

Supporting Information for

C(sp²)-S cross-coupling reactions with nickel, visible light, and mesoporous graphitic carbon nitride

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1 General Information

All required fine chemicals were purchased from standard commercial chemical suppliers and were used without purification unless stated otherwise. The reactions employed throughout the study were conducted in dehydrated *N,N*-dimethylacetamide (DMA), which was desiccated using 3 Å molecular sieves. Percentage yields refer to the isolated product after purification, unless stated otherwise. Anhydrous NaSO₄ was used as the drying agent unless otherwise specified.

Thin Layer Chromatography

Reactions were monitored by thin layer chromatography (TLC) analysis. This was done with silica gel pre-coated aluminum sheets (ALUGRAM Xtra SIL G UV254 Ref. 818333) and visualized using UV light (254 nm).

Automated Column Chromatography

Standard flash column chromatographic procedures were conducted using an automated Biotage® Isolera™ Spektra system, outfitted with a high-performance flash purification configuration. The chromatographic medium employed was silica gel 60 M (Macherey-Nagel), with a particle size range of 40-63 µm. The elution process was carried out using a mixture of petroleum ether (PE) and ethyl acetate (EtOAc).

NMR analysis

Products were characterized by Nuclear Magnetic Resonance (NMR) spectra for ¹H (400 MHz), ¹³C (100 MHz), and ¹⁹F (376 MHz) were obtained using a Bruker Avance spectrometer, with internal referencing to the residual solvent signals (CDCl₃: ¹H: 7.26 ppm, and ¹³C: 77.07 ppm). ¹H NMR data was documented in terms of chemical shift (ppm), multiplicity, coupling constants (Hz), integral of protons and ¹³C NMR data in terms of chemical shift (ppm).

GC-FID and GC-MS

Gas chromatographic (GC) analyses were performed using a flame-ionization detector (GC-FID) as well as low-resolution mass spectrometry (GC-MS) on a capillary column (30 m in length, 0.25 mm in diameter, and 0.25 µm film thickness), with helium serving as the carrier gas. GC-FID analytics were performed on a 7890B Gas Chromatography (GC) System from

Agilent Technologies, with an oven temperature of 40 °C. GC-MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector.

HR-MS

All compounds were also characterised and confirmed by HR-MS, which was measured at the Central Analytical Laboratory of the University of Regensburg. The spectra were measured on a Jeol AccuTOF GCX, Agilent Q-TOF 6540 UHD, Finnigan MAT SSQ 710 A, or a ThermoQuest Finnigan TSQ 7000 instrument.

2 Photochemical Reaction Setup

Photochemical reactions were conducted using OSRAM Oslon SSL 80 LDCQ7P-1U3U blue LEDs with a peak wavelength of 455 (± 15) nm, the maximum current (I_{\max}) of 1000 mA and the radiant power of approximately 600 mW.

General setup for small-scale reaction for the dual-catalyzed thioetherification cross-coupling reactions.



Figure S1: A depiction of the standard photochemical reaction setup. The illumination of 5 mL crimp cap reaction vials occurs from the bottom using blue LEDs with a wavelength of 455 (± 15) nm and a radiant power of 600 mW. The reaction temperature was maintained at either 25 °C or 60 °C through a custom-made aluminum cooling blocks linked to a thermostat.

Gram scale reaction setup for the thioetherification cross-coupling reaction of 4-bromobenzonitrile with mesitylmethanethiol.



Figure S2: From right to left: A depiction of the standard photochemical reaction setup. The illumination of 15 mL crimp cap reaction vial occurs from the bottom using blue LEDs with a wavelength of 455 (\pm 15) nm and a radiant power of 1500 mW. The reaction temperature was 60 °C through a custom-made aluminum cooling blocks linked to a thermostat.

Commercial photo-setup (7 W) without temperature control for the thioetherification cross-coupling reaction of 4-bromobenzonitrile with ethyl 3-mercaptopropionate.

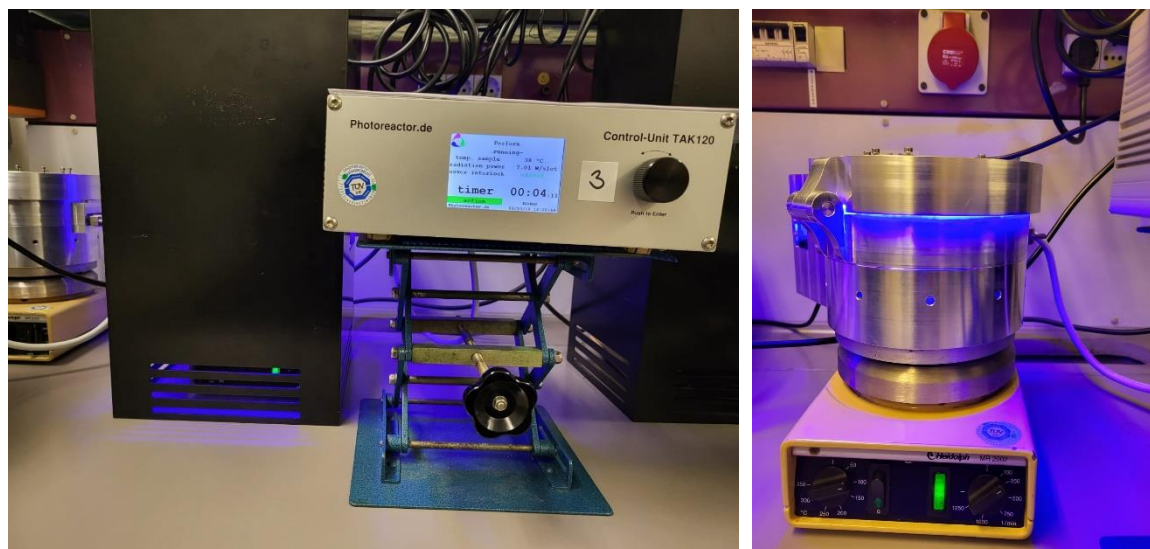


Figure S3: A depiction of the commercial photochemical reaction setup. The illumination of 5 mL crimp cap reaction vials occurs from the bottom using blue LEDs with a wavelength of 455 (\pm 15) nm and a radiant power of 7 W. The setup reaction temperature shut off was set to 60 °C.

3 Reaction Optimization

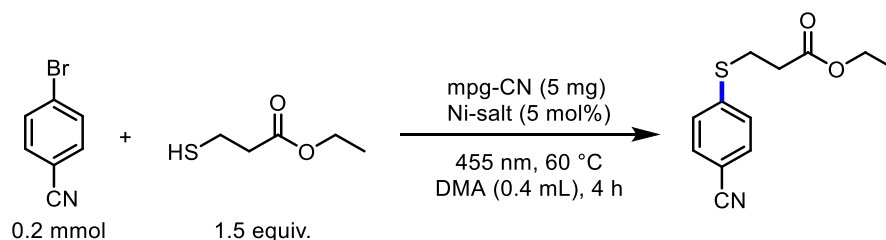
General Procedure A: Synthesis of thioethers

(Het)aryl halide (0.2 mmol, 1.0 equiv.), the respective thiol (0.3-0.5 mmol, 1.5-2.5 equiv.), mpg-CN (5 mg) and 0.4 mL of a stock solution containing NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA were mixed in a 5 mL crimp top vial charged with a magnetic stirring bar. The reaction vial was crimped, and the reaction mixture was degassed, set under nitrogen atmosphere via syringe needle and irradiated at 25 °C or 60 °C through the plane bottom side of the snap vial using a single blue LED (455 (± 15) nm). The reaction progress was monitored by GC-FID analysis. After completion, the reaction mixture was centrifuged and the photocatalyst was washed with ethyl acetate (3 × 1 mL) together with the reaction vial. The organic fractions were collected in a separating funnel, diluted with ethyl acetate (approx. 15 mL) and washed with water (approx. 20 mL). The water layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered and solvent was removed under reduced pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent.

General procedure B: Recycling of mpg-CN

The recovered mpg-CN used in General Procedure I was collected in a 15 mL centrifuge vial and washed with ethyl acetate (1 × 15 mL), DMA (1 × 15 mL), water (1 × 15 mL) and DCM (3 × 15 mL) and centrifuged after each washing for approximately 1-10 minutes. The solvent was removed before every next washing cycle. After the last washing cycle, mpg-CN was dried in the oven at 60 °C.

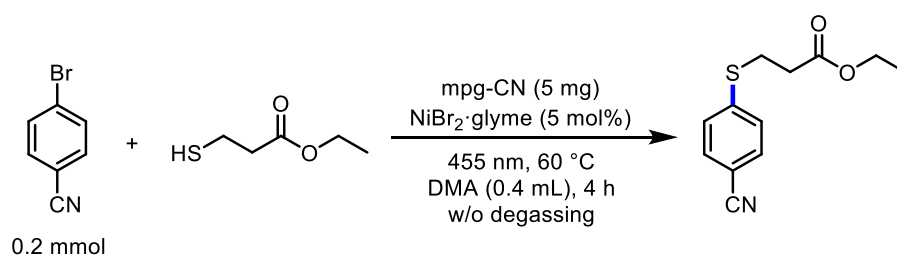
Table S1. Investigating the influence of nickel salts with 4-bromobenzonitrile and ethyl 3-mercaptopropionate.



Entry	Ni-salt	Yield ^a (%)
1	NiBr ₂ •3H ₂ O	97
2	Ni(OAc) ₂	60
3	NiCl ₂ •xH ₂ O	87
4	NiCl ₂ •glyme	93
5	Ni(BF ₄) ₂ •6H ₂ O	67
6	Ni(acac) ₂	78

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

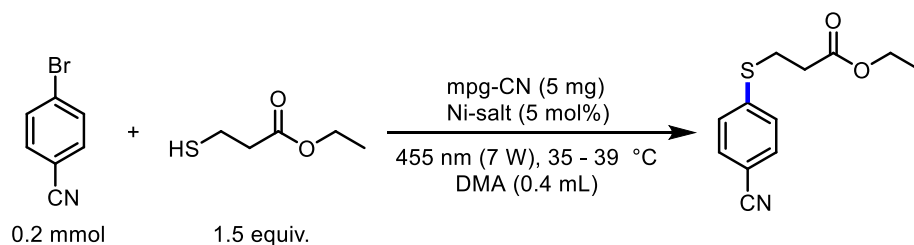
Table S2. Investigating the influence of ambient air with 4-bromobenzonitrile and ethyl 3-mercaptopropionate.



Entry	Equiv. of ethyl 3-mercaptopropionate	Yield ^a (%)
1	1.5	36
2	3	79
3	5	72

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

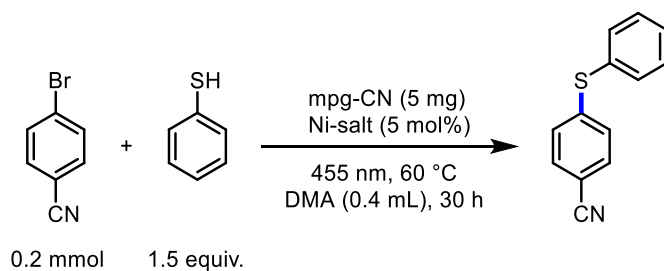
Table S3. Commercial photo-setup (7W) without temperature control with 4-bromobenzonitrile and ethyl 3-mercaptopropionate.



Entry	Reaction Time (Mins.)	Yield ^a (%)
1	20	4
2	35	45
3	55	62

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard. Reaction mixture was degassed before irradiation and maintained under dinitrogen.

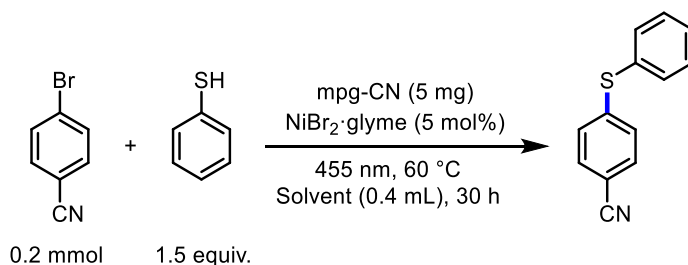
Table S4. Influence of nickel salts of thioetherification reaction of 4-bromobenzonitrile with thiophenol.



Entry	Ni-salt	Yield ^a (%)
1	NiBr ₂ •3H ₂ O	84
2	Ni(OAc) ₂	83
3	NiCl ₂ •xH ₂ O	73
4	NiCl ₂ •glyme	76
5	Ni(BF ₄) ₂ •6H ₂ O	80
6	Ni(acac) ₂	76

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

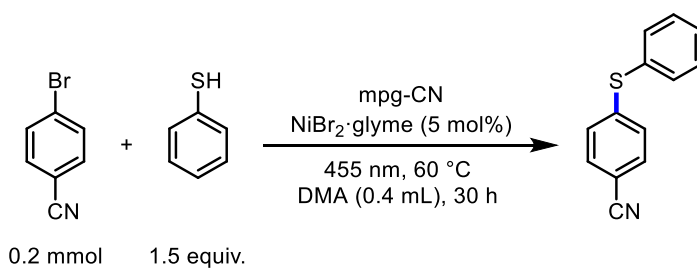
Table S5. Solvent screening of thioetherification reaction of 4-bromobenzonitrile with thiophenol.



Entry	Solvent	Yield ^a (%)
1	DMF	48
2	ACN	3
3	DMSO	0
4	pyridine	24

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

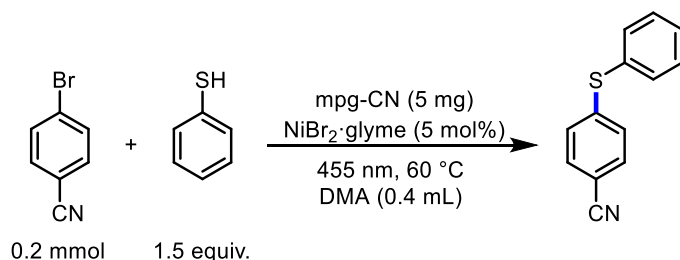
Table S6. Photocatalyst loading of thioetherification reaction of 4-bromobenzonitrile with thiophenol.



Entry	mpg-CN (mg)	Yield ^a (%)
1	0	29
2	1	41
3	2.5	52
4	5	76

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

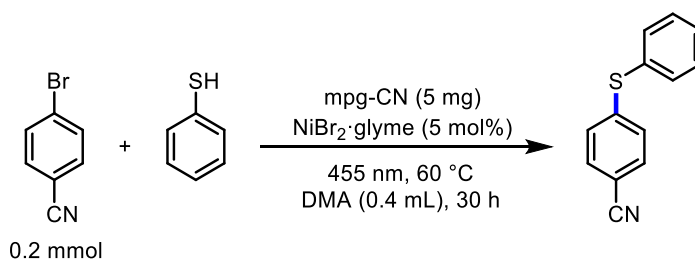
Table S7. Reaction time of dual nickel catalyzed photoredox thioetherification reaction of 4-bromobenzonitrile with thiophenol.



Entry	Reaction Time (h)	Yield ^a (%)
1	1	71
2	3	69
3	12	72
4	30	76

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

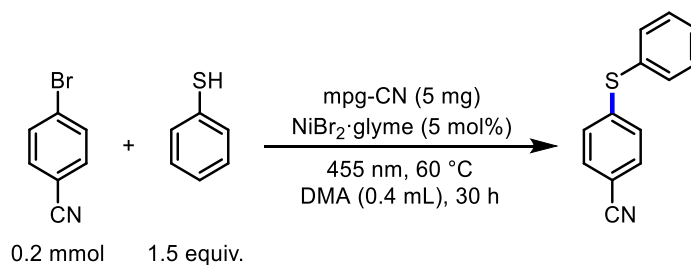
Table S8. Varying the equivalence of thioetherification reaction of 4-bromobenzonitrile with thiophenol.



Entry	Thiophenol (equiv.)	Yield ^a (%)
1	1.0	55
2	1.5	65
3	2.0	62

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

Table S9. Control experiments of thioetherification reaction of 4-bromobenzonitrile with thiophenol.



Entry	Deviation from standard conditions	Yield ^a (%)
1	w/o Ni	2
2	w/o light	4
3	w/o mpg-CN	29
4	w/o degassing	44

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

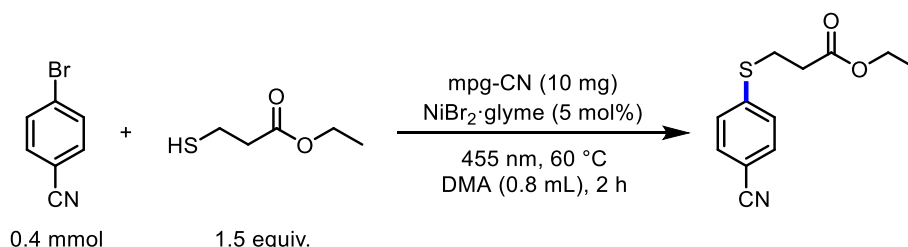
w/o: without

4 Evaluation of Catalyst Recycling

a) for the same thioetherification cross-coupling reaction: reaction conditions and catalyst recycling procedure

4-bromobenzonitrile (0.4 mmol, 1 equiv.), ethyl 3-mercaptopronionate (0.6 mmol, 1.5 equiv.) and mpg-CN (10 mg) were placed in a custom-made flat-bottom 10 mL Schlenk flask charged with a magnetic stirring bar. 0.8 mL of the stock solution containing NiBr₂-glyme (6.4 mg, 0.02 mmol, 0.05 equiv.) in DMA was added, and the reaction mixture was degassed, set under nitrogen atmosphere, and irradiated at 60 °C for 2 hours through the plane bottom side of the flask using a single blue LED (455 (± 15) nm). After completion, 0.4 mL of the 1 M stock solution of 1,3,5-trimethoxybenzene was added to the reaction mixture and mpg-CN was filtered using glass frit installed in the custom-made Schlenk flask. The reaction mixture was analyzed with GC-FID without further work-up. The mpg-CN was washed in the reaction vessel with acetone (3 × 5 mL), dried *in vacuo* and used in the next catalytic cycle.

Table S10: Determined yields over 18 catalytic cycles.



Catalytic Cycle	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Yield ^a , %	92	95	89	95	97	92	94	95	96	97	92	97	97	95	92	96	87	95

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard.

Catalyst recycling

For the same reaction

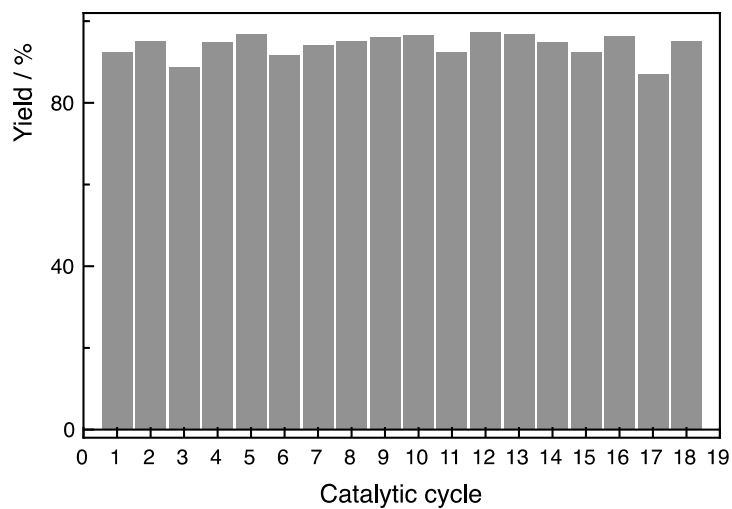
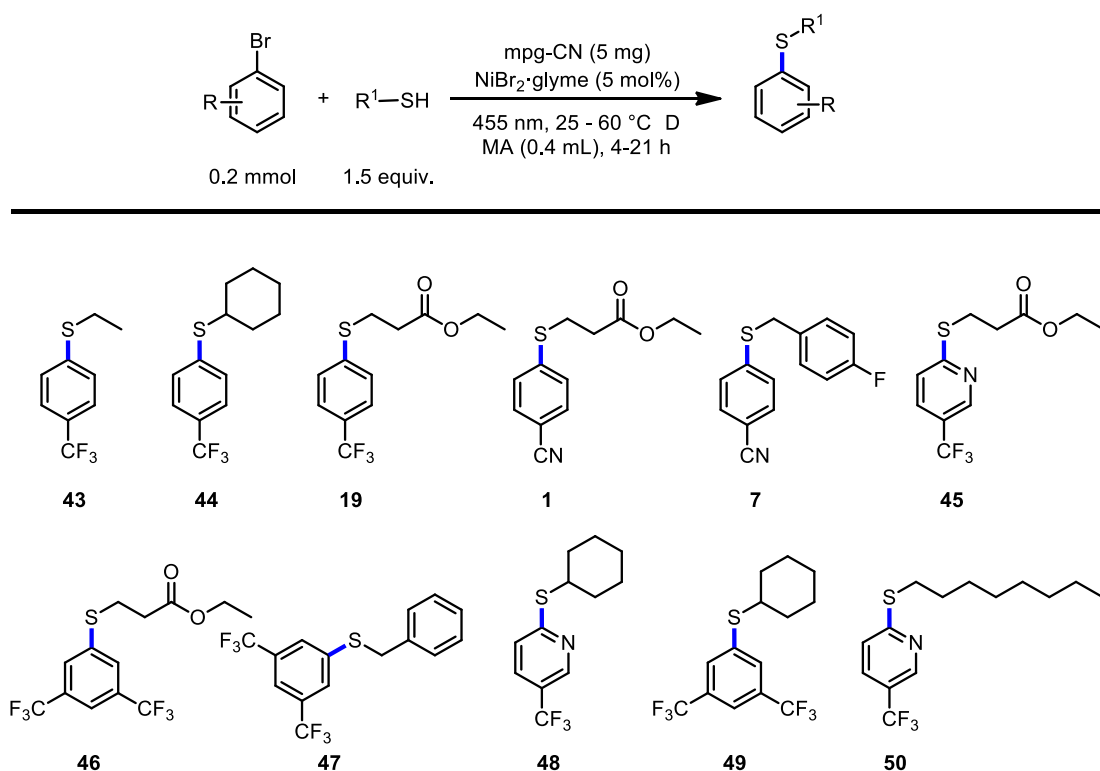


Figure S4: **Left.** Evaluation of catalyst recycling for the thioetherification cross-coupling reaction of 4-bromobenzonitrile with ethyl 3-mercaptopronionate. The yields were determined by GC-FID analysis using 1,3,5-trimethoxybenzene as an internal standard. **Right.** Custom-made flat-bottom 5 mL Schlenk flask used for the evaluation of catalyst recycling.

b) for different thioetherification cross-coupling reactions: reaction conditions and catalyst recycling procedure

(Het)aryl halide (0.2 mmol, 1.0 equiv.), the respective thiol (0.3 mmol, 1.5 equiv.), mpg-CN (5 mg) and 0.4 mL of a stock solution containing NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA were mixed in a 5 mL crimp top vial charged with a magnetic stirring bar. The reaction vial was crimped, and the reaction mixture was degassed, set under nitrogen atmosphere via syringe needle and irradiated at 25 °C or 60 °C through the plane bottom side of the snap vial using a single blue LED (455 (± 15) nm). After completion, 0.2 mmol of 2,2,2-trifluoroethan-1-ol and 0.4 mL of CDCl₃ were added (note: for the catalytic cycle 4 0.2 mL of the 1 M stock solution of 1,3,5-trimethoxybenzene was added and the yield was determined with GC-FID analysis), and the reaction mixture was centrifuged for approximately 1-10 minutes. The supernatant liquid was analyzed with ¹⁹F NMR spectroscopy, and the product formation was confirmed by GC-MS analysis. The photocatalyst was washed with ethyl acetate (4 × 1 mL), dried, and reused in the subsequent cycle. Intrinsic yield was determined by corresponding analytical method under the same reaction conditions using mpg-CN from the batch.

Table S11: Reaction conditions and yields of thioetherification cross-coupling reactions selected for the evaluation of catalyst recycling.



Reaction cycle	Compound	Time, h	Temperature, °C	Intrinsic yield, %	Yield with recovered mpg-CN, %
1	43	18	25	70	64
2	44	21	25	90	91
3	19	14	25	74	79
4	1	4	60	92	91
5	7	6	60	98	98
6	45	14	60	90	94
7	46	14	60	92	95
8	47	14	60	93	95
9	48	12	60	91	92
10	49	21	60	91	93
11	50	18	60	90	95

^aYields were determined by GC-FID using 1,3,5-trimethoxybenzene as an internal standard or ¹⁹F NMR spectroscopy using 2,2,2-trifluoroethan-1-ol as an internal standard.

For different reactions in a sequence

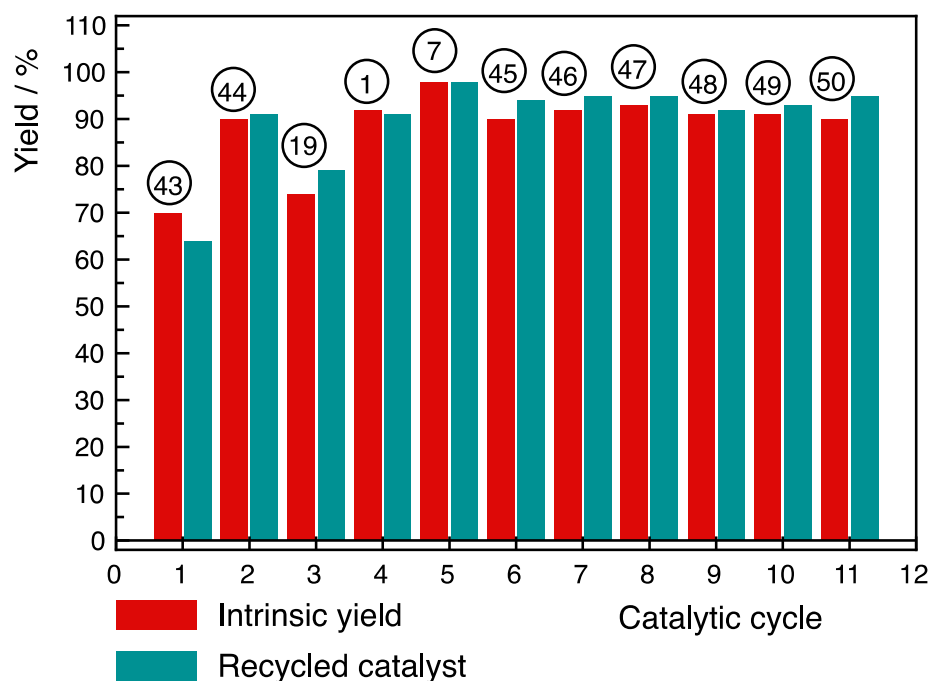


Figure S5: Evaluation of catalyst recycling for different thioetherification cross-coupling reactions. The yields were determined by either ^{19}F NMR spectroscopy using 2,2,2-trifluoroethan-1-ol as an internal standard or by GC-FID analysis using 1,3,5-trimethoxybenzene as an internal standard.

c) Evaluating the influence of the reuse of mpg-CN on the kinetic profile for the thioetherification cross-coupling reaction of 4-bromobenzonitrile with ethyl 3-mercaptopronionate

4-bromobenzonitrile (0.2 mmol, 1 equiv.), ethyl 3-mercaptopronionate (0.3 mmol, 1.5 equiv.) and mpg-CN (5 mg) were placed in a 5 mL crimp top vial charged with a magnetic stirring bar. 0.4 mL of the stock solution containing NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA was added, and the reaction mixture was degassed, set under nitrogen atmosphere, and irradiated at 25 °C. In total 5 reaction vials were prepared for the monitoring of the reaction progress over 60, 90, 120, 150, and 180 minutes. After respective amount of time, 0.2 mL of the 1 M stock solution of 1,3,5-trimethoxybenzene was added, and the reaction mixture was centrifuged for approximately 1-10 minutes. The supernatant liquid was analyzed with GC-FID analysis. The photocatalyst was washed with ethyl acetate (4 × 1 mL), dried, and reused in the subsequent cycle.

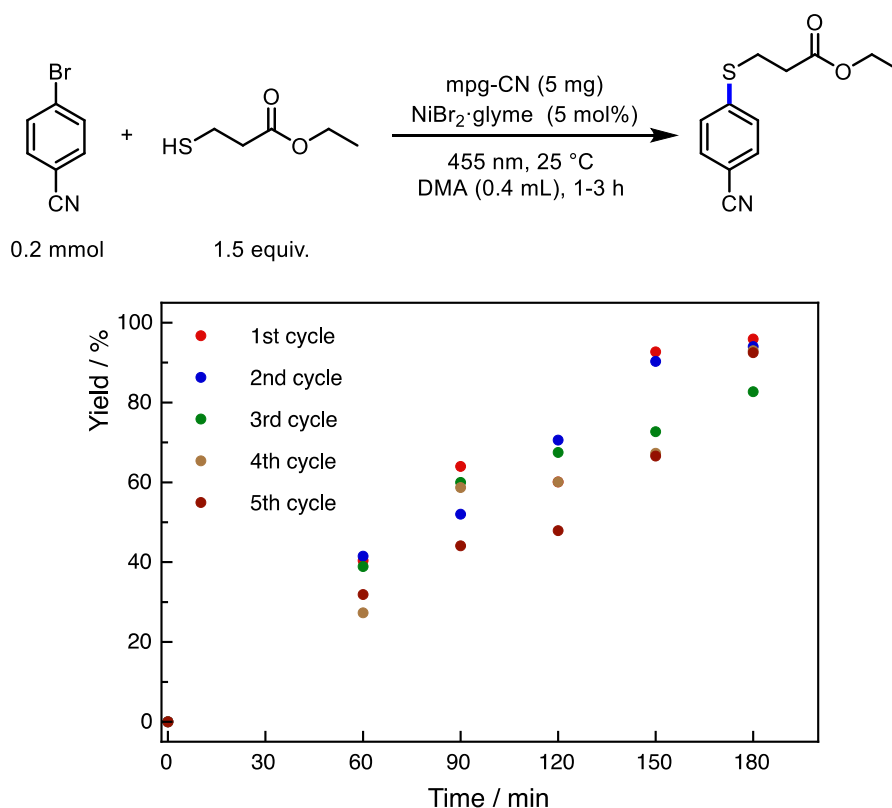


Figure S6: Evaluation of catalyst recycling for the thioetherification cross-coupling reaction of 4-bromobenzonitrile with ethyl 3-mercaptopronionate: influence of the reuse of mpg-CN on the kinetic profile (in this case, the yield of the desired product vs time). The reaction was performed with 0.2 mmol of the aryl bromide substrate. The yields were determined by GC-FID analysis using 1,3,5-trimethoxybenzene as an internal standard.

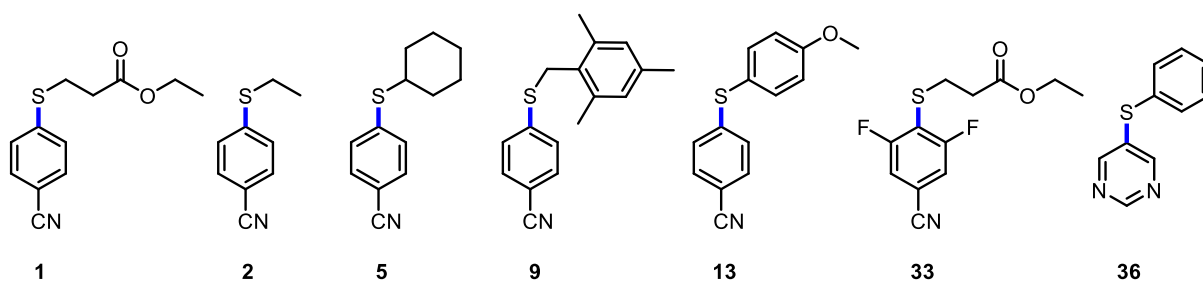
5 Calculation of the modified *E*-Factor (mod-*E*-Factor)

The modified-environmental impact factor (mod-*E*-factor) for the reaction was calculated according to the Equation 1 for the compounds listed in the Table S12 based on the general procedures described in the Section 3 (unless otherwise noted).

$$\frac{\sum m(\text{Input Materials}) - m(\text{Product})}{m(\text{Product})} \quad (1)$$

Note: It is to be noted here that for the modified *E*-factor calculations, the materials used in the purification steps are not considered. The calculations are performed considering only the mass of the "input materials" (in this case, the electrophile, i.e., aryl bromides; nucleophile, in this case, sulfur nucleophiles; catalyst, i.e., mpg-CN; solvent, in this case, DMA) and the mass of the "desired product". The mod-*E*-factor does not include the mass of the other waste, including solvents for extraction, solvents for chromatography, and every non-recycled item used in the reaction (e.g., glass vial, pipette, drying agent, filter paper, etc.). We find that providing the mod-*E*-factor makes more sense within the context of the reported reaction, as the other factors can vary depending on the person or the laboratory.

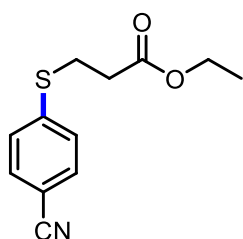
Table S12: Assessment of the modified environmental impact factor (mod-*E*-factor) for the selected compounds.



Compound	1	1 ^a	2	5	9	13	33	36
E-factor	9.3	2.2	12.6	11.8	8.4	10.2	8.0	13.4

^a40 μ L of DMA was used for the reaction conducted on a 0.2 mmol scale.

6 Synthetic Procedures



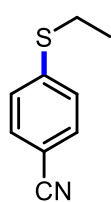
ethyl 3-((4-cyanophenyl)thio)propanoate (1): 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 4 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 97%.

ethyl 3-((4-cyanophenyl)thio)propanoate (with respective Ar-I): The compound was prepared according to the *general procedure* using 4-iodobenzonitrile (0.2 mmol, 45.8 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 10 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 83% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.23 (t, J = 7.3 Hz, 2H), 2.65 (t, J = 7.3 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.1, 143.5, 132.3, 127.2, 118.6, 108.6, 60.9, 33.6, 27.0, 14.1.

HRMS: calculated for [M]⁺: 235.0661; found: 235.0662.

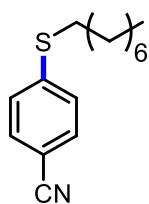


4-(ethylthio)benzonitrile (2): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), ethanethiol (0.4 mmol, 29 μ L, 2.0 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 12 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 98% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.99 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 144.9, 132.1, 126.6, 118.8, 107.8, 25.9, 13.6.

HRMS: calculated for $[M]^+$: 163.0450; found: 163.0450.

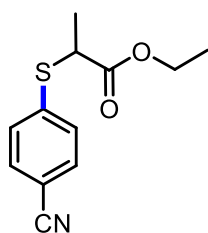


4-(octylthio)benzonitrile (3): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), octane-1-thiol (0.3 mmol, 52 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 12 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 87% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.43 (m, 2H), 7.31 – 7.20 (m, 2H), 2.97 – 2.89 (m, 2H), 1.70 – 1.61 (m, 2H), 1.47 – 1.35 (m, 2H), 1.23 – 1.32 (m, 8H), 0.90 – 0.79 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.3, 132.1, 126.5, 118.2, 107.8, 31.8, 31.7, 29.0, 29.0, 28.83, 28.5, 22.5, 14.0.

HRMS: calculated for $[M]^+$: 247.1389; found: 247.1385.

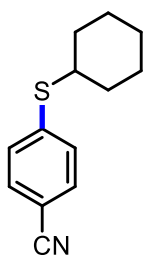


ethyl 2-((4-cyanophenyl)thio)propanoate (4): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), ethyl 2-mercaptoethanoate (0.3 mmol, 39 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 24 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.49 (m, 2H), 7.48 – 7.39 (m, 2H), 4.13 (qd, J = 7.1, 2.6 Hz, 2H), 3.93 (q, J = 7.2 Hz, 1H), 1.53 (d, J = 7.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 141.7, 132.2, 129.7, 118.4, 109.9, 61.5, 43.7, 17.1, 13.9.

HRMS: calculated for $[M]^+$: 235.0661; found: 235.0663.

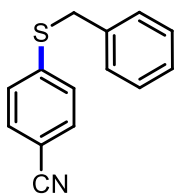


4-(cyclohexylthio)benzonitrile (5): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), cyclohexanethiol (0.3 mmol, 37 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 5 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.45 (m, 2H), 7.36 – 7.28 (m, 2H), 3.36 – 3.19 (m, 1H), 2.11 – 1.92 (m, 2H), 1.86 – 1.72 (m, 2H), 1.61 – 1.66 (m, 1H), 1.48 – 1.23 (m, 5H).

¹³C NMR (100 MHz, CDCl₃) δ 143.9, 132.1, 128.5, 118.8, 108.3, 44.8, 32.9, 25.8, 25.5.

HRMS: calculated for [M]⁺: 217.0920; found: 217.0923.



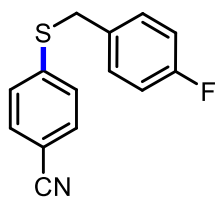
4-(benzylthio)benzonitrile (6): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), phenylmethanethiol (0.3 mmol, 35 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction

mixture was irradiated under N₂ at 60 °C for 5 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 97% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.43 (m, 2H), 7.43 – 7.19 (m, 7H), 4.20 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 144.4, 135.7, 132.2, 128.7, 128.7, 127.7, 127.3, 118.81, 108.5, 37.0.

HRMS: calculated for [M]⁺: 225.0607; found: 225.0608.



4-((4-fluorobenzyl)thio)benzonitrile (7): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), (4-fluorophenyl)methanethiol (0.3 mmol, 37 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 6 h

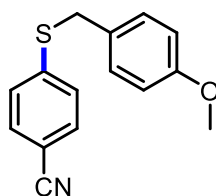
using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 94% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.44 (m, 2H), 7.37 – 7.24 (m, 4H), 7.04 – 6.94 (m, 2H), 4.16 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 163.3, 160.9, 144.0, 132.2, 131.4, 131.4, 130.3, 130.2, 127.4, 118.6, 115.7, 115.5, 108.7, 36.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.78.

HRMS: calculated for [M]⁺: 243.0513; found: 243.0510.



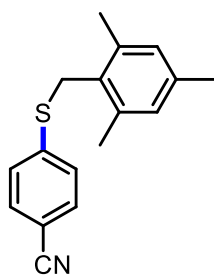
4-((4-methoxybenzyl)thio)benzonitrile (8): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), (4-methoxyphenyl)methanethiol (0.3 mmol, 42 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 6 h

using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 98% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.42 (m, 2H), 7.33 – 7.20 (m, 4H), 6.87 – 6.78 (m, 2H), 4.13 (s, 2H), 3.77 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.1, 144.6, 132.1, 129.8, 127.4, 127.2, 118.8, 114.1, 108.4, 55.2, 36.5.

HRMS: calculated for [M]⁺: 255.0712; found: 255.0716.



4-((2,4,6-trimethylbenzyl)thio)benzonitrile (9): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), mesitylmethanethiol (0.3 mmol, 49.9 mg, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 6 h using a single blue LED (455(±15) nm). The product was

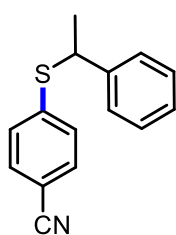
purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 93% yield.

Gram scale reaction: 4-bromobenzonitrile (4.5 mmol, 819.1 mg, 1.0 equiv.), mesitylmethanethiol (6.75 mmol, 1.12 g, 1.5 equiv.), mpg-CN (112.5 mg) and NiBr₂•glyme (72.0 mg, 0.23 mmol, 0.05 equiv.) in DMA (9 mL). The reaction mixture was irradiated under N₂ at 60 °C for 18 h using a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 91% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.52 (m, 2H), 7.42 – 7.33 (m, 2H), 6.90 (s, 2H), 4.22 (s, 2H), 2.40 (s, 6H), 2.30 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.9, 137.5, 137.3, 132.1, 129.2, 127.9, 127.0, 118.8, 108.2, 31.8, 20.9, 19.4.

HRMS: calculated for [M]⁺: 267.1076; found: 267.1071.



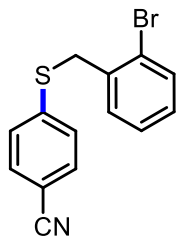
4-((1-phenylethyl)thio)benzonitrile (10): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), 1-phenylethane-1-thiol (0.3 mmol, 41 μL, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 30 h using

a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 38% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.13 (m, 5H), 4.42 (q, *J* = 7.0 Hz, 1H), 1.59 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 142.2, 132.1, 129.3, 128.7, 128.7, 127.6, 127.1, 118.7, 109.1, 46.5, 22.8.

HRMS: calculated for $[\text{M}]^+$: 239.0763; found: 239.0760.



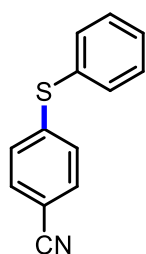
4-((2-bromobenzyl)thio)benzonitrile (11): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), (2-bromophenyl)methanethiol (0.3 mmol, 60.9 mg, 1.5 equiv.), mpg-CN (5 mg) and $\text{NiBr}_2 \bullet \text{glyme}$ (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N_2

at 60 °C for 6 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 71% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, J = 8.0, 1.3 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.38 (dd, J = 7.7, 1.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.25 (td, J = 7.5, 1.3 Hz, 1H), 7.15 (td, J = 7.7, 1.7 Hz, 1H), 4.31 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 135.2, 133.2, 132.3, 130.5, 129.3, 128.0, 127.8, 124.6, 118.7, 109.0, 37.6.

HRMS: calculated for $[\text{M}]^+$: 302.9712; found: 302.9706.



4-(phenylthio)benzonitrile (12): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), benzenethiol (0.5 mmol, 52 μL , 2.5 equiv.), mpg-CN (5 mg) and $\text{NiBr}_2 \bullet \text{glyme}$ (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N_2 at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The

product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 73% yield.

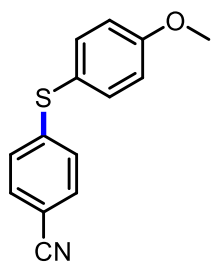
4-(phenylthio)benzonitrile (with Ar-I): 4-iodobenzonitrile (0.2 mmol, 45.8 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μL , 2.5 equiv.), mpg-CN (5 mg) and $\text{NiBr}_2 \bullet \text{glyme}$ (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N_2 at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following

the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 88% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 – 7.49 (m, 2H), 7.49 – 7.45 (m, 2H), 7.45 – 7.38 (m, 3H), 7.20 – 7.13 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.7, 134.5, 132.3, 130.8, 129.9, 129.4, 127.3, 118.8, 108.7.

HRMS: calculated for $[\text{M}]^+$: 211.0450; found: 211.0445.



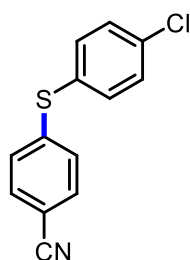
4-((4-methoxyphenyl)thio)benzonitrile (13): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), 4-methoxybenzenethiol (0.5 mmol, 62 μL , 2.5 equiv.), mpg-CN (5 mg) and $\text{NiBr}_2 \cdot \text{glyme}$ (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N_2 at 60 $^\circ\text{C}$ for

30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 85% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.38 (m, 4H), 7.10 – 7.02 (m, 2H), 7.00 – 6.92 (m, 2H), 3.85 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.9, 147.3, 137.0, 132.2, 126.0, 120.3, 118.9, 115.5, 107.9, 55.4.

HRMS: calculated for $[\text{M}]^+$: 241.0556; found: 241.0560.



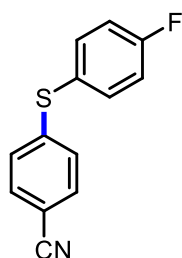
4-((4-chlorophenyl)thio)benzonitrile (14): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), 4-chlorobenzenethiol (0.5 mmol, 72.3 mg, 2.5 equiv.), mpg-CN (5 mg) and $\text{NiBr}_2 \cdot \text{glyme}$ (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N_2 at 60 $^\circ\text{C}$ for 30 h using

a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 61% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 – 7.47 (m, 2H), 7.46 – 7.35 (m, 4H), 7.21 – 7.13 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.9, 135.7, 135.6, 132.5, 130.1, 129.6, 127.6, 118.6, 109.2.

HRMS: calculated for $[\text{M}]^+$: 245.0061; found: 245.0057.



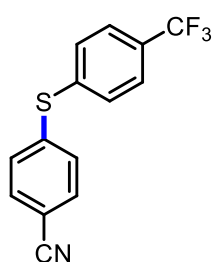
4-((4-fluorophenyl)thio)benzonitrile (15): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), 4-fluorobenzenethiol (0.5 mmol, 53 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.49 (m, 2H), 7.49 – 7.44 (m, 2H), 7.17 – 7.08 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 164.8, 162.3, 145.8, 145.8, 137.0, 137.0, 132.4, 126.8, 125.8, 125.8, 118.7, 117.3, 117.1, 108.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -110.94.

HRMS: calculated for [M]⁺: 229.0356; found: 229.0353.



4-((4-(trifluoromethyl)phenyl)thio)benzonitrile (16): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), 4-(trifluoromethyl)benzenethiol (0.5 mmol, 68 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was

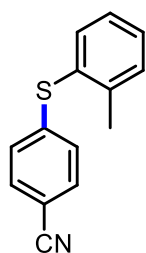
irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 59% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.60 (m, 2H), 7.59 – 7.48 (m, 4H), 7.37 – 7.27 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 142.6, 137.5, 132.7, 132.6, 131.0, 130.7, 130.4, 130.1, 129.5, 126.6, 126.5, 126.5, 126.5, 125.1, 122.4, 118.4, 110.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.30.

HRMS: calculated for [M]⁺: 279.0324; found: 279.0326.

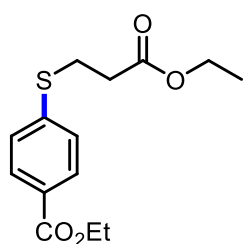


4-(o-tolylthio)benzonitrile (17): The compound was prepared according to the *general procedure* using 4-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), 2-methylbenzenethiol (0.5 mmol, 59 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 61% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H), 7.32 – 7.24 (m, 2H), 7.21 – 7.13 (m, 1H), 7.00 – 6.91 (m, 2H), 2.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.5, 142.5, 136.3, 133.4, 132.6, 132.3, 131.2, 130.2, 129.2, 127.3, 126.3, 118.8, 20.6.

