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Supporting Information

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Supporting Information

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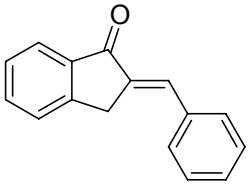
Experimental Section

General Methods

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels though a rubber septum. All of the 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 or *p*-anisaldehyde in ethanol/ 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), ^{1}H-NMR (400 MHz), ^{1}H-NMR (200 MHz), ^{19}F-NMR (188 MHz), ^{19}F-NMR (376 MHz), and ^{13}C-NMR (150.9 MHz), ^{13}C-NMR (100.6 MHz), ^{13}C-NMR (50.3 MHz) spectra for solution in $CDCl_3$ or CD_3OD were recorded on a Buruker Avance 600, a Varian Gemini-400 and a Varian Mercury 200. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or $CHCl_3$ or CH_3OH. HPLC analyses were performed on a JASCO PU-2080 Plus or SHIMADZU LC-2010A HT using 4.6 x 250 mm CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALCEL OD-H or CHIRALCEL OB-H column. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/ IR-200 spectrometer.

Allylsilanes **1a-j**were prepared according to the literature procedures. [1]

(*E*)-2-Benzylideneindan-1-one (6a)

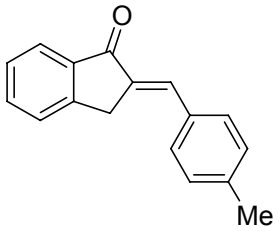


To a solution of benzaldehyde (1.22 ml, 12.0 mmol) in MeOH (30 ml), a solution of NaOMe (prepared by addition of 33 ml of MeOH to 75 mg of Na) was added at room temperature under nitrogen atmosphere. To the mixture, a solution of 1-indanone (1.5g, 11.4 mmol) was added in MeOH (30 ml) dropwise, and the reaction mixture was stirred for 15 h. The reaction mixture was then poured into water (50 ml) and the resulting suspension was acidified by the addition 2N HCl. The product was extracted into CH_2Cl_2. The combined organic layers were washed with brine and then dried over

[1]a) A. Marínez, M. Fernández, J. C. Estèvez, R. J. Estèvez, L. Castedo, *Tetrahedron* **2005**, *61*, 485–492. b) M. T. Reetz, S. H. Kyung, M. Hüllmann, *Tetrahedrone* **1986**, *42*, 2931–2935. c) B. Greely, J.-M. Paris, T. Vidal, V. Gouvernour, *Angew*. *Chem*. *Int*. *Ed*. **2003**, *42*, 3291–3294.

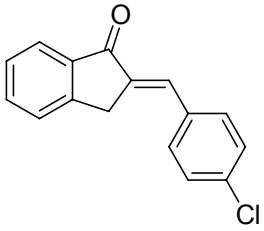
Na_2SO_4. After the removal of solvent, the residue was washed with MeOH. The compound was obtained in 69% yield (1.72 g) as white solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.06 (s, 2H), 7.38-7.69 (m, 9H), 7.91 (d, *J*=7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): 194.0, 149.4, 137.7, 135.1, 134.4, 133.6, 130.5, 129.4, 128.7, 127.4, 126.0, 124.1, 32.2; MS (EI): 220 (M^+), 219 (M^+-1); IR (KBr): 3047, 3021, 2913, 1693, 1623, 1580, 1493, 1464, 1448, 1324, 1295, 1266, 1208, 1185, 1113, 1092, 1072, 1030, 949, 932, 763, 739, 690, 673 cm^{-1}; Mp: 107-109 °C (MeOH)

(*E*)-2-(4-Methylbenzylidene)-indan-1-one (6b)



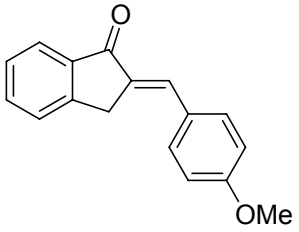
The compound **6b** was prepared by the procedure described above for **6a**. Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.40 (s, 3H), 4.02 (s, 2H), 7.23-7.65 (m, 8H), 7.89 (d, *J*=7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz):193.9, 149.2, 139.8, 137.8, 134.2, 133.7, 133.5, 132.3, 130.5, 129.4, 127.3, 125.9, 124.1, 32.6, 21.6; MS (EI): m/z 234 (M^+), 233 (M^+-1), 219 (M^+-Me); IR (KBr): 3009, 2912, 1690, 1624, 1602, 1581, 1510, 1462, 1328, 1296, 1270, 1200, 1182, 1097, 955, 819, 789, 734, 674 cm^{-1}; Mp: 137-138 °C (MeOH)

(*E*)-2-(4-Chlorobenzylidene)-indan-1-one (6c)



The compound **6c** was prepared by the procedure described above for **6a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.03 (s, 2H), 7.40-7.46 (m, 3H), 7.56-7.62 (m, 5H), 7.90 (d, *J*=7.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 193.5, 149.1, 137.6, 135.4, 134.9, 134.5, 133.6, 132.1, 131.5, 129.0, 127.5, 125.9, 124.2, 32.4; MS (EI): m/z 256 (M^++2), 254 (M^+), 253 (M^+-1), 219 (M^+-Cl); IR (KBr): 2923, 1696, 1625, 1584, 1490, 1468, 1418, 1405, 1327, 1297, 1270, 1205, 1177, 1092, 1008, 954, 820, 784, 729, 670 cm^{-1}; Mp: 179-180 °C (MeOH)

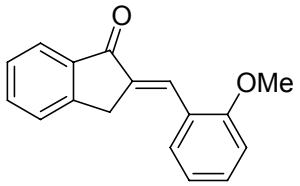
(*E*)-2-(4-Methoxybenzylidene)-indan-1-one (6d)



The compound **6d** was prepared by the procedure described above for **6a**. Pale green solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.83 (s, 3H), 4.02 (s, 2H), 6.94-7.01 (m, 2H), 7.37-7.45 (m, 1H), 7.52-7.65 (m, 5H), 7.89 (d, *J*=7.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz):193.6, 160.3, 149.0, 137.7, 133.9, 133.2, 132.1, 131.9, 127.6, 127.1, 125.7, 123.8, 114.1,

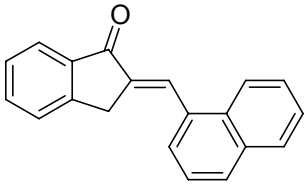
55.2, 32.4; MS (EI): m/z 250 (M^+), 249 (M^+-1), 219 (M^+-OMe); IR (KBr): 2996, 2904, 2841, 1695, 1626, 1603, 1517, 1467, 1313, 1259, 1186, 1100, 1025, 958, 823, 725 cm^{-1}; Mp: 138-139 °C (MeOH)

(*E*)-2-(2-Methoxybenzylidene)-indan-1-one (6f)



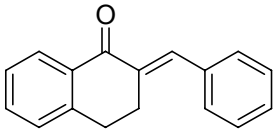
The compound **6f** was prepared by the procedure described above for **6a**. Pale green solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.89 (s, 3H), 4.00 (s, 2H), 6.94 (d, *J*=8.2 Hz, 1H), 7.02 (t, *J*=7.6 Hz, 1H), 7.32-7.44 (m, 2H), 7.49-7.62 (m, 2H), 7.67 (dd, *J*=1.5, 7.7 Hz, 1H), 7.90 (d, *J*=7.6 Hz, 1H), 8.13 (t, *J*=2.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 193.6, 158.5, 149.2, 137.8, 134.1, 133.9, 130.8, 129.2, 128.0, 127.1, 125.7, 124.0, 123.8, 120.1, 110.7, 55.4, 32.3; MS (EI): m/z 250 (M^+), 219 (M^+-OMe); IR (KBr): 2976, 2940, 1707, 1678, 1629, 1600, 1484, 1462, 1325, 1303, 1292, 1253, 1125, 1088, 1021, 957, 749, 741 cm^{-1}; Mp: 132-133 °C (MeOH)

(*E*)-2-Naphthalen-2-ylmethylene-indan-1-one (6e)



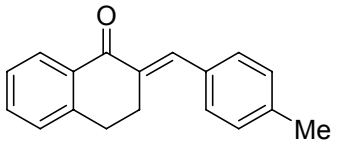
The compound **6e** was prepared by the procedure described above for **6a**. Pale green solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.15 (s, 2H), 7.39-7.66 (m, 5H), 7.74-7.94 (m, 6H), 8.12 (s, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 193.7, 149.3, 137.7, 134.5, 134.3, 133.7, 133.3, 133.0, 132.6, 131.4, 128.3, 128.2, 127.4, 127.1, 126.5, 126.4, 125.9, 124.1, 32.6; MS (EI): m/z 270 (M^+), 269 (M^+-1); IR (KBr): 3045, 1695, 1619, 1471, 1345, 1260, 1097, 973, 819, 735 cm^{-1}; Mp: 182-183 °C (MeOH)

(*E*)-2-Benzylidene-3,4-dihydro-2H-naphthalene-1-one (6i)



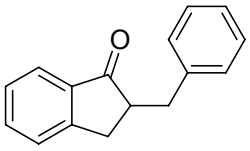
To a solution of α-tetralone (3.0 ml, 22.6 mmol) and KOH (2.53 g, 45.1 mmol) in EtOH (113 ml), benzaldehyde (2.3 ml, 22.6 mmol) was added at room temperature under nitrogen atmosphere and the reaction mixture was stirred for 14 h. The reaction mixture was filtered and washed with MeOH. The compound was obtained in 86% yield (4.52 g) as pale green solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.92-2.98 (m, 2H), 3.09-3.18 (m, 2H), 7.22-7.53 (m, 8H), 7.86 (t, *J*=1.6 Hz, 1H), 8.12 (dd, *J*=1.6, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 187.4, 143.0, 136.4,135.6, 135.2, 133.3, 133.0, 129.6, 128.3, 128.2, 128.0, 128.0, 126.8, 29.1, 27.4; MS (EI): m/z 234 (M^+), 233 (M^+-1); IR (KBr): 2942, 2844, 1661, 1605, 1590, 1492, 1460, 1297, 1247, 1223, 1161, 1141, 1023, 955, 928, 796, 757, 743, 697 cm^{-1}; Mp: 106-107 °C (MeOH)

(*E*)-2-(4-Methylbenzylidene)-3,4-dihydro-2H-naphthalene-1-one (6j)



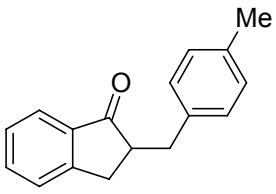
The compound **6j** was prepared by the procedure described above for **6i**. Pale green solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.34 (s, 3H), 2.93 (t, *J*=6.2 Hz, 2H), 3.14 (td, *J*=6.4, 1.4 Hz, 2H), 7.20-7.24 (m, 3H), 7.32-7.38 (m, 3H), 7.47 (td, *J*=7.4, 1.6 Hz, 1H), 7.84 (s, 1H), 8.11 (dd, *J*=1.4, 7.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 187.9, 143.2, 138.8, 136.8, 134.7, 133.6, 133.2, 133.0, 130.0, 129.2, 128.2, 128.1, 127.0, 28.8, 27.2, 21.4; MS (EI): m/z 248 (M^+), 247 (M^+-1), 233 (M^+-Me); IR (KBr): 2923, 2852, 1743, 1661, 1601, 1586, 1508, 1455, 1317, 1297, 1250, 1227, 1137, 948, 817, 741, 704 cm^{-1}; Mp: 123-124 °C (MeOH)

2-Benzylindan-1-one (7a)



Pd/C (10%, 180 mg) was added to a deoxygenated solution of (*E*)-2-benzylideneindan-1-one (**6a)** (1.8 g, 8.18 mmol) in AcOEt (180 ml) and the mixture was stirred under a hydrogen atmosphere (1 atm) at room temperature for 4h. After removal of the excess of hydrogen in vacuo, the mixture was filtered though Celite, which was eluted with MeOH. After the removal of solvent, purification by silica-gel column chromatography (Hexane/Acetone) was carried out to give **7a** in 99% yield (1.80 g) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.67 (dd, *J*=10.5, 14.0 Hz, 1H), 2.86 (dd, *J*=4.0, 17.2 Hz, 1H), 3.01 (dddd, *J*=4.0, 4.3, 7.8, 10.5 Hz, 1H), 3.17 (dd, *J*=7.8, 17.2 Hz, 1H), 3.40 (dd, *J*=4.3, 14.0 Hz, 1H), 7.21-7.26 (m, 4H), 7.29-7.31 (m, 2H), 7.36-7.41 (m, 2H), 7.57 (t, *J*=7.4 Hz, 1H), 7.78 (d, *J*=7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 207.2, 153.3, 139.4, 136.3, 134.5, 128.6, 128.3, 127.2, 126.3, 126.1, 123.8, 49.0, 37.1, 32.3; MS (EI): m/z 222 (M^+); IR (neat): 3061, 3027, 2921, 2853, 1712, 1608, 1496, 1464, 1454, 1433, 1329, 1291, 1151, 1092, 1031, 1002, 777, 743, 701, 608 cm^{-1}

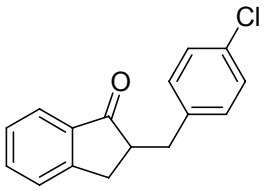
2-(4-Methybenzyl)-indan-1-one (7b)



The compound **7b** was prepared by the procedure described above for **7a**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.32 (s, 3H), 2.63 (dd, *J*=10.5, 14.0 Hz, 1H), 2.85 (dd, *J*=4.0, 17.2 Hz, 1H), 2.97 (dddd, *J*=4.0, 4.3, 7.8, 10.5 Hz, 1H), 3.15 (dd, *J*=7.8, 17.3 Hz, 1H), 3.35 (dd, *J*=4.3, 14.0 Hz, 1H), 7.10 (d, *J*=8.0 Hz, 2H), 7.13 (d, *J*=8.0 Hz, 2H), 7.36 (t, *J*=7.4 Hz, 1H), 7.39 (d, *J*=7.6 Hz, 1H), 7.56 (t, *J*=7.4 Hz, 1H), 7.77 (d, *J*=7.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 207.4, 153.4, 136.3, 136.3, 135.6, 134.5, 129.0, 128.6, 127.2, 126.4, 123.8, 49.1, 36.7, 32.3, 21.2; MS (EI): m/z 280 (M^+); IR (neat): 3020, 2921, 2848, 1712, 1608, 1515, 1464, 1434, 1327, 1273, 1207, 1150, 1092, 1042, 1005, 806, 758,

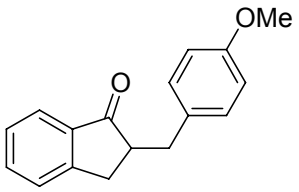
725, 679 cm^{-1}

2-(4-Chlorobenzyl)-indan-1-one (7c)



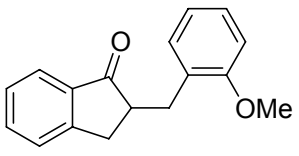
The compound **7c** was prepared by the procedure described above for **7a**. White solid; ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.69 (dd, *J*=10.1, 14.1 Hz, 1H), 2.82 (dd, *J*=4.1, 17.2 Hz, 1H), 2.96 (dddd, *J*=4.1, 4.4, 7.9, 10.1 Hz, 1H), 3.17 (dd, *J*=7.9, 17.2 Hz, 1H), 3.33 (dd, *J*=4.4, 14.1 Hz, 1H), 7.17 (d, *J*=8.3 Hz, 2H), 7.26 (d, *J*=8.3 Hz, 2H), 7.37 (t, *J*=7.4 Hz, 1H), 7.40 (d, *J*=7.7 Hz, 1H), 7.57 (t, *J*=7.4 Hz, 1H), 7.77 (d, *J*=7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 206.9, 153.1, 137.7, 136.2, 134.7, 131.9, 130.0, 128.4 127.3, 126.4, 123.8, 48.8, 36.3, 32.2; MS (EI): m/z 256 (M^++2), 256 (M^+); IR (KBr): 3045, 2930, 2843, 1703, 1606, 1493, 1465, 1429, 1406, 1320, 1290, 1210, 1092, 1015, 870, 797, 760, 725 cm^{-1}; Mp: 70-71 °C (CH_2Cl_2)

2-(4-Methoxybenzyl)-indan-1-one (7d)



The compound **7d** was prepared by the procedure described above for **7a**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.64 (dd, *J*=10.2, 14.1 Hz, 1H), 2.85 (dd, *J*=4.0, 17.2 Hz, 1H), 2.96 (dddd, *J*=4.0, 4.4, 7.8, 10.2 Hz, 1H), 3.16 (dd, *J*=7.8, 17.2 Hz, 1H), 3.31 (dd, *J*=4.4, 14.0 Hz, 1H), 3.78 (s, 3H), 6.83 (d, *J*=8.6 Hz, 2H), 7.15 (d, *J*=8.5 Hz, 2H), 7.36 (t, *J*=7.4 Hz, 1H), 7.39 (d, *J*=7.7 Hz, 1H), 7.56 (t, *J*=7.4 Hz, 1H), 7.77 (d, *J*=7.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 206.8, 157.5, 153.0, 136.0, 134.1, 130.9, 129.3, 126.8, 126.1, 123.3, 113.4, 54.8, 48.8, 35.8, 31.9; MS (EI): m/z 252 (M^+); IR (neat): 2933, 2841, 1712, 1610, 1513, 1464, 1248, 1178, 1035, 814, 760, 729 cm^{-1}

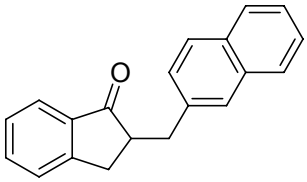
2-(2-Methoxybenzyl)-indan-1-one (7e)



The compound **7e** was prepared by the procedure described above for **7a**. White solid; ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.61-2.66 (m, 1H), 2.83-2.88 (m, 1H), 3.08-3.14 (m, 2H), 3.42 (dd, *J*=4.2, 13.8 Hz, 1H), 3.82 (s, 3H), 6.87 (d, *J*=8.2 Hz, 1H), 6.90 (dt, *J*=1.0, 7.4 Hz, 1H), 7.18 (dd, *J*=1.5, 7.4 Hz, 1H), 7.22 (dt, *J*=1.6, 7.8 Hz, 1H), 7.36 (t, *J*=7.4 Hz, 1H), 7.39 (dd, *J*=0.7, 7.7 Hz, 1H), 7.56 (dt, *J*=1.1, 7.4 Hz, 1H), 7.78 (d, *J*=7.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 207.3, 157.0, 136.1, 134.0, 129.9, 127.5, 127.1, 126.7, 126.1, 123.3, 119.9, 109.9, 54.9, 47.3, 32.1, 31.5; MS (EI): m/z 252

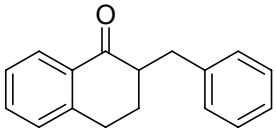
(M^+); IR (KBr): 3045, 2925, 2900, 2832, 1703, 1601, 1492, 1464, 1438, 1290, 1239, 1207, 1178, 1109, 1031, 762, 737 cm^{-1}; Mp: 75-76 °C (CH_2Cl_2)

2-Naphthalen-2-ylmethylene-indanone-1-one (7f)



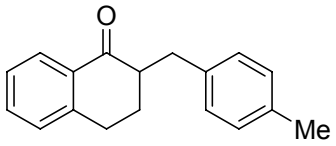
The compound **7f** was prepared by the procedure described above for **7a**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.84 (dd, *J*=10.3, 14.0 Hz, 1H), 2.91 (dd, *J*=3.7, 17.0 Hz, 1H), 2.97 (dddd, *J*=3.7, 4.2, 7.8, 10.3 Hz, 1H), 3.17 (dd, *J*=7.8, 16.9 Hz, 1H), 3.56 (dd, *J*=4.2, 14.0 Hz, 1H), 7.36-7.39 (m, 3H), 7.42-7.48 (m, 2H), 7.56 (t, *J*=7.4 Hz, 1H), 7.67 (s,1H), 7.78-7.82 (m, 4H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 206.4, 152.8, 136.6, 135.8, 134.0, 132.9, 131.5, 127.5, 127.0, 126.9, 126.7, 126.6, 126.5, 125.9, 125.5, 124.8, 123.2, 48.4, 36.7, 31.9; MS (EI): m/z 272 (M^+); IR (neat): 3045, 2918, 2843, 1711, 1606, 1464, 1276, 818, 758 cm^{-1}

2-Benzyl-3,4-dihydro-2*H*-naphthalene-1-one (7i)



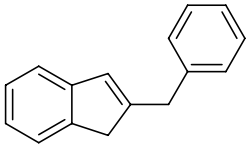
The compound **7i** was prepared by the procedure described above for **7a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.70-1.85 (m, 1H), 2.08 (dq, *J*=13.2, 4.4 Hz, 1H), 2.56-2.80 (m, 2H), 2.86-2.93 (m, 2H), 3.48 (dd, *J*=3.4, 12.8 Hz, 1H), 7.14-7.32 (m, 7H), 7.42 (dd, *J*=7.4, 1.6 Hz, 1H), 8.05 (dd, *J*=1.4, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 198.7, 143.6, 139.7, 132.9, 132.2, 128.9, 128.4, 128.1, 127.2, 126.3, 125.8, 49.4, 35.7, 28.7, 27.8; MS (EI): m/z 236 (M^+); IR (KBr): 3027, 2947, 2911, 2862, 1681, 1597, 1495, 1451, 1284, 1220, 1155, 1029, 926, 777, 745, 702 cm^{-1}; Mp: 50-51 °C (CH_2Cl_2)

2-(4-Methylbenzyl)-3,4-dihydro-2*H*-naphthalene-1-one (7j)



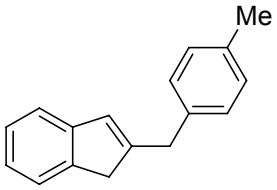
The compound **7j** was was prepared by the procedure described above for **7a**. White solid; ^{1}H-NMR ($CDCl_3$, 600 MHz): 1.74-1.81 (m, 1H), 2.10 (dq, *J*=4.5, 13.3 Hz, 1H), 2.32 (s, 3H), 2.61 (dd, *J*=9.6, 13.9 Hz, 1H), 2.69-2.74 (m, 1H), 2.87- 2.96 (m, 2H), 3.44 (dd, *J*=4.1, 13.9 Hz, 1H), 7.11 (s, 4H), 7.20 (d, *J*=7.6 Hz, 1H), 7.30 (t, *J*=7.5 Hz, 1H), 7.45 (td, *J*=7.4, 1.3 Hz, 1H), 8.06 (d, *J*=7.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 198.9, 143.7, 136.6, 135.3, 133.0, 132.3, 128.9, 128.8, 128.5, 127.3, 126.4, 49.6, 35.3, 28.7, 27.8, 21.2; MS (EI): m/z 250 (M^+); IR (KBr): 3020, 2952, 2920, 1682, 1601, 1514, 1454, 1361, 1302, 1287, 1219, 1107, 998, 935, 805, 761, 603 cm^{-1}; Mp: 76-77 °C (CH_2Cl_2)

2-Benzylindene (8a)



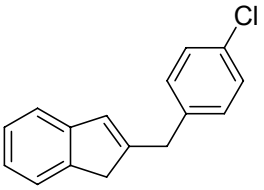
Small portions of $NaBH_4$ (320 mg, 10.5 mmol) were added to a solution of 2-benzylindan-1-one (**7a**) (1.17 g, 5.26 mmol) in MeOH (53 ml) at room temperature. The mixture was stirred for 5 min and poured into water and acetone. The methanol was evaporated in vacuo and the remaining suspension was extracted with CH_2Cl_2. The combined organic layers were dried by Na_2SO_4 and the solvents evaporated under reduced pressure. The resulting solid was mixed with 9M H_2SO_4 (73 ml) and the stirred suspension was heated at 110-120 °C for 30 min. 20% aq NaOH was added to give a basic pH and the suspension was extracted with CH_2Cl_2. The combined organic layers were dried by Na_2SO_4 and the solvents evaporated under reduced pressure. Purification by silica-gel column chromatography (Hexane/ CH_2Cl_2) was carried out to give (**8a)** in 73% yield (790 mg) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.24 (s, 2H), 3.77 (s, 2H), 6.47 (d, *J*=0.8 Hz, 1H), 7.05-7.32 (m, 9H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 148.9, 145.0, 143.1, 139.7, 128.6, 128.2, 127.6, 126.1, 126.0, 123.7, 123.4, 120.0, 40.9, 38.1; MS m/z (EI): 206 (M^+); IR (neat): 3059, 3025, 2900, 2820, 1610, 1493, 1460, 1429, 1391, 1206, 1073, 1029, 907, 789, 751, 716, 699 cm^{-1}

2-(4-Methylbenzyl)-indene (8b)



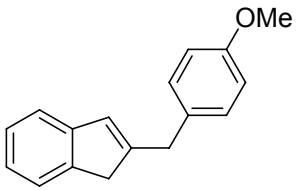
The compound **8b** was prepared by the procedure described above for **8a**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.32 (s, 3H), 3.26 (d, *J*=0.6 Hz, 2H), 3.76 (s, 2H), 6.48 (d, *J*=0.6 Hz, 1H), 7.06-7.33 (m, 8H); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): 149.6, 145.4, 143.4, 136.9, 135.7, 129.1, 128.7, 127.6, 126.2, 123.8, 123.4, 120.1, 40.8, 37.5, 21.0; MS (EI): m/z 220 (M^+); IR (neat): 3047, 3021, 2925, 2888, 2832, 1608, 1515, 1460, 1432, 1389, 1211, 1106, 903, 816, 752, 718 cm^{-1}

2-(4-Chlorobenzyl)-indene (8c)



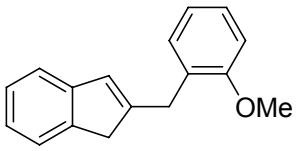
The compound **8c** was prepared by the procedure described above for **8a**. White solid; ^{1}H -NMR ($CDCl_3$, 200 MHz): 3.25 (s, 2H), 3.77 (s, 2H), 6.48 (d, *J*=0.8 Hz, 1H), 7.12-7.35 (m, 8H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 148.3, 144.8, 143.0, 138.2, 131.8, 130.0, 128.4, 127.9, 127.1, 123.8, 123.3, 120.1, 40.9, 37.4; MS (EI): m/z 242, 240 (M^+); IR (neat): 3057, 3017, 2829, 2827, 1612, 1491, 1461, 1389, 1211, 1086, 1015, 910, 822, 784, 752, 717, 661 cm^{-1}; Mp: 58-59 °C (CH_2Cl_2)

2-(4-Methoxybenzyl)-indene (8d)



The compound **8d** was prepared by the procedure described above for **8a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.26 (s, 2H), 3.74 (s, 2H), 3.79 (s, 3H), 6.47 (d, *J*=0.6 Hz, 1H), 6.81-6.87 (m, 2H), 7.03-7.33 (m, 6H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 157.7, 149.5, 145.1, 143.1, 131.8, 129.5, 127.3, 126.0, 123.6, 123.2, 119.9, 113.7, 55.3, 40.9, 37.1; MS (EI): m/z 236 (M^+); IR (KBr): 3006, 2931, 2882, 2836, 1607, 1509, 1460, 1388, 1297, 1243, 1178, 1106, 1032, 898, 835, 764, 720 cm^{-1}; Mp: 64-65 °C (CH_2Cl_2)

2-(2-Methoxybenzyl)-indene (8e)

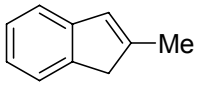


The compound **8e** was prepared by the procedure described above for **8a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.30 (s, 2H), 3.80 (s, 2H), 3.82 (s, 3H), 6.44 (d, *J*=0.6 Hz, 1H), 6.88 (t, *J*=7.5 Hz, 2H), 7.05-7.24 (m, 4H), 7.32 (d, *J*=7.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 157.0, 149.1, 145.3, 143.2, 130.1, 128.3, 127.3, 127.1, 125.9, 123.4, 123.2, 120.3, 120.0, 110.3, 55.4, 41.2, 31.8; MS (EI): m/z 236 (M^+); IR (KBr): 3000, 2940, 2883, 2836, 1599, 1494, 1465, 1435, 1294, 1245, 1123, 1100, 1030, 905, 837, 754, 717 cm^{-1}; Mp: 64-65 °C (CH_2Cl_2)

2-Naphtylmethylindene (8f)

The compound **8f** was prepared by the procedure described above for **8a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.30 (s, 2H), 3.97 (s, 2H), 6.54 (s, 1H), 7.04-7.48 (m, 7H), 7.67 (s, 1H), 7.75-7.82 (m, 3H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 148.8, 145.0, 143.2, 137.3, 133.4, 131.9, 127.8, 127.4, 127.3, 127.3, 126.8, 126.1, 125.8, 125.2, 123.7, 123.3, 120.0, 41.0, 38.2; MS (EI): m/z 256 (M^+); IR (KBr): 3052, 2904, 2876, 2820, 1598, 1507, 1459, 1423, 1388, 1211, 1014, 959, 906, 861, 816, 750, 717 cm^{-1}; Mp: 87-88 °C (CH_2Cl_2)

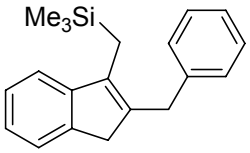
2-Methyl-indene (8g)



$TiCl_4$ (1.1 ml, 10.0 mmol) was added by syringe to dry Et_2O (50 ml) at –80 °C, and stirred for 15 min. To the solution was slowly added MeLi (8.8 ml, 10.0 mmol), and stirred for 15 min at –80 °C. The mixture was allowed to come to –50 °C, 2-indanone (1.32 g, 10.0 mmol) was then added, and allowed to come to room temperature, and stirred for 9h. The reaction mixture was poured into water, followed by extracted with ether. The combined organic layers were dried by Na_2SO_4 and the solvents evaporated under reduced pressure to give 2-methyl-indane-2-ol as crude yellow solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.51 (s, 3H), 3.02 (s, 4H), 7.14-7.24 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): 141.5,

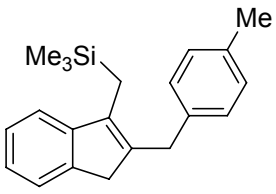
126.4, 124.8, 79.9, 48.1, 27.3; MS (EI): m/z 149 (M^+); IR (KBr): 3319, 3023, 2968, 2938, 2901, 1604, 1481, 1460, 1423, 1375, 1283, 1244, 1193, 1128, 1077, 951, 929, 886, 736, 688 cm^{-1}; Mp: 48-50 °C (CH_2Cl_2). The crude solid (500 mg, 3.37 mmol) was mixed with 9M H_2SO_4 (47 ml) and the stirred suspension was heated at 110-120 °C for 30 min. 20% aq NaOH was added to give a basic pH and the suspension was extracted with CH_2Cl_2. The combined organic layers were dried by Na_2SO_4 and the solvents evaporated under reduced pressure. Purification by silica-gel column chromatography (Hexane/ CH_2Cl_2) was carried out to give (**8g)** in 94% yield (412 mg) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.14 (d, J=0.6 Hz, 3H), 3.27 (s, 2H), 6.46 (t, J=0.6 Hz, 1H), 7.02-7.36 (m, 4H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 145.9, 143.3, 127.1, 126.1, 123.4, 123.2, 119.6, 42.6, 16.6; MS (EI): m/z 130 (M^+); IR (neat): 3059, 3009, 2960, 2909, 1613, 1462, 1443, 1391, 1211, 1036, 909, 826, 750, 716 cm^{-1}

2-Benzyl-3*H*-inden-1-ylmethyl)trimethylsilane (1a)



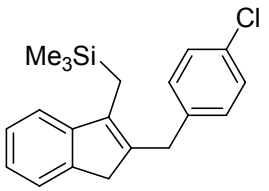
To a solution of 2-benzylindene **8a** (780 mg, 3.78 mmol) in THF (7.6 ml) at 0 °C was added dropwise *n*-BuLi in hexane (2.8 ml, 3.86 mmol). The reaction mixture was then allowed to warm to room temperature and stirred for 4h. The anion solution was then added dropwise to solution of bromomethyl-trimethyl-silane (0.54 ml, 3.78 mmol) in THF (6.0 ml) at –80 °C. After the addition, the reaction mixture was warmed to room temperature and stirred for 13h. The reaction mixture was concentrated under reduced pressure and residue dissolved in CH_2Cl_2. After filtration through Celite, removal of the solvent under reduced pressure. Purification by silica-gel column chromatography (Hexane/CH_2Cl_2) was carried out and further purification was done by kugel-rohr (160 °C/ 0.4 kpa) to give **1a** in 53% yield (584 mg) as Pale yellow oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.06 (s, 9H), 2.10 (s, 2H), 3.16 (s, 2H), 3.75 (s, 2H), 7.07-7.30 (m, 9H); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): 147.0, 143.0, 140.8, 137.5, 135.8, 128.7, 128.4, 125.9, 125.8, 123.7, 123.0, 119.1, 40.1, 35.2, 15.8, –0.6; MS (EI): m/z 292 (M^+); IR (neat): 3066, 3025, 2953, 2892, 1604, 1494, 1466, 1398, 1248, 1160, 1076, 1036, 843, 755, 721, 699 cm^{-1}

[2-(4-Methylbenzyl)-3*H*-inden-1-ylmethyl]trimethylsilane (1b)



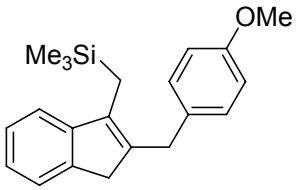
The compound **1b** was prepared by the procedure described above for **1a**. A pale yellow oil (180 °C/ 0.3 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.30 (s, 9H), 2.34 (s, 2H), 2.55 (s, 3H), 3.41 (s, 2H), 3.95 (s, 2H), 7.28-7.36 (m, 5H), 7.44-7.54 (m, 3H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 146.7, 142.7, 137.5, 137.4, 135.4, 135.1, 128.9, 128.5, 128.3, 125.5, 123.5, 122.8, 118.9, 40.2, 34.9, 21.2, 16.0, –0.3; MS (EI): m/z 306 (M^+); IR (neat): 3045, 3019, 2952, 2920, 1608, 1513, 1465, 1408, 1248, 1160, 1021, 843, 755, 720, 693 cm^{-1}

[2-(4-Chlorobenzyl)-3*H*-inden-1-ylmethyl]trimethylsilane (1c)



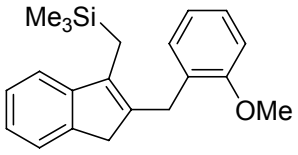
The compound **1c** was prepared by the procedure described above for **1a**. A yellow oil (190 °C/ 0.3 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.29 (s, 9H), 2.32 (s, 2H), 3.38 (s, 2H), 3.95 (s, 2H), 7.30-7.37 (m, 3H), 7.42-7.55 (m, 5H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 146.5, 142.6, 139.0, 136.4, 136.1, 131.5, 129.8, 128.3, 125.7, 123.7, 122.9, 119.0, 40.1, 34.7, 16.1, –0.3; MS (EI): m/z 328, 326 (M^+); IR (neat): 3045, 3021, 2953, 2893, 1607, 1489, 1466, 1407, 1248, 1160, 1093, 1015, 873, 797, 774, 755, 723, 694 cm^{-1}

[2-(4-Methoxybenzyl)-3*H*-inden-1-ylmethyl]trimethylsilane (1d)



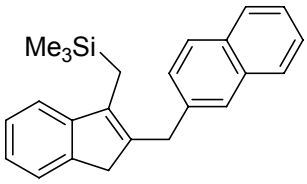
The compound **1d** was prepared by the procedure described above for **1a**. A yellow oil (210 °C/ 0.5 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0. 30 (s, 9H), 2.33 (s, 2H), 3.39 (s, 2H), 3.92 (s, 2H), 3.96 (s, 3H), 7.00-7.06 (m, 2H), 7.28-7.52 (m, 6H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 157.6, 146.8, 142.7, 137.7, 135.2, 132.6, 129.3, 125.5, 123.5, 122.8, 118.9, 113, 7, 55.2, 40.2, 34.4, 16.0, –0.3; MS (EI): m/z 322 (M^+); IR (neat): 3059, 3020, 2952, 2898, 2833, 1609, 1583, 1510, 1465, 1415, 1300, 1247, 1175, 1038, 843, 775, 756, 720, 693 cm^{-1}

[2-(2-Methoxybenzyl)-3*H*-inden-1-ylmethyl]trimethylsilane (1e)



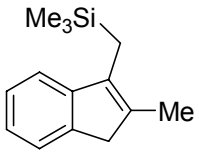
The compound **1e** was prepared by the procedure described above for **1a**. A yellow oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.05 (s, 9H), 2.09 (s, 2H), 3.17 (s, 2H), 3.73 (s, 2H), 3.83 (s, 2H), 6.80-6.87 (m, 2H), 7.03-7.29 (m, 6H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 157.0, 147.0, 142.8, 137.3, 135.4, 129.7, 128.9, 127.0, 125.5, 123.3, 122.8, 120.2, 118.7, 110.0, 55.3, 40.3, 29.2, 15.8, –0.3; MS (EI): m/z 322; IR (neat): 3052, 3019, 2952, 2834, 1600, 1492, 1465, 1438, 1287, 1245, 1161, 1105, 1050, 1031, 843, 753, 721, 693 cm^{-1}

(3*H*-Inden-2-naphtylmethyl-1-ylmethyl)trimethylsilane (1f)



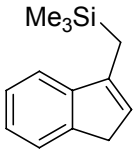
The compound **1f** was prepared by the procedure described above for **1a**. A yellow oil (255 °C/ 0.5 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0. 08 (s, 9H), 2.16 (s, 2H), 3.19 (s, 2H), 3.91 (s, 2H), 7.04-7.12 (m, 2H), 7.20-7.32 (m, 3H), 7.38-7.44 (m, 2H), 7.60 (s, 1H), 7.71-7.80 (m, 3H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 146, 7, 142.7, 138.1, 137.0, 135.8, 133.4, 131.9, 127.8, 127.8, 127.4, 127.2, 126.4, 125.7, 125.6, 125.0, 123.6, 122.9, 118.9, 40.3, 35.5, 16.1, –0.2; MS (EI): m/z 342 (M^+); IR (neat): 3052, 3017, 2952, 2893, 1602, 1508, 1466, 1415, 1248, 1160, 960, 843, 815, 754, 718, 693 cm^{-1}

(3*H*-inden-1-ylmethyl)trimethylsilane (1g)



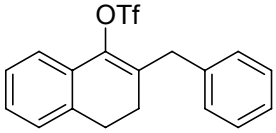
The compound **1g** was prepared by the procedure described above for **1a**. A colorless oil (100 °C/ 0.4 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.30 (s, 9H), 2.29 (d, *J*=1.4 Hz, 2H), 3.59 (d, *J*=1.4 Hz, 2H); 6.00 (s, 1H); 7.10-7.42 (m, 4H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 145.9, 144.1, 141.3, 125.6, 125.6, 124.0, 123.3, 119.1, 37.8, 17.8, –0.9; MS (EI): m/z 202 (M^+); IR (neat): 3063, 3017, 2953, 2892, 1602, 1460, 1406, 1352, 1248, 1172, 1155, 962, 848, 767, 718, 693 cm^{-1}

Trimethyl-(2-methyl-3*H*-inden-1-ylmethyl)silane (1h)



The compound **1h** was prepared by the procedure described above for **1a**. A pale yellow oil (95 °C/ 0.2 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.01 (s, 9H), 1.94 (s, 2H), 2.00 (s, 3H), 3.25 (s, 2H), 7.06-7.34 (m, 4H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 147.2, 142.4, 134.5, 134.3, 125.5, 123.1, 122.6, 118.4, 42.5, 15.8, 14.7, –0.4; MS (EI): m/z 216 (M^+); IR (KBr): 3059, 3019, 2954, 2907, 1621, 1466, 1398, 1313, 1248, 1165, 1084, 1020, 890, 842, 773, 754, 719, 693 cm^{-1}

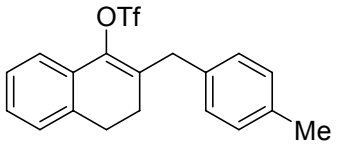
Trifluoro-methanesulfonic acid 2-benzyl-3,4-dihydro-naphthalen-1-yl ester (9i)



To a solution of 2-benzyl-3,4-dihydro-2*H*-naphthalene-1-one (**7i**) (1.69 g, 7.1 mmol) and 2,6-di-*t*-butyl-4-methyl pyridine (2.38 g, 11.6 mmol) in CH_2Cl_2 (29 ml), triflic anhydride (1.83 ml, 10.9 mmol) was added and the reaction mixture stirred at room temperature for 17h. The solvent was removed and the residue was dissolved in hexane. Purification by silica-gel column chromatography (Hexane/ AcOEt) was carried out to give **9i** in 94% yield (2.47 g) as a

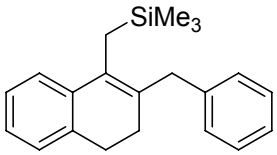
pale yellow oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.25 (t, *J*=7.9 Hz, 2H), 2.78 (t, *J*=7.8 Hz, 2H), 3.75 (s, 2H), 7.09-7.42 (m, 9H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 140.7, 136.9, 135.4, 131.6, 129.3, 128.8, 128.4, 128.2, 127.1, 126.6, 126.5, 121.3, 118.4 (d, *J*=319.2 Hz), 37.1, 27.6, 27.4; ^{19}F-NMR ($CDCl_3$, 188 MHz): –73.4 (s, 3F); MS (EI): m/z 368 (M^+); IR (neat): 3066, 3030, 2943, 2834, 1657, 1603, 1244, 1455, 1416, 1244, 1214, 1139, 1034, 1010, 950, 894, 848, 814, 764, 732, 697, 659, 606 cm^{-1}

Trifluoro-methanesulfonic acid 2-(4-methylbenzyl)-3,4-dihydro-naphthalen-1-yl ester (9j)



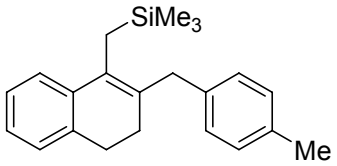
The compound **9j** was prepared by the procedure described above for **9i**. A pale yellow oil (220 °C/ 0.4 kpa); ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.24 (t, *J*=7.9 Hz, 2H), 2.32 (s, 3H), 2.77 (t, *J*=7.8 Hz, 2H), 3.70 (s, 2H), 7.09-7.29 (m, 7H), 7.39 (d, *J*=7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 140.5, 136.0, 135.4, 133.8, 131.8, 129.4, 129.1, 128.6, 128.1, 127.1, 126.5, 121.2, 118.4 (q, *J*=318.7 Hz), 36.6, 27.5, 27.3, 21.1; MS (EI): m/z 382 (M^+); IR (neat): 3024, 2942, 2835, 1734, 1656, 1514, 1416, 1243, 1213, 1139, 1035, 1010, 896, 872, 815, 763, 605 cm^{-1}

(2-Benzyl-3,4-dihydro-naphthalen-1-ylmethyl)trimethylsilane (1i)



To a suspension of sublimed aluminium chloride (373 mg, 2.79 mmol) in 1,2-dichloroethane (20 ml) under an argon atmosphere, trimethylsilyl methyl lithium (1.00 M in pentane, 8.6 ml, 8.58 mmol) was added. The resulting mixture was stirred at room temperature for 30 min and then treated rapidly via cannula transfer with a solution of **9i** and $Pd(PPh_3)_4$ catalyst which was prepared in a separate flask as follows: A solution of $Pd(PPh_3)_4$ (230 mg, 0.020 mmol) in benzene (5 ml) was treated with a solution of the **9i** (735 mg, 2.00 mmol) in benzene (5 ml). This solution was immediately transferred via cannula to the preformed aluminium reagent. The resulting solution was stirred at room temperature for 14 h and then diluted with CH_2Cl_2 (50 ml). The reaction mixture was washed sequentially with aqueous 0.2 M HCl (20 ml), water (20 ml) and brine (20 ml). The solvent removed under reduced pressure. Purification by silica-gel column chromatography (Hexane) was carried out and further purification was done by kugel rohr (190 °C/ 0.6 kpa) to give **1i** in 51% yield (315 mg) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): –0.01 (s, 9H), 2.12 (t, *J*=7.2 Hz, 2H), 2.17 (s, 2H), 2.69 (t, *J*=7.2 Hz, 2H), 3.62 (s, 2H), 7.08-7.30 (m, 9H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 139.8, 136.5, 136.0, 131.2, 129.2, 128.4, 128.1, 126.8, 126.0, 125.8, 125.6, 123.6, 40.6, 29.2, 28.7, 18.1, –0.2; MS (EI): m/z 306 (M^+); IR (neat): 3060, 3026, 2952, 2889, 2829, 1621, 1601, 1487, 1452, 1426, 1487, 1160, 1073, 1028, 934, 906, 855, 837, 755, 731, 701 cm^{-1}

(2-Benzyl-3,4-dihydro-naphthalen-1-ylmethyl)trimethylsilane (1j)

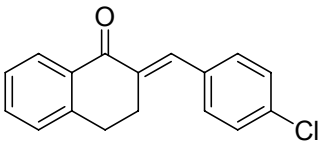


The compound **1j** was prepared by the procedure described above for **1i**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): –0.03 (s, 9H), 2.10 (t, *J*=7.6 Hz, 3H), 2.14 (s, 2H), 2.31 (s, 3H), 2.66 (t, *J*=7.6 Hz, 2H), 3.56 (s, 2H), 7.07-7.24 (m, 8H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 136.9, 136.8, 136.3, 135.4, 131.7, 129.2, 129.0, 128.5, 127.0, 125.9, 125.8, 123.8, 40.1, 29.1, 28.4, 21.0, 17.8, –0.5; MS (EI): m/z 320 (M^+); IR (neat): 3018, 2953, 2925, 2830, 1623, 1512, 1487, 1451, 1429, 1248, 1159, 1114, 1024, 930, 888, 856, 838, 756, 733, 692 cm^{-1}

Preparation of Silyl enol ethers

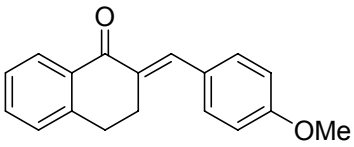
Silyl enol ethers **1k-p** were prepared according to the literature procedures[2].

(*E*)-2-(4-Chrolobenzylidene)-3,4-dihydro-2H-naphthalene-1-one (6m)



The compound **6m** was prepared by the procedure described above for **6a**. A pale yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.95 (dd, *J*=5.8, 7.0 Hz, 2H), 3.06-3.14 (m, 2H), 7.23-7.41 (m, 6H), 7.50 (td, *J*=7.4, 1.6 Hz, 1H), 7.79 (t, *J*=1.6 Hz, 1H), 8.11 (dd, *J*=1.4, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 187.6, 143.1, 136.0, 135.2, 134.5, 134.3, 133.4, 133.3, 131.1, 128.7, 128.3, 128.2, 127.1, 28.8, 27.2; MS (EI): m/z 268, 270 (M^+), 267 (M^+-1); IR (KBr): 2947, 1668, 1602, 1490, 1403, 1318, 1299, 1251, 1224, 1094, 1012, 949, 841, 743, 707 cm^{-1}; Mp: 137-138 °C (MeOH)

(*E*)-2-(4-Methoxybenzylidene)-3,4-dihydro-2H-naphthalene-1-one (6n)



The compound **6n** was prepared by the procedure described above for **6a**. Yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.94 (dd, *J*=5.6, 6.8 Hz, 2H), 3.11-3.17 (m, 2H), 3.85 (s, 3H), 6.94 (d, *J*=8.8 Hz, 2H), 6.30-6.51 (m, 5H), 7.83 (s, 1H), 8.10 (dd, *J*=1.2, 7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 187.3, 159.6, 142.7, 136.3, 133.3, 133.2, 132.8, 131.4, 128.1, 127.8, 126.7, 113.7, 55.3, 28.9, 27.3; MS (EI): m/z 264 (M^+), 263 (M^+-1); IR (KBr): 3067, 3028, 2996, 2947, 2909, 2836, 1666, 1601, 1508, 1454, 1439, 1415, 1301, 1252, 1223, 1202, 1176, 1137, 1110, 1033, 998, 963, 950, 907, 886, 841, 822, 787, 743, 725, 703 cm^{-1}; Mp: 110-111 °C (MeOH)

(*E*)-2-Naphthylmethylidene-3,4-dihydro-2H-naphthalene-1-one (6o)

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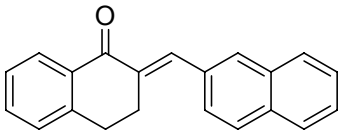
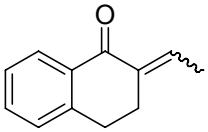
[2] Marínez, A.; Fernández, M.; Estèvez, J. C.; Estèvez, R. J.; Castedo, L. *Tetrahedron*. **2005**, *61*, 485–492.



