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Supporting Information

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A fluorous phase, Pummerer cyclative-capture strategy for the synthesis of *N*-heterocycles

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Experimental

General Considerations

All experiments were performed under an atmosphere of Ar or N_2, using anhydrous solvents, unless stated otherwise. Reactions were carried out using oven-dried glassware. THF was distilled from sodium/benzophenone, CH_2Cl_2 was distilled from CaH_2, Et_2O was distilled from CaH_2, $^iPrNH_2$ was distilled from CaH_2. Et_3N was distilled from CaH_2 and stored over KOH and under Ar/N_2. DMSO was distilled from CaH_2 and stored over molecular sieves and under Ar/N_2.

^1H NMR and ^{13}C NMR were recorded on a Fourier transform spectrometer, with chemical shift values being reported in ppm relative to residual chloroform (δ_H = 7.27 or δ_C = 77.2) as internal standard unless otherwise stated. NMR signals were assigned using DEPT-135, HMQC and COSY spectra. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra and microanalyses were recorded at the University of Glasgow. IR spectra were recorded using a JASCO FT/IR 410 spectrometer.

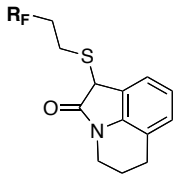
Column chromatography was carried out using Fischer Matrex silica gel 60 and FluoroFlash silica. Macherey-Nagel aluminium backed plates, pre-coated with silica gel 60 (UV_{254}) were used for thin layer chromatography and were visualised by UV or staining with alkali $KMnO_4$.

$R_F = C_8F_{17}$

Formation of fluorous-tagged *N*-heterocycles

General Procedure A : the cyclative-capture of glyoxamides

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one



To a solution of oxalyl chloride (0.18 ml, 2.10 mmol, 1.1 eq.) in CH_2Cl_2 (5 ml) at -78 ^{O}C was added DMSO (0.27 ml, 3.78 mmol, 2 eq.) in CH_2Cl_2 (3 ml). After 30 minutes, a solution of 2-hydroxy-*N*-(3,4-dihydroquinolin-1-(2*H*)-yl)acetamide (361 mg, 1.89 mmol, 1 eq.) in CH_2Cl_2 (4 ml) was added. After 1 hour, NEt_3 (1.32 ml, 9.45 mmol, 5 eq.) was added and the reaction mixture was allowed to warm to room temperature. After 1.5 hours, CH_2Cl_2 (20 ml) was added to the reaction mixture and the organic layer washed with aqueous saturated $NaHCO_3$. The organic layer was then dried ($MgSO_4$) and concentrated *in vacuo* to give the crude glyoxamide as a yellow oil which was used without further purification. CH_2Cl_2 (20 ml) and $C_8F_{17}CH_2CH_2SH$ (0.39 ml, 1.32 mmol, 0.7 eq.) were then added to the crude glyoxamide at room temperature. After 18 hours, TFAA (2.50 ml, 17.0 mmol, 9 eq.) was added. After a further hour, $BF_3.OEt_2$ (1.19 ml, 9.45 mmol, 5 eq.) was added. After 1 hour, the reaction was quenched with aqueous saturated $NaHCO_3$. The organic layer was separated and washed with aqueous saturated $NaHCO_3$. The organic layer was then dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (559 mg, 0.86 mmol, 65 % over 2 steps) as a yellow solid:

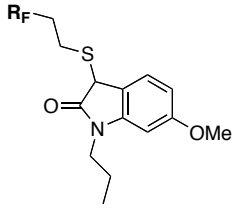
^{1}H NMR (400 MHz, $CDCl_3$) 7.12 (1H, d, J 7.6, Ar*H*), 7.00 (1H, d, J 7.6, Ar*H*), 6.91 (1H, t, J 7.6, Ar*H*), 4.43 (1H, s, C*H*-S), 3.71-3.60 (2H, m CH_2-N), 2.90-2.81 (1H, m, 1H of CH_2-R_F), 2.79-2.68 (3H, m, Ar-CH_2 and 1H of CH_2-R_F), 2.39-2.25 (2H, m, CH_2-CH_2-R_F), 1.99-1.89 (2H, m, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) 173.8 (*C*=O), 139.8 (Ar*C*), 128.2 (Ar*C*H), 123.8 (Ar*C*), 122.7 (Ar*C*H), 122.6 (Ar*C*H), 120.7 (Ar*C*), 46.0 (*C*H-S), 39.1 (*C*H_2-N), 32.0 (t, J 21.5, *C*H_2-R_F), 24.3 (Ar-*C*H_2), 21.1 (*C*H_2-CH_2-R_F and *C*H_2).

IR ν_{max} (Golden Gate)/cm^{-1} 2965, 1713 (C=O), 1623, 1502, 1469, 1364, 1199, 1145, 1102.

MS *m/z* (EI mode) 651 (M^+, 11 %), 144 (14) and 173 (100); (Found: M^+, 651.0526 $C_{21}H_{14}ONF_{17}S$ requires 651.0525).

3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-6-methoxy-1-propyl-1,3-dihydro-indol-2-one



As for general procedure A. *N*-(3-Methoxy-phenyl)-2-oxo-*N*-propyl-acetamide (0.15 g, 0.70 mmol, 1 eq.) on treatment with $C_8F_{17}CH_2CH_2SH$ (0.82 ml, 2.80 mmol, 4 eq.), TFAA (0.93 ml, 6.29 mmol,

9 eq.) and $BF_3.OEt_2$ (0.44 ml, 3.50 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-6-methoxy-1-propyl-1,3-dihydro-indol-2-one (0.36 g, 0.52 mmol, 75 %) as a pale yellow oil and as a 5:1 mixture of isomers: (For major isomer)

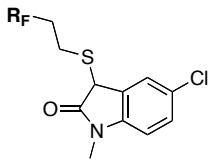
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (1H, m, Ar*H*), 6.52-6.50 (1H, dd, J 8.2, 2.3, Ar*H*), 6.35-6.35 (1H, d, J 2.3, Ar*H*), 4.21 (1H, s, C*H*-S), 3.76 (3H, s, CH_3-O), 3.67-3.50 (2H, m, N-CH_2), 2.96-2.69 (2H, m, CH_2-CH_2-R_F), 2.39-2.26 (2H, m, CH_2-R_F), 1.68-1.59 (2H, m, N-CH_2-CH_2), 0.92-0.88 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0 (*C*=O), 161.5 (Ar*C*-OMe), 145.2 (Ar*C*), 126.3 (Ar*C*H), 117.3 (Ar*C*), 106.8 (Ar*C*H), 97.3 (Ar*C*H), 56.0 (*C*H_3-O), 44.9 (*C*H-S), 42.3 (N-*C*H_2), 32.4 (t, J 22.0, *C*H_2-R_F), 21.3 (*C*H_2-CH_2-R_F), 21.1 (N-CH_2-*C*H_2), 11.7 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2965, 1713 (C=O), 1623, 1502, 1469, 1364, 1199, 1145, 1102.

MS *m/z* (EI mode) 683 (M^+, 52 %), 132 (18), 162 (32), 204 (100), 205 (100), 640 (17), 664 (12) and 684 (14); (Found: M^+, 683.0785 $C_{22}H_{18}O_2NF_{17}S$ requires 683.0787).

5-Chloro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1,3-dihydro-indol-2-one



As for general procedure A. *N*-(4-Chloro-phenyl)-2-hydroxy-*N*-methyl-acetamide (0.20 g, 1.00 mmol, 1 eq.) was oxidised to give crude glyoxamide which on treatment with $C_8F_{17}CH_2CH_2SH$ (0.12 ml, 0.50 mmol, 0.5 eq.), TFAA (1.27 ml, 9.00 mmol, 9 eq.) and $BF_3.OEt_2$ (0.60 ml, 4.50 mmol, 4.5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 5-chloro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1,3-dihydro-indol-2-one (280 mg, 0.40 mmol, 79 % over 2 steps) as a white solid:

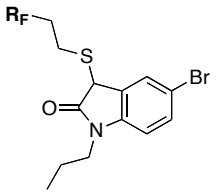
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, s, Ar*H*), 7.24 (1H, dd, J 8.3, 2.0, Ar*H*), 6.69 (1H, d, J 8.3, Ar*H*), 4.24 (1H, s, C*H*-S), 3.14 (3H, s, N-CH_3), 2.94-2.86 (1H, m, 1H of CH_2-CH_2-R_F), 2.80-2.73 (1H, m, 1H of CH_2-CH_2-R_F), 2.41-2.33 (2H, m, CH_2-R_F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9 (*C*=O), 142.9 (Ar*C*), 129.8 (Ar*C*H), 128.9 (Ar*C*), 127.1 (Ar*C*), 125.9 (Ar*C*H), 109.7 (Ar*C*H), 45.1 (*C*H-S), 32.3 (t, J 21.9, *C*H_2-R_F), 26.9 (N-*C*H_3), 21.6 (*C*H_2-CH_2-R_F).

IR ν_{max} (Golden Gate)/cm^{-1} 1706 (C=O), 1610, 1488, 1238, 1199, 1145.

MS *m/z* (EI mode) 659 (M^+, 12 %), 83 (13), 117 (13), 181 (100) and 183 (83); (Found: M^+, 658.9978 $C_{19}H_{11}ONF_{17}SCl$ requires 658.9978).

5-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one 2



As for general procedure A. *N*-(4-Bromophenyl)-*N*-propyl-2-hydroxyacetamide (1.10 g, 4.1 mmol, 1 eq.) was oxidised to give crude glyoxamide which on treatment with $C_8F_{17}CH_2CH_2SH$ (0.52 ml, 1.77 mmol, 0.7 eq.), TFAA (3.36 ml, 2.27 mmol, 9 eq.) and $BF_3.OEt_2$ (1.61 ml, 12.7 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one **2** (1.10 g, 1.51 mmol, 85 % over 2 steps) as a orange solid:

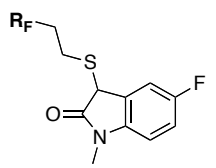
^{1}H NMR (400 MHz, $CDCl_3$) □ 7.44 (1H, s, ArC*H*), 7.37 (1H, dd, J 8.3, 1.9, ArC*H*), 6.66 (1H, d, J 8.3, ArC*H*), 4.24 (1H, s, C*H*-S), 3.66-3.52 (2H, m, N-CH_2), 2.94-2.87 (1H, m, 1H of CH_2-CH_2-R_F), 2.78-2.78 (1H, m, 1H of CH_2-CH_2-R_F), 2.42-2.28 (2H, m, CH_2-R_F), 1.67-1.58 (2H, m, N-CH_2-CH_2), 0.90 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) □ 174.7 (*C*=O), 142.9 (Ar*C*), 132.7 (Ar*C*H), 128.8 (Ar*C*H), 127.7 (Ar*C*), 115.8 (Ar*C*), 110.5 (Ar*C*H), 44.9 (*C*H-S), 42.4 (N-*C*H_2), 32.3 (t, J 22.0, *C*H_2-R_F), 21.5 (*C*H_2-CH_2-R_F), 21.0 (N-CH_2-*C*H_2), 11.7 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2967, 2935, 2877, 1714 (C=O), 1606, 1481, 1238, 1203, 1145.

MS *m/z* (EI mode) 731 (M^+, 15 %), 210 (11), 253 (100) and 733 (18); (Found: M^+, 730.9781 $C_{21}H_{15}ONF_{17}SBr$ requires 730.9786).

5-Fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1,3-dihydro-indol-2-one 4



As for general procedure A. *N*-(4-Fluorophenyl)-*N*-methyl-2-hydroxyacetamide (1.00 g, 5.47 mmol, 1 eq.) was oxidised to give crude glyoxamide which on treatment with $C_8F_{17}CH_2CH_2SH$

(0.89 ml, 3.05 mmol, 0.7 eq.), TFAA (5.80 ml, 39.2 mmol, 9 eq.) and $BF_3.OEt_2$ (2.75 ml, 21.8 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1,3-dihydro-indol-2-one **4** (1.96 g, 2.44 mmol, 80 % over 2 steps) as a white solid:

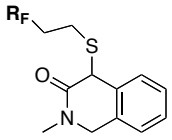
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (1H, d, J 7.7, Ar*H*), 7.07 (1H, td, J 6.7, 2.0, Ar*H*), 6.79 (1H, dd, J 8.5, 4.0, Ar*H*), 4.30 (1H, s, C*H*-S), 3.24 (3H, s, N-CH_3), 3.00-2.95 (1H, m, 1H of CH_2-CH_2-R_F), 2.90-2.80 (1H, m, 1H of CH_2-CH_2-R_F), 2.48-2.37 (2H, m, CH_2-R_F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0 (*C*=O), 159.8 (d, J 240.4, Ar*C*F), 127.1 (d, J 8.6, Ar*C*), 140.3 (Ar*C*), 116.2 (d, J 23.4, Ar*C*H), 113.6 (d, J 25.1, Ar*C*H), 109.3 (d, J 7.9, Ar*C*H), 45.4 (*C*H-S), 32.2 (t, J 21.8, *C*H_2-R_F), 26.9 (N-*C*H_3), 21.5 (*C*H_2-CH_2-R_F).

IR ν_{max} (Golden Gate)/cm^{-1} 2932, 1714 (C=O), 1494, 1265, 1240, 1211, 1149.

MS *m/z* (EI mode) 643 (M^+, 10 %), 109 (10), 164 (62) and 165 (100); (Found: M^+, 643.0265 $C_{19}H_{11}ONF_{18}S$ requires 643.0274).

4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-2-methyl-1,2-dihydroisoquinolin-3(4H)-one



As for general procedure A. *N*-Benzyl-*N*-methyl-2-hydroxyacetamide (500 mg, 2.8 mmol, 1 eq.) was oxidised to give crude glyoxamide which on treatment with $C_8F_{17}CH_2CH_2SH$ (0.41 ml, 1.40 mmol, 0.7 eq.), TFAA (2.70 ml, 18.0 mmol, 9 eq.) and $BF_3.OEt_2$ (1.27 ml, 10 mmol, 5 eq.) and after purification by using silica (eluting with CH_2Cl_2) gave 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-2-methyl-1,2-dihydroisoquinolin-3(4H)-one (402 mg, 0.64 mmol, 45 % over 2 steps) as a yellow solid:

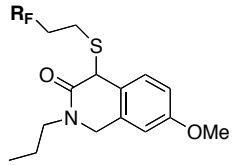
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.09 (4H, m, 4 x Ar*H*), 4.78 (1H, d, J 15.8, 1H of ArCH_2-N), 4.49 (1H, s, C*H*-S), 4.15 (1H, d, J 15.9, 1H of ArCH_2-N), 3.06 (3H, s, N-CH_3), 3.06-2.97 (1H, m, 1H of CH_2-CH_2-R_F), 2.88-2.78 (1H, m, 1H of CH_2-CH_2-R_F), 2.50-2.30 (2H, m, CH_2-R_F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7 (*C*=O), 132.8 (Ar*C*), 132.5 (Ar*C*), 128.6 (Ar*C*H), 128.4 (Ar*C*H), 128.3 (Ar*C*H), 125.9 (Ar*C*H), 52.6 (Ar*C*H_2-N), 46.9 (*C*H-S), 35.2 (N-*C*H_3), 32.0 (t, J 21.8, *C*H_2-R_F), 23.5 (*C*H_2-CH_2-R_F).

IR ν_{max} (Golden Gate)/cm^{-1} 1654 (C=O), 1195, 1143.

MS *m/z* (CI mode, isobutane) 640 ($(M+H)^+$, 100 %), 107 (5), 162 (45) and 178 (15); (Found: $(M+H)^+$, 640.0604 $C_{20}H_{15}NOF_{17}S$ requires 640.0603).

4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-7-methoxy-2-propyl-1,4-dihydro-2*H*-isoquinolin-3-one



As for general procedure A. *N*-(3-Methoxybenzyl)-2-oxo-*N*-propyl-acetamide (0.28 g, 1.21 mmol, 1 eq.) on treatment with $C_8F_{17}CH_2CH_2SH$ (0.25 ml, 0.85 mmol, 0.7 eq.), TFAA (1.61 ml, 10.89 mmol, 9 eq.) and $BF_3.OEt_2$ (0.77 ml, 6.05 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-7-methoxy-2-propyl-1,4-dihydro-2*H*-isoquinolin-3-one (0.30 g, 0.44 mmol, 51 %) as a yellow oil and as a ~2:1 mixture of isomers: (For major isomer)

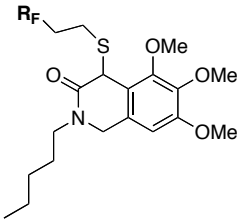
^{1}H NMR (400 MHz, $CDCl_3$) □ 7.23-7.12 (1H, m, Ar*H*), 6.79-6.62 (2H, m, Ar*H*), 4.77-4.73 (1H, d, J 15.6, 1H of ArC*H*$_2$-N), 4.44 (1H, s, C*H*-S), 4.08-4.04 (1H, d, J 15.6, 1H of ArC*H*$_2$-N), 3.73 (3H, s, C*H*$_3$-O), 3.64-3.54 (1H, m, 1H of N-C*H*$_2$), 3.31-3.21 (1H, m, 1H of N-C*H*$_2$), 3.07-2.96 (1H, m, 1H of C*H*$_2$-CH$_2$-R_F), 2.83-2.76 (1H, m, 1H of C*H*$_2$-CH$_2$-R_F), 2.49-2.36 (2H, m, C*H*$_2$-R_F), 1.63-1.55 (2H, m, N-CH$_2$-C*H*$_2$), 0.89-0.85 (3H, t, J 8.1, CH$_2$-C*H*$_3$).

^{13}C NMR (100MHz, $CDCl_3$) □ 167.7 (*C*=O), 159.8 (Ar*C*-OMe), 134.7 (Ar*C*), 129.7 (Ar*C*H), 124.5 (Ar*C*), 114.1 (Ar*C*H), 111.4 (Ar*C*H), 55.8 (*C*H$_3$-O), 50.6 (Ar*C*H$_2$-N), 49.2 (N-*C*H$_2$), 47.0 (*C*H-S), 32.1 (t, J 20.0, *C*H$_2$-R_F), 23.5 (*C*H$_2$-CH$_2$-R_F), 21.0 (N-CH$_2$-*C*H$_2$), 11.5 (CH$_2$-*C*H$_3$).

IR ν_{max} (Golden Gate)/cm^{-1} 1650 (C=O), 1598, 1469, 1439, 1353, 1331, 1282, 1236, 1200, 1146, 1114.

MS *m/z* (CI mode, isobutane) 698 ((M+H)$^+$, 99 %), 218 (52), 219 (25), 220 (34), 236 (15), 699 (38) and 700 (12); (Found: (M+H)$^+$, 698.1005 $C_{23}H_{21}O_2NF_{17}S$ requires 698.1022).

4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one 9



As for general procedure A. 2-Oxo-*N*-pentyl-*N*-(3,4,5-trimethoxy-benzyl)-acetamide (0.34 g, 1.05 mmol, 1 eq.) on treatment with $C_8F_{17}CH_2CH_2SH$ (0.22 ml, 0.74 mmol, 0.7 eq.), TFAA (1.40 ml, 9.48 mmol, 9 eq.) and $BF_3.OEt_2$ (0.67 ml, 5.27 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one **9** (0.34 g, 0.44 mmol, 60 %) as a dark yellow oil:

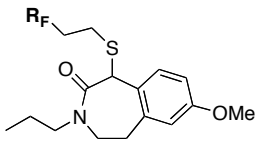
^{1}H NMR (400 MHz, $CDCl_3$) □ 6.41 (1H, s, Ar*H*), 4.71-4.68 (2H, m, C*H*-S and 1H of ArCH_2-N), 4.02-3.98 (1H, d, J 15.6, 1H of ArCH_2-N), 3.91 (3H, s, CH_3-O), 3.78 (3H, s, CH_3-O), 3.78 (3H, s, CH_3-O), 3.64-3.57 (1H, m, 1H of N-CH_2), 3.30-3.22 (1H, m, 1H of N-CH_2), 3.09-3.02 (1H, m, 1H of CH_2-CH_2-R_F), 2.85-2.77 (1H, m, 1H of CH_2-CH_2-R_F), 2.57-2.44 (2H, m, CH_2-R_F), 1.57-1.52 (2H, m, N-CH_2-CH_2), 1.28-1.18 (4H, m, CH_2-CH_2-CH_3 and CH_2-CH_2-CH_3), 0.84-0.81 (3H, t, J 6.9, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) □ 167.8 (*C*=O), 154.0 (Ar*C*-OMe), 151.0 (Ar*C*-OMe), 141.8 (Ar*C*-OMe), 129.2 (Ar*C*), 118.6 (Ar*C*), 104.6 (Ar*C*H), 61.9 (*C*H_3-O), 61.2 (*C*H_3-O), 56.5 (*C*H_3-O), 50.5 (Ar*C*H_2-N), 47.6 (N-*C*H_2), 41.6 (*C*H-S), 32.1 (t, J 22.5, *C*H_2-R_F), 29.2 (*C*H_2-CH_2-CH_3), 27.4 (N-CH_2-*C*H_2), 23.6 (*C*H_2-CH_2-R_F), 22.8 (*C*H_2-CH_3), 14.3 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2934, 2387, 2349, 1650 (C=O), 1465, 1415, 1353, 1200, 1146, 1121.

MS *m/z* (FAB mode, NOBA, NaI) 808 ((M+Na)$^+$, 56 %), 181 (34), 306 (100), 328 (14) and 784 (16); (Found: (M+Na)$^+$, 808.1348 $C_{27}H_{28}O_4NF_{17}SNa$ requires 808.1348).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-7-methoxy-3-propyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one



As for general procedure A. *N*-[2-(3-Methoxy-phenyl)-ethyl]-2-oxo-*N*-propyl-acetamide (0.25 g, 1.01 mmol, 1 eq.) on treatment with $C_8F_{17}CH_2CH_2SH$ (0.21 ml, 0.71 mmol, 0.7 eq.), TFAA (1.35 ml, 9.09 mmol, 9 eq.) and $BF_3.OEt_2$ (0.64 ml, 5.05 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-7-methoxy-3-propyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one (0.38 g, 0.53 mmol, 76 %) as a yellow oil and as a ~2:1 mixture of isomers: (For major isomer)

^{1}H NMR (400 MHz, $CDCl_3$) □ 7.12-7.04 (1H, m, Ar*H*), 6.69-6.53 (2H, m, Ar*H*), 4.74 (1H, s, C*H*-S), 4.71-4.64 (1H, m, 1H of ring CH_2-N), 3.70 (3H, s, CH_3-O), 3.56-3.49 (1H, m, 1H of N-CH_2), 3.27-

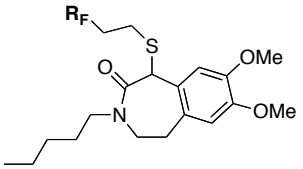
3.14 (2H, m, 1H of ring CH_2-N and 1H of N-CH_2), 3.07-2.81 (4H, m, ArCH_2 and CH_2-CH_2-R_F), 2.54-2.39 (2H, m, CH_2-R_F), 1.60-1.52 (2H, m, N-CH_2-CH_2), 0.88-0.84 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 169.9 (*C*=O), 159.5 (Ar*C*-OMe), 139.2 (Ar*C*), 134.2 (Ar*C*H), 124.2 (Ar*C*), 115.8 (Ar*C*H), 113.3 (Ar*C*H), 56.0 (*C*H-S), 55.6 (*C*H_3-O), 50.7 (N-*C*H_2), 45.6 (ring *C*H_2-N), 34.2 (Ar*C*H_2), 32.1 (t, J 21.0, *C*H_2-R_F), 24.6 (*C*H_2-CH_2-R_F), 21.5 (N-CH_2-*C*H_2), 11.6 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2936, 2360, 2340, 1641 (C=O), 1504, 1438, 1364, 1200, 1146, 1114.

MS *m/z* (CI mode, isobutane) 712 ((M+H)$^+$, 100 %), 204 (44), 232 (58), 231 (57), 230 (16), 713 (28) and 754 (11); (Found: (M+H)$^+$, 712.1174 $C_{24}H_{23}O_2NF_{17}S$ requires 712.1178).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one 7



As for general procedure A. *N*-[2-(3,4-Dimethoxy-phenyl)-ethyl]-2-oxo-*N*-pentyl-acetamide (0.38 g, 1.22 mmol, 1 eq.) on treatment with $C_8F_{17}CH_2CH_2SH$ (0.25 ml, 0.86 mmol, 0.7 eq.), TFAA (1.63 ml, 11.0 mmol, 9 eq.) and $BF_3.OEt_2$ (0.77 ml, 6.11 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one **7** (0.65 g, 0.85 mmol, 98 %) as a pale yellow solid:

^{1}H NMR (400 MHz, $CDCl_3$) 6.57 (1H, s, Ar*H*), 6.46 (1H, s, Ar*H*), 4.74-4.67 (2H, m, C*H*-S and 1H of ring CH_2-N), 3.80 (3H, s, CH_3-O), 3.77 (3H, s, CH_3-O), 3.61-3.54 (1H, m, 1H of N-CH_2), 3.27-3.16 (2H, m, 1H of ring CH_2-N and 1H of N-CH_2), 3.04-2.84 (4H, m, ArCH_2 and CH_2-CH_2-R_F), 2.57-2.35 (2H, m, CH_2-R_F), 1.56-1.49 (2H, m, N-CH_2-CH_2), 1.31-1.18 (4H, m, CH_2-CH_2-CH_3 and CH_2-CH_2-CH_3), 0.85-0.81 (3H, t, J 6.9, CH_2-CH_3).

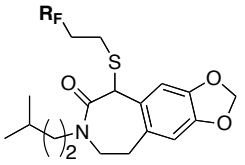
^{13}C NMR (100 MHz, $CDCl_3$) 169.7 (*C*=O), 149.2 (Ar*C*-OMe), 148.0 (Ar*C*-OMe), 130.2 (Ar*C*), 123.6 (Ar*C*), 115.1 (Ar*C*H), 113.3 (Ar*C*H), 56.4 (*C*H-S), 56.3 (*C*H_3-O), 56.2 (*C*H_3-O), 49.1 (N-*C*H_2), 45.5 (ring *C*H_2-N), 33.7 (Ar*C*H_2), 32.0 (t, J 21.5, *C*H_2-R_F), 29.4 (*C*H_2-CH_2-CH_3), 28.1 (N-CH_2-*C*H_2), 24.7 (*C*H_2-CH_2-R_F), 22.8 (CH_2-*C*H_2-CH_3), 14.3 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2935, 1919, 1635 (C=O), 1520, 1462, 1365.

MS *m/z* (EI mode) 769 (M$^+$, 8 %), 262 (98), 263 (17), 290 (21) and 291 (32); (Found: M$^+$, 769.1514 $C_{27}H_{28}O_3NF_{17}S$ requires 769.1518).

Anal. calcd for $C_{27}H_{28}O_3NF_{17}S$: C, 42.14; H, 3.67; N, 1.82. Found C, 42.08; H, 3.75; N, 1.88 %.

