Synthesis and Application of a Fluorous Lawesson's Reagent: Convenient Chromatography-Free Product Purification

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General Information: All structures were verified by one- and two-dimensional NMR experiments. NMR spectra were recorded on a 400 MHz (for ¹H) Varian INOVA spectrometer using a Varian 5mm ¹H-¹⁹F/{¹⁵N-³¹P} Z-gradient indirect detection probe as well as a direct detection Varian ¹⁵N-³¹P/{¹H-¹⁹F} switchable broadband probe. ¹H and ¹³C chemical shifts are referenced to the residual solvent signals. Fluorine shifts are given relative to CFCl₃ (δ_{CFCl₃} = 0.0 ppm). ³¹P chemical shifts are referenced to the external reference: 85% H₃PO₄ in capillary. For ³¹P decoupled ¹H-NMR spectra the WURST adiabatic heteronuclear decoupling scheme was used.¹ Infrared spectra were recorded on a Thermo Nicolet Avatar 320 FT-IR spectrometer and are reported in frequency in wavenumbers. Mass spectra and high resolution mass spectra were obtained on VG ZAB2-SEQ tandem mass spectrometer. Melting points were determined by a Büchi apparatus and are uncorrected. All weights for small scale reactions were measured on a Mettler Toledo AX 105 DeltaRange®. All microwave experiments were conducted in Prolabo Synthewave S402 with constant 600W irradiation.

2-Methoxybenzaldehyde, anisaldehyde, 2,4-dimethoxybenzaldehyde, 2-methoxycinnamaldehyde, 10% Pd/C were obtained from Aldich and used as received. The 99.95 % quality perdeuterated solvents were purchased from Cambridge Isotope Laboratories. Fluorous reverse phase silica gel (FluoroFlashTM SPE cartridge 2 grams, 8 cc tube) was purchased from Fluorous Technologies Inc.. After fluorous solid phase extractions the neutral alumine was discarded and the cartridges were regenerated by washing subsequently with acetone, THF methanol and THF. THF was distilled from sodium/benzophenone prior to use.

1-[(1E/Z)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundec-1-en-1-yl]-2-methoxybenzene (I)

A 250 mL round bottom flask was charged with 2-methoxybenzaldehyde (1.360 g, 10.0 mmol), $R_{18}CH_2CH_2PPh_3I^2$ (**5**, 9.00 g, 10.8 mmol), K_2CO_3 (1.93 g, 14.0 mmol) and 200 mL of dioxane under an atmosphere of nitrogen. After establishing vigorous stirring, H_2O (0.8 mL) was added via syringe and the flask was moved to 90 °C oil bath. After 12 hours the flask was cooled to near ambient temperature, volatiles were evaporated. The residue was taken up in $CHCl_3$ and water, the phases were partitioned, and the aqueous layer was further extracted with $CHCl_3$ two times. The combined organic layers were washed with water, dried over Na_2SO_4 , and evaporated under reduced pressure. The residue was suspended in hot hexanes, and placed on a short plug of hexanes packed silica gel (5×5 cm), and eluted with hexanes. This filtrate was concentrated in vacuo to provide **I** as a colorless oil (5.124 g, 91 %).

(Z-isomer) 1H -NMR ($CDCl_3$, 400 MHz): 3.05 (dt, $J = 18.6, 7.1$ Hz, 2H, CH_2), 3.85 (s, 3H, CH_3), 5.81 (dt, $J = 11.4, 7.1$ Hz, 1H, =CH), 6.89 (d, $J = 11.4$ Hz, 1H, =CH), 6.93 (d, $J = 8.2$ Hz, 1H, Ar-H), 6.95-7.01 (m, 1H, Ar-H), 7.18 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.28-7.34 (m, 1H, Ar-H). ^{13}C -NMR ($CDCl_3$, 100 MHz):* 30.8 (t, $^2J_{C-F} = 22.1$ Hz, CH_2), 55.3 (CH_3), 110.7 (CH), 118.1 (t, $^3J_{C-F} = 4.2$ Hz, CH), 120.3 (CH), 124.8 (C), 129.2 (CH), 129.5 (CH), 131.5 (CH), 157.1 (C).

* CF carbons are not listed

IR (KBr) cm^{-1} ; 1601, 1491, 1467, 1206, 1151, 754.

MS (EI, 70 eV) m/z (rel intensity) 566 (M^+ , 96), 547 ($[M-F]^+$, 16), 147 ($[M-R_{18}]^+$, 100);

HRMS (EI, 70 eV) calcd. for $(C_{18}H_{11}F_{17}O)$: 566.0538, found: 566.0523.

1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyl)-2-methoxybenzene (3a)

A 500 mL round bottom flask was charged with **I** (2.830 g, 5.0 mmol), 200 mL of ethanol, 100 mL of ethylacetate and 10% Pd/C (280 mg). The flask was evacuated and back-filled with H₂ (3×, 1 bar). The reaction mixture was stirred for 12 h at room temperature. The flask was flushed with nitrogen and the reaction mixture was filtered over a short pad of Celite (ethyl acetate eluent) and the solvent was evaporated in vacuo to afford pure **3a** as a colorless oil (2.755 g, 97%).

¹H-NMR (CDCl₃, 400 MHz): 1.89-2.01 (m, 2H, CH₂), 2.05-2.21 (m, 2H, CH₂), 2.75 (t, *J* = 7.6 Hz, 2H, CH₂), 3.86 (s, 3H, CH₃), 6.90 (d, *J* = 8.2 Hz, 1H, Ar-H), 6.91-6.96 (m, 1H, Ar-H), 7.16 (dd, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.22-7.28 (m, 1H, Ar-H). ¹³C-NMR (CDCl₃, 100 MHz)*: 20.4 (t, ³*J*_{C-F} = 3.4 Hz, CH₂), 29.7 (CH₂), 30.6 (t, ²*J*_{C-F} = 21.9 Hz, CH₂), 55.1 (CH₃), 110.3 (CH), 120.5 (CH), 127.6 (CH), 129.2 (C), 129.9 (CH), 157.5 (C).

* CF carbons are not listed

IR (KBr) 2950, 1603, 1496, 1468, 1245, 1146, 1032, 753, 658 cm⁻¹;

MS (EI, 70 eV) *m/z* (rel intensity): 568 (M⁺, 47), 549 ([M-F]⁺, 11), 121 ([M-R₈-CH₂-CH₂]⁺, 100)

HRMS (EI, 70 eV) calcd. for(C₁₈H₁₃F₁₇O): 568.0695, found: 568.0710.

1-[1(E/Z)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundec-1-en-1-yl]-4-methoxybenzene (II)

A 250 mL round bottom flask was charged with anisaldehyde (680 mg, 5.0 mmol), $R_{f8}CH_2CH_2PPh_3I$ ² (**5**, 4.500 g, 5.4 mmol), K_2CO_3 (0.966 g, 7.0 mmol) and 130 mL of dioxane under an atmosphere of nitrogen. After establishing vigorous stirring, H_2O (0.4 mL) was added via syringe and the flask was moved to 90 °C oil bath. After 12 hours the flask was cooled to near ambient temperature, volatiles were evaporated. The residue was taken up in $CHCl_3$ and water, the phases were partitioned, and the aqueous layer was further extracted with $CHCl_3$ two times. The combined organic layers were washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was suspended in hot hexanes, and placed on a short plug of hexanes packed silica gel (1×1 cm), and eluted with hexanes. This filtrate was concentrated in vacuo to provide **II** as a colorless oil (1.650 g, 58 %);

(Z-isomer) 1H -NMR ($CDCl_3$, 400 MHz): 3.12 (dt, $J = 18.4, 6.9$ Hz, 2H, CH_2), 3.83 (s, 3H, CH_3), 5.63 (dt, $J = 11.4, 7.1$ Hz, 1H, =CH), 6.77 (d, $J = 11.4$ Hz, 1H, =CH), 6.90-6.95 (m, 2H, Ar-H), 7.17-7.22 (m, 2H, Ar-H). ^{13}C -NMR ($CDCl_3$, 100 MHz)*: 30.6 (t, $^2J_{C-F} = 22.8$ Hz, CH_2), 55.2 (CH_3), 113.9 (CH), 116.4 (t, $^3J_{C-F} = 4.8$ Hz, CH), 129.7 (CH), 134.9 (CH), 159.1 (C).

* CF carbons are not listed

IR (KBr) 1610, 1513, 1243, 1207, 1177, 1151, 1114 cm^{-1} ;

MS (EI, 70 eV) m/z (rel intensity) 566 (M^+ , 88), 547 ($[M-F]^+$, 24), 147 ($[M-R_{f8}]^+$, 100);

HRMS (EI, 70 eV) calcd. for($C_{18}H_{11}F_{17}O$): 566.0538, found: 566.0518.

1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyl)-4-methoxybenzene (**3b**)

A 250 mL round bottom flask was charged with **II** (1415 mg, 2.5 mmol), 100 mL of ethanol, 50 mL of ethylacetate and 10% Pd/C (140 mg). The flask was evacuated and back-filled with H_2 (3×, 1 bar). The reaction mixture was stirred for 12 h at room temperature. The flask was flushed with nitrogen and the reaction mixture was filtered over a short pad of Celite (ethyl acetate eluent) and the solvent was evaporated in vacuo to afford pure **3b** as a white solid (1392 mg, 98%). mp: 36-37 °C;

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): 1.89-1.99 (m, 2H, CH_2), 2.01-2.18 (m, 2H, CH_2), 2.65 (t, $J = 7.6$ Hz, 2H, CH_2), 3.80 (s, 3H, CH_3), 6.83-6.91 (m, 2H, Ar-H), 7.10-7.16 (m, 2H, Ar-H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz)*: 22.1 (t, $^3J_{\text{C-F}} = 3.6$ Hz, CH_2), 30.3 (t, $^2J_{\text{C-F}} = 22.4$ Hz, CH_2), 34.1 (CH_2), 55.2 (CH_3), 114.0 (CH), 129.3 (CH), 132.7 (C), 158.1 (C).

* CF carbons are not listed

IR (KBr) 2962, 1610, 1515, 1245, 1202, 1148, 1115, 1027, 664 cm^{-1} ;

HRMS (EI, 70 eV) calcd. for ($\text{C}_{18}\text{H}_{13}\text{F}_{17}\text{O}$): 568.0695, found: 568.0698.

1-[(1E/Z)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundec-1-en-1-yl]-2,4-dimethoxybenzene (III)

A 250 mL round bottom flask was charged with 2,4-dimethoxybenzaldehyde (830 mg, 5.0 mmol), $\text{R}_{18}\text{CH}_2\text{CH}_2\text{PPh}_3\text{I}^2$ (**5**, 6.270 g, 7.5 mmol), K_2CO_3 (1.035 g, 7.5 mmol) and 130 mL of dioxane under an atmosphere of nitrogen. After establishing vigorous stirring, H_2O (0.4 mL) was added via syringe and the flask was moved to 90 $^\circ\text{C}$ oil bath. After 3 days the flask was cooled to near ambient temperature, volatiles were evaporated. The residue was taken up in CHCl_3 and water, the phases were partitioned, and the aqueous layer was further extracted with CHCl_3 two times. The combined organic layers were washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was suspended in hot hexanes, and placed on a short plug of hexanes packed silica gel (5 $\times$ 5 cm), and eluted with hexanes. This filtrate was concentrated in vacuo to provide **III** as a colorless oil (2.740 g, 92 %);

(Z-isomer) $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): 3.04 (dt, $J = 18.9, 7.1$ Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 5.72 (dt, $J = 11.3, 7.2$ Hz, 1H, =CH), 6.44-6.53 (m, 2H, Ar-H), 6.81 (d, $J = 11.3$ Hz, 1H, =CH), 7.09 (d, $J = 9.3$ Hz, 1H, Ar-H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz)*: 30.8 (t, $^2J_{\text{C-F}} = 22.6$ Hz, CH_2), 55.3 (CH_3), 55.4 (CH_3), 98.6 (CH), 104.0 (CH), 116.9 (t, $^3J_{\text{C-F}} = 4.5$ Hz, CH), 117.6 (C), 129.9 (CH), 131.0 (CH), 158.2 (C), 160.7 (C).

* CF carbons are not listed

IR (KBr) cm^{-1} 1613, 1506, 1468, 1210, 1152, 1038.

MS (EI, 70 eV) m/z (rel intensity) 596 (M^+ , 58), 577 ($[\text{M}-\text{F}]^+$, 14), 177 ($[\text{M}-\text{R}_{\text{f8}}]^+$, 50), 151 ($[\text{M}-\text{R}_{\text{f8}}-\text{CH}=\text{CH}]^+$, 100);

HRMS (EI, 70 eV) calcd. for($\text{C}_{19}\text{H}_{13}\text{F}_{17}\text{O}_2$): 596.0644, found: 596.0633.

1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyl)-2,4-dimethoxybenzene (3c)

A 250 mL round bottom flask was charged with **III** (1.788 g, 3.0 mmol), 100 mL of ethanol, 50 mL of ethylacetate and 10% Pd/C (180 mg). The flask was evacuated and back-filled with H_2 (3 $\times$, 1 bar). The reaction mixture was stirred for 12 h at room temperature. The flask was flushed with nitrogen and the reaction mixture was filtered over a short pad of Celite (ethyl acetate eluent) and the solvent was evaporated in vacuo to afford pure **3c** as a white solid (1.758 g, 98%). mp: 28-30 $^{\circ}\text{C}$;

^1H -NMR (CDCl_3 , 400 MHz): 1.84-1.95 (m, 2H, CH_2), 2.01-2.18 (m, 2H, CH_2), 2.66 (t, $J = 7.6$ Hz, 2H, CH_2), 3.82 (s, 6H, CH_3), 6.46 (dd, $J = 8.0, 2.1$ Hz, 1H, Ar-H), 6.49 (d, $J = 2.1$ Hz, 1H, Ar-H), 7.03 (d, $J = 8.0$ Hz, 1H, Ar-H). ^{13}C -NMR (CDCl_3 , 100 MHz)*: 20.6 (t, $^3J_{\text{C-F}} = 3.4$ Hz, CH_2), 29.0 (CH_2), 30.5 (t, $^2J_{\text{C-F}} = 22.5$ Hz, CH_2), 55.1 (CH_3), 55.3 (CH_3), 98.6 (CH), 103.9 (CH), 121.5 (C), 130.1 (CH), 158.4 (C), 159.6 (C).

* CF carbons are not listed

IR (KBr) 2962, 1512, 1245, 1202, 1148, 1115, 1027, 664 cm^{-1} ;

MS (EI, 70 eV) m/z (rel intensity) 598 (M^+ , 52), 579 ($[\text{M}-\text{F}]^+$, 21), 151 ($[\text{M}-\text{R}_{\text{f8}}-\text{CH}_2-\text{CH}_2]^+$, 100), 121 ($[\text{M}-\text{R}_{\text{f8}}-58]^+$, 22);

HRMS (EI, 70 eV) calcd. for($\text{C}_{19}\text{H}_{15}\text{F}_{17}\text{O}_2$): 598.0801, found: 598.0829.

1-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptafluorotrideca-1,3-dien)-1-yl-2-methoxybenzene (6)

A 1 L round bottom flask was charged with 2-methoxycinnamaldehyde (**4**, 3.240 g, 20.0 mmol), $R_{f8}CH_2CH_2PPh_3I^2$ (**5**, 20.90 g, 25.0 mmol), K_2CO_3 (5.520 g, 40.0 mmol) and 500 mL of dioxane under an atmosphere of nitrogen. After establishing vigorous stirring, H_2O (5.0 mL) was added via syringe and the flask was moved to 90 °C oil bath. After 12 hours the flask was cooled to near ambient temperature, volatiles were evaporated. The residue was taken up in $CHCl_3$ and water, the phases were partitioned, and the aqueous layer was further extracted with $CHCl_3$ two times. The combined organic layers were washed with water, dried over Na_2SO_4 . and evaporated under reduced pressure. The residue was suspended in hot hexanes, and placed on a short plug of hexanes packed silica gel (6×6 cm), and eluted with hexanes. This filtrate was concentrated in vacuo to provide **6** as a white solid (10.250 g, 86%) mp: 81-82°C;

(E,Z-isomer) 1H -NMR ($CDCl_3$, 400 MHz): 3.12 (dt, $J = 18.6, 8.3$ Hz, 2H, CH_2), 3.88 (s, 3H, CH_3), 5.50 (dt, $J = 10.6, 7.6$ Hz, 1H, =CH), 6.51-6.59 (m, 1H, =CH), 6.91 (d, $J = 8.3$ Hz, 1H, Ar-H), 6.95-7.01 (m, 1H, Ar-H), 7.02-7.06 (m, 2H, =CH), 7.25-7.31 (m, 1H, Ar-H), 7.52 (d, $J = 7.8$ Hz, 1H, Ar-H). ^{13}C -NMR ($CDCl_3$, 100 MHz)*: 30.1 (t, $^2J_{C-F} = 23.4$ Hz, CH_2), 55.3 (CH_3), 110.9 (CH), 116.0 (t, $^3J_{C-F} = 4.1$ Hz, CH), 120.7 (CH), 123.3 (CH), 125.9 (C), 127.0 (CH), 129.2 (CH), 130.7 (CH), 135.7(C), 157.2 (C).

* CF carbons are not listed

IR (KBr) 1597, 1491, 1251, 1202, 1148, 752, 657 cm^{-1} ;

MS (EI, 70 eV) m/z (rel intensity) 592 (M^+ , 94), 573 ($[M-F]^+$, 10), 173 ($[M-R_{f8}]^+$, 40), 159 ($[M-R_{f8}-CH_2]^+$, 100), 144 ($[173-29]^+$, 13);

HRMS (EI, 70 eV) calcd. for($C_{20}H_{13}F_{17}O$): 592.0695, found: 592.0672.

1-(6,6,7,7,8,8,9,10,10,11,11,12,12,13,13,13-heptafluorotridecyl)-2-methoxybenzene (7).

A 1.0 L autoclave was charged with **6** (9.500 g, 16.0 mmol) 300 mL of ethanol, 200 mL of ethylacetate and 10% Pd/C (950 mg). The autoclave was evacuated and back-filled with H₂ (3×, 5 bar). The reaction mixture was stirred for 12 h at room temperature. The flask was flushed with nitrogen and the reaction mixture was filtered over a short pad of Celite (ethyl acetate eluent). After removal of volatiles the crude product was bulb-to-bulb distilled (200 °C at 2.1*10⁻¹ mbar) in a Kugelrohr apparatus to yield pure **7** as a white solid (9.046 g, 95%). mp: 29-30 °C;

¹H-NMR (CDCl₃, 400 MHz): 1.40-1.50 (m, 2H, CH₂), 1.59-1.72 (m, 4H, CH₂), 1.98-2.16 (m, 2H, CH₂), 2.61-2.68 (m, 2H, CH₂), 3.84 (s, 3H, CH₃), 6.86 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.88-6.93 (m, 1H, Ar-H), 7.13 (dd, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.17-7.23 (m, 1H, Ar-H). ¹³C-NMR (CDCl₃, 100 MHz)*: 19.9 (t, ³*J*_{C-F} = 3.9 Hz, CH₂), 28.8 (CH₂), 29.4 (CH₂), 29.8 (CH₂), 30.8 (t, ²*J*_{C-F} = 22.5 Hz, CH₂), 55.2 (CH₃), 110.2 (CH), 120.4 (CH), 127.0 (CH), 129.8 (CH), 130.6 (C), 157.4 (C).

* CF carbons are not listed

IR (KBr) 1497, 1471, 1245, 1209, 1146, 1038, 755, 659 cm⁻¹;

MS (EI, 70 eV) *m/z* (rel intensity) 596 (M⁺, 37), 577 ([M-F]⁺, 10), 122 ([M-R₈-(CH₂)₄]⁺, 100), 91 ([122-30]⁺, 31);

HRMS (EI, 70 eV) calcd. for(C₂₀H₁₇F₁₇O): 596.1008, found: 596.1007.

2,4-bis[3-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptafluorotridecyl)-4-methoxyphenyl]-1,3,2,4-dithiadiphosphetane 2,4-disulfide (8).

A 50 mL round bottom flask was charged with **7** (8.940 g, 15.0 mmol), phosphorous pentasulfide (**2**, 341 mg, 1.5 mmol), and 10 mL of dry 1,2-dichlorobenzene under an atmosphere of argon. The reaction mixture was stirred at 150 °C for 4 hours then cooled to ambient temperature. The resulted precipitate was filtered off and washed with anhydrous hexanes to yield **8** as pale yellow solid (937 mg, 0.68 mmol, 45%). mp: 115-118 (dec.). The filtrate was concentrated in vacuo and bulb-to-bulb distilled (200 °C at 2.1×10^{-1} mbar) in a Kugelrohr apparatus to recover the starting material **7** (6.711 g, 82% efficiency).

The NMR characterization of fluororous Lawesson's reagent (**8**) is rather difficult due to its low solubility in organic solvents (solubility $\leq$ ca. 3 mM) and the high tendency to hydrolyze. When **8** was dissolved into THF- d_8 a single component (probably a monomer) was observed (**Figure S18**). Its ^{31}P shift in C_6D_6 was 17.5 ppm. (**Figure S17**) which is consistent with literature data, however, in THF- d_8 different shift was observed (79.4 ppm, **Figure S20**). Nevertheless THF- d_8 proved to be the best solvent appropriate for reproducible characterization of **8** with respect to sample purity. Additional we note that at room temperature it was not possible to run direct ^{13}C experiments due to the low solubility. However, we gained further structural details by two dimensional proton detected heterocorrelated spectra ^1H - ^{13}C -HSQC, ^1H - ^{13}C -HMQC and ^1H -DOSY NMR. With the latter method aliphatic and aromatic protons were correlated in the diffusion dimension. The DOSY experiment was carried out at 25 °C in a 2 mm capillary inserted in a 3 mm NMR tube to minimize convection effects. Performa I. gradient amplifier

(max. 20 gauss/cm) was used. The gradient strength was calibrated by using 5w/w% sucrose in D₂O at 25 °C ($D=5.22E^{-10}$ m²/s). The *bipolar pulse-pair stimulated echo* (Dbppste) sequence was used for acquiring diffusion data with 50 ms diffusion delay, 16 squared increments for gradient levels and 64 transients. The Varian DOSY package was used for the processing.

¹H-NMR (THF-d₈, 400 MHz, 3mM): 1.43-1.52 (m, 2H, CH₂), 1.60-1.70 (m, 4H, CH₂), 2.10-2.27 (m, 2H, CH₂), 2.64-2.72 (m, 2H, CH₂), 3.87 (s, 3H, CH₃), 6.99 (dd, $J_{H-H}=8.4$ Hz, $J_{H-P}=3.6$, 1H, Ar-H), 7.76 (dd, $J_{H-H}=1.9$ Hz, $J_{H-P}=15.1$, 1H, Ar-H), 8.73 (ddd, $J_{H-H}=8.4$, $J_{H-H}=1.9$ Hz, $J_{H-P}=14.9$, 1H, Ar-H). ¹³C-NMR (THF-d₈, 100 MHz, HSQC/HMQC)*: 21.0 (CH₂), 29.7 (CH₂), 30.4 (CH₂), 30.9 (CH₂), 31.5 (CH₂), 55.9 (CH₃), 110.4 (CH), 130.7, (d, $J_{C-P}=28.5$ Hz, CH) 131.2 (C), 132.4 (CH), 161.4 (C). ¹⁹F-NMR (THF-d₈, 376MHz): -81.4 (t, $J=10.0$ Hz, 3F), -114.7 (m, 2F), -122.3 (m, 2F), -122.4 (m, 4F), -123.3 (m, 2F), -124.0 (m, 2F), -126.7 (m, 2F). ³¹P-NMR (THF-d₈, 30°C, 162 MHz): 79.4 (t, $J_{H-P}=15.0$ Hz, 1P).

* CF carbons are not listed

IR (KBr) 2937, 2859, 2853, 1588, 1489, 1255, 1203, 1150, 1111, 1032, 818, 681, 624 cm⁻¹;

MS (EI, 70 eV) m/z (rel intensity) 690 ([M/2]⁺, 100), 627 ([M/2-PS]⁺, 76), 215 ([M/2-R₈-(CH₂)₅]⁺, 41), 152 ([215-PS]⁺, 17);

HRMS (EI, 70 eV) monomer calcd. for (C₂₀H₁₆F₁₇OPS₂): 690.0109, found: 690.0136; (monomer-PS) calcd. for (C₂₀H₁₆F₁₇OS): 627.0650, found: 627.0642.

General procedures for use of fluoros Lawesson's reagent (**8**), thermal thionation reactions.

Under an argon atmosphere a Schlenk tube was charged with the corresponding amide **9a-g** (0.2 mmol), fluoros Lawesson's reagent **8** (138 mg, 0.1 mmol) and 4 mL of anhydrous THF. After the reaction was complete 2.0 g of neutral aluminium oxide (Brockmann II, neutral) was added and the solvent was evaporated to dryness. The resulting solid was placed on a short column packed with FluoroFlashTM SPE silica (2.0 g). The column was eluted with methanol/water 8/2 and evaporated to dryness to give the pure product **10a-g**.

N,N-Dimethylthioacetamide (**10a**)⁴

The reaction was carried out for 1.5 h according to the general thermal thionation procedure.

$^1\text{H-NMR}$: (CDCl_3 , 200 MHz) δ 3.48 (s, 3H, N- CH_3), 3.29 (s, 3H, N- CH_3); 2.64 (s, 3H, CH_3); IR (KBr) 2932, 1535, 1420, 1390, 1362, 1278, 1180, 1124, 1015, 864, 656 cm^{-1} ; MS (EI, 70 eV) m/z (rel intensity) 103 (M^+ , 100), 88 ($[\text{M}-\text{CH}_3]^+$, 9), 70 ($[\text{M}-\text{SH}]^+$, 27), 59 ($[\text{CH}_3\text{CS}]^+$, 36), 44 ($[\text{N}(\text{CH}_3)_2]^+$, 30).

N-methylpyrrolidine-2-thione (10b)⁵

The reaction was carried out for 2 h according to the general thermal thionation procedure.

$^1\text{H-NMR}$: (CDCl_3 , 200 MHz) δ 3.72 (t, $J = 7.2\text{ Hz}$, 2H, CH_2), 3.24 (s, 3H, N- CH_3), 3.02 (m, 2H, CH_2), 2.13-1.96 (m, 2H, CH_2); IR (KBr) 2930, 2876, 1529, 1323, 1307, 1126, 1096 cm^{-1} ; MS (EI, 70 eV) m/z (rel intensity) 115 (M^+ , 100), 100 ($[\text{M}-\text{CH}_3]^+$, 26), 82 ($[\text{M}-\text{SH}]^+$, 48).

Azepane-2-thione (10c)³

The reaction was carried out for 2 h according to the general thermal thionation procedure.

$^1\text{H-NMR}$: (CDCl_3 , 200 MHz) δ 9.05 (br s, 1H, N-H), 3.40-3.32 (m, 2H, CH_2), 3.00-2.94 (m, 2H, CH_2), 1.85-1.56 (m, 6H); IR (KBr) 3182, 2936, 2927, 1560, 1440, 1409, 1369, 1348, 1333, 1315, 1261, 1175, 1114, 1070, 980, 779 cm^{-1} ; MS (EI, 70 eV) m/z (rel intensity) 129 (M^+ , 100), 114 ($[\text{M}-\text{NH}]^+$, 45), 101 ($[\text{M}-28]^+$, 49), 96 ($[\text{M}-\text{SH}]^+$, 65), 41 (84), 39 (68), 58 (26), 71 (38), 68 (35).

Thiobenzamide (10d)³

The reaction was carried out for 1.5 h according to the general thermal thionation procedure.

$^1\text{H-NMR}$: (CDCl_3 , 200 MHz) δ 7.86 (m, 2H, Ar-H), 7.55-7.35 (m, 3H, Ar-H); IR (KBr) 3363, 3285, 3161, 1623, 1450, 1400, 1325, 1280, 887, 774, 708, 688, 637, 568 cm^{-1} ; MS (EI, 70 eV) m/z (rel intensity) 137 (M^+ , 100), 121 ($[\text{M-NH}_2]^+$, 35), 104 ($[\text{M-SH}]^+$, 54).

Pyridine-3-carbothioamide (10e)³

The reaction was carried out for 2 h according to the general thermal thionation procedure.

$^1\text{H-NMR}$: (CD_3COCD_3 , 200 MHz) δ 9.20 (br s, 2H, NH_2), 9.12 (d, $J = 1.4$ Hz, 1H, Ar-H), 8.67 (dd, $J = 4.8, 1.4$ Hz, 1H, Ar-H), 8.30 (dt, $J = 8.0, 1.4$ Hz, 1H, Ar-H), 7.4 (dd, $J = 8.0, 4.8$ Hz, 1H, Ar-H); IR (KBr) 3236, 3029, 2961, 2810, 1677, 1588, 1457, 1400, 1311, 1029, 913, 736, 700, 630 cm^{-1} ; MS (EI, 70 eV) m/z (rel intensity) 138 (M^+ , 100), 122 ($[\text{M-NH}_2]^+$, 12), 105 ($[\text{M-SH}]^+$, 65), 78 (Pyr^+ , 20).

6-methyl-2H-1,4-benzoxazine-3(4H)-thione (10f)

The reaction was carried out for 1 h according to the general thermal thionation procedure.

$^1\text{H-NMR}$: (CDCl_3 , 200 MHz) δ 10.45 (br s, 1H, N-H), 6.86 (m, 2H, Ar-H), 6.74 (m, 1H, Ar-H), 4.85 (s, 2H, CH_2), 2.29 (s, 3H, CH_3); $^{13}\text{C-NMR}$: (CDCl_3 , 50 MHz) δ 191.7 (CS), 143.3 (C), 132.7 (C), 126.7 (CH), 125.6 (C), 116.8 (CH), 116.3 (CH), 72.9 (CH_2), 20.8 (CH_3); IR (KBr) 3185, 3133, 3031, 2918, 1557, 1509, 1392, 1274, 1231, 1138, 1106, 1009, 860, 808, 788, 644 cm^{-1} ; MS (EI, 70 eV) m/z (rel intensity) 179 (M^+ , 100), 146 ($[\text{M-SH}]^+$, 58), 134 ($[\text{M-CSH}]^+$, 10). HRMS (EI, 70 eV) calcd. for 179.0405, found: 179.0409.

Thioacetanilide (10g)³

The reaction was carried out for 4 h according to the general thermal thionation procedure.

Mixture of Z/E isomers. ¹H-NMR: (CDCl₃, 200 MHz) δ 9.95 (br s, 0.7H, N-H), 9.19 (br s, 0.9H, N-H), 7.68-7.62 (m, 1.7 H, Ar-H), 7.45-7.32 (m, 3.9H, Ar-H), 7.29-7.12 (m, 2.6H, Ar-H), 2.70 (s, 3H, N-CH₃); 2.49 (s, 2.3H, CH₃); IR (KBr) 3167, 3118, 3001, 2967, 1593, 1537, 1494, 1448, 1368, 1151, 706 cm⁻¹; MS (EI, 70 eV) *m/z* (rel intensity) 151 (M⁺, 100), 150 ([M-H]⁺, 71), 136 ([M-CH₃]⁺, 4), 118 ([M-SH]⁺, 31).

General procedures for use fluorous Lawesson's reagent (8) in microwave.

The preparation of thiocoumarin (**10h**) is a representative of the method employed.

A mixture of coumarin (**9h**, 29.22 mg, 0.2 mmol) and fluorous Lawesson's reagent **8** (138 mg, 0.1 mmol) was taken in a glass tube and mixed thoroughly with a spatula. The glass tube was then placed in the microwave oven and irradiated for 3 minutes. On completion of the reaction, followed by TLC, the colored material was mixed with 2.0 g of neutral aluminium oxide (Brockmann II, neutral) and was placed on a short column packed with FluoroFlashTM SPE silica (2.0 g). The column was eluted with methanol/water 8/2 and evaporated to dryness to give the pure **10h**.

Thioacetanilide (10g)³

The reaction was carried out for 3 minutes according to the general method.

Thiocoumarin (10h)⁶

The reaction was carried out for 3 minutes according to the general method .

¹H-NMR: (CDCl₃, 200 MHz) δ 7.65-7.45 (m, 3H, Ar-H), 7.45 (d, J = 9.2 Hz, 1H, =CH), 7.37-7.27 (m, 1H, Ar-H), 7.22 (d, J = 9.2 Hz, 1H, =CH); IR (KBr) 1607, 1552, 1415, 1252, 1206, 1194, 1127, 1094, 816, 764, 749, 592, 456 cm⁻¹; MS (EI, 70 eV) m/z (rel intensity) 162 (M⁺, 90), 118 ([M-CS]⁺, 100), 90 (18), 89 (18).

Thiobenzophenone (10i)⁷

The reaction was carried out for 3 minutes according to the general procedure. The column was eluted with anhydrous acetonitrile to give the product. The product purity was 80 % based upon NMR measurement (20 % starting material left).

¹H-NMR: (CDCl₃, 200 MHz) δ 7.75-7.69 (m, 4H, Ar-H), 7.61-7.52 (m, 2H, Ar-H), 7.44-7.34 (m, 4H, Ar-H);

¹³C-NMR: (CDCl₃, 50 MHz) δ 238.5 (CS), 147.4, 132.1, 129.7, 128.1;

MS (EI, 70 eV) m/z (rel intensity): 198, (M⁺, 95), 165 ([M-SH]⁺, 100), 121 ([M-Ph]⁺, 90), 77 (Ph⁺, 38)

General procedures for the preparation of pyrazoles using fluorous Lawesson's reagent (8).

To a mixture of the corresponding β -ketoamide **9j,k** (0.1 mmol), phenylhydrazine hydrochloride (16 mg, 0.11 mmol) and fluorous Lawesson's reagent **8** (152 mg, 0.11 mmol) was added 1.0 mL of dry THF/pyridine (95/5) solution via syringe. The reaction was stirred at room temperature for 15 min and the flask was transferred to a heating block. After the vial was kept at 55 °C for 14 h, 2.0 g of neutral aluminium oxide (Brockmann II, neutral) was added and the solvent was evaporated. The resulting solid was placed on a short column packed with FluoroFlashTM SPE silica (2.0 g). The column was eluted with methanol/water 8/2 product evaporated to dryness to give the pure product **10j,k**.

N,N-diethyl-3-methyl-1-phenyl-1H-pyrazol-5-amine (10j)^{8,9}

¹H-NMR: (CDCl₃, 200 MHz) δ 7.68 (m, 2H, Ar-H), 7.41 (m, 2H, Ar-H), 7.28 (m, 1H, Ar-H), 5.72 (s, 1H, Pyraz-H), 2.90 (q, J = 7.0 Hz, 4H, N-CH₂), 2.32 (s, 3H, Pyraz-CH₃), 0.99 (t, J = 7.0 Hz, 6H, CH₂-CH₃); IR (KBr) 2973, 2933, 1599, 1554, 1504, 1454, 1382, 1364, 1206, 763, 693 cm⁻¹; MS (EI, 70 eV) m/z (rel intensity) 229 (M⁺, 85), 214 ([M-CH₃]⁺, 100), 200 ([M-C₂H₅]⁺, 10), 186 (8), 184 (9), 77 (24).

3-methyl-N,1-diphenyl-1H-pyrazol-5-amine (10k)^{8,10}

¹H-NMR: (CDCl₃, 200 MHz) δ 7.58-7.21 (m, 7H, Ar-H), 6.99-6.92 (m, 3H, Ar-H), 5.99 (s, 1H, Pyraz-H), 2.33 (s, 3H, Pyraz-CH₃); IR (KBr) 3229, 1594, 1561, 1498, 1417, 1363, 1304, 1260, 750, 696 cm⁻¹; MS (EI, 70 eV) m/z (rel intensity) 249 (M⁺, 100), 116 (9), 91 (6), 77 (30).

Spectra:

Figure S1. ^1H NMR spectra of compound **I**.

Figure S2. ^{13}C NMR spectra of compound I

Figure S3. ^1H NMR spectra of compound **3a**.

Figure S4. ^{13}C NMR spectra of compound **3a**

Figure S5. ¹H NMR spectra of compound **II**.

Figure S6. ¹³C NMR spectra of compound **II**

Figure S7. ¹H NMR spectra of compound **3b**.

Figure S8. ¹³C NMR spectra of compound **3b**

Figure S9. ¹H NMR spectra of compound **III**.

Figure S10. ¹³C NMR spectra of compound **III**

Figure S11. ^1H NMR spectra of compound **3c**

Figure S12. ^{13}C NMR spectra of compound **3c**

Figure S13. ^1H NMR spectra of compound **6**

Figure S14. ^{13}C NMR spectra of compound **6**

Figure S15. ¹H NMR spectra of compound **7**

Figure S16. ¹³C NMR spectra of compound **7**

Figure S17. ^1H - ^{31}P -gHMQC spectrum (C_6D_6 , 25 $^\circ\text{C}$, 400 MHz) of compound **8**. The three bond P-H correlation (15 Hz optimized) is shown as a crosspeak. The horizontal and vertical scales represent the ^{31}P and ^1H chemical shift dimensions respectively.

Figure S18. ¹H-NMR spectrum (25 °C, 400 MHz) of compound **8** when dissolved in THF-d₈

Figure S19. Aromatic region of the ^1H -NMR spectrum (THF- d_8 , 25 °C, 400 MHz) of compound **8**, (a) without ^{31}P decoupling and (b) with ^{31}P bandselective adiabatic heteronuclear decoupling (WURST). Experiment (b) has clarified the unambiguous assignment of the spin system.

Figure S20. Full and partial ^{31}P -NMR spectra (30 °C, 400 MHz) of compound **8** when dissolved in THF- d_8 , (a) and (b) are magnified regions with and without ^1H -decoupling respectively.

Figure S21. ^1H - ^{13}C -gHSQC spectrum (THF- d_8 , 25 $^\circ\text{C}$, 400 MHz) of compound **8**. Direct C-H correlations are shown as crosspeaks. The horizontal and vertical scales represent the ^1H and ^{13}C chemical shift dimensions respectively.

Figure S22. ^1H - ^{13}C -gHMQC spectrum (THF- d_8 , 25 $^\circ\text{C}$, 400 MHz) of compound **8**. Three bond C-H correlations (8 Hz optimized) are shown as crosspeaks. The horizontal and vertical scales represent the ^1H and ^{13}C chemical shift dimensions respectively.

Figure S23. ^1H -DOSY spectrum (THF- d_8 , 25 $^\circ\text{C}$, 400 MHz) of compound **8**. Horizontal scale represents the ^1H chemical shift dimension whereas the vertical scale shows the diffusion dimension ($\times 10^{-10} \text{ m}^2/\text{s}$)

Figure S24. ^1H NMR spectra of compound **10f**

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