Supporting information for:

Catalytic Asymmetric Inverse-Electron-Demand Diels-Alder Reactions of N-Sulfonyl-1-Aza-1,3-dienes

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Experimental Section

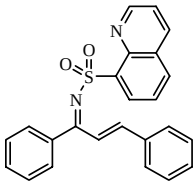
General methods.

Melting points were taken in open-end capillary tubes. NMR spectra were recorded [300 MHz (^{1}H), 75 MHz (^{13}C)] at room temperature in $CDCl_3$ calibrated at 7.26 ppm (^{1}H) or 77.0 ppm (^{13}C). Mass spectra (MS) were determined at an ionizing voltage of 70 eV. All the reactions were carried out in anhydrous solvents and under argon atmosphere. CH_2Cl_2 and CH_3CN were dried and stored over microwave-activated 4Å molecular sieves. Flash column chromatography was performed using silica gel (230-400 mesh). Enantiomeric excesses were determined by HPLC using Chiralpak AD (0.46 cm x 25 cm) and Chiralpak AS (0.46cm x 25 cm) as the chiral stationary phases.

General procedure for the synthesis of the sulfonyl imines of chalcones.[1]

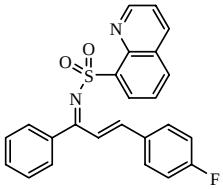
To a solution of sulfonamide (5.0 mmol) and α,β-unsaturated ketone (5.0 mmol) in CH_2Cl_2 (15 ml), cooled to 0 ºC, were successively added Et_3N (10 mmol) and $TiCl_4$ (5.0 mmol). The reaction mixture was heated at reflux overnight. Then the solution was cooled to room temperature, quenched with water (100 ml) and extracted with CH_2Cl_2 (3x 30 ml). The combined organic phase was dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography to afford pure α,β-unsaturated ketimines. Imines **1a**, **1b, 1c** and **1d** were described in a previous paper[2]

(*E*)-1,3-Diphenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (1e).



Chromatography: *n*-hexane-EtOAc 2:1. Yield: 76%. White solid; mp= 150-151 ºC. ^{1}H NMR: δ 9.09 (dd, *J*= 4.0 and 1.4 Hz, 1H), 8.59 (bs, 1H), 8.19 (dd, *J*= 8.2 and 1.3 Hz 1H), 7.99 (d, *J*= 7.9 Hz, 1H), 7.75-7.20 (m, 13H), 7.06 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR: δ 177.3, 151.2, 148.4, 143.9, 137.8, 136.2, 134.5, 133.6, 130.8, 130.5, 128.8, 128.5, 128.1, 125.1, 121.8. MS (FAB+) m/z 399.1 (M^+ +H, 100). FAB+ HRMS for $C_{24}H_{19}N_2O_2S$ (M^+): Calcd: 399.11672. Found: 399,11659.

(*E*)-3-(4-Fluorophenyl)-1-phenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (6e).

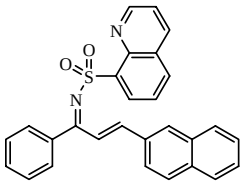


Chromatography: *n*-hexane-EtOAc 2:1. Yield: 71%.White solid; mp= 164-165 ºC. ^{1}H NMR: δ 9.01 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.51 (bs, 1H), 8.13 (dd, *J*= 8.4 and 1.7 Hz 1H), 7.95 (dd, *J*= 8.3 and 1.2 Hz, 1H), 7.60-

[1] (a) Ram, R. N.; Khan, A. A. *Synth. Commun.* **2001**, *31*, 841. (b) Sandrinelli, F.; Perrio S.; Belsin P. *J. Org. Chem.* **1997**, *62*, 8626. (c) Jennings, W. B.; Lovely, C. J. *Tetrahedron* **1991**, *29*, 5561.
[2] Esquivias, J.; Gómez Arrayás, R.; Carretero, J. C. *J. Org. Chem.* **2005**, *70*, 7451

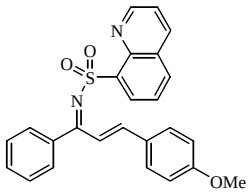
7.40 (m, 7H), 7.35-7.22 (m, 5H), 6.95 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR: δ 176.1, 151.3, 148.4, 144.1, 137.8, 136.3, 134.5, 133.8, 131.1, 130.7, 129.0, 128.7, 128.6, 125.3, 122.0. MS (FAB+) m/z 417.0 (M^+ +H, 100). FAB+ HRMS for $C_{24}H_{18}FN_2O_2S$ (M^+): Calcd: 417.10730. Found: 417.10821.

(*E*)-3-(2-Naphthyl)-1-phenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (7e).



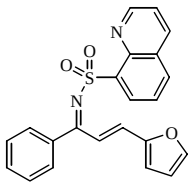
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 71%. Yellow solid; mp= 168-170 ºC. ^{1}H NMR: δ 8.99 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.50 (bs, 1H), 8.14 (dd, *J*= 8.3 and 1.7 Hz 1H), 7.87 (dd, *J*= 8.0 and 1.0 Hz, 1H), 7.84-7.20 (m, 15H), 7.11 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR: δ 177.4, 151.3, 148.7, 144.1, 138.0, 136.3, 134.5, 133.7, 133.2, 132.3, 130.8, 130.7, 128.9, 128.8, 128.7, 128.2, 127.8, 127.6, 126.8, 125.3, 123.9, 122.0. MS (FAB+) m/z 449.0 (M^+ +H, 42). FAB+ HRMS for $C_{28}H_{21}N_2O_2S$ (M^++1): Calcd: 449.13237. Found: 449.13098.

(*E*)-3-(4-Methoxyphenyl)-1-phenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (8e).



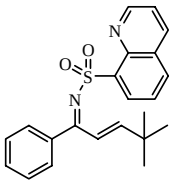
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 68%. Yellow solid; mp= 78-80 ºC. ^{1}H NMR: δ 9.00 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.48 (bs, 1H), 8.07 (dd, *J*= 8.3 and 1.7 Hz 1H), 7.88 (d, *J*= 7.0, 1H), 7.54-7.20 (m, 10H), 6.92 (d, *J*= 16.1 Hz, 1H), 6.78 (d, *J*= 8.7 Hz, 2H) 3.71 (s, 3H). ^{13}C NMR: δ 177.7, 162.1, 151.3, 148.9, 144.1, 138.2, 136.3, 133.6, 130.8, 130.6, 130.0, 129.0, 128.2, 128.1, 125.2, 121.9, 114.5, 55.5.

(*E*)- 3-(2-Furyl)-1-phenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (9e).



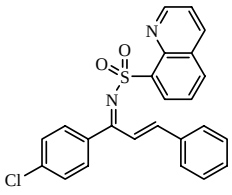
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 71%. Yellow solid; mp= 168-170 ºC. ^{1}H NMR: δ 9.03 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.50 (bs, 1H), 8.12 (dd, *J*= 8.3 and 1.7 Hz 1H), 7.94 (d, *J*= 8.2 Hz, 1H), 7.6-7.20 (m, 9H), 6.74 (d, *J*= 16.1 Hz, 1H), 6.57 (d, *J*= 3.4 Hz, 1H), 6.41 (dd, *J*= 3.4 and 1.8 Hz, 1H). ^{13}C NMR: δ 176.9, 151.3, 151.2, 146.0, 144.1, 138.3, 136.2, 134.5, 133.6, 131.2, 130.7, 129.8, 128.9, 128.1, 125.2, 121.9, 116.6, 112.8.

(*E*)-4,4-Dimethyl-1-phenyl-*N*-[(8-quinolyl)sulfonyl]pent-2-en-1-imine (10e).



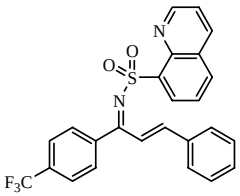
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 76%. White solid; mp= 148-150 ºC. ^{1}H NMR: δ 9.09 (dd, *J*= 4.0 and 1.6 Hz, 1H), 8.59 (bs, 1H), 8.21 (dd, *J*= 8.4 and 1.3 Hz 1H), 8.03 (d, *J*= 8.1 Hz, 1H), 7.70-7.30 (m, 8H), 6.03 (d, *J*= 16.1 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR: δ 178.2, 163.6, 151.4, 144.1, 138.3, 136.2, 133.6, 130.7, 128.9, 128.0, 125.3, 121.9, 34.9, 28.6.

(*E*)-1-(4-Chlorophenyl)-3-phenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (11e).



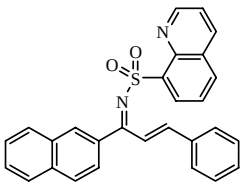
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 78%. White solid; mp= 130-132 ºC. ^{1}H NMR: δ 9.01 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.51 (bs, 1H), 8.13 (dd, *J*= 8.4 and 1.7 Hz 1H), 7.95 (dd, *J*= 8.3 and 1.2 Hz, 1H), 7.59-7.40 (m, 6H), 7.35-7.23 (m, 7H), 6.95 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR: δ 176.1, 151.3, 148.4, 144.1, 137.8, 136.3, 134.5, 133.8, 131.1, 130.7, 129.0, 128.7, 128.5, 125.3, 122.0.

(*E*)-3-Phenyl-*N*-[(8-quinolyl)sulfonyl]-1-[4-(trifluoromethyl)phenyl]prop-2-en-1-imine (12e).



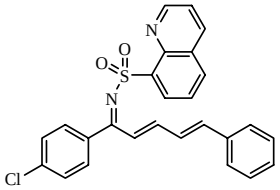
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 71%. Yellow solid; mp= 78-80 ºC. ^{1}H NMR: δ 9.02 (dd, *J*= 4.3 and 1.9 Hz, 1H), 8.54 (bs, 1H), 8.14 (dd, *J*= 8.3 and 1.1 Hz 1H), 7.97 (d, *J*= 8.3 Hz, 1H), 7.60-7.28 (m, 12H), 6.95 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR: δ 175.9, 151.4, 149.3, 144.1, 137.8, 136.4, 134.4, 134.0, 131.4, 130.8, 129.1, 128.9, 128.6, 125.4, 122.1. MS (FAB+) m/z 467.0 (M^{+} +H, 100). FAB+ HRMS for $C_{25}H_{18}F_3N_2O_2S$ (M^{+}): Calcd: 467.10411. Found: 467.10628.

(*E*)-1-(2-Naphthyl)-3-phenyl-*N*-[(8-quinolyl)sulfonyl]prop-2-en-1-imine (13e).



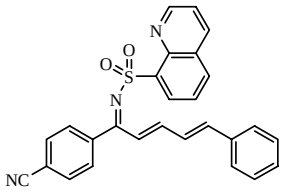
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 73%. Yellow solid; mp= 83-85 ºC. ^{1}H NMR: δ 9.06 (dd, *J*= 4.3 and 1.8 Hz, 1H), 8.54 (bs, 1H), 8.14 (d, *J*= 8.3 Hz 1H), 7.88 (d, *J*= 7.0 Hz, 1H), 7.54-7.20 (m, 15H), 7.02 (d, *J*= 16.1 Hz, 1H). ^{13}C NMR: δ 177.4, 151.3, 148.4, 144.2, 136.3, 134.8, 133.6, 132.3, 130.9, 130.8, 129.1, 129.0, 128.7, 128.0, 127.7, 126.7, 125.3, 122.0.

(2*E*,4*E*)-1-(*p*-chlorophenyl)-5-phenyl-*N*-[(8-quinolyl)sulfonyl]penta-2,4-dien-1-imine (14e).



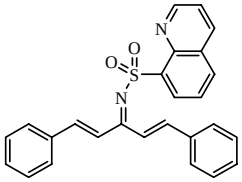
Chromatography: *n*-hexane-EtOAc 2:1. Yield: 69%. yellow solid; mp= 118-120 ºC. ^{1}H NMR: δ 9.15 (dd, *J*= 4.3 and 1.8 Hz, 1H), 8.62 (bs, 1H), 8.26 (dd, *J*= 8.3 and 1.6 Hz 1H), 8.09 (d, *J*= 8.2 Hz, 1H), 7.7-7.31 (m, 12H), 7.15 (m, 1H), 6.92 (m, 2H). ^{13}C NMR: δ 175.9, 151.4, 149.2, 144.1, 142.8, 137.9, 136.4, 135.7, 133.9, 131.3, 130.8, 129.7, 129.0, 128.9, 128.5, 127.6, 127.4, 125.3, 122.0.

(2*E*,4*E*)-1-(*p*-cyanophenyl)-5-phenyl-*N*-[(8-quinolyl)sulfonyl]penta-2,4-dien-1-imine (15e).



Chromatography: *n*-hexane-EtOAc 2:1. Yield: 72%. yellow solid; mp= 158-160 ºC. ^{1}H NMR: δ 9.13 (dd, *J*= 4.3 and 1.8 Hz, 1H), 8.60 (bs, 1H), 8.22 (dd, *J*= 8.3 and 1.6 Hz 1H), 8.04 (d, *J*= 8.2 Hz, 1H), 7.65-7.30 (m, 12H), 7.01 (m, 1H), 6.91 (m, 2H). ^{13}C NMR: δ 175.9, 151.4, 149.2, 144.1, 142.8, 137.9, 136.4, 135.7, 133.9, 131.3, 130.7, 129.7, 129.0, 128.9, 128.5, 127.6, 127.4, 125.3, 122.0.

(1*E*,4*E*)-1,5-diphenyl-*N*-[(8-quinolyl)sulfonyl]penta-1,4-dien-3-imine (16e).

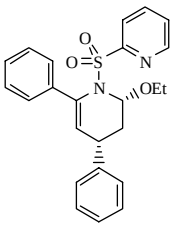


Chromatography: *n*-hexane-EtOAc 2:1. Yield: 62%. yellow solid; mp= 150-152 ºC. ^{1}H NMR: δ 9.10 (dd, *J*= 4.3 and 1.8 Hz, 1H), 8.69 (d, *J*= 7.4 Hz, 1H), 8.22 (dd, *J*= 8.3 and 1.6 Hz 1H), 8.04 (d, *J*= 8.2 Hz, 1H), 7.70-7.28 (m, 16H). ^{13}C NMR: δ 172.8, 151.4, 144.2, 144.0, 138.2, 136.4, 134.9, 133.8, 130.8, 130.6, 129.0, 128.9, 128.5, 125.4, 128.5, 123.9, 122.0.

General procedure for the asymmetric inverse electron demand ADAR.

A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.02 mmol) and (*R*,*R*)-DBFOX (9.2 mg, 0.022 mmol) in CH_2Cl_2 (1 ml) was stirred at room temperature for 4 h in a schlenk flask. Then a solution of ketimine (0.2 mmol) in CH_2Cl_2 (1 ml) was added, followed by the vinyl ether (5 equiv). The reaction was stirred at room temperature until consumption of the starting imine (72 h in all cases, except for azadiene **21e** and azatrienes **25e** and **26e** which required 120 h). Then, the mixture was quenched with saturated aqueous NH_4Cl and extracted several times with CH_2Cl_2. The combined organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography using CH_2Cl_2 in deactivated SiO_2.

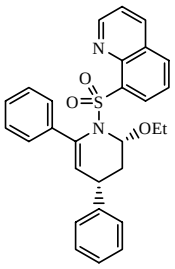
2-Ethoxy-4,6-diphenyl-1-[(2-pyridyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**2d**).



Yield: 85%; white solid; mp= 69-71 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (ddd, *J*= 4.6, *J*= 1.6 and *J*= 0.8 Hz, 1H), 7.80 (m, 1H), 7.65 (m, 1H), 7.53 (ddd, *J*= 7.5, 4.6 and 1.1 Hz, 1H), 7.34-7.05 (m, 10H), 5.98 (dd, *J*= 6.1 and 4.2 Hz, 1H), 5.96 (d, *J*= 3.4 Hz, 1H), 4.19 (dq, *J*= 9.5 and 7.0 Hz, 1H), 3.83 (dq, *J*= 9.5 and 7.0 Hz, 1H), 2.87 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.62 (ddd, *J*= 14.0, 7.1 and 5.9 Hz, 1H), 2.07 (ddd, *J*= 14.0, 7.8 and 4.2 Hz, 1H), 1.27 (t, *J*= 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.3, 150.0, 144.0, 138.6, 137.6, 136.6, 128.4, 127.9, 127.7,

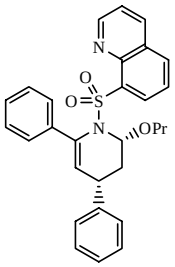
127.5, 126.9, 126.6, 126.5, 123.6, 85.4, 63.9, 40.2, 37.6, 14.9. $[\alpha]_D^{20}$ = -43 (*c* 0.65, $CHCl_3$). Enantiomeric excess: 66% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 15.7 (*minor*), t_R 23.1 (*major*). MS FAB$^+$ *m/z*: 375.0 (M^+-OEt, 100). FAB HRMS for $C_{24}H_{25}N_2O_3S$ (M^+): Calcd: 421,15076. Found: 421,15104.

2-Ethoxy-4,6-diphenyl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**2e**).



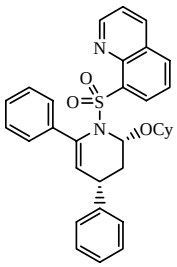
Yield 73%; white solid; mp= 65-67 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.32 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.11 (dd, *J*=7.4 and 1.4 Hz, 1H), 8.06 (dd, *J*=8.2 and 1.3 Hz, 1H), 7.63 (dd, *J*= 8.3 and 4.2 Hz, 1H), 7.47 (m, 1H), 7.31-7.12 (m, 9H), 6.89 (dd, *J*= 7.9 and 1.7 Hz, 1H), 6.55 (dd, *J*= 5.7 and 4.3 Hz, 1H), 5.87 (d, *J*= 3.3 Hz, 1H), 4.22 (dq, *J*= 9.6 and 7.1 Hz, 1H), 3.91 (dq, *J*= 9.6 and 7.1 Hz, 1H), 2.73-2.55 (m, 2H), 2.08 (ddd, *J*= 13.2, 7.4 and 3.4 Hz, 1H), 1.27 (t, *J*= 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.3, 144.0, 139.0, 137.4, 136.7, 133.9, 133.8, 128.9, 128.2, 127.9, 127.7, 126.9, 126.8, 126.3, 125.4, 122.2, 85.1, 63.7, 41.3, 37.8, 15.2. $[\alpha]_D^{20}$= -22 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 88% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 32.3 (*minor*), t_R 37.3 (*major*). MS FAB$^+$ *m/z*: 425.1 (M^+-OEt, 85), FAB HRMS for $C_{28}H_{28}O_3N_2S$ (M^+): Calcd: 471.17424. Found: 471.17582.

4,6-Diphenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**3e**).



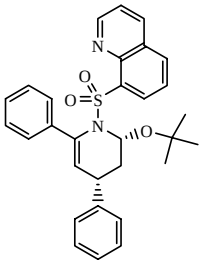
Yield 66%; white solid; mp= 53-55 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.22 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.98 (dd, *J*=7.4 and 1.3 Hz, 1H), 7.94 (dd, *J*=8.2 and 1.3 Hz, 1H), 7.53 (dd, *J*= 8.3 and 4.2 Hz, 1H), 7.37 (m, 1H), 7.21-7.02 (m, 9H), 6.83 (dd, *J*= 7.9 and 1.7 Hz, 1H), 6.39 (dd, *J*= 5.6 and 3.8 Hz, 1H), 5.74 (d, *J*= 3.4 Hz, 1H), 4.02 (dq, *J*= 9.5 and 6.7 Hz, 1H), 3.69 (dq, *J*= 9.5 and 6.7 Hz, 1H), 2.65 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.48 (ddd, *J*= 15.0, 7.2 and 1.4 Hz, 1H), 1.98 (ddd, *J*= 13.9, 7.2 and 3.8 Hz, 1H), 1.56 (m, 2H), 0.86 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.6, 144.0, 139.0, 137.4, 137.3, 136.6, 133.9, 133.7, 128.9, 128.2, 127.9, 127.7, 127.6, 126.9, 126.4, 126.2, 125.4, 122.2, 85.2, 70.1, 40.8, 37.7, 22.9, 10.9. $[\alpha]_D^{20}$= -35 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 91% ee; HPLC (AS column) 0.8 ml/min (*n*-hexane-isopropanol, 97/3): t_R 40.0 (*minor*), t_R 44..8 (*major*). MS FAB$^+$ *m/z*: 425.1 (M^+-OPr, 75), FAB HRMS for $C_{26}H_{21}O_2N_2S$ (M^+): Calcd: 425.1318. Found: 425.1312. Anal. Calcd for $C_{29}H_{28}O_3N_2S$: C 71.87, H 5.82, N 5.78, S 6.62; found: C 71.57, H 6.13, N 5.53, S 6.24.

2-Cyclohexyloxy-4,6-diphenyl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**4e**).



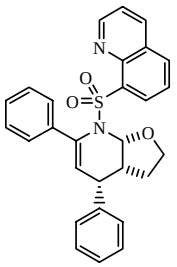
Yield 70%; yellow solid; m.p= 78-80. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.22 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.95 (m, 2H), 7.52 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.36 (t, *J*= 7.8 Hz, 1H), 7.20-7.03 (m, 8H), 6.89 (m, 2H), 6.46 (dd, , *J*= 5.4 and 3.6 Hz, 1H), 5.75 (d, *J*= 3.4 Hz, 1H), 4.11 (m, 1H), 2.75 (m, 1H), 2.46 (m, 1H), 2.00 (m, 1H), 1.85-1.55 (m, 4H), 1.25-1.15 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.9, 144.0, 139.1, 137.5, 137.0, 136.6, 133.8, 133.7, 128.8, 128.1, 128.0, 127.6, 127.5, 126.8, 126.3, 126.0, 125.3, 122.0, 81.6, 73.1, 40.7, 37.6, 33.2, 31.6, 29.1, 25.9, 22.6. $[\alpha]_D^{20}$= -33 (*c* 0.15, $CHCl_3$). Enantiomeric excess: 88% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 17.6 (*minor*), t_R 20.5 (*major*).

2-*tert*-Butoxy-4,6-diphenyl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**5e**).



Yield 35%; white solid; m.p= 66-68 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.07 (dd, *J*= 4.1 and 1.7 Hz, 1H), 8.18 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.01 (dd, *J*=7.4 and 1.3 Hz, 1H), 7.92 (dd, *J*=8.3 and 1.3 Hz, 1H), 7.49 (dd, *J*= 8.3 and 4.3 Hz, 1H), 7.36 (t, *J*=7.7 Hz, 1H), 7.26 (m, 2H), 7.15-6.93 (m, 8H), 6.37 (dd, *J*= 4.5 and 3.0 Hz, 1H), 5.65 (d, *J*= 3.4 Hz, 1H), 2.76 (m, 1H), 2.34 (ddd, *J*= 13.4, 8.5 and 4.5 Hz, 1H), 1.83 (ddd, *J*= 13.8, 4.3 and 3.2 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 145.4, 139.6, 139.4, 136.4, 134.2, 133.7, 128.3, 127.9, 127.6, 127.5, 127.1, 125.9, 125.4, 124.6, 122.0, 78.8, 75.7, 40.8, 37.4, 28.7. $[\alpha]_D^{20}$= -13 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 68% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 98/2): t_R 54.7 (*minor*), t_R 78.1 (*major*). MS FAB$^+$ *m/z*: 425.1 (M^+-O^{t}Bu, 100), FAB HRMS for $C_{26}H_{21}O_2N_2S$ (M^+): Calcd: 425.1318. Found: 425.1306.

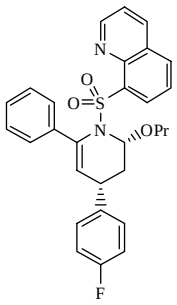
2,3,3a,4,7,7a-hexahydro-4,6-diphenyl-7-[(8-quinolyl)sulfonyl]furo[2,3-b]pyridine.



Yield 83%; white solid; m.p= 65-67 ºC. ^{1}H NMR (300 MHz, $CDCL_3$): δ 9.25 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.31 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.06 (dd, *J*= 7.5 and 1.4 Hz, 1H), 8.03 (dd, *J*= 8.1 and 1.4 Hz, 1H), 7.65 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.44 (t, *J*= 7.8 Hz, 1H), 7.31-7.15 (m, 9H), 6.95 (m, 2H), 6.09 (dd, *J*= 3.9 and 0.8, 1H), 3.96 (m, 1H), 3.63 (m, 1H), 3.22 (m, 2H), 1.89 (m, 1H), 1.55 (m, 1H). ^{13}C NMR (75 MHz, $CDCL_3$): 151.1, 143.8, 141.0, 138.0, 137.6, 136.5, 133.6, 133.3, 128.9, 128.6, 128.0, 127.7, 127.6, 126.7, 126.6, 125.3, 125.2, 122.2, 90.3, 67.3, 52.4, 41.2, 26.8. $[\alpha]_D^{20}$= -15 (*c* 0.26, $CHCl_3$). Enantiomeric excess: 58% ee; HPLC (AD column) 1.0 ml/min (*n*-hexane-isopropanol, 70/30): t_R 26.9 (*major*), t_R 38.8

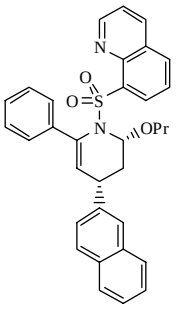
(*minor*). MS FAB$^+$ *m/z*: 469.0 (M^+ +H, 7), FAB HRMS for $C_{28}H_{25}O_3N_2S$ (M^+): Calcd: 469.15859. Found: 469.15815.

4-(*p*-Fluorophenyl)-6-phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (17e).



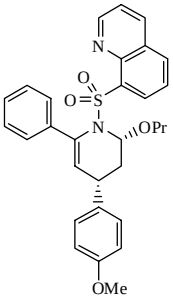
Yield 75%; white solid; m.p= 62-64 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.20 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.93 (m, 2H), 7.52 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.42 (t, *J*= 7.8 Hz, 1H), 7.16-7.01 (m, 5H), 6.89 (m, 2H), 6.78 (m, 2H), 6.30 (dd, *J*= 5.1 and 3.3 Hz, 1H), 5.65 (d, *J*= 3.3 Hz, 1H), 3.94 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.67 (dq, *J*= 9.4 and 6.6 Hz, 1H), 2.85 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.46 (ddd, *J*= 13.6, 7.2 and 5.6 Hz, 1H), 2.02 (ddd, *J*= 13.9, 5.5 and 3.4 Hz, 1H), 1.52 (m, 2H), 0.82 (t, *J*= 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.0, 144.0, 140.7, 138.9, 137.5, 137.2, 136.6, 133.8, 133.7, 133.5, 129.6, 129.5, 128.8, 127.7, 127.6, 127.0, 125.4, 124.8, 122.2, 114.9, 114.7, 84.7, 70.2, 39.7, 36.7, 22.9, 10.8. $[\alpha]_D^{20}$= -81 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 92% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 31.9 (*minor*), t_R 42.7 (*major*). MS FAB$^+$ *m/z*: 443.0 (M^+-OPr, 78), FAB HRMS for $C_{29}H_{28}O_3N_2FS$ (M^+): Calcd: 503.18043. Found: 503.18046.

4-(2-Napthyl)-6-phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (18e)



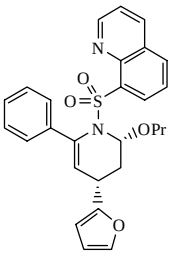
Yield 69%; white solid; m.p= 68-70 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.32 (dd, *J*= 8.4 and 1.7 Hz, 1H), 8.06 (m, 2H), 7.83 7.61 (m, 4H), 7.51-7.33 (m, 4H), 7.26-7.10 (m, 6H), 6.46 (dd, *J*= 5.5 and 3.8 Hz, 1H), 5.92 (d, *J*= 3.3 Hz, 1H), 4.10 (dq, *J*= 9.5 and 6.6 Hz, 1H), 3.79 (dq, *J*= 9.5 and 6.6 Hz, 1H), 3.04 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.65 (ddd, *J*= 13.6, 7.5 and 5.7 Hz, 1H), 2.22 (ddd, *J*= 13.7, 7.1 and 3.7 Hz, 1H), 1.65 (m, 2H), 0.94 (t, *J*= 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.0, 142.2, 139.1, 137.5, 137.3, 136.6, 133.8, 133.7, 133.3, 132.1, 128.8, 127.8, 127.7, 127.6, 127.5, 127.0, 126.6, 126.3, 125.9, 125.5, 125.4, 122.2, 85.0, 70.2, 40.1, 37.7, 22.9, 10.9. $[\alpha]_D^{20}$= -97 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 90% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 33.7 (*minor*), t_R 42.1 (*major*). MS FAB$^+$ *m/z*: 475.1 (M^+-OPr, 78), FAB HRMS for $C_{33}H_{31}O_3N_2S$ (M^+): Calcd: 535.20554. Found: 535.20674. Anal. Calcd for $C_{33}H_{31}O_3N_2S$: C 74.13, H 5.66, N 5.24, S 6.00; found: C 73.89, H 5.94, N 4.87, S 5.69.

4-(*p*-Methoxyphenyl)-6-phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**19e**).



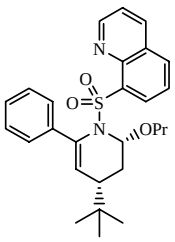
Yield 65%; white solid; m.p= 72-74 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.21 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.96 (m, 2H), 7.52 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.36 (t, *J*= 7.9 Hz, 1H), 7.20-7.03 (m, 5H), 6.75 (d, *J*= 8.7 Hz, 2H), 6.62 (d, *J*= 8.7 Hz, 2H), 6.36 (dd, *J*= 5.6 and 3.8 Hz, 1H), 5.65 (d, *J*= 3.3 Hz, 1H), 3.99 (dq, *J*= 9.5 and 6.7 Hz, 1H), 3.69 (dq, *J*= 9.5 and 6.7 Hz, 1H), 3.64 (s, 3H), 2.61 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.46 (ddd, *J*= 13.5, 7.1 and 5.6 Hz, 1H), 1.95 (ddd, *J*= 13.7, 5.5 and 3.4 Hz, 1H), 1.54 (m, 2H), 0.86 (t, *J*= 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 155.7, 148.7, 141.7, 136.7, 135.1, 134.7, 134.4, 131.6, 131.3, 126.5, 125.3, 124.6, 124.4, 123.0, 119.8, 111.2, 82.8, 67.8, 52.9, 38.5, 34.5, 20.6, 8.5. $[\alpha]_D^{20}$= -27 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 80% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 50.12. (*minor*), t_R 55.5 (*major*). Anal. Calcd for $C_{30}H_{30}N_2O_4S$: C 70.01, H 5.88, N 5.44, S 6.23; found: C 69.86, H 6.01, N 5.22, S 5.89.

4-(2-Furyl)-6-phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**20e**).



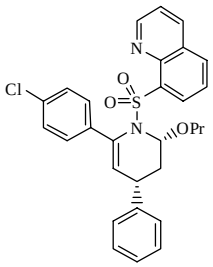
Yield 52%; white solid; m.p= 56-58 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.17 (dd, *J*= 8.4 and 1.8 Hz, 1H), 7.90 (m, 2H), 7.50 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.31 (t, *J*= 7.9 Hz, 1H), 7.14-7.01 (m, 6H), 6.30 (dd, *J*= 4.7 and 3.5 Hz, 1H), 6.11 (dd, *J*= 3.1 and 1.9 Hz, 1H), 5.81 (d, *J*= 2.5, 1H), 5.67 (d, *J*= 3.4 Hz, 1H), 3.89 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.65 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.04 (td, *J*= 8.0 and 5.2 Hz, 1H), 2.42 (ddd, *J*= 13.9, 7.8 and 5.6 Hz, 1H), 1.95 (ddd, *J*= 13.9, 5.3 and 3.4 Hz, 1H), 1.50 (m, 2H), 0.79 (t, *J*= 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.2, 151.0, 143.8, 140.6, 138.9, 137.4, 137.1, 136.5, 133.7, 128.8, 127.7, 127.5, 127.3, 127.2, 125.3, 122.1, 121.1, 110.1, 104.8, 84.4, 69.9, 35.8, 30.9, 22.9, 10.8. $[\alpha]_D^{20}$= -17 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 77% ee; HPLC (AS column) 1.0 ml/min (*n*-hexane-isopropanol, 94/6): t_R 71.12. (*minor*), t_R 74.5 (*major*). MS FAB^+ *m/z*: 416.1 (M^+-OPr, 100), FAB HRMS for $C_{27}H_{27}N_2O_4S$ (M^+): Calcd: 475,16133. Found: 475.16105.

4-*tert*Butyl-6-phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**21e**).