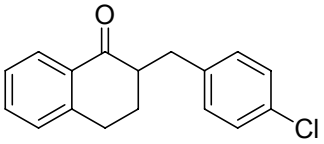
The compound **6o** was prepared by the procedure described above for **6a**. Yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.97 (dd, *J*=6.0, 6.8 Hz, 2H), 3.20-3.27 (m, 2H), 7.25 (d, *J*=6.8 Hz, 1H), 7.38 (d, *J*=7.6 Hz, 1H), 7.45-7.56 (m, 4H), 7.82-7.90 (m, 4H), 8.01 (s, 1H), 8.15 (dd, *J*=1.6, 7.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 187.3, 142.9, 136.4, 135.4, 133.2, 133.1, 133.0, 132.8, 132.8, 129.3, 128.0, 128.0, 127.9, 127.8, 127.4, 127.0, 126.8, 126.5, 126.2, 29.0, 27.5; MS (EI): m/z 284 (M^+), 283 (M^+-1); IR (KBr): 3053, 2948, 2848, 1659, 1603, 1583, 1507, 1455, 1376, 1334, 1314, 1296, 1243, 1177, 1136, 1029, 962, 942, 932, 897, 862, 823, 788, 756, 739, 714, 649, 613 cm^{-1}; Mp: 133-134 °C (MeOH)

2-Ethylidene-3,4-dihydro-2*H*-naphthalene-1-one (6p)



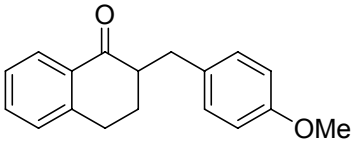
The compound **6p** was prepared by the procedure described above for **6a**. A yellow oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.88 (d, *J*=7.4 Hz, 3H), 2.79 (dd, *J*=5.6, 7.0 Hz, 2H), 2.95 (dd, *J*=5.8, 7.2 Hz, 2H), 7.02 (q, *J*=7.4 Hz, 1H), 7.23 (d, *J*=7.4 Hz, 1H), 7.30 (dd, *J*=7.2, 7.8 Hz, 1H), 7.45 (ddd, *J*=1.2, 7.3, 7.4 Hz, 1H), 8.07 (dd, *J*=1.2, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 186.8, 186.5, 143.1, 142.9, 139.4, 135.6, 135.3, 134.1, 133.0, 132.5, 132.4, 131.5, 127.8, 127.7, 127.5, 127.4, 126.6, 126.3, 28.8, 28.6, 25.5, 25.1, 19.1, 13.9; MS (EI): m/z 172 (M^+); IR (neat): 2928, 2848, 1676, 1625, 1456, 1315, 1297, 1245, 912, 739, 707 cm^{-1}

2-(4-Chlorobenzyl)-3,4-dihydro-2*H*-naphthalene-1-one (7m)



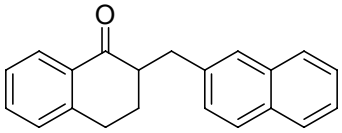
The compound **7m** was prepared by the procedure described above for **7a**. White solid; ^{1}H-NMR ($CDCl_3$, 600 MHz): 1.73-1.80 (m, 1H), 2.08 (dq, *J*=4.4, 13.3 Hz, 1H), 2.64-2.73 (m, 2H), 2.89- 2.96 (m, 2H), 3.41 (dd, *J*=3.8, 13.3 Hz, 1H), 7.15 (d, *J*=8.3 Hz, 2H), 7.21 (d, *J*=7.6 Hz, 1H), 7.26 (d, *J*=8.3 Hz, 1H), 7.30 (t, *J*=7.6 Hz, 1H), 7.45 (td, *J*=7.5, 1.3 Hz, 1H), 8.05 (d, *J*=7.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 198.5, 143.6, 138.2, 133.1, 132.1, 131.6, 130.4, 128.5, 128.2, 127.3, 126.4, 49.4, 35.2, 28.8, 27.9; MS (EI): m/z 270, 272 (M^+); IR (KBr): 2953, 2926, 1683, 1599, 1491, 1457, 1359, 1286, 1219, 1090, 1014, 932, 801, 749, 654 cm^{-1}; Mp: 89-90 °C (CH_2Cl_2)

2-(4-Methoxybenzyl)-3,4-dihydro-2*H*-naphthalene-1-one (7n)



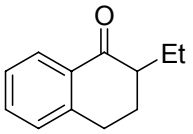
The compound **7n** was prepared by the procedure described above for **7a**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 600 MHz): 2.62 (dd, *J*=9.6, 13.8 Hz, 1H), 2.68-2.73 (m, 1H), 2.88-2.98 (m, 2H), 3.40 (dd, *J*=4.2, 13.8 Hz, 1H), 6.85 (d, *J*=7.8 Hz, 2H), 7.14 (d, *J*=7.8 Hz, 2H), 7.22 (d, *J*=7.8 Hz, 1H), 7.31 (dd, *J*=7.2, 7.8 Hz, 1H), 7.46 (dd, *J*=1.2, 7.5 Hz, 1H); 8.06 (dd, *J*=1.2, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 198.9, 157.6, 143.7, 132.9, 132.2, 131.6, 129.9, 128.4, 127.2, 126.3, 113.6, 55.2, 49.6, 34.8, 28.7, 27.7; MS (EI): m/z 266 (M^+); IR (neat): 3051, 2929, 2862, 1682, 1599, 1508, 1455, 1359, 1286, 1231, 1162, 1120, 1029, 1008, 965, 944, 909, 858, 810, 742 cm^{-1}

2-Naphthylmethylidene-3,4-dihydro-2*H*-naphthalene-1-one (7o)



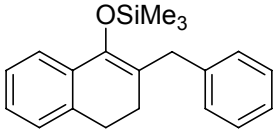
The compound **7o** was prepared by the procedure described above for **7a**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 600 MHz): 1.79-1.86 (m, 1H), 2.13 (qd, *J*=4.2, 13.2 Hz, 1H), 2.82 (dd, *J*=9.6, 22.2 Hz, 1H), 2.81-2.98 (m, 3H), 3.67 (dd, *J*=4.8, 12.6 Hz, 1H), 7.22 (d, *J*=7.2 Hz, 1H), 7.33 (dd, *J*=7.2, 7.8 Hz, 1H), 7.38 (dd, *J*=1.2, 7.8 Hz, 1H), 7.42-7.48 (m, 3H), 7.67 (s, 1H), 7.79 (dd, *J*=2.4, 8.4 Hz, 2H), 7.82 (d, *J*=7.8 Hz, 1H), 8.09 (dd, *J*=1.2, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 198.8, 143.7, 137.3, 133.3, 133.0, 132.3, 131.9, 128.5, 127.8, 127.4, 127.3, 127.2, 126.4, 125.8, 125.1, 49.5, 36.0, 28.8, 27.9; MS (EI): m/z 288, 286 (M^+); IR (neat): 3066, 3028, 2932, 2862, 2834, 1682, 1610, 1512, 1455, 1360, 1295, 1247, 1177, 1107, 1036, 931, 839, 812, 759, 736 cm^{-1}

2-Ehtyl-3,4-dihydro-2*H*-naphthalene-1-one (7p)



The compound **6p** was prepared by the procedure described above for **5a**. Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 600 MHz): 0.99 (t, *J*=7.2 Hz, 3H), 1.56 (hept., *J*=7.2 Hz, 1H), 1.84-1.90 (m, 1H), 1.92-2.00 (m, 1H), 2.21 (dq, *J*=12.6, 4.8 Hz, 1H), 2.35-2.40 (m, 1H), 2.92-2.98 (m, 2H), 7.20 (d, *J*=7.2 Hz, 1H), 7.26 (dd, *J*=7.2, 7.8 Hz, 1H), 7.42 (dd, *J*=7.2, 7.8 Hz, 1H), 8.02 (d, *J*=7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 200.0, 143.8, 132.9, 132.4, 128.5, 127.2, 126.3, 48.7, 28.2, 27.6, 22.3, 11.3; MS (EI): m/z 174 (M^+), 146 (M^+-Et+1); IR (neat): 2931, 2862, 1683, 1601, 1455, 1359, 1296, 1224, 909, 741 cm^{-1}

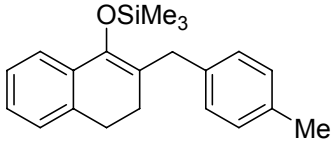
2-Benzyl-1-trimethylsilyoxytetral-1-ene (1k)



2-Benzyl-3,4-dihydro-2*H*-naphthalene-1-one **(7i)** (1.0 g, 4.53 mmol) was added to a solution of Et_3N (0.79 ml, 5.66 mmol) in CH_3CN (1 ml) and the mixture was stirred under nitrogen atmosphere at room temperature for 20 min. TMS-Cl (0.72 ml, 5.66 mmol) was then added dropwise to the mixture, and it was stirred for 20 min. A solution of NaI (850 mg, 5.66 mmol) in CH_3CN (5 ml) was next added to the mixture. After 19h, the reaction mixture was extracted with hexane (20 ml x 3). After the removal of solvent, purification by silica-gel column chromatography

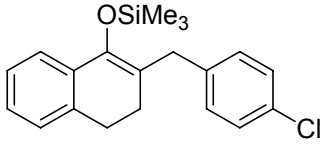
(Hexane/AcOEt) was carried out and further purification was done by kugel rohr (193-202 °C/ 0.3-0.4 kpa) to give **1k** in 89% yield (1.07 g) as a colorless oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.23 (s, 9H), 2.12 (t, *J*=7.7 Hz, 2H), 2.72 (t, *J*=7.7 Hz, 2H), 3.64 (s, 2H), 7.09-7.41 (m, 9H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 143.2, 139.9, 136.1, 134.0, 128.6, 128.1, 126.6, 126.4, 125.9, 125.7, 121.9, 119.0, 36.9, 28.5, 26.9, 0.9; MS (EI): m/z 308 (M^+); IR (neat): 3062, 3025, 2956, 2883, 2831, 1644, 1602, 1487, 1453, 1303, 1253, 1194, 1137, 1086, 1028, 911, 874, 845, 757, 703 cm^{-1}

2-(4-methylbenzyl)-1-trimethylsilyoxytetral-1-ene (1l)



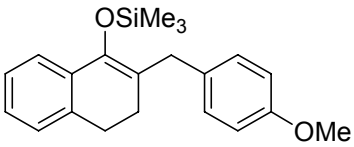
The compound **1l** was prepared by the procedure described above for **1k**. A colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.21 (s, 9H), 2.10 (t, *J*=7.8 Hz, 2H), 2.30 (s, 3H), 2.65 (t, *J*=7.8 Hz, 2H), 3.59 (s, 2H), 7.03-7.22 (m, 7H), 7.38 (d, *J*=7.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 143.1, 136.7, 136.0, 135.1, 134.1, 128.8, 128.5, 126.5, 126.3, 125.8, 124.9, 121.9, 119.2, 36.4, 28.5, 26.8, 21.2, 0.9; MS (EI): m/z 322 (M^+), 307 (M^+-Me); IR (neat): 3017, 2956, 2834, 1644, 1513, 1486, 1303, 1253, 1136, 1084, 911, 846, 758 cm^{-1}

2-(4-Chlorobenzyl)-1-trimethylsilyoxytetral-1-ene (1m)



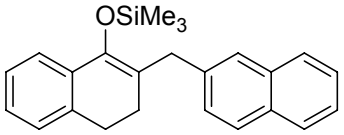
The compound **1m** was prepared by the procedure described above for **1k**. White solid; ^{1}H -NMR ($CDCl_3$, 200 MHz): 0.20 (s, 9H), 2.08 (t, *J*=7.9 Hz, 2H), 2.71 (t, *J*=7.8 Hz, 2H), 3.58 (s, 2H), 7.05-7.24 (m, 7H), 7.37 (d, *J*=6.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 143.5, 138.4, 136.0, 133.8, 131.4, 129.9, 128.2, 126.6, 126.5, 125.9, 122.0, 118.3, 36.3, 28.4 26.8, 0.9; MS m/z (EI): 342, 344 (M^+), 314, 316 (M^+-Cl); IR (KBr): 2960, 2931, 2890, 2827, 1647, 1487, 1304, 1253, 1135, 1088, 1014, 911, 844, 768 cm^{-1}; Mp: 51-52 °C (Hexane)

2-(4-Methoxybenzyl)-1-trimethylsilyoxytetral-1-ene (1n)



The compound **1n** was prepared by the procedure described above for **1k**. White solid; ^{1}H -NMR ($CDCl_3$, 200 MHz): 0.21 (s, 9H), 2.09 (dd, *J*=7.4, 8.4 Hz, 2H), 2.70 (dd, *J*=7.4, 8.4 Hz, 2H), 6.79 (d, *J*=8.8 Hz, 2H), 7.04-7.23 (m, 5H), 7.37 (d, *J*=7.2 Hz); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 157.5, 142.9, 136.0, 134.0, 131.8, 129.4, 126.5, 126.3, 125.8, 121.8, 121.8, 119.4, 113.5, 55.3, 36.0, 27.5, 26.8, 0.9; MS m/z (EI): 338 (M^+); IR (KBr): 2955, 2882, 2833, 1642, 1610, 1585, 1509, 1484, 1466, 1439, 1301, 1248, 1219, 1194, 1174, 1132, 1083, 909, 879, 847, 758, 737, 716, 688 cm^{-1}; Mp: 42-43 °C (Hexane)

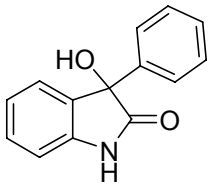
2Naththylmethyl-1-trimethylsilyoxytetral-1-ene (1o)



The compound **1o** was prepared by the procedure described above for **1k**. Pale yellow solid; ^{1}H -NMR ($CDCl_3$, 200 MHz): 0.24 (s, 9H), 2.13 (dd, *J*=7.2, 8.2 Hz, 2H), 2.71 (dd, *J*=7.2, 8.2 Hz, 2H), 7.04-7.21 (m, 3H), 7.31-7.46 (m, 4H), 7.63 (s, 1H), 7.70-7.79 (m, 3H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 143.4, 137.4, 136.1, 134.0, 133.3, 131.9, 127.7, 127.4, 127.2, 126.6, 126.6, 126.4, 125.9, 125.6, 124.9, 121.9, 118.8, 37.1, 28.5, 26.8, 1.0; MS m/z (EI): 358 (M^+); IR (KBr): 3045, 2954, 2928, 2878, 2830, 1915, 1643, 1601, 1507, 1485, 1450, 1407, 1362, 1331, 1304, 1253, 1225, 1196, 1136, 1086, 1028, 971, 912, 896, 879, 845, 820, 768, 754, 735, 692, 627 cm^{-1}; Mp: 66-67 °C (Hexane)

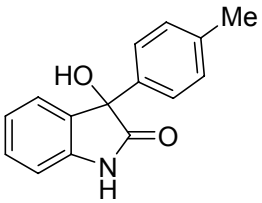
Oxindoles **3a-f**were prepared according to the literature procedures[3].

3-Hydroxy-3-phenylindolin-2-one (10a)



To a solution of isatin (2.0 g, 13.6 mmol) in THF (27 ml), NaH (652 mg, 16.3 mmol) was added at –15 °C and stirred for 45 min. PhMgBr (6.0 ml, 2.7 M, 16.3 mmol) was then added to the reaction mixture and stirred for 1h. A solution of 2N HCl. (30 ml) was added and the mixture was extracted with ether, washed saturated aqueous sodium bicarbonate solution and brine. The combined organic layers were dried by Na_2SO_4 and the solvent was evaporated under reduced pressure. Purification by flash silica-gel column chromatography (Hexane/Acetone) was carried out and further purification by recrystallization (Acetone:Hexane) to give **10a** in 87% yield (2.65 g) as orange solid. ^{1}H-NMR (CD_3OD, 200 MHz): 6.86 (d, *J*=8.0 Hz, 1H), 6.95 (dd, *J*=1.0, 7.5 Hz, 1H), 7.06 (d, *J*=6.8 Hz, 1H), 7.11-7.32 (m, 6H); ^{13}C-NMR (CD_3OD, 50.3 MHz): 181.1, 142.6, 141.6, 134.5, 130.4, 129.0, 128.6, 126.4, 125.8, 123.7, 111.1, 79.2; MS (EI): m/z 225 (M^+); IR (KBr): 3445, 2925, 2853, 1707, 1620, 1508, 1472, 1339, 1184, 1066, 930, 758, 659 cm^{-1}; Mp: 213-214 °C (Acetone/Hexane)

3-Hydroxy-3-(4-methylphenyl)-indolin-2-one (10b)

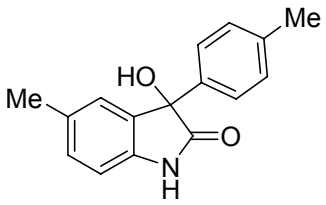


The compound **10b** was prepared by the procedure described above for **10a**. White solid; ^{1}H-NMR (CD_3OD, 200

[3] Y. Hamashima, T. Suzuki, H. Takano, Y. Simura, M. Sodeoka, *J. Am. Chem. Soc.* **2005**, *127*, 10164–10165.

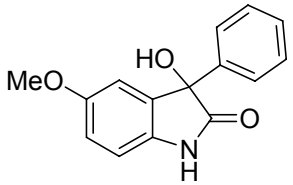
MHz): 2.29 (s, 3H), 6.88-7.34 (m, 8H); ^{13}C-NMR (CD_3OD, 50.3 MHz): 181.7, 143.0, 138.9, 138.8, 134.9, 130.6, 129.9, 126.7, 126.1, 124.0, 111.3, 79.2, 21.1; MS m/z (EI): 239 (M^+); IR (KBr): 3360, 1712, 1620, 1470, 1340, 1178, 1106, 1079, 925, 810, 753, 698, 652 cm^{-1}; Mp: 206-207 °C (Acetone/ Hexane)

3-Hydroxy-3-(4-methylphenyl)-5-methyl-indolin-2-one (10c)



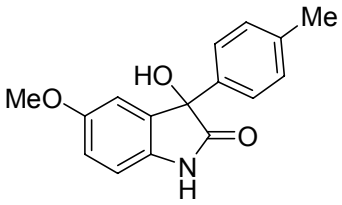
The compound **10c** was prepared by the procedure described above for **10a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 2.25 (s, 3H), 2.31 (s, 3H), 3.64 (s, 1H), 6.75 (d, *J*=8.4 Hz, 1H), 7.03-7.13 (m, 4H), 7.28 (d, *J*=8.4 Hz, 1H), 8.42 (s, 1H) ^{13}C-NMR (CD_3OD, 50.3 MHz): 181.3, 140.0, 138.7, 138.3, 134.6, 133.3, 130.5, 129.5, 126.3, 110.8, 79.2, 21.2; MS m/z (EI): 253 (M^+); IR (KBr): 3420, 3200, 2916, 1702, 1625, 1493, 1336, 1207, 1148, 1057, 958, 820, 775, 698, 649, 507 cm^{-1}; Mp: 206-208 °C (Acetone/ Hexane)

3-Hydroxy-5-methoxy-3-phenylindolin-2-one (10d)



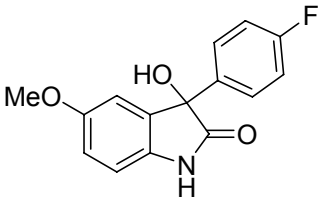
The compound **10d** was prepared by the procedure described above for **10a**. Orange solid; ^{1}H-NMR (CD_3OD, 200 MHz): 3.71 (s, 3H), 6.75-6.77 (m, 1H), 6.85-6.87 (m, 2H), 7.26-7.35 (m, 5H); ^{13}C-NMR (CD_3OD, 150.9 MHz): 181.6, 157.8, 142.0, 136.1, 136.1, 129.3, 128.9, 126.6, 115.6, 112.6, 111.9, 79.8, 56.2; MS (EI): m/z 255 (M^+); IR (KBr): 3346, 3270, 2948, 1710, 1605, 1491, 1300, 1262, 1203, 1165, 1130, 1066, 1029, 812, 762, 734, 696, 665 cm^{-1}; Mp: 213-214 °C (Acetone/ Hexane)

3-Hydroxy-3-(4-methoxyphenyl)-5-methyl-indolin-2-one (10e)



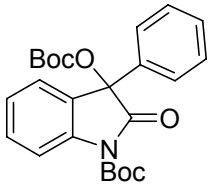
The compound **10e** was prepared by the procedure described above for **10a**. Pale orange solid; ^{1}H-NMR (CD_3OD, 400 MHz): 2.32 (s, 3H), 3.71 (s, 3H), 6.77-6.83 (m, 3H), 7.13 (d, *J*=10.4 Hz, 2H), 7.29 (d, *J*=11.2 Hz, 1H), 8.36 (s, 1H); ^{13}C-NMR (CD_3OD, 50.3 MHz): 181.2, 157.3, 138.6, 138.4, 135.7, 135.7, 129.6, 126.3, 115.3, 112.4, 111.6, 79.6, 56.1, 21.2; MS (EI): m/z 269 (M^+); IR (KBr): 3307, 3218, 1694, 1614, 1494, 1437, 1362, 1332, 1282, 1205, 1184, 1160, 1115, 1073, 1029, 980, 953, 894, 826, 778, 704, 635 cm^{-1}; Mp: 185-186 °C (Acetone/ Hexane)

3-(4-Fluorophenyl)-3-hydroxy-5-methyl-indolin-2-one (10f)



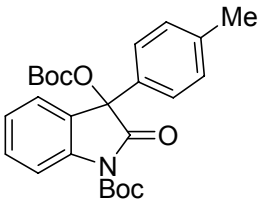
The compound **10f** was prepared by the procedure described above for **10a**. Orange solid; ^{1}H-NMR (CD_3OD, 200 MHz), 3.69 (s, 3H), 6.74 (s, 1H), 6.86 (m, 2H), 7.00 (t, *J*=8.8 Hz, 2H), 7.30-7.37 (m, 2H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 180.9, 163.4 (d, *J*=244.3 Hz), 157.4, 137.6 (d, *J*=2.8 Hz), 135.7, 135.4, 128.5 (d, *J*=8.3 Hz), 115.9, 115.5, 115.5, 112.1 (d, *J*=27.1 Hz), 79.2, 56.1; ^{19}F-NMR (CD_3OD, 188 MHz): –114.4- –114.0 (m, 1F); MS (EI): m/z 273 (M^+); IR (KBr): 3322, 3234, 2925, 1707, 1603, 1508, 1491, 1289, 1204, 1156, 1120, 1029, 841, 814, 784, 617 cm^{-1}; Mp: 189-190 °C (Acetone/ Hexane)

1-(*t*-Butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl *t*-butyl carbonate (11a)



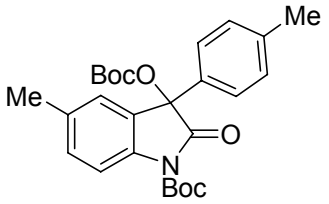
To a solution of 3-hydroxy-3-phenylindolin-2-one (**10a**) (2.65 g, 11.8 mmol) in CH_2Cl_2 (100 ml), DMAP (144 mg, 1.18 mmol), and $(Boc)_2O$ (5.66 g, 11.8 mmol) were added at room temperature, and the mixture was stirred for 1h. After the removal of solvent, the residue was purified by column chromatography on silica-gel (Hexane/AcOEt) to give **11a** in 85% yield (4.25 g) as pale yellow solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.38 (s, 9H), 1.60 (s, 9H), 7.22-7.31 (m, 6H), 7.40-7.48 (m, 1H), 7.97 (d, *J*=8.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz); 171.1, 150.7, 148.8, 140.4, 135.7, 130.1, 128.9, 128.3, 127.1, 126.5, 124.8, 123.9, 115.3, 84.5, 53.9, 28.2, 27.7; MS (EI): m/z 425 (M^+); IR (KBr): 2983, 2934, 1786, 1733, 1610, 1468, 1396, 1371, 1346, 1294, 1251, 1149, 1102, 1003, 977, 955, 938, 903, 857, 756, 714, 693, 622 cm^{-1}; Mp: 135-137 °C (CH_2Cl_2)

1-(*t*-Butoxycarbonyl)-2-oxo-3-(4-methylphenyl)-indolin-3-yl *t*-butyl carbonate (11b)



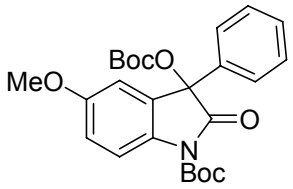
The compound **11b** was prepared by the procedure described above for **11a**. Pale yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.37 (s, 9H), 1.60 (s, 9H), 2.31 (s, 1H), 7.08-7.31 (m, 6H), 7.43 (td, *J*=8.1, 2.0 Hz, 1H), 7.96 (d, *J*=8.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 171.2, 150.7, 148.8, 140.3, 138.8, 132.8, 130.0, 129.0, 127.2, 126.4, 124.7, 123.8, 115.2, 84.3, 83.7, 81.5, 28.2, 27.7, 21.3; MS (EI): m/z 439 (M^+); IR (KBr): 2978, 2933, 1786, 1749, 1727, 1608, 1469, 1370, 1345, 1295, 1253, 1147, 1104, 1001, 957, 937, 860, 816, 759 cm^{-1}; Mp: 143-145 °C (CH_2Cl_2)

1-(*t*-Butoxycarbonyl)-2-oxo-3-(4-methylphenyl)-5-methyl-indolin-3-yl *t*-butyl carbonate (11c)



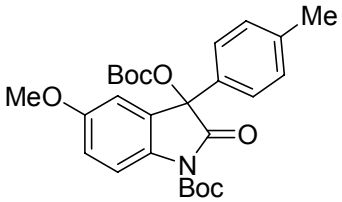
The compound **11c** was prepared by the procedure described above for **11a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.38 (s, 9H), 1.59 (s, 9H), 2.31 (s, 1H), 2.35 (s, 3H), 7.08-7.25 (m, 6H), 7.82 (d, *J*=8.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 171.4, 150.7, 148.9, 138.7, 138.0, 134.4, 133.0, 130.6, 129.0, 127.3, 126.4, 124.2, 115.0, 84.2, 83.8, 81.7, 28.2, 27.7, 21.3, 21.2; MS (EI): m/z 453 (M^+); IR (KBr): 2980, 2932, 2870, 1790, 1753, 1726, 1494, 1371, 1338, 1293, 1253, 1147, 1123, 1023, 959, 822, 797, 734, 485 cm^{-1}; Mp: 170-172 °C (CH_2Cl_2)

1-(*t*-Butoxycarbonyl)-2-oxo-5-methoxy-3-phenylindolin-3-yl *t*-butyl carbonate (11d)



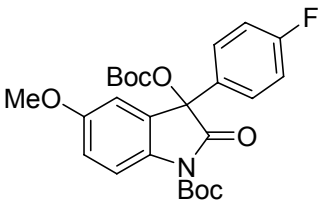
The compound **11d** was prepared by the procedure described above for **11a**. Yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.39 (s, 9H), 1.59 (s, 9H), 3.78 (m, 3H), 6.84 (d, *J*=2.6 Hz, 1H), 6.95 (dd, *J*=2.6, 7.2 Hz, 1H), 7.31 (s, 5H), 7.88 (d, *J*=9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 171.2, 156.9, 150.6, 148.8, 135.6, 133.6, 128.9, 128.3, 126.5, 116.3, 115.2, 109.6, 84.3, 84.0, 55.7, 28.2, 27.7; MS (EI): m/z 455 (M^+); IR (KBr): 2984, 2932, 1787, 1748, 1725, 1601, 1490, 1456, 1370, 1337, 1294, 1251, 1154, 1119, 1011, 992, 957, 854, 787, 752, 734, 713, 692, 648 cm^{-1}; Mp: 153-155 °C (CH_2Cl_2)

1-(*t*-Butoxycarbonyl)-2-oxo-3-(4-methylphenyl)-5-methoxy-indolin-3-yl *t*-butyl carbonate (11e)



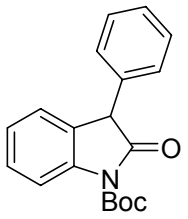
The compound **11e** was prepared by the procedure described above for **11a**. Yellow solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.38 (s, 9H), 1.59 (s, 9H), 2.31 (s, 1H), 2.35 (s, 3H), 7.08-7.25 (m, 6H), 7.82 (d, *J*=8.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 171.1, 156.8, 150.5, 148.8, 138.7, 133.5, 132.7, 128.9, 128.3, 126.3, 116.2, 115.0, 109.5, 84.0, 83.7, 81.6, 55.5, 28.1, 27.6, 21.1; MS (EI): m/z 469 (M^+); IR (KBr): 2981, 2935, 1731, 1602, 1492, 1395, 1371, 1339, 1281, 1252, 1153, 1115, 1042, 1011, 955, 921, 859, 795, 766, 735 cm^{-1}; Mp: 163-164 °C (CH_2Cl_2)

1-(*t*-Butoxycarbonyl)-2-oxo-3-(4-fluorophenyl)-5-methoxy-indolin-3-yl *t*-Butyl Carbonate (11f)



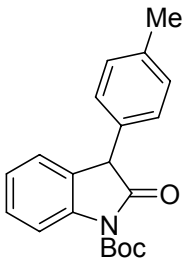
The compound **11f** was prepared by the procedure described above for **11a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.39 (s, 9H), 1.60 (s, 9H), 3.79 (s, 1H), 6.84 (d, *J*=3.0 Hz, 1H), 6.93-6.03 (m, 3H), 7.24-7.33 (m, 3H), 7.89 (d, *J*=8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 170.9, 162.7 (d, *J*=248.2 Hz), 156.9, 150.4, 148.6, 133.5, 131.4 (d, *J*=3.2 Hz), 128.5 (d, *J*=8.4 Hz), 127.8, 116.3, 115.2 (d, *J*=22.0 Hz), 115.2, 109.5, 84.2, 84.0, 81.1, 55.6, 28.1, 27.6; ^{19}F-NMR ($CDCl_3$, 188 MHz): –111.9- –111.8 (m, 1F); MS (EI): m/z 473 (M^+); IR (KBr): 2981, 2941, 1748, 1725, 1605, 1508, 1494, 1456, 1439, 1396, 1370, 1336, 1299, 1228, 1150, 1119, 1043, 1013, 992, 957, 922, 862, 848, 816, 801, 788, 769, 736 cm^{-1}; Mp: 152-154 °C (CH_2Cl_2)

***N-t*-Butoxycarbonyl-3-phenyl-2-oxindole (3a)**



To a solution of 1-(*t*-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl *t*-butyl carbonate **11a** (756 mg, 1.78 mmol) in MeOH (18 ml), Pd/C (10%, 76 mg) was added and resulting mixture was stirred under hydrogen atmosphere for 18 h at room temperature. The reaction mixture was filtered through Celite to remove Pd/C. After removal of the solvent, **3a** was obtained in 60% yield (331 mg) as white solid. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.62 (s, 9H), 4.71 (s, 1H), 7.14-7.35 (m, 8H), 7.91 (d, *J*=8.0 Hz, 1H); ^{13}C-NMR (CD_3OD, 50.3 MHz): 173.4, 149.1, 140.2, 136.0, 128.6, 128.4, 127.6, 127.2, 124.8, 124.3, 114.9, 84.3, 52.6, 28.2; MS (EI): m/z 309 (M^+); IR (KBr): 3053, 2984, 2925, 1769, 1726, 1607, 1479, 1463, 1371, 1348, 1333, 1291, 1256, 1149, 1089, 1024, 845, 830, 765, 722, 695 cm^{-1}; Mp: 112-113 °C (AcOEt/ Hexane)

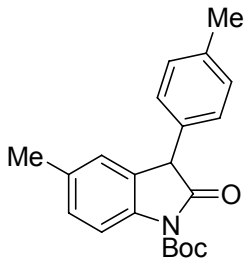
***N-t*-Butoxycarbonyl-3-(4-methylphenyl)-2-oxindole (3b)**



The compound **3b** was prepared by the procedure described above for **3a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.62 (s, 9H), 2.32 (s, 3H), 4.71 (s, 1H), 7.04-7.15 (m, 6H), 7.32-7.36 (m, 1H), 7.90 (d, *J*=8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 173.6, 149.1, 140.2, 137.3, 133.0, 129.3, 128.3, 128.2, 127.4, 124.8, 124.3, 114.9, 84.2, 52.3, 28.2, 21.3; MS m/z (EI): 323 (M^+); IR (KBr): 3045, 2986, 2925, 1770, 1731, 1604, 1514, 1479, 1462, 1345, 1297, 1253, 1150,

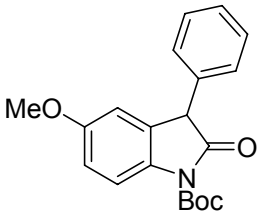
1089, 1023, 849, 774, 755 cm^{-1}; Mp: 113-114 °C (AcOEt/ Hexane)

***N-t*-Butoxycarbonyl-3-(4-methylphenyl)-5-methyl-2-oxindole (3c)**



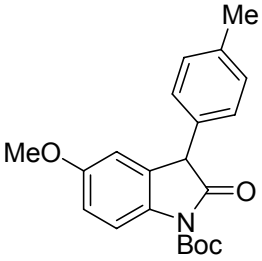
The compound **3c** was prepared by the procedure described above for **3a**. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.61 (s, 9H), 2.30 (s, 3H), 2.33 (s, 3H), 4.64 (s, 1H), 6.95 (s, 1H), 7.04-7.16 (m, 5H), 7.77 (d, *J*=8.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 173.8, 149.1, 137.8, 137.3, 134.0, 133.3, 129.4, 128.8, 128.3, 127.4, 125.3, 114.6, 84.1, 52.4, 28.2, 21.3, 21.2; MS m/z (EI): 337 (M^+); IR (KBr): 2981, 2925, 1768, 1730, 1514, 1488, 1369, 1339, 1300, 1281, 1252, 1155, 1104, 1023, 819, 756 cm^{-1}; Mp: 111-112 °C (AcOEt/ Hexane)

***N-t*-Butoxycarbonyl-5-methoxy-3-phenyl-2-oxindole (3d)**



The compound **3d** was prepared by the procedure described above for **3a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.62 (s, 9H), 3.76 (s, 3H), 4.69 (s, 1H), 6.71 (d, *J*=2.4 Hz, 1H), 6.87 (dd, *J*=8.9, 2.6 Hz, 1H), 7.17-7.34 (m, 3H), 7.83 (d, *J*=9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 173.3, 156.4, 148.9, 135.9, 133.4, 128.5, 128.2, 127.5, 115.7, 113.3, 110.7, 83.9, 55.4, 52.7, 28.1; MS (EI): m/z 339 (M^+), 239 (M^++1–COO^{t}Bu); IR (KBr): 3051, 2984, 2936, 2839, 1766, 1723, 1598, 1489, 1455, 1353, 1302, 1159, 1035, 847, 720 cm^{-1}; Mp: 127-128 °C ($AcOEt_2$/ Hexane)

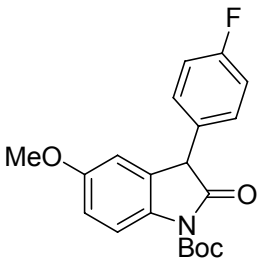
***N-t*-Butoxycarbonyl-5-methoxy-3-(4-methylphenyl)-2-oxindole (3e)**



The compound **3e** was prepared by the procedure described above for **3a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.61 (s, 9H), 2.33 (s, 3H), 3.75 (s, 3H), 4.65 (s, 1H), 6.70 (dd, *J*=1.0, 2.6 Hz, 1H), 6.86 (dd, *J*=2.6, 8.5 Hz, 1H), 7.06 (d, *J*=7.8 Hz, 2H), 7.14 (d, *J*=7.8 Hz, 2H), 7.82 (d, *J*=9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 173.5, 156.5, 149.1, 137.2, 133.5, 132.9, 129.3, 128.5, 128.5, 115.7, 113.3, 110.7, 83.9, 55.5, 52.5, 28.1, 21.2; MS m/z (EI): m/z 353 (M^+), 253 (M^++1–COO^{t}Bu); IR (KBr): 2982, 2937, 1768, 1721, 1597, 1487, 1369, 1353, 1302, 1280, 1252, 1160, 1106, 1040,

850, 820, 779, 742 cm^{-1}; Mp: 115-116 °C (CH_2Cl_2)

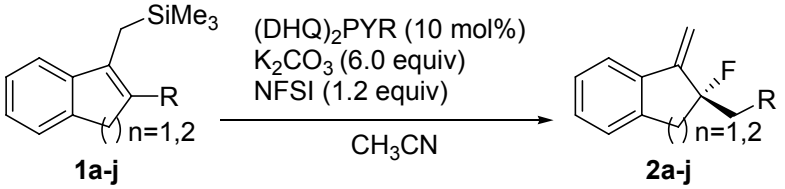
***N*-*t*-Butoxycarbonyl-3-(4-fluorophenyl)-5-methoxy-2-oxindole (3f)**



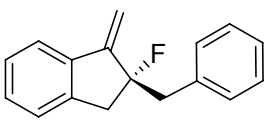
The compound **3f** was prepared by the procedure described above for **3a**. White solid; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.62 (s, 1H), 3.77 (s, 3H), 4.67 (s, 1H), 6.69 (d, *J*=1.8 Hz, 1H), 6.88 (dd, *J*=8.9, 2.9 Hz, 1H), 7.00 (d, *J*=8.6 Hz, 1H), 7.04 (d, *J*=8.6 Hz, 1H), 7.13-7.20 (m, 2H), 7.83 (d, *J*=8.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 173.4, 162.1 (d, *J*=246.2 Hz), 156.7, 149.0, 133.5, 131.6 (d, *J*=3.6 Hz), 130.0 (d, *J*=8.4 Hz), 128.1, 116.0, 115.7 (d, *J*=21.6 Hz), 113.5, 110.8, 84.3, 55.7, 52.1, 28.2; ^{19}F-NMR ($CDCl_3$, 188 MHz): –113.9- –113.8 (m, 1F); MS (EI): m/z 357 (M^+), 257 (M^++1–COO^{t}Bu); IR (KBr): 2932, 1766, 1722, 1597, 1512, 1489, 1352, 1302, 1282, 1230, 1157, 856, 805 cm^{-1}; Mp: 128-129 °C (AcOEt/ Hexane)

General procedure for the catalytic enantioselective fluorination of allylsilanes:

$(DHQ)_2PYR$ (10 mol%) and *N*-fluorobenzensulfonimide (1.2 equiv) in CH_3CN (1.0 ml) were stirred under nitrogen atmosphere at room temperature for 30 min. K_2CO_3 (6.0 equiv) was then added to the solution, and the reaction mixture stirred for 30 min at –20 °C or –40 °C. A solution of allylsilane **1a—j** (0.084–0.131 mmol) in CH_3CN (1.0 ml) was added to the catalyst solution. The reaction was stirred at the temperature for 12h to 5 days with monitoring by TLC. The reaction mixture was filtrated through alumina and the solvent was evaporated under reduced pressure. The residue was purified by alumina PTLC or column chromatography on alumina eluting with hexane to give **2a—j**. The ee of the product **2a—j** was determined by chiral HPLC on CHIRALCEL OD-H or OJ and CHIRALPAK AD-H column.



(*R*)-2-Benzyl-2-fluoro-1-methylen-indan (2a)

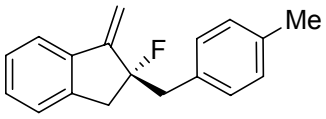


Pale yellow solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 3.00 (dd, *J*=14.5, 28.6 Hz, 1H), 3.07 (dd, *J*=17.2, 25.3 Hz, 1H), 3.21 (dd, *J*=15.1, 17.1 Hz, 1H), 3.32 (dd, *J*=14.5, 17.8 Hz, 1H), 5.28 (d, *J*=4.0 Hz, 1H), 5.71 (d, *J*=4.3 Hz, 1H), 7.17-7.18 (m, 1H),

7.23-7.31 (m, 7H), 7.49-7.51 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 151.1 (d, *J*=17.5 Hz), 140.9 (d, *J*=3.4 Hz), 138.3 (d, *J*=2.9 Hz), 136.0, 130.5 (d, *J*=1.5 Hz), 129.3, 128.1, 127.2, 126.8, 125.2 (d, *J*=1.7 Hz), 121.1, 107.1 (d, *J*=5.6 Hz), 101.8 (d, *J*=184.0 Hz), 44.3 (d, *J*=26.9 Hz), 41.9 (d, *J*=24.4 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –137.3 (dddd, *J*=15.1, 17.8, 25.3, 28.6 Hz, 1F); MS (EI): m/z 238 (M^+); HPLC: (OJ-H, Hexane/ ^{i}PrOH=99/1, 0.5 ml/ min, 254 nm) t_R (minor-isomer)=21.6 min, t_R (major-isomer)=23.9 min (94% ee); $[\alpha]_D^{25}$ +22.3 (*c*=0.240, $CHCl_3$ 94% ee, *R*); IR (KBr): 3061, 3024, 2912, 1809, 1648, 1602, 1496, 1462, 1455, 1417, 1307, 1286, 1209, 1113, 1078, 1049, 1025, 1011, 1001, 902, 875, 795, 780, 764, 734, 700, 623 cm^{-1}; Mp: 60-61 °C (Hexane)

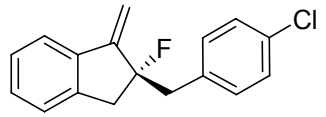
(*R*)-2-Fluoro-2-(4-methylbenzyl)-1-methylen-indan (2b)



Pale yellow solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.33 (s, 3H), 2.95 (dd, *J*=14.5, 29.0 Hz, 1H), 3.06 (dd, *J*=17.2, 25.4 Hz, 1H), 3.20 (dd, *J*=15.8, 16.7 Hz, 1H), 3.28 (dd, *J*=14.6, 17.4 Hz, 1H), 5.29 (d, *J*=4.0 Hz, 1H), 5.71 (d, *J*=4.3 Hz, 1H), 7.11 (d, *J*=7.7 Hz, 2H), 7.17 (d, *J*=7.3 Hz, 3H), 7.23-7.24 (m, 2H), 7.49-7.50 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 151.2 (d, *J*=17.5 Hz), 141.0 (d, *J*=3.3 Hz), 138.3 (d, *J*=2.9 Hz), 136.3, 132.9, 130.4 (d, *J*=1.5 Hz), 129.2, 128.8, 127.2, 125.2 (d, *J*=1.7 Hz), 121.1, 107.0 (d, *J*=5.6 Hz), 101.9 (d, *J*=183.5 Hz), 43.8 (d, *J*=27.0 Hz), 41.8 (d, *J*=24.4 Hz), 21.1; ^{19}F-NMR ($CDCl_3$, 188 MHz): –137.0 (dddd, *J*=15.8, 17.4, 25.4, 29.0 Hz, 1F); MS (EI): m/z 252 (M^+); HPLC: (AD-H, Hexane =100, 1.0 ml/ min, 254 nm) t_R (minor-isomer)=12.1 min, t_R (major-isomer)=14.0 min (95% ee); $[\alpha]_D^{25}$ +6.0 (*c*=0.386, $CHCl_3$ 95% ee); IR (KBr): 3024, 2913, 2853, 1814, 1646, 1604, 1514, 1465, 1420, 1308, 1292, 1227, 1106, 1048, 1023, 1011, 906, 816, 783, 759, 734, 677, 634 cm^{-1}; Mp: 54-55 °C (Hexane)

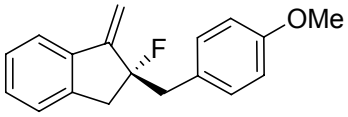
(*R*)-2-(4-Chlorobenzyl)-2-fluoro-1-methylen-indan (2c)



Pale yellow solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.98 (dd, *J*=14.4, 27.9 Hz, 1H), 3.09 (dd, *J*=17.4, 25.2 Hz, 1H), 3.16 (dd, *J*=15.0, 16.8 Hz, 1H), 3.25 (dd, *J*=14.4, 18.6 Hz, 1H), 5.22 (d, *J*=4.2 Hz, 1H), 5.70 (d, *J*=4.0 Hz, 1H), 7.17-7.27 (m, 7H), 7.48-7.50 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 150.8 (d, *J*=17.7 Hz), 140.6 (d, *J*=3.6 Hz), 138.2 (d, *J*=2.9 Hz), 134.4, 132.8, 131.8 (d, *J*=1.7 Hz), 129.4, 128.2, 127.3, 125.2 (d, *J*=1.7 Hz), 121.1, 107.2 (d, *J*=5.6 Hz), 101.6 (d, *J*=184.7 Hz), 43.7 (d, *J*=27.2 Hz), 42.0 (d, *J*=24.3 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –138.2 (dddd, *J*=15.0, 18.6, 25.2, 27.9 Hz, 1F); MS (EI): m/z 272 (M^+); HPLC: (AD-H, Hexane/ ^{i}PrOH=99/1, 0.5 ml/ min, 254 nm) t_R (minor-isomer)=12.6 min, t_R (major-isomer) =14.1 min (94% ee); $[\alpha]_D^{25}$ +23.9 (*c*=0.252, $CHCl_3$ 94% ee); IR (KBr): 3052, 3024, 2925, 2899, 1648, 1492, 1414, 1291, 1219, 1092, 1011, 909, 822, 780, 735, 622 cm^{-1}; Mp: 54-55 °C (Hexane)

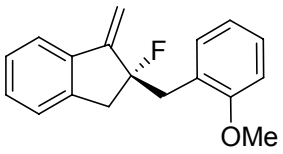
(*R*)-2-Fluoro-2-(4-methoxylbenzyl)-1-methylen-indan (2d)



Pale yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.97 (dd, *J*=14.4, 28.8 Hz, 1H), 3.10 (dd, *J*=16.8, 25.2 Hz, 1H), 3.22 (dd, *J*=15.0, 16.2 Hz, 1H), 3.27 (dd, *J*=14.4, 18.0 Hz, 1H), 5.29 (d, *J*=4.2 Hz, 1H), 5.73 (d, *J*=4.2 Hz, 1H), 6.86 (d, *J*=9.0 Hz, 2H), 7.19-7.21 (m, 1H), 7.22 (d, *J*=8.4 Hz, 2H), 7.25-7.27 (m, 2H), 7.51-7.53 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 58.5, 151.1 (d, *J*=17.5 Hz), 140.9 (d, *J*=3.5 Hz), 138.4 (d, *J*=3.0 Hz), 131.5 (d, *J*=1.5 Hz), 129.2, 128.1 (d, *J*=1.2 Hz), 127.2, 125.2 (d, *J*=1.7 Hz), 121.1, 113.5, 107.0 (d, *J*=5.6 Hz), 102.0 (d, *J*=188.0 Hz), 55.2, 43.5 (d, *J*=27.2 Hz), 41.9 (d, *J*=24.3 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –137.4 (dddd, J=15.0, 18.0, 25.2, 28.8 Hz, 1F); MS (EI): m/z 268 (M^+); HPLC: (AD-H, Hexane/ ^{i}PrOH=95/5, 0.5 ml/ min, 254 nm) t_R (minor-isomer)=10.9 min, t_R (major-isomer)=13.2 min (90% ee); $[\alpha]_D^{25}$ +7.7 (*c*=0.249, $CHCl_3$ 90% ee); IR (neat): 3009, 2947, 2913, 2837, 2252, 1611, 1513, 1465, 1303, 1251, 1179, 1116, 1035, 910, 833, 779, 734, 650 cm^{-1}

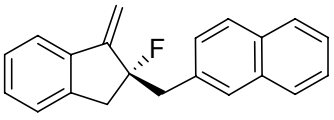
(*S*)-2-Fluoro-2-(2-methoxylbenzyl)-1-methylen-indan (2e)



Pale yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 3.06 (dd, *J*=16.8, 25.2 Hz, 1H), 3.25 (d, *J*=24.0 Hz, 2H), 3.27 (t, *J*=16.2 Hz, 2H), 6.87 (d, *J*=8.4 Hz, 1H), 6.92 (t, *J*=7.5 Hz, 1H), 7.17-7.18 (m, 1H), 7.22-7.25 (m, 3H), 7.36 (d, *J*=7.2 Hz, 1H), 7.49-7.51 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 157.8, 151.5 (d, *J*=17.3 Hz), 141.4, 138.5, 132.3, 129.1, 128.0, 127.0, 125.1, 124.6, 121.0, 120.3, 110.4, 106.5 (d, *J*=5.7 Hz), 102.2 (d, *J*=183.2 Hz), 55.2, 41.8 (d, *J*=24.4 Hz), 36.7 (d, *J*=26.9 Hz); ^{19}F-NMR ($CDCl_3$,188 MHz): –136.3 (ddt, *J*=25.2, 24.0, 16.2 Hz, 1F); HPLC: (OJ-H, Hexane/ ^{i}PrOH=90/10, 1.0 ml/ min, 254 nm) t_R (major-isomer)=8.4 min, t_R (minor-isomer)=10.4 min (93% ee); MS (EI): m/z 268; IR (neat): 3066, 3024, 2923, 2834, 1654, 1602, 1494, 1464, 1291, 1246, 1124, 1051, 1025, 895, 778, 754, 730cm^{-1}

(*R*)-2-Fluoro-2-naphthylmethyl-1-methylen-indan (2f)

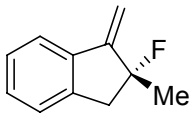


White solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 3.08 (dd, *J*=17.4, 25.8 Hz, 1H), 3.16 (dd, *J*=14.4, 28.8 Hz, 1H), 3.25 (dd, *J*=15.0, 16.8 Hz, 1H), 3.48 (dd, *J*=14.4, 18.0 Hz, 1H), 5.31 (d, *J*=3.6 Hz, 1H), 5.72 (d, *J*=4.2 Hz, 1H), 7.16 (t, *J*=4.2 Hz, 1H), 7.22-7.25 (m, 2H), 7.43-7.48 (m, 3H), 7.51 (dd, *J*=3.0, 6.0 Hz, 1H), 7.71 (s, 1H), 7.77-7.83 (m, 3H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 151.2 (d, *J*=17.5 Hz), 140.9 (d, *J*=3.5 Hz), 138.3 (d, *J*=3.0 Hz), 133.7, 133.3, 132.4, 129.3, 129.2, 128.8 (d, *J*=2.1 Hz), 127.7, 127.6, 127.2, 125.9, 125.6, 125.2 (d, *J*=1.7 Hz), 121.1, 107.2 (d, *J*=5.6 Hz), 102.0 (d, *J*=184.1 Hz), 44.5 (d, *J*=26.7 Hz), 24.4 (d, *J*=42.0 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –136.9 (dddd, *J*=25.8, 28.8, 15.0, 18.0 Hz, 1F);

MS (EI): m/z 288 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=95/5, 0.5 ml/ min, 254 nm) t_R (major-isomer)=13.4 min, t_R (minor-isomer)=14.7 min (91% ee); $[\alpha]_D^{25}$ +11.4 (*c*=0.304, $CHCl_3$ 91% ee); IR (KBr): 3059, 3023, 2922, 2861, 1647, 1599, 1507, 1473, 1464, 1413, 1371, 1308, 1291, 1226, 1207, 1054, 1026, 1010, 904, 888, 822, 779, 759, 738, 686 cm^{-1}; Mp: 87–88 °C (Hexane)

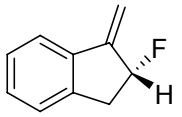
2-Fluoro-2-methyl-1-methylen-indan (2g)



Yellow oil

^{1}H-NMR ($CDCl_3$, 400 MHz): 1.67 (d, *J*=20.8 Hz, 3H), 3.13 (t, *J*=17.8 Hz, 1H), 3.36 (dd, *J*=17.2, 25.6 Hz, 1H), 5.40 (d, *J*=4.4 Hz, 1H), 5.68 (d, *J*=4.8 Hz, 1H), 7.22-7.29 (m, 3H), 7.49-7.52 (m, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 151.6 (d, *J*=17.2 Hz), 140.7, 138.1, 129.1, 127.0, 125.0, 121.0, 106.1 (d, *J*=6.0 Hz), 100.1 (d, *J*=175.9 Hz), 44.9 (d, *J*=25.2 Hz), 25.3 (d, *J*=29.9 Hz); ^{19}F-NMR ($CDCl_3$, 376 MHz): –130.9 (ddq, *J*=17.8, 25.6, 20.8 Hz, 1F); MS (EI): m/z 162 (M^+); HPLC: (OD-H, Hexane=100, 1.0 ml/ min, 254 nm) t_R (major-isomer)=14.2 min, t_R (minor-isomer)=15.9 min (72% ee); $[\alpha]_D^{25}$ –14.2 (*c*=0.200, $CHCl_3$ 72% ee); IR (neat): 2925, 2853, 1735, 1465, 1376, 1260, 1076, 1022, 892, 803, 777, 728 cm^{-1}

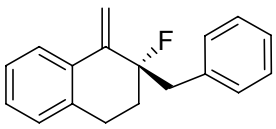
2-Fluoro-1-methylen-indan (2h)



Yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 3.15 (ddd, *J*=2.4, 17.4, 28.2 Hz, 1H), 3.32 (ddd, *J*=6.6, 17.4, 23.4 Hz, 1H), 5.49 (dd, *J*=1.2, 5.4 Hz, 1H), 5.64 (dddt, *J*=54.6, 2.4, 2.6, 1.2 Hz. 1H), 5.76 (dd, *J*=1.2, 5.4 Hz, 1H), 7.23-7.27 (m, 3H), 7.51 (d, *J*=6.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 148.4 (d, *J*=13.6 Hz), 141.9, 138.1 (d, *J*=2.3 Hz), 129.2, 127.2, 125.4 (d, *J*=1.4 Hz), 121.1, 109.4 (d, *J*=7.8 Hz), 94.0 (d, *J*=177.4 Hz), 38.1 (d, *J*=22.9 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –166.5 (ddd, *J*=28.2, 23.4, 54.6 Hz, 1F); MS (EI): m/z 148 (M^+); HPLC: (OD-H, Hhexane=100, 0.5 ml/ min, 254 nm) t_R (major-isomer)=29.5 min, t_R (minor-isomer)=36.0 min (51% ee); IR (neat): 3066, 3031, 2925, 2853, 1734, 1649, 1465, 1420, 1321, 1259, 1217, 1170, 1017, 898, 779, 728 cm^{-1}

(*S*)-2-Benzyl-2-fluoro-1-methylene-1,2,3,4-tetrahydro-naphthalene (2i)

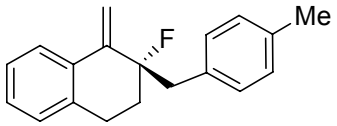


Colorless oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.00-2.10 (m, 2H), 2.91-2.98 (m, 2H), 2.95 (dd, *J*=14.4, 27.0 Hz, 1H), 3.08 (dd, *J*=14.4, 24.0 Hz, 1H), 5.26 (s, 1H), 5.55 (d, *J*=3.0 Hz, 1H), 7.14-7.16 (m, 1H), 7.20 (d, *J*=7.8 Hz, 2H), 7.22-7.25 (m, 3H), 7.28 (t, *J*=7.8 Hz, 2H), 7.59-7.61 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 145.7 (d, *J*=17.4 Hz), 135.9, 134.6 (d, *J*=1.4 Hz),

133.6 (d, *J*=3.9 Hz), 130.6 (d, *J*=1.5 Hz), 128.7, 128.0, 127.9, 126.6, 126.5, 125.1 (d, *J*=2.1 Hz), 108.5 (d, *J*=12.1 Hz), 95.8 (d, *J*=182.7 Hz), 43.1 (d, *J*=24.4 Hz), 32.3 (d, *J*=21.9 Hz), 27.0 (d, *J*=10.9 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –145.3- –145.6 (m, 1F); MS (EI): m/z 252 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=97/3, 1.0 ml/ min, 254 nm) t_R (major-isomer)=9.3 min, t_R (minor-isomer)=13.0 min (81% ee); $[\alpha]_D^{25}$ +30.0 (*c*=0.400, $CHCl_3$ 79% ee); IR (neat): 3062, 3029,2929, 2850, 1956, 1816, 1730, 1631, 1604, 1496, 1485, 1455, 1239, 1216, 1147, 1119, 1082, 1022, 963, 903, 868, 774, 747, 729, 702, 631cm^{-1}

(*S*)-2-Fluoro 2-(4-Methylbenzyl)-1-methylene-1,2,3,4-tetrahydro-naphthalene (2j)

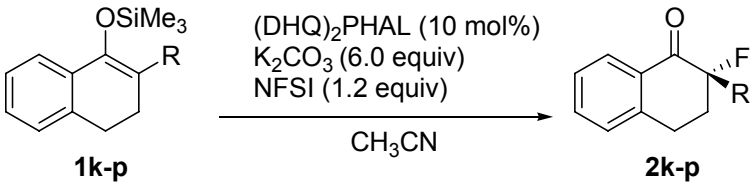


Colorless oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.00-2.07 (m, 2H), 2.33 (s, 3H), 2.90 (dd, *J*=14.4, 27.6 Hz, 1H), 2.94-2.97 (m, 2H), 3.04 (dd, *J*=14.4, 23.4 Hz, 1H), 5.28 (s, 1H), 5.56 (d, *J*=4.2 Hz, 1H), 7.09 (s, 4H), 7.13-7.15 (m, 1H), 7.22-7.24 (m, 2H), 7.59-7.61 (m, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 145.9 (d, *J*=17.2 Hz), 136.1, 134.7, 133.6 (d, *J*=3.9 Hz), 132.8, 130.4 (d, *J*=1.2 Hz), 128.7, 128.7, 128.0, 126.5, 125.1 (d, *J*=1.5 Hz), 108.5 (d, *J*=11.9 Hz), 95.8 (d, *J*=182.4 Hz), 42.7 (d, *J*=24.6 Hz), 32.1 (d, *J*=22.0 Hz), 27.0 (d, *J*=11.0 Hz), 21.1; ^{19}F-NMR ($CDCl_3$, 188 MHz): –145.3- –145.6 (m, 1F); MS (EI): m/z 266 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=95/5, 0.5 ml/ min, 254 nm) t_R (minor-isomer)=17.9 min, t_R (major-isomer)=24.9 min (81% ee); $[\alpha]_D^{25}$ +21.3 (*c*=0.244, $CHCl_3$ 81% ee); IR (neat): 3022, 2923, 2862, 1630, 1515, 1487, 1455, 1238, 1120, 1025, 963, 903, 872, 819, 773, 757, 729, 626 cm^{-1}

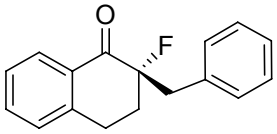
General procedure for the catalytic enantioselective fluorination of silyl enol ethers:

$(DHQ)_2PHAL$ (20 mol%) and *N*-fluorobenzensulfonimide (1.2 equiv) in CH_3CN (1.0 ml) were stirred under nitrogen atmosphere at room temperature for 30 min. K_2CO_3 (6.0 equiv) was then added to the solution, and the reaction mixture was stirred for 30 min at –40 °C. A solution of silyl enol ether **1k—p** (0.075–0.123 mmol) in CH_3CN (1.0 ml) was added to the catalyst solution. The reaction was stirred at the temperature for 6 days to 10 days with monitoring by TLC, it was stopped by the addition of 1N HCl. The reaction mixture was then diluted with AcOEt, washed with saturated aqueous sodium bicarbonate solution, brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hexane/AcOEt or Hexane/CH_2Cl_2 to give **2k—p.** The ee of the product **2k—p** was determined by chiral HPLC on CHIRALCEL OJ-H or OB-H column.



