Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Redox-Active Alkyl Xanthate Esters Enable Practical C-S Cross-Coupling by Nickel Catalysis

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1. General Information

All the NMR spectra were taken with Bruker Avance 400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR). All ^{1}H NMR experiments were measured in relative to the signal of $CDCl_3$ (7.26 ppm), ^{13}C NMR experiments were measured relative to the signal of $CDCl_3$ (77.16 ppm), Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Most of the High-resolution mass spectrometry (HRMS) was performed on either a SCIEX X500R LC-Q-TOF, ESI ion Source. The diastereomeric and regioisomeric ratios were determined by NMR, GC, or GC-MS analysis of unpurified reaction mixtures. Infrared (IR) spectra were recorded on a Bruker ALPHA II FT-IR Spectrometer, max in cm^{-1}.

2. Catalysts, Reagents, and Solvents

Benzoyl chloride was purchased from Bidepharm and was distilled before use.

Benzoic acid was purchased from Energy Chemical and recrystallization before use.

$NiCl_2$(DME) was purchased from Bidepharm and used as received.

$NiBr_2$(diglyme) was purchased from Bidepharm and used as received.

$MgCl_2$ was purchased from Bidepharm and used as received.

KI was purchased from Heowms and used as received.

Zn was purchased from Aladdin and activated by treatment with con. HCl (37%).

6,6'-Dimethyl-2,2'-dipyridyl was purchased from Bidepharm and used as received.

1,10-Phenanthroline was purchased from Adamas and used as received.

DMA (Dimethylacetamide, 99.8%, Extra Dry, with molecular sieve, Water ≤ 50 ppm) was purchased from J&K and used as received.

DMPU (1,3-Dimethyl-Tetrahydropyrimidin-2(1H)-one) was distilled over NaH and stored in a glovebox.

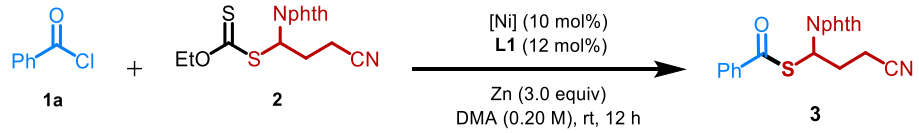
DMI (1,3-Dimethyl-2-imidazolidinone) was purchased from J&K, 99%, stored in a glovebox, and used as received.

DLP (CAS# 105-74-8, Dilauroyl peroxide, 98%) was purchased from Energy Chemical and used as received.

Note: Unless otherwise noted, reagents received from commercial suppliers were used as received. All reactions were performed under an atmosphere of dry nitrogen.

3. Screening of Reaction Conditions (from Benzoyl Chloride 1a)

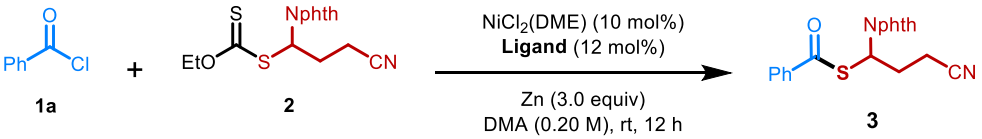
Table S-1. Optimization of nickel catalysts (from Benzoyl chloride 1a).[a]

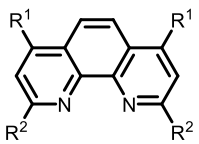


entry	[Ni]	yield of **3** (%)[b]
1	-	-
2	$NiCl_2$	40
3	$Ni(COD)_2$	30
4	$Ni(OTf)_2$	2
5	$NiCl_2(PPh_3)_2$	27
6	$NiCl_2$(dppe)	10
7	**$NiCl_2$(DME)**	**53**
8	$NiBr_2$(diglyme)	47
9	$NiBr_2$(DME)	41
10	$Ni(acac)_2$	35
11	$Ni(OAc)_2$	34

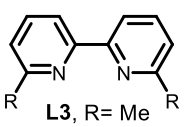
[a] Reaction conditions (unless otherwise stated): **1a** (0.12 mmol, 1.2 equiv), **2** (0.1 mmol, 1.0 equiv), [Ni] (10 mol%), **L1** (12 mol%), Zn (0.30 mmol, 3.0 equiv), DMA (0.50 mL), rt, 12 h; [b] Yields were determined by GC analysis with a calibrated internal standard.

Table S-2. Optimization of ligands (from Benzoyl chloride 1a).[a]

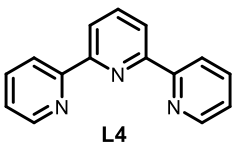




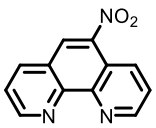
L1, $R^1 = R^2 = H$
L2, R^1 = Ph, R^2 = Me
L6, R^1 = H, R^2 = Me



L3, R= Me
L5, R= H



L4

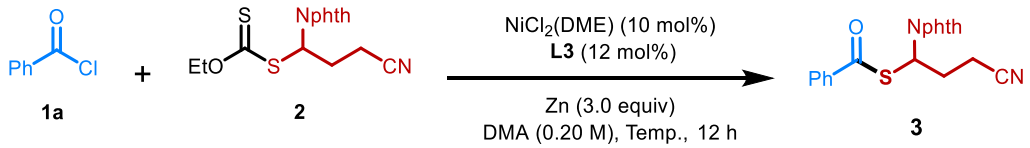


L7

entry	Ligand	yield of **3** (%)[b]
1	-	-
2	**L1**	53
3	**L2**	54
4	**L3**	**57**
5	**L4**	41
6	**L5**	26
7	**L6**	51
8	**L7**	37

[a] Reaction conditions (unless otherwise stated): **1a** (0.12 mmol, 1.2 equiv), **2** (0.10 mmol, 1.0 equiv), $NiCl_2$(DME) (10 mol%), Ligand (12 mol%), Zn (0.30 mmol, 3.0 equiv), DMA (0.50 mL), rt, 12 h; [b] Yields were determined by GC analysis with a calibrated internal standard.

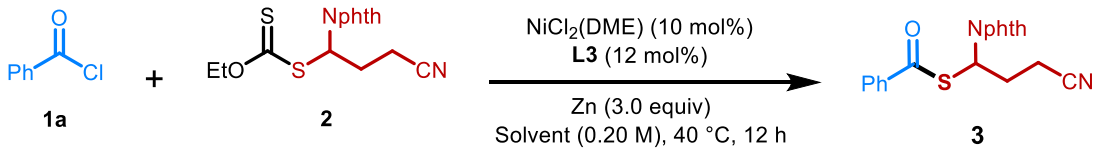
Table S-3. Optimization of temperature (from Benzoyl chloride 1a).[a]



entry	TEMP./ °C	yield of **3** (%)[b]
1	rt	56
2	**40**	**67**
3	50	62

[a] Reaction conditions (unless otherwise stated): **1a** (0.12 mmol, 1.2 equiv), **2** (0.10 mmol, 1.0 equiv), $NiCl_2$(DME) (10 mol%), **L3** (12 mol%), Zn (0.30 mmol, 3.0 equiv), DMA (0.50 mL), Temp., 12 h; [b] Yields were determined by GC analysis with a calibrated internal standard.

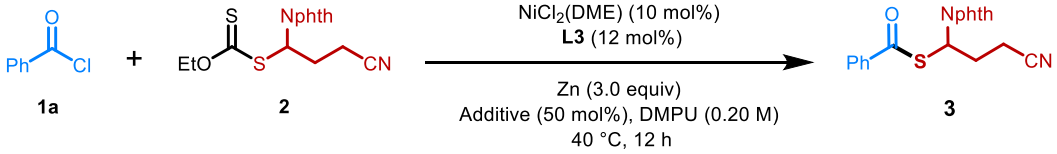
Table S-4. Optimization of solvents (from acyl chloride 1a).[a]



entry	Solvent	yield of **3** (%)[b]
1	DMA	67
2	DMF	26
3	**DMPU**	**79**
4	NMP	59
5	THF	-

[a] Reaction conditions (unless otherwise stated): **1a** (0.12 mmol, 1.2 equiv), **2** (0.10 mmol, 1.0 equiv), $NiCl_2$(DME) (10 mol%), **L3** (12 mol%), Zn (0.30 mmol, 3.0 equiv), Solvent (0.50 mL), 40 °C, 12 h; [b] Yields were determined by GC analysis with a calibrated internal standard.

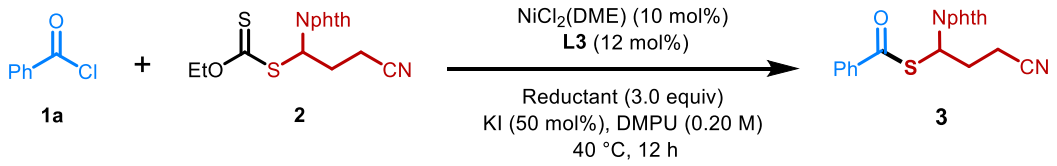
Table S-5. Optimization of additives (from Benzoyl chloride 1a).[a]



entry	additive	yield of **3** (%)[b]
1	-	79
2	$MgCl_2$	12
3	$MgBr_2$	32
4	$FeBr_2$	63
5	NaBr	58
6	NaI	63
7	**KI**	**84**
8	DMBA	40

[a] Reaction conditions (unless otherwise stated): **1a** (0.12 mmol, 1.2 equiv), **2** (0.1 mmol, 1.0 equiv), $NiCl_2$(DME) (10 mol%), **L3** (12 mol%), Zn (0.3 mmol, 3 equiv), DMPU (0.50 mL), Additive (50 mol%), 40 °C, 12 h; [b] Yields were determined by GC analysis with a calibrated internal standard.

Table S-6. Optimization of reductants (from Benzoyl chloride 1a).[a]

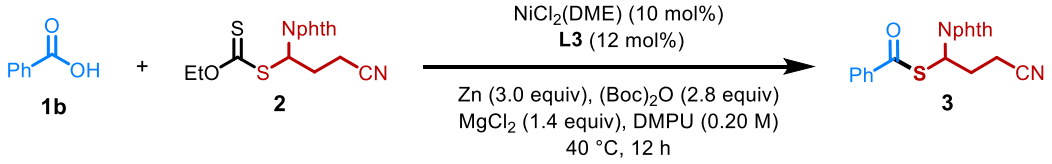


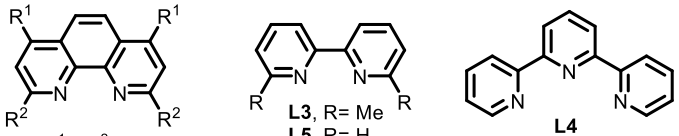
entry	reductant	yield of **3** (%)[b]
1	-	-
2	**Zn**	**84**
3	Mn	-

[a] Reaction conditions (unless otherwise stated): **1a** (0.12 mmol, 1.2 equiv), **2** (0.1 mmol, 1.0 equiv), $NiCl_2$(DME) (10 mol%), **L3** (12 mol%), reductant (0.3 mmol, 3.0 equiv), DMPU (0.50 mL), KI (50 mol%), 40 °C, 12 h. [b] Yields were determined by GC analysis with a calibrated internal standard.

4. Screening of Reaction Conditions (from Benzoic Acid 1b)

Table S-7. Optimization reaction conditions (from Benzoic acid 1b).[a]





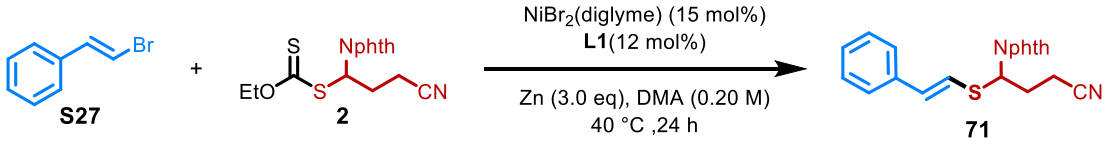
entry	variation from standard conditions	yield of **3** (%)[b]
1	-	**75**
2	$NiCl_2$ instead of $NiCl_2$(DME)	38
3	$Ni(COD)_2$ instead of $NiCl_2$(DME)	64
4	$NiBr_2$(DME) instead of $NiCl_2$(DME)	70
5	$NiCl_2(PPh_3)_2$ instead of $NiCl_2$(DME)	71
6	**L1** instead of **L3**	69
7	**L2** instead of **L3**	71

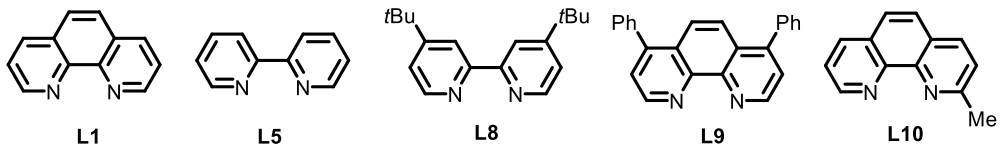
8	**L4** instead of **L3**	73
9	**L5** instead of **L3**	69
10	**L6** instead of **L3**	68
11	rt instead of 40℃	68
12	50℃ instead of 40℃	60
13	DMF instead of DMPU	70
14	DMA instead of DMPU	39
15	NMP instead of DMPU	42
16	DMI instead of DMPU	3
17	KI instead of $MgCl_2$	69
18	$FeCl_2$ instead of $MgCl_2$	2
19	TBAI instead of $MgCl_2$	22
20	Mn instead of Zn	-
21	No Zn or No Ligand	-

[a] Reaction conditions (unless otherwise stated): **1b** (0.12 mmol, 1.4 equiv), **2** (0.1 mmol, 1.0 equiv), $(Boc)_2O$ (2.8 equiv), $NiCl_2$(DME) (10 mol%), **L3** (12 mol%), Zn (0.3 mmol, 3.0 equiv), DMPU (0.50 mL), $MgCl_2$ (1.4 equiv), 40 °C, 12 h. [b] Yields were determined by GC analysis with a calibrated internal standard.

5. Screening of Reaction Conditions of Vinyl Sulfide

Table S-8. Optimization of the synthesis of 30.[a]





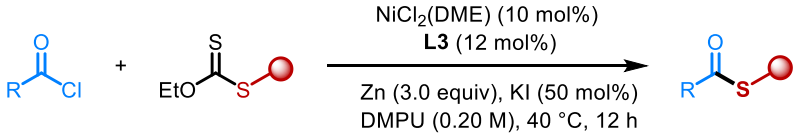
entry	variation from standard conditions	yield of **71** (%)[b]
1	-	**73**
2	$Ni(OTf)_2$ instead of $NiBr_2$(diglyme)	5

3	$Ni(COD)_2$ instead of $NiBr_2$(diglyme)	38
4	$NiBr_2$ instead of $NiBr_2$(diglyme)	47
5	$NiCl_2$(DME) instead of $NiBr_2$(diglyme)	62
6	**L5** instead of **L1**	52
7	**L8** instead of **L1**	47
8	**L9** instead of **L1**	54
9	**L10** instead of **L1**	52
10	DMF instead of DMA	69
11	DMPU instead of DMA	21
12	NMP instead of DMA	54
13	THF instead of DMA	-
14	KI	10
15	$MgCl_2$	54
16	TBAI	13
17	No Ligand or No Zn	-

[a] Reaction conditions (unless otherwise stated): **S27** (0.12 mmol, 1.2 equiv), **2** (0.1 mmol, 1.0 equiv), $NiBr_2$(diglyme) (15 mol%), **L1** (12 mol%), Zn (0.3 mmol, 3.0 equiv), DMA (0.50 mL), 40 °C, 24 h; [b] Yields were determined by GC analysis with a calibrated internal standard.

6. Condition for the Synthesis of Thioesters

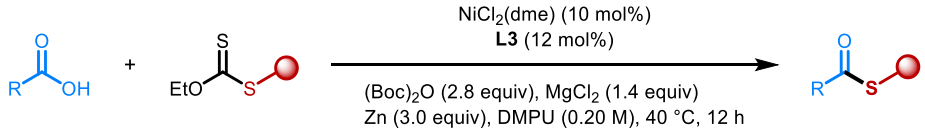
■ Condition for the synthesis of thioester from acid chloride (Condition A)



To an oven-dried 100 x 16 mm screw-capped vial with a magnetic stir bar was added alkyl xanthate esters (0.30 mmol, 1.0 equiv). Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Next, ligand **L3** (6.6 mg, 0.036 mmol, 12 mol%), $NiCl_2$(DME) (6.6 mg, 0.030 mmol, 10 mol%), KI (24.9 mg, 0.15 mmol, 50 mol%), Zn (58.9 mg, 0.90 mmol, 3.0 equiv) and DMPU (1.5 mL, 0.20 M) were added to the vial sequentially. The vial was removed from the glove box and added acid chloride (0.36 mmol, 1.2 equiv) through a microsyringe. The reaction was stirred at 40 °C for 12 h, then quenched upon the addition of H_2O (15 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4,

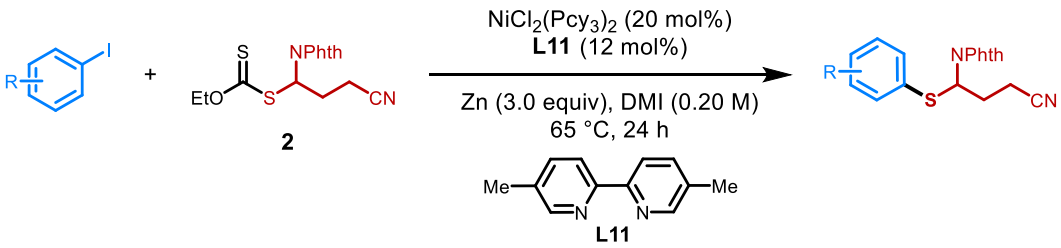
gravity filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel.

■ Condition for the synthesis of thioesters from carboxylic acids (Condition B)



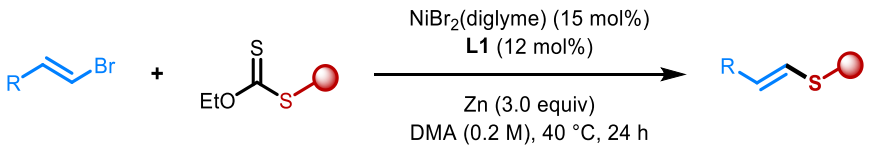
An oven-dried 100 x 16 mm screw-capped vial was charged with a magnetic stir bar. Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Next, ligand **L3** (6.6 mg, 0.036 mmol, 12 mol%), $NiCl_2$(DME) (6.6 mg, 0.030 mmol, 10 mol%), DMPU (1.5 mL, 0.20 M) were added to the vial sequentially. Alkyl xanthate ester (0.30 mmol, 1.0 equiv) was added after the reaction was stirred for 10 minutes. After further 10 minutes, carboxylic acid (0.42 mmol, 1.4 equiv), $(Boc)_2O$ (0.20 ml, 0.84 mmol, 2.8 equiv), $MgCl_2$ (39.99 mg, 0.42 mmol, 1.4 equiv), Zn (58.9 mg, 0.90 mmol, 3.0 equiv) were added. The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at 40 ℃ for 12 h, then quenched upon the addition of H_2O (15 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel.

7. Condition for the Synthesis of Aryl Sulfide (Condition C)



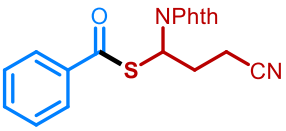
An oven-dried 100 x 16 mm screw-capped vial with a magnetic stir bar was transferred to an N_2-filled glovebox. First, **L11** (6.6 mg, 0.036 mmol, 12 mol%), $NiCl_2(PCy_3)_2$ (41.4 mg, 0.060 mmol, 20 mol%), Zn (117.9 mg, 0.90 mmol, 3.0 equiv), and DMI (1.50 mL, 0.20 M) were added to the vial sequentially. Next, Aryl halide (0.48 mmol, 1.6 equiv) and xanthate ester (0.30 mmol, 1.0 equiv) were added. The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at 65 ℃ for 24 h, then quenched upon the addition of H_2O (15 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL), and the combined organic layers were extracted with H_2O (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel.

8. Condition for the Synthesis of Vinyl Sulfide (Condition D)

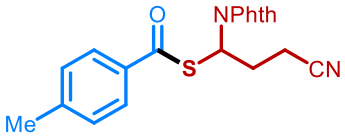


To an oven-dried 100 x 16 mm screw-capped vial with a magnetic stir bar was added alkyl xanthate esters (0.30 mmol, 1.0 equiv). Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Next, Ligand **L1** (6.6 mg, 0.036 mmol, 12 mol%), $NiBr_2$(diglyme) (15.9 mg, 0.045 mmol, 15 mol%), Zn (58.9 mg, 0.90 mmol, 3.0 equiv), ally halide (0.036 mmol, 1.2 equiv) and DMA (1.50 mL, 0.20 M) were added to the vial sequentially. The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at 40 ℃ for 24 h, then quenched upon the addition of H_2O (15 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel.

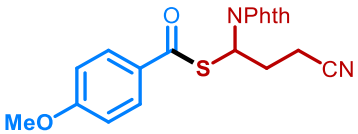
9. Characterization Data for Products:



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) benzothioate (3):**
The title compound **3** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.2) to give brown viscous oil (82.1 mg, 0.234 mmol, 78% yield). When from **Condition B** (79.4 mg, 0.226 mmol, 75% yield). **IR (neat):** 2360, 1780, 1714, 1468, 1207, 901, 773, 716, 684, 646. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 – 7.92 (m, 2H), 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.41 (m, 2H), 6.41 – 6.31 (m, 1H), 2.81 – 2.66 (m, 1H), 2.64 – 2.41 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 189.06, 167.03, 135.82, 134.74, 134.35, 131.60, 128.96, 127.69, 124.02, 118.20, 50.90, 30.29, 15.19. **HRMS (ESI):** Calcd for $C_{19}H_{15}N_2O_3S$ $[M+H]^+$ 351.0798, found 351.0797.

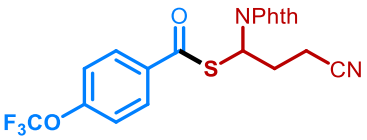


***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 4-methylbenzothioate (5):**
The title compound **5** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.2) to give brown viscous oil (78.8 mg, 0.216 mmol, 72% yield). **IR (neat):** 3853, 3649, 2988, 2360, 2341, 1699, 1395, 1066, 669, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.38 – 6.29 (m, 1H), 2.83 – 2.64 (m, 1H), 2.66 – 2.46 (m, 3H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.57, 167.05, 145.45, 134.71, 133.28, 131.62, 129.62, 127.77, 124.00, 118.25, 50.81, 30.34, 21.90, 15.19. **HRMS (ESI):** Calcd for $C_{20}H_{17}N_2O_3S$ $[M+H]^+$ 365.0955, found 365.0954.



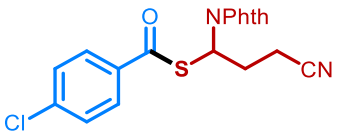
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 4-methoxybenzothioate (6):**
The title compound **6** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.3) to give brown viscous oil (57.2 mg, 0.150 mmol, 50% yield). **IR (neat):** 3853, 3649, 2968, 2902, 2360, 2342, 1717, 1376, 1066, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 – 7.87 (m, 4H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.95 – 6.88 (m, 2H), 6.39 – 6.30 (m, 1H), 3.86 (s, 3H), 2.76 – 2.63 (m, 1H), 2.61 – 2.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 187.34, 167.07, 164.54, 134.71, 131.66, 130.01, 128.61, 124.00, 118.28, 114.15,

55.74, 50.84, 30.40, 15.21. **HRMS (ESI):** Calcd for $C_{20}H_{17}N_2O_4S$ $[M+H]^+$ 381.0904, found 381.0905.



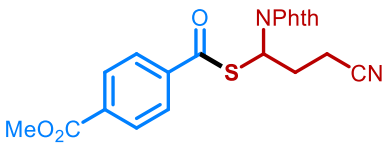
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl)4-(trifluoromethoxy) benzothioate (7):**

The title compound **7** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.3) to give brown viscous oil (83.9 mg, 0.193 mmol, 64% yield). **IR (neat):** 3853, 2988, 2968, 2360, 2342, 1717, 1653, 1066, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H), 6.37 – 6.31 (m, 1H), 2.85 – 2.68 (m, 1H), 2.64 – 2.43 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 187.70, 166.97, 153.47, 134.81, 133.97, 131.55, 129.72, 124.06, 121.60, 120.67, 119.02, 118.10, 51.06, 30.21, 15.19. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -57.61. **HRMS (ESI):** Calcd for $C_{20}H_{14}F_3N_2O_4S$ $[M+H]^+$ 435.0621, found 435.0621.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 4-chlorobenzothioate (8):**

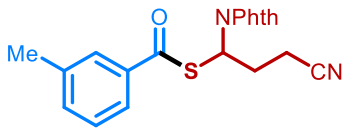
The title compound **8** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.2) to give brown viscous oil (73.5 mg, 0.191 mmol, 64% yield). **IR (neat):** 3853, 2987, 2360, 2342, 1717, 1653, 1599, 1066, 669, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 6.40 – 6.31 (m, 1H), 2.82 – 2.68 (m, 1H), 2.68 – 2.44 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 187.96, 166.96, 140.82, 134.78, 134.13, 131.53, 129.29, 128.99, 124.03, 118.12, 50.98, 30.21, 15.17. **HRMS (ESI):** Calcd for $C_{19}H_{14}ClN_2O_3S$ $[M+H]^+$ 385.0408, found 385.0410.



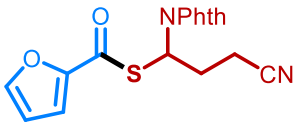
Methyl 4-(((3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) thio) carbonyl) benzoate (9):

The title compound **9** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown viscous oil (85.9 mg, 0.210 mmol, 70% yield). **IR (neat):** 3853, 3675, 2987, 2360, 2342, 1716, 1653, 1541, 1066, 903, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.90 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77

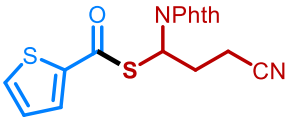
(dd, J = 5.5, 3.0 Hz, 2H), 6.42 – 6.31 (m, 1H), 3.94 (s, 3H), 2.83 – 2.70 (m, 1H), 2.62 – 2.43 (m, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 188.73, 166.99, 166.00, 139.05, 135.02, 134.83, 131.56, 130.15, 127.62, 124.09, 118.08, 52.74, 51.06, 31.09, 30.21, 15.20. **HRMS (ESI):** Calcd for $C_{21}H_{17}N_2O_5S$ $[M+H]^+$ 409.0853, found 409.0855.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 3-methylbenzothioate (10):**
The title compound **10** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.2) to give brown viscous oil (78.1 mg, 0.214 mmol, 71% yield). **IR (neat):** 3853, 3675, 2987, 2360, 2341, 1717, 1653, 1599, 1066, 669. **^{1}H NMR (400 MHz, CDCl$_3$):** 7.89 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.73 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 6.35 – 6.31 (m, 1H), 2.79 – 2.67 (m, 1H), 2.62 – 2.47 (m, 3H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 189.16, 167.04, 138.92, 135.83, 135.13, 134.73, 131.62, 128.83, 128.18, 124.88, 124.01, 118.22, 50.87, 30.32, 21.39, 15.18. **HRMS (ESI):** Calcd for $C_{20}H_{17}N_2O_3S$ $[M+H]^+$ 365.0955, found 365.0954.

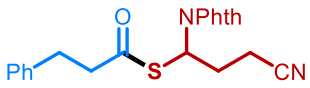


***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) furan-2-carbothioate (11):**
The title compound **11** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (59.6 mg, 0.175 mmol, 58% yield). **IR (neat):** 3649, 2924, 2987, 2360, 2342, 1780, 1715, 1460, 1377, 1066, 839, 716. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.89 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.59 – 7.58 (m, 1H), 7.24 – 7.22 (m, 1H),6.56 – 6.55 (m, 1H), 6.34 – 6.30 (m, 1H), 2.78 – 2.64 (m, 1H), 2.60 – 2.38 (m, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 177.51, 166.94, 149.80, 147.15, 134.75, 131.60, 124.03, 118.15, 117.25, 112.81, 49.97, 30.36, 15.14. **HRMS (ESI):** Calcd for $C_{18}H_{13}N_2O_4S$ $[M+H]^+$ 341.0591, found 341.0590.

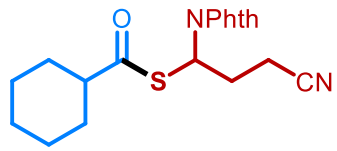


***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) thiophene-2-carbothioate(12):**
The title compound **12** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (68.9 mg, 0.193 mmol, 64% yield). **IR (neat):** 3649, 2925, 2360, 2341, 1714, 1652, 1468, 1206, 1053, 882, 714. **^{1}H NMR (400 MHz, CDCl$_3$):** δ

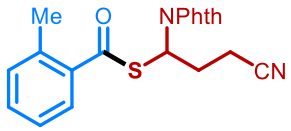
7.89 (m, 2H), 7.81 – 7.72 (m, 3H), 7.68 (m, 1H), 7.15 – 7.07 (m, 1H), 6.32 (m, 1H), 2.77 – 2.64 (m, 1H), 2.60 – 2.45 (m, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 180.95, 166.95, 140.59, 134.77, 134.30, 132.27, 131.60, 128.29, 124.05, 118.16, 50.97, 30.39, 15.18. **HRMS (ESI):** Calcd for $C_{17}H_{13}N_2O_3S_2$ $[M+H]^+$ 357.0362, found 357.0347.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 3-phenylpropanethioate (13):**
The title compound **13** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (79.9 mg, 0.211 mmol, 70% yield). **IR (neat):** 2930, 2360, 2341, 1780, 1715, 1460, 1377, 1103, 982, 716, 528. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.19 – 7.12 (m, 3H), 6.16 – 6.05 (m, 1H), 3.02 – 2.93 (m, 2H), 2.91 – 2.79 (m, 2H), 2.61 – 2.50 (m, 1H), 2.45 – 2.30 (m, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 195.82, 166.89, 139.47, 134.73, 131.55, 128.71, 128.45, 126.66, 123.99, 118.14, 50.53, 45.43, 31.26, 30.08, 14.98. **HRMS (ESI):** Calcd for $C_{21}H_{19}N_2O_3S$ $[M+H]^+$ 379.1111, found 379.1109.

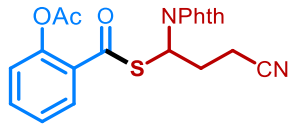


***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) cyclohexanecarbothioate(14):**
The title compound **14** was prepared according to Condition A. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.4) to give brown viscous oil (60.4 mg, 0.169 mmol, 56% yield). **IR (neat):** 3853, 2987, 2360, 2342, 1717, 1559, 1507, 1066, 669, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.86 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 dd, J = 5.5, 3.1 Hz, 2H), 6.10 – 6.02 (m, 1H), 2.69 – 2.57 (m, 1H), 2.50 – 2.34 (m, 4H), 1.97 – 1.81 (m, 2H), 1.81 – 1.72 (m, 2H), 1.52 – 1.37 (m, 2H), 1.30 – 1.16 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 200.16, 167.00, 134.69, 131.59, 123.97, 118.22, 52.67, 50.26, 30.30, 29.49, 29.32, 25.60, 25.49, 25.44, 15.10. **HRMS (ESI):** Calcd for $C_{19}H_{21}N_2O_3S$ $[M+H]^+$ 357.1268, found 357.1269.



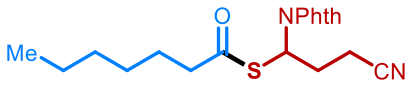
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 2-methylbenzothioate (15):**
The title compound **15** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown viscous oil (71.9 mg, 0.197 mmol, 66% yield). **IR (neat):** 3853, 3675, 2987, 2360, 2342, 1717, 1653, 1559, 1066, 669, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.90 (dd, J = 5.4, 3.1 Hz, 2H), 7.80 – 7.74 (m, 3H), 7.43 – 7.39 (m, 1H), 7.25 – 7.22

(m, 2H), 6.32 – 6.21 (m, 1H), 2.81 – 2.67 (m, 1H), 2.66 – 2.51 (m, 3H), 2.49 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 190.63, 167.06, 138.01, 135.69, 134.72, 132.75, 132.03, 131.61, 128.95, 126.06, 123.99, 118.24, 51.21, 30.29, 21.10, 15.18. **HRMS (ESI):** Calcd for $C_{20}H_{17}N_2O_3S$ $[M+H]^+$ 365.0955, found 365.0954.



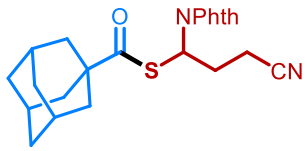
2-(((3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) thio) carbonyl) phenyl acetate (16):

The title compound **16** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown viscous oil (67.5 mg, 0.165 mmol, 55% yield). **IR (neat):** 3853, 2921, 2360, 2342, 1771, 1716, 1457, 1183, 1067, 717. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.92 – 7.86 (m, 3H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.33 – 7.29 (m, 1H), 7.14 – 7.12 (m, 1H), 6.33 – 6.21 (m, 1H), 2.75– 2.66 (m, 1H), 2.61 – 2.44 (m, 3H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 187.19, 169.45, 166.99, 148.41, 134.76, 134.56, 131.63, 129.77, 129.05, 126.37, 124.20, 124.02, 118.21, 50.95, 30.28, 21.32, 15.08. **HRMS (ESI):** Calcd for $C_{22}H_{17}N_2O_5S$ $[M+H]^+$ 409.0853, found 409.0855.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) heptanethioate (17):**

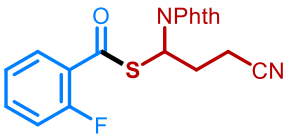
The title compound **17** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.4) to give brown viscous oil (69.9 mg, 0.171 mmol, 58% yield). **IR (neat):** 3853, 2928, 2857, 2248, 1779, 1713, 1422, 1328, 881, 716, 529. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.11 – 6.08 (m, 1H), 2.73 – 2.55 (m, 4H), 2.51 – 2.37 (m, 3H), 1.69 – 1.63 (m, 1H), 1.27 (d, *J* = 7.7 Hz, 6H), 0.85 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 196.79, 166.98, 134.73, 131.56, 123.99, 118.18, 50.50, 44.06, 31.44, 30.17, 28.67, 25.32, 22.50, 15.10, 14.11. **HRMS (ESI):** Calcd for $C_{19}H_{23}N_2O_3S$ $[M+H]^+$ 409.0853, found 409.0855.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) (3r,5r,7r)-adamantane-1-carbothi -oate (18):**

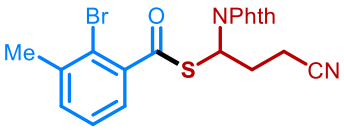
The title compound **18** was prepared according to **Condition A**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (81.5 mg, 0.202 mmol, 67% yield). **IR (neat):** 3853, 2987, 2361, 2341, 1780, 1717, 1653, 1457, 1066, 669, 420. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.10 – 6.00 (m, 1H), 2.70

– 2.60 (m, 1H), 2.52 – 2.36 (m, 3H), 2.08 – 1.99 (m, 3H), 1.92 – 1.83 (m, 6H), 1.78 – 1.61 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.59, 167.06, 134.66, 131.61, 123.95, 118.28, 50.08, 49.06, 39.13, 36.38, 30.36, 28.13, 15.11. **HRMS (ESI):** Calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$ 409.1581, found 409.1586.



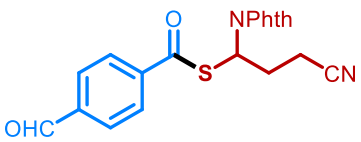
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 2-fluorobenzothioate (19):**

The title compound **19** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.2) to give brown viscous oil (88.2 mg, 0.239 mmol, 80% yield). **IR (neat):** 2943, 2360, 2341, 1780, 1715, 1376, 1270, 1198, 908, 715. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.28 – 7.26 (m, 1H), 6.99 – 6.93 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.99 – 6.93 (m, 1H), 6.68 – 6.62 (m, 1H), 6.59 – 6.54 (m, 1H), 5.83 – 5.69 (m, 1H), 2.24 – 2.08 (m, 1H), 2.08 – 1.83 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 186.03, 185.98, 166.99, 162.14, 159.56, 135.51, 135.42, 134.74, 131.59, 130.09, 124.59, 124.55, 124.02, 118.17, 117.28, 117.06, 50.77, 50.73, 30.07, 15.16. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -108.96. **HRMS (ESI):** Calcd for $C_{19}H_{14}FN_2O_3S$ $[M+H]^+$ 369.0704, found 369.0704.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl)2-bromo-3-methylbenzothioate (20):**

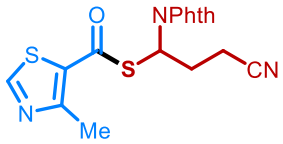
The title compound **20** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown solid (79.7 mg, 0.180 mmol, 60% yield). **IR (neat):** 3853, 2987, 2360, 2342, 1717, 1559, 1507, 1376, 903, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 6.33 – 6.22 (m, 1H), 2.76 – 2.66 (m, 1H), 2.63 – 2.46 (m, 3H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.99, 166.96, 140.26, 139.37, 134.81, 133.77, 131.58, 127.18, 126.30, 124.08, 121.03, 118.21, 51.50, 30.32, 23.64, 15.13. **HRMS (ESI):** Calcd for $C_{20}H_{16}BrN_2O_3S$ $[M+H]^+$ 443.0060, found 443.0061.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 4-formylbenzothioate (21):**

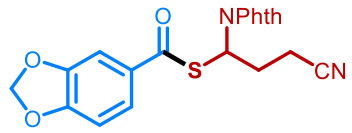
The title compound **21** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown viscous oil (51.9 mg, 0.137 mmol, 46% yield). **IR (neat):** 3853, 3675,

2987, 2360, 2342, 1717, 1559, 1395, 1066, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.09 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.40 – 6.29 (m, 1H), 2.84 – 2.70 (m, 1H), 2.61 – 2.45 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.34, 188.68, 166.97, 140.06, 139.92, 134.87, 131.53, 130.06, 128.26, 124.11, 118.04, 51.13, 30.18, 15.20. **HRMS (ESI):** Calcd for $C_{20}H_{15}N_2O_4S$ $[M+H]^+$ 379.0747, found 379.0749.



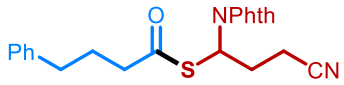
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl)4-methylthiazole-5-carbothioate (22):**

The title compound **22** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown solid (76.6 mg, 0.206 mmol, 68% yield). **IR (neat):** 3853, 2987, 2360, 2342, 1717, 1559, 1507, 1066, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.78 (s, 1H), 7.90 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.36 – 6.25 (m, 1H), 2.78 (s, 3H), 2.75 – 2.67 (m, 1H), 2.59 – 2.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 180.62, 166.91, 159.66, 155.70, 134.86, 131.55, 124.12, 118.03, 51.63, 30.26, 18.46, 15.20. **HRMS (ESI):** Calcd for $C_{17}H_{14}N_3O_3S$ $[M+H]^+$ 372.0471, found 372.0470.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) benzo[β] [1,3] dioxole-5-carbo -thioate (23):**

The title compound **23** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (79.7 mg, 0.202 mmol, 67% yield). **IR (neat):** 3587, 3567, 1749, 1653, 1559, 1508, 1474, 1457, 1419, 528. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.57 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.36 – 6.27 (m, 1H), 6.05 (s, 2H), 2.81 – 2.63 (m, 1H), 2.60 – 2.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 187.16, 167.04, 152.87, 148.41, 134.73, 131.63, 130.29, 124.16, 124.02, 118.23, 108.32, 107.52, 102.30, 51.00, 30.33, 15.20. **HRMS (ESI):** Calcd for $C_{20}H_{15}N_2O_5S$ $[M+H]^+$ 395.0696, found 395.0704.



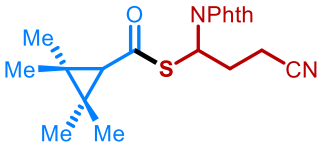
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 4-phenylbutanethioate (24):**

The title compound **24** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (90.1 mg, 0.226 mmol, 75% yield). **IR (neat):** 2920, 2360,

2342, 1760, 1377, 1084, 882, 750, 717, 528. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.24 (s, 1H), 7.19 – 7.12 (m, 3H), 6.12 – 6.08 (m, 1H), 2.69 – 2.54 (m, 5H), 2.54 – 2.35 (m, 3H), 2.04 – 1.93 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.40, 166.95, 140.86, 134.74, 131.57, 128.59, 126.29, 124.00, 118.14, 50.54, 43.23, 34.94, 30.16, 26.76, 15.11. **HRMS (ESI):** Calcd for $C_{22}H_{21}N_2O_3S$ $[M+H]^+$ 399.1268, found 399.1276.

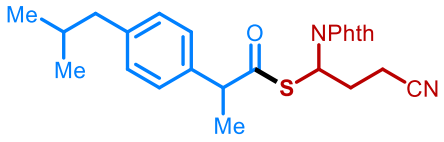
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) dec-9-enethioate (25):**

The title compound **25** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (79.4 mg, 0.202 mmol, 67% yield). **IR (neat):** 2926, 2855, 2360, 2341, 1717, 1377, 882, 717, 528. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.14 – 6.03 (m, 1H), 5.83 – 5.73 (m, 1H), 4.94 (dd, *J* = 21.7, 13.6 Hz, 2H), 2.66 – 2.53 (m, 3H), 2.53 – 2.37 (m, 3H), 2.01 (m, 2H), 2.03 – 1.98 (m, 2H), 1.34 – 1.19 (m, 8H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 196.71, 166.95, 139.14, 134.71, 131.57, 123.97, 118.16, 114.37, 50.52, 44.02, 33.82, 30.19, 29.10, 28.93, 28.90, 28.88, 25.32, 15.09. **HRMS (ESI):** Calcd for $C_{22}H_{27}N_2O_3S^+$ $[M+H]^+$ 399.1737, found 399.1735.



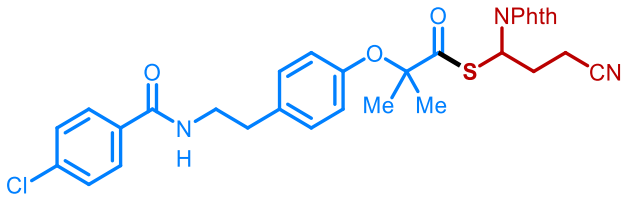
***S*-(2-cyano-1-(1,3-dioxoisoindolin-2-yl)ethyl)2,2,3,3-tetramethylcyclopropane-1-carbothioate (26):**

The title compound **26** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give yellow oil (54.7 mg, 0.152 mmol, 51% yield). **IR (neat):** 3735, 2924, 1718, 1508, 1377, 1076,719, 418. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.10 – 6.03 (m, 1H), 2.63 – 2.36 (m, 5H), 1.25 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H), 1.16 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.37, 167.03, 134.60, 131.64, 123.88, 118.35, 50.65, 46.08, 35.98, 35.95, 30.41, 23.54, 16.92, 16.89, 15.07. **HRMS (ESI):** Calcd for $C_{20}H_{26}N_3O_3S$ $[M+NH_4]^+$ 388.1689, found 388.1690.



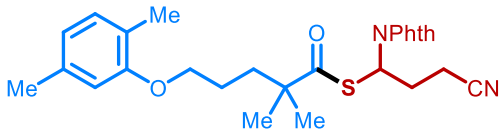
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl)-2-(4-isobutylphenyl) propaneth -ioate (27):**

The title compound **27** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.3) to give white solid (87.2 mg, 0.200 mmol, 67% yield) (dr =1:1). **IR (neat):** 2971, 2360, 2342, 1716, 1653, 1507, 1457, 1066, 669, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (ddd, *J* = 13.9, 5.5, 3.1 Hz, 2H), 7.74 (ddd, *J* = 13.9, 5.5, 3.1 Hz, 2H), 7.18 – 7.10 (m, 3H), 7.05 (d, *J* = 8.1 Hz,1H), 6.10 – 5.97 (m, 1H), 3.93 – 3.72 (m, 1H), 2.64 – 2.51 (m, 1H), 2.48 – 2.39 (m, 3H), 2.37 – 2.25 (m, 2H), 1.82 (m, 1H), 1.51 (dd, *J* = 14.5, 7.1 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.92, 198.73, 166.96, 166.92, 141.61, 141.47, 136.15, 135.88, 134.71, 134.66, 131.59, 131.55, 129.77, 129.65, 127.87, 127.86, 123.99, 123.95, 118.18, 118.12, 54.19, 54.13, 50.82, 50.78, 45.18, 45.15, 30.36, 30.30, 30.25, 30.12, 22.53, 22.51, 18.48, 18.31, 15.08, 14.94. **HRMS (ESI):** Calcd for $C_{25}H_{27}N_2O_3S$ $[M+H]^+$ 435.1737, found 435.1731.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 2-(4-(2-(4-chlorobenzamido) ethyl) phenoxy)-2-methylpropanethioate (28):**

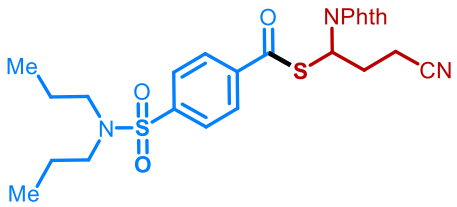
The title compound **28** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:2 EA/PE, R_f = 0.2) to give white solid (125.1 mg, 0.212 mmol, 70% yield) (dr =1:1). **IR (neat):** 3734, 2969, 2360, 2342, 1717, 1653, 1243, 1066, 718, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.18 – 6.02 (m, 1H), 3.66 (d, 6.9 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H), 2.74 – 2.62 (m, 1H), 2.55 – 2.35 (m, 3H), 1.51 (s, 3H), 1.45 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.10, 167.04, 166.51, 152.69, 137.81, 134.77, 134.19, 133.03, 131.56, 129.66, 128.98, 128.37, 124.00, 121.98, 118.17, 85.98, 50.64, 41.33, 34.97, 30.00, 25.30, 15.15. **HRMS (ESI):** Calcd for $C_{31}H_{29}ClN_3O_5S$ $[M+H]^+$ 590.1511, found 590.1502.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 5-(2,5-dimethylphenoxy)-2,2-dime -thylpentanethioate (29):**

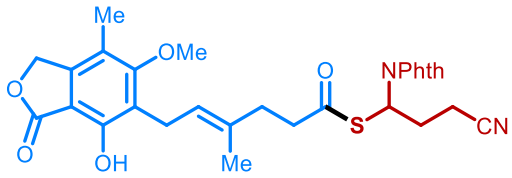
The title compound **29** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give white solid (125.5 mg, 0.263 mmol, 87% yield). **IR (neat):** 2925, 1717, 1377, 1285, 1103, 1085, 937, 882, 692, 519. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* =

5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.04 – 6.97 (m, 1H), 6.71 – 6.61 (m, 1H), 6.57 (s, 1H), 6.07 – 6.04 (m, 1H), 3.97 – 3.78 (m, 2H), 2.70 – 2.61 (m, 1H), 2.53 – 2.34 (m, 3H), 2.29 (s, 3H), 2.14 (s, 3H), 1.79 – 1.74 (m, 2H), 1.73 – 1.65 (m, 2H), 1.25 (s, 3H), 1.25 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 203.58, 167.01, 156.83, 136.55, 134.66, 131.52, 130.38, 123.94, 123.60, 120.82, 118.20, 111.91, 67.57, 50.60, 50.10, 37.45, 30.21, 25.18, 25.16, 24.89, 21.51, 15.90, 15.08. **HRMS (ESI):** Calcd for $C_{27}H_{31}N_2O_4S$ $[M+H]^+$ 479.1999, found 479.1993.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (30):**

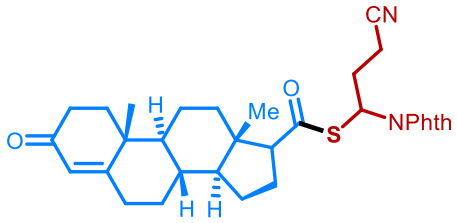
The title compound **30** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown viscous oil (68.3 mg, 0.133 mmol, 44% yield). **IR (neat):** 3735, 2968, 2360, 2342, 1717, 1457, 1203, 908, 717, 669. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.09 – 8.00 (m, 2H), 7.94 – 7.84 (m, 4H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.42 – 6.27 (m, 1H), 3.07 (t, *J* = 15.2 Hz, 4H), 2.80 – 2.70 (m, 1H), 2.62 – 2.49 (m, 3H), 1.53 (dd, *J* = 15.2, 7.4 Hz, 4H), 0.85 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 188.26, 166.95, 145.47, 138.51, 134.88, 131.53, 128.28, 127.55, 124.11, 118.02, 51.15, 50.02, 30.17, 22.04, 15.20, 11.28. **HRMS (ESI):** Calcd for $C_{25}H_{28}N_3O_5S$ $[M+H]^+$ 514.1465, found 514.1456.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl)propyl)-(E)-6-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enethioate (31):**

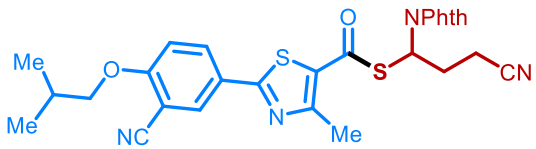
The title compound **31** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown solid (94.4 mg, 0.172 mmol, 57% yield). **IR (neat):** 3902, 3839, 3567, 2372, 2157, 1717, 1653, 1508, 1489, 1362, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.11 – 6.00 (m, 1H), 5.21 (s, 2H), 5.17 – 5.09 (m, 1H), 3.77 (s, 3H), 3.36 (t, *J* = 6.4 Hz, 2H), 2.73 – 2.54 (m, 3H), 2.50 – 2.27 (m, 5H), 2.18 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 196.19, 166.93, 153.66, 150.99, 146.05, 144.25, 134.73, 133.82, 131.52, 123.98, 122.86, 118.17, 116.89, 113.90, 106.50, 70.21, 61.15, 50.49, 42.59, 34.86, 30.13, 27.80, 22.70,

15.01, 11.94. **HRMS (ESI):** Calcd for $C_{29}H_{29}N_2O_7S$ $[M+H]^+$ 549.1690, found 549.1699.



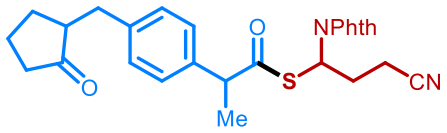
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl)propyl)(8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-17-carbothioate (32):**

The title compound **32** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give brown viscous oil (72.5 mg, 0.133 mmol, 44% yield, dr = 1:1). **IR (neat):** 3735, 2968, 2360, 2342, 1717, 1507, 1376, 1051, 789, 669, 419. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.18 – 6.04 (m, 1H), 5.71 (d, *J* = 5.8 Hz, 1H), 3.22 (d, *J* = 40.9 Hz, 1H), 2.94 (s, 1H), 2.67 – 2.50 (m, 2H), 2.48 – 2.35 (m, 5H), 2.30 – 2.11 (m, 3H), 2.06 – 1.95 (m, 2H), 1.87 – 1.61 (m, 5H), 1.51 – 1.42 (m, 1H), 1.33 – 1.23 (m, 4H), 1.19 – 1.13 (m, 3H), 0.75 – 0.62 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.58, 199.55, 197.15, 196.80, 170.88, 170.87, 166.96, 166.96, 134.71, 131.55, 131.54, 124.09, 124.06, 123.97, 123.96, 118.20, 118.14, 64.47, 64.36, 55.62, 55.55, 53.66, 53.64, 50.60, 50.55, 45.00, 44.92, 38.68, 38.64, 38.39, 38.20, 35.80, 35.76, 35.73, 35.67, 34.04, 34.01, 32.82, 31.94, 31.92, 30.16, 30.11, 24.62, 24.61, 23.96, 23.90, 21.01, 20.92, 17.47, 17.43, 15.13, 15.09, 13.49, 13.29. **HRMS (ESI):** Calcd for $C_{32}H_{37}N_2O_4S$ $[M+H]^+$ 545.2469, found 545.2467.



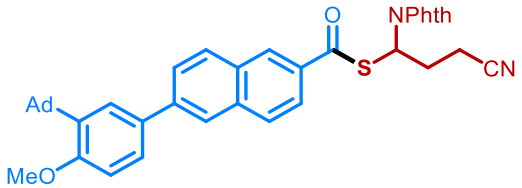
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl)propyl)2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbothioate (33):**

The title compound **33** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give white solid (94.8 mg, 0.173 mmol, 58% yield). **IR (neat):** 3735, 2987, 2360, 2342, 1717, 1507, 1457, 1066, 669, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 2.3 Hz, 1H), 8.06 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.91 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.33 – 6.29 (m, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.76 (s, 3H), 2.74 – 2.68 (m, 1H), 2.61 – 2.43 (m, 3H), 2.20 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 180.03, 167.95, 166.92, 162.97, 160.39, 134.84, 132.92, 132.45, 131.54, 128.74, 125.53, 124.11, 118.09, 115.35, 112.81, 103.24, 75.88, 51.61, 30.28, 28.26, 19.17, 18.69, 15.19. **HRMS (ESI):** Calcd for $C_{28}H_{25}N_4O_4S$ $[M+H]^+$ 545.1312, found 545.1306.



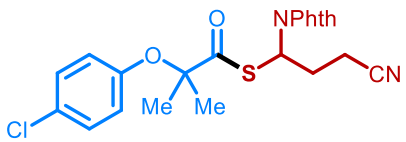
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl)2-(4-((2-oxocyclopentyl)methyl)ph -enyl)propanethioate (34):**

The title compound **34** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.3) to give yellow solid (61.3 mg, 0.129 mmol, 43% yield, dr = 1:1). **IR (neat):** 3735, 2923, 2360, 2341, 1717, 1377, 1067, 937, 669, 420. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.86 (ddd, J = 12.8, 5.3, 3.1 Hz, 2H), 7.78 – 7.72 (ddd, J = 12.8, 5.3, 3.1 Hz, 2H), 7.19 - 7.14 (m, 3H), 7.09 – 7.07 (m, 1H), 6.05 – 6.00 (m, 1H), 3.89 – 3.78 (m, 1H), 3.19 – 3.03 (m, 1H), 2.61 – 2.52 (m, 1H), 2.51 – 2.26 (m, 6H), 2.16 – 2.04 (m, 2H), 1.98 – 1.66 (m, 3H), 1.51 (dd, J = 14.9, 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 198.77, 198.61, 166.95, 166.92, 139.94, 139.80, 136.75, 136.48, 134.74, 134.71, 131.55, 131.51, 129.56, 129.45, 128.23, 128.22, 124.00, 123.96, 118.17, 118.11, 54.12, 54.07, 51.08, 51.05, 50.80, 50.76, 38.32, 38.30, 35.36, 35.32, 30.34, 30.11, 29.41, 29.36, 20.68, 20.65, 18.49, 18.32, 15.08, 14.96. **HRMS (ESI):** Calcd for $C_{27}H_{27}N_2O_4S$ $[M+H]^+$ 475.1686, found 475.1685.



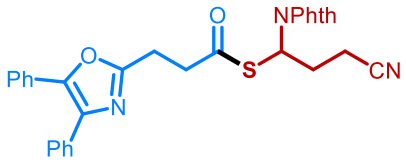
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 6-(3-((3r,5r,7r)-adamantan-1-yl)-4 -methoxyphenyl) naphthalene-2-carbothioate (35):**

The title compound **35** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give white solid (0.164 mg, 0.256 mmol, 85% yield). **IR (neat):** 3735, 2987, 2360, 2341, 1717, 1507, 1457, 1066, 669, 420. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.51 (s, 1H), 8.00 – 7.94 (m, 3H), 7.93 – 7.87 (m, 3H), 7.81 (dd, J = 8.6, 1.7 Hz, 1H), 7.76 (dd, J = 5.5, 3.1 Hz, 2H), 7.59 (d, J = 2.3 Hz, 1H), 7.53 (dd, J = 8.5, 2.3 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.44 – 6.40 (m, 1H), 3.90 (s, 3H), 2.83 – 2.73 (m, 1H), 2.68 – 2.48 (m, 3H), 2.18 – 2.16 (m, 6H), 2.10 (s, 3H), 1.80 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 188.73, 167.08, 159.16, 142.25, 139.14, 136.65, 134.73, 132.56, 132.29, 131.61, 131.12, 130.11, 129.37, 128.91, 127.08, 126.08, 125.87, 124.82, 124.01, 123.45, 118.28, 112.20, 55.28, 50.95, 40.67, 37.31, 37.21, 30.36, 29.18, 15.22. **HRMS (ESI):** Calcd for $C_{40}H_{37}N_2O_4S$ $[M+H]^+$ 641.2469, found 641.2469.



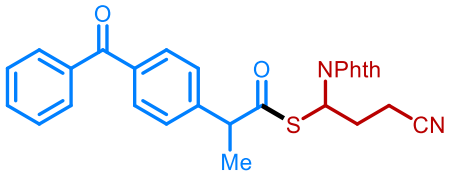
***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 2-(4-chlorophenoxy)-2-methylpro -panethioate (36):**

The title compound **36** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.3) to give white solid (0.109 mg, 0.247 mmol, 82% yield). **IR (neat):** 2987, 2360, 2341, 1716, 1487, 1377, 1225, 1066, 716, 519. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.09 – 6.04 (m, 1H), 2.75 – 2.60 (m, 1H), 2.56 – 2.36 (m, 3H), 1.51 (s, 3H), 1.45 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.72, 167.00, 152.55, 134.76, 131.54, 129.36, 129.01, 124.01, 122.95, 118.11, 86.27, 50.65, 29.98, 25.37, 25.08, 15.16. **HRMS (ESI):** Calcd for $C_{22}H_{20}ClN_2O_4S$ $[M+H]^+$ 443.0827, found 443.0830.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 3-(4,5-diphenyloxazol-2-yl) prop-anethioate (37):**

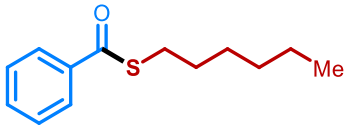
The title compound **37** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give white solid (66.8 mg, 0.128 mmol, 42% yield). **IR (neat):** 3587, 3567, 1659, 1417, 1203, 1173, 907, 773, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.59 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.54 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.39 – 7.28 (m, 6H), 6.21 – 6.10 (m, 1H), 3.32 – 3.08 (m, 4H), 2.68 – 2.56 (m, 1H), 2.52 – 2.35 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.03, 166.91, 160.96, 145.76, 135.25, 134.76, 132.37, 131.54, 128.92, 128.80, 128.72, 128.70, 128.27, 127.96, 126.62, 124.04, 118.08, 50.64, 40.33, 30.18, 23.43, 15.06. **HRMS (ESI):** Calcd for $C_{30}H_{24}N_3O_4S$ $[M+H]^+$ 522.1482, found 522.1476.



***S*-(3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) 3-(4,5-diphenyloxazol-2-yl) prop -anethioate (38):**

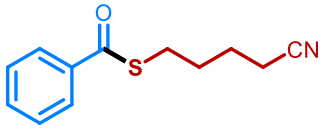
The title compound **38** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:3 EA/PE, R_f = 0.2) to give white solid (0.122 mg, 0.251 mmol, 84% yield, dr = 1:1). **IR (neat):** 3735, 2977, 2360, 2341, 1716, 1377, 1280, 1017, 712, 528. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (ddd, *J* = 14.5, 5.4, 3.1 Hz, 2H), 7.80 – 7.78 (m, 1H), 7.77 – 7.70 (m, 4H), 7.68 – 7.65 (m, 1H), 7.63 – 7.55 (m, 1H), 7.53-7.51 (m, 1H), 7.49-7.46 (m, 2H), 7.45-7.38 (m, 1H), 6.10 – 5.96 (m, 1H), 3.97-3.89 (m, 1H), 2.66 – 2.51 (m, 1H), 2.50 – 2.24 (m, 3H), 1.56

(dd, J = 13.7, 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.12, 198.05, 196.32, 196.30, 166.87, 166.83, 139.22, 138.96, 138.23, 138.11, 137.37, 137.33, 134.72, 134.69, 132.75, 132.69, 132.02, 131.97, 131.47, 131.42, 130.16, 129.77, 129.73, 129.65, 128.98, 128.92, 128.46, 128.43, 123.96, 123.94, 118.09, 118.02, 54.17, 54.15, 50.81, 30.23, 30.00, 18.46, 18.37, 15.03, 14.97. **HRMS (ESI):** Calcd for $C_{28}H_{23}N_2O_4S$ $[M+NH_4]^+$ 500.1668, found 500.1630.



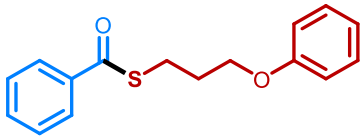
***S*-hexyl benzothioate (39):**

The title compound **39** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (39.6 mg, 0.178 mmol, 59% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01-7.93 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 3.07 (t, J = 7.3Hz, 2H), 1.73-1.61 (m, 2H), 1.46 – 1.38 (m, 2H), 1.34 – 1.29 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H), and spectral data were in accordance with the literature values.[1]



***S*-(4-cyanobutyl) benzothioate (40):**

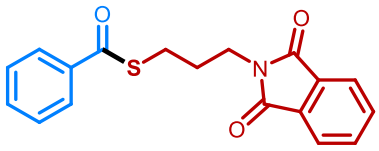
The title compound **40** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (37.2 mg, 0.169 mmol, 56% yield). **IR (neat):** 2906, 2870, 2360, 2341, 1658, 1448, 1205, 1175, 908, 773, 687. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 – 7.90 (m, 2H), 7.59 (m, 1H), 7.46 (m, 2H), 3.11 (t, J = 6.7 Hz, 2H), 2.42 (t, J = 6.7 Hz, 2H), 1.89 – 1.76 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.76, 136.97, 133.66, 128.79, 127.36, 119.48, 28.87, 27.91, 24.50, 16.97. **HRMS (ESI):** Calcd for $C_{12}H_{14}NOS$ $[M+H]^+$ 220.0791, found 220.0783.



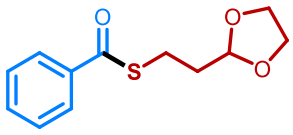
***S*-(3-phenoxypropyl) benzothioate (41):**

The title compound **41** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (49.7 mg, 0.182 mmol, 61% yield). **IR (neat):** 3735, 2970, 2360, 2341, 1717, 1507, 1243, 1040, 687, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 – 7.95 (m, 2H), 7.61 – 7.55 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.33 –

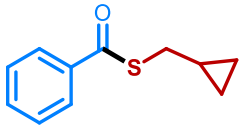
7.27 (m, 2H), 6.98 – 6.89 (m, 3H), 4.08 (t, J = 6.0 Hz, 2H), 3.27 (t, J = 7.1 Hz, 2H), 2.25 – 2.08 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 191.88, 158.78, 137.05, 133.40, 129.48, 128.63, 127.22, 120.80, 114.51, 66.11, 29.39, 25.80. **HRMS (ESI):** Calcd for $C_{16}H_{17}O_2S$ $[M+H]^+$ 273.0944, found 273.0944.



***S*-(3-(1,3-dioxoisoindolin-2-yl) propyl) benzothioate (42):**
The title compound **42** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/500 EA/PE, R_f = 0.8) to give yellow oil (50.4 mg, 0.149 mmol, 49% yield). **IR (neat):** 3567, 2156, 1750, 1717, 1699, 1508, 1457, 1419, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.95 (d, J = 7.7 Hz, 2H), 7.86 (dd, J = 5.1, 3.1 Hz, 2H), 7.72 (dd, J = 5.1, 3.1 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.83 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 7.1 Hz, 2H), 2.13 – 1.98 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 191.70, 168.50, 137.07, 134.14, 133.53, 132.18, 128.72, 127.38, 123.45, 37.11, 28.88, 26.43. **HRMS (ESI):** Calcd for $C_{18}H_{16}NO_3S$ $[M+H]^+$ 343.1111, found 343.1110.

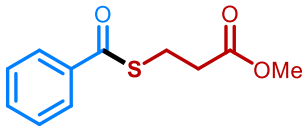


***S*-(2-(1,3-dioxolan-2-yl) ethyl) benzothioate (43):**
The title compound **43** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (40.4 mg, 0.169 mmol, 56% yield). **IR (neat):** 2957, 2883, 2360, 2341, 1660, 1581, 1206, 1133, 912, 774, 689. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.02 – 7.92 (m, 2H), 7.61 – 7.52 (m, 1H), 7.50 – 7.40 (m, 2H), 5.00 (t, J = 4.5 Hz, 1H), 4.06 – 3.83 (m, 4H), 3.20 – 3.16 (m, 2H), 2.12 – 1.99 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 191.87, 137.16, 133.46, 128.72, 127.33, 103.25, 100.11, 65.19, 33.86, 23.58. **HRMS (ESI):** Calcd for $C_{12}H_{15}O_3S$ $[M+H]^+$ 239.0737, found 239.0735.



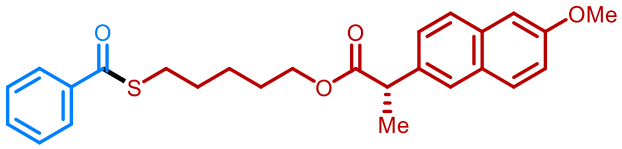
***S*-(cyclopropylmethyl) benzothioate (44):**
The title compound **44** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (28.8 mg, 0.150 mmol, 50% yield). **IR (neat):** 3735, 2924, 1719, 1658, 1448, 1204, 910, 828, 772, 687, 616. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.99 (t, J = 6.4 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.50 – 7.40 (m, 2H), 3.05 (t, J

= 8.5 Hz, 2H), 1.17 – 1.01 (m, 1H), 0.66 – 0.50 (m, 2H), 0.41 – 0.21 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.38, 137.30, 133.37, 128.68, 127.34, 34.87, 28.33, 10.96, 5.96. **HRMS (ESI):** Calcd for $C_{11}H_{13}OS$ $[M+H]^+$ 193.0682, found 193.0682.



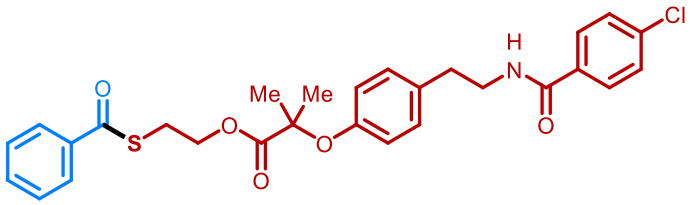
Methyl 3-(benzoylthio) propanoate (45):

The title compound **45** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.6) to give yellow oil (41.5 mg, 0.185 mmol, 62% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 – 7.88 (m, 2H), 7.65 – 7.51 (m, 1H), 7.44 (t, J = 7.1 Hz, 2H), 3.71 (s, 3H), 3.31 (td, J = 6.9, 1.2 Hz, 2H), 2.74 (td, J = 6.9, 1.2 Hz, 2H), and spectral data were in accordance with the literature values.[2]



5-(benzoylthio) pentyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (46):

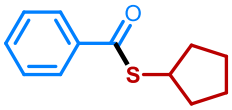
The title compound **46** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/100 EA/PE, R_f = 0.4) to give yellow oil (94.3 mg, 0.216 mmol, 72% yield). **IR (neat):** 3735, 2926, 2368, 2156, 1717, 1699, 1508, 1419, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 – 7.94 (m, 2H), 7.76 – 7.66 (m, 3H), 7.61-7.53 (t, J = 7.4 Hz, 1H), 7.50 – 7.38 (m, 3H), 7.17 – 7.10 (m, 2H), 4.11 (t, J = 6.5 Hz, 2H), 3.90 (s, 3H), 3.85 (q, J = 7.1 Hz, 1H), 2.94 (t, J = 7.3 Hz, 2H), 1.65 – 1.59 (m, 4H), 1.57 (d, J = 7.1 Hz, 3H), 1.39 – 1.32 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.09, 174.83, 157.73, 137.29, 135.90, 133.80, 133.40, 129.39, 129.04, 128.70, 127.30, 127.24, 126.38, 126.05, 119.10, 105.71, 64.65, 55.42, 45.63, 29.25, 28.84, 28.22, 25.30, 18.55. **HRMS (ESI):** Calcd for $C_{26}H_{32}NO_4S$ $[M+NH_4]^+$ 454.2046, found 454.2048.



2-(benzoylthio)ethyl 2-(4-(2-(4-chlorobenzamido) ethyl) phenoxy)-2-methyl propanoate (47):

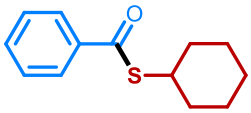
The title compound **47** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/100 EA/PE, R_f = 0.3) to give yellow oil (69.4 mg, 0.13 mmol, 44% yield). **IR**

(neat): 3725, 2935, 1728, 1658, 1605, 1030, 910, 852, 773, 521. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.64-7.56 (m, 3H), 7.53 – 7.41 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.80 (t, *J* = 8.7 Hz, 2H), 6.10 (s, 1H), 4.37 (t, *J* = 6.5 Hz, 2H), 3.71 -3.60 (m, 2H), 3.31 (t, *J* = 6.5 Hz, 2H), 2.90 – 2.76 (m, 2H), 1.60 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.00, 174.07, 166.49, 154.24, 137.74, 136.66, 133.86, 133.11, 132.57, 129.66, 128.93, 128.84, 128.36, 127.39, 119.54, 79.28, 63.68, 41.34, 34.84, 27.64, 25.56. **HRMS (ESI):** Calcd for $C_{28}H_{29}ClNO_5S$ $[M+H]^+$ 526.1450, found 526.1448.



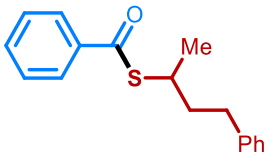
***S*-cyclopentyl benzothioate (48):**

The title compound **48** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.7) to give yellow oil (46.2 mg, 0.224 mmol, 75% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ7.93 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 3.99 – 3.85 (m, 1H), 2.29 – 2.11 (m, 2H), 1.82 – 1.59 (m, 6H), and spectral data were in accordance with the literature values.[3]



***S*-cyclohexyl benzothioate (49):**

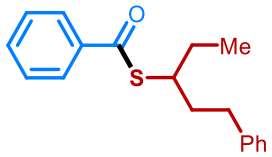
The title compound **49** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.7) to give yellow oil (34.8 mg, 0.158 mmol, 53% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 3.84 – 3.67 (m, 1H), 2.09 – 1.98 (m, 2H), 1.84 – 1.71(m, 2H), 1.68 – 1.60 (m, 1H), 1.54 – 1.42 (m, 4H), 1.37 – 1.27 (m, 1H)., and spectral data were in accordance with the literature values.[3]



***S*-(4-phenylbutan-2-yl) benzothioate (50):**

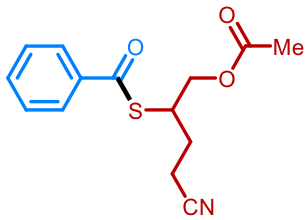
The title compound **50** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (56.4 mg, 0.208 mmol, 69% yield). **IR (neat):** 2960, 2924, 2360, 2341, 1656, 1447, 1205, 906, 687, 647. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 3H), 3.90 – 3.78 (m, 1H), 2.87 – 2.68 (m, 2H), 2.08 – 1.93

(m, 2H), 1.46 (d, J = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 191.98, 141.68, 137.47, 133.36, 128.69, 128.55, 128.52, 127.32, 126.08, 39.49, 38.59, 33.60, 21.76. **HRMS (ESI):** Calcd for $C_{17}H_{19}OS$ $[M+H]^+$ 271.1151, found 271.1147.



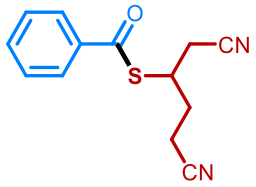
***S*-(1-phenylpentan-3-yl) benzothioate (51):**

The title compound **51** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.8) to give yellow oil (59.6 mg, 0.209 mmol, 70% yield). **IR (neat):** 2924, 1725, 1448, 1212, 1112, 1056, 996, 719, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.01 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.33 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 3.82 – 3.76 (m, 1H), 2.84 – 2.67 (m, 2H), 2.10 – 1.91 (m, 2H), 1.87 – 1.69 (m , 2H), 1.03 (t, J = 7.4 Hz, 3H).**^{13}C NMR (100 MHz, CDCl$_3$):** δ 192.12, 141.91, 137.51, 133.34, 128.69, 128.53, 127.39, 126.03, 100.11, 46.10, 36.57, 33.49, 28.24, 11.38. **HRMS (ESI):** Calcd for $C_{18}H_{21}OS$ $[M+H]^+$ 285.1308, found 285.1311.



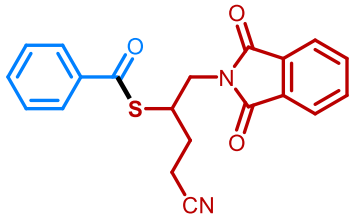
2-(benzoylthio)-4-cyanobutyl acetate (52):

The title compound **52** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/40 EA/PE, R_f = 0.3) to give yellow oil (47.0 mg, 0.169 mmol, 56% yield). **IR (neat):** 2929, 2247, 1772, 1709, 1661, 1204, 1174, 773, 666, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.95 (d, J = 7.7 Hz, 2H), 7.66 – 7.55 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 4.40 – 4.19 (m, 2H), 4.12 – 2.99 (m, 1H), 2.62 – 2.44 (m, 2H), 2.34 – 2.19 (m, 1H), 2.11 (s, 3H), 2.08 – 1.94 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 189.99, 170.65, 136.31, 134.15, 128.92, 127.57, 118.94, 65.84, 41.88, 27.98, 20.89, 15.19. **HRMS (ESI):** Calcd for $C_{14}H_{16}NO_3S$ $[M+H]^+$ 278.0846, found 278.0847.



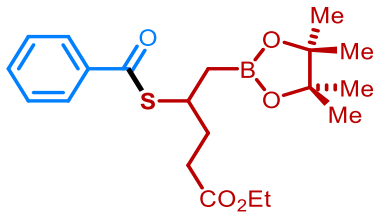
***S*-(1,4-dicyanobutan-2-yl) benzothioate (53):**

The title compound **53** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/20 EA/PE, R_f = 0.3) to give white solid (58.1 mg, 0.238 mmol, 79% yield). **IR (neat):** 3567, 1654, 1419, 1208, 902, 775, 666, 458, 419. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.44 (m, 2H), 4.01 (td, *J* = 10.5, 5.6 Hz, 1H), 2.92 (d, *J* = 5.6 Hz, 2H), 2.74 – 2.50 (m, 2H), 2.37 – 2.09 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 189.61, 135.92, 134.58, 129.07, 127.68, 118.23, 116.60, 39.09, 29.27, 24.87, 15.40. **HRMS (ESI):** Calcd for $C_{13}H_{16}N_3OS$ $[M+NH_4]^+$ 262.1008, found 262.1010.



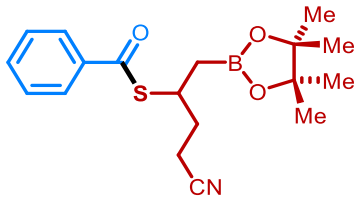
***S*-(4-cyano-1-(1,3-dioxoisoindolin-2-yl) butan-2-yl) benzothioate (54):**

The title compound **54** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/10 EA/PE, R_f = 0.2) to give brown viscous oil (75.8 mg, 0.208 mmol, 69% yield). **IR (neat):** 2952, 1657, 1248, 1205, 1174, 906, 772, 687, 647, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 – 7.82 (m, 4H), 7.78 – 7.69 (m, 2H), 7.63 – 7.51 (m, 1H), 7.47 – 7.41(m, 2H), 4.22 – 4.13 (m, 1H), 4.08 – 3.96 (m, 2H), 2.69 – 2.47 (m, 2H), 2.32 – 2.20 (m, 1H), 2.16 – 1.97 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.08, 168.17, 136.36, 134.38, 134.02, 131.81, 128.83, 127.60, 123.71, 119.01, 42.66, 40.98, 28.81, 15.10. **HRMS (ESI):** Calcd for $C_{20}H_{17}N_2O_3S$ $[M+H]^+$ 365.0955, found 365.0960.



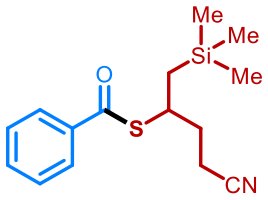
Ethyl 4-(benzoylthio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (55):

The title compound **55** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/30 EA/PE, R_f = 0.2) to give brown viscous oil (63.6 mg, 0.162 mmol, 54% yield). **IR (neat):** 3735, 2978, 2929, 1732, 1660, 1368, 1204, 1109, 908, 846, 689, 648. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 – 7.90 (m, 2H), 7.62 – 7.49 (m, 1H), 7.48 – 7.38 (m, 2H), 4.15 – 4.06 (m, 2H), 4.05 3.94 (m, 1H), 2.49 – 2.39 (m, 2H), 2.20 – 2.05 (m, 1H), 2.07 – 1.98 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 12H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.56, 173.36, 137.37, 133.30, 128.66, 127.36, 83.63, 60.51, 40.69, 32.47, 32.16, 24.97, 24.88, 14.34. **HRMS (ESI):** Calcd for $C_{20}H_{31}BO_5S$ $[M+H]^+$ 393.1902, found 393.1891.



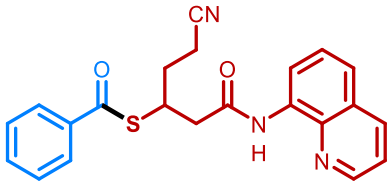
***S*-(4-cyano-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butan-2-yl) benzothio -ate (56):**

The title compound **56** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/30 EA/PE, R_f = 0.3) to give brown viscous oil (63.9 mg, 0.185 mmol, 61% yield). **IR (neat):** 2978, 1661, 1370, 1330, 1206, 1174, 908, 846, 666, 420. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95 – 7.91 (m, 2H), 7.57 (d, J = 7.4 Hz, 1H), 7.49 – 7.40 (m, 2H), 4.03 – 3.94 (m, 1H), 2.51 – 2.44 (m, 2H), 2.23 – 2.06 (m, 2H), 1.29 – 1.38 (m, 2H), 1.23 (d, J = 7.1 Hz, 12H) **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.28, 136.94, 133.68, 128.80, 127.43, 83.86, 40.23, 33.19, 24.97, 24.89, 15.20. **HRMS (ESI):** Calcd for $C_{18}H_{25}BNO_3S$ $[M+H]^+$ 346.1650, found 346.1463.



***S*-(4-cyano-1-(trimethylsilyl) butan-2-yl) benzothioate (57):**

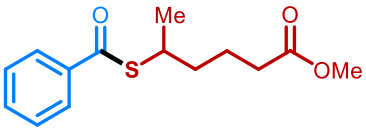
The title compound **57** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/30 EA/PE, R_f = 0.4) to give brown viscous oil (53.6 mg, 0.184 mmol, 61% yield). **IR (neat):** 1772, 1708, 1661, 1392, 1354, 1204, 1174, 903, 666. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 – 7.88 (m, 2H), 7.59 (m, 1H), 7.46 (m, 2H), 3.91 (m, 1H), 2.54 – 2.39 (m, 2H), 2.23 – 1.86 (t, J = 7.6 Hz, 2H), 1.22 – 0.99 (m, 2H), 0.10 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.39, 136.89, 133.76, 128.84, 127.42, 119.58, 40.85, 34.55, 23.56, 14.95, -0.64. **HRMS (ESI):** Calcd for $C_{15}H_{22}NOSSi$ $[M+H]^+$ 292.1186, found 292.1180.



***S*-(5-cyano-1-oxo-1-(quinolin-8-ylamino) pentan-3-yl) benzothioate (58):**

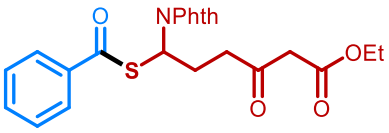
The title compound **58** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica

gel (1/10 EA/PE, R_f = 0.2) to give brown viscous oil (55.7 mg, 0.143 mmol, 48% yield). **IR (neat):** 3735, 2922, 2373, 2156, 1698, 1524, 1370, 1207, 907, 669, 418. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.22 – 8.08 (m, 1H), 7.99 – 7.91 (m, 2H), 7.81 (dd, *J* = 18.9, 7.9 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.50 – 7.38 (m, 3H), 7.15 (t, *J* = 7.7 Hz, 1H), 4.29 (td, *J* = 10.6, 6.2 Hz, 1H), 3.74 – 3.59 (m, 2H), 2.64 – 2.48 (m, 2H), 2.43 – 2.14 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 191.15, 173.47, 150.64, 143.91, 136.25, 133.77, 129.19, 128.83, 128.79, 128.62, 128.43, 128.12, 127.51, 126.23, 121.79, 119.52, 43.07, 39.53, 30.76, 15.39. **HRMS (ESI):** Calcd for $C_{22}H_{19}N_3O_2S$ $[M+H]^+$ 390.1271, found 390.1269.



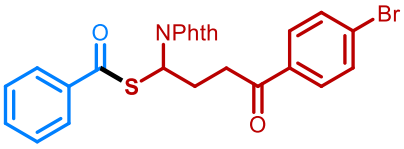
Methyl 5-(benzoylthio) hexanoate (59):

The title compound **59** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (100% PE, R_f = 0.5) to give yellow oil (40.8 mg, 0.152 mmol, 51% yield). **IR (neat):** 2952, 1735, 1656, 1447, 1254, 1204, 1172, 907, 667, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.94(m, 2H), 7.59 – 7.52 (m, 1H), 7.43 (m, 2H), 3.85 – 3.74 (m, 1H), 3.66 (s, 3H), 2.35 (t, *J* = 6.6 Hz, 2H), 1.84 – 1.66 (m, 4H), 1.40 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 191.99, 173.92, 137.37, 133.36, 128.66, 127.29, 51.70, 39.27, 36.16, 33.82, 22.57, 21.51. **HRMS (ESI):** Calcd for $C_{14}H_{19}O_3S$ $[M+H]^+$ 267.1050, found 267.1044.

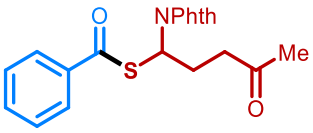


Ethyl 6-(benzoylthio)-6-(1,3-dioxoisoindolin-2-yl)-3-oxohexanoate (60):

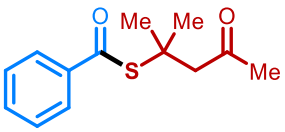
The title compound **60** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/5 EA/ PE, R_f = 0.2) to give brown viscous oil (72.1 mg, 0.164 mmol, 55% yield). **IR (neat):** 3735, 3568, 2370, 1717, 1686, 1540, 1510, 1456, 419. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.49 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 6.44 – 6.37 (m, 1H), 4.13 (q, *J* = 7.9 Hz, 2H), 3.43 (s, 2H), 2.95 – 2.78 (m, 2H), 2.64 – 2.45 (m, 2H), 1.25 (t, *J* = 7.9 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 206.56, 189.74, 167.00, 134.74, 134.33, 132.91, 131.67, 128.92, 128.27, 127.48, 123.85, 61.06, 57.20, 41.27, 30.12, 28.25, 13.45. **HRMS (ESI):** Calcd for $C_{23}H_{21}NO_6S$ $[M+H]^+$ 440.1163, found 440.1167.



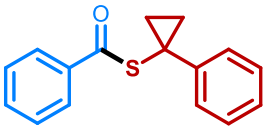
***S*-(4-(4-bromophenyl)-1-(1,3-dioxoisoindolin-2-yl)-4-oxobutyl) benzothioate (61):**
The title compound **61** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/5 EA/ PE, R_f = 0.2) to give yellow solid (118.4 mg, 0.233 mmol, 78% yield). **IR (neat):** 3735, 3567, 2370, 1717, 1684, 1541, 1508, 1457, 418. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (dd, J = 5.5, 3.1 Hz, 2H), 7.87 (dd, J = 5.5, 3.1 Hz, 2H), 7.78-7.70 (m, 4H), 7.60 – 7.52 (m, 3H), 7.47 – 7.40 (m, 2H), 7.25 (s, 1H), 6.38 (m, 1H), 3.22 – 2.99 (m, 2H), 2.81 – 2.61 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.03, 189.66, 167.06, 136.17, 135.36, 134.49, 134.09, 132.04, 131.75, 129.70, 128.87, 128.51, 127.66, 123.83, 51.86, 35.64, 28.89. **HRMS (ESI):** Calcd for $C_{25}H_{19}BrNO_4S$ $[M+H]^+$ 508.0213, found 508.0225.



***S*-(1-(1,3-dioxoisoindolin-2-yl)-4-oxopentyl) benzothioate (62):**
The title compound **62** was prepared according to **Condition B**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/5 EA/ PE, R_f = 0.3) to give yellow solid (71.4 mg, 0.294 mmol, 65% yield). **IR (neat):** 3735, 2987, 2360, 2342, 1653, 1507, 1457, 1066, 669, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 – 7.91 (m, 2H), 7.87 (dd, J = 5.5, 3.1 Hz, 2H), 7.75 (dd, J = 5.5, 3.1 Hz, 2H), 7.57 (m, 1H), 7.43 (m, 2H), 6.26 (m, 1H), 2.69 – 2.45 (m, 4H), 2.13 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 206.52, 189.69, 167.06, 136.15, 134.49, 134.07, 131.73, 128.85, 127.63, 123.81, 51.70, 40.54, 30.10, 28.34. **HRMS (ESI):** Calcd for $C_{20}H_{18}NO_4S$ $[M+H]^+$ 368.0951, found 368.0957.

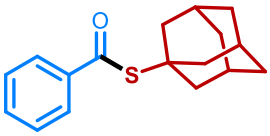


***S*-(2-methyl-4-oxopentan-2-yl) benzothioate (63):**
The title compound **63** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/500 EA/ PE, R_f = 0.7) to give yellow oil (31.7 mg, 0.134 mmol, 45% yield). **IR (neat):** 2924, 1714, 1651, 1361, 1202, 1120, 906, 773, 690. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 – 7.84 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.4 Hz, 2H), 3.24 (s, 2H), 2.15 (s, 3H), 1.63 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 206.75, 193.21, 137.99, 133.37, 128.68, 127.12, 52.08, 49.03, 31.95, 27.96. **HRMS (ESI):** Calcd for $C_{13}H_{17}O_2S$ $[M+H]^+$ 237.0944, found 237.0948.



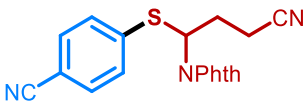
***S*-(1-phenylcyclopropyl) benzothioate (64):**

The title compound **64** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/500 EA/ PE, R_f = 0.6) to give yellow oil (30.0 mg, 0.118 mmol, 39% yield). **IR (neat):** 2925, 1969, 1658, 1463, 1119, 908, 780, 691, 521. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.70 – 7.60 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.38 (m, 2H), 7.37 – 7.27 (m, 2H), 7.25 – 7.17 (m, 1H), 1.55 – 1.48 (m, 2H), 1.46 – 1.36 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.04, 143.47, 137.05, 133.44, 128.92, 128.68, 128.31, 127.17, 127.00, 100.10, 26.32, 16.84. **HRMS (ESI):** Calcd for $C_{16}H_{15}OS$ $[M+H]^+$ 255.0838, found 255.0839.



