Supplementary Information

C(sp^3)–heteroatom bond formation by iron-catalyzed soft couplings

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This PDF includes:

Supplementary Methods
Supplementary Discussion
Supplementary Fig. 1–199
Supplementary Table 1–5
Supplementary References

Supplementary Information – Table of Contents

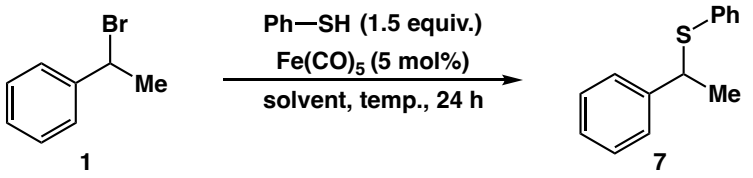
1. Supplementary Methods

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. All work-up and purification procedures used reagent grade solvents purchased from Fisher, VWR or Sigma-Aldrich. Reagents and catalyst used were purchased from the following vendors and used as received: diphenyl disulfide (99.9%), iron (III) acetylacetonate (99.9%), triphenyl phosphine (99%), carbon tetrabromide (99%), bis(cyclooctadiene)nickel(0) (95%), phenylethanol (98%), pinacolone (98%), magnesium chloride (98%), aluminum chloride (99%), benzyl bromide (98%), 4-chlorobenzaldehyde (97%), tetrakis(triphenylphosphine)nickel(0) (95%), phenylacetic acid (99%), aniline (99.5%), *N*-methylaniline (99%), thiophenol (97%), benzaldehyde (99%), pivaldehyde (96%), phenylmagnesium chloride (2M in THF), ethylmagnesium chloride (3M in ether), triethylamine (99.5%), cyclohexylmagnesium chloride (1M in MeTHF), methylmagnesium chloride (3M in THF), methylmagnesium iodide, lithium bromide (99%), hydrogen bromide (48% in water), nitropropane (98.5%), ethyl acetoacetate (99%), ethyl malonate (99%), naphthalen-2-yl-ethanol (98%), 2-methyl-1-phenylpropanone (97%), tetrakis(triphenylphosphine)palladium(0) (99%), trimethylsilyl bromide (98%), and trimethylsilyl chloride (98%) were purchased from Sigma Aldrich. Iron (II) chloride (99.5%), iron(III) bromide (98%), iron (0) pentacarbonyl (99.5%), chlorobenzenethiol (97%), 4-dimethylaminopyridine (99%), benzhydryl bromide (90%), and copper (II) bromide (99%) were purchased from Alfa Aesar. Bromoethylbenzene (95%), 4-cholorobenzenethiol (98%), 4-nitrobenzenethiol (95%), ethyl mercaptan (98%), cyclohexanethiol (98%), 4-mercaptobenzonitrile (98%), 4-mercaptobenzoic acid (95%), 4-chlorobenzylmercaptan (98%), 2-propanethiol (96%), 2-bromobenzaldehyde (98%), 3-bromobenzaldehyde (98%), 4-bromophenylethanol (97%), 4-acetylbenzonitrile (97%) were purchased from TCI chemicals. *N,N′*-diisopropylcarbodiimide (>99%) was acquired from Advanced ChemTech. Anthracenyl bromide (98%), 1-bromoethyl-4-fluorobenzene, iron(II) trifluoromethanesulfonate (98%), iron(III) trifluoromethanesulfonate (98%), Ibuprofen (99%), 5-trifluoromethyl-2-mercaptopyridine (98.87%), 3-bromo-6-mercaptopyridine (95%), 4-methoxythiophenol (97%), 3-methoxythiophenol (97%), 2-methoxythiophenol (95%), 2-pyridinethiol (97%), 2-naphthalenethiol (98%) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (97%) were obtained from Ambeed. Iron (III) chloride (98%), iron (II) bromide (97%), diiron nanocarbonyl (98%), 2-methyl-

2-propanethiol (99%), toluenethiol (98%), 4-fluorothiophenol were purchased from Thermo Scientific. Iron (II) fluoride (99%), iron (III) fluoride (99%), and 4-benzenethiol (98%) were purchased from Strem Chemicals, and 4-(trifluoromethyl)thiophenol (95%) were purchased from Matrix Scientific. Reaction temperatures were controlled using IKA Plates (RCT digital) and the built-in temperature modulators. Thin layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV light, potassium permanganate, phosphomolybdic acid, and p-anisaldehyde staining. Silicycle Silica flash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on a Mercury (400 MHz), or Varian spectrometers (500, 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Mercury (100 MHz), or Varian spectrometers (125 MHz, 150 MHz) and are reported relative to deuterated solvent signals. ^{19}F spectra were recorded on a Varian spectrometer (564 MHz). IR data were collected on an Agilent Cary 630 FTIR Spectrometer and Mettler Toledo ReactIR 720L. All IR data are reported in terms of frequency absorption (cm^{-1}). Melting points were recorded on a VWR melting point apparatus, high resolution mass (HRMS) spectra were obtained on an Agilent 6545Q-TOF LC/MS, and chiral SFC data were collected on an Agilent 1260 Hybrid SFC/UHPLC system equipped with the following chiral columns: ChiralPak IA-3, 4.6x250mm, 3 mic; ChiralPak IB N-3, 4.6x250mm, 3 mic; ChiralPak IC-3, 4.6x250mm, 3 mic; ChiralPak IH-3, 4.6x250mm, 3 mic; ChiralPak IG-3, 4.6x250mm, 3 mic; ChiralPak IJ-3, 4.6x250mm, 3 mic; and ChiralPak IK-3, 4.6x250mm, 3 mic.

A. Optimization procedures

A.1. Solvent evaluation



Supplementary Fig. 1. **General scheme for reaction discovery.**

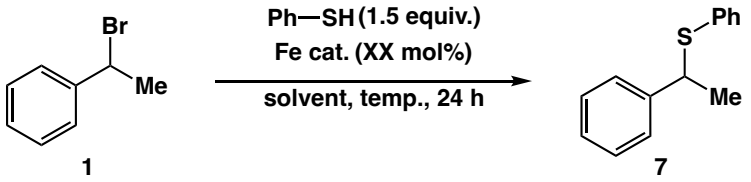
To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (4.9 mg, 0.025 mmol, 5 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 68 uL, 1.0 equiv.), and thiophenol (**85**) (82.6 mg, 0.75 mmol, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 40 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield a crude mixture including phenyl thioether **7**. The mixture was analyzed by NMR using 1,3,5-trimethoxybenzene as an internal standard.

Entry	Solvent	Yield (%)[1]
1	acetone	20
2	pinacolone	27
3	tetrahydrofuran	6
4	diethyl ether	35
5	acetonitrile	24
6	dichloromethane	31
7	1,4-dioxane	NR

[1] Yields are NMR yields determined with 1,3,5-trimethoxybenzene as an internal standard. Me, methyl group; Ph, phenyl group; NR, no reaction.

Supplementary Table 1**. Solvent screen.**

A.2. Catalyst loading and temperature optimization



Supplementary Fig. 2. **General scheme for catalyst loading and temperature optimization.**

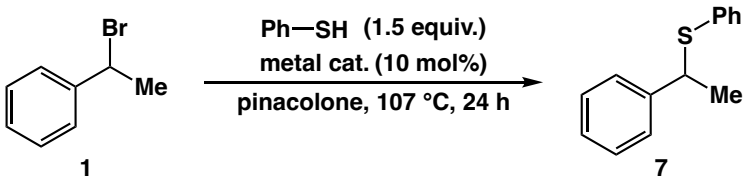
To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (0.025 mmol, 5 mol% or 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 68 uL, 1.0 equiv.), and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at the designated temperature for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield a crude mixture including phenyl thioether **7**. The mixture was analyzed by NMR using 1,3,5-trimethoxybenzene as an internal standard.

Entry	Iron source (XX mol%)	Solvent	Temperature	Yield (%)[1]
1	$Fe(CO)_5$ (5 mol%)	acetone	40 °C	20
2	$Fe(CO)_5$ (5 mol%)	acetone	55 °C	25
3	$Fe(CO)_5$ (5 mol%)	pinacolone	55 °C	32
4	$Fe(CO)_5$ (10 mol%)	acetone	55 °C	37
5	$Fe(CO)_5$ (10 mol%)	pinacolone	55 °C	51
6	$Fe(CO)_5$ (10 mol%)	pinacolone	80 °C	82
7	$Fe(CO)_5$ (10 mol%)	pinacolone	100 °C	85
8	$Fe(CO)_5$ (5 mol%)	pinacolone	107 °C	76
9	$Fe(CO)_5$ (10 mol%)	pinacolone	107 °C	92

[1] NMR yields determined using 1,3,5-trimethoxybenzene as an internal standard.
Me, methyl group; Ph, phenyl group.

Supplementary Table 2. **Reaction optimization, catalyst loading and temperature.**

A.3. Iron and additive evaluation



Supplementary Fig. 3. **General scheme for metal evaluation.**

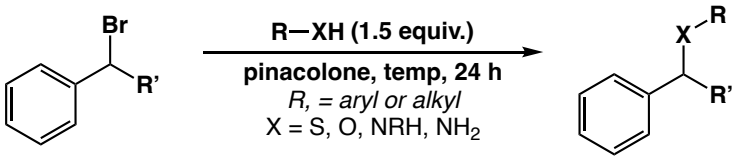
To a flame-dried 4 mL dram vial equipped with a stir bar was added a metal catalyst (0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 68 uL, 1.0 equiv.), and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77.0 uL, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield a crude mixture including phenyl thioether **7**. The mixture was analyzed by NMR using 1,3,5-trimethoxybenzene as an internal standard.

Entry	Variation From Standard Conditions	Yield (%)[1]
1	none	92(91)*
2	$Fe_2(CO)_9$	72
3	$Fe(OAc)_2$	79
4	$Fe(OTf)_2$	75
5	FeF_2	76
6	$FeCl_2$	81
7	$FeBr_2$	70
8	$Fe(acac)_3$	76
9	FeF_3	79
10	$FeCl_3$	54
11	$FeBr_3$	68
12	with Cs_2CO_3	79
13	with K_2CO_3	62
14	no Fe cat.	trace
15	with H_2O (1 uL)	78
16	$MgCl_2$	11
17	$AlCl_3$	10
18	Camphorsulfonic acid	19

[1] NMR yield determined using 1,3,5-trimethoxybenzene as an internal standard. (*) Isolated yield. Me, methyl group; Ph, phenyl group; OTf, triflate group; acac, acetyl acetonate; cod, 1,5-cyclooctadiene.

Supplementary Table 3. **Iron and additive evaluation.**

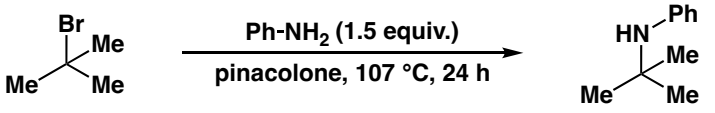
A.4. Background reactivity experiments



Entry	R'	Nucleophile	Temperature	Yield (%)[1]
1	Me	thiophenol	107 °C	trace
2	Me	benzyl alcohol	80 °C	trace
3	Me	aniline	107 °C	69
4	Me	piperidine	107 °C	78
5	H	thiophenol	107 °C	8

[1] Yields are NMR yields determined with 1,3,5-trimethoxybenzene as an internal standard. Me, methyl group.

Supplementary Table 4**. Control experiments without iron catalyst.**

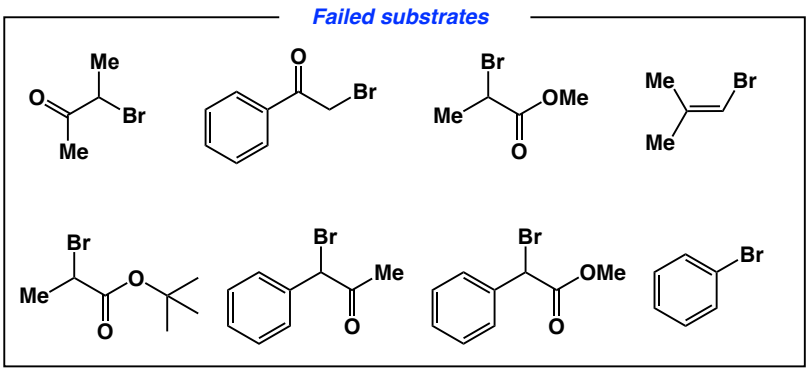


Entry	Nucleophile	Yield (%)[1]
1	aniline	NR

[1] Yields are NMR yields determined with 1,3,5-trimethoxybenzene as an internal standard. Me, methyl group; NR, no reaction.

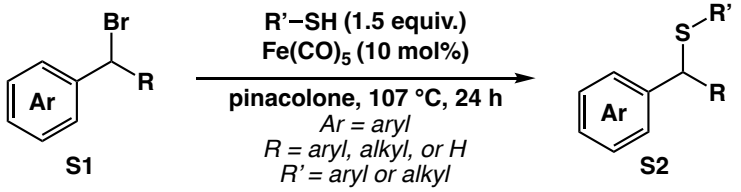
Supplementary Table 5**. Control experiments without iron catalyst.**

A.5. Incompatible electrophiles



Supplementary Fig. 4. **Incompatible bromide substrate classes.**

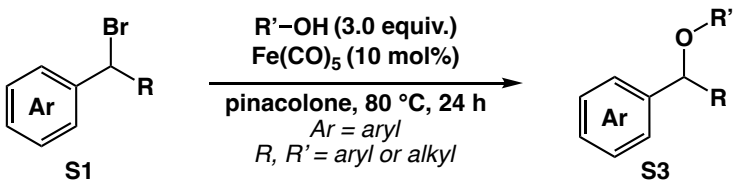
B. General, optimized procedure for thiol coupling



Supplementary Fig. 5. **General scheme for optimized thiol coupling procedure.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (10.0 mg, 0.025 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL), bromide coupling partner (**S1**) (0.5 mmol, 1.0 equiv.), and thiol (0.75 mmol, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture was purified by silica flash chromatography to yield thioethers **S2**.

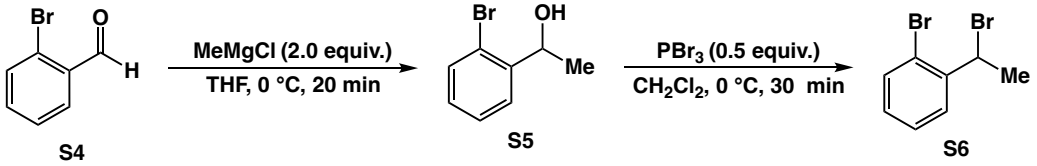
C. General, optimized procedure for alcohol coupling



Supplementary Fig. 6. **General scheme for optimized alcohol coupling procedure.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (10.0 mg, 0.025 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL), bromide coupling partner (**S1**) (0.5 mmol, 1.0 equiv.), and alcohol (1.5 mmol, 3.0 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 80 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture was purified by silica flash chromatography to yield ether **S3**.

D. Substrate synthesis and characterization

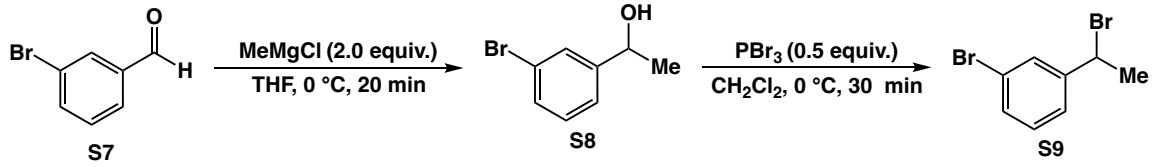


Supplementary Fig. 7. **Synthesis of bromide S6.**

1-Bromo-2-(1-bromoethyl)benzene (S6). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added 2-bromobenzaldehyde (**S4**) (926 mg, 5.0 mmol, 1.0 equiv.) and THF (4.0 mL). The mixture was cooled to 0 ℃ under a positive pressure of N_2 and MeMgCl (3.0 M in THF, 3.3 mL, 10.0 mmol, 2.0 equiv.) was then added dropwise over 5 min. The mixture was stirred for

additional 20 min at 0 °C. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (10.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (1:4 EtOAc:hexane) to yield alcohol **S5** as a pale-yellow oil (667 mg, 66% yield).

The resultant alcohol **S5** was added to a flame-dried 50 mL round-bottom-flask equipped with a stir bar. CH_2Cl_2 (10.0 mL) was added, and the solution was cooled to 0 °C. PBr_3 (156 µL, 1.7 mmol, 0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 30 min at 0 °C. The reaction was quenched with water (10.0 mL) and extracted with CH_2Cl_2 (10.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography with 100%hexane to yield bromide **S6** as a light-yellow oil (573 mg, 65% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.16 – 7.12 (m, 1H), 5.61 (q, *J* = 6.9 Hz, 1H), 2.04 (d, *J* = 6.9 Hz, 3H). Spectral data matched those reported previously.[1]

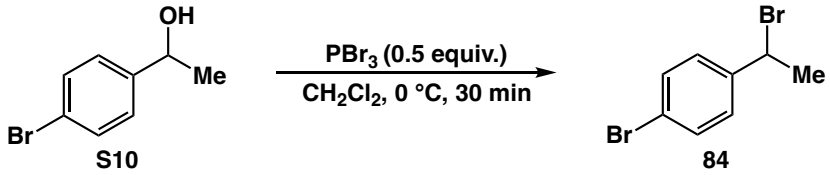


Supplementary Fig. 8. **Synthesis of bromide S9.**

1-Bromo-3-(1-bromoethyl)benzene (S9). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added 3-bromobenzaldehyde (**S7**) (926 mg, 5.0 mmol, 1.0 equiv.) and THF (4.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and MeMgCl (3.0 M in THF, 3.3 mL, 10.0 mmol, 2.0 equiv.) was then added dropwise over 5 min. The mixture was stirred for additional 20 min at 0 °C. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (10.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (1:4 EtOAc:hexane) to yield alcohol **S8** as a pale-yellow oil (402 mg, 40% yield).

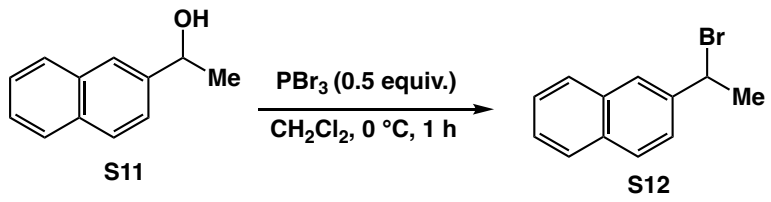
The resultant alcohol **S8** was added to a flame-dried 50 mL round-bottom-flask equipped with a stir bar. CH_2Cl_2 (10.0 mL) was added, and the solution was cooled to 0 °C. PBr_3 (94 µL, 1.0 mmol,

0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 30 min at 0 °C. The reaction was quenched with water (10.0 mL) and extracted with CH_2Cl_2 (10.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography with 100%hexane to yield bromide **S9** as a light-yellow oil (225 mg, 49% yield). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.58 (s, 1H), 7.44–7.39 (m, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 5.12 (q, *J* = 6.9 Hz, 1H), 2.02 (d, *J* = 6.9 Hz, 3H). Spectral data matched those reported previously.[2]



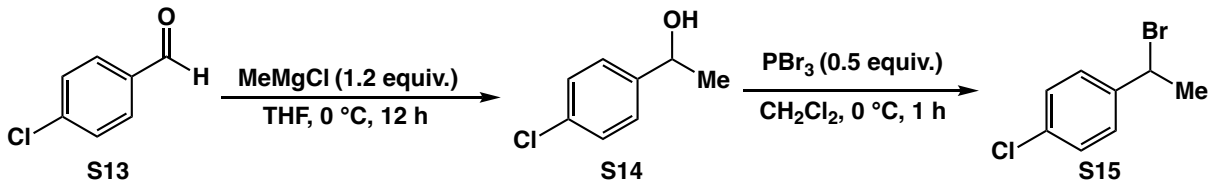
Supplementary Fig. 9. **Synthesis of bromide 84.**

1-Bromo-4-(1-bromoethyl)benzene (84). To a flame-dried 20 mL vial equipped with a stir bar was added 1-(4-bromophenyl)ethan-1-ol (**S10**) (1.05 g, 5.0 mmol, 1.0 equiv.) and CH_2Cl_2 (30.0 mL). The solution was cooled to 0 °C. PBr_3 (280 μL, 2.5 mmol, 0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 30 min at 0 °C. The reaction was quenched with water (20.0 mL) and extracted with CH_2Cl_2 (20.0 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **84** as a light yellow oil (1.12 g, 85% yield). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.47 (d, *J* = 6. 7 Hz, 2H), 7.31 (d, *J* = 7.1 Hz, 2H), 5.15 (q, *J* = 7.3 Hz, 1H), 2.02 (d, *J* = 7.2 Hz, 3H). Spectral data matched those reported previously.[3]



Supplementary Fig. 10. **Synthesis of bromide S12.**

2-(1-Bromoethyl)naphthalene (S12). To a flame-dried 20 mL vial equipped with a stir bar was added 1-(naphthalen-2-yl)ethan-1-ol (**S11**) (172.22 mg, 1.0 mmol, 1.0 equiv.) and CH_2Cl_2 (3.0 mL). The reaction mixture was cooled to 0 °C under a positive pressure of N_2 and PBr_3 (47.0 uL, 0.5 mmol, 0.5 equiv.) was added to the solution dropwise. The reaction was then stirred for 1 hour at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Bromide **S12** was unstable to silica flash chromatography purification conditions and was used without further purification. **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.86–7.80 (m, 4H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.52–7.46 (m, 2H), 5.40 (q, *J* = 6.3 Hz, 1H), 2.15 (d, *J* = 6.9 Hz, 3H). Spectral data matched those reported previously.[1]

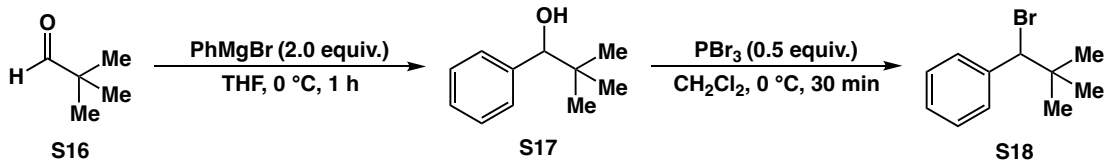


Supplementary Fig. 11. **Synthesis of bromide S15.**

1-(1-Bromoethyl)-4-chlorobenzene (S15). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added 4-chlorobenzaldehyde (**S13**) (500 mg, 3.6 mmol, 1.0 equiv.) and THF (12.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and MeMgCl (3.0 M in THF, 1.0 mL, 3.0 mmol, 1.2 equiv.) was then added dropwise over 30 min. The mixture was then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (5.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was

purified by silica flash chromatography (9:1 to 7:3 hexanes:EtOAc) to yield alcohol **S14** as a pale yellow oil (357 mg, 63% yield).

The resultant alcohol **S14** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (11.0 mL) was added and the solution was cooled to 0 °C. PBr_3 (104 uL, 1.1 mmol, 0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 ℃. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **S15** as a colorless oil (215 mg, 43% yield). **^{1}H NMR (600 MHz, $CDCl_3$).** δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 5.18 (q, *J* = 7.1 Hz, 1H), 2.03 (d, *J* = 7.1 Hz, 3H). Spectral data matched those reported previously.[2]

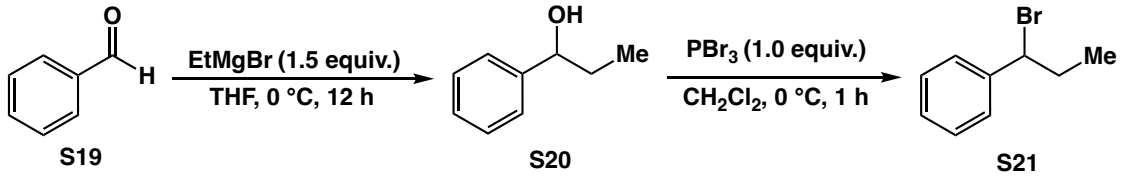


Supplementary Fig. 12. **Synthesis of bromide S18.**

(1-Bromo-2,2-dimethylpropyl)benzene (S18). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added pivalaldehyde (**S16**) (1000 mg, 11.6 mmol, 1.0 equiv.) and THF (4 mL). The mixture was cooled to 0 ℃ under a positive pressure of N_2 and PhMgBr (3.0 M in THF, 6.8 mL, 20.3 mmol, 3.5 equiv.) was then added dropwise over 10 min. The mixture was stirred at 0 °C for an additional 1 h. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (10.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (9:1 hexanes:EtOAc) to yield alcohol **S17** as a pale yellow oil (1.52 g, 80% yield).

The resultant alcohol **S17** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (25.0 mL) was added and the solution was cooled to 0 °C. PBr_3 (609 µL, 4.64 mmol, 0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 30 min at 0 ℃. extracted with CH_2Cl_2 (3.0 mL x 3). The reaction was quenched with water (20.0 mL) and extracted with CH_2Cl_2 (20.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and

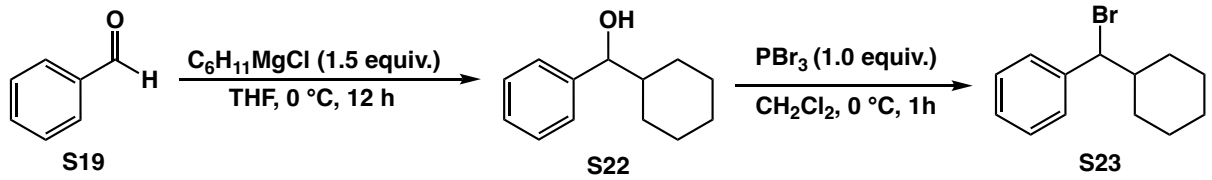
concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **S18** as a light yellow oil (255 mg, 49% yield). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.37–7.23 (m, 5H), 5.26 (s, 1H), 1.08 (s, 9H), Spectral data matched those reported previously.[1]



Supplementary Fig. 13. **Synthesis of bromide S21.**

(1-Bromopropyl)benzene (S21). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added benzaldehyde (**S19**) (500 mg, 4.7 mmol, 1.0 equiv.) and THF (12.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and EtMgBr (3.0 M in diethyl ether, 7.1 mL, 7.06 mmol, 1.5 equiv.) was then added dropwise over 30 min. The mixture was then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (5.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (8:2 hexanes:EtOAc) to yield alcohol **S20** as a pale yellow oil and used directly in the next step.

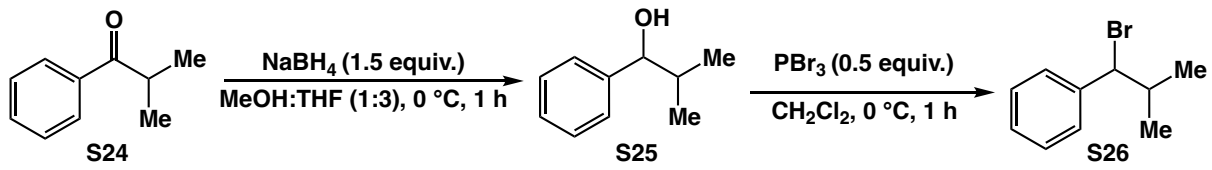
The resultant alcohol **S20** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (12.0 mL) was added and the solution was cooled to 0 °C. PBr_3 (174 uL, 4.7 mmol, 1.0 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **S21** as a colorless oil (511 mg, 55% yield, 2 steps). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.41–7.37 (m, 2H), 7.36–7.31 (m, 2H), 7.30–7.27 (m, 1H), 4.88 (t, *J* = 7.4 Hz, 1H), 2.36–2.32 (m, 1H), 2.22–2.10 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H), Spectral data matched those reported previously.[1]



Supplementary Fig. 14. **Synthesis of bromide S23.**

(Bromo(cyclohexyl)methyl)benzene (S23). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added benzaldehyde (**S19**) (500 mg, 4.7 mmol, 1.0 equiv.) and THF (12.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and $C_6H_{11}MgCl$ (1.0 M in THF, 7.06 mL, 7.06 mmol, 1.5 equiv.) was then added dropwise over 30 min. The mixture was then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (5.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (8:2 hexanes:EtOAc) to yield alcohol **S22** as a pale yellow oil and used directly in the next step.

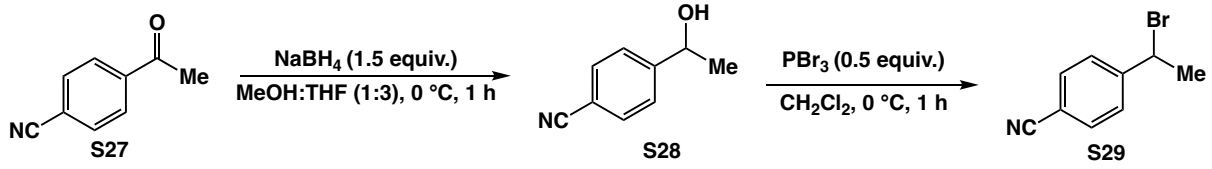
The resultant alcohol **S22** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (12.0 mL) was added and the solution was cooled to 0 °C. PBr_3 (174 uL, 4.7 mmol, 1.0 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **S23** as a colorless oil (396 mg, 33% yield, 2 steps). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.44–7.27 (m, 5H), 4.71 (d, *J* = 9.2 Hz, 1H), 2.35–2.25 (m, 1H), 2.02–1.90 (m, 1H), 1.84–1.76 (m, 1H), 1.70–1.57 (m, 2H), 1.51–1.43 (m, 1H), 1.32–0.97 (m, 4H), 0.93–0.78 (m, 1H), Spectral data matched those reported previously.[1]



Supplementary Fig. 15. **Synthesis of bromide S26.**

(1-Bromo-2-methylpropyl)benzene (S26). To a flame-dried 20 mL vial equipped with a stir bar was added 2-methyl-1-phenylpropan-1-one (**S24**) (444.6 mg, 3.0 mmol, 1.0 equiv.) along with THF (6.0 mL) and MeOH (2.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and $NaBH_4$ (170.2 mg, 4.5 mmol. 1.5 equiv.) was added. The mixture was stirred for 1 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with EtOAc (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant mixture was purified by silica flash chromatography (1:4 EtOAc:hexane) to yield alcohol **S25** as a pale yellow oil (357 mg, 80.0% yield).

The resultant alcohol **S25** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (6.0 mL) was added and the solution was cooled to 0 °C. PBr_3 (120 uL, 1.2 mmol, 0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (1:9 to 1:5 EtOAc:hexane) to yield bromide **S26** as a colorless oil (267 mg, 49% yield). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.39–7.23 (m, 5H), 4.72 (d, *J* = 8.5 Hz, 1H), 2.32 (oct, 6.5 Hz, 1H), 1.19 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H). Spectral data matched those reported previously.[1]

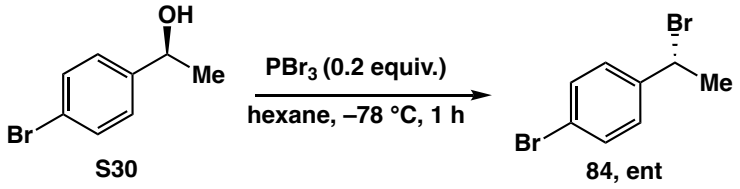


Supplementary Fig. 16. **Synthesis of bromide S29.**

4-(1-Bromoethyl)benzonitrile (S29). To a flame-dried 20 mL vial equipped with a stir bar was added 4-acetylbenzonitrile (**S27**) (436 mg, 3.0 mmol, 1.0 equiv.) along with THF (6.0 mL) and

MeOH (2.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and $NaBH_4$ (170.2 mg, 4.5 mmol. 1.5 equiv.) was added. The mixture was stirred for 1 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with EtOAc (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant mixture was purified by silica flash chromatography (1:5 to 1:1 EtOAc:hexane) to yield alcohol **S28** as a pale-yellow oil (410 mg, 94% yield).

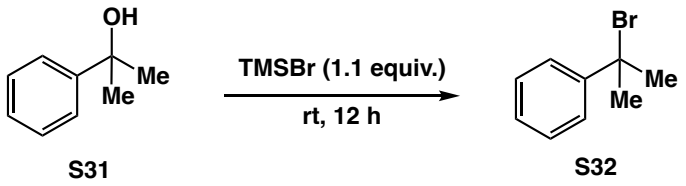
The resultant alcohol **S28** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (6.0 mL) was added and the solution was cooled to 0 °C. PBr_3 (130 uL, 1.36 mmol, 0.5 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (1:5 EtOAc:hexane) to yield bromide **S29** as a colorless oil (311 mg, 55% yield). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.68–7.51 (m, 4H), 5.16 (q, *J* = 6.9, 1H), 2.03 (d, *J* = 6.9 Hz, 3H). Spectral data matched those reported previously.[3]



Supplementary Fig. 17. **Synthesis of bromide 84, ent.**

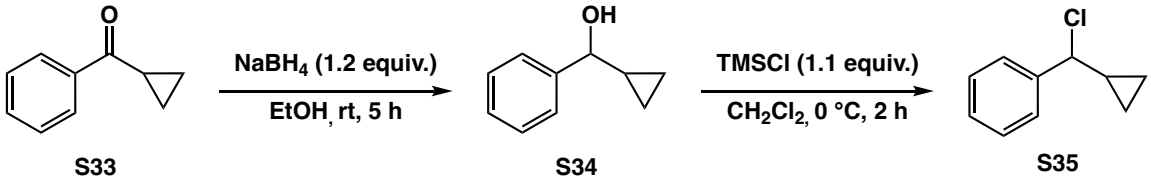
Enantioenriched 1-Bromo-4-(1-bromoethyl)benzene (84, ent). Enantiopure alcohol **S30** was added to a flame-dried 20 mL vial equipped with a stir bar. Hexane (3.0 mL) was added and the solution was cooled to –78 °C. PBr_3 (3 uL, 0.032 mmol, 0.2 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at –78 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **84, ent** as a colorless oil (53 mg, 80% yield, 24% ee). Chiral SFC: 250 mm ChiralPak IG–3, 5% MeOH, 3.0 mL/min, λ = 254 nm, 35 °C, nozzle pressure = 140 bar CO_2, tR1 (major) = 2.24 min, tR2 (minor) = 2.65 min. **^{1}H NMR**

(400 MHz, $CDCl_3$). δ = 7.47 (d, *J* = 6. 7 Hz, 2H), 7.31 (d, *J* = 7.1 Hz, 2H), 5.15 (q, *J* = 7.3 Hz, 1H), 2.02 (d, *J* = 7.2 Hz, 3H). Spectral data matched those reported previously.[3]



Supplementary Fig. 18. **Synthesis of bromide S32.**

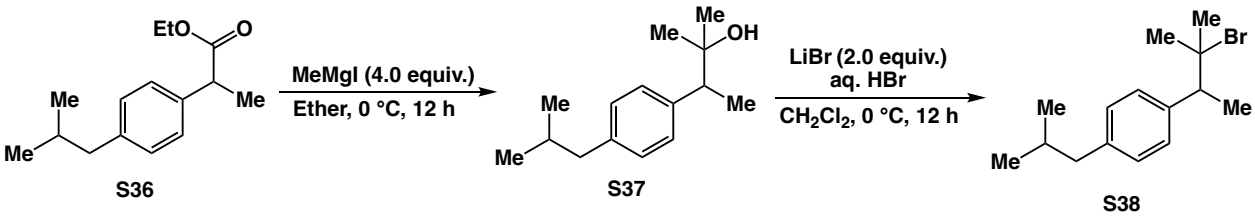
(2-bromopropan-2-yl)benzene (S32). To a flame-dried 20 mL vial equipped with a stir bar was added 2-phenylpropan-2-ol (**S31**) (272 mg, 2.0 mmol, 1.0 equiv.) along with trimethylsilyl bromide TMSBr (337 mg, 2.2 mmol, 1.1 equiv.). The mixture was stirred at room temperature for 12 hours. The reaction was quenched with water (5.0 mL) and extracted with EtOAc (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to yield bromide **S32** as a colorless oil (395 mg, 99% yield). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.66 (d, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 2.24 (s, 6H). Spectral data matched those reported previously.[4]



Supplementary Fig. 19. **Synthesis of chloride S35.**

(Chloro(cyclopropyl)methyl)benzene (S35). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added cyclopropylphenylmethanone (**33**) (0.5 g, 3.3 mmol, 1.0 equiv.) and EtOH (13 mL) followed by $NaBH_4$ (0.15 g, 4.0 mmol, 1.2 equiv.) in portions, and the mixture was stirred at room temperature for 5 h before cooled in an ice bath. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (5.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to yield alcohol **S34** as a pale yellow oil and used directly in the next step.

The resultant alcohol **S34** was added to a flame-dried 20 mL vial equipped with a stir bar. CH_2Cl_2 (12.0 mL) was added and the solution was cooled to 0 °C. TMSCl (454 uL, 3.6 mmol, 1.1 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 2 h at 0 °C. The reaction was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (3.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to yield chloride **S35** as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.43–7.24 (m, 5H), 4.27 (d, *J* = 9.2 Hz, 1H), 1.58–1.49 (m, 1H), 0.82–0.75 (m, 1H), 0.69–0.62 (m, 1H), 0.58–0.52 (m, 1H), 0.43–0.36 (m, 1H). Spectral data matched those reported previously.[1]

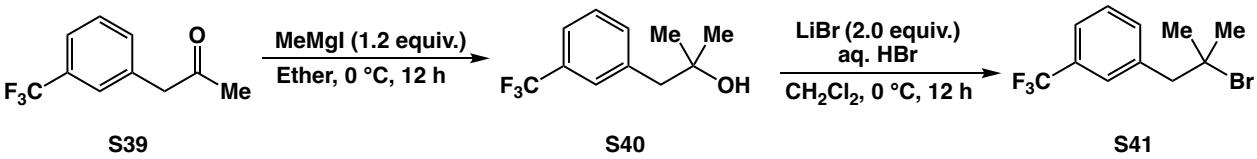


Supplementary Fig. 20. **Synthesis of bromide S38.**

1-(3-bromo-3-methylbutan-2-yl)-4-isobutylbenzene (S38). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added ethyl 2-(4-isobutylphenyl)propanoate (**S36**) (1.0 g, 4.3 mmol, 1.0 equiv.) and diethyl ether (30.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and MeMgI (3.0 M in ether, 5.7 mL, 17.07 mmol, 4.0 equiv.) was then added dropwise over 30 min. The mixture was then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (15.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (8:2 hexanes:EtOAc) to yield alcohol **S37** as a colorless oil and used directly in the next step.

To a 50-mL round-bottom flask equipped with a stir bar was charged with LiBr (2.0 equiv.) and aqueous HBr (48% wt; 8.0 mL). The solution was cooled to 0 °C, and then the alcohol **(S37)** was dissolved in a minimal amount of CH_2Cl_2, and added over 5 min. The reaction mixture was allowed to warm to rt, and it was stirred for 12 h. The mixture was then diluted with Et_2O (10 mL) and water (10 mL), and the organic layer was separated. The combined organic layers were washed with brine (50 mL), dried over MgSO4, filtered, and concentrated to provide the crude product.

The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide **S38** as a colorless oil (161 mg, 29% yield, 2 steps). (R_f= 0.66, hexanes:EtOAc 9:1). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.18 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.98 (q, *J* = 7.0 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dp, *J* = 13.5, 6.2 Hz, 1H), 1.75 (s, 3H), 1.62 (s, 3H), 1.52 (d, *J* = 7.0 Hz, 3H), 0.90 (dd, *J* = 6.6, 2.1 Hz, 6H) **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 140.4, 139.6, 129.0, 128.7, 72.9, 52.7, 45.2, 34.5, 31.5, 30.3, 22.6, 22.5, 18.6. **IR (Neat).** 3088, 2955, 2898, 1509, 1459, 1367, 1176, 1123, 1101, 1088, 920, 847, 805, 797, 738. cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + H]^+$ calcd for $C_{15}H_{24}Br^+$, 383.1061; found 383.0968.



S39 **S40** **S41**

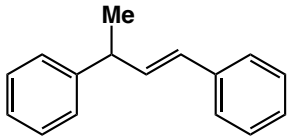
Supplementary Fig. 21. **Synthesis of bromide S41.**

1-(2-bromo-2-methylpropyl)-3-(trifluoromethyl)benzene (S41). To a flame-dried 50 mL round-bottom-flask equipped with a stir bar was added 1-(3-(trifluoromethyl)phenyl)propan-2-one (**S39**) (1.5 g, 7.4 mmol, 1.0 equiv.) and diethyl ether (30.0 mL). The mixture was cooled to 0 °C under a positive pressure of N_2 and MeMgI (3.0 M in ether, 5.9 mL, 17.9 mmol, 1.2 equiv.) was then added dropwise over 30 min. The mixture was then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with saturated NH_4Cl (10.0 mL) and extracted with EtOAc (15.0 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (9:1 hexanes:EtOAc) to yield alcohol **S40** as a colorless oil and used directly in the next step.

To a 50-mL round-bottom flask equipped with a stir bar was charged with LiBr (2.0 equiv.) and aqueous HBr (48% wt; 8.0 mL). The solution was cooled to 0 °C, and then the alcohol **(S40)** was dissolved in a minimal amount of CH_2Cl_2, and added over 5 min. The reaction mixture was allowed to warm to rt, and it was stirred for 12 h. The mixture was then diluted with Et_2O (10 mL) and water (10 mL), and the organic layer was separated. The combined organic layers were washed with brine (50 mL), dried over MgSO4, filtered, and concentrated to provide the crude product. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield bromide

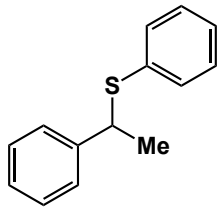
S41 as a colorless oil (1.3 g, 62% yield, 2 steps). (R_f = 0.85, hexanes:EtOAc 8:2). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.55 (d, *J* = 7.8 Hz, 1H), 7.53 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 3.22 (s, 2H), 1.78 (s, 6H), **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 138.2, 134.3, 130.5, 128.5, 127.6, 125.2, 124.0, 123.4, 65.3, 52.8, 34.0. **^{19}F NMR (470 MHz, $CDCl_3$).** δ = –62.6. Spectral data matched those reported previously.[5]

E. Product characterization



1d

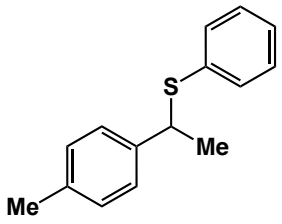
(*E*)-but-1-ene-1,3-diyldibenzene (1d). To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (10.0 mg, 0.025 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL) and bromide **1** (0.5 mmol, 1.0 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 2 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard (34% NMR yield, **1d**). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.38–7.17 (m, 10H), 6.45–6.41 (m, 2H), 3.69–3.63 (m, 1H), 1.47 (d, *J* = 7.1 Hz, 3H), Spectral data matched those reported previously.[6]



7

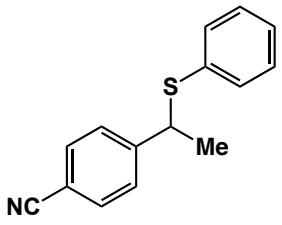
Phenyl(1-phenylethyl)sulfane (7). Thioether **7** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **7** was obtained as a colorless liquid (97.8 mg, 91% yield) upon purification by flash chromatography on silica gel

with 100% hexane. (R_f = 0.30, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.31–7.19 (m, 10H), 4.34 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H), **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 143.4, 135.3, 132.6, 128.8, 128.5, 127.4, 127.3, 127.2, 48.1, 22.5. Spectral data matched those reported previously.[7]



8

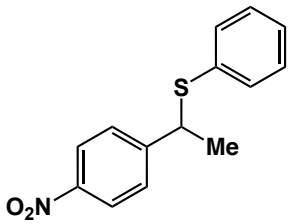
phenyl(1-(p-tolyl)ethyl)sulfane (8). Thioether **8** was synthesized following the optimized procedure outlined in section 5 with 1-(1-bromoethyl)-4-methylbenzene (99.6 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **5** was obtained as a colorless liquid (96.7 mg, 85% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.16, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.31 (d, *J* = 6.8 Hz, 2H), 7.25–7.19 (m, 5H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 1.62 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 140.3, 136.9, 135.6, 132.4, 129.2, 128.8, 127.3, 127.1, 47.8, 22.6, 21.2. Spectral data matched those reported previously.[8]



9

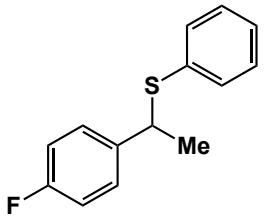
4-(1-(phenylthio)ethyl)benzonitrile (9). Thioether **9** was synthesized following the optimized procedure outlined in section 5 with 4-(1-bromoethyl)benzonitrile (105 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **9** was obtained as a colorless liquid (77.6 mg, 65% yield) upon purification by flash chromatography on silica gel

with 100% hexane to 95:5 Hexane:EtOAc (R_f= 0.29, 95:5 hexanes:EtOAc). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.53 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.24–7.19 (m, 5H), 4.31 (q, *J* = 7.1 Hz, 1H), 1.63 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 149.1, 133.9, 133.3, 132.3, 129.0, 128.2, 128.0, 118.9, 110.9, 48.1, 21.8. Spectral data matched those reported previously.[9]



10

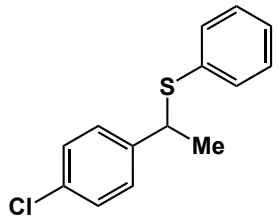
(1-(4-nitrophenyl)ethyl)(phenyl)sulfane (10). Thioether **10** was synthesized following the optimized procedure outlined in section 5 with 1-(1-bromoethyl)-4-nitrobenzene (115 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **10** was obtained as a colorless liquid (79.8 mg, 63% yield) upon purification by flash chromatography on silica gel with 100% hexane to 9:1 hexane:EtOAc. (R_f = 0.59, 9:1 hexanes:EtOAc). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 8.10 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.25–7.20 (m, 5H), 4.37 (q, *J* = 7.0 Hz, 1H), 1.66 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 151.2, 133.7, 133.3, 129.1, 128.2, 128.1, 127.9, 123.8, 47.8, 21.9. Spectral data matched those reported previously.[10]



11

(1-(4-fluorophenyl)ethyl)(phenyl)sulfane (11). Thioether **11** was synthesized following the optimized procedure outlined in section 5 with 1-(1-bromoethyl)-4-fluorobenzene (102 mg, 0.5

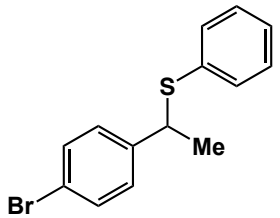
mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **11** was obtained as a colorless liquid (108.2 mg, 93% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.19, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.31–7.22 (m, 7H), 6.97 (t, *J* = 8.7 Hz, 2H), 4.35 (q, *J* = 7.0 Hz, 1H), 1.64 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 162.9, 161.0, 139.1 (d, *J* = 3.2 Hz), 134.8, 129.0, 128.9 (d, *J* = 2.9 Hz), 127.5, 115.3 (d, *J* = 21.4 Hz), 47.5, 22.5. **^{19}F NMR (470 MHz, $CDCl_3$).** δ = –115.2. Spectral data matched those reported previously.[11]



12

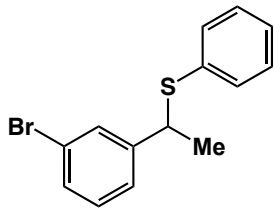
(1-(4-chlorophenyl)ethyl)(phenyl)sulfane (12). Thioether **12** was synthesized following the optimized procedure outlined in section 5 with 1-(1-bromoethyl)-4-chlorobenzene (110 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **12** was obtained as a colorless liquid (109 mg, 87% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.20, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.32–7.23 (m, 9H), 4.33 (q, *J* = 7.1 Hz, 1H), 1.64 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125**

MHz, $CDCl_3$). δ = 142.0, 134.7, 132.9, 132.8, 128.9, 128.7, 128.6, 127.5, 47.6, 22.3. Spectral data matched those reported previously.[10]



13

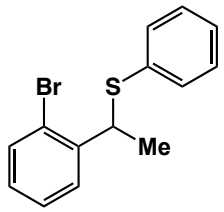
(1-(4-Bromophenyl)ethyl)(phenyl)sulfane (13). Thioether **13** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-4-(1-bromoethyl)benzene (132 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **13** was obtained as a colorless liquid (134.9 mg, 92% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.31–7.23 (m, 5H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.30 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.6, 134.7, 132.9, 131.6, 129.1, 128.9, 127.5, 120.9, 47.6, 22.3. Spectral data matched those reported previously.[7]



14

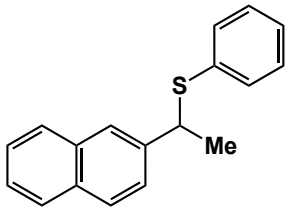
(1-(3-Bromophenyl)ethyl)(phenyl)sulfane (14). Thioether **14** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-3-(1-bromoethyl)benzene (132 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **14** was obtained as a colorless liquid (119 mg, 81% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.44 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.31–7.25 (m, 5H), 7.22 (d, *J* = 7.8 Hz, 1H),

7.15 (t, J = 7.8 Hz, 1H), 4.29 (q, J = 7.0 Hz, 1H), 1.63 (d, J = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 145.8, 134.6, 132.9, 130.5, 130.3, 130.0, 128.9, 127.6, 126.1, 122.5, 47.9, 22.3. Spectral data matched those reported previously.[8]



15

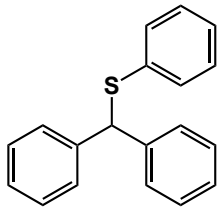
(1-(2-Bromophenyl)ethyl)(phenyl)sulfane (15). Thioether **15** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-2-(1-bromoethyl)benzene (132 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **15** was obtained as a colorless liquid (108 mg, 74% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.56 (ddd, J = 11.3, 7.9, 1.5 Hz, 2H), 7.35–7.21 (m, 6H), 7.10 (ddd, J = 8.0, 7.3, 1.7 Hz, 1H), 4.92 (q, J = 7.0 Hz, 1H), 1.62 (d, J = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.2, 134.9, 132.9, 132.1, 128.9, 128.6, 128.5, 127.9, 127.2, 124.2, 46.3, 21.9. Spectral data matched those reported previously.[8]



16

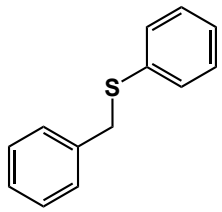
(1-(naphthalen-2-yl)ethyl)(phenyl)sulfane (16). Thioether **16** was synthesized following the optimized procedure outlined in section 5 with 2-(1-bromoethyl)naphthalene (118 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **16** was obtained as a colorless liquid (107 mg, 81% yield) upon purification by flash chromatography on

silica gel with 100% hexane. (R_f = 0.19, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.80 (d, *J* = 8.2 Hz, 2H), 7.76–7.74 (m, 1H), 7.63 (s, 1H), 7.54 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.46–7.44 (m, 2H), 7.31–7.27 (m, 2H), 7.23–7.15 (m, 3H), 4.51 (q, *J* = 7.0 Hz, 1H), 1.73 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 140.8, 135.2, 133.4, 132.8, 132.7, 128.8, 128.4, 127.9, 127.7, 127.3, 126.2, 125.9, 125.8, 125.7, 48.4, 22.5. Spectral data matched those reported previously.[8]



17

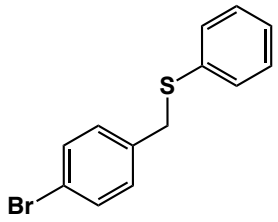
Benzhydryl(phenyl)sulfane (17). Thioether **17** was synthesized following the optimized procedure outlined in section 5 with (bromomethylene)dibenzene (124 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **17** was obtained as a white solid (102 mg, 74% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.12, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.45 (d, *J* = 7.4 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.28–7.22 (m, 4H), 7.21–7.15 (m, 3H), 5.58 (s, 1H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 141.2, 136.3, 130.7, 128.9, 128.7, 128.6, 127. 4, 126.7, 57.6. Spectral data matched those reported previously.[8]



18

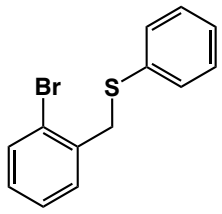
Benzyl(phenyl)sulfane (18). Thioether **18** was synthesized following the optimized procedure outlined in section 5 with (bromomethyl)benzene (86 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **18** was obtained as a white solid

(77.9 mg, 78% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.21, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.33–7.17 (m, 10H), 4.13 (s, 2H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 137.6, 136.5, 129.9, 129.0, 128.9, 128.6, 127.3, 126.5, 39.2. Spectral data matched those reported previously.[12]



19

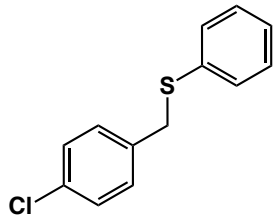
(4-bromobenzyl)(phenyl)sulfane (19). Thioether **19** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-4-(bromomethyl)benzene (125 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **19** was obtained as a white solid (109 mg, 74% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.21, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.33–7.17 (m, 9H), 4.13 (s, 2H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 137.6, 136.5, 129.9, 129.0, 128.9, 128.6, 127.3, 126.5, 39.2. Spectral data matched those reported previously.[12]



20

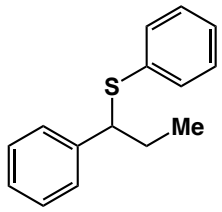
(2-bromobenzyl)(phenyl)sulfane (20). Thioether **20** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-2-(bromomethyl)benzene (125 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **20** was obtained as a colorless liquid (93 mg, 67% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.59 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.32–7.21 (m, 5H), 7.13 (td, J = 7.6, 7.5, 1.8 Hz,

1H), 4.26 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$).** 10 of 11 signals observed: δ = 136.9, 135.8, 133.1, 130.9, 129.0, 128.9, 127.5, 126.9, 124.7, 39.9. Spectral data matched those reported previously.[12]



21

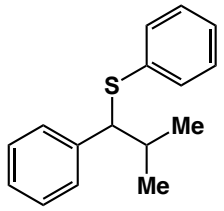
(4-chlorobenzyl)(phenyl)sulfane (21). Thioether **21** was synthesized following the optimized procedure outlined in section 5 with 1-chloro-4-(chloromethyl)benzene (81 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **21** was obtained as a white solid (88 mg, 75% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.24, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.33–7.21 (m, 9H), 4.09 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 136.3, 135.8, 133.1, 130.4, 130.3, 129.1, 128.7, 126.8, 38.7. Spectral data matched those reported previously.[12]



22

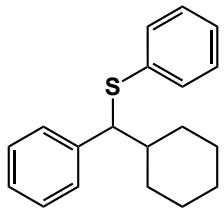
Phenyl(1-phenylpropyl)sulfane (22). Thioether **22** was synthesized following the optimized procedure outlined in section 5 with (1-bromopropyl)benzene (99.5 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **22** was obtained as a colorless liquid (100.4 mg, 88% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.19, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.32–7.18 (m, 10H), 4.08 (dd, J = 8.7, 6.0 Hz, 1H), 2.09–1.92 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR (125**

MHz, $CDCl_3$). δ = 142.1, 135.3, 132.4, 128.8, 128.4, 128.0, 127.2, 127.1, 55.5, 29.6, 12.4. Spectral data matched those reported previously.[11]



23

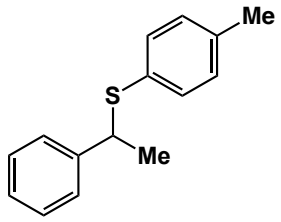
(2-methyl-1-phenylpropyl)(phenyl)sulfane (23). Thioether **23** was synthesized following the optimized procedure outlined in section 5 with (1-bromo-2-methylpropyl)benzene (106.6 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **23** was obtained as a colorless liquid (85.4 mg, 71% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.19, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.29–7.13 (m, 10H), 4.01 (d, *J* = 7.4 Hz, 1H), 2.23 (dq, *J* = 13.7, 6.8 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 141.7, 135.9, 131.8, 128.8, 128.1, 126.9, 126.6, 61.6, 34.1, 21.2, 20.7. Spectral data matched those reported previously.[13]



24

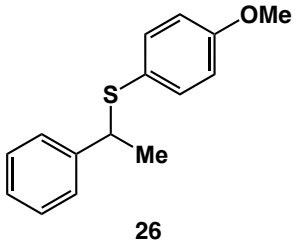
(Cyclohexyl(phenyl)methyl)(phenyl)sulfane (24). Thioether **24** was synthesized following the optimized procedure outlined in section 5 with (bromo(cyclohexyl)methyl)benzene (127 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **24** was obtained as a colorless liquid (110 mg, 77% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.28, 100% hexanes). **^{1}H NMR (500 MHz,**

$CDCl_3$). δ = 7.30–7.14 (m, 10H), 4.02 (d, *J* = 7.9 Hz, 1H), 2.25–2.22 (m, 1H), 1.88–1.79 (m, 2H), 1.72–1.27 (m, 4H) 1.26–0.96 (m, 4H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 141.8, 136.0, 131.9, 128.7, 128.6, 128.1, 126.8, 126.6, 60.9, 43.6, 31.8, 31.2, 26.4. Spectral data matched those reported previously.[13]



25

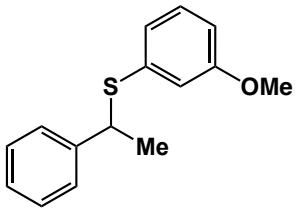
(1-Phenylethyl)(*p*-tolyl)sulfane (25). Thioether **25** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-methylbenzenethiol (93.2 mg, 0.75 mmol, 1.5 equiv.). Thioether product **25** was obtained as a colorless liquid (97.4 mg, 85% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.30, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.30–7.22 (m, 5H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 4.28 (q, *J* = 7.0 Hz, 1H), 2.31 (s, 3H), 1.62 (d, *J* = 7.0 Hz, 3H), **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 143.5, 137.5, 133.3, 131.4, 129.6, 128.5, 127.4, 127.2, 48.5, 22.3, 21.2. Spectral data matched those reported previously.[7]



26

(4-Methoxyphenyl)(1-phenylethyl)sulfane (26). Thioether **26** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-methoxythiophenol (**85**) (105 mg, 0.75 mmol, 1.5 equiv.). Thioether product **26** was obtained as a colorless liquid (101 mg, 83% yield) upon purification by flash chromatography

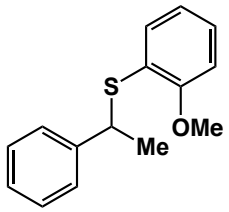
on silica gel with 100% hexane to 8:2 hexane:EtOAc. (R_f= 0.40, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.32–7.21 (m, 7H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.21 (q, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 159.7, 143.5, 136.1, 132.8, 128.4, 127.5, 127.1, 114.3, 55.4, 49.3, 21.9. Spectral data matched those reported previously.[7]



27

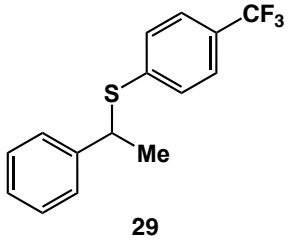
(3-Methoxyphenyl)(1-phenylethyl)sulfane (27). Thioether **27** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 3-methoxythiophenol (**85**) (105 mg, 0.75 mmol, 1.5 equiv.). Thioether product **27** was obtained as a colorless liquid (89.4 mg, 72% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. (R_f= 0.40, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.34 (d, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.25–7.22 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.92 (ddt, *J* = 7.7, 1.8, 0.8 Hz, 1H), 6.80 (s, 1H), 6.77–6.74 (m, 1H), 4.38 (q, *J* = 7.0 Hz, 1H), 3.71 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 159.6, 143.4, 136.5, 129.6, 128.5, 127.4, 127.3, 124.5, 117.2, 113.3, 55.3, 47.9, 22.5. **IR (Neat).** 3065,

2966, 2838, 1587, 1477, 1282, 1244, 1174 cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{15}H_{16}AgOS^+$, 350.9967; found 350.9966.