1k-p **2k-p**

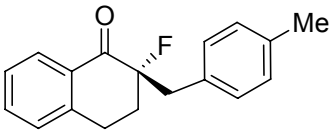
(*S*)-2-Benzyl-2-fluoro-3,4-dihydro-2*H*-naphthalene-1-one (2k)



Yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.10-2.17 (m, 1H), 2.27-2.33 (m, 1H), 3.01-3.09 (m, 3H), 3.32 (dd, *J*=15.0, 17.0 Hz, 1H), 7.26-7.33 (m, 6H), 7.37 (t, *J*=7.6 Hz, 1H), 7.54 (t, *J*=7.5 Hz, 1H), 8.09 (d, *J*=7.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 194.0 (d, *J*=18.0 Hz), 142.7, 134.5, 134.1, 130.9, 130.5, 130.5, 128.7, 128.4, 127.1, 127.1, 95.1 (d, *J*=184.8 Hz), 39.4 (d, *J*=23.0 Hz), 31.3 (d, *J*=22.9 Hz), 25.9 (d, *J*=9.8 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –156.7 (dddd, *J*=5.3, 15.7, 15.8, 31.6 Hz, 1F); MS (EI): m/z 254 (M^+); HPLC: (OJ-H, Hexane/ ^{i}PrOH=90/10, 0.5 ml/ min, 254 nm) t_R (major-isomer-isomer)=30.3 min, t_R (minor-isomer)=37.0 min (82% ee); $[\alpha]_D^{25}$ +26.5 (*c*=0.490, $CHCl_3$ 74% ee, *S*), Lit[4]. $[\alpha]_D^{26}$ –32.5 (*c*=0.578, $CHCl_3$ 88% ee, *R*); IR (neat): 3063, 3029, 2927, 2855, 1698, 1602, 1496, 1455, 1294, 1223, 1083, 918, 758, 704 cm^{-1}

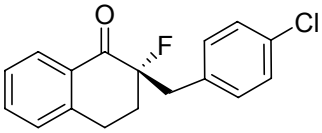
(*S*)-2-Fluoro-2-(4-methylbenzyl)-3,4-dihydro-2*H*-naphthalene-1-one (2l)



Yellow oil

^{1}H-NMR ($CDCl_3$, 400 MHz): 2.10-2.19 (m, 1H), 2.25-2.31 (m, 1H), 2.34 (s, 3H), 2.96-3.08 (m, 3H), 3.27 (dd, *J*=14.8, 17.2 Hz, 1H), 7.13 (d, *J*=8.4 Hz, 2H), 7.17 (d, *J*=8.0 Hz, 2H), 7.26 (d, *J*=7.6 Hz, 1H), 7.37 (t, *J*=7.4 Hz, 1H), 7.53 (dt, *J*=1.2, 7.4 Hz, 1H), 8.09 (d, *J*=8.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): 194, 2 (d, *J*=17.5 Hz), 142.7, 136.7, 134.1, 131.3, 130.9, 130.3 (d, *J*=1.1 Hz), 129.1, 128.7, 128.3, 127.1, 95.2 (d, *J*=184.8 Hz), 38.9 (d, *J*=22.9 Hz), 31.3 (d, *J*=22.9 Hz), 25.9 (d, *J*=9.6 Hz), 21.1; ^{19}F-NMR ($CDCl_3$, 188 MHz): –156.5- –156.9 (m, 1F); MS (EI): m/z 268 (M^+); HPLC: (OJ-H, Hexane/ ^{i}PrOH=90/10, 1.0 ml/ min, 254 nm) t_R (major-isomer)=22.0 min, t_R (minor-isomer) =41.9 min (82% ee); $[\alpha]_D^{25}$ +32.3 (*c*=0.228, $CHCl_3$ 82% ee); IR (neat): 2925, 1698, 1603, 1521, 1455,1296, 1223, 918, 756 cm^{-1}

(*S*)-2-(Chlorobenzyl)-2-fluoro-3,4-dihydro-2*H*-naphthalene-1-one (2m)



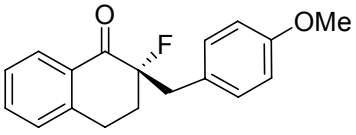
Yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.09-2.16 (m, 1H), 2.29-2.35 (m, 1H), 2.99-3.12 (m, 3H), 3.30 (dd, *J*=14.8, 17.6 Hz, 1H), 7.21 (d, *J*=8.2 Hz, 1H), 7.26-7.30 (m, 4H), 7.38 (t, *J*=7.5 Hz, 1H), 7.55 (t, *J*=7.5 Hz, 1H), 8.08 (d, *J*=7.7 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 193.6 (d, *J*=17.8 Hz), 142.6, 134.2, 131.8 (d, *J*=1.3 Hz), 130.8, 128.8, 128.6, 128.4, 127.2, 94.9 (d, *J*=184.7 Hz), 38.8 (d, *J*=23.0 Hz), 31.4 (d, *J*=22.6 Hz), 25.8 (d, *J*=9.5 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –157.0- –157.4 (m, 1F); MS (EI): m/z 288 (M^+); HPLC: (OJ-H, Hexane/ ^{i}PrOH=95/5, 1.0 ml/ min, 254 nm) t_R (major-isomer)=23.9 min, t_R (minor-isomer)=26.3 min (86% ee); $[\alpha]_D^{25}$ +25.6 (*c*=0.232, $CHCl_3$ 71% ee); IR (neat):

[4] Y. Takeuchi, T. Suzuki, A, Satoh, T. Shiragami, N. Shibata, *J. Org. Chem*. **1999**, *64*, 5708–5711.

2932, 1695, 1603, 1493, 1224, 1093, 1014, 918, 741 cm^{-1}

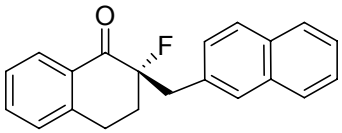
(*S*)-2-Fluoro-2-(4-methoxybenzyl)-3,4-dihydro-2*H*-naphthalene-1-one (2n)



Yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.11-2.18 (m, 1H), 2.27-2.33 (m, 1H), 3.00 (dd, *J*=14.4, 31.8 Hz, 1H), 3.05-3.07 (m, 2H), 3.25 (dd, *J*=15.0, 17.4 Hz, 1H), 3.80 (s, 3H), 6.86 (d, *J*=9.0 Hz, 2H), 7.20 (d, *J*=8.4 Hz, 2H), 7.26 (d, *J*=7.8 Hz, 1H), 7.37 (t, *J*=7.2 Hz, 1H), 7.54 (dt, *J*=1.2, 7.2 Hz, 1H), 8.09 (dd, *J*=0.6, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 194.2 (d, *J*=194.2 Hz), 158.7, 142.7, 134.1, 131.4, 130.9, 128.7, 128.3, 127.1, 126.4, 113.8, 95.3 (d, *J*=184.2 Hz), 38.5 (d, *J*=23.2 Hz), 31.3 (d, *J*=22.6 Hz), 25.9 (d, *J*=10.0 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –156.9- –156.5 (m, 1F); MS (EI): m/z 284 (M^+); HPLC: (OJ-H, Hexane/ ^{i}PrOH=90/10, 1.0 ml/ min, 254 nm) t_R (minor-isomer)=22.0 min, t_R (major-isomer)=24.4 min (85% ee); $[\alpha]_D^{25}$ +32.7 (*c*=0.763, $CHCl_3$ 85% ee); IR (neat): 2933, 2834, 1698, 1604, 1514, 1455, 1300, 1253, 1179, 1034, 919, 835, 782, 760, 742 cm^{-1}

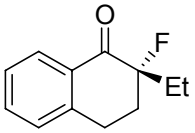
(*S*)-2-Fluoro-2-naphthylmethyl-3,4-dihydro-2*H*-naphthalene-1-one (2o)



White solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.13-2.19 (m, 1H), 2.29-2.36 (m, 1H), 3.08-3.10 (m, 2H), 3.22 (dd, *J*=15.0, 33.0 Hz, 1H), 3.49 (dd, *J*=15.0, 16.8 Hz, 1H), 7.27 (d, *J*=7.8 Hz, 1H), 7.38 (t, *J*=7.2 Hz, 1H), 7.44-7.49 (m, 3H), 7.55 (dt, *J*=1.2, 8.1 Hz, 1H), 7.73 (s, 1H), 7.80-7.84 (m, 3H), 8.12 (dd, *J*=1.2, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 194.0 (d, *J*=17.8 Hz), 142.8, 134.2, 133.3, 132.5, 132.2, 130.9, 129.2, 128.8, 128.5 (d, *J*=1.7 Hz), 128.4, 128.0, 127.6, 127.6, 127.2, 126.1, 125.8, 95.3 (d, *J*=184.7 Hz), 39.5 (d, *J*=22.9 Hz), 31.4 (d, *J*=22.6 Hz), 25.9 (d, *J*=9.7 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –156.5- –156.1 (m, 1F); MS (EI): m/z 304 (M^+); HPLC: (OJ-H, Hexane/ ^{i}PrOH=90/10, 1.0 ml/ min, 254 nm) t_R (minor-isomer)=29.5 min, t_R (major-isomer)=37.9 min (84% ee); $[\alpha]_D^{25}$ +32.2 (*c*=0.450, $CHCl_3$ 84% ee); IR (KBr): 3058, 2959, 2930, 2901, 2850, 1687, 1601, 1508, 1457, 1432, 1371, 1224, 1159, 1137, 2052, 962, 946, 927, 910, 892, 854, 827, 819, 754, 739, 688, 660; Mp: 80-81 °C (CH_2Cl_2)

(*R*)-2-Ethyl-2-fluoro-3,4-dihydro-2*H*-naphthalene-1-one (2p)

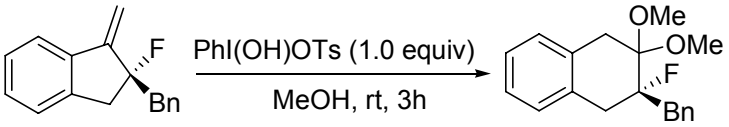


Yellow oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 1.04 (t, *J*=7.2 Hz, 3H), 1.86 (dq, *J*=24.6, 7.2 Hz, 1H), 1.95 (dq, *J*=21.6, 7.2 Hz, 1H), 2.34-2.46 (m, 2H), 3.02 (ddd, *J*=5.4, 10.8, 16.8 Hz, 1H), 3.12 (td, *J*=4.2, 17.4 Hz, 1H), 7.25 (d, *J*=7.8 Hz, 1H), 7.35 (t, *J*=7.8 Hz, 1H), 7.51 (dt, *J*=1.2, 7.8 Hz, 1H), 8.06 (dt, *J*=0.6, 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 194.9 (d,

J=17.5 Hz), 142.5, 133.9, 131.1, 128.6, 128.2 (d, *J*=1.5 Hz), 127.0, 96.0 (d, *J*=184.2 Hz), 31.9 (d, *J*=22.6 Hz), 26.4 (d, *J*=24.6 Hz), 26.4, 8.0 (d, *J*=4.8 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –161.7- –162.1 (m, 1F); MS (EI): m/z 192 (M^+); HPLC: (OB-H, Hexane/ ^{i}PrOH=99/1, 1.0 ml/ min, 254 nm) t_R (major-isomer)=19.0 min, t_R (minor-isomer)=24.6 min (67% ee); $[\alpha]_D^{25}$ +32.3 (*c*=0.417, $CHCl_3$ 67% ee); IR (neat): 3066, 3024, 2938, 2876, 1702, 1603, 1456, 1303, 1274, 1223, 1195, 1146, 1097, 983, 935, 900.6, 854, 774, 742, 691, 641 cm^{-1}

(*R*)-2-Benzyl-2-fluoro-3,3-dimethoxy-1,2,3,4-tetrahydro-naphthalene (5a)



2a (99% ee) **5a** (74%, 99% ee)

[Hydroxy(tosyloxy)iodo]benzene[5] (12.7 mg, 0.031 mmol) was added to a solution of **(*R*)-2a** (7.4 mg, 99% ee) in MeOH (0.24 ml). The solution was stirred at room temperature for 3 h with monitoring by TLC, it was stopped by the addition of H_2O. The reaction mixture was then diluted with CH_2Cl_2, washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/AcOEt) to give **5a** in 74% yield with 99% ee.

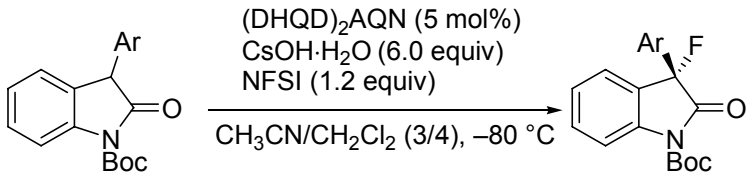
Colorless oil

^{1}H-NMR ($CDCl_3$, 600 MHz): 2.70 (dd, *J*=14.4, 40.2 Hz, 1H), 2.76 (dd, *J*=13.2, 16.2 Hz, 1H), 2.99 (t, *J*=15.6 Hz, 1H), 3.04 (d, *J*=17.4 Hz, 1H), 3.40 (dd, *J*=4.8, 17.4 Hz, 1H), 3.43 (dd, *J*=11.4, 14.4 Hz, 1H), 3.46 (d, *J*=2.4 Hz, 3H), 3.47 (d, *J*=1.8 Hz, 3H), 7.00 (d, *J*=6.0 Hz, 1H), 7.11-7.18 (m, 5H), 7.24-7.31 (m, 3H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 135.8, 133.6, 133.6, 132.5, 131.0, 128.7 (d, *J*=21.9 Hz), 128.0, 126.5 (d, *J*=19.8 Hz), 126.3, 100.4 (d, *J*=17.7 Hz), 98.8 (d, *J*=98.8 Hz), 50.7 (d, *J*=3.6 Hz), 50.2 (d, *J*=2.9 Hz), 38.5 (d, *J*=22.0 Hz), 36.4 (d, *J*=24.3 Hz), 35.6 (d, *J*=4.1 Hz); ^{19}F-NMR ($CDCl_3$, 188 MHz): –164.4- –163.8 (m, 1F); MS (EI): m/z 300 (M^+); HPLC: (AD-H, Hexane/ ^{i}PrOH=99/1, 1.0 ml/ min, 254 nm) t_R (minor-isomer)=5.7 min, t_R (major-isomer)=8.7 min (99% ee); $[\alpha]_D^{25}$ +14.9 (*c*=0.230, $CHCl_3$ 99% ee); IR (neat): 3052, 3024, 2924, 2855, 1604, 1496, 1455, 1337, 1213, 1146, 1118, 1055, 909, 881, 846, 826, 742, 710, 657 cm^{-1}

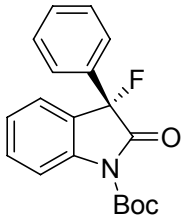
General procedure for the catalytic enantioselective fluorination of oxindole:

$(DHQD)_2AQN$ (5 mol%) and *N*-fluorobenzensulfonimide (1.2 equiv) in CH_3CN/CH_2Cl_2 (3/4, 1.0 ml) were stirred under argon atmosphere at room temperature for 30 min. $CsOH{\cdot}H_2O$ (6.0 equiv) was then added to the solution, and the reaction mixture stirred for 30 min at –80 °C. A solution of oxindole **3a—f** (0.100–0.145 mmol) in CH_3CN/CH_2Cl_2 (3/4, 1 ml) was added to the catalyst solution. The solution was stirred at the temperature for 5–5.5 days with monitoring by TLC, and it was stopped by the addition of water. The reaction mixture was then diluted with AcOEt, washed with 2N HCl, saturated aqueous sodium bicarbonate solution, brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/AcOEt, 1% Et_3N) to give **4a—f**. The ee of the product **4a—f** was determined by chiral HPLC on CHIRALCEL OD-H column.

[5] M. W. Justik. G. F. Koser, *Molecules* **2005**, *10*, 217–225.



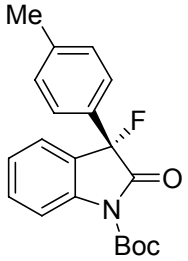
(*S*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-phenyl-2-oxindole (4a)



White solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 1.62 (s, 9H), 7.28 (d, *J*=7.6 Hz, 1H), 7.35-740 (m, 6H), 7.50-7.52 (m, 1H), 8.01 (d, *J*=8.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 170.1 (d, *J*=25.1 Hz), 148.9, 141.0 (d, *J*=5.1 Hz), 135.6 (d, *J*=27.9 Hz), 131.8 (d, *J*=3.1 Hz), 129.5, 128.6, 126.3, 126.2, 125.5 (d, *J*=17.8 Hz), 125.3 (d, *J*=2.7 Hz), 115.6, 92.7 (d, *J*=187.8 Hz), 85.0, 28.0; ^{19}F-NMR ($CDCl_3$, 188 MHz): –144.6 (s, 1F); MS (EI): m/z 327 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (minor-isomer)=27.5 min, t_R (major-isomer)=29.9 min (87% ee); $[\alpha]_D^{25}$ +82.9 (*c*=0.450, $CHCl_3$ 87% ee), Lit.[3] $[\alpha]_D^{27}$ –70.4 (*c*=0.77, $CHCl_3$ 79% ee, *R*); IR (KBr): 3062, 2981, 2926, 2854, 1784, 1733, 1610, 1481, 1467, 1346, 1290, 1252, 1150, 1099, 1003, 838, 766, 695 cm^{-1}; Mp: 70-72 °C (CH_2Cl_2/ Hexane)

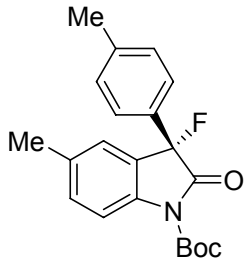
(*S*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-2-oxindole (4b)



White solid

^{1}H-NMR ($CDCl_3$, 600 MHz): 1.61 (s, 9H), 2.35 (s, 3H), 7.19 (d, *J*=7.9 Hz, 2H), 7.26-7.28 (m, 1H), 7.25 (d, *J*=7.9 Hz, 2H), 7.37 (d, *J*=6.7 Hz, 1H), 7.49-7.51 (m, 1H), 8.00 (d, *J*=8.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 170.3 (d, *J*=25.5 Hz), 148.9, 140.9 (d, *J*=5.2 Hz), 139.6 (d, *J*=1.7 Hz), 132.6 (d, *J*=28.0 Hz), 131.7 (d, *J*=3.0 Hz), 129.3, 126.3 (d, *J*=5.6 Hz), 126.2, 125.6 (d, *J*=17.8 Hz), 125.2 (d, *J*=2.7 Hz), 115.6, 92.6 (d, *J*=187.4 Hz), 84.9, 28.0, 21.0; ^{19}F-NMR ($CDCl_3$, 188 MHz): –143.8 (s, 1F); MS (EI): m/z 341 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (minor-isomer)=24.6 min, t_R (major-isomer)=29.9 min (83% ee); $[\alpha]_D^{25}$ +73.5 (*c*=0.217, $CHCl_3$ 83% ee), Lit.[3] $[\alpha]_D^{26}$ –70.7 (*c*=0.685, $CHCl_3$ 85% ee, *R*), IR (KBr): 2992, 2932, 1788, 1737, 1609, 1481, 1344, 1291, 1251, 1151, 1098, 1003, 815, 773, 754 cm^{-1}; Mp: 91-93 °C (CH_2Cl_2/ Hexane)

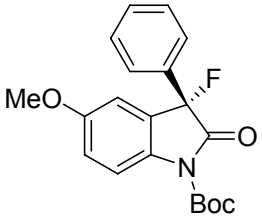
(*S*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-5-methyl-2-oxindole (4c)



White solid

^{1}H-NMR ($CDCl_3$, 200 MHz): 1.60 (s, 9H), 2.35 (s, 6H), 7.17 (d, *J*=7.8 Hz, 2H), 7.22-7.30 (m, 4H), 7.85 (d, *J*=8.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 170.1 (d, *J*=25.2 Hz), 148.7, 139.3 (d, *J*=2.0 Hz), 138.3 (d, *J*=5.2 Hz), 134.9 (d, *J*=2.8 Hz), 132.6 (d, *J*=28.0 Hz), 132.0 (d, *J*=2.8 Hz), 129.1, 126.4, 126.0 (d, *J*=5.6 Hz), 125.4 (d, *J*=18.0 Hz), 115.3, 92.8 (d, *J*=186.8 Hz), 84.7, 28.2, 21.4, 21.2; ^{19}F-NMR ($CDCl_3$, 188 MHz): –144.2 (s, 1F); MS (EI): m/z 355 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.5 ml/ min, 210 nm) t_R (minor-isomer)=12.5 min, t_R (major-isomer)=15.5 min (81% ee); $[\alpha]_D^{25}$ +95.2 (*c*=0.500, $CHCl_3$ 81% ee); IR (KBr): 2924, 2853, 1779, 1741, 1598, 1483, 1369, 1335, 1280, 1253, 1150, 1116, 961, 886, 835, 779, 761, 739 cm^{-1}; Mp: 109-111 °C (CH_2Cl_2/ Hexane)

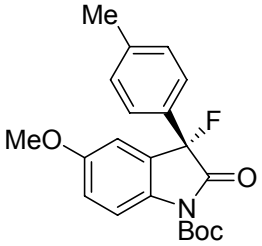
(*S*)-*N*-*t*-Butoxycarbonyl-3-fluoro-5-methoxy-3-phenyl-2-oxindole (4d)



Colorless oil

^{1}H-NMR ($CDCl_3$, 200 MHz): 1.60 (s, 9H), 3.79 (s, 3H), 6.89 (t, *J*=2.3 Hz, 1H), 7.04 (dt, *J*=9.0, 2.3 Hz, 1H), 7.33-7.41 (m, 5H), 7.91 (dd, *J*=9.0, 1.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz): 170.2 (d, *J*=25.2 Hz), 157.4 (d, *J*=2.9 Hz), 149.0, 135.6 (d, *J*=27.8 Hz), 134.1 (d, *J*=5.3 Hz), 129.5, 128.6, 126.6 (d, *J*=17.5 Hz), 126.2 (d, *J*=5.9 Hz), 117.4 (d, *J*=3.0 Hz), 116.8, 115.4, 92.9 (d, *J*=188.6 Hz), 84.8, 55.7, 28.0; ^{19}F-NMR ($CDCl_3$, 188 MHz): –145.4 (s, 1F); MS (EI): m/z 357 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (minor-isomer)=45.0 min, t_R (major-isomer)=48.4 min (84% ee); $[\alpha]_D^{25}$ +107.7 (*c*=0.554, $CHCl_3$ 84% ee); IR (neat): 2983, 1784, 1732, 1601, 1488, 1394, 1370, 1336, 1280, 1251, 1153, 1119, 1013, 891, 845, 768, 720, 696, 650 cm^{-1}

(*S*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-5-methoxy-2-oxindole (4e)

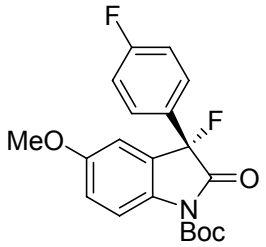


White solid

H-NMR ($CDCl_3$, 200 MHz): 1.60 (s, 9H), 2.35 (s, 3H), 3.78 (s, 3H), 6.89 (t, *J*=2.4 Hz, 1H), 7.01 (dt, *J*=9.0, 2.4 Hz, 1H),

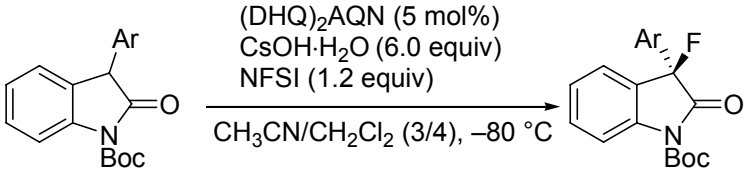
7.17 (d, *J*=8.4 Hz, 2H), 7.25 (d, *J*=8.6 Hz, 2H), 7.90 (dd, *J*=9.0, 1.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 150.9 MHz):170.3 (d, *J*=25.4 Hz), 157.3 (d, *J*=2.7 Hz), 149.0, 139.6, 134.1 (d, *J*=5.3 Hz), 132.6 (d, *J*=27.9 Hz), 129.3, 126.6 (d, *J*=17.4 Hz), 126.2 (d, *J*=5.6 Hz), 117.3 (d, *J*=2.9 Hz), 116.8, 92.9 (d, *J*=188.0 Hz), 84.7, 55.7, 28.0, 21.2; ^{19}F-NMR ($CDCl_3$, 188 MHz): –144.6 (s, 1F); MS m/z 371 (M^+); HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (minor-isomer)=31.5 min, t_R (major-isomer)=35.7 min (79% ee); $[\alpha]_D^{25}$ +102.1 (*c*=0.398, $CHCl_3$ 79% ee); IR (neat): 2981, 1785, 1733, 1602, 1493, 1395, 1371, 1336, 1298, 1281, 1250, 1153, 1110, 1042, 1013, 968, 892, 847, 824, 792, 732, 695, 615 cm^{-1}; Mp 129-130 °C (CH_2Cl_2/ Hexane)

(*S*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-fluorophenyl)-5-methoxy-2-oxindole (4f)

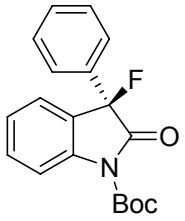


White solid

^{1}H-NMR ($CDCl_3$, 200 MHz): 1.61 (s, 9H), 3.80 (s, 3H), 6.88 (t, *J*=2.2 Hz, 1H), 6.99-7.11 (m, 3H), 7.31-7.38 (m, 2H), 7.91 (dd, *J*=1.4, 9.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 50.3 MHz): 169.7 (d, *J*=25.6 Hz), 163.2 (dd, *J*=2.0, 263.7 Hz), 157.1 (d, *J*=2.8 Hz), 148.6, 133.9 (d, *J*=5.2 Hz), 131.3 (dd, *J*=3.2, 28.3 Hz), 128.3 (dd, *J*=6.3, 8.4 Hz), 125.9 (d, *J*=17.6 Hz), 117.3 (d, *J*=3.2 Hz), 116.7, 115.5 (d, *J*=21.5 Hz), 111.3, 92.3 (d, *J*=188.0 Hz), 84.9, 55.8, 28.2; ^{19}F-NMR ($CDCl_3$, 188 MHz): –143.1 (s, 1F), –111.2- –111.0 (m, 1F); MS (EI): m/z 375 (M^+), 275 (M^++1–Boc); HPLC: (CHIRALCEL OD-H, Hexane/ ^{i}PrOH=99.5/0.5, 1.0 ml/ min, 254 nm) t_R (minor-isomer)=10.5 min, t_R (major-isomer)=14.1 min (81% ee); $[\alpha]_D^{25}$ +114.6 (*c*=0.442, $CHCl_3$ 81% ee); IR (KBr): 2979, 2932, 1834, 1781, 1735, 1602, 1510, 1493, 1372, 1335, 1281, 1251, 1153, 1127, 1013, 800, 768, 741 cm^{-1}; Mp: 113-114 °C (CH_2Cl_2/ Hexane)



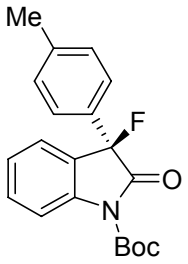
(*R*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-phenyl-2-oxindole (4a)



White solid

HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (major-isomer)=24.5 min, t_R (minor-isomer)=26.3 min (85% ee); $[\alpha]_D^{25}$ –69.8 (*c*=0.648, $CHCl_3$ 85% ee)

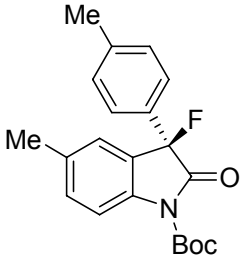
(*R*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-2-oxindole (4b)



White solid

HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (major-isomer)=23.8 min, t_R (minor-isomer)=27.9 min (86% ee); $[\alpha]_D^{25}$ –74.1 (*c*=0.520, $CHCl_3$ 86% ee)

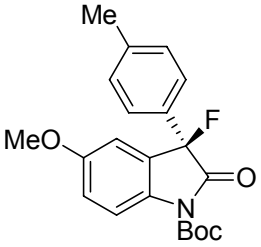
(*R*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-5-methyl-2-oxindole (4c)



White solid

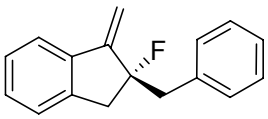
HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.5 ml/ min, 210 nm) t_R (major-isomer)=11.1 min, t_R (minor-isomer)=13.4 min (84% ee); $[\alpha]_D^{25}$ –91.0 (*c*=0.606, $CHCl_3$ 84% ee)

(*R*)-*N*-*t*-Butoxycarbonyl-3-fluoro-3-(4-methylphenyl)-5-methoxy-2-oxindole (4e)



White foam

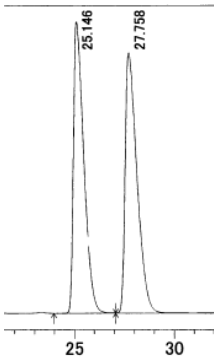
HPLC: (OD-H, Hexane/ ^{i}PrOH=99/1, 0.25 ml/ min, 254 nm) t_R (minor-isomer)=29.4 min, t_R (major-isomer)=33.7 min (85% ee); $[\alpha]_D^{25}$ –107.3 (*c*=0.434, $CHCl_3$ 85% ee)

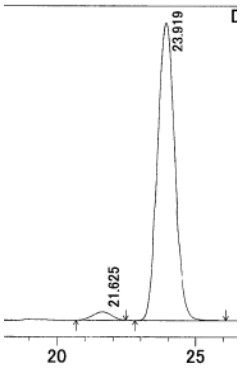


2a

HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.5 ml/min, λ=254 nm)

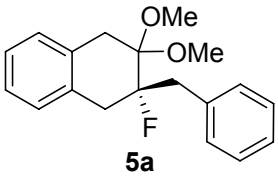




racemic compound of **2a**

No.	tR (min)	Area (%)	High (%)
1	25.1	50.460	47.035
2	27.8	49.540	52.965

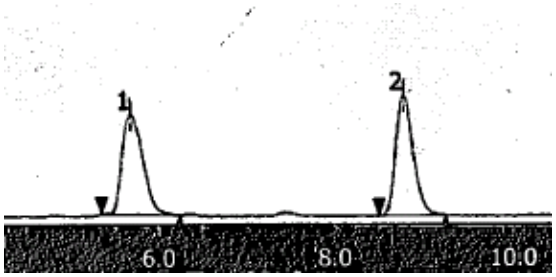
No.	tR (min)	Area (%)	High (%)
1	21.6	2.980	2.743
2	23.9	97.020	97.257

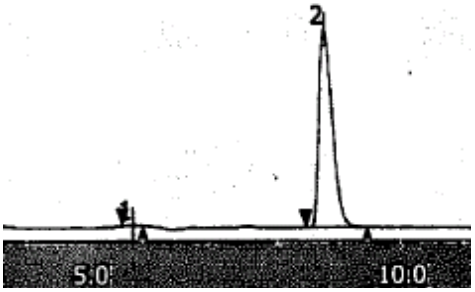


5a

HPLC using an AD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 1.0 ml/min, λ=207 nm)

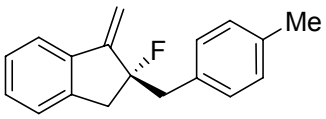




racemic compound of **5a**

No.	tR (min)	Area (%)	High (%)
1	5.7	49.932	45.488
2	8.8	50.068	54.512

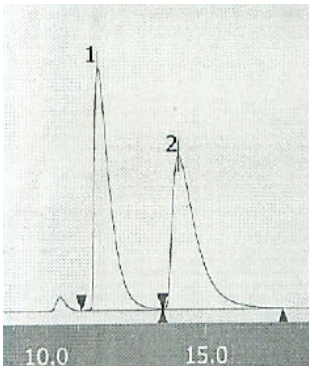
No.	tR (min)	Area (%)	High (%)
1	5.7	0.477	0.787
2	8.7	99.523	99.213

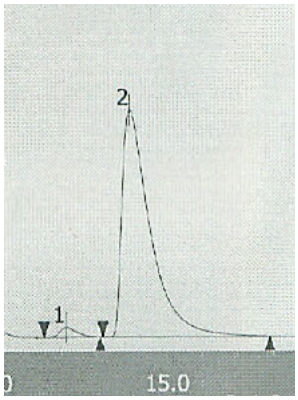


2b

HPLC using an AD-H

(*n*-Hexane=100, flow rate 1.0 ml/min, λ=254 nm)

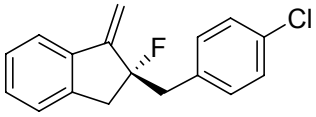




racemic compound of **2b**

No.	tR (min)	Area (%)	High (%)
1	11.7	50.290	61.357
2	14.2	49.710	38.643

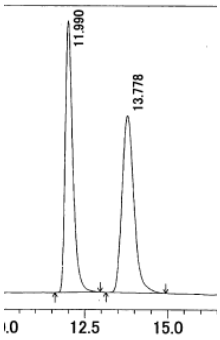
No.	tR (min)	Area (%)	High (%)
1	12.1	2.624	4.211
2	14.0	97.376	95.789

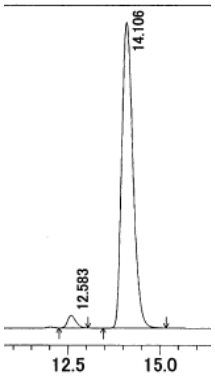


2c

HPLC using an AD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.5 ml/min, λ=254 nm)

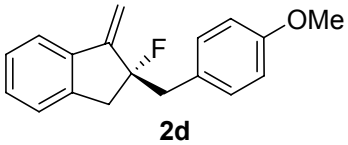




racemic compound of **2c**

No.	tR (min)	Area (%)	High (%)
1	12.0	49.475	60.592
2	13.8	50.525	39.408

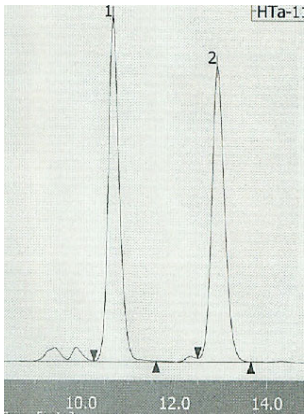
No.	tR (min)	Area (%)	High (%)
1	12.6	2.981	3.935
2	14.1	97.019	96.065



2d

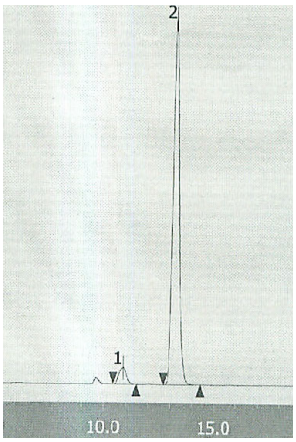
HPLC using an AD-H

(*n*-Hexane/^{i}PrOH=95/5, flow rate 0.5 ml/min, λ=254 nm)

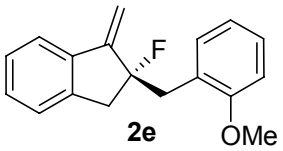


racemic compound of **2d**

No.	tR (min)	Area (%)	High (%)
1	10.7	50.003	53.804
2	12.9	49.997	46.196



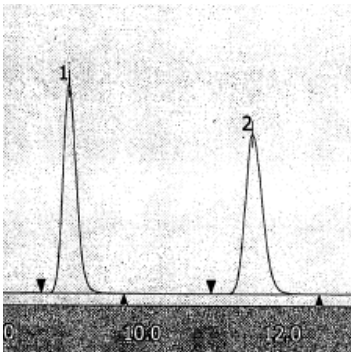
No.	tR (min)	Area (%)	High (%)
1	10.9	5.198	4.393
2	13.2	94.802	95.607



2e

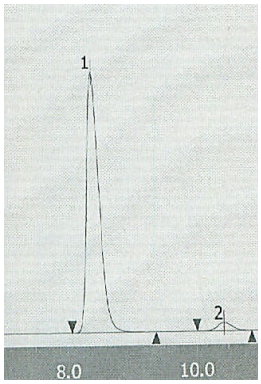
HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=90/10, flow rate 1.0 ml/min, λ=254 nm)

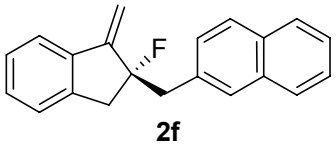


racemic compound of **2e**

No.	tR (min)	Area (%)	High (%)
1	9.0	49.752	56.788
2	11.6	50.248	43.212



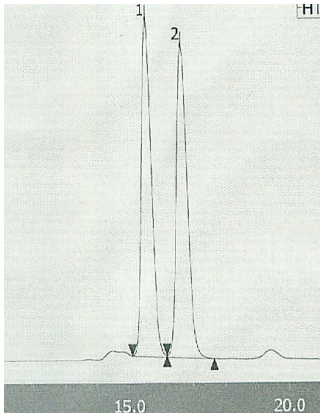
No.	tR (min)	Area (%)	High (%)
1	8.4	96.312	94.752
2	10.4	3.688	5.248

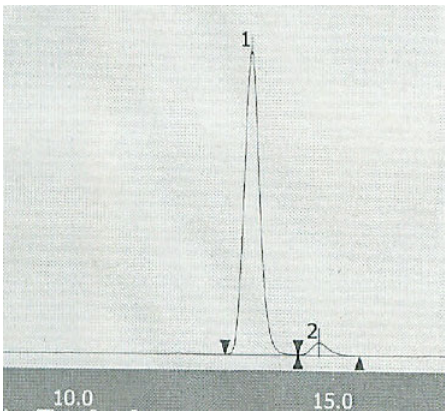


2f

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=95/5, flow rate 0.5 ml/min, λ=254 nm)

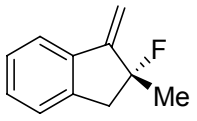




racemic compound of **2f**

No.	tR (min)	Area (%)	High (%)
1	15.6	49.644	51.950
2	16.7	50.356	48.050

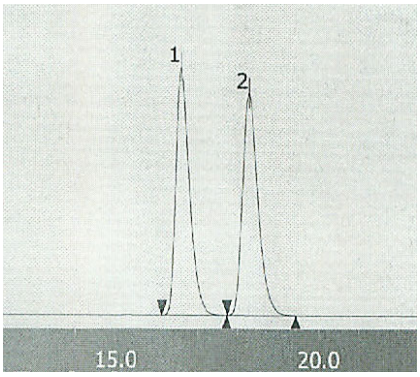
No.	tR (min)	Area (%)	High (%)
1	13.4	95.490	96.066
2	14.7	4.510	3.934

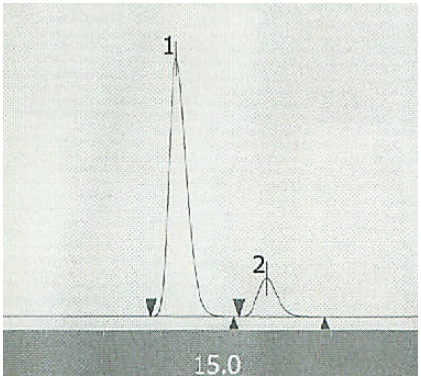


2g

HPLC using an OD-H

(*n*-Hexane=100, flow rate 1.0 ml/min, λ=254 nm)

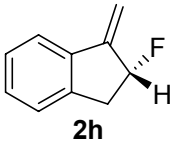




racemic compound of **2g**

No.	tR (min)	Area (%)	High (%)
1	16.6	49.985	52.773
2	18.3	50.015	47.227

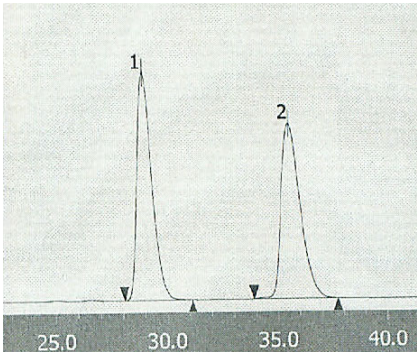
No.	tR (min)	Area (%)	High (%)
1	14.3	85.969	82.014
2	15.9	14.031	12.986

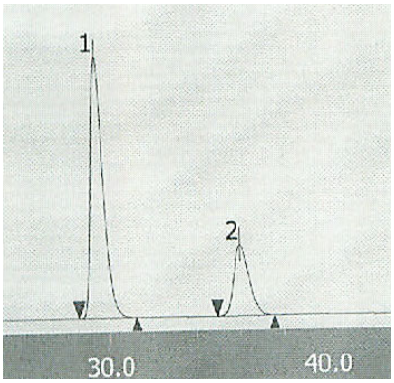


2h

HPLC using an OD-H

(*n*-Hexane=100, flow rate 0.5 ml/min, λ=254 nm)

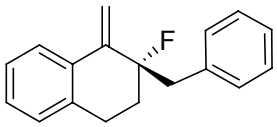




racemic compound of **2h**

No.	tR (min)	Area (%)	High (%)
1	29.0	49.951	56.587
2	35.6	50.049	43.413

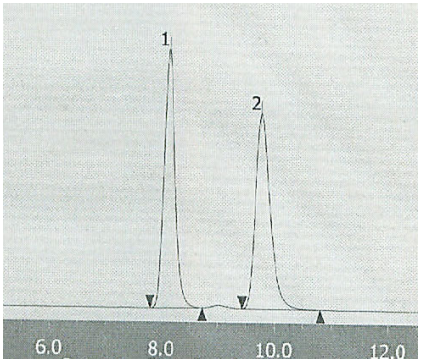
No.	tR (min)	Area (%)	High (%)
1	29.5	75.577	78.680
2	36.0	24.423	21.320

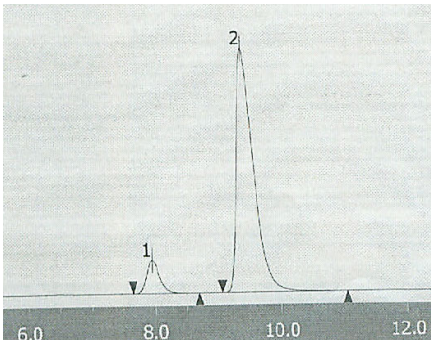


2i

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=97/3, flow rate 1.0 ml/min, λ=254 nm)

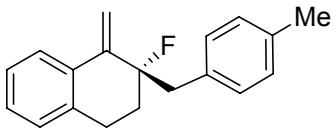




racemic compound of **2i**

No.	tR (min)	Area (%)	High (%)
1	8.1	50.132	57.046
2	9.7	49.868	42.954

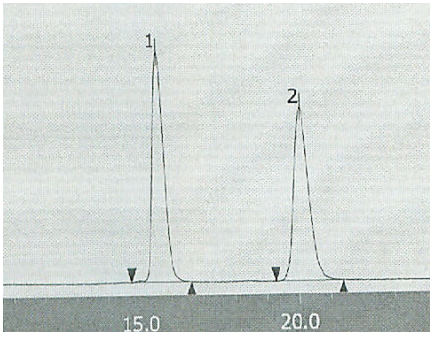
No.	tR (min)	Area (%)	High (%)
1	8.0	9.358	11.993
2	9.4	90.642	88.007

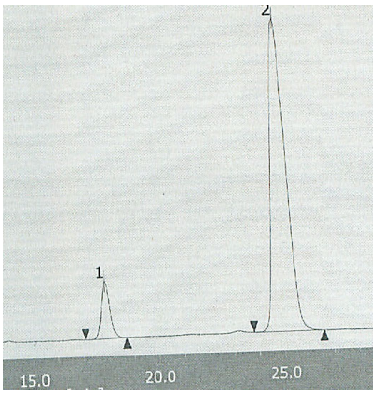


2j

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=95/5, flow rate 0.5 ml/min, λ=254 nm)

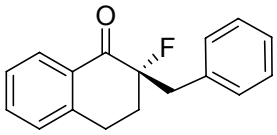




racemic compound of **2j**

No.	tR (min)	Area (%)	High (%)
1	15.6	50.103	57.021
2	20.0	49.897	42.979

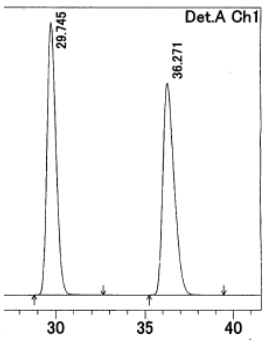
No.	tR (min)	Area (%)	High (%)
1	17.9	9.384	15.512
2	24.9	90.616	84.488

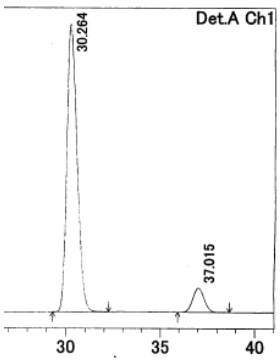


2k

HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=90/10, flow rate 0.5 ml/min, λ=254 nm)

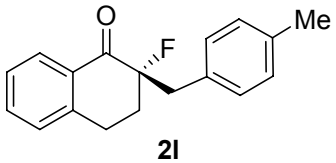




racemic compound of **2k**

No.	tR (min)	Area (%)	High (%)
1	29.7	49.889	56.242
2	36.2	50.111	43.758

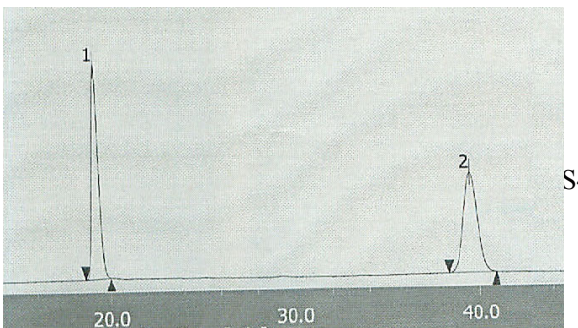
No.	tR (min)	Area (%)	High (%)
1	30.3	91.141	92.179
2	37.0	8.859	7.821

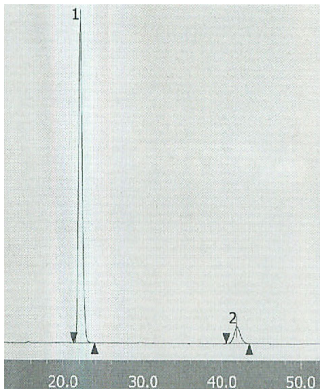


2l

HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=90/10, flow rate 1.0 ml/min, λ=254 nm)

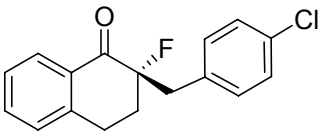




racemic compound of **2l**

No.	tR (min)	Area (%)	High (%)
1	19.2	49.985	68.260
2	36.5	50.015	31.740

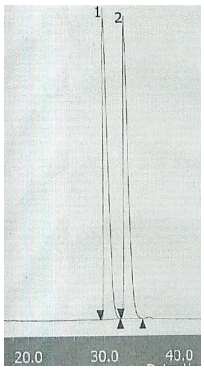
No.	tR (min)	Area (%)	High (%)
1	22.0	91.134	95.071
2	41.9	8.866	4.929

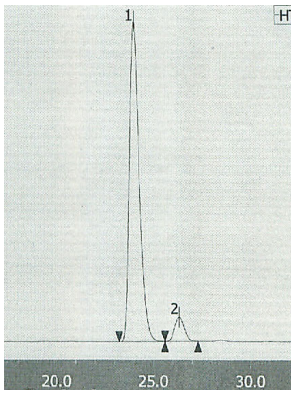


2m

HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=95/5, flow rate 1.0 ml/min, λ=254 nm)

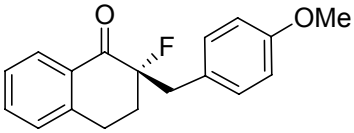




racemic compound of **2m**

No.	tR (min)	Area (%)	High (%)
1	30.4	50.026	50.742
2	33.1	49.974	49.258

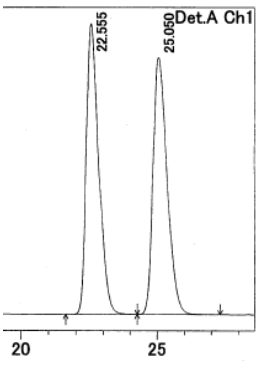
No.	tR (min)	Area (%)	High (%)
1	23.9	92.997	92.968
2	26.3	7.003	7.032

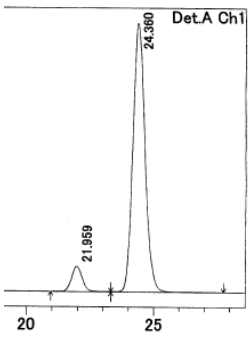


2n

HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=90/10, flow rate 1.0 ml/min, λ=254 nm)

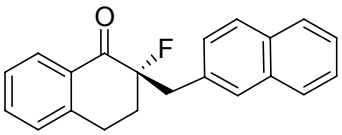




racemic compound of **2n**

No.	tR (min)	Area (%)	High (%)
1	22.6	49.789	53.105
2	25.0	50.211	46.895

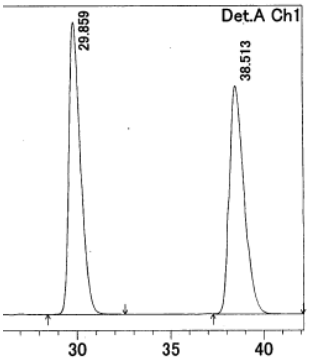
No.	tR (min)	Area (%)	High (%)
1	22.0	7.576	8.516
2	24.4	92.428	91.484

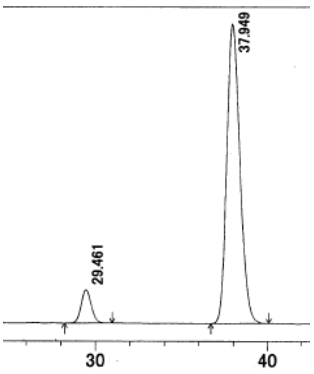


2o

HPLC using an OJ-H

(*n*-Hexane/^{i}PrOH=90/10, flow rate 1.0 ml/min, λ=254 nm)

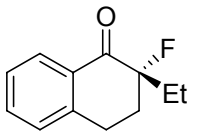




racemic compound of **2o**

No.	tR (min)	Area (%)	High (%)
1	29.9	49.846	56.076
2	38.5	50.154	43.924

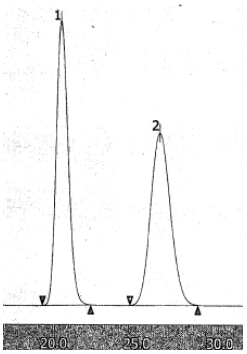
No.	tR (min)	Area (%)	High (%)
1	29.5	7.866	10.635
2	37.9	92.134	89.965

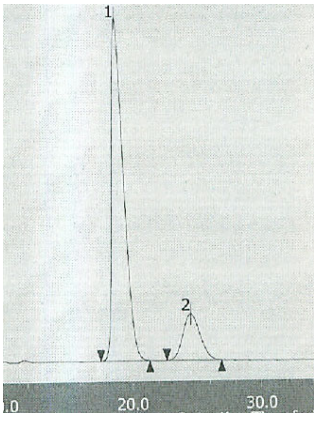


2p

HPLC using an OB-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 1.0 ml/min, λ=254 nm)

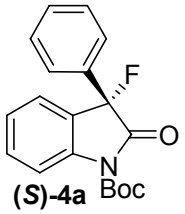




racemic compound of **2p**

No.	tR (min)	Area (%)	High (%)
1	20.5	49.984	62.334
2	26.4	50.016	37.666

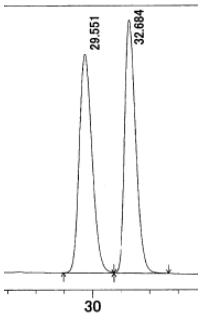
No.	tR (min)	Area (%)	High (%)
1	19.0	83.491	87.991
2	24.6	16.509	12.009

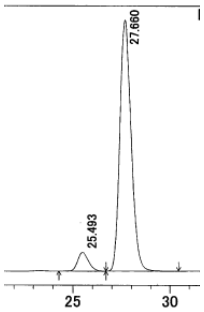


(*S*)-4a

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)

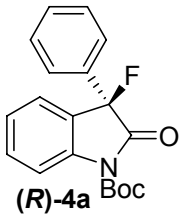




racemic compound of **4a**

No.	tR (min)	Area (%)	High (%)
1	29.6	49.976	46.343
2	32.7	50.024	53.657

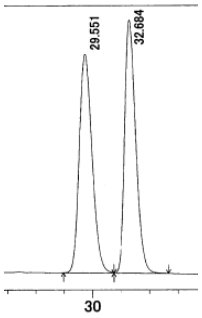
No.	tR (min)	Area (%)	High (%)
1	25.5	6.552	6.928
2	27.7	93.448	93.072

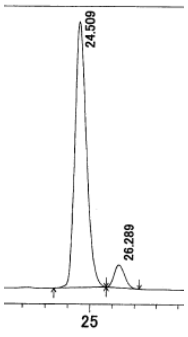


(*R*)-4a

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)

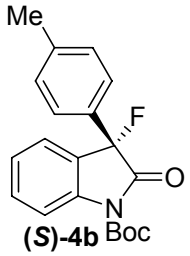




racemic compound of **4a**

No.	tR (min)	Area (%)	High (%)
1	29.6	49.976	46.343
2	32.7	50.024	53.657

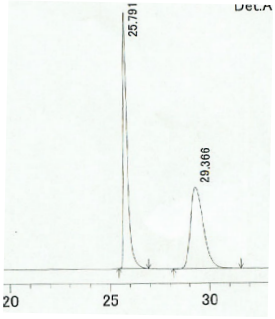
No.	tR (min)	Area (%)	High (%)
1	24.5	92.639	92.040
2	26.3	7.361	7.960

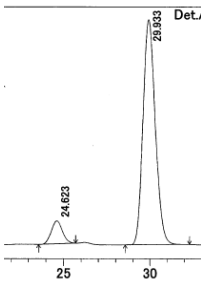


(*S*)-4b

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)

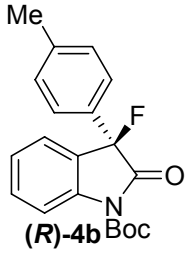




racemic compound of **4b**

No.	tR (min)	Area (%)	High (%)
1	25.8	50.794	75.872
2	29.4	49.206	24.128

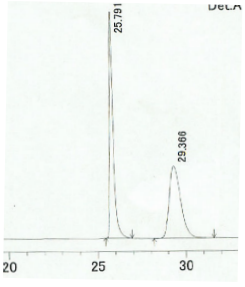
No.	tR (min)	Area (%)	High (%)
1	24.6	8.385	9.287
2	29.9	91.615	90.713

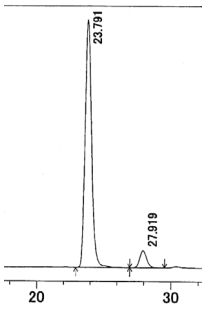


(*R*)-4b

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)





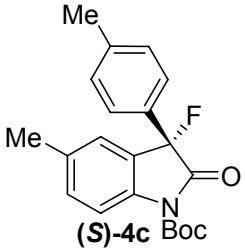
racemic compound of **4b**

No.	tR (min)	Area (%)	High (%)

No.	tR (min)	Area (%)	High (%)

1	25.8	50.794	75.872
2	29.4	49.206	24.128

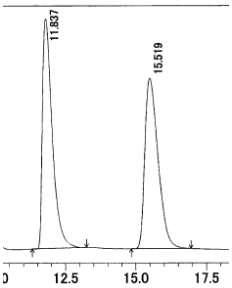
1	23.8	93.232	93.549
2	27.9	6.768	6.451

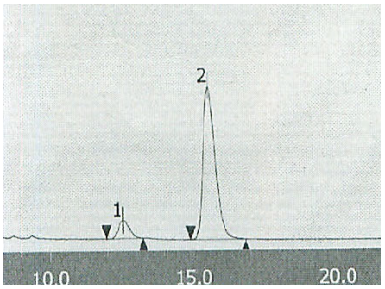


(*S*)-4c

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.5 ml/min, λ=210 nm)

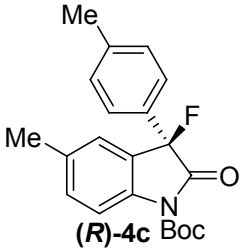




racemic compound of **4c**

No.	tR (min)	Area (%)	High (%)
1	11.8	50.307	57.362
2	15.5	49.693	42.638

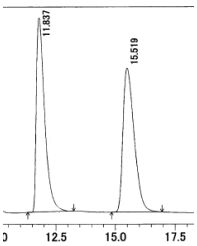
No.	tR (min)	Area (%)	High (%)
1	12.5	9.581	10.546
2	15.5	90.419	89.454

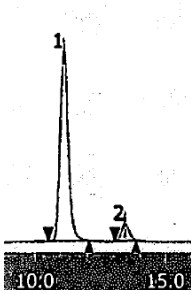


(*R*)-4c

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.5 ml/min, λ=210 nm)

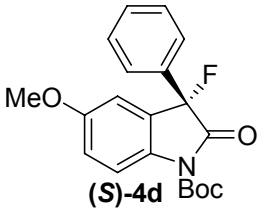




racemic compound of **4c**

No.	tR (min)	Area (%)	High (%)
1	11.8	50.307	57.362
2	15.5	49.693	42.638

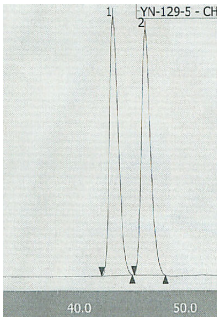
No.	tR (min)	Area (%)	High (%)
1	11.1	91.939	91.853
2	13.4	8.061	8.147



