Electronic Supplementary Information

Use of Dipyridyldithiocarbonate (DPDTC) as an Environmentally Responsible Reagent Leading to Esters and Thioesters under Green Chemistry Conditions

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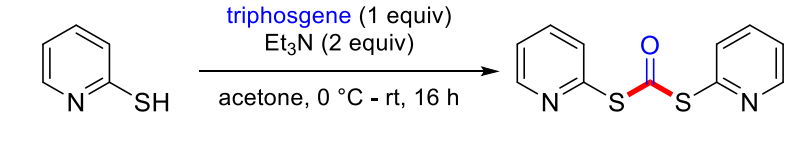
1. General Information

A solution of 2 wt % surfactant/H_2O was prepared by dissolving the surfactant in degassed HPLC grade water and was stored under argon. TPGS-750-M was obtained from PHT International, but is also available from Sigma-Aldrich (catalog #733857). All commercially available reagents were purchased from Sigma-Aldrich, Combi-Blocks, Ambeed Inc., Acros Organics, BLD Pharma, Fischer Scientific, or ChemScene and used without further purification. Thin layer chromatography (TLC) was done using Silica Gel 60 F254 plates (Merck, 0.25 mm thick). The developed TLC plate was analyzed by a UV lamp (254 nm). The plates were further analyzed with the use of a bromocresol green stain and developed with a heat gun. All commercially available reagents were used without further purification. Flash chromatography was performed using Silicycle Silicaflash® P60 unbonded grade silica.

^1H, ^{13}C, and ^{19}F NMR were recorded at 25 °C on either an Agilent Technologies 400 MHz, a Bruker Avance III HD 400 MHz, or a Agilent Technologies 500 MHz, a Bruker Avance III HD 400 MHz spectrometer in $CDCl_3$, with residual $CHCl_3$ (^1H = 7.26 ppm, ^{13}C = 77.16 ppm), the internal standard. Chemical shifts are reported in parts per million (ppm, or Hz). The data presented will be reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (if applicable), and integration. High-resolution mass analyses (HRMS) were recorded on a Waters GCT Premier GC TOF, Agilent 6230 TOF LC/MS System, or Xevo G2-XS UPLC-QTOF.

2. Synthesis of di-2-pyridyldithiocarbonate (DPDTC)[2]



2-mercaptopyridine

1
DPDTC
89% yield, 6.5 g scale

All glassware was flame dried. To a 500 mL round-bottom flask equipped with a PTFE-coated magnetic stir bar was added 2-mercaptopyridine (6 equiv, 60 mmol, 6.67 g), after which the flask was sealed with a rubber septum and anhydrous acetone (100 mL) was added via syringe under a positive flow of argon, followed by anhydrous Et_3N (6 equiv, 60 mmol, 8.36 mL) and the solution was stirred until all components were fully dissolved. An ice bath was used to cool the resulting solution, an argon balloon was affixed to the septum via a needle, then a solution of triphosgene (1 equiv, 10 mmol, 2.967 g, from TCI) in acetone (12.5 mL) was slowly added over the course of

15 min. The ice was replaced as needed to keep the solution cool during addition of triphosgene to prevent excessive generation of phosgene gas. Upon full addition, triethylammonium chloride was observed to precipitate. The reaction was allowed to warm to rt and stir overnight. Upon completion, the septum was removed inside a fume hood and the reaction was allowed to expel any excess phosgene gas, then the reaction mixture was filtered to remove triethylammonium chloride and the filtrate was concentrated *in vacuo* to afford a crude oil containing crystals of remaining triethylammonium chloride. The crude residue was redissolved in EtOAc in 10 mL portions and filtered into a separatory funnel. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (100 mL), followed by DI water (100 mL), followed by saturated brine (100 mL). The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* and residual solvent was removed under high vacuum overnight to afford DPDTC as a light-yellow solid (6.596 g, 89% yield).

There is no odor whatsoever associated with the use of DPDTC or the byproduct, 2-mercaptopyridine.

Caution: Triphosgene is acutely toxic and releases toxic phosgene gas on contact with moisture. It should be handled on small scale in a fume hood or glove box and weighed out using a pre-weighed, tightly sealed container.

Note: Inexpensive 2-mercaptopyridine obtained from commercial sources may require purification prior to use due to the presence of the corresponding disulfide. This can be accomplished via recrystallization from EtOAc.

3. General procedures

General procedure for thioester bond formation under neat conditions:

The initially formed 2-pyridylthioester was made according to previously reported procedures as follows.[2] To a 1-dram vial, a PTFE-coated stir bar, carboxylic acid (1 equiv, 0.25 mmol) and DPDTC (1.05 equiv, 0.26 mmol, 65.2 mg) were added. The reaction mixture was stirred at 60 °C until full consumption of the acid, as determined by TLC (ca. 3-6 h). Because the reaction is neat, the stirring should not be too vigorous to cause splashing on the sides of the vial (150 rpm).

Subsequent thioesterification or esterification was carried out as follows using one of three general methods.

3.1 Thioesters

Method A – Formation under neat conditions

Upon complete consumption of the thioester, the thiol (1.05 equiv, 0.26 mmol) was directly added in 1-pot to the vial and stirred until complete consumption of the intermediate thioester.

The crude product was directly purified via silica gel chromatography (the eluent varied per substrate).

Method B – Formation using 2 M EtOAc

Upon complete consumption of the thioester, thiol (1.05 equiv, 0.26 mmol), followed by EtOAc (forming a 2 M solution, 125 µL) was directly added and the mixture was stirred at 60 °C until complete consumption of the intermediate thioester. The crude product was directly purified via silica gel chromatography (the eluent varied per substrate).

Method C– Formation under aqueous micellar conditions, TPGS-750-M

After complete consumption of the thioester, a 2 wt % TPGS-750-M/H_2O solution was added (leading to a 0.5 M global concentration, 0.5 mL) and the reaction was neutralized to a pH of 8-10. Thiol (1.05 equiv, 0.26 mmol) was added and the reaction was stirred at 60 °C until complete consumption of the intermediate thioester. The crude reaction mixture was extracted with EtOAc. The combined extracts were directly purified via silica gel chromatography (the eluent varied per substrate).

Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.2 mol %), was used to form all thioesters made using aliphatic thiols.

3.2 Esters

Method A – Formation using neat conditions

Upon complete consumption of the thioester, the alcohol (1.05 equiv , 0.26 mmol) was directly added, followed by either 1,4-diazabicyclo[2.2. 2]octane (DABCO) (10 mol %, 0.025 mmol or 1 equiv, 0.25 mmol) or 4-*N,N*-dimethylaminopyridine (DMAP; 10 mol %, 0.025 mmol) in 1-pot to the vial and stirred until complete consumption of the intermediate thioester. The crude reaction mixture was purified via silica gel chromatography (the eluent varied per substrate). This method was used if the alcohol was liquid, which provided sufficient stirring without the use of an added solvent. In the case of alcohols such as methanol, ethanol, etc. excess alcohol (5 equiv) was used to ensure sufficient stirring.

Method B – Formation using 2 M EtOAc

Upon complete consumption of the thioester, the alcohol was added (1.05 equiv, 0.26 mmol), followed by either 1,4-diazabicyclo[2.2.2]octane (DABCO; 10 mol %, 0.025 mmol or 1 equiv, 0.25 mmol) or 4-*N,N*-dimethylaminopyridine (DMAP; 10 mol %, 0.025 mmol) and EtOAc (2 M, 125 µL) was directly added, and the reaction mixture was stirred at 60 °C until complete consumption of the intermediate thioester. The crude reaction product is purified via silica gel chromatography (the eluent varied per substrate). This method was used when the alcohol was a solid.

Either DABCO or DMAP could be used. All esters from phenols, benzylic alcohols, and methanol were made using DABCO (10 mol %). All esters from aliphatic alcohols were made using 1 equiv

of DABCO unless otherwise stated. DMAP was used when noted, if DABCO did not form the ester product.

4. Optimization of reaction conditions

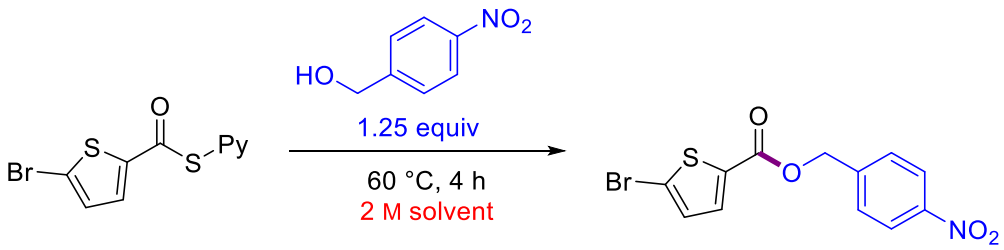
4.1 Optimization of ester formation

General procedure for ester bond formation from *S*-(2-pyridyl) thioesters:
To a 1-dram vial, a PTFE-coated stir bar, pyridyl thioester (1 equiv, 0.10 mmol, 31.0 mg) and 4-nitrophenol or 4-nitrobenzyl alcohol (1 equiv, 0.125 mmol, 17.39, 19.14 mg, respectively) was added. The contents were stirred at various temperatures, times, and in various solvents. Upon completion 1,3,5-trimthoxybenzene and $CDCl_3$ was added to the reaction vial and stirred for 15 min until fully homogeneous. The NMR was then directly taken.
For all reactions, ^1H NMR yields were calculated using 1,3,5-trimethoxybenzene as the internal standard.

Optimization per type of alcohol

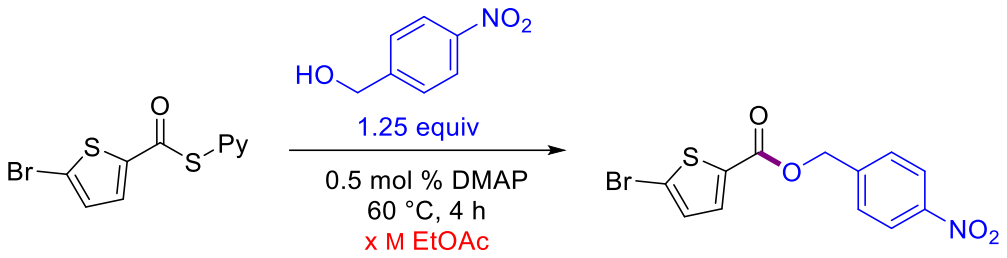
Phenol and benzyl alcohols

Table 1. Solvent



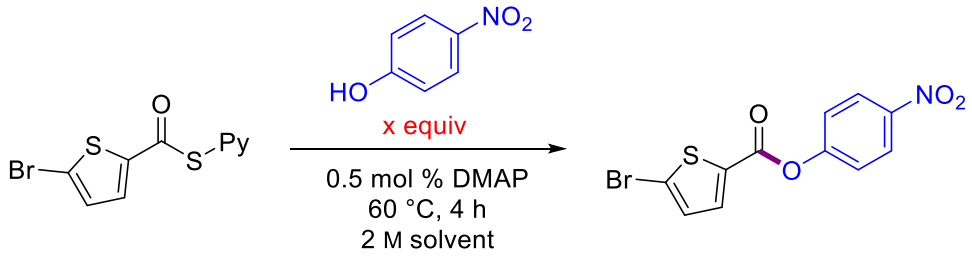
entry	solvent	NMR yield (%)
1	**ethyl acetate**	**34 (4 h), 87 (24 h)**
2	acetone	29
3	isopropyl acetate	18
4	cyrene	26

Table 2. Reaction concentration



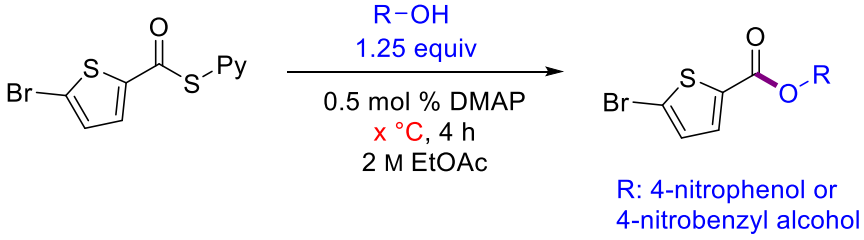
entry	concentration (M)	NMR yield (%)
1	**2**	**97**
2	1.5	61
3	1	48
4	0.5	40

Table 3. Equivalents of alcohol



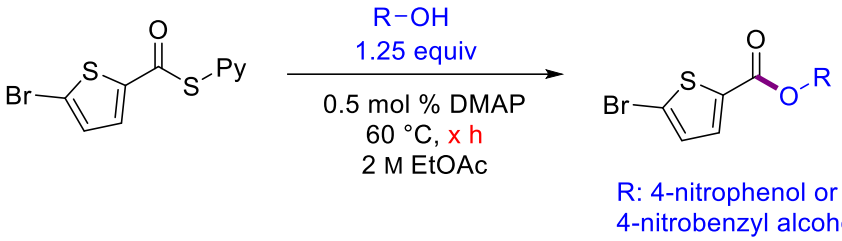
entry	alcohol (equiv)	NMR yield (%)
1	1	98
2	**1.05**	**97**
3	1.1	96
4	1.25	97

Table 4. Reaction temperature



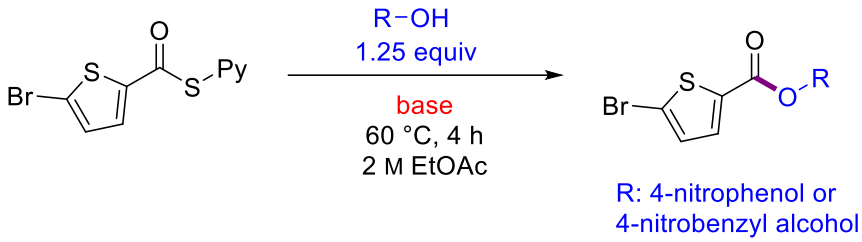
entry	temperature (°C)	phenol NMR yield (%)	benzyl alcohol NMR yield (%)
1	rt	0	0
2	40	19	24
3	50	56	41
4	**60**	**99**	**97**

Table 5. Reaction time



Entry	time (h)	phenol NMR yield (%)	benzyl alcohol NMR yield (%)
1	1	>99	61
2	2	93	87
3	3	>99	92
4	**4**	**99**	**96**

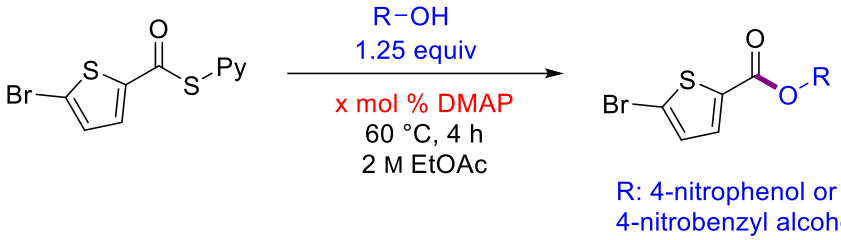
Table 6. Additive screen



entry	additive	phenol NMR yield (%)	benzyl alcohol NMR yield (%)
1	[a]DMAP	99	>99
2	TEA (2 M)	82	95
3	TEA (1 equiv)	90	93
4	NMM (2 M)	71	100
5	NMM (1 equiv)	95	78
6	[a]DBU	95	92
7	[b]DABCO	97	95
8	none	47	34

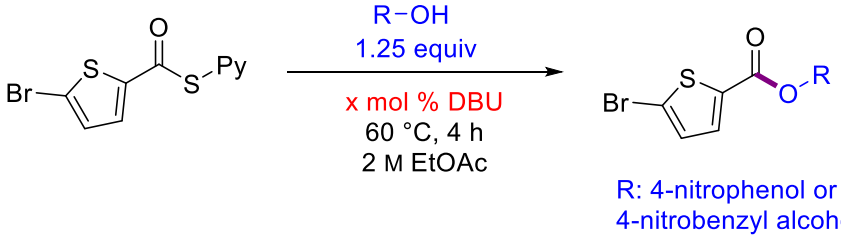
[a] 2 mol %; [b] 10 mol %.

Table 7. Loading of DMAP



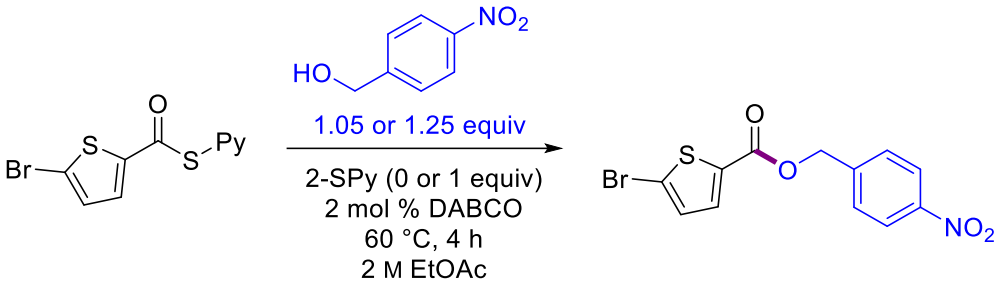
entry	DMAP (equiv)	phenol NMR yield (%)	benzyl alcohol NMR yield (%)
1	2 mol %	79	> 99
2	1 mol %	92	92
3	**0.5 mol %**	**99**	**97**
4	0.25 mol %	59	67
5	0.1 mol %	56	58

Table 8. Loading of DBU



entry	DBU (mol %)	phenol NMR yield (%)	benzyl alcohol NMR yield (%)
1	2 mol %	95	92
2	1 mol %	94	87
3	**0.5 mol %**	**85**	**70**
4	0.25 mol %	74	59

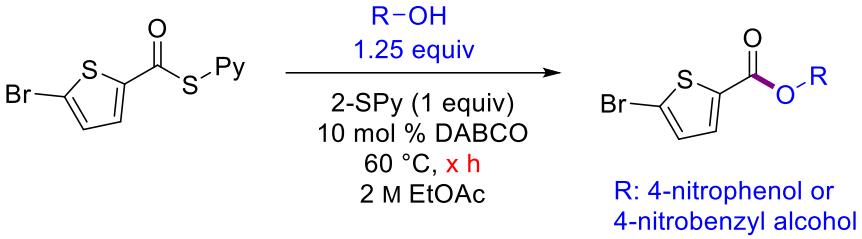
Table 9. Effect of added 2-mercaptopyridine



entry	alcohol (equiv)	2-SPy (equiv)	NMR yield (%)
1	1.05	n/a	95, 90[a]
2	1.05	1	42
3	1.25	1	46
4	1.05	n/a	38[a,b]

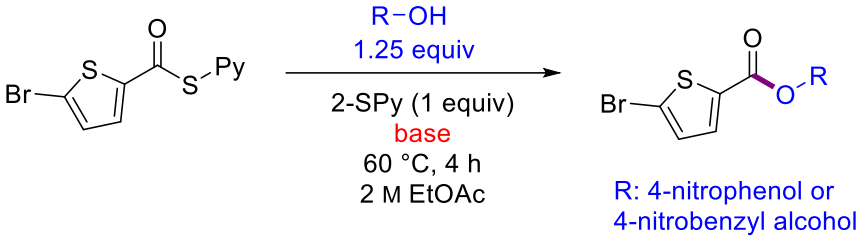
[a] Isolated yield; [b] One-pot, starting from carboxylic acid and DPDTC.

Table 10. Time with added 2-mercatopyridine



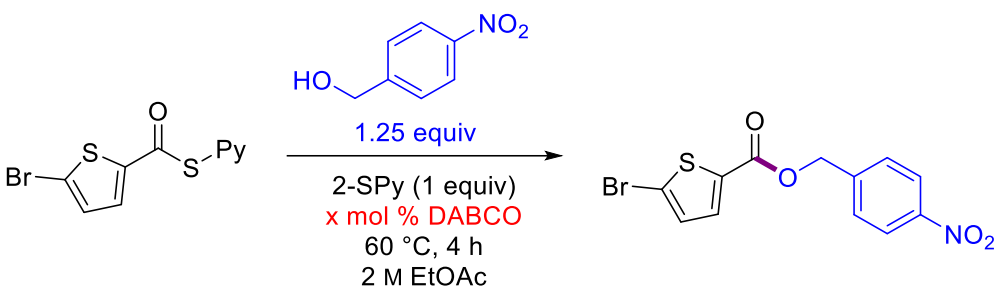
entry	time (h)	4-nitrophenol NMR Yield (%)	4-nitrobenzyl alcohol NMR yield (%)
1	1	99	61
2	2	93	87
3	3	99	92
4	4	99	96

Table 11. Base screening with 2-mercaptopyridine



entry	base	4-nitrophenol NMR yield (%)	4-nitrobenzyl alcohol NMR yield (%)
1	None	47	34
2	DMAP	99	>99
3	DBU	95	92
4	TEA	99	99
5	**DABCO**	**93**	**98**

Table 12. Loading of DBU with 2-mercatopyridine

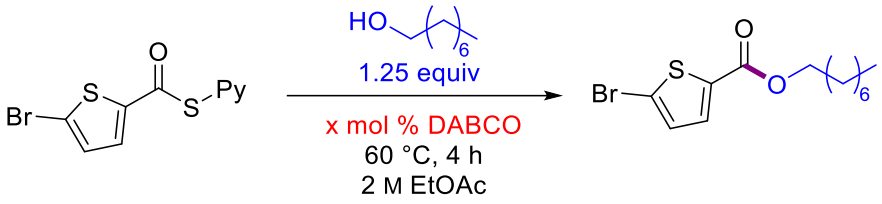


entry	DABCO (mol %)	benzyl alcohol NMR yield (%)
1	5	88
2	**10**	**92**
3	20	93
4	1[a]	95

[a] equivalent.

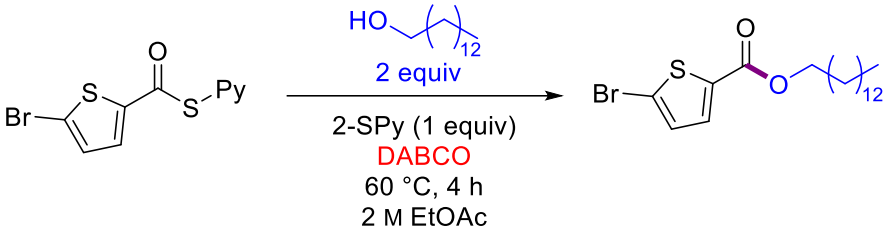
Aliphatic alcohols

Table 13. Base Screen using with 1-octanol



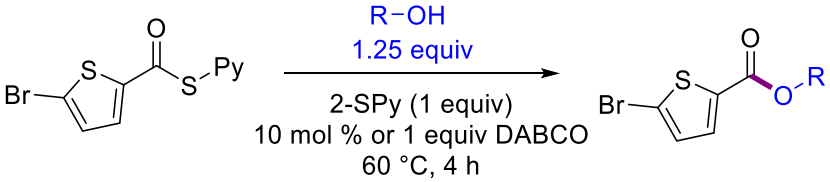
entry	DABCO (equiv)	NMR yield (%)
1	30 mol %	75
2	**10 mol %**	**75**
3	1 mol %	47

Table 14. Base screening with dodecanol



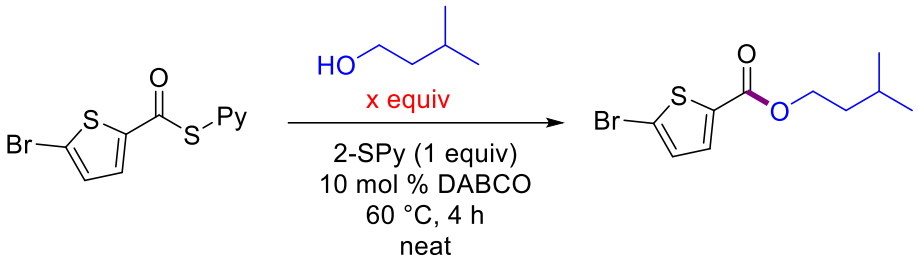
entry	dodecanol (equiv)	DABCO (equiv)	NMR yield (%)
1	2	10 mol %	69
2	**2**	**1**	**88**
3	2	2	90

Table 15. Base screen with common alcohol solvents



entry	alcohol	NMR yield (%) (10 mol % DABCO)	NMR yield (%) (1 equiv DABCO)
1	methanol	95	100
2	ethanol	76	93
3	*t*-butanol	13	47

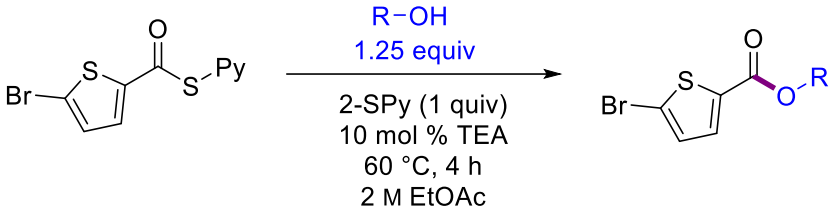
Table 16. Equivalents of aliphatic alcohols, neat conditions



entry	alcohol (equiv)	NMR yield (%)
1	1.25	26% ester remaining, 46
2	1.25	54
3	1.25	63
4	**2**	**87**
5	3	83

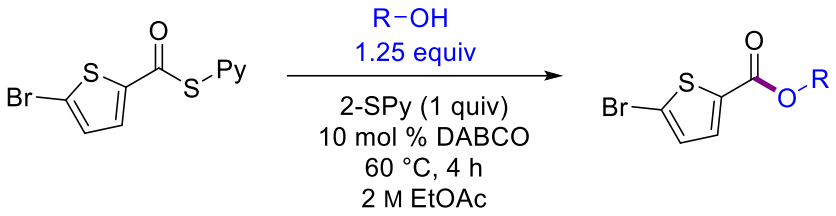
NMR yield based on remaining thioester.

Table 17. Alcohol screening with TEA as activating agent



entry	alcohol	NMR yield (%)
1	nerol	61
2	1-octanol	32
3	cholesterol	39
4	benzyl alcohol	88
5	4-nitrophenol	97
6	4-nitrobenzyl alcohol	98
7	4-MeO-phenol	99
8	4-Br-2,6-xylenol	69
9	phenol	81

Table 18. Alcohol screening using DABCO as activating agent



entry	alcohol	NMR yield (%)
1	nerol	90
2	1-octanol	76
3	2-octanol	23
4	3-methylbutanol	87
5	borneal	19
6	cholesterol	46
7	benzyl alcohol	90
8	4-nitrophenol	98
9	4-nitrobenzyl alcohol	93

4.2 Optimization of ester bond formation

General Procedure for thioester bond formation from S-(2-pyridyl) thioesters:

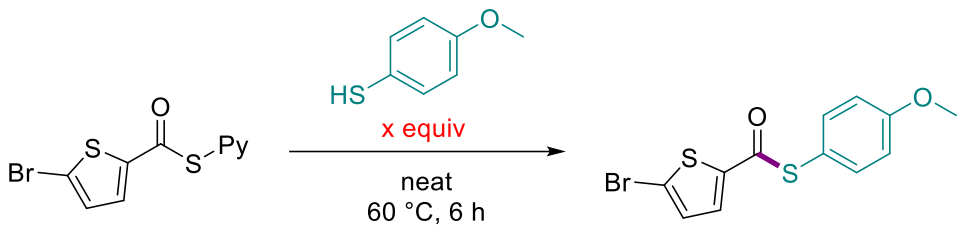
To a 1-dram vial, a PTFE-coated stir bar, pyridyl thioester (1 equiv, 0.10 mmol, 31.0 mg) and thiol (1-1.1 equiv, 0.1-0.11 mmol) were added. The contents were stirred at various temperatures, times, and in various solvents. Upon completion, 1,3,5-trimthoxybenzene and $CDCl_3$ were added to the reaction vial and stirred for 15 min until fully homogeneous. The NMR was then recorded.

For all reactions, ^{1}H NMR yields were calculated using the 1,3,5-trimethoxybenzene present as internal standard.

