SUPPORTING INFORMATION FOR

Aza-Morita-Baylis-Hillman Reactions and Cyclizations of Conjugated Dienes Activated by Sulfone, Ester and Keto Groups

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Contents:

General Experimental Section. Mass spectra were obtained by EI unless indicated otherwise. Chromatographic separations were performed by flash chromatography on silica gel (230-400 mesh). Anhydrous DMF was either distilled over CaH_2 and subsequently stored over molecular sieves, or was obtained directly as DriSolv® EMD™ (Aldrich Co.). THF was freshly distilled over lithium aluminum hydride.

***N*-Phenylsulfonyl-1-(3-pyridyl)-2-(*p*-toluenesulfonyl)-2,4-pentadienylamine (4j).** This product was prepared by the same general procedure as used for **4a**,[2] but it could not be obtained in a pure state. It was therefore cyclized directly to the corresponding piperidine **5j** without isolation and purification (vide infra).

The following piperidine derivatives were prepared by the same procedure as **5a**, **5b** and **5h**, which were described in the Supporting Information of our preliminary communication.[2]

***N*-(Benzenesulfonyl)-2-(*m*-chlorophenyl)-3-(*p*-toluenesulfonyl)-3,4-dehydropiperidine (5c).** White solid, mp 124-127 °C (from ethyl acetate-hexanes); IR (film) 1645, 1317, 1149, 1088 cm^{-1}; ^1H NMR (300 MHz) δ 7.74 (d, *J* = 7.2 Hz, 2 H), 7.60-7.55 (m, 1 H), 7.48-7.38, (m, 4 H), 7.12-7.08 (m, 6 H), 6.66 (s, 1 H), 5.99 (s, 1 H), 3.78 (dd, *J* = 15.4, 6.7 Hz, 1 H), 2.98 (m, 1 H), 2.36 (s, 3 H), 2.28-2.05 (m, 2 H); ^{13}C NMR (75 MHz) δ 145.0, 140.3, 139.6, 139.0, 138.5, 136.1, 134.1, 133.2, 129.9, 129.8, 129.5, 128.5, 128.4, 128.3, 127.7, 127.2, 54.8, 36.1, 24.3, 21.7; mass spectrum (*m/z*, %) 487 (1, M^+), 376 (26), 346 (85), 190 (33), 91 (39), 77 (100); HRMS calcd for $C_{24}H_{22}ClNO_4S_2$: 487.0679; found: 487.0669.

***N*-(Benzenesulfonyl)-2-(*o*-chlorophenyl)-3-(*p*-toluenesulfonyl)-3,4-dehydropiperidine (5d).** White solid; mp 144-147 °C (from ethyl acetate-hexanes); IR (film) 1645, 1447, 1319, 1151, 1088 cm^{-1}; ^1H NMR (300 MHz) δ 7.73-7.70 (m, 2 H), 7.59-7.52 (m, 3 H), 7.44-7.39 (m, 2 H), 7.33 (d, *J* = 7.7 Hz, 1 H), 7.19-7.12 (m, 4 H), 6.98-6.89 (m, 2 H), 6.35 (s, 1 H), 3.69-3.62 (m, 1 H), 3.12 (m, 1 H), 2.37 (s, 3 H), 2.30-2.29 (m, 2H); ^{13}C NMR (75 MHz) δ 144.7, 139.9, 139.8, 138.7, 136.1, 134.8, 134.1, 133.2, 130.8, 130.6, 129.9, 129.8, 129.2, 128.5, 127.9, 126.2, 52.0, 36.3, 24.2, 21.8; mass spectrum (*m/z*, %) 487 (1, M^+), 346 (93), 190 (35), 128 (45), 91 (37), 77 (100); HRMS calcd for $C_{24}H_{22}{}^{35}ClNO_4S_2$: 487.0679; found: 487.0661.

***N*-(Benzenesulfonyl)-2-(*p*-methoxyphenyl)-3-(*p*-toluenesulfonyl)-3,4-dehydropiperidine (5e).** White solid; mp 171-174 °C (from ethyl acetate-hexanes); IR (film) 1642, 1338, 1147, 1028 cm^{-1}; ^1H NMR (300 MHz) δ 7.69-7.66 (m, 2 H), 7.58-7.53 (m, 1 H), 7.45-7.40, (m, 4 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 7.06 (m, 1 H), 6.94 (d, *J* = 8.7 Hz, 2 H), 6.61 (d, *J* = 8.7 Hz, 2 H), 5.92 (s, 1 H), 3.75 (s, 3 H, superimposed on m, 1 H), 3.04 (m, 1 H), 2.38, (s, 3 H), 2.24-2.09 (m, 2 H); ^{13}C NMR (75 MHz) δ 159.5, 144.2, 140.3, 140.2, 138.1, 136.4, 132.8, 130.0, 129.4, 129.1, 128.5, 128.3, 127.0, 113.5, 55.2, 54.7, 35.7, 24.3, 21.5; mass spectrum (*m/z*, %) 483 (7, M^+), 342 (100), 186 (51), 91 (23), 77 (65); HRMS calcd for $C_{25}H_{25}NO_5S_2$: 483.1174; found: 483.1188.

***N*-(Benzenesulfonyl)-2-(*p*-carbomethoxyphenyl)-3-(*p*-toluenesulfonyl)-3,4-dehydropiperidine (5g).** White crystals; mp 189-190 °C (from ethyl acetate-hexanes); IR (film) 1721, 1645, 1283, 1151, 1107, 1087 cm^{-1}; ^1H NMR δ (300 MHz) 7.76 (d, *J* = 8.2 Hz, 2 H), 7.68 (d, *J* = 7.7 Hz, 2 H), 7.59-7.54 (m, 1 H), 7.45-7.39 (m, 4 H), 7.12-7.08 (m, 5 H), 6.00 (s, 1 H), 3.91 (s, 3 H), 3.76 (dd, *J* = 15.4, 7.2 Hz, 1 H), 2.98 (m, 1 H), 2.35 (s, 3 H), 2.28-2.00 (m, 2 H); ^{13}C NMR (75 MHz) δ 166.7, 145.0, 141.4, 140.3, 139.7, 139.0, 136.2, 133.2, 130.0, 129.8, 129.6, 129.5, 128.9, 128.5, 127.2, 54.9, 52.4, 36.1, 24.3, 21.7; MS (*m/z*, %): 511 (2, M^+), 480 (2), 370 (72), 91(28), 77 (100); HRMS calcd for $C_{26}H_{25}NO_6S_2$: 511.1123; found 511.1118.

***N*-(Benzenesulfonyl)-1-(1-naphthyl)-2-(*p*-toluenesulfonyl)-3,4-dehydropiperidine (5i)**. Colorless crystals; mp 184-187 °C (from chloroform); IR (film) 1645, 1334, 1161, 1087 cm^{-1}; ^1H NMR (300 MHz) δ 8.75 (d, *J* = 8.7 Hz, 1 H), 7.84-7.82 (m, 3 H), 7.69-7.64, (m, 2 H), 7.59-7.52 (m, 2 H), 7.44 (t, *J* = 7.7 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.09 (t, *J* = 3.6 Hz, 1 H), 6.98-6.90 (m, 4 H), 6.78 (d, *J* = 6.7 Hz, 1 H), 3.64-3.58 (m, 1 H), 3.21-3.10 (m, 1 H), 2.27 (s, 3 H), 2.20-2.15 (m, 2 H); ^{13}C NMR (75 MHz) δ 144.3, 140.4, 139.5, 138.0, 136.1, 134.1, 133.1, 131.3, 131.2, 129.3, 129.2, 129.0, 128.5, 128.1, 127.7, 127.5, 127.2, 126.1, 124.0, 123.8, 51.4, 36.0, 23.6, 21.4; mass spectrum (*m/z*, %) 503 (M^+, 36), 362 (72), 206 (100), 178 (49), 91 (24), 77 (79); HRMS calcd for $C_{28}H_{25}NO_4S_2$: 503.1225; found: 503.1243.

***N*-(Benzenesulfonyl)-1-(3-pyridyl)-2-(*p*-toluenesulfonyl)-3,4-dehydropiperidine (5j).** The crude adduct 4j was cyclized in the usual manner without prior purification to afford an overall yield of 30% of the piperidine derivative **5j**: viscous yellow oil; IR (film) 1643, 1595, 1335, 1157, 1089 cm^{-1}; ^1H NMR (300 MHz) δ 8.43 (br s, 1 H), 8.21 (br s, 1 H), 7.68 (d, *J* = 7.2 Hz, 2 H), 7.60-7.55 (m, 1 H), 7.50-7.42 (m, 5 H), 7.18-7.08 (m, 4 H), 5.97 (s, 1 H), 3.80 (dd, *J* = 15.4, 6.7 Hz, 1 H), 2.96 (m, 1 H), 2.39 (s, 3 H), 2.31-2.05 (m, 2 H); ^{13}C NMR (75 MHz) δ 149.5, 149.1, 144.9, 139.9, 139.0, 138.9, 136.2, 135.8, 133.1, 129.8, 129.3, 128.3, 127.0, 123.2, 123.1, 53.2, 35.8, 24.2, 21.6; mass spectrum (*m/z*, %) 454 (5, M^+), 376 (28), 313 (81), 157 (33), 91 (23), 77 (100); HRMS calcd for $C_{23}H_{22}N_2O_4S_2$: 454.1021; found: 454.0998.

Preparation of 3,5-hexadien-2-one (7). To a solution of 3-phenylseleno-5-hexen-2-one[3] (4.63 g, 18.3 mmol) in THF (90 mL) was added dropwise 30% H_2O_2 (7.5 mL) at room temperature. After an hour, the reaction mixture was washed with water, dried ($MgSO_4$) and concentrated. Chromatography (elution with hexanes-ether, 3:1) afforded 1.54 g (88%) of dienone **7**.[4]

Preparation of 1-phenyl-2,4-pentadien-1-one (8). 1-Phenyl-2-phenylseleno-4-penten-1-one[3] (2.62 g, 8.31 mmol) was treated as in the preceding procedure to afford 1.12 g (85%) of dienone **8**.[5]

Ester (*E*)-13b. White solid; mp 129-132 °C (from toluene-ethyl acetate); IR (Nujol) 3270, 1716, 1161cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2 H), 7.54-7.50 (m, 1 H), 7.43-7.38 (m, 2 H), 7.25-7.18 (m, 4 H), 7.07 (d, *J* = 11.8 Hz, 1 H), 6.71 (dt, *J* = 16.4, 10.5 Hz, 1 H), 6.35 (d, *J* = 10.3 Hz, 1 H, exchanged with D_2O), 5.72-5.64 (m, 3 H), 3.58 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 141.7, 140.8, 137.3, 133.4, 132.6,

130.2, 129.0, 128.8, 128.6, 128.0, 127.3, 126.9, 53.3, 52.0; mass spectrum (*m/z,* %) 391 (M^+, 1), 252 (45), 250 (95), 218 (34), 141 (67), 77 (100); HRMS calc'd for $C_{19}H_{18}NO_4S^{35}Cl$ (M^+): 391.0645; found: 391.0627.

Ester (*E*)-13e. White solid; mp 140-142 °C (from toluene-ethyl acetate); IR (film) 3292, 1716, 1160cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2 H), 7.52-7.47 (m, 1 H), 7.41-7.36 (m, 2 H), 7.18 (d, *J* = 8.7 Hz, 2 H), 7.04 (d, *J* = 11.8 Hz, 1 H), 6.80-6.66 (m, 3 H), 6.41 (d, *J* = 10.3 Hz, 1 H, exchanged with D_2O), 5.72-5.59 (m, 3 H), 3.75 (s, 3 H), 3.56 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 158.8, 141.1, 140.8, 132.3, 130.6, 130.3, 128.6, 128.4, 128.3, 127.0, 126.9, 113.7, 55.1, 53.2, 51.8; mass spectrum (*m/z,* %) 387 (M^+, 2), 276 (13), 246 (100), 214 (72), 186 (71), 134 (75), 77 (92); HRMS calc'd for $C_{20}H_{21}NO_5S$ (M^+): 387.1140; found: 387.1142.

Ester (*E*)-13f. White solid; mp 124-127 °C (from benzene-hexanes); IR (film): 3295, 1717, 1521, 1164 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 2 H), 7.82-7.76 (m, 2 H), 7.57-7.40 (m, 5 H), 7.13 (d, *J* = 11.3 Hz, 1 H), 6.73 (dt, *J* = 16.4, 10.5 Hz, 1 H), 6.38 (d, *J* = 9.7 Hz, 1 H, exchanged with D_2O), 5.81-5.69 (m, 3 H), 3.59 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.3, 146.2, 142.1, 132.7, 129.9, 129.7, 129.0, 128.9, 127.6, 127.0, 126.9, 126.8, 123.6, 53.5, 52.1; mass spectrum (*m/z,* %) 402 (M^+, 4), 261 (93), 229 (39), 141 (46), 77 (100); HRMS calc'd for $C_{19}H_{18}N_2O_6S$ (M^+): 402.0886; found: 402.0875.

Ester (*E*)-13h. Viscous colorless oil; IR (film) 3296, 2229, 1717, 1608, 1165 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2 H), 7.56-7.50 (m, 3 H), 7.43-7.37 (m, 4 H), 7.10 (d, *J* = 11.3 Hz, 1 H), 6.69 (dt, *J* = 16.4, 10.6 Hz, 1 H), 6.43 (d, *J* = 10.3 Hz, 1 H, exchanged with D_2O), 5.76-5.65 (m, 3 H), 3.56 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 144.3, 142.1, 140.5, 132.7, 132.2, 129.9, 129.6, 128.9, 127.5, 126.8, 126.6, 118.4, 111.3, 53.4, 52.1; mass spectrum (*m/z,* %) 366 (M^+-O, 1), 270 (1), 225 (3), 141 (15), 102 (16), 77 (100), 51 (60); HRMS calc'd for $C_{14}H_{10}N_2O_2S$ (M^+ - $C_6H_8O_2$): 270.0463; found: 270.0440.

Methyl ketone (*E*)-14b. White solid; mp 172-176 °C (from ethyl acetate-toluene); IR (film) 3215, 1653, 1340, 1165 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2 H), 7.51 (d, *J* = 7.7 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 7.27-7.13 (m, 4 H), 6.92-6.78 (m, 2 H), 6.42 (d, *J* = 10.2 Hz, 1 H, exchanged with D_2O), 5.79-5.72 (m, 2 H), 5.64 (d, *J* = 10.3 Hz, 1 H), 2.03 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 143.0, 141.1, 137.6, 136.8, 133.4, 132.6, 130.9, 129.7, 129.0, 128.7, 127.4, 127.2, 54.0, 26.2; mass spectrum (*m/z*, %) 332 (0.4), 280 (2), 234 (60), 77 (100); HRMS calc'd for $C_{13}H_{13}{}^{35}ClNO$ (M^+ - $C_6H_5SO_2$) 234.0686; found: 234.0694.

Methyl ketone (*E*)-14f. White solid; mp 137-140° C (from ethyl acetate-toluene); IR (film) 3284, 1653, 1347, 1163, 1092 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 2 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.57-7.52 (m, 1 H), 7.46-7.39 (m, 4 H), 6.97 (d, *J* = 10.8 Hz, 1 H), 6.90-6.77 (dt, *J* = 15.9, 10.8 Hz, 1 H), 6.40 (d, *J* = 10.2 Hz, 1 H, exchanges with D_2O), 5.86-5.72 (m, 3 H), 2.05 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8. 147.3, 146.6, 143.6, 140.9, 136.4, 132.8, 130.64, 130.59, 129.1, 127.1, 126.8,

123.8, 54.0, 26.1; mass spectrum (*m/z*, %) 245 (M^+ - $C_6H_5SO_2$, 8), 141 (10), 93 (25), 77 (100); HRMS calc'd for $C_{13}H_{13}N_2O_3$ (M^+ - $C_6H_5SO_2$): 245.0926; found: 245.0905.

Methyl ketone (*E*)-14h. Yellow solid; mp 152-155 ^oC (from ethyl acetate-toluene); IR (film) 3280, 2229, 1645, 1340, 1164, 1093 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2 H), 7.56-7.52 (m, 3 H), 7.43 (t, *J* = 7.7 Hz, 1 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 6.95 (d, *J* = 11.3 Hz, 1 H), 6.88-6.72 (m, 1 H), 6.37 (d, *J* = 10.3 Hz, 1 H, exchanged with D_2O), 5.84-5.77 (m, 2 H), 5.69 (d, *J* = 10.2 Hz, 2 H), 2.04 (s, 3 H); the sample was shaken with D_2O and irradiation of the signal at δ 6.88-6.72 ppm resulted in an nOe of 13% for the signal at δ 5.69. Irradiation of the signal at δ5.69 ppm resulted in an nOe of 10% for the signal at δ 6.88-6.72 ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 144.6, 143.6, 141.0, 136.4, 132.8, 132.4, 130.7, 130.4, 129.1, 127.1, 126.7, 118.7, 111.4, 54.1, 26.1; mass spectrum (*m/z, %*) 366 (M^+, 0.3), 225 (51), 141 (38), 77 (100); HRMS calc'd for $C_{14}H_{13}N_2O$ (M^+ - $C_6H_5SO_2$): 225.1028; found: 225.1046.

Phenyl ketone (*E*)-15a. White solid, mp 159-162 ^oC (from ethyl acetate-toluene); IR (film) 3205, 1633, 1341, 1164, 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 2 H), 7.53-7.43 (m, 2 H), 7.41-7.18 (m, 12 H), 6.92-6.78 (dt, *J* = 16.4, 11.3 Hz, 1 H), 6.76 (d, *J* = 10.3 Hz, 1 H, exchanged with D_2O), 6.64 (d, *J* = 11.3 Hz, 1 H), 5.88 (d, *J* = 10.3 Hz, 1 H), 5.61 (m, 1 H); the sample was shaken with D_2O and irradiation of the signal at δ 5.88 ppm resulted in an nOe of 23% for the signal at δ 6.92-6.78. Irradiation of the signal at δ 6.92-6.78 ppm resulted in an nOe of 26% for the signal at δ 5.88 ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 144.6, 141.4, 139.1, 137.8, 136.3, 132.5, 132.4, 130.8, 129.3, 129.0, 128.9, 128.7, 128.4, 127.6, 127.1, 126.2, 55.0; mass spectrum (*m/z*, %) 403 (M^+, 1), 262 (38), 105 (78), 77 (100); HRMS calc'd for $C_{24}H_{21}NO_3S$ (M^+): 403.1242; found: 403.1226.

Phenyl ketone (*E*)-15b. White solid, mp 155-157 ^oC (from ethyl acetate-toluene); IR (film) 3283, 1662, 1338, 1164, 1092 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2 H), 7.54-7.50 (m, 2 H), 7.48-7.21 (m, 10 H), 6.85-6.76 (m, 1 H), 6.71-6.64 (m, 2 H, 1 H exchanged with D_2O, leaving a d, *J* = 10.8 Hz), 5.83 (d, *J* = 10.3 Hz, 1 H), 5.67-5.57 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 144.8, 141.3, 137.7, 137.6, 135.9, 133.5, 132.6, 132.5, 130.6, 129.4, 129.3, 129.1, 128.9, 128.4, 127.6, 127.1, 54.5; mass spectrum (*m/z, %*) 437 (M^+, 2), 296 (61), 141 (13), 105 (81), 77 (100); HRMS calc'd for $C_{24}H_{20}{}^{35}ClNO_3S$ (M^+): 437.0852; found: 437.0862.

Phenyl ketone (*Z*)-15e. White solid; mp 153-156 ^oC (from ethyl acetate-toluene); IR (film) 3282, 1649, 1328, 1163, 1092 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2 H), 7.61 (d, *J* = 8.2 Hz, 2 H), 7.51-7.45 (m, 2 H), 7.41-7.33 (m, 4 H), 7.06 (d, *J* = 8.2 Hz, 2 H), 6.74 (d, *J* = 9.2 Hz, 2 H), 6.36 (d, *J* = 11.3 Hz, 1 H), 5.94-5.82 (m, 2 H, 1 H exchanged with D_2O), 5.27-5.24 (m, 2 H), 5.09 (d, *J* = 9.8 Hz, 1 H), 3.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 159.3, 140.6, 137.6, 137.5, 135.2, 133.7, 132.6, 132.3, 130.4, 129.6, 129.0, 128.8, 128.1, 127.3, 123.4, 114.1, 61.6, 55.3; mass spectrum (*m/z*, %) 327 (1), 292 (39), 105 (57), 77 (100); HRMS calc'd for $C_{25}H_{23}NO_4S$ (M^+): 433.1348; found: 433.1344.

Phenyl ketone (*E*)-15f. Off-white solid; mp 163-167 °C (from ethyl acetate-toluene); IR (film) 3280, 1653, 1348, 1164, 1093 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 2 H), 7.81 (d, *J* = 7.2 Hz, 2 H), 7.55-7.49 (m, 4 H), 7.44-7.35 (m, 3 H), 7.29-7.26 (m, 3 H), 6.90-6.65 (m, 3 H, one H exchanged with D_2O), 5.92 (d, *J* = 10.3 Hz, 1 H), 5.73-5.62 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 147.4, 146.7, 145.6, 141.1, 137.2, 135.4, 132.9, 132.8, 130.3, 129.24, 129.22, 128.6, 127.1, 127.0, 123.9, 54.6; mass spectrum (*m/z*, %) 157 (11), 141 (21), 105 (45), 77 (100); HRMS calc'd for $C_{18}H_{15}N_2O_3$ (M^+ -$C_6H_5SO_2$) 307.1083; found: 307.1054.

Phenyl ketone (*E*)-15h. Yellow solid; mp 142-147 °C (from ethyl acetate-toluene); IR (film) 3283, 2228, 1653, 1345, 1164, 1092 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2 H), 7.58-7.49 (m, 4 H), 7.46-7.35 (m, 6 H), 7.27 (d, *J* = 7.2 Hz, 2 H), 6.88-6.65 (m, 2 H, one H exchanged with D_2O), 5.88 (d, *J* = 10.3 Hz, 1 H), 5.71-5.62 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): 198.3, 145.5, 144.7, 141.1, 137.3, 135.4, 132.8, 132.7, 132.5, 130.3, 130.1, 129,2, 128.5, 127.0, 126.9, 118.6, 111.6, 54.7; mass spectrum (*m/z*, %) 428 (0.9), 287 (53), 105 (67), 77 (100); HRMS calc'd for $C_{25}H_{20}N_2O_3S$ (M^+): 428.1195; found: 428.1183.

Piperidine 16b. Clear viscous oil; IR (film) 1717, 1343, 1271, 1162, 1088 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 2 H), 7.58-7.53 (m, 1 H), 7.47-7.42 (m, 2 H), 7.29-7.21 (m, 4 H), 7.05 (t, *J* = 3.6 Hz, 1 H), 5.96 (s, 1 H), 3.80 (dd, *J* = 14.3, 4.6 Hz, 1 H), 3.66 (s, 3 H), 3.00-2.90 (m, 1 H), 2.18-2.13 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 140.7, 139.4, 137.3, 134.0, 132.7, 129.5, 129.3, 129.0, 128.6, 127.0, 54.4, 52.0, 36.7, 24.1; mass spectrum (*m/z*, %) 391 (M^+, 1), 280 (36), 252 (32), 250 (100), 77 (83); HRMS calc'd for $C_{19}H_{18}{}^{35}ClNO_4S$ (M^+): 391.0645; found: 391.0634.

Piperidine 16e. Clear viscous oil; IR (film) 1717, 1339, 1255, 1160, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 2 H), 7.56-7.51 (m, 1 H), 7.46-7.41 (m, 2 H), 7.20 (d, *J* = 8.7 Hz, 2 H), 7.01 (t, *J* = 3.1 Hz, 1 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 5.96 (s, 1 H), 3.78 (s, 3 H), 3.78-3.74 (m, 1 H), 3.65 (s, 3 H), 3.06-2.95 (m, 1 H), 2.19-2.11 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 159.3, 140.9, 138.7, 132.5, 130.7, 129.9, 129.3, 128.9, 127.0, 113.7, 55.2, 54.5, 51.9, 36.6, 24.1; mass spectrum (*m/z*, %) 387 (M^+, 7), 246 (80), 245 (67), 230 (34), 214 (44), 186 (31), 77 (100); HRMS calc'd for $C_{20}H_{21}NO_5S$ (M^+): 387.1140; found: 387.1164.

Piperidine 16f. Pale-yellow oil; IR (film) 1717, 1348, 1274, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 2 H), 7.80 (d, *J* = 7.7 Hz, 2 H), 7.60-7.55 (m, 1 H), 7.50-7.45 (m, 4 H). 7.13 (t, *J* = 3.6 Hz, 1 H), 6.05 (s, 1 H), 3.86-3.79 (m, 1 H), 3.67 (s, 3 H), 2.98-2.90 (m, 1 H), 2.18-2.16 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 147.6, 146.0, 140.4, 140.2, 133.0, 129.2, 129.0, 128.6, 127.0, 123.7, 54.3, 52.2, 36.9, 24.0; mass spectrum (*m/z*, %) 402 (M^+, 1), 280 (27), 277 (19), 261 (41), 77 (100); HRMS calc'd for $C_{19}H_{18}N_2O_6S$ (M^+): 402.0886; found: 402.0906.

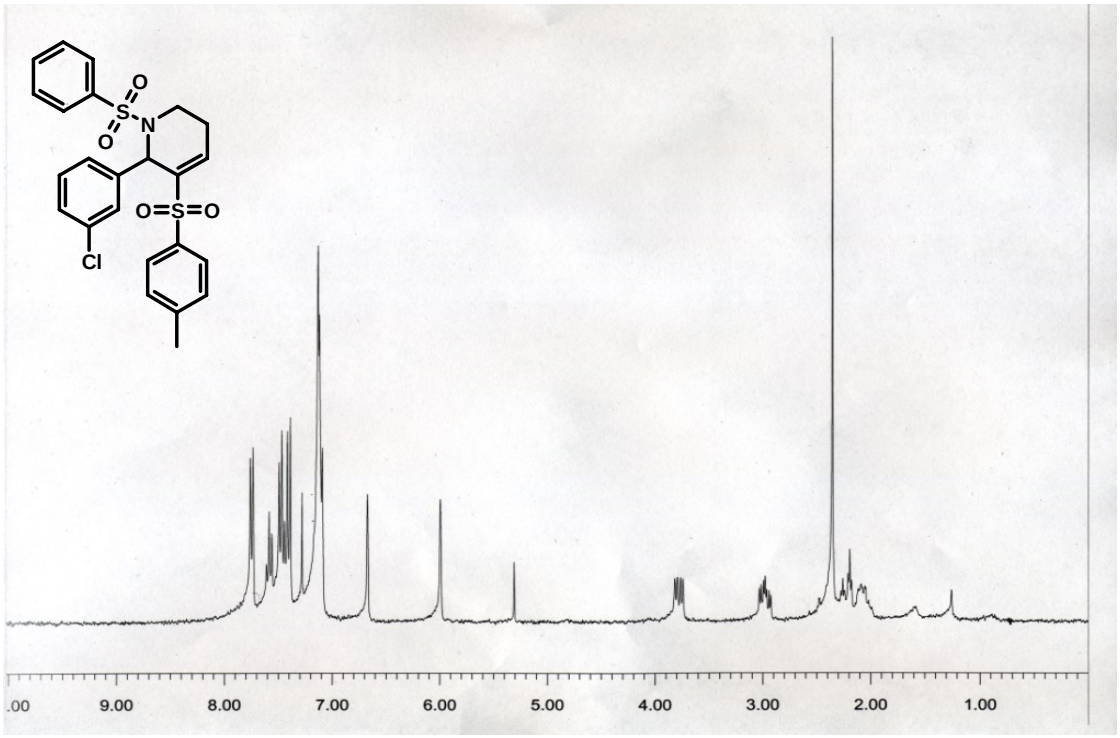
Piperidine 16h. White solid; mp 140-144 °C (from ethyl acetate-hexanes); IR (film) 2231, 1717, 1340, 1275, 1161 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 2 H), 7.62-7.55 (m, 3 H), 7.49-7.41 (m, 4 H), 7.10 (t, *J* = 3.1 Hz, 1 H), 6.01 (s, 1 H), 3.85-3.79 (m, 1 H), 3.67 (s, 3 H), 2.96-2.86 (m, 1 H), 2.17-2.12 (m, 2 H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 164.8, 144.1, 140.4, 140.1, 132.9, 132.3, 129.1, 128.8, 128.6, 126.9, 118.5, 112.0, 54.5, 52.1, 36.9, 23.9; mass spectrum (*m/z*, %) 382 (M^+, 1), 280 (49), 181 (18), 154 (33), 77 (100); HRMS calc'd for $C_{20}H_{18}N_2O_4S$ (M^+): 382.0987; found: 382.0972.

