d, J = 6.3 Hz, 0.53H), 5.82 (d, J = 6.5 Hz, 0.47H), 4.44 (d, J = 6.3 Hz, 0.53H), 4.29 (d, J = 6.5 Hz, 0.47H), 2.83–2.65 (m, 2H), 2.62–2.53 (m, 0.47H), 2.39–2.25 (m, 1.53H), 2.11 (dd, J_{HF} = 3.5, 3.5 Hz, 1.41H), 1.72 (dd, J_{HF} = 2.8, 2.8 Hz, 1.59H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.1 (d, J_{CF} = 2 Hz), 147.0 (d, J_{CF} = 3 Hz), 144.7, 144.0, 143.7, 142.7, 141.6, 141.2, 132.82, 132.80, 128.9, 128.82, 128.77, 128.77, 128.38, 128.38, 128.38, 128.36, 128.32, 128.294, 128.285, 128.28, 127.3, 126.7, 126.6, 126.03, 125.96, 124.8 (dd, J_{CF} = 28, 26 Hz), 124.56, 124.54 (dd, J_{CF} = 28, 26 Hz), 124.53, 122.5 (dd, J_{CF} = 264, 250 Hz), 122.4 (dd, J_{CF} = 261, 253 Hz), 106.2, 106.0, 42.0, 41.5, 38.2 (dd, J_{CF} = 5, 2 Hz), 38.1, 35.0, 33.1, 20.5, 19.7 (dd, J_{CF} = 5, 2 Hz).

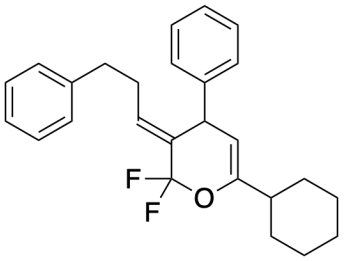
^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.9 (d, J = 164 Hz, 1.06F), 104.3 (d, J = 164 Hz, 0.47F), 102.5 (d, J = 164 Hz, 0.47F).

IR (neat): $\tilde{\nu}$ = 2938, 1795, 1647, 1600, 1451, 1318, 1140, 650 cm^{-1}.

HRMS (EI): *m*/*z* calcd. for $C_{27}H_{24}F_2O$ $[M]^+$: 402.1790; found: 402.1787, 402.1788.

3–4. (*E*)-6-Cyclohexyl-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3d**

Synthesized from 1,1-difluoroallene **1a** (58 mg, 0.32 mmol), enone **2b** (64 mg, 0.30 mmol), AuCl(IPr) (4 mg, 0.006 mmol), $AgSbF_6$ (2 mg, 0.006 mmol), and MS 4A (121 mg).



3d

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).

A yellow liquid, 101 mg, 85% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23–7.08 (m, 8H), 7.00 (d, J = 7.0 Hz, 2H), 6.19 (br t, J = 7.0 Hz, 1H), 4.77 (br d, J = 3.8 Hz, 1H), 4.24 (br s, 1H), 2.60–2.47 (m, 2H), 2.42–2.25 (m, 2H), 1.99–1.93 (m, 1H), 1.85–1.78 (m, 2H), 1.72–1.66 (m, 2H), 1.62–1.58 (m, 1H), 1.22–1.08 (m, 5H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 154.3 (d, J_{CF} = 4 Hz), 141.9, 141.0, 131.0 (dd, J_{CF} = 6, 6 Hz), 128.9 (dd, J_{CF} = 32, 22 Hz), 128.5, 128.4, 128.3, 127.59, 127.57, 127.5, 127.3, 127.1, 126.6, 126.1, 120.0 (dd, J_{CF} = 257, 248 Hz), 99.9, 41.2, 39.5 (d, J_{CF} = 3 Hz), 34.6, 30.3, 30.1, 30.0, 26.03, 25.97.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.8 (d, J = 158 Hz, 1F), 81.8 (d, J = 158 Hz, 1F).

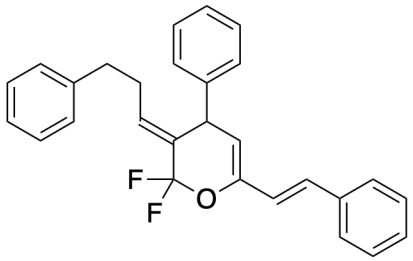
IR (neat): $\tilde{\nu}$ = 2930, 1725, 1453, 1154, 1059 cm^{-1}.

HRMS (EI): m/z calcd. for $C_{26}H_{28}F_2O$ $[M]^+$: 394.2103; found: 394.2093.

3–5. (*E,E*)-2,2-Difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-6-(2-phenylvinyl)-3,4-dihydro-2*H*-pyran **3e**

Synthesized from 1,1-difluoroallene **1a** (58 mg, 0.32 mmol), enone **2c** (70 mg, 0.32 mmol), AuCl(IPr) (4 mg, 0.006 mmol), $AgSbF_6$ (2 mg, 0.006 mmol), and MS 4A (128 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).



3e

A pale yellow liquid, 131 mg, quantitative yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (dd, J = 7.1, 1.4 Hz, 2H), 7.22–7.06 (m, 11H), 6.97 (dd, J = 7.1, 1.4 Hz, 2H), 6.91 (d, J = 15.9 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H), 6.25 (t, J = 6.5 Hz, 1H), 5.13 (br d, J = 4.6 Hz, 1H), 4.37 (br s, 1H), 2.56–2.46 (m, 2H), 2.40–2.25 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.6 (d, J_{CF} = 4 Hz), 141.2, 140.8, 136.3, 131.8 (dd, J_{CF} = 6, 6 Hz), 129.6, 128.70, 128.65, 128.5, 128.3, 128.1, 127.7, 127.6, 126.9, 126.8, 126.2, 120.8, 120.1 (dd, J_{CF} = 259, 250 Hz), 107.5, 40.3 (d, J_{CF} = 3 Hz), 34.5 (d, J_{CF} = 1 Hz), 30.0.

^{19}F NMR ($CDCl_3$, 470 MHz) δ 104.8 (d, J = 158 Hz, 1F), 82.3 (d, J = 158 Hz, 1F).

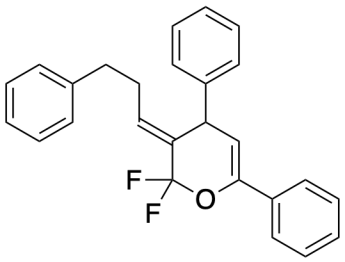
IR (neat): $\tilde{\nu}$ = 2928, 1495, 1452, 1329, 1264, 1153, 484 cm^{-1}.

HRMS (EI): m/z calcd. for $C_{28}H_{24}F_2O$ $[M]^+$: 414.1790; found: 414.1797.

3–6. (*E*)-2,2-Difluoro-4,6-diphenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3f**

Synthesized from 1,1-difluoroallene **1a** (186 mg, 1.03 mmol), enone **2d** (218 mg, 1.05 mmol), AuCl(IPr) (12 mg, 0.020 mmol), $AgSbF_6$ (7 mg, 0.019 mmol), and MS 4A (401 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).



3f

A colorless liquid, 399 mg, quantitative yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (d, J = 7.4 Hz, 2H), 7.25– 7.05 (m, 11H), 6.96 (d, J = 7.4 Hz, 2H), 7.25 (br t, J = 3.2 Hz, 1H), 5.52 (br d, J = 3.4 Hz, 1H), 4.38 (br s, 1H), 2.55–2.45 (m, 2H), 2.42–2.26 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.1 (d, J_{CF} = 4 Hz), 141.3, 140.8, 132.9, 131.6 (dd, J_{CF} = 6, 6 Hz), 128.9, 128.6, 128.4, 128.31, 128.27, 127.65, 127.64, 126.8, 126.1, 124.7, 120.3 (dd, J_{CF} = 259, 250 Hz), 102.9, 40.1, 34.4, 30.0.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.3 (d, J = 157 Hz, 1F), 81.9 (d, J = 157 Hz, 1F).

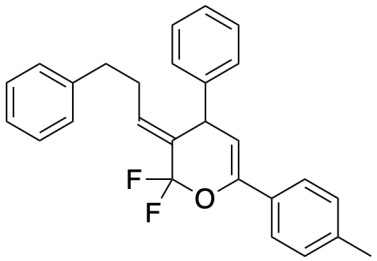
IR (neat): $\tilde{\nu}$ = 3028, 3015, 1677, 1496, 1323, 1163, 1059 cm^{-1}.

HRMS (EI): m/z calcd. for $C_{26}H_{22}F_2O$ $[M]^+$: 388.1634; found: 388.1653.

3–7. (*E*)-2,2-Difluoro-6-(4-methylphenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3g**

Synthesized from 1,1-difluoroallene **1a** (56 mg, 0.031 mmol), enone **2e** (69 mg, 0.31 mmol), AuCl(IPr) (4 mg, 0.006 mmol), $AgSbF_6$ (3 mg, 0.008 mmol), and MS 4A (122 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).



3g

A yellow liquid, 126 mg, quantitative yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40 (d, J = 8.0 Hz, 2H), 7.23–7.08 (m, 8H), 7.06 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 7.1 Hz, 2H), 6.26 (br t, J = 6.0 Hz, 1H), 5.50 (br d, J = 3.6 Hz, 1H), 4.40 (br s, 1H), 2.59–2.47 (m, 2H), 2.47–2.27 (m, 2H), 2.25 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.3 (d. J_{CF} = 9 Hz), 141.5, 140.9, 138.9, 131.5 (dd, J_{CF} = 6, 6 Hz), 131.4, 129.0, 128.6, 128.4, 128.3, 127.71, 127.69, 126.8, 126.1, 124.7, 120.2 (dd, J_{CF} = 259, 250 Hz), 102.0, 40.1 (d, J_{CF} = 3 Hz), 34.6, 30.1, 21.2.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.1 (d, J = 158 Hz, 1F), 81.8 (d, J = 158 Hz, 1F).

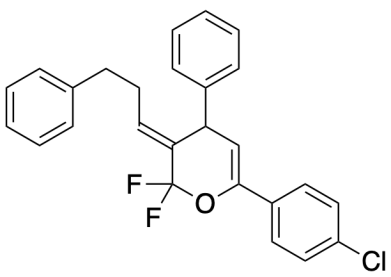
IR (neat): $\tilde{\nu}$ = 3030, 1495, 1453, 1319, 1163, 1058, 758 cm^{-1}.

HRMS (EI): m/z calcd. for $C_{27}H_{24}F_2O$ $[M]^+$: 402.1790; found: 402.1783.

3–8. (*E*)-6-(4-Chlorophenyl)-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3h**

Synthesized from 1,1-difluoroallene **1a** (59 mg, 0.33 mmol), enone **2f** (74 mg, 0.30 mmol), AuCl(IPr) (5 mg, 0.008 mmol), $AgSbF_6$ (2 mg, 0.006 mmol), and MS 4A (122 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).



3h

A pale yellow liquid, 125 mg, 97% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (d, J = 8.5 Hz, 2H), 7.24–7.11 (m, 9H), 7.08 (t, J = 7.0 Hz, 1H), 6.98 (d, J = 7.5 Hz, 2H), 6.27 (br t, J = 6.5 Hz, 1H), 5.53 (br d, J = 2.8 Hz, 1H), 4.40 (br s, 1H), 2.58–2.47 (m, 2H), 2.44–2.28 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.3 (d, J_{CF} = 5 Hz), 141.1, 140.8, 134.8, 131.9 (dd, J_{CF} = 6, 6 Hz), 131.5, 128.7, 128.6, 128.4, 128.3, 128.2 (dd, J_{CF} = 31, 22 Hz), 127.6 (d, J_{CF} = 3 Hz), 127.0, 126.14, 126.07, 120.1 (dd J_{CF} = 259, 250 Hz), 103.4, 40.2, 34.5, 30.1.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 103.9 (d, J = 158 Hz, 1F), 81.7 (d, J = 158 Hz, 1F).

IR (neat): $\tilde{\nu}$ = 2930, 1675, 1493, 1315, 1161, 834 cm^{-1}.

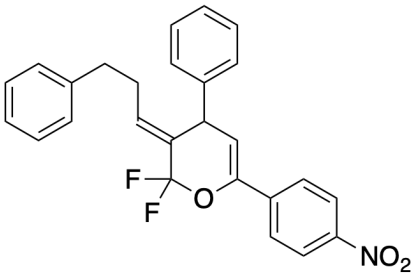
HRMS (EI): m/z calcd. for $C_{26}H_{21}ClF_2O$ $[M]^+$: 422.1244; found: 422.1229.

3–9. (*E*)-2,2-Difluoro-6-(4-nitrophenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3i**

Synthesized from 1,1-difluoroallene **1a** (60 mg, 0.33 mmol), enone **2g** (79 mg, 0.31 mmol), AuCl(IPr) (4 mg, 0.006 mmol), $AgSbF_6$ (2 mg, 0.006 mmol), and MS 4A (120 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).

A yellow liquid, 106 mg, 78% yield.



3i

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.27–7.15 (m, 7H), 7.11 (t, J = 7.0 Hz, 1H), 7.00 (d, J = 5.8 Hz, 2H), 6.33 (br t, J = 6.8 Hz, 1H), 5.78 (br d, J = 4.5 Hz, 1H), 4.46 (br s, 1H), 2.62–2.50 (m, 2H), 2.46–2.30 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.8, 145.4 (d, J_{CF} = 5 Hz), 140.7, 140.5, 138.9, 132.5 (dd, J_{CF} = 6, 6 Hz), 128.9, 128.5, 128.3, 127.64, 127.63 (dd, J_{CF} = 30, 26 Hz), 127.2, 126.2, 125.4, 123.7, 120.0 (dd J_{CF} = 260, 251 Hz), 107.1, 40.4 (d, J_{CF} = 3 Hz), 34.5, 30.1.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 103.7 (d, J = 158 Hz, 1F), 81.5 (d, J = 158 Hz, 1F).

IR (neat): $\tilde{\nu}$ = 3027, 1599, 1522, 1348, 1217, 1162, 771 cm^{-1}.

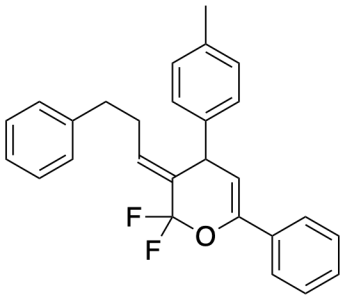
HRMS (EI): m/z calcd. for $C_{26}H_{21}F_2NO_3$ $[M]^+$: 433.1485; found: 433.1504.

3–10. (*E*)-2,2-Difluoro-4-(4-methylphenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3j**

Synthesized from 1,1-difluoroallene **1a** (54 mg, 0.30 mmol), enone **2h** (68 mg, 0.31 mmol), AuCl(IPr) (4 mg, 0.006 mmol), $AgSbF_6$ (3 mg, 0.009 mmol), and MS 4A (121 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).

A colorless liquid, 116 mg, 96% yield.



3j

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (dd, J = 8.3, 1.5 Hz, 2H), 7.25–7.05 (m, 8H), 7.00–6.98 (m,

4H), 6.24 (br t, J = 6.6 Hz, 1H), 5.53 (br d, J = 4.5 Hz, 1H), 4.36 (br s, 1H), 2.54–2.50 (m, 2H), 2.42–2.28 (m, 2H), 2.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.1 (d, J_{CF} = 5 Hz), 140.9, 138.3, 136.5, 133.0, 131.4 (dd, J_{CF} = 6, 6 Hz) , 129.3, 128.8, 128.6 (dd, J_{CF} = 32, 21 Hz), 128.4, 128.3, 127.58, 127.56, 126.1, 124.7, 120.2 (dd, J_{CF} = 259, 250 Hz) , 103.0, 39.8 (d, J_{CF} = 3 Hz), 34.6, 30.0, 21.0.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.1 (d, J = 157 Hz, 1F), 81.9 (d, J = 157 Hz, 1F).

IR (neat): $\tilde{\nu}$ = 3013, 2976, 1326, 1163, 1059 cm^{-1}.

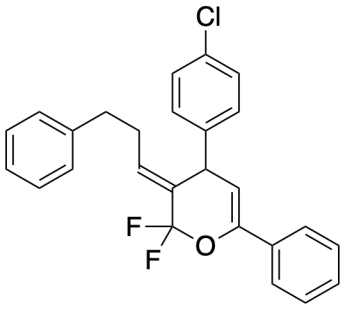
HRMS (EI): m/z calcd. for $C_{27}H_{24}F_2O$ $[M]^+$: 402.1790; found: 402.1777.

3–11. (*E*)-4-(4-Chlorophenyl)-2,2-difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3k**

Synthesized from 1,1-difluoroallene **1a** (58 mg, 0.32 mmol), enone **2i** (72 mg, 0.30 mmol), AuCl(IPr) (5 mg, 0.007 mmol), $AgSbF_6$ (2 mg, 0.007 mmol), and MS 4A (128 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).

A yellow liquid, 131 mg, quantitative yield.



3k

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53–7.43 (m, 2H), 7.28–6.93 (m, 12H), 6.25 (br t, J = 6.4 Hz, 1H), 5.47 (br d, J = 4.6 Hz, 1H), 4.34 (br s, 1H), 2.56–2.52 (m, 2H), 2.44–2.27 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.6 (d, J_{CF} = 5 Hz), 140.6, 139.7, 132.8, 132.7, 131.8 (dd, J_{CF} = 6, 6 Hz), 129.1, 129.0 (d, J_{CF} = 3 Hz), 128.7, 128.5, 128.4, 128.3, 128.1 (dd, J_{CF} = 31, 22 Hz), 126.2, 124.8, 120.1 (dd, J_{CF} = 259, 250 Hz), 102.1, 39.4 (d, J_{CF} = 3 Hz), 34.6, 30.0.

^{19}F NMR ($CDCl_3$, 470 MHz) δ 104.3 (d, J = 158 Hz, 1F), 81.5 (d, J = 158 Hz, 1F).

IR (neat): $\tilde{\nu}$ = 3028, 1677, 1491, 1324, 1162, 1035, 752 cm^{-1}.

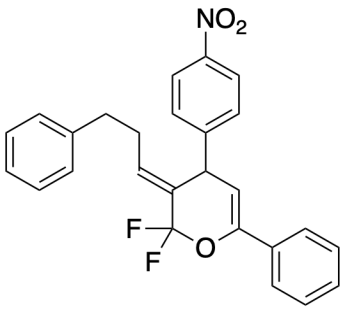
HRMS (EI): m/z calcd. for $C_{26}H_{21}ClF_2O$ $[M]^+$: 422.1244; found: 422.1250.

3–12. (*E*)-2,2-Difluoro-4-(4-nitrophenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3l**

Synthesized from 1,1-difluoroallene **1a** (60 mg, 0.33 mmol), enone **2j** (78 mg, 0.31 mmol), AuCl(IPr) (5 mg, 0.008 mmol), $AgSbF_6$ (2 mg, 0.007 mmol), and MS 4A (123 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).

A yellow liquid, 89 mg, 67% yield.



3l

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, J = 8.8 Hz, 2H), 7.54–7.52 (m, 2H), 7.35–7.28 (m, 5H), 7.20–7.11 (m, 3H), 7.02 (d, J = 7.2 Hz, 2H), 6.35 (br t, J = 6.2 Hz, 1H), 5.52 (br d, J = 4.6 Hz, 1H), 4.47 (br s, 1H), 2.66–2.63 (m, 2H), 2.51–2.32 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 148.5 (d, J_{CF} = 6 Hz, 1H), 148.4, 146.8, 140.4, 132.6 (d, J_{CF} = 6 Hz), 132.5 (d, J_{CF} = 5 Hz), 129.4, 128.6, 128.5, 128.4, 128.3, 127.3 (dd, J_{CF} = 32, 22 Hz), 126.3, 124.9, 123.9, 119.9 (dd, J_{CF} = 258, 251 Hz), 100.6, 39.5 (d, J_{CF} = 3 Hz), 34.6, 30.2.

^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.5 (d, J = 158 Hz, 1F), 80.9 (d, J = 158 Hz, 1F).

IR (neat): $\tilde{\nu}$ = 2928, 1523, 1349, 1265, 1164, 909 cm^{-1}.

HRMS (EI): *m*/*z* calcd. for $C_{26}H_{21}F_2NO_3$ $[M]^+$: 433.1485; found: 433.1487.

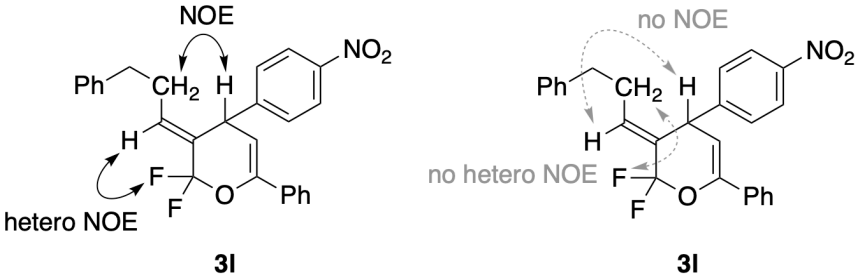


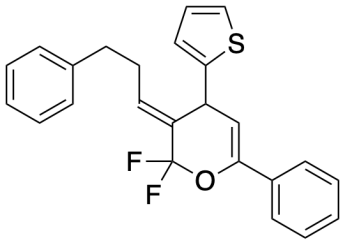
Figure S1.

