Supporting Information

Nickel-Catalyzed Selective Disulfides Formation by Reductive Cross-Coupling of Thiosulfonates

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1. General Information

Reagents

Unless otherwise noted, all commercially available compounds were used directly without further purification. Solvents for chromatography were technical grade and distilled prior to use. *N*,*N*-Dimethylacetamide (DMA) and 1,2-dichloroethane (DCE, 99.5% extra dry over molecular sieve) used in reactions were purchased from Acros, bubbled for 30 min with N_2, and stored at room temperature. *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (MeCN) and toluene used in reaction optimization were acquired from the solvent purification system MBraun SPS-5.

Thin layer chromatography (TLC)

Analytical thin layer chromatography (TLC) was corried out on Macherey-Nagel ALUGRAM Xtra SIL G/UV F254, visualised by irradiation with UV light.

Flash column chromatography (FCC)

Column chromatography was performed on silica gel (Macherey-Nagel, particle size 0.040-0.063 mm). The eluents for column chromatography were presented as ratios of solvent volumes.

NMR spectra

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian VNMRS-300, VNMRS-400 and VNMRS-600 spectrometer in $CDCl_3$ and $(CD_3)_2SO$. Spectra were calibrated relative to residual proton signal of the deuterated solvents: δH = 7.26 ppm and δC =77.16 ppm for $CDCl_3$; δH = 2.50 ppm and δC = 39.52 ppm for $(CD_3)_2SO$. Coupling constants (J) are reported in hertz (Hz). The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet).

Infrared (IR) spectra

Infrared (IR) spectra were conducted on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption.

Gas chromatography (GC)

Gas chromatography were conducted on a Shimadzu GC-2010 chromatograph.

Mass spectra (MS)

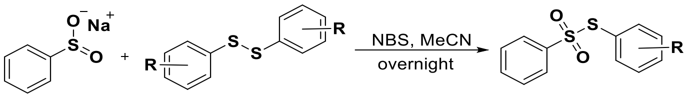
Mass spectra were performed on a Finnigan SSQ 7000 spectrometer.

High resolution mass spectrometer (HRMS)

High resolution mass spectrometer were acquired on a ThermoFisher Scientific LTQOrbitrap XL (ESI), Finnigan MAT SSQ7000 (EI/CI), maXis II Bruker (APCI).

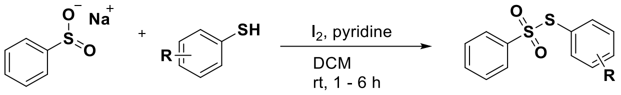
2. Preparation and Characterization of Thiosulfonates

General procedure A for the preparation of thiosulfonates (SM1-4)



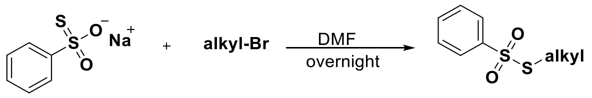
The thiosulfonates were synthesized from the corresponding disulfide according to the procedure in literature.[1] An oven-dried 50 mL round-bottom flask was charged with $PhSO_2Na$ (4.0 equiv.), disulfide (1.0 equiv.), NBS (2.0 equiv.) and MeCN. The mixture was stirred at room temperature and monitored by TLC. Upon completion, the crude mixture was quenched by the addition of water and extracted with ethyl acetate (EtOAc). Then the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by rotary evaporation and then was purified by column chromatography on silica to afford the desired products.

General procedure C for the preparation of thiosulfonates (SM5-9, SM23)

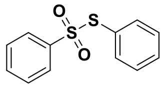


The thiosulfonates were synthesized from the corresponding thiol according to the procedure in literature.[2] Iodine (2.0 equiv.) was added to the oven-dried 50 mL round-bottom flask equipped with thiol (2.0 equiv.) and pyridine (1.05 equiv.) in DCM (1 M in respect to the thiol) slowly. The mixture was stirred at room temperature and then sodium benzenesulfinate or sodium 4-methylbenzenesulfinate (1.70 equiv.) was added to the mixture. The mixture was monitored by TLC, after all the disulfide intermediate was consumed, the reaction mixture was quenched by addition of water and extracted with ethyl acetate. The organic phase was washed with water, saturated $Na_2S_2O_3$ solution, then, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by rotary evaporation and then was purified by column chromatography on silica to obtain the desired products.