Optimization per type of thiol –

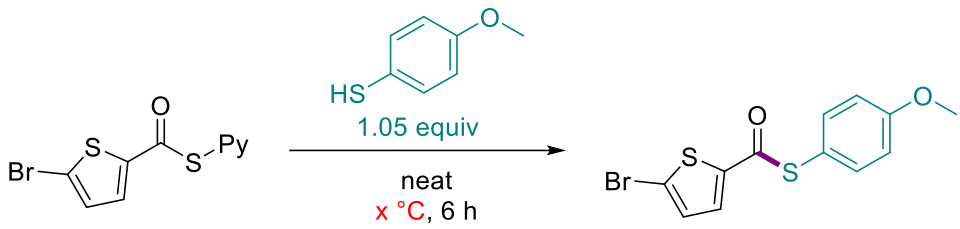
Phenylthiols

Table 19. Equivalents of thiol



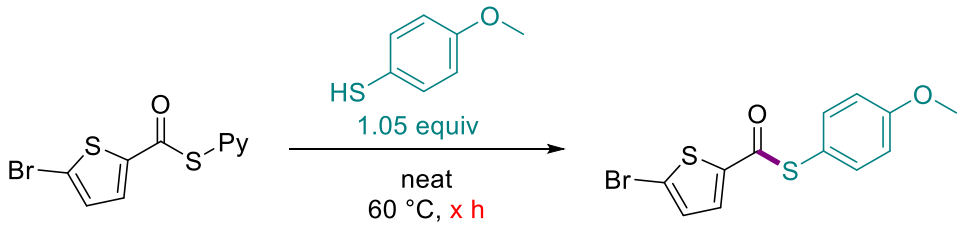
entry	thiol (equiv)	time (h)	NMR yield (%)
1	1	6	99
2	1.05	6	99

Table 20. Reaction temperature



entry	temp (°C)	NMR yield (%)
1	40	82
2	50	93
3	**60**	**99**

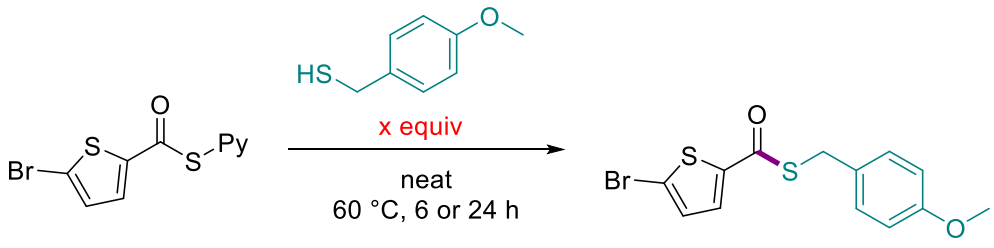
Table 21. Reaction time



entry	time (h)	NMR yield (%)
1	1	81
2	3	95
3	6	99

Benzylic thiols

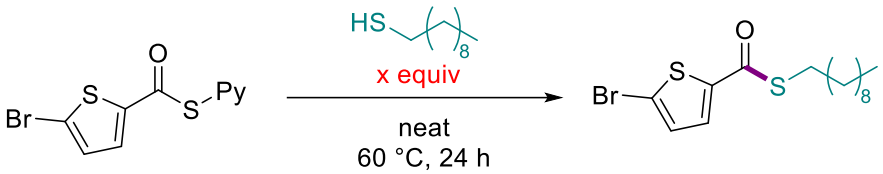
Table 22. Equivalents of benzylic thiol



entry	thiol (equiv)	time (h)	NMR yield (%)
1	1	6	70
2	1	24	85
3	1.05	6	90
4	1.05	24	96
5	1.1	6	88
6	1.1	24	95

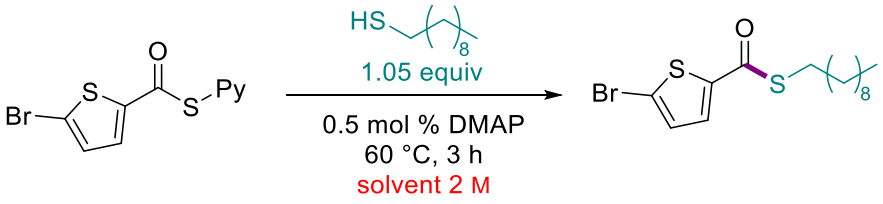
Aliphatic thiols

Table 23. Equivalents of thiol (decanethiol)



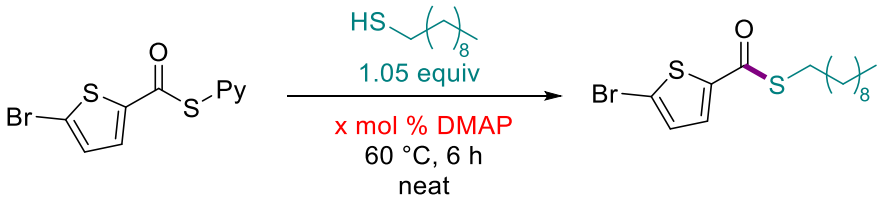
entry	thiol (equiv)	NMR yield (%)
1	**1.05**	**52**
2	1.1	42
3	1.2	51

Table 24. Solvent



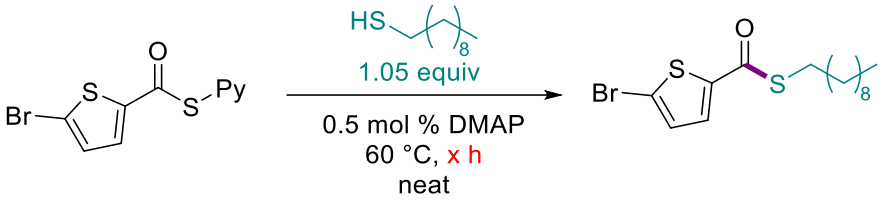
entry	Solvent	NMR yield (%)
1	**EtOAc**	**91**
2	acetone	90
3	isopropyl Acetate	80
4	2-MeTHF	75

Table 25. Loading of DMAP



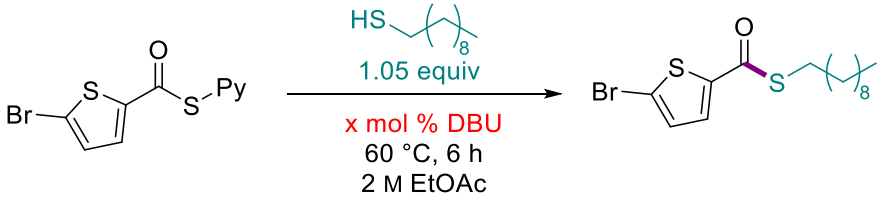
entry	DMAP (mol %)	NMR yield (%)
1	10	100
2	5	89
3	2.5	91
4	1	55
5	**0.5**	**91**
6	0.2	66

Table 26. Reaction time



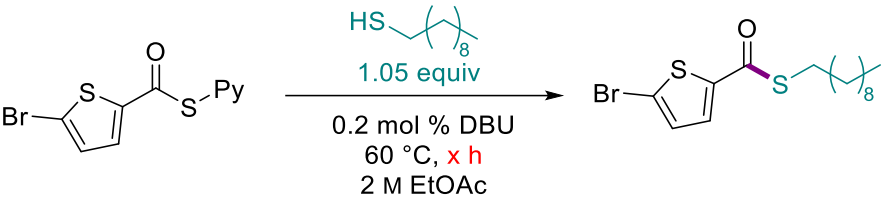
entry	time (h)	NMR yield (%)
1	1	83
2	2	82
3	**3**	**91**
4	6	91

Table 27. Loading of DBU



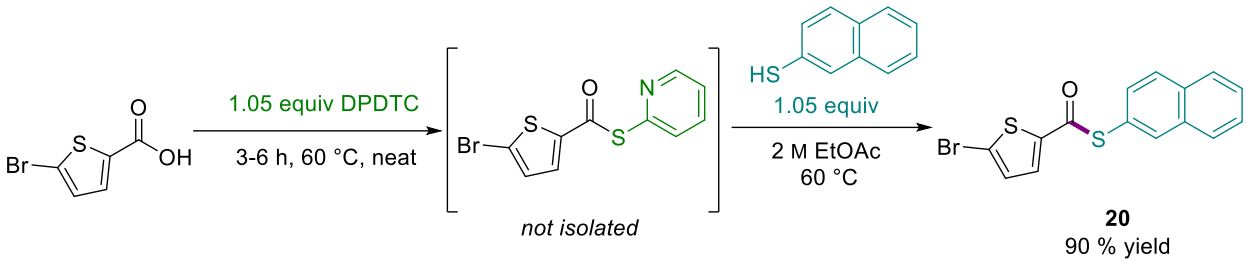
entry	DBU (mol %)	NMR yield (%)
1	1	100
2	0.5	95
3	**0.2**	**95**

Table 28. Reaction time (DBU)



entry	time (h)	NMR yield (%)
1	2	90
2	**3**	**95**
3	6	95

5. Gram-scale synthesis of a thioester



To a 25 mL round-bottom flask, a PTFE-coated stir bar, 5-bromothiophene carboxylic acid (1 equiv, 3.00 mmol, 621.1 mg) and DPDTC (1.05 equiv, 3.15 mmol, 782.2 mg) were added. The reaction mixture was stirred at 60 °C until full consumption of the acid, as determined by TLC (ca. 3-6 h). Upon consumption of the thioester, 2-naphthalenethiol (1.05 equiv, 3.15 mmol, 504.7 mg) was directly added to the round-bottom flask and stirring continued until complete consumption of the intermediate thioester. The crude reaction mixture was then dissolved in EtOAc and washed with 1 M NaOH (1 mL x 3), dried over anhydrous Na_2SO_4 and concentrated via rotary evaporation. The crude product was purified by flash chromatography (gradient hexanes to hexanes/EtOAc 95:5) to afford **2** (944.6 mg, 90% yield) as a white solid; R_f: 0.40 (hexanes/EtOAc) 95:5).

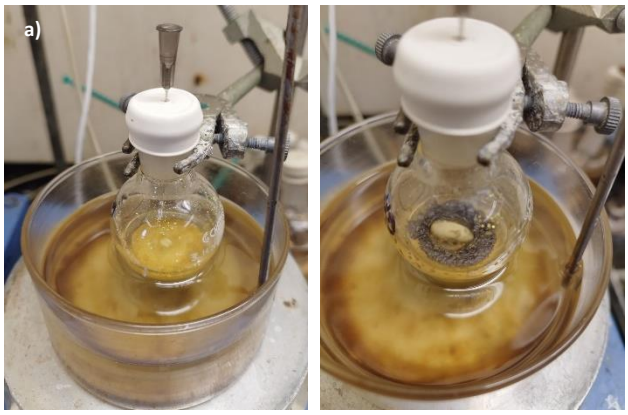
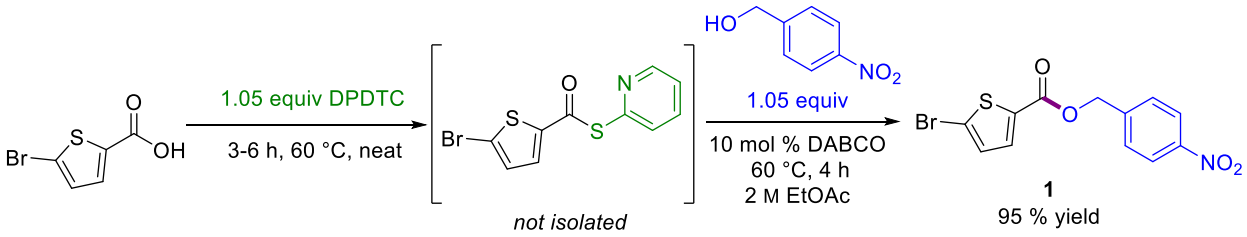


Figure 1. a) Initial reaction; b) After thioester formation

6. Recovery of EtOAc



To a 25 mL round-bottom flask, a PTFE-coated stir bar, 5-bromothiophene carboxylic acid (1 equiv, 10 mmol, 2.07 g) and DPDTC (1.1 equiv, 10.1 mmol, 2.7315 g) were added. The reaction mixture was stirred at 60 °C until full consumption of the acid, as determined by TLC (ca. 3-6 h).

Upon complete consumption of the thioester the 4-nitrobenzyl alcohol (1.1 equiv, 10.1 mmol, 1.6845 g) and EtOAc (5 mL, leading to a 2 M reaction mixture) was directly added to the round-bottom flask and stirring continued until complete consumption of the intermediate thioester. The crude reaction was attached to a distillation head and heated in an oil bath at 100 C to distill off EtOAc (3.1 mL, or 62% of the EtOAc was recovered). The crude reaction mixture was directly purified by flash column chromatography (gradient hexanes to hexanes/ EtOAc 95:5) afforded **2** (3.2506 g, 95% yield) as a white solid; R_f: 0.71 (hexanes/ EtOAc 50:50).

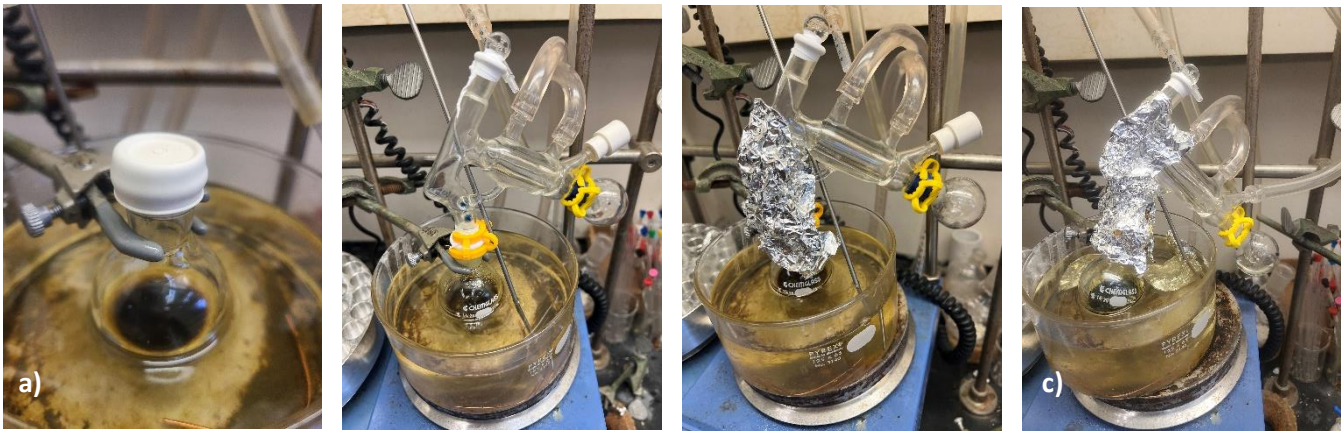
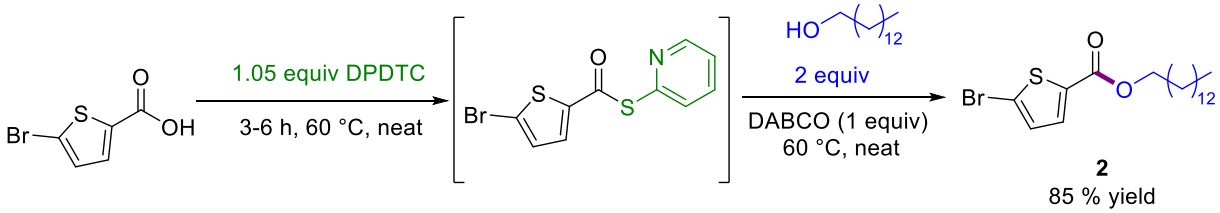


Figure 2. a) After thioester formation, with addition of alcohol and EtOAc; b-1) distillation set up; b-2) with foil added; c) with distillate collected

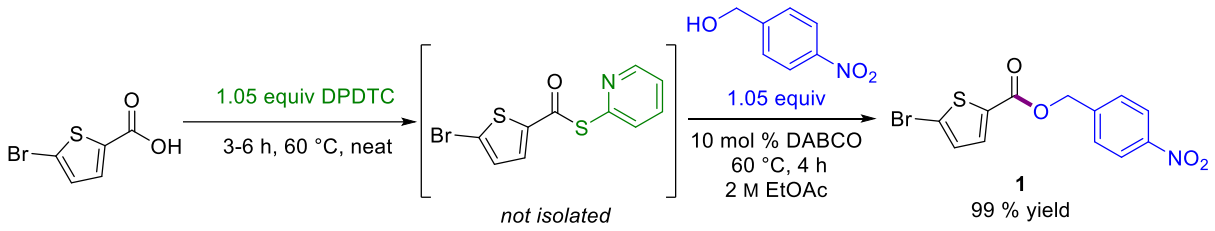
7. PMI/E Factor calculations

PMI for a neat reaction (conditions a) – ester



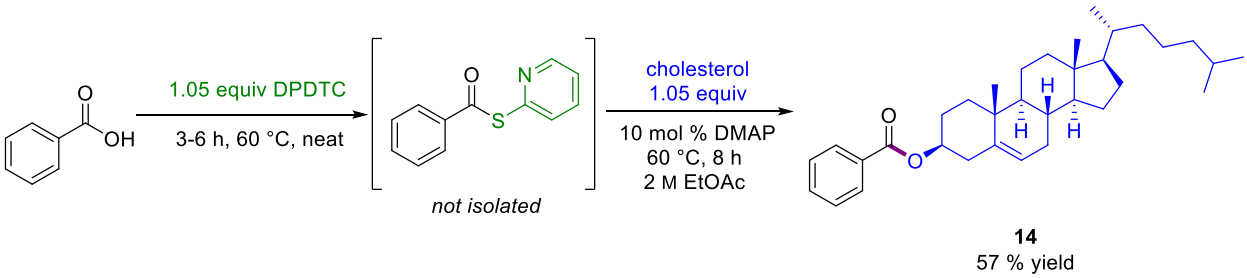
$$PMI = \frac{total\ mass\ reaction}{mass\ product} = \frac{(mass_{DPDTC} + mass_{alcohol} + mass_{carboxylic\ acid} + mass_{DABCO})}{(mass product)} = \frac{0.0652\ g + 0.0774 g + 0.0518 g + 0.0112\ g}{0.0738} = 2.786$$

PMI for a reaction using 2 M EtOAc (conditions b) – ester



$$PMI = \frac{total\ mass\ reaction}{mass\ product} = \frac{(mass_{DPDTC} + mass_{alcohol} + mass_{carboxylic\ acid} + mass_{DABCO} + mass_{EtOAc})}{(mass_{product})} = \frac{0.0652\ g + 0.0478g + 0.0518g + 0.0028\ g + 0.1386\ g}{0.0874} = 3.471$$

PMI for a reaction using 2 M EtOAc (conditions b) – ester, direct comparison

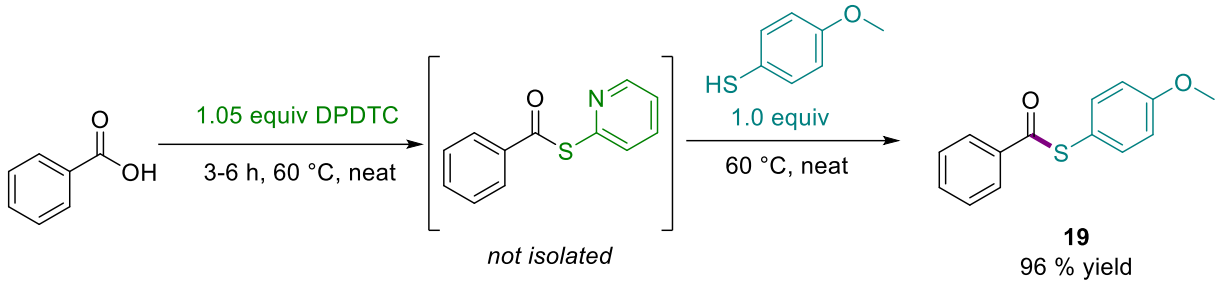


$$E\ Factor = \frac{total\ mass\ reaction}{mass\ product} = \frac{(mass_{DPDTC} + mass_{alcohol} + mass_{carboxylic\ acid} + mass_{DMAP} + mass_{EtOAc}) - (mass_{product})}{(mass_{product})} = \frac{(0.0652\ g + 0.0966g + 0.0305g + 0.0031\ g + 0.1386\ g) - 0.0700}{0.0700} = 3.336$$

$$PMI = \frac{total\ mass\ reaction}{mass\ product} = \frac{(mass_{DPDTC} + mass_{alcohol} + mass_{carboxylic\ acid} + mass_{DMAP} + mass_{EtOAc})}{(mass_{product})} = \frac{0.0652\ g + 0.0966g + 0.0305g + 0.0031\ g + 0.1386\ g}{0.0700} = 4.336$$

$$RME = \frac{mass\ product}{total\ mass\ reagents} = \frac{(mass_{prodcut})}{(mass_{DPDTC} + mass_{alcohol} + mass_{carboxylic\ acid} + mass_{DMAP})} \times 100 = \frac{0.0700}{(0.0652\ g + 0.0966g + 0.0305g + 0.0031\ g)} \times 100 = 35.8$$

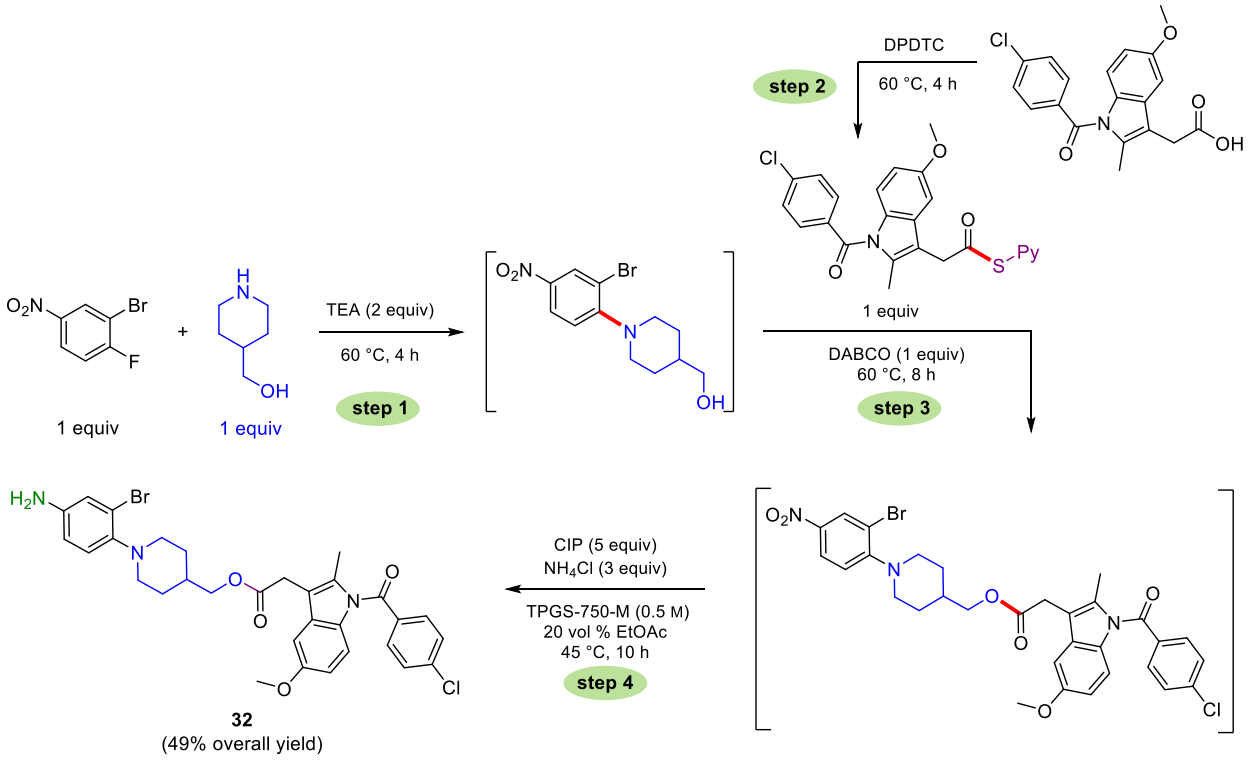
PMI for a neat reaction (conditions a) – thioester



$$PMI = \frac{total\ mass\ reaction}{mass\ product} = \frac{(mass_{DPDTC} + mass_{thiol} + mass_{carboxylic\ acid})}{(mass_{product})} =$$

$$\frac{0.0652\ g + 0.0351g + 0.0305g}{0.0586} = 2.232$$

8. One-pot chemocatalysis sequence

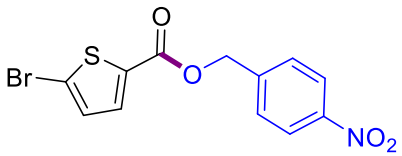


To a 1-dram vial, a PTFE-coated stir bar, 1-fluoro-2-bromo-4-nitrobenzene (1 equiv, 0.5 mmol, 110 mg), 4-piperidinemethanol (1 equiv, 0.5 mmol, 57.6 mg) and triethylamine (TEA; 1 mmol, 139.4 µL) were added.[3] The reaction mixture was stirred at 60 °C until full consumption of both starting materials as determined by TLC (ca. 4 h). To a 2-dram vial, a PTFE-coated stir bar, indomethacin (0.5 mmol, 178.9 mg) and DPDTC (0.525 mmol, 130.37 mg) were added and stirred at 60 °C until full consumption of the acid and DPDTC. Upon consumption of starting materials,

the crude S_NAr reaction was transferred with EtOAc to the 2-dram vial (crude thioester), the EtOAc was concentrated *in vacuo*, and then DABCO (0.5 mmol, 56 mg) and EtOAc (2 M, 250 µL) were directly added to the 2-dram vial and stirred until complete consumption of the intermediate thioester. The crude reaction mixture was then washed with 1 M NaOH (1 mL x 2), and 1 M HCl (1 mL x 1). Then EtOAc (20 vol %, 200 µL) and 2 wt % TPGS-750-M (0.5 M, 1 mL) were added and stirred until emulsified. CIP (5 equiv, 2.5 mmol, 139.63 mg) and NH_4Cl (3 equiv, 1.5 mmol, 80.24 mg) were added and stirred at 45 °C until complete consumption of the starting material (ca. 4 h).[4] The crude product was filtered through Celite and purified by flash chromatography (gradient hexanes/EtOAc 80:20 to hexanes/EtOAc 70:30) to afford **32** (154 mg, 49% yield) as a yellow oil; R_f: 0.18 (hexanes/EtOAc 70:30).

9. Analytical data

9.1 Esters

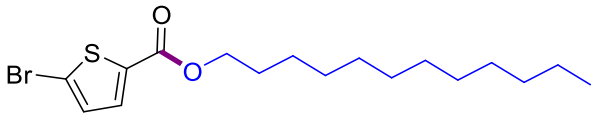


4-Nitrobenzyl 5-bromothiophene-2-carboxylate (1): Compound **1** was prepared according to Method B. The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) afforded **1** (84.7 mg, 99% yield) as a white solid; R_f: 0.71 (hexanes/EtOAc 50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.13 (m, 2H), 7.66 – 7.49 (m, 3H), 7.09 (d, *J* = 4.0 Hz, 1H), 5.40 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.54, 147.82, 142.77, 134.41, 133.83, 131.19, 128.39, 123.91, 121.17, 77.35, 77.09, 76.84, 65.41.

HRMS: *m/z* calcd for $C_{12}H_8BrO_4S$; 340.935742 [M]: found 340.9357.

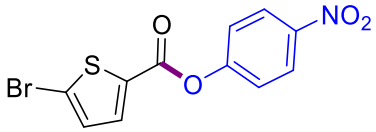


Dodecyl 5-bromothiophene-2-carboxylate (2): Compound **2** was prepared according to Method A with the following modifications: 2 equiv alcohol (0.5 mmol, 112 µL) and 1 equiv DABCO (0.25 mmol, 28 mg). The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **2** (73.8 mg, 85% yield) as a yellow oil; R_f: 0.83 (hexanes/EtOAc 50:50).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 4.0 Hz, 1H), 4.28 (t, *J* = 6.7 Hz, 2H), 1.80 – 1.69 (m, 2H), 1.34 – 1.24 (m, 18H), 0.90 (t, *J* = 6.9 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.19, 135.19, 133.44, 130.84, 120.01, 77.30, 77.05, 76.79, 65.56, 31.94, 29.71, 29.69, 29.68, 29.66, 29.58, 29.52, 29.38, 29.37, 29.24, 28.64, 25.93, 22.71, 14.14.

HRMS: *m/z* calcd for $C_{17}H_{27}BrO_2S$; 374.091512 [M]: found 374.0915.

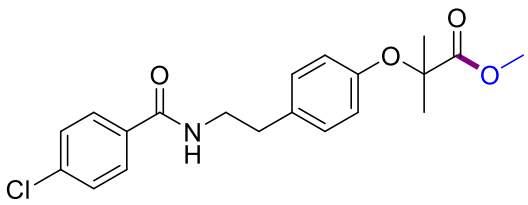


4-Nitrophenyl 5-bromothiophene-2-carboxylate (3): Compound **3** was prepared according to Method B. The crude product was purified by flash column chromatography (hexanes/EtOAc 90:10) afforded **3** (79.8 mg, 97.3%) as a white solid; R_f: 0.57 (hexanes/EtOAc 70:30).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 4.1 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.40, 155.02, 145.55, 135.80, 132.70, 131.53, 125.59, 125.33, 122.80, 122.45, 77.29, 77.04, 76.79.

HRMS: *m/z* calcd for $C_{11}H_6BrNO_4S$; 326.920092 [M]: found 326.9201.

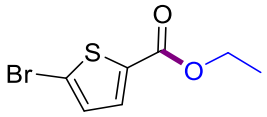


Methyl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (4): Compound **4** was prepared according to Method A, with the following modifications: 5 equiv methanol (1.25 mmol, 50.6 µL) was used. The crude product was purified by flash column chromatography (hexanes/EtOAc 80:20) to afford **4** (87.5 mg, 93% yield) as a white solid; R_f: 0.61 (hexanes/EtOAc 50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.55 (m, 2H), 7.43 – 7.31 (m, 2H), 7.13 – 7.04 (m, 2H), 6.85 – 6.73 (m, 2H), 6.12 (t, *J* = 5.9 Hz, 1H), 3.76 (s, 3H), 3.65 (q, *J* = 6.6 Hz, 2H), 2.85 (t, *J* = 6.9 Hz, 2H), 1.58 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.80, 166.40, 154.05, 149.58, 137.63, 133.01, 132.52, 129.54, 128.81, 128.27, 119.58, 79.18, 77.31, 77.06, 76.80, 52.52, 41.23, 34.74, 25.36.

All spectral data were in agreement with literature data.[5]

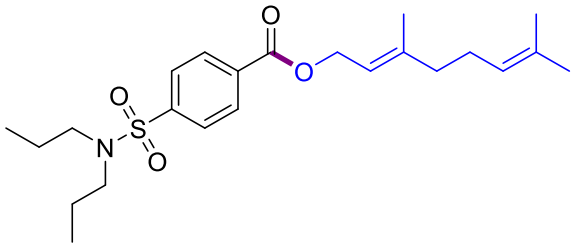


Ethyl 5-bromothiophene-2-carboxylate (5): Compound **5** was prepared according to Method A, with the following modifications: 5 equiv ethanol (1.25 mmol, 73 µL) was used and 1 equiv DABCO (0.25 mmol, 28 mg). The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **5** (58.7 mg, quant.) as a colorless oil; R_f: 0.66 (hexanes/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.15, 135.17, 133.49, 130.85, 120.04, 77.31, 77.05, 76.80, 61.43, 14.29, 14.14.

All spectral data were in agreement with literature data.[6]

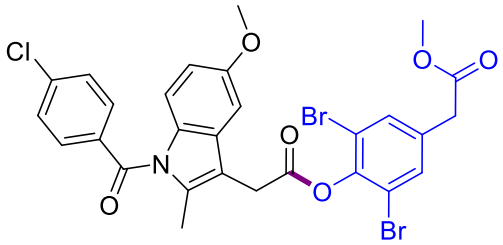


(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 4-(*N,N*-dipropylsulfamoyl)benzoate (6): Compound **6** was prepared according to Method A with the following modifications: 2 equiv alcohol (0.5 mmol, 87.5 µL) and 1 equiv DABCO (0.25 mmol, 28 mg). The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **6** (98 mg, 93% yield) as a colorless oil; R_f: 0.83 (hexanes/EtOAc 50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 – 8.07 (m, 2H), 7.89 – 7.77 (m, 2H), 5.51 – 5.42 (m, 1H), 5.09 (td, *J* = 6.9, 3.3 Hz, 1H), 4.82 (d, *J* = 7.3 Hz, 2H), 3.15 – 2.96 (m, 4H), 2.24 – 2.04 (m, 4H), 1.78 (s, 3H), 1.58 (s, 3H), 1.51 (p, *J* = 7.5 Hz, 4H), 0.84 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.25, 144.11, 143.42, 133.83, 132.26, 130.21, 126.93, 123.48, 118.76, 77.34, 77.09, 76.83, 62.16, 49.88, 32.22, 26.64, 25.68, 23.54, 21.89, 17.67, 11.14.

HRMS: *m/z* calcd for $C_{23}H_{35}NO_4SNa$; 444.218451 [M+Na]: found 444.2184.

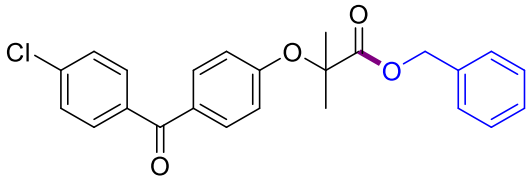


2,6-Dibromo-4-(2-methoxy-2-oxoethyl)phenyl-2-(1-(4-methoxybenzoyl)-2-methyl-1H-indol-3-yl)acetate (7): Compound **7** was prepared according to Method B. The crude product was purified by flash column chromatography (hexanes/EtOAc 85:15) to afford **7** (164 mg, 99% yield) as a white solid; R_f: 0.70 (hexanes/EtOAc 50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 4.0 Hz, 4H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.01 (s, 2H), 3.84 (s, 3H), 3.70 (s, 3H), 3.55 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.57, 168.33, 167.06, 156.09, 145.22, 139.36, 136.43, 134.63, 133.84, 133.23, 131.24, 130.83, 130.58, 129.17, 117.47, 114.98, 111.98, 111.38, 101.28, 77.32, 77.06, 76.81, 55.76, 52.43, 39.74, 29.81, 13.57.

HRMS: *m/z* calcd for $C_{28}H_{23}Br_2ClNO_6$; 661.958064 [M+1]: found 661.9581.

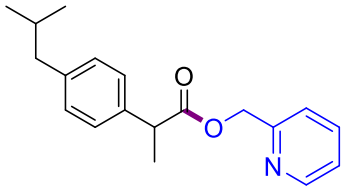


Benzyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (8): Compound **8** was prepared according to Method B with the following modification: 1.25 equiv alcohol (0.256 mmol, 32.5 µL). The crude product was purified by flash column chromatography (hexanes/EtOAc 80:20) to afford **8** (89.3 mg, 87.4% yield) as a white solid; R_f: 0.62 (hexanes/EtOAc 70:30).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 2H), 7.69 – 7.64 (m, 2H), 7.51 – 7.45 (m, 2H), 7.32 (q, *J* = 3.1 Hz, 3H), 7.28 (d, *J* = 3.8 Hz, 3H), 6.82 – 6.77 (m, 2H), 5.23 (s, 2H), 1.70 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 194.20, 173.47, 159.53, 138.40, 136.38, 135.10, 131.97, 131.18, 130.34, 128.56, 128.55, 128.49, 128.46, 117.27, 79.44, 77.28, 77.03, 76.77, 67.36, 25.44.