3–13. (*E*)-2,2-Difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-4-(2-thienyl)-3,4-dihydro-2*H*-pyran **3m**

Synthesized from 1,1-difluoroallene **1a** (47 mg, 0.26 mmol), enone **2k** (57 mg, 0.26 mmol), AuCl(IPr) (4 mg, 0.006 mmol), $AgSbF_6$ (2 mg, 0.006 mmol), and MS 4A (122 mg).

Purified by column chromatography (SiO_2, hexane/ethyl acetate = 30:1).

A yellow liquid, 94 mg, 91% yield.



3m

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.52 (d, J = 8.0 Hz, 2H), 7.30–7.23 (m, 3H), 7.19 (dd, J = 7.5, 7.5 Hz, 2H), 7.13–7.05 (m, 4H), 6.83–6.78 (m, 2H), 6.26 (td, J = 7.5, 2.5 Hz, 1H), 5.59 (dd, J = 9.5, 1.5 Hz, 1H), 4.62 (br s, 1H), 2.70–2.58 (m, 2H), 2.52–2.45 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.7 (d, J_{CF} = 5 Hz), 144.4, 140.7, 132.8, 131.4 (dd, J_{CF} = 6, 6 Hz), 129.1, 128.5, 128.2, 128.0 (dd, J_{CF} = 32, 22 Hz), 126.7, 126.2, 124.9, 124.7 (d, J_{CF} = 2 Hz), 124.2, 119.9 (dd, J_{CF} = 260, 250 Hz), 101.6, 35.0 (d, J_{CF} = 3 Hz), 34.6, 30.0.

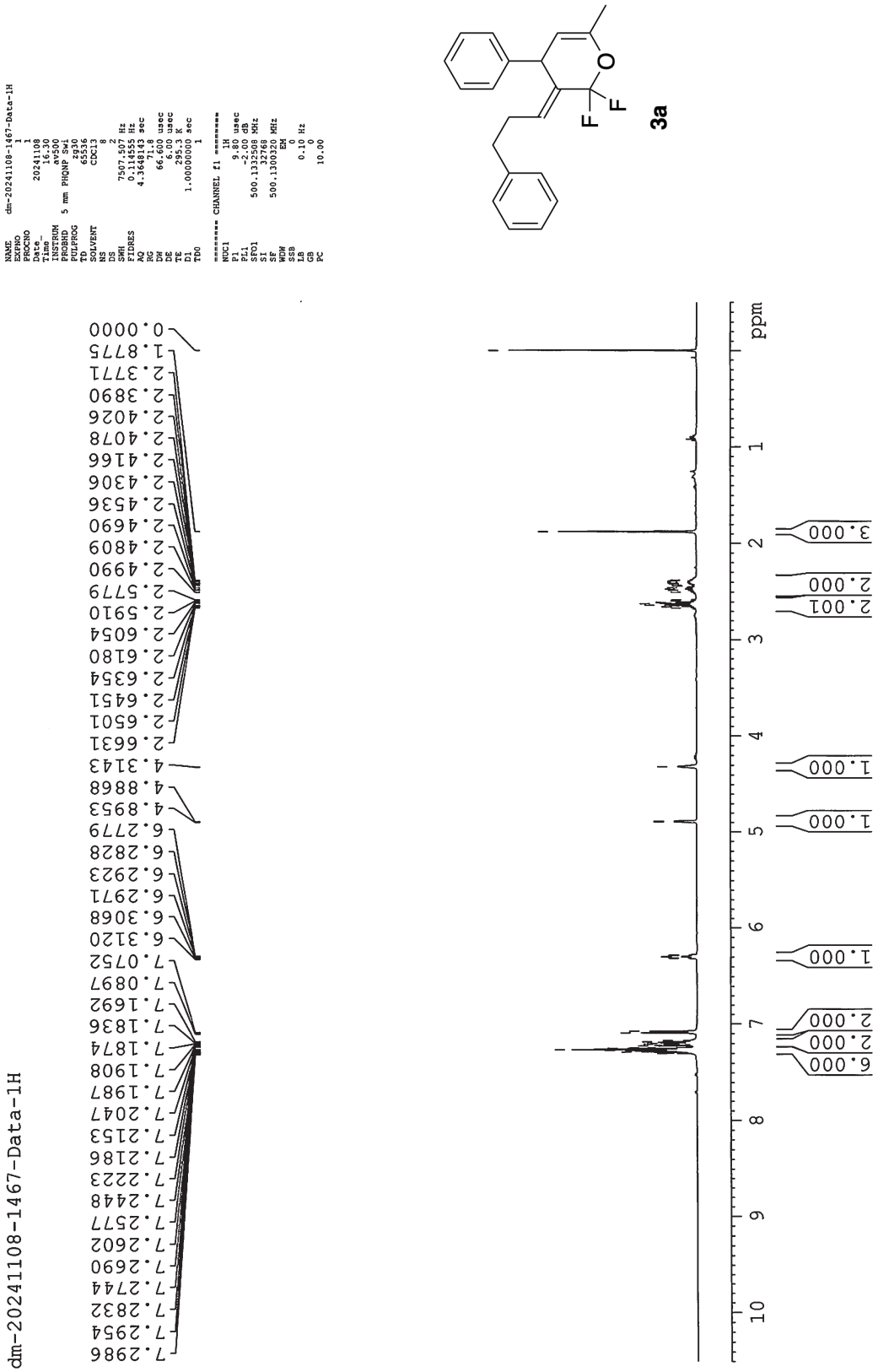
^{19}F NMR ($CDCl_3$, 471 MHz) δ 104.1 (d, J = 156 Hz, 1F), 79.8 (d, J = 156 Hz, 1F).

IR (neat): $\tilde{\nu}$ = 2929, 1496, 1323, 1165, 1063, 699 cm^{-1}.

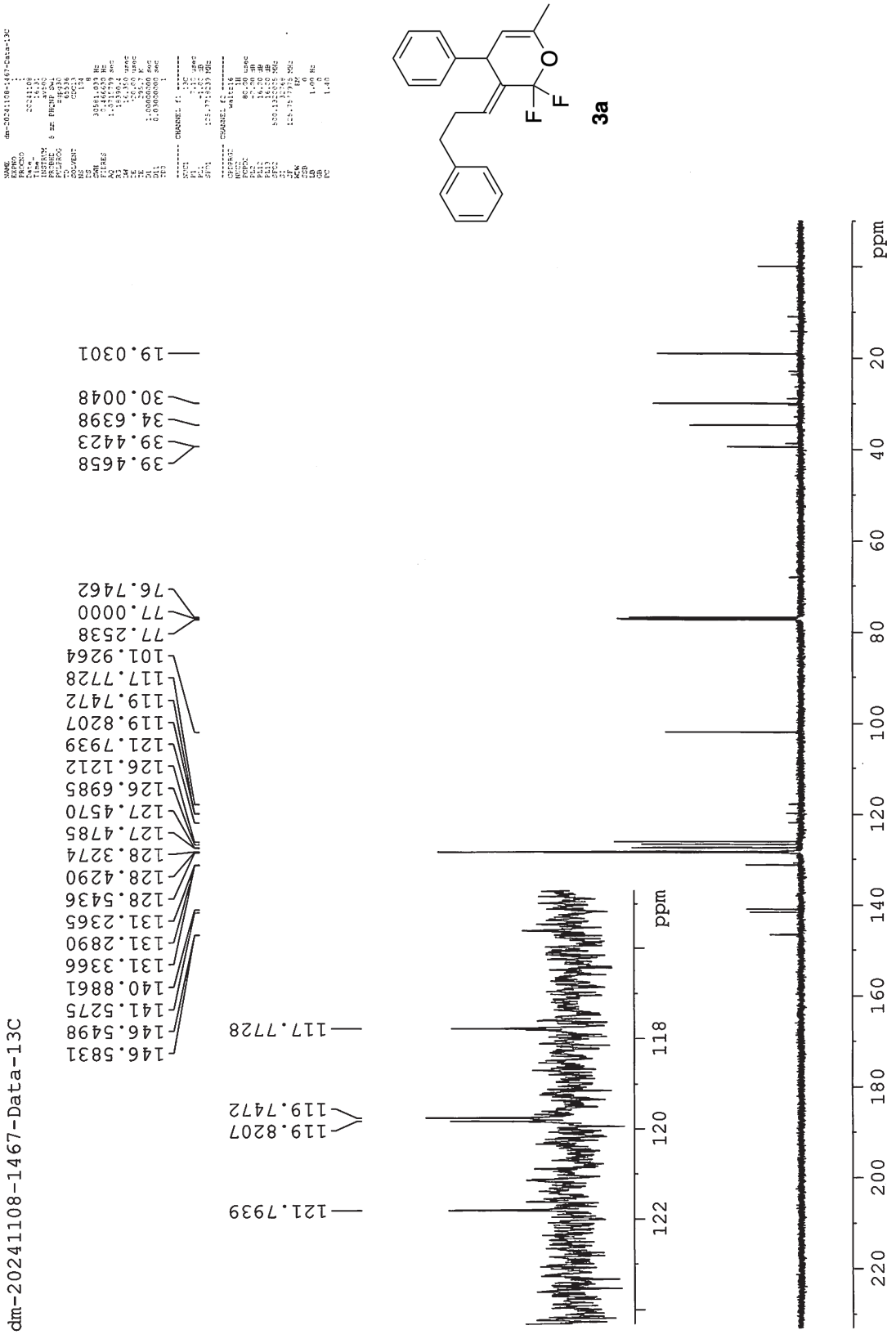
HRMS (EI): *m*/*z* calcd. for $C_{24}H_{20}F_2OS$ $[M]^+$: 394.1197; found: 394.1204.

4. NMR Spectra of Products

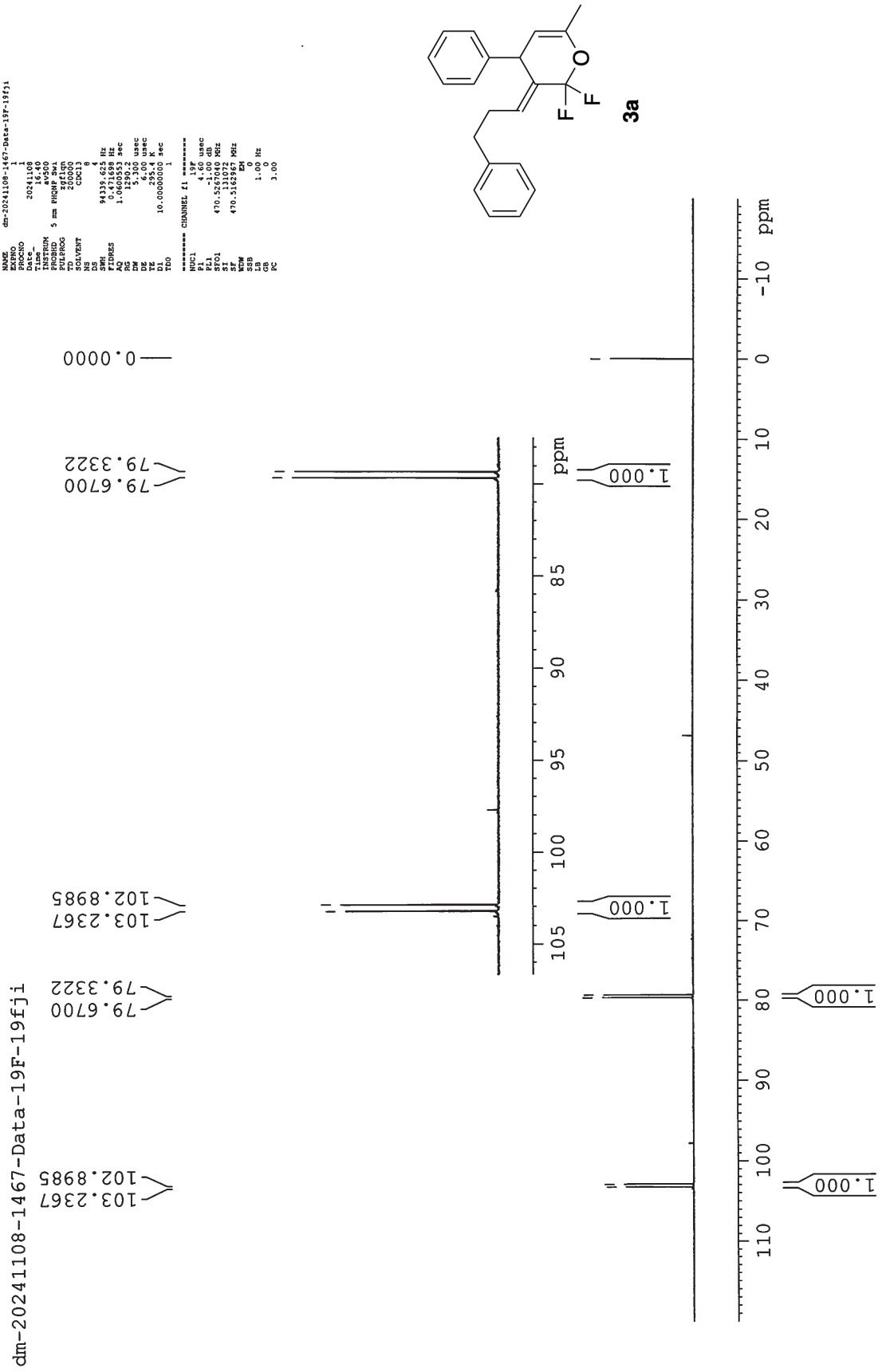
^{1}H NMR Spectrum of (*E*)-2,2-Difluoro-6-methyl-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3a**



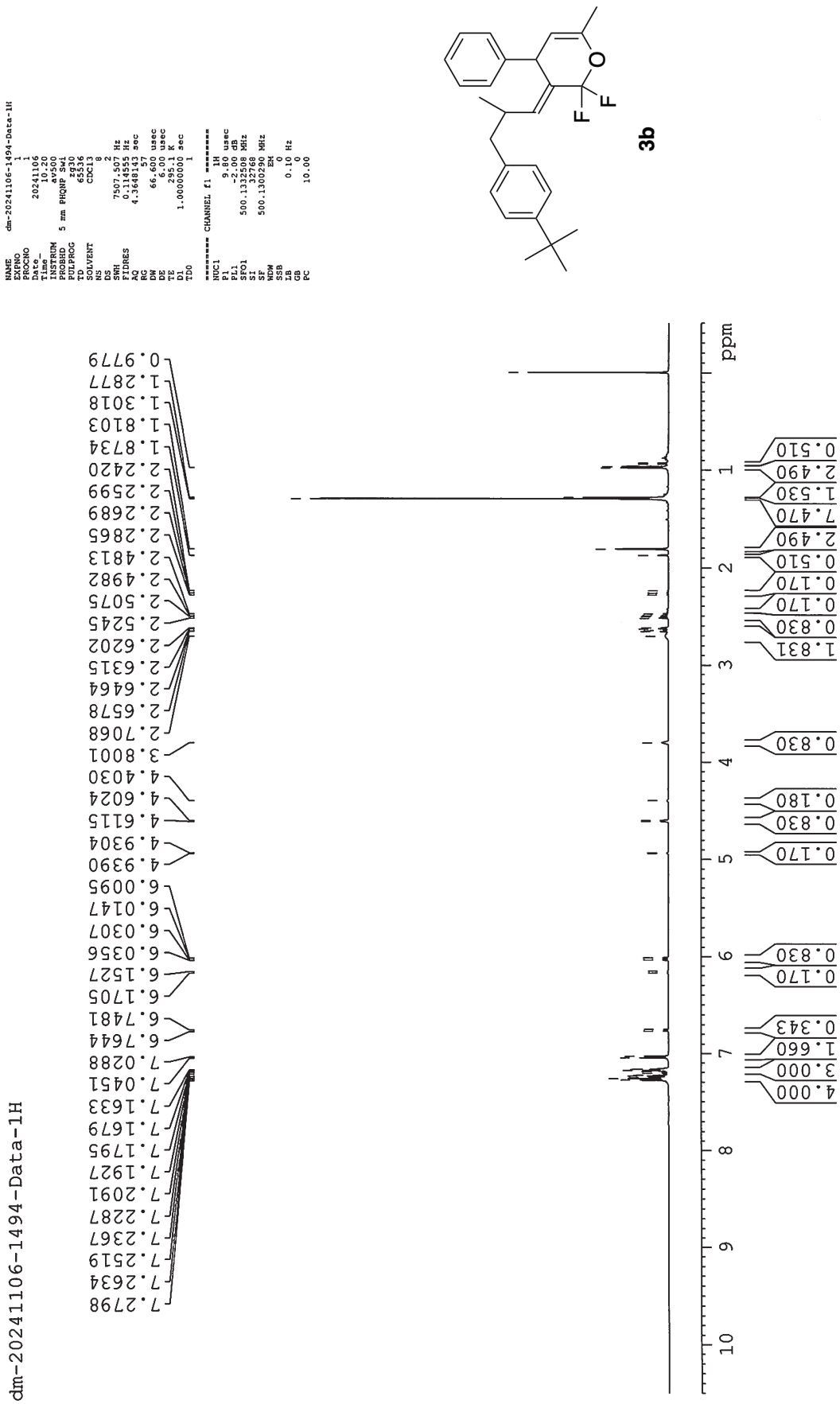
^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-6-methyl-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3a**



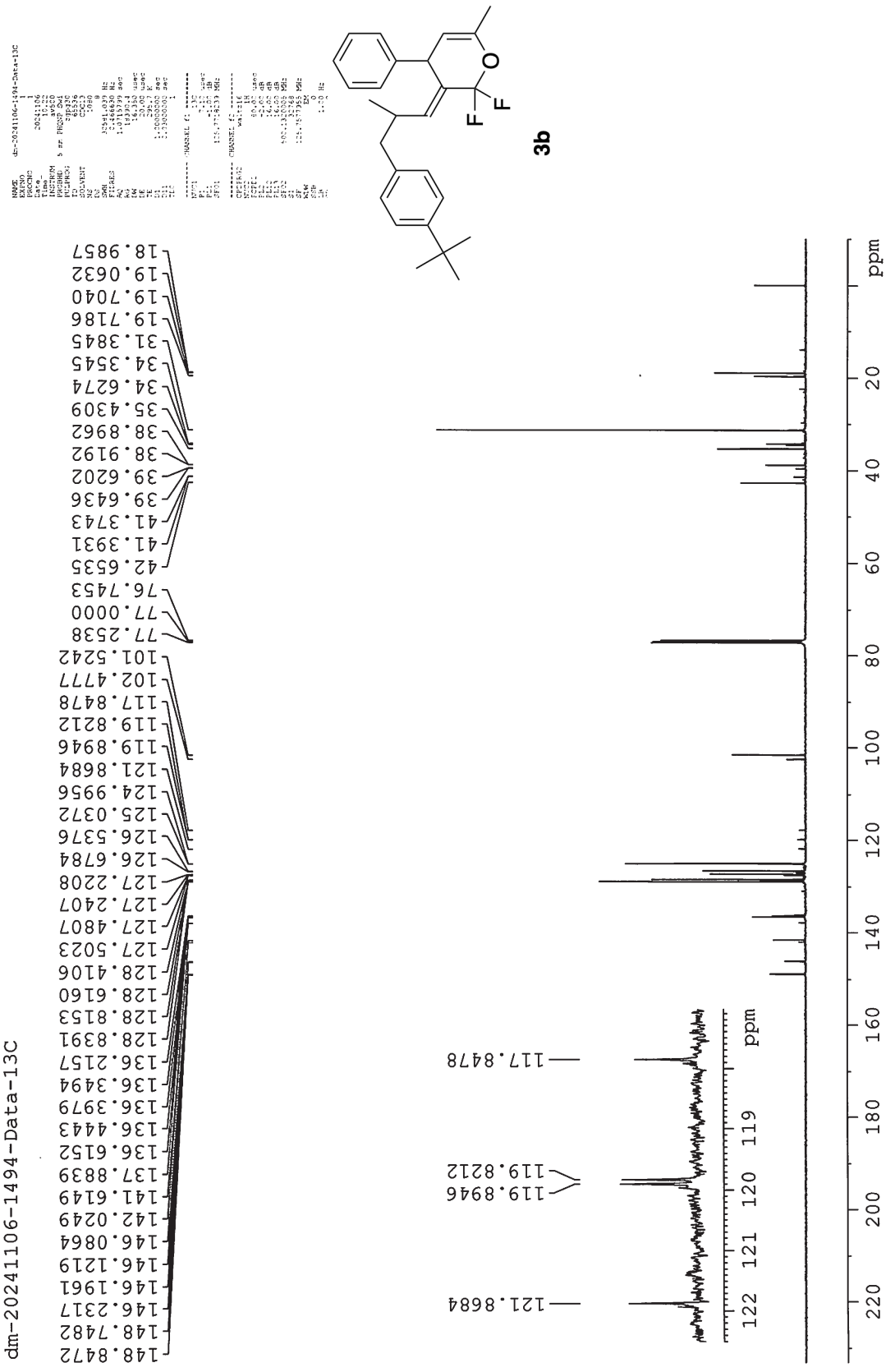
^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-6-methyl-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3a**