General procedure B for the preparation of thiosulfonates (SM10-22)



The thiosulfonates were synthesized from the corresponding alkyl bromide according to the procedure in literature. An oven-dried 50 mL round-bottom flask was equipped with $PhSO_2SNa$ (1.0 equiv.), alkyl bromide (2.0 equiv.) and DMF. The mixture was stirred at room temperature and monitored by TLC. Upon completion, the mixture was diluted with ethyl acetate and washed with water. Then the organic phase was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by rotary evaporation and then was purified by column chromatography on silica to afford the desired products. *S*-(pent-4-yn-1-yl) benzenesulfonothioate was synthesized according to the procedure in literature.[3]



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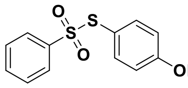

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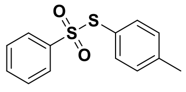

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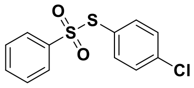

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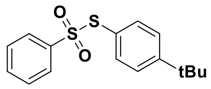

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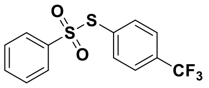

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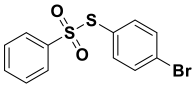

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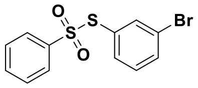

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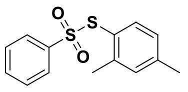

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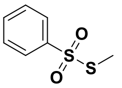

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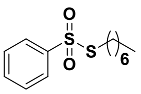

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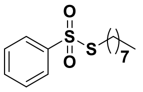

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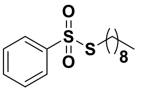

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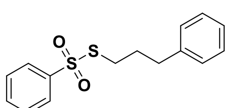

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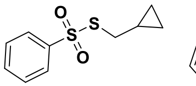

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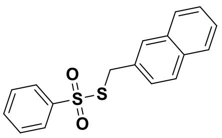

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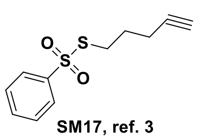

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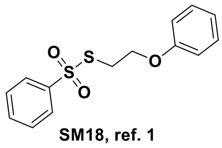

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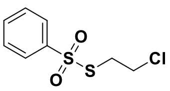
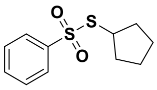


SM19



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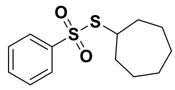
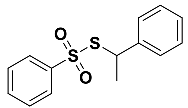


SM21



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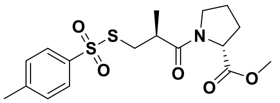
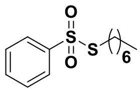


SM23

S-heptyl benzenesulfonothioate (SM11)



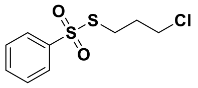
Following general procedure C**,** the title compound (4.23 g, 78% yield) was isolated as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.98 – 7.87 (m, 2H), 7.65 – 7.59 (m, 1H), 7.58 – 7.51 (m, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.53 (m, , 2H), 1.28 – 1.17 (m 8H), 0.84 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.0, 133.7, 129.3, 127.0, 36.2, 31.6, 28.6, 28.6, 28.5, 22.6, 14.1.

IR (ATR) : ν 3434, 2931, 2869, 1655, 1497, 1439, 1388, 1254, 1096, 660 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{13}H_{21}O_2S_2^+$ [M +H]$^+$: 273.09775; found: 273.09827.