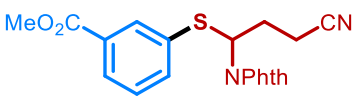
***S*-((3*S*,5*S*,7*S*)-adamantan-1-yl) benzothioate (65):**

The title compound **65** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/500 EA/ PE, R_f = 0.6) to give yellow oil (36.8 mg, 0.135 mmol, 45% yield). **IR (neat):** 3735, 2924, 2357, 1970, 1717, 1653, 1458, 1231, 718. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 2H), 2.27 (s, 6H), 2.10 (s, 3H), 1.85 (d, *J* = 12.6 Hz, 3H), 1.71 (d, *J* = 11.8 Hz, 3H), and spectral data were in accordance with the literature values.[3]

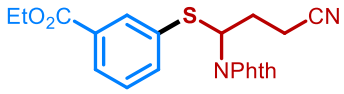


4-((3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) thio) benzonitrile (66):

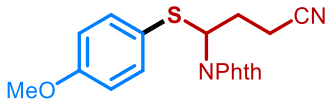
The title compound **66** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give brown viscous oil (58.2 mg, 0.168 mmol, 56% yield). **IR (neat):** 3649, 2359, 1774, 1715, 1616, 1559, 1377, 718, 418. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 – 7.84 (m, 2H), 7.78 – 7.74 (m, 2H), 7.66 (s, 1H), 7.56 – 7.50 (m, 4H), 5.80 (t, *J* = 7.9 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.57 – 2.50 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.97, 139.66, 134.93, 132.84, 131.39, 128.96, 124.05, 118.35, 117.86, 111.43, 56.27, 29.12, 15.46. **HRMS (ESI):** Calcd for $NaC_{19}H_{13}N_3O_2S$ $[M+Na]^+$ 370.0620, found 370.0618.



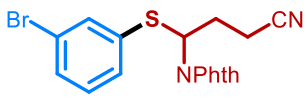
Methyl 3-((3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) thio) benzoate (67):
The title compound **67** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.2) to give brown viscous oil (41.1 mg, 0.11 mmol, 36% yield). **IR (neat):** 3735, 3567, 2360, 1717, 1559, 1508, 1457, 1419,728, 429. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.83-7.80 (m, 2H), 7.77 – 7.72 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 5.61-5.5 (m, 1H), 3.83 (s, 3H), 2.82 – 2.61 (m, 2H), 2.58 – 2.47 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.99, 166.08, 138.14, 134.89, 134.66, 132.80, 131.46, 131.32, 130.10, 129.59, 123.88, 118.07, 58.01, 52.43, 28.93, 15.48. **HRMS (ESI):** Calcd for $C_{20}H_{20}N_3O_4S$ $[M+NH_4]^+$ 398.1169, found 398.1164.



Ethyl 3-((3-cyano-1-(1,3-dioxoisoindolin-2-yl) propyl) thio) benzoate (68):
The title compound **68** was prepared according to **Condition C**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.2) to give brown viscous oil (50.9 mg, 0.13 mmol, 43% yield). **IR (neat):** 2934, 2248, 1712, 1419, 1257, 1104, 881, 716, 600, 418. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 (t, *J* = 1.6 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.83-7.80 (m, 2H), 7.76 – 7.71 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 5.65 – 5.57 (m, 1H), 4.34 – 4.23 (m, 2H), 2.78 – 2.63 (m, 2H), 2.59 – 2.50 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.98, 165.59, 137.92, 134.71, 134.65, 132.75, 131.67, 131.45, 130.03, 129.53, 123.86, 118.07, 61.36, 57.99, 28.94, 15.47, 14.36. **HRMS (ESI):** Calcd for $C_{21}H_{22}N_3O_4S$ $[M+NH_4]^+$ 412.1325, found 412.1321.

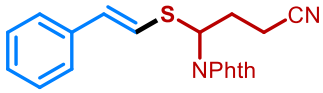


4-(1,3-dioxoisoindolin-2-yl)-4-((4-methoxyphenyl) thio) butanenitrile (69):
The title compound **69** was prepared according to **Condition C**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.2) to give brown viscous oil (38.1 mg, 0.109 mmol, 36% yield). **IR (neat):** 3735, 2923, 2249, 1713, 1379, 1288, 1112, 717, 642, 520. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 5.53 – 5.39 (m, 1H), 3.75 (s, 3H), 2.82 – 2.58 (m, 2H), 2.61 – 2.50 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.09, 160.66, 136.69, 134.56, 131.54, 123.76, 122.29, 118.25, 114.96, 58.78, 55.45, 28.62, 15.48. **HRMS (ESI):** Calcd for $C_{19}H_{17}N_2O_3S$ $[M+H]^+$ 353.0955, found 353.0960.



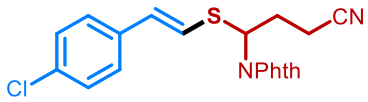
4-((3-bromophenyl) thio)-4-(1,3-dioxoisoindolin-2-yl) butanenitrile (70):

The title compound **70** was prepared according to **Condition C**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.2) to give brown viscous oil (69.8 mg, 0.173 mmol, 58% yield). **IR (neat):** 2934, 2248, 1712, 1419, 1257, 1104, 881, 716, 600, 420. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 – 7.80 (m, 2H), 7.81 – 7.68 (m, 2H), 7.48 – 7.38 (m, 2H), 7.31 – 7.28 (m, 1H), 7.24 – 7.22 (m, 1H), 5.72 – 5.52 (m, 1H), 2.84 – 2.59 (m, 2H), 2.57 – 2.45 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.05, 136.20, 134.75, 134.61, 133.94, 132.13, 132.11, 131.95, 131.50, 130.80, 129.45, 128.96, 123.80, 118.19, 58.09, 29.02, 15.48. **HRMS (ESI):** Calcd for $C_{18}H_{13}BrN_2O_2S$ $[M+NH_4]^+$ 418.0219, found 418.0252.



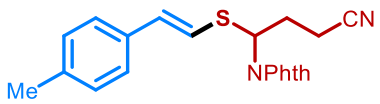
(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-(styrylthio) butanenitrile (71):

The title compound **71** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.3) to give yellow viscous oil (75.8 mg, 0.217 mmol, 72% yield). **IR (neat):** 2968, 2360, 2342, 1717 1604, 1507, 1457, 1066, 669. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0Hz, 2H), 7.31 – 7.26 (m, 3H), 7.26 – 7.19 (m, 2H), 6.85 (d, *J* = 15.5 Hz, 1H), 6.66 (d, *J* = 15.5 Hz, 1H), 5.60 (t, *J* = 7.9 Hz, 1H), 2.73 – 2.67 (m, 2H), 2.58 – 2.54 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.37, 136.06, 134.71, 133.81, 131.54, 128.80, 128.03, 126.25, 123.94, 120.61, 118.15, 55.38, 28.60, 15.50. **HRMS (ESI):** Calcd for $C_{20}H_{17}N_2O_2S$ $[M+H]^+$ 349.1005, found 349.1009.



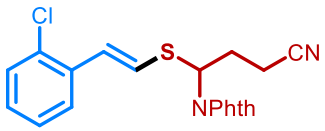
(*E*)-4-((4-chlorostyryl) thio)-4-(1,3-dioxoisoindolin-2-yl) butanenitrile (72):

The title compound **72** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:6 EA/PE, R_f = 0.2) to give yellow viscous oil (83.4 mg, 0.218 mmol, 72% yield). **IR (neat):** 2926, 1710, 1378, 1326, 1088, 1011, 952, 681, 660, 528. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.21 (m, 1H), 7.20 – 7.17 (m, 2H), 6.85 (d, *J* = 15.5 Hz, 1H), 6.60 (d, *J* = 15.5 Hz, 1H), 5.60 (t, *J* = 7.9 Hz, 1H), 2.72 – 2.63 (m, 2H), 2.63 – 2.51 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.35, 134.77, 134.57, 133.64, 132.05, 131.52, 128.97, 127.38, 123.96, 121.63, 118.09, 55.37, 28.60, 15.51. **HRMS (ESI):** Calcd for $C_{20}H_{16}ClN_2O_2S$ $[M+H]^+$ 383.0616, found 383.0623.

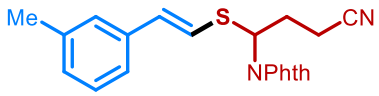


(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-((4-methylstyryl) thio) butanenitrile (73):

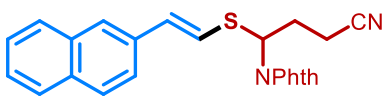
The title compound **73** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.3) to give brown viscous oil (62.8 mg, 0.173 mmol, 58% yield). **IR (neat):** 3735, 3649, 3567, 1716, 1508, 1457, 1379, 716, 527, 418. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 15.5 Hz, 1H), 6.64 (d, *J* = 15.5 Hz, 1H), 5.57 (t, *J* = 7.9 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.62 – 2.52 (m, 2H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 167.36, 138.06, 134.67, 134.35, 133.31, 131.56, 129.48, 126.21, 123.90, 119.19, 118.17, 55.45, 28.60, 21.36, 15.49. **HRMS (ESI):** Calcd for $C_{21}H_{19}N_2O_2S$ $[M+H]^+$ 363.1162, found 363.1167.



(*E*)-4-((2-chlorostyryl) thio)-4-(1,3-dioxoisoindolin-2-yl) butanenitrile (74):
The title compound **74** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:6 EA/PE, R_f = 0.2) to give yellow viscous oil (60.6 mg, 0.158 mmol, 52% yield). **IR (neat):** 3735, 2926, 2248, 1714, 1377, 1321, 1066, 882, 689, 529. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.12 (m, 3H), 7.02 (d, *J* = 15.5 Hz, 1H), 6.90 (d, *J* = 15.5 Hz, 1H), 5.62 (t, *J* = 7.9 Hz, 1H), 2.74 – 2.68 (m, 2H), 2.59 – 2.56 (m, 2H) **^{13}C NMR (100 MHz, CDCl$_3$):** δ 167.37, 134.76, 134.39, 132.61, 131.55, 129.85, 128.92, 127.11, 126.73, 125.09, 123.98, 123.62, 118.10, 55.44, 28.61, 15.51. **HRMS (ESI):** Calcd for $C_{20}H_{16}ClN_2O_2S$ $[M+H]^+$ 383.0616, found 383.0624.

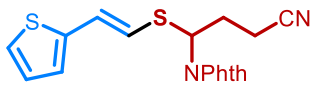


(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-((3-methylstyryl) thio) butanenitrile (75):
The title compound **75** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.3) to give brown viscous oil (78.3 mg, 0.22 mmol, 72% yield). **IR (neat):** 3735, 2928, 2247, 1772, 1709, 1662, 1392, 1205, 903, 667. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.14 – 6.98 (m, 3H), 6.82 (d, *J* = 15.5 Hz, 1H), 6.64 (d, *J* = 15.5 Hz, 1H), 5.59 (t, *J* = 7.9 Hz, 1H), 2.72 – 2.67 (m, 2H), 2.61 – 2.50 (m, 2H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 167.35, 138.40, 136.00, 134.68, 134.16, 131.57, 128.87, 128.68, 126.98, 123.92, 123.42, 120.26, 118.15, 55.41, 28.65, 21.49, 15.49. **HRMS (ESI):** Calcd for $C_{21}H_{19}N_2O_2S$ $[M+H]^+$ 363.1162, found 363.1166.



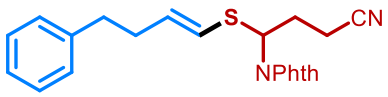
(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-((2-(naphthalen-2-yl) vinyl) thio) butanenitrile (76):

The title compound **76** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.3) to give brown viscous oil (65.0 mg, 0.163 mmol, 54% yield). **IR (neat):** 3735, 3567, 2369, 2156, 1716, 1473, 1396, 882, 688, 418. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, J = 5.5, 3.1 Hz, 2H), 7.79 – 7.73 (m, 6H), 7.49 – 7.42 (m, 3H), 6.98 (d, J = 15.5 Hz, 1H), 6.82 (d, J = 15.5 Hz, 1H), 5.64 (t, J = 7.9 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.62 – 2.56 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.38, 134.69, 133.76, 133.52, 133.50, 133.06, 131.52, 128.50, 128.13, 127.77, 126.53, 126.23, 123.92, 123.16, 121.01, 118.17, 55.43, 28.60, 15.48. **HRMS (ESI):** Calcd for $C_{24}H_{19}N_2O_2S$ $[M+H]^+$ 399.1162, found 399.1168.



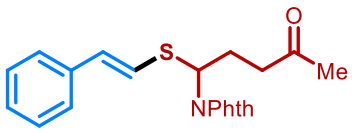
(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-((2-(thiophen-2-yl) vinyl) thio) butanenitrile (77):

The title compound **77** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.2) to give brown oil (50.7 mg, 0.143 mmol, 48% yield). **IR (neat):** 2927, 2247, 1777, 1709, 1377, 1325, 1104, 881, 714, 529. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.16 – 7.15(m, 1H), 6.96 – 6.86 (m, 2H), 6.80 (d, *J* = 15.2 Hz, 1H), 6.65 (d, *J* = 15.2 Hz, 1H), 5.54 (t, *J* = 7.9 Hz, 1H), 2.72 – 2.65 (m, 2H), 2.58 – 2.50 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.31, 140.82, 134.71, 131.56, 127.92, 127.59, 125.94, 125.20, 123.95, 119.44, 118.12, 55.52, 28.65, 15.48. **HRMS (ESI):** Calcd for $C_{18}H_{15}N_2O_2S_2$ $[M+H]^+$ 355.0570, found 355.0564.



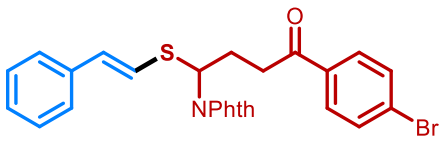
(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-((4-phenylbut-1-en-1-yl)thio)butanenitrile (78):

The title compound **78** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:5 EA/PE, R_f = 0.4) to give brown viscous oil (67.3 mg, 0.175 mmol, 58% yield). **IR (neat):** 3736, 2929, 2248, 1777, 1710, 1379, 1106, 881, 716, 530. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), ,7.31 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 6.14 – 6.06 (m, 1H), 5.90 (dd, *J* = 15.5 ,1.4 Hz, 1H), 5.65 (t, *J* = 7.9 Hz, 1H), 3.12 – 2.73 (m, 4H), 2.68 – 2.54 (m, 2H), 2.42 – 2.31 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.37, 139.47, 134.79, 131.55, 128.90, 128.84, 128.45, 126.77, 123.90, 120.67, 118.14, 55.41, 31.26, 30.08, 28.63, 15.53. **HRMS (ESI):** Calcd for $C_{22}H_{24}N_3O_2S$ $[M+NH_4]^+$ 394.1583, found 394.1588.



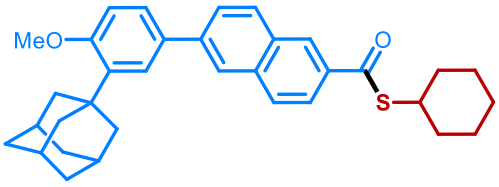
(*E*)-4-(1,3-dioxoisoindolin-2-yl)-4-((2-(naphthalen-2-yl)vinyl)thio)butanenitrile (79):

The title compound **79** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.3) to give brown viscous oil (81.4 mg, 0.204 mmol, 68% yield). **IR (neat):** 3735, 2917, 1707, 1378, 1350, 1327, 1163, 944, 716, 691. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, J = 5.5, 3.1 Hz, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.26 – 7.16 (m, 4H), 6.84 (d, J = 15.5 Hz, 1H), 6.61 (d, J = 15.5 Hz, 1H), 5.54 (t, J = 7.9 Hz, 1H), 2.68 – 2.47 (m, 4H), 2.14 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 206.75, 167.47, 136.41, 134.49, 132.09, 131.67, 128.74, 127.68, 126.10, 123.75, 121.89, 56.07, 40.64, 30.15, 26.94. **HRMS (ESI):** Calcd for $C_{21}H_{23}N_2O_3S$ $[M+NH_4]^+$ 416.1427, found 416.1429.



(*E*)-2-(4-(4-bromophenyl)-4-oxo-1-(styrylthio) butyl) isoindoline-1,3-dione (80):

The title compound **80** was prepared according to **Condition D**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1:4 EA/PE, R_f = 0.2) to give brown viscous solid (98.5 mg, 0.193 mmol, 64% yield). **IR (neat):** 3735, 2926, 2361, 1716, 1684, 1541, 1473, 1419, 1396, 688, 419. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (dd, J = 5.5, 3.1 Hz, 2H), 7.80 – 7.78 (m, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 7.58 – 7.55 (m, 2H), 7.39 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 6.86 (d, J = 15.5 Hz, 1H), 6.62 (d, J = 15.5 Hz, 1H), 5.65 (t, J = 7.9 Hz, 1H), 3.17 – 3.07 (m, 2H), 2.84 – 2.68 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.26, 167.47, 136.39, 135.35, 134.49, 132.33, 132.08, 131.71, 129.71, 128.75, 128.41, 127.72, 126.12, 123.77, 121.85, 56.23, 35.72, 27.50. **HRMS (ESI):** Calcd for $C_{26}H_{24}BrN_2O_3S$ $[M+NH_4]^+$ 523.0685, found 523.0693.



***S*-cyclohexyl 6-(3-((3*R*,5*R*,7*R*)-adamantan-1-yl)-4-methoxyphenyl) naphthalene-2-carbothioate (83):**

The title compound **83** was prepared according to **Condition B** but **L2** was used instead of **L3**. The pure product was isolated by preparative thin-layer chromatography on silica gel (1/500 EA/ PE, R_f = 0.8) to give yellow oil (78.4 mg, 0.154 mmol, 51% yield). **IR (neat):** 3735, 2926, 2358, 1717, 1684, 1508, 1457, 1230, 717. **^{1}H NMR (400 MHz,**

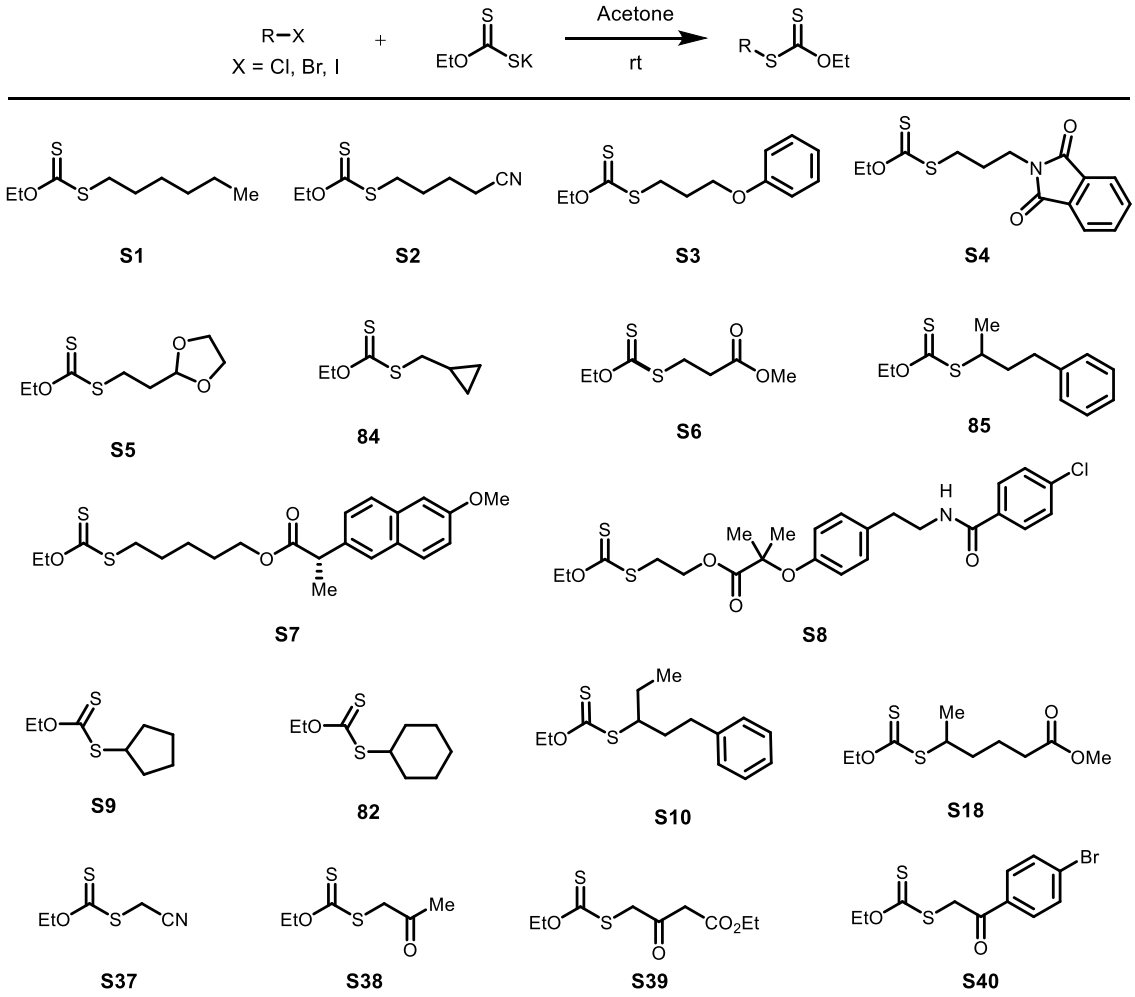
$CDCl_3$): δ 8.73 (s, 1H), 8.29 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.00 (d, *J* = 9.4 Hz, 2H), 7.87 – 7.76 (m, 1H), 7.63 – 7.53 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.79 – 3.67 (m, 1H), 2.18 (s, 6H), 2.08 (s, 3H), 1.80 (s, 6H), 1.63 – 1.55 (m, 10H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.90, 159.04, 139.11, 135.98, 135.34, 132.68, 131.79, 131.24, 130.36, 129.42, 127.85, 126.59, 126.07, 125.87, 125.83, 124.76, 112.21, 68.81, 55.31, 40.73, 37.34, 37.26, 29.85, 29.23, 14.07. **HRMS (ESI):** Calcd for $C_{34}H_{39}O_2S$ $[M+H]^+$ 511.2666, found 511.2675.

10. Synthesis and Characterization of Substrates

■ Methods for the Synthesis of Alkyl Xanthate Esters

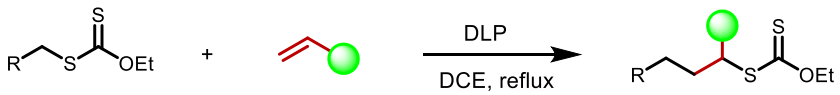
Note: Generally, the identical alkyl xanthate ester can be prepared by a few alternative synthetic methods. However, the exact synthetic procedure adopted in the paper for each alkyl xanthate ester has been carefully indicated before the characterization data.

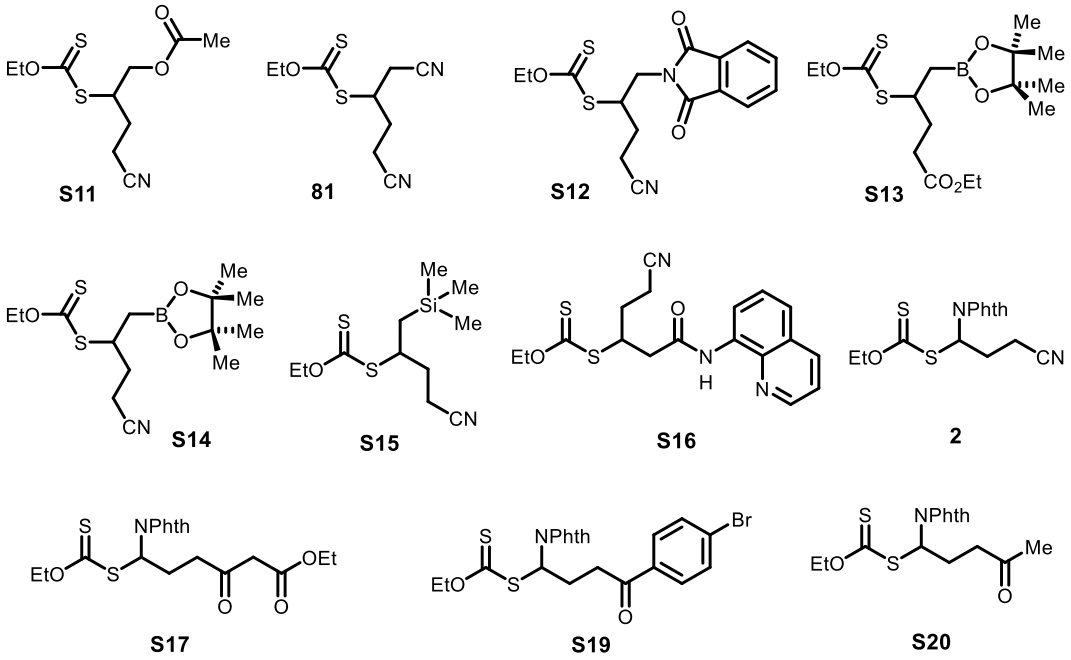
Condition E [4]



Note: *Alternatively, these substrates can be prepared using condition E.*
To a solution of potassium ethyl xanthate esters (1.5 equiv) in acetone (0.75 M) was added alkyl bromide (1.0 equiv). The mixture was stirred at rt until consumption of the alkyl bromide as determined by TLC. The mixture was concentrated and taken up in EtOAc and washed with H_2O, brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel.

Condition F[5]

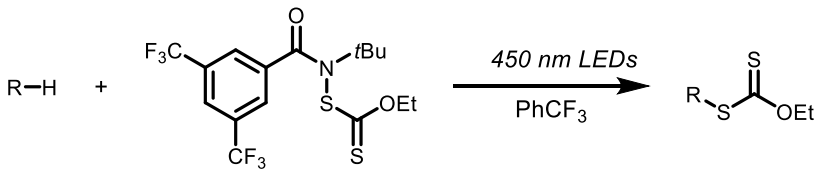


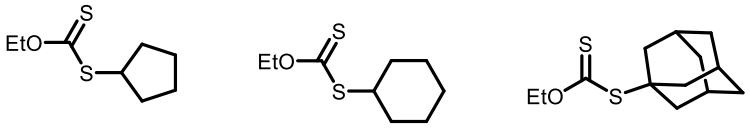


Note: *Alternatively, these substrates can be prepared using condition F.*

To a solution of alkene (1.0 equiv) in DCE (0.50 M) was added ethyl xanthate esters (2.0 equiv). Then the solution was refluxed for 15 min. DLP (5 mol%) was added, and additional DLP (di-lauroyl peroxide, 5 mol%) was added every 60 min until consumption of alkene (TLC monitored). The mixture was then cooled to room temperature, evaporating the solvent under reduced pressure. The residue was purified by flash chromatography on silica gel.

Condition G [6]

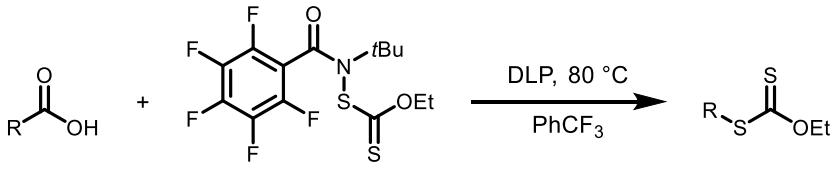


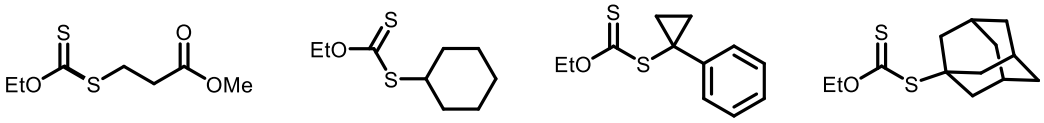


Note: *Alternatively, these substrates can be prepared using condition G.*

According to the reported method.[6] To a solution of xanthylamide (1.5 equiv) in $PhCF_3$ (1.0 M), the hydrocarbon (1.0 equiv) was added. Then the resulting solution was irradiated with 450 nm LEDs. Upon completion (GC analysis), the reaction was concentrated in vacuo, and the crude residue was purified by flash column chromatography to afford the desired product.

Condition H[7]



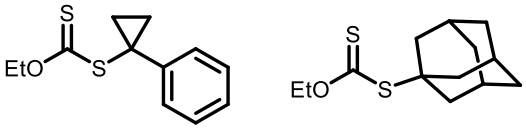


S6 **82** **S22** **S23**

Note: *Alternatively, these substrates can be prepared using condition H.*

According to the reported method.[7] To a solution of carboxylic acid (1.0 equiv) in $PhCF_3$ (0.1 M), DLP (10 mol %) and xanthylamide (1.5 equiv) was added. Then the mixture was heated at 80 ℃ for 4 hours. Upon completion (TLC analysis), the reaction was concentrated in vacuo, and the crude residue was purified by flash column chromatography to afford the desired product.

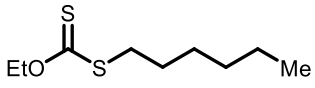
Condition I[9]



S22 **S23**

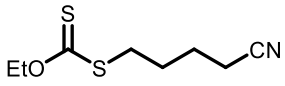
Note: *Alternatively, these substrates can be prepared using condition I.*

To a solution of acyl chloride (1.1 equiv) in acetone (0.25 M), potassium ethyl xanthate esters (1.0 equiv) in acetone (0.20 M) were added dropwise at room temperature. The mixture was stirred for 1 hour at -35 °C, then slowly heated to room temperature for 12 h. After filtration through Celite and concentration, the crude acyl xanthate was dissolved in octane (0.35 M) and irradiated by a 300 W tungsten lamp for 5 h. The solution was then concentrated under a vacuum, and the crude residue was purified by flash column chromatography to afford the desired product.

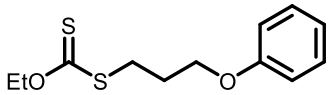


***O*-ethyl *S*-hexyl carbonodithioate (S1):**

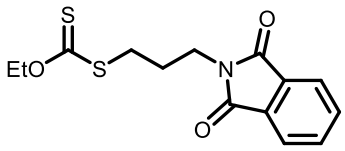
Prepared from 1-bromohexane according to **Condition E** (1.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (0.180 g, 0.870 mmol, 87% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 1.67 (q, *J* = 7.5 Hz, 2H), 1.48 – 1.37 (m, 5H), 1.33 – 1.27 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H), and spectral data were in accordance with the literature values.[4]



***S*-(4-cyanobutyl) *O*-ethyl carbonodithioate (S2):**
Prepared from 5-bromopentanenitrile according to **Condition E** (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a yellow oil (0.272 g, 1.34 mmol, 67% yield). **IR (neat):** 2937, 1455, 1209, 1145, 1110, 1040, 853, 431. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 4.64 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.39 (t, *J* = 6.9 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.82 – 1.72 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 214.49, 119.34, 70.22, 34.78, 27.68, 24.51, 16.94, 13.88. **HRMS (ESI):** Calcd for $C_8H_{14}NOS_2$ $[M+H]^+$ 204.0512, found: 204.0518.

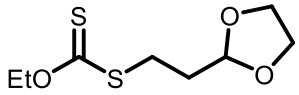


***O*-ethyl *S*-(3-phenoxypropyl) carbonodithioate (S3):**
Prepared from (3-bromopropoxy) benzene according to **Condition E** (3.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.5) to give a yellow oil (0.400 g, 1.56 mmol, 52% yield). **IR (neat):** 2932, 1600, 1586, 1496, 1469, 1386, 1290, 1210, 1172, 1047, 812,691. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.28 (dd, *J* = 13.5, 5.7 Hz, 2H), 7.05 – 6.86 (m, 3H), 4.65 (q, *J* = 7.1 Hz, 2H), 4.08 (dt, *J* = 11.9, 5.8 Hz, 2H), 3.41 – 3.27 (m, 2H), 2.29 – 2.12 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 214.80, 158.81, 129.61, 120.96, 114.59, 70.11, 66.09, 32.59, 28.47, 13.94. **HRMS (ESI):** Calcd for $[M+H]^+$ $C_{12}H_{17}O_2S_2$ 257.0665, found: 257.0665.



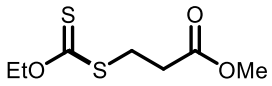
***S*-(3-(1,3-dioxoisoindolin-2-yl) propyl) *O*-ethyl carbonodithioate (S4):**
Prepared from 2-(3-bromopropyl) isoindoline-1,3-dione according to **Condition E** (2.0 mmol scale). The pure product was isolated by column chromatography (1/50 EA/PE, R_f = 0.4) to give a yellow oil (0.433 g, 1.40 mmol, 70% yield). **IR (neat):** 1771, 1704, 1467, 1435, 1392, 1361, 1289, 1209, 1108, 1044, 1011,714. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.86 (dd, J = 5.5, 3.0 Hz, 2H), 7.73 (dd, J = 5.4, 3.1 Hz, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 3.80 (t, *J* = 6.8 Hz, 2H), 3.14 (dd, *J* = 8.1, 6.8 Hz, 2H), 2.09 (m, *J* = 13.4, 6.7

Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 214.53,168.48, 134.18, 132.15, 123.45, 70.17, 37.10, 33.10, 28.07, 13.90. **HRMS (ESI):** Calcd for $C_{14}H_{16}NO_3S_2$ $[M+H]^+$ 310.0566, found: 310.0557.



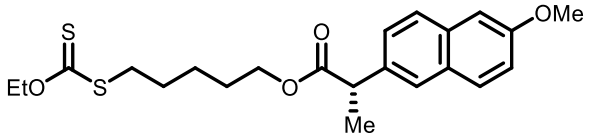
***O*-ethyl *S*-(3-phenoxypropyl) carbonodithioate (S5):**

Prepared from 2-(2-bromoethyl)-1,3-dioxolane according to **Condition E** (1.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a yellow oil (0.135 g, 0.610 mmol, 61% yield).**IR (neat):** 2882, 1390, 1206, 1110, 1043, 942, 867, 1210, 443.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.97 (t, J = 4.3 Hz, 1H), 4.64 (q, J = 7.1 Hz, 2H), 4.02 – 3.94 (m, 2H), 3.92 – 3.82 (m, 2H), 3.24 – 3.19 (m, 2H), 2.07 (td, J = 7.5, 4.6 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 214.76, 103.08, 70.02, 65.18, 32.72, 30.21, 13.93. **HRMS (ESI):** Calcd for $C_8H_{16}O_3S_2$ $[M+H]^+$ 223.0457, found: 223.0453.



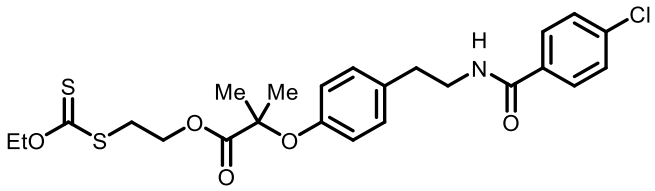
Methyl 3-((ethoxycarbonothioyl)thio) propanoate (S6):

Prepared from 4-methoxy-4-oxobutanoic acid according to **Condition H** (2.0 mmol scale). The pure product was isolated by column chromatography (1/40 EA/PE, R_f = 0.6) to give a yellow oil (0.358 g, 1.72 mmol, 86% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.63 (q, J = 7.1 Hz, 2H), 3.71 (s, 3H), 3.37 (t, J = 7.1 Hz, 2H), 2.87 (t, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[7]



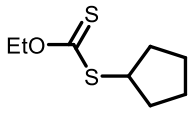
5-((ethoxycarbonothioyl)thio)pentyl(*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (S7):

Prepared from **S33** (1.0 mmol scale) according to **Condition E**. The pure product was isolated by column chromatography (1/4 EA/PE, R_f = 0.6) to give a brown viscous oil (0.215 g, 0.510 mmol, 51% yield). **IR (neat):** 2937, 2926, 2156, 1699, 1568, 1419, 1117, 518. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 – 7.61 (m, 3H), 7.40 (d, J = 8.4 Hz, 1H), 7.22 – 7.08 (m, 2H), 4.63 (q, J = 7.1 Hz, 2H), 4.17 – 3.98 (m, 2H), 3.91 (s, 3H), 3.88 – 3.82 (m, 1H), 3.05 – 2.87 (m, 2H), 1.67 – 1.55 (m, 7H), 1.45 – 1.36 (q, J = 7.1 Hz, 3H), 1.36 – 1.24 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 215.12, 174.79, 157.72, 135.86, 133.78, 129.36, 129.02, 127.24, 126.34, 126.04, 119.11, 105.69, 69.93, 64.54, 55.43, 45.62, 35.68, 28.19, 28.06, 25.25, 18.53, 13.93. **HRMS (ESI):** Calcd for $C_{22}H_{29}O_4S_2$ $[M+H]^+$ 421.1502, found: 421.1504.



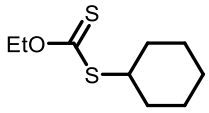
2-((ethoxycarbonothioyl)thio)ethyl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate (S8):

Prepared from **S33** (1.0 mmol scale) according to **Condition E**. The pure product was isolated by column chromatography (1/5 EA/PE, R_f = 0.6) to give a brown viscous oil (0.296 g, 0.58 mmol, 58% yield). **IR (neat):** 2932, 2926, 2832, 1717, 1658, 1601, 912, 851, 519. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 6.13 (s, 1H), 4.62 (q, J = 7.1 Hz, 2H), 4.40 (t, J = 6.4 Hz, 2H), 3.68 – 3.63 (m, 2H), 3.36 (t, J = 6.4 Hz, 2H), 2.84 (d, J = 6.4 Hz, 2H), 1.60 (s, 6H), 1.44 – 1.37 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 213.50, 174.10, 166.50, 154.13, 137.71, 133.07, 132.62, 129.69, 128.90, 128.39, 119.43, 79.19, 70.57, 62.90, 41.36, 34.82, 34.30, 25.51, 13.87. **HRMS (ESI):** Calcd for $C_{24}H_{29}ClNO_5S_2$ $[M+H]^+$ 510.1170, found: 510.1158.



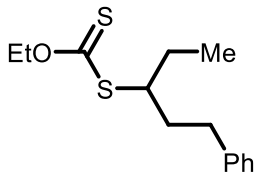
***S*-cyclopentyl *O*-ethyl carbonodithioate (S9):**

Prepared from cyclopentane according to **Condition G** (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.4) to give a yellow oil (0.228 g, 1.20 mmol, 60% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.63 (q, J = 7.1 Hz, 2H), 3.97 – 3.84 (m, 1H), 2.16 (dt, J = 9.0, 5.1 Hz, 2H), 1.69 – 1.65 (m, 6H), 1.41 (t, J = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[6]



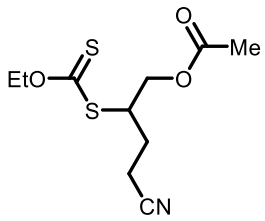
***S*-cyclohexyl *O*-ethyl carbonodithioate (82):**

Prepared from bromocyclohexane according to **Condition E** (1.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a yellow oil (0.151 g,0.74 mmol, 74% yield). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 4.63 (q, J = 7.1 Hz, 2H), 3.97 – 3.84 (m, 1H), 2.16 (dt, J = 9.0, 5.1 Hz, 2H), 1.67 (m, 2H), 1.63 – 1.51 (m, 6H), 1.40 (t, J = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[6]



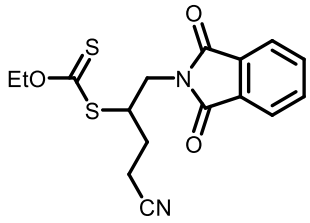
***O*-ethyl *S*-(4-phenylbutan-2-yl) carbonodithioate (S10):**

Prepared from (3-bromobutyl) benzene according to **Condition E** (3.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (0.532 g, 1.98 mmol, 66% yield). **IR (neat):** 2964, 1496, 1453, 1205, 1144, 1109, 1041, 746, 698, 474. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 3H), 4.64 (q, *J* = 7.1 Hz, 2H), 3.87 – 3.59 (m, 1H), 2.84 – 2.64 (m, 2H), 2.07 – 1.89 (m, 2H), 1.76 (d, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 214.71, 141.59, 128.47, 126.03, 69.74, 52.35, 35.59, 33.28, 27.31, 13.87, 11.26. **HRMS (ESI):** Calcd 269.1028 for $C_{14}H_{21}OS_2$ $[M+H]^+$ found: 269.1023.



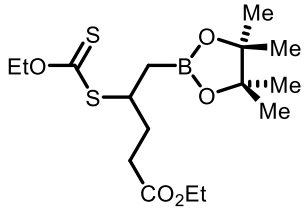
Methyl 5-((ethoxycarbonothioyl)thio) hexanoate (S11):

Prepared from *S*-(cyanomethyl) *O*-ethyl and allyl acetate according to **Condition F** (1.5 mmol scale). The pure product was isolated by column chromatography (1/40 EA/PE, R_f = 0.4) to give a yellow viscous oil (0.288 g, 1.10 mmol, 71% yield). **IR (neat):** 3335, 2929, 1739, 1681, 1522, 1484, 1423, 1386, 1323, 1213, 1110,1041. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.65 (q, *J* = 7.1 Hz, 2H), 4.33 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.27 – 4.18 (m, 1H), 4.14 – 3.94 (m, 1H), 2.61 – 2.46 (m, 2H), 2.26 – 2.14 (m, 1H), 2.08 (s, 3H), 2.03 – 1.91 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 211.60, 170.54, 118.77, 70.86, 65.11, 48.20, 27.20, 20.82, 15.14, 13.80. **HRMS (ESI):** Calcd for $C_{10}H_{19}N_2O_3S_2$ $[M+NH_4]^+$ 279.0831, found: 279.0820.



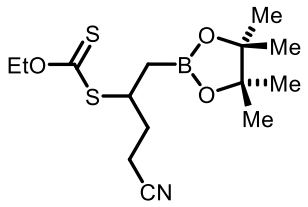
***S*-(4-cyano-1-(1,3-dioxoisoindolin-2-yl) butan-2-yl) *O*-ethyl carbonodithioate (S12):**

Prepared from *S*-(cyanomethyl) *O*-ethyl and 2-allylisoindoline-1,3-dionecarbonodithi - oate according to **Condition F** (2.0 mmol scale). The pure product was isolated by column chromatography (1/10 EA/PE, R_f = 0.4) to give a yellow oil (0.523 g, 1.50 mmol, 75% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, *J* = .5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5,3.0 Hz, 2H), 4.63 (q, *J* = 7.1 Hz, 2H), 4.24 (m, 1H), 4.03 (dd *J* = 14.1, 7.1 Hz, 1H), 3.96 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.76 (m, 1H), 2.56 (m, 1H), 2.19 (m, 1H), 2.00 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[10]



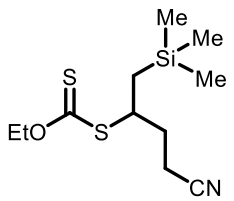
Ethyl 4-((ethoxycarbonothioyl)thio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentanoate (S13):

Prepared from ethy 1,2-((ethoxycarbonothioyl)thio)acetate and 2-allyl-4,4,5,5-tetrame -thyl-1,3,2-dioxaborolane according to **Condition F** (1.0 mmol scale). The pure product was isolated by column chromatography (1/30 EA/PE, R_f = 0.4) to give a yellow viscous oil (0.192 g, 0.51 mmol, 51% yield). **IR (neat):** 2978, 1733, 1366, 1327, 1208, 1141, 1109, 1045, 967, 848, 672. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.62 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 4.01 – 3.90 (m, 1H), 2.48 – 2.38 (m, 2H), 2.13 – 1.96 (m, 2H), 1.41 (t, J = 7.1 Hz, 3H), 1.28 (dd, J = 11.5, 4.4 Hz, 3H), 1.23 (d, J = 3.6 Hz, 14H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 214.24, 173.21, 83.68, 69.74, 60.54, 47.13, 31.89, 31.46, 24.91, 24.86, 14.34, 13.90. **HRMS (ESI):** Calcd for $C_{16}H_{30}BO_5S_2$ $[M+H]^+$ 377.1622, found: 377.1615.



***S*-(4-cyano-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butan-2-yl) *O*-ethyl carbonodithioate (S14):**

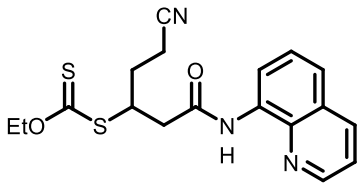
Prepared from *S*-(cyanomethyl) *O*-ethyl and 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxa -borolane according to **Condition F** (2.0 mmol scale). The pure product was isolated by column chromatography (1/30 EA/PE, R_f = 0.3) to give a yellow oil (0.382 g, 1.16 mmol, 58% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.65 (q, J = 7.1 Hz, 2H), 4.06 – 3.93 (m, 1H), 2.48 (t, J = 7.6 Hz, 2H), 2.23 – 2.02 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.24 (d, J = 3.5 Hz, 12H), and spectral data were in accordance with the literature values.[11]



***O*-ethyl *S*-(4-isocyano-1-(trimethylsilyl) butan-2-yl) carbonodithioate (S15):**

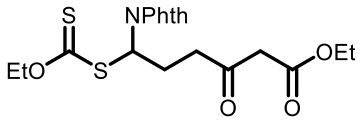
Prepared from *S*-(cyanomethyl) *O*-ethyl and allyltrimethylsilane according to

Condition F (1.0 mmol scale). The pure product was isolated by column chromatography (1/30 EA/PE, R_f = 0.4) to give a yellow oil (0.174 g, 0.630 mmol, 63% yield). **IR (neat):** 2953, 1444, 1248, 1212, 1110, 1045, 839, 695. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.64 (q, *J* = 7.1 Hz, 2H), 3.93-3.89 (m, 1H), 2.49 (t, J = 7.6 Hz, 2H), 2.18-2.09 (m, 1H), 2.04-1.95 (m, 1H), 1.43 (t, J = 7.1 Hz, 3H), 1.10 (dd, J = 15.0, 8.2 Hz, 1H), 0.99 (dd, J = 15.0, 7.3 Hz, 1H), 0.08 (d, J = 10.7 Hz, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 213.31, 119.41, 70.23, 47.26, 33.50, 22.64, 14.86, 13.92, -0.66. **HRMS (ESI):** Calcd for $C_{11}H_{25}N_2OS_2Si$ $[M+NH_4]^+$ 293.1172, found: 293.1166.



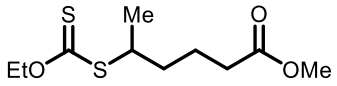
***O*-ethyl *S*-(5-isocyano-1-oxo-1-(quinolin-8-ylamino) pentan-3-yl) carbonodithioate (S16):**

Prepared from *S*-(cyanomethyl) *O*-ethyl and *N*-(quinolin-8-yl) but-3-enamide according to **Condition F** (2.0 mmol scale). The pure product was isolated by column chromatography (1/10 EA/PE, R_f = 0.3) to give a yellow oil (0.306 g, 0.820 mmol, 41% yield). **IR (neat):** 3336, 2926, 1681, 1522, 1484, 1423, 1386, 1323, 1214, 1147, 1110,1042. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.95 (s, 1H), 8.81 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.76 – 8.71 (m, 1H), 8.18 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.67 (q, *J* = 7.1 Hz, 2H), 4.33 (m, 1H), 3.15 (dd, *J* = 15.5, 5.1 Hz, 1H), 2.98 (dd, *J* = 15.5, 7.7 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.41 – 2.33 (m, 1H), 2.26 – 2.17 (m, 1H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 212.64, 167.88, 148.39, 136.61, 134.09, 128.06, 127.48, 122.12, 121.88, 119.06, 116.85, 70.66, 46.38, 42.49, 29.82, 15.45, 13.92. **HRMS (ESI):** Calcd for $C_{18}H_{20}N_3O_2S_2$ $[M+H]^+$ 374.0992, found: 374.0982.

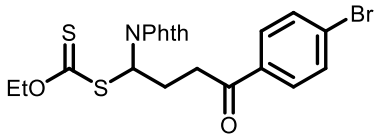


Ethyl 6-(1,3-dioxoisoindolin-2-yl)-6-((ethoxycarbonothioyl)thio)-3-oxohexanoate (S17):

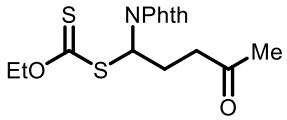
Prepared from ethyl 4-((ethoxycarbonothioyl)thio)-3-oxobutanoate and 2-vinylisoino - line-1,3-dione according to **Condition F** (3.0 mmol scale). The pure product was isolated by column chromatography (1/3 EA/PE, R_f = 0.3) to give a yellow oil (0.534 g, 1.26 mmol, 42% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 – 7.82 (m, 2H), 7.81 – 7.68 (m, 2H), 6.28 (t, *J* = 7.8 Hz, 1H), δ 4.65 (q, *J* = 7.1 Hz, 2H), 4.28 – 4.03 (m, 2H), 3.43 (d, *J* = 14.0 Hz, 2H), 2.82 – 2.58 (m, 2H), 2.55 – 2.44 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.20 (m, 3H), and spectral data were in accordance with the literature values.[5]



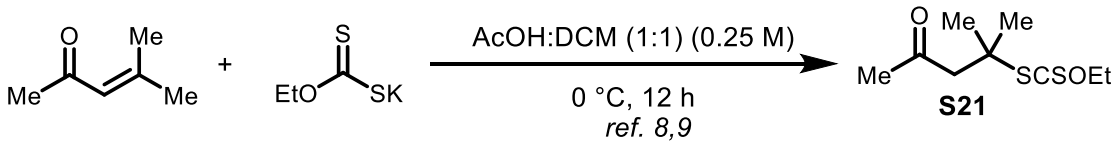
Methyl 5-((ethoxycarbonothioyl)thio) hexanoate (S18):
Prepared from methyl 5-bromohexanoate according to **Condition E** (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a yellow oil (0.250 g, 1.00 mmol, 50% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.60 (q, *J* = 7.1 Hz, 2H), 3.70 (dd, *J* = 13.5, 6.7 Hz, 1H), 3.63 (d, *J* = 7.4 Hz, 3H), 2.31 (q, *J* = 6.8 Hz, 2H), 1.77 – 1.61 (m, 4H), 1.37 (m, *J* = 16.8, 7.1 Hz, 6H), and spectral data were in accordance with the literature values.[6]



***S*-(4-(4-bromophenyl)-1-(1,3-dioxoisoindolin-2-yl)-4-oxobutyl) *O*-ethyl carbonodi -thioate (S19):**
Prepared from *S*-(2-(4-bromophenyl)-2-oxoethyl) *O*-ethyl carbonodithioate and 2-vinylisoindoline-1,3-dione according to **Condition F** (5.0 mmol scale). The pure product was isolated by column chromatography (1/3 EA/PE, R_f = 0.2) to give a yellow solid (1.92 g, 3.90 mmol, 78% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.80 – 7.71 (m, 4H), 7.57 (d, *J* = 8.6 Hz, 2H), 6.38 (t, *J* = 7.9 Hz, 1H), 4.61 (dq, *J* = 7.1, 2.6 Hz, 2H), 3.17 – 3.02 (m, 2H), 2.72 – 2.56 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[5]

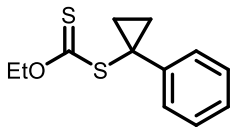


***S*-(1-(1,3-dioxoisoindolin-2-yl)-4-oxopentyl) *O*-ethyl carbonodithioate (S20):**
Prepared from *O*-ethyl *S*-(2-oxopropyl) carbonodithioate and 2-vinylisoindoline -1,3-dione according to **Condition F** (3.0 mmol scale). The pure product was isolated by column chromatography (1/4 EA/PE, R_f = 0.3) to give a brown viscous oil (0.654 g, 1.86 mmol, 62% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.26 (t, *J* = 7.8 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 2.66-2.55 (m, 2H), 2.52 – 2.40 (m, 2H), 2.13 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[5]



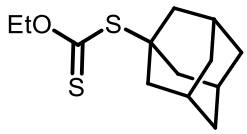
To a solution of 4-methylpent-3-en-2-one (0.196 g, 2.0 mmol, 1.0 equiv) in a mixture of DCM and acetic acid (8 mL, V/V= 1:1, 0.25M), was added KSCSOEt (0.641 g, 4.0

mmol, 2.0 equiv) at 0 °C. Then the reaction was stirred for 12 hours at this temperature. Upon completion, the reaction was concentrated in vacuo, and the crude residue was purified by flash column chromatography (1/500 EA/PE, R_f = 0.6) to afford the desired product **S21** as a yellow viscous oil (0.304 g,1.38 mmol, 69% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.69 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 2H), 2.17 (s, 3H), 1.58 (s, 6H), 1.48 (t, *J* = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[8-9]



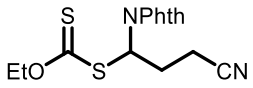
***O*-ethyl *S*-(1-phenylcyclopropyl) carbonodithioate (S22):**

Prepared from 1-phenylcyclopropane-1-carboxylic acid according to **Condition H** (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.6) to give a yellow oil (0.377 g,1.58 mmol, 79% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.43 (m, 2H), 7.28 (dd, *J* = 13.2, 5.6 Hz, 2H), 7.23 – 7.19(m, 1H), 4.65 – 4.53 (q, *J* = 7.1 Hz, 2H), 1.48 – 1.43 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[7]



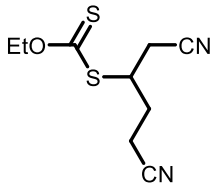
***S*-((1*S*,3*S*)-adamantan-1-yl) *O*-ethyl carbonodithioate (S23):**

Prepared from cyclopentane according to **Condition G** (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a white solid (0.385 g,1.50 mmol, 75% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.63 (q, *J* = 7.1 Hz, 2H), 3.97 – 3.84 (m, 1H), 2.16 (dt, *J* = 9.0, 5.1 Hz, 2H), 1.67 (m, *J* = 19.8, 10.7, 4.4 Hz, 6H), 1.41 (t, *J* = 7.1 Hz, 3H). and spectral data were in accordance with the literature values.[6]



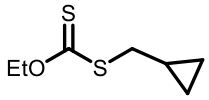
***S*-[3-Cyano-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-propyl]-*O*-ethyl dithiocarbo -nate (2):**

Prepared from *S*-(cyanomethyl) *O*-ethyl and 2-vinylisoindoline-1,3-dione according to **Condition F** (20 mmol scale). The pure product was isolated by column chromatography (1/5 EA/PE, R_f = 0.2) to give a yellow viscous oil (4.75 g, 14.2 mmol, 71% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.39 – 6.33 (m, 1H), 4.65 (q, J = 7.1 Hz, 2H), 2.69 – 2.54 (m, 2H), 2.53-2.46 (m, 2H), 1.42 (t, J = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[5]



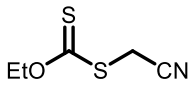
***S*-(1-cyano-4-isocyanobutan-2-yl) *O*-ethyl carbonodithioate (81):**

Prepared from *S*-(cyanomethyl) *O*-ethyl and but-3-enenitrile according to **Condition F** (20.0 mmol scale). The pure product was isolated by column chromatography (1/20 EA/PE, R_f = 0.5) to give a yellow viscous oil (3.27 g, 17 mmol, 85% yield). **IR (neat):** 2933, 2249, 1420, 1365, 1219, 1148, 1110, 1039, 999, 851. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.67 (q, J = 7.1 Hz, 2H), 4.09 – 3.97 (m, 1H), 3.00 – 2.87 (m, 2H), 2.66-2.53 (m, 2H), 2.35 – 2.21 (m, 1H), 2.18 – 2.04 (m, 1H), 1.44 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 210.64, 118.17, 116.51, 71.20, 45.39, 28.48, 24.09, 15.27, 13.82. **HRMS (ESI):** Calcd for $C_9H_{16}N_3OS_2$ $[M+NH_4]^+$ 246.0729, found: 246.0720.



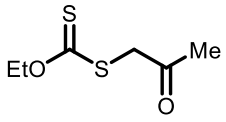
***S*-(cyclopropylmethyl) *O*-ethyl carbonodithioate (84):**

Prepared from (bromomethyl) cyclopropane according to **Condition E** (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (0.194 g, 1.10 mmol, 55% yield). **IR (neat):** 2924, 1495, 1453, 1377, 1206, 1145, 1109, 1048, 746, 697, 508. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.64 (q, J = 7.1 Hz, 2H), 3.08 (d, J = 7.3 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H), 1.16-1.06 (m, 1H), 0.65 – 0.55 (m, 2H), 0.34 – 0.25 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 215.41, 69.91, 42.01, 13.96, 9.60, 5.90. **HRMS (ESI):** Calcd for $C_7H_{13}OS_2$ $[M+H]^+$ 177.0403, found: 177.0401.



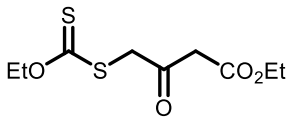
***S*-(cyanomethyl) O-ethyl carbonodithioate (S37):**

Prepared from 2-bromoacetonitrile according to **Condition E** (20.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (2.90 g, 18 mmol, 90% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.73 (q, *J*= 7.1 Hz, 2H), 3.89 (s, 2H), 1.47 (t, *J*= 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[4]

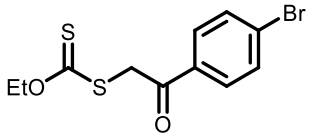


***O*-ethyl *S*-2-oxopropyl carbonodithioate (S38):**

Prepared from chloroacetone according to **Condition E** (5.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (0.802 g, 4.45 mmol, 89% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.72 (q, *J* = 7.1 Hz, 2H), 3.96 (*s*, 2H), 2.29 (s, 3H), 1.47 (t, *J*= 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[4]



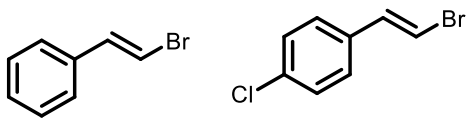
Ethyl 4-((ethoxycarbonothioyl)thio)-3-oxobutanoate (S39):
Prepared from ethyl 4-chloroacetoacetate according to **Condition E** (8.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (0.876 g, 3.52 mmol, 44% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** 4.64 (q, *J*= 7.1 Hz, 2H), 4.20 (q, *J*= 7.1 Hz, 2H), 4.12 (s, 2H), 3.65 (s, 2H), 1.42 (t, *J*= 7.1 Hz, 3H),1.30 (t, *J*= 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[14]



***S*-(2-(4-bromophenyl)-2-oxoethyl) *O*-ethyl carbonodithioate (S40):**
Prepared from 2,4'-dibromoacetophenone according to **Condition E** (10.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (2.27 g, 7.10 mmol, 71% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.90-7.85 (m, 2H), 7.66-7.63 (m, 2H), 4.64 (q, *J* = 7.1 Hz, 2H), 4.61 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), and spectral data were in accordance with the literature values.[15]

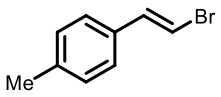
■ Synthesis of Vinyl Bromide

Vinyl bromides **S24** and **S25** were prepared according to reported procedures.[16]

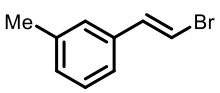


S24 **S25**

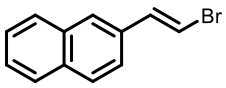
Vinyl bromides **S26-31** were prepared according to reported procedures.[17-20]



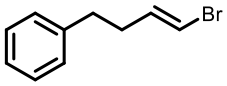
S26[18]



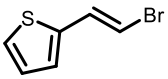
S27[18]



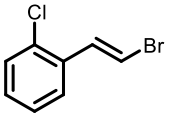
S28[18]



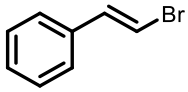
S29[18]



S30[17]

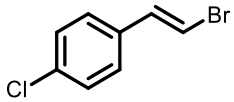


S31[20]



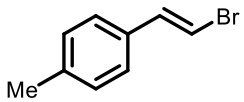
(*E*)-(2-bromovinyl)benzene (S24):

Prepared from cinnamic acid according to reported procedures.[16] (20 mmol scales). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a colorless oil (3.19 g, 17.4 mmol, 87% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.37 – 7.27 (m, 5H), 7.15 – 7.08 (m, 1H), 6.78 (d, J = 14.0 Hz, 1H), and spectral data were in accordance with the literature values.[16]



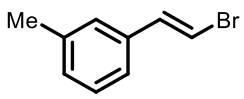
(*E*)-1-(2-bromovinyl)-4-chlorobenzene (S25):

Prepared from (*E*)-3-(4-chlorophenyl)acrylic acid according to reported procedures.[16] (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a colorless oil (0.331 g, 1.52 mmol, 76% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 7.06 (d, J = 14.0 Hz, 1H), 6.77 (d, J = 14.0 Hz, 1H), and spectral data were in accordance with the literature values.[16]



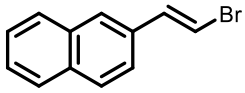
(*E*)-1-(2-bromovinyl)-4-methylbenzene (S26):

Prepared from 4-methylbenzaldehyde according to reported procedures.[18] (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a white solid (0.288 g, 1.46 mmol, 73% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.19 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 14.0 Hz, 1H), 6.71 (d, J = 14.0 Hz, 1H), 2.33 (s, 3H), and spectral data were in accordance with the literature values.[18]



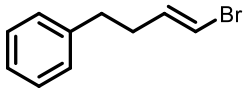
(*E*)-1-(2-bromovinyl)-3-methylbenzene (S27):

Prepared from (E)-3-(m-tolyl)acrylic acid according to reported procedures.[19] (3.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a white solid (0.520 g, 2.64 mmol, 88% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 – 7.28 (m, 2H), 7.24 – 7.14 (m, 3H), 6.64 (d, *J* = 13.8 Hz, 1H), 2.34 (s, 3H), and spectral data were in accordance with the literature values.[19]



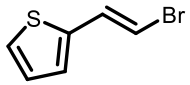
(*E*)-2-(2-Bromovinyl)naphthalene (S28):

Prepared from 2-naphthaldehyde according to reported procedures.[18] (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a white solid (0.326 g, 1.40 mmol, 70% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 – 7.77 (m, 3H), 7.69 (s, 1H), 7.52 – 7.45 (m, 3H), 7.26 (d, *J* = 14.0 Hz, 1H), 6.90 (d, *J* = 14.0 Hz, 1H), and spectral data were in accordance with the literature values.[18]



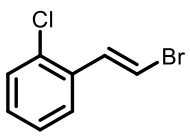
(E)-(4-bromobut-3-en-1-yl)benzene (S29):

Prepared from 2-naphthaldehyde according to reported procedures.[18] (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a white solid (0.232 g, 1.10 mmol, 55% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 – 7.27 (m, 2H), 7.21 (s, 3H), 6.21 (dt, *J*= 13.5, 7.2 Hz, 1H), 6.04 (dd, *J*= 13.5 ,1.4 Hz, 1H), 2.74 – 2.68 (m, 2H), 2.39 – 2.32 (m, 2H**),** and spectral data were in accordance with the literature values.[18]



(*E*)-2-(2-Bromovinyl)thiophene (S30):

Prepared from thiophene-2-carbaldehyde according to reported procedures.[17] (2.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a brown oil (0.185 g, 0.98 mmol, 49% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24-7.19 (m, 2H), 7.01-6.99 (m, 2H), 6.67-6.62 (d, 1H), and spectral data were in accordance with the literature values.[17]

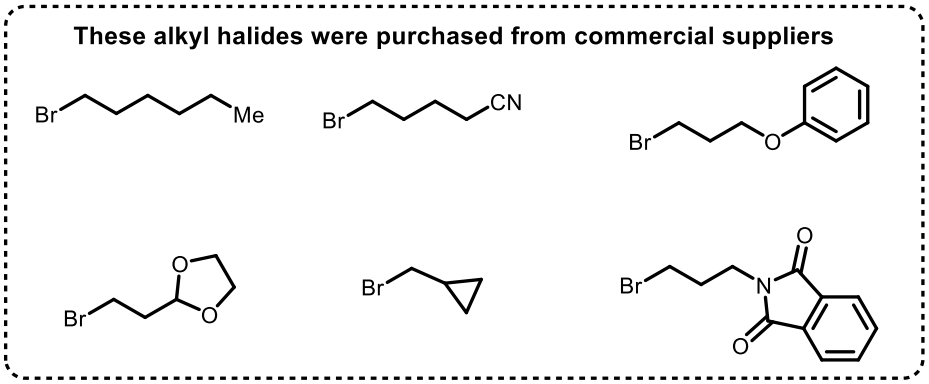


(*E*)-1-(2-bromovinyl)-2-chlorobenzene (S31):

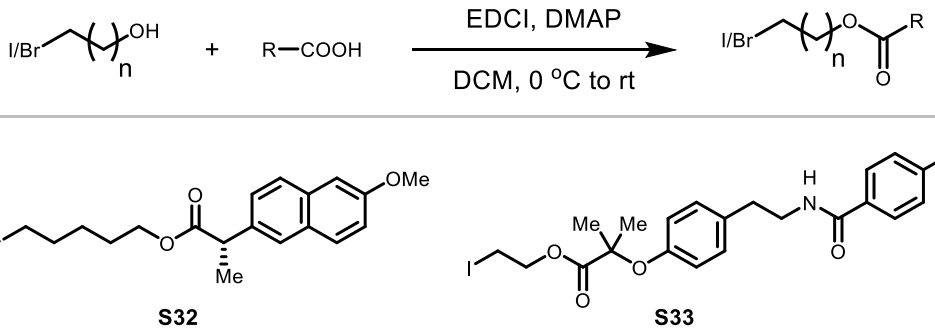
Prepared from 1-(bromomethyl)-2-chlorobenzene according to reported procedures.[20] (4.0 mmol scale). The pure product was isolated by column chromatography (100% PE,

R_f = 0.7) to give a colorless oil (0.478 g, 2.20 mmol, 55% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 (t, *J* = 13.2 Hz, 1H), 7.38 (m, *J* = 8.4, 7.6, 4.3 Hz, 2H), 7.23 (m, *J* = 9.4, 4.4 Hz, 2H), 6.80 (d, *J* = 14.0 Hz, 1H), and spectral data were in accordance with the literature values.[20]

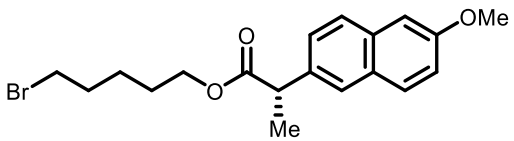
■ **Synthesis of Alkyl halides**



Condition J:

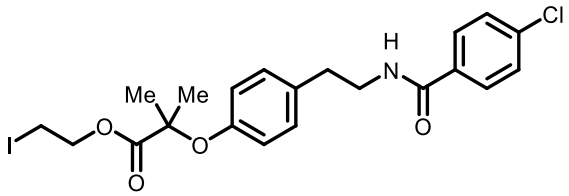


To a solution of halohydrin (1.0 equiv) in DCM (0.10 M) was added corresponding acid (1.5 equiv) and DMAP (10 mol%) at 0℃. Then, EDCI (1.5 equiv) was added to the reaction mixture over 30 min. The resulting mixture was stirred at room temperature for 24 hours. The reaction was quenched by saturated NH_4Cl solution and extracted with DCM three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified with flash chromatography on silica gel to give the desired product.



5-Bromopentyl (*S*)-2-(6-methoxynaphthalen-2-yl) propanoate (S32):
Prepared from (*S*)-2-(6-methoxynaphthalen-2-yl) propanoic acid and 5-bromopentan-1-ol according to **Condition J** (2.0 mmol scale). The pure product was isolated by silica gel column chromatography (1:5 EA/PE, R_f = 0.3) to give a colorless oil. (0.508 g, 1.34 mmol, 67% yield). **IR (neat):** 2937, 2156, 1699, 1717, 1419, 1157, 682, 518. **^{1}H NMR**

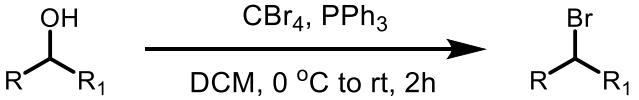
(400 MHz, $CDCl_3$): δ 7.73 – 7.65 (m, 3H), 7.40 (m, 1H), 7.18 – 7.09 (m, 2H), 4.12 – 4.03 (m, 2H), 3.92 (s, 3H), 3.84 (q, *J* = 7.1 Hz, 1H), 3.25 (t, *J* = 6.7 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.60 – 1.54 (m, 5H), 1.39 – 1.31 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 174.82, 157.74, 135.85, 133.79, 129.37, 129.02, 127.25, 126.36, 126.06, 119.14, 105.66, 64.52, 55.46, 45.63, 33.59, 32.31, 27.82, 24.62, 18.52. **HRMS (ESI):** Calcd for $C_{19}H_{23}BrO_3$ $[M+H]^+$ 379.0904, found: 379.0916.



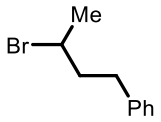
2-Bromoethyl 2-(4-(2-(4-chlorobenzamido) ethyl) phenoxy)-2-methylpropanoate (S33):

Prepared from 2-(4-(2-(4-chlorobenzamido) ethyl) phenoxy)-2-methylpropanoic acid and 2-iodoethan-1-oll according to **Condition J** (2.0 mmol scale). The pure product was isolated by silica gel column chromatography (1:5 EA/PE, R_f = 0.3) to give a colorless oil. (0.815 g, 1.58 mmol, 79% yield). **IR (neat):** 2932, 2832, 1711, 1612, 912, 851, 519. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (dd, J = 8.6, 2.3 Hz, 2H), 7.37 (dd, J = 8.5, 2.0 Hz, 2H), 7.012 7.04 (m, 2H), 6.86 – 6.74 (m, 2H), 6.08 (s, 1H), 4.42 (t, J = 6.7 Hz, 1H), 3.66 (q, J = 6.7 Hz, 2H), 3.28 (t, J = 6.7 Hz, 2H), 2.85 (t, J = 6.9 Hz, 2H), 1.60 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 212.64, 167.88, 148.39, 136.61, 134.09, 128.06, 127.48, 122.12, 121.88, 119.06, 116.85, 70.66, 46.38, 42.49, 29.82, 15.45, 13.92. **HRMS (ESI):** Calcd for $C_{21}H_{24}ClINO_4$ $[M+H]^+$ 516.0433, found: 516.0419.

<u>Condition K</u>:

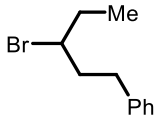


To a solution of alcohol (1.0 equiv) in DCM (0.20 M) was added CBr_4 (1.1 equiv). The solution was stirred at 25 °C for 5 min. PPh_3 (1.1 equiv) in DCM was added dropwise at 0 °C, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel to give the desired product.

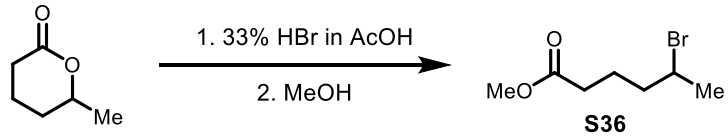


(3-bromobutyl) benzene (S34):

Prepared from 4-phenyl-2-butanol according to **Condition K** (3.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a colorless oil (0.339 g, 1.59 mmol, 53% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 – 7.25 (m, 2H), 7.21 (d, *J* = 6.6 Hz, 3H), 4.14 – 4.03 (m, 1H), 2.95 – 2.64 (m, 5.3 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.20 – 2.01 (m, 2H), 1.74 (d, *J* = 6.7 Hz, 3H), and spectral data were in accordance with the literature values.[12-23]



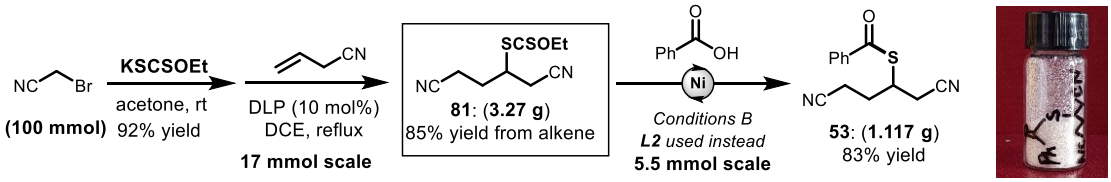
(3-bromopentyl) benzene (S35):
Prepared from 1-phenyl-3-pentanol according to **Condition K** (3.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.7) to give a colorless oil (0.463 g, 2.04 mmol, 68% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.32 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 4.00 – 3.87 (m, 1H), 2.93 – 2.80 (m, 1H), 2.79 – 2.70 (m, 1H), 2.17 – 2.06 (m, 2H), 1.91 – 1.83 (m, 2H), 1.03 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 141.03, 128.55, 128.49, 126.08, 59.44, 40.44, 33.85, 32.31, 12.09.



Hexalactone (0.228 g, 2.0 mmol, 1.0 equiv) was added to a flask containing a solution of 33% HBr in AcOH (0.57 mL, 3.5 M) and was heated to 75 °C for 4 h. Then cooled to room temperature, at which MeOH (0.40 mL, 5.0 M) was added, and the mixture was stirred at room temperature overnight. The reaction was then partially concentrated under reduced pressure, taken up in EtOAc, washed three times with aqueous $NaHCO_3$, brine, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purified by column chromatography (1/40 EA/PE, R_f = 0.3) on silica gel to give the desired product **S36** as a colorless oil (0.201 g, 0.96 mmol, 48% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.15 – 4.05 (m, 1H), 3.66 (s, 3H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.91 – 1.72 (m, 4H), 1.69 (d, *J* = 6.7 Hz, 3H), and spectral data were in accordance with the literature values.[22]

11. Gram Scale Synthesis and Comparison with Reported Methods

■ Gram Scale Synthesis

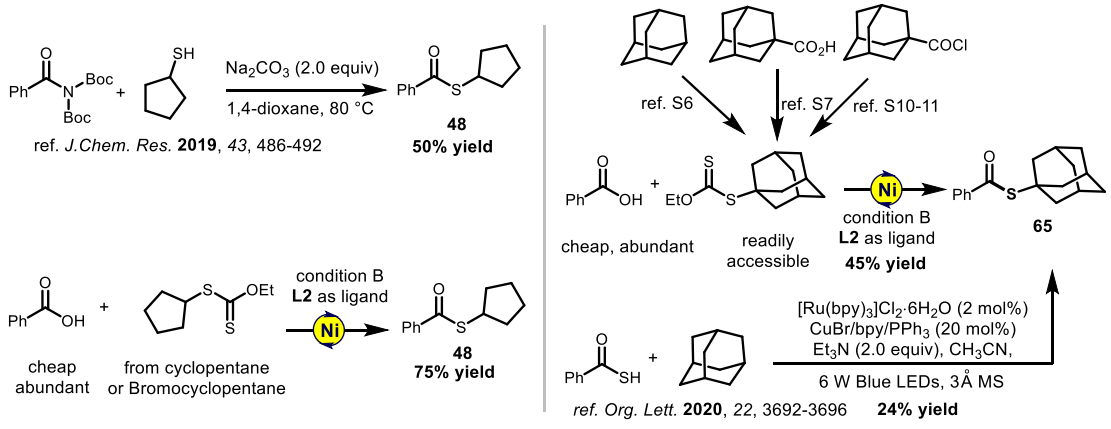


Step 1: To a solution of alkyl 2-bromoacetonitrile (12.0 g, 100 mmol, 1.0 equiv) in acetone (130 mL, 0.75 M) was added potassium ethyl xanthate esters (24.0 g, 150 mmol, 1.5 equiv). The mixture was stirred at room temperature until consumption of the alkyl bromide as determined by TLC. The mixture was concentrated and taken up in EtOAc and washed with H_2O, brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the alkyl xanthate ester (14.7 g, 92 mmol, 92% yield).

Step 2: To a solution of but-3-enenitrile (1.14 g, 17 mmol, 1.0 equiv) in DCE (34 mL, 0.50 M) was added the ethyl xanthate esters (5.45 g, 34 mmol, 2.0 equiv). The reaction was refluxed for 15 min. DLP (0.338 g, 0.85 mmol, 5 mol %) was then added and additional DLP (0.338 g, 0.85 mmol, 5 mol %) was added every 60 minutes until consumption of alkenes. The mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **81** as a yellow viscous oil (3.27 g, 14.4 mmol, 85% yield).

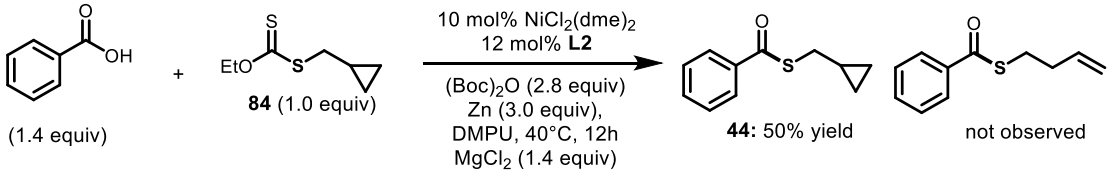
Step 3: An oven-dried flask vial with a magnetic stir bar is transferred to an N_2-filled glovebox. ligand **L2** (0.122 mg, 0.66 mmol, 12 mol%), $NiCl_2$(DME) (0.122 mg, 0.55 mmol, 10 mol%), DMPU (27.5 mL, 0.20 M) were added to the vial sequentially. After stirring for 10 minutes, the alkyl xanthate ester **81** (1.25 g, 5.5 mmol, 1.0 equiv) was added to the vial, and then the solution was stirred for another 10 minutes. Benzoic acid (0.940 g, 7.7 mmol, 1.4 equiv), $(Boc)_2O$ (3.54 mL, 15.4 mmol, 2.8 equiv), $MgCl_2$ (0.733 g, 7.7 mmol, 1.4 equiv), Zn (1.07 g, 16.5 mmol, 3.0 equiv) were added. The flask was removed from the glovebox, stirred at 40 °C for 12 h, then quenched upon adding H_2O (80 mL). The aqueous layer was extracted with EtOAc (3 x 30 mL), and the combined organic layers were washed with H_2O (3 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **53** as a yellow viscous oil (1.12 g, 4.57 mmol, 83% yield).

■ Comparison with reported methods

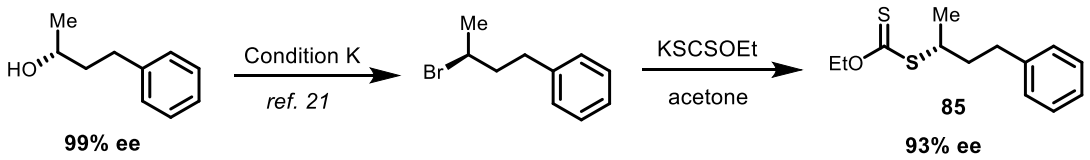


12. Mechanistic Investigations

■ **Radical clock experiment**



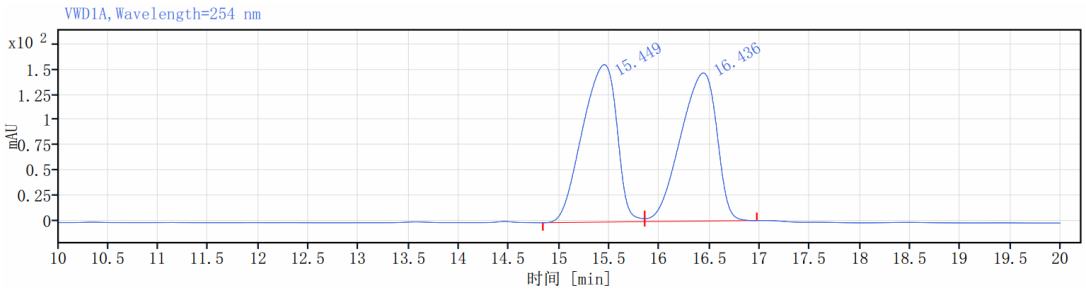
An oven-dried 100 x 16 mm screw-capped vial was charged with a magnetic stir bar. Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Next, ligand **L2** (6.6 mg, 0.036 mmol, 12 mol%), $NiCl_2$(DME) (6.6 mg, 0.030 mmol, 10 mol%), DMPU (1.5 mL, 0.20 M) were added to the vial sequentially. After stirring for 10 minutes, **84** (51.4 mg, 0.30 mmol, 1.0 equiv) was added. After additional 10 minutes, benzoic acid (51.3 mg, 0.42 mmol, 1.4 equiv), $(Boc)_2O$ (0.20 mL, 0.84 mmol, 2.8 equiv), $MgCl_2$ (40.0 mg, 0.42 mmol, 1.4 equiv), Zn (58.9 mg, 0.90 mmol, 3.0 equiv). The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at 40 ℃ for 12 h, then quenched upon the addition of H_2O (15 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel to give yellow oil **44** (28.8 mg, 0.15 mmol, 50% yield).



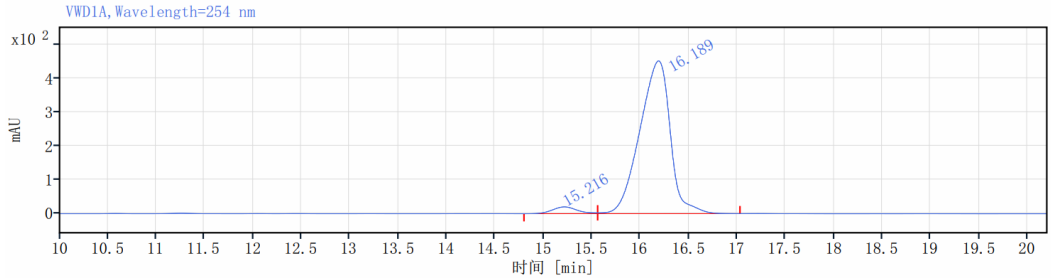
***O*-ethyl *S*-(4-phenylbutan-2-yl) carbonodithioate (85):**

Prepared from (3-bromobutyl) benzene[23-24] according to **Condition E** (3.0 mmol scale). The pure product was isolated by column chromatography (100% PE, R_f = 0.8) to give a yellow oil (0.505 g, 1.98 mmol, 66% yield). **IR (neat):** 2924, 1495, 1453, 1377, 1206, 1145, 1109, 1048, 746, 697,476. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 (d, J = 7.0 Hz, 2H), 7.22 (t, J = 7.6 Hz, 3H), 4.63 (q, J = 7.1 Hz, 2H), 3.83 – 3.74 (m, 1H), 2.77 (t, J = 7.9 Hz, 2H), 2.09 – 2.00 (m, 1H), 1.98 – 1.89 (m, 1H), 1.48 – 1.38 (m, 6H).**^{13}C NMR (100 MHz, $CDCl_3$):** δ 214.34, 141.42, 128.61, 128.52, 128.50, 126.10, 69.68, 45.45, 37.83, 33.42, 20.66, 13.89. **HRMS (ESI):** Calcd for $C_{13}H_{19}OS_2$ $[M+H]^+$ 255.0872; Found: 255.0868. **HPLC analysis:** The enantiomeric excess (93% ee) was determined on a Lux®5μm i-Amylose-1 column (0.5% iPrOH in hexane, 0.39 mL/min, 35 ℃, λ = 254 nm), t_R (minor) = 15.22, t_R (major) = 16.19 min.

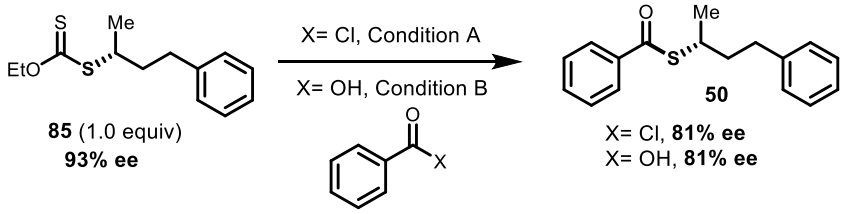
HPLC traces for Compound 85



Resolution Time (min)	Width (min)	Area	Height	Area %
15.449	1.016	3724.8	155.1	50.32
16.436	1.119	3676.9	145.9	49.68



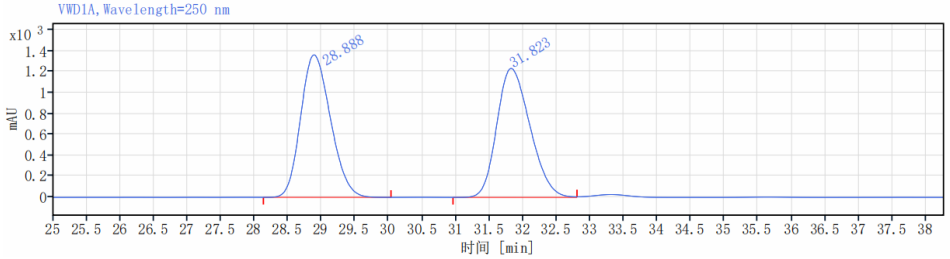
Resolution Time (min)	Width (min)	Area	Height	Area %
15.216	0.277	361.7	20.2	3.54
16.189	1.470	9846.1	451.0	96.46



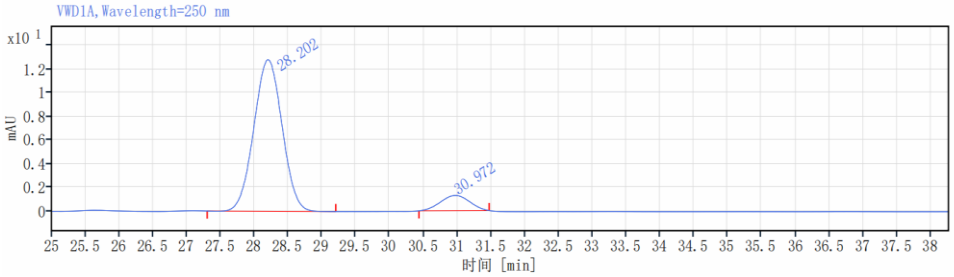
S-(4-phenylbutan-2-yl) benzothioate (50):

HPLC analysis: The enantiomeric excess (81% ee) was determined on a Lux®5µm i-Amylose-1 column (2% iPrOH in hexane, 0.25 mL/min, 35 °C, λ = 250 nm), t_R (major) = 28.2 min, t_R (minor) = 30.9 min.