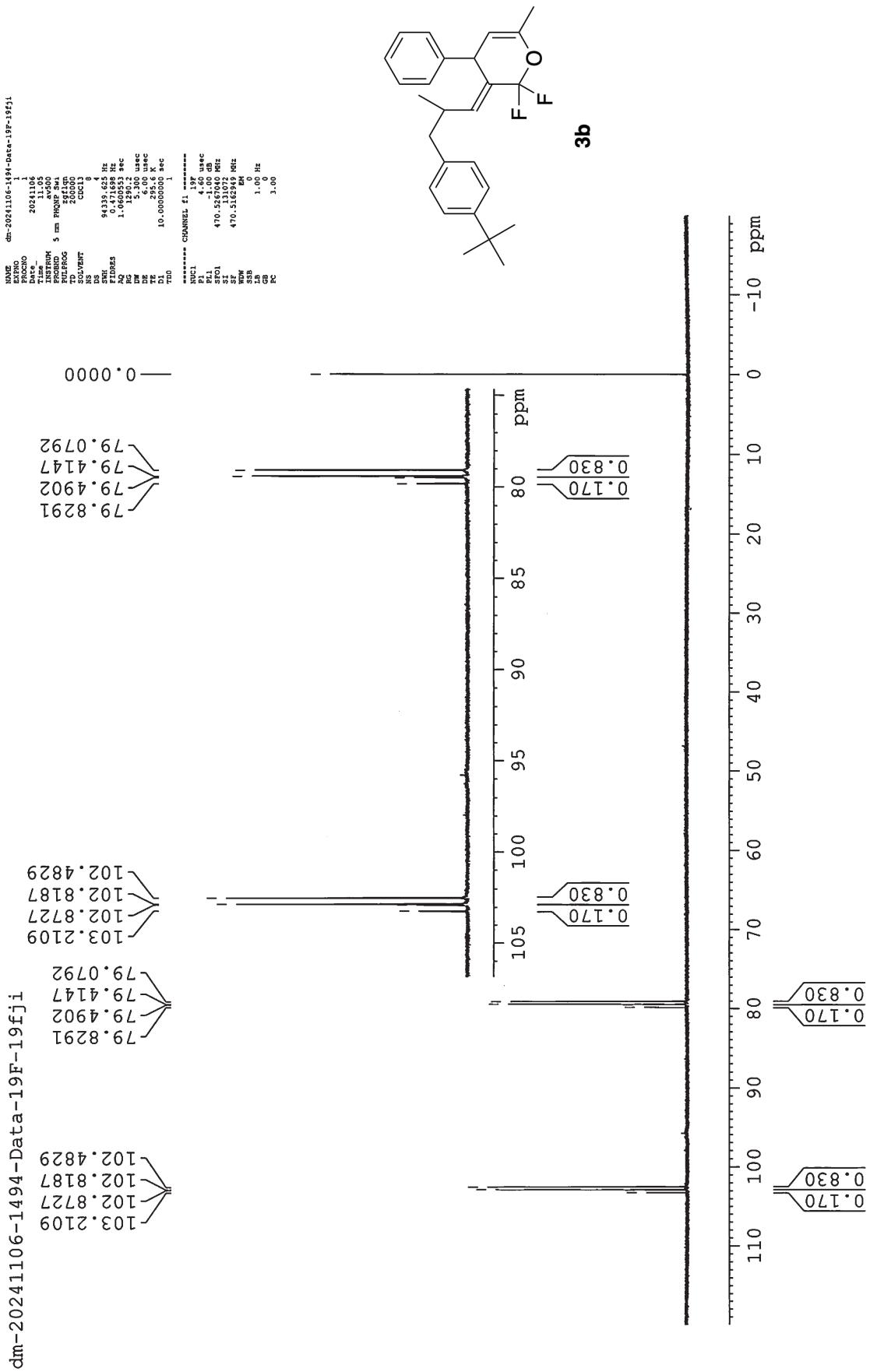
^{1}H NMR Spectrum of (*E*)-3-[3-(4-tert-Butylphenyl)-2-methylpropan-1-ylidene]-2,2-difluoro-6-methyl-7-phenyl-3,4-dihydro-2*H*-pyran **3b** (dr = 83:17)



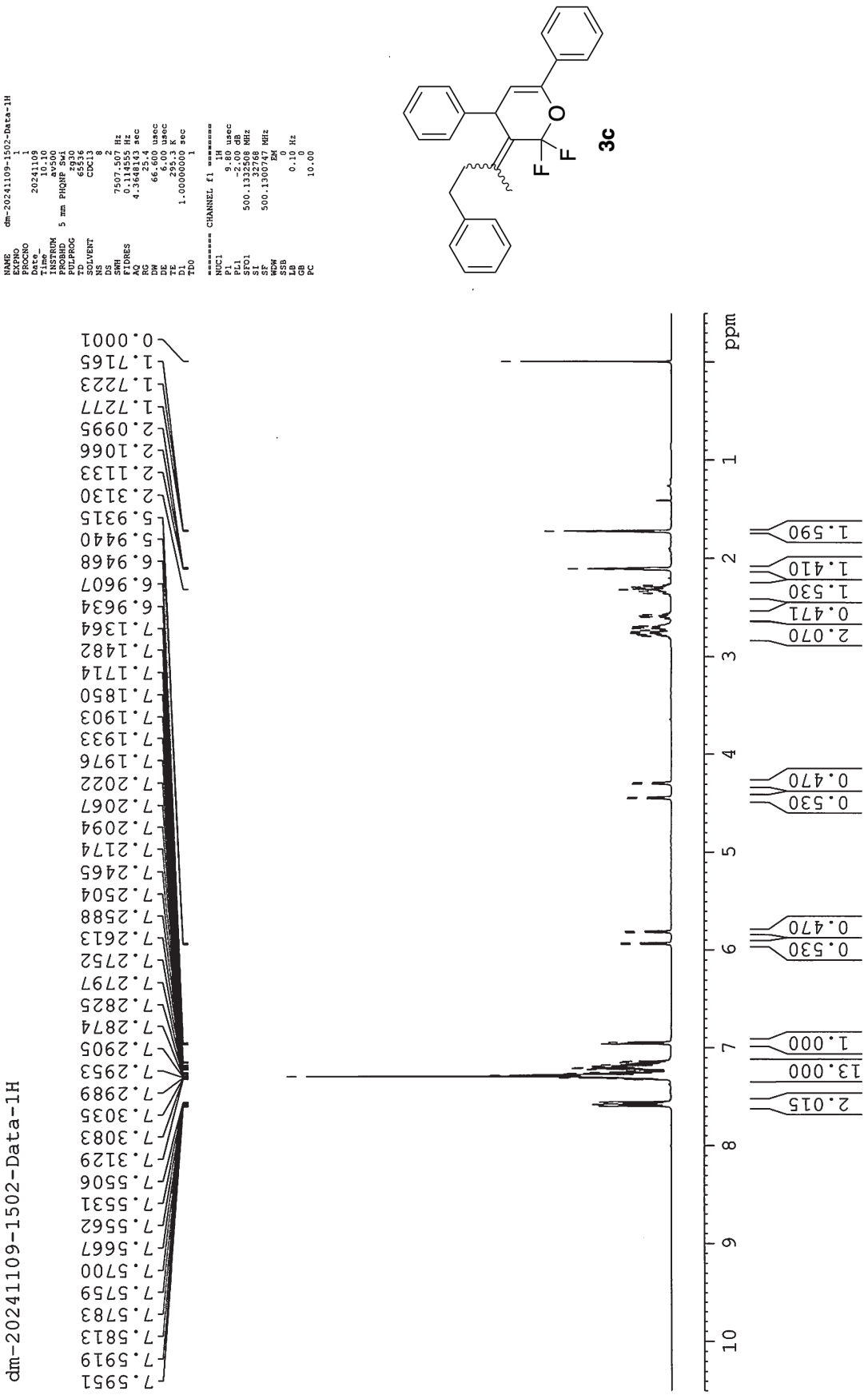
^{13}C NMR Spectrum of (*E*)-3-[3-(4-tert-Butylphenyl)-2-methylpropan-1-ylidene]-2,2-difluoro-6-methyl-7-phenyl-3,4-dihydro-2*H*-pyran **3b** (dr = 83:17)



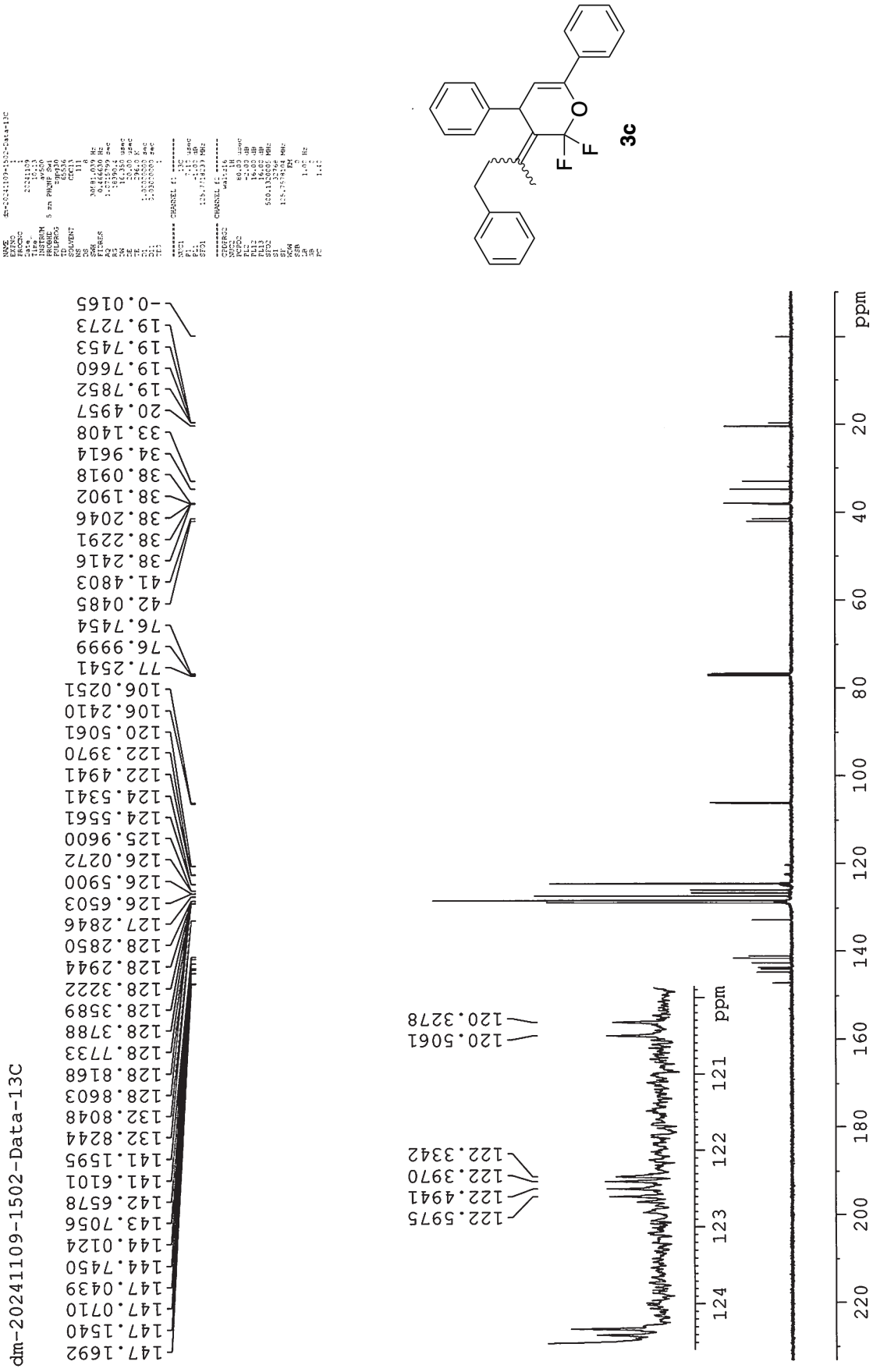
^{19}F NMR Spectrum of (*E*)-3-[3-(4-*tert*-Butylphenyl)-2-methylpropan-1-ylidene]-2,2-difluoro-6-methyl-7-phenyl-3,4-dihydro-2*H*-pyran **3b** (dr = 83:17)



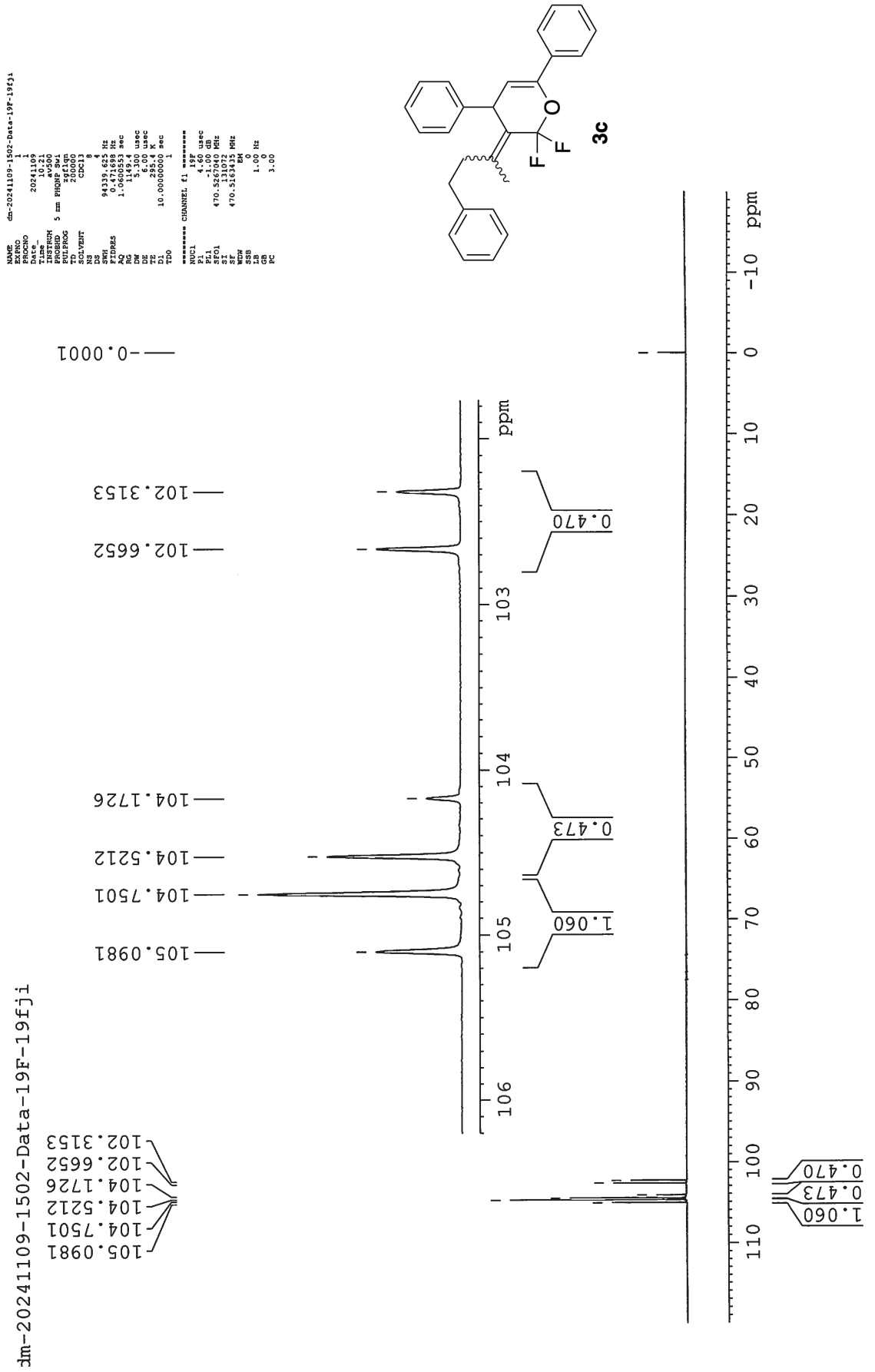
^{1}H NMR Spectrum of 2,2-Difluoro-4,6-diphenyl-3-(4-phenylbutan-2-ylidene)-3,4-dihydro-2*H*-pyran **3c** (*E*/*Z* = 53:47)



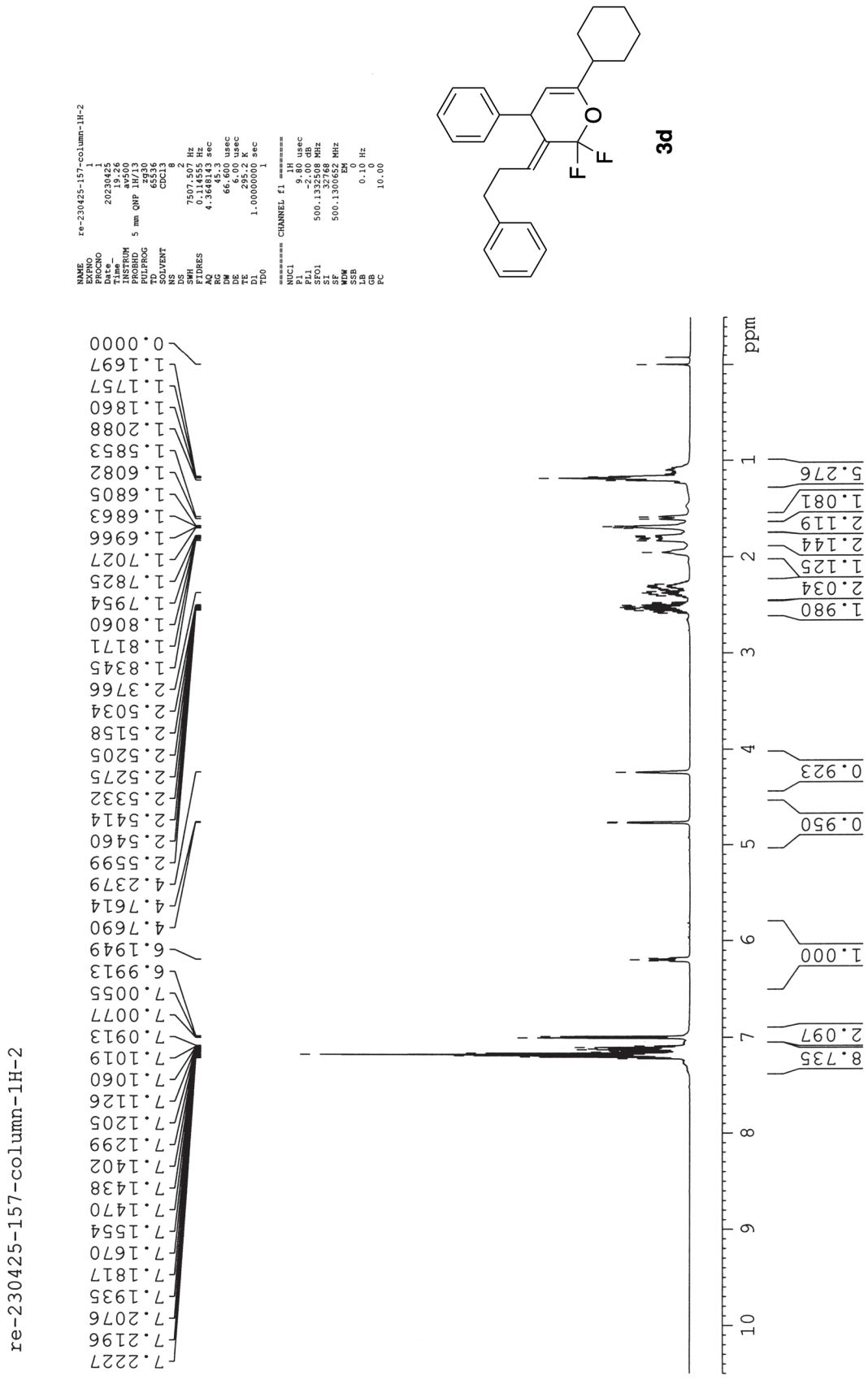
^{13}C NMR Spectrum of 2,2-Difluoro-4,6-diphenyl-3-(4-phenylbutan-2-ylidene)-3,4-dihydro-2H-pyran **3c** (*E*/*Z* = 53:47)



