SUPPORTING INFORMATION

for

Thionation using Fluorous Lawesson's Reagent

Zoltán Kaleta,^{†,‡} Brian T. Makowski,[†] Tibor Soós,^{*,‡} and Roman Dembinski^{*,†}

[†]) *Department of Chemistry, Oakland University, 2200 N. Squirrel Rd., Rochester, Michigan 48309-4477, USA*

[‡]) *Institute of Biomolecular Chemistry, Chemical Research Center of Hungarian Academy of Science, P.O. Box 17, 1525 Budapest, Hungary*

Email: dembinsk@oakland.edu

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General Information. Commercial chemicals were treated as follows: DMF, distilled from CaH₂ and degassed (freeze and thaw) three times prior to use; THF, ether, hexanes distilled from Na/benzophenone.

4-Bromo-1-butene, 1,2-dichlorobenzene (TCI America), perfluorohexyl iodide (Fluorous Technologies Inc.), phosphorus pentasulfide (Acros Organics), 1-phenyl-1,4-pentanedione, phenol 99+%, 1,2-dibenzoylthane (Lancaster), *N,N'*-bis(*p*-toluoyl)hydrazine (Alfa Aesar), *N*-acetylbenzohydrazide, *N*-(4-methylbenzoyl)glycine (4-methylhippuric acid) (Aldrich), *p*-dioxane (anhydrous, EMD Chemicals), silica gel (J. T. Baker, 60-200 mesh), TLC plates Analtech GF, cat. number 2521 or Merck 60, cat. number 5715, alumina neutral Brockmann activity I, 60-325 mesh (Fisher), were used as received. *N*-(1-Methyl-2-oxohexyl)benzamide (**7a**), *N*-[2-(4-methoxyphenyl)-2-oxoethyl]-4-methylbenzamide¹ (**7b**), 2',3',5'-tri-*O*-acetyl-2'-deoxyuridine² (**11a**), 3',5'-di-*O*-acetyl-5-iodo-2'-deoxyuridine² (**11b**), and heptadecafluorododecyl bromide³ were prepared by known methods.

Fluorous reverse phase (FRP) purification: A glass column (1.5 × 10 cm) or a cartridge packed with Fluorochrom (SiliCycle, fluorous reverse phase silica gel; cartridges SiliaBond Fluorochrom - SiliCycle or FluoroFlash - Fluorous Technologies Inc. can be also used), was wetted with ether and washed with acetonitrile prior to use. The microwave reaction was carried out in an unmodified household microwave oven (Samsung MW5351G, 1.2 kW) at atmospheric pressure.

The NMR spectra were recorded on a Bruker DPX Avance 200 spectrometer (200 MHz for ¹H and 50 MHz for ¹³C). IR spectra were recorded on a Bio Rad FTS-175C spectrometer. Mass spectra and high resolution mass spectra were recorded on a VG ZAB2-SEQ tandem mass high resolution spectrometer instrument or GC/MS Hewlett Packard HP 6890 GC instrument with 5973 mass selective detector. Microanalyses were conducted by Atlantic Microlab. M.p. were recorded on a Büchi apparatus.

1-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyloxy)benzene (1-f₈).

¹ (a) Farouz-Grant, F.; P. S. Portoghese, P. S. *J. Med. Chem.* **1997**, *40*, 1977-1981. (b) Rapoport, H.; Knudsen, C. G. *J. Org. Chem.* **1983**, *48*, 2260-2266.

² (a) Chang, P. K.; Welch, A. D. *J. Med. Chem.* **1963**, *6*, 428-430. (b) Esho, N.; Desaulniers, J.-P.; Davies, B.; Chui, H. M.-P. Rao, M. S.; Chow, C. S.; Szafert, S.; Dembinski, R. *Bioorg. Med. Chem.* **2005**, *13*, 1231-1238.

³ Wilson, S. R.; Cayetano, V.; Yurchenko, M. *Tetrahedron* **2002**, *58*, 4041-4047.