HPLC traces for Compound 50

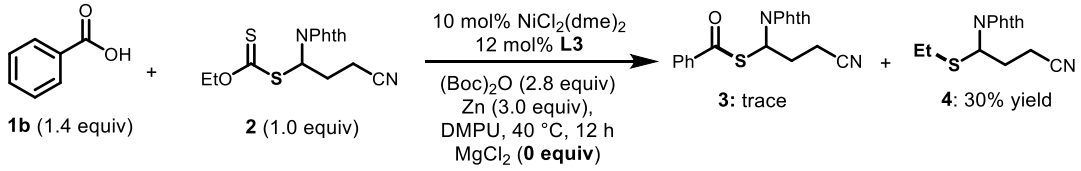


Resolution Time (min)	Width (min)	Area	Height	Area %
28.888	1.900	42160.9	1360.2	49.89
31.823	1.846	42346.1	1231.1	50.11
		Total VWD1A	84507.0	



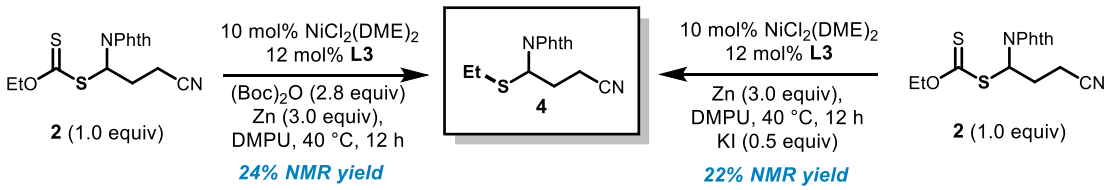
Resolution Time (min)	Width (min)	Area	Height	Area %
28.202	0.455	373.2	12.8	90.59
30.972	0.471	38.8	1.3	9.41
		Total VWD1A	411.9	

■ Control experiments

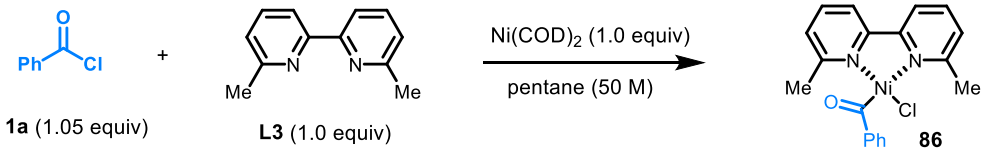


An oven-dried 100 x 16 mm screw-capped vial was charged with a magnetic stir bar. Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Next, ligand **L3** (6.6 mg, 0.036 mmol, 12 mol%), $NiCl_2$(DME) (6.6 mg, 0.030 mmol, 10 mol%), DMPU (1.5 mL, 0.20 M) were added to the vial sequentially. After stirring for 10 minutes, **2** (0.30 mmol, 1.0 equiv) was added. After additional 10 minutes, benzoic acid (0.42 mmol, 1.4 equiv), $(Boc)_2O$ (0.20 mL, 0.84 mmol, 2.8 equiv), Zn (58.9 mg, 0.90 mmol, 3.0 equiv) were added. The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The reaction was stirred at 40 °C for 12 h, then quenched upon adding H_2O (15 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel to give by-product **4** (25 mg, 0.09 mmol, 30% yield). **IR (neat):** 2926, 2247, 1777, 1710, 1378, 1322, 1165, 765, 717, 529. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (dd, J = 5.5, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.1 Hz, 2H), 5.44 – 5.33 (m, 1H), 2.75 – 2.66 (m, 1H), 2.66 – 2.51 (m, 6H), 1.27 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 7.99, 7.97, 7.58, 7.54, 7.46, 7.45, 3.05, 3.03, 1.14, 1.10, 0.61, 0.59, 0.33, 0.31. **HRMS (ESI):** Calcd for $C_{14}H_{15}N_2O_2S$ $[M+H]^+$ 275.0849, found 275.0844.

The following two reactions were carried out according to the standard condition A or B in the absence of **1a** or **1b**.

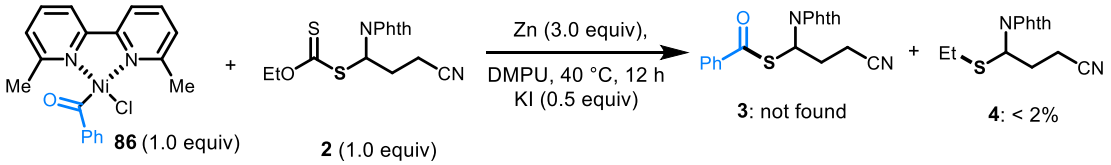


■ Stoichiometric experiment with pre-generated acyl-Ni(II) complex (86)



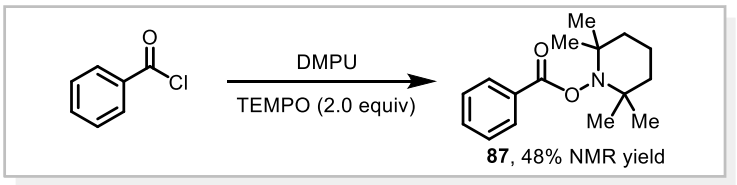
Synthesis of acyl-Ni complex (86): The nickel complex **86** was readily synthesized according to the literature method.[26-28] In a N_2-filled glovebox, anhydrous pentane (15 mL) was added to a 25 mL Schlenk tube that contained **L3** (55.3 mg, 0.30 mmol, 1.0 equiv) and $Ni(COD)_2$ (82.5 mg, 0.30 mmol, 1.0 equiv). The resulting dark solution was

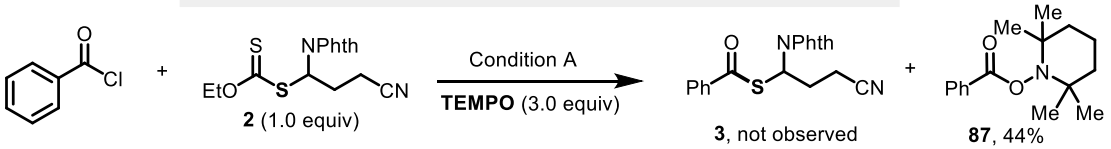
stirred at room temperature for 1 h. The corresponding freshly distilled benzoyl chloride (44.3 mg, 0.32 mmol, 1.05 equiv) was then added, and the reaction mixture was stirred for 10 minutes, resulting in the precipitation of an orange solid. The orange solid was collected on a fritted filter, washed with anhydrous pentane (3.0 mL x 3), and dried under reduced pressure (57.5 mg, 50% yield), which can be used directly without further purification. ***Note***: This complex slowly degrades in the air or moisture but can be stored in a nitrogen-filled glove box. Unfortunately, we failed to obtain the X-ray crystallography after extensive trials. Besides, our efforts to obtain the appropriate NMR spectra proved to be unsuccessful because of the broad signal.



Stoichiometric experiment: To an oven-dried 100 x 16 mm screw-capped vial with a magnetic stir bar was added alkyl xanthate esters (33.3 mg, 0.10 mmol, 1.0 equiv). Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Complex **86** (38.4 mg, 0.1 mmol, 1.0 equiv), KI (28.3 mg, 0.05 mmol, 50 mol%), Zn (19.5 mg, 0.30 mmol, 3.0 equiv) and DMPU (0.5 mL, 0.20 M) were added to the vial sequentially. The reaction was stirred at 40 °C for 12 h, then quenched upon the addition of H_2O (5.0 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The crude mixture was determined by ^1H NMR using dibromomethane as an internal standard. We did not find thioester **3**, yet a trace amount of thioether **4** was observed.

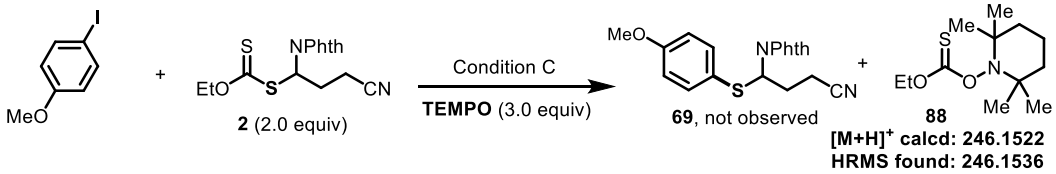
■ Radical trap experiments





To an oven-dried 100 x 16 mm screw-capped vial with a magnetic stir bar was added alkyl xanthate esters esters (33.4 mg, 0.10 mmol, 1.0 equiv). Then the vial was sealed with a rubber septum, evacuated and backfilled with nitrogen three times on a Schlenk line, and finally transferred to an N_2-filled glovebox. Next, TEMPO (46.9 mg, 0.30 mmol, 3.0 equiv), Ligand **L3** (2.2 mg, 0.012 mmol, 12 mol%), $NiCl_2$(DME) (3.3 mg, 0.010 mmol, 10 mol%), KI (8.3 mg, 0.050 mmol, 50 mol%), Zn (19.6 mg, 0.30 mmol,

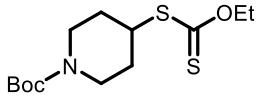
3.0 equiv) and DMPU (0.50 mL, 0.20 M) were added to the vial sequentially. The vial was removed from the glovebox and added acid chloride (13.9 μL, 0.12 mmol, 1.2 equiv) through microsyringe. The reaction was stirred at 40 ℃ for 12 h, then quenched upon the addition of H_2O (5.0 mL). The aqueous layer was extracted with EtOAc (3 x 3.0 mL), and the combined organic layers were extracted with H_2O (3 x 5.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel to give a colorless oil **87** (12.0 mg, 44% yield). Spectral data matched those reported in the literature.[25]



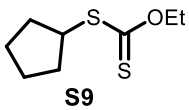
An oven-dried 100 x 16 mm screw-capped vial with a magnetic stir bar was transferred to an N_2-filled glovebox. First, ligand **L11** (6.6 mg, 0.036 mmol, 12 mol%), $NiCl_2(PCy_3)_2$ (41.4 mg, 0.060 mmol, 20 mol%), Zn (58.9 mg, 0.90 mmol, 3.0 equiv) and DMI (1.5 mL, 0.20 M) were added to the vial sequentially. Next, 4-Iodoanisole (70.2 mg, 0.30 mmol, 1.0 equiv), **2** (200.4 mg, 0.60 mmol, 2.0 equiv) and TEMPO (13.95 mg, 0.90 mmol, 3.0 equiv) were transferred to vials. The vial was sealed with a Teflon-lined screw cap, removed from the glovebox. The reaction was stirred at 65℃ for 24 h, then quenched upon the addition of H_2O (15.0 mL). The aqueous layer was extracted with EtOAc (3 x 15.0 mL), and the combined organic layers were extracted with H_2O (3 x 30.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, gravity filtered, and concentrated under reduced pressure. The residue for **HRMS** analysis, **HRMS (ESI):** Calcd for $C_{12}H_{24}NO_2S$ $[M+H]^+$ 246.1522, found 246.1536, and **69** not observed.

13. Cyclic Voltammetry

General experimental details: All the solutions were prepared in the N_2-filled glove box prior to measurements. Cyclic voltammogram for alkyl xanthate esters (**S9**) [0.1 M] in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Pt electrode working electrode, $Ag/AgNO_3$ ($AgNO_3$ 0.01 M in CH_3CN) reference electrode, Pt wire auxiliary electrode. E_{red} ($Ag/AgNO_3$) = +0.283 V vs SCE) was measured as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE). E_{red} [Ni^{II}/Ni^0] = –1.1 V versus SCE in DMF, implying that the reduction of Ni^{II} to Ni^I occurs at a more positive potential.[29]

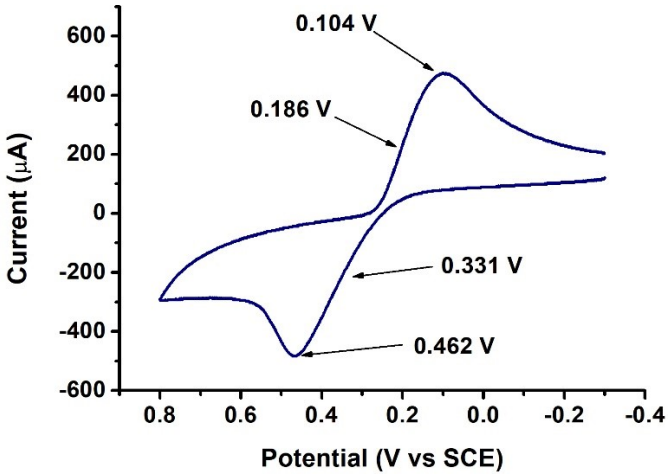


(E_{red} = -1.95 V vs SCE)[30]

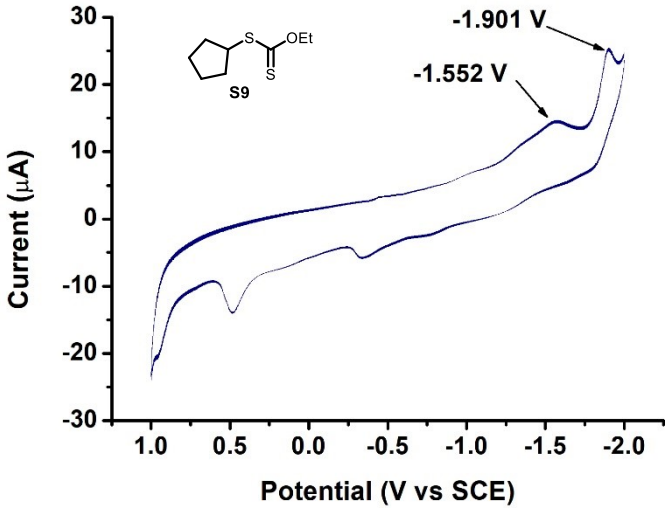


S9

(E_{red} = -1.27 V vs SCE in CH_3CN)



Cyclic voltammogram of $AgNO_3$ (17.0 mg, 2 mmol) at a scan rate of 500 mV/s.



Cyclic voltammogram of alkyl xanthate esters (**S9**) (190.32 mg, 1.0 mmol) at a scan rate of 100 mV/s. E_{red}(**S9**/**S9**$^{\cdot-}$) = −1.27 V vs SCE in CH_3CN).

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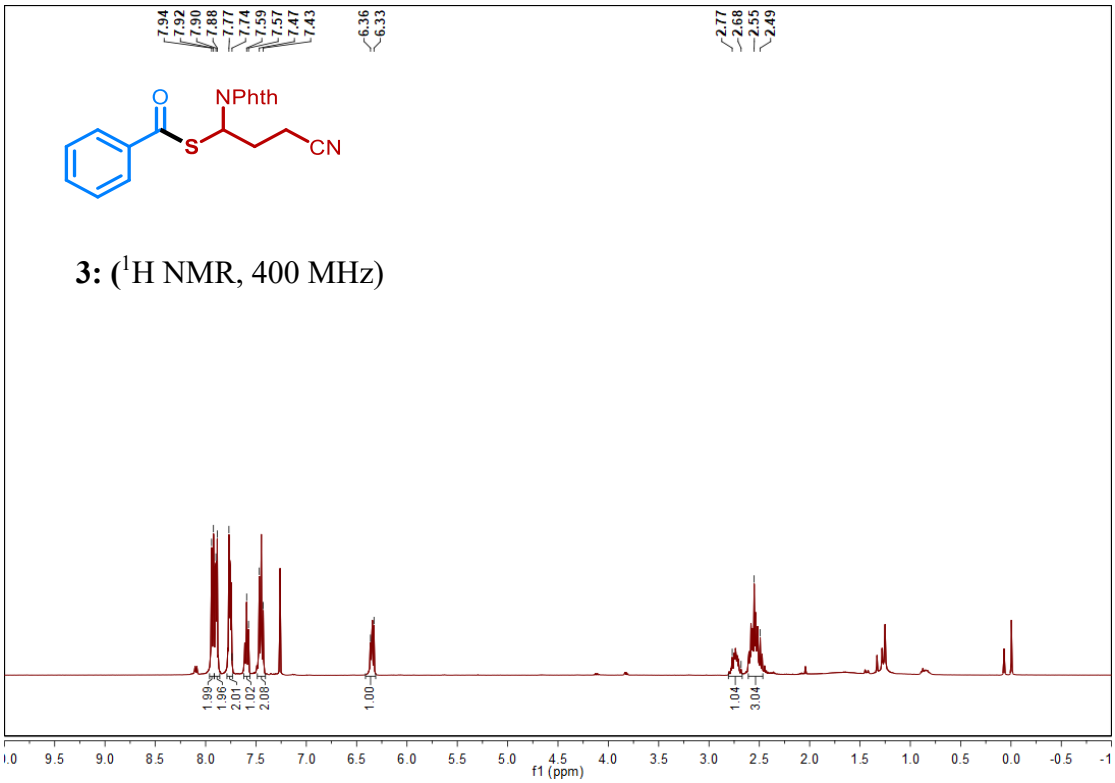
15. Copies of NMR Spectra



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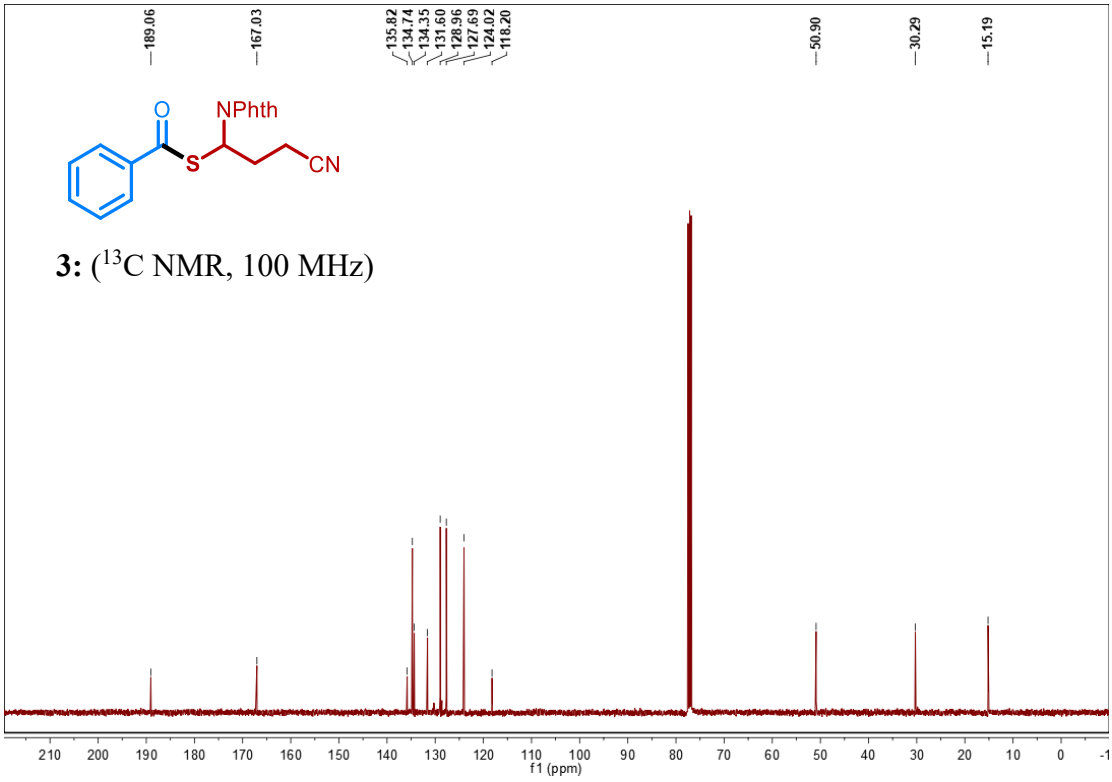

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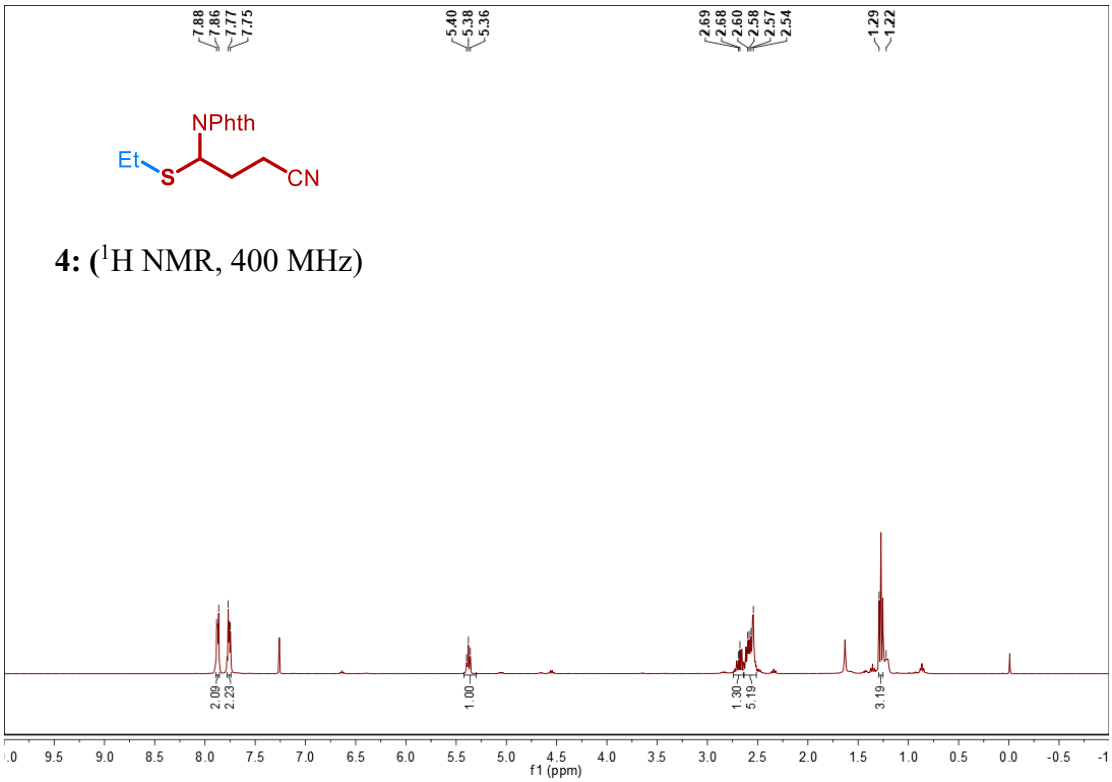

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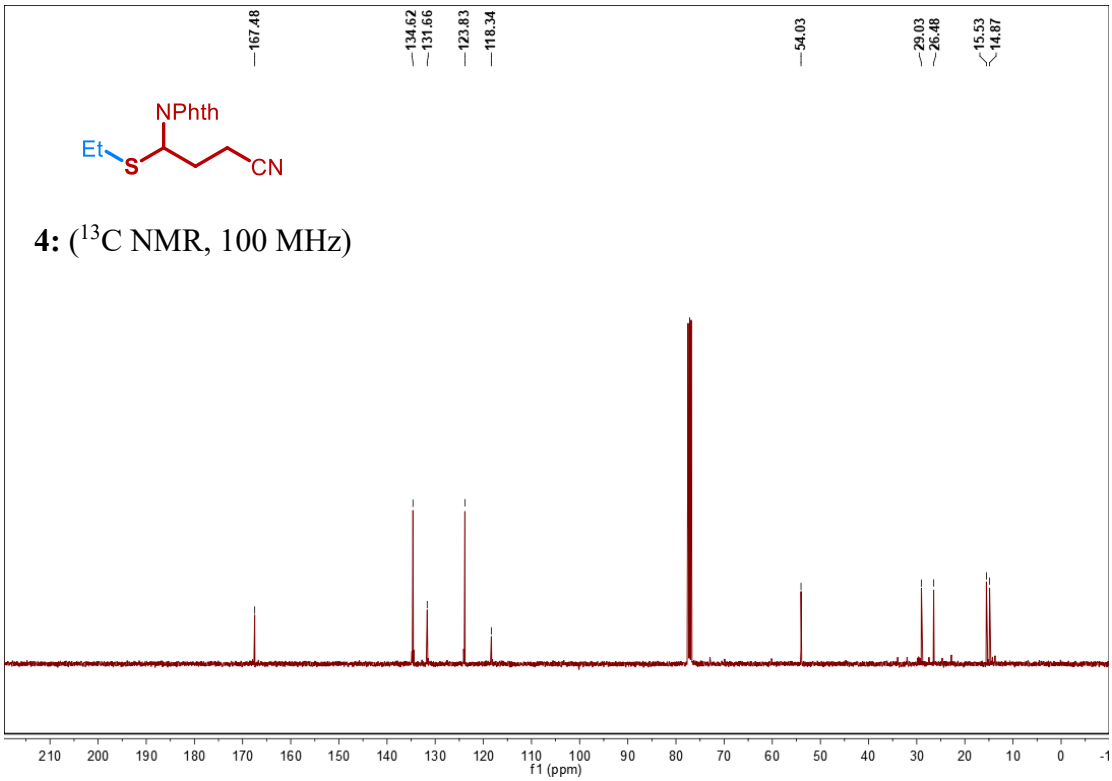

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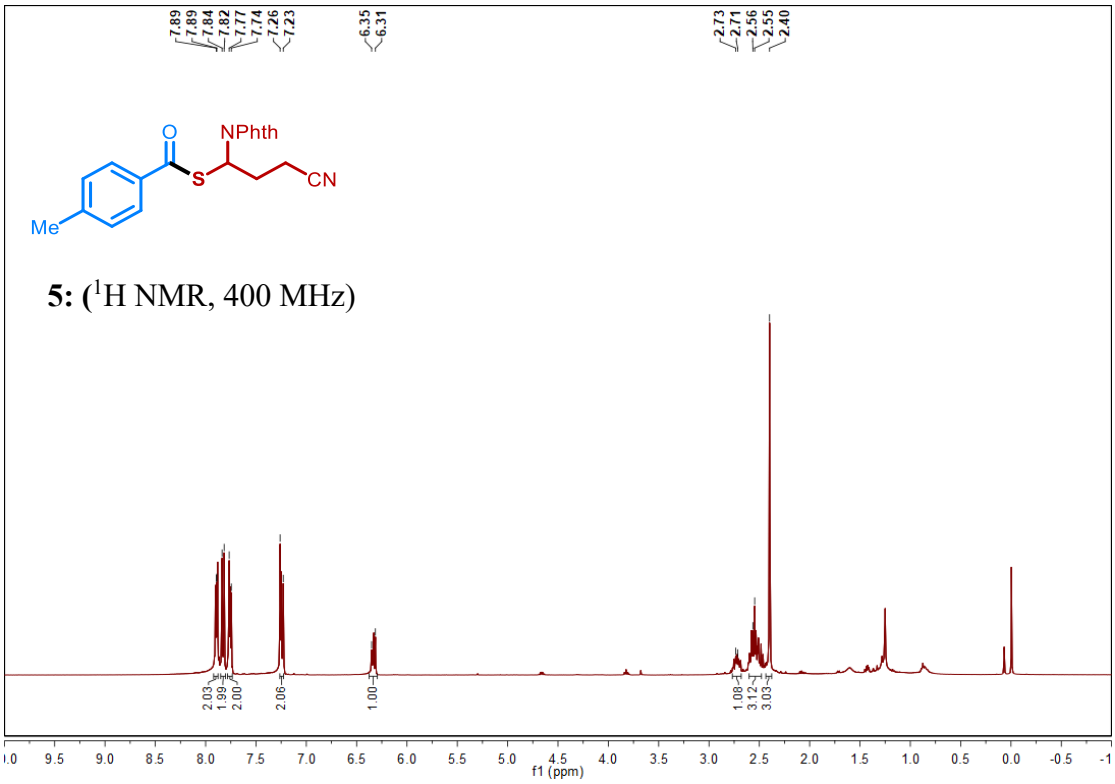

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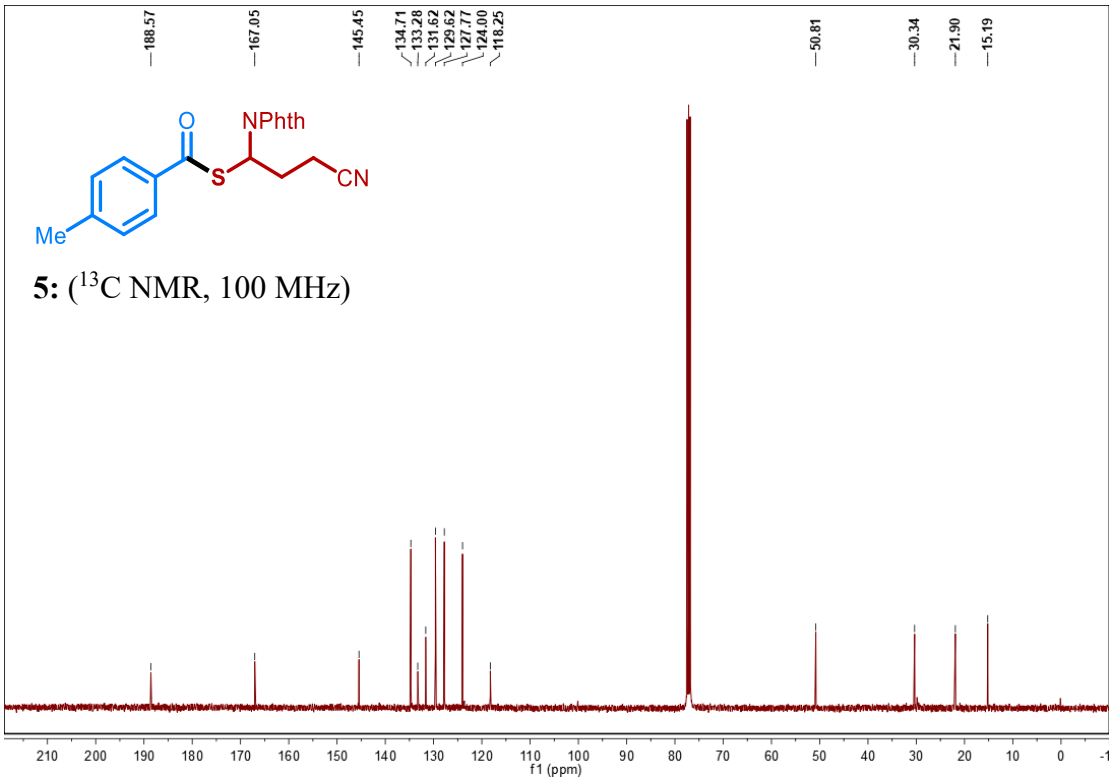

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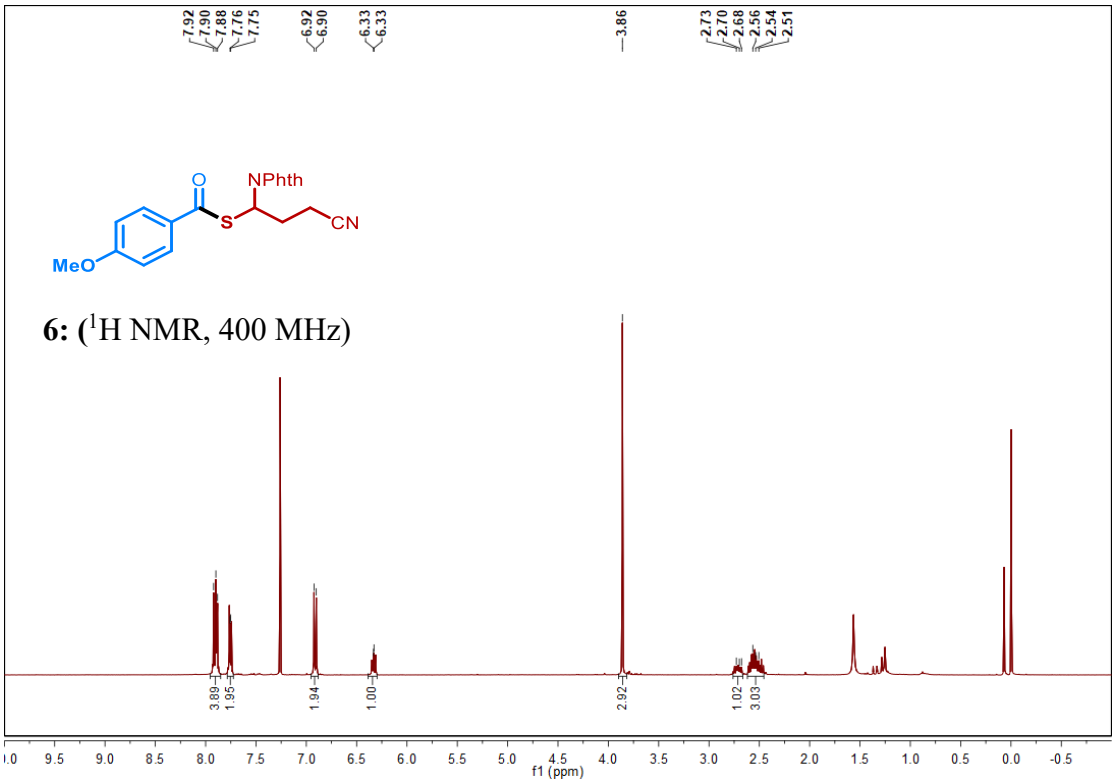

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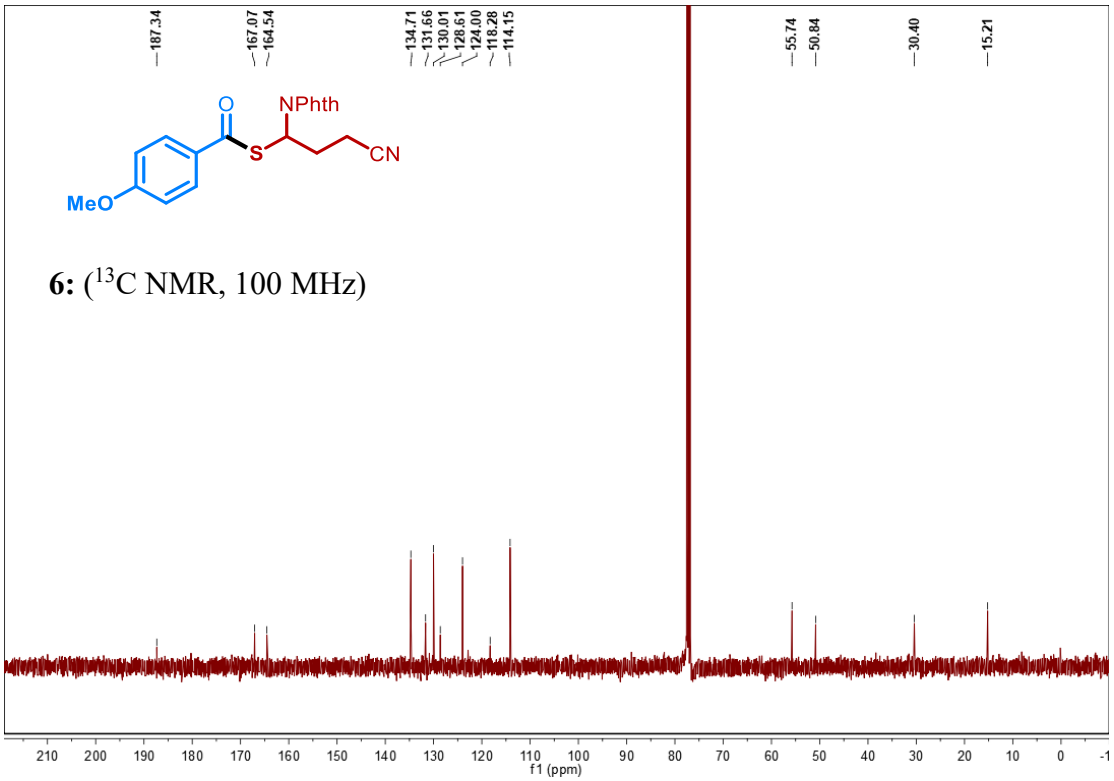

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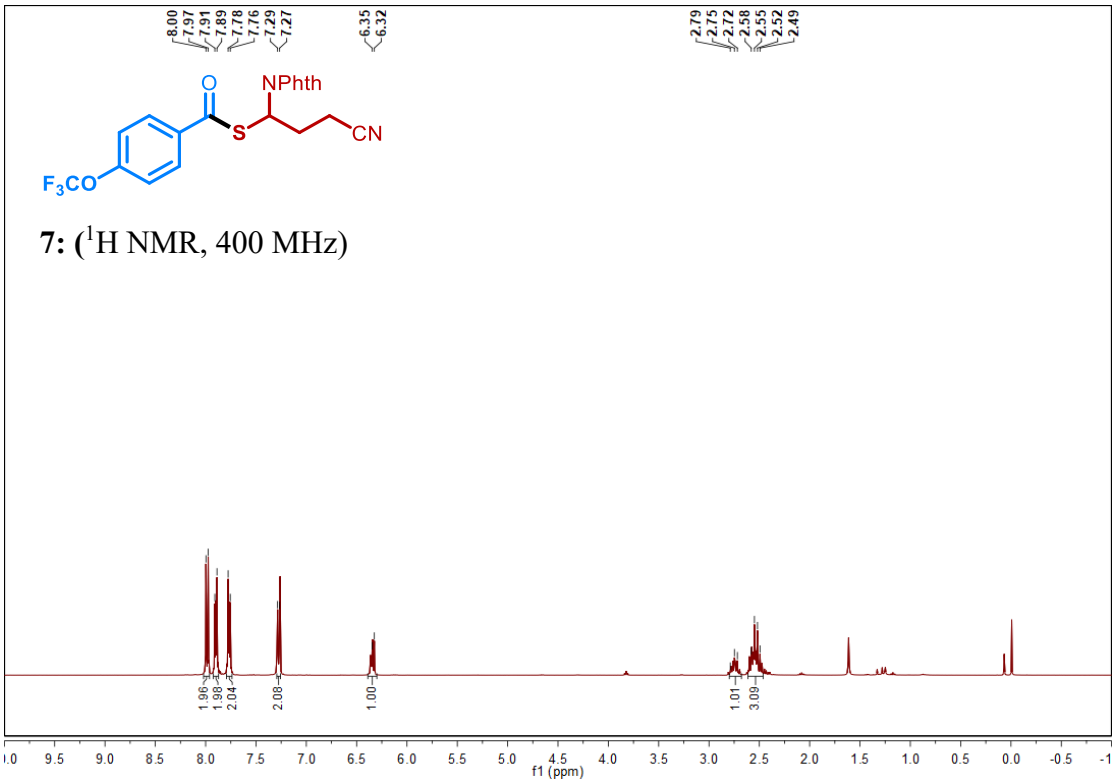

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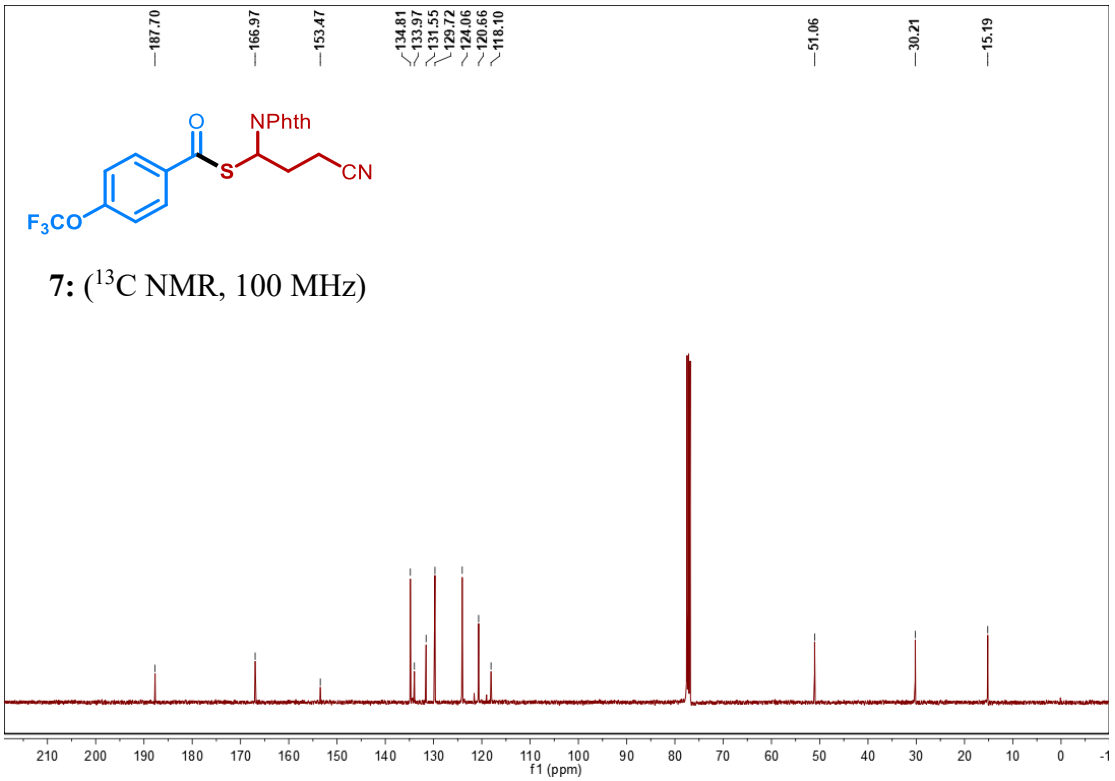

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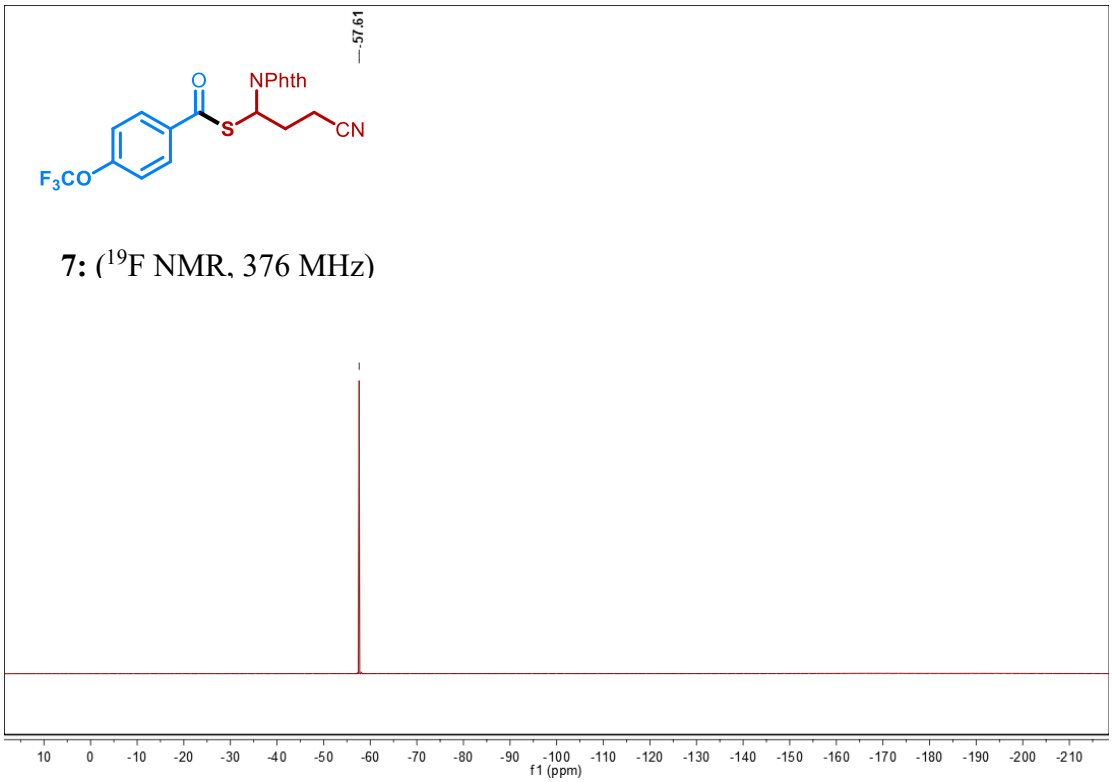

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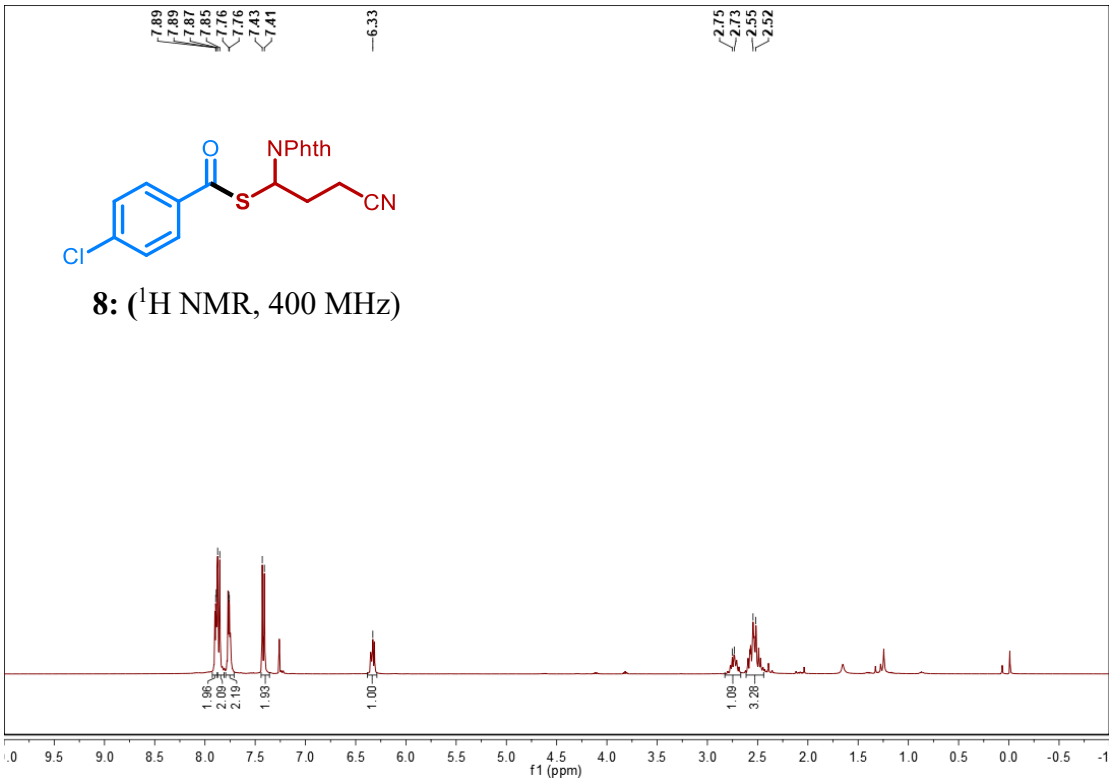

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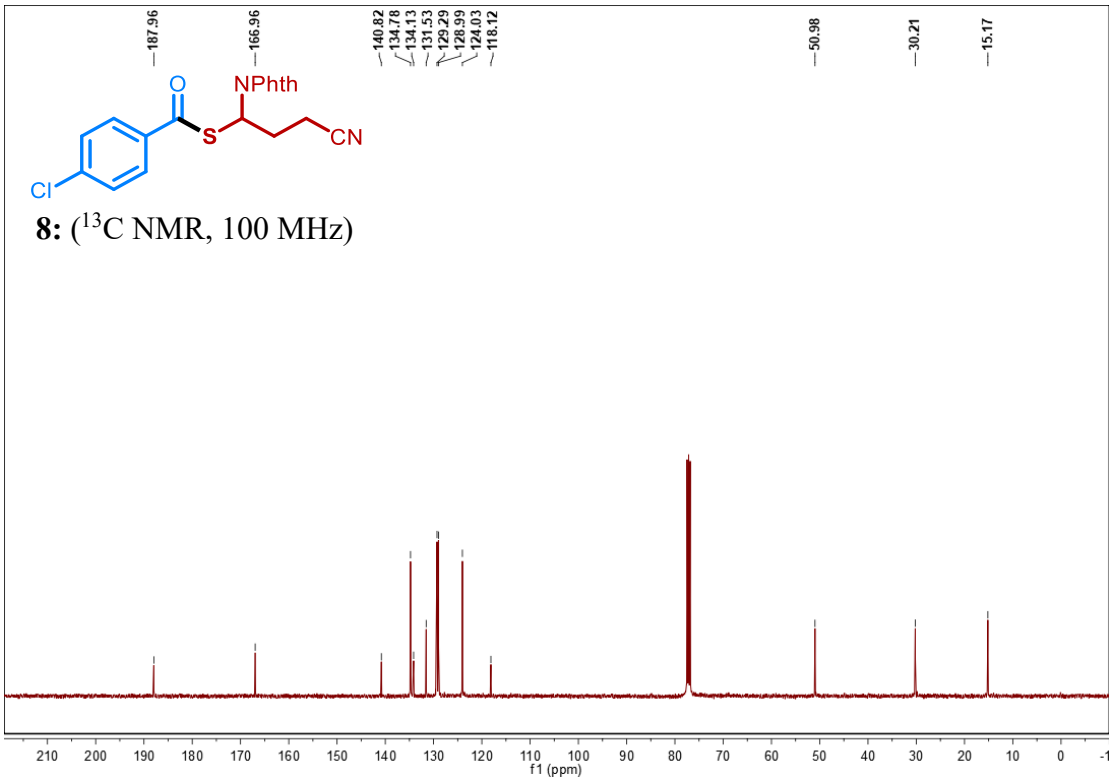

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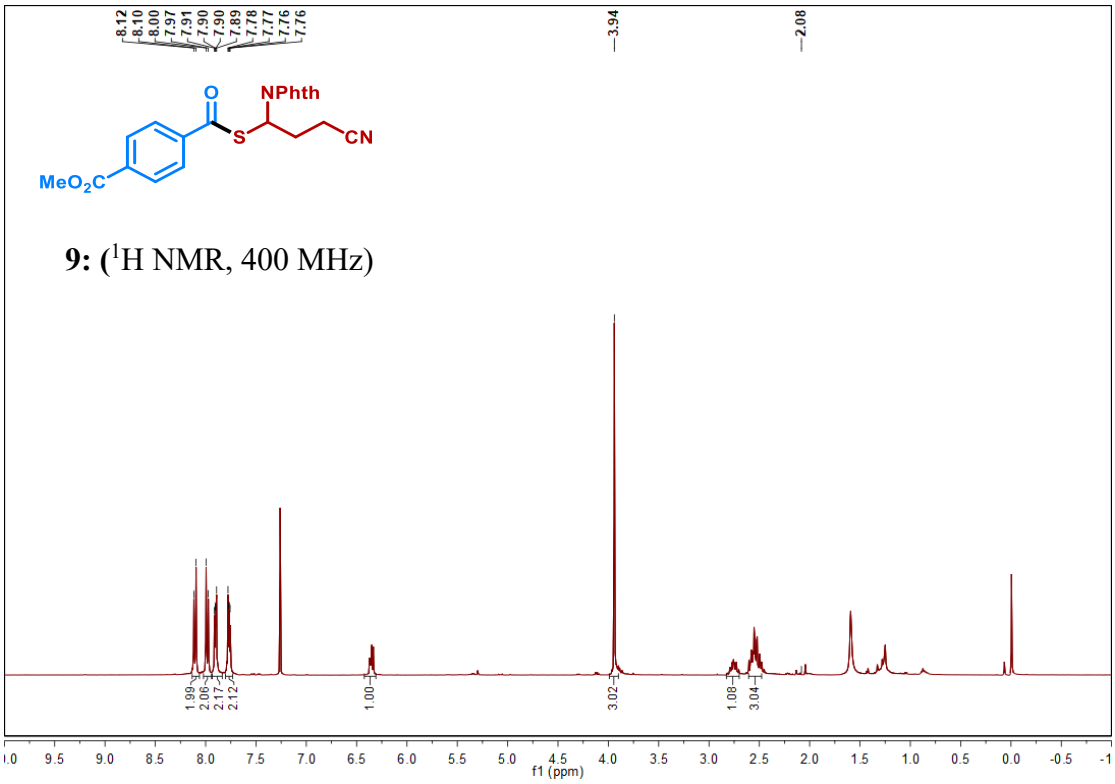

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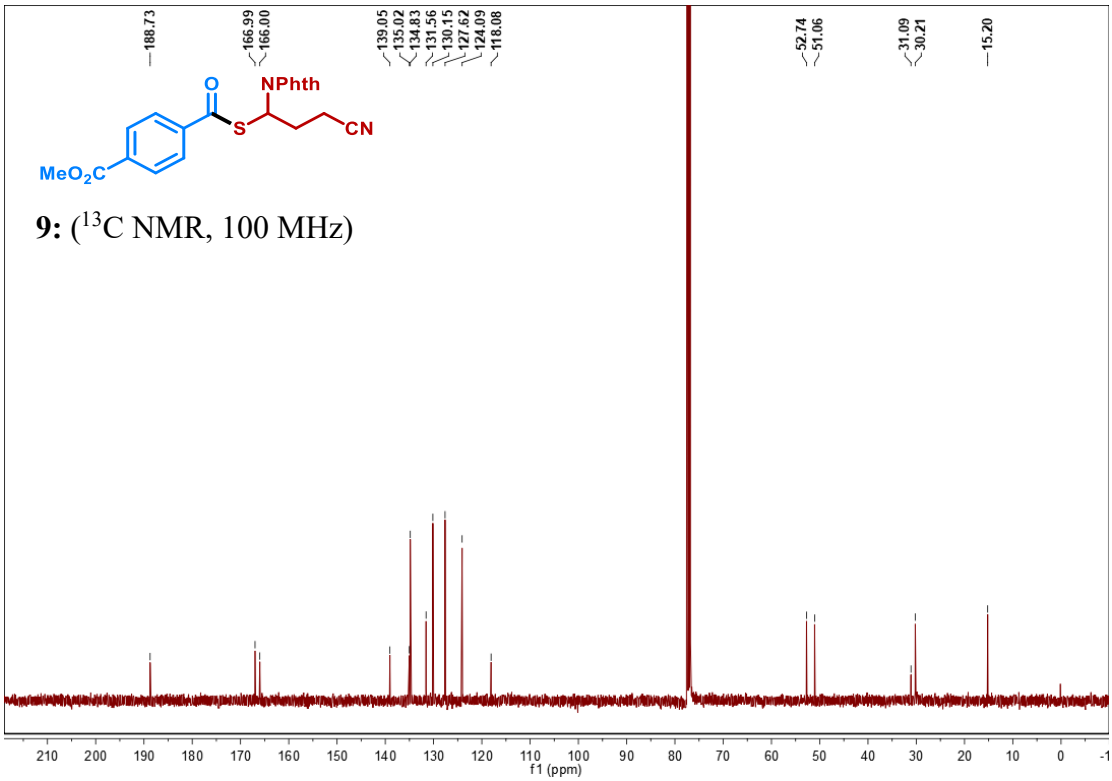

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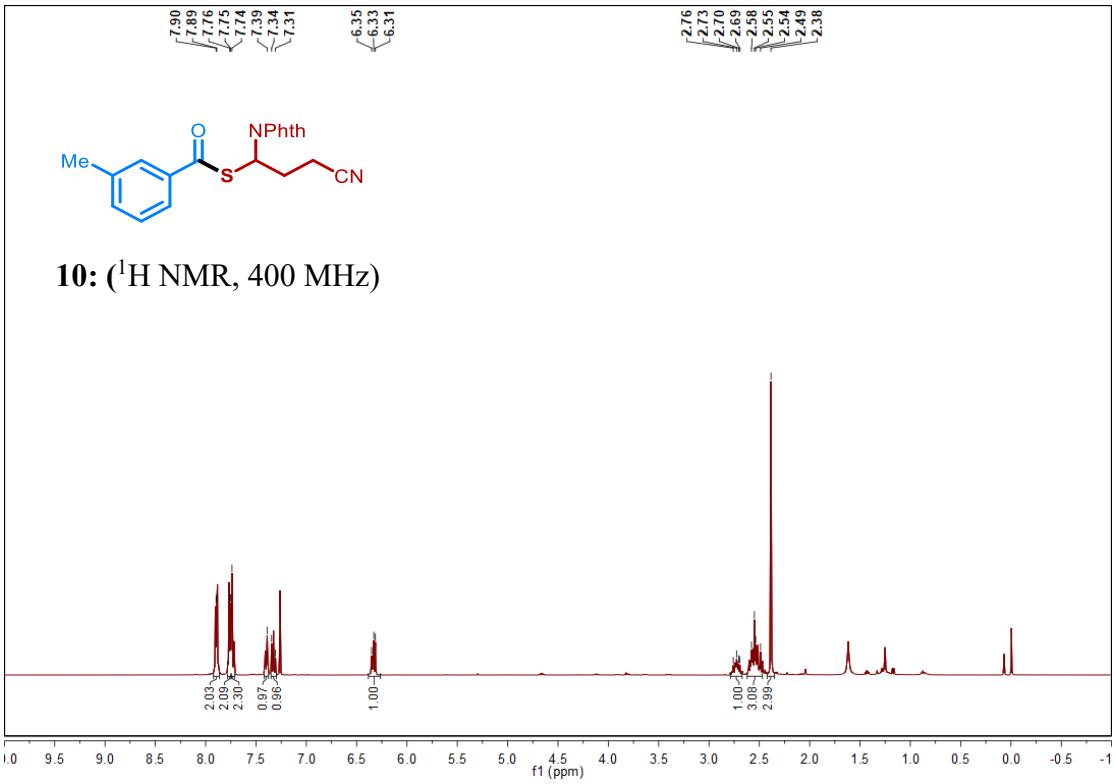

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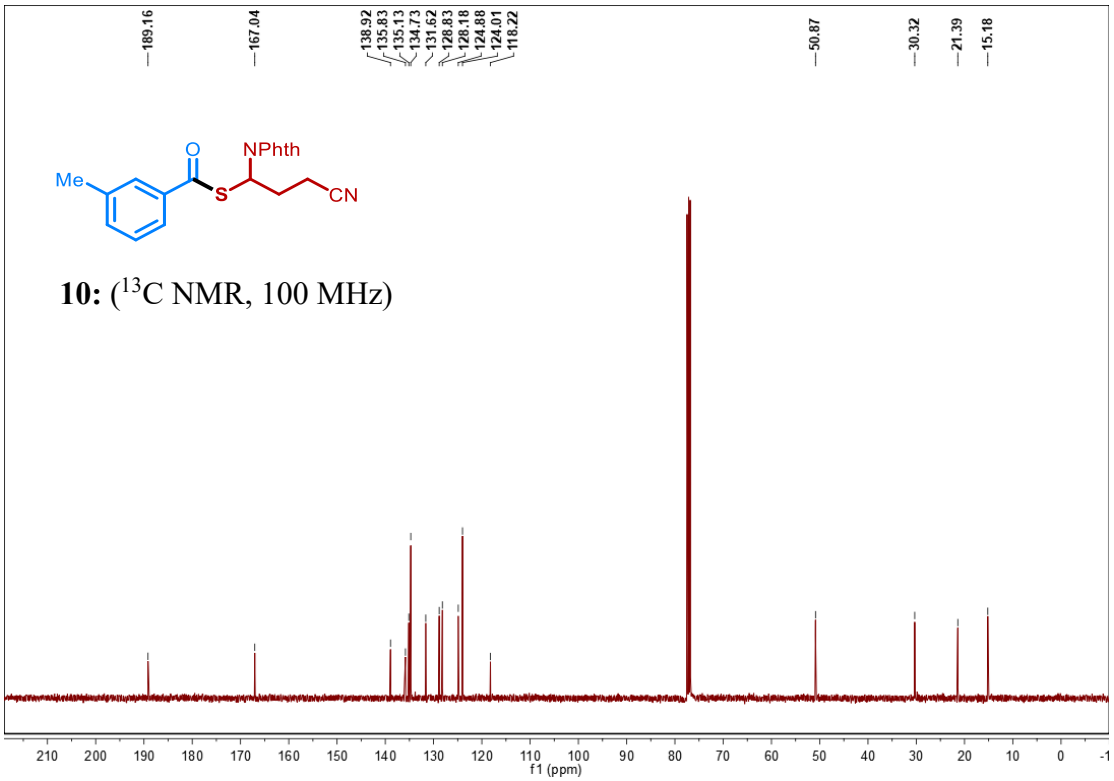

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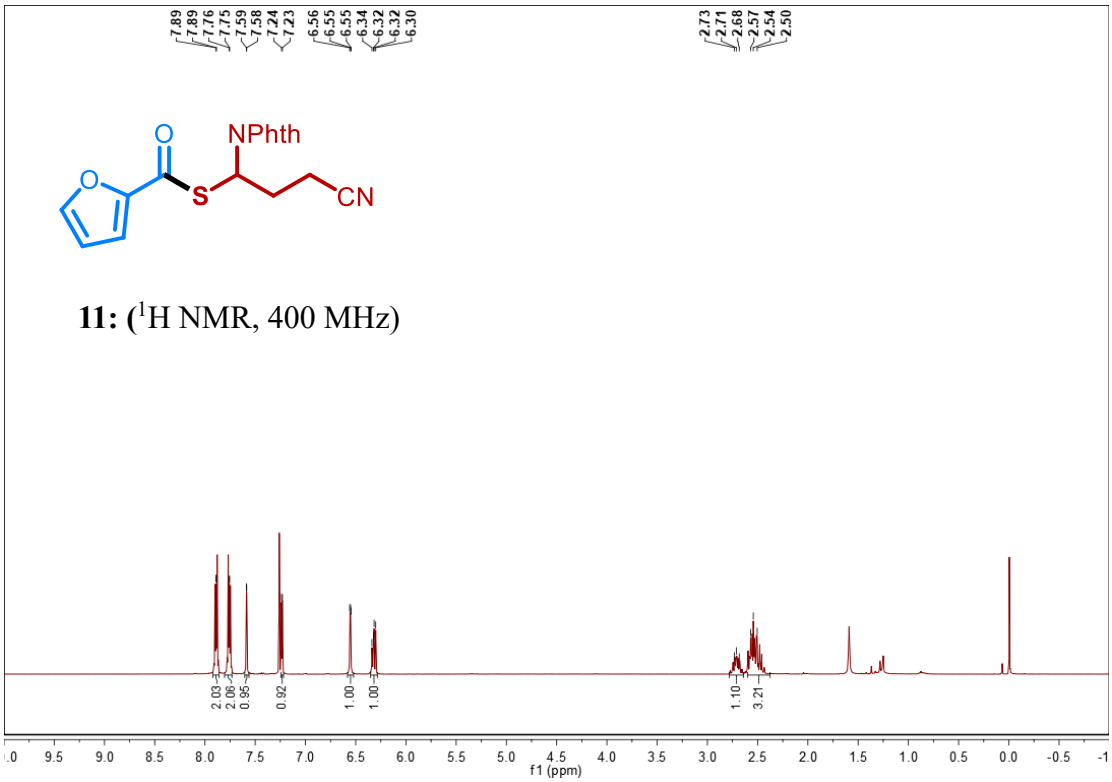

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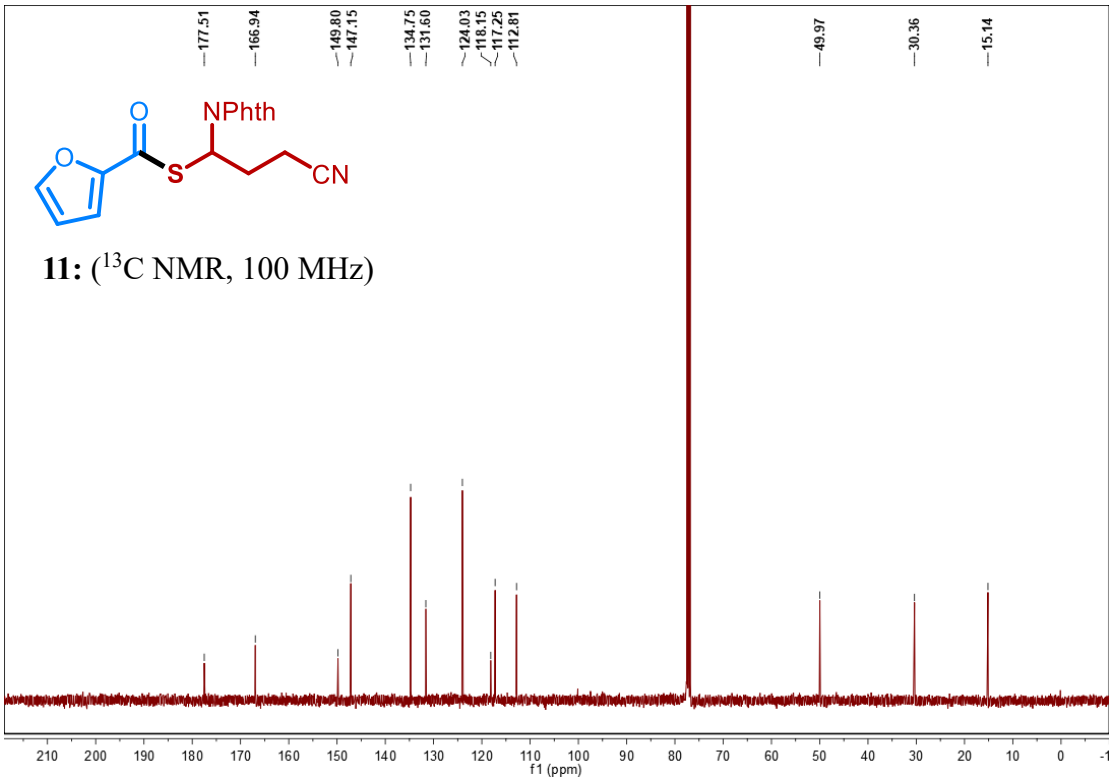

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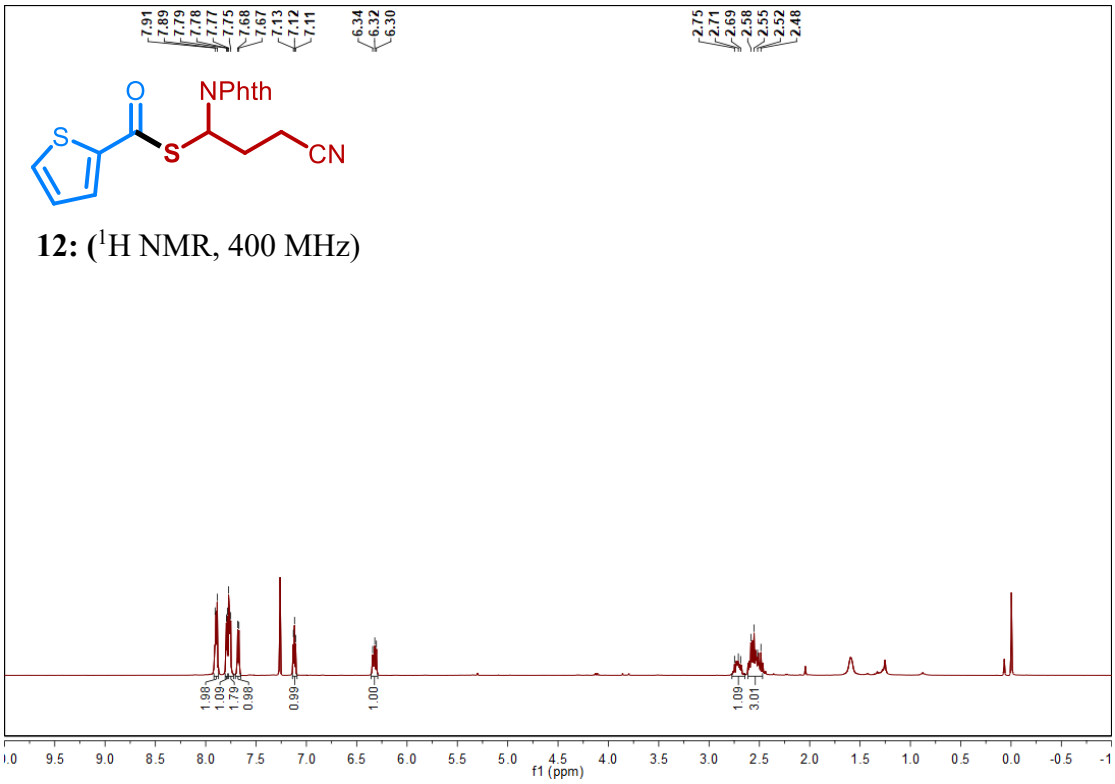

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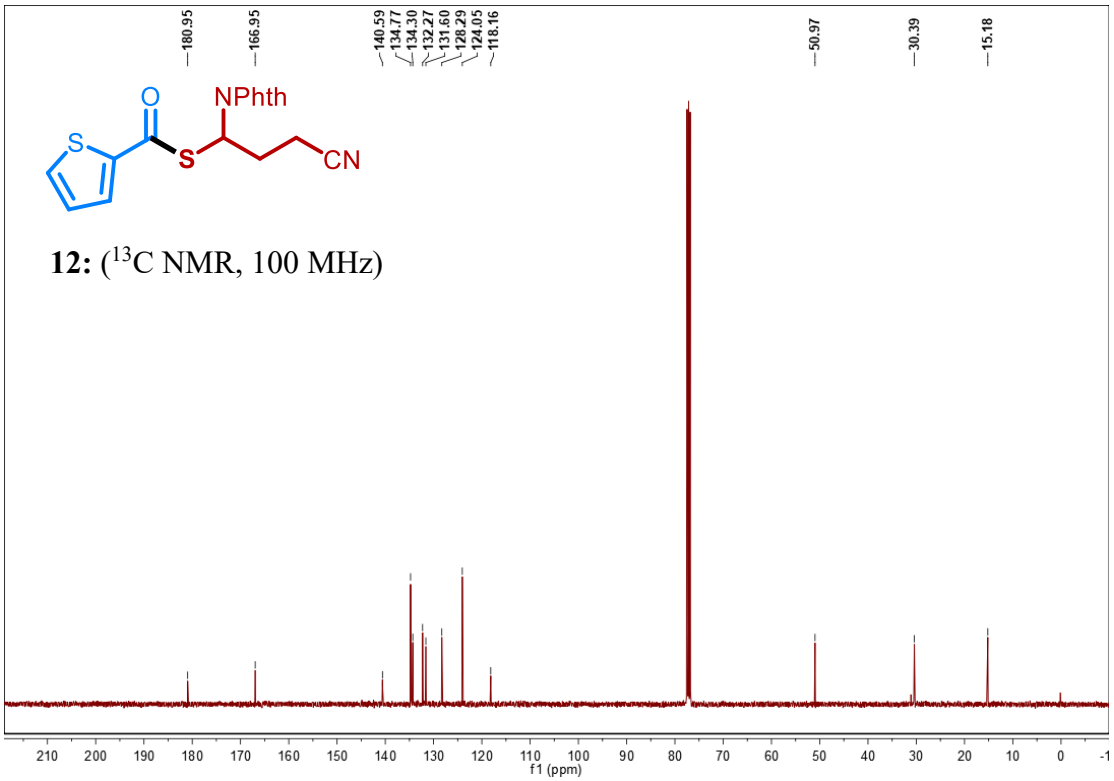

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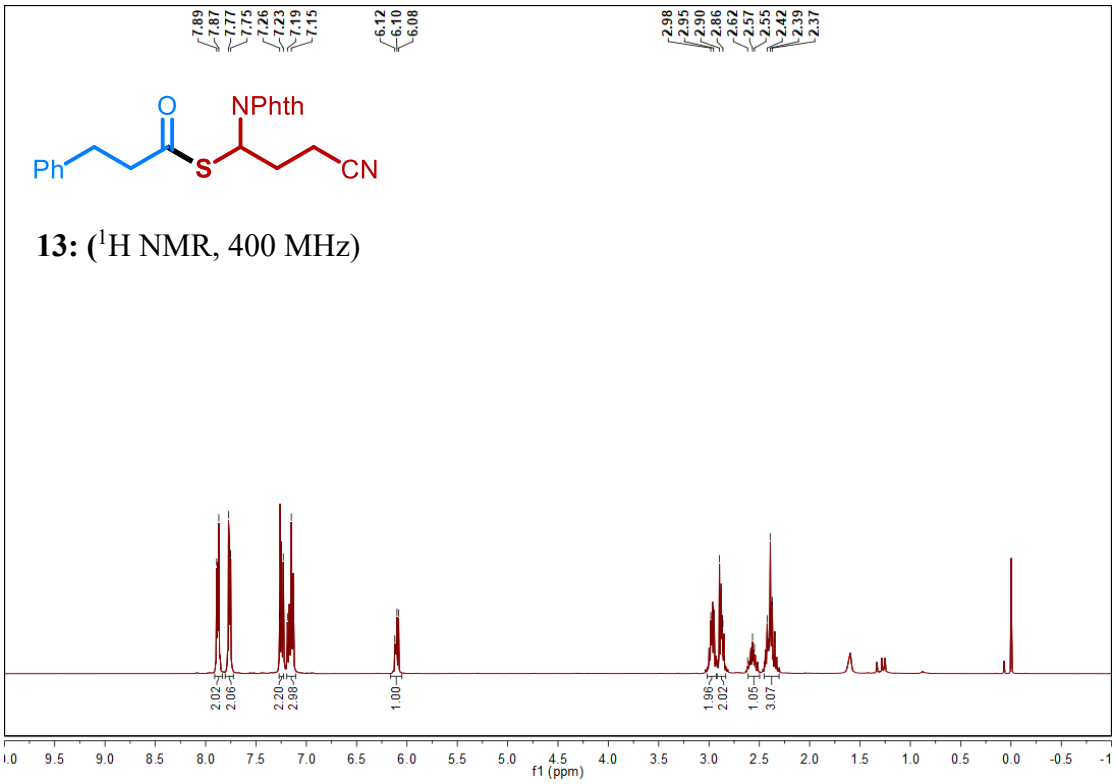

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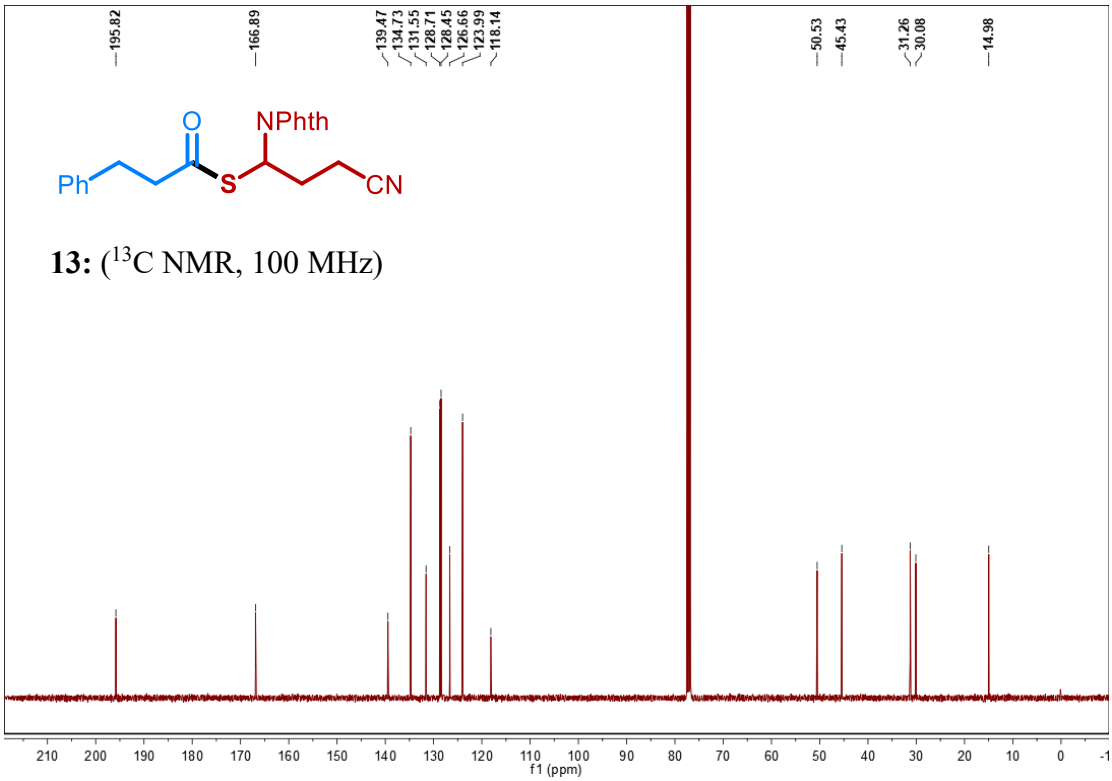

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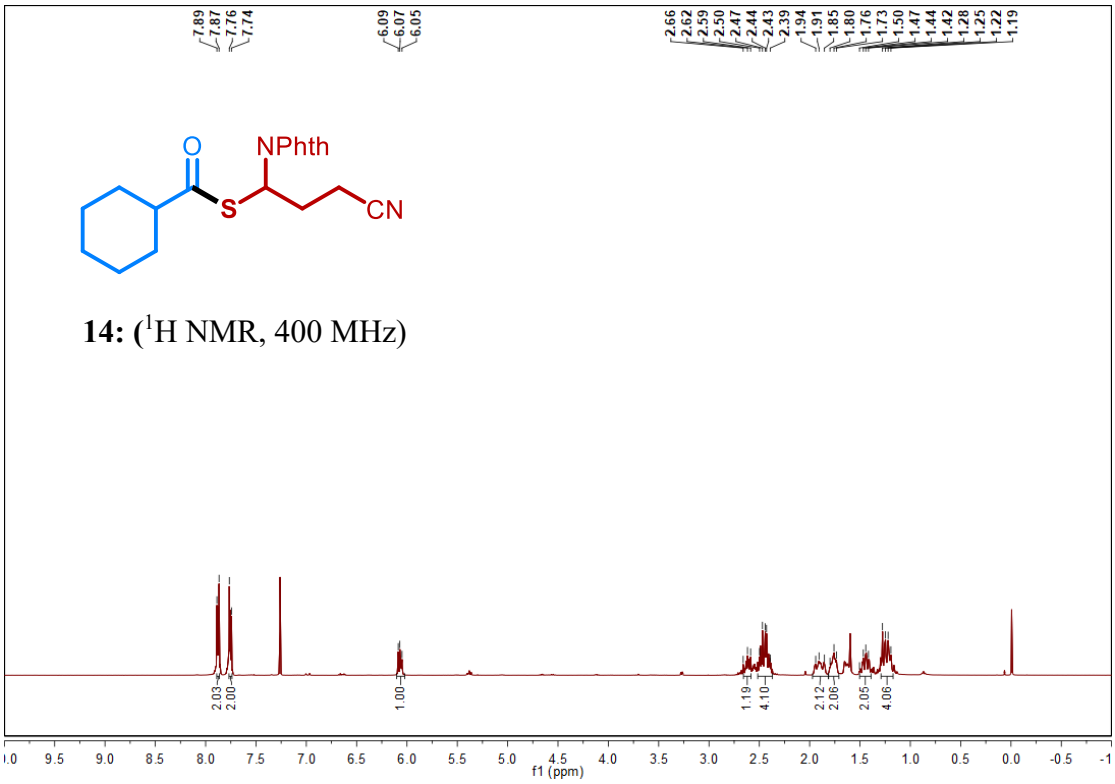

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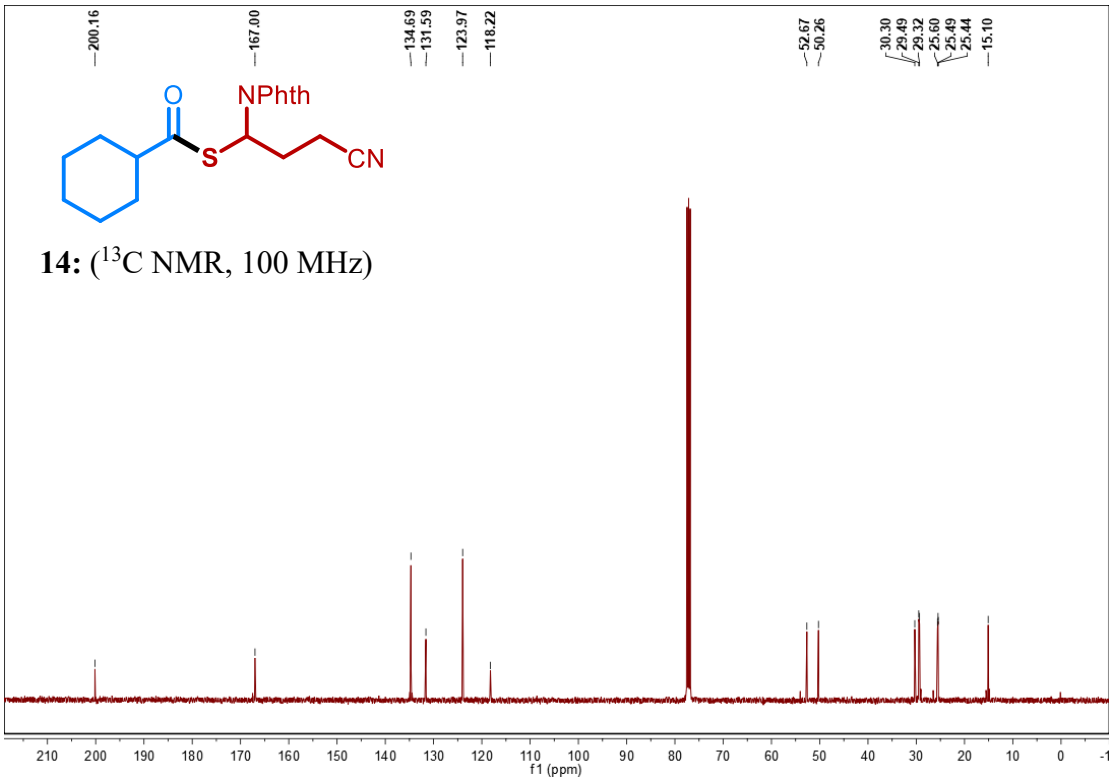

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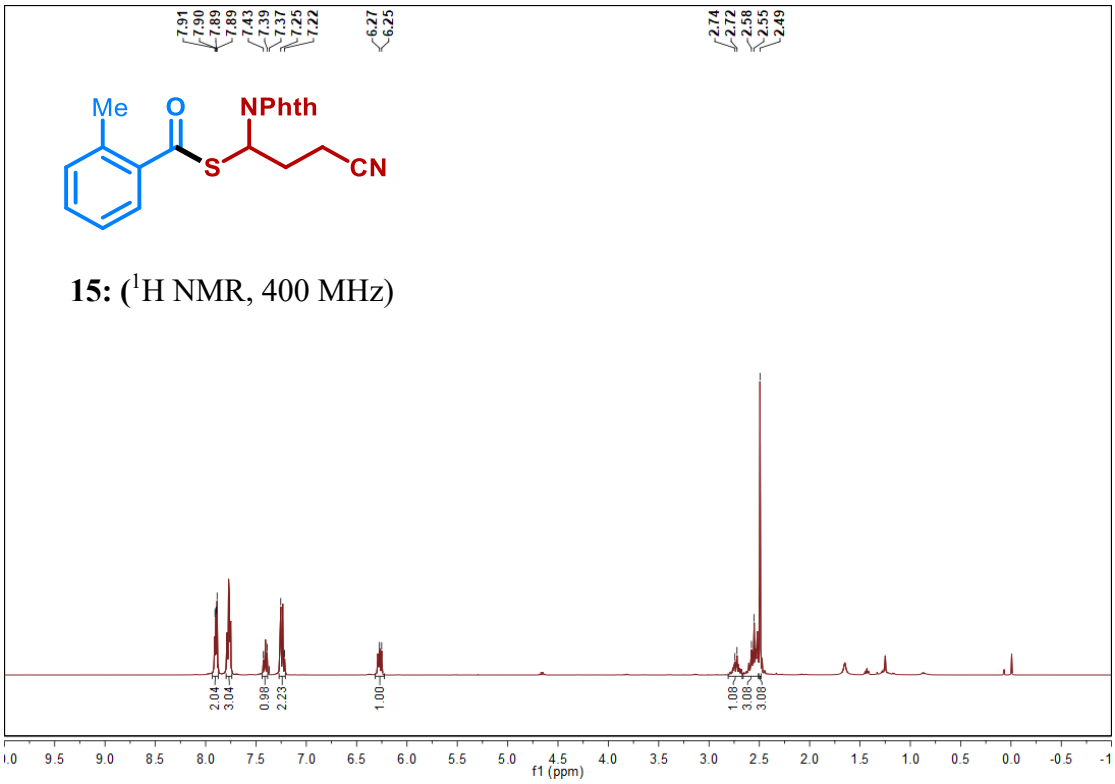

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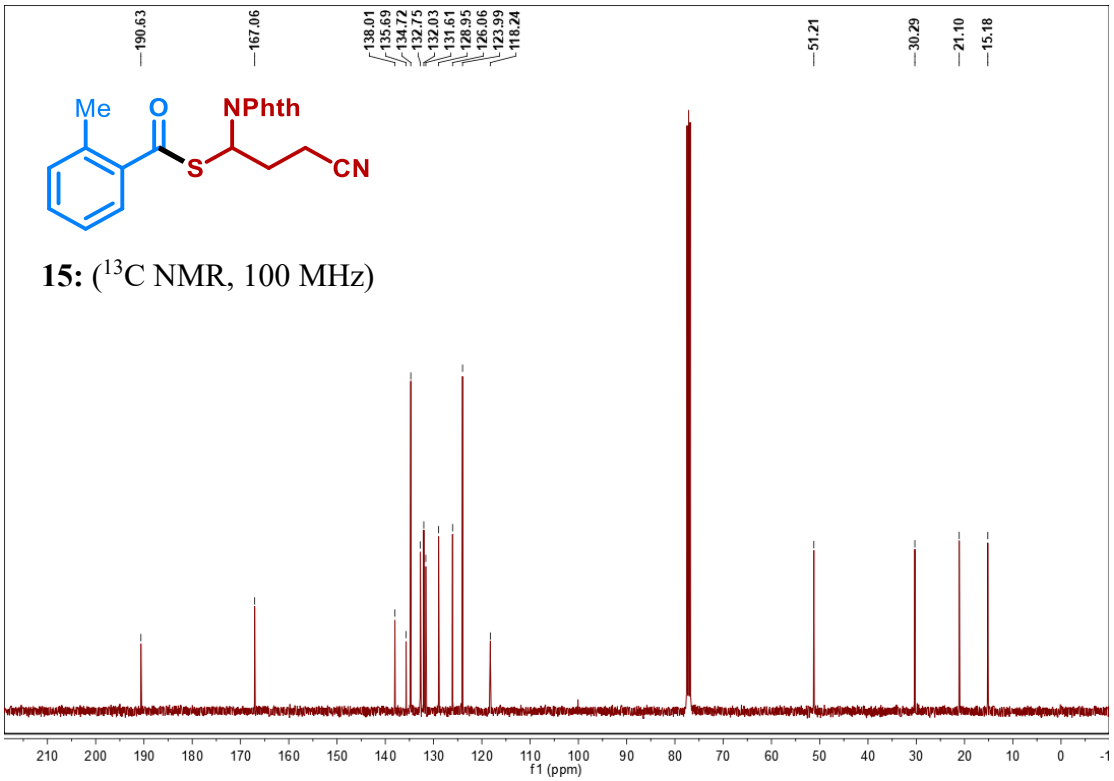