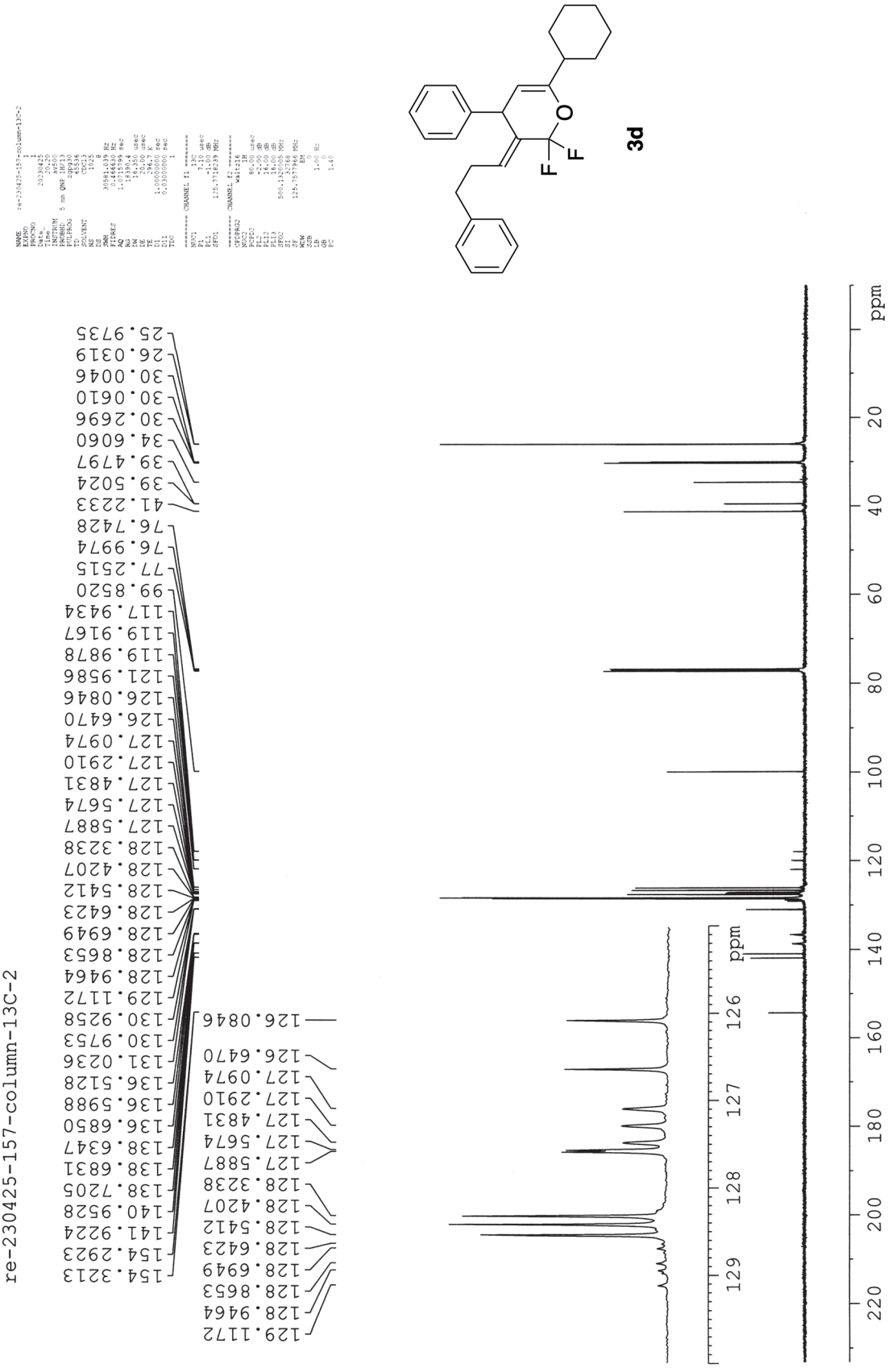
^{19}F NMR Spectrum of 2,2-Difluoro-4,6-diphenyl-3-(4-phenylbutan-2-ylidene)-3,4-dihydro-2H-pyran **3c** (*E*/*Z* = 53:47)



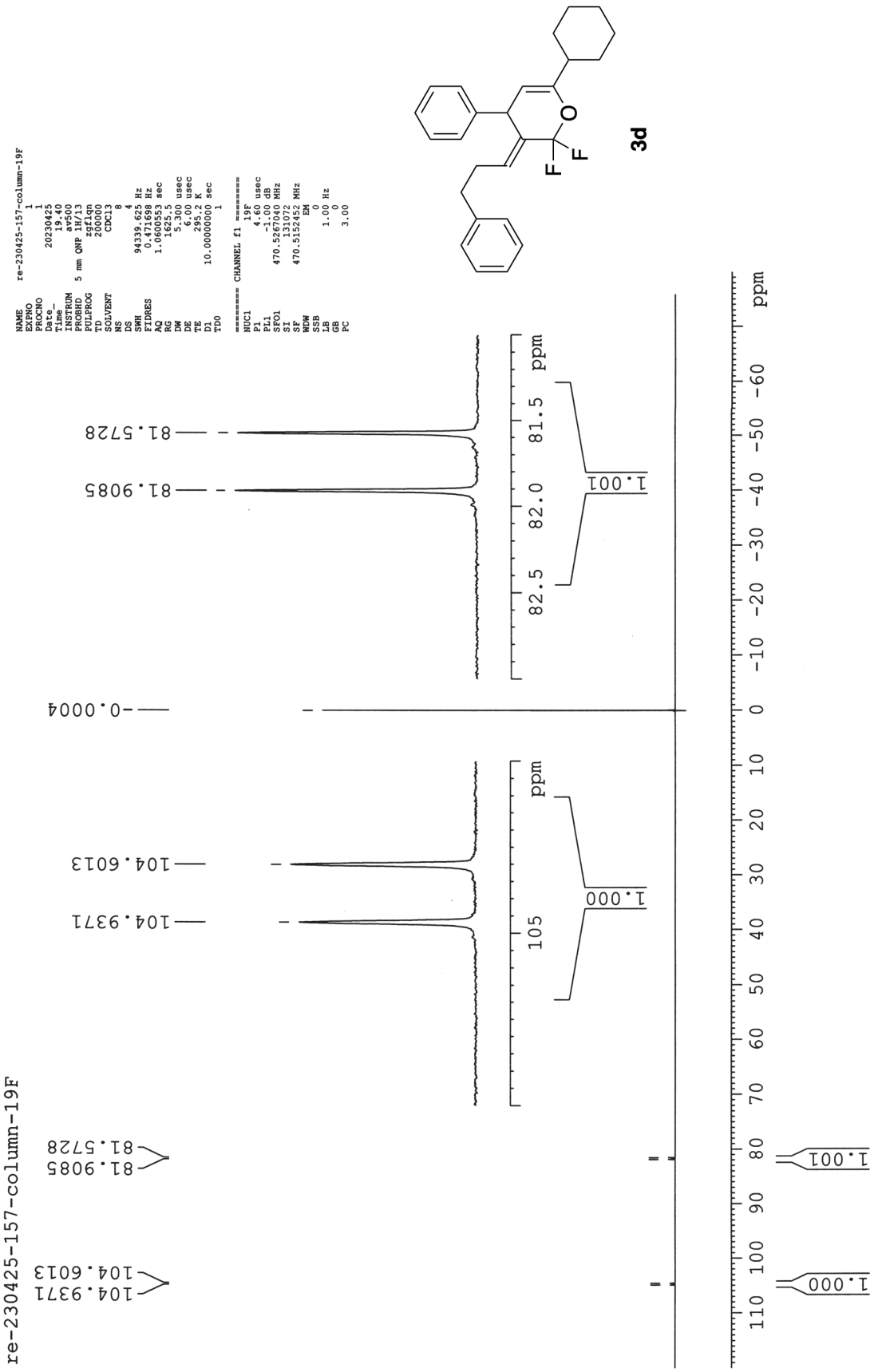
[1]H NMR Spectrum of (*E*)-6-Cyclohexyl-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3d**



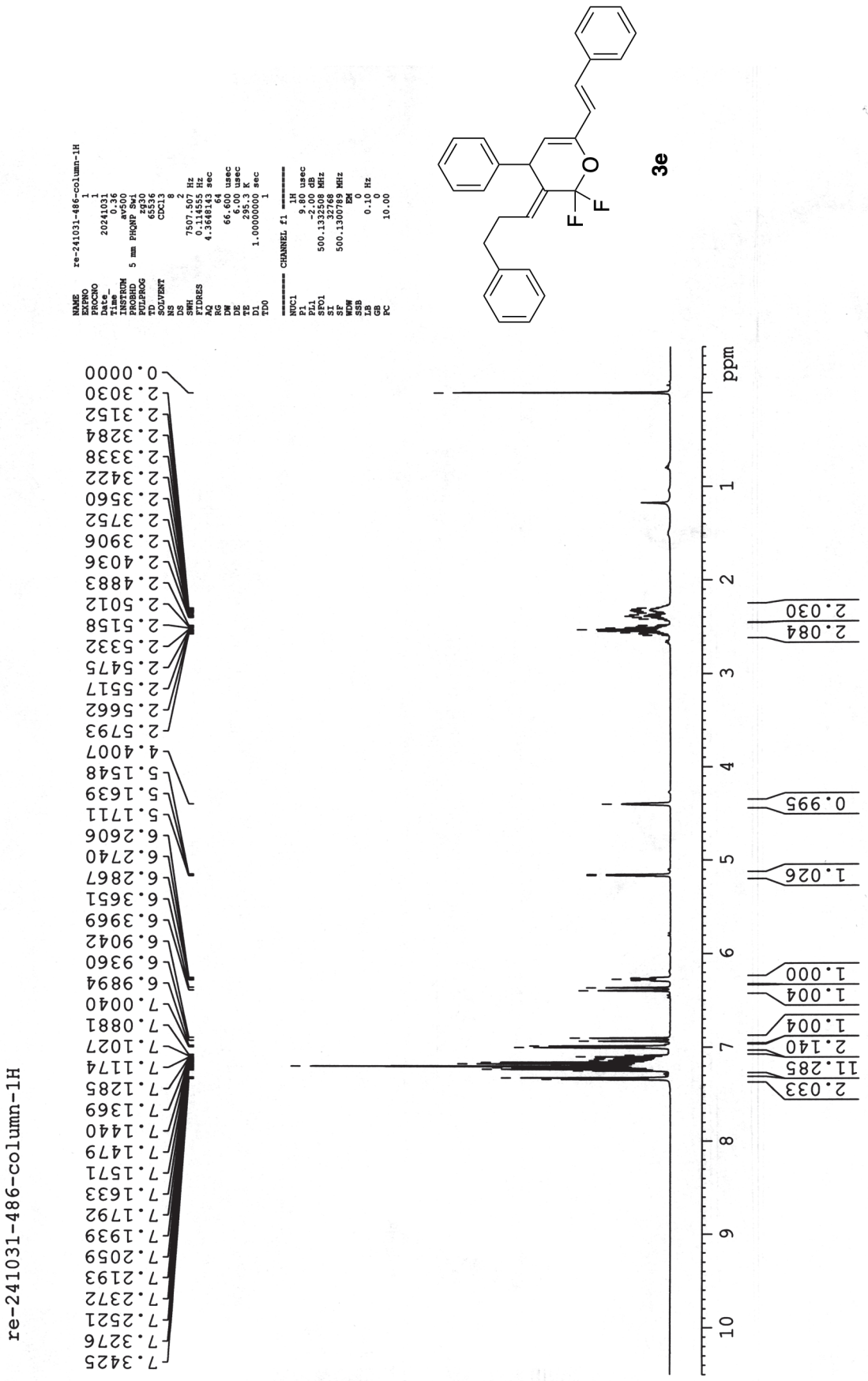
^{13}C NMR Spectrum of (*E*)-6-Cyclohexyl-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3d**



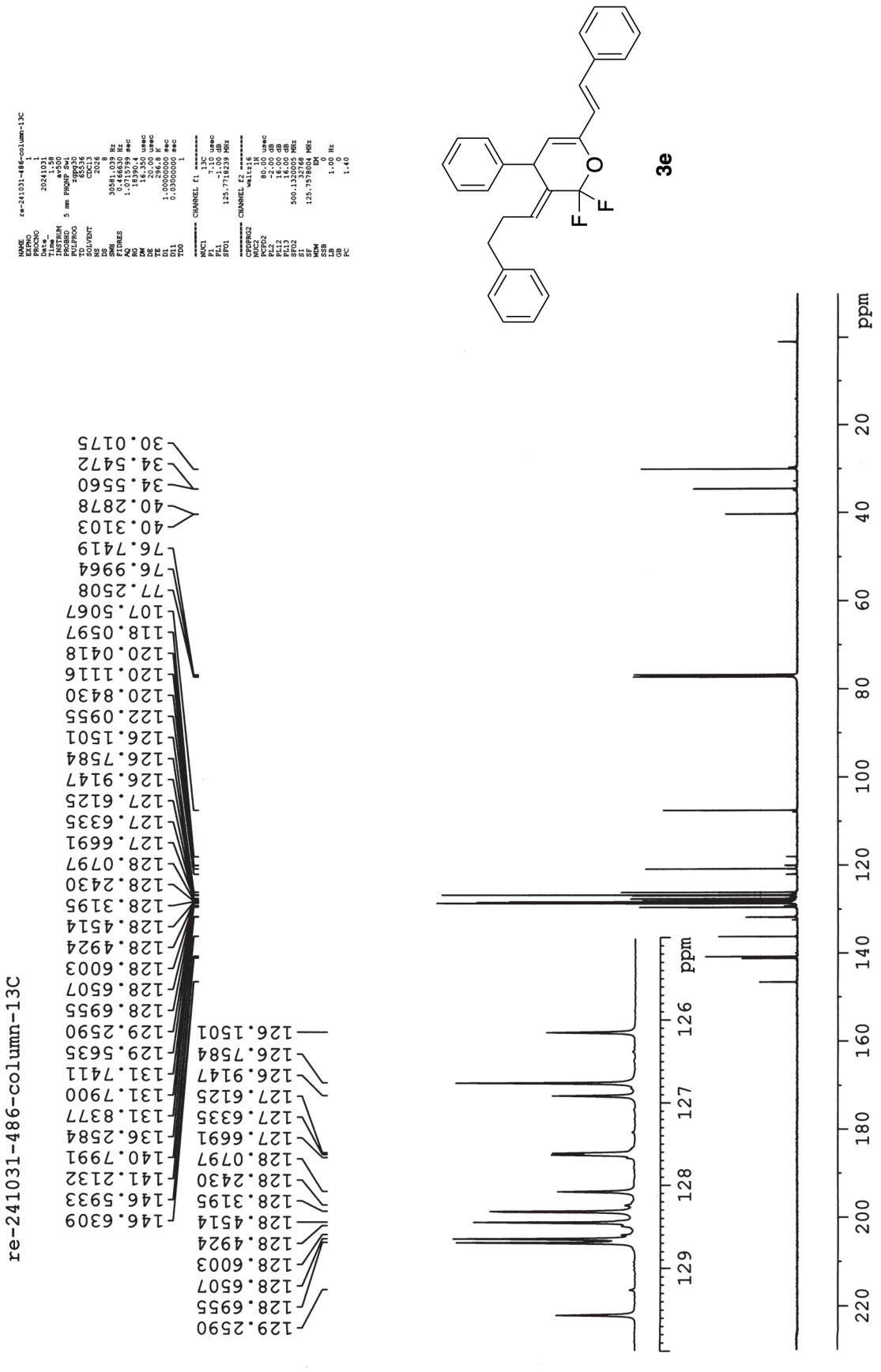
^{19}F NMR Spectrum of (*E*)-6-Cyclohexyl-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3d**



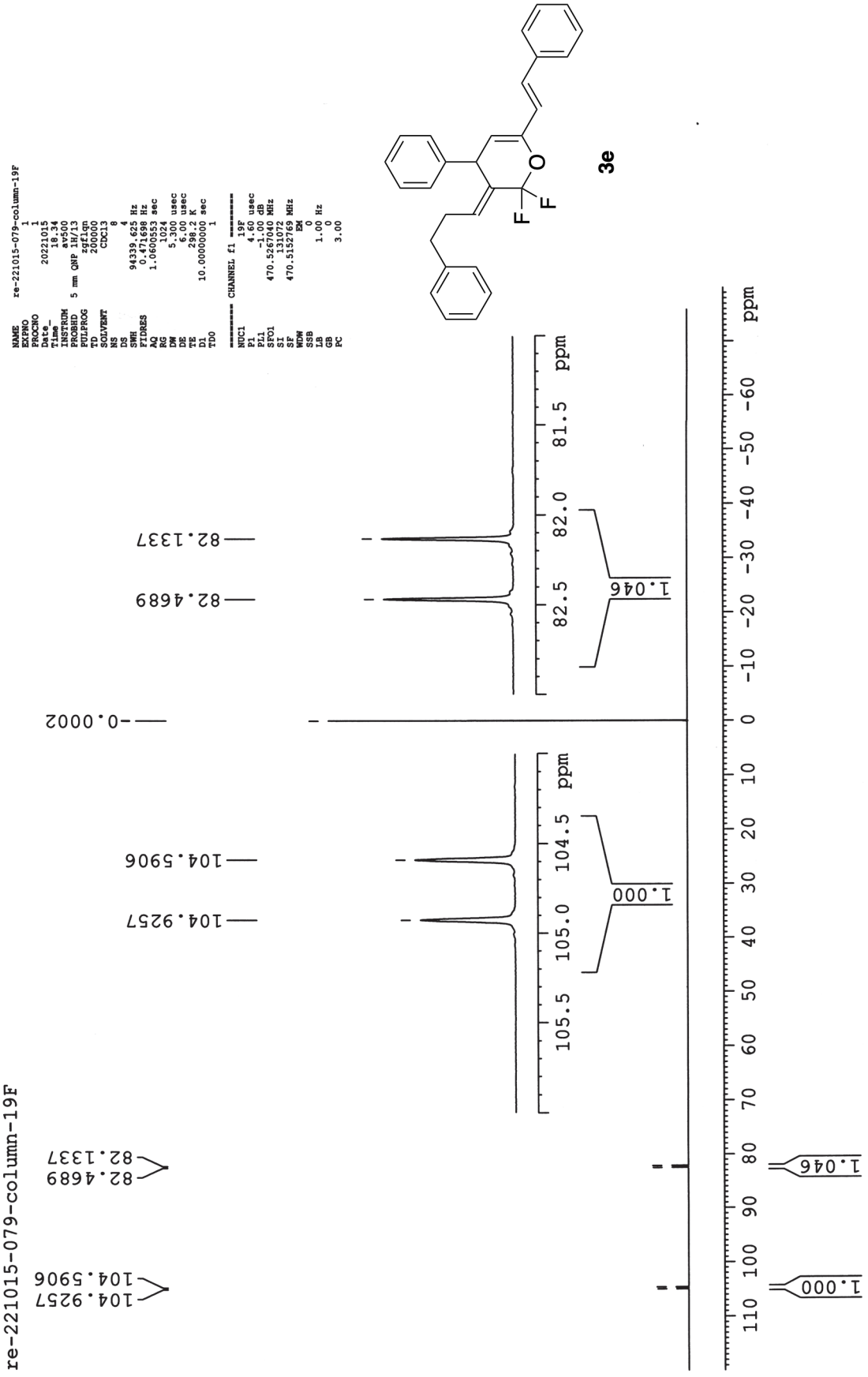
^{1}H NMR Spectrum of (*E,E*)-2,2-Difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-6-(2-phenylvinyl)-3,4-dihydro-2*H*-pyran **3e**



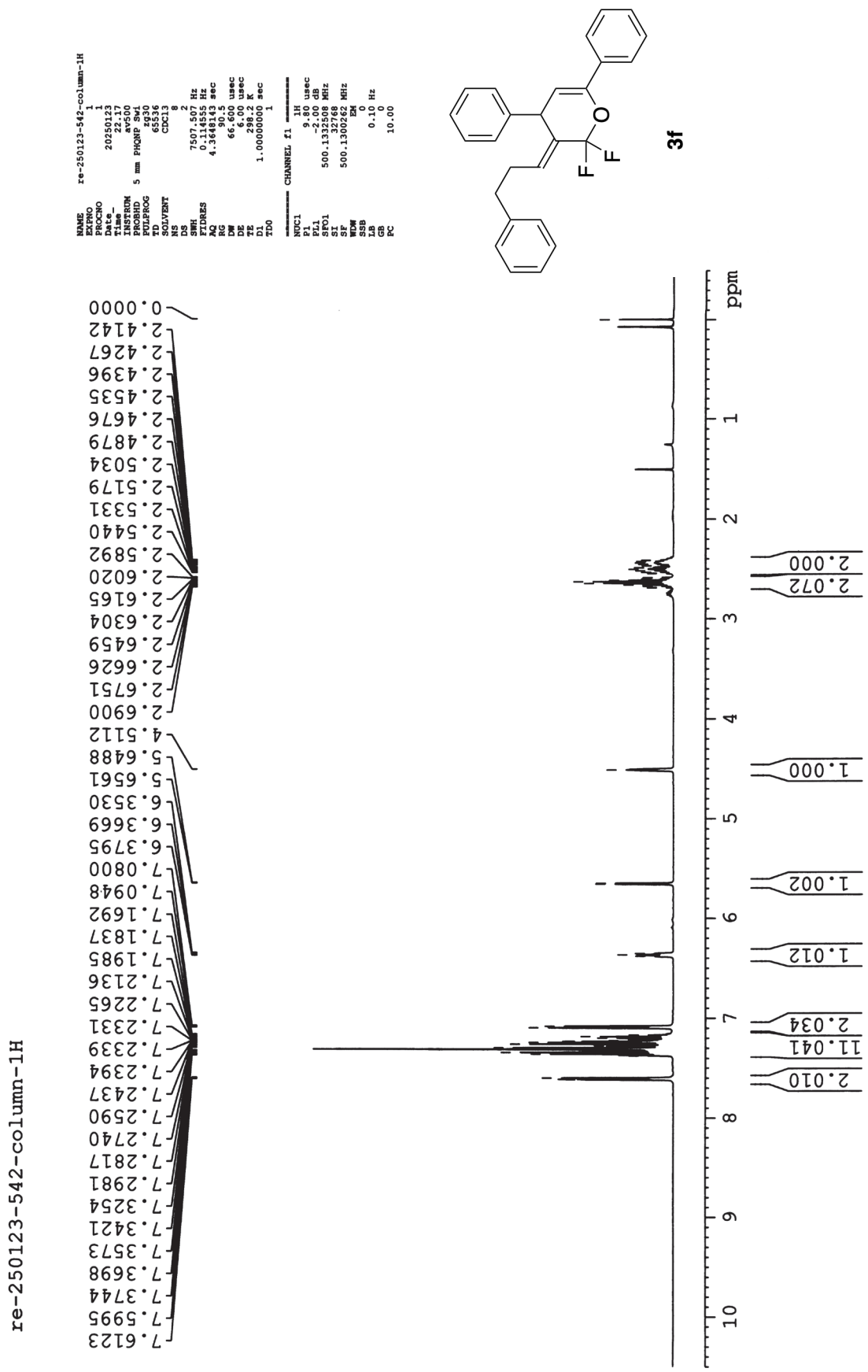
^{13}C NMR Spectrum of (*E,E*)-2,2-Difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-6-(2-phenylvinyl)-3,4-dihydro-2*H*-pyran **3e**