(*S*)-4d

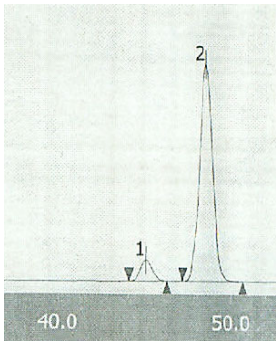
HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)

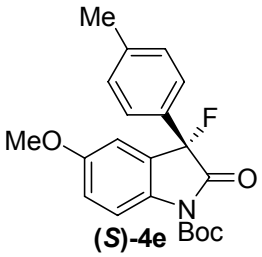


racemic compound of **4d**

No.	tR (min)	Area (%)	High (%)
1	43.3	50.205	51.312
2	46.3	49.795	48.688



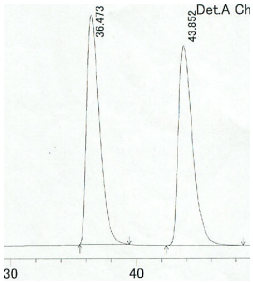
No.	tR (min)	Area (%)	High (%)
1	45.0	8.241	8.989
2	48.4	91.759	91.011



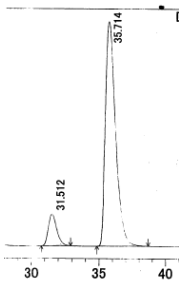
(*S*)-4e

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)



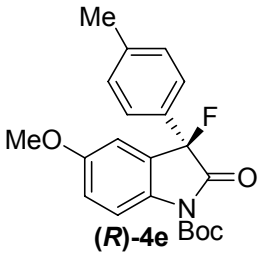
racemic



compound of **4e**

No.	tR (min)	Area (%)	High (%)
1	36.5	50.553	53.455
2	43.9	49.447	46.545

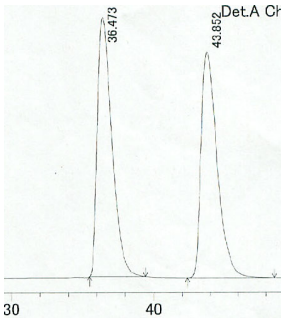
No.	tR (min)	Area (%)	High (%)
1	31.5	10.444	12.464
2	35.7	89.556	87.536

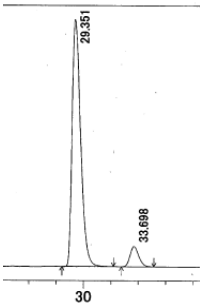


(*R*)-4e

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99/1, flow rate 0.25 ml/min, λ=254 nm)

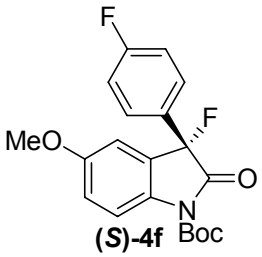




racemic compound of **4e**

No.	tR (min)	Area (%)	High (%)
1	36.5	50.553	53.455
2	43.9	49.447	46.545

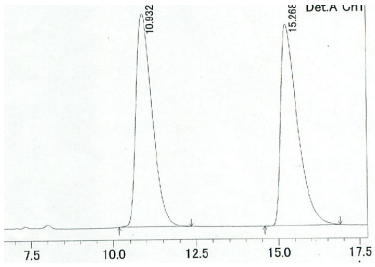
No.	tR (min)	Area (%)	High (%)
1	29.4	92.310	92.397
2	33.7	7.690	7.603

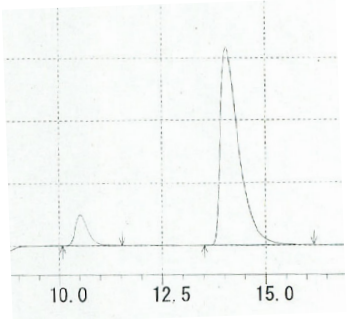


(*S*)-4f

HPLC using an OD-H

(*n*-Hexane/^{i}PrOH=99.5/0.5, flow rate1.0 ml/min, λ=254 nm)

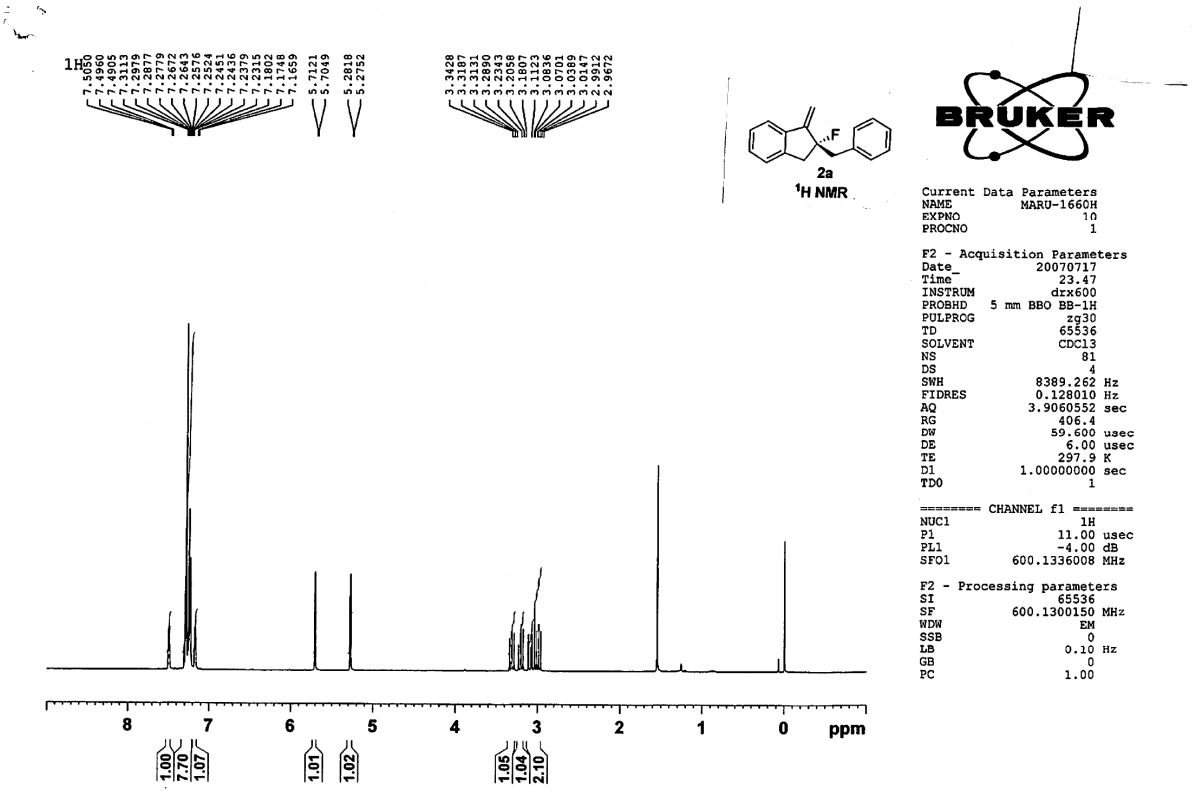




racemic compound of **4e**

No.	tR (min)	Area (%)	High (%)
1	10.9	50.094	51.450
2	15.3	49.906	48.550

No.	tR (min)	Area (%)	High (%)
1	10.5	9.489	13.516
2	14.1	90.511	86.484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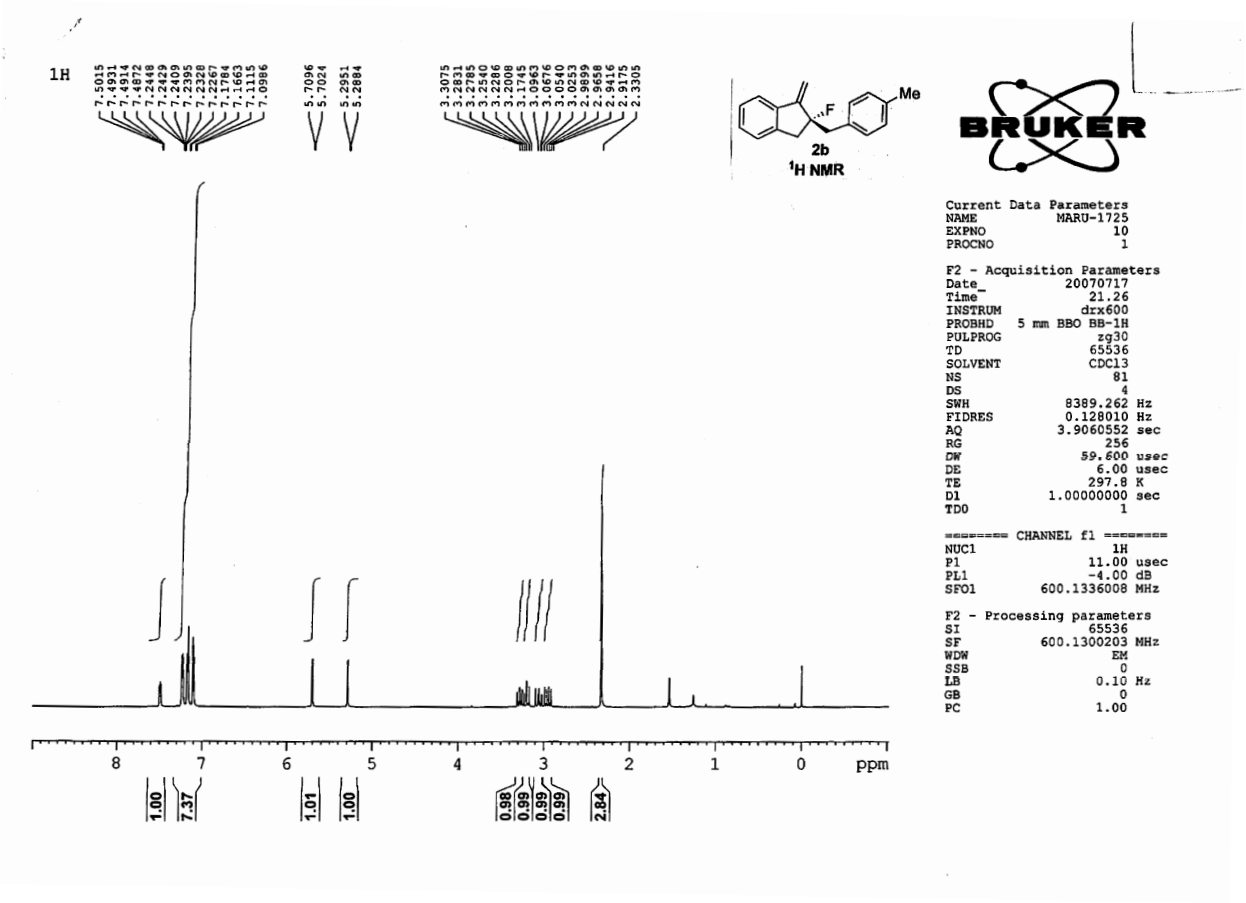
7.4905
7.3113
7.2979
7.2877
7.2779
7.2673
7.2643
7.2576
7.2524
7.2451
7.2436
7.2379
7.2315
7.1802
7.1748
7.1659
5.7121
5.7049
5.2818
5.2752
3.3428
3.3187
3.3131
3.2890
3.2343
3.2058
3.1607
3.1223
3.0836
3.0701
3.0389
3.0147
2.9912
2.9672
F
2a
1H NMR
BRUKER
Current Data Parameters
NAME MARU-1660H
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070717
Time 23.47
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 81
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 406.4
DW 59.600 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300150 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.00
7.70
1.07
1.01
1.02
1.05
1.04
2.10


1H
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7.4931
7.4914
7.4872
7.2448
7.2429
7.2409
7.2395
7.2268
7.2267
7.1784
7.1663
7.1115
7.0986
5.7096
5.7024
5.2951
5.2884
3.3075
3.2831
3.2785
3.2540
3.2286
3.2008
3.1745
3.0963
3.0676
3.0540
3.0253
2.9899
2.9658
2.9416
2.9175
2.3305
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Me
2b
1H NMR
BRUKER
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PROCNO 1
F2 - Acquisition Parameters
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Time 21.26
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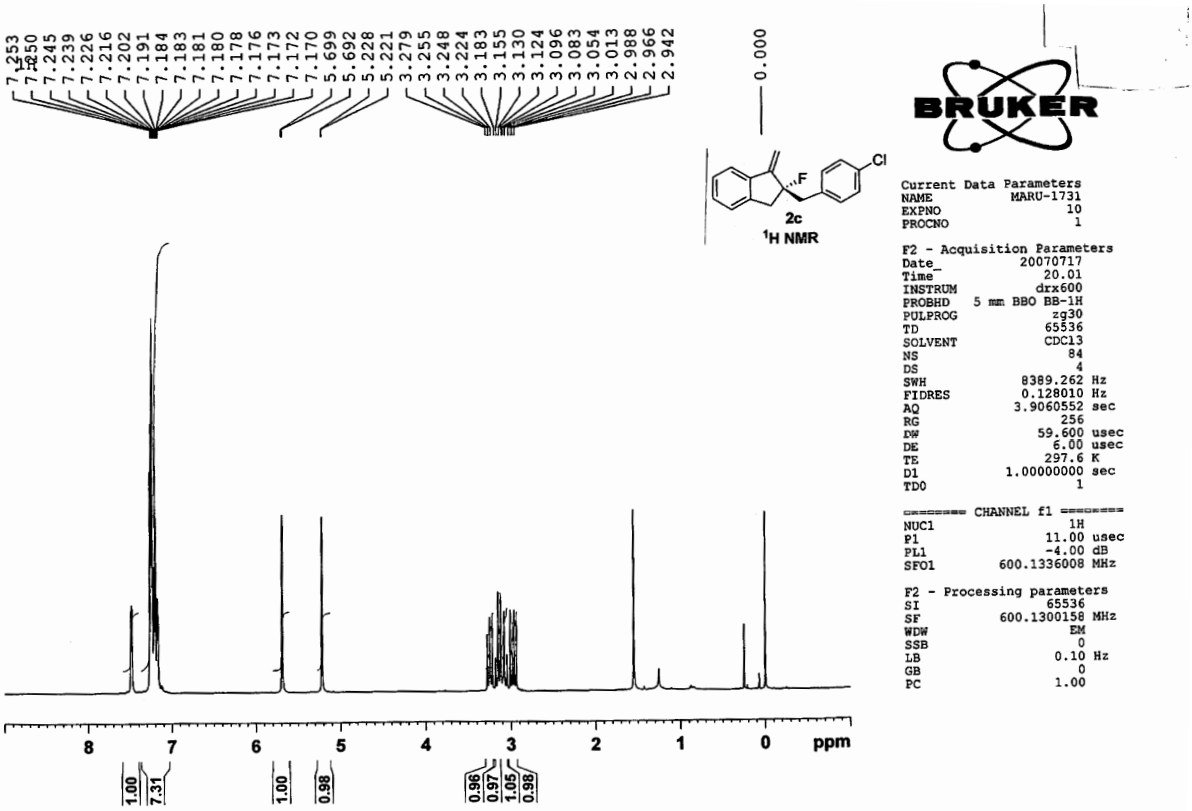
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 81
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300203 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.00
7.37
1.01
1.00
0.98
0.99
0.99
2.84


7.253
7.250
7.245
7.239
7.226
7.216
7.202
7.191
7.184
7.183
7.181
7.180
7.178
7.176
7.173
7.172
7.170
5.699
5.692
5.228
5.221
3.279
3.255
3.248
3.224
3.183
3.155
3.130
3.124
3.096
3.083
3.054
3.013
2.988
2.966
2.942
0.000
F
Cl
2c
1H NMR
BRUKER
Current Data Parameters
NAME MARU-1731
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PROCNO 1
F2 - Acquisition Parameters
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Time 20.01
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PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 84
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300158 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
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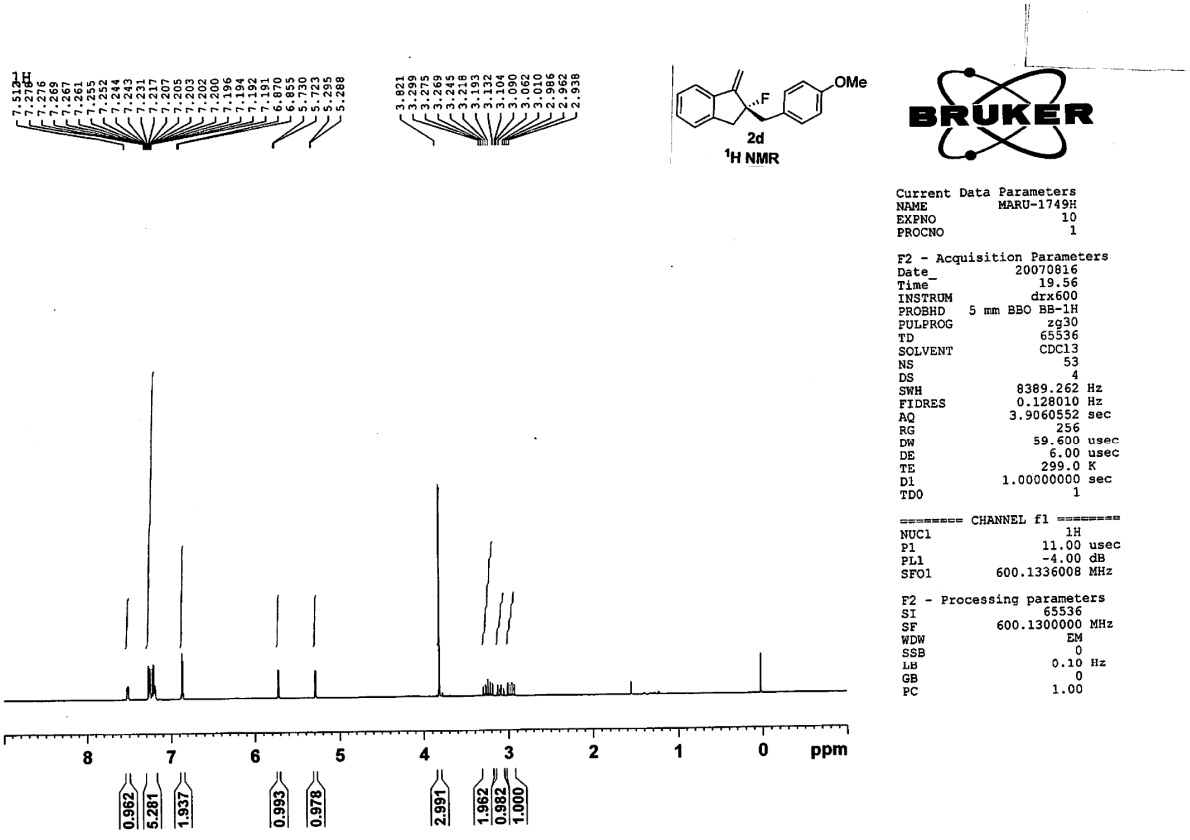
1H
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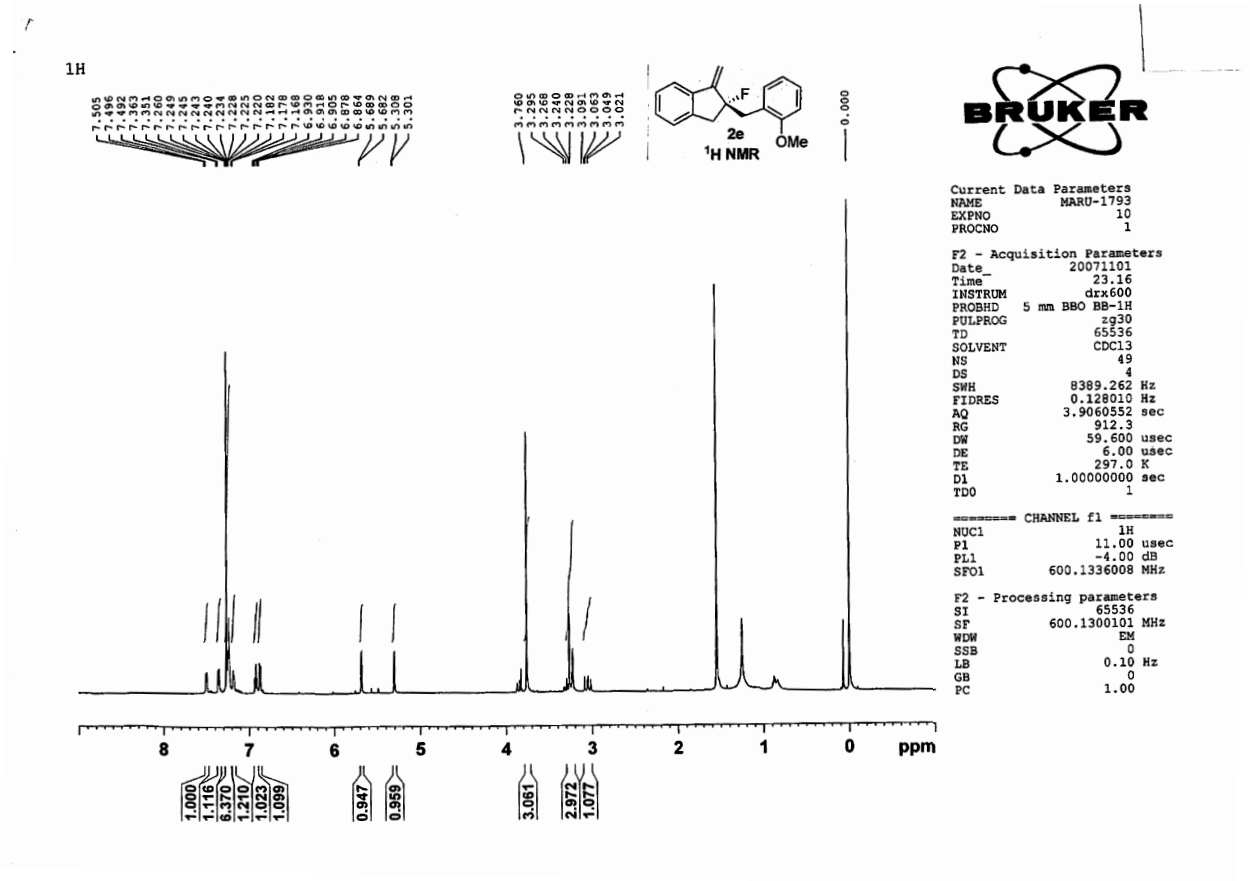
7.278
7.276
7.269
7.267
7.261
7.255
7.252
7.244
7.243
7.231
7.217
7.207
7.205
7.203
7.202
7.200
7.196
7.194
7.192
7.191
6.870
6.855
5.730
5.723
5.295
5.288
3.821
3.299
3.275
3.269
3.245
3.218
3.193
3.132
3.104
3.090
3.062
3.000
2.986
2.962
2.938
F
OMe
2d
1H NMR
BRUKER
Current Data Parameters
NAME MARU-1749H
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070816
Time 19.56
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 53
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 299.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
0.962 5.281 1.937 0.993 0.978 2.991 1.962 0.982 1.000


1H
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7.496
7.492
7.363
7.351
7.260
7.249
7.245
7.243
7.240
7.234
7.228
7.225
7.220
7.182
7.178
7.168
6.930
6.918
6.905
6.878
6.864
5.689
5.682
5.308
5.301
3.760
3.295
3.268
3.240
3.228
3.091
3.063
3.049
3.021
0.000
F
2e
OMe
1H NMR
BRUKER
Current Data Parameters
NAME MARU-1793
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071101
Time 23.16
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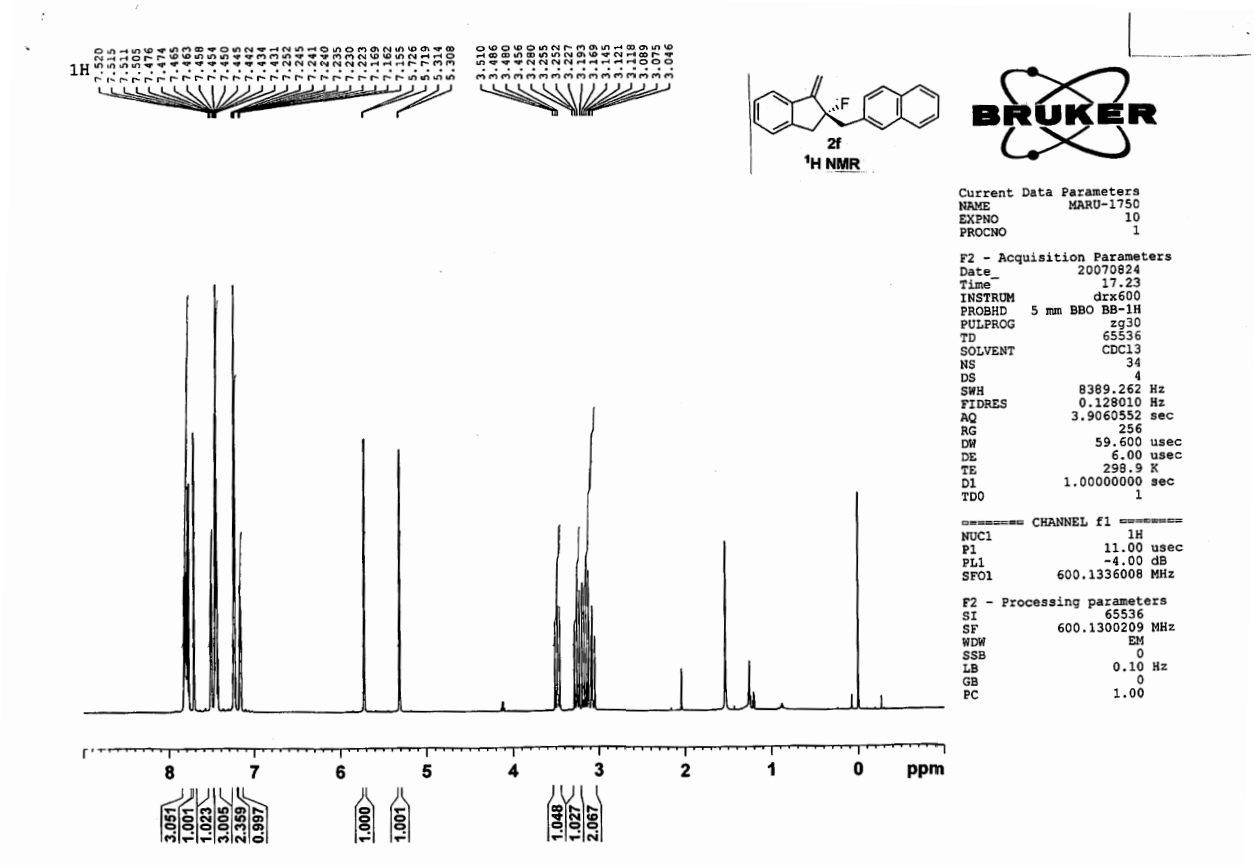
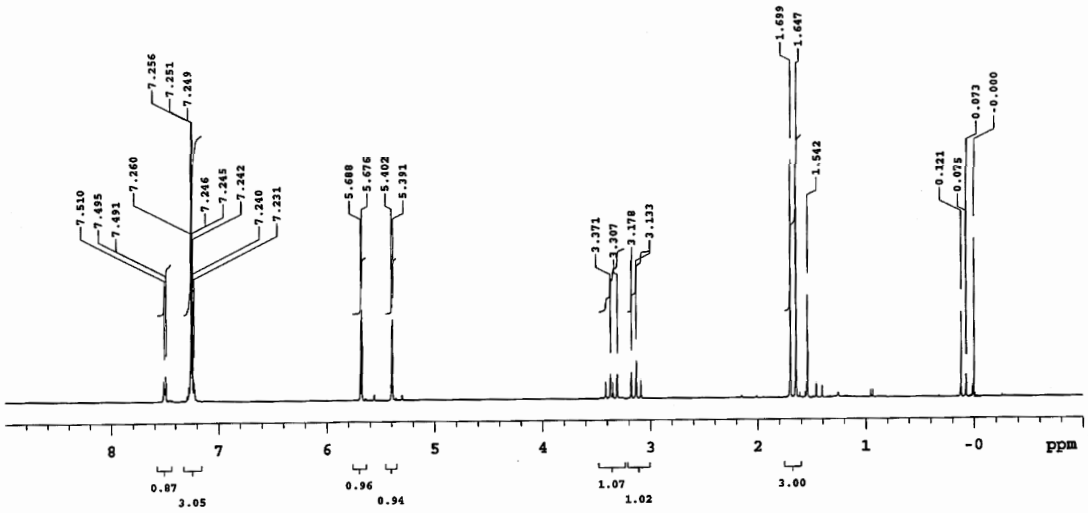
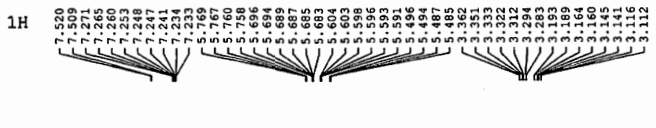
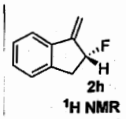
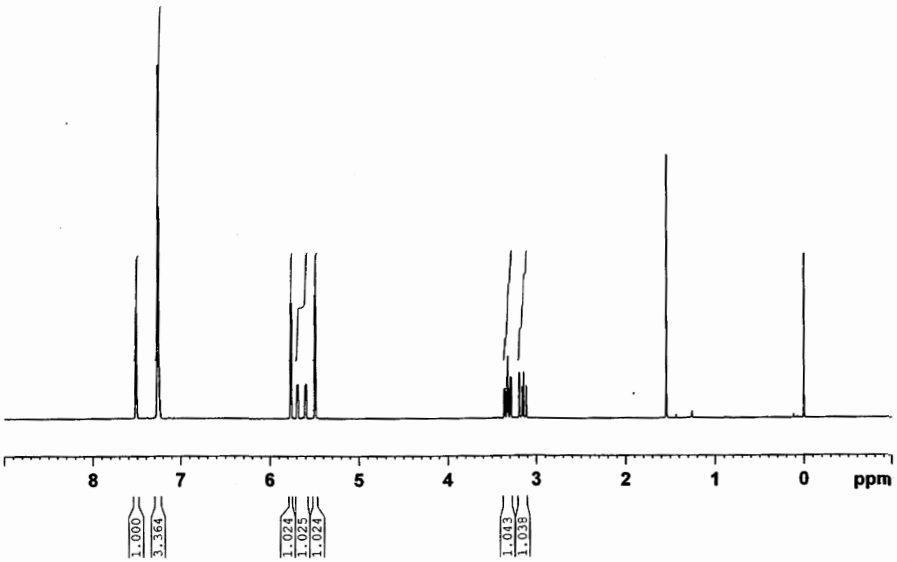
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 49
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 912.3
DW 59.600 usec
DE 6.00 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300101 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.000
1.116
6.370
1.210
1.023
1.099
0.947
0.959
3.061
2.972
1.077


1H
7.520
7.515
7.511
7.505
7.476
7.474
7.465
7.463
7.458
7.454
7.450
7.445
7.442
7.434
7.431
7.252
7.245
7.241
7.240
7.235
7.230
7.223
7.169
7.162
7.155
5.726
5.719
5.314
5.308
3.510
3.486
3.480
3.456
3.280
3.255
3.252
3.227
3.193
3.169
3.145
3.121
3.118
3.099
3.075
3.046
F
2f
1H NMR
BRUKER
Current Data Parameters
NAME MARU-1750
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070824
Time 17.23
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 34
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 298.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300209 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
3.051
1.001
1.023
3.005
2.369
0.997
1.000
1.001
1.048
1.027
2.067

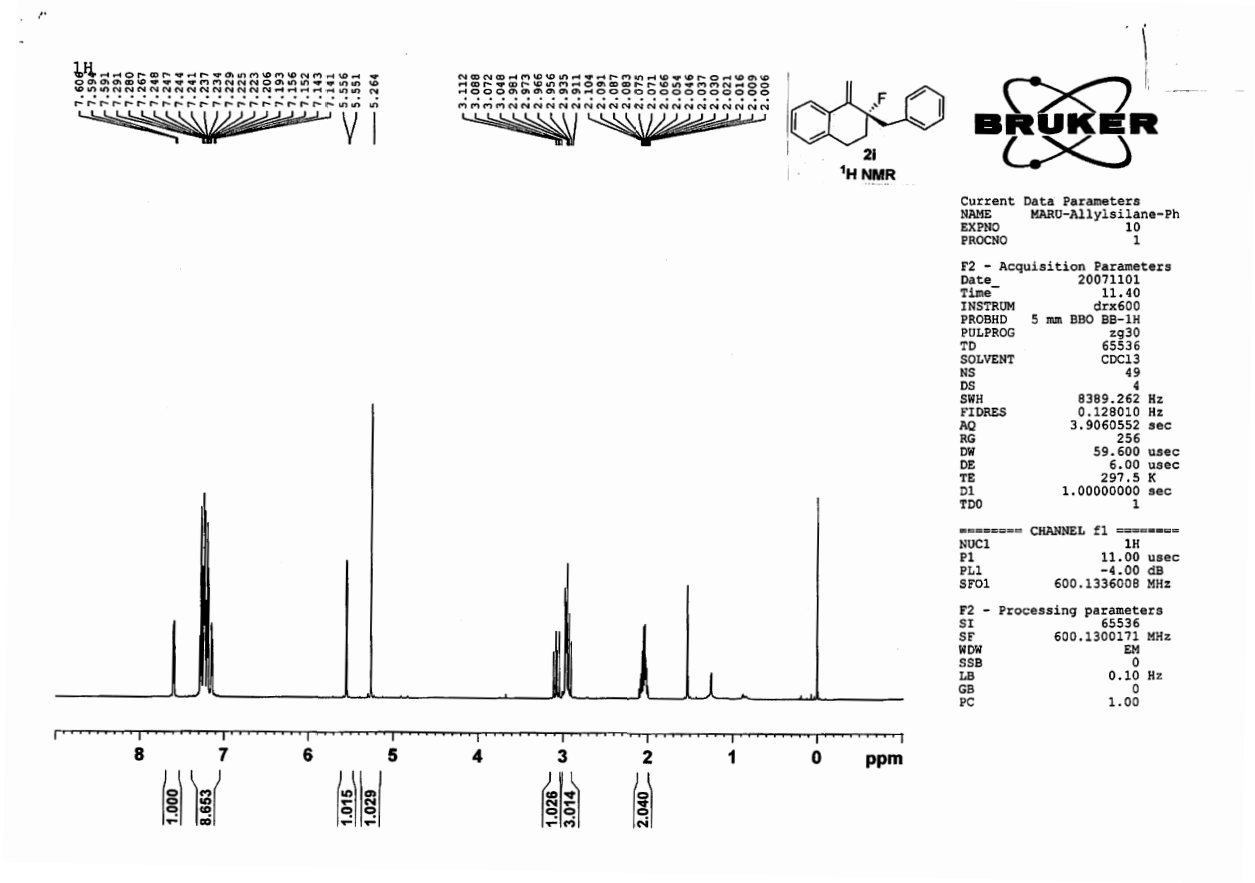


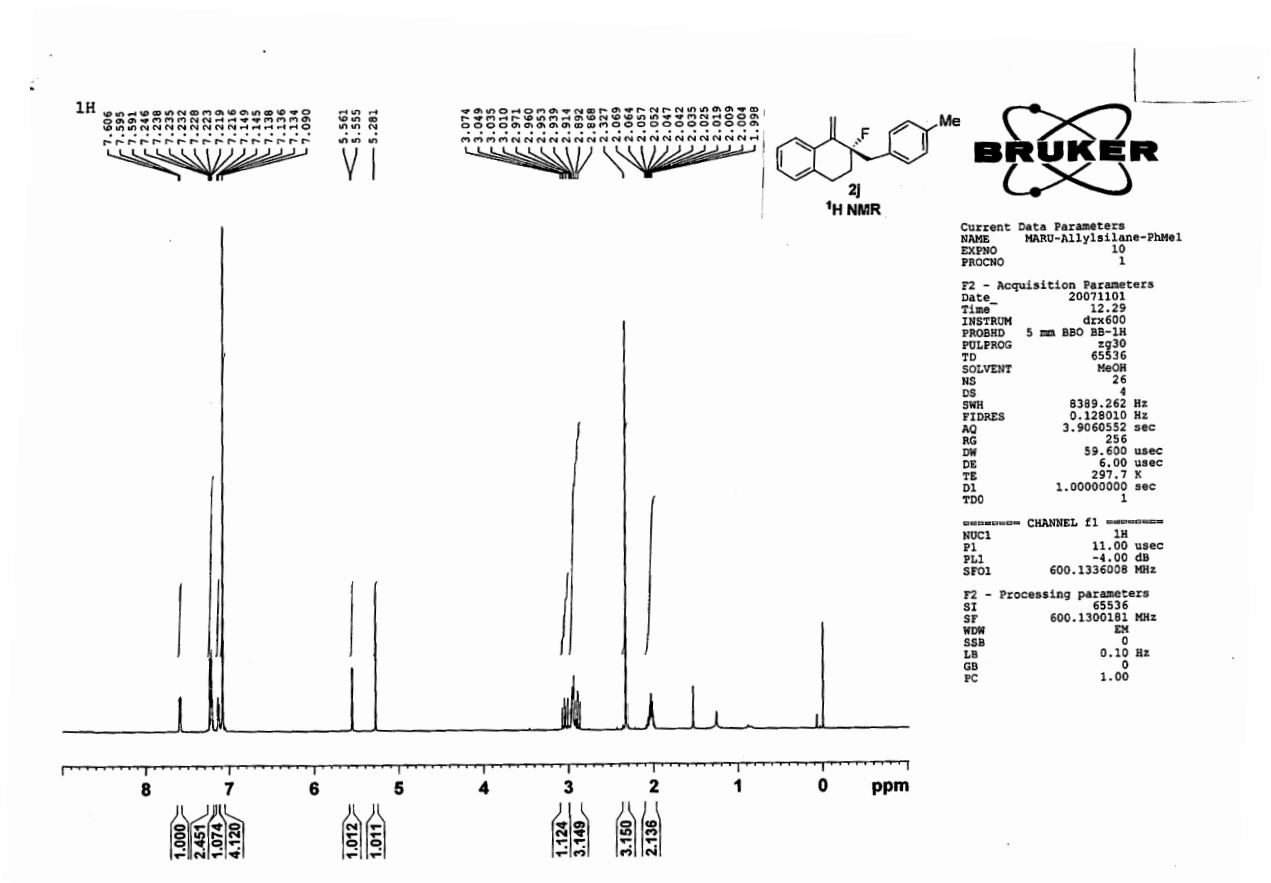


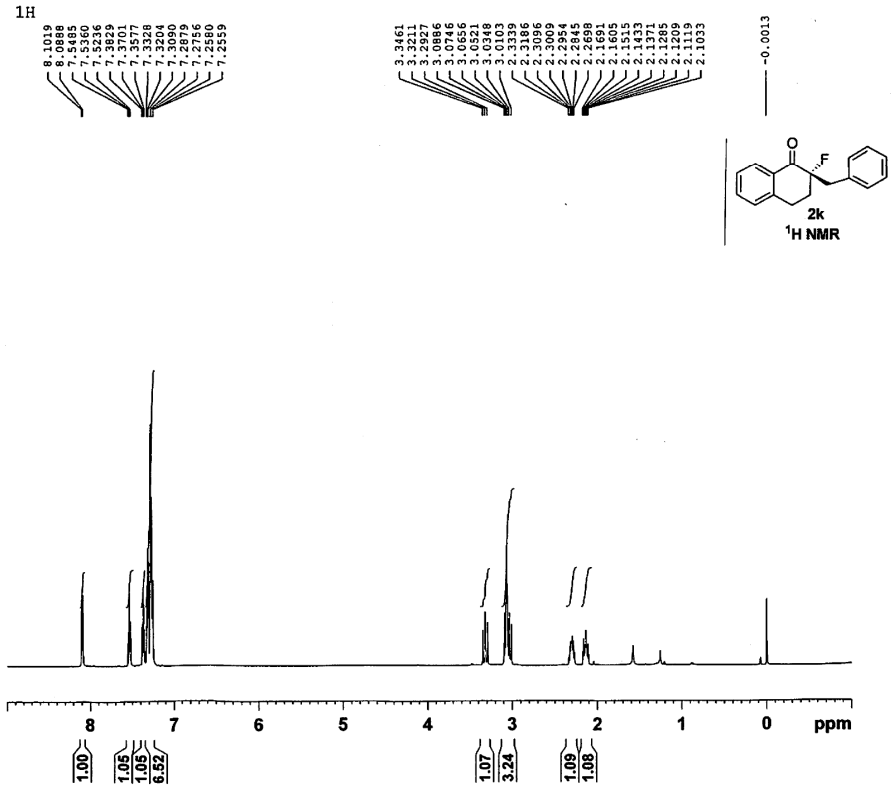




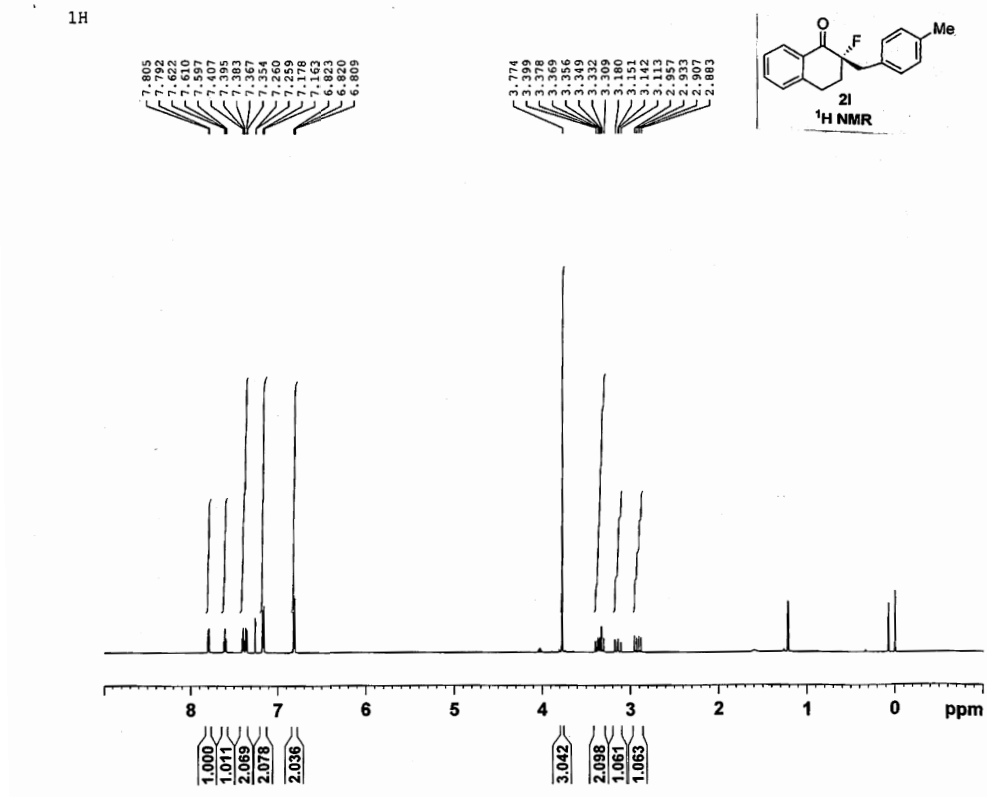

```
Current Data Parameters
NAME      MARU-monofluoro
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070824
Time_              17.40
INSTRUM          drx600
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   33
DS                    4
SWH            8389.262 Hz
FIDRES        0.128010 Hz
AQ            3.9060552 sec
RG                456.1
DW               59.600 usec
DE                6.00 usec
TE               298.9 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.00 usec
PL1               -4.00 dB
SFO1         600.1336008 MHz

F2 - Processing parameters
SI                65536
SF           600.1300136 MHz
WDW                  EM
SSB                   0
LB                0.10 Hz
GB                    0
PC                 1.00
```


1H
7.606
7.594
7.591
7.291
7.280
7.267
7.248
7.247
7.244
7.241
7.237
7.234
7.229
7.225
7.223
7.206
7.193
7.156
7.152
7.143
7.141
5.556
5.551
5.264
3.112
3.088
3.072
3.048
2.981
2.973
2.966
2.956
2.935
2.911
2.104
2.091
2.087
2.083
2.075
2.071
2.066
2.054
2.046
2.037
2.030
2.021
2.016
2.009
2.006
F
2i
1H NMR
BRUKER
Current Data Parameters
NAME MARU-Allylsilane-Ph
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071101
Time 11.40
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 49
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 297.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300171 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.000
8.653
1.015
1.029
1.026
3.014
2.040

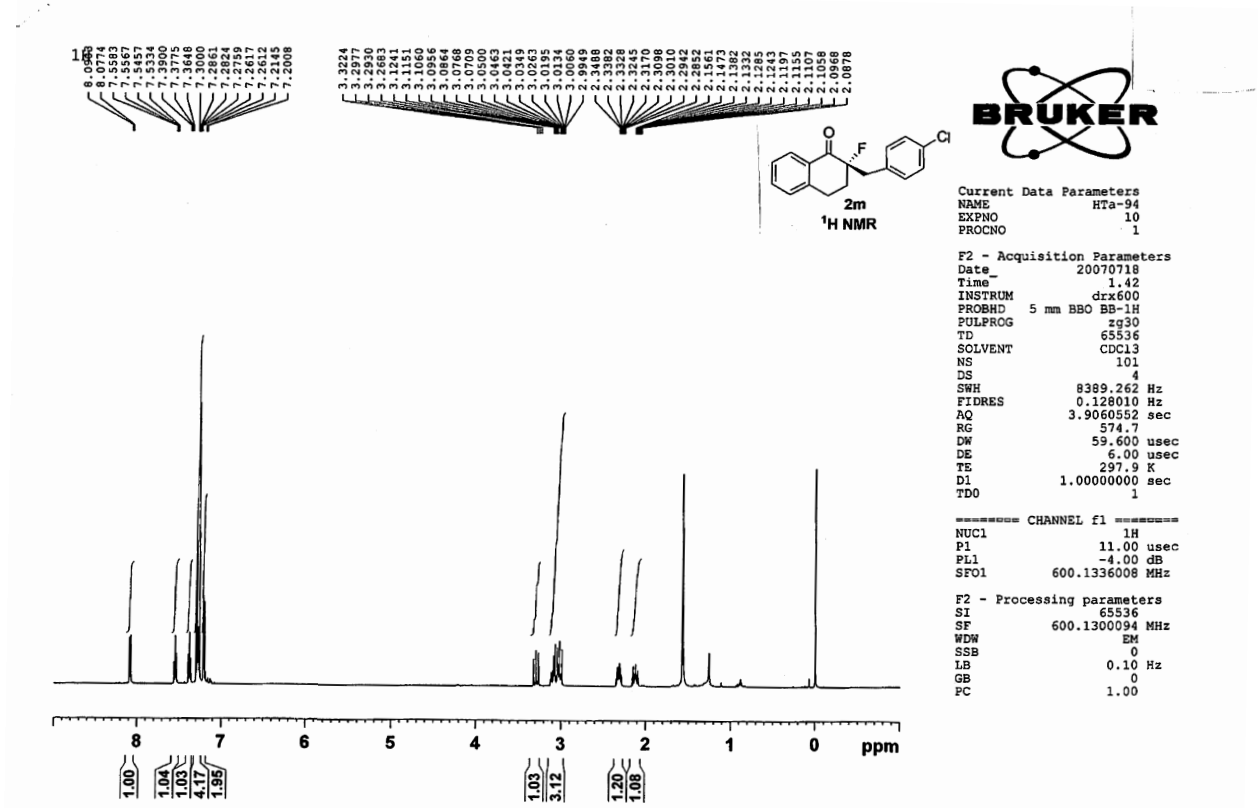

1H
7.606
7.595
7.591
7.246
7.238
7.235
7.232
7.228
7.223
7.219
7.216
7.149
7.145
7.138
7.136
7.134
7.090
5.561
5.555
5.281
3.074
3.049
3.035
3.010
2.971
2.960
2.953
2.939
2.914
2.892
2.868
2.327
2.069
2.064
2.057
2.052
2.047
2.042
2.035
2.025
2.019
2.009
2.004
1.998
F
Me
2j
1H NMR
BRUKER
Current Data Parameters
NAME MARU-Allylsilane-PhMe1
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071101
Time 12.29
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT MeOH
NS 26
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 297.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300181 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.000
2.451
1.074
4.120
1.012
1.011
1.124
3.149
3.150
2.136

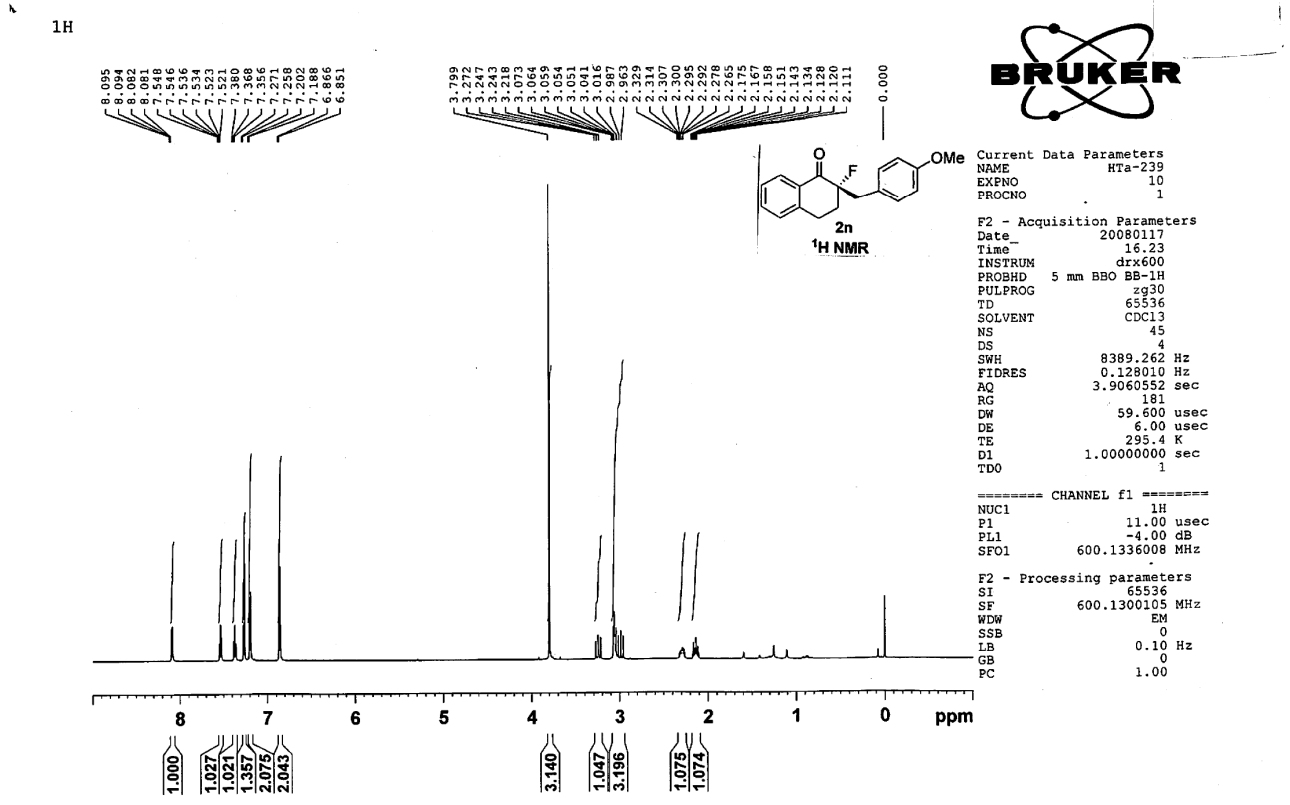


```
Current Data Parameters
NAME                  MARU-4
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070519
Time                   0.25
INSTRUM              drx600
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        4
SWH                8389.262 Hz
FIDRES             0.128010 Hz
AQ                 3.9060552 sec
RG                      256
DW                   59.600 usec
DE                    6.00 usec
TE                   297.4 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                  -4.00 dB
SFO1          600.1336008 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300120 MHz
WDW                      EM
SSB                       0
LB                     0.10 Hz
GB                        0
PC                     1.00
```

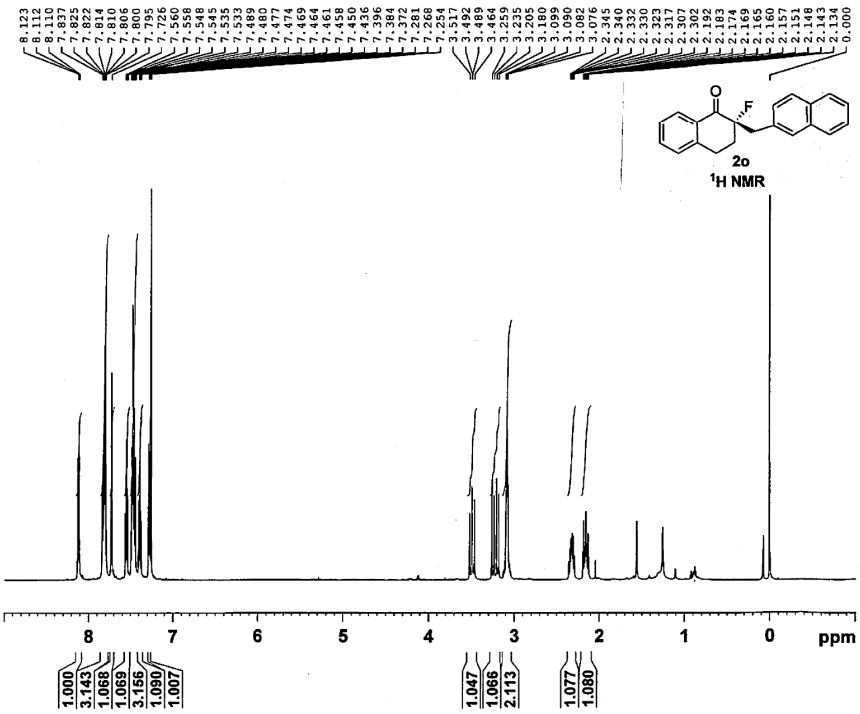


```
Current Data Parameters
NAME                  HTa-180
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20071031
Time                  23.49
INSTRUM              drx600
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       49
DS                        4
SWH                8389.262 Hz
FIDRES             0.128010 Hz
AQ                 3.9060552 sec
RG                      256
DW                   59.600 usec
DE                    6.00 usec
TE                   297.6 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                  -4.00 dB
SFO1          600.1336008 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300100 MHz
WDW                      EM
SSB                       0
LB                     0.10 Hz
GB                        0
PC                     1.00
```


1H
2m
1H NMR
Current Data Parameters
NAME HTa-94
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070718
Time 1.42
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 101
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 574.7
DW 59.600 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300094 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
ppm


1H
2n
1H NMR
Current Data Parameters
NAME HTa-239
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080117
Time 16.23
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 45
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 181
DW 59.600 usec
DE 6.00 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz
F2 - Processing parameters
SI 65536
SF 600.1300105 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
ppm