A round bottom flask (100 mL) was charged with phenol (0.660 g, 7.01 mmol), K₂CO₃ (2.900 g, 21.00 mmol), and DMF (50 mL) under N₂ atmosphere. A vigorous stirring was established and the flask was placed in a 70°C oil bath. 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl bromide³ (3.608 g, 6.500 mmol) was added via syringe. After 12 h the mixture was cooled to an ambient temperature, and brine (40 mL) and ether (40 mL) were added. The aqueous layer was washed in a separatory funnel with ether (2 × 20 mL). The combined three organic layers were washed with brine (3 × 30 mL), saturated aqueous Na₂CO₃ (3 × 30 mL), and dried over Na₂SO₄. Solvent was removed by rotary evaporation and the residue was recrystallized from methanol (20 mL) to give **1-f₈** as a white solid (2.629 g, 4.626 mmol, 71%), mp 62-63°C. Anal. Calcd for C₁₈H₁₃F₁₇O: C, 38.04; H, 2.31. Found: C 38.09; H 2.26. MS (EI, 70 eV) *m/z* (rel intensity) 568 (M⁺, 1), 94 (PhOH⁺, 100). IR (KBr) 2884, 1604, 1586, 1502, 1478, 1465, 1384, 1372, 1346, 1327, 1151, 1082, 1071, 1038, 1014, 954, 753, 694, 656 cm⁻¹. NMR (CDCl₃): ¹H 7.21 (t, *J* = 7.9 Hz, 2H, C₆H₅), 6.92-6.78 (m, 3H, C₆H₅), 3.92 (t, *J* = 5.5 Hz, 2H, OCH₂), 2.22-1.91 (m, 2H, CH₂CF₂), 1.90-1.70 (m, 4H, CH₂CH₂CH₂CH₂CF₂); ¹³C{¹H} 159.0, 129.6, 121.0, 114.6, 67.2, 30.8 (t, *J* = 22 Hz), 28.9, 17.5.

2,4-Bis(4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyloxy)phenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (f₈-LR).

A round bottom flask (10 mL) was charged with **1-f₈** (2.273 g, 4.000 mmol), phosphorus pentasulfide (0.0909 g, 0.400 mmol), and 1,2-dichlorobenzene (4 mL), under N₂ atmosphere. After establishing vigorous stirring the flask was heated at 170°C (oil bath). After 1 h the mixture became homogenous. After an additional 3 h the mixture was cooled to an ambient temperature. The precipitate was filtered off and washed with hexanes (3 × 5 mL) to give **f₈-LR** as a pale yellow solid (0.264 g, 0.202 mmol, 51%), mp 146-148°C dec.

The filtrate was placed on a short plug of silica gel (2 × 6 cm) and eluted with hexanes. Low boiling solvent was removed by rotary evaporation to afford the residual **1-f₈** in 1,2-dichlorobenzene. This material can be reused for the same synthesis.

***f*₈-LR** data: MS (EI, 70 eV) *m/z* (rel intensity) 662 ([M/2]⁺, 95), 599 ([M/2-PS]⁺, 7), 125 (100), 63 (PS⁺, 36); HRMS (EI, 70 eV) monomer calcd. for (C₁₈H₁₂F₁₇OPS₂): 661.9796, found: 661.9813. IR (KBr) 2958, 1592, 1562, 1498, 1471, 1409, 1371, 1310, 1295, 1259, 1096, 956, 829, 701, 644, 566 cm⁻¹.

NMR (THF-*d*₈): ¹H 8.48 (dd, *J* = 16.7, 8.7 Hz, 4H, C₆H₄), 7.20 (dd, *J* = 8.7, 3.7 Hz, 4H, C₆H₄), 4.20 (t, *J* = 5.6 Hz, 2H, OCH₂), 2.48-2.12 (m, 4H, CH₂CF₂), 2.04-1.70 (m, 8H, CH₂CH₂CH₂CF₂); ¹³C{¹H} 164.4, 135.6 (d, *J* = 17.2 Hz), *ipso* not observed, 115.6 (d, *J* = 18.8 Hz), 55.1, 31.3 (t, *J* = 21.7 Hz), 29.5, 18.2; ³¹P{¹H} 16.7.

(But-3-en-1-yloxy)benzene⁴ (but-3-en-1-yl phenyl ether, 2).