HRMS: *m/z* calcd for $C_{24}H_{21}ClO_4$; 408.11284 [M]: found 408.1128.

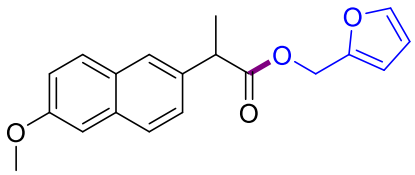


Ibuprofen piconol (9): Compound **9** was prepared according to Method A. The crude product was purified by flash column chromatography (hexanes/EtOAc 70:30) to afford **9** (57 mg, 77% yield) as a colorless oil; $R_{f:}$ 0.35 (hexanes/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.6 Hz, 1H), 7.61 – 7.49 (m, 1H), 7.23 (s, 1H), 7.15 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 5.34 – 5.07 (m, 2H), 3.82 (q, *J* = 7.1 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 7H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.27, 156.10, 149.25, 140.69, 137.50, 136.62, 129.38, 127.31, 122.63, 121.09, 77.34, 77.09, 76.83, 66.74, 45.10, 45.04, 30.22, 22.38, 18.36.

HRMS: *m/z* calcd for $C_{19}H_{23}NO_2$; 297.172878 [M]: found 297.1729.

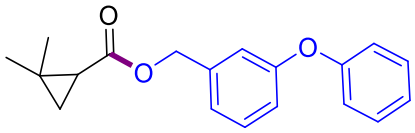


Furan-2-ylmethyl 2-(6-methoxynaphthalen-2-yl)propanoate (10): Compound **10** was prepared according to Methods A and C (thioester section). Method A was followed with the following modification: 10 mol % DMAP was used (0.025 mmol, 3.1 mg). Method C was followed with the following modification: in step 2: the pH is adjusted to 9 with triethylamine. The crude product was purified by flash column chromatography (hexanes/EtOAc 85:15) to afford **10** (74.5 mg, 96% yield, Method A, 65.2 mg, 84% yield, Method C) as a white solid; $R_{f:}$ 0.57 (hexanes/EtOAc 70:30).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 – 7.62 (m, 3H), 7.45 – 7.36 (m, 2H), 7.21 – 7.10 (m, 2H), 6.37 (dd, *J* = 8.3, 2.6 Hz, 2H), 5.17 (d, *J* = 13.2 Hz, 1H), 5.03 (d, *J* = 13.2 Hz, 1H), 3.94 (s, 4H), 1.60 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.34, 157.65, 149.49, 143.16, 135.46, 133.71, 129.32, 128.93, 127.15, 126.24, 125.98, 118.96, 110.56, 110.52, 105.59, 77.31, 77.05, 76.80, 58.41, 55.32, 45.32, 18.69.

HRMS: *m/z* calcd for $C_{24}H_{21}ClO_4$; 408.112838 [M]: found 408.1128.

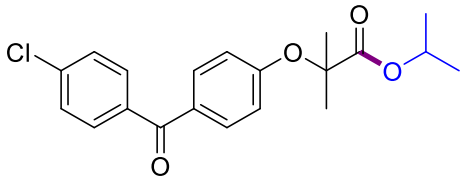


3-Phenoxybenzyl 2,2-dimethylcyclopropane-1-carboxylate (11): Compound **11** was prepared according to Method A with the following modification: 10 mol % DMAP was used (0.025 mmol, 3.1 mg). The crude product was purified by flash column chromatography (hexanes/EtOAc 90:10) afforded **11** (74 mg, quant. yield) as a yellow/brown oil; $R_{f:}$ 0.67 (hexanes/EtOAc 70:30).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.33 (m, 3H), 7.15 (ddt, *J* = 13.8, 7.5, 1.3 Hz, 2H), 7.09 – 7.03 (m, 3H), 6.99 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 5.14 (d, *J* = 1.4 Hz, 2H), 1.60 (dd, *J* = 8.0, 5.5 Hz, 1H), 1.25 (s, 3H), 1.20 (s, 3H), 1.16 (dd, *J* = 5.5, 4.3 Hz, 1H), 0.91 (dd, *J* = 8.0, 4.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.61, 157.55, 157.01, 138.45, 129.88, 129.83, 123.47, 122.67, 119.08, 118.31, 118.25, 77.37, 77.12, 76.86, 65.60, 26.97, 26.84, 23.42, 22.75, 22.36, 18.86.

HRMS: *m/z* calcd for $C_{19}H_{20}O_3$; 296.141245 [M]: found 296.1412.

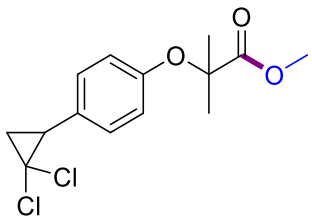


Isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (12): Compound **12** was prepared according to Method A, with the following modification: 5 equiv alcohol (1.25 mmol, 95.6 µL) and 10 mol % DAMP (0.025, 3.1 mg). The crude product was purified by flash column chromatography (hexanes/EtOAc 90:10) to afford **12** (59.5 mg, 66% yield) as a yellow/brown oil; R_f 0.29 (hexanes/EtOAc 90:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 12.8, 8.4 Hz, 4H), 7.44 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.09 (dq, *J* = 12.5, 6.3 Hz, 1H), 1.65 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 194.26, 173.10, 159.75, 138.35, 136.44, 131.95, 131.17, 130.23, 128.54, 117.26, 79.43, 77.30, 77.05, 76.80, 69.35, 25.38, 21.53.

All spectral data were in agreement with literature data.[7]

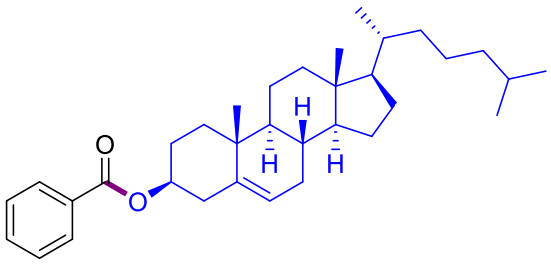


Methyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (13): Compound **13** was prepared according to Method A, with the following modification: 5 equiv methanol (1.25 mmol, 50.6 µL) was used. The crude product was purified by flash column chromatography (hexanes/EtOAc 90:10) afforded **13** (69.5 mg, 91.7% yield) as a colorless oil; R_f: 0.80 (hexanes/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 3.76 (s, 3H), 2.82 (dd, *J* = 10.7, 8.4 Hz, 1H), 1.93 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.77 (t, *J* = 7.9 Hz, 1H), 1.59 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.75, 154.85, 129.70, 128.31, 118.80, 79.18, 77.32, 77.06, 76.81, 60.86, 52.51, 34.84, 25.85, 25.40, 25.38.

All spectral data were in agreement with literature data.[8]



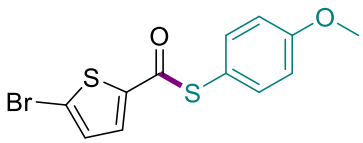
Cholesteryl benzoate (14): Compound **14** was prepared according to Method B with the following modification: 10 mol % DMAP (0.025 mmol, 3.1 mg) The crude product was purified by flash column chromatography (hexanes) to afford **14** (70 mg, 57% yield) as a white solid; R_f: 0.74 (hexanes/EtOAc 70:30).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 – 8.02 (m, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.45 (d, *J* = 5.0 Hz, 1H), 4.89 (dtd, *J* = 12.0, 8.5, 4.5 Hz, 1H), 2.50 (d, *J* = 8.2 Hz, 2H), 2.03 (tt, *J* = 15.8, 4.4 Hz, 3H), 1.94 (dt, *J* = 13.5, 3.6 Hz, 1H), 1.90 – 1.82 (m, 1H), 1.82 – 1.72 (m, 1H), 1.65 – 1.45 (m, 6H), 1.42 – 1.14 (m, 12H), 1.10 (s, 4H), 1.04 (tt, *J* = 11.1, 5.7 Hz, 4H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.90 (dd, *J* = 6.6, 2.3 Hz, 7H), 0.72 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.00, 139.67, 132.72, 130.87, 129.56, 128.27, 122.80, 77.30, 77.04, 76.79, 74.59, 56.72, 56.17, 50.07, 42.35, 39.77, 39.55, 38.25, 37.07, 36.68, 36.22, 35.83, 31.96, 31.91, 28.27, 28.04, 27.91, 24.32, 23.87, 22.85, 22.60, 21.08, 19.40, 18.75, 11.89.

All spectral data were in agreement with literature data.[9]

9.2 Thioesters

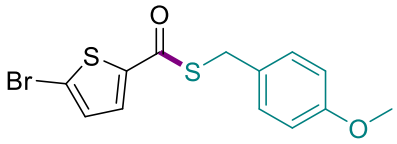


***S*-(4-Methoxyphenyl)-5-bromothiophene-2-carbothioate (15):** Compound **15** was prepared according to Method A with the following modification: 1.0 equiv (0.25 mmol, 31.2 µL) thiol was added. The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **15** (82.3 mg, 86% yield) as a white solid; R_f: 0.70 (hexanes/EtOAc 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 4.0 Hz, 1 H), 7.42-7.40 (m, 2H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.98-6.96 (m, 2H), 3.84 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 182.07, 161.03, 142.58, 136.68, 131.57, 131.09, 121.99, 116.83, 115.04, 77.29, 77.03, 76.78, 55.42.

HRMS: *m/z* calcd for $C_{12}H_9BrO_2S_2$; 327.9227 [M]: found 327.9227.

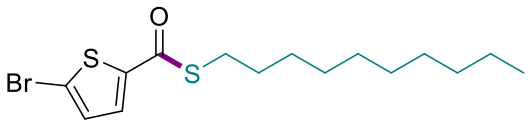


***S*-(4-Methoxybenzyl)-5-bromothiophene-2-carbothioate (16):** Compound **16** was prepared according to Method A. The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **16** (74.0 mg, 87% yield) as a yellow solid; R_f: 0.60 (hexanes/EtOAc 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 4.1 Hz, 1H), 7.29-7.27 (m, 2H), 7.06 (d, *J* = 4.1 Hz, 1H), 6.86-6.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 182.06, 161.03, 142.58, 136.68, 131.58, 131.09, 121.98, 116.83, 115.04, 77.36, 77.04, 76.72, 55.42.

HRMS: *m/z* calcd for $C_{13}H_{11}BrO_2S_2$; 341.9384 [M]: found 341.9384

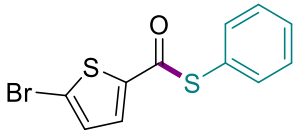


***S*-Decyl-5-bromothiophene-2-carbothioate (17):** Compound **17** was prepared according to Method B. The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **17** (78.6 mg, 87% yield) as a white solid; R_f: 0.70 (hexanes/EtOAc 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 4.1 Hz, 1H), 7.08 (d, *J* = 4.1 Hz, 1H), 3.07-3.03 (t, *J* = 7.25 Hz, 2H), 1.69-1.62 (pentet, *J* = 7.61, 2H), 1.44-1.36 (m, 2H), 1.30-1.25 (m, 12H), 0.89-0.86 (t, *J* = 6.81 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 183.15, 143.53, 130.92, 130.88, 121.16, 77.30, 77.05, 76.79, 31.90, 29.60, 29.55, 29.50, 29.31, 29.25, 29.13, 28.86, 22.70, 14.13.

HRMS: *m/z* calcd for $C_{15}H_{23}BrOS_2$; 362.0374 [M]: found 362.0374.

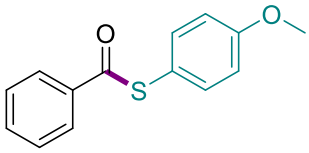


***S*-Phenyl-5-bromothiophene-2-carbothioate (18):** Compound **18** was prepared according to Method A. The crude product was purified by flash column chromatography (gradient hexanes to hexanes/EtOAc 95:5) to afford **18** (74.8 mg, 90% yield) as a yellow solid; R_f: 0.60 (hexanes/EtOAc 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 4.1 Hz, 1H), 7.52-7.50 (m, 2H), 7.46-7.44 (m, 3H), 7.14 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 181.12, 142.55, 135.07, 131.71, 131.13, 129.84, 129.35, 126.36, 122.18, 77.30, 77.05, 76.79.

HRMS: *m/z* calcd for $C_{11}H_7BrOS_2$; 297.912170 [M]: found 297.9122.

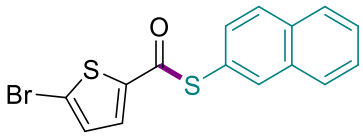


***S*-(4-Methoxyphenyl) benzothioate (19):** Compound **19** was prepared according to Method C with the following modification. In step 2: pH is adjusted to 10 with triethylamine. The crude product was purified by flash column chromatography (hexanes/AcOEt 95:5) to afford **19** (58.6 mg, 96% yield) as a colorless oil; **R_f**: 0.40 (hexanes/EtOAc 95:5).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 – 8.02 (m, 2H), 7.67 – 7.58 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.05 – 6.97 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 191.07, 160.82, 136.69, 136.65, 133.58, 128.73, 127.48, 117.91, 114.99, 77.29, 77.03, 76.78, 55.41.

All spectral data were in agreement with literature data.[10]

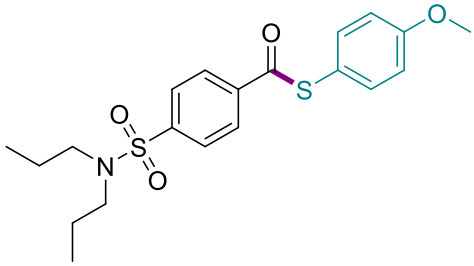


***S*-Naphtyl-5-bromothiophene-2-carbothioate (20):** Compound **20** was prepared according to Method A. The crude product was purified by flash column chromatography (gradient hexanes to hexanes/EtOAc 90:10) to afford **20** (79.3 mg, 91% yield) as a white solid; $\mathbf{R_f}$: 0.50 (hexanes/EtOAc 90:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.92-7.89 (d, *J* = 8.6 Hz, 1 H), 7.89-7.84 (m, 2H) 7.70 (d, *J* = 4.1 Hz, 1H), 7.56-7.52 (m, 3H), 7.16 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 181.29, 142.57, 135.10, 133.62, 133.55, 131.81, 131.20, 128.98, 128.06, 127.87, 127.40, 126.70, 123.69, 122.27, 77.33, 77.08, 76.82.

HRMS: *m/z* calcd for $C_{15}H_9BrOS_2$; 347.9278 [M]: found 347.9278.

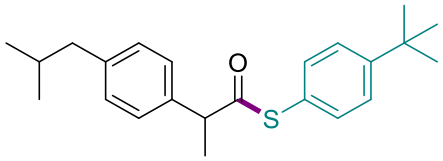


***S*-(4-Methoxyphenyl)-4-(*N,N*-dipropylsulfamoyl)benzothioate (21):** Compound **21** was prepared according to Method A. The crude product was purified by flash column chromatography (hexanes/EtOAc 80:20) to afford **21** (83.5 mg, 82% yield) as a white solid; $\mathbf{R_f}$: 0.40 (hexanes/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.10 (m, 2H), 7.93-7.90 (m, 2H), 7.42-7.40 (m, 2H), 7.01-6.99 (m, 2H), 3.86 (s, 3H), 3.13-3.09 (m, 4H), 1.59-1.53 (sextet, *J* = 7.5 Hz, 4H), 0.90-0.86 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 190.19, 161.08, 144.67, 139.45, 136.53, 128.03, 127.38, 116.98, 115.16, 55.44, 49.99, 21.99, 11.18.

All spectral data were in agreement with literature data.[11]

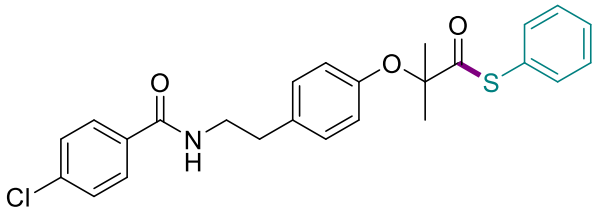


***S*-(4-*t*-Butylphenyl)-2-(4-isobutylphenyl)propanethioate (22):** Compound **22** was prepared according to Method A. The crude product was purified by flash column chromatography (hexanes/EtOAc 80:20) to afford **22** (76.7 mg, 93% yield) as a white oil; $R_{f:}$ 0.80 (hexanes/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.28-7.27 (m, 2H), 7.25-7.24 (m, 2H), 7.13-7.11 (m, 2H), 2.48-2.46 (d, *J* = 7.1 Hz, 2H), 1.57-1.55 (d, *J* = 7.1 Hz, 2H), 1.30 (s, 9H), 0.92-0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.76, 152.48, 141.06, 136.90, 134.19, 129.52, 127.80, 126.26, 124.67, 77.39, 77.13, 76.88, 53.73, 45.17, 34.78, 31.28, 30.26, 22.50, 18.79.

HRMS: *m/z* calcd for $C_{23}H_{30}O_3S$; 354.2017 [M]: found 354.2018.

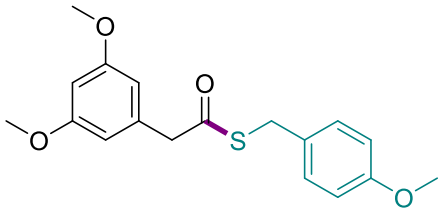


***S*-Phenyl-2-[4-[2-(4-chlorobenzamido)ethyl]phenoxy]-2-methylpropanethioate (23):**
Compound **23** was prepared according to Method A. The crude product was purified by flash column chromatography (hexanes/EtOAc 50:50) to afford **23** (89.1 mg, 79% yield) as a white solid; $R_{f:}$ 0.50 (hexanes/EtOAc 50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.43 (s, 5H), 7.39-7.36 (m, 2H), 7.17-7.15 (m, 2H), 7.02-7.00 (m, 2H), 6.10 (s, 1H), 3.72-3.67 (q, *J* = 6.7 Hz, 2H) 2.90-2.89 (t, *J* = 7.0 Hz, 2H), 1.58 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.44, 166.40, 153.13, 137.69, 134.84, 133.70, 132.99, 129.55, 129.39, 129.23, 128.85, 128.26, 127.87, 121.61, 86.03, 77.30, 77.05, 76.80, 41.25, 34.88, 25.45.

HRMS: *m/z* calcd for $C_{25}H_{24}ClNO_3SNa$; 476.1063 [M+23]: found 476.1063.

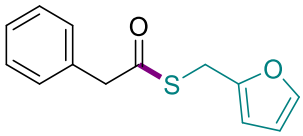


***S*-(4-Methoxybenzyl)-3,5-dimethoxyphenylethanethioate (24):** Compound **24** was prepared according to Method A. The crude product was purified by flash column chromatography (gradient hexanes/EtOAc 95:5 to hexanes/EtOAc 80:20) to afford **24** (74.1 mg, 86% yield) as a white solid; R_f: 0.40 (hexanes/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2H), 6.82-6.80 (m, 2H), 6.43 (d, *J* = 2.2 Hz, 2H), 6.39-6.38 (t, *J* = 2.2 Hz, 1H), 4.06 (s, 2H), 3.77 (s, 9H), 3.75 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.70, 160.89, 158.85, 135.56, 130.04, 129.27, 114.03, 107.64, 99.53, 55.34, 55.28, 50.48, 33.18.

HRMS: *m/z* calcd for $C_{18}H_{20}O_4S$; 332.1082 [M]: found 332.1082.

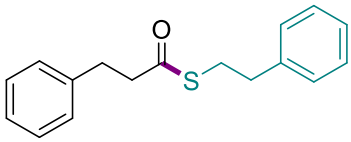


***S*-(Furan-2-ylmethyl)-2-phenylethanethioate (25):** Compound **25** was prepared according to Method A. The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **25** (53.0 mg, 91% yield) as a pale brown solid; R_f: 0.6 (hexanes/EtOAc 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 6H), 6.28-6.27 (dd, *J* = 3.3, 1.9 Hz,1H), 6.20-6.19 (d, *J* = 3.2 Hz, 1H), 4.13 (s, 2H), 3.85 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.33, 150.20, 142.25, 133.25, 129.68, 128.72, 127.55, 110.63, 108.04, 50.27, 26.06.

HRMS: *m/z* calcd for $C_{13}H_{12}O_2S$; 232.0558 [M]: found 232.0558.

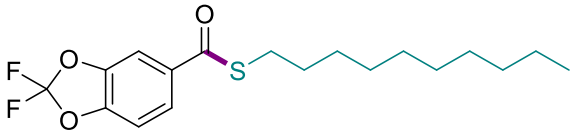


***S*-Phenethyl 3-phenylpropanethioate (26):** Compound **26** was prepared according to Method B. The crude product was purified by flash column chromatography (gradient hexanes, then hexanes/EtOAc 85:15 afforded **26** (56 mg, 83% yield) as a white solid; R_f: 0.72 (hexanes/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 4H), 7.28 – 7.17 (m, 6H), 3.16 (dd, *J* = 8.7, 6.7 Hz, 2H), 3.01 (dd, *J* = 8.8, 6.1 Hz, 2H), 2.89 (ddd, *J* = 7.2, 6.0, 3.0 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.44, 140.11, 140.00, 128.66, 128.59, 128.54, 128.38, 126.58, 126.40, 77.43, 77.11, 76.80, 45.59, 35.92, 31.49, 30.36.

All spectral data were in agreement with literature data.[12]



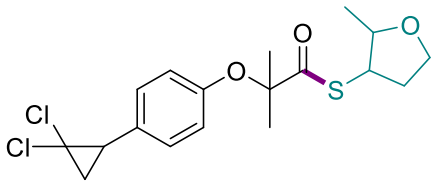
***S*-(Decyl)benzo[d][1,3]dioxole-5-carbothioate (27):** Compound **27** was prepared according to Method B. The crude product was purified by flash column chromatography (gradient hexanes/EtOAc 90:10 to hexanes/EtOAc 80:20) to afford **27** (80.4 mg, 90% yield) as a white solid; R_f: 0.80 (hexanes/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.11-7.09 (d, *J* = 8.4 Hz, 1H), 3.08-3.05 (t, *J* = 7.5 Hz, 2H), 1.70-1.62 (quintet, *J* = 7.4 Hz, 2H), 1.43-1.37 (quintet, *J* = 7.1 Hz, 2H), 1.26 (s, 12H), 0.89-0.85 (t, *J* = 6.7 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$): δ -49.74.

^{13}C NMR (126 MHz, $CDCl_3$): δ 189.98, 147.11, 143.94, 133.67, 131.67, 124.17, 109.19, 108.46, 31.91, 29.56, 29.51, 29.47, 29.40, 29.33, 29.16, 28.93, 22.70, 14.11.

HRMS: *m/z* calcd for $C_{28}H_{24}F_2O_3S$; 358.1414 [M]: found 358.1414.

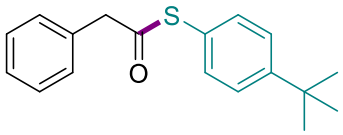


***S*-(2-Methyl-3-tetrahydrofuranyl)-2-[4-(2,2-dichlorocyclopropyl)phenoxy]-2-methylpropanethioate (*cis*- and *trans*- mixture) (28):** Compound **28** was prepared according to Method B with the following modification: 2.5 mol % DBU was added. The crude product was purified by flash column chromatography (hexanes/EtOAc 90:10) to afford **28** (61.1 mg, 63% yield) as a yellow oil; R_f: 0.30 (hexanes/EtOAc 90:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.13 (dd, *J* = 8.9, 2.6 Hz, 2H), 6.95-6.91 (m, 2H), 4.23-3.91 (m, 2H), 3.85-3.48 (m, 2H), 2.87-2.82 (t, *J* = 9.8 Hz, 1H), 2.55-2.45 (m, 1H), 1.98-1.85 (m, 2H), 1.81-1.77 (t, *J* = 7.7 Hz, 1H), 1.53-1.52 (d, *J* = 3.1 Hz, 6H), 1.31-1.29 (d, *J* = 6.2 Hz, 2H), 1.20 (d, *J* = 6.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 204.86, 204.78, 153.90, 153.80, 129.63, 129.60, 121.01, 121.00, 120.90, 120.88, 85.83, 85.81, 80.23, 66.81, 66.06, 60.77, 46.21, 45.59, 34.86, 33.32, 33.25, 29.71, 25.91, 25.61, 25.60, 25.47, 25.44, 25.41, 25.39, 25.33, 25.31, 19.43, 16.85.

HRMS: *m/z* calcd for $C_{18}H_{22}Cl_2O_3S$; 388.0667 [M]: found 388.0667.

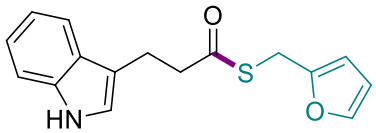


***S*-(4-*t*-Butylphenyl)-2-phenylethanethioate (29):** Compound **29** was prepared according to Method C with the following modification. In step 2: pH is adjusted to 9 with triethylamine. The crude product was purified by flash column chromatography (hexanes/EtOAc 95:5) to afford **29** (61.6 mg, 87% yield) as a yellow oil; R_f: 0.50 (hexanes/EtOAc 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.36-7.30 (m, 6H), 3.92 (s, 2H), 1.32 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.83, 152.68, 134.10, 133.42, 129.67, 128.71, 126.32, 124.32, 50.07, 34.78, 31.22.

All spectral data were in agreement with literature data.[7]

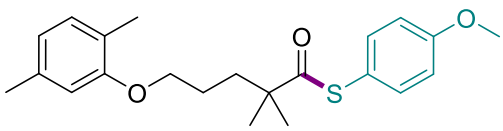


***S*-(Furan-2-ylmethyl)indole-3-propanethioate (30):** Compound **30** was prepared according to Method C with the following modification: in step 2: pH is adjusted to 9 with triethylamine. The crude product was purified by flash column chromatography (hexanes/AcOEt 70:30) to afford **30** (62.7 mg, 88% yield) as a yellow solid; R_f: 0.60 (hexanes/AcOEt 70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.62-7.60 (d, *J* = 7.8 Hz, 1H), 7.37-7.34 (m, 2H), 7.24-7.20 (t, *J* = 7.5 Hz, 1H), 7.17-7.13 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.32-6.31 (dd, *J* = 3.1, 1.6 Hz, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 4.19 (s, 2H), 3.19-3.16 (t, *J* = 7.6 Hz, 2H), 3.01-2.98 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.96, 150.56, 142.24, 136.29, 127.10, 122.17, 121.61, 119.46, 118.68, 114.36, 111.23, 110.68, 107.94, 44.42, 25.68, 21.13.

HRMS: *m/z* calcd for $C_{16}H_{15}NO_2S$; 285.0824 [M]: found 285.0854.

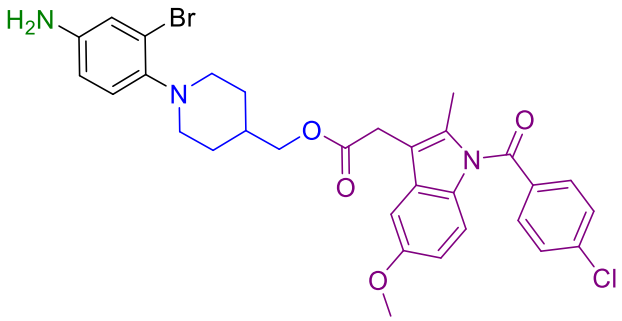


***S*-(4-Methoxyphenyl)-[5-(2',5'-dimethylphenoxy)-2,2-dimethylpentanethioate (31):**
Compound **31** was prepared according to Method C with the following modification: in step 2, pH is adjusted to 10 with triethylamine. The crude product was purified by flash column chromatography (hexanes/AcOEt 95:5) to afford **31** (56.9 mg, 61% yield) as a white oil; $R_{f:}$ 0.40 (hexanes/AcOEt 95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.03-7.01 (d, *J* = 7.5 Hz, 1H), 6.95-6.93 (m, 2H), 6.68-6.66 (d, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 3.97-3.94 (t, *J* = 5.5 Hz, 2H), 3.83 (s, 3H), 2.32 (s, 3H), 2.20 (s, 3H), 1.86-1.81 (m, 4H), 1.34 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 205.11, 160.53, 156.93, 136.53, 130.35, 123.65, 120.74, 118.62, 114.84, 111.95, 67.80, 55.37, 49.92, 37.68, 25.40, 24.95, 21.44, 15.86.

HRMS: *m/z* calcd for $C_{22}H_{28}O_3S$; 372.1759 [M+1]: found 372.1759.

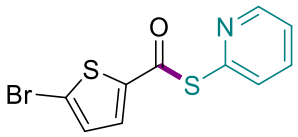


Ester 32: Compound **32** was prepared according to section 8. The crude product was purified by flash column chromatography with a gradient of 20% to 30% EtOAc/hexanes by 5% increases, to afford **32** as a yellow oil; $R_{f:}$ 0.18 (hexanes/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.02 – 6.94 (m, 1H), 6.94 – 6.79 (m, 3H), 6.71 – 6.63 (m, 1H), 6.57 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.03 (d, *J* = 5.9 Hz, 2H), 3.83 (s, 3H), 3.69 (s, 2H), 3.53 (s, 2H), 3.17 (d, *J* = 11.1 Hz, 2H), 2.52 (t, *J* = 11.4 Hz, 2H), 2.40 (s, 3H), 1.72 (s, 3H), 1.48 (tt, *J* = 14.0, 7.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.97, 168.33, 156.07, 143.22, 142.93, 139.24, 135.90, 133.93, 131.20, 130.83, 130.66, 129.13, 121.67, 121.26, 120.05, 115.01, 114.78, 112.72, 111.75, 101.29, 77.36, 77.10, 76.85, 69.38, 55.74, 52.53, 35.23, 30.43, 29.32, 13.42.

HRMS: *m/z* calcd for $C_{31}H_{31}BrClN_3O_4$; 624.1265 [M+1]: found 624.1259.



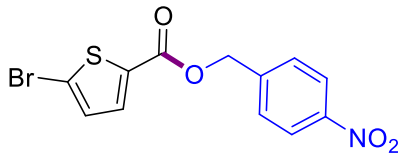
***S*-(Pyridin-2-yl) 5-bromothiophene-2-carbothioate (33): C**ompound **33** was prepared according to general procedure for intermediate thioester formation. The crude product was purified by silica plug chromatography (hexanes/EtOAc 90:10) to afford **33** as a white solid; $R_{f:}$ 0.53 (hexanes/EtOAc 50:50).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 – 8.63 (m, 1H), 7.85 – 7.73 (m, 2H), 7.69 (d, *J* = 4.1 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.17 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 180.11, 150.59, 150.56, 142.36, 137.29, 132.18, 131.25, 130.66, 123.86, 122.82, 77.29, 77.04, 76.78.

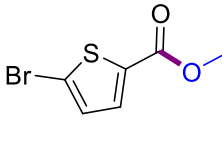
HRMS: *m/z* calcd for $C_{10}H_6BrNOS_2$; 298.9074 [M+1]: found 298.9074.