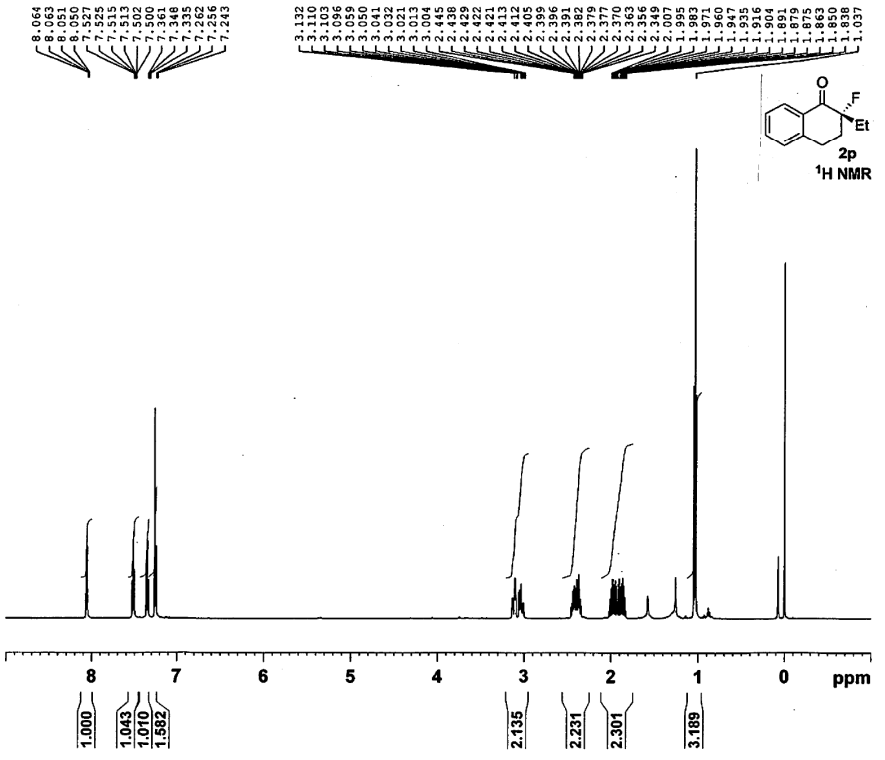
1H



BRUKER

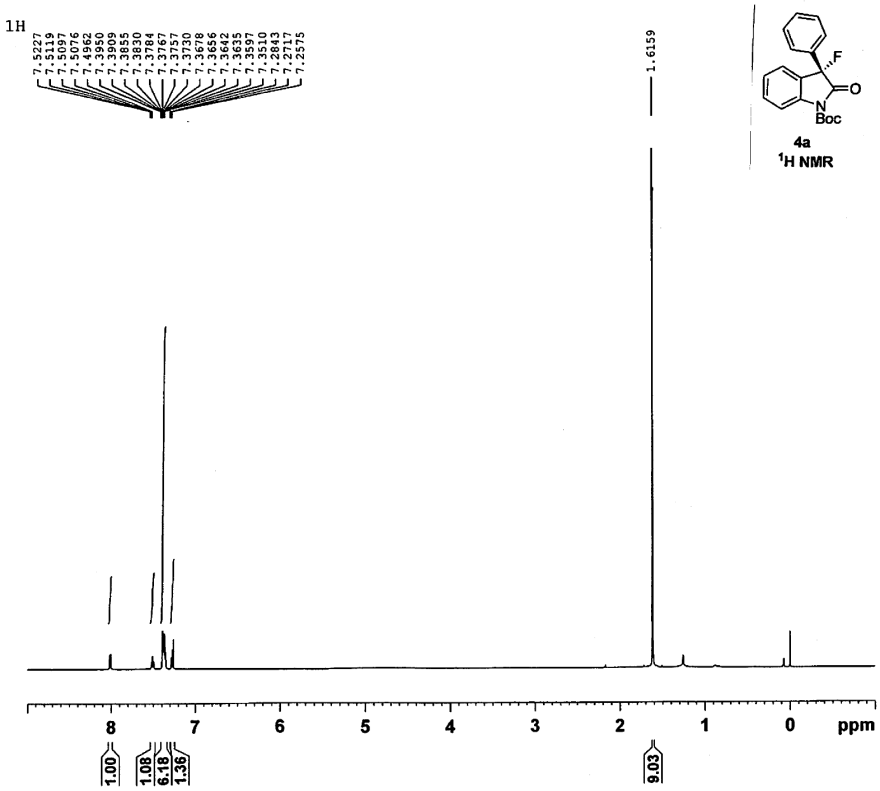
```
Current Data Parameters
NAME                  HTa-240
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20080117
Time                   16.54
INSTRUM               drx600
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       25
DS                        4
SWH                8389.262 Hz
FIDRES             0.128010 Hz
AQ                 3.9060552 sec
RG                       256
DW                    59.600 usec
DE                     6.00 usec
TE                    295.4 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.00 usec
PL1                    -4.00 dB
SFO1           600.1336008 MHz

F2 - Processing parameters
SI                        65536
SF             600.1300128 MHz
WDW                          EM
SSB                           0
LB                     0.10 Hz
GB                            0
PC                         1.00
```

1H



BRUKER

```
Current Data Parameters
NAME                  HTa-141
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20071113
Time                   17.37
INSTRUM               drx600
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       65
DS                        4
SWH                8389.262 Hz
FIDRES             0.128010 Hz
AQ                 3.9060552 sec
RG                     456.1
DW                    59.600 usec
DE                     6.00 usec
TE                    297.2 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     11.00 usec
PL1                    -4.00 dB
SFO1           600.1336008 MHz

F2 - Processing parameters
SI                        65536
SF             600.1300084 MHz
WDW                          EM
SSB                           0
LB                     0.10 Hz
GB                            0
PC                         1.00
```



4a
^{1}H NMR

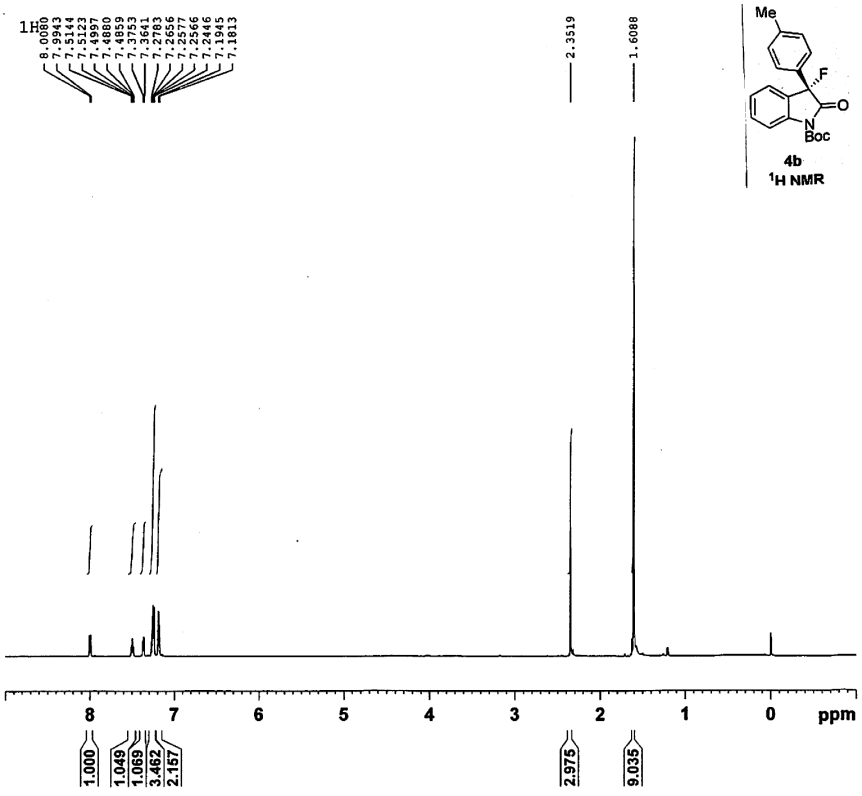
BRUKER

Current Data Parameters
NAME MARU-2
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070519
Time 0.05
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 256
DW 59.600 usec
DE 6.00 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz

F2 - Processing parameters
SI 65536
SF 600.1300114 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00



4b
^{1}H NMR

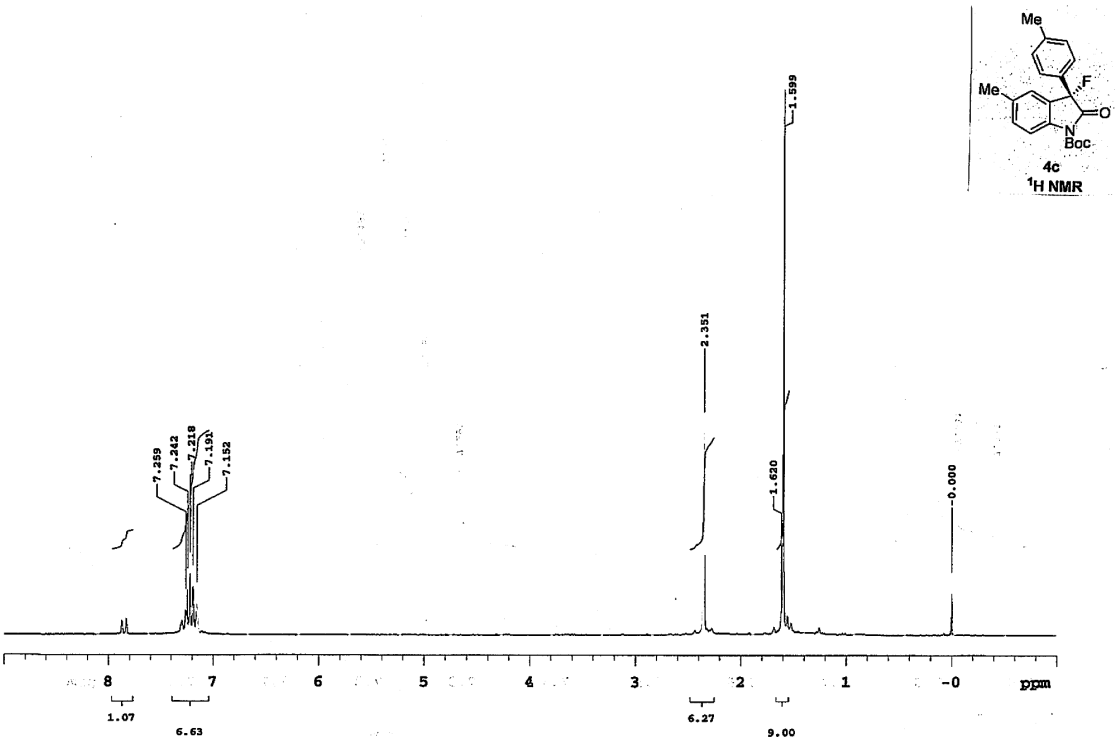
BRUKER

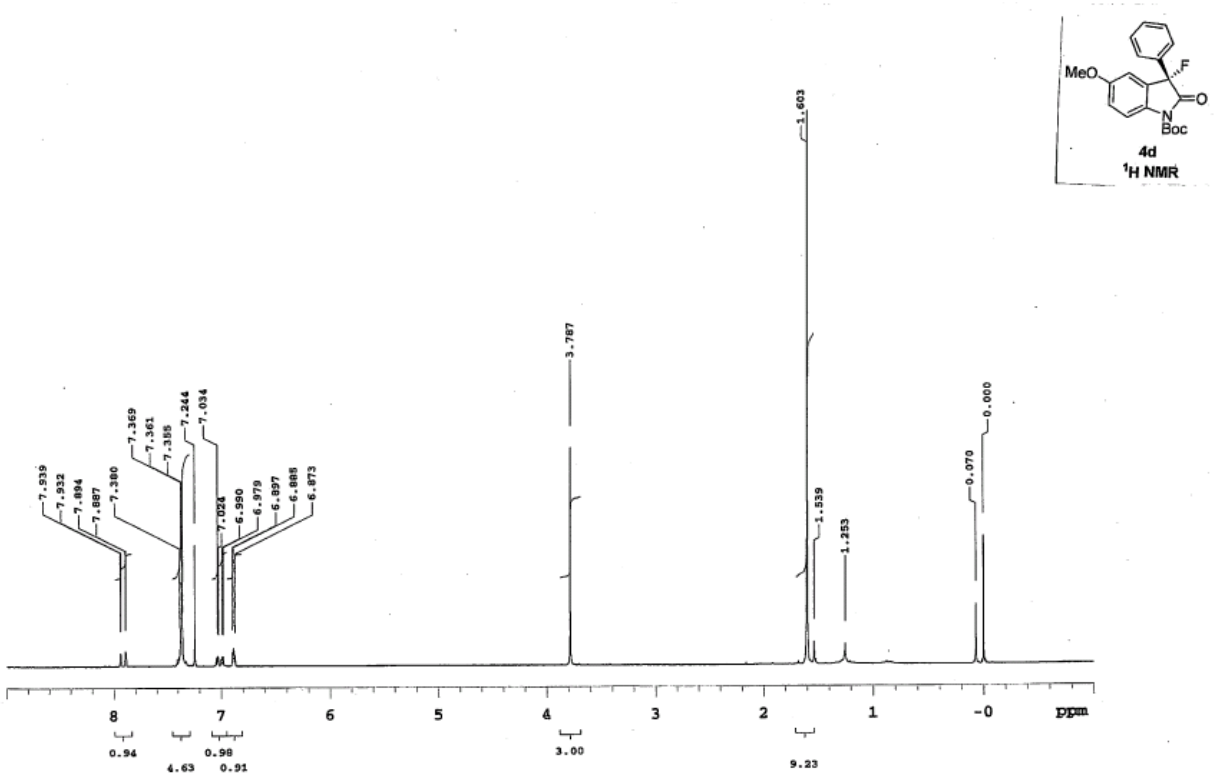
Current Data Parameters
NAME MARU-1733
EXPNO 10
PROCNO 1

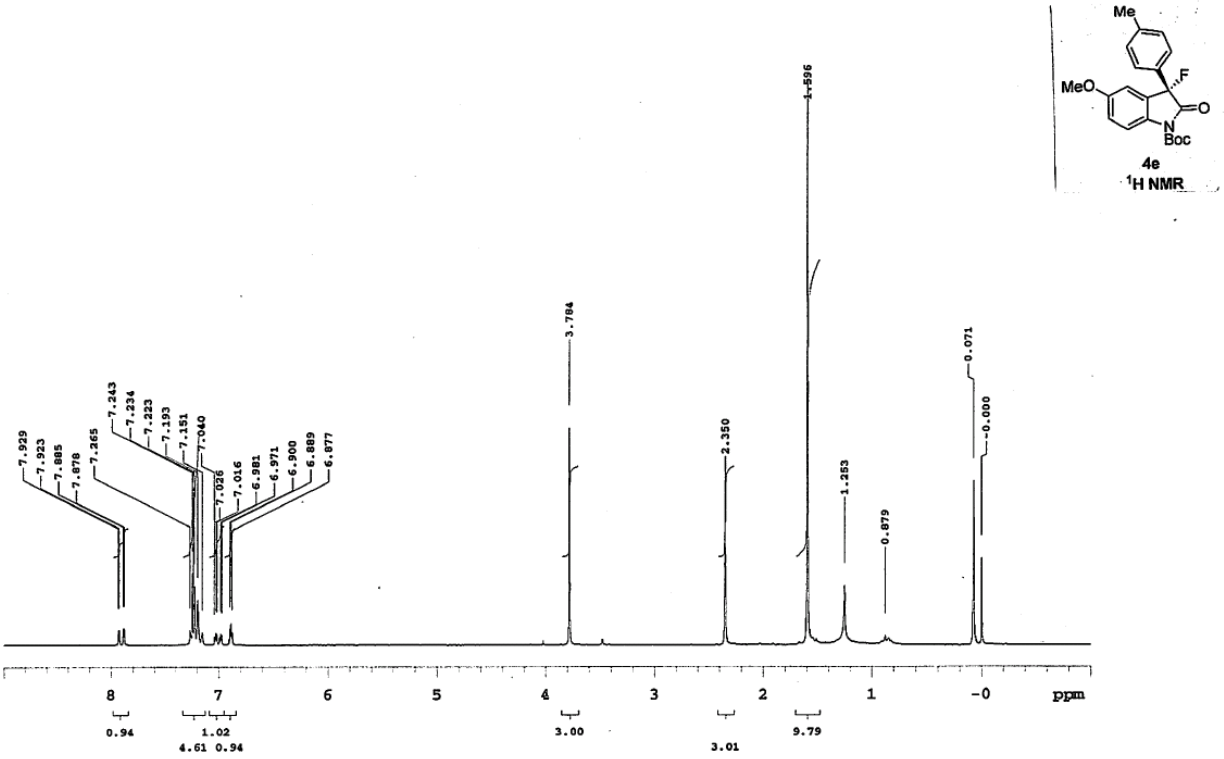
F2 - Acquisition Parameters
Date_ 20070721
Time 6.52
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 8389.262 Hz
FIDRES 0.128010 Hz
AQ 3.9060552 sec
RG 181
DW 59.600 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

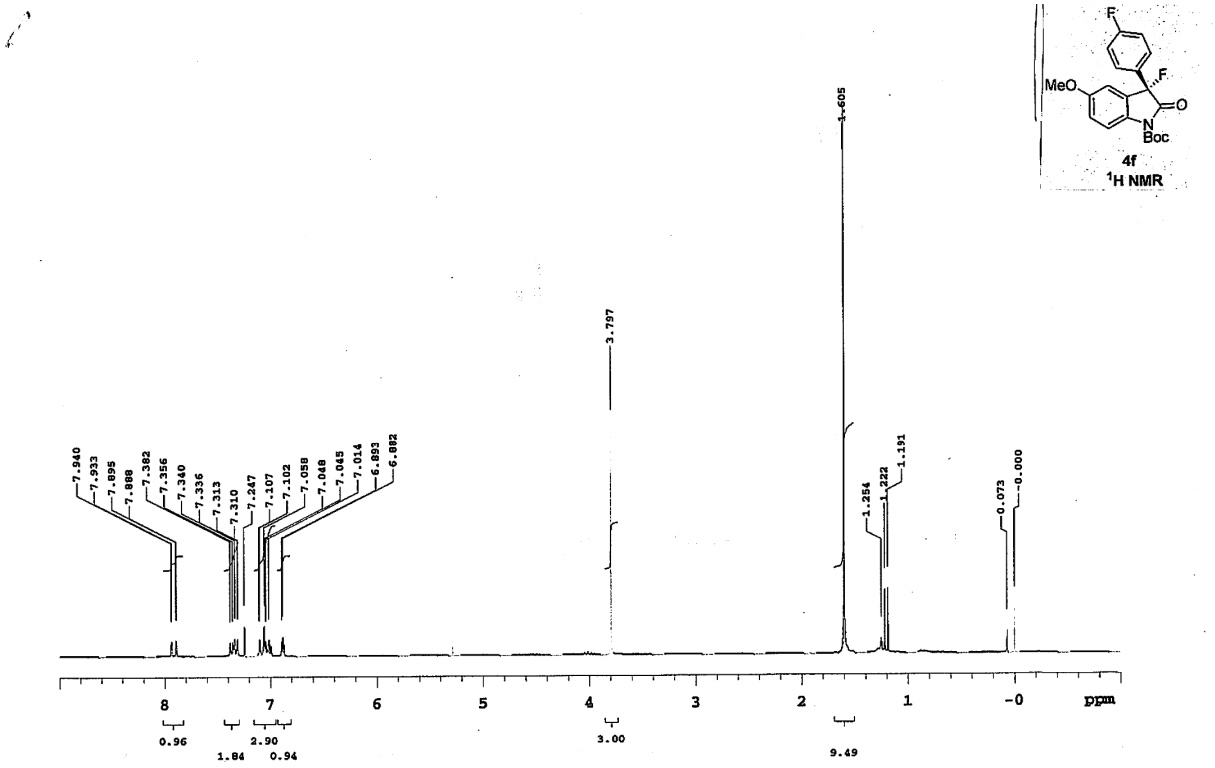
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -4.00 dB
SFO1 600.1336008 MHz

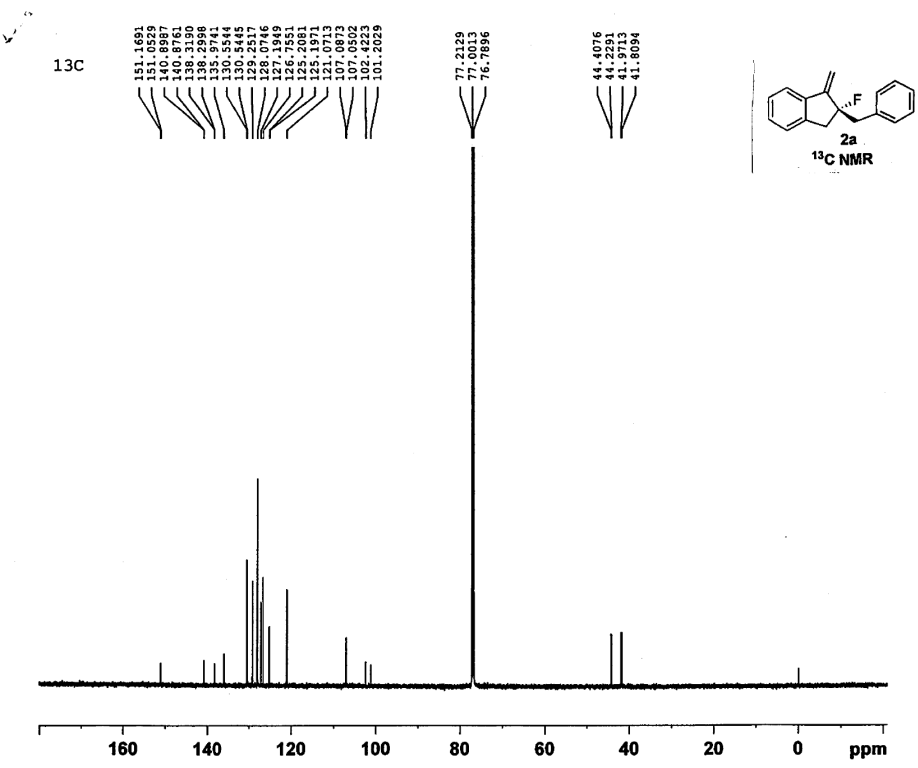
F2 - Processing parameters
SI 65536
SF 600.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


Me
Me
F
O
N
Boc
4c
1H NMR
7.359
7.242
7.218
7.191
7.152
2.351
1.620
1.599
0.000
8
7
6
5
4
3
2
1
-0
ppm
1.07
6.63
6.27
9.00


MeO
F
O
N
Boc
4d
1H NMR
7.939
7.932
7.894
7.887
7.380
7.369
7.361
7.355
7.244
7.034
7.024
6.990
6.979
6.897
6.888
6.873
3.787
1.603
1.539
1.253
0.079
0.000
8
7
6
5
4
3
2
1
-0
ppm
0.94
4.63
0.98
0.91
3.00
9.23

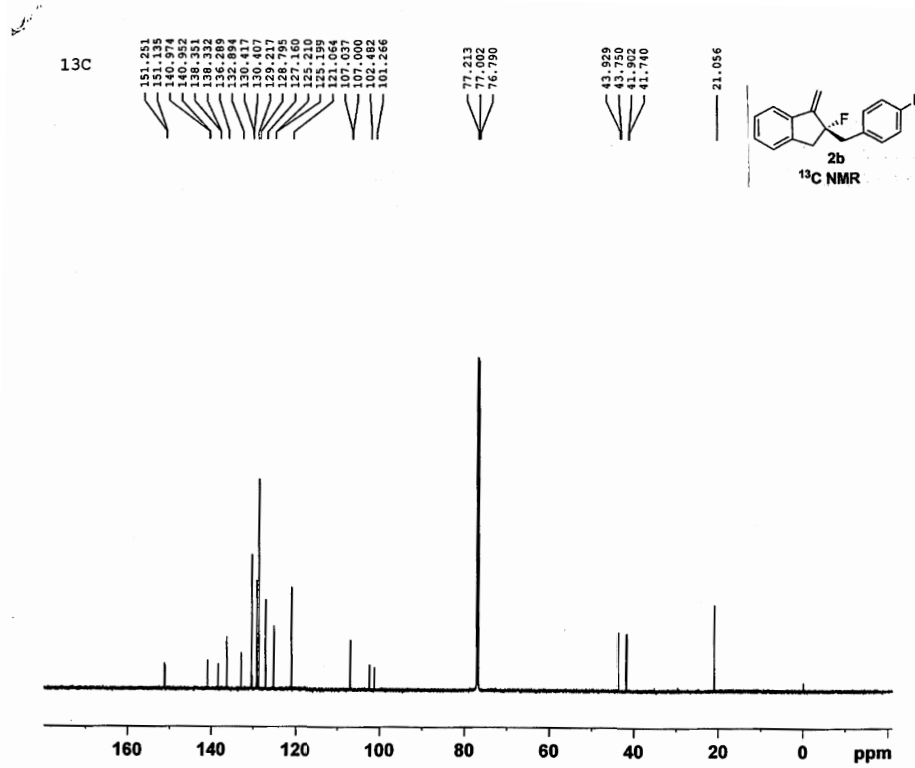

Me
MeO
F
O
N
Boc
4e
^{1}H NMR
7.929
7.923
7.885
7.878
7.365
7.243
7.234
7.223
7.193
7.151
7.040
7.026
7.016
6.981
6.971
6.900
6.889
6.877
3.784
2.350
1.596
1.253
0.879
0.071
-0.000
8
7
6
5
4
3
2
1
-0
ppm
0.94
1.02
4.61
0.94
3.00
3.01
9.79


F
MeO
F
O
N
Boc
4f
^{1}H NMR
7.940
7.933
7.895
7.888
7.382
7.356
7.340
7.336
7.313
7.310
7.247
7.107
7.102
7.058
7.048
7.045
7.014
6.893
6.892
3.797
1.605
1.254
1.222
1.191
0.073
-0.000
8
7
6
5
4
3
2
1
-0
ppm
0.96
2.90
1.84
0.94
3.00
9.49



BRUKER

```
Current Data Parameters
NAME                  MARU-1660C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20070718
Time                        0.00
INSTRUM                   drx600
PROBHD     5 mm BBO BB-1H
PULPROG                   zgpg30
TD                        131072
SOLVENT                    CDCl3
NS                          2103
DS                             4
SWH                  45454.547 Hz
FIDRES                0.346791 Hz
AQ                    1.4418530 sec
RG                       5160.6
DW                     11.000 usec
DE                      6.00 usec
TE                      298.1 K
D1                  0.60000002 sec
d11                 0.03000000 sec
DELTA               0.50000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                        8.20 usec
PL1                       4.50 dB
SFO1                150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    82.00 usec
PL2                      -4.00 dB
PL12                     15.00 dB
PL13                     15.00 dB
SFO2                600.1324005 MHz

F2 - Processing parameters
SI                          131072
SF                  150.9028114 MHz
WDW                           EM
SSB                            0
LB                         1.00 Hz
GB                             0
PC                          1.40
```



BRUKER

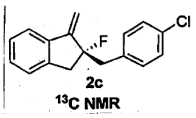
```
Current Data Parameters
NAME                  MARU-1725C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20070717
Time                       21.41
INSTRUM                   drx600
PROBHD     5 mm BBO BB-1H
PULPROG                   zgpg30
TD                        131072
SOLVENT                    CDCl3
NS                          1263
DS                             4
SWH                  45454.547 Hz
FIDRES                0.346791 Hz
AQ                    1.4418530 sec
RG                          3251
DW                     11.000 usec
DE                      6.00 usec
TE                      298.2 K
D1                  0.60000002 sec
d11                 0.03000000 sec
DELTA               0.50000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                        8.20 usec
PL1                       4.50 dB
SFO1                150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    82.00 usec
PL2                      -4.00 dB
PL12                     15.00 dB
PL13                     15.00 dB
SFO2                600.1324005 MHz

F2 - Processing parameters
SI                          131072
SF                  150.9028131 MHz
WDW                           EM
SSB                            0
LB                         1.00 Hz
GB                             0
PC                          1.40
```

13C

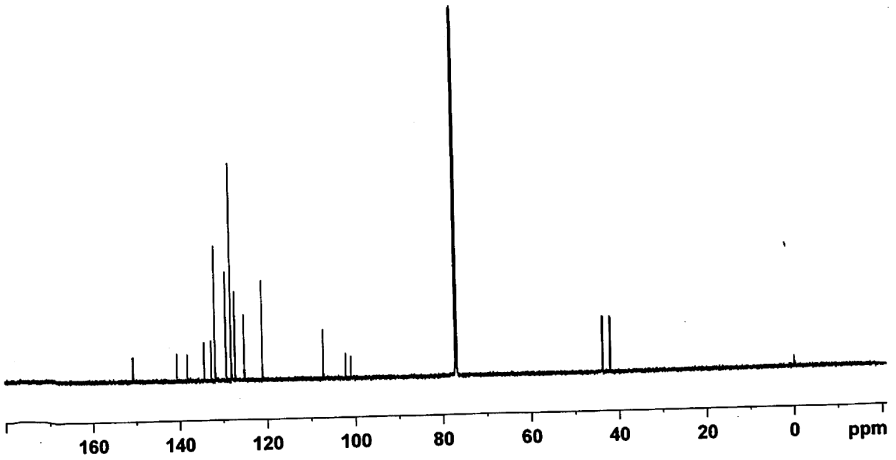
150.834
150.717
140.635
140.611
138.176
138.157
134.379
132.755
131.844
131.833
129.354
128.213
127.304
125.212
125.201
121.090
107.239
107.202
102.190
100.966

77.213
77.002
76.790

43.806
43.626
42.048
41.887



2c
^{13}C NMR



BRUKER

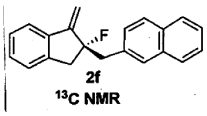
```
Current Data Parameters
NAME                  MARU-1731C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20070717
Time                       20.29
INSTRUM                   drx600
PROBHD     5 mm BBO BB-1H
PULPROG                 zgpg30
TD                        131072
SOLVENT                   CDCl3
NS                          1208
DS                             4
SWH                 45454.547 Hz
FIDRES               0.346791 Hz
AQ                   1.4418530 sec
RG                        4597.6
DW                     11.000 usec
DE                      6.00 usec
TE                        298.0 K
D1                  0.60000002 sec
d11                 0.03000000 sec
DELTA               0.50000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                      8.20 usec
PL1                      4.50 dB
SFO1               150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                  82.00 usec
PL2                     -4.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
SFO2               600.1324005 MHz

F2 - Processing parameters
SI                        131072
SF                 150.9028124 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                          1.40
```

13C

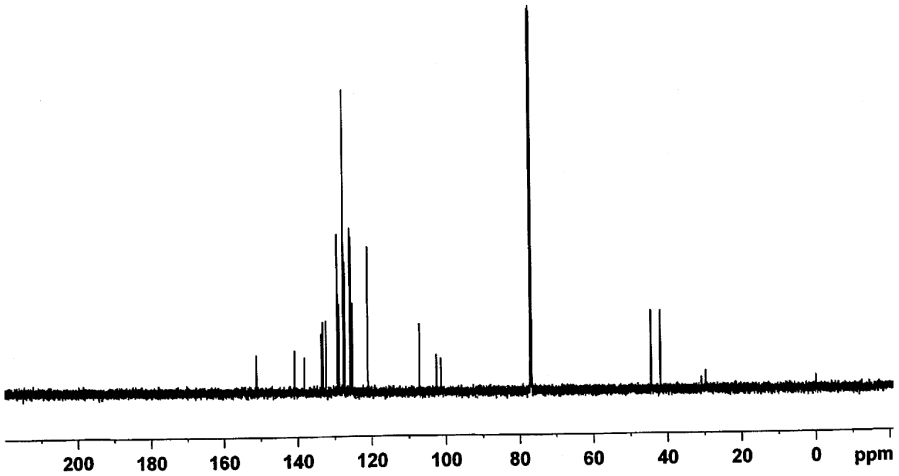
151.217
151.101
140.900
140.877
138.296
138.276
133.272
132.397
129.290
129.183
128.851
128.837
127.681
127.588
127.231
125.921
125.582
125.245
125.234
121.108
107.177
107.140
102.186
101.366

77.213
77.002
76.790

44.563
44.386
42.057
41.895

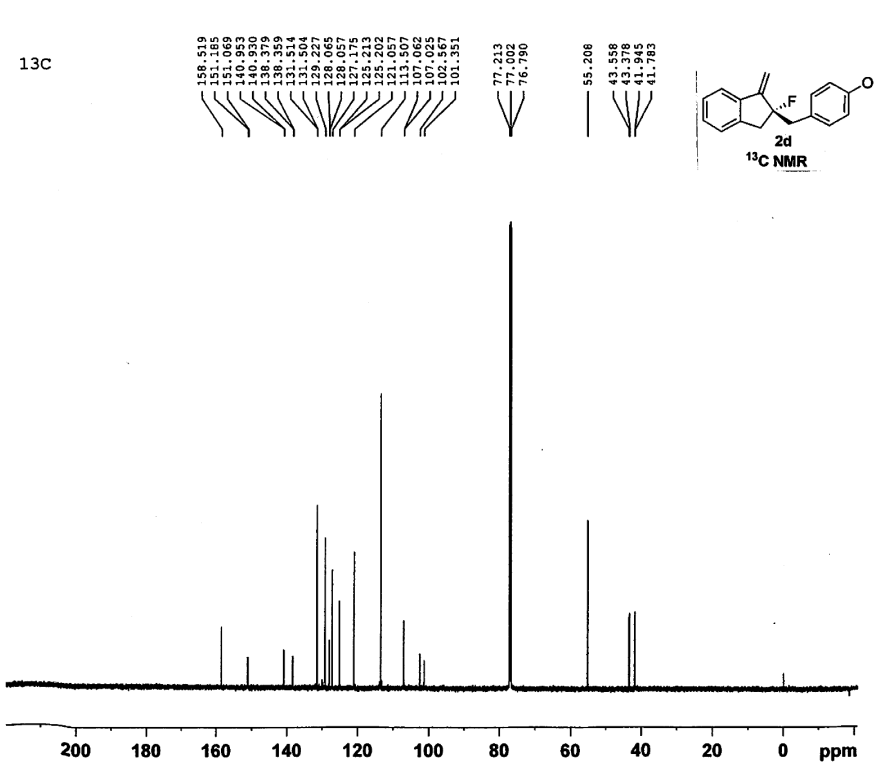


2f
^{13}C NMR



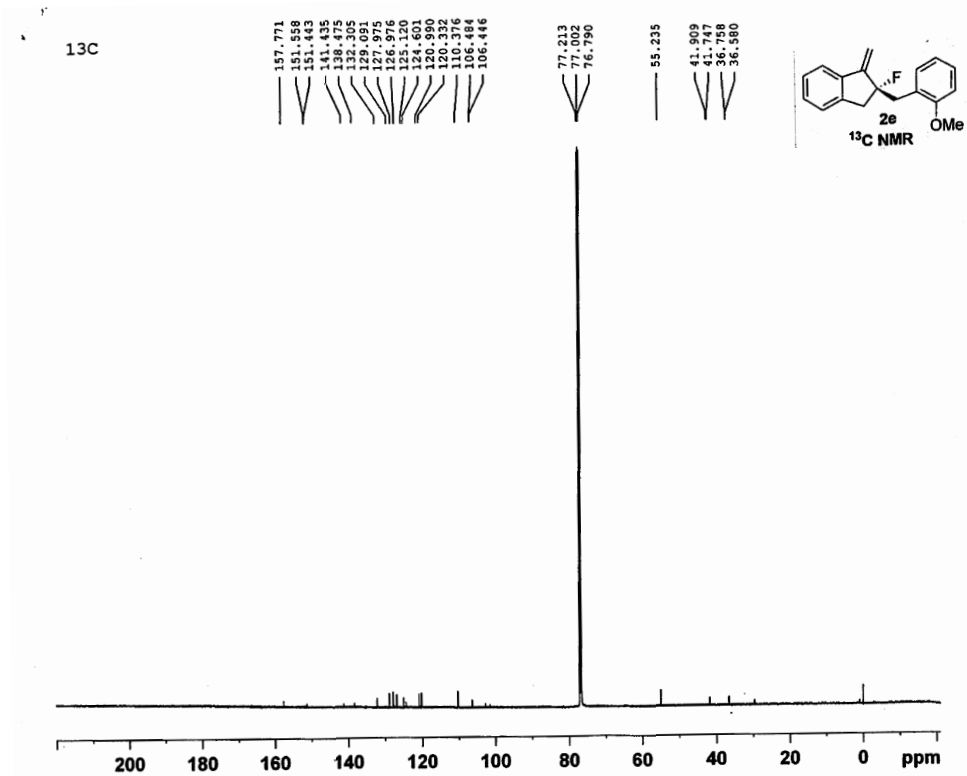
BRUKER

```
Current Data Parameters
NAME                  MARU-1750C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20070818
Time                       15.01
INSTRUM                   drx600
PROBHD     5 mm BBO BB-1H
PULPROG                 zgpg30
TD                        131072
SOLVENT                   CDCl3
NS                           204
DS                             4
SWH                 45454.547 Hz
FIDRES               0.346791 Hz
AQ                   1.4418530 sec
RG                        2298.8
DW                     11.000 usec
DE                      6.00 usec
TE                        299.4 K
D1                  0.60000002 sec
d11                 0.03000000 sec
DELTA               0.50000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                      8.20 usec
PL1                      4.50 dB
SFO1               150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                  82.00 usec
PL2                     -4.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
SFO2               600.1324005 MHz

F2 - Processing parameters
SI                        131072
SF                 150.9028127 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                          1.40
```



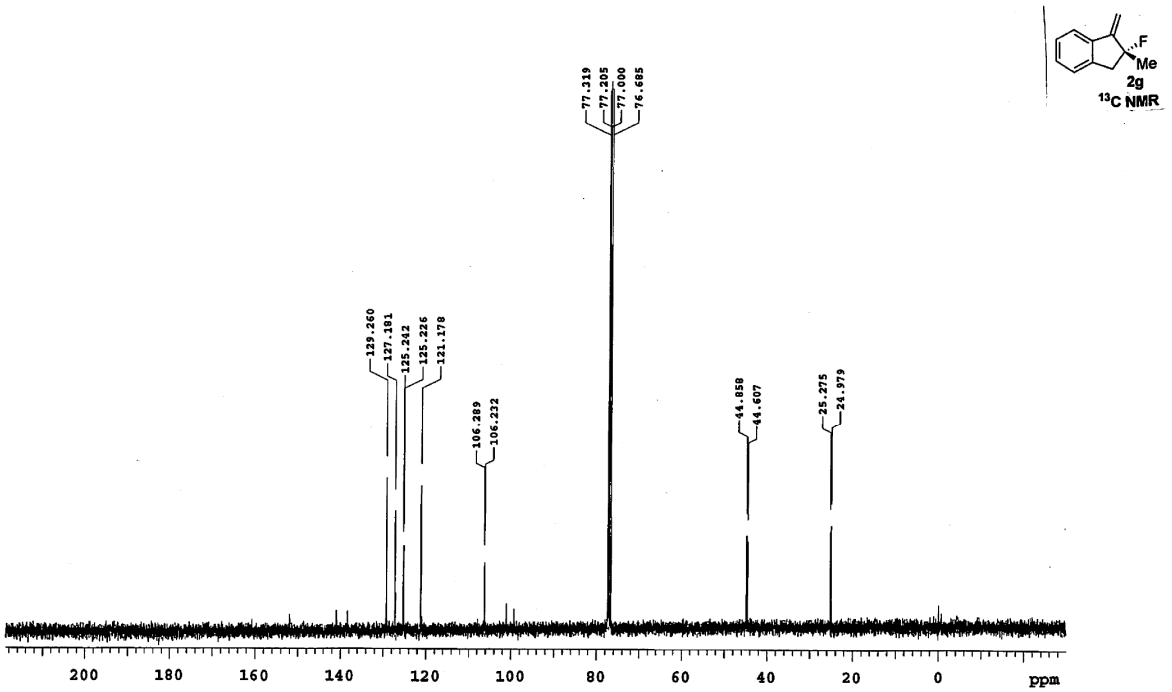
BRUKER

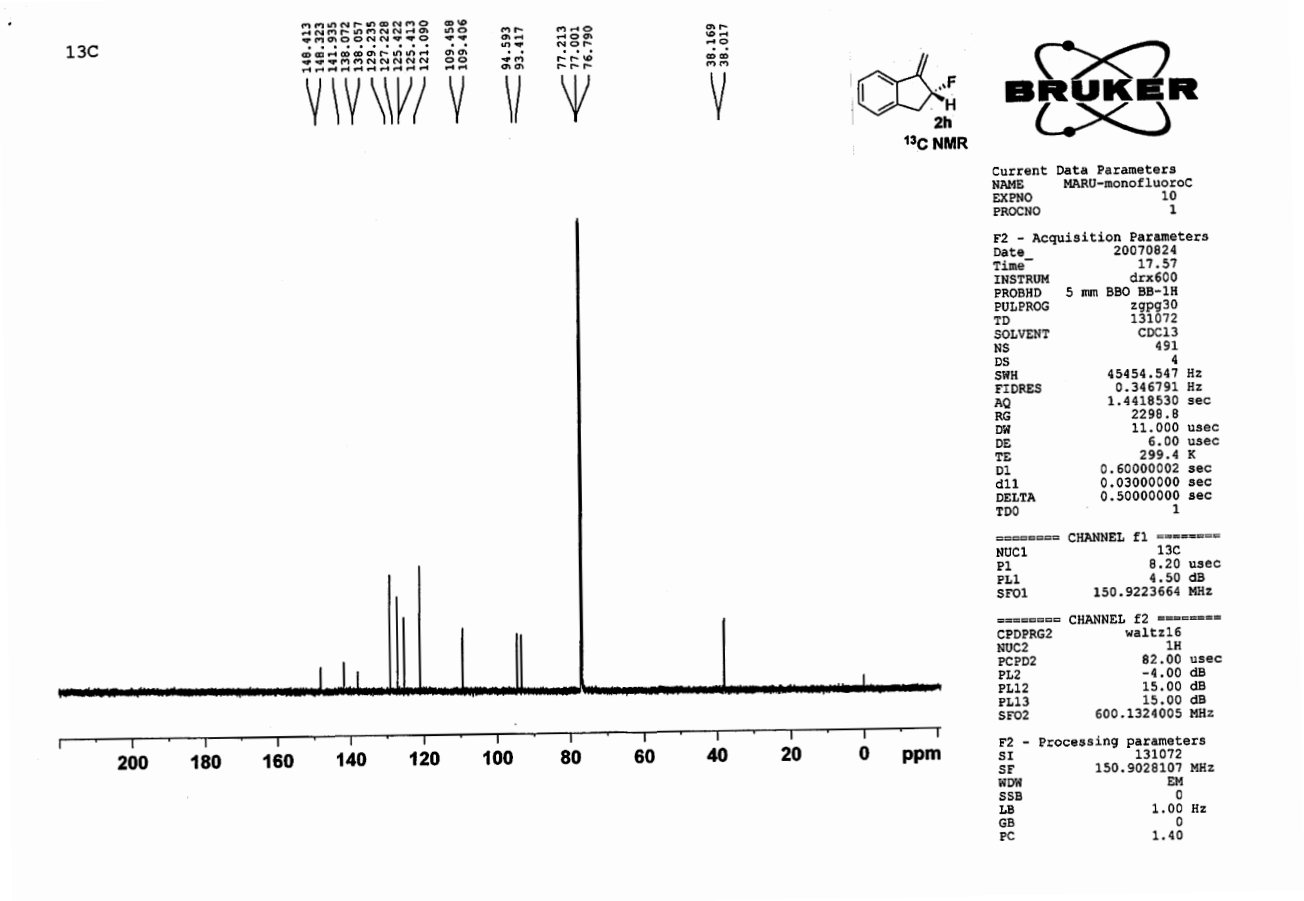
```
Current Data Parameters
NAME          MARU-1749C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070816
Time               20.52
INSTRUM           drx600
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                  1301
DS                     4
SWH            45454.547 Hz
FIDRES          0.346791 Hz
AQ             1.4418530 sec
RG                  3251
DW                11.000 usec
DE                 6.00 usec
TE                299.7 K
D1             0.60000002 sec
d11            0.03000000 sec
DELTA          0.50000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.20 usec
PL1                4.50 dB
SFO1         150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             82.00 usec
PL2               -4.00 dB
PL12              15.00 dB
PL13              15.00 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI               131072
SF         150.9028104 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



BRUKER

```
Current Data Parameters
NAME          MARU-1793C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071102
Time               9.56
INSTRUM           drx600
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                 14957
DS                     4
SWH            45454.547 Hz
FIDRES          0.346791 Hz
AQ             1.4418530 sec
RG                3649.1
DW                11.000 usec
DE                 6.00 usec
TE                298.0 K
D1             0.60000002 sec
d11            0.03000000 sec
DELTA          0.50000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.20 usec
PL1                4.50 dB
SFO1         150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             82.00 usec
PL2               -4.00 dB
PL12              15.00 dB
PL13              15.00 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI               131072
SF         150.9028101 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

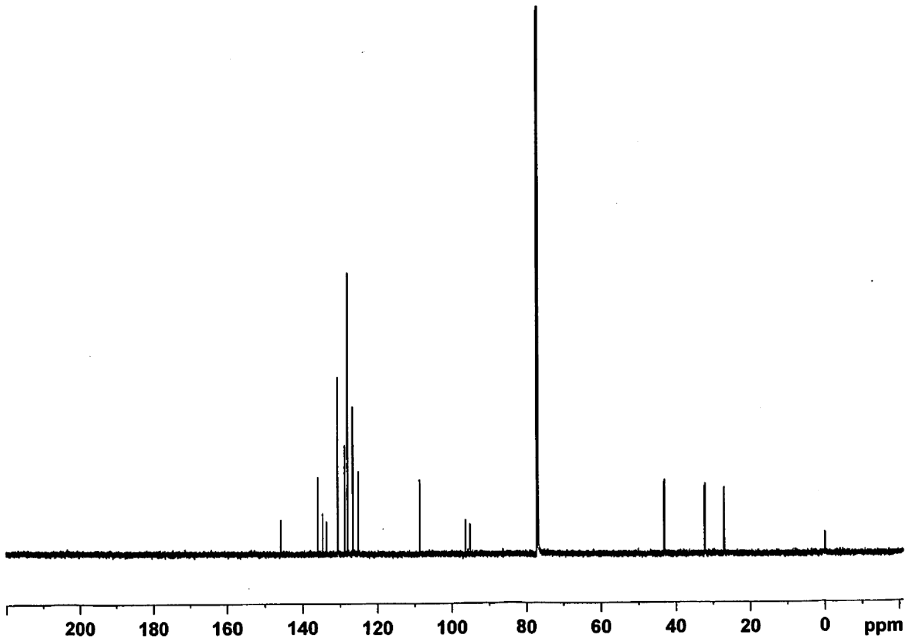




BRUKER

```
Current Data Parameters
NAME      MARU-monofluoroC
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20070824
Time              17.57
INSTRUM           drx600
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD               131072
SOLVENT             CDCl3
NS                    491
DS                      4
SWH           45454.547 Hz
FIDRES        0.346791 Hz
AQ            1.4418530 sec
RG               2298.8
DW               11.000 usec
DE                6.00 usec
TE               299.4 K
D1            0.60000002 sec
d11           0.03000000 sec
DELTA         0.50000000 sec
TD0                     1

========== CHANNEL f1 ==========
NUC1                  13C
P1                 8.20 usec
PL1                4.50 dB
SFO1         150.9223664 MHz

========== CHANNEL f2 ==========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             82.00 usec
PL2               -4.00 dB
PL12              15.00 dB
PL13              15.00 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 131072
SF           150.9028107 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

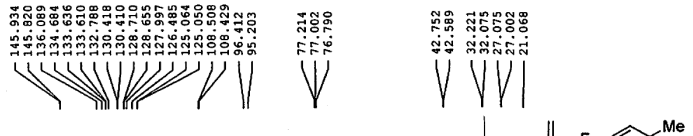
13C

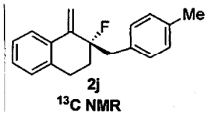


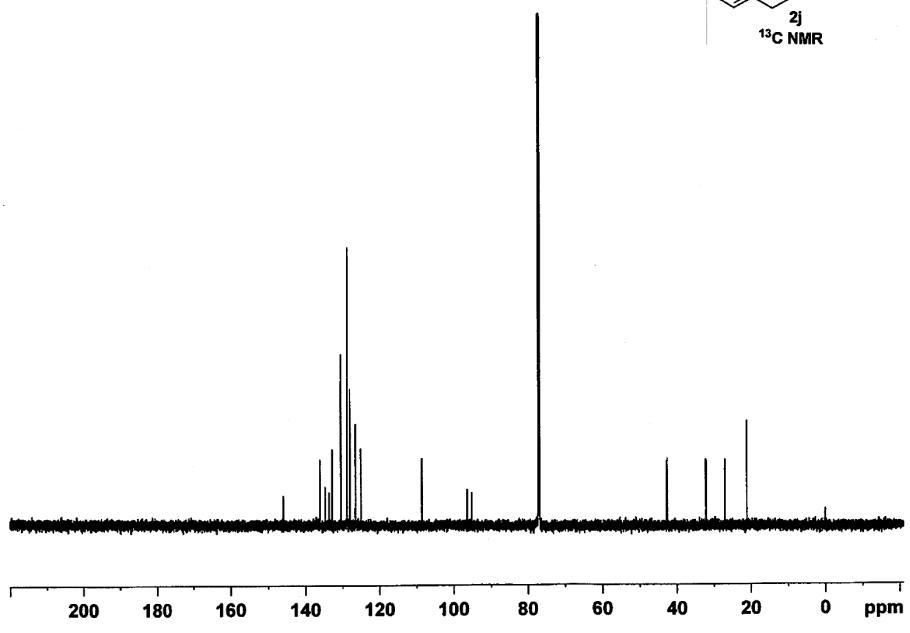
BRUKER

```
Current Data Parameters
NAME      MARU-Allylsilane-PhC
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20071101
Time              11.51
INSTRUM           drx600
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                   823
DS                     4
SWH           45454.547 Hz
FIDRES         0.346791 Hz
AQ            1.4418530 sec
RG                  8192
DW                11.000 usec
DE                 6.00 usec
TE                297.9 K
D1            0.60000002 sec
d11           0.03000000 sec
DELTA         0.50000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.20 usec
PL1                 4.50 dB
SFO1         150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              82.00 usec
PL2                -4.00 dB
PL12               15.00 dB
PL13               15.00 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 131072
SF           150.9028124 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