A round bottom flask (100 mL) was charged with phenol (3.01 g, 32.0 mmol) and anhydrous ethanol (50 mL) under N₂ atmosphere. After establishing vigorous stirring, sodium (0.690 g, 30.0 mmol) was added slowly. After the sodium was totally dissolved, 4-bromo-1-butene (4.050 g, 30.00 mmol) was added via syringe and the flask was placed in an 80°C oil bath. After 12 h the pH of the mixture was still basic, and 4-bromo-1-butene (2.025 g, 15.00 mmol) was added via syringe. After 12 h the pH became neutral and the solvent was removed via rotary evaporation. Brine (40 mL) and ether (40 mL) were added, and the mixture was transferred to a separatory funnel. The aqueous layer was washed with ether (3 × 20 mL). The combined four organic layers were washed with brine (2 × 40 mL), saturated aqueous Na₂CO₃ (40 mL), and dried over Na₂SO₄. Solvent was removed by rotary evaporation to give **2** as a colorless oil (2.00 g, 13.5 mmol, 45%). ¹H and ¹³C NMR spectral data matched those previously reported.⁴

1-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyloxy)benzene (1-*f*₆).

⁴ Westwell, A. D.; Williams, J. M. J. *Tetrahedron* **1997**, 53, 13063-13078.

A Schlenk flask (25 mL) was charged under N₂ atmosphere with **2** (2.964 g, 20.00 mmol), perfluorohexyliodide (9.811 g, 22.00 mmol), and AIBN (0.131 g, 0.798 mmol). The resulting mixture was degassed (freeze and thaw) three times. The flask was placed into a 85°C oil bath. Progress of the reaction was monitored by ¹H NMR. After completion, the volatiles were removed by rotary evaporation, and the crude iodide was used for further reaction.

A 250 mL round bottom flask was charged with lithium aluminum hydride (3.04 g, 80.0 mmol) and ether (80 mL). Crude iodide diluted in ether (40 mL) was added dropwise with stirring. After 2 h water (3 mL) was added carefully, followed by NaOH (15% solution in water, 3 mL) and water (9 mL). The resulting suspension was stirred for 1 h. The solid was filtered off, and the solvent was evaporated from the filtrate by rotary evaporation. The product was crystallized from methanol (20 mL) to give **1-f₆** as a white solid (3.00 g, 6.41 mmol, 32%), mp 44-45°C. Calcd for C₁₈H₁₃F₁₇O: C, 41.04; H, 2.80. Found: C 41.12; H 2.78. MS (EI, 70 eV) *m/z* (rel intensity) 468 (M⁺, 1), 94 (PhOH⁺, 100). IR (KBr) 2958, 2881, 1602, 1587, 1499, 1477, 1386, 1367, 1144, 1083, 1041, 1011, 753, 692 cm⁻¹.

NMR (CDCl₃): ¹H 7.21 (t, *J* = 7.9 Hz, 2H, C₆H₅), 6.92-6.77 (m, 3H, C₆H₅), 3.91 (t, *J* = 5.5 Hz, 2H, OCH₂), 2.22-1.90 (m, 2H, CH₂CF₂), 1.90-1.70 (m, 4H, CH₂CH₂CH₂CH₂CF₂); ¹³C{¹H} 159.0, 129.6, 121.0, 114.6, 67.2, 30.8 (t, *J* = 22 Hz), 28.9, 17.5.

2,4-Bis(4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)phenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (f₆-LR).

A 25 mL round bottom flask was charged with **1-f₆** (5.62 g, 12.0 mmol), phosphorus pentasulfide (0.454 g, 2.00 mmol), and 1,2-dichlorobenzene (8 mL) under N₂ atmosphere. After establishing vigorous stirring the flask was heated at 170°C (oil bath). After 1 h the mixture became homogenous and after an additional 3 h was cooled to an ambient temperature. The precipitate was filtered off and washed with hexanes (3 × 5 mL) to give **f₆-LR** as a pale yellow solid (0.871 g, 0.774 mmol, 39%), mp 184°C.

The filtrate was placed on a short plug of silica gel (2 × 6 cm), and eluted with hexanes. Low boiling solvent was removed by rotary evaporation to afford the residual **1-f₆** in 1,2-dichlorobenzene. This material can be reused for the same synthesis.

f₆-LR data: MS (EI, 70 eV) *m/z* (rel intensity) 562 ([M/2]⁺, 100), 499 ([M/2-PS]⁺, 10), 125 (90), 63 (PS⁺, 67); HRMS (EI, 70 eV) monomer calcd. for (C₁₆H₁₂F₁₃OPS₂): 561.9860, found: 561.9868. IR (KBr) 2958, 1591, 1497, 1471, 1409, 1367, 1311, 1295, 1261, 1184, 1144, 1097, 829, 698, 645, 567 cm⁻¹.