28

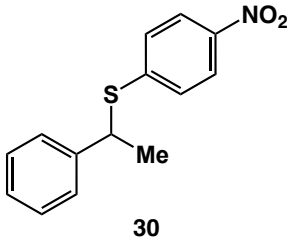
(2-Methoxyphenyl)(1-phenylethyl)sulfane (28). Thioether **28** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 2-methoxythiophenol (**85**) (105 mg, 0.75 mmol, 1.5 equiv.). Thioether product **28** was obtained as a colorless liquid (79 mg, 65% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. (R_f = 0.40, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.33−6.79 (m, 9H), 4.48 (q, J = 7.0 Hz, 1H), 3.87 (s, 3H), 1.63 (d, J = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 158.7, 143.5, 133.5, 128.6, 128.4, 127.4, 127.1, 123.4, 120.9, 110.6, 55.8, 45.7, 22.4. Spectral data matched those reported previously.[8]



29

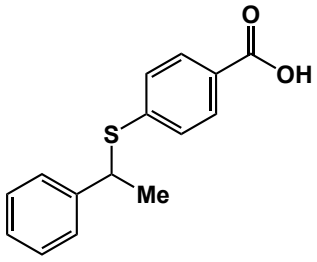
(1-Phenylethyl)(4-(trifluoromethyl)phenyl)sulfane (29). Thioether **29** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-(trifluoromethyl)benzenethiol (134 mg, 0.75 mmol, 1.5 equiv.). Thioether product **29** was obtained as a colorless liquid (119 mg, 84% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.30, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.47 (d, J = 7.8 Hz, 2H), 7.39–7.31 (m, 6H), 7.28–7.25 (m, 1H), 4.49 (q, J =

7.0 Hz, 1H), 1.69 (d, J = 6.9 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.7, 141.1, 130.5, 128.8, 128.4, 127.6, 127.3, 125.6 (q, J = 3.8 Hz), 123.6, 47.3, 22.8. **^{19}F NMR (470 MHz, $CDCl_3$).** δ = –62.5. Spectral data matched those reported previously.[7]



30

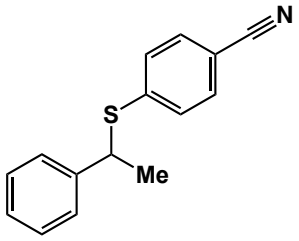
(4-Nitrophenyl)(1-phenylethyl)sulfane (30). Thioether **30** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-nitrobenzenethiol (116.4 mg, 0.75 mmol, 1.5 equiv.). Thioether product **30** was obtained as a colorless liquid (112 mg, 86% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. ($R_{f=}$ 0.59, hexanes:EtOAc 9:1). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 8.03 (d, J = 9.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.33–7.23 (m, 5H), 4.56 (q, J = 7.0 Hz, 1H), 1.69 (d, J = 7.1 Hz, 3H). **^{13}C NMR (150 MHz, CDCl3)**. δ = 146.4, 145.6, 142.2, 128.9, 128.6, 127.8, 127.2, 123.8, 46.5, 22.9. Spectral data matched those reported previously.[7]



31

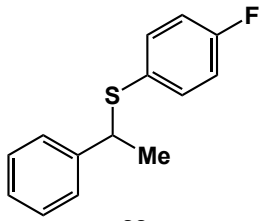
4-((1-phenylethyl)thio)benzoic acid (31). Thioether **31** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-mercaptobenzoic acid (116 mg, 0.75 mmol, 1.5 equiv.). Thioether product **31** was obtained as a white solid (155 mg, 86% yield) after purification by flash chromatography on silica gel with

100% CH_2Cl_2 to 7:3 CH_2Cl_2:EtOAc (R_f = 0.49, 50% EtOAc/CH_2Cl_2). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 11.9 (brs, 1H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.32–7.29 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 4.53 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 171.1, 144.2, 142.7, 130.5, 129.0, 128.8, 127.6, 127.3, 126.6, 46.6, 22.9. Spectral data matched those reported previously.[14]



32

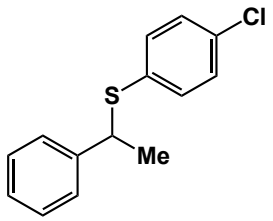
4-((1-phenylethyl)thio)benzonitrile (32). Thioether **32** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-mercaptobenzonitrile (99.5 mg, 0.75 mmol, 1.5 equiv.). Thioether product **32** was obtained as a colorless liquid (99.3 mg, 83% yield) after purification by flash chromatography on silica gel with 100% Hexanes to 9:1 Hexanes:EtOAc (R_f = 0.49, 10% EtOAc/Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.45 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.33–7.23 (m, 5H), 4.50 (q, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 143.6, 142.3, 132.2, 129.5, 128.9, 127.8, 127.2, 118.8, 109.3, 46.7, 22.9. Spectral data matched those reported previously.[15]



33

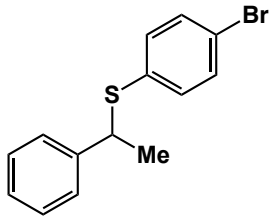
(4-Fluorophenyl)(1-phenylethyl)sulfane (33). Thioether **33** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-fluorobenzenethiol (96.2 mg, 0.75 mmol, 1.5 equiv.). Thioether product **33** was

obtained as a colorless liquid (96.3 mg, 83% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.30, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.29–7.23 (m, 3H), 7.22–7.18 (m, 4H), 6.91 (t, *J* = 8.7 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 1H), 1.62 (d, *J* = 6.7 Hz, 3H), **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 162.7 (d, *J* = 241.6 Hz), 143.2, 135.8 (d, *J* = 15.1 Hz), 129.9 (d, *J* = 3.0 Hz), 128.5, 127.4, 127.3, 115.8 (d, *J* = 15.1 Hz), 49.1, 22.1. **^{19}F NMR (564 MHz, $CDCl_3$).** δ = –114.0. Spectral data matched those reported previously.[7]



34

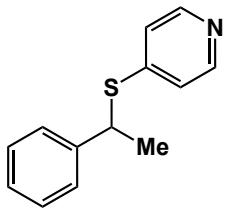
(4-Chlorophenyl)(1-phenylethyl)sulfane (34). Thioether **34** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 4-chlorobenzenethiol (109 mg, 0.75 mmol, 1.5 equiv.). Thioether product **34** was obtained as a colorless liquid (112 mg, 90% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.40, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.30–7.27 (m, 4H), 7.24–7.20 (m, 1H), 7.19–7.17 (m, 4H), 4.30 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.0, 134.1, 133.7, 133.5, 128.9, 128.6, 127.4, 127.4, 48.4, 22.3. Spectral data matched those reported previously.[7]



35

(4-Bromophenyl)(1-phenylethyl)sulfane (35). Thioether **35** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol,

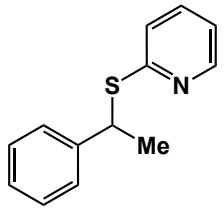
1.0 equiv.) and 4-bromobenzenethiol (142 mg, 0.75 mmol, 1.5 equiv.). Thioether product **35** was obtained as a colorless liquid (122.5 mg, 84% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.30, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.33 (d, *J* = 8.5 Hz, 2H), 7.30–7.27 (m, 4H), 7.24–7.20 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.0, 134.4, 134.2, 131.9, 128.6, 127.4, 127.3 121.5, 48.3, 22.4. Spectral data matched those reported previously.[7]



36

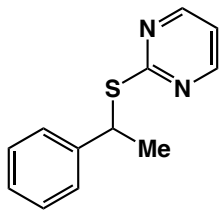
4-((1-Phenylethyl)thio)pyridine (36). Thioether **36** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and pyridine-4-thiol (83.4 mg, 0.75 mmol, 1.5 equiv.). Thioether product **36** was obtained as a colorless liquid (93.7 mg, 87% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. ($R_{f=}$ 0.59, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 8.35 (d, *J* = 6.3 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 3.7 Hz, 1H), 7.09 (d, *J* = 6.2 Hz, 2H), 4.59 (q, *J* = 7.1 Hz, 1H), 1.71 (d, *J* = 7.1 Hz, 3H), **^{13}C NMR (125**

MHz, $CDCl_3$). δ = 149.4, 148.4, 142.3, 128.9, 127.8, 127.2, 122.2, 45.1, 23.1. Spectral data matched those reported previously.[7]



37

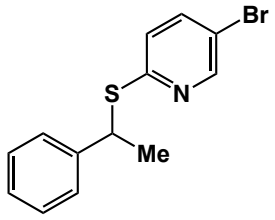
2-((1-Phenylethyl)thio)pyridine (37). Thioether **37** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and pyridine-2-thiol (83.4 mg, 0.75 mmol, 1.5 equiv.). Thioether product **37** was obtained as a colorless liquid (102.4 mg, 95% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. (R_f = 0.60, hexanes:EtOAc 9:1). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 8.46 (ddd, *J* = 5.0, 1.9, 1.0 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.44–7.42 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.25–7.22 (m, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.97 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 5.13 (q, *J* = 7.1 Hz, 1H), 1.76 (d, *J* = 7.1 Hz, 3H), **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 159.0, 149.6, 143.4, 136.0, 128.6, 127.5, 127.2, 122.9, 119.7, 43.8, 22.7. Spectral data matched those reported previously. [10]



38

2-((1-phenylethyl)thio)pyrimidine (38). Thioether **38** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and pyrimidine-2-thiol (84.1 mg, 0.75 mmol, 1.5 equiv.). Thioether product **38** was obtained as a pale-yellow liquid (71.9 mg, 67% yield) upon purification by flash chromatography on silica gel

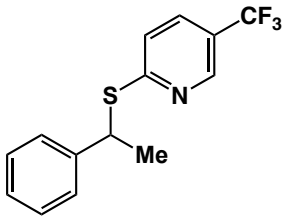
with 100% hexane to 75:25 hexane:EtOAc. . (R_f= 0.40, 9:1 hexane:EtOAc). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 8.50 (d, *J* = 4.8, 1.8 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.25–7.23 (m, 1H), 6.93 (t, *J* = 4.8 Hz, 1H), 5.08 (q, *J* = 7.1 Hz, 1H), 1.78 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 172.4, 143.1, 128.6, 127.6, 127.3, 117.6, 44.3, 22.5. Spectral data matched those reported previously.[7]



39

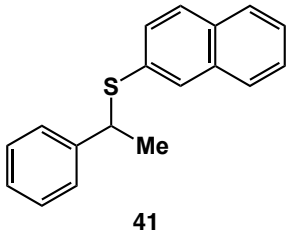
5-bromo-2-((1-phenylethyl)thio)pyridine (39). Thioether **39** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 5-bromopyridine-2-thiol (143 mg, 0.75 mmol, 1.5 equiv.). Thioether product **39** was obtained as a colorless liquid (131.9 mg, 90% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. (R_f= 0.77, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 8.50 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25–7.21 (m, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 5.05 (q, *J* = 7.1 Hz, 1H), 1.73 (d, *J* = 7.1 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 157.8, 150.4, 143.1, 138.6, 128.7,

127.5, 127.4, 123.9, 116.4, 44.1, 22.6. **IR (Neat).** 3060, 2972, 2925, 1558, 1492, 1440, 1349, 1112 cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{13}H_{12}AgBrNS^+$, 399.8919; found 399.8910.



40

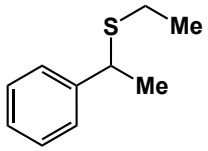
2-((1-phenylethyl)thio)-5-(trifluoromethyl)pyridine (40). Thioether **40** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 5-(trifluoromethyl)pyridine-2-thiol (134 mg, 0.75 mmol, 1.5 equiv.). Thioether product **40** was obtained as a colorless liquid (123 mg, 87% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. (R_f = 0.66, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 8.70 (s, 1H), 7.63 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28–7.24 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 5.20 (q, *J* = 7.1 Hz, 1H), 1.78 (d, *J* = 7.1 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 164.2, 146.4 (q, *J* = 4.3 Hz), 142.9, 132.7 (q, *J* = 3.4 Hz), 128.7, 127.5 (d, *J* = 1.9 Hz), 125.0, 122.5, 122.3, 121.8, 43.7, 22.6. **^{19}F NMR (470 MHz, $CDCl_3$).** δ = –62.2. **IR (Neat).** 3056, 2985, 2935, 1599, 1550, 1464, 1325, 1112 cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{14}H_{12}AgF_3NS^+$, 389.9688; found 389.9718.



41

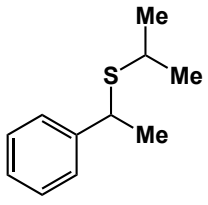
Naphthalen-2-yl(1-phenylethyl)sulfane (41). Thioether **41** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol,

1.0 equiv.) and naphthalene-2-thiol (120 mg, 0.75 mmol, 1.5 equiv.). Thioether product **41** was obtained as a white solid (100 mg, 76% yield) upon purification by flash chromatography on silica gel with 100% hexane to 8:2 hexane:EtOAc. ($R_{f=}$ 0.51, hexanes:EtOAc 9:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.78–7.68 (m, 4H), 7.46–7.20 (m, 7H), 4.45 (q, *J* = 7.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.3, 133.7, 132.8, 132.4, 131.2, 129.9, 128.6, 128.3, 127.8, 127.6, 127.5, 127.3, 126.5, 126.2, 48.1, 22.5. Spectral data matched those reported previously.[8]



42

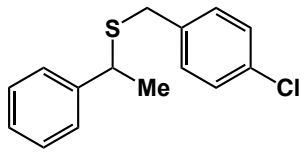
Ethyl(1-phenylethyl)sulfane (42). Thioether **42** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and ethanethiol (46.6 mg, 0.75 mmol, 1.5 equiv.). Thioether product **42** was obtained as a colorless liquid (69 mg, 83% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.30, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.37–7.29 (m, 4H), 7.25–7.20 (m, 1H), 3.98 (q, *J* = 7.0 Hz, 1H), 2.39–2.28 (m, 2H), 1.57 (d, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 144.3, 128.6, 127.4, 127.1, 43.8, 25.3, 22.7, 14.6. Spectral data matched those reported previously.[7]



43

Isopropyl(1-phenylethyl)sulfane (43). Thioether **43** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and propane-2-thiol (57 mg, 0.75 mmol, 1.5 equiv.). Thioether product **43** was obtained as a

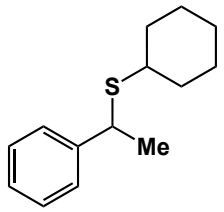
colorless liquid (48.5 mg, 54% yield) upon purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.35, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 2.61 (hept, *J* = 6.7 Hz, 1H), 1.55 (d, *J* = 7.0 Hz, 3H), 1.25 (d, *J* = 6.6, Hz, 3H). 1.13 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 144.7, 128.6, 127.3, 127.0, 43.2, 34.3, 23.7, 23.2 (d, *J* = 2.3 Hz). Spectral data matched those reported previously.[7]



44

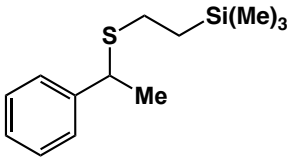
(4-chlorobenzyl)(1-phenylethyl)sulfane (44). Thioether **44** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and (4-chlorophenyl)methanethiol (119 mg, 0.75 mmol, 1.5 equiv.). Thioether product **44** was obtained as a colorless liquid (125 mg, 95% yield) after purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.30, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.35–7.24. (m, 7H), 7.14 (d, *J* = 6.5 Hz, 2H), 3.79 (q, *J* = 7.1 Hz, 1H), 3.49 (d, *J* = 13.8 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 1.53 (d, *J* = 7.1 Hz, 3H) **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 143.7, 137.1, 132.7, 130.4, 128.7, 128.6, 127.6, 127.3, 43.8, 35.2, 22.7. **IR (Neat).** 3060, 2970,

2925, 1597, 1489, 1451, 1224, 1090 cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{15}H_{15}AgClS^+$, 368.9629; found 368.9614.



45

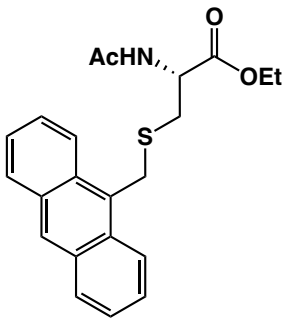
Cyclohexyl(1-phenylethyl)sulfane (45). Thioether **45** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and cyclohexanethiol (87.2 mg, 0.75 mmol, 1.5 equiv.). Thioether product **45** was obtained as a colorless liquid (88.8 mg, 80% yield) after purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.40, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.35 (d, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.24–7.21 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 1H), 2.42–2.38 (m, 1H), 1.99–1.95 (m, 1H), 1.75–1.72 (m, 2H), 1.68–1.64 (m, 1H), 1.56 (d, *J* = 7.1 Hz, 3H), 1.35–1.17 (m, 6H) **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 144.8, 128.5, 127.3, 127.0, 42.9, 42.6, 34.0, 33.4, 26.0, 23.3. Spectral data matched those reported previously.[16]



46

Trimethyl(2-((1-phenylethyl)thio)ethyl)silane (46). Thioether **46** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 2-(trimethylsilyl)ethane-1-thiol (141 mg, 0.75 mmol, 1.5 equiv.). Thioether product **46** was obtained as a colorless liquid (101 mg, 59% yield) after purification by flash chromatography on silica gel with 100% Hexanes. (R_f = 0.30, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.34–7.21 (m, 5H), 3.98 (q, *J* = 7.1 Hz, 1H), 2.39–2.29 (m, 2H), 1.58 (d, *J* =

7.1 Hz, 3H), 0.87–0.72 (m, 2H), -0.05 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 144.3, 128.5, 127.4, 127.1, 43.9, 26.9, 22.6, 17.3, -1.7. **IR (Neat).** 3088, 3060, 2939, 2877, 1604, 1489, 1451, 1248, 1162, 1026. cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{13}H_{22}AgSSi^+$, 345.0262; found 345.0297.

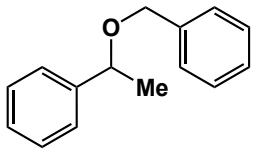


47

Ethyl N-acetyl-S-(anthracen-9-ylmethyl)-L-cysteinate (47). Method A: To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (9.8 mg, 0.05 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1 mL), 9-(bromomethyl)anthracene (135.4 mg, 0.50 mmol, 1.0 equiv.), and cysteine thiol (143 mg, 0.75 mmol, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica flash chromatography (9:1 to 2:5 hexanes:EtOAc) to yield thioether **47** as a yellow solid (154 mg, 81% yield).

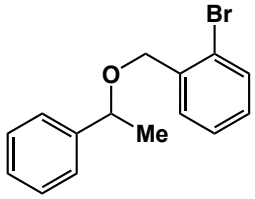
Method B: To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (9.8 mg, 0.05 mmol, 7 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1 mL), 9-(bromomethyl)anthracene (135.4 mg, 0.50 mmol, 1.0 equiv.), and cysteine thiol (143 mg, 0.75 mmol, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 40 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica flash chromatography (9:1 to 2:5 hexanes:EtOAc) to yield thioether **47** as a yellow solid (112 mg, 59%

yield). (R_f = 0.40, hexanes:EtOAc 1:1). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 8.41 (s, 1H), 8.29 (d, *J* = 8.9 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.59–7.56 (m, 2H), 7.49–7.46 (m, 2H), 6.26 (d, *J* = 7.8 Hz, 1H), 4.92 (q, *J* = 5.4 Hz, 1H), 4.78 (s, 2H), 4.24–4.15 (m, 2H), 3.16 (qd, *J* = 13.9, 5.1 Hz, 2H), 1.99 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 171.1, 170.0, 131.6, 130.1, 129.4, 128.4, 127.9, 126.5, 125.2, 124.2, 62.1, 52.1, 35.6, 29.8, 23.3, 14.2. Spectral data matched those reported previously.[7]



48

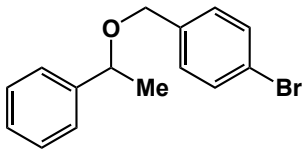
(1-(benzyloxy)ethyl)benzene (48). Ether **48** was synthesized following the optimized procedure outlined in section 6 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and benzyl alcohol (162.2 mg, 1.5 mmol, 3.0 equiv.). Ether product **48** was obtained as a colorless liquid (80.6 mg, 76% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. (R_f = 0.15, 100% hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.41–7.27 (m, 10H), 4.51 (q, *J* = 6.5 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.9, 138.8, 128.6, 128.5, 127.8, 127.6, 127.6, 126.5, 77.4, 70.5, 24.4. Spectral data matched those reported previously.[17]



49

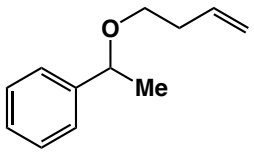
1-bromo-2-((1-phenylethoxy)methyl)benzene (49). Ether **49** was synthesized following the optimized procedure outlined in section 6 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and (2-bromophenyl)methanol (281 mg, 1.5 mmol, 3.0 equiv.). Ether product **49** was

obtained as a light-yellow liquid (74.6 mg, 53% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. (R_f= 0.15, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.55–7.50 (m, 2H), 7.41–7.27 (m, 6H), 7.18–7.10 (m, 1H), 4.57 (q, *J* = 6.4 Hz, 1H), 4.45 (s, 2H), 1.53 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.7, 138.2, 132.6, 129.3, 128.9, 128.7, 127.7, 127.5, 126.4, 122.9, 78.2, 70.1, 24.3. Spectral data matched those reported previously.[18]



50

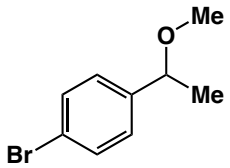
1-bromo-4-((1-phenylethoxy)methyl)benzene (50). Ether **50** was synthesized following the optimized procedure outlined in section 6 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and (4-bromophenyl)methanol (281 mg, 1.5 mmol, 3.0 equiv.). Ether product **50** was obtained as a light-yellow liquid (103 mg, 73% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. (R_f= 0.15, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.51–7.42 (m, 2H), 7.40–7.15 (m, 7H), 4.48 (q, *J* = 6.5 Hz, 1H), 4.38 (d, *J* = 12.1 Hz, 1H), 4.25 (d, *J* = 12.0 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.6, 137.8, 131.6, 129.4, 128.7, 127.8, 126.4, 121.4, 77.6, 69.7, 24.3. Spectral data matched those reported previously.[19]



51

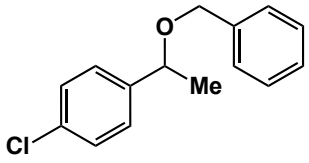
(1-(but-3-en-1-yloxy)ethyl)benzene (51). Ether **51** was synthesized following the optimized procedure outlined in section 6 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and but-3-en-1-ol (108.2 mg, 1.5 mmol, 3.0 equiv.). Ether product **51** was obtained as a light-

yellow liquid (50.2 mg, 61% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. (R_f = 0.15, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.38–7.26 (m, 5H), 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.09-5.03 (m, 1H), 5.03-4.99 (m, 1H), 4.41 (q, *J* = 6.5 Hz, 1H), 3.36 (td, *J* = 6.9, 2.1 Hz, 2H), 2.33 (q, *J* = 6.8 Hz, 2H), 1.44 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 144.1, 135.4, 128.4, 127.3, 126.1, 116.2, 78.0, 68.0, 34.4, 24.1. Spectral data matched those reported previously.[20]



52

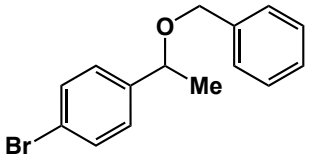
1-bromo-4-(1-methoxyethyl)benzene (52). Ether **52** was synthesized following the optimized procedure outlined in section 6 with 1-bromo-4-(1-bromoethyl)benzene (132 mg, 0.5 mmol, 1.0 equiv.) and methanol (48.1 mg, 60μL, 1.5 mmol, 3.0 equiv.). Ether product **52** was obtained as a light-yellow liquid (77.9 mg, 72% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. (R_f = 0.15, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.47 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 4.26 (q, *J* = 6.5 Hz, 1H), 3.21 (s, 3H), 1.40 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.8, 131.7, 128.1, 121.3, 79.2, 56.6, 23.9. Spectral data matched those reported previously.[21]



53

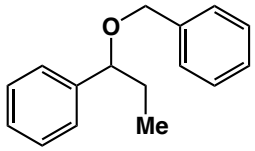
1-(1-(benzyloxy)ethyl)-4-chlorobenzene (53). Ether **53** was synthesized following the optimized procedure outlined in section 6 with 1-(1-bromoethyl)-4-chlorobenzene (110 mg, 0.5 mmol, 1.0 equiv.) and benzyl alcohol (162.2 mg, 1.5 mmol, 3.0 equiv.). Ether product **53** was obtained as a colorless liquid (103 mg, 73% yield) after purification by flash chromatography on silica gel with

100% hexane to 98:2 hexane:EtOAc ($R_{f=}$ 0.15, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.41–7.23 (m, 9H), 4.48 (q, *J* = 6.5 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.30 (d, *J* = 11.9 Hz, 1H), 1.46 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.4, 138.5, 133.3, 128.9, 128.6, 127.9, 127.8, 127.7, 76.7, 70.5, 24.3. Spectral data matched those reported previously.[18]



54

1-(1-(benzyloxy)ethyl)-4-bromobenzene (54). Ether **54** was synthesized following the optimized procedure outlined in section 6 with 1-bromo-4-(1-bromoethyl)benzene (132 mg, 0.5 mmol, 1.0 equiv.) and benzyl alcohol (162.21 mg, 0.156 mL, 1.5 mmol, 3.0 equiv.). Ether product **54** was obtained as a light-yellow liquid (98.3 mg, 68% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. ($R_{f=}$ 0.15, 100% hexanes). **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.53–7.46 (m, 2H), 7.38–7.22 (m, 7H), 4.47 (q, *J* = 6.5 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.30 (d, *J* = 11.8 Hz, 1H), 1.46 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.8, 138.3, 131.6, 128.4, 128.1, 127.7, 127.6, 121.2, 76.6, 70.4, 24.1. Spectral data matched those reported previously.[18]

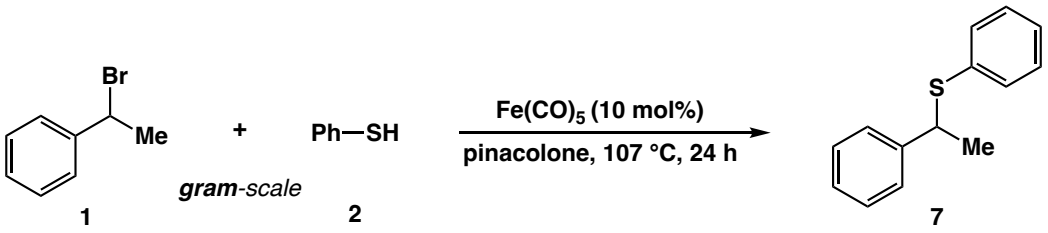


55

(1-(benzyloxy)propyl)benzene (55). Ether **55** was synthesized following the optimized procedure outlined in section 6 with (1-bromopropyl)benzene (100 mg, 0.5 mmol, 1.0 equiv.) and benzyl alcohol (162.2 mg, 1.5 mmol, 3.0 equiv.). Ether product **55** was obtained as a colorless liquid (73.1 mg, 53% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc ($R_{f=}$ 0.15, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.42–7.26 (m, 10H),

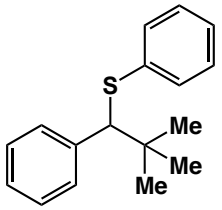
4.48 (d, *J* = 11.9 Hz, 1H), 4.28 (d, *J* = 11.9 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 1H), 1.97-1.85 (m, 1H), 1.79-1.67 (m, 1H), 0.93 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.6, 138.9, 128.5, 128.4, 127.9, 127.6, 127.6, 127.0, 83.1, 70.5, 31.3, 10.5. Spectral data matched those reported previously.[22]

F. Synthetic application procedures



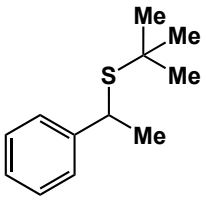
Supplementary Fig. 22. **Gram-scale reaction.**

Gram-Scale Procedure. To a flame-dried 20 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (118 mg, 0.60 mmol, 81 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (12 mL), (1-bromoethyl)benzene (**1**) (1.11 g, 6.0 mmol, 822 uL, 1.0 equiv.), and thiophenol (**85**) (992 mg, 9.0 mmol, 918 uL, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (5.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 5.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant oil was purified by silica flash chromatography (100% hexanes) to yield thioether **7** as a colorless oil (1.19 g, 93% yield). Compound tabulation can be found above.



56

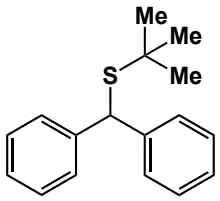
(2,2-Dimethyl-1-phenylpropyl)(methyl)sulfane (56). Thioether **56** was synthesized following the optimized procedure outlined in section 5 with (1-bromo-2,2-dimethylpropyl)benzene (114 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **56** was obtained as a colorless liquid (87.3 mg, 68% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.30, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.38 (d, *J* = 7.0 Hz, 2H), 7.29–7.18 (m, 5H), 7.14 (td, *J* = 7.4, 1.0 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 4.05 (s, 1H), 1.11 (s, 9H) **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 141.3, 136.9, 130.9, 129.8, 128.7, 127.7, 126.8, 126.2, 66.2, 36.2, 28.6. Spectral data matched those reported previously.[23]



57

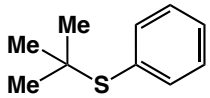
***tert*-Butyl(1-phenylethyl)sulfane (57).** Thioether **57** was synthesized following the optimized procedure outlined in section 5 with 1-(bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.) and 2-methylpropane-2-thiol (67.6 mg, 0.75 mmol, 1.5 equiv.). Thioether product **57** was obtained as a colorless liquid (43 mg, 44% yield) after purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.30, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.38–7.25 (m, 5H), 4.03 (q, *J* = 7.0 Hz, 1H), 1.70 (d, *J* = 7.0 Hz, 3H), 1.34 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$).**

δ = 142.6, 128.6, 127.8, 127.6, 51.3, 48.0, 30.2, 21.3. Spectral data matched those reported previously.[7]



58

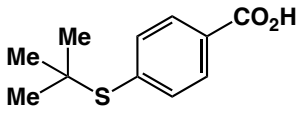
Benzhydryl(tert-butyl)sulfane (58). Thioether **58** was synthesized following the optimized procedure outlined in section 5 with (bromomethylene)dibenzene (124 mg, 0.5 mmol, 1.0 equiv.) and 2-methylpropane-2-thiol (67.6 mg, 0.75 mmol, 1.5 equiv.). Thioether product **58** was obtained as a colorless liquid (44 mg, 34% yield) after purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.20, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.44 (d, J = 7.7 Hz, 4H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.21–7.18 (m, 2H), 5.21 (s, 1H), 1.27 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 143.3, 128.6, 128.5, 126.9, 52.3, 44.8, 31.5. Spectral data matched those reported previously.[24]



59

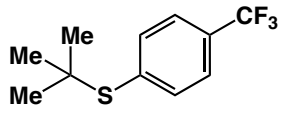
tert-butyl(phenyl)sulfane (59). Thioether **59** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and thiophenol (**85**) or diphenyldisulfide (0.75 mmol, 1.5 equiv.). Thioether product **59** was obtained as a colorless liquid (67.6 mg, 81% yield or 65.9 mg, 79% yield, respectively) after purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.30, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.55–7.53 (m, 2H), 7.38–7.31 (m, 3H), 1.29 (s, 9H).**^{13}C NMR (125 MHz,**

$CDCl_3$). δ = 137.6, 132.8, 128.8, 128.6, 46.0, 31.1. Spectral data matched those reported previously.[25]



60

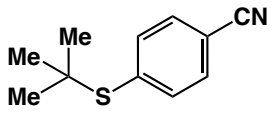
4-(tert-butylthio)benzoic acid (60). Thioether **60** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-mercaptobenzoic acid (116 mg, 0.75 mmol, 1.5 equiv.). Thioether product **60** was obtained as a colorless liquid (83 mg, 79% yield) after purification by flash chromatography on silica gel with 100% CH_2Cl_2 to 9:1 CH_2Cl_2:EtOAc. ($R_{f=}$ 0.29, 10% EtOAc/CH_2Cl_2). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 12.3 (brs, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 9H).**^{13}C NMR (150 MHz, $CDCl_3$).** δ = 172.1, 140.6, 136.8, 130.2, 129.3, 47.1, 31. Spectral data matched those reported previously.[25]



61

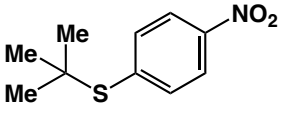
tert-butyl(4-(trifluoromethyl)phenyl)sulfane (61). Thioether **61** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-(trifluoromethyl)benzenethiol (134 mg, 0.75 mmol, 1.5 equiv.). Thioether product **61** was obtained as a colorless liquid (74 mg, 72% yield) after purification by flash chromatography on silica gel with 100% Hexanes. ($R_{f=}$ 0.40, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.65 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 1.31 (s, 9H).**^{13}C NMR (150 MHz, $CDCl_3$).** δ =

137.6, 137.3, 130.7, 130.5, 125.2 (q, J = 3.7 Hz), 46.7, 31.0. **^{19}F NMR (564 MHz, $CDCl_3$).** δ = –62.7. Spectral data matched those reported previously.[26]



62

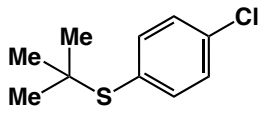
4-(tert-butylthio)benzonitrile (62). Thioether **62** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-mercaptobenzonitrile (99.5 mg, 0.75 mmol, 1.5 equiv.). Thioether product **62** was obtained as a colorless liquid (67 mg, 70% yield) after purification by flash chromatography on silica gel with 100% Hexanes to 9:1 Hexanes:EtOAc (R_f = 0.57, 10% EtOAc/Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.63–7.59 (m, 4H), 1.32 (s, 9H).**^{13}C NMR (150 MHz, $CDCl_3$).** δ = 139.9, 137.3, 130.0, 118.6, 112.3, 47.4, 31.2. Spectral data matched those reported previously.[25]



63

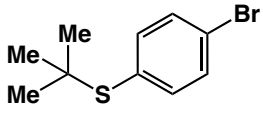
tert-butyl(4-nitrophenyl)sulfane (63). Thioether **63** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-nitrobenzenethiol (116 mg, 0.75 mmol, 1.5 equiv.). Thioether product **63** was obtained as a yellow liquid (67 mg, 63% yield) after purification by flash chromatography on silica gel with 100% Hexanes to 9:1 Hexanes:EtOAc (R_f = 0.57, 10% EtOAc/Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 8.16 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 1.35 (s, 9H).**^{13}C NMR (150 MHz,**

$CDCl_3$). δ = 147.9, 142.5, 137.0, 123.5, 47.7, 31.3. Spectral data matched those reported previously. [25]



64

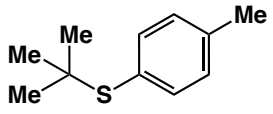
tert-butyl(4-chlorophenyl)sulfane (64). Thioether **64** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-chlorobenzenethiol (109 mg, 0.75 mmol, 1.5 equiv.). Thioether product **64** was obtained as a colorless liquid (84 mg, 83% yield) after purification by flash chromatography on silica gel with 100% Hexanes. ($R_{f=}$ 0.40, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 1.28 (s, 9H).**^{13}C NMR (150 MHz, $CDCl_3$).** δ = 138.8, 135.3, 131.4, 128.8, 46.3, 31.0. Spectral data matched those reported previously. [25]



65

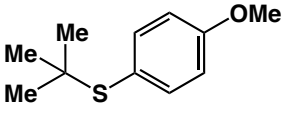
(4-bromophenyl)(tert-butyl)sulfane (65). Thioether **65** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-bromobenzenethiol (142 mg, 0.75 mmol, 1.5 equiv.). Thioether product **65** was obtained as a colorless liquid (106 mg, 87% yield) after purification by flash chromatography on silica gel with 100% Hexanes. ($R_{f=}$ 0.40, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.46 (d, *J* =

8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 1.28 (s, 9H).**^{13}C NMR (150 MHz, $CDCl_3$).** δ = 139.1, 132.0, 131.8, 123.6, 46.3, 31.0. Spectral data matched those reported previously. [25]



66

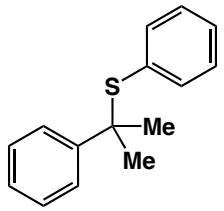
tert-butyl(p-tolyl)sulfane (66). Thioether **66** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-methylbenzenethiol (93.2 mg, 0.75 mmol, 1.5 equiv.). Thioether product **66** was obtained as a colorless liquid (66.6 mg, 74% yield) after purification by flash chromatography on silica gel with 100% Hexanes. (R_f = 0.29, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.42 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 1.28 (s, 9H).**^{13}C NMR (150 MHz, $CDCl_3$).** δ = 138.9, 137.6, 129.4, 129.3, 45.7, 31.0, 21.4. Spectral data matched those reported previously.[26]



67

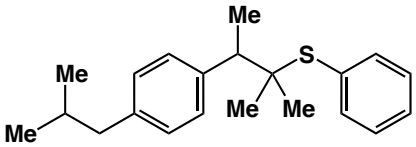
tert-butyl(4-methoxyphenyl)sulfane (67). Thioether **67** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and 4-methoxythiophenol (105 mg, 0.75 mmol, 1.5 equiv.). Thioether product **67** was obtained as a yellow liquid (64 mg, 65% yield) after purification by flash chromatography on silica gel with 100% Hexanes to 9:1 Hexanes:EtOAc (R_f = 0.57, 10% EtOAc/Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.44 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.26 (s, 9H).**^{13}C NMR**

(150 MHz, $CDCl_3$). δ = 160.4, 139.0, 123.8, 114.1, 55.4, 45.6, 30.9. Spectral data matched those reported previously. [26]



68

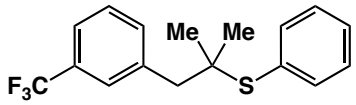
Phenyl(2-phenylpropan-2-yl)sulfane (68). Thioether **68** was synthesized following the optimized procedure outlined in section 5 with (2-bromopropan-2-yl)benzene (100 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). Thioether product **68** was obtained as a colorless liquid (81.1 mg, 71% yield) after purification by flash chromatography on silica gel with 100% hexane. ($R_{f=}$ 0.25, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.44 (d, *J* = 7.7 Hz, 2H), 7.32–7.28 (m, 3H), 7.25–7.16 (m, 5H), 1.72 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 146.5, 136.6, 133.0, 128.6, 128.4, 128.0, 126.70, 126.67, 51.1, 29.8. Spectral data matched those reported previously.[8]



69

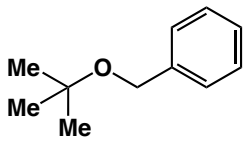
(3-(4-isobutylphenyl)-2-methylbutan-2-yl)(phenyl)sulfane (69). Thioether **69** was synthesized following the optimized procedure outlined in section 5 with 1-(3-bromo-3-methylbutan-2-yl)-4-isobutylbenzene (**S38**) (141 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.5 mg, 0.75 mmol, 1.5 equiv.). Thioether product **69** was obtained as a colorless liquid (106 mg, 68% yield) after purification by flash chromatography on silica gel with 100% Hexanes. ($R_{f=}$ 0.26, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 6.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.88 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.1

Hz, 2H), 1.85 (dp, J = 13.4, 6.7 Hz, 1H), 1.53 (d, J = 7.2 Hz, 3H), 1.22 (s, 3H), 1.07 (s, 3H), 0.90 (dd, J = 6.6, 1.1 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 140.5, 139.9, 137.9, 132.7, 129.1, 128.8, 128.6, 128.6, 53.4, 48.6, 45.2, 30.3, 29.5, 24.6, 22.6, 22.6, 16.9. **IR (Neat).** 3088, 3062, 2959, 2927, 2870, 1742, 1507, 1459, 1371, 1241, 1116, 847, 747, 693. cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{21}H_{28}AgS^+$, 419.0963; found 419.0968.



70

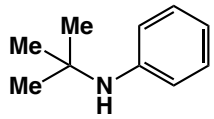
(2-methyl-1-(3-(trifluoromethyl)phenyl)propan-2-yl)(phenyl)sulfane (70). Thioether **70** was synthesized following the optimized procedure outlined in section 5 with 1-(2-bromo-2-methylpropyl)-3-(trifluoromethyl)benzene (**S41**) (109 mg, 0.5 mmol, 1.0 equiv.) and thiophenol (**85**) (82.5 mg, 0.75 mmol, 1.5 equiv.). Thioether product **70** was obtained as a colorless liquid (119 mg, 77% yield) after purification by flash chromatography on silica gel with 100% Hexanes. ($R_{f=}$ 0.26, 100% Hexanes). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (dt, J = 7.3, 1.3 Hz, 2H), 7.50 (d, J = 7.3 Hz, 1H), 7.43 – 7.33 (m, 6H), 2.94 (s, 2H), 1.21 (s, 6H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.8, 137.8, 134.2, 131.9, 130.4 (q, J = 32.0 Hz), 129.1, 128.8, 128.4, 127.4 (q, J = 3.8 Hz), 125.3, 123.5 (q, J = 3.5 Hz), 49.0, 48.8, 28.2. **^{19}F NMR (564 MHz, $CDCl_3$).** δ = –62.6. **IR (Neat).** 3080, 2972, 2929, 2875, 1436, 1328, 1159, 1116, 1073. cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M + Ag]^+$ calcd for $C_{17}H_{17}AgF_3S^+$, 417.0054; found 417.0551.



71

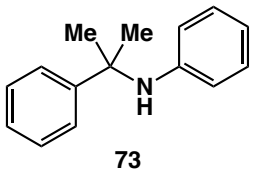
(1-(benzyloxy)propyl)benzene (71). Ether **71** was synthesized following the optimized procedure outlined in section 6 with 2-bromo-2-methylpropane (69 mg, 0.75 mmol, 1.5 equiv.) and benzyl alcohol (162.2 mg, 1.5 mmol, 3.0 equiv.). Ether product **71** was obtained as a colorless liquid (51.7

mg, 63% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. ($R_{f=}$ 0.33, 95:5 hexanes:EtOAc). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.41–7.21 (m, 5H), 4.48 (s, 2H), 1.33 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ = 140.1, 128.5, 127.2, 127.2, 73.5, 64.3, 27.3. Spectral data matched those reported previously.[27]



72

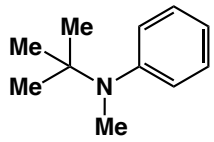
***N*-(tert-butyl)aniline (72).** Amine **72** was synthesized following the optimized procedure outlined in section 5 with 2-bromo-2-methylpropane (69 mg, 0.5 mmol, 1.0 equiv.) and aniline (70 mg, 0.75 mmol, 1.5 equiv.). Amine product **72** was obtained as a orange liquid (108.9 mg, 73% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. ($R_{f=}$ 0.40, 9:1 hexanes:EtOAc). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.28 (t, *J* = 7.9 Hz, 2H), 7.04-6.99 (m, 1H), 6.64 (d, J = 8.4 Hz, 2H), 4.01 (s, br 1H), 1.35 (s, 9H). Spectral data matched those reported previously.[28]



73

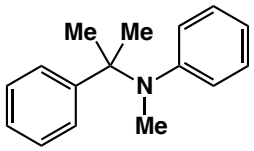
***N*-(2-phenylpropan-2-yl)aniline (73).** Amine **73** was synthesized following the optimized procedure outlined in section 5 with (2-bromopropan-2-yl)benzene (100 mg, 0.5 mmol, 1.0 equiv.) and aniline (70 mg, 0.75 mmol, 1.5 equiv.). Amine product **73** was obtained as a colorless liquid (131 mg, 67% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. ($R_{f=}$ 0.40, 9:1 hexanes:EtOAc). **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.51 (d, *J* = 7.6 Hz, 2H), 7.34 –7.32 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.01–6.99 (m, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 2H) 4.03 (s, br 1H), 1.64 (s, 6H). **^{13}C NMR (150 MHz, $CDCl_3$).** δ

= 147.6, 146.2, 128.8, 128.7, 126.4, 125.7, 117.2, 115.5, 55.9, 30.8. Spectral data matched those reported previously.[29]



74

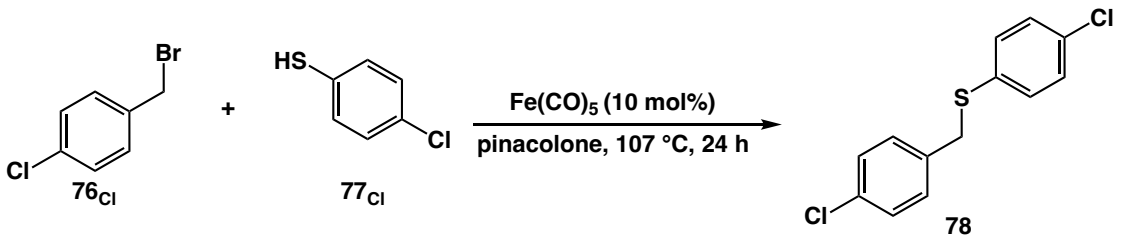
***N*-(tert-butyl)-N-methylaniline (74).** Amine **74** was synthesized following the optimized procedure outlined in section 6 with 2-bromo-2-methylpropane (69 mg, 0.5 mmol, 1.0 equiv.) and *N*-methylaniline (80.3 mg, 0.75 mmol, 1.5 equiv.). Amine product **74** was obtained as a orange liquid (67 mg, 41% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. ($R_{f=}$ 0.40, 9:1 hexanes:EtOAc). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.28 (t, *J* = 7.9 Hz, 2H), 7.04-6.99 (m, 1H), 6.64 (d, J = 8.4 Hz, 2H), 2.71 (s, 3H), 1.31 (s, 9H). Spectral data matched those reported previously.[30]



75

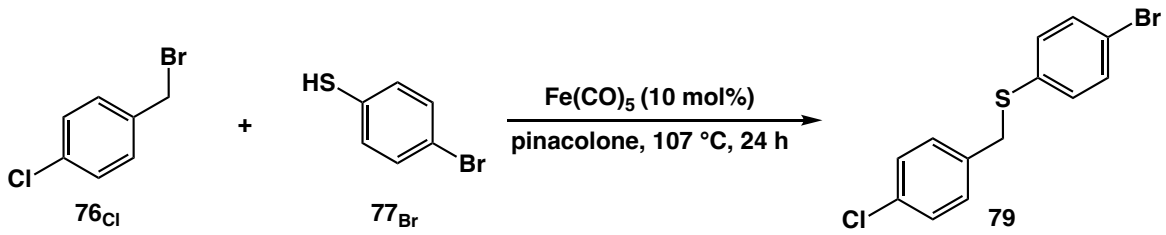
***N*-methyl-N-(2-phenylpropan-2-yl)aniline (75).** Amine **75** was synthesized following the optimized procedure outlined in section 5 with (2-bromopropan-2-yl)benzene (100 mg, 0.5 mmol, 1.0 equiv.) and *N*-methylaniline (80.3 mg, 0.75 mmol, 1.5 equiv.). Amine product **75** was obtained as a colorless liquid (128.4 mg, 60% yield) after purification by flash chromatography on silica gel with 100% hexane to 98:2 hexane:EtOAc. ($R_{f=}$ 0.40, 9:1 hexanes:EtOAc). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.28–7.24 (m, 5H), 7.17–7.14 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 2.83 (s, 3H), 1.65 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 151.5, 147.1, 139.8, 128.0, 127.7, 126.9, 125.5, 112.3, 42.3, 31.1, 30.9. Spectral data matched those reported previously.[31]

Rapid Chlorbenside Analog Synthesis



Supplementary Fig. 23. **Thioether (Chlorbenside) 78 synthesis.**

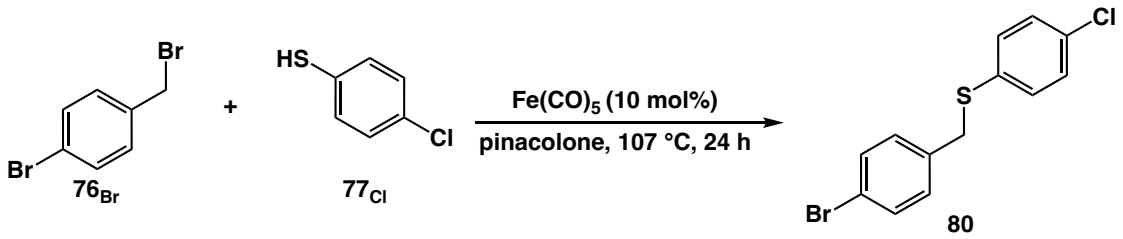
(4-chlorobenzyl)(4-chlorophenyl)sulfane (78). Thioether **78** was synthesized following the optimized procedure outlined in section 5 with 1-(bromomethyl)-4-chlorobenzene (**76$_{Cl}$**) (102 mg, 0.5 mmol, 1.0 equiv.) and 4-chlorobenzenethiol **(77 $_{Cl}$)** (109 mg, 0.75 mmol, 1.5 equiv.). Thioether product **78** was obtained as a white solid (107 mg, 79% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.29–7.19 (m, 8H), 4.05 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 136.0, 134.1, 133.2, 133.0, 131.9, 130.2, 129.2, 128.8, 38.9. Spectral data matched those reported previously.[32]



Supplementary Fig. 24. **Thioether (Chlorbenside analog) 79 synthesis.**

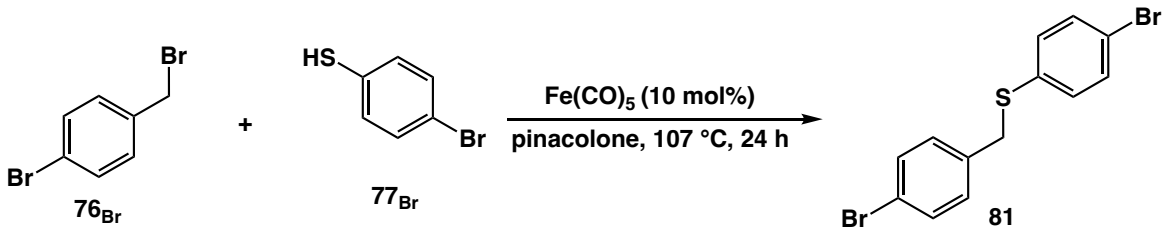
(4-bromophenyl)(4-chlorobenzyl)sulfane (79). Thioether **79** was synthesized following the optimized procedure outlined in section 5 with 1-(bromomethyl)-4-chlorobenzene (**76$_{Cl}$**) (102 mg, 0.5 mmol, 1.0 equiv.) and 4-bromobenzenethiol **(77$_{Br}$)** (142 mg, 0.75 mmol, 1.5 equiv.). Thioether product **79** was obtained as a white solid (132 mg, 84% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.38 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.14 (d, J

= 8.5 Hz, 2H), 4.04 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 135.8, 134.9, 133.2, 132.1, 132.0, 130.2, 128.2, 120.8, 38.7. Spectral data matched those reported previously.[33]