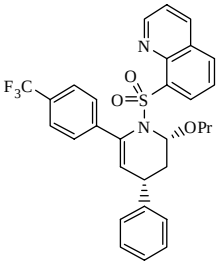
Yield 61%; white solid; m.p= 65-67 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.16 (m, 2H), 7.95 (d, *J*= 8.1 Hz, 1H), 7.49 (m, 2H), 7.38-7.15 (m, 5H), 7.00 (m, 1H), 6.57 (dd, *J*= 7.7 and 5.8 Hz, 1H), 5.78 (d, *J*= 4.0 Hz, 1H), 4.12 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.79 (dq, *J*= 9.4 and 6.6 Hz, 1H), 2.25 (m, 1H), 1.67 (m, 1H), 1.22 (m, 1H), 0.98 (t, *J*= 7.3 Hz, 3H), 0.82 (m, 2H), 0.26 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.2, 139.3, 138.3, 137.0, 136.6, 134.2, 133.5, 129.2, 128.9, 127.8, 127.7, 127.3, 126.1, 125.2, 121.9, 87.5, 69.9, 42.1, 36.9, 30.3, 26.8, 22.9, 10.9. $[\alpha]_D^{20}$= 82 (*c* 0.5, $CHCl_3$). Enantiomeric excess: 84% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 11.6 (*major*), t_R 15.9 (*minor*).

6-(*p*-Chlorophenyl)-4-phenyl-2-propoxy-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**22e**).



Yield 73%; white solid; m.p= 58-60 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.24 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.02 (m, 2H), 7.53 (dd, *J*= 8.4 and 4.2 Hz, 1H), 7.42 (m, 1H), 7.28-7.0 (m, 7H), 6.83 (m, 2H), 6.34 (dd, *J*= 5.6 and 3.8 Hz, 1H), 5.74 (d, *J*= 3.4 Hz, 1H), 3.96 (dq, *J*= 9.5 and 6.7 Hz, 1H), 3.67 (dq, *J*= 9.5 and 6.7 Hz, 1H), 2.63 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.44 (ddd, *J*= 13.6, 7.2 and 5.6 Hz, 1H), 1.99 (ddd, *J*= 13.5, 7.2 and 3.8 Hz, 1H), 1.56 (m, 2H), 0.86 (t, *J*= 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.2, 143.9, 137.6, 137.3, 136.7, 136.3, 133.9, 133.8, 133.5, 128.8, 128.2, 128.1, 127.9, 127.8, 126.9, 126.4, 125.4, 122.2, 85.2, 70.1, 40.7, 37.6, 22.9, 10.9. $[\alpha]_D^{20}$= -35 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 90% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 30.8 (*major*), t_R 37.0 (*minor*). MS FAB$^+$ *m/z*: 459.1 (M^+-OPr, 100), FAB HRMS for $C_{29}H_{28}O_3N_2ClS$ (M^+): Calcd: 519.1503. Found: 519.1547. Anal. Calcd for $C_{29}H_{27}O_3N_2ClS$: C 67.10, H 5.29, N 5.40, S 6.18; found: C 67.48, H 5.53, N 5.03, S 5.84.

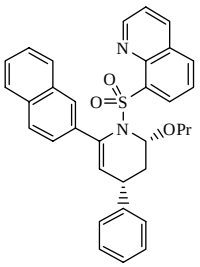
4-Phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-6-[*p*-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydropyridine (**23e**).



Yield 69%; white solid; m.p= 68-70 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.23 (dd, *J*= 8.3 and 1.6 Hz, 1H), 7.99 (m, 2H), 7.55 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.44-7.28 (m, 6H), 7.14-7.02 (m, 3H), 6.83 (m, 2H), 6.32 (dd, *J*= 5.5 and 3.6 Hz, 1H), 5.83 (d, *J*= 3.4

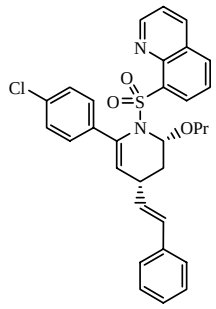
Hz, 1H), 3.98 (dq, *J*= 9.5 and 6.7 Hz, 1H), 3.69 (dq, *J*= 9.5 and 6.7 Hz, 1H), 2.69 (td, *J*= 7.2 and 3.4 Hz, 1H), 2.41 (ddd, *J*= 13.6, 7.6 and 5.6 Hz, 1H), 1.99 (ddd, *J*= 13.8, 6.9 and 3.7 Hz, 1H), 1.55 (m, 2H), 0.86 (t, *J*= 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.1, 144.0, 142.7, 137.2, 136.7, 136.3, 133.9, 133.8, 129.3, 128.9, 128.3, 128.1, 127.9, 127.0, 126.4, 125.4, 124.7, 124.6, 122.3, 85.1, 70.3, 40.3, 37.7, 22.9, 10.8. $[\alpha]_D^{20}$= -43 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 91% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 37.8 (*major*), t_R 40.4 (*minor*). MS FAB$^+$ *m/z*: 494.1 (M^+-OPr, 100), FAB HRMS for $C_{30}H_{28}F_3N_2O_3S$ (M^+): Calcd: 553,16945. Found: 553,16913.

6-(2-Napthyl)-4-phenyl-2-propoxy-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**24e**).



Yield 67%, white solid; m.p= 78-80 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.13 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.21 (dd, *J*= 8.4 and 1.7 Hz, 1H), 7.89 (m, 2H), 7.69 (m, 1H), 7.60-7.41 (m, 4H), 7.40-7.28 (m, 3H), 7.26-7.03 (m, 4H), 6.88 (m, 2H), 6.45 (dd, *J*= 5.5 and 3.8 Hz, 1H), 5.90 (d, *J*= 3.3 Hz, 1H), 4.09 (dq, *J*= 9.5 and 6.6 Hz, 1H), 3.75 (dq, *J*= 9.5 and 6.6 Hz, 1H), 2.77 (td, *J*= 7.3 and 3.4 Hz, 1H), 2.57 (ddd, *J*= 13.6, 7.5 and 5.7 Hz, 1H), 2.06 (ddd, *J*= 13.7, 7.1 and 3.7 Hz, 1H), 1.59 (m, 2H), 0.88 (t, *J*= 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.5, 137.4, 137.2, 136.6, 136.4, 133.9, 133.6, 133.0, 132.8, 128.8, 128.2, 128.0, 127.9, 127.5, 127.1, 127.0, 126.3, 125.8, 125.6, 125.3, 125.2, 124.6, 122.1, 85.2, 70.2, 40.8, 37.8, 23.0, 10.9. Enantiomeric excess: 6% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 45.8 (*major*), t_R 60.2 (*minor*).

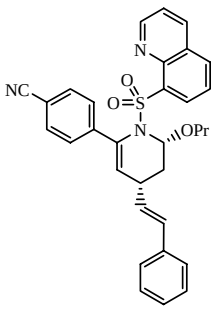
6-(*p*-Chlorophenyl)-2-propoxy-4-styryl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**25e**).



Yield 63%; white solid; m.p= 65-67 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.19 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.95 (dd, *J*= 8.1 and 1.3 Hz, 1H), 7.86 (dd, *J*= 7.5 and 1.4 Hz, 1H), 7.51 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.35 (t, *J*= 7.9 Hz, 1H), 7.20-7.15 (m, 4H), 7.00-6.95 (m, 4H), 6.16 (m, 3H), 5.36 (d, *J*= 3.6 Hz, 1H), 3.87 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.70 (dq, *J*= 9.4 and 6.6 Hz, 1H), 2.66 (m, 1H), 2.13 (ddd, *J*= 14.0, 7.7 and 3.8 Hz, 1H), 1.96 (dt, = 14.0 and 2.7 Hz, 1H), 1.55 (m, 3H), 0.87 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 143.9, 137.9, 137.4, 136.5, 135.0, 133.8, 133.6, 133.4, 133.3, 129.2, 128.8, 128.6, 128.5, 128.4, 128.0, 127.4, 126.0, 125.3, 122.4, 122.2, 84.3, 70.1, 35.6, 35.1, 23.1, 10.9. $[\alpha]_D^{20}$= -140 (*c* 0.2, $CHCl_3$).

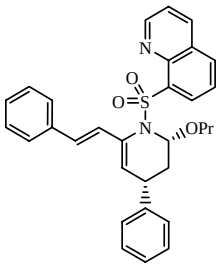
Enantiomeric excess: 92% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 28.7 (*major*), t_R 38.1 (*minor*).

6-(*p*-Cyanophenyl)-2-propoxy-4-styryl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**26e**).



Yield 70%; yellow solid; m.p= 85-86 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.21 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.96 (m, 2H), 7.52 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.40 (t, *J*= 7.8 Hz, 1H), 7.37 (d, *J*= 8.4 Hz, 2H), 7.26 (d, *J*= 8.4 Hz, 2H), 7.15 (m, 5H), 6.16 (m, 2H), 6.05 (m, 1H), 5.51 (d, *J*= 3.6 Hz, 1H), 3.86 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.68 (dq, *J*= 9.4 and 6.6 Hz, 1H), 2.62 (m, 1H), 1.92 (m, 1H), 1.55 (m, 3H), 0.87 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.2, 144.4, 143.9, 137.2, 136.6, 134.9, 134.2, 133.3, 133.0, 131.5, 129.6, 128.9, 128.5, 127.7, 127.2, 126.0, 125.4, 124.7, 122.4, 119.0, 110.9, 84.3, 70.2, 35.7, 34.7, 23.0, 10.9. $[\alpha]_D^{20}$= -102 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 92% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 45.9 (*minor*), t_R 53.5 (*major*).

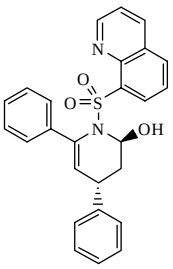
4-Phenyl-2-propoxy-4-styryl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**27e**).



Yield 68%; yellow solid; m.p= 80-81 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.05 (dd, *J*= 4.2 and 1.8 Hz, 1H), 8.35 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.02 (d, *J*= 8.3 Hz, 1H), 7.93 (d, *J*= 8.4 Hz, 1H), 7.52 (dd, *J*= 8.3 and 4.1 Hz, 1H), 7.40 (t, *J*= 7.8 Hz, 1H), 7.21-7.00 (m, 7H), 6.90 (m, 3H), 6.36 (d, *J*= 16.0 Hz, 1H), 6.25 (dd, *J*= 5.0 and 4.3 Hz, 1H), 5.70 (d, *J*= 3.5 Hz, 1H), 3.78 (dq, *J*= 9.4 and 6.6 Hz, 1H), 3.50 (dq, *J*= 9.4 and 6.6 Hz, 1H), 2.70 (m, 1H), 2.52 (m, 1H), 2.03 (ddd, *J*= 13.7, 6.0 and 3.3 Hz, 1H), 1.49 (m, 3H), 0.82 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.2, 144.7, 143.9, 137.4, 136.9, 136.7, 135.3, 134.3, 133.9, 129.4, 128.9, 128.5, 128.2, 127.9, 127.6, 127.4, 126.6, 125.5, 123.2, 122.2, 85.0, 69.7, 39.4, 42.1, 26.0, 10.8. $[\alpha]_D^{20}$= -13 (*c* 0.4, $CHCl_3$). Enantiomeric excess: 20% ee; HPLC (AD column) 0.7 ml/min (*n*-hexane-isopropanol, 90/10): t_R 24.2 (*major*), t_R 43.4 (*minor*).

2-Hydroxy-4,6-diphenyl-1-[(8-quinolyl)sulfonyl]-1,2,3,4-tetrahydropyridine (**29**).

To a solution of compound **3e** (91% ee**,** 0.21 mmol) in CH_2Cl_2 (2 ml) at 0 ºC was added $BF_3.OEt_2$ (0.21 mmol). The mixture was stirred at 0 ºC for 2 h before the mixture was quenched with saturated aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic phase was dried (Na_2SO_4) and concentrated. The residue was

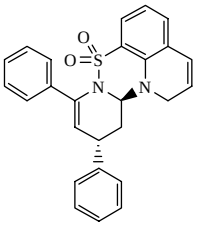


purified by flash chromatography in deactivated SiO_2 (*n*-hexane-AcOEt 3:1) to afford **29** as a white solid (88% yield); m.p.: 67-69 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.00 (dd, *J*= 4.2 and 1.7 Hz, 1H), 8.22 (dd, *J*= 8.3 and 1.7 Hz, 1H), 7.84 (dd, *J*=7.4 and 1.3 Hz, 1H), 7.54 (dd, *J*=8.2 and 1.3 Hz, 1H), 7.44 (dd, *J*= 8.3 and 4.2 Hz, 1H), 7.21-7.02 (m, 6H), 6.91-6.62 (m, 5H), 5.65 (s, 1H), 5.05 (dd, *J*= 2.7 and 1.3 Hz, 1H), 3.83 (ddd, *J*= 9.5, 6.7 and 2.8 Hz, 1H), 2.51 (dddd, *J*= 14.0, 6.7, 3.0 and 1.4 Hz, 1H), 2.08 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 151.1, 144.7, 144.3, 139.0, 137.5, 137.3, 135.9, 133.9, 133.2, 128.9, 128.2, 128.0, 127.7, 127.6, 126.9, 126.4, 126.2, 125.4, 122.2, 85.2, 71.4, 45.2, 33.4. $[\alpha]_D^{20}$= +17 (*c* 0.4, $CHCl_3$).

General procedure for the preparation of tetracyclic compounds 30-32.

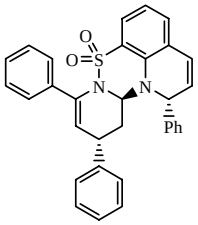
To a solution of compound **3e** (91% ee, 0.21 mmol) in CH_2Cl_2 (2 ml) at 0 ºC was added $BF_3.OEt_2$ (0.21 mmol). The mixture was stirred at 0 ºC for 2 h before the mixture was cooled to -78 ºC and treated with a solution of the nucleophile (1.2 equiv) in CH_2Cl_2 (1 mL). The mixture was stirred for 30 min at -78 ºC and it was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography in deactivated SiO_2 (*n*-hexane-AcOEt 3:1).

Compound 30a.



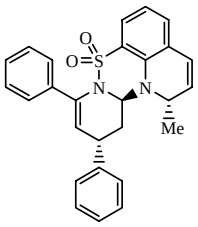
Yield 82%; white solid; mp= 76-78 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15-6.94 (m, 12H), 6.78 (dd, *J*= 7.4 and 1.4 Hz, 1H), 6.44 (t, *J*= 7.5 Hz, 1H), 6.18 (m, 1H), 5.59 (ddd, *J*= 7.9, 4.9 and 2.9 Hz, 1H), 5.21 (dd, *J*= 2.7 and 0.8 Hz, 1H), 5.16 (dd, *J*= 6.8 and 2.5 Hz, 1H), 4.01 (ddd, *J*= 15.4, 4.9 and 1.2 Hz, 1H), 3.82 (ddd, *J*= 15.3, 2.6 and 0.8 Hz, 1H), 3.60 (m, 1H), 2.73 (dtd, *J*= 13.9, 6.1 and 1.0 Hz, 1H), 1.91 (ddd, *J*= 14.2, 8.4. and 2.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 144.0, 140.8, 138.0, 136.9, 130.8, 128.8, 127.9, 127.7, 127.6, 127.5, 127.4, 127.0, 125.8, 123.7, 123.4, 122.6, 121.0, 119.5, 117.4, 72.9, 45.6, 36.4, 31.6. $[\alpha]_D^{20}$= -203 (*c* 0.4, $CHCl_3$).MS FAB$^+$ *m/z*: 427.1 (M^+ +H, 100), FAB HRMS for $C_{26}H_{23}N_2O_2S$ (M^+): Calcd: 427.1403. Found: 427.1435

Compound 31a.



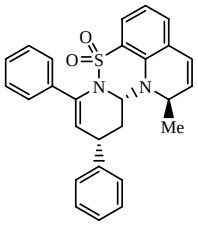
Yield 71%, white solid; m.p.: 83-85 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.18 (m, 16H), 6.94 (dd, *J*= 7.4 and 1.5 Hz, 1H), 6.63 (t, *J*= 7.6 Hz, 1H), 6.22 (dd, *J*= 10.0 and 1.5 Hz, 1H), 5.77 (d, *J*= 3.8 Hz, 1H), 5.65 (dd, *J*= 9.8 and 4.9 Hz, 1H), 5.25 (dd, *J*= 5.1 and 1.1 Hz, 1H), 4.20 (m, 1H), 3.66 (ddd, *J*= 10.5, 5.0 and 2.2 Hz, 1H), 2.80 (dtd, *J*= 14.2, 5.2 and 1.2 Hz, 1H), 2.04 (ddd, *J*= 14.2, 10.6. and 2.2 Hz, 1H), 1.15 (d, *J*= 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 143.8, 139.8, 138.1, 137.4, 130.8, 128.8, 128.3, 128.0, 127.8, 127.5, 127.0, 124.1, 123.8, 122.0, 118.5, 117.2, 70.8, 49.2, 36.1, 32.4, 17.7. $[\alpha]_D^{20}$= -323 (*c* 0.34, $CHCl_3$).

Compound 32a.



Yield 60%; white solid; mp= 79-81 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.12 (m, 11H), 7.01 (dd, *J*= 7.4 and 1.4 Hz, 1H), 6.61 (t, *J*= 7.6 Hz, 1H), 6.36 (d, *J*= 9.6 Hz, 1H), 5.82 (dd, *J*= 9.6 and 5.9 Hz, 1H), 5.75 (dd, *J*= 5.1 and 2.2 Hz, 1H), 5.12 (dd, *J*= 1.9 and 1.5 Hz, 1H), 4.20 (m, 1H), 3.66 (ddd, *J*= 10.5, 5.0 and 2.2 Hz, 1H), 2.80 (dtd, *J*= 14.2, 5.2 and 1.2 Hz, 1H), 2.04 (ddd, *J*= 14.2, 10.6. and 2.2 Hz, 1H), 1.15 (d, *J*= 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 143.8, 139.8, 138.1, 137.4, 130.8, 128.8, 128.3, 128.0, 127.8, 127.5, 127.0, 124.1, 123.8, 122.0, 118.5, 117.2, 70.8, 49.2, 36.1, 32.4, 17.7. $[\alpha]_D^{20}$= -354 (*c* 0.3, $CHCl_3$).Anal. Calcd for $C_{27}H_{24}N_2O_2S$: C 73.61, H 5.49, N 6.36, S 7.28; found: C 73.28, H 5.68, N 6.04, S 7.89.

Compound 32b.

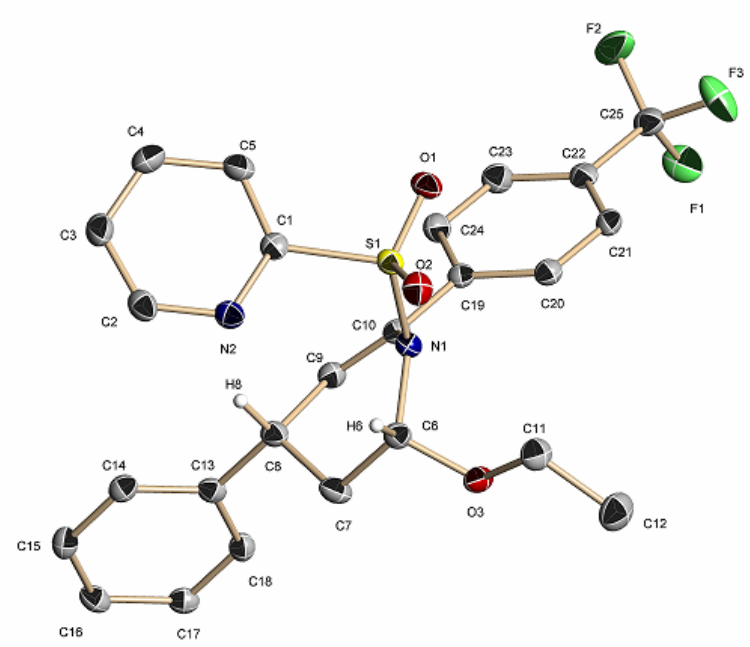


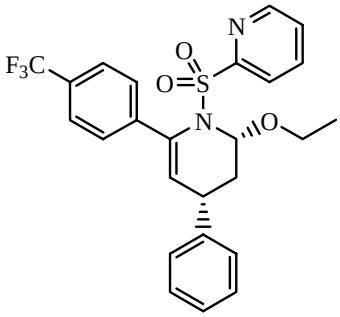
Yield 15%; white solid; mp= 83-85 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.15 (m, 11H), 6.94 (dd, *J*= 7.2 and 1.4 Hz, 1H), 6.64 (dd, *J*= 7.8 and 7.3 Hz, 1H), 6.23 (d, *J*= 9.8 Hz, 1H), 5.81 (d, *J*= 3.6 Hz, 1H), 5.62 (dd, *J*= 9.7 and 5.4 Hz, 1H), 5.18 (dd, *J*= 11.2 and 3.1 Hz, 1H), 4.09 (m, 1H), 3.76 (ddd, *J*= 10.4, 7.0 and 3.6 Hz, 1H), 2.74 (m, 1H), 2.30 (ddd, *J*= 13.4, 7.1. and 3.3 Hz, 1H), 1.30 (d, *J*= 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 144.0, 140.2, 138.3, 136.9, 131.8, 128.8, 127.8, 127.7, 127.6, 127.2, 127.4, 127.0, 125.8, 123.7, 123.4, 122.6, 121.0, 119.5, 117.4, 72.9, 36.4, 31.4, 18.3. $[\alpha]_D^{20}$= -134 (*c* 0.4, $CHCl_3$).

Determination of the stereochemistry of the products

a) Stereochemistry *endo*

It is well-known that the Diels-Alder reaction of N-sulfonyl-1-aza-1,3-dienes takes place with very high endo-selectivity[3]. We have confirmed this stereochemistry by X-ray diffraction analysis of (±)-**I** (see below). Data of X-ray structure of **I** are found at the end of the Supporting Information.



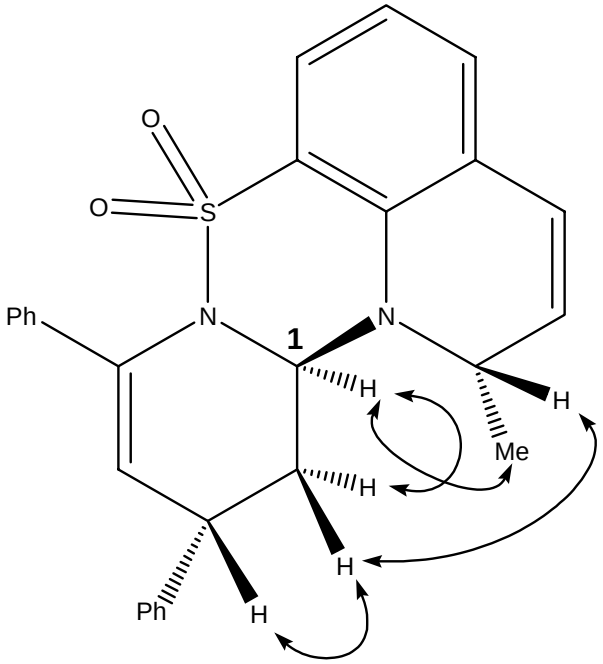


I

b) Relative stereochemistry of the tetracyclic products **30-32**

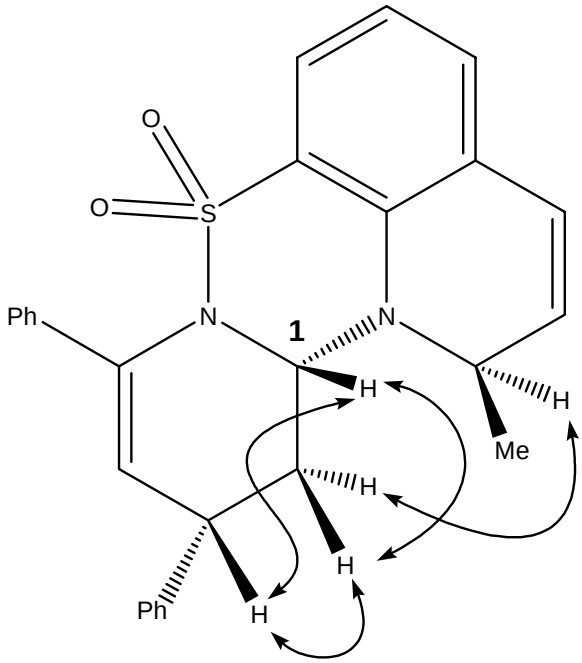
The relative stereochemistry of both diastereomers **32a** and **32b** has been established by NMR. ^{13}C-^{1}H Heteronuclear correlation and ^{1}H-COSY experiments allowed proton assignment, while the 2D-NOESY experiments were decisive for determination of the relative stereochemistry. Some critical diagnostic criteria, such as coupling constants for the key aminal proton and strong NOE contacts are shown in the Figure below. The stereochemical assignments of the related derivatives **30a** and **31a** have been established by chemical analogy and similarity of their ^{1}H NMR spectra with that of **32a**. On the other hand, these relative stereochemistries are in agreement with the attack of the Grignard reagent to the less hindered convex face of the quinolinium intermediate **28**. Furthermore, as shown later, this stereochemical assignment has been unequivocally confirmed by X-ray crystallographic analysis of **32b**.

[3] Boger et al. *J. Am. Chem. Soc.* **2006**, 2587; *J. Org. Chem.* **1993**, 2068 and *J. Am. Chem. Soc*. **1991**, *113*, 1713.



32a

δ H^1 = 5.75 ppm ($CDCl_3$)
J = 5.1 and 2.2 Hz

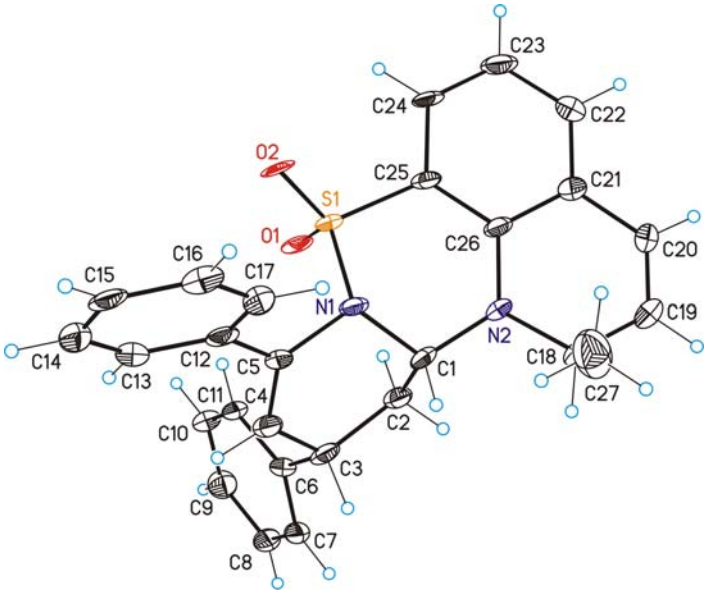


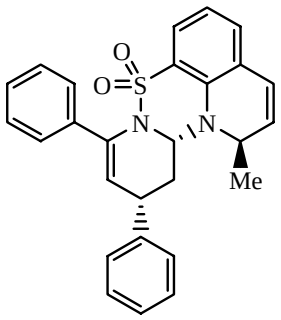
32b

δ H^1 = 5.18 ppm ($CDCl_3$)
J = 11.2 and 3.1 Hz

C) Absolute stereochemistry

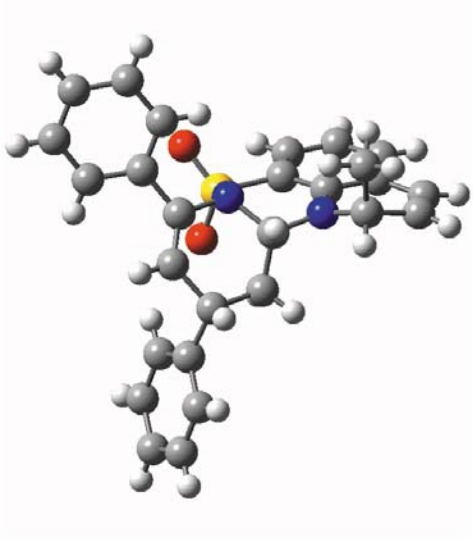
The absolute stereochemistry has been unequivocally established by X-ray crystallographic analysis of an enantiopure sample of the crystalline product **32b** (see below). Data of X-ray structure of **32b** are found at the end of the Supporting Information.