NMR (THF-*d*₈): ¹H 8.47 (dd, *J* = 16.8, 8.7 Hz, 4H, C₆H₄), 7.20 (dd, *J* = 8.7, 3.7 Hz, 4H, C₆H₄), 4.19 (t, *J* = 5.7 Hz, 4H, OCH₂), 2.49-2.11 (m, 4H, CH₂CF₂), 2.02-1.70 (m, 8H, CH₂CH₂CH₂CF₂); ¹³C{¹H} 164.6, 135.7 (d, *J* = 17.2 Hz), *ipso* not observed, 115.6 (d, *J* = 18.8 Hz), 55.3, 31.3 (t, *J* = 21.7 Hz), 29.4, 18.2; ³¹P{¹H} 16.7.

Thiobenzamide⁵ (**4a**) (synthesis with the use of **f₈-LR**).

A Schlenk tube was charged under N₂ atmosphere with the benzamide (**3a**) (0.0242 g, 0.200 mmol), **f₈-Lawesson's reagent** (**f₈-LR**) (0.132 g, 0.100 mmol), THF (4 mL), and stirred at 55°C. After 4 h, when the reaction was completed as determined by TLC, alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **4a** as a yellow solid (0.0258 g, 0.188 mmol, 94%). ¹H and ¹³C NMR spectral data matched a commercial sample.⁶ NMR (CDCl₃): ¹H 7.98-7.83 (m, 2H, C₆H₅), 7.55-7.35 (m, 3H, C₆H₅); ¹³C{¹H} 203.0, 139.3, 132.2, 128.6, 127.0.

Thiobenzamide⁵ (**4a**) (synthesis with the use of **f₆-LR**).

⁵ Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, 87, 229-238.

⁶ <http://www.sigmaaldrich.com/spectra/fnmr/FNMR001416.PDF>

A Schlenk tube was charged under N₂ atmosphere with the benzamide (**3a**) (0.0242 g, 0.200 mmol), *f*₆-Lawesson's reagent (**f₆-LR**) (0.112 g, 0.100 mmol), THF (4 mL), and placed into a 55°C oil bath. After 4 h, when the reaction was completed as determined by TLC, alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **4a** as a yellow solid (0.0253 g, 0.184 mmol, 92%). ¹H and ¹³C NMR spectral data matched a commercial sample.⁶

Thioacetanilide⁵ (**4b**).

A Schlenk tube was charged under N₂ atmosphere with the acetanilide (**3b**) (0.0270 g, 0.200 mmol), *f*₆-Lawesson's reagent (**f₆-LR**) (0.112 g, 0.100 mmol), THF (4 mL), and placed into a 55°C oil bath. After 6 h, when the reaction was completed as determined by TLC, alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **4b** as a yellow solid (0.0295 g, 0.195 mmol, 97%). ¹H and ¹³C NMR spectral data matched a commercial sample.⁷

NMR (CDCl₃): ¹H 9.81 (br s, 1H, NH), 8.97 (br s, 1.2H, NH), 7.7-7.6 (m, 1.3H, C₆H₅), 7.45-7.33 (m, 3.0H, C₆H₅), 7.3-7.1 (m, 1.9H, C₆H₅), 2.73 (s, 2.6H, CH₃), 2.51 (s, 2.0H, CH₃); ¹³C{¹H} 204.7, 200.6, 138.7, 138.1, 129.7, 129.0, 128.1, 127.1, 125.2, 124.0, 36.2, 30.1.

2-Methyl-5-phenylthiophene⁸ (**6a**).

A Schlenk tube was charged under N₂ atmosphere with the 1-phenyl-1,4-pentanedione (**5a**) (0.0352 g, 0.200 mmol), *f*₆-Lawesson's reagent (**f₆-LR**) (0.225 g, 0.200 mmol), THF (4 mL), and placed into a 55°C oil bath. After 4 h, when the reaction was completed as determined by TLC,

⁷ <http://www.sigmaaldrich.com/spectra/fnmr/FNMR001958.PDF>

⁸ Liu, W.-D.; Chi, C.-C.; Pai, I.-F.; Wu, A.-T.; Chung, W.-S. *J. Org. Chem.* **2002**, 67, 9267-9275.

alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **6a** as a white solid (0.0307 g, 0.176 mmol, 88%). ^1H and ^{13}C NMR spectral data matched those reported.⁸

NMR (CDCl_3): ^1H 7.54 (d, $J = 7.2$ Hz, 2H, C_6H_5), 7.34 (t, $J = 7.2$ Hz, 2H, C_6H_5); 7.27-7.19 (m, 1H, C_6H_5), 7.09 (d, $J = 3.3$ Hz, 1H, SC_4H_2), 6.71 (d, $J = 3.3$ Hz, 1H, SC_4H_2), 2.50 (3H, s); $^{13}\text{C}\{^1\text{H}\}$ 142.1, 139.6, 134.8, 128.9, 127.1, 126.3, 125.6, 123.0, 15.6.