13C



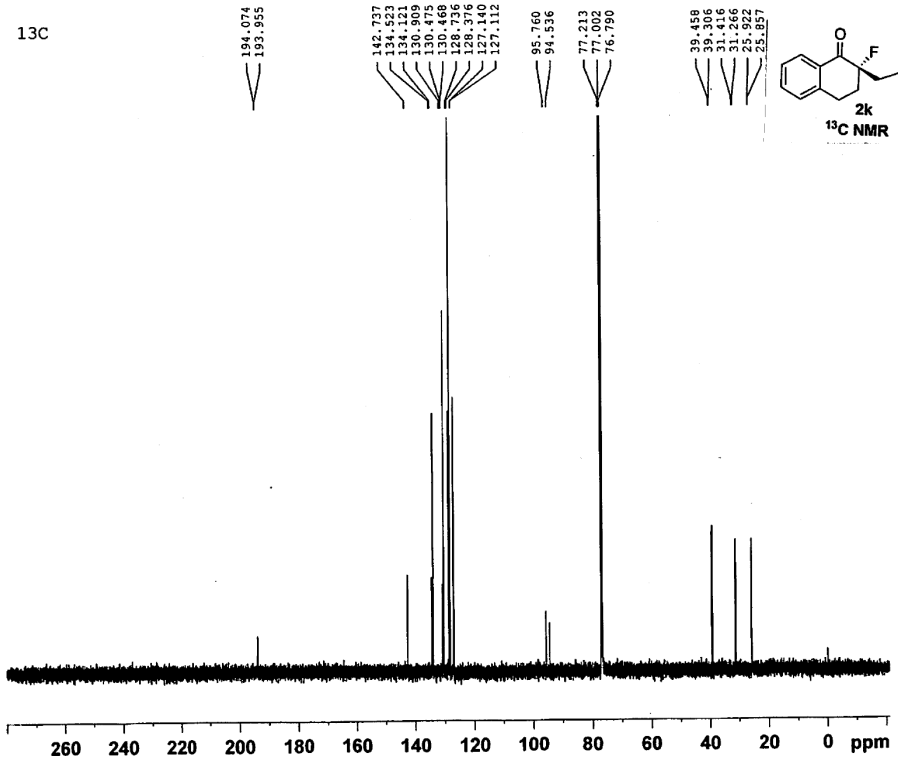




BRUKER

```
Current Data Parameters
NAME      MARU-Allylsilane-PhMeC
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20071101
Time              12.40
INSTRUM           drx600
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                   244
DS                     4
SWH           45454.547 Hz
FIDRES         0.346791 Hz
AQ            1.4418530 sec
RG                  4597.6
DW                11.000 usec
DE                 6.00 usec
TE                298.1 K
D1            0.60000002 sec
d11           0.03000000 sec
DELTA         0.50000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.20 usec
PL1                 4.50 dB
SFO1         150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              82.00 usec
PL2                -4.00 dB
PL12               15.00 dB
PL13               15.00 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 131072
SF           150.9028124 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

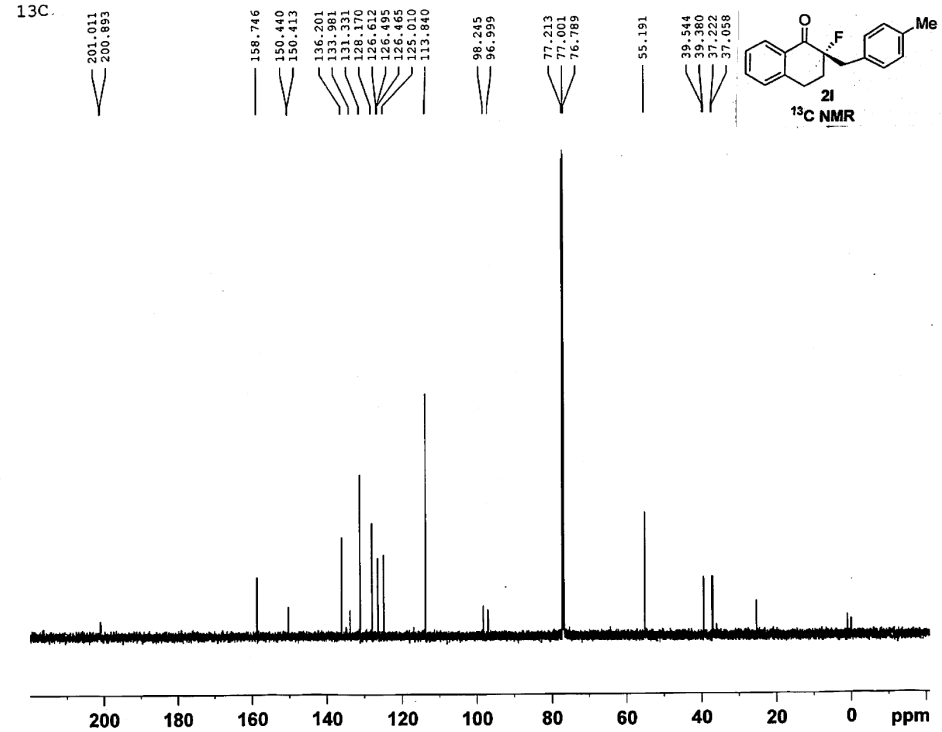
13C



BRUKER

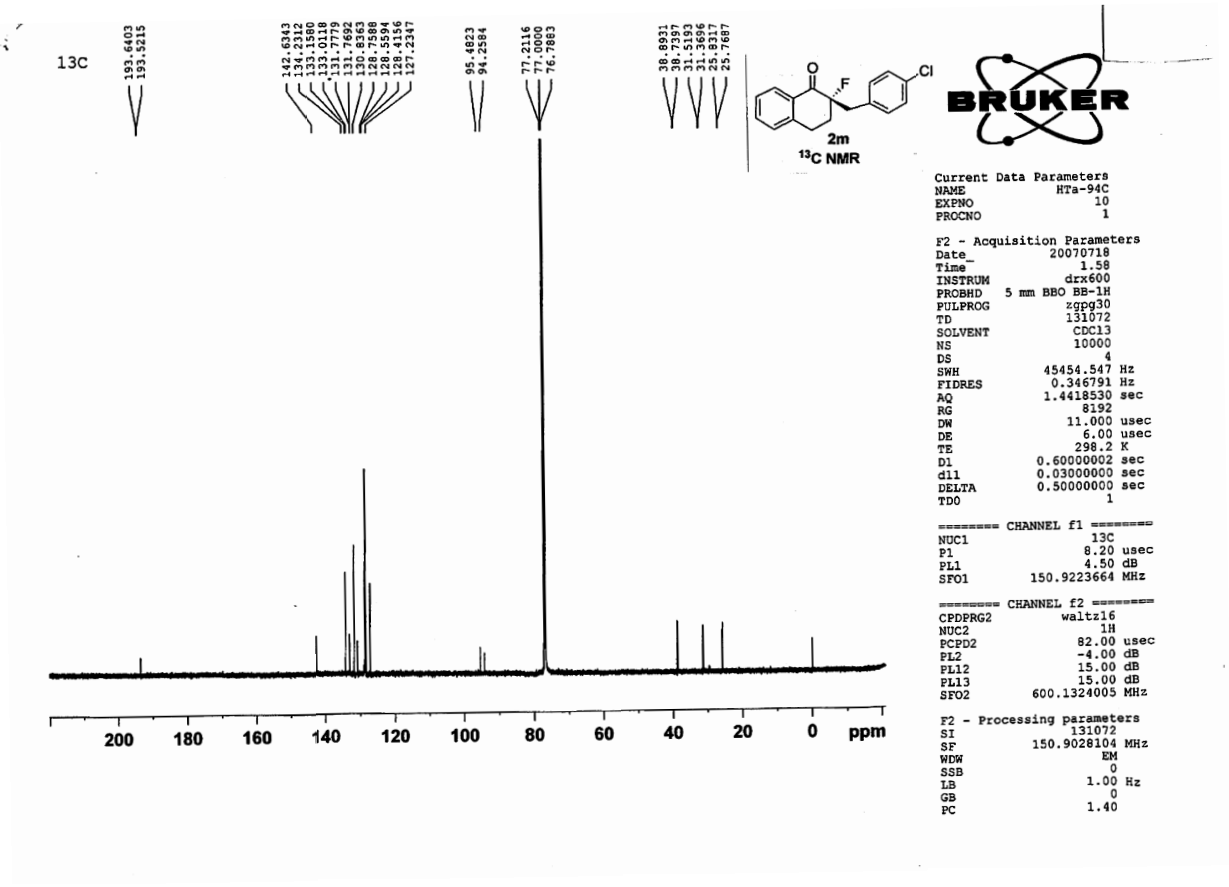
```
Current Data Parameters
NAME      MARU-tetra-benzyl C
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20070522
Time                   17.50
INSTRUM                drx600
PROBHD    5 mm BBO BB-1H
PULPROG                zgpg30
TD                     131072
SOLVENT                CDCl3
NS                       512
DS                         4
SWH                45454.547 Hz
FIDRES             0.346791 Hz
AQ                 1.4418530 sec
RG                     16384
DW                    11.000 usec
DE                     6.00 usec
TE                    297.9 K
D1                 0.60000002 sec
d11                0.03000000 sec
DELTA              0.50000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       8.20 usec
PL1                      4.50 dB
SFO1              150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   82.00 usec
PL2                     -4.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
SFO2              600.1324005 MHz

F2 - Processing parameters
SI                       131072
SF                150.9028133 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                         1.40
```

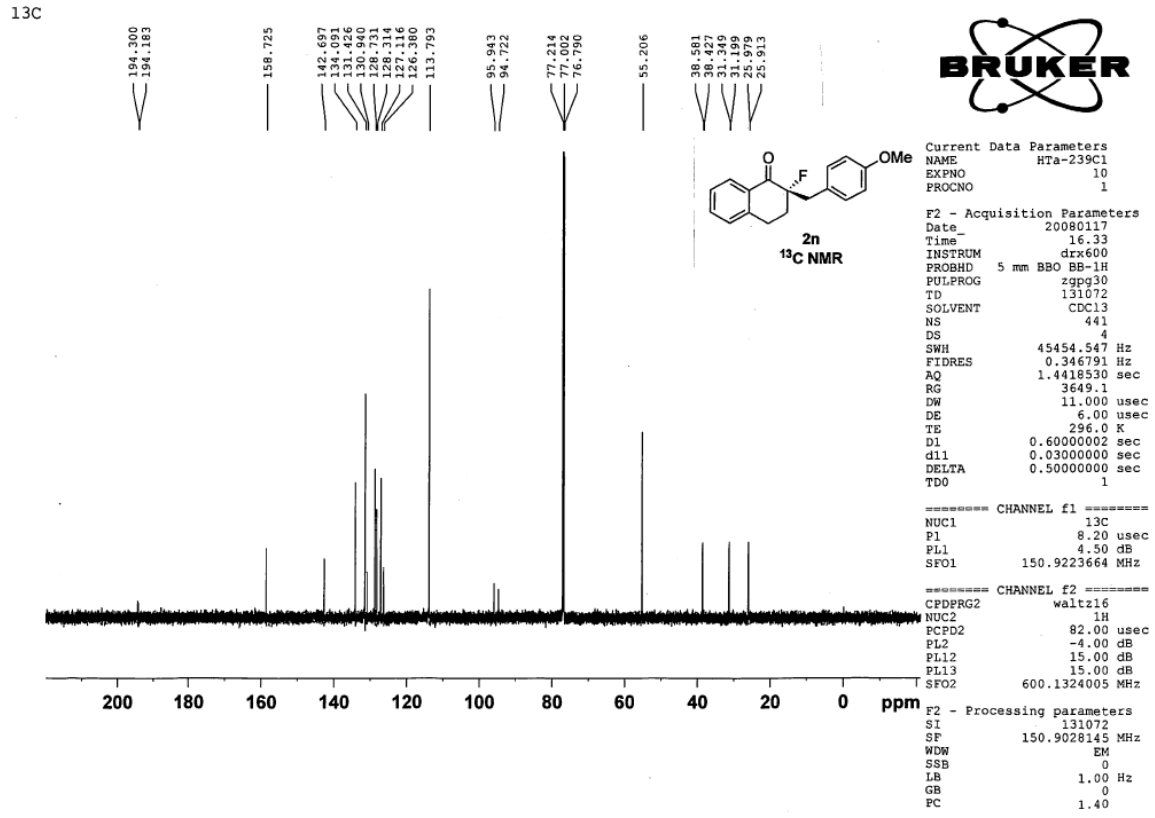
13C

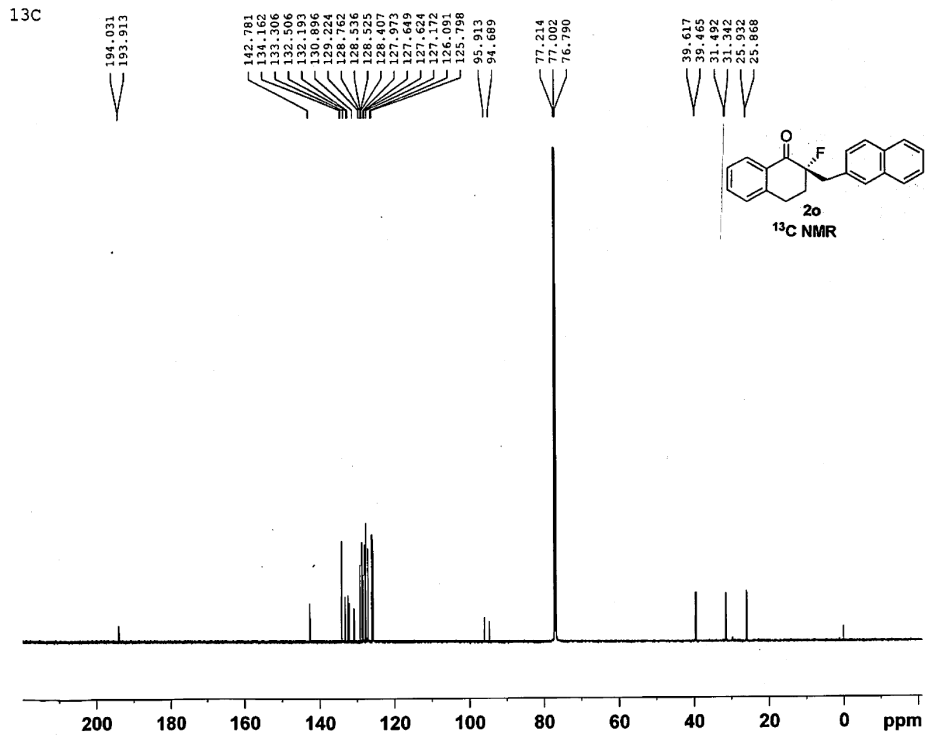


BRUKER

```
Current Data Parameters
NAME                   HTa-180C
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_               20071101
Time                    0.00
INSTRUM                drx600
PROBHD    5 mm BBO BB-1H
PULPROG                zgpg30
TD                     131072
SOLVENT                CDCl3
NS                       194
DS                         4
SWH                45454.547 Hz
FIDRES             0.346791 Hz
AQ                 1.4418530 sec
RG                      6502
DW                    11.000 usec
DE                     6.00 usec
TE                    298.0 K
D1                 0.60000002 sec
d11                0.03000000 sec
DELTA              0.50000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       8.20 usec
PL1                      4.50 dB
SFO1              150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   82.00 usec
PL2                     -4.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
SFO2              600.1324005 MHz

F2 - Processing parameters
SI                       131072
SF                150.9028125 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                         1.40
```


13C
193.6403
193.5215
142.6343
134.2342
133.1580
133.1018
131.7779
131.7692
130.8363
128.7588
128.5594
128.4156
127.2347
95.4823
94.2584
77.2116
77.0000
76.7883
38.8931
38.7397
31.5193
31.3656
25.8317
25.7687
O
F
Cl
2m
13C NMR
BRUKER
Current Data Parameters
NAME HTa-94C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070718
Time 1.58
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDC13
NS 10000
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 8192
DW 11.000 usec
DE 6.00 usec
TE 298.2 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028104 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm


13C
194.300
194.183
158.725
142.697
134.091
131.426
130.940
128.731
128.314
127.116
126.380
113.793
95.943
94.722
77.214
77.002
76.790
55.206
38.581
38.427
31.349
31.199
25.979
25.913
O
F
OMe
2n
13C NMR
BRUKER
Current Data Parameters
NAME HTa-239C1
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080117
Time 16.33
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDC13
NS 441
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 3649.1
DW 11.000 usec
DE 6.00 usec
TE 296.0 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028145 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm



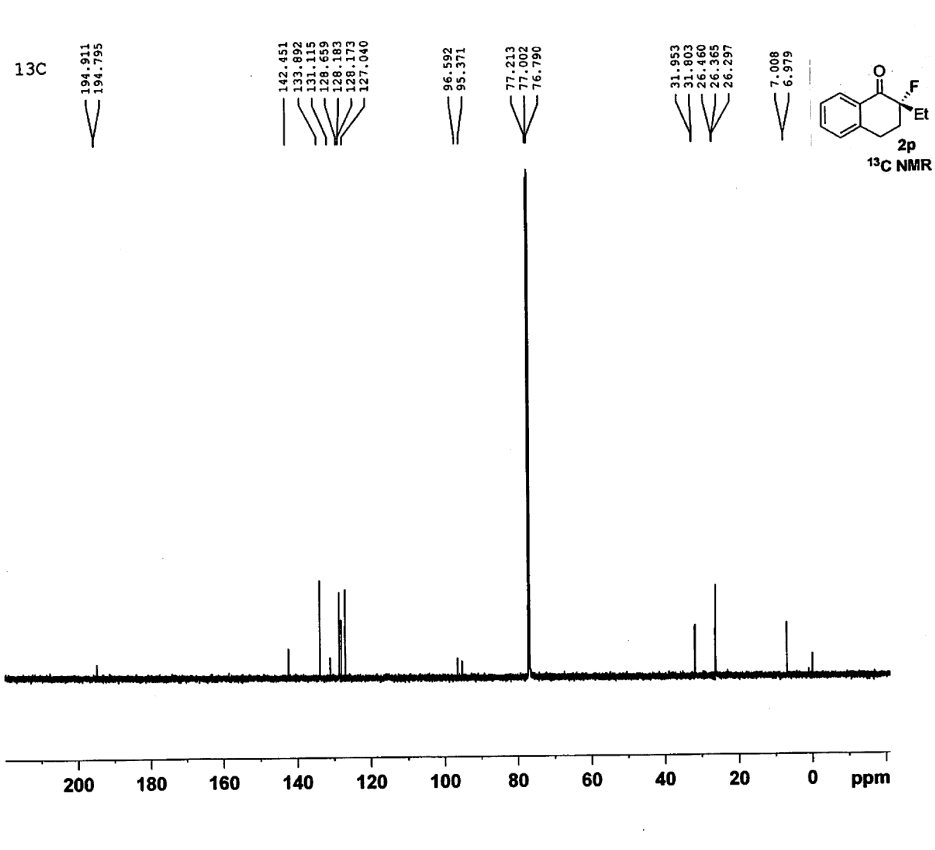
Current Data Parameters
NAME HTa-240C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080117
Time 17.02
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 3481
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 10321.3
DW 11.000 usec
DE 6.00 usec
TE 295.9 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz

F2 - Processing parameters
SI 131072
SF 150.9028131 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



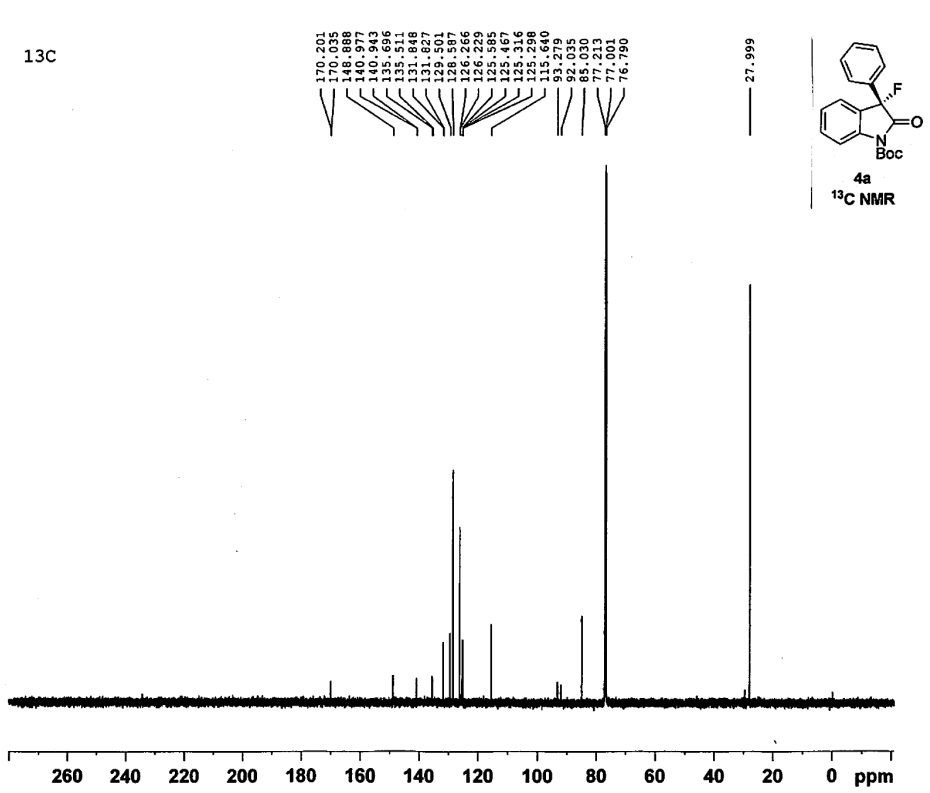
Current Data Parameters
NAME HTa-141C
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20071113
Time 17.48
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 512
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 2298.8
DW 11.000 usec
DE 6.00 usec
TE 297.6 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz

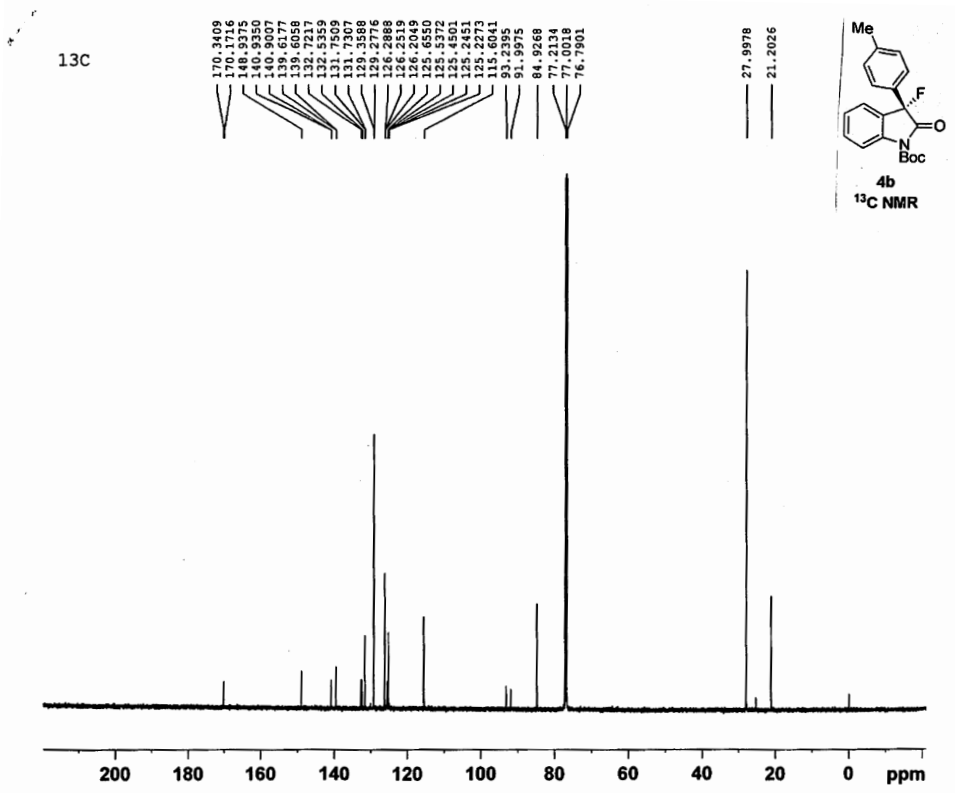
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz

F2 - Processing parameters
SI 131072
SF 150.9028110 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



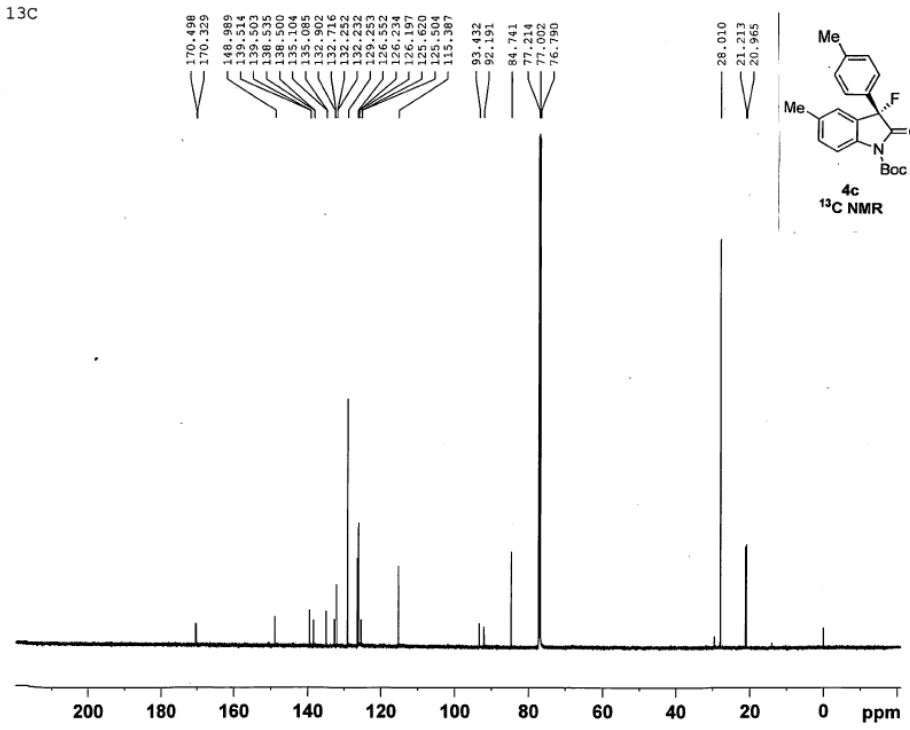
BRUKER

```
Current Data Parameters
NAME                  MARU-2 C
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_               20070522
Time                   20.25
INSTRUM                drx600
PROBHD    5 mm BBO BB-1H
PULPROG                zgpg30
TD                     131072
SOLVENT                 CDCl3
NS                        512
DS                          4
SWH                45454.547 Hz
FIDRES              0.346791 Hz
AQ                  1.4418530 sec
RG                      16384
DW                     11.000 usec
DE                      6.00 usec
TE                     297.5 K
D1                 0.60000002 sec
d11                0.03000000 sec
DELTA              0.50000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        8.20 usec
PL1                       4.50 dB
SFO1               150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    82.00 usec
PL2                      -4.00 dB
PL12                     15.00 dB
PL13                     15.00 dB
SFO2               600.1324005 MHz

F2 - Processing parameters
SI                         131072
SF                 150.9028121 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



BRUKER

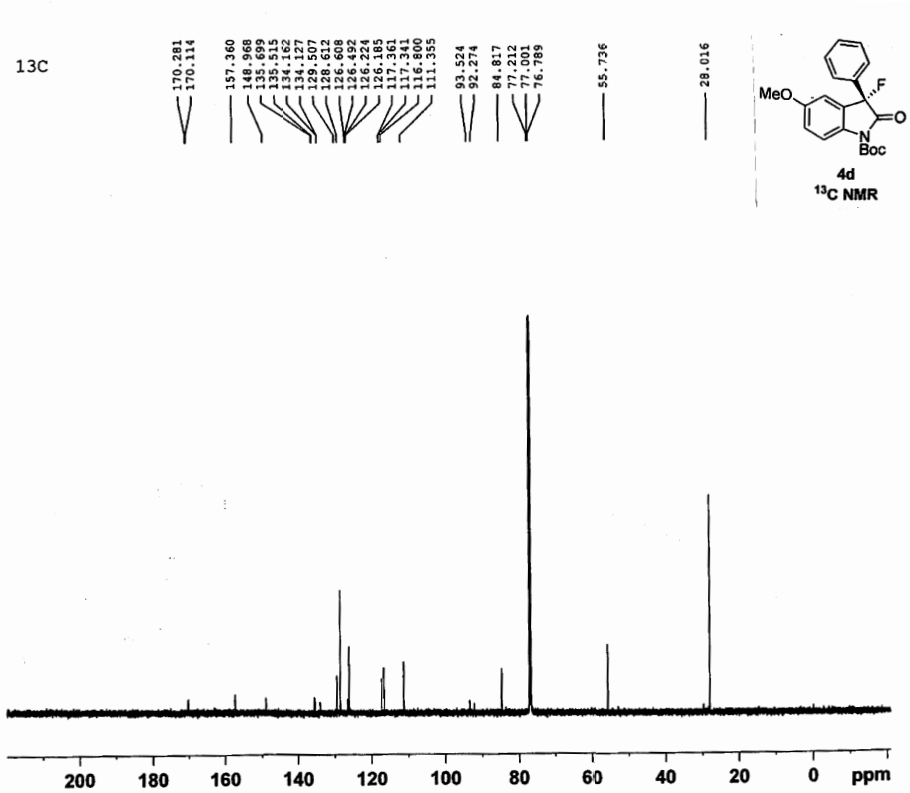
```
Current Data Parameters
NAME                MARU-1733C
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_               20070721
Time                    8.33
INSTRUM                drx600
PROBHD    5 mm BBO BB-1H
PULPROG                zgpg30
TD                     131072
SOLVENT                 CDCl3
NS                       1912
DS                          4
SWH                45454.547 Hz
FIDRES              0.346791 Hz
AQ                  1.4418530 sec
RG                       8192
DW                     11.000 usec
DE                      6.00 usec
TE                     298.8 K
D1                 0.60000002 sec
d11                0.03000000 sec
DELTA              0.50000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        8.20 usec
PL1                       4.50 dB
SFO1               150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    82.00 usec
PL2                      -4.00 dB
PL12                     15.00 dB
PL13                     15.00 dB
SFO2               600.1324005 MHz

F2 - Processing parameters
SI                         131072
SF                 150.9028121 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



4c
^{13}C NMR

BRUKER

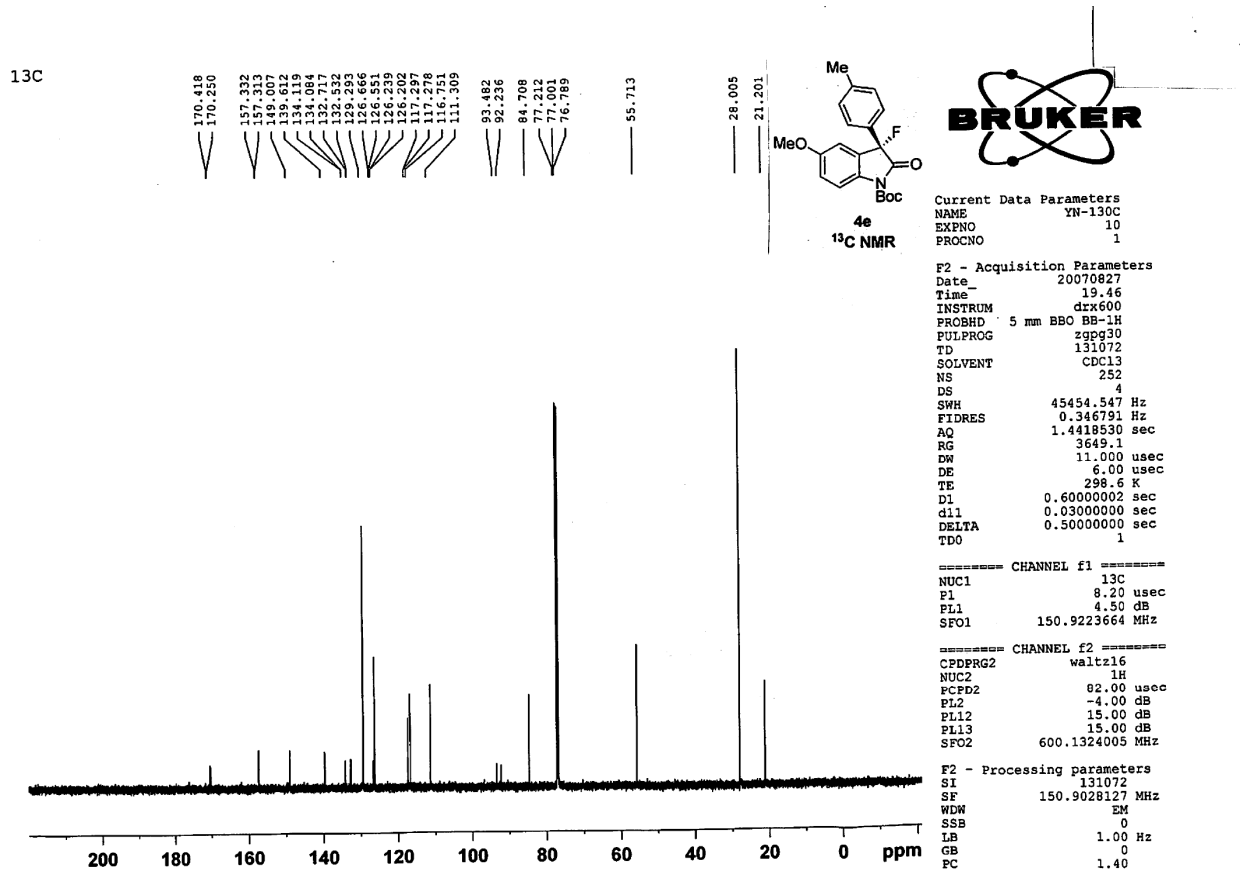
```
Current Data Parameters
NAME                  MARU-1845C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                  20080208
Time                      16.16
INSTRUM                  drx600
PROBHD    5 mm BBO BB-1H
PULPROG                 zgpg30
TD                      131072
SOLVENT                   CDCl3
NS                         2411
DS                            4
SWH                 45454.547 Hz
FIDRES               0.346791 Hz
AQ                   1.4418530 sec
RG                      7298.2
DW                     11.000 usec
DE                      6.00 usec
TE                      297.2 K
D1                  0.60000002 sec
d11                 0.03000000 sec
DELTA               0.50000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         8.20 usec
PL1                        4.50 dB
SFO1               150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     82.00 usec
PL2                       -4.00 dB
PL12                      15.00 dB
PL13                      15.00 dB
SFO2               600.1324005 MHz

F2 - Processing parameters
SI                         131072
SF                 150.9028121 MHz
WDW                            EM
SSB                             0
LB                          1.00 Hz
GB                              0
PC                           1.40
```

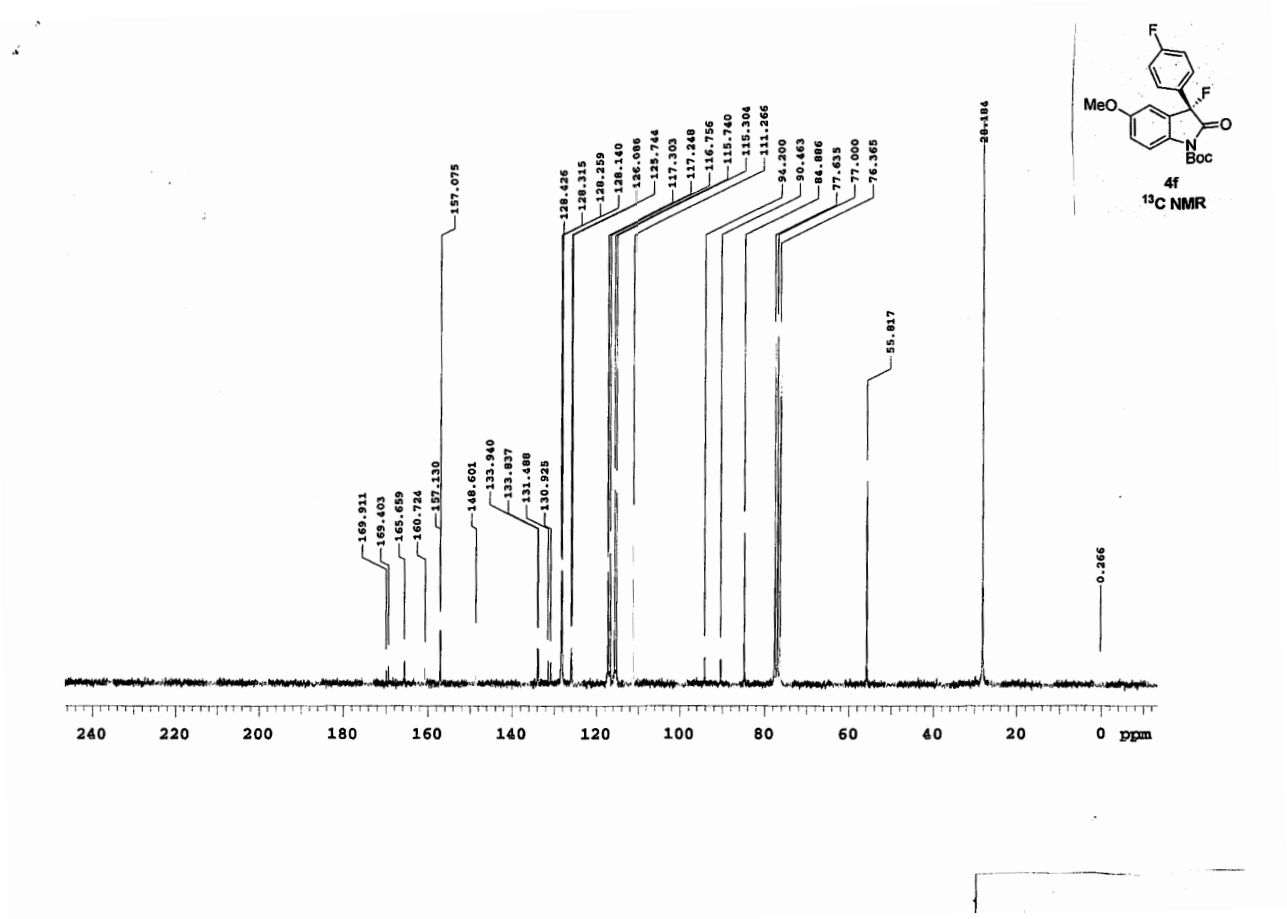


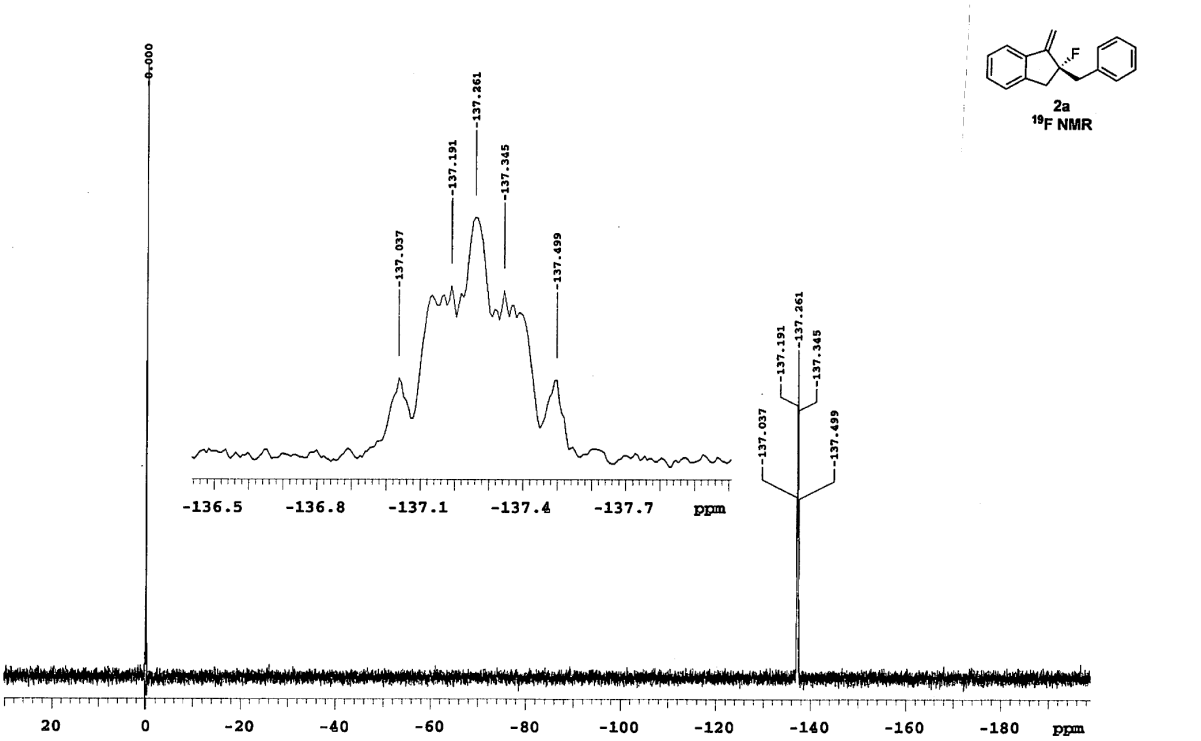
4d
^{13}C NMR

BRUKER

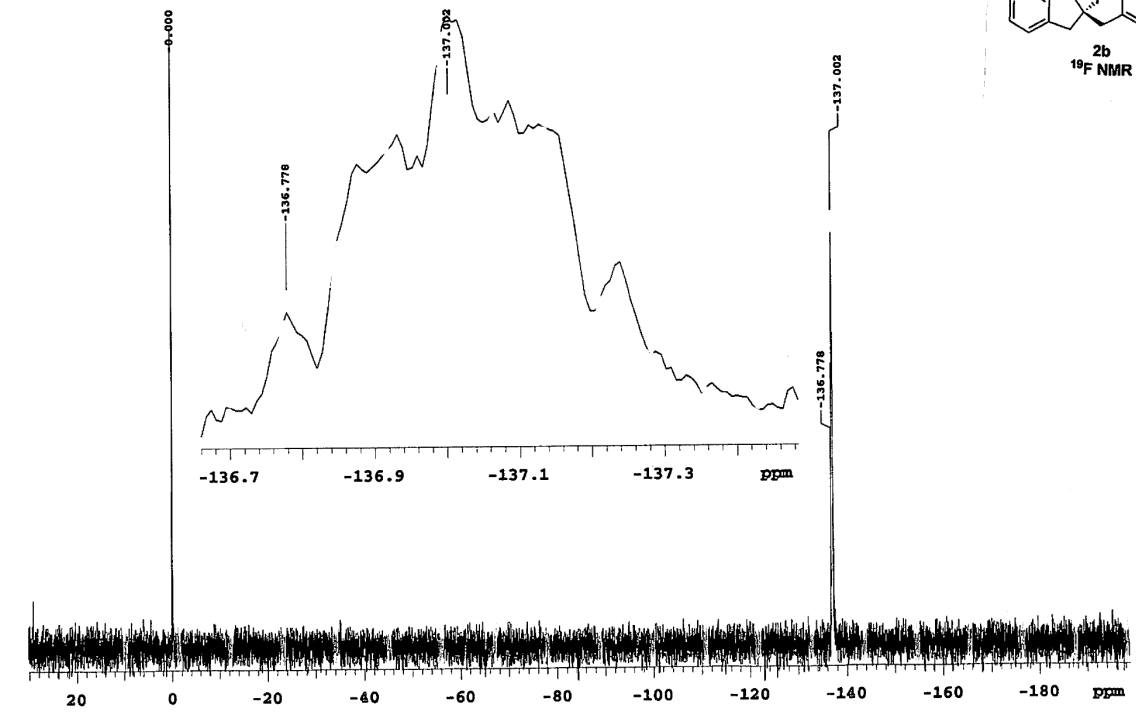
```
Current Data Parameters
NAME                   YN-121C
EXPNO                         10
PROCNO                         1

F2 - Acquisition Parameters
Date_                  20070827
Time                      19.26
INSTRUM                  drx600
PROBHD    5 mm BBO BB-1H
PULPROG                 zgpg30
TD                      131072
SOLVENT                   CDCl3
NS                          405
DS                            4
SWH                 45454.547 Hz
FIDRES               0.346791 Hz
AQ                   1.4418530 sec
RG                      5792.6
DW                     11.000 usec
DE                      6.00 usec
TE                      298.1 K
D1                  0.60000002 sec
d11                 0.03000000 sec
DELTA               0.50000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         8.20 usec
PL1                        4.50 dB
SFO1               150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     82.00 usec
PL2                       -4.00 dB
PL12                      15.00 dB
PL13                      15.00 dB
SFO2               600.1324005 MHz

