Supporting Information

General procedures for synthesis of 3,6-dihydro-1-oxa-3,4-diazin-2-ones (2):

N-Carboethoxy-N-phenylhydrazine:

A mixture of benzaldehyde (5 g, 47 mmol) and phenylhydrazine (5.10 g, 47 mmol) in HOAc (50 mL) was stirred at rt for 1h, then filtered. The crystals were washed with HOAc and H_2O then dried to give benzaldehyde phenylhydrazone as bright yellow crystals (8.5 g, 92%), mp 156 °C (lit[1] 156 °C): ^{1}H NMR (300 MHz, $CDCl_3$):δ 7.72 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.41 (s, 1H), 7.35 (t, J = 9.0 Hz, 1H), 7.32 (t, J = 9.0 Hz, 2H), 7.15 (d, J = 9.0 Hz, 2H), 6.90 (t, J = 7.5 Hz, 1H).

To the solution of the above benzaldehyde phenylhydrazone (1.0 g, 5 mmol) in THF was added 1.6M *n*-butyl lithium in hexane (3.15 mL, 5 mmol) at -78 °C. A yellow solid was formed during the addition. The mixture was stirred for 15 min, then ethyl chloroformate (0.7 mL, 8 mmol) was added. The resulting yellow solution was warmed to rt and quenched by adding H_2O. The solution was extracted with EtOAc. The extracts were combined, washed with H_2O and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a white solid which was recrystalized from cyclohexane to give benzaldehyde N-(carboethoxy)-N-phenylhydrazone as white crystals (1.33 g, 97 %), mp 97-98 °C (lit[1] mp 98.5 °C) which were used as obtained.

To the solution of the above N-(carboethoxy)benzaldehyde phenylhydrazone (1.33 g, 4.96 mmol) in 25 mL of 10% aq HCl/ethanol (1:2 v/v) was warmed to 40 °C until tlc indicated no hydrazone remained (3-5 h). The reaction mixture was diluted with 10 mL of water and partitioned four times with 30 mL of ether. After warming the aqueous solution to expell residual ether, the aqueous solution was basified to pH > 12 and extracted four times with 25 mL of ether. The combined extracts were dried over $MgSO_4$. The solvent was removed *in vacuo* to give 652.5 mg (73%) of the semisolid N-(carboethoxy)-N-phenylhydrazine.[2]

2-Phenylacetophenone phenylhydrazone:

To a suspension of phenylhydrazine hydrochloride (21.7 g, 0.15 mol) in HOAc (600 mL) were added 2-phenylacetophenone (29.5 g, 0.15 mol) and NaOAc trihydrate (20.4 g, 0.15 mol). The resulting mixture was stirred at rt for 12 h. The mixture was then poured into H_2O (3 L). The solid formed was filtered and washed with H_2O and hexane to give the title hydrazone as light yellow solid (40 g, 93%), mp 114 - 116 °C (lit[3] mp 116 °C): ^{1}H NMR (300 MHz, $CDCl_3$): 7.88 (d, 2H), 7.75 (s, 1H), 7.40 (t, 2H), 7.39 - 7.21 (m, 8H), 7.11 (d, 2H), 6.89 (t, 1H), 4.19 (s, 2H); ^{13}C NMR ($CDCl_3$): 32.5, 113.3, 120.3, 125.7, 127.1, 127.91, 127.94, 128.4, 129.2, 129.3, 135.3, 139.0, 142.5, 145.0.

2-phenylacetophenone N-(Carboethoxy)-N-phenylhydrazone (**4a**):

To a solution of 2-phenylacetophenone phenylhydrazone (5 g, 17.46 mmol) in THF (50 ml) was added 1.6 M *n*-butyl lithium in hexane (12 mL, 19.25 mmol) at - 78 °C. The resulting mixture was stirred for 15 min, then quenched by addition of ethyl chloroformate (2.67 mL, 28 mmol) and gradually warmed to rt. The resulting yellow solution was diluted with EtOAc, then washed with H_2O, brine and dried over $MgSO_4$. Solvent was evaporated and the oily residue was purified by column chromatography (silica gel,

elution by 10% EtOAc in hexane) to give 4.08 g (66%) of **4a** as a yellow oil: ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.80 (d, J = 6.5Hz, 2H), 7.50-7.10 (m, 11H), 6.95 (d, J = 6.6 Hz, 1H), 4.17 (s, 2H), 4.96 (q, J = 7.2 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H) which was used as obtained.