HRMS: calculated for [M]⁺: 225.0607; found: 225.0606.

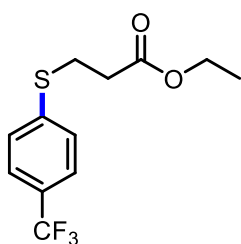


ethyl 4-((3-ethoxy-3-oxopropyl)thio)benzoate (18): The compound was prepared according to the *general procedure* using ethyl 4-bromobenzoate (0.2 mmol, 32.7 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 20 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 92% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.93 (m, 2H), 7.33 – 7.31 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.25 (t, J = 7.4 Hz, 2H), 2.66 (t, J = 7.4 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.5, 166.2, 142.5, 130.0, 127.7, 127.2, 60.9 (d, J = 5.2 Hz), 34.0, 27.4, 14.3 (d, J = 15.2 Hz).

HRMS: calculated for [M]⁺: 282.0920; found: 282.0926.



ethyl 3-((4-(trifluoromethyl)phenyl)thio)propanoate (19): The compound was prepared according to the *general procedure* using 1-bromo-4-(trifluoromethyl)benzene (0.2 mmol, 28 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL).

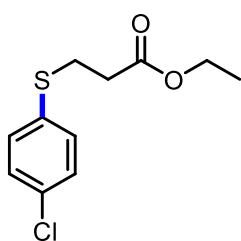
The reaction mixture was irradiated under N₂ at 25 °C for 20 h using a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 78% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.51 (m, 2H), 7.40 – 7.37(m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.23 (t, J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.4, 141.1 (d, J = 1.6 Hz), 128.4, 128.1, 127.8, 127.4, 125.86, 125.8 (q, J = 3.8 Hz), 125.4, 122.7, 120.0, 60.9, 34.0, 27.8, 14.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0.

HRMS: calculated for [M]⁺: 278.0582; found: 278.0587.



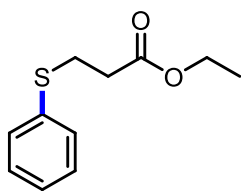
ethyl 3-((4-chlorophenyl)thio)propanoate (20): The compound was prepared according to the *general procedure* using 1-bromo-4-chlorobenzene (0.2 mmol, 38.3 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The

reaction mixture was irradiated under N₂ at 60 °C for 20 h using a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 69% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.24 (m, 4H), 4.13 (q, J = 7.1 Hz, 2H), 3.14 (t, J = 7.4 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.5, 133.8, 132.6, 131.5, 129.1, 60.8, 34.3, 29.3, 14.2

HRMS: calculated for [M]⁺: 244.0319; found: 244.0319.

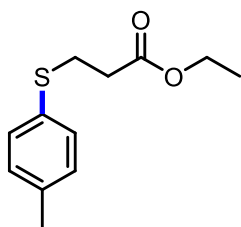


ethyl 3-(phenylthio)propanoate (21): The compound was prepared according to the *general procedure* using bromobenzene (0.2 mmol, 21.1 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 12 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 52% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.19 (m, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.17 (t, J = 7.5 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 135.3, 130.1, 129.0, 126.6, 60.7, 34.5, 29.1, 14.2.

HRMS: calculated for [M]⁺: 210.0709; found: 210.0704.

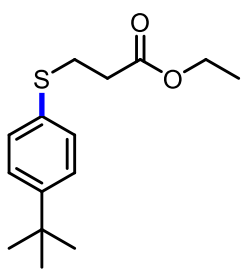


ethyl 3-(p-tolylthio)propanoate (22): The compound was prepared according to the *general procedure* using 4-Bromotoluene (0.2 mmol, 34.2 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 46% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 8.1 Hz, 2H), 7.13 – 7.010 (m, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.11 (t, J = 7.4 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 2.32 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 136.8, 131.4, 131.0, 129.8, 60.6, 34.5, 29.8, 21.0, 14.2.

HRMS: calculated for [M]⁺: 224.0865; found: 224.0865.

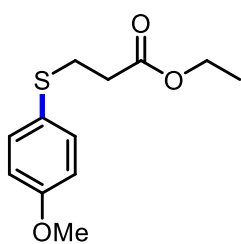


ethyl 3-((4-(tert-butyl)phenyl)thio)propanoate (23): The compound was prepared according to the *general procedure* using 1-bromo-4-(tert-butyl)benzene (0.2 mmol, 34.7 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h using a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 31% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.32 (s, 4H), 4.13 (q, J = 7.1 Hz, 2H), 3.13 (t, J = 7.4 Hz, 2H), 2.61 (t, J = 7.4 Hz, 2H), 1.31 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 150.0, 131.5, 130.5, 126.1, 60.7, 34.7, 34.5, 31.3, 29.5, 14.2.

HRMS: calculated for [M]⁺: 266.1346; found: 266.1344.



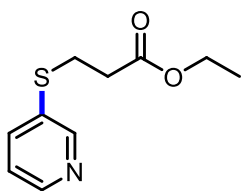
ethyl 3-((4-methoxyphenyl)thio)propanoate (24): The compound was prepared according to the *general procedure* using 4-Bromoanisole (0.2 mmol, 25.0 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was

irradiated under N₂ at 60 °C for 48 h using a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 59% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.36 (m, 2H), 6.86 – 6.84 (m, 2H), 4.12 (q, J = 7.3 Hz, 2H), 3.79 (s, 3H), 3.04 (t, J = 7.4 Hz, 2H), 2.55 (t, J = 7.4 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.9, 159.3, 134.2, 125.2, 114.6, 60.6, 55.3, 34.6, 31.1, 14.2.

HRMS: calculated for [M]⁺: 240.0814; found: 240.0817.

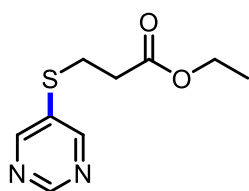


ethyl 3-(pyridin-3-ylthio)propanoate (25): The compound was prepared according to the *general procedure* using 3-bromopyridine (0.2 mmol, 31.6 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 8 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 66% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.61 – 8.60 (m, 1H), 8.46 (dd, J = 4.8, 1.6 Hz, 1H), 7.70 (ddd, J = 8.0, 2.4, 1.5 Hz, 1H), 7.23 (ddd, J = 8.0, 4.8, 0.8 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.17 (t, J = 7.3 Hz, 2H), 2.61 (t, J = 7.3 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.4, 151.0, 147.7, 138.0, 132.6, 123.7, 60.9, 34.4, 29.3, 14.2.

HRMS: calculated for [M]⁺: 211.0661; found: 211.0668.

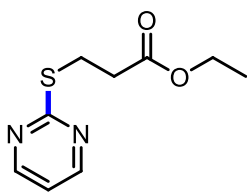


ethyl 3-(pyrimidin-5-ylthio)propanoate (26): The compound was prepared according to the *general procedure* using 5-bromopyrimidine (0.2 mmol, 31.8 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 8 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 54% yield.

¹H NMR (400 MHz, CDCl₃) δ 9.06 (s, 1H), 8.72 (s, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.21 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.0, 157.9, 156.6, 131.9, 61.1, 34.3, 29.1, 14.2.

HRMS: calculated for [M]⁺: 212.0614; found: 212.0616.

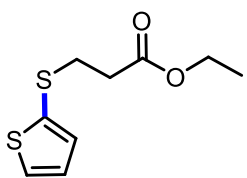


ethyl 3-(pyrimidin-2-ylthio)propanoate (27): The compound was prepared according to the *general procedure* using 2-bromopyrimidine (0.2 mmol, 31.8 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 8 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, J = 4.9 Hz, 2H), 6.96 (t, J = 4.8 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.38 (t, J = 7.2 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.9, 157.3, 116.5, 60.7, 34.4, 25.9, 14.2.

HRMS: calculated for [M]⁺: 212.0614; found: 212.0614:

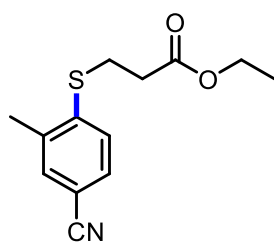


ethyl 3-(thiophen-2-ylthio)propanoate (28): The compound was prepared according to the *general procedure* using 2-bromothiophene (0.2 mmol, 19.4 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 12 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 76% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, J = 5.4, 1.2 Hz, 1H), 7.14 (dd, J = 3.6, 1.3 Hz, 1H), 6.97 (dd, J = 5.4, 3.5 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.00 (t, J = 7.3 Hz, 2H), 2.60 (t, J = 7.3 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.5, 134.6, 133.1, 129.9, 127.6, 60.7, 34.5, 33.6, 14.2.

HRMS: calculated for [M]⁺: 216.0273; found: 216.0274.



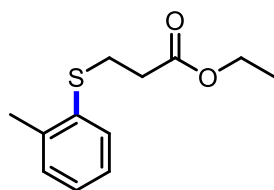
ethyl 3-((4-cyano-2-methylphenyl)thio)propanoate (29): The compound was prepared according to the *general procedure* using 4-bromo-3-methylbenzonitrile (0.2 mmol, 39.2 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL).

The reaction mixture was irradiated under N₂ at 60 °C for 20 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, J = 8.2, 1.9 Hz, 1H), 7.42-7.41 (m, 1H), 7.29-7.28 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.27 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.2, 143.0, 137.1, 132.8, 130.0, 125.0, 119.0, 108.1, 61.0, 33.5, 26.6, 19.9, 14.2.

HRMS: calculated for [M]⁺: 249.0818; found: 249.0819.



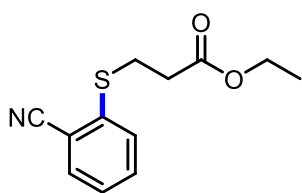
ethyl 3-(o-tolylthio)propanoate (30): The compound was prepared according to the *general procedure* using 2-Bromotoluene (0.2 mmol, 24.1 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol,

0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 37% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.31 (m, 1H), 7.20 – 7.10 (m, 3H), 4.14 (q, J = 7.2 Hz, 2H), 3.15 (t, J = 7.4 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 138.5, 134.6, 130.3, 129.2, 126.5, 126.4, 60.7, 34.3, 28.3, 20.4, 14.2.

HRMS: calculated for [M]⁺: 224.0865; found: 224.0868.

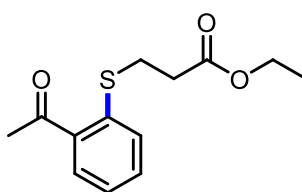


ethyl 3-((2-cyanophenyl)thio)propanoate (31): The compound was prepared according to the *general procedure* using 2-Brombenzotrinitril (0.2 mmol, 36.4 mg, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 25 °C for 20 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 69% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.61 (m, 1H), 7.54 – 7.46(m, 2H), 7.31 – 7.27(m, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.27 (t, J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.2, 140.3, 133.8, 132.9, 130.0, 126.7, 117.0, 114.5, 60.9, 34.1, 28.9, 14.1.

HRMS: calculated for [M]⁺: 235.0661; found: 235.0661.

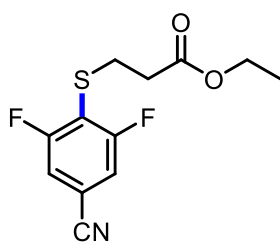


ethyl 3-((2-acetylphenyl)thio)propanoate (32): The compound was prepared according to the *general procedure* using 1-(2-bromophenyl)ethan-1-one (0.2 mmol, 27 μ L, 1.0 equiv.), ethyl 3-mercaptopropanoate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 20 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 82% yield.

¹H NMR (400 MHz, CDCl₃) δ ppm 7.78 (dd, J = 7.8, 1.5 Hz, 1H), 7.45 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H), 7.39 (dd, J = 8.2, 1.3 Hz, 1H), 7.22 (ddd, J = 7.8, 7.1, 1.3 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.18 (t, J = 7.2 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.61 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 199.5, 171.7, 139.5, 136.0, 132.2, 130.8, 126.5, 124.3, 60.9, 33.3, 28.5, 27.4, 14.2.

HRMS: calculated for [M]⁺: 252.0814; found: 252.0817.



ethyl 3-((4-cyano-2,6-difluorophenyl)thio)propanoate (33): The compound was prepared according to the *general procedure* using 4-bromo-3,5-difluorobenzonitrile (0.2 mmol, 43.6 mg, 1.0 equiv.), ethyl 3-mercaptothioacetate (0.3 mmol, 38 μ L, 1.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL).

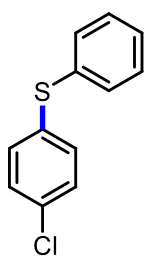
The reaction mixture was irradiated under N₂ at 25 °C for 20 h using a single blue LED (455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.21 (m, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.24 (t, J = 7.2 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 171.0, 163.8 (d, J = 6.0 Hz), 161.3 (d, J = 6.0 Hz), 118.8 (t, J = 21.6 Hz), 115.6, 115.6, 115.5, 115.4, 115.3, 115.3, 112.50 (t, J = 11.9 Hz), 61.0, 35.0, 29.1 (t, J = 3.7 Hz), 14.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -101.6.

HRMS: calculated for [M]⁺: 271.0473; found: 271.0468.



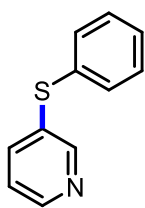
(4-chlorophenyl)(phenyl)sulfane (34): The compound was prepared according to the *general procedure* using 1-bromo-4-chlorobenzene (0.2 mmol, 38.3 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h using a single blue LED

(455(±15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a yellow solid in 16% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.14 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 135.1, 134.7, 133.0, 132.0, 131.3, 129.3, 129.3, 127.4.

HRMS: calculated for [M]⁺: 220.0108; found: 220.0108.

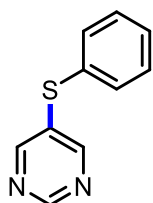


3-(phenylthio)pyridine (35): The compound was prepared according to the *general procedure* using 3-bromopyridine (0.2 mmol, 31.6 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless solid in 91% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.36 (d, J = 4.8 Hz, 1H), 7.55 – 7.42 (m, 1H), 7.34 – 7.15 (m, 5H), 7.14 – 7.04 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 151.0, 147.8, 137.8, 133.9, 133.6, 131.7, 129.5, 127.8, 123.8.

HRMS: calculated for [M]⁺: 187.0450; found: 187.0445.

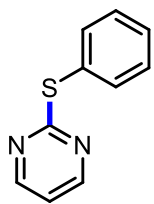


5-(phenylthio)pyrimidine (36): The compound was prepared according to the *general procedure* using 5-bromopyrimidine (0.2 mmol, 31.8 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a yellowish oil in 82% yield.

¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.56 (s, 2H), 7.48 – 7.28 (m, 5H).

¹³C NMR (100 MHz, CDCl₃) δ 157.0, 156.2, 133.4, 132.6, 131.6, 129.8, 128.7.

HRMS: calculated for [M]⁺: 188.0403; found: 188.0402.



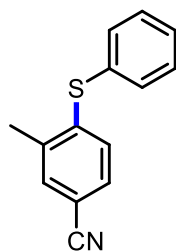
2-(phenylthio)pyrimidine (37): The compound was prepared according to the *general procedure* using 2-bromopyrimidine (0.2 mmol, 31.8 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was

irradiated under N₂ at 60 °C for 30 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 4.8 Hz, 2H), 7.69 – 7.59 (m, 2H), 7.49 – 7.39 (m, 3H), 6.95 (t, J = 4.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.8, 157.5, 135.2, 129.3, 129.3, 129.2, 116.9.

HRMS: calculated for [M]⁺: 188.0403; found: 188.0387.



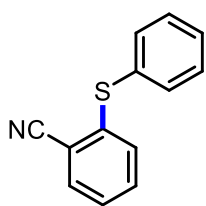
3-methyl-4-(phenylthio)benzonitrile (38): The compound was prepared according to the *general procedure* using 4-bromo-3-methylbenzonitrile (0.2 mmol, 39.2 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h using

a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 42% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.38 (m, 6H), 7.31 – 7.24 (m, 1H), 6.87 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 144.6, 136.6, 134.2, 132.9, 131.0, 129.9, 129.8, 129.1, 127.4, 118.9, 108.6, 19.9.

HRMS: calculated for [M]⁺: 225.0607; found: 225.0605.



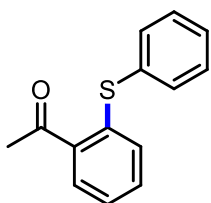
2-(phenylthio)benzonitrile (39): The compound was prepared according to the *general procedure* using 2-bromobenzonitrile (0.2 mmol, 36.4 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The

reaction mixture was irradiated under N₂ at 60 °C for 48 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 33% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.7, 1.2 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.44 – 7.36 (m, 4H), 7.26 (td, J = 7.6, 1.2 Hz, 1H), 7.17 – 7.09 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 142.3, 133.7, 133.6, 133.0, 131.9, 130.0, 129.8, 128.9, 126.5, 116.9, 112.9.

HRMS: calculated for [M]⁺: 211.0450; found: 211.0442.



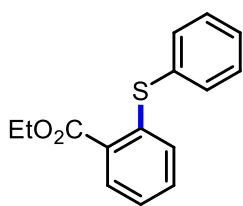
1-(2-(phenylthio)phenyl)ethan-1-one (40): The compound was prepared according to the *general procedure* using 1-(2-bromophenyl)ethan-1-one (0.2 mmol, 39.8 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in

DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a yellow solid in 33% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 7.8, 1.5 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.48 – 7.37 (m, 3H), 7.31 – 7.23 (m, 1H), 7.19 (td, J = 7.5, 1.3 Hz, 1H), 6.92 (dd, J = 8.1, 1.0 Hz, 1H), 2.68 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 199.1, 141.9, 135.1, 134.6, 133.2, 132.0, 130.5, 129.6, 128.9, 128.2, 124.4, 28.2.

HRMS: calculated for [M]⁺: 228.0603; found: 228.0603.



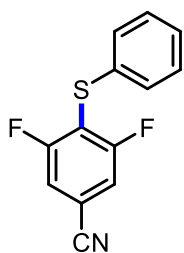
ethyl 2-(phenylthio)benzoate (41): The compound was prepared according to the *general procedure* using ethyl 2-bromobenzoate (0.2 mmol, 45.8 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol,

0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a colorless oil in 21% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, J = 7.8, 1.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.47 – 7.38 (m, 3H), 7.26 – 7.18 (m, 1H), 7.12 (td, J = 7.5, 1.2 Hz, 1H), 6.82 (dd, J = 8.1, 1.2 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.5, 143.0, 135.5, 132.7, 132.2, 131.0, 129.7, 129.0, 127.5, 127.2, 124.3, 61.3, 14.3.

HRMS: calculated for [M]⁺: 258.0709; found: 258.0701.



3,5-difluoro-4-(phenylthio)benzonitrile (42): The compound was prepared according to the *general procedure* using 4-bromo-3,5-difluorobenzonitrile (0.2 mmol, 43.6 mg, 1.0 equiv.), thiophenol (0.5 mmol, 52 μ L, 2.5 equiv.), mpg-CN (5 mg) and NiBr₂•glyme (3.2 mg, 0.01 mmol, 0.05 equiv.) in DMA (0.4 mL). The reaction mixture was irradiated under N₂ at 60 °C for 48 h

using a single blue LED (455(\pm 15) nm). The product was purified following the *general procedure* by column flash chromatography on silica gel using petroleum ether/ethyl acetate solvent mixture as an eluent and obtained as a white solid in 32% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 2H), 7.25 – 7.19 (m, 3H), 7.19 – 7.11 (m, 2H).

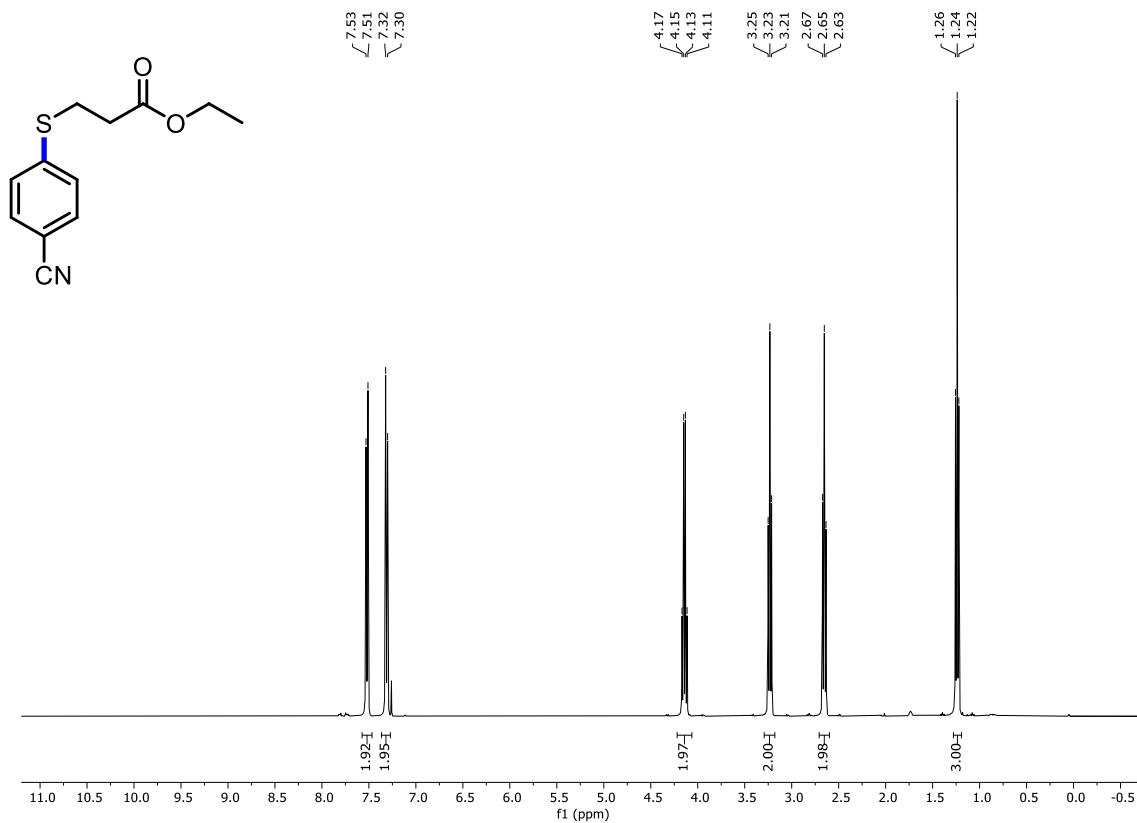
¹³C NMR (100 MHz, CDCl₃) δ 163.7, 163.7, 161.2, 161.2, 132.5, 130.8, 129.3, 128.07, 119.1, 118.9, 118.7, 116.3, 116.3, 116.2, 115.9, 115.9, 115.8, 115.7, 115.6, 115.6, 113.4, 113.3, 113.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -100.52.

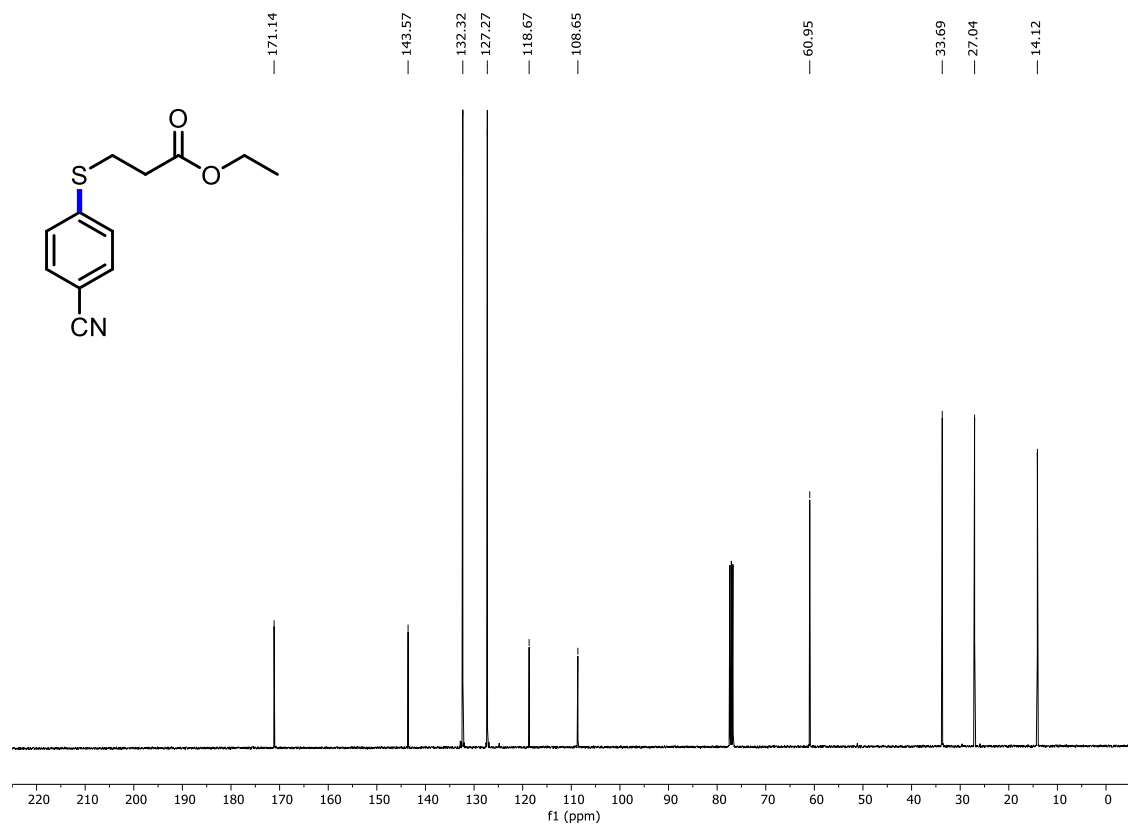
HRMS: calculated for [M]⁺: 247.0262; found: 247.0260.

7 NMR Spectra

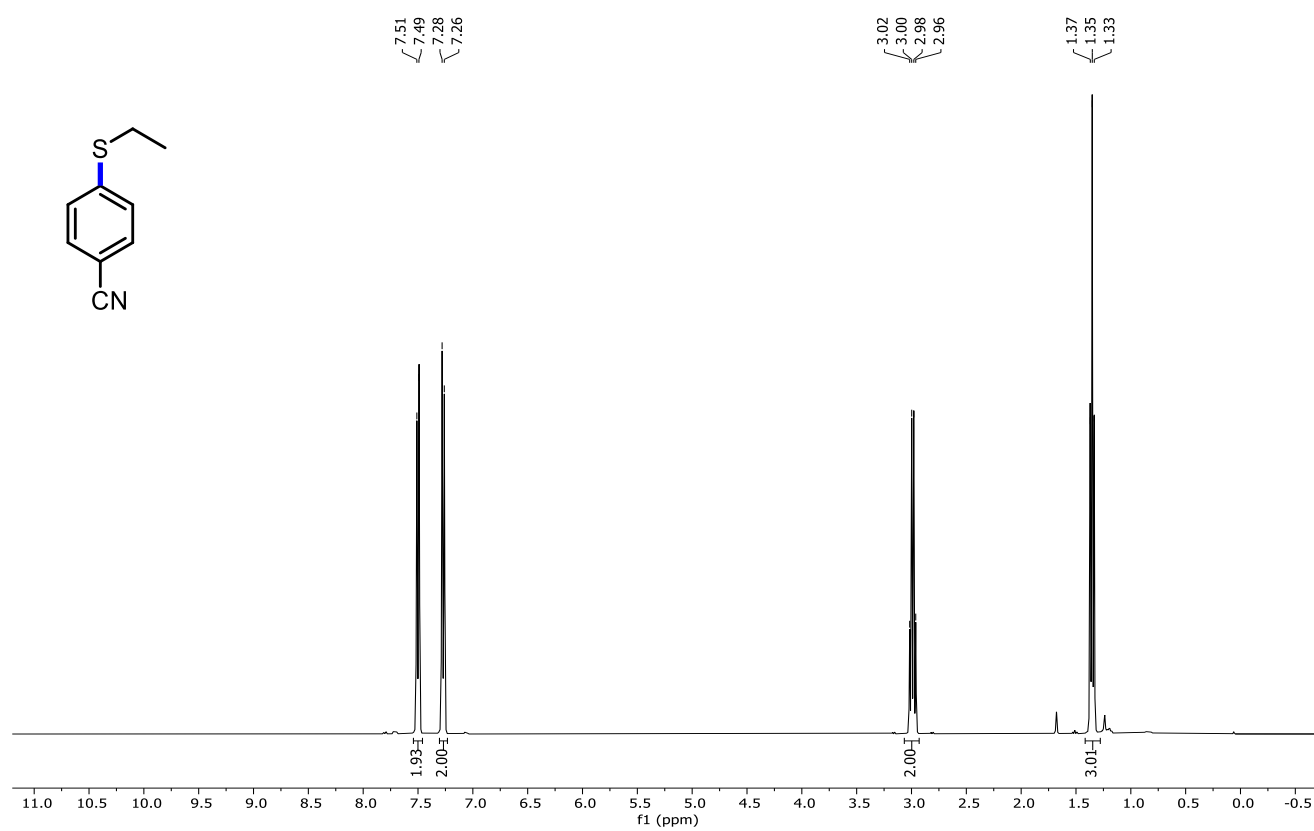
Ethyl 3-((4-cyanophenyl)thio)propanoate (1): ^1H NMR (400 MHz), CDCl_3 .



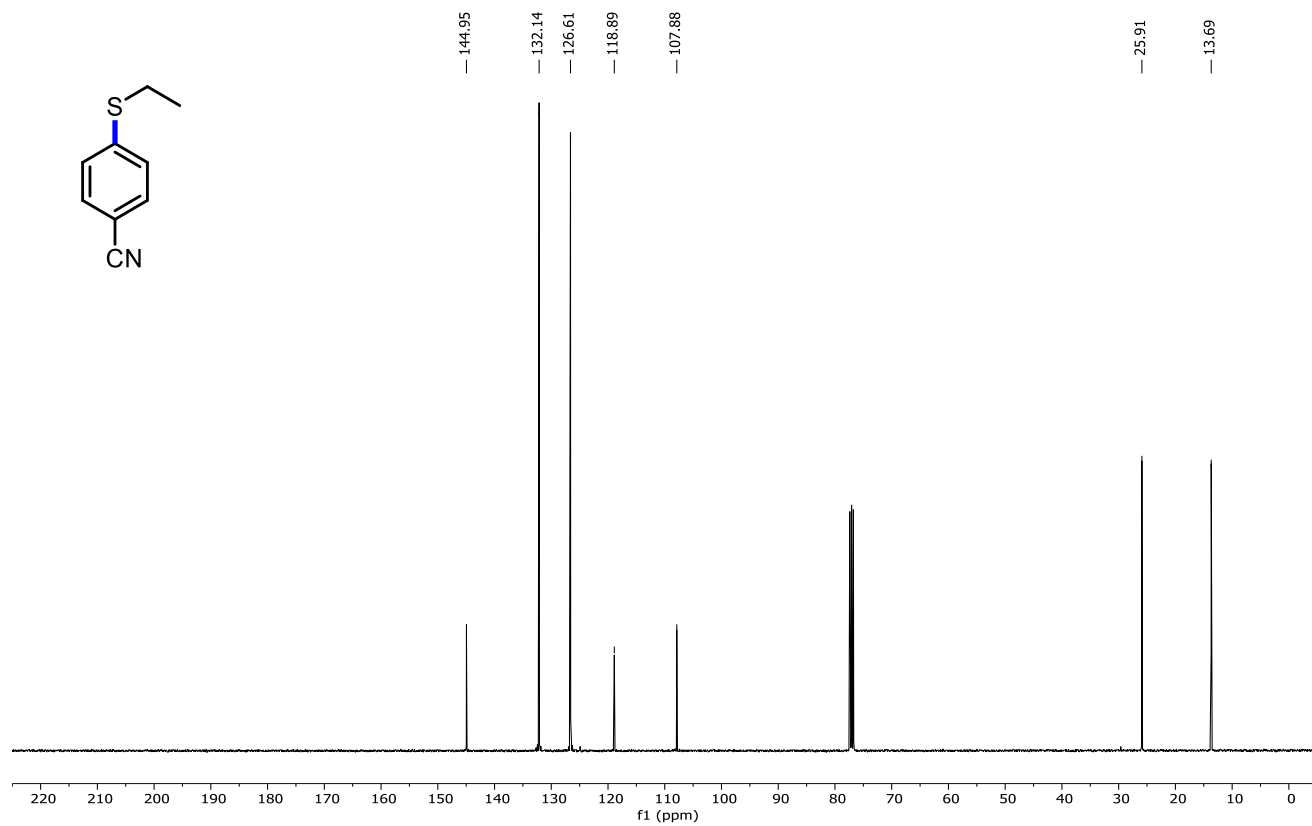
Ethyl 3-((4-cyanophenyl)thio)propanoate (1): ^{13}C NMR (100 MHz), CDCl_3 .



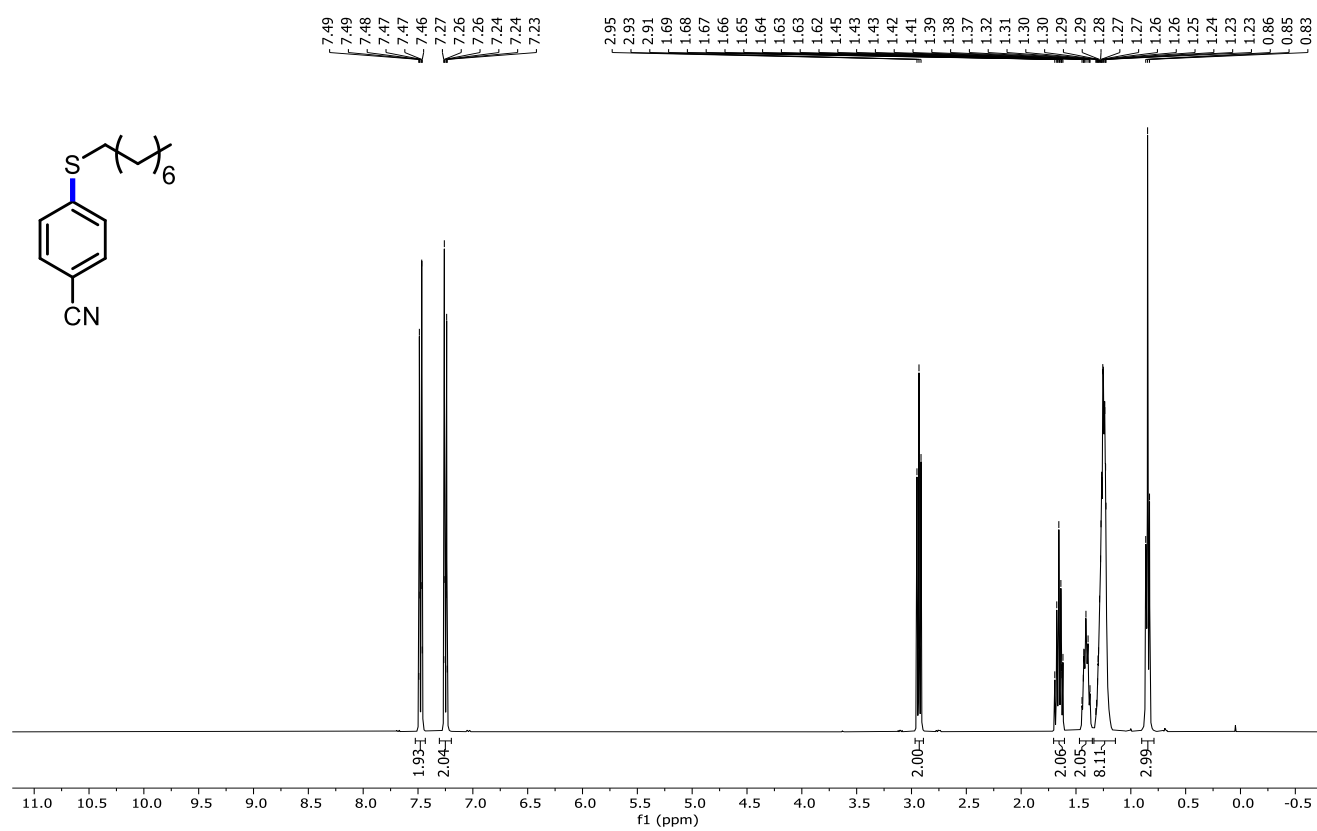
4-(ethylthio)benzonitrile (2): ^1H NMR (400 MHz), CDCl_3 .



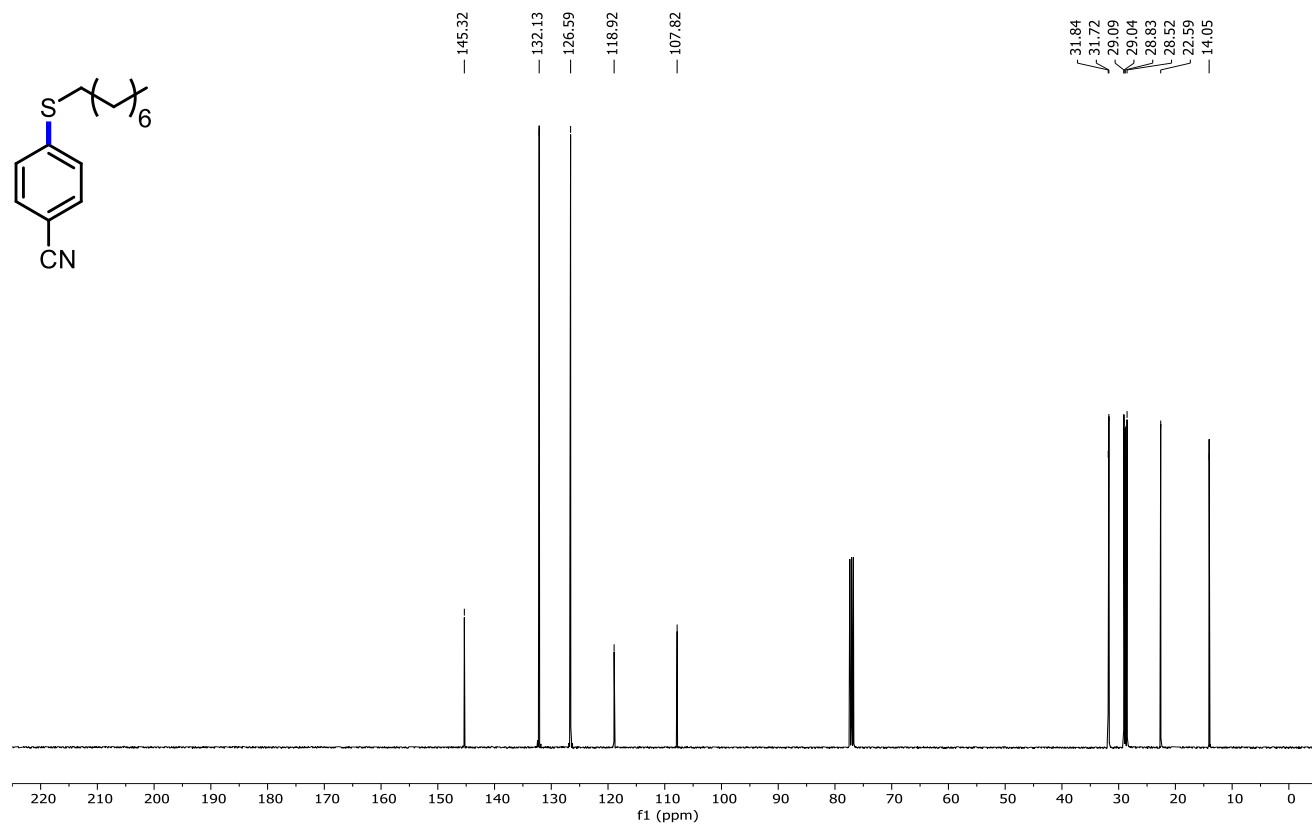
4-(ethylthio)benzonitrile (2): ^{13}C NMR (100 MHz), CDCl_3 .



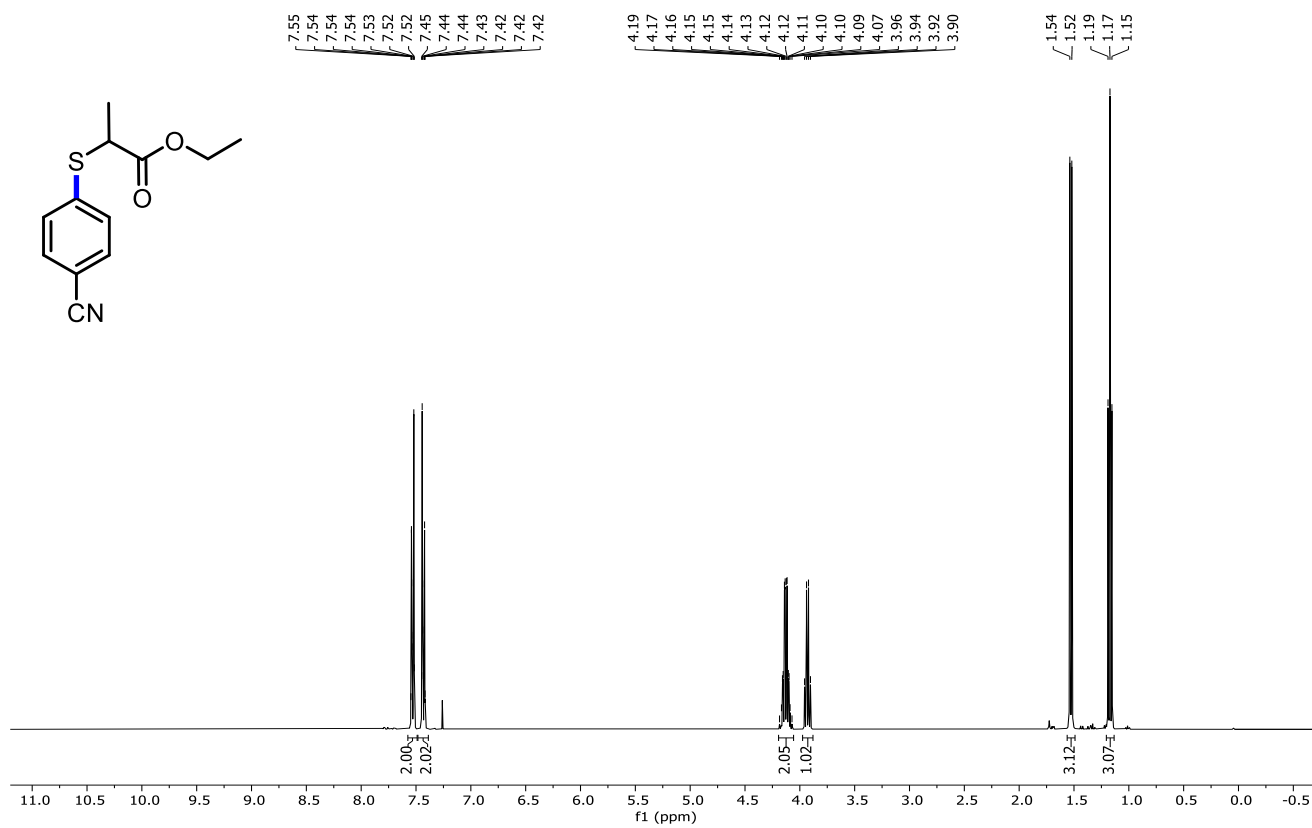
4-(octylthio)benzonitrile (3): ^1H NMR (400 MHz), CDCl_3 .



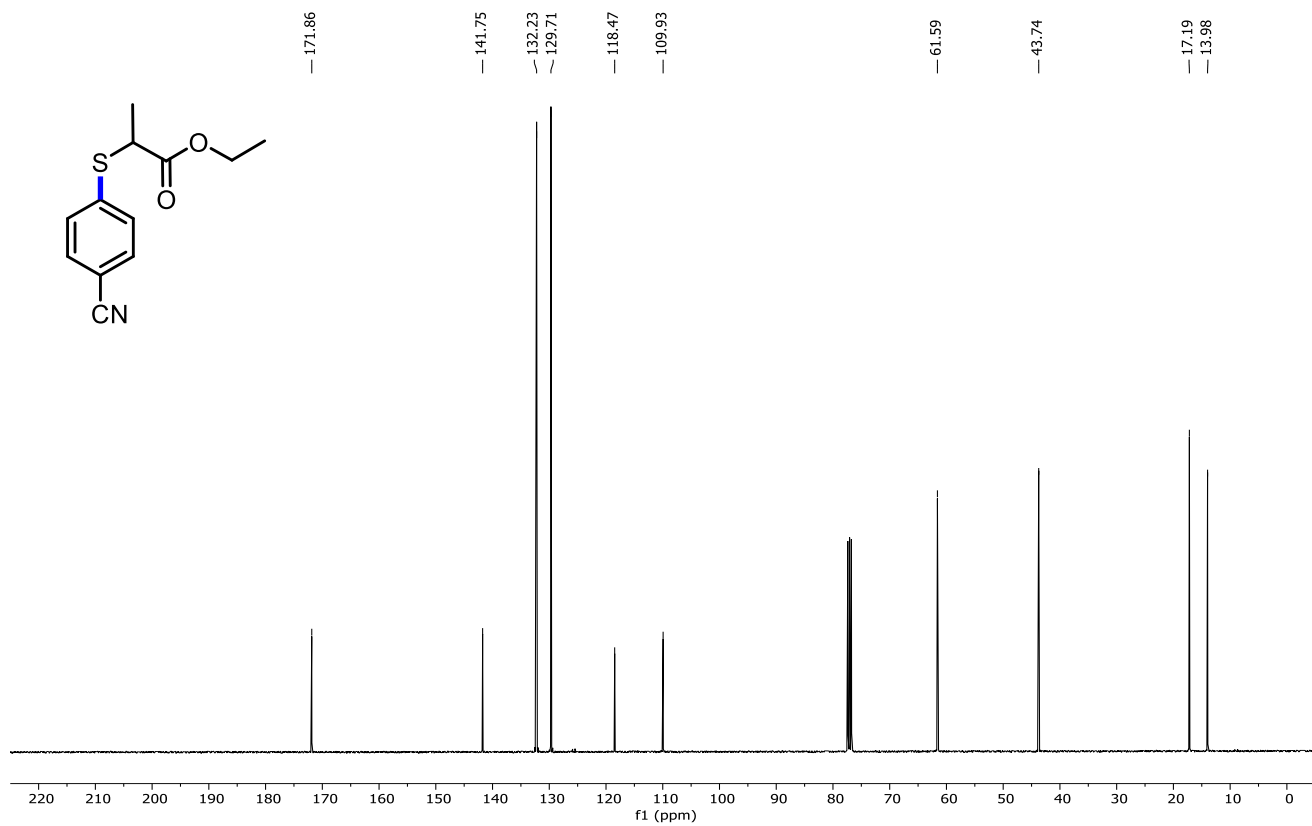
4-(octylthio)benzonitrile (3): ^{13}C NMR (100 MHz), CDCl_3 .