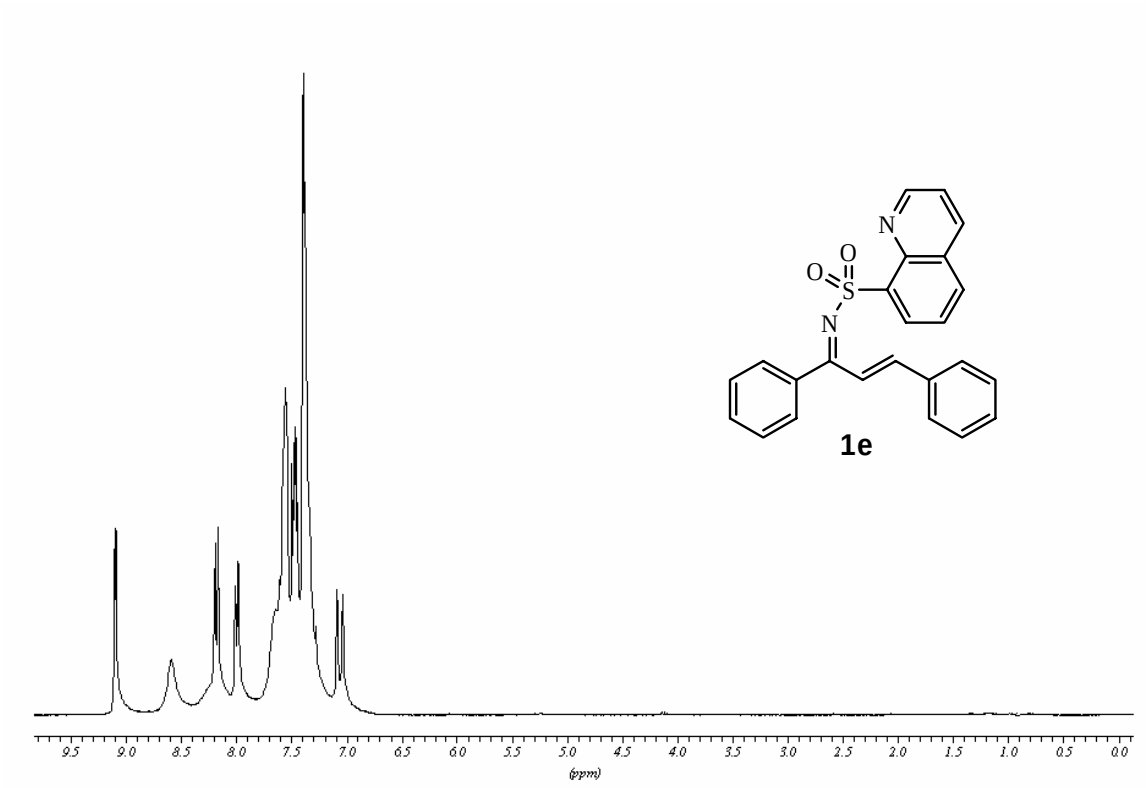


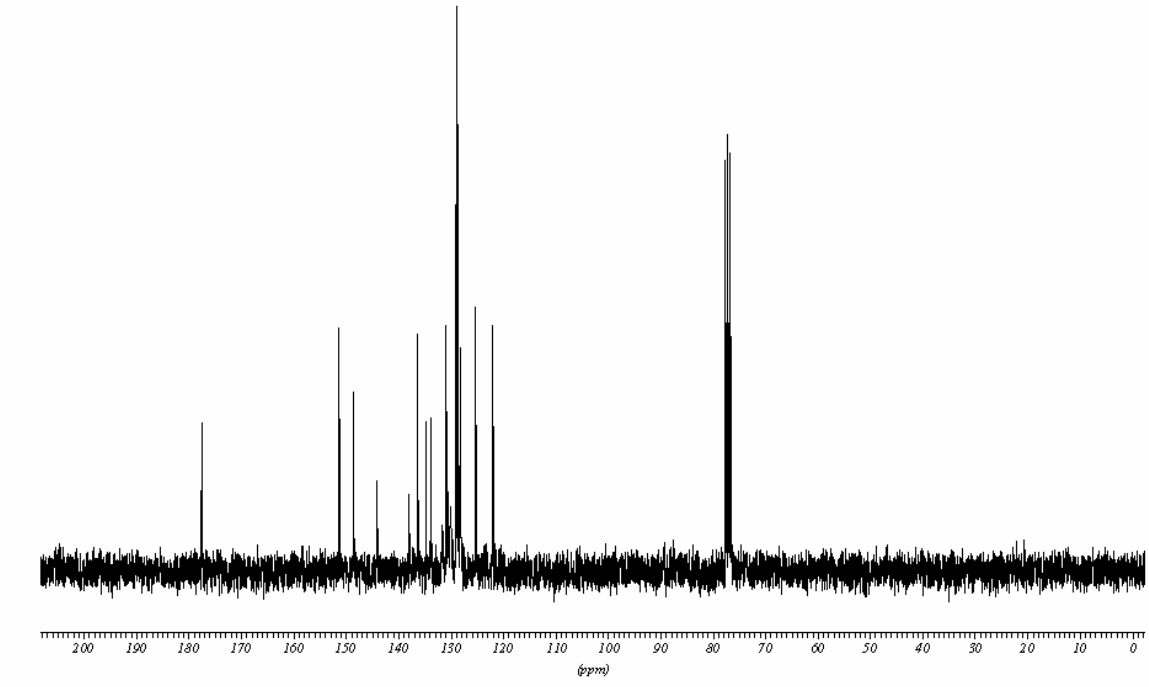
32b

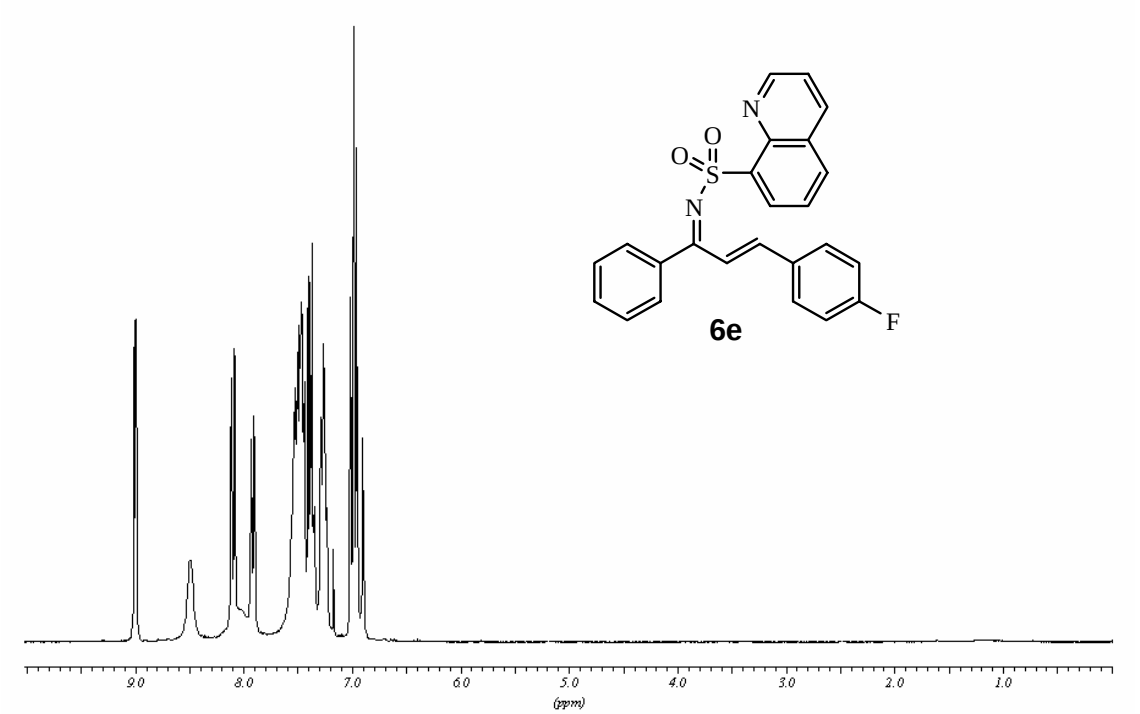
Sticks and balls view of crystal structure of compound **32b**



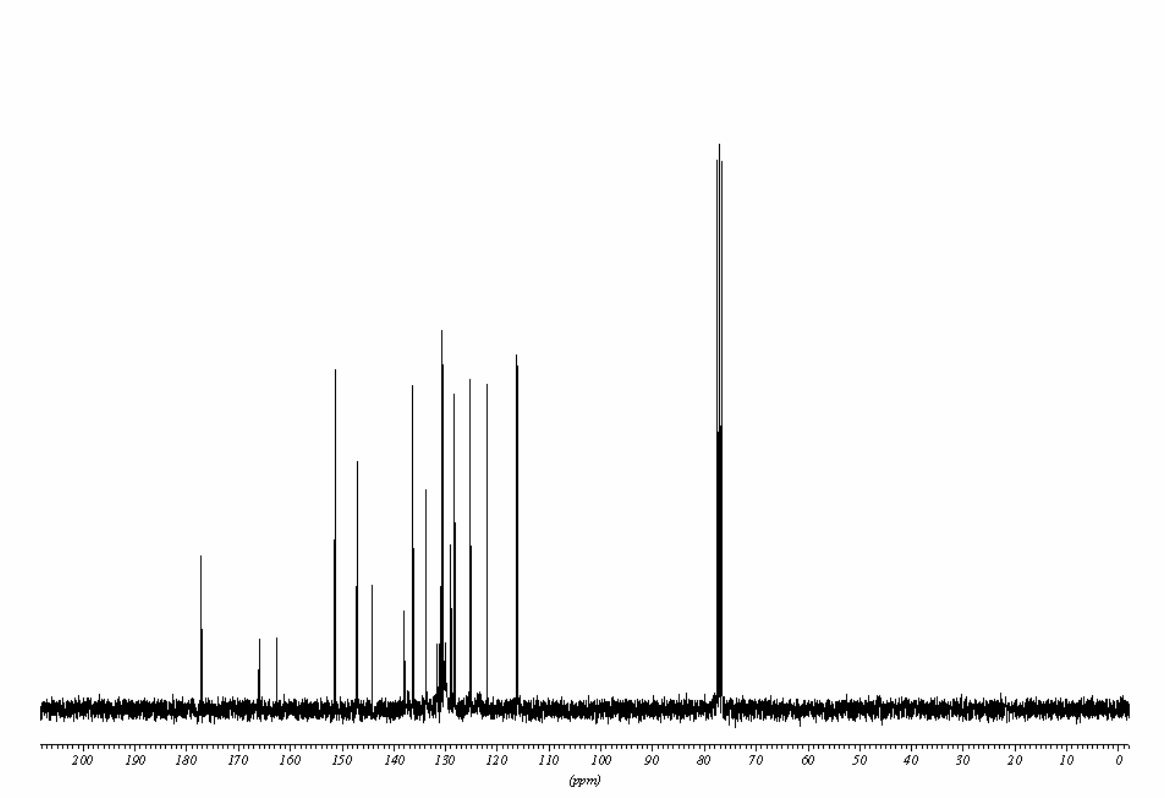
NMR Spectra

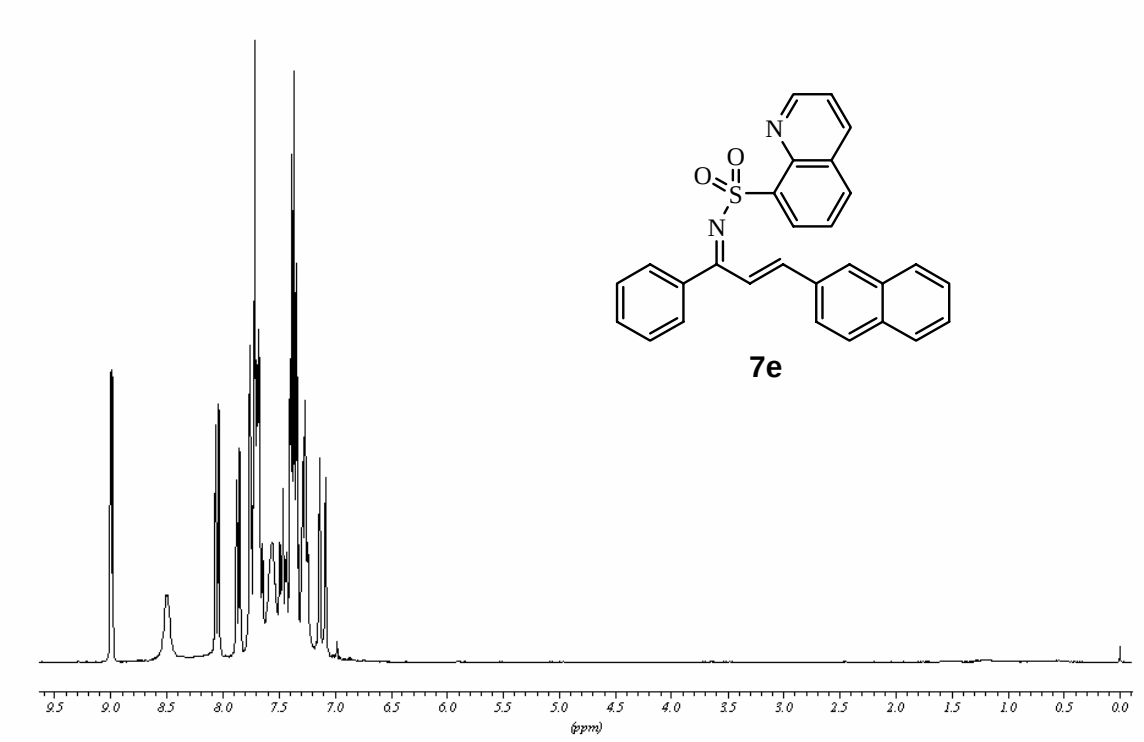

N
O
O
S
N
1e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

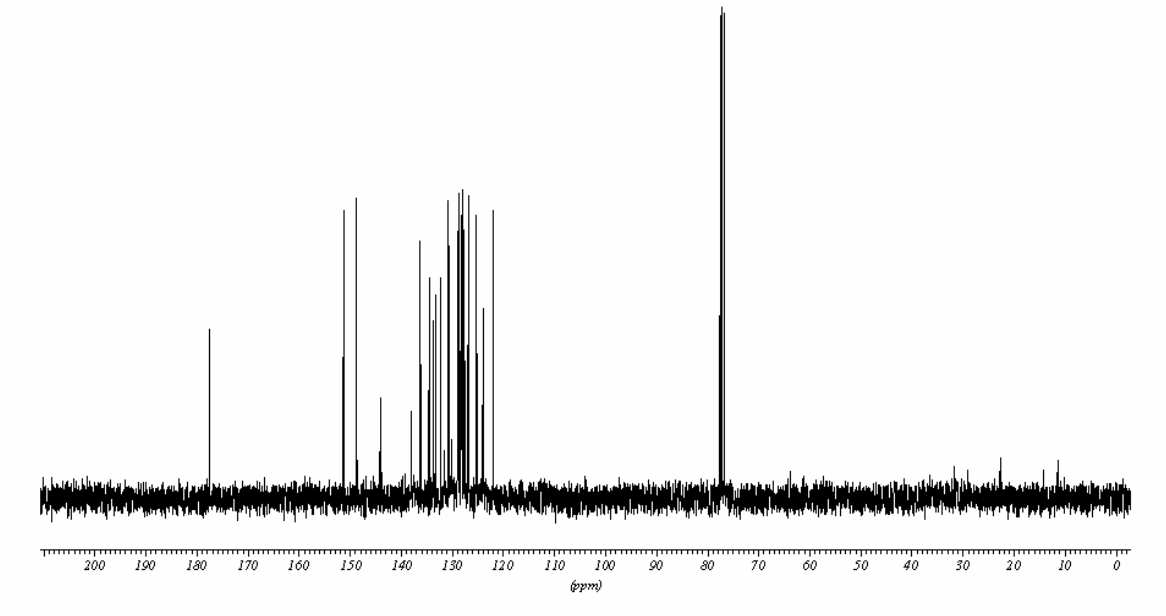

N
O
O
S
N
F
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

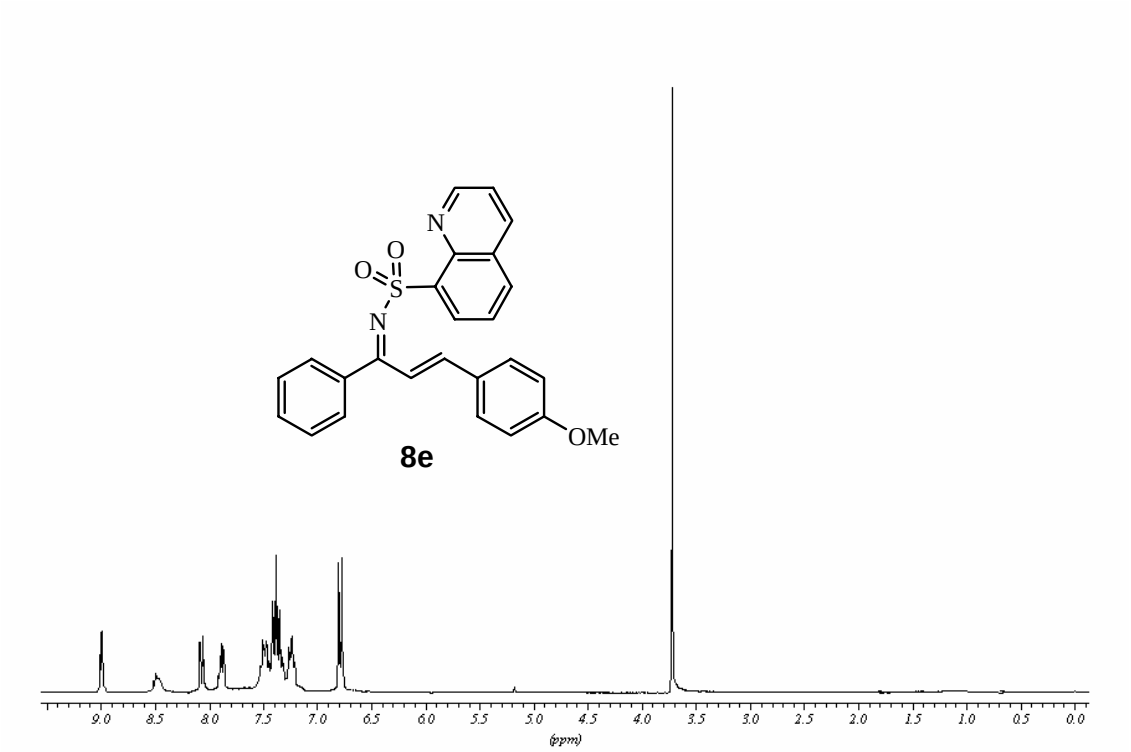
6e


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

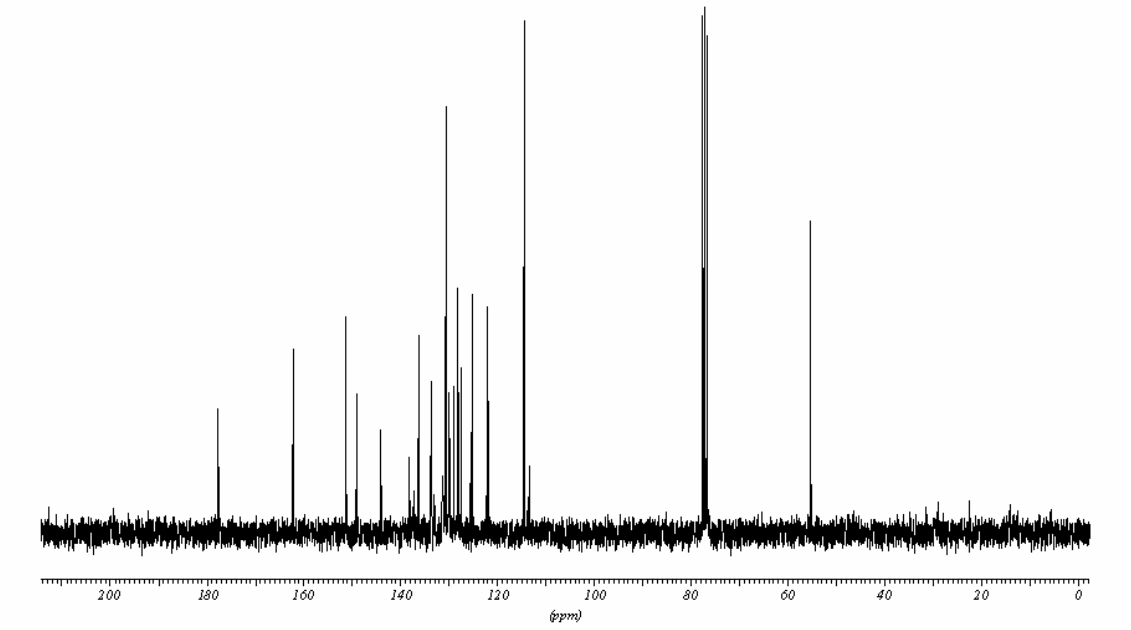

N
O
O
S
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

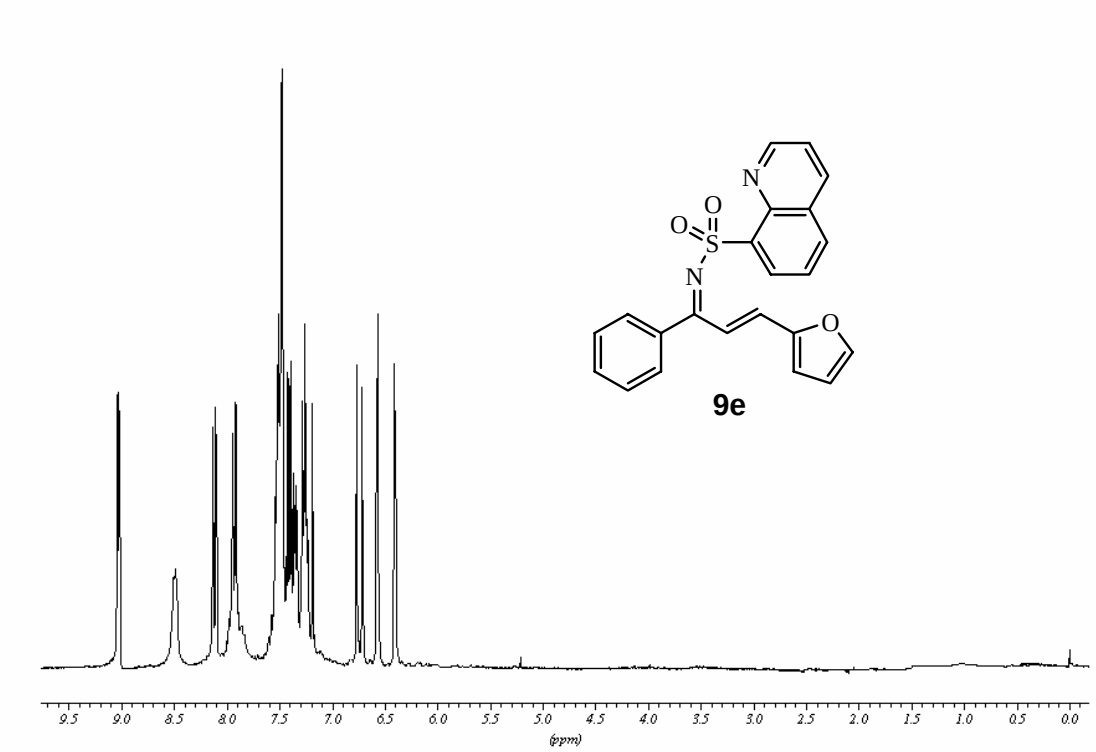
7e


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

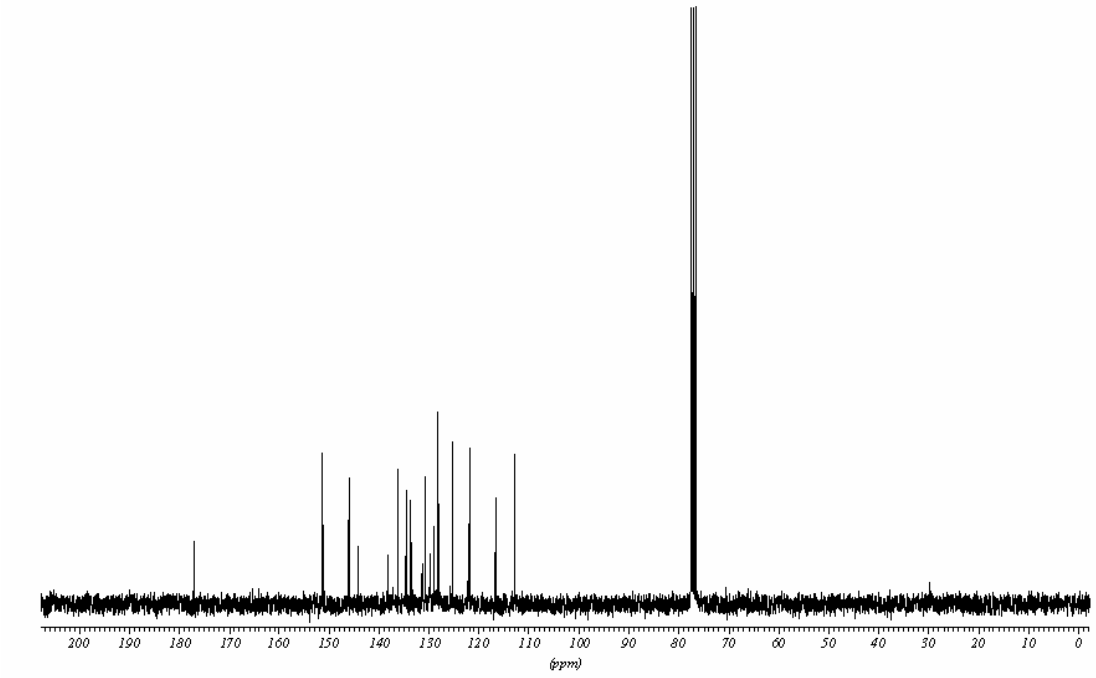

N
O
O
S
N
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

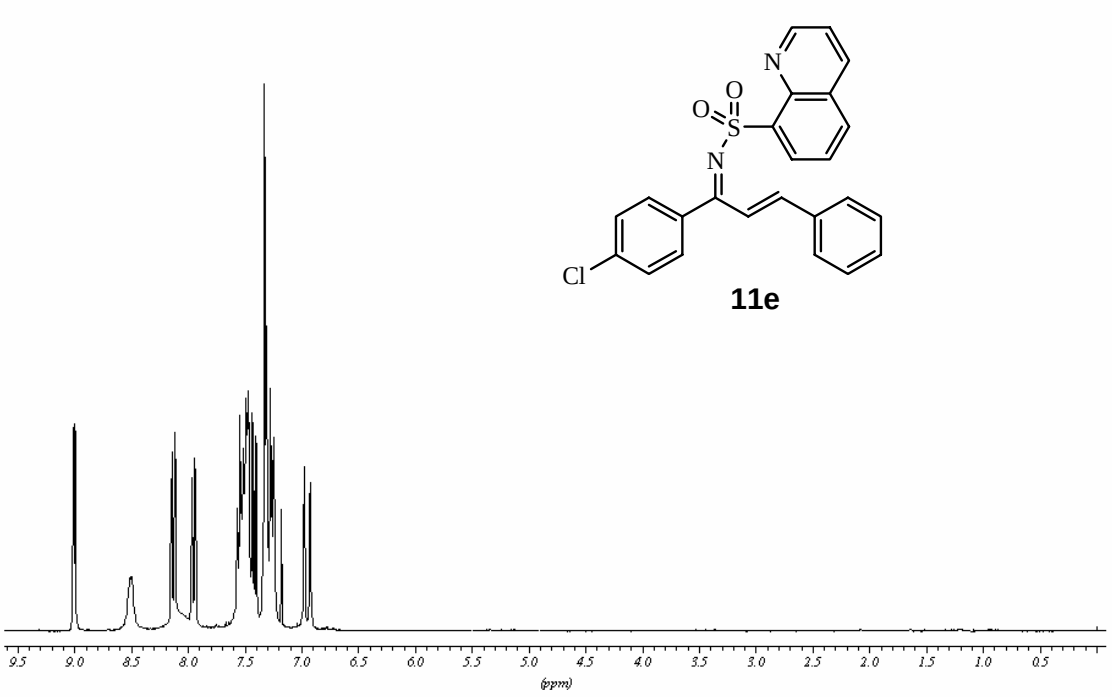
8e


200
180
160
140
120
100
80
60
40
20
0
(ppm)