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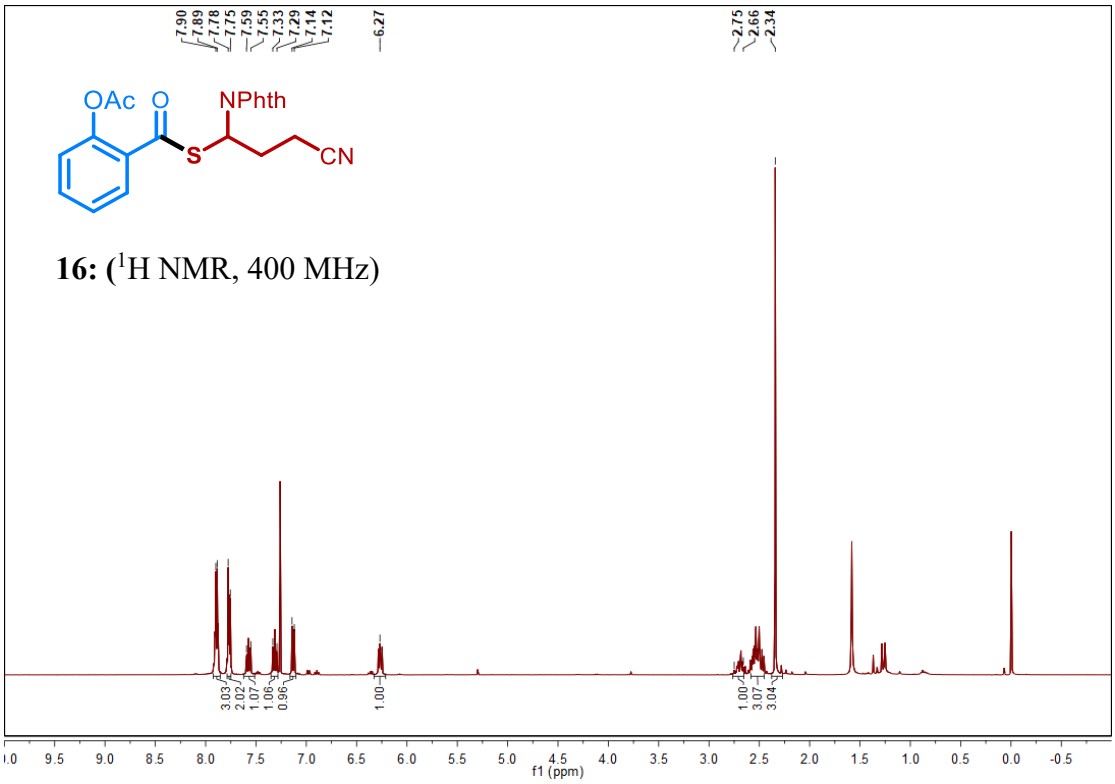

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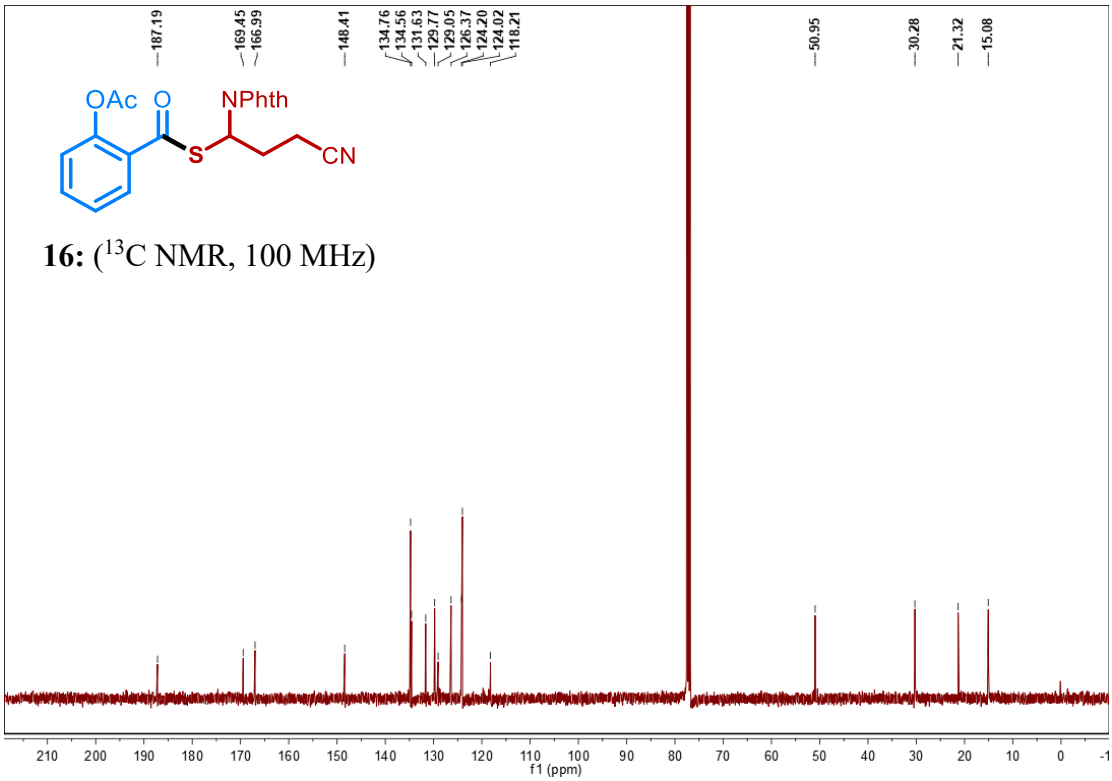

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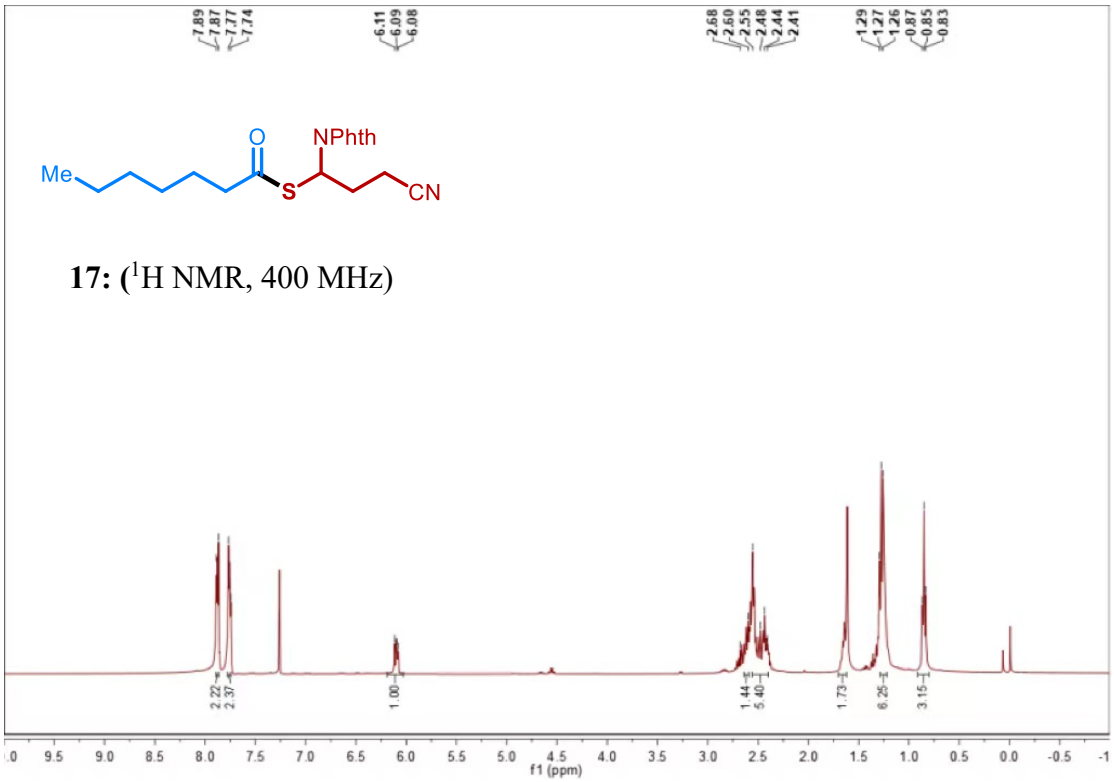

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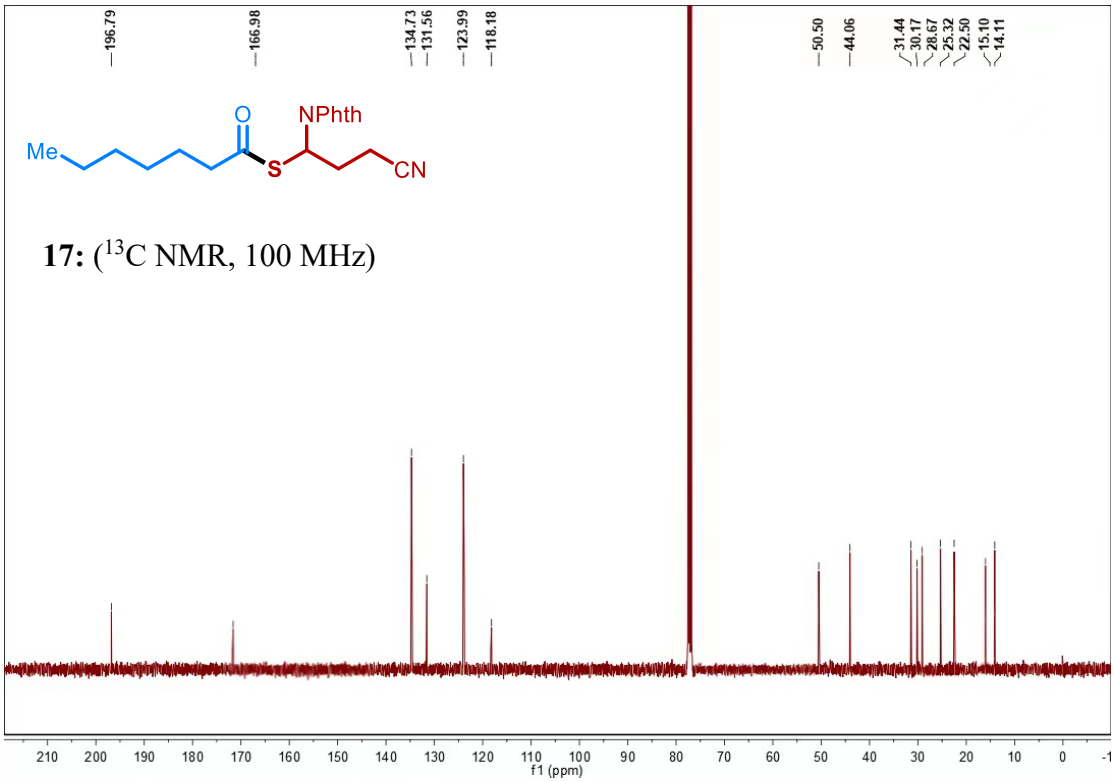

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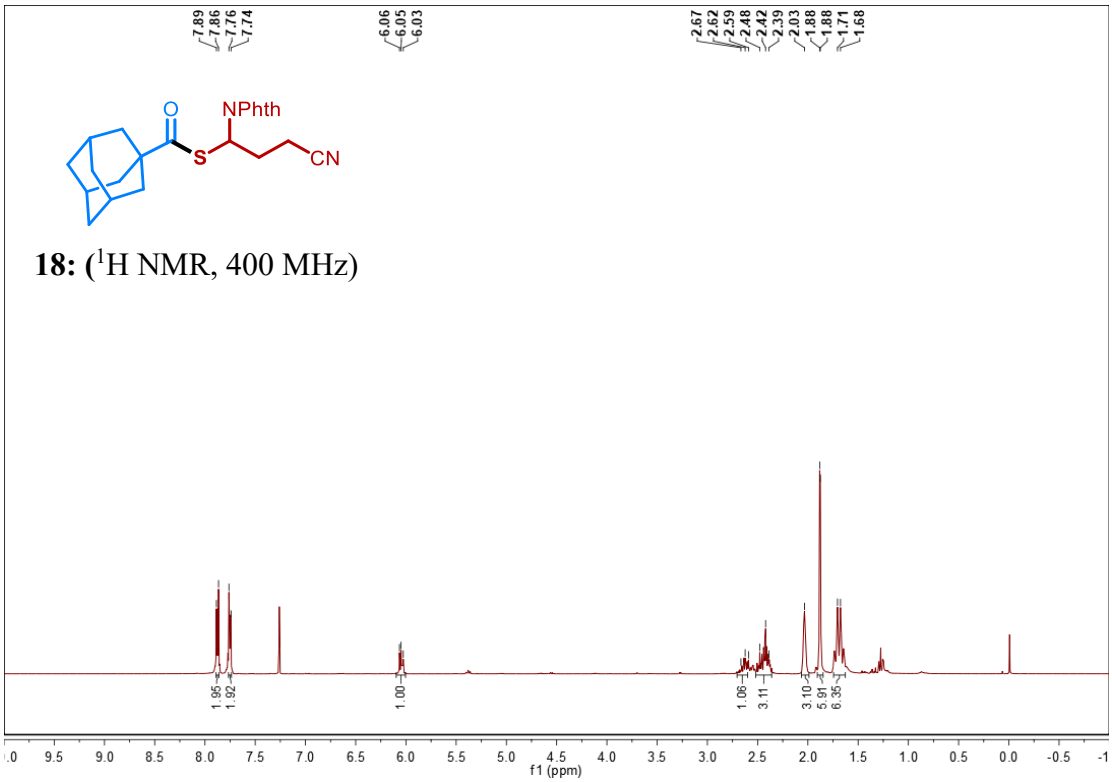
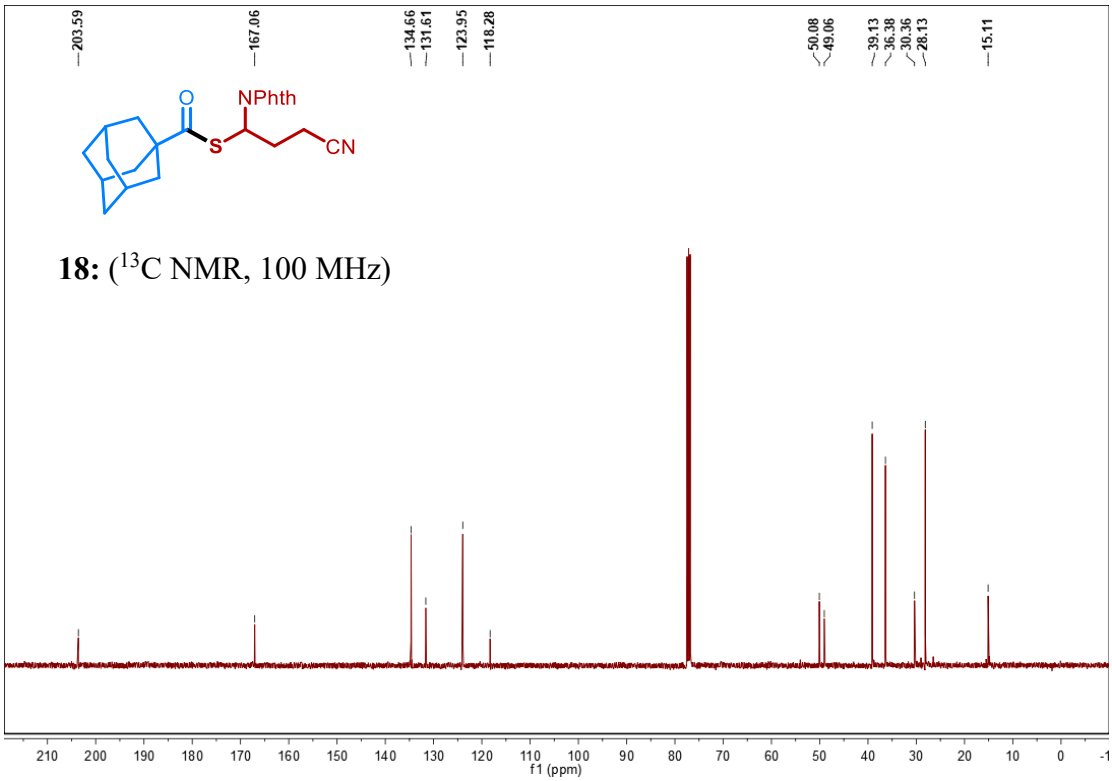
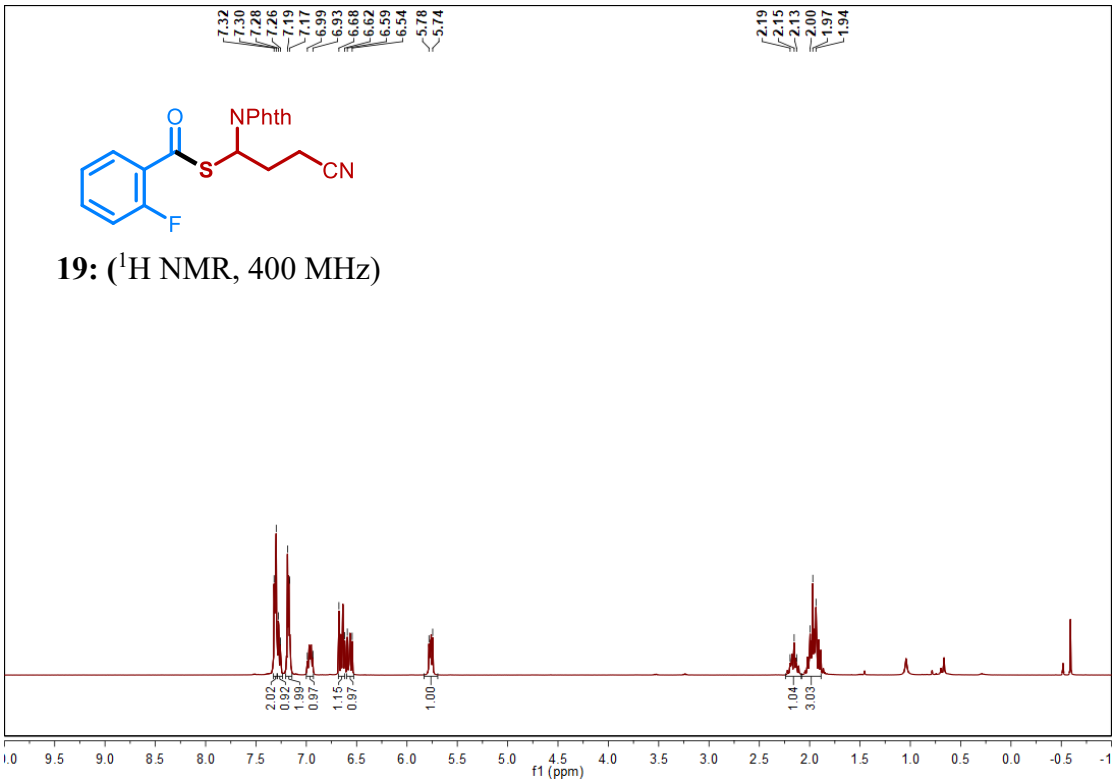


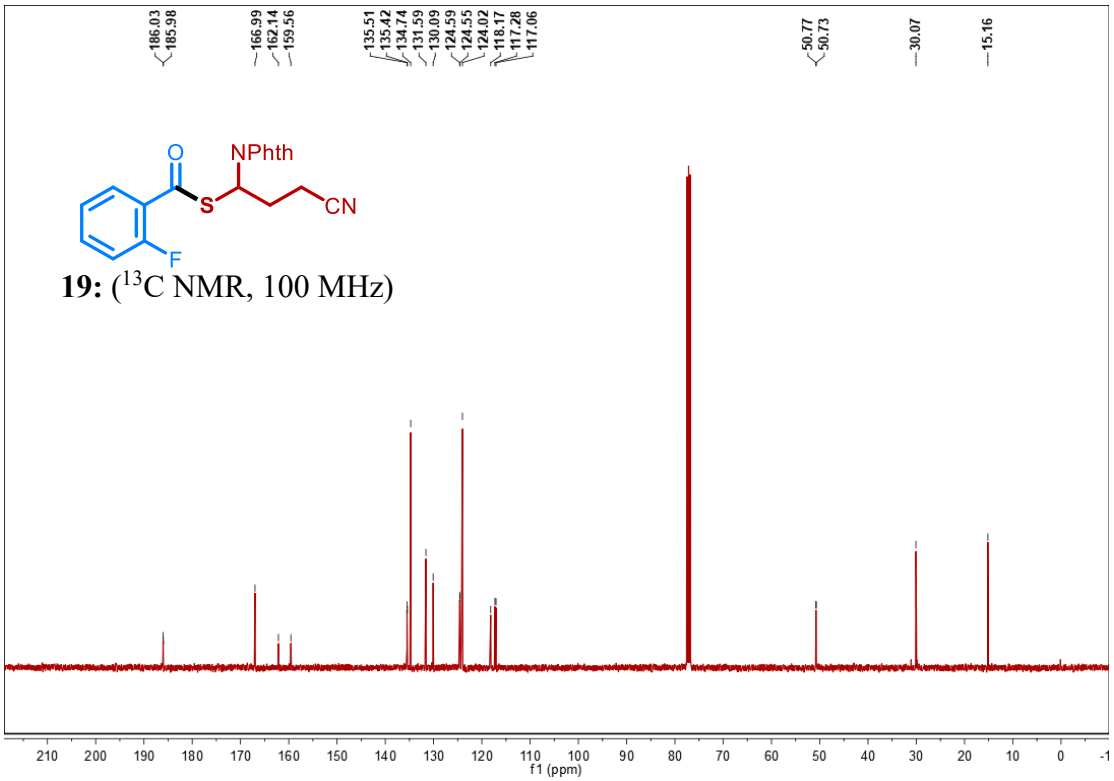
18: (^{1}H NMR, 400 MHz)



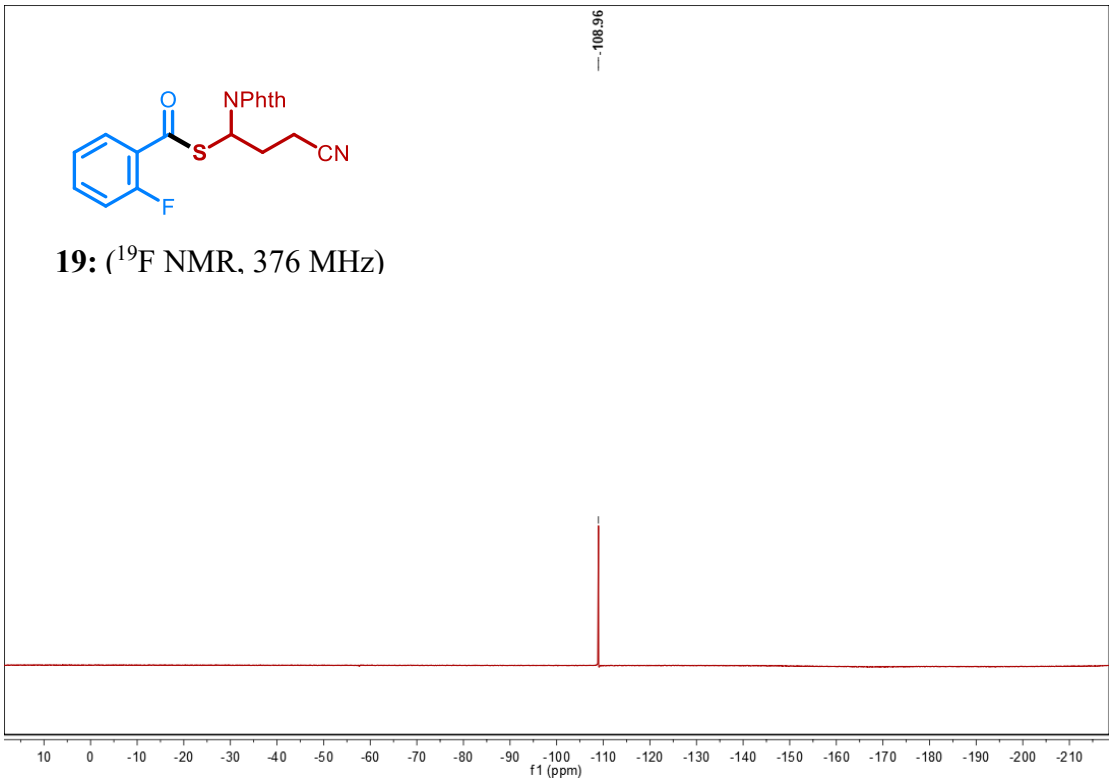
18: (^{13}C NMR, 100 MHz)



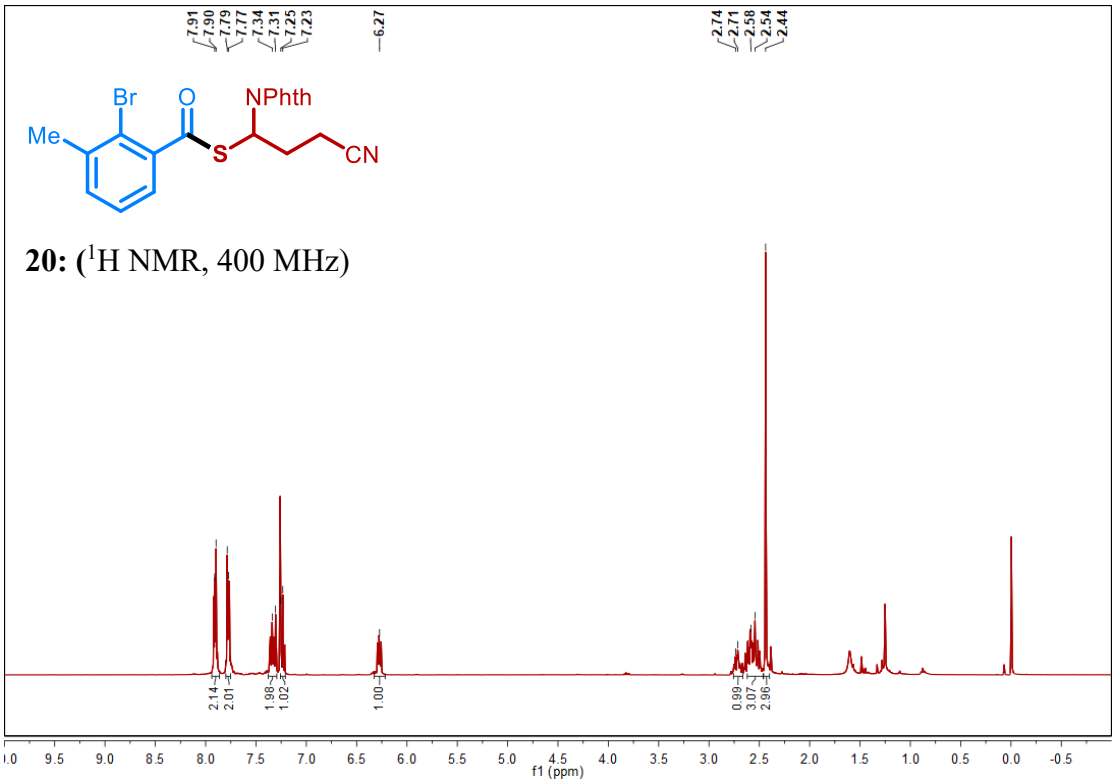
19: (^{1}H NMR, 400 MHz)



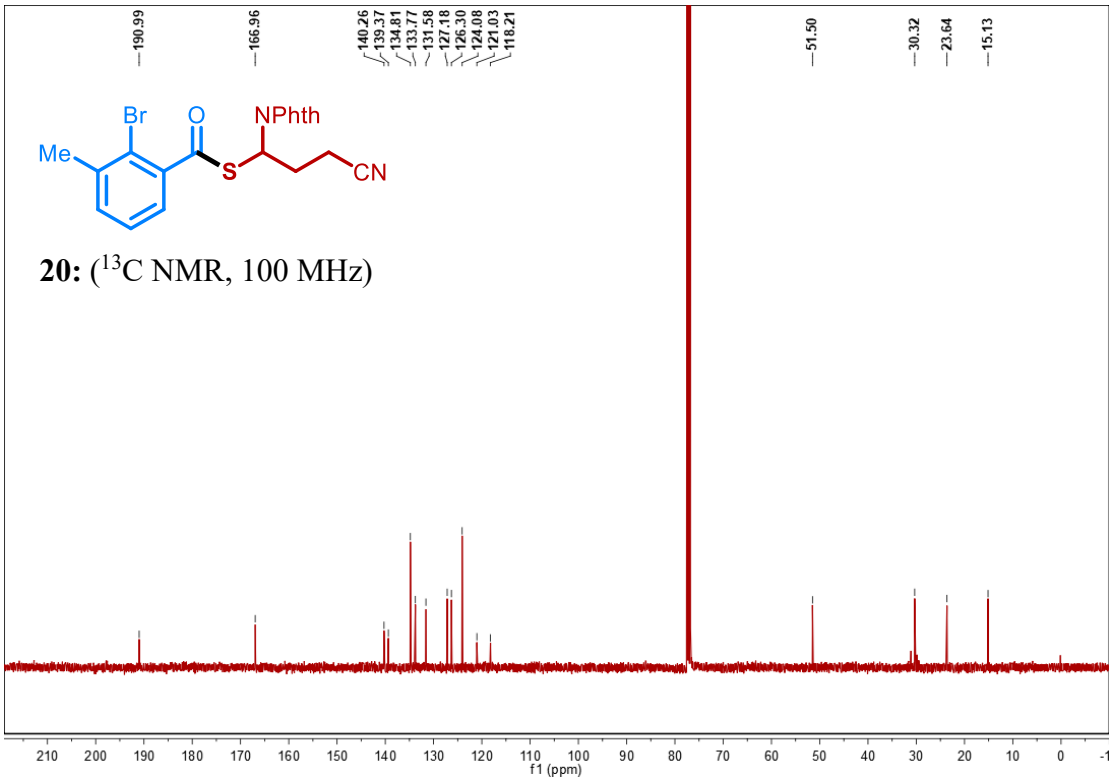
19: (^{13}C NMR, 100 MHz)



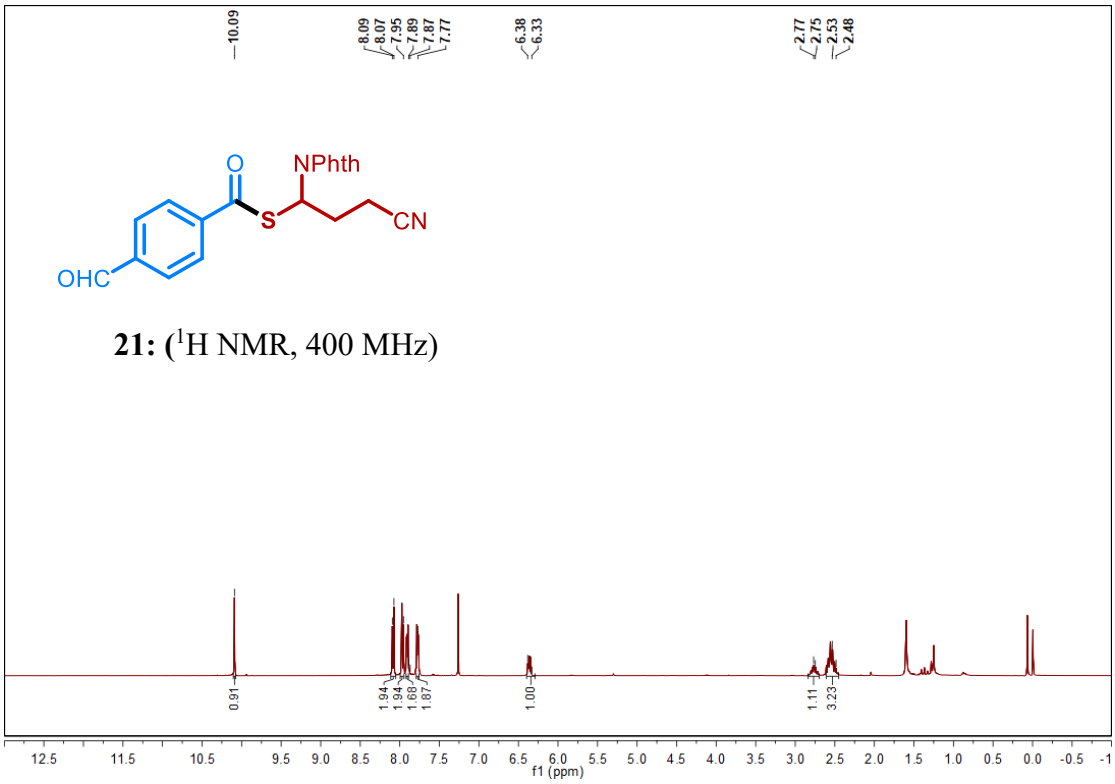
19: (^{19}F NMR, 376 MHz)



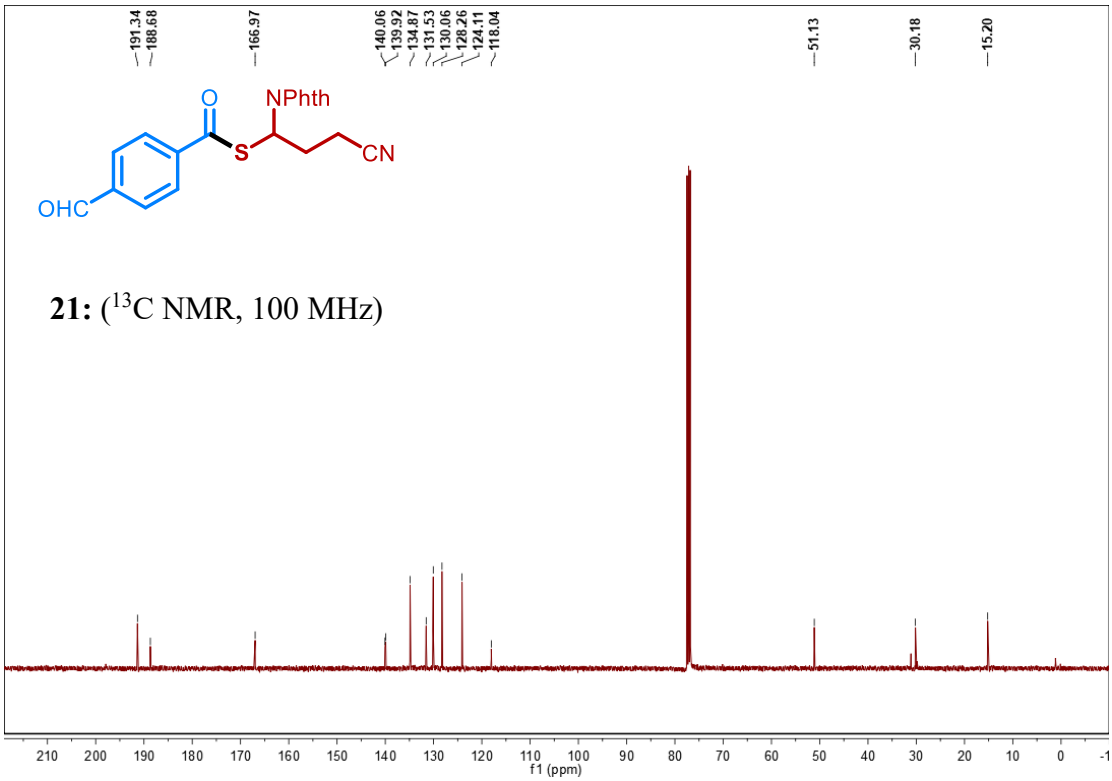
20: (^{1}H NMR, 400 MHz)



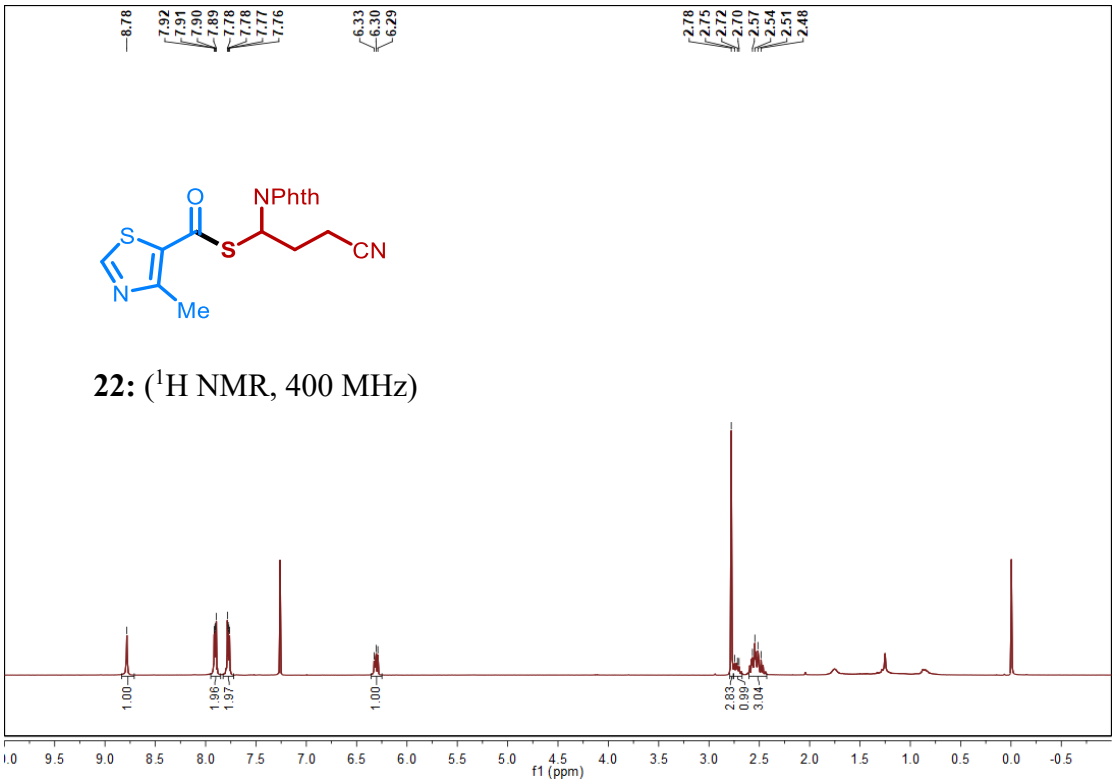
20: (^{13}C NMR, 100 MHz)



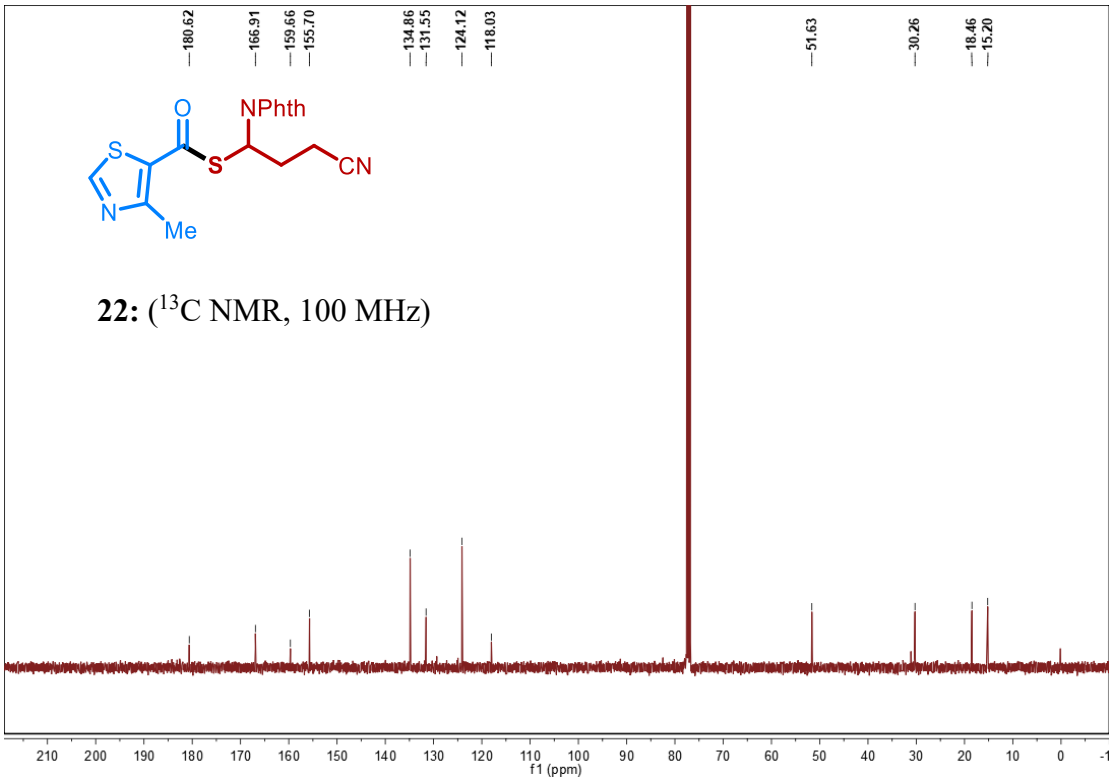
21: (^{1}H NMR, 400 MHz)



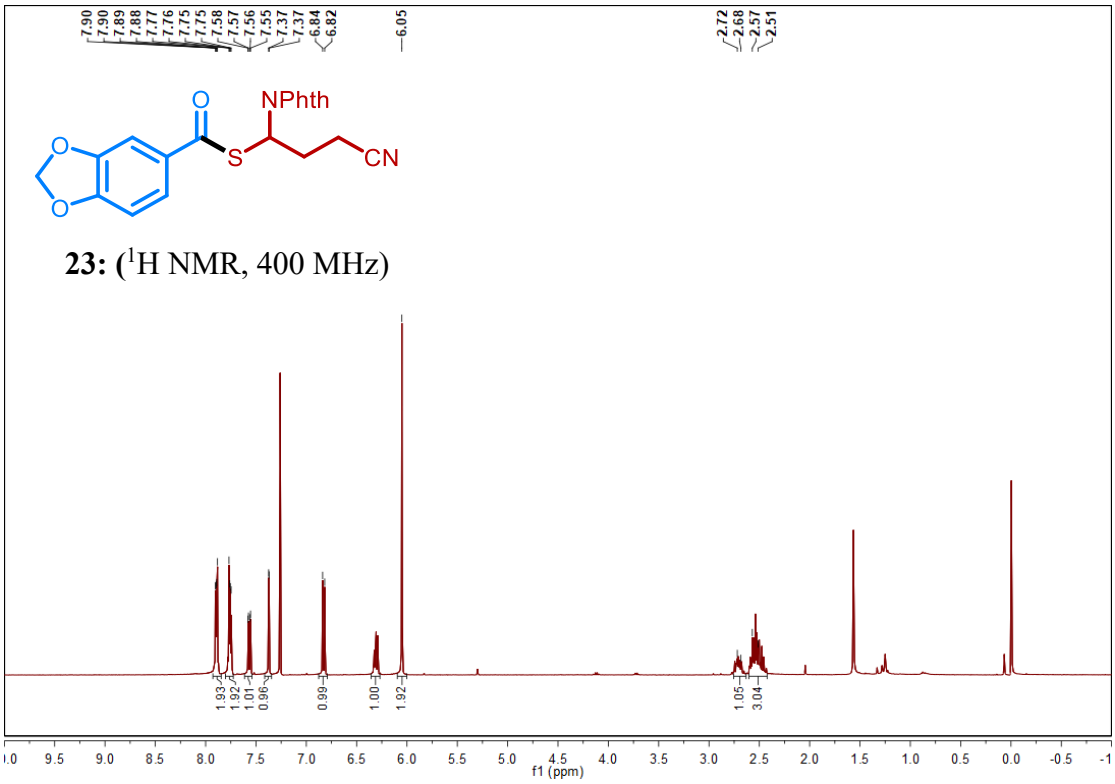
21: (^{13}C NMR, 100 MHz)



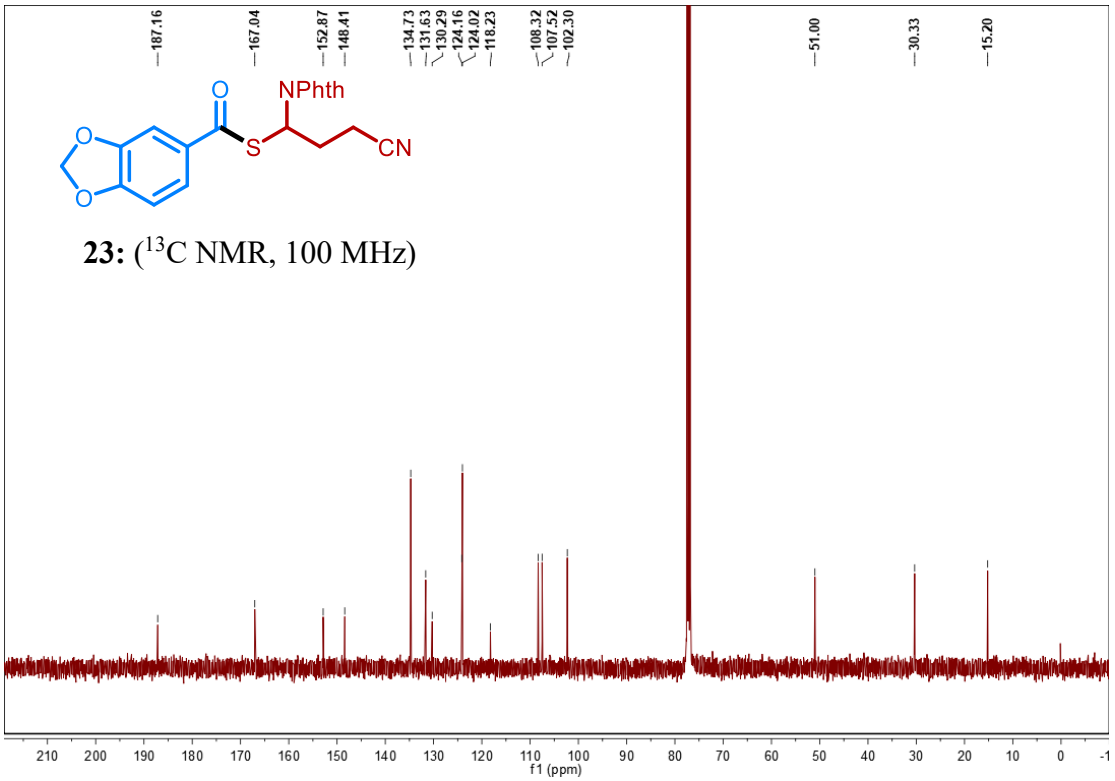
22: (^{1}H NMR, 400 MHz)



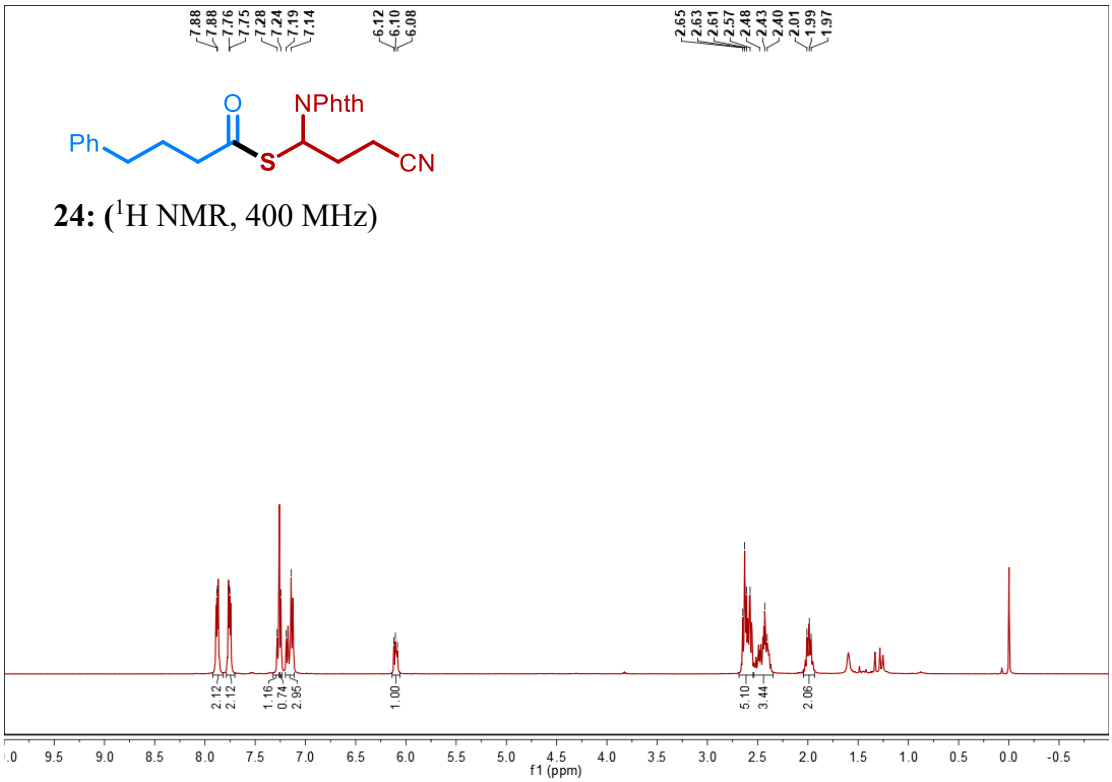
22: (^{13}C NMR, 100 MHz)



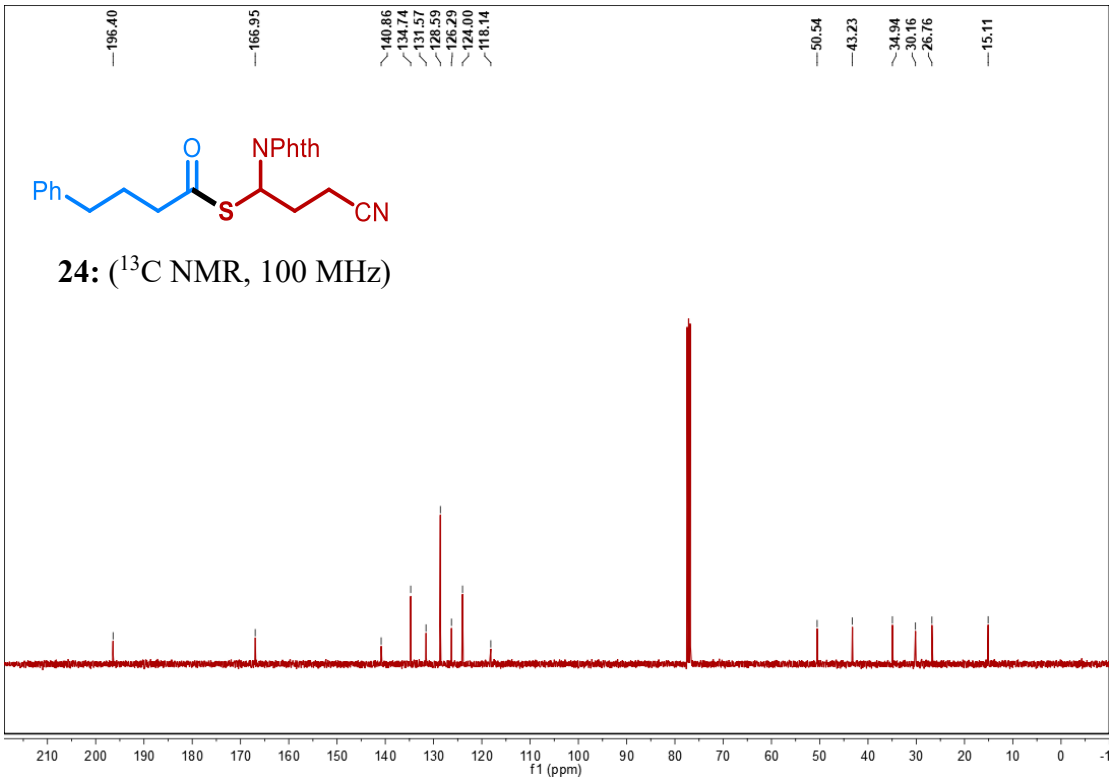
23: (^{1}H NMR, 400 MHz)



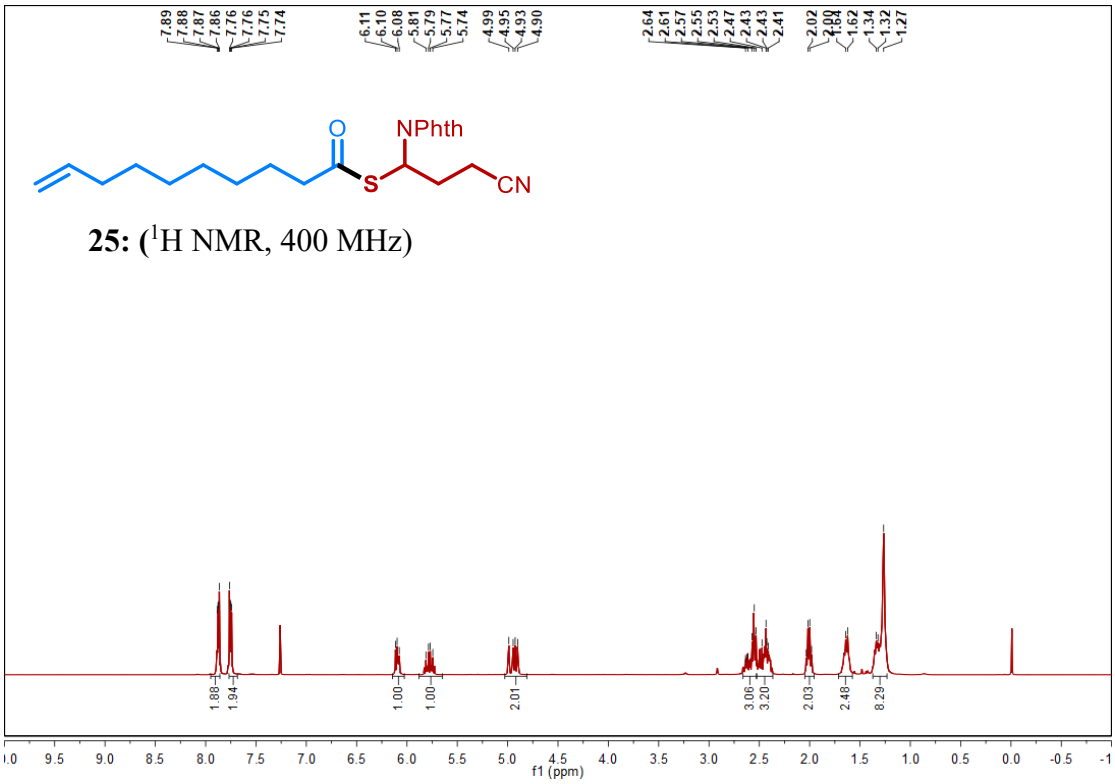
23: (^{13}C NMR, 100 MHz)



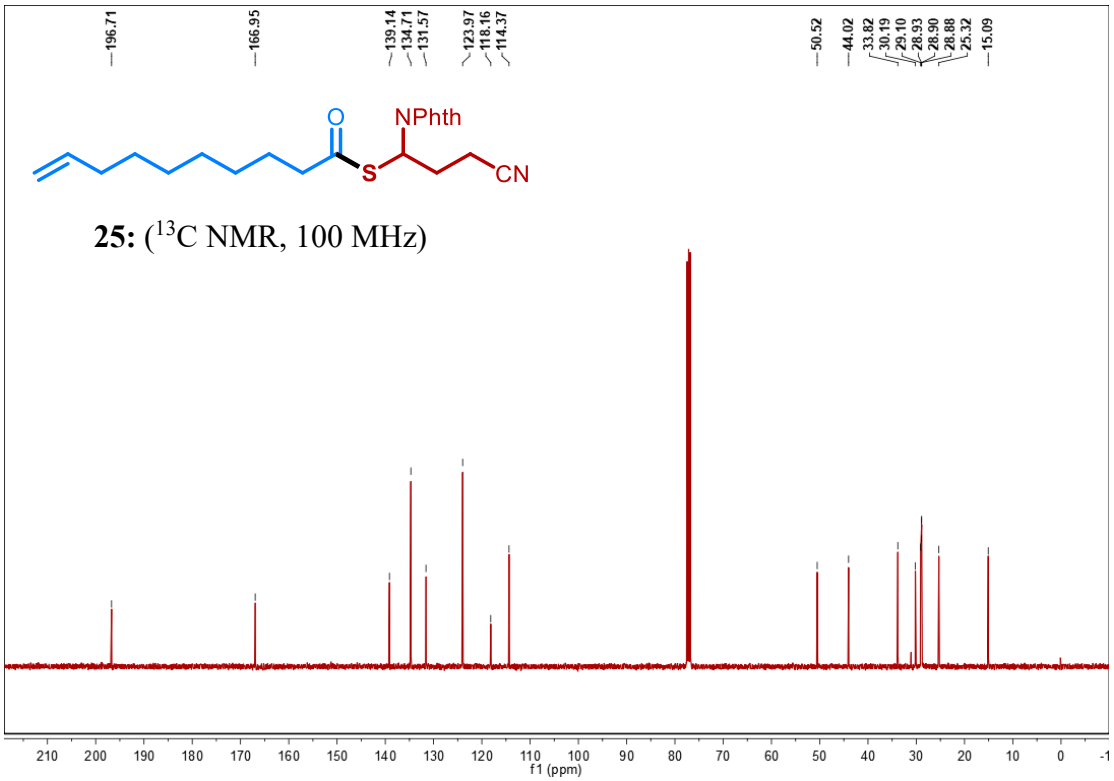
24: (^{1}H NMR, 400 MHz)



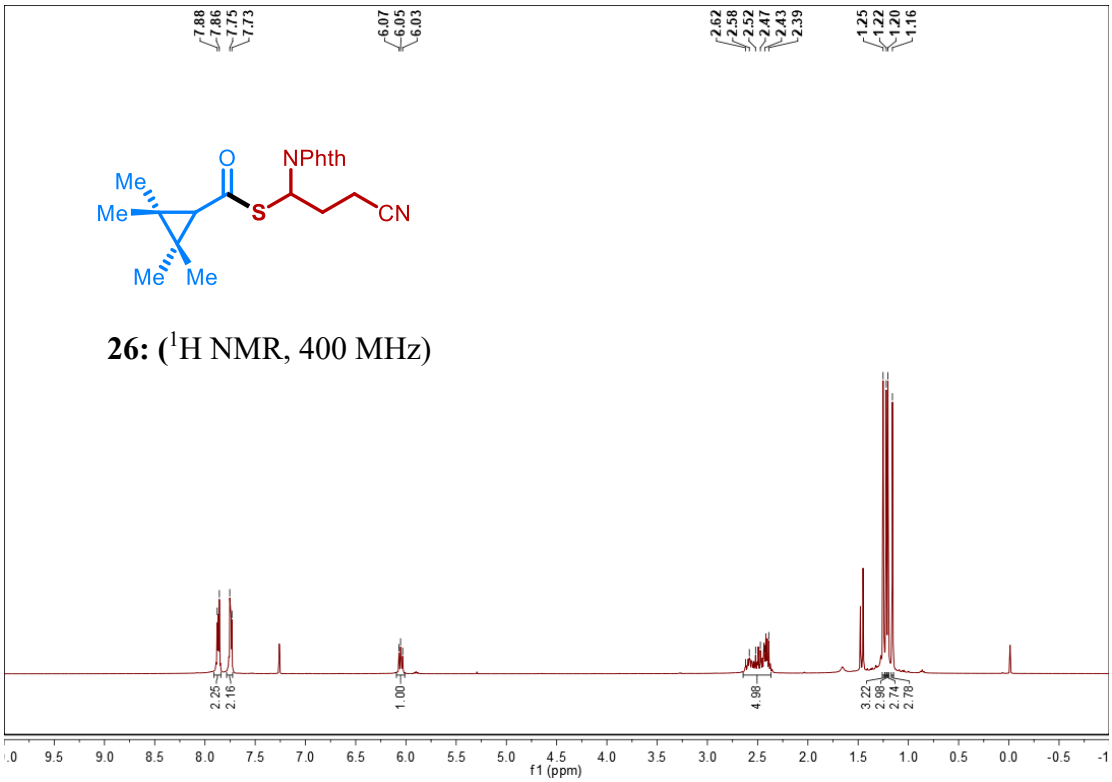
24: (^{13}C NMR, 100 MHz)



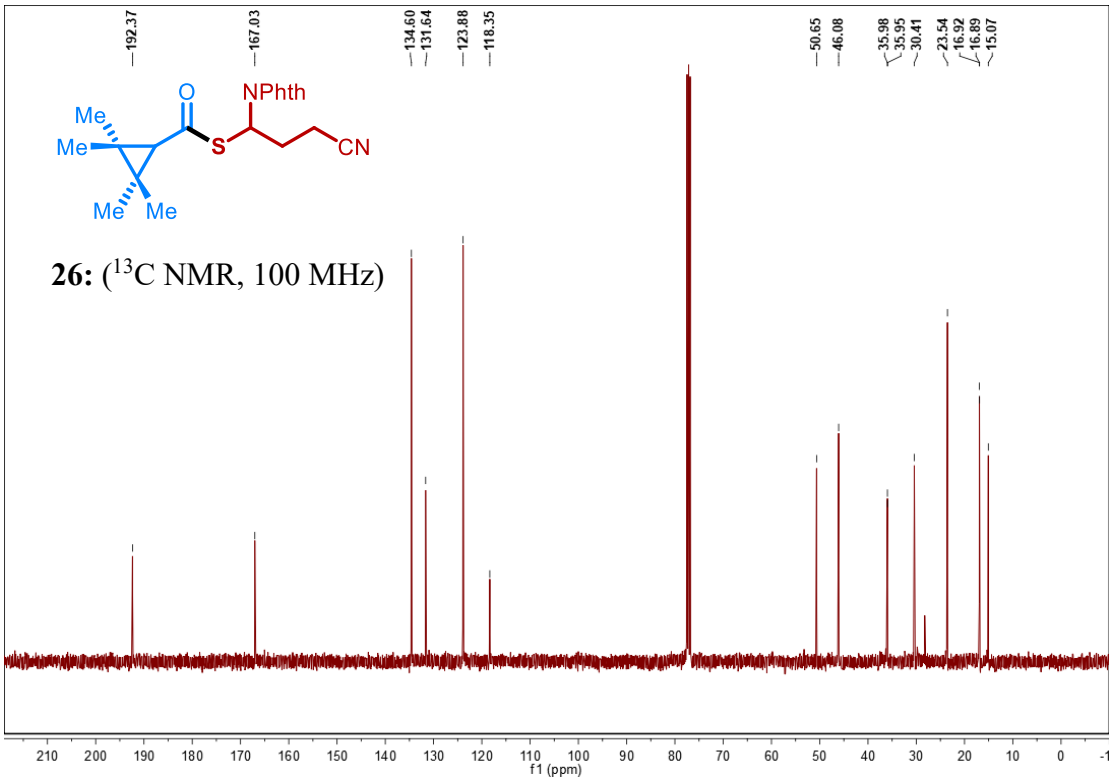
25: (^{1}H NMR, 400 MHz)



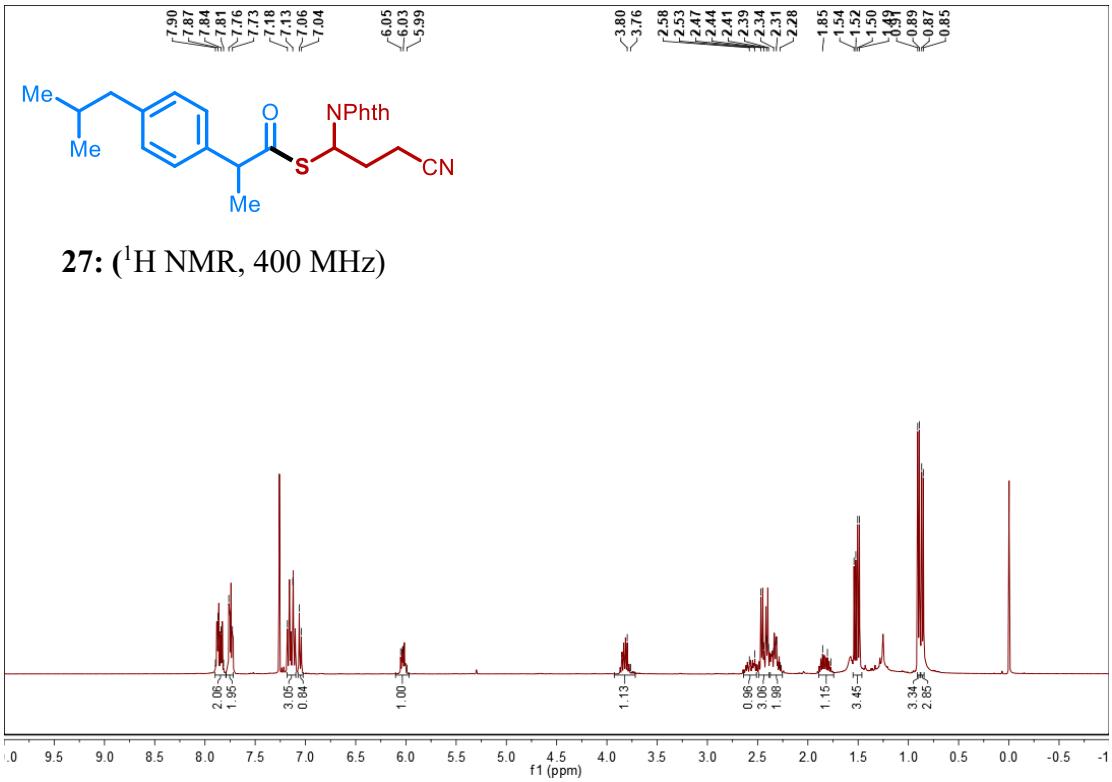
25: (^{13}C NMR, 100 MHz)



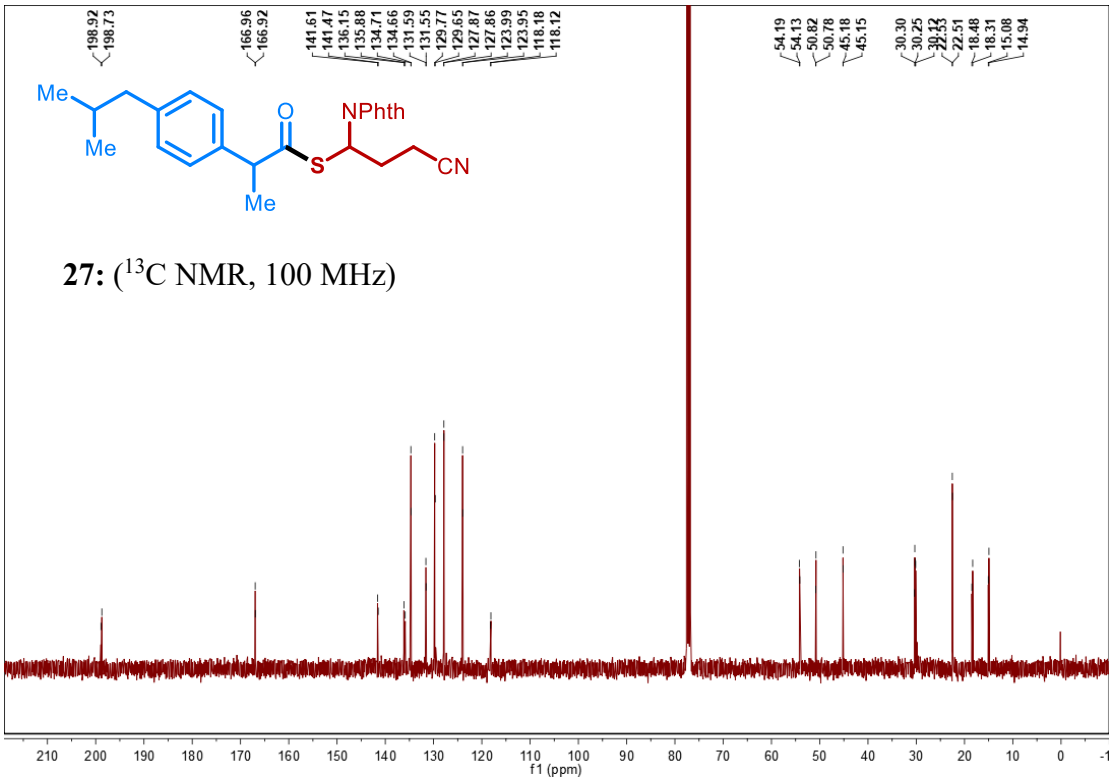
26: (^{1}H NMR, 400 MHz)



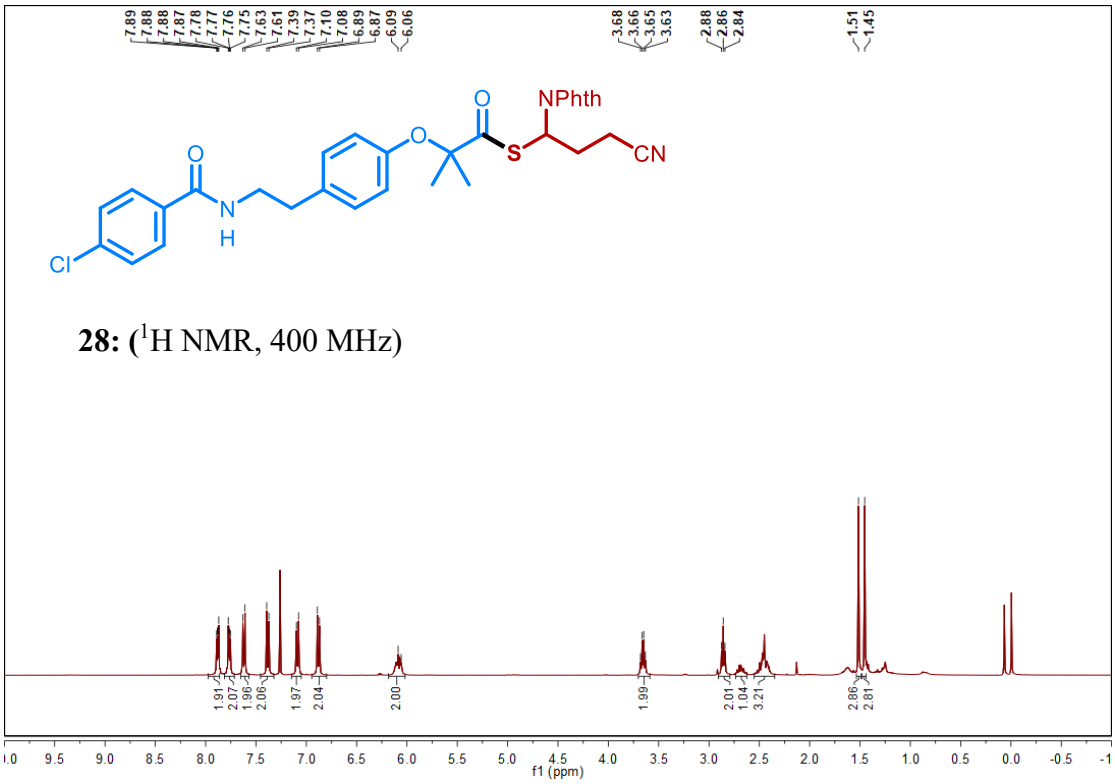
26: (^{13}C NMR, 100 MHz)



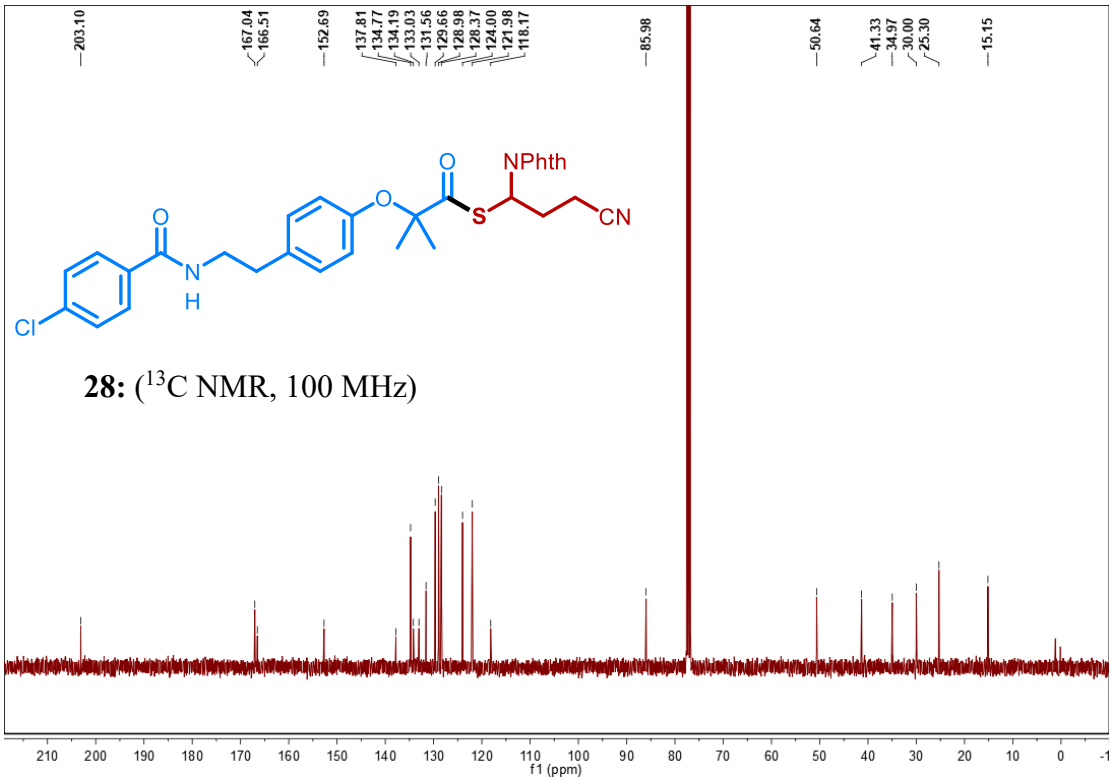
27: (^{1}H NMR, 400 MHz)



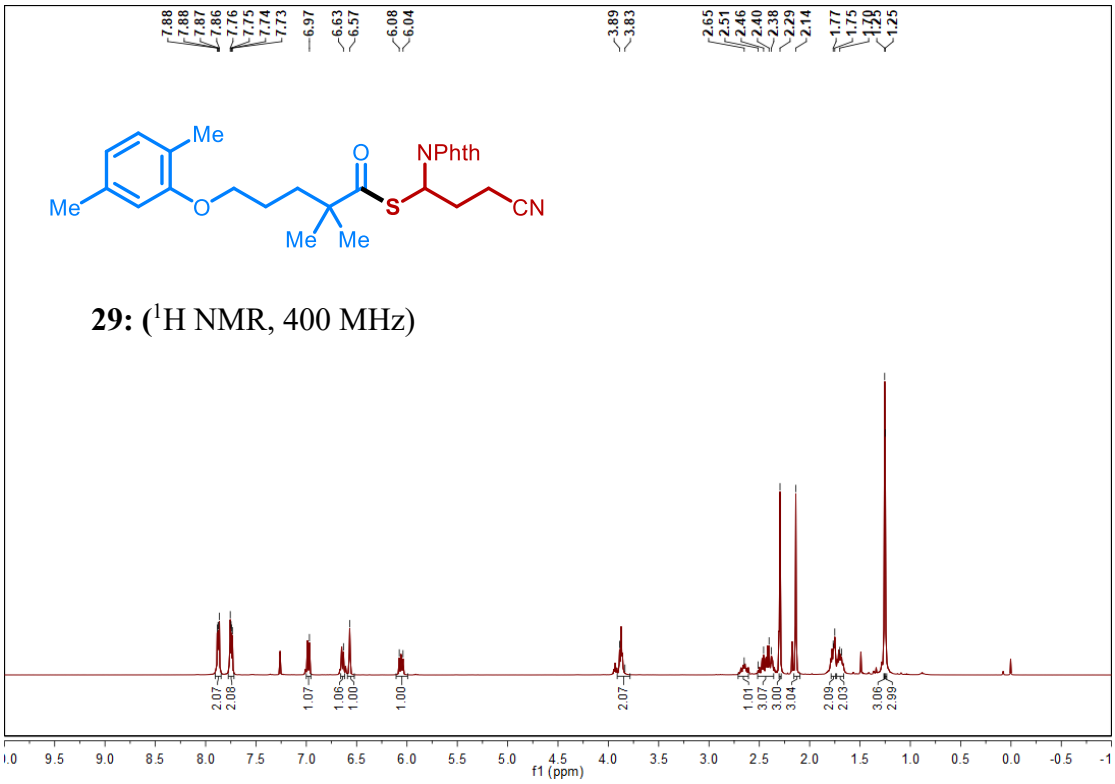
27: (^{13}C NMR, 100 MHz)



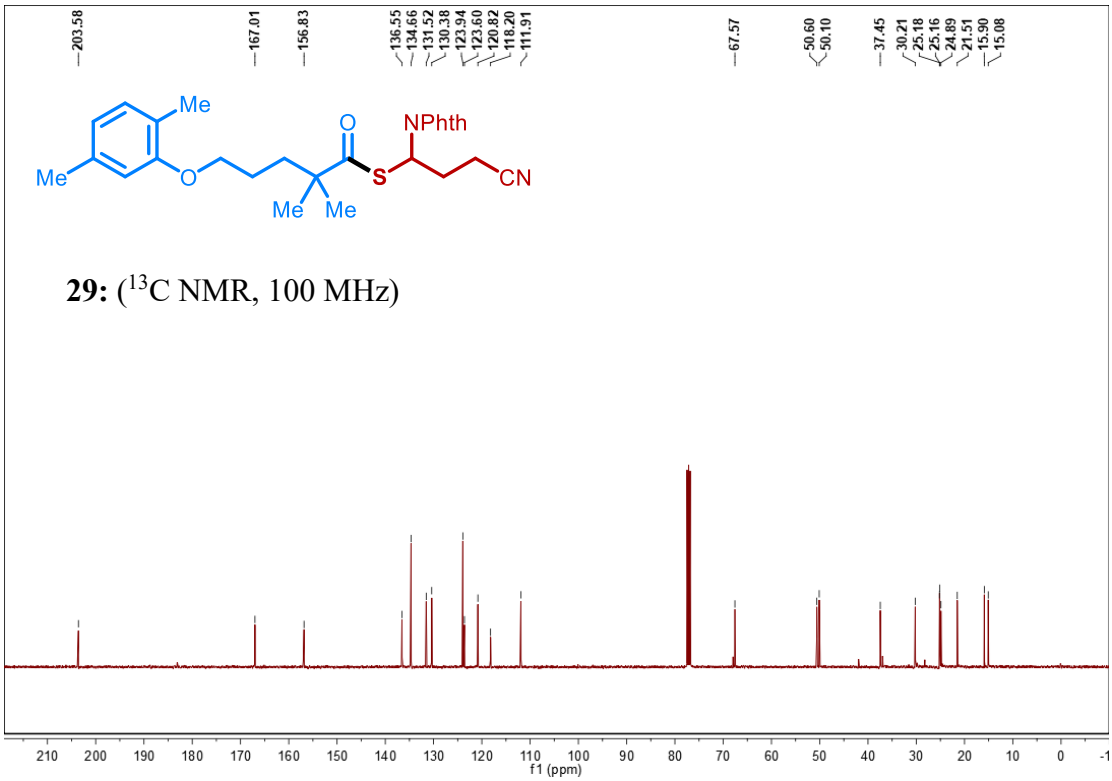
28: (^{1}H NMR, 400 MHz)



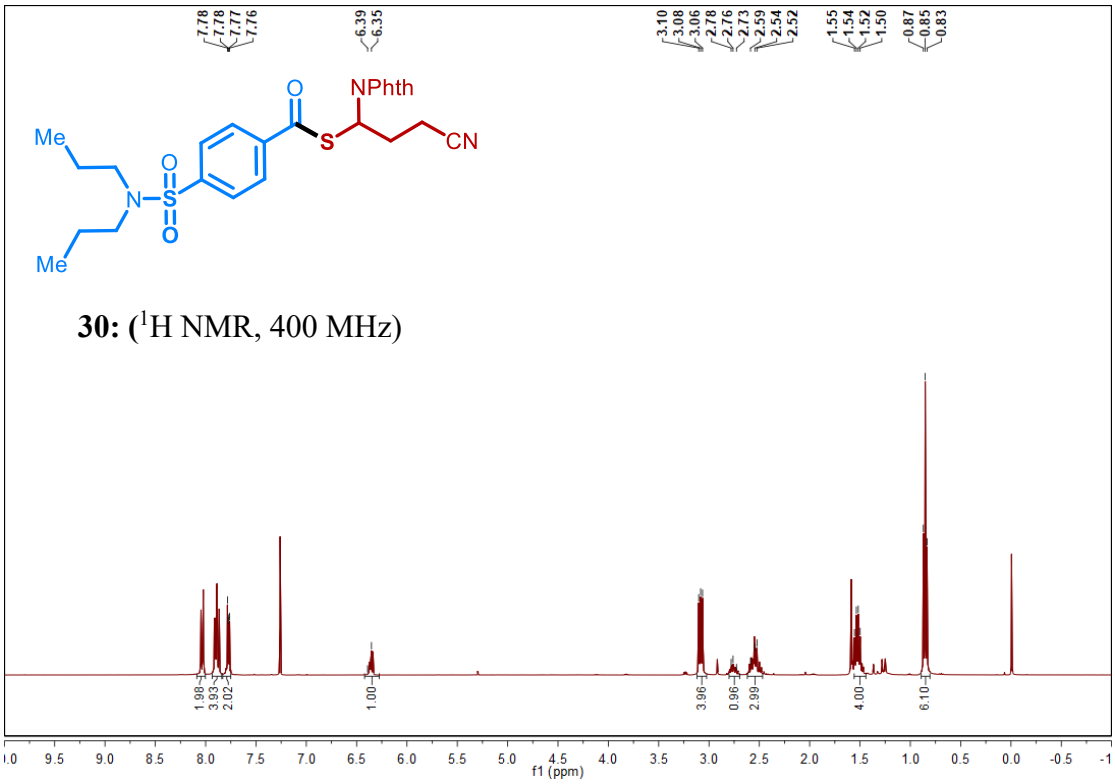
28: (^{13}C NMR, 100 MHz)



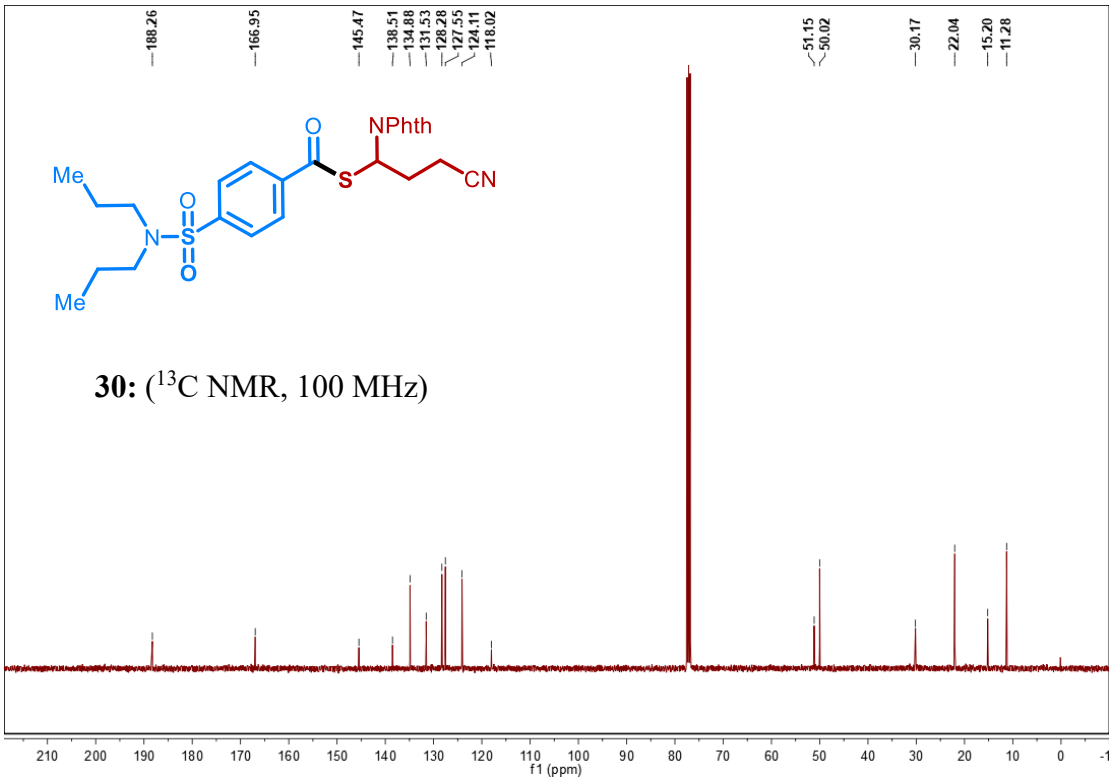
29: (^{1}H NMR, 400 MHz)



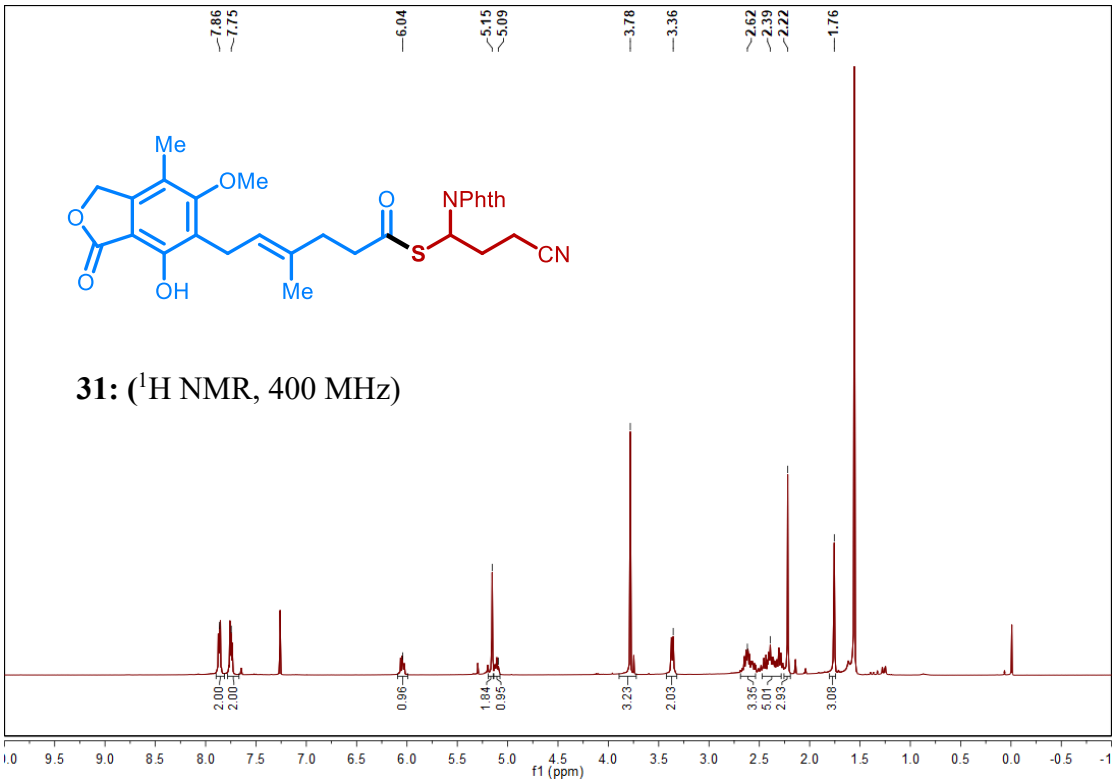
29: (^{13}C NMR, 100 MHz)