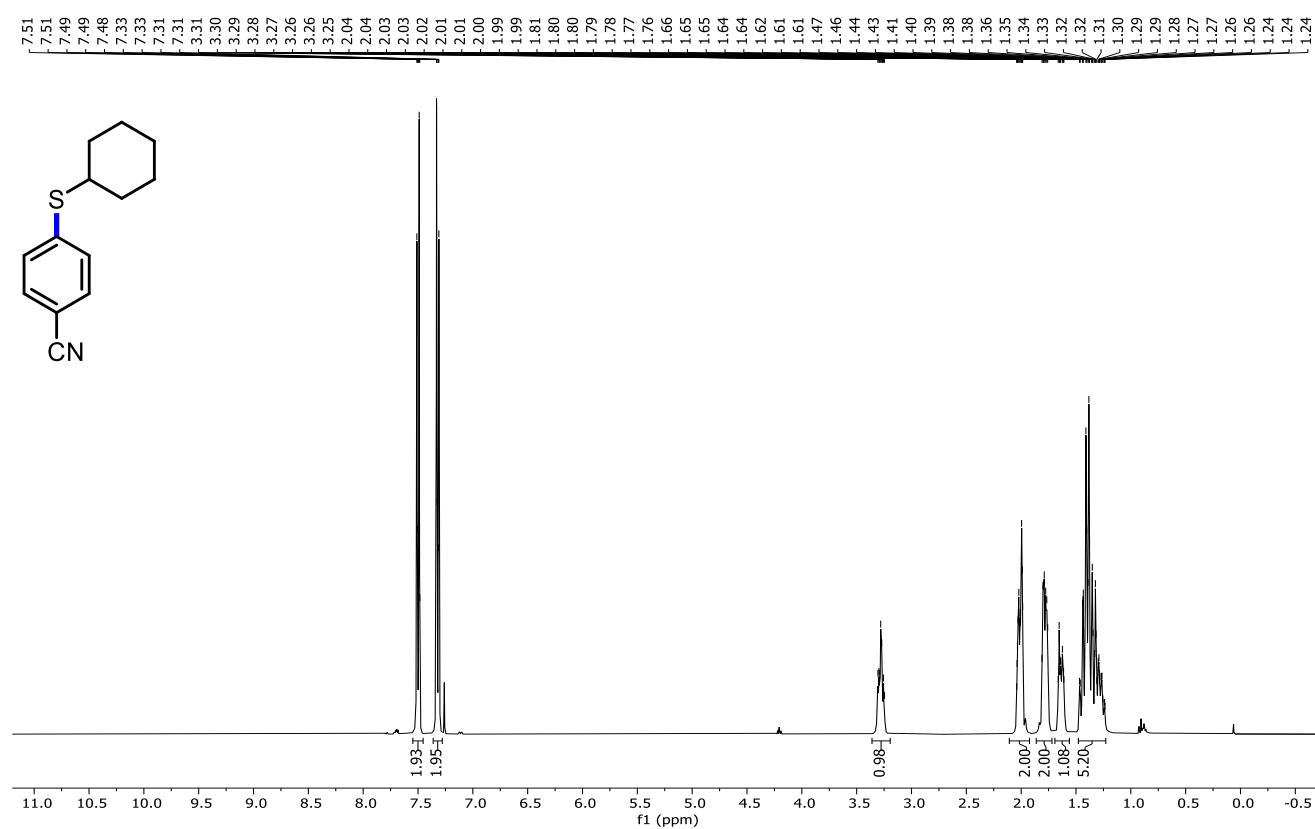
Ethyl 2-((4-cyanophenyl)thio)propanoate (4): ^1H NMR (400 MHz), CDCl_3 .



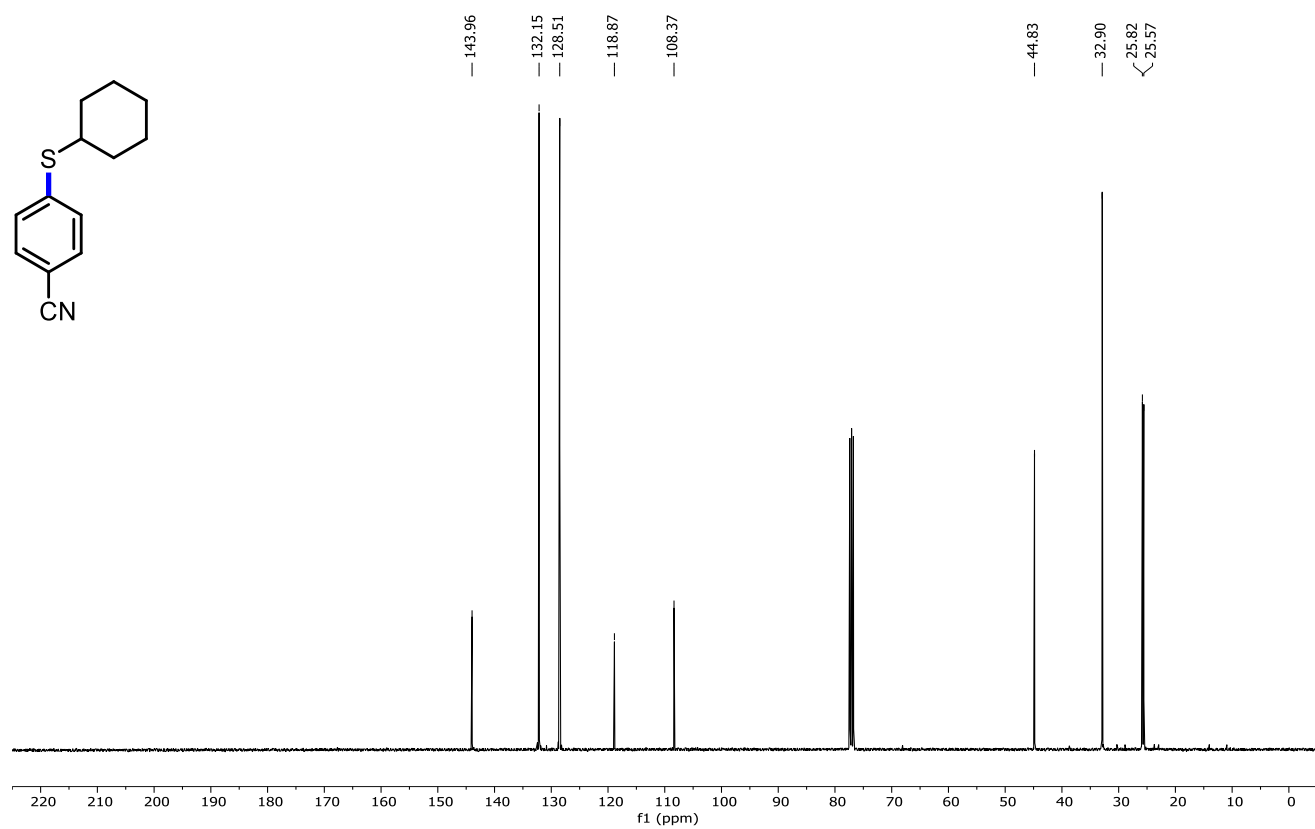
Ethyl 2-((4-cyanophenyl)thio)propanoate (4): ^{13}C NMR (100 MHz), CDCl_3 .



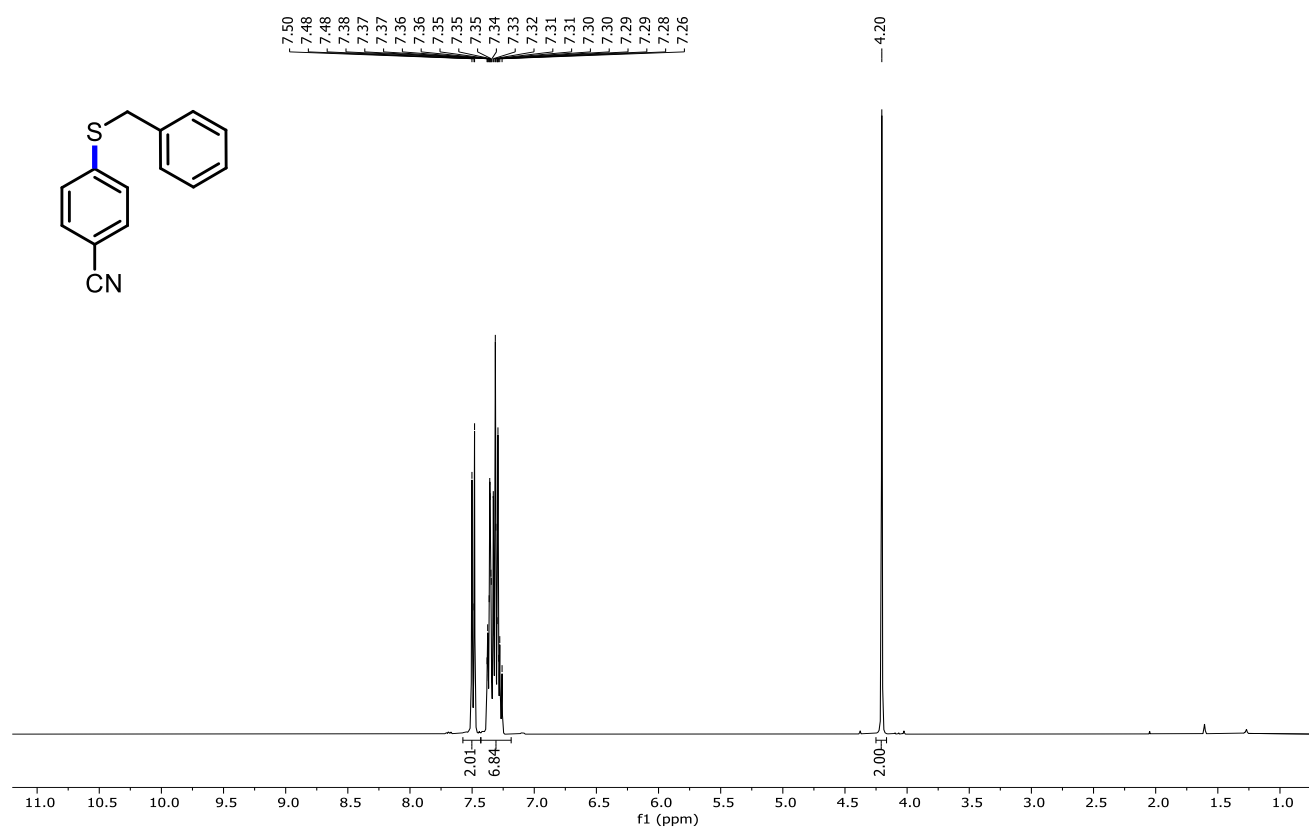
4-(cyclohexylthio)benzonitrile (5): ^1H NMR (400 MHz), CDCl_3 .



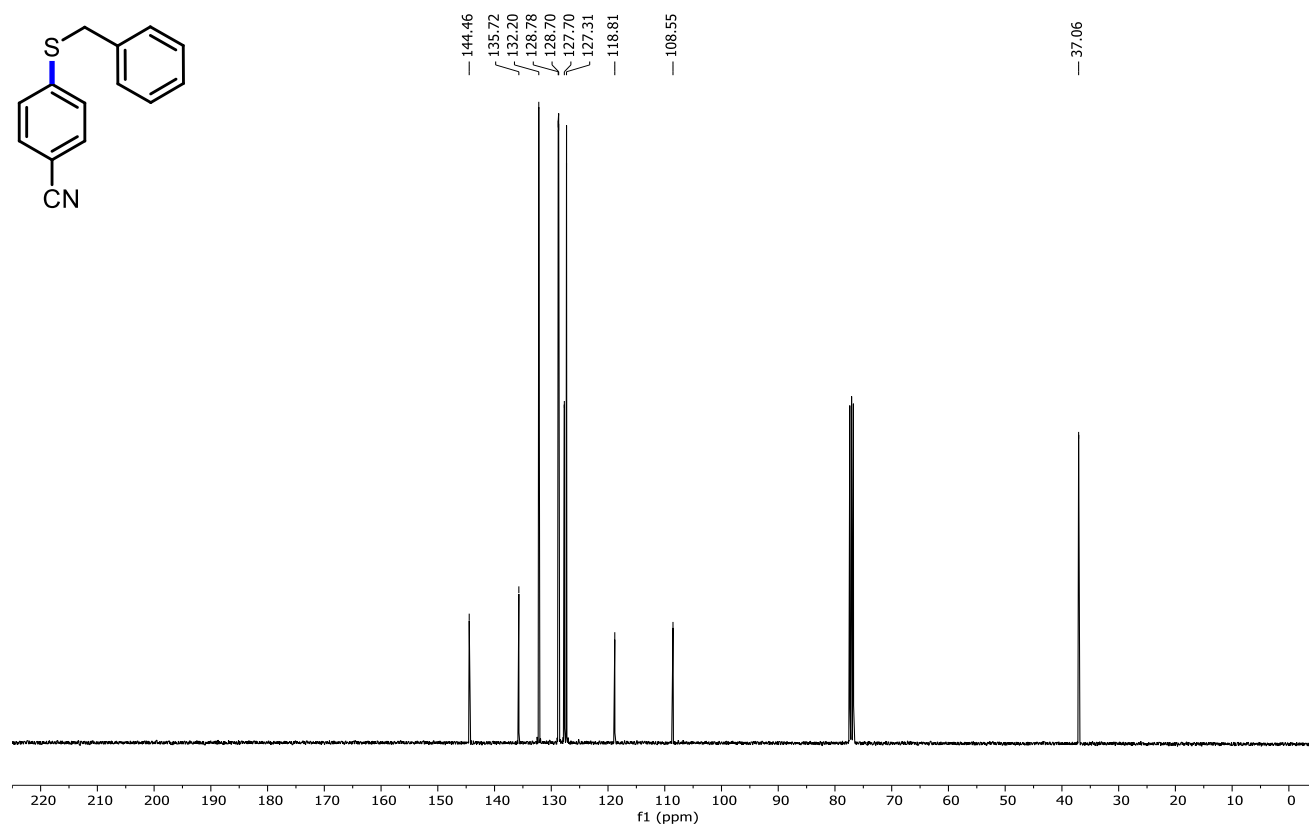
4-(cyclohexylthio)benzonitrile (5): ^{13}C NMR (100 MHz), CDCl_3 .



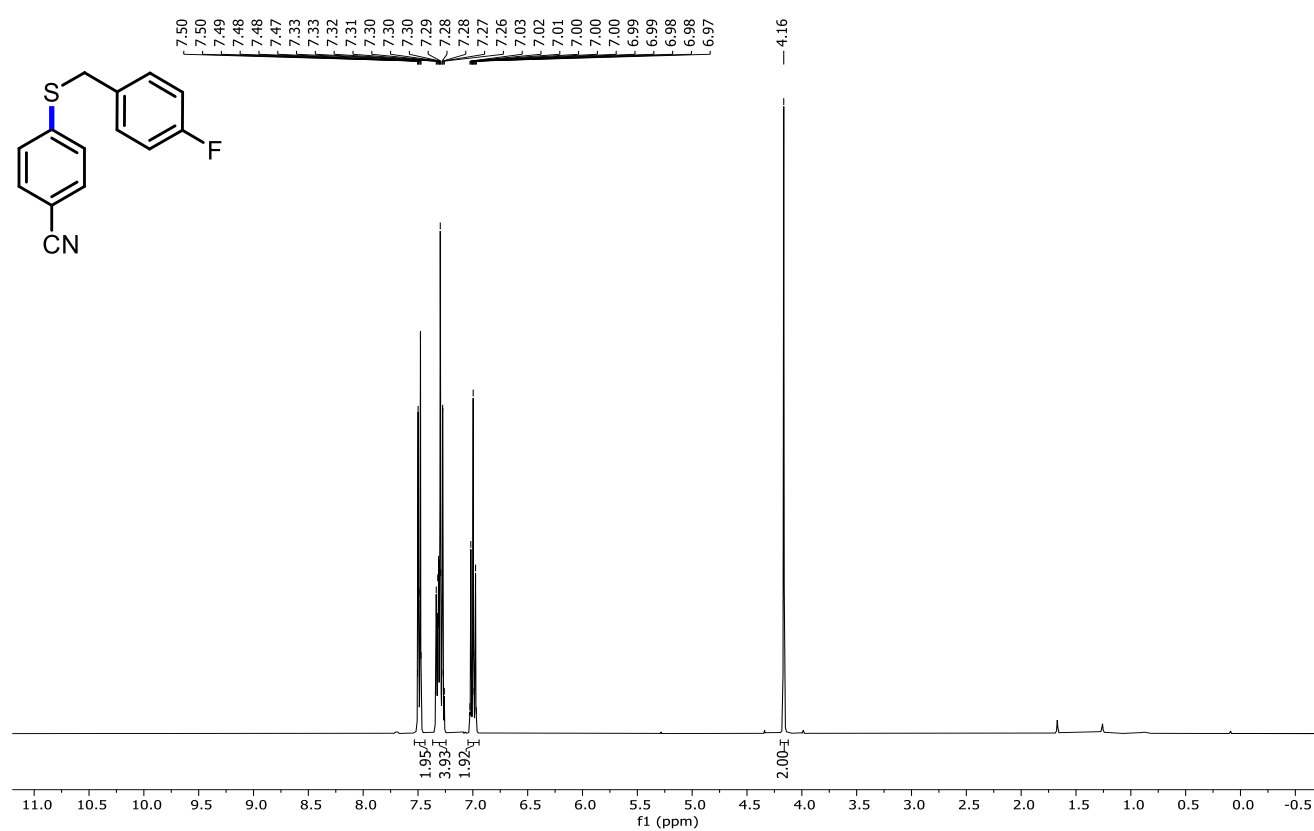
4-(benzylthio)benzonitrile (6): ^1H NMR (400 MHz), CDCl_3 .



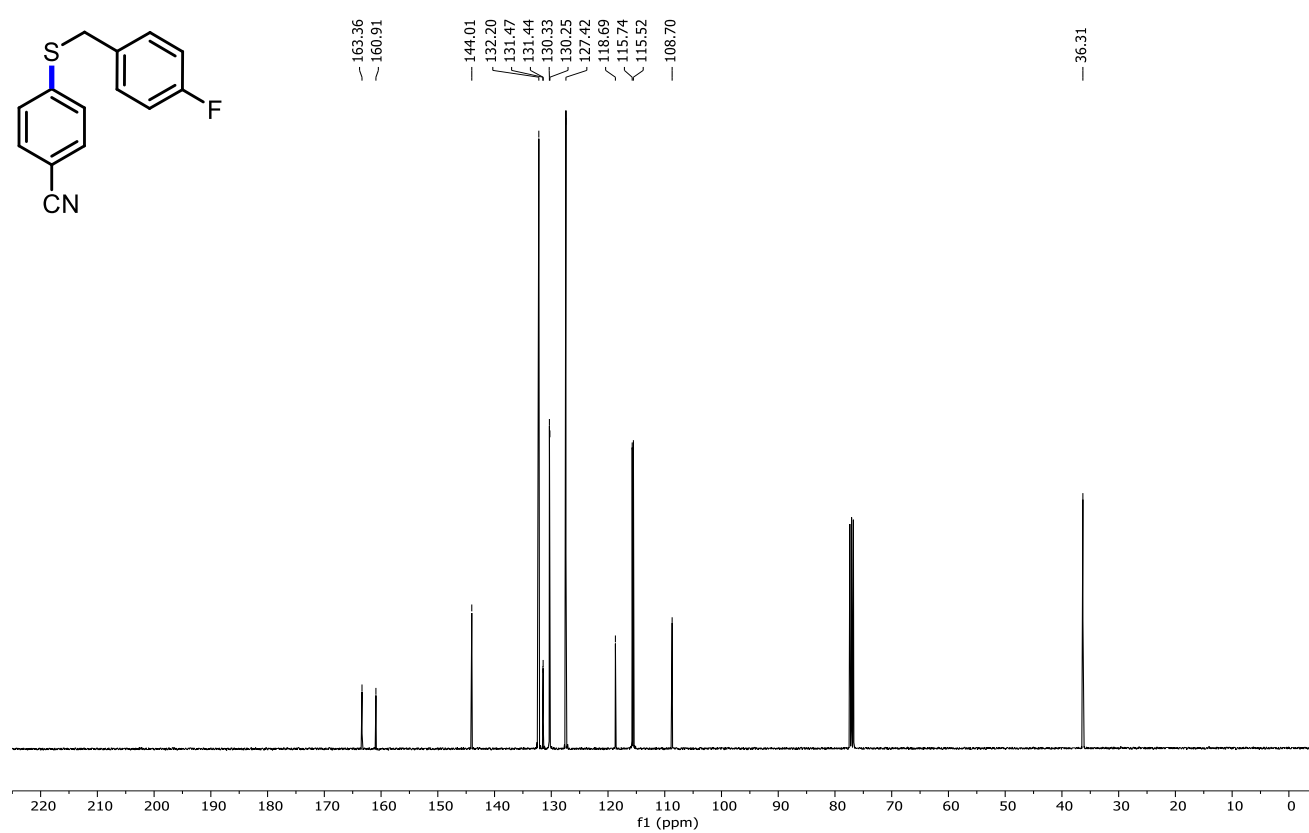
4-(benzylthio)benzonitrile (6): ^{13}C NMR (100 MHz), CDCl_3 .



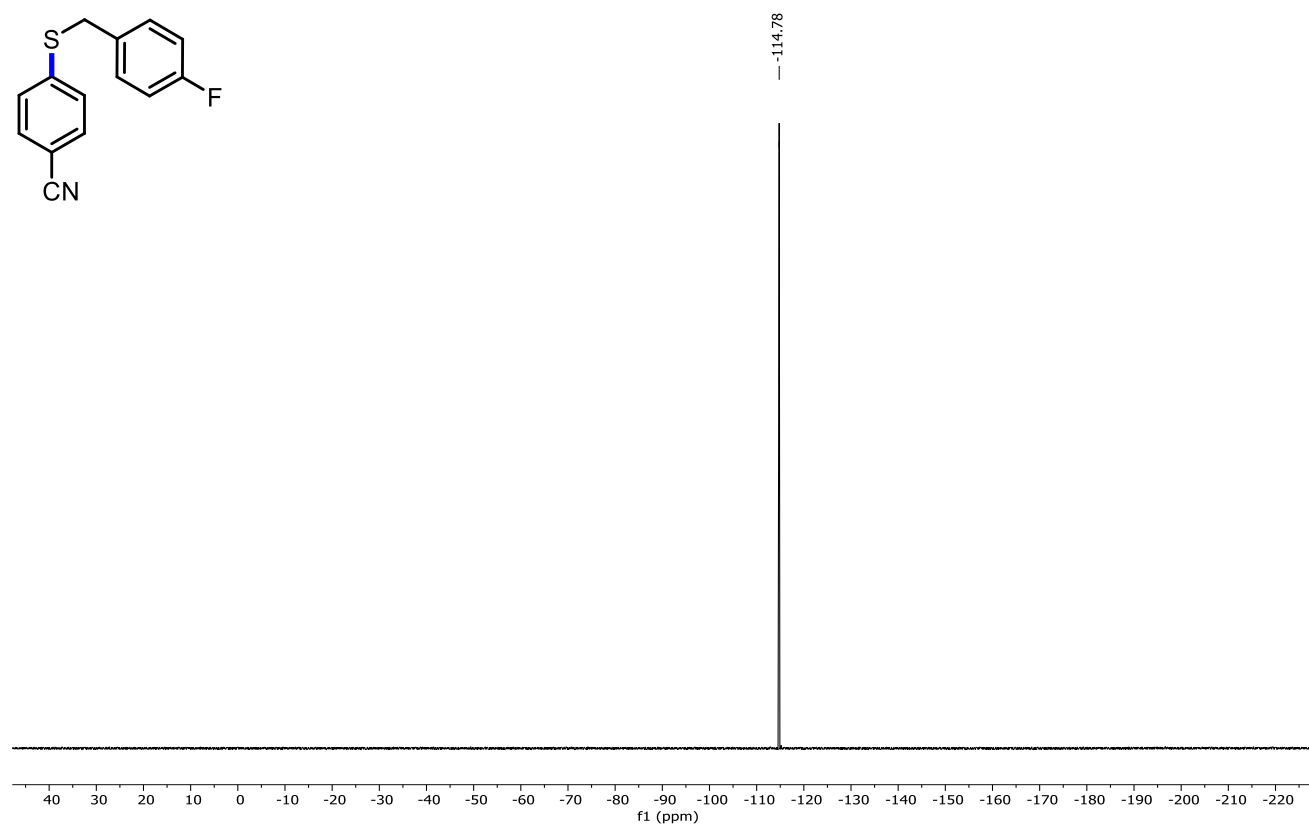
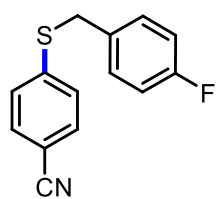
4-((4-fluorobenzyl)thio)benzonitrile (7): ¹H NMR (400 MHz), CDCl₃.



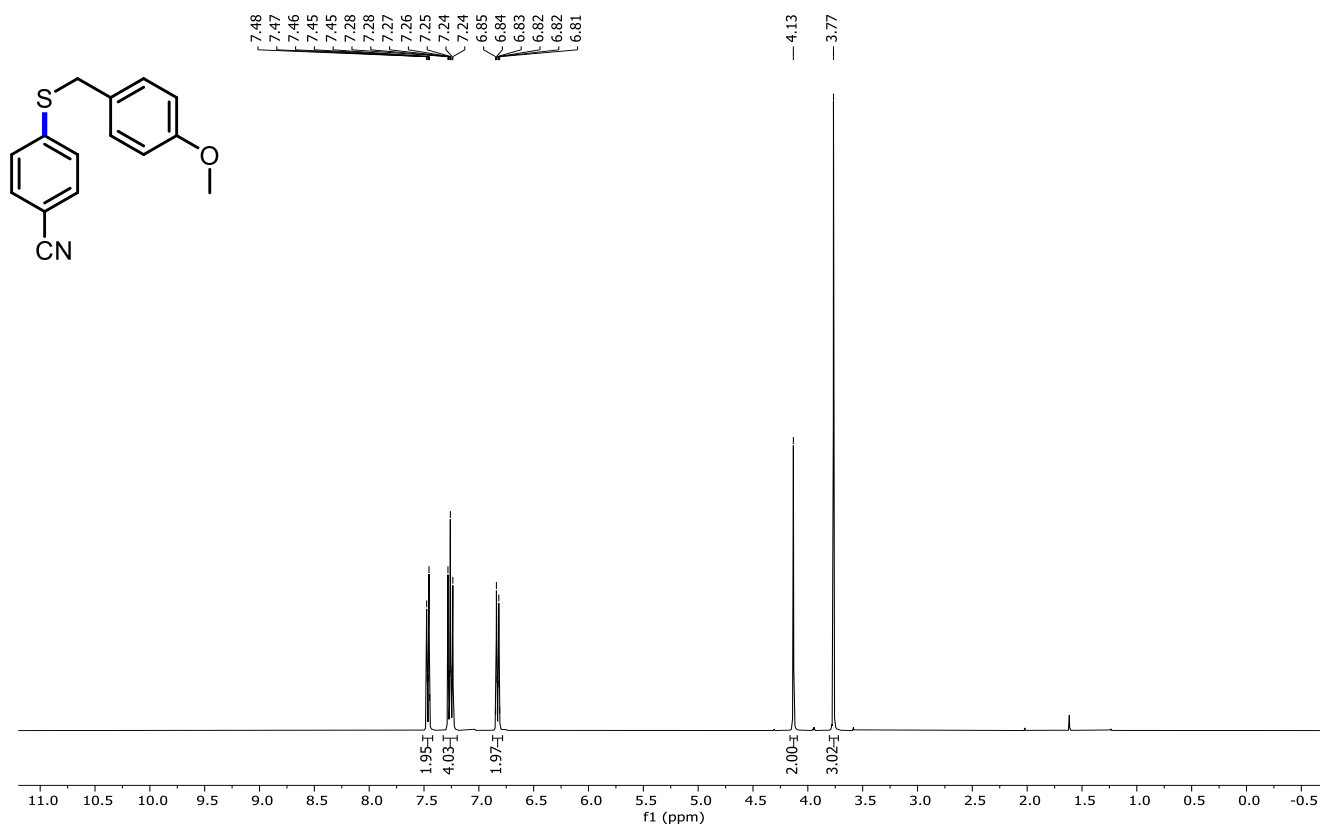
4-((4-fluorobenzyl)thio)benzonitrile (7): ¹³C NMR (100 MHz), CDCl₃.



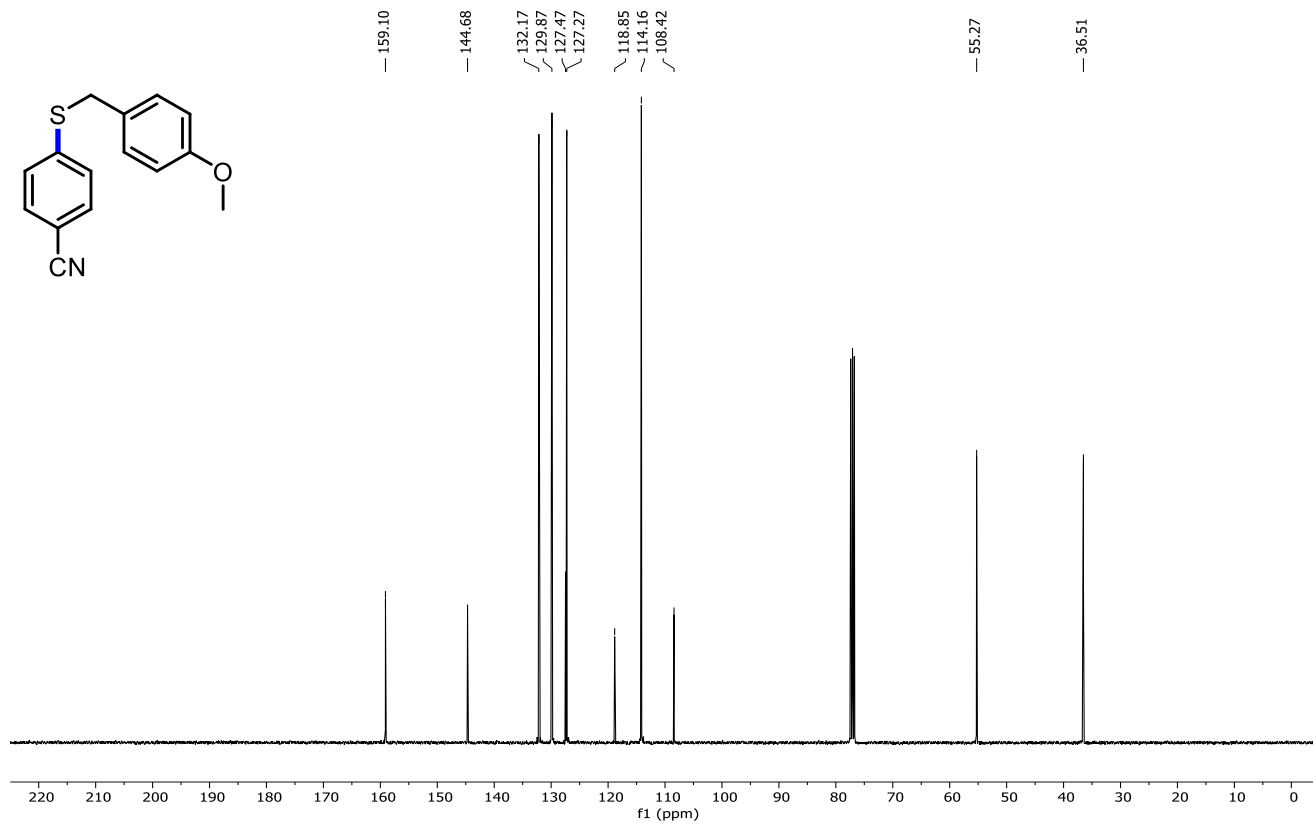
4-((4-fluorobenzyl)thio)benzonitrile (**7**): ^{19}F NMR (376 MHz), CDCl_3 .



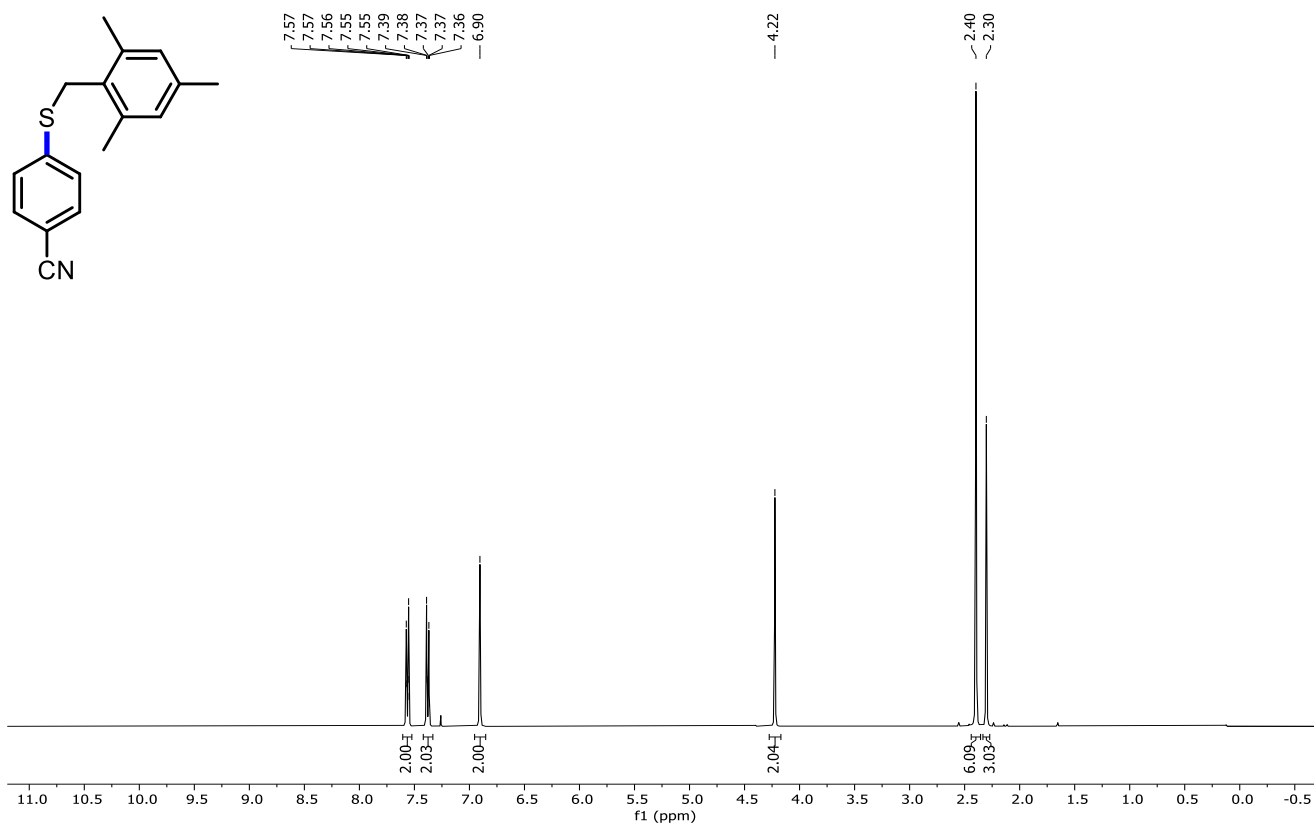
4-((4-methoxybenzyl)thio)benzonitrile (8): ^1H NMR (400 MHz), CDCl_3 .



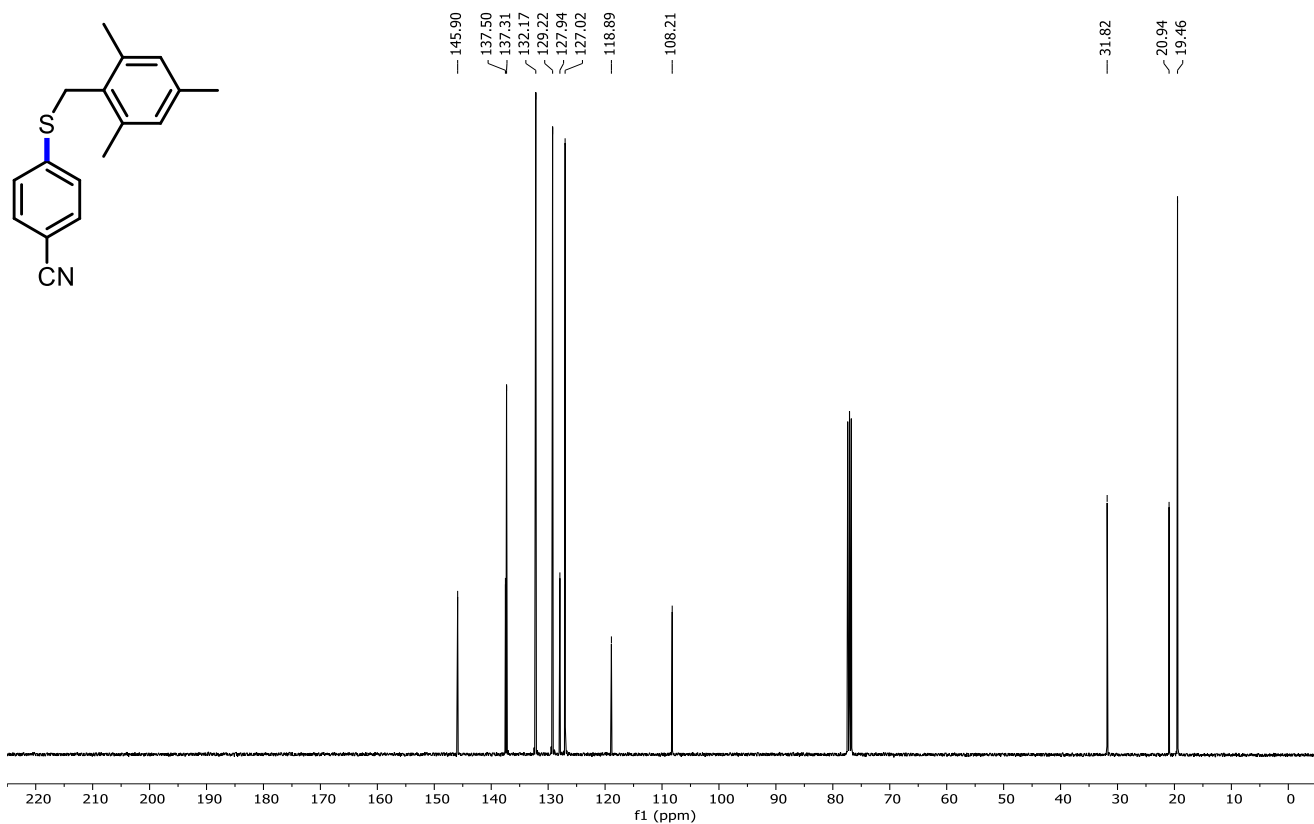
4-((4-methoxybenzyl)thio)benzonitrile (8): ^{13}C NMR (100 MHz), CDCl_3 .



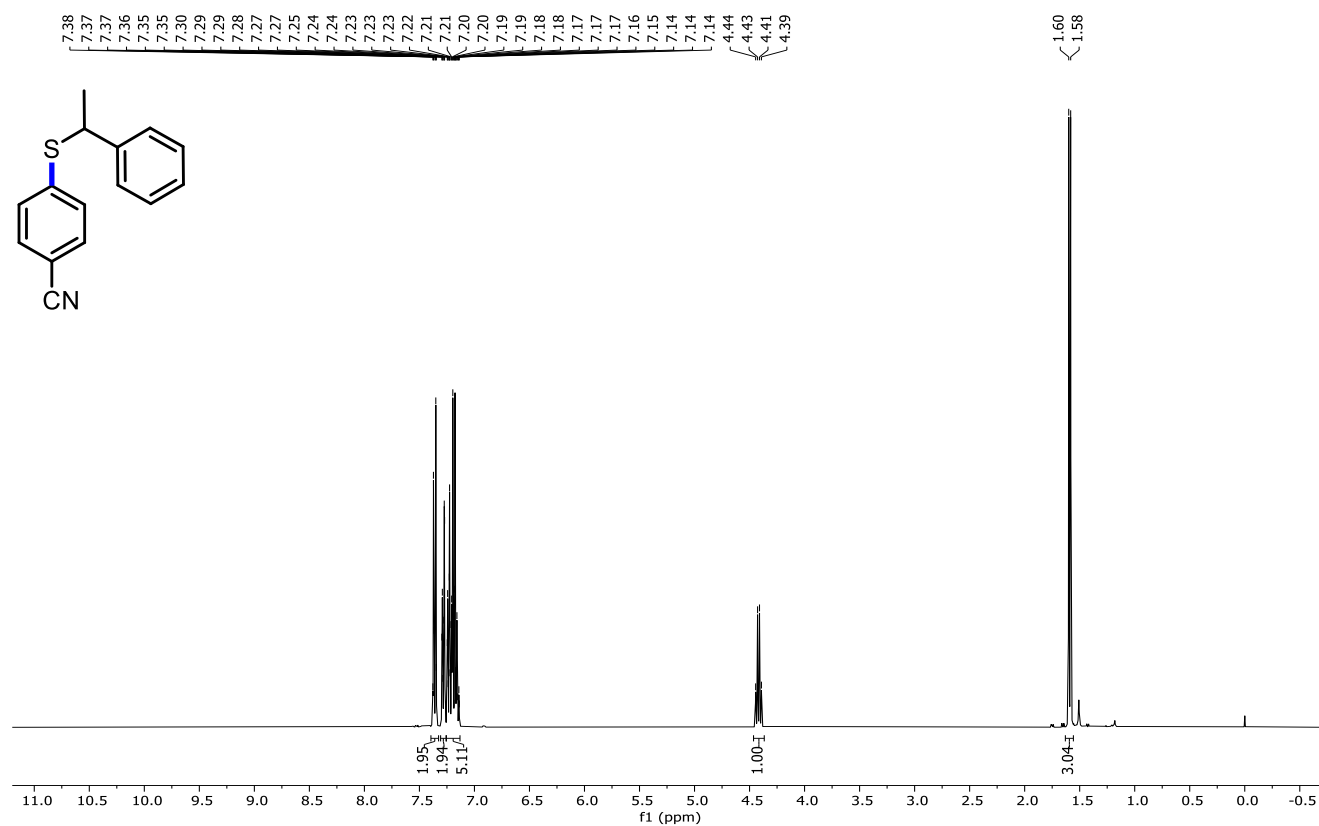
4-((2,4,6-trimethylbenzyl)thio)benzonitrile (9): ^1H NMR (400 MHz), CDCl_3 .



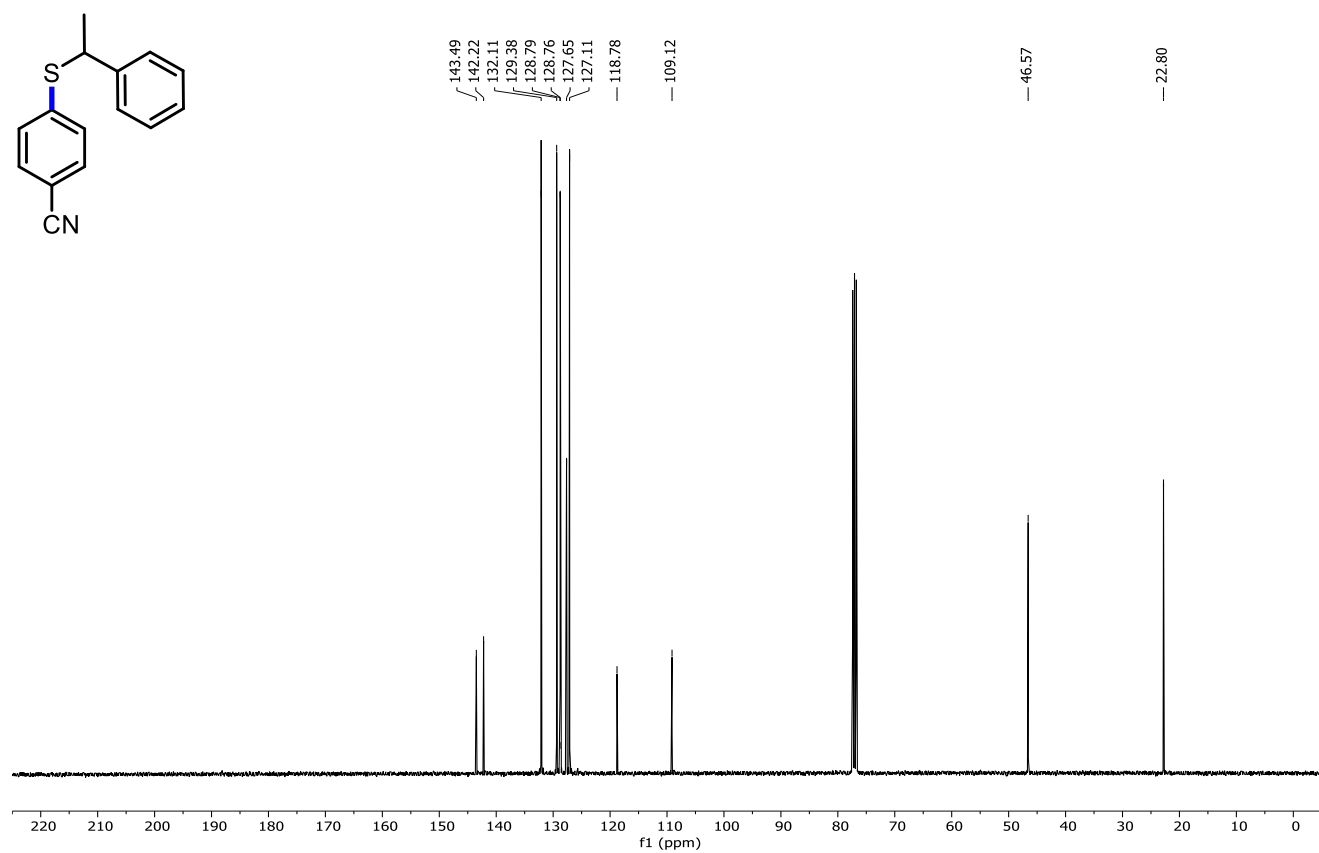
4-((2,4,6-trimethylbenzyl)thio)benzonitrile (9): ^{13}C NMR (100 MHz), CDCl_3 .