Supplementary Fig. 25. **Thioether (Chlorbenside analog) 80 synthesis.**

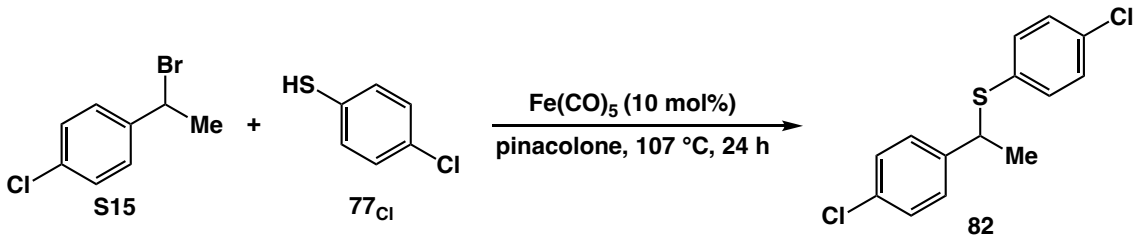
(4-bromobenzyl)(4-chlorophenyl)sulfane (80). Thioether **80** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-4-(bromomethyl)benzene (**76_{Br}**) (125 mg, 0.5 mmol, 1.0 equiv.) and 4-chlorobenzenethiol **(77_{Cl})** (109 mg, 0.75 mmol, 1.5 equiv.). Thioether product **80** was obtained as a white solid (122 mg, 76% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.40 (d, *J* = 8.4 Hz, 2H), 7.23–7.18 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.01 (s, 2H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 136.5, 134.1, 133.1, 132.0, 131.8, 130.6, 129.2, 121.4, 39.0. Spectral data matched those reported previously.[34]



Supplementary Fig. 26. **Thioether (Chlorbenside analog) 81 synthesis.**

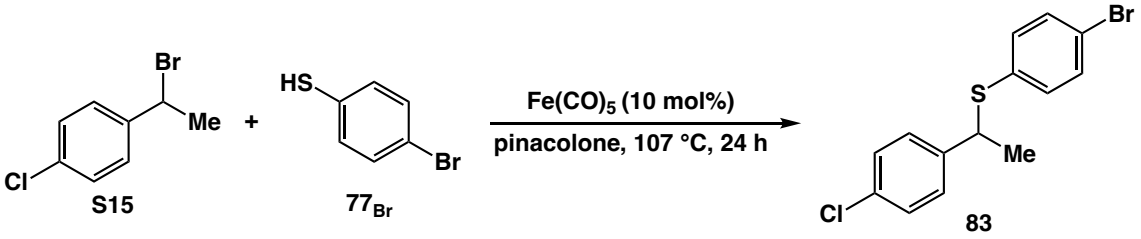
(4-bromobenzyl)(4-bromophenyl)sulfane (81). Thioether **81** was synthesized following the optimized procedure outlined in section 5 with 1-bromo-4-(bromomethyl)benzene **(76_{Br})** (125 mg, 0.5 mmol, 1.0 equiv.) and 4-bromobenzenethiol **(77_{Br})** (142 mg, 0.75 mmol, 1.5 equiv.). Thioether product **81** was obtained as a white solid (156.7 mg, 87% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.39 (dd, *J* = 16.7, 8.5 Hz, 4H), 7.13 (dd, *J* = 8.4, 3.6 Hz, 4H), 4.01 (s, 2H), **^{13}C NMR**

(125 MHz, $CDCl_3$). δ = 136.4, 134.5, 132.1, 132.0, 131.8, 130.6, 121.4, 120.9, 38.8. Spectral data matched those reported previously.[34]



Supplementary Fig. 27. **Thioether (Chlorbenside analog) 82 synthesis.**

(4-chlorophenyl)(1-(4-chlorophenyl)ethyl)sulfane (82). Thioether **82** was synthesized following the optimized procedure outlined in section 5 with 1-(1-bromoethyl)-4-chlorobenzene (125 mg, 0.5 mmol, 1.0 equiv.) and 4-chlorobenzenethiol **(77_{Cl})** (109 mg, 0.75 mmol, 1.5 equiv.). Thioether product **82** was obtained as a white solid (127 mg, 88% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.29–7.19 (m, 8H), 4.28 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.0 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 141.7, 134.3, 133.8, 133.1, 133.0, 130.2, 129.1, 128.7 (d, J = 1.9 Hz) , 47.8, 22.2. Spectral data matched those reported previously.[11]

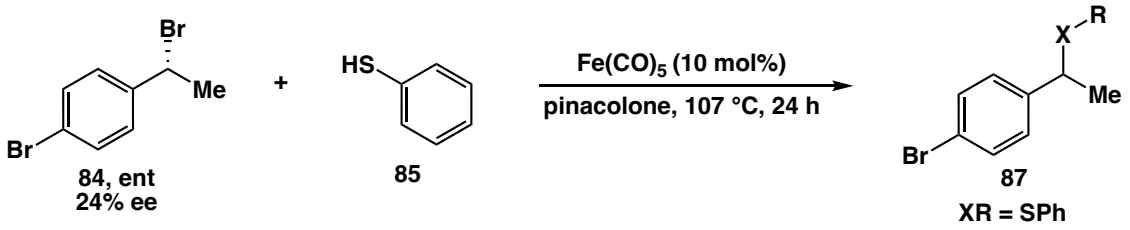


Supplementary Fig. 28. **Thioether (Chlorbenside analog) 83 synthesis.**

(4-bromophenyl)(1-(4-chlorophenyl)ethyl)sulfane (83). Thioether **83** was synthesized following the optimized procedure outlined in section 5 with 1-(1-bromoethyl)-4-chlorobenzene (125 mg, 0.5 mmol, 1.0 equiv.) and 4-bromobenzenethiol **(77_{Br})** (142 mg, 0.75 mmol, 1.5 equiv.). Thioether product **83** was obtained as a white solid (152 mg, 93% yield) upon purification by flash chromatography on silica gel with 100% hexane. (R_f = 0.29, 100% hexanes). **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.34 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.26 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).**

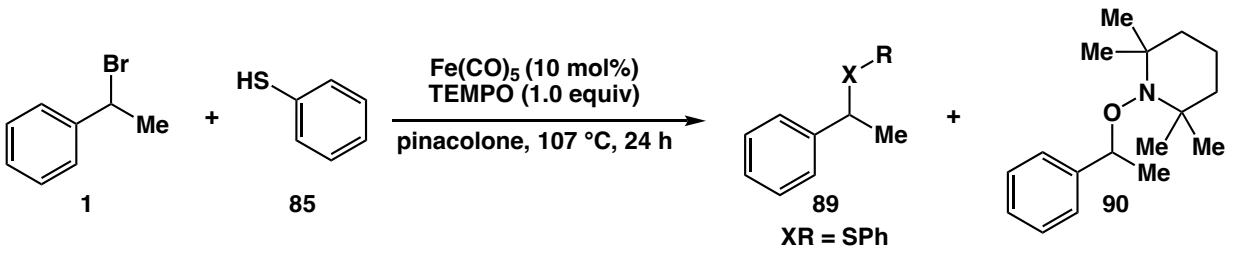
δ = 141.6, 134.4, 133.8, 133.0, 132.0, 130.2, 128.7, 121.8, 47.7, 22.3. Spectral data matched those reported previously.[11]

G. Mechanistic study procedures



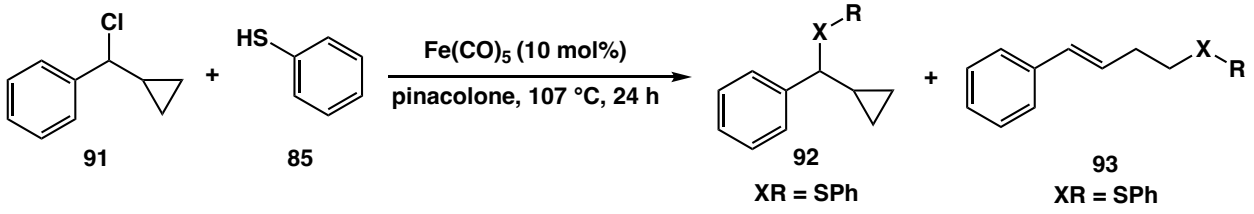
Supplementary Fig. 29. **Examination of thiol coupling stereospecificity.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), 1-bromo-4-(1-bromoethyl)benzene (**84, ent**) (132.0 mg, 0.5 mmol, 1.0 equiv., 24% ee), and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture was purified by silica flash chromatography (100% hexanes) to yield thioether **87** as a colorless oil (134.9 mg, 92% yield, 0% ee). Chiral SFC: 250 mm ChiralPak IJ–3, 10% MeOH, 3.0 mL/min, λ = 210 nm, 35 °C, nozzle pressure = 140 bar CO_2, tR1 = 4.22 min, tR2 = 4.73 min. **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.31–7.23 (m, 5H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.30 (q, *J* = 7.0 Hz, 1H), 1.63 (d, *J* = 7.1 Hz, 3H). Spectral data matched those reported previously.[7]



Supplementary Fig. 30. **Thiol coupling spin trap experiment.**

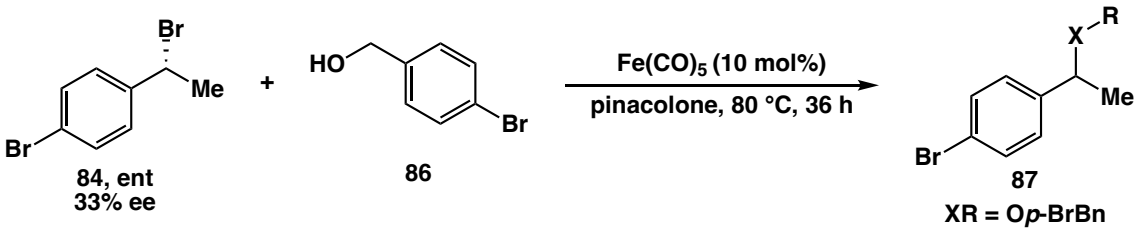
To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.), thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.), and TEMPO (78.1 mg, 0.5 mmol, 1.0 equiv). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture containing thioether **89** and TEMPO adduct **90** was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard (39% NMR yield, **89**) (51% NMR yield, **90**). Thioether **89** is tabulated above. TEMPO adduct **90**: **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.35-7.21 (m, 5H), 4.85 (q, J= 6.4 Hz, 1H), 1.46 (d, J= 6.4 Hz, 3H), 1.41-1.25 (m, 6H), 1.29 (s, 3H), 1.16 (s, 3H), 1.02 (s, 3H), 0.65 (s, 3H). Spectral data matched those reported previously.[7]



Supplementary Fig. 31. **Thiol coupling radical clock experiment.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), (chloro(cyclopropyl)methyl)benzene (**91**) (83.3 mg, 0.5 mmol, 1.0 equiv.), and thiophenol (**85**) (82.6 mg, 0.75 mmol, 77 uL, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24

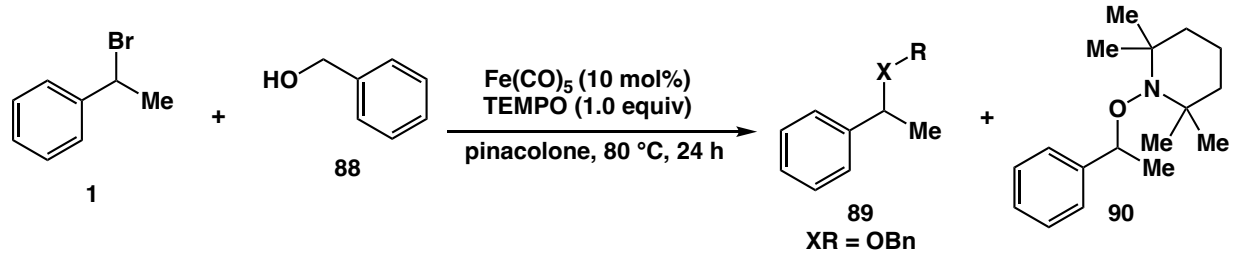
hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture containing thioether **92** and radical clock adduct **93** was analyzed by NMR using 1,3,5-trimethoxy benzene (20% NMR yield, **92**) (76% NMR yield, **93**). Thioether **92** **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.34-7.15 (m, 10H), 3.51 (d, *J* = 9.5 Hz, 1H), 1.35–.90 (m, 1H), 0.70–0.50 (m, 2H), 0.36–0.23 (m, 2H). Spectral data matched those reported previously[35] Radical clock adduct **93**: **^{1}H NMR (600 MHz, $CDCl_3$).** δ = 7.36-7.15 (m, 10H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.23–6.18 (m, 1H), 3.08–3.00 (m, 2H), 2.56–2.47 (m, 2H). Spectral data matched those reported previously.[36]



Supplementary Fig. 32. **Examination of alcohol coupling stereospecificity.**

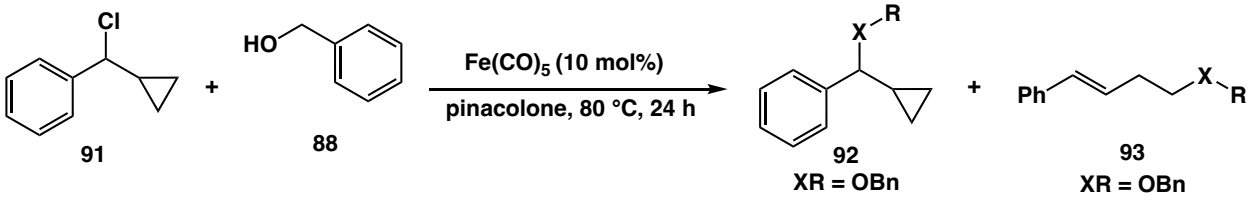
To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), 1-bromo-4-(1-bromoethyl)benzene (**84, ent**) (132.0 mg, 0.5 mmol, 1.0 equiv., 33% ee), and 4-bromobenzyl alcohol (281 mg, 1.5 mmol, 3.0 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 80 °C for 36 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture was purified by silica flash chromatography (100% hexanes) to yield ether **87** as a colorless oil (98.3 mg, 78% yield, 0% ee). Chiral SFC: 250 mm ChiralPak IJ–4, 05%MeOH, 3.0 mL/min, λ = 210 nm, 35 °C, nozzle pressure = 140 bar CO_2, tR1 = 2.62 min, tR2 = 3.13 min. **^{1}H NMR (500 MHz, $CDCl_3$).** δ = 7.52–7.43 (m, 4H), 7.24–7.20 (m, 2H), 7.19–7.15 (m, 2H), 4.44 (q, *J* = 6.5 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.24 (d, *J* = 12.0 Hz, 1H), 1.45 (d, *J* = 6.5 Hz, 3H), **^{13}C NMR (125 MHz, $CDCl_3$).** δ = 142.7, 137.5, 131.9, 131.7, 129.4, 128.2, 121.6, 76.9, 69.8, 24.2. **IR (Neat).** 3082, 2935, 2879,

1589, 1477, 1401, 1380, 1203, 1088, 1066. cm^{-1}. **HRMS-QTOF-ESI** (m/z) $[M+H]^+$ calcd for $C_{15}H_{15}Br_2O^+$, 368.9490; found 368.9498.



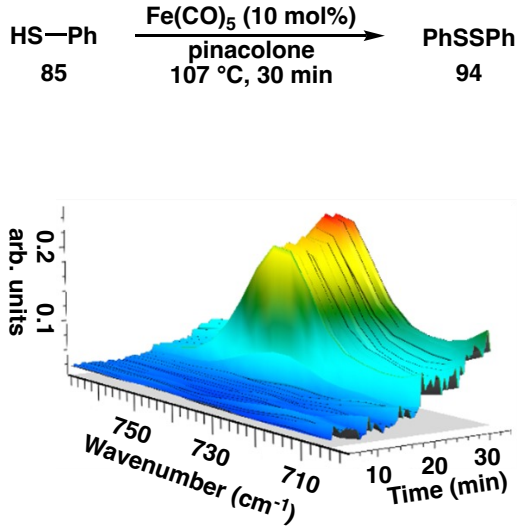
Supplementary Fig. 33. **Alcohol coupling spin trap experiment.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.), and benzyl alcohol (162.2 mg, 1.5 mmol, 3.0 equiv.), and TEMPO (78.1 mg, 0.5 mmol, 1.0 equiv). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 80 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture containing ether **89** and TEMPO adduct **90** was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard (45% NMR yield, **89**) (34% NMR yield, **90**). Ether **89** is tabulated above. TEMPO adduct **90**: **^{1}H NMR (400 MHz, $CDCl_3$).** δ = 7.35-7.21 (m, 5H), 4.85 (q, J= 6.4 Hz, 1H), 1.46 (d, J= 6.4 Hz, 3H), 1.41-1.25 (m, 6H), 1.29 (s, 3H), 1.16 (s, 3H), 1.02 (s, 3H), 0.65 (s, 3H). Spectral data matched those reported previously.[7]



Supplementary Fig. 34. **Alcohol coupling radical clock experiment.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), (chloro(cyclopropyl)methyl)benzene (**91**) (83.3 mg, 0.5 mmol, 1.0 equiv.), and benzyl alcochol (162.2 mg, 1.5 mmol, 3.0 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard. NMR yields were determined for ether **92** (0% NMR yield) and radical clock adduct **93** (100% NMR yield). Radical clock adduct **93**: **^{1}H NMR (500 MHz, $CDCl_3$).** δ = δ = 7.39–7.27 (m, 9H), 7.25–7.20 (m, 1H), 6.48 (d, J = 16.9 Hz, 1H), 6.29-6.17 (m,1H), 4.55 (s, 2H), 3.63 (t, J = 6.8 Hz, 2H), 2.54 (q, J = 6.7 Hz, 2H). Spectral data matched those reported previously.[37]



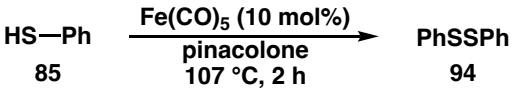
Supplementary Fig. 35. **In-situ infrared spectroscopy studies.**

To a vial equipped with a stir bar and the ReactIR probe was added pinacolone (2.0 mL). The solution was and equilibrated to 107 °C for approximately 14 minutes and Fe(CO)5 (196 mg, 1.0 mmol, 140 uL) was added. After an additional 7 minutes, thiophenol (**85**) (110 mg, 1.0 mmol, 1.0 equiv) was added to the solution and stirred for 20 minutes. Results were monitored using in situ infrared spectroscopy.

Note: *Unfortunately, control experiments where the full reaction was run in the presence of ReactIR test kit equipment demonstrated that the system was not compatible.*

The initial masses of gold leaf and C-22 were 21.45 mg and 3,309.91 mg, respectively.

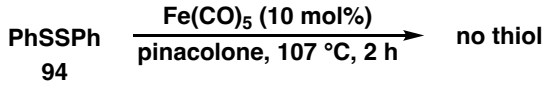
The recovered masses of gold leaf and C-22 were 21.06 mg and 3,295.35 mg, respectively. This represents a loss of 0.39 mg (1.8%) and 14.56 mg (0.5%), respectively. Such decomposition was not observed when stirring iron with thiol or disulfide in the absence of substrate.



Supplementary Fig. 36. **Thiol to disulfide interconversion studies with $Fe(CO)_5$.**

Thiol to disulfide interconversion procedure

To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), and thiophenol (**85**) (55 mg, 0.5 mmol, 51 uL, 1.0 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 2 hours. The mixture was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over silica plug, and concentrated under reduced pressure. The resultant mixture containing thiol **85** and disulfide **94** was analyzed by NMR using 1,3,5-trimethoxy benzene (5% NMR yield, **94**).

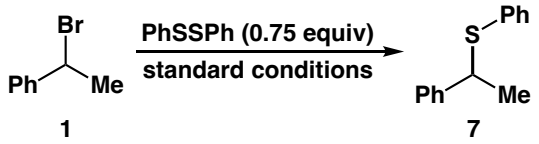


Supplementary Fig. 37. **Disulfide to thiol interconversion studies with $Fe(CO)_5$.**

Disulfide to thiol interconversion procedure

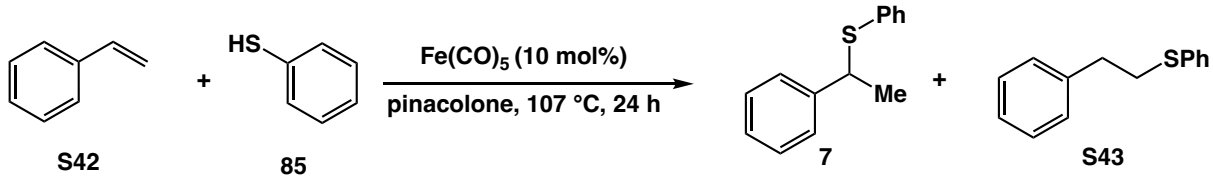
To a flame-dried 4 mL dram vial equipped with a stir bar was added an iron catalyst (6.8 uL, 0.05 mmol, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added solvent (1.0 mL), and diphenyl disulfide (110 mg, 0.5 mmol, 1.0 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at

107 °C for 2 hours. The mixture was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over silica plug, and concentrated under reduced pressure. The resultant mixture containing disulfide **94** was analyzed by NMR using 1,3,5-trimethoxy benzene with full recovery of disulfide **94** and no formation of thiol **85**.



Supplementary Fig. 38. **Limited disulfide coupling.**

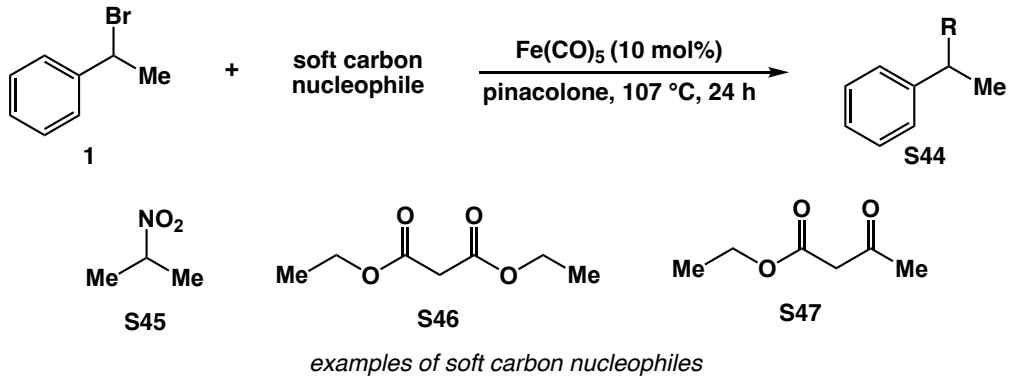
To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (10.0 mg, 0.025 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.), and thiophenol (**85**) (0.375 mmol, 0.75 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture containing thioether **7** (40% NMR yield) was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard.



Supplementary Fig. 39. **Failed Markovnikov 1,2-addition.**

To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (10.0 mg, 0.025 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL), styrene (**S42**) (52.1 mg, 0.5 mmol, 1.0 equiv.), and thiophenol (**85**) (0.75 mmol, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched

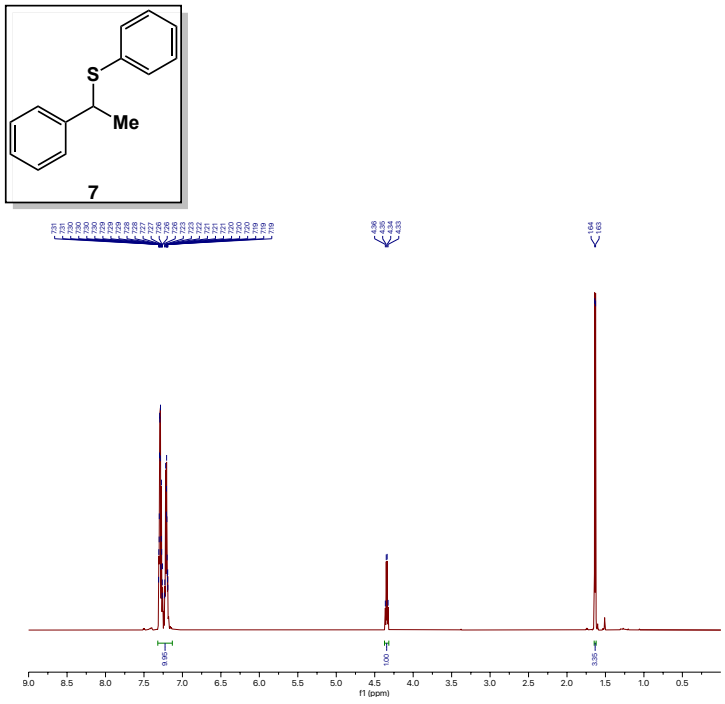
with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture containing thioether **S43** (16% NMR yield) was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard; no formation of thioether **7** was observed.



Supplementary Fig. 40. **Failed soft carbon nucleophiles.**

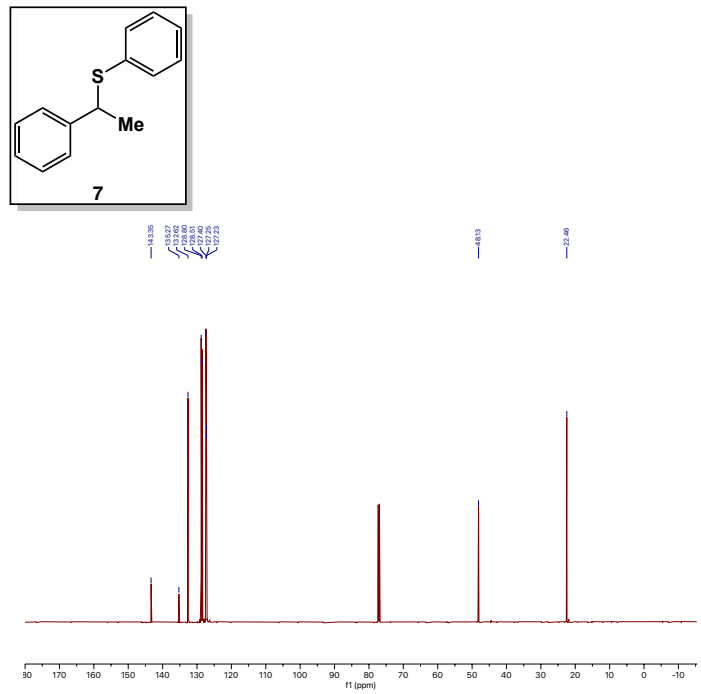
To a flame-dried 4 mL dram vial equipped with a stir bar was added $Fe(CO)_5$ (10.0 mg, 0.025 mmol, 6.8 uL, 10 mol%) in a glove box. The vial was taken out of the glove box and placed under N_2 in a fume-hood. To the vial was added pinacolone (1.0 mL), (1-bromoethyl)benzene (**1**) (92.5 mg, 0.5 mmol, 1.0 equiv.), and corresponding carbon nucleophile (**S45**, **S46**, or **S47**, 0.75 mmol, 1.5 equiv.). The reaction vessel was sealed with a teflon screw cap and the mixture was stirred at 107 °C for 24 hours. The mixture was quenched with water (1.0 mL) and the aqueous layer was extracted with diethyl ether (3 x 1.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resultant mixture containing was analyzed by NMR using 1,3,5-trimethoxy benzene as an internal standard no formation of desired product **S44**.

H. ^{1}H, ^{13}C, and ^{19}F NMR data



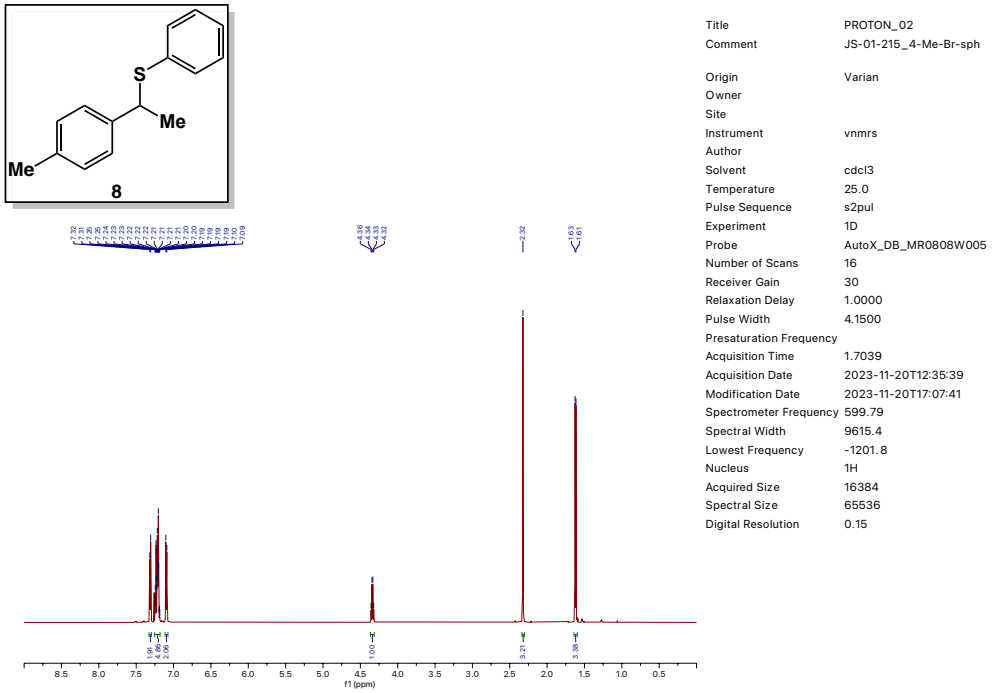
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Acquisition Time	1.7039
Acquisition Date	2023-10-06T14:07:24
Modification Date	2023-10-06T18:03:37
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1212.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 41. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 7.**



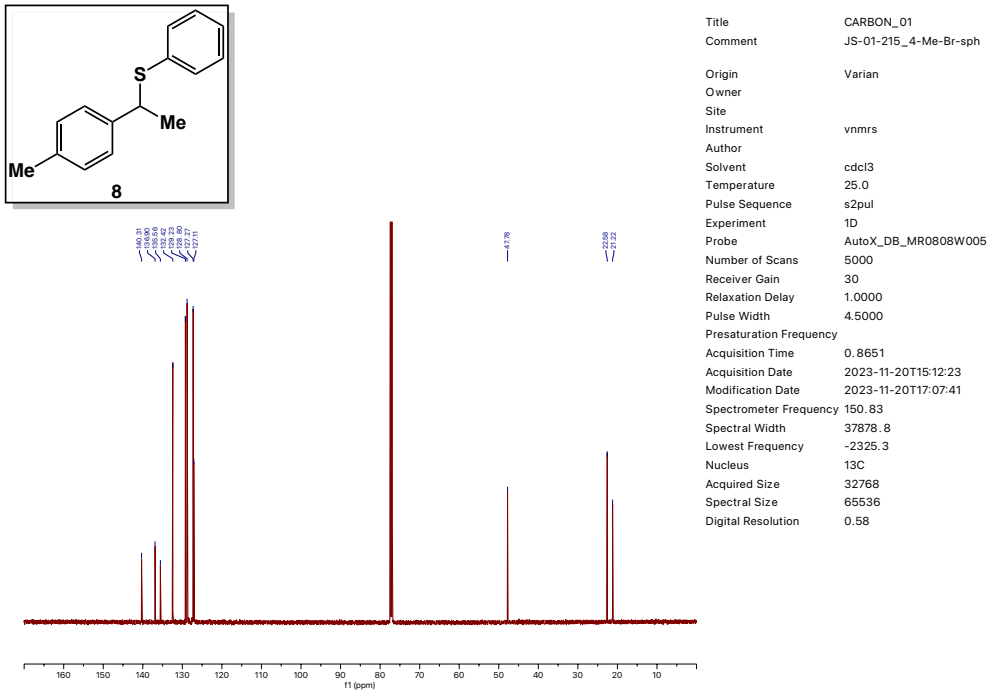
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	4000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Acquisition Time	0.8651
Acquisition Date	2023-10-06T16:13:40
Modification Date	2023-10-06T18:03:37
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2329.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 42. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 7.**



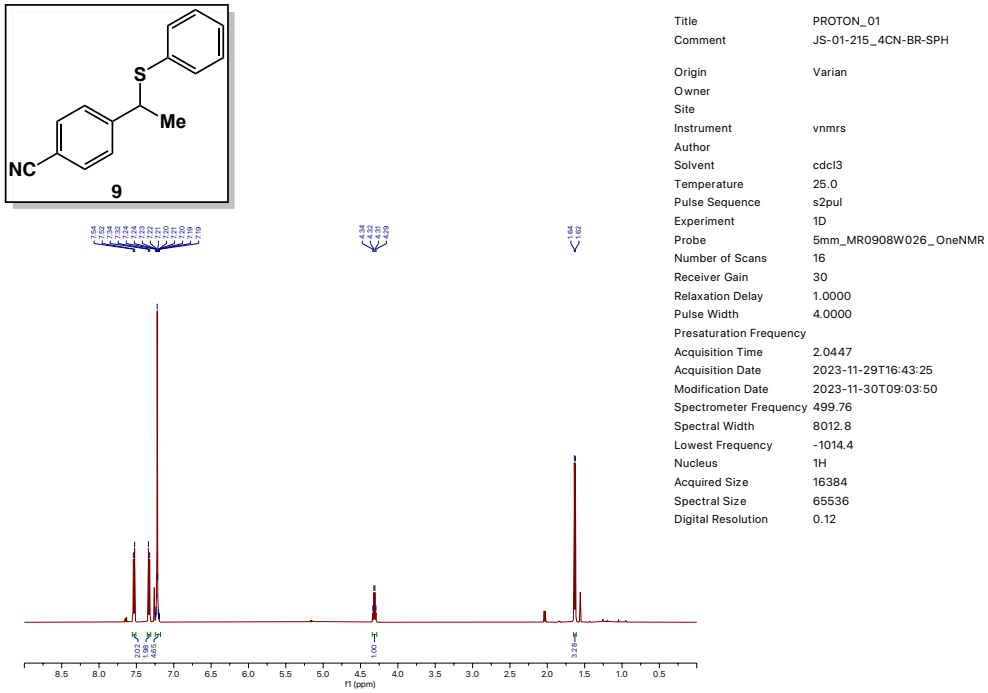
Title	PROTON_02
Comment	JS-01-215_4-Me-Br-sph
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2023-11-20T12:35:39
Modification Date	2023-11-20T17:07:41
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1201.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 43. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 8.**



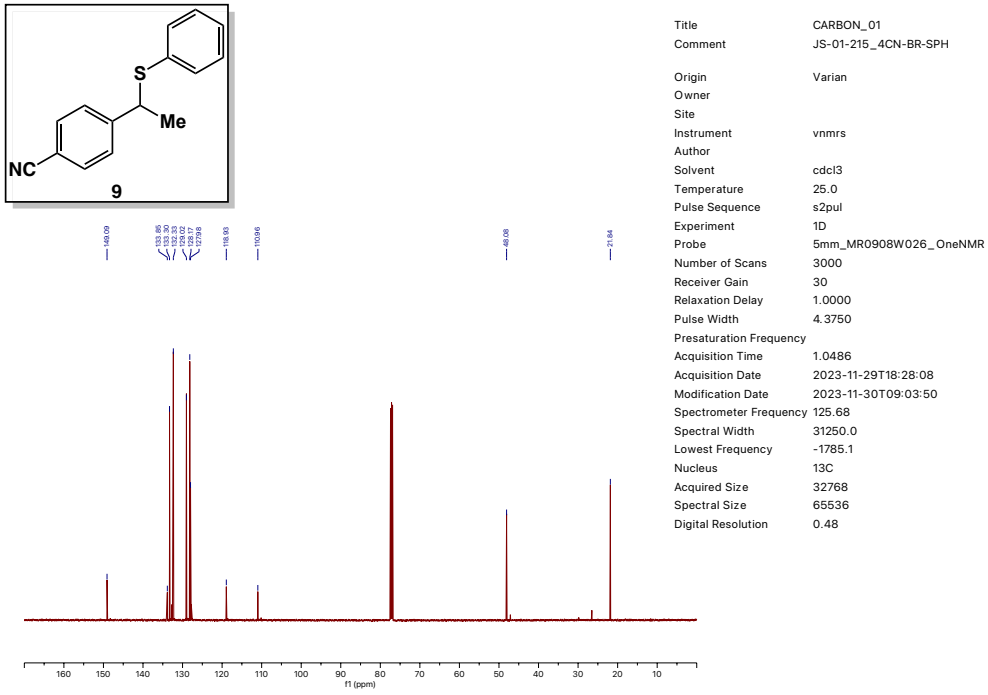
Title	CARBON_01
Comment	JS-01-215_4-Me-Br-sph
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2023-11-20T15:12:23
Modification Date	2023-11-20T17:07:41
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2325.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 44. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 8.**



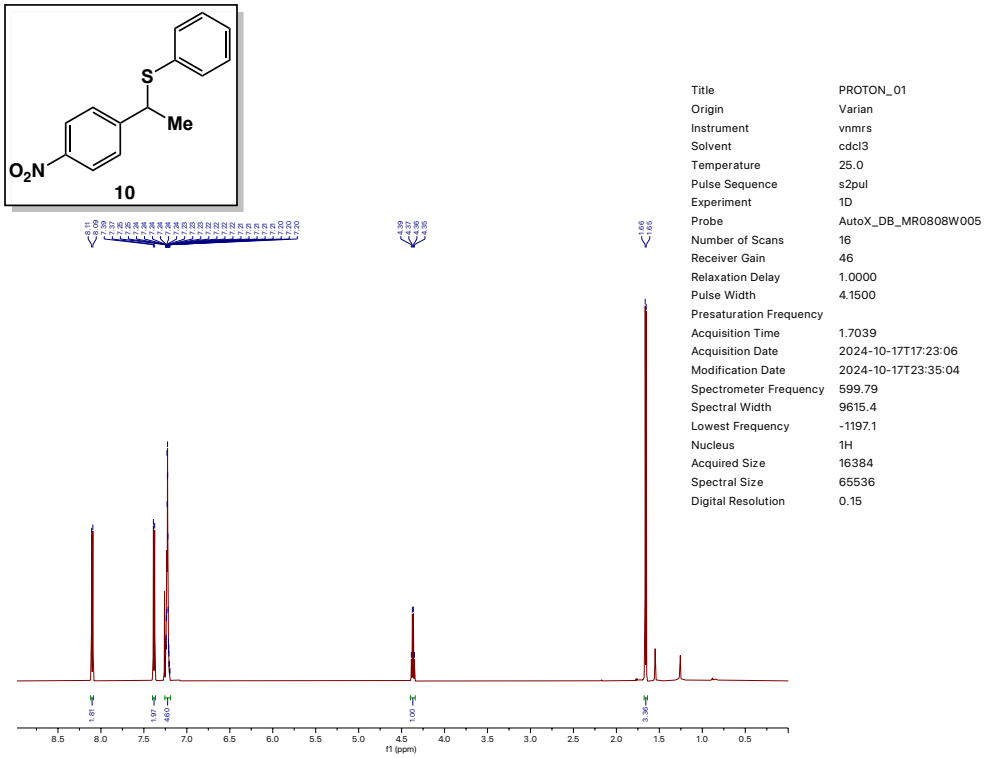
Title	PROTON_01
Comment	JS-01-215_4CN-BR-SPH
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-11-29T16:43:25
Modification Date	2023-11-30T09:03:50
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1014.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 45. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 9.**



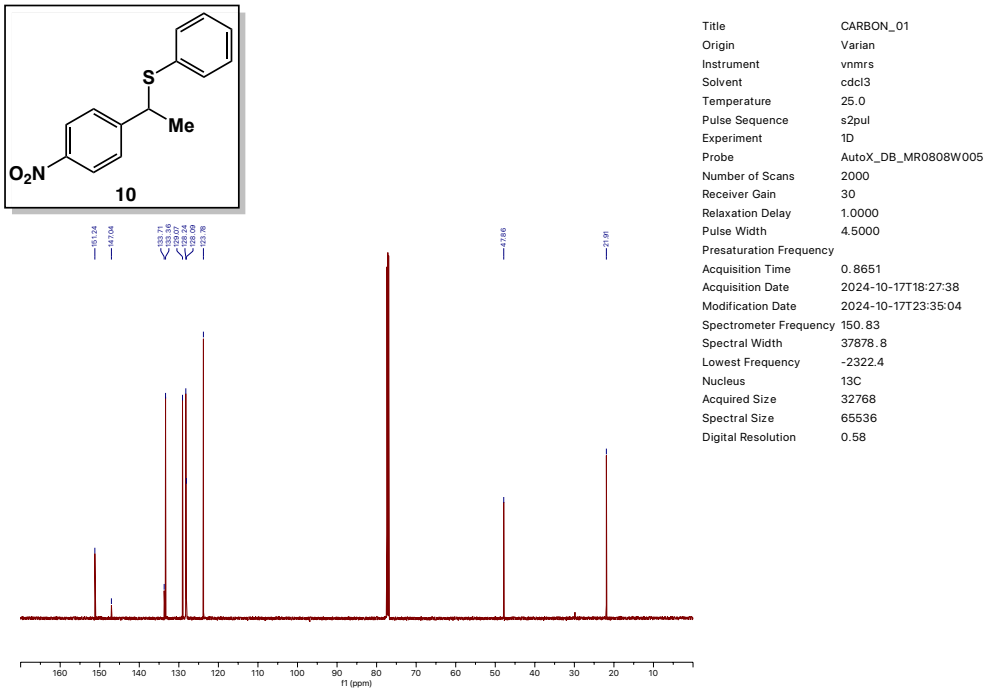
Title	CARBON_01
Comment	JS-01-215_4CN-BR-SPH
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2023-11-29T18:28:08
Modification Date	2023-11-30T09:03:50
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1785.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 46. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 9.**



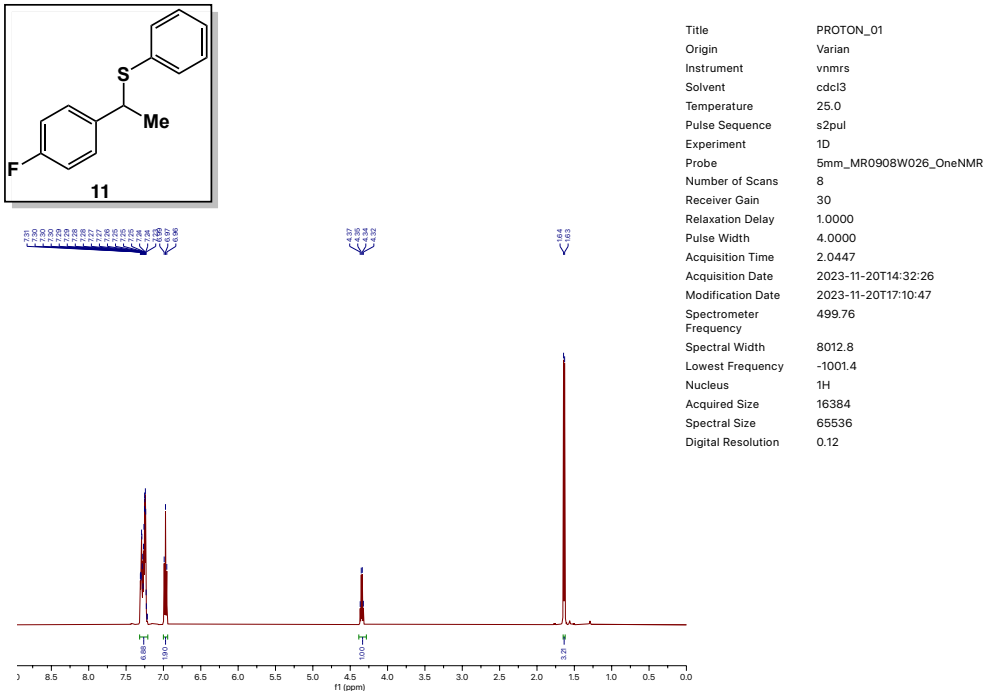
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-17T17:23:06
Modification Date	2024-10-17T23:35:04
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1197.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 47. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 10.**

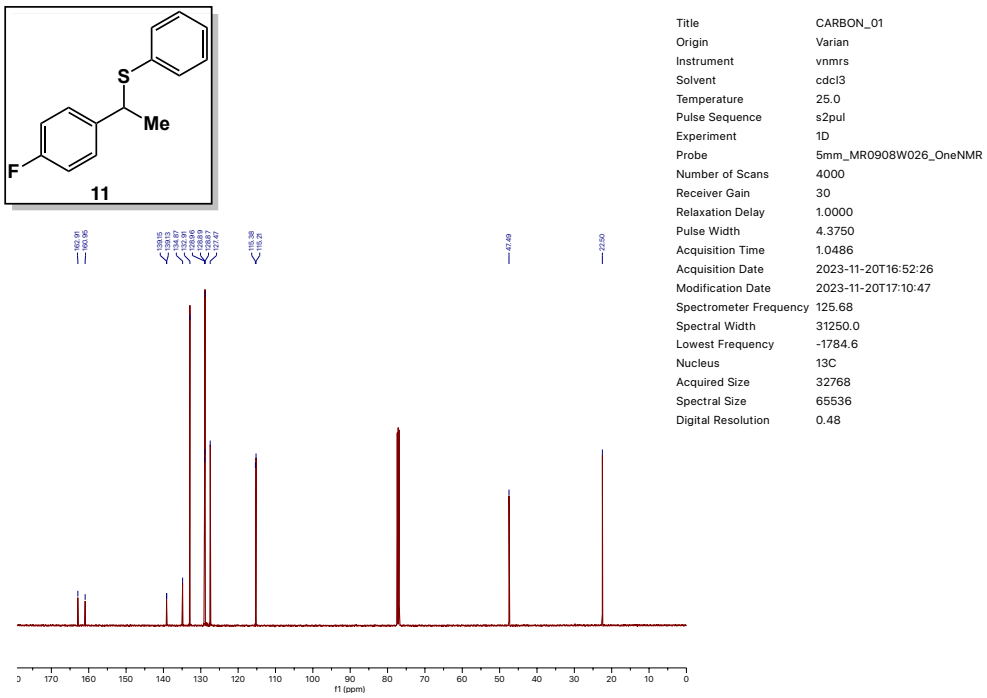


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-17T18:27:38
Modification Date	2024-10-17T23:35:04
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2322.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

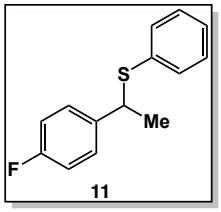
Supplementary Fig. 48. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 10.**



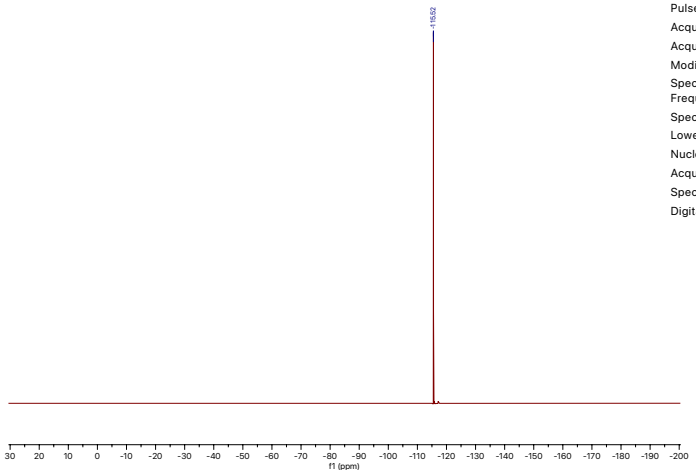
Supplementary Fig. 49. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 11.**



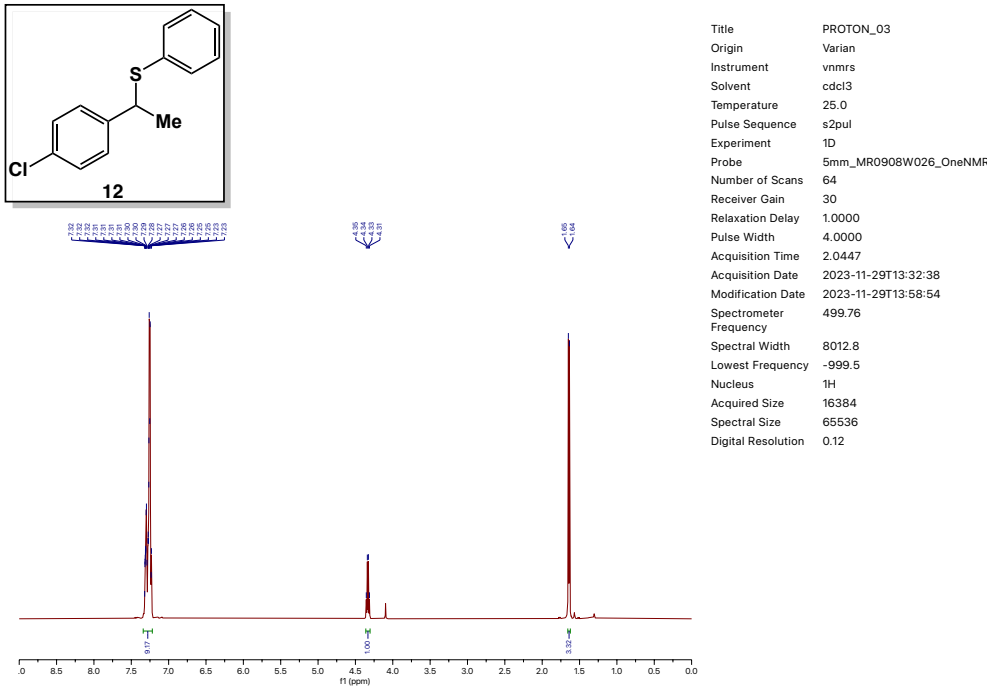
Supplementary Fig. 50. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 11.**



Title	FLUORINE_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	32
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2023-11-20T16:56:14
Modification Date	2023-11-20T17:10:48
Spectrometer Frequency	470.20
Spectral Width	108695.7
Lowest Frequency	-94318.4
Nucleus	19F
Acquired Size	65536
Spectral Size	131072
Digital Resolution	0.83

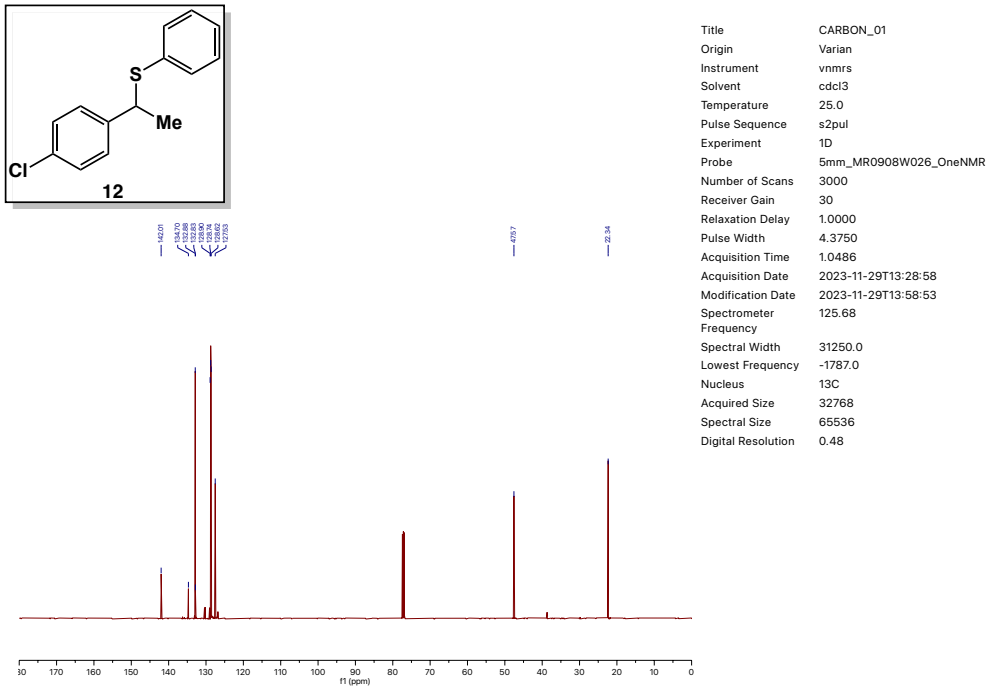


Supplementary Fig. 51. **^{19}F NMR (470 MHz, $CDCl_3$) spectrum of thioether 11**.