F2 - Processing parameters
SI                         131072
SF                 150.9028114 MHz
WDW                            EM
SSB                             0
LB                          1.00 Hz
GB                              0
PC                           1.40
```


13C
170.418
170.250
157.332
157.313
149.007
139.612
134.119
134.084
132.717
132.532
129.293
126.666
126.551
126.239
125.297
117.278
116.751
111.309
93.482
92.236
84.708
77.212
77.001
76.789
55.713
28.005
21.201
Me
MeO
F
O
N
Boc
4e
13C NMR
BRUKER
Current Data Parameters
NAME YN-130C
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070827
Time 19.46
INSTRUM drx600
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 252
DS 4
SWH 45454.547 Hz
FIDRES 0.346791 Hz
AQ 1.4418530 sec
RG 3649.1
DW 11.000 usec
DE 6.00 usec
TE 298.6 K
D1 0.60000002 sec
d11 0.03000000 sec
DELTA 0.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.20 usec
PL1 4.50 dB
SFO1 150.9223664 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 82.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 131072
SF 150.9028127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

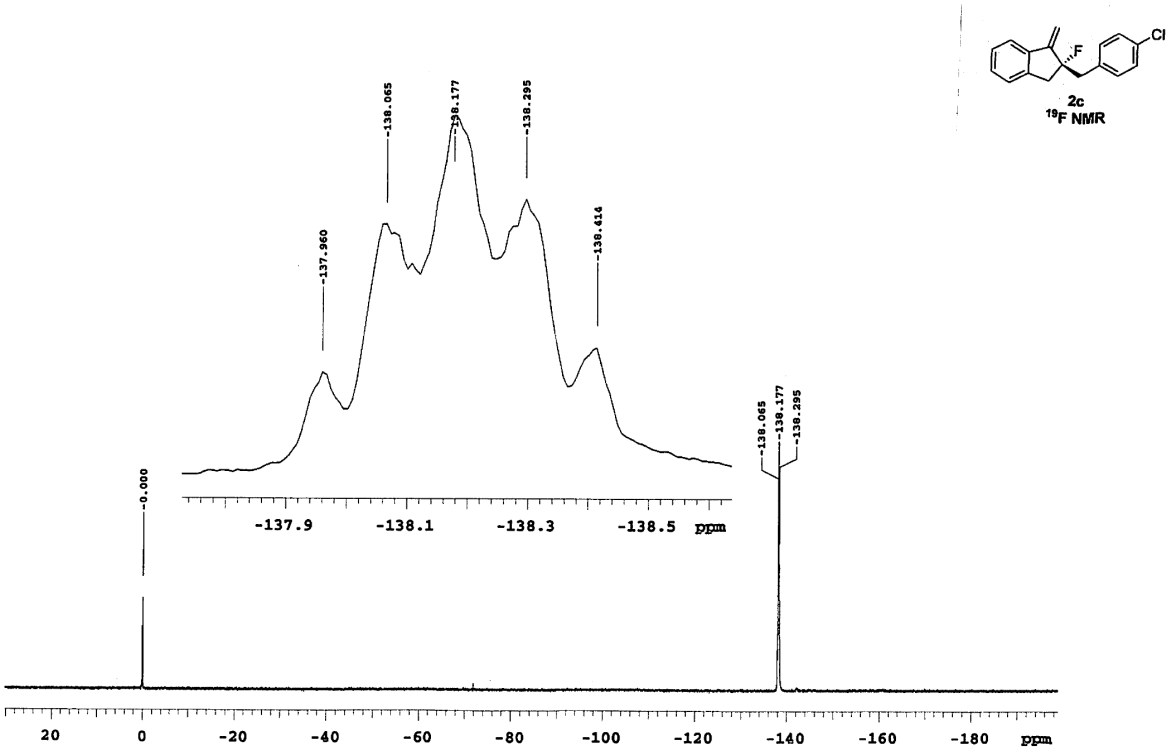

F
MeO
F
O
N
Boc
4f
13C NMR
169.911
169.403
165.659
160.724
157.139
157.075
148.601
133.940
133.837
131.488
130.925
128.426
128.315
128.259
128.140
126.086
125.744
117.303
117.248
116.756
115.740
115.304
111.266
94.200
90.463
84.886
77.635
77.000
76.365
55.817
28.184
0.266
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm



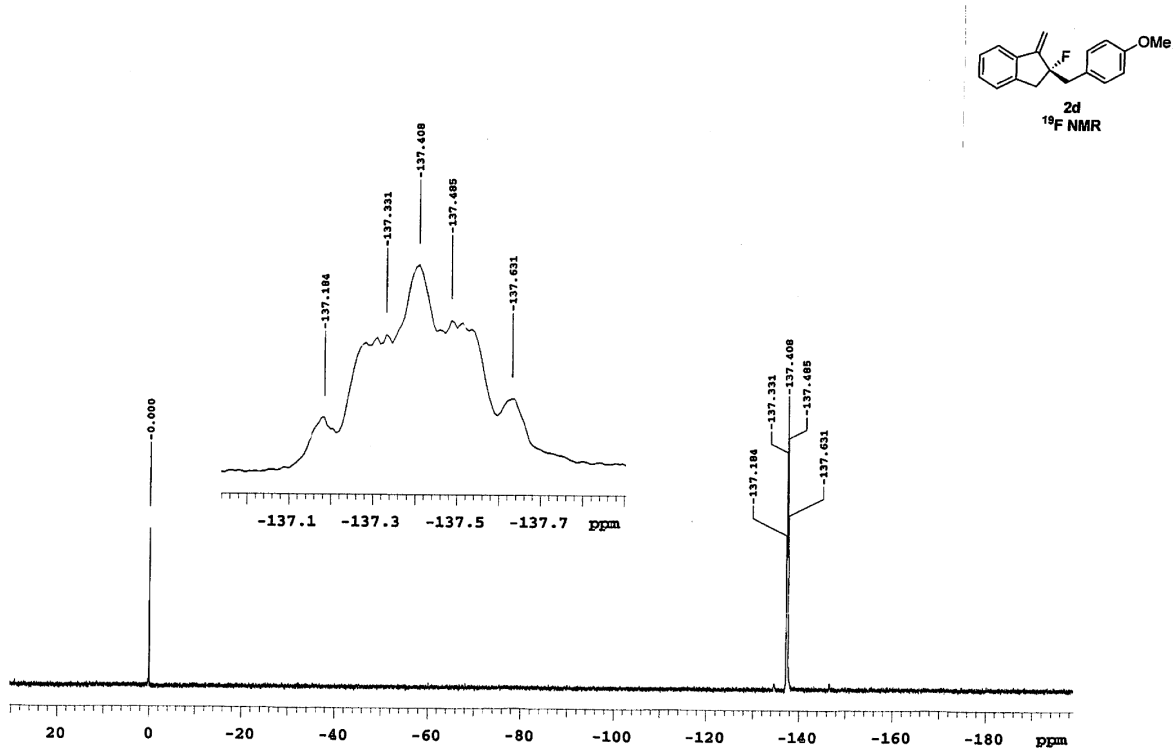
2a
^{19}F NMR

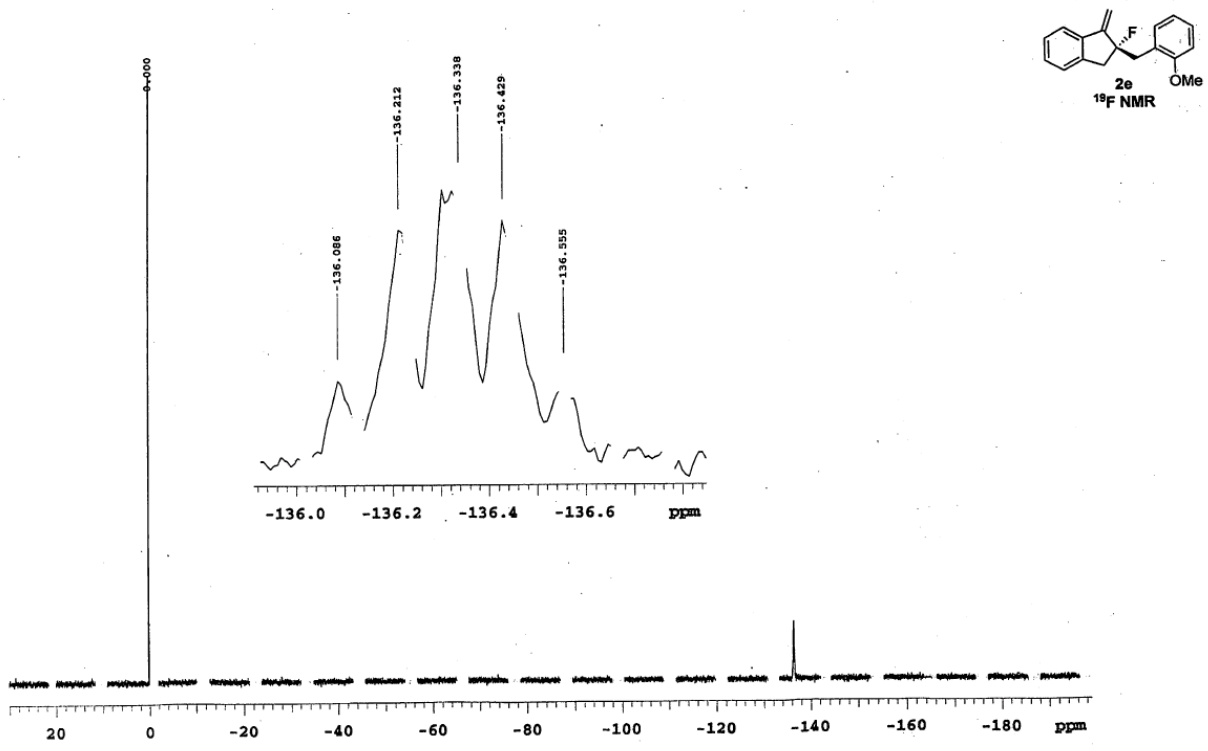


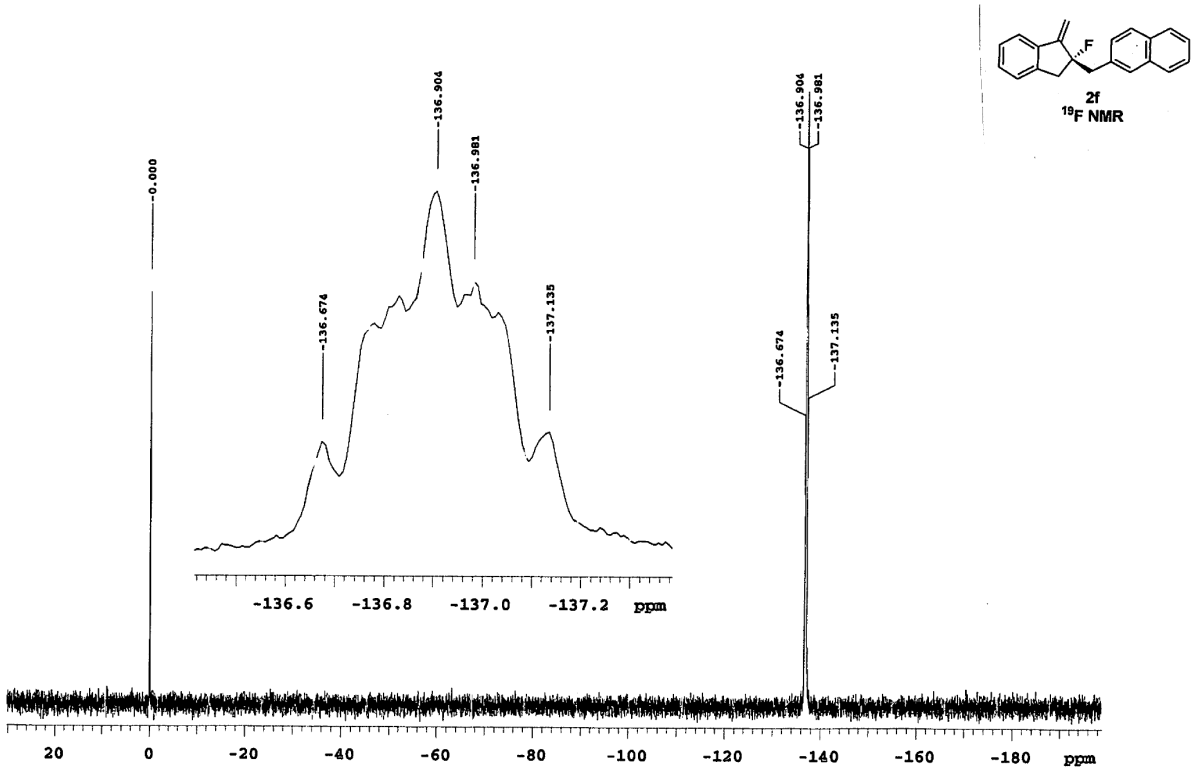
2b
^{19}F NMR

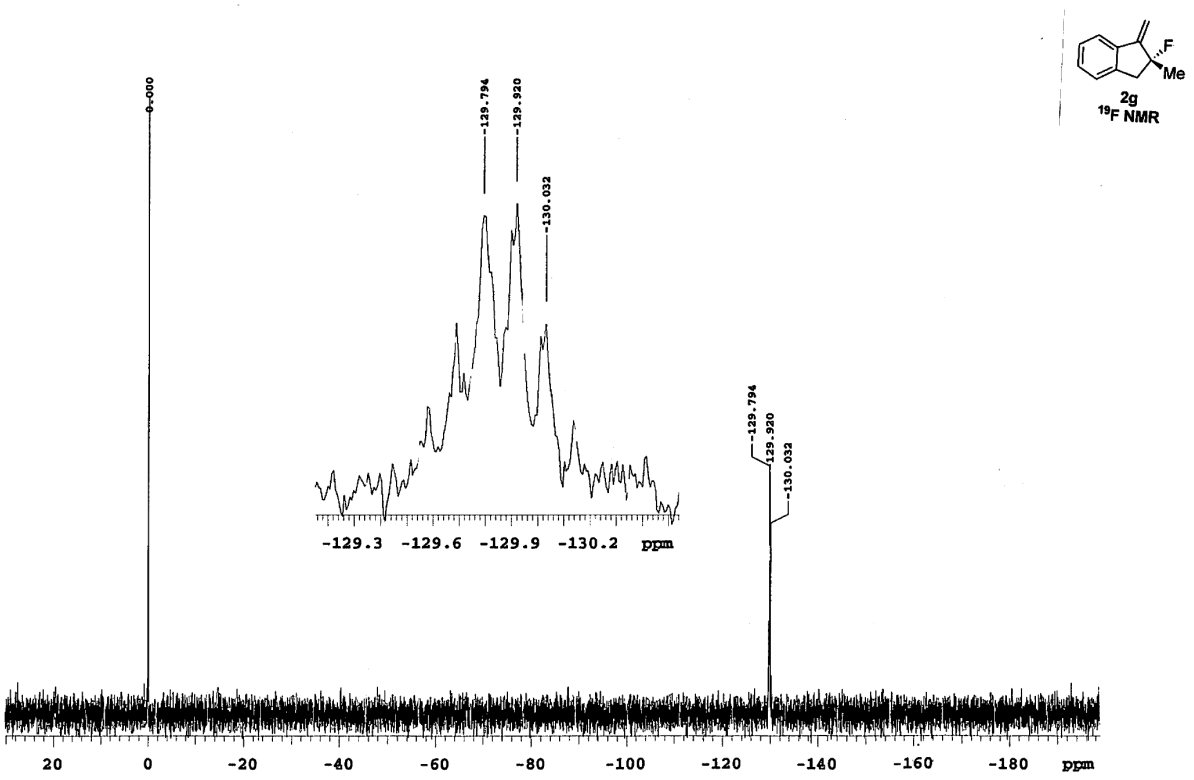


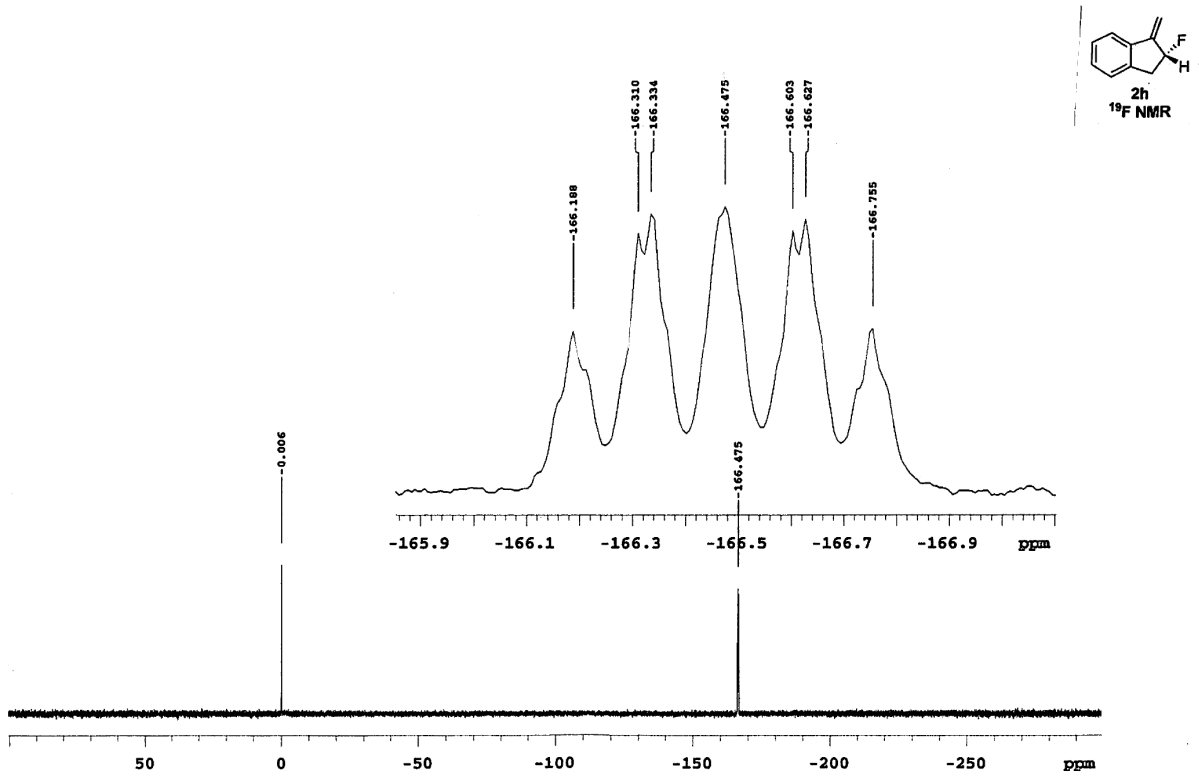
SVff ' MARC- 1751 ')

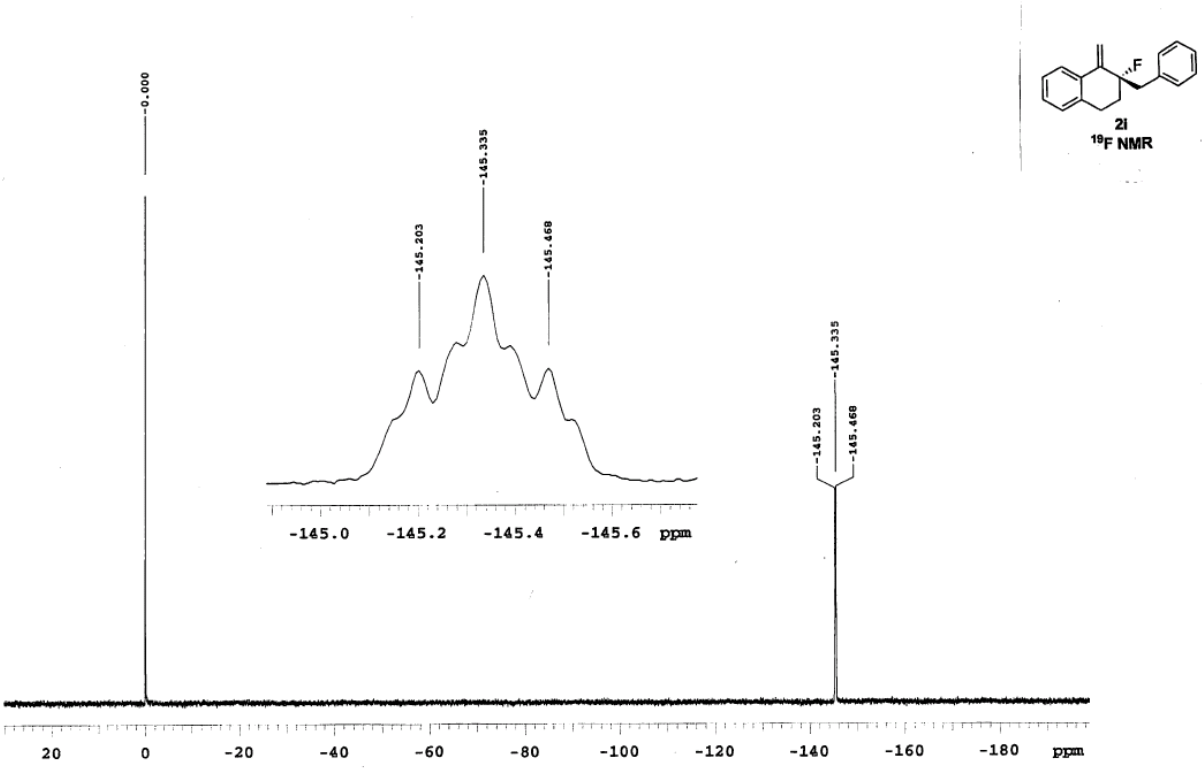



F
OMe
2e
^{19}F NMR
-0.000
-136.086
-136.212
-136.338
-136.429
-136.555
-136.0
-136.2
-136.4
-136.6
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

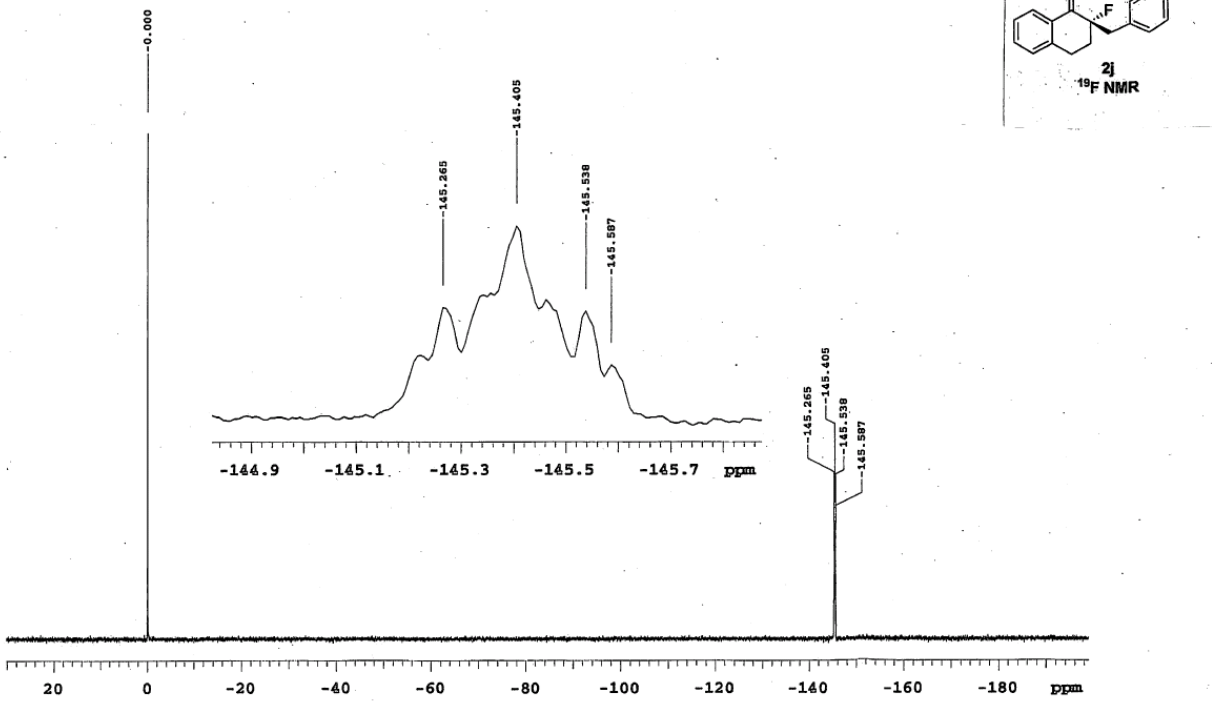

F
2f
^{19}F NMR
-0.000
-136.674
-136.904
-136.981
-137.135
-136.6
-136.8
-137.0
-137.2
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


F
Me
2g
19F NMR
0.000
-129.794
-129.920
-130.032
-129.3 -129.6 -129.9 -130.2 ppm
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

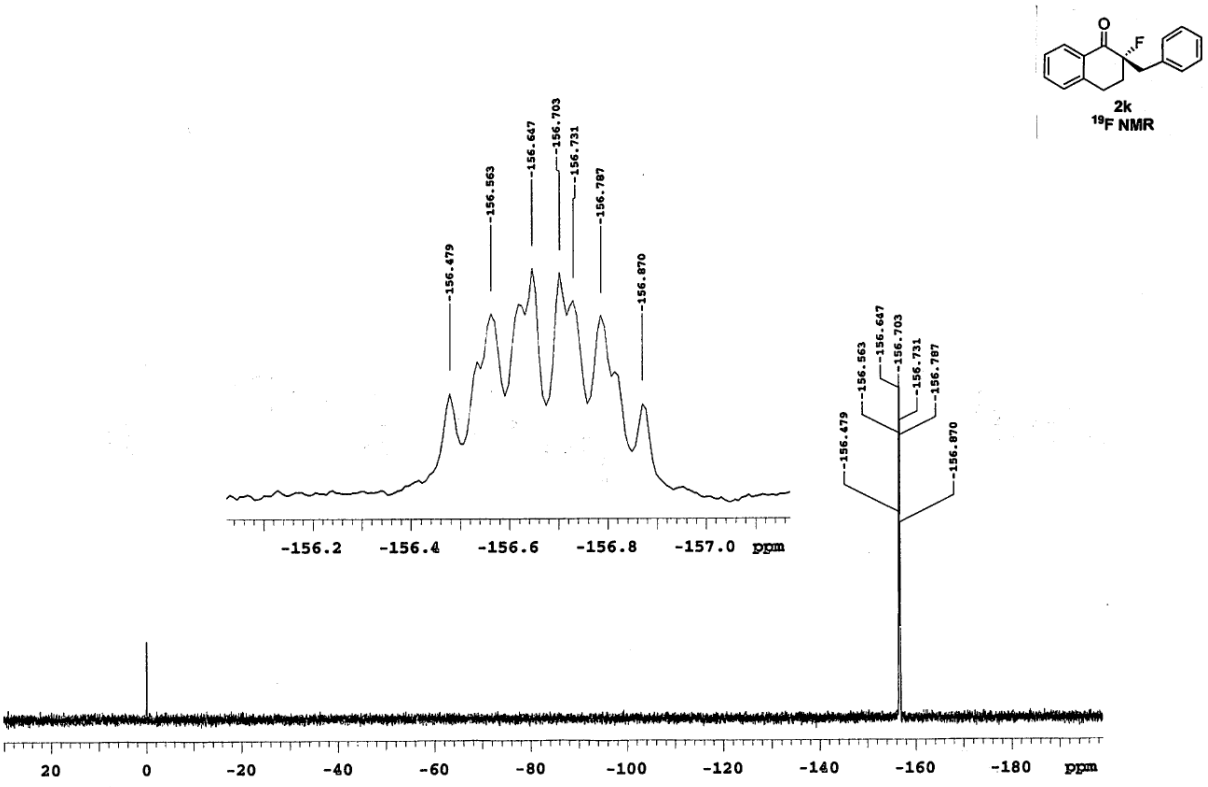

F
H
2h
19F NMR
-166.188
-166.310
-166.334
-166.475
-166.603
-166.627
-166.755
-0.006
-166.475
-165.9 -166.1 -166.3 -166.5 -166.7 -166.9 ppm
50 0 -50 -100 -150 -200 -250 ppm

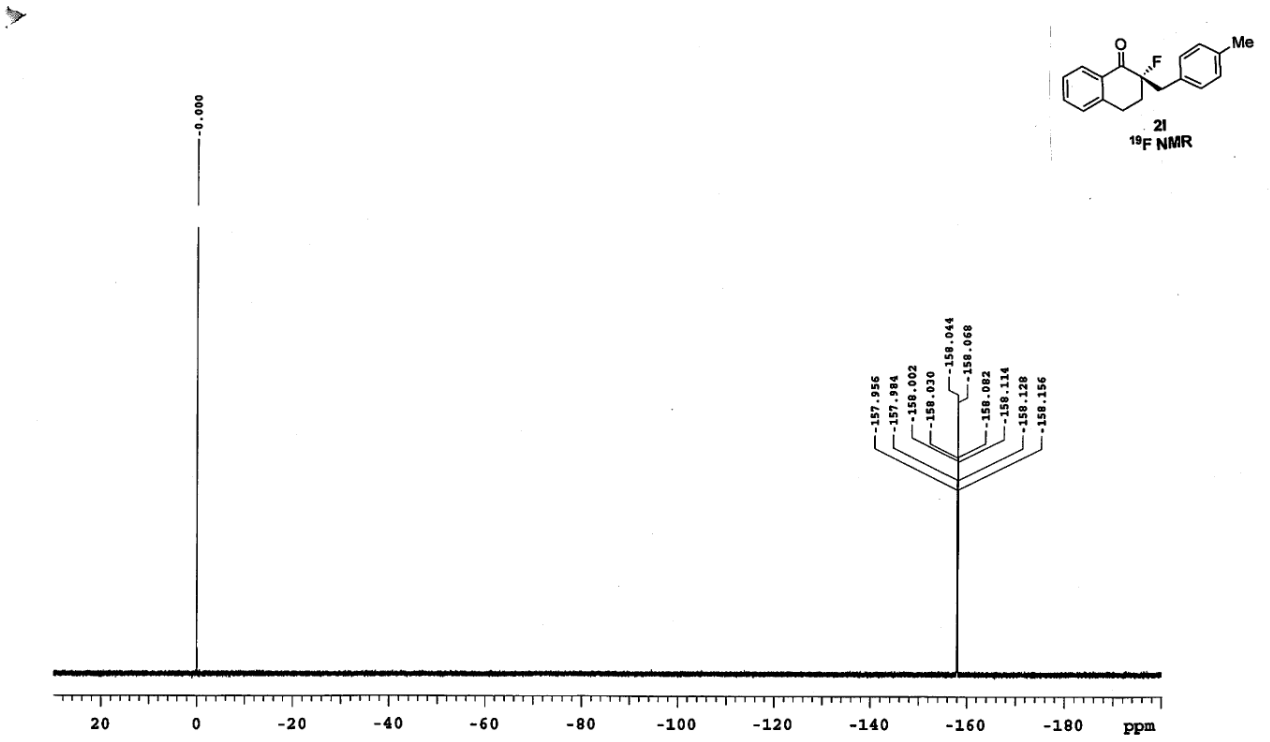

-0.000
-145.203
-145.335
-145.468
-145.0
-145.2
-145.4
-145.6
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

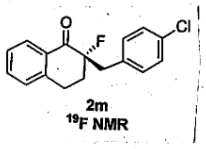
F
2i
19F NMR


-0.000
-145.265
-145.405
-145.538
-145.587
-144.9
-145.1
-145.3
-145.5
-145.7
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

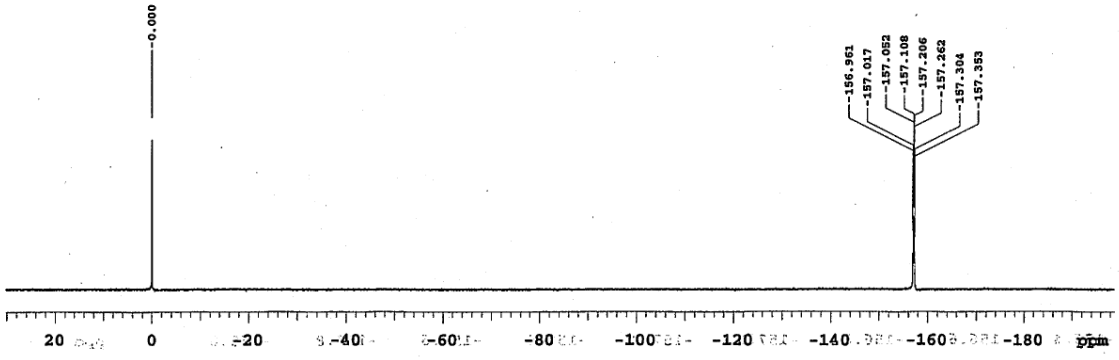
Me
F
2j
19F NMR

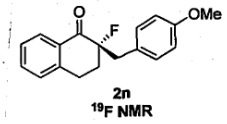

2k
19F NMR
-156.479
-156.563
-156.647
-156.703
-156.731
-156.787
-156.870
-156.2
-156.4
-156.6
-156.8
-157.0
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


2l
19F NMR
-0.000
-157.956
-157.984
-158.002
-158.030
-158.044
-158.068
-158.082
-158.114
-158.128
-158.156
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

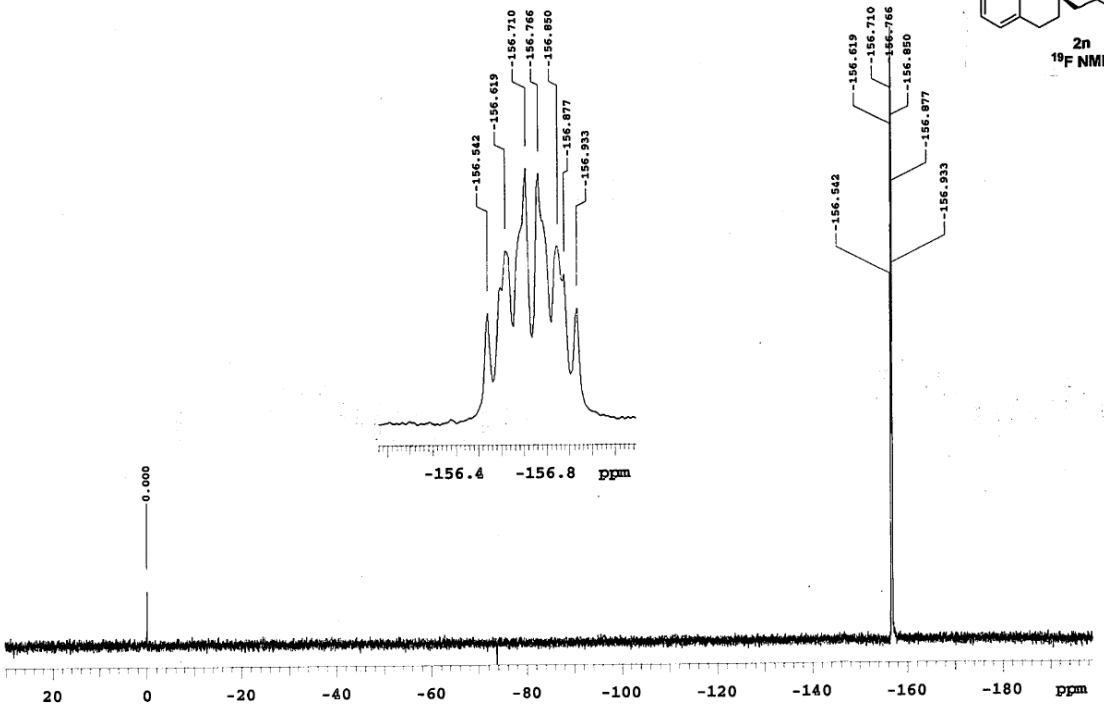


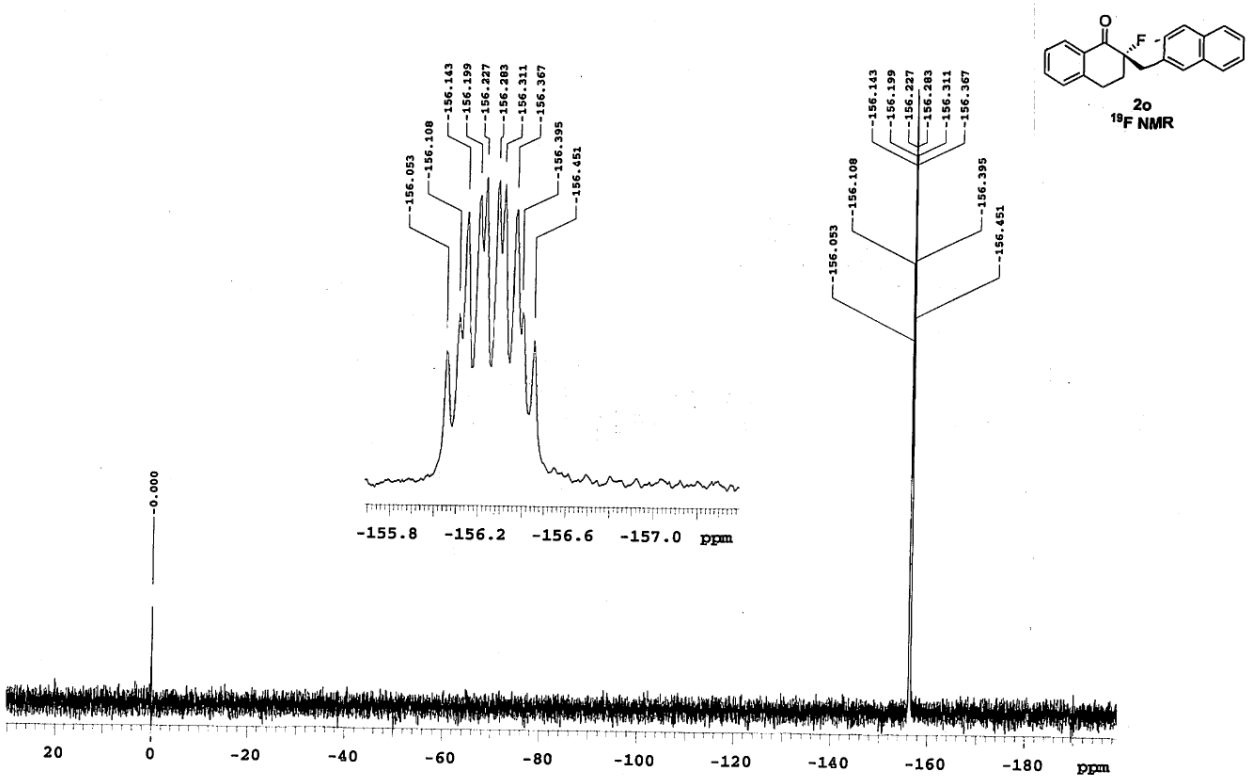
2m
^{19}F NMR

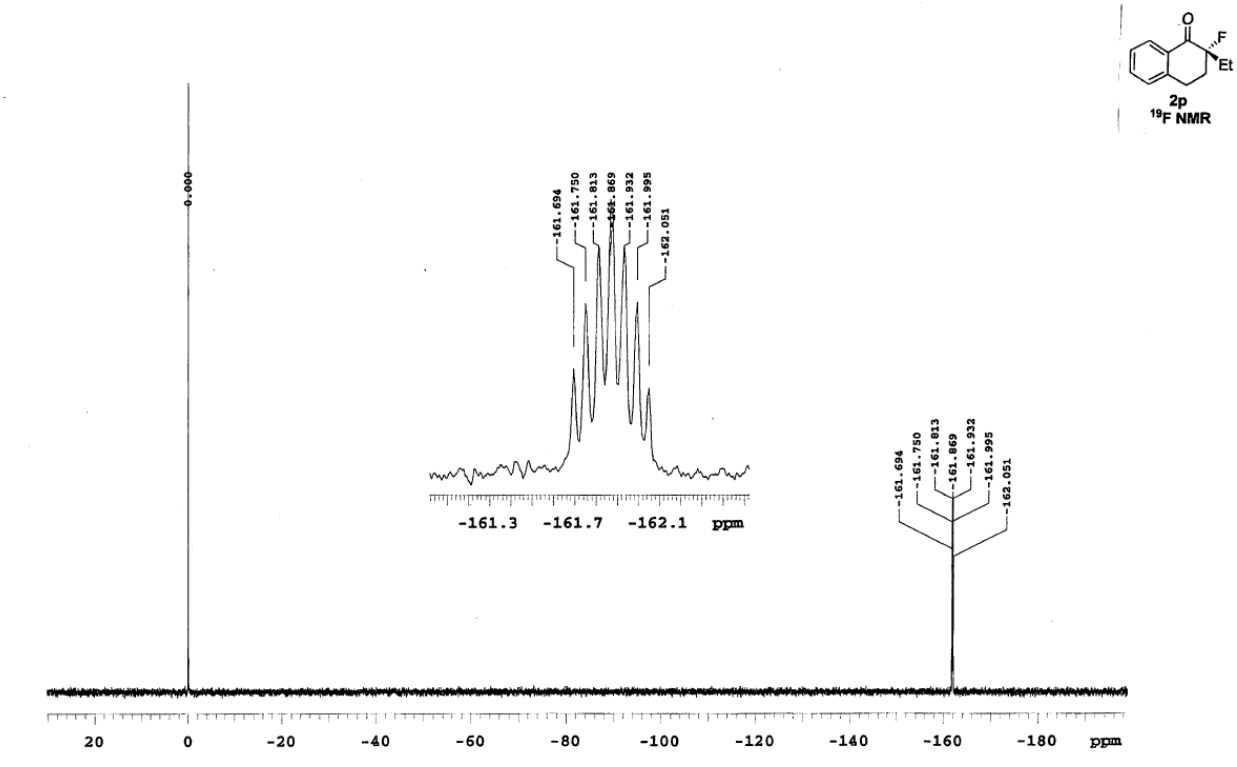


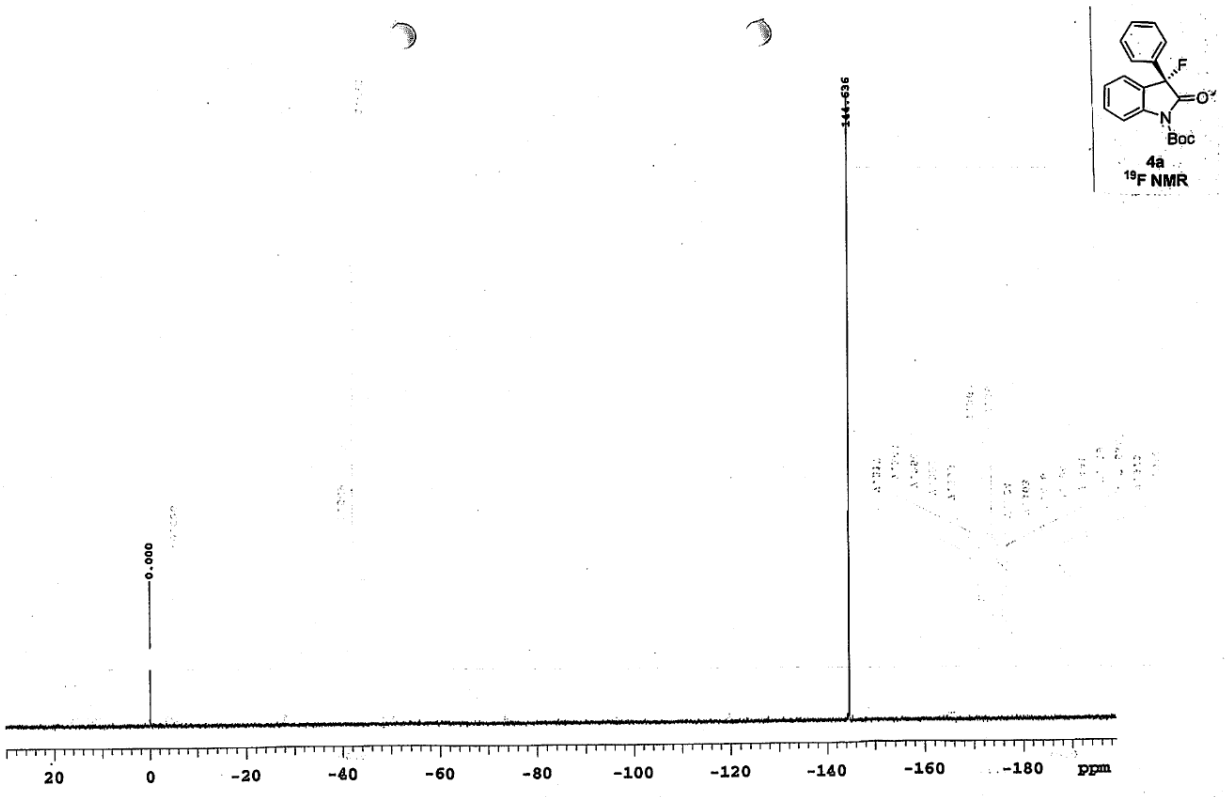


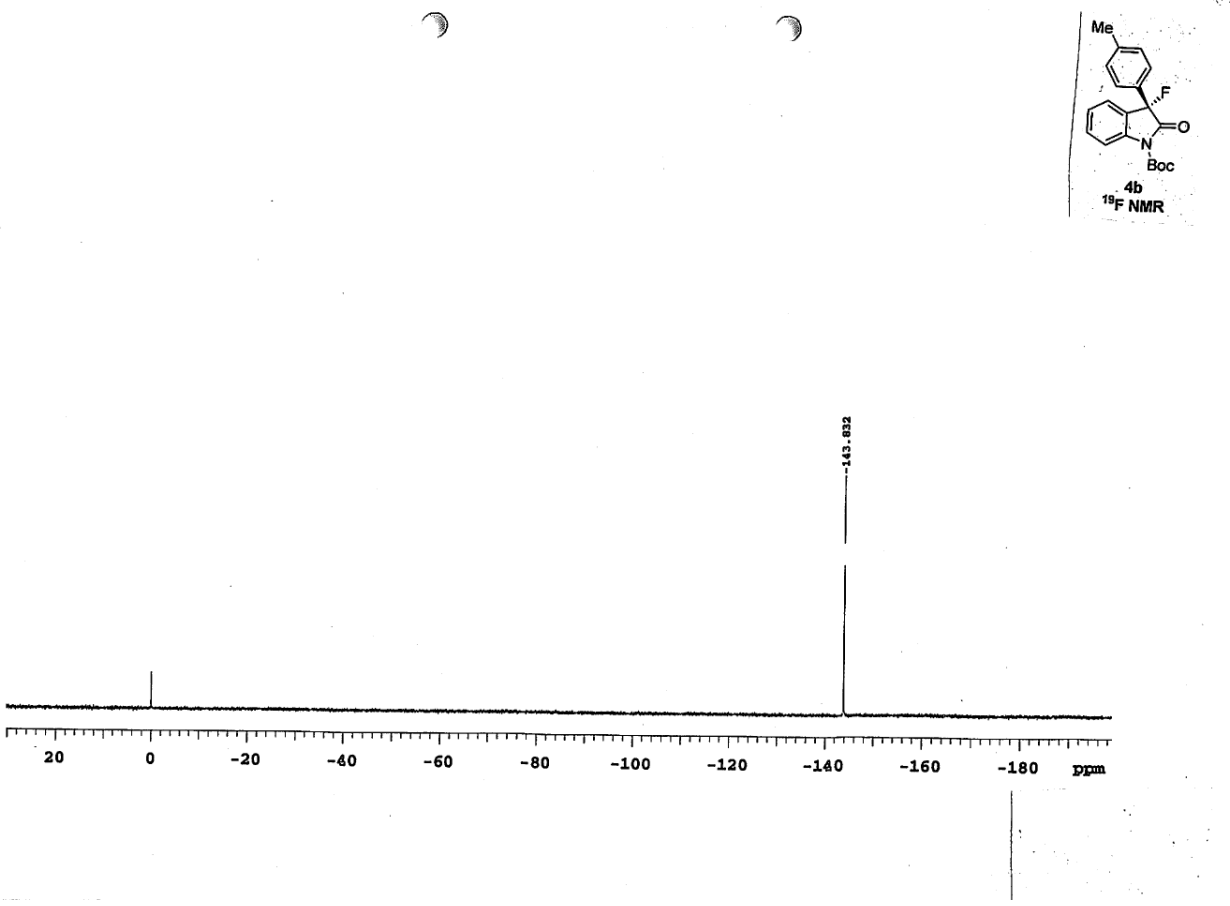
2n
^{19}F NMR

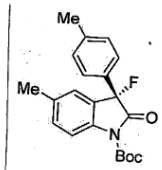



2o
19F NMR
-156.053
-156.108
-156.143
-156.199
-156.227
-156.283
-156.311
-156.367
-156.395
-156.451
-0.000
-155.8
-156.2
-156.6
-157.0
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


2p
19F NMR
-0.000
-161.694
-161.750
-161.813
-161.869
-161.932
-161.995
-162.051
-161.3
-161.7
-162.1
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

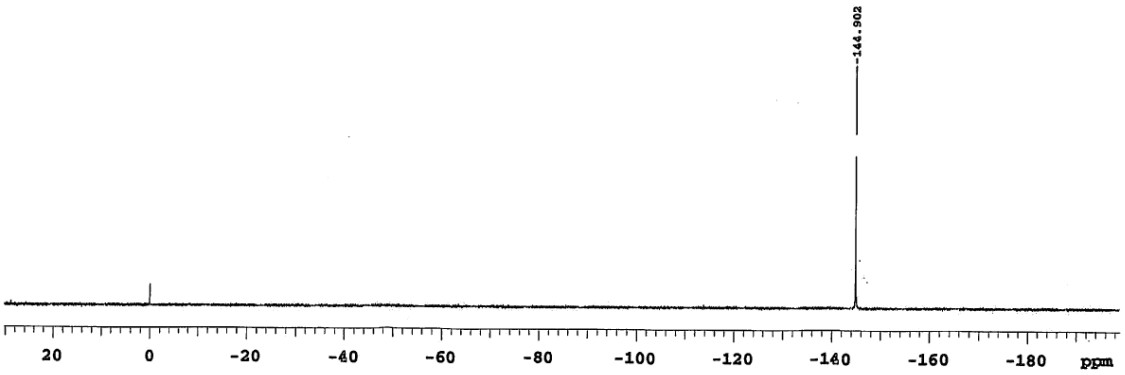

-144.636
0.000
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
F
O
N
Boc
4a
^{19}F NMR

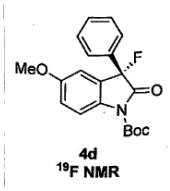

-143.832
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
Me
F
O
N
Boc
4b
^{19}F NMR



4c

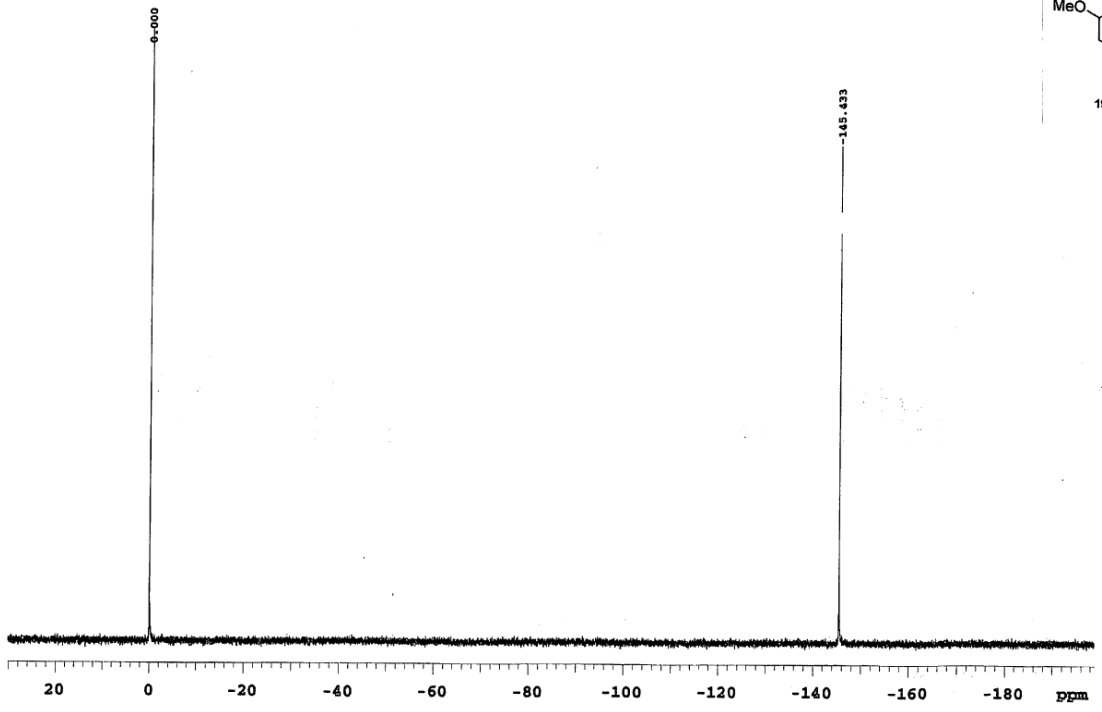
^{19}F NMR

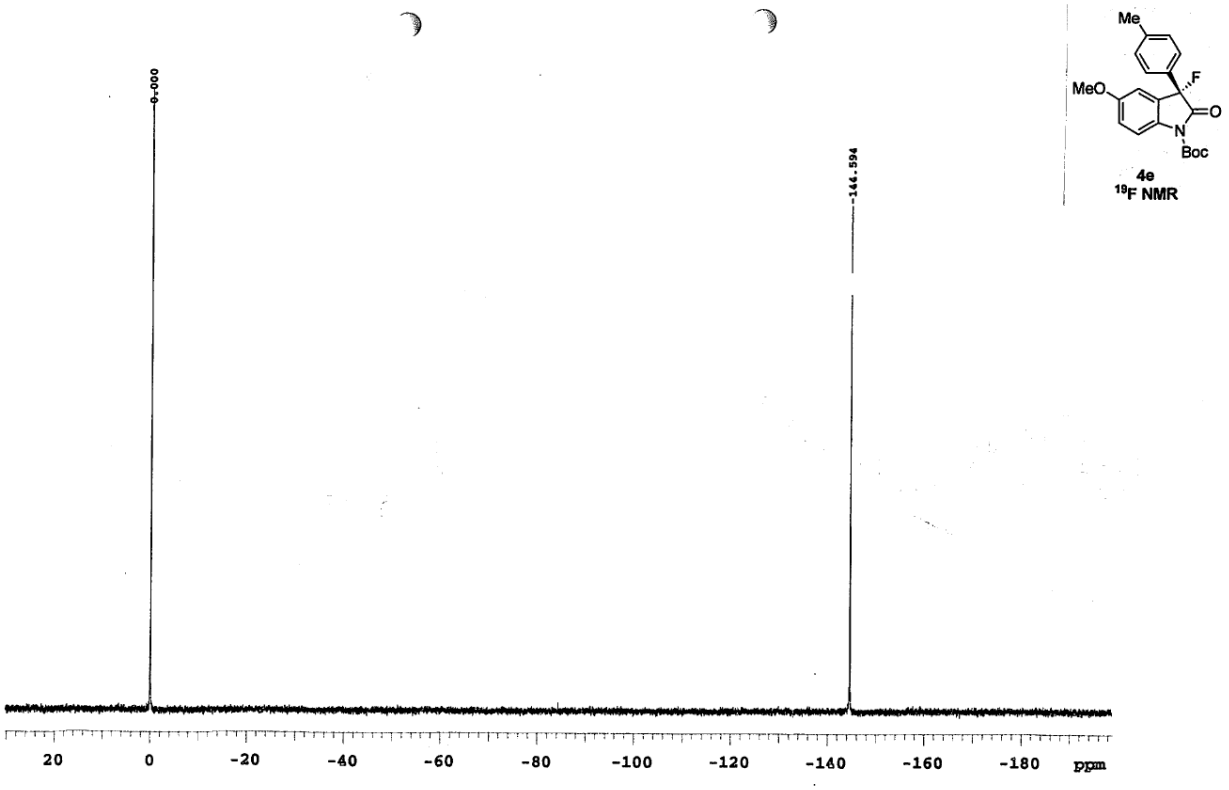




4d

^{19}F NMR

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0
-20
-40
-60
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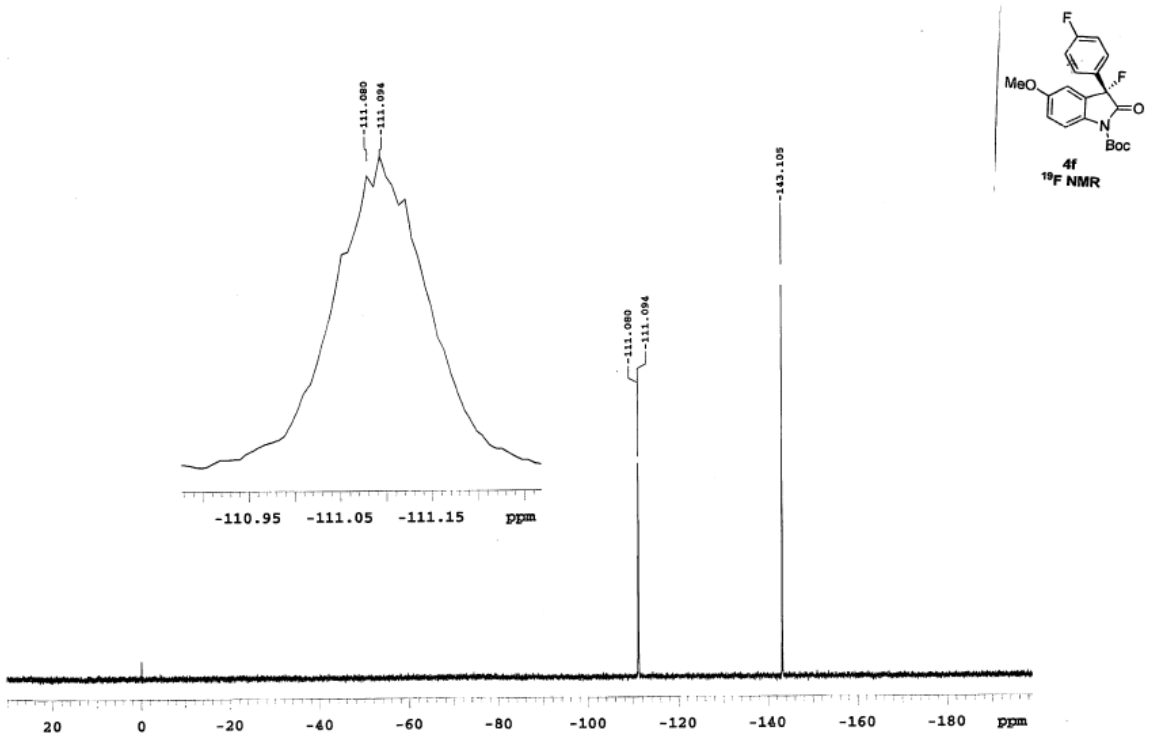
-180
ppm
Me
MeO
F
O
N
Boc
4e
19F NMR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ppm
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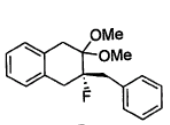
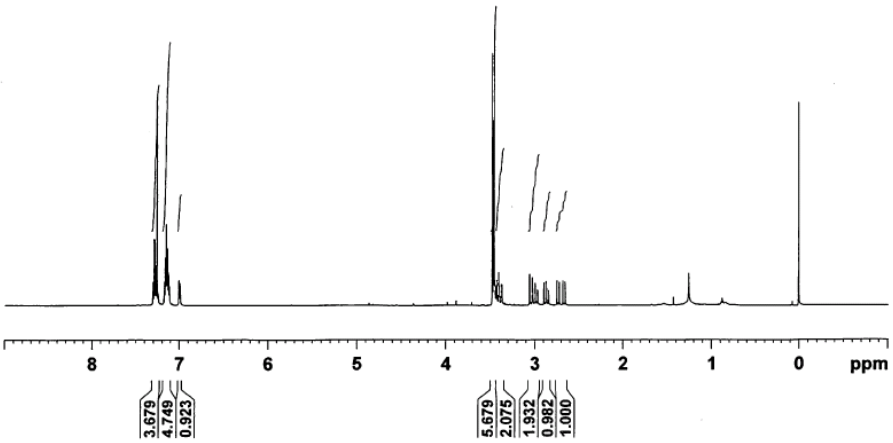
MeO
F
O
N
Boc
4f
19F NMR

1H



5a
^{1}H NMR

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PROCNO                        1

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SOLVENT                 CDCl3
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DS                          4
SWH                  8389.262 Hz
FIDRES               0.128010 Hz
AQ                   3.9060552 sec
RG                        256
DW                     59.600 usec
DE                      6.00 usec
TE                     296.6 K
D1                1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        1H
P1                      11.00 usec
PL1                     -4.00 dB
SFO1             600.1336008 MHz

F2 - Processing parameters
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SSB                             0
LB                         0.10 Hz
GB                              0
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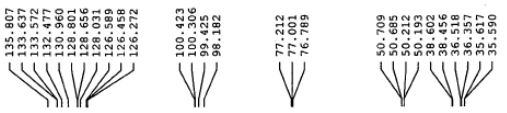
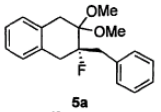
13C





5a
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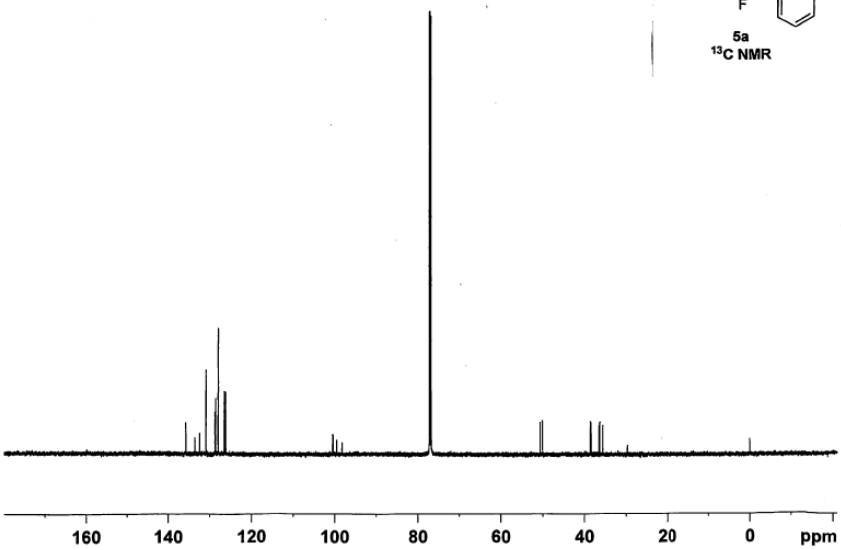


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SOLVENT               CDCl3
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AQ                1.4418530 sec
RG                    16384
DW                  11.000 usec
DE                   6.00 usec
TE                  296.8 K
D1             0.60000002 sec
d11            0.03000000 sec
DELTA          0.50000000 sec
TD0                          1

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NUC1                       13C
P1                      8.20 usec
PL1                     4.50 dB
SFO1          150.9223664 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                  82.00 usec
PL2                     -4.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
SFO2          600.1324005 MHz

F2 - Processing parameters
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SF            150.9028111 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
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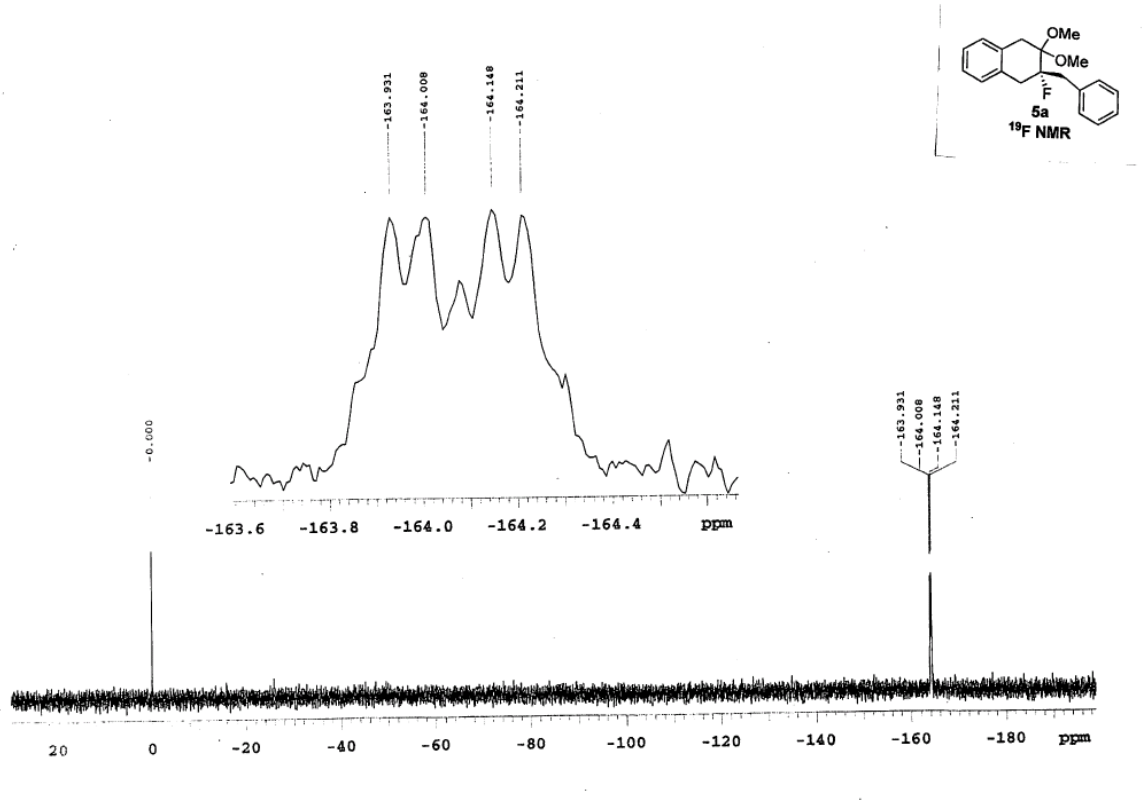
OMe
OMe
F
5a
19F NMR
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-164.0
-164.2
-164.4
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

Sample: RGK1528[(DHQ)2PYR]

X-ray Structure Report

for

Professor Shibata

NITEC

January 31, 2008

Experimental

Data Collection

A colorless block crystal of $C_{60}H_{68}N_6O_6$ having approximate dimensions of 0.20 x 0.18 x 0.15 mm was mounted in a loop. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα radiation.

Indexing was performed from 3 oscillations that were exposed for 36 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

a = 11.4810(2) Å
b = 17.5152(2) Å
c = 25.6075(7) Å
V = 5149.46(18) Å^3

For Z = 4 and F.W. = 969.23, the calculated density is 1.250 g/cm^3. The systematic absences of:

h00: h ± 2n
0k0: k ± 2n
00l: l ± 2n

uniquely determine the space group to be:

$P2_12_12_1$ (#19)

The data were collected at a temperature of -180 ± 1^{o}C to a maximum 2θ value of 136.5^o. A total of 90 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0^o in 10.0^o step, at χ=0.0^o and ϕ = 0.0^o. The exposure rate was 6.0 [sec./^{o}]. A second sweep was performed using ω scans from 80.0 to

260.0° in 10.0° step, at χ=54.0° and ϕ = 0.0°. The exposure rate was 6.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ=54.0° and ϕ = 90.0°. The exposure rate was 6.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ=54.0° and ϕ = 180.0°. The exposure rate was 6.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ=54.0° and ϕ = 270.0°. The exposure rate was 6.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 46937 reflections that were collected, 9386 were unique (R_{int} = 0.033); equivalent reflections were merged.

The linear absorption coefficient, μ, for Cu-Kα radiation is 6.457 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.811 to 0.908. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 9336 observed reflections and 652 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0449 \quad (I>2.00\sigma(I))$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma \, w(Fo^2)^2]^{1/2} = 0.1101$$

The standard deviation of an observation of unit weight[4] was 1.09. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.38 and -0.37 $e^-/Å^3$, respectively. The absolute configuration was confirmed based on Flack parameter, 0.07(19), refined by using 4133 Friedel pairs.[5]

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf'' were those of Creagh and McAuley[8]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[9]. All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL-97[11].

References

(1) SIR2002: Burla, M.C., Camalli, M., Carrozzini, B., Cascarano, G.L., Giacovazzo, C., Polidori, G., Spagna., R. (2003).

(2) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) Flack, H. D. (1983), Acta Cryst. A39, 876-881.

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.

(11) SHELX97: Sheldrick, G.M. (1997).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{60}H_{68}N_6O_6$
Formula Weight	969.23
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 X 0.18 X 0.15 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 36.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 11.4810(2) Å b = 17.5152(2) Å c = 25.6075(7) Å V = 5149.46(18) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.250 g/cm^3
F_{000}	2072.00
μ(CuKα)	6.457 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Detector Aperture	460 mm x 256 mm
Data Images	90 exposures
ω oscillation Range (χ=0.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	6.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	6.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0^{o}
Exposure Rate	6.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 260.0^{o}
Exposure Rate	6.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	80.0 - 260.0^{o}
Exposure Rate	6.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	136.5^{o}
No. of Reflections Measured	Total: 46937 Unique: 9336 (R_{int} = 0.033)

	Friedel pairs: 4133
Corrections	Lorentz-polarization Absorption (trans. factors: 0.811 - 0.908)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0435 \cdot P)^2 + 2.3976 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.5^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	9336
No. Variables	652
Reflection/Parameter Ratio	14.32
Residuals: R1 ($I>2.00\sigma(I)$)	0.0449
Residuals: R (All reflections)	0.0528
Residuals: wR2 (All reflections)	0.1101
Goodness of Fit Indicator	1.086
Flack Parameter (Friedel pairs = 4133)	0.07(19)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.38 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.37 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
O1	0.33303(14)	0.31684(9)	0.60172(6)	1.97(2)	
O2	0.04092(15)	0.00945(9)	0.67160(6)	2.60(3)	
O3	0.20477(14)	0.57103(9)	0.59452(6)	2.11(2)	
O4	0.38394(15)	0.66149(11)	0.43327(6)	2.92(3)	
O5	0.8245(4)	-0.1136(2)	0.19320(16)	3.87(10)	0.506(6)
O5A	0.7814(4)	-0.0950(3)	0.1991(2)	5.86(14)	0.494(6)
O6A	0.8134(3)	-0.0043(2)	0.24728(16)	3.08(9)	0.494(6)
O6	0.8370(3)	0.01216(16)	0.2238(2)	3.80(10)	0.506(6)
N1	0.14263(16)	0.34724(11)	0.61948(7)	1.91(3)	
N2	0.07560(17)	0.47539(11)	0.61505(7)	2.00(3)	
N3	0.33696(18)	0.16051(12)	0.53747(7)	2.39(3)	
N4	0.31437(18)	0.20971(13)	0.78480(7)	2.52(3)	
N5	0.09233(18)	0.76258(11)	0.62327(8)	2.26(3)	
N6	-0.09112(19)	0.68066(13)	0.46211(8)	2.85(3)	
C1	0.0598(2)	0.40020(13)	0.62292(8)	1.93(3)	
C2	0.2486(2)	0.37059(13)	0.60614(8)	1.80(3)	
C3	0.2785(2)	0.44663(13)	0.59688(8)	1.84(3)	
C4	0.1837(2)	0.49623(13)	0.60272(8)	1.91(3)	
C5	-0.0594(2)	0.37335(14)	0.63569(8)	2.02(3)	
C6	-0.0808(2)	0.29598(14)	0.64332(9)	2.24(4)	
C7	-0.1923(2)	0.26989(15)	0.65370(9)	2.60(4)	
C8	-0.2830(2)	0.32121(16)	0.65758(9)	2.66(4)	
C9	-0.2636(2)	0.39847(16)	0.65023(9)	2.79(4)	
C10	-0.1519(2)	0.42426(15)	0.63882(9)	2.54(4)	
C11	0.3986(2)	0.47227(13)	0.58284(9)	2.10(4)	
C12	0.4627(2)	0.43330(14)	0.54468(9)	2.31(4)	
C13	0.5751(2)	0.45632(15)	0.53224(10)	2.80(4)	
C14	0.6247(2)	0.51878(16)	0.55640(11)	3.16(5)	
C15	0.5619(2)	0.55863(15)	0.59403(11)	3.10(4)	
C16	0.4491(2)	0.53494(14)	0.60750(10)	2.66(4)	
C17	0.3000(2)	0.23959(12)	0.61617(8)	1.91(3)	
C18	0.3815(2)	0.18160(14)	0.58981(9)	2.11(3)	
C19	0.5108(2)	0.20438(14)	0.58846(9)	2.18(4)	
C20	0.5592(2)	0.17992(14)	0.53523(9)	2.33(4)	
C21	0.5006(2)	0.22884(15)	0.49325(9)	2.71(4)	
C22	0.3671(2)	0.21941(15)	0.49881(9)	2.66(4)	
C23	0.3958(2)	0.08896(15)	0.52175(10)	2.71(4)	

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C24	0.5311(2)	0.09510(14)	0.52455(9)	2.46(4)	
C25	0.5835(2)	0.03931(15)	0.56299(10)	2.83(4)	
C26	0.7163(2)	0.04073(18)	0.56510(12)	3.77(5)	
C27	0.30228(19)	0.23134(13)	0.67496(9)	1.87(3)	
C28	0.3671(2)	0.27846(14)	0.70656(9)	2.14(4)	
C29	0.3692(2)	0.26572(15)	0.76094(9)	2.41(4)	
C30	0.2493(2)	0.16202(14)	0.75387(9)	2.18(4)	
C31	0.1919(2)	0.09999(15)	0.77827(10)	2.69(4)	
C32	0.1249(2)	0.05078(15)	0.74989(10)	2.65(4)	
C33	0.1116(2)	0.06179(14)	0.69528(9)	2.26(4)	
C34	0.1681(2)	0.11952(13)	0.67043(9)	2.01(3)	
C35	0.2389(2)	0.17099(13)	0.69901(9)	1.88(3)	
C36	0.0194(2)	0.01999(16)	0.61711(10)	2.88(4)	
C37	0.1108(2)	0.62610(13)	0.60040(9)	2.05(3)	
C38	0.1737(2)	0.69795(13)	0.61994(9)	2.20(4)	
C39	0.2363(2)	0.68405(16)	0.67281(10)	2.97(4)	
C40	0.1929(2)	0.74393(15)	0.71223(9)	2.78(4)	
C41	0.0623(2)	0.73311(17)	0.71834(10)	3.07(5)	
C42	0.0051(2)	0.75102(16)	0.66463(9)	2.81(4)	
C43	0.1606(2)	0.83059(14)	0.63676(10)	2.73(4)	
C44	0.2161(2)	0.82523(15)	0.69219(9)	2.66(4)	
C45	0.3443(2)	0.84739(18)	0.69242(11)	3.47(5)	
C46	0.3689(2)	0.92768(19)	0.67359(15)	4.73(7)	
C47	0.0445(2)	0.63853(13)	0.55039(9)	2.07(3)	
C48	-0.0752(2)	0.64005(14)	0.55161(10)	2.42(4)	
C49	-0.1390(2)	0.66074(15)	0.50702(10)	2.83(4)	
C50	0.0276(2)	0.67778(15)	0.45973(9)	2.54(4)	
C51	0.0806(2)	0.70019(16)	0.41171(10)	2.99(4)	
C52	0.1966(2)	0.69506(17)	0.40489(10)	3.18(5)	
C53	0.2688(2)	0.66754(15)	0.44582(9)	2.48(4)	
C54	0.2221(2)	0.64989(14)	0.49349(9)	2.28(4)	
C55	0.1003(2)	0.65520(13)	0.50160(9)	2.14(4)	
C56	0.4612(2)	0.64013(15)	0.47436(10)	2.70(4)	
C57	0.9768(3)	-0.0819(2)	0.24233(17)	5.88(9)	
C58	0.8613(3)	-0.06367(18)	0.22104(12)	4.19(6)	
C59	0.7332(4)	0.0501(3)	0.20402(16)	4.06(14)	0.506(6)
C59A	0.6989(4)	0.0029(2)	0.2235(2)	3.95(14)	0.494(6)

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
C60	0.6540(2)	0.0761(2)	0.24797(14)	4.89(7)	
H1	-0.0183	0.2606	0.6414	2.69	
H2	-0.2062	0.2168	0.6581	3.12	
H3	-0.3593	0.3034	0.6654	3.20	
H4	-0.3262	0.4337	0.6530	3.34	
H5	-0.1388	0.4772	0.6331	3.05	
H6	0.4291	0.3908	0.5272	2.77	
H7	0.6183	0.4288	0.5068	3.36	
H8	0.7013	0.5345	0.5474	3.79	
H9	0.5954	0.6019	0.6106	3.72	
H10	0.4069	0.5618	0.6336	3.19	
H11	0.2187	0.2301	0.6037	2.30	
H18	0.3772	0.1341	0.6114	2.53	
H19A	0.5190	0.2602	0.5930	2.61	
H19B	0.5538	0.1785	0.6169	2.61	
H20	0.6454	0.1880	0.5343	2.80	
H21A	0.5260	0.2121	0.4581	3.25	
H21B	0.5225	0.2831	0.4978	3.25	
H22A	0.3324	0.2687	0.5096	3.20	
H22B	0.3335	0.2053	0.4645	3.20	
H23A	0.3726	0.0759	0.4856	3.25	
H23B	0.3696	0.0470	0.5448	3.25	
H24	0.5625	0.0823	0.4892	2.95	
H25A	0.5578	-0.0129	0.5536	3.40	
H25B	0.5527	0.0508	0.5982	3.40	
H26A	0.7424	0.0896	0.5796	4.53	
H26B	0.7477	0.0346	0.5298	4.53	
H26C	0.7441	-0.0011	0.5873	4.53	
H28	0.4103	0.3194	0.6918	2.57	
H29	0.4133	0.3000	0.7818	2.89	
H31	0.2001	0.0925	0.8148	3.22	
H32	0.0872	0.0092	0.7667	3.18	
H34	0.1601	0.1254	0.6337	2.41	
H36A	-0.0334	-0.0200	0.6046	3.46	
H36B	0.0931	0.0171	0.5979	3.46	
H36C	-0.0163	0.0701	0.6114	3.46	
H37	0.0558	0.6078	0.6280	2.46	

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

atom	x	y	z	B_{eq}	occ
H38	0.2346	0.7114	0.5936	2.64	
H39A	0.2189	0.6320	0.6857	3.56	
H39B	0.3217	0.6887	0.6682	3.56	
H40	0.2324	0.7363	0.7466	3.33	
H41A	0.0317	0.7680	0.7455	3.68	
H41B	0.0449	0.6800	0.7289	3.68	
H42A	-0.0468	0.7083	0.6547	3.37	
H42B	-0.0432	0.7976	0.6679	3.37	
H43A	0.1094	0.8760	0.6352	3.28	
H43B	0.2231	0.8375	0.6106	3.28	
H44	0.1737	0.8616	0.7155	3.19	
H45A	0.3746	0.8420	0.7284	4.17	
H45B	0.3876	0.8111	0.6701	4.17	
H46A	0.3435	0.9329	0.6372	5.67	
H46B	0.4527	0.9379	0.6759	5.67	
H46C	0.3266	0.9643	0.6954	5.67	
H48	-0.1151	0.6270	0.5829	2.91	
H49	-0.2216	0.6604	0.5093	3.40	
H51	0.0332	0.7190	0.3841	3.58	
H52	0.2303	0.7099	0.3726	3.81	
H54	0.2715	0.6341	0.5212	2.73	
H56A	0.4528	0.6759	0.5035	3.24	
H56B	0.5416	0.6414	0.4616	3.24	
H56C	0.4422	0.5884	0.4862	3.24	
H57A	0.9708	-0.1263	0.2655	7.05	
H57B	1.0063	-0.0380	0.2621	7.05	
H57C	1.0304	-0.0935	0.2136	7.05	
H59A	0.6900	0.0146	0.1810	4.88	0.506
H59B	0.7566	0.0949	0.1829	4.88	0.506
H59C	0.6485	-0.0411	0.2323	4.75	0.494
H59D	0.7046	0.0076	0.1850	4.75	0.494
H60A	0.5853	0.1014	0.2333	5.86	0.506
H60B	0.6961	0.1119	0.2705	5.86	0.506
H60C	0.6294	0.0318	0.2685	5.86	0.506
H60D	0.5758	0.0871	0.2346	5.86	0.494
H60E	0.7064	0.1184	0.2391	5.86	0.494
H60F	0.6508	0.0701	0.2860	5.86	0.494

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy (continued)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0289(8)	0.0204(8)	0.0257(7)	0.0023(6)	0.0035(6)	-0.0004(6)
O2	0.0379(9)	0.0288(9)	0.0322(8)	-0.0079(7)	0.0003(7)	-0.0006(7)
O3	0.0315(8)	0.0210(8)	0.0276(8)	0.0037(6)	0.0034(6)	0.0020(6)
O4	0.0348(10)	0.0487(11)	0.0275(8)	-0.0008(8)	0.0031(7)	0.0076(7)
N1	0.0292(10)	0.0248(10)	0.0187(8)	0.0012(8)	0.0029(7)	-0.0008(7)
N2	0.0309(10)	0.0251(10)	0.0202(9)	-0.0008(8)	0.0019(7)	0.0009(7)
N3	0.0334(11)	0.0307(11)	0.0268(10)	0.0016(9)	-0.0023(8)	-0.0064(8)
N4	0.0329(11)	0.0383(12)	0.0244(10)	-0.0018(9)	-0.0013(8)	-0.0041(8)
N5	0.0333(10)	0.0272(10)	0.0253(9)	0.0071(8)	-0.0044(8)	-0.0024(8)
N6	0.0367(12)	0.0380(12)	0.0337(11)	-0.0033(10)	-0.0069(9)	-0.0006(9)
C1	0.0320(12)	0.0248(12)	0.0165(10)	-0.0021(9)	-0.0019(9)	0.0005(8)
C2	0.0296(12)	0.0223(11)	0.0166(10)	-0.0000(9)	-0.0002(8)	-0.0001(8)
C3	0.0285(12)	0.0244(11)	0.0172(10)	0.0016(9)	-0.0008(9)	0.0006(8)
C4	0.0345(13)	0.0207(11)	0.0174(10)	-0.0026(9)	-0.0027(9)	0.0024(8)
C5	0.0290(12)	0.0324(13)	0.0154(10)	0.0035(10)	0.0010(8)	0.0005(9)
C6	0.0344(13)	0.0311(12)	0.0196(10)	-0.0008(10)	-0.0000(9)	0.0010(9)
C7	0.0417(14)	0.0358(14)	0.0214(11)	-0.0073(11)	0.0030(10)	0.0023(10)
C8	0.0295(13)	0.0500(16)	0.0216(11)	-0.0083(12)	0.0016(9)	0.0027(11)
C9	0.0274(13)	0.0491(17)	0.0294(13)	0.0021(11)	0.0037(10)	0.0017(11)
C10	0.0384(14)	0.0343(14)	0.0239(11)	0.0027(11)	0.0022(10)	0.0019(10)
C11	0.0294(12)	0.0239(12)	0.0264(11)	-0.0009(10)	-0.0022(9)	0.0058(9)
C12	0.0308(12)	0.0300(13)	0.0271(12)	0.0012(10)	-0.0003(10)	0.0057(10)
C13	0.0319(14)	0.0377(15)	0.0367(14)	0.0027(11)	-0.0001(11)	0.0102(11)
C14	0.0299(13)	0.0391(15)	0.0511(16)	-0.0031(12)	-0.0036(12)	0.0132(12)
C15	0.0347(14)	0.0307(14)	0.0523(16)	-0.0046(11)	-0.0112(12)	0.0043(12)
C16	0.0350(13)	0.0284(13)	0.0377(14)	0.0029(11)	-0.0052(11)	0.0019(10)
C17	0.0333(12)	0.0173(11)	0.0222(11)	-0.0023(9)	0.0025(9)	0.0026(8)
C18	0.0340(12)	0.0253(12)	0.0209(10)	0.0023(10)	0.0019(9)	-0.0012(9)
C19	0.0296(12)	0.0286(13)	0.0245(11)	0.0021(9)	0.0009(9)	-0.0014(9)
C20	0.0297(13)	0.0317(13)	0.0271(11)	-0.0006(10)	0.0052(9)	-0.0025(10)
C21	0.0425(15)	0.0341(14)	0.0264(12)	0.0050(11)	0.0076(10)	0.0011(10)
C22	0.0410(14)	0.0359(14)	0.0243(11)	0.0054(12)	-0.0010(10)	-0.0022(10)
C23	0.0376(14)	0.0322(13)	0.0330(13)	-0.0006(11)	0.0013(11)	-0.0106(11)
C24	0.0363(13)	0.0310(13)	0.0262(12)	0.0000(11)	0.0071(10)	-0.0051(10)
C25	0.0415(15)	0.0306(14)	0.0355(14)	0.0047(11)	0.0043(11)	-0.0043(10)
C26	0.0460(17)	0.0445(17)	0.0528(17)	0.0135(14)	-0.0061(14)	-0.0019(14)
C27	0.0228(11)	0.0238(12)	0.0245(11)	0.0032(9)	0.0008(9)	-0.0017(9)

Table 2. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C28	0.0269(12)	0.0272(12)	0.0273(11)	-0.0014(10)	0.0024(9)	-0.0032(9)
C29	0.0285(12)	0.0344(14)	0.0286(12)	-0.0024(11)	-0.0014(10)	-0.0063(10)