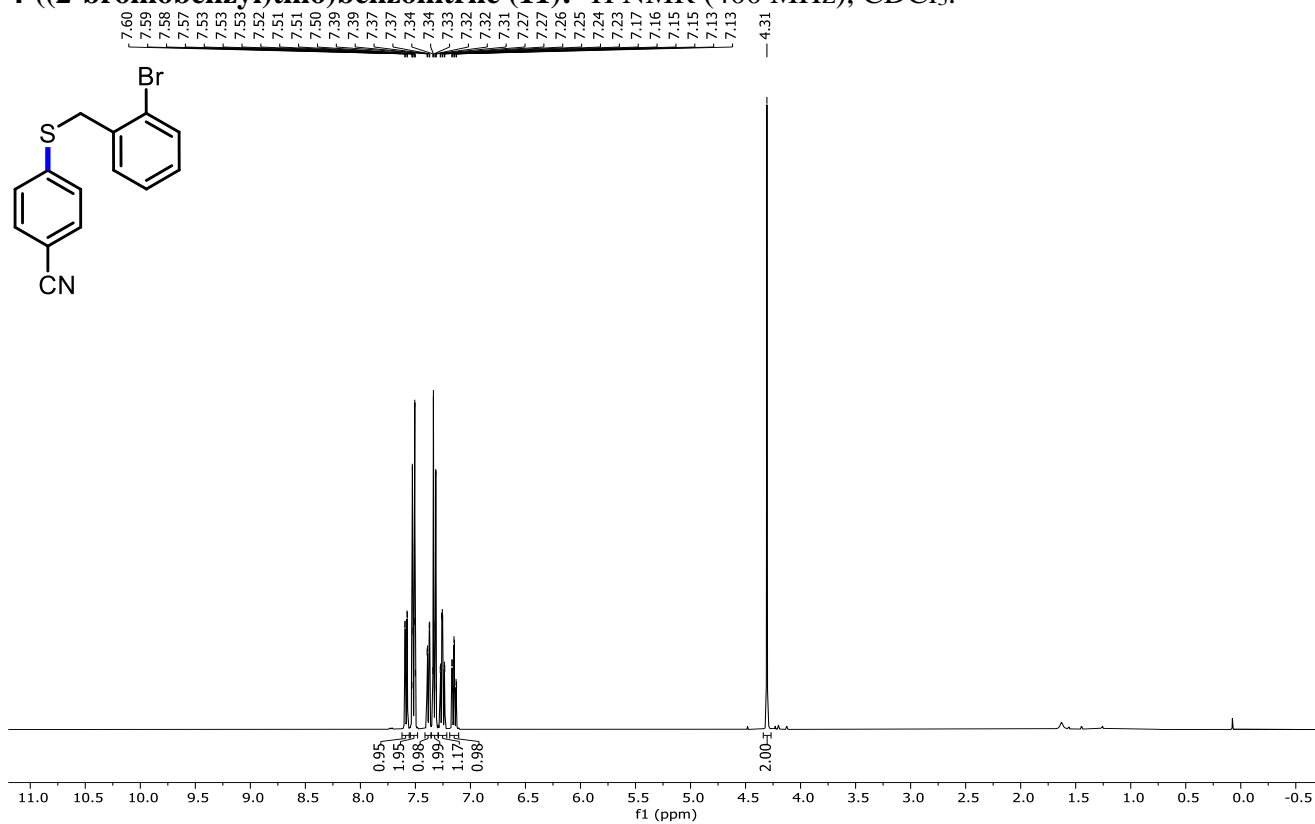
4-((1-phenylethyl)thio)benzonitrile (10): ^1H NMR (400 MHz), CDCl_3 .



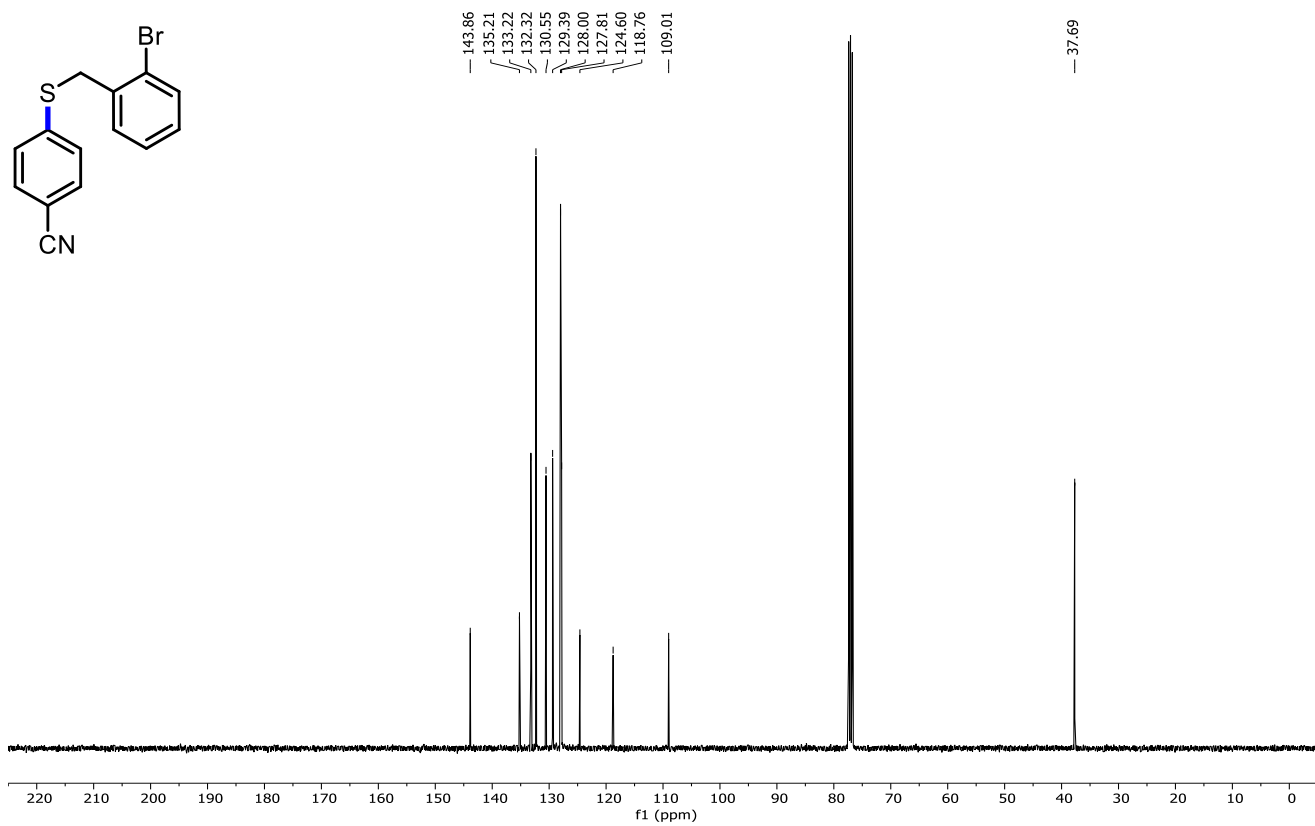
4-((1-phenylethyl)thio)benzonitrile (10): ^{13}C NMR (100 MHz), CDCl_3 .



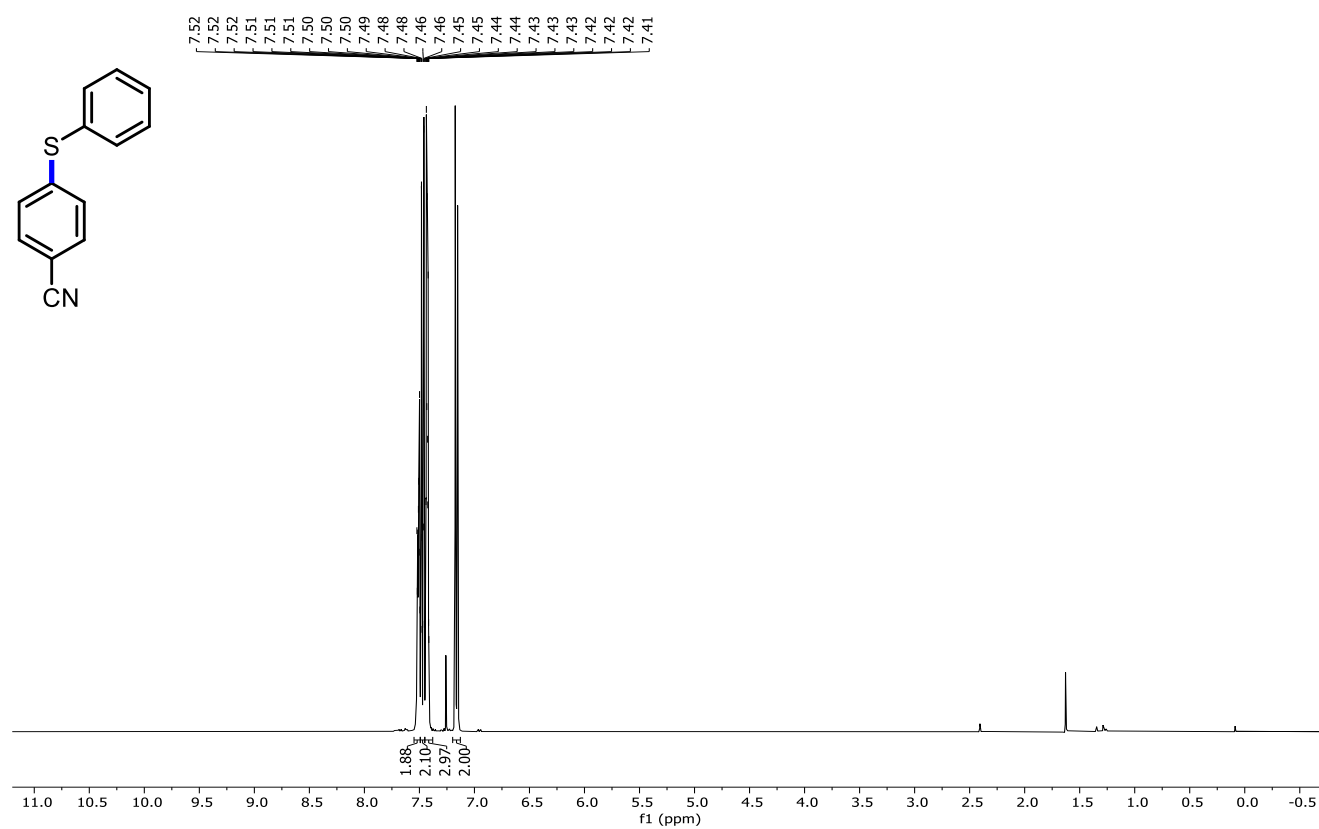
4-((2-bromobenzyl)thio)benzonitrile (11): ^1H NMR (400 MHz), CDCl_3 .



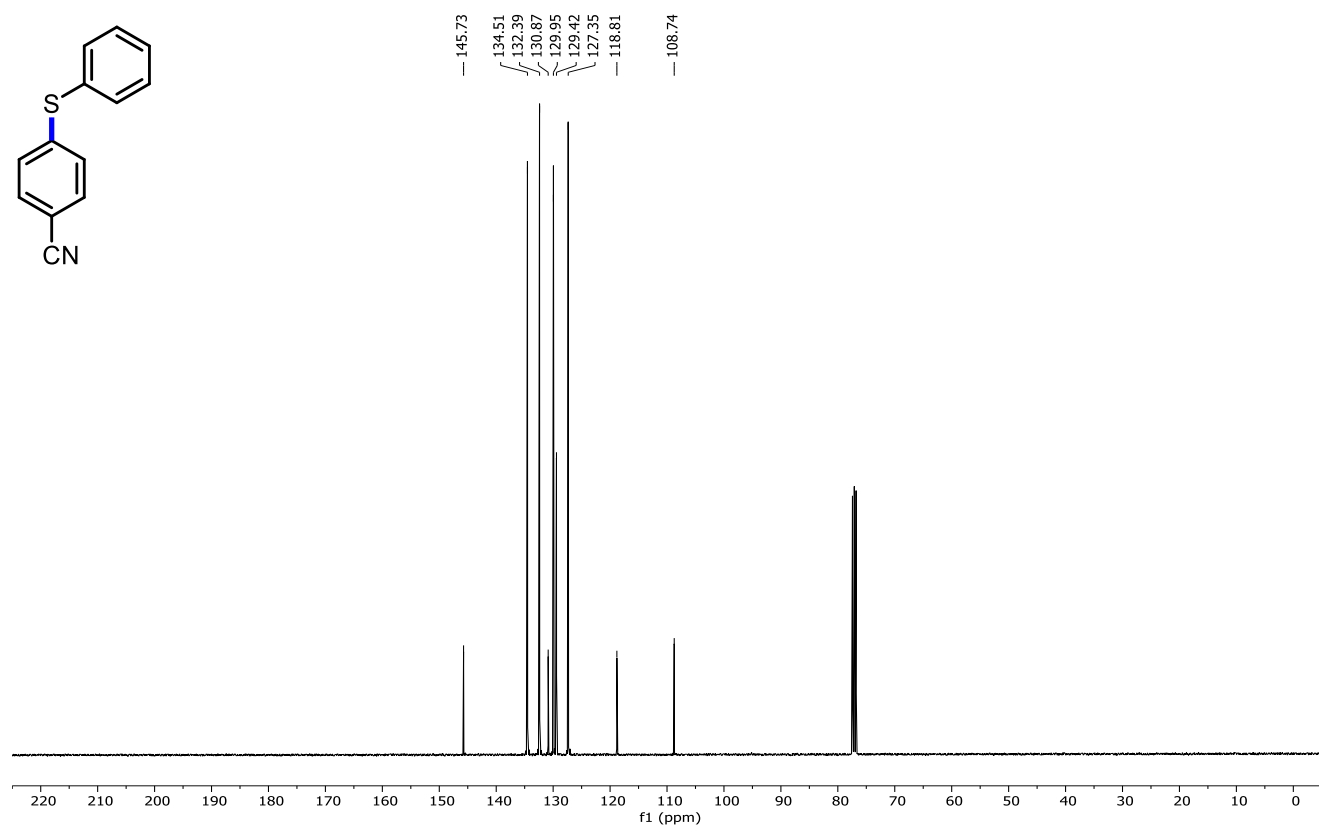
4-((2-bromobenzyl)thio)benzonitrile (11): ^{13}C NMR (100 MHz), CDCl_3 .



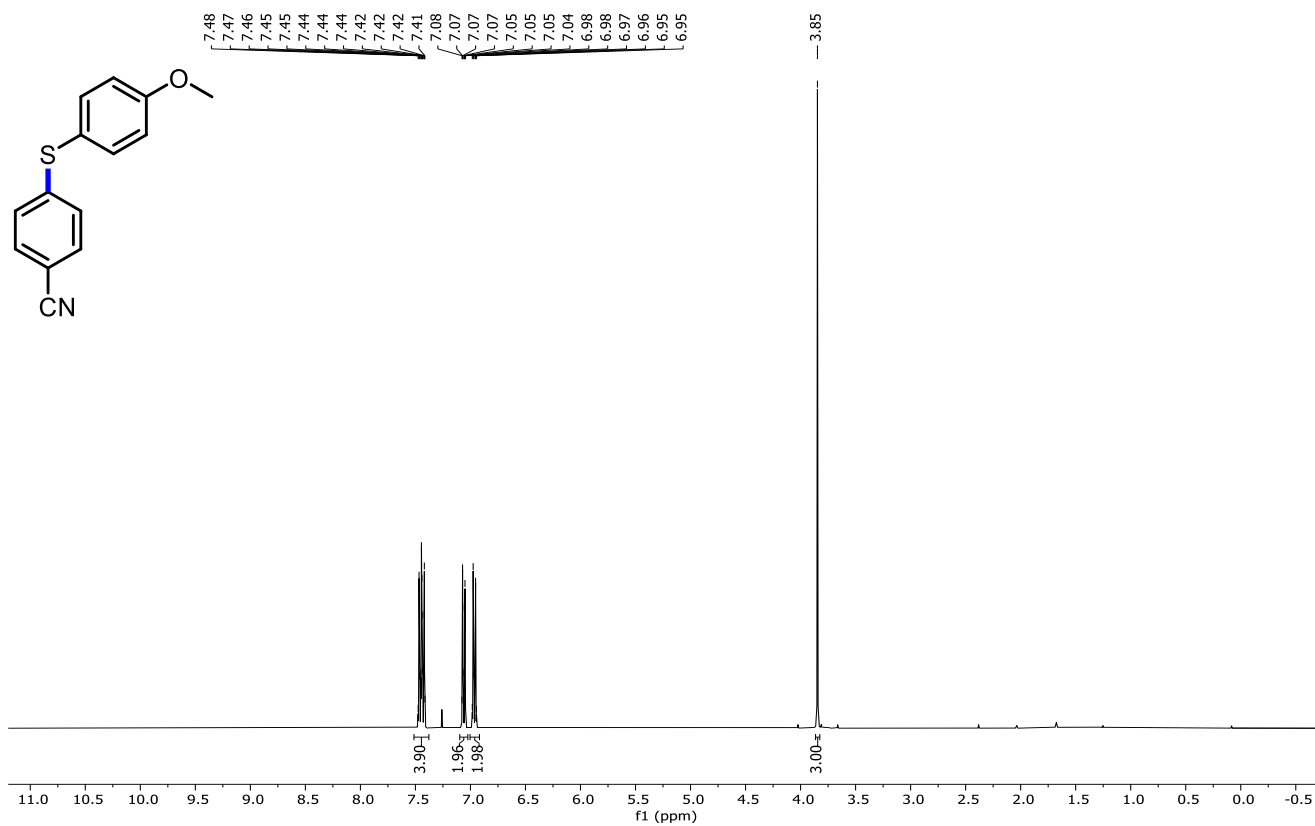
4-(phenylthio)benzonitrile (12): ^1H NMR (400 MHz), CDCl_3 .



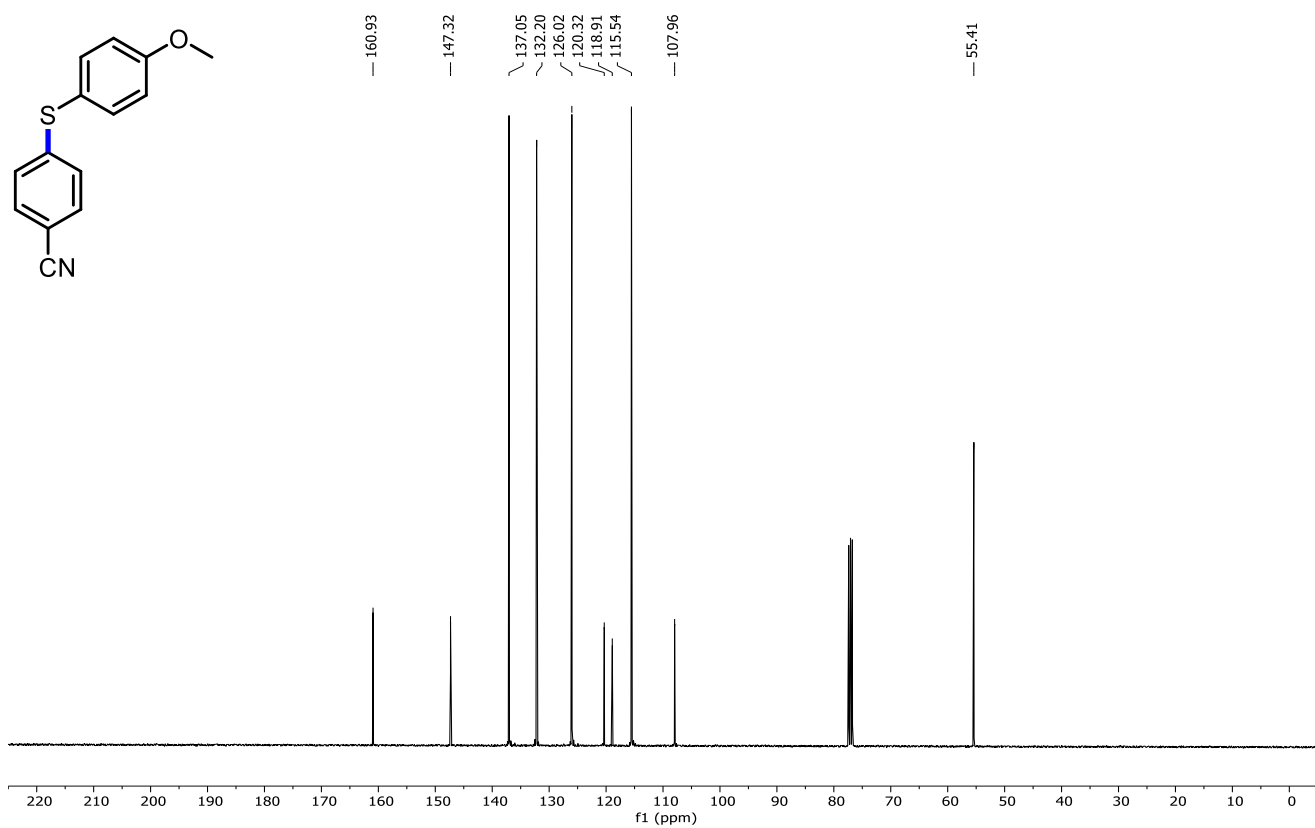
4-(phenylthio)benzonitrile (12): ^{13}C NMR (100 MHz), CDCl_3 .



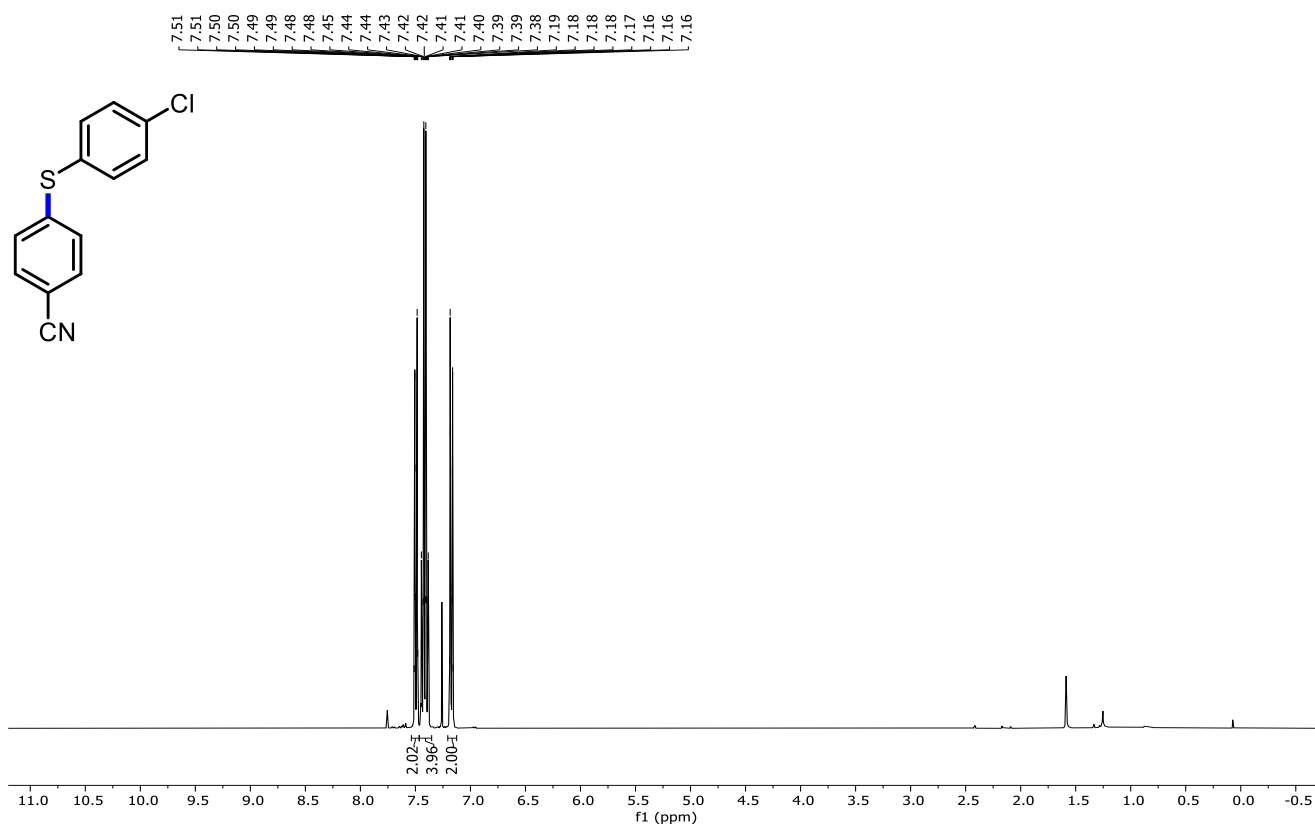
4-((4-methoxyphenyl)thio)benzonitrile (13): ^1H NMR (400 MHz), CDCl_3 .



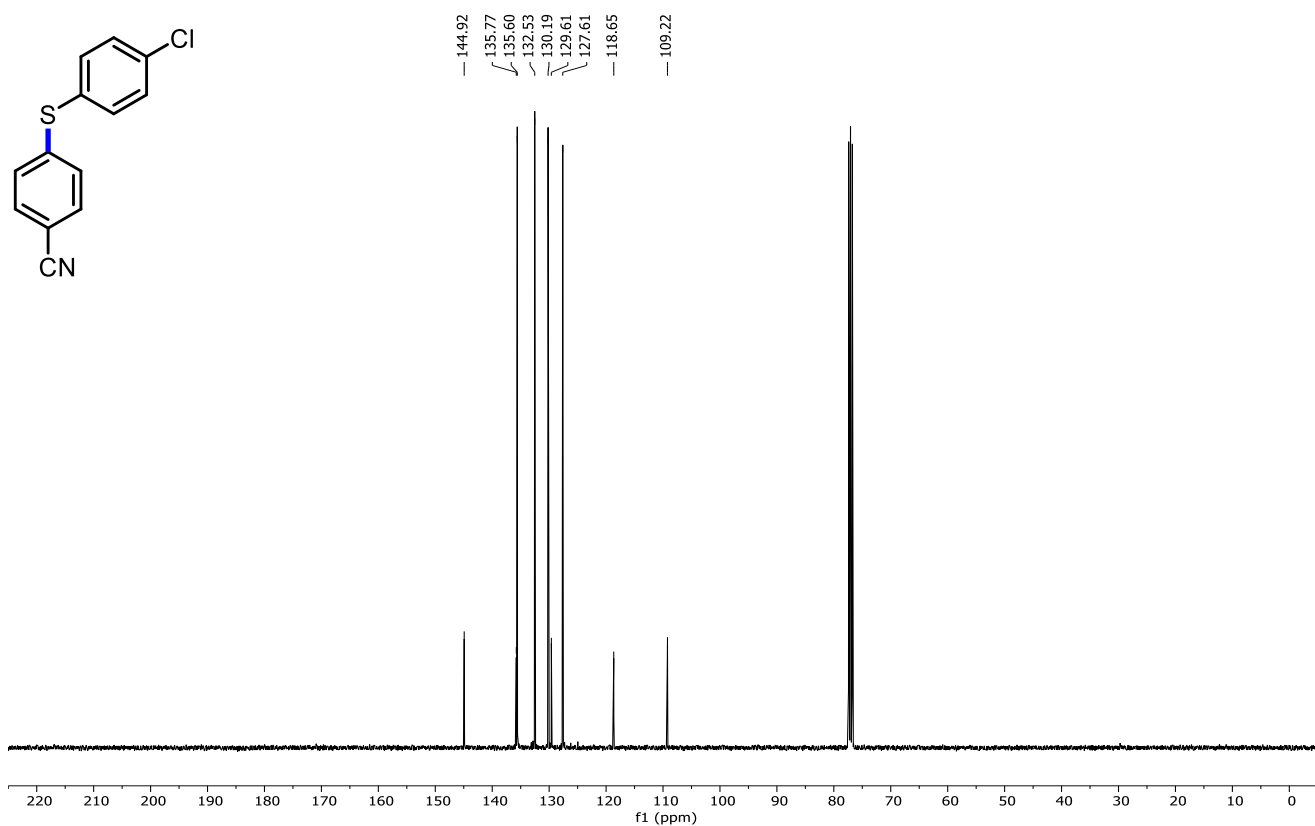
4-((4-methoxyphenyl)thio)benzonitrile (13): ^{13}C NMR (100 MHz), CDCl_3 .



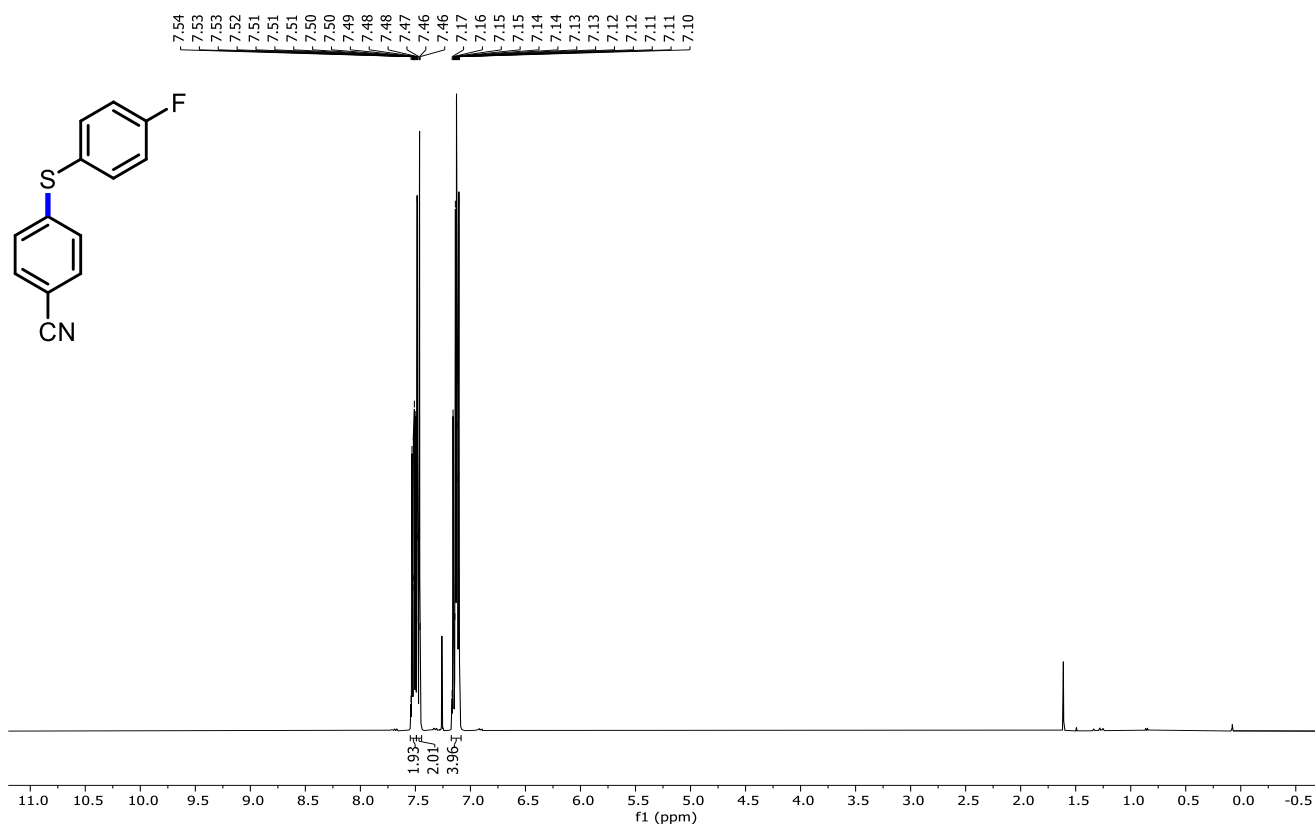
4-((4-chlorophenyl)thio)benzonitrile (14): ^1H NMR (400 MHz), CDCl_3



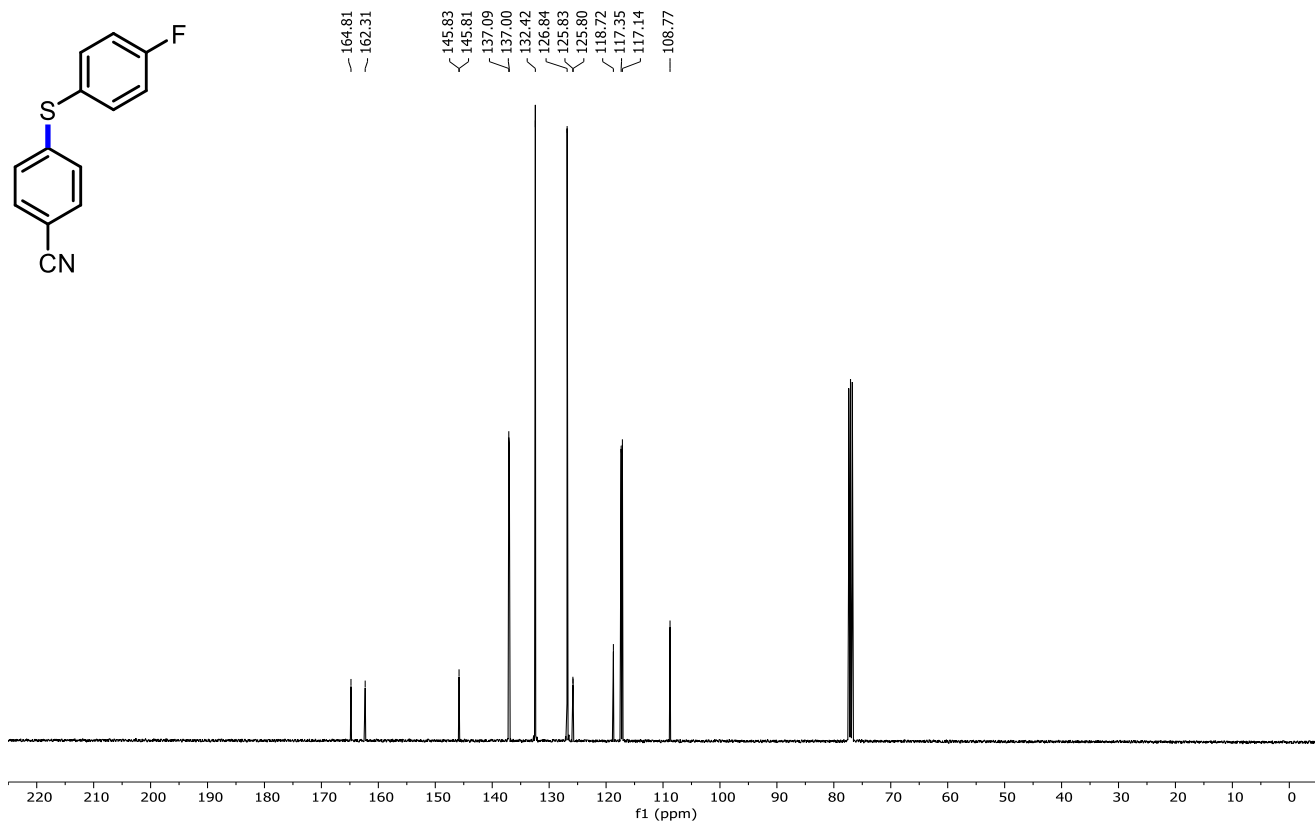
4-((4-chlorophenyl)thio)benzonitrile (14): ^{13}C NMR (100 MHz), CDCl_3



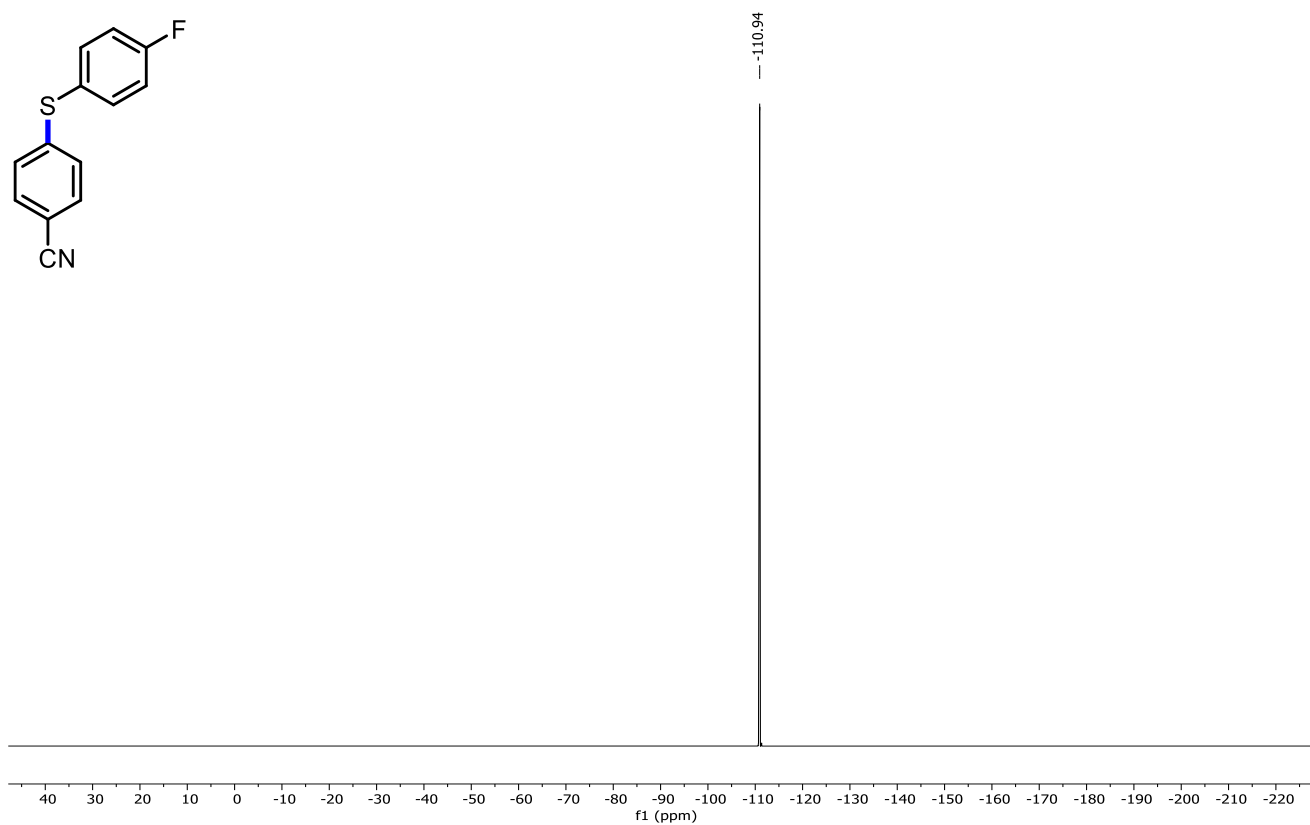
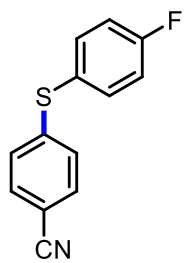
4-((4-fluorophenyl)thio)benzonitrile (15): ^1H NMR (400 MHz), CDCl_3



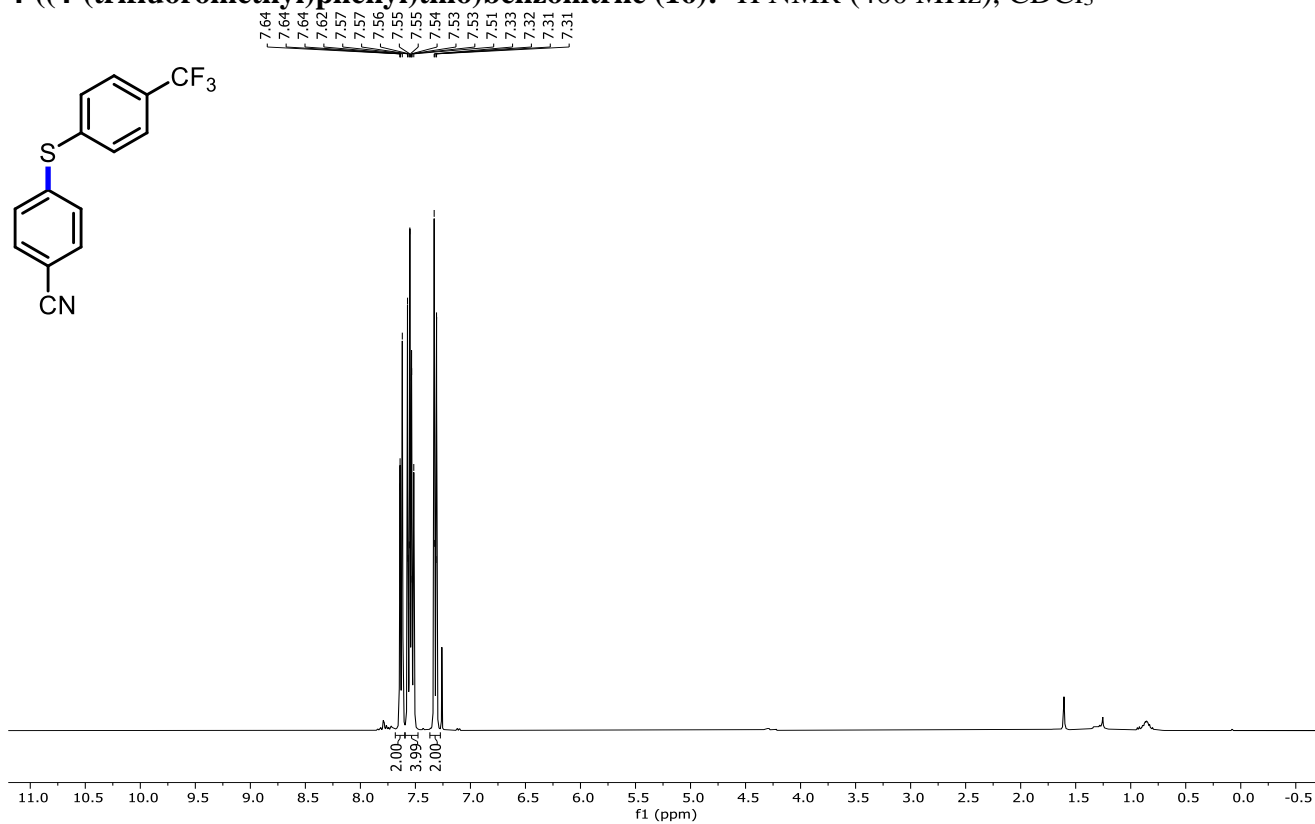
4-((4-fluorophenyl)thio)benzonitrile (15): ^{13}C NMR (100 MHz), CDCl_3 .



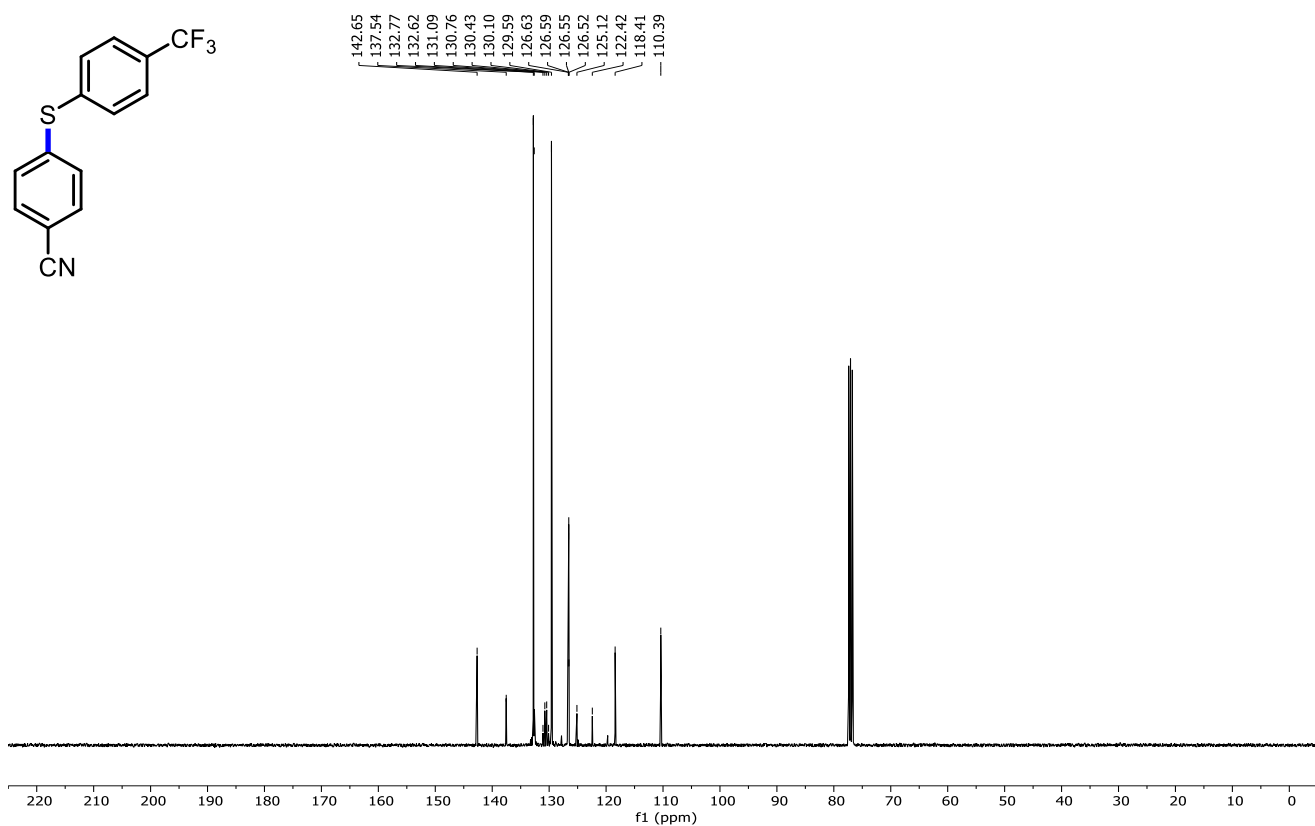
4-((4-fluorophenyl)thio)benzonitrile (15): ^{19}F NMR (376 MHz), CDCl_3 .