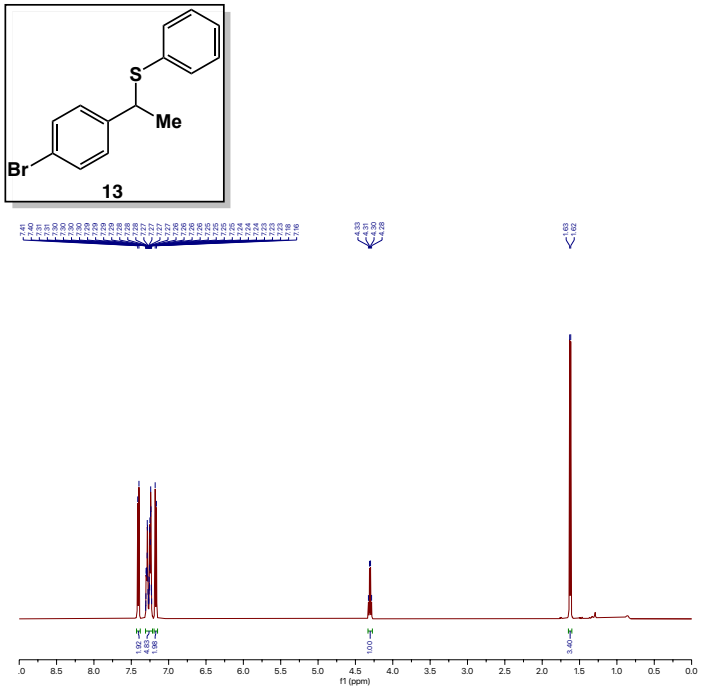
Title	PROTON_03
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-11-29T13:32:38
Modification Date	2023-11-29T13:58:54
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-999.5
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 52. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 12.**



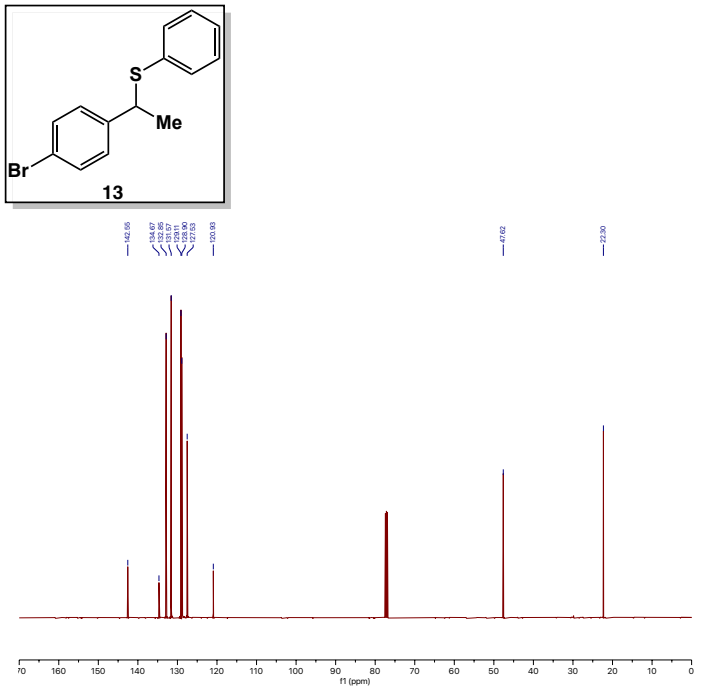
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-11-29T13:28:58
Modification Date	2023-11-29T13:58:53
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1787.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 53. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 12.**



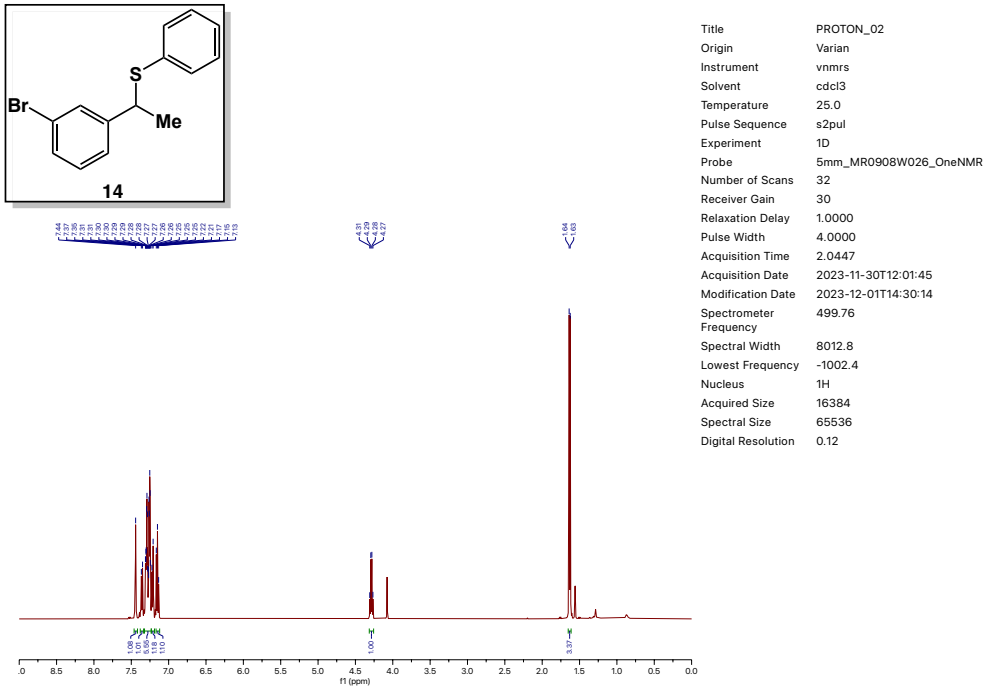
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-11-28T17:01:48
Modification Date	2023-11-29T09:57:21
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1001.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 54. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 13.**



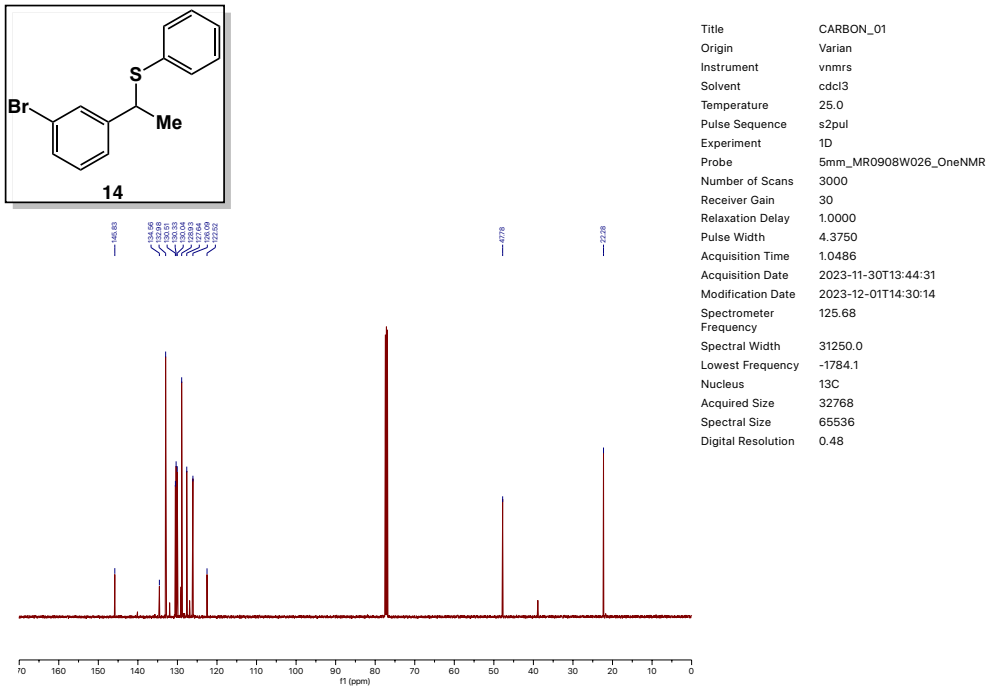
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	4000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-11-28T19:20:28
Modification Date	2023-11-29T09:57:21
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1786.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 55. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 13.**



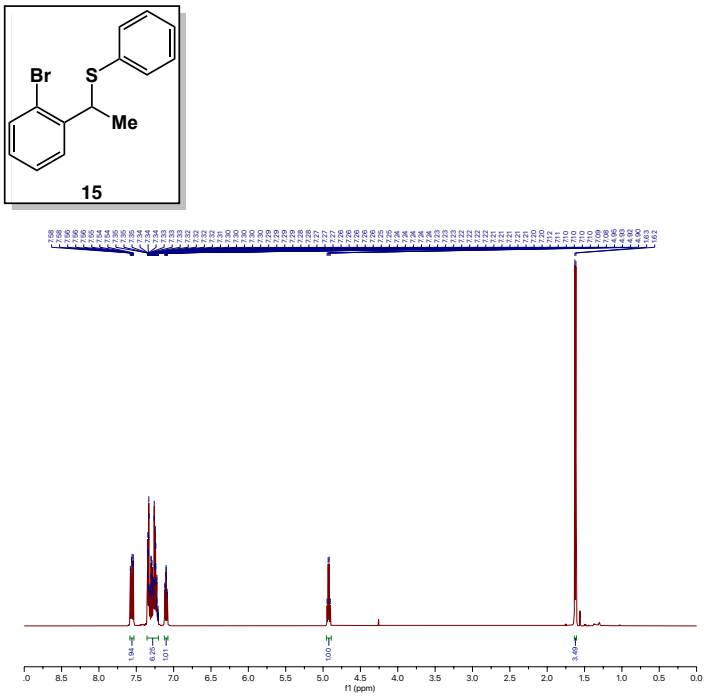
Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	32
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-11-30T12:01:45
Modification Date	2023-12-01T14:30:14
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1002.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 56. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 14.**



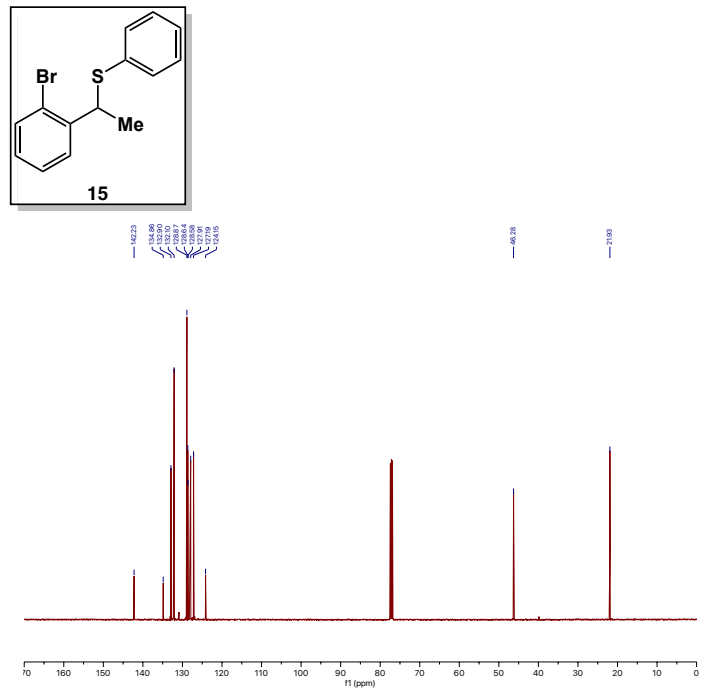
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-11-30T13:44:31
Modification Date	2023-12-01T14:30:14
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 57. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 14.**



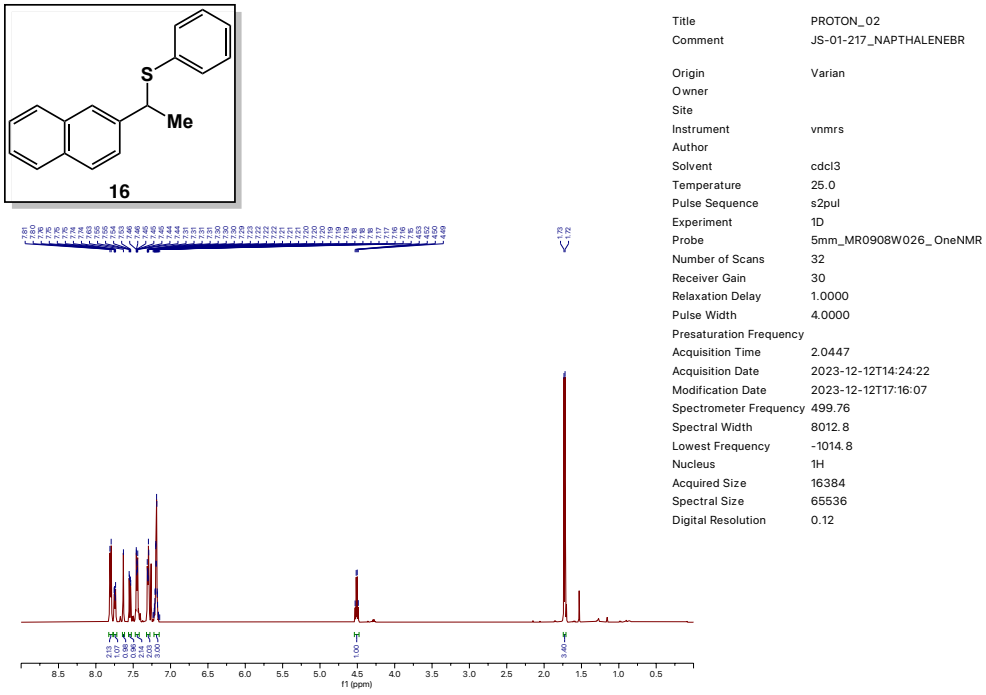
Title	PROTON_03
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-11-30T18:23:44
Modification Date	2023-12-01T14:29:12
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-998.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 58. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 15.**

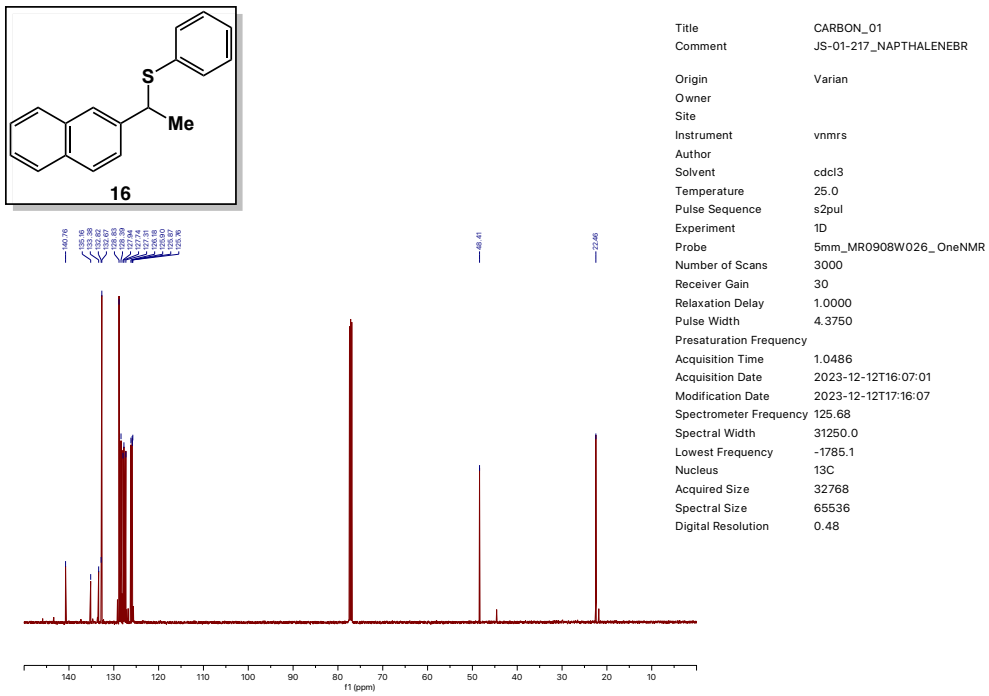


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-11-30T18:20:03
Modification Date	2023-12-01T14:29:12
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1785.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

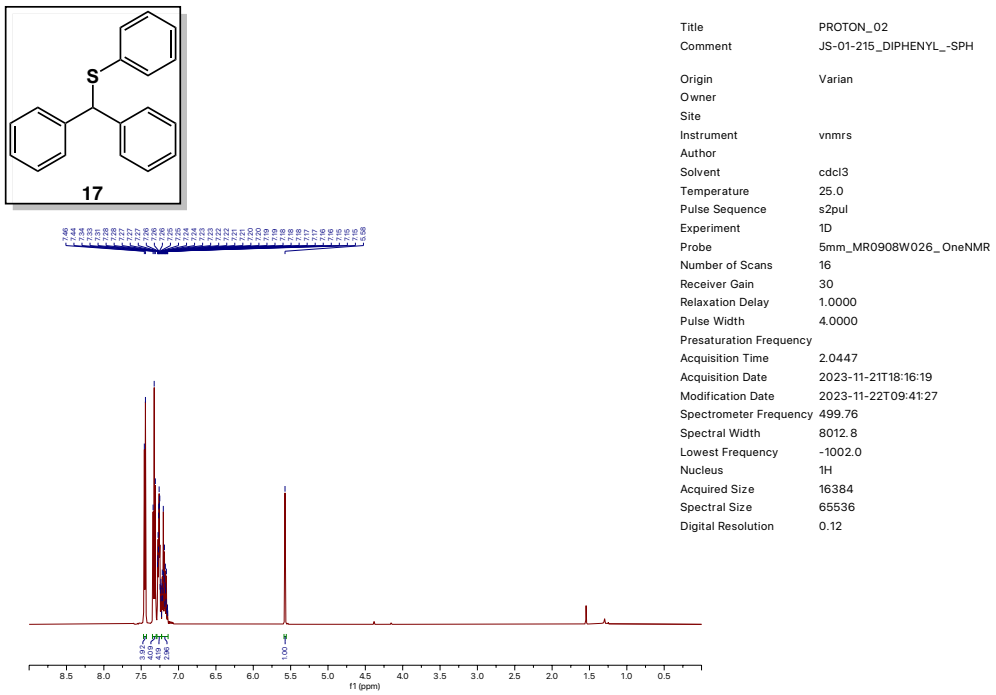
Supplementary Fig. 59. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 15.**



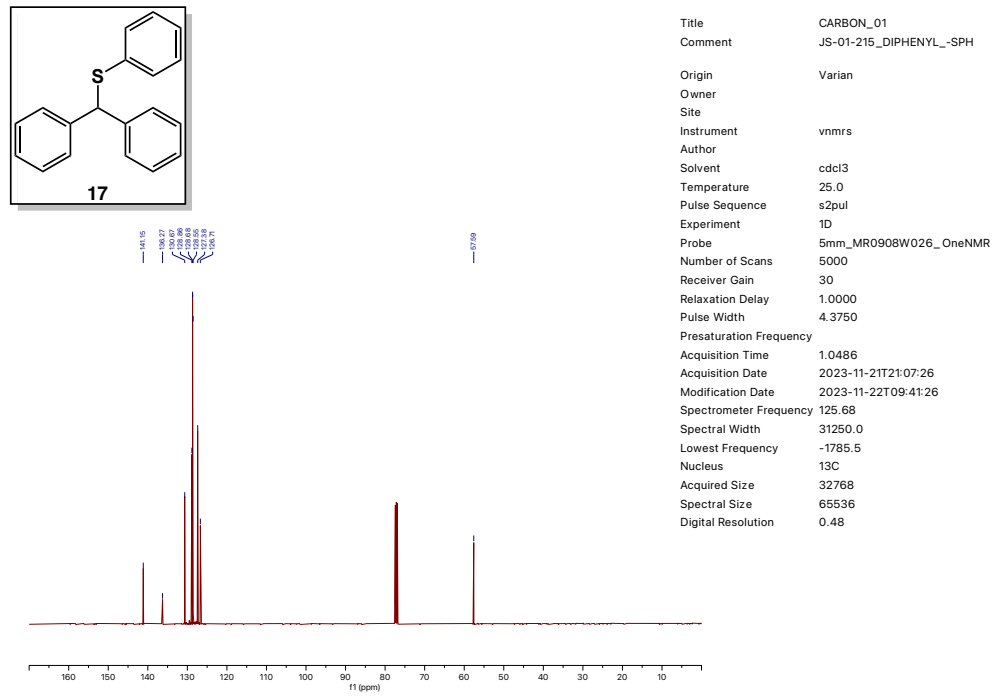
Supplementary Fig. 60. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 16.**



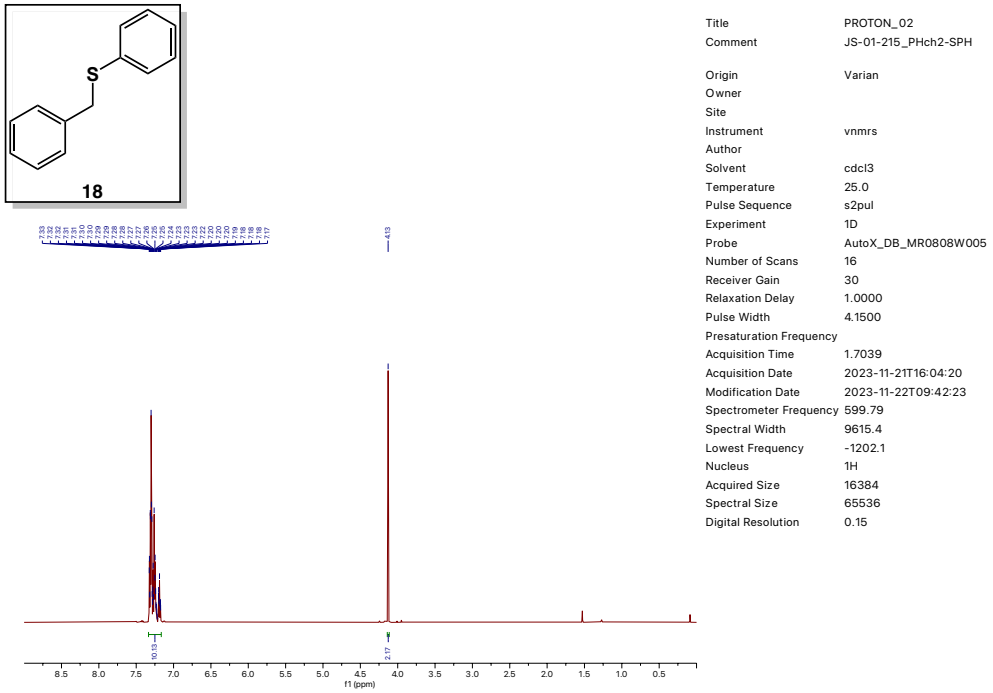
Supplementary Fig. 61. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 16.**



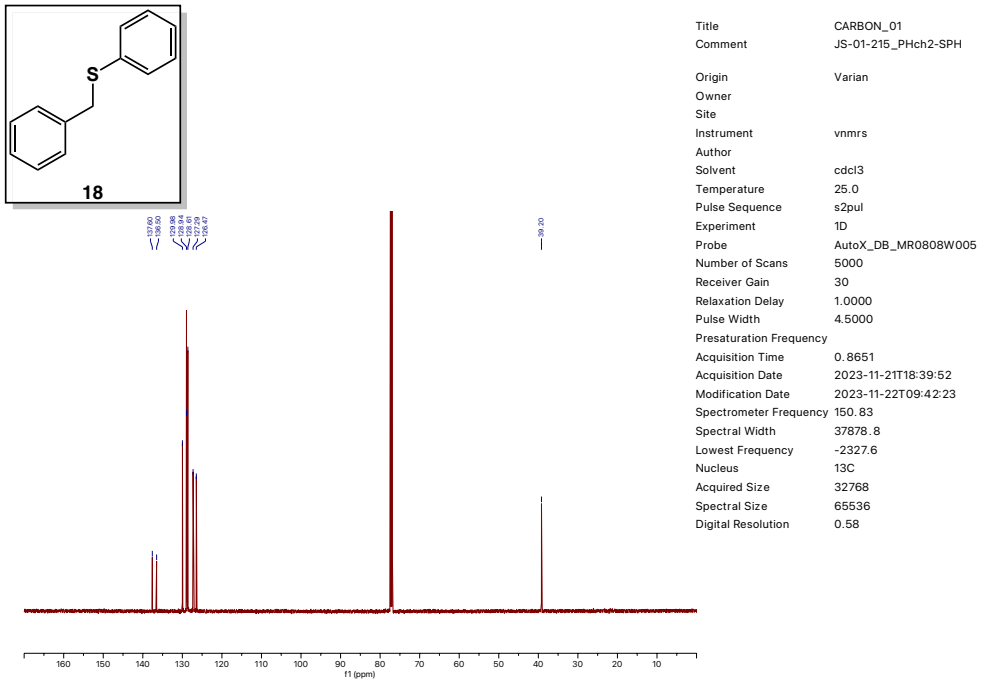
Supplementary Fig. 62. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 17.**



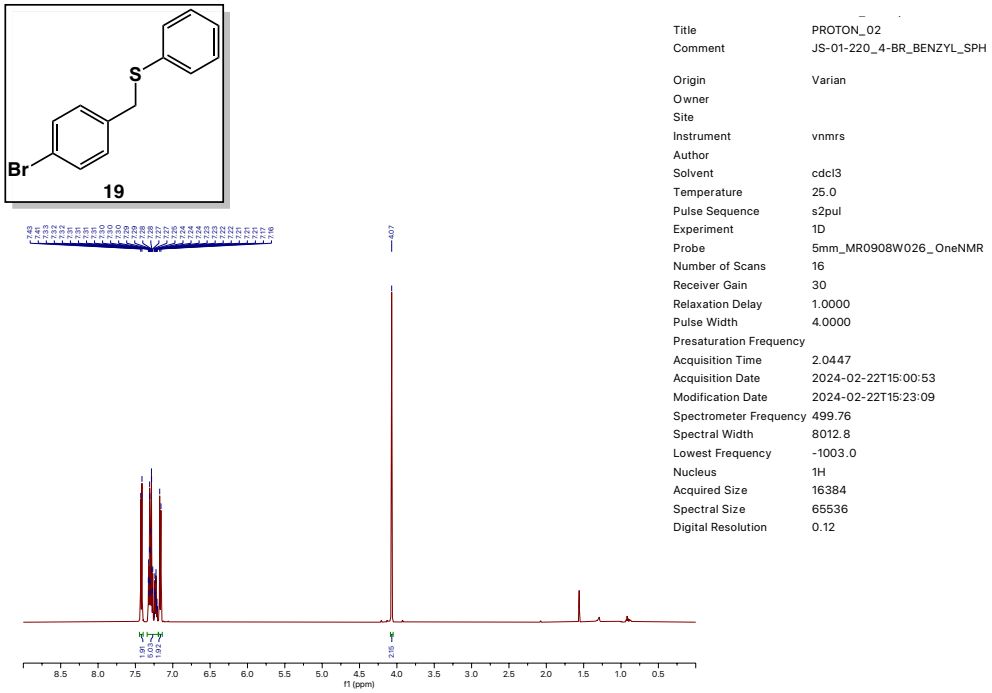
Supplementary Fig. 63. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 17.**



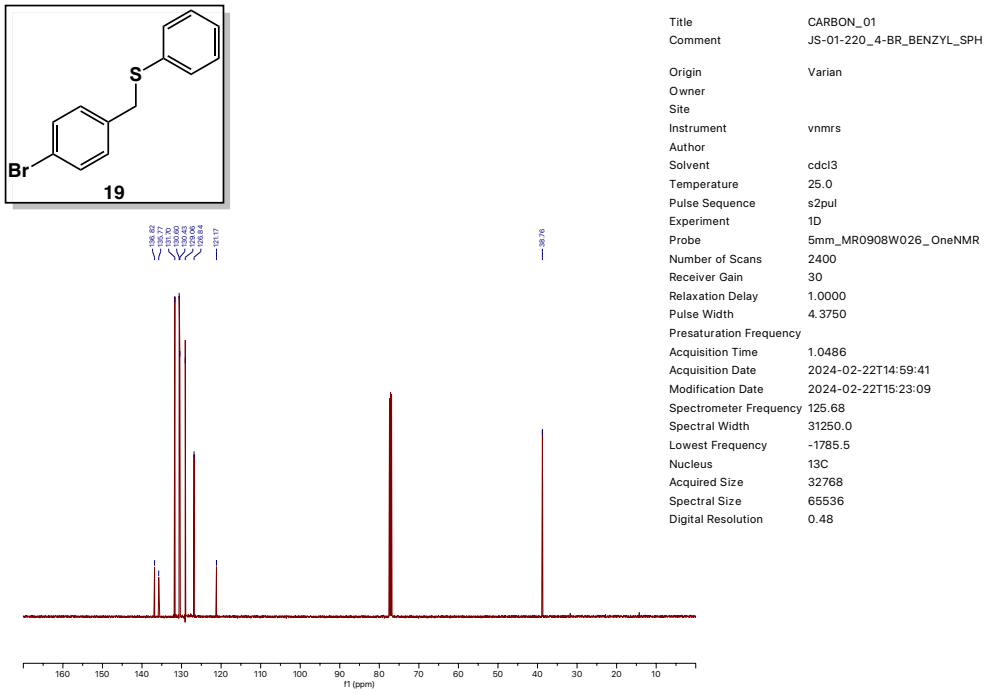
Supplementary Fig. 64. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 18.**



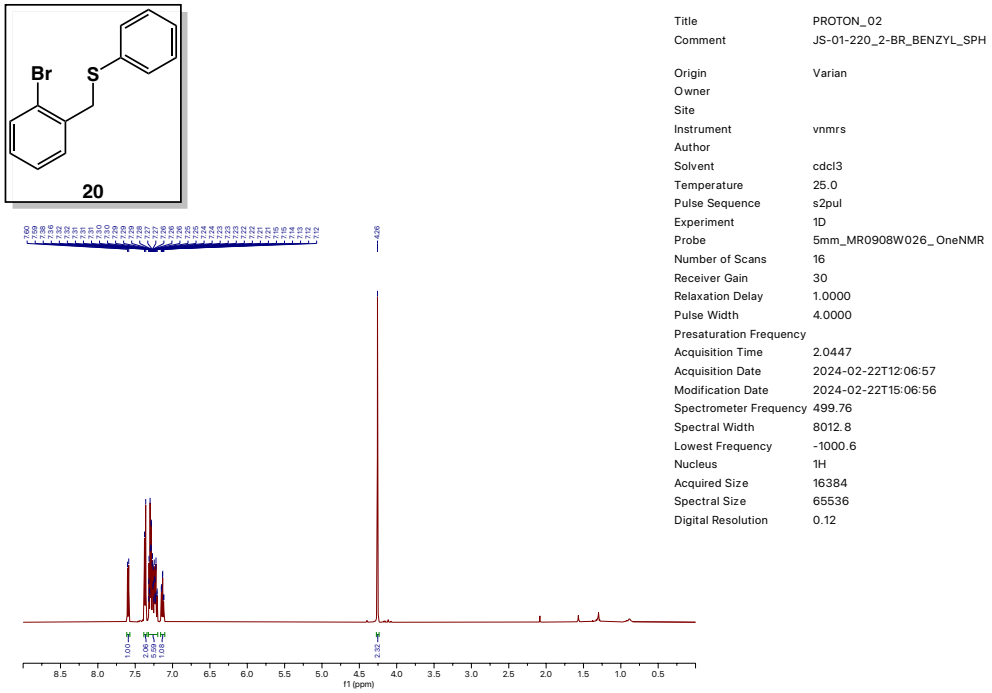
Supplementary Fig. 65. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 18.**



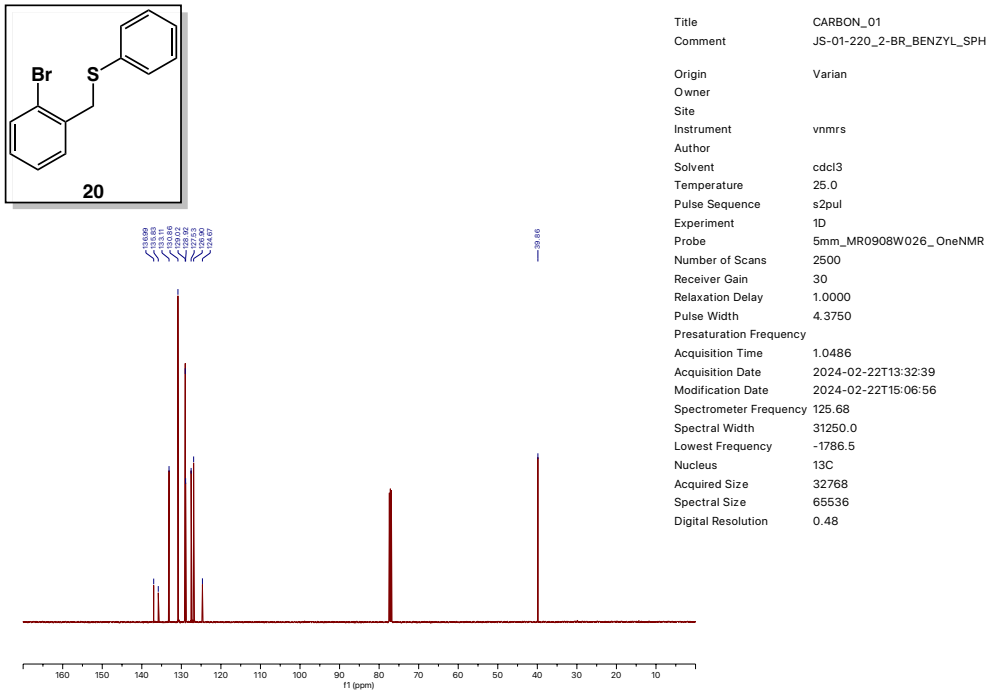
Supplementary Fig. 66. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 19.**



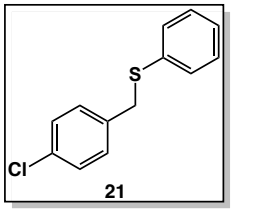
Supplementary Fig. 67. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 19.**

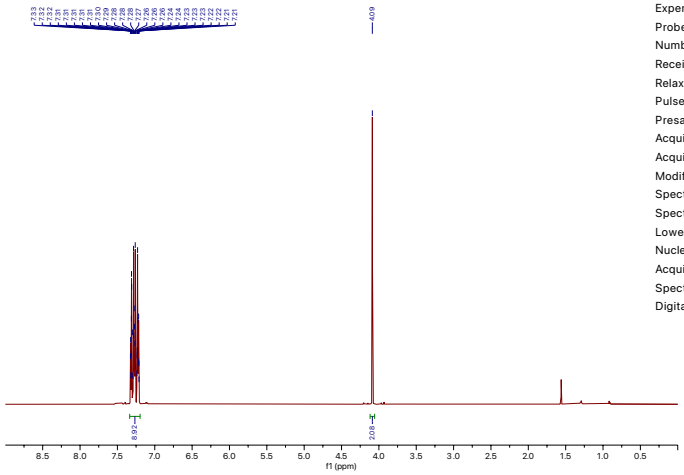


Supplementary Fig. 68. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 20.**



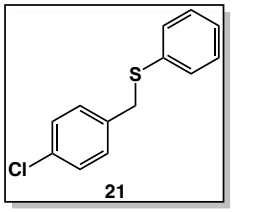
Supplementary Fig. 69. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 20.**

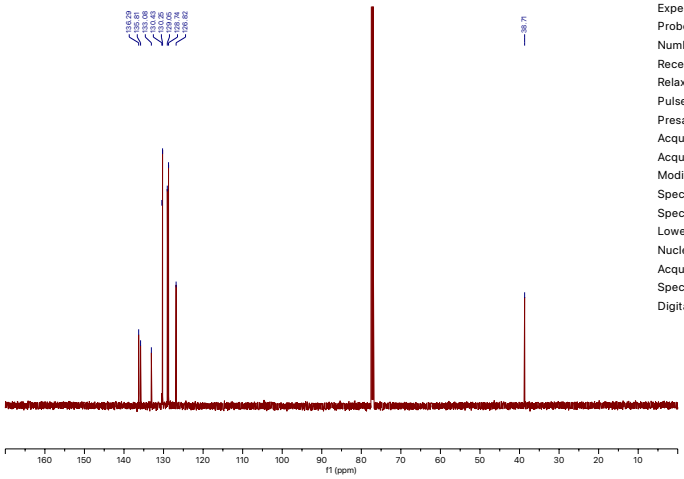




Title	PROTON_02
Comment	JS-01-220_4CL-BENZYL_SPH
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	32
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-02-22T14:40:21
Modification Date	2024-02-22T16:12:50
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1186.5
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

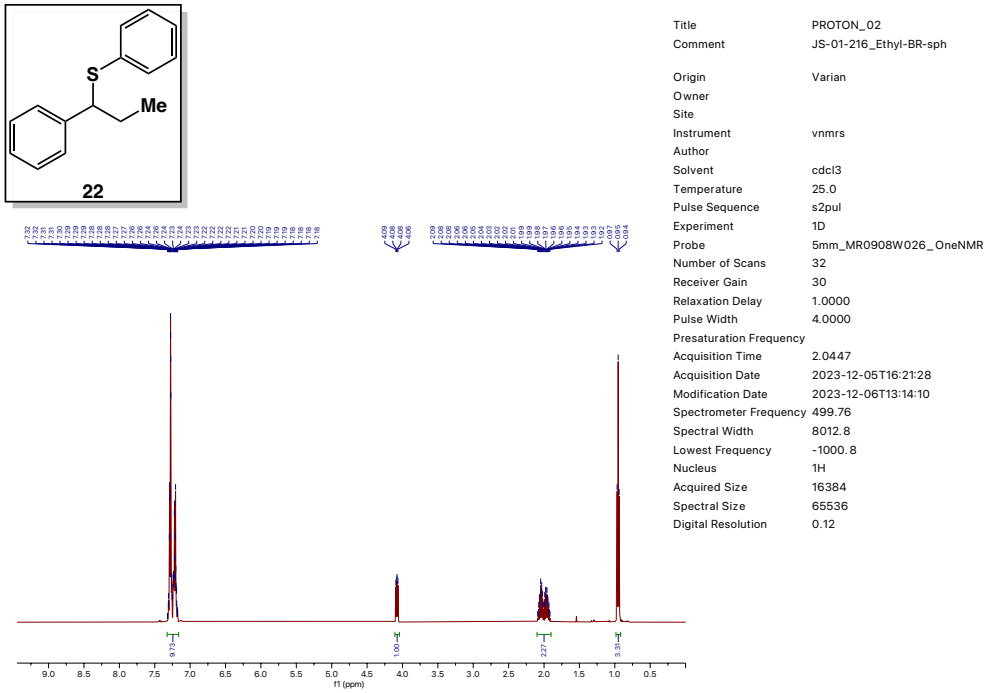
Supplementary Fig. 70. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 21.**



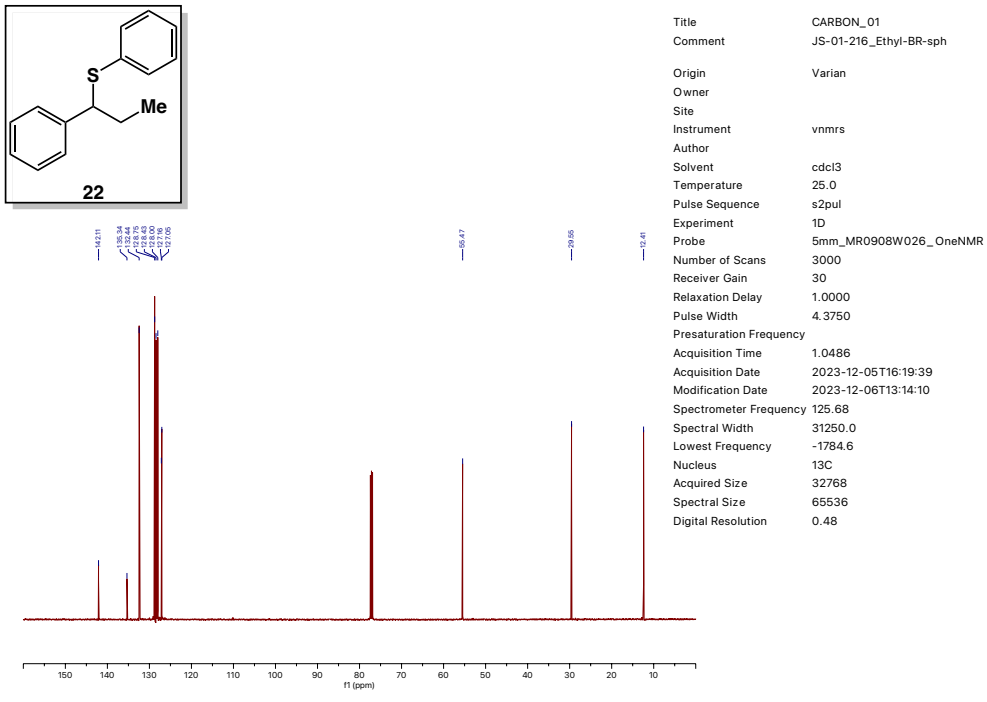


Title	CARBON_01
Comment	JS-01-220_4CL-BENZYL_SPH
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-02-22T15:58:10
Modification Date	2024-02-22T16:12:50
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2325.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

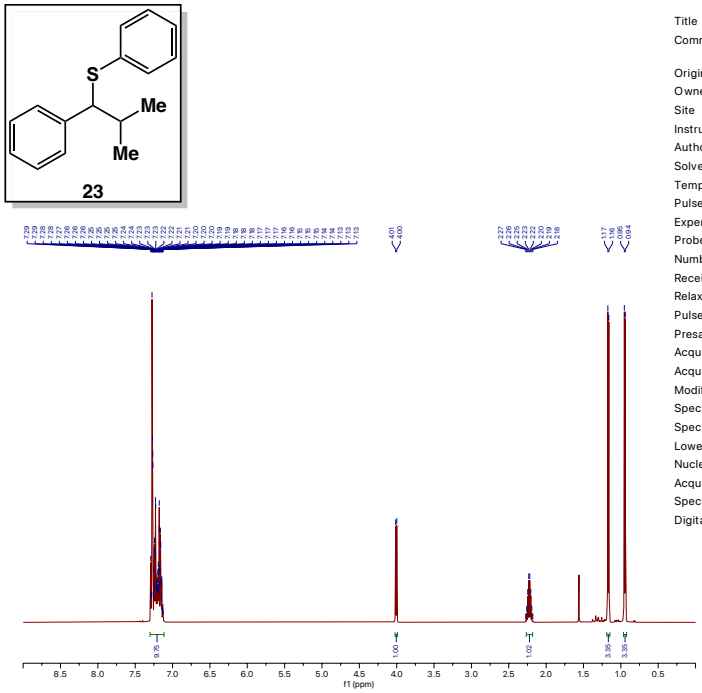
Supplementary Fig. 71. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 21.**



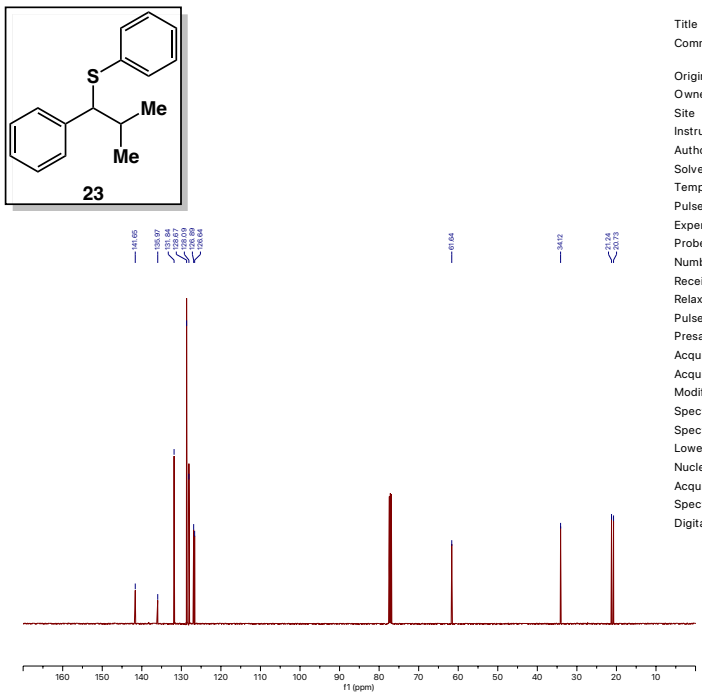
Supplementary Fig. 72. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 22.**



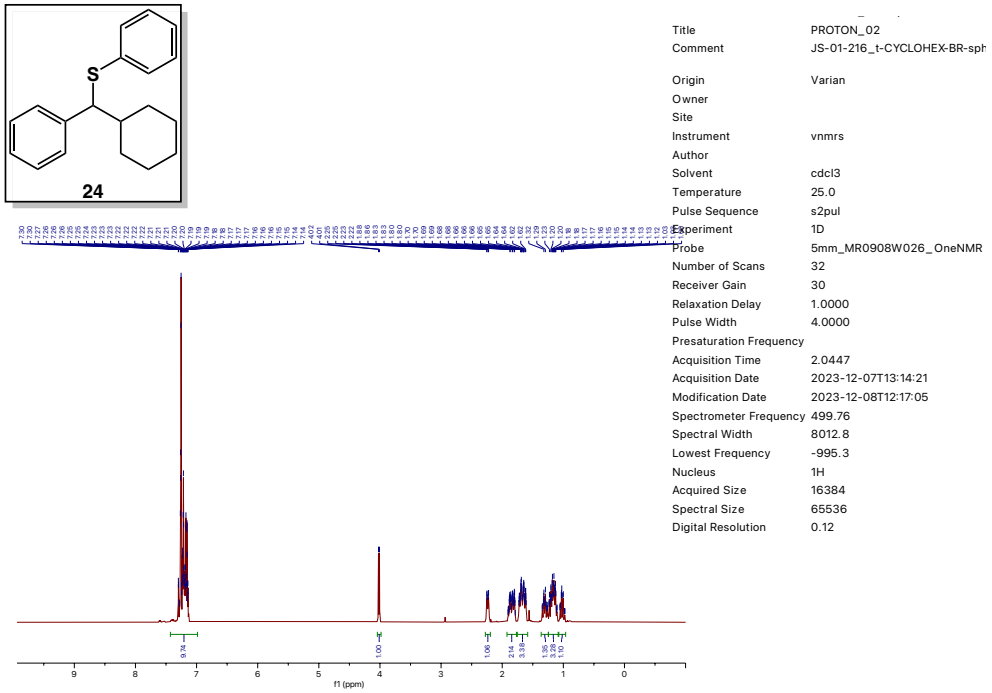
Supplementary Fig. 73. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 22.**



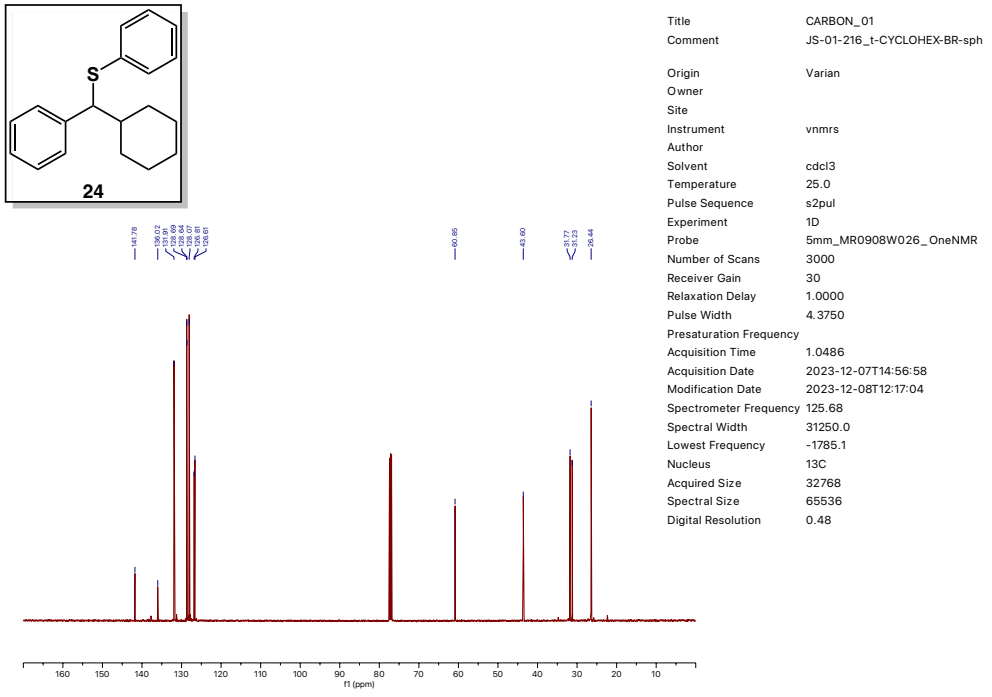
Supplementary Fig. 74. **^{13}C NMR (500 MHz, $CDCl_3$) spectrum of thioether 23.**



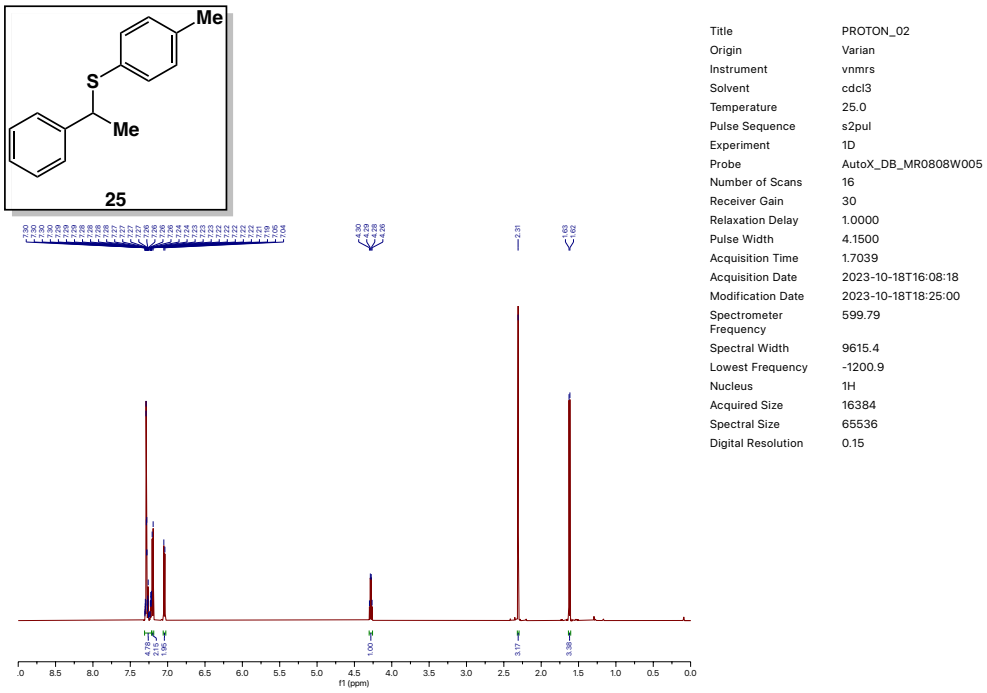
Supplementary Fig. 75. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 23.**



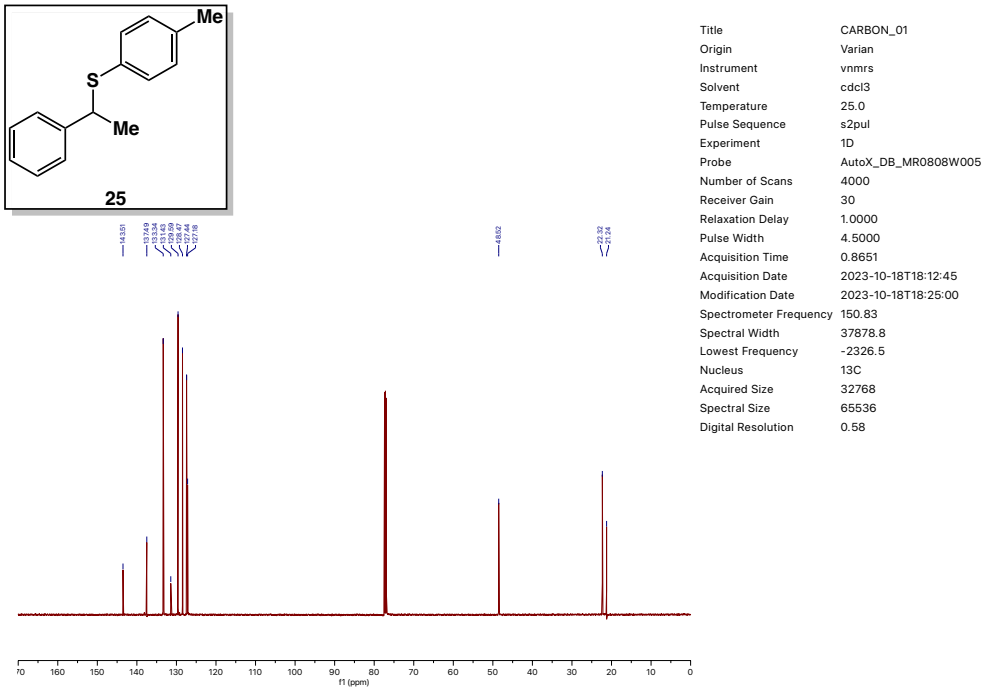
Supplementary Fig. 76. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 24.**



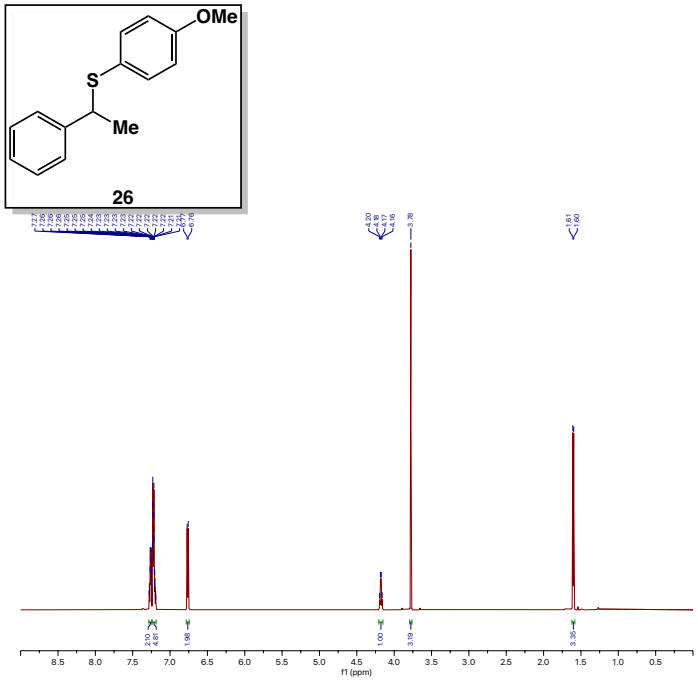
Supplementary Fig. 77. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 24.**



Supplementary Fig. 78. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 25.**

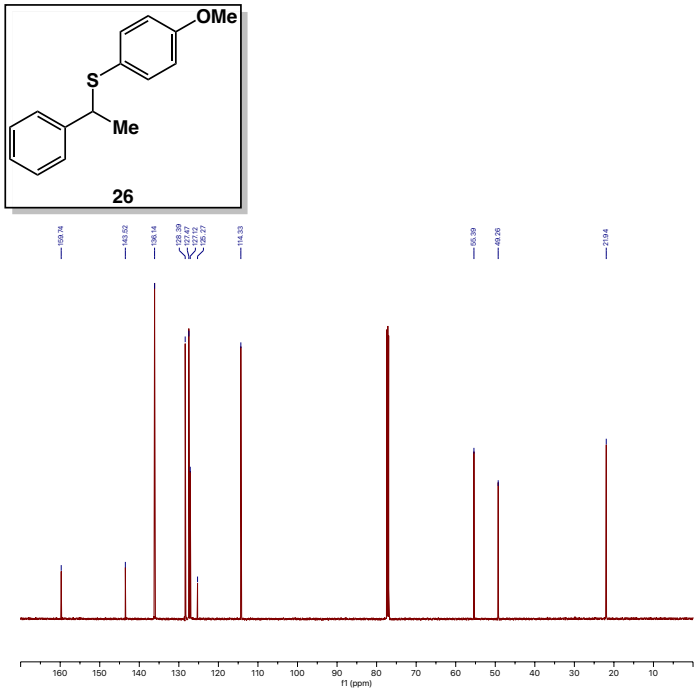


Supplementary Fig. 79. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 25.**



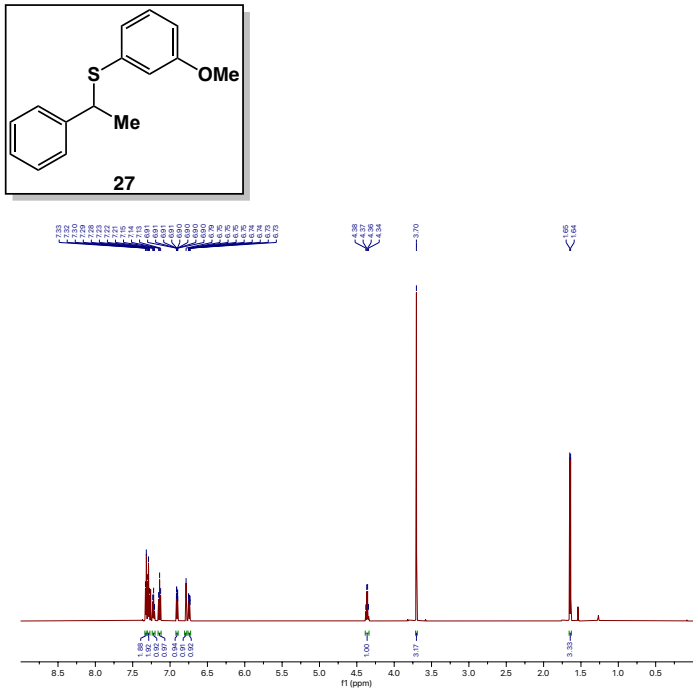
Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	32
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-18T13:44:22
Modification Date	2024-10-18T23:46:33
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1200.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 80. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 26.**