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfanyl)-7,8-methylenedioxy-3-(3-methyl-butyl)-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one



As for general procedure A. *N*-[2-(3,4-Methylenedioxy-phenyl)-ethyl]-2-oxo-*N*-(3-methyl-butyl)-acetamide (0.36 g, 1.23 mmol, 1 eq.) on treatment with $C_8F_{17}CH_2CH_2SH$ (0.25 ml, 0.86 mmol, 0.7 eq.), TFAA (1.64 ml, 11.06 mmol, 9 eq.) and $BF_3.OEt_2$ (0.78 ml, 6.15 mmol, 5 eq.) and after purification using fluorous silica (eluting with 80 % $MeCN/H_2O$ then MeCN) gave 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-7,8-methylenedioxy-3-(3-methyl-butyl)-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one (0.53 g, 0.71 mmol, 82 %) as a yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) □ 6.67 (1H, s, Ar*H*), 6.54 (1H, s, Ar*H*), 5.96-5.95 (2H, m, O-C*H*$_2$-O), 4.74 (1H, s, C*H*-S), 4.74-4.64 (1H, m, 1H of ring C*H*$_2$-N), 3.68-3.61 (1H, m, 1H of N-C*H*$_2$), 3.36-3.28 (2H, m, 1H of ring C*H*$_2$-N and 1H of N-C*H*$_2$), 3.10-2.91 (4H, m, C*H*$_2$-CH_2-R_F and ArC*H*$_2$), 2.61-2.45 (2H, m, C*H*$_2$-R_F), 1.66-1.50 (1H, m, C*H*-$(CH_3)_2$), 1.49-1.43 (2H, m, N-CH_2-C*H*$_2$), 0.97-0.95 (3H, d, J 6.6, CH_3 of CH-(C*H*$_3$)$_2$), 0.96-0.94 (3H, d, J 6.6, CH_3 of CH-(C*H*$_3$)$_2$).

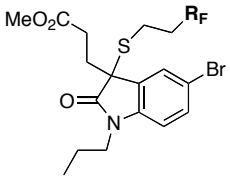
^{13}C NMR (100 MHz, $CDCl_3$) □ 169.4 (*C*=O), 148.1 (Ar*C*-O), 147.0 (Ar*C*-O), 131.6 (Ar*C*), 124.9 (Ar*C*), 111.9 (Ar*C*H), 110.2 (Ar*C*H), 101.7 (O-*C*H$_2$-O), 56.6 (*C*H-S), 47.5 (N-*C*H$_2$), 45.6 (ring *C*H$_2$-N), 37.1 (N-CH_2-*C*H$_2$), 34.2 (Ar*C*H$_2$), 32.0 (t, J 22.0, *C*H$_2$-R_F), 26.4 (*C*H-$(CH_3)_2$), 24.7 (*C*H$_2$-CH_2-R_F), 22.9 (CH_3 of CH-(*C*H$_3$)$_2$), 22.9 (CH_3 of CH-(*C*H$_3$)$_2$).

IR ν_{max} (Golden Gate)/cm^{-1} 2959, 1641 (C=O), 1505, 1487, 1425, 1367, 1202.

MS *m/z* (EI mode) 753 (M^+, 6 %), 161 (14), 246 (100), 247 (18), 274 (12), 275 (74) and 276 (13); (Found: M^+, 753.1207 $C_{26}H_{24}O_3NF_{17}S$ requires 753.1205).

Modification of fluorous tagged *N*-heterocycles

Methyl-3-(5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-2-oxo-1-propyl-2,3-dihydro-1*H*-indol-3-yl)propanoate 3



To solution of 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one **2** (84 mg, 0.11 mmol, 1 eq.) in MeOH (5 ml) at 0 ^{O}C was added NaOMe (15 mg, 0.28 mmol, 2.5 eq.) and methyl acrylate (13 ml, 0.14 mmol, 1.3 eq.). The reaction was allowed to stir for 18 h gradually warming up to room temperature. The reaction was quenched with aqueous saturated NH_4Cl. The aqueous layer was then extracted with CH_2Cl_2 and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give methyl-3-(5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-2-oxo-1-propyl-2,3-dihydro-1*H*-indol-3-yl)propanoate **3** (64 mg, 0.08 mmol, 71 %) as a white solid:

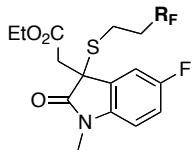
^{1}H NMR (400 MHz, $CDCl_3$) 7.38 (1H, dd, J 8.3, 2.0, Ar*H*), 7.35 (1H, d, J 2.0, Ar*H*), 6.69 (1H, d, J 8.3, Ar*H*), 3.60 (2H, t, J 7.3, N-CH_2), 3.52 (3H, s, CH_3-O), 2.71-2.56 (2H, m, CH_2-CH_2-R_F), 2.43-2.28 (2H, m, N-CH_2-CH_2), 2.21-2.08 (3H, m, 1H of CH_2-CS and CH_2-R_F), 2.03-1.95 (1H, m, 1H of CH_2-CS), 1.67-1.58 (2H, m, C(O)-CH_2), 0.90 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 175.7 (*C*=O), 172.5 (*C*=O), 142.1 (Ar*C*), 132.9 (Ar*C*H), 130.7 (Ar*C*), 127.9 (Ar*C*H), 116.1 (Ar*C*), 110.6 (Ar*C*H), 53.6 (*C*S), 52.2 (*C*H_3-O), 42.4 (N-*C*H_2), 31.8 (t, 21.7, *C*H_2-R_F), 31.1 (C(O)-*C*H_2), 29.7 (*C*H_2-CS), 21.1 (N-CH_2-*C*H_2), 20.0 (*C*H_2-CH_2-R_F), 11.7 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2938, 1735 (C=O), 1708 (C=O), 1604, 1481,1195, 1143.

MS *m/z* (FAB mode, NOBA) 818 ((M+H)$^{+}$, 60 %), 70 (28), 236 (20), 278 (83). 306 (100), and 340 (85); (Found: M^{+}, 818.0213 $C_{25}H_{22}O_3NBrF_{17}S$ requires 818.0232).

Ethyl 2-(5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)acetate 5



To a solution of diisopropylamine (0.05 ml, 0.34 mmol, 1.2 eq.) in THF (3 ml) at –78 ^{O}C was added *n*-BuLi (0.14 ml, 2.46 M in THF, 0.34 mmol, 1.2 eq.). After 45 minutes, a solution of 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1,3-dihydro-indol-2-one **4** (178 mg, 0.28 mmol, 1 eq.) in THF (5 ml) was added by cannula. After 1 hour, ethyl bromoacetate (0.09 ml, 0.84 mmol, 1.1 eq.) was added. The reaction was allowed to stir for 2.5 hours gradually warming to room temperature. The reaction was then quenched with aqueous saturated NH_4Cl. The aqueous layer was extracted with ethyl acetate. The organic layers were combined, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give ethyl 2-(5-fluoro-3-

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)acetate **5** (181 mg, 0.25 mmol, 89 %) as an orange oil:

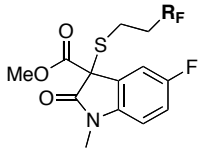
^{1}H NMR (400 MHz, $CDCl_3$) □ 6.97 (2H, m, Ar*H*), 6.73 (1H, m, Ar*H*), 3.93-3.80 (2H, m, CH_3-C*H*$_2$-O), 3.27 (1H, d, J 16.6, 1H of C(O)-C*H*$_2$), 3.20 (3H, s, N-C*H*$_3$), 3.02 (1H, d, J 16.6, 1H of C(O)-C*H*$_2$), 2.76-2.68 (1H, m, 1H of C*H*$_2$-CH_2-R_F), 2.65-2.57 (1H, m, 1H of C*H*$_2$-CH_2-R_F), 2.20-2.07 (2H, m, C*H*$_2$-R_F), 0.99 (3H, t, J 7.1, C*H*$_3$-CH_2-O).

^{13}C NMR (100 MHz, $CDCl_3$) □ 176.1 (ester *C*=O), 168.6 (amide *C*=O), 159.7 (d, J 240.5, Ar*C*F), 140.0 (d, J 1.8, Ar*C*), 130.2 (d, J 8.0, Ar*C*), 116.3 (d, J 23.7, Ar*C*H), 111.9 (d, J 25.1, Ar*C*H), 109.4 (d, J 7.8, Ar*C*H), 61.5 (CH_3-*C*H_2-O), 50.9 (*C*S), 40.3 (C(O)-*C*H_2), 31.8 (t, J 21.9, *C*H_2-R_F), 27.1 (N-*C*H_3), 19.9 (*C*H_2-CH_2-R_F), 14.2 (*C*H_3-CH_2-O).

IR ν_{max} (Golden Gate)/cm^{-1} 1715 (amide and ester C=O), 1613, 1496, 1194, 1144.

MS *m/z* (EI mode) 729 (M^+, 27 %), 148 (20), 177 (55), 178 (100) and 251 (65); (Found: M^+, 729.0639 $C_{23}H_{17}O_3NF_{18}S$ requires 729.0642).

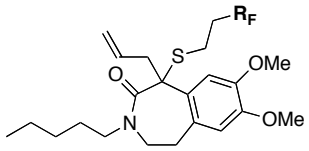
Methyl 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole-3-carboxylate 6



To a solution of 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1,3-dihydro-indol-2-one **4** (293 mg, 0.47 mmol, 1 eq.) in CH_2Cl_2 (10 ml) was added NEt_3 (0.26 ml, 1.88 mmol, 4 eq.) and methyl chloroformate (0.15 ml, 1.88 mmol, 4 eq.) at room temperature. After 3 hours, the reaction mixture was washed with aqueous saturated $NaHCO_3$, dried ($MgSO_4$) and concentrated *in vacuo* to give 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1H-indol-2-yl methyl carbonate (323 mg, 0.46 mmol, 98 %) as a yellow oil which was used without further purification. To a solution of 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-1H-indol-2-yl methyl carbonate (154 mg, 0.22 mmol, 1 eq.) in toluene (6 ml) was added dimethylaminopyridine (9 mg, 0.07 mmol, 30 mol %). The reaction was heated at 70 ^{O}C for 3 hours. After cooling, CH_2Cl_2 (10 ml) was added. The organic layer was then washed with H_2O, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give methyl 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole-3-carboxylate **6** (92 mg, 0.13 mmol, 60 %) as a yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) □ 7.10-6.99 (2H, m, 2 x Ar*H*), 6.74 (1H, dd, J 8.6, 4.0, Ar*H*), 3.72 (3H, s, C*H*$_3$-O), 3.20 (3H, s, N-C*H*$_3$), 3.00 (2H, t, J 8.1, C*H*$_2$-CH$_2$-R$_F$), 2.39-2.26 (2H, m, C*H*$_2$-R$_F$).
^{13}C NMR (100 MHz, $CDCl_3$) □ 171.9 (*C*=O), 167.1 (*C*=O), 159.7 (d, J 241.4, Ar*C*), 139.6 (Ar*C*), 126.8 (d, J 8.5, Ar*C*), 117.2 (d, J 23.3, Ar*C*H), 113.5 (d, J 25.3, Ar*C*H), 109.8 (d, J 8.0, Ar*C*H), 58.0 (*C*S), 54.4 (*C*H$_3$-O), 31.8 (t, J 21.7, *C*H$_2$-R$_F$), 27.3 (N-*C*H$_3$), 20.9 (*C*H$_2$-CH$_2$-R$_F$).
IR ν_{max} (Golden Gate)/cm^{-1} 1746 (C=O), 1716 (C=O), 1495, 1198, 1144.
MS *m/z* (EI mode) 701 (M$^+$, 10 %), 135 (10), 191 (100) and 642 (20); (Found: M$^+$, 701.0328 $C_{21}H_{13}O_3NF_{18}S$ requires 701.0328).

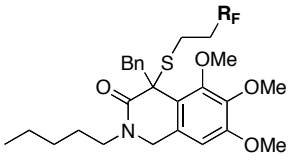
1-Allyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one 8



To a solution of 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one **7** (88 mg, 0.11 mmol, 1 eq.) in THF (3 ml) and DMF (0.3 ml) was added NaH (55 mg, 0.23 mmol, 2.0 eq.) and allyl bromide (22 □L, 0.26 mmol, 2.2 eq). The reaction mixture was then refluxed at 80 ^{O}C under an atmosphere of argon. After 18 hours, THF was evaporated and H_2O added (10 ml). The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 1-allyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one **8** (71 mg, 0.09 mmol, 77 %) as a brown oil:
^{1}H NMR (400 MHz, $CDCl_3$) □ 7.12 (1H, s, Ar*H*), 6.39 (1H, s, Ar*H*), 5.42-5.32 (1H, m, C*H*=CH$_2$), 4.91-4.81 (2H, m, CH=C*H*$_2$), 4.20-4.14 (1H, m, 1H of ring C*H*$_2$-N), 3.81 (3H, s, C*H*$_3$-O), 3.78 (3H, s, C*H*$_3$-O), 3.62-3.55 (1H, m, 1H of N-C*H*$_2$), 3.31-3.20 (2H, m, 1H of ring C*H*$_2$-N and 1H of N-C*H*$_2$), 2.99-2.72 (6H, m, ArC*H*$_2$, C*H*$_2$-CH$_2$-R$_F$ and C*H*$_2$CH=CH$_2$), 2.31-2.18 (2H, m, C*H*$_2$-R$_F$), 1.57-1.48 (2H, m, N-CH$_2$-C*H*$_2$), 1.31-1.17 (4H, m, C*H*$_2$-CH$_2$-CH$_3$ and CH$_2$-C*H*$_2$-CH$_3$), 0.85-0.81 (3H, t, J 7.0, CH$_2$-C*H*$_3$).
^{13}C NMR (100 MHz, $CDCl_3$) □ 169.7 (*C*=O), 148.3 (Ar*C*-OMe), 147.5 (Ar*C*-OMe), 135.3 (*C*H=CH$_2$), 133.8 (Ar*C*), 127.6 (Ar*C*), 118.1 (CH=*C*H$_2$), 115.1 (Ar*C*H), 113.0 (Ar*C*H), 61.4 (*C*-S), 56.4 (*C*H$_3$-O), 56.1 (*C*H$_3$-O), 51.5 (N-*C*H$_2$), 48.4 (ring *C*H$_2$-N), 46.1 (*C*H$_2$CH=CH$_2$), 36.6 (Ar*C*H$_2$), 31.7 (t, J 22.0, *C*H$_2$-R$_F$), 29.5 (*C*H$_2$-CH$_2$-CH$_3$), 27.8 (N-CH$_2$-*C*H$_2$), 22.8 (CH$_2$-*C*H$_2$-CH$_3$), 22.1 (*C*H$_2$-CH$_2$-R$_F$), 14.3 (CH$_2$-*C*H$_3$).

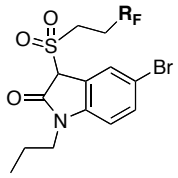
IR ν_{max} (Golden Gate)/cm^{-1} 2935, 1630 (C=O), 1521, 1467, 1439, 1396.
MS *m/z* (FAB mode, NOBA, NaI) 832 ((M+Na)$^+$, 50 %), 70 (13), 217 (16), 260 (23), 302 (47), 330 (100) and 768 (26); (Found: (M+Na)$^+$, 832.1740 $C_{30}H_{32}O_3NF_{17}SNa$ requires 832.1729).

4-Benzyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-5,6,7-trimethoxy-3-pentyl-1,4-dihydro-2*H*-isoquinolin-2-one 10



To a solution of 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one **9** (100 mg, 0.13 mmol, 1 eq.) in THF (3 ml) at –78 ^{O}C was added LiHMDS (0.32 ml, 1.0 M in THF, 0.32 mmol, 2.5 eq.). After 0.5 hour, BnBr (34 □L, 0.28 mmol, 2.2 eq). After 7 hours, the reaction was quenched with aqueous saturated NH_4Cl and THF was evaporated. The aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 4-benzyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one **10** (94 mg, 0.11 mmol, 85 %) as a pale yellow solid:
^{1}H NMR (400 MHz, $CDCl_3$) □ 6.81-6.73 (5H, m, Ar*H*), 5.91 (1H, s, Ar*H*), 4.09-4.05 (1H, d, J 8.3, 1H of ring CH_2-N), 3.86-3.53 (12H, m, 1H of ring CH_2-N, CH_2-Ph and 3 x CH_3-O), 3.30-3.23 (1H, m, 1H of N-CH_2), 3.15-3.08 (1H, m, 1H of N-CH_2), 2.68-2.49 (2H, m, CH_2-CH_2-R_F), 2.05-1.82 (2H, m, CH_2-R_F), 1.35-1.26 (2H, m, N-CH_2-CH_2), 1.14-0.97 (4H, m, CH_2-CH_2-CH_3 and CH_2-CH_2-CH_3), 0.68-0.65 (3H, t, J 7.2, CH_2-CH_3).
^{13}C NMR (100 MHz, $CDCl_3$) □ 168.5 (*C*=O), 153.8 (Ar*C*-OMe), 153.1 (Ar*C*-OMe), 138.0 (Ar*C*-OMe), 130.3 (2 x Ar*C*H), 129.2 (Ar*C*), 128.0 (2 x Ar*C*H), 126.6 (Ar*C*H), 126.3 (Ar*C*), 120.4 (Ar*C*), 102.9 (Ar*C*H), 61.6 (*C*H_3-O), 60.8 (*C*H_3-O), 56.1 (*C*H_3-O), 55.1 (*C*-S), 50.4 (ring *C*H_2-N), 48.4 (N-*C*H_2), 41.7 (*C*H_2-Ph), 32.1 (t, J 19.5, *C*H_2-R_F), 29.4 (*C*H_2-CH_2-CH_3), 26.7 (N-CH_2-*C*H_2), 22.8 (*C*H_2-CH_3), 22.1 (*C*H_2-CH_2-R_F), 14.3 (CH_2-*C*H_3).
IR ν_{max} (Golden Gate)/cm^{-1} 2941, 1632 (C=O), 1601, 1491, 1451, 1407, 1363, 1238, 1198, 1146, 1123, 1084.
MS *m/z* (FAB mode, NOBA, NaI) 898 ((M+Na)$^+$, 28 %), 91 (12), 181 (14), 283 (61), 395 (25), 396 (100), 784 (20) and 874 (13); (Found: (M+Na)$^+$, 898.1831 $C_{34}H_{34}O_4NF_{17}SNa$ requires 898.1835).
M.pt. 88-91 ^{O}C.

5-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-1,3-dihydro-indol-2-one



To a solution of 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-propyl-1,3-dihydro-indol-2-one (564 mg, 0.77 mmol, 1 eq.) in CH_2Cl_2 (15 ml) was added *m*CPBA (709 mg, 57-86 % *m*CPBA, ~3.08 mmol, ~4 eq.) at room temperature. After 2 hours, the reaction mixture was washed with aqueous saturated $NaHCO_3$, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-1,3-dihydro-indol-2-one (463 mg, 0.61 mmol, 79 %) as an orange solid:

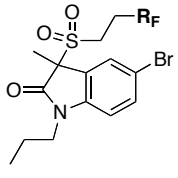
^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (1H, d, J 0.9, Ar*H*), 7.49 (1H, dd, J 8.4, 1.5, Ar*H*), 6.71 (1H, d, J 8.4, Ar*H*), 4.76 (1H, s, C*H*), 3.86-3.79 (1H, m, 1H of CH_2-CH_2-R_F), 3.74-3.52 (3H, m, N-CH_2 and 1H of CH_2-CH_2-R_F), 2.76-2.63 (2H, m, CH_2-R_F), 1.68-1.59 (2H, m, N-CH_2-CH_2), 0.89 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 167.0 (*C*=O), 144.2 (Ar*C*), 134.4 (Ar*C*H), 130.6 (Ar*C*H), 118.9 (Ar*C*), 116.5 (Ar*C*), 111.1 (Ar*C*H), 65.6 (*C*H), 44.4 (*C*H_2-CH_2-R_F), 42.7 (N-*C*H_2), 24.7 (t, J 22.6, *C*H_2-R_F), 20.9 (N-CH_2-*C*H_2), 11.5 (CH_2-CH_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2971, 2922, 1731 (C=O), 1482, 1197, 1138.

MS *m/z* (EI mode) 763 (M^+, 8 %), 116 (10), 173 (11), 210 (10) and 252 (100); (Found: M^+, 762.9683 $C_{21}H_{15}O_3NBrF_{17}S$ requires 762.9685).

5-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one 15



To a solution of 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-1,3-dihydro-indol-2-one (321 mg, 0.41 mmol, 1 eq.) in DMF (8 ml) was added K_2CO_3 (0.567 mg, 4.1 mmol, 10 eq.) and methyl iodide (0.25 ml, 4.10 mmol, 10 eq.). The reaction was

heated at 40 ^{O}C. After 2 hours, EtOAc (10 ml) was added to the reaction. The organic layer was then washed with water, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one **15** (292 mg, 0.38 mmol, 92 %) as an orange solid:

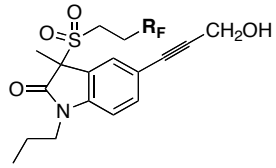
^{1}H NMR (400 MHz, $CDCl_3$) 7.62 (1H, d, J 2.0, Ar*H*), 7.49 (1H, dd, J 8.4, 2.0, Ar*H*), 6.75 (1H, d, J 8.4, Ar*H*), 3.80-3.69 (2H, m, 1H of N-CH_2 and 1H of CH_2-CH_2-R_F), 3.58-3.51 (1H, m, 1H of N-CH_2), 3.38-3.30 (1H, m, 1H of CH_2-CH_2-R_F), 2.66-2.54 (2H, m, CH_2-R_F), 1.84 (3H, s, CH_3-CS), 1.70-1.61 (2H, m, N-CH_2-CH_2), 0.89 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 171.2 (*C*=O), 143.2 (Ar*C*), 134.3 (Ar*C*H), 129.8 (Ar*C*H), 125.0 (Ar*C*), 116.5 (Ar*C*), 111.0 (Ar*C*H), 70.3 (CH_3-*C*S), 42.8 (N-*C*H_2), 40.4 (*C*H_2-CH_2-R_F), 24.2 (t, 24.0, *C*H_2-R_F), 20.9 (N-CH_2-*C*H_2), 18.8 (*C*H_3-CS), 11.5 (CH_2-C*H*$_3$).

IR ν_{max} (Golden Gate)/cm^{-1} 2976, 2943, 1707 (C=O), 1482, 1197, 1145.

MS *m/z* (FAB mode) 778 ((M+H)$^+$, 14 %), 69 (28), 188 (27) and 266 (100); (Found: M$^+$, 777.9904 $C_{22}H_{18}O_3NBrF_{17}S$ requires 777.9919).

3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfonyl)-5-(3-hydroxyprop-1-ynyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one 11a



A flask containing 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one **15** (66 mg, 0.08 mmol, 1 eq.) and palladium (0) tetrakis(triphenylphosphine) (18 mg, 0.02 mmol, 20 mol %) was flushed with argon. Propargyl alcohol (14 ml, 0.16 mmol, 3 eq.) and triethylamine (3 ml) were then added. The reaction was heated at 80 ^{O}C for 18 hours. The reaction was allowed to cool and CH_2Cl_2 was added. The organic layer was washed with water, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-5-(3-hydroxyprop-1-ynyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one **11a** (33 mg, 0.05 mmol, 59 %) as a yellow oil:

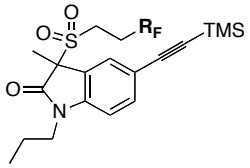
^{1}H NMR (400 MHz, $CDCl_3$) 7.57 (1H, d, J 1.5, Ar*H*), 7.44 (1H, dd, J 8.2, 1.5, Ar*H*), 6.82 (1H, d, J 8.2, Ar*H*), 4.42 (2H, s, CH_2-OH), 3.79-3.70 (2H, m, 1H of N-CH_2 and 1H of CH_2-CH_2-R_F), 3.60-3.52 (1H, m, 1H of N-CH_2), 3.37-3.30 (1H, m, 1H of CH_2-CH_2-R_F), 2.66-2.53 (2H, m, CH_2-R_F), 1.83 (3H, s, CH_3), 1.70-1.61 (2H, m, N-CH_2-CH_2), 0.90 (3H, t, J 8.1, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (*C*=O), 144.1 (Ar*C*), 135.1 (Ar*C*H), 130.0 (Ar*C*H), 123.4 (Ar*C*), 118.3 (Ar*C*), 109.6 (Ar*C*H), 87.9 (alkyne *C*), 85.2 (alkyne *C*), 70.1 (*C*-S), 52.0 (*C*H_2-OH), 42.8 (N-*C*H_2), 40.4 (*C*H_2-CH_2-R_F), 24.2 (t, J 22.0, *C*H_2-R_F), 21.0 (N-CH_2-*C*H_2), 18.7 (C-*C*H_3), 11.5 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2938, 1711 (C=O), 1490, 1197, 1142, 1089.

MS *m/z* (EI mode) 753 (M^+, 5 %), 77 (2), 200 (3) and 242 (100); (Found: M^+, 753.0845 $C_{25}H_{20}O_4NF_{17}S$ requires 753.0842).

3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-5-(2-(trimethylsilyl)ethynyl)-1,3-dihydro-indol-2-one 11b



A flask containing 5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one **15** (49 mg, 0.06 mmol, 1 eq.) and palladium (0) tetrakis(triphenylphosphine) (15 mg, 0.02 mmol, 20 mol %) and copper (I) iodide (2 mg, 0.01 mmol, 20 mol %) was flushed with argon. Trimethyl silylacetylene (0.09 ml, 0.63 mmol, 10 eq.) and triethylamine (3 ml) were then added. The reaction was heated at 60 ^{O}C for 18 hours. The reaction was allowed to cool and CH_2Cl_2 was added. The organic layer was washed with water, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-5-(2-(trimethylsilyl)ethynyl)-1,3-dihydro-indol-2-one **11b** (41 mg, 0.05 mmol, 82 %) as a yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (1H, d, J 1.4, Ar*H*), 7.55 (1H, dd, J 8.2, 1.4, Ar*H*), 6.87 (1H, d, J 8.2, Ar*H*), 3.85-3.77 (2H, m, N-C*H*$_2$), 3.66-3.60 (1H, m, 1H of C*H*$_2$-CH_2-R_F), 3.43-3.36 (1H, m, 1H of C*H*$_2$-CH_2-R_F), 2.73-2.60 (2H, m, C*H*$_2$-R_F), 1.91 (3H, s, C*H*$_3$), 1.78-1.69 (2H, m, N-CH_2-C*H*$_2$), 0.97 (3H, t, J 7.4, CH_2-C*H*$_3$), 0.26 (9H, s, Si-(C*H*$_3$)$_3$).

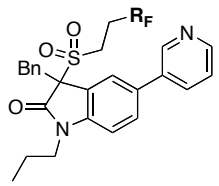
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (*C*=O), 143.7 (Ar*C*), 135.0 (Ar*C*H), 129.8 (Ar*C*H), 123.0 (Ar*C*), 118.7 (Ar*C*), 109.1 (Ar*C*H), 104.1 (alkyne *C*), 94.7 (alkyne *C*), 69.8 (*C*-S), 42.9 (N-*C*H_2), 40.1 (*C*H_2-CH_2-R_F), 23.9 (t, J 22.0, *C*H_2-R_F), 20.7 (N-CH_2-*C*H_2), 18.3 (*C*H_3), 11.2 (CH_2-*C*H_3), 0.00 (Si-(*C*H_3)$_3$).