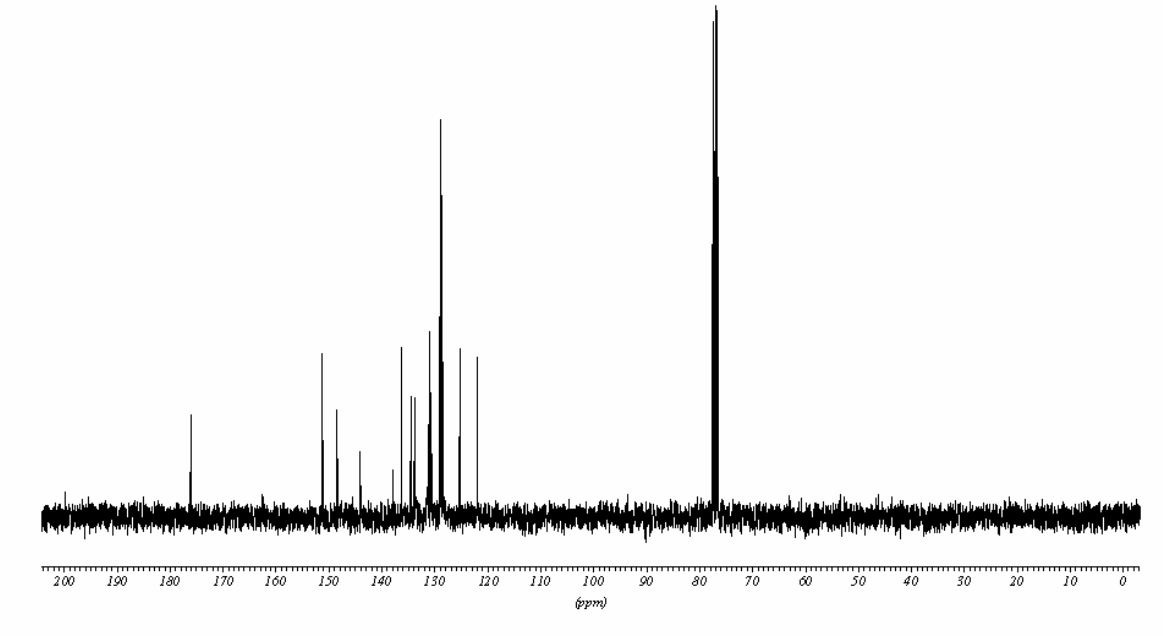

N
O
O
S
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

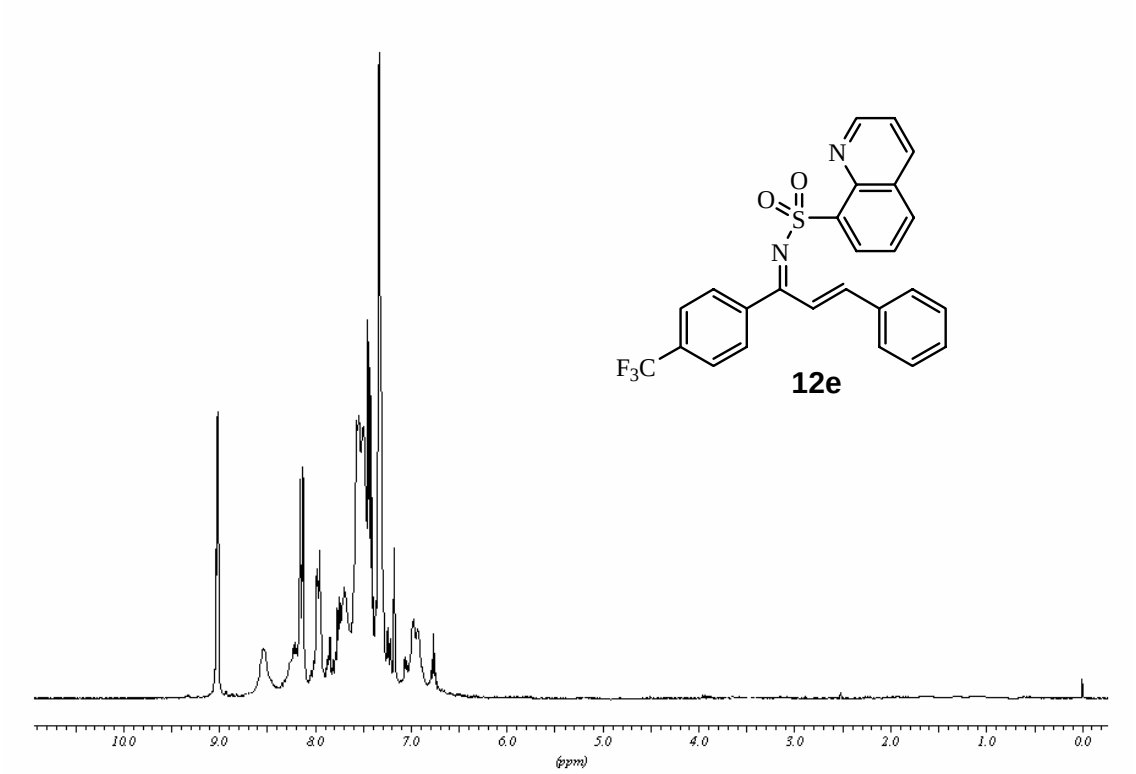
9e


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

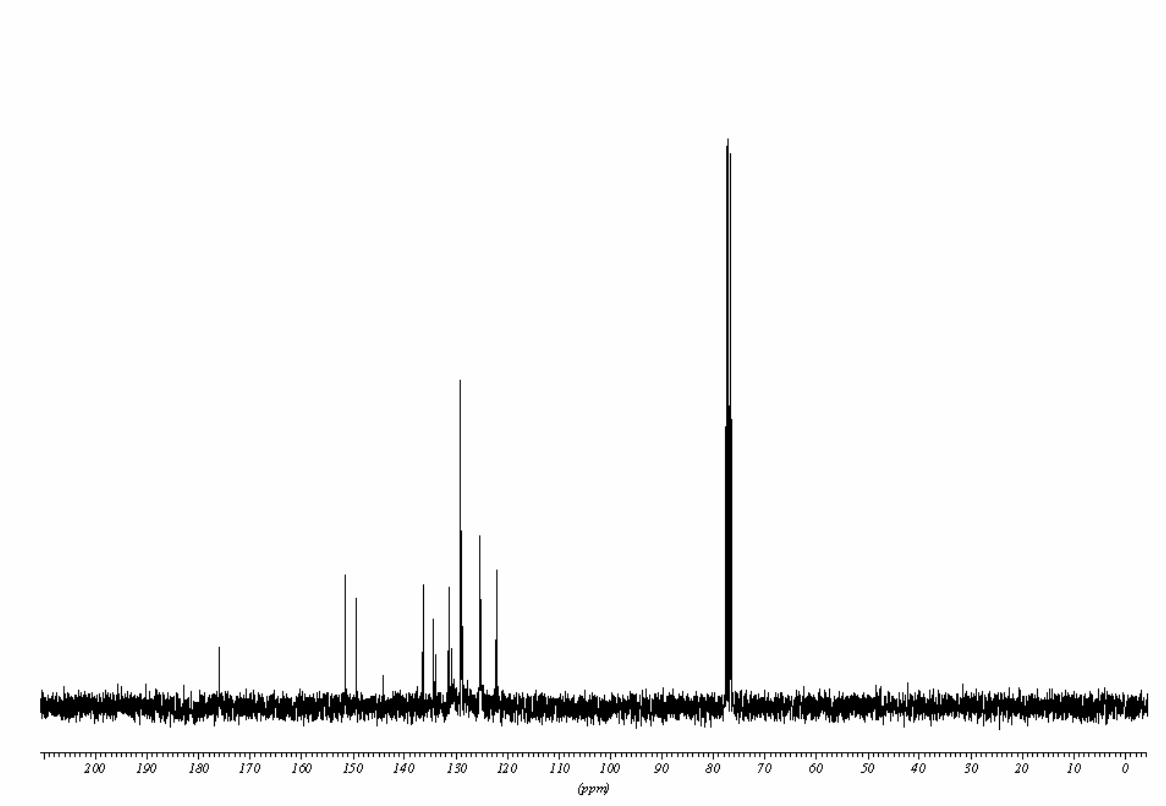

N
O
O
S
N
Cl
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

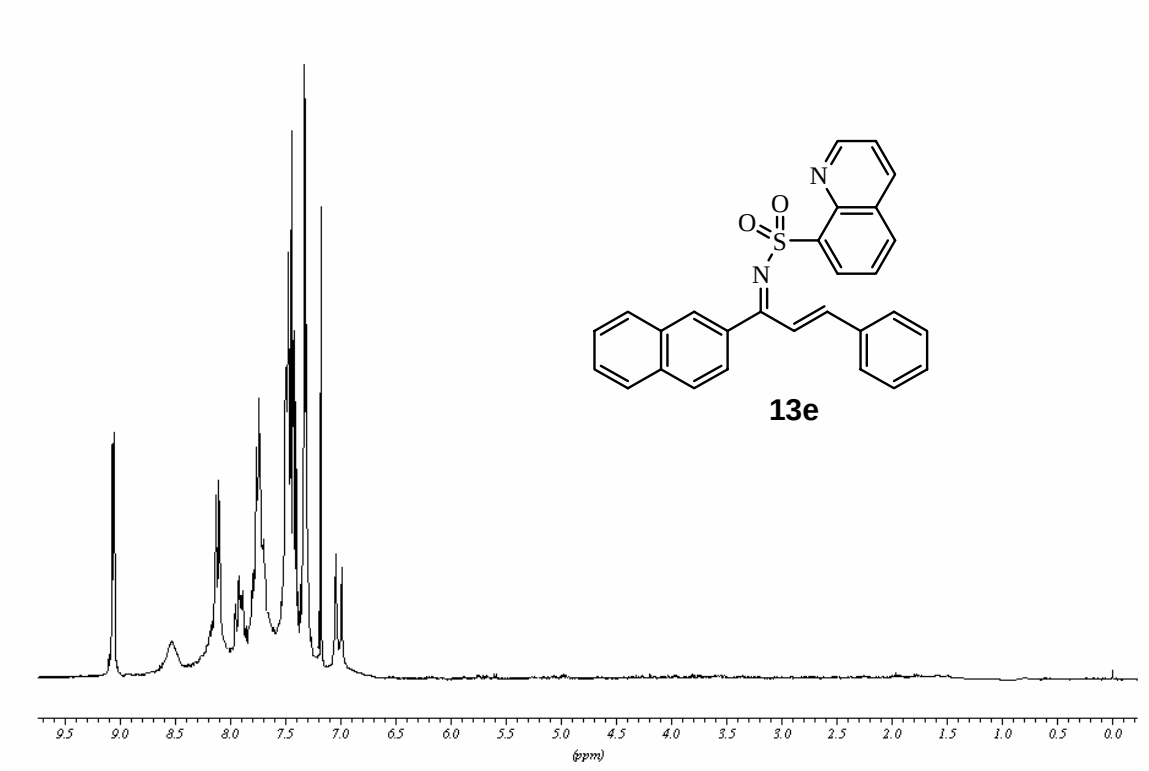
11e


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

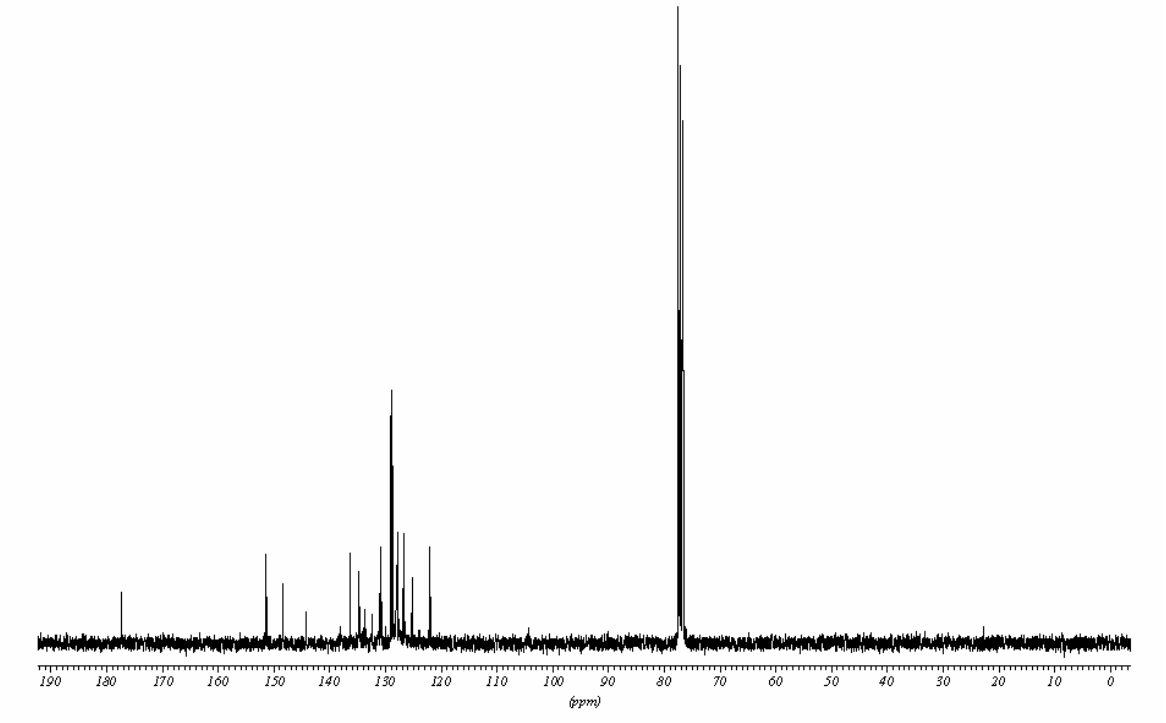

N
O
O
S
N
F3C
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

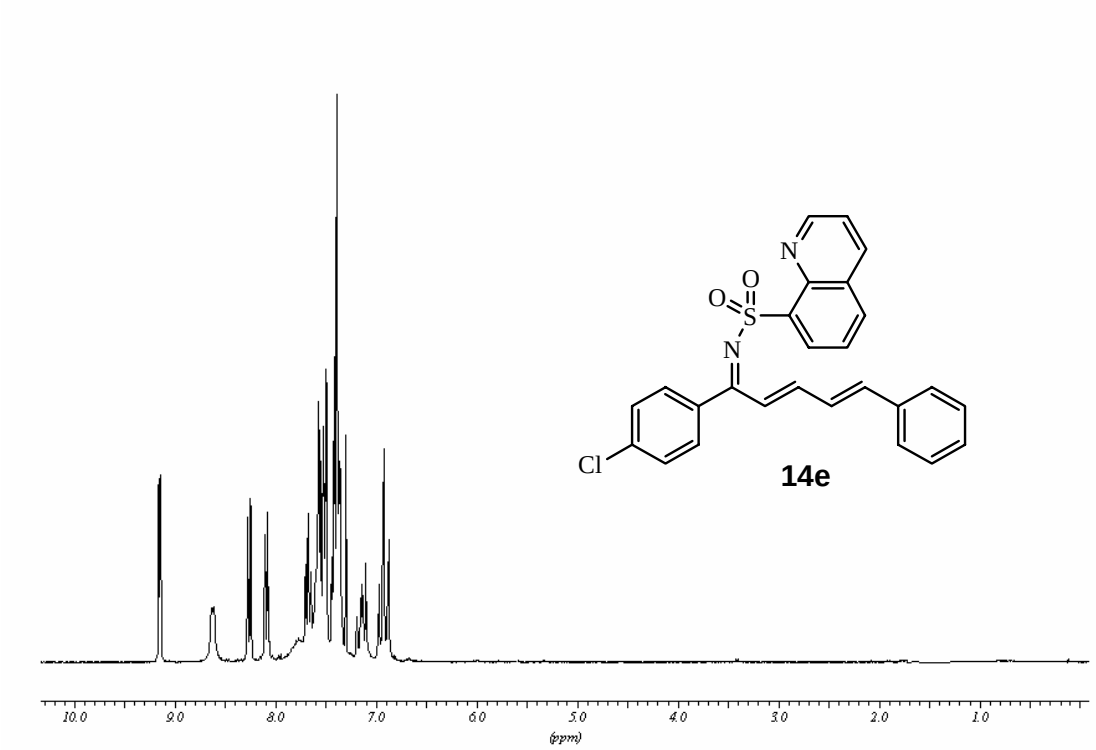
12e

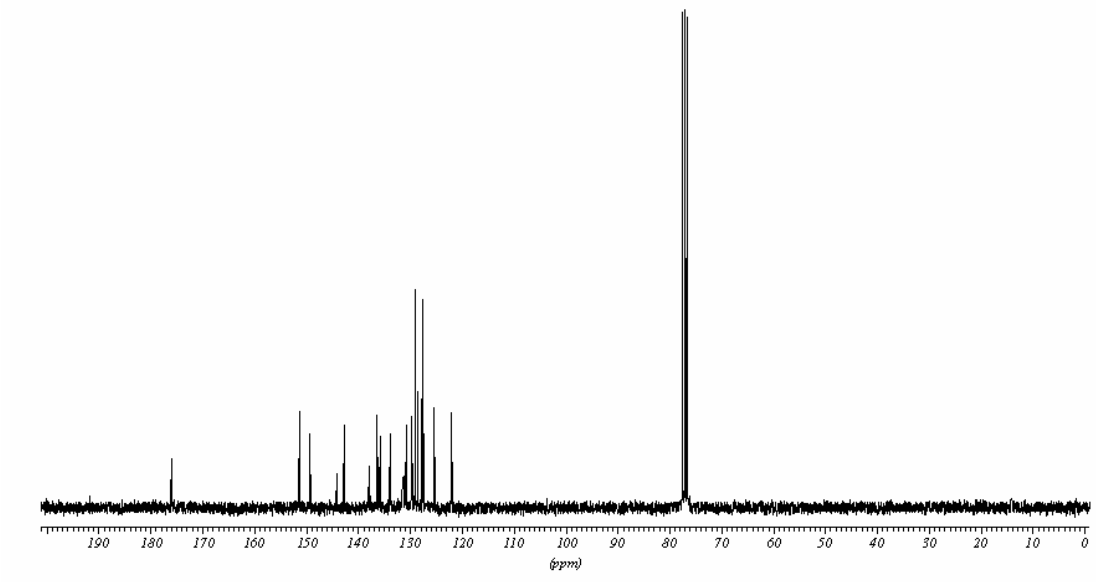

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

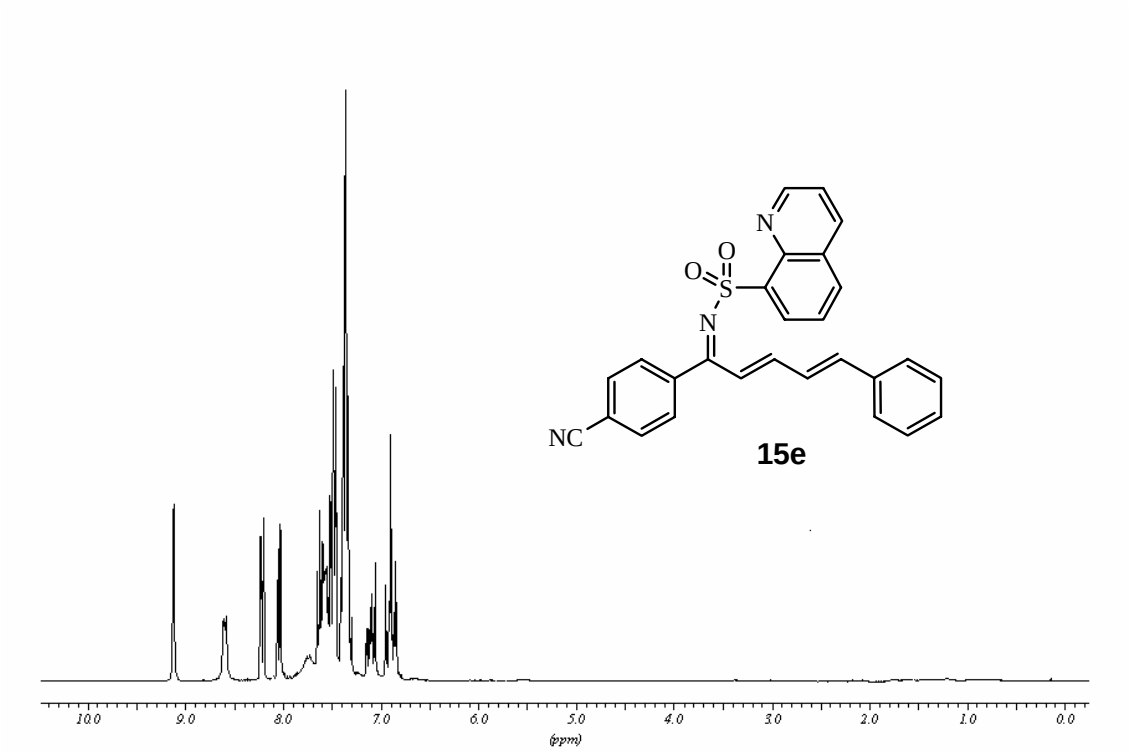

N
O
O
S
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

13e

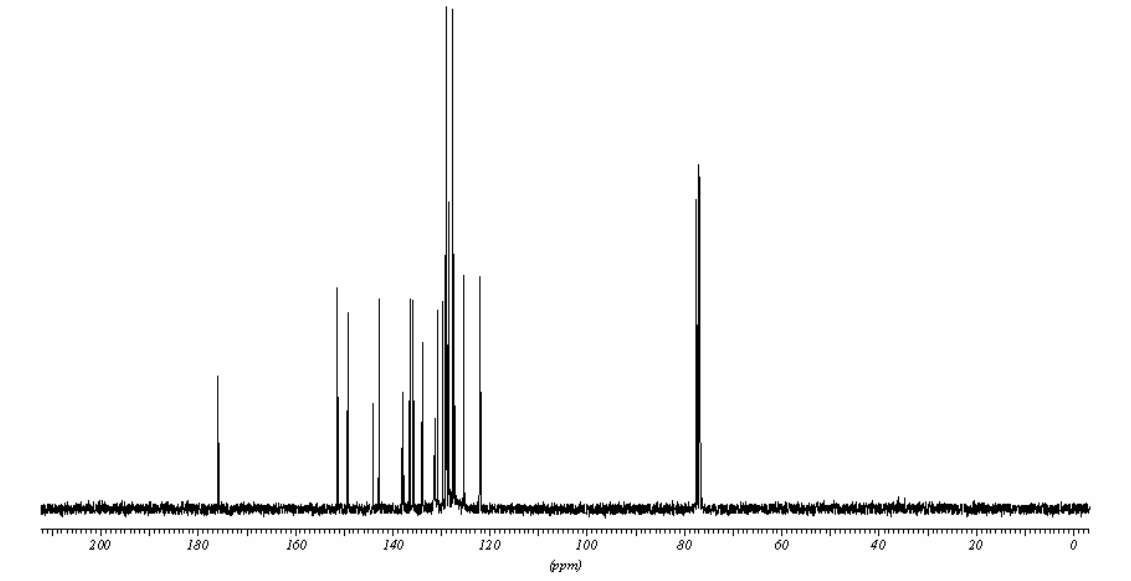

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

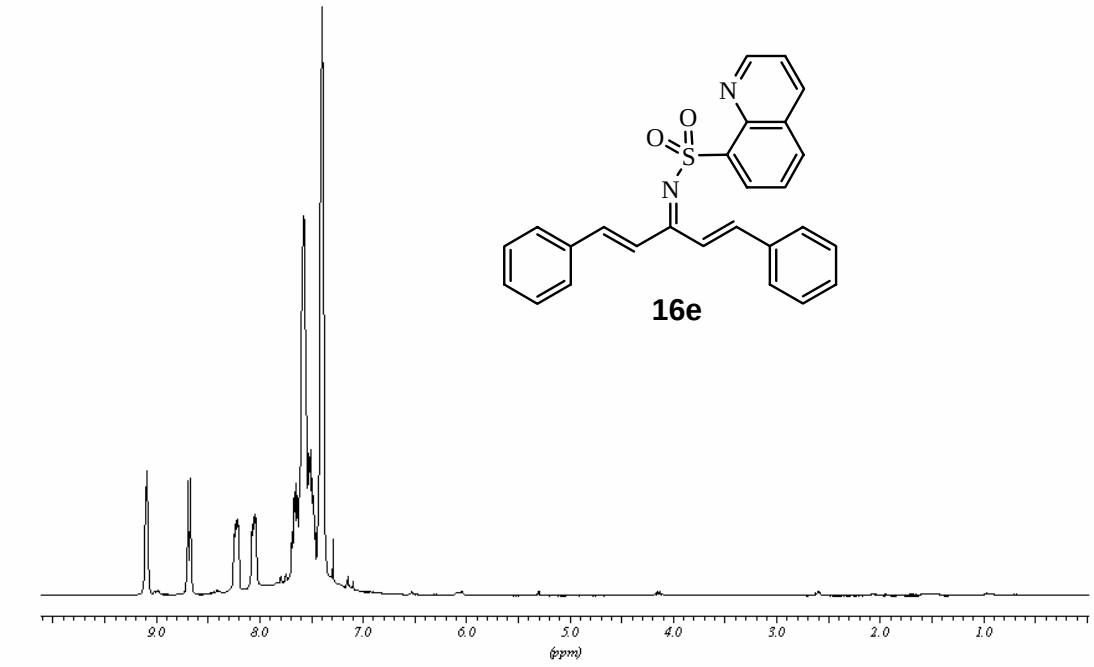

N
O
O
S
N
Cl
14e
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

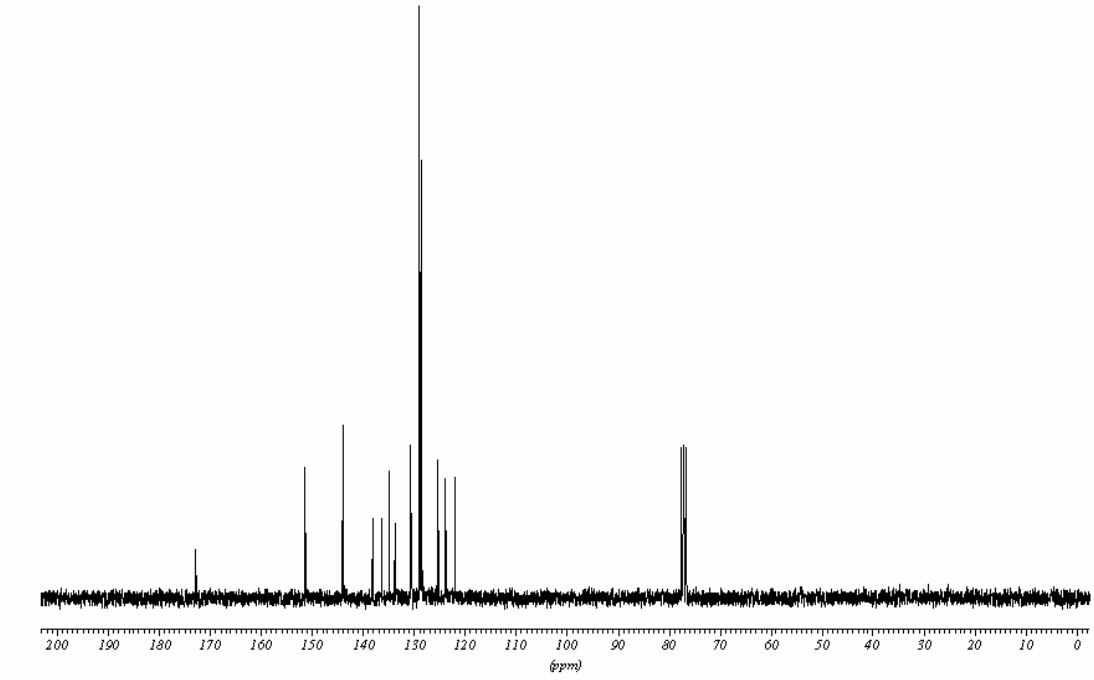

N
O
O
S
N
NC
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

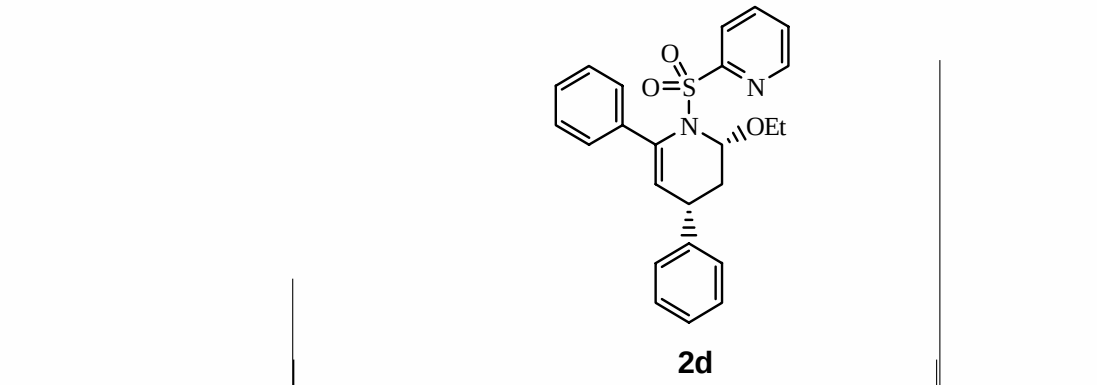
15e


200
180
160
140
120
100
80
60
40
20
0
(ppm)


N
O
O
S
N
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

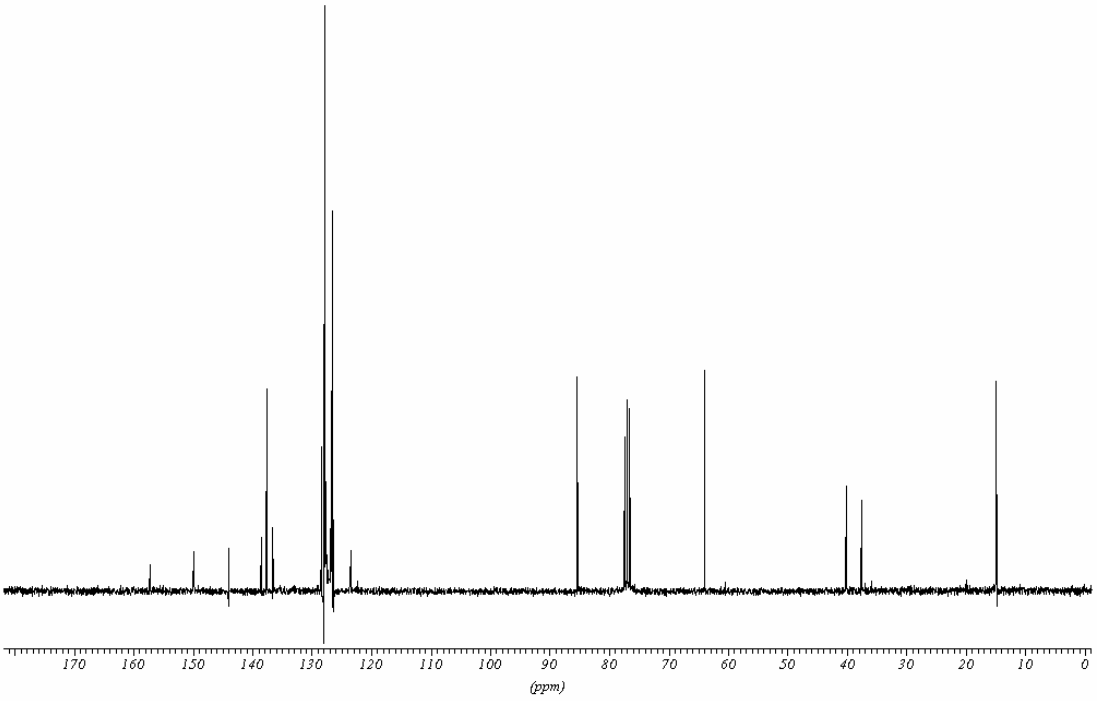
16e

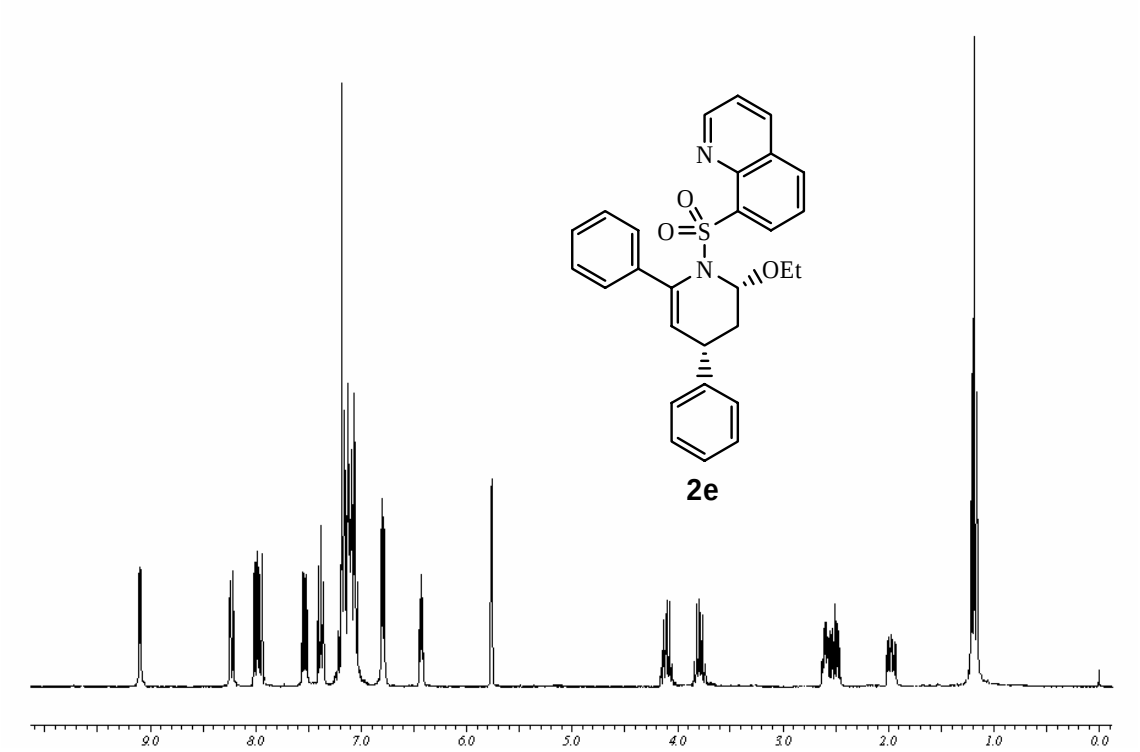

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


O
O
S
N
N
OEt

2d

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)


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


N
O
O=S
N
OEt
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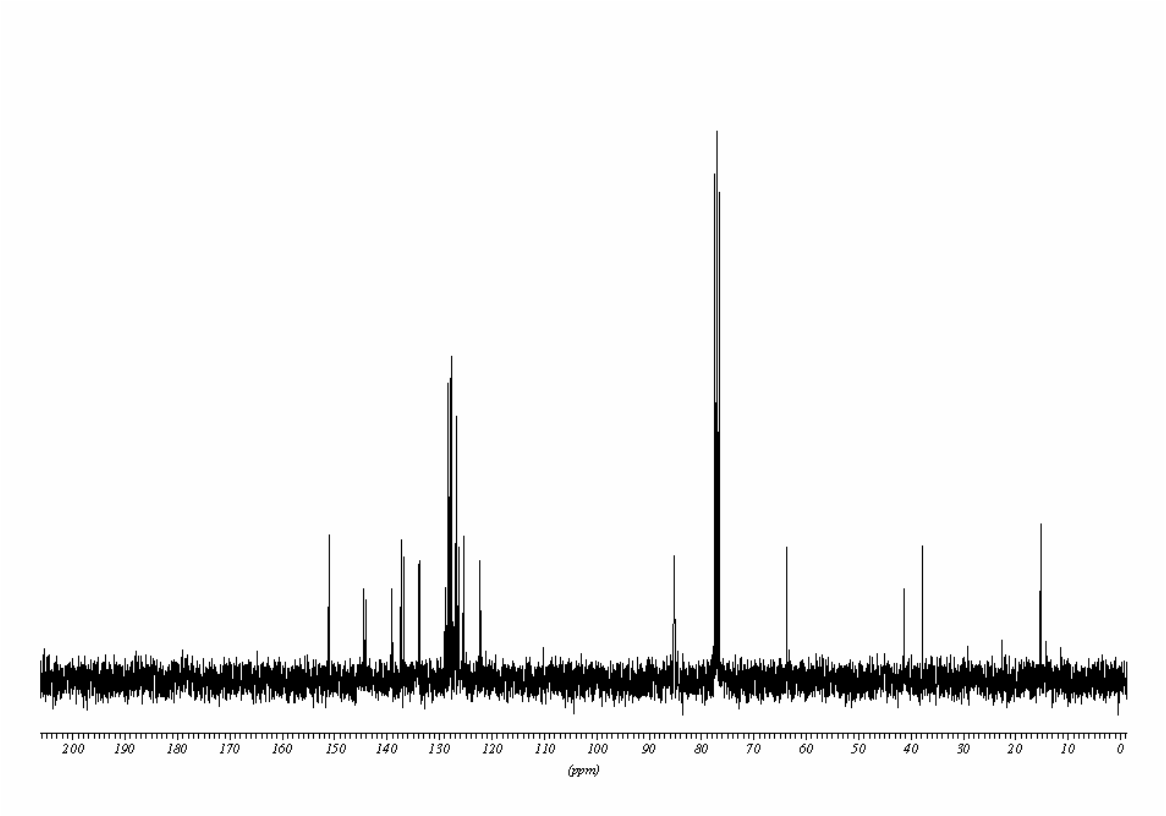
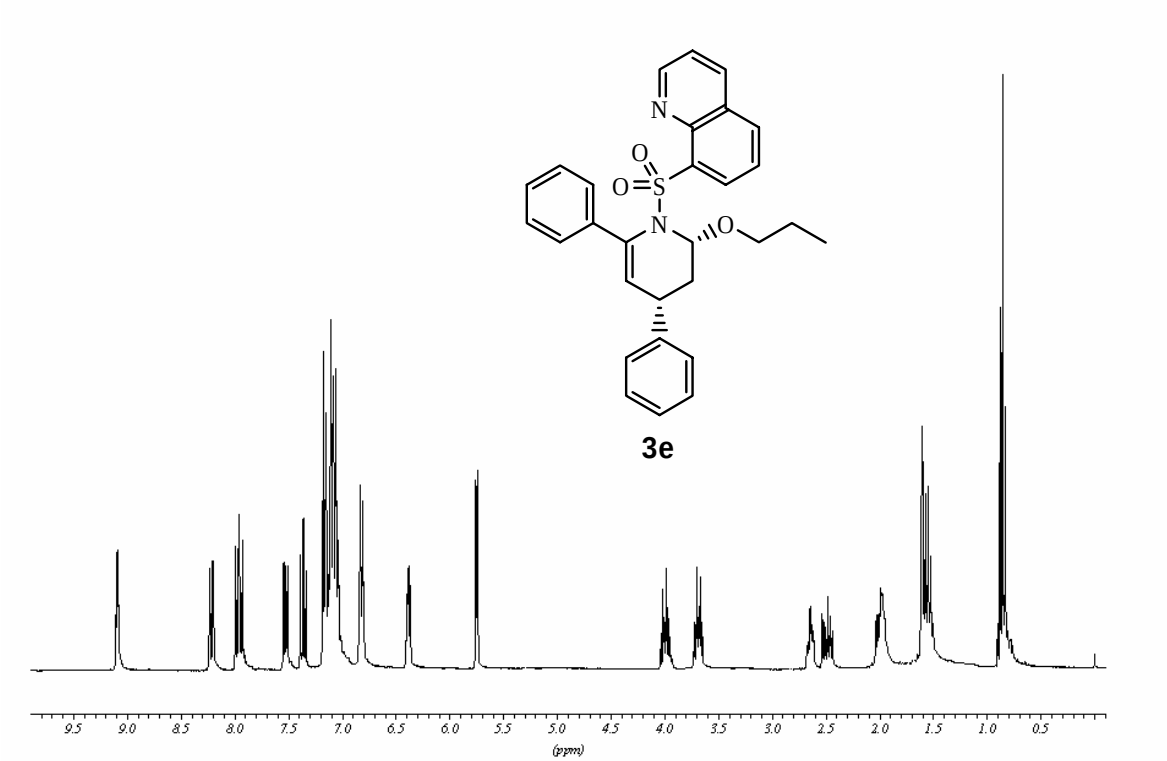
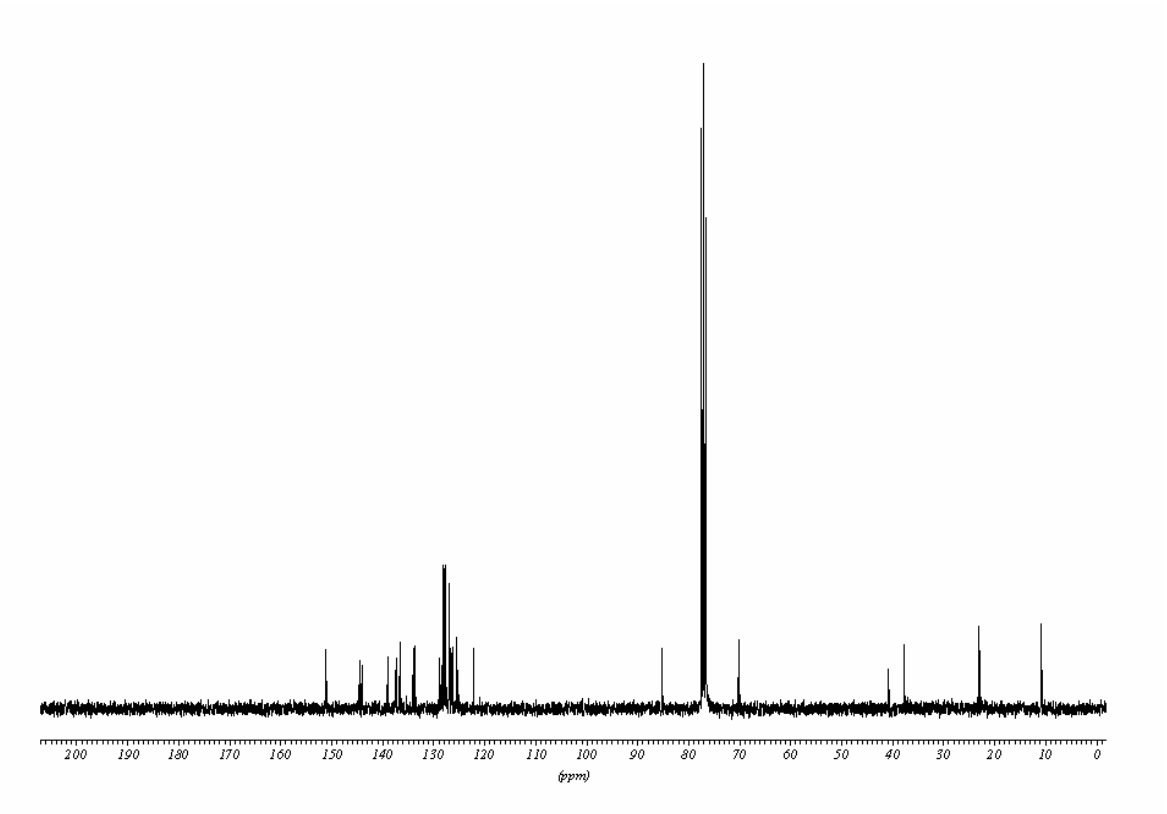
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

