Friedel–Crafts-Type Cyclization of 2,2-Difluorovinyl Ketones via α -Fluorocarocations and its Application in Domino Cyclizations

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Supporting Information

General: NMR spectra were obtained at the indicated field strengths. Chemical shift values were given in ppm relative to internal Me₄Si (for ¹H NMR: δ 0.00), CDCl₃ (for ¹³C NMR: δ 77.0), and C₆F₆ (for ¹⁹F NMR: δ_F 0.00). Tetrahydrofuran and diethyl ether were distilled from sodium diphenylketyl prior to use. Hexamethylphosphoric triamide (HMPA) and 1,2-dichloroethane (CH₂ClCH₂Cl) were distilled from CaH₂, and stored over molecular sieves 4Å. Dichloromethane (CH₂Cl₂) was distilled twice from P₂O₅ and from CaH₂, and then stored over molecular sieves 4Å. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled from molecular sieves 4Å, and stored over molecular sieves 4Å. Benzene was distilled to remove water azeotropically, and stored over molecular sieves 4Å. Column chromatography and preparative thin-layer chromatography (PTLC) were performed on silica gel.

Typical experimental procedure for the preparation of 2,2-difluorovinylketones **1** is as follows: Butyllithium (6.09 ml, 1.71 M in hexane, 10.4 mmol) was added to a solution of 2,2,2-trifluoroethyl *p*-toluenesulfonate (1.26 g, 4.96 mmol) in THF (25 ml) at –78 °C over 10 min under nitrogen. The reaction mixture was stirred for 30 min at –78 °C and then a trialkylborane was added at –78 °C over 10 min (The trialkylborane was prepared as below: Borane–THF complex (5.5 ml, 1.0 M in THF, 5.5 mmol) was added to a solution of prop-1-en-2-ylbenzene (1.95 g, 16.5 mmol) in THF (2.5 ml) at 0 °C, and the mixture was stirred at room temperature for 2 h.). After being stirred for 1 h, the reaction mixture was warmed up to room temperature and stirred for an additional 3 h. The obtained difluorovinylborane solution was cooled to 0 °C and treated with HMPA (8.5 ml) and cuprous iodide (1.89 g, 9.92 mmol). After 30 min at the same temperature, the reaction mixture was treated with benzoyl chloride (837 mg, 5.95 mmol) and stirred at room temperature for 0.5 h. The reaction mixture was quenched with phosphate buffer (pH 7), and aqueous hydrogen peroxide (3.0 ml, 30%) was added dropwise at 0 °C. After being stirred at room temperature for 20 min, the mixture was filtered. Organic materials were extracted with ethyl acetate (AcOEt) three times. The combined extracts were washed with aqueous Na₂S₂O₃ and brine, and then dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane–Et₂O, 40:1) to give 3,3-difluoro-1-phenyl-2-(2-phenylpropyl)prop-2-en-1-one (**1a**; 787 mg, 55%).

3-Benzoyl-4-fluoro-1-methyl-1,2-dihydronaphthalene (2a)

TMSOTf (139 μ l, 0.79 mmol) was added to a solution of **1a** ($R^1 = \text{Me}$, $R^2 = R^3 = R^4 = \text{H}$, $R^5 = \text{Ph}$; 222 mg, 0.79 mmol) in CH_2Cl_2 –HFIP (1:1, 7.0 ml) at 0 °C under nitrogen. After the reaction mixture was stirred for 25 min, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with water, and then dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane– Et_2O 10:1) to give **2a** (162 mg, 84%). ^1H NMR (500 MHz, CDCl_3): δ 1.35 (3H, d, $J = 6.9$ Hz), 2.54–2.66 (1H, m), 2.85–2.96 (1H, m), 3.10 (1H, ddq, $J = 6.9, 6.9, 6.9$ Hz), 7.23–7.28 (2H, m), 7.34–7.57 (5H, m), 7.83–7.88 (2H, m). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 50.7 (s). ^{13}C NMR (126 MHz, CDCl_3): δ 19.8, 31.8, 31.9 (d, $J_{\text{CF}} = 2$ Hz), 112.7 (d, $J_{\text{CF}} = 7$ Hz), 123.0 (d, $J_{\text{CF}} = 6$ Hz), 126.3 (d, $J_{\text{CF}} = 4$ Hz), 126.7, 127.0 (d, $J_{\text{CF}} = 25$ Hz), 128.3, 128.8 (d, $J_{\text{CF}} = 3$ Hz), 130.9, 132.6, 139.2 (d, $J_{\text{CF}} = 2$ Hz), 143.5 (d, $J_{\text{CF}} = 7$ Hz), 157.6 (d, $J_{\text{CF}} = 267$ Hz), 195.0. IR (NaCl, neat): 3080, 2975, 1635, 1600, 1490, 1360, 1340, 1145, 1065, 775, 700 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{FO}$: C, 81.18; H, 5.68%. Found: C, 80.96; H, 5.76%.

3-Benzoyl-4-fluoro-1,2-dihydronaphthalene (2b)

Compound **2b** was prepared by the method described for **2a** in 89% yield. ^1H NMR (500 MHz, CDCl_3): δ 2.72–2.82 (2H, m), 2.89–2.99 (2H, m), 7.18–7.34 (3H, m), 7.35–7.56 (4H, m), 7.83–7.87 (2H, m). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 51.4 (s). ^{13}C NMR (126 MHz, CDCl_3): δ 24.6 (d, $J_{\text{CF}} = 4$ Hz), 27.5, 114.3 (d, $J_{\text{CF}} = 7$ Hz), 122.9 (d, $J_{\text{CF}} = 6$ Hz), 127.0, 127.8 (d, $J_{\text{CF}} = 4$ Hz), 128.0 (d, $J_{\text{CF}} = 25$ Hz), 128.4, 128.9, 130.7, 132.7, 138.8 (d, $J_{\text{CF}} = 7$ Hz), 139.2 (d, $J_{\text{CF}} = 2$ Hz), 158.4 (d, $J_{\text{CF}} = 267$ Hz), 195.1. IR (NaCl, neat): 3080, 2950, 1635, 1605, 1580, 1495, 1455, 1365, 1350, 1330, 1290, 1275, 1140, 1080, 770, 700 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{FO}$: C, 80.93; H, 5.19%. Found: C, 80.69; H, 5.26%.