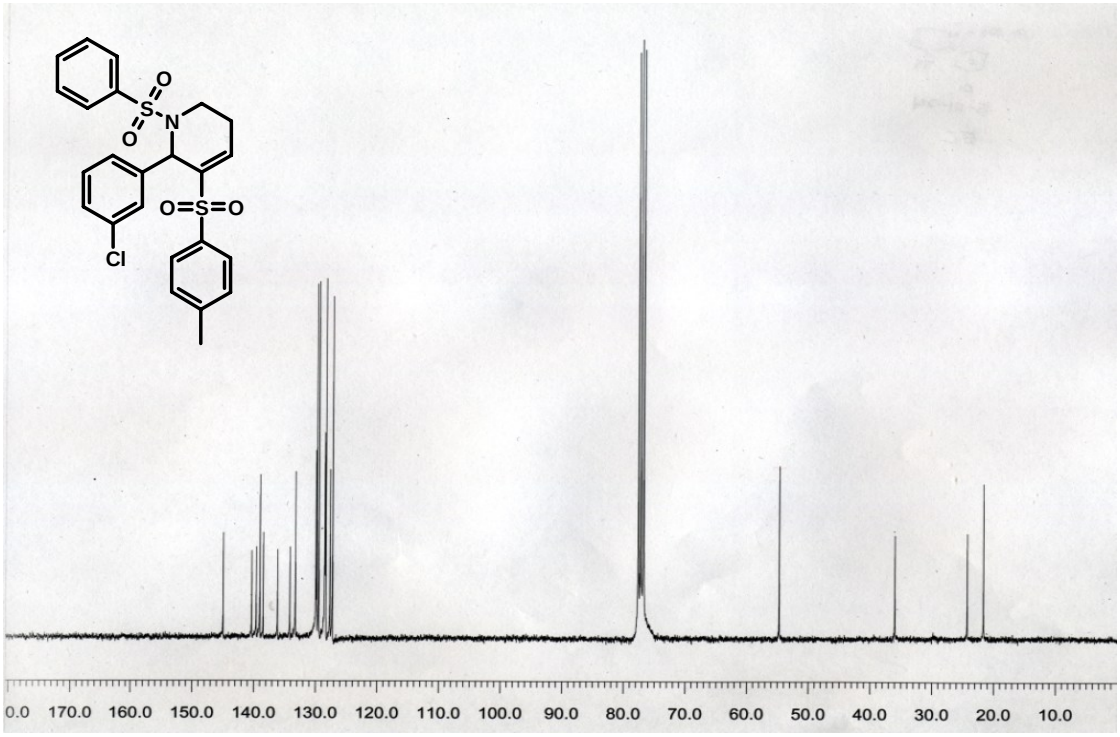
References for the Supporting Information

1. Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth*. **1988**, *66*, 203-210.
2. Back, T. G.; Rankic, D. A.; Sorbetti, J. M.; Wulff, J. E. *Org. Lett.* **2005**, *7*, 2377-2379.
3. Ponthieux, S.; Outurquin, F.; Paulmier, C. *Tetrahedron* **1997**, *53*, 6365-6376.
4. Bloch, R.; Abecassis, J.; Hassan, D. *Can. J. Chem.* **1984**, *62*, 2019-2024.
5. Yu, Y.; Lin, R.; Zhang, Y. *Tetrahedron Lett.* **1993**, *34*, 4547-4550.