S-(3-chloropropyl) benzenesulfonothioate (SM19)



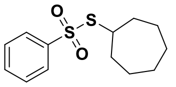
Following general procedure C**,** the title compound (1.33 g, 52% yield) was isolated as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.58 – 7.54 ((m, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.13 – 2.06 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 144.5, 134.0, 129.5, 127.0, 42.8, 33.0, 31.5.

IR (ATR) : ν 2959, 1444, 1319, 1140, 1075, 755, 713, 684 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_9H_{12}O_2ClS_2^+$ [M +H]$^+$: 250.99618; found: 250.99691.

S-cycloheptyl benzenesulfonothioate (SM21)



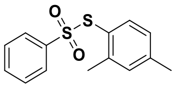
Following general procedure C**,** the title compound (1.49 g, 55% yield) was isolated as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.94 (d, *J* = 7.3 Hz, 2H), 7.66 – 7.62 (m,1H), 7.58 – 7.54 (m, 2H), 3.57 – 3.50 (m, 1H), 2.00 – 1.95 (m, 2H), 1.72 – 1.64 (m, 2H), 1.58 - 1.46 (m, 8H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.7, 133.6, 129.3, 127.0, 52.6, 35.4, 28.0, 25.6.

IR (ATR) : ν 2926, 2856, 1447, 1323, 1141, 1076, 754, 714, 685 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{13}H_{19}O_2S_2^+$ [M +H]$^+$: 271.08210; found: 271.08240.

S-(2,4-dimethylphenyl) benzenesulfonothioate(SM9)



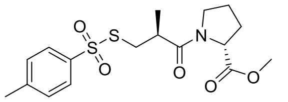
Following general procedure B**,** the title compound (2.57 g, 92% yield) was isolated as a white solid. **^{1}H NMR (300 MHz, CDCl$_3$)** δ = 7.72 – 7.51 (m, 3H), 7.48 – 7.39 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 2.33 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 144.1, 143.7, 142.7, 138.3, 133.7, 132.0, 129.0, 128.0, 127.61, 21.5, 20.6.

IR (ATR) : ν 3041, 2921, 1598, 1473, 1443, 1315, 1140, 1072, 996, 824, 760, 713, 685 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{14}H_{15}O_2S_2^+$ [M +H]$^+$: 279.05080; found: 279.05100.

methyl ((S)-2-methyl-3-(tosylthio)propanoyl)-D-prolinate(SM23)



Following general procedure B**,** the title compound (2.23 g, 58% yield) was isolated as a colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.80 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.49 (dd, *J* = 8.6, 4.0 Hz, 1H), 3.70 (s, 3H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.25 (dd, *J* = 13.9, 9.1 Hz, 1H), 3.17 – 3.08 (m, 1H), 2.88 (dd, *J* = 13.9, 4.9 Hz, 1H), 2.45 (s, 3H), 2.25 – 2.17 (m, 1H), 2.09 – 1.94 (m, 3H), 1.20 (d, *J* = 6.9 Hz, 3H).

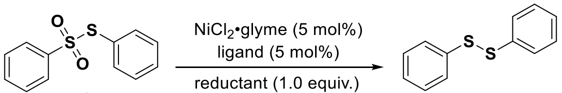
^{13}C NMR (101 MHz, CDCl$_3$) δ 173.0, 172.7, 145.0, 141.8, 130.0, 127.2, 58.8, 52.3, 47.0, 38.7, 38.6, 29.2, 25.0, 21.8, 17.0.

IR (ATR) : ν 3477, 2972, 2879, 1743, 1637, 1596, 1432, 1367, 1321, 1177, 1137, 1077, 814, 752, 703 cm^{-1}.

HRMS (ESI) *m/z* Calcd for $C_{15}H_{16}ONaS_2^+$ [M +Na]$^+$: 299.05348; found: 299.05311.

3. Optimizations of Nickel-Catalyzed Reduction Homo-Coupling Reaction

Table S1. Optimizations of homo-coupling reaction.