3-Benzoyl-4-fluoro-6-methyl-1,2-dihydronaphthalene (2c)

Compound **2c** was prepared by the method described for **2a** in 71% yield. ^1H NMR (500 MHz, CDCl_3): δ 2.33 (3H, s), 2.77 (2H, td, $J = 8.5$ Hz, $J_{\text{HF}} = 5.5$ Hz), 2.91 (2H, t, $J = 8.5$ Hz), 7.12 (1H, d, $J = 8.6$ Hz), 7.15 (1H, d, $J = 8.6$ Hz), 7.29 (1H, s), 7.45 (2H, dd, $J = 7.6, 7.6$ Hz), 7.55 (1H, tt, $J = 7.6, 1.2$ Hz), 7.85 (2H, dd, $J = 7.6, 1.2$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 51.7 (br. s). ^{13}C NMR (126 MHz, CDCl_3): δ 21.1, 24.6 (d, $J_{\text{CF}} = 3$ Hz), 27.0, 114.1 (d, $J_{\text{CF}} = 7$ Hz), 123.4 (d, $J_{\text{CF}} = 5$ Hz), 127.5 (d, $J_{\text{CF}} = 4$ Hz), 128.2 (d, $J_{\text{CF}} = 25$ Hz), 128.3, 128.8 (d, $J_{\text{CF}} = 3$ Hz), 131.3, 132.5, 135.8 (d, $J_{\text{CF}} = 7$ Hz), 136.5, 139.2 (d, $J_{\text{CF}} = 2$ Hz), 158.5 ($J_{\text{CF}} = 268$ Hz), 195.1. IR (NaCl, neat): 3075, 2950, 1635, 1600, 1585, 1455, 1365, 1290, 1140, 1085, 700 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{FO}$: C, 81.18; H, 5.68%. Found: C, 81.08; H, 5.85%.

2-Benzoyl-1-fluoro-4-methyl-3,4-dihydrophenanthrene (2d)

Compound **2d** was prepared by the method described for **2a** in 86% yield. ^1H NMR (500 MHz, CDCl_3): δ 1.36 (3H, d, $J = 7.3$ Hz), 2.85 (1H, ddd, $J = 16.2, 5.2$ Hz, $J_{\text{HF}} = 1.2$ Hz), 3.10 (1H, ddd, $J = 16.2, 6.1$ Hz, $J_{\text{HF}} = 6.1$ Hz), 3.85 (1H, qdd, $J = 7.3, 6.1, 5.2$ Hz), 7.63 (2H, dd, $J = 7.5, 7.5$ Hz),

7.50–7.64 (4H, m), 7.75 (1H, d, $J = 8.4$ Hz), 7.85 (1H, d, $J = 8.4$ Hz), 7.89 (2H, d, $J = 7.5$ Hz), 8.09 (1H, d, $J = 8.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 52.8 (br. s). ^{13}C NMR (126 MHz, CDCl_3): δ 19.5, 27.8, 31.0 (d, $J_{\text{CF}} = 3$ Hz), 110.7 (d, $J_{\text{CF}} = 7$ Hz), 119.9 (d, $J_{\text{CF}} = 7$ Hz), 123.3 (d, $J_{\text{CF}} = 25$ Hz), 123.8, 127.0, 127.1, 127.2, 128.3, 128.8 (d, $J_{\text{CF}} = 2$ Hz), 129.0, 130.0 (d, $J_{\text{CF}} = 4$ Hz), 132.5, 134.8, 139.5 (d, $J_{\text{CF}} = 2$ Hz), 141.4 (d, $J_{\text{CF}} = 7$ Hz), 158.1 (d, $J_{\text{CF}} = 267$ Hz), 195.1. IR (KBr): 3060, 2960, 2930, 1640, 1600, 1510, 1450, 1320, 1275, 1140, 820, 720 cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{FO}$: C, 83.52; H, 5.42%. Found: C, 83.70; H, 5.65%.

3-Cyclohexanecarbonyl-4-fluoro-1-methyl-1,2-dihydronaphthalene (2e)

Compound **2e** was prepared by the method described for **2a** in 70% yield. ^1H NMR (500 MHz, CDCl_3): δ 1.05–1.55 (6H, m), 1.25 (3H, d, $J = 6.9$ Hz), 1.55–2.07 (4H, m), 2.47 (1H, ddd, $J = 16.2$, 6.9 Hz, $J_{\text{HF}} = 5.3$ Hz), 2.76 (1H, ddd, $J = 16.2$, 6.9 Hz, $J_{\text{HF}} = 5.3$ Hz), 2.97 (1H, ddq, $J = 6.9$, 6.9, 6.9 Hz), 3.05–3.25 (1H, m), 7.24 (1H, dd, $J = 7.9$, 1.2 Hz), 7.29 (1H, ddd, $J = 7.9$, 7.9, 1.2 Hz), 7.38 (1H, ddd, $J = 7.9$, 7.9, 1.2 Hz), 7.59 (1H, dd, $J = 7.9$, 1.2 Hz). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 49.9 (br. s). ^{13}C NMR (126 MHz, CDCl_3): δ 19.5, 26.0, 26.1, 29.2 (d, $J_{\text{CF}} = 4$ Hz), 30.1 (d, $J_{\text{CF}} = 4$ Hz), 31.6, 50.4 (d, $J_{\text{CF}} = 9$ Hz), 112.9 (d, $J_{\text{CF}} = 6$ Hz), 123.3 (d, $J_{\text{CF}} = 7$ Hz), 126.1 (d, $J_{\text{CF}} = 4$ Hz), 126.6, 127.4 (d, $J_{\text{CF}} = 26$ Hz), 130.9, 144.1 (d, $J_{\text{CF}} = 7$ Hz), 159.7 (d, $J_{\text{CF}} = 271$ Hz), 203.1 (d, $J_{\text{CF}} = 4$ Hz). IR (NaCl, neat): 2950, 2875, 1635, 1600, 1580, 1455, 1380, 1340, 1175, 1065, 770 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{FO}$: C, 79.38; H, 7.77%. Found: C, 79.13; H, 7.85%.