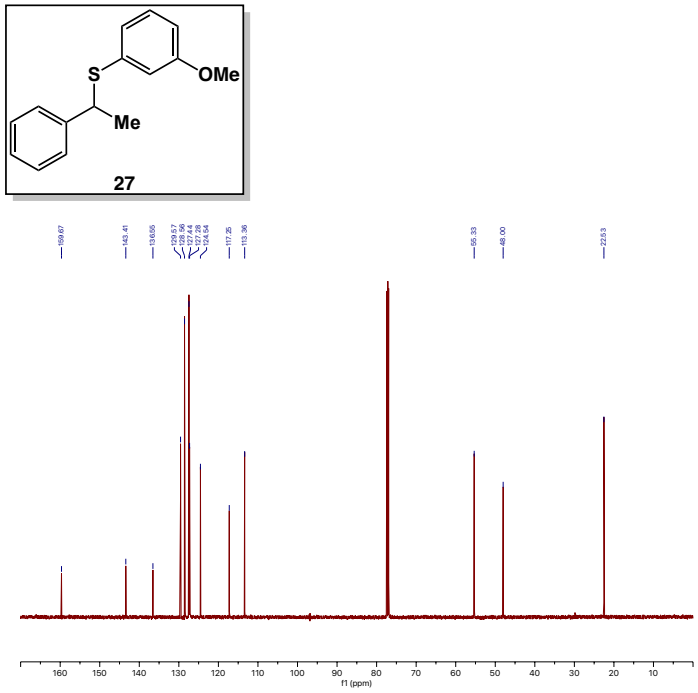
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2300
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-18T13:42:46
Modification Date	2024-10-18T23:46:32
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2325.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 81. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 26.**



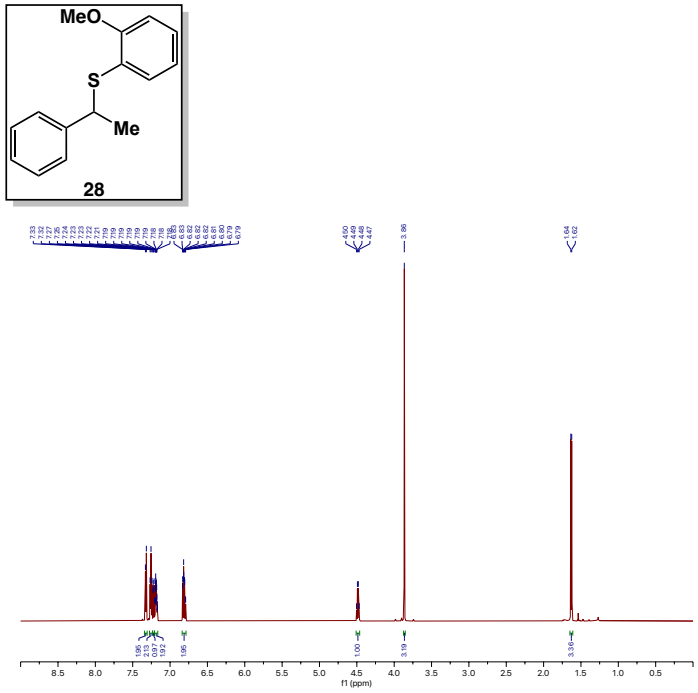
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-23T11:28:30
Modification Date	2024-10-23T14:17:37
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1204.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 82. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 27.**



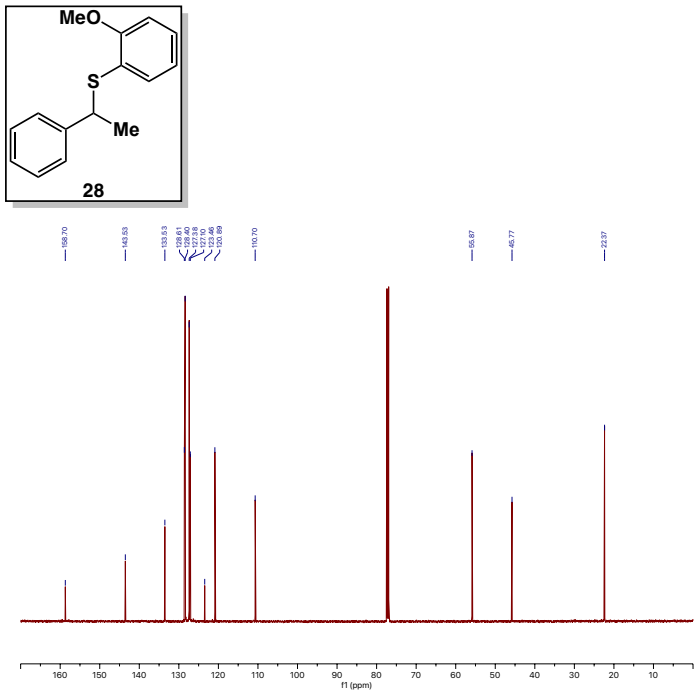
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	950
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-23T12:00:16
Modification Date	2024-10-23T14:17:37
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2325.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 83. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 27.**



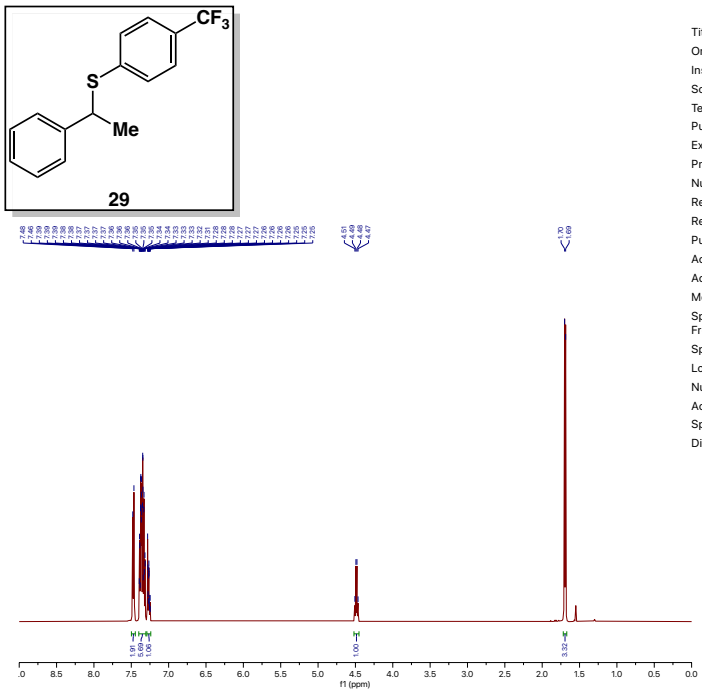
Title	PROTON_03
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-18T15:18:18
Modification Date	2024-10-18T23:46:22
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1200.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 84. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 28.**



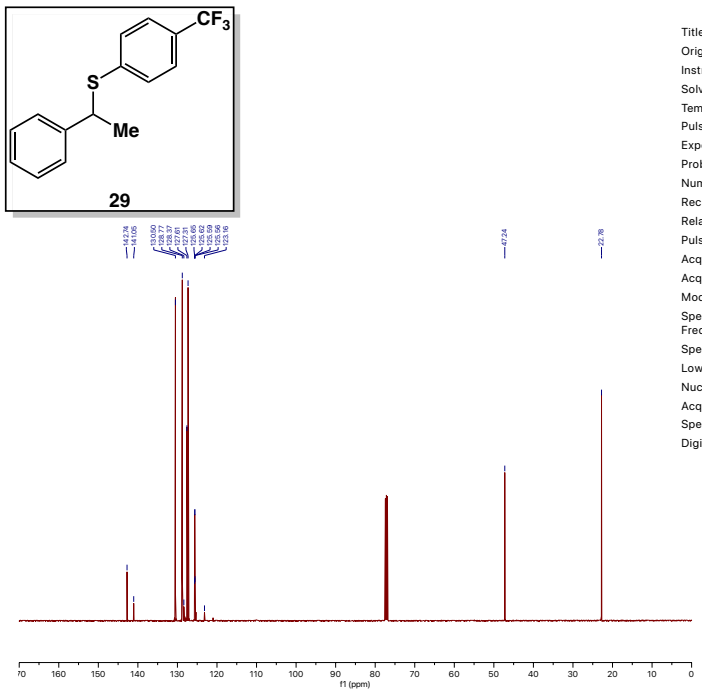
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-18T15:15:15
Modification Date	2024-10-18T23:46:14
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2326.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 85. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 28.**



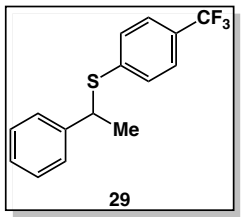
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-09T18:28:24
Modification Date	2023-10-10T13:50:50
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1001.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 86. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 29.**

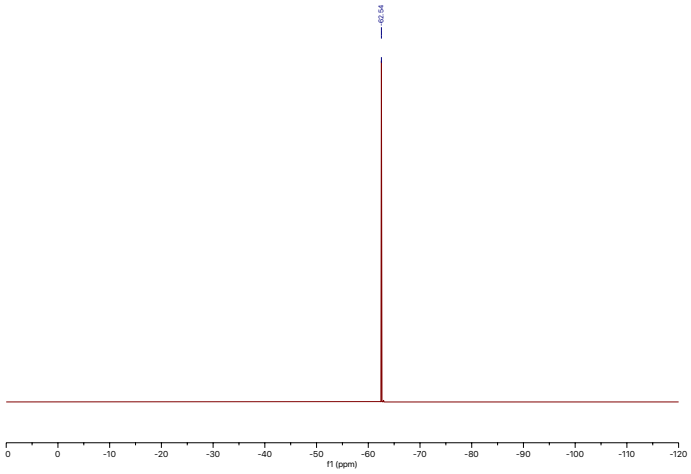


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-10-09T21:29:16
Modification Date	2023-10-10T13:50:51
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1783.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

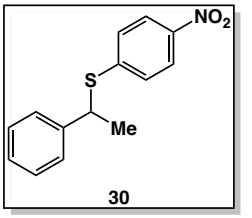
Supplementary Fig. 87. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 29.**

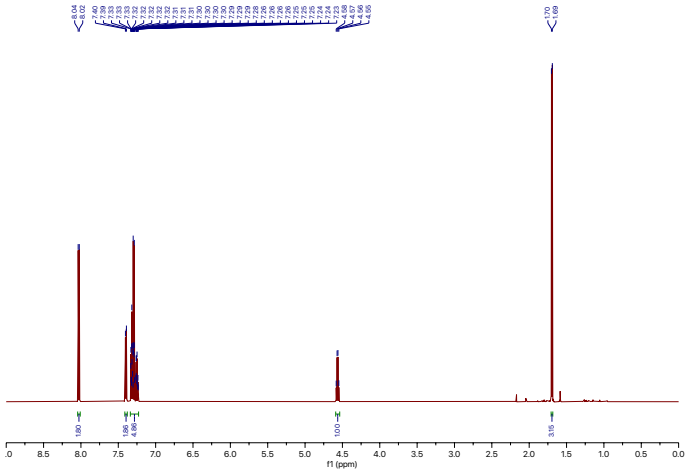


Title	FLUORINE_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	64
Receiver Gain	48
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2023-10-09T18:35:28
Modification Date	2023-10-10T13:50:51
Spectrometer Frequency	470.20
Spectral Width	108695.7
Lowest Frequency	-94318.4
Nucleus	19F
Acquired Size	65536
Spectral Size	131072
Digital Resolution	0.83



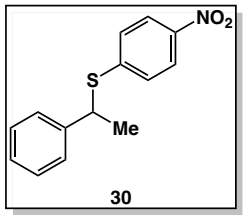
Supplementary Fig. 88. **^{19}F NMR (470 MHz, $CDCl_3$) spectrum of thioether 29.**

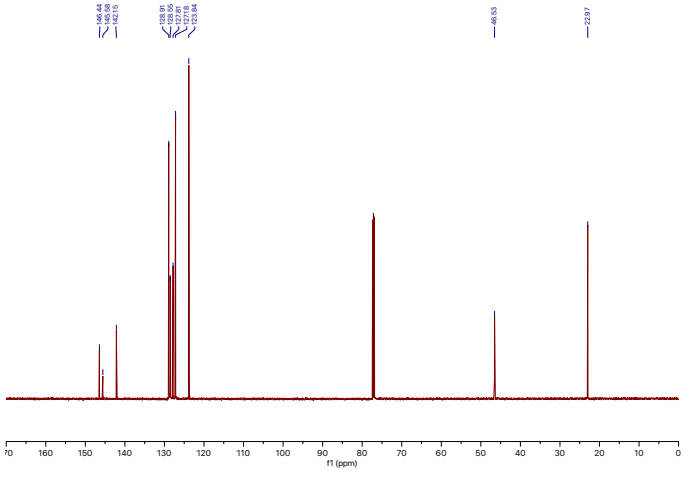




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Acquisition Time	1.7039
Acquisition Date	2023-10-13T15:47:23
Modification Date	2023-10-14T21:49:13
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1203.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

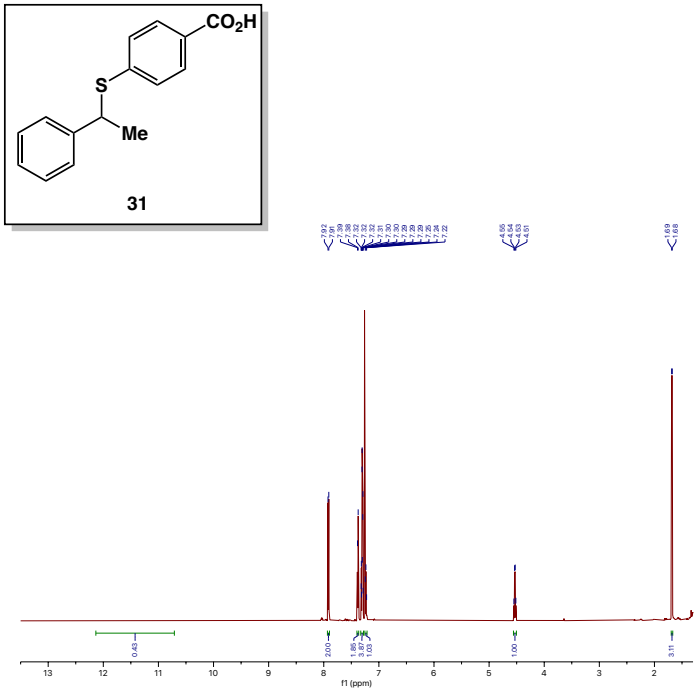
Supplementary Fig. 89. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 30.**





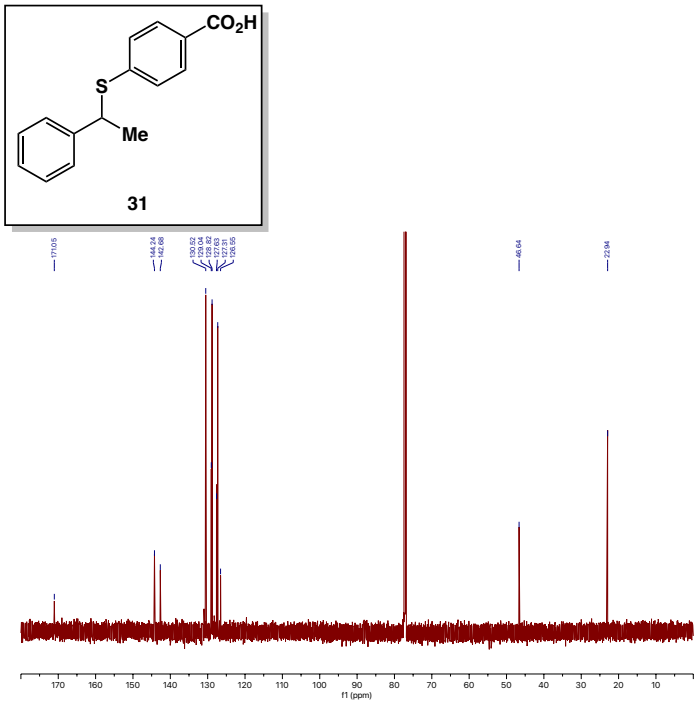
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Acquisition Time	0.8651
Acquisition Date	2023-10-13T17:22:53
Modification Date	2023-10-14T21:49:13
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2333.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 90. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 30.**



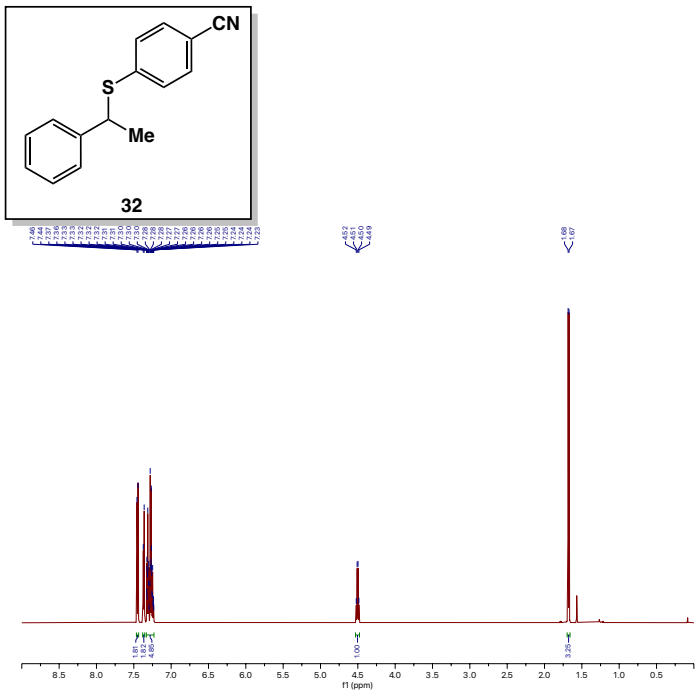
Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	32
Receiver Gain	50
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-24T09:44:17
Modification Date	2024-10-24T10:52:35
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1200.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 91. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 31.**



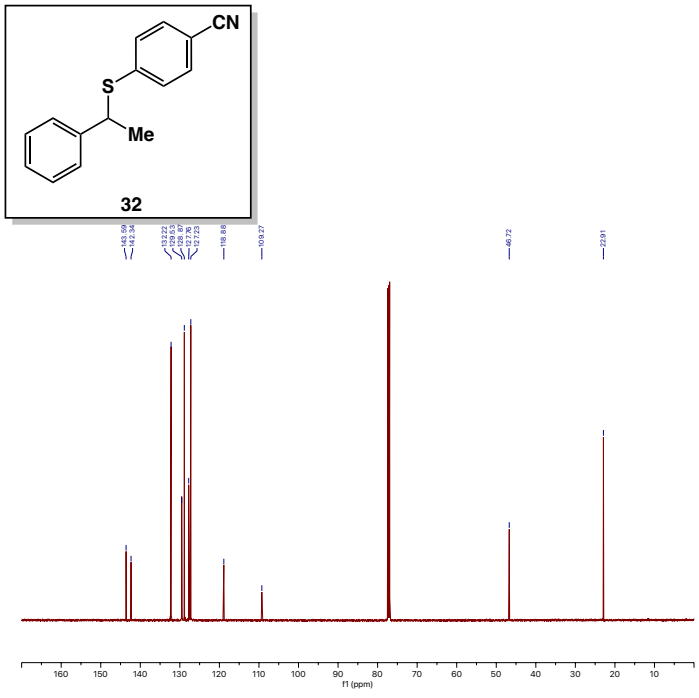
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	1500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-11T15:59:36
Modification Date	2024-10-11T16:07:58
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2321.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 92. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 31.**



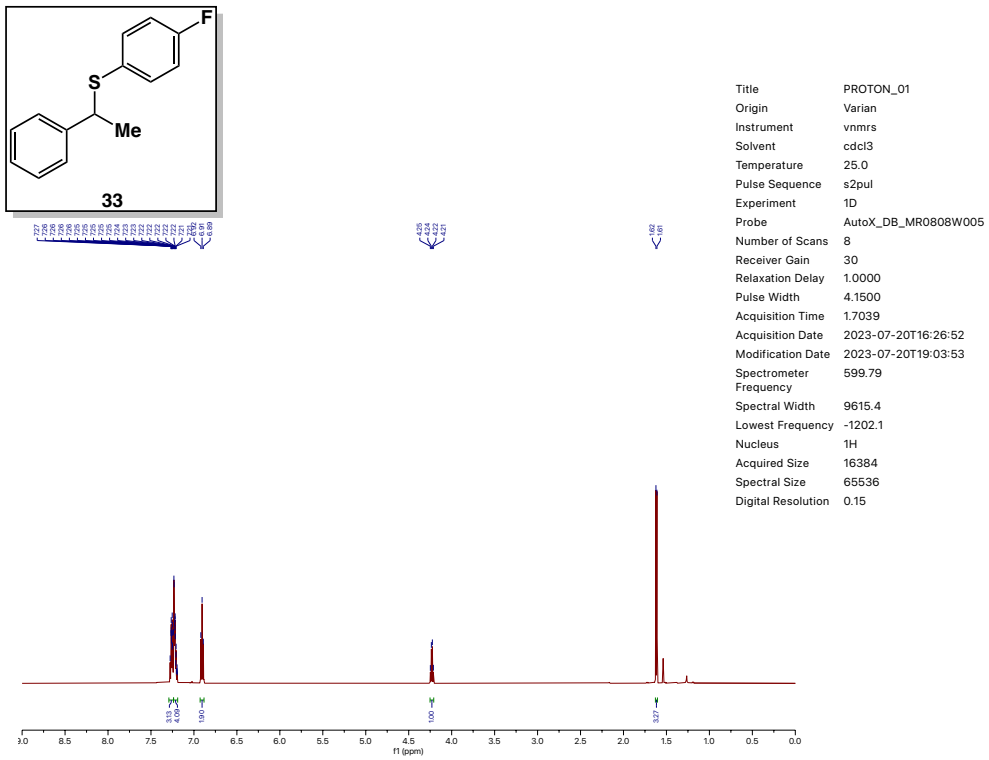
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-11T12:55:18
Modification Date	2024-10-11T16:07:58
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1198.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 93. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 32.**

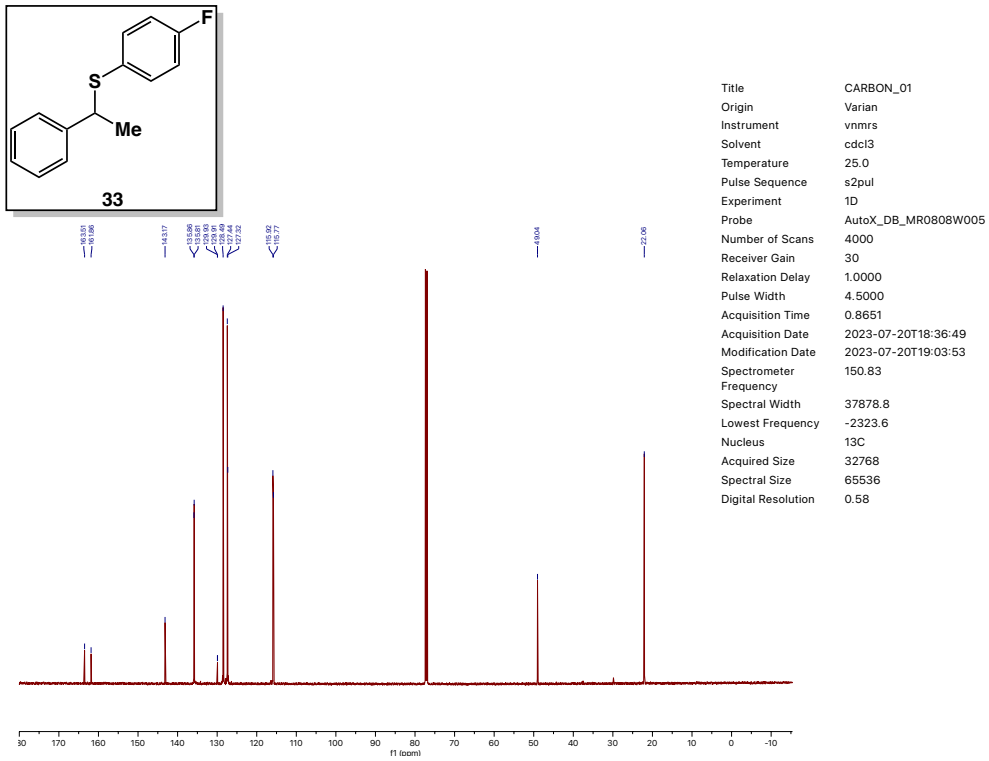


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-11T14:16:46
Modification Date	2024-10-11T16:07:58
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2326.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

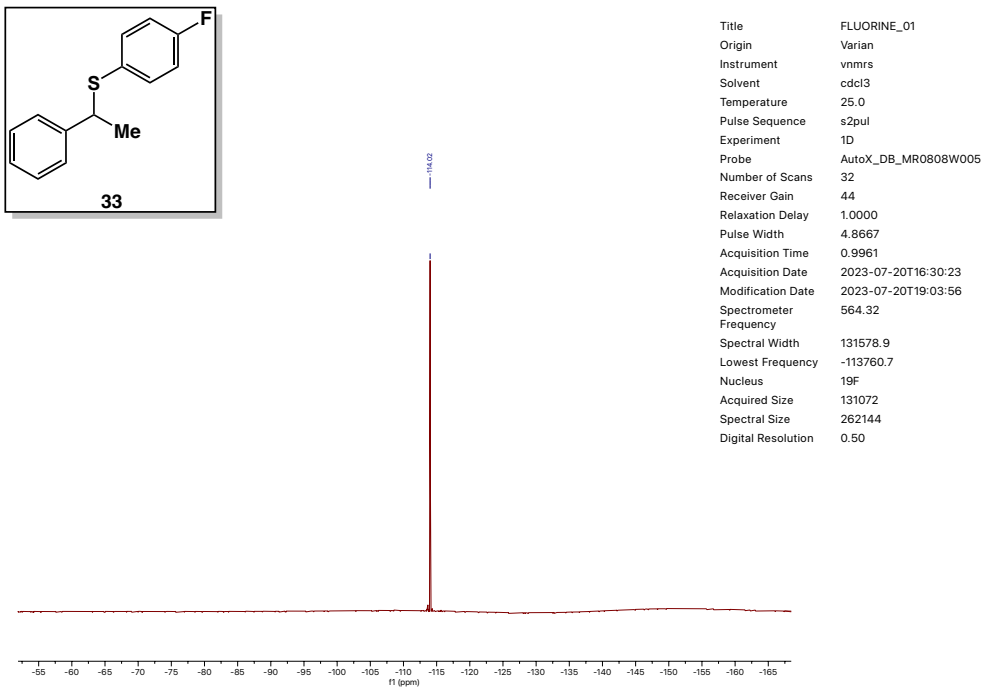
Supplementary Fig. 94. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 32.**



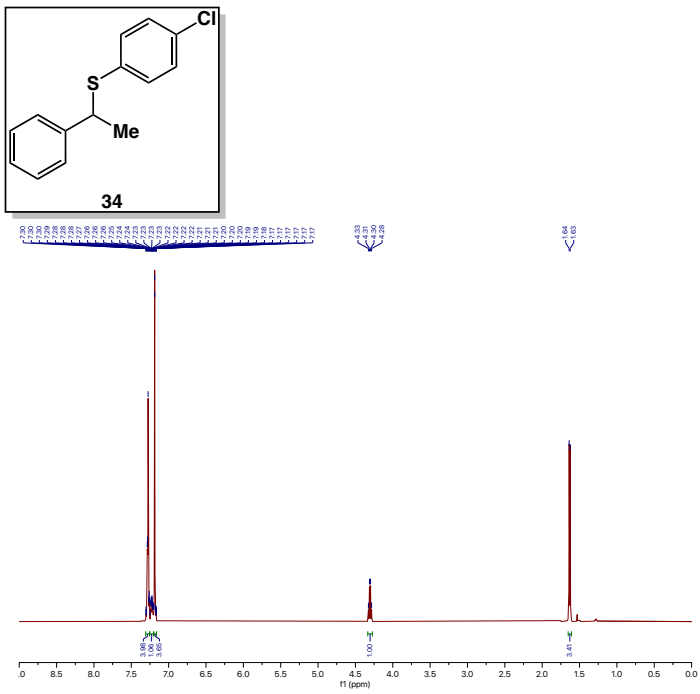
Supplementary Fig. 95. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 33.**



Supplementary Fig. 96. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 33.**

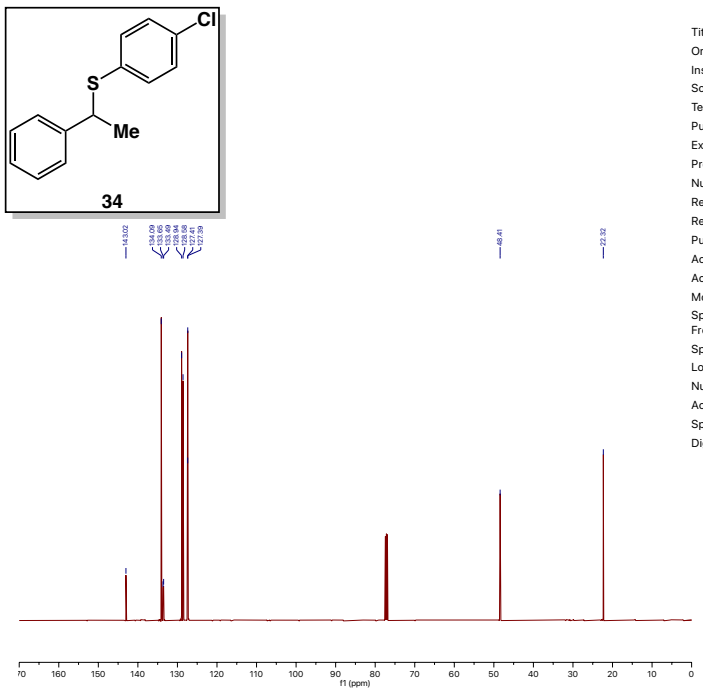


Supplementary Fig. 97. **^{19}F NMR (564 MHz, $CDCl_3$) spectrum of thioether 33.**



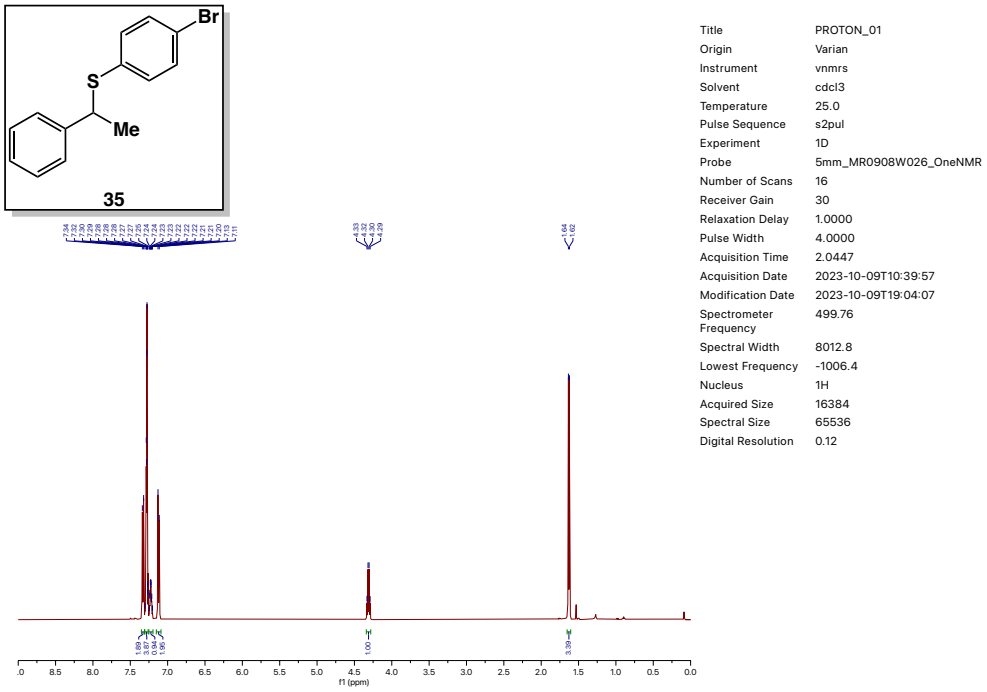
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-09T15:19:55
Modification Date	2023-10-09T19:04:35
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1012.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 98. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 34.**



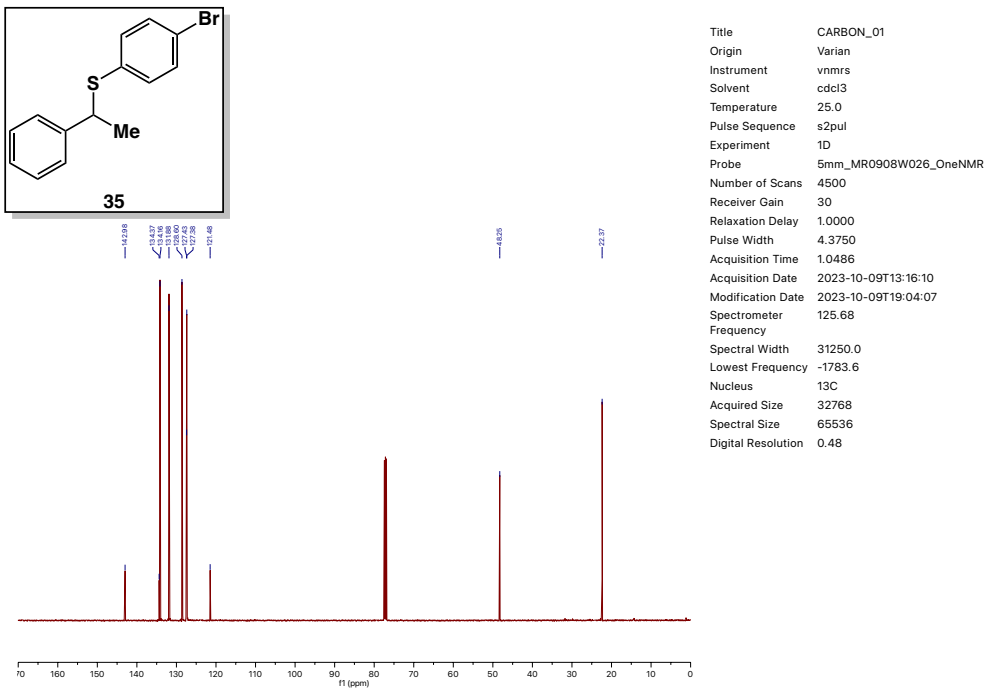
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-10-09T18:13:06
Modification Date	2023-10-09T19:04:36
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1785.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 99. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 34.**



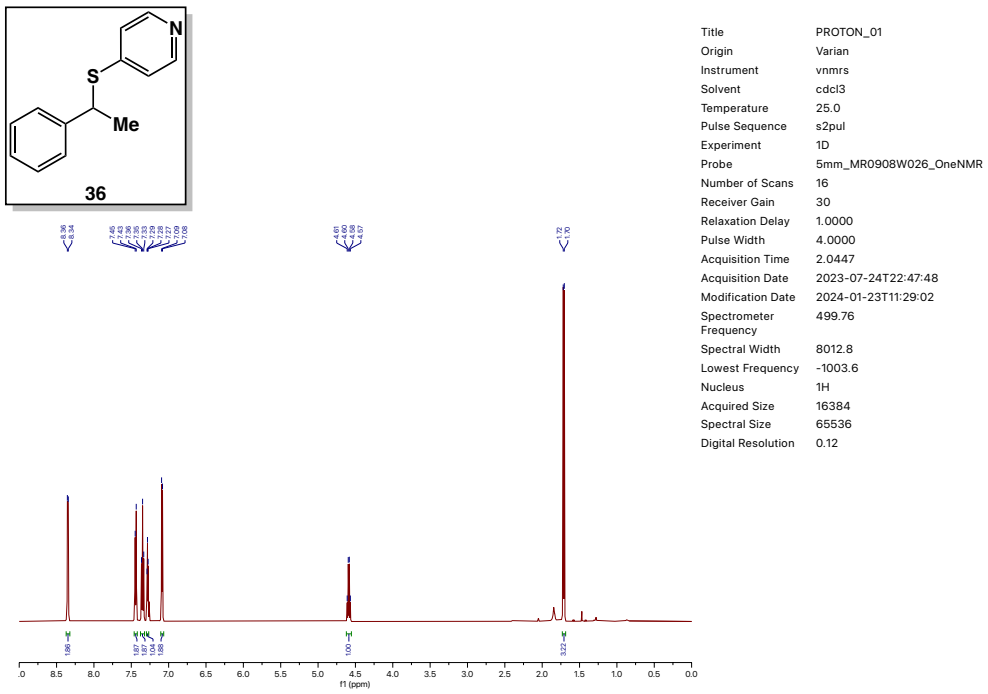
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-09T10:39:57
Modification Date	2023-10-09T19:04:07
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1006.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 100. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 35.**



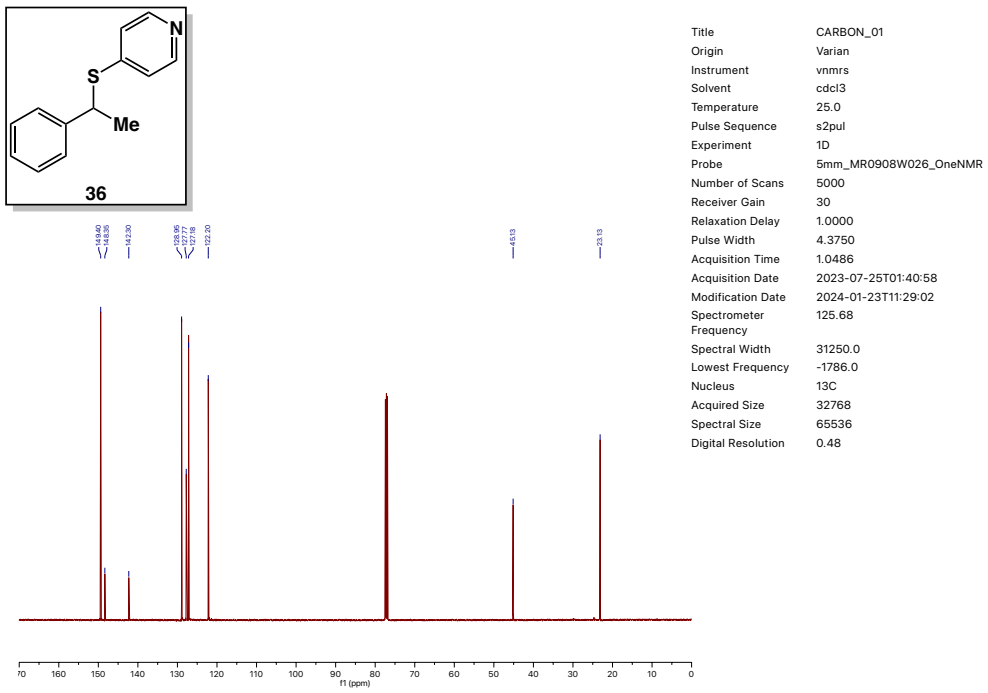
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	4500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-10-09T13:16:10
Modification Date	2023-10-09T19:04:07
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1783.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 101. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 35.**



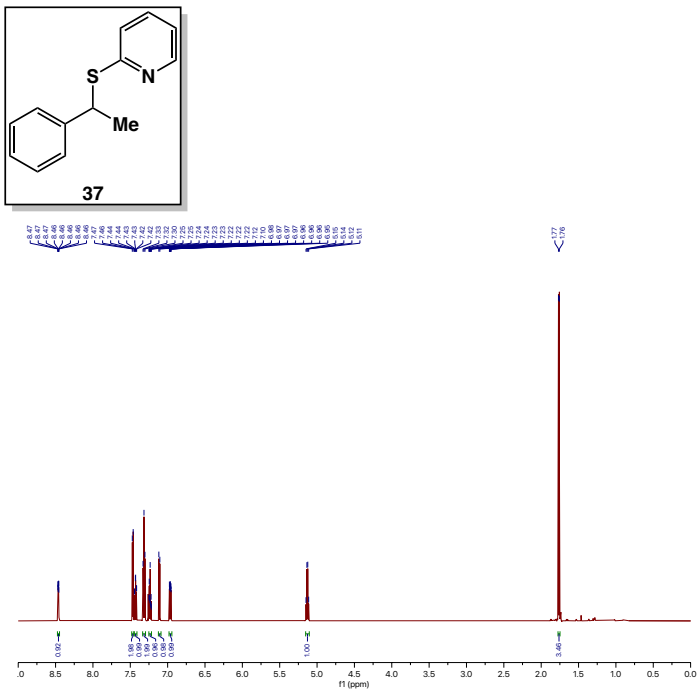
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-07-24T22:47:48
Modification Date	2024-01-23T11:29:02
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1003.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 102. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 36.**



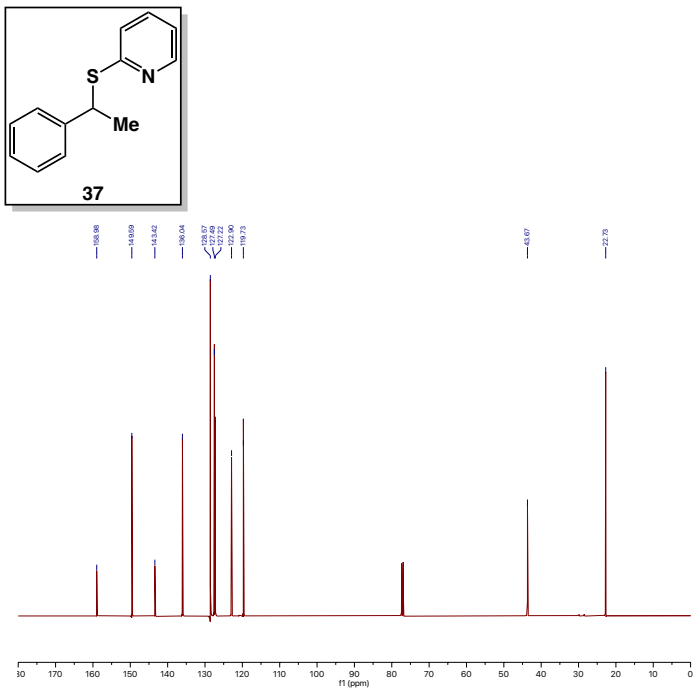
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-07-25T01:40:58
Modification Date	2024-01-23T11:29:02
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1786.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 103. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 36.**



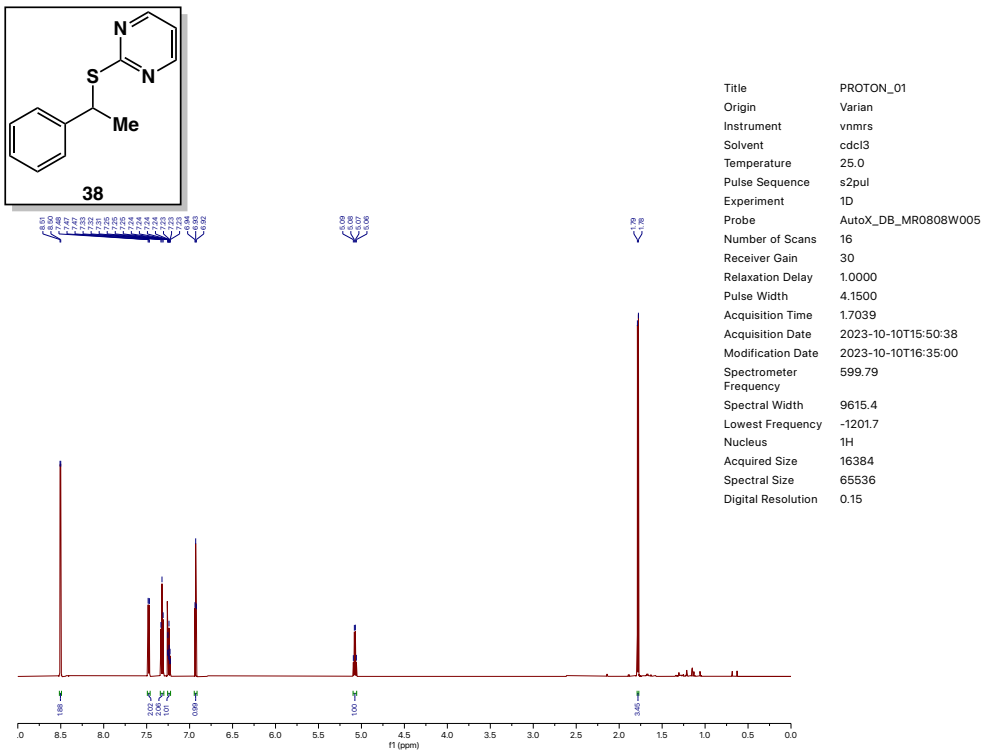
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Acquisition Time	1.7039
Acquisition Date	2023-10-12T10:02:16
Modification Date	2024-01-23T11:26:45
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1201.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 104. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 37.**

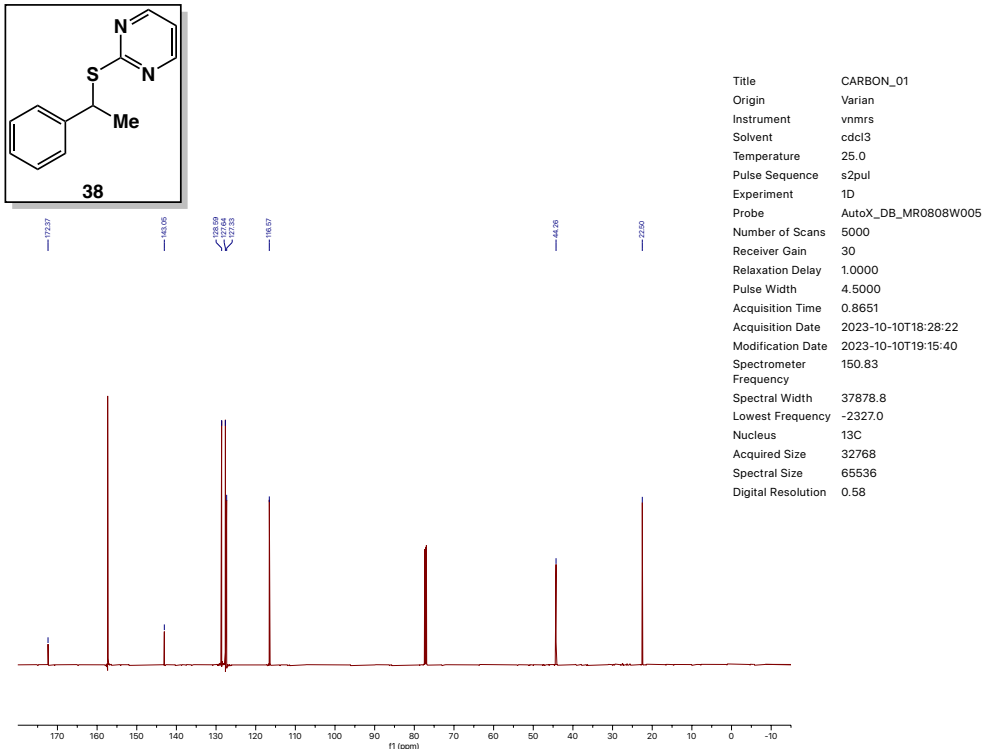


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Acquisition Time	0.8651
Acquisition Date	2023-10-12T12:40:03
Modification Date	2024-01-23T11:26:45
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2332.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

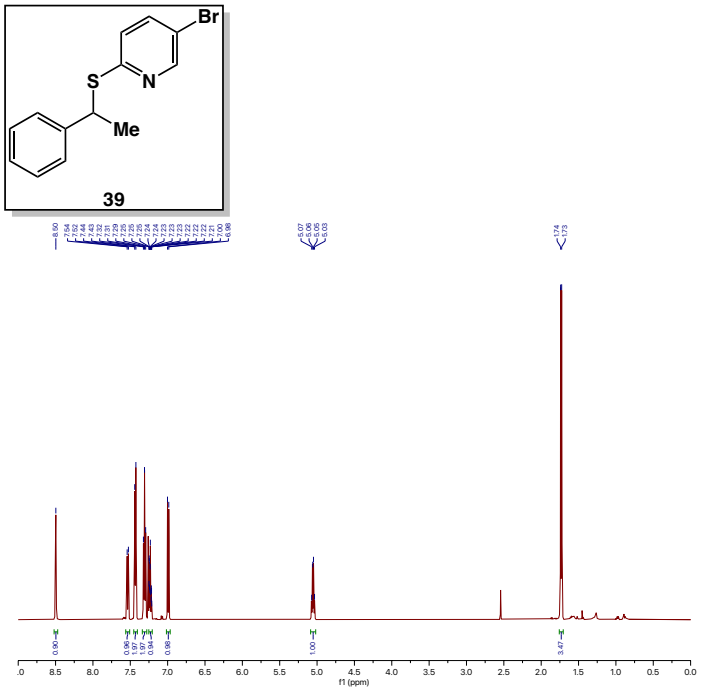
Supplementary Fig. 105. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 37.**



Supplementary Fig. 106. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 38.**

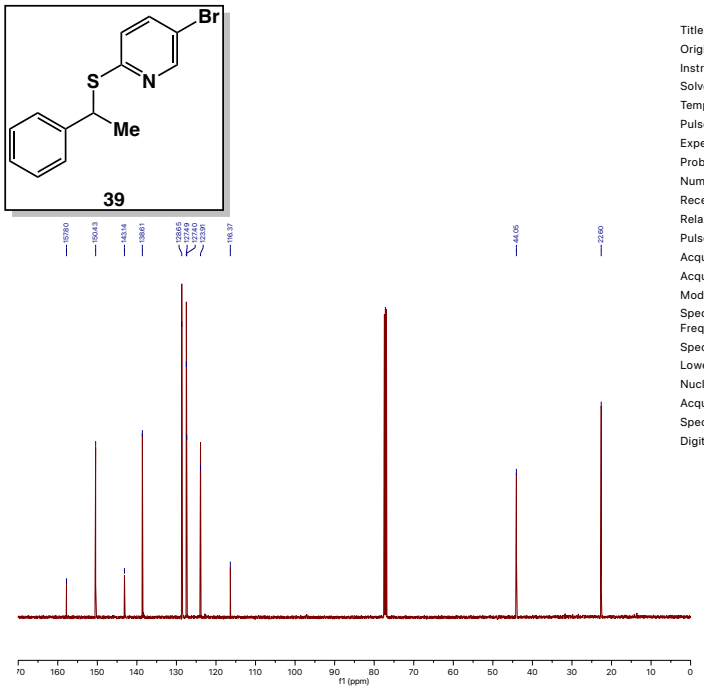


Supplementary Fig. 107. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 38.**



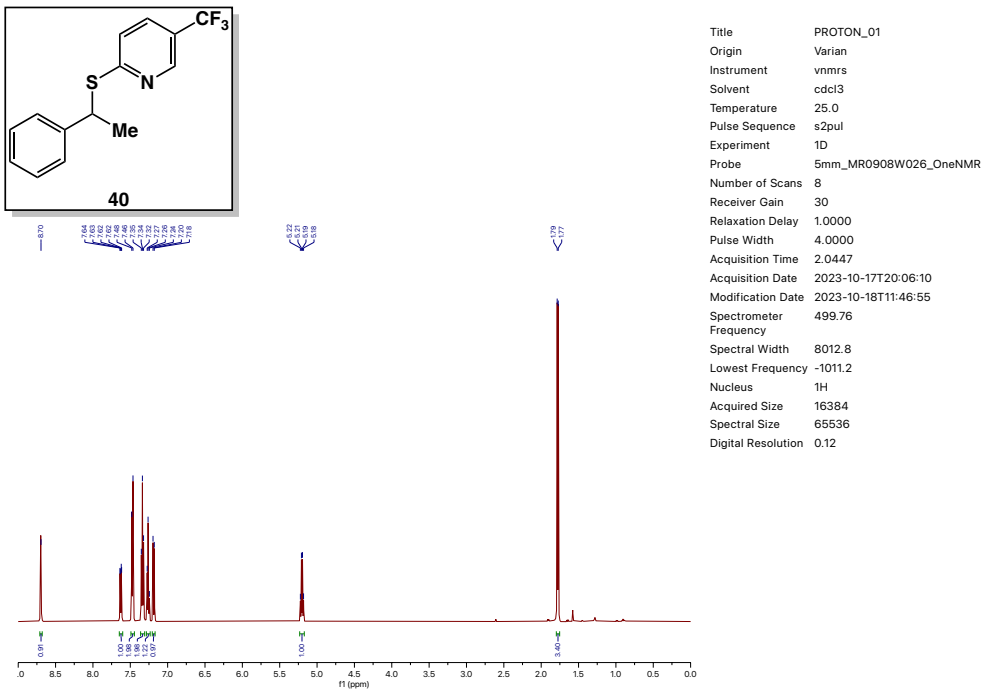
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-19T17:51:14
Modification Date	2023-10-20T12:50:32
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1013.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 108. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 39.**



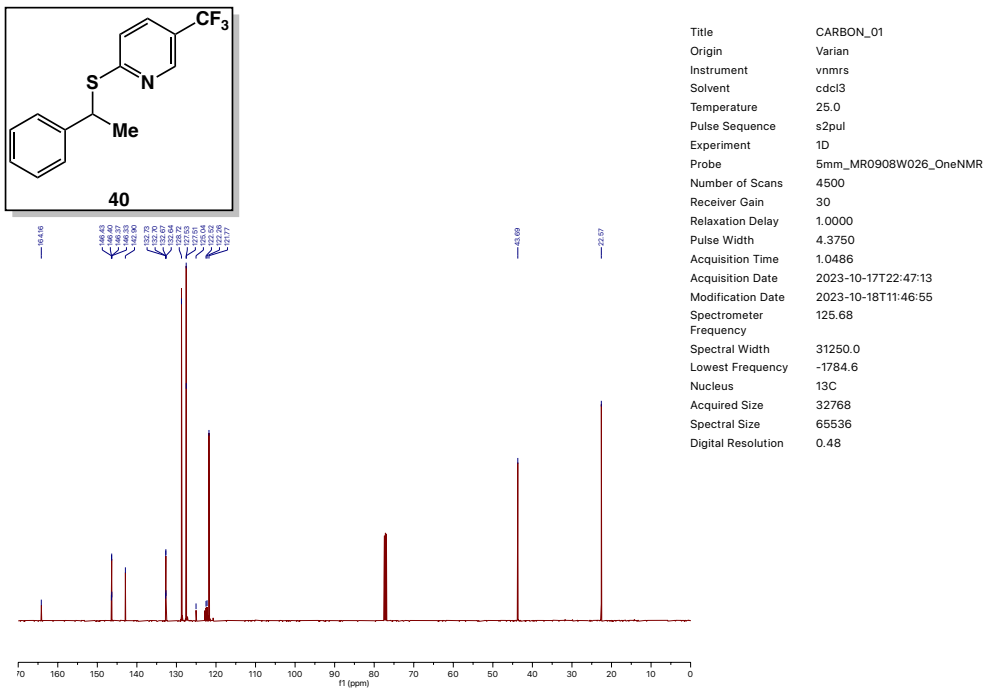
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	4000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-10-19T20:11:05
Modification Date	2023-10-20T12:50:32
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 109. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 39.**



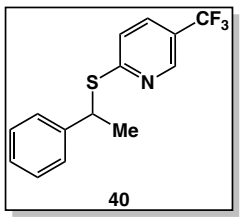
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-17T20:06:10
Modification Date	2023-10-18T11:46:55
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1011.2
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 110. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 40.**