2,5-Diphenylthiophene⁹ (**6b**).

A Schlenk tube was charged under N_2 atmosphere with 1,2-dibenzoyl-ethane (**5b**) (0.0238 g, 0.100 mmol), f_6 -Lawesson's reagent (**f₆-LR**) (0.112 g, 0.100 mmol), THF (4 mL), and placed into a 55°C oil bath. After 6 h, when the reaction was completed as determined by TLC, alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **6b** as a white solid (0.0217 g, 0.0918 mmol, 92%). ^1H and ^{13}C NMR spectral data matched those reported.⁸

NMR (CDCl_3): ^1H 7.66-7.55 and 7.43-7.20 (2m, 12H, $2\text{C}_6\text{H}_5$ and SC_4H_2); $^{13}\text{C}\{^1\text{H}\}$ 145.1, 135.7, 130.4, 129.0, 127.1, 125.4.

5-Butyl-4-methyl-2-phenyl-1,3-thiazole (**8a**).

A Schlenk tube was charged under N_2 atmosphere with *N*-(1-methyl-2-oxohexyl)benzamide¹ (**7a**) (0.1165 g, 0.5000 mmol), f_6 -Lawesson's reagent (**f₆-LR**) (0.675 g, 0.600 mmol), THF (16 mL), and placed into a 55°C oil bath. After 6 h, when the reaction was completed as determined by TLC, alumina (4 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile

⁹ Kiryanov, A. A.; Sampson, P.; Seed, A. J. *J. Org. Chem.* **2001**, 66, 7925-7929.

(30 mL). Solvent was evaporated and the residue was purified by silica gel column chromatography (2 × 22 cm, hexanes/ethyl acetate 8:2) to give **8a** ($R_f = 0.7$) as a white solid (0.0555 g, 0.240 mmol, 48%). Second fraction ($R_f = 0.6$) was assigned as an analogous oxazole based upon GC/MS (0.0051 g, 0.024 mmol, 5%).

Data for **8a**: MS (EI, 70 eV) m/z (rel intensity) 231 (M^+ , 100), 188 ($[M-C_3H_7]^+$, 100), 121 ($PhCS^+$, 15), 104 ($PhCNH^+$, 27). HRMS (EI, 70 eV) calcd. for ($C_{14}H_{17}NS$): 231.1082, found: 231.1076. IR (KBr) 2957, 2930, 2872, 2858, 1542, 1502, 1461, 1439, 1378, 1245, 1002, 994, 761, 720, 690 cm^{-1} .

NMR ($CDCl_3$): 1H 7.91-7.86 (m, 2H, C_6H_5), 7.42-7.34 (m, 3H, C_6H_5); 2.75 (t, $J = 7.4$ Hz, 2H, $SC_3HNCH_2CH_2$), 2.40 (s, 3H, CH_3), 1.64 (p, $J = 7.4$ Hz, 2H, $SC_3HNCH_2CH_2$), 1.40 (hex, $J = 7.4$ Hz, 2H, $CH_2CH_2CH_3$), 0.95 (t, $J = 7.4$ Hz, 2H, CH_2CH_3); $^{13}C\{^1H\}$ 163.6, 148.7, 134.1, 132.9, 129.4, 128.9, 126.2, 33.9, 26.3, 22.3, 15.1, 13.9.

5-(4-Methoxyphenyl)-2-*p*-tolylthiazole¹⁰ (**8b**).

A Schlenk tube was charged under N_2 atmosphere with *N*-[2-(4-methoxyphenyl)-2-oxoethyl]-4-methylbenzamide (**7b**) (0.0283 g, 0.100 mmol), f_6 -Lawesson's reagent (**f_6 -LR**) (0.122 g, 0.10 mmol), and placed into an alumina bath inside the microwave oven. After 3 × 1 min full power (1200 W) irradiation alumina (2 g) was added and mixed thoroughly with spatula. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL). Solvent was removed from the filtrate by rotary evaporation and the residue was recrystallized from methanol (1 mL) to give **8b** as a white solid (0.0231 g, 0.0821 mmol, 82%).