5-Benzoyl-6-fluoro-2,3,3a,4-tetrahydrophenalene (2f)

Compound **2f** was prepared by the method described for **2a** in 84% yield. ^1H NMR (500 MHz, CDCl_3): δ 1.53 (1H, dddd, $J = 13.4$, 13.4, 2.4, 0.7 Hz), 1.69–1.81 (1H, m), 2.04–2.11 (1H, m), 2.12–2.18 (1H, m), 2.47 (1H, ddd, $J = 15.9$, 15.9 Hz, $J_{\text{HF}} = 5.5$ Hz), 2.77 (1H, ddd, $J = 15.9$, 5.5 Hz, $J_{\text{HF}} = 5.5$ Hz), 2.82–2.85 (2H, m), 2.97–3.05 (1H, m), 7.13–7.21 (2H, m), 7.32 (1H, dd, $J = 7.3$, 1.8 Hz), 7.46 (2H, dd, $J = 7.5$, 7.5 Hz), 7.56 (1H, tt, $J = 7.5$, 1.2 Hz), 7.85 (2H, dd, $J = 7.5$, 1.2 Hz). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 52.8 (br. s). ^{13}C NMR (126 MHz, CDCl_3): δ 22.6, 28.9, 29.4, 31.7 (d, $J_{\text{CF}} = 3$ Hz), 34.1, 114.3 (d, $J_{\text{CF}} = 6$ Hz), 120.7 (d, $J_{\text{CF}} = 6$ Hz), 126.3, 127.4 (d, $J_{\text{CF}} = 25$ Hz), 128.3, 128.8 (d, $J_{\text{CF}} = 3$ Hz), 131.5, 132.5, 136.3 (d, $J_{\text{CF}} = 3$ Hz), 137.3 (d, $J_{\text{CF}} = 7$ Hz), 139.2 (d, $J_{\text{CF}} = 2$ Hz), 158.4 (d, $J_{\text{CF}} = 268$ Hz), 195.1. IR (NaCl, neat): 3075, 2950, 2875, 1635, 1600, 1470, 1365, 1330, 1140, 1065, 720 cm^{-1} . HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{FO}$ 292.1263 (M^+); found 292.1256.

2-Butyl-3,3,3-(2,4-dimethoxyphenyl)-3-fluoro-1-phenylprop-2-en-1-one (4),

2-Butyl-3,3-bis(2,4-dimethoxyphenyl)-1-phenylprop-2-en-1-one (5)

$\text{BF}_3 \cdot \text{OEt}_2$ (85 mg, 0.60 mmol) was added to a solution of 2-butyl-3,3-difluoro-1-phenyl-prop-2-en-1-one (**3**, 122 mg, 0.54 mmol) and *m*-dimethoxybenzene (83 mg, 0.599 mmol) in CH_2Cl_2 (3.0 ml) at 0 °C under nitrogen. After the reaction mixture was stirred for 1.5 h, phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane– Et_2O 10:1) to give **4** (135 mg, 72%, *E:Z* = 75:25) and **5** (14

mg, 5%).

4 (E-isomer): ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{CO}$): δ 0.91 (3H, t, $J = 7.3$ Hz), 1.36–1.54 (4H, m), 2.61 (2H, td, $J = 7.5$ Hz, $J_{\text{HF}} = 2.8$ Hz), 3.68 (3H, s), 3.68 (3H, s), 6.24 (1H, d, $J = 1.6$ Hz), 6.33 (1H, dd, $J = 8.5$, 1.6 Hz), 7.04 (1H, d, $J = 8.5$ Hz), 7.24 (2H, dd, $J = 7.8$, 7.8 Hz), 7.35 (1H, tt, $J = 7.8$, 1.4 Hz), 7.66 (2H, dd, $J = 7.8$, 1.4 Hz). ^{19}F NMR (470 MHz, $(\text{CD}_3)_2\text{CO}$): δ_{F} 74.0 (s). ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{CO}$): δ 14.1, 23.3, 28.1 (d, $J_{\text{CF}} = 4$ Hz), 31.5 (d, $J_{\text{CF}} = 2$ Hz), 55.5, 55.7, 98.8, 105.4, 115.1 (d, $J_{\text{CF}} = 29$ Hz), 122.3 (d, $J_{\text{CF}} = 23$ Hz), 128.6, 129.6, 132.9, 133.0, 139.0, 159.5, 160.1 (d, $J_{\text{CF}} = 262$ Hz), 163.8, 196.8 (d, $J_{\text{CF}} = 11$ Hz). IR (NaCl, neat): 2975, 2880, 1650, 1610, 1580, 1510, 1470, 1330, 1220, 1170, 1040, 940, 840, 700 cm^{-1} . MS (70 eV) m/z 342 (M^+), 342 (base peak), 311.

4 (Z-isomer): ^1H NMR (270 MHz, CDCl_3): δ 0.91 (3H, t, $J = 7.3$ Hz), 1.21–1.56 (4H, m), 2.66 (2H, td, $J = 7.3$ Hz, $J_{\text{HF}} = 2.6$ Hz), 3.62 (3H, s), 3.65 (3H, s), 6.07 (1H, d, $J = 2.1$ Hz), 6.33 (1H, dd, $J = 8.5$, 2.1 Hz), 7.07 (1H, d, $J = 8.5$ Hz), 7.17 (2H, dd, $J = 7.5$, 7.5 Hz), 7.29 (1H, t, $J = 7.5$ Hz), 7.68 (2H, d, $J = 7.5$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 71.8 (s). ^{13}C NMR (126 MHz, CDCl_3): δ 13.9, 23.0, 30.1, 32.8, 54.9, 55.3, 98.1, 104.0, 114.6 (d, $J_{\text{CF}} = 28$ Hz), 121.9 (d, $J_{\text{CF}} = 20$ Hz), 127.7, 128.9, 132.1, 132.2, 138.0 (d, $J_{\text{CF}} = 3$ Hz), 158.2, 159.1 (d, $J_{\text{CF}} = 263$ Hz), 162.5, 197.3 (d, $J_{\text{CF}} = 11$ Hz). IR (NaCl, neat): 2975, 2880, 1650, 1610, 1580, 1510, 1470, 1330, 1220, 1170, 1040, 940, 840, 700 cm^{-1} . MS (70 eV) m/z 342 (M^+), 342 (base peak), 311.