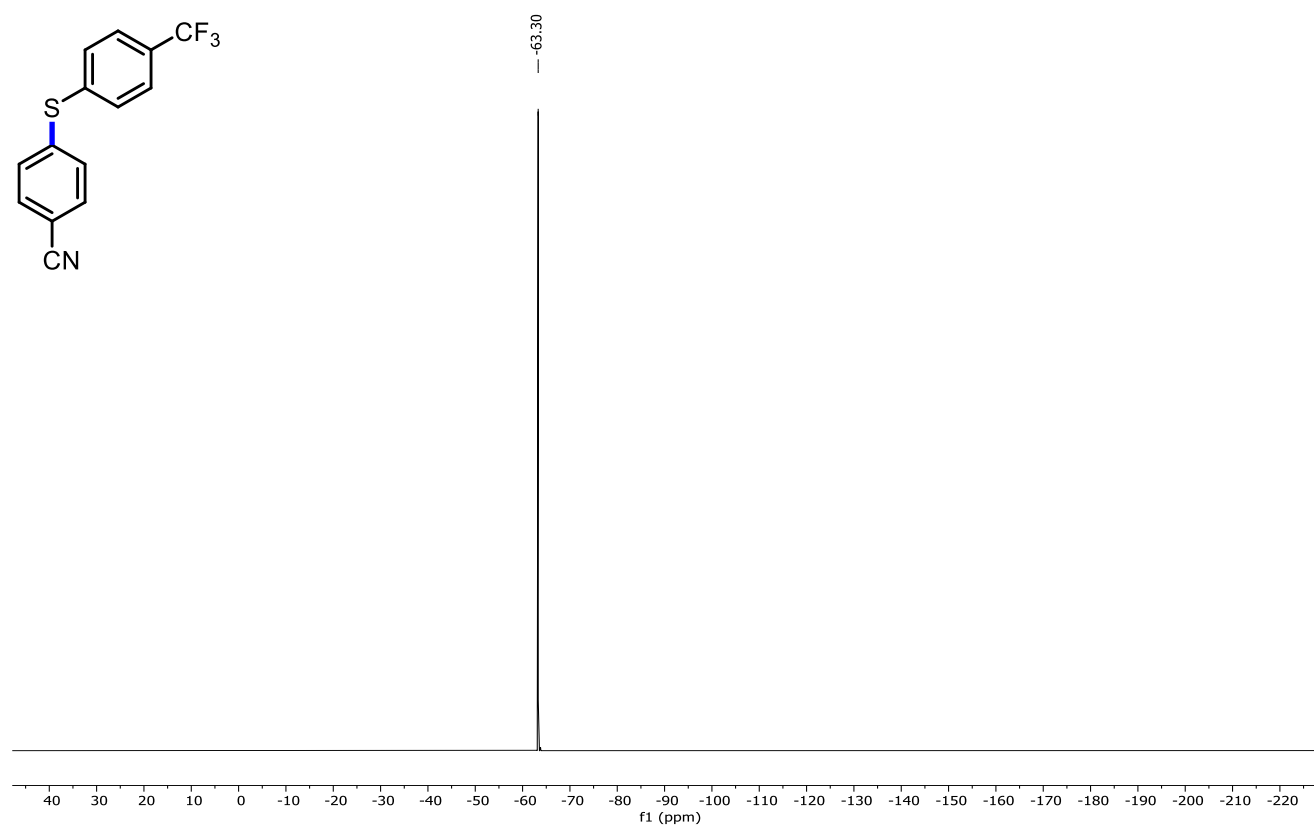
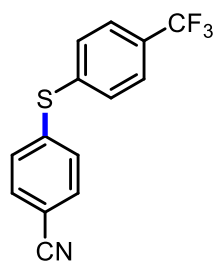
4-((4-(trifluoromethyl)phenyl)thio)benzonitrile (16): ^1H NMR (400 MHz), CDCl_3



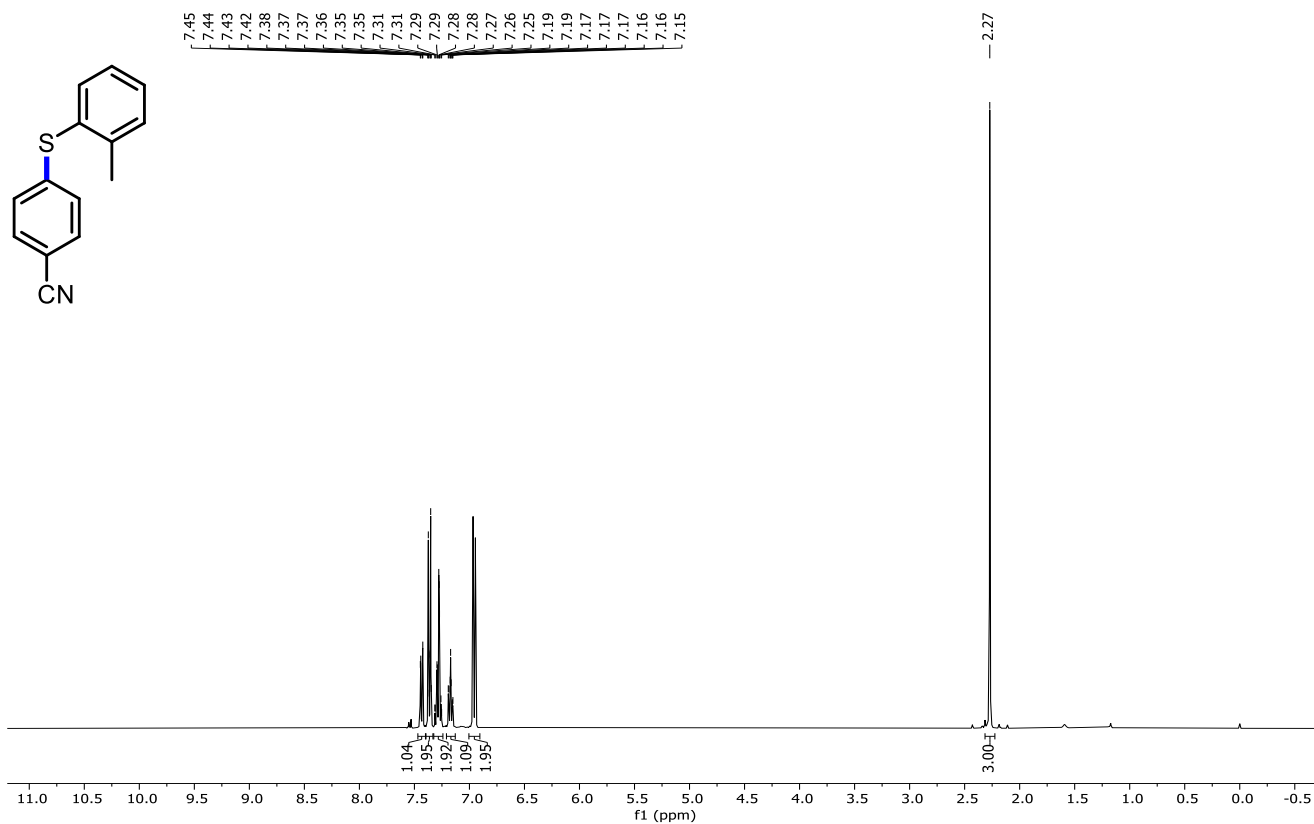
4-((4-(trifluoromethyl)phenyl)thio)benzonitrile (16): ^{13}C NMR (100 MHz), CDCl_3



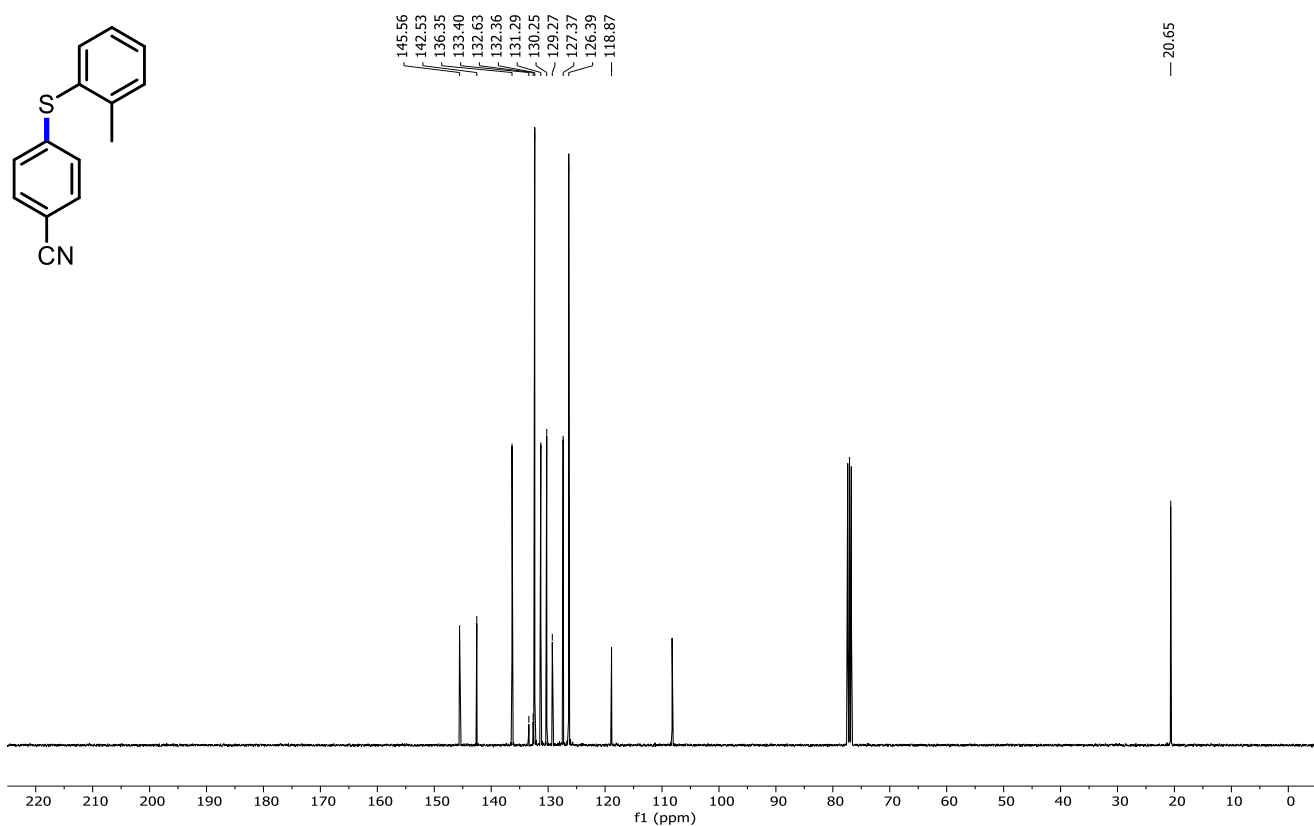
4-((4-(trifluoromethyl)phenyl)thio)benzonitrile (16): ^{19}F NMR (376 MHz), CDCl_3 .



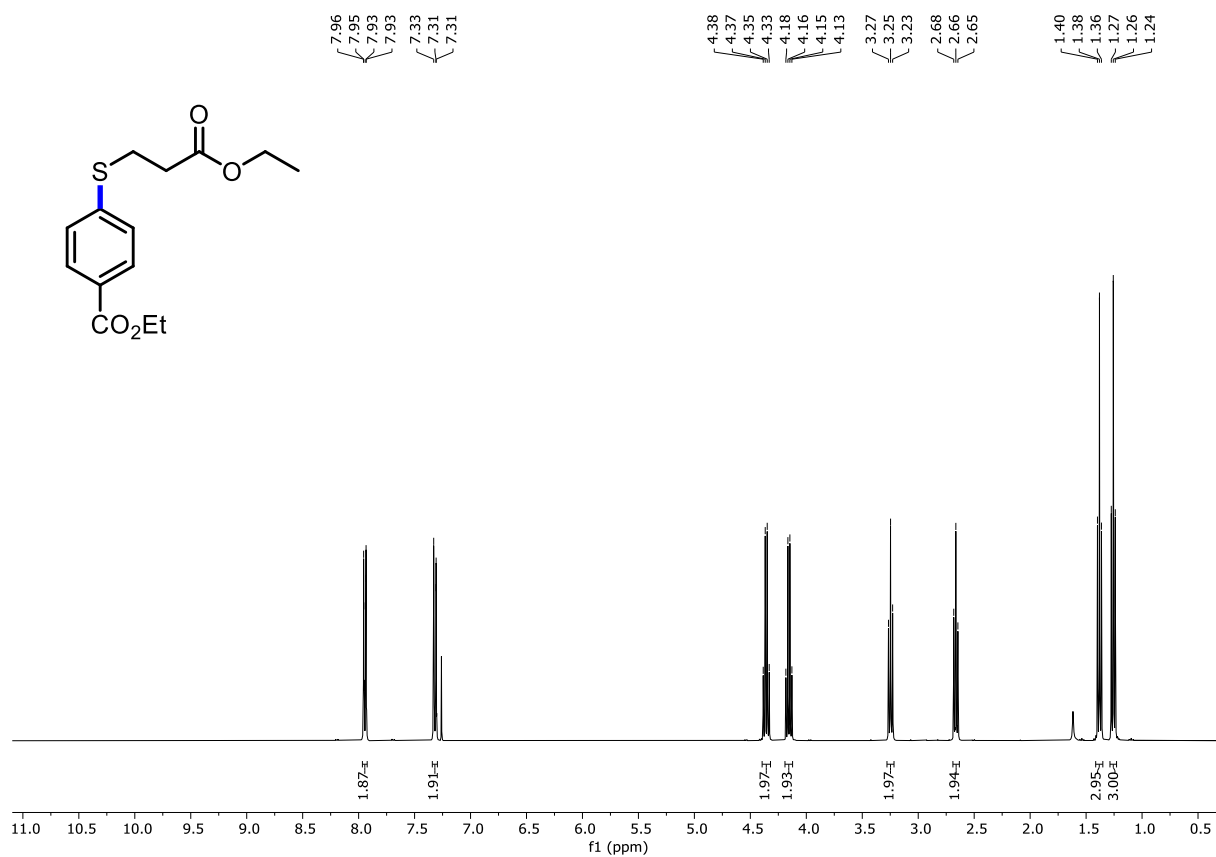
4-(o-tolylthio)benzotrile (17): ^1H NMR (400 MHz), CDCl_3



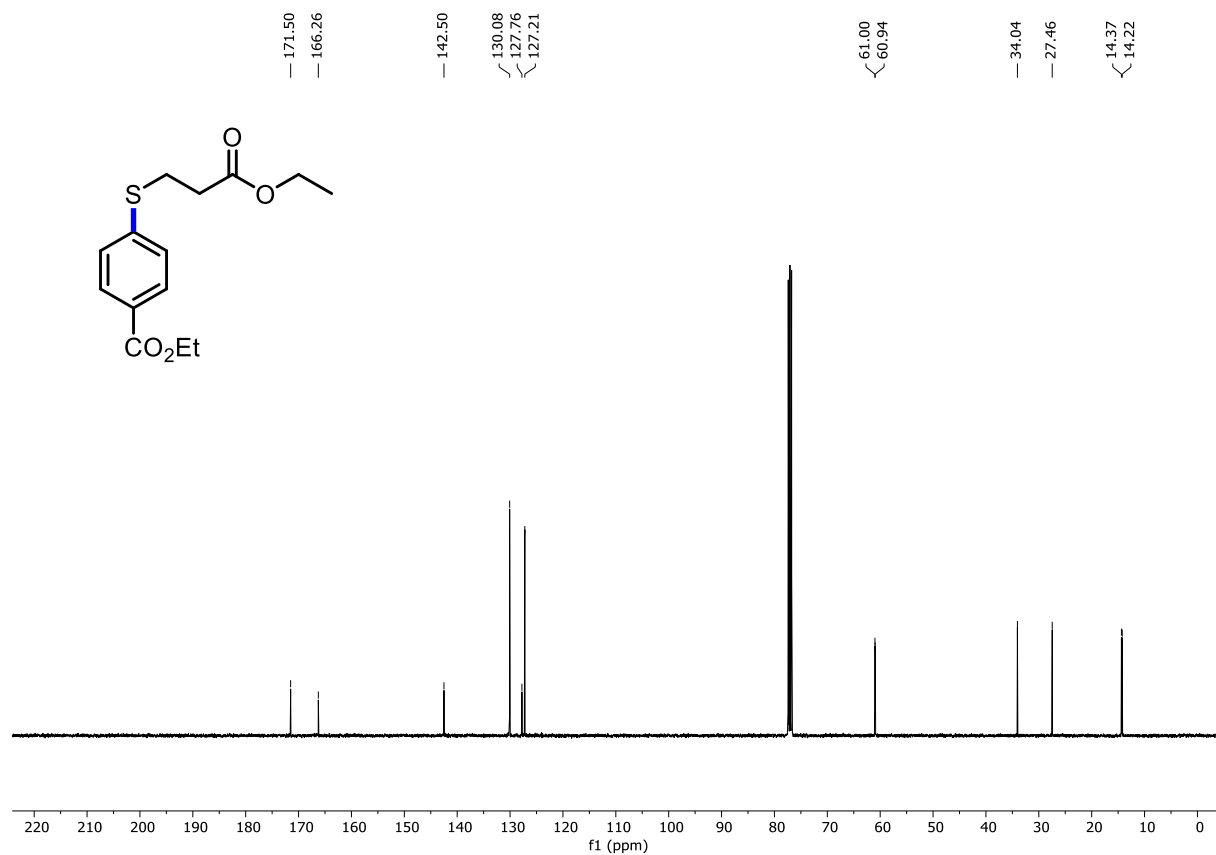
4-(o-tolylthio)benzotrile (17): ^{13}C NMR (100 MHz), CDCl_3 .



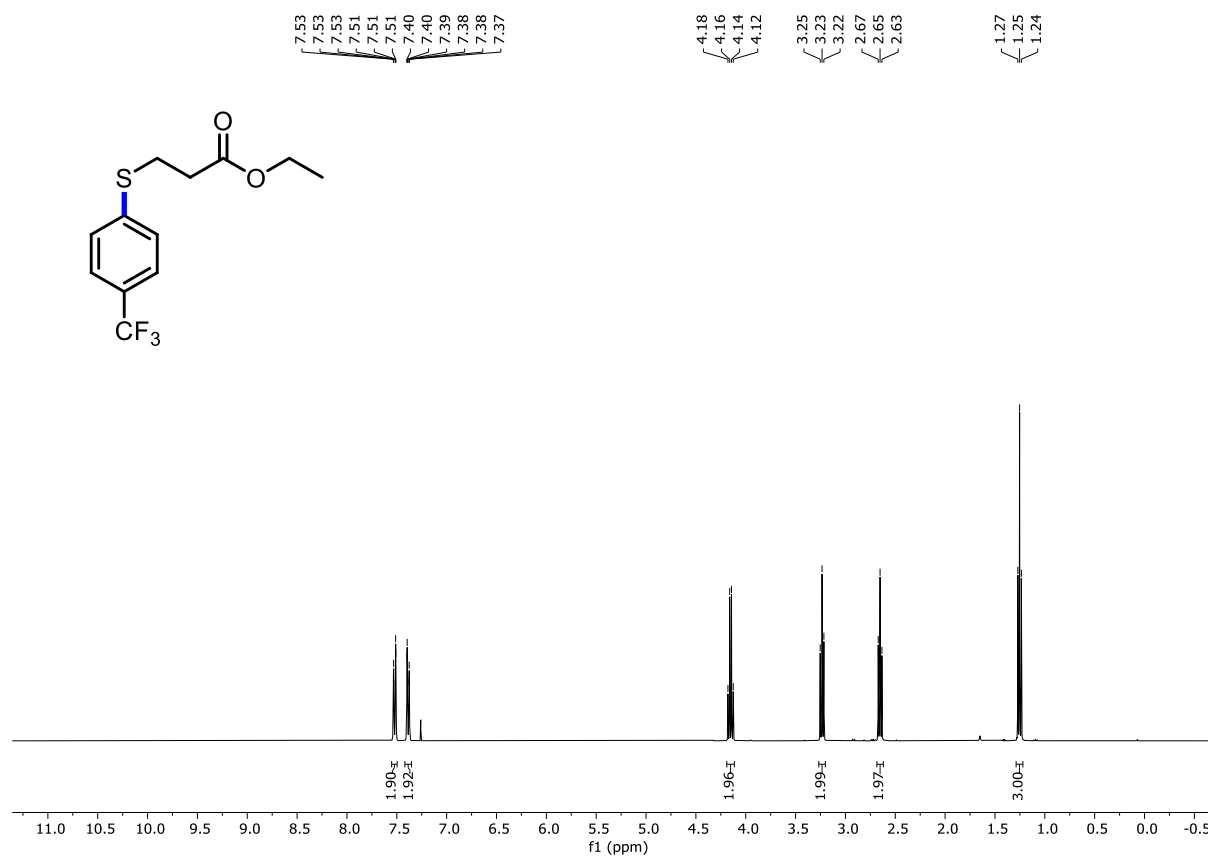
Ethyl 4-((3-ethoxy-3-oxopropyl)thio)benzoate (18): ^1H NMR (400 MHz), CDCl_3 .



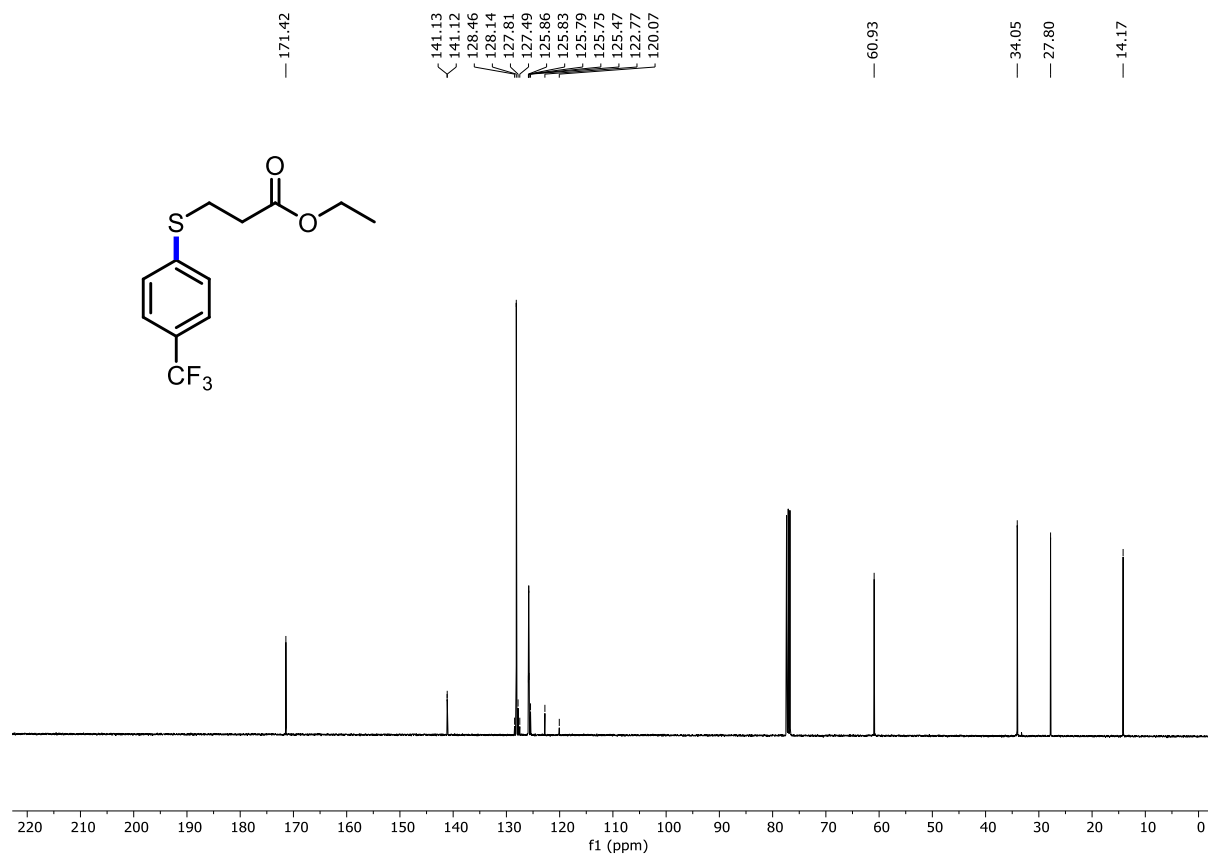
Ethyl 4-((3-ethoxy-3-oxopropyl)thio)benzoate (18): ^{13}C NMR (100 MHz), CDCl_3 .



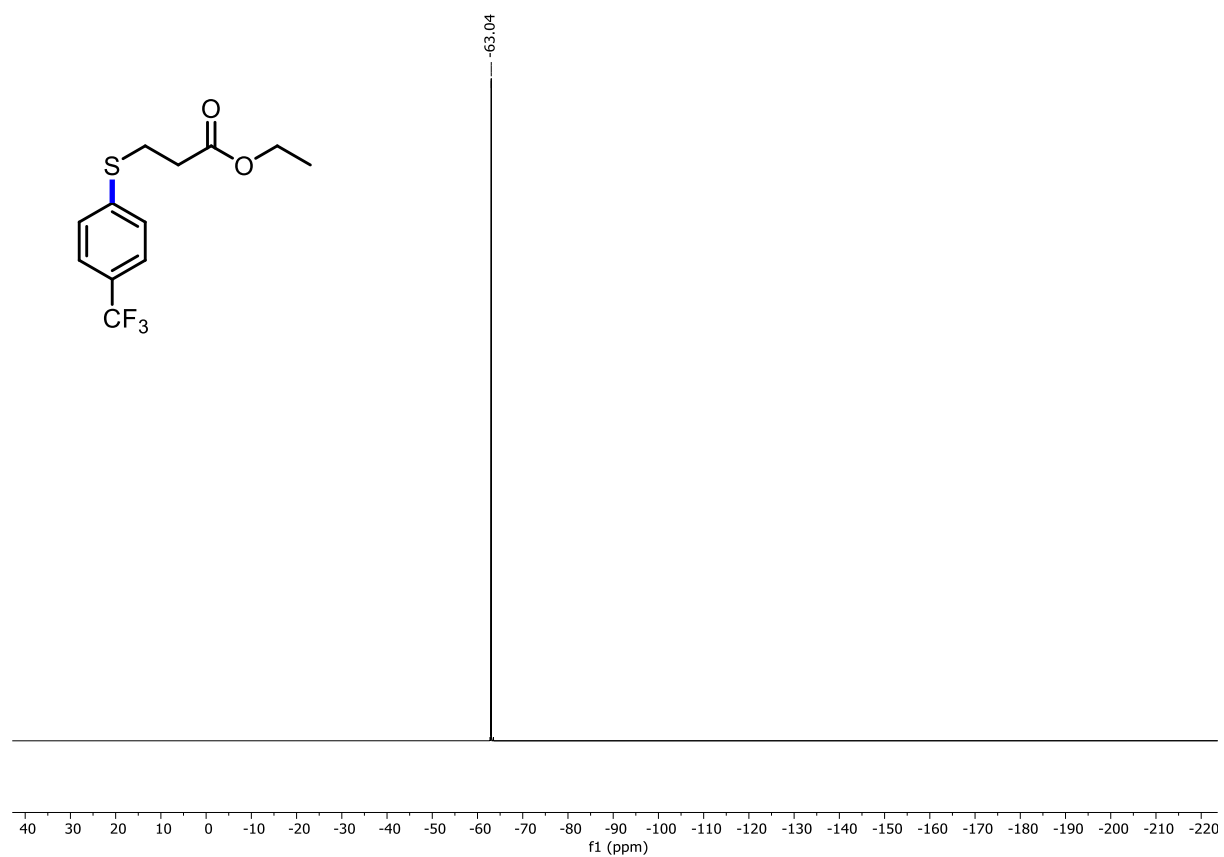
Ethyl 3-((4-(trifluoromethyl)phenyl)thio)propanoate (19): ^1H NMR (400 MHz), CDCl_3 .



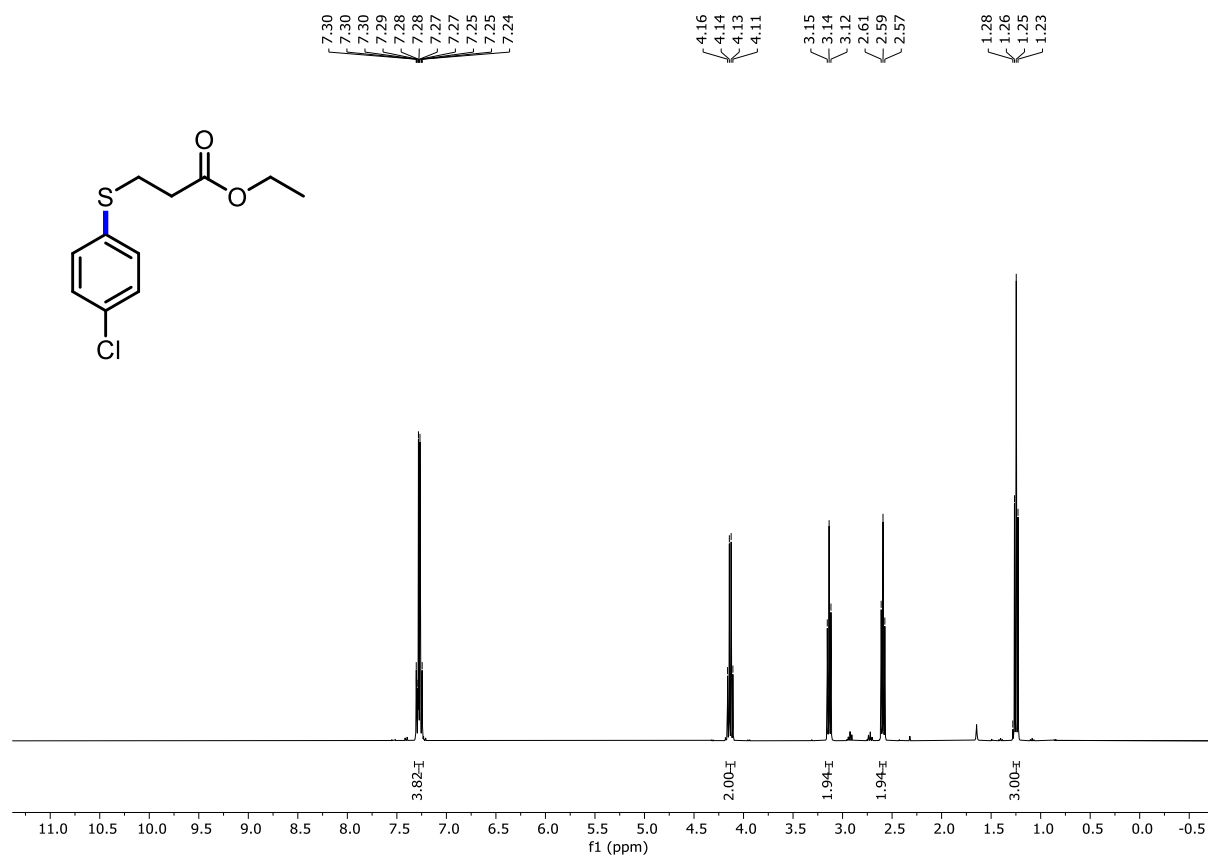
Ethyl 3-((4-(trifluoromethyl)phenyl)thio)propanoate (19): ^{13}C NMR (100 MHz), CDCl_3 .



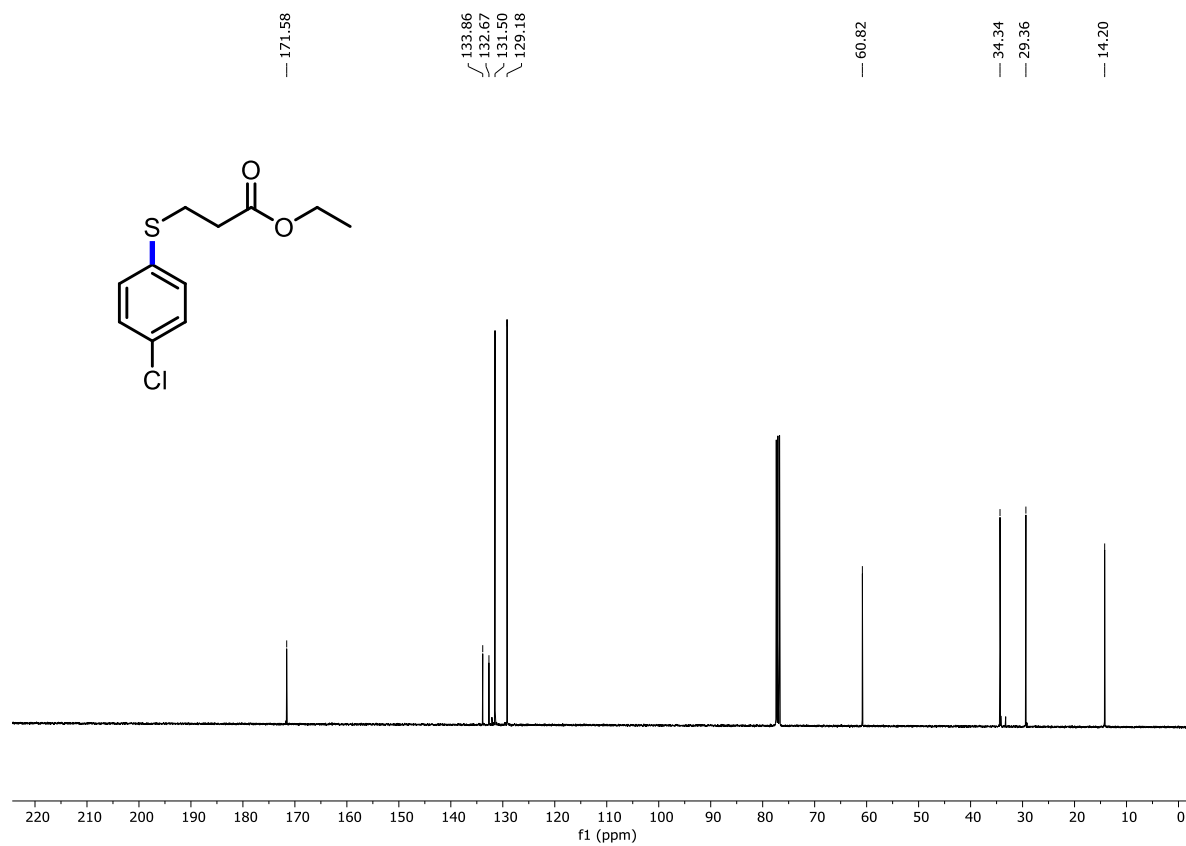
Ethyl 3-((4-(trifluoromethyl)phenyl)thio)propanoate (19): ^{19}F NMR (376 MHz), CDCl_3 .



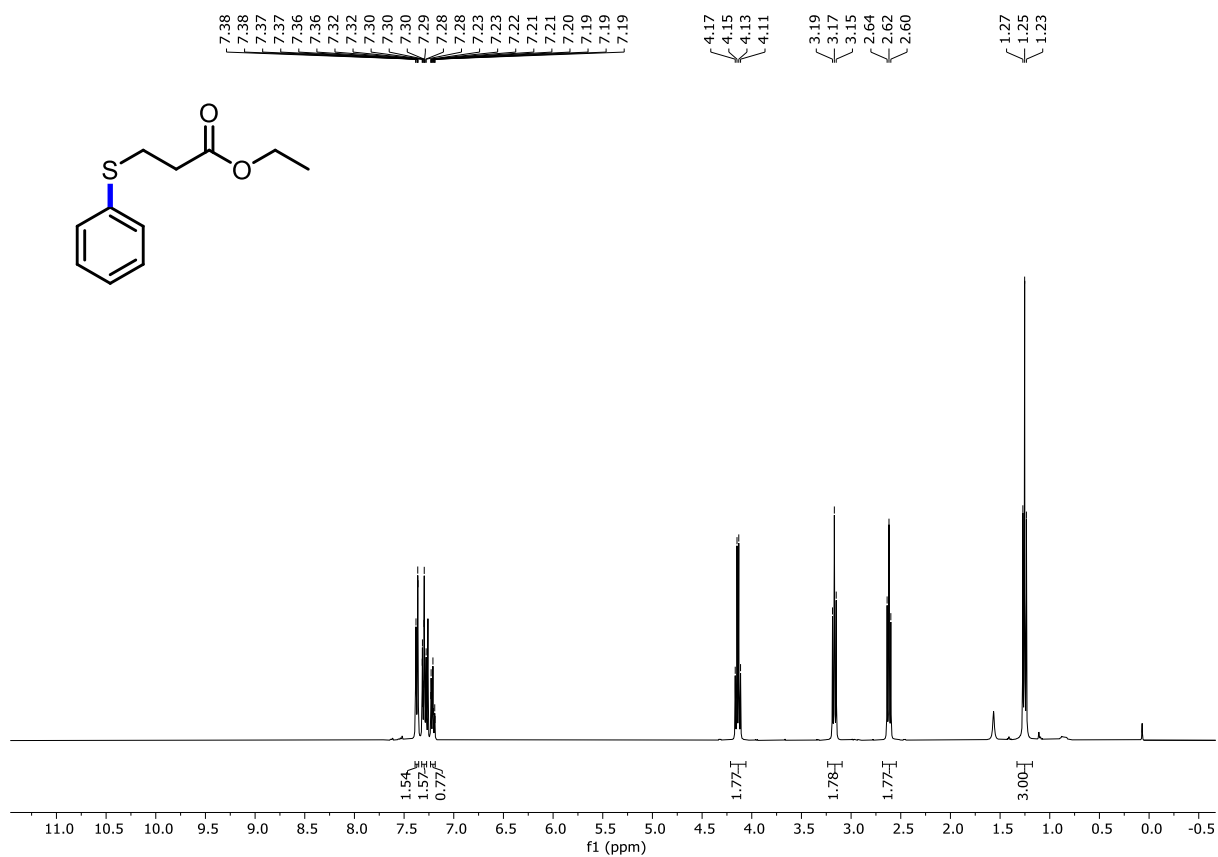
Ethyl 3-((4-chlorophenyl)thio)propanoate (20): ^1H NMR (400 MHz), CDCl_3 .



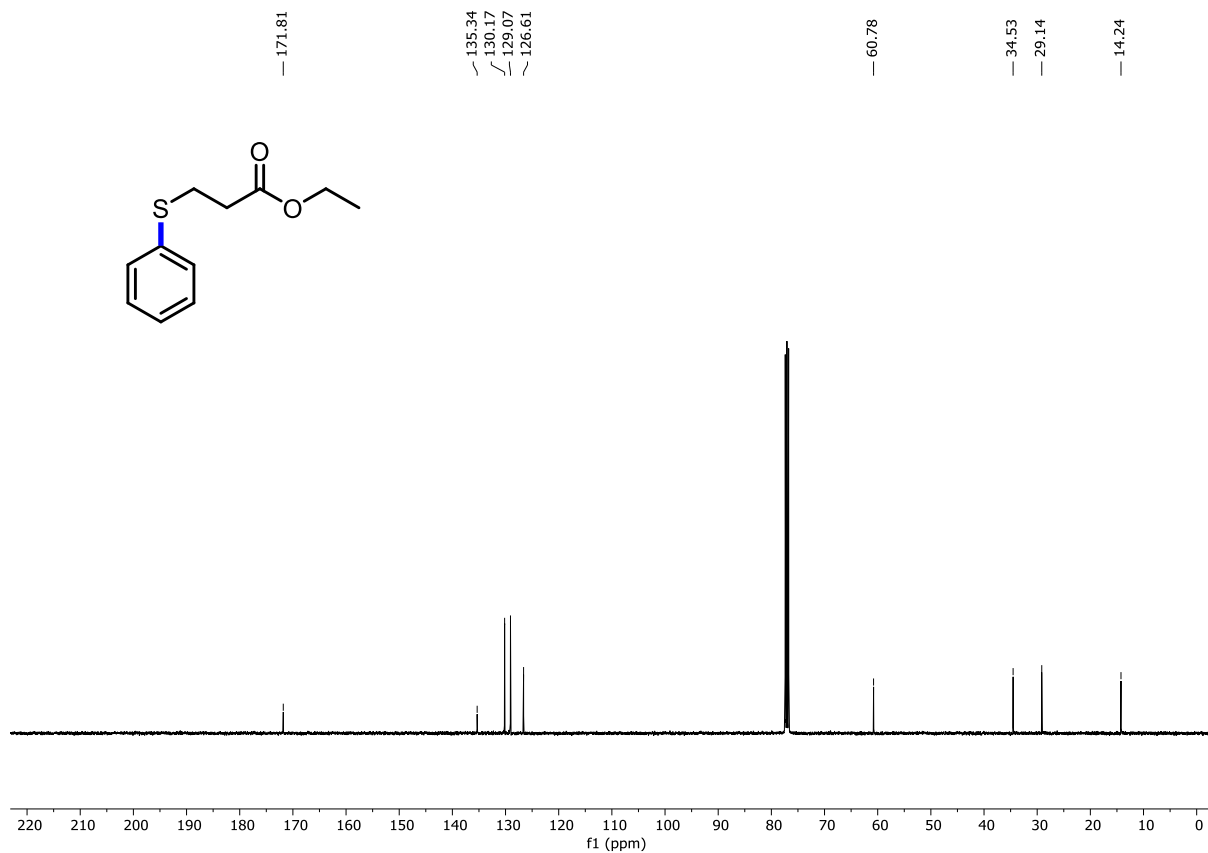
Ethyl 3-((4-chlorophenyl)thio)propanoate (20): ^{13}C NMR (100 MHz), CDCl_3 .



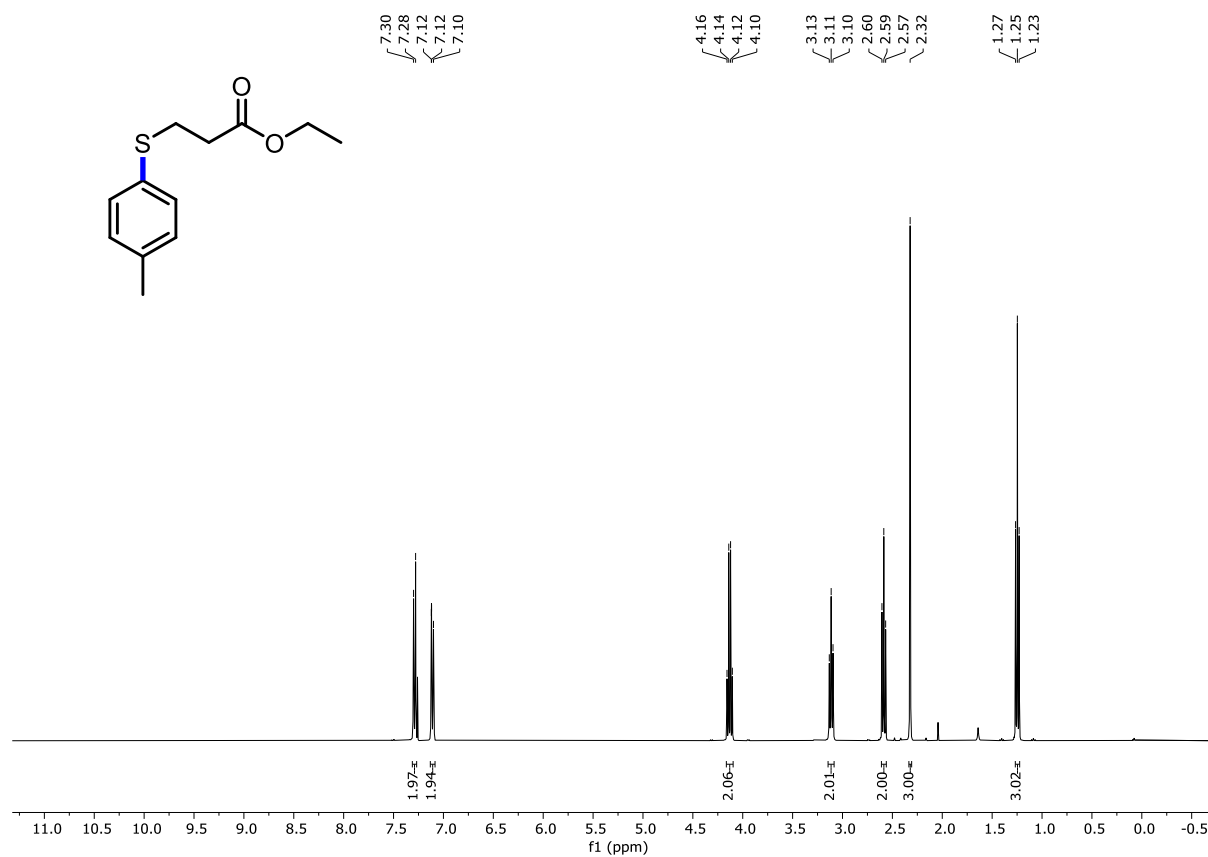
Ethyl 3-(phenylthio)propanoate (21): ^1H NMR (400 MHz), CDCl_3 .