10. NMR Spectra



1

^{1}H NMR (400 MHz, $CDCl_3$)



1

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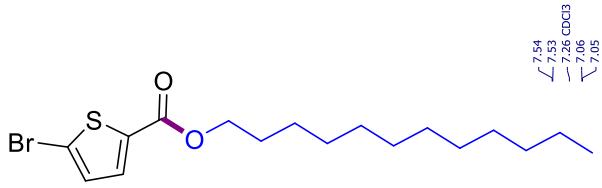

2

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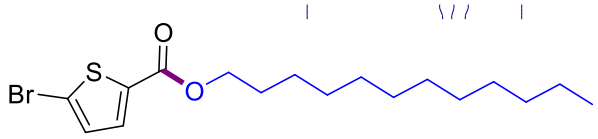
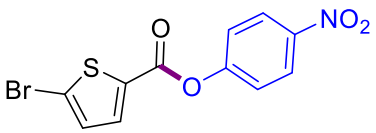


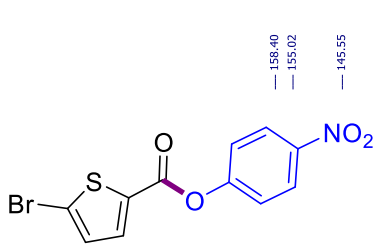
2

^{13}C NMR (126 MHz, $CDCl_3$)



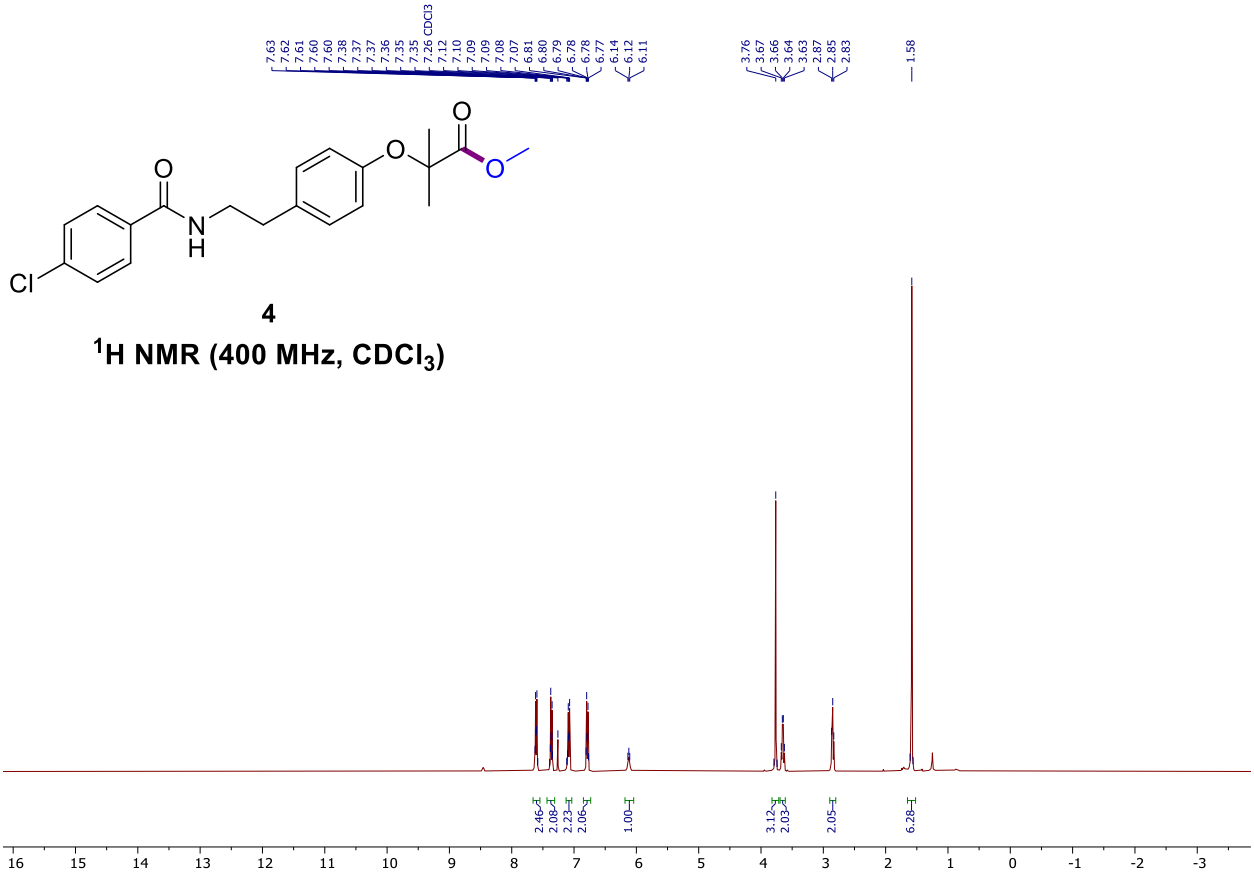
3

^{1}H NMR (500 MHz, $CDCl_3$)



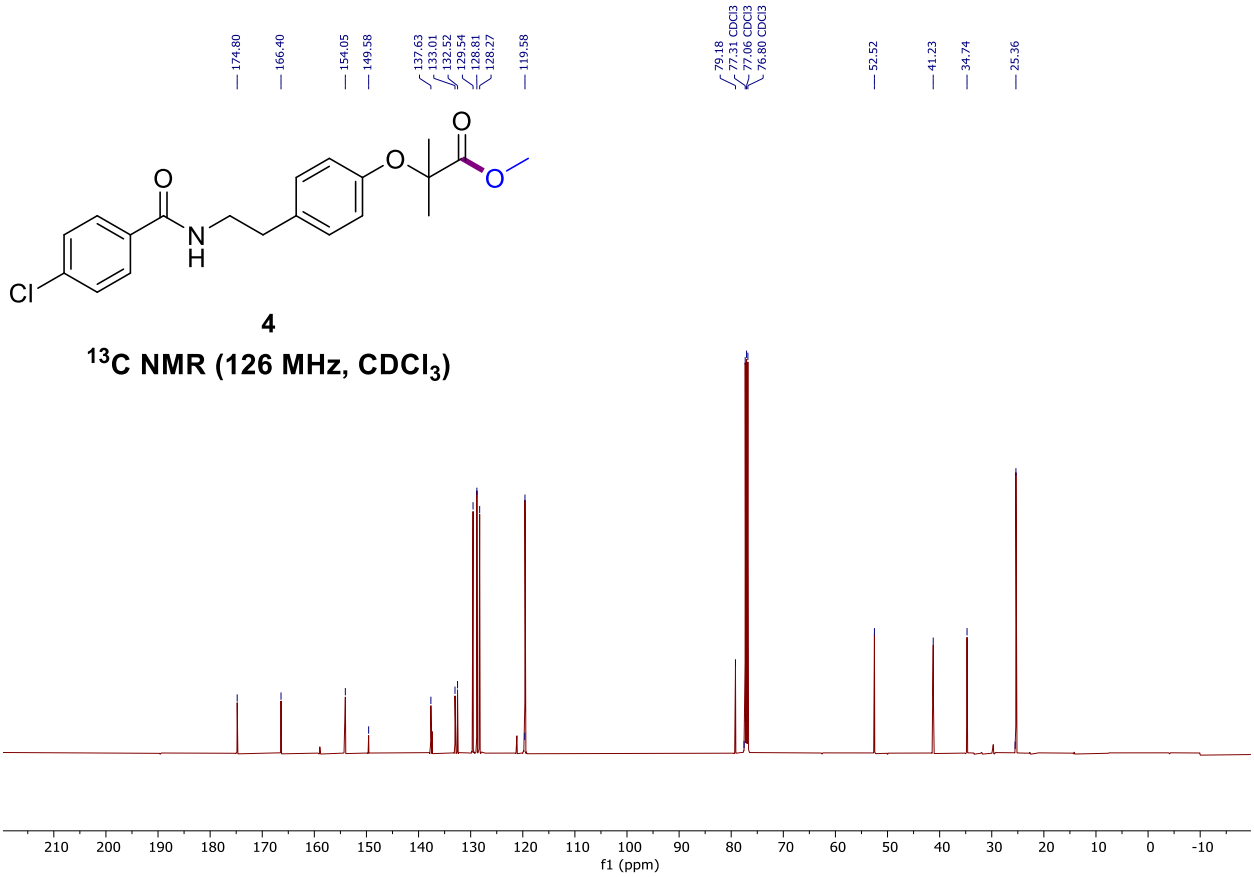
3

^{13}C NMR (126 MHz, $CDCl_3$)



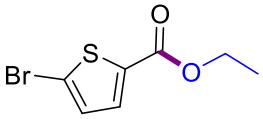
4

^{1}H NMR (400 MHz, $CDCl_3$)



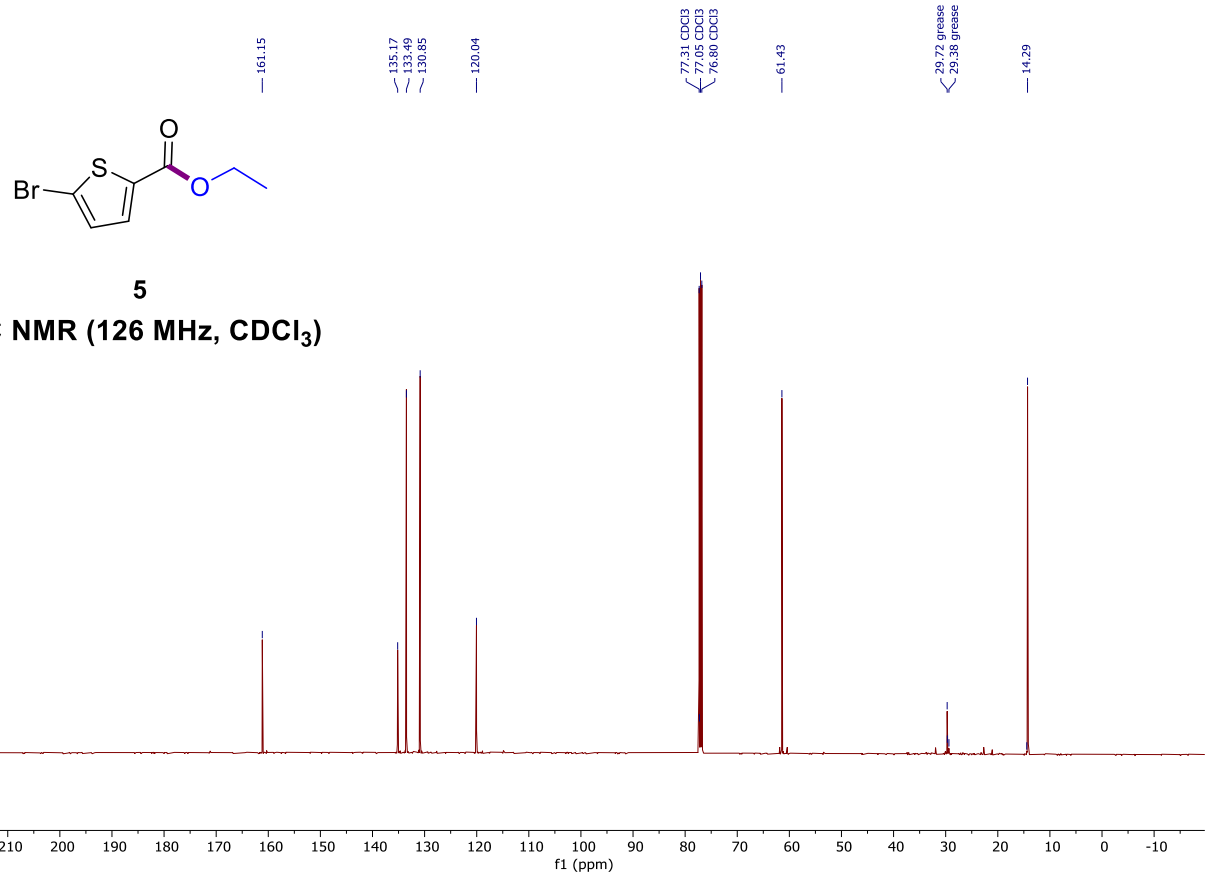
4

^{13}C NMR (126 MHz, $CDCl_3$)



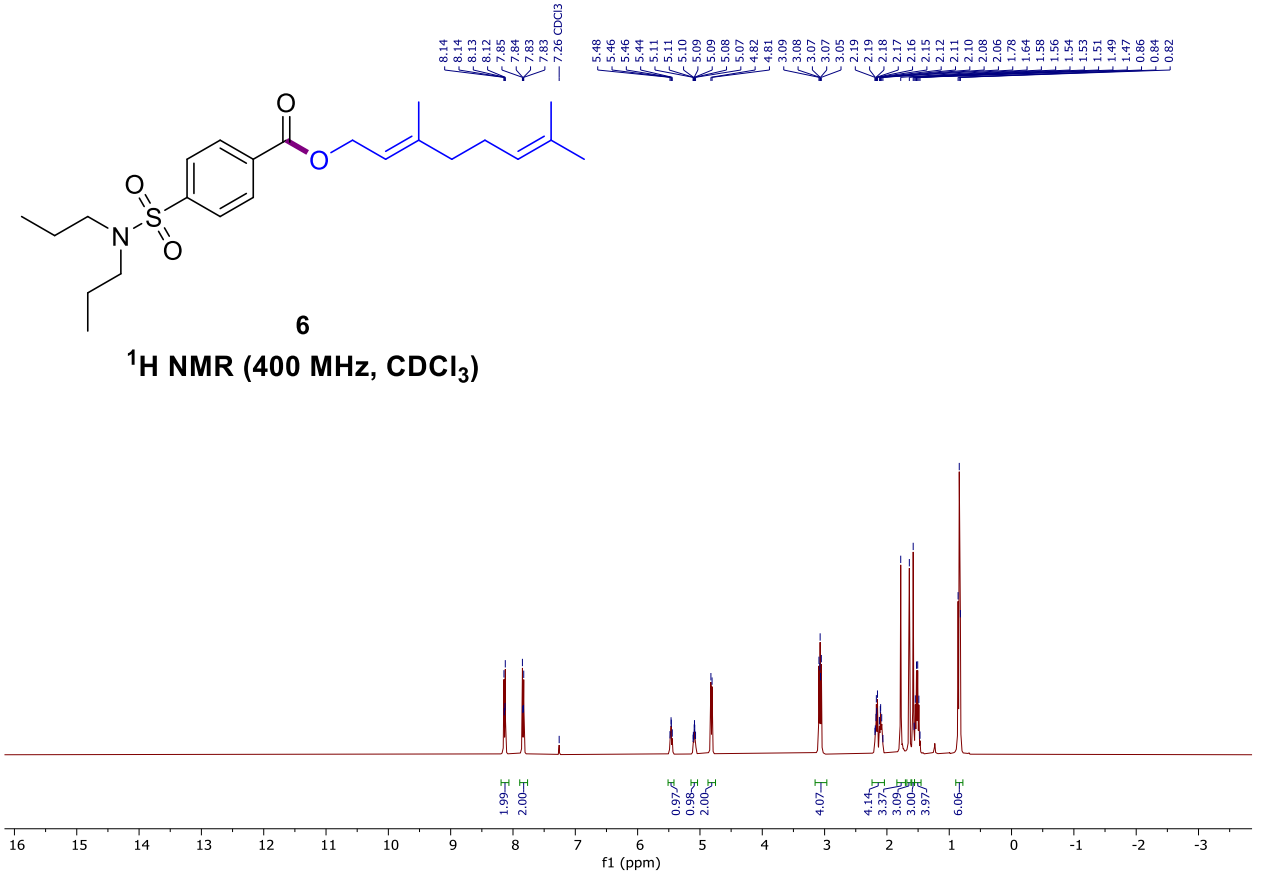
5

^{1}H NMR (400 MHz, $CDCl_3$)



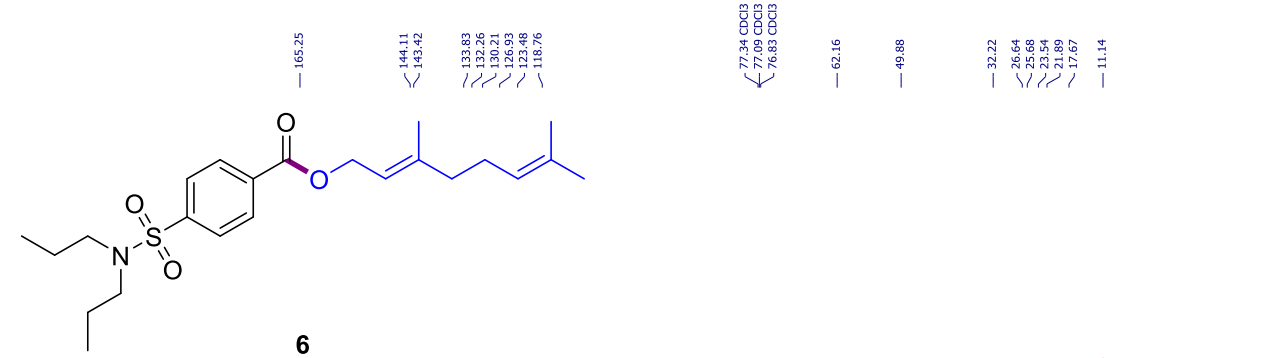
5

^{13}C NMR (126 MHz, $CDCl_3$)



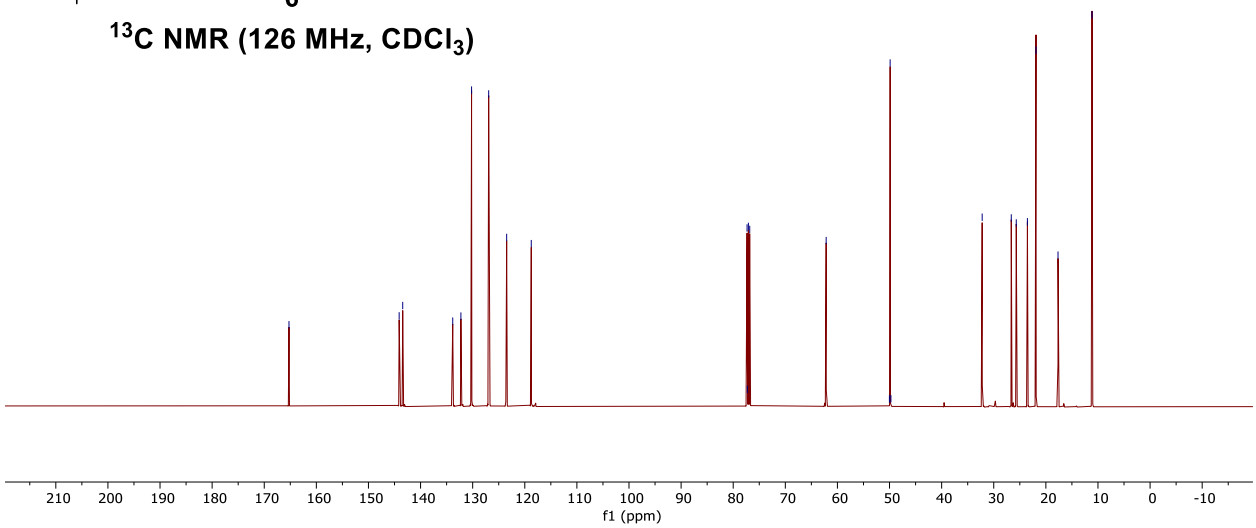
6

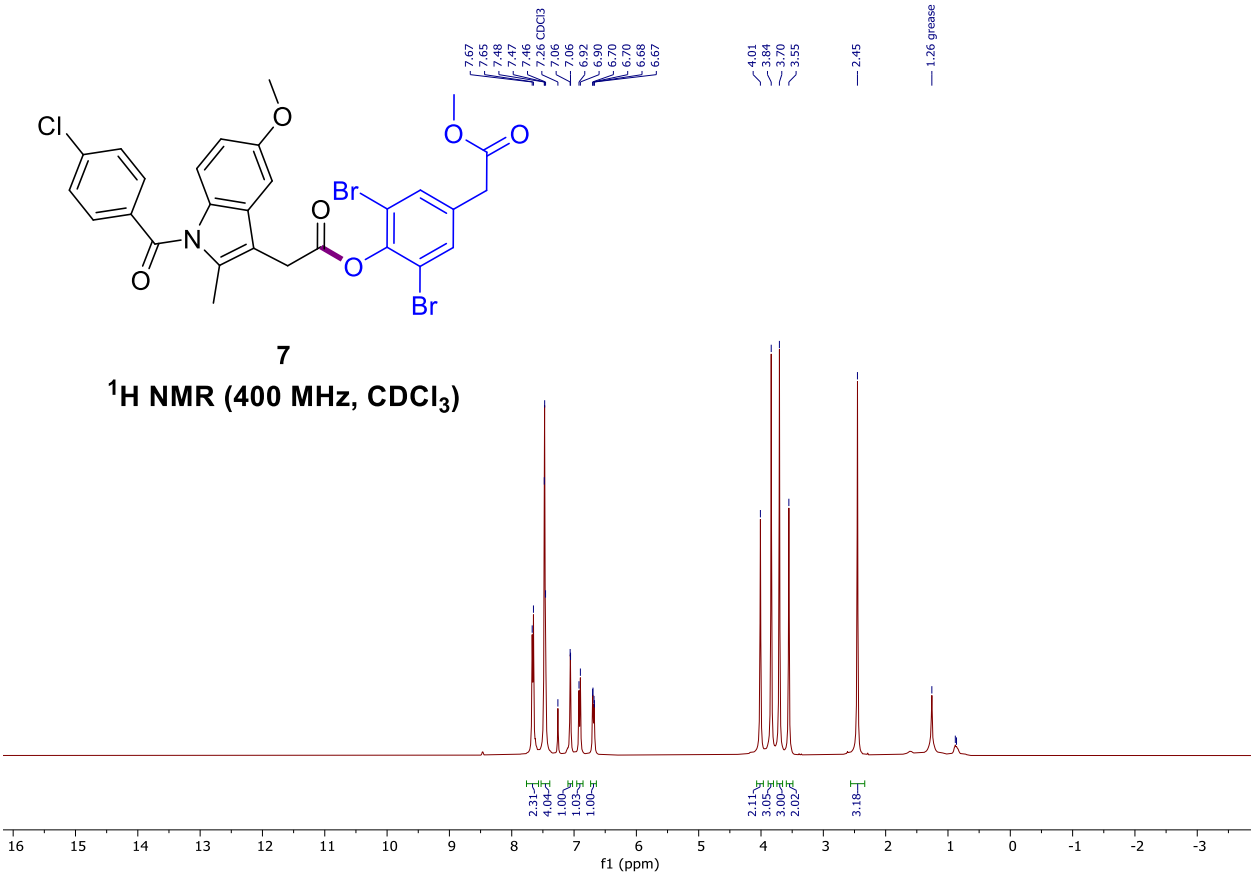
^{1}H NMR (400 MHz, $CDCl_3$)



6

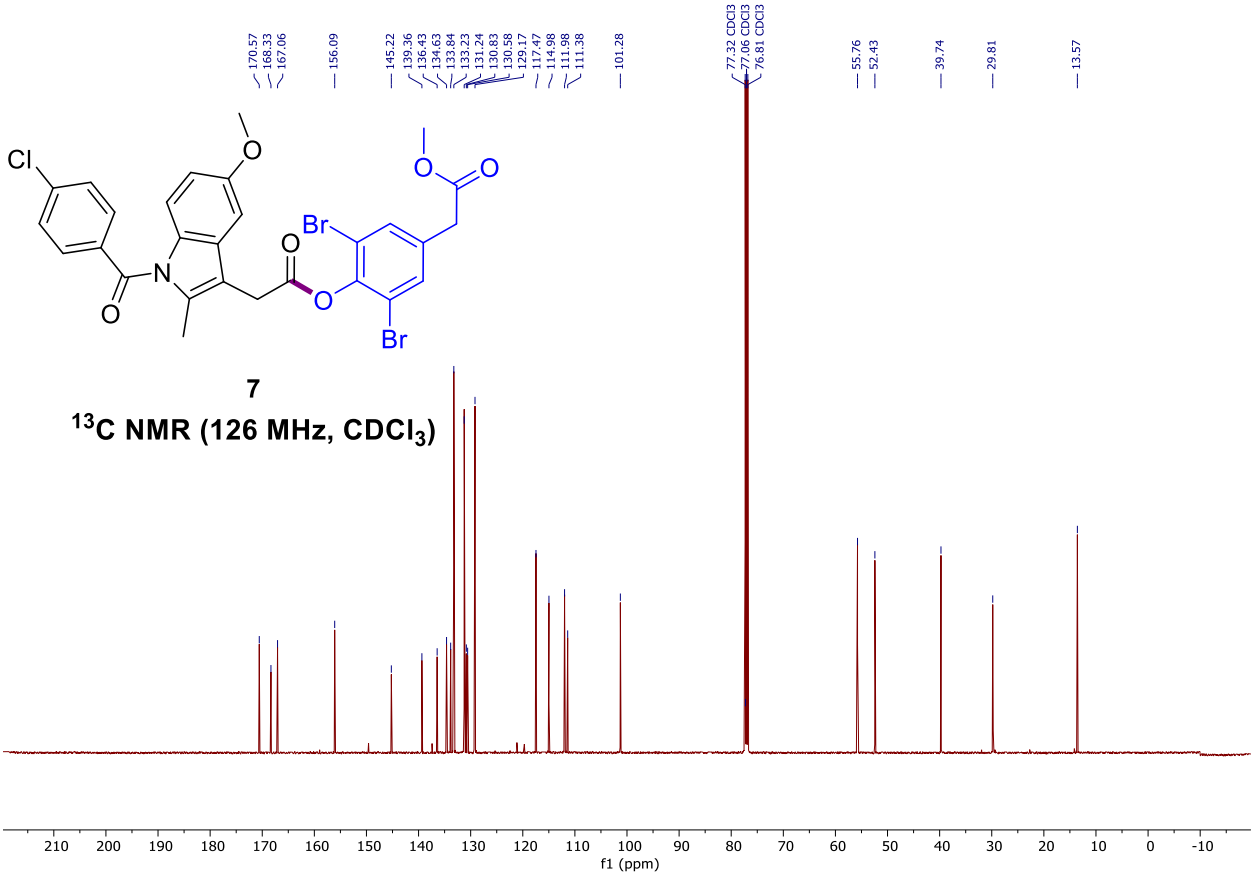
^{13}C NMR (126 MHz, $CDCl_3$)





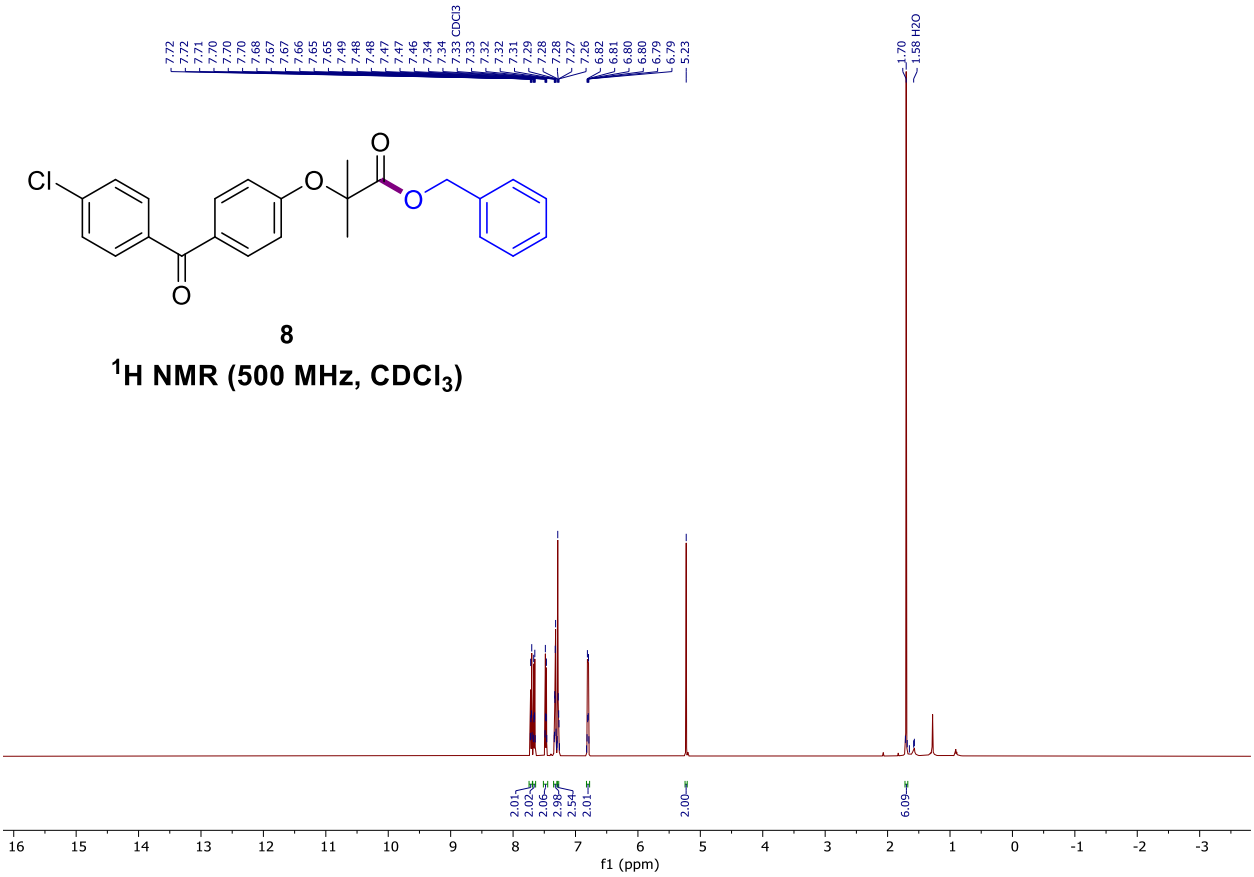
7

^{1}H NMR (400 MHz, $CDCl_3$)



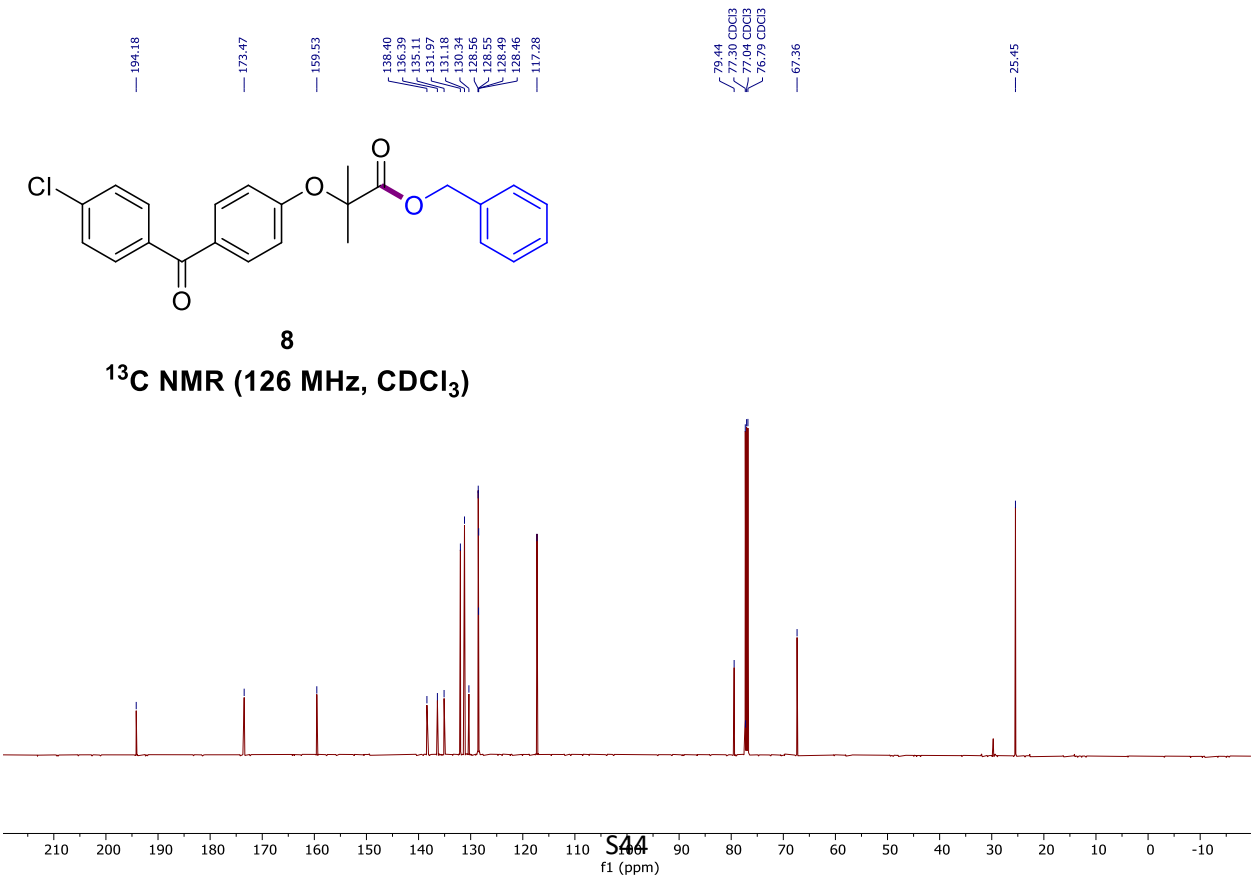
7

^{13}C NMR (126 MHz, $CDCl_3$)