C30	0.0302(12)	0.0305(13)	0.0221(11)	0.0003(10)	0.0038(9)	-0.0022(9)
C31	0.0420(14)	0.0379(15)	0.0221(11)	0.0018(12)	0.0059(11)	0.0032(10)
C32	0.0402(14)	0.0340(14)	0.0266(12)	-0.0070(11)	0.0070(11)	0.0038(10)
C33	0.0312(13)	0.0277(12)	0.0268(11)	-0.0013(10)	0.0021(10)	-0.0024(9)
C34	0.0297(12)	0.0236(11)	0.0230(11)	0.0043(9)	0.0033(9)	-0.0015(9)
C35	0.0260(11)	0.0230(12)	0.0225(10)	0.0046(9)	0.0029(8)	-0.0010(9)
C36	0.0412(15)	0.0358(14)	0.0324(13)	-0.0051(12)	-0.0078(11)	-0.0002(11)
C37	0.0289(12)	0.0233(11)	0.0256(11)	0.0047(9)	0.0028(9)	0.0018(9)
C38	0.0358(13)	0.0242(12)	0.0237(11)	0.0050(10)	-0.0046(10)	-0.0005(9)
C39	0.0449(15)	0.0372(14)	0.0307(13)	0.0139(12)	-0.0112(11)	-0.0019(11)
C40	0.0397(14)	0.0438(16)	0.0220(12)	0.0087(12)	-0.0058(10)	-0.0062(10)
C41	0.0467(16)	0.0458(16)	0.0241(12)	0.0038(13)	-0.0018(11)	-0.0032(11)
C42	0.0396(14)	0.0398(15)	0.0272(12)	0.0121(11)	-0.0043(11)	-0.0059(11)
C43	0.0457(15)	0.0249(13)	0.0333(13)	0.0049(11)	-0.0094(11)	-0.0051(10)
C44	0.0331(13)	0.0401(15)	0.0280(12)	0.0099(11)	-0.0036(10)	-0.0114(11)
C45	0.0347(15)	0.0560(19)	0.0412(15)	0.0050(13)	0.0017(12)	-0.0096(13)
C46	0.0420(17)	0.057(2)	0.081(2)	-0.0063(15)	-0.0008(16)	-0.0225(18)
C47	0.0282(12)	0.0202(11)	0.0304(12)	0.0002(9)	-0.0027(10)	-0.0024(9)
C48	0.0321(13)	0.0272(13)	0.0328(12)	-0.0017(10)	-0.0005(10)	-0.0003(10)
C49	0.0302(13)	0.0367(15)	0.0408(14)	-0.0028(11)	-0.0063(11)	-0.0047(11)
C50	0.0345(14)	0.0320(14)	0.0302(12)	-0.0021(11)	-0.0057(10)	-0.0042(10)
C51	0.0402(15)	0.0456(16)	0.0276(12)	-0.0012(12)	-0.0094(11)	0.0050(11)
C52	0.0438(15)	0.0527(17)	0.0243(12)	-0.0068(13)	-0.0034(11)	0.0040(11)
C53	0.0319(13)	0.0362(14)	0.0263(12)	-0.0027(11)	0.0002(10)	0.0022(10)
C54	0.0348(13)	0.0287(12)	0.0230(11)	-0.0026(10)	-0.0026(9)	-0.0013(9)
C55	0.0327(12)	0.0226(12)	0.0259(11)	-0.0013(9)	-0.0029(9)	-0.0034(9)
C56	0.0332(13)	0.0390(15)	0.0305(12)	-0.0005(11)	0.0007(10)	0.0004(10)
C57	0.072(2)	0.058(2)	0.093(2)	0.0248(19)	0.041(2)	0.022(2)
C58	0.064(2)	0.0447(18)	0.0509(17)	-0.0175(16)	0.0182(16)	-0.0054(14)
C60	0.0421(17)	0.068(2)	0.075(2)	-0.0018(16)	-0.0069(16)	-0.0306(19)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
O1	C2	1.356(2)	O1	C17	1.453(2)
O2	C33	1.367(2)	O2	C36	1.429(2)
O3	C4	1.349(2)	O3	C37	1.455(2)
O4	C53	1.364(3)	O4	C56	1.426(3)
N1	C1	1.331(2)	N1	C2	1.328(2)
N2	C1	1.345(2)	N2	C4	1.331(3)
N3	C18	1.481(2)	N3	C22	1.471(3)
N3	C23	1.480(3)	N4	C29	1.316(3)
N4	C30	1.372(3)	N5	C38	1.470(3)
N5	C42	1.471(3)	N5	C43	1.467(3)
N6	C49	1.321(3)	N6	C50	1.366(3)
C1	C5	1.483(3)	C2	C3	1.396(3)
C3	C4	1.401(3)	C3	C11	1.494(3)
C5	C6	1.391(3)	C5	C10	1.389(3)
C6	C7	1.384(3)	C7	C8	1.380(3)
C8	C9	1.384(3)	C9	C10	1.390(3)
C11	C12	1.401(3)	C11	C16	1.393(3)
C12	C13	1.389(3)	C13	C14	1.380(3)
C14	C15	1.391(3)	C15	C16	1.403(3)
C17	C18	1.538(3)	C17	C27	1.513(3)
C18	C19	1.537(3)	C19	C20	1.533(3)
C20	C21	1.531(3)	C20	C24	1.545(3)
C21	C22	1.548(3)	C23	C24	1.559(3)
C24	C25	1.512(3)	C25	C26	1.527(3)
C27	C28	1.375(3)	C27	C35	1.423(3)
C28	C29	1.411(3)	C30	C31	1.416(3)
C30	C35	1.419(3)	C31	C32	1.365(3)
C32	C33	1.420(3)	C33	C34	1.359(3)
C34	C35	1.418(3)	C37	C38	1.535(3)
C37	C47	1.505(3)	C38	C39	1.552(3)
C39	C40	1.539(3)	C40	C41	1.519(3)
C40	C44	1.537(3)	C41	C42	1.556(3)
C43	C44	1.559(3)	C44	C45	1.522(3)
C45	C46	1.513(4)	C47	C48	1.375(3)
C47	C55	1.434(3)	C48	C49	1.404(3)
C50	C51	1.427(3)	C50	C55	1.415(3)
C51	C52	1.347(3)	C52	C53	1.421(3)

Table 3. Bond lengths (Å) (continued)

atom	atom	distance	atom	atom	distance
C53	C54	1.369(3)	C54	C55	1.417(3)
C57	C58	1.469(5)	O5	C58	1.204(5)
O6	C58	1.359(4)	O6	C59	1.455(6)
C59	C60	1.517(5)	O5A	C58	1.207(6)
O6A	C58	1.355(4)	O6A	C59A	1.454(6)
C59A	C60	1.518(6)			

Table 4. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C6	H1	0.950	C7	H2	0.950
C8	H3	0.950	C9	H4	0.950
C10	H5	0.950	C12	H6	0.950
C13	H7	0.950	C14	H8	0.950
C15	H9	0.950	C16	H10	0.950
C17	H11	1.000	C18	H18	1.000
C19	H19A	0.990	C19	H19B	0.990
C20	H20	1.000	C21	H21A	0.990
C21	H21B	0.990	C22	H22A	0.990
C22	H22B	0.990	C23	H23A	0.990
C23	H23B	0.990	C24	H24	1.000
C25	H25A	0.990	C25	H25B	0.990
C26	H26A	0.980	C26	H26B	0.980
C26	H26C	0.980	C28	H28	0.950
C29	H29	0.950	C31	H31	0.950
C32	H32	0.950	C34	H34	0.950
C36	H36A	0.980	C36	H36B	0.980
C36	H36C	0.980	C37	H37	1.000
C38	H38	1.000	C39	H39A	0.990
C39	H39B	0.990	C40	H40	1.000
C41	H41A	0.990	C41	H41B	0.990
C42	H42A	0.990	C42	H42B	0.990
C43	H43A	0.990	C43	H43B	0.990
C44	H44	1.000	C45	H45A	0.990
C45	H45B	0.990	C46	H46A	0.980
C46	H46B	0.980	C46	H46C	0.980
C48	H48	0.950	C49	H49	0.950
C51	H51	0.950	C52	H52	0.950
C54	H54	0.950	C56	H56A	0.980
C56	H56B	0.980	C56	H56C	0.980
C57	H57A	0.980	C57	H57B	0.980
C57	H57C	0.980	C59	H59A	0.990
C59	H59B	0.990	C59A	H59C	0.990
C59A	H59D	0.990	C60	H60A	0.980
C60	H60B	0.980	C60	H60C	0.980
C60	H60D	0.980	C60	H60E	0.980
C60	H60F	0.980			

Table 5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C2	O1	C17	116.00(17)	C33	O2	C36	116.70(18)
C4	O3	C37	119.64(17)	C53	O4	C56	116.69(18)
C1	N1	C2	117.18(19)	C1	N2	C4	115.46(19)
C18	N3	C22	110.66(18)	C18	N3	C23	107.44(18)
C22	N3	C23	107.67(18)	C29	N4	C30	116.50(19)
C38	N5	C42	111.61(18)	C38	N5	C43	107.42(19)
C42	N5	C43	107.80(19)	C49	N6	C50	116.4(2)
N1	C1	N2	125.2(2)	N1	C1	C5	116.9(2)
N2	C1	C5	117.9(2)	O1	C2	N1	117.55(19)
O1	C2	C3	118.21(19)	N1	C2	C3	124.2(2)
C2	C3	C4	112.5(2)	C2	C3	C11	123.7(2)
C4	C3	C11	123.8(2)	O3	C4	N2	118.1(2)
O3	C4	C3	116.5(2)	N2	C4	C3	125.4(2)
C1	C5	C6	120.2(2)	C1	C5	C10	121.0(2)
C6	C5	C10	118.8(2)	C5	C6	C7	120.8(2)
C6	C7	C8	119.8(2)	C7	C8	C9	120.3(2)
C8	C9	C10	119.7(2)	C5	C10	C9	120.6(2)
C3	C11	C12	120.4(2)	C3	C11	C16	120.8(2)
C12	C11	C16	118.8(2)	C11	C12	C13	120.4(2)
C12	C13	C14	120.7(2)	C13	C14	C15	119.7(2)
C14	C15	C16	120.0(2)	C11	C16	C15	120.4(2)
O1	C17	C18	110.13(17)	O1	C17	C27	109.74(16)
C18	C17	C27	111.29(18)	N3	C18	C17	110.59(18)
N3	C18	C19	112.19(18)	C17	C18	C19	115.24(19)
C18	C19	C20	107.31(18)	C19	C20	C21	107.97(19)
C19	C20	C24	110.51(19)	C21	C20	C24	108.80(19)
C20	C21	C22	108.12(19)	N3	C22	C21	111.7(2)
N3	C23	C24	112.6(2)	C20	C24	C23	106.42(19)
C20	C24	C25	115.1(2)	C23	C24	C25	112.4(2)
C24	C25	C26	114.2(2)	C17	C27	C28	122.6(2)
C17	C27	C35	119.51(19)	C28	C27	C35	117.9(2)
C27	C28	C29	119.7(2)	N4	C29	C28	124.6(2)
N4	C30	C31	117.8(2)	N4	C30	C35	123.4(2)
C31	C30	C35	118.9(2)	C30	C31	C32	120.8(2)
C31	C32	C33	120.0(2)	O2	C33	C32	114.2(2)
O2	C33	C34	125.1(2)	C32	C33	C34	120.7(2)
C33	C34	C35	120.3(2)	C27	C35	C30	117.9(2)

Table 5. Bond angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C27	C35	C34	122.8(2)	C30	C35	C34	119.3(2)
O3	C37	C38	103.18(17)	O3	C37	C47	112.49(18)
C38	C37	C47	113.36(18)	N5	C38	C37	110.54(19)
N5	C38	C39	111.38(19)	C37	C38	C39	111.95(19)
C38	C39	C40	108.4(2)	C39	C40	C41	107.6(2)
C39	C40	C44	110.87(19)	C41	C40	C44	108.7(2)
C40	C41	C42	107.5(2)	N5	C42	C41	112.1(2)
N5	C43	C44	112.6(2)	C40	C44	C43	106.78(19)
C40	C44	C45	113.8(2)	C43	C44	C45	112.6(2)
C44	C45	C46	114.6(2)	C37	C47	C48	119.2(2)
C37	C47	C55	123.0(2)	C48	C47	C55	117.5(2)
C47	C48	C49	120.5(2)	N6	C49	C48	124.0(2)
N6	C50	C51	117.0(2)	N6	C50	C55	124.4(2)
C51	C50	C55	118.6(2)	C50	C51	C52	121.0(2)
C51	C52	C53	120.3(2)	O4	C53	C52	114.7(2)
O4	C53	C54	124.9(2)	C52	C53	C54	120.4(2)
C53	C54	C55	120.2(2)	C47	C55	C50	117.0(2)
C47	C55	C54	123.7(2)	C50	C55	C54	119.3(2)
O5	C58	O6	131.9(4)	O5	C58	C57	112.2(3)
O6	C58	C57	112.3(3)	C58	O6	C59	126.7(4)
O6	C59	C60	111.7(3)	O5A	C58	O6A	105.7(4)
O5A	C58	C57	139.4(4)	O6A	C58	C57	110.4(3)
C58	O6A	C59A	103.0(3)	O6A	C59A	C60	101.9(3)
O6A[1)]	C59A[1)]	C60[1)]	101.9(3)				

Symmetry Operators:

(1) X+Y+Z,X+Y+Z,X+Y+Z

Table 6. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C5	C6	H1	119.6	C7	C6	H1	119.6
C6	C7	H2	120.1	C8	C7	H2	120.1
C7	C8	H3	119.8	C9	C8	H3	119.8
C8	C9	H4	120.2	C10	C9	H4	120.2
C5	C10	H5	119.7	C9	C10	H5	119.7
C11	C12	H6	119.8	C13	C12	H6	119.8
C12	C13	H7	119.7	C14	C13	H7	119.6
C13	C14	H8	120.2	C15	C14	H8	120.2
C14	C15	H9	120.0	C16	C15	H9	120.0
C11	C16	H10	119.8	C15	C16	H10	119.8
O1	C17	H11	108.5	C18	C17	H11	108.5
C27	C17	H11	108.5	N3	C18	H18	106.0
C17	C18	H18	106.0	C19	C18	H18	106.0
C18	C19	H19A	110.3	C18	C19	H19B	110.2
C20	C19	H19A	110.3	C20	C19	H19B	110.3
H19A	C19	H19B	108.5	C19	C20	H20	109.8
C21	C20	H20	109.8	C24	C20	H20	109.8
C20	C21	H21A	110.1	C20	C21	H21B	110.1
C22	C21	H21A	110.1	C22	C21	H21B	110.1
H21A	C21	H21B	108.4	N3	C22	H22A	109.3
N3	C22	H22B	109.3	C21	C22	H22A	109.3
C21	C22	H22B	109.3	H22A	C22	H22B	107.9
N3	C23	H23A	109.1	N3	C23	H23B	109.1
C24	C23	H23A	109.1	C24	C23	H23B	109.1
H23A	C23	H23B	107.8	C20	C24	H24	107.5
C23	C24	H24	107.5	C25	C24	H24	107.5
C24	C25	H25A	108.7	C24	C25	H25B	108.7
C26	C25	H25A	108.7	C26	C25	H25B	108.7
H25A	C25	H25B	107.6	C25	C26	H26A	109.5
C25	C26	H26B	109.5	C25	C26	H26C	109.5
H26A	C26	H26B	109.5	H26A	C26	H26C	109.5
H26B	C26	H26C	109.5	C27	C28	H28	120.1
C29	C28	H28	120.1	N4	C29	H29	117.7
C28	C29	H29	117.7	C30	C31	H31	119.6
C32	C31	H31	119.6	C31	C32	H32	120.0
C33	C32	H32	120.0	C33	C34	H34	119.8
C35	C34	H34	119.8	O2	C36	H36A	109.5

Table 6. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
O2	C36	H36B	109.5	O2	C36	H36C	109.5
H36A	C36	H36B	109.5	H36A	C36	H36C	109.5
H36B	C36	H36C	109.5	O3	C37	H37	109.2
C38	C37	H37	109.2	C47	C37	H37	109.2
N5	C38	H38	107.6	C37	C38	H38	107.6
C39	C38	H38	107.6	C38	C39	H39A	110.0
C38	C39	H39B	110.0	C40	C39	H39A	110.0
C40	C39	H39B	110.0	H39A	C39	H39B	108.4
C39	C40	H40	109.9	C41	C40	H40	109.9
C44	C40	H40	109.9	C40	C41	H41A	110.2
C40	C41	H41B	110.2	C42	C41	H41A	110.2
C42	C41	H41B	110.2	H41A	C41	H41B	108.5
N5	C42	H42A	109.2	N5	C42	H42B	109.2
C41	C42	H42A	109.2	C41	C42	H42B	109.2
H42A	C42	H42B	107.9	N5	C43	H43A	109.1
N5	C43	H43B	109.1	C44	C43	H43A	109.1
C44	C43	H43B	109.1	H43A	C43	H43B	107.8
C40	C44	H44	107.8	C43	C44	H44	107.8
C45	C44	H44	107.8	C44	C45	H45A	108.6
C44	C45	H45B	108.6	C46	C45	H45A	108.6
C46	C45	H45B	108.6	H45A	C45	H45B	107.6
C45	C46	H46A	109.5	C45	C46	H46B	109.5
C45	C46	H46C	109.5	H46A	C46	H46B	109.5
H46A	C46	H46C	109.5	H46B	C46	H46C	109.5
C47	C48	H48	119.7	C49	C48	H48	119.8
N6	C49	H49	118.0	C48	C49	H49	118.0
C50	C51	H51	119.5	C52	C51	H51	119.5
C51	C52	H52	119.9	C53	C52	H52	119.8
C53	C54	H54	119.9	C55	C54	H54	119.9
O4	C56	H56A	109.5	O4	C56	H56B	109.5
O4	C56	H56C	109.5	H56A	C56	H56B	109.5
H56A	C56	H56C	109.5	H56B	C56	H56C	109.5
C58	C57	H57A	109.5	C58	C57	H57B	109.5
C58	C57	H57C	109.5	H57A	C57	H57B	109.5
H57A	C57	H57C	109.5	H57B	C57	H57C	109.5
O6	C59	H59A	109.3	O6	C59	H59B	109.3
C60	C59	H59A	109.3	C60	C59	H59B	109.3

Table 6. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
H59A	C59	H59B	107.9	O6A	C59A	H59C	111.4
O6A	C59A	H59D	111.4	H59C	C59A	H59D	109.3
C59	C60	H60A	109.5	C59	C60	H60B	109.5
C59	C60	H60C	109.5	H60A	C60	H60B	109.5
H60A	C60	H60C	109.5	H60B	C60	H60C	109.5
C59A	C60	H60D	109.5	C59A	C60	H60E	109.5
C59A	C60	H60F	109.5	H60D	C60	H60E	109.5
H60D	C60	H60F	109.5	H60E	C60	H60F	109.5

Table 7. Distances beyond the asymmetric unit out to 3.60 Å

atom	atom	distance	atom	atom	distance
O2	C43[1)]	3.535(2)	O2	C59[2)]	3.418(5)
O2	C59A[2)]	3.065(5)	O2	C60[2)]	3.328(3)
O4	N5[3)]	3.097(2)	O4	C42[3)]	3.251(2)
O4	C48[3)]	3.529(3)	O4	C49[3)]	3.479(3)
O5	C7[4)]	3.290(5)	O5	C26[5)]	3.551(5)
O5A	C7[4)]	3.433(6)	O5A	C26[5)]	3.561(6)
N1	C21[6)]	3.573(3)	N4	C52[7)]	3.501(3)
N4	C57[8)]	3.456(4)	N5	C56[9)]	3.379(3)
N6	C56[9)]	3.586(3)	C1	C60[6)]	3.503(4)
C7	C40[10)]	3.463(3)	C8	C19[11)]	3.595(3)
C9	C14[11)]	3.444(3)	C30	C57[8)]	3.456(4)
C49	C53[9)]	3.410(3)			

Symmetry Operators:

(1) X,Y-1,Z
(2) -X+1/2,-Y,Z+1/2
(3) X+1/2,-Y+1/2+1,-Z+1
(4) -X+1/2,-Y,Z+1/2-1
(5) -X+1/2+1,-Y,Z+1/2-1
(6) X+1/2-1,-Y+1/2,-Z+1
(7) -X+1/2,-Y+1,Z+1/2
(8) -X+1/2+1,-Y,Z+1/2
(9) X+1/2-1,-Y+1/2+1,-Z+1
(10) -X,Y+1/2-1,-Z+1/2+1
(11) X-1,Y,Z

Table 8. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
O2	H43A[1)]	2.635	O2	H44[1)]	3.209
O2	H46C[1)]	3.428	O2	H59A[2)]	2.695
O2	H59C[2)]	2.730	O2	H59D[2)]	2.856
O2	H60A[2)]	2.892	O2	H60C[2)]	3.241
O2	H60D[2)]	2.694	O4	H26C[3)]	3.278
O4	H36A[4)]	2.825	O4	H42A[5)]	3.303
O4	H42B[5)]	2.814	O4	H43A[5)]	3.196
O4	H59B[6)]	3.579	O5	H2[7)]	2.434
O5	H3[7)]	3.424	O5	H19B[8)]	2.657
O5	H25B[8)]	3.018	O5	H26A[8)]	3.037
O5	H26C[8)]	3.466	O5	H39A[4)]	3.345
O5	H40[4)]	2.848	O5A	H2[7)]	2.530
O5A	H19B[8)]	3.186	O5A	H25B[8)]	3.301
O5A	H26A[8)]	3.073	O5A	H26C[8)]	3.335
O5A	H39A[4)]	3.103	O5A	H40[4)]	2.893
O6A	H10[4)]	3.387	O6A	H39A[4)]	3.021
O6A	H46B[9)]	3.450	O6	H29[4)]	3.408
O6	H46B[9)]	2.846	N1	H21A[3)]	2.612
N1	H24[3)]	3.180	N1	H60B[3)]	2.971
N1	H60C[3)]	3.569	N1	H60F[3)]	2.822
N2	H23A[3)]	3.589	N2	H24[3)]	2.858
N2	H60B[3)]	3.584	N2	H60C[3)]	3.047
N2	H60F[3)]	2.793	N3	H7[3)]	3.167
N4	H9[10)]	3.437	N4	H42A[11)]	3.441
N4	H51[12)]	3.330	N4	H52[12)]	2.701
N4	H57A[13)]	2.910	N4	H57C[13)]	3.262
N4	H59B[3)]	3.583	N4	H60E[3)]	3.314
N5	H56B[14)]	2.809	N6	H25A[3)]	3.424
N6	H38[14)]	3.100	N6	H43B[14)]	2.848
N6	H45B[14)]	3.396	N6	H46A[14)]	3.315
N6	H56A[14)]	2.709	C1	H21A[3)]	2.886
C1	H23A[3)]	3.537	C1	H24[3)]	2.887
C1	H60B[3)]	3.153	C1	H60C[3)]	3.128
C1	H60F[3)]	2.608	C2	H21A[3)]	3.367
C2	H24[3)]	3.348	C2	H60B[3)]	3.230
C2	H60F[3)]	3.157	C3	H24[3)]	3.356
C3	H26B[3)]	3.279	C3	H60F[3)]	3.351

Table 8. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C4	H24[3)]	3.060	C4	H26B[3)]	3.513
C4	H60C[3)]	3.391	C4	H60F[3)]	3.101
C5	H21A[3)]	2.995	C5	H22B[3)]	3.162
C5	H23A[3)]	3.323	C5	H24[3)]	3.576
C5	H32[15)]	3.466	C5	H41A[11)]	3.573
C5	H60F[3)]	3.290	C6	H21A[3)]	2.876
C6	H22B[3)]	2.932	C6	H40[11)]	3.473
C6	H41A[11)]	2.944	C7	H19B[16)]	3.456
C7	H22B[3)]	3.073	C7	H40[11)]	2.659
C7	H41A[11)]	3.173	C8	H19A[16)]	3.006
C8	H19B[16)]	3.292	C8	H22B[3)]	3.433
C8	H40[11)]	2.927	C8	H44[11)]	3.555
C8	H45A[11)]	3.124	C9	H8[16)]	3.574
C9	H31[15)]	3.590	C9	H32[15)]	3.520
C9	H45A[11)]	3.501	C10	H8[16)]	3.471
C10	H22B[3)]	3.490	C10	H23A[3)]	3.198
C10	H31[15)]	3.225	C10	H32[15)]	2.937
C11	H26B[3)]	3.366	C12	H26B[3)]	3.169
C13	H4[17)]	3.316	C13	H23A[4)]	3.492
C13	H36B[4)]	3.372	C14	H4[17)]	2.942
C14	H5[17)]	3.430	C14	H23A[4)]	3.466
C14	H49[17)]	3.275	C15	H4[17)]	2.952
C16	H4[17)]	3.340	C16	H57B[3)]	3.404
C19	H3[17)]	3.019	C20	H22A[4)]	3.459
C21	H1[4)]	3.459	C21	H11[4)]	3.599
C22	H20[3)]	3.135	C23	H7[3)]	3.283
C23	H8[3)]	3.577	C26	H36A[17)]	3.227
C26	H36C[17)]	3.331	C26	H59A[13)]	3.302
C26	H59D[13)]	3.312	C27	H57C[13)]	3.240
C27	H60B[3)]	3.312	C28	H3[17)]	3.343
C28	H45A[10)]	3.579	C28	H57A[13)]	3.585
C28	H57C[13)]	3.451	C28	H60B[3)]	2.808
C28	H60E[3)]	2.934	C29	H45A[10)]	3.243
C29	H45B[10)]	3.399	C29	H51[12)]	3.358
C29	H52[12)]	3.108	C29	H57A[13)]	3.059
C29	H57C[13)]	3.449	C29	H59B[3)]	3.115
C29	H60B[3)]	3.031	C29	H60E[3)]	2.760

Table 8. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C30	H41B[11)]	3.420	C30	H42A[11)]	3.398
C30	H57A[13)]	3.288	C30	H57B[13)]	3.555
C30	H57C[13)]	2.983	C31	H5[11)]	3.186
C31	H41B[11)]	3.063	C31	H42A[11)]	3.053
C31	H46C[1)]	3.541	C31	H57C[13)]	3.595
C32	H5[11)]	3.266	C32	H41B[11)]	3.035
C32	H44[1)]	3.474	C32	H46C[1)]	3.098
C32	H59C[2)]	3.176	C32	H60C[2)]	3.293
C32	H60D[2)]	3.361	C33	H41B[11)]	3.359
C33	H43A[1)]	3.599	C33	H46C[1)]	3.001
C33	H59C[2)]	3.155	C33	H60D[2)]	3.528
C34	H46C[1)]	3.333	C35	H57C[13)]	2.999
C36	H7[3)]	3.488	C36	H26A[16)]	3.538
C36	H26C[16)]	3.273	C36	H43A[1)]	2.764
C36	H56B[3)]	3.480	C36	H56C[3)]	3.375
C36	H59A[2)]	2.970	C36	H59C[2)]	3.543
C36	H59D[2)]	3.142	C39	H57A[3)]	3.281
C40	H2[15)]	3.357	C41	H2[15)]	3.580
C41	H60A[12)]	3.379	C41	H60D[12)]	3.550
C42	H52[14)]	3.366	C42	H60A[12)]	3.293
C42	H60D[12)]	3.480	C43	H36A[18)]	3.533
C43	H36B[18)]	3.501	C43	H56B[14)]	2.906
C45	H29[19)]	2.978	C45	H51[5)]	3.147
C46	H25B[18)]	3.581	C46	H29[19)]	3.544
C46	H51[5)]	3.514	C46	H57B[20)]	3.305
C46	H57C[20)]	3.290	C47	H25A[3)]	3.458
C48	H8[16)]	3.165	C48	H56A[14)]	3.533
C49	H8[16)]	3.053	C49	H43B[14)]	3.402
C49	H56A[14)]	3.060	C50	H25A[3)]	2.929
C50	H56A[14)]	2.861	C51	H9[14)]	3.517
C51	H25A[3)]	3.409	C51	H29[21)]	3.327
C51	H45B[14)]	3.055	C51	H56A[14)]	3.401
C51	H59B[6)]	3.573	C52	H26C[3)]	3.446
C52	H29[21)]	3.396	C52	H42B[5)]	3.523
C52	H49[5)]	3.482	C52	H59B[6)]	2.902
C53	H26C[3)]	3.049	C53	H49[5)]	3.227
C53	H59B[6)]	3.545	C54	H25A[3)]	3.282

Table 8. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C54	H26B[3)]	3.300	C54	H26C[3)]	3.336
C54	H49[5)]	3.386	C55	H25A[3)]	2.907
C55	H56A[14)]	3.411	C56	H36A[4)]	2.919
C56	H43A[5)]	3.294	C57	H10[4)]	3.296
C57	H39A[4)]	3.596	C57	H39B[4)]	3.452
C57	H46B[9)]	3.148	C57	H46C[9)]	3.284
C58	H2[7)]	3.600	C58	H19B[8)]	3.479
C58	H25B[8)]	3.304	C58	H39A[4)]	3.131
C58	H40[4)]	3.466	C58	H46B[9)]	3.279
C59	H26C[8)]	3.122	C59	H29[4)]	3.362
C59	H36A[7)]	3.467	C59	H42B[21)]	3.568
C59	H52[22)]	3.443	C59A	H26C[8)]	3.549
C59A	H32[7)]	3.473	C59A	H39A[4)]	3.324
C60	H32[7)]	3.183	C60	H41A[21)]	3.464
C60	H42B[21)]	3.274	H1	H21A[3)]	2.641
H1	H22B[3)]	3.257	H1	H41A[11)]	2.905
H2	H19B[16)]	3.026	H2	H22B[3)]	3.455
H2	H26A[16)]	3.059	H2	H40[11)]	2.481
H2	H41A[11)]	3.304	H2	H41B[11)]	3.495
H3	H19A[16)]	2.440	H3	H19B[16)]	2.705
H3	H28[16)]	2.746	H3	H40[11)]	2.930
H3	H45A[11)]	2.808	H4	H8[16)]	3.245
H4	H9[16)]	3.266	H4	H31[15)]	3.243
H4	H45A[11)]	3.480	H4	H57B[23)]	3.431
H5	H8[16)]	3.033	H5	H23A[3)]	3.181
H5	H31[15)]	2.521	H5	H32[15)]	2.693
H6	H26A[3)]	3.492	H6	H26B[3)]	2.857
H7	H22B[4)]	3.487	H7	H23A[4)]	2.927
H7	H23B[4)]	3.202	H7	H36B[4)]	2.860
H7	H36C[4)]	3.400	H8	H23A[4)]	2.885
H8	H23B[4)]	3.369	H8	H48[17)]	2.810
H8	H49[17)]	2.569	H9	H31[19)]	3.031
H9	H48[17)]	3.427	H9	H49[17)]	3.493
H9	H51[5)]	3.220	H9	H57A[3)]	3.507
H9	H57B[3)]	3.595	H10	H57A[3)]	2.914
H10	H57B[3)]	2.935	H11	H21A[3)]	2.903
H11	H21B[3)]	3.447	H18	H57C[13)]	2.912

Table 8. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

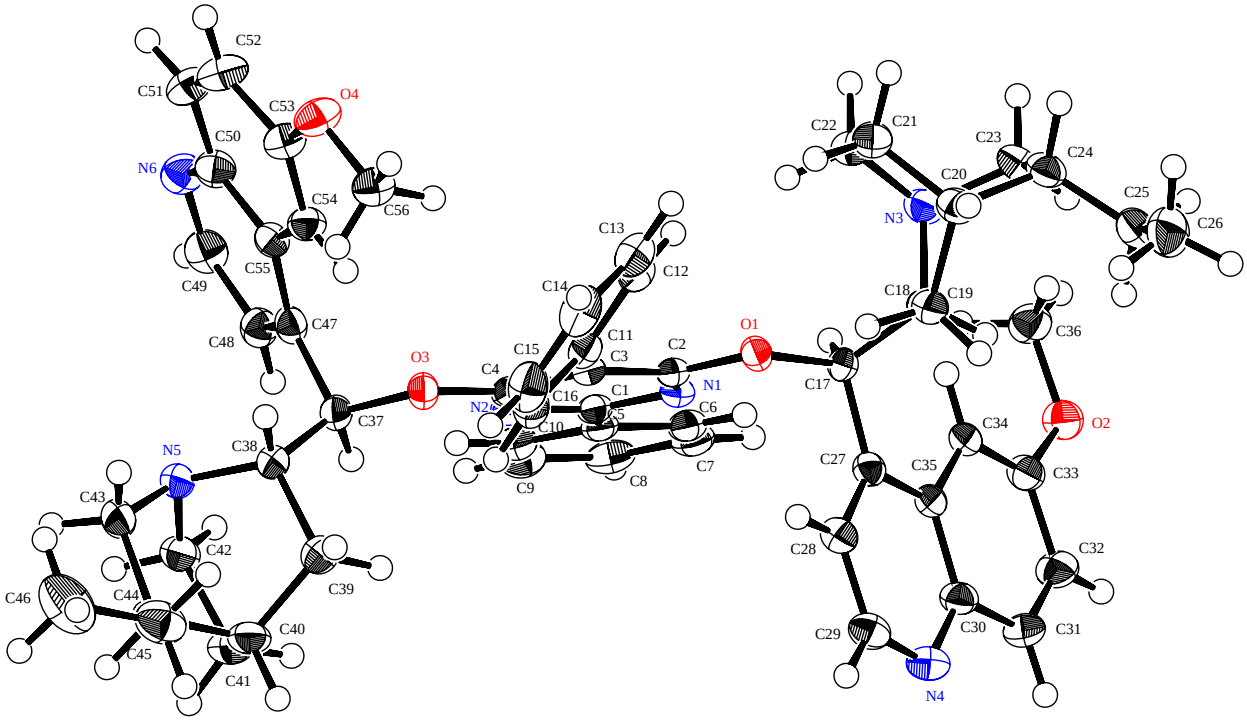
atom	atom	distance	atom	atom	distance
H19B	H57C[13)]	3.046	H20	H22A[4)]	2.539
H20	H22B[4)]	2.856	H22A	H26A[3)]	3.528
H23B	H46A[1)]	3.112	H25A	H46A[1)]	3.397
H25A	H46B[1)]	3.465	H25B	H46A[1)]	3.321
H25B	H46B[1)]	3.031	H25B	H57C[13)]	3.193
H26A	H36A[17)]	3.274	H26A	H36C[17)]	2.907
H26A	H59A[13)]	3.266	H26A	H59D[13)]	3.247
H26B	H36A[17)]	3.303	H26B	H36C[17)]	3.478
H26B	H54[4)]	3.242	H26B	H56C[4)]	3.131
H26C	H36A[17)]	2.614	H26C	H36C[17)]	3.083
H26C	H56C[4)]	3.325	H26C	H59A[13)]	2.528
H26C	H59B[13)]	2.949	H26C	H59D[13)]	2.574
H28	H45A[10)]	3.229	H28	H60B[3)]	2.902
H28	H60E[3)]	3.130	H28	H60F[3)]	3.597
H29	H45A[10)]	2.558	H29	H45B[10)]	2.605
H29	H46B[10)]	3.061	H29	H51[12)]	2.712
H29	H52[12)]	2.855	H29	H57A[13)]	3.347
H29	H59B[3)]	2.729	H29	H60B[3)]	3.224
H29	H60E[3)]	2.825	H31	H37[11)]	3.293
H31	H41B[11)]	3.392	H31	H42A[11)]	2.796
H31	H48[11)]	2.860	H32	H41B[11)]	3.356
H32	H44[1)]	3.063	H32	H46C[1)]	3.391
H32	H59C[2)]	2.900	H32	H60A[2)]	2.900
H32	H60C[2)]	2.589	H32	H60D[2)]	2.649
H32	H60F[2)]	3.105	H36A	H42B[1)]	3.584
H36A	H43A[1)]	2.572	H36A	H56B[3)]	2.851
H36A	H56C[3)]	2.632	H36A	H59A[2)]	2.659
H36A	H59B[2)]	3.507	H36A	H59D[2)]	2.855
H36A	H60D[2)]	3.564	H36B	H43A[1)]	2.655
H36B	H43B[1)]	3.498	H36B	H46A[1)]	3.384
H36B	H56B[3)]	3.221	H36B	H56C[3)]	3.326
H36C	H59A[2)]	3.058	H36C	H59C[2)]	3.484
H36C	H59D[2)]	3.174	H38	H49[5)]	3.498
H39A	H57A[3)]	3.152	H39A	H59C[3)]	2.756
H39A	H60C[3)]	3.265	H39B	H51[5)]	3.211
H39B	H57A[3)]	2.647	H40	H57A[3)]	3.362
H40	H59C[3)]	3.592	H41A	H60A[12)]	2.670

Table 8. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H41A	H60B[12)]	3.416	H41A	H60D[12)]	2.835
H41A	H60E[12)]	3.385	H41B	H59C[3)]	2.885
H42A	H52[14)]	3.016	H42B	H52[14)]	2.802
H42B	H59B[12)]	3.113	H42B	H60A[12)]	2.483
H42B	H60B[12)]	3.535	H42B	H60D[12)]	2.672
H42B	H60E[12)]	3.001	H43A	H56B[14)]	2.616
H43A	H60A[12)]	3.385	H43A	H60D[12)]	3.379
H43B	H49[5)]	3.134	H43B	H56B[14)]	2.810
H44	H60A[12)]	3.077	H44	H60D[12)]	3.041
H45A	H51[5)]	3.574	H45B	H51[5)]	2.236
H46A	H51[5)]	3.482	H46B	H51[5)]	3.282
H46B	H57B[20)]	2.858	H46B	H57C[20)]	2.899
H46B	H59B[20)]	3.391	H46C	H57B[20)]	2.875
H46C	H57C[20)]	2.835	H48	H52[14)]	3.552
H49	H56A[14)]	3.512	H49	H56B[16)]	3.000
H51	H56A[14)]	3.537	H52	H59B[6)]	2.469
H52	H60E[6)]	3.358			

Symmetry Operators:

(1) X,Y-1,Z
(2) -X+1/2,-Y,Z+1/2
(3) X+1/2-1,-Y+1/2,-Z+1
(4) X+1/2,-Y+1/2,-Z+1
(5) X+1/2,-Y+1/2+1,-Z+1
(6) -X+1,Y+1/2,-Z+1/2
(7) -X+1/2,-Y,Z+1/2-1
(8) -X+1/2+1,-Y,Z+1/2-1
(9) -X+1/2+1,-Y+1,Z+1/2-1
(10) -X+1,Y+1/2-1,-Z+1/2+1
(11) -X,Y+1/2-1,-Z+1/2+1
(12) -X+1/2,-Y+1,Z+1/2
(13) -X+1/2+1,-Y,Z+1/2
(14) X+1/2-1,-Y+1/2+1,-Z+1
(15) -X,Y+1/2,-Z+1/2+1
(16) X-1,Y,Z
(17) X+1,Y,Z
(18) X,Y+1,Z
(19) -X+1,Y+1/2,-Z+1/2+1
(20) -X+1/2+1,-Y+1,Z+1/2
(21) -X+1/2,-Y+1,Z+1/2-1
(22) -X+1,Y+1/2-1,-Z+1/2
(23) X+1/2-2,-Y+1/2,-Z+1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C51
C53
O4
C50
N6
C54
C56
C55
C49
C47
C48
O3
C37
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N5
C43
C42
C46
C44
C39
C40
C45
C41
C13
C12
C14
C11
C15
C3
C4
C2
O1
C16
C1
N1
N2
C10
C5
C6
C9
C8
C7
C22
C21
C23
C24
C20
C25
N3
C26
C18
C19
C36
C17
C34
O2
C27
C35
C33
C28
C32
C29
C30
C31
N4