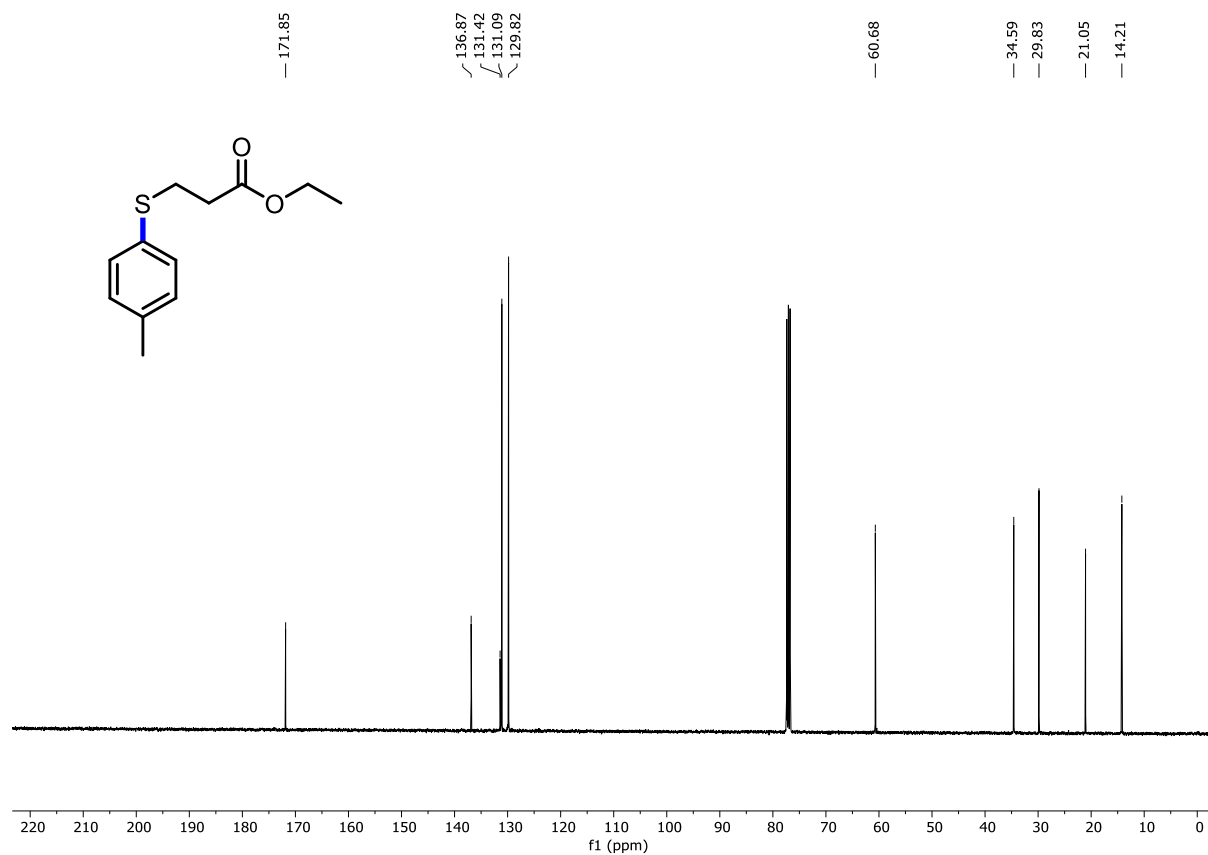
Ethyl 3-(phenylthio)propanoate (21): ^{13}C NMR (100 MHz), CDCl_3 .



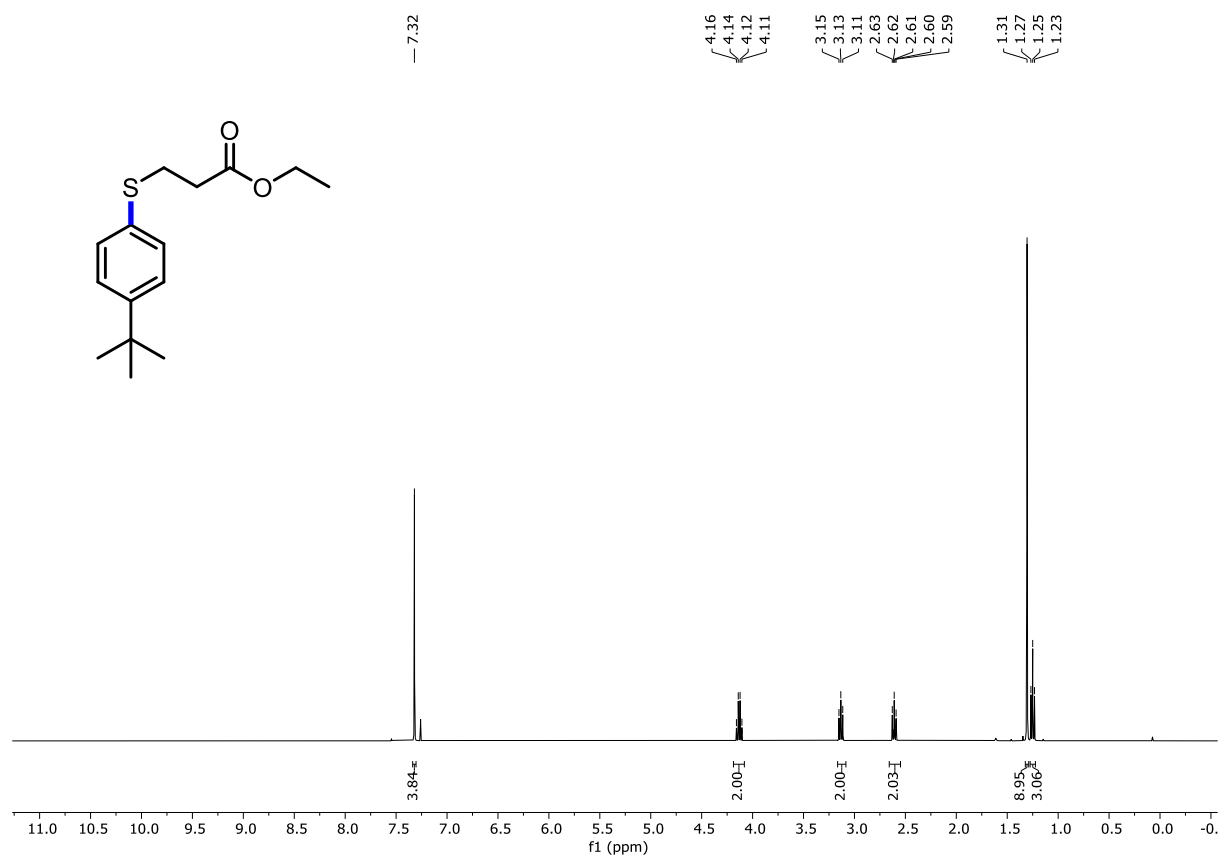
Ethyl 3-(p-tolylthio)propanoate (22): ^1H NMR (400 MHz), CDCl_3 .



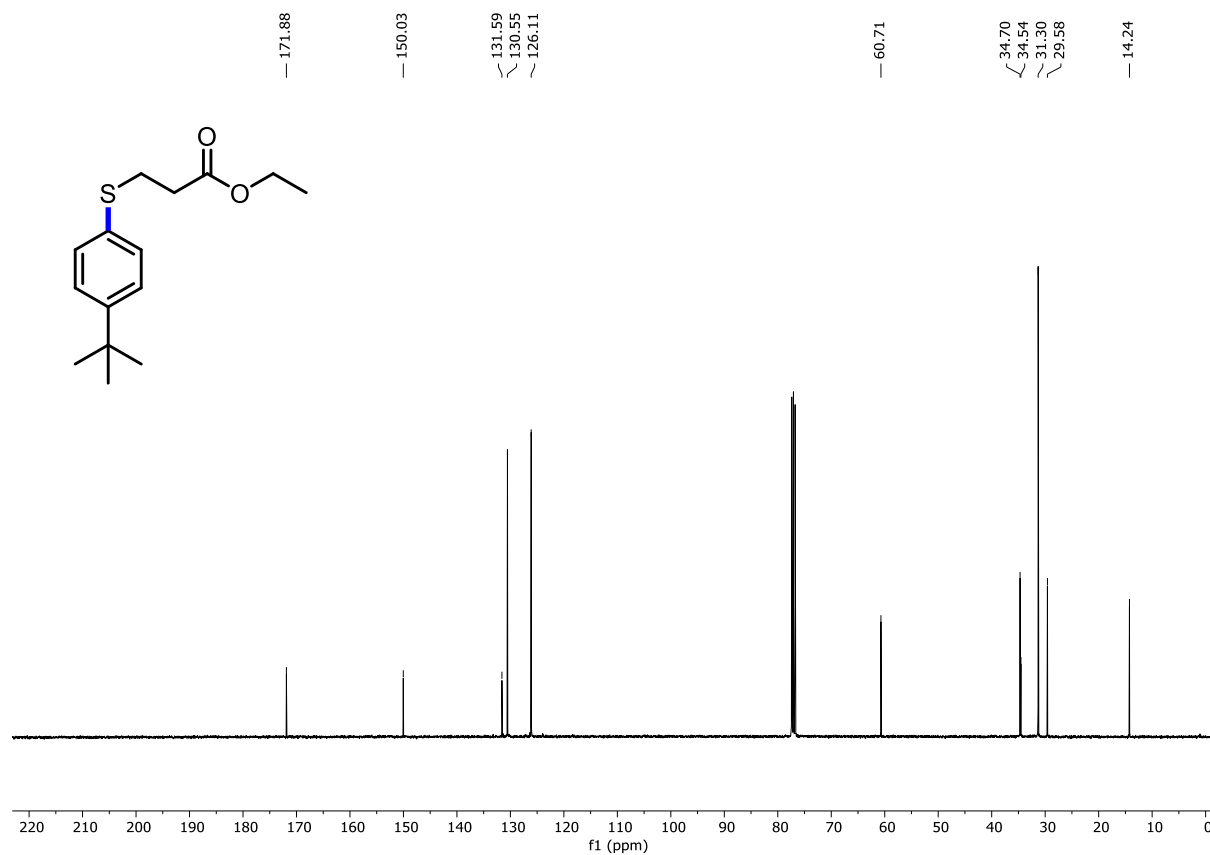
Ethyl 3-(p-tolylthio)propanoate (22): ^{13}C NMR (100 MHz), CDCl_3 .



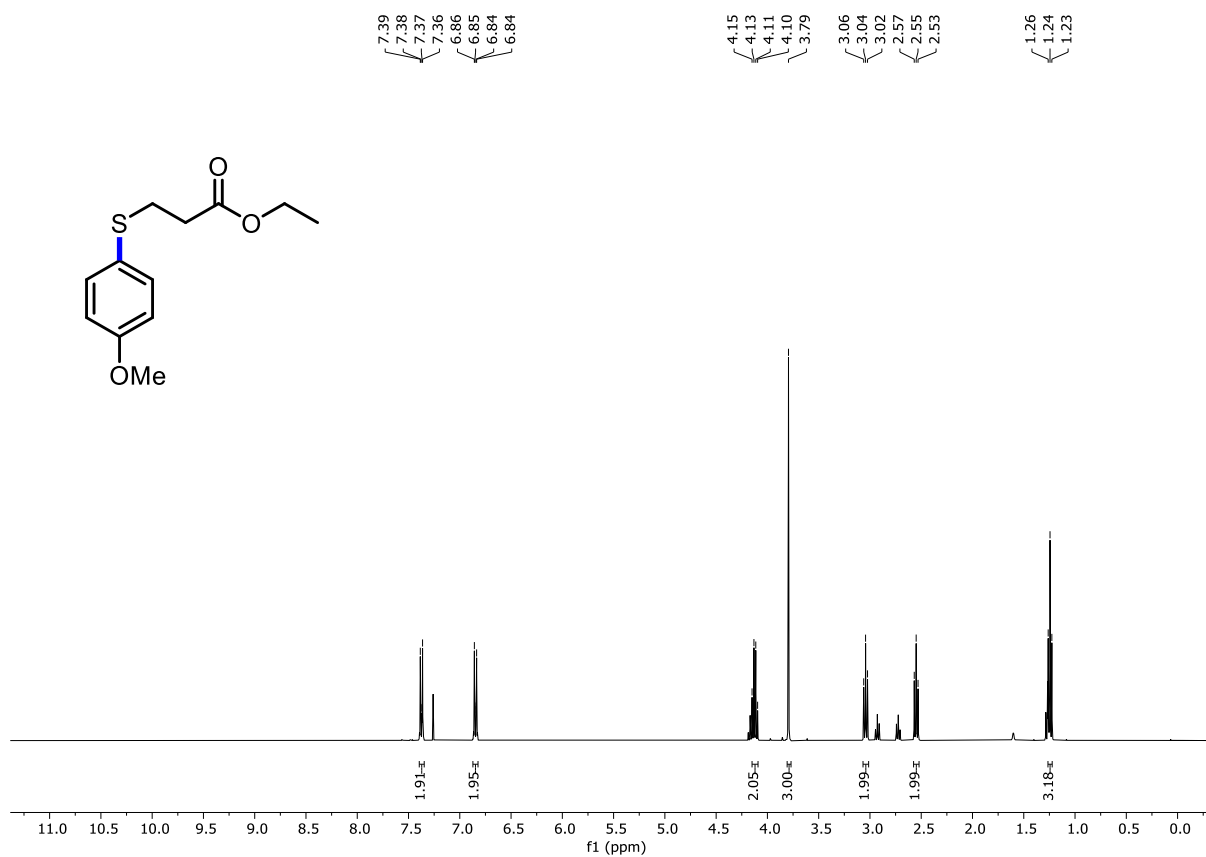
Ethyl 3-((4-(tert-butyl)phenyl)thio)propanoate (23): ^1H NMR (400 MHz), CDCl_3 .



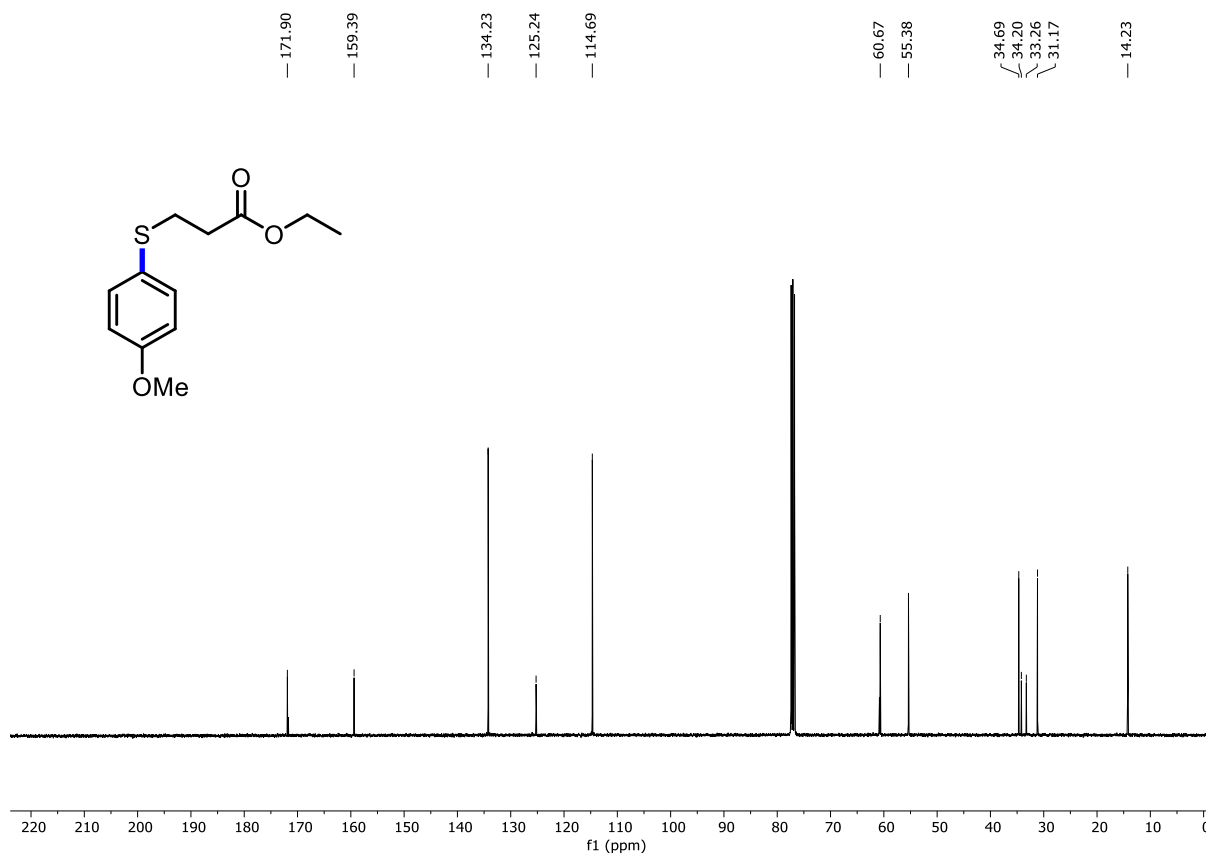
Ethyl 3-((4-(tert-butyl)phenyl)thio)propanoate (23): ^{13}C NMR (100 MHz), CDCl_3 .



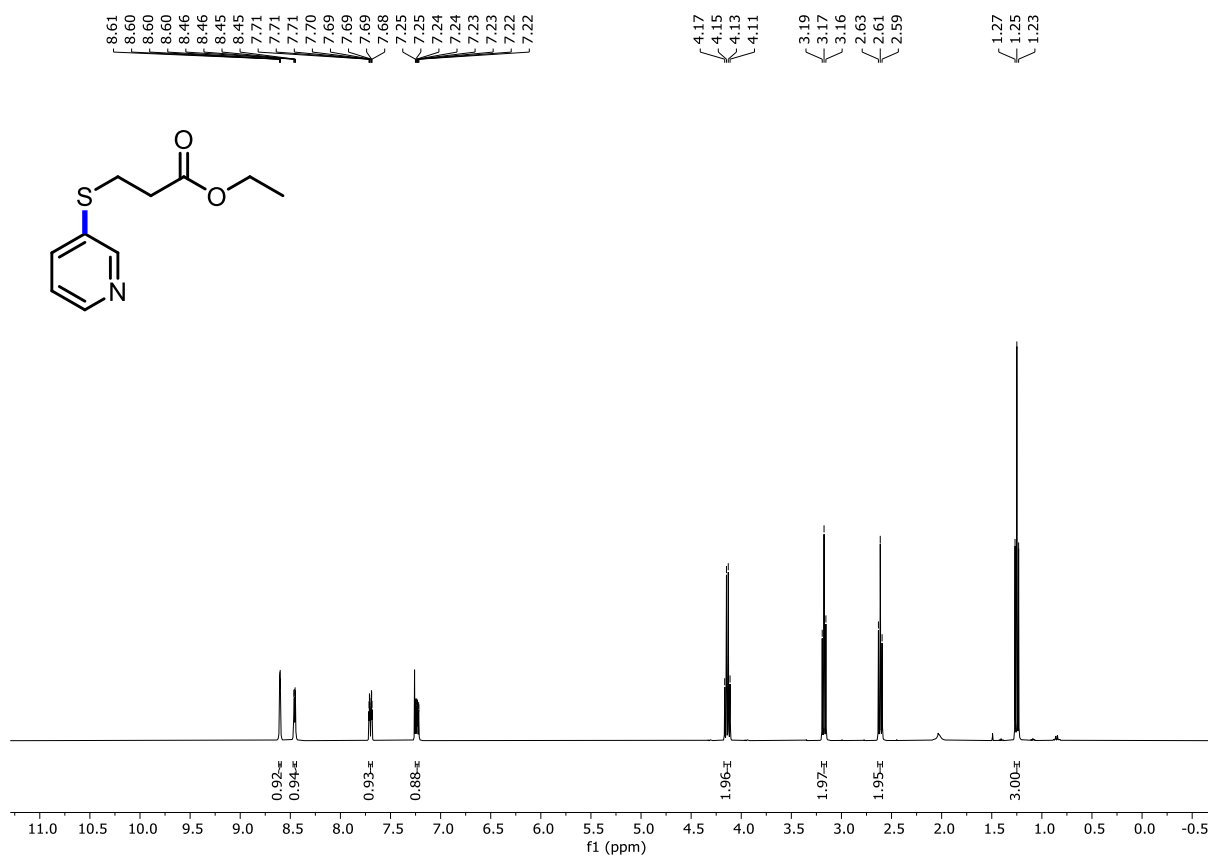
Ethyl 3-((4-methoxyphenyl)thio)propanoate (24): ^1H NMR (400 MHz), CDCl_3 .



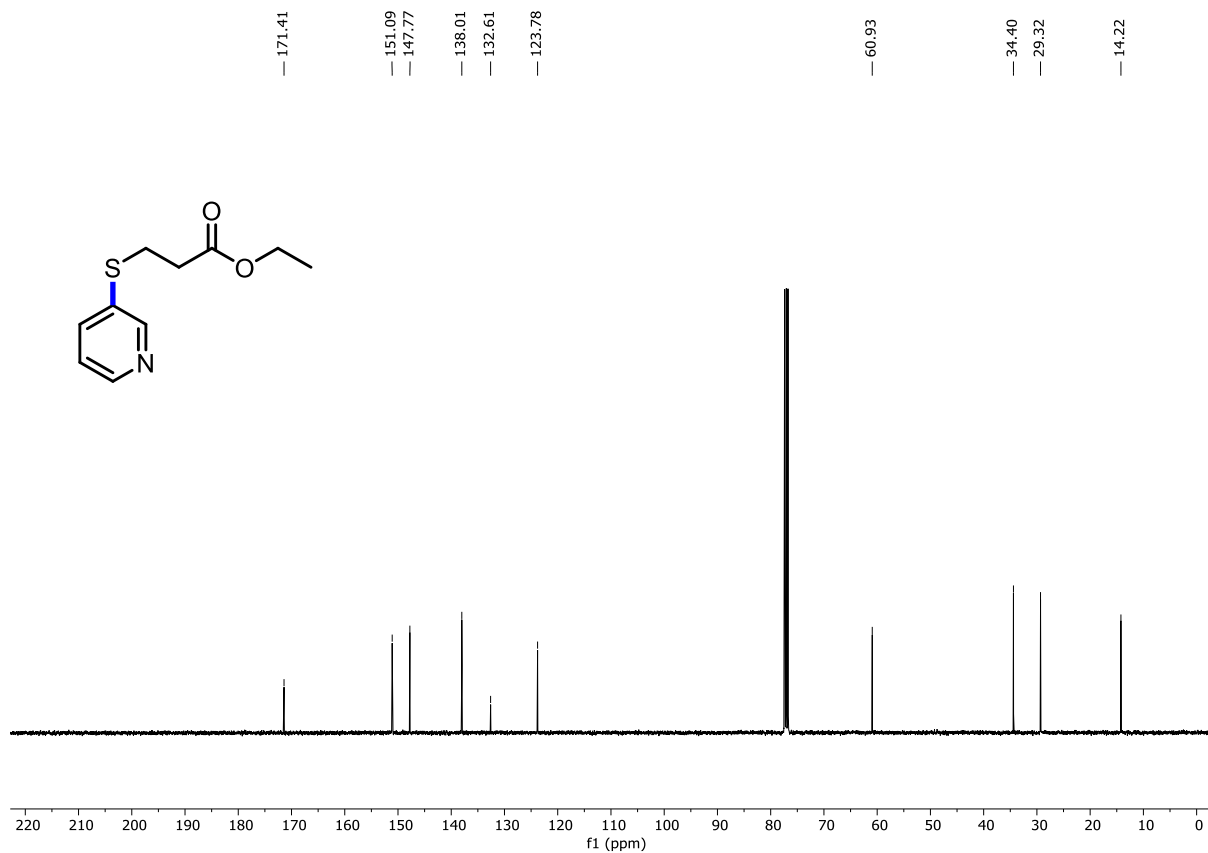
Ethyl 3-((4-methoxyphenyl)thio)propanoate (24): ^{13}C NMR (100 MHz), CDCl_3 .



Ethyl 3-(pyridin-3-ylthio)propanoate (25): ^1H NMR (400 MHz), CDCl_3 .



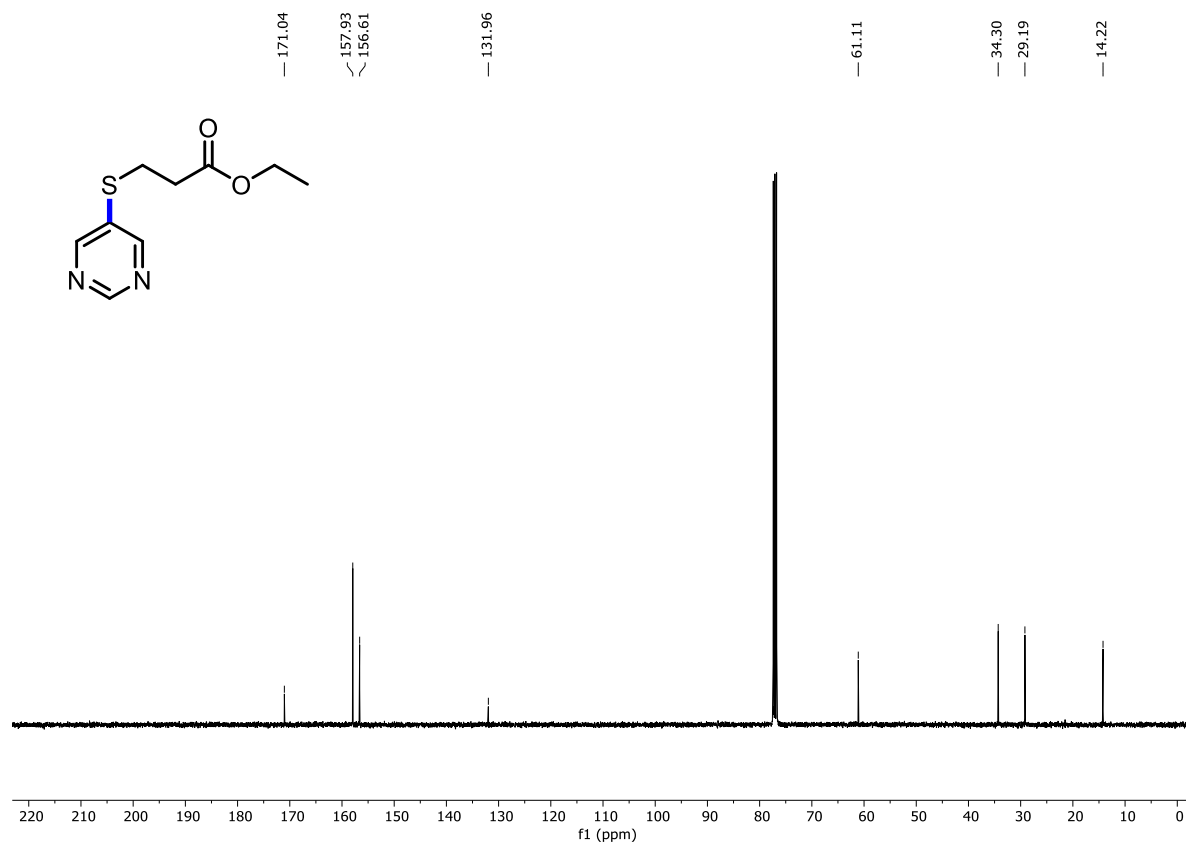
Ethyl 3-(pyridin-3-ylthio)propanoate (25): ^{13}C NMR (100 MHz), CDCl_3 .



Ethyl 3-(pyrimidin-5-ylthio)propanoate (26): ^1H NMR (400 MHz), CDCl_3 .



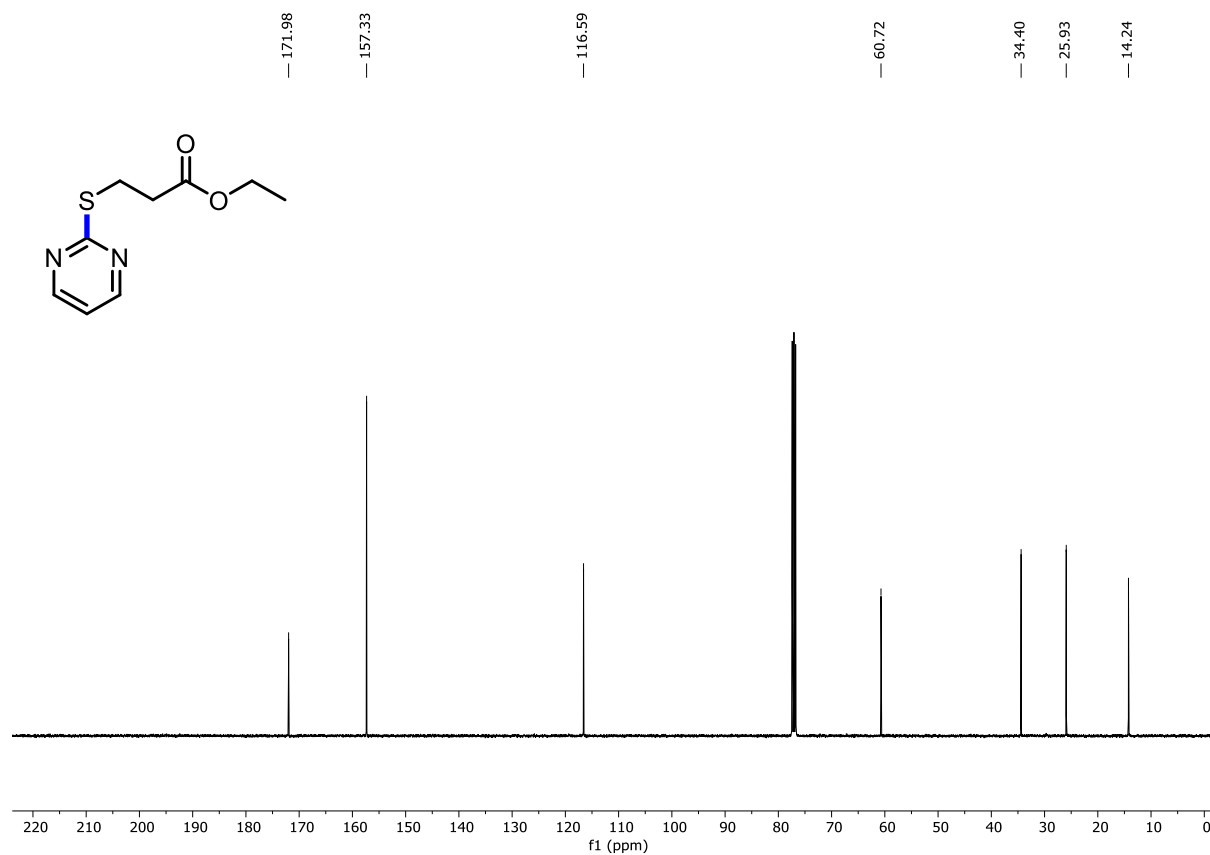
Ethyl 3-(pyrimidin-5-ylthio)propanoate (26): ^{13}C NMR (100 MHz), CDCl_3 .



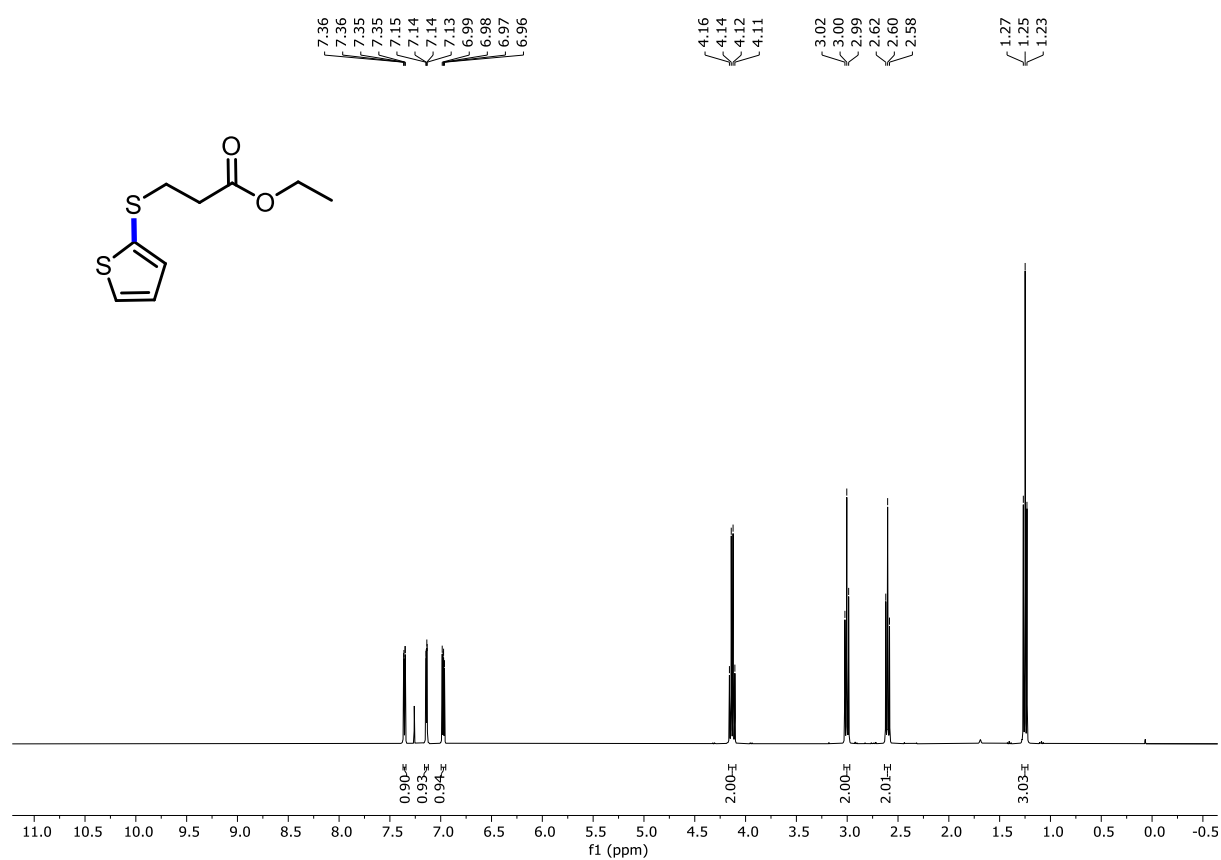
Ethyl 3-(pyrimidin-2-ylthio)propanoate (27): ^1H NMR (400 MHz), CDCl_3 .



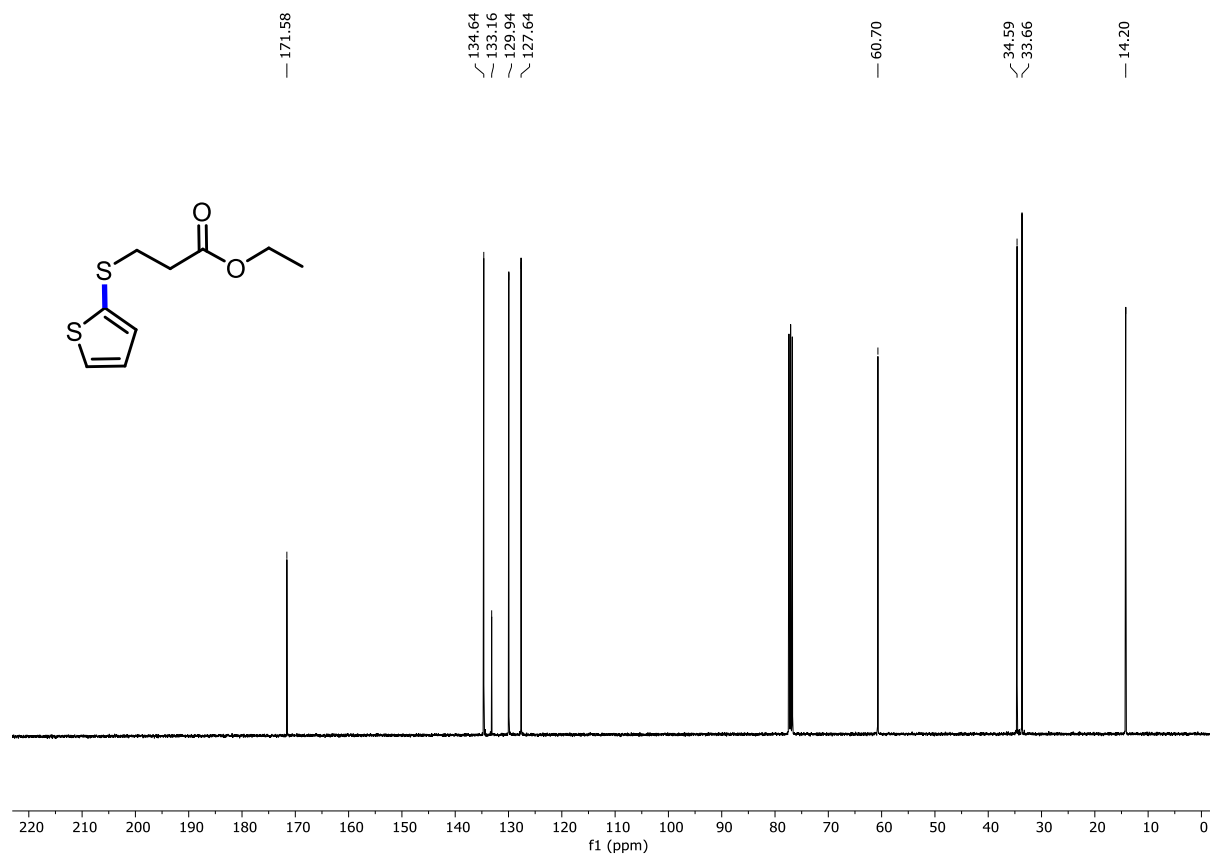
Ethyl 3-(pyrimidin-2-ylthio)propanoate (27): ^{13}C NMR (100 MHz), CDCl_3 .



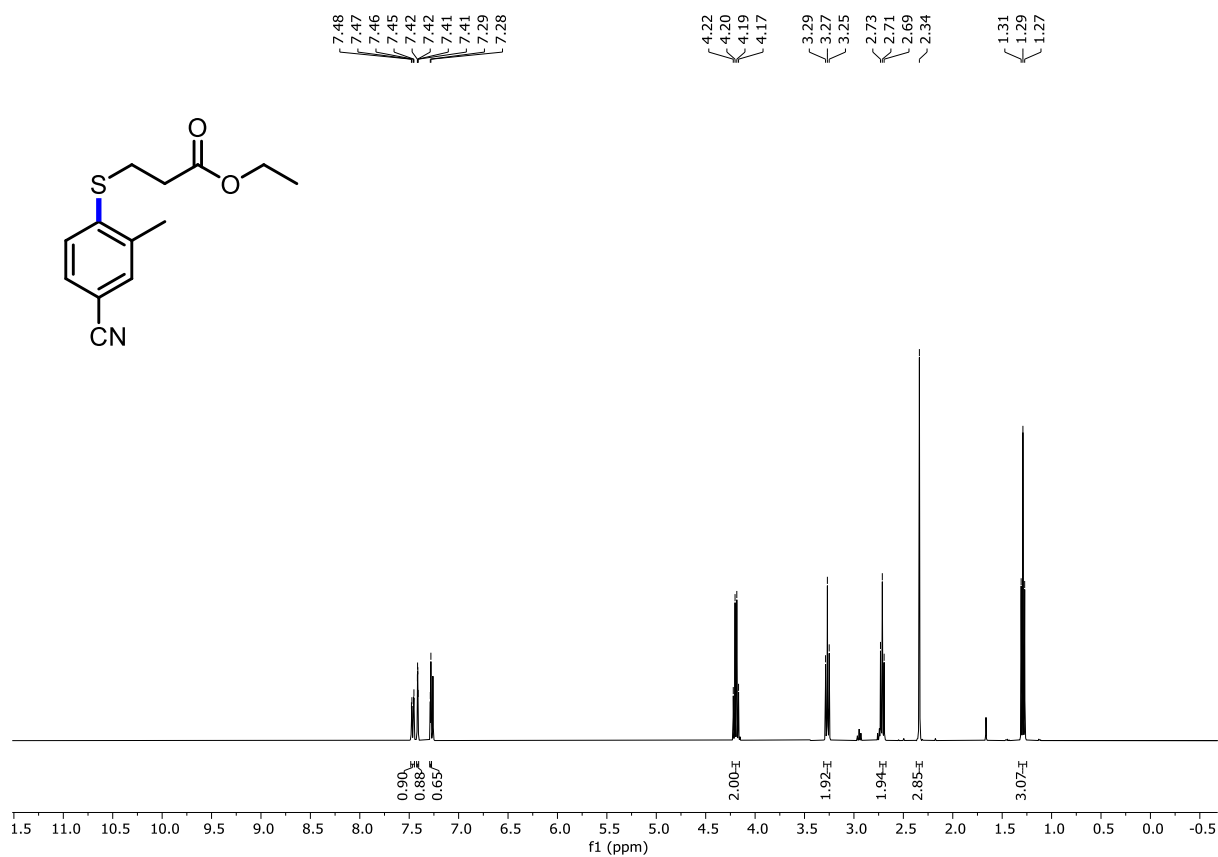
Ethyl 3-(thiophen-2-ylthio)propanoate (28): ^1H NMR (400 MHz), CDCl_3 .



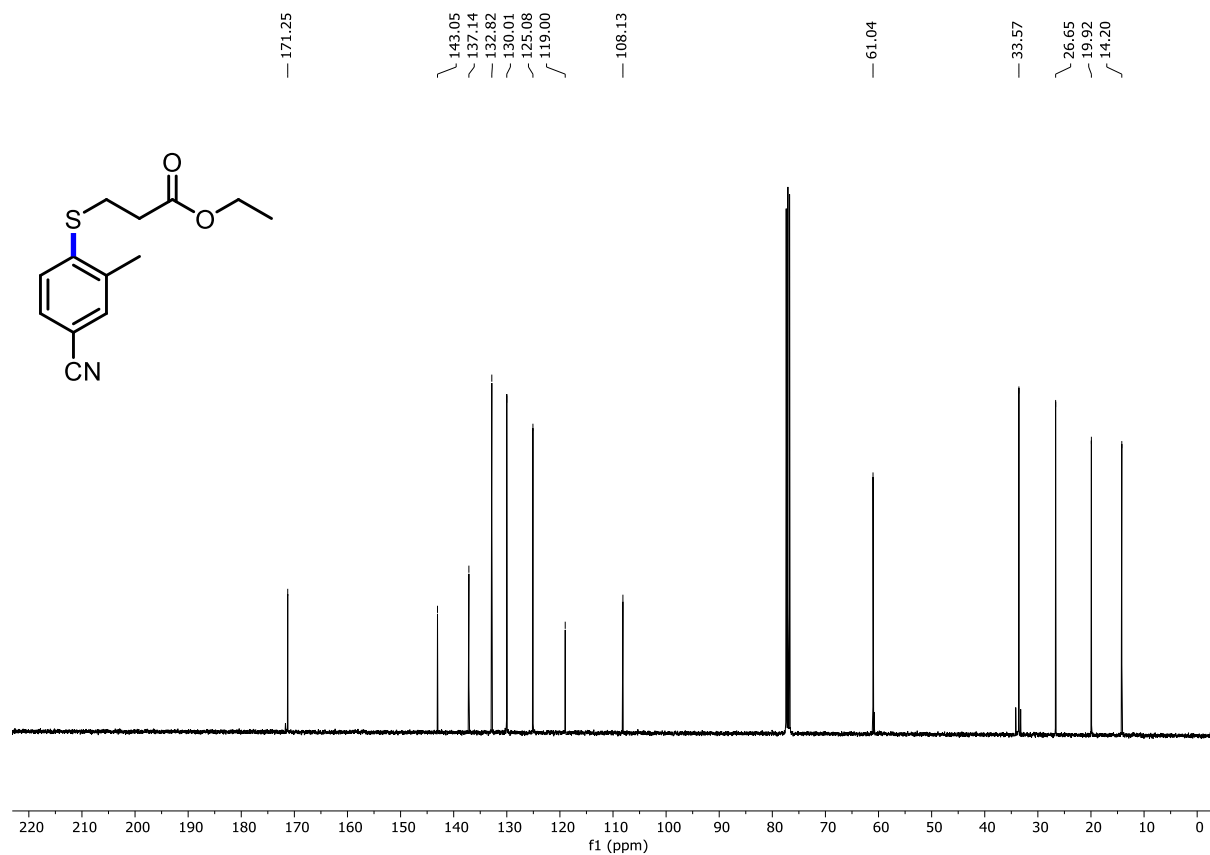
Ethyl 3-(thiophen-2-ylthio)propanoate (28): ^{13}C NMR (100 MHz), CDCl_3 .



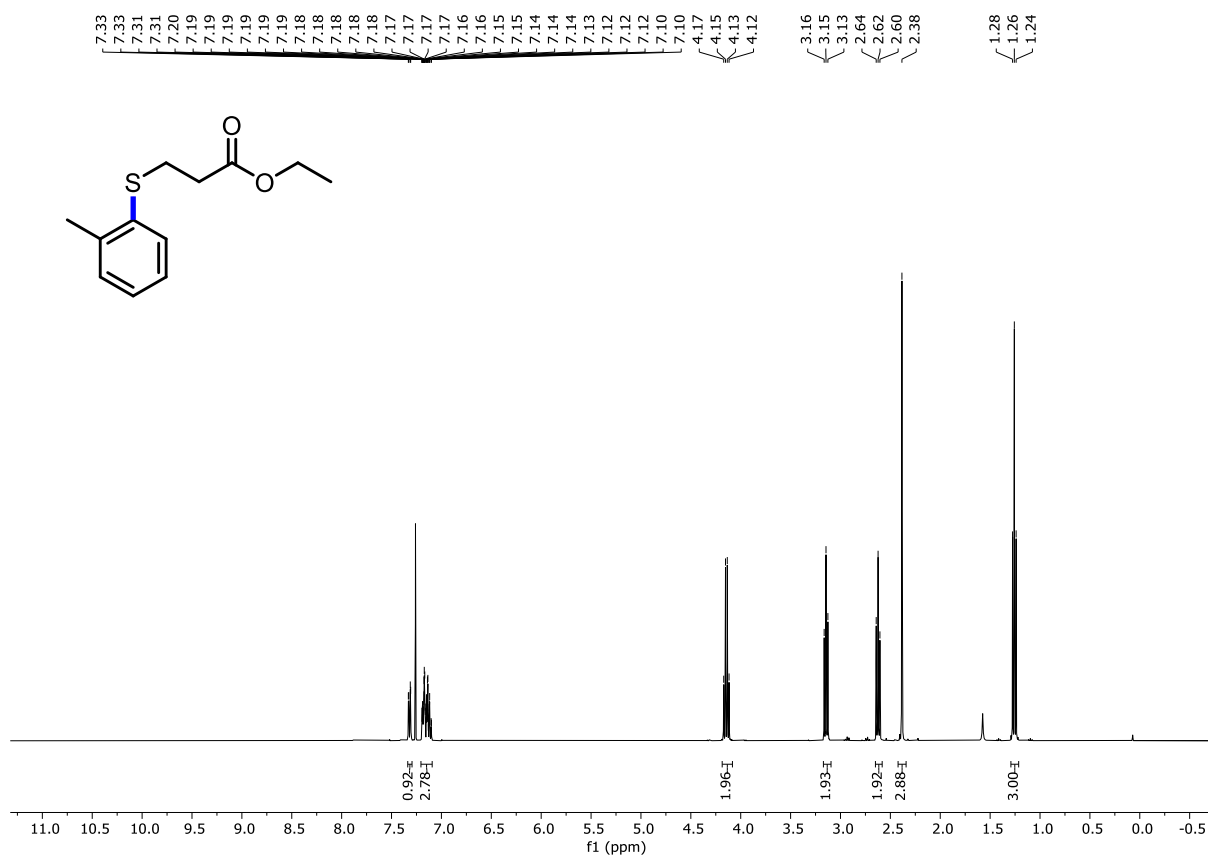
Ethyl 3-((4-cyano-2-methylphenyl)thio)propanoate (29): ^1H NMR (400 MHz), CDCl_3 .