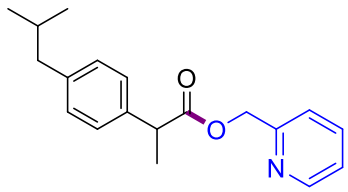
8

^{1}H NMR (500 MHz, $CDCl_3$)



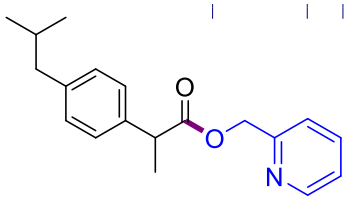
8

^{13}C NMR (126 MHz, $CDCl_3$)



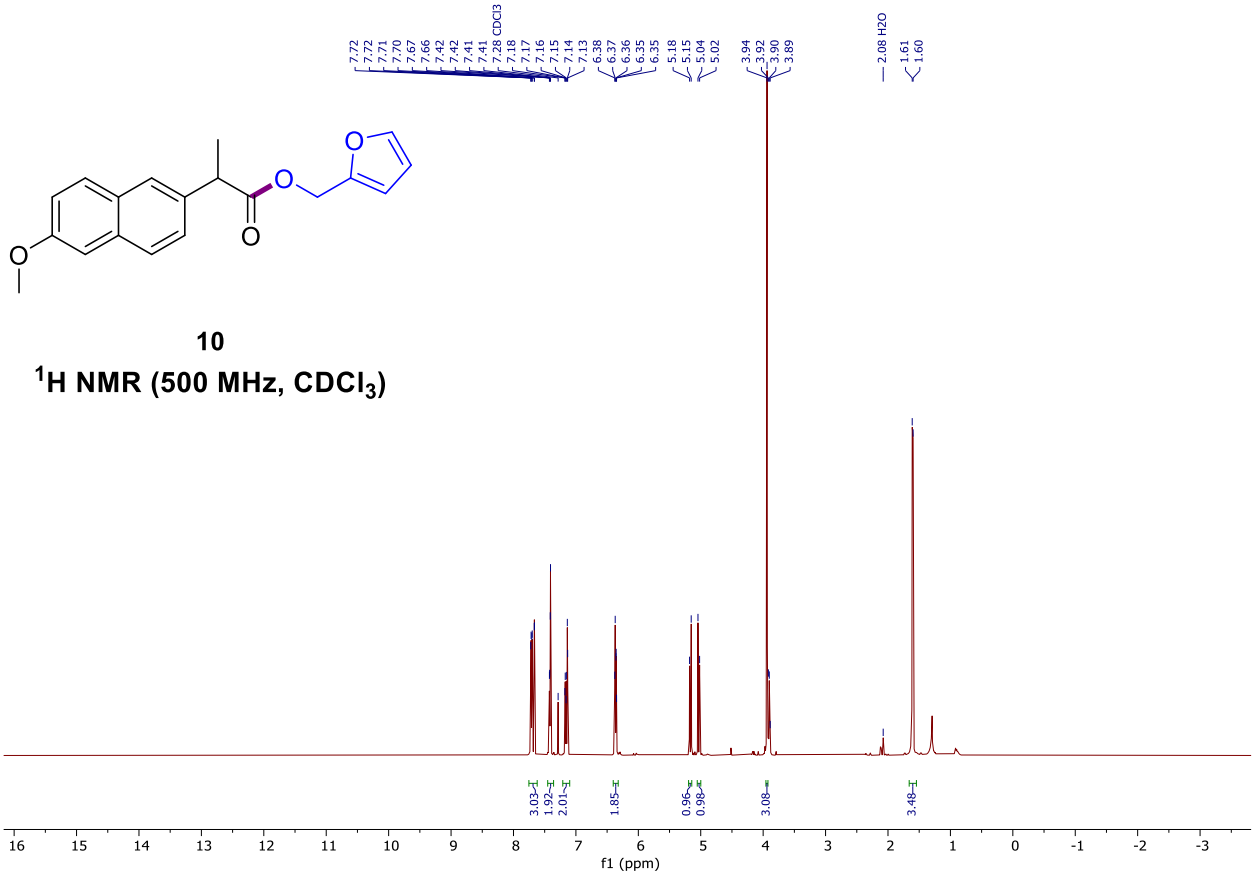
9

^{1}H NMR (400 MHz, $CDCl_3$)



9

^{13}C NMR (126 MHz, $CDCl_3$)



10

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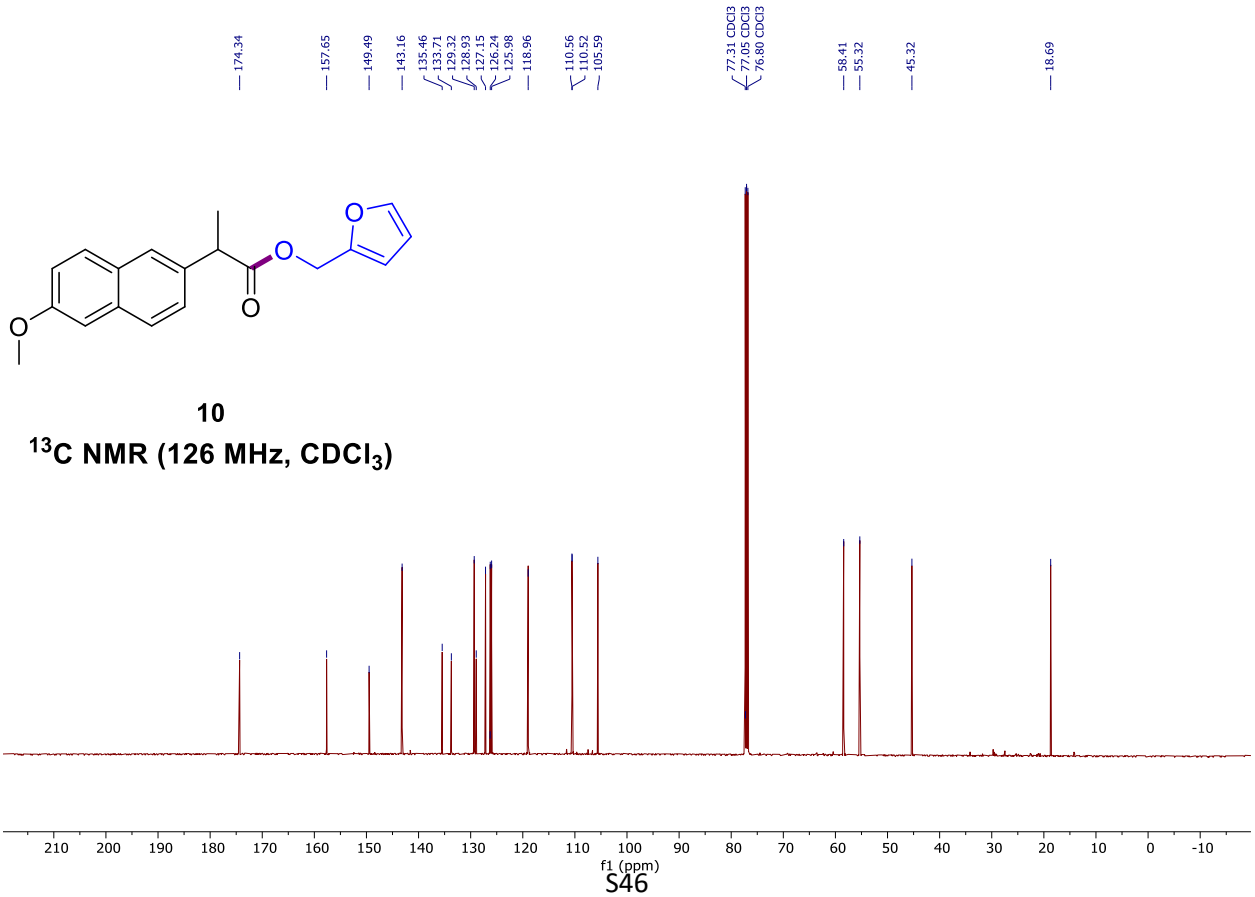

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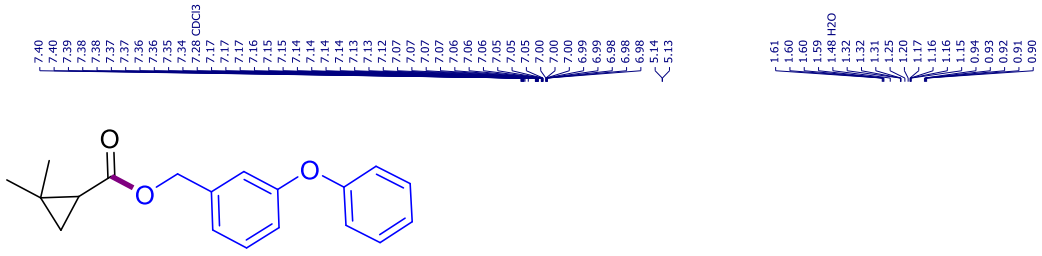
^{13}C NMR (126 MHz, $CDCl_3$)



11

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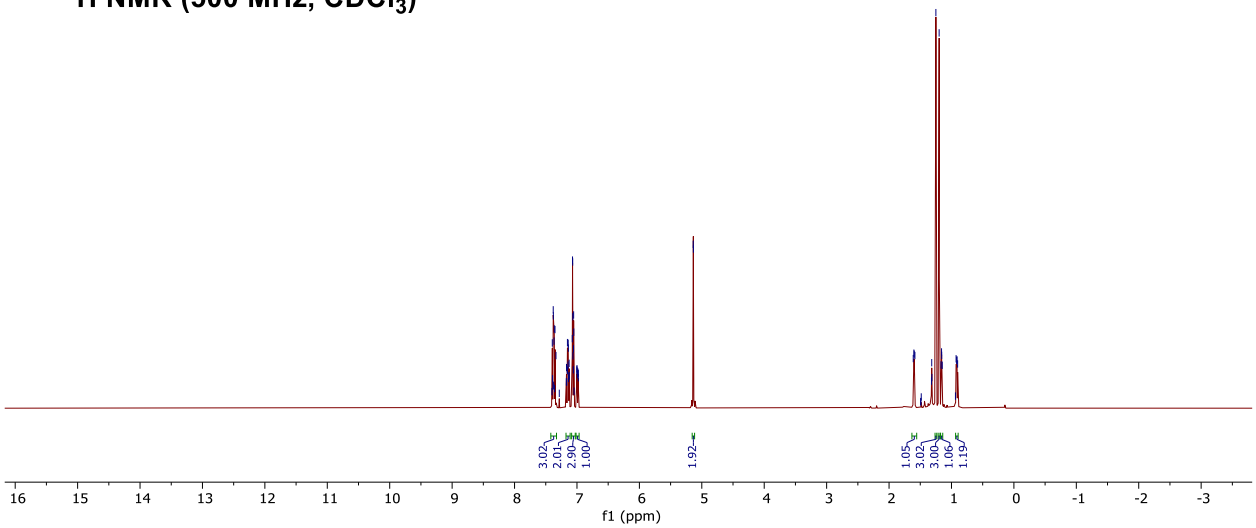
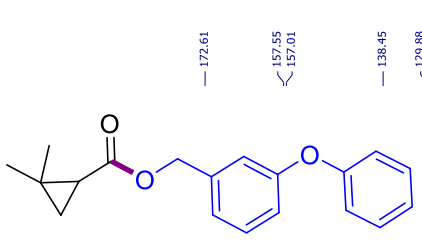
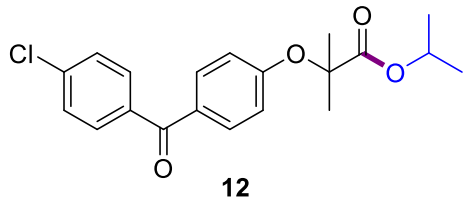




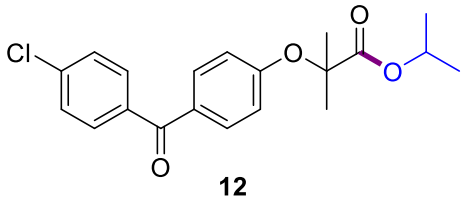
11

^{13}C NMR (126 MHz, $CDCl_3$)



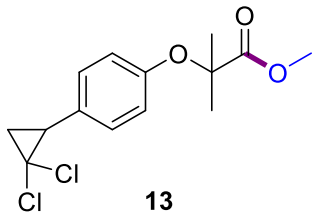
12

^{1}H NMR (400 MHz, $CDCl_3$))



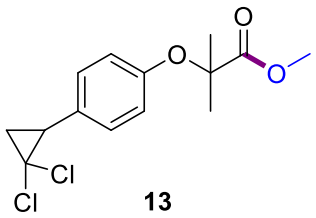
12

^{13}C NMR (126 MHz, $CDCl_3$)



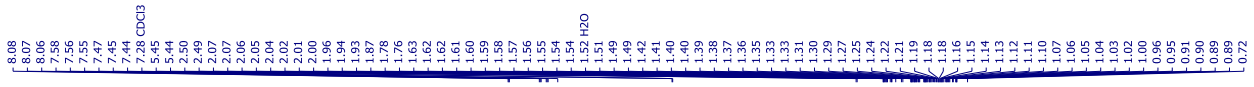
13

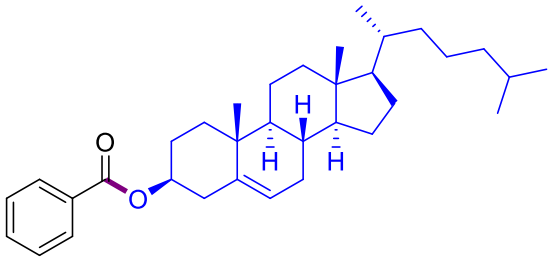
^{1}H NMR (400 MHz, $CDCl_3$)



13

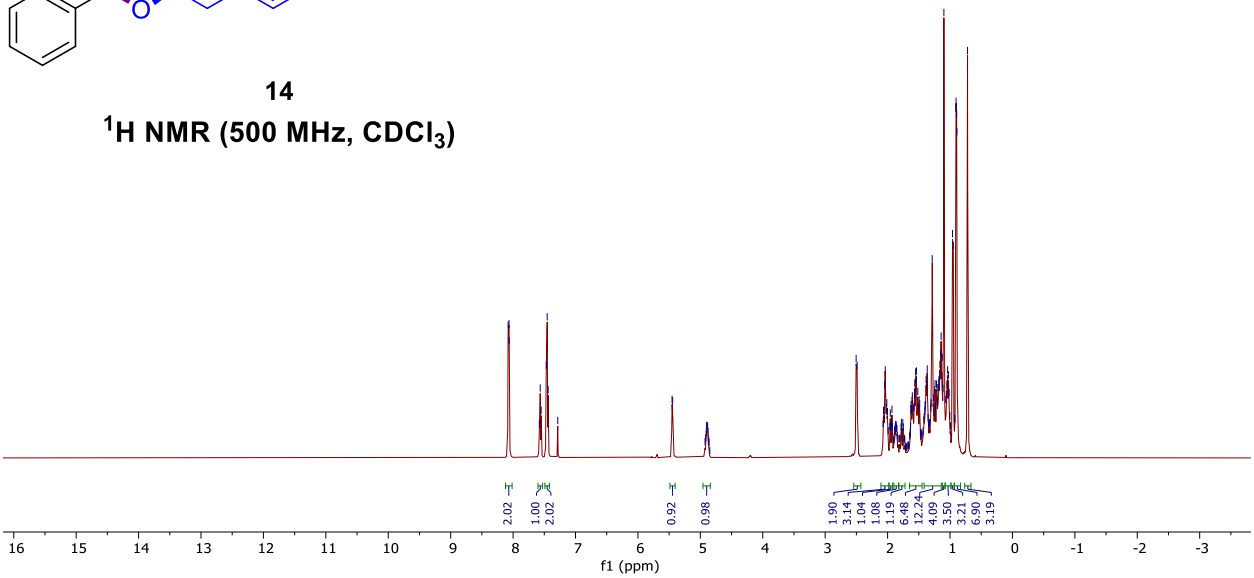
^{13}C NMR (126 MHz, $CDCl_3$)

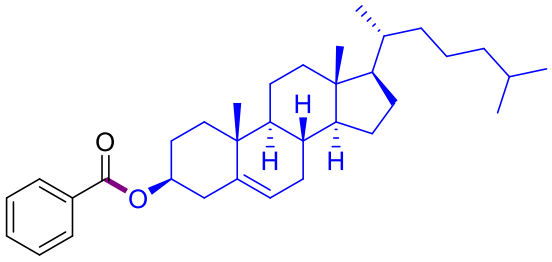




14

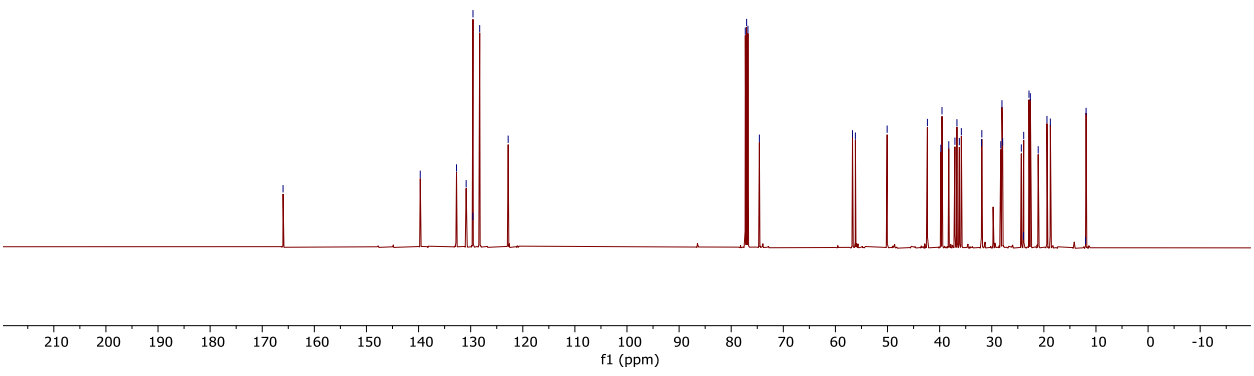
^{1}H NMR (500 MHz, $CDCl_3$)

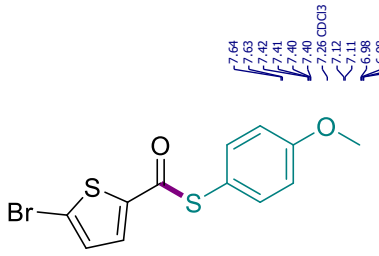




14

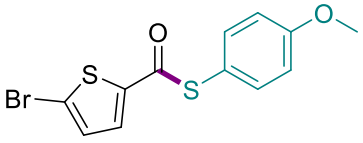
^{13}C NMR (126 MHz, $CDCl_3$)





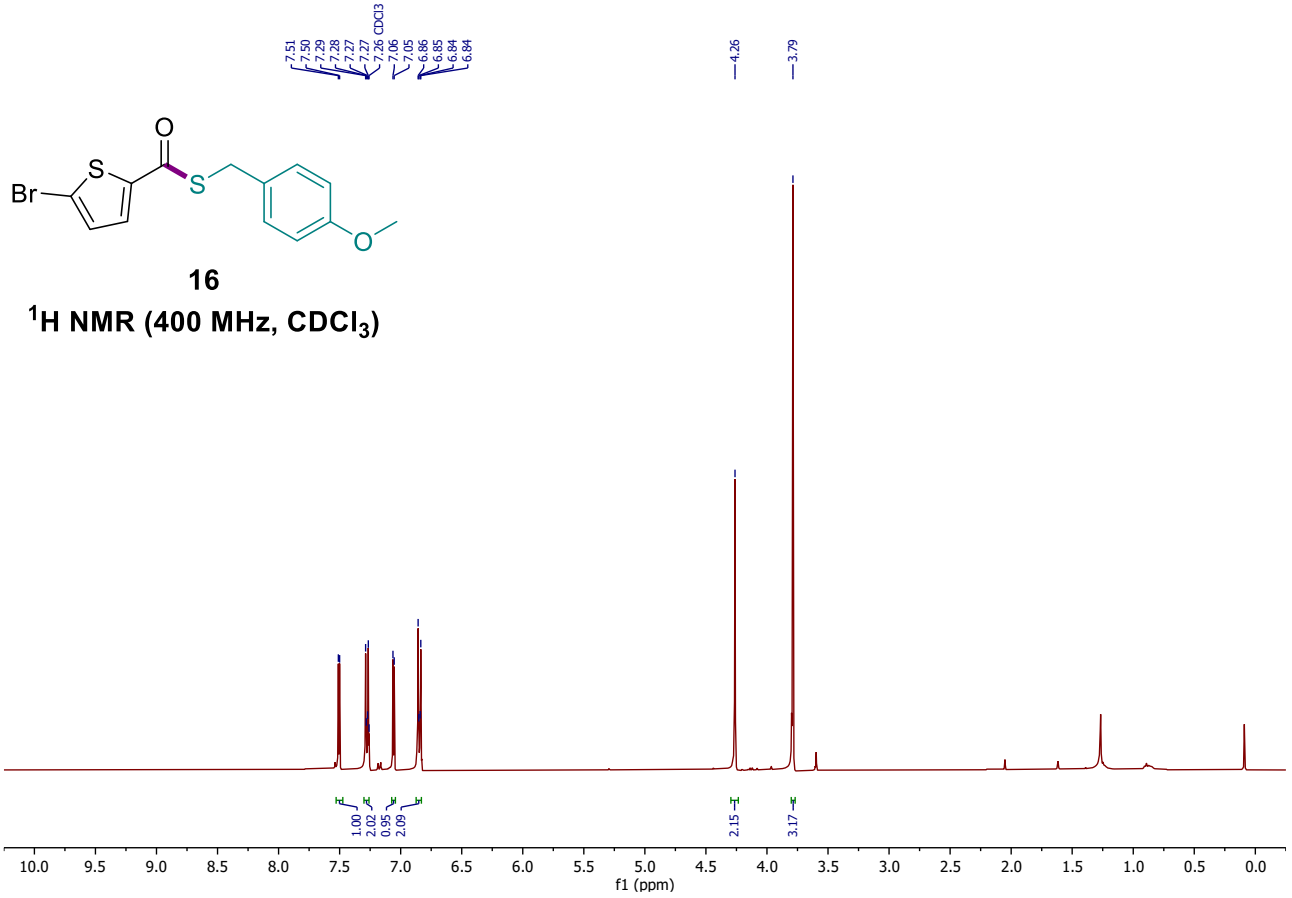
15

^{1}H NMR (400 MHz, $CDCl_3$)



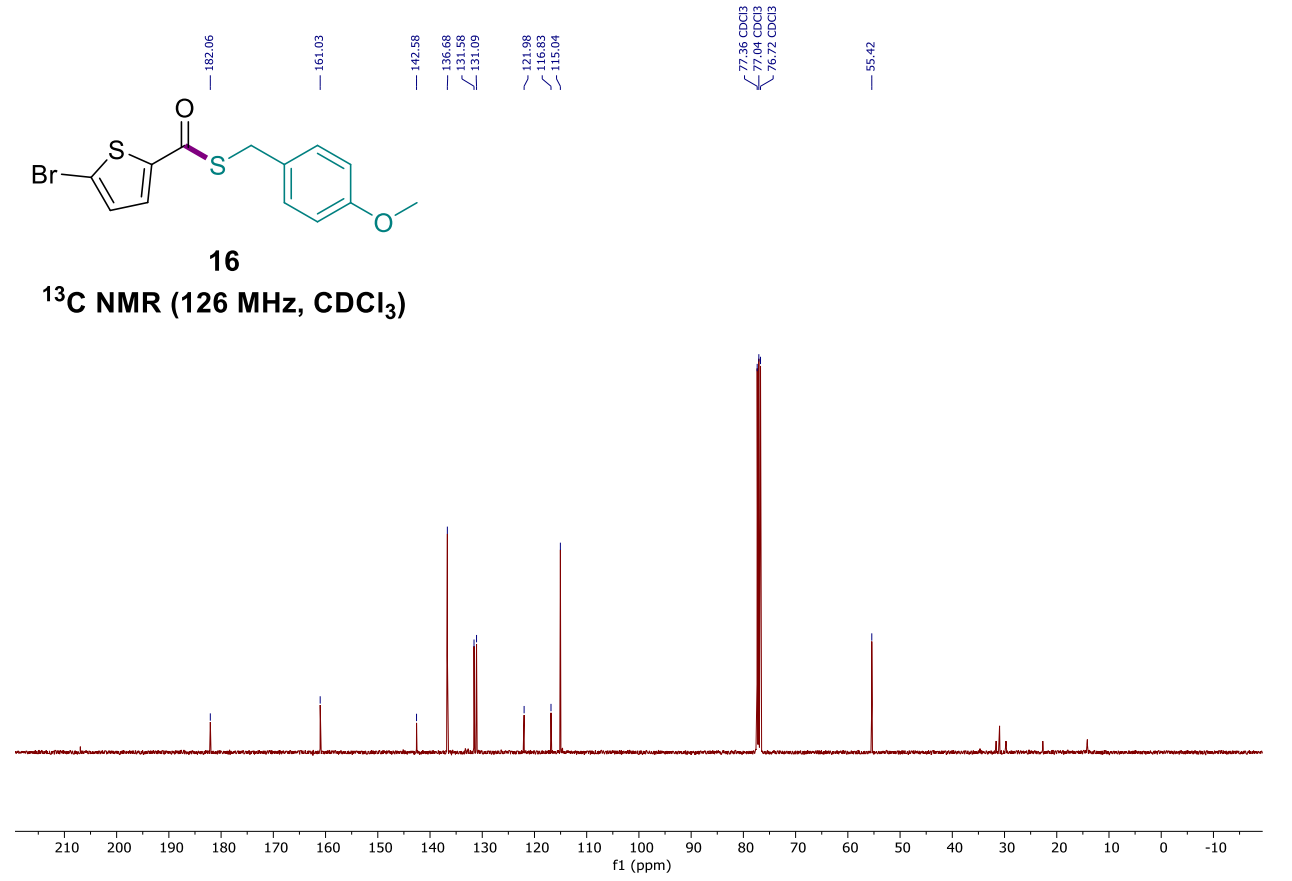
15

^{13}C NMR (126 MHz, $CDCl_3$)



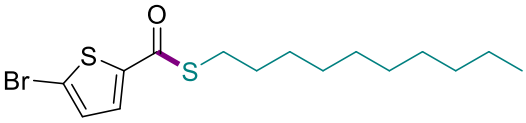
16

^{1}H NMR (400 MHz, $CDCl_3$)



16

^{13}C NMR (126 MHz, $CDCl_3$)

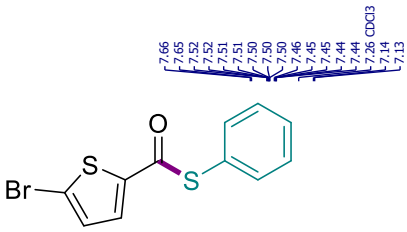


17

^{1}H NMR (400 MHz, $CDCl_3$)

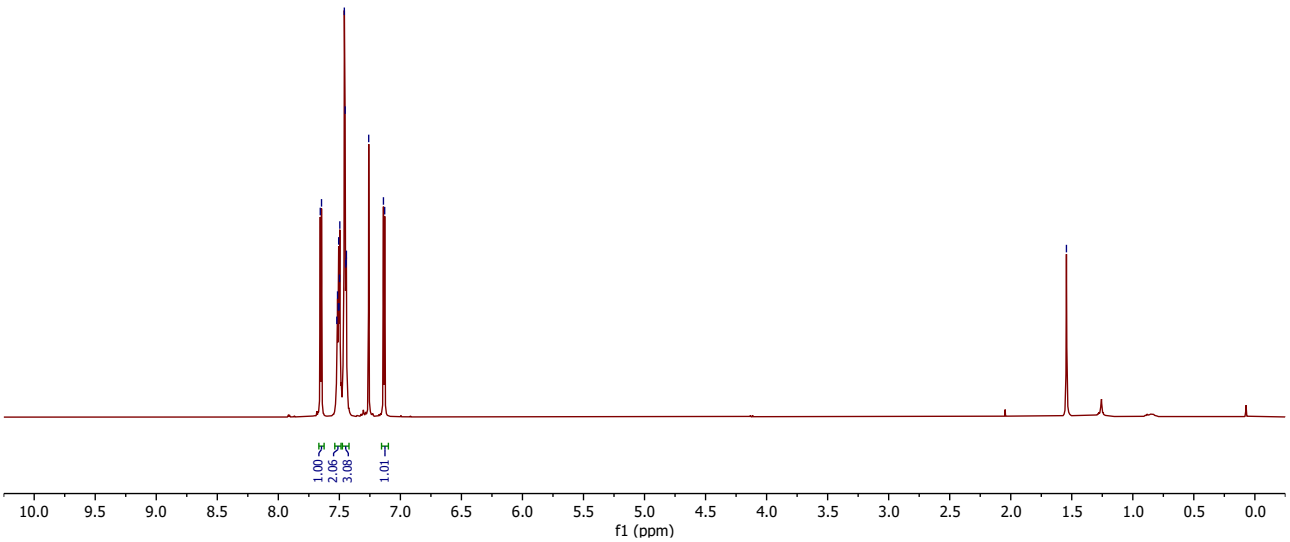
17

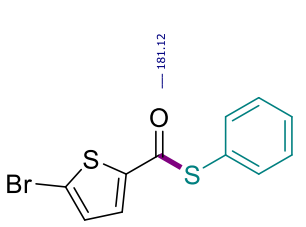
^{13}C NMR (126 MHz, $CDCl_3$)