5: ^1H NMR (500 MHz, CDCl_3): δ 0.76 (3H, t, $J = 7.3$ Hz), 1.25 (2H, tq, $J = 7.3$, 7.3 Hz), 1.69 (2H, tt, $J = 7.3$, 7.3 Hz), 2.71 (2H, t, $J = 7.3$ Hz), 3.11 (3H, s), 3.13 (3H, s), 3.35 (3H, s), 3.38 (3H, s), 5.98 (1H, d, $J = 2.2$ Hz), 6.11 (1H, dd, $J = 8.4$, 2.2 Hz), 6.41 (1H, dd, $J = 8.4$, 2.2 Hz), 6.50 (1H, d, $J = 2.2$ Hz), 6.98–7.06 (3H, m), 7.30 (1H, d, $J = 8.4$ Hz), 7.36 (1H, d, $J = 8.4$ Hz), 8.25 (2H, dd, $J = 7.9$, 1.8 Hz). ^{13}C NMR (126 MHz, CDCl_3): δ 13.9, 23.0, 30.1, 32.8, 54.9, 55.1, 55.3, 55.5, 98.3, 98.4, 103.4, 103.9, 123.0, 124.0, 127.5, 128.9, 131.0, 131.8, 132.5, 136.8, 138.4, 141.3, 157.5, 157.6, 160.0, 160.3, 201.1. IR (NaCl, neat): 2950, 2880, 1740, 1660, 1610, 1585, 1505, 1420, 1215, 1160, 1040, 940, 835, 700 cm^{-1} . MS (70 eV) m/z 460 (M^+), 460 (base peak), 429, 105, 77.

(E)-3-Fluoro-1-phenyl-2-(2-phenylpropyl)prop-2-en-1-one (6)

Sodium borohydride (22 mg, 0.59 mmol) was added to a solution of 3,3-difluoro-2-(2-phenylpropyl)-1-phenylpropan-1-one (**1a**, 305 mg, 1.07 mmol) in THF–HMPA (10:1) 6 mL at -78 $^{\circ}\text{C}$ under nitrogen. After the reaction mixture was stirred for 1 h, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with water, and then dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 10:1) to give **6** (182 mg, 64 %) as a colorless liquid. ^1H NMR (500 MHz, CDCl_3): δ 1.31 (3H, d, $J = 7.3$ Hz), 2.71–2.89 (2H, m), 3.01 (1H, qdd, $J = 7.3$, 7.3, 7.3 Hz), 7.14–7.19 (2H, m), 7.22–7.28 (4H, m), 7.42 (2H, dd, $J = 7.3$, 1.5 Hz), 7.47 (2H, dd, $J = 7.3$, 1.5 Hz), 7.54 (1H, tt, $J = 7.3$, 1.5 Hz). ^{19}F NMR (470 MHz, CDCl_3): δ_{F} 50.9 (d, $J = 82$ Hz). ^{13}C NMR (126 MHz, CDCl_3): δ 22.2, 32.6 (d, $J_{\text{CF}} = 2$ Hz), 39.2 (d, $J_{\text{CF}} = 2$ Hz), 126.1 (d, $J_{\text{CF}} = 4$ Hz), 127.1, 127.8, 129.1, 129.2, 129.8, 132.9, 139.4, 147.1, 161.7 (d, $J_{\text{CF}} = 279$ Hz), 195.3 (d, $J_{\text{CF}} = 17$ Hz). IR (NaCl, neat): 3050, 2990, 1715, 1650, 1605, 1500, 1460, 1330, 1165, 1135, 705 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{FO}$: C, 80.57; H, 6.39%. Found: C, 80.78; H, 6.21%.

1-Phenyl-2-(2-phenylpropyl)prop-2-en-1-one (7)

¹H NMR (500 MHz, CDCl₃): δ 2.77–2.87 (4H, m), 5.58 (1H, s), 5.79 (1H, s), 7.18 (1H, t, *J* = 7.6 Hz), 7.20 (2H, d, *J* = 7.6 Hz), 7.27 (2H, dd, *J* = 7.6, 7.6 Hz), 7.40 (2H, dd, *J* = 7.6, 7.6 Hz), 7.51 (1H, tt, *J* = 7.6, 1.3 Hz), 7.68 (2H, dd, *J* = 7.6, 1.3 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 34.0, 34.4, 126.0, 126.6, 128.2, 128.4, 128.6, 129.5, 132.2, 137.8, 141.3, 147.3, 198.2. IR (NaCl, neat): 3050, 2950, 1660, 1600, 1500, 1455, 1330, 1210, 980, 760, 700 cm⁻¹. Anal. Calcd for C₁₇H₁₆O: C, 86.41; H, 6.82%. Found: C, 86.32; H, 6.92%.

5-Methyl-3-phenyl-4,5-dihydro-1H-benzo[g]indazole (8a)

Hydrazine monohydrate (26 mg, 0.52 mmol) was added to a solution of **2a** (46 mg, 0.17 mmol) in benzene (3 ml) at room temperature under nitrogen. After the mixture was stirred for 14 h at reflux, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine, and dried over Na₂SO₄. After removal of solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 3:1) to give **8a** (41 mg, 92%). ¹H NMR (500 MHz, CDCl₃): δ 1.18 (3H, d, *J* = 7.0 Hz), 2.68 (1H, dd, *J* = 15.0, 6.2 Hz), 3.00 (1H, dd, *J* = 15.0, 6.2 Hz), 3.05 (1H, qdd, *J* = 7.0, 6.2, 6.2 Hz), 7.08 (1H, dd, *J* = 7.6, 7.6 Hz), 7.20 (1H, t, *J* = 7.6, 7.6 Hz), 7.22–7.32 (4H, m), 7.53 (2H, d, *J* = 7.6 Hz), 7.68 (1H, d, *J* = 7.6 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 21.2, 27.7, 34.1, 112.1, 122.3, 126.6, 126.7, 127.0, 127.7, 127.8, 127.9, 128.7, 131.1, 141.3, 142.1, 146.3. IR (KBr): 3100, 2950, 1470, 1440, 1260, 1150, 1080, 980, 750, 700 cm⁻¹. HRMS calcd for C₁₈H₁₆N₂ 260.1313 (M⁺); found 260.1289.