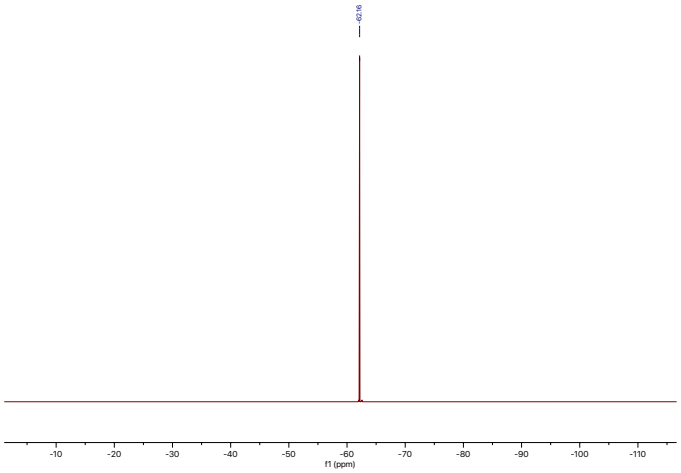


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	4500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-10-17T22:47:13
Modification Date	2023-10-18T11:46:55
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

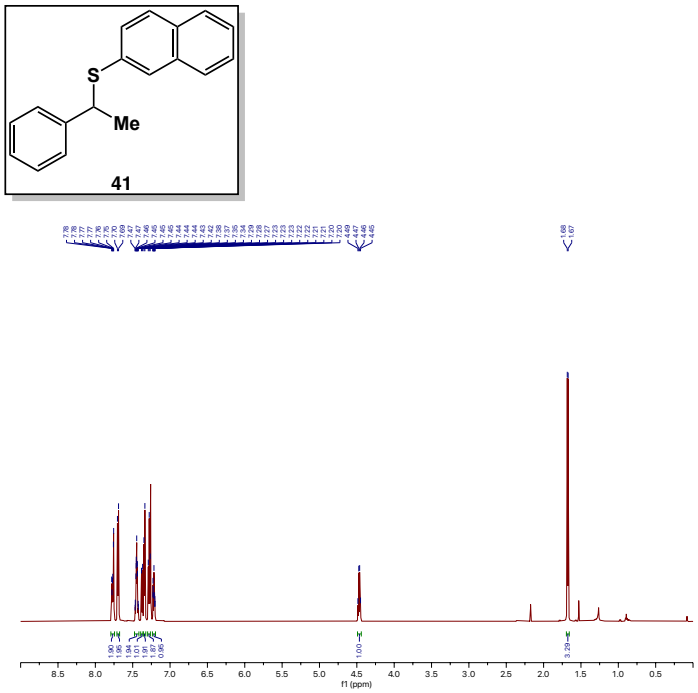
Supplementary Fig. 111. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 40.**



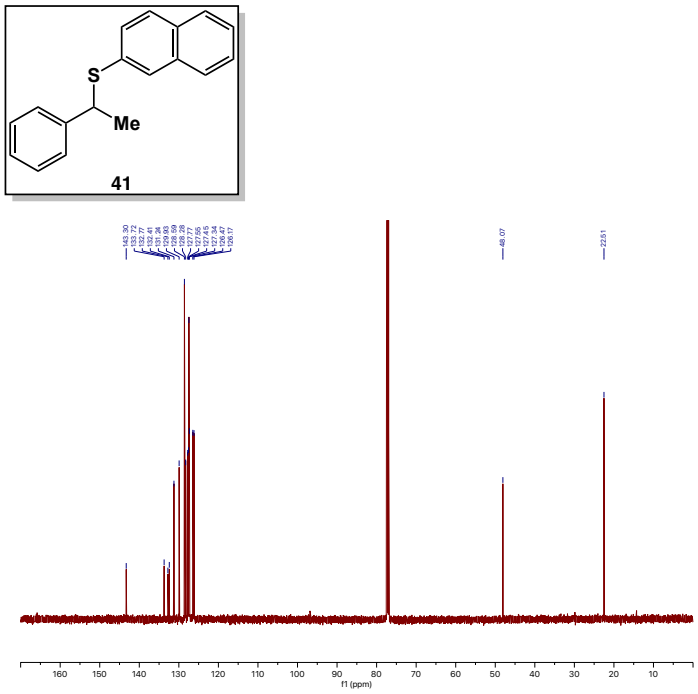
Title	FLUORINE_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	32
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	3.3667
Acquisition Time	0.6029
Acquisition Date	2023-10-17T20:10:13
Modification Date	2023-10-18T11:46:55
Spectrometer Frequency	470.20
Spectral Width	108695.7
Lowest Frequency	-94318.4
Nucleus	19F
Acquired Size	65536
Spectral Size	131072
Digital Resolution	0.83



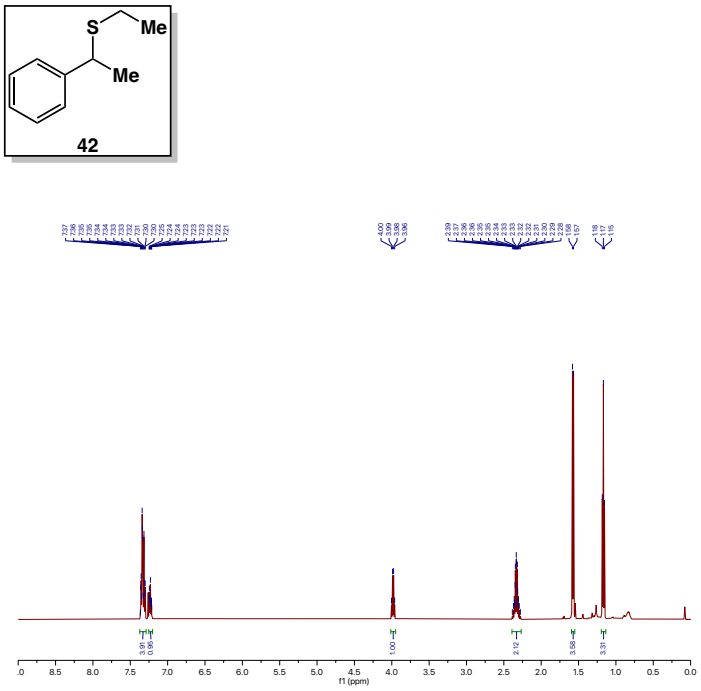
Supplementary Fig. 112. **^{19}F NMR (470 MHz, $CDCl_3$) spectrum of thioether 40.**



Supplementary Fig. 113. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 41.**

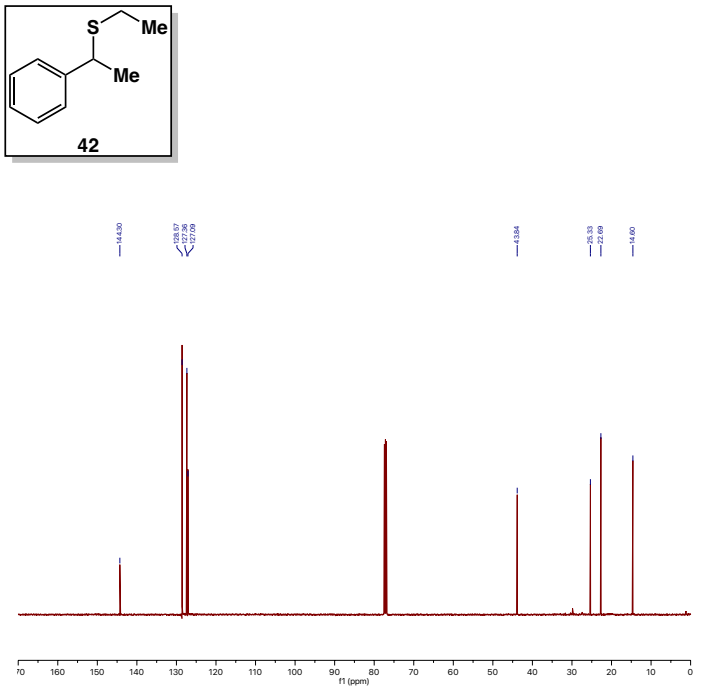


Supplementary Fig. 114. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 41.**



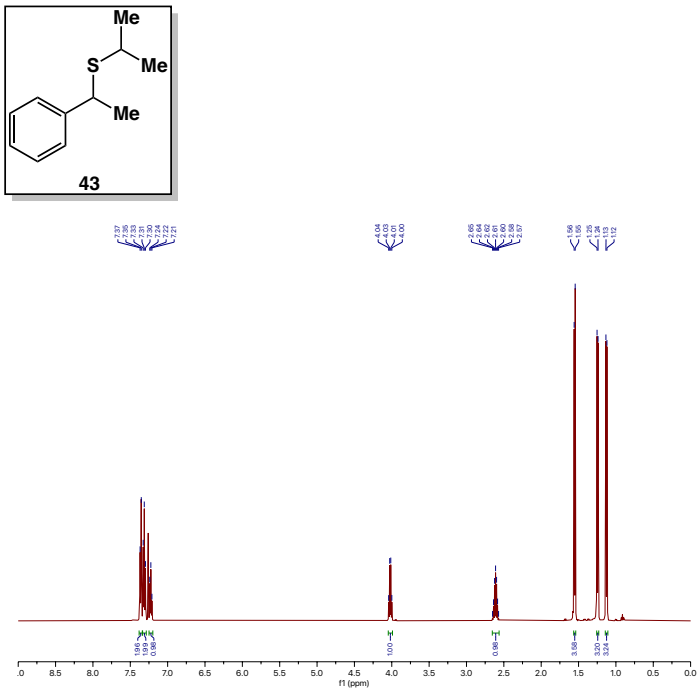
Title	PROTON_03
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-12-08T13:35:22
Modification Date	2023-12-13T10:37:35
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1015.3
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 115. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 42.**



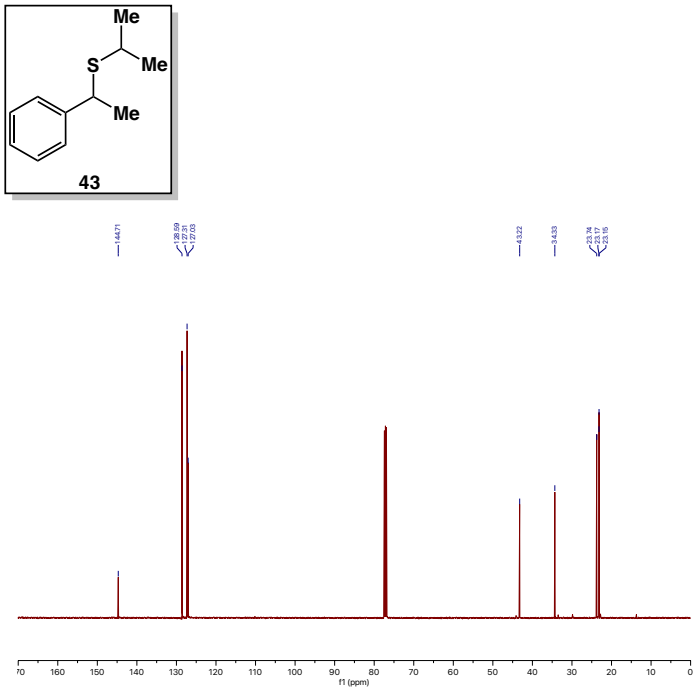
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-12-08T13:31:49
Modification Date	2023-12-13T10:37:35
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1785.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 116. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 42.**



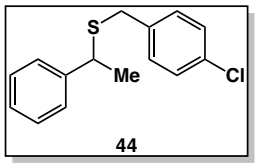
Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Acquisition Time	2.0447
Acquisition Date	2023-10-13T19:07:20
Modification Date	2023-10-14T21:47:54
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1014.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

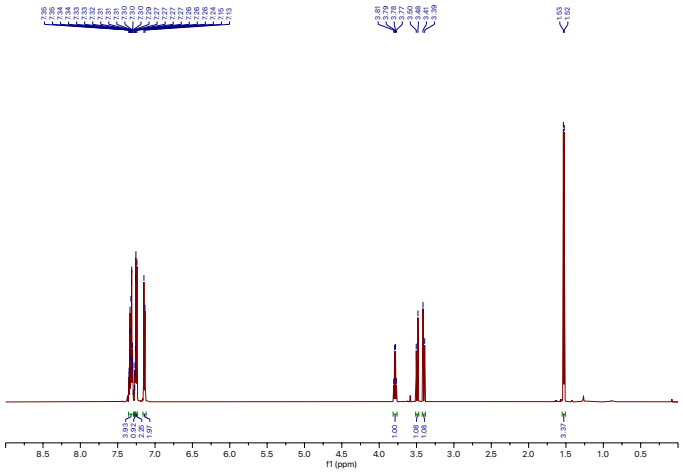
Supplementary Fig. 117. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 43.**



Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Acquisition Time	1.0486
Acquisition Date	2023-10-13T22:00:04
Modification Date	2023-10-14T21:47:54
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

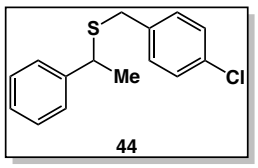
Supplementary Fig. 118. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 43.**

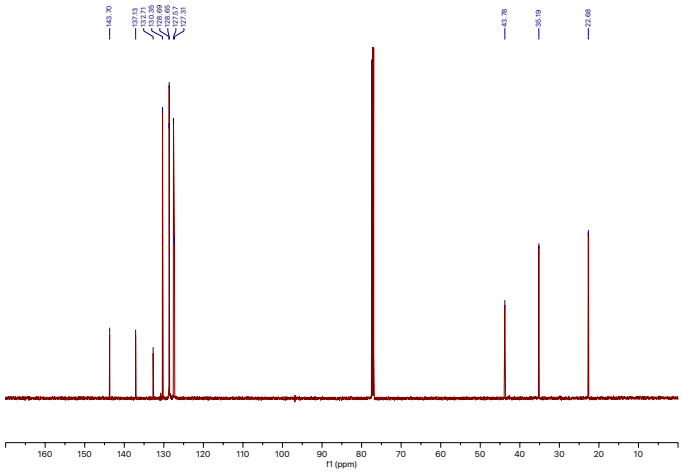




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-31T17:58:50
Modification Date	2024-10-31T22:18:58
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1203.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

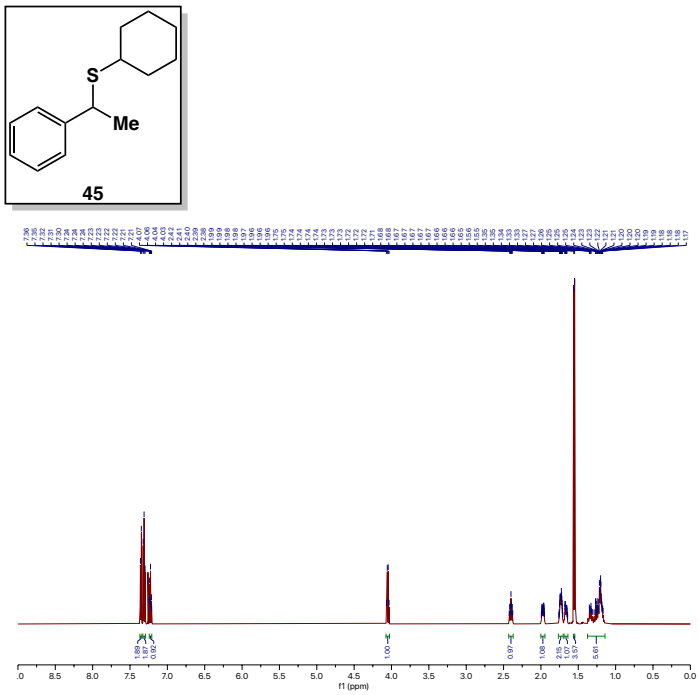
Supplementary Fig. 119. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 44.**





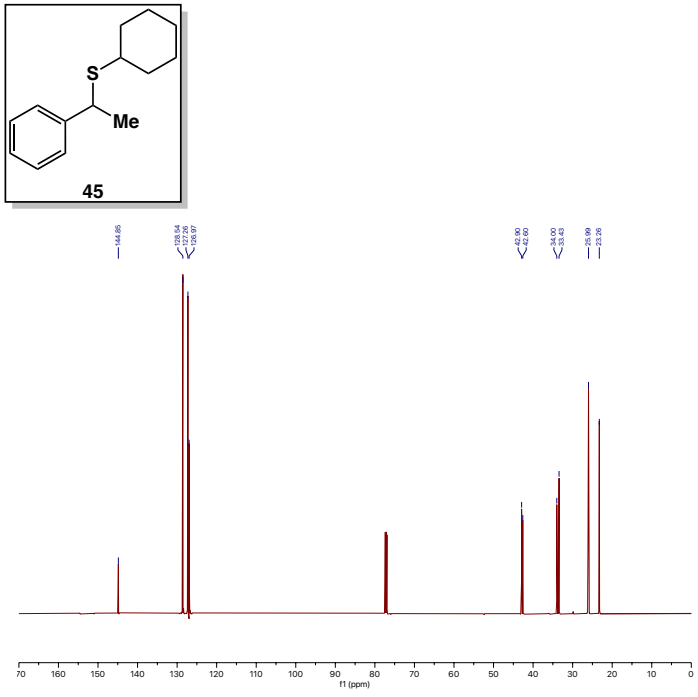
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	1200
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-31T18:38:40
Modification Date	2024-10-31T22:18:59
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2325.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 120. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 44.**



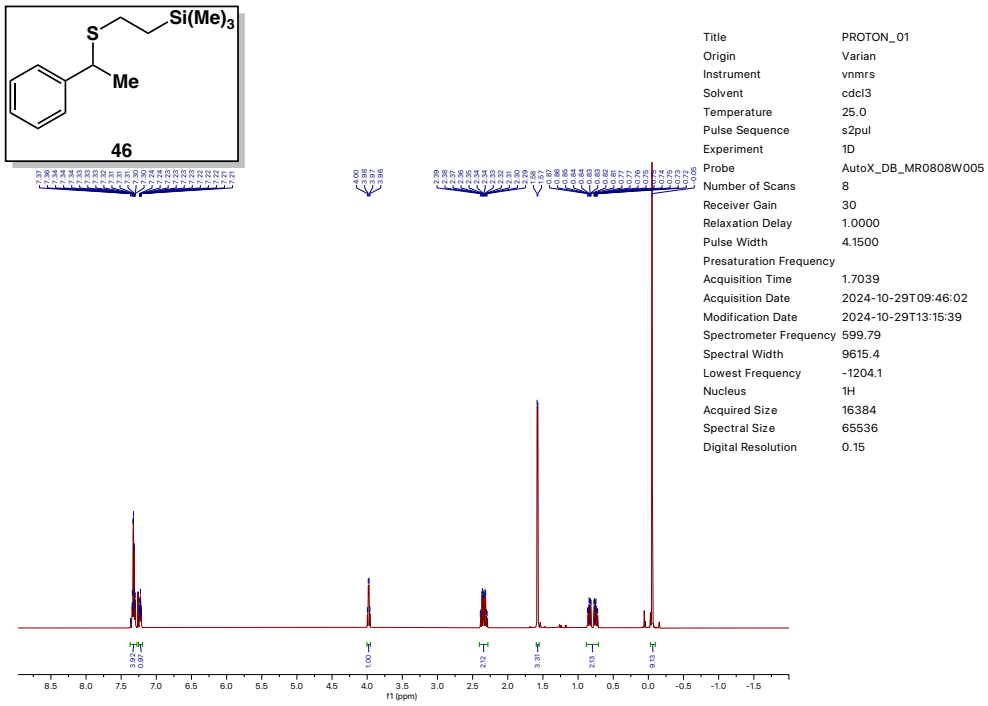
Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Acquisition Time	1.7039
Acquisition Date	2023-10-09T15:07:26
Modification Date	2023-10-09T19:06:13
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1201.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

Supplementary Fig. 121. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 45.**

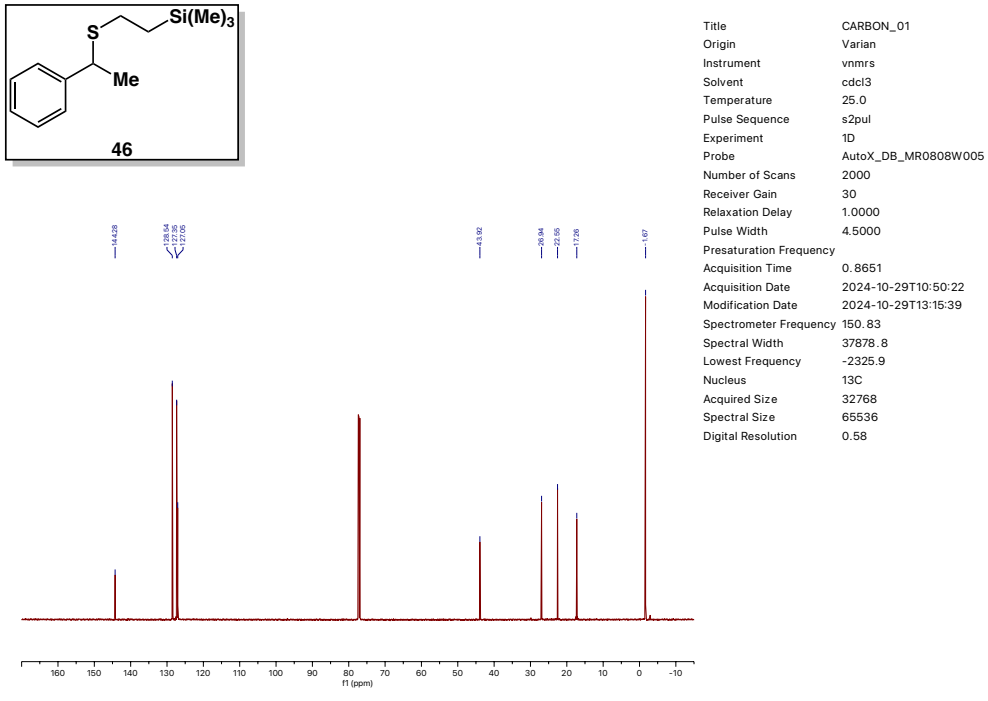


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Acquisition Time	0.8651
Acquisition Date	2023-10-09T17:44:56
Modification Date	2023-10-09T19:06:13
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2327.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

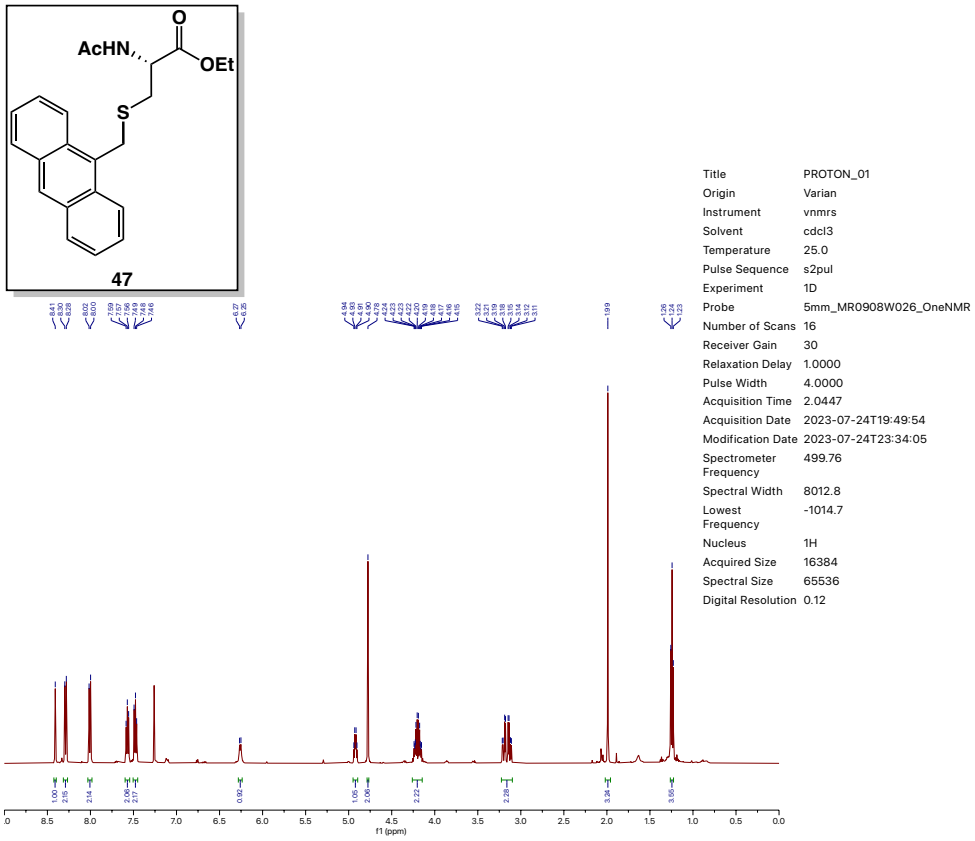
Supplementary Fig. 122. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 45.**



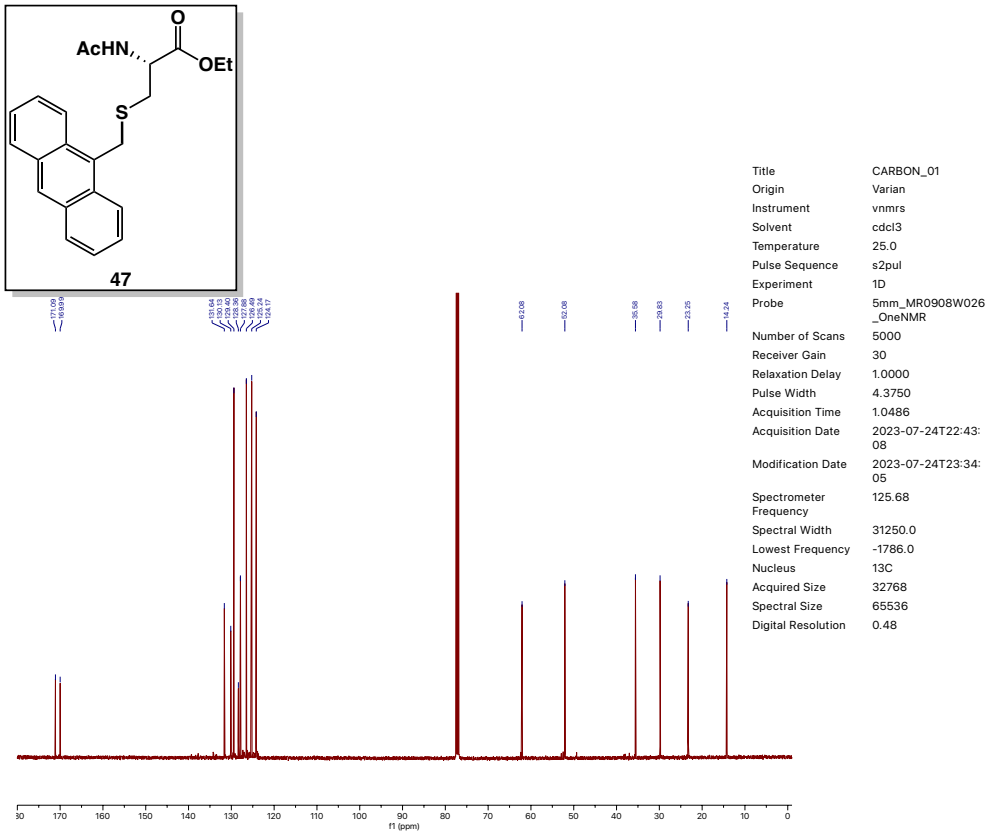
Supplementary Fig. 123. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 46.**



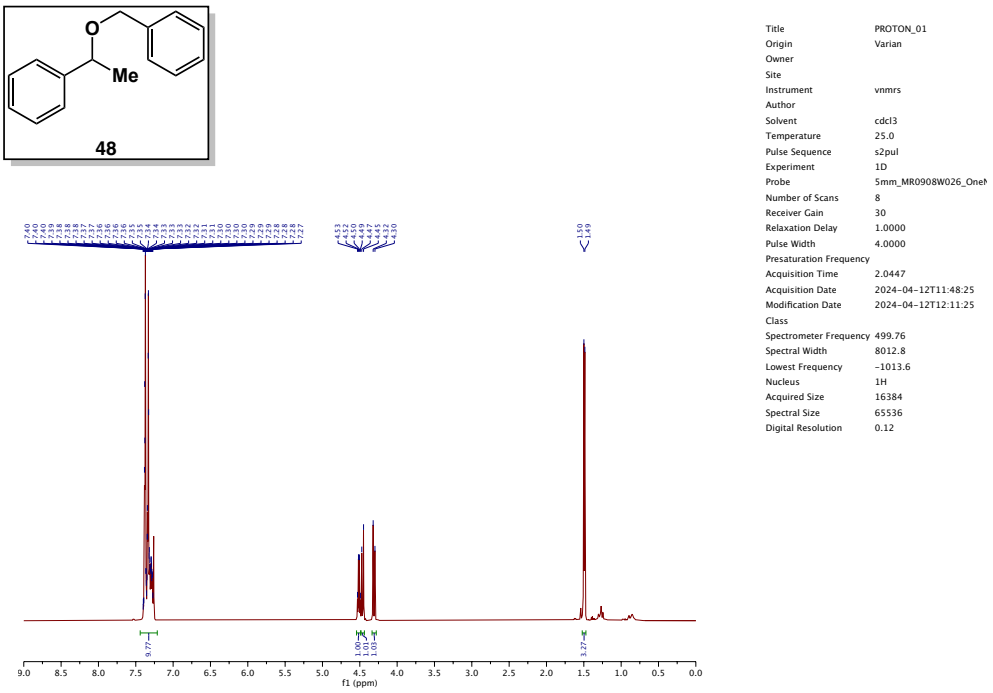
Supplementary Fig. 124. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 46.**



Supplementary Fig. 125. **^{13}C NMR (500 MHz, $CDCl_3$) spectrum of thioether 47.**

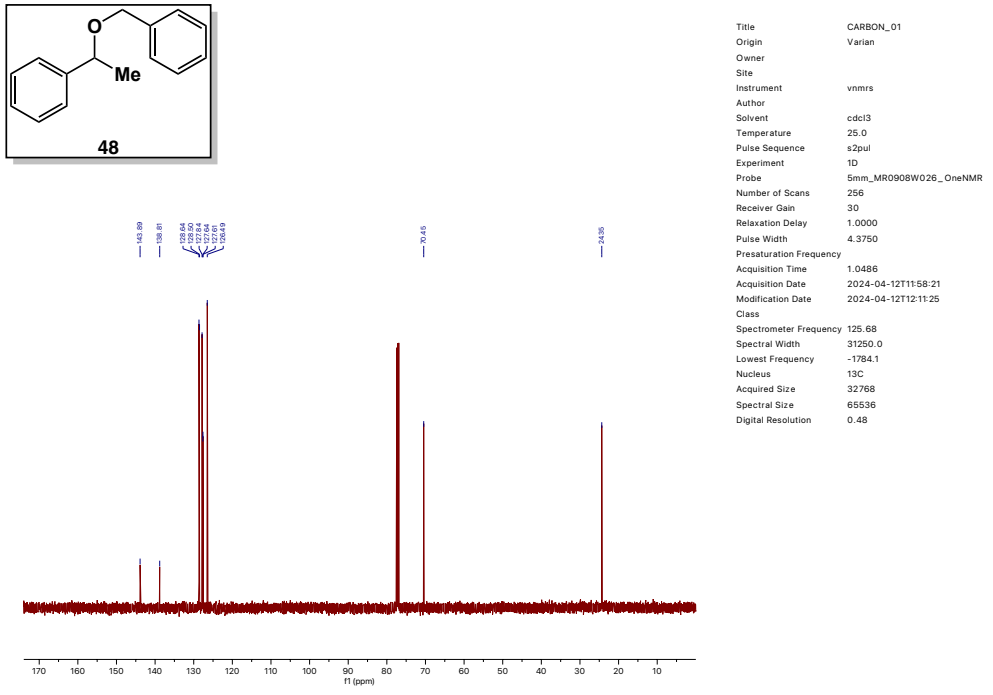


Supplementary Fig. 126. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 47.**



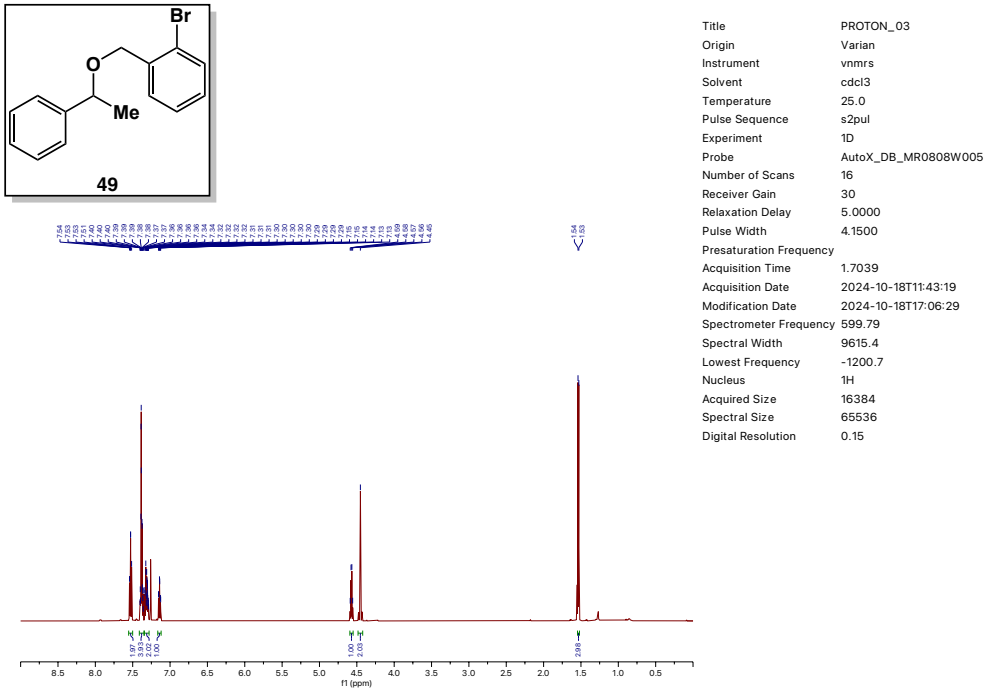
Title	PROTON_01
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_One
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2024-04-12T11:48:25
Modification Date	2024-04-12T12:11:25
Class	
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1013.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 127. **^{13}C NMR (500 MHz, $CDCl_3$) spectrum of ether 48.**

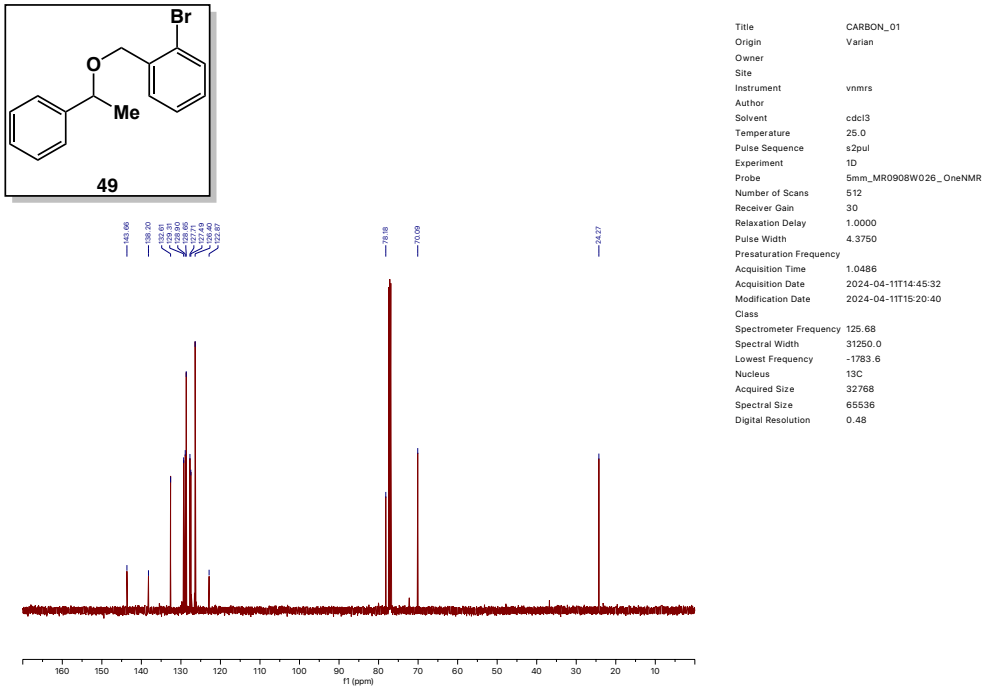


Title	CARBON_01
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2024-04-12T11:58:21
Modification Date	2024-04-12T12:11:25
Class	
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

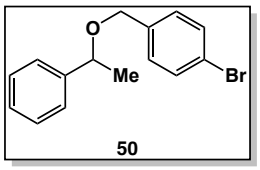
Supplementary Fig. 128. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 48.**

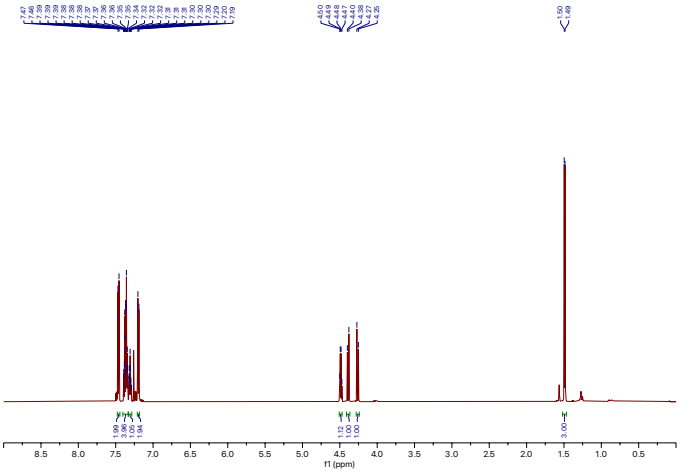


Supplementary Fig. 129. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ether 49.**



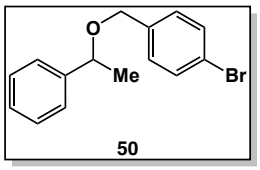
Supplementary Fig. 130. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 49.**

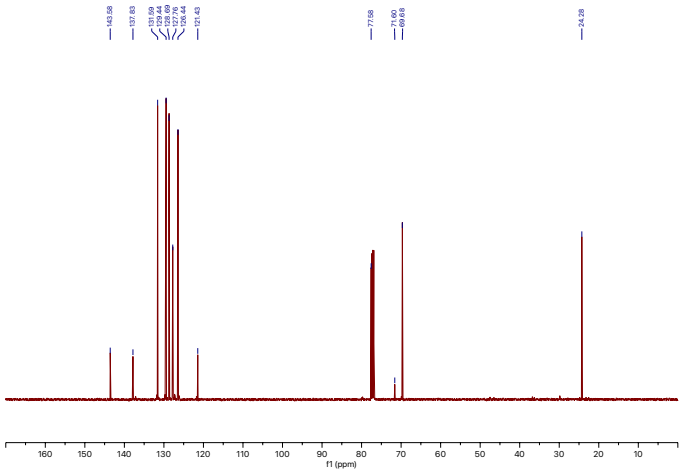




Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	58
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-21T17:58:26
Modification Date	2024-10-21T18:21:21
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1200.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

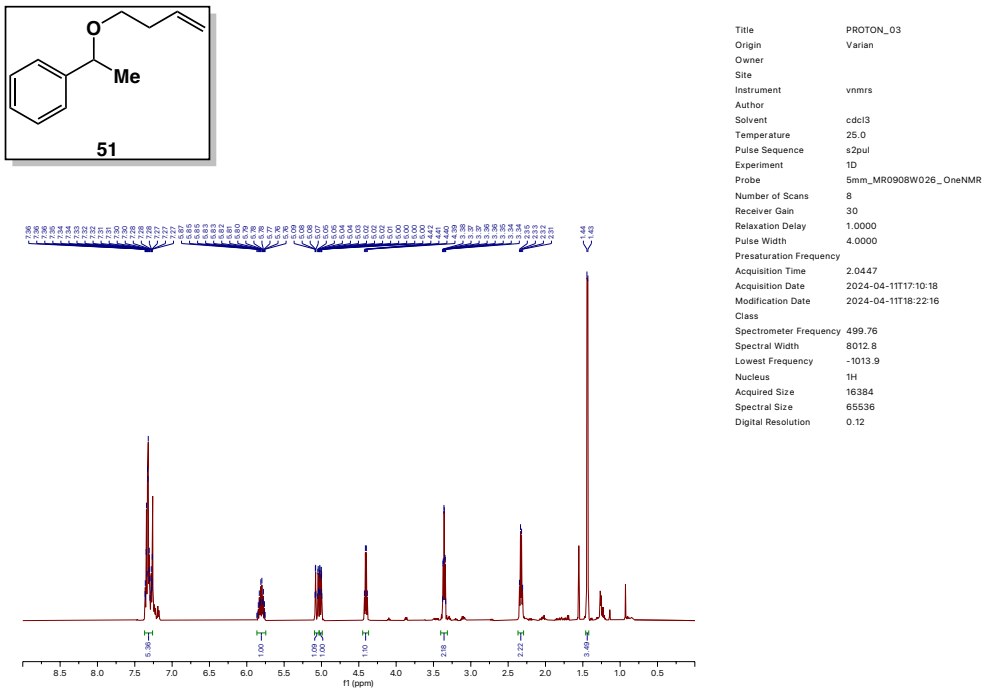
Supplementary Fig. 131. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ether 50.**



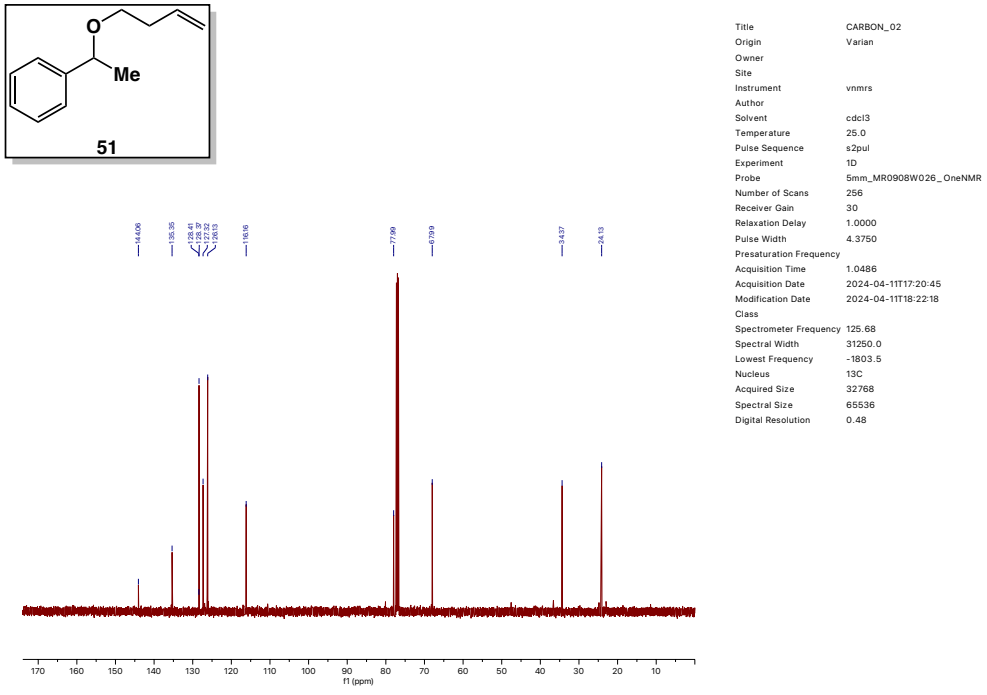


Parameter	Value
Title	CARBON_01
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_ OneNMR
Number of Scans	2000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2023-12-04T13:51:56
Modification Date	2023-12-05T10:06:50
Class	
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1785.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

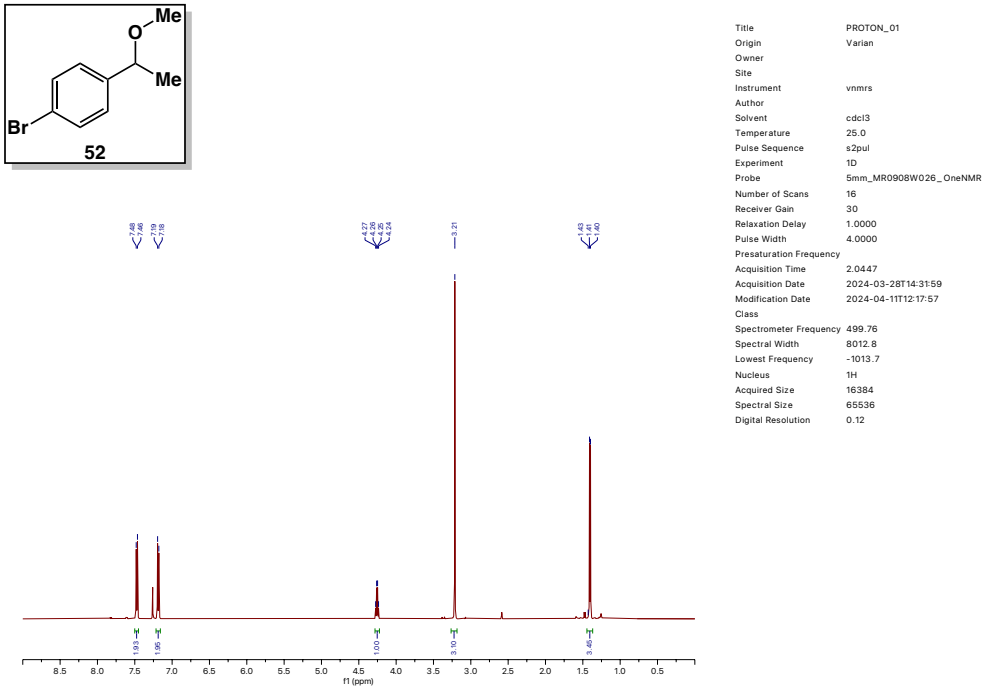
Supplementary Fig. 132. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 50.**



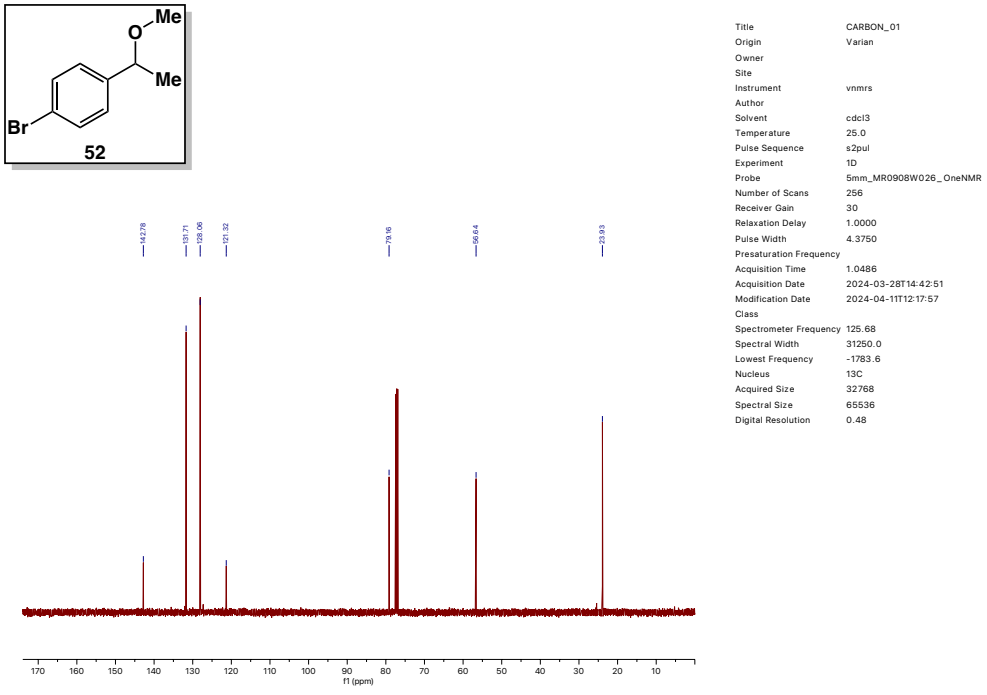
Supplementary Fig. 133. **^{1}H NMR (125 MHz, $CDCl_3$) spectrum of ether 51.**



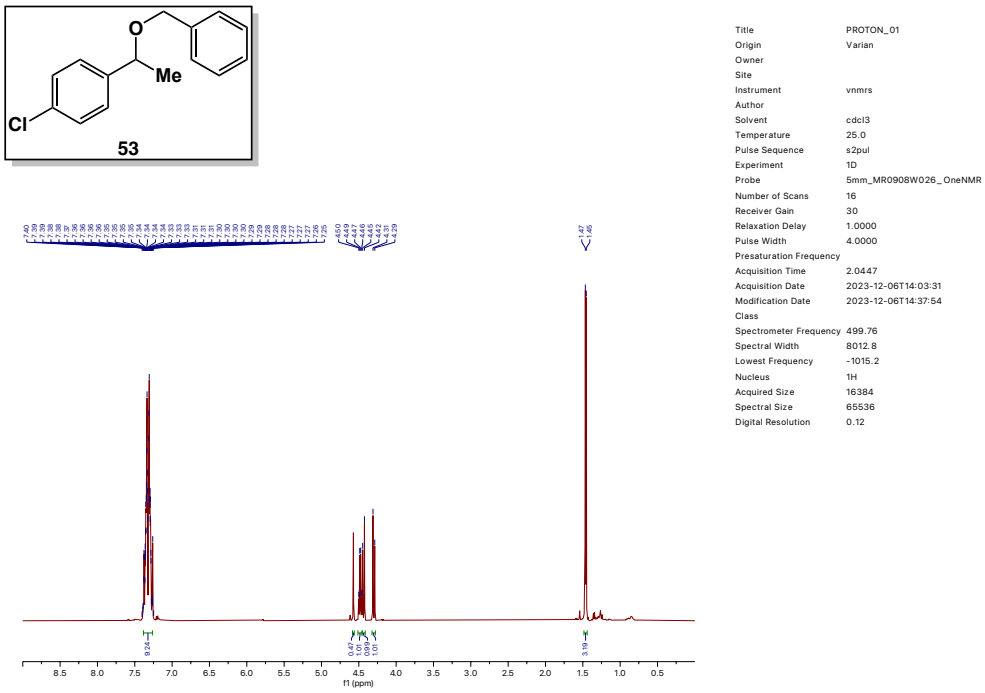
Supplementary Fig. 134. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 51.**



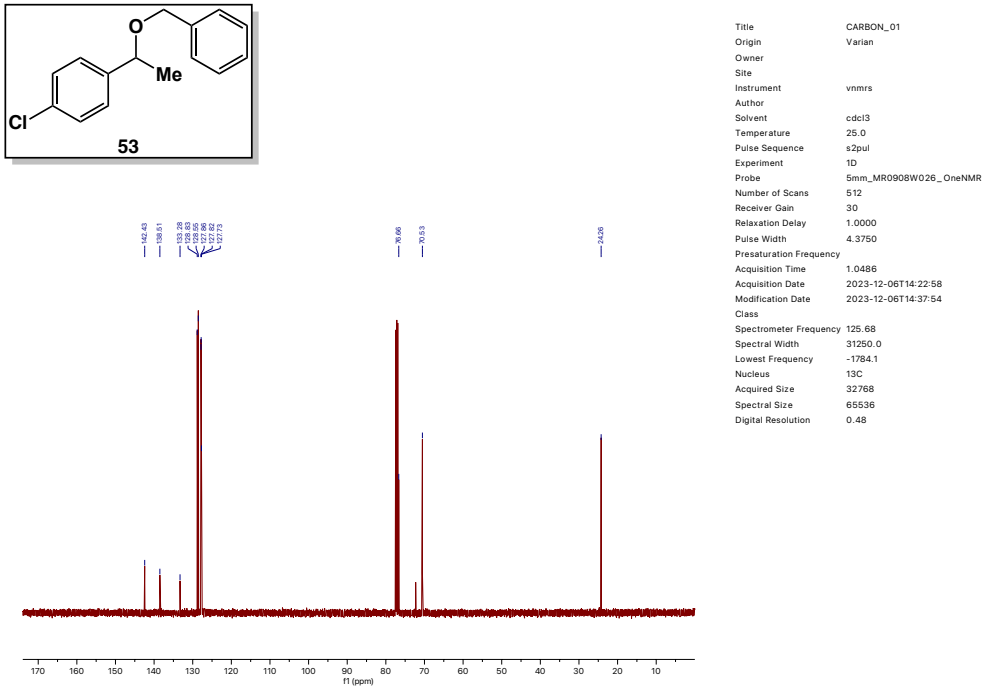
Supplementary Fig. 135. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ether 52.**



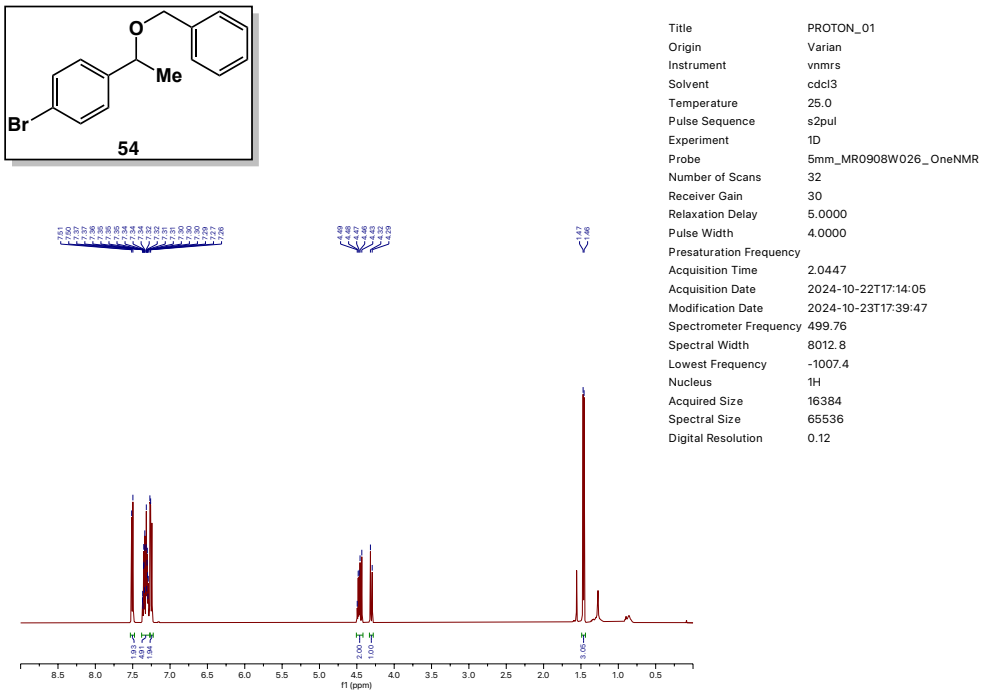
Supplementary Fig. 136. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 52.**