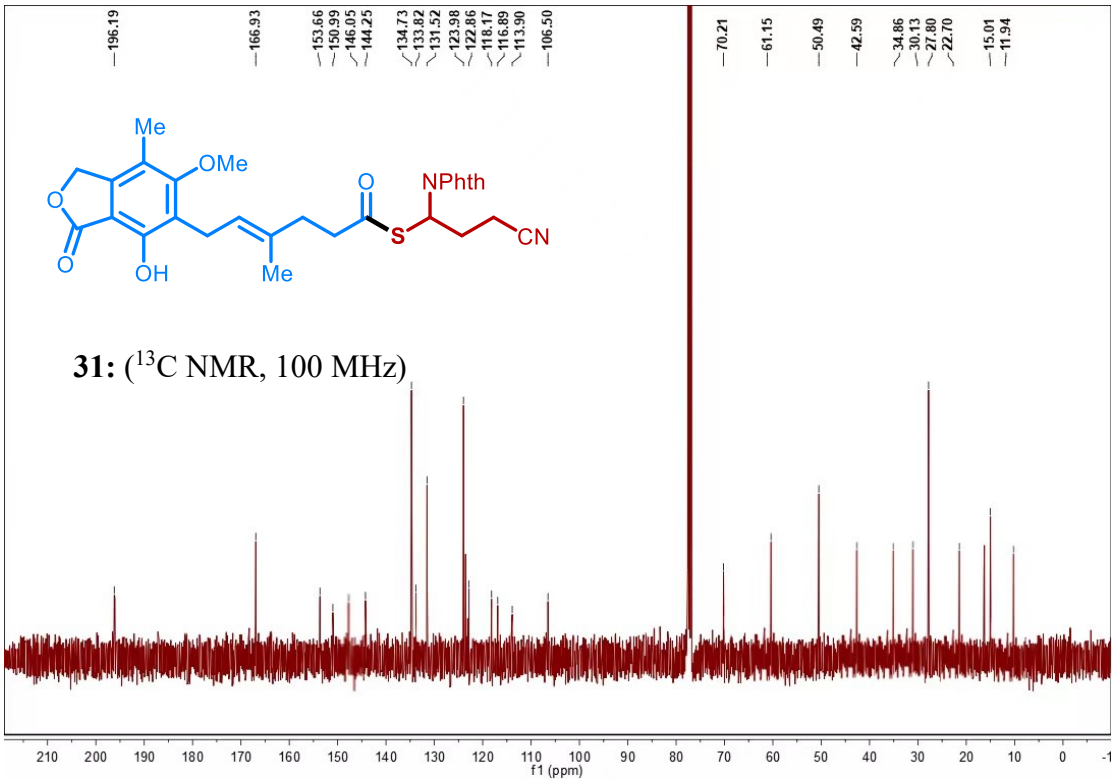
30: (^{1}H NMR, 400 MHz)



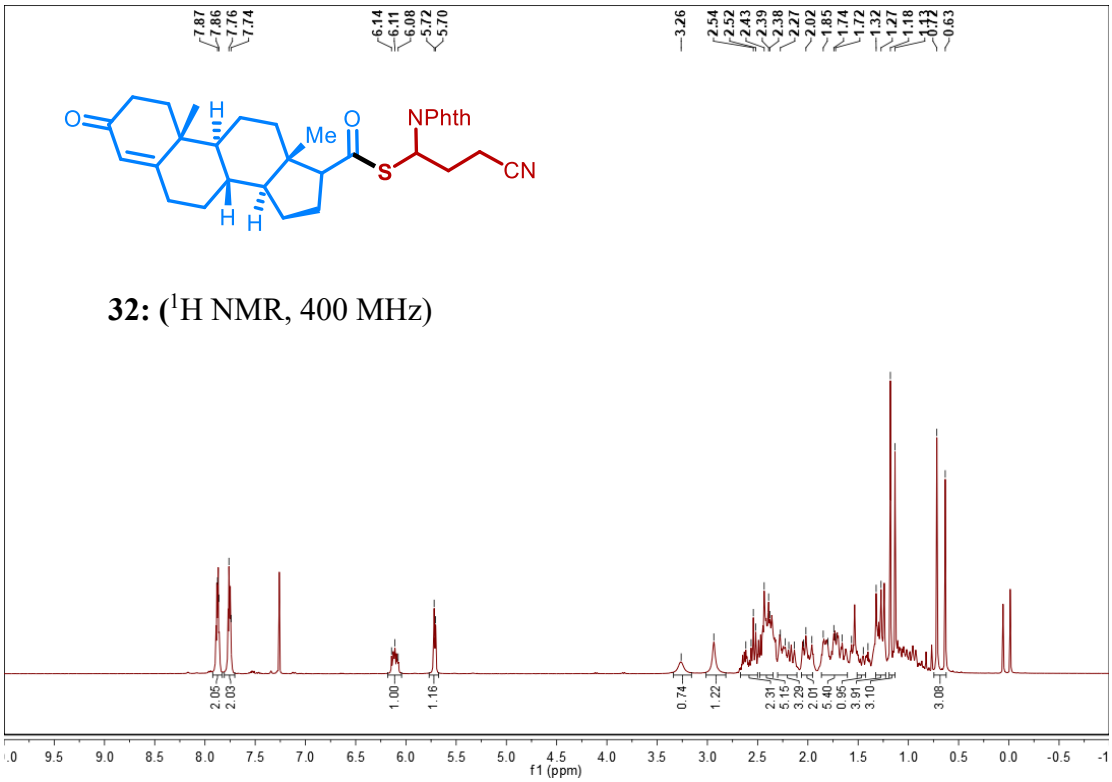
30: (^{13}C NMR, 100 MHz)



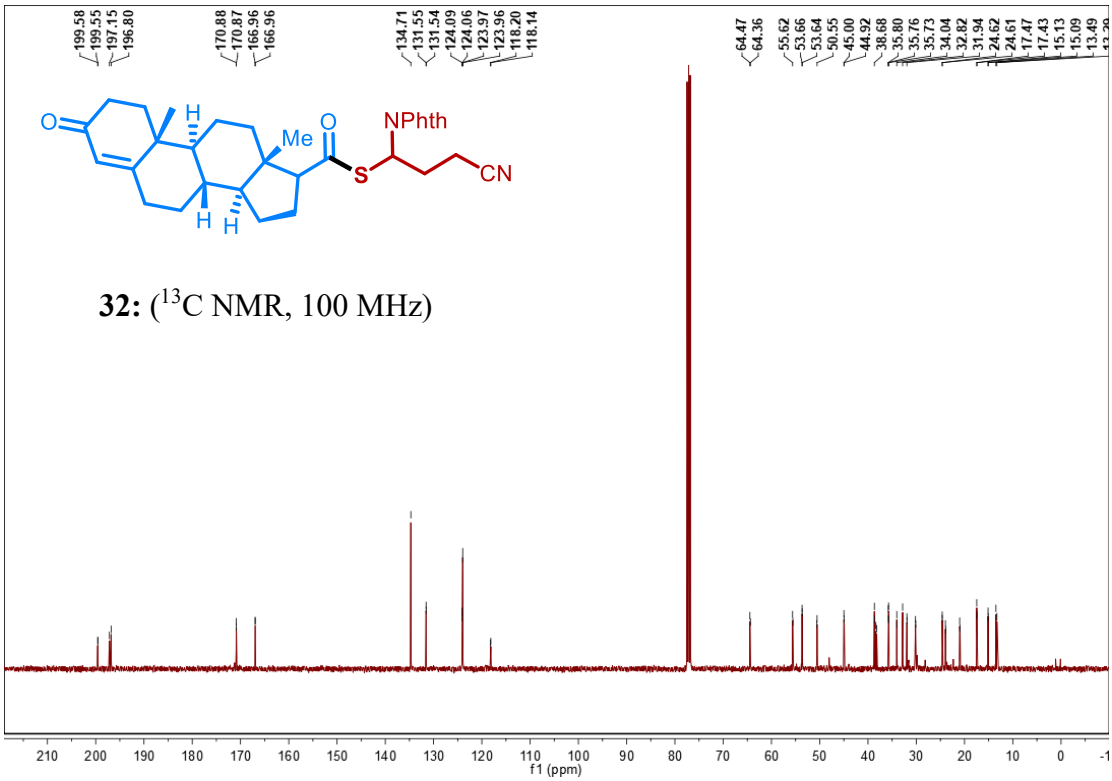
31: (^{1}H NMR, 400 MHz)



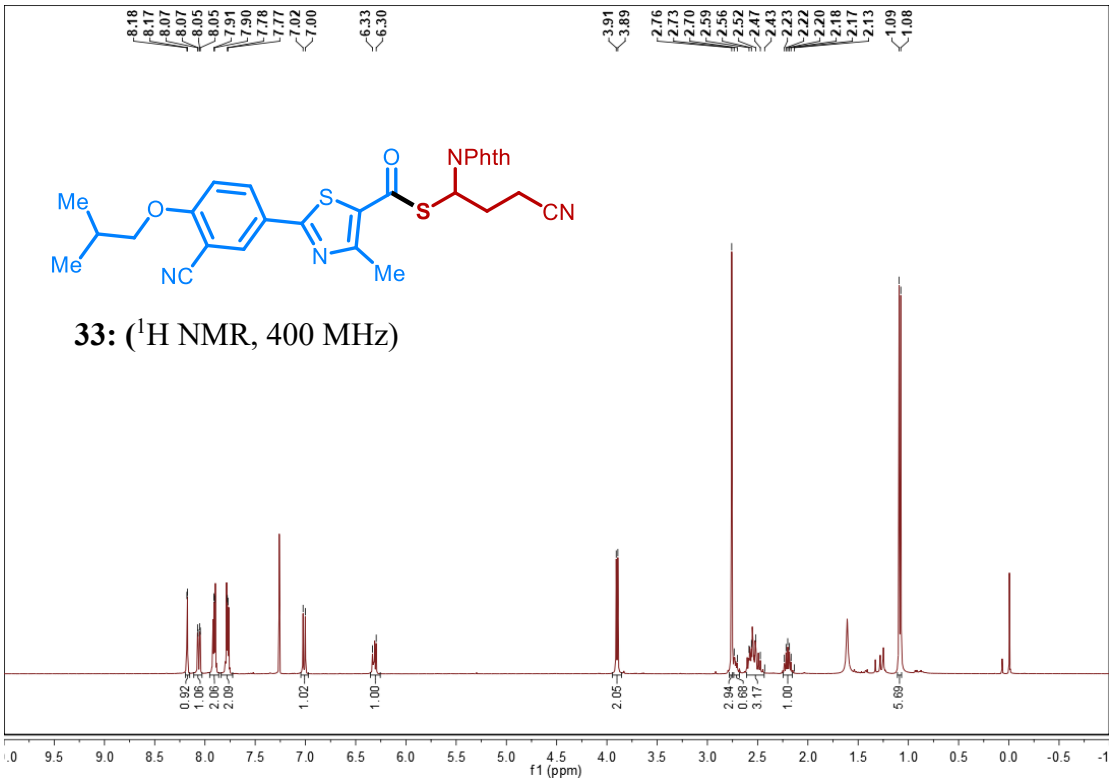
31: (^{13}C NMR, 100 MHz)



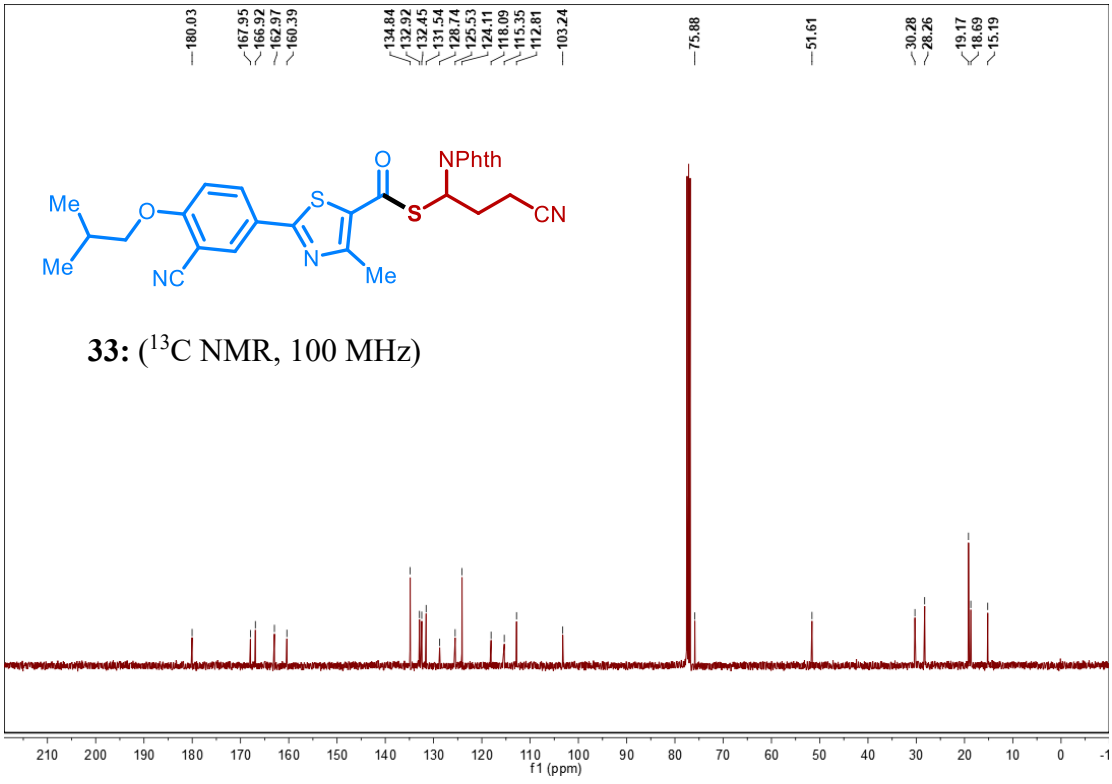
32: (^{1}H NMR, 400 MHz)



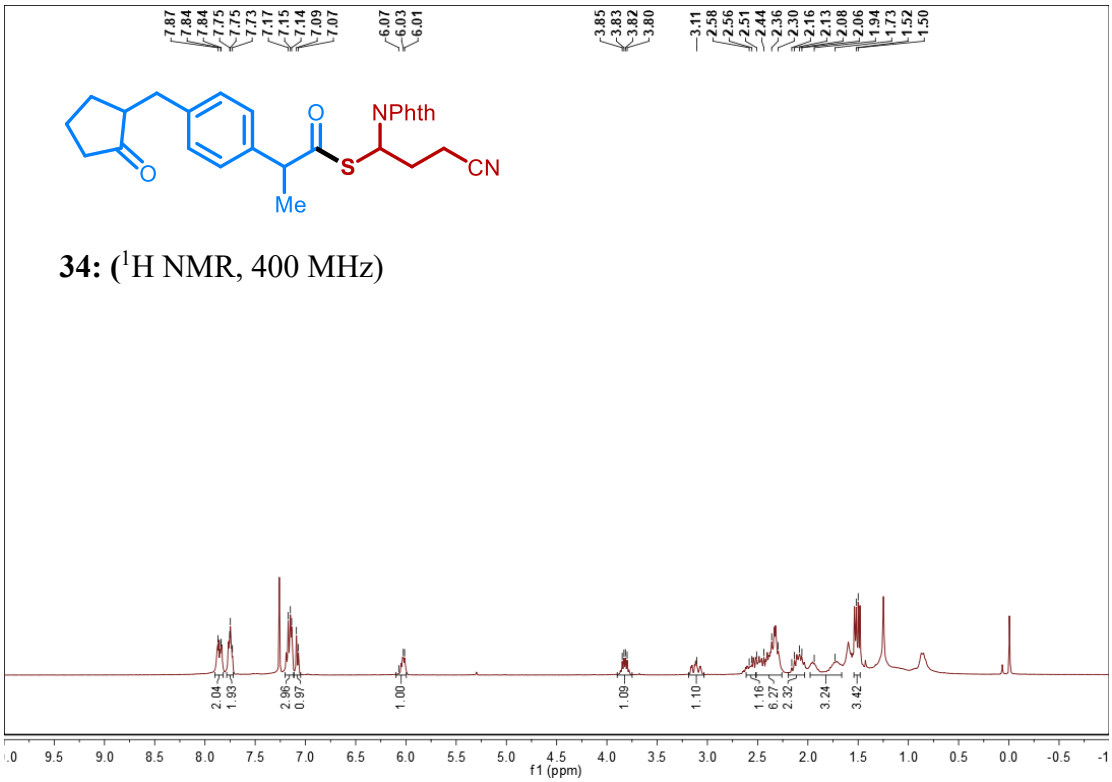
32: (^{13}C NMR, 100 MHz)



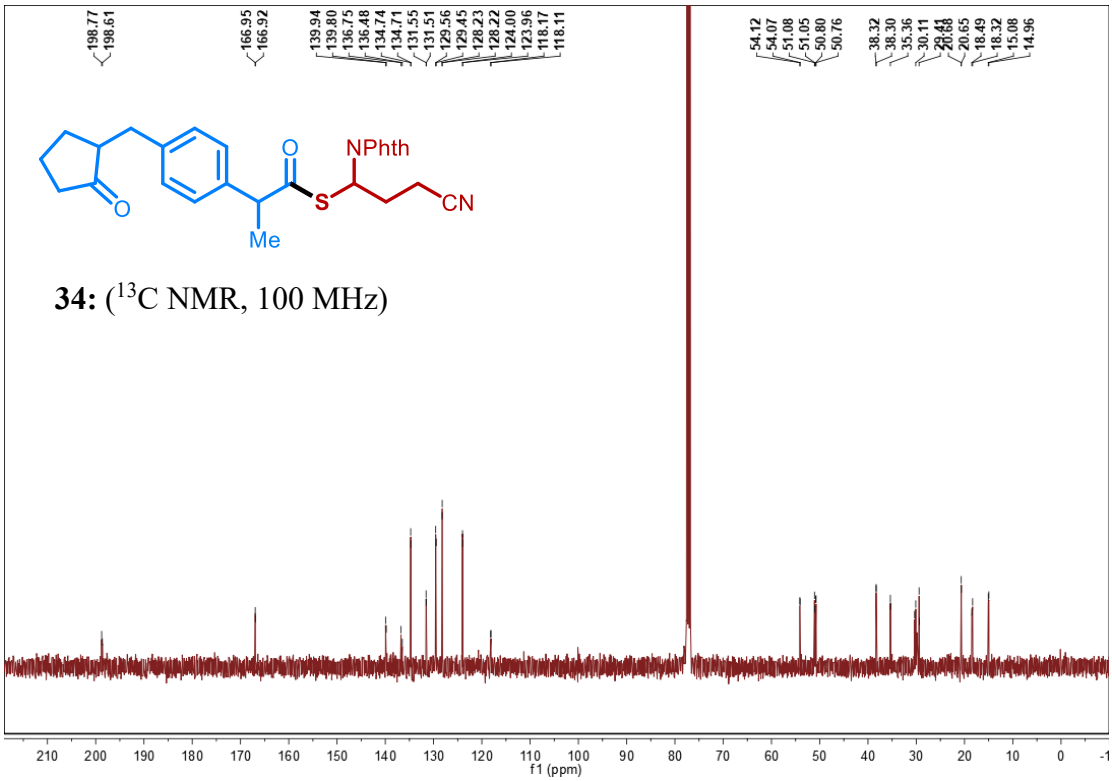
33: (^{1}H NMR, 400 MHz)



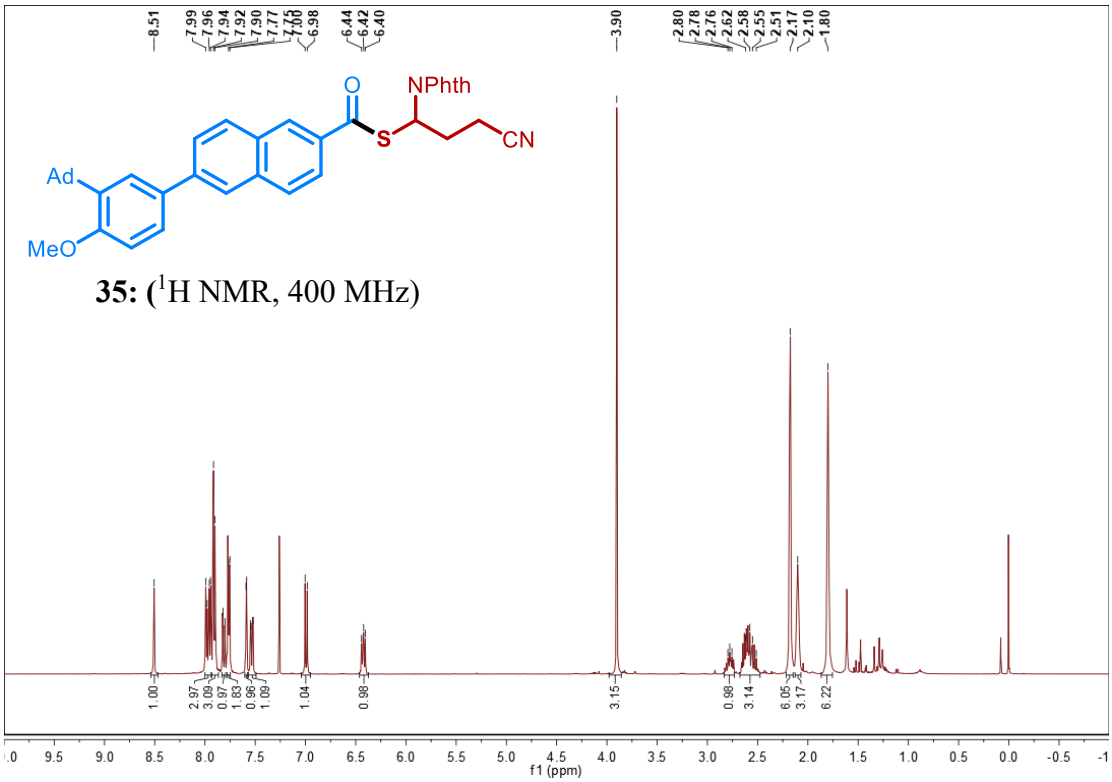
33: (^{13}C NMR, 100 MHz)



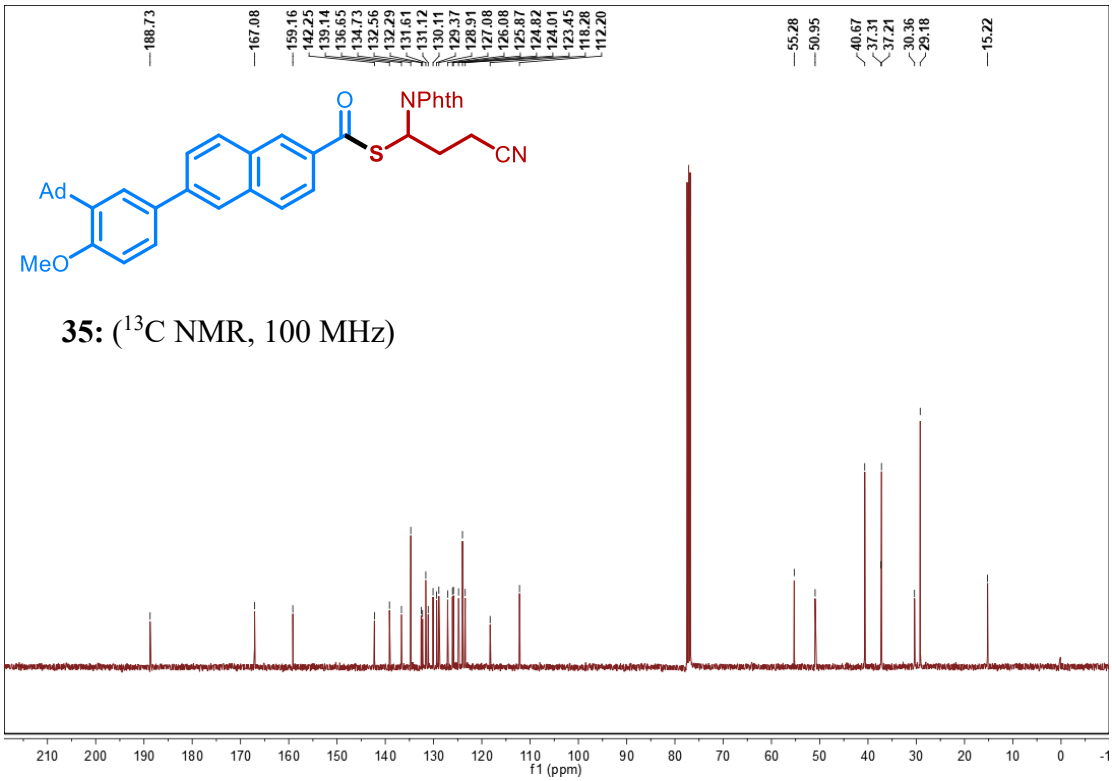
34: (^{1}H NMR, 400 MHz)



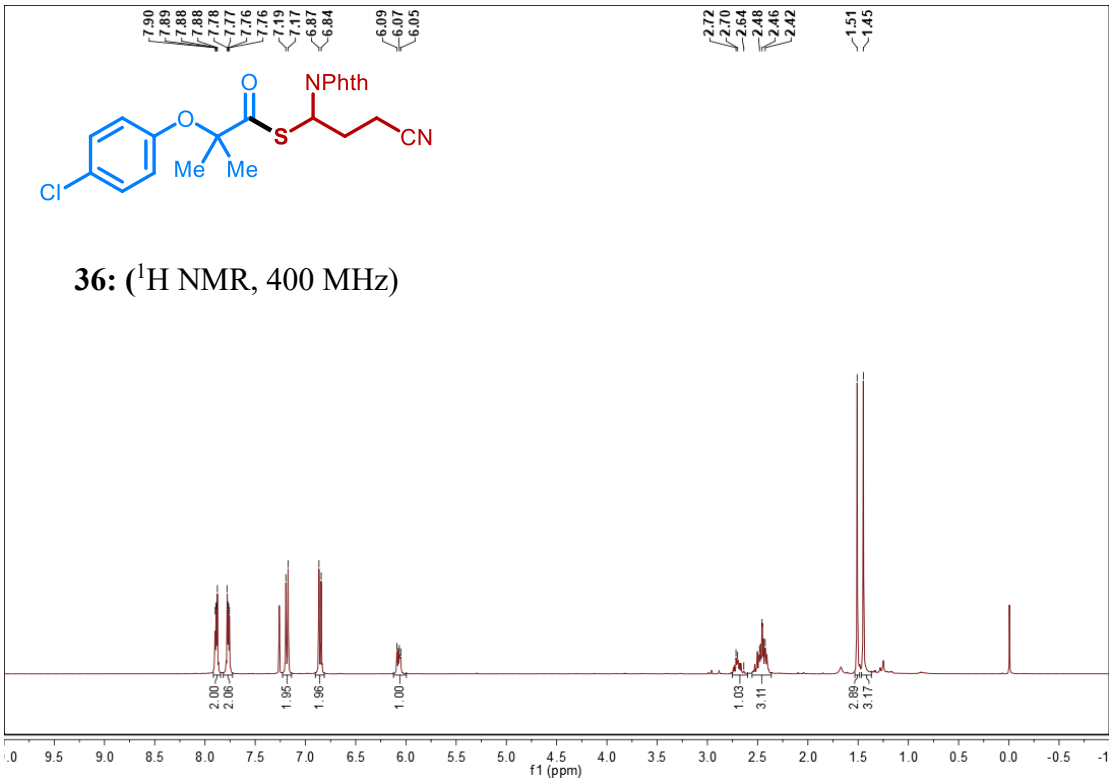
34: (^{13}C NMR, 100 MHz)



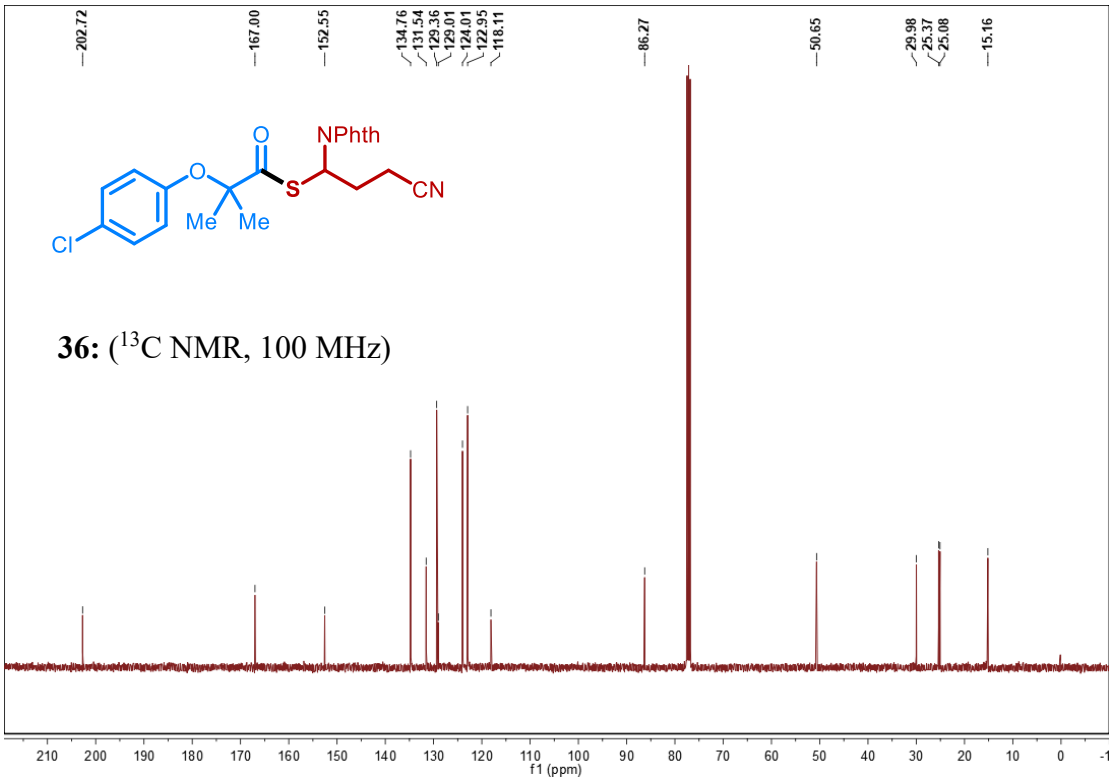
35: (^{1}H NMR, 400 MHz)



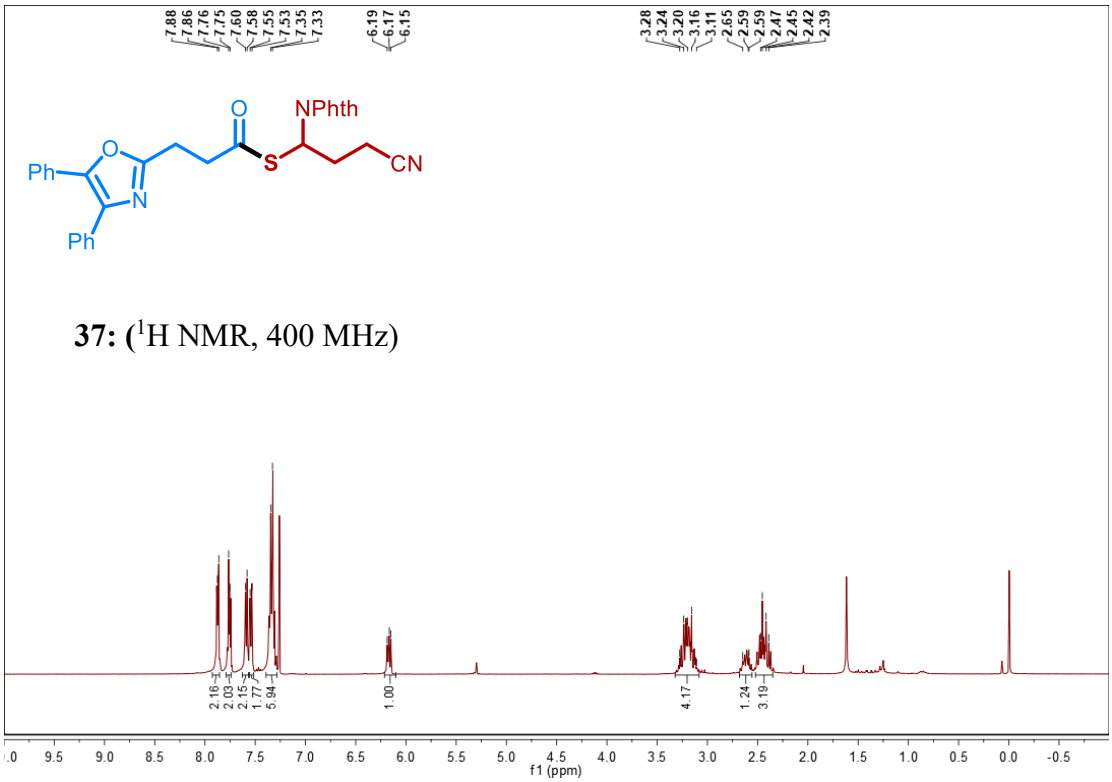
35: (^{13}C NMR, 100 MHz)



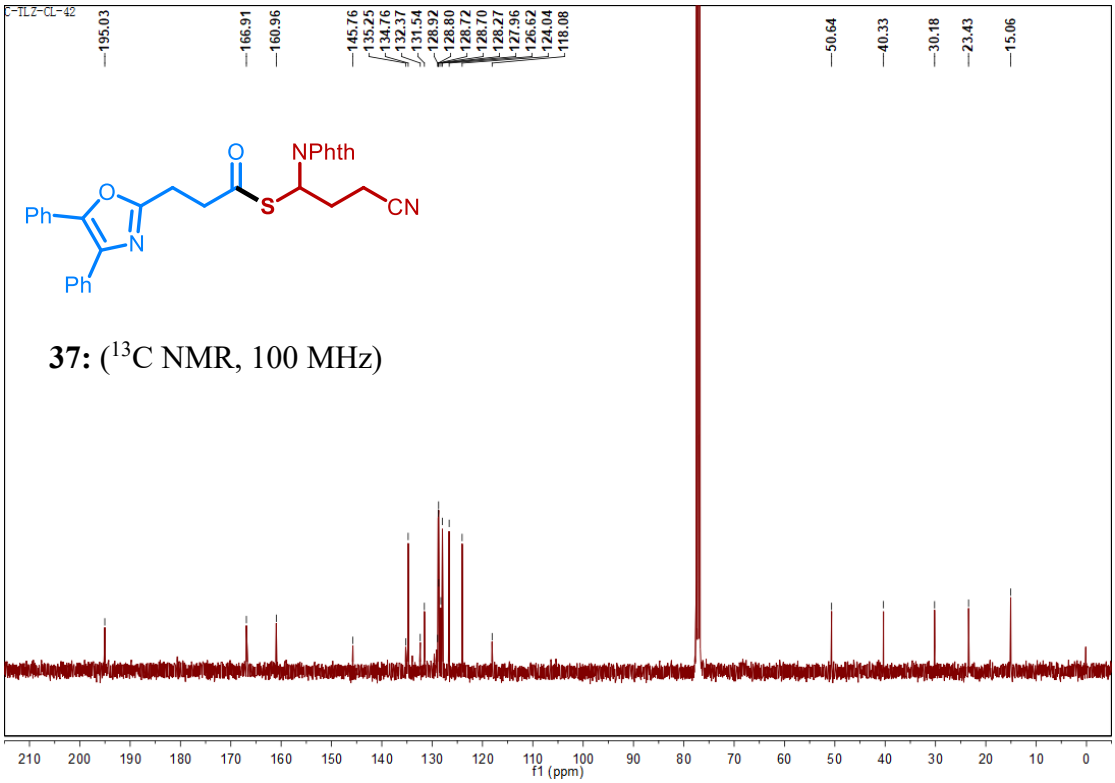
36: (^{1}H NMR, 400 MHz)



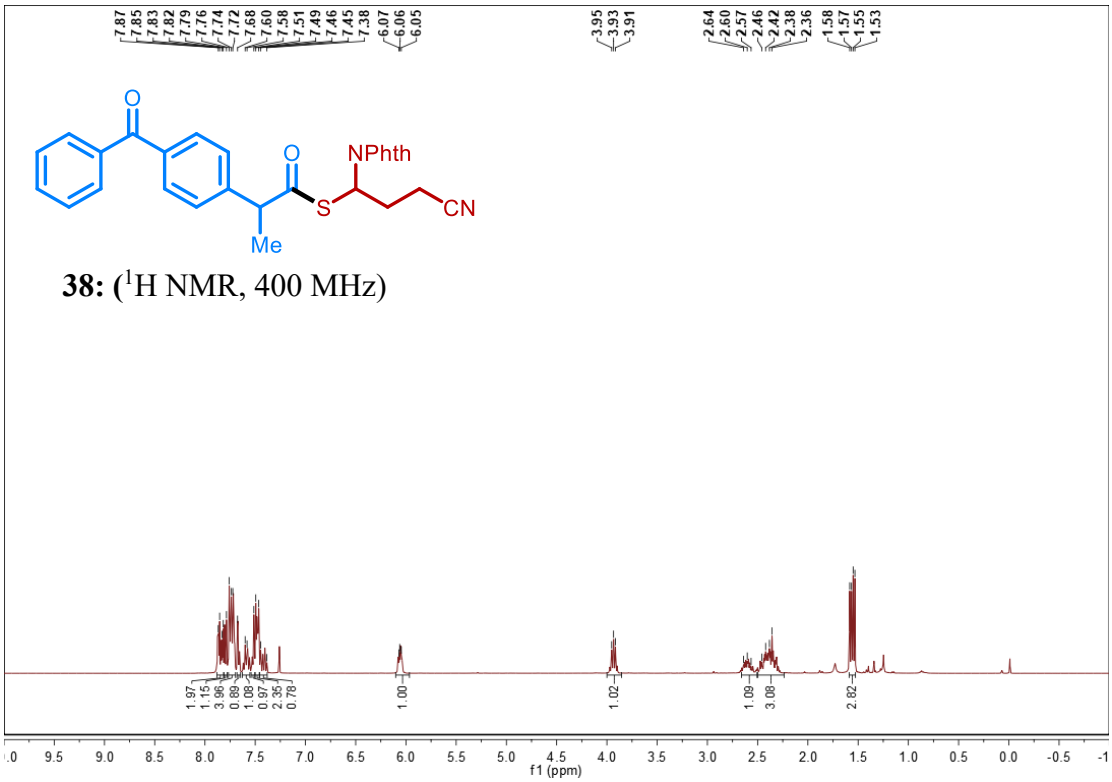
36: (^{13}C NMR, 100 MHz)



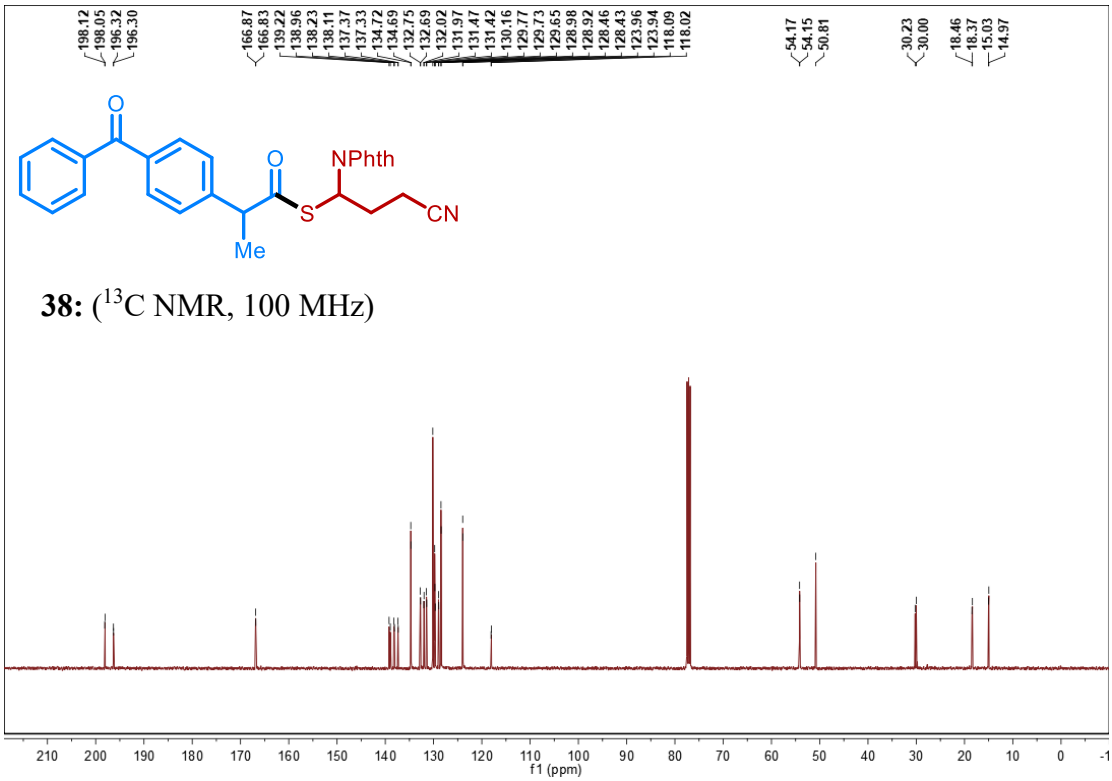
37: (^{1}H NMR, 400 MHz)



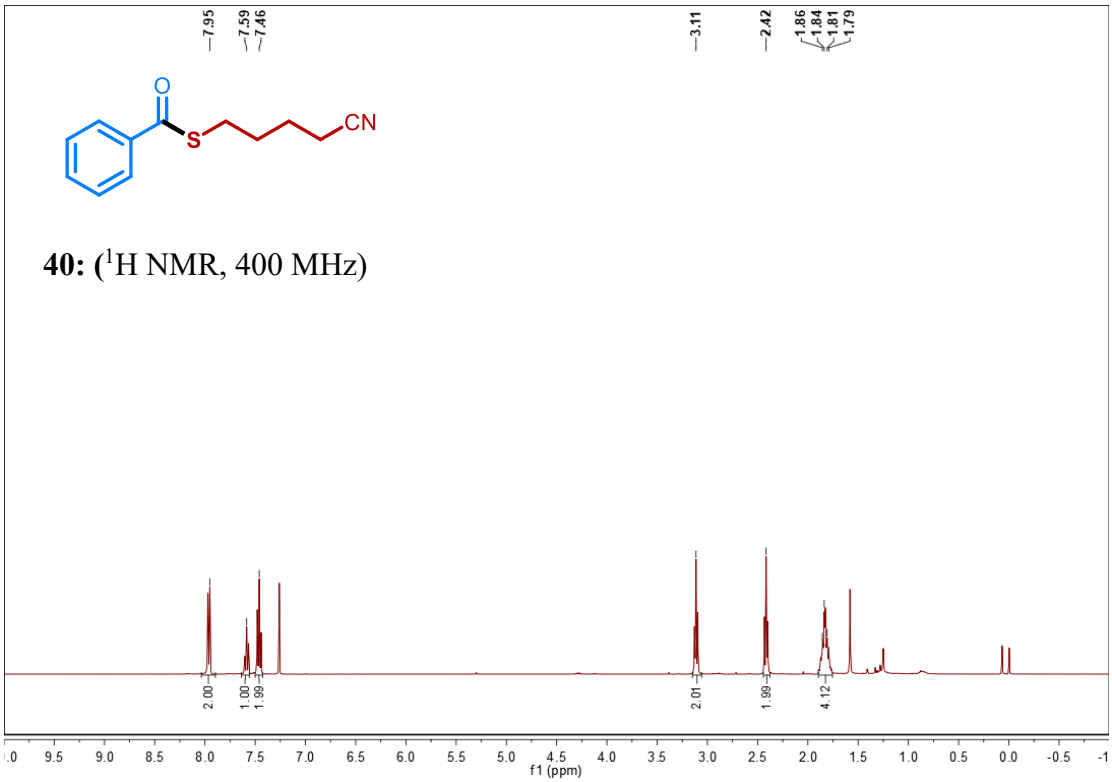
37: (^{13}C NMR, 100 MHz)



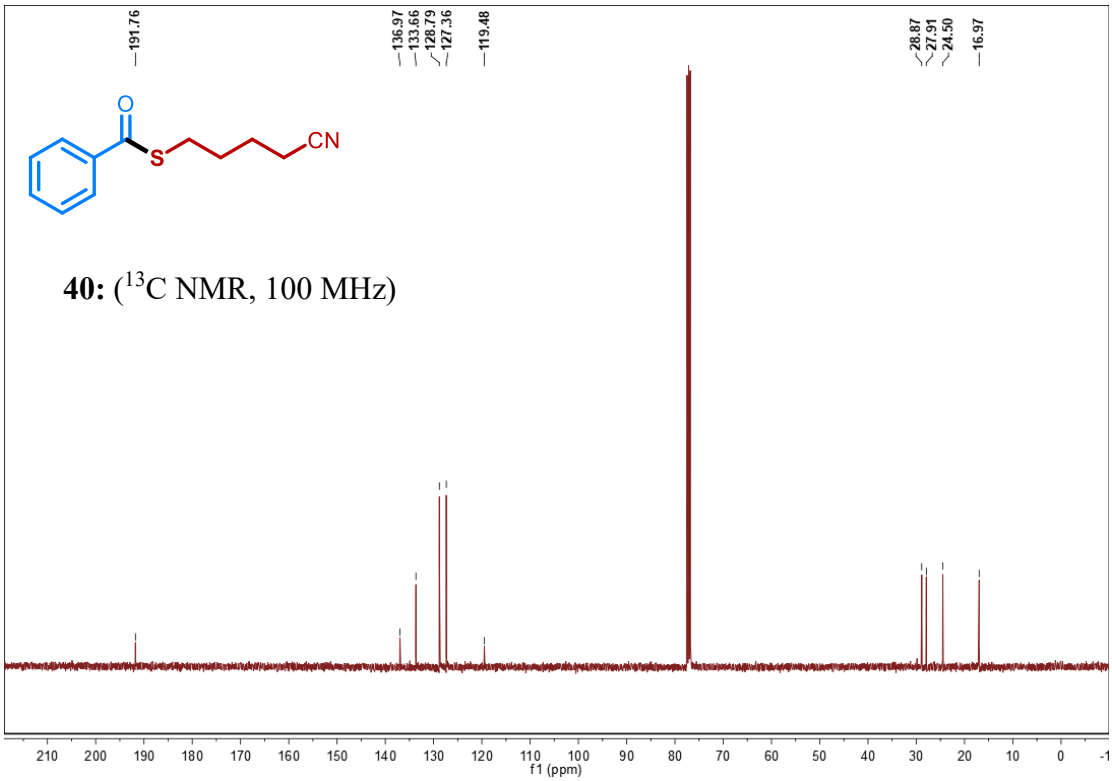
38: (^{1}H NMR, 400 MHz)



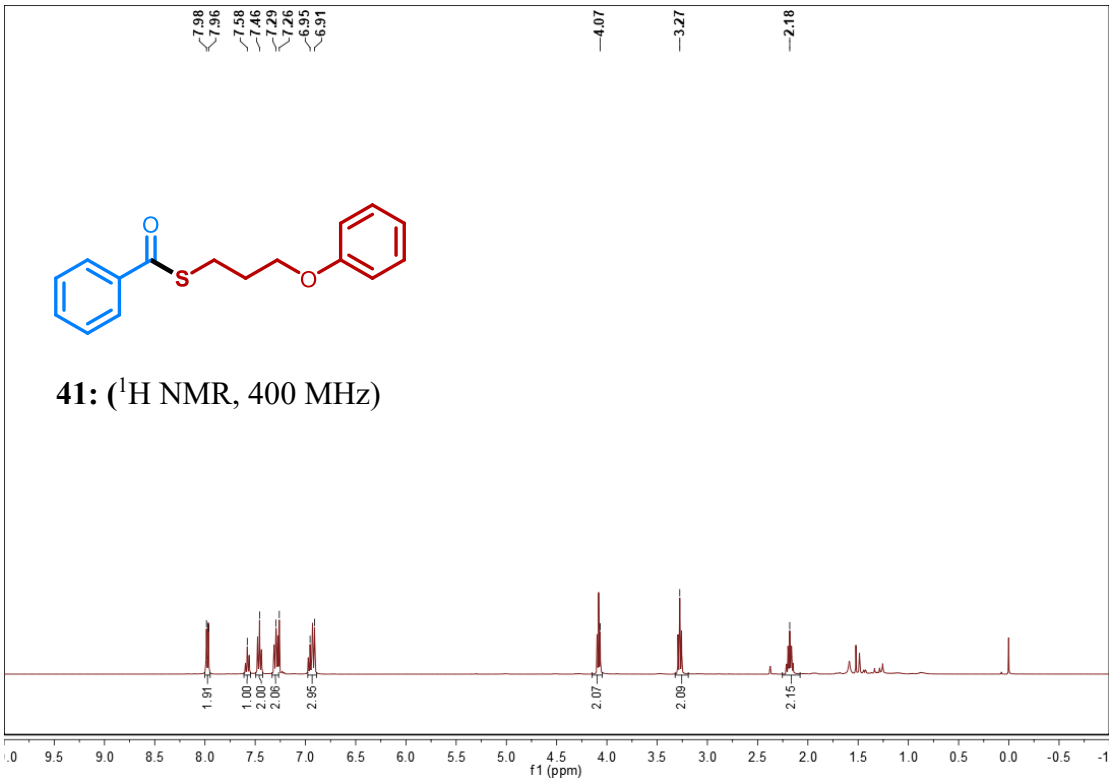
38: (^{13}C NMR, 100 MHz)



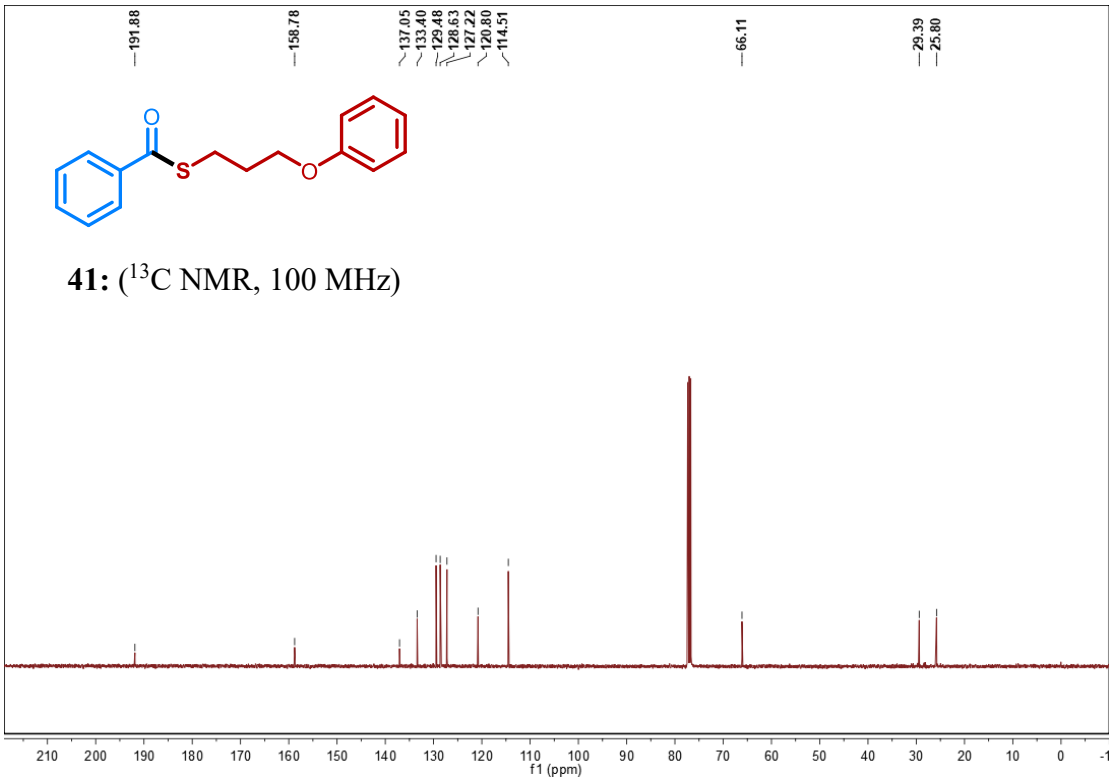
40: (^{1}H NMR, 400 MHz)



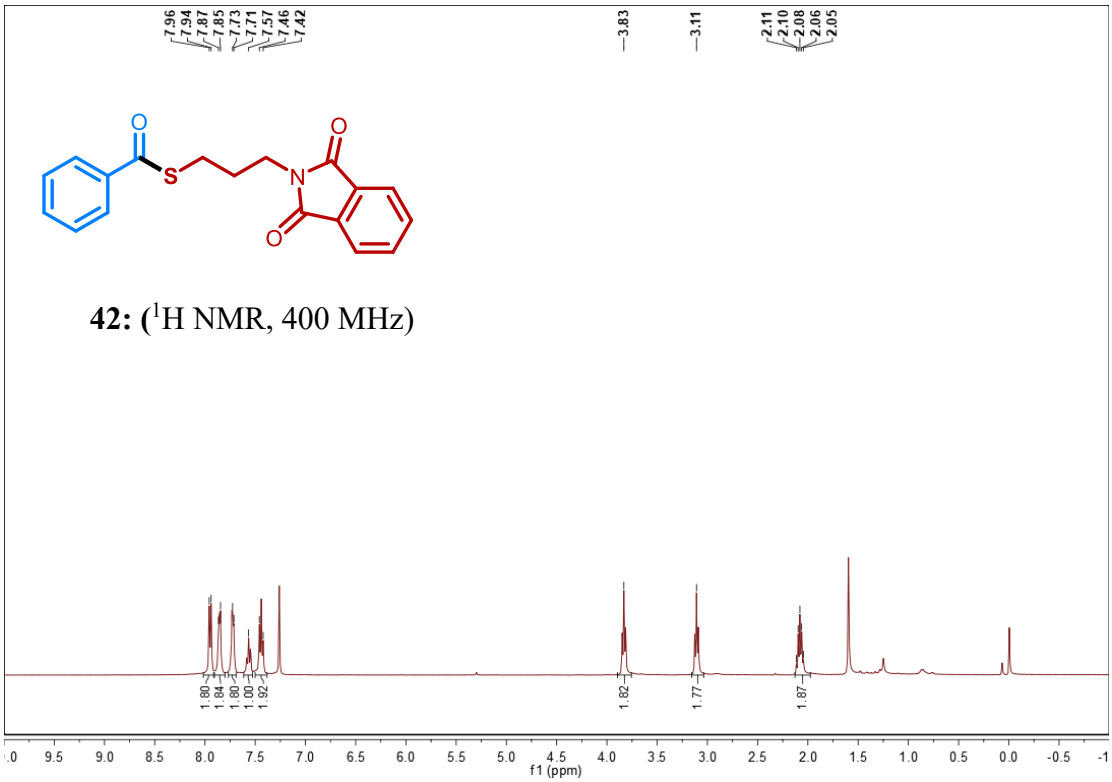
40: (^{13}C NMR, 100 MHz)



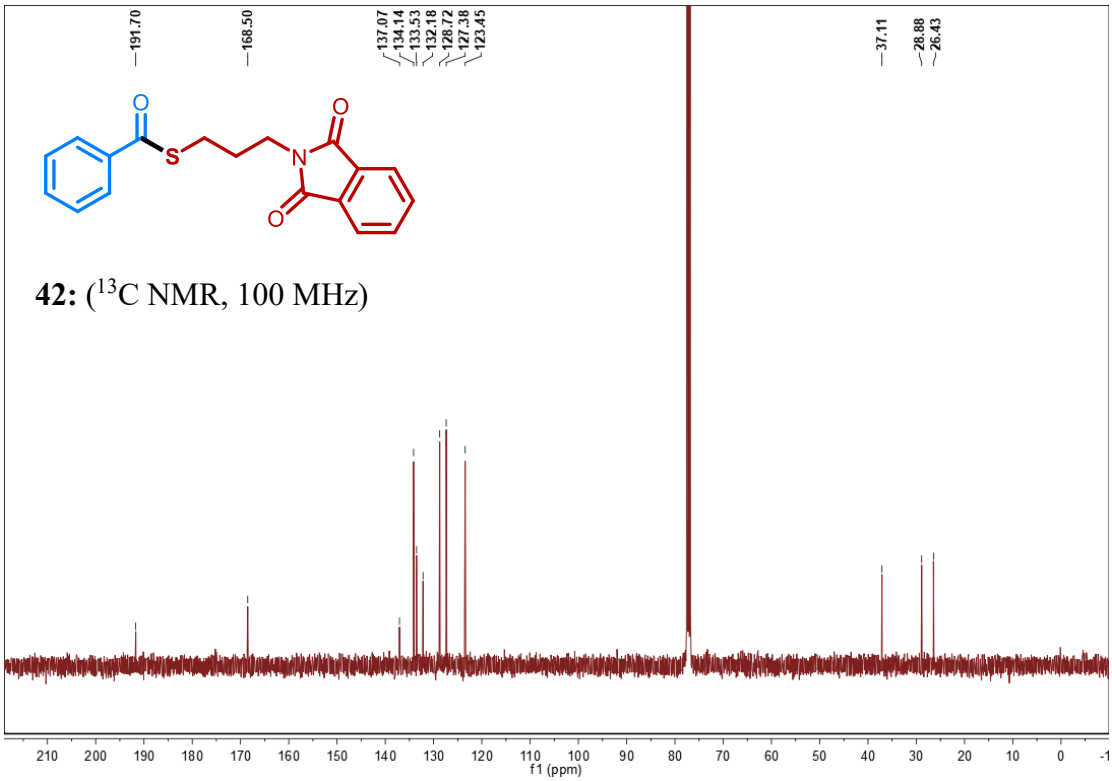
41: (^{1}H NMR, 400 MHz)



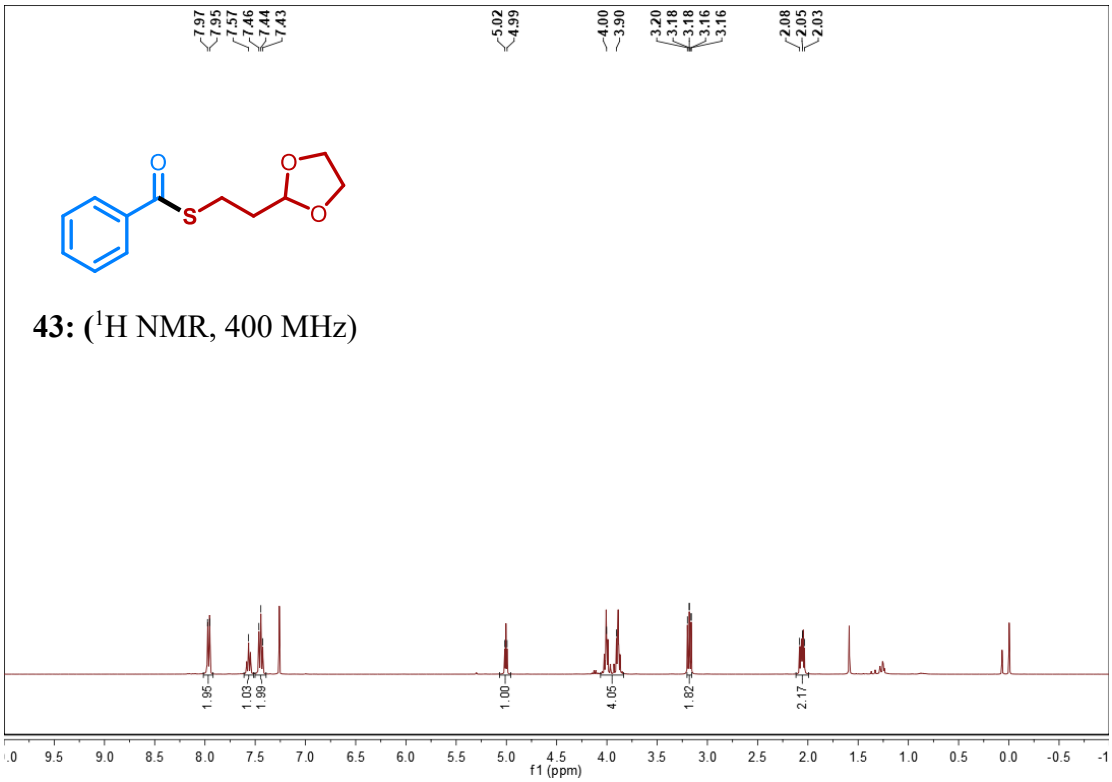
41: (^{13}C NMR, 100 MHz)



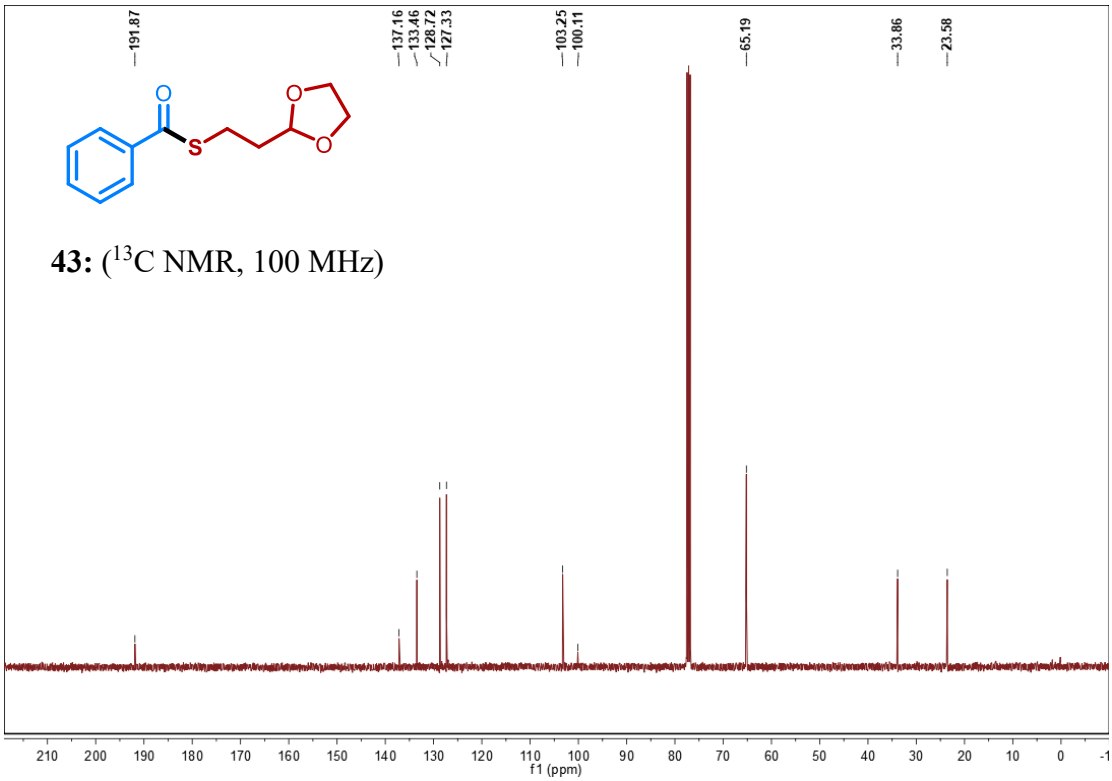
42: (^{1}H NMR, 400 MHz)



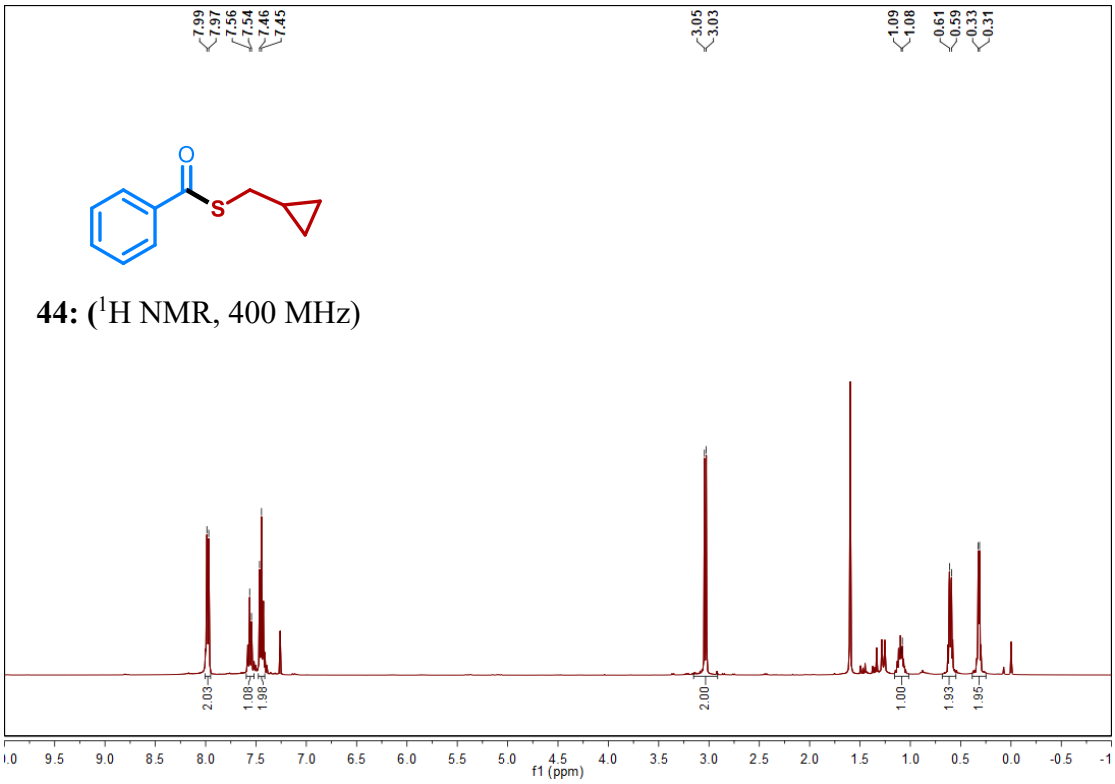
42: (^{13}C NMR, 100 MHz)



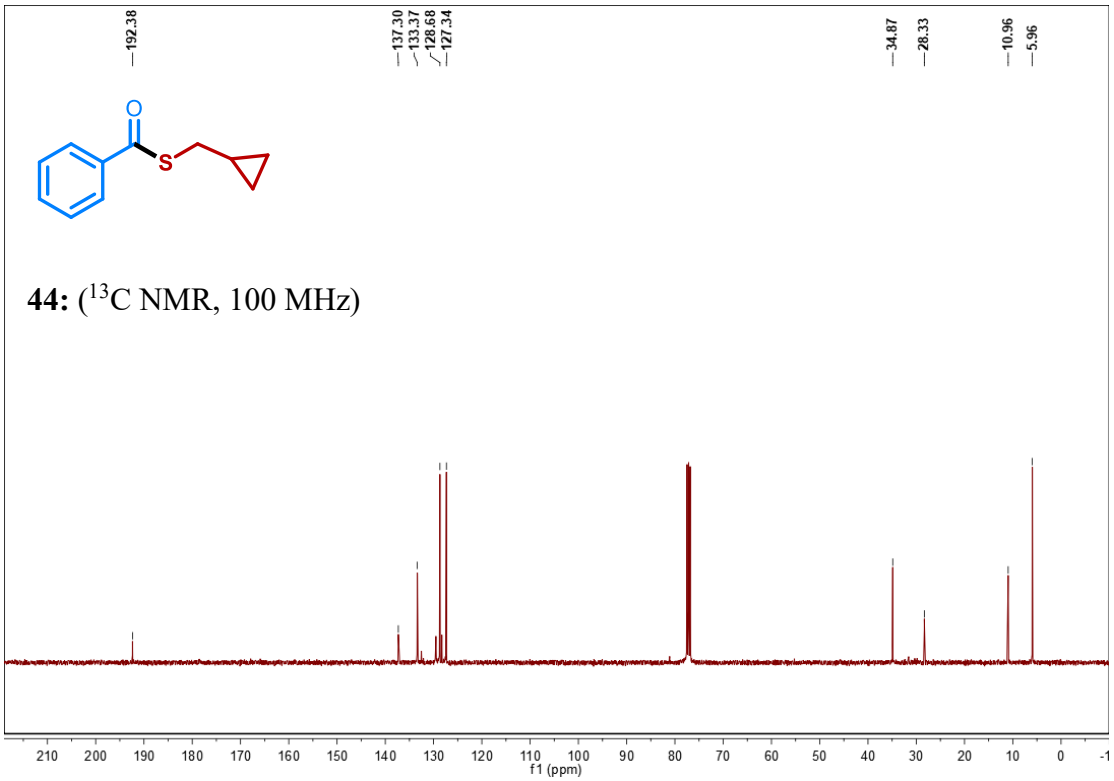
43: (^{1}H NMR, 400 MHz)



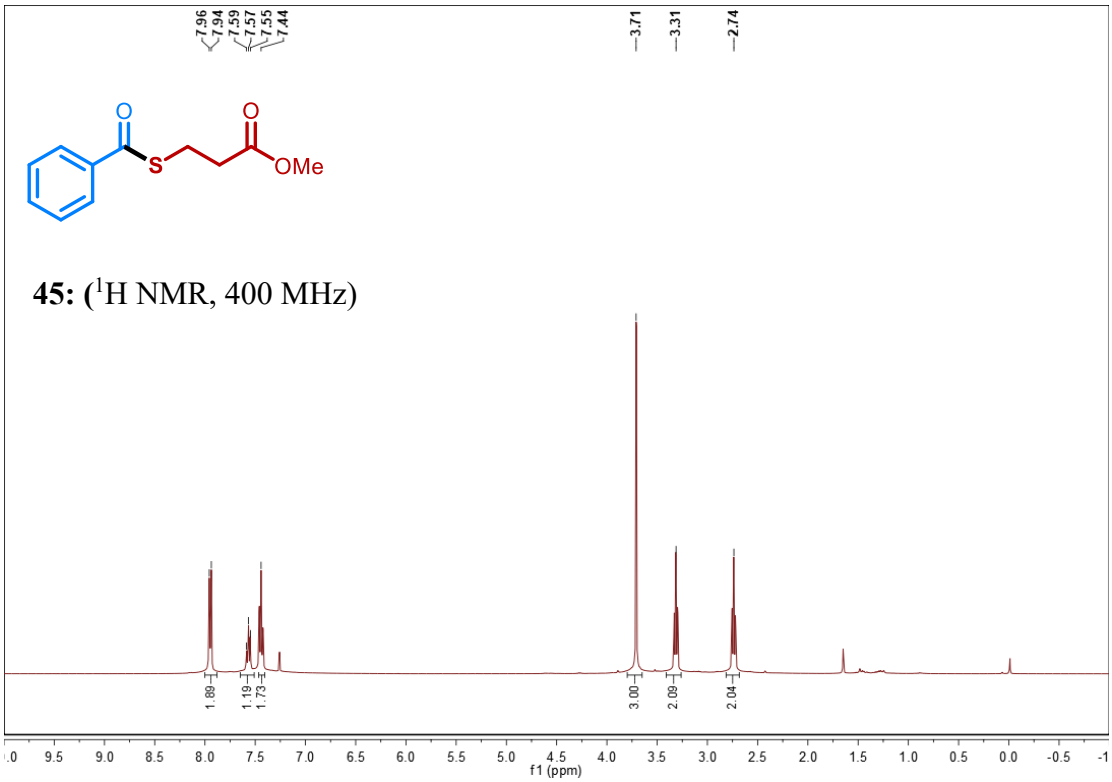
43: (^{13}C NMR, 100 MHz)



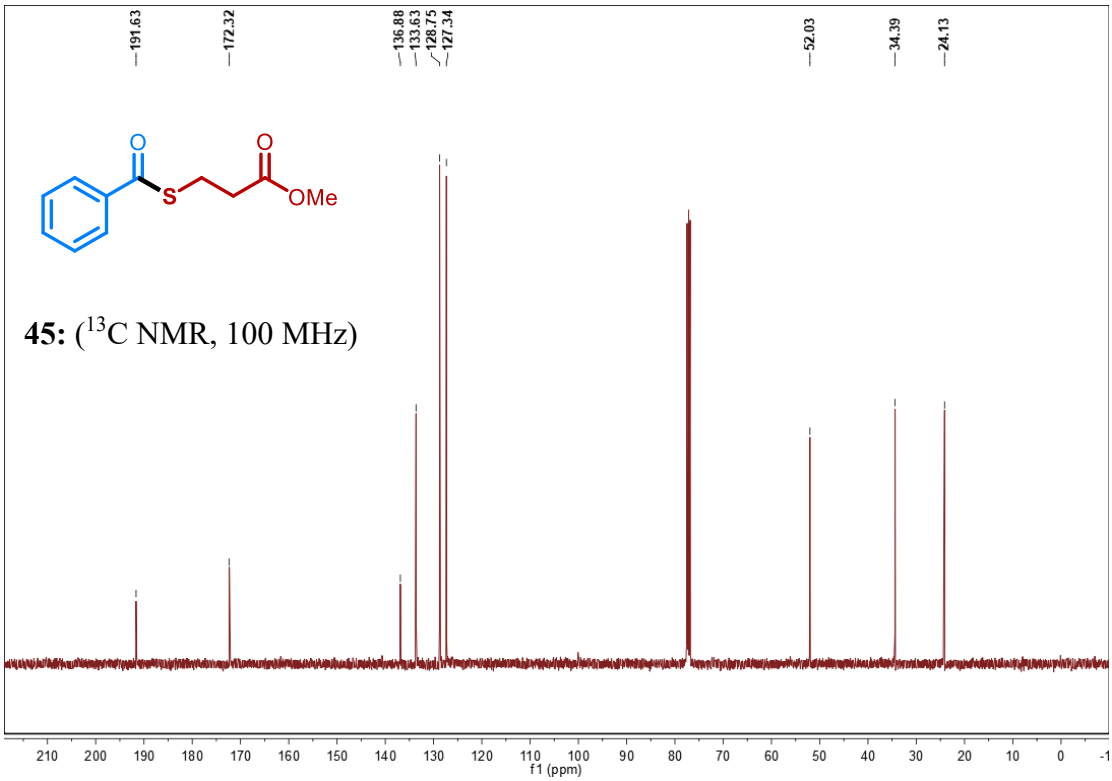
44: (^{1}H NMR, 400 MHz)



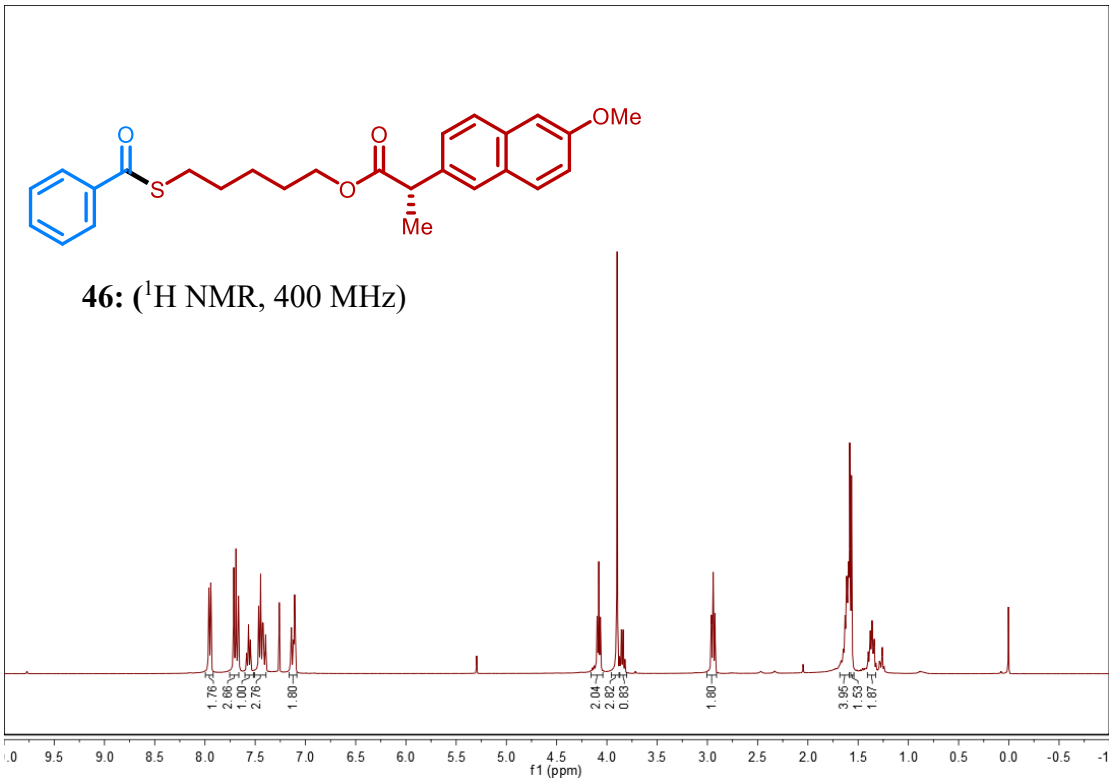
44: (^{13}C NMR, 100 MHz)



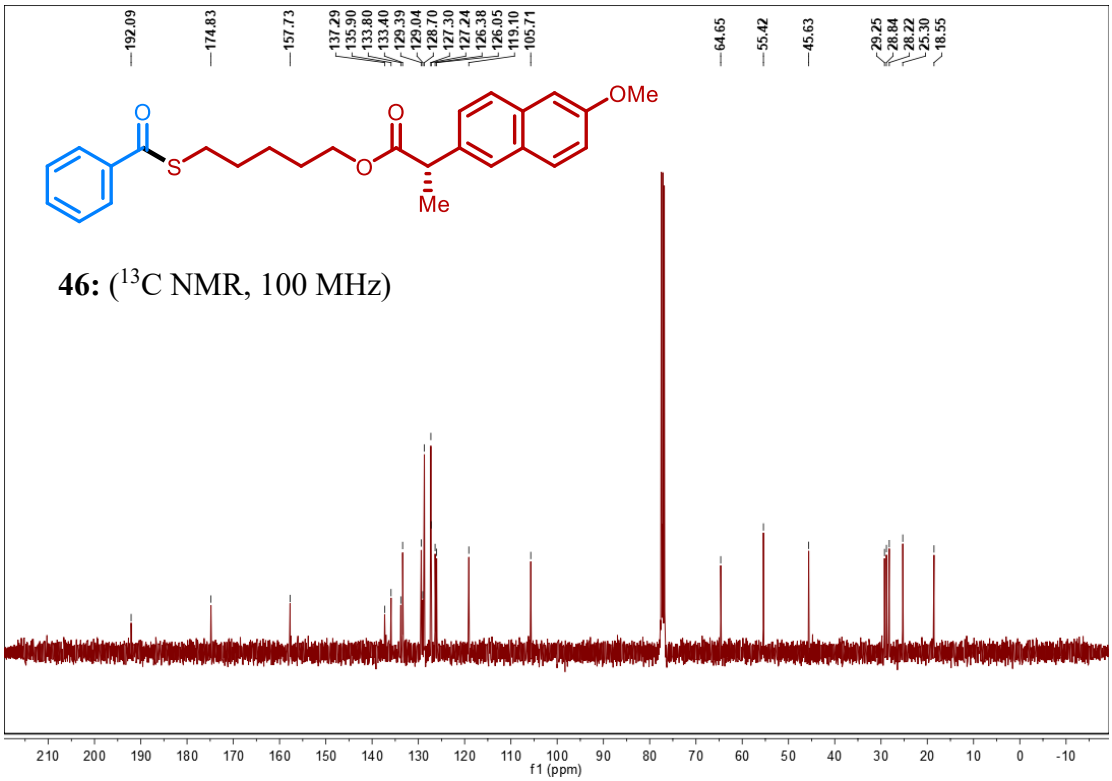
45: (^{1}H NMR, 400 MHz)



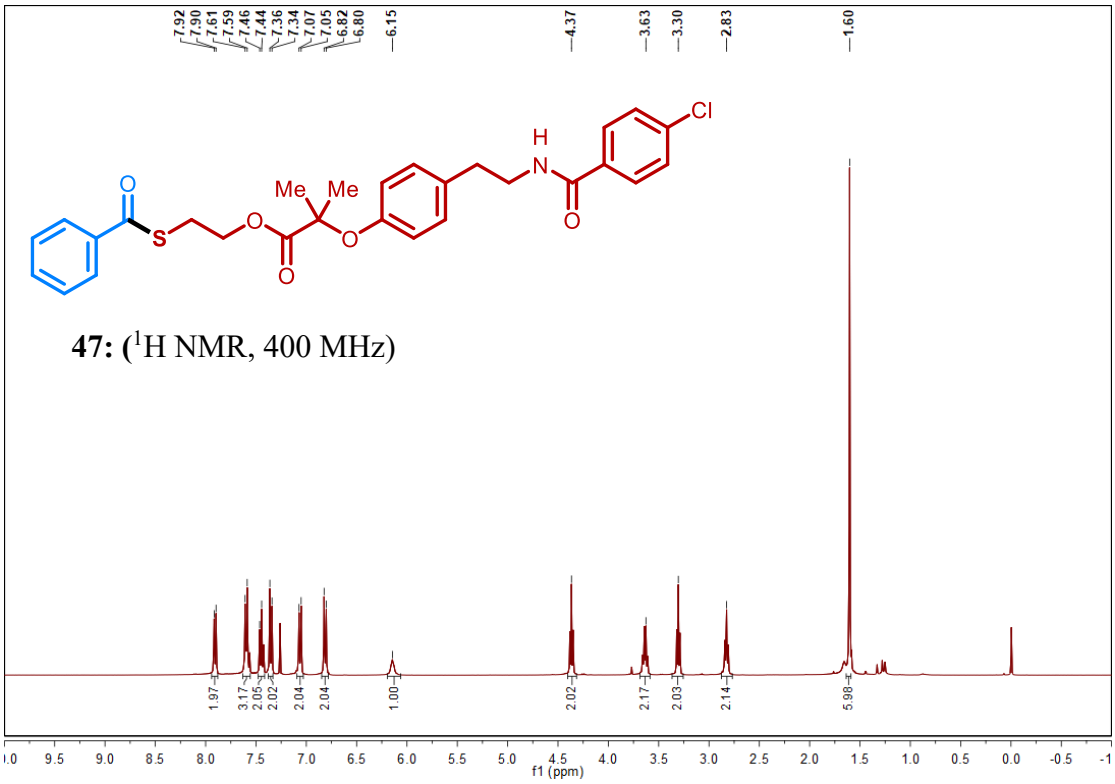
45: (^{13}C NMR, 100 MHz)



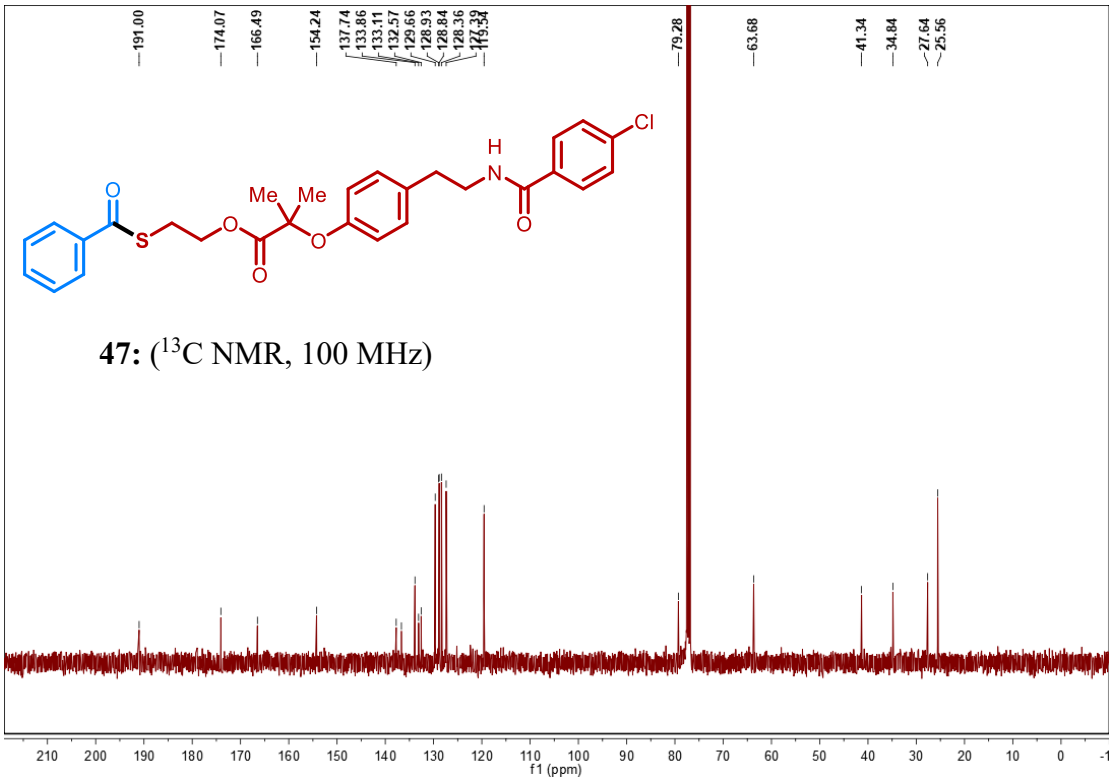
46: (^{1}H NMR, 400 MHz)



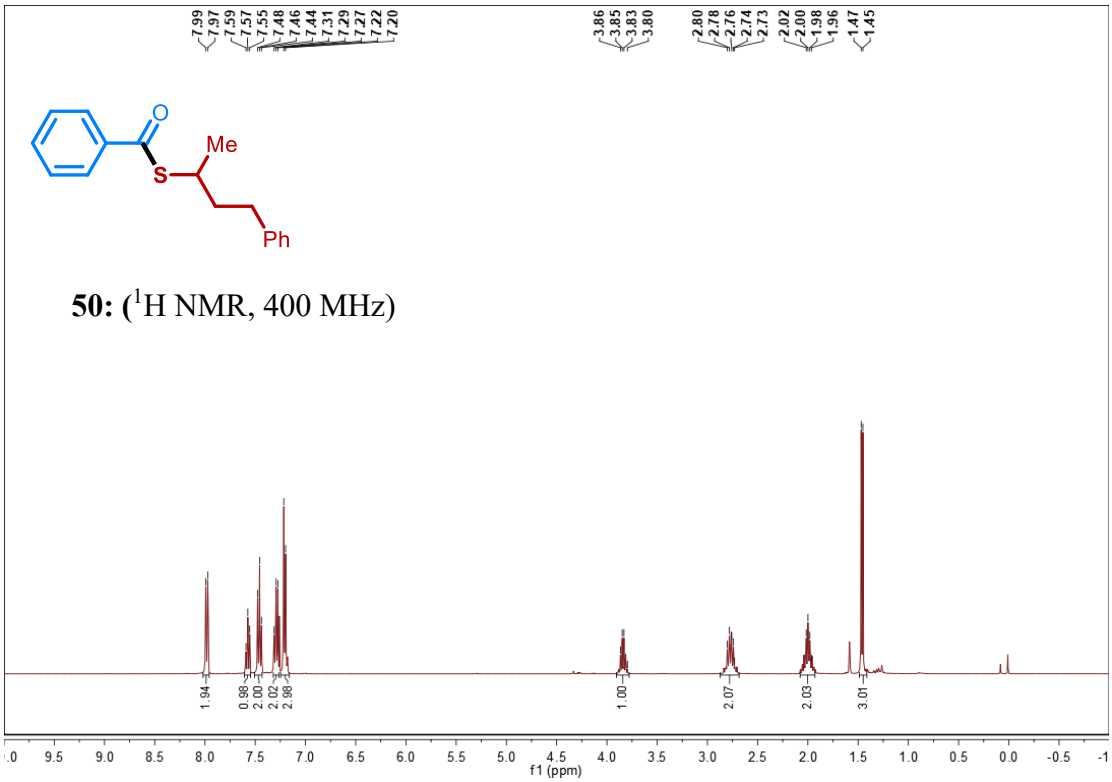
46: (^{13}C NMR, 100 MHz)