IR ν_{max} (Golden Gate)/cm^{-1} 2969, 2882, 1716 (C=O), 1614, 1489, 1199, 1143.

MS *m/z* (FAB mode, NOBA, NaI) 818 ((M+Na)$^+$, 2 %), 73 (30), 212 (32), 284 (100) and 796 (9); (Found: (M+Na)$^+$, 818.1016 $C_{27}H_{26}O_3NF_{17}SSiNa$ requires 818.1029).

General Procedure B for the Pd-catalysed Suzuki cross-couplings

3-Benzyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-5-(pyridin-3-yl)-1,3-dihydro-indol-2-one 13



A flask containing 3-benzyl-5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-1,3-dihydro-indol-2-one **12** (82 mg, 0.10 mmol, 1 eq.), palladium (0) tetrakis(triphenylphosphine) (23 mg, 0.02 mmol, 20 mol %) and pyridine-3-boronic acid (37 mg, 0.30 mmol, 3 eq.) was flushed with argon. Na_2CO_3 (0.15 ml of a 2 M soln., 0.30 mmol, 3 eq.), H_2O (1 ml) and 1,4-dioxane (5 ml) were then added. The reaction was heated at 80 ^{O}C for 3.5 hours. The reaction was allowed to cool and CH_2Cl_2 was added. The organic layer was washed with water, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was purified using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) to give 3-benzyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-5-(pyridin-3-yl)-1,3-dihydro-indol-2-one **13** (59 mg, 0.07 mmol, 70 %) as a white solid:

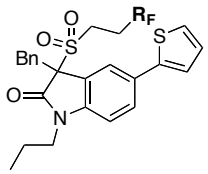
^{1}H NMR (400 MHz, $CDCl_3$) □ 8.89 (1H, s, pyridine Ar*H*), 8.66 (1H, s, pyridine Ar*H*), 7.94-7.90 (2H, m, 2 x Ar*H*), 7.57 (1H, dd, J 8.2, 1.8, Ar*H*), 7.44-7.41 (1H, m, Ar*H*), 7.14-7.06 (3H, m, 3 x Ar*H*), 6.95 (1H, d, J 1.7, Ar*H*), 6.91 (1H, s, Ar*H*), 6.82 (1H, d, J 8.2, Ar*H*), 4.03-3.98 (1H, m, 1H of CH_2-CH_2-R_F), 3.82 (1H, d, J 12.8, 1H of CH_2-Ph), 3.74 (1H, d, J 12.8, 1H of CH_2-Ph), 3.69-3.62 (1H, m, 1H of N-CH_2), 3.55-3.46 (2H, m, 1H of N-CH_2 and 1H of CH_2-CH_2-R_F), 2.81-2.70 (2H, m, CH_2-R_F), 1.51-1.42 (2H, m, N-CH_2-CH_2), 0.76 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) □ 170.2 (*C*=O), 149.0 (Ar*C*H), 148.5 (Ar*C*H), 144.7 (Ar*C*), 136.1 (Ar*C*), 134.6 (Ar*C*H), 133.5 (Ar*C*), 132.3 (Ar*C*), 130.4 (2 x Ar*C*H), 130.3 (Ar*C*H), 128.7 (2 x Ar*C*H), 128.0 (Ar*C*H), 126.0 (Ar*C*H), 124.1 (Ar*C*H), 121.7 (Ar*C*), 110.0 (Ar*C*H), 75.5 (*C*-S), 42.7 (N-*C*H_2), 41.0 (*C*H_2-CH_2-R_F), 37.8 (*C*H_2-Ph), 24.2 (t, J 21.9, *C*H_2-R_F), 20.8 (N-CH_2-*C*H_2), 11.5 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2935, 1713 (C=O), 1617, 1199, 1135.

MS *m/z* (FAB mode) 853 (M^+, 85 %), 91 (5), 265 (14) and 342 (100); (Found: M^+, 853.1396 $C_{33}H_{26}O_3N_2F_{17}S$ requires 853.1393).

3-Benzyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-5-(thiophen-2-yl)-1,3-dihydro-indol-2-one 14



As for general procedure B. 3-Benzyl-5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-1,3-dihydro-indol-2-one **12** (123 mg, 0.14 mmol, 1 eq.) on treatment with palladium (0) tetrakis(triphenylphosphine) (35 mg, 0.03 mmol, 20 mol %), thiophene-2-boronic acid (54 mg, 0.42 mmol, 3 eq.), Na_2CO_3 (0.21 ml of a 2 M soln., 0.42 mmol, 3 eq.), H_2O (1 ml) and 1,4-dioxane (5 ml) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-benzyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-5-(thiophen-2-yl)-1,3-dihydro-indol-2-one **14** (110 mg, 0.13 mmol, 92 %) as a clear oil:

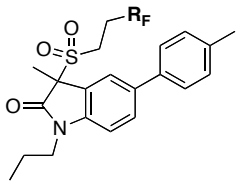
^{1}H NMR (400 MHz, $CDCl_3$) □ 7.88 (1H, d, J 1.8, Ar*H*), 7.49 (1H, dd, J 8.2, 1.8, Ar*H*), 7.25-7.22 (2H, m, 2 x Ar*H*), 7.04-6.95 (4H, m, 4 x Ar*H*), 6.87 (1H, d, J 1.2, Ar*H*), 6.85 (1H, d, J 1.7, Ar*H*), 6.61 (1H, d, J 8.2, Ar*H*), 3.88-3.80 (1H, m, 1H of C*H*$_2$-CH$_2$-R$_F$), 3.70 (1H, d, J 12.8 Hz, 1H of C*H*$_2$-Ph), 3.63 (1H, d, J 12.8, 1H of C*H*$_2$-Ph), 3.58-3.49 (1H, m, 1H of N-C*H*$_2$), 3.45-3.31 (2H, m, 1H of N-C*H*$_2$ and 1H of C*H*$_2$-CH$_2$-R$_F$), 2.69-2.59 (2H, m, C*H*$_2$-R$_F$), 1.28-1.37 (2H, m, N-CH$_2$-C*H*$_2$), 0.64 (3H, t, J 7.4, CH$_2$-C*H*$_3$).

^{13}C NMR (100 MHz, $CDCl_3$) □ 170.0 (*C*=O), 143.8 (Ar*C*), 143.7 (Ar*C*), 132.3 (Ar*C*), 130.5 (2 x Ar*C*H), 130.4 (Ar*C*), 129.1 (Ar*C*H), 128.6 (2 x Ar*C*H), 128.5 (Ar*C*H), 128.0 (Ar*C*H), 125.2 (Ar*C*H), 124.8 (Ar*C*H), 123.5 (Ar*C*H), 121.5 (Ar*C*), 109.8 (Ar*C*H), 75.5 (*C*-S), 42.6 (N-*C*H$_2$), 41.1 (*C*H$_2$-CH$_2$-R$_F$), 37.7 (*C*H$_2$-Ph), 24.3 (t, J 22.3, *C*H$_2$-R$_F$), 20.8 (N-CH$_2$-*C*H$_2$), 11.5 (CH$_2$-*C*H$_3$).

IR ν_{max} (Golden Gate)/cm^{-1} 1710 (C=O), 1489, 1200, 1136.

MS *m/z* (FAB mode) 858 (M$^+$, 16 %), 69 (20), 288 (10), 318 (26) and 346 (100); (Found: M$^+$, 858.1007 $C_{32}H_{25}O_3NF_{17}S$ requires 858.1004).

3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-5-(4-methylphenyl)-1,3-dihydro-indol-2-one 16



As for general procedure B. 5-Bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-1,3-dihydro-indol-2-one **15** (106 mg, 0.14 mmol, 1 eq.) on treatment with palladium (0) tetrakis(triphenylphosphine) (35 mg, 0.03 mmol, 20 mol %), methylbenzene boronic acid (57 mg, 0.42 mmol, 3 eq.), Na_2CO_3 (0.21 ml of a 2 M soln., 0.42 mmol, 3 eq.), H_2O (1 ml) and 1,4-dioxane (5 ml) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-5-(4-methylphenyl)-1,3-dihydro-indol-2-one **16** (95 mg, 0.12 mmol, 87 %) as a white solid:

^{1}H NMR (400 MHz, $CDCl_3$) □ 7.79 (1H, d, J 1.8, Ar*H*), 7.65 (1H, dd, J 8.2, 1.8, Ar*H*), 7.46 (2H, apparent d, J 8.1, 2 x Ar*H*), 7.26 (2H, apparent d, J 8.0, 2 x Ar*H*), 7.01 (1H, d, J 8.2, Ar*H*), 3.90-3.86 (2H, m, 1H of N-CH_2 and 1H of CH_2-CH_2-R_F), 3.74-3.67 (1H, m, 1H of N-CH_2), 3.51-3.41 (1H, m, 1H of CH_2-CH_2-R_F), 2.76-2.63 (2H, m, CH_2-R_F), 2.42 (3H, s, Ar-CH_3), 1.98 (3H, s, C-S), 1.84-1.75 (2H, m, N-CH_2-CH_2), 1.01 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) □ 171.6 (*C*=O), 143.0 (Ar*C*), 137.7 (Ar*C*), 137.6 (Ar*C*), 137.5 (Ar*C*), 130.0 (2 x Ar*C*H), 129.9 (Ar*C*H), 127.2 (2 x Ar*C*H), 125.4 (Ar*C*H), 123.7 (Ar*C*), 109.8 (Ar*C*H), 70.4 (*C*-CH_3), 42.8 (N-*C*H_2), 40.4 (*C*H_2-CH_2-R_F), 24.1 (t, J 22.7, *C*H_2-R_F), 21.5 (Ar-*C*H_3), 21.0 (N-CH_2-*C*H_2), 18.8 (C-*C*H_3), 11.6 (CH_2-*C*H_3).

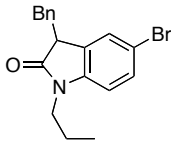
IR ν_{max} (Golden Gate)/cm^{-1} 2972, 2941, 1721 (C=O), 1488, 1198, 1143.

MS *m/z* (FAB mode, NOBA, NaI) 812 ((M+Na)$^+$, 100 %), 69 (20), 220 (20), 278 (100) and 301 (55); (Found: (M+Na)$^+$, 812.1101 $C_{29}H_{24}O_3NF_{17}SNa$ requires 812.1103).

Traceless removal of the fluorous phase-tag

General Procedure C(i) for the cleavage of N-heterocycles

3-Benzyl-5-bromo-1-propyl-1,3-dihydro-indol-2-one 17



To a solution of 3-benzyl-5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-1,3-dihydro-indol-2-one **12** (140 mg, 0.16 mmol, 1 eq.) in THF (5 ml) was added SmI_2 (3.5 ml, 0.1 M soln. in THF, 0.35 mmol, 2.2 eq.) at room temperature. After 18 hours, aqueous saturated $NaHCO_3$ was added. The organic layer was then extracted with EtOAc. The organic layers were then combined, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified through a short pad of silica (eluting with 30 % EtOAc/petroleum

ether (40-60)) to give 3-benzyl-5-bromo-1-propyl-1,3-dihydro-indol-2-one **17** (54 mg, 0.16 mmol, 98 %) as a yellow oil:

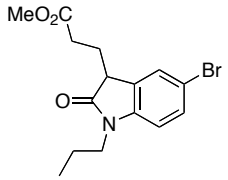
^{1}H NMR (400 MHz, $CDCl_3$) □ 7.24 (1H, d, J 8.3, Ar*H*), 7.19-7.10 (3H, m, 3 x Ar*H*), 7.07-7.03 (2H, m, 2 x Ar*H*), 6.92 (1H, s, Ar*H*), 6.53 (1H, d, J 8.3, Ar*H*), 3.64-3.54 (2H, m, 1H of N-CH_2 and C*H*), 3.43-3.33 (2H, m, 1H of Ph-CH_2 and 1H of N-CH_2)**,** 2.90 (1H, dd, J 13.7, 8.5, 1H of Ph-CH_2), 1.53-1.41 (2H, m, N-CH_2-CH_2), 0.75 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) □ 176.6 (*C*=O), 143.3 (Ar*C*), 137.4 (Ar*C*), 131.1 (Ar*C*), 130.9 (Ar*C*), 129.8 (2 x Ar*C*H), 128.7 (2 x Ar*C*H), 128.1 (Ar*C*H), 127.2 (Ar*C*H), 114.8 (Ar*C*), 109.9 (Ar*H*), 47.3 (*C*H), 41.9 (N-*C*H_2), 36.9 (Ph-*C*H_2), 20.9 (N-CH_2-*C*H_2), 11.6 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 1697 (C=O), 1604, 1482, 1350, 1102.

MS *m/z* (EI mode) 343 (M^+, 32 %), 65 (5), 91 (100) and 252 (22); (Found: M^+, 343.0560 $C_{18}H_{18}ONBr$ requires 343.0572).

Methyl 3-(5-bromo-2-oxo-1-propyl-2,3-dihydro-1*H*-indol-3-yl)propanoate 18



As for general procedure C(i). Methyl-3-(5-bromo-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-2-oxo-1-propylindol-3-yl)propanoate **3** (37 mg, 0.05 mmol, 1 eq.) on treatment with SmI_2 (1.30 ml, 0.1 M soln. in THF, 0.13 mmol, 2.5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave methyl 3-(5-bromo-2-oxo-1-propyl-2,3-dihydro-1*H*-indol-3-yl)propanoate **18** (13 mg, 0.038 mmol, 76 %) as a yellow oil:

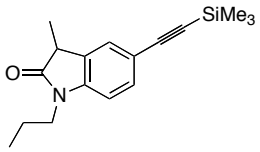
^{1}H NMR (400 MHz, $CDCl_3$) □ 7.32 (2H, m, 2 x Ar*H*), 6.64 (1H, d, J 8.2, Ar*H*), 3.64-3.50 (5H, m, N-CH_2 and CH_3-O), 2.44-2.35 (1H, m, 1H of C(O)-CH_2), 3.44 (1H, t, J 6.0, C*H*-C(O)), 2.31-2.09 (3H, m, CH-CH_2 and 1H of C(O)-CH_2), 1.66-1.56 (2H, m, N-CH_2-CH_2), 0.89 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) □ 176.9 (ester *C*=O), 173.5 (amide *C*=O), 143.3 (Ar*C*), 131.3 (Ar*C*H), 130.7 (Ar*C*), 127.7 (Ar*C*H), 115.3 (Ar*C*), 110.1 (Ar*C*H), 52.0 (*C*H_3-O), 44.7 (*C*H-C(O)), 42.0 (N-*C*H_2), 30.3 (C(O)-*C*H_2), 26.0 (CH-*C*H_2), 21.1 (N-CH_2-*C*H_2), 11.8 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2963, 2930, 1734 (ester C=O), 1701 (amide C=O), 1605, 1482, 1339.

MS *m/z* (EI mode) 339 (M^+, 36 %), 116 (20), 210 (20), 238 (33), 265 (99), 267 (100) and 309 (44); (Found: M^+, 339.0476 $C_{15}H_{18}O_4NBr$ requires 339.0470).

3-Methyl-1-propyl-5-(2-(trimethylsilyl)ethynyl)-1,3-dihydro-indol-2-one 19



As for general procedure C(i). 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-5-(2-(trimethylsilyl)ethynyl)-1,3-dihydro-indol-2-one **11b** (75 mg, 0.09 mmol, 1 eq.) on treatment with SmI_2 (2.30 ml, 0.1 M soln. in THF, 0.23 mmol, 2.5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-methyl-1-propyl-5-(2-(trimethylsilyl)ethynyl)-1,3-dihydro-indol-2-one **19** (23 mg, 0.08 mmol, 88 %) as a yellow oil:

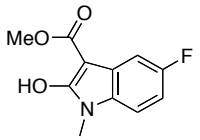
^{1}H NMR (400 MHz, $CDCl_3$) 7.31 (1H, dd, J 8.1, 1.6, Ar*H*), 7.27 (1H, s, Ar*H*), 6.68 (1H, d, J 8.1, Ar*H*), 3.58 (2H, t, J 7.4, N-CH_2), 3.32 (1H, q, J 7.6, CH_3-C*H*), 1.66-1.56 (2H, m, N-CH_2-CH_2), 1.38 (3H, d, J 7.6, CH_3-CH), 0.88 (3H, t, J 7.4, CH_2-CH_3), 0.18 (9H, s, (3 x CH_3-Si).

^{13}C NMR (100 MHz, $CDCl_3$) 178.5 (*C*=O), 143.7 (Ar*C*), 132.1 (Ar*C*H), 130.7 (Ar*C*), 127.2 (Ar*C*H), 116.7 (Ar*C*), 107.9 (Ar*C*H), 105.2 (alkyne *C*), 93.0 (alkyne *C*), 41.5 (N-*C*H_2), 40.2 (CH_3-*C*H), 20.7 (N-CH_2-*C*H_2), 15.4 (*C*H_3-CH), 11.3 (CH_2-*C*H_3), 0.00 ((*C*H_3)$_3$-Si).

IR ν_{max} (Golden Gate)/cm^{-1} 2965, 1715 (C=O), 1615, 1488, 1347.

MS *m/z* (EI mode) 285 (M^+, 100 %), 73 (7), 106 (8), 228 (22) and 270 (85); (Found: M^+, 285.1548 $C_{17}H_{23}ONSi$ requires 285.1549).

Methyl 5-fluoro-1-methyl-2-hydroxy-indol-3-carboxylate 20

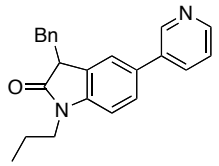


As for general procedure C(i). Methyl 5-fluoro-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-indole-3-carboxylate **6** (114 mg, 0.16 mmol, 1 eq.) on treatment with SmI_2 (4.00 ml, 0.1 M soln. in THF, 0.40 mmol, 2.5 eq.) and after filtration (precipitation occurs on addition of 80 % MeCN/H_2O), gave methyl 5-fluoro-1-methyl-2-hydroxy-indol-3-carboxylate **20** (33 mg, 0.15 mmol, 92 %) as a clear oil: (For both tautomers)

^{1}H NMR (400 MHz, $CDCl_3$) 7.31 (1H, d, J 8.6 , Ar*H*), 7.06-6.92 (3H, m, 3 x Ar*H*), 6.79 (1H, td, J 9.2, 2.4, Ar*H*), 6.70 (1H, dd, J 8.4, 4.4, Ar*H*), 4.37 (1H, s, C*H*), 3.89 (3H, s, CH_3-O, one tautomer), 3.73 (3H, s, CH_3-O, one tautomer), 3.53 (3H, s, N-CH_3, one tautomer), 3.15 (3H, s, N-CH_3, one tautomer).

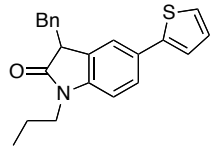
^{13}C NMR (100 MHz, $CDCl_3$) □ 170.1 (*C*=O), 166.8 (*C*=O), 159.7 (d, J 235.0, Ar*C*F), 159.2 (d, J 240.0, Ar*C*F), 140.6 (Ar*C*), 128.4 (Ar*C*), 124.6 (Ar*C*), 124.5 (Ar*C*), 115.6 (d, J 23.0, Ar*C*H), 113.0 (d, J 25.0, Ar*C*H), 109.3 (d, J 9.0, Ar*C*H), 108.9 (d, J 8.0, Ar*C*H), 108.5 (d, J 25.0, Ar*C*H), 105.6 (d, J 26.0, Ar*C*H), 84.6 (Ar*C*), 53.2 (*C*H_3-O), 52.3 (*C*H), 51.3 (*C*H_3-O), 27.5 (N-*C*H_3), 26.7 (N-*C*H_3).
IR ν_{max} (Golden Gate)/cm^{-1} 3229 (OH), 1650 (broad) (ester and amide C=O), 1541, 1458, 1214.
MS *m/z* (EI mode) 223 (M^+, 50 %), 84 (35), 109 (19), 135 (35), 164 (45) and 191 (100); (Found: M^+, 223.0646 $C_{11}H_{10}O_3NF$ requires 223.0645).

3-Benzyl-1-propyl-5-(pyridin-3-yl)-1,3-dihydro-indol-2-one 21



As for general procedure C(i). 3-Benzyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-5-(pyridin-3-yl)-1,3-dihydro-indol-2-one **13** (87 mg, 0.10 mmol, 1 eq.) on treatment with SmI_2 (2.50 ml, 0.1 M soln. in THF, 0.25 mmol, 2.5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-benzyl-1-propyl-5-(pyridin-3-yl)-1,3-dihydro-indol-2-one **21** (24 mg, 0.071 mmol, 71 %) as a clear oil:
^{1}H NMR (400 MHz, $CDCl_3$) □ 8.61 (1H, s, Ar*H*), 8.47 (1H, s, Ar*H*), 7.65-7.62 (1H, m, Ar*H*), 7.36 (1H, dd, J 8.1, 1.3, Ar*H*), 7.27-7.10 (6H, m, 6 x Ar*H*), 6.85 (1H, s, Ar*H*), 6.79 (1H, d, J 8.1, Ar*H*), 3.72-3.62 (2H, m, 1H of N-CH_2 and C*H*), 3.55-3.46 (2H, m, 1H of Ph-CH_2 and 1H of N-CH_2), 2.87 (1H, dd, J 13.5, 9.2, 1H of Ph-CH_2), 1.60-1.49 (2H, m, N-CH_2-CH_2), 0.82 (3H, t, J 7.4, CH_2-CH_3).
^{13}C NMR (100 MHz, $CDCl_3$) □ 175.8 (*C*=O), 146.8 (Ar*C*H), 146.7 (Ar*C*H), 143.0 (Ar*C*), 136.6 (2 x Ar*C*), 132.9 (2 x Ar*C*H), 130.3 (Ar*C*), 128.5 (2 x Ar*C*H), 128.4 (Ar*C*), 127.3 (Ar*C*H), 125.6 (Ar*C*H), 125.8 (Ar*C*H), 122.6 (Ar*C*H), 122.5 (Ar*C*H), 107.7 (Ar*C*H), 40.1 (*C*H), 40.6 (N-*C*H_2), 35.9 (Ph-*C*H_2), 19.7 (N-CH_2-*C*H_2), 10.3 (CH_2-*C*H_3).
IR ν_{max} (Golden Gate)/cm^{-1} 2965, 2930, 1702 (C=O), 1617, 1475, 1350.
MS *m/z* (EI mode) 342 (M^+, 100 %), 47 (5), 84 (31), 91 (32), 194 (15), 209 (18) and 251 (83); (Found: M^+, 342.1733 $C_{23}H_{22}O_2N$ requires 342.1732).

3-Benzyl-1-propyl-5-(thiophen-2-yl)-1,3-dihydro-indol-2-one 22



As for general procedure C(i). 3-Benzyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfonyl)-1-propyl-5-(thiophen-2-yl)-1,3-dihydro-indol-2-one **14** (82 mg, 0.10 mmol, 1 eq.) on treatment with SmI_2 (2.40 ml, 0.1 M soln. in THF, 0.24 mmol, 2.5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-benzyl-1-propyl-5-(thiophen-2-yl)-1,3-dihydro-indol-2-one **22** (27 mg, 0.077 mmol, 82 %) as a yellow oil:

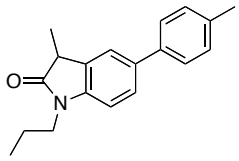
^{1}H NMR (400 MHz, $CDCl_3$) 7.38 (1H, dd, J 8.1, 1.2, Ar*H*), 7.37-7.05 (6H, m, 6 x Ar*H*), 7.00-6.88 (3H, m , 3 x Ar*H*), 6.67 (1H, d, J 8.1, Ar*H*), 3.67-3.56 (2H, m, 1H of N-CH_2 and C*H*), 3.50-3.43 (2H, m, 1H of Ph-CH_2 and 1H of N-CH_2), 2.95-2.85 (1H, m, 1H of Ph-CH_2), 1.43-1.56 (2H, m, N-CH_2-CH_2), 0.78 (3H, m, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 177.1 (*C*=O), 144.8 (Ar*C*), 143.7 (Ar*C*), 138.0 (Ar*C*), 130.0 (2 x Ar*C*H), 129.5 (Ar*C*), 128.8 (Ar*C*), 128.7 (2 x Ar*C*H), 128.4 (Ar*C*H), 127.1 (Ar*C*H), 126.0 (Ar*C*H), 124.4 (Ar*C*H), 122.9 (Ar*C*H), 122.5 (Ar*C*H), 108.8 (Ar*C*H), 53.8 (*C*H), 42.0 (N-*C*H_2), 37.2 (Ph-*C*H_2), 21.0 (N-CH_2-*C*H_2), 11.7 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2961, 2924, 2873, 1701 (C=O), 1486, 1339, 1103.

MS *m/z* (CI mode, isobutane) 348 ((M+H)$^+$, 100 %); (Found: (M+H)$^+$, 348.1423 $C_{22}H_{22}ONS$ requires 348.1422).

3-Methyl-1-propyl-5-(4-methylphenyl)-1,3-dihydro-indol-2-one 23



As for general procedure C(i). 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylsulfonyl)-3-methyl-1-propyl-5-(4-methylphenyl)-1,3-dihydro-indol-2-one **16** (75 mg, 0.09 mmol, 1 eq.) on treatment with SmI_2 (2.30 ml, 0.1 M soln. in THF, 0.23 mmol, 2.5 eq.) and after purification using fluorous silica (eluting with 80 % MeCN/H_2O then MeCN) gave 3-methyl-1-propyl-5-(4-methylphenyl)-1,3-dihydro-indol-2-one **23** (24 mg, 0.085 mmol, 94 %) as a clear oil:

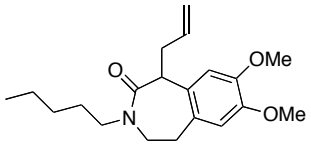
^{1}H NMR (400 MHz, $CDCl_3$) 7.40-7.38 (4H, m, 4 x Ar*H*), 7.16 (2H, d, J 8.0, 2 x Ar*H*), 6.81 (1H, d, J 8.2, Ar*H*), 3.63 (2H, t, J 7.0, N-CH_2), 3.41 (1H, q, J 7.6, CH_3-C*H*), 2.32 (3H, s, CH_3-Ar), 1.70-1.60 (2H, m, N-CH_2-CH_2), 1.44 (3H, d, J 7.6, CH_3-CH), 0.91 (3H, t, J 7.4, CH_2-CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) 170.0 (*C*=O), 140.0 (Ar*C*), 138.6 (Ar*C*), 137.2 (Ar*C*), 136.0 (Ar*C*), 131.7 (Ar*C*), 129.9 (2 x Ar*C*H), 127.1 (2 x Ar*C*H), 126.8 (Ar*C*H), 122.8 (Ar*C*H), 108.9 (Ar*C*H), 41.9 (N-*C*H_2), 41.1 (*C*H), 21.5 (*C*H_3-Ar), 21.2 (N-CH_2-*C*H_2), 16.0 (*C*H_3-CH), 11.8 (CH_2-*C*H_3).

IR ν_{max} (Golden Gate)/cm^{-1} 2965, 2930, 2872, 1706 (C=O), 1617, 1486, 1348, 1207.
MS *m/z* (EI mode) 279 (M^+, 100 %), 207 (14), 222 (65) and 250 (10); (Found: M^+, 279.1625 $C_{19}H_{21}ON$ requires 279.1623).