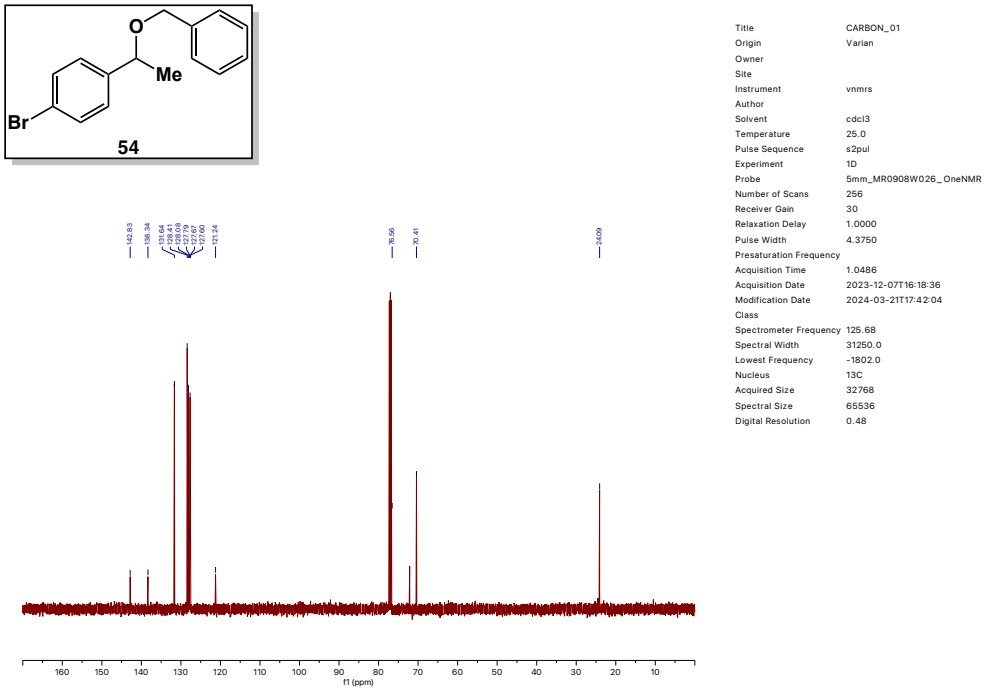
Supplementary Fig. 137. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ether 53.**



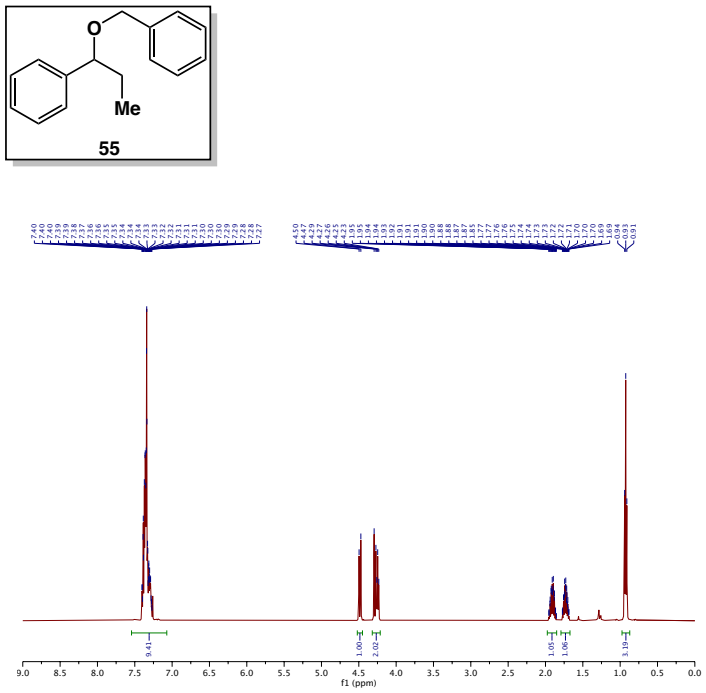
Supplementary Fig. 138. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 53.**



Supplementary Fig. 139. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ether 54.**

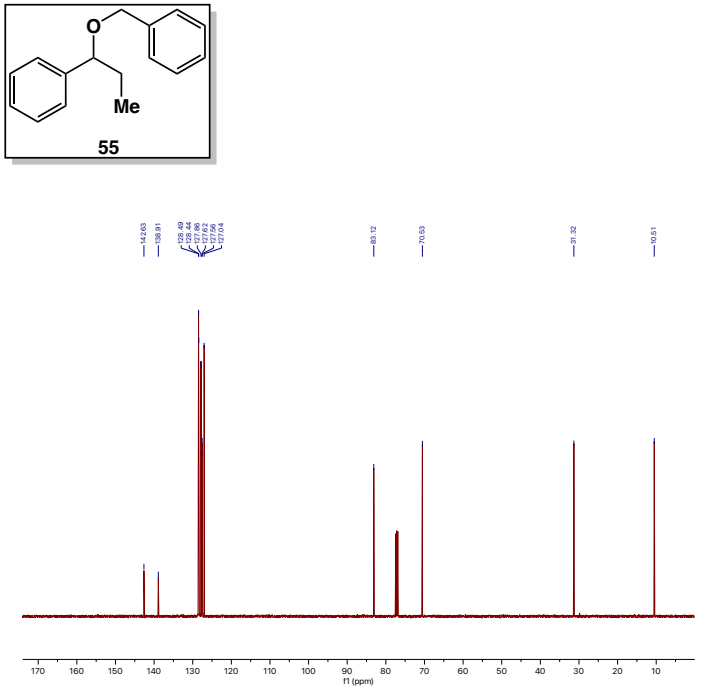


Supplementary Fig. 140. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 54.**



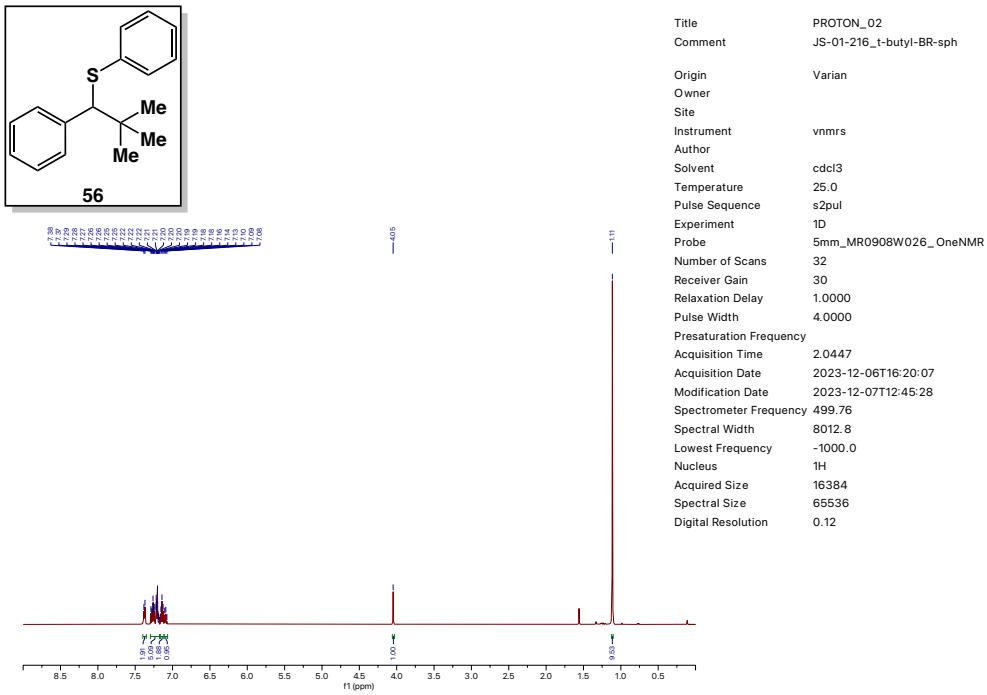
Title	PROTON_01
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-12-12T16:42:11
Modification Date	2023-12-12T17:54:52
Class	
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1015.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 141. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ether 55.**



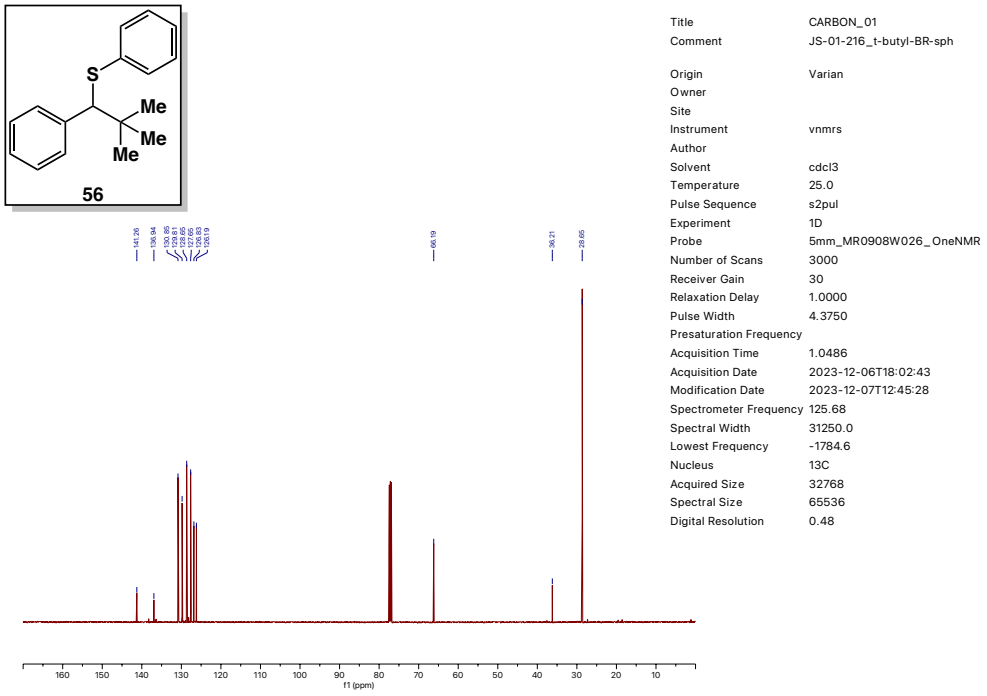
Title	CARBON_01
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	512
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2023-12-12T17:02:27
Modification Date	2023-12-12T17:54:52
Class	
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1787.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 142. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 55.**



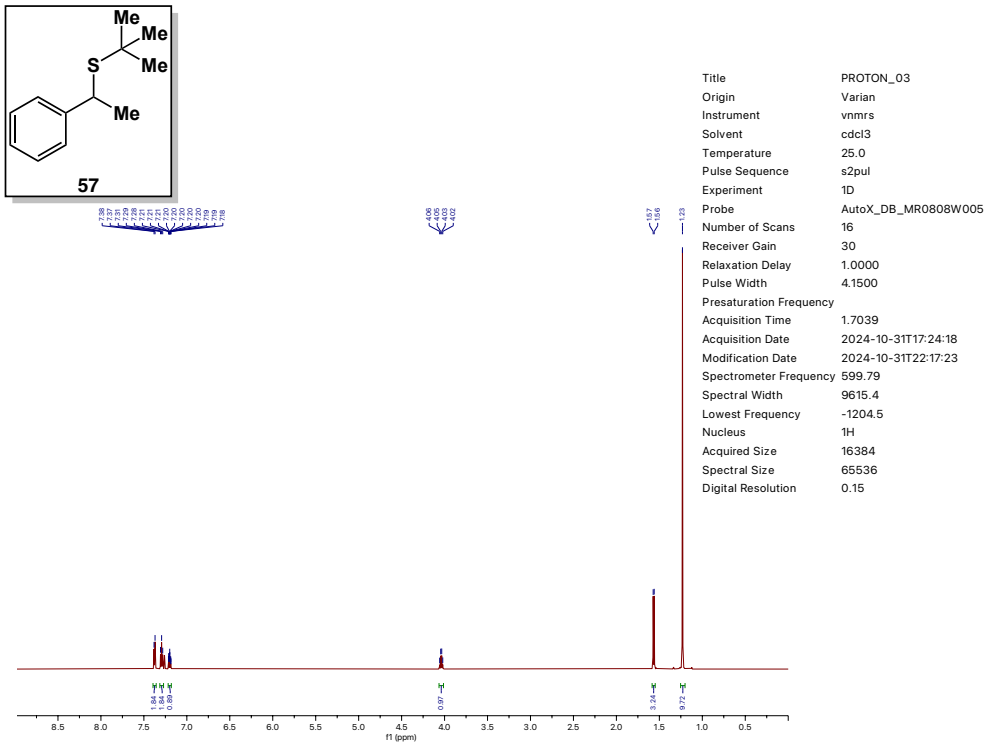
Title	PROTON_02
Comment	JS-01-216_t-butyl-BR-sph
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	32
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-12-06T16:20:07
Modification Date	2023-12-07T12:45:28
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1000.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

Supplementary Fig. 143. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 56.**

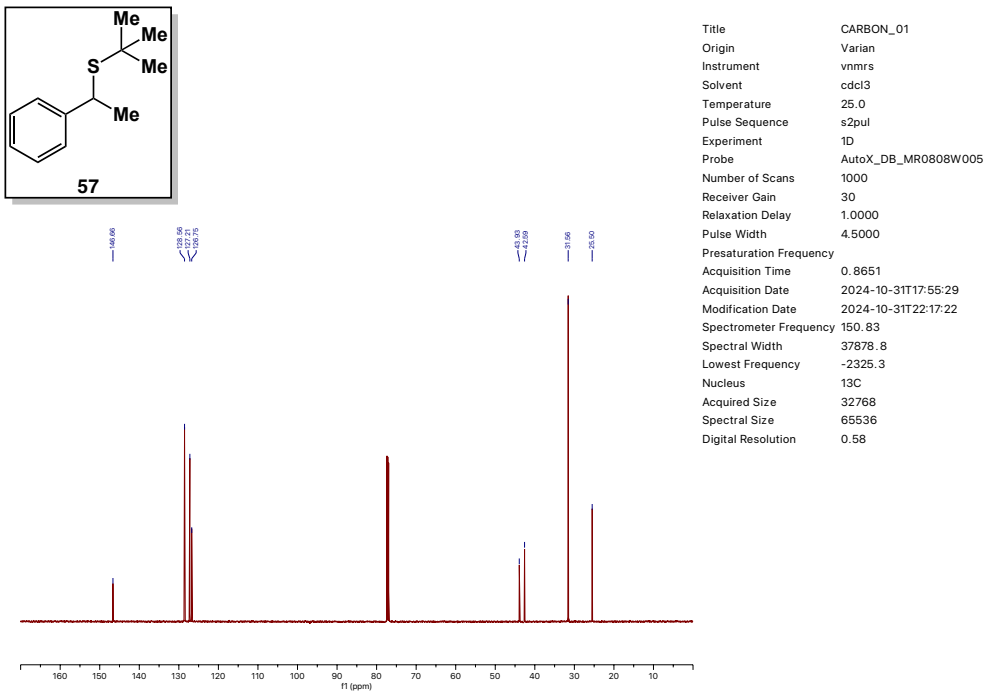


Title	CARBON_01
Comment	JS-01-216_t-butyl-BR-sph
Origin	Varian
Owner	
Site	
Instrument	vnmrs
Author	
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	3000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2023-12-06T18:02:43
Modification Date	2023-12-07T12:45:28
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

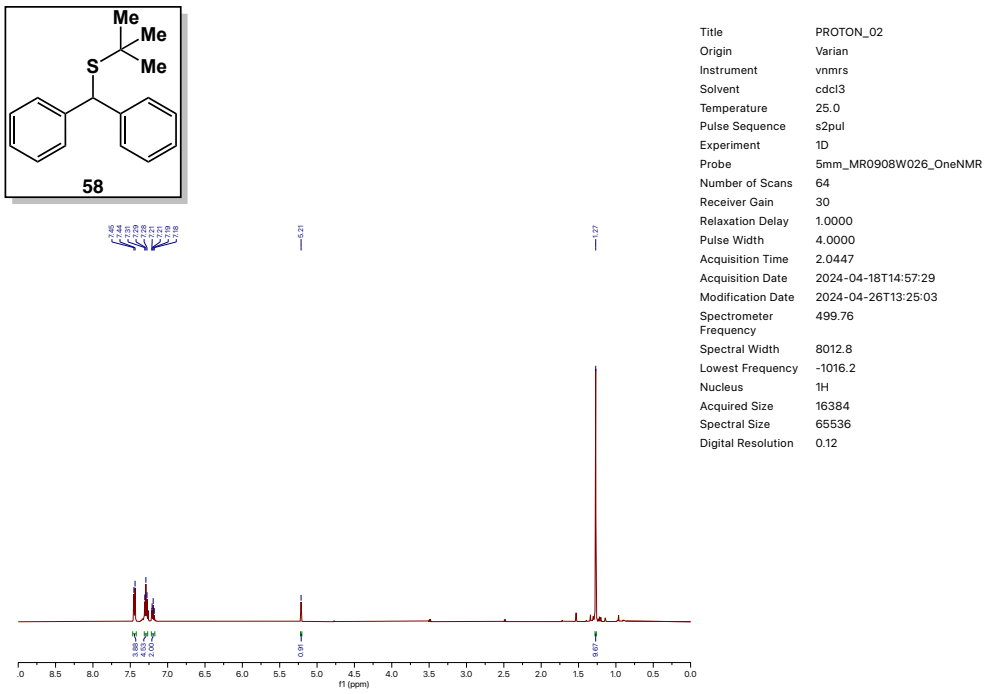
Supplementary Fig. 144. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 56.**



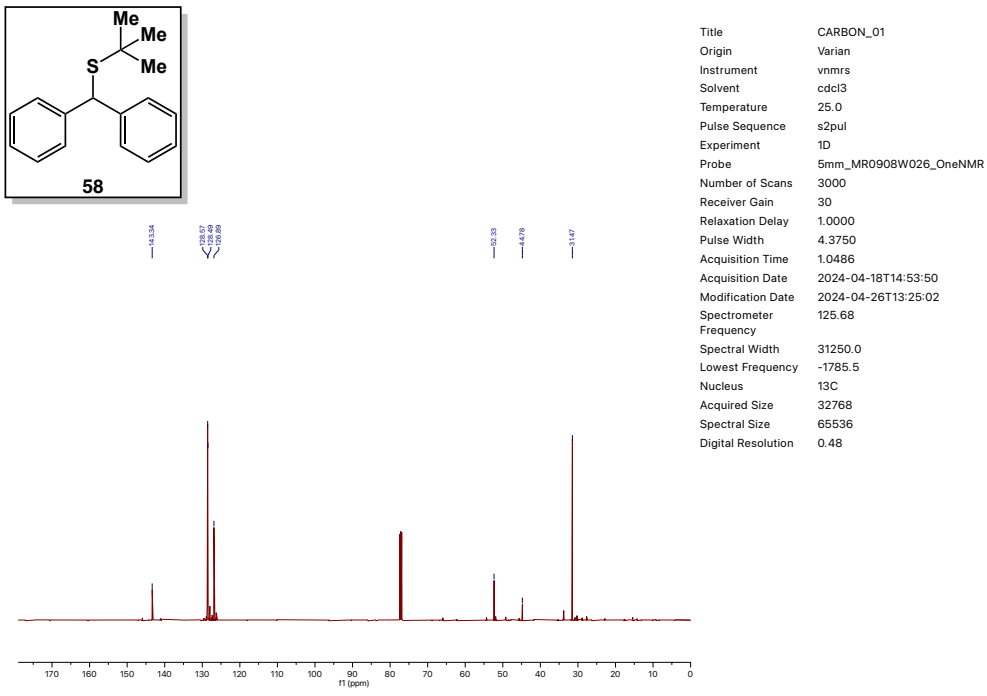
Supplementary Fig. 145. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 57.**



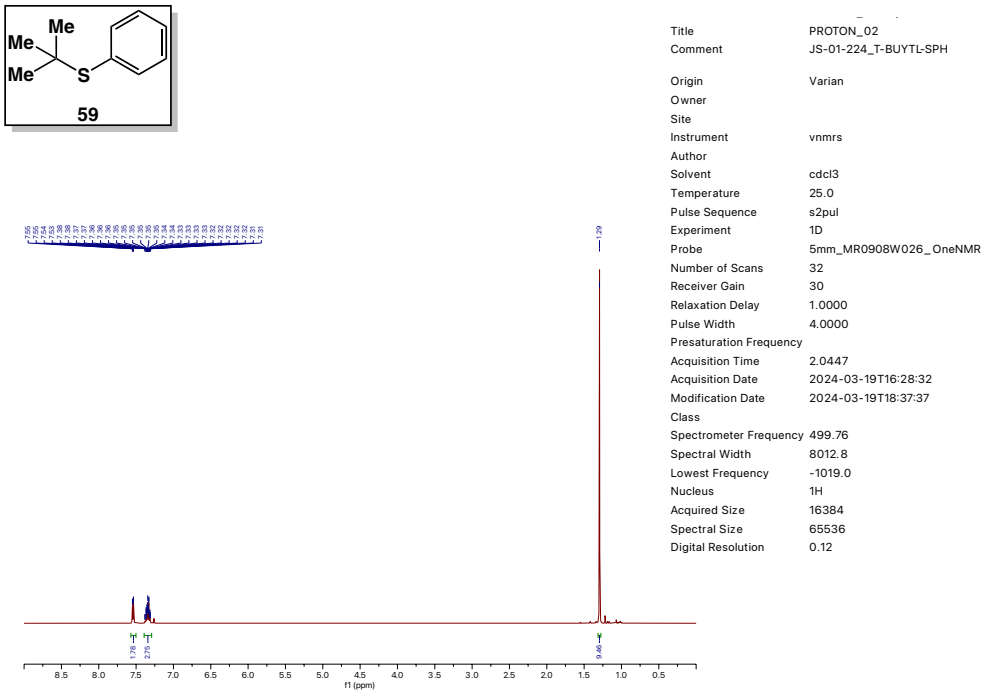
Supplementary Fig. 146. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 57.**



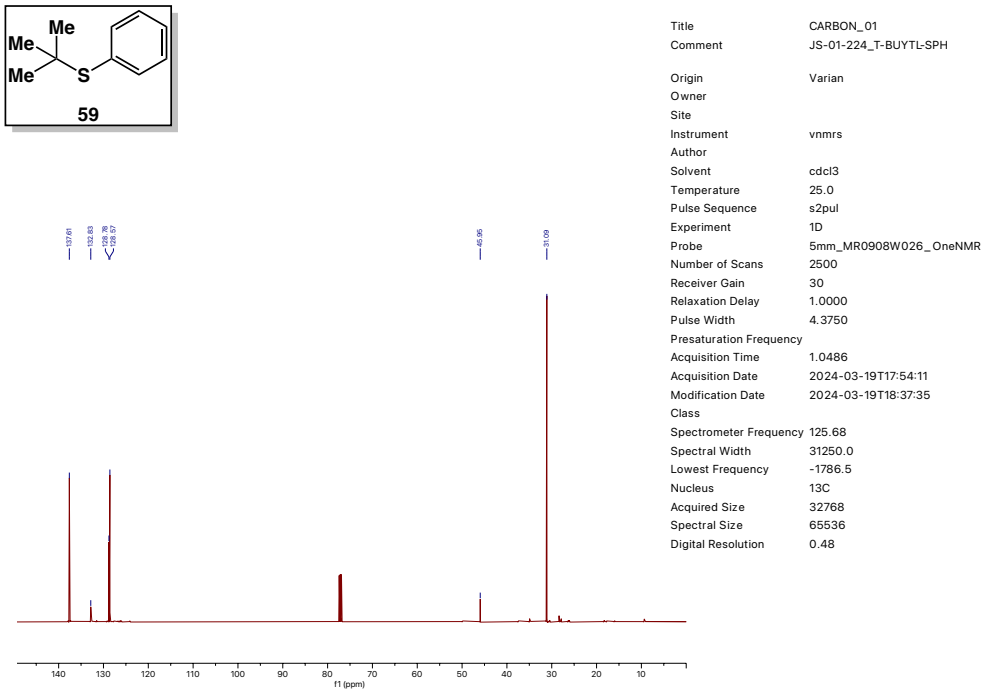
Supplementary Fig. 147. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 58.**



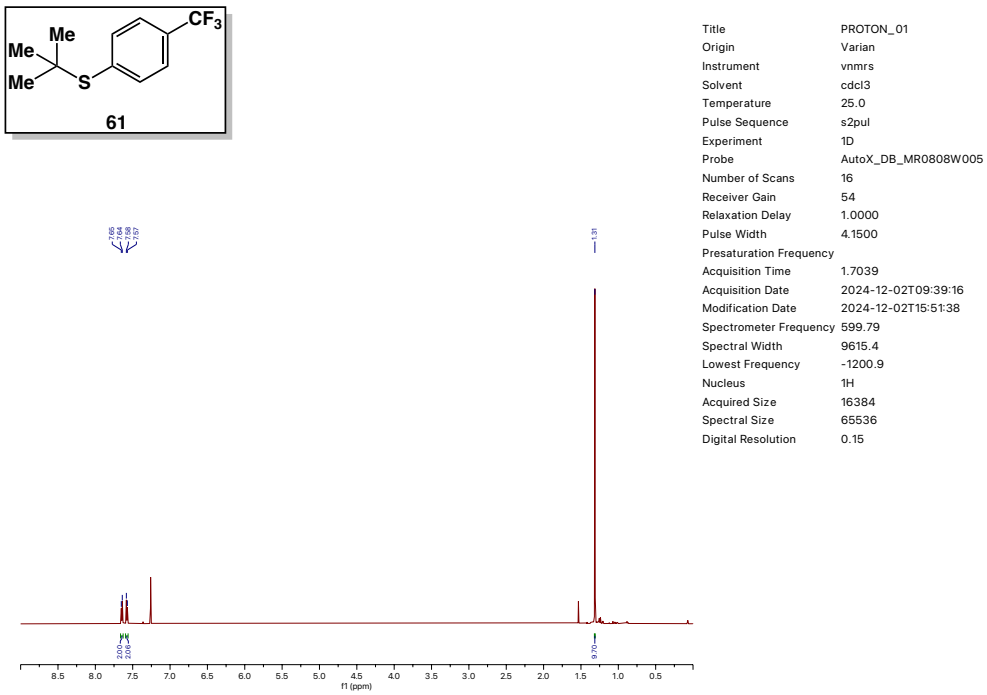
Supplementary Fig. 148. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 58.**



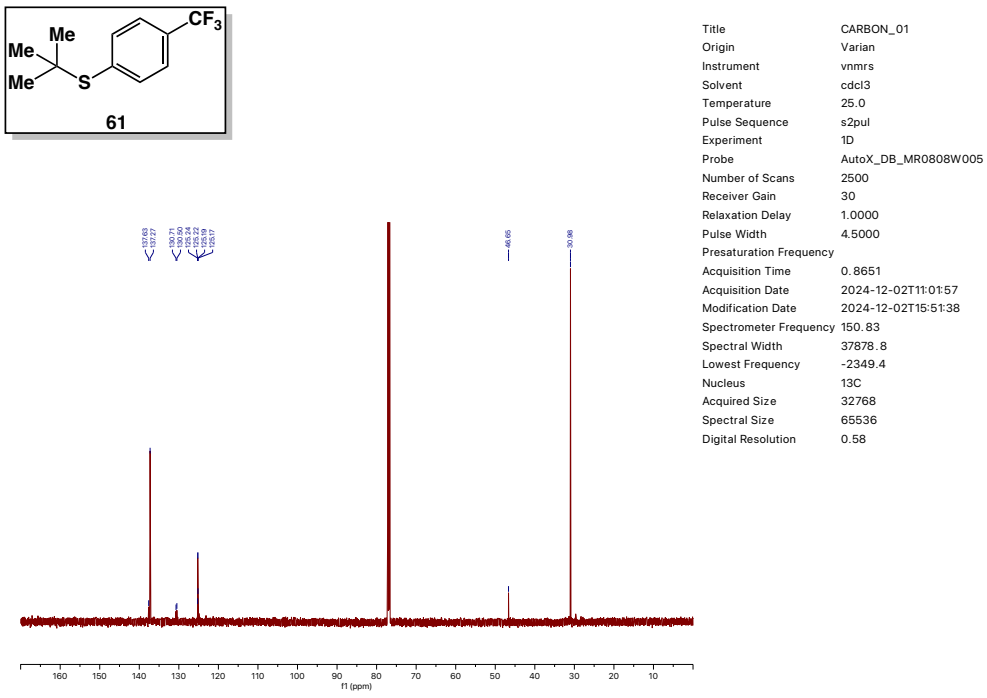
Supplementary Fig. 149. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 59.**



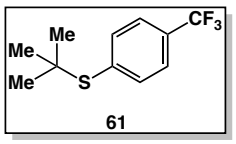
Supplementary Fig. 150. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 59.**



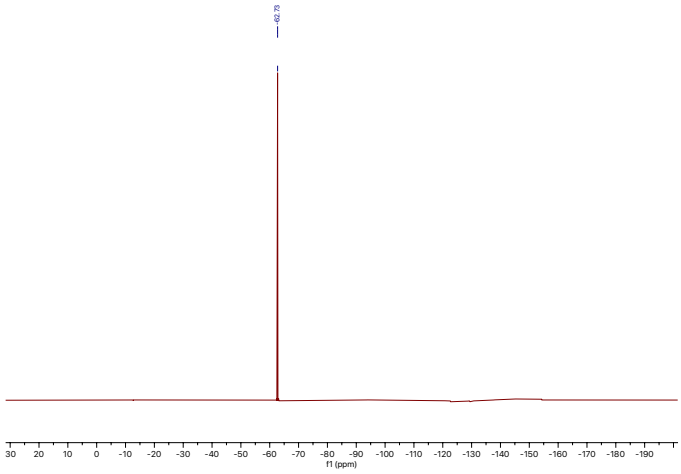
Supplementary Fig. 151. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 61.**



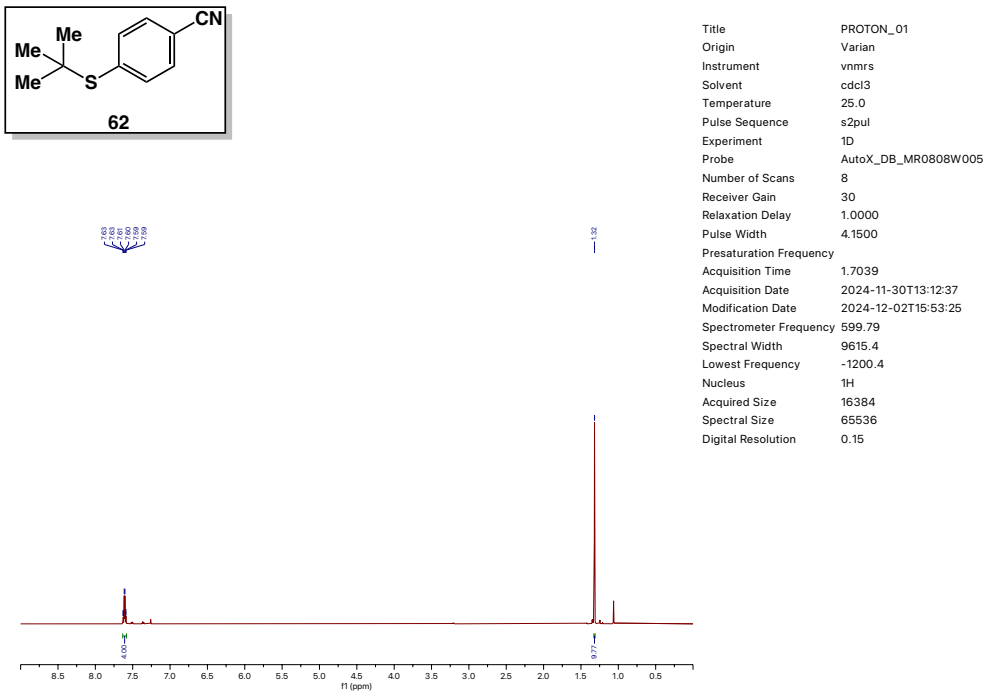
Supplementary Fig. 152. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 61.**



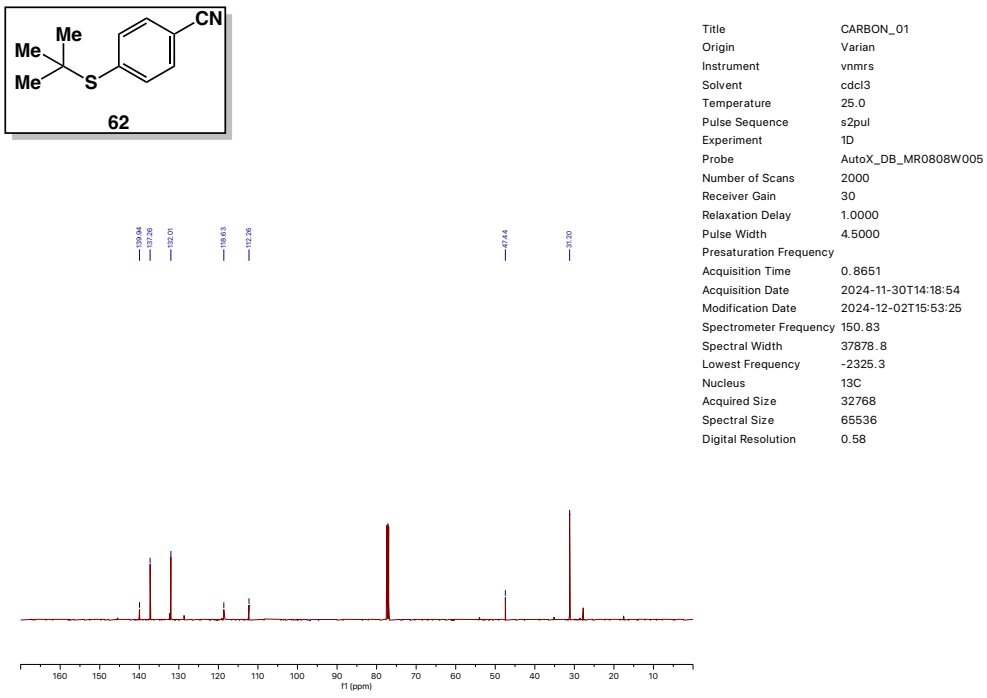
Title	FLUORINE_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	4.8667
Presaturation Frequency	
Acquisition Time	0.9961
Acquisition Date	2024-12-02T09:42:19
Modification Date	2024-12-02T15:51:38
Spectrometer Frequency	564.32
Spectral Width	131578.9
Lowest Frequency	-113760.7
Nucleus	19F
Acquired Size	131072
Spectral Size	262144
Digital Resolution	0.50



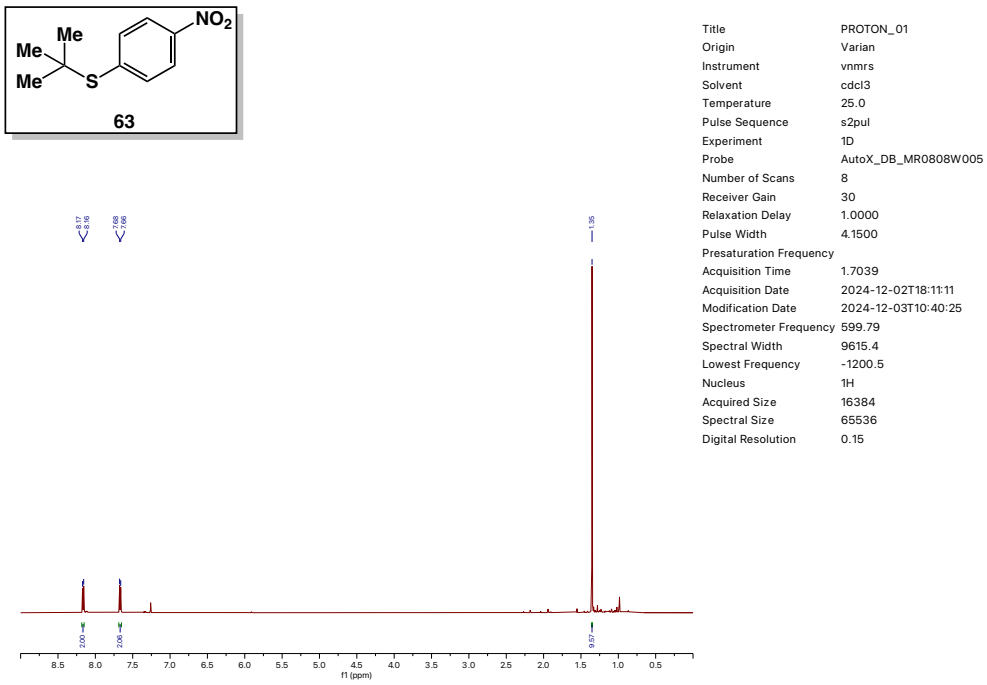
Supplementary Fig. 153. **^{19}F NMR (564 MHz, $CDCl_3$) spectrum of thioether 61.**



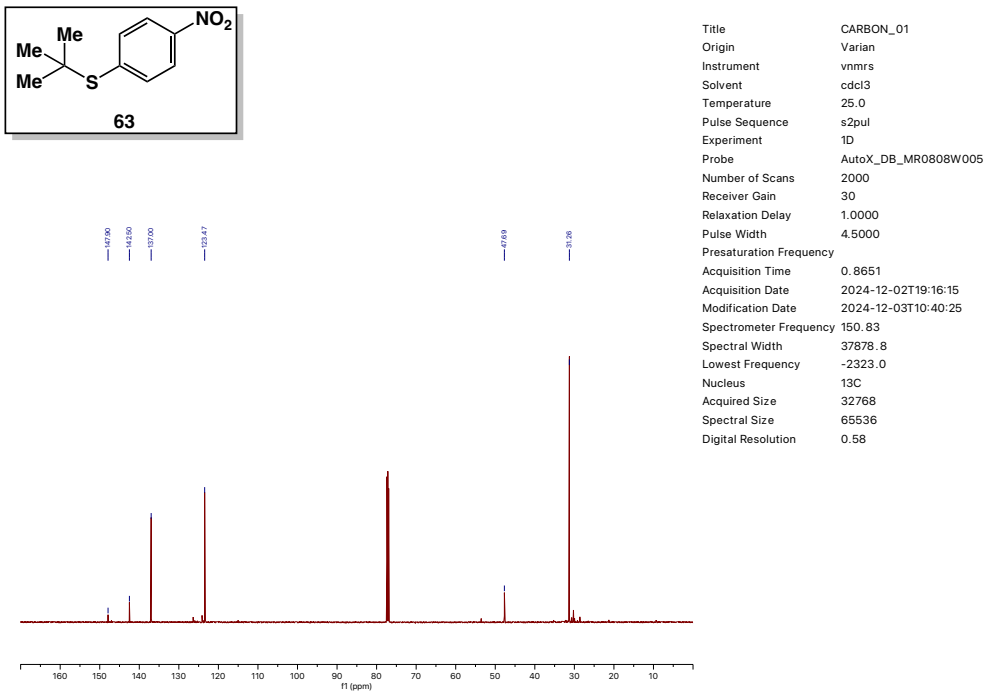
Supplementary Fig. 154. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 62.**



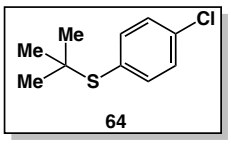
Supplementary Fig. 155. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 62.**

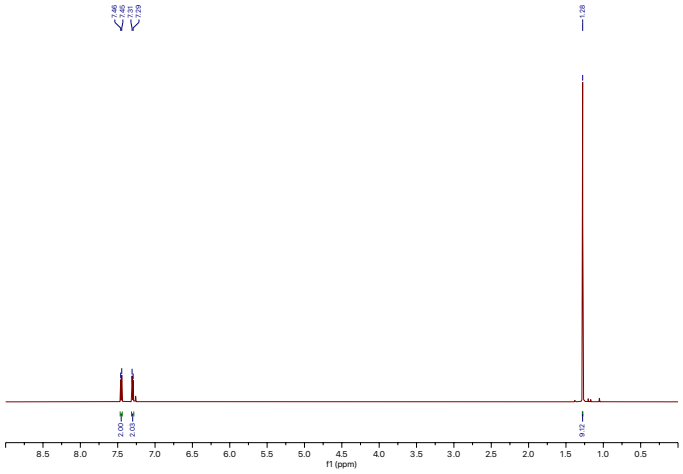


Supplementary Fig. 156. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 63.**



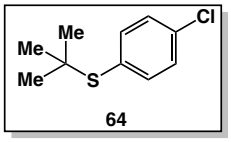
Supplementary Fig. 157. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 63.**

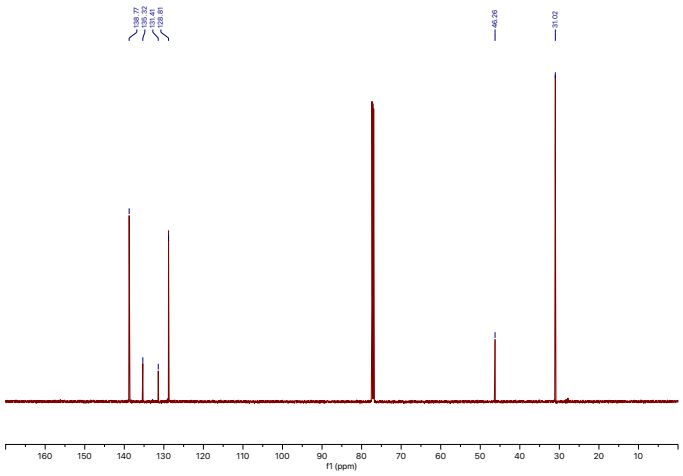




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-11-30T14:31:28
Modification Date	2024-12-02T15:51:48
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1200.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

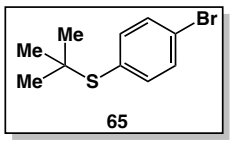
Supplementary Fig. 158. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 64.**

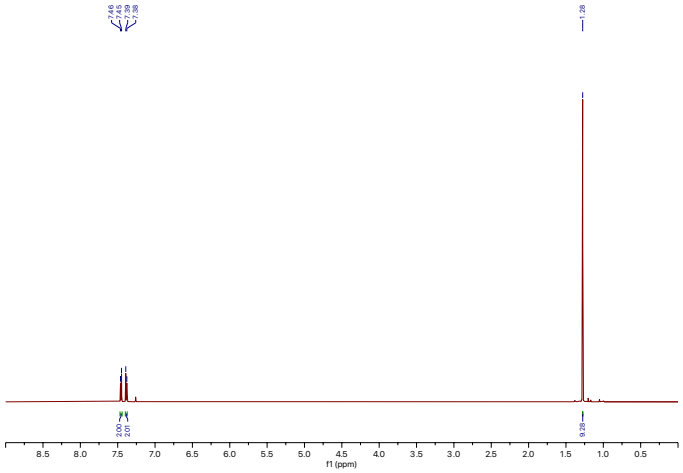




Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-11-30T15:35:01
Modification Date	2024-12-02T15:51:48
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2323.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

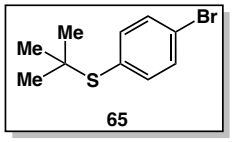
Supplementary Fig. 159. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 64.**

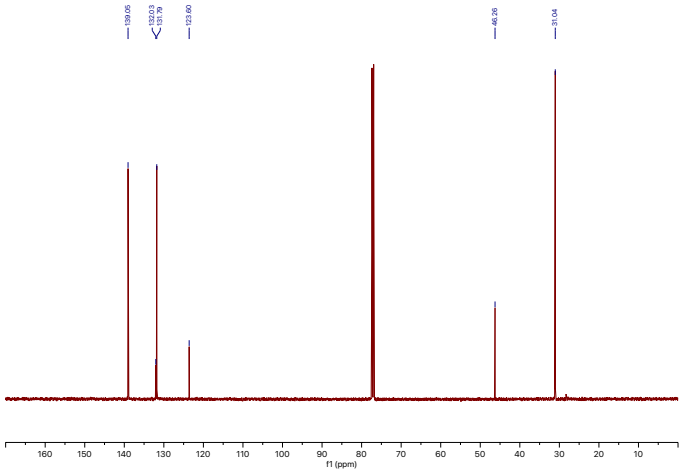




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-11-30T12:04:53
Modification Date	2024-12-02T15:51:21
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1200.5
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

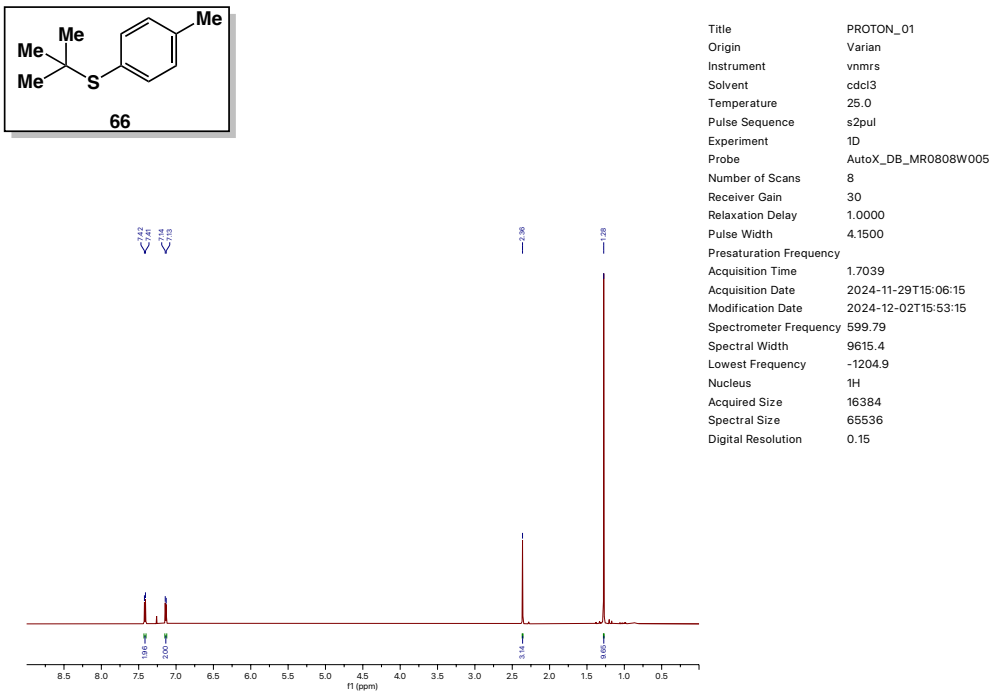
Supplementary Fig. 160. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 65.**



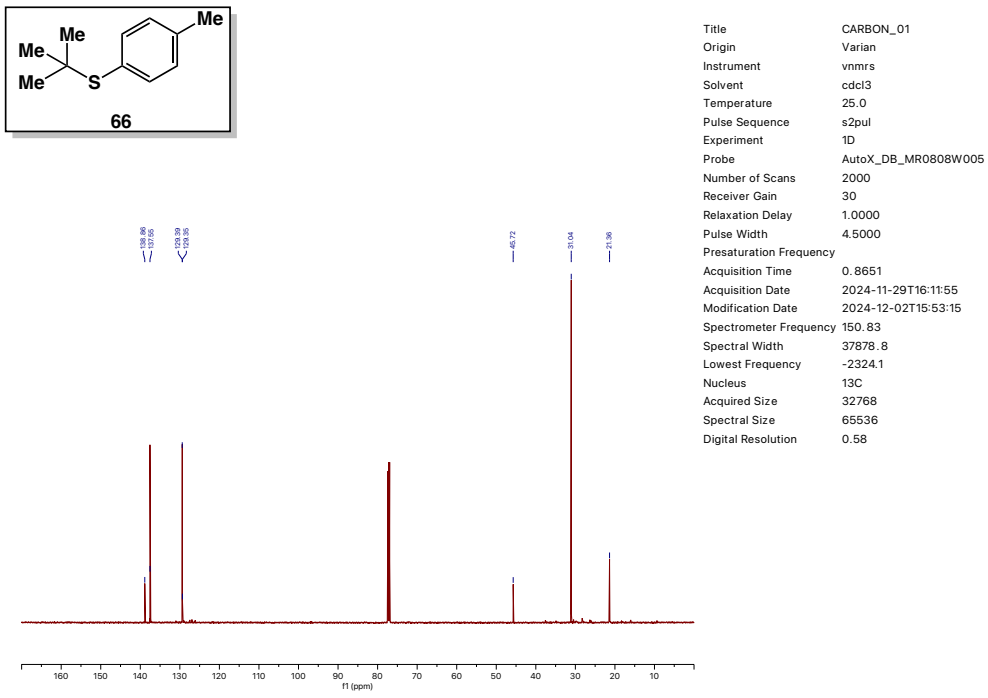


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-11-30T13:08:38
Modification Date	2024-12-02T15:51:21
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2323.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

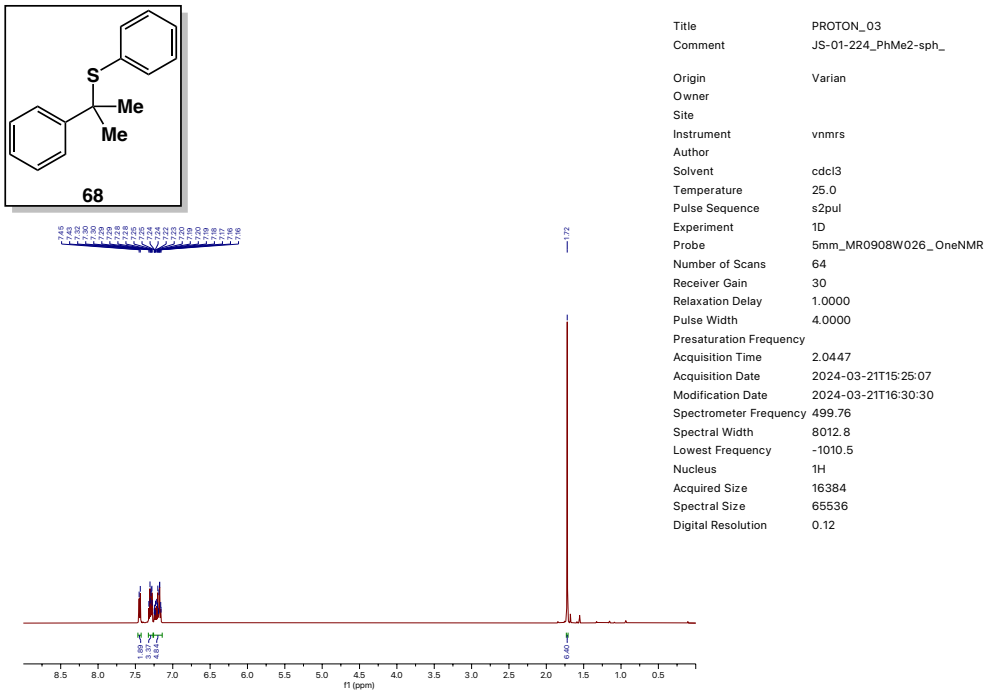
Supplementary Fig. 161. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 65.**



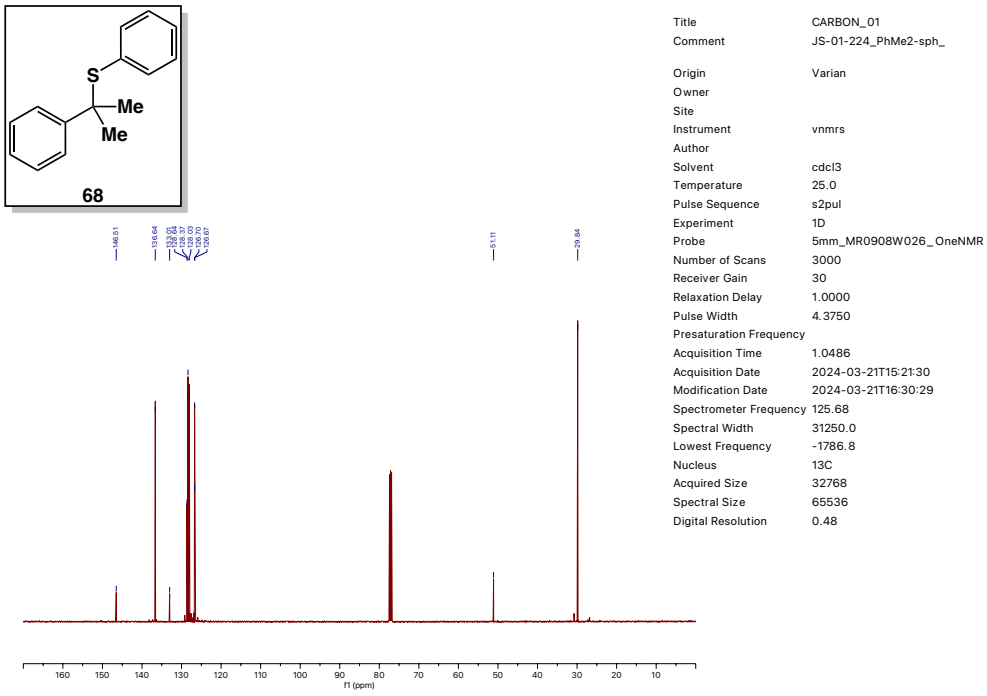
Supplementary Fig. 162. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 66.**



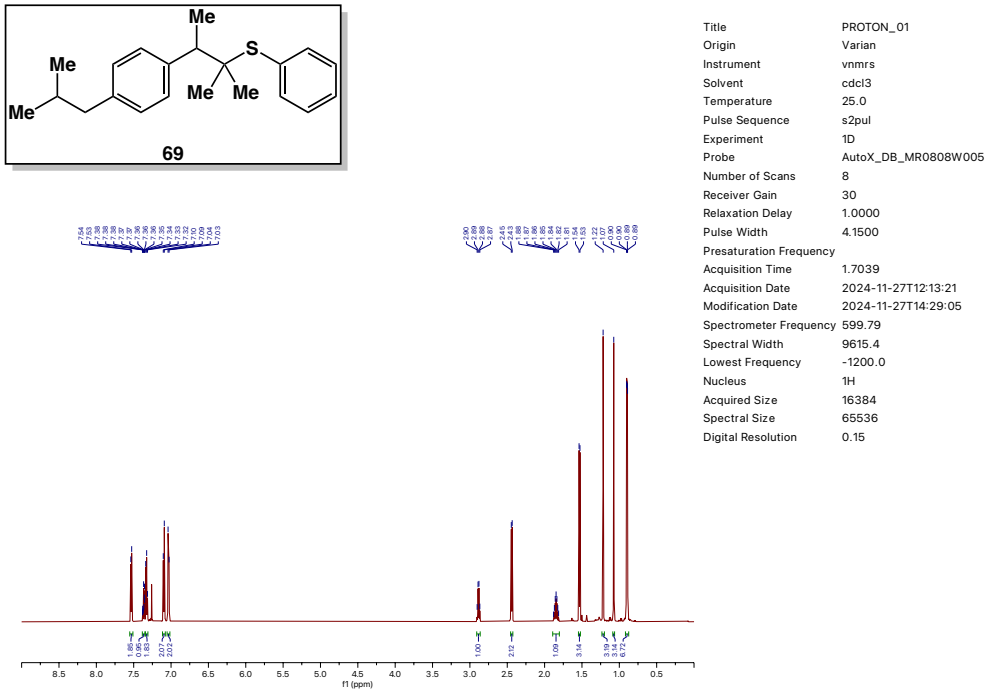
Supplementary Fig. 163. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 66.**