1
0.2 mmol

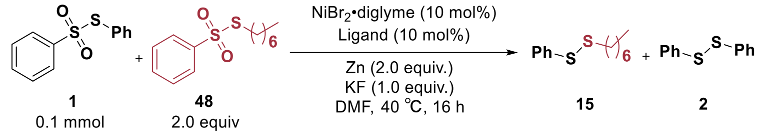
36

entry	Ni-Cat	ligand	solvent	reductant	yield (%) ^{a}
1	$NiCl_2$·glyme	6,6′-di-Me-2,2′-bpy	DMF	Mn	92
2	$NiCl_2$·glyme	6,6′-di-Me-2,2′-bpy	DMA	Mn	90
3	$NiCl_2$·glyme	6,6′-di-Me-2,2′-bpy	DMSO	Mn	84
4	$NiCl_2$·glyme	6,6′-di-Me-2,2′-bpy	THF	Mn	23
5	$NiCl_2$·glyme	bpy	DMF	Mn	18
6	$NiCl_2$·glyme	dtbbpy	DMF	Mn	55
7	$NiCl_2$·glyme	6,6′-di-Me-2,2′-bpy	DMF	Mg	82
8	-	6,6′-di-Me-2,2′-bpy	DMF	Mn	29
9	$NiCl_2$·glyme	-	DMF	Mn	44
10	$NiCl_2$·glyme	6,6′-di-Me-2,2′-bpy	DMF	-	30

^{a} GC yield using n-decane (0.1 mmol) as the internal standard.

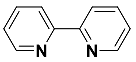
4. Optimizations of Nickel-Catalyzed Reduction Cross-Coupling Reaction

Table S2. Optimization of ligands.



entry	ligand	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	**L1**	7/1	21	3
2	**L2**	3.5/1	7	2
3	**L3**	15/1	15	1
4	**L4**	1.5/1	3	2
5	**L5**	5.3/1	21	4
6	**L6**	4.5/1	9	2
7	**L7**	5/1	5	1
8	**L8**	5/1	15	3
9	**L9**	4.7/1	14	3
10	**L10**	12/1	12	1

[a] Yields determined by GC analysis using decane as internal standard.



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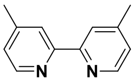
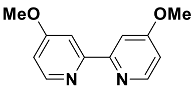


L2



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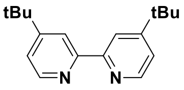

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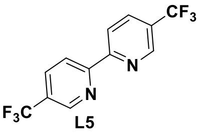

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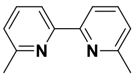
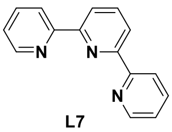
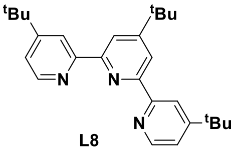


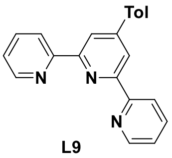
L6



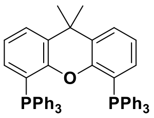
L7



L8

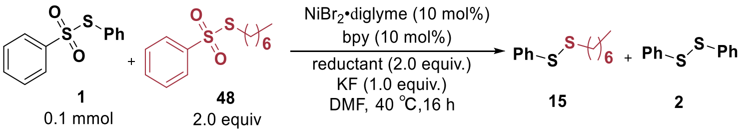


L9



L10

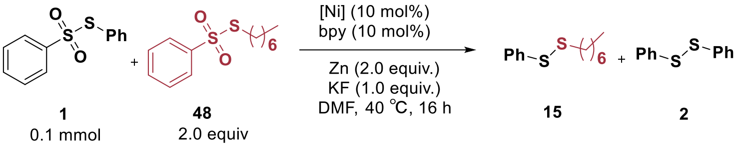
Table S3. Optimization of reductants.



entry	reductant	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	Zn	7/1	21	3
2	Mn	1/1	4	4
3	Mg	0.8/1	4	5
4	Fe	1/1	5	5

[a] Yields determined by GC analysis using decane as internal standard.