NMR ($CDCl_3$): 1H 7.89 (s, 1H, SC_3NH), 7.84 (d, $J = 8.2$ Hz, 2H, C_6H_4), 7.53 (d, $J = 8.2$ Hz, 2H, C_6H_4), 7.25 (d, $J = 8.2$ Hz, 2H, C_6H_4), 6.94 (d, $J = 8.2$ Hz, 2H, C_6H_4), 3.85 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3); $^{13}C\{^1H\}$ 166.6, 159.8, 140.2, 138.8, 138.2, 131.3, 129.8, 128.1, 126.3, 124.2, 114.6, 55.5, 21.6.

¹⁰ Dölling, K.; Zäschke, H.; Schubert, H. *J. Prakt. Chem.* **1979**, 321, 643-654.

2-Methyl-5-phenyl-1,3,4-thiadiazole¹¹ (**10a**).

A Schlenk tube was charged under N₂ atmosphere with *N'*-acetylbenzohydrazide (**9a**) (0.0356 g, 0.200 mmol), *f*₆-Lawesson's reagent (**f₆-LR**) (0.225 g, 0.200 mmol), THF (4 mL), and placed into a 55°C oil bath. After 6 h, when the reaction was completed as determined by TLC, alumina (2 g) was added and the solvent was removed by rotary evaporation. The resulting solid was placed on a column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL). Solvent was removed by rotary evaporation to give **10a** as a white solid (0.0331 g, 0.188 mmol, 94%).

NMR (CDCl₃): ¹H 8.09-7.94 (m, 2H, C₆H₅), 7.59-7.39 (m, 3H, C₆H₅), 2.60 (s, 3H, CH₃); ¹³C{¹H} 165.0, 163.7, 131.6, 129.1, 126.8, 124.0, 11.2.

2,5-Bis(4-methylphenyl)-1,3,4-thiadiazole¹² (**10b**).

A Schlenk tube was charged under N₂ atmosphere with the 4-methyl-*N'*-(4-methylbenzoyl)benzohydrazine (**9b**) (0.0537 g, 0.200 mmol), *f*₆-Lawesson's reagent (**f₆-LR**) (0.225 g, 0.100 mmol), THF (4 mL), and placed into a 55°C oil bath. After 6 h, when the reaction was completed as determined by TLC, alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **10b** as a white solid (0.0496 g, 0.186 mmol, 93%).

NMR (CDCl₃): ¹H 7.91 (d, *J* = 8.2 Hz, 4H, C₆H₅), 7.31 (d, *J* = 8.1 Hz, 4H, C₆H₅), 2.44 (s, 6H, CH₃); ¹³C{¹H} 168.0, 141.6, 129.9, 127.9, 127.6, 21.6.

¹¹ (a) Ikeda, N.; Yada, A.; Takase, K. *Yakugaku Zasshi* **1970**, 90, 95-98; *Chem. Abstr.* **1970**, 72, 90374p. (b) Moss, S. F.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. I* **1982**, 1987-1991. (c) Demchuk, D. V.; Lutsenko, A. I.; Troyanskii, E. I.; Nikishin, G. I. *Izv. Akad. Nauk SSSR Ser. Khim.* **1989**, 1843-1848; *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1989**, 38, 1690-1695.

¹² Okuma, K.; Nagakura, K.; Nakajima, Y.; Kubo, K.; Shioji, K. *Synthesis* **2004**, 1929-1931.

2',3',5'-Tri-*O*-acetyl-4-thiouridine¹³ (12a).

A Schlenk tube was charged under N₂ atmosphere with 2',3',5'-tri-*O*-acetyl-uridine **11a** (0.0741 g, 0.200 mmol), *f*₆-Lawesson's reagent (***f*₆-LR**) (0.225 g, 0.200 mmol), THF (4 mL), and placed into a 55°C oil bath. The reaction, monitored by TLC, was completed after 17 h. Alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL) to give **12a** as a yellow solid (0.0728 g, 0.188 mmol, 94%).