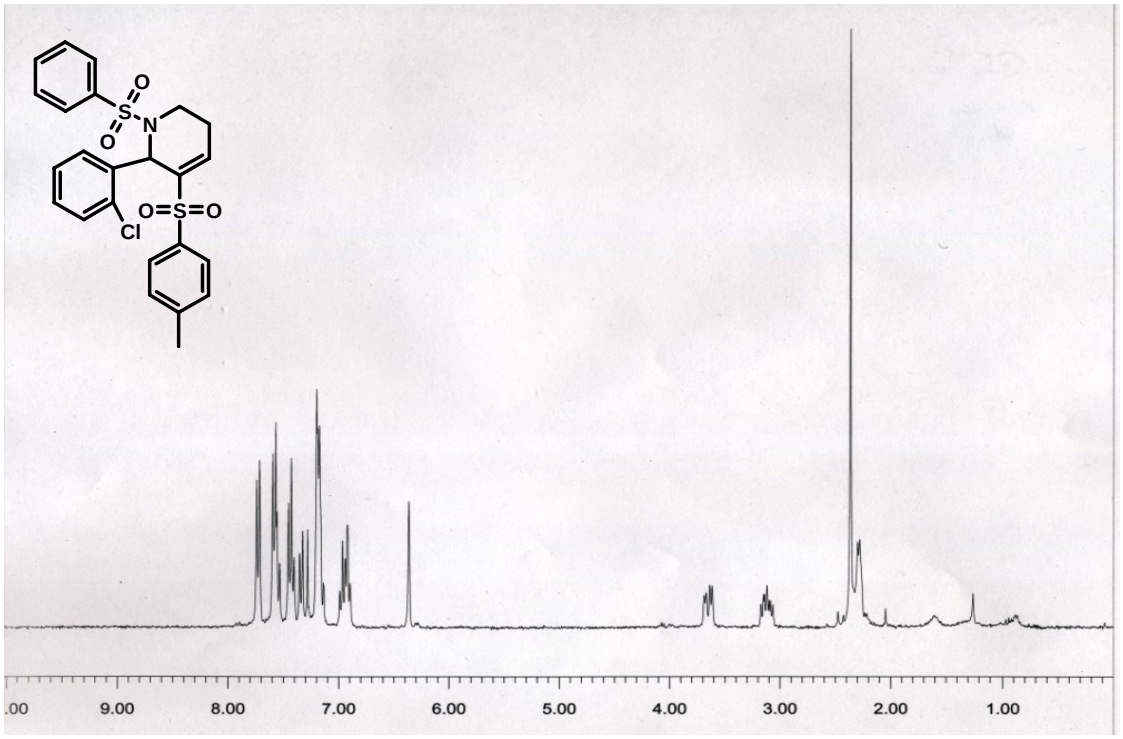
^{1}H NMR Spectrum of **5c**



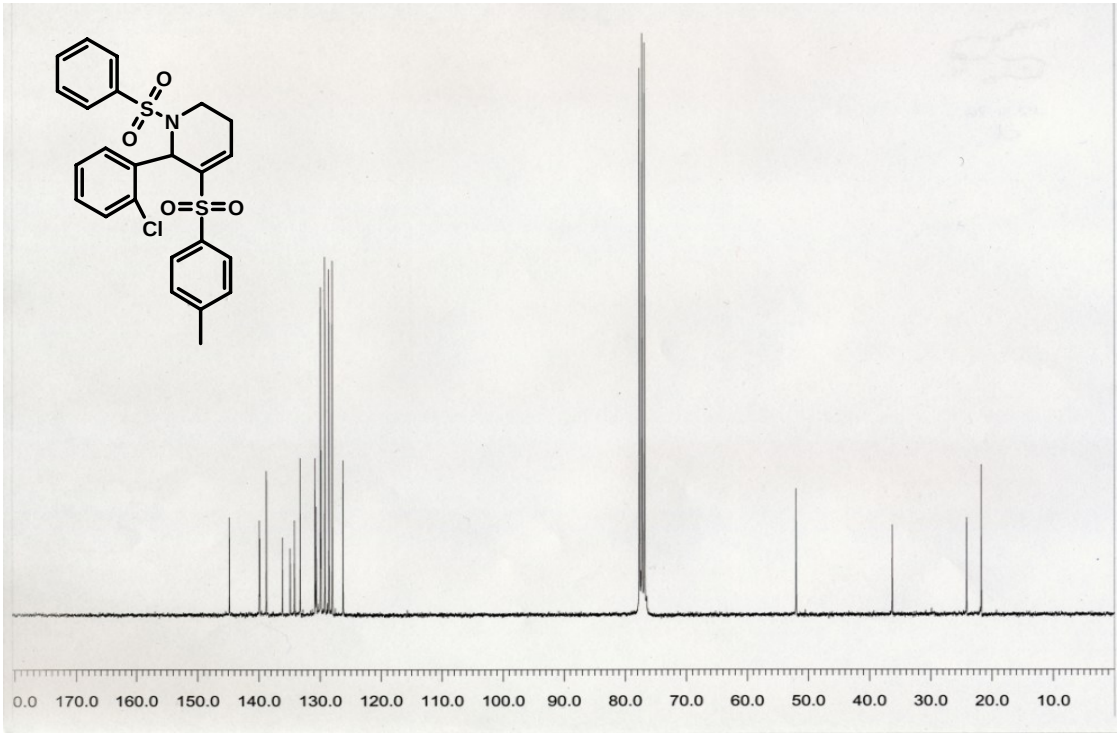
^{13}C NMR Spectrum of **5c**



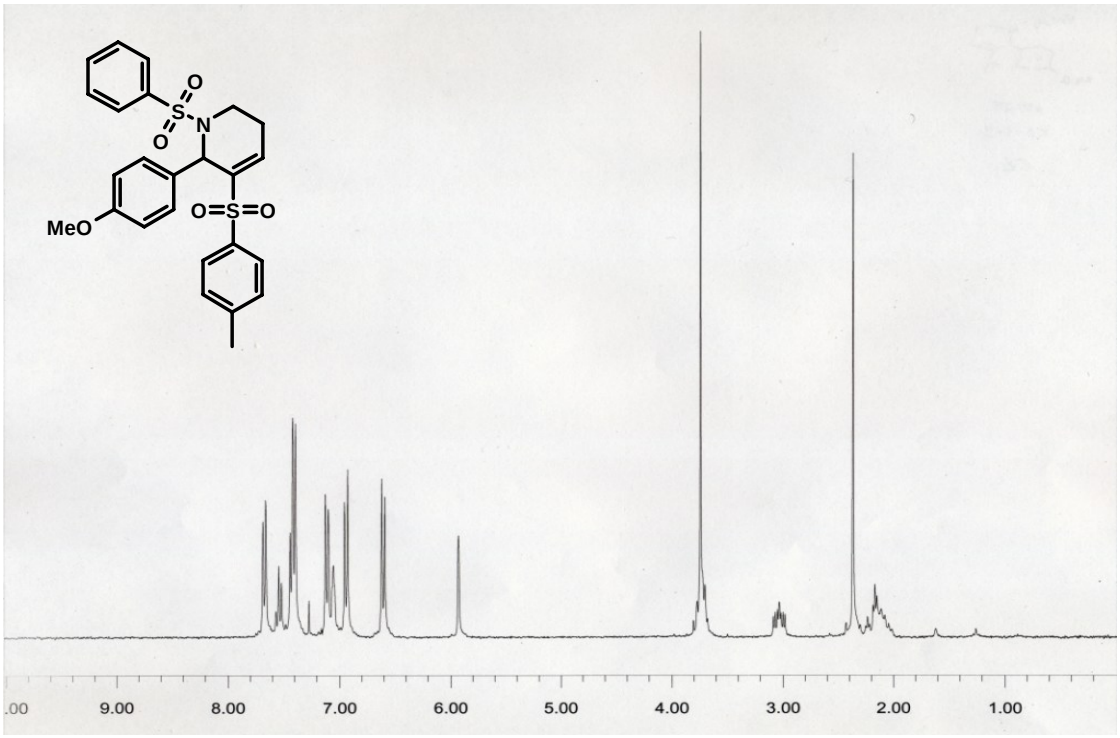
^{1}H NMR Spectrum of **5d**



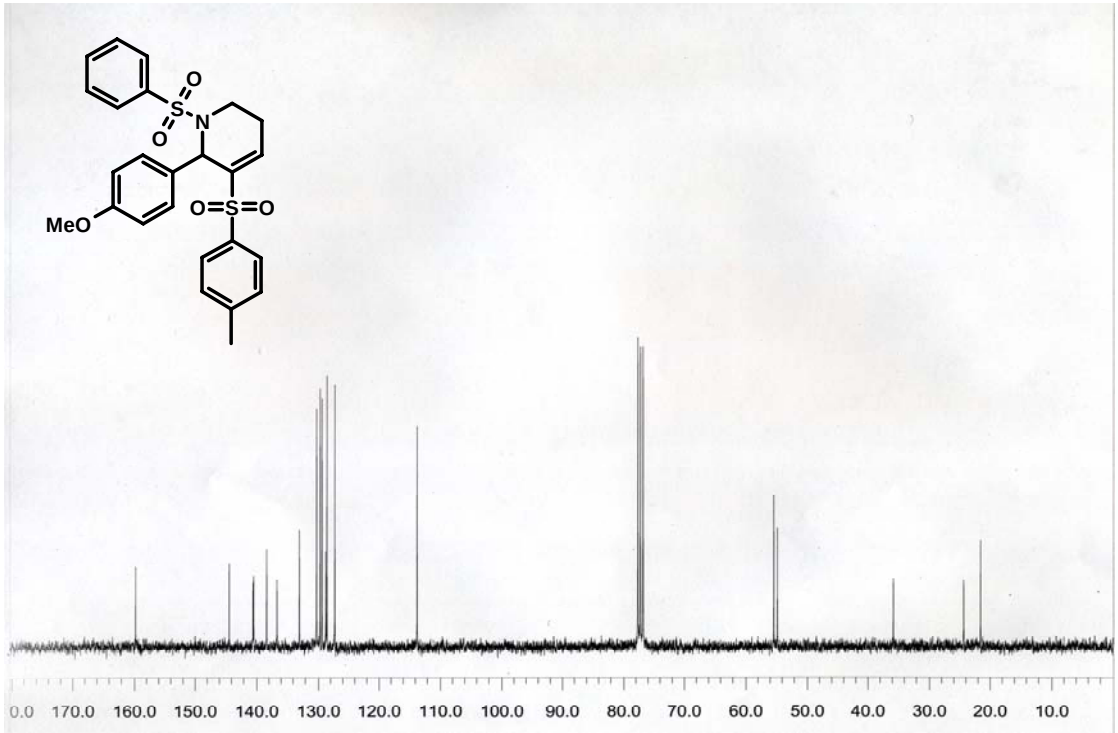
^{13}C NMR Spectrum of **5d**



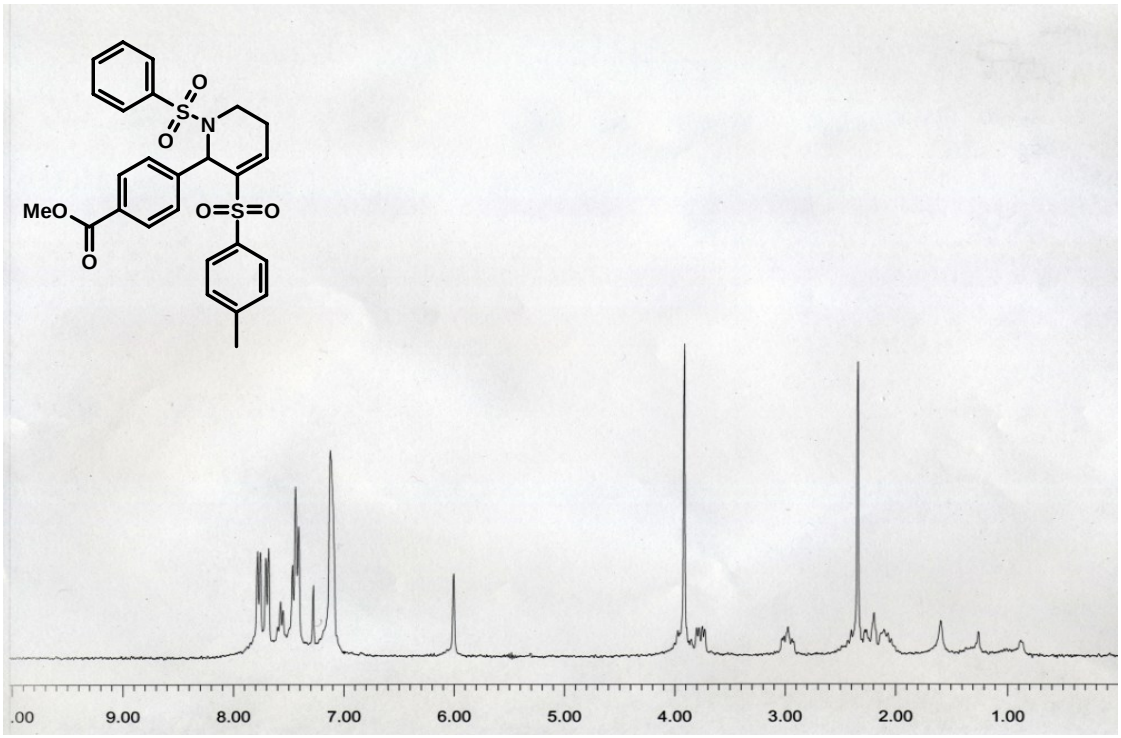
^{1}H NMR Spectrum of **5e**



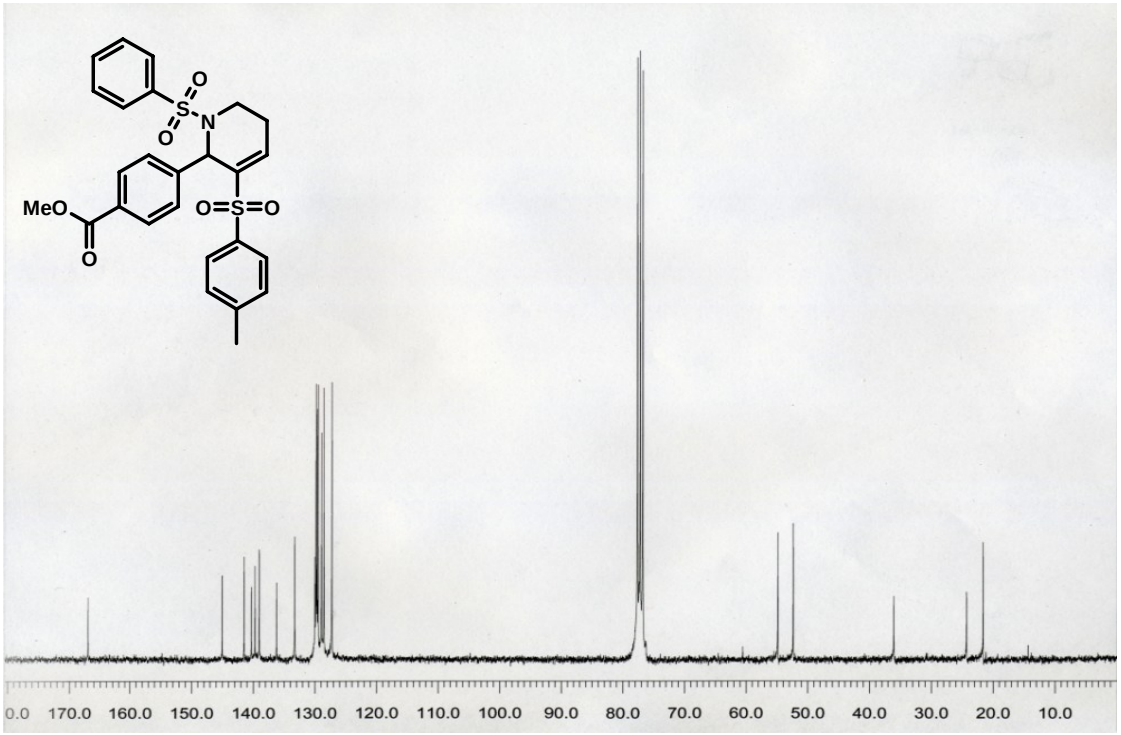
^{13}C NMR Spectrum of **5e**



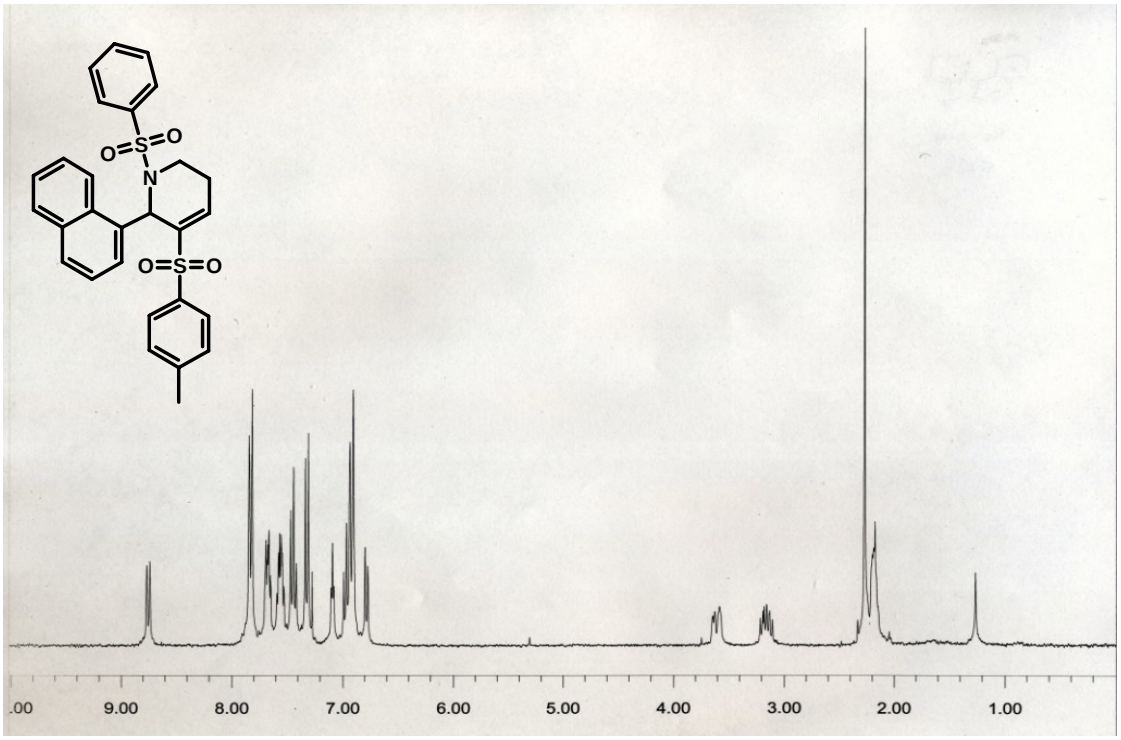
^{1}H NMR Spectrum of **5g**



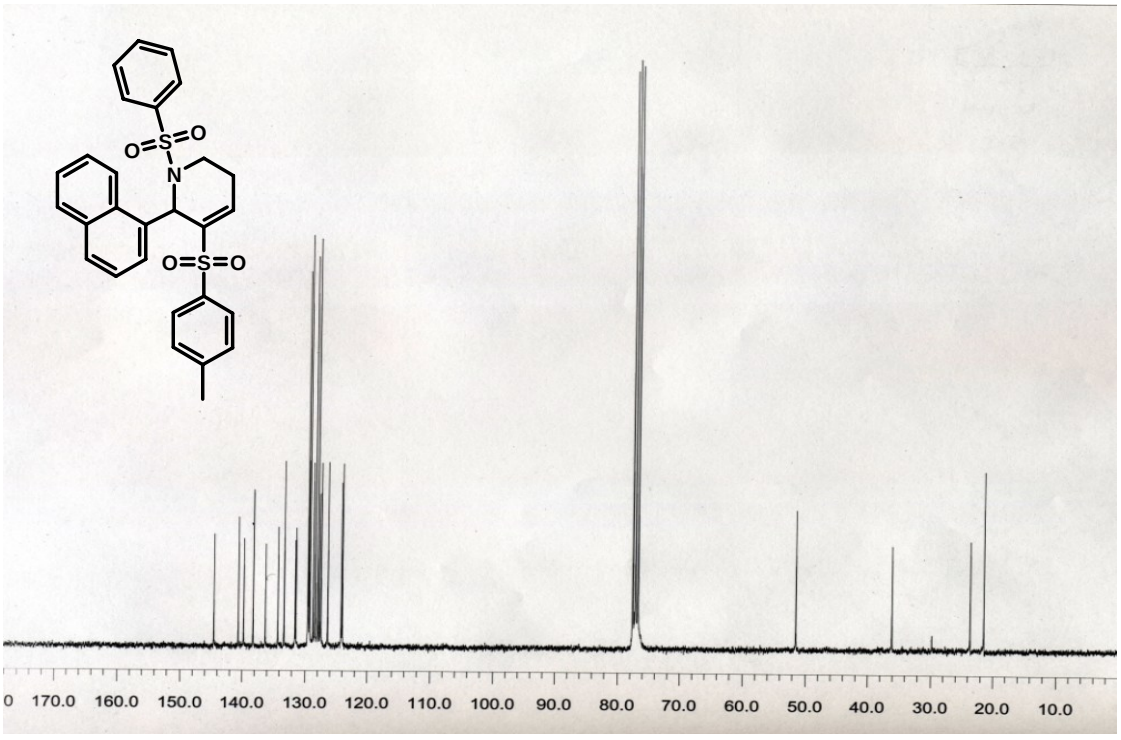
^{13}C NMR Spectrum of **5g**



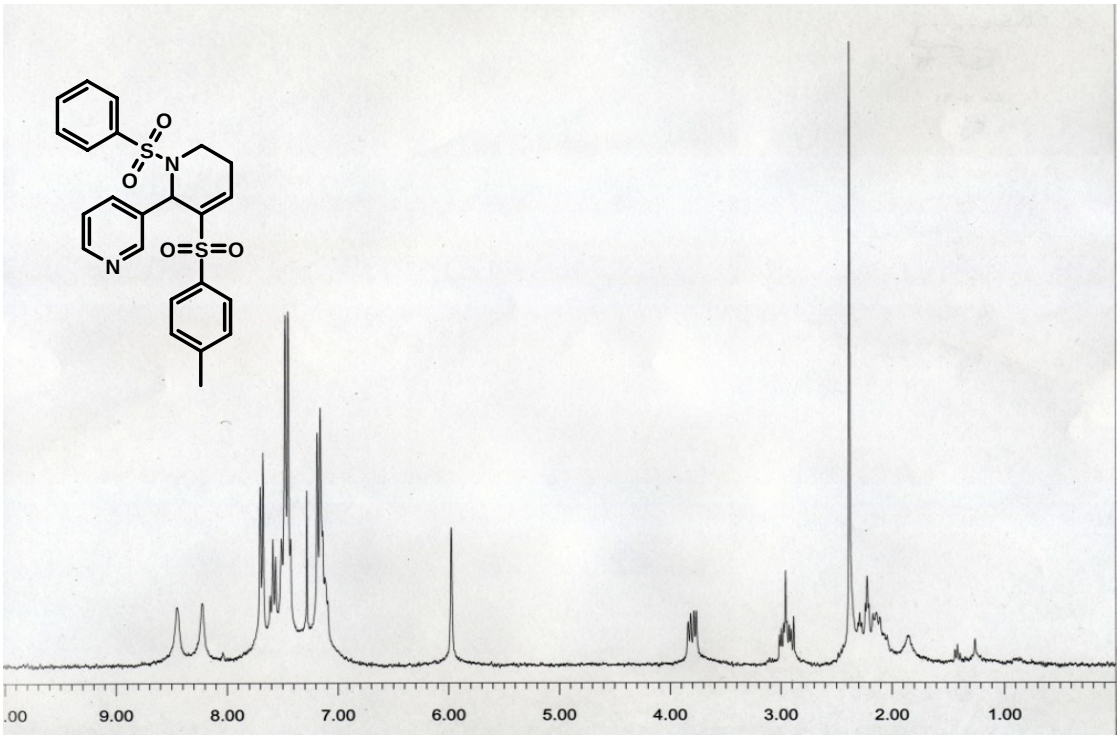
^{1}H NMR Spectrum of **5i**



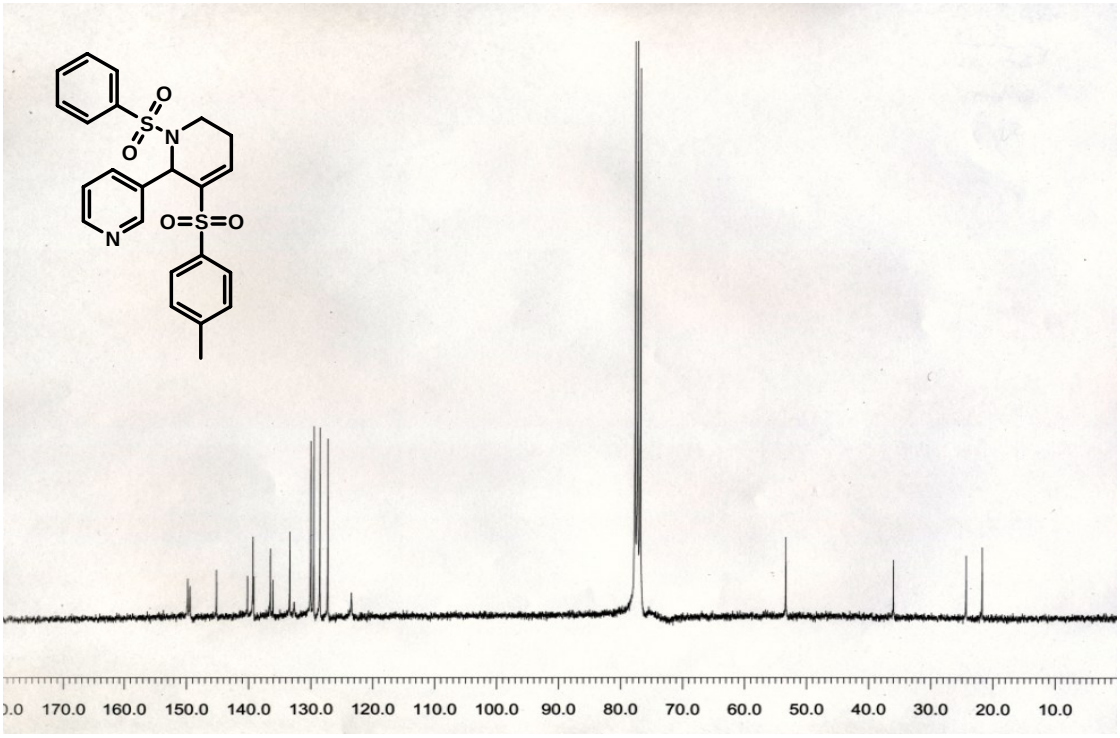
^{13}C NMR Spectrum of **5i**



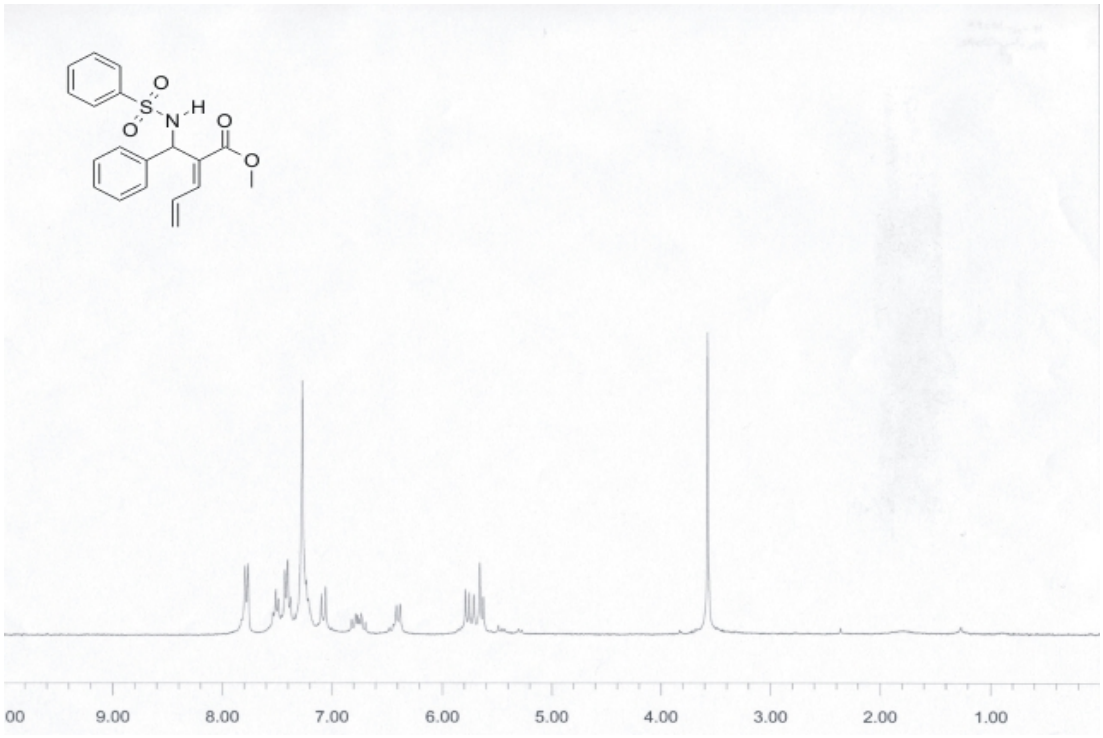
^{1}H NMR Spectrum of **5j**



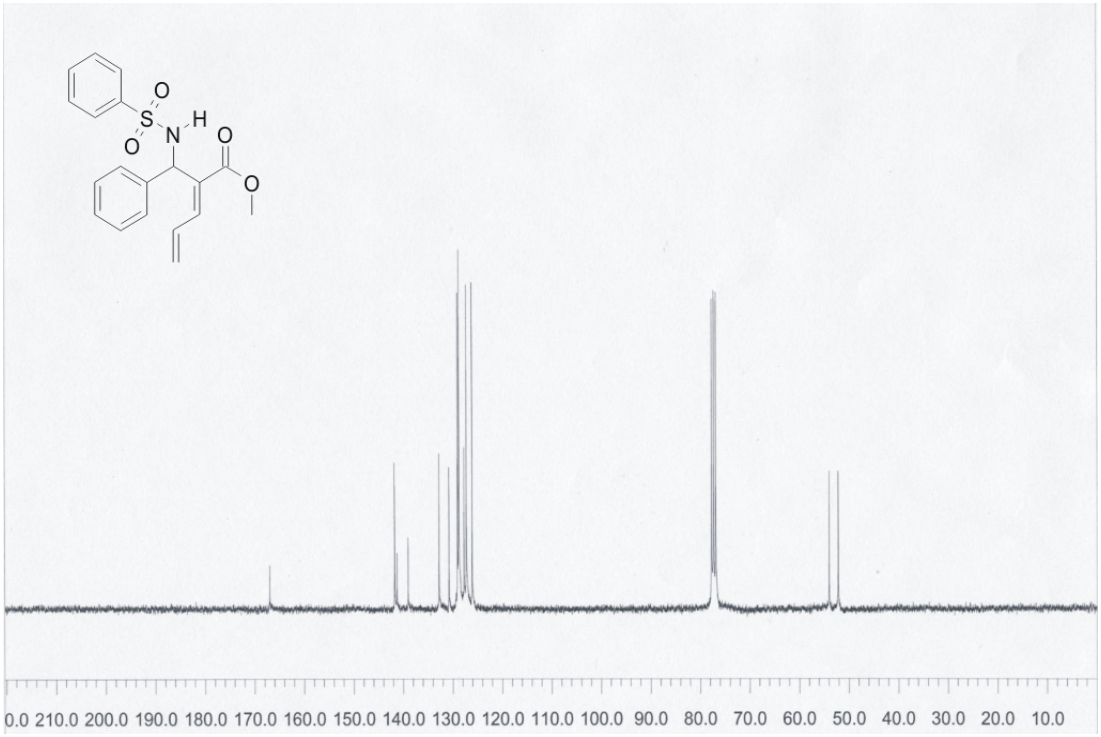
^{13}C NMR Spectrum of **5j**



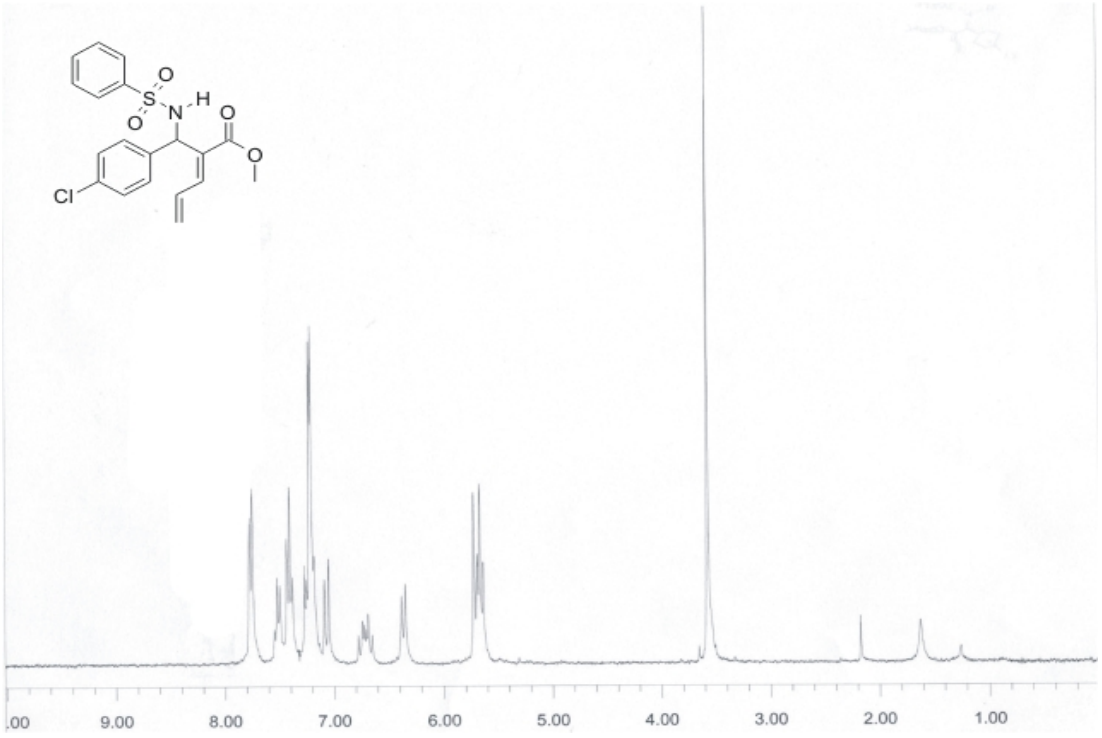
^{1}H NMR Spectrum of (*E*)-**13a**



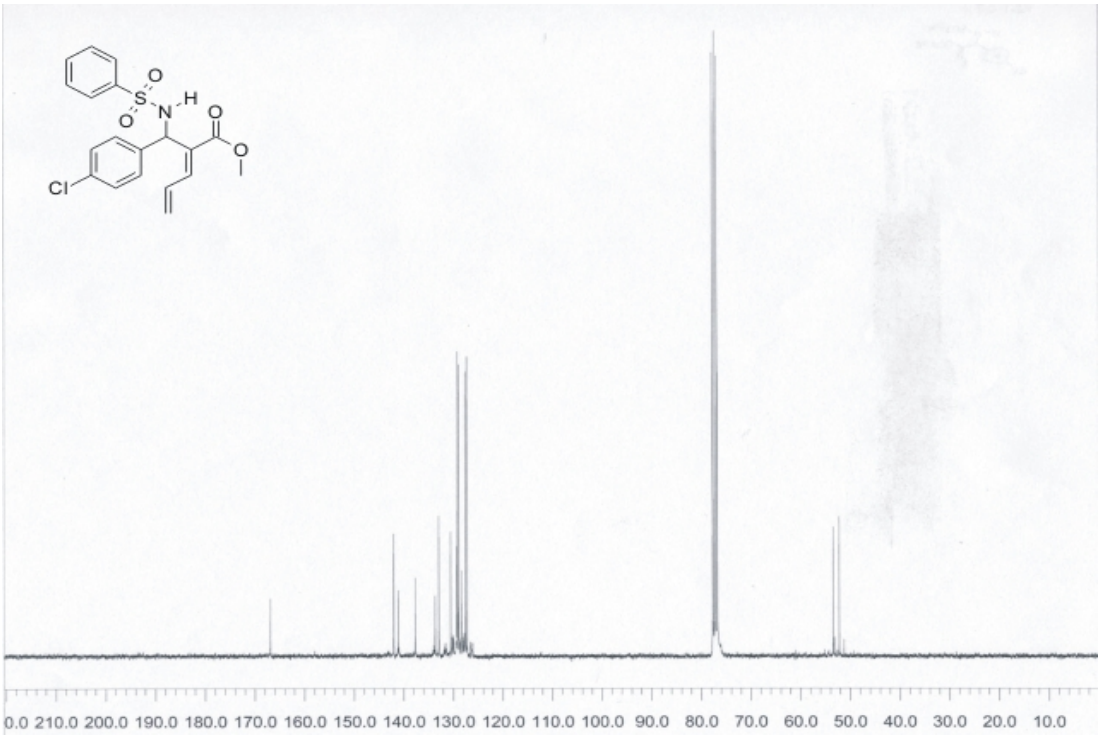
^{13}C NMR Spectrum of (*E*)-**13a**



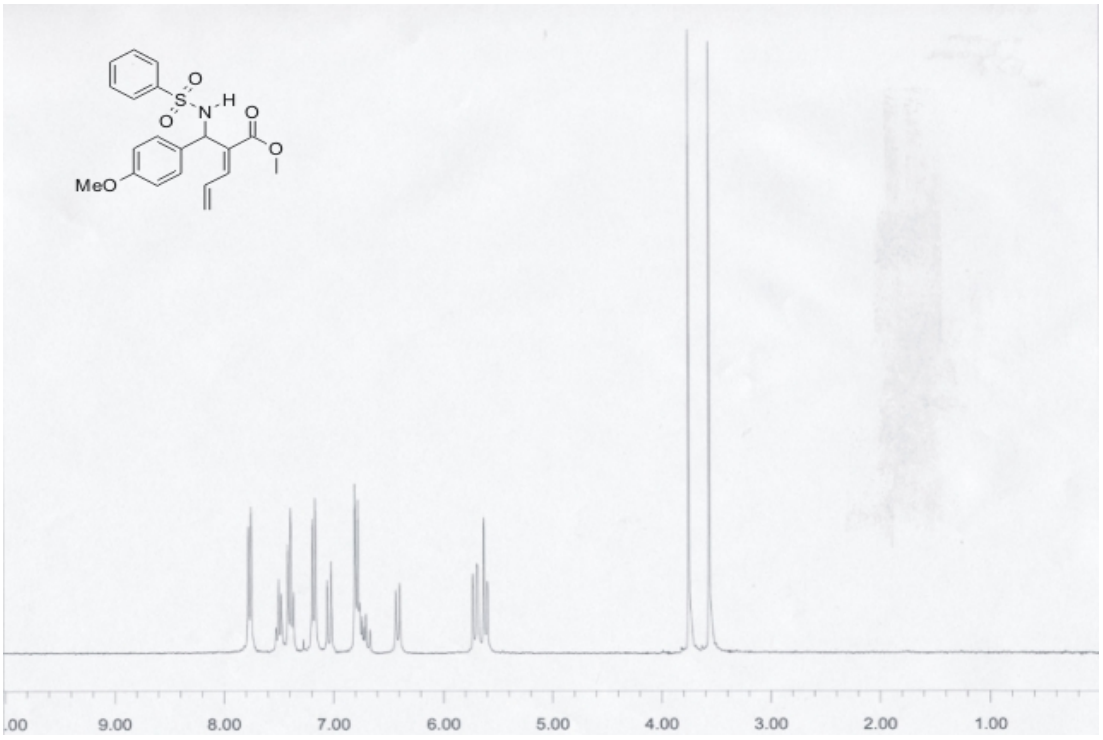
^{1}H NMR Spectrum of (*E*)-**13b**