3,5,6-Triphenyl-3,6-dihydro-1-oxa-3,4-diazin-2-one (**2a**):

To a solution of 290 mg (1.05 mmol) of **4a** in 3 mL of THF was added 403 mg (1.05 mmol) of phenyltrimethylammonium tribromide (PTAB) at rt. The resulting mixture was stirred for 10 min, then diluted with DMF (2.5 mL) and heated to reflux for 20 min. After cooling to rt, 30 mL of ethyl acetate/hexane (1:1 v/v) was added. The mixture was then washed with H_2O, brine and dried over $MgSO_4$. The solvent was evaporated and the residual oil was purified by silica gel column (eluting with a gradient of 10% to 20% ethyl acetate in hexane) to give 235 mg (91%) of **2a** as off-white solid, mp 54-56 °C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (dd, J_1 = 8.1, J_2 = 2.1 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.50-7.30 (m, 11H), 6.47 (s, 1H).

Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.68; H, 4.87; N, 8.49.

α-(4-Nitrophenoxy)acetophenone N-(Carboethoxy)-N-phenylhydrazone (**4f**):

Method A:

To a solution of acetophenone N-(carboethoxy)-N-phenylhydrazone (11.7g, 0.04 mol) in THF (250 mL) was added PTAB (16 g, 0.04 mol) at rt. The resulting mixture was stirred for 10 min, then filtered. The filtrate was diluted with 500 mL of EtOAc, washed twice with H_2O, and dried over $MgSO_4$. Concentration *in vacuo* gave the bromide as a yellow oil which was used directly for the next step.

To a solution of the above bromide in 200 mL of DMF was added 4-nitrophenol (11.54 g, 0.08 mol) and potassium carbonate (11.2 g, 0.08 mol). The mixture was stirred at rt for 10 h then diluted with 600 mL of EtOAc and 150 mL of H_2O. The organic phase was separated, washed with 5% potassium carbonate until the aqueous wash was colorless, and then finally once with H_2O. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo* to give an oily residue which was purified by column chromatography (silica gel, elution with a gradient of 10% to 20% EtOAc in hexane) to afford 9.9 g (57 %) of **4f** as a yellow oil. ^{1}H NMR analysis shows that **4f** exists as E,Z hydrazone isomers in the ratio of 2:1 in $CDCl_3$, but as a single isomer in d_6-DMSO; ^{1}H NMR (300 MHz, $CDCl_3$) minor isomer: δ 8.21 (d, J = 9.3 Hz, 2H), 7.53 - 7.03 (overlap with other isomer, 12H), 5.19 (s, 2H), 4.13 (q, J = 6.9 Hz, 2H), 1.18 (t, J = 6.9 Hz, 3H); major isomer: 8.10 (d, J = 9.3 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.53 - 7.03 (overlap with other isomer, 8H), 6.81 (d, J = 9.3 Hz, 2H), 5.21 (s, 2H), 4.31 (q, J = 6.9 Hz, 2H), 1.32 (t, J = 6.9 Hz, 3H).

HRMS. Calcd for $C_{23}H_{21}N_3O_5$: 419.1481. Found: 419.1479.

Method B:

To a solution of ethyl chloroformate (0.3 mL, 3 mmol) in CH_2Cl_2 (20 mL) was added 4-dimethylaminopyridine (0.4 g, 3.3 mmol). The resulting solution was stirred at rt for 10 min, then α-(*p*-

nitrophenoxy)acetophenone phenylhydrazone (347 mg, 1 mmol) was added. The yellow solution was stirred for 36 h and evaporated to dryness. The residual solid was dissolved in EtOAc (80 mL) and partitioned with 0.5N HCl (10 mL). The organic phase was separated, washed with H_2O, brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and residual oil was purified by column chromatography (silica gel, elution by 20% EtOAc in hexane) to give 224 mg (53%) of **4f** which was spectrocopically identical to that obtained by method A above. α-(4-Nitrophenoxy)acetophenone (40 mg) was also recovered during the purification.