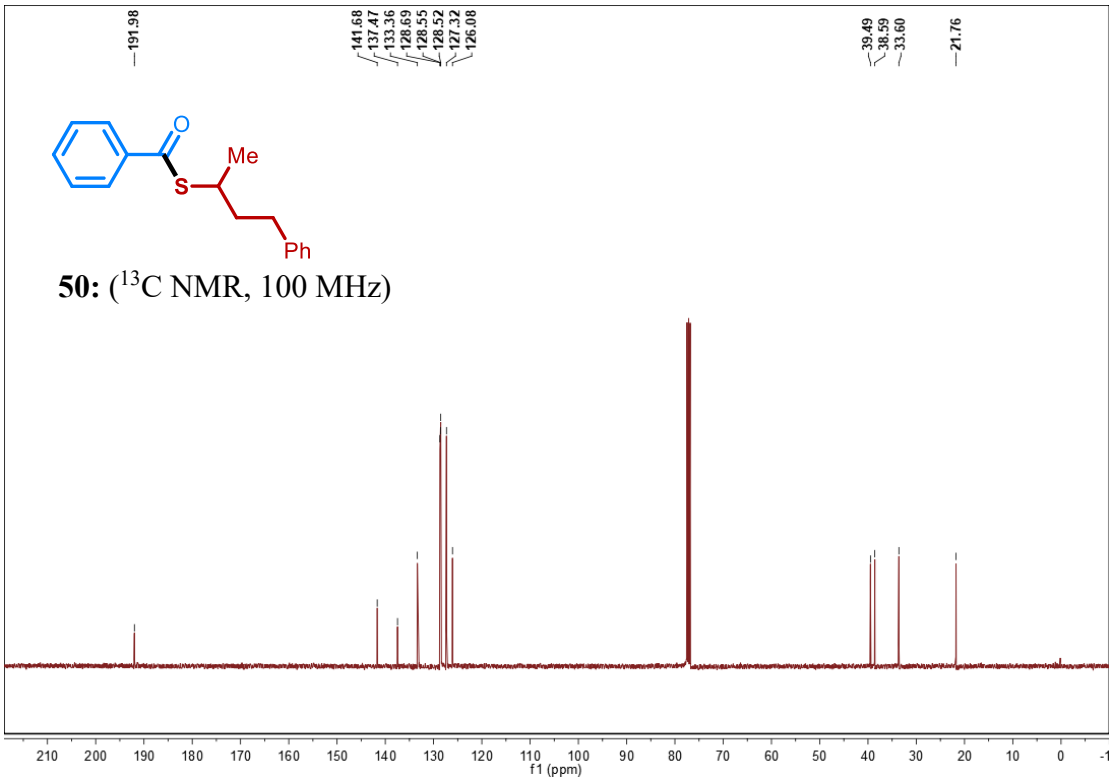
47: (^{1}H NMR, 400 MHz)



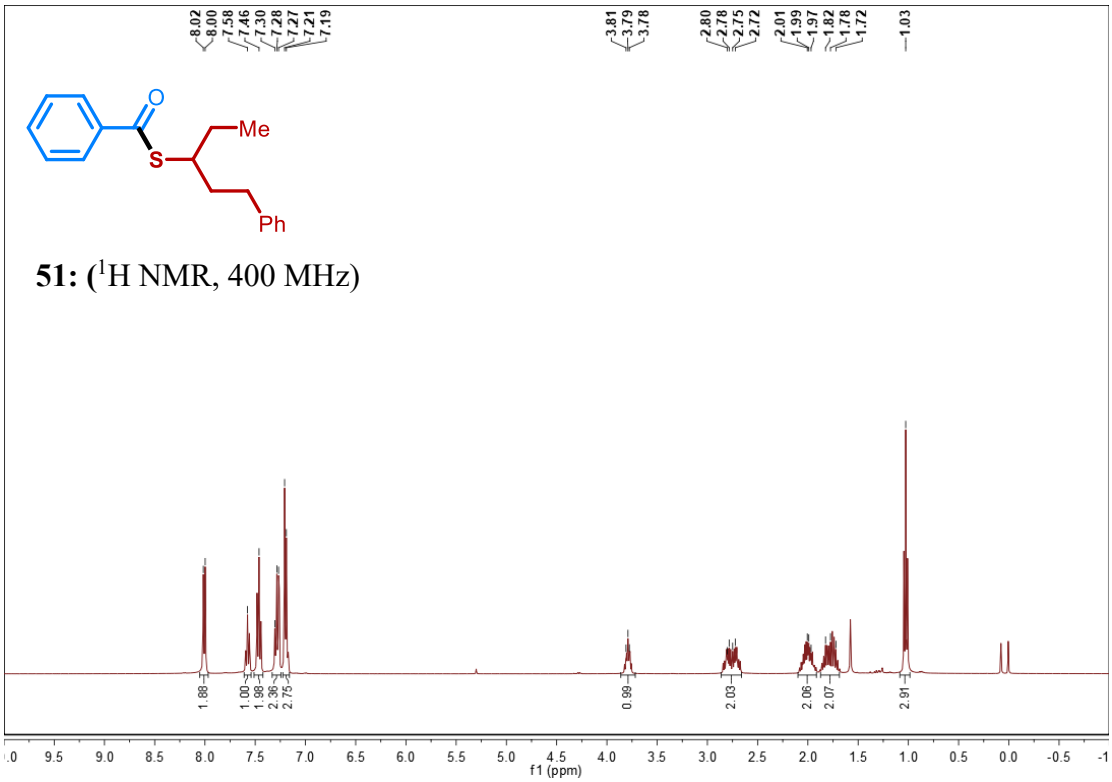
47: (^{13}C NMR, 100 MHz)



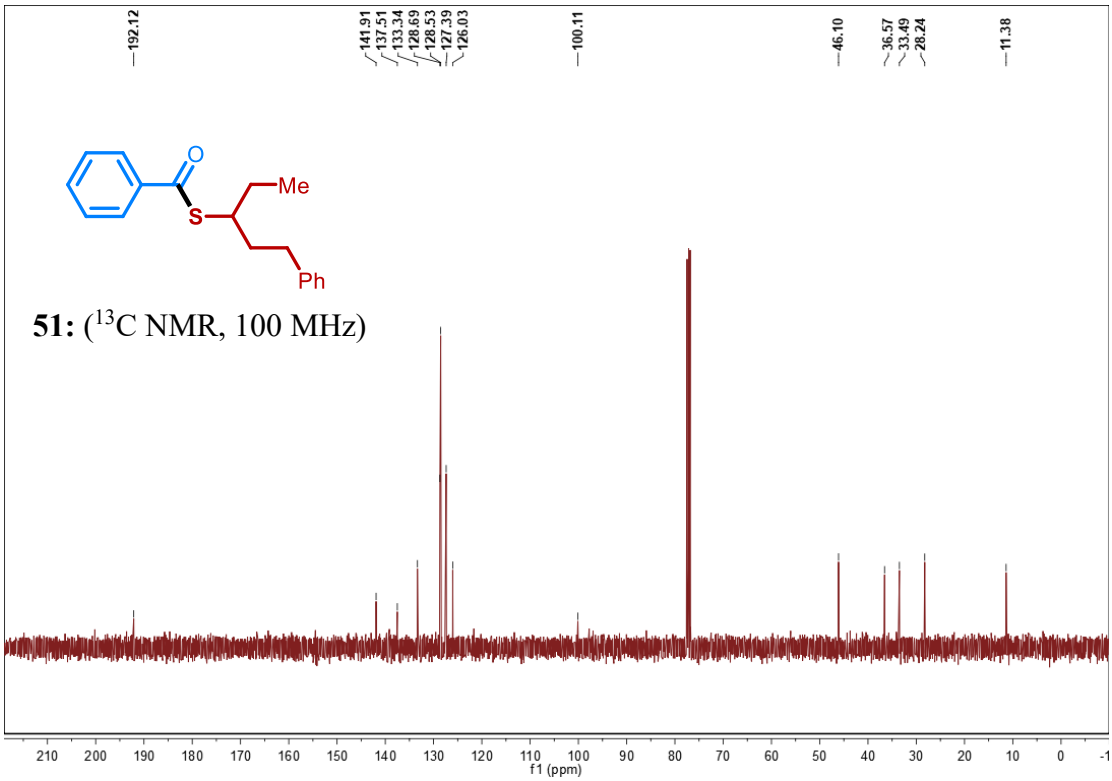
50: (^{1}H NMR, 400 MHz)



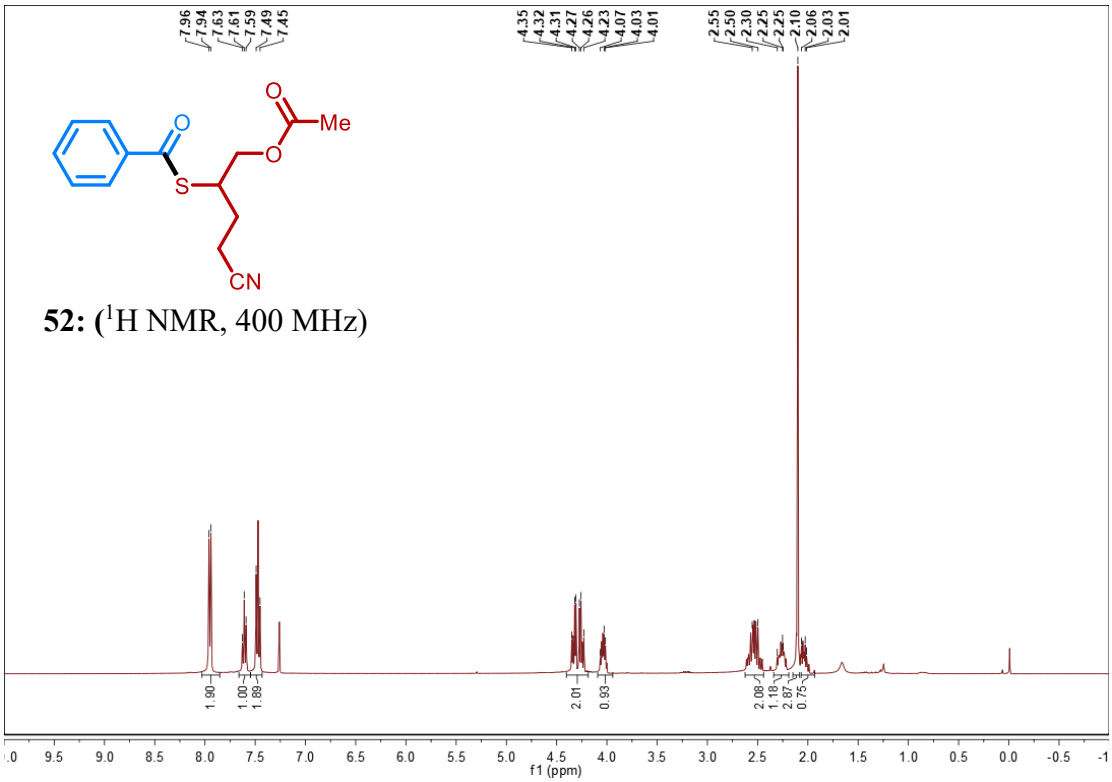
50: (^{13}C NMR, 100 MHz)



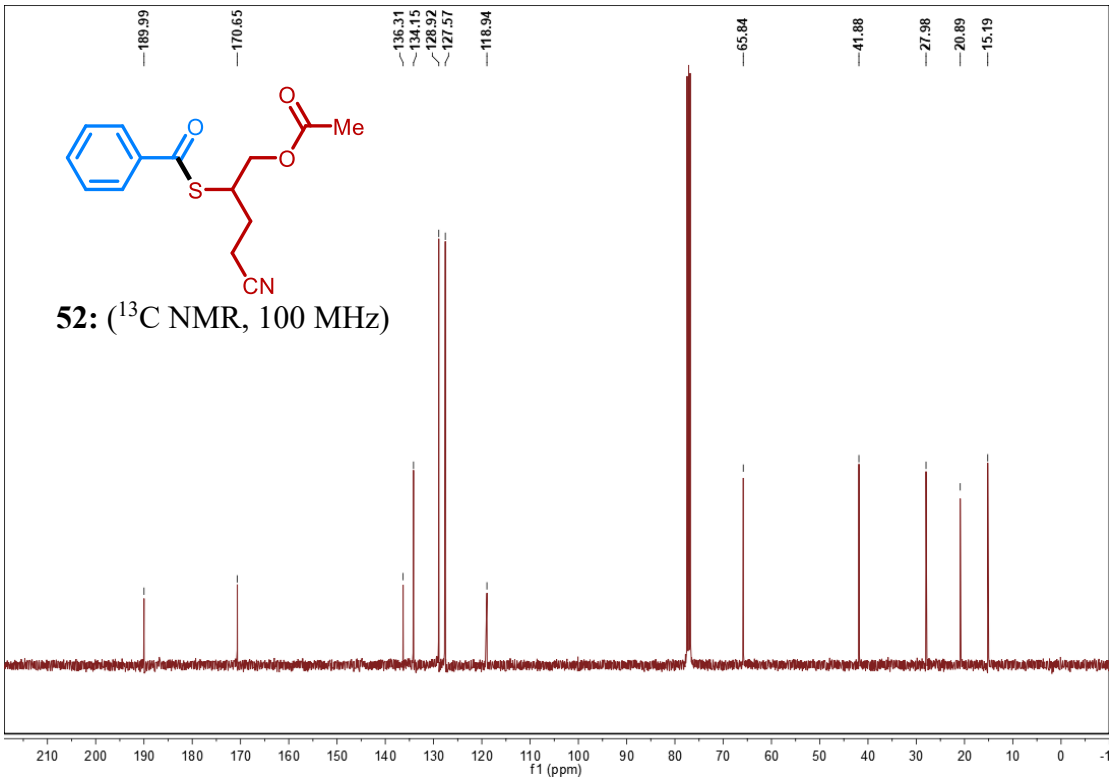
51: (^{1}H NMR, 400 MHz)



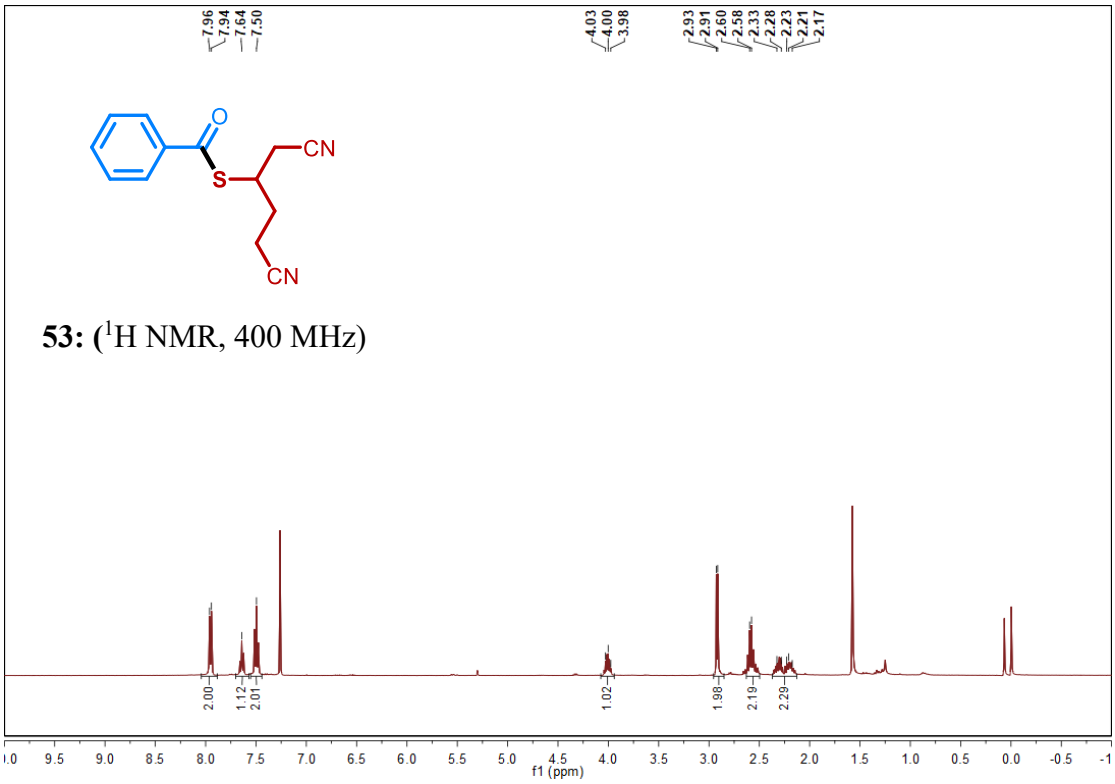
51: (^{13}C NMR, 100 MHz)



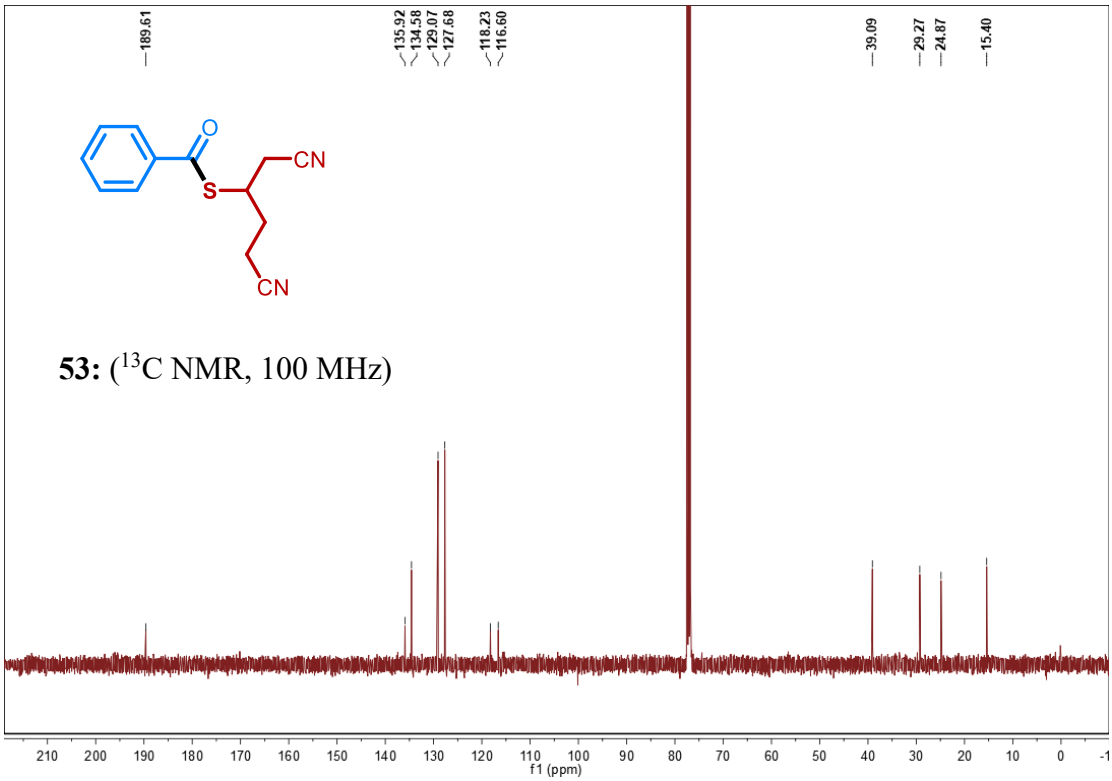
52: (^{1}H NMR, 400 MHz)



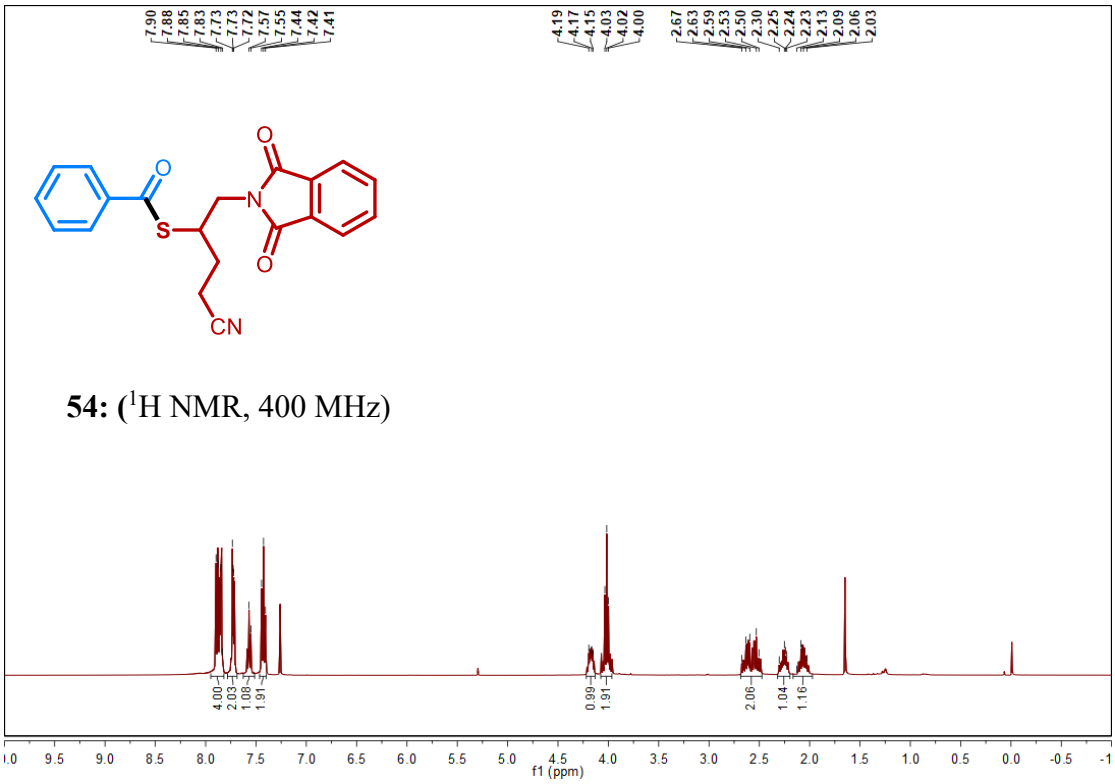
52: (^{13}C NMR, 100 MHz)



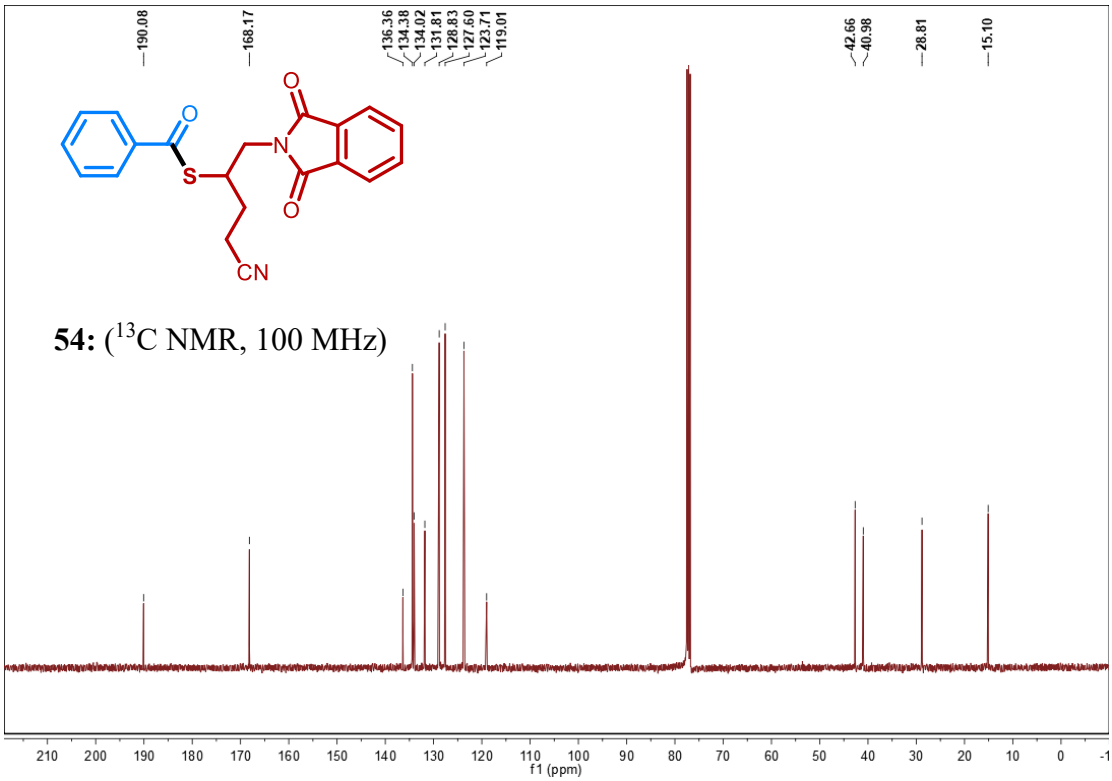
53: (^{1}H NMR, 400 MHz)



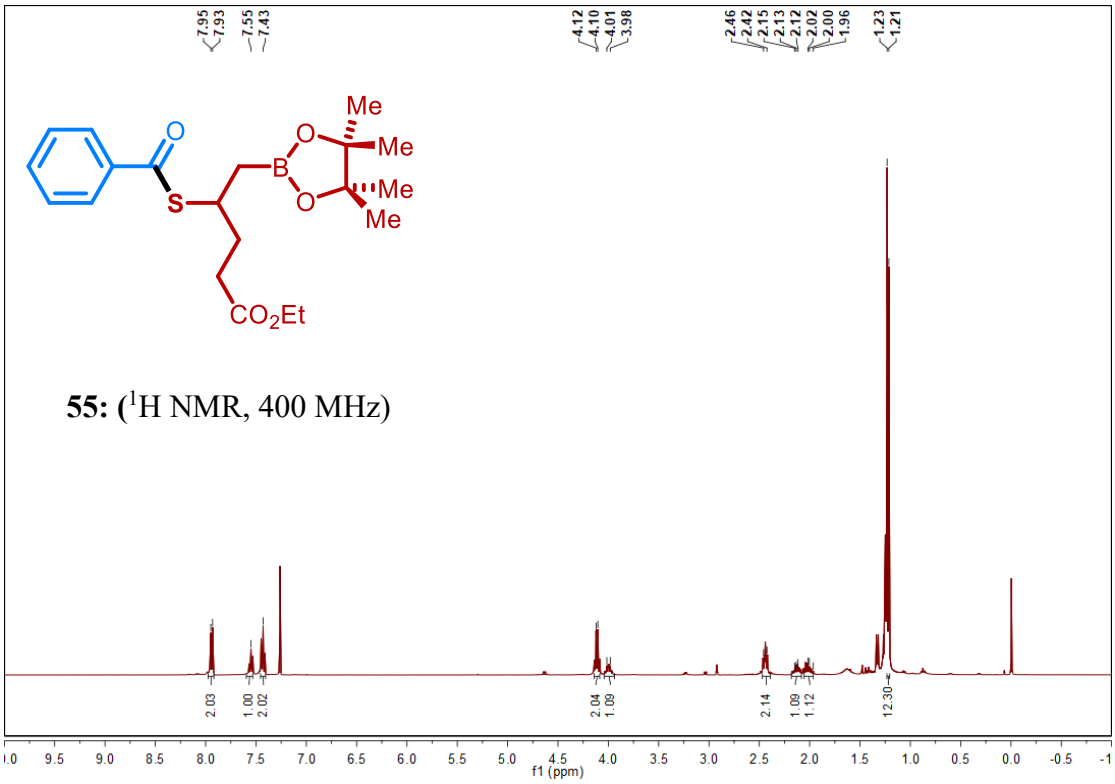
53: (^{13}C NMR, 100 MHz)



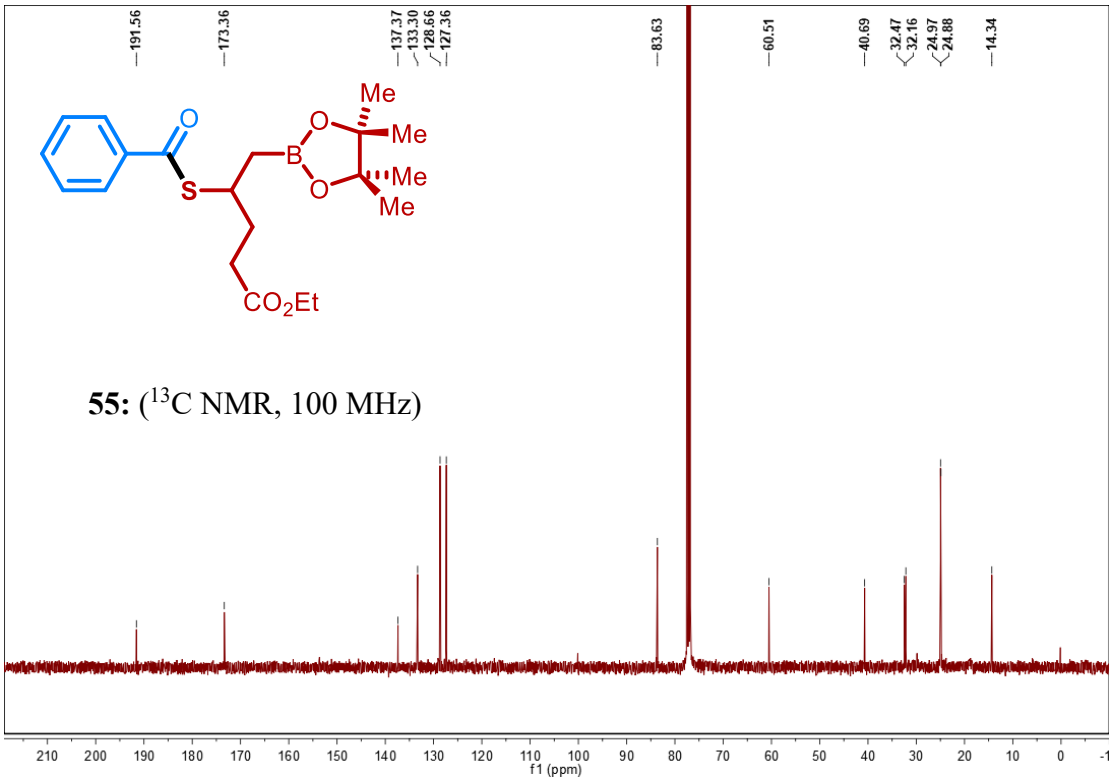
54: (^{1}H NMR, 400 MHz)



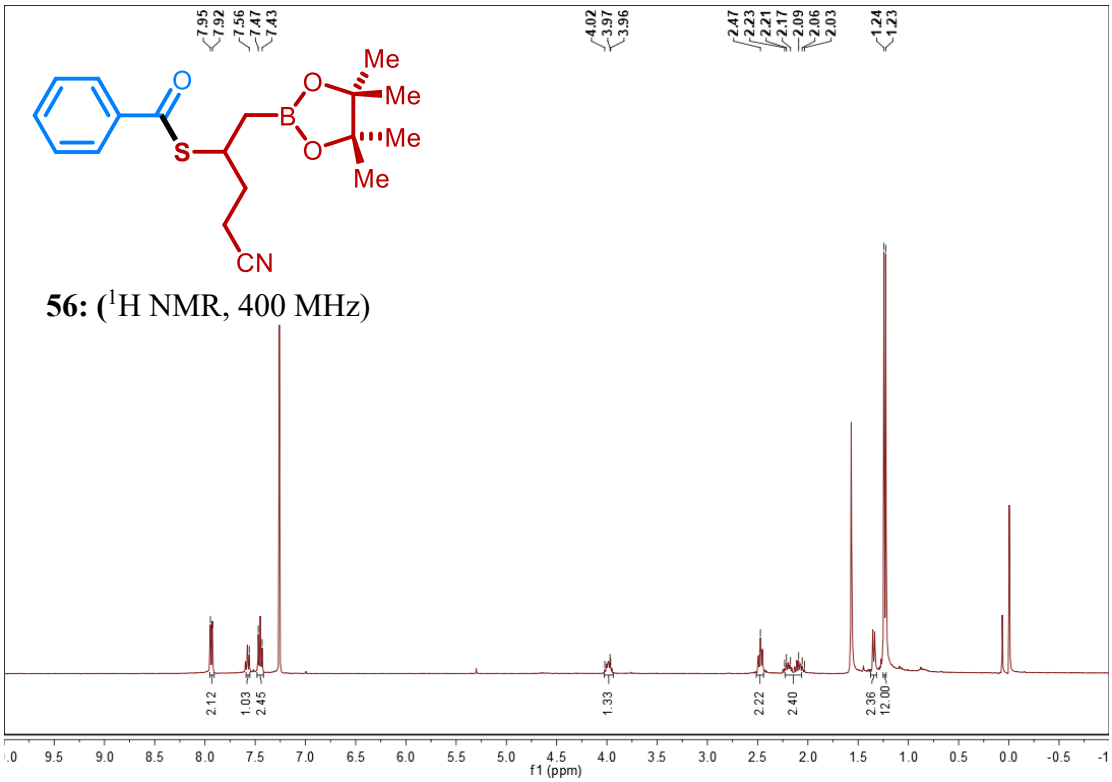
54: (^{13}C NMR, 100 MHz)



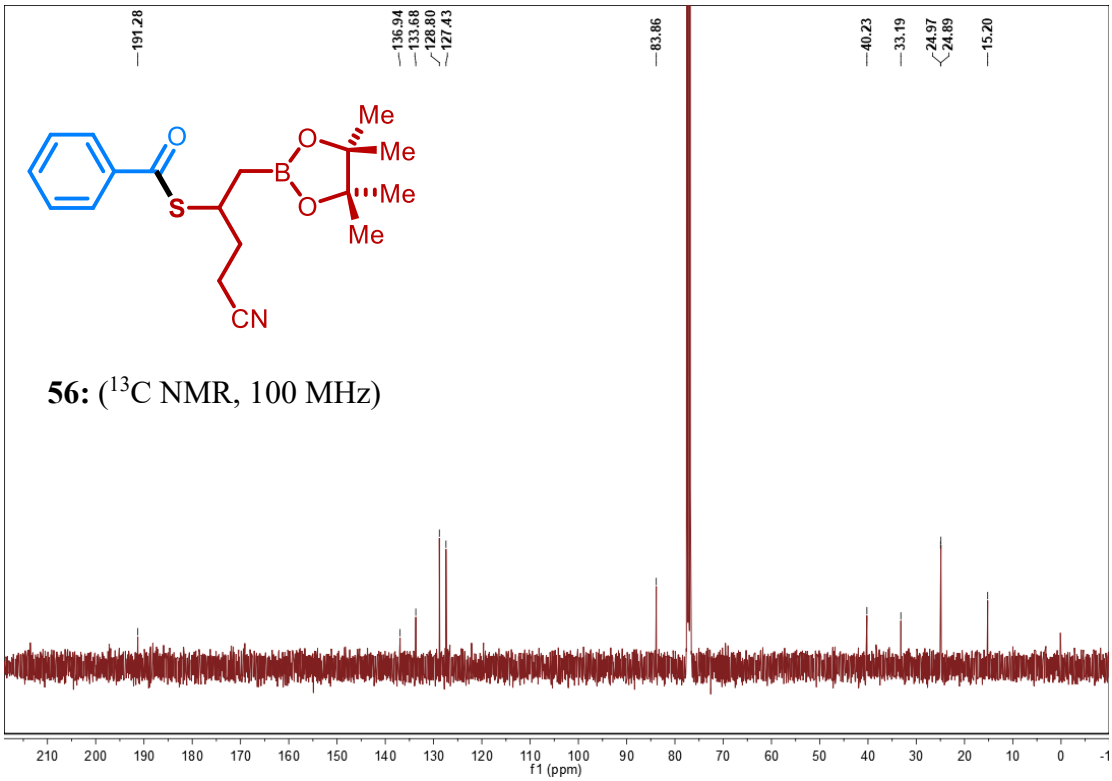
55: (^{1}H NMR, 400 MHz)



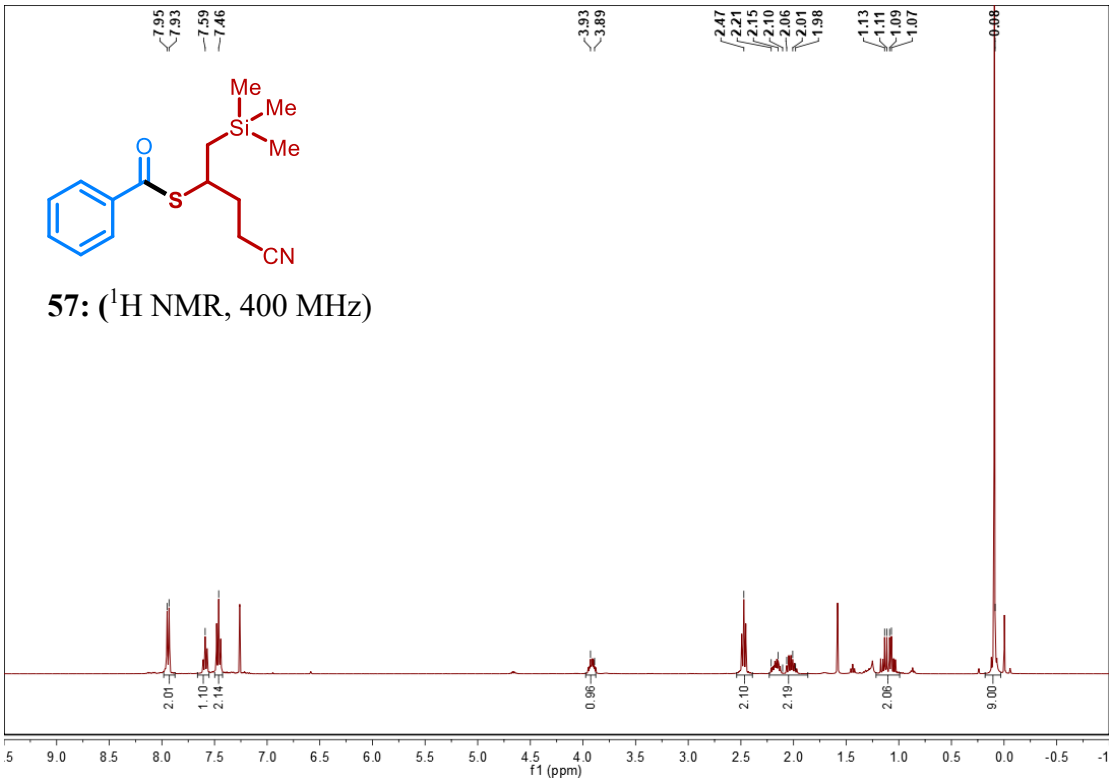
55: (^{13}C NMR, 100 MHz)



56: (^{1}H NMR, 400 MHz)



56: (^{13}C NMR, 100 MHz)



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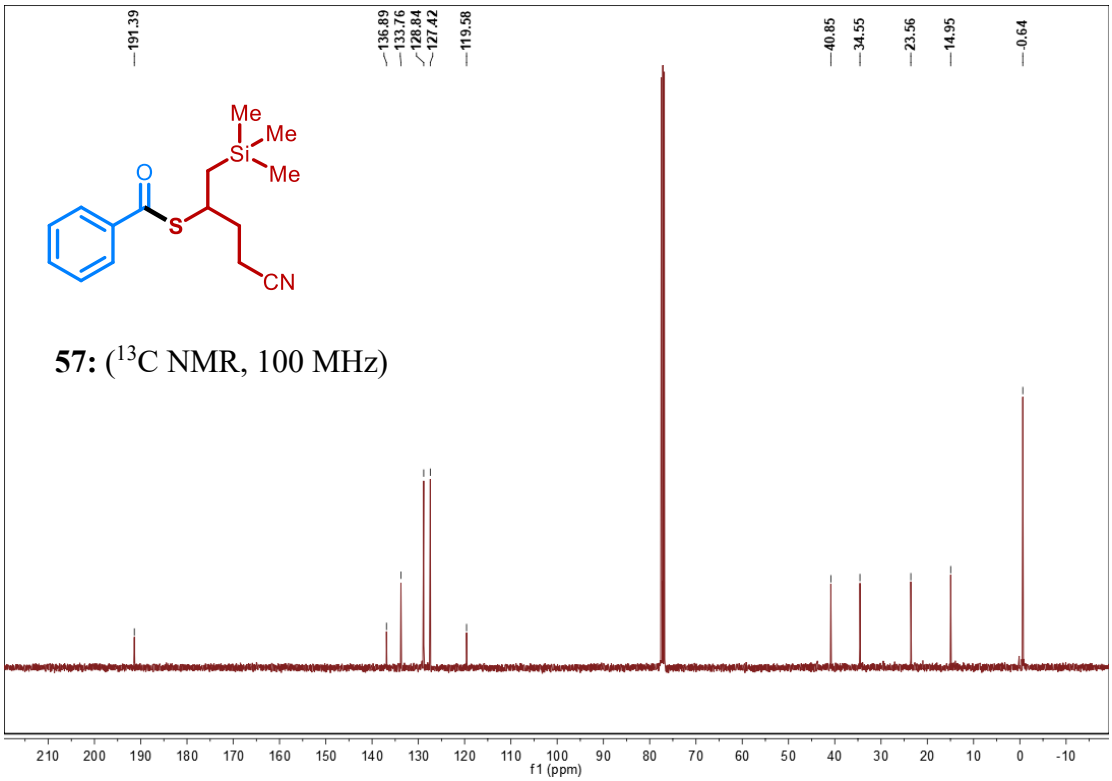

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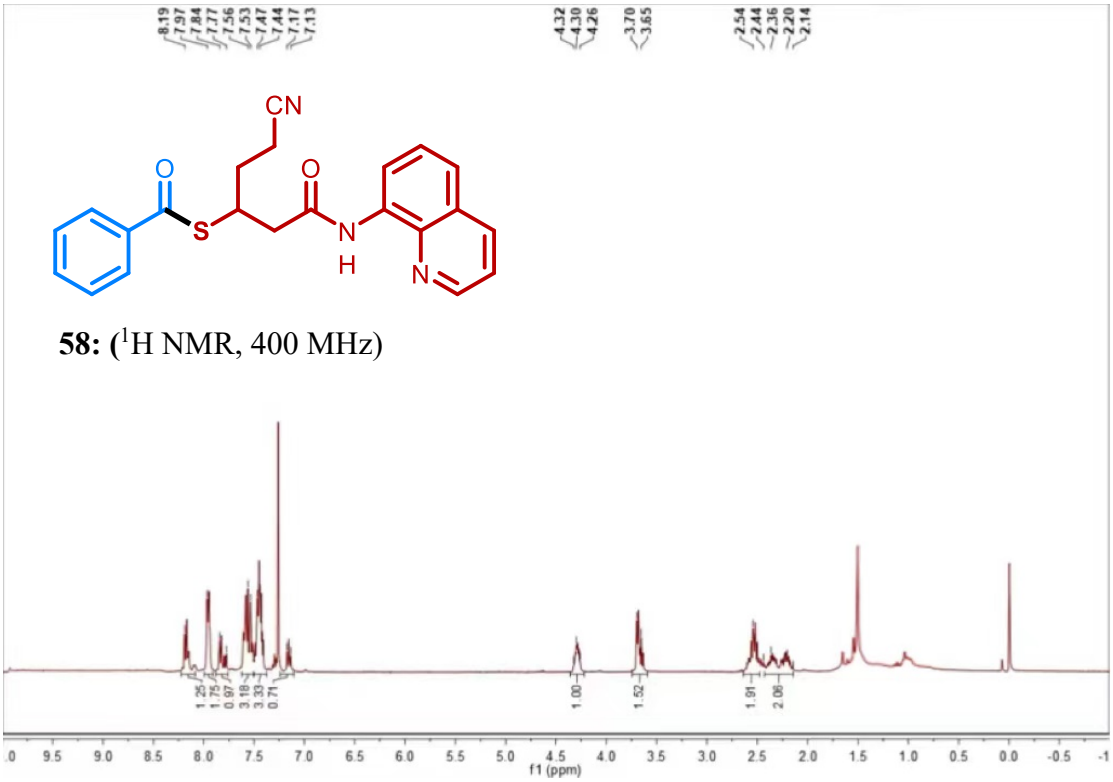
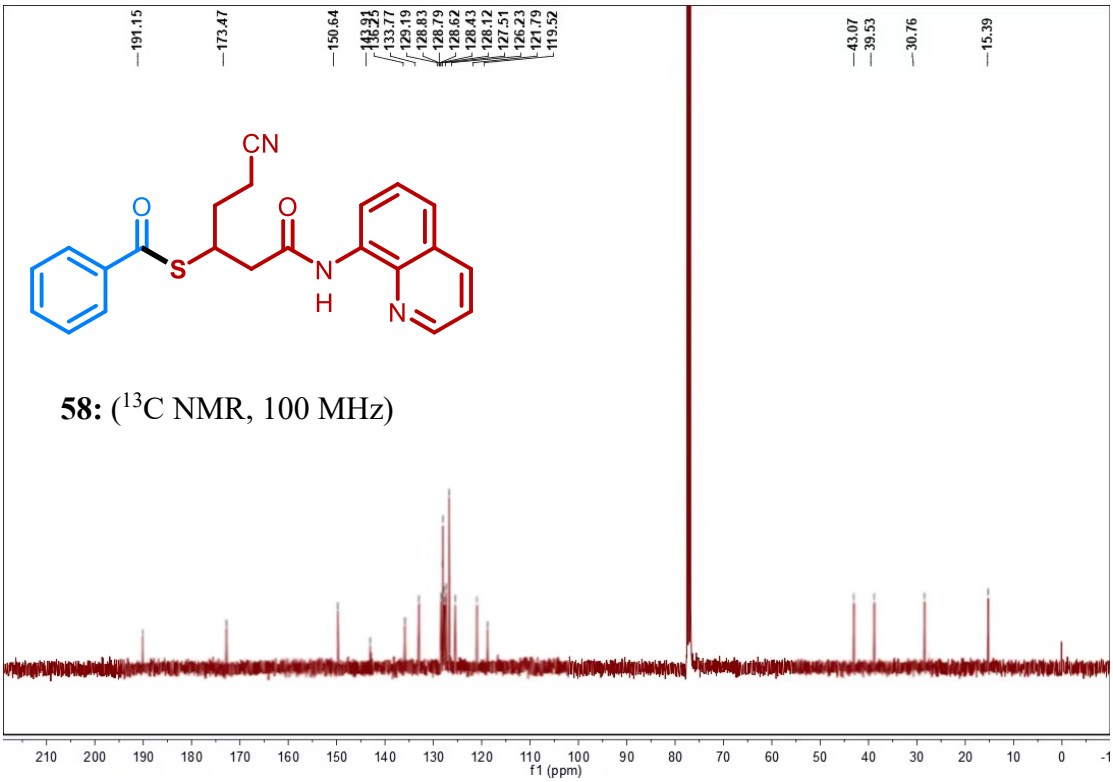


58: (^{1}H NMR, 400 MHz)



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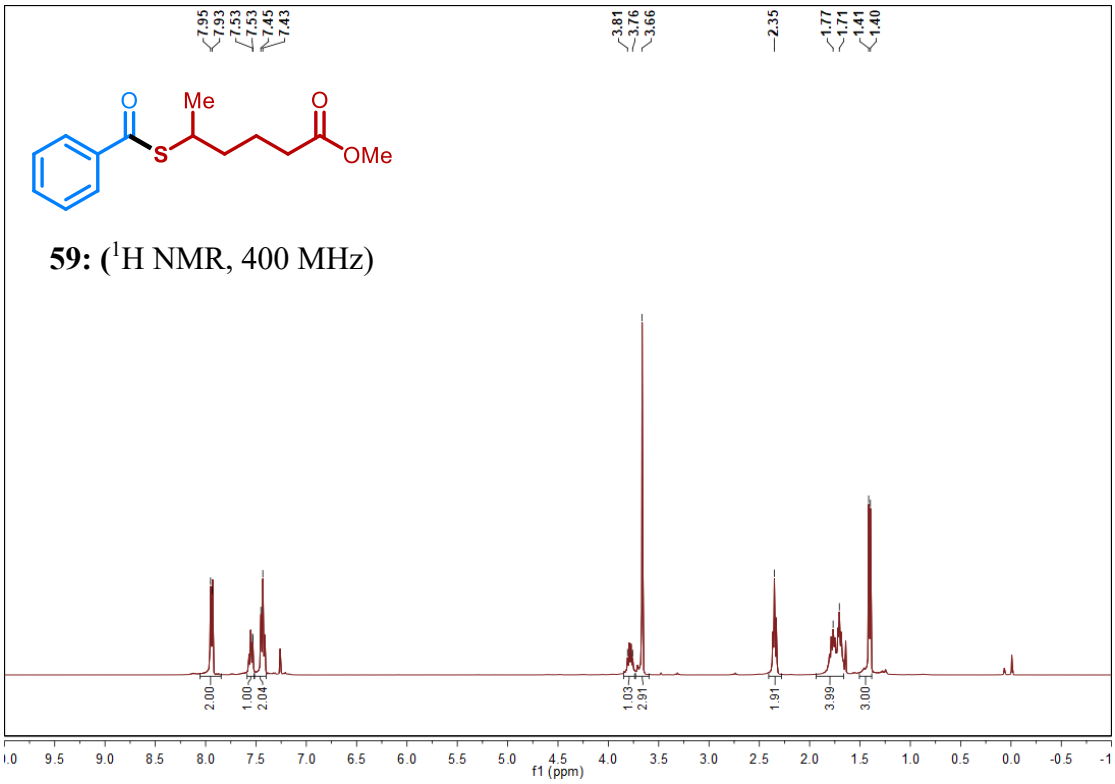
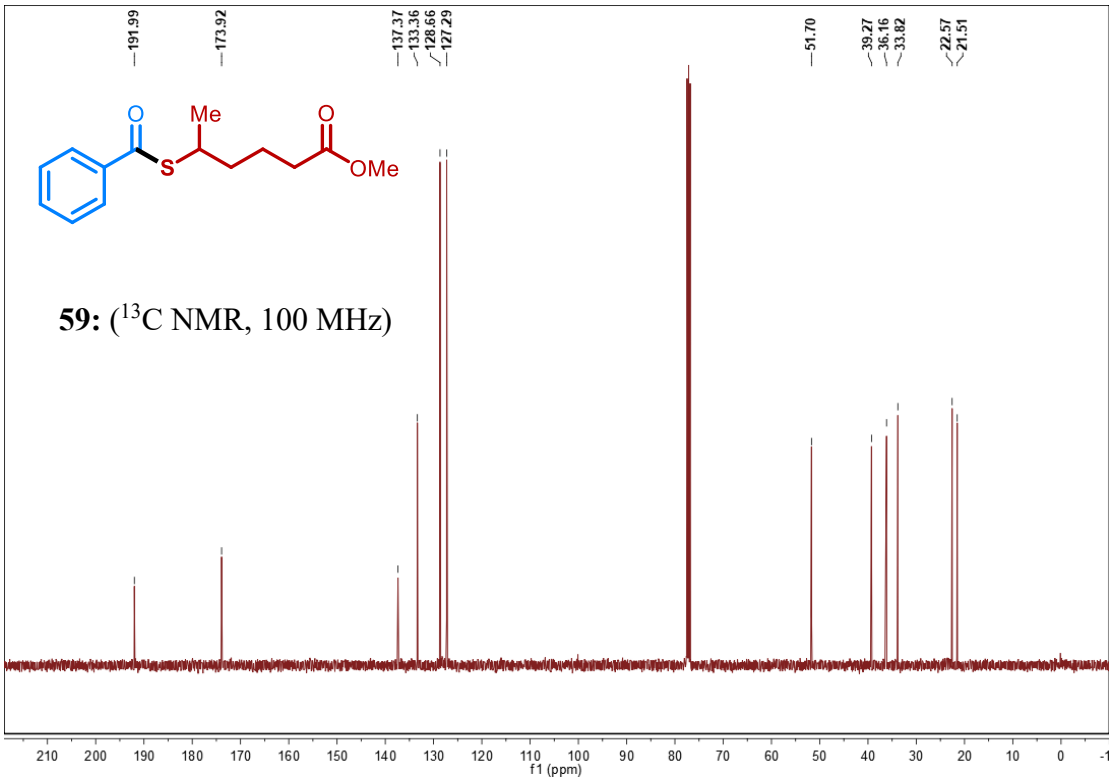
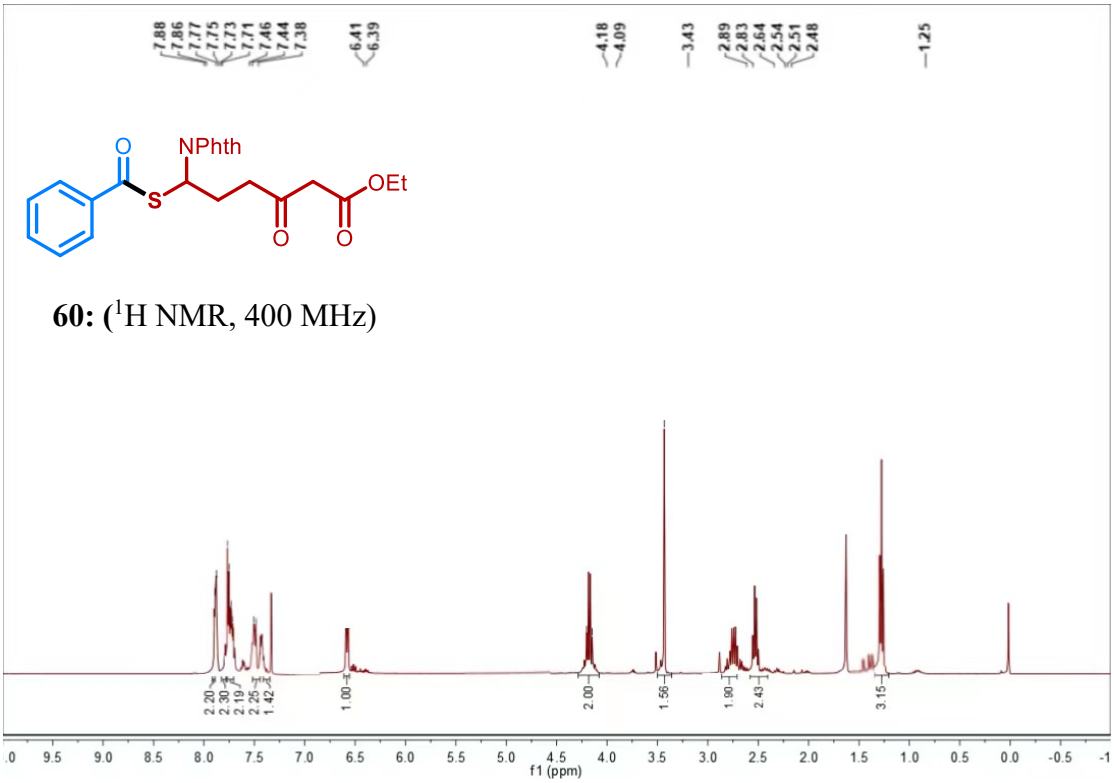


59: (^{1}H NMR, 400 MHz)



59: (^{13}C NMR, 100 MHz)



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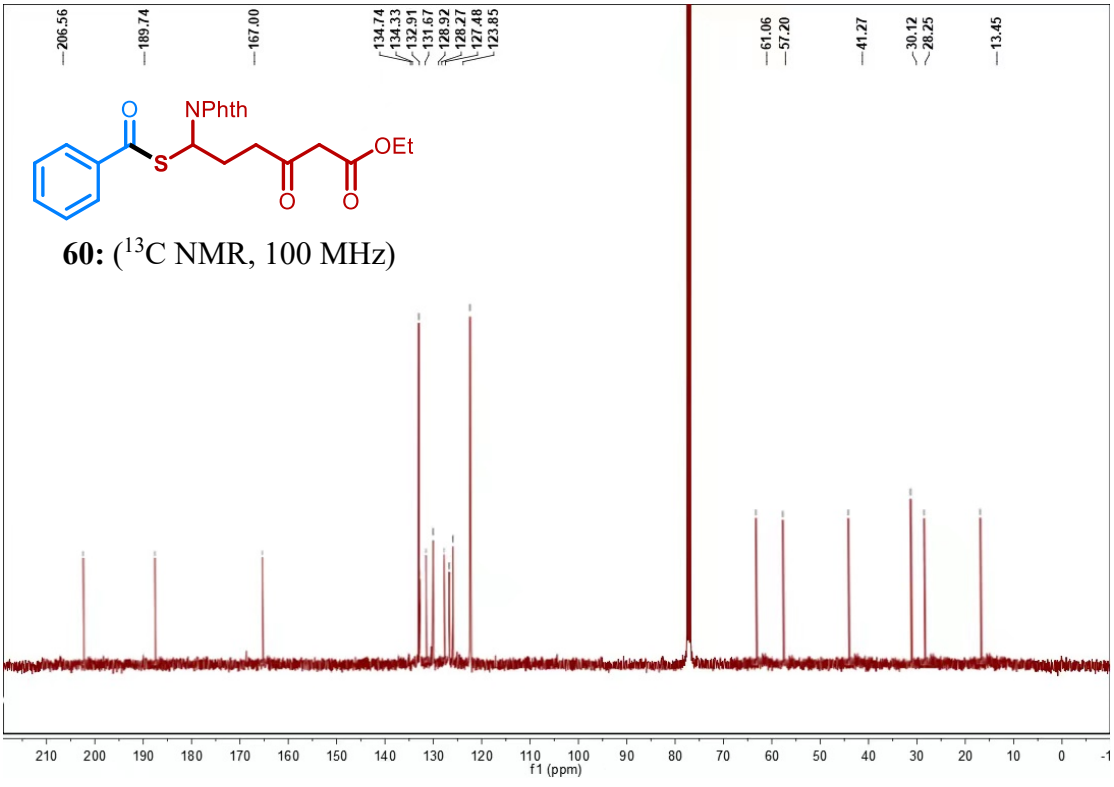

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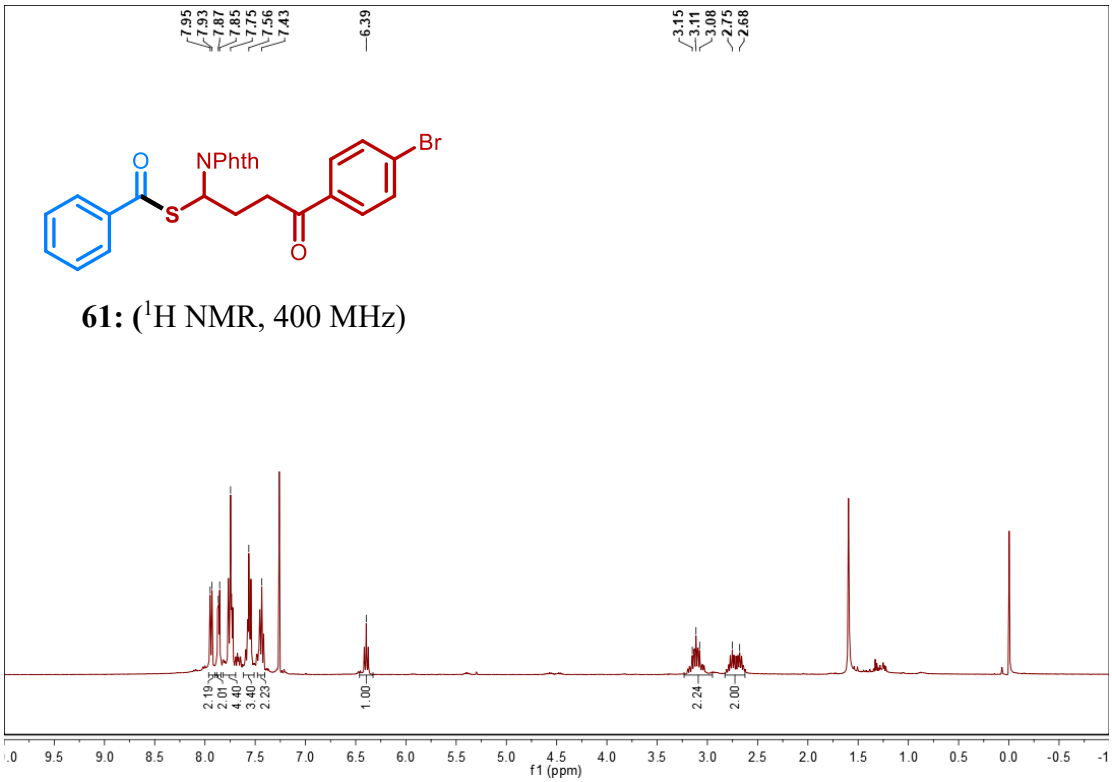
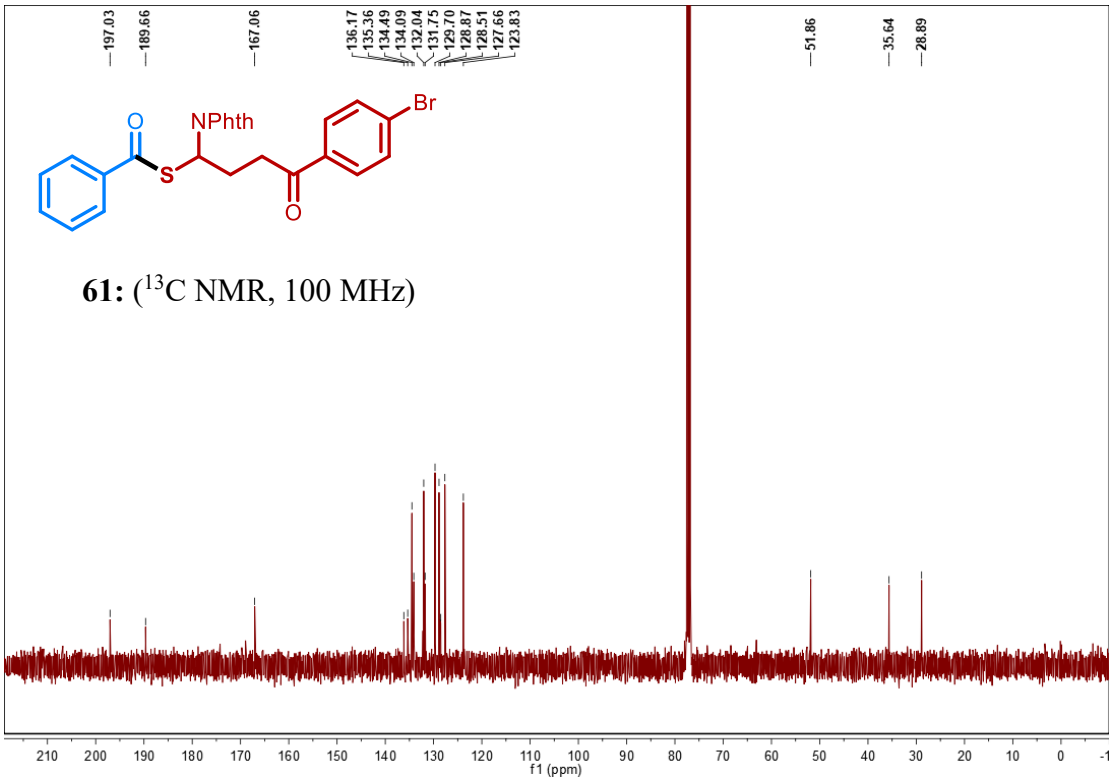
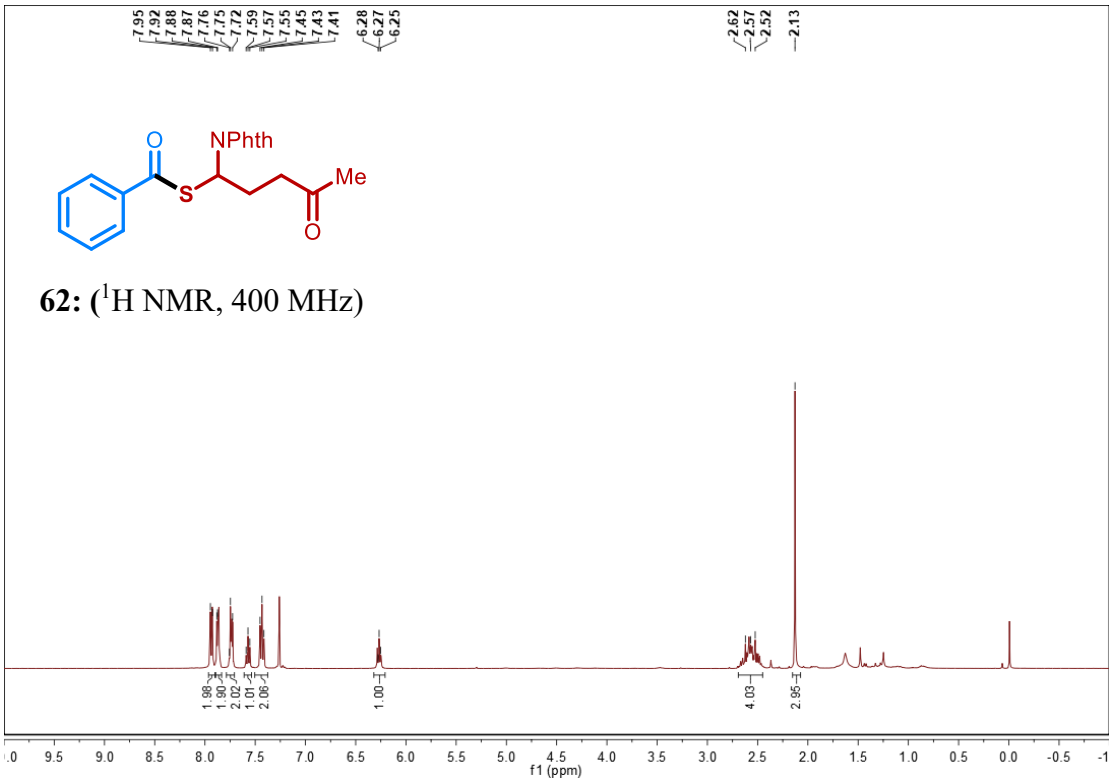


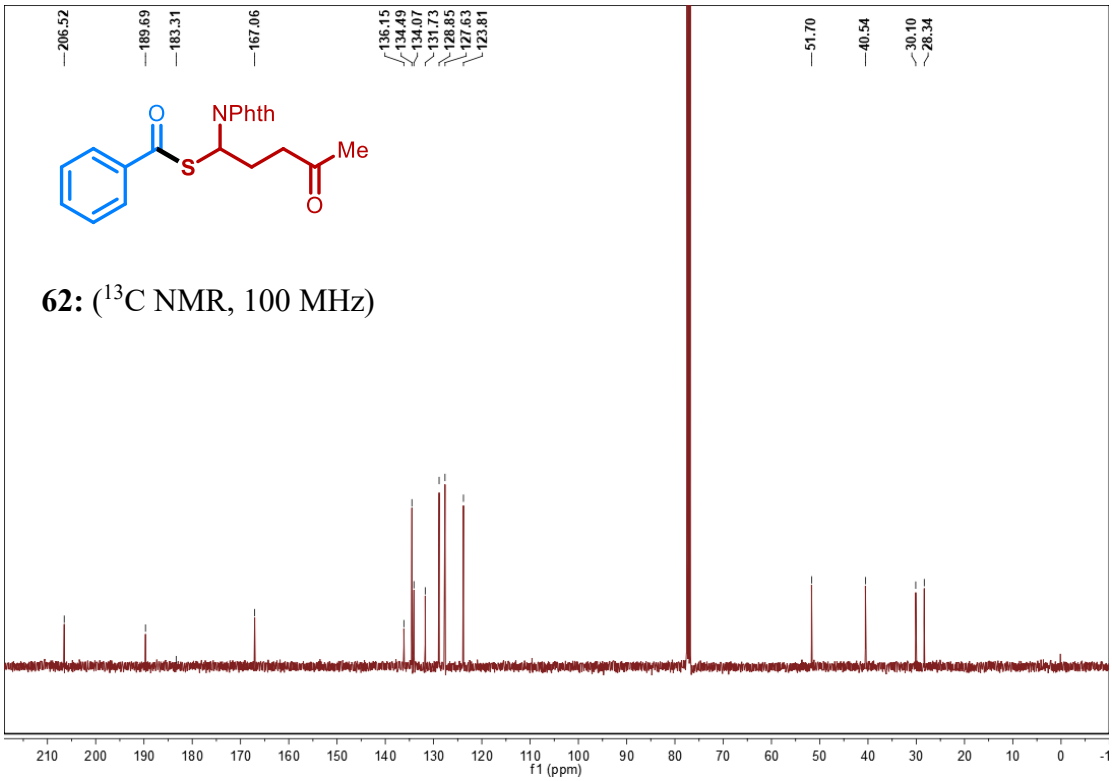
61: (^{1}H NMR, 400 MHz)



61: (^{13}C NMR, 100 MHz)



62: (^{1}H NMR, 400 MHz)



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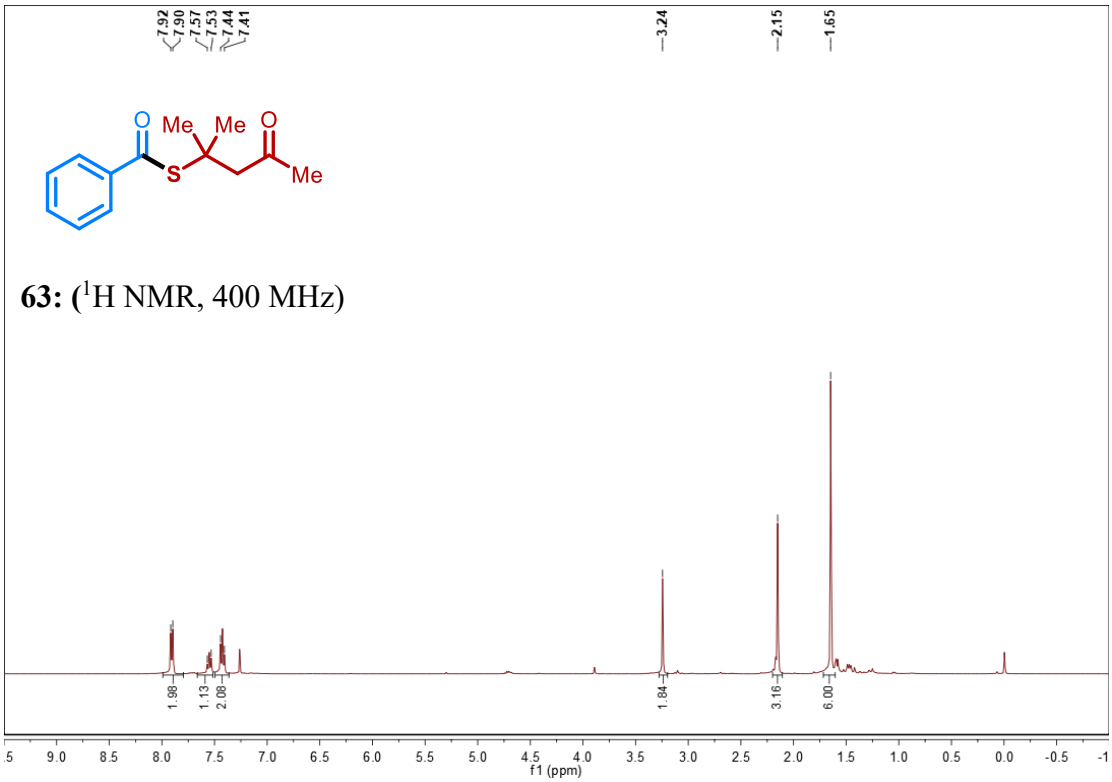
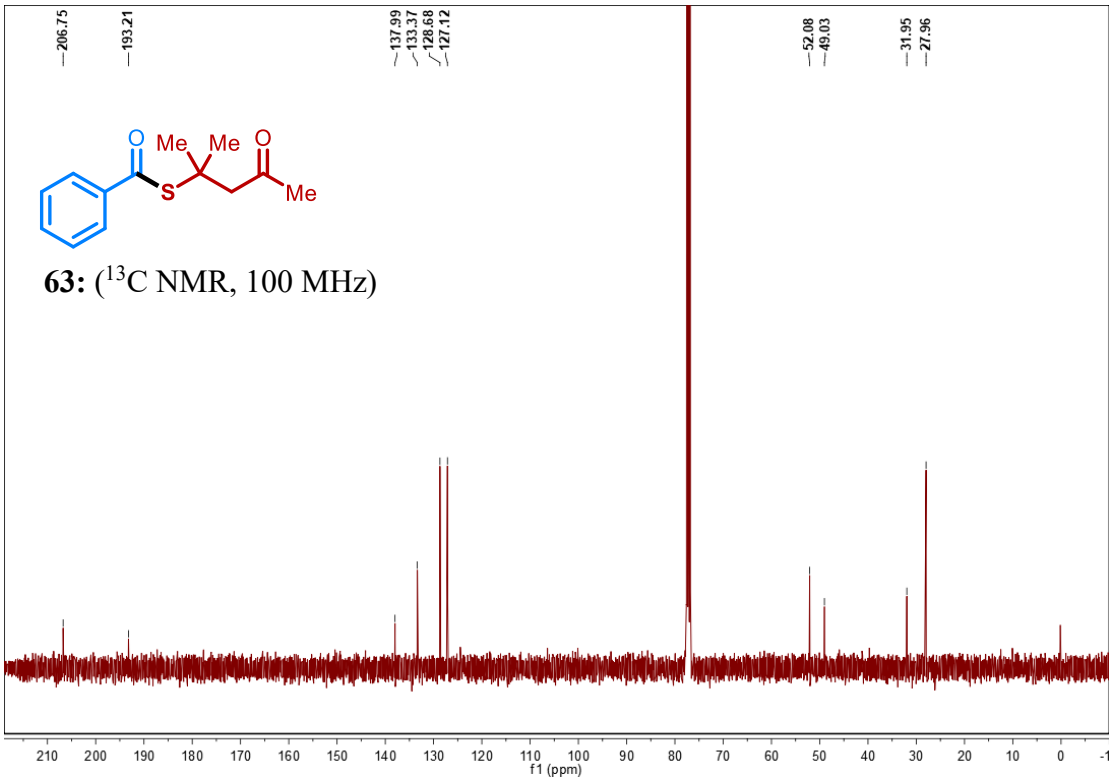


63: (^{1}H NMR, 400 MHz)



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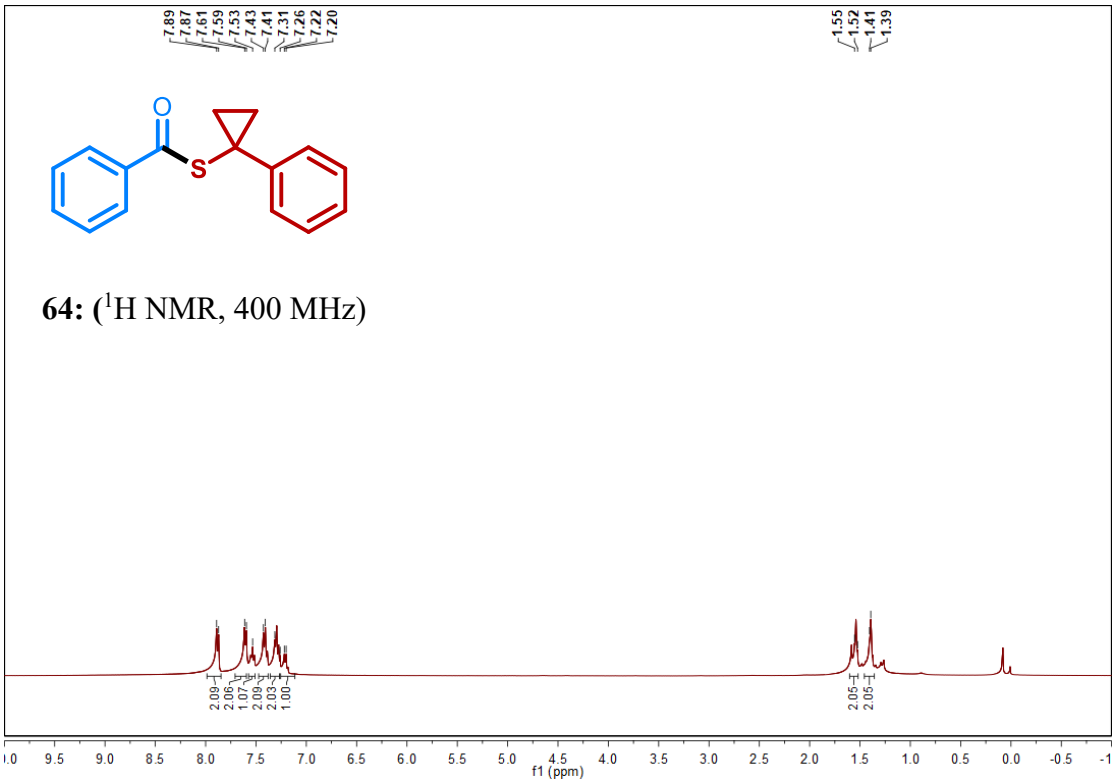
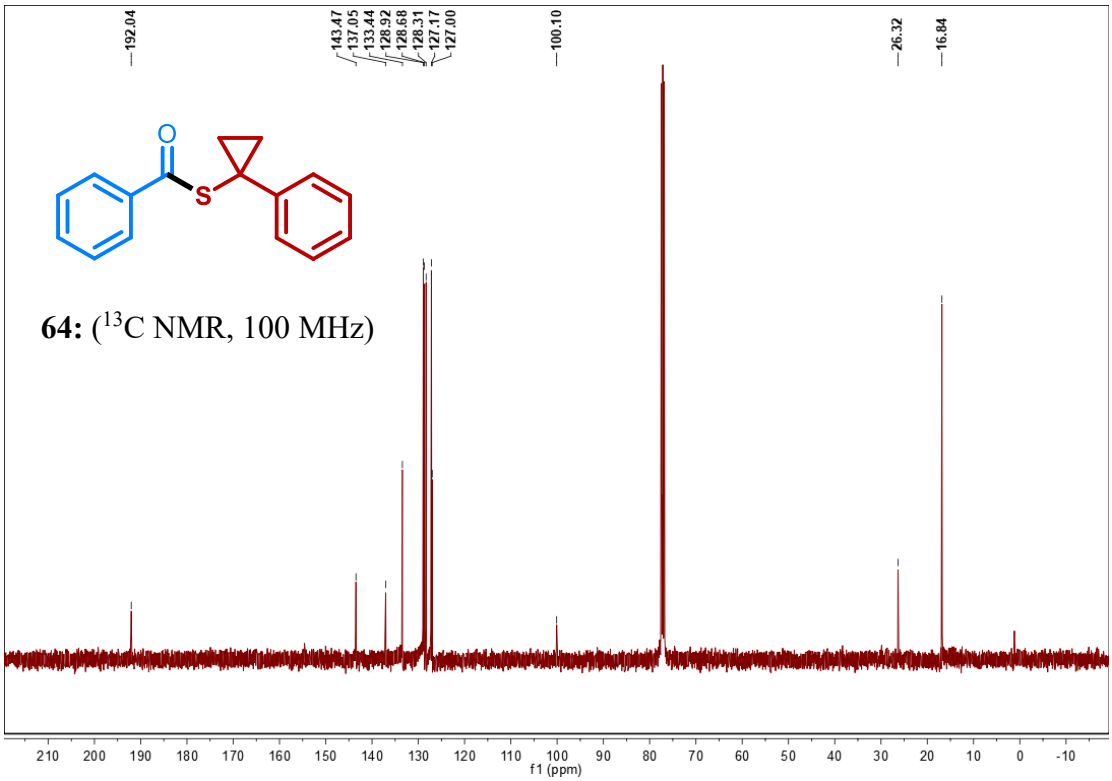


64: (^{1}H NMR, 400 MHz)



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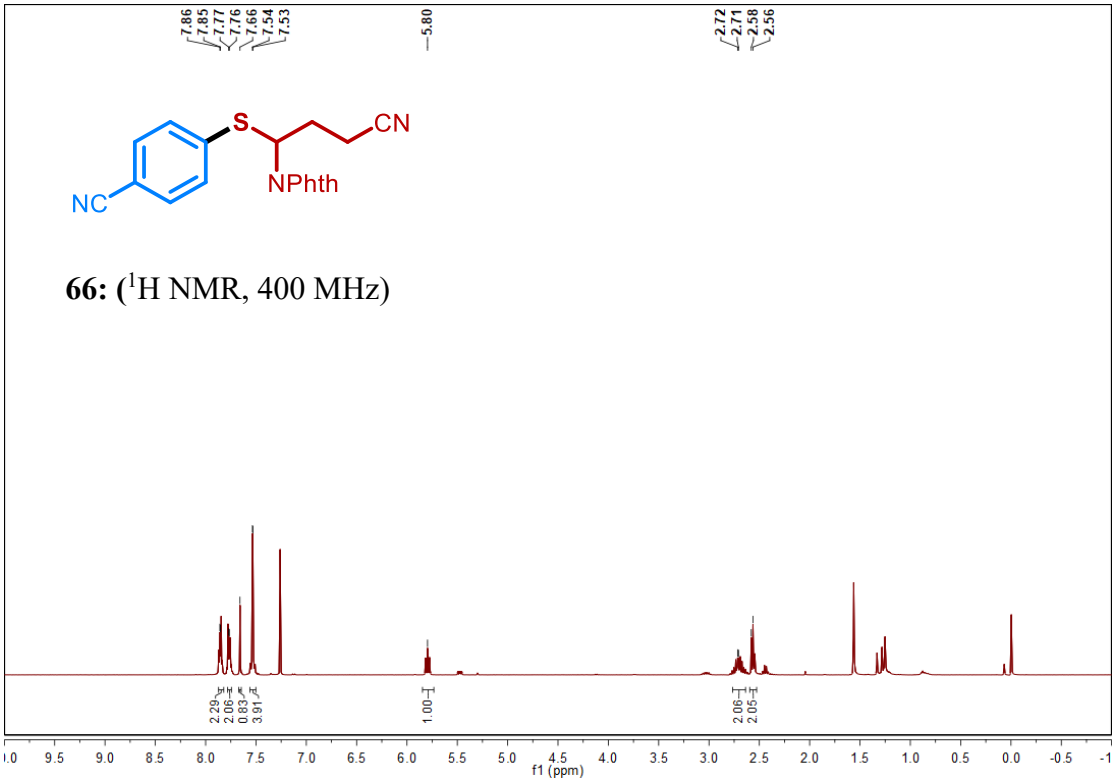
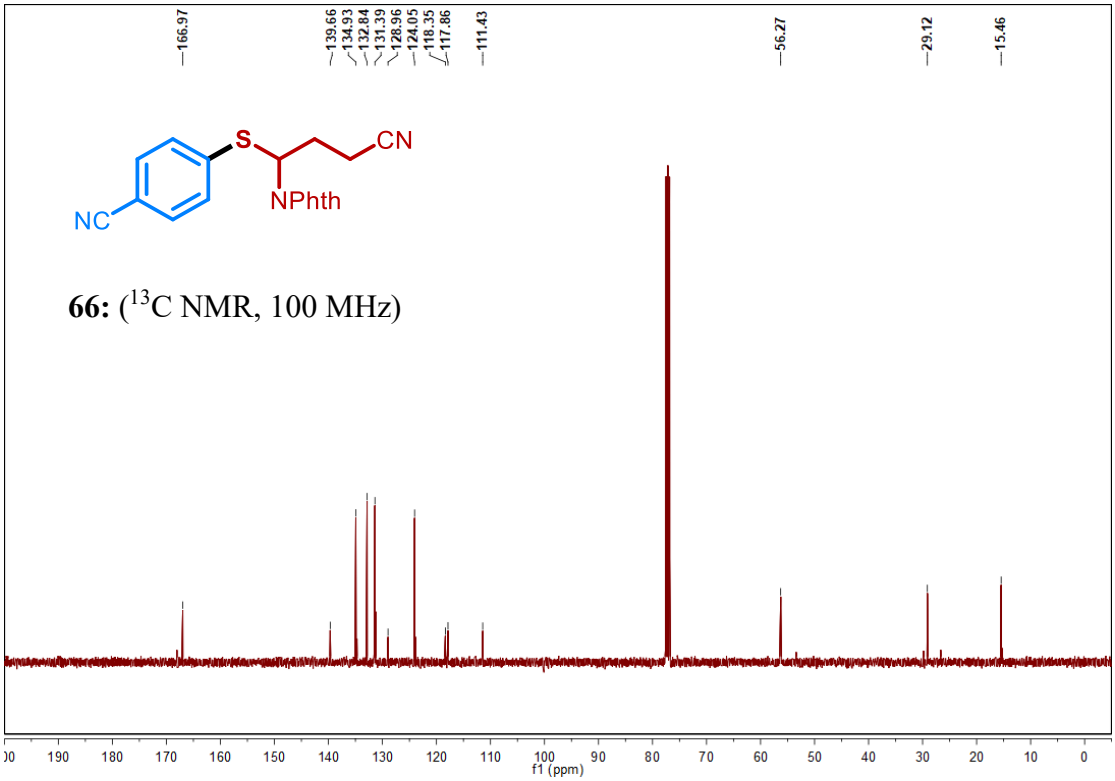


66: (^{1}H NMR, 400 MHz)