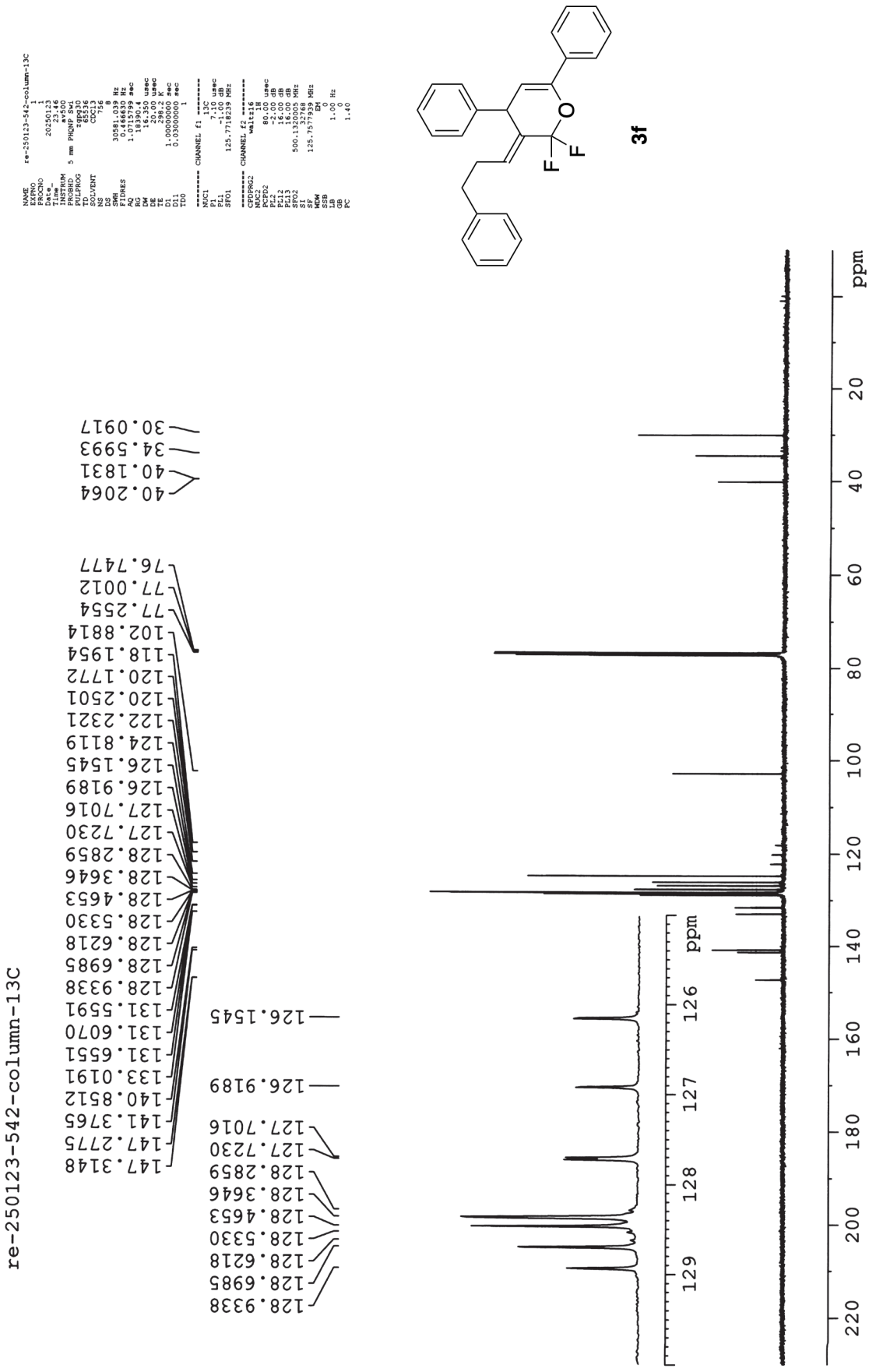
^{19}F NMR Spectrum of (*E,E*)-2,2-Difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-6-(2-phenylvinyl)-3,4-dihydro-2*H*-pyran **3e**



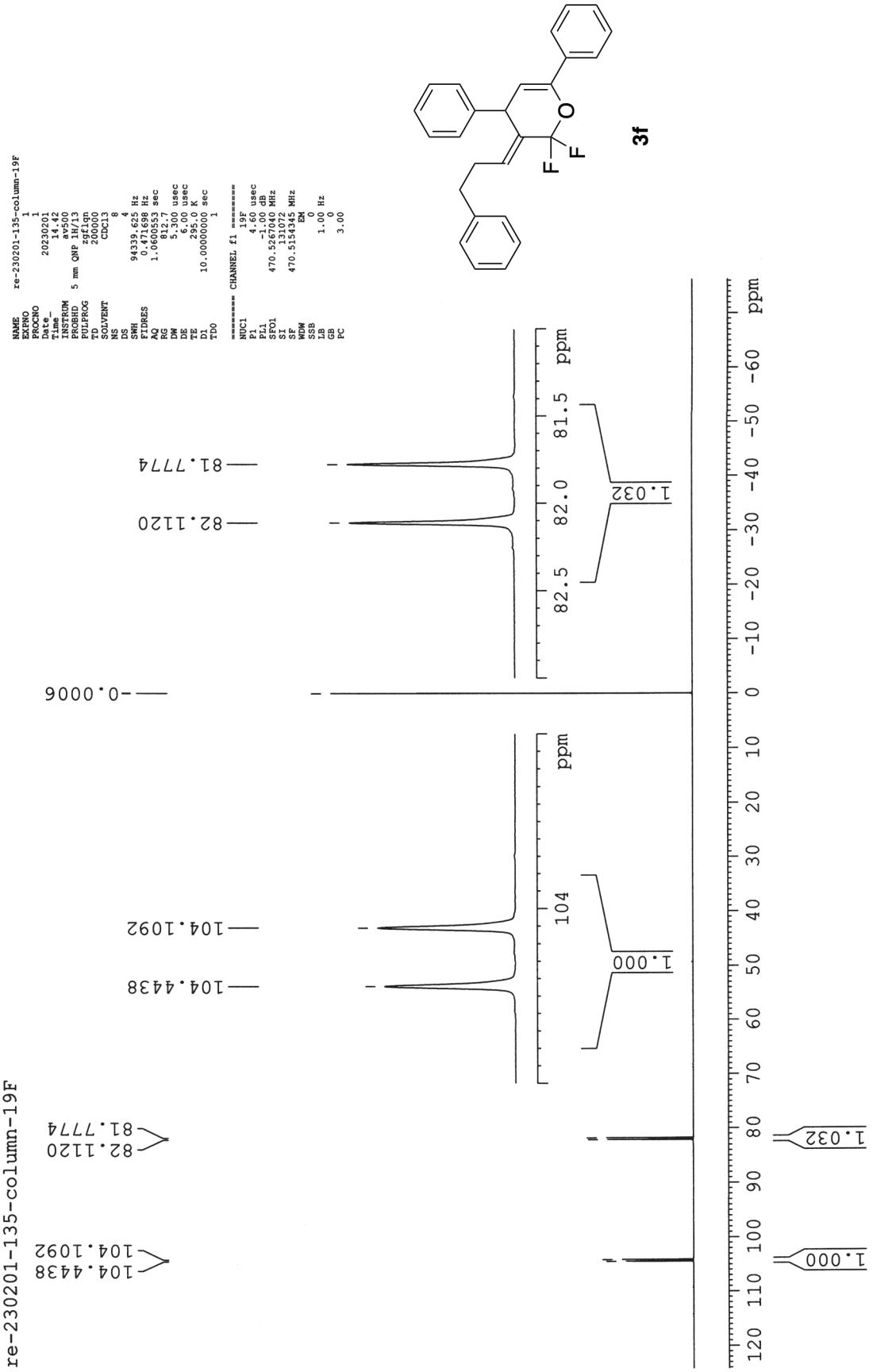
[1]H NMR Spectrum of (*E*)-2,2-Difluoro-4,6-diphenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3f**



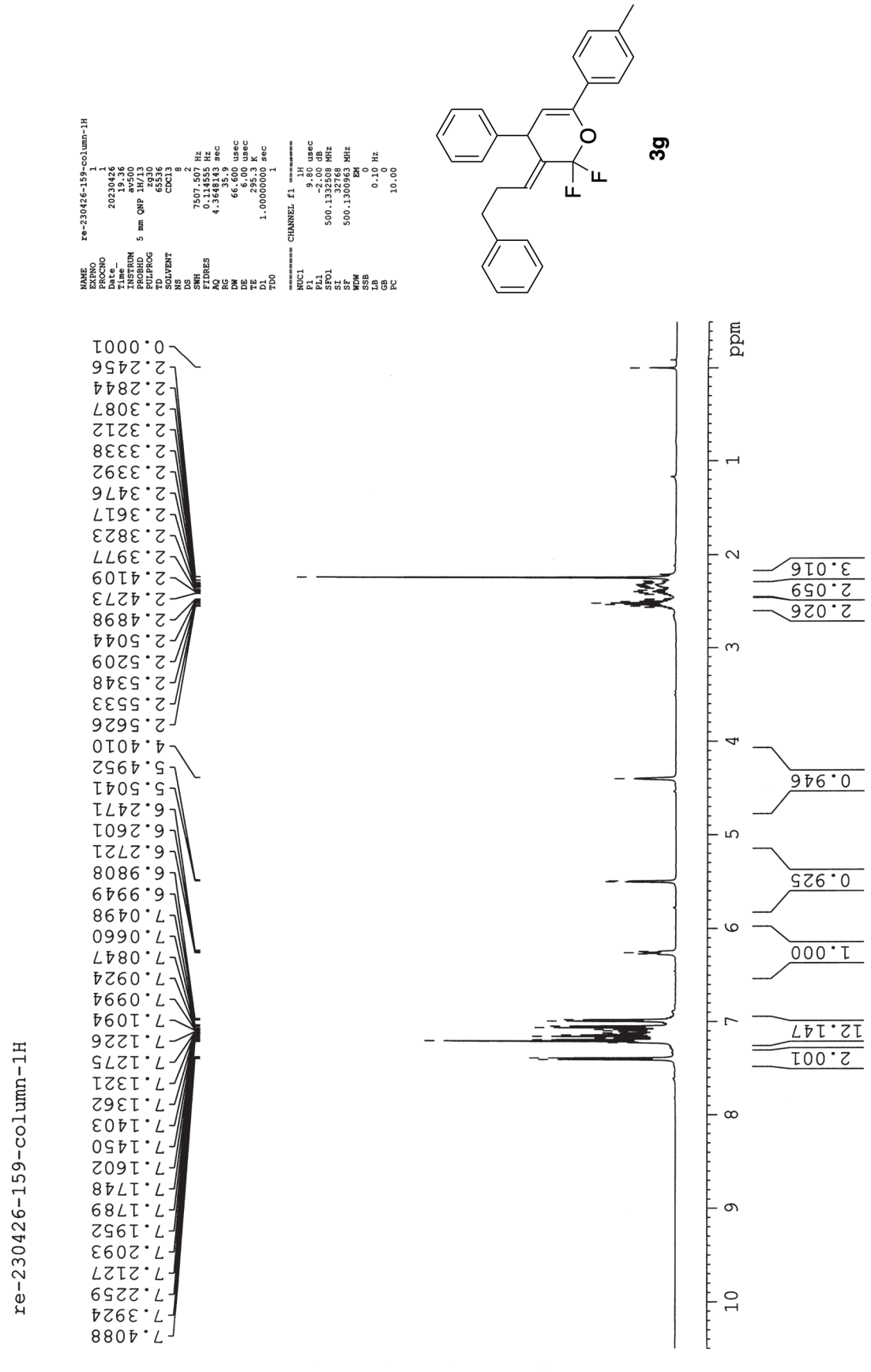
^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-4,6-diphenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3f**



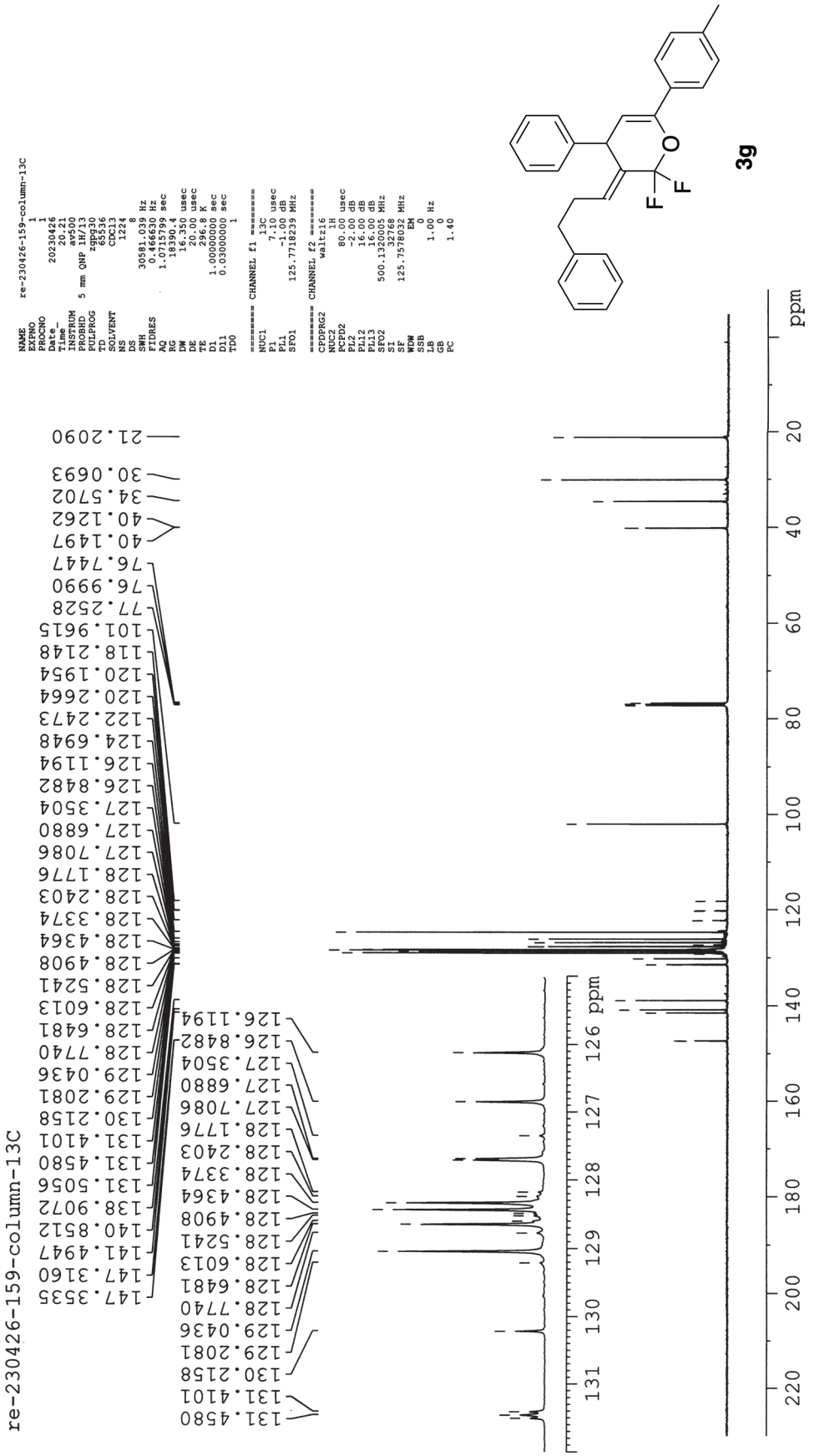
^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-4,6-diphenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3f**



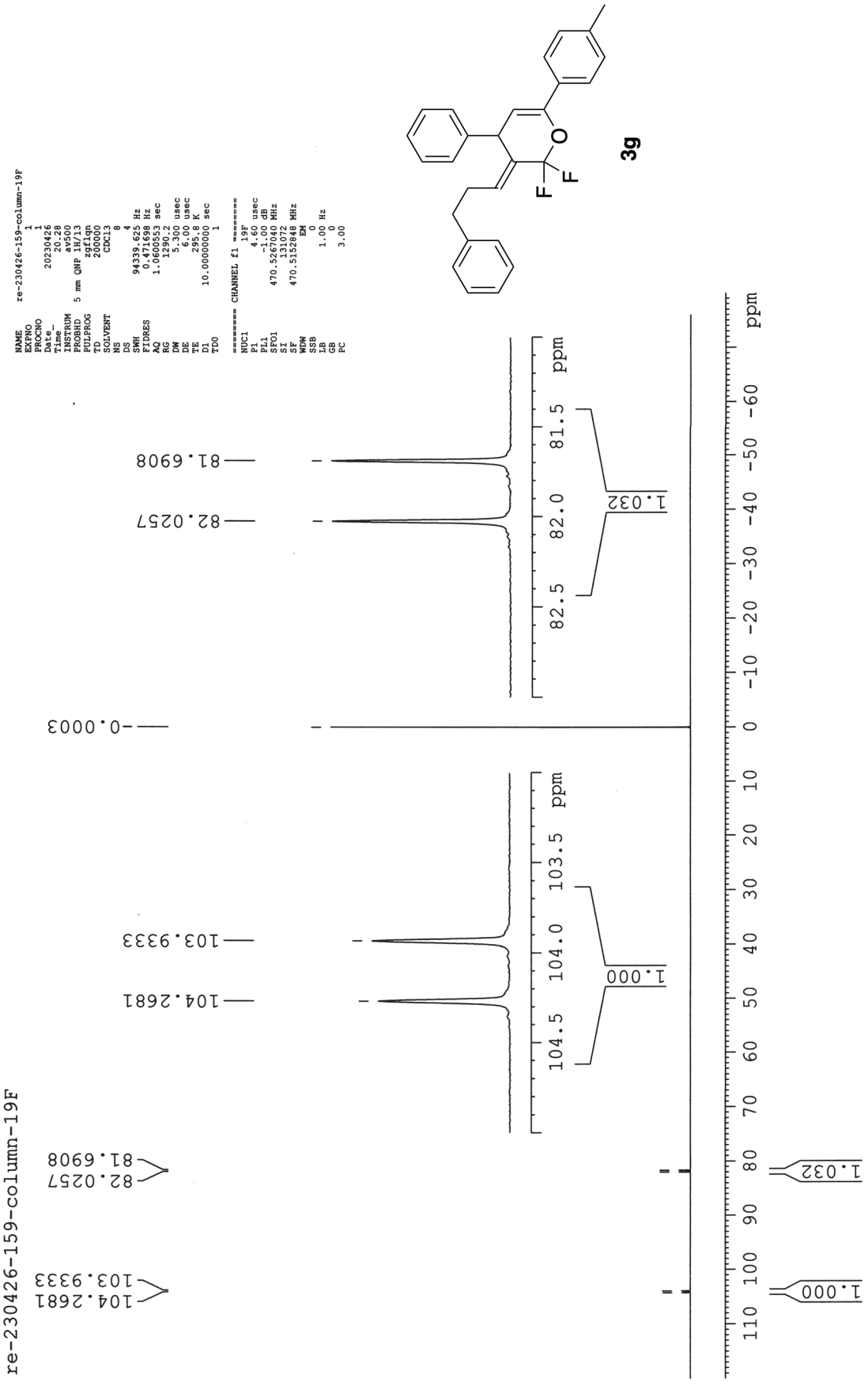
^{1}H NMR Spectrum of (*E*)-2,2-Difluoro-6-(4-methylphenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3g**



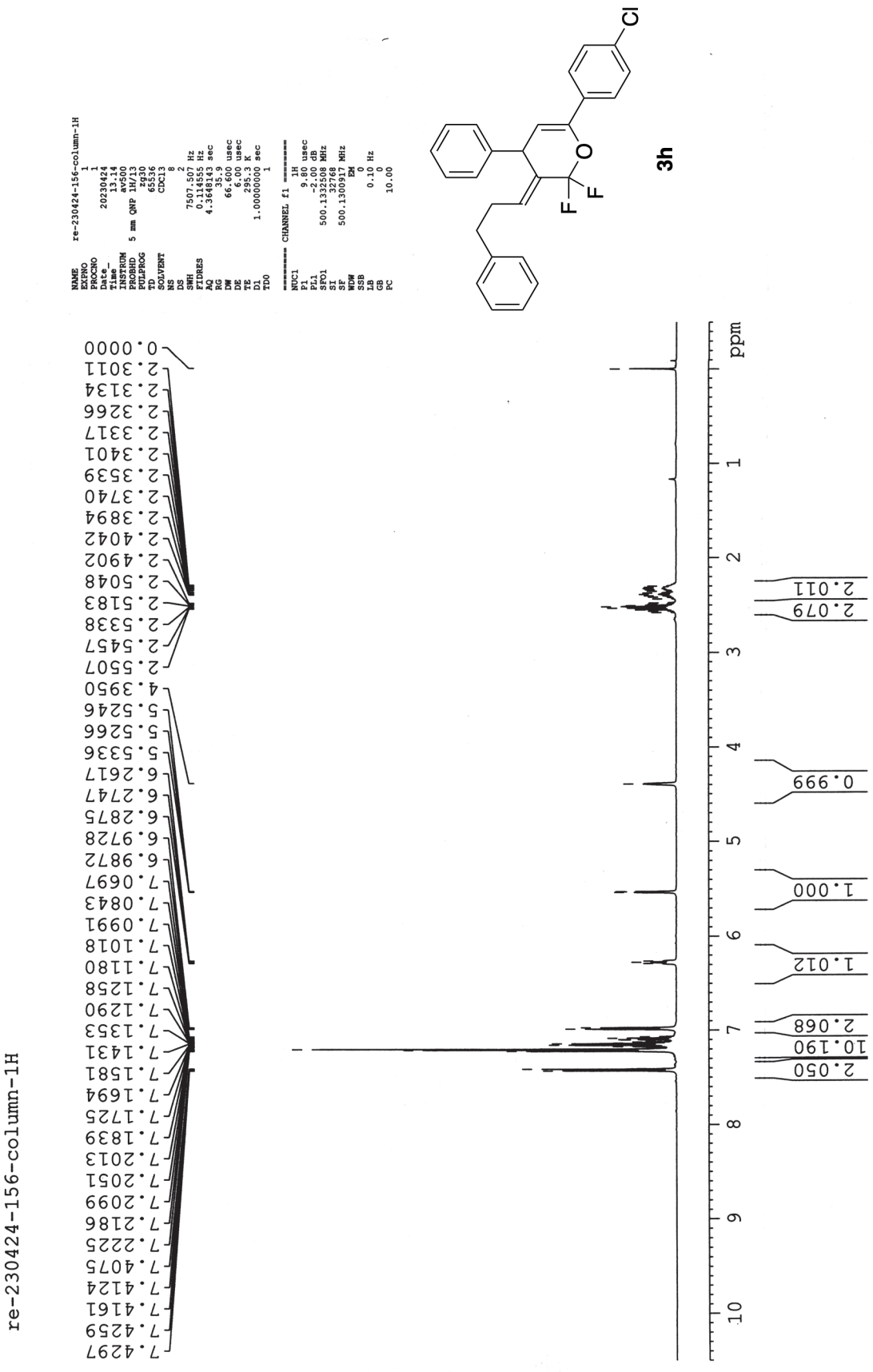
^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-6-(4-methylphenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3g**