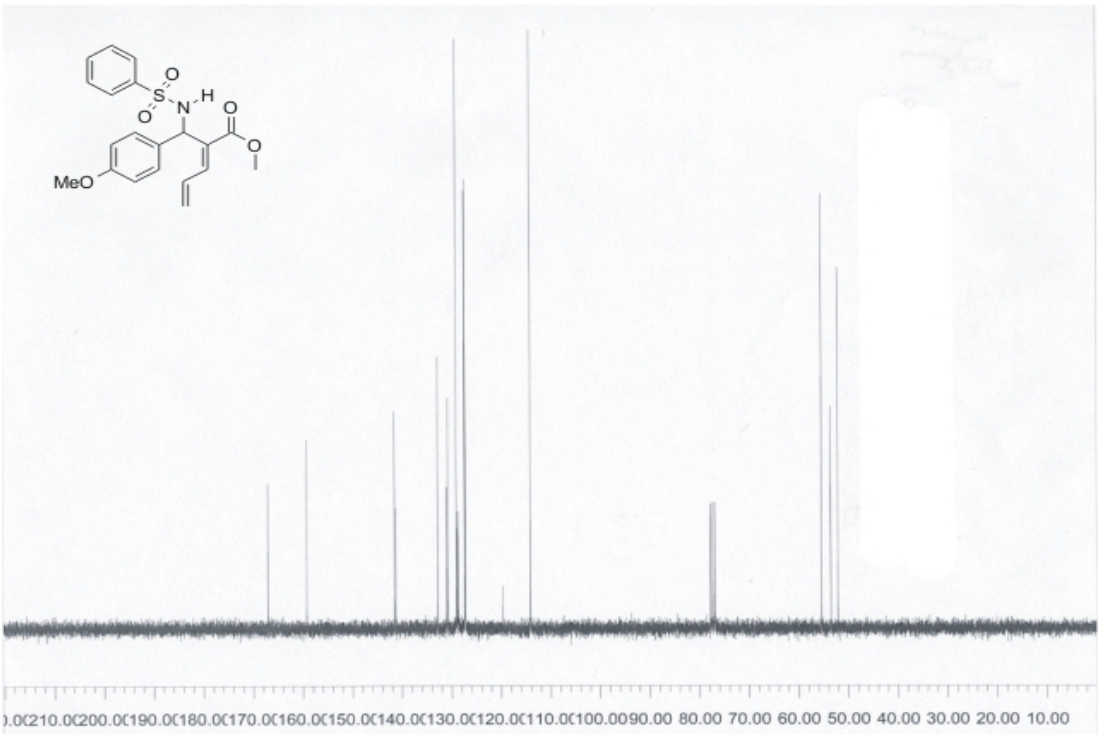
^{13}C NMR Spectrum of (*E*)-**13b**



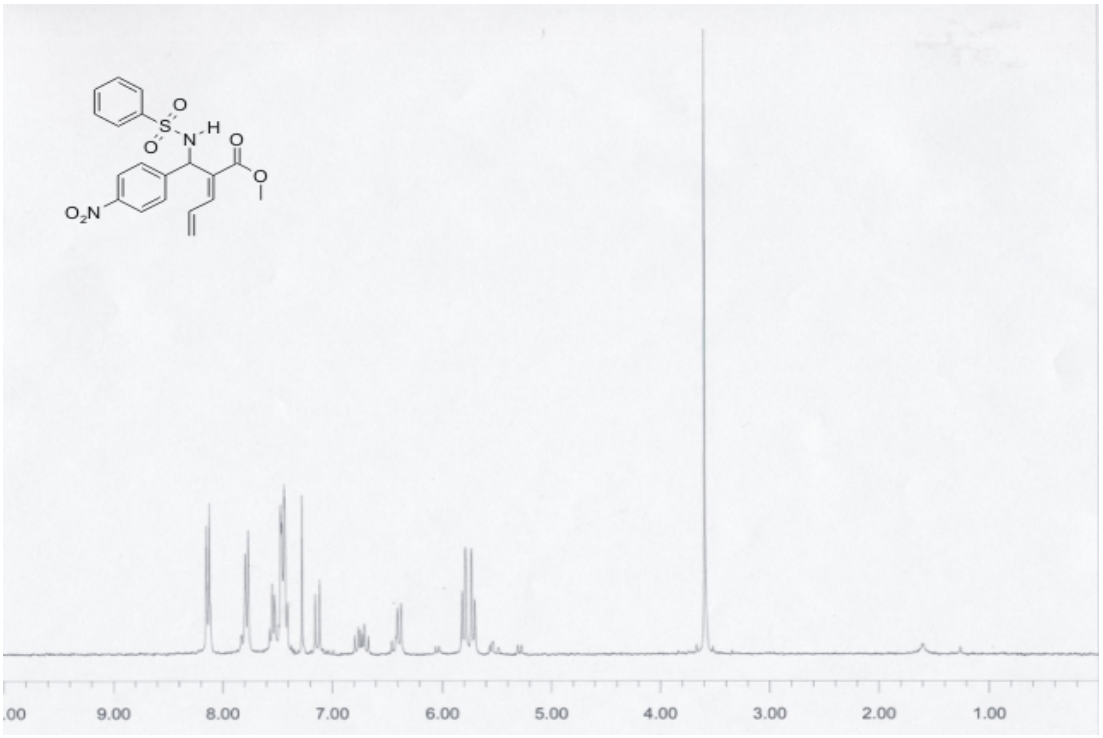
^{1}H NMR Spectrum of (*E*)-**13e**



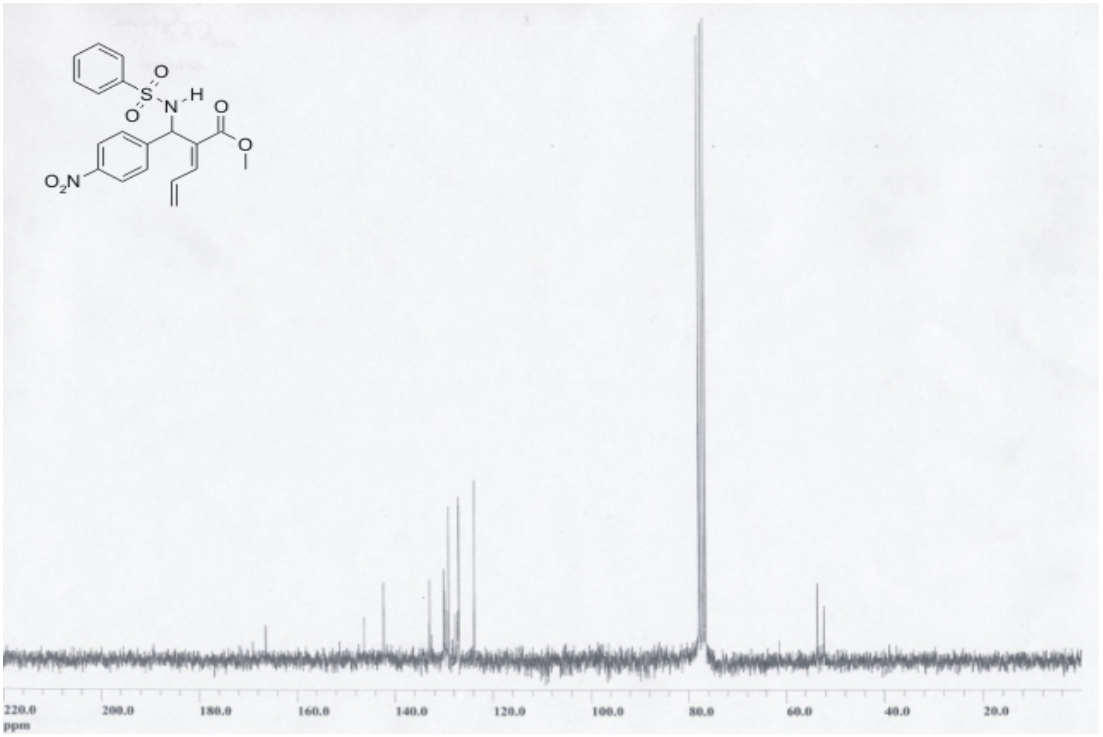
^{13}C NMR Spectrum of (*E*)-**13e**



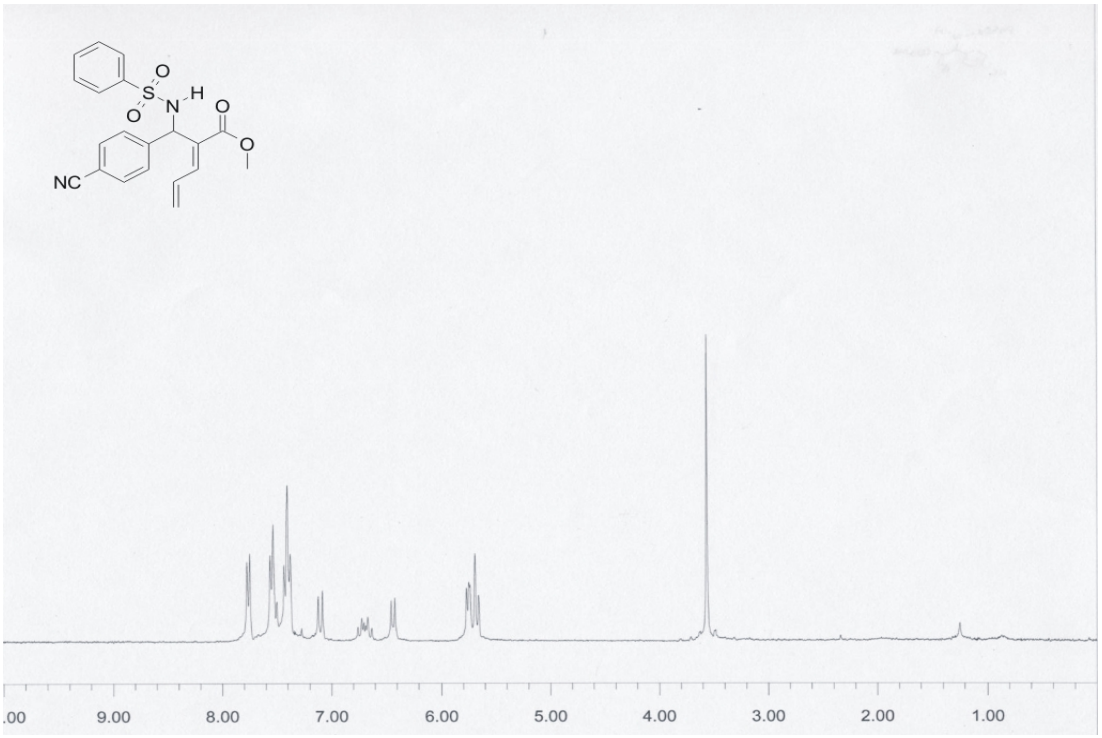
^{1}H NMR Spectrum of (*E*)-**13f**



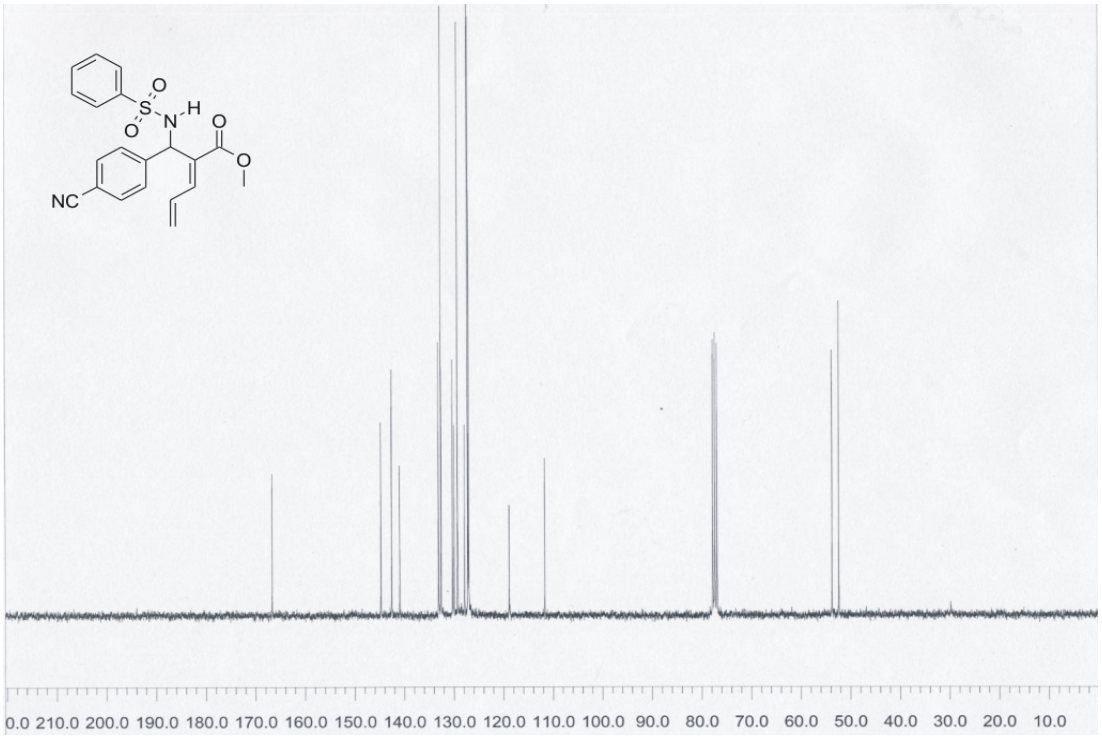
^{13}C NMR Spectrum of (*E*)-**13f**



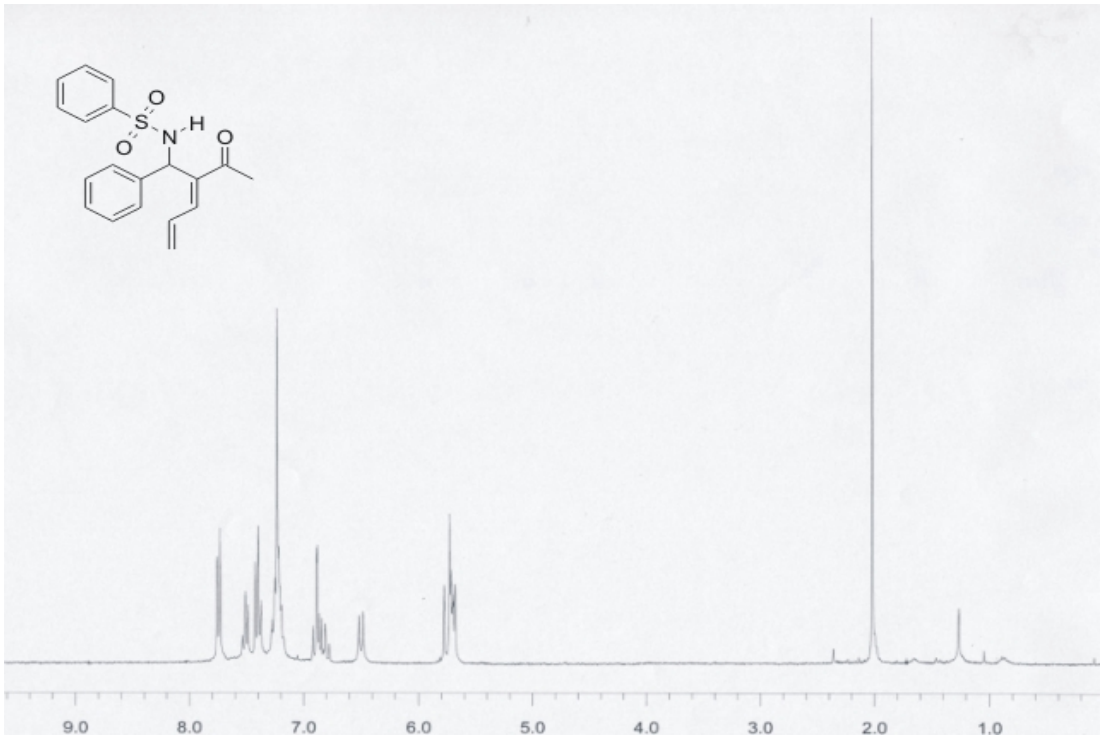
^{1}H NMR Spectrum of (*E*)-**13h**



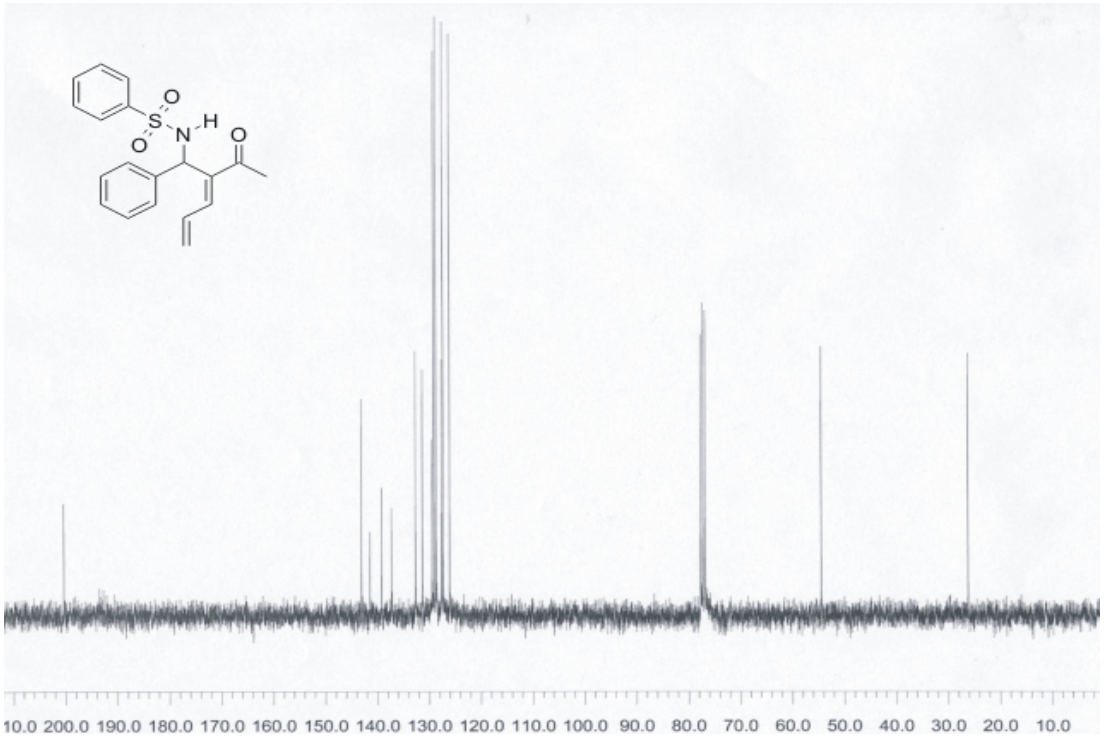
^{13}C NMR Spectrum of (*E*)-**13h**



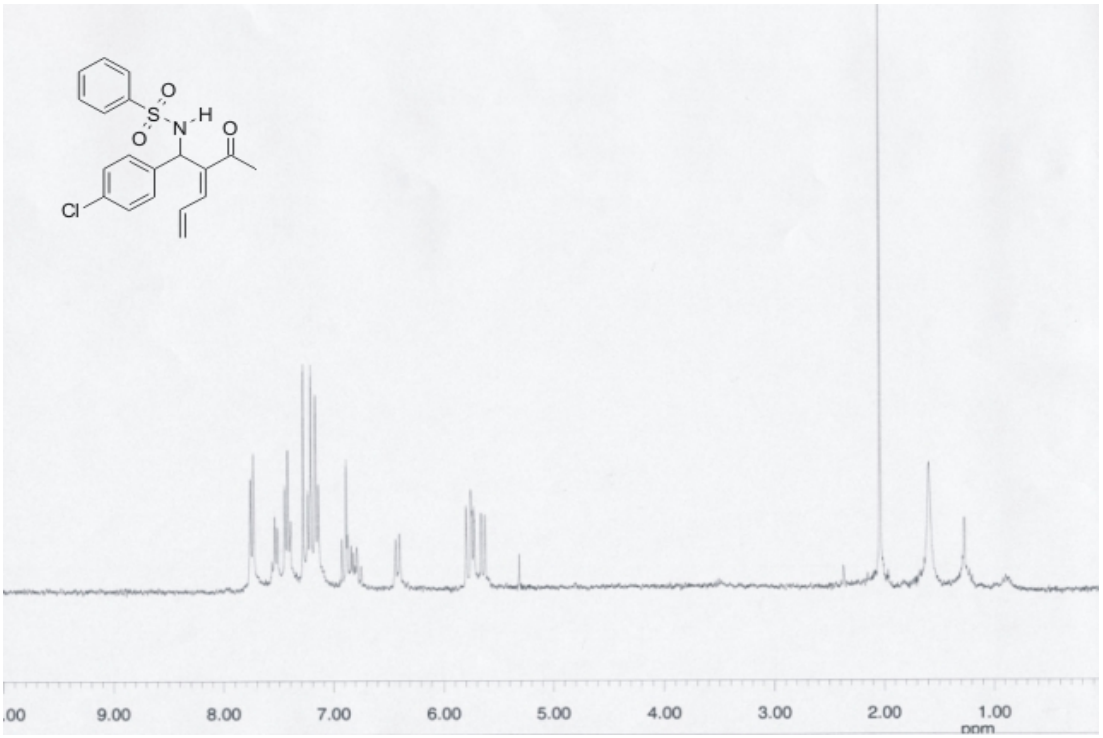
^{1}H NMR Spectrum of (*E*)-**14a**



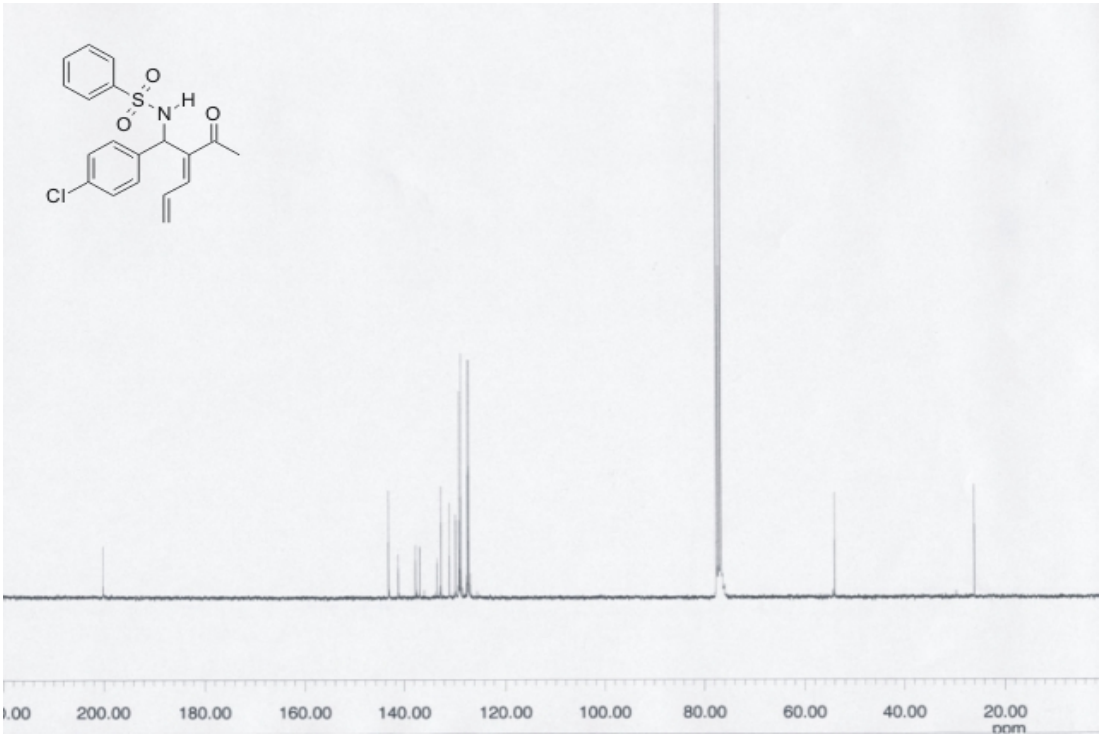
^{13}C NMR Spectrum of (*E*)-**14a**



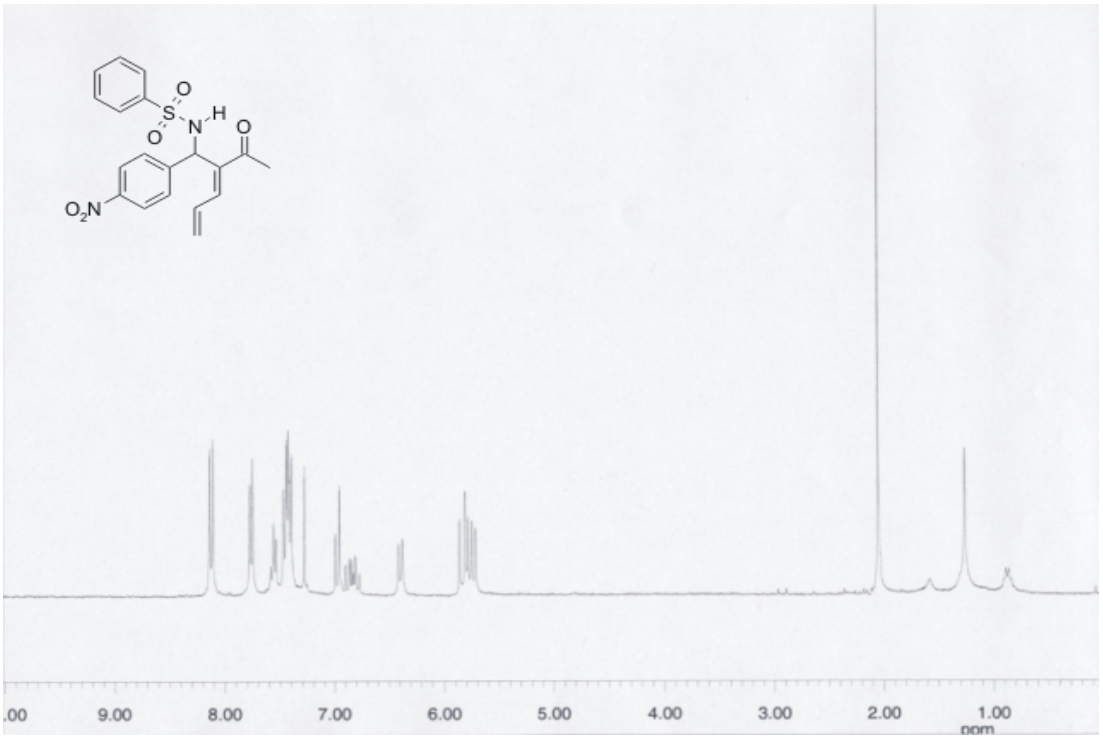
^{1}H NMR Spectrum of (*E*)-**14b**



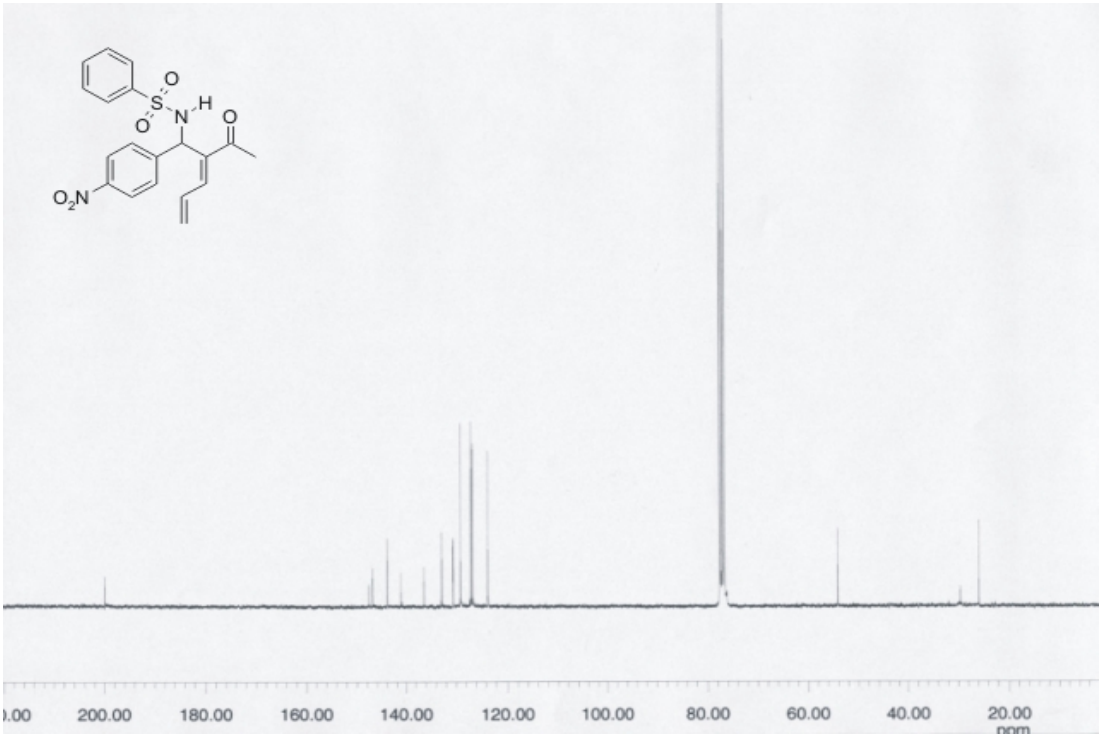
^{13}C NMR Spectrum of (*E*)-**14b**



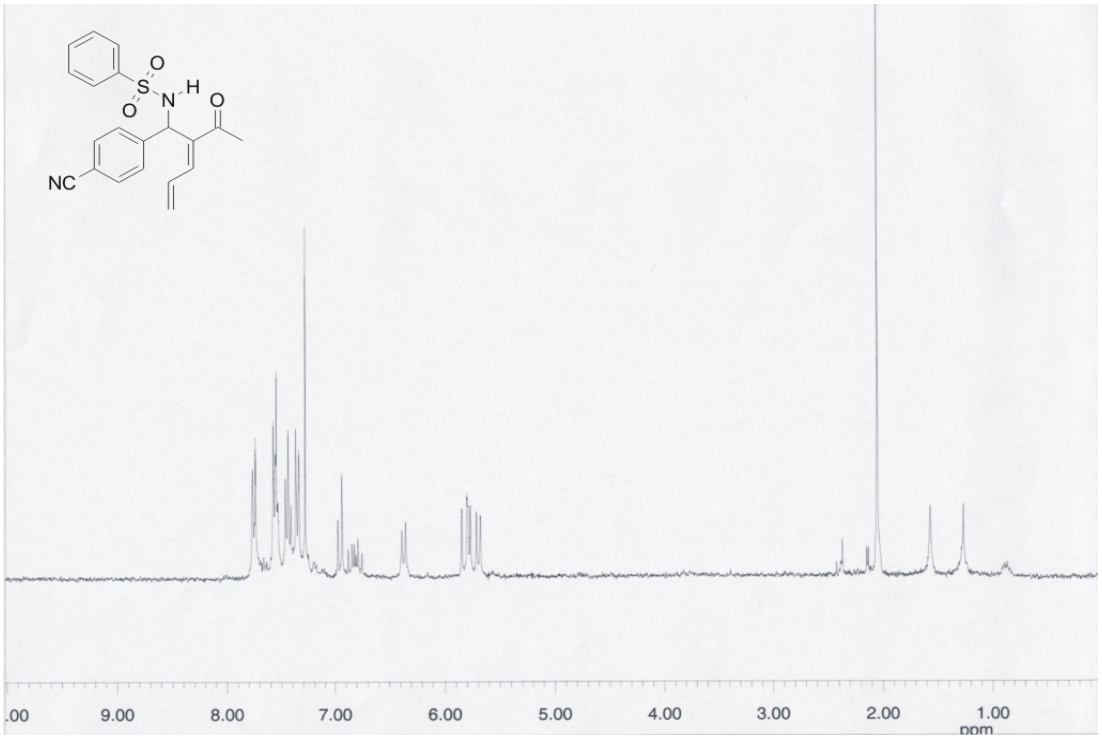
^{1}H NMR Spectrum of (*E*)-**14f**



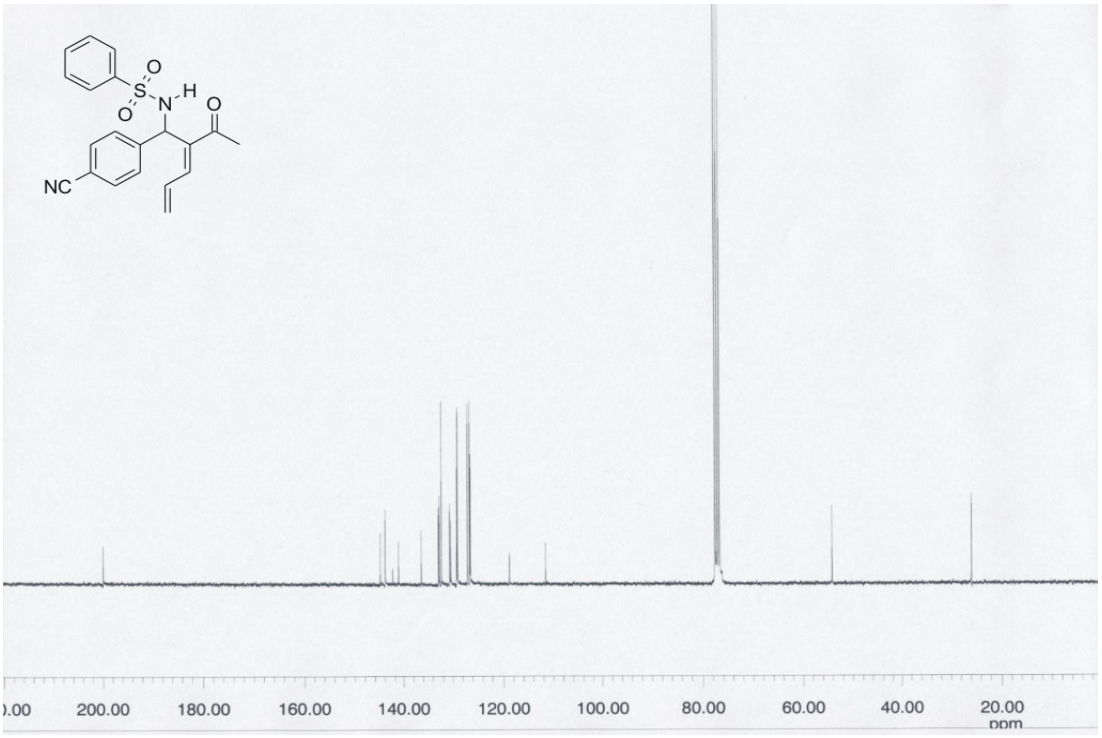
^{13}C NMR Spectrum of (*E*)-**14f**



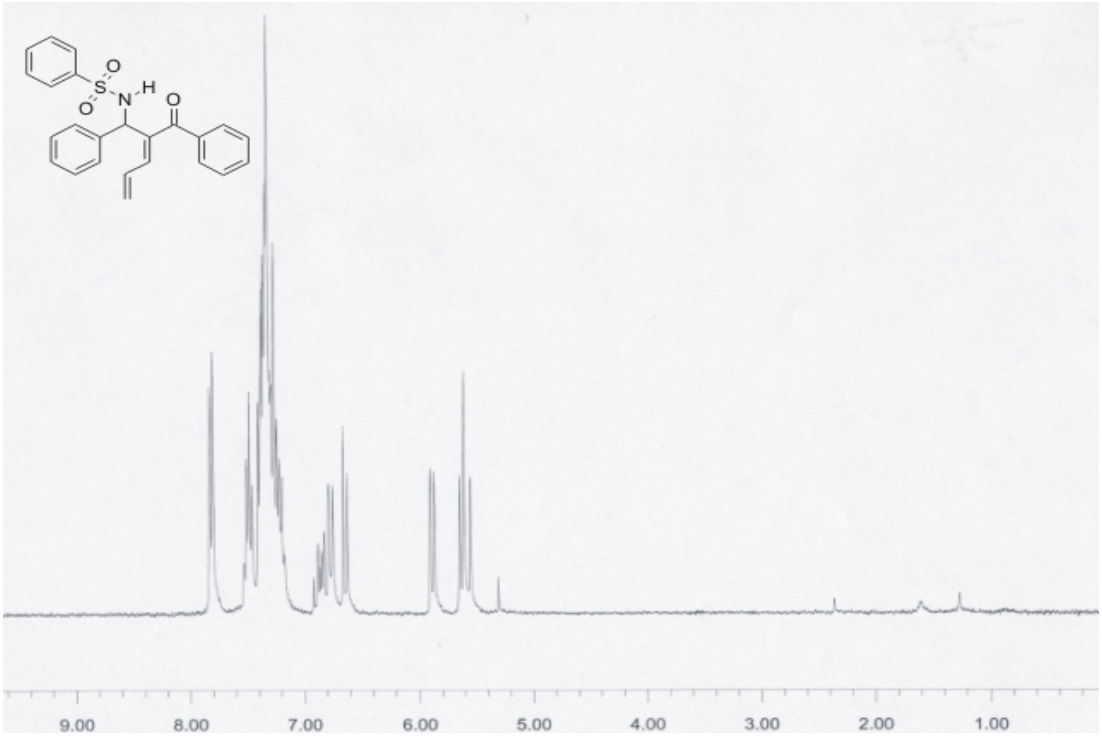
^{1}H NMR Spectrum of (*E*)-**14h**



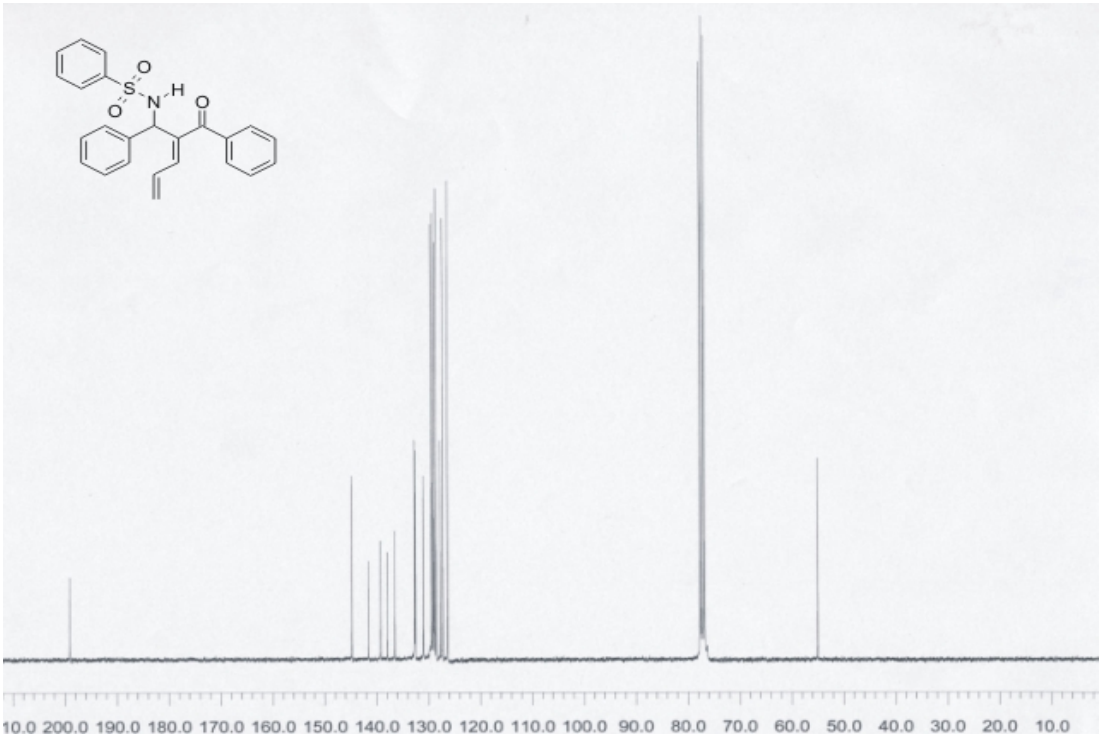