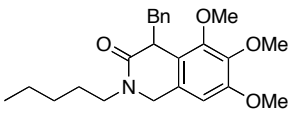
General Procedure C(ii) for the cleavage of N-heterocycles

1-Allyl-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one 24



To a solution of 1-allyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylsulfanyl)-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one **8** (68 mg, 0.08 mmol, 1 eq.) in THF (2 ml) was added SmI_2 (3.70 ml, 0.1 M soln. in THF, 0.37 mmol, 4.4 eq.) at room temperature. After 18 hours, the reaction mixture was concentrated and CH_2Cl_2 (20 ml) was added. The organic layer was then washed with H_2O, dried ($MgSO_4$) and after purification through a short pad of silica (eluting with DCM then 50 % EtOAc/petroleum ether (40-60))) gave 1-allyl-7,8-dimethoxy-3-pentyl-1,3,4,5-tetrahydro-benzo[*d*]azepin-2-one **24** (25 mg, 0.08 mmol, 90 %) as a pale yellow oil:
^{1}H NMR (400 MHz, $CDCl_3$) □ 6.64 (1H, s, Ar*H*), 6.50 (1H, s, Ar*H*), 5.91-5.81 (1H, m, C*H*=CH_2), 5.10-4.97 (2H, m, CH=CH_2), 4.11-4.07 (1H, m, C*H*-C(O)), 4.00-3.92 (1H, m, 1H of ring CH_2-N), 3.78 (3H, s, CH_3-O), 3.76 (3H, s, CH_3-O), 3.46-3.25 (3H, m, 1H of ring CH_2-N and N-CH_2), 3.14-3.07 (1H, m, 1H of ArCH_2), 3.01-2.85 (2H, m, 1H of ArCH_2 and 1H of CH_2CH=CH_2), 2.62-2.55 (1H, m, 1H of CH_2CH=CH_2), 1.46-1.39 (2H, m, N-CH_2-CH_2), 1.26-1.06 (4H, m, CH_2-CH_2-CH_3 and CH_2-CH_2-CH_3), 0.80-0.76 (3H, t, J 7.2, CH_2-CH_3).
^{13}C NMR (100 MHz, $CDCl_3$) □ 173.1 (*C*=O), 148.0 (Ar*C*-OMe), 147.7 (Ar*C*-OMe), 137.2 (*C*H=CH_2), 128.6 (Ar*C*), 128.4 (Ar*C*), 116.8 (CH=*C*H_2), 113.8 (Ar*C*H), 111.0 (Ar*C*H), 56.3 (2 x *C*H_3-O), 48.1 (N-*C*H_2), 47.2 (*C*H-C(O)), 46.6 (ring *C*H_2-N), 34.5 (*C*H_2CH=CH_2), 33.0 (Ar*C*H_2), 29.3 (*C*H_2-CH_2-CH_3), 28.3 (N-CH_2-*C*H_2), 22.8 (CH_2-*C*H_2-CH_3), 14.4 (CH_2-*C*H_3).
IR ν_{max} (Thin Film)/cm^{-1} 2931 (C=C-H), 1654 (C=O), 1519, 1483, 1450.
MS *m/z* (EI mode) 331 (M^+, 85 %), 43 (12), 83 (15), 146 (11), 177 (25), 246 (15), 262 (100) 263 (51), 290 (19) and 332 (20); (Found: M^+, 331.2148 $C_{20}H_{29}O_3N$ requires 331.2147).

4-Benzyl-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one 25



As for general procedure C(ii). 4-Benzyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylsulfanyl)-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one **10** (83 mg, 0.10 mmol, 1 eq.) on treatment with SmI_2 (6.27 ml, 0.1 M soln. in THF, 0.63 mmol, 6.6 eq.) and after purification through a short pad of silica (eluting with DCM then 50 % EtOAc/petroleum ether (40-60))) gave 4-benzyl-5,6,7-trimethoxy-2-pentyl-1,4-dihydro-2*H*-isoquinolin-3-one **25** (29 mg, 0.07 mmol, 76 %) as a yellow oil:

^{1}H NMR (400 MHz, $CDCl_3$) 7.10-7.05 (1H, m, Ar*H*), 7.02-6.98 (2H, m, Ar*H*), 6.69-6.67 (2H, m, Ar*H*), 6.13 (1H, s, Ar*H*), 4.04-4.00 (1H, m, C*H*-C(O)), 3.84 (3H, s, CH_3-O), 3.82 (3H, s, CH_3-O), 3.74 (3H, s, CH_3-O), 3.62-3.58 (1H, d, J 15.5, 1H of ring CH_2-N), 3.29-3.15 (3H, m, 1H of CH_2-Ph and N-CH_2), 3.03-2.96 (2H, m, 1H of ring CH_2-N and 1H of CH_2-Ph), 1.44-1.10 (6H, m, N-CH_2-CH_2, CH_2-CH_2-CH_3 and CH_2-CH_2-CH_3), 0.84-0.80 (3H, t, J 7.2, CH_2-CH_3).

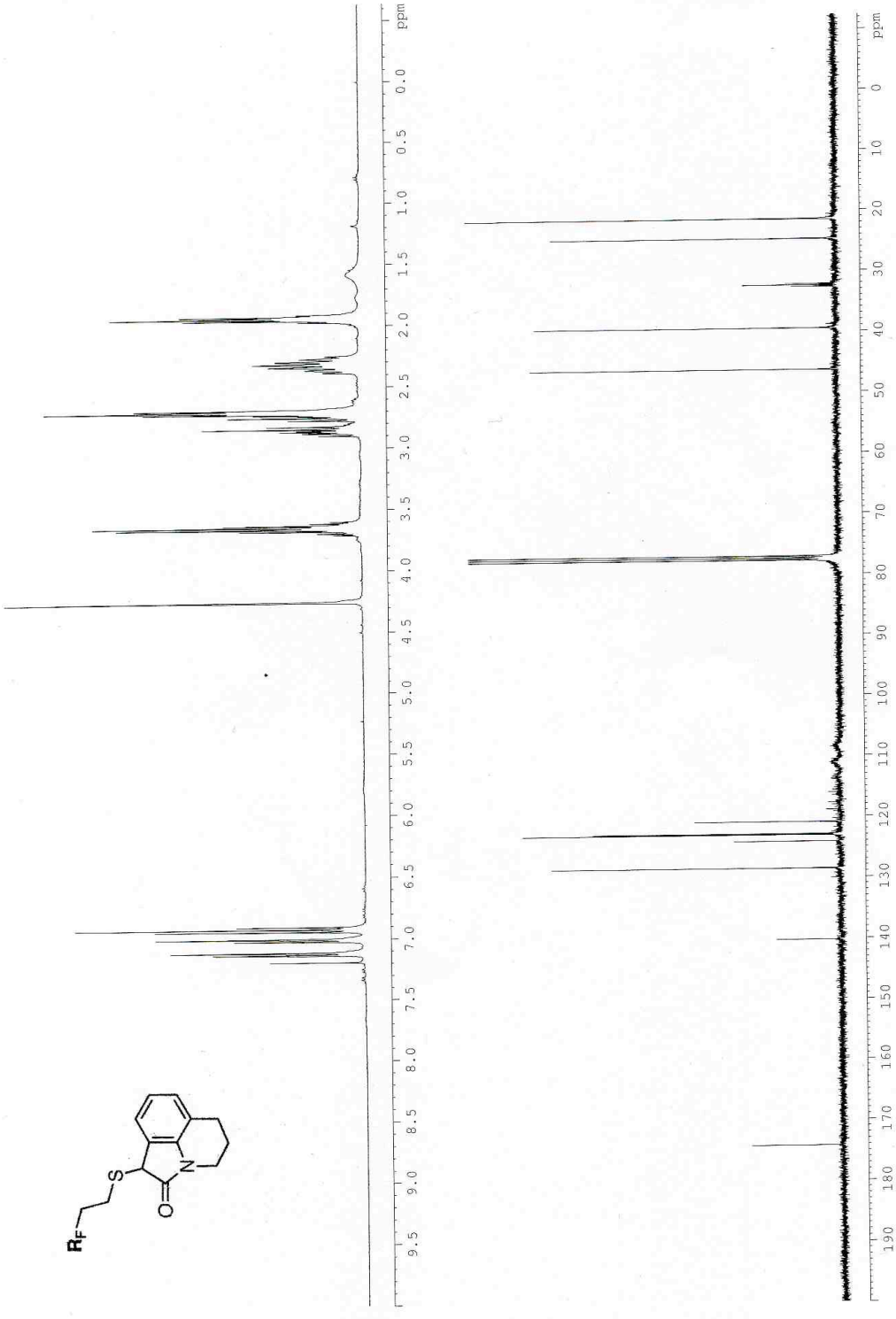
^{13}C NMR (100 MHz, $CDCl_3$) 171.0 (*C*=O), 152.9 (Ar*C*-OMe), 150.8 (Ar*C*-OMe), 141.5 (Ar*C*), 138.1 (Ar*C*-OMe), 130.2 (2 x Ar*C*H), 128.1 (Ar*C*), 128.0 (2 x Ar*C*H), 126.8 (Ar*C*H), 121.3 (Ar*C*), 103.6 (Ar*C*H), 61.3 (*C*H_3-O), 56.4 (2 x *C*H_3-O), 50.6 (ring *C*H_2-N), 47.5 (N-*C*H_2), 43.4 (*C*H-C(O)), 40.3 (*C*H_2-Ph), 29.5 (*C*H_2-CH_2-CH_3), 27.1 (N-CH_2-*C*H_2), 22.8 (*C*H_2-CH_3), 14.3 (CH_2-*C*H_3).

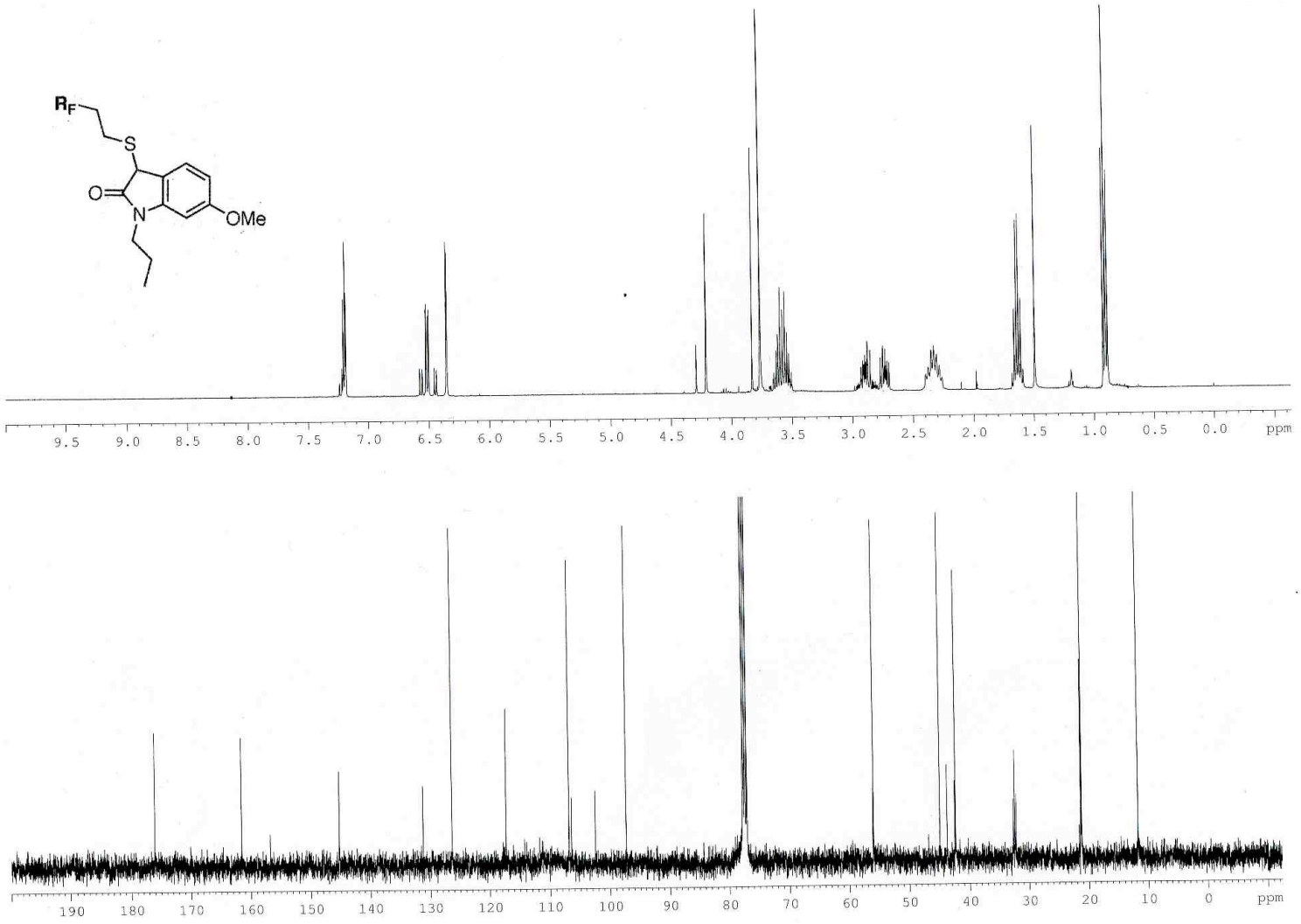
IR ν_{max} (Thin Film)/cm^{-1} 2933, 2859, 1644 (C=O), 1604, 1492, 1463, 1414, 1358, 1314, 1240, 1120.

MS *m/z* (EI mode) 397 (M^+, 11 %), 91 (11), 181 (10), 278 (26), 306 (100) and 307 (19); (Found: M^+, 397.2256 $C_{24}H_{31}O_4N$ requires 397.2253).

^{1}H and ^{13}C spectra

Fluorous-tagged *N*-heterocycles




R_F
S
O
N
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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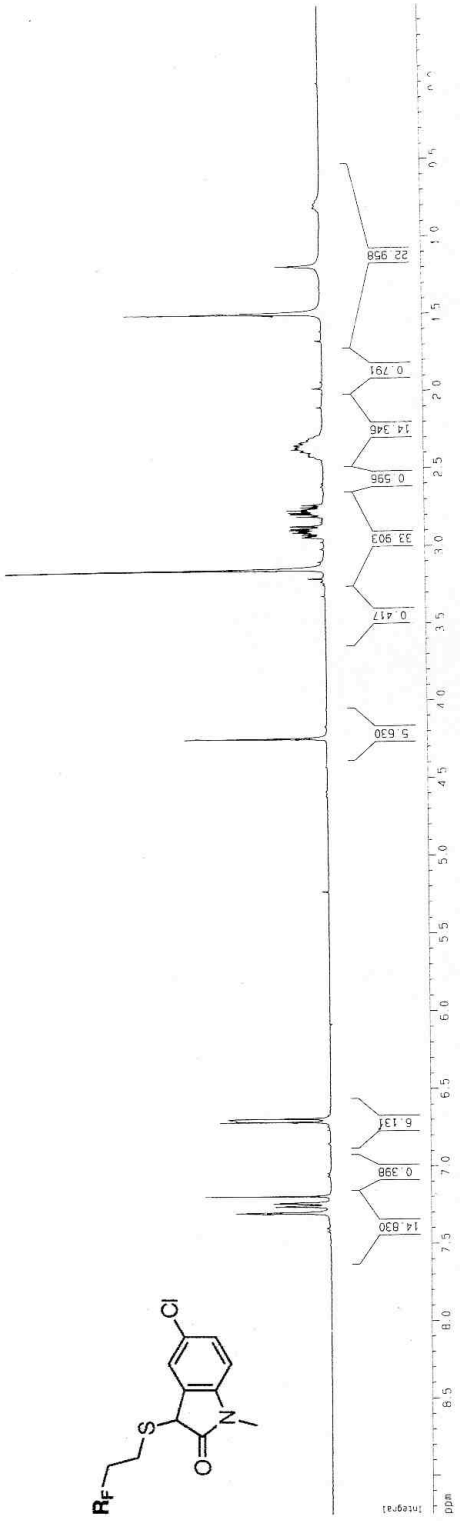
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N
O
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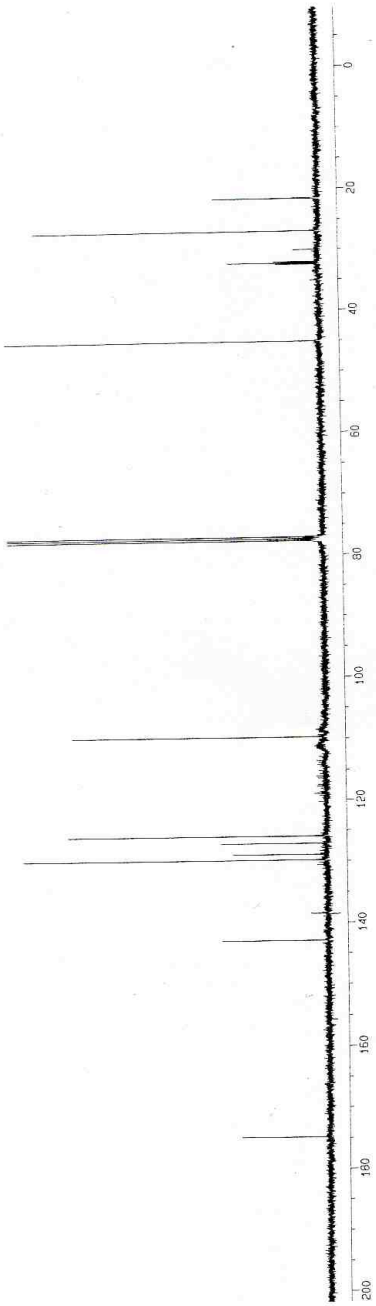
integral
ppm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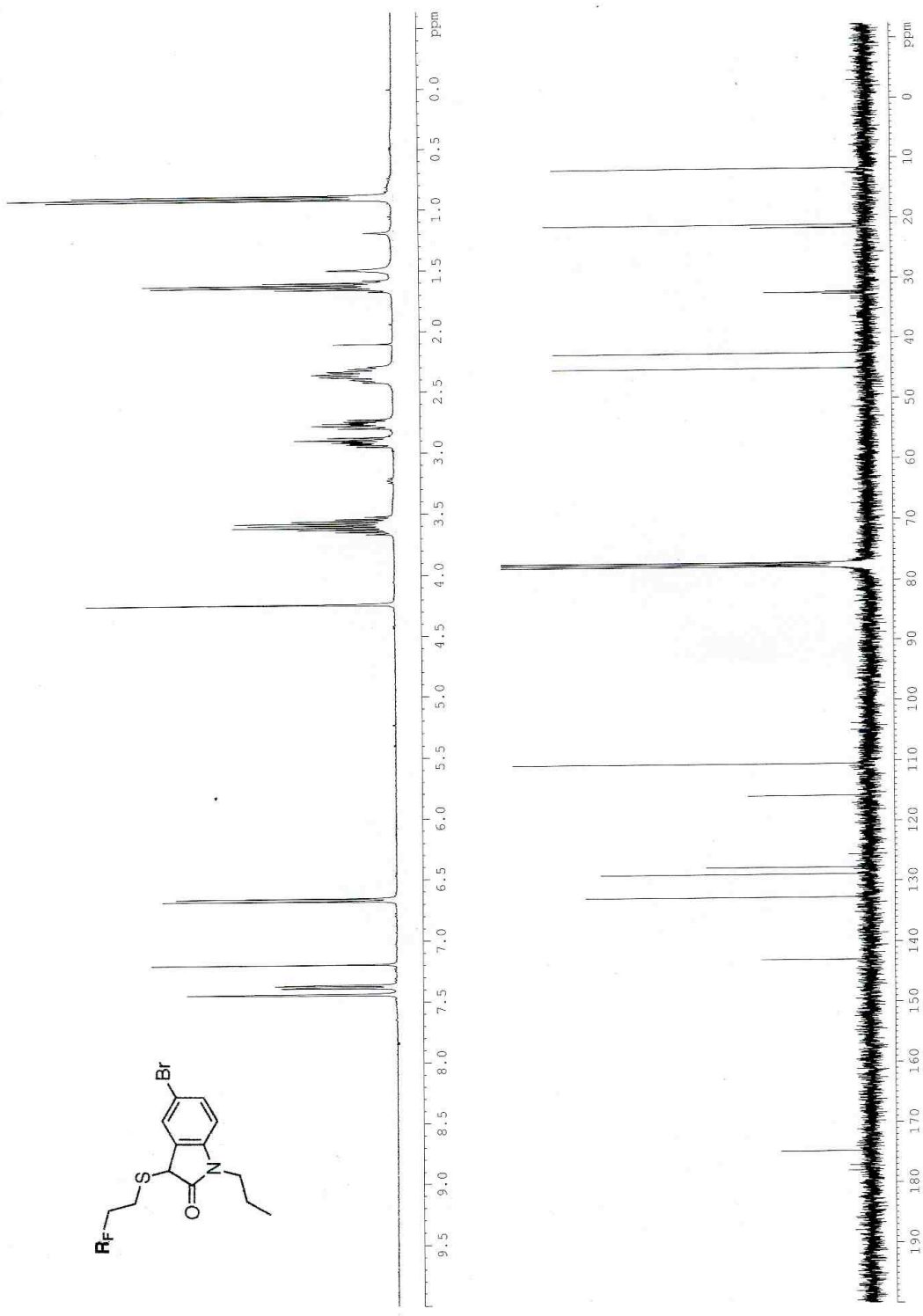
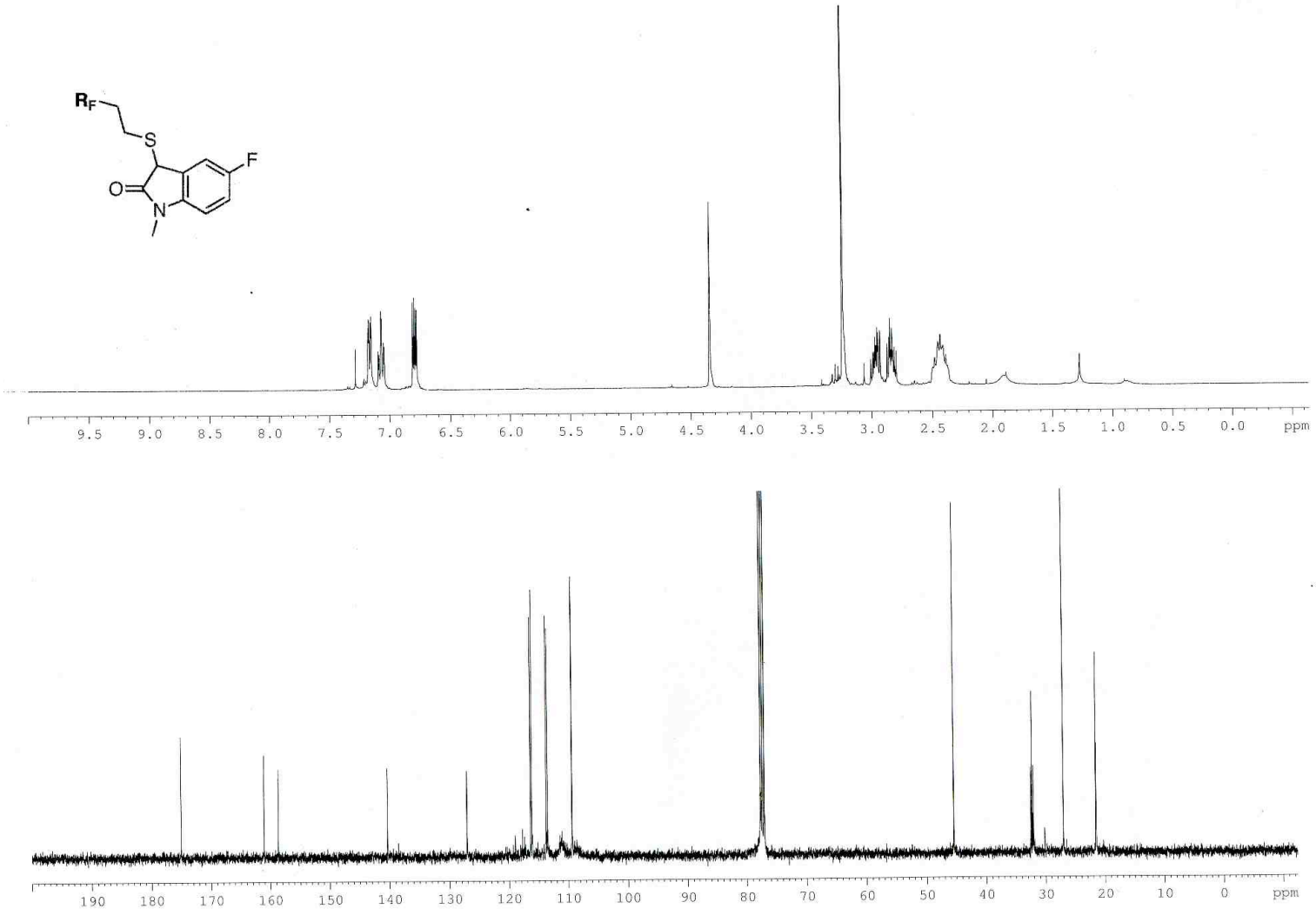
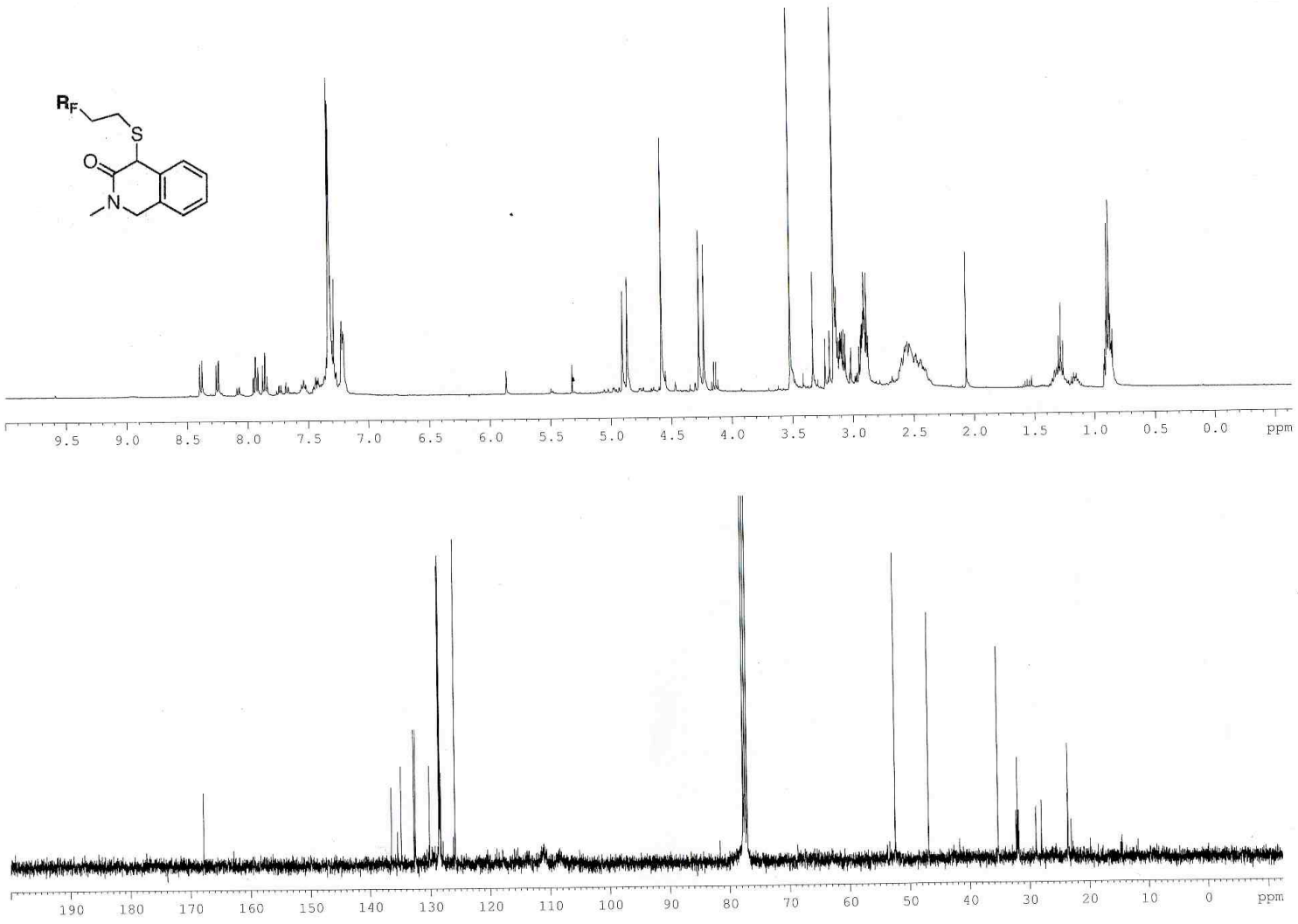
20
40
60
80
100
120
140
160
180
200