Method C:

A solution of 257.3 mg (1 mmol) of α-(4-nitrophenoxy)acetophenone in 5 mL of toluene was combined with 270.3 mg (1.5 mmol) of N-(carboethoxy)-N-phenylhydrazine and a catalytic amount of trifluoroacetic acid, and heated at reflux for 1-2 h until tlc indicated consumption of the ketone. The reaction mixture was washed with 5 mL of sat $NaHCO_3$, dried over $MgSO_4$, and evaporated to afford 293.6 mg (70%) of **4f** spectroscopically identical to that obtained by method A above.

3,5-Diphenyl-6-(4-nitrophenoxy)-3,6-dihydro-1-oxa-3,4-diazin-2-one (**2f**):

To a solution of **4f** (3.97 g, 9.47 mmol) in THF (100 mL) was added PTAB (3.67 g, 9.47 mmol) at rt. The resulting mixture was stirred for 10 min then filtered. The filtrate was evaporated to a volume of 30 mL, diluted with 250 mL of EtOAc, washed twice with H_2O, 50% brine, and dried over $MgSO_4$. Concentration to dryness *in vacuo* followed by trituration with hexane/ether afforded 2.50 g of **2f**. The filtrate was evaporated to dryness and purified by column chromatography (elution with 20% EtOAc in hexane) to give an additional 0.65 g of **2f**, affording a combined yield of 3.15 g (86 %) of **2e** as white crystals, mp 170 - 172 °C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 8.1 Hz, 2H), 7.53 - 7.48 (m, 5H), 7.40 (d, J = 9.0 Hz, 2H), 7.38 (t, 1H), 7.35 (d, J = 7.5 Hz, 2H), 6.80 (s, 1H), 3.34 (d, J = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 92.4, 117.3, 124.3, 125.8, 126.2, 127.5, 128.9, 129.2, 130.8, 131.2, 140.4, 141.6, 144.1, 144.3, 160.0; IR (cm-$^{1)}$: 1728; MS m/z : 412 (M+23).

Anal. Calcd for $C_{21}H_{15}N_3O_5$: C, 64.78; H, 3.88; N, 10.79. Found: C, 64.96; H, 3.99; N, 10.78.

General procedure for preparation of 8, 10, and 11, the sulfur analogues of 2f: :

3,5-Diphenyl-6-(4-nitrophenoxy)-3,6-dihydro-1-oxa-3,4-diazin-2-thione (**8**)

Method A: The mixture of **2f** (2 g, 5.14 mmol) and Lawesson's reagent[4] (4.16 g, 10.3 mmol) in dry toluene (50 mL) was heated to reflux for 12 h. Toluene was removed and the red residue was dissolved in EtOAc and partitioned with H_2O. The organic phase was separated and dried over $MgSO_4$. Removal of solvent *in vacuo* afforded an oily residue which was purified by column chromatography (silica gel, elution with a gradient of 10% to 20% EtOAc in hexane) and the resulting solid recrystallized from 50% EtOAc in hexane to give 1.28 g (61 %) of **8** as yellow crystals, mp 185-187 °C (dec.): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, J = 9.3 Hz, 2H), 7.75 (d, J = 7.5 Hz, 2H), 7.61 - 7.47 (m, 10H), 6.70 (s, 1H).

Anal. Calcd for $C_{21}H_{15}N_3O_4S$: C, 62.21; H, 3.73; N, 10.36; S, 7.91. Found: C, 62.09; H, 3.70; N, 10.14; S, 7.41.

Method B:

t-Butyl chlorothioformate:

To a stirred solution of 2,2-dimethylpropanethiol (11.3 mL, 0.1mol) in 50 mL of dry 1,2-dichloroethane at - 5 °C is added 51.4 mL (0.1 mol) of a 1.93 M solution of phosgene in toluene. The resulting mixture was treated with 14 mL of dry triethylamine (10.1 g 0.1mol) dropwise at -5 °C and the resulting mixture stirred at -5 °C for 1 h then slowly warmed to rt. The resulting precipitate was collected by filtration and the solids washed with additional dry 1,2-dichloroethane. The filtrate was then washed successively with 30 mL of 0.5 N aq HCl solution and three 30 mL portions of H_2O, followed by drying over $MgSO_4$. After concentration *in vacuo*, the residue was distilled to afford 8.2 g (54%) of *t*-butyl chlorothioformate as an colorless liquid, bp 55 - 58 °C / 21 mm (lit[5] 43 °C / 12 mm).