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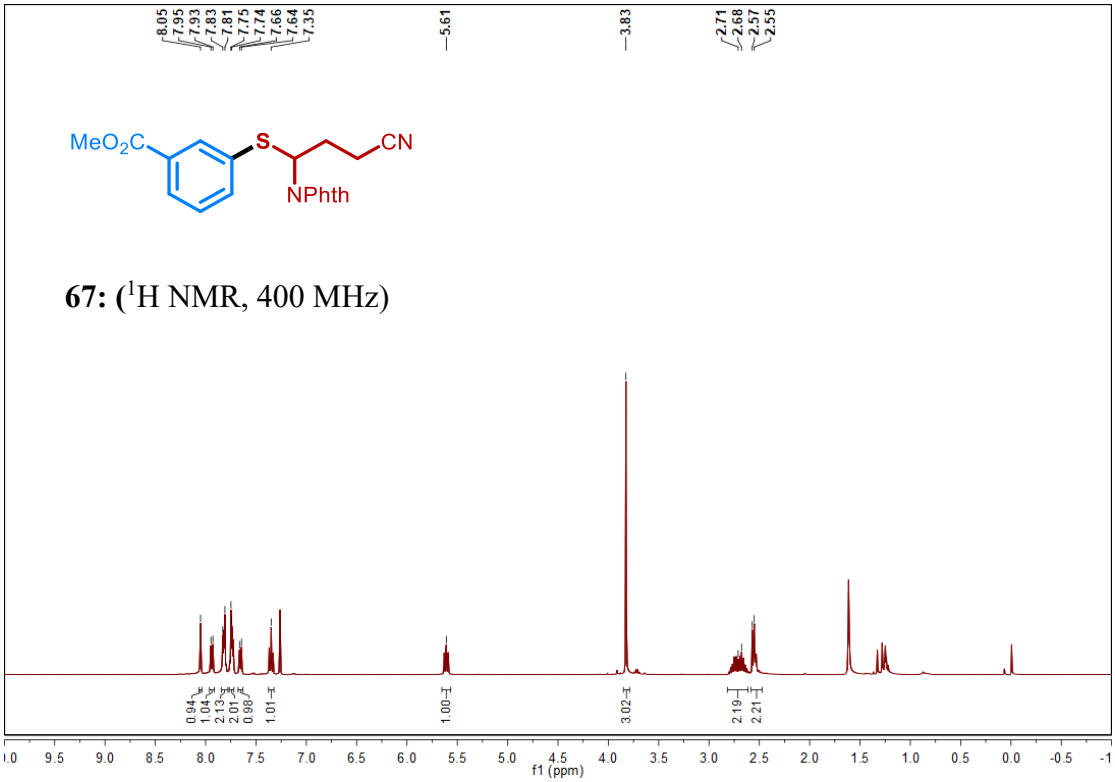
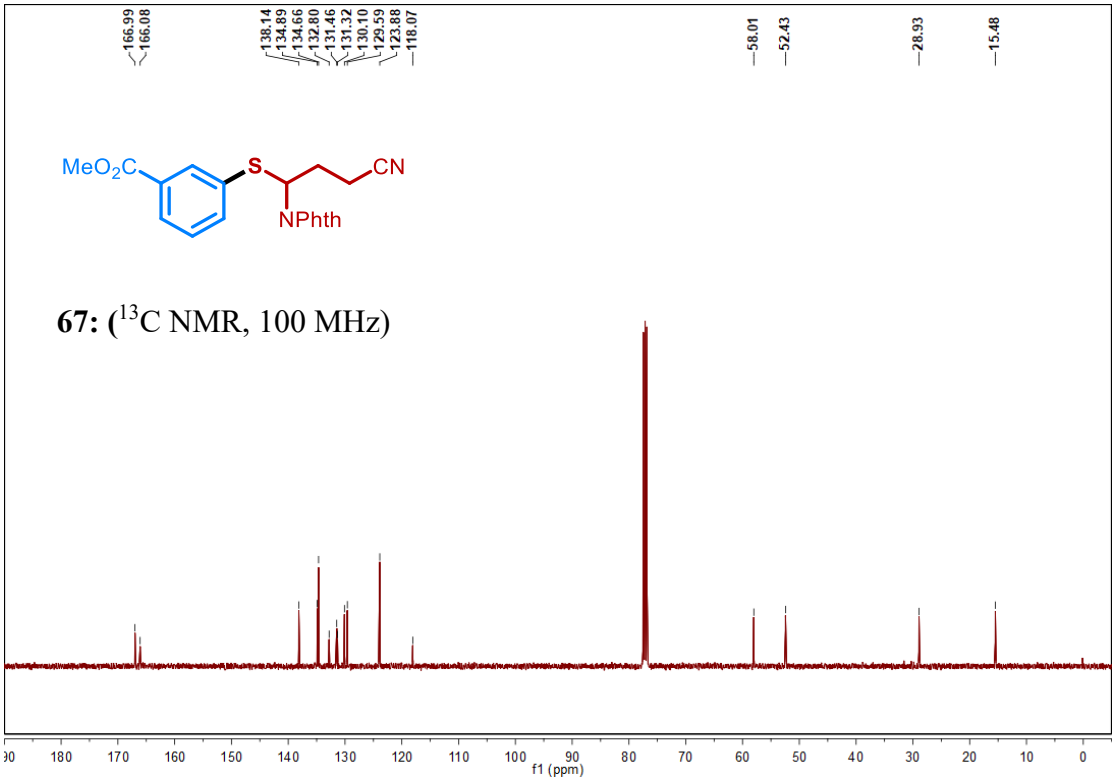
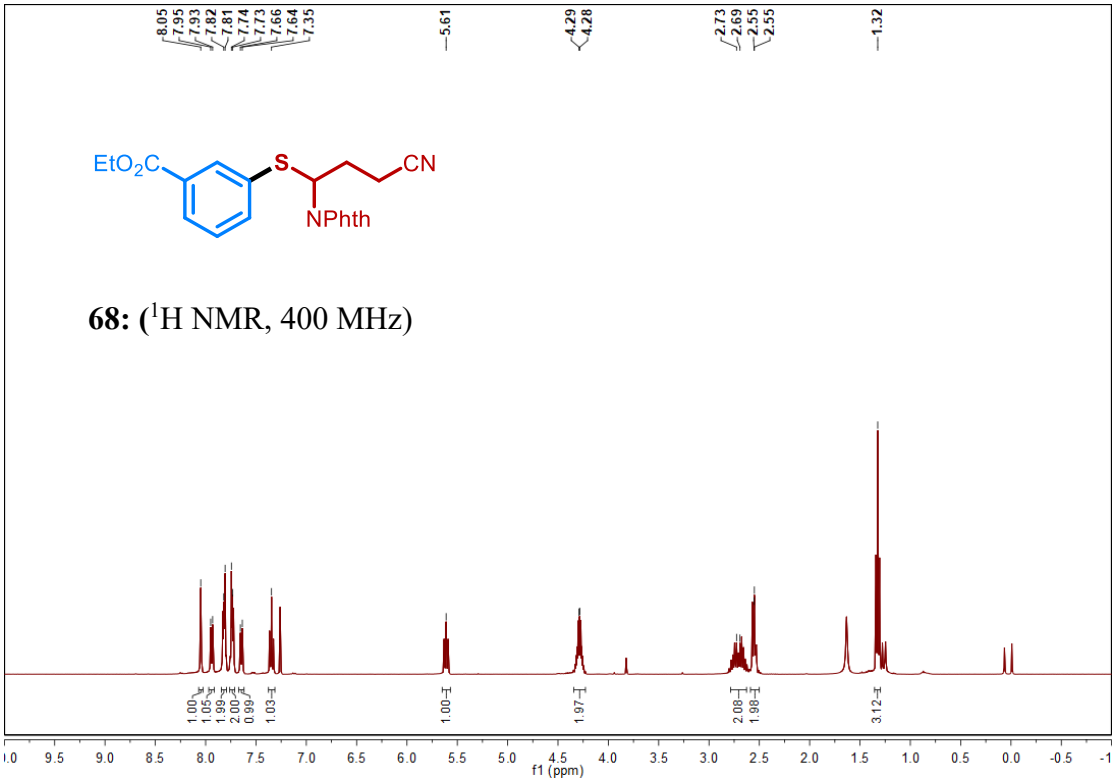


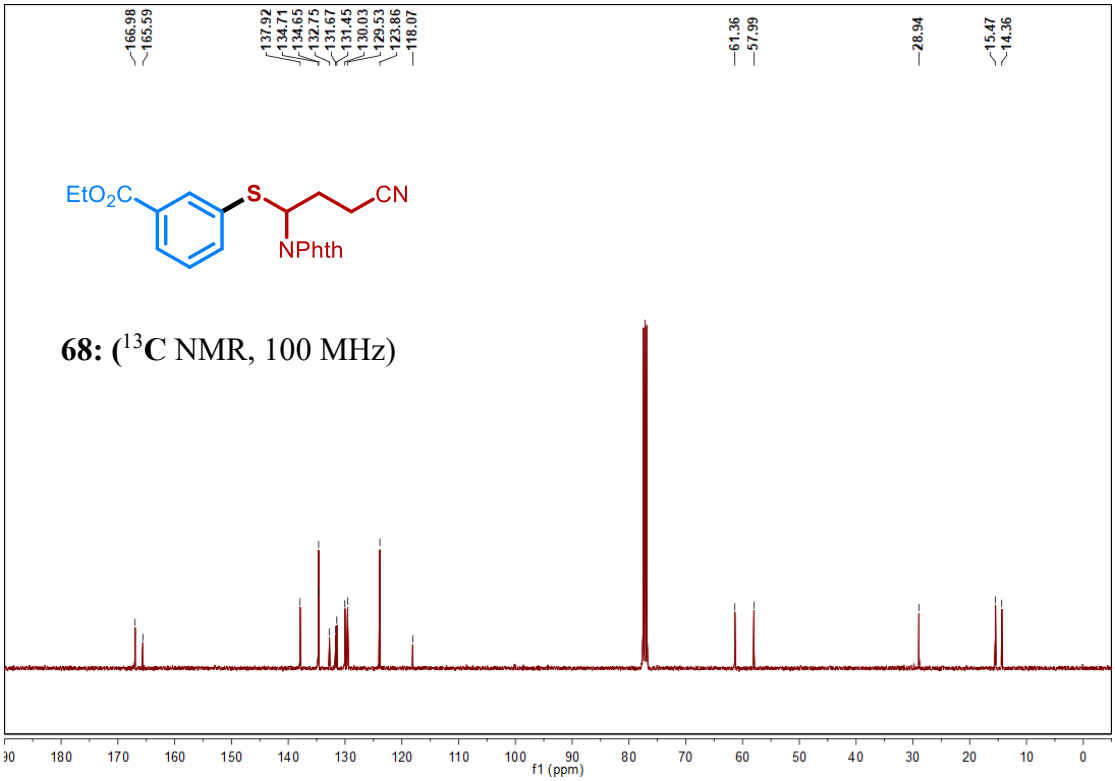
67: (^{1}H NMR, 400 MHz)



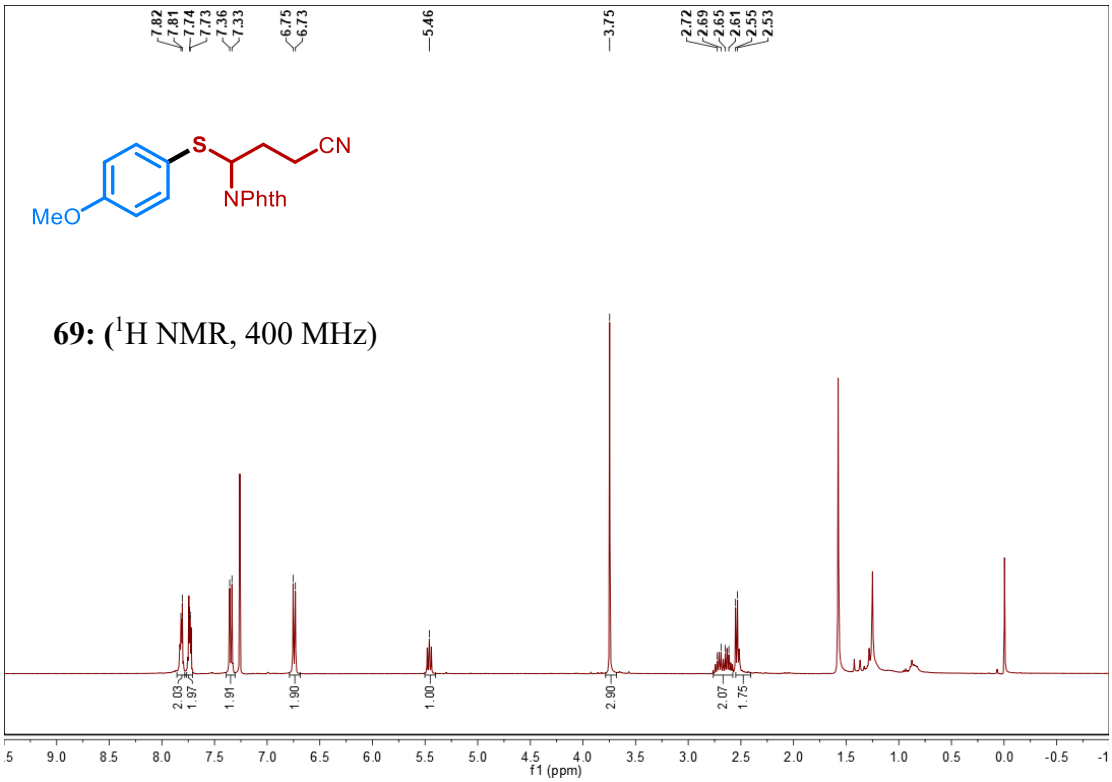
67: (^{13}C NMR, 100 MHz)



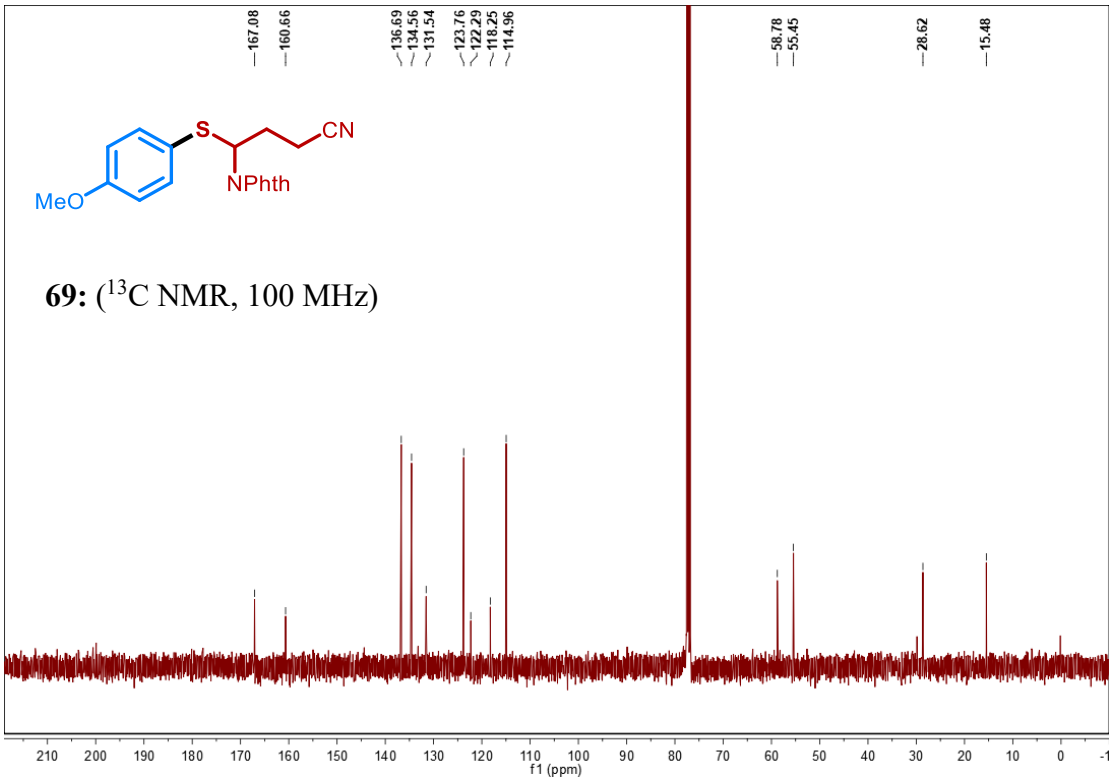
68: (^{1}H NMR, 400 MHz)



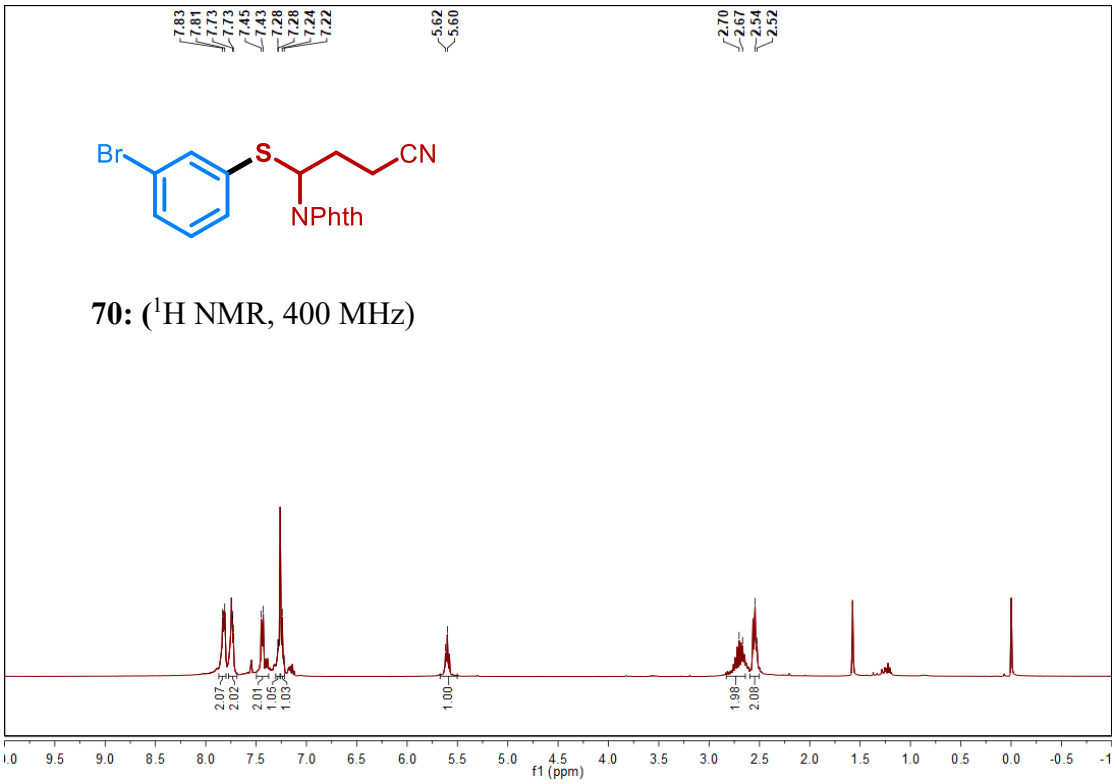
68: (^{13}**C** NMR, 100 MHz)



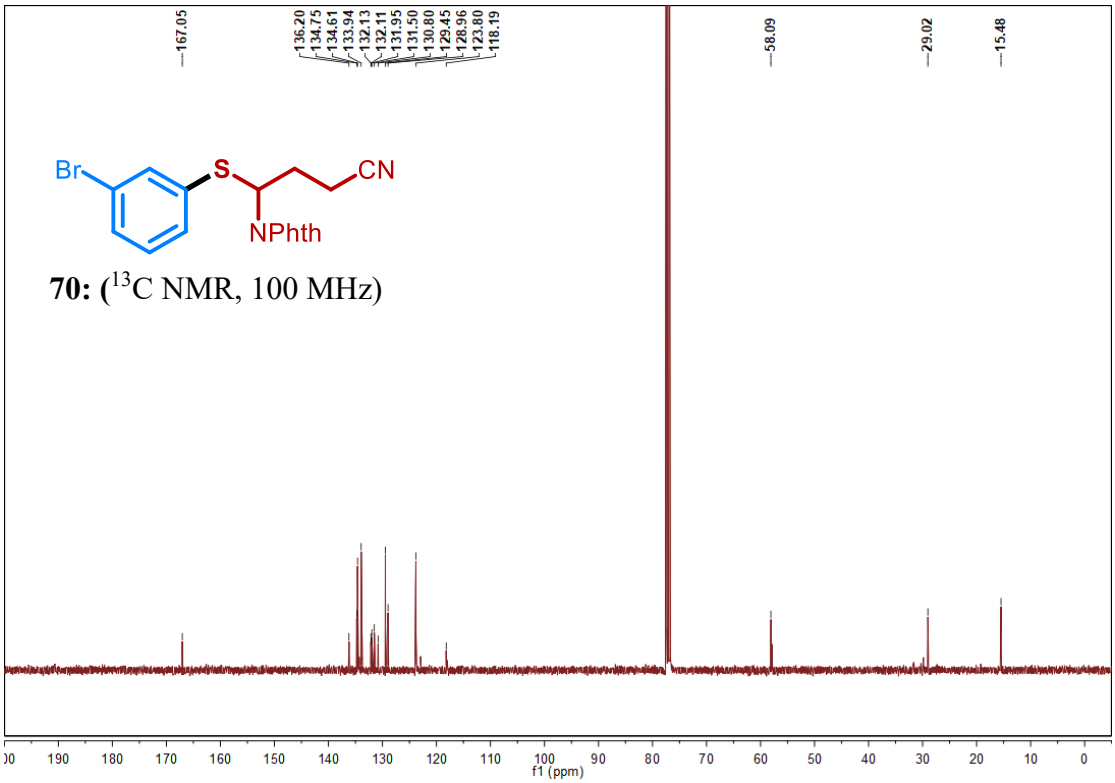
69: (^{1}H NMR, 400 MHz)



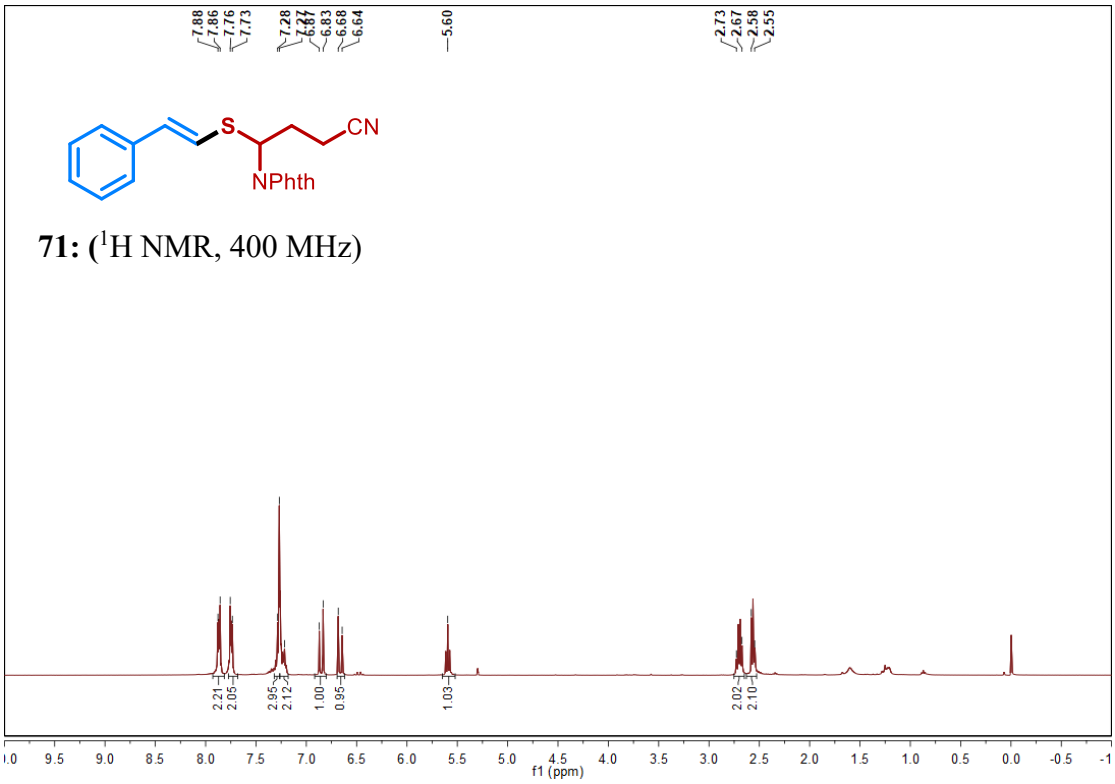
69: (^{13}C NMR, 100 MHz)



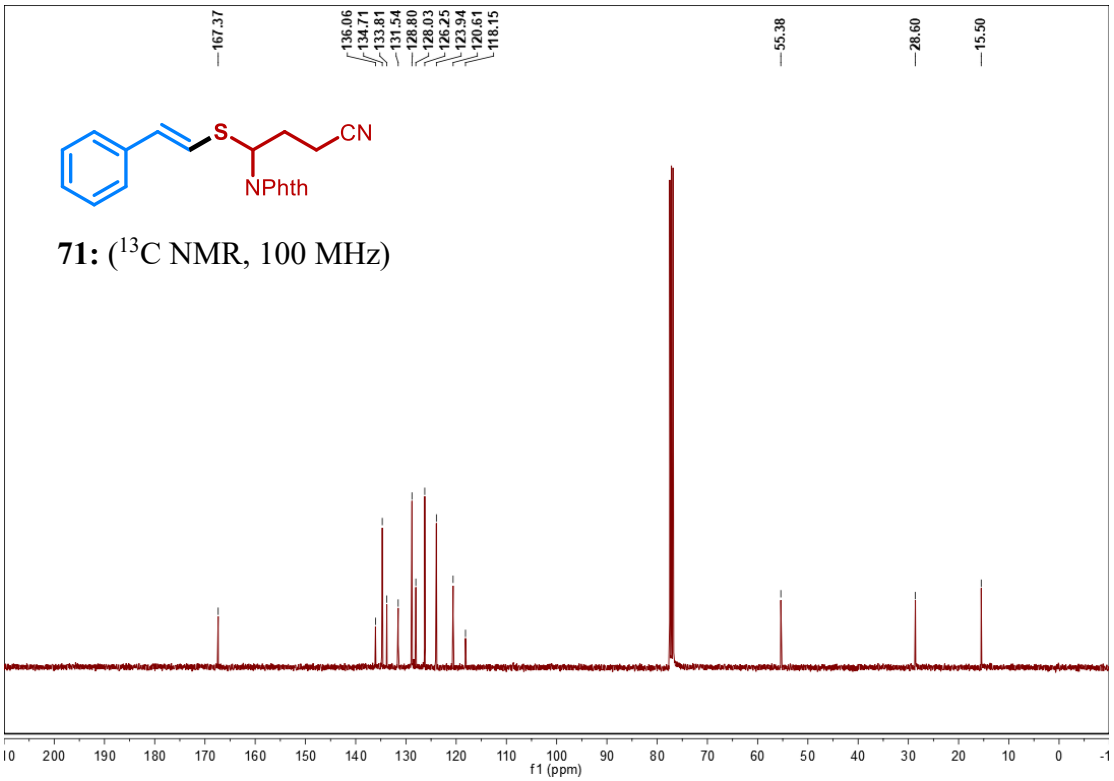
70: (^{1}H NMR, 400 MHz)



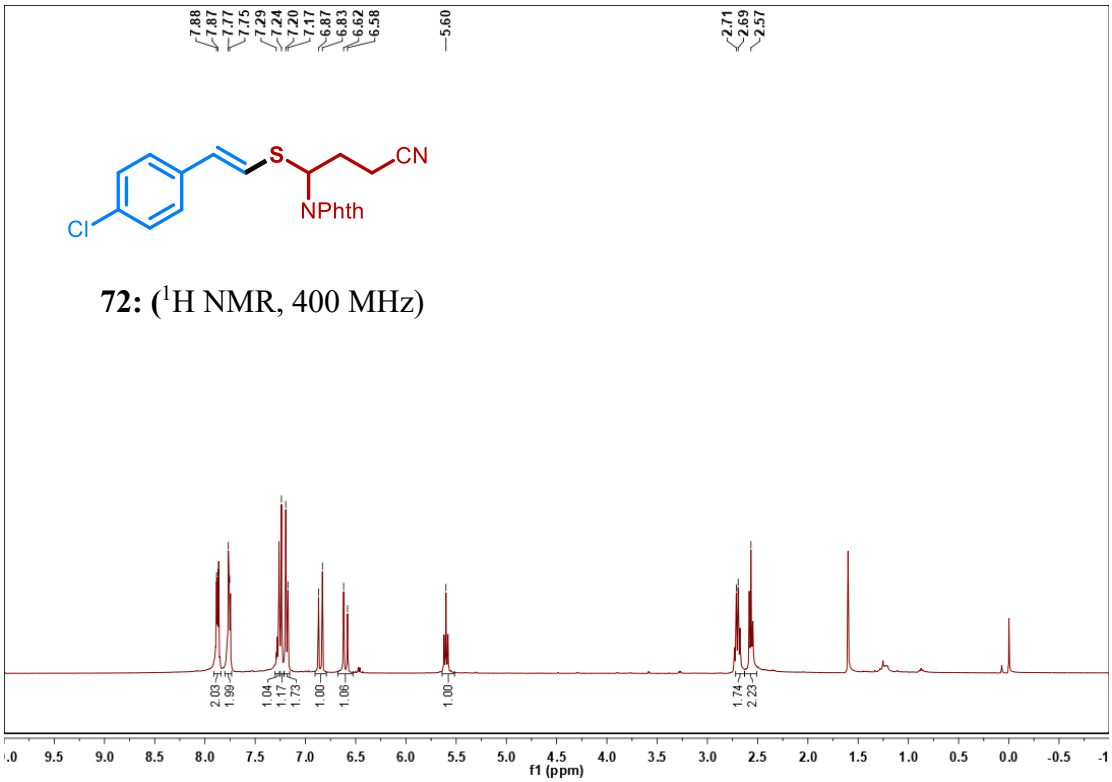
70: (^{13}C NMR, 100 MHz)



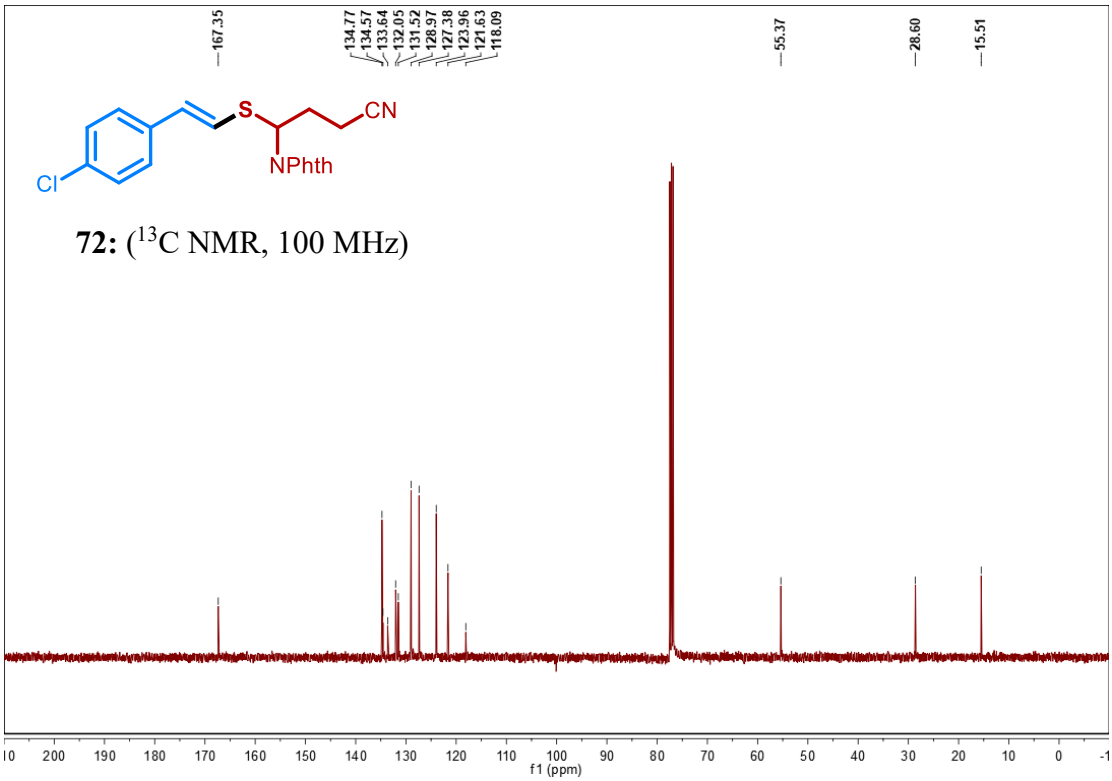
71: (^{1}H NMR, 400 MHz)



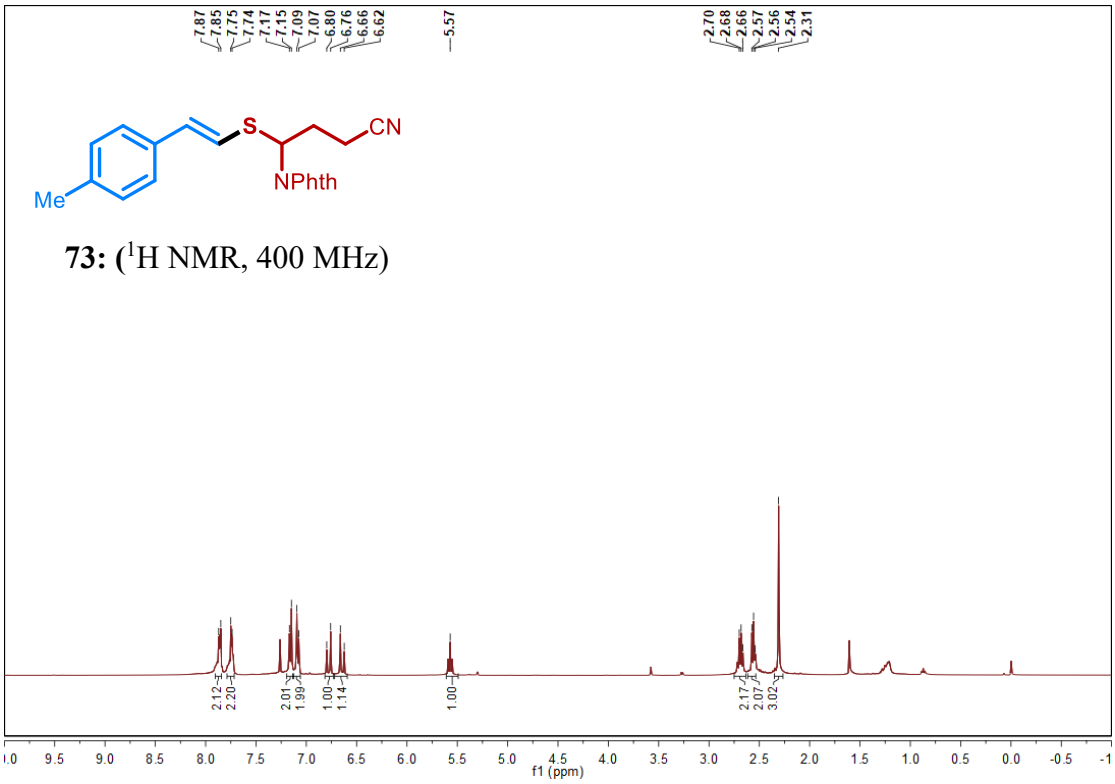
71: (^{13}C NMR, 100 MHz)



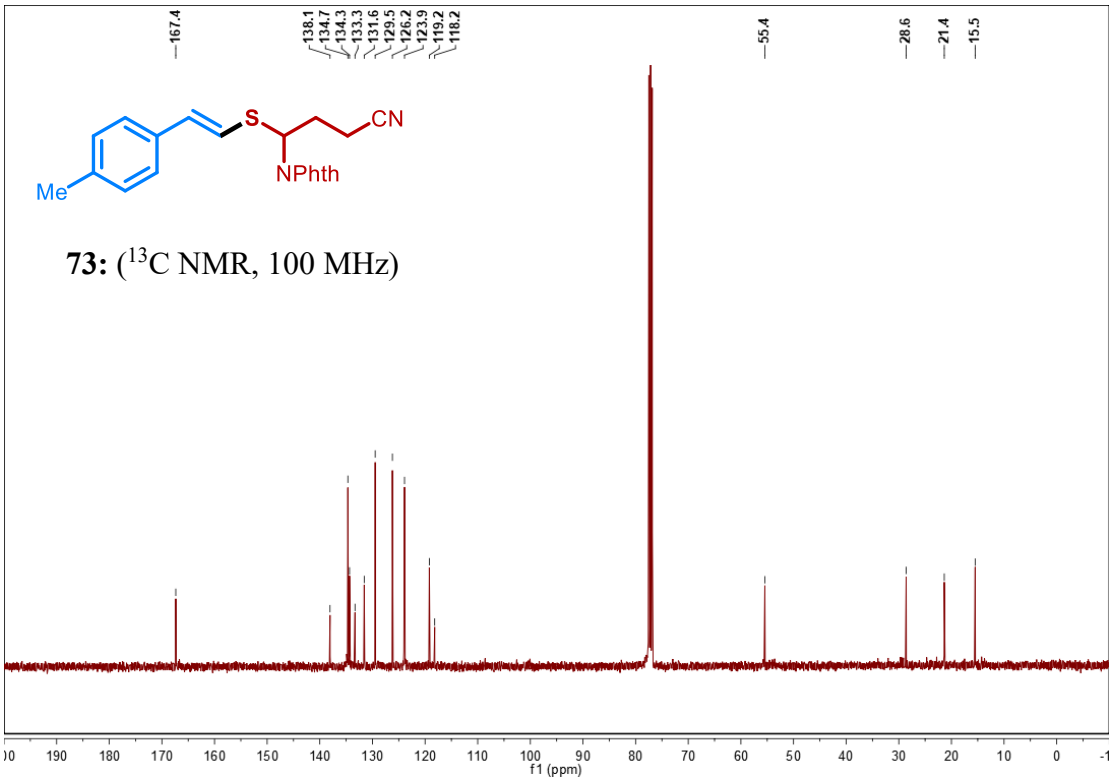
72: (^{1}H NMR, 400 MHz)



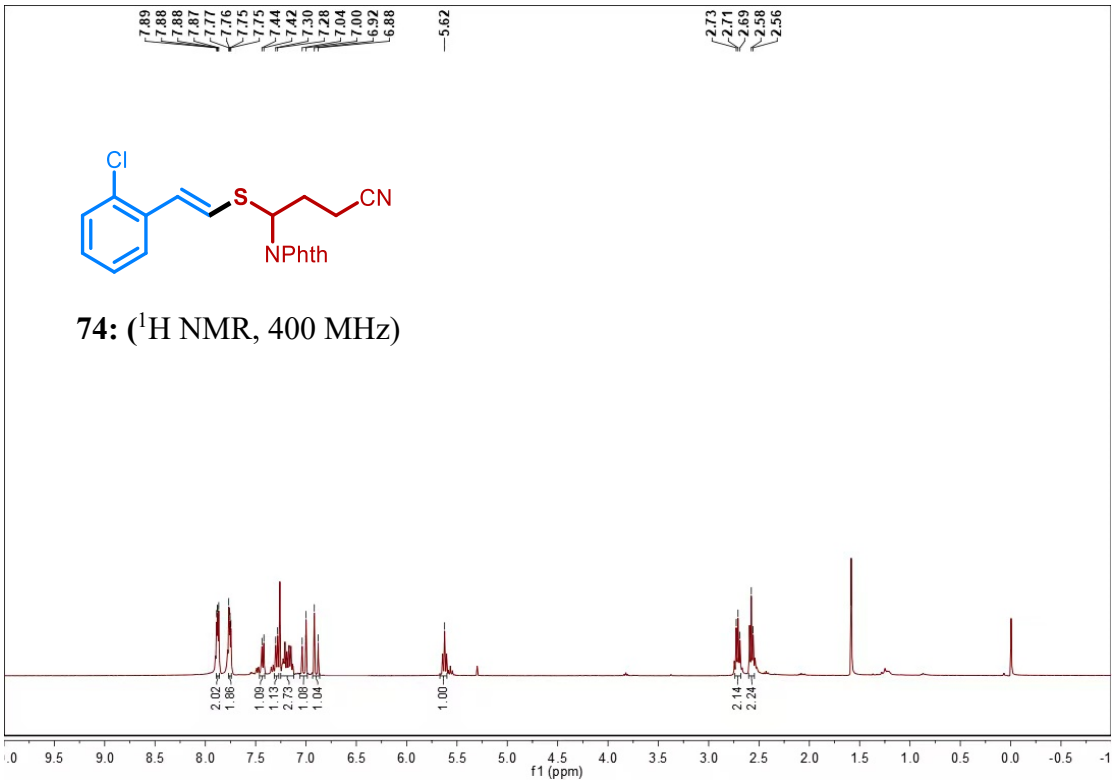
72: (^{13}C NMR, 100 MHz)



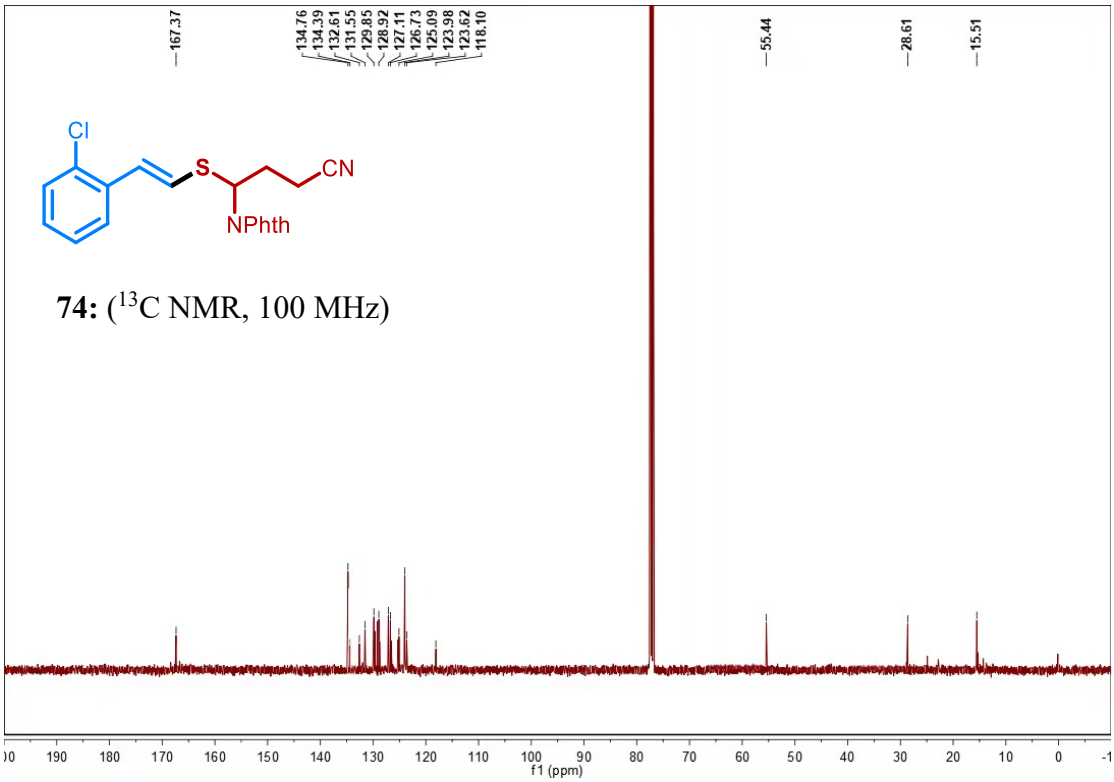
73: (^{1}H NMR, 400 MHz)



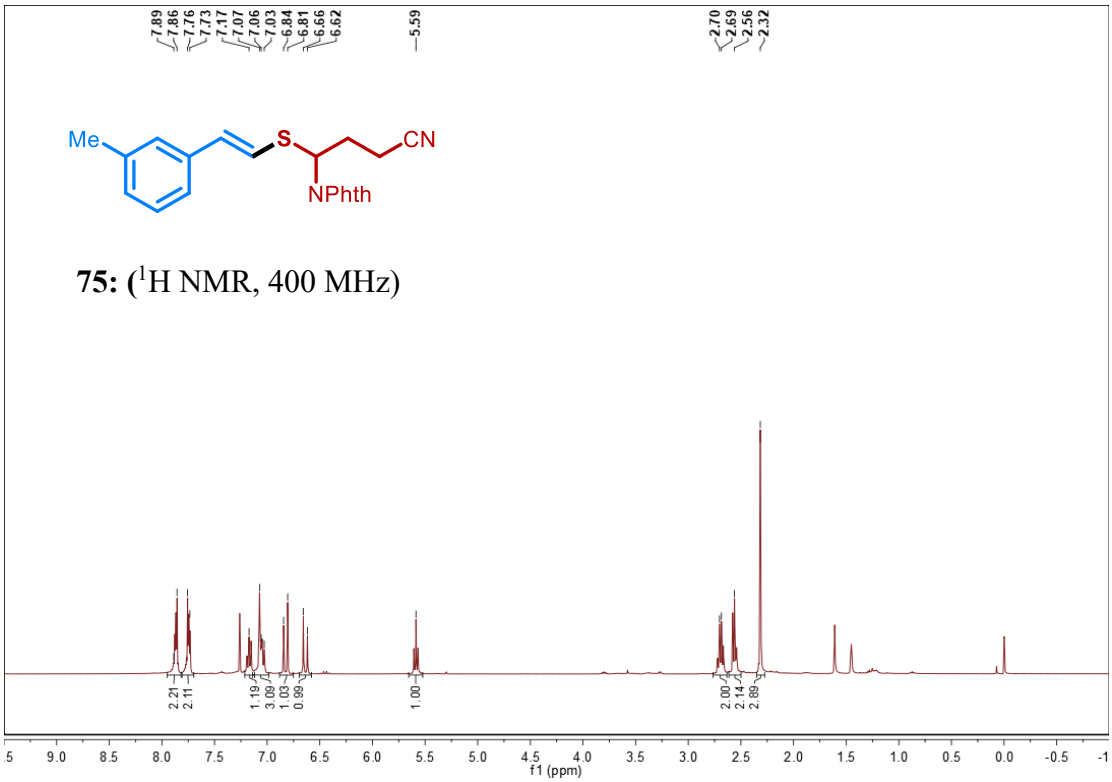
73: (^{13}C NMR, 100 MHz)



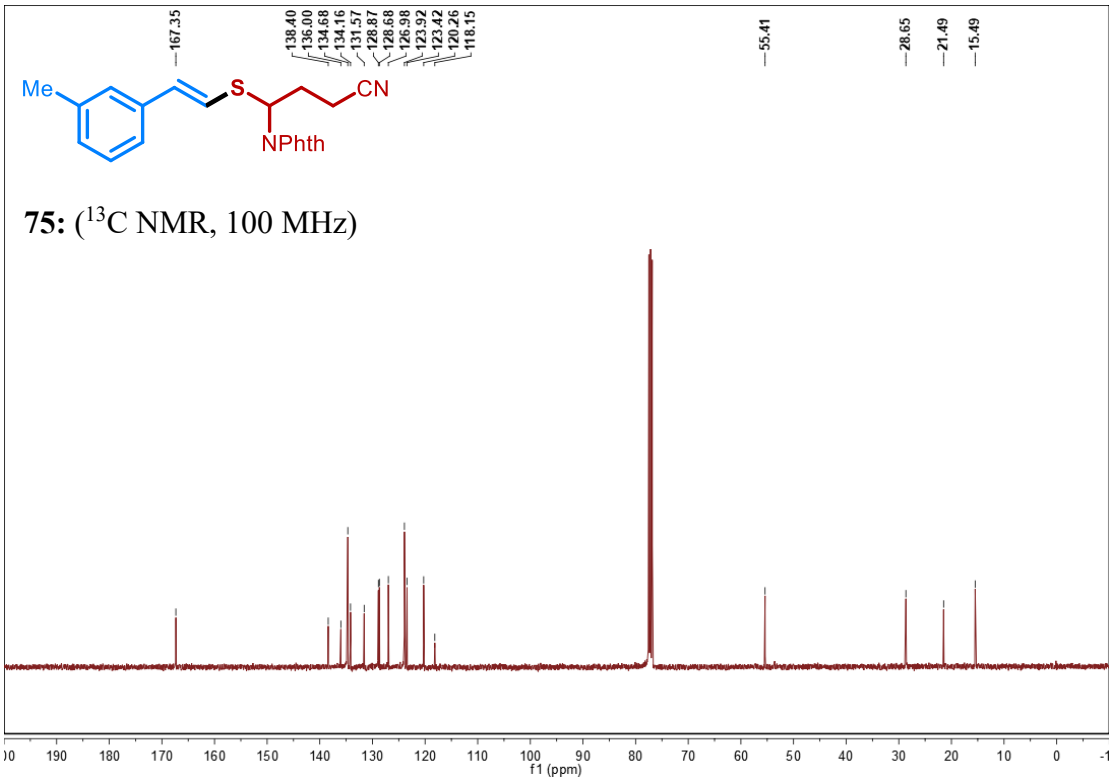
74: (^{1}H NMR, 400 MHz)



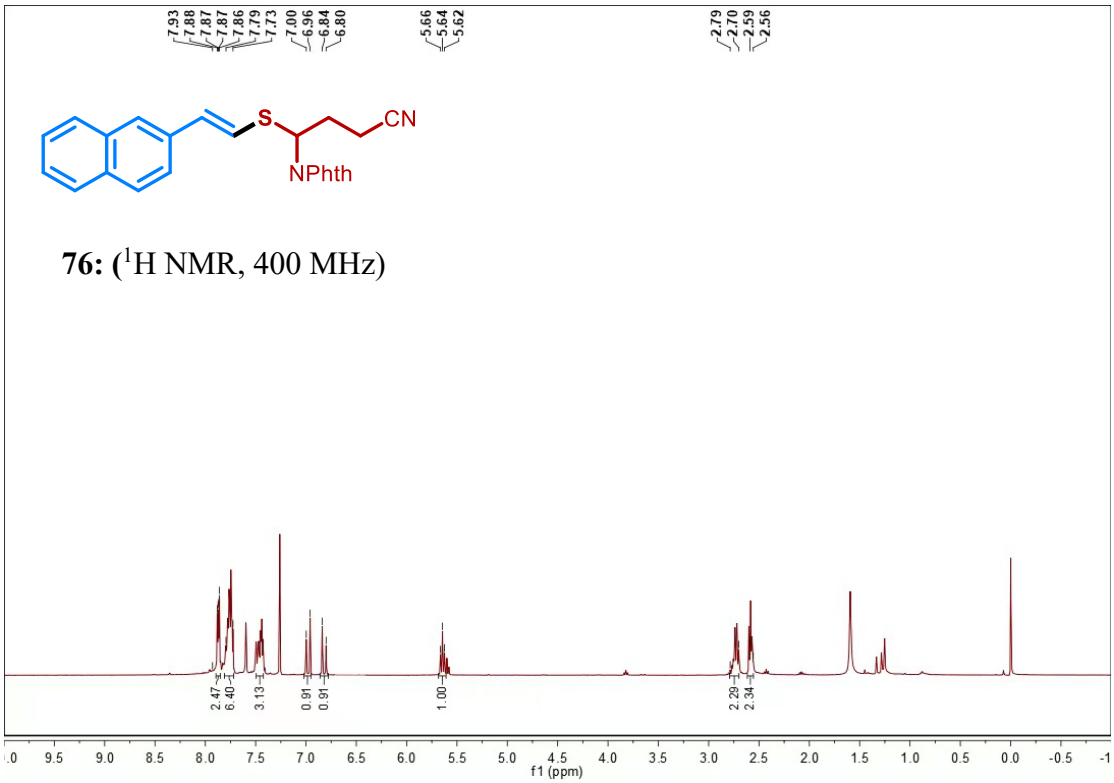
74: (^{13}C NMR, 100 MHz)



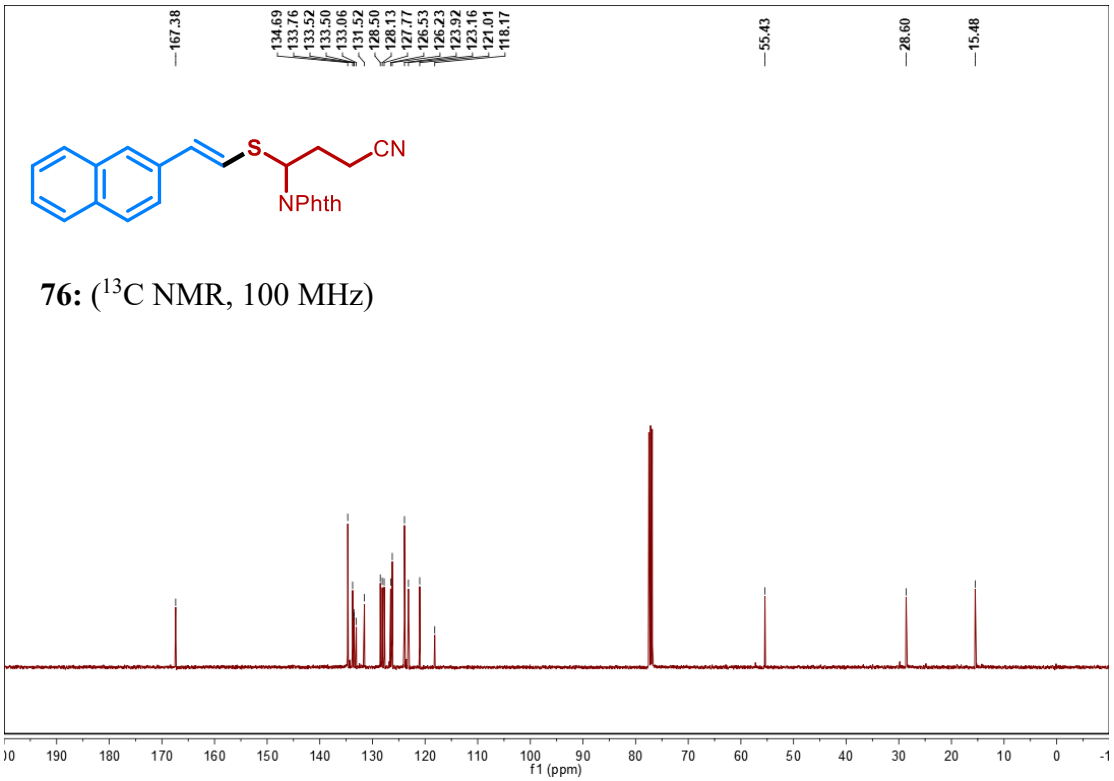
75: (^{1}H NMR, 400 MHz)



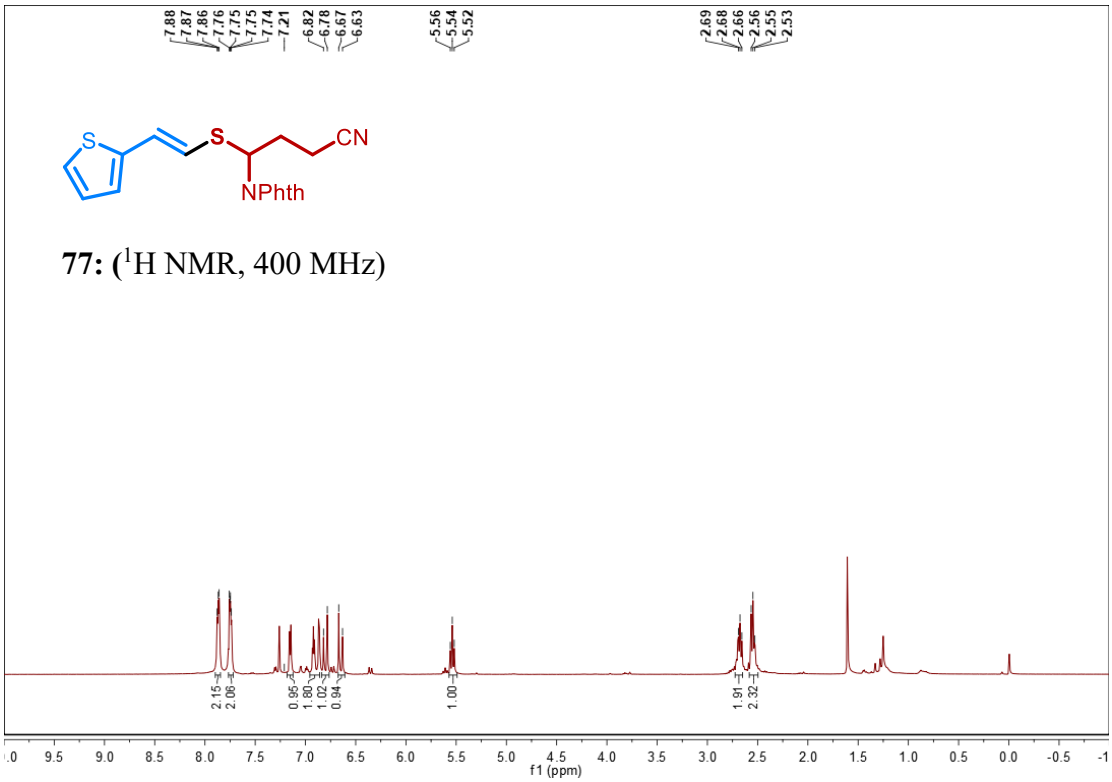
75: (^{13}C NMR, 100 MHz)



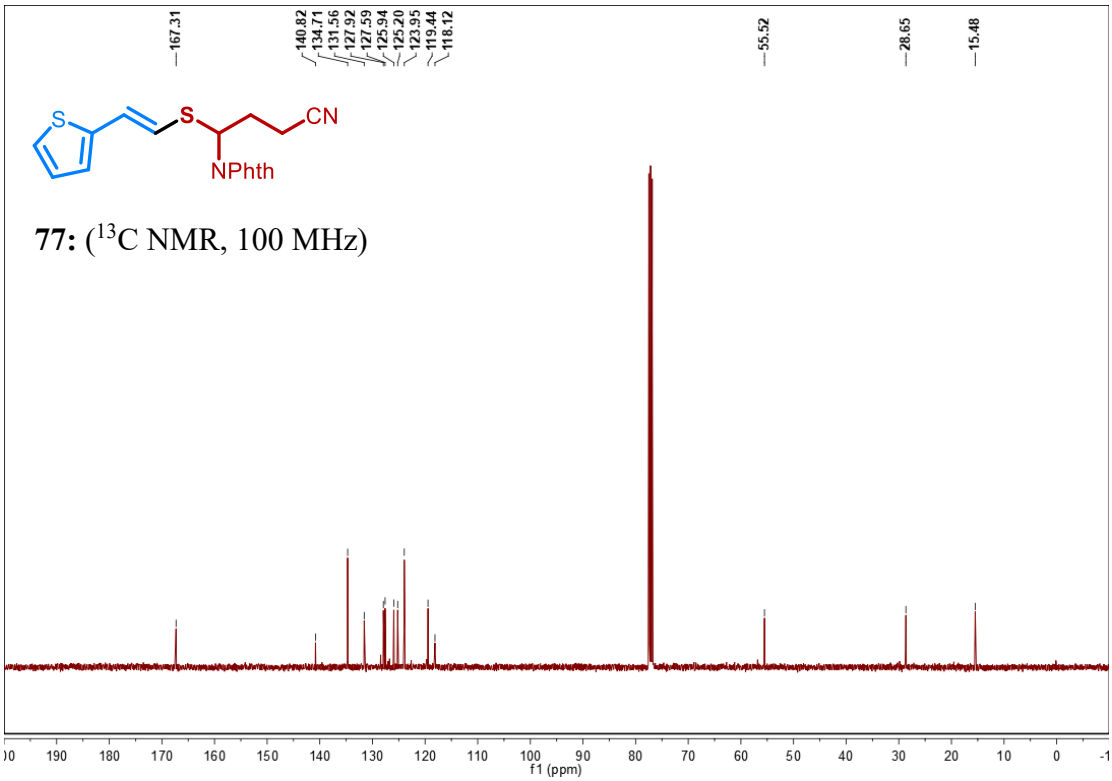
76: (^{1}H NMR, 400 MHz)



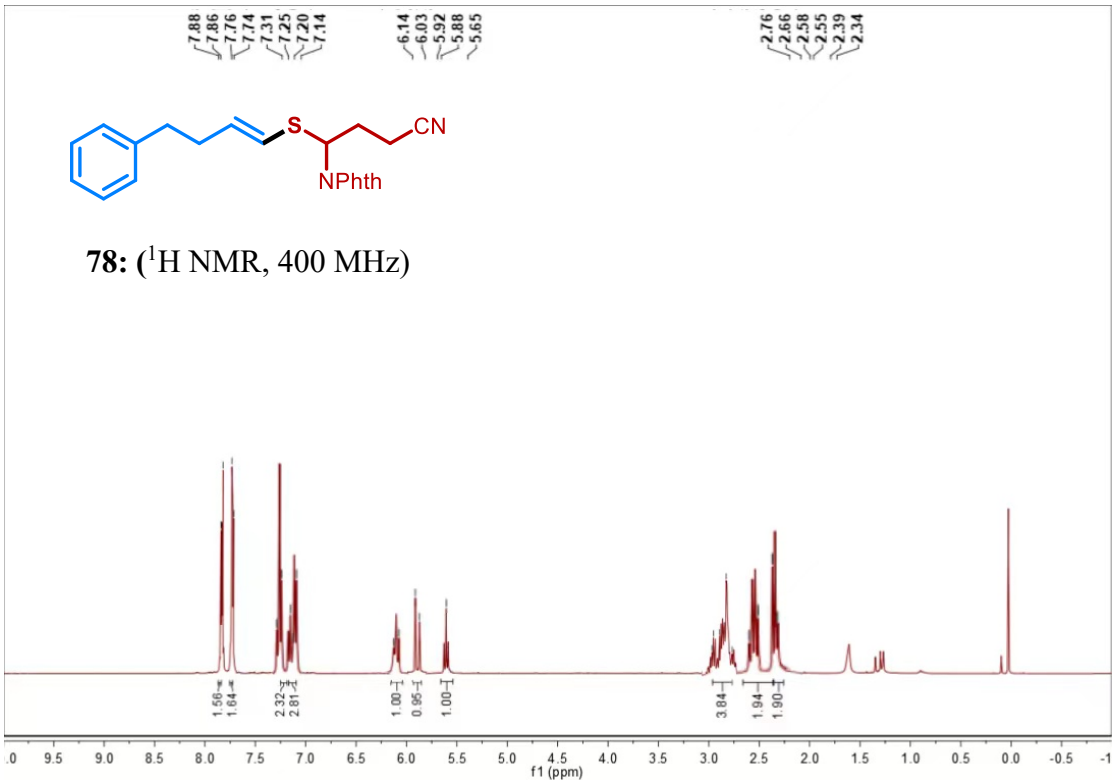
76: (^{13}C NMR, 100 MHz)



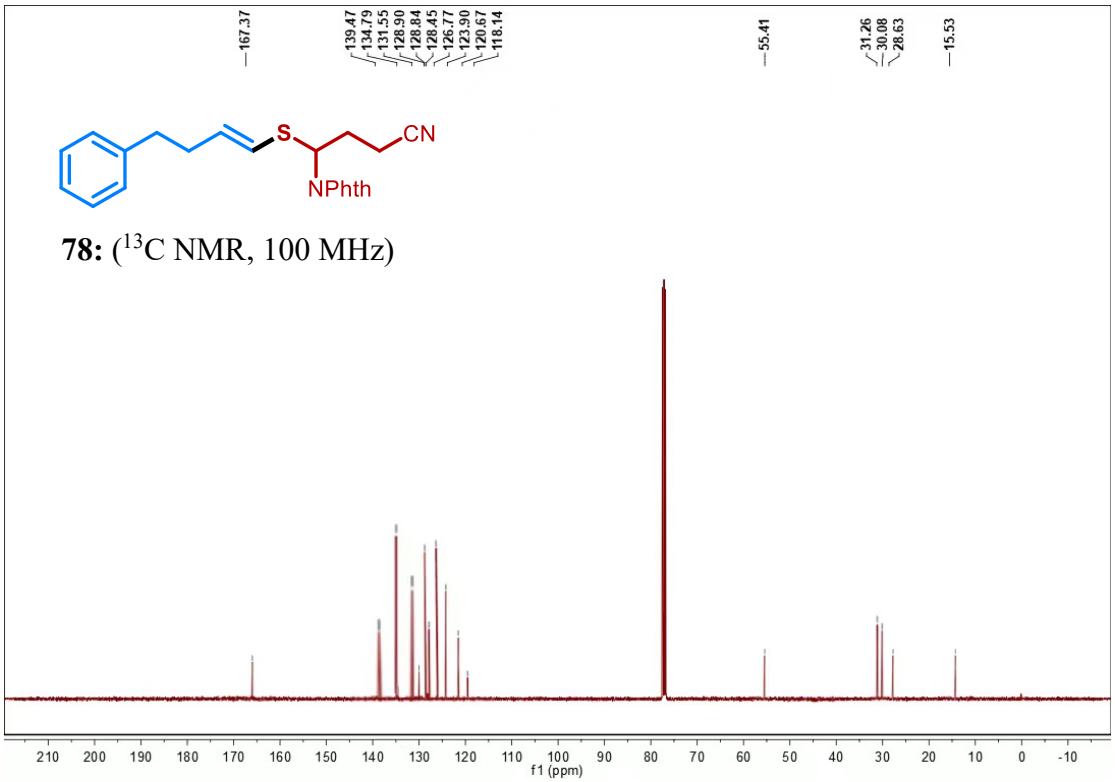
77: (^{1}H NMR, 400 MHz)



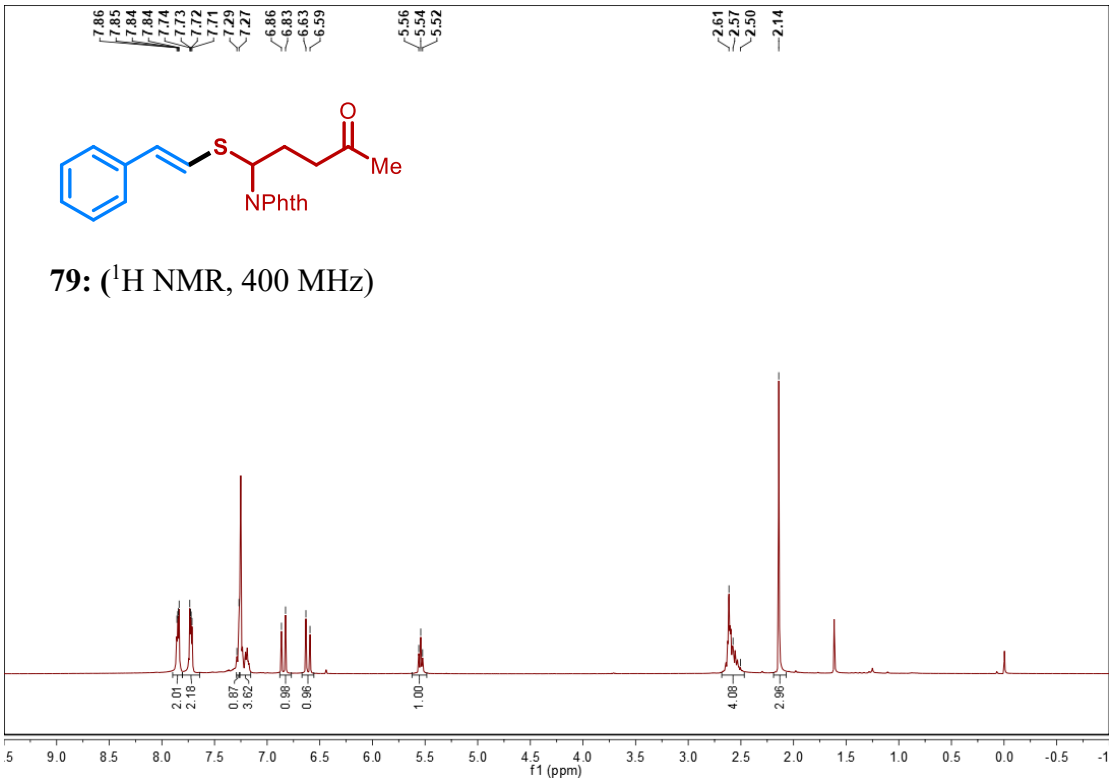
77: (^{13}C NMR, 100 MHz)



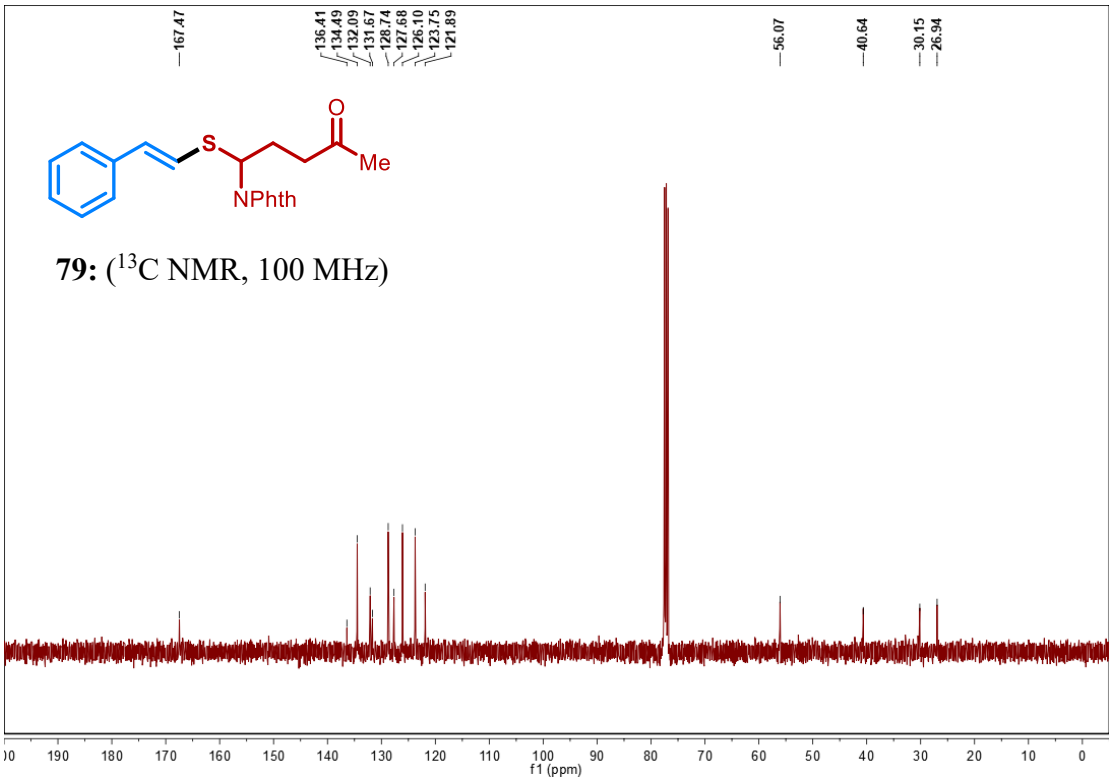
78: (^{1}H NMR, 400 MHz)



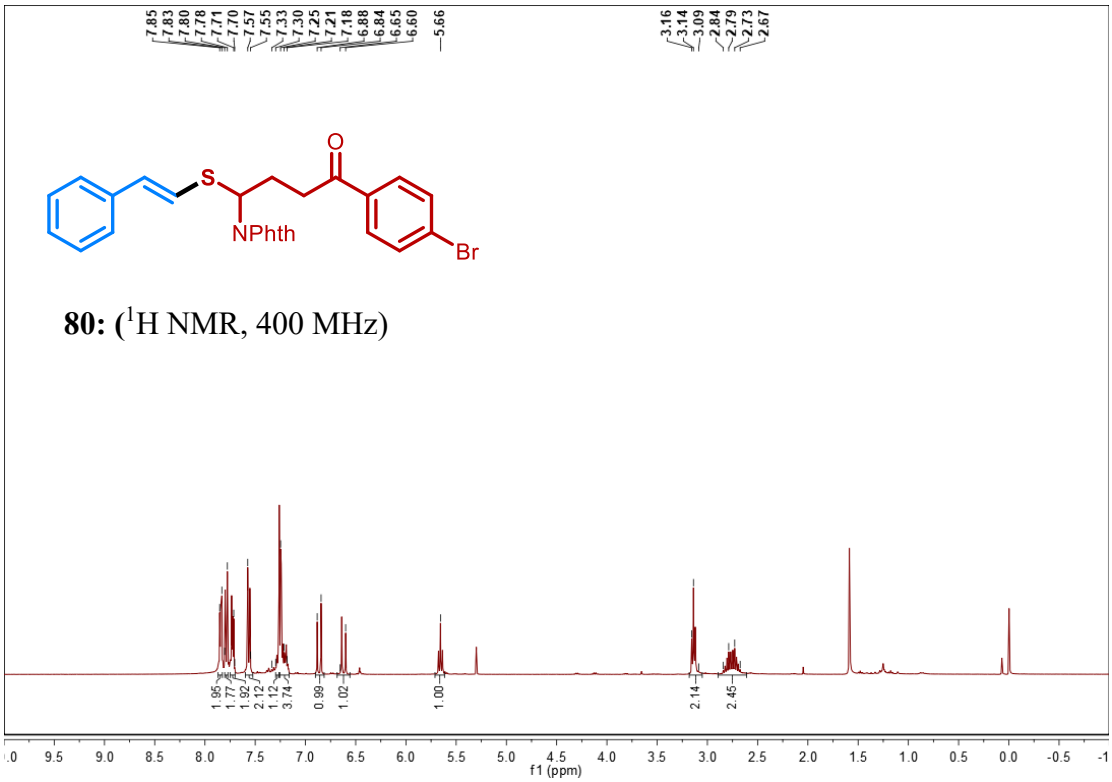
78: (^{13}C NMR, 100 MHz)



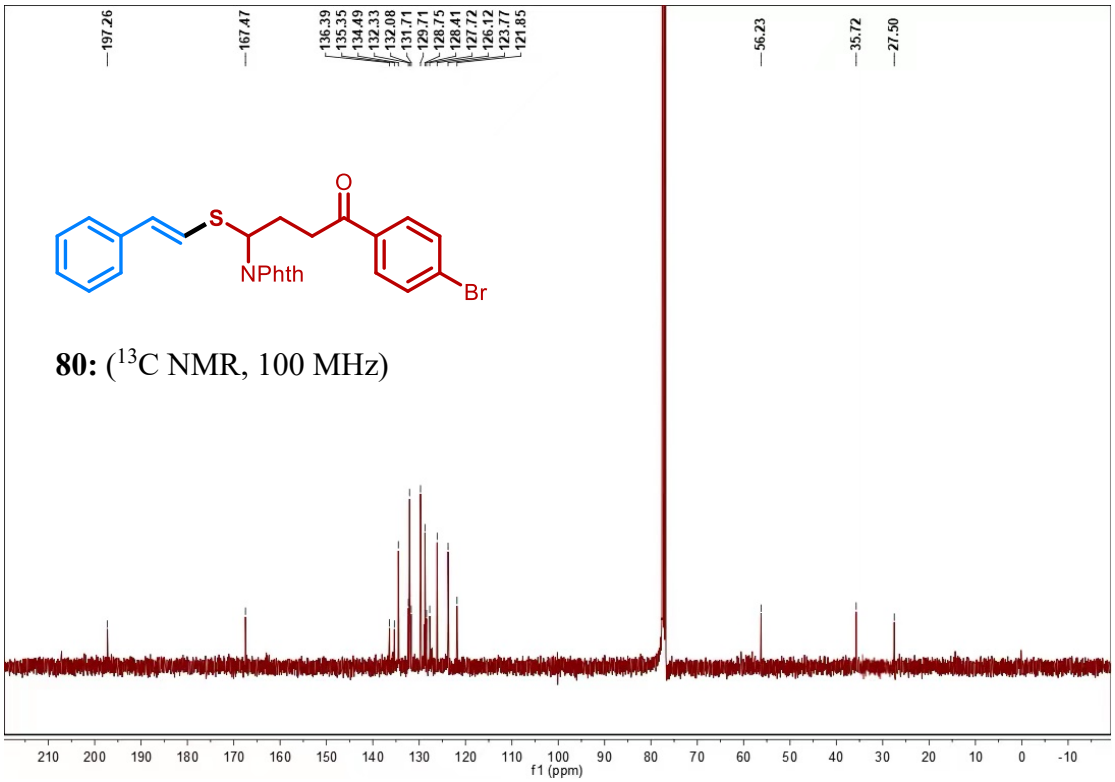
79: (^{1}H NMR, 400 MHz)



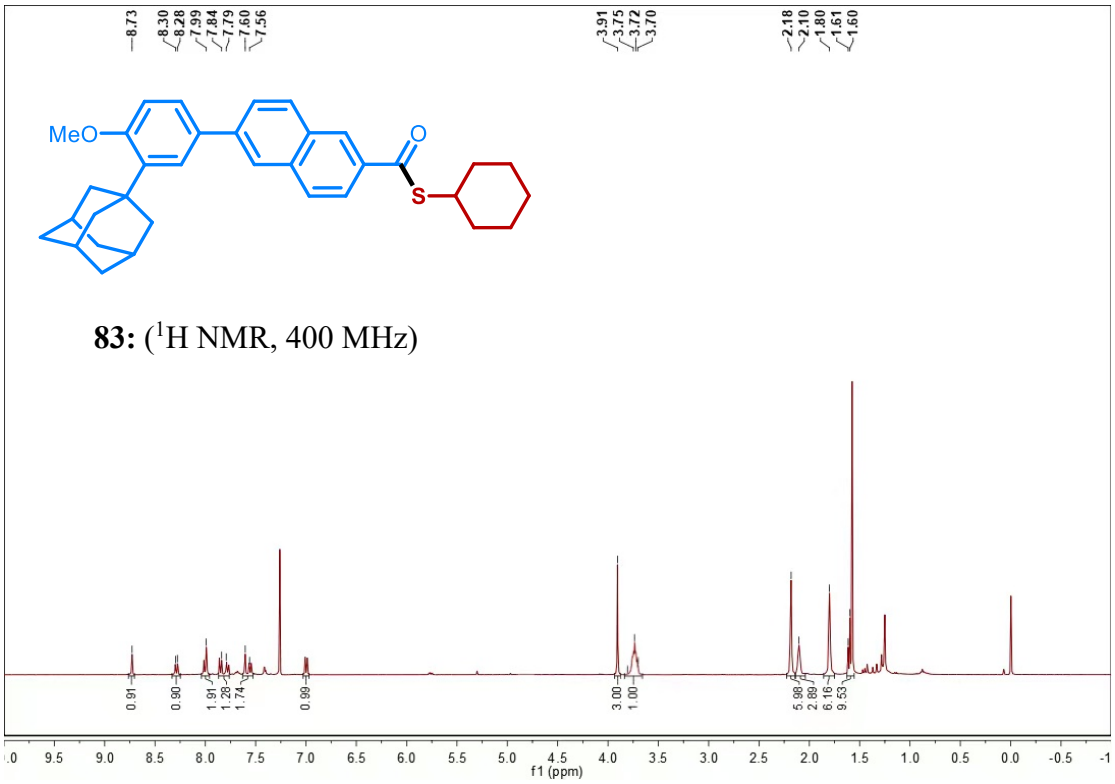
79: (^{13}C NMR, 100 MHz)



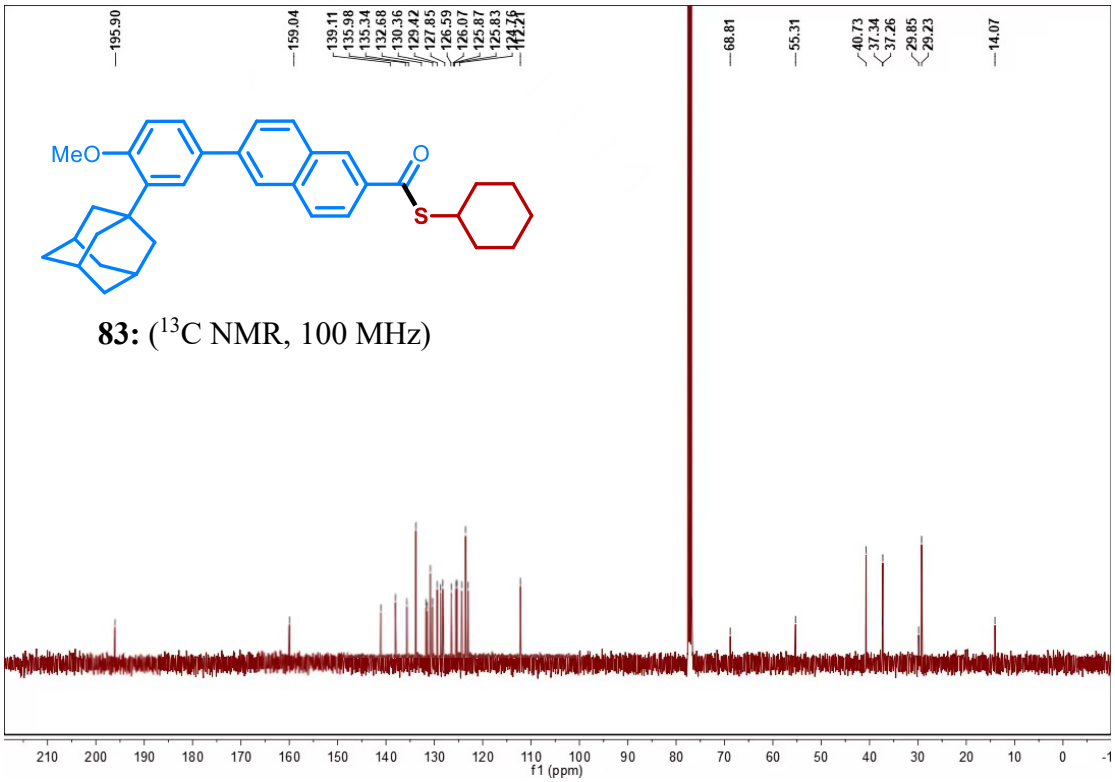
80: (^{1}H NMR, 400 MHz)



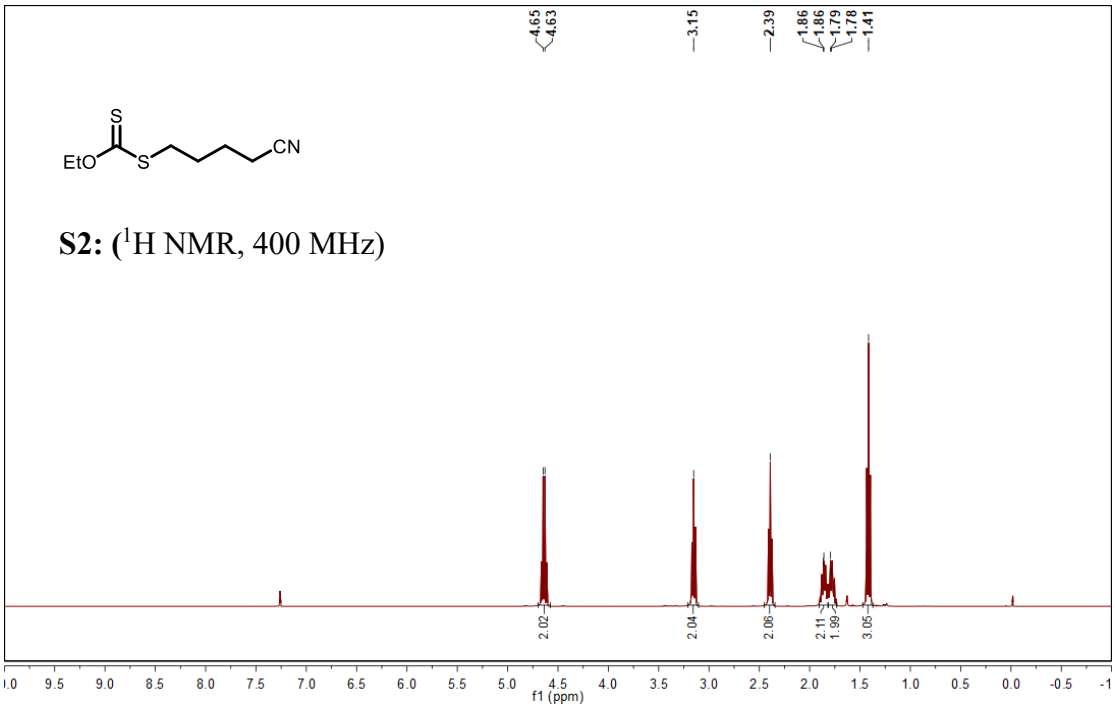
80: (^{13}C NMR, 100 MHz)



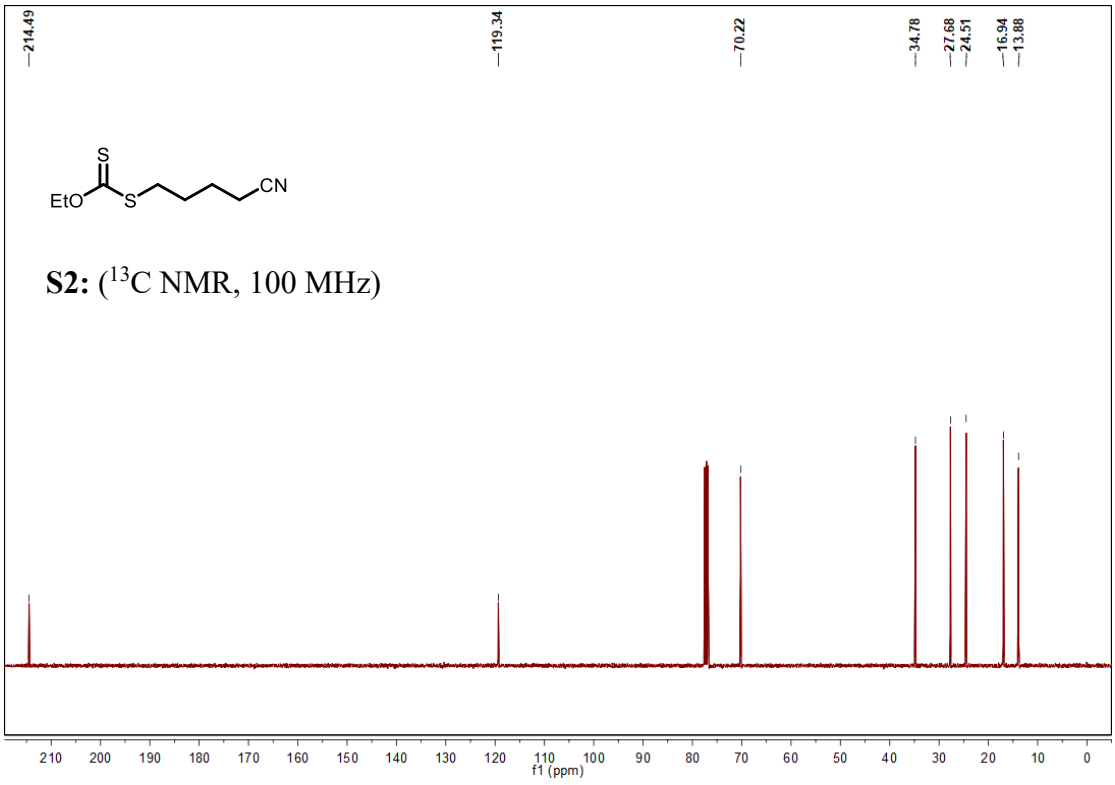
83: (^{1}H NMR, 400 MHz)