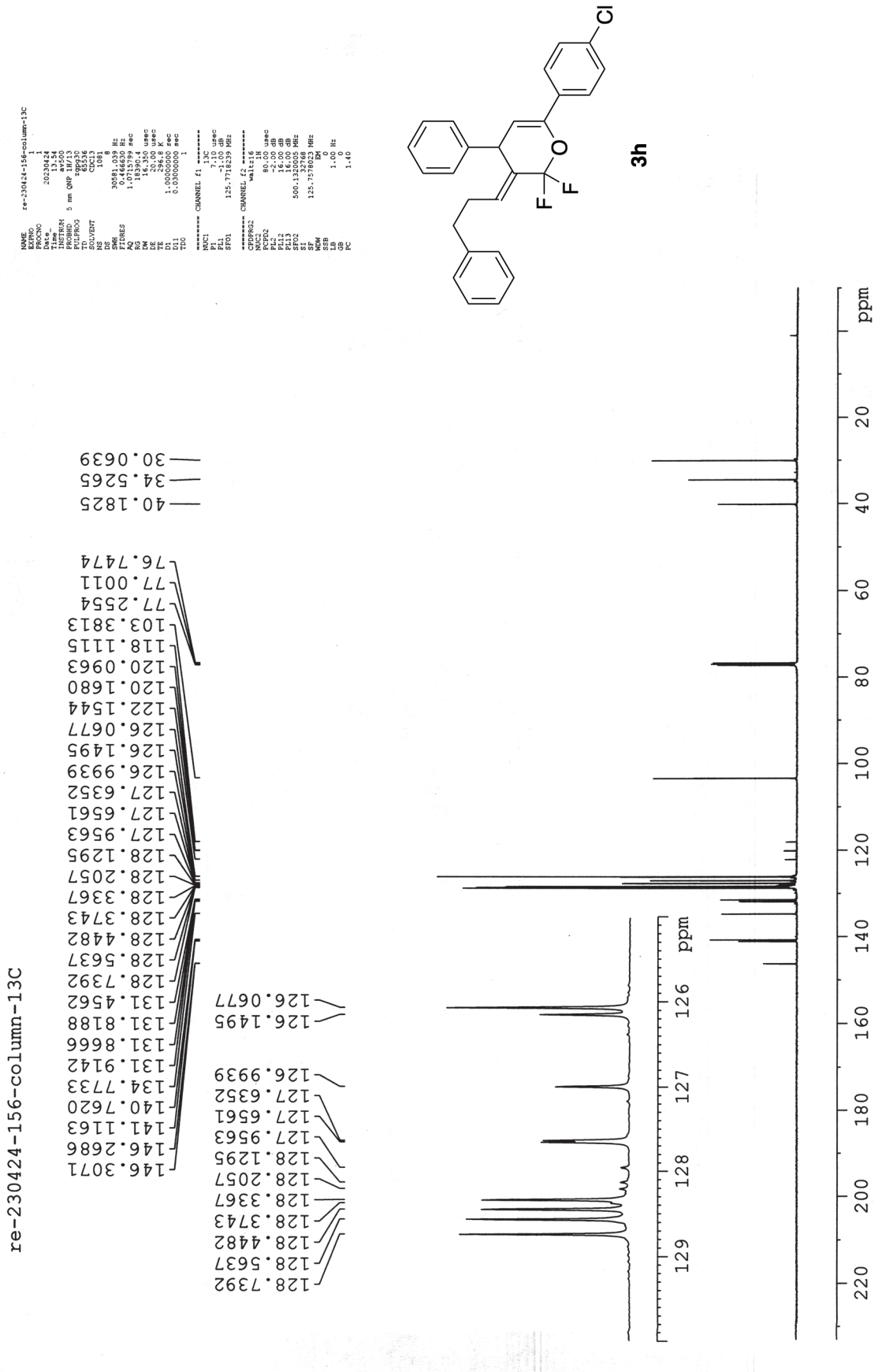
^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-6-(4-methylphenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3g**



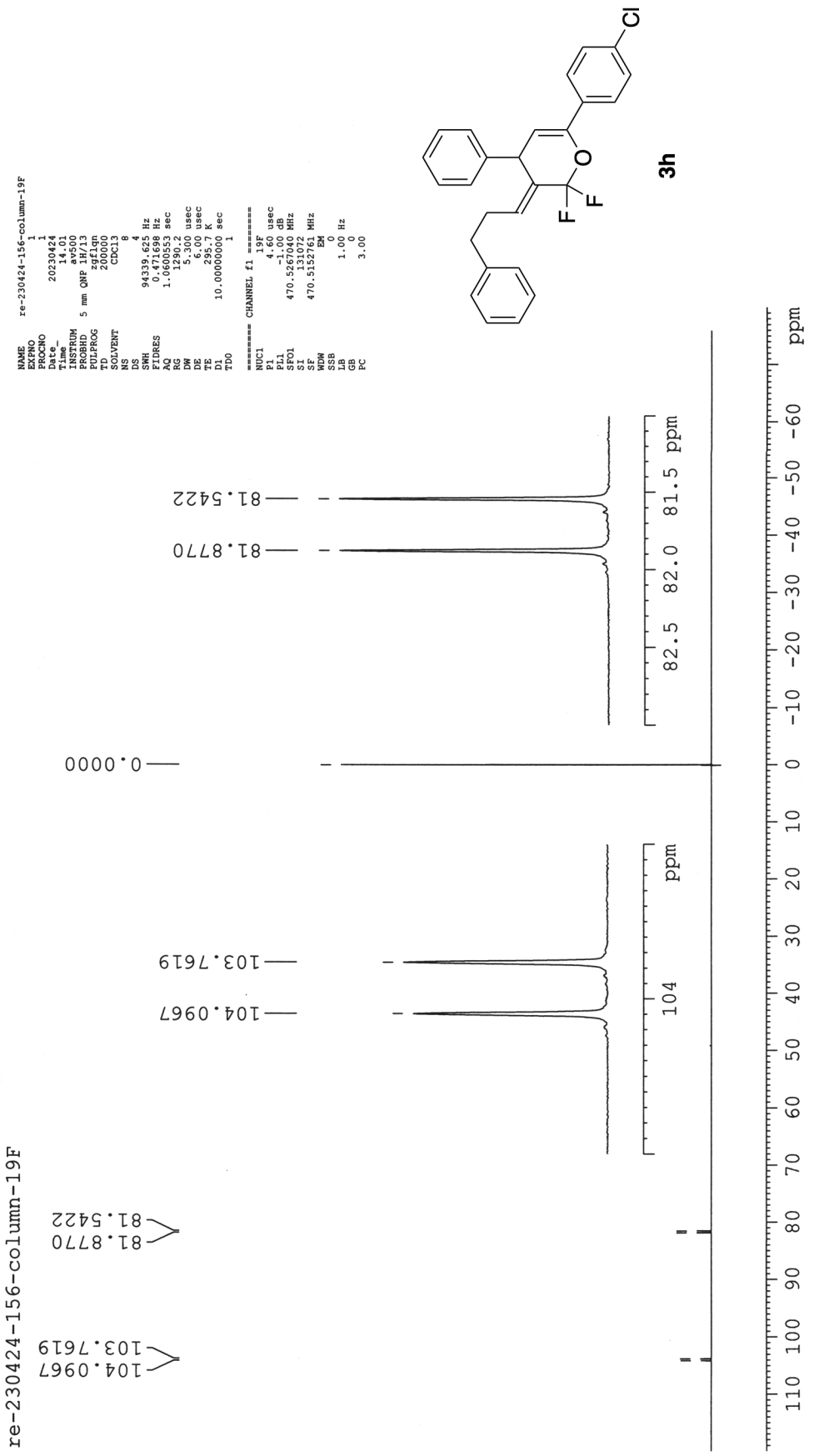
^{1}H NMR Spectrum of (*E*)-6-(4-Chlorophenyl)-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3h**



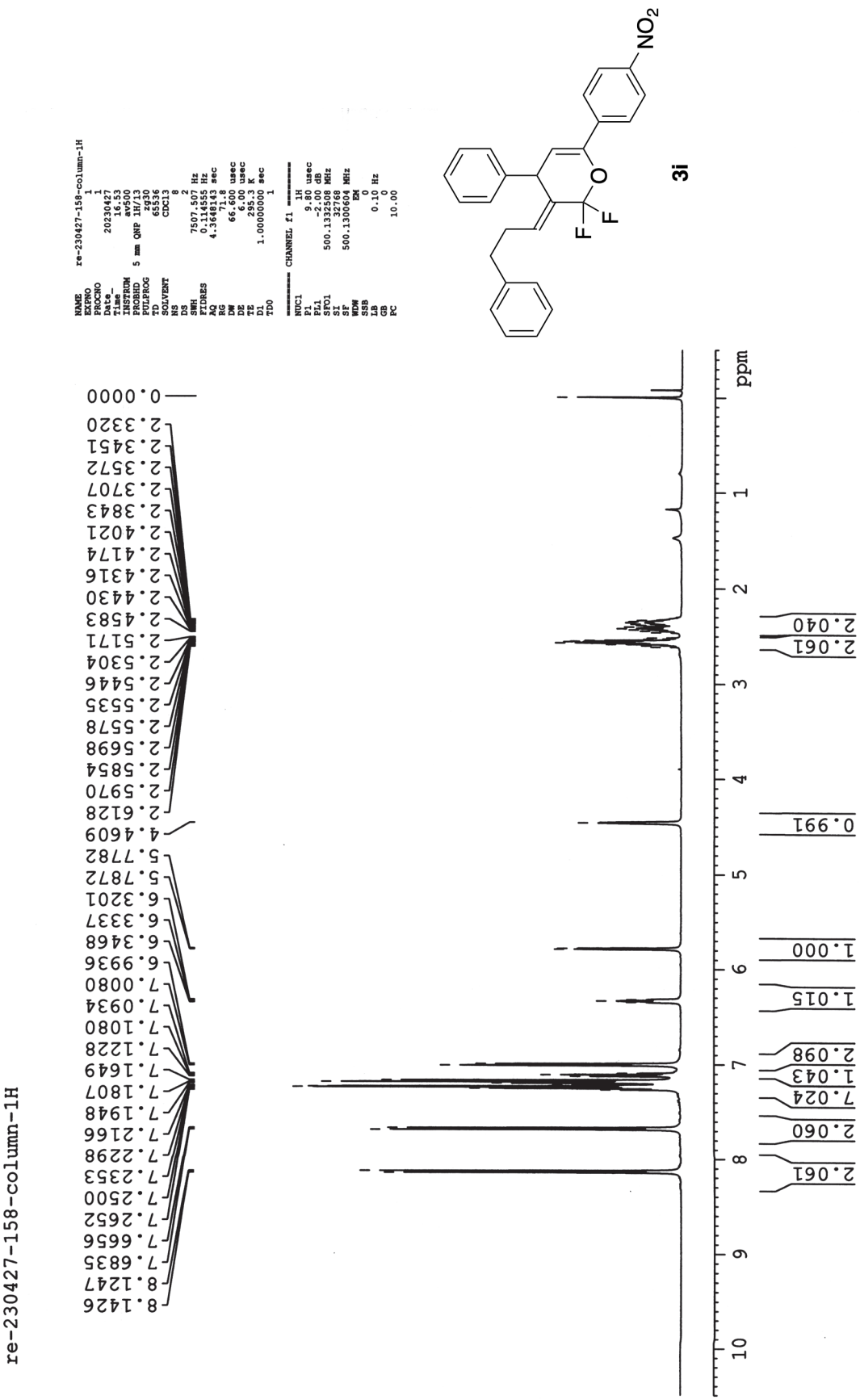
^{13}C NMR Spectrum of (*E*)-6-(4-Chlorophenyl)-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3h**



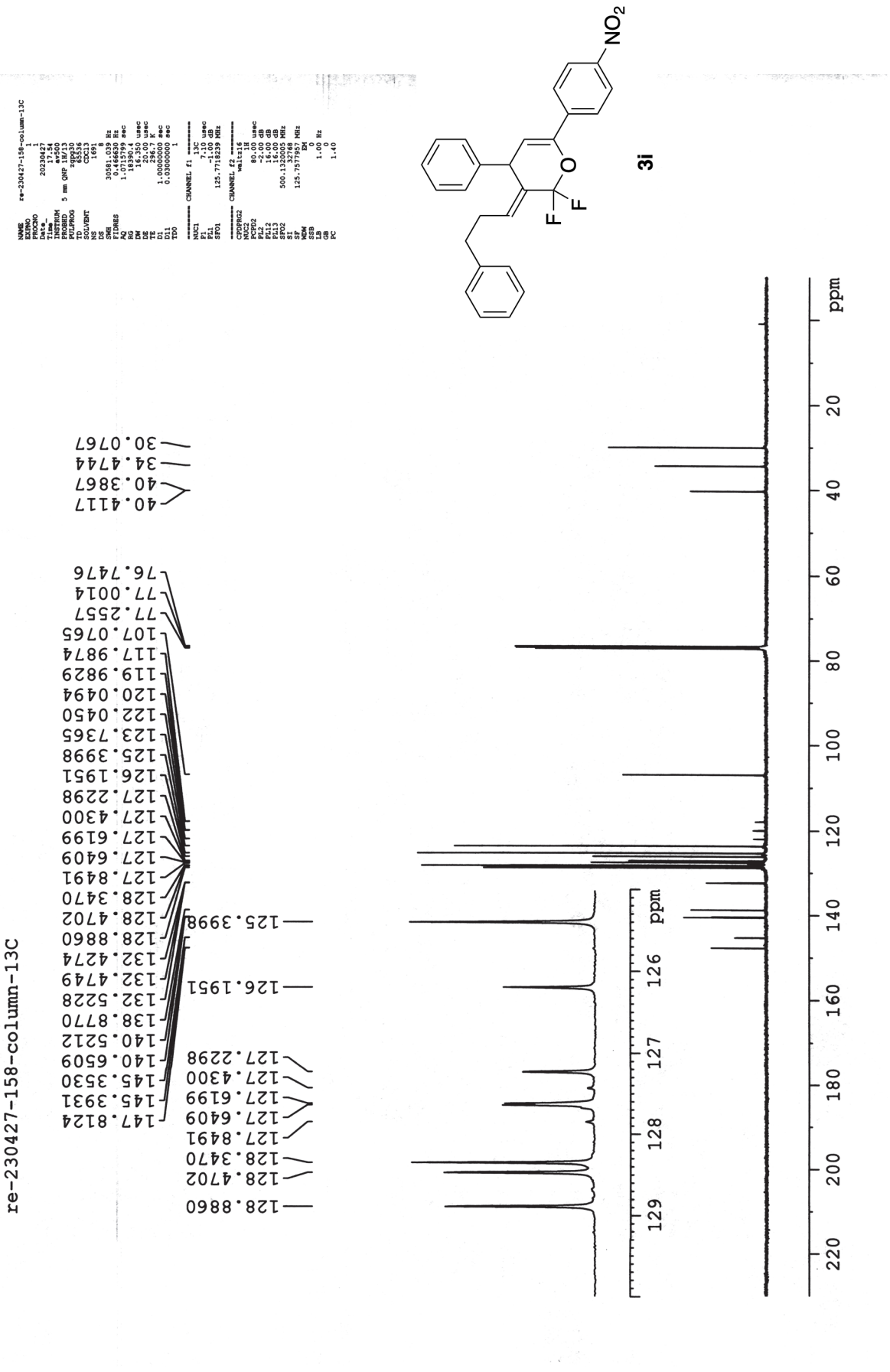
^{19}F NMR Spectrum of (*E*)-6-(4-Chlorophenyl)-2,2-difluoro-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3h**



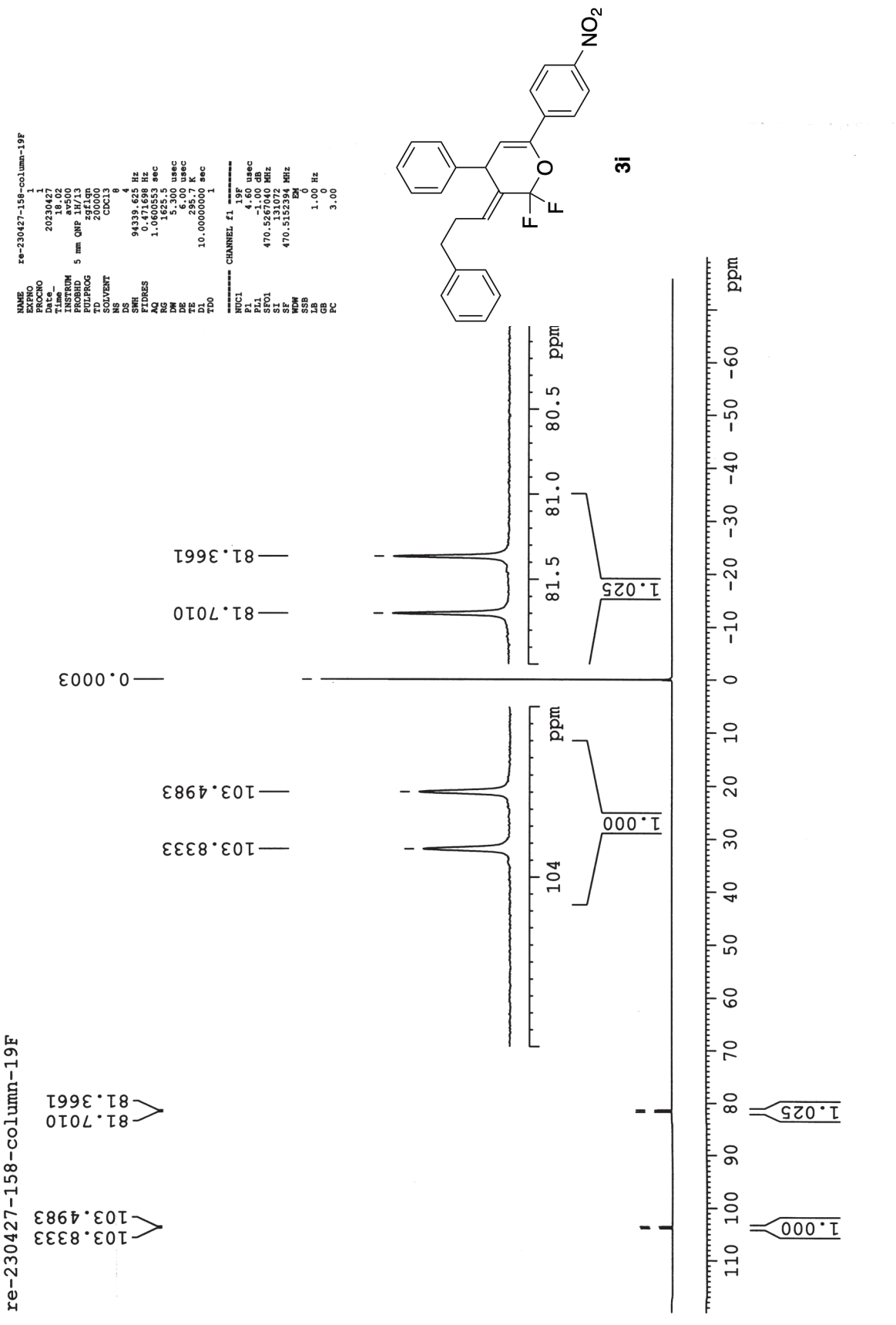
[1]H NMR Spectrum of (*E*)-2,2-Difluoro-6-(4-nitrophenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3i**