α-(4-Nitrophenoxy)acetophenone N-(*t*-butylthiocarboxy)-N-phenylhydrazone:

To a solution of *t*-butyl chlorothioformate (1.72 g, 11.3 mmol) in CH_2Cl_2 (30 mL) was added 4-dimethylaminopyridine (1.45 g, 11.9 mmol). The resulting solution was stirred at rt for 10 min, then α-(*p*-nitrophenoxy)acetophenone phenylhydrazone (2.3 g, 6.63 mmol) was added. The yellow solution was stirred for 18 h at which time tlc analysis indicated that the hydrazone was almost completely consumed. The reaction mixture was evaporated to dryness *in vacuo*. The residue was partitioned between EtOAc (80 mL) and 0.5 N HCl (15 mL). The aqueous phase was extracted twice with 10 mL portions of EtOAc. The combined organic phases were washed successively with 25 mL portions of H_2O and brine, and dried over $MgSO_4$. During concentration *in vacuo* to a volume of ~5 mL, a light yellow solid separated. The solid was collected with suction and washed with ~5 mL of EtOAc to give 1.68 g of solid. The filtrate was evaporated and purified by column chromatography (silica gel, elution by 10% EtOAc in hexane) to afford another 0.90 g of solid. The combined solids were recrystallized from hexane/ether to afford 2.51 g (82 %) of pure hydrazone, mp 145 - 147 °C which was used as obtained.

To a solution of 50 mg (0.1 mmol) of α-(4-nitrophenoxy)-acetophenone N-(*t*-butylthiocarboxy)-N-phenylhydrazone in THF (1.5 mL) was added PTAB (41 mg, 0.1 mmol) at rt. The resulting mixture was stirred for 10 min, then filtered. The filtrate was diluted with 40 mL of dichloroethane and concentrated to ~5 mL volume below 20 °C. The light yellow solution was again diluted with 40 mL of dichloroethane and heated at reflux for 30 min. The solvent was removed *in vacuo* and the resulting yellow residue was purified by column chromatography (silica gel, elution by 10% EtOAc in hexane) to give 18 mg (42 %) of **7** which was spectroscopically identical to that obtained by method A.

Ethyl chlorodithioformate:

To a stirred solution of thiophosgene in benzene (90 mL) was added dropwise a solution of ethanethiol (40 mL, 0.524 mol) in benzene (75 mL) at the temperature below 10 °C. The resulting solution was stirred for 20 h at 0 °C then evaporated to remove benzene. The residue was distilled to give 49.3 g (67%) of the chlorodithioformate as an orange liquid, bp 117 °C / 25 mm (lit[6] 63-64 °C / 5.8(8) mm): ^1H NMR (300 MHz, $CDCl_3$): 3.23 (q, J = 6.9 Hz, 2H), 1.40 (t, J = 6.9 Hz, 3H).

α-(4-nitrophenoxy)acetophenone N-(ethyldithiocarboxy)-N-phenylhydrazone:

To a solution of ethyl chlorodithioformate (6.32 g, 45 mmol) in CH_2Cl_2 (150 mL) was added 4-dimethylaminopyridine (5.86 g, 48 mmol). The resulting solution was stirred at rt for 10 min, then α-(*p*-nitrophenoxy)acetophenone phenylhydrazone (10.4 g, 30 mmol) was added. The yellow solution was stirred at rt for 2 h, then evaporated to dryness. The solid residue was suspended in 150 mL of EtOAc and partitioned with 100 mL of 0.25 N HCl. The resulting bright yellow precipitate was collected with suction, washed three times with H_2O, then EtOAc/hexane (1:1) and dried in air to give 9.2 g of the dithiocarboxyhydrazone. The organic phase was separated and diluted with additional EtOAc, washed successively with H_2O, brine, and dried over $MgSO_4$. During concentration of the organic phase, an additional 4 g of the dithiocarboxyhydrazone separated as bright yellow solid. The solids were combined, washed on a filter with a small amount of EtOAc, and dried in air to afford 13.2 g (98%) of the dithiocarboxyhydrazone, mp 146 - 147 °C. ^{1}H NMR in d_3-acetonitrile showed two E,Z hydrazone isomers present in about equal amount: ^{1}H NMR (300 MHz, CD_3CN): δ 8.20 (d, J= 9.3 Hz, 1H), 8.10 (d, J= 9.3 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.55 - 7.44 (m, 4H), 7.39 (t, J = 6.9 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.18 - 7.07 (m, 3H), 6.85 (d, J = 9.3 Hz, 1H), 6.68 (d, J = 7.2 Hz, 1H), 5.24 and 5.12 (s, 2H), 3.25 and 3.23 (q, J = 6.9 Hz, 2H), 1.32 and 1.31 (t, J = 6.9 Hz, 3H) which was used as obtained.