18

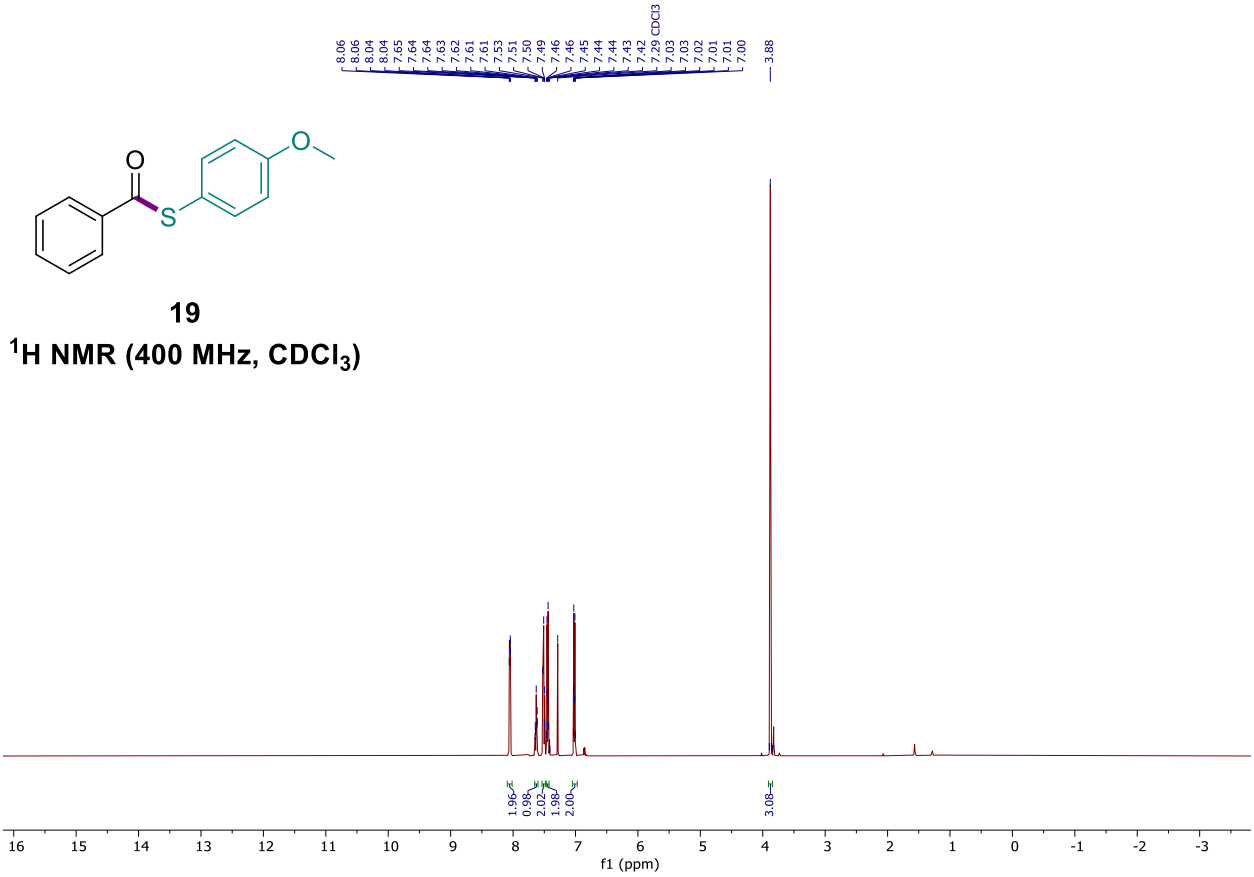
^{1}H NMR (400 MHz, $CDCl_3$)





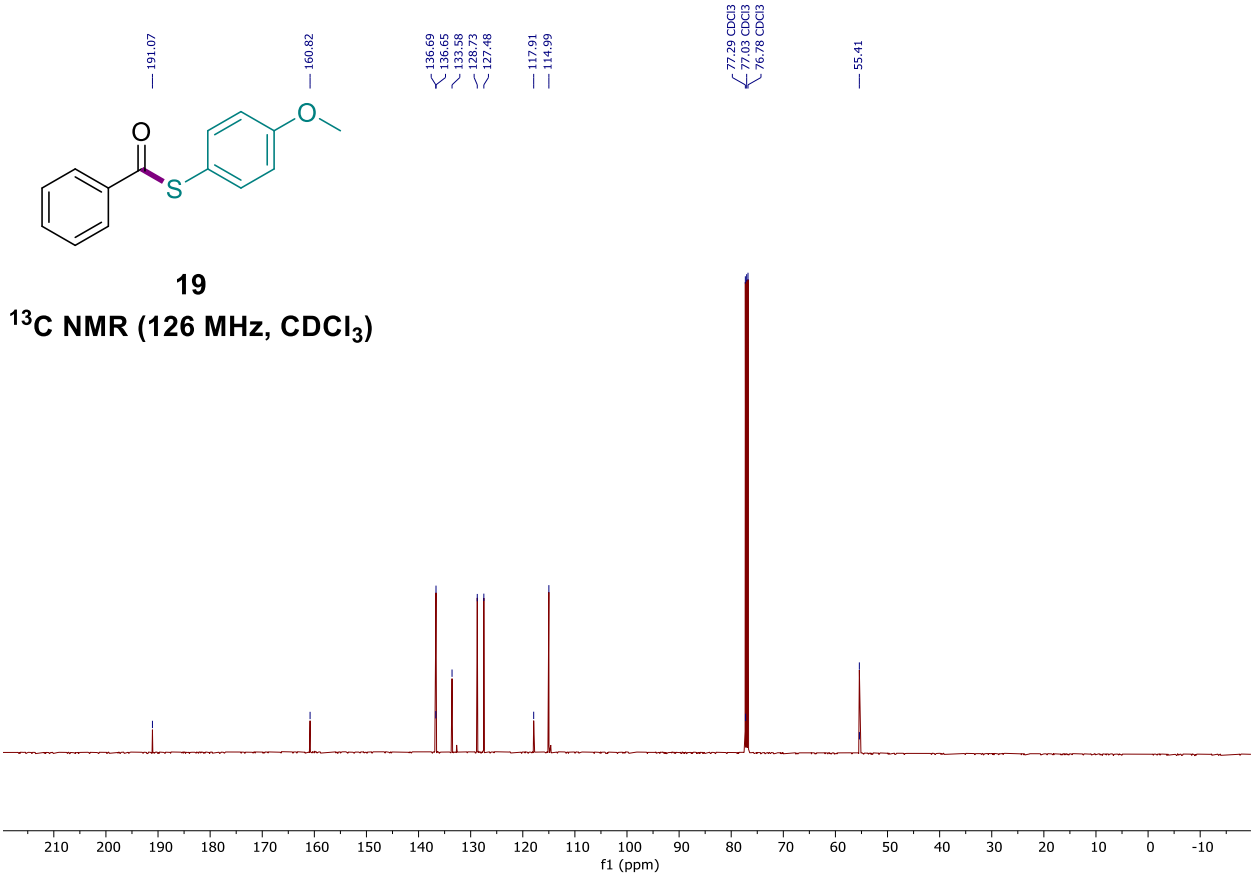
18

^{13}C NMR (126 MHz, $CDCl_3$)



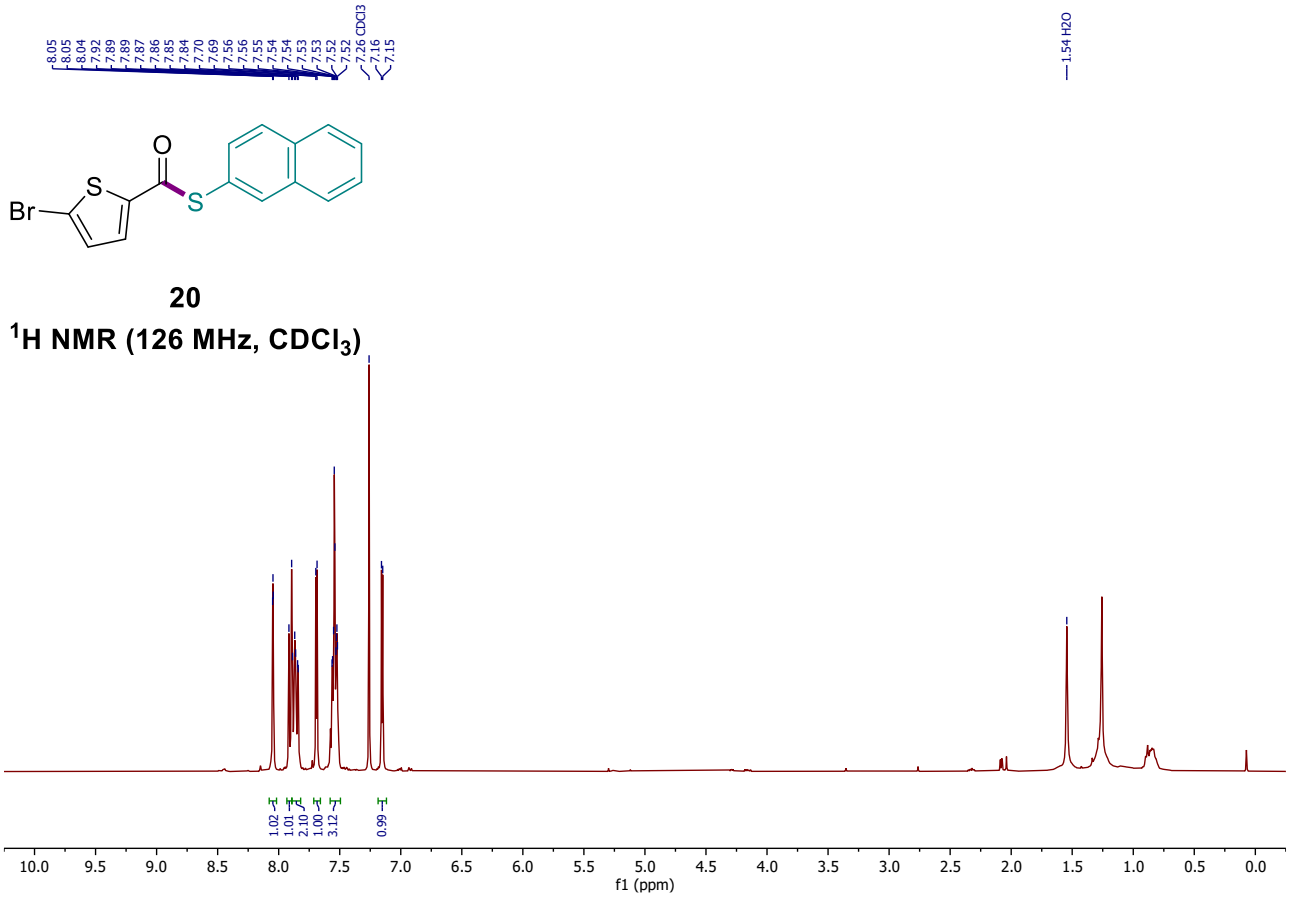
19

^{1}H NMR (400 MHz, $CDCl_3$)



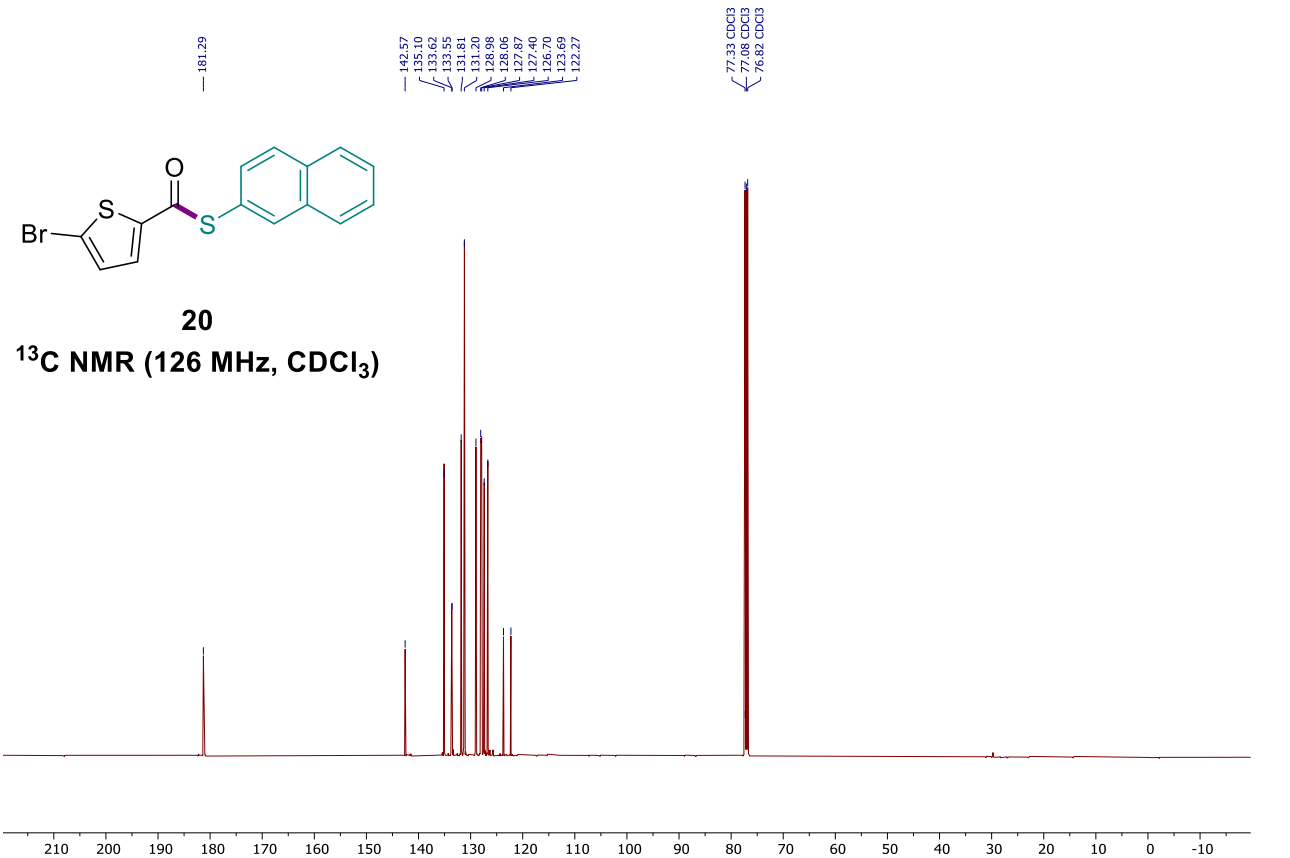
19

^{13}C NMR (126 MHz, $CDCl_3$)



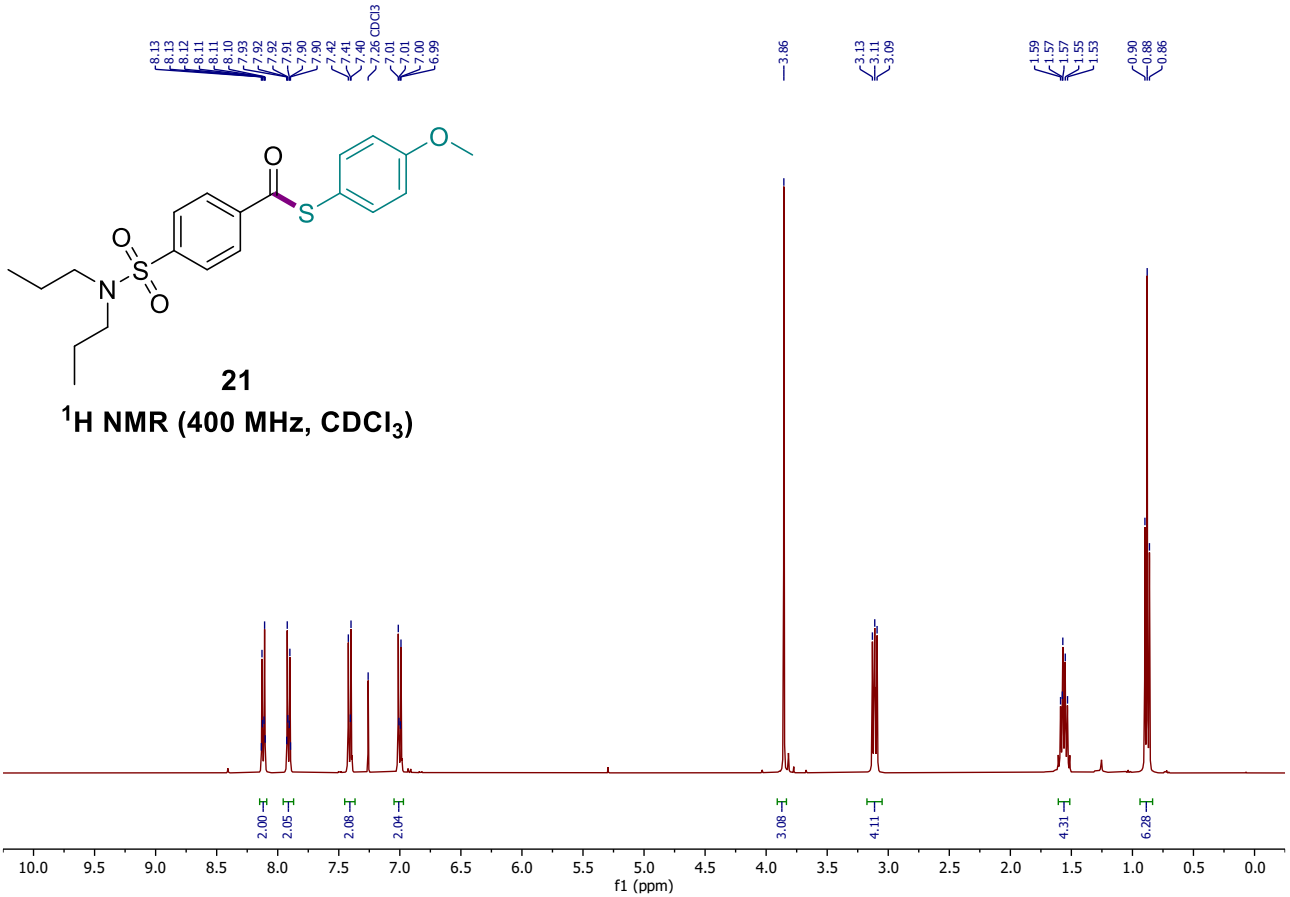
20

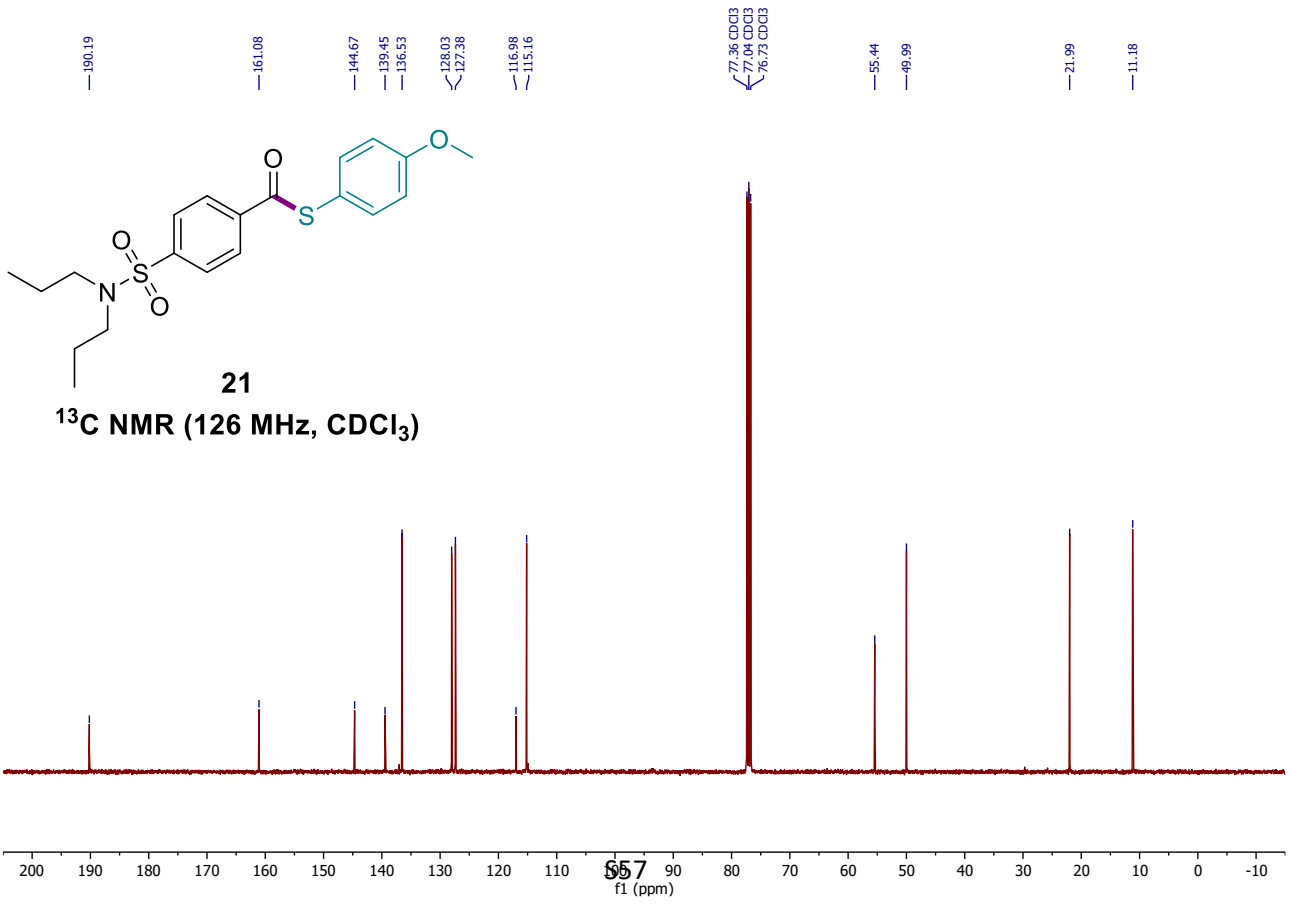
^{1}H NMR (126 MHz, $CDCl_3$)

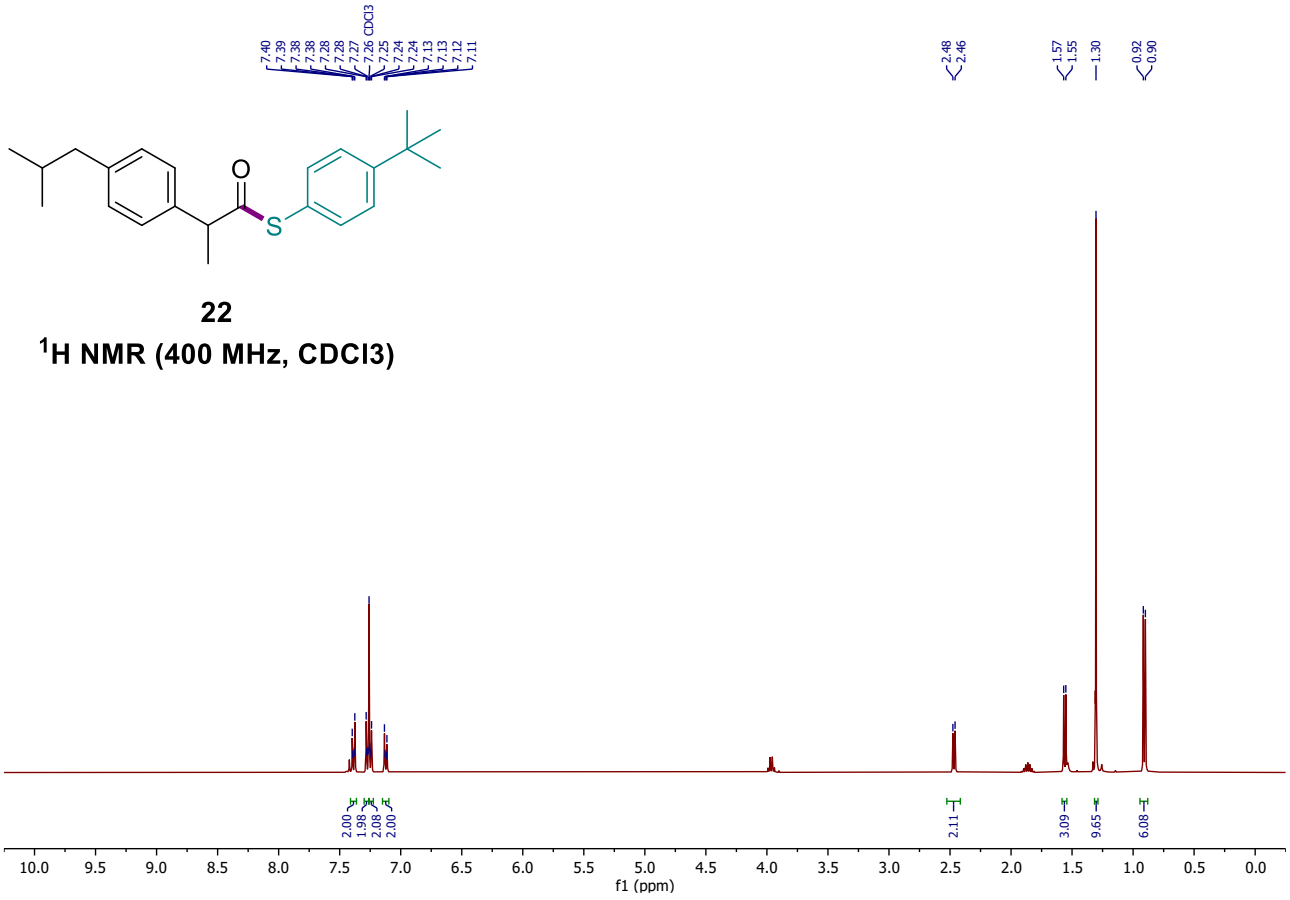


20

^{13}C NMR (126 MHz, $CDCl_3$)

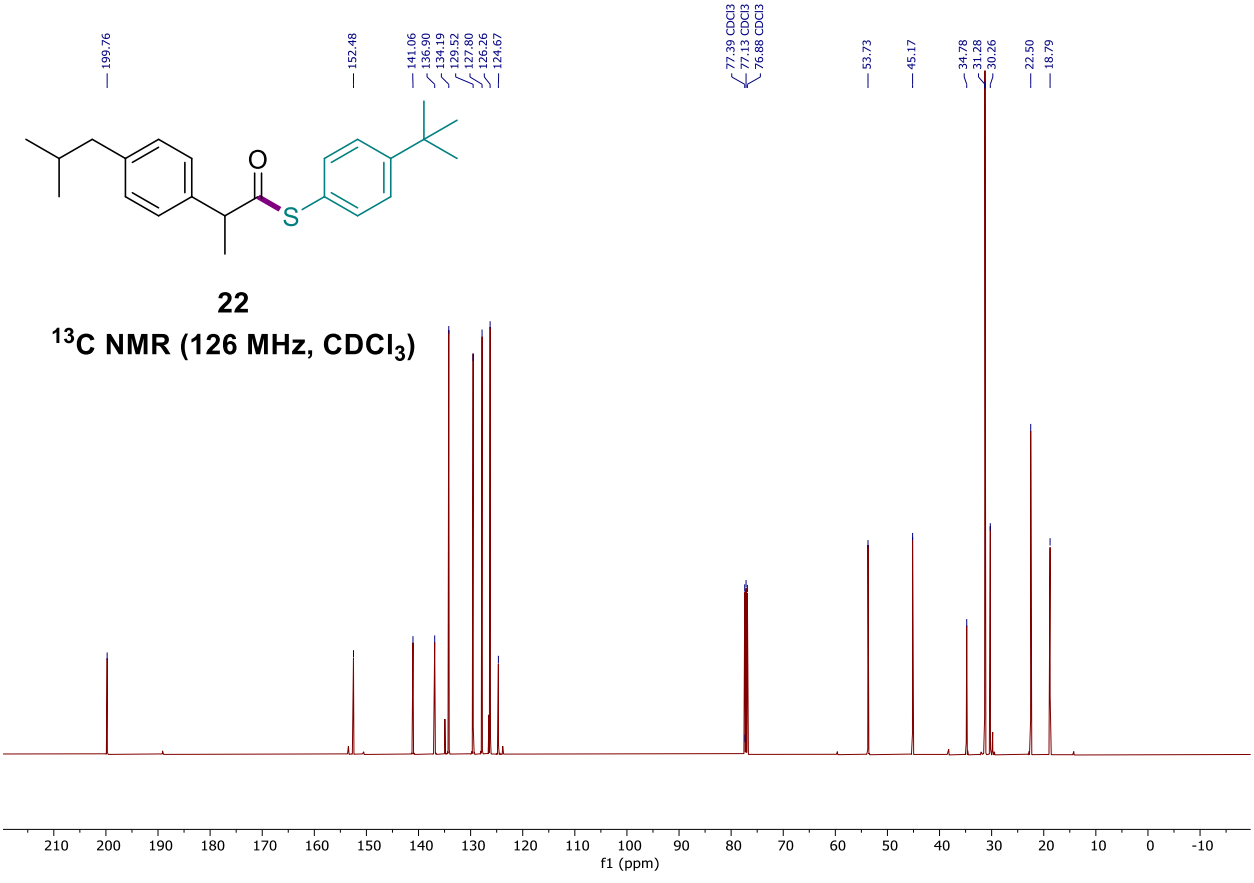

8.13
8.13
8.12
8.11
8.11
8.10
7.93
7.92
7.92
7.91
7.90
7.90
7.42
7.41
7.40
7.26 CDCl3
7.01
7.01
7.00
6.99
3.86
3.13
3.11
3.09
1.59
1.57
1.57
1.55
1.53
0.90
0.88
0.86
O
O
S
O
N
O
S
O
O
21
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.05
2.08
2.04
3.08
4.11
4.31
6.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.19
161.08
144.67
139.45
136.53
128.03
127.38
116.98
115.16
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
55.44
49.99
21.99
11.18
O
O
S
O
N
O
S
O
O
21
^{13}C NMR (126 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



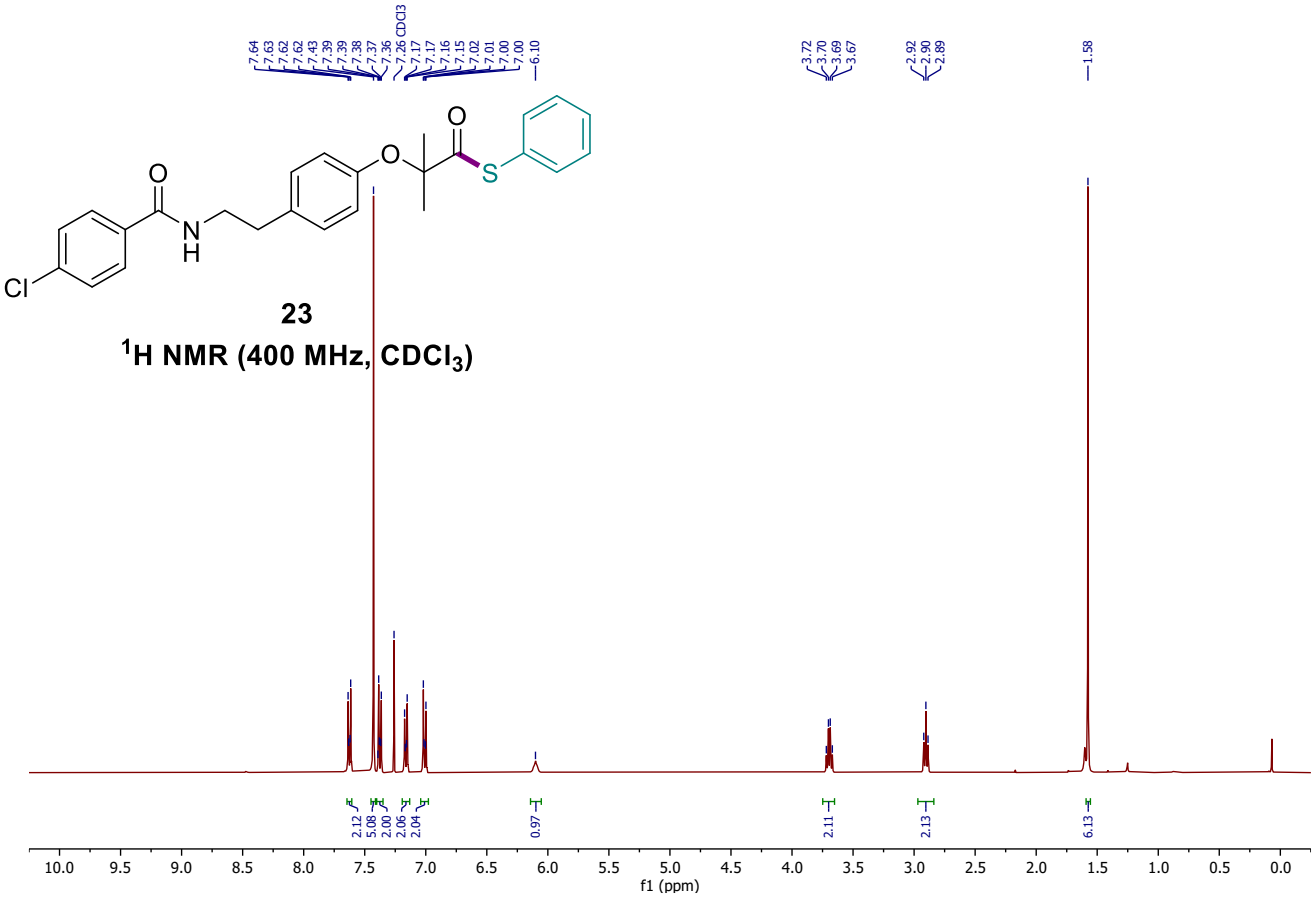
22

^{1}H NMR (400 MHz, CDCl3)