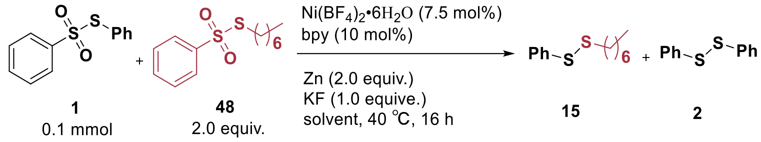
Table S4. Optimization of catalyst precursors



entry	[Ni]	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	$NiBr_2$·diglyme	7.7/1	23	3
2	$NiCl_2$·glyme	6.7/1	20	3
3	$NiCl_2$·$6H_2O$	6/1	24	4
4 [b]	$Ni(BF_4)_2$·$6H_2O$	6.8/1	27	4
5	$Ni(acac)_2$	1.1/1	14	13
6	$Ni(OAc)_2$·$4H_2O$	5/1	20	4
7	$NiBr_2$·$3H_2O$	4.8/1	29	6
8	$NiCl_2$	5/1	25	5

[a] Yields determined by GC analysis using decane as internal standard. [b] [Ni] (7.5 mol%).

Table S5. Optimization of solvent

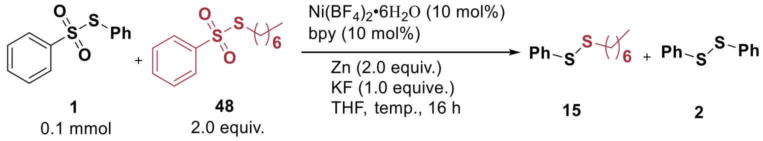


entry	solvent	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	DMF	6/1	24	4
2	DMA	3.6/1	36	10
3	THF	2.1/1	64	30
4 [b]	THF	3.5/1	77	22
5	MeCN	1.0/1	26	25
6	Toluene	0.8/1	19	23

[a] Yields determined by GC analysis using decane as internal standard.

[b] $Ni(BF_4)_2$·$6H_2O$ (10 mol%).

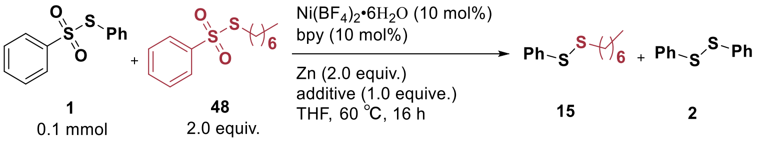
Table S6. Optimization of temperature



entry	temp. (℃)	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	rt	0.8/1	5	7
2	40	3.9/1	77	20
3	60	86/1	89 (77)	1
4	100	3.8/1	42	11

[a] Yields determined by GC analysis using decane as internal standard. The value in parentheses indicates the isolated yield.

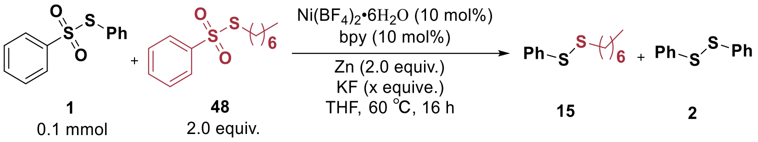
Table S7. Optimization of the additives



entry	additives	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	KF	89/1	89	1
2	LiF	3.1/1	58	19
3	NaF	3.5/1	53	15
4	CsF	5.1/1	36	7
5	KI	3.1/1	58	19
6	K_2CO_3	3.6/1	43	12

[a] Yields determined by GC analysis using decane as internal standard.

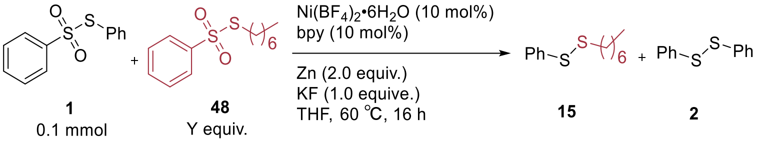
Table S8. Optimization of the amount of KF



entry	X =	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	0	3.2/1	51	16
2	0.5	4.8/1	62	13
3	1	44.5/1	89	2
4	1.5	4.8/1	72	15
5	2	12.3/1	86	7

[a] Yields determined by GC analysis using decane as internal standard.