1,5-Dimethyl-3-phenyl-4,5-dihydro-1H-benzo[g]indazole (8b)

Methylhydrazine (23 mg, 0.49 mmol) was added to a solution of **2a** (65 mg, 0.25 mmol) in benzene (3 ml) at room temperature under nitrogen. After the mixture was stirred for 19 h at room temperature, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine, and dried over Na₂SO₄. After removal of solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 7:1) to give **8b** (62 mg, 93%). ¹H NMR (500 MHz, CDCl₃): δ 1.24 (3H, d, *J* = 6.7 Hz), 2.72 (1H, dd, *J* = 14.9, 6.1 Hz), 3.03 (1H, dd, *J* = 14.9, 6.1 Hz), 3.07 (1H, qdd, *J* = 6.7, 6.1, 6.1 Hz), 4.21 (3H, s), 7.24–7.38 (4H, m), 7.43 (2H, dd, *J* = 7.6, 7.6 Hz), 7.60 (1H, dd, *J* = 7.6, 0.9 Hz), 7.71 (2H, d, *J* = 7.6 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 20.4, 28.2, 35.0, 39.5, 114.4, 122.4, 126.6, 126.7, 127.1, 127.3, 127.6, 127.7, 128.5, 133.8, 138.5, 142.3, 146.9. IR (KBr): 3050, 2950, 1600, 1520, 1470, 1360, 1310, 770, 700 cm⁻¹. MS (70 eV) *m/z* 274 (M⁺), 274 (base peak), 259, 170, 156, 77.

5-Methyl-1,3-diphenyl-4,5-dihydro-1H-benzo[g]indazole (8c)

Butyllithium (0.29 ml, 1.57 M in hexane, 0.46 mmol) was added to a solution of phenylhydrazine (50 mg, 0.46 mmol) in THF (3 ml) at –78 °C under nitrogen. After being stirred for 10 min, the mixture was added to a solution of **2a** (61 mg, 0.23 mmol) in THF (0.5 ml) at –78 °C. The reaction mixture was stirred for 2 h at room temperature, and phosphate buffer (pH 7) was then

added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine, and then dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 7:1) to give **8c** (63 mg, 81%). ¹H NMR (500 MHz, CDCl₃): δ 1.36 (3H, d, *J* = 7.0 Hz), 2.78 (1H, dd, *J* = 15.3, 7.0 Hz), 3.10 (1H, dd, *J* = 15.3, 6.5 Hz), 3.16 (1H, qdd, *J* = 7.0, 7.0, 6.5 Hz), 6.85 (1H, dd, *J* = 7.6, 1.2 Hz), 7.00 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.19 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.33 (1H, d, *J* = 7.6 Hz), 7.35 (1H, tt, *J* = 6.7, 1.2 Hz), 7.38–7.51 (5H, m), 7.57 (2H, dd, *J* = 7.6, 1.2 Hz), 7.78 (2H, dd, *J* = 7.6, 1.2 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 20.3, 28.5, 34.8, 116.1, 123.4, 125.9, 126.1, 126.2, 127.1, 127.4, 127.6, 127.7, 128.2, 128.5, 129.3, 133.5, 138.4, 140.9, 141.9, 149.2. IR (KBr): 3050, 2925, 1590, 1505, 1470, 1370, 1275, 1195, 1070, 765, 700 cm⁻¹. MS (70 eV) *m/z* 336 (M⁺), 336 (base peak), 321, 214, 132, 77. Crystal data: C₂₄H₂₀N₂, *M* = 336.44, monoclinic, *a* = 8.314(2), *b* = 20.024(1), *c* = 10.969(1) Å, *U* = 1782.8(4) Å³, *T* = 293.1 K, space group *P*2₁/*a*, *Z* = 4, *μ*(CuKα) = 5.65 cm⁻¹, 2957 reflections measured, 2858 unique (*R*_{int} = 0.021) which were used in all calculations. The final *wR*(*F*²) was 0.0310 (all data). The largest residual electron density hole was –0.13 e.Å⁻³.

2,6-Dimethyl-4-phenyl-5,6-dihydrobenzo[*h*]quinazoline (9a)

Sodium hydride (17 mg, 62% dispersion in mineral oil, 0.45 mmol) was added to a solution of acetamidine monohydrochloride (43 mg, 0.45 mmol) in THF (3.0 ml) under nitrogen. After the mixture was stirred for 6 h at room temperature, the solvent was evaporated under reduced pressure. A solution of **2a** (60 mg, 0.23 mmol) in benzene (3.0 ml) was added. The mixture was heated at reflux for 17 h, and phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine, and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 7:1) to give **9a** (60 mg, 93%). ¹H NMR (500 MHz, CDCl₃): δ 1.19 (3H, d, *J* = 6.7 Hz), 2.81 (1H, dd, *J* = 15.0, 6.1 Hz), 2.82 (3H, s), 2.97–3.11 (2H, m), 7.28 (1H, dd, *J* = 7.5, 1.4 Hz), 7.36–7.52 (5H, m), 7.58 (2H, dd, *J* = 7.9, 1.5 Hz), 8.43 (1H, dd, *J* = 7.5, 1.4 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 20.0, 26.2, 31.9, 32.0, 121.2, 126.0, 126.2, 127.1, 128.4, 128.9, 129.0, 131.1, 132.2, 138.1, 144.0, 159.7, 164.8, 165.7. IR (KBr): 3075, 2950, 1600, 1580, 1540, 1400, 1380, 1220, 1160, 1020, 760, 710 cm⁻¹. HRMS calcd for C₂₀H₁₈N₂ 286.1470 (M⁺); found 286.1452.

6-Methyl-2,4-diphenyl-5,6-dihydrobenzo[*h*]quinazoline (9b)

Sodium hydride (18 mg, 62% dispersion in mineral oil, 0.47 mmol) was added to a solution of benzamidine monohydrochloride (73 mg, 0.47 mmol) in THF (3.0 ml) under nitrogen. After the mixture was stirred for 6 h at room temperature, the solvent was evaporated under reduced pressure. A solution of **2a** (62 mg, 0.23 mmol) in benzene (3.0 ml) was added. The mixture was heated at reflux for 16 h, and phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with AcOEt three times. The combined extracts were washed with brine, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 7:1) to give **9b** (76 mg, 93%). ¹H NMR (500 MHz,

CDCl₃): δ 1.22 (3H, d, J = 7.0 Hz), 2.92 (1H, dd, J = 15.6, 7.0 Hz), 3.08 (1H, qdd, J = 7.0, 7.0, 6.5 Hz), 3.17 (1H, dd, J = 15.6, 6.5 Hz), 7.31 (1H, d, J = 6.9 Hz), 7.42–7.56 (8H, m), 7.73 (2H, dd, J = 6.9, 1.5 Hz), 8.63 (1H, d, J = 6.9 Hz), 8.66 (2H, dd, J = 6.9, 1.5 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 20.1, 32.1, 32.3, 122.3, 126.2, 126.2, 127.1, 128.1, 128.3, 128.4, 129.2, 129.2, 130.2, 131.1, 132.5, 138.2, 138.4, 144.0, 159.8, 162.1, 164.8. IR (KBr): 3060, 2960, 1605, 1580, 1540, 1400, 1380, 1200, 1030, 760, 700 cm⁻¹. HRMS calcd for C₂₅H₂₀N₂ 348.1627 (M⁺); found 348.1634.