^{13}C NMR Spectrum of (*E*)-**14h**



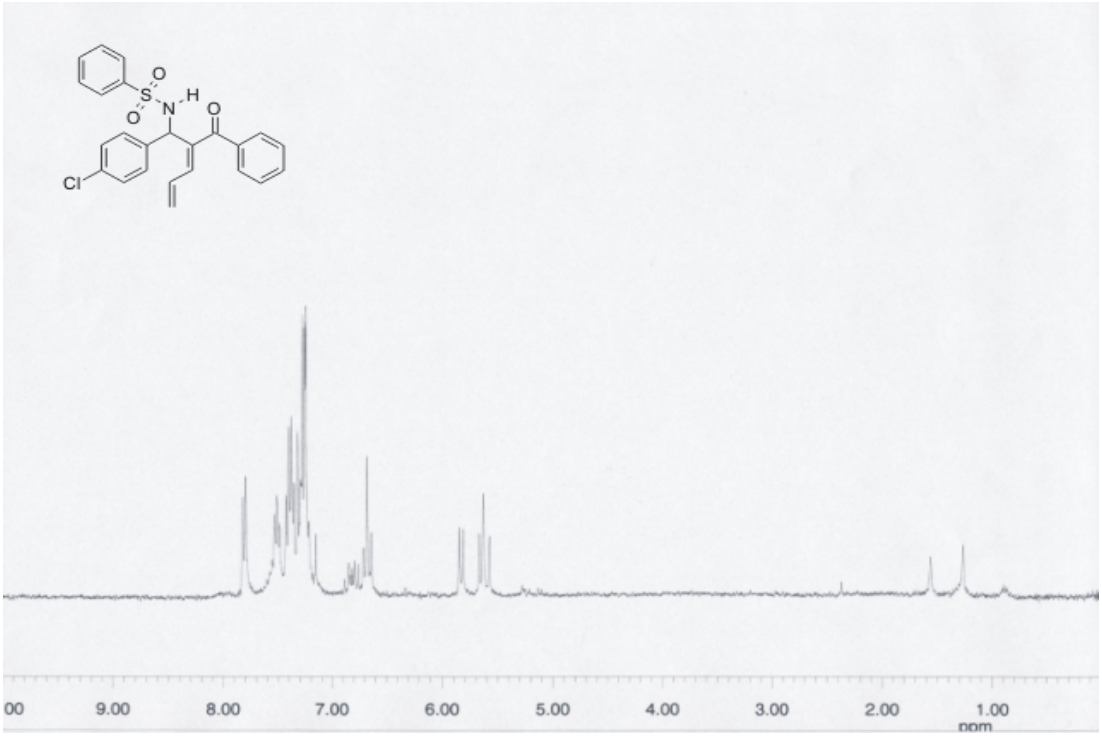
^{1}H NMR Spectrum of (*E*)-**15a**



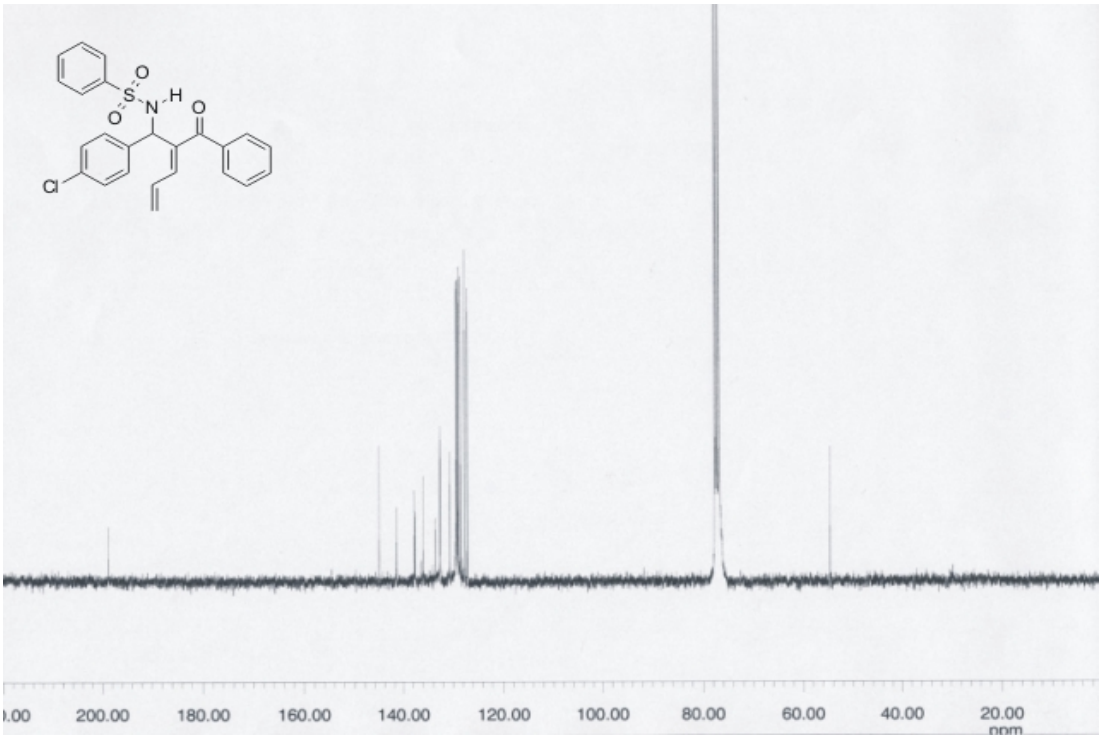
^{13}C NMR Spectrum of (*E*)-**15a**



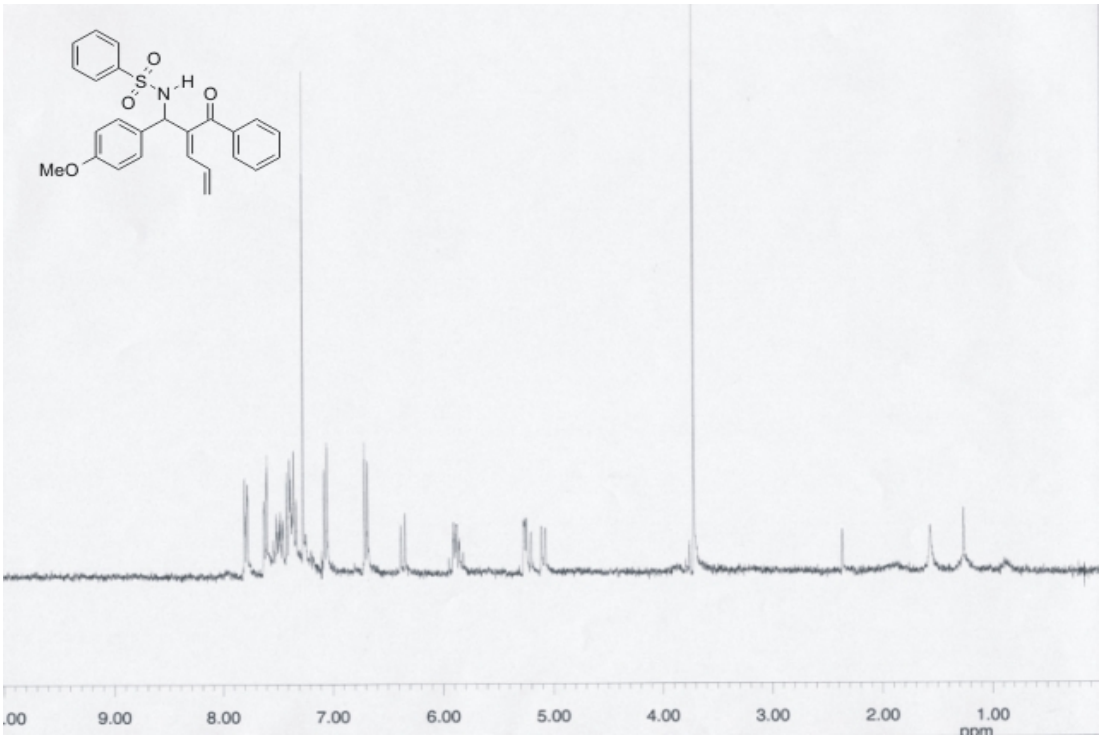
^{1}H NMR Spectrum of (*E*)-**15b**



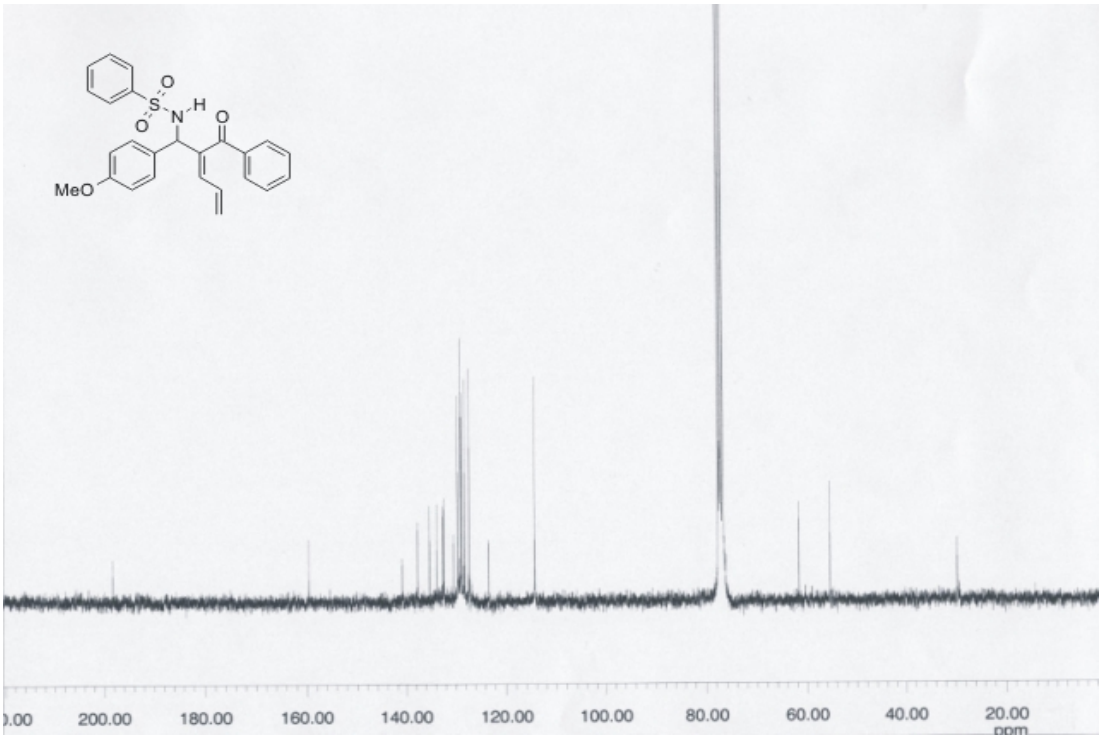
^{13}C NMR Spectrum of (*E*)-**15b**



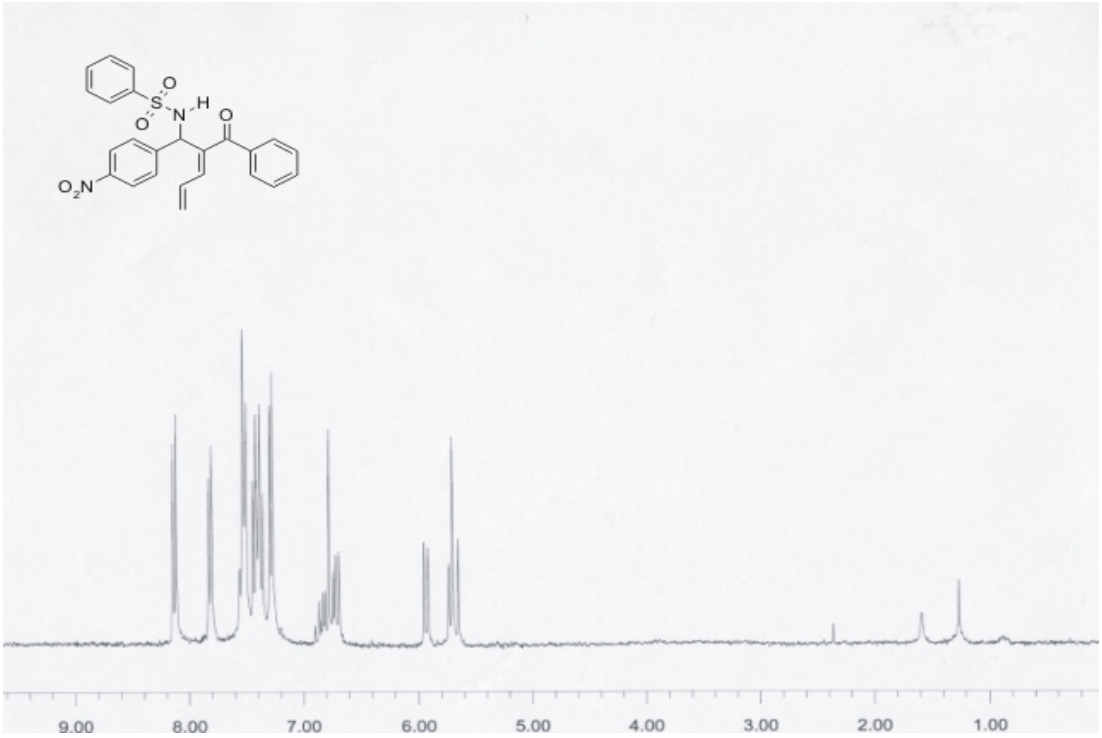
^{1}H NMR Spectrum of (*Z*)-**15e**



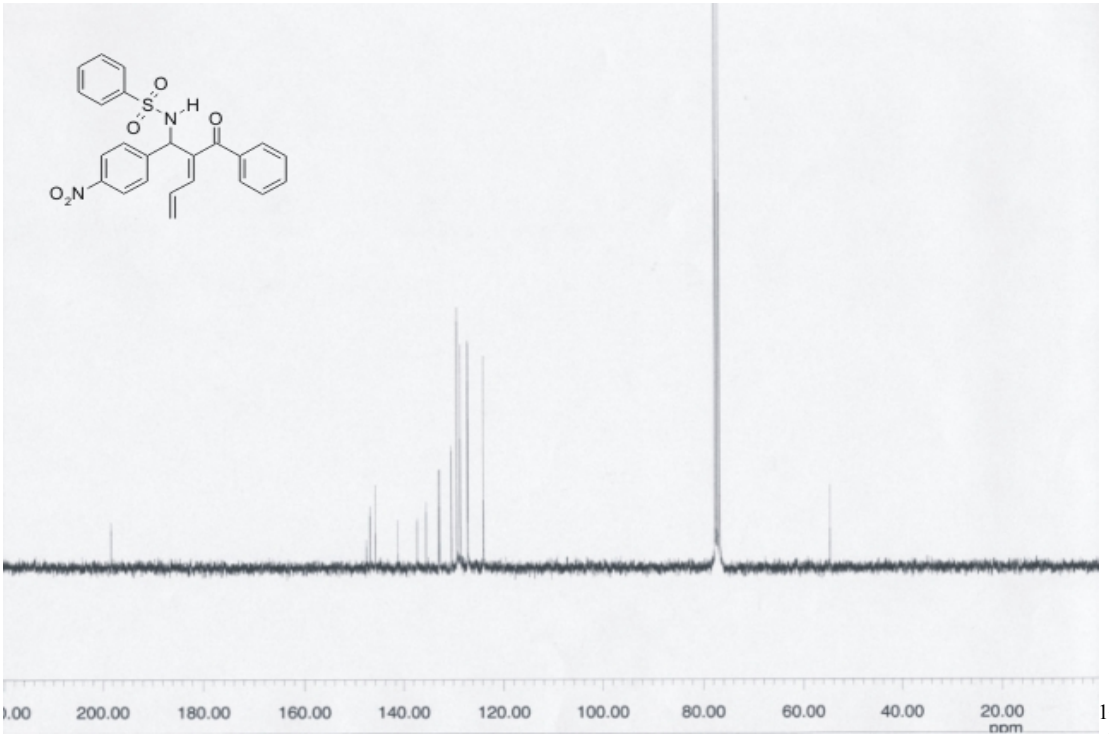
^{13}C NMR Spectrum of (*Z*)-**15e**



^{1}H NMR Spectrum of (*E*)-**15f**

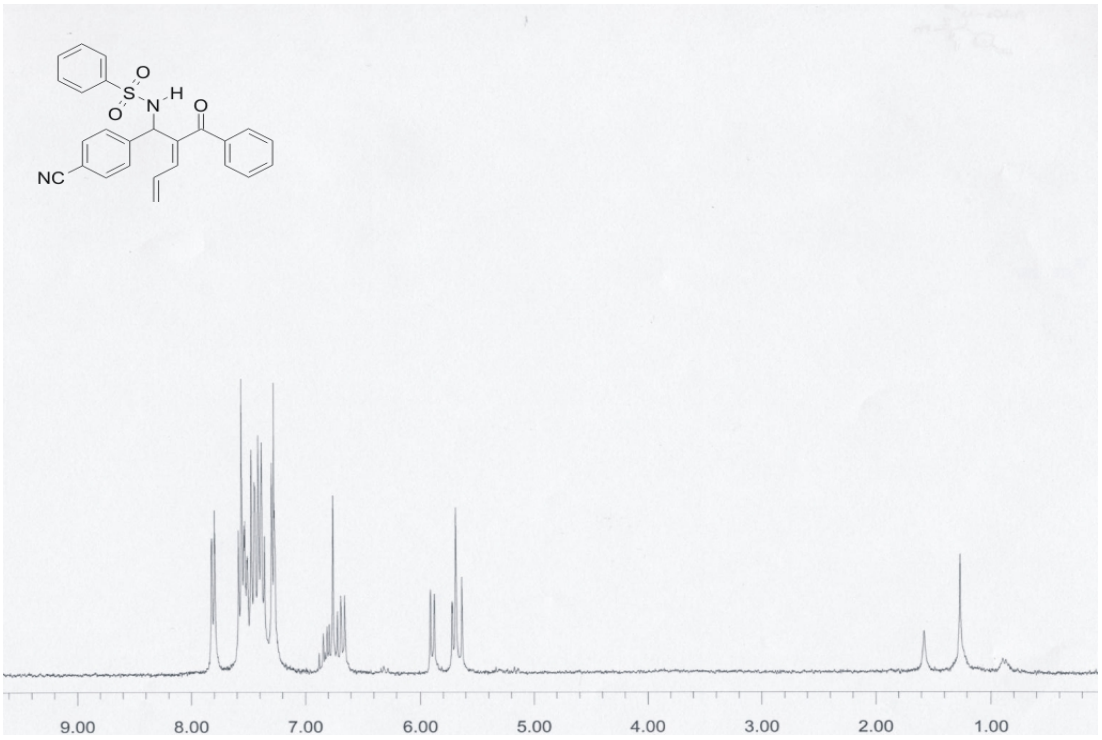


^{13}C NMR Spectrum of (*E*)-**15f**

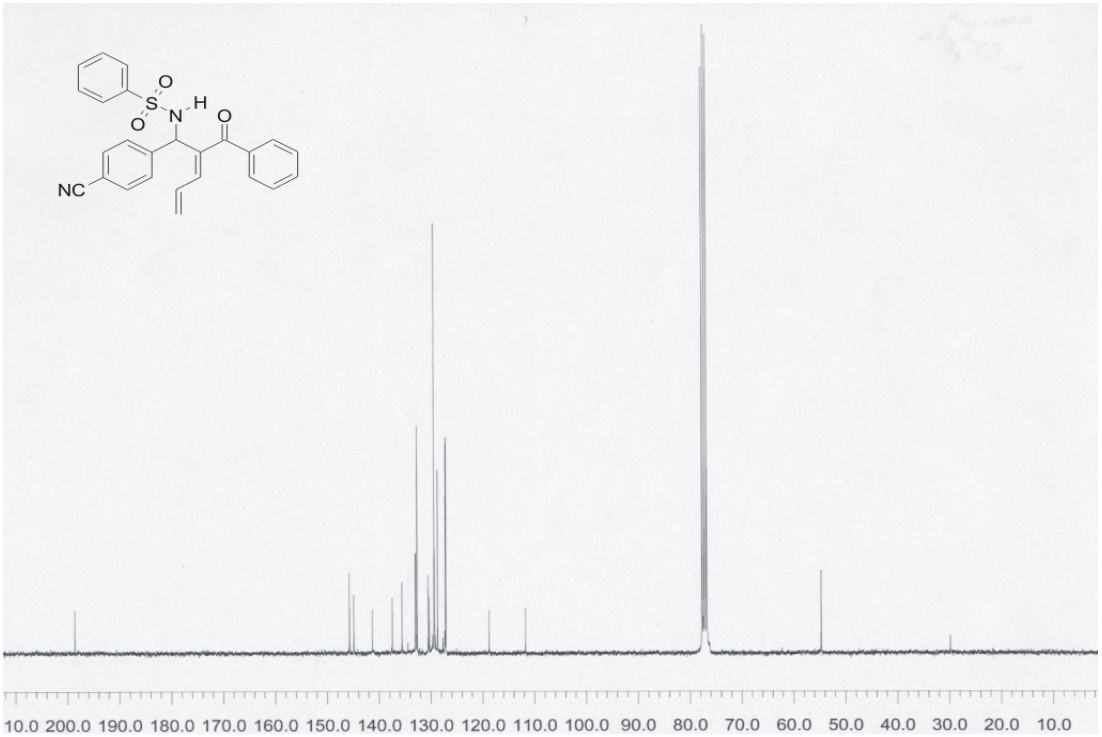


^{1}H

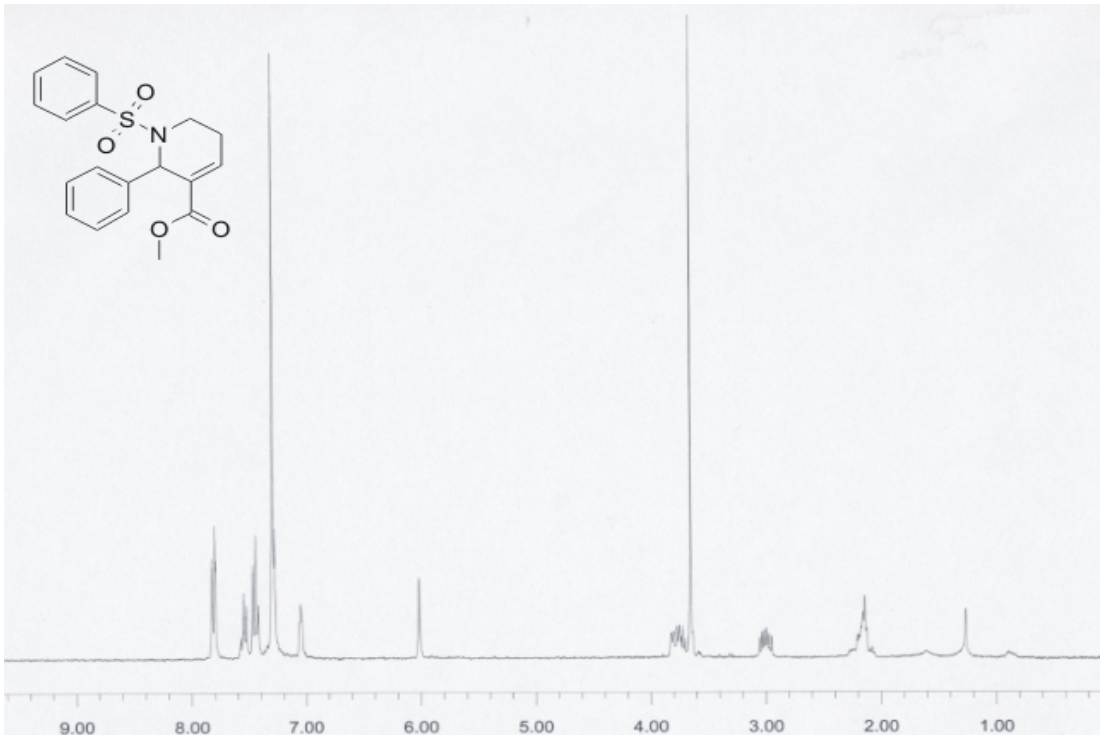
NMR Spectrum of (*E*)-**15h**



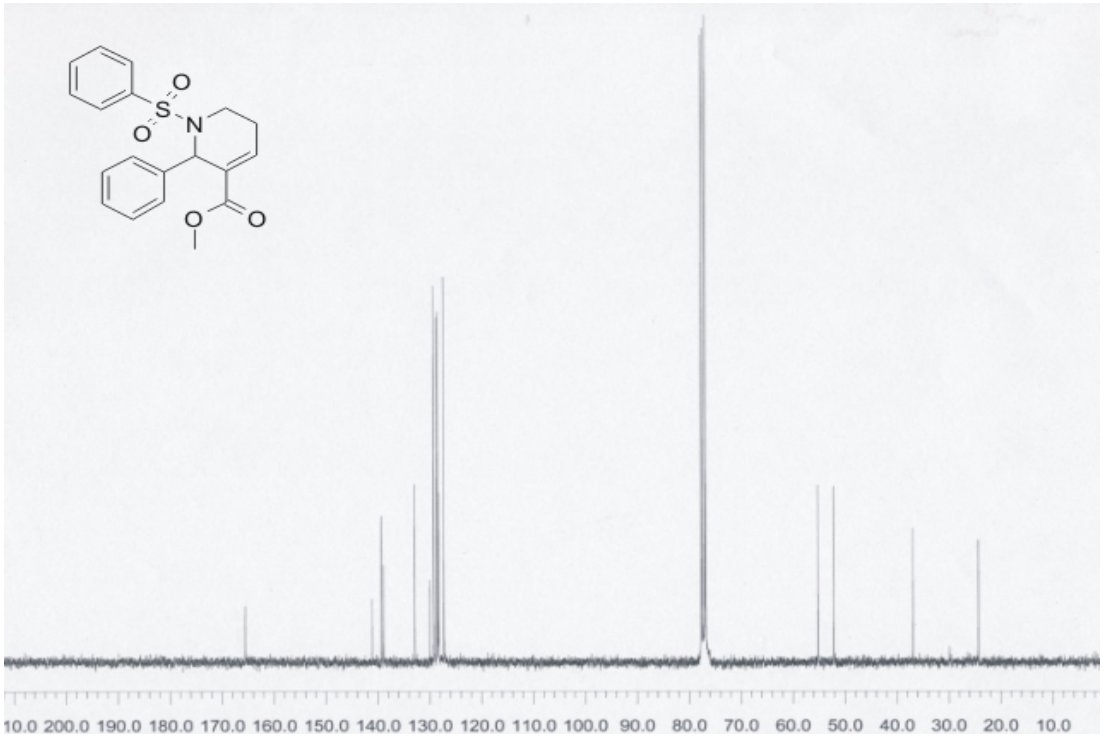
^{13}C NMR Spectrum of (*E*)-**15h**



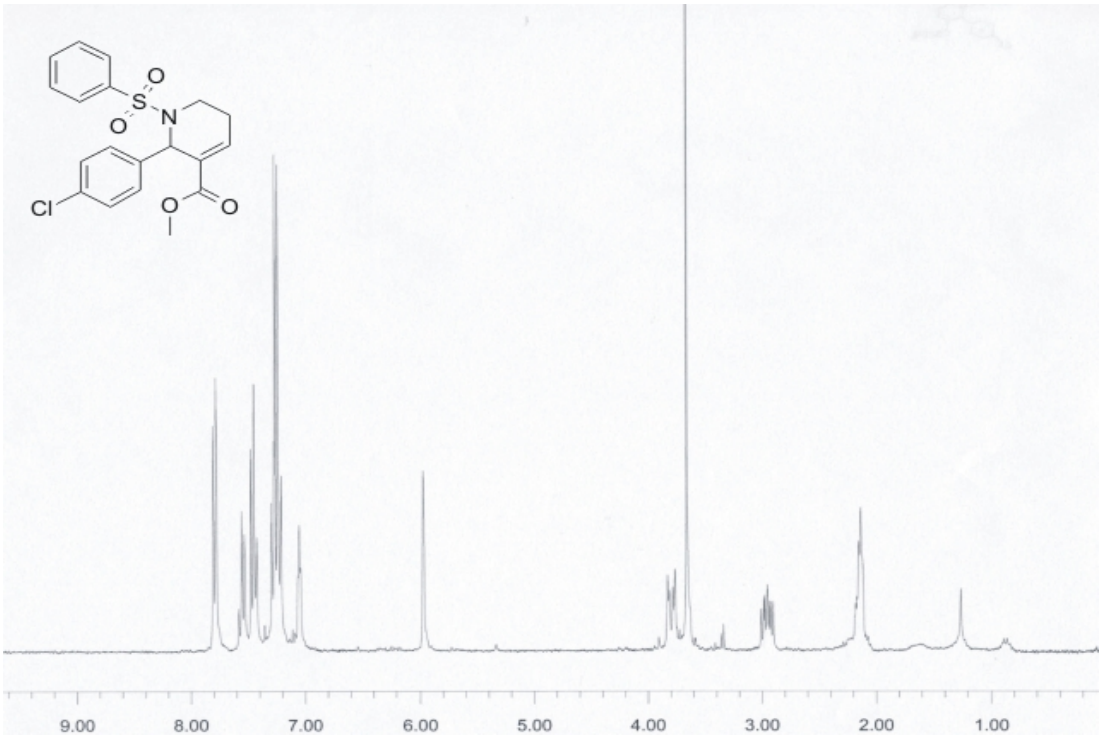
^{1}H NMR Spectrum of **16a**



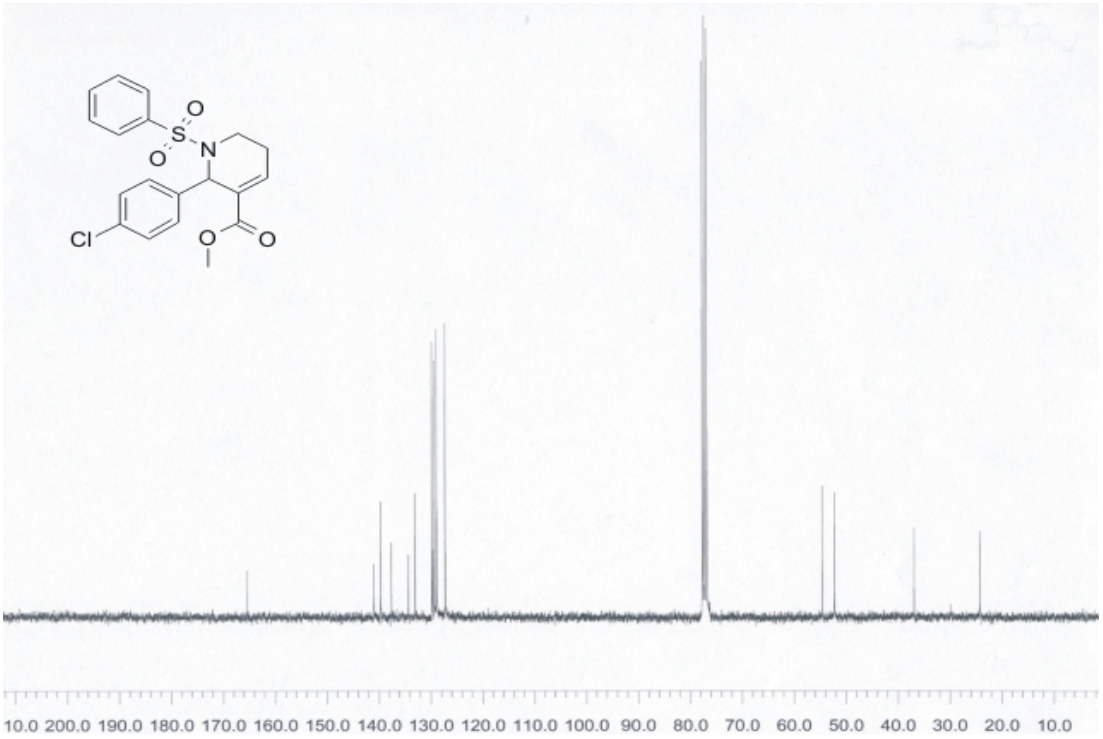
^{13}C NMR Spectrum of **16a**



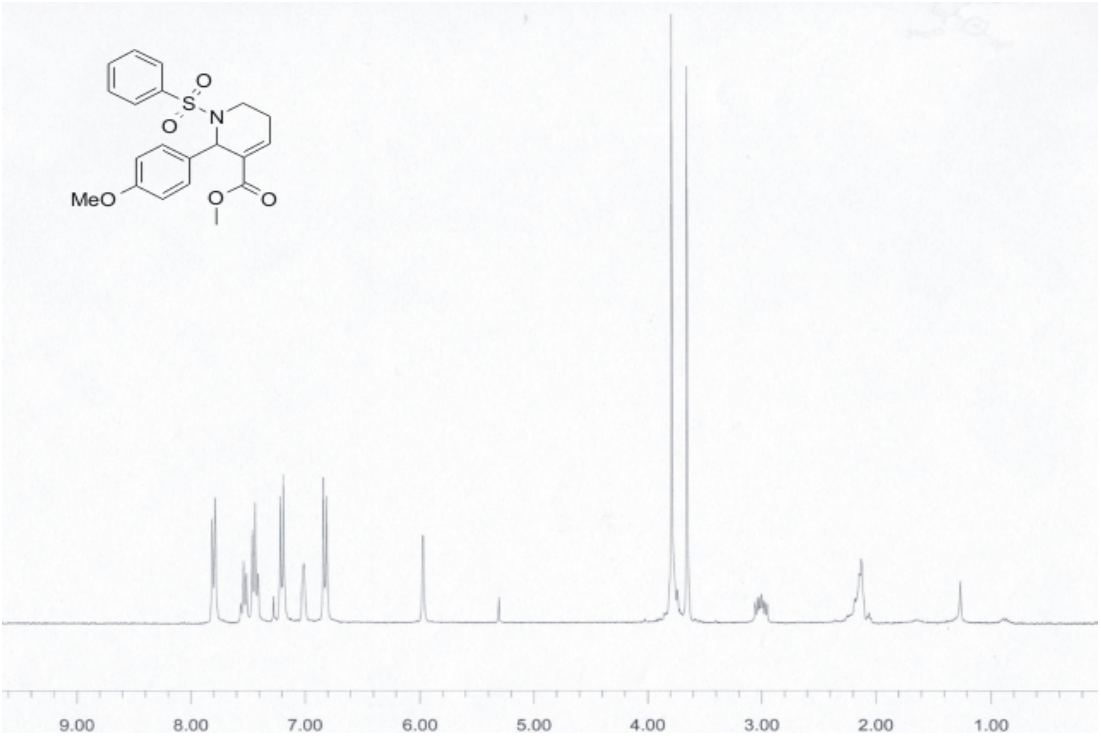
^{1}H NMR Spectrum of **16b**



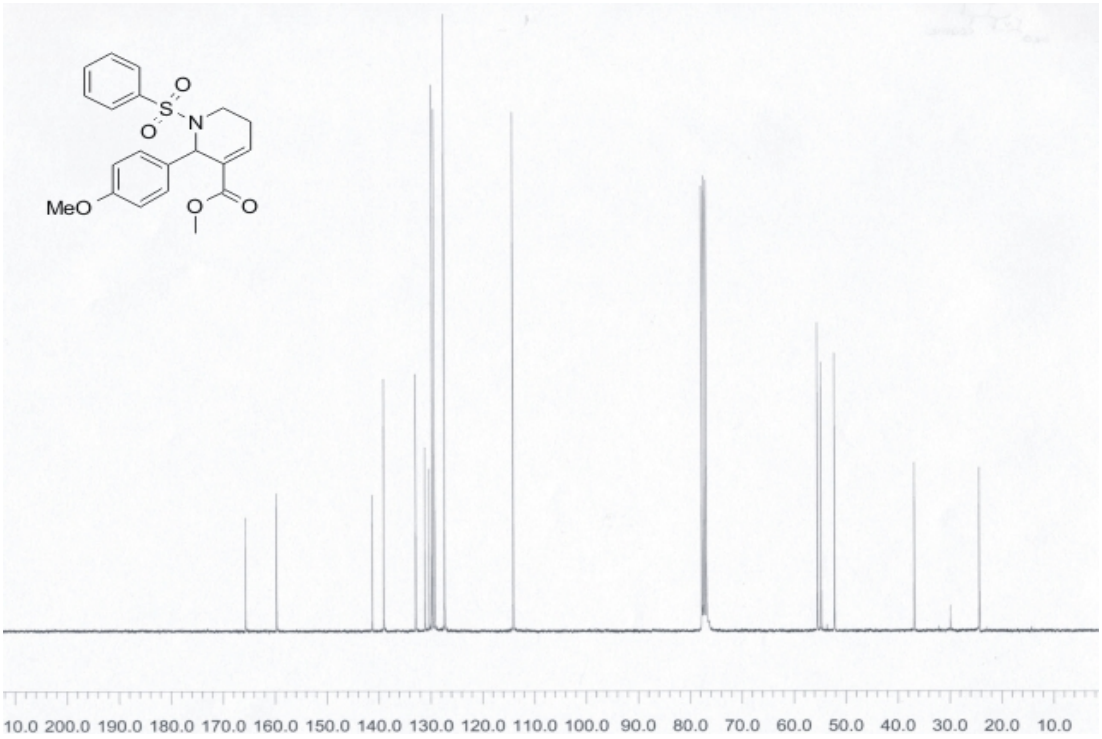
^{13}C NMR Spectrum of **16b**