Br
S
N
O
R_F
ppm
ppm


R_F
S
F
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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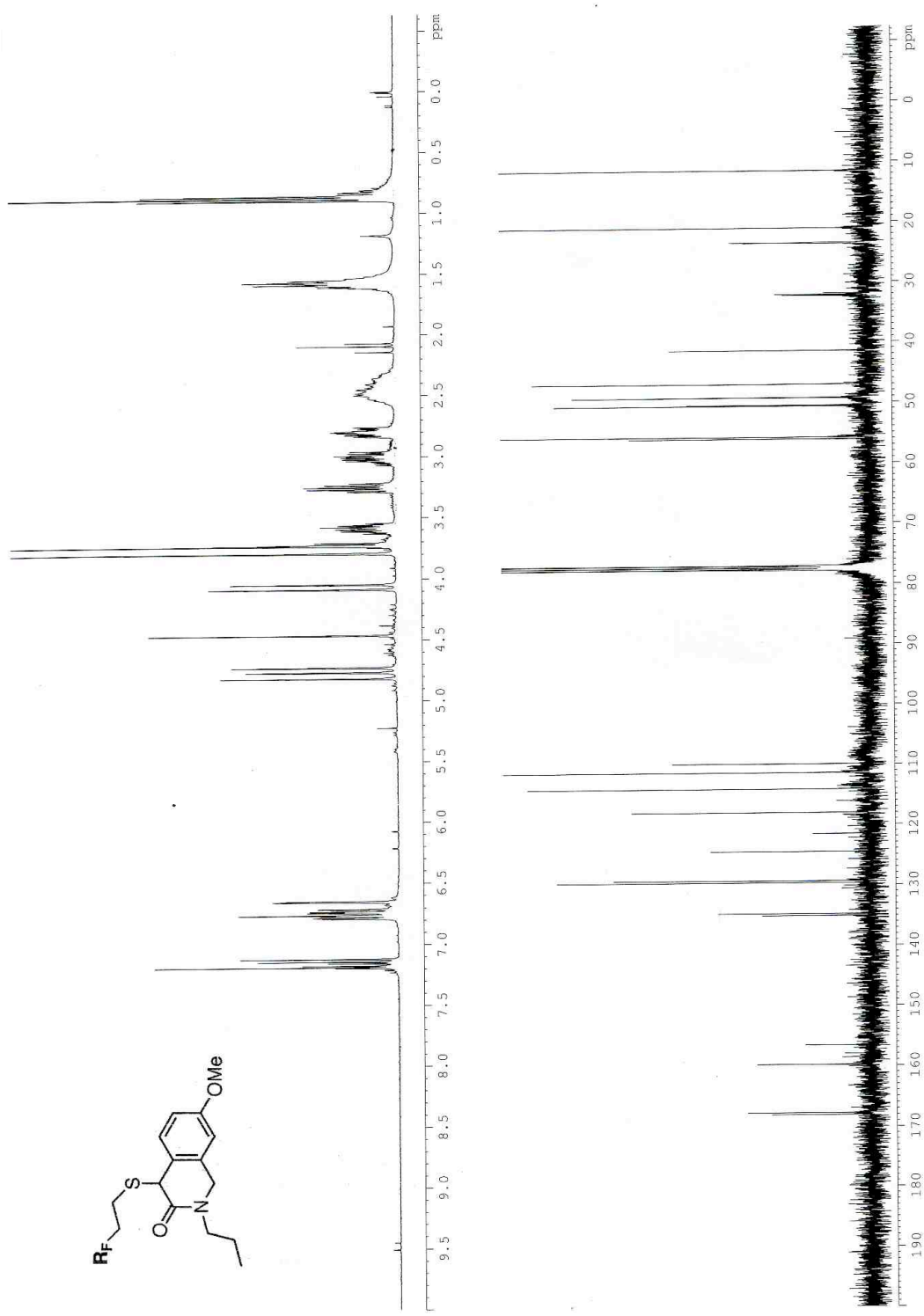
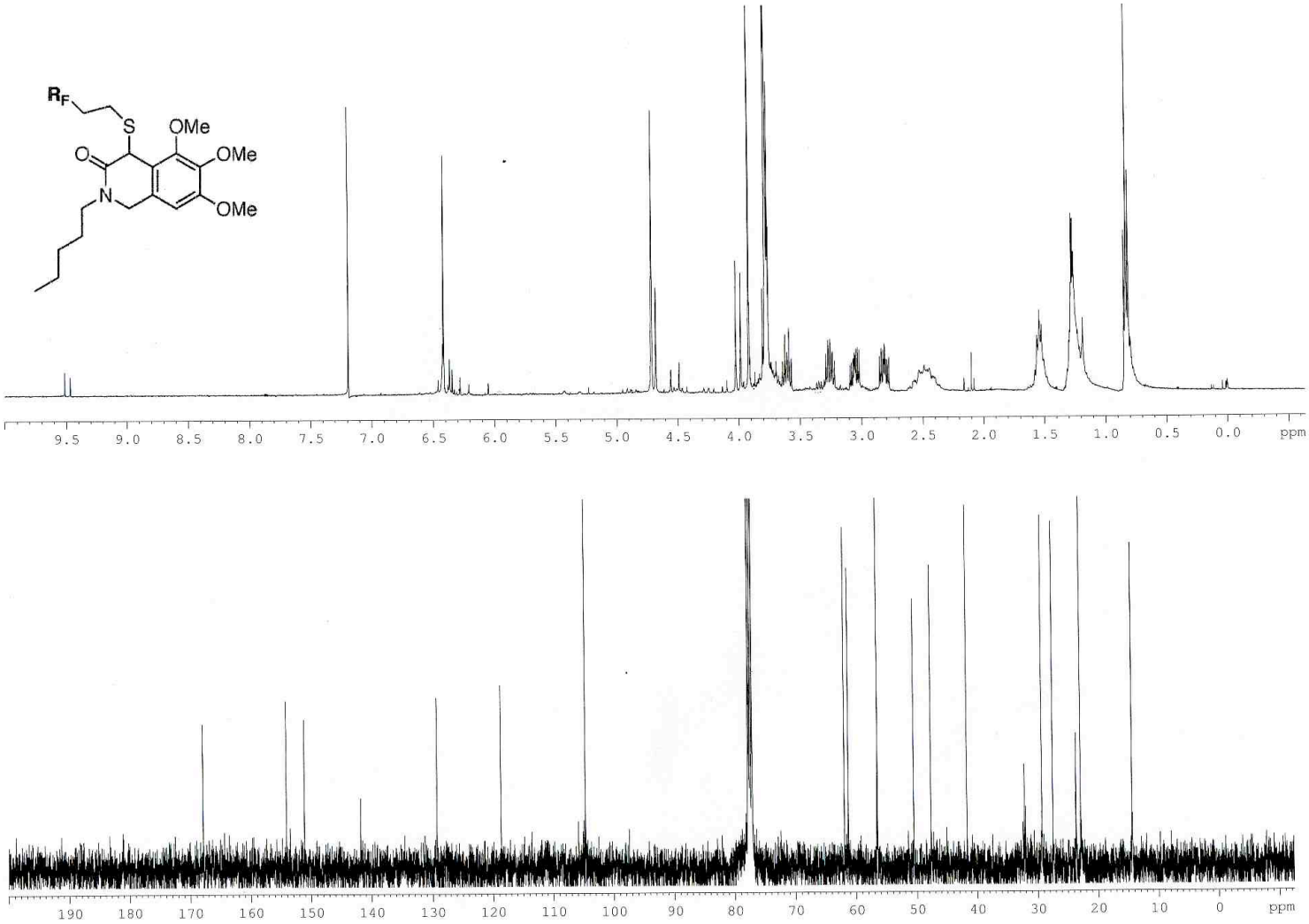
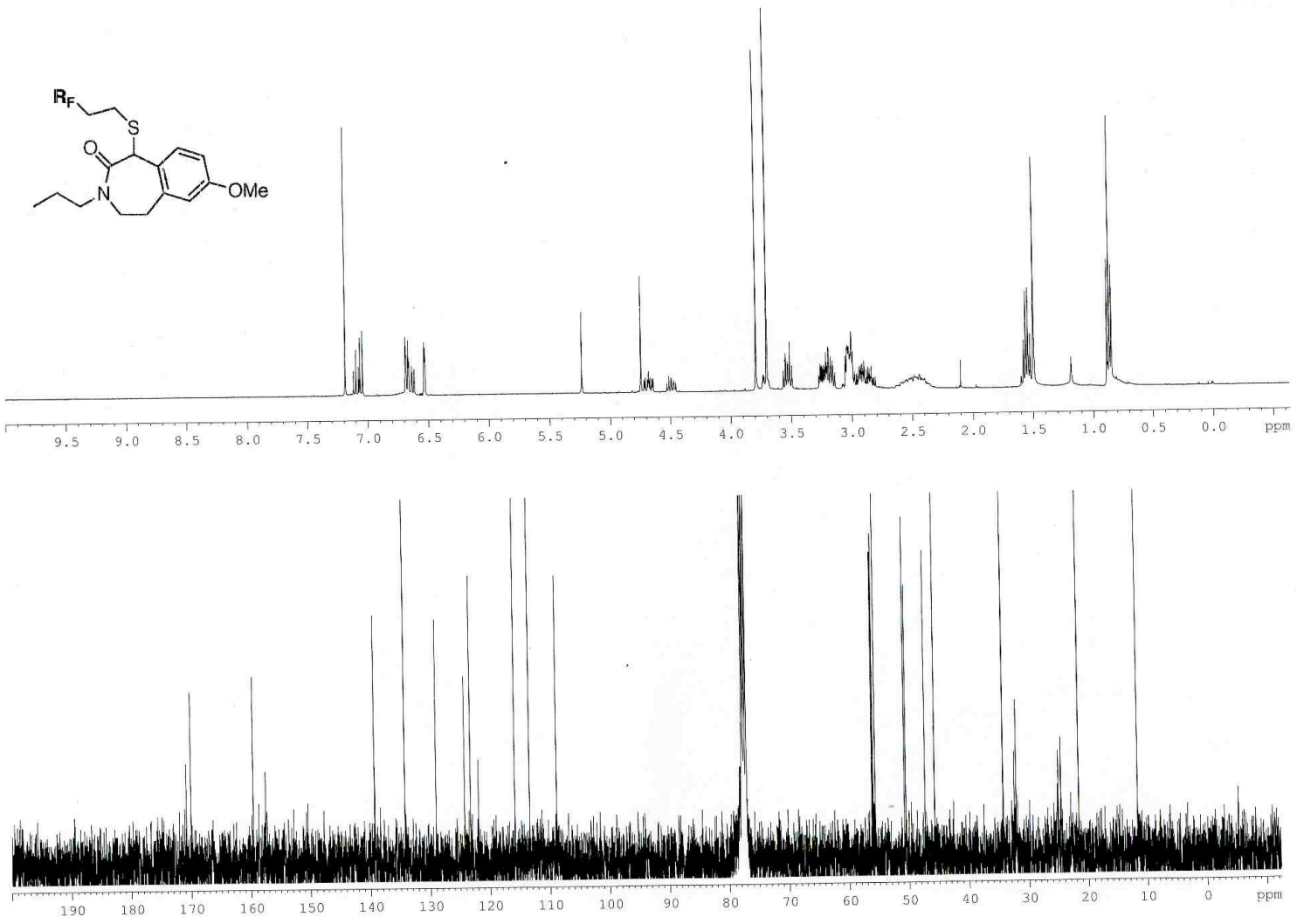
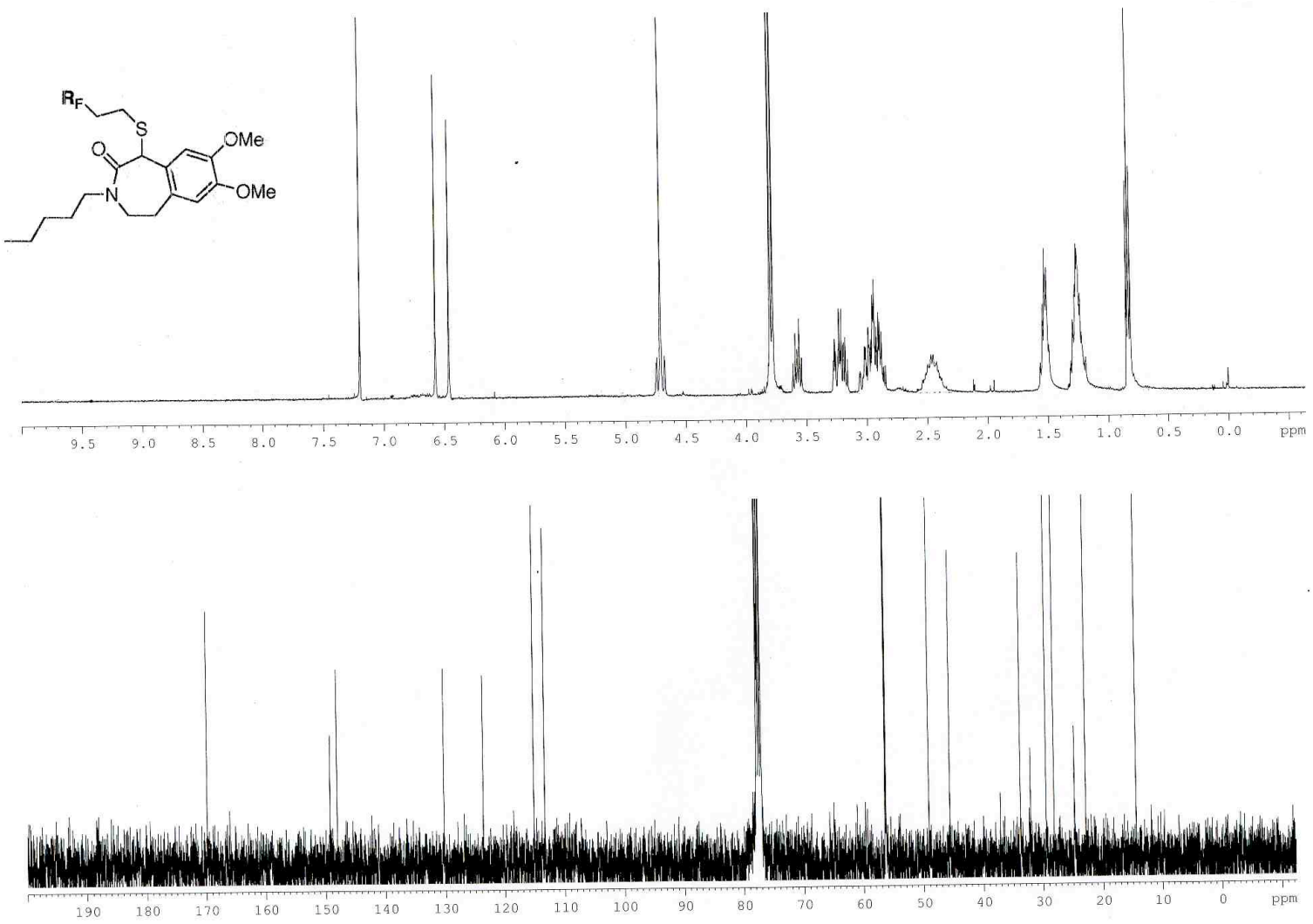
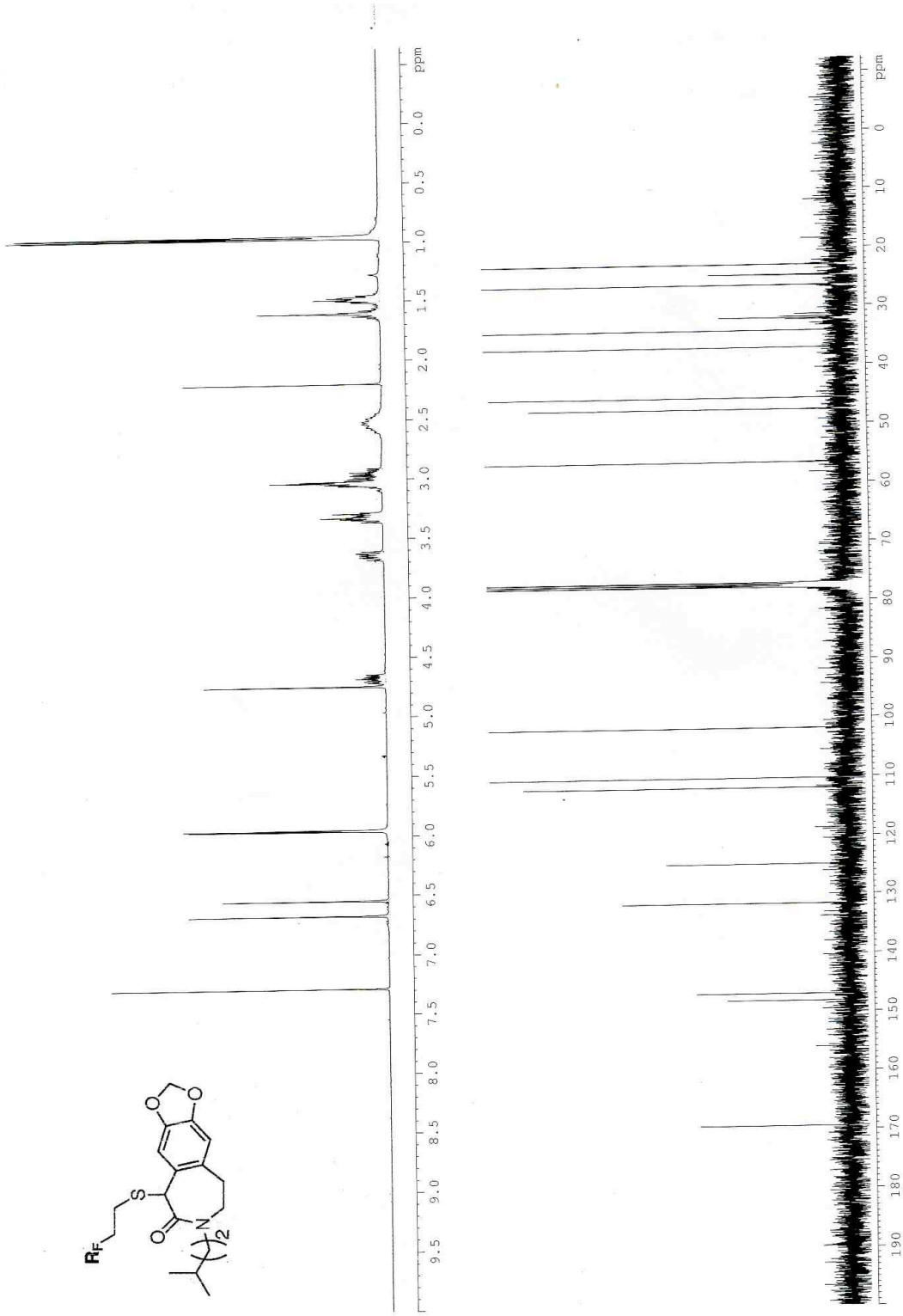
S
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OMe
S
N
O
R_F
ppm
ppm