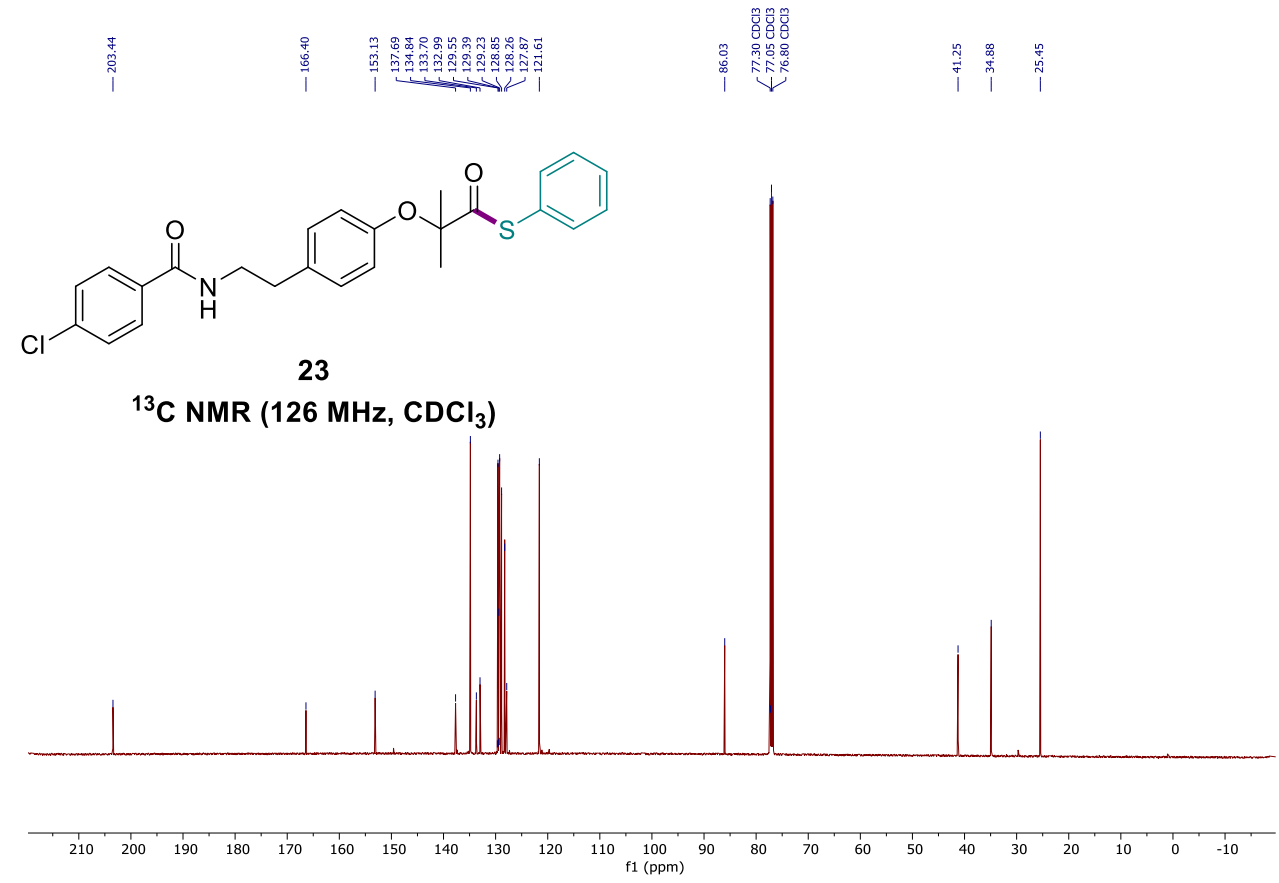
22

^{13}C NMR (126 MHz, $CDCl_3$)



23

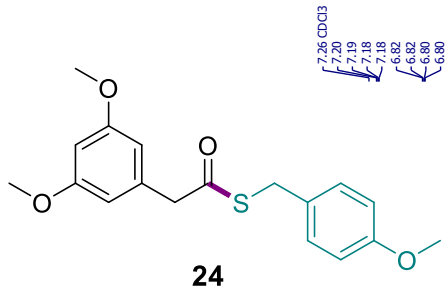
^{1}H NMR (400 MHz, $CDCl_3$)



23

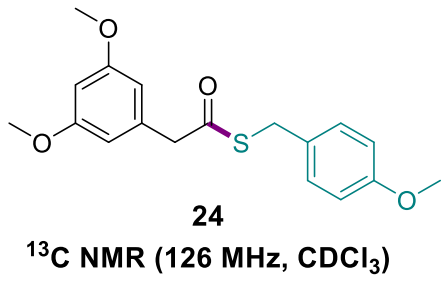
^{13}C NMR (126 MHz, $CDCl_3$)

SS



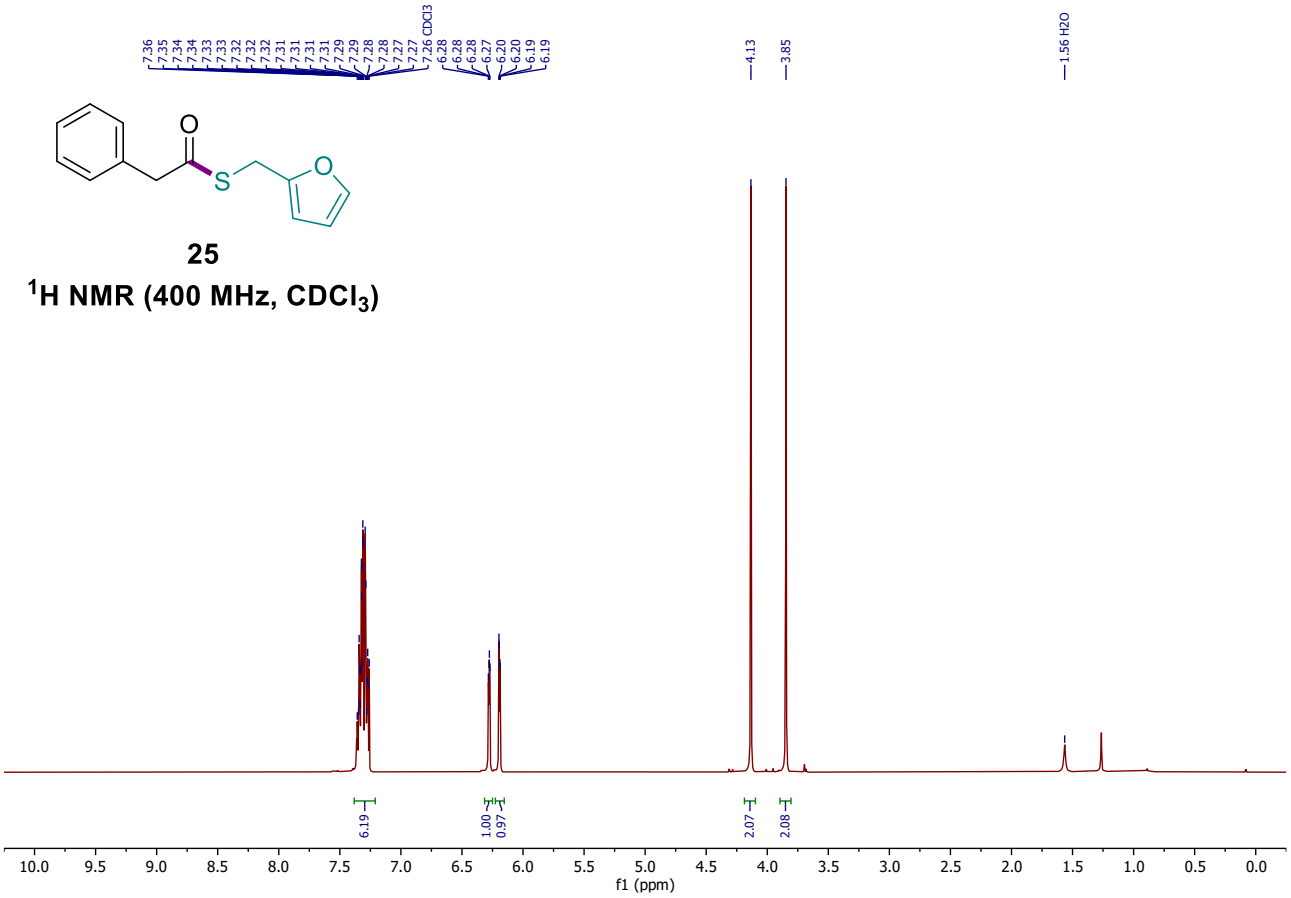
24

^{1}H NMR (400 MHz, $CDCl_3$)



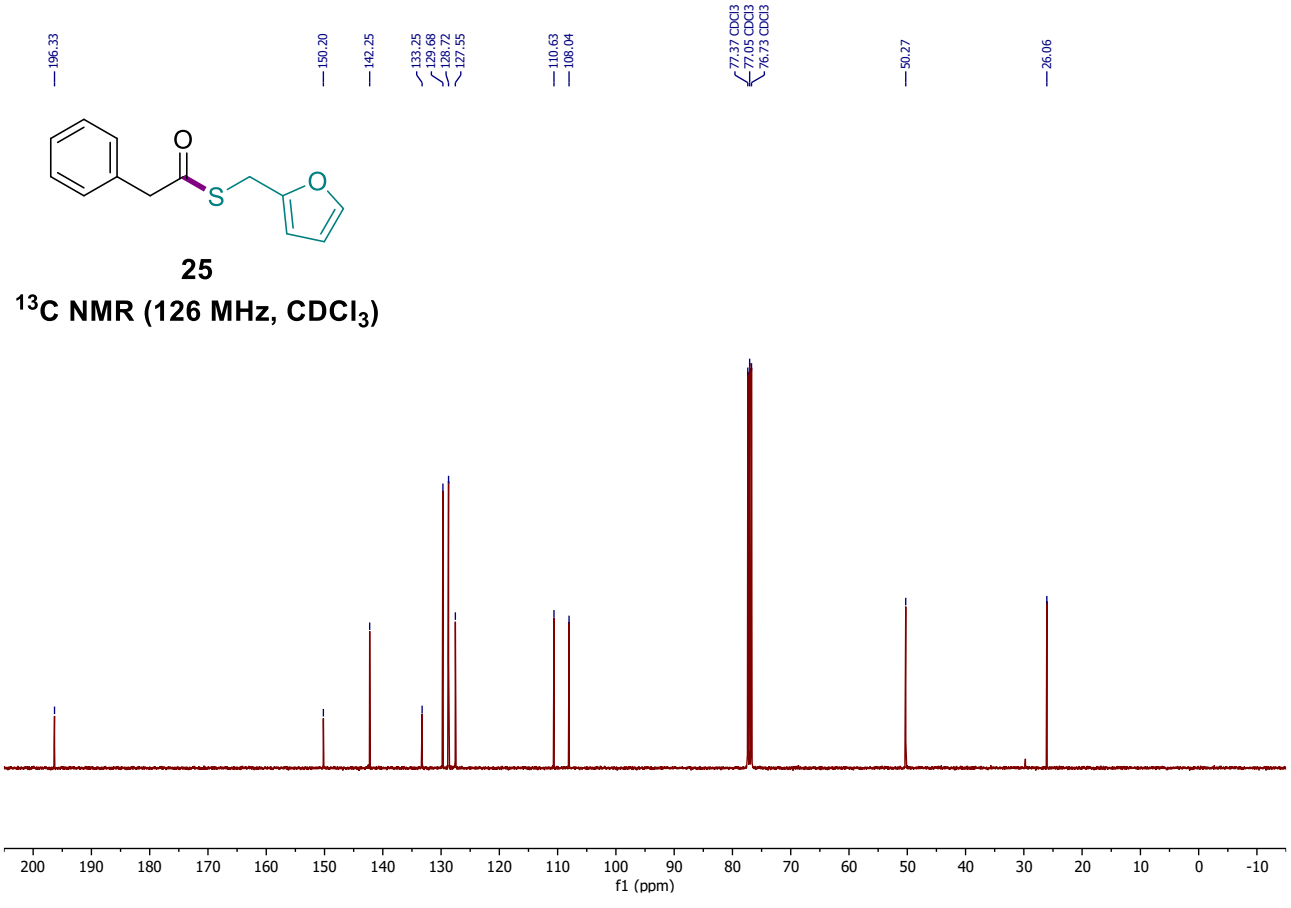
24

^{13}C NMR (126 MHz, $CDCl_3$)



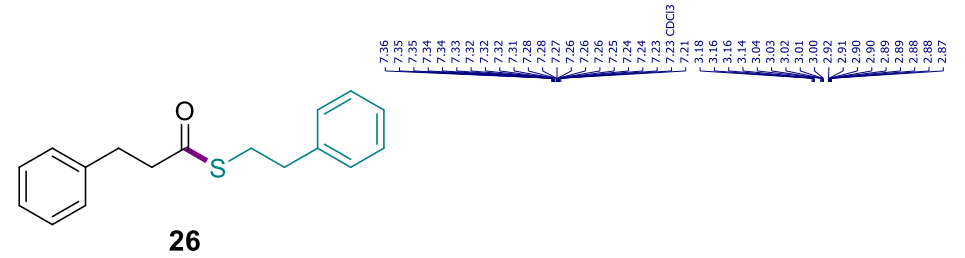
25

^{1}H NMR (400 MHz, $CDCl_3$)



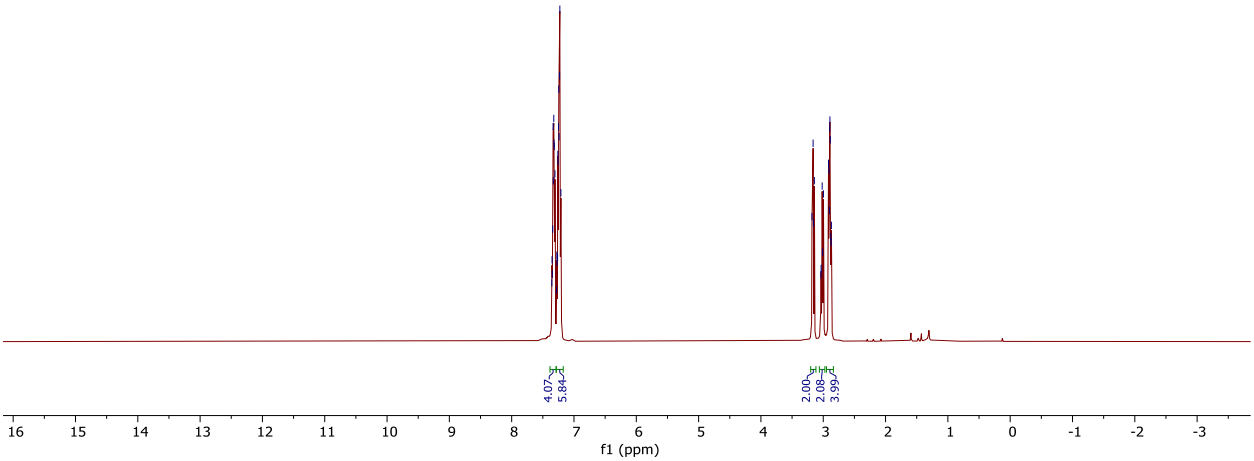
25

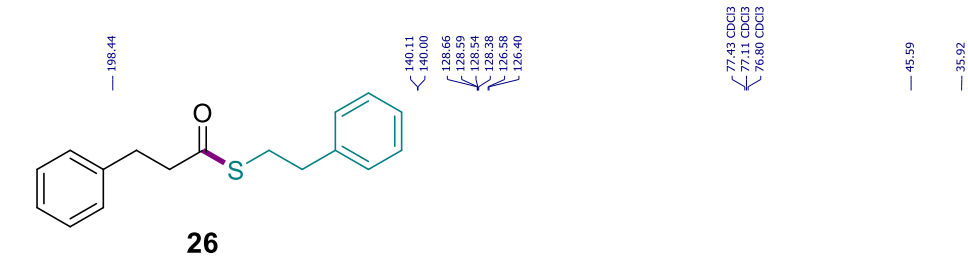
^{13}C NMR (126 MHz, $CDCl_3$)



26

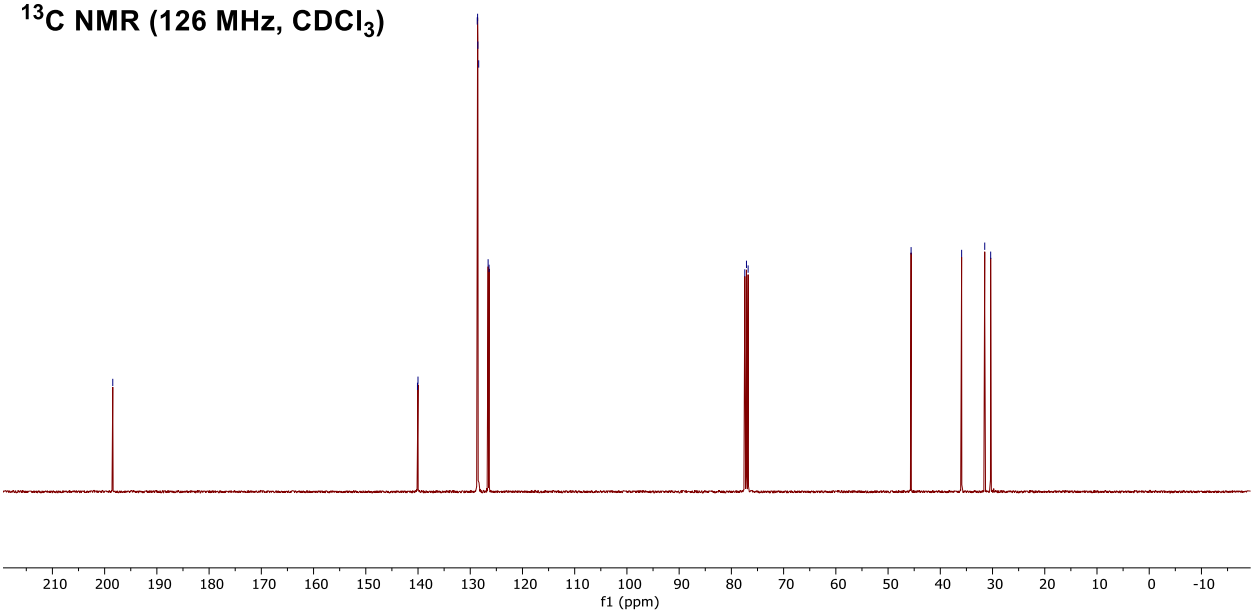
^{1}H NMR (400 MHz, $CDCl_3$)

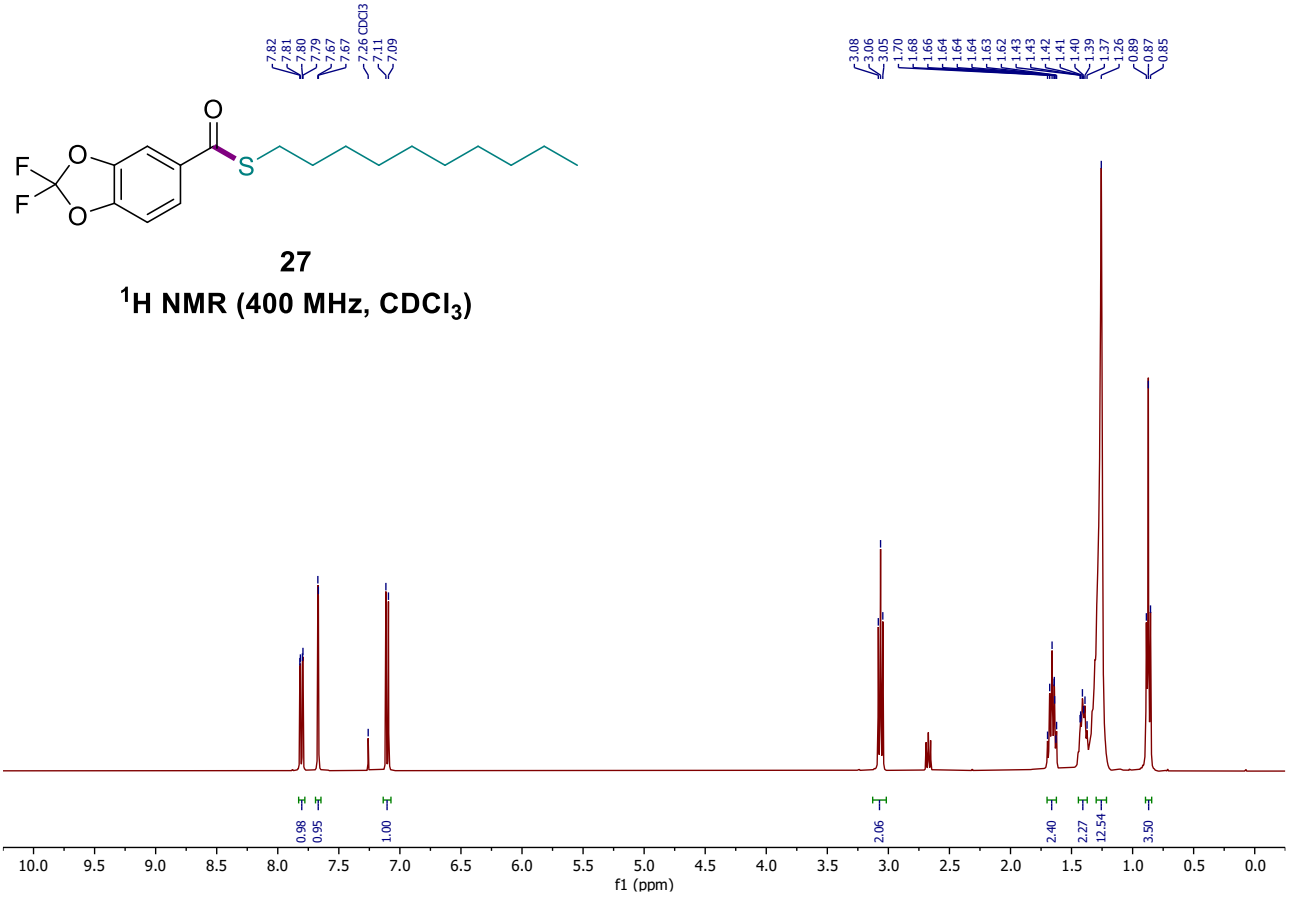




26

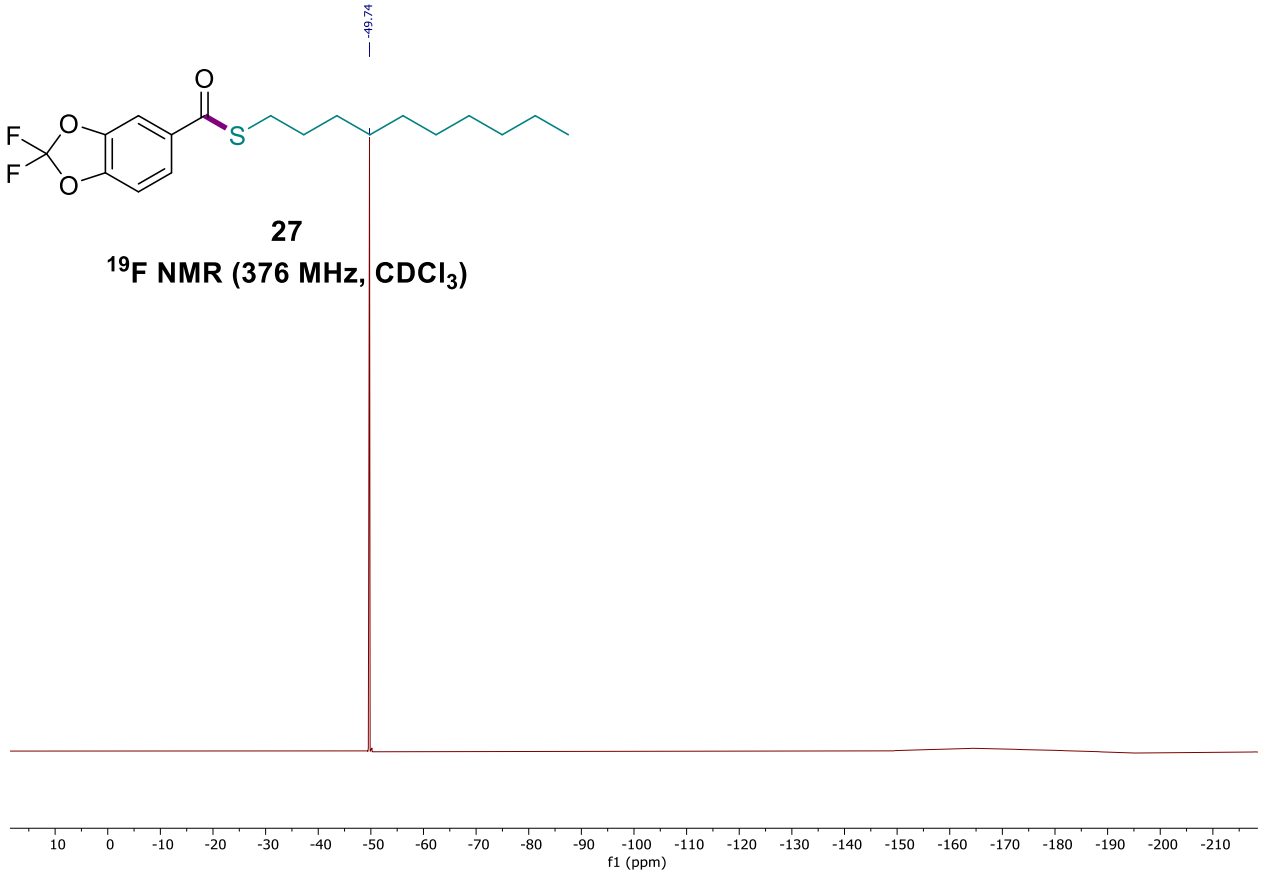
^{13}C NMR (126 MHz, $CDCl_3$)





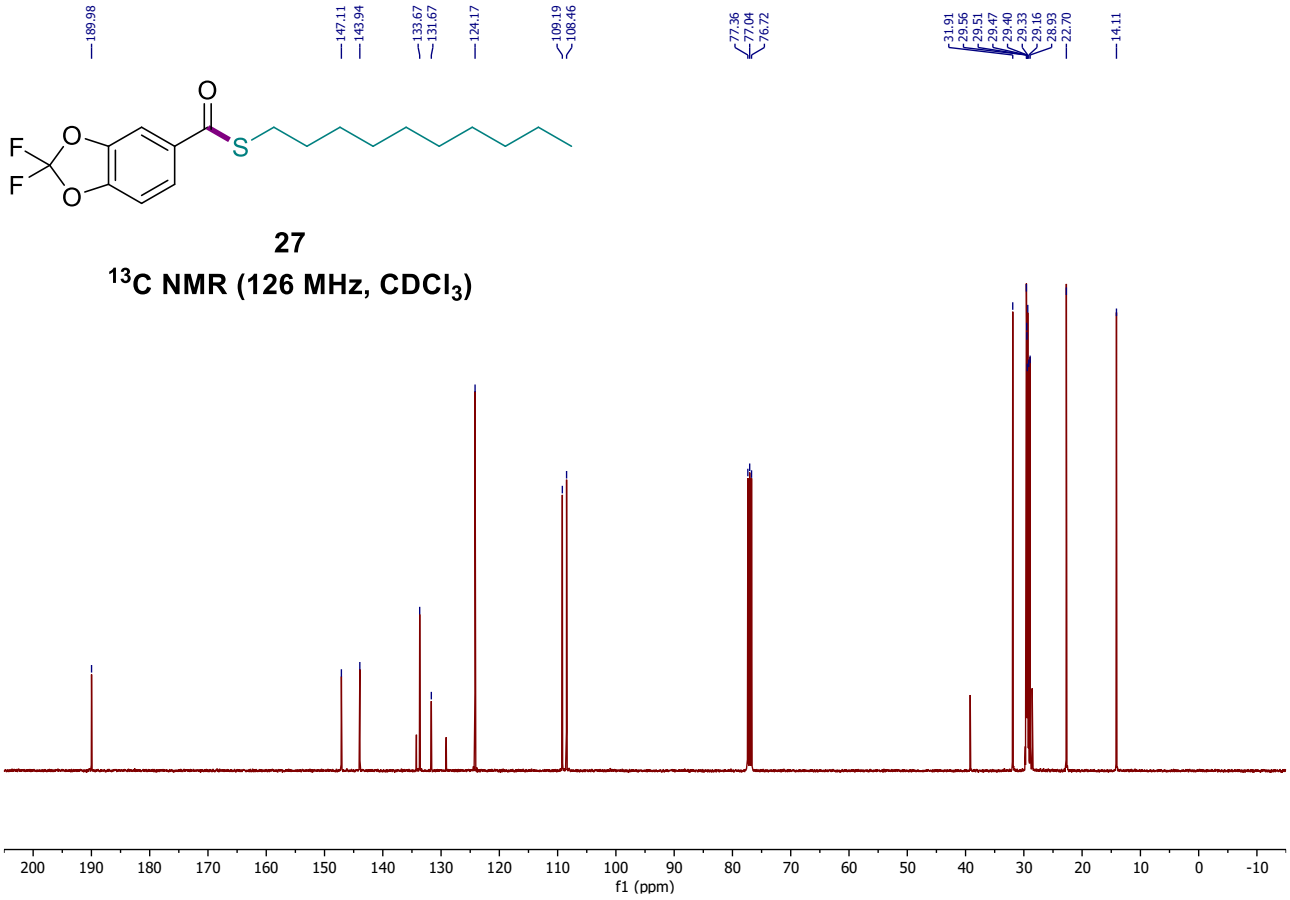
27

^{1}H NMR (400 MHz, $CDCl_3$)