Table S9. Optimization of the amount of **2a**

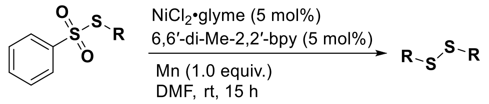


entry	Y =	**15/2**	yield **15** (%) [a]	yield **2** (%) [a]
1	1.0	1.4/1	14	10
2	1.2	2/1	26	13
3	1.5	2.6/1	36	14
4	2.0	86/1	86 (78)	1

[a] Yields determined by GC analysis using decane as internal standard. The value in parentheses indicates the isolated yield.

5. General Procedure for the Homo-Coupling Reaction

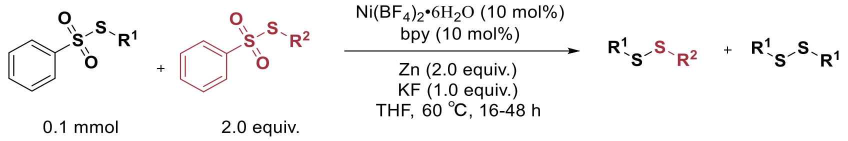
General Procedure D



A oven-dried vial containing a teflon coated stirring bar was equipped with benzenesulfonothioate (0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (0.01 mmol, 5 mol%), Mn (0.2 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed DMF (1.0 mL) was added via syringe. The septum and the vial were sealed with parafilm and then was stirred at rt for 16 h. Upon completion, the crude reaction mixture was concentrated by rotary evaporation and then was purified by column chromatography on silica to using hexane: Et_2O as eluent to obtain the desired products.

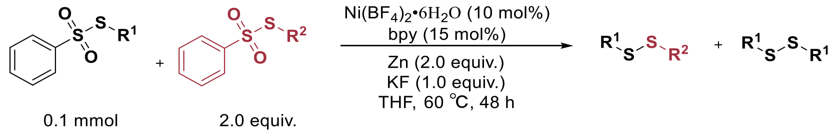
6. General Procedure for the Cross-Coupling Reaction

General Procedure E for the Cross-Coupling Reaction



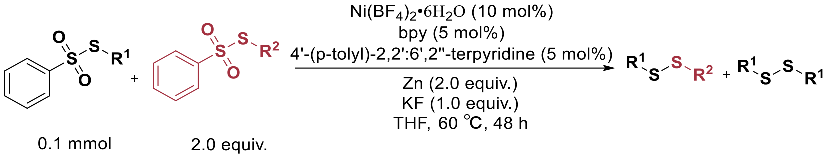
A oven-dried vial containing a teflon coated stirring bar was equipped with benzenesulfonothioate (black) (0.1 mmol, 1.0 equiv., if solid), benzenesulfonothioate (red) (0.2 mmol, 2.0 equiv., if solid), $Ni(BF_4)_2$·$6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1 mL) and benzenesulfonothioate (black) (0.1 mmol, 1.0 equiv., if liquid), benzenesulfonothioate (red) (0.2 mmol, 2.0 equiv., if liquid) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 16-48 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, the crude mixture was purified by column chromatography on silica to afford the desired products.

General Procedure F for the Cross-Coupling Reaction



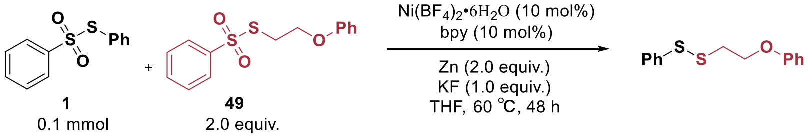
A oven-dried vial containing a teflon coated stirring bar was equipped with benzenesulfonothioate (black) (0.1 mmol, 1.0 equiv., if solid), benzenesulfonothioate (red) (0.2 mmol, 2.0 equiv., if solid), $Ni(BF_4)_2$·$6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.015 mmol, 15 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL), benzenesulfonothioate (black) (0.1 mmol, 1.0 equiv., if liquid), benzenesulfonothioate (red) (0.2 mmol, 2.0 equiv., if liquid) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 48 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, the crude mixture was purified by column chromatography on silica to afford the desired products.