(E)-16-Butylidene-11-methyl-11,12,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (10a)

TMSOTf (0.219 ml, 1.13 mmol) was added to a solution of **1** (R⁶ = H, R⁷ = *n*-Pr, R⁸ = H; 129 mg, 0.38 mmol) in HFIP (3.0 ml) at room temperature under nitrogen. After being stirred for 5 min, the mixture was heated at reflux for 2 h. Phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with CH₂Cl₂ three times. The combined extracts were washed with water, and then dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 4:1) to give **10a** (76 mg, 67%). ¹H NMR (500 MHz, CDCl₃): δ 1.01 (3H, t, J = 7.3 Hz), 1.16 (3H, d, J = 7.0 Hz), 1.59 (2H, qt, J = 7.3, 7.3 Hz), 2.31 (2H, td, J = 7.3, 7.3 Hz), 2.69 (1H, ddd, J = 17.1, 7.6, 3.7 Hz), 2.80 (1H, d, J = 17.1 Hz), 3.42 (1H, d, J = 20.1 Hz), 3.63 (1H, dd, J = 20.1, 3.7 Hz), 3.98 (1H, dq, J = 7.6, 7.0 Hz), 6.71 (1H, t, J = 7.3 Hz), 7.45–7.60 (3H, m), 7.78 (1H, d, J = 7.9 Hz), 7.85 (1H, d, J = 7.9 Hz), 8.14 (1H, d, J = 7.9 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 14.1, 20.9, 22.0, 25.4, 28.1, 29.3, 31.8, 122.0, 124.2, 126.8, 126.9, 127.1, 127.2, 129.0, 130.7, 134.5, 135.1, 136.3, 137.6, 141.3, 158.8, 195.3. IR (NaCl, neat): 2960, 2940, 2870, 1685, 1655, 1630, 1610, 1560, 1510, 1400, 1270, 1180, 820, 750 cm⁻¹. HRMS calcd for C₂₂H₂₂O 302.1671 (M⁺); found 302.1650. The configuration of the exocyclic double bond in **10a** was assigned by ¹H NMR measurement on the basis of the chemical shift of the vinylic proton (δ 6.71).^{4a}

11-methyl-16-(propan-2-ylidene)-11,12,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (10b)

Compound **10b** was prepared by the method described for **10a** in 61% yield. ¹H NMR (500 MHz, CDCl₃): δ 1.15 (3H, d, J = 7.3 Hz), 2.00 (3H, s), 2.41 (3H, s), 2.67 (1H, ddd, J = 17.1, 7.3, 3.6 Hz), 2.76 (1H, d, J = 17.1 Hz), 3.39 (1H, d, J = 20.1 Hz), 3.61 (1H, dd, J = 20.1, 3.6 Hz), 3.97 (1H, dq, J = 7.3, 7.3 Hz), 7.51 (1H, dd, J = 7.9, 7.9 Hz), 7.54 (1H, d, J = 7.9 Hz), 7.56 (1H, dd, J = 7.9, 7.9 Hz), 7.77 (1H, d, J = 7.9 Hz), 7.85 (1H, d, J = 7.9 Hz), 8.14 (1H, d, J = 7.9 Hz). ¹³C NMR (126 MHz, CDCl₃): δ 19.9, 20.9, 24.2, 25.4, 28.1, 31.4, 121.9, 124.1, 126.6, 126.8, 127.1, 127.2, 129.0, 130.3, 130.8, 134.9, 138.9, 140.8, 145.2, 155.6, 196.0. IR (NaCl, neat): 2970, 2930, 1670, 1630, 1560, 1510, 1400, 1380, 1180, 1100, 980, 750 cm⁻¹. HRMS calcd for C₂₁H₂₀O 288.1514 (M⁺); found 288.1484.

(5*R,S*,11*aSR*)-5-Methyl-5,6,9,10,11,11*a*-hexahydroindeno[1,2-*a*]phenanthren-7-one (10c)

Compound **10c** was prepared by the method described for **10a** in 60% yield (single diastereomer). ¹H NMR (500 MHz, CDCl₃): δ 1.13 (3H, d, J = 7.3 Hz), 1.47 (1H, ddd, J = 11.9, 11.9, 3.1 Hz), 1.81–1.93 (1H, m), 2.10–2.18 (1H, m), 2.27–2.38 (1H, m), 2.44–2.53 (1H, m), 2.66 (1H, ddd, J =

17.3, 7.3, 3.7 Hz), 2.82 (1H, d, $J = 17.3$ Hz), 2.87–2.94 (1H, m), 3.43–3.51 (1H, m), 3.98 (1H, dq, $J = 7.3, 7.3$ Hz), 6.79 (1H, s), 7.52 (1H, dd, $J = 8.1, 8.1$ Hz), 7.56 (1H, dd, $J = 8.1, 8.1$ Hz), 7.75 (1H, d, $J = 8.1$ Hz), 7.84 (1H, d, $J = 8.1$ Hz), 7.88 (1H, d, $J = 8.1$ Hz), 8.15 (1H, d, $J = 8.1$ Hz). ^{13}C NMR (126 MHz, CDCl_3): δ 20.8, 23.4, 24.9, 25.2, 28.3, 28.7, 41.5, 123.3, 124.4, 126.8, 126.8, 126.9, 128.3, 128.8, 130.8, 131.7, 134.7, 137.9, 141.5, 141.9, 160.5, 193.8. IR (neat): 2958, 2925, 2863, 1678, 1602, 1396, 1315, 1261, 908, 817, 728 cm^{-1} . MS (70 eV) m/z 300 (M^+), 300 (base peak), 285. HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{21}\text{O}$ 301.1593 ($[\text{M} + \text{H}]^+$); found 301.1586.