2e


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


N
O
O
S
N
O
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
(ppm)

3e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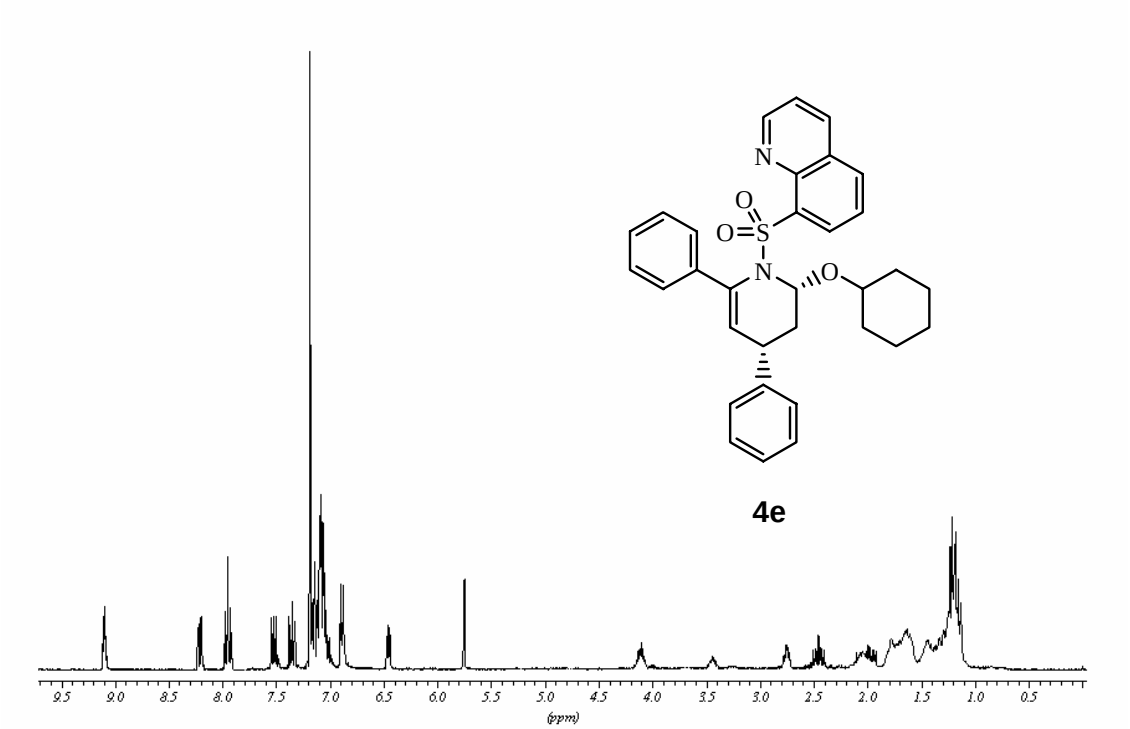
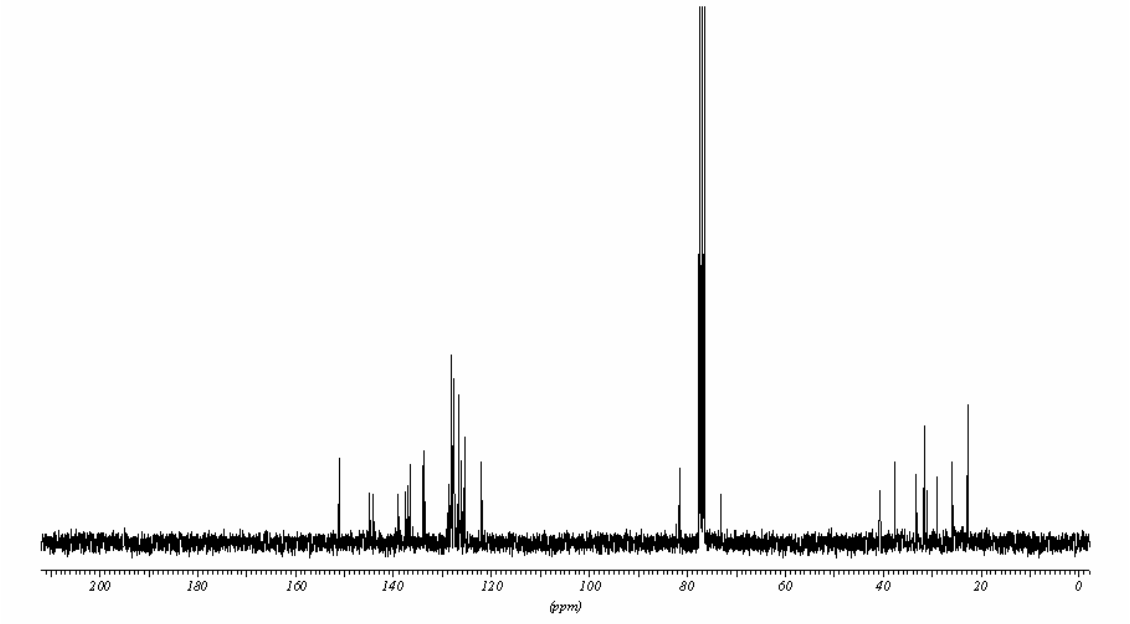
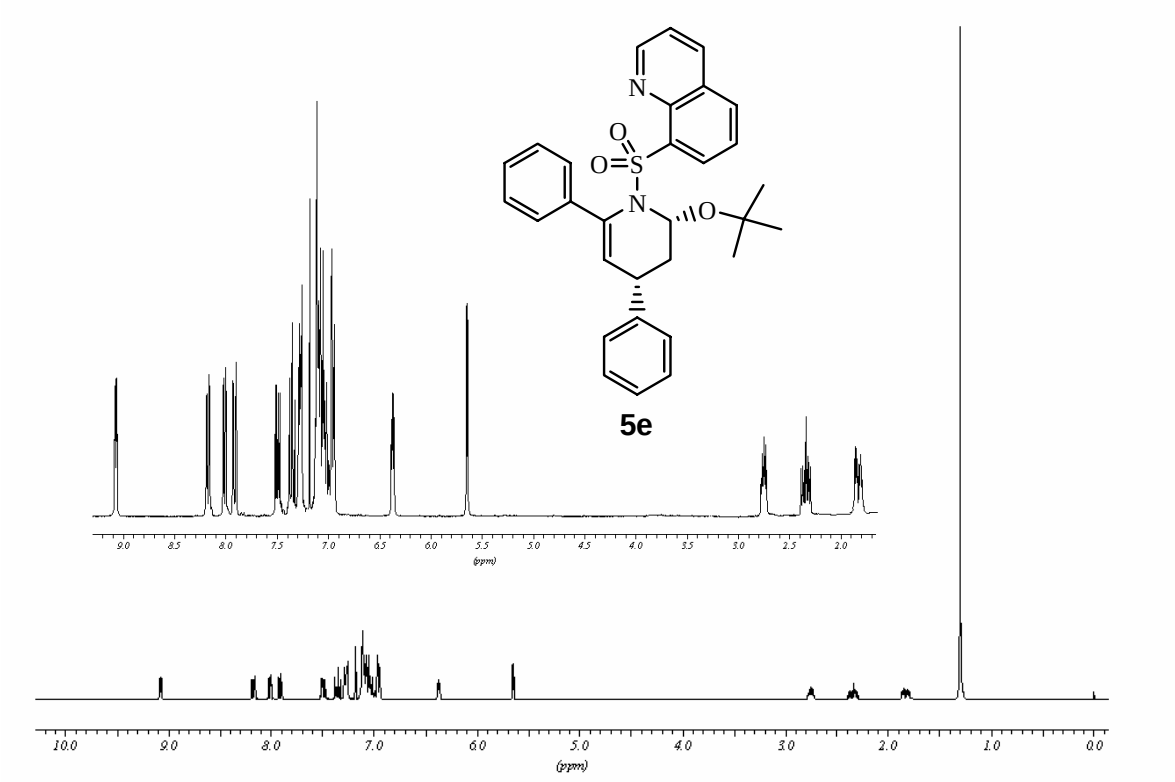
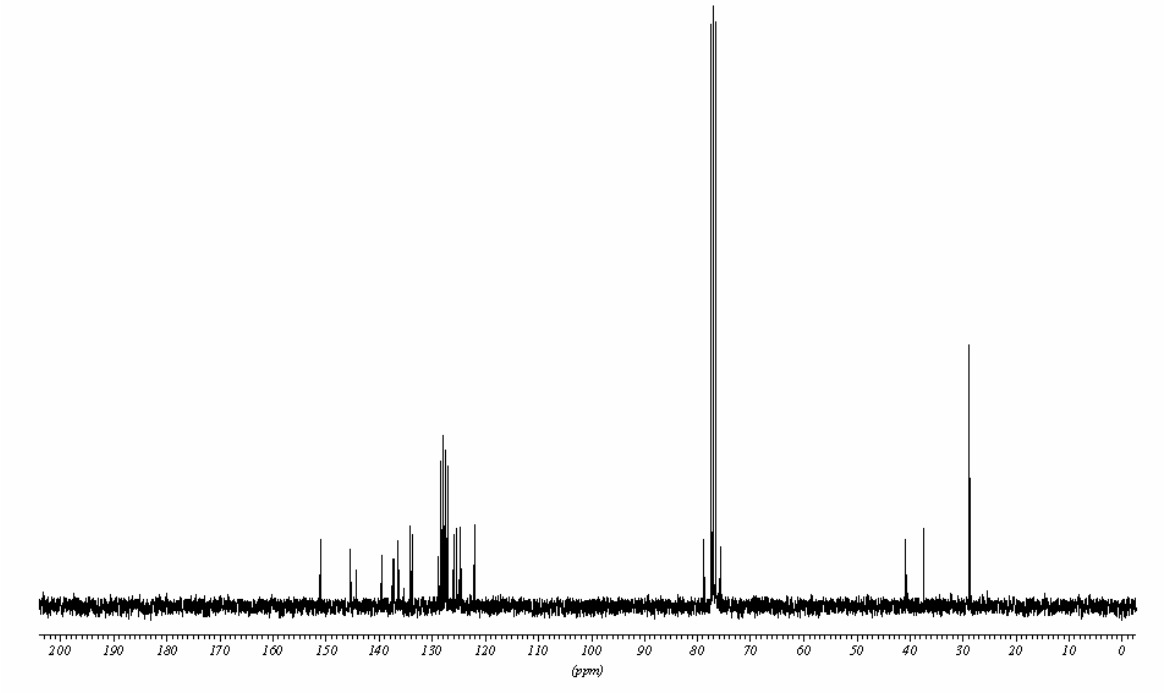
(ppm)

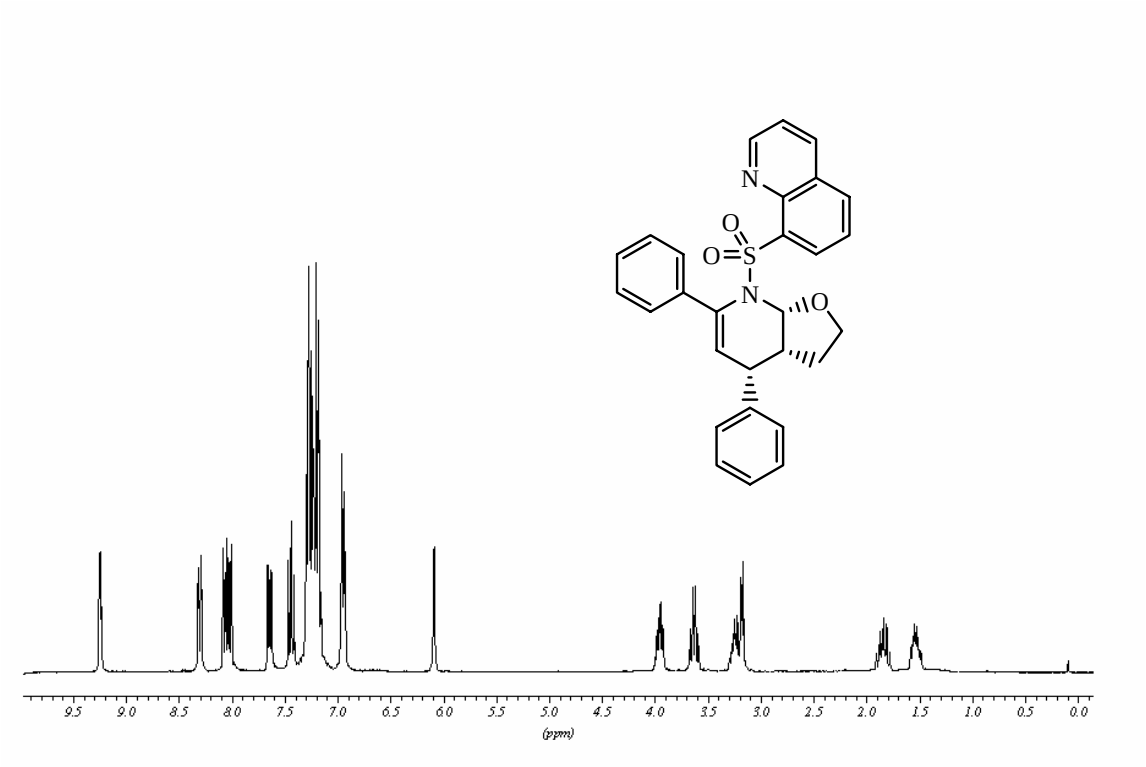

N
O
O=S
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

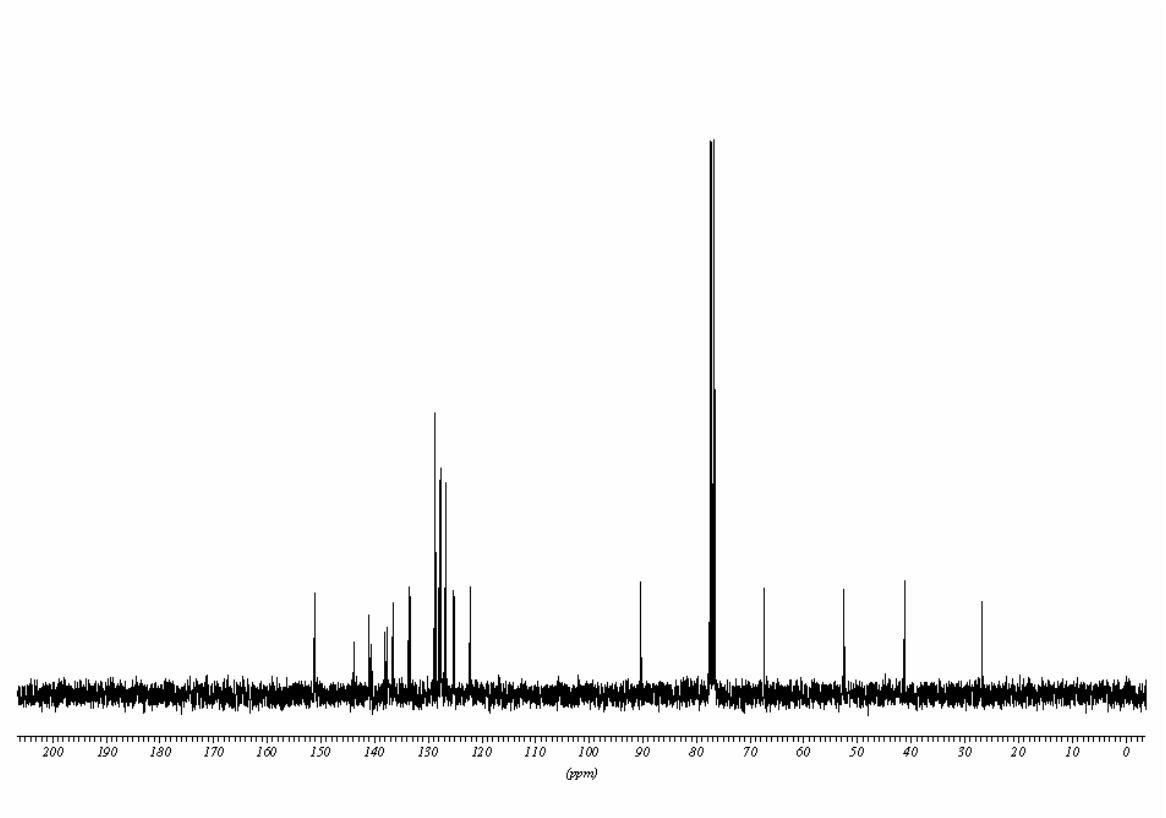
4e

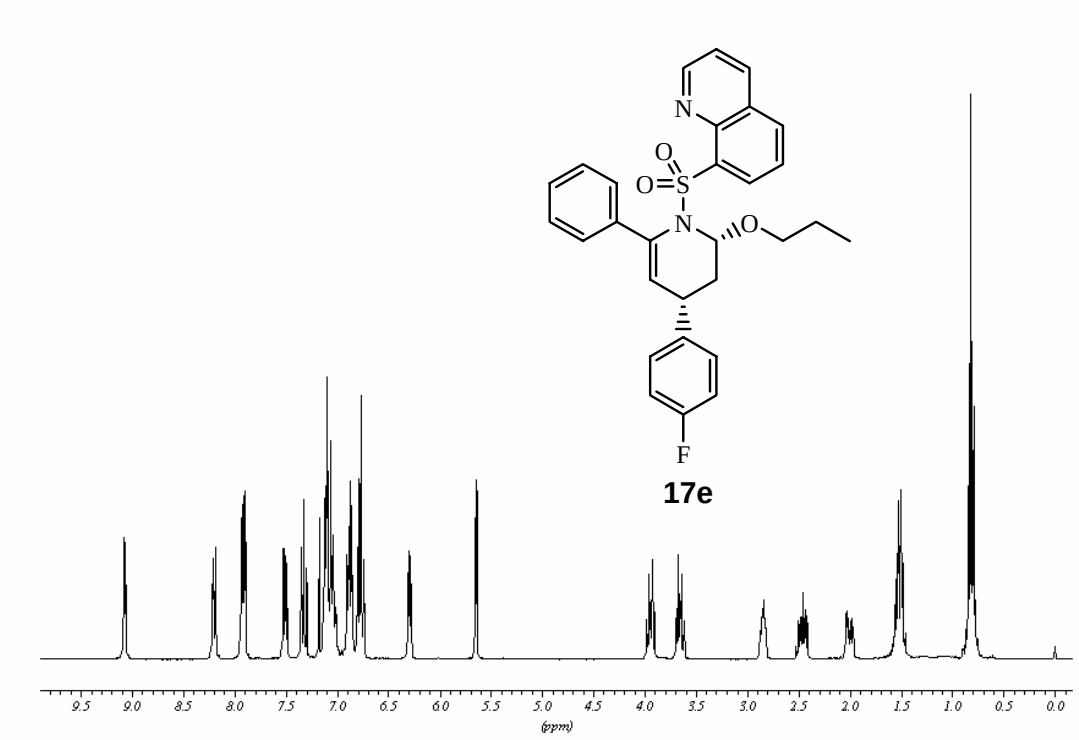

200 180 160 140 120 100 80 60 40 20 0
(ppm)


N
O
O=S
N
O
5e
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
(ppm)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