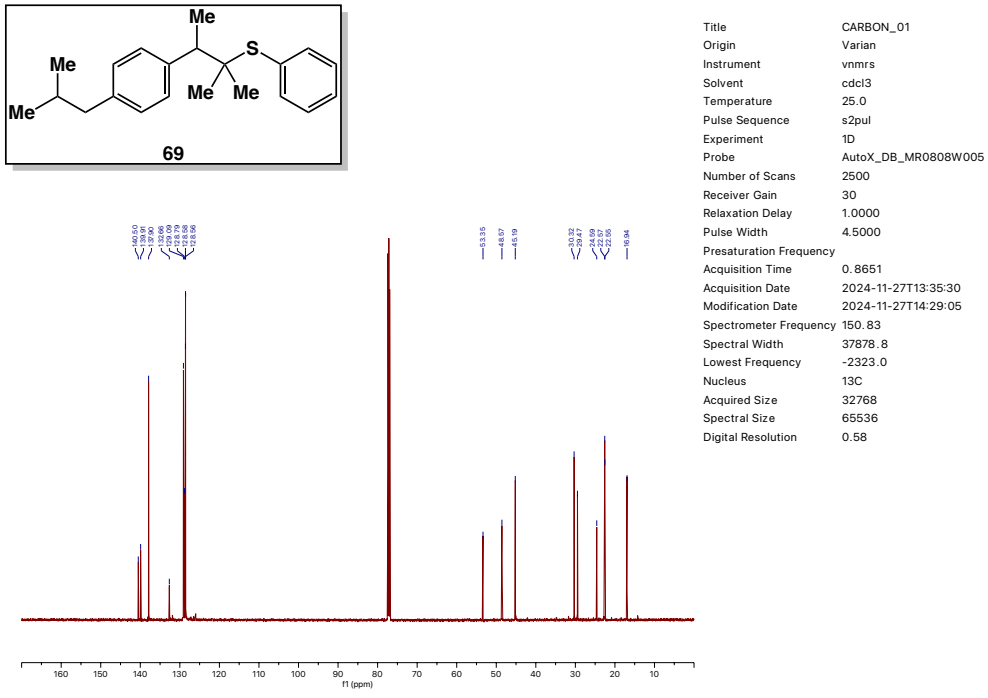
Supplementary Fig. 164. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 68.**



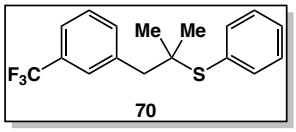
Supplementary Fig. 165. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 68.**

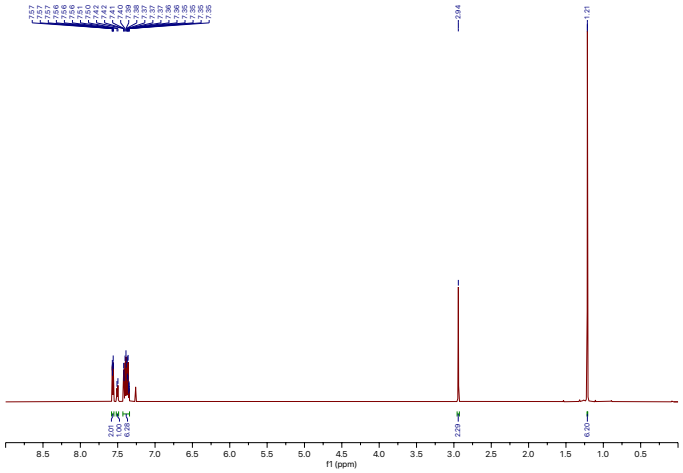


Supplementary Fig. 166. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 69.**



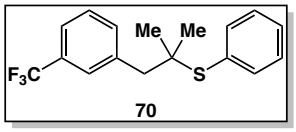
Supplementary Fig. 167. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 69.**

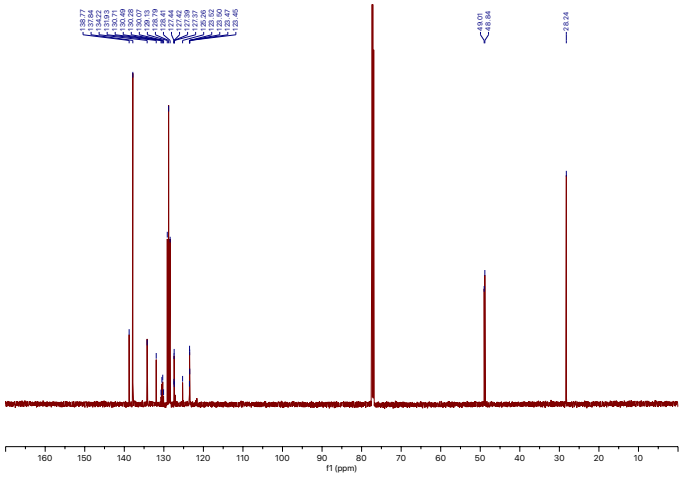




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-12-01T10:49:08
Modification Date	2024-12-02T15:47:26
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1201.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

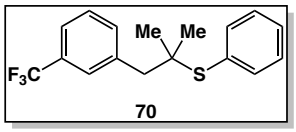
Supplementary Fig. 168. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 70.**





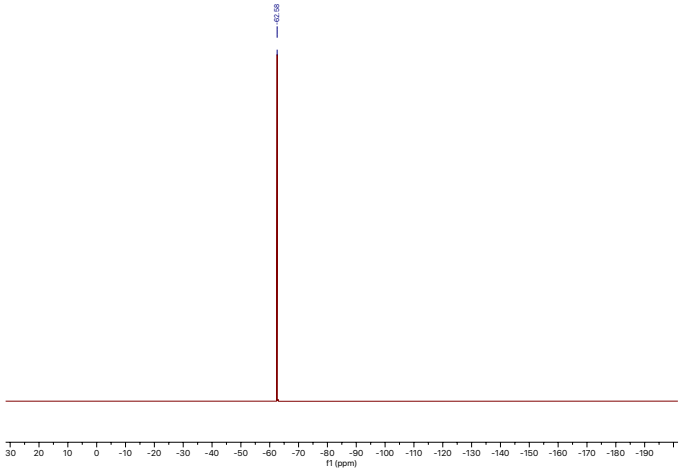
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-12-01T12:09:58
Modification Date	2024-12-02T15:47:26
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2323.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 169. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 70.**

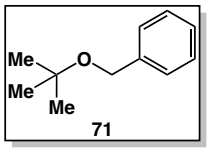


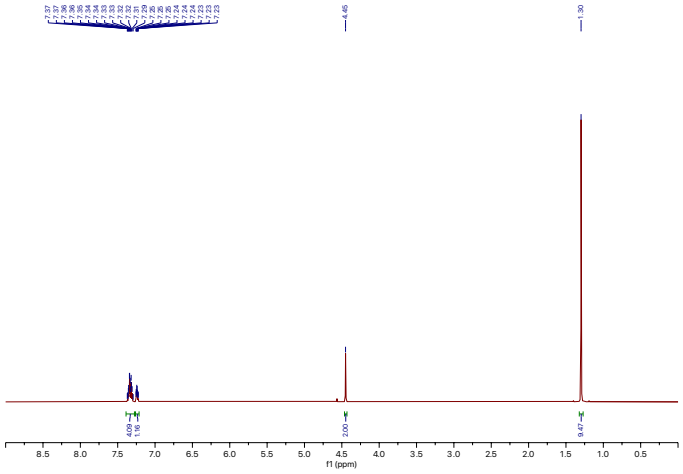
70

Title	FLUORINE_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	4.8667
Presaturation Frequency	
Acquisition Time	0.9961
Acquisition Date	2024-12-01T12:12:53
Modification Date	2024-12-02T15:47:26
Spectrometer Frequency	564.32
Spectral Width	131578.9
Lowest Frequency	-113760.7
Nucleus	19F
Acquired Size	131072
Spectral Size	262144
Digital Resolution	0.50



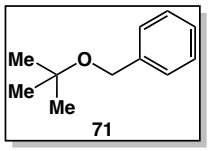
Supplementary Fig. 170. **^{19}F NMR (564 MHz, $CDCl_3$) spectrum of thioether 70.**

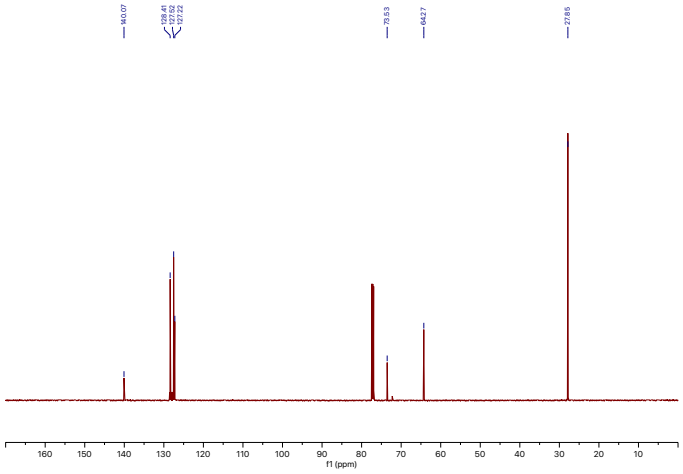




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-10-31T13:34:37
Modification Date	2024-10-31T14:11:54
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1208.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

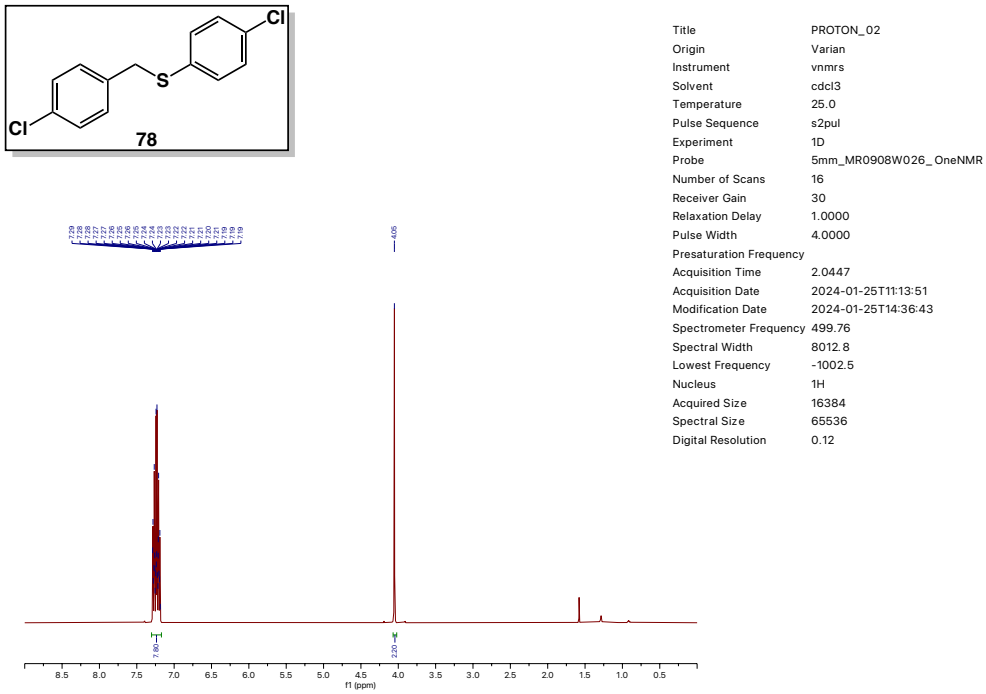
Supplementary Fig. 171. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of thioether 71.**



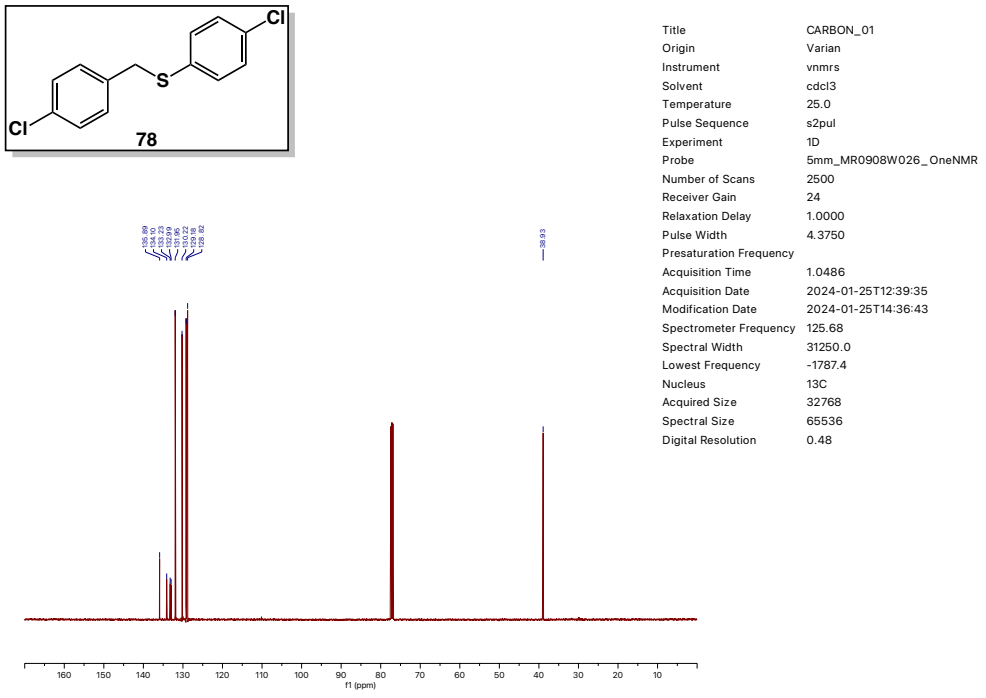


Title	CARBON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	1500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-10-31T15:13:13
Modification Date	2024-10-31T15:38:22
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2327.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

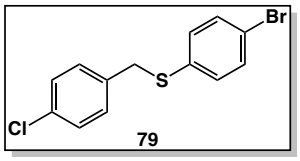
Supplementary Fig. 172. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of thioether 71.**

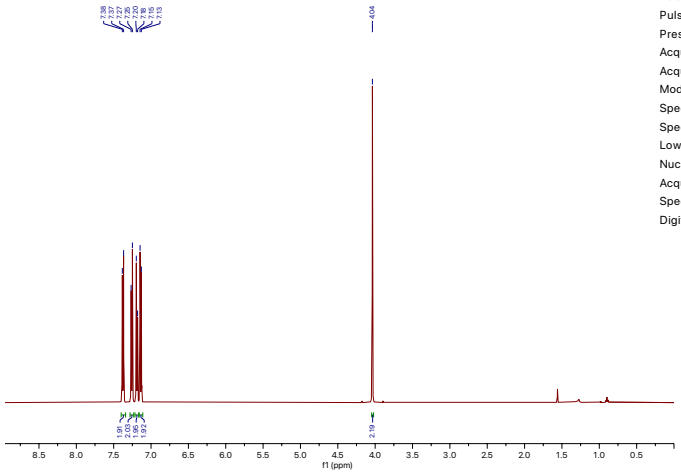


Supplementary Fig. 173. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 78.**



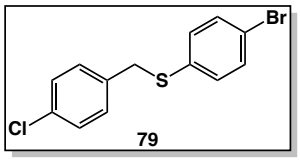
Supplementary Fig. 174. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 78.**

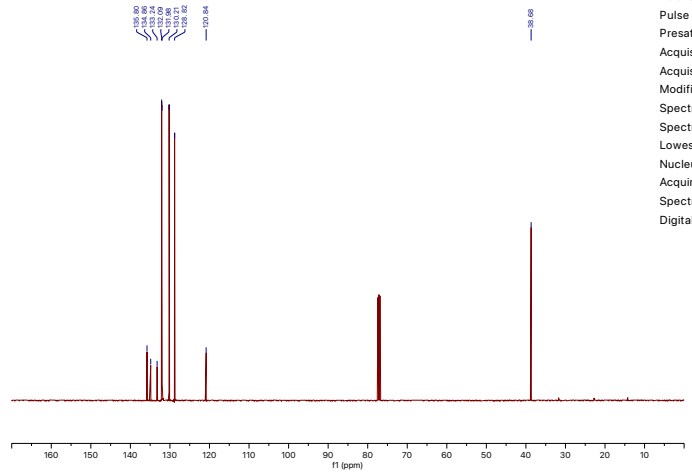




Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2024-01-25T12:48:51
Modification Date	2024-01-25T14:36:43
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1012.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

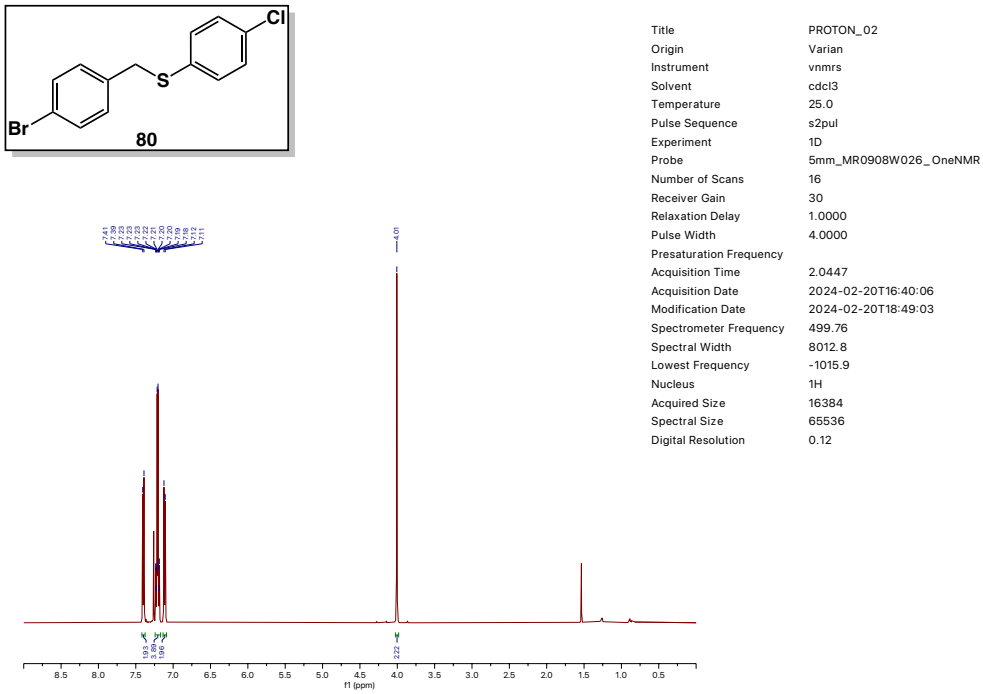
Supplementary Fig. 175. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 79.**





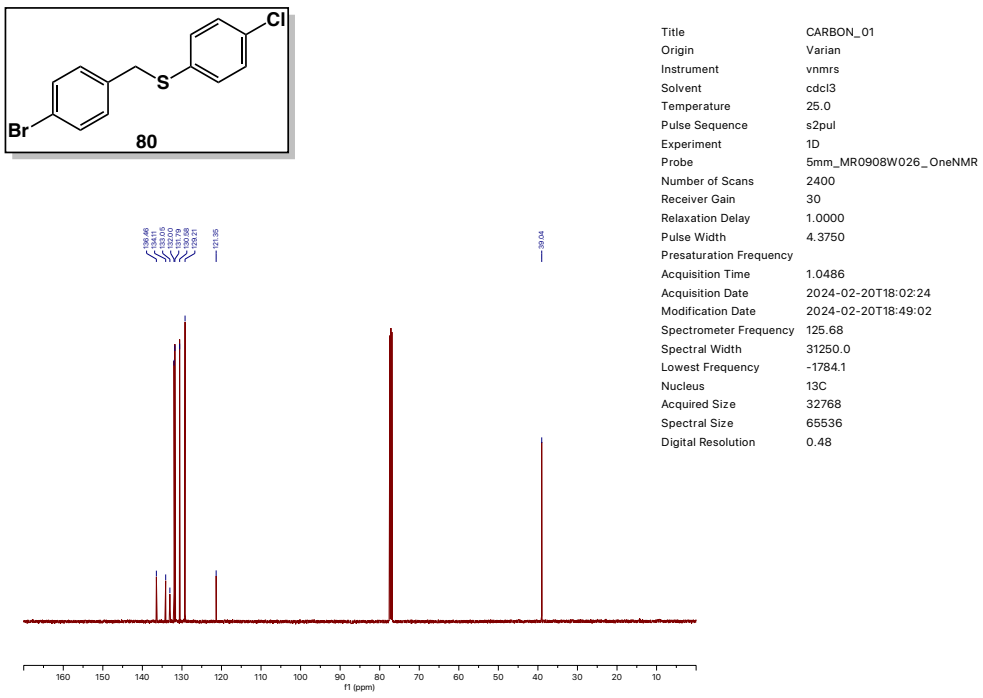
Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2024-01-25T14:14:33
Modification Date	2024-01-25T14:36:43
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1789.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

Supplementary Fig. 176. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 79.**



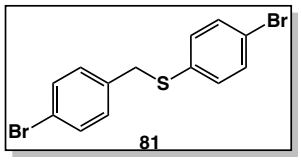
Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2024-02-20T16:40:06
Modification Date	2024-02-20T18:49:03
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1015.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

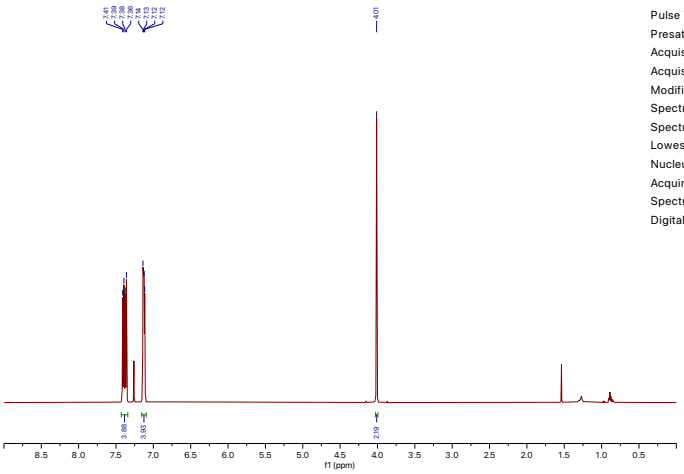
Supplementary Fig. 177. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 80.**



Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	2400
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2024-02-20T18:02:24
Modification Date	2024-02-20T18:49:02
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1784.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

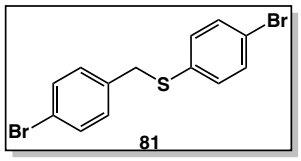
Supplementary Fig. 178. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 80.**

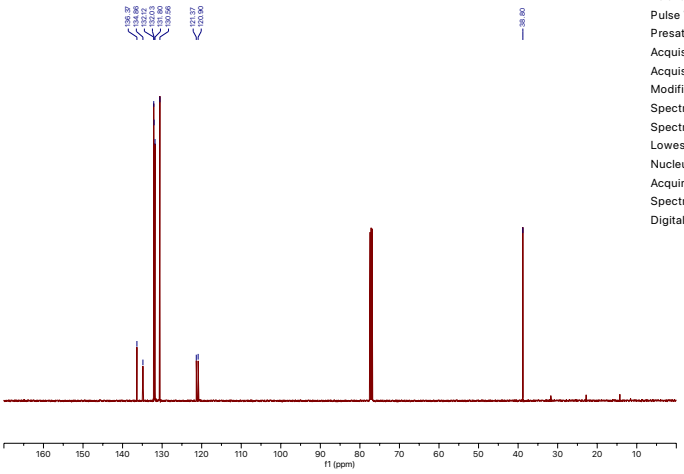




Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2024-02-20T15:05:16
Modification Date	2024-02-20T18:49:54
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1015.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

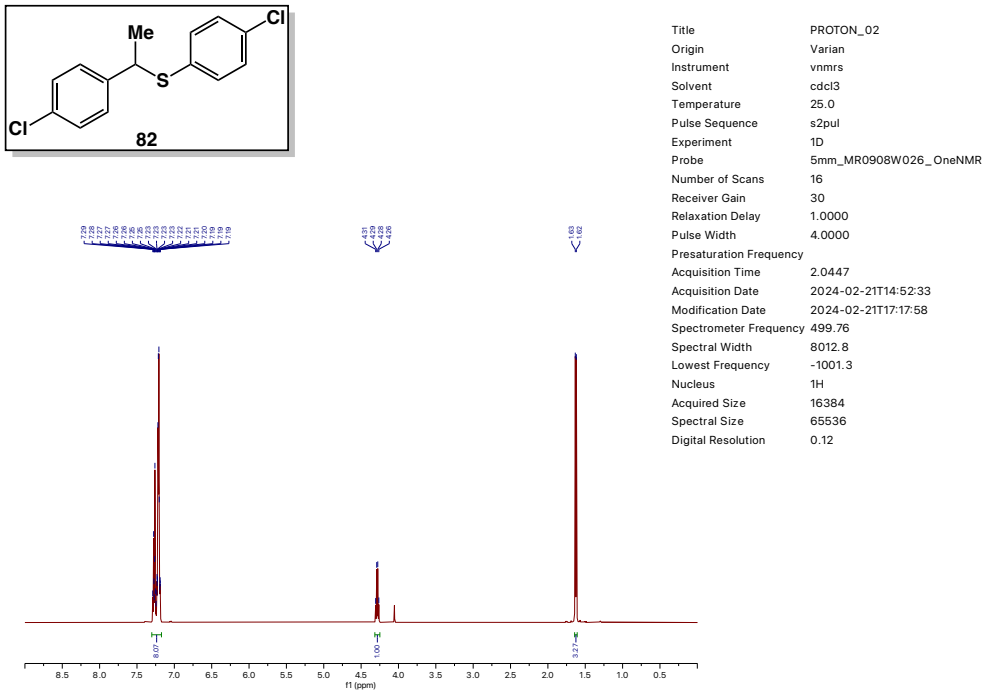
Supplementary Fig. 179. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 81.**



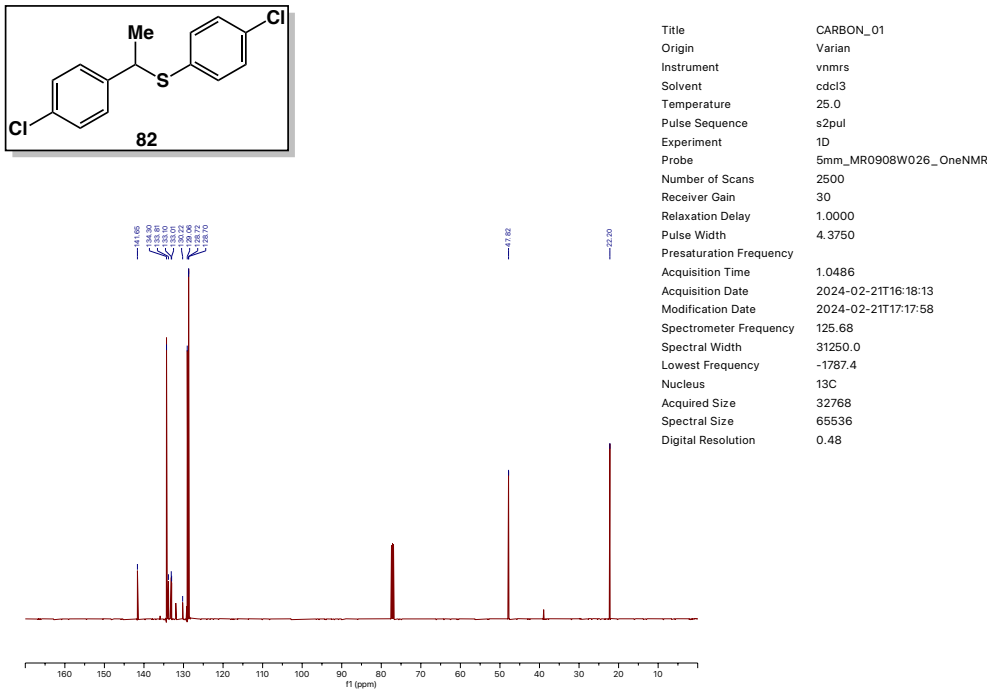


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2024-02-20T16:33:01
Modification Date	2024-02-20T18:49:54
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1785.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

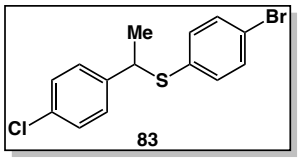
Supplementary Fig. 180. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 81.**



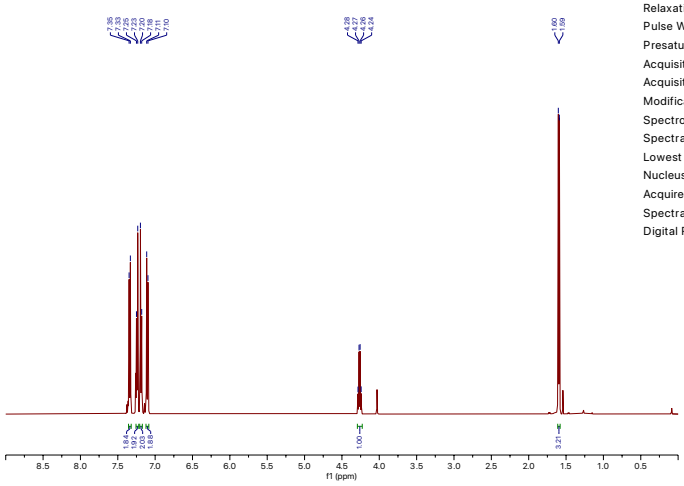
Supplementary Fig. 181. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 82.**



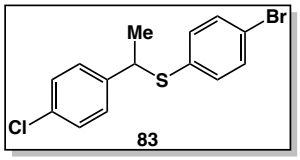
Supplementary Fig. 182. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 82.**



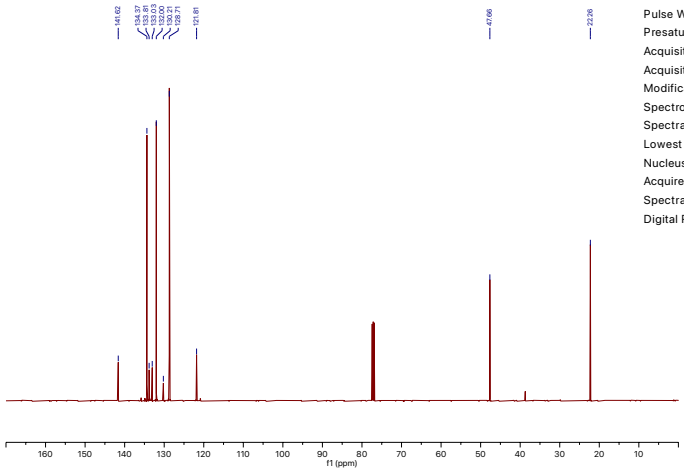
Title	PROTON_02
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2024-02-21T13:18:18
Modification Date	2024-02-21T17:17:58
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1015.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12



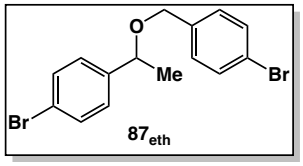
Supplementary Fig. 183. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of thioether 83.**

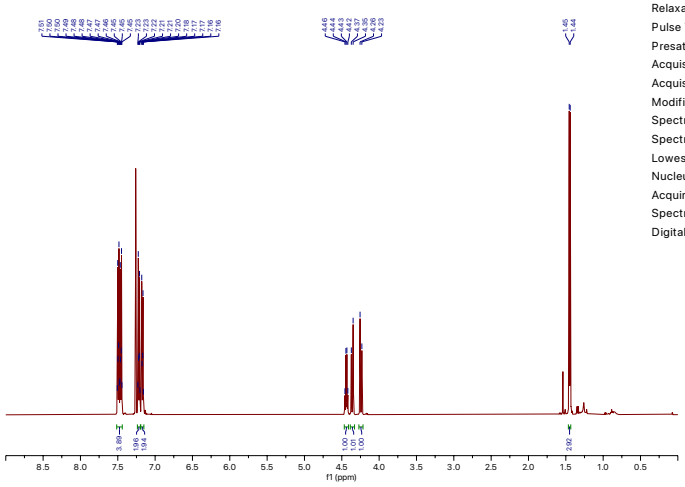


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	2500
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2024-02-21T14:43:58
Modification Date	2024-02-21T17:17:58
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1787.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48



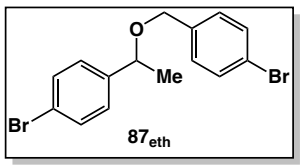
Supplementary Fig. 184. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of thioether 83.**

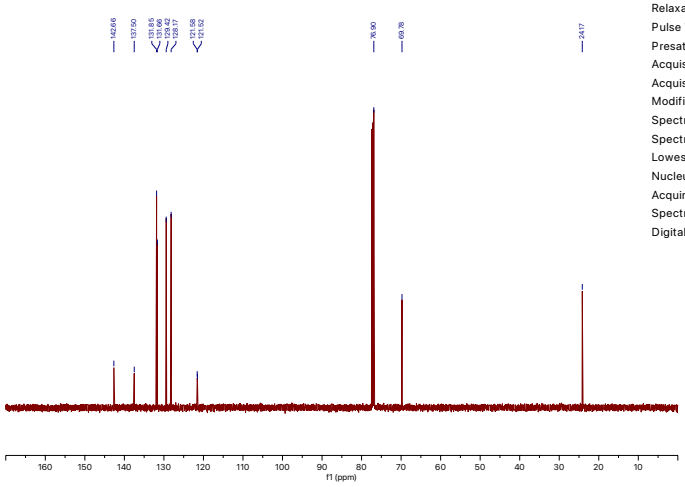




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	32
Receiver Gain	30
Relaxation Delay	5.0000
Pulse Width	4.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2024-10-26T12:49:18
Modification Date	2024-10-26T13:52:07
Spectrometer Frequency	499.76
Spectral Width	8012.8
Lowest Frequency	-1012.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.12

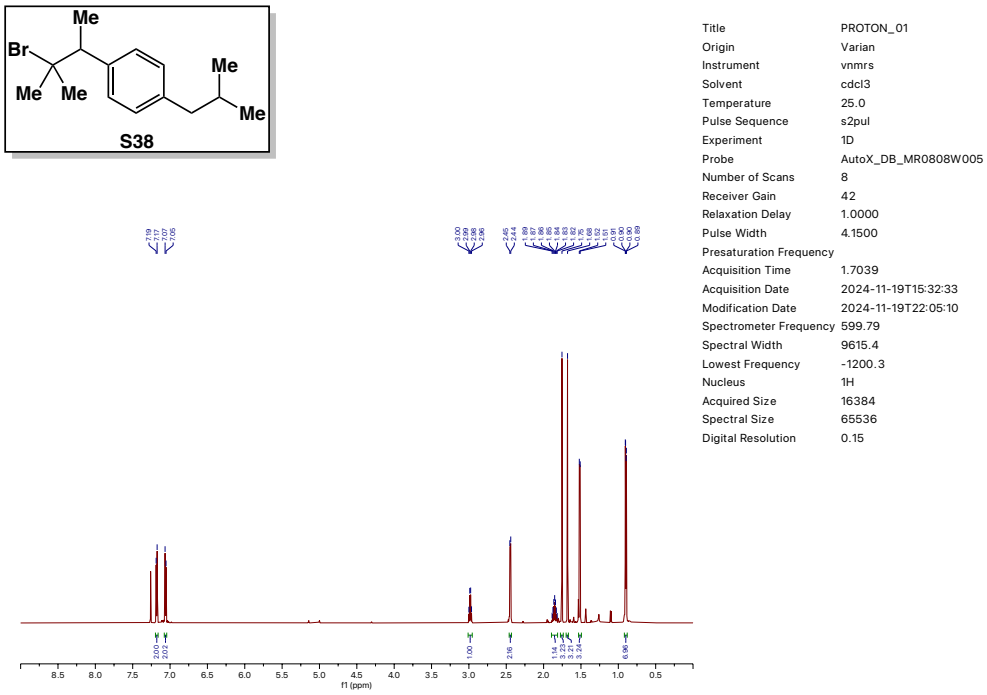
Supplementary Fig. 185. **^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ether 87$_{eth}$.**



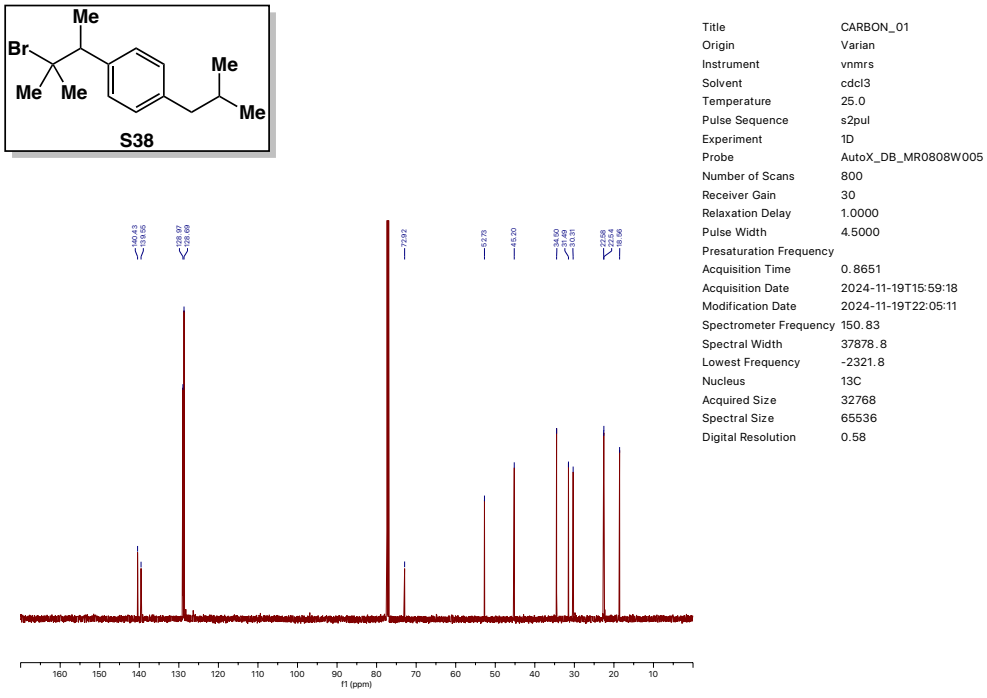


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	5mm_MR0908W026_OneNMR
Number of Scans	512
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.3750
Presaturation Frequency	
Acquisition Time	1.0486
Acquisition Date	2024-10-26T13:10:05
Modification Date	2024-10-26T13:52:07
Spectrometer Frequency	125.68
Spectral Width	31250.0
Lowest Frequency	-1783.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.48

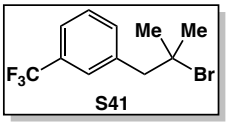
Supplementary Fig. 186. **^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ether 87$_{eth}$.**

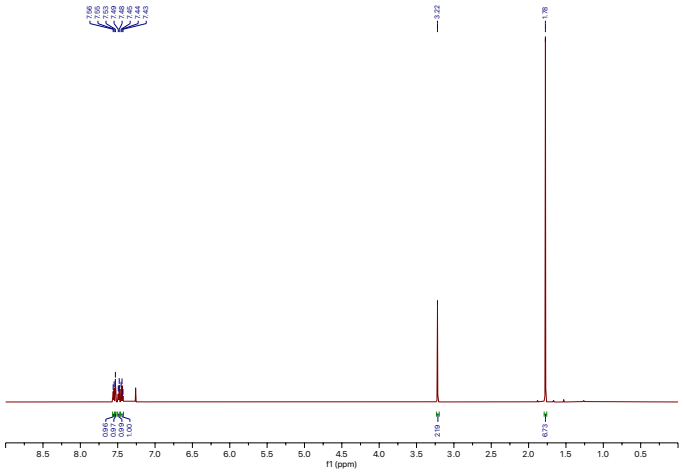


Supplementary Fig. 187. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of bromide S38.**



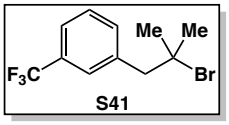
Supplementary Fig. 188. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of bromide S38.**

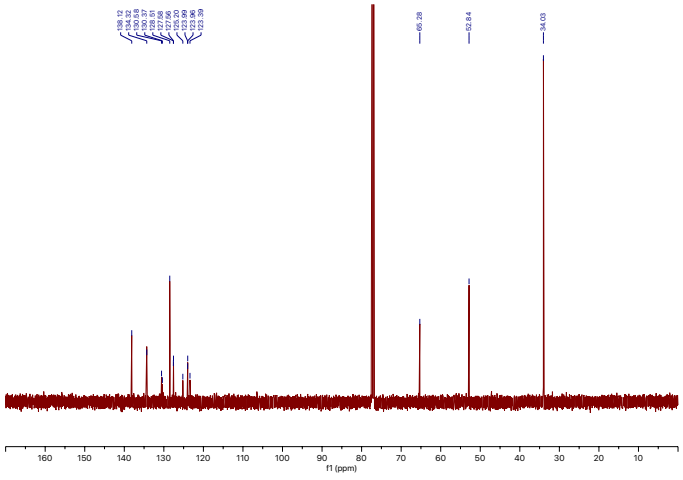




Title	PROTON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	8
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	4.1500
Presaturation Frequency	
Acquisition Time	1.7039
Acquisition Date	2024-11-28T12:07:36
Modification Date	2024-12-02T15:50:24
Spectrometer Frequency	599.79
Spectral Width	9615.4
Lowest Frequency	-1206.2
Nucleus	1H
Acquired Size	16384
Spectral Size	65536
Digital Resolution	0.15

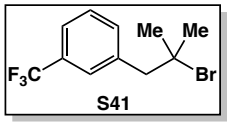
Supplementary Fig. 189. **^{1}H NMR (600 MHz, $CDCl_3$) spectrum of bromide S41.**



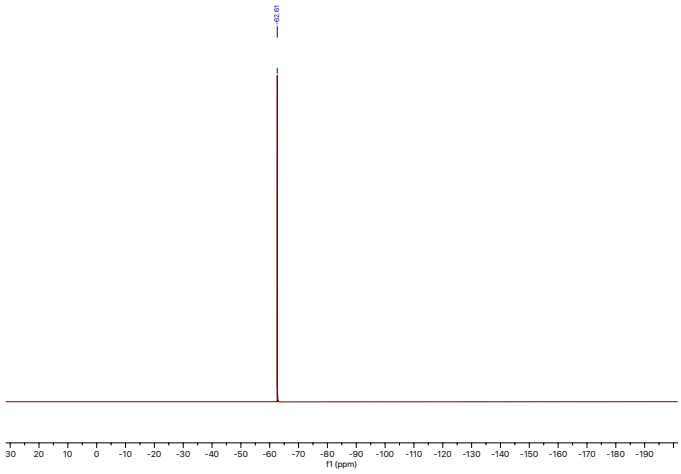


Title	CARBON_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	1000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.5000
Presaturation Frequency	
Acquisition Time	0.8651
Acquisition Date	2024-11-28T12:41:59
Modification Date	2024-12-02T15:50:24
Spectrometer Frequency	150.83
Spectral Width	37878.8
Lowest Frequency	-2323.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.58

Supplementary Fig. 190. **^{13}C NMR (150 MHz, $CDCl_3$) spectrum of bromide S41.**

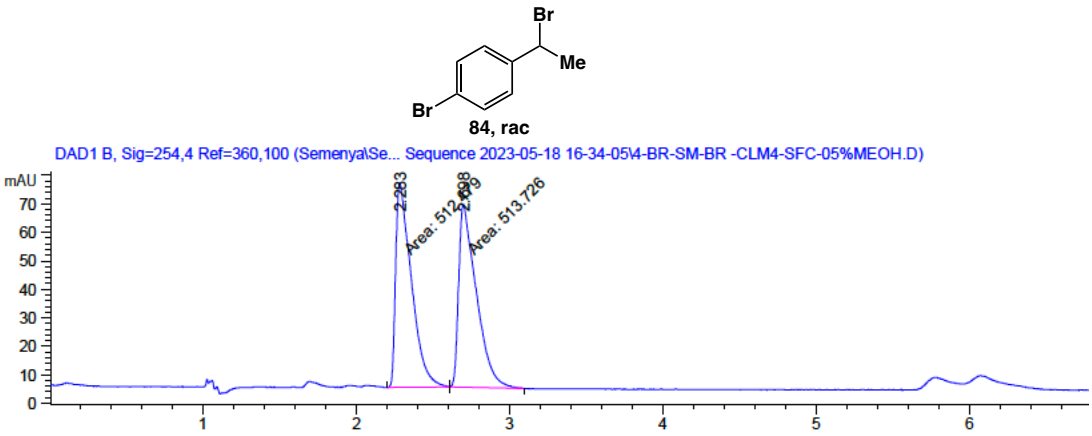


Title	FLUORINE_01
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	AutoX_DB_MR0808W005
Number of Scans	16
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	4.8667
Presaturation Frequency	
Acquisition Time	0.9961
Acquisition Date	2024-11-28T12:43:41
Modification Date	2024-12-02T15:50:24
Spectrometer Frequency	564.32
Spectral Width	131578.9
Lowest Frequency	-113760.7
Nucleus	19F
Acquired Size	131072
Spectral Size	262144
Digital Resolution	0.50



Supplementary Fig. 191. **^{19}F NMR (564 MHz, $CDCl_3$) spectrum of bromide S41.**

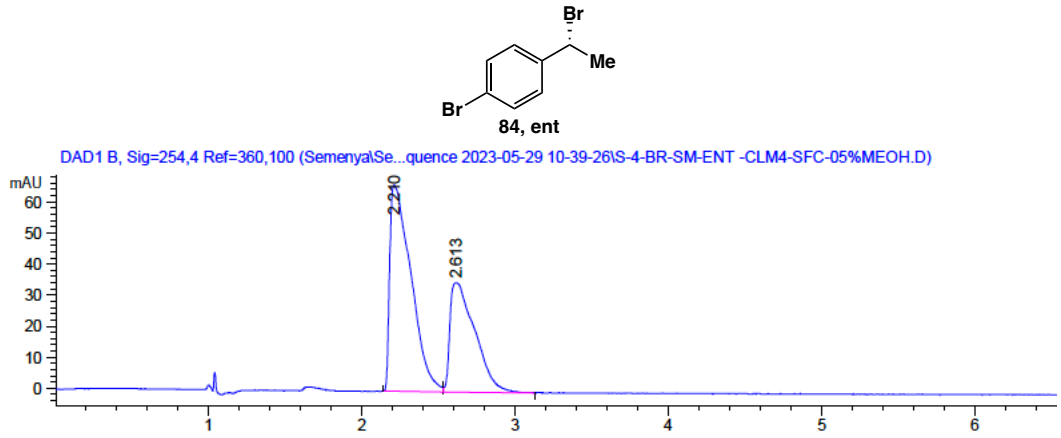
I. SFC data



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.283	MM	0.1188	512.47937	71.89185	49.9393
2	2.698	MM	0.1337	513.72620	64.01808	50.0607
Totals :				1026.20557	135.90993	

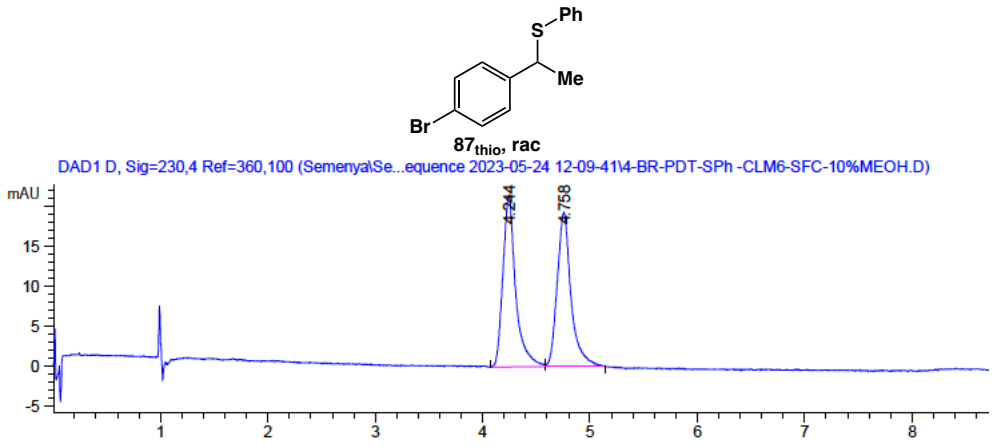
Supplementary Fig. 192. **SFC data of racemic bromide 84.**



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.210	BV	0.1350	639.29968	66.30545	61.7159
2	2.613	VV R	0.1455	396.57468	35.03807	38.2841
Totals :				1035.87436	101.34352	

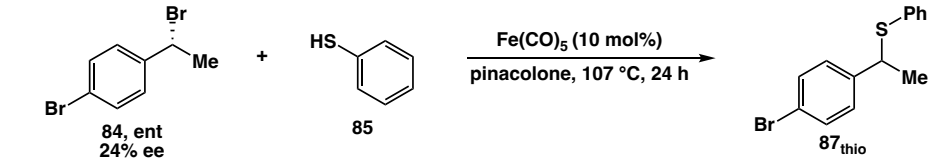
Supplementary Fig. 193. **SFC data of enantiomeric bromide 84.**

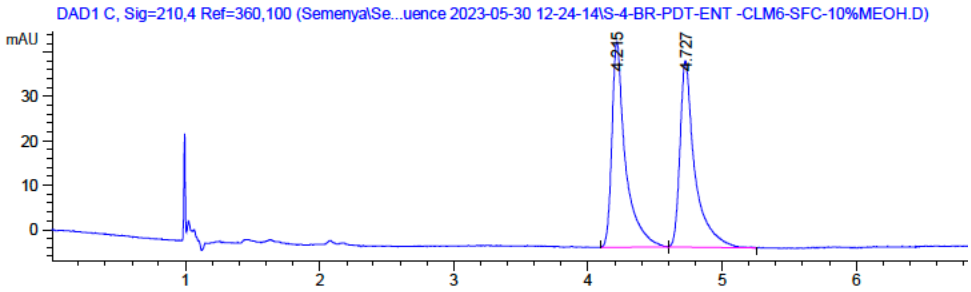


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.244	BV	0.1156	176.66917	21.44798	50.5049
2	4.758	VV R	0.1209	173.13667	19.25885	49.4951
Totals :				349.80585	40.70683	

Supplementary Fig. 194. **SFC data of racemic thioether 87.**

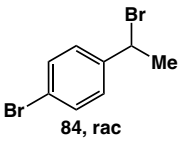




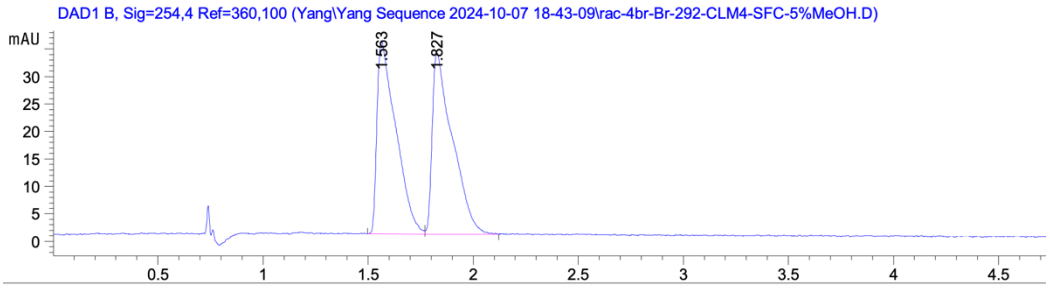
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.215	BB	0.1001	325.49915	46.28148	50.1396
2	4.727	BV R	0.1105	323.68665	41.98196	49.8604
Totals :				649.18579	88.26344	

Supplementary Fig. 195. **SFC data of thioether 87.**



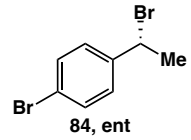
84, rac



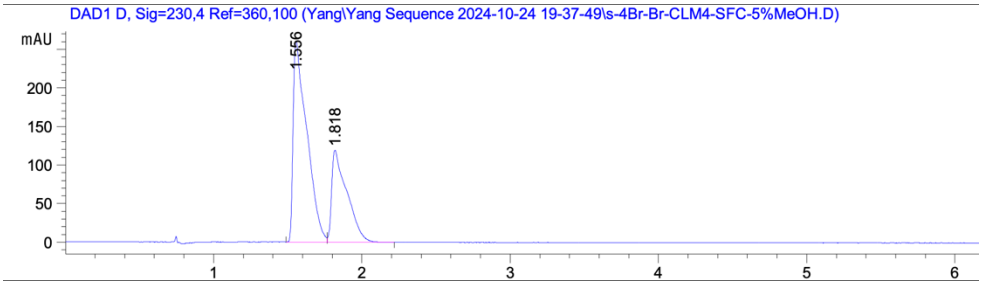
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.563	BV	0.0839	219.88115	35.19555	49.9082
2	1.827	VV R	0.0910	220.68973	33.00345	50.0918
Totals :				440.57088	68.19900	

Supplementary Fig. 196. **SFC data of racemic bromide 84**



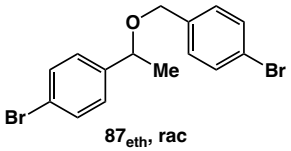
84, ent



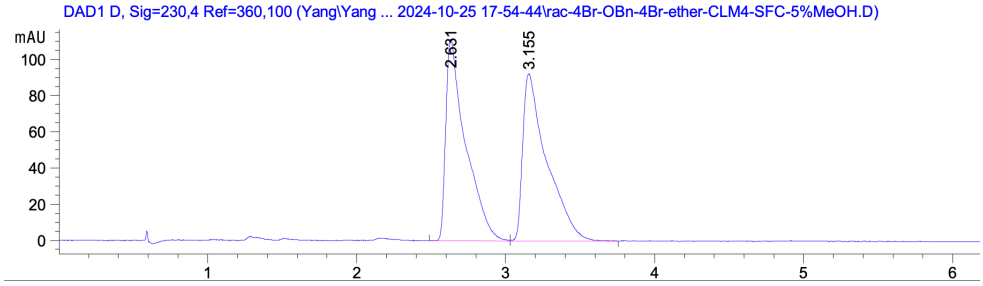
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.556	BV	0.0867	1677.45593	260.41177	66.2398
2	1.818	VV R	0.0952	854.94324	119.20483	33.7602
Totals :				2532.39917	379.61661	

Supplementary Fig. 197. **SFC data of enantiomeric bromide 84.**



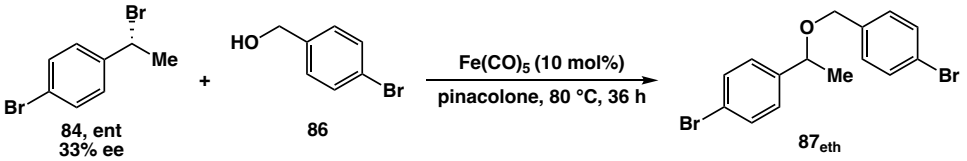
87$_{eth}$, rac

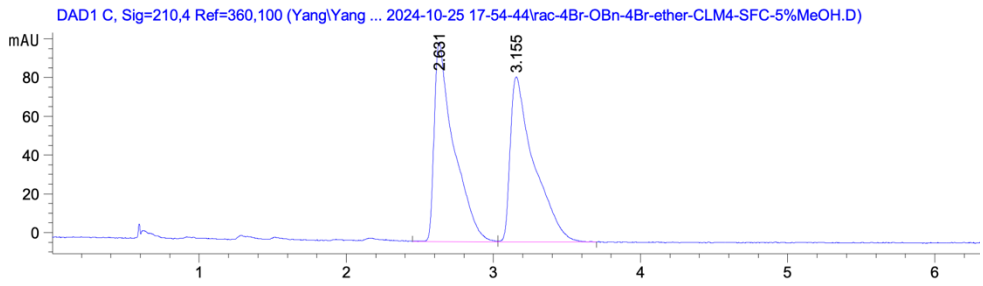


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.631	BV	0.1279	1029.30273	111.28088	49.8333
2	3.155	VV R	0.1509	1036.18713	92.35968	50.1667
Totals :				2065.48987	203.64056	

Supplementary Fig. 198. **SFC data of racemic ether 87.**





Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.631	VV R	0.1269	950.59943	102.76118	49.9611
2	3.155	VV R	0.1499	952.08063	85.15626	50.0389
Totals :				1902.68005	187.91744	

Supplementary Fig. 199. **SFC data of ether 87.**

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