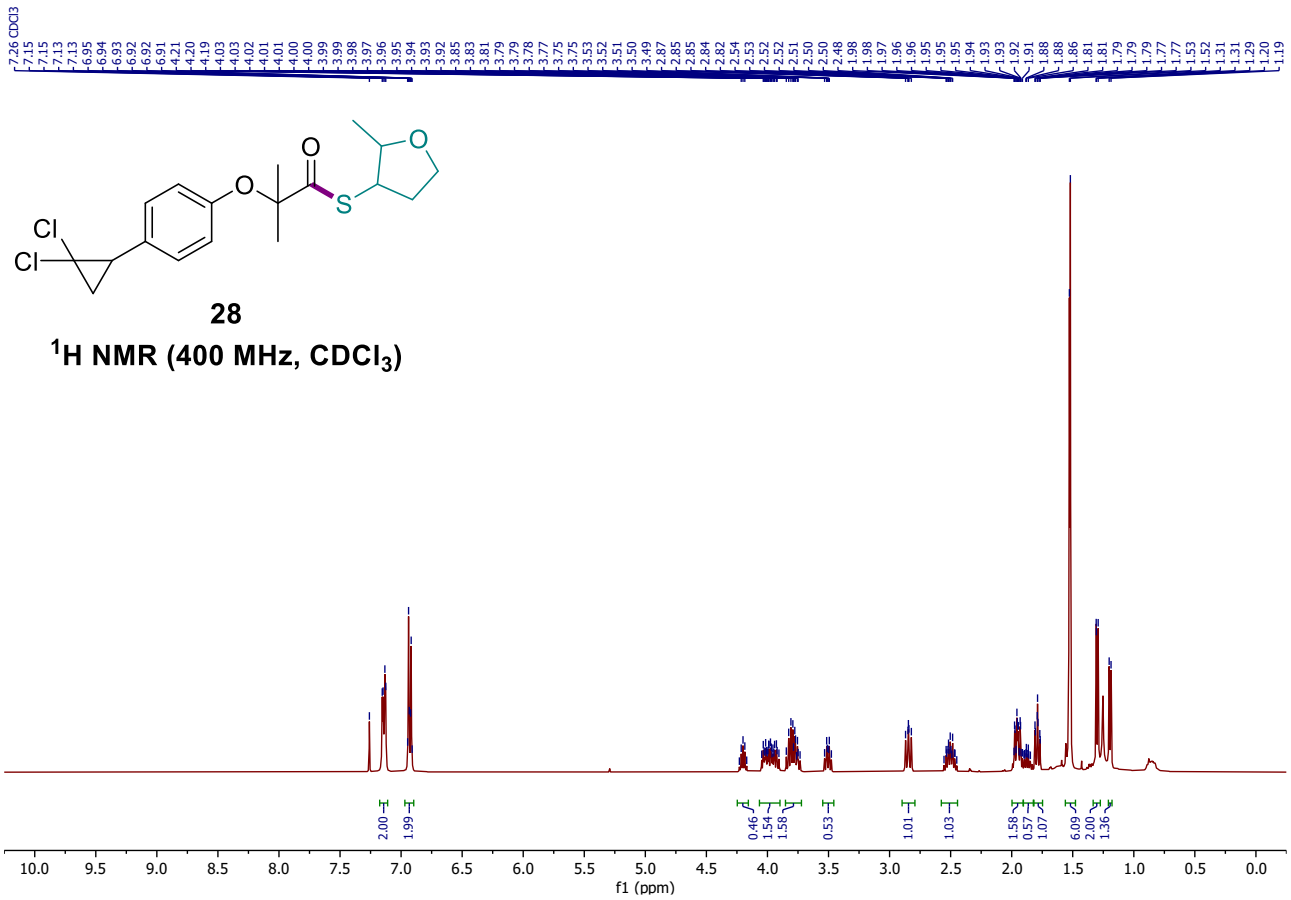
27

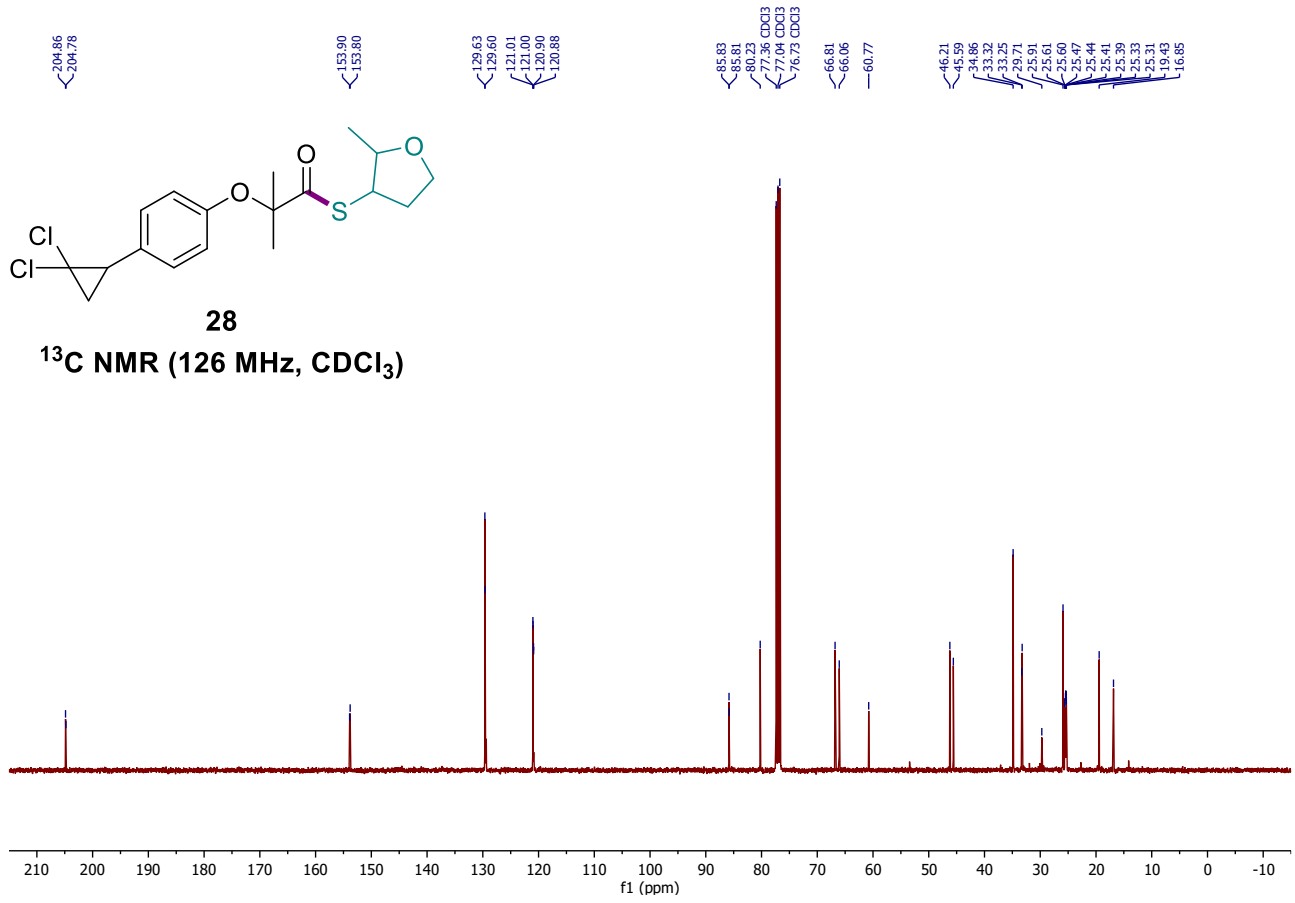
^{19}F NMR (376 MHz, $CDCl_3$)

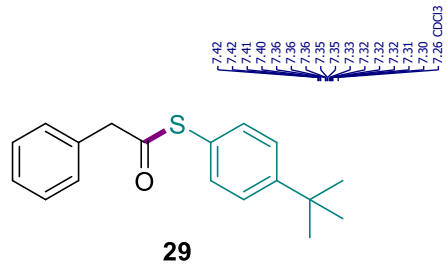


27

^{13}C NMR (126 MHz, $CDCl_3$)

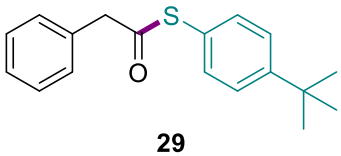

Cl
Cl
O
O
S
O
28
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Cl
Cl
O
O
S
O
28
13C NMR (126 MHz, CDCl3)
f1 (ppm)



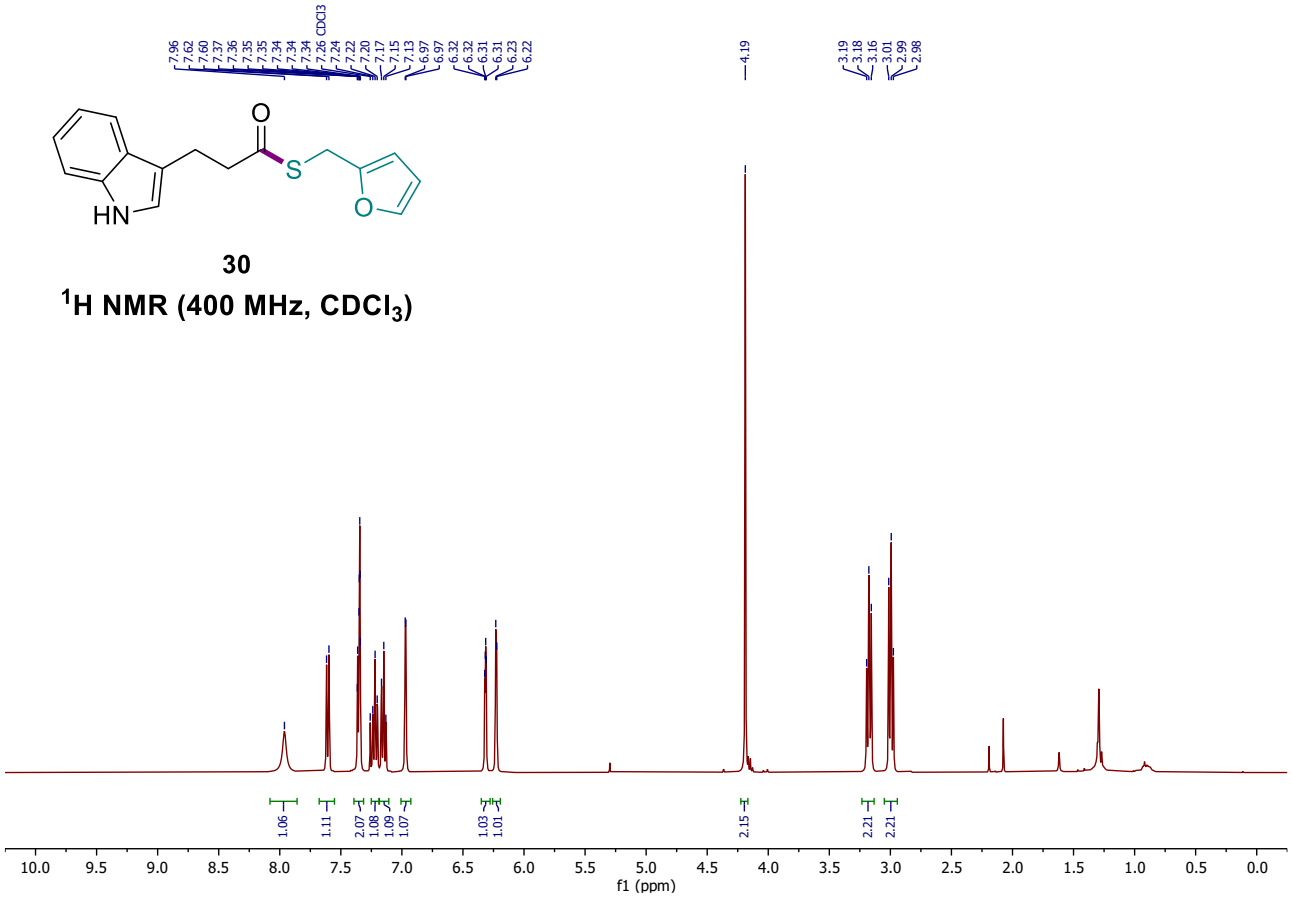
29

^{1}H NMR (400 MHz, $CDCl_3$)



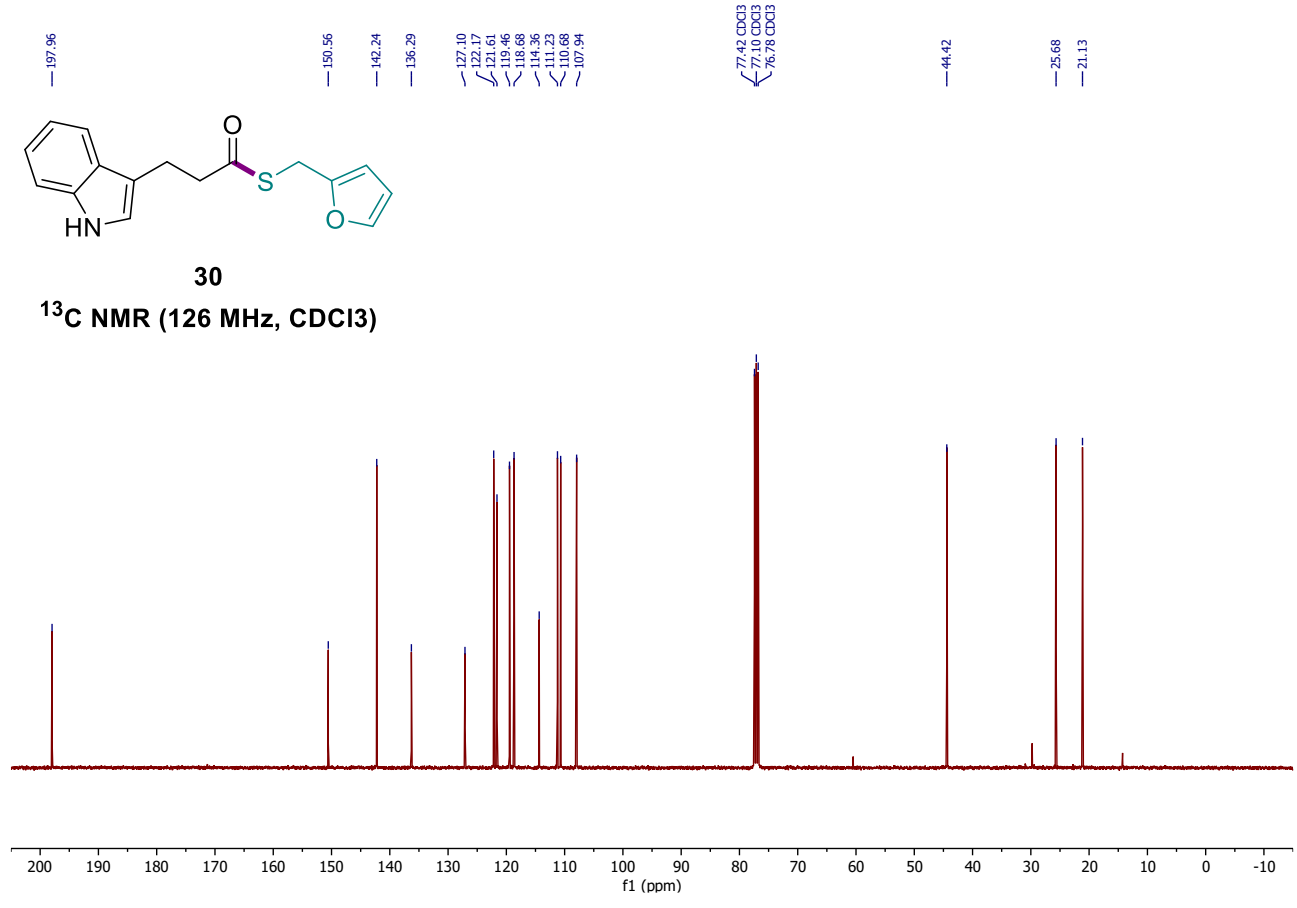
29

^{13}C NMR (126 MHz, CDCl3)



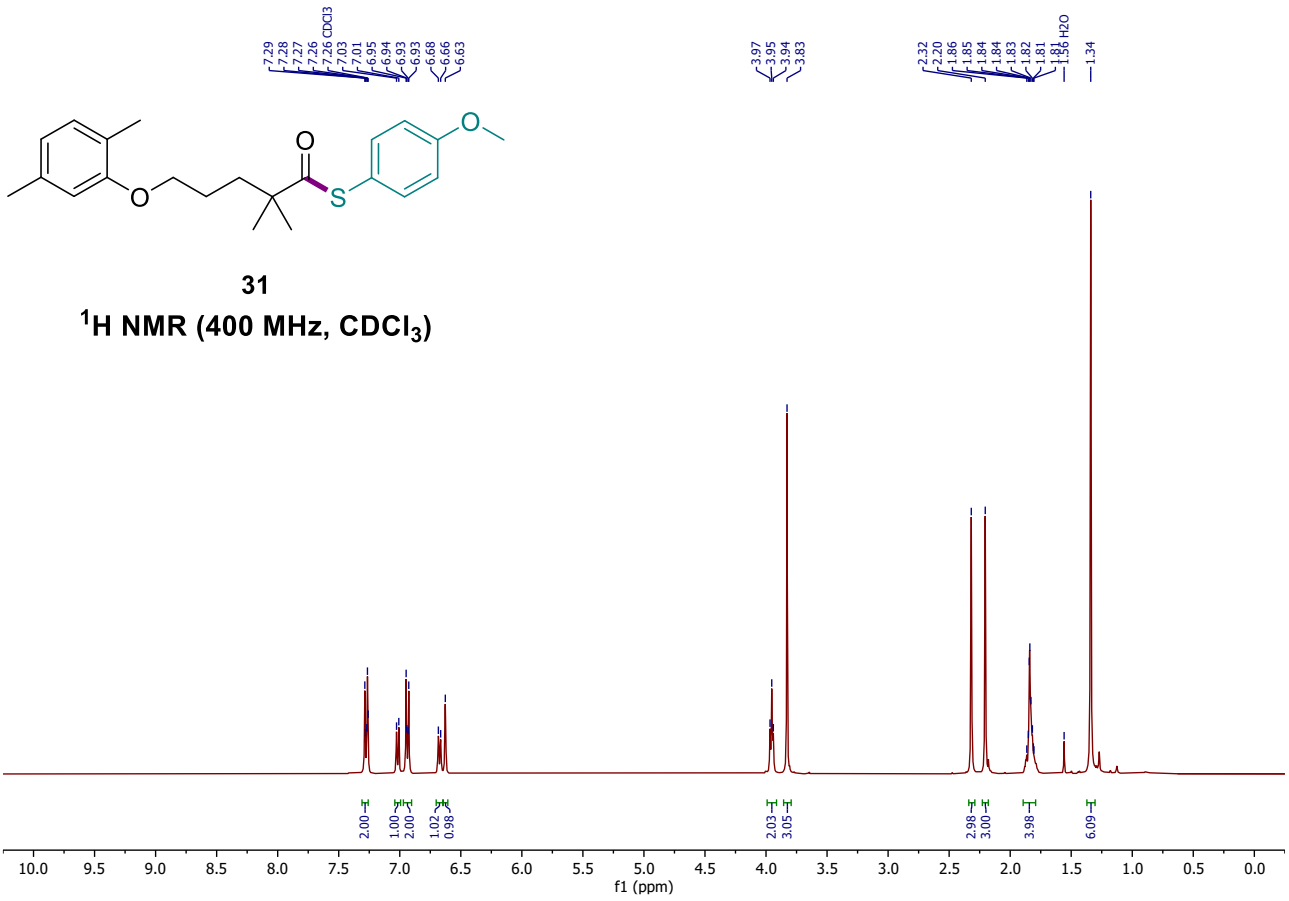
30

^{1}H NMR (400 MHz, $CDCl_3$)



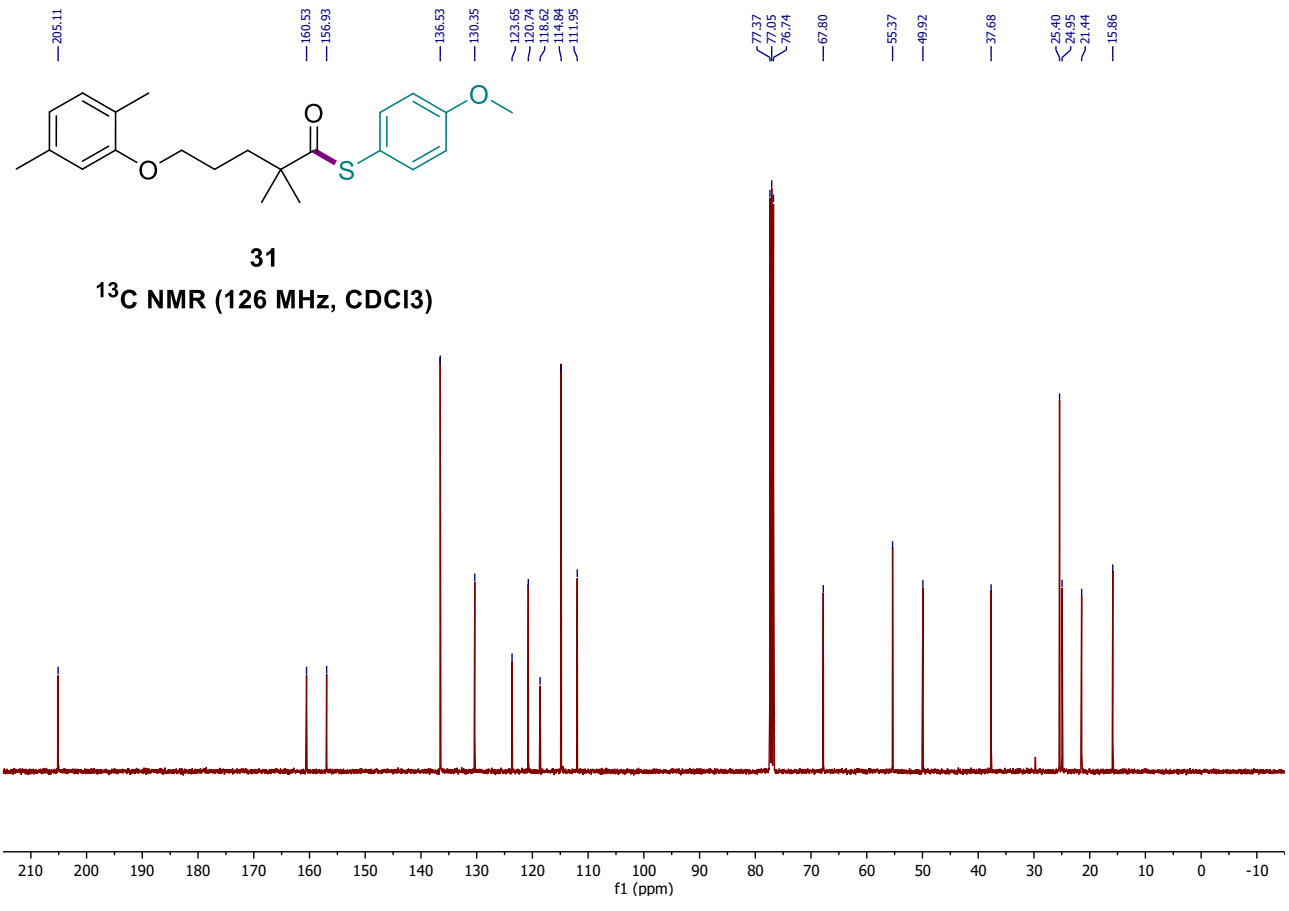
30

^{13}C NMR (126 MHz, CDCl3)



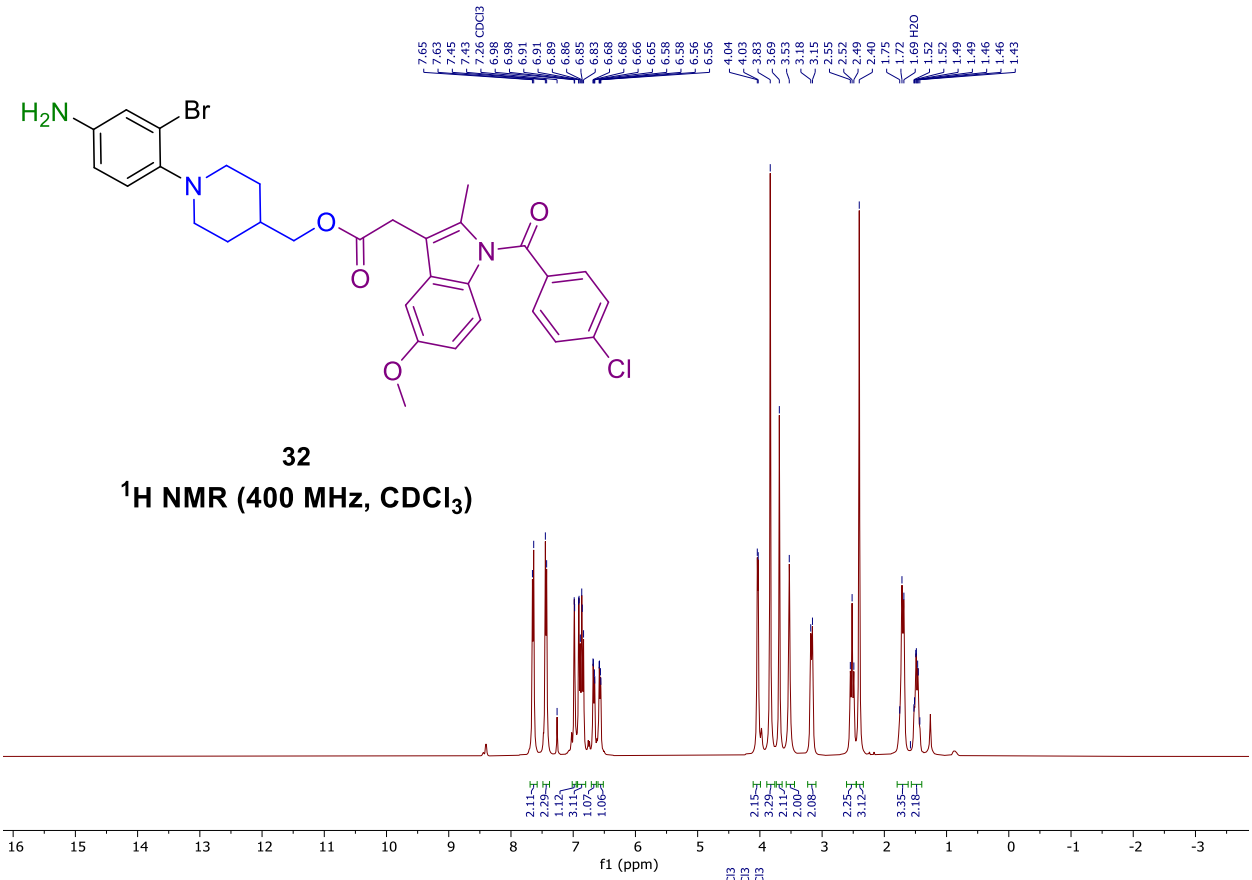
31

^{1}H NMR (400 MHz, $CDCl_3$)



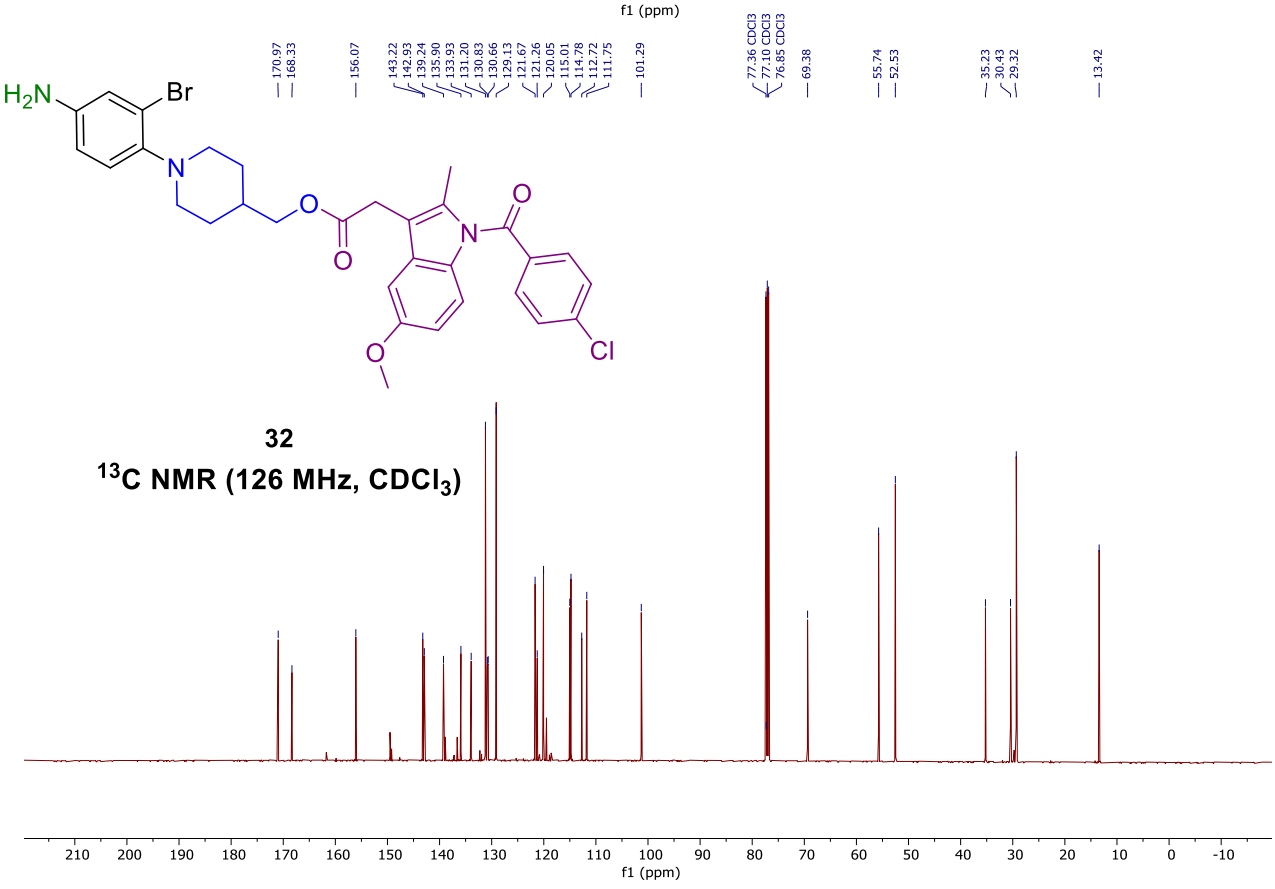
31

^{13}C NMR (126 MHz, CDCl3)



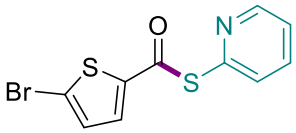
32

^{1}H NMR (400 MHz, $CDCl_3$)



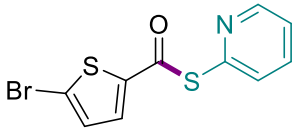
32

^{13}C NMR (126 MHz, $CDCl_3$)



33

^{1}H NMR (400 MHz, $CDCl_3$)



33

^{13}C NMR (126 MHz, $CDCl_3$)

11. References

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2. K. M. Freiberg, R. D. Kavthe, R. M. Thomas, D. M. Fialho, P. Dee and M. Scurria, *Chem. Sci.***,** 2023, **14**, 3462-3469.
3. N. A. Isley, R. T. H. Linstadt, S. M. Kelly, F. Gallou‡, and B. H. Lipshutz, *Org. Lett.,* 2015, **17**, 4734–4737.
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