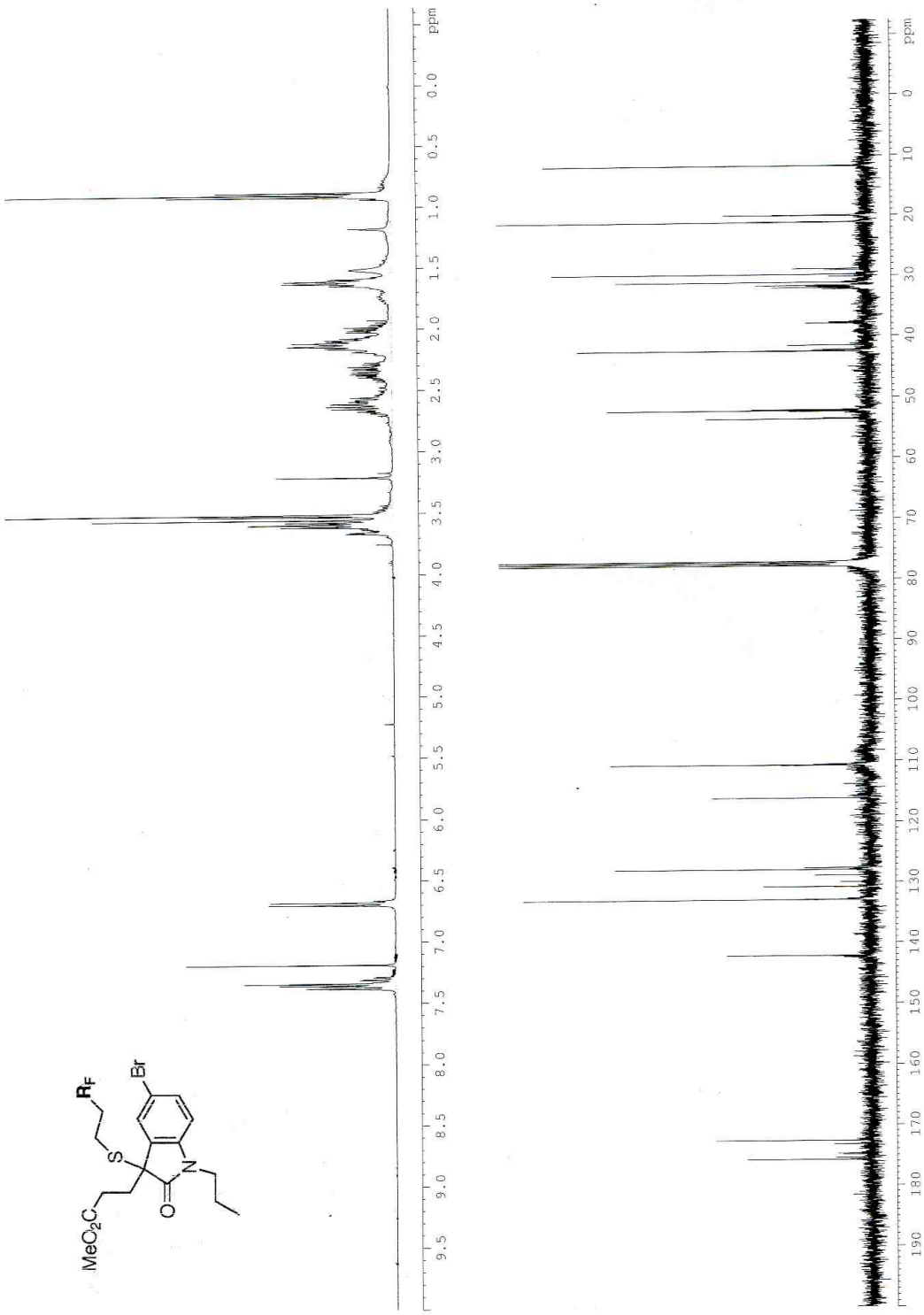

R_F
S
OMe
OMe
OMe
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

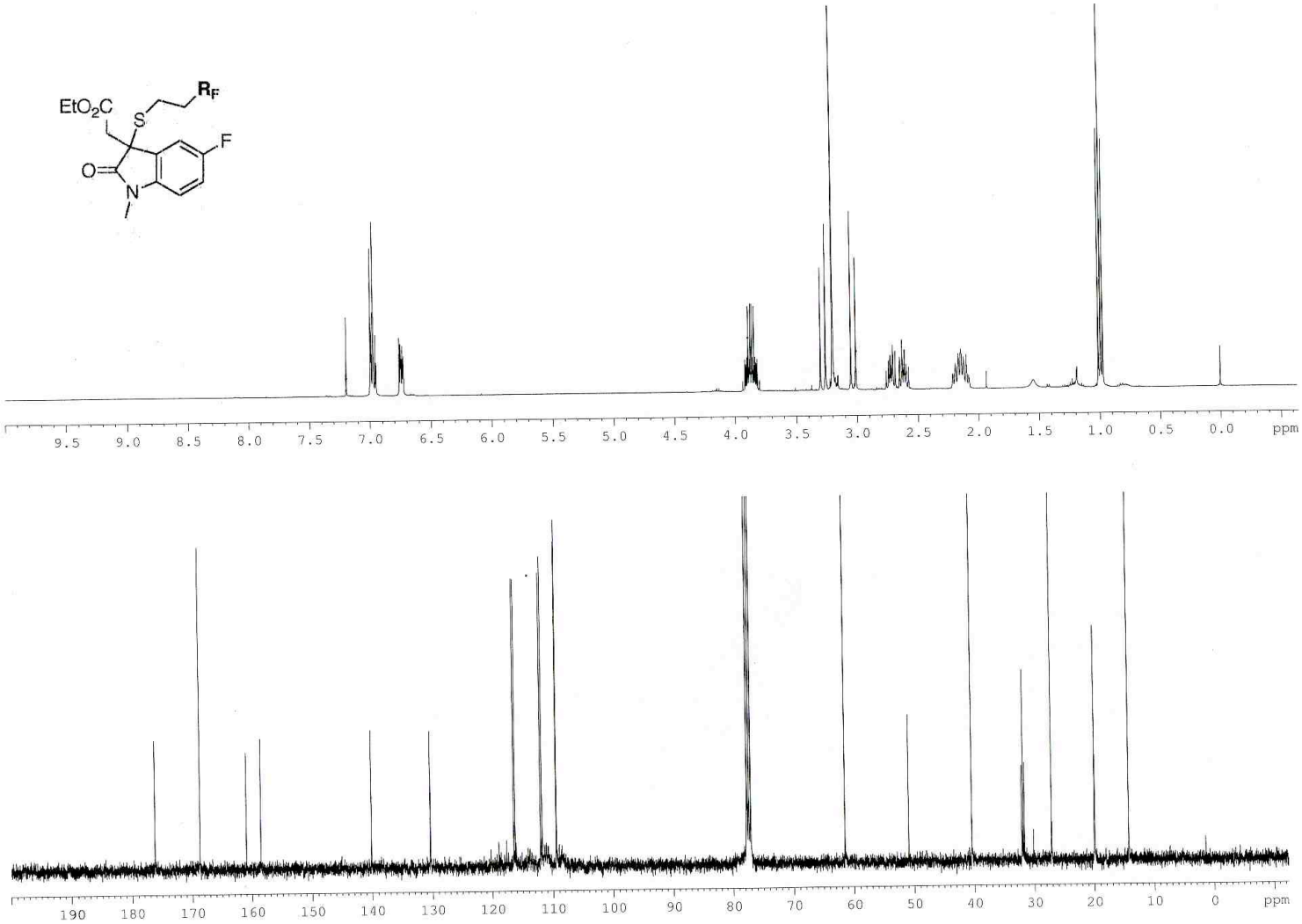

R_F
S
O
N
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

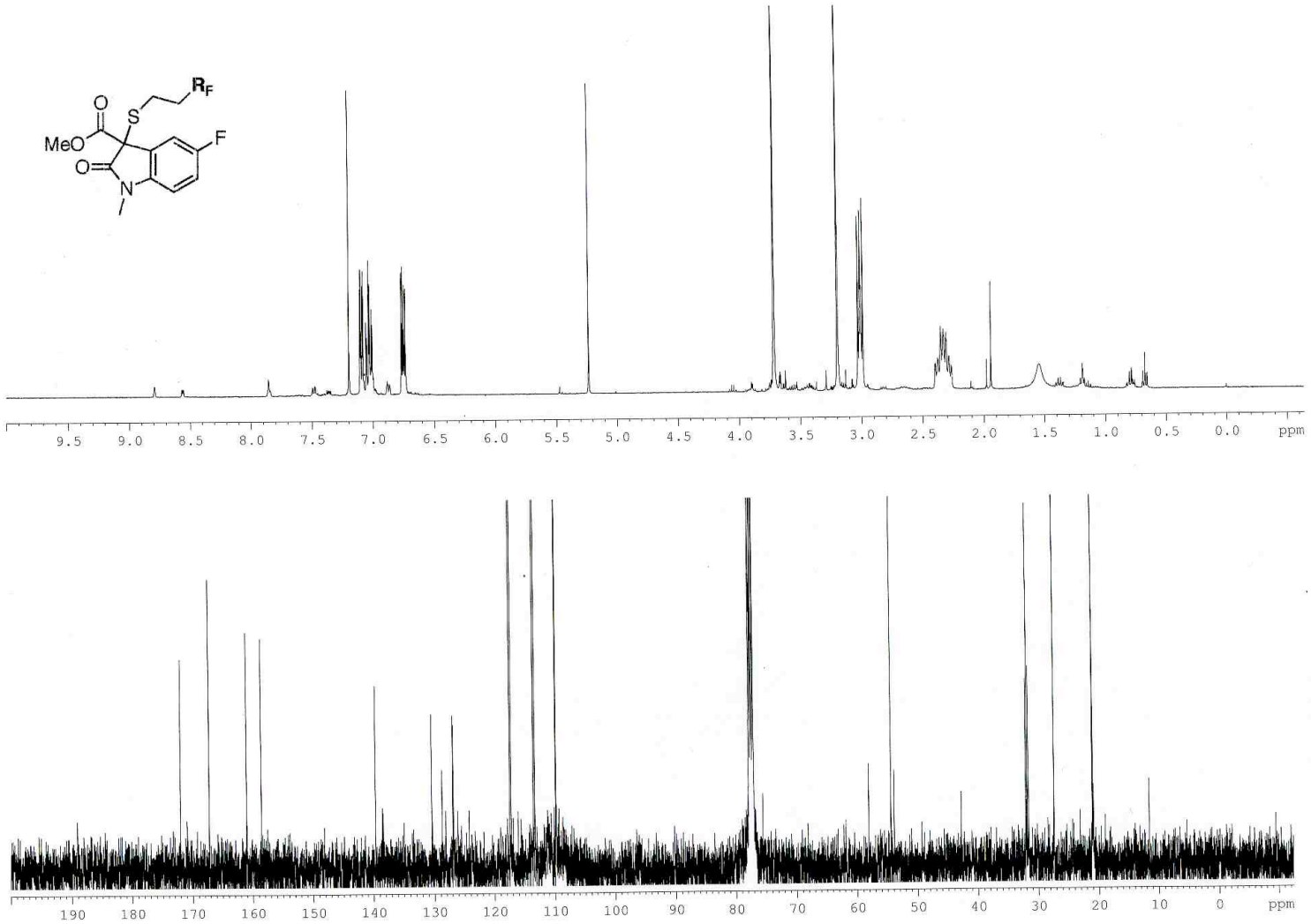

R_F
S
O
N
OMe
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

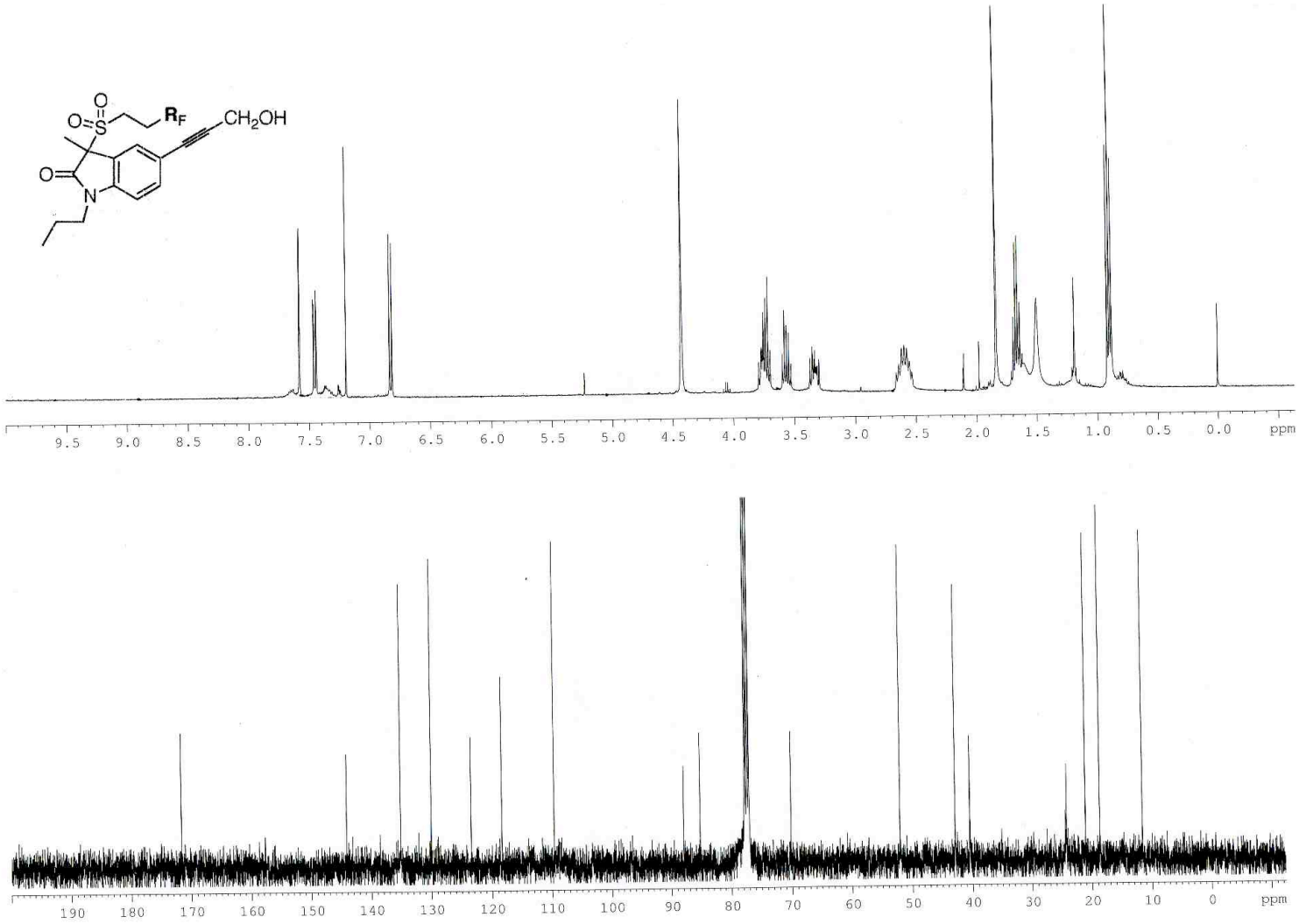

ppm
ppm

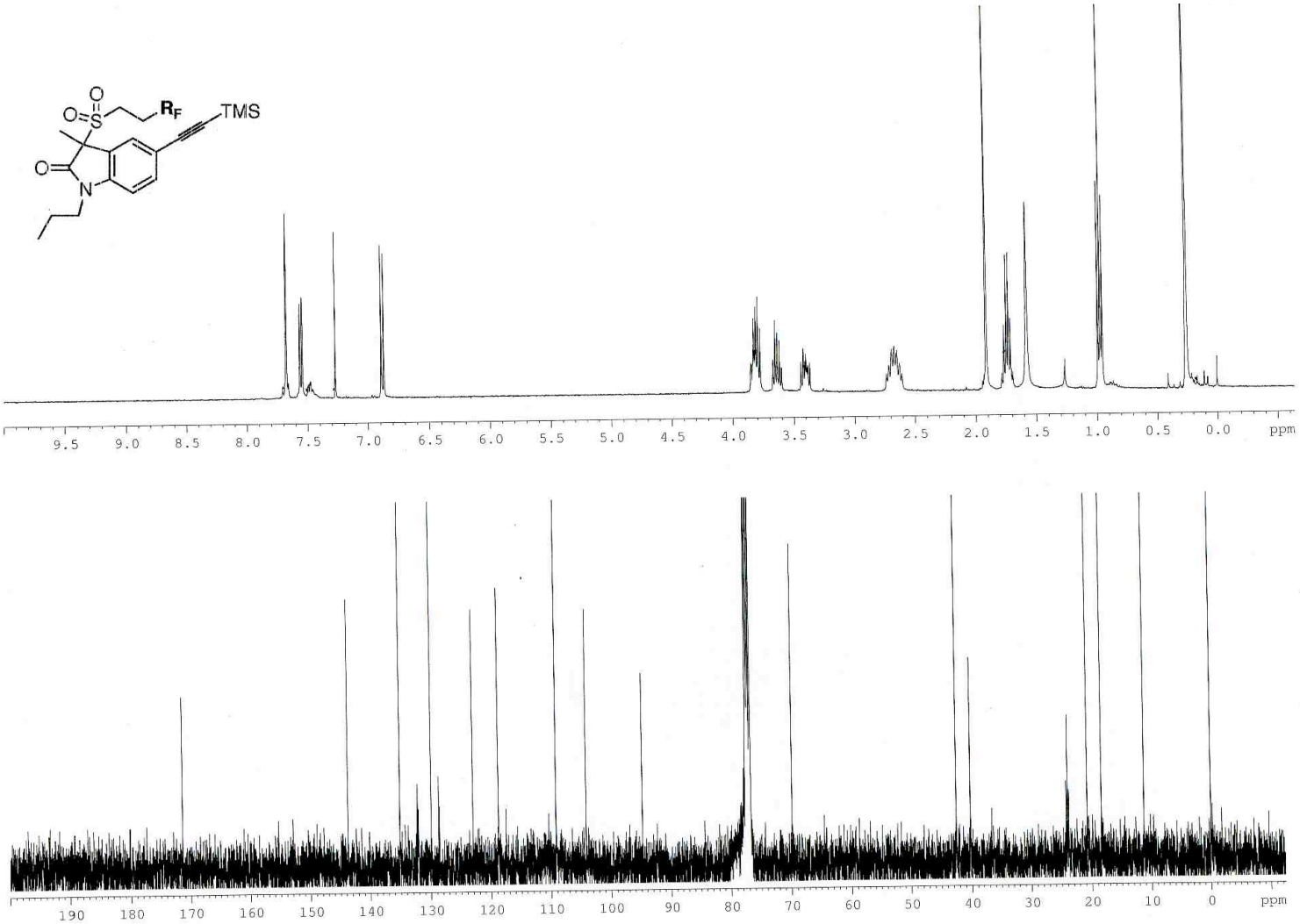
Modified fluorous tagged *N*-heterocycles