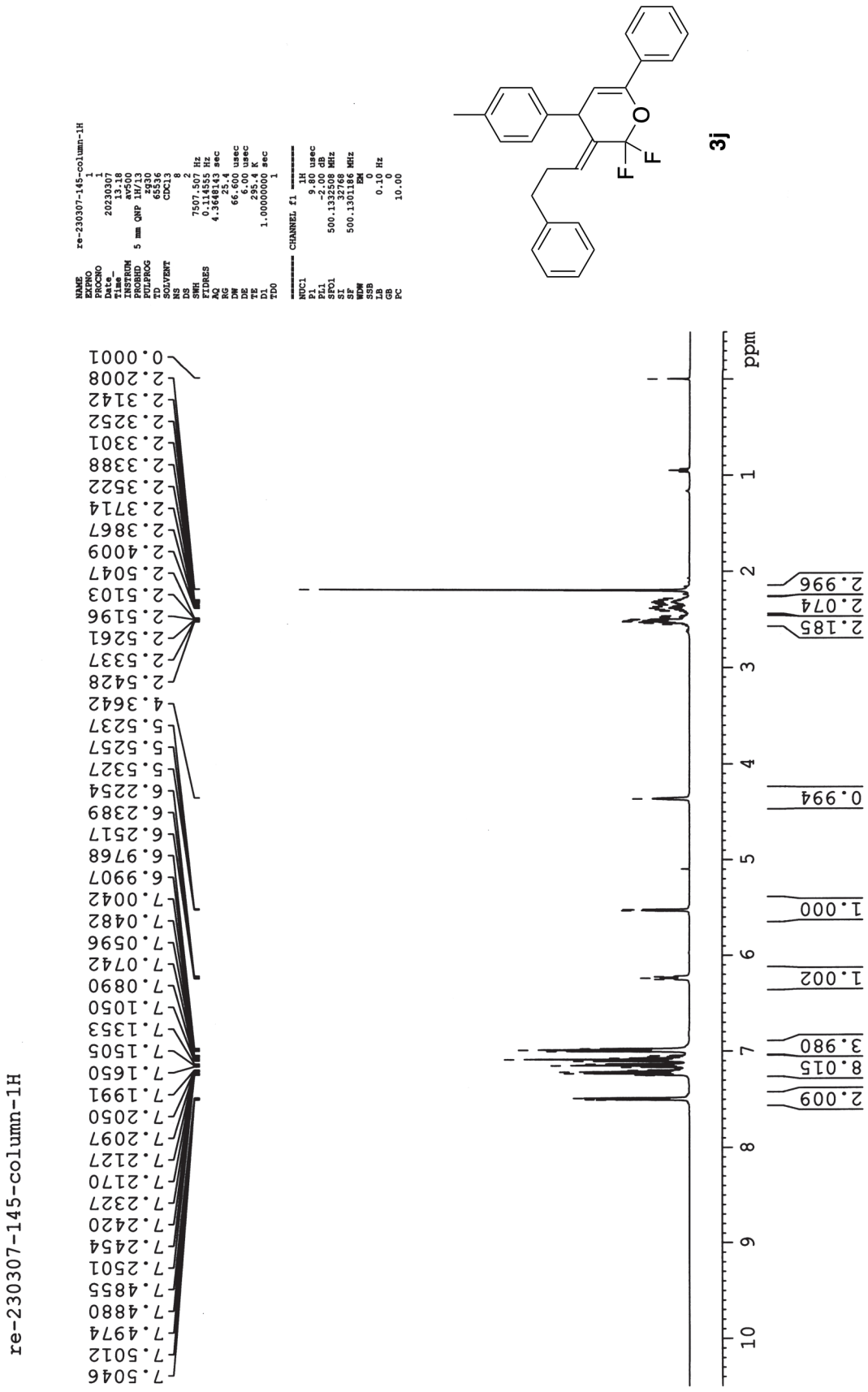
^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-6-(4-nitrophenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3i**



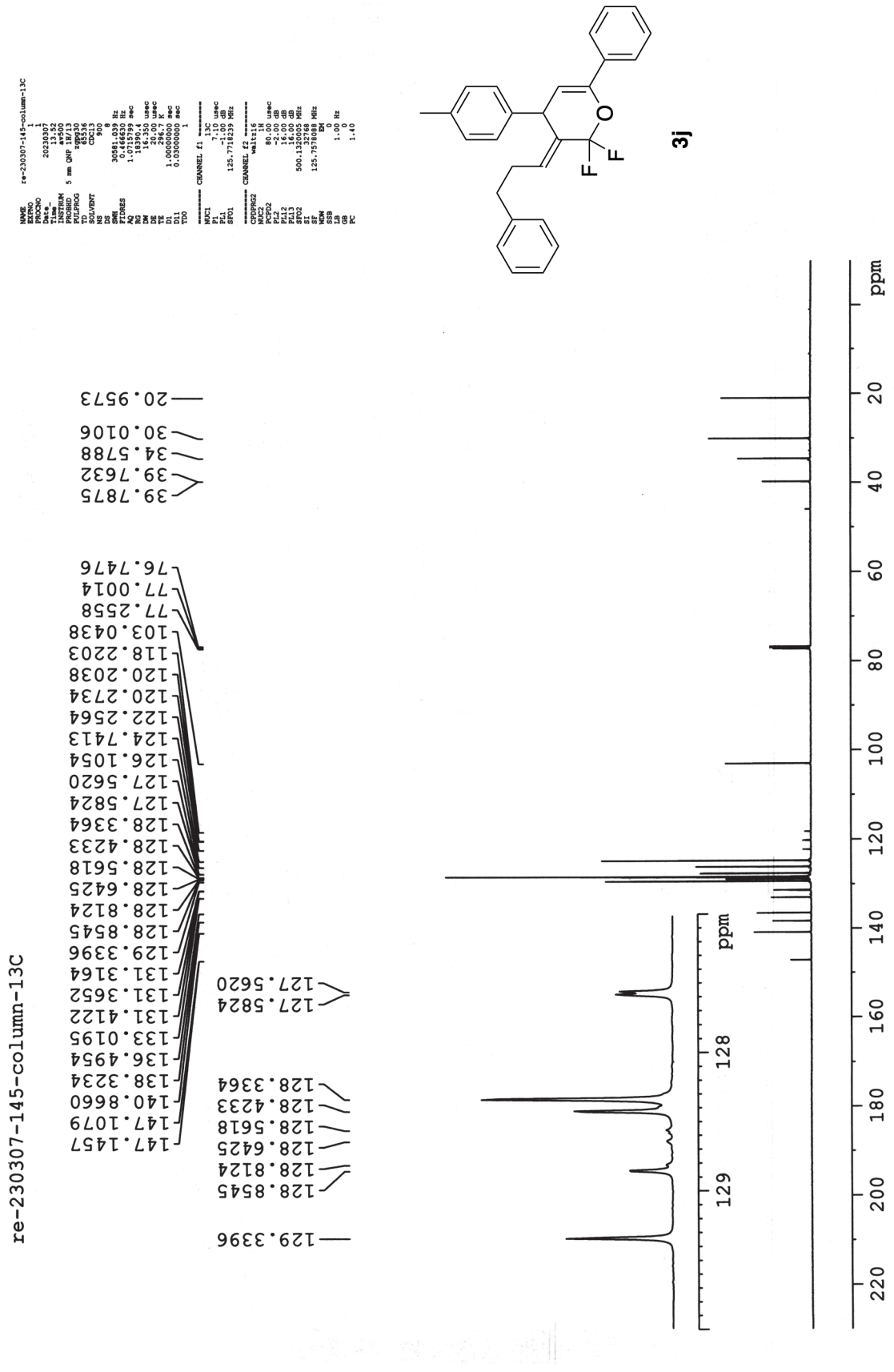
^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-6-(4-nitrophenyl)-4-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3i**



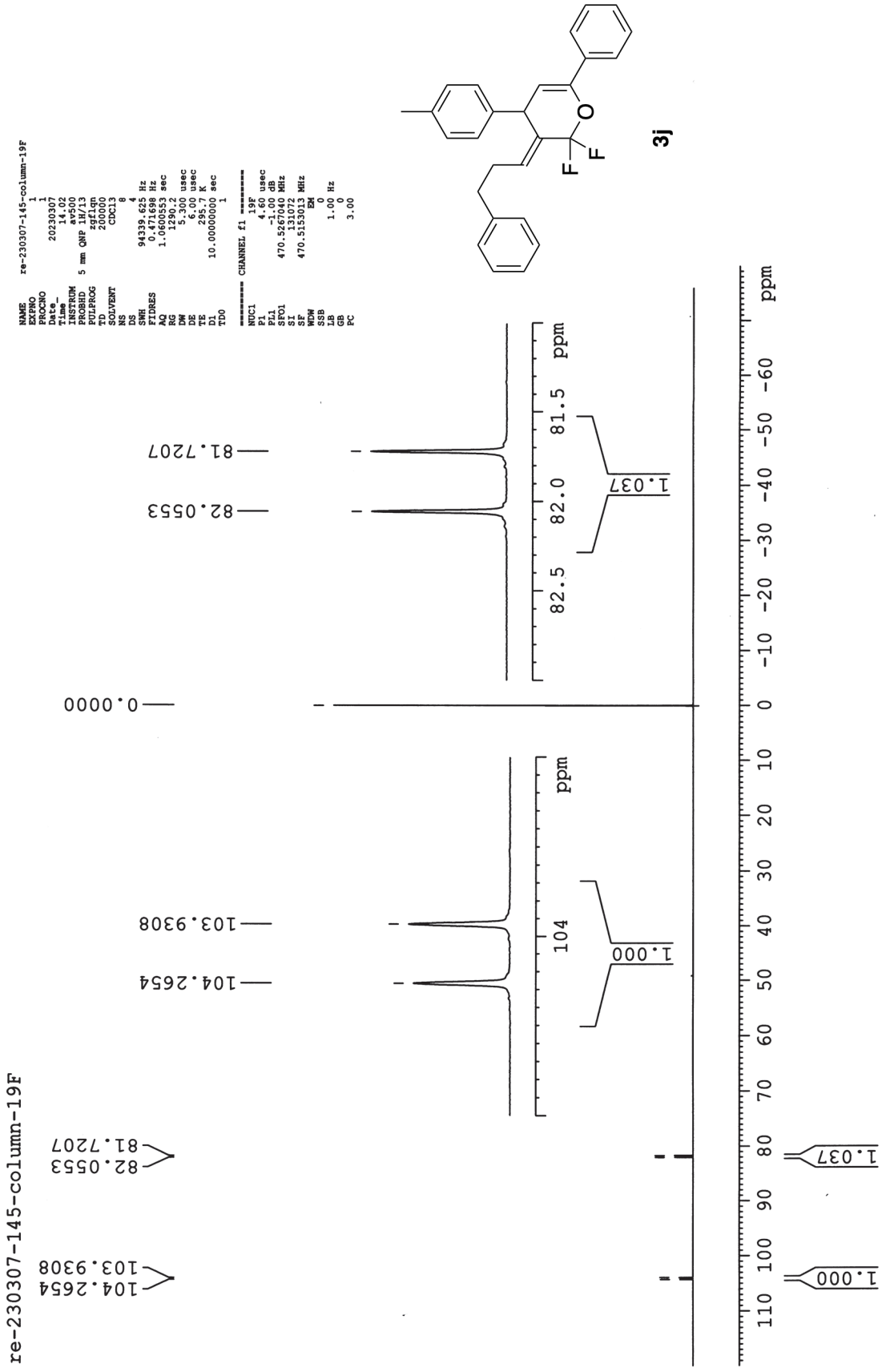
[1]H NMR Spectrum of (*E*)-2,2-Difluoro-4-(4-methylphenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3j**



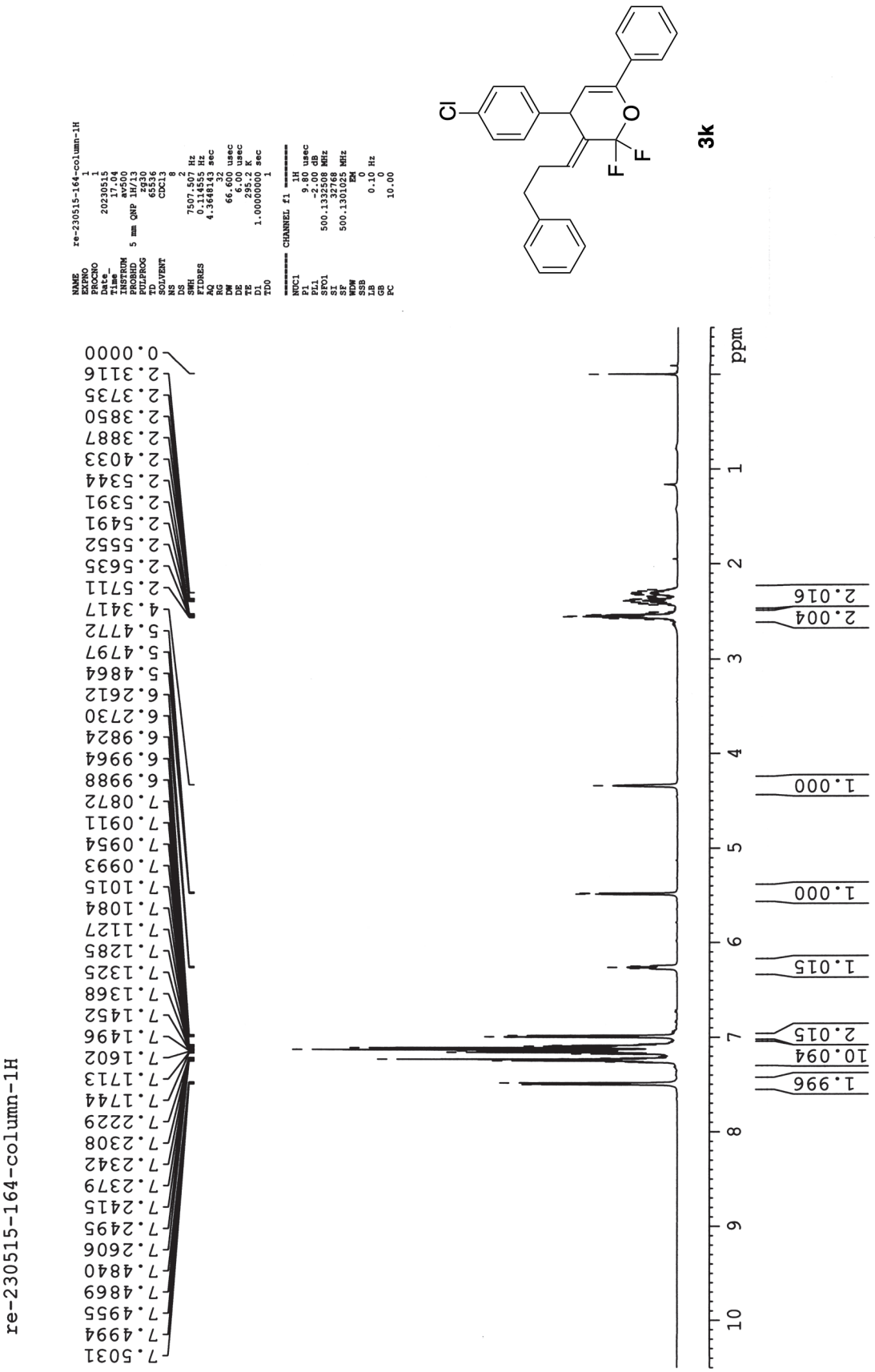
^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-4-(4-methylphenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3j**



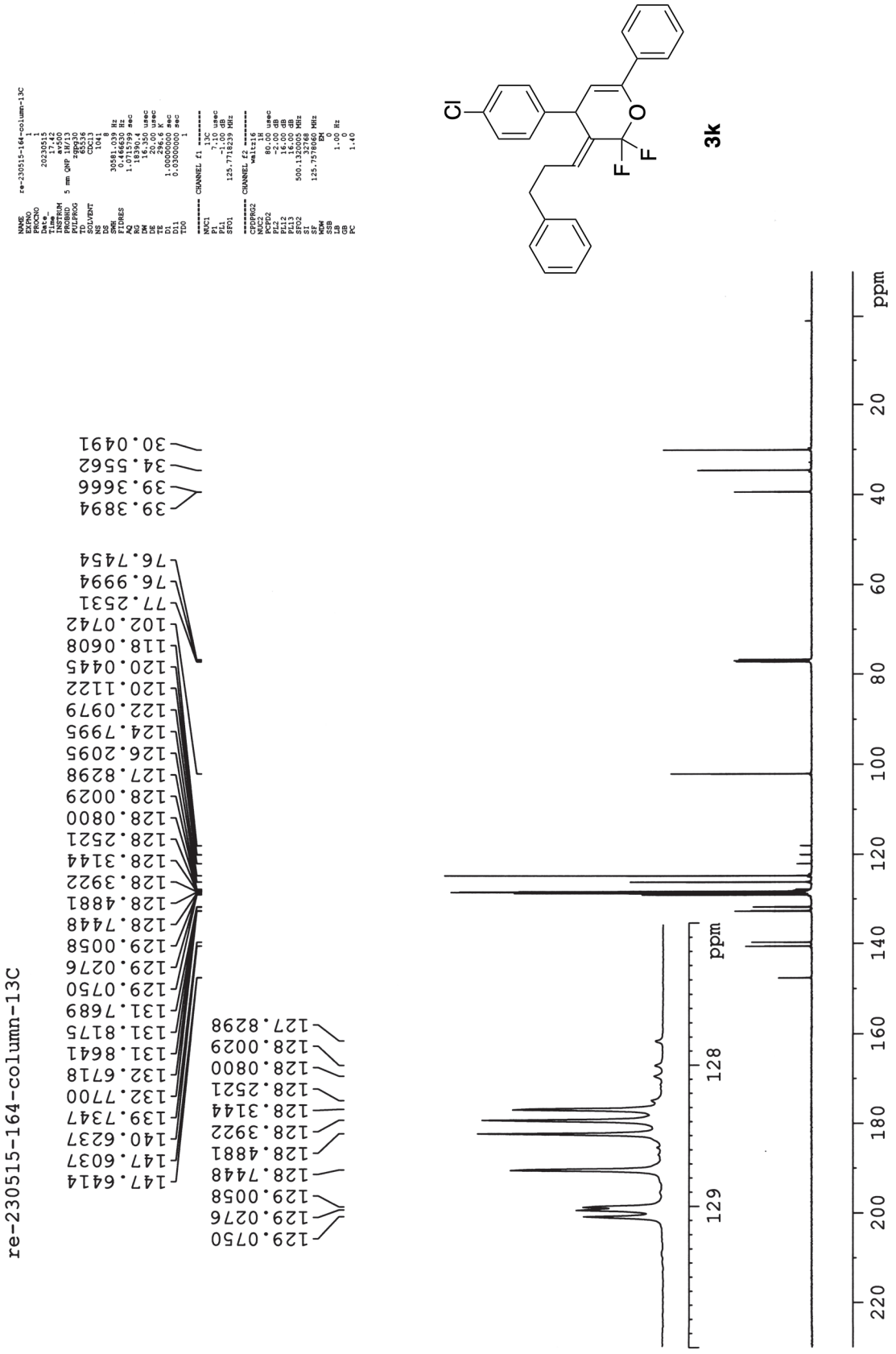
^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-4-(4-methylphenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3j**



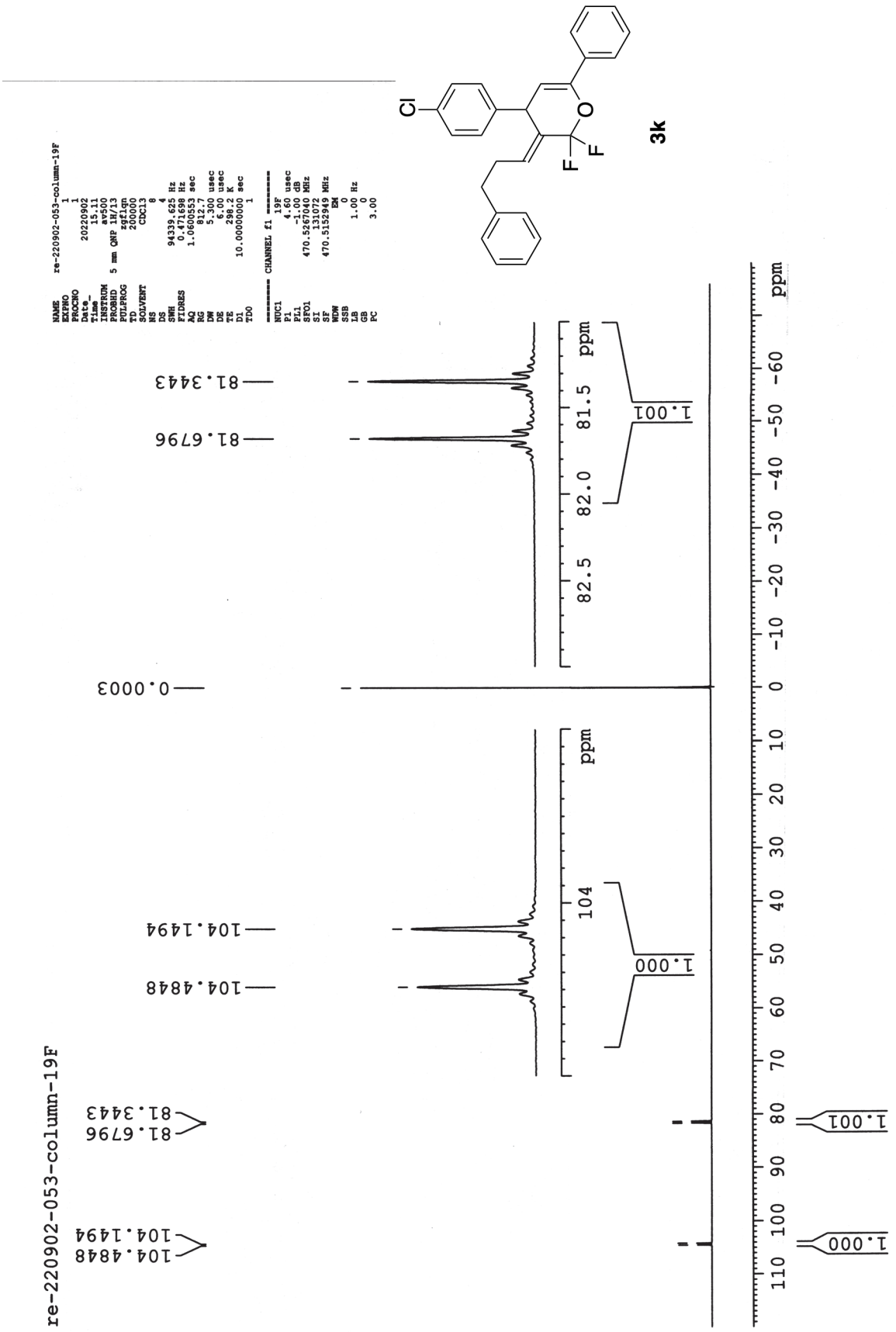
[1]H NMR Spectrum of (*E*)-4-(4-Chlorophenyl)-2,2-difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3k**