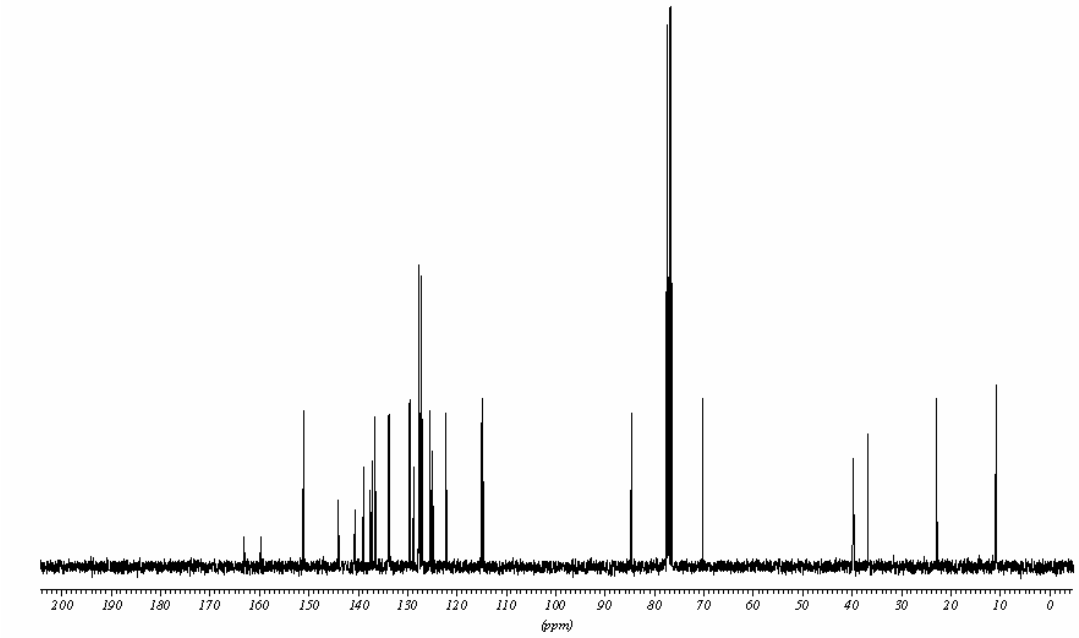

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

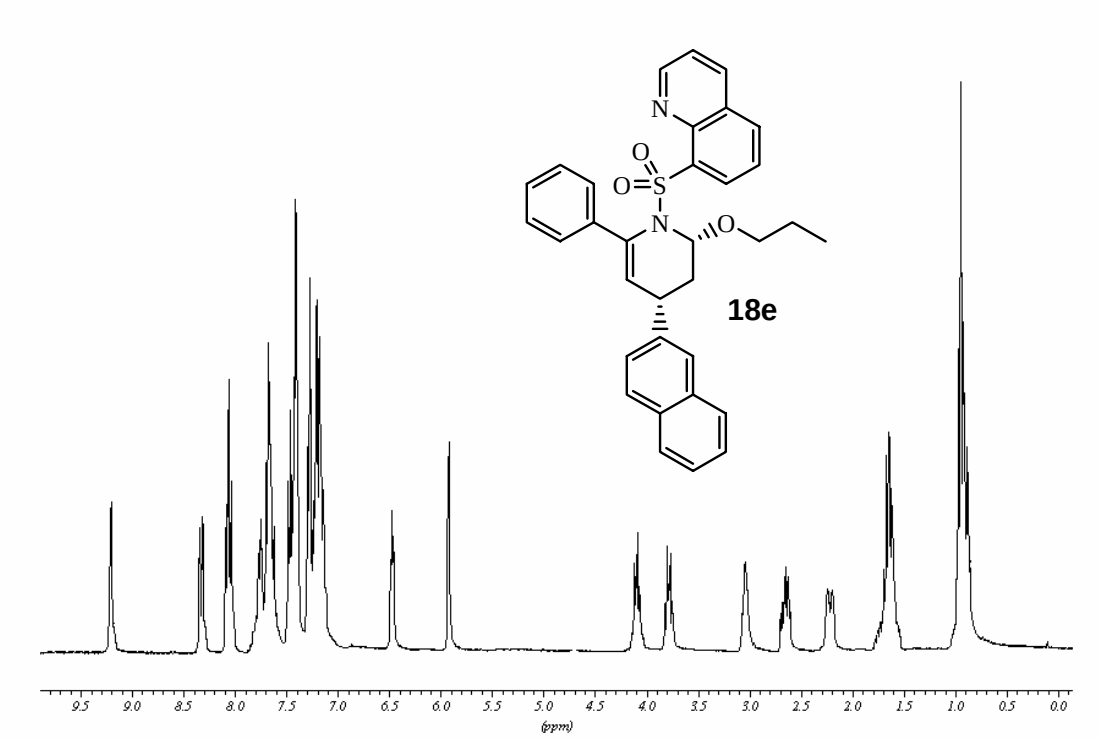

N
O
O=S
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

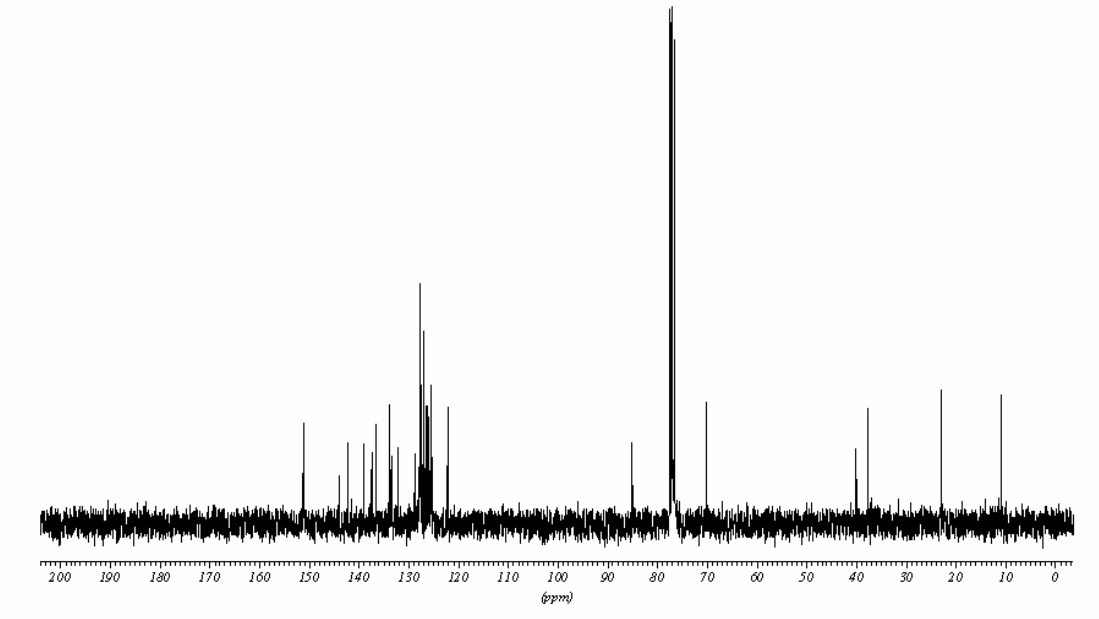

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

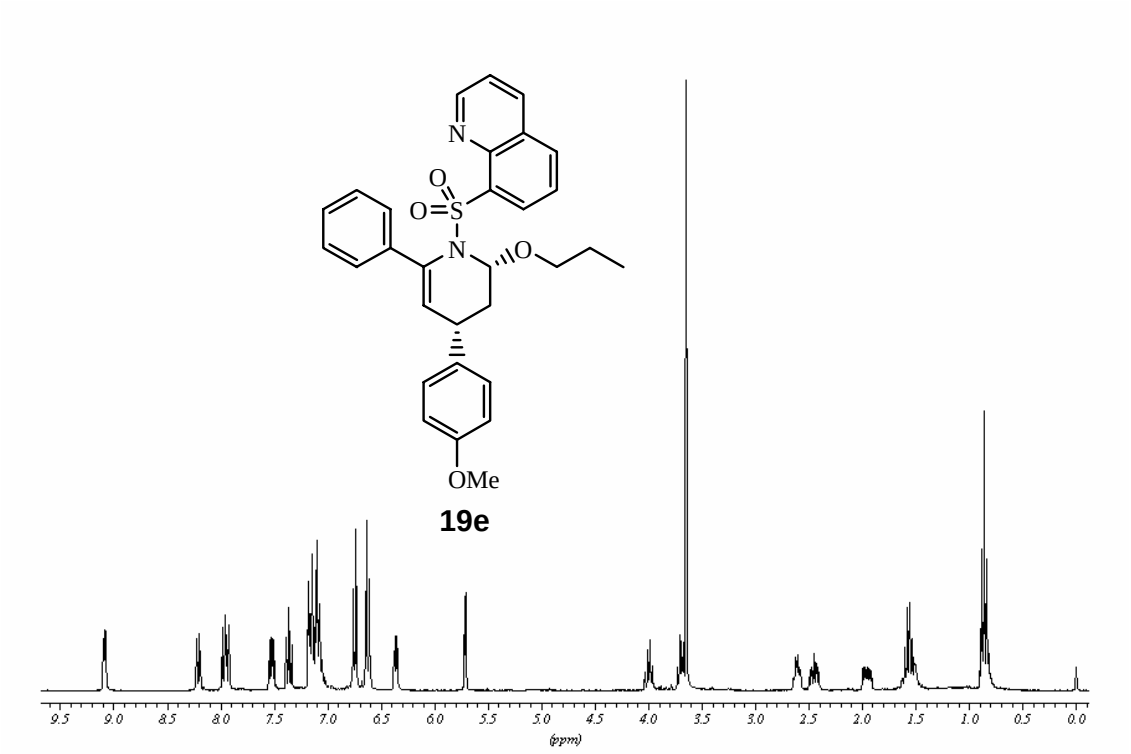

N
O
O=S
N
O
F
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

17e


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

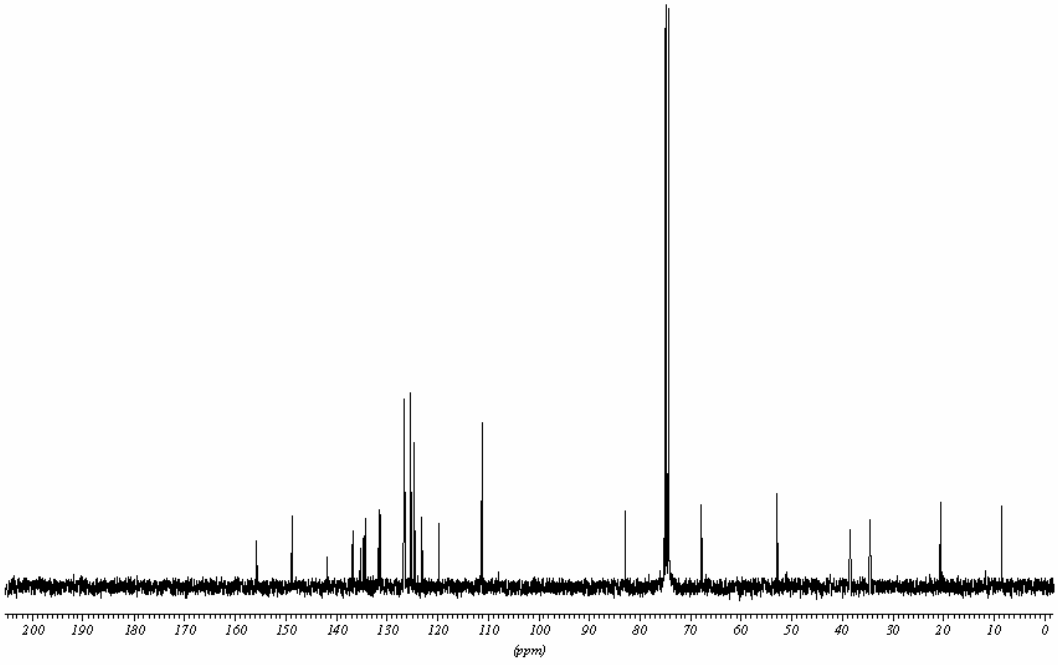

N
O
O=S
N
O
18e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

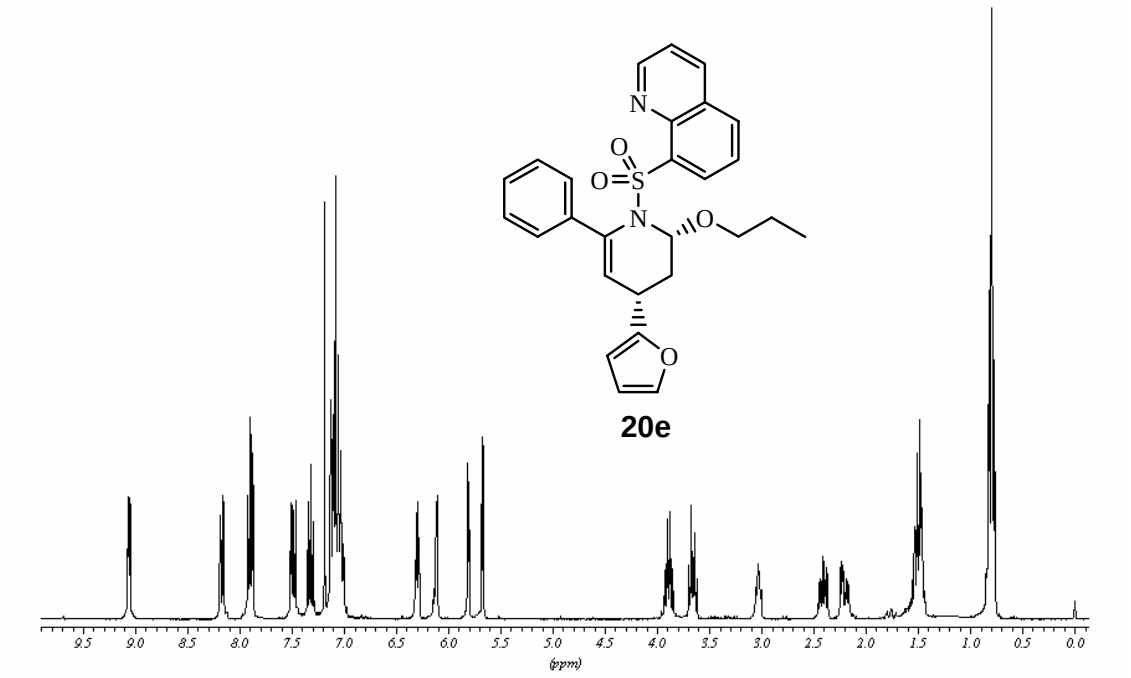

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


N
O
O=S
N
O
OMe

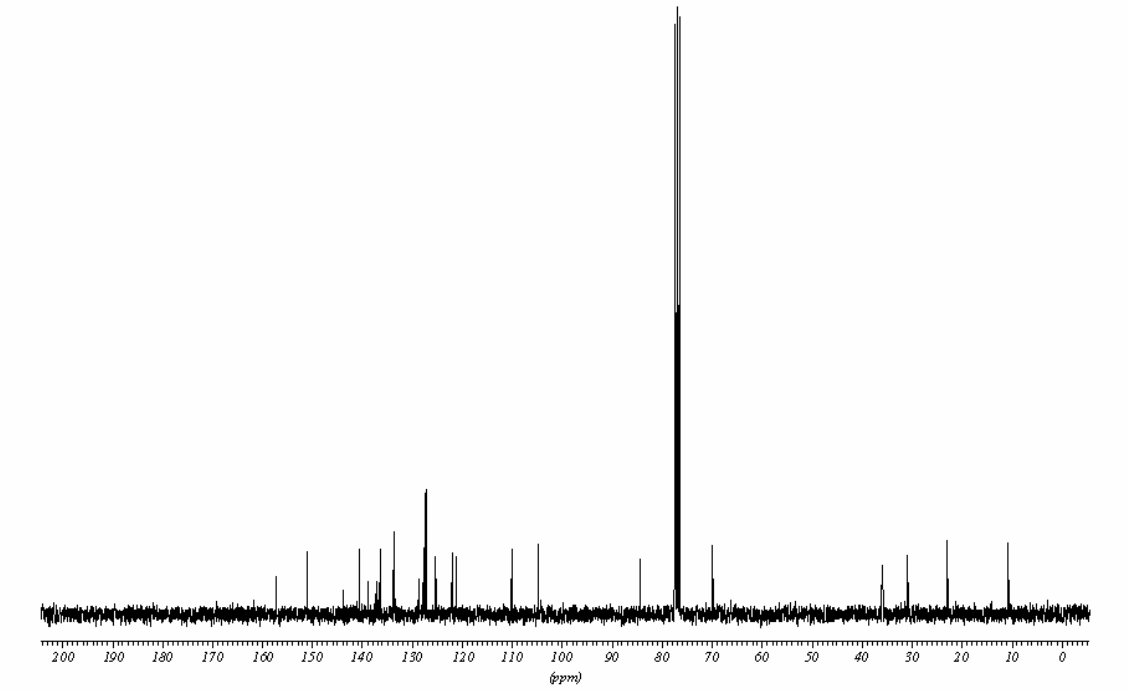
19e

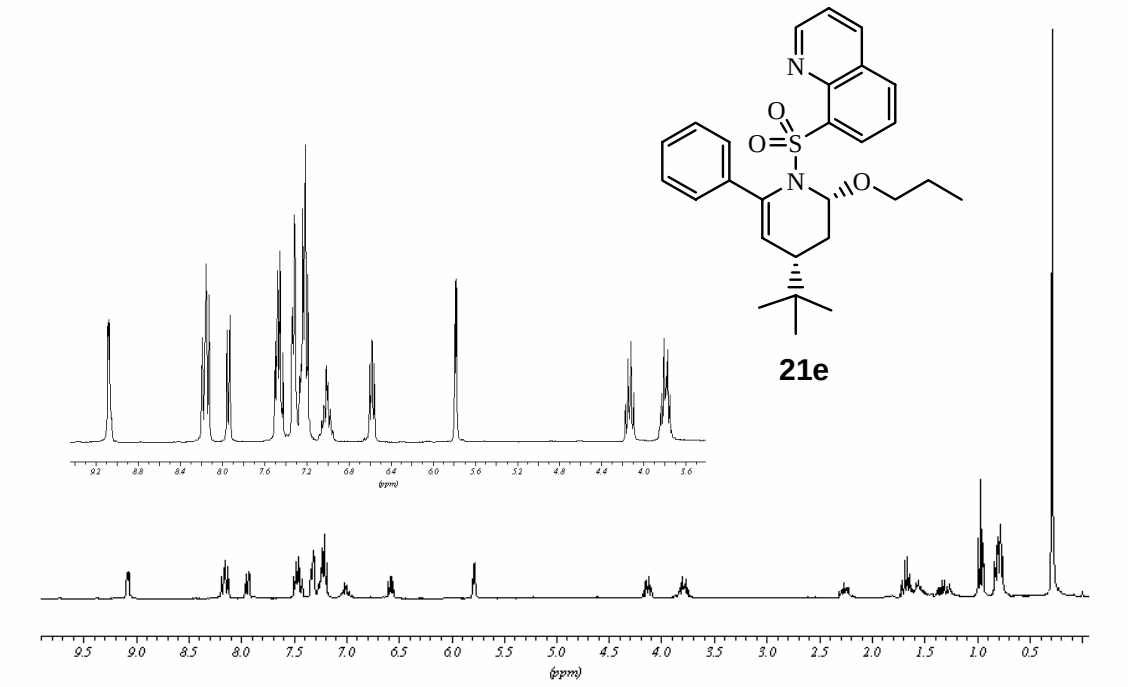
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

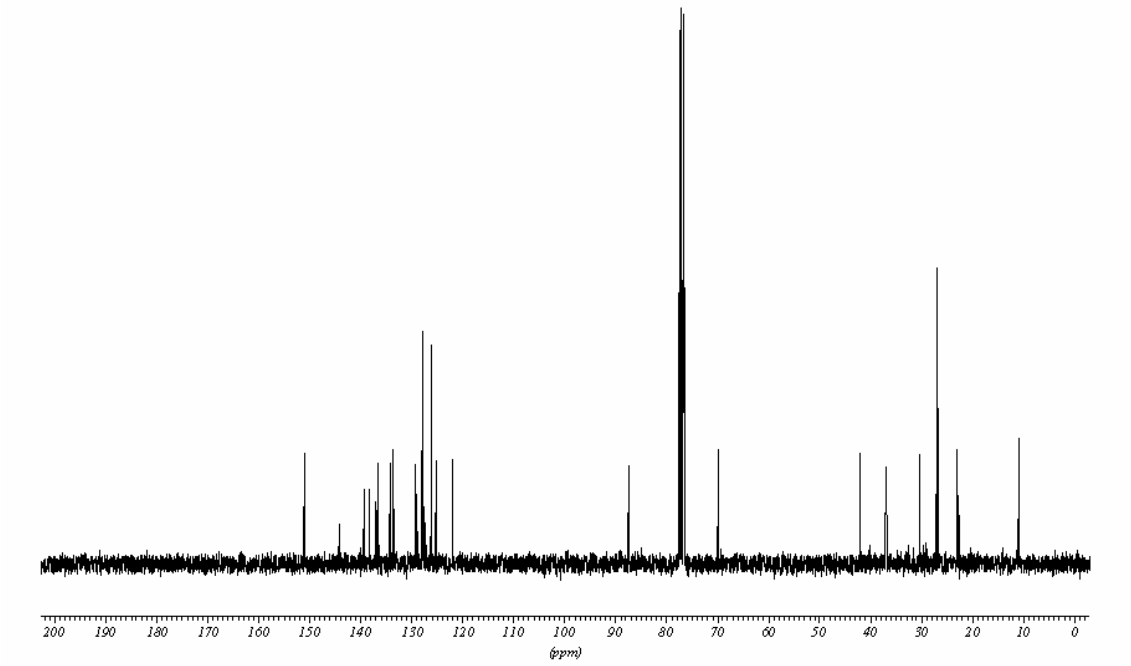

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


N
O
O=S
N
O
O
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)

20e


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


N
O
O=S
N
O
21e
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
(ppm)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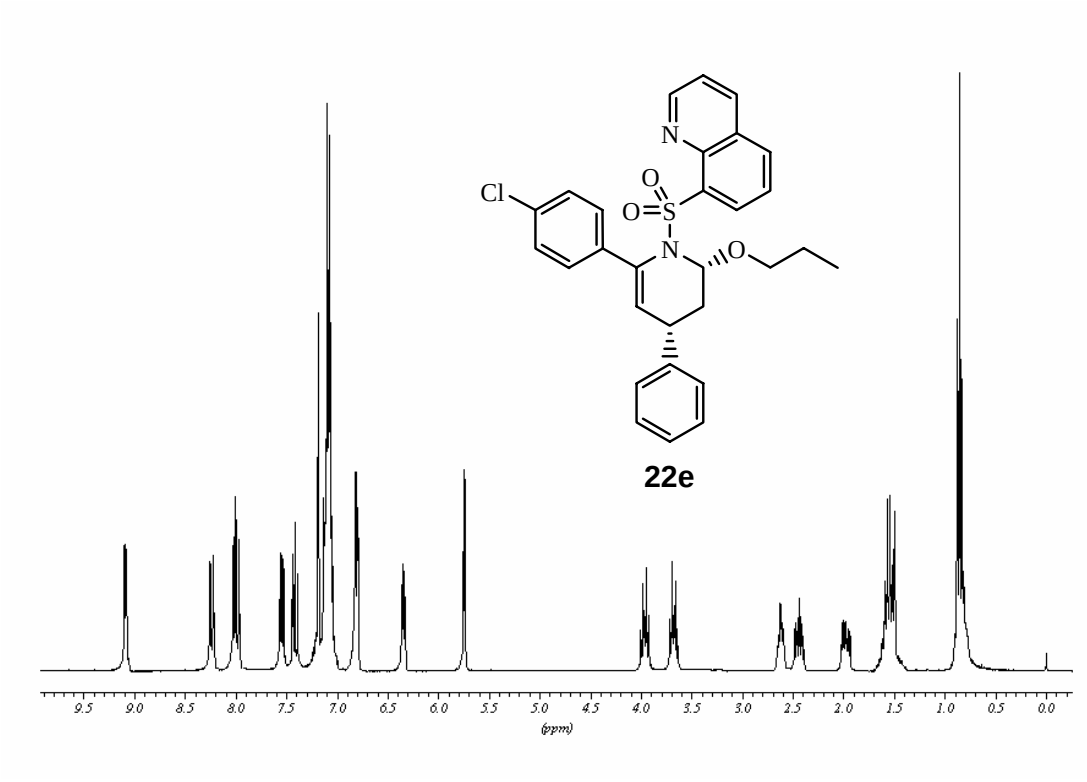
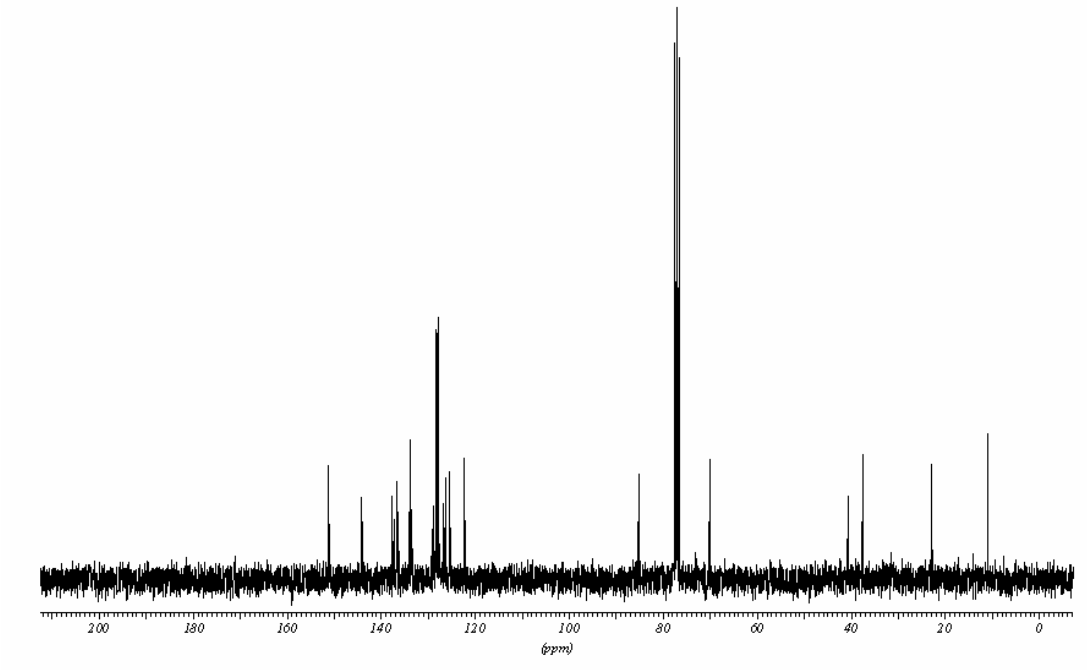
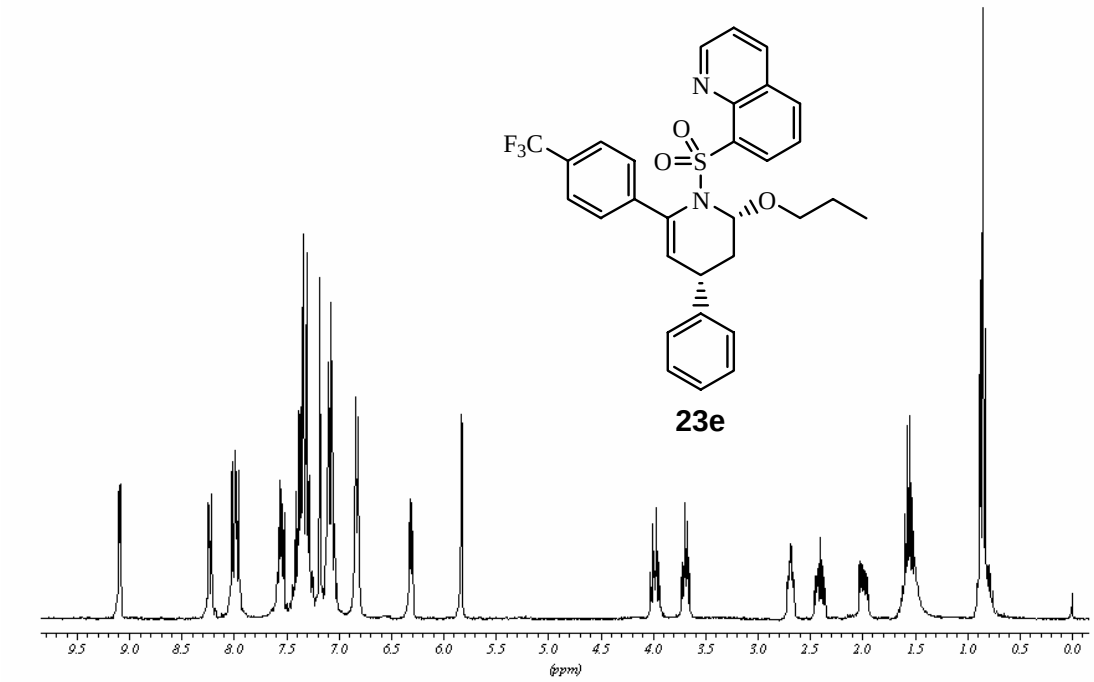
(ppm)

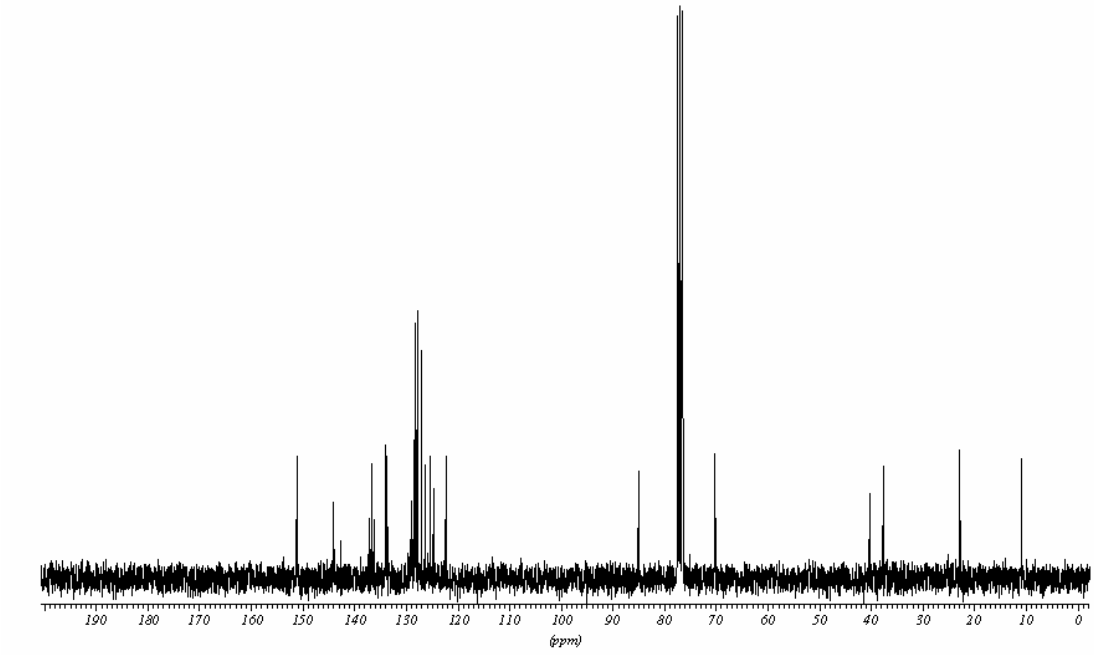

Cl
O
O=S
N
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

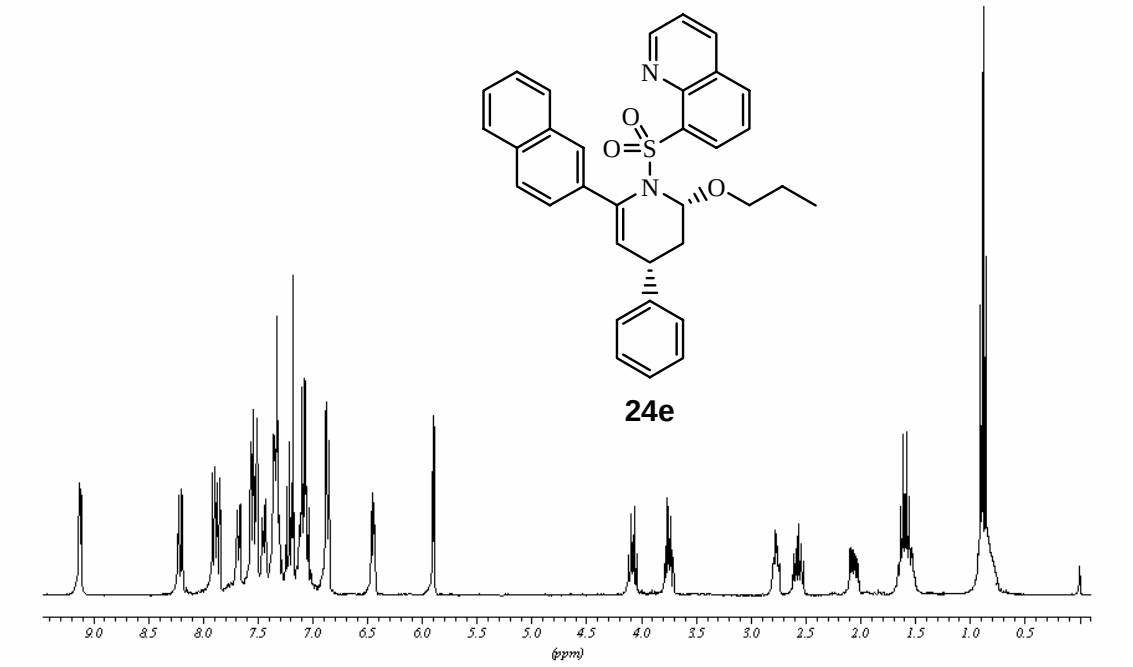
22e


200 180 160 140 120 100 80 60 40 20 0
(ppm)

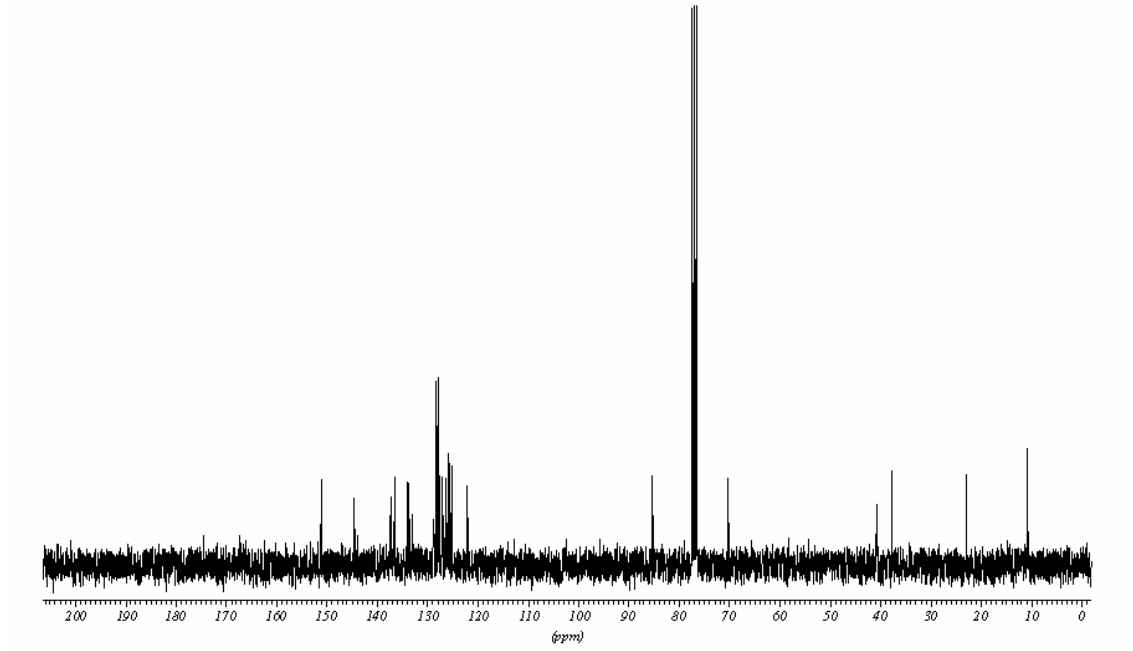

N
O
O=S
F3C
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

23e


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


N
O
O=S
N
O
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
(ppm)

24e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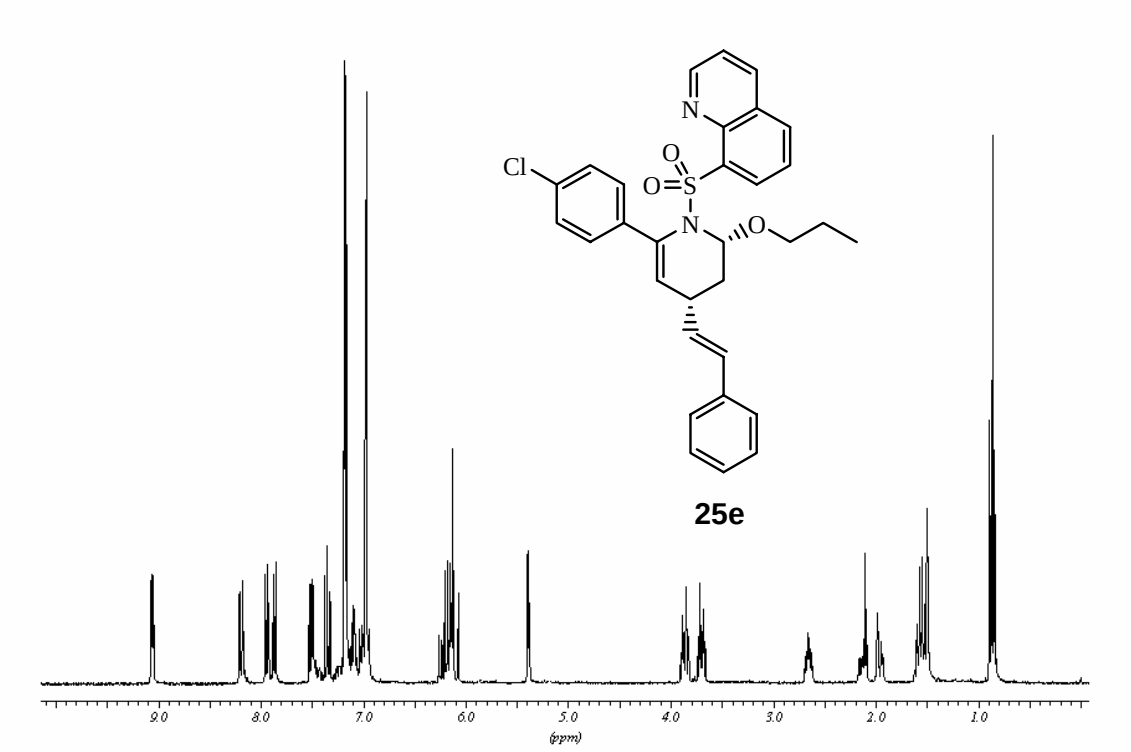
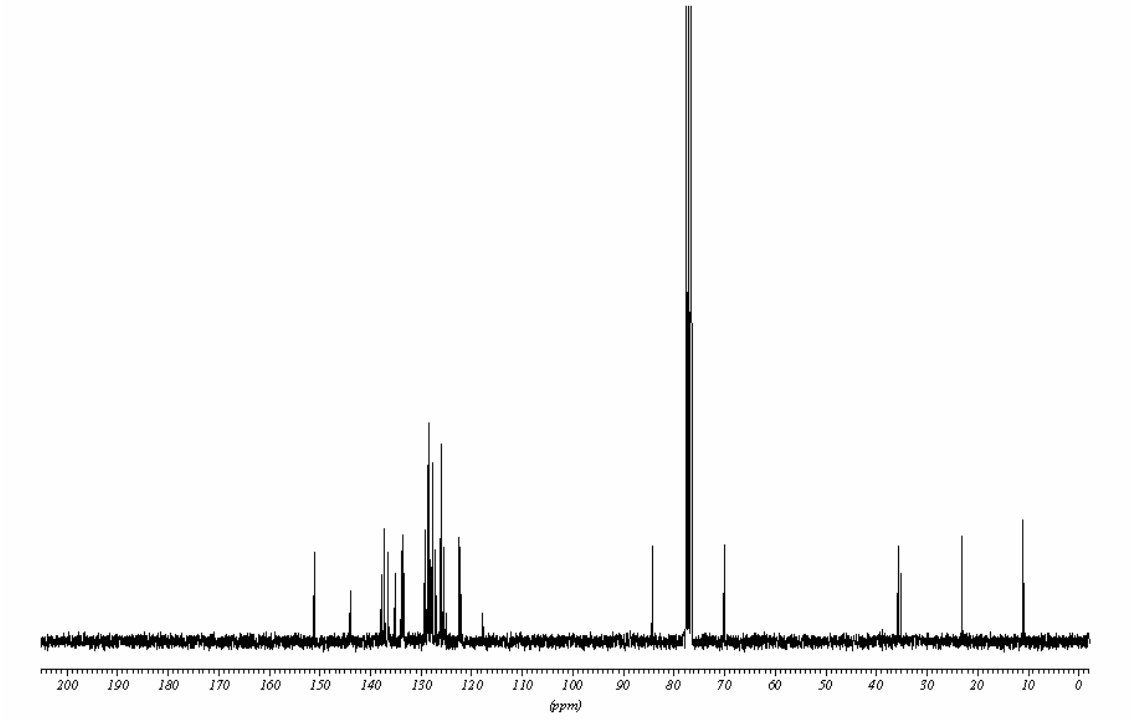
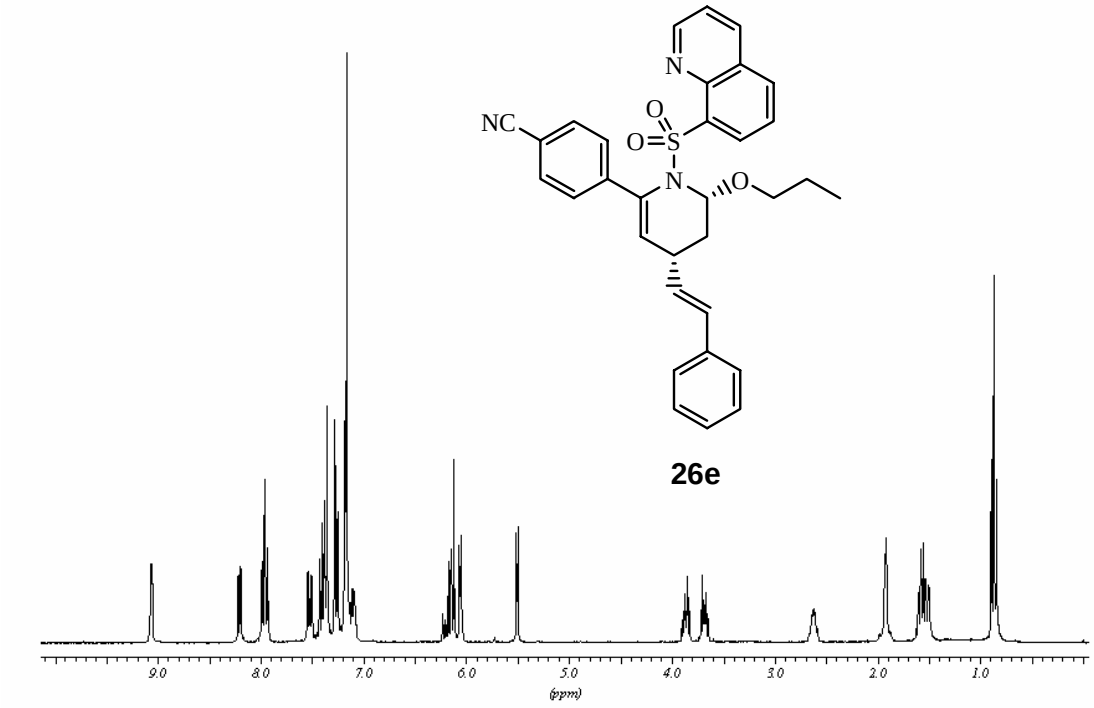
(ppm)


N
O
Cl
O=S
N
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)