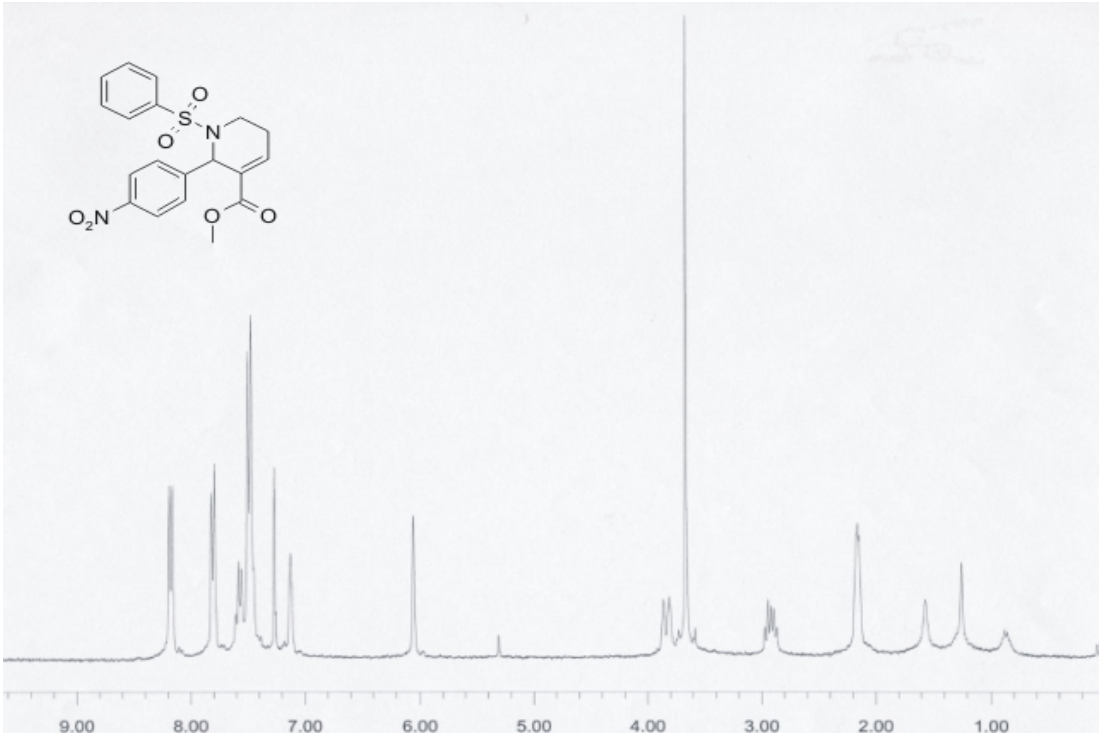
^{1}H NMR Spectrum of **16e**



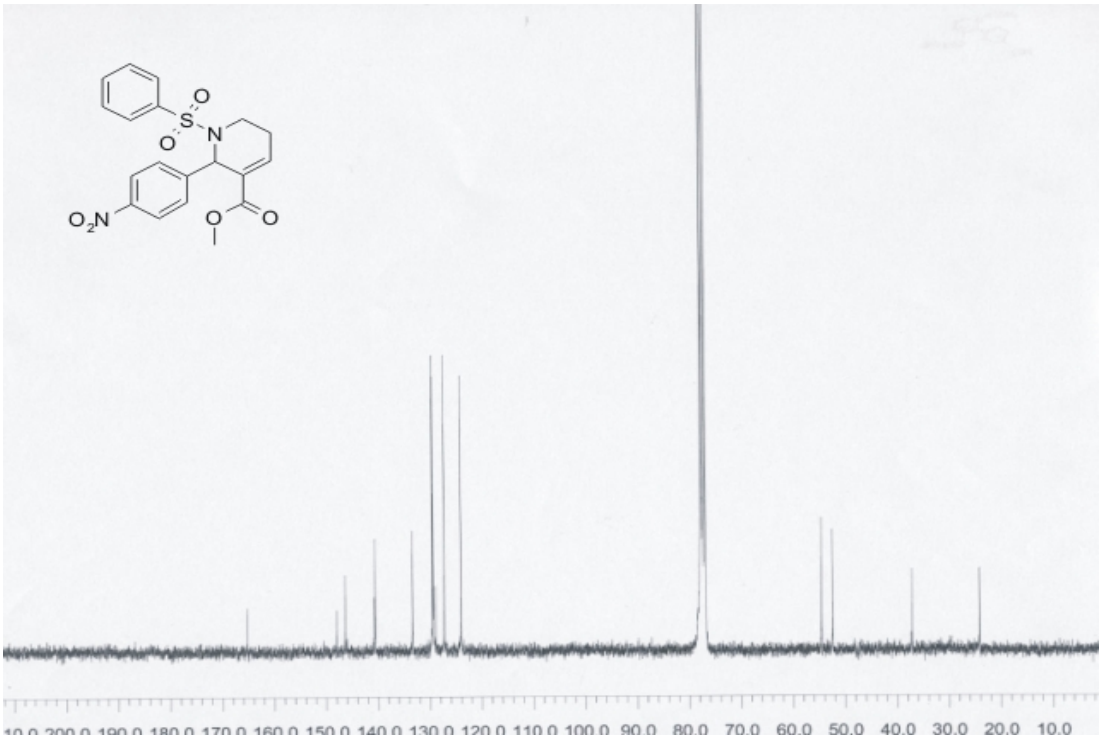
^{13}C NMR Spectrum of **16e**



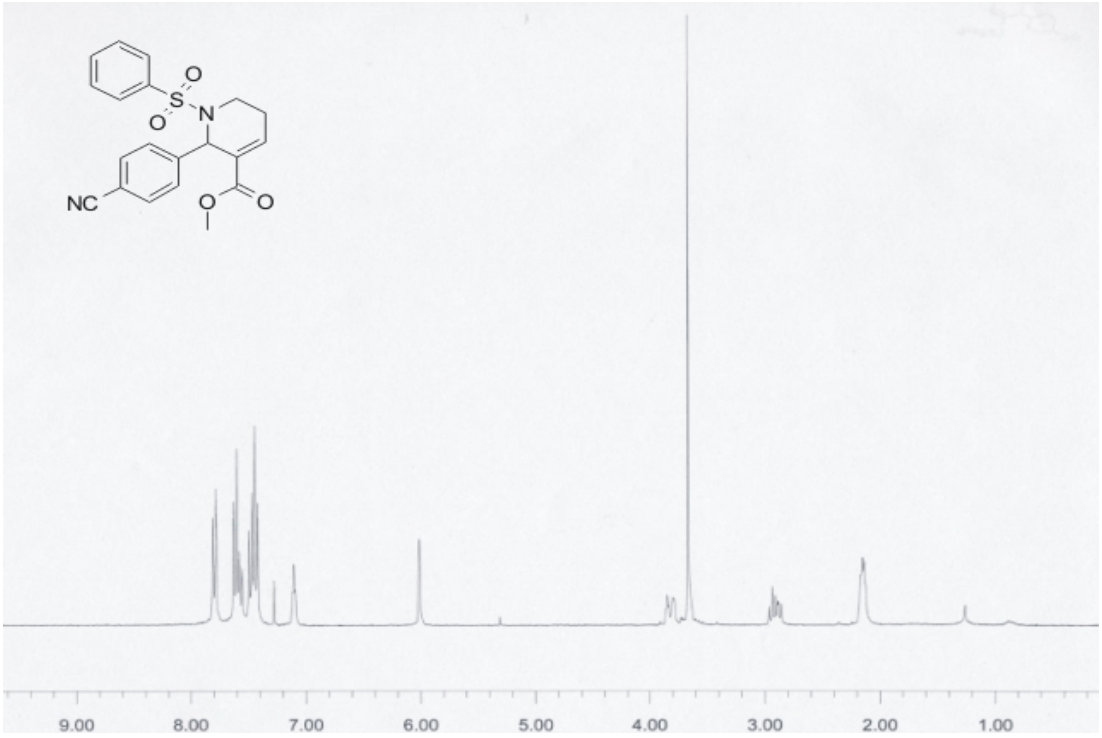
^{1}H NMR Spectrum of **16f**



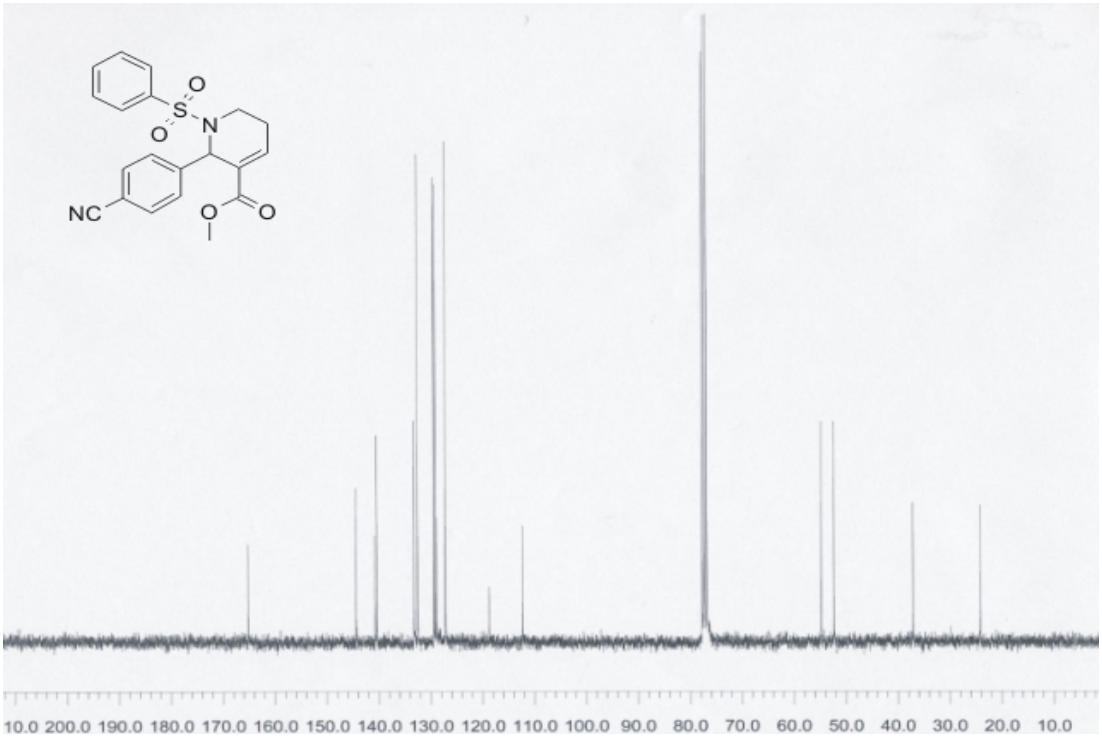
^{13}C NMR Spectrum of **16f**



^{1}H NMR Spectrum of **16h**

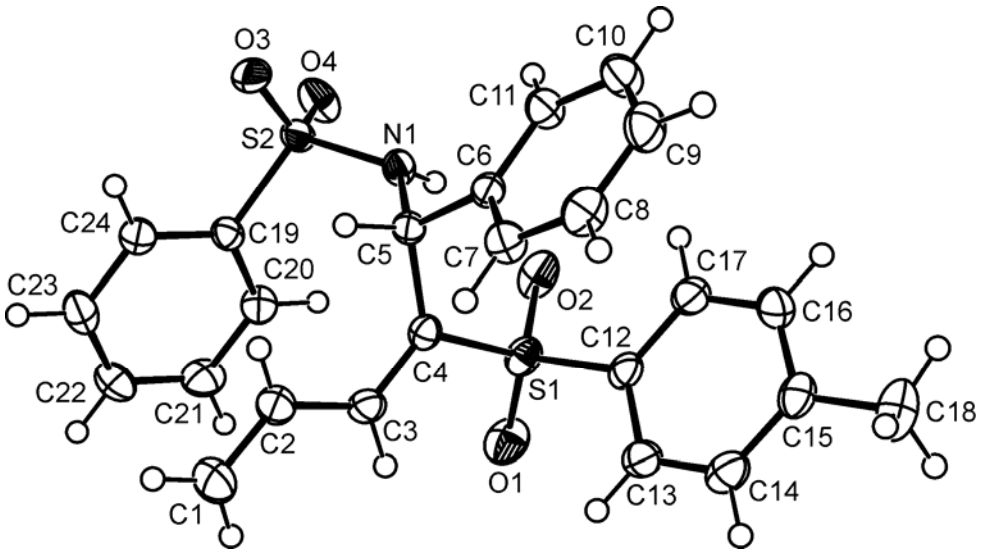


^{13}C NMR Spectrum of **16h**



X-Ray Structure Report on (*E*)-4a

ORTEP Diagram of **(*E*)-4a**:



Experimental:

A colorless prismatic crystal of $C_{24}H_{23}NO_4S_2$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. Cell constants obtained from the refinement[1] of 9572 reflections in the range $3.3 < \theta < 27.5°$ corresponded to a primitive monoclinic cell; details of crystal data and structure refinement have been provided in Table 1. The space group was uniquely determined from the systematic absences. The data were collected[2] at a temperature of 173(2) K using the ω and φ scans to a maximum θ value of 27.5°. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method[1]. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary.