General Procedure G for the Cross-Coupling Reaction



A oven-dried vial containing a teflon coated stirring bar was equipped with benzenesulfonothioate (black) (0.1 mmol, 1.0 equiv., if solid), benzenesulfonothioate (red) (0.2 mmol, 2.0 equiv., if solid), $Ni(BF_4)_2·6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.005 mmol, 5 mol%), 4'-(p-tolyl)-2,2':6',2''-terpyridine (0.005 mmol, 5 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL) and benzenesulfonothioate (black) (0.1 mmol, 1.0 equiv., if liquid), benzenesulfonothioate (red) (0.2 mmol, 2.0 equiv., if liquid) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 48 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, the crude mixture was purified by column chromatography on silica to afford the desired products.

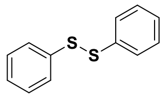
General Procedure F for the Scale-up Reaction



A 250 mL flask containing a teflon coated stirring bar was equipped with benzenesulfonothioate **1** (5 mmol, 1.0 equiv.), benzenesulfonothioate **49** (10 mmol, 2.0 equiv.), $Ni(BF_4)_2·6H_2O$ (0.5 mmol, 10 mol%), 2,2'-bipyridine (0.5 mmol, 10 mol%), Zn (10 mmol, 2.0 equiv.), KF (5 mmol, 1.0 equiv.). The flask was introduced to a glovebox which with Argon atmosphere. Then, anhydrous THF (25 mL) were added via syringe. The flask was close with a rubber septum and removed from the glovebox. The flask then was stirred at 60 °C for 48 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (20 mL), the mixture was concentrated by rotary evaporation. Then, the crude mixture was purified by column chromatography on silica (eluent: 80:1 to 50:1 hexane: Et_2O) to afford **27’** as a white solid in 65% yield (852 mg).

7. Specific Procedures and Spectroscopic Data of the Products

1,2-Diphenyldisulfane (2)



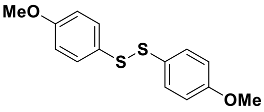
Following general procedure D, the title compound (19.4 mg, 89% yield) was isolated as a white solid after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.55 – 7.44 (m, 4H), 7.32 – 7.28 (m, 4H), 7.23 (dd, *J* = 8.5, 3.3 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.2, 129.2, 127.7, 127.3.

The data is consistent with the literature.[9]

1,2-Bis(4-methoxyphenyl)disulfane (3)



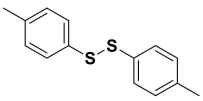
Following general procedure D, the title compound (24.9 mg, 90% yield) was isolated as a yellow solid after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 (dd, *J* = 8.7, 1.8 Hz, 4H), 6.84 (dd, *J* = 8.7, 1.8 Hz, 4H), 3.80 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 132.8, 128.5, 114.7, 55.5.

The data is consistent with the literature.[9]

1,2-Di-p-tolyldisulfane (4)



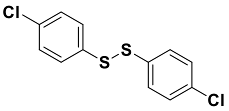
Following general procedure D, the title compound (20.8 mg, 85% yield) was isolated as a pale yellow solid after flash chromatography on silica gel (eluent: hexane), starting from *S*-(p-tolyl) benzenesulfonothioate (52.8 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 2.33 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 134.0, 129.9, 128.7, 21.2.

The data is consistent with the literature.[9]

1,2-Bis(4-chlorophenyl)disulfane (5)



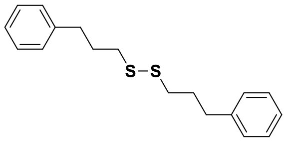
Following general procedure D, the title compound (28.4 mg, 99% yield) was isolated as a pale yellow solid after flash chromatography on silica gel (eluent: hexane), starting from *S*-(4-chlorophenyl) benzenesulfonothioate (56.9 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h. The data of are consistent with the literature.[9]

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.42 – 7.38 (m, 4H), 7.30 – 7.26 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.3, 133.8, 129.4.