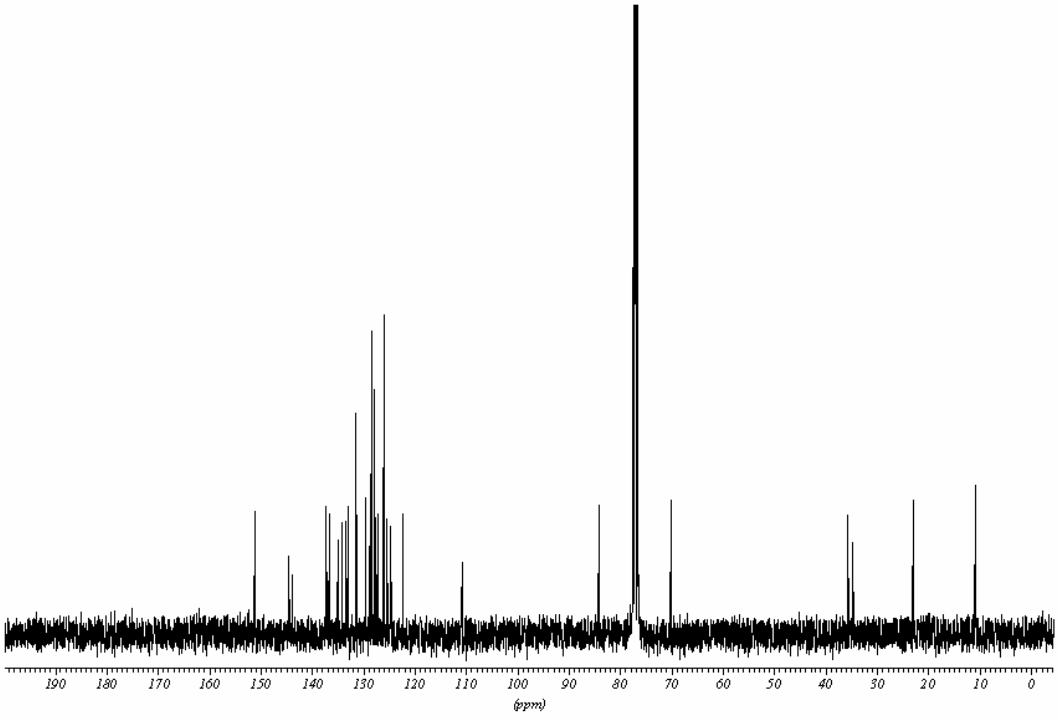
25e

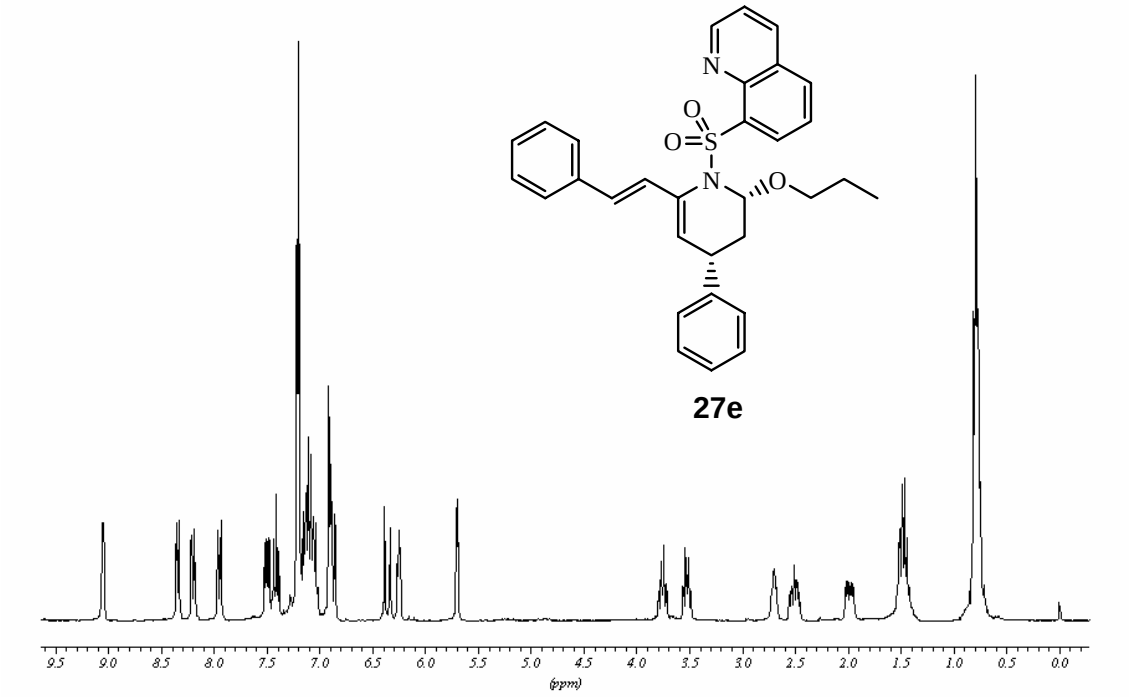

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


N
O
O=S
NC
N
O

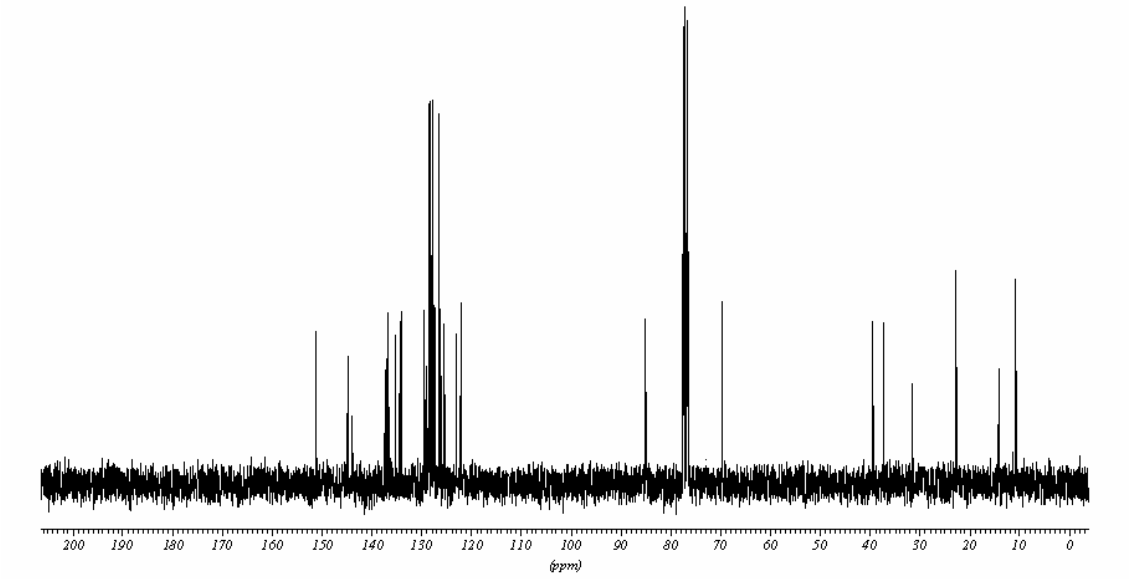
26e

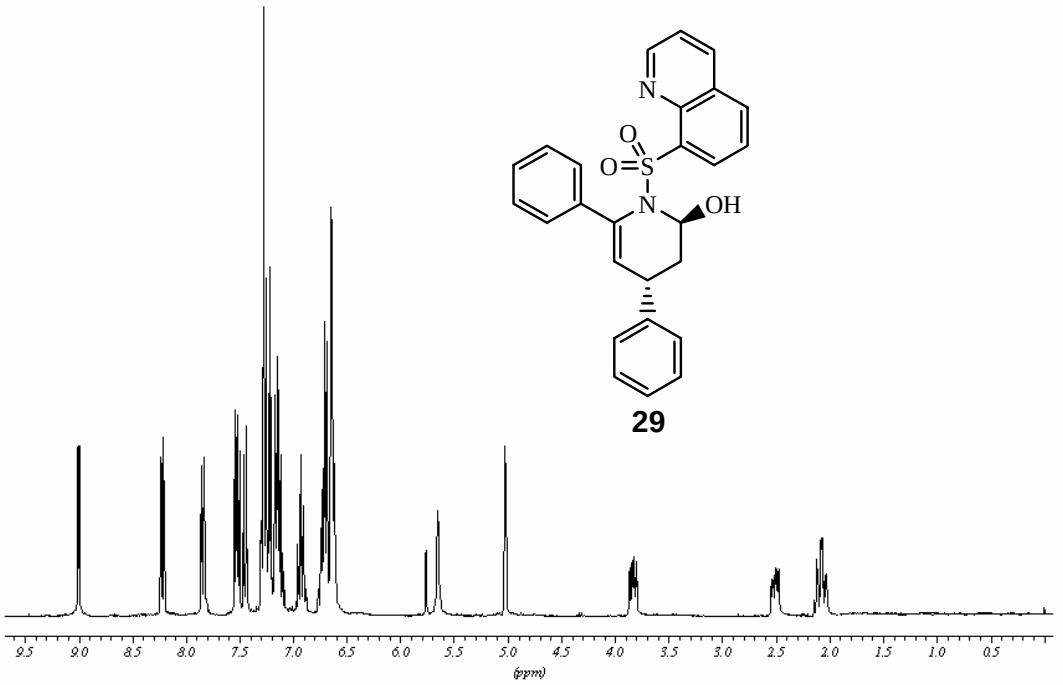
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
(ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

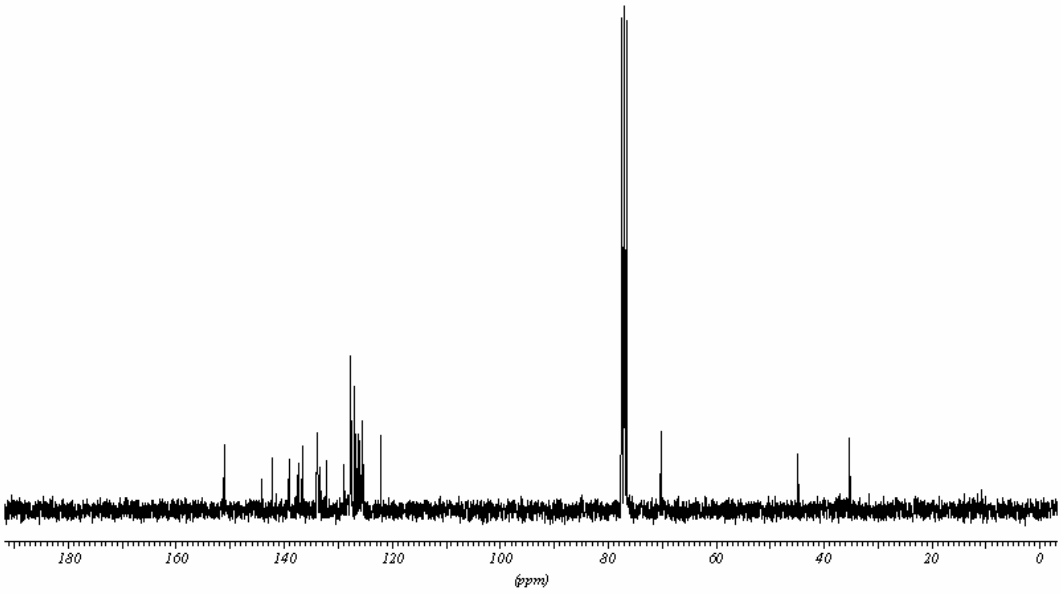

N
O
O
S
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

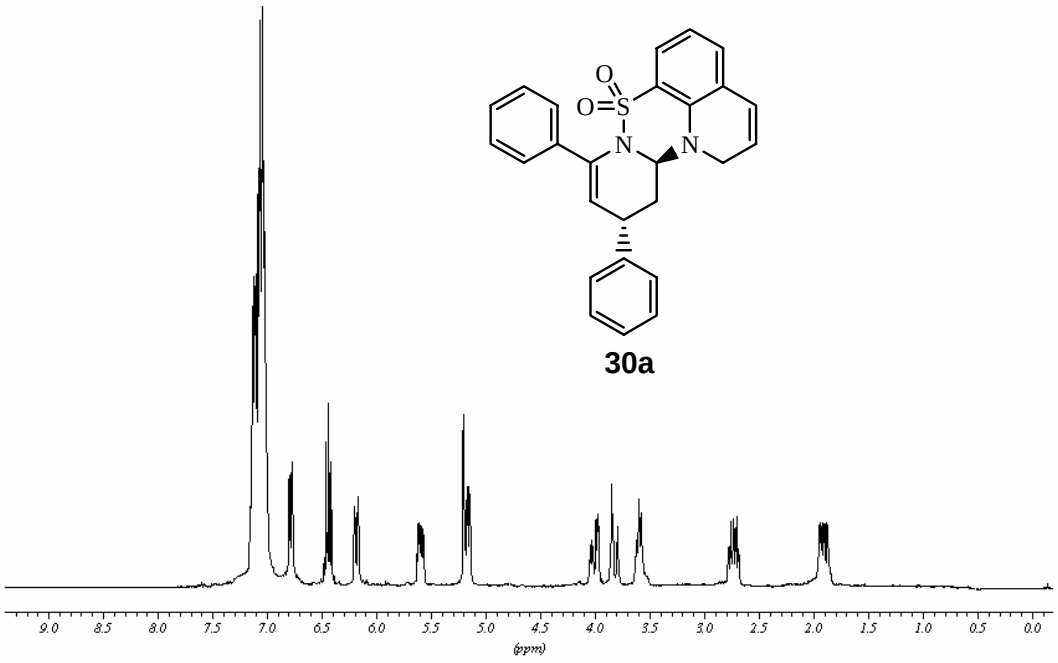
27e


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

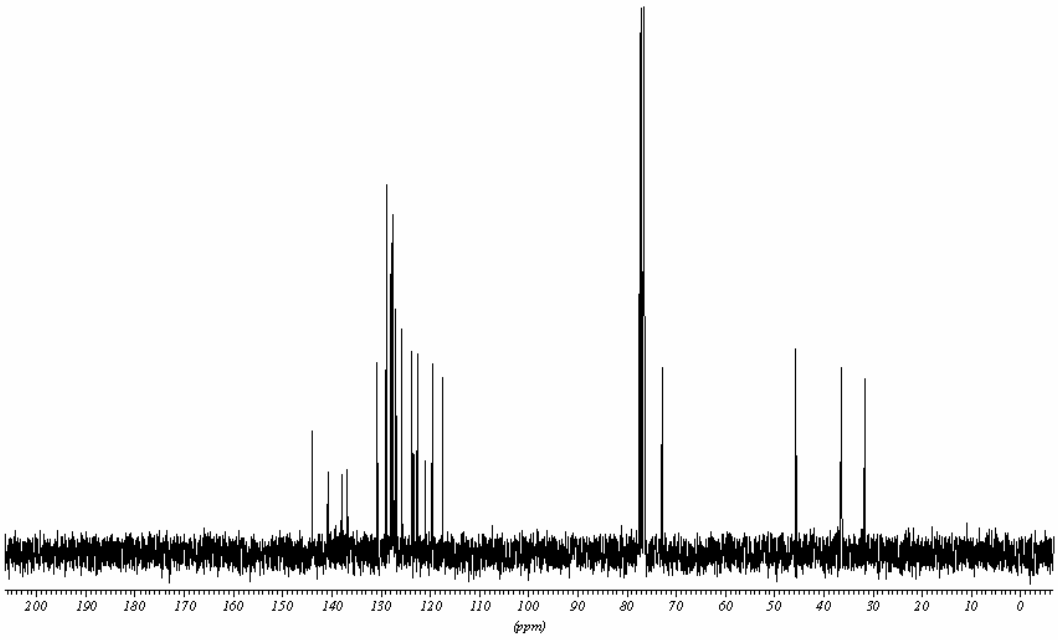

N
O
O=S
N
OH
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

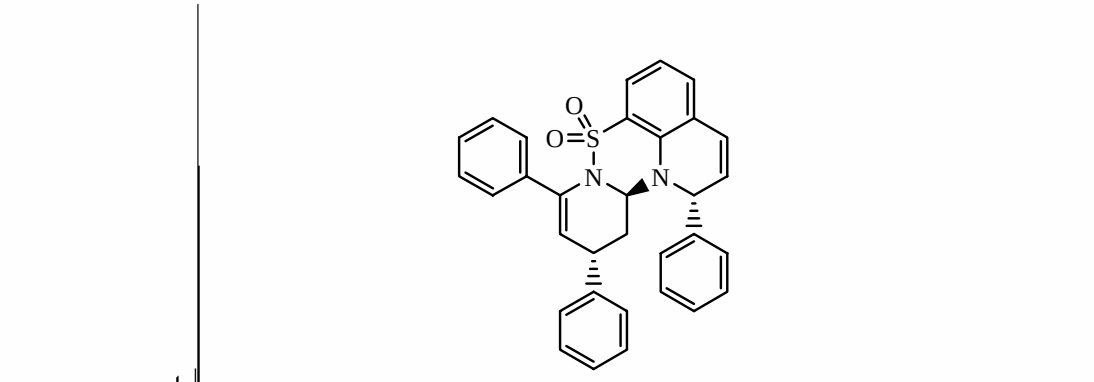
29


180 160 140 120 100 80 60 40 20 0
(ppm)

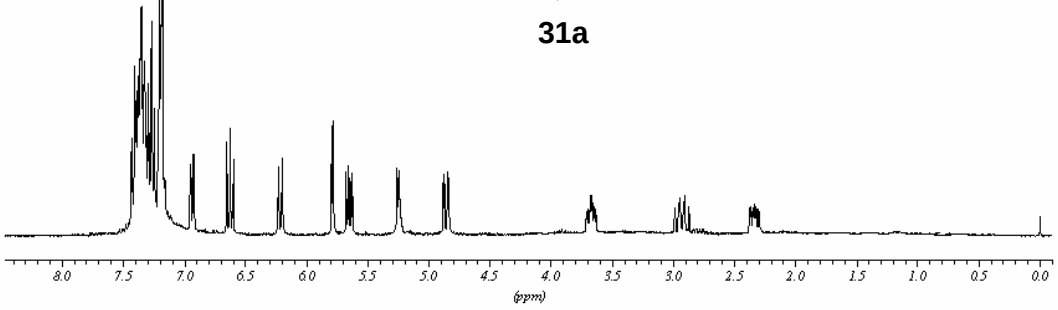

O
O=S
N
N
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

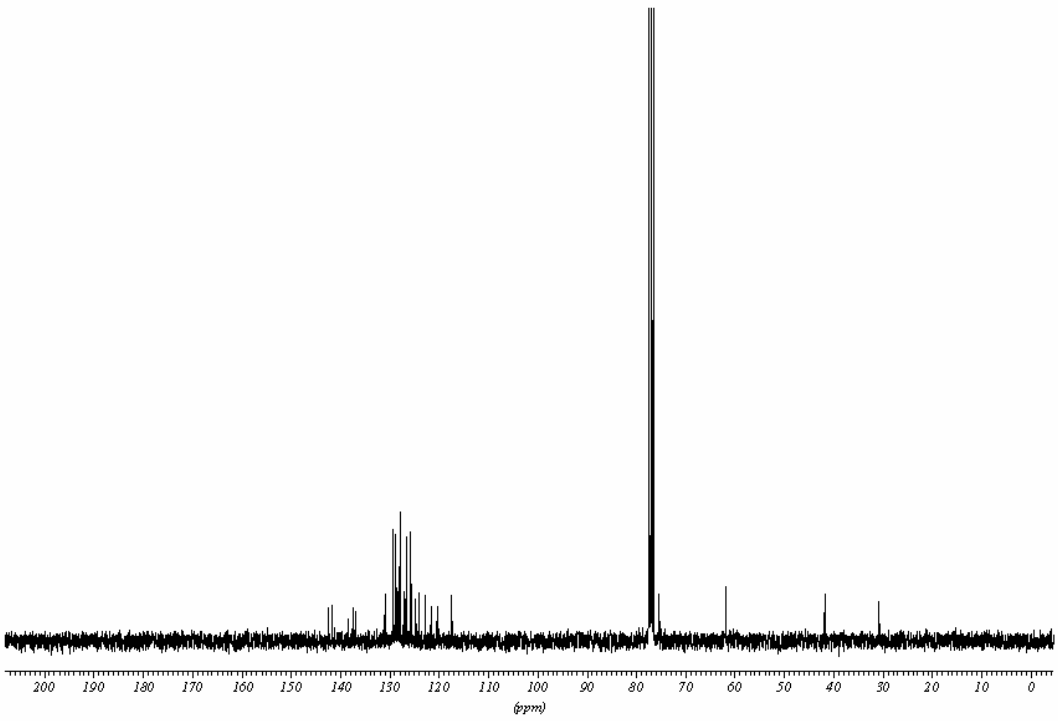
30a

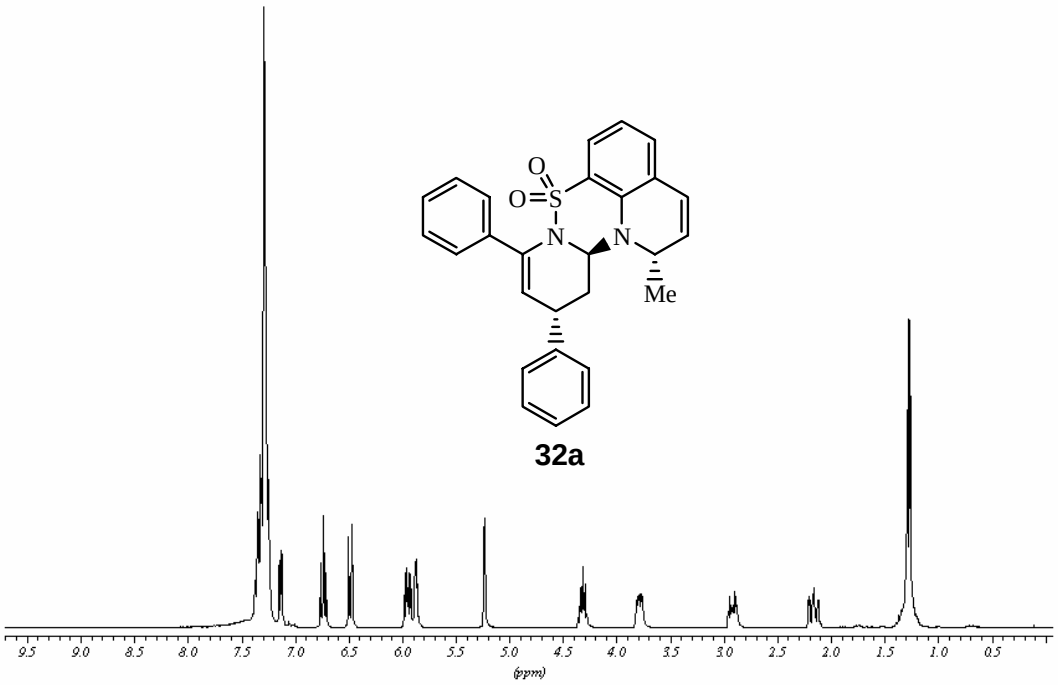

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)



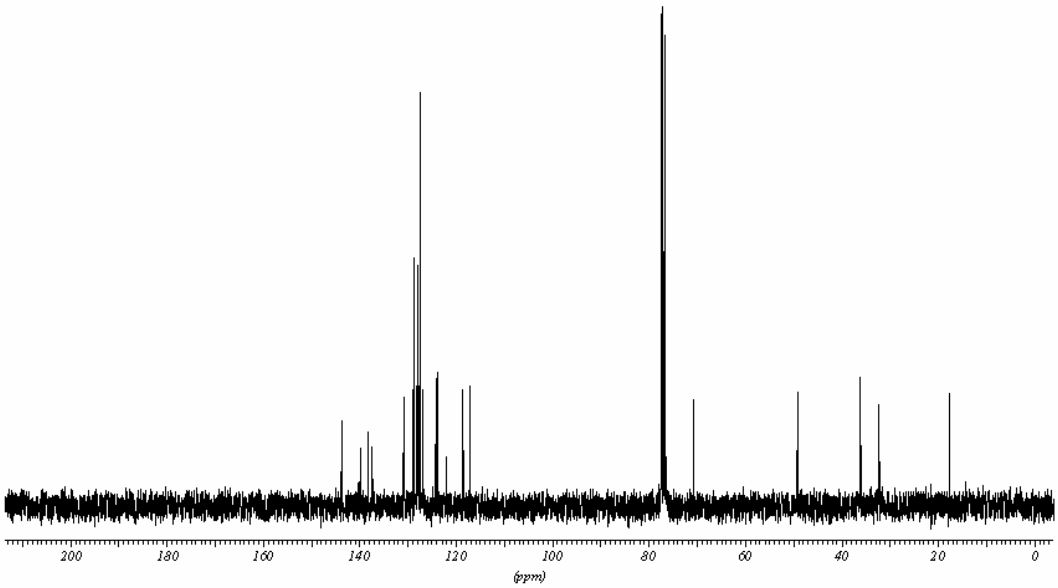
31a

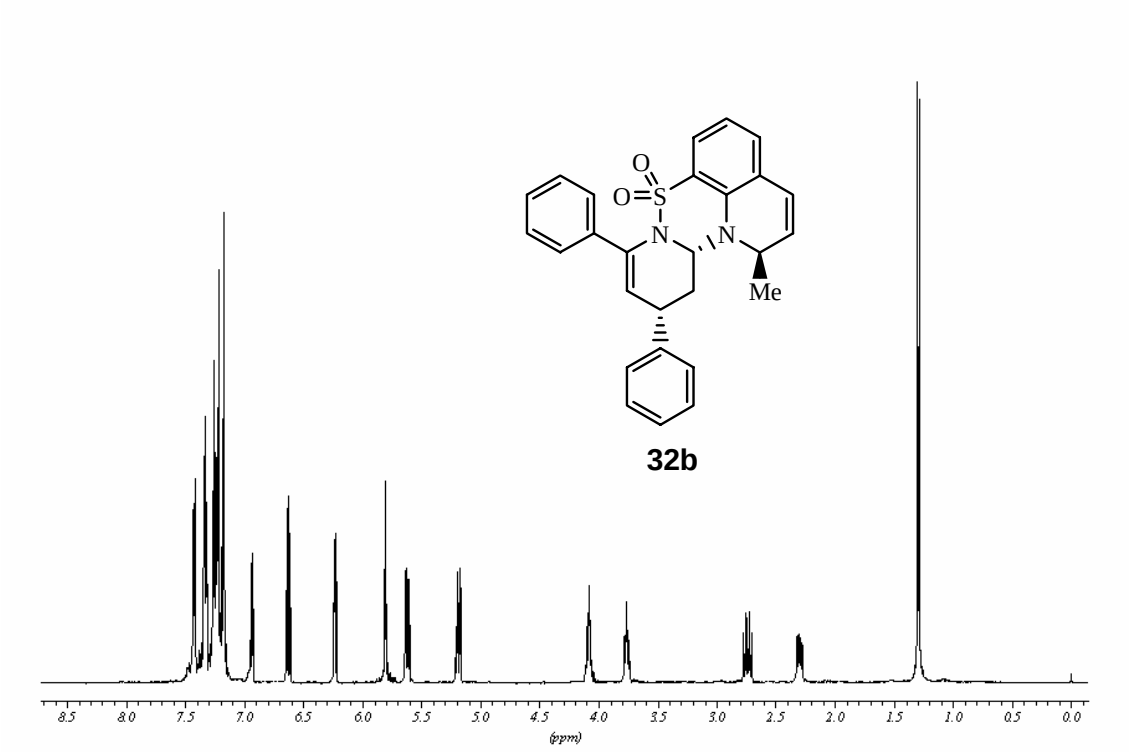

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

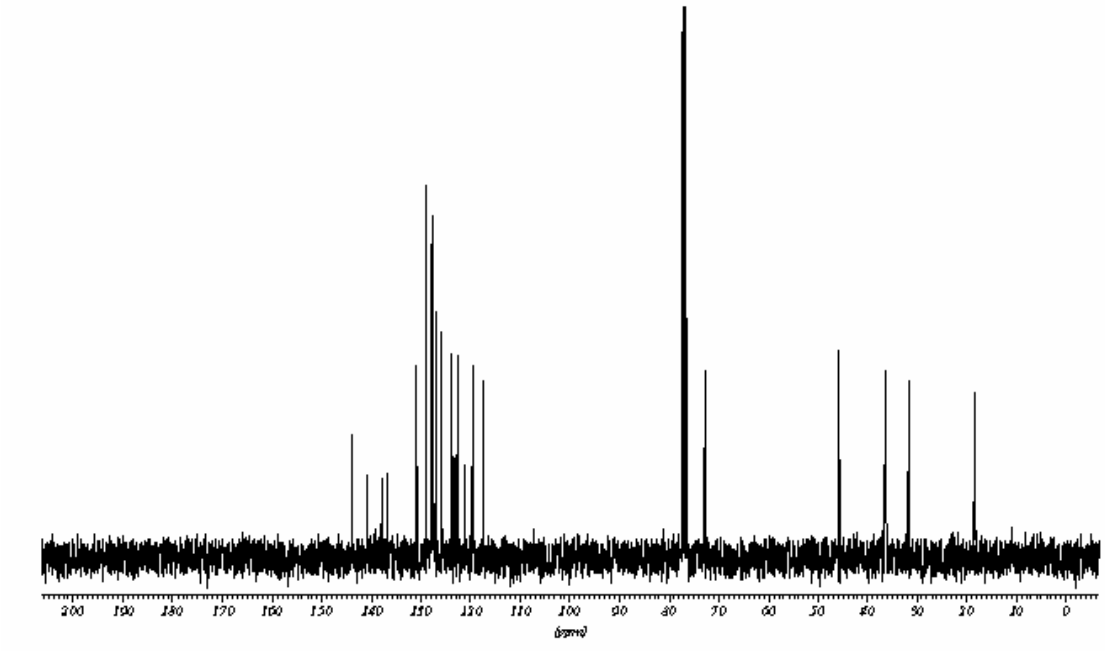

O
O
S
N
N
Me
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

32a


200 180 160 140 120 100 80 60 40 20 0
(ppm)


O
O
S
N
N
Me
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)

32b


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

X-ray data for compound **I**

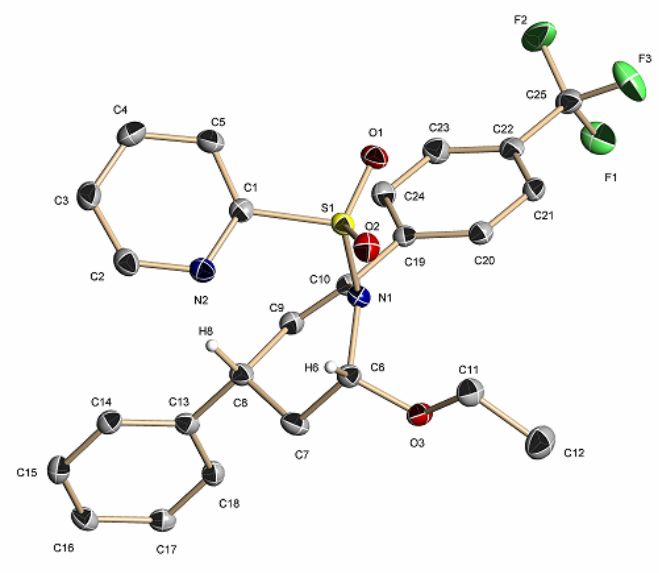


Table 1. Crystal data and structure refinement for I.