The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from a difference map, were included at geometrically idealized positions and were not refined except for the one bonded to N1 that was allowed to refine. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.042 and wR = 0.110 (all data), respectively, and goodness of fit, S = 1.02. The weighting scheme was based on counting statistics and the final difference map was free of any chemically significant features. The figure was plotted with the aid of ORTEPII[6].

Table 1. Crystal data and structure refinement for $C_{24}H_{23}NO_4S_2$.

Empirical formula	$C_{24}H_{23}NO_4S_2$
Formula weight	453.55
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.798(3) Å	α= 90°.
	b = 16.267(5) Å	β= 106.329(15)°.
	c = 13.239(3) Å	γ = 90°.
Volume	2231.6(11) $Å^3$	
Z	4	
Density (calculated)	1.350 Mg/m^3	
Absorption coefficient	0.270 mm^{-1}	
F(000)	952	
Crystal size	0.20 x 0.18 x 0.16 mm^3	
Theta range for data collection	3.3 to 27.5°.	
Index ranges	-13<=h<=13, -20<=k<=21, -17<=l<=17	
Reflections collected	9572	
Independent reflections	5079 [R(int) = 0.033]	
Completeness to theta = 27.5°	99.6 %	
Absorption correction	Multi-scan method	
Max. and min. transmission	0.958 and 0.948	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5079 / 0 / 283	
Goodness-of-fit on F^2	1.02	
Final R indices [I>2sigma(I)]	R1 = 0.042, wR2 = 0.097	
R indices (all data)	R1 = 0.067, wR2 = 0.110	
Largest diff. peak and hole	0.31 and -0.40 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{24}H_{23}NO_4S_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	3273(1)	2035(1)	4105(1)	29(1)
S(2)	3658(1)	1144(1)	7431(1)	26(1)
O(1)	3282(2)	2905(1)	3922(1)	42(1)
O(2)	4473(1)	1649(1)	4687(1)	39(1)
O(3)	2907(2)	560(1)	7811(1)	36(1)
O(4)	5027(1)	1186(1)	7897(1)	39(1)
N(1)	3500(2)	948(1)	6199(1)	24(1)
C(1)	-461(2)	3047(2)	5357(2)	50(1)
C(2)	230(2)	2390(1)	5293(2)	35(1)
C(3)	1249(2)	2412(1)	4775(1)	28(1)
C(4)	2121(2)	1823(1)	4797(1)	23(1)
C(5)	2240(2)	1015(1)	5397(1)	22(1)
C(6)	1966(2)	271(1)	4667(1)	23(1)
C(7)	783(2)	244(1)	3891(2)	29(1)
C(8)	492(2)	-403(1)	3187(2)	35(1)
C(9)	1373(2)	-1034(1)	3242(2)	36(1)
C(10)	2534(2)	-1017(1)	4023(2)	35(1)
C(11)	2832(2)	-367(1)	4730(2)	28(1)
C(12)	2757(2)	1539(1)	2877(1)	26(1)
C(13)	1799(2)	1899(1)	2073(2)	30(1)
C(14)	1387(2)	1503(1)	1111(2)	34(1)
C(15)	1920(2)	753(1)	935(2)	32(1)
C(16)	2876(2)	410(1)	1750(2)	36(1)
C(17)	3303(2)	794(1)	2720(2)	34(1)
C(18)	1495(3)	333(2)	-122(2)	48(1)
C(19)	2984(2)	2117(1)	7530(1)	23(1)
C(20)	3428(2)	2804(1)	7114(2)	29(1)
C(21)	2922(2)	3570(1)	7232(2)	36(1)
C(22)	2003(2)	3643(1)	7771(2)	39(1)
C(23)	1574(2)	2961(1)	8191(2)	39(1)

C(24)	2053(2)	2190(1)	8065(2)	30(1)

Table 3. Bond lengths [Å] and angles [°] for $C_{24}H_{23}NO_4S_2$.

S(1)-O(1)	1.4363(16)
S(1)-O(2)	1.4501(15)
S(1)-C(12)	1.759(2)
S(1)-C(4)	1.7744(19)
S(2)-O(3)	1.4291(15)
S(2)-O(4)	1.4347(15)
S(2)-N(1)	1.6224(16)
S(2)-C(19)	1.7617(19)
N(1)-C(5)	1.476(2)
N(1)-H(1)	0.83(2)
C(1)-C(2)	1.321(3)
C(1)-H(1A)	0.9500
C(1)-H(1B)	0.9500
C(2)-C(3)	1.451(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.338(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.522(3)
C(5)-C(6)	1.525(3)
C(5)-H(5)	1.0000
C(6)-C(11)	1.384(3)
C(6)-C(7)	1.397(3)
C(7)-C(8)	1.382(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.387(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.383(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.388(3)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-C(13)	1.388(3)
C(12)-C(17)	1.389(3)
C(13)-C(14)	1.384(3)

C(13)-H(13)	0.9500
C(14)-C(15)	1.397(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.384(3)
C(15)-C(18)	1.508(3)
C(16)-C(17)	1.384(3)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(18)-H(18D)	0.9800
C(18)-H(18E)	0.9800
C(18)-H(18F)	0.9800
C(19)-C(24)	1.388(3)
C(19)-C(20)	1.389(3)
C(20)-C(21)	1.386(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.382(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.378(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(3)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500

O(1)-S(1)-O(2)	117.90(10)
O(1)-S(1)-C(12)	108.16(9)
O(2)-S(1)-C(12)	107.28(9)
O(1)-S(1)-C(4)	108.46(9)
O(2)-S(1)-C(4)	107.02(9)
C(12)-S(1)-C(4)	107.61(9)
O(3)-S(2)-O(4)	119.84(10)
O(3)-S(2)-N(1)	108.26(9)
O(4)-S(2)-N(1)	104.26(9)
O(3)-S(2)-C(19)	106.52(9)

O(4)-S(2)-C(19)	108.81(9)
N(1)-S(2)-C(19)	108.80(8)
C(5)-N(1)-S(2)	121.59(13)
C(5)-N(1)-H(1)	113.5(15)
S(2)-N(1)-H(1)	112.2(15)
C(2)-C(1)-H(1A)	120.0
C(2)-C(1)-H(1B)	120.0
H(1A)-C(1)-H(1B)	120.0
C(1)-C(2)-C(3)	121.9(2)
C(1)-C(2)-H(2)	119.1
C(3)-C(2)-H(2)	119.1
C(4)-C(3)-C(2)	126.48(19)
C(4)-C(3)-H(3)	116.8
C(2)-C(3)-H(3)	116.8
C(3)-C(4)-C(5)	125.83(17)
C(3)-C(4)-S(1)	116.21(15)
C(5)-C(4)-S(1)	117.91(13)
N(1)-C(5)-C(4)	111.40(15)
N(1)-C(5)-C(6)	111.91(14)
C(4)-C(5)-C(6)	112.43(14)
N(1)-C(5)-H(5)	106.9
C(4)-C(5)-H(5)	106.9
C(6)-C(5)-H(5)	106.9
C(11)-C(6)-C(7)	118.86(17)
C(11)-C(6)-C(5)	123.36(16)
C(7)-C(6)-C(5)	117.78(16)
C(8)-C(7)-C(6)	120.50(19)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	120.36(19)
C(7)-C(8)-H(8)	119.8
C(9)-C(8)-H(8)	119.8
C(10)-C(9)-C(8)	119.26(19)
C(10)-C(9)-H(9)	120.4
C(8)-C(9)-H(9)	120.4
C(9)-C(10)-C(11)	120.57(19)

C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(6)-C(11)-C(10)	120.42(18)
C(6)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(13)-C(12)-C(17)	120.63(18)
C(13)-C(12)-S(1)	119.31(16)
C(17)-C(12)-S(1)	120.06(15)
C(14)-C(13)-C(12)	119.14(19)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	121.26(19)
C(13)-C(14)-H(14)	119.4
C(15)-C(14)-H(14)	119.4
C(16)-C(15)-C(14)	118.28(19)
C(16)-C(15)-C(18)	120.5(2)
C(14)-C(15)-C(18)	121.2(2)
C(17)-C(16)-C(15)	121.5(2)
C(17)-C(16)-H(16)	119.2
C(15)-C(16)-H(16)	119.2
C(16)-C(17)-C(12)	119.18(19)
C(16)-C(17)-H(17)	120.4
C(12)-C(17)-H(17)	120.4
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(15)-C(18)-H(18D)	109.5
H(18A)-C(18)-H(18D)	141.1
H(18B)-C(18)-H(18D)	56.3
H(18C)-C(18)-H(18D)	56.3
C(15)-C(18)-H(18E)	109.5
H(18A)-C(18)-H(18E)	56.3
H(18B)-C(18)-H(18E)	141.1

H(18C)-C(18)-H(18E)	56.3
H(18D)-C(18)-H(18E)	109.5
C(15)-C(18)-H(18F)	109.5
H(18A)-C(18)-H(18F)	56.3
H(18B)-C(18)-H(18F)	56.3
H(18C)-C(18)-H(18F)	141.1
H(18D)-C(18)-H(18F)	109.5
H(18E)-C(18)-H(18F)	109.5
C(24)-C(19)-C(20)	120.88(18)
C(24)-C(19)-S(2)	119.23(15)
C(20)-C(19)-S(2)	119.83(15)
C(21)-C(20)-C(19)	119.23(19)
C(21)-C(20)-H(20)	120.4
C(19)-C(20)-H(20)	120.4
C(22)-C(21)-C(20)	119.9(2)
C(22)-C(21)-H(21)	120.1
C(20)-C(21)-H(21)	120.1
C(23)-C(22)-C(21)	120.7(2)
C(23)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(22)-C(23)-C(24)	120.1(2)
C(22)-C(23)-H(23)	119.9
C(24)-C(23)-H(23)	119.9
C(23)-C(24)-C(19)	119.19(19)
C(23)-C(24)-H(24)	120.4
C(19)-C(24)-H(24)	120.4

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{24}H_{23}NO_4S_2$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	25(1)	36(1)	26(1)	2(1)	9(1)	-4(1)
S(2)	31(1)	23(1)	20(1)	-2(1)	3(1)	6(1)
O(1)	54(1)	34(1)	41(1)	2(1)	18(1)	-15(1)
O(2)	20(1)	68(1)	30(1)	5(1)	6(1)	1(1)
O(3)	60(1)	22(1)	30(1)	3(1)	18(1)	3(1)
O(4)	31(1)	45(1)	33(1)	-12(1)	-6(1)	14(1)
N(1)	22(1)	29(1)	20(1)	-3(1)	4(1)	3(1)
C(1)	47(1)	63(2)	43(1)	6(1)	15(1)	27(1)
C(2)	30(1)	44(1)	30(1)	5(1)	9(1)	12(1)
C(3)	30(1)	28(1)	23(1)	2(1)	3(1)	3(1)
C(4)	21(1)	26(1)	20(1)	0(1)	5(1)	-1(1)
C(5)	20(1)	24(1)	20(1)	1(1)	5(1)	3(1)
C(6)	26(1)	23(1)	21(1)	0(1)	8(1)	-1(1)
C(7)	23(1)	33(1)	29(1)	-2(1)	4(1)	0(1)
C(8)	32(1)	40(1)	28(1)	-4(1)	2(1)	-7(1)
C(9)	44(1)	33(1)	32(1)	-10(1)	11(1)	-6(1)
C(10)	39(1)	28(1)	38(1)	-5(1)	11(1)	3(1)
C(11)	27(1)	29(1)	28(1)	-3(1)	5(1)	2(1)
C(12)	25(1)	34(1)	23(1)	5(1)	11(1)	1(1)
C(13)	26(1)	34(1)	30(1)	7(1)	10(1)	4(1)
C(14)	27(1)	45(1)	28(1)	7(1)	6(1)	2(1)
C(15)	36(1)	37(1)	28(1)	1(1)	16(1)	-6(1)
C(16)	44(1)	33(1)	38(1)	3(1)	23(1)	7(1)
C(17)	33(1)	40(1)	30(1)	9(1)	13(1)	10(1)
C(18)	55(2)	60(2)	35(1)	-10(1)	22(1)	-14(1)
C(19)	24(1)	22(1)	21(1)	-4(1)	4(1)	1(1)
C(20)	30(1)	28(1)	30(1)	-2(1)	10(1)	-4(1)
C(21)	46(1)	22(1)	40(1)	0(1)	10(1)	-7(1)
C(22)	51(1)	24(1)	45(1)	-5(1)	16(1)	8(1)
C(23)	45(1)	36(1)	43(1)	-3(1)	23(1)	8(1)

C(24)	35(1)	26(1)	30(1)	1(1)	13(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{24}H_{23}NO_4S_2$.

Atom	x	y	z	U(eq)
H(1)	4110(20)	1131(13)	6002(17)	29
H(1A)	-298	3553	5059	60
H(1B)	-1123	3014	5701	60
H(2)	55	1888	5594	42
H(3)	1302	2893	4381	33
H(5)	1565	1021	5781	26
H(7)	173	673	3846	35
H(8)	-316	-416	2662	42
H(9)	1181	-1473	2749	44
H(10)	3134	-1454	4076	42
H(11)	3635	-361	5260	34
H(13)	1431	2410	2182	36
H(14)	729	1747	559	40
H(16)	3248	-100	1642	43
H(17)	3961	550	3271	40
H(18A)	815	659	-602	73
H(18B)	1161	-216	-39	73
H(18C)	2232	282	-413	73
H(18D)	1990	-175	-100	73
H(18E)	1645	699	-664	73
H(18F)	574	201	-290	73
H(20)	4070	2749	6754	35
H(21)	3208	4043	6941	43
H(22)	1662	4170	7854	47
H(23)	948	3020	8567	47
H(24)	1749	1717	8342	36

Table 6. Torsion angles [°] for $C_{24}H_{23}NO_4S_2$.

O(3)-S(2)-N(1)-C(5)	63.52(17)
O(4)-S(2)-N(1)-C(5)	-167.84(14)
C(19)-S(2)-N(1)-C(5)	-51.86(17)
C(1)-C(2)-C(3)-C(4)	169.7(2)
C(2)-C(3)-C(4)-C(5)	-1.7(3)
C(2)-C(3)-C(4)-S(1)	-178.88(16)
O(1)-S(1)-C(4)-C(3)	17.63(18)
O(2)-S(1)-C(4)-C(3)	145.81(15)
C(12)-S(1)-C(4)-C(3)	-99.16(16)
O(1)-S(1)-C(4)-C(5)	-159.83(13)
O(2)-S(1)-C(4)-C(5)	-31.65(16)
C(12)-S(1)-C(4)-C(5)	83.38(15)
S(2)-N(1)-C(5)-C(4)	99.65(17)
S(2)-N(1)-C(5)-C(6)	-133.52(14)
C(3)-C(4)-C(5)-N(1)	-118.1(2)
S(1)-C(4)-C(5)-N(1)	59.08(18)
C(3)-C(4)-C(5)-C(6)	115.4(2)
S(1)-C(4)-C(5)-C(6)	-67.46(18)
N(1)-C(5)-C(6)-C(11)	-2.8(2)
C(4)-C(5)-C(6)-C(11)	123.51(19)
N(1)-C(5)-C(6)-C(7)	177.91(16)
C(4)-C(5)-C(6)-C(7)	-55.8(2)
C(11)-C(6)-C(7)-C(8)	-1.1(3)
C(5)-C(6)-C(7)-C(8)	178.25(18)
C(6)-C(7)-C(8)-C(9)	0.0(3)
C(7)-C(8)-C(9)-C(10)	1.4(3)
C(8)-C(9)-C(10)-C(11)	-1.5(3)
C(7)-C(6)-C(11)-C(10)	1.0(3)
C(5)-C(6)-C(11)-C(10)	-178.37(18)
C(9)-C(10)-C(11)-C(6)	0.4(3)
O(1)-S(1)-C(12)-C(13)	-37.36(18)
O(2)-S(1)-C(12)-C(13)	-165.52(15)
C(4)-S(1)-C(12)-C(13)	79.62(17)
O(1)-S(1)-C(12)-C(17)	142.86(16)

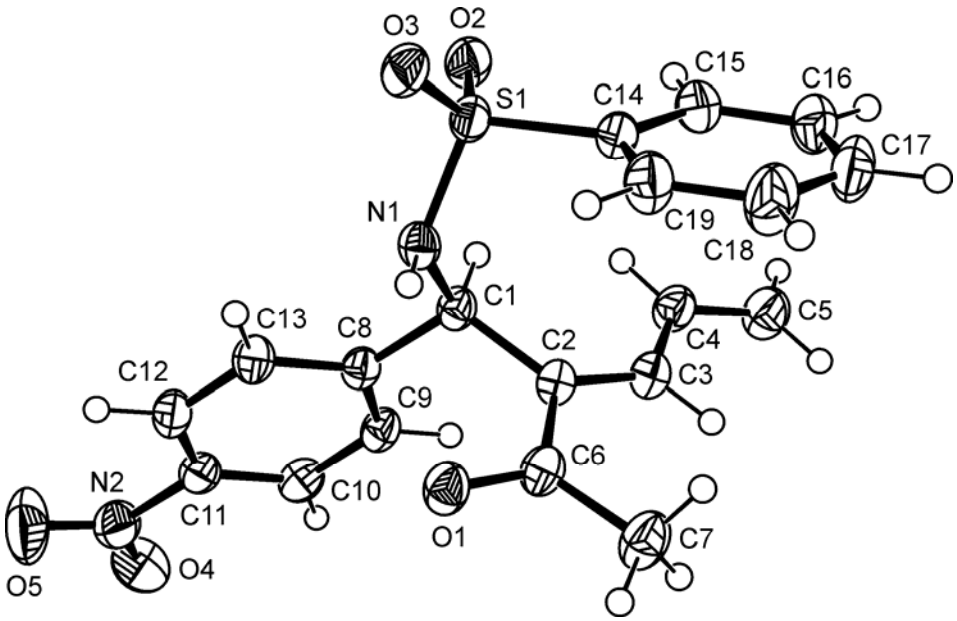
O(2)-S(1)-C(12)-C(17)	14.70(18)
C(4)-S(1)-C(12)-C(17)	-100.16(17)
C(17)-C(12)-C(13)-C(14)	0.3(3)
S(1)-C(12)-C(13)-C(14)	-179.43(15)
C(12)-C(13)-C(14)-C(15)	-0.2(3)
C(13)-C(14)-C(15)-C(16)	0.0(3)
C(13)-C(14)-C(15)-C(18)	-178.4(2)
C(14)-C(15)-C(16)-C(17)	0.1(3)
C(18)-C(15)-C(16)-C(17)	178.5(2)
C(15)-C(16)-C(17)-C(12)	0.1(3)
C(13)-C(12)-C(17)-C(16)	-0.3(3)
S(1)-C(12)-C(17)-C(16)	179.50(16)
O(3)-S(2)-C(19)-C(24)	9.55(18)
O(4)-S(2)-C(19)-C(24)	-120.94(16)
N(1)-S(2)-C(19)-C(24)	126.05(16)
O(3)-S(2)-C(19)-C(20)	-173.31(15)
O(4)-S(2)-C(19)-C(20)	56.20(17)
N(1)-S(2)-C(19)-C(20)	-56.80(17)
C(24)-C(19)-C(20)-C(21)	-0.6(3)
S(2)-C(19)-C(20)-C(21)	-177.65(15)
C(19)-C(20)-C(21)-C(22)	1.0(3)
C(20)-C(21)-C(22)-C(23)	-0.4(3)
C(21)-C(22)-C(23)-C(24)	-0.7(4)
C(22)-C(23)-C(24)-C(19)	1.1(3)
C(20)-C(19)-C(24)-C(23)	-0.5(3)
S(2)-C(19)-C(24)-C(23)	176.60(16)

Table 7. Hydrogen bonds for $C_{24}H_{23}NO_4S_2$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(2)	0.83(2)	2.07(2)	2.756(2)	140(2)

X-Ray Structure Report on (*E*)-14f

ORTEP Diagram of **(*E*)-14f**:



Experimental:

A colorless prismatic crystal of $C_{19}H_{18}N_2O_5S$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. Cell constants obtained from the refinement[1] of 8005 reflections in the range $3.2 < \theta < 27.5°$ corresponded to a primitive triclinic cell; details of crystal data and structure refinement have been provided in Table 1. The data were collected[2] at a temperature of 173(2) K using ω and φ scans to a maximum θ value of 27.5°. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method[1]. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary.

The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined except for the hydrogen bonded to N1 that was allowed to refine. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.046 and wR = 0.117 (all data), respectively, and goodness of fit, S = 1.03. The weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless. The figures were plotted with the aid of ORTEPII[6].

Table 1. Crystal data and structure refinement for $C_{19}H_{18}N_2O_5S$.

Empirical formula	$C_{19}H_{18}N_2O_5S$	
Formula weight	386.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.390(4) Å	α= 99.10(2)°.
	b = 10.134(4) Å	β= 104.52(2)°.
	c = 11.986(5) Å	γ = 105.71(2)°.
Volume	921.3(7) $Å^3$	
Z	2	
Density (calculated)	1.393 Mg/m^3	
Absorption coefficient	0.209 mm^{-1}	
F(000)	404	
Crystal size	0.22 x 0.12 x 0.08 mm^3	
Theta range for data collection	3.2 to 27.5°.	
Index ranges	-10<=h<=10, -12<=k<=13, -15<=l<=15	
Reflections collected	8005	
Independent reflections	4202 [R(int) = 0.034]	
Completeness to theta = 27.5°	98.4 %	
Absorption correction	Multi-scan method	
Max. and min. transmission	0.984 and 0.955	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4202 / 0 / 248	
Goodness-of-fit on F^2	1.03	
Final R indices [I>2sigma(I)]	R1 = 0.046, wR2 = 0.104	
R indices (all data)	R1 = 0.071, wR2 = 0.117	
Largest diff. peak and hole	0.30 and -0.34 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{19}H_{18}N_2O_5S$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	2513(1)	704(1)	7825(1)	29(1)
O(1)	40(2)	1316(1)	10531(1)	35(1)
O(2)	3888(2)	1775(2)	7658(1)	36(1)
O(3)	2585(2)	-703(1)	7742(1)	37(1)
O(4)	6849(2)	6067(2)	15005(1)	51(1)
O(5)	7136(3)	4027(2)	15046(2)	80(1)
N(1)	2427(2)	1236(2)	9153(1)	28(1)
N(2)	6597(2)	4843(2)	14527(2)	42(1)
C(1)	2507(2)	2699(2)	9594(2)	27(1)
C(2)	707(2)	2867(2)	9339(2)	27(1)
C(3)	197(3)	3756(2)	8717(2)	30(1)
C(4)	1191(3)	4790(2)	8239(2)	35(1)
C(5)	477(3)	5602(2)	7647(2)	44(1)
C(6)	-516(2)	1963(2)	9830(2)	31(1)
C(7)	-2419(3)	1815(2)	9462(2)	41(1)
C(8)	3584(2)	3237(2)	10907(2)	26(1)
C(9)	3774(2)	4597(2)	11509(2)	30(1)
C(10)	4752(3)	5136(2)	12693(2)	33(1)
C(11)	5535(2)	4292(2)	13270(2)	31(1)
C(12)	5395(3)	2952(2)	12700(2)	32(1)
C(13)	4424(3)	2434(2)	11515(2)	31(1)
C(14)	532(2)	633(2)	6824(2)	29(1)
C(15)	528(3)	1641(2)	6168(2)	34(1)
C(16)	-1044(3)	1609(2)	5415(2)	44(1)
C(17)	-2552(3)	580(3)	5320(2)	53(1)
C(18)	-2538(3)	-433(3)	5973(2)	53(1)
C(19)	-990(3)	-409(2)	6739(2)	42(1)

Table 3. Bond lengths [Å] and angles [°] for $C_{19}H_{18}N_2O_5S$.