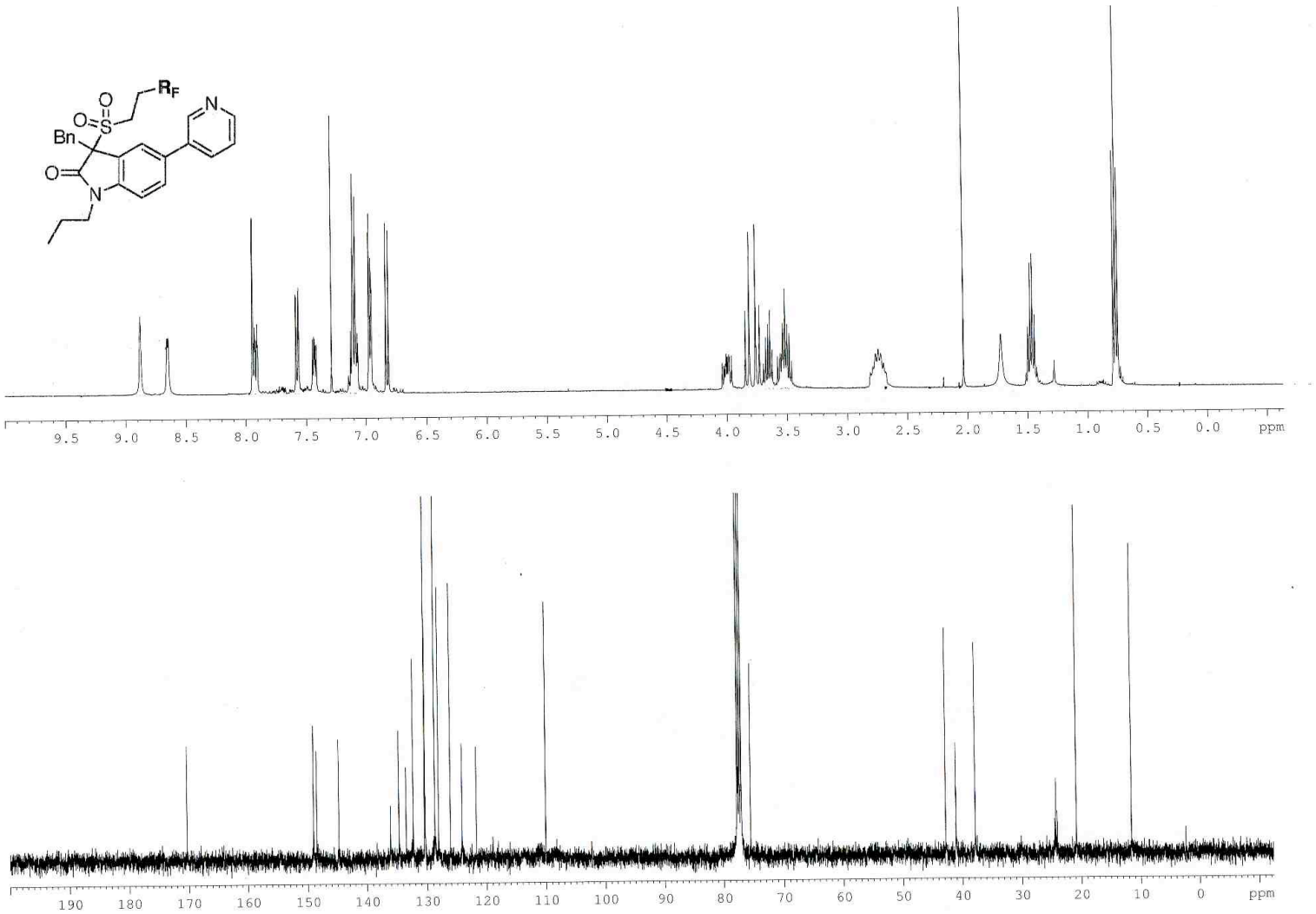


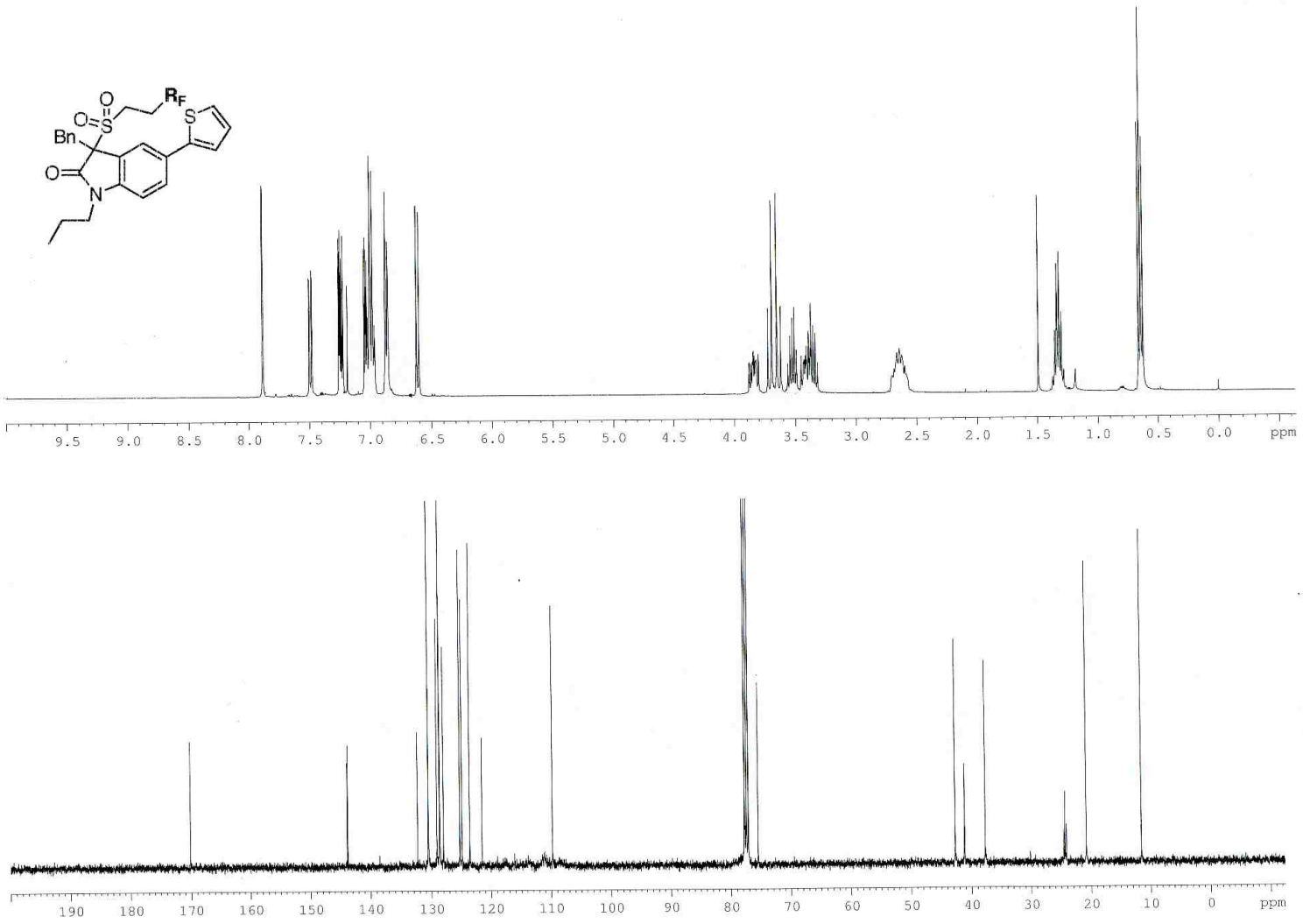

EtO2C
S
RF
F
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

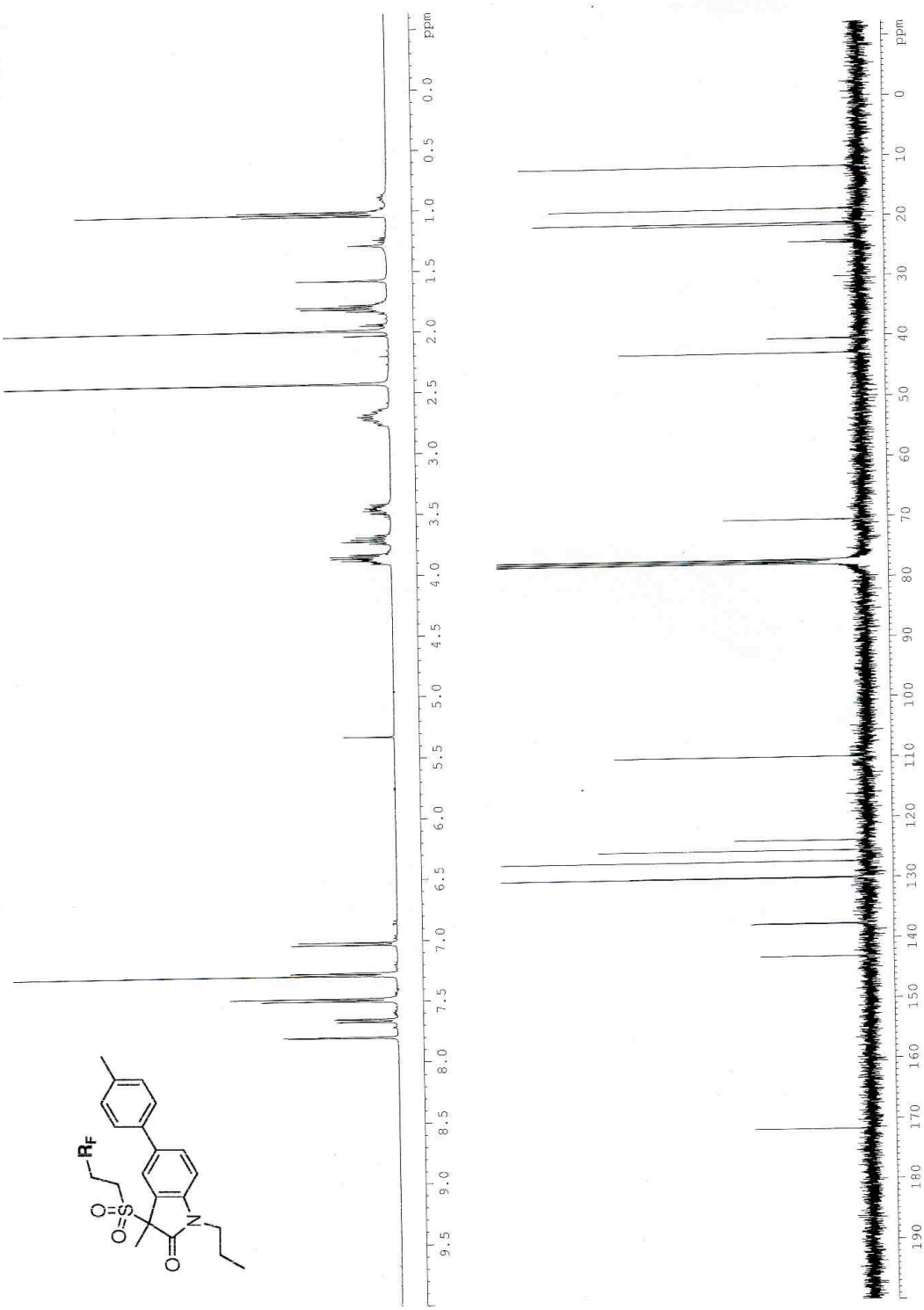

MeO
O
O
S
N
F
R_F
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

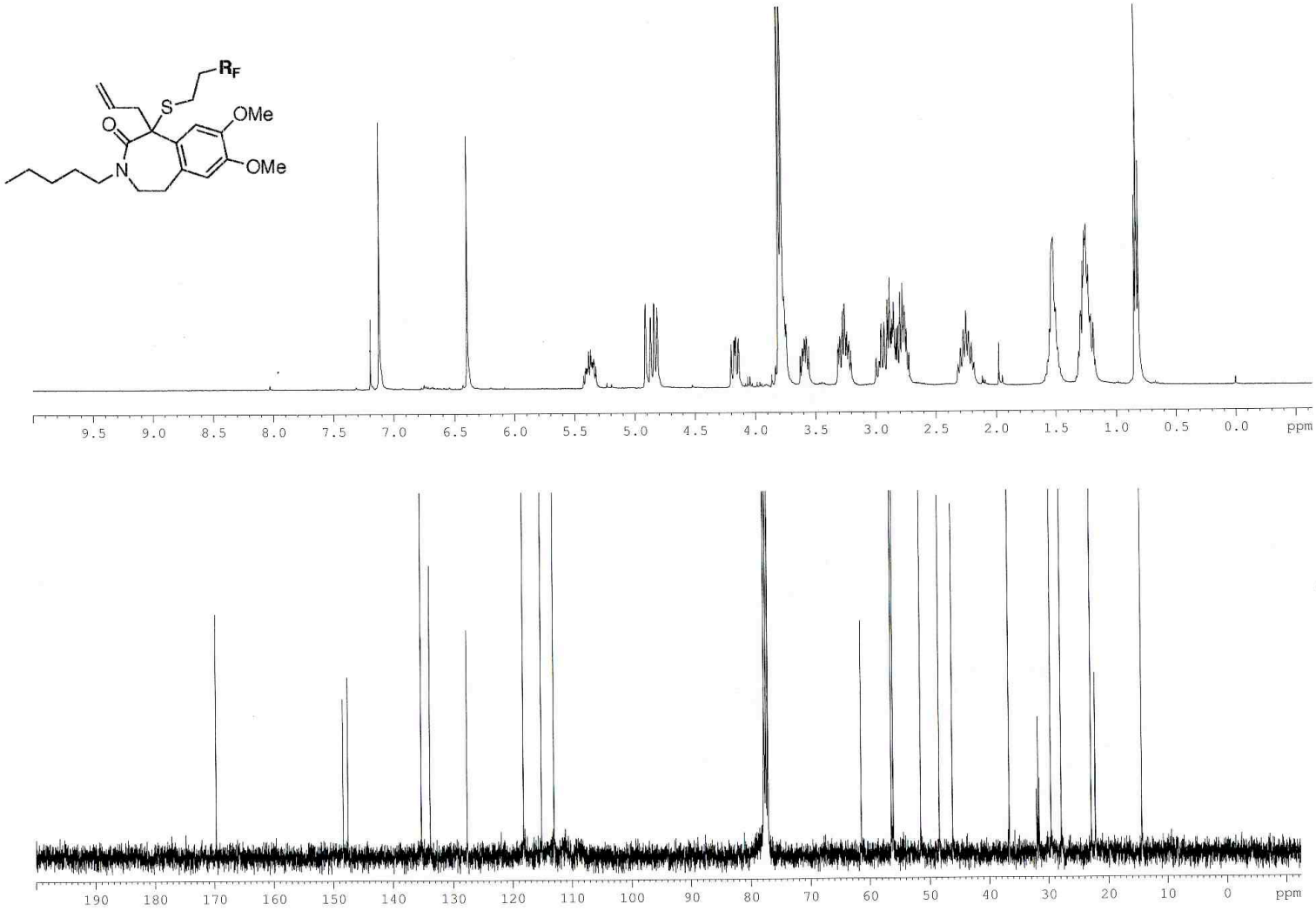

O
O=S
R_F
CH_2OH
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

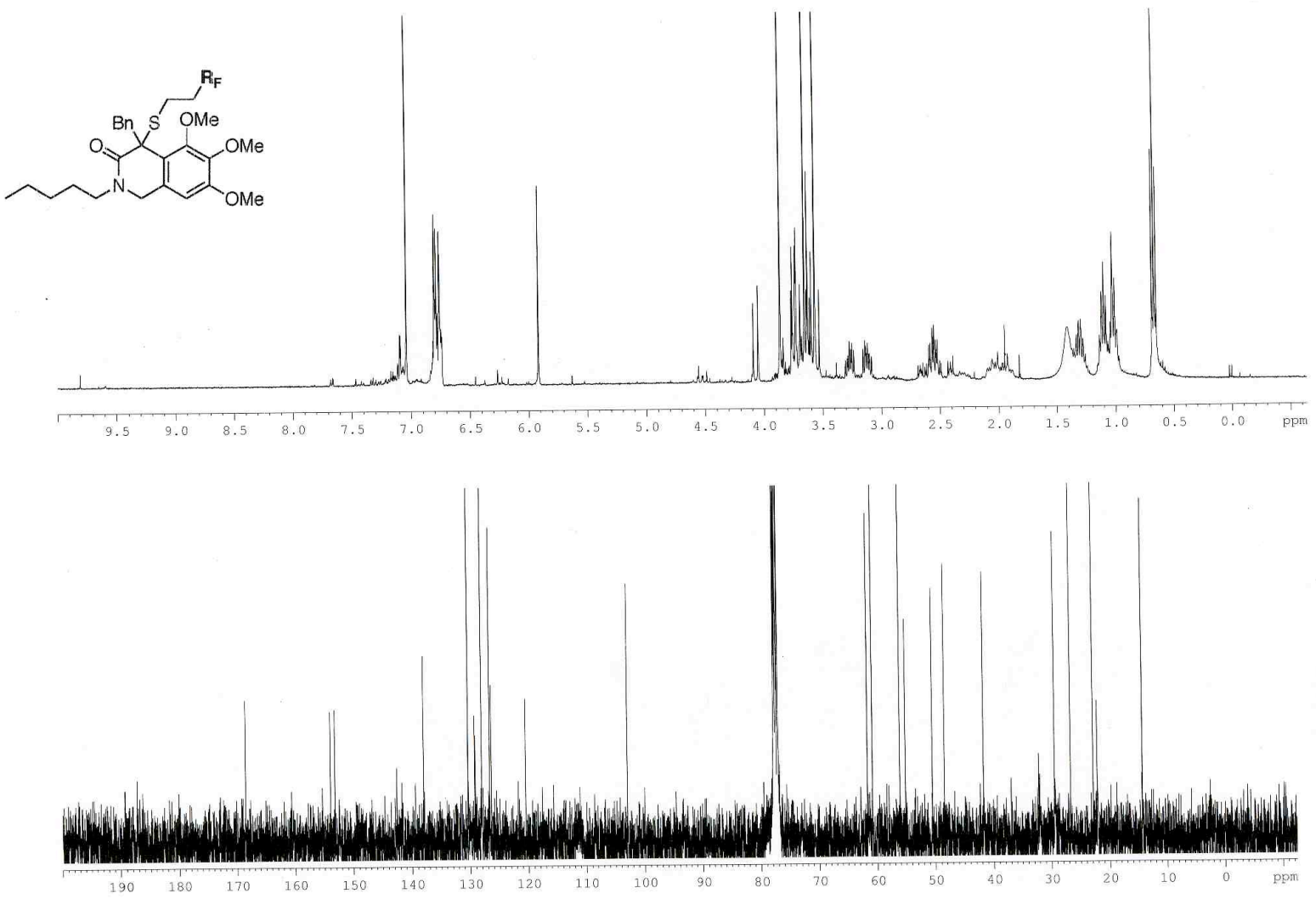

O
O=S
R_F
TMS
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Bn
O
O
S
O
N
N
R_F
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