3,5-Diphenyl-6-(4-nitrophenoxy)-3,6-dihydro-1-thia-3,4-diazin-2-thione (**10**) :

To a solution of 4.51 g (10 mmol) of α-(*p*-nitrophenoxy)acetophenone N-(ethyldithiocarboxy)-N-phenylhydrazone in 200 mL of THF was added 3.76 g (10 mmol) of PTAB at rt. The resulting mixture was stirred for 10 min, then DMF (50 mL) was added. The mixture was heated at reflux (oil bath temperature 95 - 100 °C) for 45 min, cooled to rt, and concentrated *in vacuo* to a volume of ~50 mL. The yellow solution was diluted with 500 mL of EtOAc, washed successively twice with H_2O, 50% brine, brine, and dried over $MgSO_4$. During concentration *in vacuo*, **10** precipitated as a bright yellow solid. The solids were collected by suction with the aid of a minimum amount of EtOAc/hexane (1:1 v/v) to afford 4.09 g (97%) of **10**, mp 214-6 °C (dec.): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.56 - 7.47 (m, 8H), 7.21 (d, J = 9.0 Hz, 2H), 6.41 (s, 1H); MS (m/z): 421 (M+).

Anal. Calcd for $C_{21}H_{15}N_3O_3S_2$: C, 59.84; H, 3.59; N, 9.97; S, 15.21. Found: C, 60.04; H, 3.67; N, 9.91; S, 15.54.

3,5-Diphenyl-6-(4-nitrophenoxy)-3,6-dihydro-1-thia-3,4-diazin-2-one (**11**):

Method A:

To a suspension of **10** (100 mg, 0.237 mmol) in acetone (3 mL) was added a solution of 91 mg (0.284 mmol) of $Hg(OAc)_2$ in HOAc (3 mL). The resulting mixture was heated to 60 °C for 20 min, cooled to rt and filtered. The filtrate was diluted with H_2O and extracted three times with 20 mL portions of EtOAc. The combined extracts were washed with H_2O and dried over $MgSO_4$. During concentration *in vacuo* to a volume of ~1 mL, **11** precipitated as light yellow crystals. The crystals were collected by suction, washed with EtOAc, and dried under vacuum to afford 88 mg (92 %) of **11**, mp 195 - 197 °C (dec.): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, J = 9.3 Hz, 2H), 7.76 (dd, J_1 = 8.1, J_2 = 2.1 Hz, 2H),

7.59 (d, J = 7.8 Hz, 1H), 7.53 - 7.45 (m, 6H), 7.40 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 9.3 Hz, 2H), 6.65 (s, 1H); MS (m/z): 405 (M+).

Anal. Calcd for $C_{21}H_{15}N_3O_4S$: C, 62.21; H, 3.73; N, 10.36. Found: C, 62.06 H, 3.78; N, 10.26.

Method B:

To a suspension of **10** (100 mg, 0.237 mmol) in EtOAc (1.5 mL) and THF (5mL) was added 30% H_2O_2 (0.5 mL), then Na_2WO_4 (78 mg, 0.237 mmol). The resulting mixture was stirred at rt for 10 h. The yellow solution was evaporated and the residue was dissolved in 20 mL of EtOAc, washed with 10 mL of H_2O and the organic phase was dried over $MgSO_4$. During concentration *in vacuo* to a volume of ~1 mL, **11** precipitated as light yellow crystals. The crystals were collected by suction, washed with EtOAc, and dried under vacuum to give 88 mg (92 %) of **11** which was spectroscopically identical to that otained using method A.

General procedures for synthesis of 2,5-dihydro-1-thia-2,3-diazole-1,1-dioxides (3):

Acetophenonesulfonic acid phenylhydrazone, sodium salt:[7]

α-Acetophenonesulfonic acid, sodium salt (3 g, 13.5 mmol) was suspended in 250 mL of ethanol and heated to reflux. A 1.33 mL portion of phenylhydrazine (1.46 g, 13.5 mmol) was added and heating continued at reflux for 4 h. The volume of the reaction mixture was reduced to ~100 mL by distillation of ethanol. The mixture was cooled and stirred at rt for 36 h. The resulting solids were collected by suction and recrystallized from aq ethanol to afford 2.74 (65 %) of the hydrazone sodium salt which was used as obtained in the next step.