S(1)-O(3)	1.4316(15)
S(1)-O(2)	1.4336(15)
S(1)-N(1)	1.6241(18)
S(1)-C(14)	1.765(2)
O(1)-C(6)	1.223(2)
O(4)-N(2)	1.219(2)
O(5)-N(2)	1.225(2)
N(1)-C(1)	1.470(2)
N(1)-H(1N)	0.86(2)
N(2)-C(11)	1.471(3)
C(1)-C(2)	1.526(3)
C(1)-C(8)	1.530(3)
C(1)-H(1)	0.9601
C(2)-C(3)	1.347(3)
C(2)-C(6)	1.484(3)
C(3)-C(4)	1.441(3)
C(3)-H(3)	0.9600
C(4)-C(5)	1.333(3)
C(4)-H(4)	0.9600
C(5)-H(5A)	0.9599
C(5)-H(5B)	0.9600
C(6)-C(7)	1.504(3)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(13)	1.390(2)
C(8)-C(9)	1.398(3)
C(9)-C(10)	1.383(3)
C(9)-H(9)	0.9600
C(10)-C(11)	1.381(3)
C(10)-H(10)	0.9600
C(11)-C(12)	1.381(3)
C(12)-C(13)	1.382(3)
C(12)-H(12)	0.9600

C(13)-H(13)	0.9600
C(14)-C(15)	1.384(3)
C(14)-C(19)	1.387(3)
C(15)-C(16)	1.387(3)
C(15)-H(15)	0.9600
C(16)-C(17)	1.370(3)
C(16)-H(16)	0.9600
C(17)-C(18)	1.387(3)
C(17)-H(17)	0.9600
C(18)-C(19)	1.381(3)
C(18)-H(18)	0.9600
C(19)-H(19)	0.9599

O(3)-S(1)-O(2)	120.02(9)
O(3)-S(1)-N(1)	105.62(9)
O(2)-S(1)-N(1)	107.11(9)
O(3)-S(1)-C(14)	108.78(9)
O(2)-S(1)-C(14)	107.86(9)
N(1)-S(1)-C(14)	106.72(9)
C(1)-N(1)-S(1)	120.68(13)
C(1)-N(1)-H(1N)	117.2(14)
S(1)-N(1)-H(1N)	110.8(14)
O(4)-N(2)-O(5)	123.5(2)
O(4)-N(2)-C(11)	118.64(18)
O(5)-N(2)-C(11)	117.83(19)
N(1)-C(1)-C(2)	112.39(15)
N(1)-C(1)-C(8)	109.96(14)
C(2)-C(1)-C(8)	113.26(16)
N(1)-C(1)-H(1)	106.1
C(2)-C(1)-H(1)	109.0
C(8)-C(1)-H(1)	105.6
C(3)-C(2)-C(6)	120.07(17)
C(3)-C(2)-C(1)	124.53(17)
C(6)-C(2)-C(1)	115.39(15)
C(2)-C(3)-C(4)	129.39(19)
C(2)-C(3)-H(3)	119.5

C(4)-C(3)-H(3)	111.1
C(5)-C(4)-C(3)	121.6(2)
C(5)-C(4)-H(4)	119.3
C(3)-C(4)-H(4)	119.1
C(4)-C(5)-H(5A)	120.4
C(4)-C(5)-H(5B)	119.6
H(5A)-C(5)-H(5B)	120.0
O(1)-C(6)-C(2)	119.00(17)
O(1)-C(6)-C(7)	119.98(18)
C(2)-C(6)-C(7)	121.01(17)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(13)-C(8)-C(9)	118.71(18)
C(13)-C(8)-C(1)	122.16(17)
C(9)-C(8)-C(1)	119.10(16)
C(10)-C(9)-C(8)	121.23(17)
C(10)-C(9)-H(9)	119.0
C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	118.19(18)
C(11)-C(10)-H(10)	121.5
C(9)-C(10)-H(10)	120.3
C(12)-C(11)-C(10)	122.17(19)
C(12)-C(11)-N(2)	118.41(18)
C(10)-C(11)-N(2)	119.40(18)
C(11)-C(12)-C(13)	118.83(18)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	121.6
C(12)-C(13)-C(8)	120.85(18)
C(12)-C(13)-H(13)	119.3
C(8)-C(13)-H(13)	119.9
C(15)-C(14)-C(19)	121.65(19)
C(15)-C(14)-S(1)	119.17(15)

C(19)-C(14)-S(1)	119.15(15)
C(14)-C(15)-C(16)	118.8(2)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	121.2
C(17)-C(16)-C(15)	120.0(2)
C(17)-C(16)-H(16)	120.4
C(15)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	120.9(2)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.1
C(19)-C(18)-C(17)	120.0(2)
C(19)-C(18)-H(18)	119.4
C(17)-C(18)-H(18)	120.7
C(18)-C(19)-C(14)	118.6(2)
C(18)-C(19)-H(19)	121.4
C(14)-C(19)-H(19)	120.0

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{19}H_{18}N_2O_5S$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	27(1)	32(1)	30(1)	10(1)	7(1)	13(1)
O(1)	32(1)	36(1)	43(1)	19(1)	12(1)	13(1)
O(2)	27(1)	45(1)	39(1)	16(1)	11(1)	10(1)
O(3)	43(1)	34(1)	39(1)	9(1)	10(1)	22(1)
O(4)	55(1)	43(1)	40(1)	0(1)	9(1)	3(1)
O(5)	108(2)	90(2)	40(1)	4(1)	-10(1)	69(1)
N(1)	30(1)	25(1)	29(1)	11(1)	9(1)	10(1)
N(2)	37(1)	50(1)	35(1)	5(1)	7(1)	17(1)
C(1)	26(1)	25(1)	31(1)	11(1)	9(1)	10(1)
C(2)	25(1)	26(1)	29(1)	7(1)	5(1)	9(1)
C(3)	28(1)	30(1)	34(1)	9(1)	7(1)	12(1)
C(4)	33(1)	38(1)	42(1)	18(1)	14(1)	17(1)
C(5)	40(1)	48(1)	55(2)	30(1)	19(1)	19(1)
C(6)	29(1)	26(1)	37(1)	7(1)	7(1)	10(1)
C(7)	28(1)	42(1)	57(1)	20(1)	13(1)	12(1)
C(8)	22(1)	26(1)	30(1)	11(1)	8(1)	7(1)
C(9)	28(1)	27(1)	37(1)	12(1)	10(1)	12(1)
C(10)	30(1)	28(1)	40(1)	7(1)	12(1)	9(1)
C(11)	24(1)	37(1)	30(1)	7(1)	7(1)	9(1)
C(12)	29(1)	35(1)	35(1)	14(1)	7(1)	13(1)
C(13)	32(1)	26(1)	34(1)	9(1)	8(1)	11(1)
C(14)	27(1)	32(1)	29(1)	8(1)	6(1)	13(1)
C(15)	35(1)	34(1)	33(1)	11(1)	8(1)	12(1)
C(16)	45(1)	52(1)	43(1)	22(1)	10(1)	25(1)
C(17)	32(1)	80(2)	51(2)	28(1)	6(1)	25(1)
C(18)	29(1)	71(2)	60(2)	30(1)	10(1)	11(1)
C(19)	33(1)	49(1)	45(1)	23(1)	9(1)	12(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{19}H_{18}N_2O_5S$.

Atom	x	y	z	U(eq)
H(1N)	1710(30)	580(20)	9335(19)	33
H(1)	3160	3259	9182	32
H(3)	-985	3753	8546	36
H(4)	2394	4890	8344	42
H(5A)	1160	6281	7332	53
H(5B)	-725	5507	7540	53
H(7A)	-2552	2750	9638	50
H(7B)	-3008	1215	9901	50
H(7C)	-2936	1385	8608	50
H(9)	3216	5171	11099	35
H(10)	4880	6075	13093	39
H(12)	5973	2404	13131	38
H(13)	4328	1506	11111	37
H(15)	1602	2340	6234	41
H(16)	-1070	2324	4979	53
H(17)	-3632	535	4775	63
H(18)	-3599	-1152	5904	64
H(19)	-953	-1089	7210	50

Table 6. Torsion angles [°] for $C_{19}H_{18}N_2O_5S$.

O(3)-S(1)-N(1)-C(1)	174.14(14)
O(2)-S(1)-N(1)-C(1)	45.12(16)
C(14)-S(1)-N(1)-C(1)	-70.19(16)
S(1)-N(1)-C(1)-C(2)	91.11(18)
S(1)-N(1)-C(1)-C(8)	-141.73(14)
N(1)-C(1)-C(2)-C(3)	-122.5(2)
C(8)-C(1)-C(2)-C(3)	112.1(2)
N(1)-C(1)-C(2)-C(6)	57.5(2)
C(8)-C(1)-C(2)-C(6)	-67.9(2)
C(6)-C(2)-C(3)-C(4)	175.0(2)
C(1)-C(2)-C(3)-C(4)	-5.0(3)
C(2)-C(3)-C(4)-C(5)	-179.4(2)
C(3)-C(2)-C(6)-O(1)	-169.66(19)
C(1)-C(2)-C(6)-O(1)	10.3(3)
C(3)-C(2)-C(6)-C(7)	11.5(3)
C(1)-C(2)-C(6)-C(7)	-168.51(18)
N(1)-C(1)-C(8)-C(13)	4.0(2)
C(2)-C(1)-C(8)-C(13)	130.64(19)
N(1)-C(1)-C(8)-C(9)	-177.92(16)
C(2)-C(1)-C(8)-C(9)	-51.3(2)
C(13)-C(8)-C(9)-C(10)	-1.1(3)
C(1)-C(8)-C(9)-C(10)	-179.24(18)
C(8)-C(9)-C(10)-C(11)	-0.3(3)
C(9)-C(10)-C(11)-C(12)	1.2(3)
C(9)-C(10)-C(11)-N(2)	179.41(18)
O(4)-N(2)-C(11)-C(12)	173.69(19)
O(5)-N(2)-C(11)-C(12)	-8.5(3)
O(4)-N(2)-C(11)-C(10)	-4.6(3)
O(5)-N(2)-C(11)-C(10)	173.2(2)
C(10)-C(11)-C(12)-C(13)	-0.7(3)
N(2)-C(11)-C(12)-C(13)	-178.97(18)
C(11)-C(12)-C(13)-C(8)	-0.7(3)
C(9)-C(8)-C(13)-C(12)	1.5(3)
C(1)-C(8)-C(13)-C(12)	179.65(18)

O(3)-S(1)-C(14)-C(15)	-138.91(17)
O(2)-S(1)-C(14)-C(15)	-7.24(19)
N(1)-S(1)-C(14)-C(15)	107.57(17)
O(3)-S(1)-C(14)-C(19)	42.9(2)
O(2)-S(1)-C(14)-C(19)	174.53(17)
N(1)-S(1)-C(14)-C(19)	-70.66(19)
C(19)-C(14)-C(15)-C(16)	0.5(3)
S(1)-C(14)-C(15)-C(16)	-177.68(17)
C(14)-C(15)-C(16)-C(17)	-0.8(3)
C(15)-C(16)-C(17)-C(18)	0.4(4)
C(16)-C(17)-C(18)-C(19)	0.4(4)
C(17)-C(18)-C(19)-C(14)	-0.7(4)
C(15)-C(14)-C(19)-C(18)	0.3(3)
S(1)-C(14)-C(19)-C(18)	178.45(19)

Table 7. Hydrogen bonds for $C_{19}H_{18}N_2O_5S$ [Å and °].

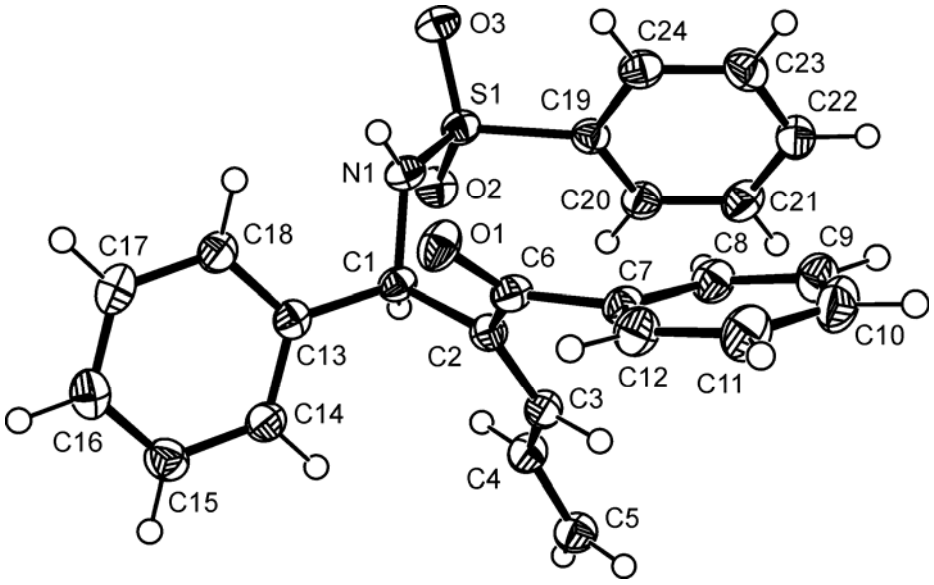
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.86(2)	2.13(2)	2.986(2)	168(2)
N(1)-H(1N)...O(1)	0.86(2)	2.41(2)	2.906(2)	116.8(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2

X-Ray Structure Report on (*E*)-15a

ORTEP Diagram of **(*E*)-15a**:



Experimental:

A colorless plate crystal of $C_{24}H_{21}NO_3S$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. Cell constants obtained from the refinement[1] of 7261 reflections in the range $3.7 < \theta < 27.5°$ corresponded to a primitive monoclinic cell; details of crystal data and structure refinement have been provided in Table 1. The data were collected[2] at a temperature of 173(2) K using ω and φ scans to a maximum θ value of 27.5°. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method[1]. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary.

The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined; methyl H-atoms were disordered over six sites.. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.047 and wR = 0.118 (all data), respectively, and goodness of fit, S = 1.03. The weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless. The figures were plotted with the aid of ORTEPII[6].

Table 1. Crystal data and structure refinement for $C_{24}H_{21}NO_3S$.

Empirical formula	$C_{24}H_{21}NO_3S$	
Formula weight	403.48	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.779(8) Å	α= 90°.
	b = 10.326(4) Å	β= 94.06(2)°.
	c = 15.405(9) Å	γ = 90°.
Volume	2027.7(19) $Å^3$	
Z	4	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	0.185 mm^{-1}	
F(000)	848	
Crystal size	0.19 x 0.14 x 0.07 mm^3	
Theta range for data collection	3.7 to 27.5°.	
Index ranges	-16<=h<=16, -10<=k<=13, -19<=l<=19	
Reflections collected	7261	
Independent reflections	4620 [R(int) = 0.037]	
Completeness to theta = 27.5°	99.3 %	
Absorption correction	Multi-scan method	
Max. and min. transmission	0.987 and 0.966	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4620 / 0 / 262	
Goodness-of-fit on F^2	1.03	
Final R indices [I>2sigma(I)]	R1 = 0.047, wR2 = 0.103	
R indices (all data)	R1 = 0.073, wR2 = 0.118	
Largest diff. peak and hole	0.50 and -0.57 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{24}H_{21}NO_3S$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	4705(1)	-487(1)	2435(1)	25(1)
O(1)	4663(1)	1370(1)	-152(1)	33(1)
O(2)	4078(1)	-9(1)	3101(1)	31(1)
O(3)	4866(1)	-1851(1)	2344(1)	33(1)
N(1)	4183(1)	20(1)	1512(1)	25(1)
C(1)	3727(2)	1328(2)	1447(1)	23(1)
C(2)	4521(2)	2348(2)	1211(1)	24(1)
C(3)	4688(2)	3455(2)	1667(1)	26(1)
C(4)	4196(2)	3846(2)	2446(1)	28(1)
C(5)	4323(2)	5016(2)	2797(1)	32(1)
C(6)	5055(2)	2120(2)	403(1)	25(1)
C(7)	6082(2)	2749(2)	256(1)	24(1)
C(8)	6895(2)	2780(2)	908(1)	28(1)
C(9)	7884(2)	3203(2)	719(1)	34(1)
C(10)	8051(2)	3653(2)	-103(2)	38(1)
C(11)	7240(2)	3655(2)	-751(2)	37(1)
C(12)	6263(2)	3184(2)	-574(1)	31(1)
C(13)	2714(2)	1366(2)	860(1)	23(1)
C(14)	2074(2)	2454(2)	909(1)	28(1)
C(15)	1109(2)	2519(2)	438(1)	32(1)
C(16)	779(2)	1501(2)	-97(1)	31(1)
C(17)	1412(2)	424(2)	-156(1)	31(1)
C(18)	2377(2)	355(2)	318(1)	28(1)
C(19)	5966(2)	213(2)	2616(1)	25(1)
C(20)	6149(2)	1142(2)	3261(1)	30(1)
C(21)	7163(2)	1607(2)	3439(2)	35(1)
C(22)	7975(2)	1143(2)	2978(1)	34(1)
C(23)	7783(2)	218(2)	2336(1)	34(1)
C(24)	6778(2)	-246(2)	2146(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for $C_{24}H_{21}NO_3S$.

S(1)-O(3)	1.4319(15)
S(1)-O(2)	1.4334(15)
S(1)-N(1)	1.6142(18)
S(1)-C(19)	1.771(2)
O(1)-C(6)	1.234(2)
N(1)-C(1)	1.472(2)
N(1)-H(1N)	0.8800
C(1)-C(2)	1.524(3)
C(1)-C(13)	1.525(3)
C(1)-H(1)	0.9600
C(2)-C(3)	1.350(3)
C(2)-C(6)	1.480(3)
C(3)-C(4)	1.452(3)
C(3)-H(3)	0.9600
C(4)-C(5)	1.329(3)
C(4)-H(4)	0.9599
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9599
C(6)-C(7)	1.495(3)
C(7)-C(12)	1.391(3)
C(7)-C(8)	1.394(3)
C(8)-C(9)	1.386(3)
C(8)-H(8)	0.9600
C(9)-C(10)	1.379(3)
C(9)-H(9)	0.9600
C(10)-C(11)	1.387(3)
C(10)-H(10)	0.9600
C(11)-C(12)	1.384(3)
C(11)-H(11)	0.9600
C(12)-H(12)	0.9600
C(13)-C(18)	1.387(3)
C(13)-C(14)	1.396(3)
C(14)-C(15)	1.387(3)
C(14)-H(14)	0.9600

C(15)-C(16)	1.383(3)
C(15)-H(15)	0.9599
C(16)-C(17)	1.382(3)
C(16)-H(16)	0.9599
C(17)-C(18)	1.389(3)
C(17)-H(17)	0.9599
C(18)-H(18)	0.9600
C(19)-C(20)	1.388(3)
C(19)-C(24)	1.390(3)
C(20)-C(21)	1.390(3)
C(20)-H(20)	0.9600
C(21)-C(22)	1.384(3)
C(21)-H(21)	0.9600
C(22)-C(23)	1.384(3)
C(22)-H(22)	0.9600
C(23)-C(24)	1.384(3)
C(23)-H(23)	0.9600
C(24)-H(24)	0.9600

O(3)-S(1)-O(2)	120.03(9)
O(3)-S(1)-N(1)	106.63(9)
O(2)-S(1)-N(1)	107.57(9)
O(3)-S(1)-C(19)	106.33(9)
O(2)-S(1)-C(19)	107.17(9)
N(1)-S(1)-C(19)	108.75(9)
C(1)-N(1)-S(1)	119.66(13)
C(1)-N(1)-H(1N)	120.2
S(1)-N(1)-H(1N)	120.2
N(1)-C(1)-C(2)	112.51(15)
N(1)-C(1)-C(13)	112.31(14)
C(2)-C(1)-C(13)	113.10(16)
N(1)-C(1)-H(1)	105.0
C(2)-C(1)-H(1)	108.5
C(13)-C(1)-H(1)	104.7
C(3)-C(2)-C(6)	120.45(17)
C(3)-C(2)-C(1)	122.94(17)

C(6)-C(2)-C(1)	116.44(16)
C(2)-C(3)-C(4)	127.18(18)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	113.0
C(5)-C(4)-C(3)	122.81(19)
C(5)-C(4)-H(4)	118.2
C(3)-C(4)-H(4)	119.0
C(4)-C(5)-H(5A)	120.3
C(4)-C(5)-H(5B)	119.7
H(5A)-C(5)-H(5B)	120.0
O(1)-C(6)-C(2)	119.61(17)
O(1)-C(6)-C(7)	119.05(17)
C(2)-C(6)-C(7)	121.31(16)
C(12)-C(7)-C(8)	119.37(19)
C(12)-C(7)-C(6)	118.98(18)
C(8)-C(7)-C(6)	121.28(18)
C(9)-C(8)-C(7)	120.02(19)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	120.1
C(10)-C(9)-C(8)	120.1(2)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	120.3
C(9)-C(10)-C(11)	120.3(2)
C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	119.7
C(12)-C(11)-C(10)	119.8(2)
C(12)-C(11)-H(11)	120.9
C(10)-C(11)-H(11)	119.3
C(11)-C(12)-C(7)	120.4(2)
C(11)-C(12)-H(12)	120.1
C(7)-C(12)-H(12)	119.5
C(18)-C(13)-C(14)	118.67(18)
C(18)-C(13)-C(1)	123.54(17)
C(14)-C(13)-C(1)	117.71(17)
C(15)-C(14)-C(13)	120.89(19)
C(15)-C(14)-H(14)	119.6

C(13)-C(14)-H(14)	119.5
C(16)-C(15)-C(14)	119.87(19)
C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	119.6
C(17)-C(16)-C(15)	119.7(2)
C(17)-C(16)-H(16)	120.4
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(18)	120.56(19)
C(16)-C(17)-H(17)	120.5
C(18)-C(17)-H(17)	118.9
C(13)-C(18)-C(17)	120.33(18)
C(13)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	119.7
C(20)-C(19)-C(24)	120.97(19)
C(20)-C(19)-S(1)	120.02(15)
C(24)-C(19)-S(1)	118.87(15)
C(19)-C(20)-C(21)	119.19(19)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.8
C(22)-C(21)-C(20)	120.1(2)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	120.1
C(23)-C(22)-C(21)	120.3(2)
C(23)-C(22)-H(22)	119.5
C(21)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	120.36(19)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(19)	119.14(19)
C(23)-C(24)-H(24)	121.0
C(19)-C(24)-H(24)	119.9

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{24}H_{21}NO_3S$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	28(1)	21(1)	25(1)	1(1)	4(1)	-1(1)
O(1)	34(1)	36(1)	30(1)	-11(1)	9(1)	-10(1)
O(2)	32(1)	35(1)	27(1)	1(1)	9(1)	0(1)
O(3)	39(1)	21(1)	38(1)	2(1)	3(1)	-1(1)
N(1)	30(1)	21(1)	23(1)	-3(1)	3(1)	0(1)
C(1)	26(1)	20(1)	23(1)	-3(1)	5(1)	0(1)
C(2)	23(1)	23(1)	24(1)	0(1)	2(1)	0(1)
C(3)	25(1)	25(1)	26(1)	-1(1)	2(1)	-2(1)
C(4)	29(1)	28(1)	28(1)	-3(1)	6(1)	-2(1)
C(5)	34(1)	30(1)	32(1)	-7(1)	7(1)	2(1)
C(6)	28(1)	20(1)	27(1)	-2(1)	4(1)	0(1)
C(7)	27(1)	21(1)	26(1)	-4(1)	5(1)	-1(1)
C(8)	32(1)	28(1)	26(1)	-4(1)	4(1)	-2(1)
C(9)	31(1)	35(1)	36(1)	-7(1)	-3(1)	-4(1)
C(10)	31(1)	40(1)	45(1)	-6(1)	11(1)	-12(1)
C(11)	39(1)	39(1)	36(1)	5(1)	11(1)	-8(1)
C(12)	32(1)	32(1)	29(1)	2(1)	3(1)	-4(1)
C(13)	22(1)	25(1)	22(1)	3(1)	7(1)	-3(1)
C(14)	29(1)	25(1)	31(1)	-1(1)	3(1)	-2(1)
C(15)	30(1)	32(1)	34(1)	5(1)	3(1)	2(1)
C(16)	27(1)	40(1)	27(1)	7(1)	1(1)	-6(1)
C(17)	32(1)	34(1)	26(1)	-4(1)	4(1)	-11(1)
C(18)	25(1)	28(1)	31(1)	-5(1)	7(1)	-3(1)
C(19)	26(1)	23(1)	25(1)	2(1)	4(1)	1(1)
C(20)	31(1)	29(1)	31(1)	-4(1)	6(1)	1(1)
C(21)	40(1)	31(1)	36(1)	-6(1)	4(1)	-5(1)
C(22)	29(1)	34(1)	38(1)	1(1)	1(1)	-3(1)
C(23)	29(1)	37(1)	36(1)	-1(1)	8(1)	4(1)
C(24)	35(1)	27(1)	28(1)	-3(1)	5(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{24}H_{21}NO_3S$.

Atom	x	y	z	U(eq)
H(1N)	4172	-483	1050	30
H(1)	3512	1515	2018	28
H(3)	5171	4087	1474	31
H(4)	3764	3236	2726	34
H(5A)	3986	5237	3314	38
H(5B)	4751	5643	2529	38
H(8)	6774	2507	1488	34
H(9)	8456	3183	1158	41
H(10)	8731	3965	-229	46
H(11)	7364	3991	-1315	45
H(12)	5706	3152	-1026	37
H(14)	2307	3171	1270	34
H(15)	672	3267	490	38
H(16)	114	1549	-428	38
H(17)	1194	-287	-528	37
H(18)	2809	-399	271	33
H(20)	5580	1452	3578	36
H(21)	7298	2259	3877	42
H(22)	8679	1442	3113	40
H(23)	8349	-87	2012	40
H(24)	6636	-884	1699	36

Table 6. Torsion angles [°] for $C_{24}H_{21}NO_3S$.

O(3)-S(1)-N(1)-C(1)	167.71(13)
O(2)-S(1)-N(1)-C(1)	37.73(16)
C(19)-S(1)-N(1)-C(1)	-78.01(15)
S(1)-N(1)-C(1)-C(2)	90.28(18)
S(1)-N(1)-C(1)-C(13)	-140.74(14)
N(1)-C(1)-C(2)-C(3)	-128.76(19)
C(13)-C(1)-C(2)-C(3)	102.7(2)
N(1)-C(1)-C(2)-C(6)	56.0(2)
C(13)-C(1)-C(2)-C(6)	-72.6(2)
C(6)-C(2)-C(3)-C(4)	177.28(18)
C(1)-C(2)-C(3)-C(4)	2.2(3)
C(2)-C(3)-C(4)-C(5)	-172.4(2)
C(3)-C(2)-C(6)-O(1)	-155.71(19)
C(1)-C(2)-C(6)-O(1)	19.7(3)
C(3)-C(2)-C(6)-C(7)	26.3(3)
C(1)-C(2)-C(6)-C(7)	-158.33(17)
O(1)-C(6)-C(7)-C(12)	40.2(3)
C(2)-C(6)-C(7)-C(12)	-141.80(19)
O(1)-C(6)-C(7)-C(8)	-132.7(2)
C(2)-C(6)-C(7)-C(8)	45.3(3)
C(12)-C(7)-C(8)-C(9)	-2.1(3)
C(6)-C(7)-C(8)-C(9)	170.86(18)
C(7)-C(8)-C(9)-C(10)	3.2(3)
C(8)-C(9)-C(10)-C(11)	-1.7(3)
C(9)-C(10)-C(11)-C(12)	-0.9(3)
C(10)-C(11)-C(12)-C(7)	2.1(3)
C(8)-C(7)-C(12)-C(11)	-0.6(3)
C(6)-C(7)-C(12)-C(11)	-173.68(18)
N(1)-C(1)-C(13)-C(18)	-12.0(3)
C(2)-C(1)-C(13)-C(18)	116.6(2)
N(1)-C(1)-C(13)-C(14)	164.66(16)
C(2)-C(1)-C(13)-C(14)	-66.7(2)
C(18)-C(13)-C(14)-C(15)	1.2(3)
C(1)-C(13)-C(14)-C(15)	-175.72(18)

C(13)-C(14)-C(15)-C(16)	-0.8(3)
C(14)-C(15)-C(16)-C(17)	0.2(3)
C(15)-C(16)-C(17)-C(18)	0.0(3)
C(14)-C(13)-C(18)-C(17)	-0.9(3)
C(1)-C(13)-C(18)-C(17)	175.80(18)
C(16)-C(17)-C(18)-C(13)	0.3(3)
O(3)-S(1)-C(19)-C(20)	-135.32(16)
O(2)-S(1)-C(19)-C(20)	-5.81(19)
N(1)-S(1)-C(19)-C(20)	110.20(17)
O(3)-S(1)-C(19)-C(24)	40.39(18)
O(2)-S(1)-C(19)-C(24)	169.91(15)
N(1)-S(1)-C(19)-C(24)	-74.08(17)
C(24)-C(19)-C(20)-C(21)	-0.6(3)
S(1)-C(19)-C(20)-C(21)	175.02(16)
C(19)-C(20)-C(21)-C(22)	-0.1(3)
C(20)-C(21)-C(22)-C(23)	0.2(3)
C(21)-C(22)-C(23)-C(24)	0.3(3)
C(22)-C(23)-C(24)-C(19)	-1.0(3)
C(20)-C(19)-C(24)-C(23)	1.1(3)
S(1)-C(19)-C(24)-C(23)	-174.55(16)

Table 7. Hydrogen bonds for $C_{24}H_{21}NO_3S$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.88	2.29	3.010(2)	138.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z

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