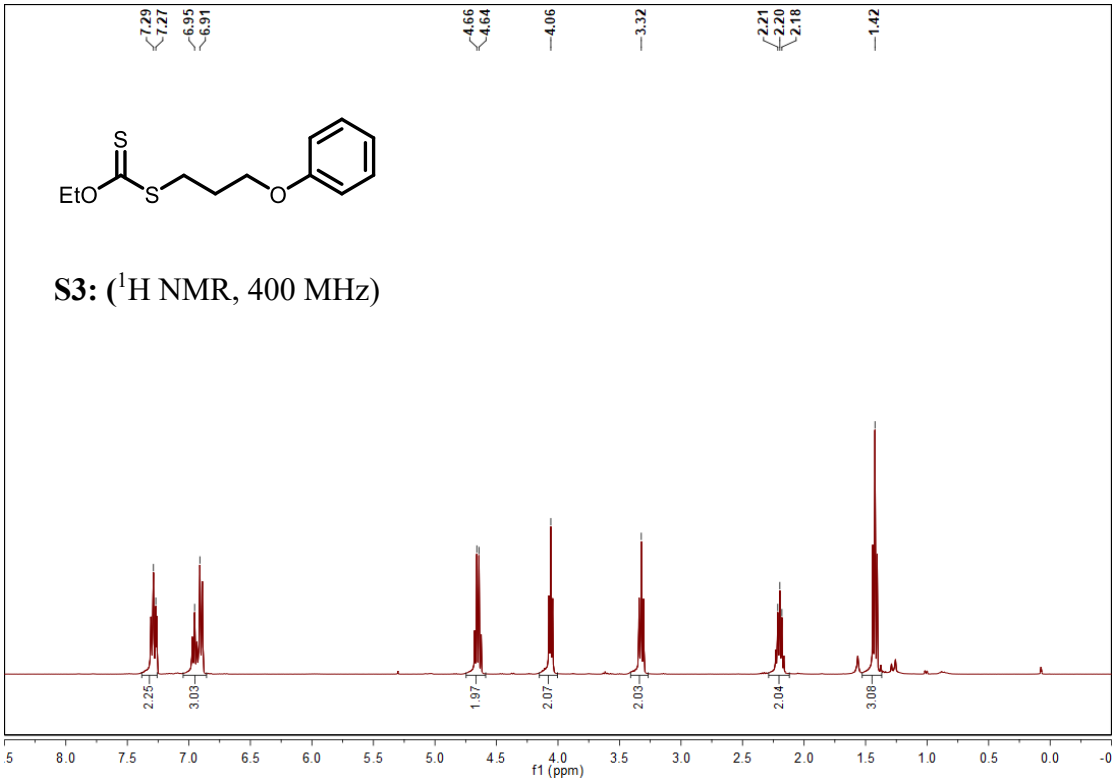
83: (^{13}C NMR, 100 MHz)



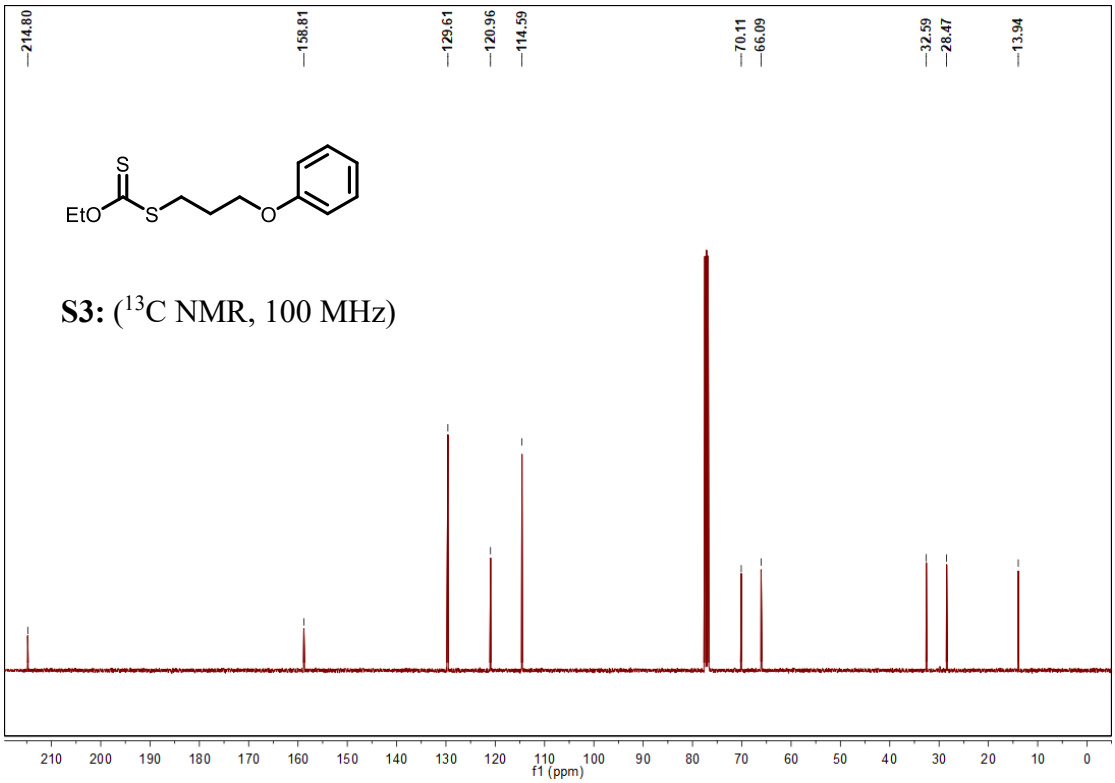
S2: (^{1}H NMR, 400 MHz)



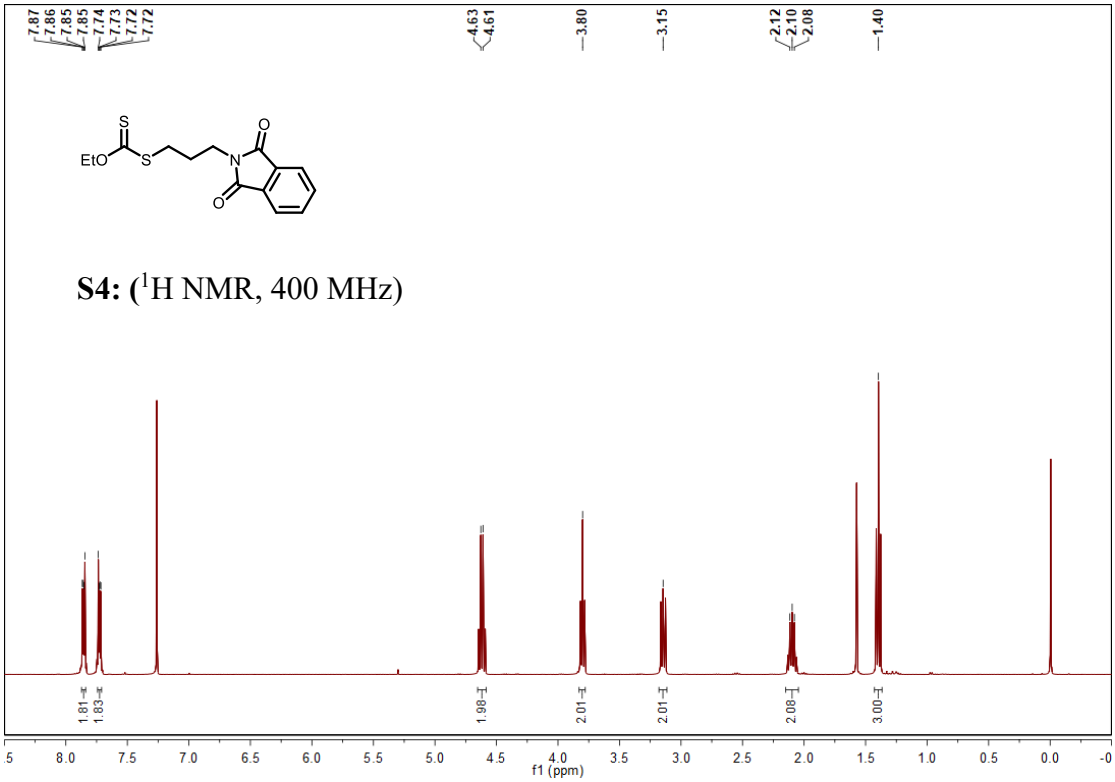
S2: (^{13}C NMR, 100 MHz)



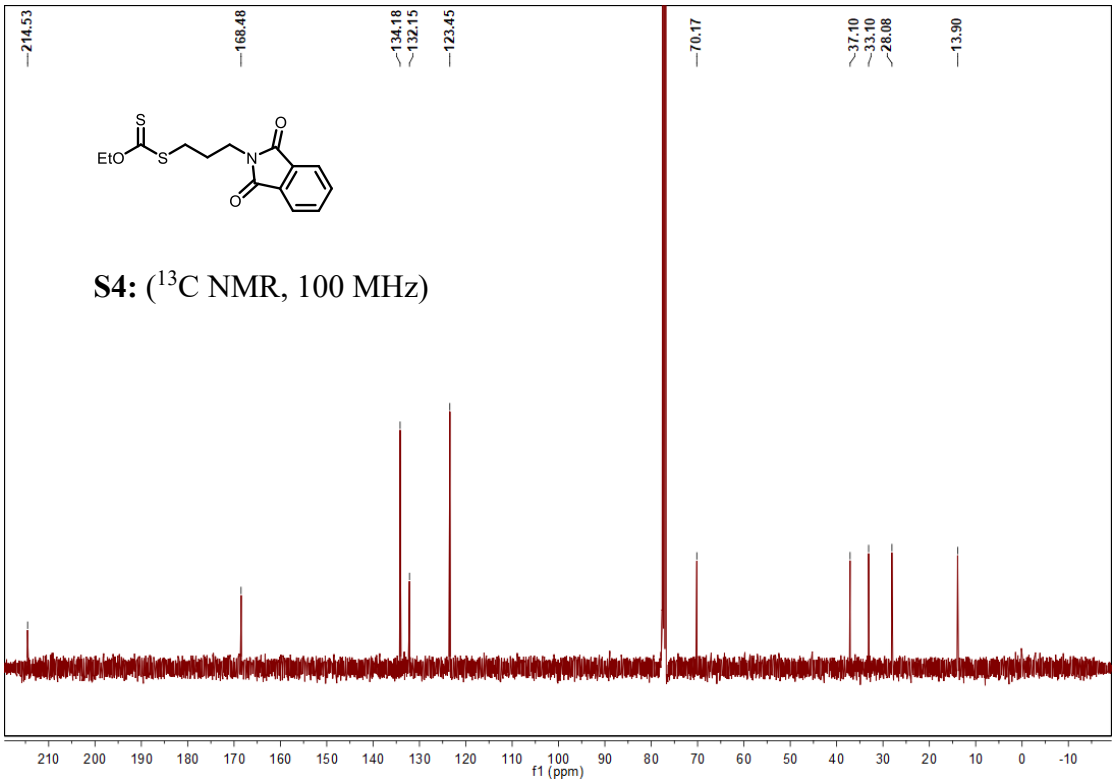
S3: (^{1}H NMR, 400 MHz)



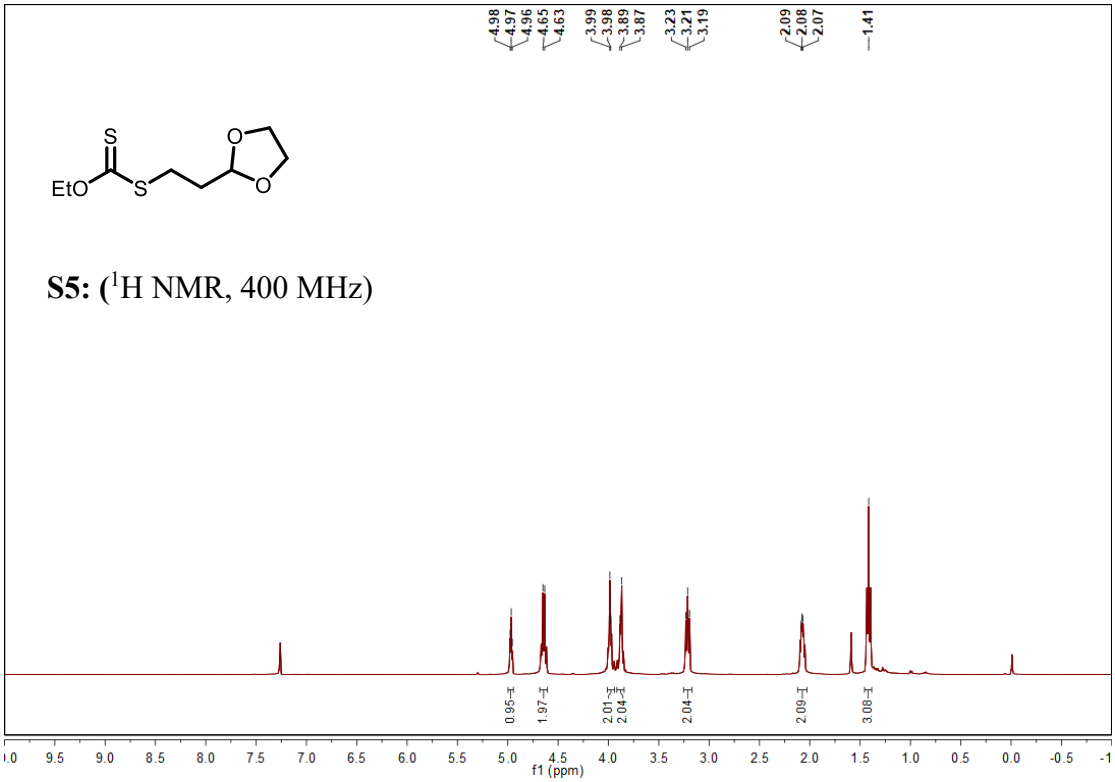
S3: (^{13}C NMR, 100 MHz)



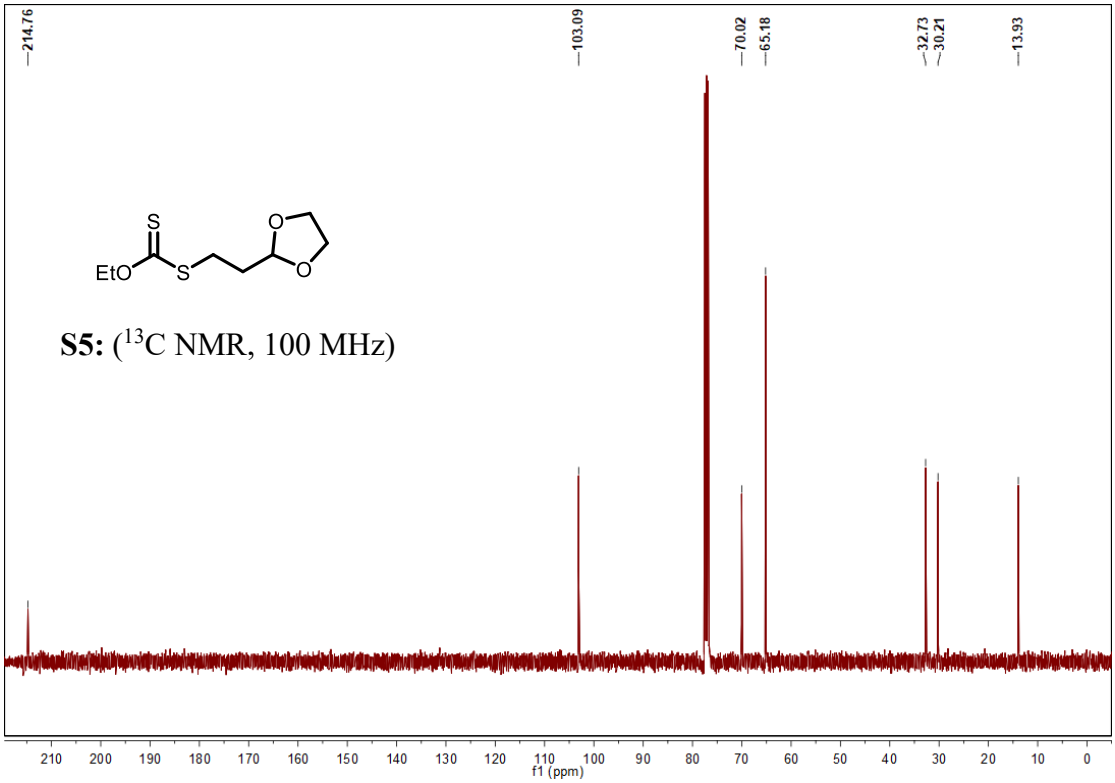
S4: (^{1}H NMR, 400 MHz)



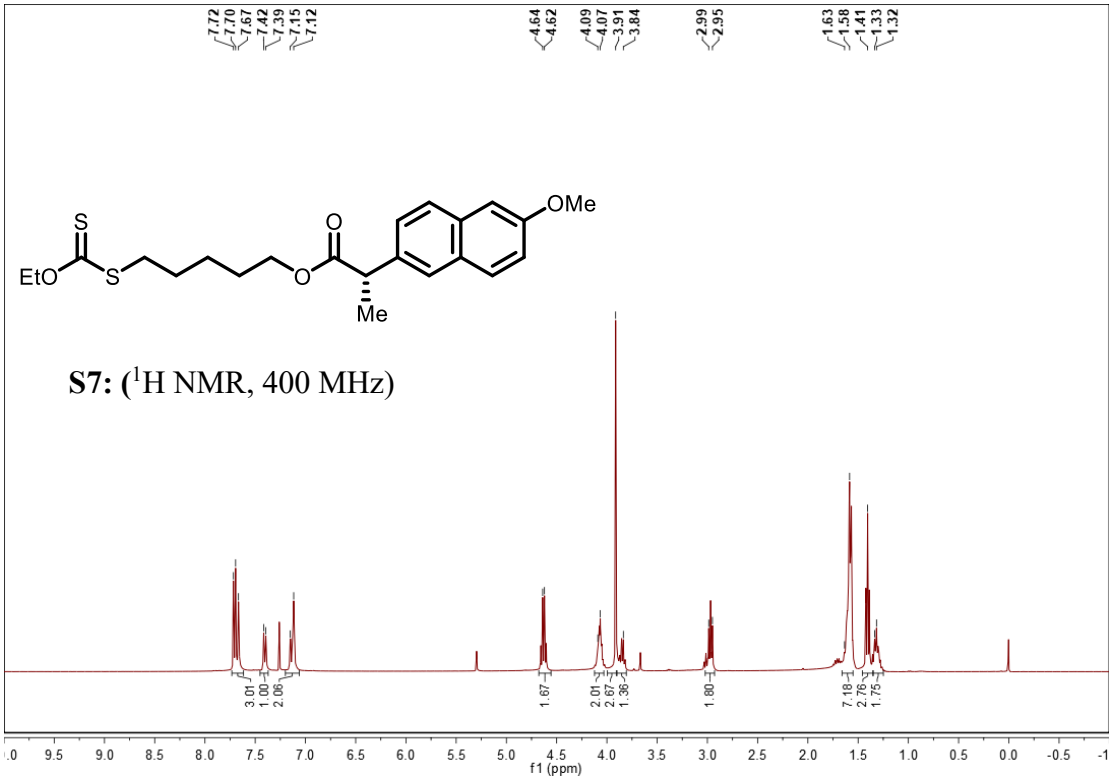
S4: (^{13}C NMR, 100 MHz)



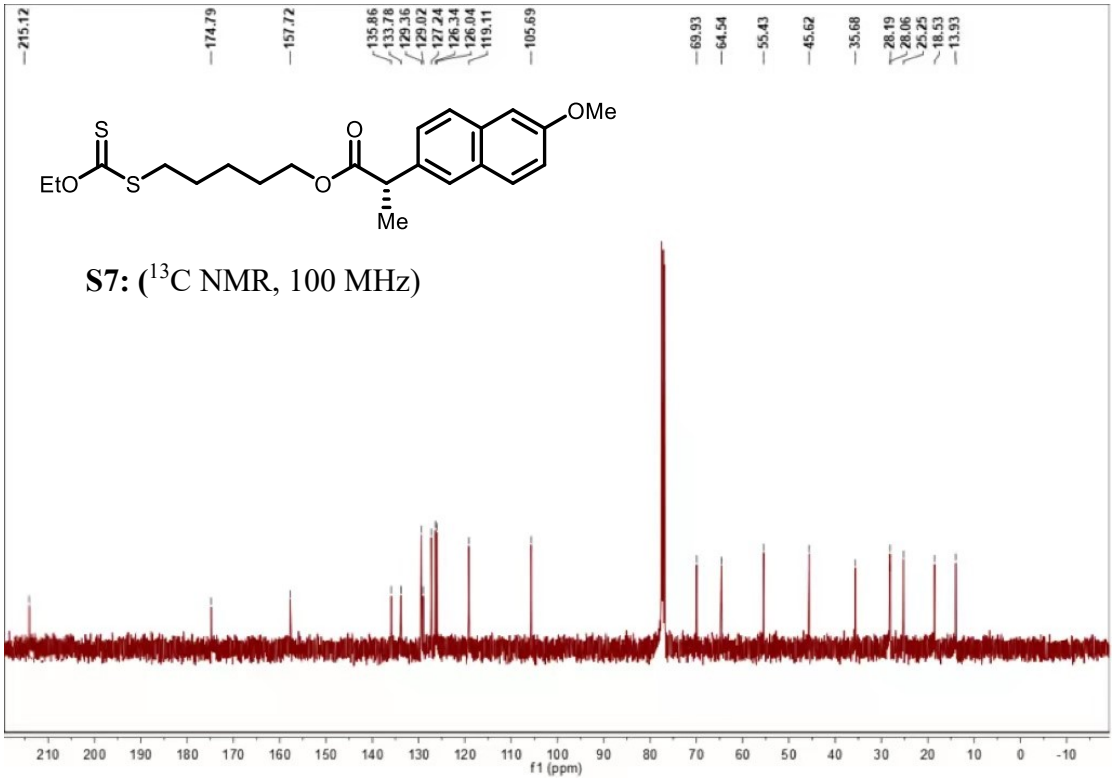
S5: (^{1}H NMR, 400 MHz)



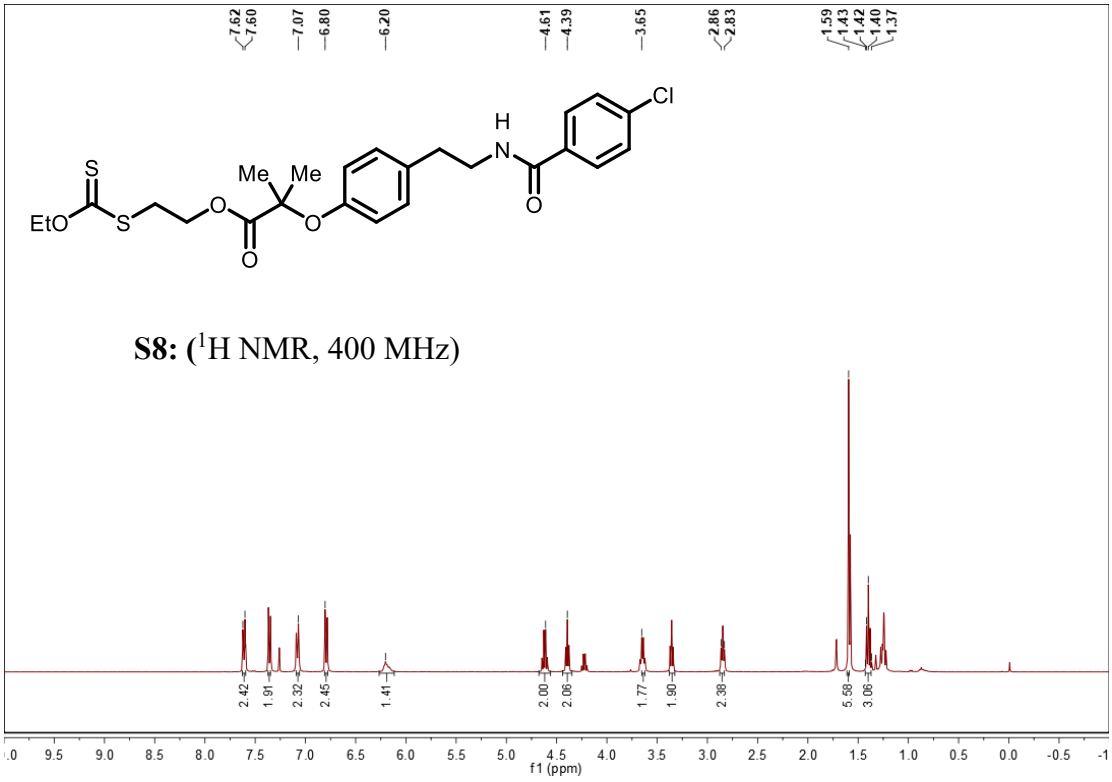
S5: (^{13}C NMR, 100 MHz)



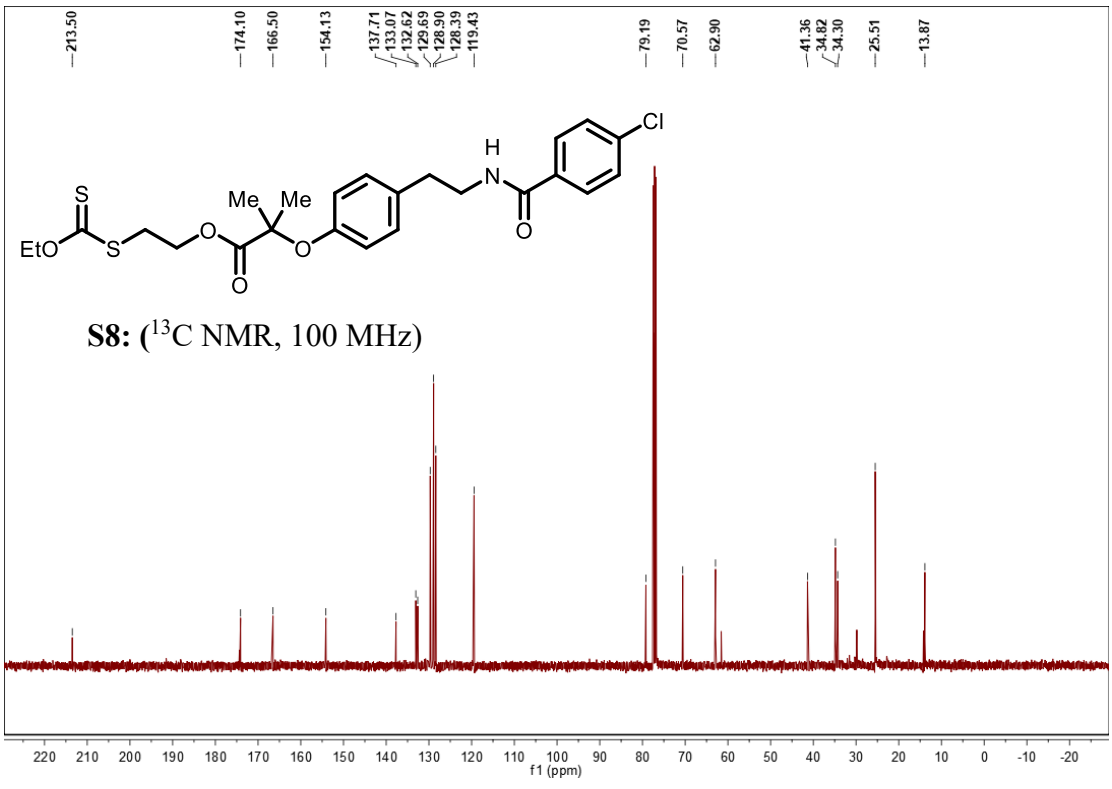
S7: (^{1}H NMR, 400 MHz)



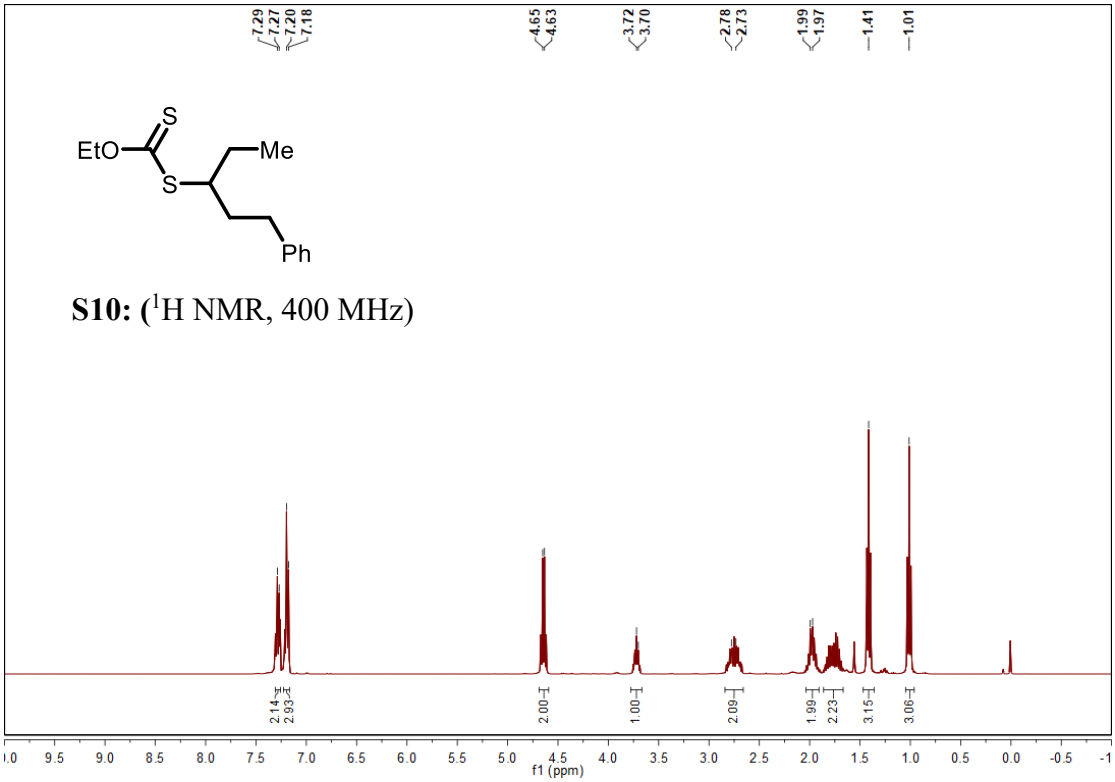
S7: (^{13}C NMR, 100 MHz)



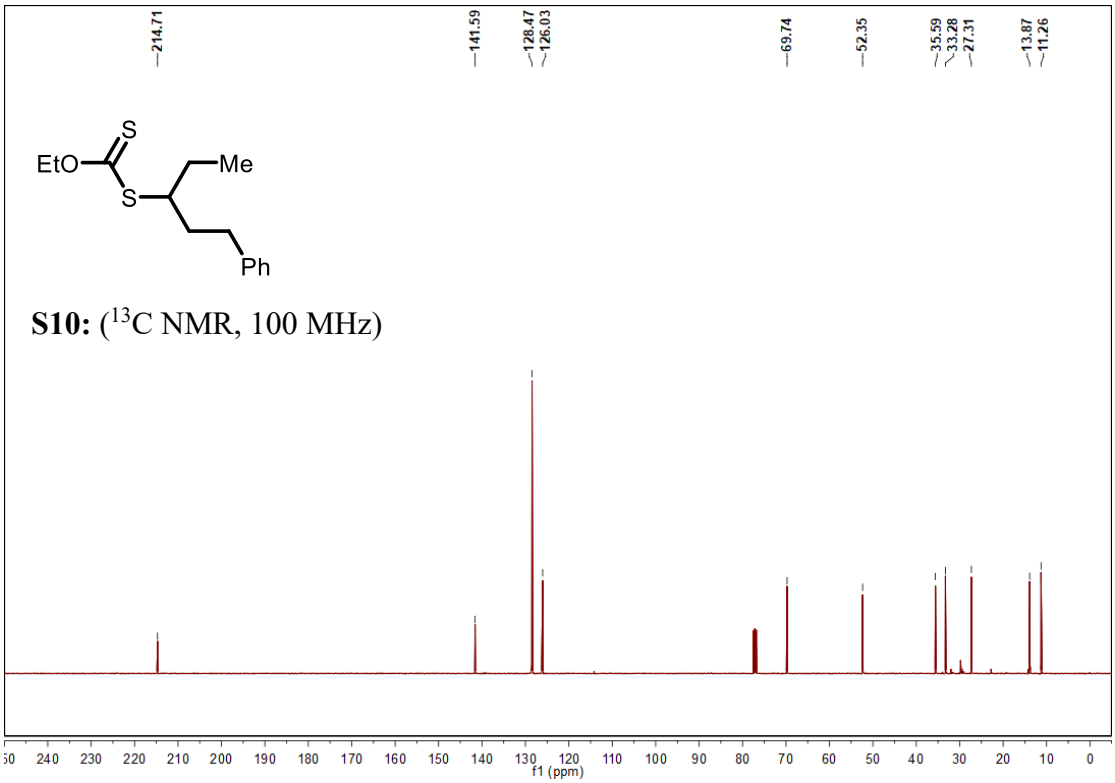
S8: (^{1}H NMR, 400 MHz)



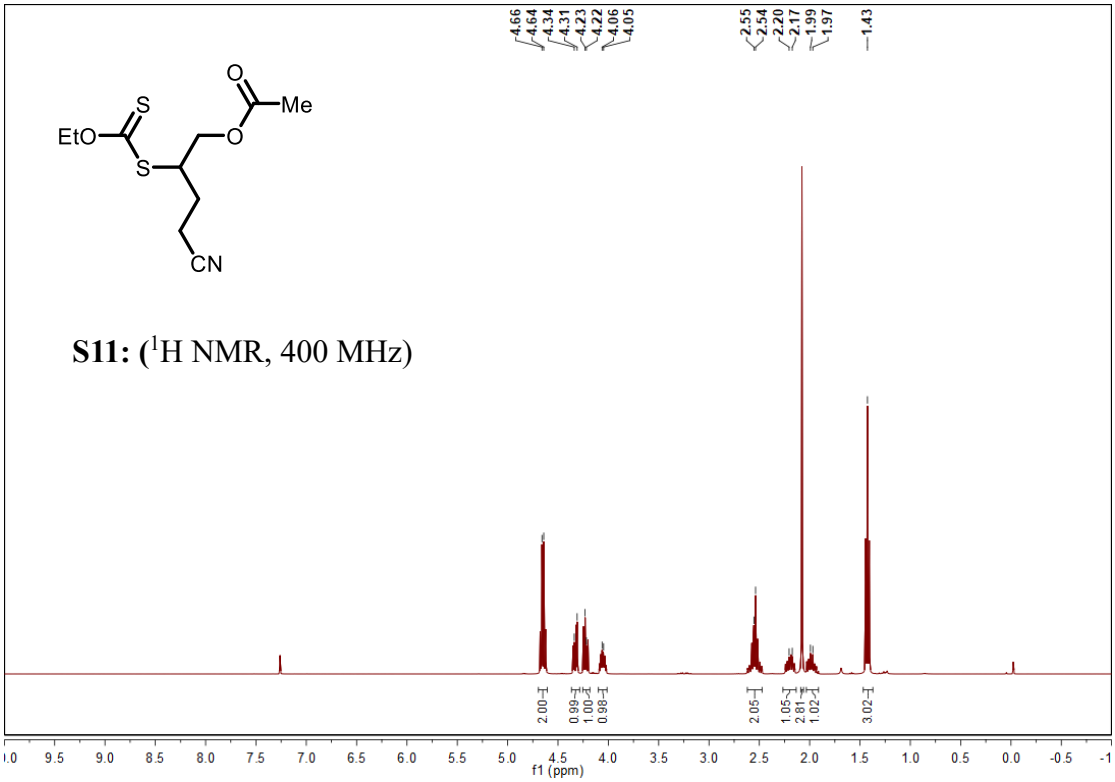
S8: (^{13}C NMR, 100 MHz)



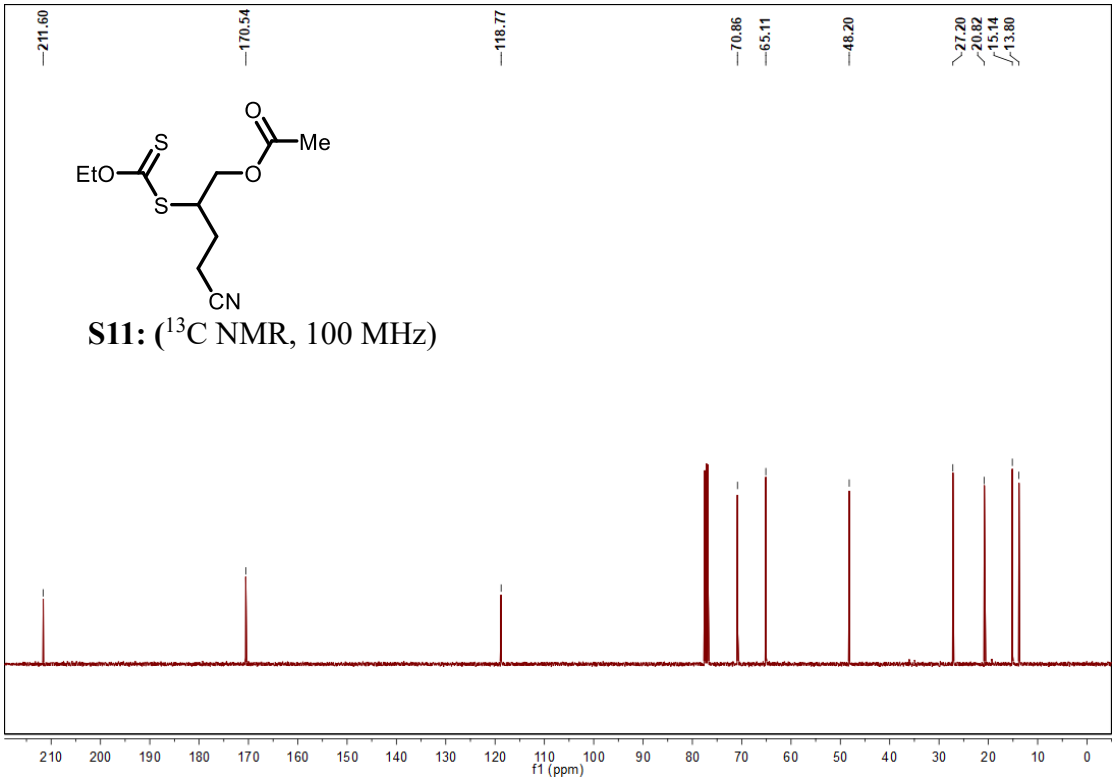
S10: (^{1}H NMR, 400 MHz)



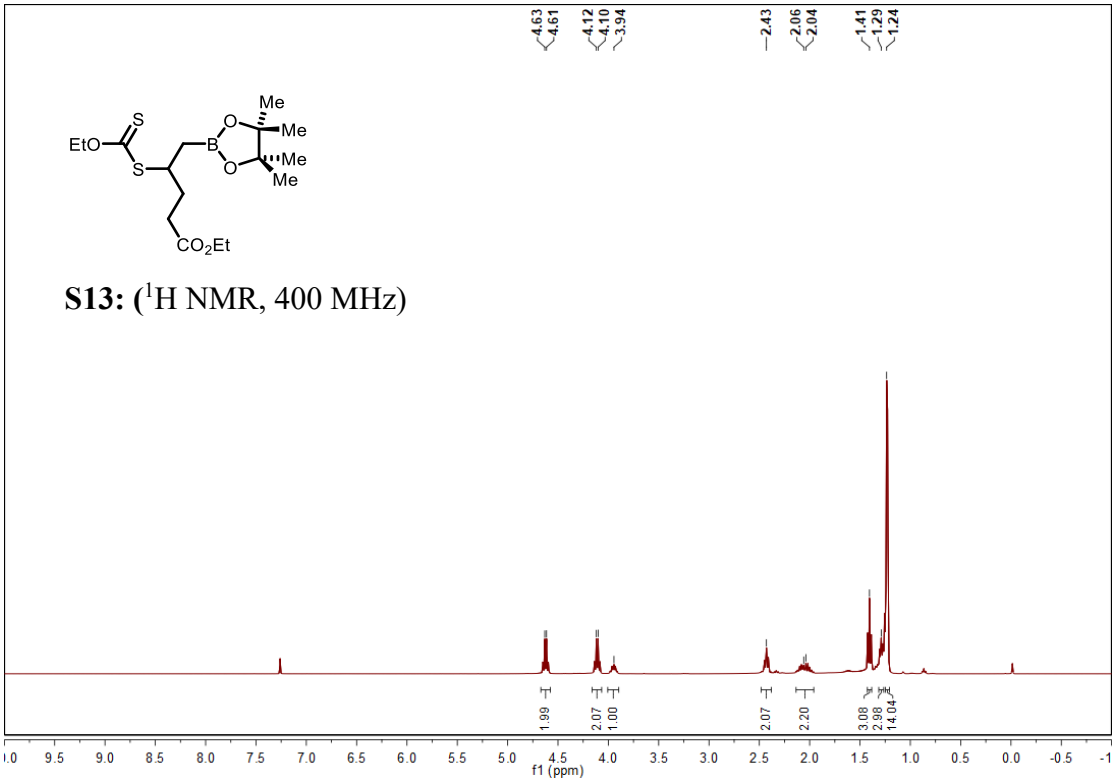
S10: (^{13}C NMR, 100 MHz)



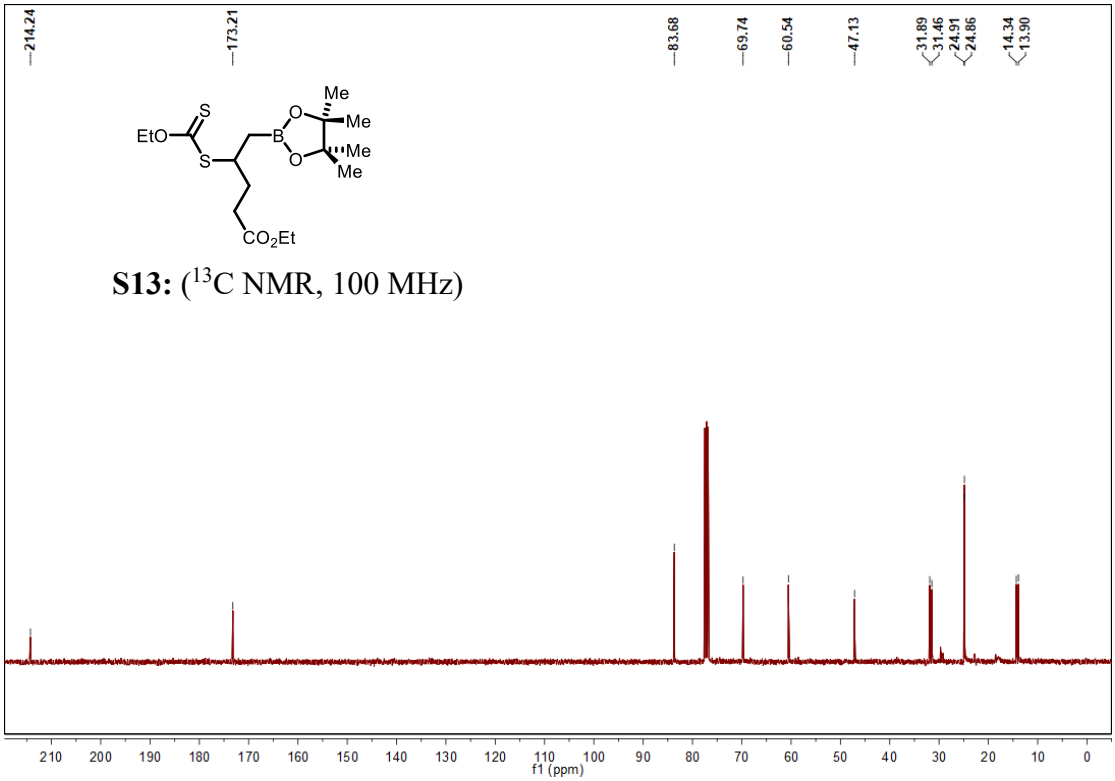
S11: (^{1}H NMR, 400 MHz)



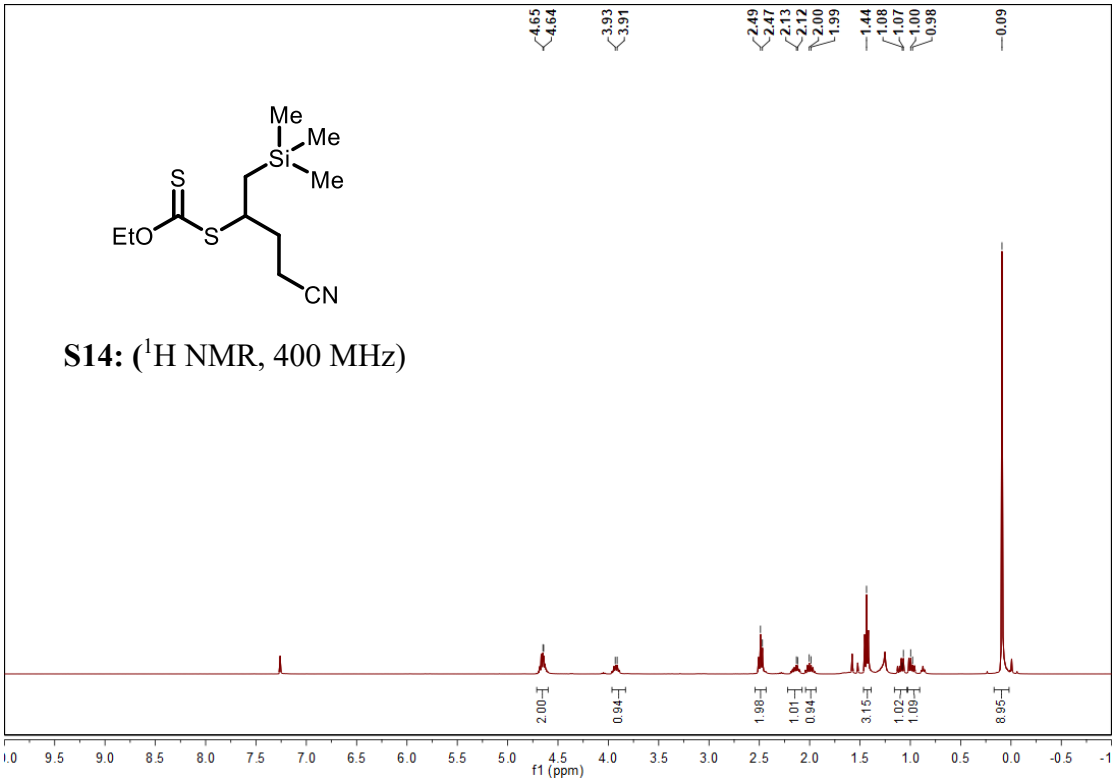
S11: (^{13}C NMR, 100 MHz)



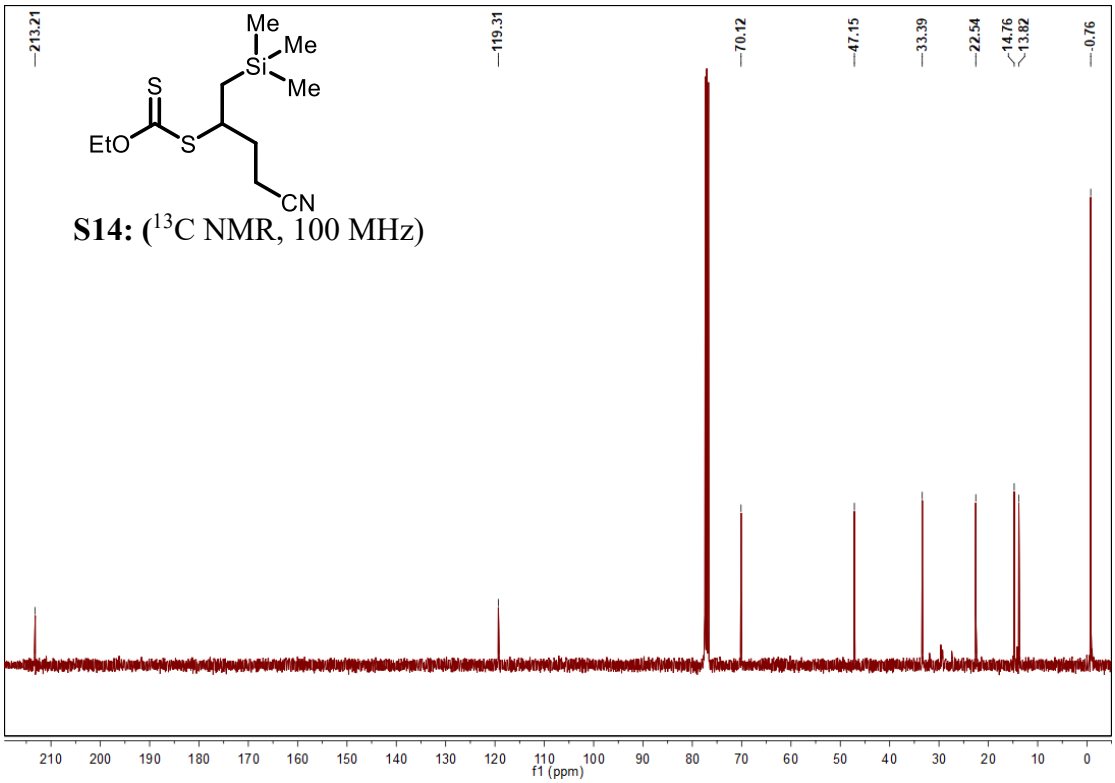
S13: (^{1}H NMR, 400 MHz)



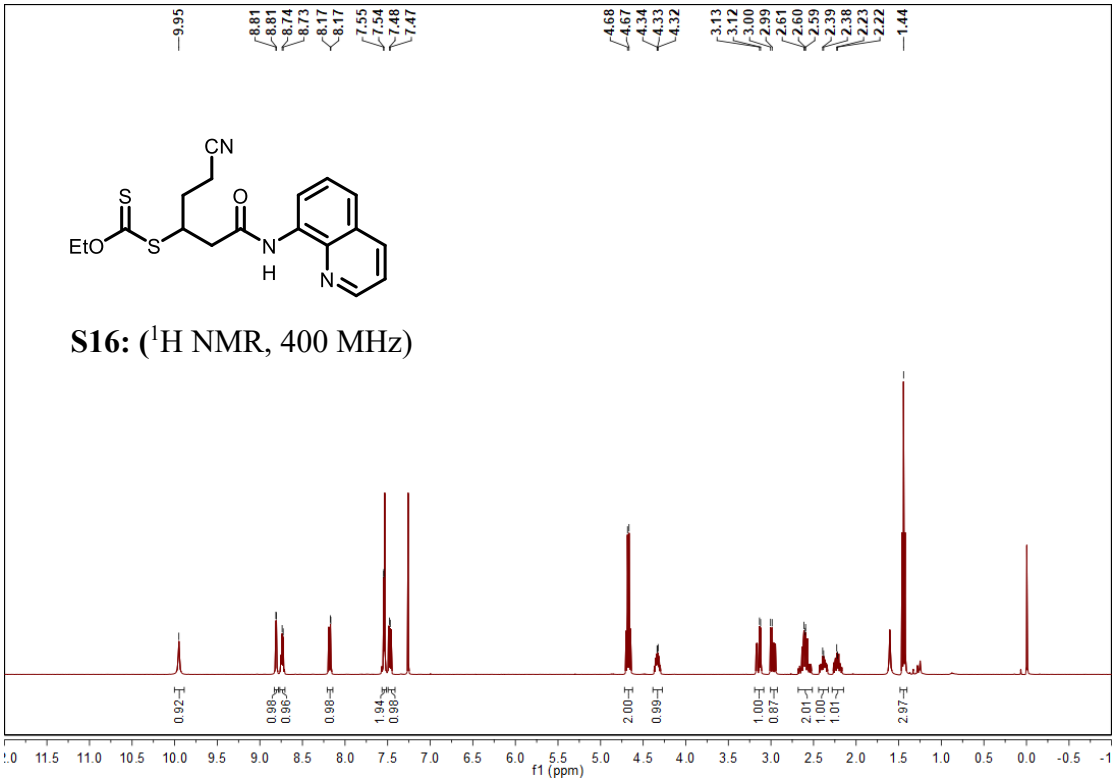
S13: (^{13}C NMR, 100 MHz)



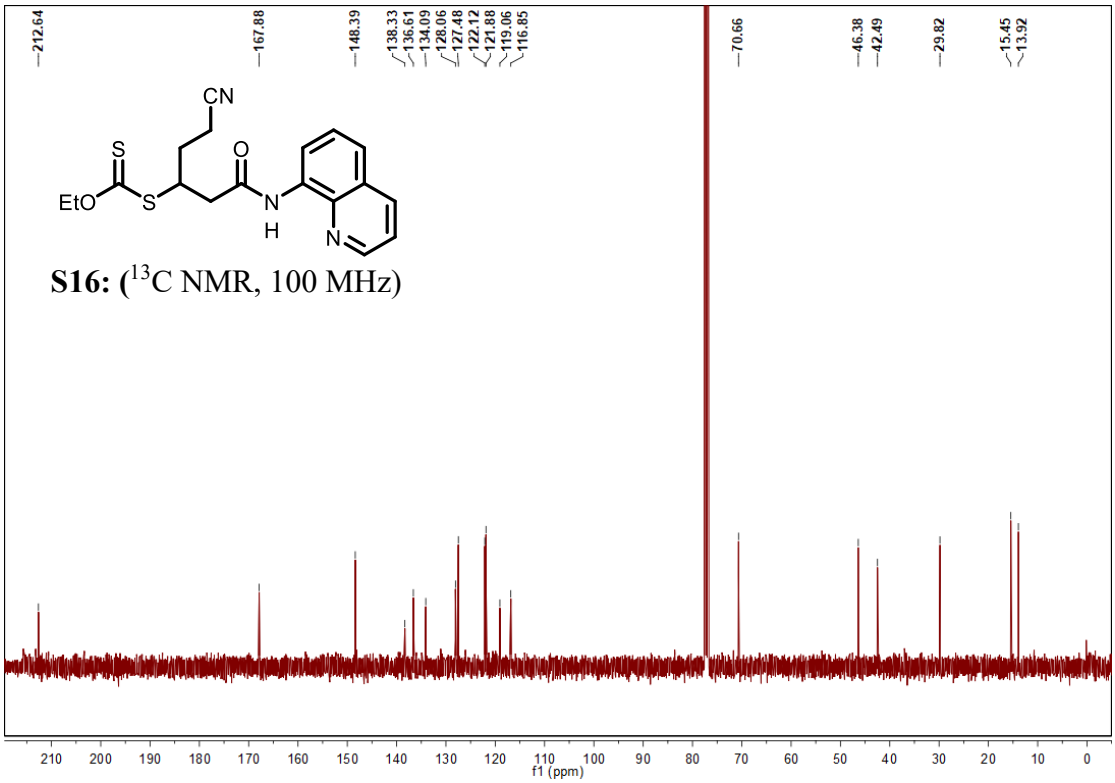
S14: (^{1}H NMR, 400 MHz)



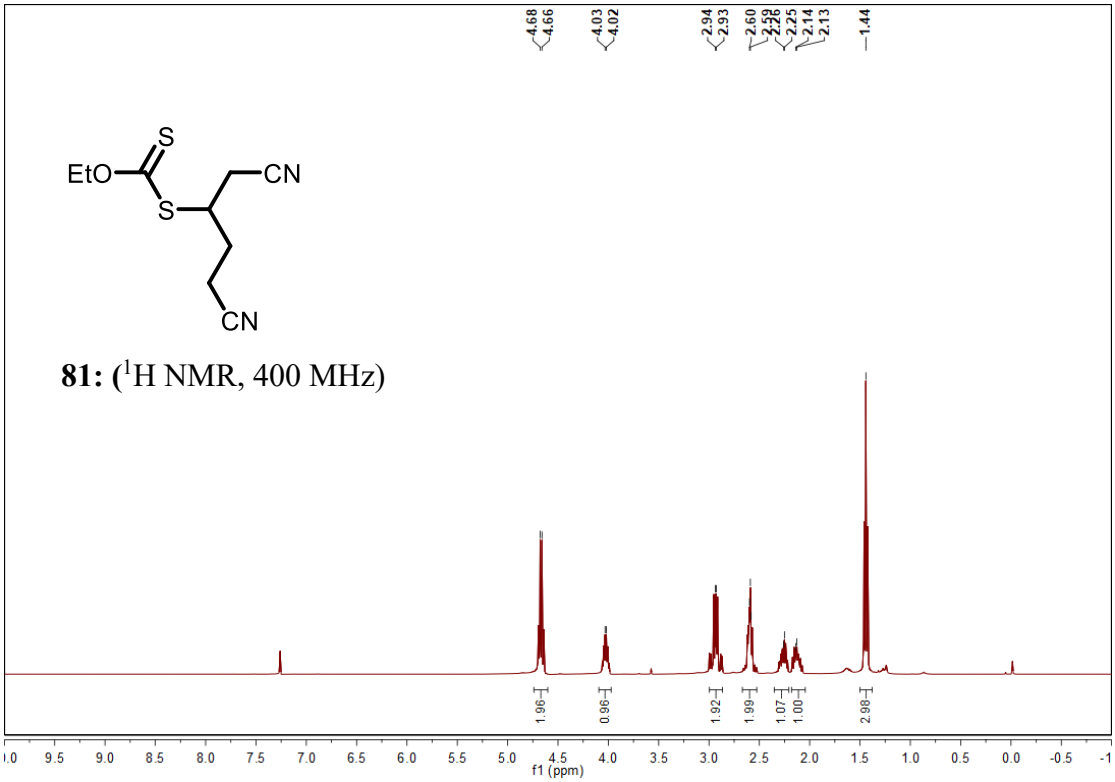
S14: (^{13}C NMR, 100 MHz)



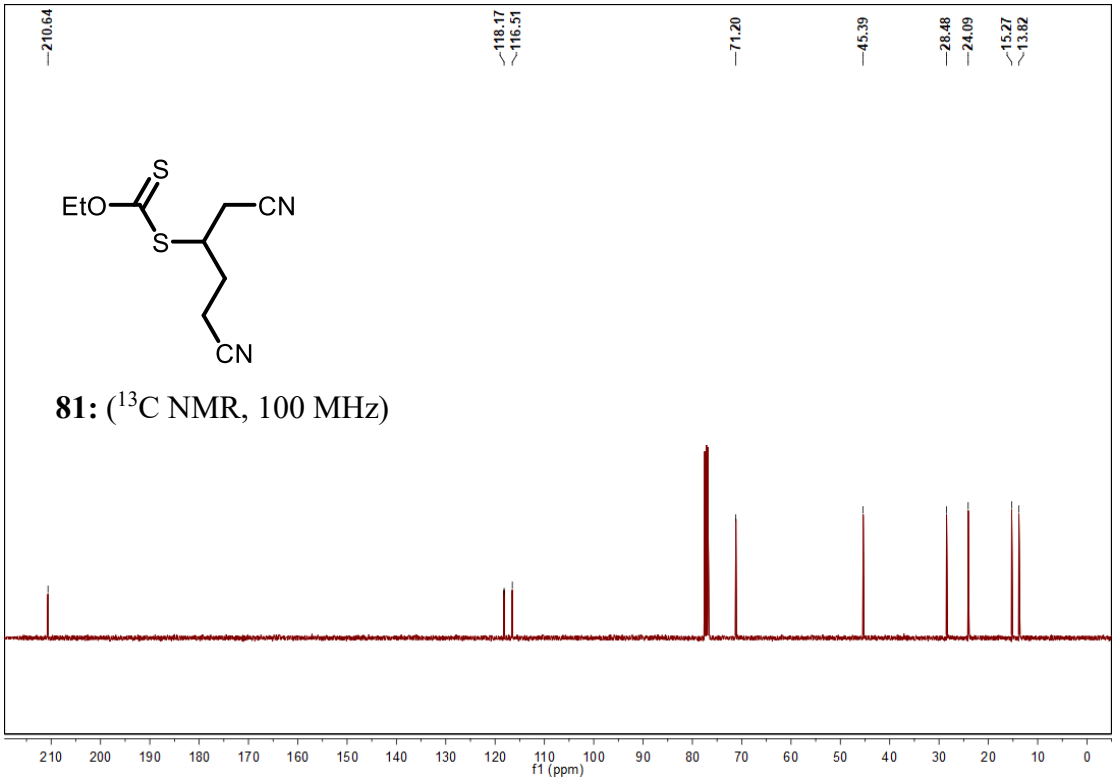
S16: (^{1}H NMR, 400 MHz)



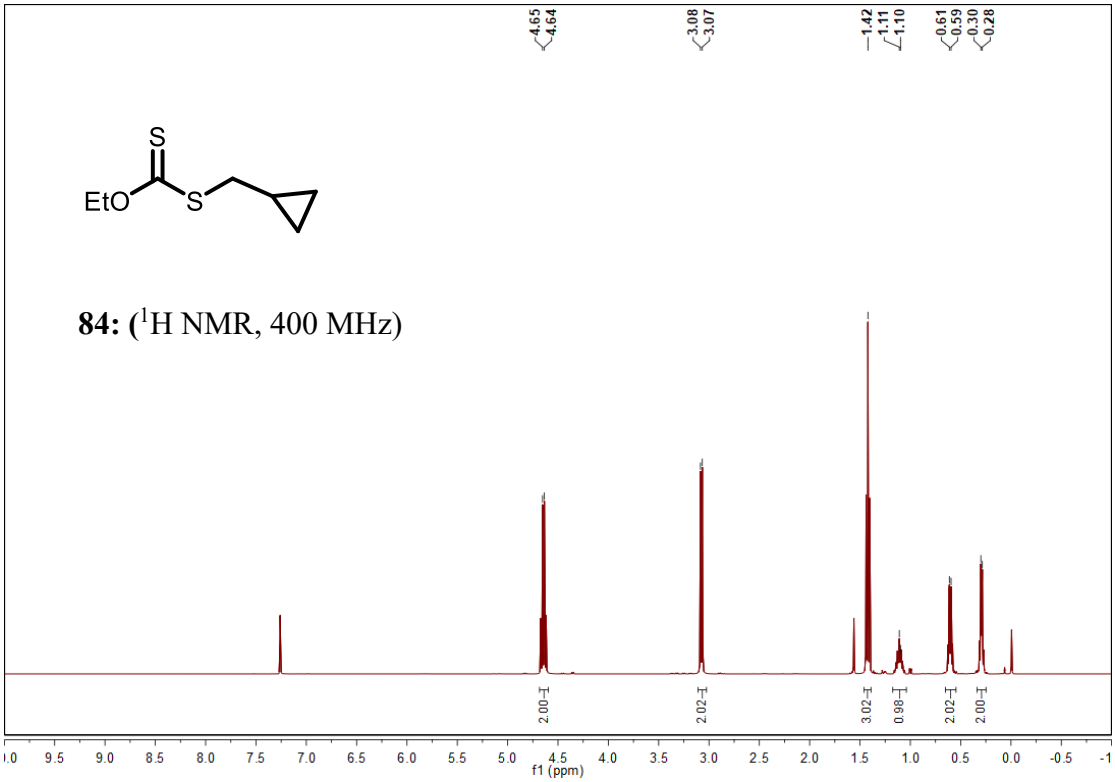
S16: (^{13}C NMR, 100 MHz)



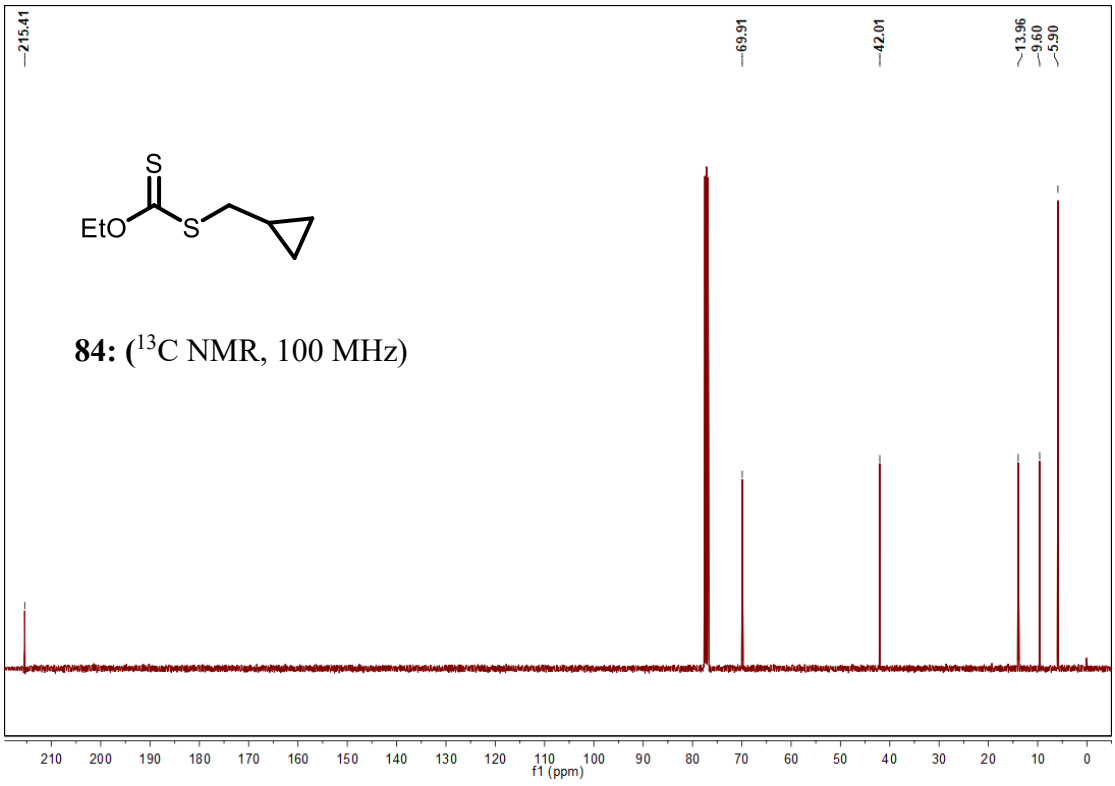
81: (^{1}H NMR, 400 MHz)



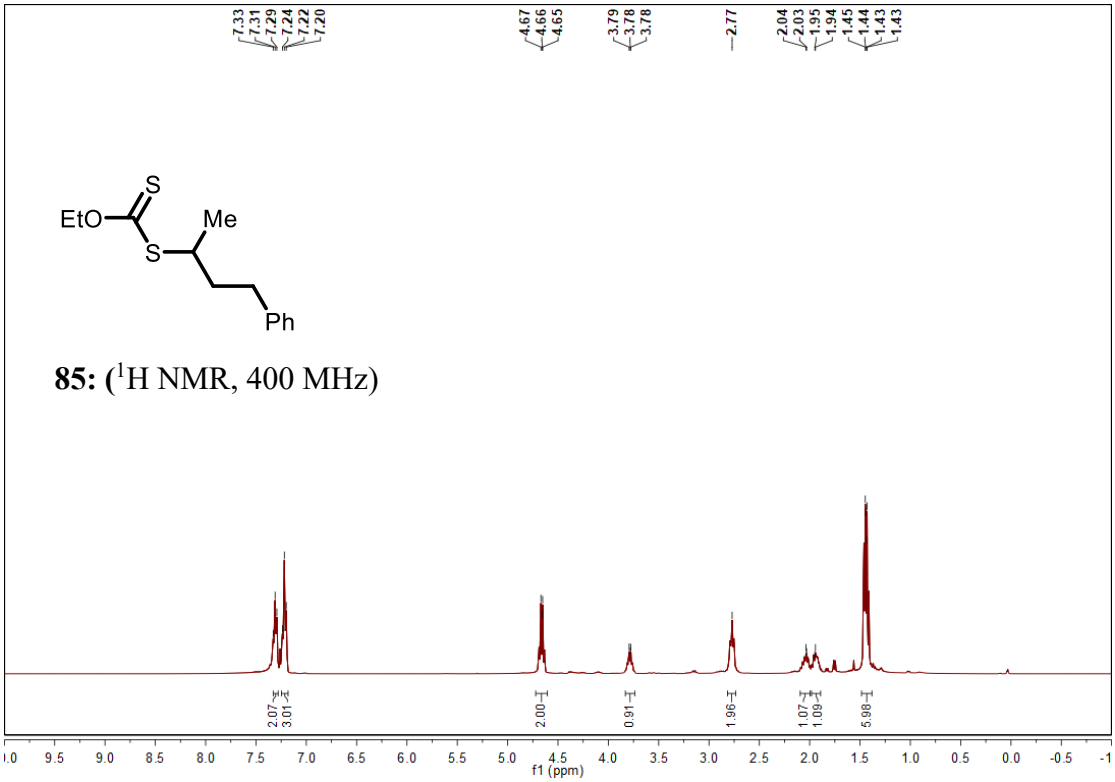
81: (^{13}C NMR, 100 MHz)



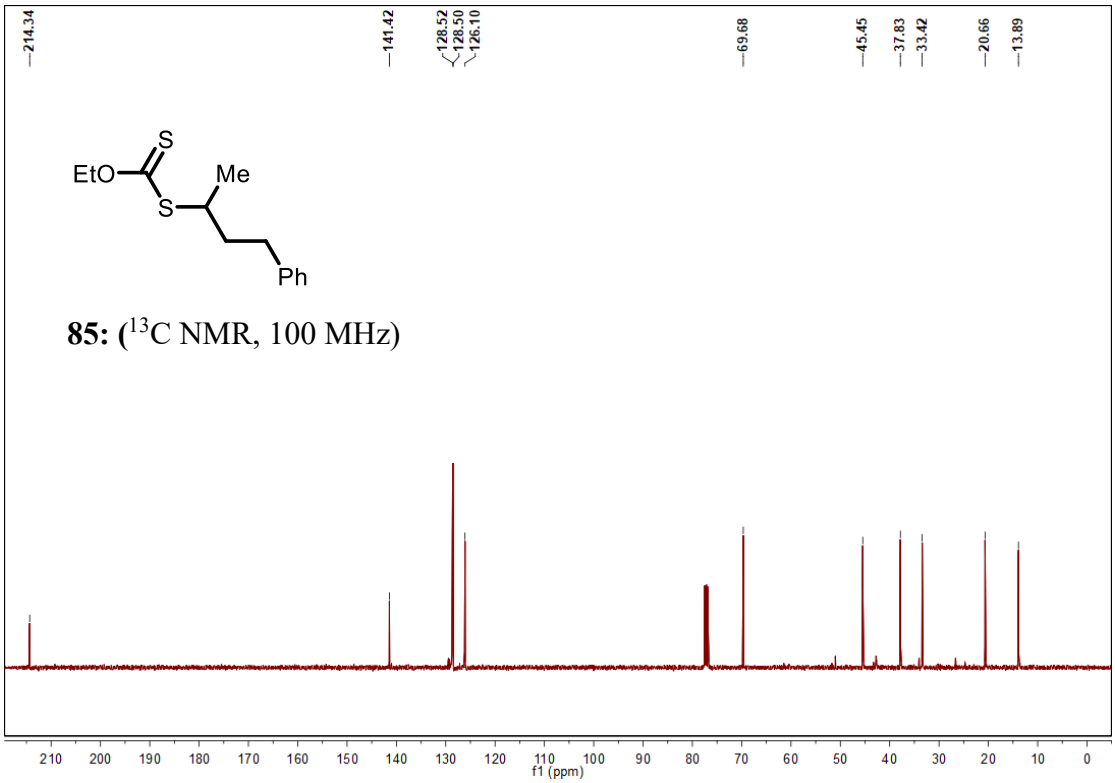
84: (^{1}H NMR, 400 MHz)



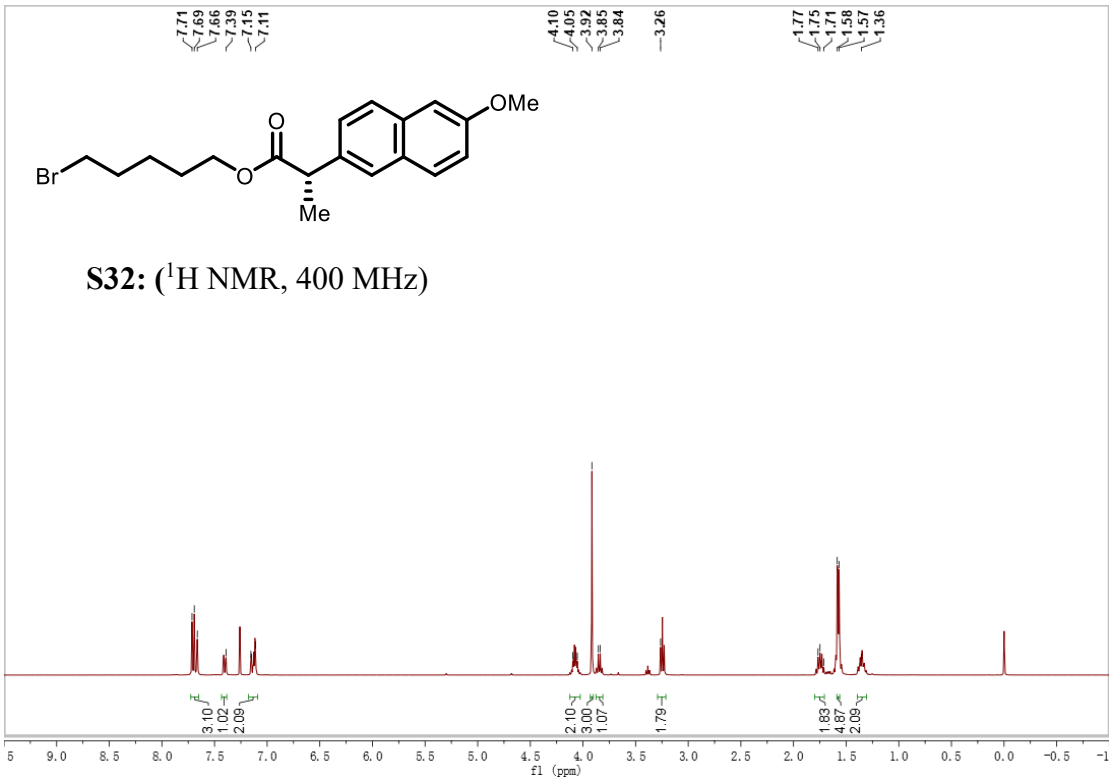
84: (^{13}C NMR, 100 MHz)



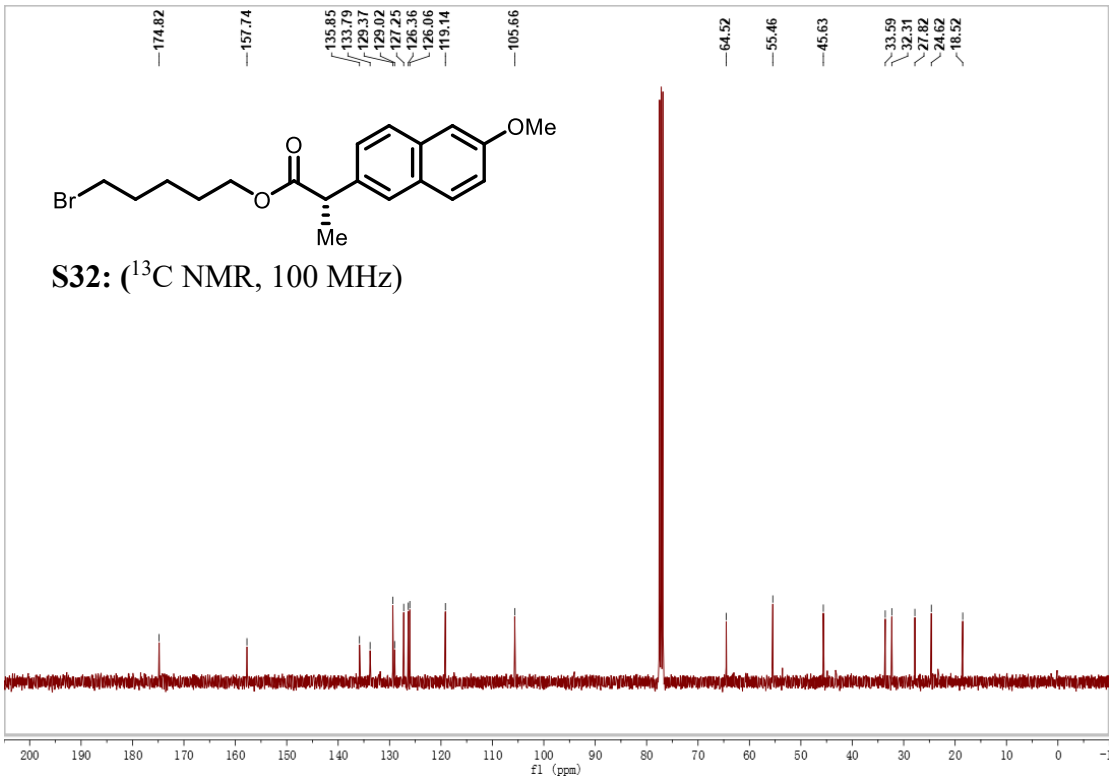
85: (^{1}H NMR, 400 MHz)



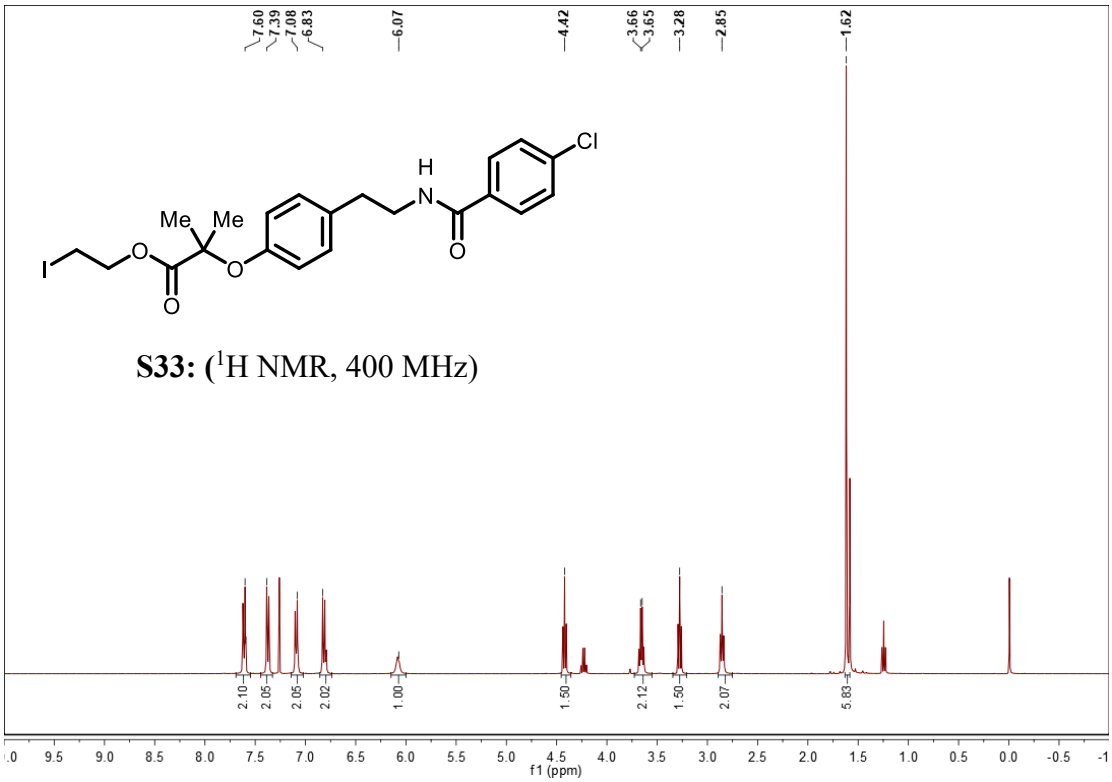
85: (^{13}C NMR, 100 MHz)



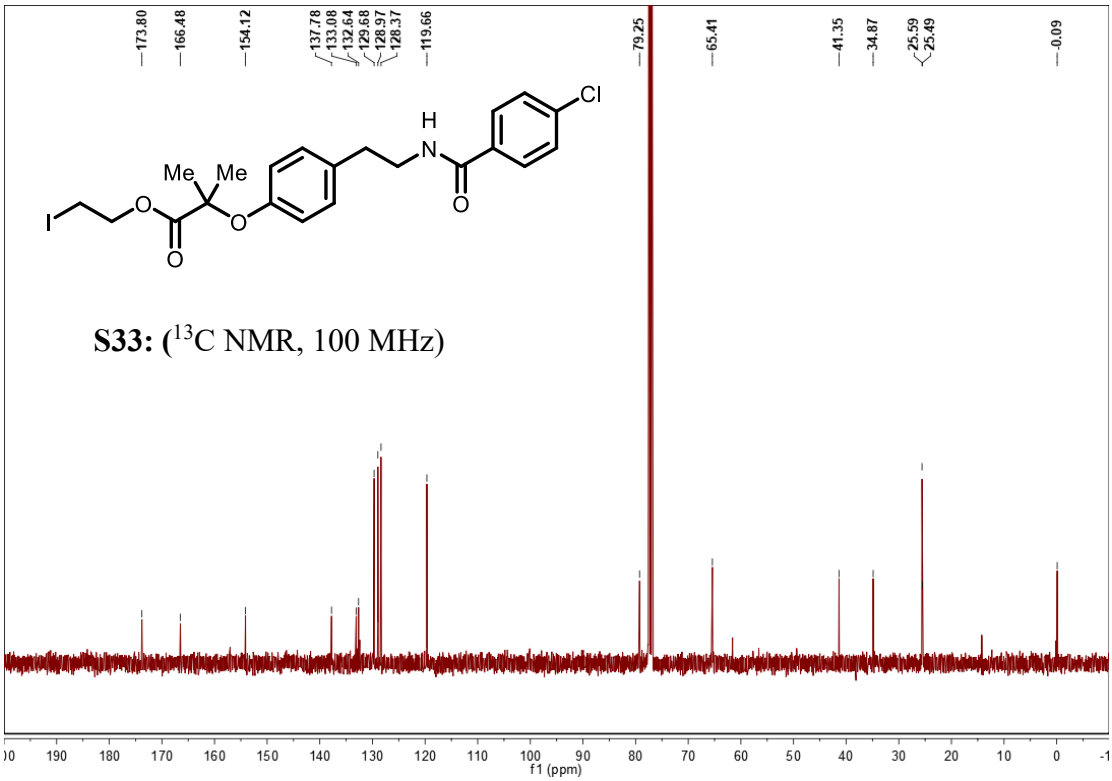
S32: (^{1}H NMR, 400 MHz)



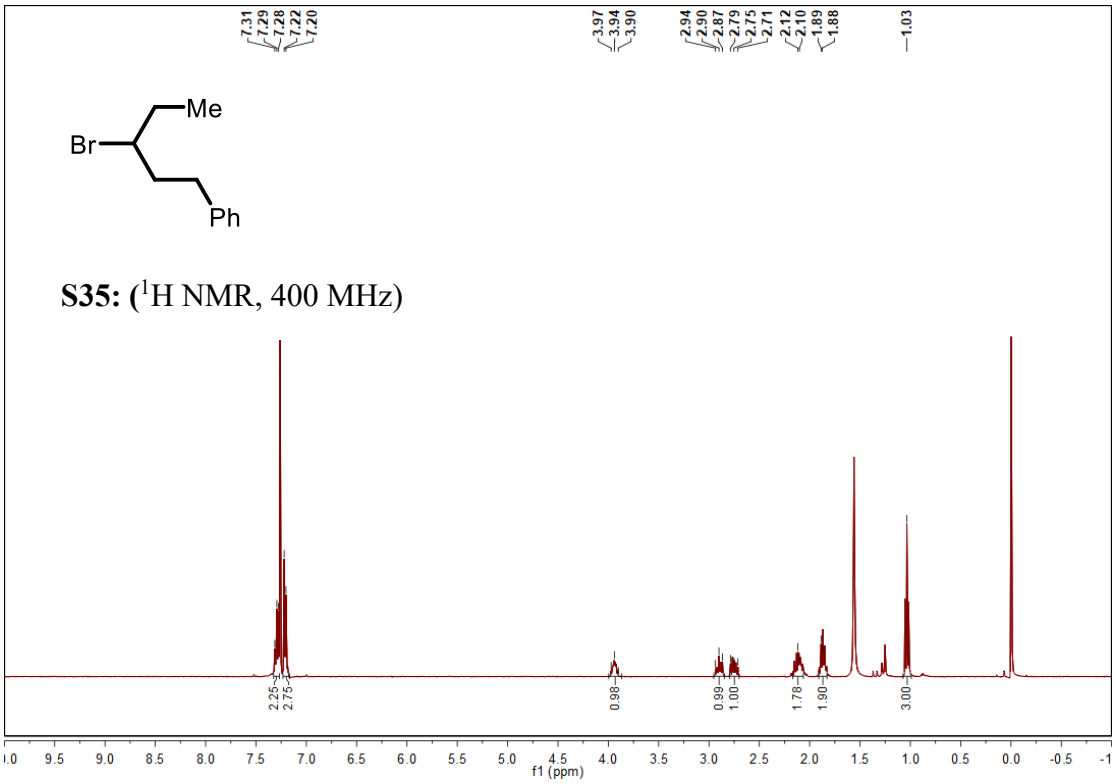
S32: (^{13}C NMR, 100 MHz)



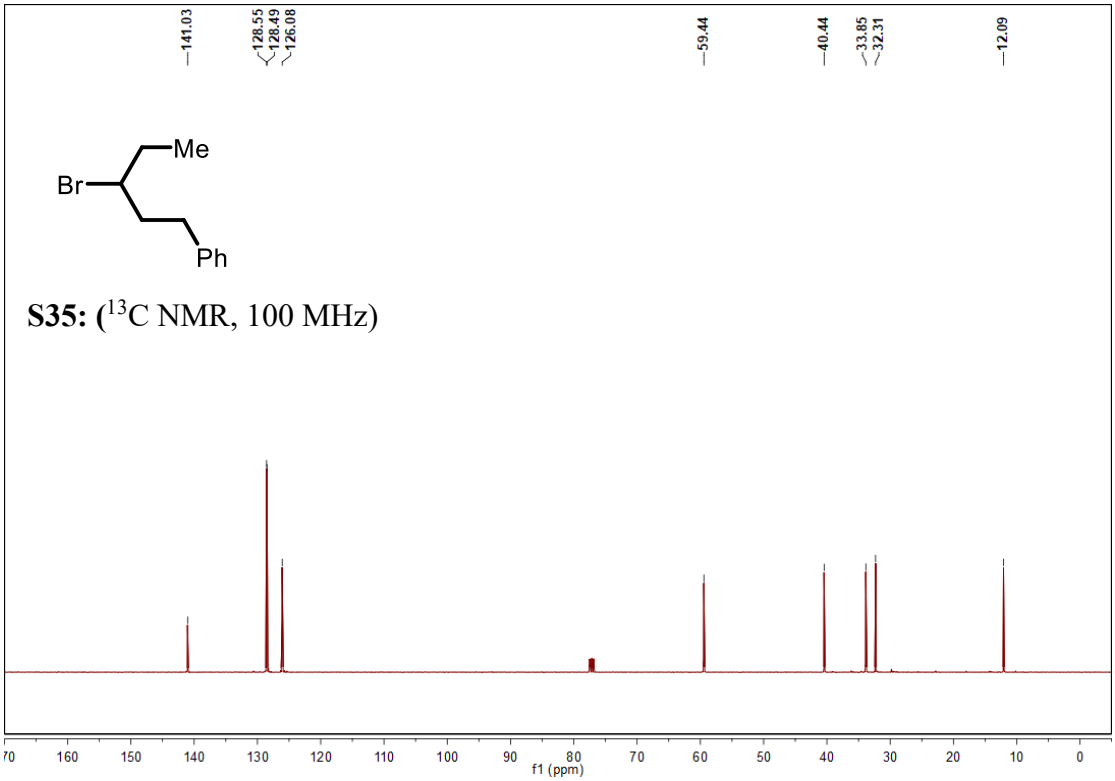
S33: (^{1}H NMR, 400 MHz)



S33: (^{13}C NMR, 100 MHz)



S35: (^{1}H NMR, 400 MHz)



S35: (^{13}C NMR, 100 MHz)