16-Hydroxy-11,16-dimethyl-11,12,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (11a)

Compound **11a** was prepared by the method described for **10a** in 25% yield [15:1 diastereomer ratio determined by ^{13}C NMR measurement (peak heights)]. Major diastereomer: ^1H NMR (500 MHz, CDCl_3): δ 1.17 (3H, d, $J = 7.3$ Hz), 1.50 (3H, s), 2.62–2.74 (1H, m), 2.75–2.90 (1H, m), 3.03 (1H, ddd, $J = 17.4, 2.4, 2.4$ Hz), 3.23 (1H, dd, $J = 17.4, 3.7$ Hz), 3.98 (1H, qdd, $J = 7.3, 7.0, 2.1$ Hz), 7.47 (1H, d, $J = 8.2$ Hz), 7.52–7.60 (2H, m), 7.78 (1H, d, $J = 8.2$ Hz), 7.86 (1H, d, $J = 8.2$ Hz), 8.14 (1H, d, $J = 8.2$ Hz). ^{13}C NMR (126 MHz, CDCl_3): δ 20.6, 25.3, 26.3, 28.0, 41.7, 76.4, 122.0, 124.2, 126.9, 127.0, 127.2, 127.4, 129.1, 130.5, 130.8, 135.4, 142.0, 163.2, 209.1. IR (NaCl, neat): 3350, 2950, 1680, 1630, 1560, 1470, 1410, 1220, 1140, 955, 815, 740 cm^{-1} . HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ 278.1307 (M^+); found 278.1310.

16-Methoxy-11,16-dimethyl-11,12,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (11b)

TMSOTf (0.206 ml, 1.07 mmol) was added to a solution of **1** ($\text{R}^6 = \text{R}^7 = \text{R}^8 = \text{H}$; 107 mg, 0.36 mmol) in HFIP (3.0 ml) at room temperature under nitrogen. After being stirred for 5 min, the reaction mixture was treated with trimethoxyborane (44.5 μl , 0.39 mmol). The mixture was stirred at reflux for 3 h, and phosphate buffer (pH 7) was then added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with water, and then dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt 4:1) to give **11b** (72 mg, 69 %, 11:1 diastereomer ratio determined by ^1H NMR measurement). Major diastereomer: ^1H NMR (500 MHz, CDCl_3): δ 1.15 (3H, d, $J = 7.3$ Hz), 1.49 (3H, s), 2.66–2.74 (2H, m), 2.86 (1H, ddd, $J = 17.7, 2.4, 2.4$ Hz), 3.28–3.35 (1H, m), 3.32 (3H, s), 3.92–4.04 (1H, m), 7.51 (1H, d, $J = 8.0$ Hz), 7.53–7.62 (2H, m), 7.80 (1H, d, $J = 8.0$ Hz), 7.87 (1H, d, $J = 8.0$ Hz), 8.15 (1H, d, $J = 8.0$ Hz). ^{13}C NMR (126 MHz, CDCl_3): δ 20.7, 23.5, 24.9, 28.0, 37.7, 52.0, 81.3, 121.9, 124.3, 127.0, 127.0, 127.2, 127.4, 129.1, 130.6, 132.6, 135.4, 141.9, 162.5, 207.0. IR (KBr): 2960, 2940, 1680, 1620, 1560, 1470, 1400, 1360, 1320, 1260, 1100, 840, 760 cm^{-1} . MS (70 eV) m/z 292 (M^+), 292 (base peak), 277, 261, 165. HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2$ 293.1542 ($[\text{M} + \text{H}]^+$); found 293.1534.

4H SINGL NON

4 (E)

26-MAR-1994 11:42:29.63
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 IRNS : 0
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 CSPED : 12 Hz
 FIELD : -9897

DFILE 5MI006801

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EXMOD NON

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POINT 32768

FREQU 5405.4 Hz

SCANS 16

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SLVNT CDCL3

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RGAIN 11

OPERATOR :

4 (Z)

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5

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 SAMPO : 32768
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 SCANS : 8
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 IRSET : 162410.00 Hz
 IRPW : 50.0 usec
 IRATN : 511
 IRNS : 0
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 IRBP2 : 6
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 XS : 289.76 Hz
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 LKLEV : 180
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 LKPHS : 260.15 deg
 LKSIG : 1042
 CTEMP : 24.6 C
 CSPED : 12 Hz
 FIELD : -9897

19-JAN-1996 14:28:12.54
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 DUMMY : 4
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 OBFRQ : 500.00 MHz
 OBSET : 162410.00 Hz
 IRNUC : 1H
 IRFRQ : 500.00 MHz
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16-DEC-1995 22:17:06.41

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IRMOD : NDN
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SCANS : 8
DUMMY : 4
ACQTM : 3.2768 sec
PD : 3.7232 sec
RGAIN : 14
PW1 : 6.25 usec

OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz

IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 28
IRBP2 : 6
IRRNS : 0

ADBIT : 16
CTEMP : 24.9 C
CSPED : 14 Hz
SLVNT : CDCL3

RESOL : 0.31 Hz
BF : 0.15 Hz
T1 : 0.00 %
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T4 : 100.00 %
REFVL : 0.00 ppm
XE : 4400.94 Hz
XS : 476.53 Hz
operator

7-JUN-1995 17:14:35.79

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EXMOD : SINGL

IRMOD : NON

POINT : 32768

FREQ : 10000.00 Hz

SCANS : 32

DUMMY : 4

ACGTM : 3.2768 sec

PD : 3.7232 sec

RGAIN : 13

PW1 : 6.25 usec

DENUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz

IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 511
IRBPW : 50.0 usec
IRBP1 : 28
IRBP2 : 6
IRBNS : 0

ADBIT : 16
CTEMP : 25.6 C
CSPED : 14 Hz
SLVNT : CDCL3

RESOL : 0.31 Hz
BF : 0.15 Hz
T1 : 0.00 %
T2 : 0.00 %
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XE : 5001.22 Hz
XS : 73.85 Hz
operator