2,4-Diphenyl-2,5-dihydro-1-thia-2,3-diazole-1,1-dioxide (**3b**):[8]

A 500 mg (1.6 mmol) portion of the above dry hydrazone sodium salt was suspended in 2 mL of neat PCl_3 (xs) and the resulting mixture heated under Ar at reflux for 4h. The volatiles were removed *in vacuo* and the residue was cautiously treated with 5 mL of sat $NaHCO_3$, and the resulting suspension extracted five times with 5 mL portions of CH_2Cl_2, the combined organic phases dried over $MgSO_4$, and the solvent removed *in vacuo*. The residue was purified by column chromatography (silica gel, elution by EtOAc/hexane (1:2, v/v)) afforded 339.9 mg (78%) of **3b** as a white solid, mp 144-145 °C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 - 7.70 (m, 2H), 7.60 (m, 1H), 7.58 (m, 1H), 7.51 - 7.43 (m, 5H), 7.32 (t J = 8.1 Hz, 1H, 4.47 (s, 2H).

HRMS. Calcd for $C_{14}H_{12}N_2O_2S$: 272.0620. Found: 272.0634.

General Procedures for Diels-Alder Reactions of 1,2-Diaza-1,3-butadienes

Method A: *In situ* generation of the diazadiene from diazinones **2** and sulfur analogue **8**

Adduct **6d**

A suspension of 36 mg (0.1 mmol) of **2d** and 87 mg (0.5 mmol) of N-phenyl maleimide in toluene (1.5 mL) was heated at reflux under Ar for 7.5 h or until tlc analysis showed no further evolution. The mixture was concentrated *in vacuo* and the residual oil was purified by chromatography (silica gel, elution by a gradient from 10% to 25% EtOAc/hexane) to afford 46 mg (95 %) of **6d** as an off-white solid, mp 233 – 235 °C (dec), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2H), 7.51-6.90 (m, 17H), 5.80 (d, J = 3.3 Hz, 1H), 5.15 (d, J = 9.0 Hz, 1H), 3.56 (dd, J_1 = 9.0, J_2 = 3.3 Hz, 1H), 2.02 (s, 3H).

HRMS. Calcd for $C_{31}H_{25}N_3O_3$: 487.1896. Found: 487.1912.

Adduct **6e** from **2f**:

A suspension of 194 mg (0.5 mmol) of **2f** and 433 mg (2.5 mmol) of N-phenyl maleimide in mesitylene (1 mL) was heated under gentle reflux for 3 h or until tlc analysis showed no further evolution. The mixture was concentrated *in vacuo* and the residual red residue was purified by chromatography (silica gel, elution by a gradient from 15% to 30% EtOAc/hexane) to afford a yellow solid which was triturated with 15% EtOAc in hexanes and dried *in vacuo* to afford 203 mg (83 %) of **6e** as an off-white solid, mp 222 - 224 °C (dec): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, J = 9.0 Hz, 2H) 7.71 (d, J= 8.4 Hz, 2H), 7.61 (d, J= 7.5 Hz, 2H), 7.47 - 7.37 (m, 8H), 7.16 (d, Jb= 6.9 Hz, 2H), 7.13 (t, 1H), 7.03 (d,, J = 9.0 Hz 2H), 6.01 (d, J = 3.3 Hz, 1H), 5.21 (d, J = 9.3 Hz, 1H), 3.65 (dd, J_1 = 9.3 Hz, J_2 = 3.6 Hz, 1H).

Anal. Calcd for $C_{34}H_{30}N_4O_7$ (**6e** + EtOAc): C, 67.32; H, 4.98; N, 9.23. Found: C, 67.57; H, 5.01; N, 9.28.

Adduct **6e** from **8**

A suspension of 202.7 mg (0.5 mmol) of **8** and 433 mg (2.5 mmol) of N-phenyl maleimide in toluene (2 mL) was heated under gentle reflux for 7 h or until tlc analysis showed no further evolution. The mixture was concentrated *in vacuo* and the residual red residue was purified by chromatography (silica gel, elution by a gradient from 15% to 30% EtOAc/hexane) to afford a yellow solid which was triturated with 15% EtOAc in hexanes and dried *in vacuo* to afford 207.2 mg (85 %) of **6e** as an off-white solid, spectroscopically indistinguishable from that obtained from **2f**.