NMR (CDCl₃): ¹H 10.42 (brs, 1H, NH), 7.27 (d, *J* = 7.6 Hz, 1H, H-6), 6.44 (d, *J* = 7.6 Hz, 1H, H-5), 5.99 (d, *J* = 4.6 Hz, 1H, H-1'), 5.45-5.30 (m, 2H, H-2', H-3'), 4.46-4.33 (m, 3H, H-4', H-5'), 2.14, 2.13, and 2.12 (3s, 9H, 3CH₃CO); ¹³C{¹H} 189.9 (C-4), 170.3 (CH₃CO), 169.8 (2CH₃CO), 147.7 (C-2), 133.8 (C-6), 114.0 (C-5), 88.2 (C-1'), 80.1 (C-2'), 73.0 (C-4'), 70.0 (C-3'), 63.1 (C-5'), 20.8 (CH₃CO), 20.5 (2CH₃CO).

3',5'-Di-*O*-acetyl-5-iodo-4-thio-2'-deoxyuridine¹⁴ (12b).

A Schlenk tube was charged under N₂ atmosphere with 3',5'-di-*O*-acetyl-5-iodo-2'-deoxyuridine (**11b**) (0.0438 g, 0.100 mmol), *f*₆-Lawesson's reagent (***f*₆-LR**) (0.112 g, 0.100 mmol) and

¹³ Sung, W. L. *J. Chem. Soc., Chem. Commun.* **1982**, 522-523.

¹⁴ Brancalle, A.; McGuigan, C.; Algain, B.; Savy, P.; Benhida, R.; Fourrey, J.-L.; Andrei, G.; Snoeck, R.; De Clercq, E.; Balzarini, J. *Bioorg. Med. Chem. Lett.* **2001**, 11, 2507-2510.

anhydrous dioxane (4 mL) and placed into a 100°C oil bath. The reaction, monitored by TLC, was completed after 4 h. Alumina (2 g) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FRP silica (2 g). The column was eluted with acetonitrile (20 mL). Solvent was removed, and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate 8:2) to give **12b** as a yellow solid (0.0254 g, 0.0559 mmol, 56%).

NMR (CDCl₃): ¹H 10.34 (brs, 1H, NH), 8.05 (s, 1H, H-6), 6.24 (dd, *J* = 8.0, 5.8 Hz, 1H, H-1'), 5.23 (dt, *J* = 6.4, 2.0 Hz, 2H, H-3'), 4.37 (m, 3H, H-4' and H-5'), 2.62 and 2.55 (2dd, *J* = 5.8, 2.0 Hz, 2H, H-2'), 2.20 (s, 3H CH₃), 2.11 (s, 3H, CH₃); ¹³C{¹H} 188.3 (C-4), 170.5 (COCH₃), 170.3 (COCH₃), 147.7 (C-2), 140.0 (C-6), 86.0 (C-1'), 83.1 (C-4'), 82.9 (C-5), 74.2 (C-3'), 63.9 (C-5'), 38.6 (C-2'), 21.3 (COCH₃), 21.0 (COCH₃).

¹³C NMR spectrum for 1-*f*₆ (CDCl₃)

Current Data Parameters

NAME Zoltan-Supp

EXPNO 38

PROCNO 1

F2 - Acquisition Parameters

Date_ 20050903

Time 15.34

INSTRUM spect

PROBHD 5 mm Multinucl

PULPROG zgdc

TD 37686

SOLVENT CDCl₃

NS 1024

DS 4

SWH 12562.814 Hz

FIDRES 0.333355 Hz

AQ 1.4999528 sec

RG 90.5

DW 39.800 usec

DE 6.00 usec

TE 300.0 K

D1 4.00000000 sec

d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 ¹³C

P1 6.00 usec

PL1 1.00 dB

SFO1 50.3285046 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16

NUC2 ¹H

PCPD2 100.00 usec

PL2 -4.00 dB

PL12 16.72 dB

SFO2 200.1300000 MHz

F2 - Processing parameters

SI 32768

SF 50.3227221 MHz

WDW EM

SSB 0

LB 3.00 Hz

GB 0

PC 1.40

¹H NMR spectrum for **1-f₆** (CDCl₃)

¹³C NMR spectrum for **1-f₈** (CDCl₃)

¹H NMR spectrum for **1-f₈** (CDCl₃)

¹³C NMR spectrum for *f*₆-LR (THF-*d*₈)

¹H NMR spectrum for *f*₆-LR (THF-*d*₈)

MS for f_6 -LR

¹³C NMR spectrum for *f*₈-LR (THF-*d*₈)

MS for *f*₈-LR

¹³C NMR spectrum for **4a** (CDCl₃)