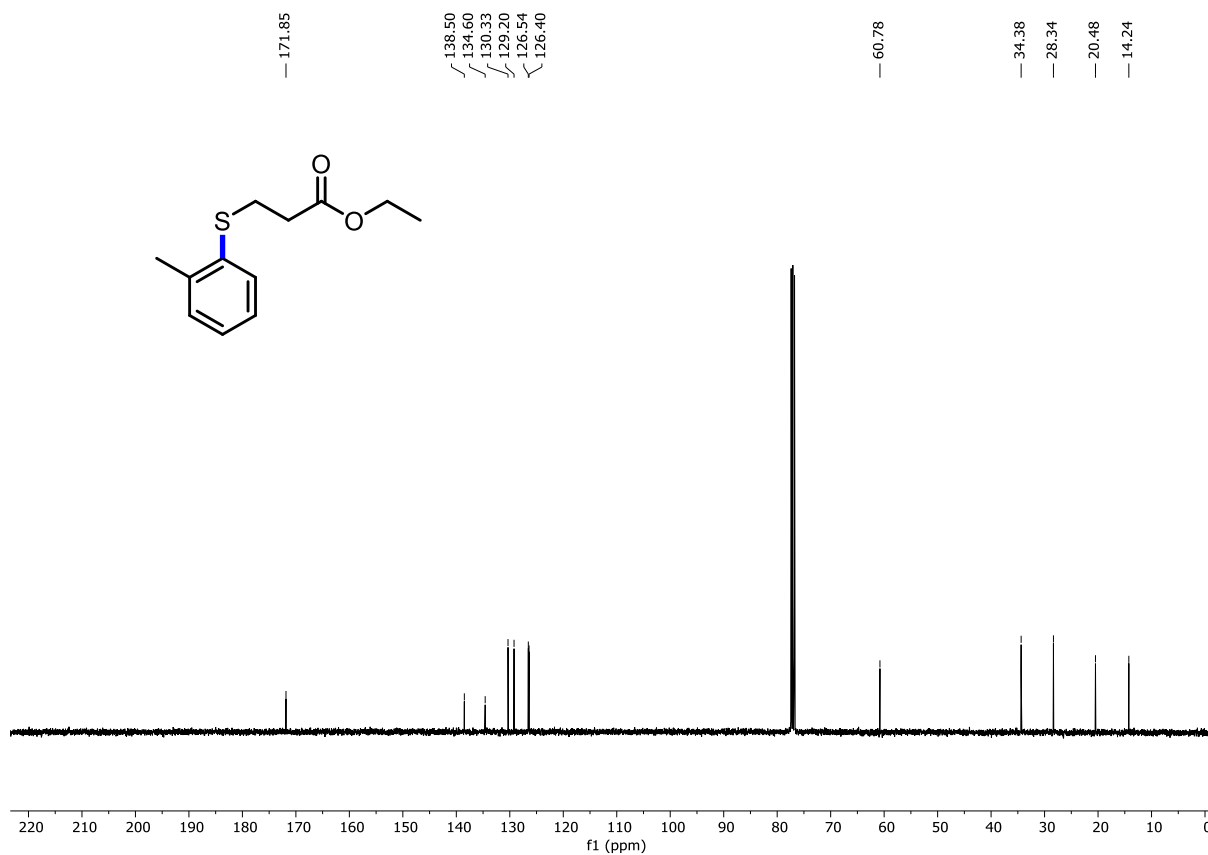
Ethyl 3-((4-cyano-2-methylphenyl)thio)propanoate (29): ^{13}C NMR (100 MHz), CDCl_3 .



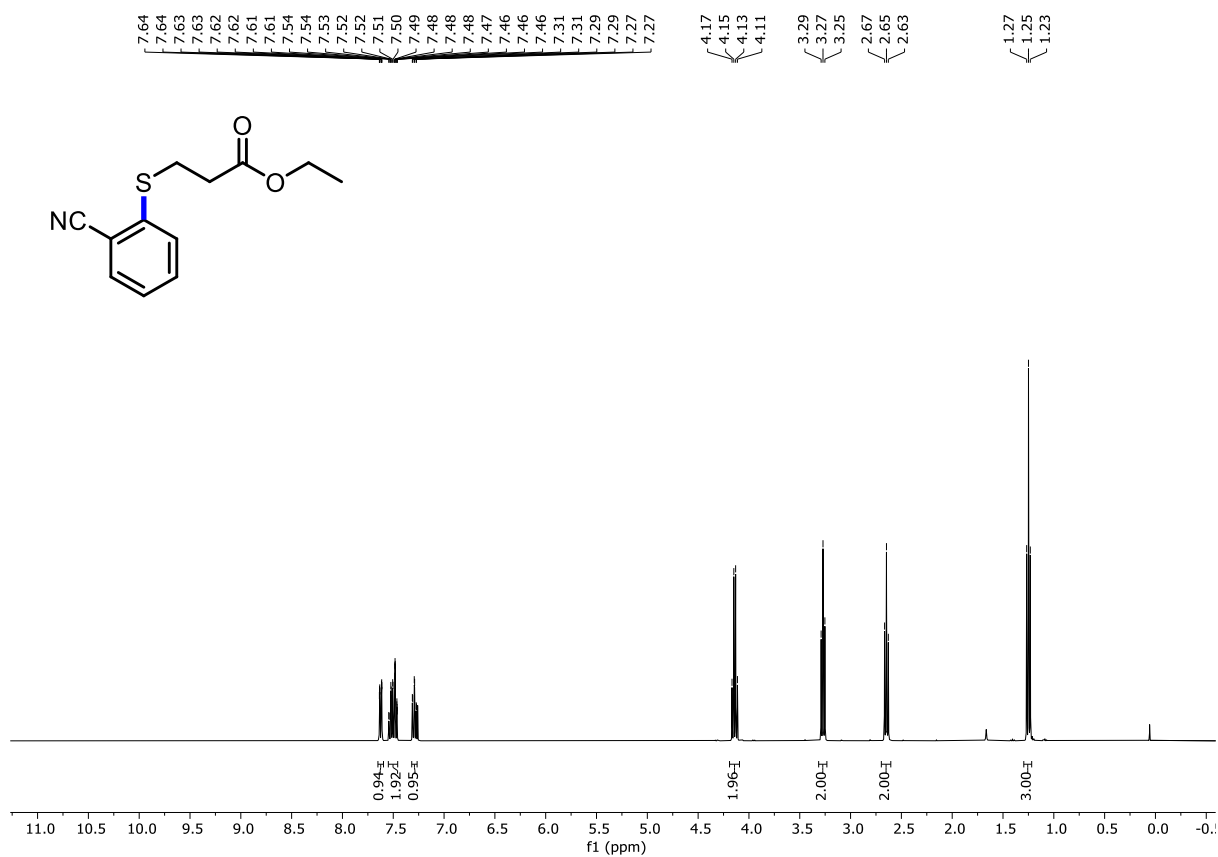
Ethyl 3-(o-tolylthio)propanoate (30): ¹H NMR (400 MHz), CDCl₃.



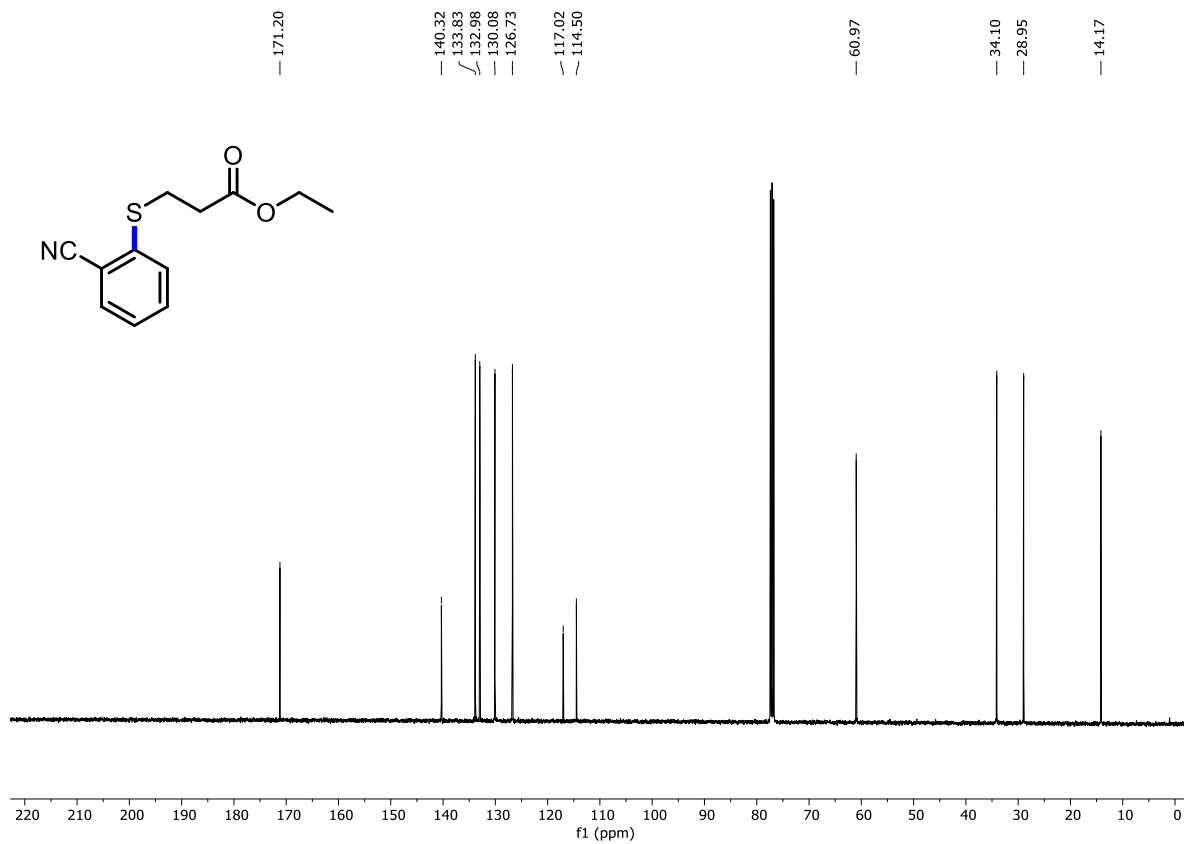
Ethyl 3-(o-tolylthio)propanoate (30): ¹³C NMR (100 MHz), CDCl₃.



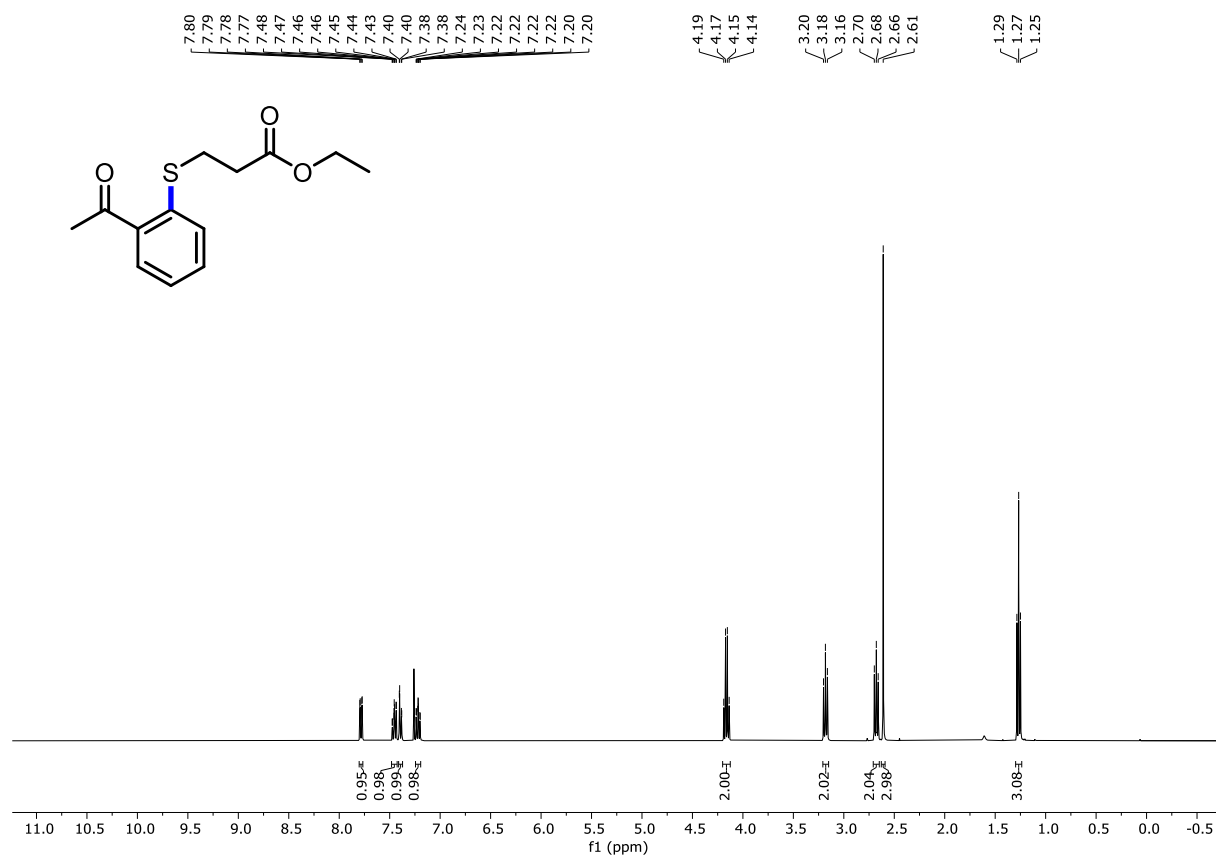
Ethyl 3-((2-cyanophenyl)thio)propanoate (31): ^1H NMR (400 MHz), CDCl_3 .



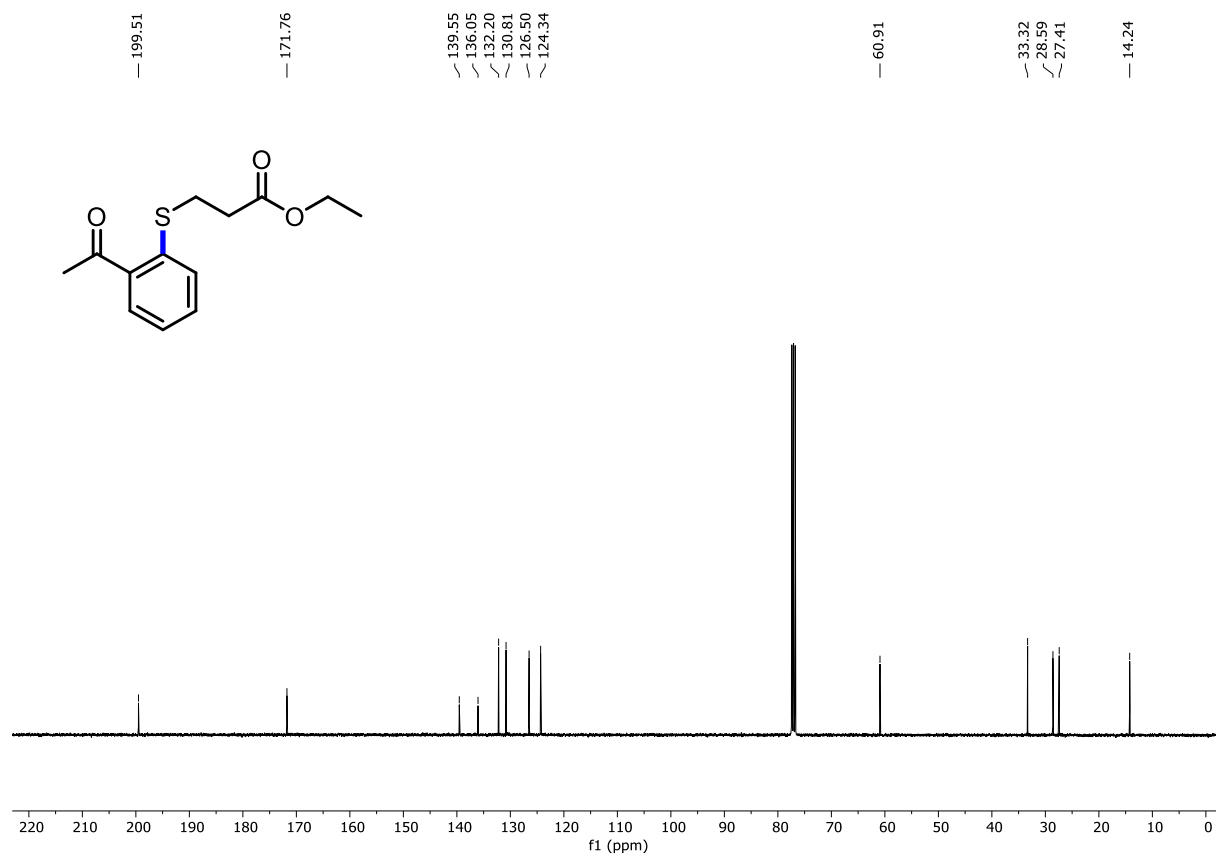
Ethyl 3-((2-cyanophenyl)thio)propanoate (31): ^{13}C NMR (100 MHz), CDCl_3 .



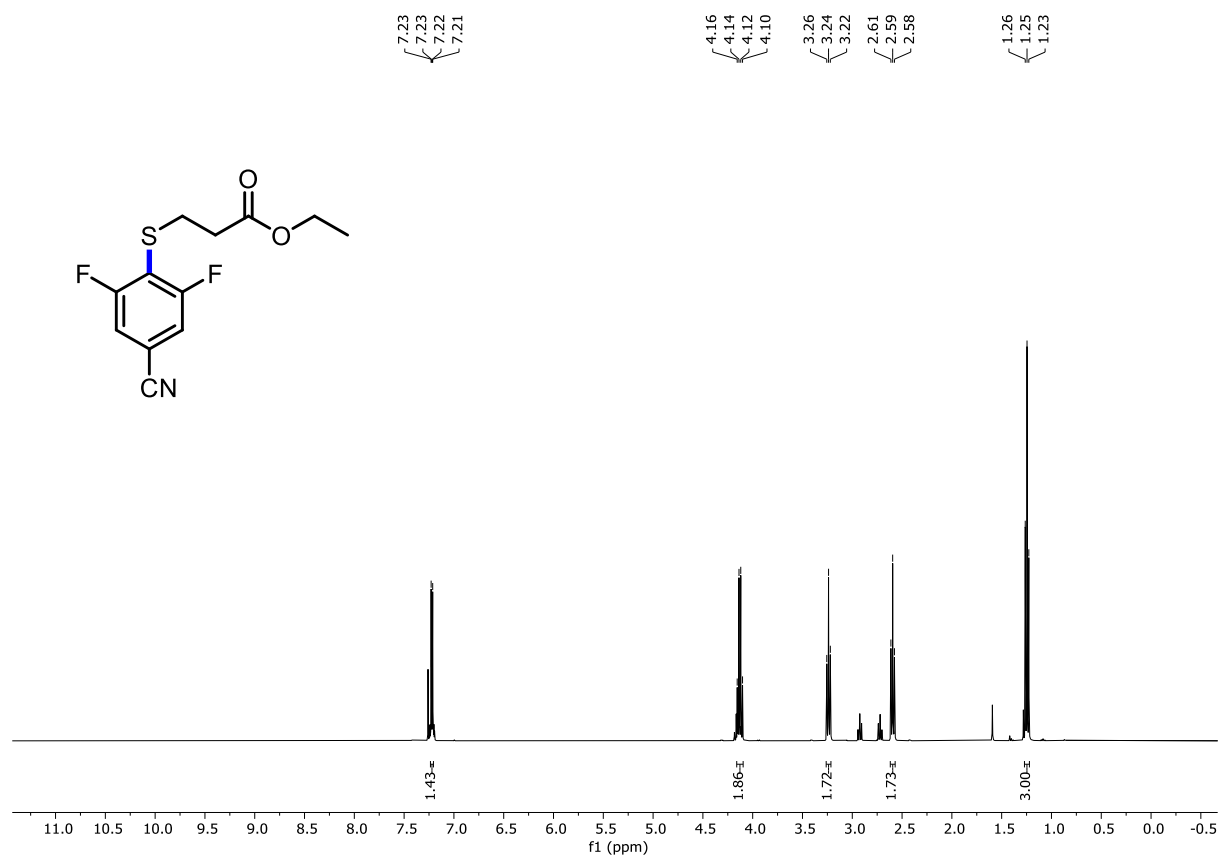
Ethyl 3-((2-acetylphenyl)thio)propanoate (32): ^1H NMR (400 MHz), CDCl_3 .



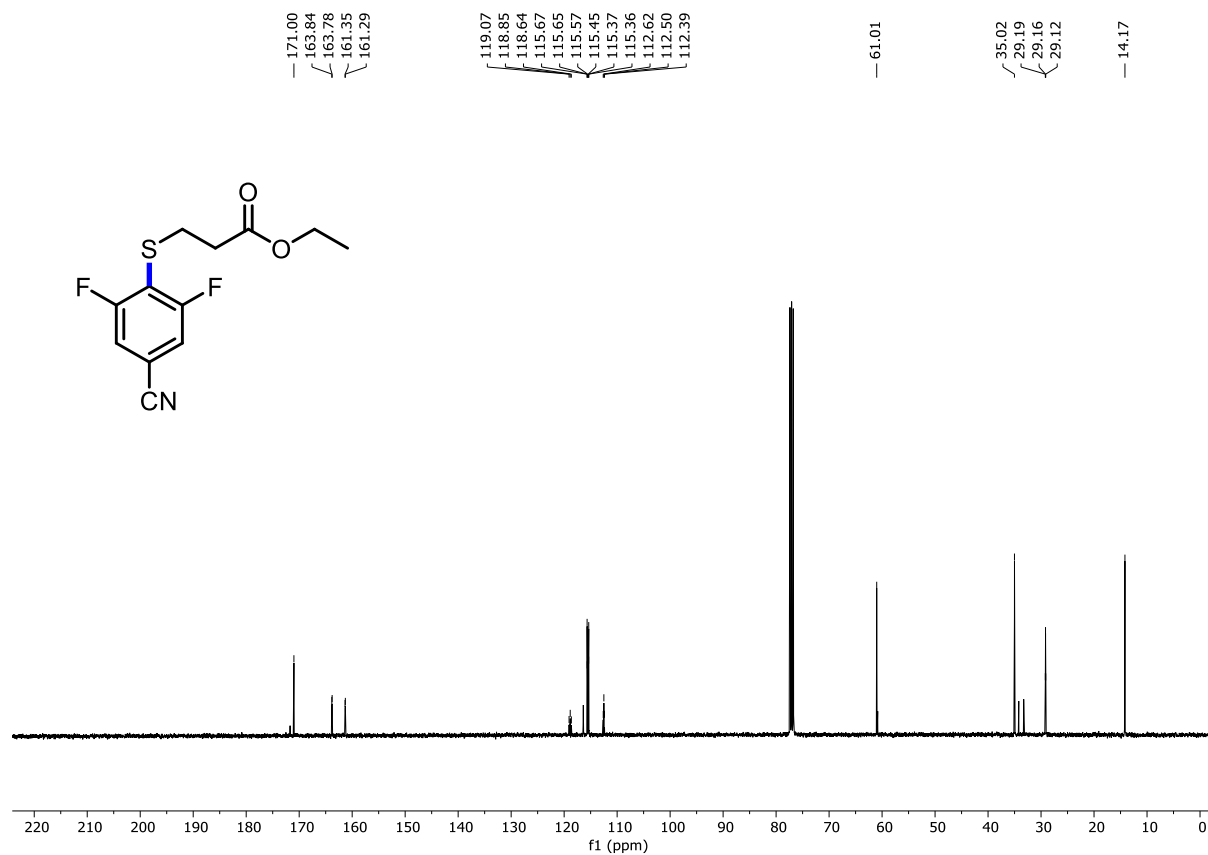
Ethyl 3-((2-acetylphenyl)thio)propanoate (32): ^{13}C NMR (100 MHz), CDCl_3 .



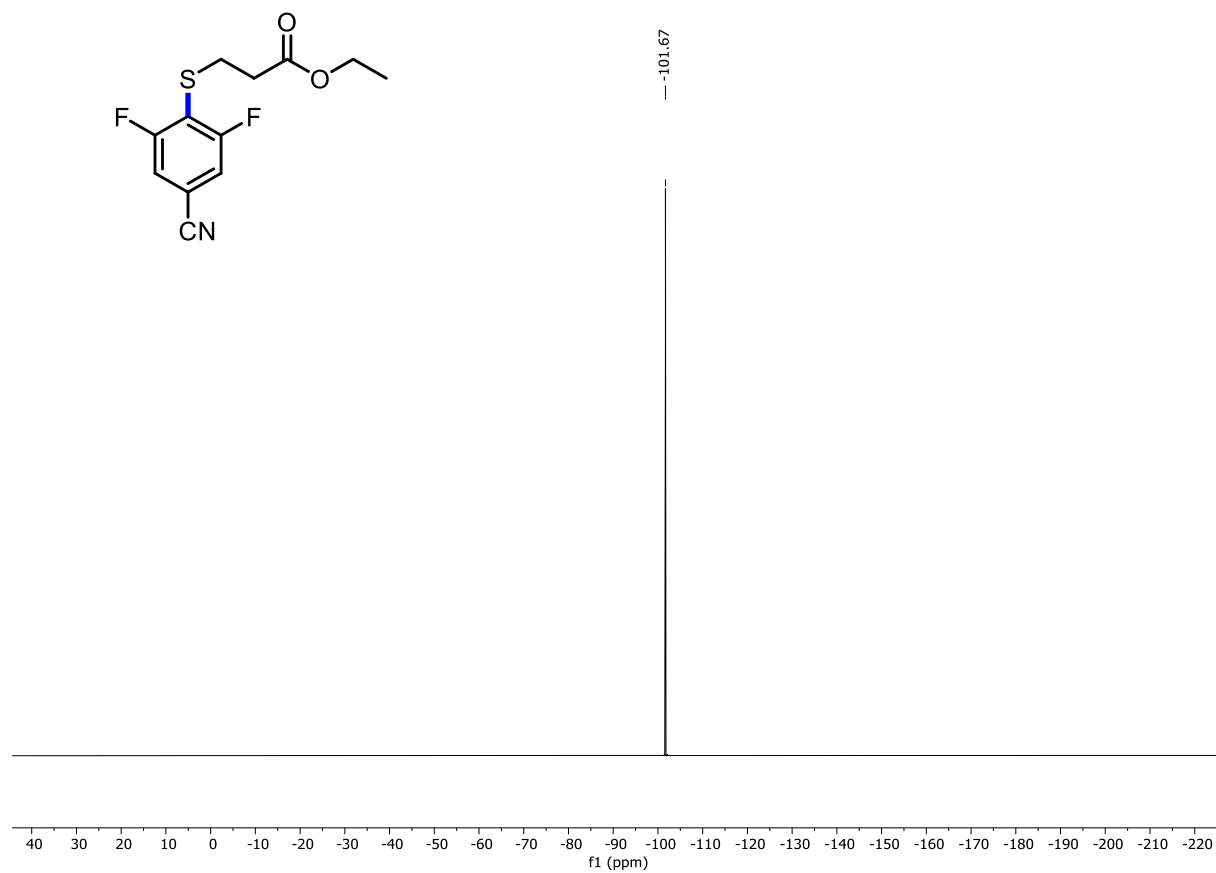
Ethyl 3-((4-cyano-2,6-difluorophenyl)thio)propanoate (33): ^1H NMR (400 MHz), CDCl_3 .



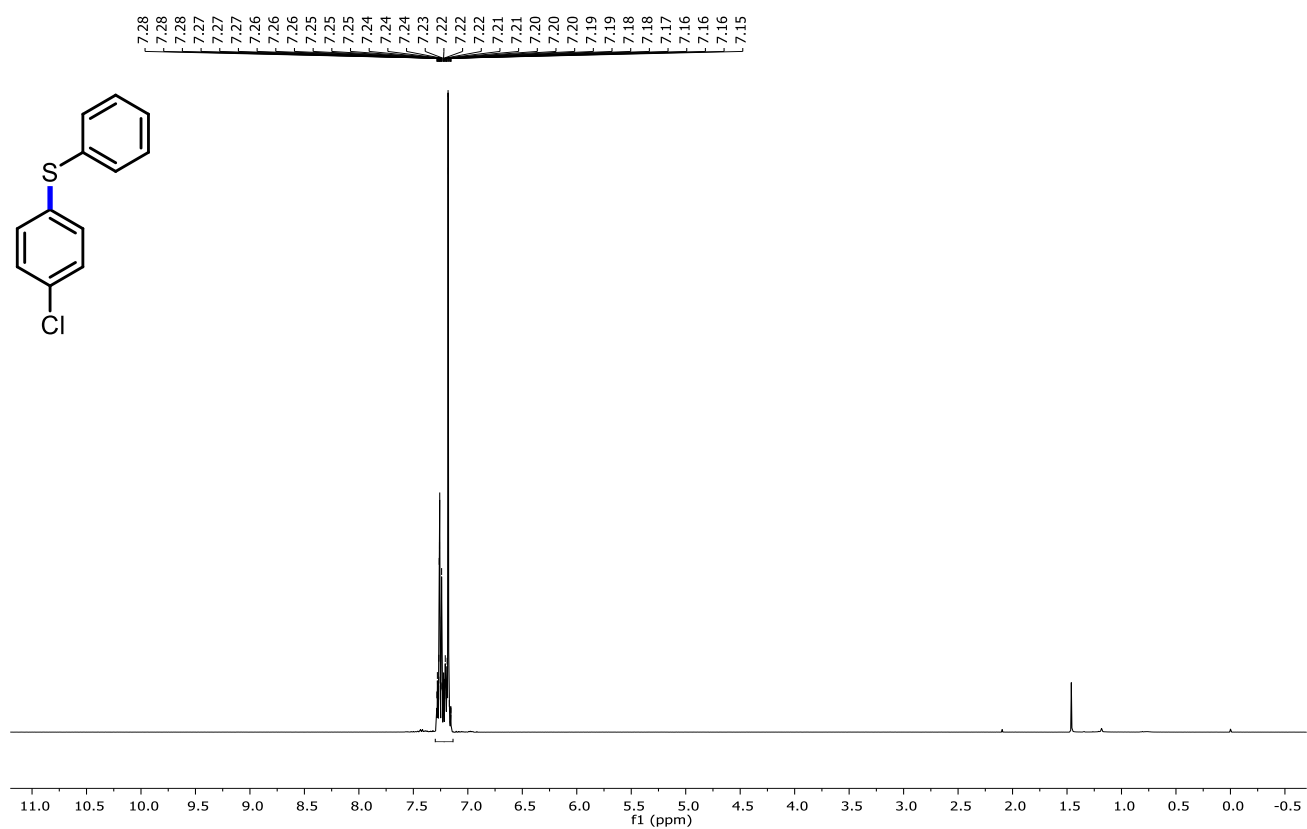
Ethyl 3-((4-cyano-2,6-difluorophenyl)thio)propanoate (33): ^{13}C NMR (100 MHz), CDCl_3 .



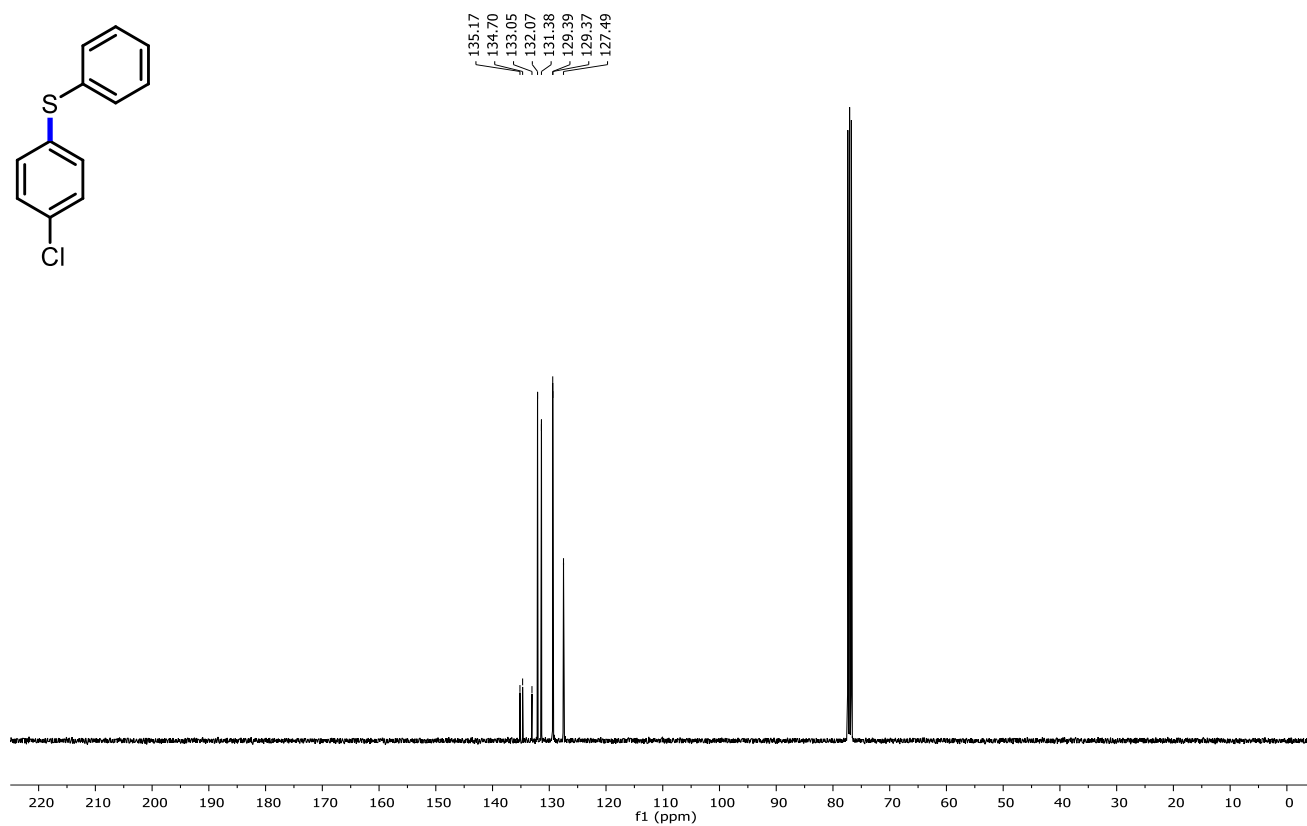
Ethyl 3-((4-cyano-2,6-difluorophenyl)thio)propanoate (33): ^{19}F NMR (376 MHz), CDCl_3 .



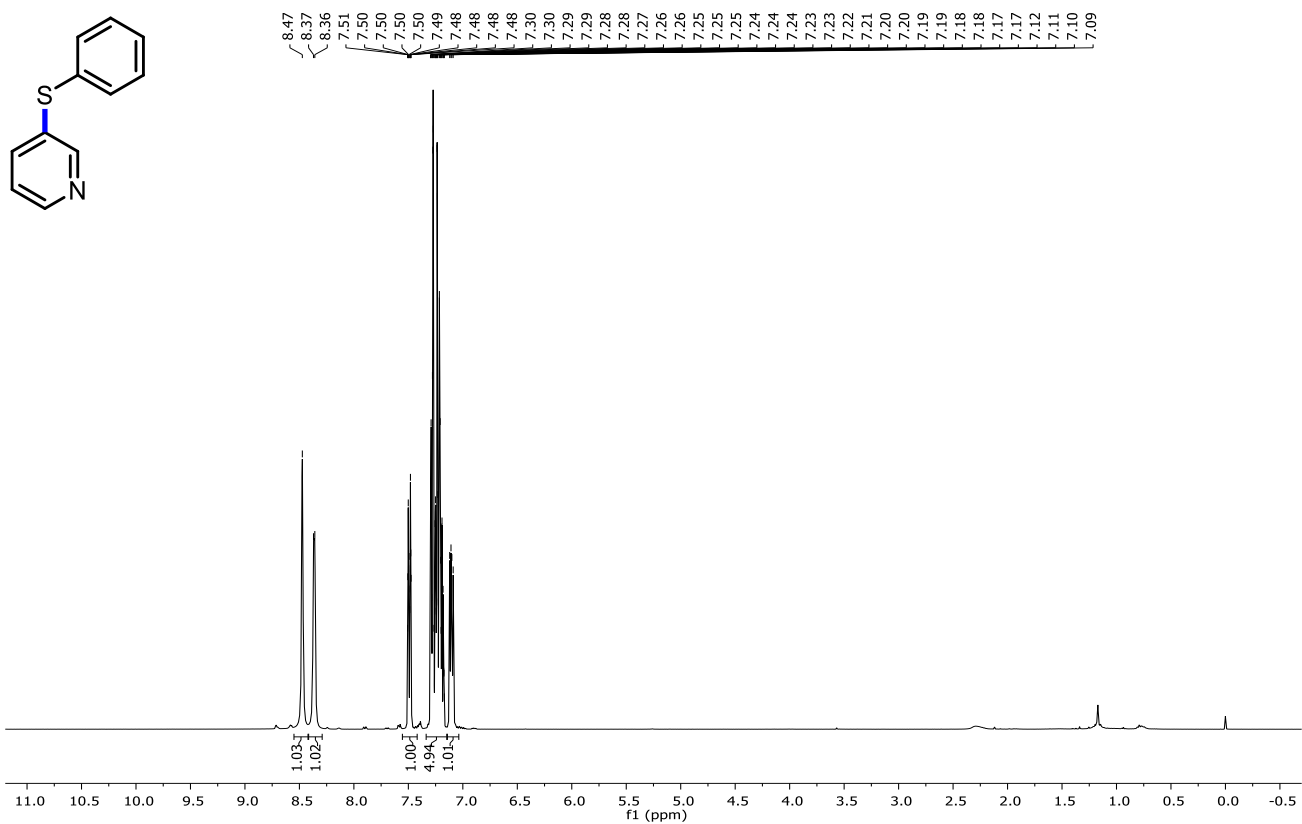
(4-chlorophenyl)(phenyl)sulfane (34): ^1H NMR (400 MHz), CDCl_3



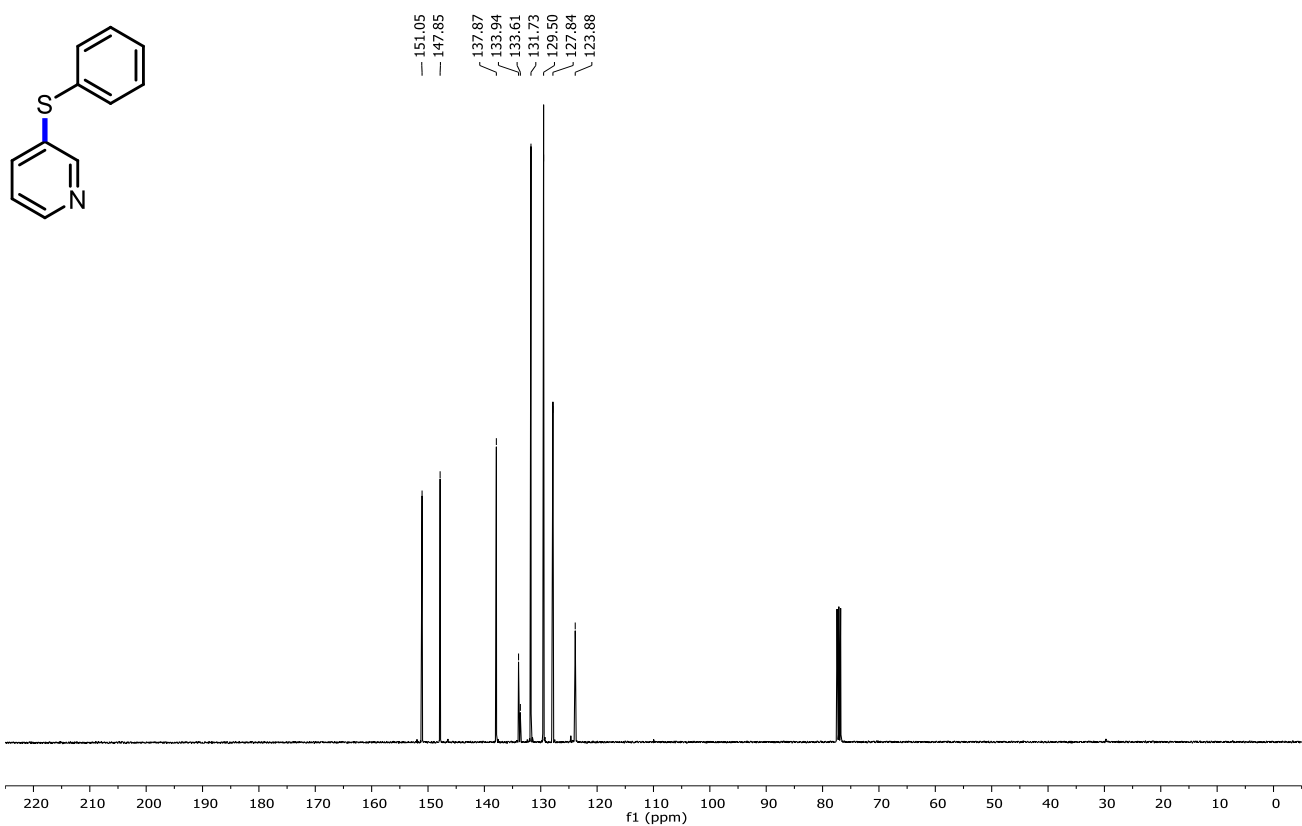
(4-chlorophenyl)(phenyl)sulfane (34): ^{13}C NMR (100 MHz), CDCl_3 .