Method B: *In situ* generation of the diazadiene from thidiazinone dioxides

Adduct **6f** from **3b**

A solution of 101 mg (0.37 mmol) of **3b** was dissolved in 2 mL of toluene and 95 mg (0.55 mmol) of N-phenylmaleimide was added. The mixture was heated at reflux under Ar for about 7h, cooled and the solvent removed *in vacuo*. The residue was purified by column chromatorgraphy to afford 123 mg

(88%) of **6f** as a white solid, mp 183 - 184 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 6.4 Hz, 2H), 7.58 (d, J = 9.8 Hz, 2H), 7.45 - 7.35 (m, 8H), 7.23 (d, J = 9.8 Hz, 2H), 7.06 (t, J = 6.4 Hz, 1H), 5.26 (d, J = 9.1 Hz, 1H), 3.71 (dd , J_1 = 9.1, J_2 = 6.0 Hz, 1H), 3.08 (dd, J_1 = 15.3, J_2 = 6.0 Hz, 1H), 3.02 (dd, J_1 = 15.3, J_2 = 6.0 Hz, 1H).

HRMS. Calcd for $C_{24}H_{19}N_3O_2$: 381.1477. Found: 381.1489.

Method C: Diels Alder Reaction of Isolated Diazadiene

Adduct **6a**

A mixture of **1** ($R_1 = R_2 = Ph$)[3] (60 mg, 0.21 mmol) and N-phenyl maleimide (146 mg, 0.84 mmol) in toluene (2 mL) was heated to gentle reflux for 24 hr. The mixture was cooled and evaporated. The resulting residue was purified by column chromatography (silica gel, elution by 25% Et_2O in hexane) afforded 86 mg (89%) of **6a** as white needles, mp 218-220 °C (dec), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, J = 7.8 Hz, 2H), 7.50-7.20 (m, 16H), 7.12 (t, J = 7.8 Hz, 1H), 6.46 (dd, J_1 = 6.0, J_2 = 2.1 Hz, 1H), 5.02 (d, J = 8.4 Hz, 1H), 4.72 (d, J = 6.6 Hz, 1H), 3.60 (dd, J_1 = 8.4, J_2 = 6.6 Hz, 1H).

HRMS. Calcd for $C_{30}H_{23}N_3O_2$: 457.1790. Found: 457.1781.

References:

1) Lawton, G.; Moody, C. J.; Pearson, C. J.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 885-97.

2) (a) Willstätter, R.; Veraguth, H. *Chem. Ber.* **1907**, *40*, 1432-1437. (b) Kuo, C. N.; Wu, M. H.; Chen, S. P.; Li, T. P.; Huang, C. Y.; Yeh, M. Y. *J. Chin. Chem. Soc. (Taipei)* **1994**, *41*, 849-56;

3) Schantl, J.; Karpellus, P. *Monatsh. Chem.* **1978**, *109*, 1081-92.

4) (a) Yde, B.; Yousif, N. M.; Pedersen, U.; Thomsen, I.; Lawesson, S. O. *Tetrahedron* **1984**, *40*, 2047-52. (b) El-Barbary, A. A.; Lawesson, S. O. *Indian J. Chem., Sect. B* **1984**, *23B*, 655-7.

5) (a) Godt, H. C., Jr.; Wann, R. E. *J. Org. Chem.* **1961**, *26*, 4047-51; (b) McKinnon, D. M.; Queen, A. *Can. J. Chem.* **1972**, *50*, 1401-6.

6) Stanley, R. L.; Tarbell, D. S. *J. Org. Chem.* **1977**, *42*, 3686-90.

7) (a) Kitamura, M.; Yoshimura, M.; Kanda, N.; Noyori, R. *Tetrahedron* **1999**, *55*, 8769-8785; (b) Parkes, G. D.; Tinsley, S. G. *J. Chem. Soc.***1934**, 1861-1864.

8) (a) Mazak, P.; Suszko, J. *Roczniki Chem.* **1929**, *9*, 431-33; (b) Mazak, P.; Suszko, J. *Bull. Intern. Acad. Polonaise* **1929A**, 131-142.