1H SINGL

26-JAN-1996 14:27:41.62

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COMNT : 1H SINGL NON 2MK80

EXMOD : SINGL

IRMOD : NON

POINT : 32768

FREQ : 10000.00 Hz

SCANS : 32

DUMMY : 4

ACGTM : 3.2768 sec

PD : 3.7232 sec

RGAIN : 14

PW1 : 6.25 usec

OBNUC : 1H

OBFRQ : 500.00 MHz

OBSET : 162410.00 Hz

IRNUC : 1H

IRFRQ : 500.00 MHz

IRSET : 162410.00 Hz

IRATN : 511

IRRPW : 50.0 usec

IRBP1 : 28

IRBP2 : 6

IRRNS : 0

ADBIT : 15

CTEMP : 24.0 C

CSPED : 13 Hz

SLVNT : CDCL3

RESOL : 0.31 Hz

BF : 0.15 Hz

T1 : 0.00 %

T2 : 0.00 %

T3 : 90.00 %

T4 : 100.00 %

REFVL : 0.00 ppm

XE : 5001.22 Hz

XS : 85.45 Hz

operator

9a

1H SINGL NON

24-JAN-1996 16:28:58.75
DFILE : ALPHA
SFIL : 2MK8041NON_E4S4
COMNT : 1H SINGL NON 2MK8
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQ : 10000.00 Hz
SCANS : 32
DUMMY : 4
ACQTM : 3.2768 sec
PD : 3.7232 sec
RGAIN : 16
PW1 : 6.25 usec

9b

OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 28
IRBP2 : 6
IRRNS : 0
ADBIT : 15
CTEMP : 23.9 c
CSPED : 13 Hz
SLVNT : CDCL3
RESOL : 0.31 Hz
BF : 0.15 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 5001.22 Hz
XS : 80.26 Hz
operator

25-JAN-1996 16:04:49.37
 DFILE : ALPHA
 SFIL : 2MK802B1NDN_E3S3
 COMNT : 1H SINGL NON 2MK80
 EXMOD : SINGL
 IRMOD : NON
 POINT : 32768
 FREQU : 10000.00 Hz
 SCANS : 32
 DUMMY : 4
 ACQTM : 3.2768 sec
 PD : 3.7232 sec
 RGAIN : 15
 PW1 : 6.25 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162410.00 Hz
 IRNUC : 1H
 IRFRQ : 500.00 MHz
 IRSET : 162410.00 Hz
 IRATN : 511
 IRPW : 50.0 usec
 IRBP1 : 28
 IRBP2 : 6
 IRBNS : 0
 AD8IT : 16
 CTEMP : 24.2 C
 CSPED : 14 Hz
 SLVNT : CDCL3
 RESOL : 0.31 Hz
 BF : 0.15 Hz
 T1 : 0.00 %
 T2 : 0.00 %
 T3 : 90.00 %
 T4 : 100.00 %
 REFVL : 0.00 ppm
 XE : 5001.22 Hz
 XS : 88.50 Hz
 operator

1H SINGL NON

3-DEC-1995 18:06:57.53
DFILE : ALPHA
SFIL : [J]MK75181NON_E2
COMNT : 1H SINGL NON [J]
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQ : 10000.00 Hz
SCANS : 8
DUMMY : 4
ACQTM : 3.2768 sec
PD : 3.7232 sec
RGAIN : 17
PW1 : 6.25 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 28
IRBP2 : 6
IRBNS : 0
ADBIT : 16
CTEMP : 24.8 C
CSPED : 14 Hz
SLVNT : CDCL3
RESOL : 0.31 Hz
BF : 0.15 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 4501.04 Hz
XS : 439.30 Hz
operator

10b

1H SINGL NON

3-DEC-1995 17:24:37.48

DFILE : ALPHA

SFILE : [J]MK72481NON_E1

COMNT : 1H SINGL NON [J]

EXMOD : SINGL

IRMOD : NON

POINT : 32768

FREQ : 10000.00 Hz

SCANS : 8

DUMMY : 4

ACQTM : 3.2768 sec

PD : 3.7232 sec

RGAIN : 18

PW1 : 6.25 usec

OBNUC : 1H

OBFRQ : 500.00 MHz

OBSET : 162410.00 Hz

IRNUC : 1H

IRFRQ : 500.00 MHz

IRSET : 162410.00 Hz

IRATN : 511

IRRPW : 50.0 usec

IRBP1 : 28

IRBP2 : 6

IRRNS : 0

ADBIT : 16

CTEMP : 24.9 C

CSPED : 13 Hz

SLVNT : CDCL3

RESOL : 0.31 Hz

BF : 0.15 Hz

T1 : 0.00 %

T2 : 0.00 %

T3 : 90.00 %

T4 : 100.00 %

REFVL : 0.00 ppm

XE : 4501.04 Hz

XS : 440.52 Hz

operator

10c

26-SEP-1995 15:13:48.42

DFILE : ALPHA
SFIL : 2WK675B1NON_E1S1

COMNT : 1H SINGL NON 2MK67
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQ : 10000.00 Hz
SCANS : 16
DUMY : 4
ACQTM : 3.2768 sec
PD : 3.7232 sec
RGAIN : 16

PW1 : 6.25 usec

OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz

IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 28
IRBP2 : 6
IRRNS : 0

ADBIT : 16
CTEMP : 26.1 C
CSPED : 10 Hz
SLVNT : CDCL3

RESOL : 0.31 Hz
BF : 0.15 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 5001.22 Hz
XS : 89.72 Hz
operator

11a

8-SEP-1995 14: 46: 37.61

DFILE : ALPHA

SFILE : 2MK50B1NON_EIS1

COMNT : 1H SINGL NON 2MK6

EXMOD : SINGL

IRMOD : NON

POINT : 32768

FREQ : 10000.00 Hz

SCANS : 16

DUMMY : 4

ACQTM : 3.2768 sec

PD : 3.7232 sec

RGAIN : 17

PW1 : 6.25 usec

OBNUC : 1H

OBFRQ : 500.00 MHz

OBSET : 162410.00 Hz

IRNUC : 1H

IRFRQ : 500.00 MHz

IRSET : 162410.00 Hz

IRATN : 511

IRRPW : 50.0 usec

IRBP1 : 28

IRBP2 : 6

IRRNS : 0

ADBIT : 15

CTEMP : 26.2 c

CSPED : 11 Hz

SLVNT : CDCL3

RESOL : 0.31 Hz

BF : 0.15 Hz

T1 : 0.00 %

T2 : 0.00 %

T3 : 90.00 %

T4 : 100.00 %

REFVL : 0.00 ppm

XE : 5001.22 Hz

XS : 91.25 Hz

operator

11b