Project name: 2005 Jorge Esquivias Jorge1 100K 70104

Project path: F:\2005\Jorge_Esquivias\70104\work\2005_Jom.*

Identification code	2005_jom	
Empirical formula	C25 H23 F3 N2 O3 S	
Formula weight	488.51	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.4345(2) Å	α= 90°.
	b = 11.1796(3) Å	β= 90°.
	c = 21.8461(6) Å	γ = 90°.
Volume	2304.19(10) $Å^3$	
Z	4	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	1.733 mm^{-1}	
F(000)	1016	
Crystal size	0.25 x 0.25 x 0.20 mm^3	
Theta range for data collection	4.05 to 70.62°.	
Index ranges	-10<=h<=10, -12<=k<=13, -24<=l<=26	
Reflections collected	12952	

Independent reflections	4224 [R(int) = 0.0273]
Completeness to theta = 70.62°	97.0 %
Absorption correction	YES, SADABS v. 2.03
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4224 / 0 / 399
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0763
R indices (all data)	R1 = 0.0305, wR2 = 0.0771
Absolute structure parameter	0.00
Largest diff. peak and hole	0.260 and -0.180 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for I. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	304(1)	3379(1)	5907(1)	17(1)
C(1)	1817(2)	2482(2)	6086(1)	18(1)
C(2)	2733(2)	1061(2)	6709(1)	24(1)
C(3)	4003(2)	1070(2)	6393(1)	26(1)
C(4)	4151(2)	1824(2)	5893(1)	29(1)
C(5)	3029(2)	2564(2)	5737(1)	24(1)
C(6)	-813(2)	3663(2)	7036(1)	19(1)
C(7)	-17(2)	3793(2)	7644(1)	24(1)
C(8)	1581(2)	4004(2)	7555(1)	19(1)
C(9)	1721(2)	5091(2)	7159(1)	19(1)
C(10)	950(2)	5175(2)	6648(1)	17(1)
C(11)	-3187(2)	3914(2)	6672(1)	25(1)
C(12)	-4546(2)	4537(2)	6844(1)	34(1)
C(13)	2337(2)	4078(2)	8166(1)	18(1)
C(14)	3286(2)	3182(2)	8331(1)	20(1)
C(15)	3939(2)	3200(2)	8902(1)	21(1)
C(16)	3667(2)	4119(2)	9310(1)	21(1)
C(17)	2723(2)	5016(2)	9146(1)	19(1)
C(18)	2058(2)	4998(2)	8580(1)	19(1)
C(19)	928(2)	6230(2)	6239(1)	17(1)
C(20)	-325(2)	6588(2)	5949(1)	19(1)
C(21)	-355(2)	7595(2)	5583(1)	20(1)

C(22)	867(2)	8265(2)	5502(1)	20(1)
C(23)	2120(2)	7929(2)	5789(1)	23(1)
C(24)	2143(2)	6915(2)	6150(1)	21(1)
C(25)	843(2)	9363(2)	5110(1)	24(1)
N(1)	-13(2)	4209(1)	6514(1)	17(1)
N(2)	1630(2)	1751(1)	6561(1)	21(1)
O(1)	724(2)	4160(1)	5422(1)	22(1)
O(2)	-888(1)	2606(1)	5833(1)	23(1)
O(3)	-2129(1)	4237(1)	7111(1)	21(1)
F(1)	657(2)	10362(1)	5429(1)	35(1)
F(2)	2044(2)	9504(1)	4795(1)	54(1)
F(3)	-212(2)	9354(1)	4697(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for I.

S(1)-O(2)	1.4271(14)
S(1)-O(1)	1.4290(13)
S(1)-N(1)	1.6463(15)
S(1)-C(1)	1.7875(19)
C(1)-N(2)	1.333(2)
C(1)-C(5)	1.378(3)
C(2)-N(2)	1.335(3)
C(2)-C(3)	1.383(3)
C(2)-H(2)	0.98(2)
C(3)-C(4)	1.386(3)
C(3)-H(3)	0.93(3)
C(4)-C(5)	1.386(3)
C(4)-H(4)	0.91(3)
C(5)-H(5)	0.95(3)
C(6)-O(3)	1.407(2)
C(6)-N(1)	1.497(2)
C(6)-C(7)	1.533(2)
C(6)-H(6)	0.98(2)
C(7)-C(8)	1.538(3)
C(7)-H(7A)	1.01(2)
C(7)-H(7B)	0.94(2)

C(8)-C(9)	1.499(3)
C(8)-C(13)	1.515(2)
C(8)-H(8)	0.90(2)
C(9)-C(10)	1.336(3)
C(9)-H(9)	0.96(2)
C(10)-N(1)	1.441(2)
C(10)-C(19)	1.479(2)
C(11)-O(3)	1.430(2)
C(11)-C(12)	1.506(3)
C(11)-H(11A)	0.99(2)
C(11)-H(11B)	1.00(2)
C(12)-H(12A)	1.01(3)
C(12)-H(12B)	0.94(3)
C(12)-H(12C)	0.92(3)
C(13)-C(14)	1.392(3)
C(13)-C(18)	1.394(3)
C(14)-C(15)	1.390(3)
C(14)-H(14)	1.00(2)
C(15)-C(16)	1.385(3)
C(15)-H(15)	0.95(2)
C(16)-C(17)	1.388(3)
C(16)-H(16)	0.96(2)
C(17)-C(18)	1.388(3)
C(17)-H(17)	0.93(2)
C(18)-H(18)	0.97(2)
C(19)-C(24)	1.392(3)
C(19)-C(20)	1.400(3)
C(20)-C(21)	1.382(3)
C(20)-H(20)	0.95(2)
C(21)-C(22)	1.385(3)
C(21)-H(21)	0.97(3)
C(22)-C(23)	1.390(3)
C(22)-C(25)	1.497(3)
C(23)-C(24)	1.381(3)
C(23)-H(23)	0.97(3)
C(24)-H(24)	0.95(2)
C(25)-F(1)	1.328(2)
C(25)-F(2)	1.336(2)

C(25)-F(3)	1.344(2)

O(2)-S(1)-O(1)	120.28(8)
O(2)-S(1)-N(1)	106.81(8)
O(1)-S(1)-N(1)	107.69(7)
O(2)-S(1)-C(1)	108.32(8)
O(1)-S(1)-C(1)	106.48(8)
N(1)-S(1)-C(1)	106.54(8)
N(2)-C(1)-C(5)	125.58(17)
N(2)-C(1)-S(1)	114.14(14)
C(5)-C(1)-S(1)	120.26(14)
N(2)-C(2)-C(3)	123.43(18)
N(2)-C(2)-H(2)	116.3(14)
C(3)-C(2)-H(2)	120.3(14)
C(2)-C(3)-C(4)	119.01(18)
C(2)-C(3)-H(3)	123.6(15)
C(4)-C(3)-H(3)	117.3(15)
C(3)-C(4)-C(5)	118.68(19)
C(3)-C(4)-H(4)	119.9(17)
C(5)-C(4)-H(4)	121.4(17)
C(1)-C(5)-C(4)	117.25(18)
C(1)-C(5)-H(5)	117.6(17)
C(4)-C(5)-H(5)	125.1(17)
O(3)-C(6)-N(1)	110.36(14)
O(3)-C(6)-C(7)	106.73(15)
N(1)-C(6)-C(7)	111.95(15)
O(3)-C(6)-H(6)	110.8(13)
N(1)-C(6)-H(6)	102.8(12)
C(7)-C(6)-H(6)	114.2(13)
C(6)-C(7)-C(8)	112.71(15)
C(6)-C(7)-H(7A)	107.1(14)
C(8)-C(7)-H(7A)	110.8(14)
C(6)-C(7)-H(7B)	105.6(14)
C(8)-C(7)-H(7B)	112.9(15)
H(7A)-C(7)-H(7B)	107.4(19)
C(9)-C(8)-C(13)	115.05(15)
C(9)-C(8)-C(7)	106.46(15)
C(13)-C(8)-C(7)	111.04(14)

C(9)-C(8)-H(8)	109.2(13)
C(13)-C(8)-H(8)	105.9(13)
C(7)-C(8)-H(8)	109.0(14)
C(10)-C(9)-C(8)	119.48(17)
C(10)-C(9)-H(9)	123.0(13)
C(8)-C(9)-H(9)	117.2(13)
C(9)-C(10)-N(1)	117.38(16)
C(9)-C(10)-C(19)	124.59(17)
N(1)-C(10)-C(19)	117.83(15)
O(3)-C(11)-C(12)	108.09(16)
O(3)-C(11)-H(11A)	108.4(14)
C(12)-C(11)-H(11A)	108.6(14)
O(3)-C(11)-H(11B)	108.3(13)
C(12)-C(11)-H(11B)	111.3(13)
H(11A)-C(11)-H(11B)	112.0(19)
C(11)-C(12)-H(12A)	110.8(17)
C(11)-C(12)-H(12B)	109.0(15)
H(12A)-C(12)-H(12B)	113(2)
C(11)-C(12)-H(12C)	112(2)
H(12A)-C(12)-H(12C)	102(3)
H(12B)-C(12)-H(12C)	110(3)
C(14)-C(13)-C(18)	118.99(16)
C(14)-C(13)-C(8)	119.45(16)
C(18)-C(13)-C(8)	121.50(16)
C(15)-C(14)-C(13)	120.50(17)
C(15)-C(14)-H(14)	120.9(12)
C(13)-C(14)-H(14)	118.6(12)
C(16)-C(15)-C(14)	120.36(17)
C(16)-C(15)-H(15)	120.8(14)
C(14)-C(15)-H(15)	118.9(14)
C(15)-C(16)-C(17)	119.31(17)
C(15)-C(16)-H(16)	118.8(13)
C(17)-C(16)-H(16)	121.9(13)
C(18)-C(17)-C(16)	120.62(17)
C(18)-C(17)-H(17)	117.0(13)
C(16)-C(17)-H(17)	122.4(13)
C(17)-C(18)-C(13)	120.22(17)
C(17)-C(18)-H(18)	120.5(12)

C(13)-C(18)-H(18)	119.3(12)
C(24)-C(19)-C(20)	118.38(16)
C(24)-C(19)-C(10)	120.76(16)
C(20)-C(19)-C(10)	120.84(16)
C(21)-C(20)-C(19)	120.77(17)
C(21)-C(20)-H(20)	119.8(14)
C(19)-C(20)-H(20)	119.4(14)
C(20)-C(21)-C(22)	119.85(17)
C(20)-C(21)-H(21)	120.8(14)
C(22)-C(21)-H(21)	119.4(14)
C(21)-C(22)-C(23)	120.28(17)
C(21)-C(22)-C(25)	120.24(17)
C(23)-C(22)-C(25)	119.48(17)
C(24)-C(23)-C(22)	119.51(17)
C(24)-C(23)-H(23)	118.4(16)
C(22)-C(23)-H(23)	122.0(16)
C(23)-C(24)-C(19)	121.22(17)
C(23)-C(24)-H(24)	121.3(14)
C(19)-C(24)-H(24)	117.5(14)
F(1)-C(25)-F(2)	106.48(17)
F(1)-C(25)-F(3)	105.12(16)
F(2)-C(25)-F(3)	106.40(16)
F(1)-C(25)-C(22)	113.01(15)
F(2)-C(25)-C(22)	112.31(16)
F(3)-C(25)-C(22)	112.94(16)
C(10)-N(1)-C(6)	118.00(14)
C(10)-N(1)-S(1)	118.10(12)
C(6)-N(1)-S(1)	118.36(12)
C(1)-N(2)-C(2)	116.02(16)
C(6)-O(3)-C(11)	115.02(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for I. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	21(1)	17(1)	14(1)	-1(1)	-1(1)	0(1)
C(1)	22(1)	15(1)	18(1)	-3(1)	0(1)	1(1)
C(2)	31(1)	19(1)	21(1)	0(1)	-3(1)	3(1)
C(3)	28(1)	25(1)	26(1)	-1(1)	-1(1)	9(1)
C(4)	25(1)	37(1)	27(1)	-1(1)	7(1)	5(1)
C(5)	28(1)	26(1)	18(1)	2(1)	3(1)	2(1)
C(6)	17(1)	22(1)	19(1)	2(1)	1(1)	-2(1)
C(7)	22(1)	32(1)	16(1)	3(1)	-1(1)	-5(1)
C(8)	21(1)	18(1)	17(1)	-1(1)	1(1)	1(1)
C(9)	18(1)	20(1)	19(1)	-1(1)	1(1)	-1(1)
C(10)	17(1)	17(1)	17(1)	-3(1)	2(1)	-1(1)
C(11)	20(1)	31(1)	24(1)	-3(1)	-4(1)	-2(1)
C(12)	22(1)	43(1)	37(1)	-6(1)	-4(1)	1(1)
C(13)	18(1)	19(1)	17(1)	2(1)	1(1)	-3(1)
C(14)	20(1)	18(1)	21(1)	-2(1)	2(1)	1(1)
C(15)	18(1)	19(1)	27(1)	2(1)	-2(1)	1(1)
C(16)	22(1)	25(1)	16(1)	2(1)	-3(1)	-5(1)
C(17)	20(1)	20(1)	19(1)	0(1)	2(1)	-4(1)
C(18)	18(1)	19(1)	21(1)	2(1)	0(1)	1(1)
C(19)	19(1)	18(1)	15(1)	-3(1)	1(1)	2(1)
C(20)	18(1)	19(1)	19(1)	-2(1)	1(1)	0(1)
C(21)	22(1)	20(1)	18(1)	-2(1)	1(1)	6(1)
C(22)	25(1)	16(1)	17(1)	-3(1)	4(1)	5(1)
C(23)	21(1)	23(1)	24(1)	1(1)	1(1)	-3(1)
C(24)	19(1)	25(1)	20(1)	1(1)	-2(1)	1(1)
C(25)	28(1)	20(1)	24(1)	-1(1)	6(1)	4(1)
N(1)	18(1)	17(1)	16(1)	0(1)	-1(1)	-1(1)
N(2)	23(1)	19(1)	20(1)	1(1)	1(1)	-1(1)
O(1)	31(1)	21(1)	16(1)	0(1)	1(1)	3(1)
O(2)	24(1)	21(1)	24(1)	-4(1)	-5(1)	-1(1)
O(3)	17(1)	29(1)	17(1)	-3(1)	0(1)	-1(1)
F(1)	54(1)	18(1)	33(1)	-3(1)	2(1)	0(1)
F(2)	48(1)	51(1)	64(1)	35(1)	37(1)	21(1)
F(3)	61(1)	28(1)	33(1)	8(1)	-20(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for I.

	x	y	z	U(eq)
H(2)	2610(20)	550(20)	7067(11)	26(6)
H(3)	4800(30)	630(20)	6510(11)	33(6)
H(4)	4990(30)	1850(20)	5686(12)	41(7)
H(5)	3030(30)	3120(20)	5411(12)	41(7)
H(6)	-940(20)	2840(20)	6902(10)	17(5)
H(7A)	-190(30)	3040(20)	7885(11)	29(6)
H(7B)	-470(30)	4420(20)	7852(10)	25(6)
H(8)	1960(20)	3370(20)	7359(9)	14(5)
H(9)	2300(20)	5740(20)	7311(10)	19(5)
H(11A)	-2880(30)	4210(20)	6265(11)	28(6)
H(11B)	-3300(20)	3020(20)	6680(10)	21(5)
H(12A)	-4400(30)	5430(30)	6869(12)	46(8)
H(12B)	-5260(30)	4310(20)	6566(11)	34(6)
H(12C)	-4820(30)	4360(30)	7238(16)	66(10)
H(14)	3460(20)	2518(19)	8038(9)	12(5)
H(15)	4570(30)	2570(20)	9007(11)	28(6)
H(16)	4140(20)	4119(18)	9696(10)	17(5)
H(17)	2510(20)	5654(19)	9405(10)	16(5)
H(18)	1390(20)	5623(19)	8468(9)	14(5)
H(20)	-1160(30)	6120(20)	5999(10)	24(6)
H(21)	-1230(30)	7850(20)	5392(10)	26(6)
H(23)	2980(30)	8390(20)	5748(12)	39(7)
H(24)	2990(30)	6650(20)	6338(10)	24(5)

Table 6. Torsion angles [°] for I.

O(2)-S(1)-C(1)-N(2)	-53.45(15)
O(1)-S(1)-C(1)-N(2)	175.87(13)
N(1)-S(1)-C(1)-N(2)	61.14(15)
O(2)-S(1)-C(1)-C(5)	125.21(15)
O(1)-S(1)-C(1)-C(5)	-5.47(17)
N(1)-S(1)-C(1)-C(5)	-120.20(15)
N(2)-C(2)-C(3)-C(4)	-0.5(3)

C(2)-C(3)-C(4)-C(5)	1.5(3)
N(2)-C(1)-C(5)-C(4)	-0.2(3)
S(1)-C(1)-C(5)-C(4)	-178.65(15)
C(3)-C(4)-C(5)-C(1)	-1.2(3)
O(3)-C(6)-C(7)-C(8)	-142.25(16)
N(1)-C(6)-C(7)-C(8)	-21.4(2)
C(6)-C(7)-C(8)-C(9)	56.3(2)
C(6)-C(7)-C(8)-C(13)	-177.74(16)
C(13)-C(8)-C(9)-C(10)	-171.52(17)
C(7)-C(8)-C(9)-C(10)	-48.1(2)
C(8)-C(9)-C(10)-N(1)	1.4(2)
C(8)-C(9)-C(10)-C(19)	176.11(17)
C(9)-C(8)-C(13)-C(14)	-126.49(18)
C(7)-C(8)-C(13)-C(14)	112.51(19)
C(9)-C(8)-C(13)-C(18)	56.3(2)
C(7)-C(8)-C(13)-C(18)	-64.7(2)
C(18)-C(13)-C(14)-C(15)	0.4(3)
C(8)-C(13)-C(14)-C(15)	-176.83(17)
C(13)-C(14)-C(15)-C(16)	-0.8(3)
C(14)-C(15)-C(16)-C(17)	0.6(3)
C(15)-C(16)-C(17)-C(18)	-0.1(3)
C(16)-C(17)-C(18)-C(13)	-0.3(3)
C(14)-C(13)-C(18)-C(17)	0.2(3)
C(8)-C(13)-C(18)-C(17)	177.33(16)
C(9)-C(10)-C(19)-C(24)	34.5(3)
N(1)-C(10)-C(19)-C(24)	-150.88(16)
C(9)-C(10)-C(19)-C(20)	-143.45(19)
N(1)-C(10)-C(19)-C(20)	31.2(2)
C(24)-C(19)-C(20)-C(21)	0.0(3)
C(10)-C(19)-C(20)-C(21)	177.93(15)
C(19)-C(20)-C(21)-C(22)	-0.2(3)
C(20)-C(21)-C(22)-C(23)	-0.2(3)
C(20)-C(21)-C(22)-C(25)	-179.58(16)
C(21)-C(22)-C(23)-C(24)	0.7(3)
C(25)-C(22)-C(23)-C(24)	-179.87(16)
C(22)-C(23)-C(24)-C(19)	-0.9(3)
C(20)-C(19)-C(24)-C(23)	0.6(3)
C(10)-C(19)-C(24)-C(23)	-177.37(16)

C(21)-C(22)-C(25)-F(1)	95.8(2)
C(23)-C(22)-C(25)-F(1)	-83.6(2)
C(21)-C(22)-C(25)-F(2)	-143.68(18)
C(23)-C(22)-C(25)-F(2)	36.9(3)
C(21)-C(22)-C(25)-F(3)	-23.3(2)
C(23)-C(22)-C(25)-F(3)	157.23(17)
C(9)-C(10)-N(1)-C(6)	39.4(2)
C(19)-C(10)-N(1)-C(6)	-135.64(16)
C(9)-C(10)-N(1)-S(1)	-113.95(16)
C(19)-C(10)-N(1)-S(1)	71.00(18)
O(3)-C(6)-N(1)-C(10)	91.90(18)
C(7)-C(6)-N(1)-C(10)	-26.8(2)
O(3)-C(6)-N(1)-S(1)	-114.81(14)
C(7)-C(6)-N(1)-S(1)	126.47(15)
O(2)-S(1)-N(1)-C(10)	-172.38(12)
O(1)-S(1)-N(1)-C(10)	-41.90(15)
C(1)-S(1)-N(1)-C(10)	72.01(14)
O(2)-S(1)-N(1)-C(6)	34.35(14)
O(1)-S(1)-N(1)-C(6)	164.84(12)
C(1)-S(1)-N(1)-C(6)	-81.25(14)
C(5)-C(1)-N(2)-C(2)	1.1(3)
S(1)-C(1)-N(2)-C(2)	179.71(13)
C(3)-C(2)-N(2)-C(1)	-0.8(3)
N(1)-C(6)-O(3)-C(11)	76.21(18)
C(7)-C(6)-O(3)-C(11)	-161.93(16)
C(12)-C(11)-O(3)-C(6)	176.08(16)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for I [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-ray data for compound **32b**

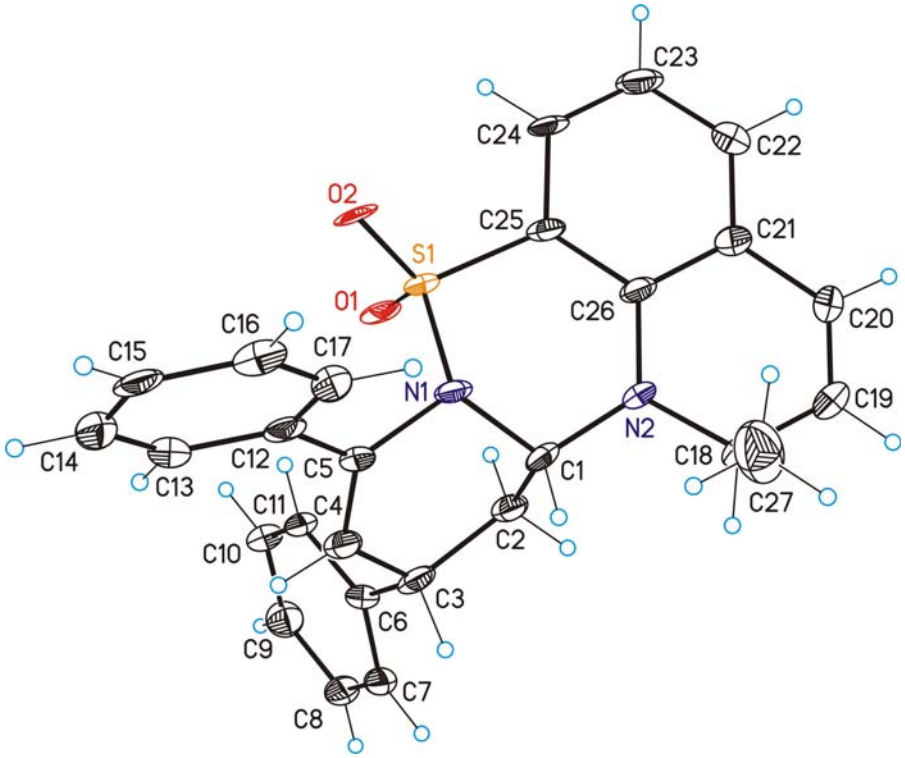


Table 1. Crystal data and structure refinement for compound **32b**

Identification code	jep002_0m	
Empirical formula	C27 H24 N2 O2 S	
Formula weight	440.54	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.123(5) Å	α= 90°.
	b = 12.226(5) Å	β= 90°.
	c = 16.556(9) Å	γ = 90°.
Volume	2251.3(18) $Å^3$	
Z	4	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.171 mm^{-1}	
F(000)	928	
Crystal size	0.30 x 0.02 x 0.01 mm^3	
Theta range for data collection	2.76 to 26.88°.	
Index ranges	-13<=h<=14, -15<=k<=13, -21<=l<=19	

Reflections collected	19072
Independent reflections	4809 [R(int) = 0.1389]
Completeness to theta = 26.88°	99.1 %
Absorption correction	SADABS (Bruker-Nonius)
Max. and min. transmission	0.9983 and 0.9505
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4809 / 0 / 290
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0762, wR2 = 0.1738
R indices (all data)	R1 = 0.1311, wR2 = 0.2115
Absolute structure parameter	0.05(17)
Largest diff. peak and hole	0.916 and -0.955 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for JEP002_0m.

S(1)-O(1)	1.413(3)
S(1)-O(2)	1.429(3)
S(1)-N(1)	1.654(4)
S(1)-C(25)	1.733(5)
N(1)-C(5)	1.454(6)
N(1)-C(1)	1.497(6)
C(1)-N(2)	1.442(6)
C(1)-C(2)	1.502(7)
N(2)-C(26)	1.371(6)
N(2)-C(18)	1.457(6)
C(2)-C(3)	1.532(7)
C(3)-C(4)	1.497(7)
C(3)-C(6)	1.503(7)
C(4)-C(5)	1.328(7)
C(5)-C(12)	1.479(7)
C(6)-C(7)	1.385(7)
C(6)-C(11)	1.393(7)
C(7)-C(8)	1.370(7)
C(8)-C(9)	1.390(7)
C(9)-C(10)	1.385(7)
C(10)-C(11)	1.366(7)
C(12)-C(17)	1.372(7)
C(12)-C(13)	1.389(7)
C(13)-C(14)	1.380(7)
C(14)-C(15)	1.362(8)
C(15)-C(16)	1.372(7)
C(16)-C(17)	1.393(7)
C(18)-C(19)	1.498(8)
C(18)-C(27)	1.511(9)
C(19)-C(20)	1.308(8)
C(20)-C(21)	1.455(7)
C(21)-C(22)	1.384(8)
C(21)-C(26)	1.414(7)
C(22)-C(23)	1.387(8)
C(23)-C(24)	1.351(7)
C(24)-C(25)	1.399(7)

C(25)-C(26)	1.395(7)

O(1)-S(1)-O(2)	116.1(2)
O(1)-S(1)-N(1)	112.3(2)
O(2)-S(1)-N(1)	107.2(2)
O(1)-S(1)-C(25)	109.3(2)
O(2)-S(1)-C(25)	110.5(2)
N(1)-S(1)-C(25)	100.4(2)
C(5)-N(1)-C(1)	110.3(4)
C(5)-N(1)-S(1)	110.7(3)
C(1)-N(1)-S(1)	115.0(3)
N(2)-C(1)-N(1)	110.9(4)
N(2)-C(1)-C(2)	114.1(4)
N(1)-C(1)-C(2)	112.6(4)
C(26)-N(2)-C(1)	122.6(4)
C(26)-N(2)-C(18)	121.5(4)
C(1)-N(2)-C(18)	115.2(4)
C(1)-C(2)-C(3)	109.3(4)
C(4)-C(3)-C(6)	112.9(4)
C(4)-C(3)-C(2)	113.0(4)
C(6)-C(3)-C(2)	110.9(4)
C(5)-C(4)-C(3)	126.0(5)
C(4)-C(5)-N(1)	120.1(4)
C(4)-C(5)-C(12)	124.4(4)
N(1)-C(5)-C(12)	115.2(4)
C(7)-C(6)-C(11)	117.6(4)
C(7)-C(6)-C(3)	120.9(5)
C(11)-C(6)-C(3)	121.3(4)
C(8)-C(7)-C(6)	121.8(5)
C(7)-C(8)-C(9)	120.2(5)
C(10)-C(9)-C(8)	118.3(5)
C(11)-C(10)-C(9)	121.3(5)
C(10)-C(11)-C(6)	120.8(4)
C(17)-C(12)-C(13)	119.0(5)
C(17)-C(12)-C(5)	119.9(4)
C(13)-C(12)-C(5)	120.9(5)
C(14)-C(13)-C(12)	120.1(5)
C(15)-C(14)-C(13)	120.7(5)

C(14)-C(15)-C(16)	119.8(5)
C(15)-C(16)-C(17)	120.0(5)
C(12)-C(17)-C(16)	120.4(5)
N(2)-C(18)-C(19)	110.3(4)
N(2)-C(18)-C(27)	112.6(5)
C(19)-C(18)-C(27)	110.8(5)
C(20)-C(19)-C(18)	122.4(5)
C(19)-C(20)-C(21)	120.9(5)
C(22)-C(21)-C(26)	119.5(5)
C(22)-C(21)-C(20)	122.5(5)
C(26)-C(21)-C(20)	117.9(5)
C(21)-C(22)-C(23)	121.8(5)
C(24)-C(23)-C(22)	119.4(5)
C(23)-C(24)-C(25)	120.3(5)
C(26)-C(25)-C(24)	121.7(4)
C(26)-C(25)-S(1)	121.4(4)
C(24)-C(25)-S(1)	116.8(4)
N(2)-C(26)-C(25)	123.3(4)
N(2)-C(26)-C(21)	119.3(4)
C(25)-C(26)-C(21)	117.4(4)

Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for JEP002_0m.

O(1)-S(1)-N(1)-C(5)	-59.7(4)
O(2)-S(1)-N(1)-C(5)	68.9(3)
C(25)-S(1)-N(1)-C(5)	-175.6(3)
O(1)-S(1)-N(1)-C(1)	66.3(4)
O(2)-S(1)-N(1)-C(1)	-165.1(3)
C(25)-S(1)-N(1)-C(1)	-49.7(4)
C(5)-N(1)-C(1)-N(2)	-173.5(4)
S(1)-N(1)-C(1)-N(2)	60.4(5)
C(5)-N(1)-C(1)-C(2)	57.2(5)
S(1)-N(1)-C(1)-C(2)	-69.0(5)
N(1)-C(1)-N(2)-C(26)	-36.4(6)
C(2)-C(1)-N(2)-C(26)	92.1(6)
N(1)-C(1)-N(2)-C(18)	134.0(4)
C(2)-C(1)-N(2)-C(18)	-97.5(5)
N(2)-C(1)-C(2)-C(3)	173.3(4)
N(1)-C(1)-C(2)-C(3)	-59.0(5)
C(1)-C(2)-C(3)-C(4)	31.1(6)
C(1)-C(2)-C(3)-C(6)	159.1(4)
C(6)-C(3)-C(4)-C(5)	-130.6(5)
C(2)-C(3)-C(4)-C(5)	-3.7(7)
C(3)-C(4)-C(5)-N(1)	1.6(8)
C(3)-C(4)-C(5)-C(12)	-171.7(5)
C(1)-N(1)-C(5)-C(4)	-27.4(6)
S(1)-N(1)-C(5)-C(4)	101.1(5)
C(1)-N(1)-C(5)-C(12)	146.6(4)
S(1)-N(1)-C(5)-C(12)	-84.9(4)
C(4)-C(3)-C(6)-C(7)	-133.5(5)
C(2)-C(3)-C(6)-C(7)	98.5(5)
C(4)-C(3)-C(6)-C(11)	51.3(6)
C(2)-C(3)-C(6)-C(11)	-76.7(6)
C(11)-C(6)-C(7)-C(8)	1.3(7)
C(3)-C(6)-C(7)-C(8)	-174.1(4)
C(6)-C(7)-C(8)-C(9)	-0.4(7)
C(7)-C(8)-C(9)-C(10)	-0.3(7)
C(8)-C(9)-C(10)-C(11)	0.1(8)
C(9)-C(10)-C(11)-C(6)	0.8(8)

C(7)-C(6)-C(11)-C(10)	-1.5(7)
C(3)-C(6)-C(11)-C(10)	173.9(4)
C(4)-C(5)-C(12)-C(17)	141.3(5)
N(1)-C(5)-C(12)-C(17)	-32.4(6)
C(4)-C(5)-C(12)-C(13)	-34.0(7)
N(1)-C(5)-C(12)-C(13)	152.3(5)
C(17)-C(12)-C(13)-C(14)	-0.1(8)
C(5)-C(12)-C(13)-C(14)	175.2(5)
C(12)-C(13)-C(14)-C(15)	0.6(8)
C(13)-C(14)-C(15)-C(16)	-0.3(8)
C(14)-C(15)-C(16)-C(17)	-0.5(8)
C(13)-C(12)-C(17)-C(16)	-0.7(7)
C(5)-C(12)-C(17)-C(16)	-176.1(5)
C(15)-C(16)-C(17)-C(12)	1.1(8)
C(26)-N(2)-C(18)-C(19)	-32.4(7)
C(1)-N(2)-C(18)-C(19)	157.1(4)
C(26)-N(2)-C(18)-C(27)	92.0(6)
C(1)-N(2)-C(18)-C(27)	-78.5(6)
N(2)-C(18)-C(19)-C(20)	24.4(8)
C(27)-C(18)-C(19)-C(20)	-101.1(7)
C(18)-C(19)-C(20)-C(21)	-5.0(9)
C(19)-C(20)-C(21)-C(22)	174.2(6)
C(19)-C(20)-C(21)-C(26)	-9.2(8)
C(26)-C(21)-C(22)-C(23)	-0.2(9)
C(20)-C(21)-C(22)-C(23)	176.4(5)
C(21)-C(22)-C(23)-C(24)	-0.2(9)
C(22)-C(23)-C(24)-C(25)	-0.1(8)
C(23)-C(24)-C(25)-C(26)	0.9(8)
C(23)-C(24)-C(25)-S(1)	-176.0(4)
O(1)-S(1)-C(25)-C(26)	-97.1(4)
O(2)-S(1)-C(25)-C(26)	134.0(4)
N(1)-S(1)-C(25)-C(26)	21.2(4)
O(1)-S(1)-C(25)-C(24)	79.8(4)
O(2)-S(1)-C(25)-C(24)	-49.1(4)
N(1)-S(1)-C(25)-C(24)	-162.0(4)
C(1)-N(2)-C(26)-C(25)	7.7(7)
C(18)-N(2)-C(26)-C(25)	-162.1(5)
C(1)-N(2)-C(26)-C(21)	-169.2(5)

C(18)-N(2)-C(26)-C(21)	21.0(7)
C(24)-C(25)-C(26)-N(2)	-178.3(4)
S(1)-C(25)-C(26)-N(2)	-1.6(7)
C(24)-C(25)-C(26)-C(21)	-1.3(7)
S(1)-C(25)-C(26)-C(21)	175.4(4)
C(22)-C(21)-C(26)-N(2)	178.1(5)
C(20)-C(21)-C(26)-N(2)	1.3(7)
C(22)-C(21)-C(26)-C(25)	1.0(7)
C(20)-C(21)-C(26)-C(25)	-175.8(5)

Symmetry transformations used to generate equivalent atoms: