Supplementary Information (SI) for Soft Matter.

The effect of thioester linkages on the stability of the ferroelectric nematic phase

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Supplemental Information

1. Thermal Data for GO compounds

For comparative purposes, a selection of compounds containing an ester link were either re-synthesised and analysed, or data extracted from previous work. These results are summarised in Table S1.

*Table S1. Transition temperatures and associated scaled entropy changes (ΔS/R) for the compounds **GO1-GO9**. The calculated dipole moments (μ) are also listed.*

	μ/D	M.P. / °C (ΔS/R)	T_{NFN} / °C *T_{NFI} / °C (ΔS/R)	T_{NI} / °C (ΔS/R)	Originally published
GO1	11.4	139 (10.0)	131 (0.18)	188 (0.16)	[1,2,3†]
GO2	12.5	166 (13.8)	140 (0.47)	155 (0.14)	[1†]
GO3	12.6	145 (11.6)	*[a]113 (1.16)	-	[4]
GO4	12.1	161 (15.0)	143 (0.40)	165 (0.19)	[3†]
GO5	12.7	192 (13.1)	132 (0.48)	139 (0.10)	[5†]
GO6	12.7	167 (15.1)	*104 (1.34)	-	[6†]
GO7	12.1	177 (11.5)	-	198 (0.14)	[1]
GO8	12.9	199 (15.8)	-	169 (0.14)	[1]
GO9	13.9	169 (11.3)	149 (0.95)	-	[1]

[a]Values extracted from DSC cooling traces. †Data extracted from relevant literature.

2. Materials & methods

Reagents All solvents, reagents and starting materials were purchased from Sigma-Aldrich, Fluorochem, TCI Chemicals, Fisher Scientific or Apollo Scientific and were used without further purification unless stated otherwise. Dry solvents were prepared by following appropriate drying procedures and stored over 3 or 4 Å molecular sieves under argon. For anhydrous reactions, glassware was pre-dried in an oven at 120 ℃ overnight and cooled in an argon atmosphere.

Thin Layer Chromatography Unless stated otherwise, reactions were monitored by thin layer chromatography (TLC) using aluminium-backed plates with a coating of Merck Kieselgel 60 F254 silica and the appropriate solvent system. The spots on the plate were visualised by UV light (254 nm), thus allowing the calculation of retention factor (R*f*) values. Some reactions required a phosphomolybdic acid stain to visualise spots.

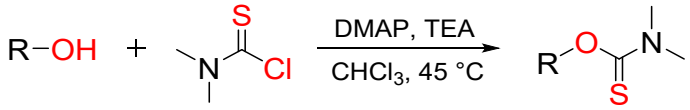
Column Chromatography The separations were carried out with Fluorochem high-purity grade 60 Å silica gel (40-63 micron) using a forced flow of appropriate eluent.

Structural Characterisation and Purity Analysis ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance III HD 400 MHz or a Bruker Avance III HD 600 MHz NMR spectrometers using either $CDCl_3$ or DMSO-*d*6 as solvent. Chemical shifts (δ) are presented in parts per million (ppm). Apparent coupling constants (*J* values) are given in Hertz (Hz) and reported to the nearest 0.1 Hz. Data for H NMR spectra are reported in the order: chemical shift (δ), multiplicity, coupling constants, number of protons. Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ). Infrared spectra were recorded using a Perkin Elmer Spectrum Two FT-IR or a Thermal Scientific Nicolet IR100 FTIR spectrometer with ATR diamond cells. High-resolution mass spectrometry was used to confirm the molecular weight for the synthesised compounds with an accepted difference of up to 5 ppm. Mass spectra were obtained at the University of Aberdeen on a Waters XEVO G2 Q-ToF mass spectrometer calibrated using sodium formate. Lock mass: leucine enkephalin, $C_{28}H_{37}N_5O_7$ [M+H]+: 556.2771.

3. Synthesis & analytical data

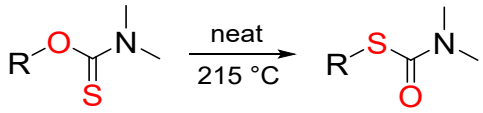
3.1 General Experimental Procedures

General Procedure A1: Preparation of Aryl Thiols (3 step reaction; step 1)



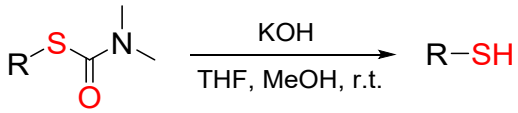
To a pre-dried round bottom flask, the indicated phenol (14.6 mmol, 1 eq.) was dissolved in chloroform (50 mL) and the atmosphere was replaced with argon. DMAP (1.46 mmol, 0.1 eq.) and TEA (43.8 mmol, 3 eq.) were added followed by dimethylthiocarbamoyl chloride (17.5 mmol, 1.2 eq.) and the solution was stirred at 45 ℃ for 72 h. The reaction progress was monitored by TLC. When the reaction was completed, the resulting mixture was cooled to room temperature, diluted with DCM (50 mL) and the organic layer was washed with water (2 x 50 mL), brine (50 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum and the crude was purified by column chromatography on silica gel using the indicated eluent to obtain the desired product.

General Procedure A2: Preparation of Aryl Thiols (3 step reaction; step 2)



To a pre-dried round bottom flask, the indicated thionoester (8 mmol, 1 eq.) was added and the atmosphere was replaced with argon. The material was heated (neat) at 215 ℃ for 2 h while stirring. The reaction progress was monitored by TLC. When the reaction was completed, the contents were cooled to room temperature and the crude was purified by column chromatography on silica gel using the indicated eluent to obtain the desired product.

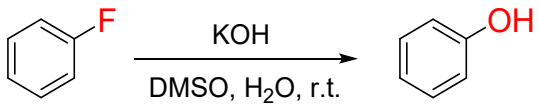
General Procedure A3: Preparation of Aryl Thiols (3 step reaction; step 3)



To a pre-dried round bottom flask, the indicated thioester (6.4 mmol, 1 eq.) was dissolved in THF (10 mL) and a solution of KOH (12.8 mmol, 2 eq.) in MeOH (13 mL)

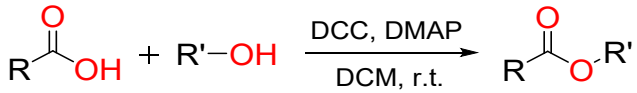
was added. The solution was stirred at room temperature for 3 h and the progress was monitored by TLC. When the reaction was completed, the mixture was acidified to pH 4 by the addition of 1 M hydrochloric acid, the organic solvents were removed under vacuum and replaced with EtOAc (100 mL). The organic layer was washed with water (2 x 50 mL), brine (50 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure to obtain the desired product.

General Procedure B: Preparation of Phenols



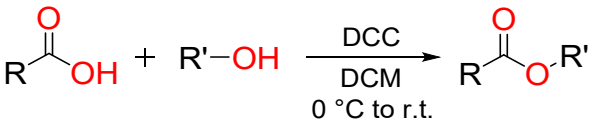
To a round bottom flask, the indicated fluorobenzene (6 mmol, 1 eq.) was dissolved in DMSO (20 mL) and a solution of KOH (12 mmol, 2 eq.) in water (5 mL) was added. The mixture was stirred at room temperature overnight and the progress was monitored by TLC. When the reaction was completed, the resulting suspension was diluted with water (100 mL), the pH was adjusted to pH 4 by the addition of 1 M hydrochloric acid and extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with water (4 x 100 mL), brine (50 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel using the indicated eluent to obtain the desired product.

General Procedure C1: Esterification Method 1



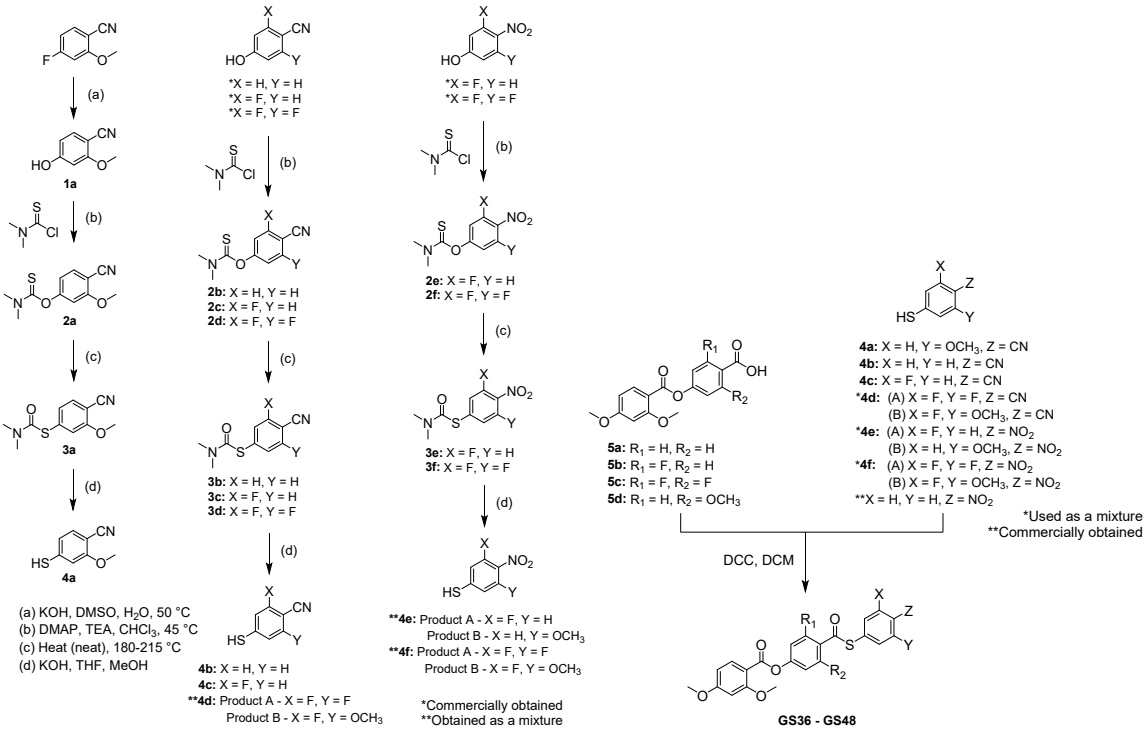
To a round bottom flask, the indicated carboxylic acid (1.1 eq.) was added and dissolved in DCM. The addition of DCC (1.3 eq.) was followed by the indicated phenol or thiophenol (1 eq.) and the mixture was allowed to stir for 2 min before adding DMAP (0.1 eq.). The reaction mixture was stirred overnight at room temperature and the progress was monitored by TLC. When the reaction was completed, the white precipitate was removed by filtration and the solvent was evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel using the indicated eluent to obtain the desired product.

General Procedure C2: Esterification Method 2



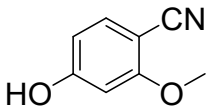
To a round bottom flask, the indicated carboxylic acid (either 1.5 or 2 eq.) was added and dissolved in DCM (50 mL). The reaction mixture was cooled to 0 ℃ before adding DCC (1 eq.) and stirred for 30 min. The indicated phenol or thiophenol (1 eq.) was added and the mixture was allowed to warm to room temperature and stirred overnight. The reaction progress was monitored by TLC. When the reaction was completed, the white precipitate was removed by filtration, and the solvent was evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel using the indicated eluent to obtain the desired product.

Synthetic procedures for GS36-48



Scheme 1. Synthetic route to GS36-48.

4-Hydroxy-2-methoxybenzonitrile (1a)



Prepared according to General Procedure **B**. Quantities used: 4-fluoro-2-methoxybenzonitrile (2.00 g, 13.2 mmol), KOH (1.48 g, 26.4 mmol), DMSO (20 mL), H_2O (5 mL). The reaction mixture was allowed to stir at 50 ℃ for 8 h and the progress was monitored by TLC (Eluent: 20% EtOAc in petroleum ether (40-60), R_f 0.18). A general work up was used with no further purification to obtain the desired product (1.39 g, 70 %). Appearance: White solid.

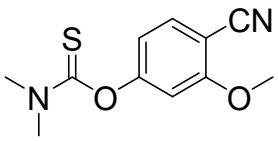
Melting point: 165 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.66 (s, 1H, OH), 7.48 (d, J = 8.5 Hz, 1H, Ar-H), 6.57 – 6.42 (m, 2H, Ar-H), 3.83 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.47, 162.77, 134.80, 117.20, 108.58, 99.44, 90.51, 55.93.

IR (v_{max}/cm^{-1}): 3262 (OH), 2941 (C-H), 2224 (CN), 1601 (Ar C=C), 1583 (Ar C=C).

***O*-(4-Cyano-3-methoxyphenyl)-dimethylcarbamothioate** (**2a**)



Prepared according to General Procedure **A1**. Quantities used: compound **1a** (1.30 g, 8.72 mmol), dimethylthiocarbamoyl chloride (1.30 g, 10.5 mmol), DMAP (0.11 g, 0.87 mmol), TEA (3.65 mL, 2.65 g, 26.2 mmol), chloroform (40 mL). The reaction mixture was allowed to stir for 72 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.38) and recrystallised from EtOH (40 mL) to obtain the desired product (1.53 g, 74 %). Appearance: White solid.

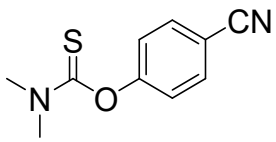
Melting point: 143 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.5 Hz, 1H, Ar-H), 6.76 – 6.70 (m, 2H, Ar-H), 3.91 (s, 3H, OCH_3), 3.45 (s, 3H, NCH_3), 3.34 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.33, 162.28, 158.53, 134.16, 116.14, 115.87, 107.31, 99.39, 56.40, 43.46, 39.06.

IR (v_{max}/cm^{-1}): 2948 (C-H), 2230 (CN), 1537 (Ar C=C), 1491 (Ar C=C).

***O*-(4-Cyanophenyl)-dimethylcarbamothioate** (**2b**)



Prepared according to General Procedure **A1**. Quantities used: 4-hydroxybenzonitrile (3.00 g, 25.2 mmol), dimethylthiocarbamoyl chloride (3.74 g, 30.2 mmol), DMAP (0.31 g, 2.52 mmol), TEA (10.5 mL, 7.64 g, 75.6 mmol), chloroform (60 mL). The reaction mixture was allowed to stir for 72 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.38) and recrystallised from EtOH (80 mL) to obtain the desired product (3.60 g, 69 %). Appearance: Off white solid.

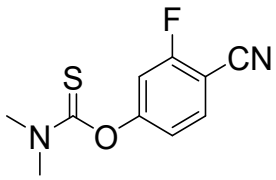
Melting point: 122 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.31 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.36 (s, 3H, NCH_3), 3.32 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 185.23, 157.05, 133.62 (2C), 124.32 (2C), 118.43, 108.48, 42.88, 38.71.

IR (v_{max}/cm^{-1}): 2934 (C-H), 2222 (CN), 1541 (Ar C=C), 1497 (Ar C=C).

***O*-(4-Cyano-3-fluorophenyl)-dimethylcarbamothioate** (**2c**)



Prepared according to General Procedure **A1**. Quantities used: 2-fluoro-4-hydroxybenzonitrile (2.00 g, 14.6 mmol), dimethylthiocarbamoyl chloride (2.17 g, 17.5 mmol), DMAP (0.18 g, 1.46 mmol), TEA (6.09 mL, 4.42 g, 43.8 mmol), chloroform (50 mL). The reaction mixture was allowed to stir for 72 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.63) and recrystallised from EtOH (60 mL) to obtain the desired product (2.77 g, 85 %). Appearance: Pale yellow solid.

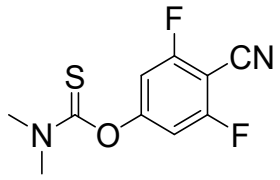
Melting point: 100 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (dd, J = 8.4, 7.7 Hz, 1H, Ar-H), 7.44 (dd, J = 10.4, 2.1 Hz, 1H, Ar-H), 7.19 (ddd, J = 8.6, 2.2, 0.7 Hz, 1H, Ar-H), 3.36 (s, 3H, NCH_3), 3.31 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 184.65, 164.01, 161.46, 158.59, 158.47, 134.23, 134.22, 120.85, 120.81, 113.69, 112.44, 112.22, 97.51, 97.36, 42.94, 38.83.

IR (v_{max}/cm^{-1}): 2932 (C-H), 2237 (CN), 1546 (Ar C=C), 1491 (Ar C=C).

***O*-(4-Cyano-3,5-difluorophenyl)-dimethylcarbamothioate (2d)**



Prepared according to General Procedure **A1**. Quantities used: 2,6-difluoro-4-hydroxybenzonitrile (3.00 g, 19.4 mmol), dimethylthiocarbamoyl chloride (2.89 g, 23.3 mmol), DMAP (0.24 g, 1.94 mmol), TEA (8.10 mL, 5.88 g, 58.2 mmol), chloroform (60 mL). The reaction mixture was allowed to stir for 72 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.55) and recrystallised from EtOH (50 mL) to obtain the desired product (2.37 g, 51 %). Appearance: White solid.

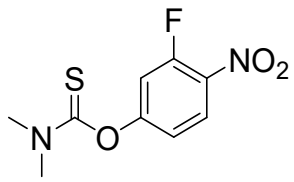
Melting point: 127 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (app d, J = 8.8 Hz, 2H, Ar-H), 3.36 (s, 3H, NCH_3), 3.31 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 184.05, 163.78, 163.71, 161.22, 161.15, 159.37, 159.22, 159.08, 109.34, 109.17, 109.13, 108.94, 108.91, 88.93, 88.73, 88.53, 43.01, 38.96.

IR (v_{max}/cm^{-1}): 2933 (C-H), 2246 (CN), 1556 (Ar C=C), 1499 (Ar C=C).

***O*-(3-Fluoro-4-nitrophenyl)-dimethylcarbamothioate (2e)**



Prepared according to General Procedure **A1**. Quantities used: 3-fluoro-4-nitrophenol (3.00 g, 19.1 mmol), dimethylthiocarbamoyl chloride (2.84 g, 22.9 mmol), DMAP (0.23 g, 1.91 mmol), TEA (7.97 mL, 5.79 g, 57.3 mmol), chloroform (60 mL). The reaction mixture was allowed to stir for 72 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.55) and recrystallised from EtOH (50 mL) to obtain the desired product (2.41 g, 52 %). Appearance: Yellow solid.

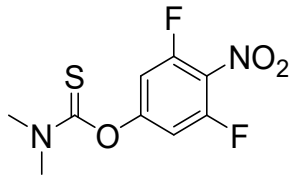
Melting point: 128 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (app t, J = 8.8 Hz, 1H, Ar-H), 7.52 (dd, J = 12.1, 2.3 Hz, 1H, Ar-H), 7.28 – 7.17 (m, 1H, Ar-H), 3.37 (s, 3H, NCH_3), 3.33 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.57, 158.66, 158.55, 157.41, 154.76, 134.96, 134.89, 126.85, 126.83, 119.70, 119.66, 113.95, 113.72, 43.55, 39.18.

IR (v_{max}/cm^{-1}): 2939 (C-H), 1599 (Ar C=C), 1520 (N-O), 1351 (N-O).

***O*-(3,5-Difluoro-4-nitrophenyl)-dimethylcarbamothioate (2f)**



Prepared according to General Procedure **A1**. Quantities used: 3,5-difluoro-4-nitrophenol (3.00 g, 17.1 mmol), dimethylthiocarbamoyl chloride (2.54 g, 20.5 mmol), DMAP (0.21 g, 1.71 mmol), TEA (7.13 mL, 5.18 g, 51.3 mmol), chloroform (60 mL). The reaction mixture was allowed to stir for 72 h. The crude was purified by column chromatography (Eluent: 20% petroleum ether (40-60) in DCM, R_f 0.75) and recrystallised from EtOH (60 mL) to obtain the desired product (2.72 g, 61 %). Appearance: Yellow solid.

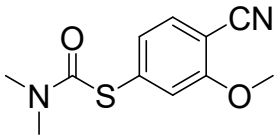
Melting point: 133 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (app d, J = 9.1 Hz, 2H, Ar-H), 3.37 (s, 3H, NCH_3), 3.32 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 184.17, 157.18, 157.04, 156.90, 155.73, 155.69, 153.15, 153.11, 126.66, 126.51, 126.37, 109.79, 109.76, 109.73, 109.59, 109.55, 109.53, 43.03, 38.96.

IR (v_{max}/cm^{-1}): 2971 (C-H), 1600 (Ar C=C), 1534 (N-O), 1301 (N-O).

***S*-(4-Cyano-3-methoxyphenyl)-dimethylcarbamothioate (3a)**



Prepared according to General Procedure **A2**. Quantities used: compound **2a** (1.49 g, 6.31 mmol). The reaction mixture was allowed to stir at 215 ℃ for 2 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.13) to obtain the desired product (0.65 g, 44 %). Appearance: Off white solid.

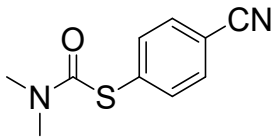
Melting point: 119 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 1H, Ar-H), 7.18 – 7.10 (m, 2H, Ar-H), 3.93 (s, 3H, OCH_3), 3.16 (s, 3H, NCH_3), 3.03 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06, 153.54, 147.85, 133.46, 127.20, 118.00, 116.16, 102.33, 56.35, 37.05, 36.78.

IR (v_{max}/cm^{-1}): 2920 (C-H), 2222 (CN), 1680 (C=O), 1591 (Ar C=C), 1557 (Ar C=C).

***S*-(4-Cyanophenyl)-dimethylcarbamothioate (3b)**



Prepared according to General Procedure **A2**. Quantities used: compound **2b** (3.20 g, 15.5 mmol). The reaction mixture was allowed to stir at 215 ℃ for 4 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.13) to obtain the desired product (1.81 g, 57 %). Appearance: Off white solid.

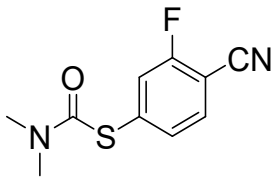
Melting point: 107 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 7.6 Hz, 2H, Ar-H), 7.65 (d, J = 7.6 Hz, 2H, Ar-H), 3.05 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.99, 135.74 (2C), 135.61, 132.25 (2C), 118.50, 112.63, 37.16, 37.04.

IR (v_{max}/cm^{-1}): 2931 (C-H), 2226 (CN), 1666 (C=O), 1590 (Ar C=C), 1482 (Ar C=C).

***S*-(4-Cyano-3-fluorophenyl)-dimethylcarbamothioate (3c)**



Prepared according to General Procedure **A2**. Quantities used: compound **2c** (1.79 g, 7.99 mmol). The reaction mixture was allowed to stir at 215 ℃ for 2 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.15) to obtain the desired product (1.45 g, 81 %). Appearance: White solid.

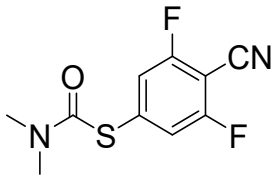
Melting point: 102 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (app t, J = 7.5 Hz, 1H, Ar-H), 7.72 (app d, J = 9.8 Hz, 1H, Ar-H), 7.51 (app d, J = 8.1 Hz, 1H, Ar-H), 3.05 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.08, 163.79, 161.19, 138.40, 138.32, 133.04, 133.03, 130.95, 130.92, 122.77, 122.56, 113.71, 101.70, 101.54, 37.26, 36.98.

IR (v_{max}/cm^{-1}): 2931 (C-H), 2232 (CN), 1661 (C=O), 1601 (Ar C=C), 1562 (Ar C=C).

***S*-(4-Cyano-3,5-difluorophenyl)-dimethylcarbamothioate (3d)**



Prepared according to General Procedure **A2**. Quantities used: compound **2d** (2.00 g, 8.26 mmol). The reaction mixture was allowed to stir at 215 ℃ for 2 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.30) to obtain the desired product (1.70 g, 85 %). Appearance: White solid.

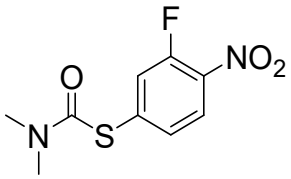
Melting point: 107 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (d, J = 8.6 Hz, 2H, Ar-H), 3.05 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.75, 163.70, 163.22, 161.14, 161.09, 139.87, 139.77, 139.66, 118.02, 117.98, 117.81, 117.77, 109.05, 92.66, 92.47, 92.27, 37.36, 36.97.

IR (v_{max}/cm^{-1}): 2932 (C-H), 2239 (CN), 1671 (C=O), 1602 (Ar C=C), 1561 (Ar C=C).

_S_-(3-Fluoro-4-nitrophenyl)-dimethylcarbamothioate (3e)



Prepared according to General Procedure **A2**. Quantities used: compound **2e** (2.10 g, 8.61 mmol). The reaction mixture was allowed to stir at 190 ℃ for 2 h. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.38) to obtain the desired product (1.89 g, 90 %). Appearance: Pale yellow solid.

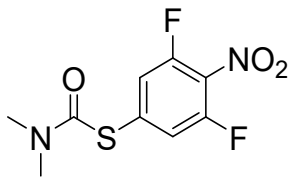
Melting point: 111 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (app t, J = 8.3 Hz, 1H, Ar-H), 7.77 (app d, J = 11.6 Hz, 1H, Ar-H), 7.53 (app d, J = 8.6 Hz, 1H, Ar-H), 3.06 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.89, 156.29, 153.64, 139.21, 139.13, 137.20, 137.13, 130.48, 130.44, 125.92, 125.90, 124.45, 124.23, 37.31, 37.01.

IR (v_{max}/cm^{-1}): 2933 (C-H), 1662 (C=O), 1585 (Ar C=C), 1514 (N-O), 1466 (Ar C=C), 1348 (N-O).

***S*-(3,5-Difluoro-4-nitrophenyl)-dimethylcarbamothioate (3f)**



Prepared according to General Procedure **A2**. Quantities used: compound **2f** (2.60 g, 9.92 mmol). The reaction mixture was allowed to stir at 190 ℃ for 2 h. The crude was purified by column chromatography (Eluent: 20% petroleum ether (40-60) in DCM, R_f 0.38) to obtain the desired product (2.23 g, 86 %). Appearance: Off white solid.

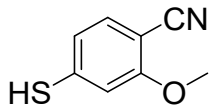
Melting point: 107 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (app d, J = 8.7 Hz, 2H, Ar-H), 3.05 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.35, 155.33, 155.30, 152.71, 152.69, 137.08, 136.98, 136.88, 129.57, 129.39, 129.26, 119.02, 118.99, 118.97, 118.82, 118.80, 118.77, 37.36, 36.96.

IR (v_{max}/cm^{-1}): 2937 (C-H), 1675 (C=O), 1602 (Ar C=C), 1575 (Ar C=C), 1528 (N-O), 1351 (N-O).

4-Mercapto-2-methoxybenzonitrile (4a)



Prepared according to General Procedure **A3**. Quantities used: compound **3a** (0.65 g, 2.75 mmol), KOH (0.31 g, 5.51 mmol), THF (10 mL), MeOH (12 mL). The reaction mixture was allowed to stir for 2 h and the progress was monitored by TLC (Eluent: 100% DCM, R_f 0.58). A general workup was used with no further purification to obtain the desired product (0.37 g, 81 %). Appearance: Pale yellow solid.

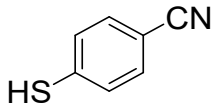
Melting point: 95 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (d, J = 8.2 Hz, 1H, Ar-H), 6.81 (d, J = 1.5 Hz, 1H, Ar-H), 6.78 (dd, J = 8.2, 1.8 Hz, 1H, Ar-H), 3.88 (s, 3H, OCH_3). SH peak is too broad to be assigned.

^{13}C NMR (101 MHz, DMSO-d_6) δ 160.09, 143.62, 134.45, 117.98, 111.50, 109.72, 99.22, 56.63.

IR (v_{max}/cm^{-1}): 2985 (C-H), 2572 (S-H), 2217 (CN), 1592 (Ar C=C), 1557 (Ar C=C).

4-Mercaptobenzonitrile (4b)



Prepared according to General Procedure **A3**. Quantities used: compound **3b** (1.63 g, 7.91 mmol), KOH (0.88 g, 15.8 mmol), THF (10 mL), MeOH (13 mL). The reaction mixture was allowed to stir for 3 h and the progress was monitored by TLC (Eluent: 20% petroleum ether (40-60) in DCM, R_f 0.63). A general workup was used with no further purification to obtain the desired product (0.72 g, 67 %). Appearance: Pale yellow solid.

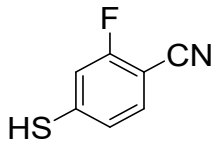
Melting point: 52 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 – 7.58 (m, 2H, Ar-H), 7.58 – 7.35 (m, 2H, Ar-H). SH peak is too broad to be assigned.

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.31, 132.51 (2C), 128.69 (2C), 118.66, 108.71.

IR (v_{max}/cm^{-1}): 3080 (C-H), 2533 (S-H), 2222 (CN), 1590 (Ar C=C), 1484 (Ar C=C).

2-Fluoro-4-mercaptobenzonitrile (4c)



Prepared according to General Procedure **A3**. Quantities used: compound **3c** (1.44 g, 6.43 mmol), KOH (0.72 g, 12.9 mmol), THF (10 mL), MeOH (13 mL). The reaction mixture was allowed to stir for 2 h and the progress was monitored by TLC (Eluent: 20% petroleum ether (40-60) in DCM, R_f 0.50). A general workup was used with no further purification to obtain the desired product (0.78 g, 79 %). Appearance: Off white solid.

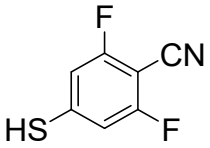
Melting point: 94 ℃

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (app t, J = 7.7 Hz, 1H), 7.51 (dd, J = 10.4, 0.7 Hz, 1H), 7.33 (dd, J = 8.2, 1.0 Hz, 1H). SH peak is too broad to be assigned.

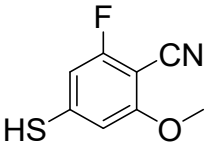
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.24, 161.64, 142.41, 142.33, 133.58, 133.57, 124.59, 124.55, 115.96, 115.74, 113.90, 98.00, 97.85.

IR (v_{max}/cm^{-1}): 3064 (C-H), 2577 (S-H), 2229 (CN), 1601 (Ar C=C), 1554 (Ar C=C).

2,6-Difluoro-4-mercaptobenzonitrile (Product A) and 2-fluoro-4-mercapto-6-methoxybenzonitrile (Product B) (4d)



Product **A**



Product **B**

Prepared according to General Procedure **A3**. Quantities used: compound **3d** (1.65 g, 6.82 mmol), KOH (0.76 g, 13.6 mmol), THF (10 mL), MeOH (13 mL). The reaction mixture was allowed to stir for 2 h and the progress was monitored by TLC. A general workup was used to obtain a mixture of products **A** and **B** (Total yield: 1.02 g, 88 %). Further purification by column chromatography was unsuccessful. Appearance: Pale orange solid.

Product **A**:

Yield: 0.54 g, 47 %

R_f 0.39 (Eluent: 20% petroleum ether (40-60) in DCM)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, J = 9.2 Hz, 2H, Ar-H). SH peak is too broad to be assigned.

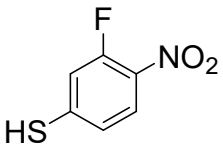
Product **B**:

Yield: 0.48 g, 41 %

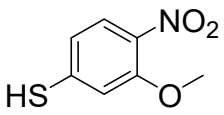
R_f 0.37 (Eluent: 20% petroleum ether (40-60) in DCM)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.25 – 7.00 (m, 2H, Ar-H), 3.92 (s, 3H, OCH_3). SH peak is too broad to be assigned.

3-Fluoro-4-nitrothiophenol (Product A) and 3-methoxy-4-nitrothiophenol (Product B) (4e)



Product **A**



Product **B**

Prepared according to General Procedure **A3**. Quantities used: compound **3e** (1.84 g, 7.54 mmol), KOH (0.85 g, 15.1 mmol), THF (10 mL), MeOH (13 mL). The reaction mixture was allowed to stir for 2 h and the progress was monitored by TLC. A general workup was used to obtain a mixture of products **A** and **B** (Total yield: 1.26 g, 97 %). Further purification by column chromatography was unsuccessful. Appearance: Yellow solid.

Product **A**:

Yield: 0.62 g, 48 %

R_f 0.51 (Eluent: 20% petroleum ether (40-60) in DCM)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (app t, J = 8.5 Hz, 1H, Ar-H), 7.55 (d, J = 12.2 Hz, 1H, Ar-H), 7.40 – 7.28 (m, 1H, Ar-H). SH peak is too broad to be assigned.

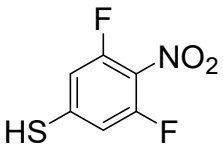
Product **B**:

Yield: 0.64 g, 49 %

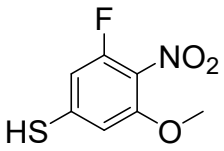
R_f 0.48 (Eluent: 20% petroleum ether (40-60) in DCM)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (d, J = 7.8 Hz, 1H, Ar-H), 7.38 – 7.27 (m, 1H, Ar-H), 7.10 – 6.96 (m, 1H, Ar-H), 3.91 (s, 3H, OCH_3). SH peak is too broad to be assigned.

3,5-Difluoro-4-nitrothiophenol (Product A) and 3-fluoro-5-methoxy-4-nitrothiophenol (Product B) (4f)



Product **A**



Product **B**

Prepared according to General Procedure **A3**. Quantities used: compound **3f** (2.00 g, 7.63 mmol), KOH (0.86 g, 15.3 mmol), THF (10 mL), MeOH (13 mL). The reaction mixture was allowed to stir for 2 h and the progress was monitored by TLC. A general workup was used to obtain a mixture of products **A** and **B** (Total yield: 1.22 g, 84 %). Further purification by column chromatography was unsuccessful. Appearance: Yellow solid.

Product **A**:

Yield: 0.46 g, 32 %

R_f 0.62 (Eluent: 20% petroleum ether (40-60) in DCM)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, J = 10.2 Hz, 2H, Ar-H). SH peak is too broad to be assigned.

Product **B**:

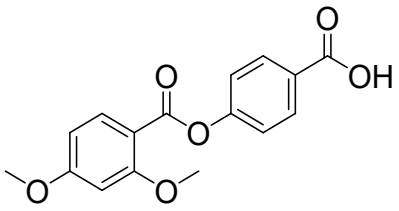
Yield: 0.76 g, 52 %

R_f 0.60 (Eluent: 20% petroleum ether (40-60) in DCM)

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32 – 7.05 (m, 2H, Ar-H), 3.92 (s, 3H, OCH_3). SH peak is too broad to be assigned.

4-((2,4-Dimethoxybenzoyl)oxy)benzoic acid (10a)

Prepared according to procedures reported elsewhere.[3]



Melting point: 202 ℃

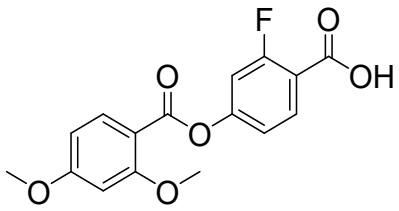
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.02 (s, 1H, COOH), 8.01 (app d, *J* = 8.8 Hz, 2H, Ar-H), 7.96 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.34 (app d, *J* = 8.8 Hz, 2H, Ar-H), 6.72 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.68 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 3.88 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.72, 164.95, 162.59, 161.75, 154.32, 134.02, 130.87 (2C), 128.15, 122.31 (2C), 109.93, 105.75, 99.05, 56.04, 55.75.

IR (v_{max}/cm^{-1}): 3011 (C-H), 2901 (broad OH), 1730 (C=O), 1587 (Ar C=C), 1576 (Ar C=C).

4-((2,4-Dimethoxybenzoyl)oxy)-2-fluorobenzoic acid (10b)

Prepared according to procedures reported elsewhere. [3]



Melting point: 183 ℃

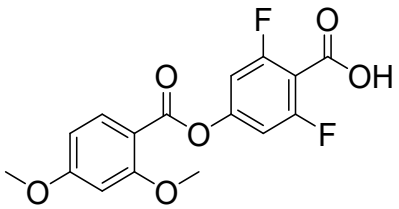
^{1}H NMR (400 MHz, DMSO-d_6): δ 13.29 (s, 1H, COOH), 8.02 – 7.89 (m, 2H, Ar-H), 7.32 (d, *J* = 11.3 Hz, 1H, Ar-H), 7.19 (d, *J* = 6.5 Hz, 1H, Ar-H), 6.76 – 6.63 (m, 2H, Ar-H), 3.87 (s, 6H, OCH_3).

^{13}C NMR (101 MHz, DMSO-d_6): δ 165.12, 164.50 (d), 162.77, 162.04, 161.92, 160.19, 154.88 (d), 134.17, 132.76 (d), 118.45 (d), 116.73 (d), 111.49, 111.23, 109.45, 105.79, 99.02, 56.04, 55.77.

IR (v_{max}/cm^{-1}): 2941 (C-H), 2888 (broad OH), 1688 (C=O), 1598 (Ar C=C).

4-((2,4-Dimethoxybenzoyl)oxy)-2,6-difluorobenzoic acid (10c)

Prepared according to procedures reported elsewhere. [3]



Melting point: 204 ℃

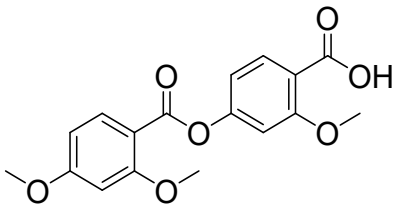
^{1}H NMR (400 MHz, DMSO-d_6): δ 13.84 (s, 1H, COOH), 7.97 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.29 – 7.20 (m, 2H, Ar-H), 6.71 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.67 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar-H), 3.88 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.25, 162.06, 161.82, 161.70, 160.91, 160.81, 158.40, 158.31, 153.37, 153.22, 153.07, 134.29, 110.11, 109.90, 109.71, 109.09, 107.53, 107.50, 107.46, 107.35, 107.27, 107.24, 105.81, 98.99, 56.04, 55.78.

IR (v_{max}/cm^{-1}): 2987 (C-H), 2847 (broad OH), 1757 (C=O), 1577 (Ar C=C).

4-((2,4-Dimethoxybenzoyl)oxy)-2-methoxybenzoic acid (10d)

Prepared according to procedures reported elsewhere. [7]



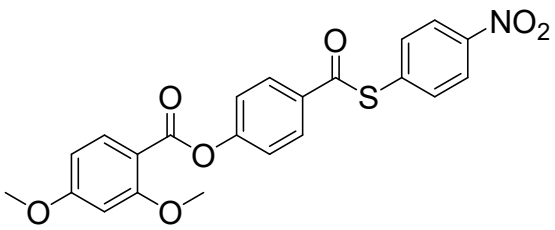
Melting point: 171 ℃

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.59 (s, 1H, COOH), 7.97 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.73 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.01 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.85 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H, Ar-H), 6.72 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.68 (dd, *J* = 8.7 Hz, 2.2 Hz, 1H, Ar-H), 3.88 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ 167.05, 165.36, 162.89, 162.20, 159.91, 154.99, 134.51, 132.29, 118.74, 114.20, 110.38, 107.32, 106.14, 99.46, 56.55, 56.47, 56.19.

IR (v_{max}/cm^{-1}): 2990 (C-H), 2863 (broad OH), 1716 (C=O), 1587 (Ar C=C).

4-(((4-Nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS36)



Prepared according to General Procedure **C1**. Quantities used: compound **5a** (0.30 g, 1.00 mmol), 4-nitrothiophenol (0.14 g, 0.91 mmol), DCC (0.24 g, 1.18 mmol), DMAP (0.01 g, 0.09 mmol), DCM (50 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 2% EtOAc in DCM, R_f 0.55) and recrystallised from EtOH (20 mL) to obtain the desired product (0.05 g, 13 %). Appearance: White solid.

Melting point: 174 ℃, T_{NI} 215 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (app d, *J* = 8.9 Hz, 2H, Ar-H), 8.11 – 8.05 (m, 3H, Ar-H), 7.72 (app d, *J* = 8.9 Hz, 2H, Ar-H), 7.37 (app d, *J* = 8.8 Hz, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.54 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).

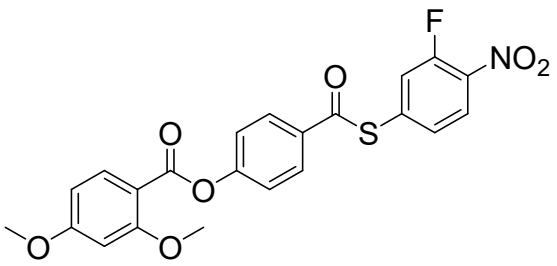
^{13}C NMR (101 MHz, $CDCl_3$) δ 187.05, 165.54, 162.87, 162.66, 156.09, 148.42, 136.18, 135.58 (2C), 134.77, 133.16, 129.28 (2C), 124.10 (2C), 122.76 (2C), 110.46, 105.13, 99.15, 56.18, 55.77.

IR (v_{max}/cm^{-1}): 2980 (C-H), 1743 (C=O), 1595 (Ar C=C), 1573 (Ar C=C), 1510 (N-O), 1346 (N-O).

M/Z: Calculated mass for $C_{22}H_{18}NO_7S$ $[M+H]^+$: 440.0822 Found: 440.0804; Difference: 4.1 ppm.

Data consistent with reported values.[8]

4-(((3-Fluoro-4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS37)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4e** (0.08 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 1% EtOAc in DCM, R_f 0.43) and recrystallised from EtOH (25 mL) to obtain the desired product (0.07 g, 33 %). Appearance: White solid.

Melting point: 186 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (app t, *J* = 8.1 Hz, 1H, Ar-H), 8.11 – 8.04 (m, 3H, Ar-H), 7.56 (dd, *J* = 10.6, 1.3 Hz, 1H, Ar-H), 7.50 – 7.44 (m, 1H, Ar-H), 7.38 (app d, *J* = 8.6 Hz, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.1 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.1 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

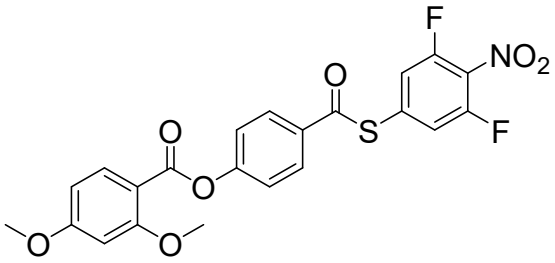
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.72, 165.21, 162.40, 162.20, 155.96, 155.08 (d, $^{1}J_{CF}$ = 266.9 Hz), 137.28 (d, $^{2}J_{CF}$ = 24.2 Hz), 137.11 (d, $^{3}J_{CF}$ = 7.2 Hz) 134.19, 132.52, 130.04 (d, $^{3}J_{CF}$ = 4.2 Hz), 128.83 (2C), 125.85 (d, $^{4}J_{CF}$ = 2.3 Hz), 123.73 (d, $^{2}J_{CF}$ = 22.4 Hz) 122.37 (2C), 110.23, 105.12, 98.90, 55.80, 55.34. .

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.11

IR (v_{max}/cm^{-1}): 2979 (C-H), 1741 (C=O), 1589 (Ar C=C), 1575 (Ar C=C), 1518 (N-O), 1349 (N-O).

M/Z: Calculated mass for $C_{22}H_{16}NO_7FSNa$ $[M+Na]^+$: 480.0542 Found: 480.0529; Difference: 2.7 ppm.

4-(((3,5-Difluoro-4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS38)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.30 g, 0.99 mmol), compound **4f** (0.13 g, 0.66 mmol), DCC (0.14 g, 0.66 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.50) and recrystallised from EtOH (30 mL) to obtain the desired product (0.07 g, 22 %). Appearance: Off white solid.

Melting point: 148 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.05 (app d, *J* = 8.7 Hz, 2H, Ar-H), 7.39 (app d, *J* = 8.7 Hz, 2H, Ar-H), 7.34 (app d, *J* = 7.6 Hz, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).

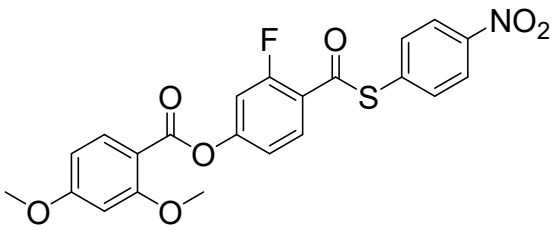
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.78, 165.61, 162.81, 162.71, 156.42, 154.34 (dd, $^{1}J_{CF}$ = 264.1 Hz, $^{3}J_{CF}$ = 2.4, (2C)), 135.19 (t, $^{3}J_{CF}$ = 9.7 Hz) 134.81, 132.62, 129.89 (t, $^{2}J_{CF}$ = 14.9 Hz), 129.37 (2C), 122.93 (2C), 118.94 (dd, $^{2}J_{CF}$ = 21.7 Hz, $^{4}J_{CF}$ = 3.7 Hz, (2C)) 110.37, 105.17, 99.16, 56.20, 55.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.76

IR (v_{max}/cm^{-1}): 2987 (C-H), 1716 (C=O), 1594 (Ar C=C), 1582 (Ar C=C), 1536 (N-O), 1363 (N-O).

M/Z: Calculated mass for $C_{22}H_{15}NO_7F_2SNa$ $[M+Na]^+$: 498.0453 Found: 498.0435; Difference: 3.6 ppm.

3-Fluoro-4-(((4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS39)



Prepared according to General Procedure **C2**. Quantities used: compound **5b** (0.15 g, 0.47 mmol), 4-nitrothiophenol (0.04 g, 0.28 mmol), DCC (0.06 g, 0.28 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 2% EtOAc in DCM, R_f 0.40) and recrystallised from EtOH (30 mL) to obtain the desired product (0.06 g, 51 %). Appearance: White solid.

Melting point: 184 ℃, T_{NI} 186 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (app d, *J* = 8.9 Hz, 2H, Ar-H), 8.06 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.98 (dd, *J* = 8.7, 8.3 Hz, 1H, Ar-H), 7.73 (app d, *J* = 8.9 Hz, 2H, Ar-H), 7.22 – 7.15 (m, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.54 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

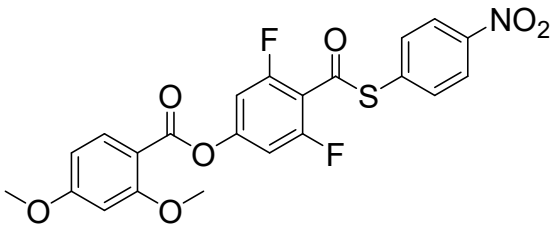
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.24 (d, $^{3}J_{CF}$ = 6.1 Hz), 165.76, 162.72, 161.73 (d, $^{1}J_{CF}$ = 259.8 Hz) 160.13, 156.49 (d, $^{2}J_{CF}$ = 11.5 Hz), 148.54, 135.87 (d, $^{3}J_{CF}$ = 5.4 Hz), 135.64 (2C), 134.84, 130.84 (d, $^{4}J_{CF}$ = 2.7 Hz), 124.14 (2C), 121.49 (d, $^{2}J_{CF}$ = 11.3 Hz), 118.59 (d, $^{3}J_{CF}$ = 3.4 Hz). 111.60, 111.35, 110.00, 105.23, 99.15, 56.19, 55.80.

^{19}F NMR (376 MHz, $CDCl_3$) δ -106.09

IR (v_{max}/cm^{-1}): 2954 (C-H), 1747 (C=O), 1601 (Ar C=C), 1573 (Ar C=C), 1504 (N-O), 1332 (N-O).

M/Z: Calculated mass for $C_{22}H_{17}NO_7FS$ $[M+H]^+$: 458.0716 Found: 458.0710; Difference: 1.3 ppm.

3,5-Difluoro-4-(((4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS40)



Prepared according to General Procedure **C2**. Quantities used: compound **5c** (0.31 g, 0.92 mmol), 4-nitrothiophenol (0.08 g, 0.54 mmol), DCC (0.11 g, 0.54 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 2% EtOAc in DCM, R_f 0.56) and recrystallised from EtOH (40 mL) to obtain the desired product (0.12 g, 49 %). Appearance: Off white solid.

Melting point: 180 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (app d, *J* = 8.9 Hz, 2H, Ar-H), 8.03 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.75 (app d, *J* = 8.9 Hz, 2H, Ar-H), 6.98 (app d, *J* = 8.6 Hz, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.54 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

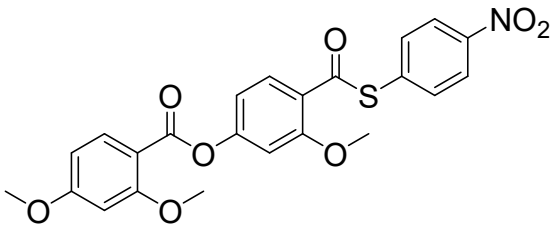
^{13}C NMR (101 MHz, $CDCl_3$) δ
182.22 (t, $^{3}J_{CF}$ = 1.9 Hz), 165.90, 162.88, 162.07, 159.90 (dd, $^{1}J_{CF}$ = 256.0 Hz, $^{4}J_{CF}$ = 8.3 Hz, 2C), 154.96 (t, $^{3}J_{CF}$ = 14.1 Hz), 148.67, 135.27 (2C), 135.22, 134.86, 124.29 (2C), 113.51 (t, $^{2}J_{CF}$ = 18.9 Hz), 109.65, 107.18 (dd, $^{2}J_{CF}$ = 25.4 Hz, $^{4}J_{CF}$ = 3.8 Hz, 2C), 105.30, 99.14, 56.19, 55.82.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.20

IR (v_{max}/cm^{-1}): 2988 (C-H), 1746 (C=O), 1600 (Ar C=C), 1577 (Ar C=C), 1518 (N-O), 1322 (N-O).

M/Z: Calculated mass for $C_{22}H_{15}NO_7F_2SNa$ $[M+Na]^+$: 498.0411 Found: 498.0435; Difference: -4.8 ppm.

3-Methoxy-4-(((4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS41)



Prepared according to General Procedure **C2**. Quantities used: compound **5d** (0.20 g, 0.60 mmol), 4-nitrothiophenol (0.05 g, 0.35 mmol), DCC (0.07 g, 0.35 mmol), DCM (30 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 2% EtOAc in DCM, R_f 0.38) and recrystallised from EtOH (40 mL) to obtain the desired product (0.13 g, 86 %). Appearance: White solid.

Melting point: 165 ℃

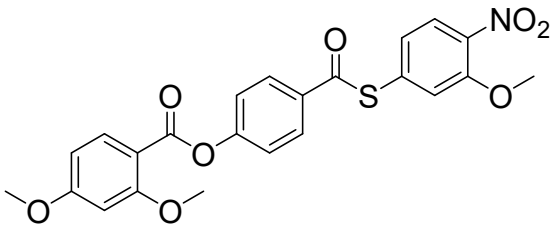
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.08 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.93 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.71 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.97 (d, *J* = 1.9 Hz, 1H, Ar-H), 6.91 (dd, *J* = 8.6, 2.1 Hz, 1H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.1 Hz, 1H, Ar-H), 4.00 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.01, 165.56, 162.80, 162.68, 159.93, 156.62, 148.22, 137.73, 135.59 (2C), 134.79, 131.42, 123.91 (2C), 122.52, 114.57, 110.42, 106.60, 105.14, 99.14, 56.23, 56.20, 55.77.

IR (v_{max}/cm^{-1}): 2945 (C-H), 1738 (C=O), 1598 (Ar C=C), 1570 (Ar C=C), 1511 (N-O), 1346 (N-O).

M/Z: Calculated mass for $C_{23}H_{19}NO_8SNa$ $[M+Na]^+$: 492.0741 Found: 492.0729; Difference: 2.4 ppm.

4-(((3-Methoxy-4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS42)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4e** (0.08 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 1% EtOAc in DCM, R_f 0.23) and recrystallised from EtOH (30 mL) to obtain the desired product (0.07 g, 36 %). Appearance: White solid.

Melting point: 151 ℃

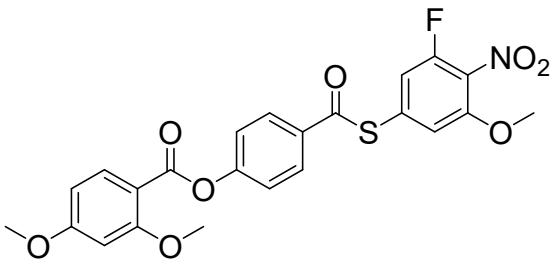
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 3H, Ar-H), 7.91 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.37 (app d, *J* = 8.8 Hz, 2H, Ar-H), 7.31 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.20 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 4.01 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.29, 165.54, 162.88, 162.66, 156.06, 153.03, 139.99, 135.13, 134.77, 133.22, 129.23 (2C), 126.35, 126.07, 122.75 (2C), 119.84, 110.45, 105.14, 99.14, 56.94, 56.18, 55.77.

IR (v_{max}/cm^{-1}): 2953 (C-H), 1743 (C=O), 1598 (Ar C=C), 1577 (Ar C=C), 1523 (N-O), 1343 (N-O).

M/Z: Calculated mass for $C_{23}H_{19}NO_8SNa$ $[M+Na]^+$: 492.0752 Found: 492.0729; Difference: 4.7 ppm.

4-(((3-Fluoro-5-methoxy-4-nitrophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS43)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.30 g, 0.99 mmol), compound **4f** (0.13 g, 0.66 mmol), DCC (0.14 g, 0.66 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 100% DCM, R_f 0.38) and recrystallised from EtOH (40 mL) to obtain the desired product (0.11 g, 34 %). Appearance: Off white solid.

Melting point: 172 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.05 (app d, *J* = 8.9 Hz, 2H, Ar-H), 7.37 (app d, *J* = 8.9 Hz, 2H, Ar-H), 7.09 – 7.03 (m, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.97 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).

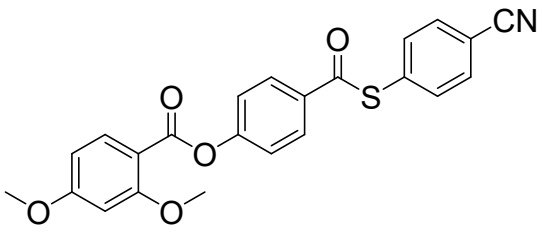
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.85, 165.57, 162.87, 162.69, 156.18, (d, $^{1}J_{CF}$ = 259.2 Hz), 152.50 (d, $^{3}J_{CF}$ = 3.2 Hz), 134.79, 133.05 (d, $^{3}J_{CF}$ = 9.8 Hz), 132.99, 131.14 (d, $^{2}J_{CF}$ = 16.3 Hz), 129.27 (2C), 122.82 (2C), 114.90 (d, $^{2}J_{CF}$ = 20.9 Hz), 114.68 (d, $^{4}J_{CF}$ = 3.3 Hz), 110.42, 105.16, 99.16, 57.30, 56.19, 55.78.

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.47

IR (v_{max}/cm^{-1}): 2987 (C-H), 1747 (C=O), 1602 (Ar C=C), 1588 (Ar C=C), 1530 (N-O), 1333 (N-O).

M/Z: Calculated mass for $C_{23}H_{19}NO_8FS$ $[M+H]^+$: 488.0838 Found: 488.0815; Difference: 4.7 ppm.

4-(((4-Cyanophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS44)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4b** (0.06 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 1% EtOAc in DCM, R_f 0.23) and recrystallised from EtOH (35 mL) to obtain the desired product (0.11 g, 59 %). Appearance: White solid.

Melting point: 191 ℃

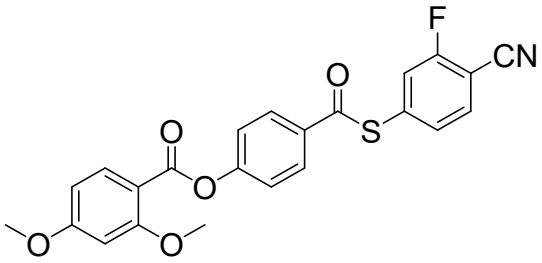
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 3H, Ar-H), 7.74 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.66 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.37 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.61 – 6.52 (m, 2H, Ar-H), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.28, 165.52, 162.88, 162.65, 156.03, 135.48 (2C), 134.77, 134.06, 133.21, 132.65 (2C), 129.24 (2C), 122.72 (2C), 118.38, 113.25, 110.48, 105.13, 99.15, 56.18, 55.76.

IR (v_{max}/cm^{-1}): 2985 (C-H), 2228 (CN), 1743 (C=O), 1598 (Ar C=C), 1570 (Ar C=C).

M/Z: Calculated mass for $C_{23}H_{17}NO_5SNa$ $[M+Na]^+$: 442.0735 Found: 442.0725; Difference: 2.3 ppm.

4-(((4-Cyano-3-fluorophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS45)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4c** (0.07 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40

mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 1% EtOAc in DCM, R_f 0.28) and recrystallised from EtOH (55 mL) to obtain the desired product (0.16 g, 80 %). Appearance: White solid.

Melting point: 212 ℃

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.06 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.70 (app t, *J* = 7.3 Hz, 1H, Ar-H), 7.48 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.44 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.38 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.60 – 6.53 (m, 2H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

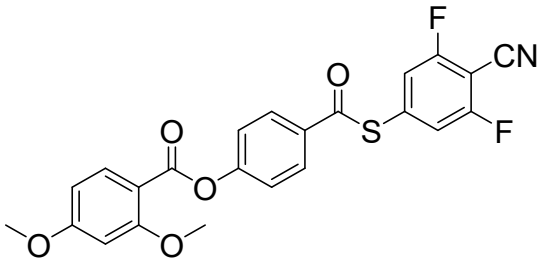
^{13}C NMR (151 MHz, $CDCl_3$) δ 186.49, 165.58, 162.87, 162.79 (d, $^1J_{CF}$ = 259.8 Hz), 162.70, 156.24, 136.68 (d, $^3J_{CF}$ = 8.2 Hz), 134.81, 133.56, 132.95, 130.86 (d, $^3J_{CF}$ = 3.7 Hz), 129.33 (2C), 122.85 (2C), 122.62 (d, $^2J_{CF}$ = 21.0 Hz), 113.60, 110.44, 105.15, 102.38 (d, $^2J_{CF}$ = 15.6 Hz), 99.17, 56.20, 55.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.14

IR (ν_{max}/cm^{-1}): 2952 (C-H), 2234 (CN), 1740 (C=O), 1600 (Ar C=C), 1573 (Ar C=C).

M/Z: Calculated mass for $C_{23}H_{17}NO_5FS$ $[M+H]^+$: 438.0832 Found: 438.0811; Difference: 4.8 ppm.

4-(((4-Cyano-3,5-difluorophenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS46)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4d** (0.08 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 1% EtOAc in DCM, R_f 0.50) and recrystallised from EtOH (30 mL) to obtain the desired product (0.07 g, 33 %). Appearance: White solid.

Melting point: 164 ℃, T_{NI} 170 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.05 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.38 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.30 (d, *J* = 7.4 Hz, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.1 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

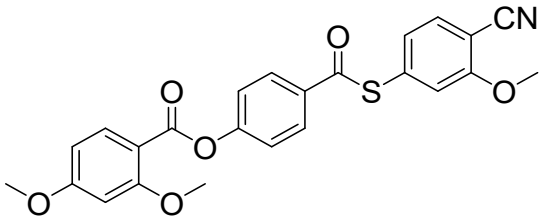
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.63, 165.60, 162.78, 162.74 (dd, $^{1}J_{CF}$ = 264.0, $^{3}J_{CF}$ = 4.6 Hz, (2C)), 162.69, 156.41, 137.98 (t, $^{3}J_{CF}$ = 10.3 Hz), 134.78, 132.61, 129.35 (2C), 122.91 (2C), 117.95 (dd, $^{2}J_{CF}$ = 21.2 Hz, $^{4}J_{CF}$ = 3.9 Hz, (2C)) 110.33, 108.89, 105.16, 99.14, 93.22 (t, $^{2}J_{CF}$ = 19.3 Hz) 56.18, 55.78.

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.01

IR (v_{max}/cm^{-1}): 2949 (C-H), 2241 (CN), 1742 (C=O), 1601 (Ar C=C), 1559 (Ar C=C).

M/Z: Calculated mass for $C_{23}H_{16}NO_5F_2S$ $[M+H]^+$: 456.0719 Found: 456.0717; Difference: 0.4 ppm.

4-(((4-Cyano-3-methoxyphenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS47)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4a** (0.07 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 2% EtOAc in DCM, R_f 0.45) and recrystallised from EtOH (25 mL) to obtain the desired product (0.06 g, 32 %). Appearance: White solid.

Melting point: 196 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 3H, Ar-H), 7.62 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.37 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.21 – 7.15 (m, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.0 Hz, 1H, Ar-H), 3.98 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).

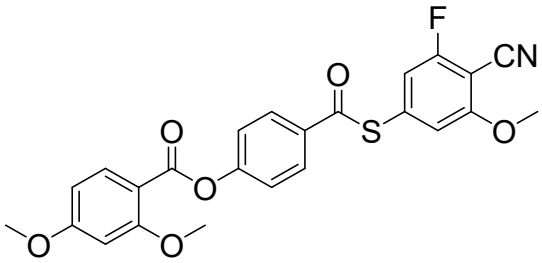
^{13}C NMR (101 MHz, $CDCl_3$) δ 187.45, 165.55, 162.92, 162.68, 161.27, 156.04, 135.32,

134.79, 133.91, 133.31, 129.24 (2C), 126.91, 122.75 (2C), 117.68, 116.05, 110.50, 105.15, 102.95, 99.18, 56.49, 56.20, 55.79.

IR (v_{max}/cm^{-1}): 2996 (C-H), 2229 (CN), 1741 (C=O), 1577 (Ar C=C), 1559 (Ar C=C).

M/Z: Calculated mass for $C_{24}H_{19}NO_6SNa$ $[M+Na]^+$: 472.0846 Found: 472.0831; Difference: 3.2 ppm.

4-(((4-Cyano-3-fluoro-5-methoxyphenyl)thio)carbonyl)phenyl-2,4-dimethoxybenzoate (GS48)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), compound **4d** (0.08 g, 0.44 mmol), DCC (0.09 g, 0.44 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 1% EtOAc in DCM, R_f 0.35) and recrystallised from EtOH (30 mL) to obtain the desired product (0.06 g, 29 %). Appearance: White solid.

Melting point: 201 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.05 (app d, *J* = 8.7 Hz, 2H, Ar-H), 7.37 (app d, *J* = 8.7 Hz, 2H, Ar-H), 7.05 – 6.96 (m, 2H, Ar-H), 6.58 (dd, *J* = 8.7, 2.3 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 3.99 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

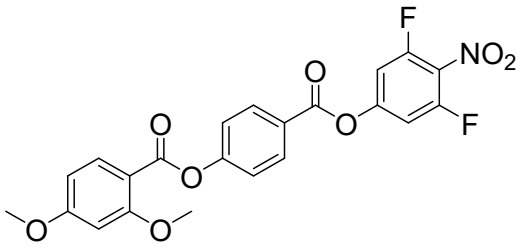
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.63, 165.57, 163.17 (d, $^1J_{CF}$ = 260.9 Hz), 162.84, 162.67, 162.03 (d, $^3J_{CF}$ = 5.2 Hz), 156.19, 136.65 (d, $^3J_{CF}$ = 10.8 Hz), 134.77, 132.98, 129.25 (2C), 122.81 (2C), 114.15 (d, $^2J_{CF}$ = 21.6 Hz), 113.15 (d, $^4J_{CF}$ = 3.3 Hz), 111.18, 110.37, 105.16, 99.13, 92.83 (d, $^2J_{CF}$ = 18.0 Hz) 57.06, 56.17, 55.77.

^{19}F NMR (376 MHz, $CDCl_3$) δ -104.59

IR (v_{max}/cm^{-1}): 2954 (C-H), 2234 (CN), 1742 (C=O), 1599 (Ar C=C), 1576 (Ar C=C).

M/Z: Calculated mass for $C_{24}H_{19}NO_6FS$ $[M+H]^+$: 468.0940 Found: 468.0917; Difference: 4.9 ppm.

Synthetic procedures for GO3, GO7-9
4-((3,5-Difluoro-4-nitrophenoxy)carbonyl)phenyl-2,4-dimethoxybenzoate (GO3)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.20 g, 0.66 mmol), 3,5-difluoro-4-nitrophenol (0.07 g, 0.39 mmol), DCC (0.08 g, 0.39 mmol), DCM (40 mL). The reaction mixture was allowed to stir overnight. The crude was purified by column chromatography (Eluent: 2% EtOAc in DCM, R*f* 0.55) and recrystallised from EtOH (25 mL) to obtain the desired product (0.06 g, 33 %). Appearance: White solid.

Melting Point: 145 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (app d, *J* = 8.8 Hz, 2H, Ar-H), 8.09 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.39 (app d, *J* = 8.8 Hz, 2H, Ar-H), 7.11 (app d, *J* = 8.3 Hz, 2H, Ar-H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH3), 3.90 (s, 3H, OCH3).

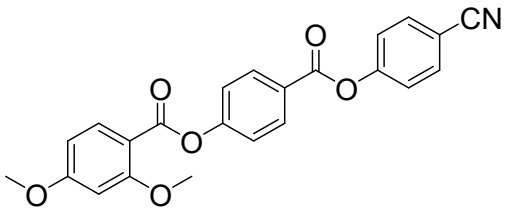
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.59, 162.99, 162.82, 162.70, 155.58 (dd, $^1J_{CF}$ = 262.0 Hz, $^3J_{CF}$ = 4.0 Hz, (2C)), 156.45, 153.78 (t, $^3J_{CF}$ = 13.0 Hz) 134.78, 132.11 (2C), 127.59 (t, $^2J_{CF}$ = 15.2 Hz), 124.88, 122.79 (2C), 110.37, 107.63 (dd, $^2J_{CF}$ = 23.6 Hz, $^4J_{CF}$ = 3.5 Hz, (2C)) 105.16, 99.14, 56.18, 55.77.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.14

IR (v_{max}/cm^{-1}): 3069 (C-H), 1746 (C=O), 1602 (Ar C=C), 1538 (N-O), 1321 (N-O).

M/Z: Calculated mass for $C_{22}H_{15}NO_8F_2Na$ $[M+Na]^+$: 482.0663. Found: 482.0685; Difference: 4.6 ppm

4-((4-Cyanophenoxy)carbonyl)phenyl-2,4-dimethoxybenzoate (GO7)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.60 g, 1.98 mmol), 4-hydroxybenzonitrile (0.12 g, 0.99 mmol), DCC (0.20 g, 0.99 mmol), DCM (50 mL). The crude was purified by column chromatography (eluent: 2 % EtOAc in DCM, R_f 0.54) and recrystallised from toluene (10 ml) to obtained the desired product (120 mg, 30 %). Appearance: white solid.

Melting Point: 177 °C

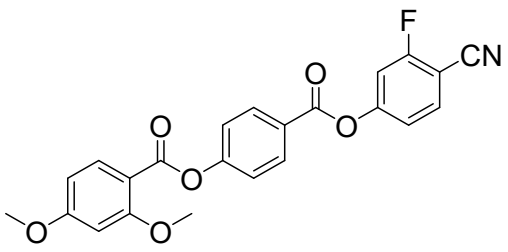
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.19 (m, 2H, Ar-H), 8.09 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.78 – 7.70 (m, 2H, Ar-H), 7.42 – 7.33 (m, 4H, Ar-H), 6.58 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-H), 6.54 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.93 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.48, 163.80, 162.89, 162.62, 156.02, 154.33, 134.73, 133.84 (2C), 131.93 (2C), 125.77, 123.05 (2C), 122.58 (2C), 118.39, 110.47, 109.93, 105.11, 99.11, 56.15, 55.74.

IR (v_{max}/cm^{-1}): 2984 (C-H stretch), 2231 (CN nitrile stretch) 1742 (C=O stretching, ester).

M/Z: Calculated mass for $C_{23}H_{18}NO_6$ $[M+H]^+$: 404.1134. Found: 404.1145; Difference: 2.7 ppm

4-((4-Cyano-3-fluorophenoxy)carbonyl)phenyl-2,4-dimethoxybenzoate (GO8)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.60 g, 1.98 mmol), 2-fluoro-4-hydroxybenzonitrile (0.14 g, 0.99 mmol), DCC (0.20 g, 0.99 mmol), DCM (50 mL). The crude was purified by column chromatography (eluent: 2 %

EtOAc in DCM, R_f 0.43) and recrystallised from toluene (10 ml) to obtained the desired product (101 mg, 24 %). Appearance: white solid.

Melting Point: 199 °C

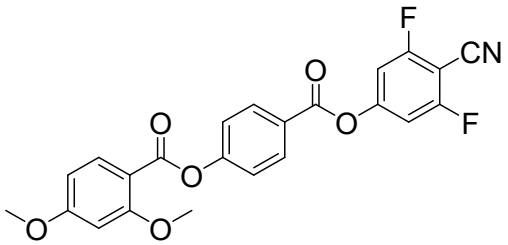
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.19 (m, 2H, Ar-H), 8.10 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.75 – 7.66 (m, 2H, Ar-H), 7.43 – 7.35 (m, 4H, Ar-H), 6.58 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar-H), 6.55 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.28

IR (v_{max}/cm^{-1}): 2988 (C-H stretch), 2234 (CN nitrile stretch) 1740 (C=O stretching, ester).

M/Z: Calculated mass for $C_{23}H_{17}NO_6F$ $[M+H]^+$: 422.1040. Found: 422.1052; Difference: 2.8 ppm

4-((4-Cyano-3,5-difluorophenoxy)carbonyl)phenyl-2,4-dimethoxybenzoate (GO9)



Prepared according to General Procedure **C2**. Quantities used: compound **5a** (0.60 g, 1.98 mmol), 2,6-difluoro-4-hydroxybenzonitrile (0.15 g, 0.99 mmol), DCC (0.20 g, 0.99 mmol), DCM (50 mL). The crude was purified by column chromatography (eluent: 2 % EtOAc in DCM, R_f 0.65) and recrystallised from toluene (10 ml) to obtain the desired product (132 mg, 30 %). Appearance: white solid.

Melting Point: 169 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (m, 2H, Ar-H), 8.09 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.39 – 7.66 (m, 2H, Ar-H), 7.07 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.61-6.52 (m, 1H, Ar-H), 3.94 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.58, 164.94, 162.91, 162.81, 162.70, 162.40, 162.34, 156.45, 156.13, 134.77, 132.11, 124.89, 122.78, 110.36, 108.89, 107.24, 107.20, 107.01, 106.97, 105.16, 99.14, 90.21, 56.18, 55.77.

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.94

IR (v_{max}/cm^{-1}): 2978 (C-H stretch), 2240 (CN nitrile stretch) 1745 (C=O stretching, ester).

M/Z: Calculated mass for $C_{23}H_{16}NO_6F_2$ $[M+H]^+$: 440.0946. Found: 440.0958; Difference: 2.7 ppm

4. References

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