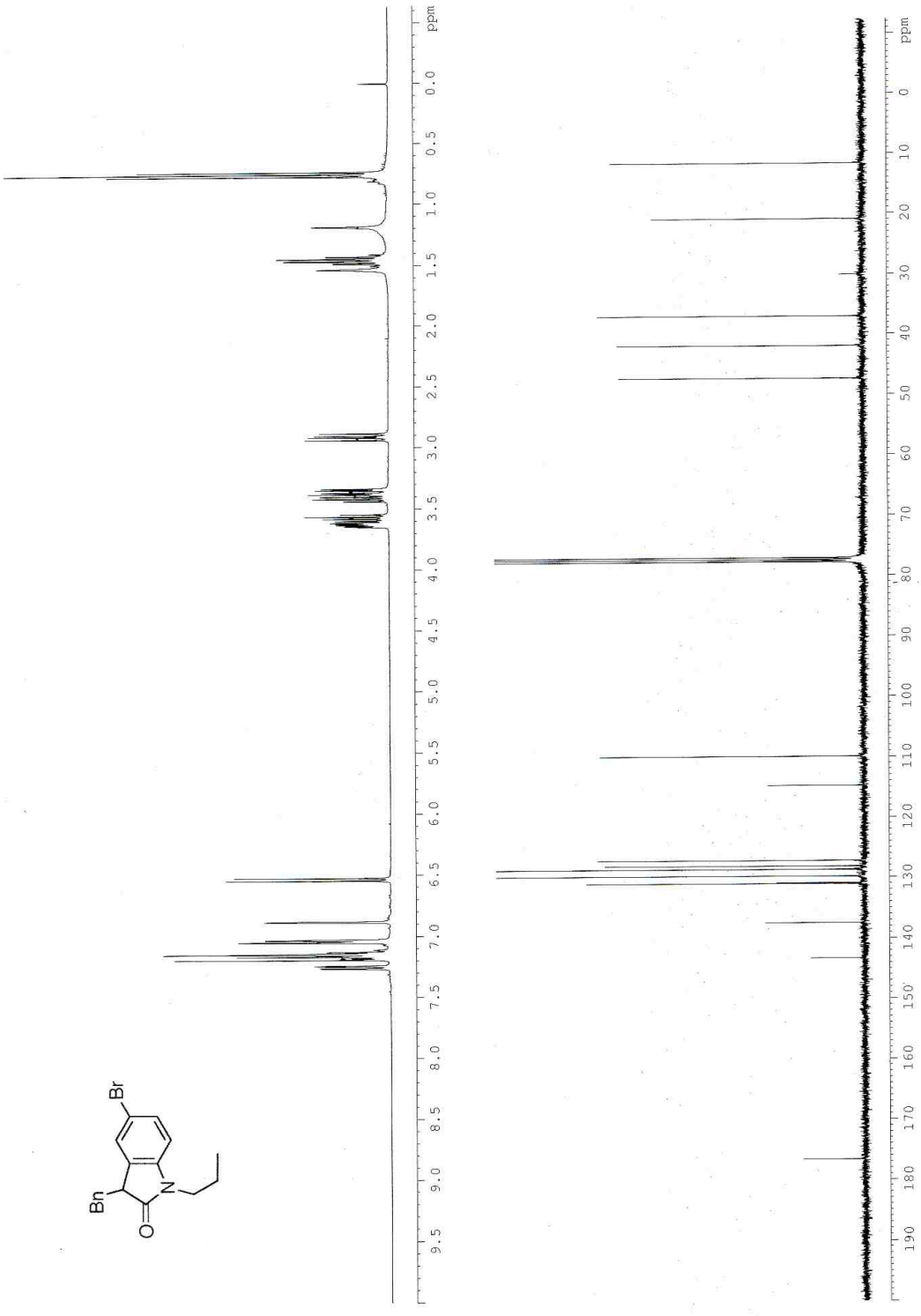

Bn
O
O
S
N
R_F
S
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

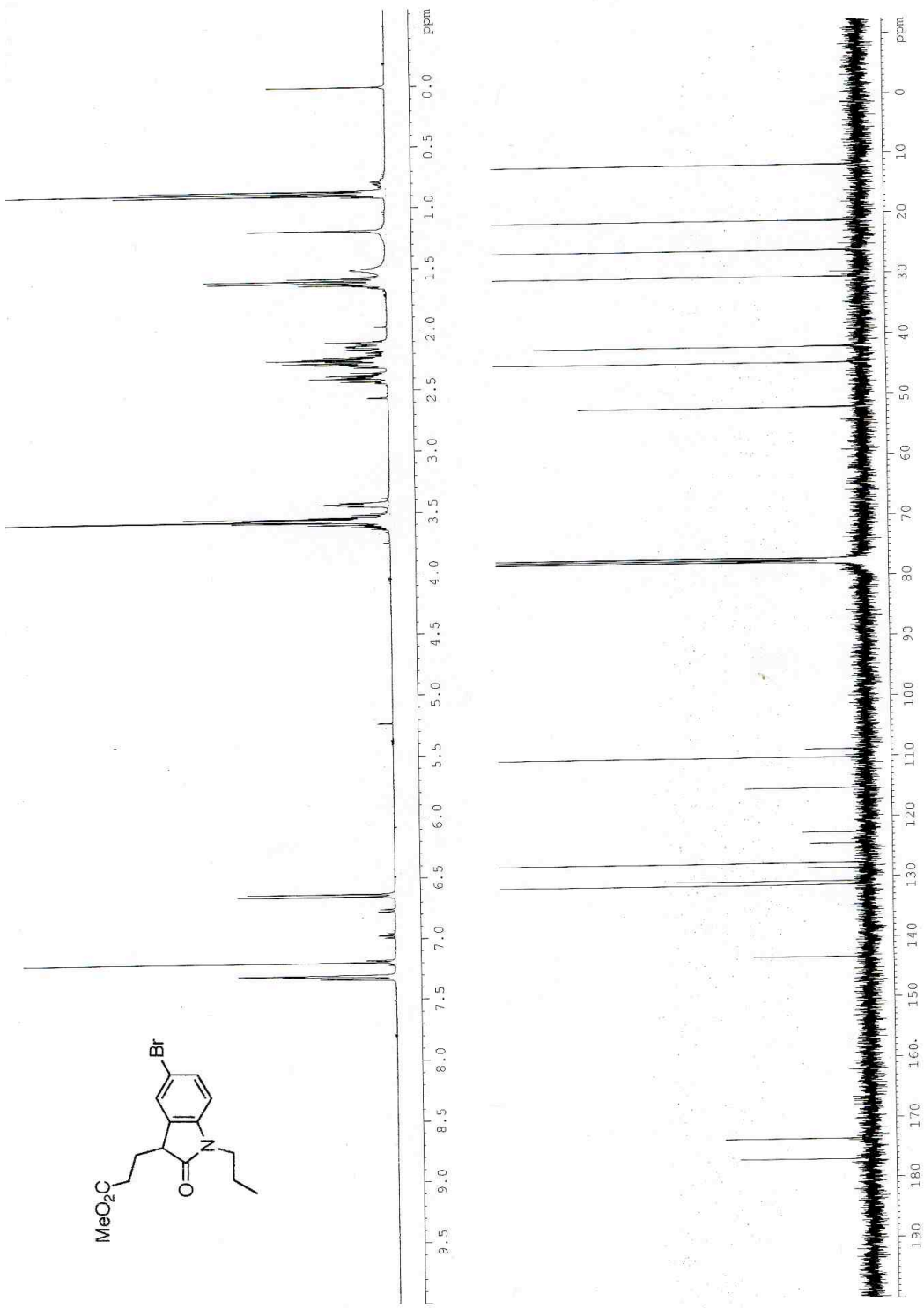

RF
O
S
O
N
O
ppm
ppm

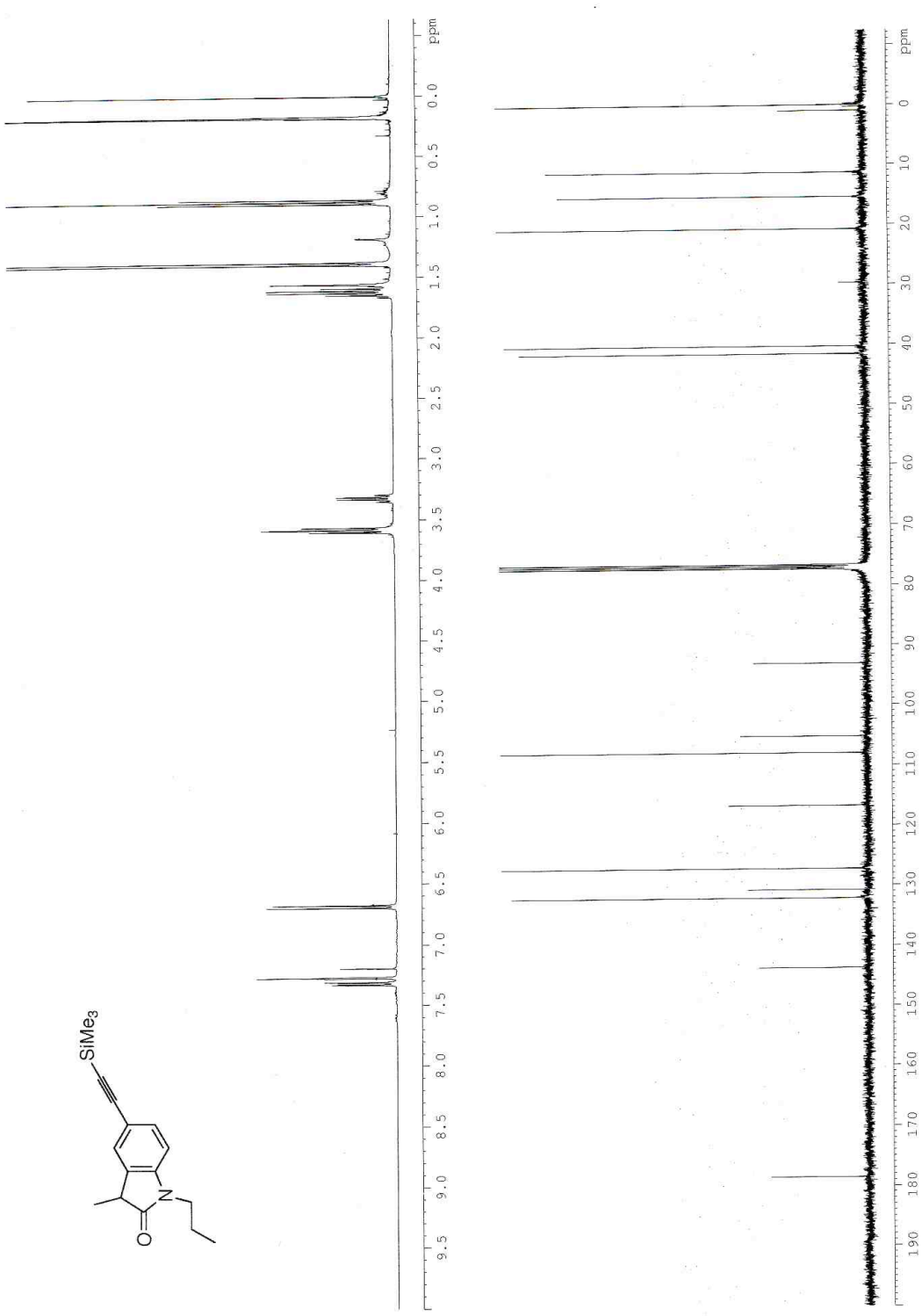

R_F
S
O
N
OMe
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

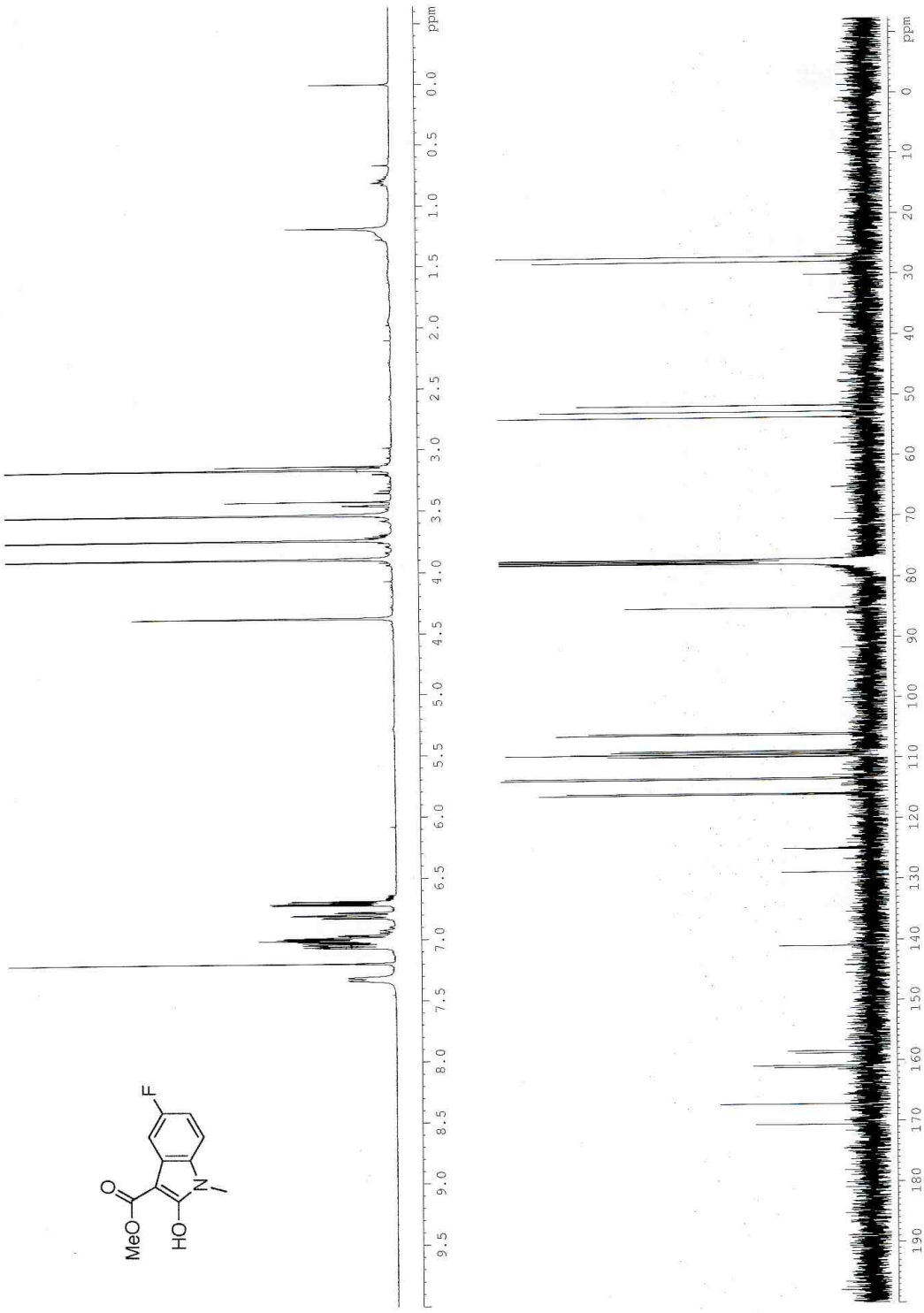

R_F
Bn
S
OMe
O
OMe
N
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

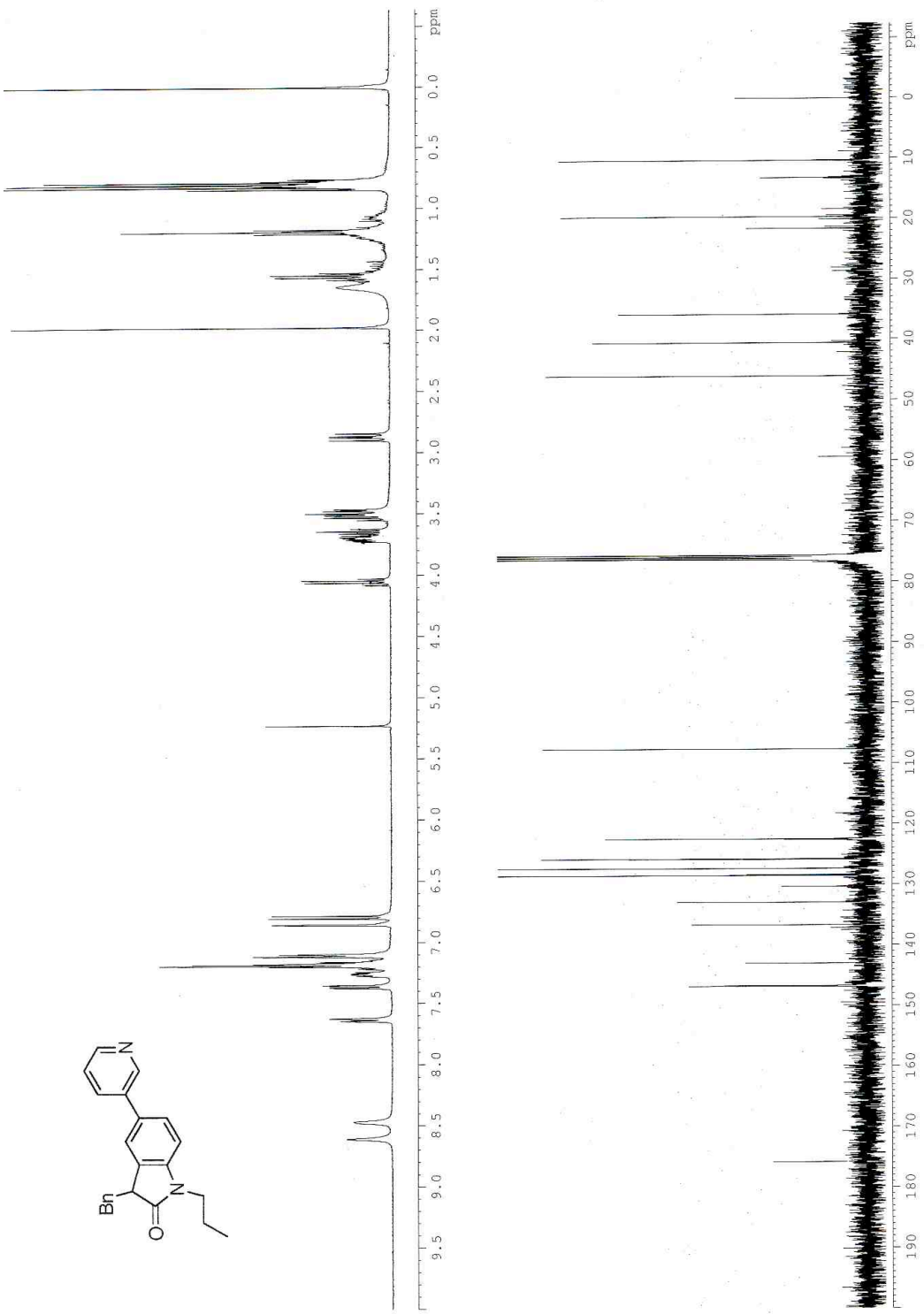
Cleaved *N*-heterocycles

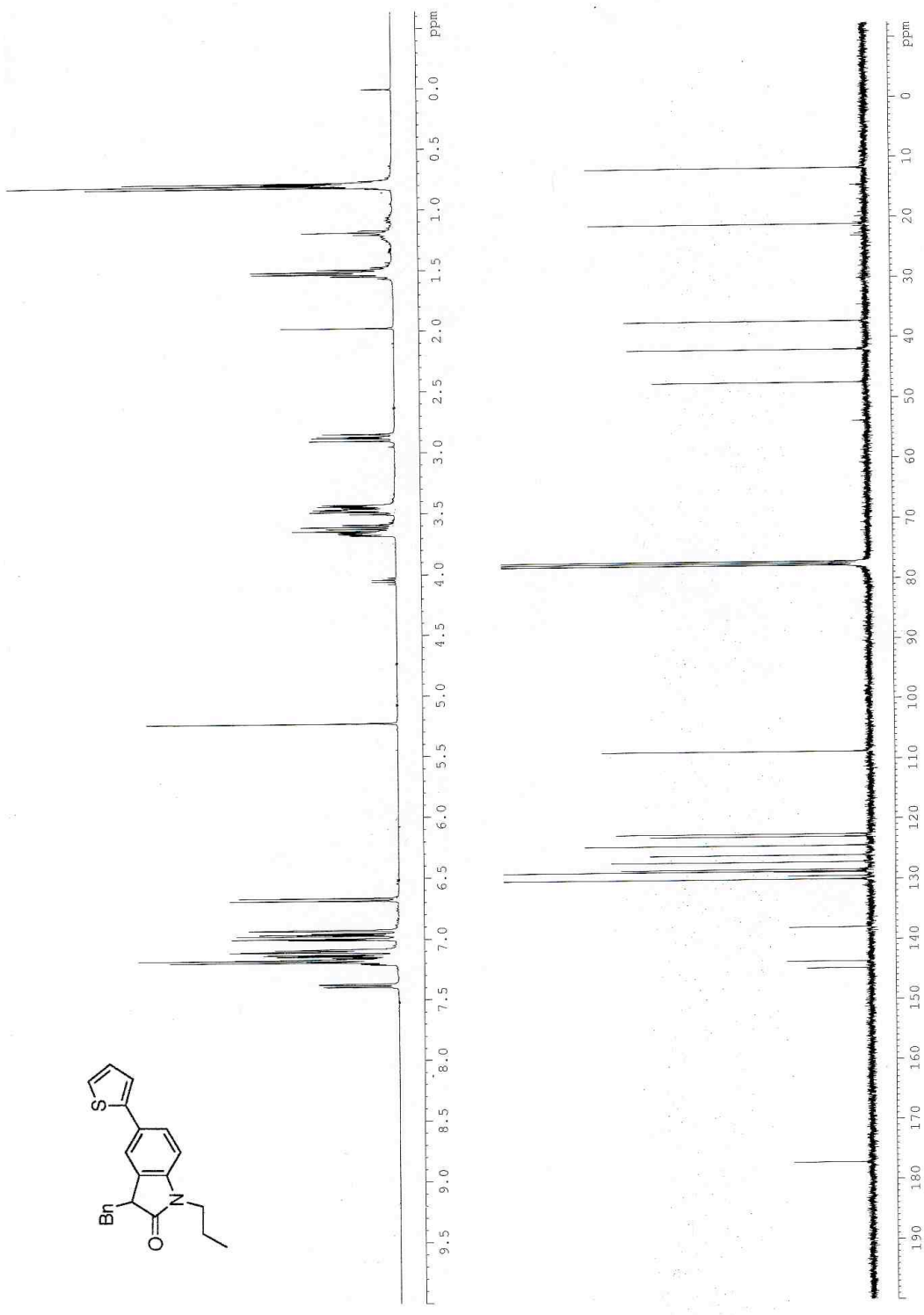


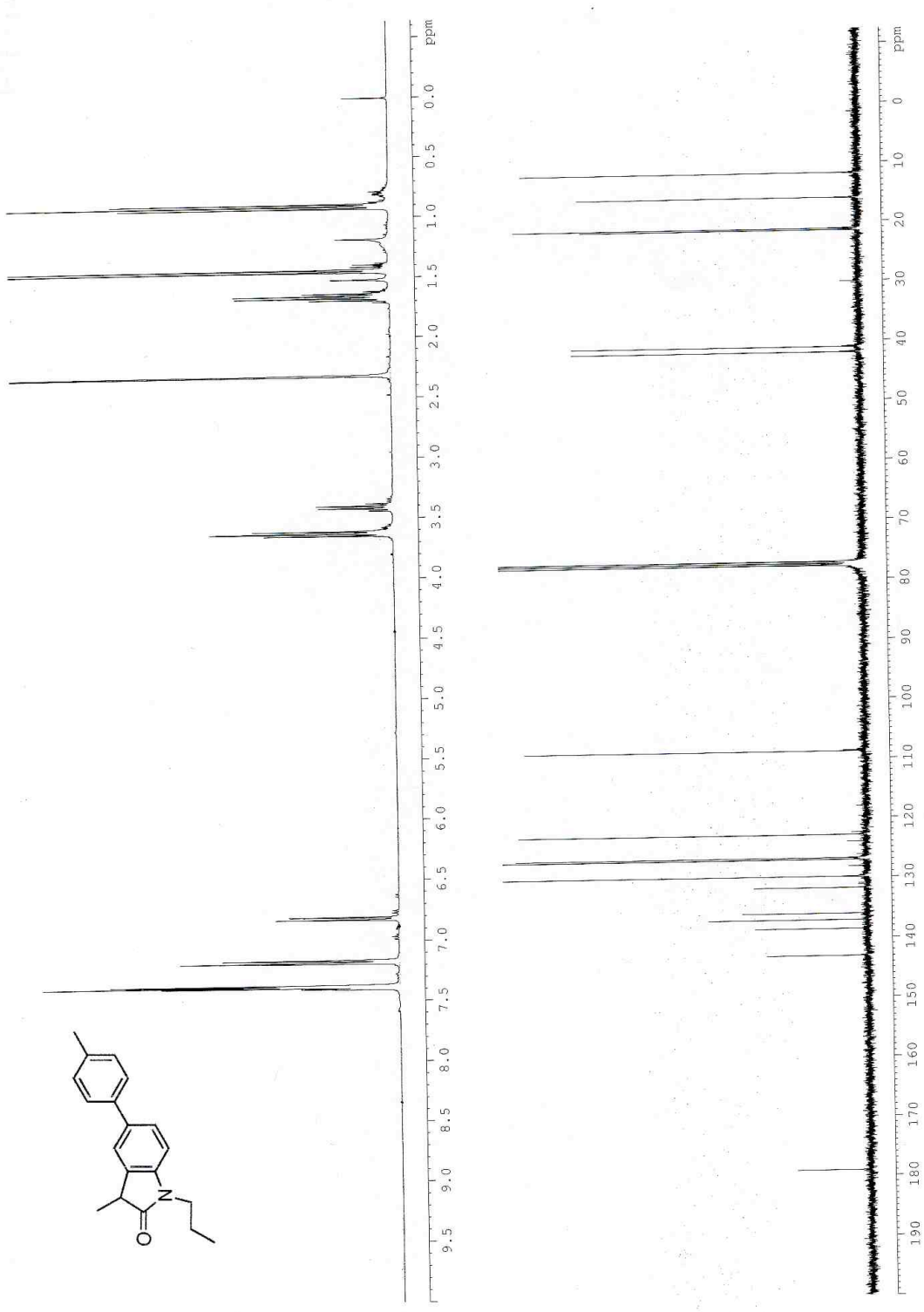

Br
MeO2C
O
N
ppm
ppm

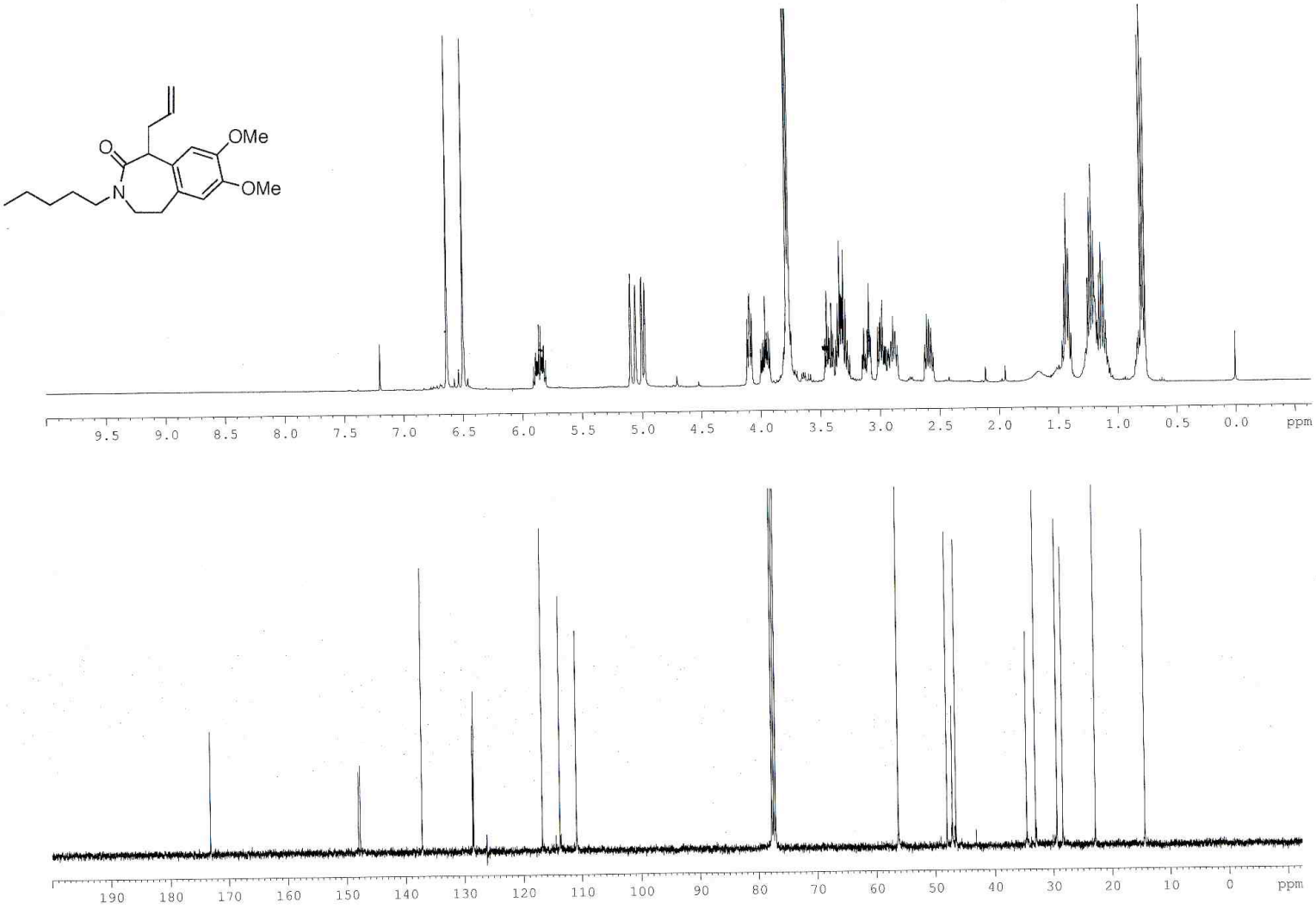

SiMe3
O
N
ppm
ppm

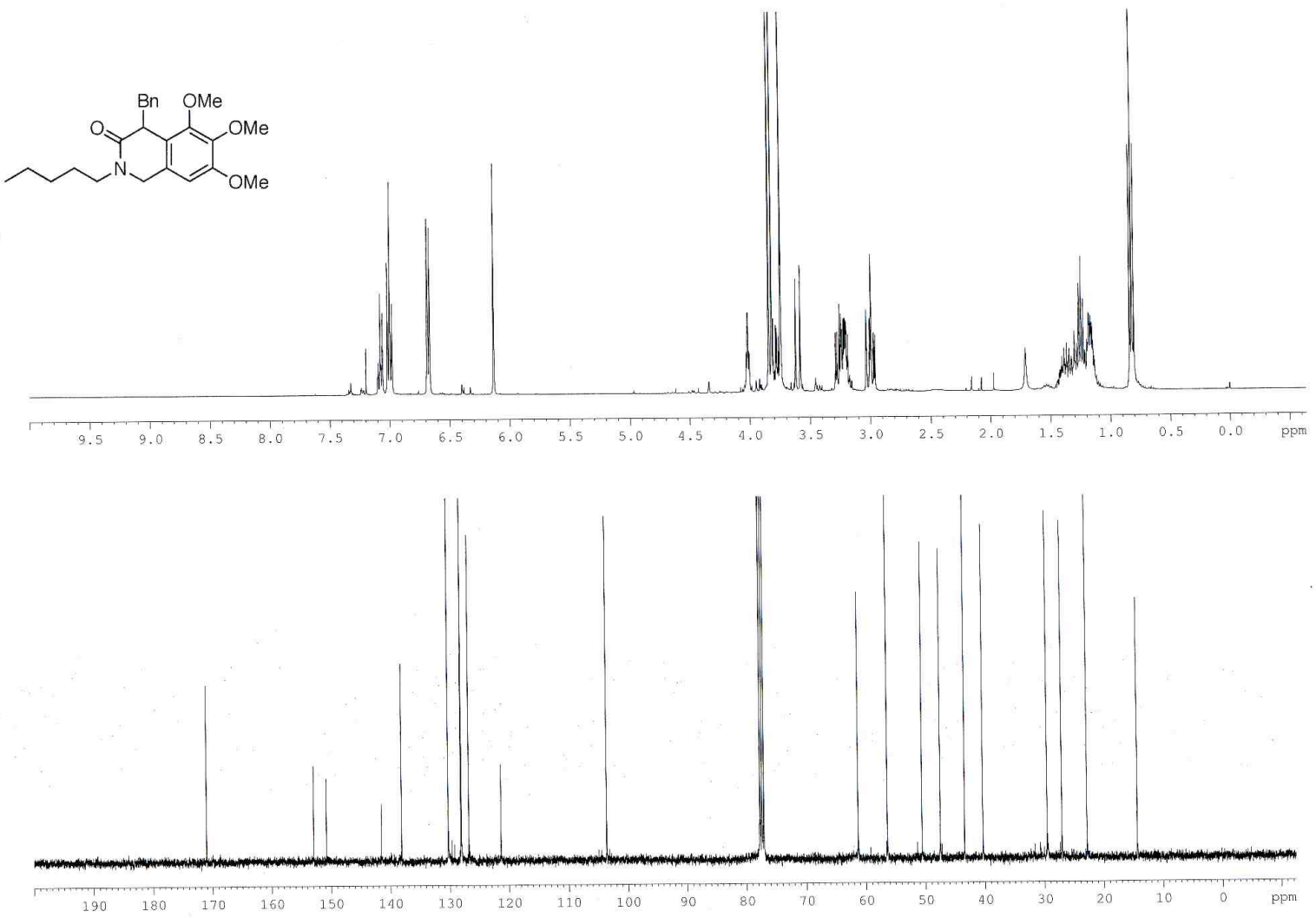

F
O
MeO
HO
N
ppm
ppm


Bn
N
O
N
ppm
ppm

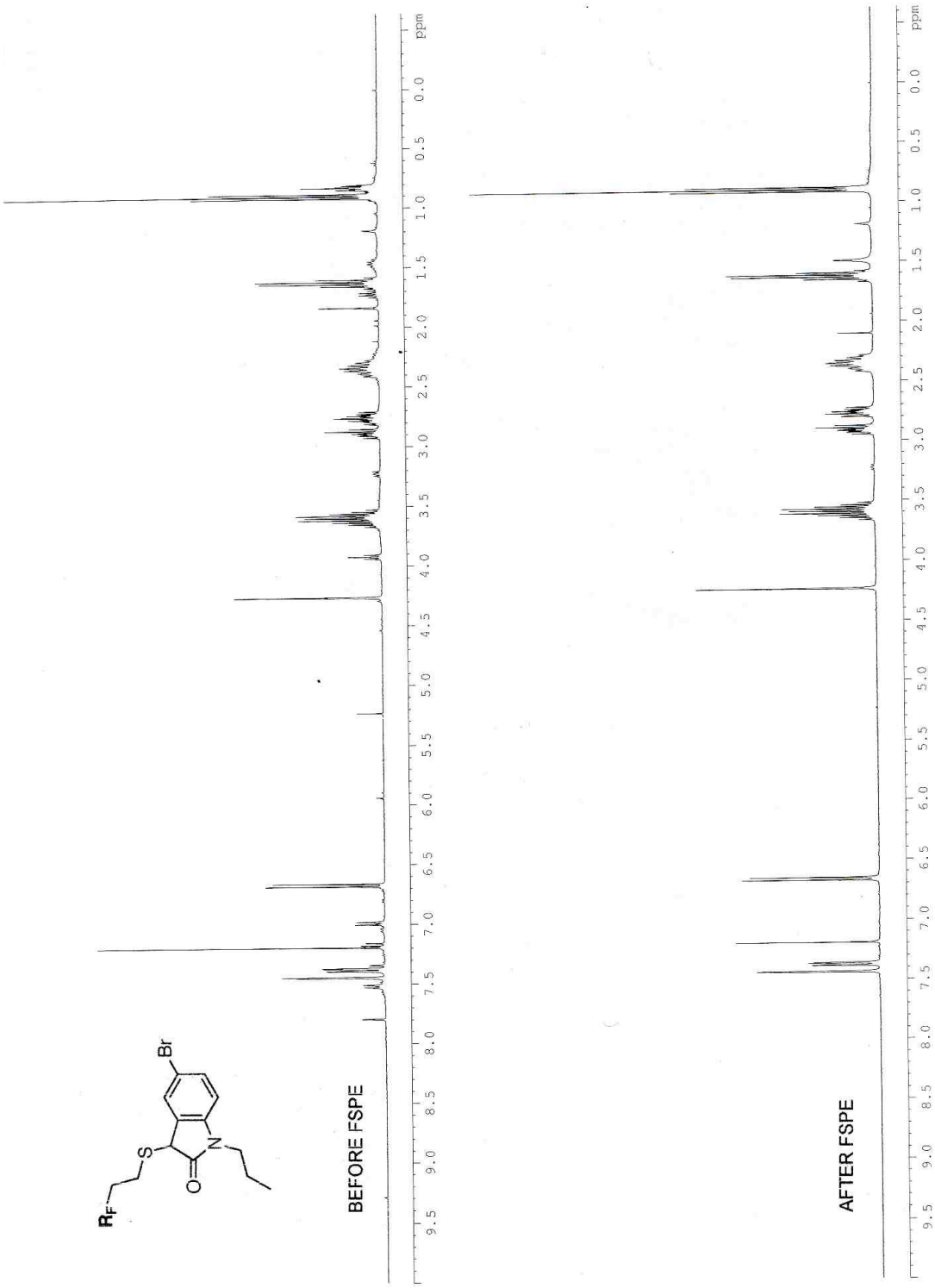

S
Bn
O
N
ppm
ppm

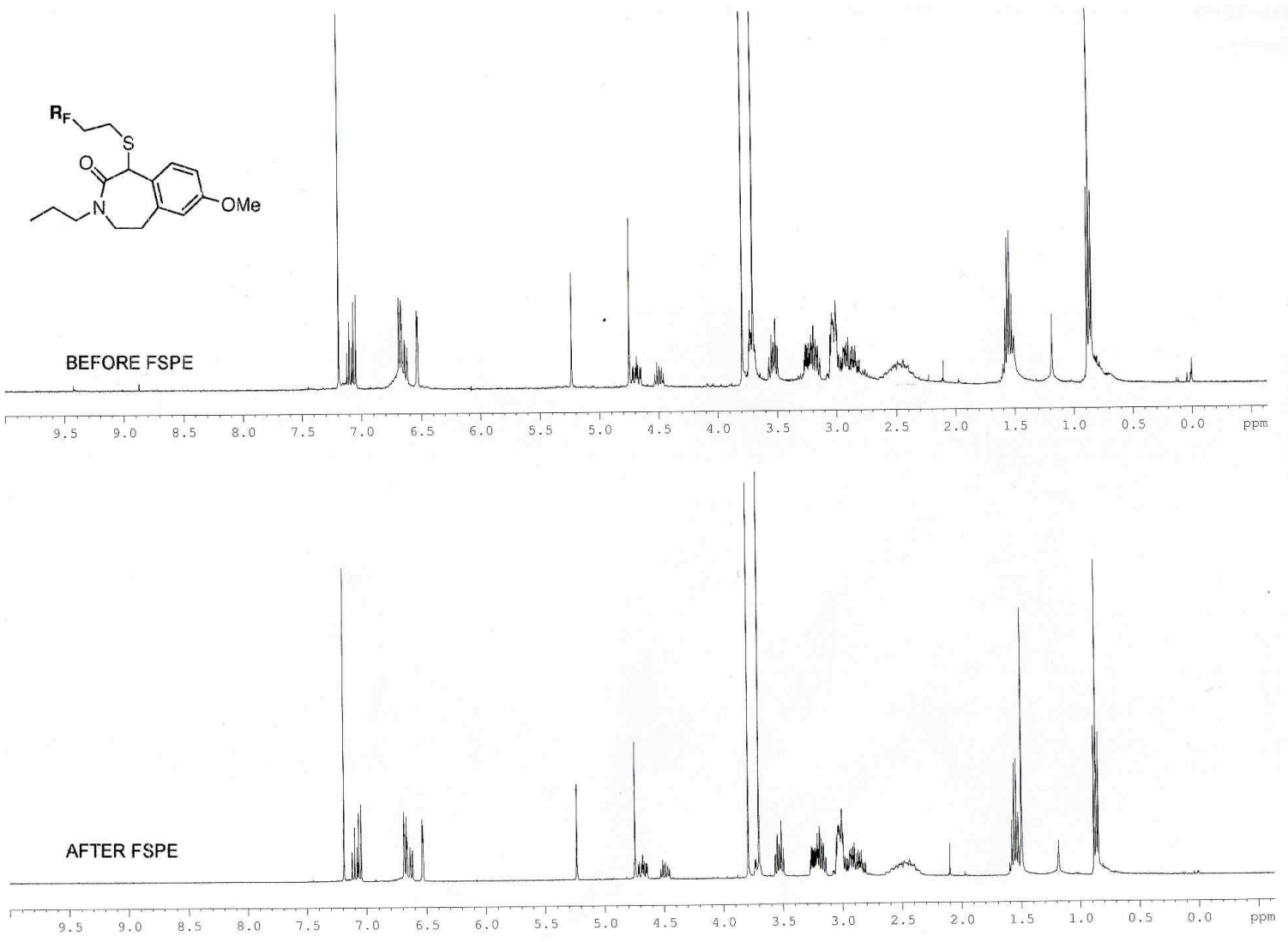

ppm
ppm


OMe
OMe
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

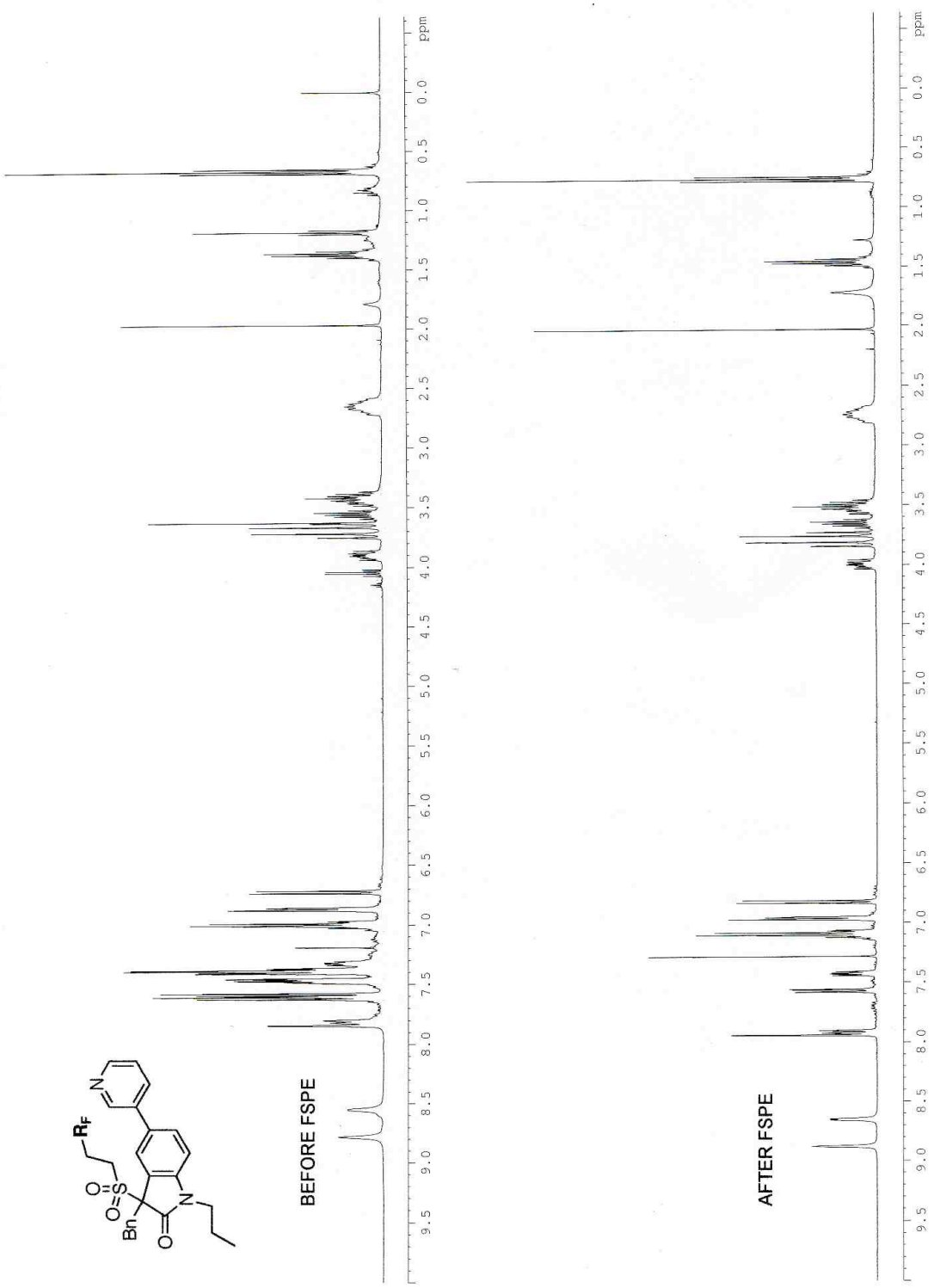

Bn
OMe
O
OMe
N
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

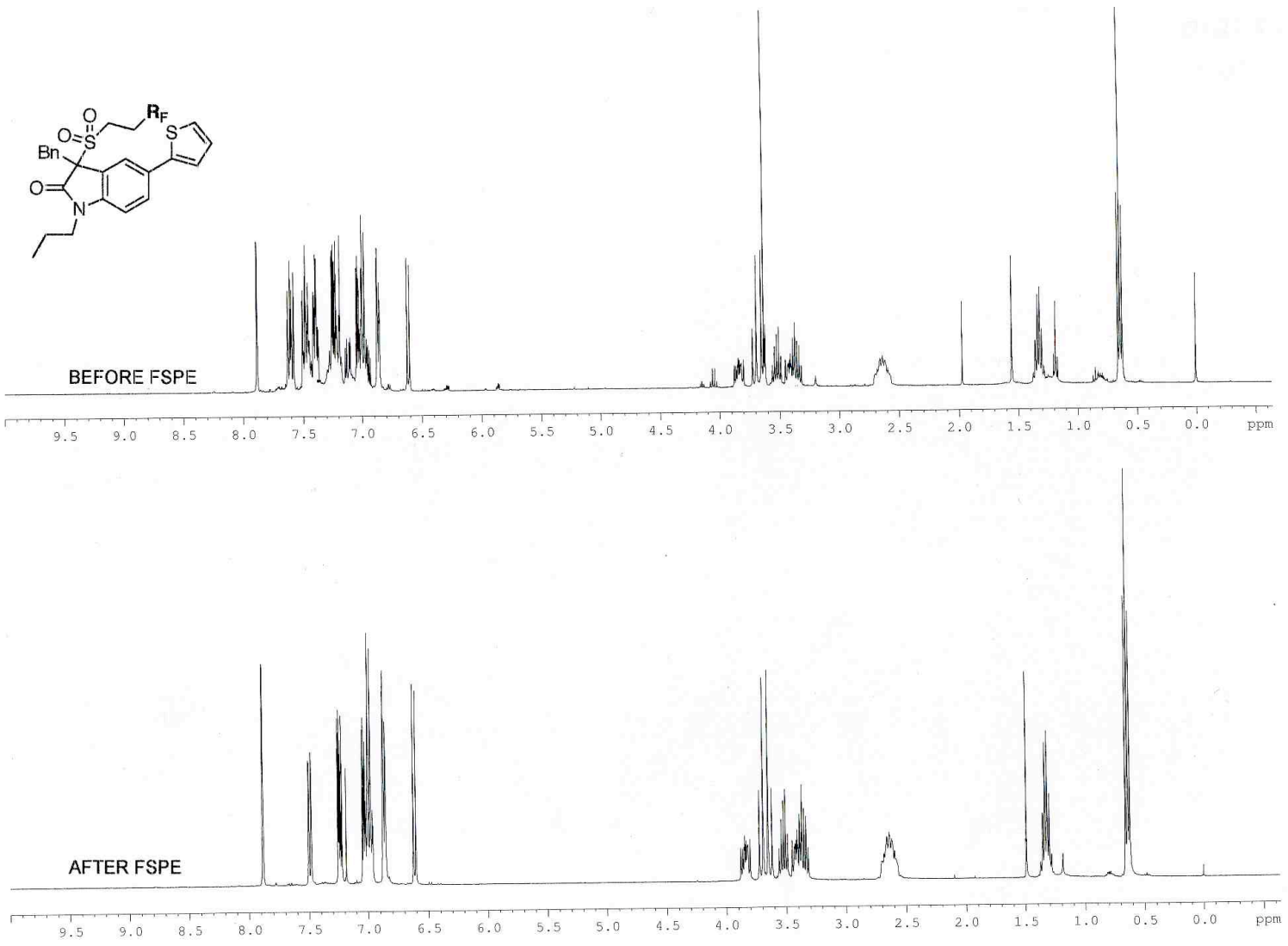
Before and after FSPE of fluorous-tagged *N*-heterocycles




R_F
S
O
N
OMe
BEFORE FSPE
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
AFTER FSPE
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

Before and after FSPE of modified fluorous-tagged *N*-heterocycles




BEFORE FSPE
AFTER FSPE
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

Before and after FSPE of cleaved *N*-heterocycles