¹³C NMR spectrum for **4b** (CDCl₃)

¹H NMR spectrum for **4b** (CDCl₃)

¹³C NMR spectrum for **6a** (CDCl₃)

¹H NMR spectrum for **6a** (CDCl₃)

2,5-diphenylthiophene

143.749
134.445
129.061
127.653
125.765
124.137
123.851

77.798
77.164
76.528

¹³C NMR spectrum for **6b** (CDCl₃)

Current Data Parameters
NAME Zoitan-Supp
EXPNO 62
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051005
Time 18.50
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgdc
TD 37686
SOLVENT CDCl3
NS 700
DS 4
SWH 12562.814 Hz
FIDRES 0.333355 Hz
AQ 1.4999528 sec
RG 90.5
DW 39.800 usec
DE 6.00 usec
TE 300.0 K
D1 4.0000000 sec
d11 0.0300000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 1.00 dB
SF01 50.3285046 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 16.72 dB
SF02 200.1300000 MHz

F2 - Processing parameters
SI 32768
SF 50.3226589 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

2,5-diphenylthiophene

7.640
7.632
7.622
7.596
7.412
7.405
7.370
7.362
7.332
7.293
7.286
7.269
7.260
7.247
7.220

Current Data Parameters
NAME Zoltan-Supp
EXPNO 61
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051005
Time 17.39
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 4096
SOLVENT CDCl3
NS 16
DS 2
SWH 2796.421 Hz
FIDRES 0.682720 Hz
AQ 0.7324148 sec
RG 724.1
DW 178.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -3.00 dB
SFO1 200.1313509 MHz

F2 - Processing parameters
SI 32768
SF 200.1300170 MHz
WDW EM
SSB 0
LB 0.03 Hz
GB 0
PC 1.00

^1H NMR spectrum for **6b** (CDCl_3)

¹³C NMR spectrum for **8a** (CDCl₃)

Current Data Parameters
 NAME Zoltan-Supp
 EXPNO 98
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051114
 Time 21.44
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 2048
 DS 4
 SWH 12562.814 Hz
 FIDRES 0.333355 Hz
 AQ 1.4999528 sec
 RG 143.7
 DW 39.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 4.0000000 sec
 d11 0.0300000 sec

==== CHANNEL f1 =====
 NUC1 13C
 P1 6.00 usec
 PL1 1.00 dB
 SF01 50.3285046 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -4.00 dB
 PL12 16.72 dB
 SF02 200.1300000 MHz

F2 - Processing parameters
 SI 32768
 SF 50.3227263 MHz
 EM
 WDW 0
 SSB 3.00 Hz
 LB 0
 GB 0
 PC 1.40

¹H NMR spectrum for **8a** (CDCl₃)

¹³C NMR spectrum for **8b** (CDCl₃)

¹H NMR spectrum for **8b** (CDCl₃)

2-methyl-5-phenyl-1,3,4-thiadiazole

```

Current Data Parameters
NAME      Zoltan-Supp
EXPNO     50
PROCNO    1

F2 - Acquisition Parameters
Date_     20050921
Time      22.36
INSTRUM   spect
PROBHD    5 mm Multinucl
PULPROG   zgdc
TD         37686
SOLVENT   CDCl3
NS         2048
DS         4
SWH        12562.814 Hz
FIDRES     0.333355 Hz
AQ         1.4999528 sec
RG         90.5
DW         39.800 usec
DE         6.00 usec
TE         300.0 K
D1         4.0000000 sec
d11        0.0300000 sec

===== CHANNEL f1 =====
NUC1       13C
P1         6.00 usec
PL1        1.00 dB
SFO1       50.3285046 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        -4.00 dB
PL12       16.72 dB
SFO2       200.1300000 MHz

F2 - Processing parameters
SI          32768
SF          50.3227263 MHz
WDW         EM
SSB         0
LB          3.00 Hz
GB          0
PC          1.40
    
```

^{13}C NMR spectrum for **10a** (CDCl_3)

¹H NMR spectrum for **10a** (CDCl₃)

¹³C NMR spectrum for **10b** (CDCl₃)

¹H NMR spectrum for **10b** (CDCl₃)

¹³C NMR spectrum for **12a** (CDCl₃)

¹H NMR spectrum for **12a** (CDCl₃)

¹³C NMR spectrum for **12b** (CDCl₃)

¹H NMR spectrum for **12b** (CDCl₃)