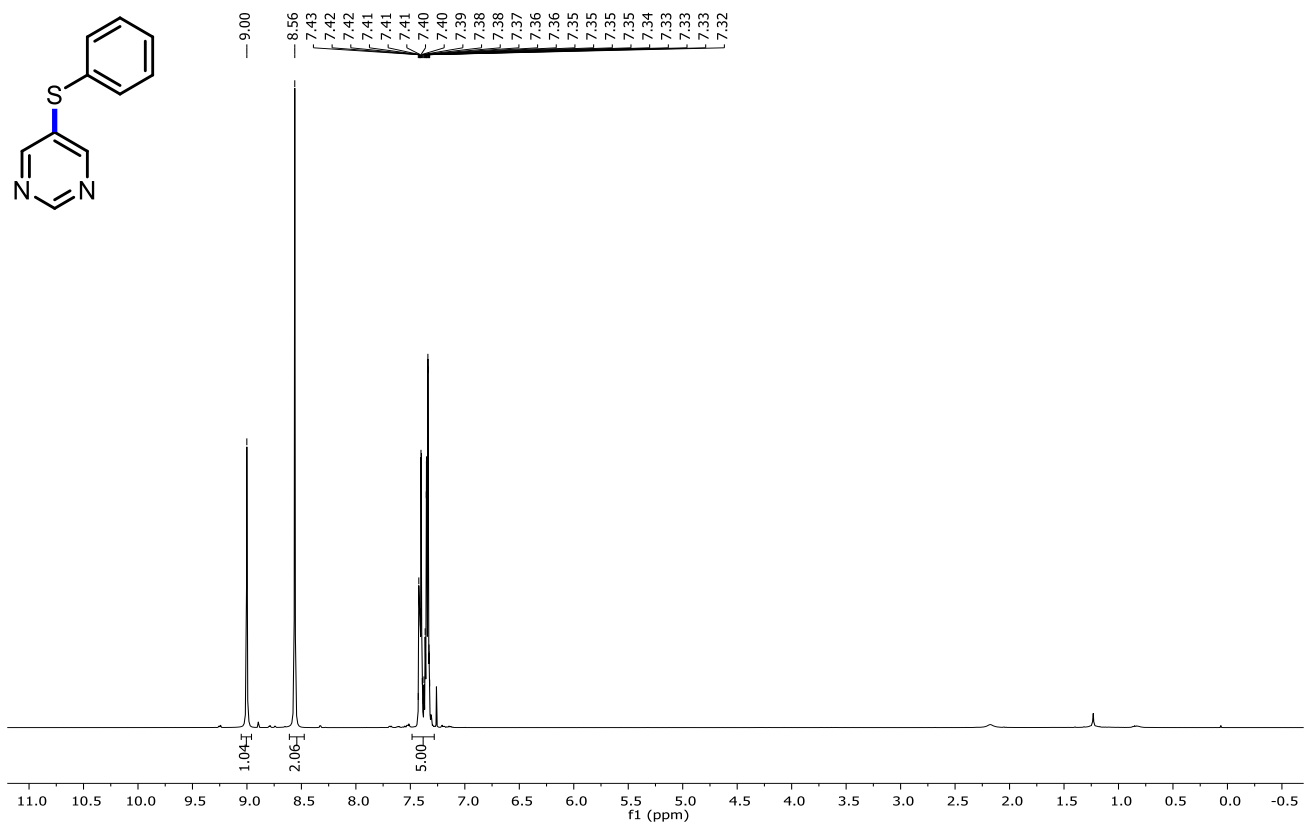
3-(phenylthio)pyridine (35): ^1H NMR (400 MHz), CDCl_3



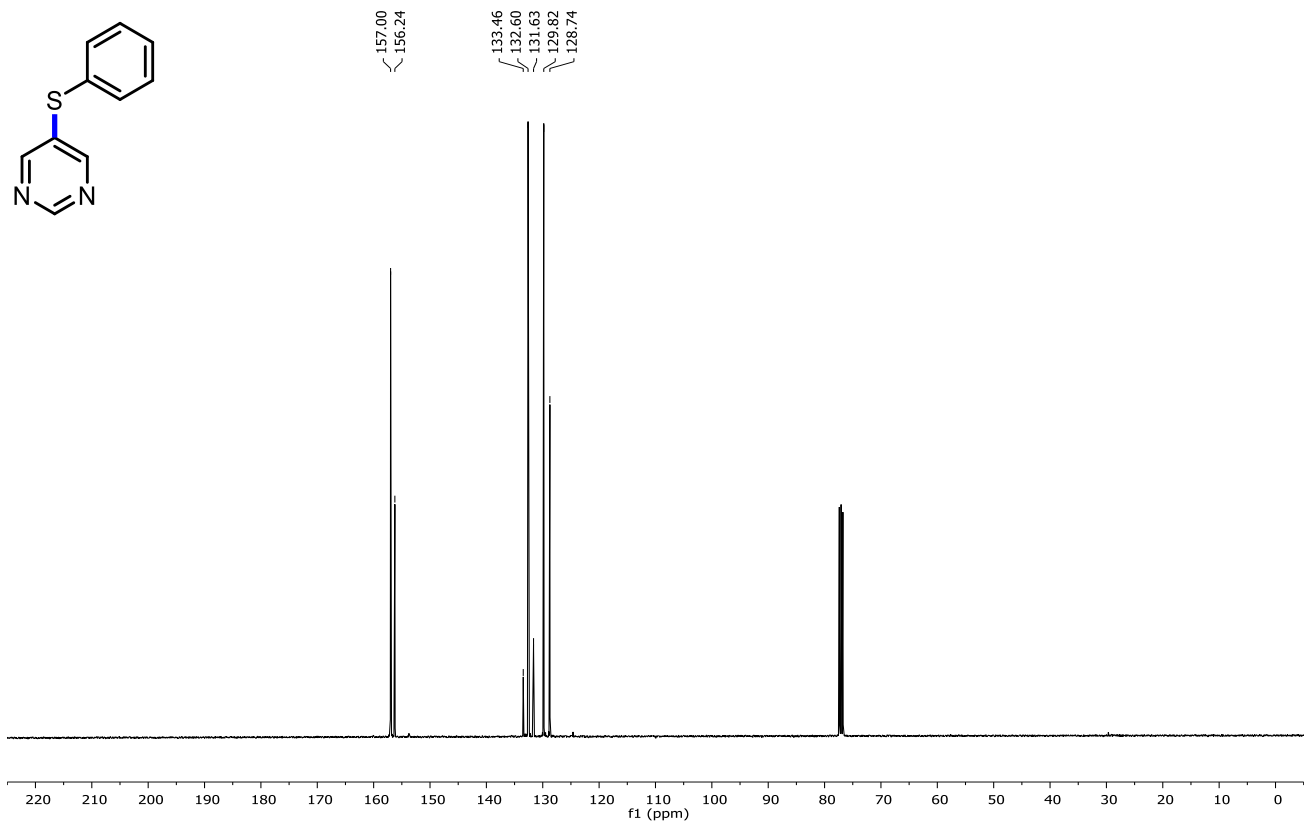
3-(phenylthio)pyridine (35): ^{13}C NMR (100 MHz), CDCl_3 .



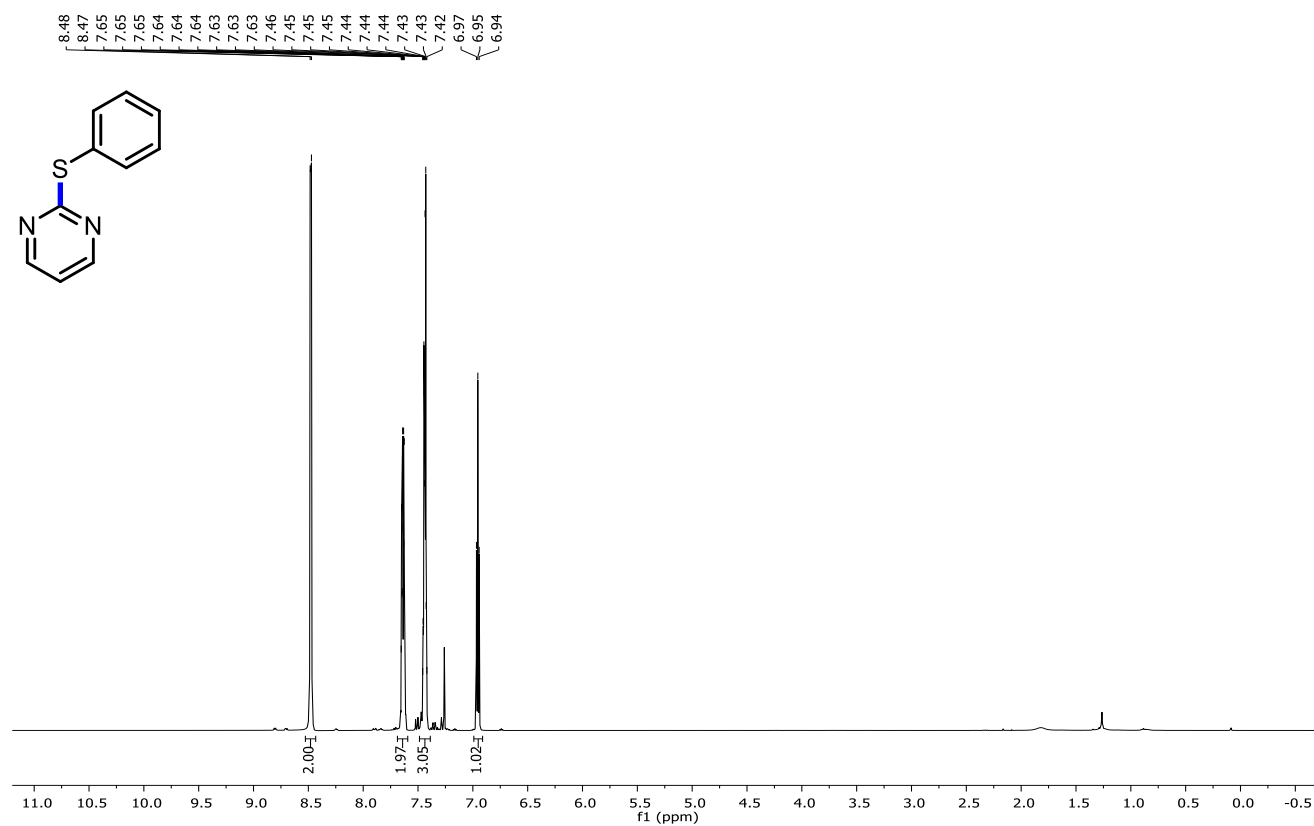
5-(phenylthio)pyrimidine (36): ^1H NMR (400 MHz), CDCl_3 .



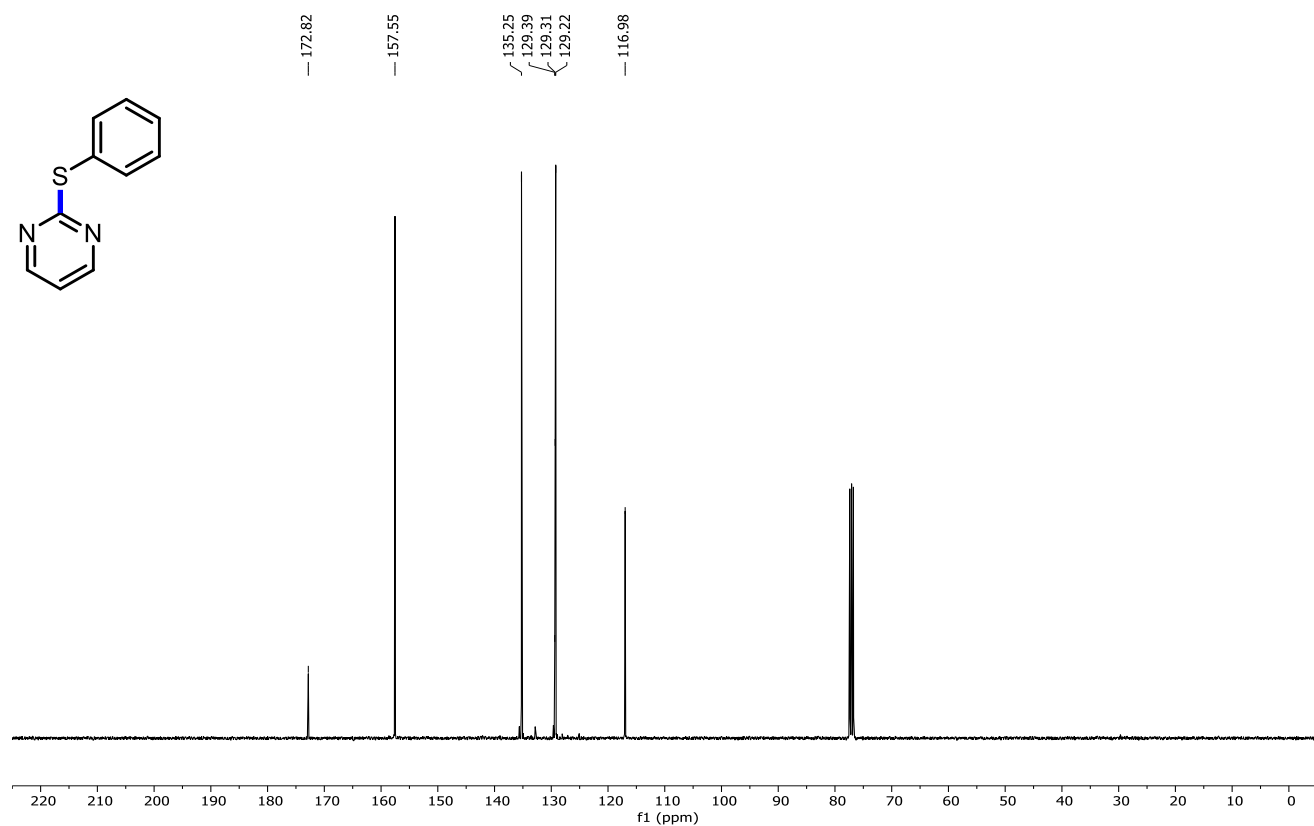
5-(phenylthio)pyrimidine (36): ^{13}C NMR (100 MHz), CDCl_3 .



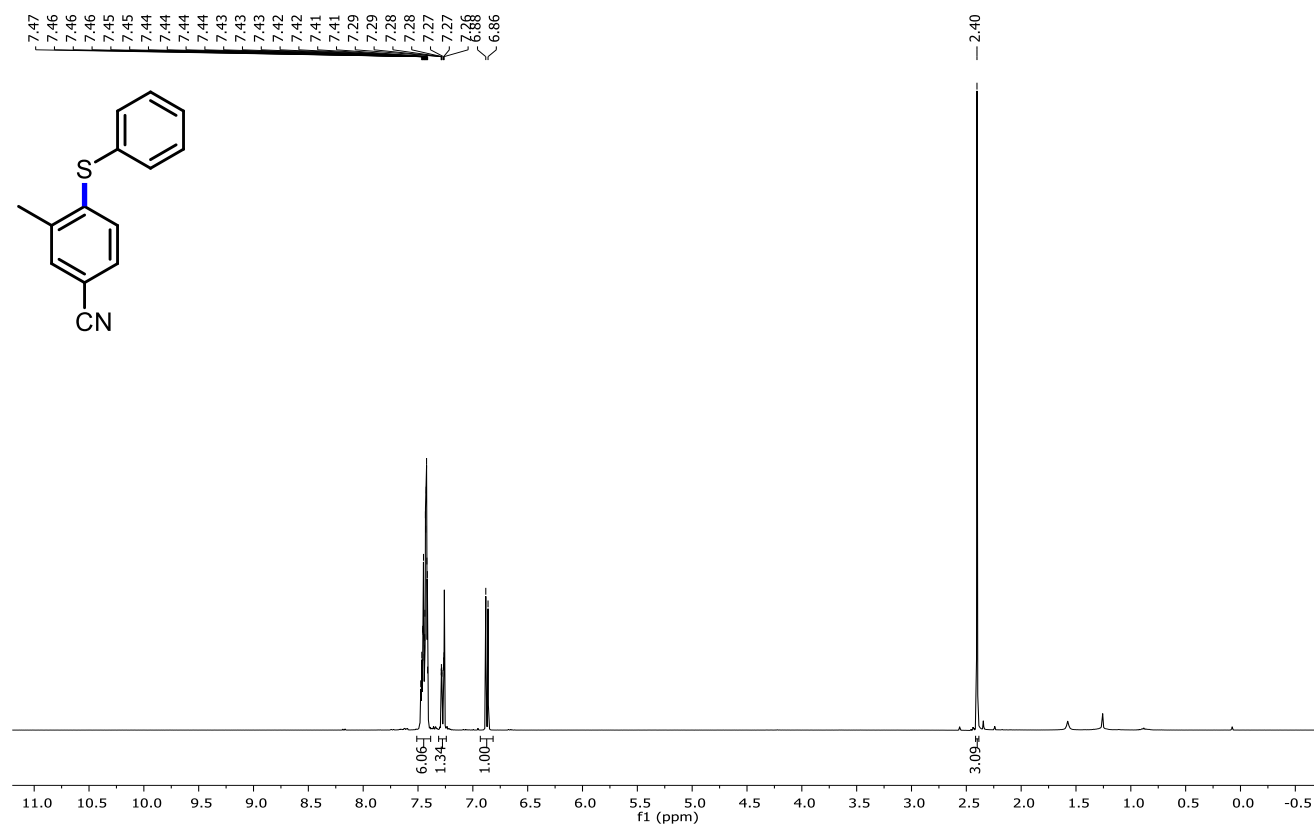
2-(phenylthio)pyrimidine (37): ^1H NMR (400 MHz), CDCl_3



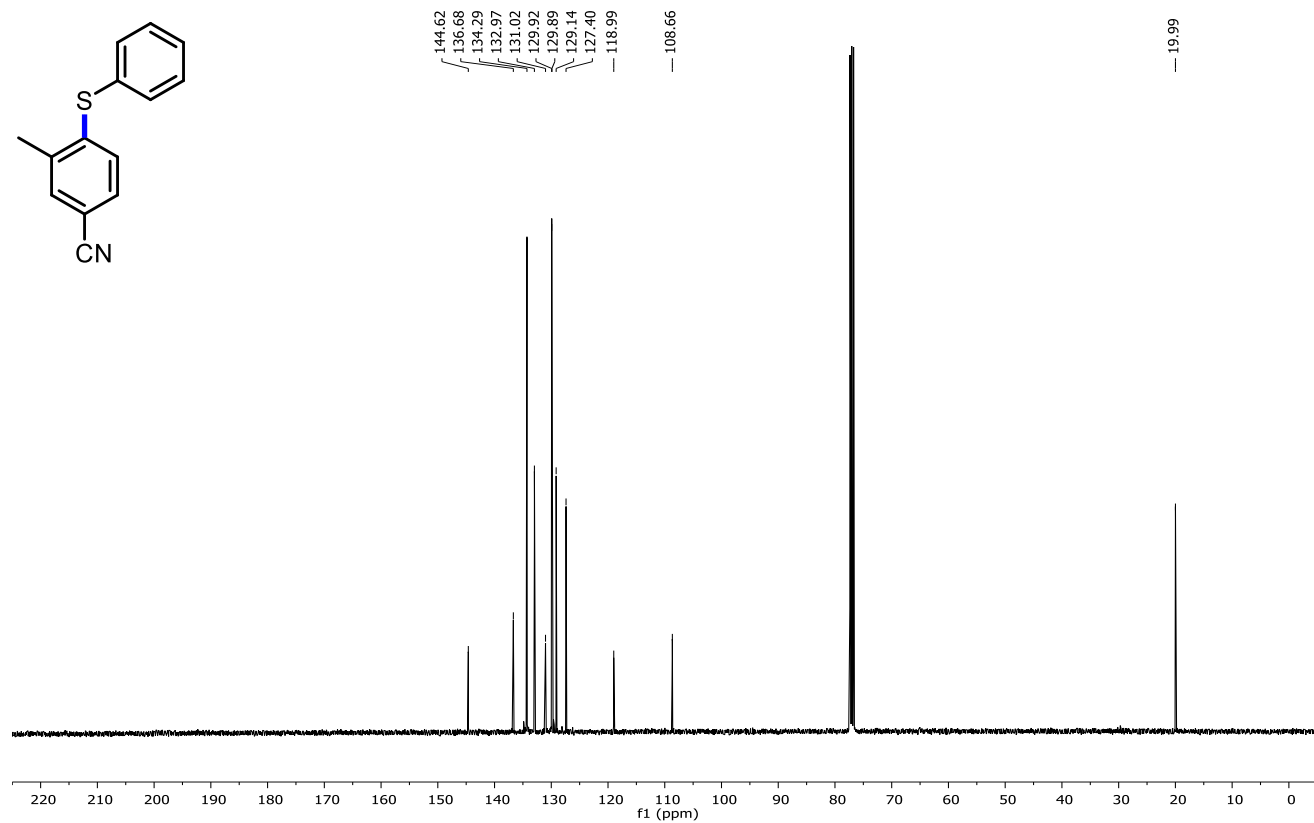
2-(phenylthio)pyrimidine (37): ^{13}C NMR (100 MHz), CDCl_3 .



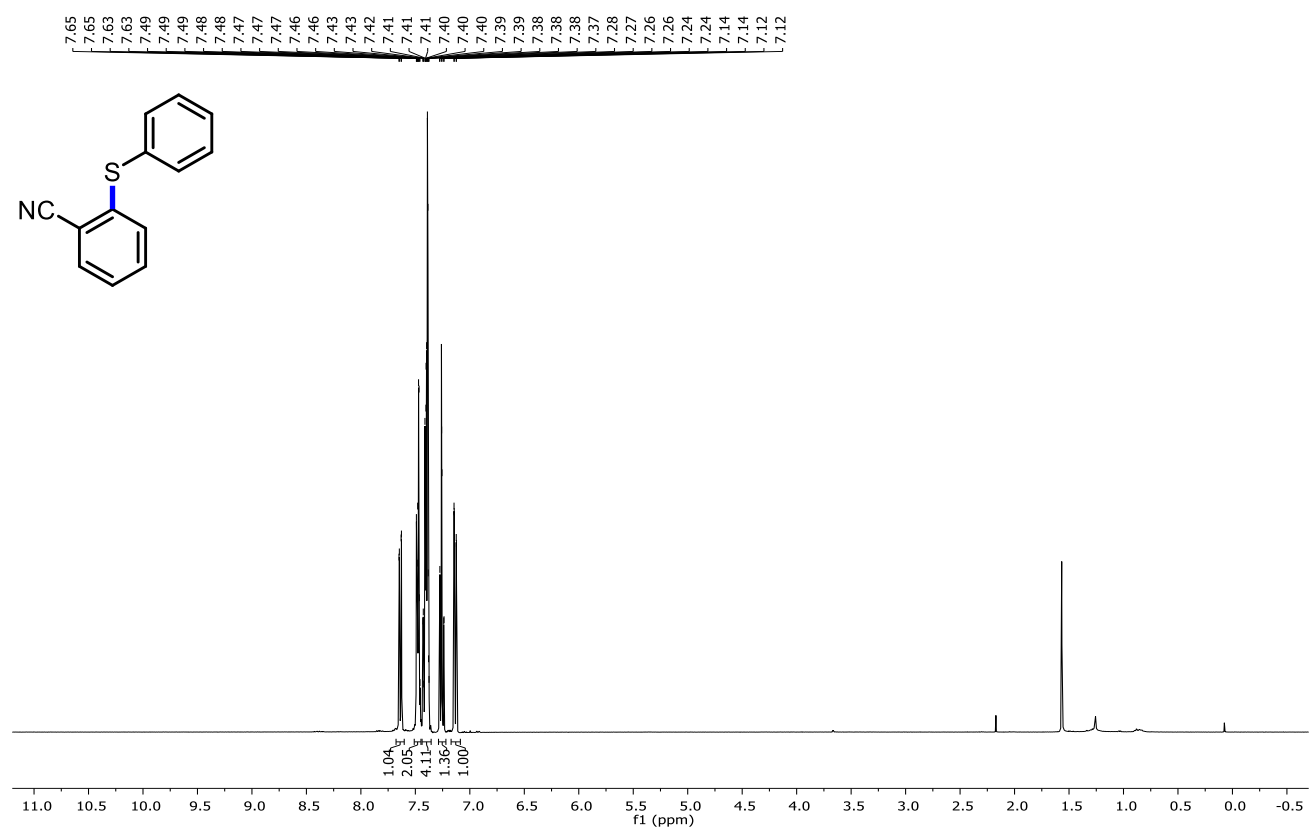
3-methyl-4-(phenylthio)benzonitrile (38): ^1H NMR (400 MHz), CDCl_3



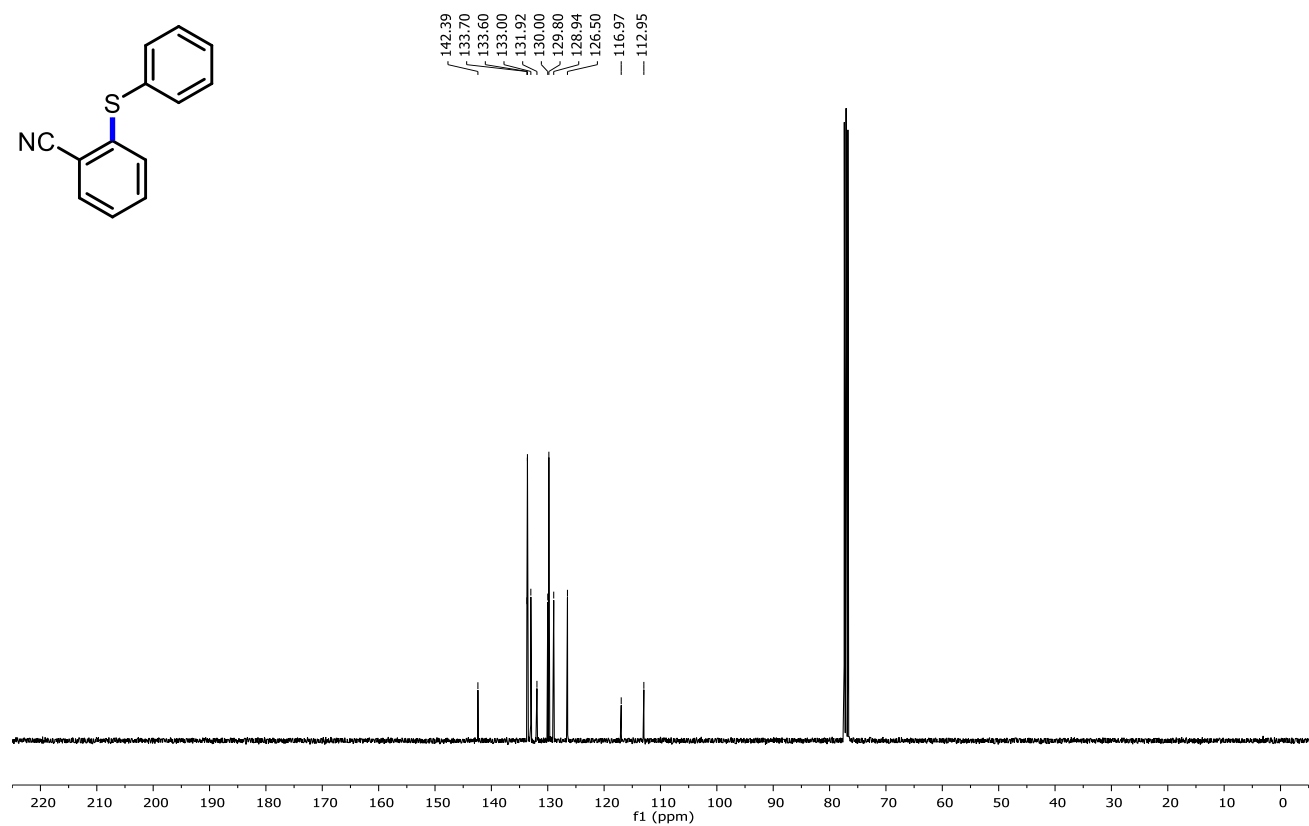
3-methyl-4-(phenylthio)benzonitrile (38): ^{13}C NMR (100 MHz), CDCl_3 .



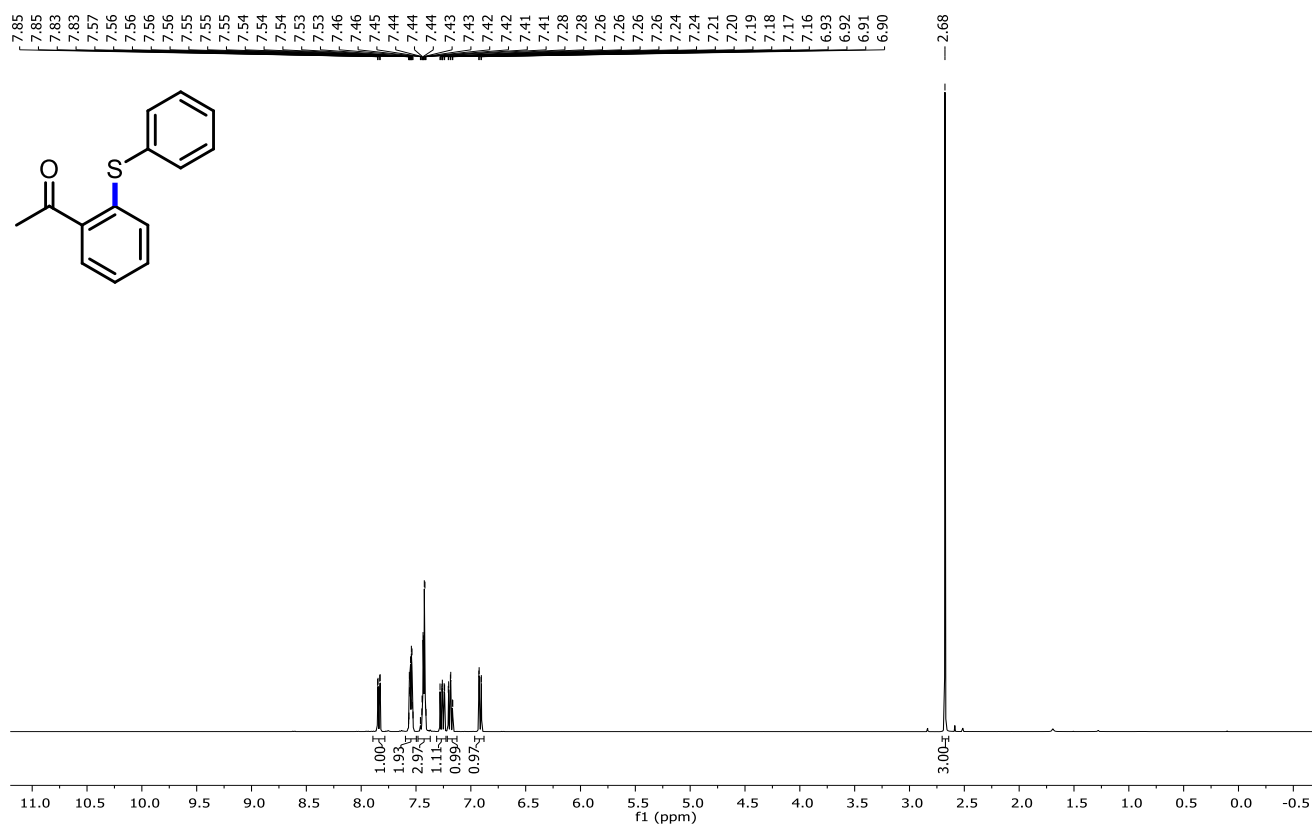
2-(phenylthio)benzonitrile (39): ^1H NMR (400 MHz), CDCl_3



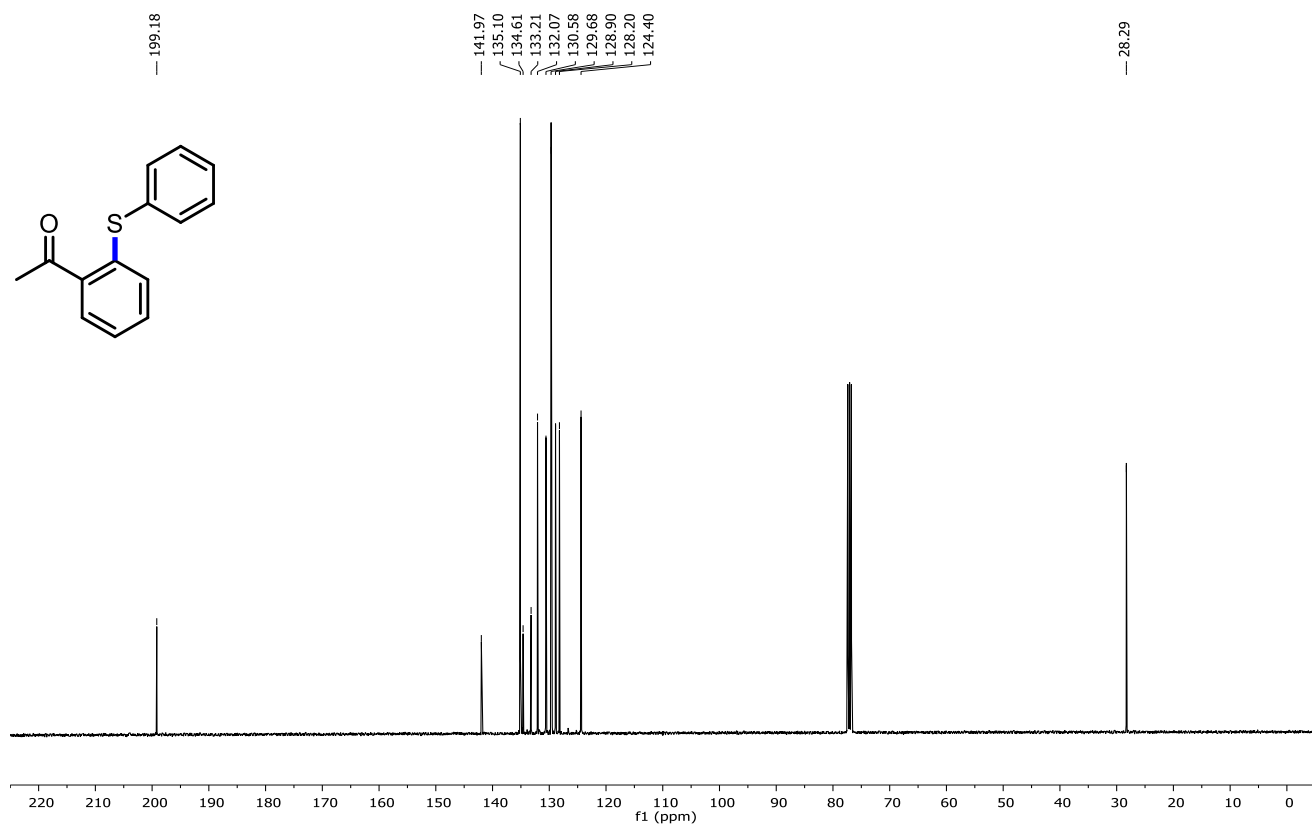
2-(phenylthio)benzonitrile (39): ^{13}C NMR (100 MHz), CDCl_3 .



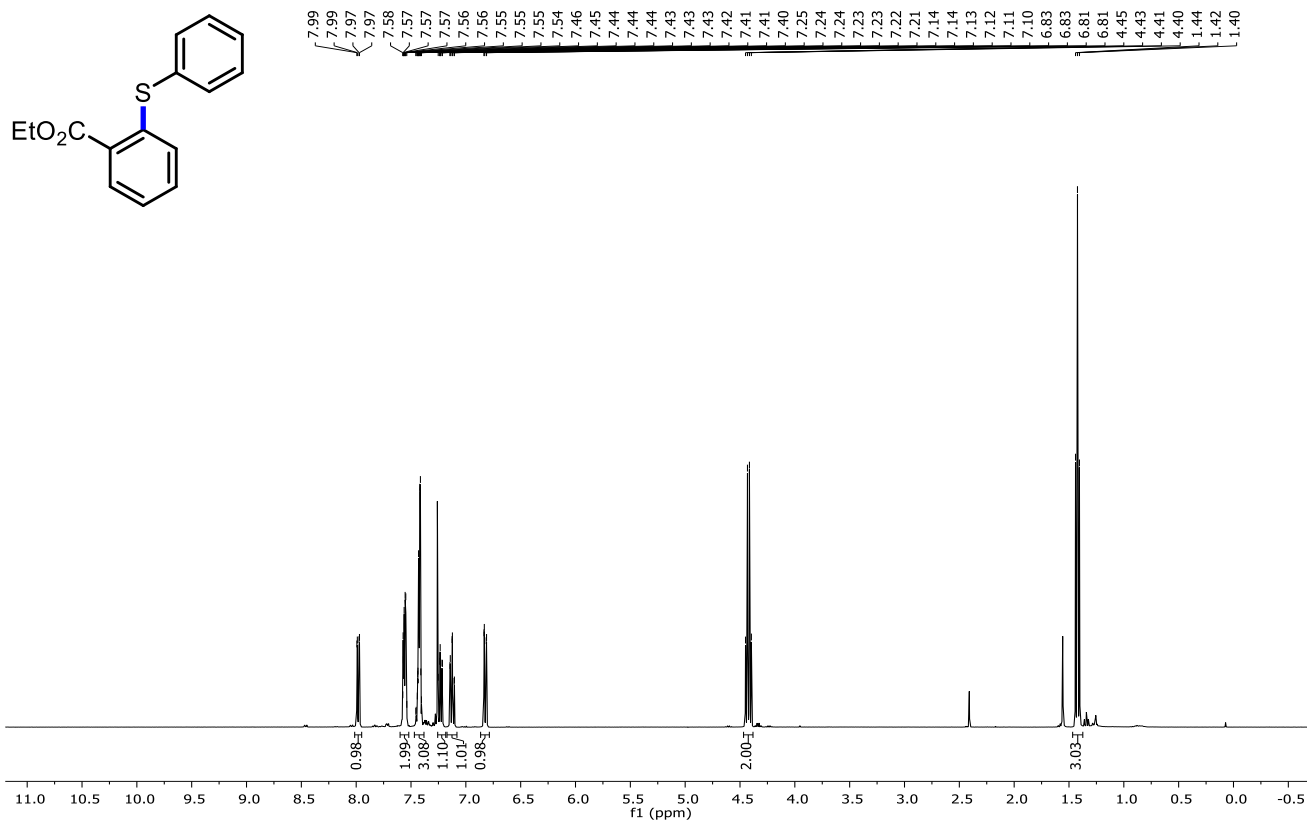
1-(2-(phenylthio)phenyl)ethan-1-one (40): ^1H NMR (400 MHz), CDCl_3



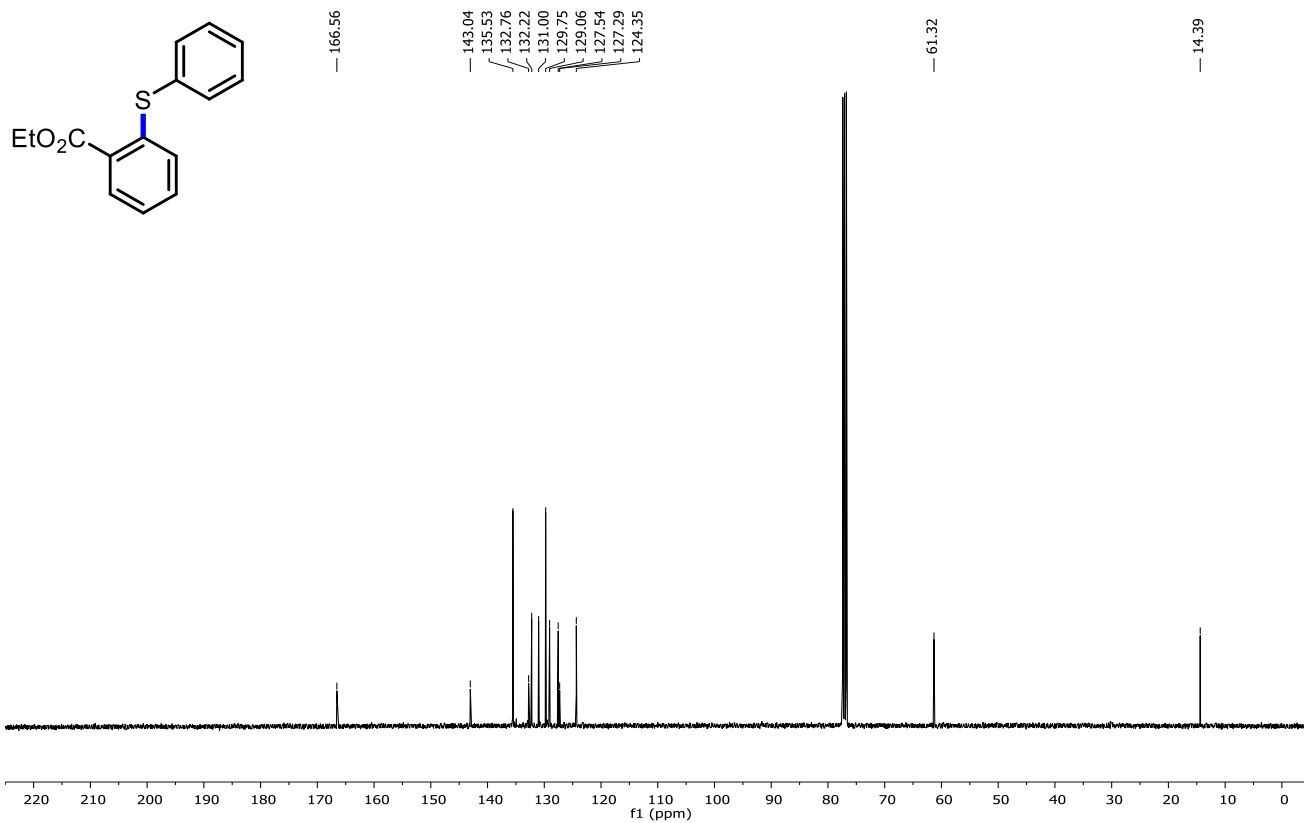
1-(2-(phenylthio)phenyl)ethan-1-one (40): ^{13}C NMR (100 MHz), CDCl_3 .



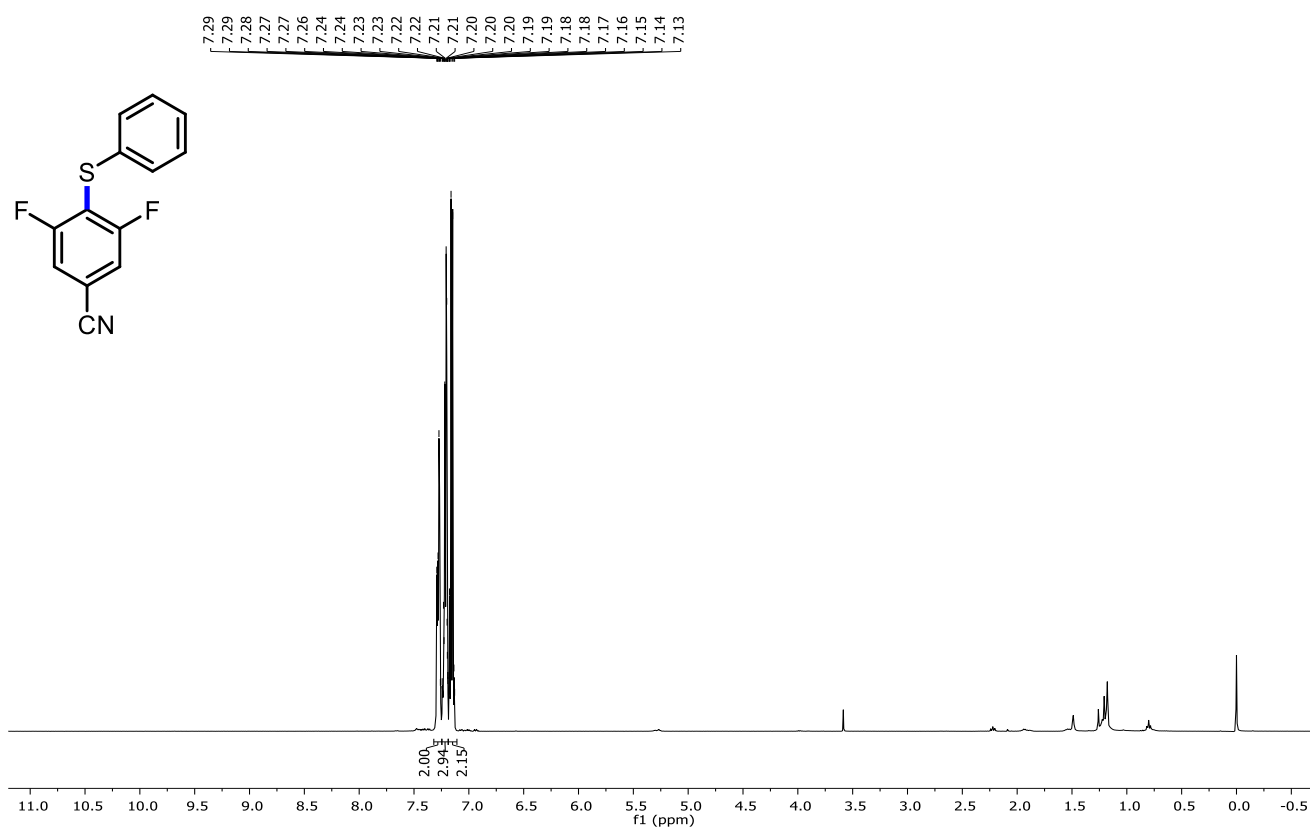
Ethyl 2-(phenylthio)benzoate (41): ^1H NMR (400 MHz), CDCl_3



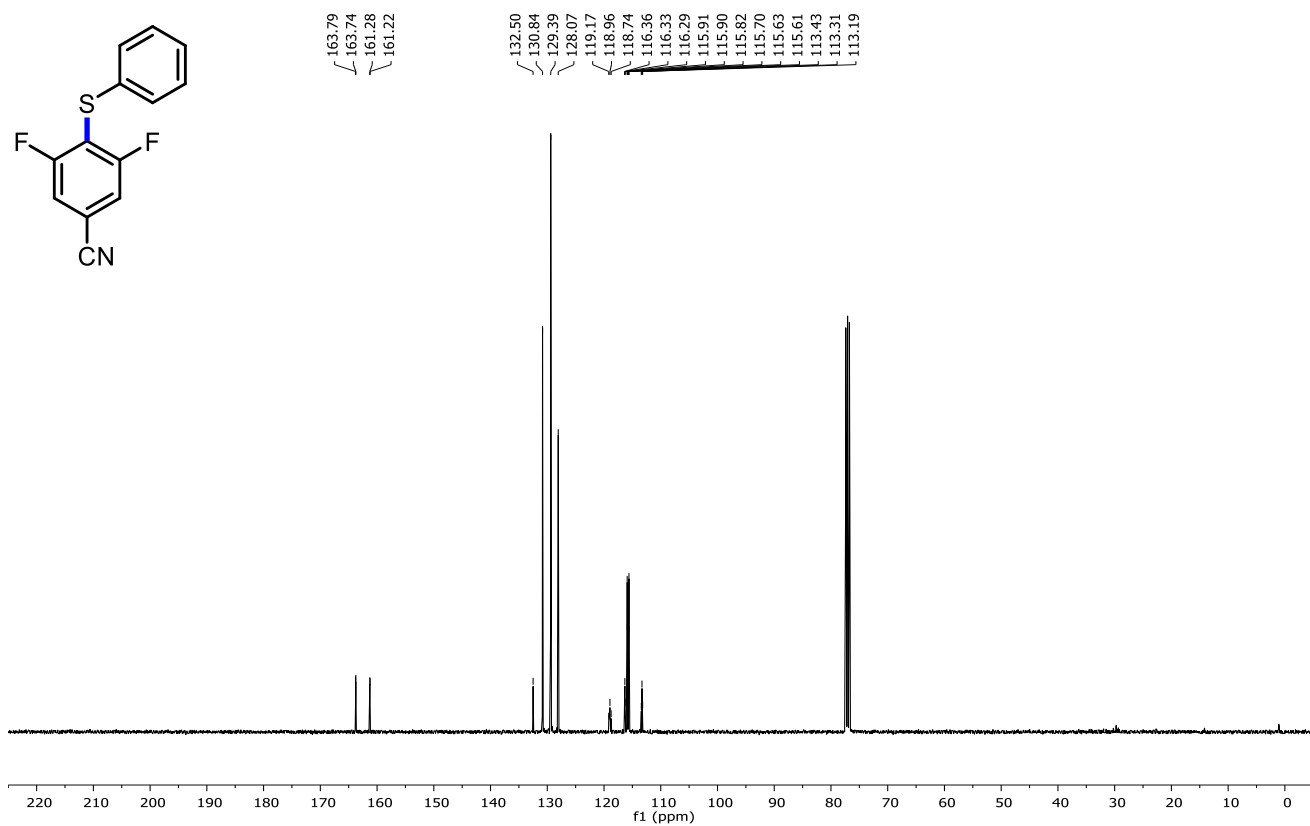
Ethyl 2-(phenylthio)benzoate (41): ^{13}C NMR (100 MHz), CDCl_3 .



3,5-difluoro-4-(phenylthio)benzonitrile (42): ^1H NMR (400 MHz), CDCl_3



3,5-difluoro-4-(phenylthio)benzonitrile (42): ^{13}C NMR (100 MHz), CDCl_3 .



3,5-difluoro-4-(phenylthio)benzonitrile (42): ^{19}F NMR (376 MHz), CDCl_3 .