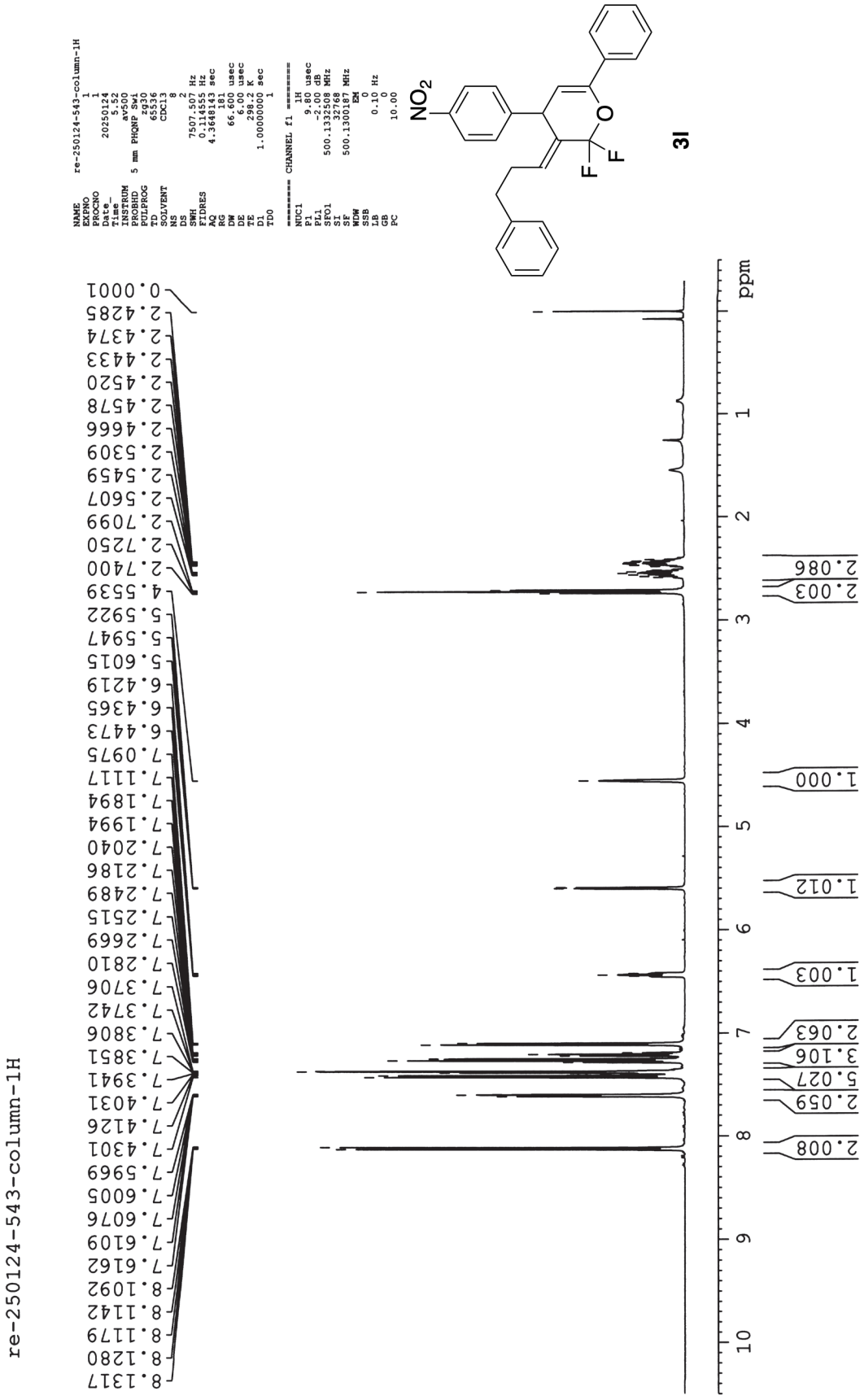
^{13}C NMR Spectrum of (*E*)-4-(4-Chlorophenyl)-2,2-difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3k**



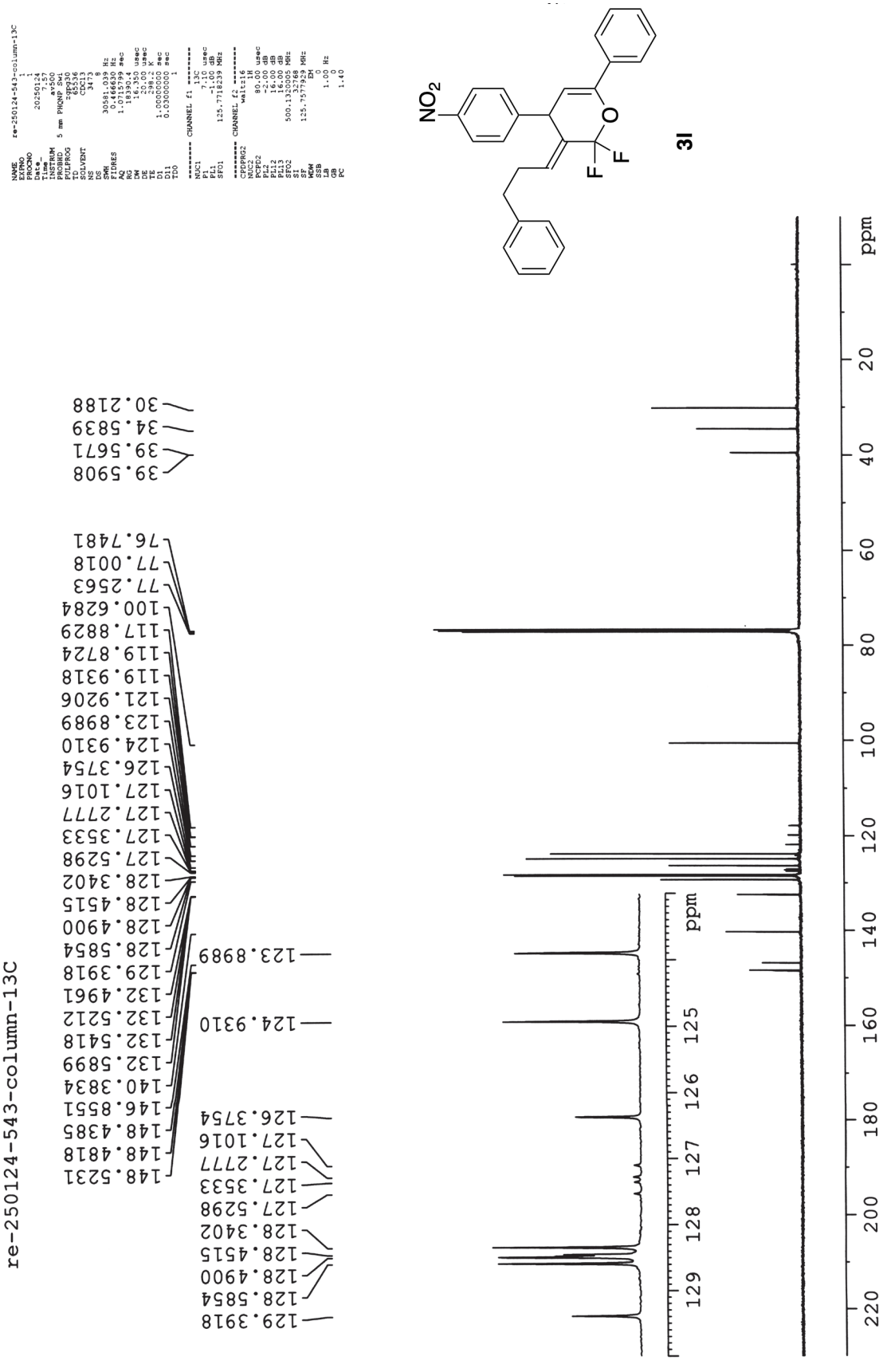
^{19}F NMR Spectrum of (*E*)-4-(4-Chlorophenyl)-2,2-difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3k**



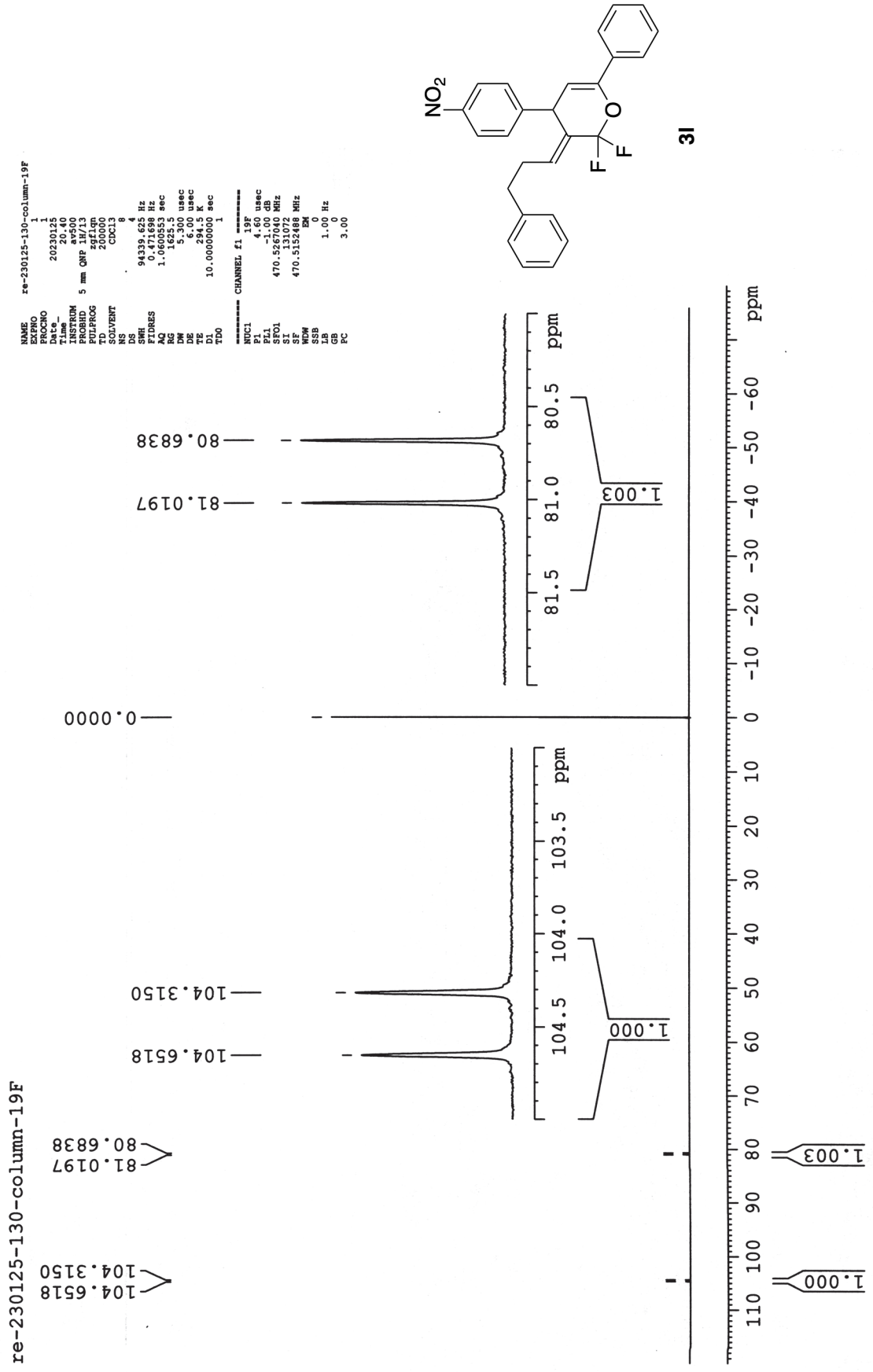
^{1}H NMR Spectrum of (*E*)-2,2-Difluoro-4-(4-nitrophenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3l**



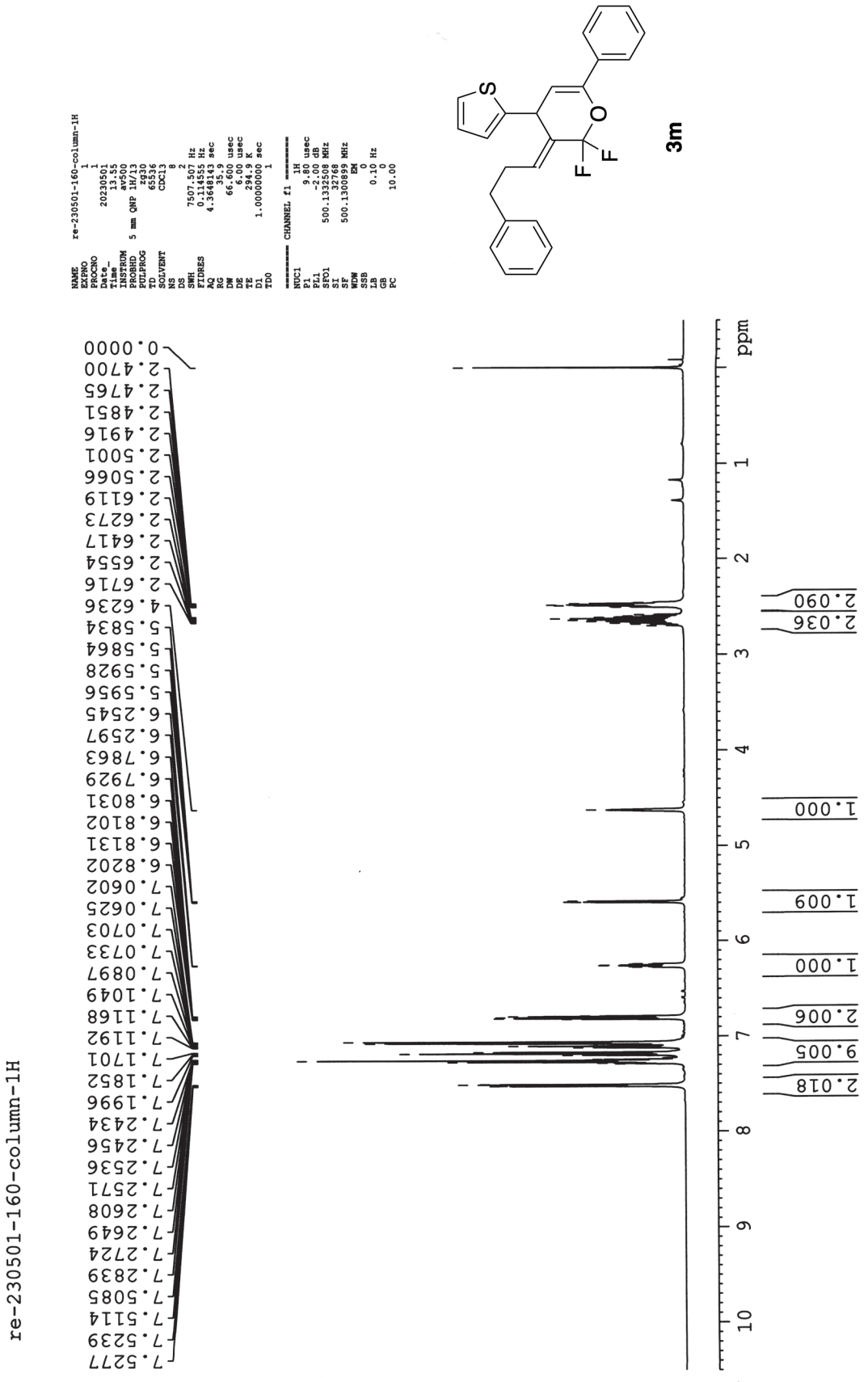
^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-4-(4-nitrophenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3l**



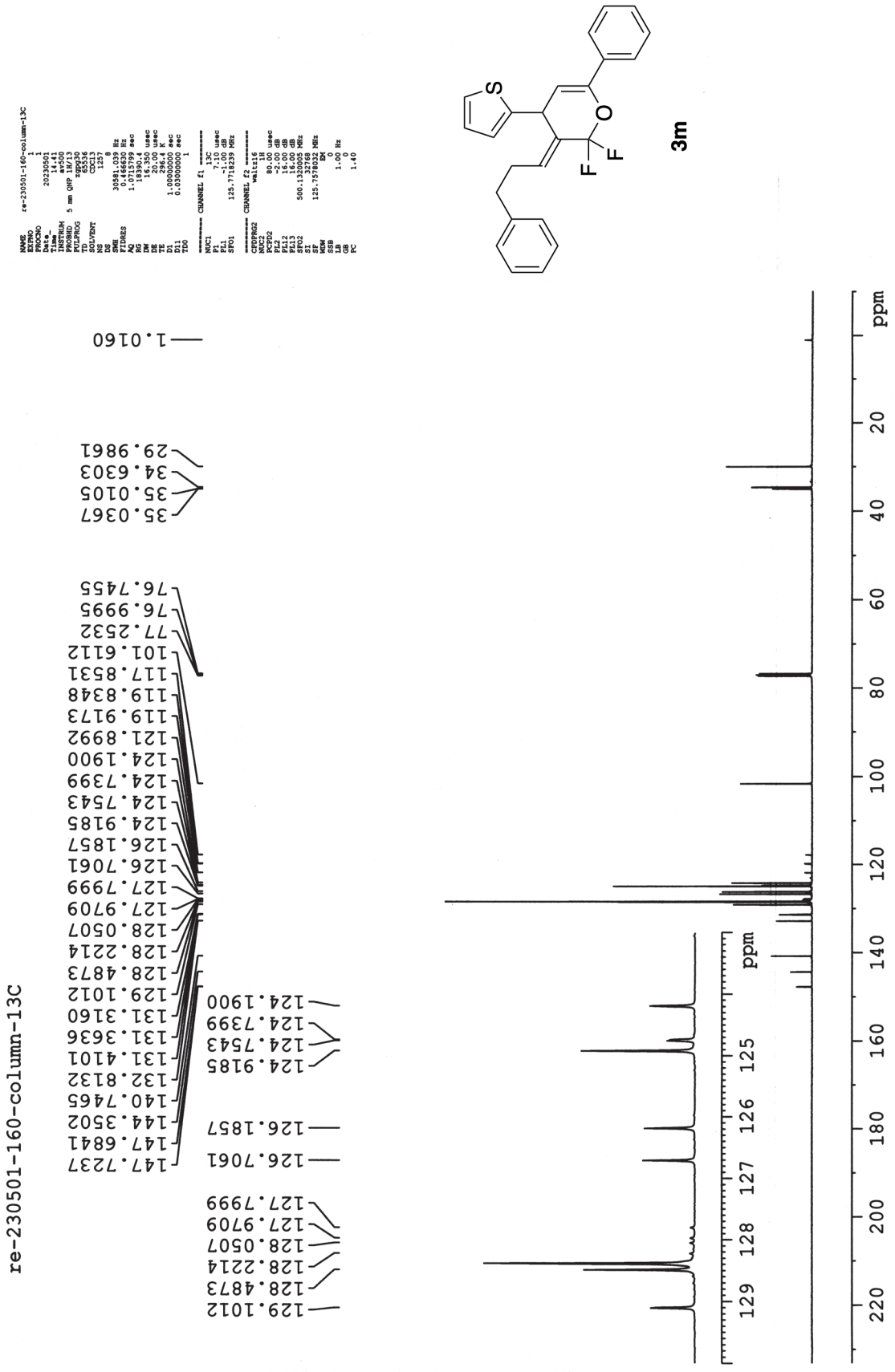
^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-4-(4-nitrophenyl)-6-phenyl-3-(3-phenylpropan-1-ylidene)-3,4-dihydro-2*H*-pyran **3l**



^{1}H NMR Spectrum of (*E*)-2,2-Difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-4-(2-thienyl)-3,4-dihydro-2*H*-pyran **3m**



^{13}C NMR Spectrum of (*E*)-2,2-Difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-4-(2-thienyl)-3,4-dihydro-2*H*-pyran **3m**



^{19}F NMR Spectrum of (*E*)-2,2-Difluoro-6-phenyl-3-(3-phenylpropan-1-ylidene)-4-(2-thienyl)-3,4-dihydro-2*H*-pyran **3m**