The data is consistent with the literature.[9]

1,2-Bis(3-phenylpropyl)disulfane (6)



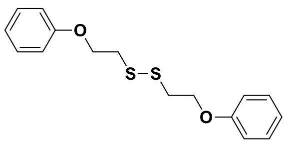
Following general procedure D, the title compound (25.3 mg, 84% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 400:1 to 200:1hexane: Et_2O), starting from *S*-(3-phenylpropyl) benzenesulfonothioate (58.5 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30 (m, 4H), 7.21 (m, 6H), 2.73 (t, *J* = 7.6 Hz, 4H), 2.69 (t, *J* = 7.2 Hz, 4H), 2.05 – 2.00 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.5, 128.6, 128.5, 126.1, 38.3, 34.5, 30.7.

The data is consistent with the literature.[10]

1,2-Bis(2-phenoxyethyl)disulfane (7)



Following general procedure D, the title compound (26.7 mg, 87% yield) was isolated as a white solid after flash chromatography on silica gel (eluent: 80:1 to 50:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (58.9 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

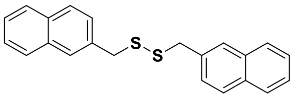
^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 – 7.27 (m, 4H), 6.99 – 6.96 (m, 2H), 6.93 (d, *J* = 8.5 Hz, 4H), 4.26 (t, *J* = 6.6 Hz, 4H), 3.10 (t, *J* = 6.6 Hz, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 129.7, 121.6, 114.8, 66.1, 38.0.

IR (ATR) : ν 2926, 1595, 1493, 1467, 1421, 1294, 1237, 1171, 1076, 1023, 824, 742, 685 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{16}H_{18}O_2S_2^+$ $[M]^+$: 306.07436; found: 306.07428.

1,2-Bis(naphthalen-2-ylmethyl)disulfane (8)



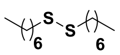
Following general procedure D, the title compound (26.5 mg, 77% yield) was isolated as a white solid after flash chromatography on silica gel (eluent: 400:1 to 20:1 hexane: Et_2O), starting from *S*-(naphthalen-2-ylmethyl) benzenesulfonothioate (62.9 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 8.6 Hz, 4H), 7.56 – 7.45 (m, 6H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 2H), 3.73 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 133.3, 132.8, 128.4, 128.4, 127.9, 127.9, 127.4, 126.4, 126.1, 43.8.

The data is consistent with the literature.[11]

1,2-Diheptyldisulfane (9)



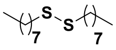
Following general procedure D, the title compound (21.7 mg, 83% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-heptyl benzenesulfonothioate (45.5 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.70 – 2.65 (m, 4H), 1.69 – 1.64 (m, 4H), 1.38 (m, 4H), 1.29 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 39.4, 31.9, 29.4, 29.1, 28.6, 22.8, 14.2.

The data is consistent with the literature.[12]

1,2-Diethyldisulfane (10)



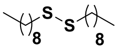
Following general procedure D, the title compound (23.9 mg, 83% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-octyl benzenesulfonothioate (57.3 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.71 – 2.64 (m, 4H), 1.69 – 1.64 (m, 4H), 1.40 – 1.24 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 39.4, 32.0, 29.4, 29.4, 29.3, 28.7, 22.8, 14.2.

The data is consistent with the literature.[12]

1,2-Dinonyldisulfane (11)



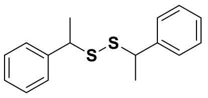
Following general procedure D, the title compound (22.8 mg, 72% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-nonyl benzenesulfonothioate (60.1 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.71 – 2.65 (m, 4H), 1.69 – 1.64 (m, 4H), 1.39 – 1.25 (m, 24H), 0.93 – 0.85 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 39.4, 32.0, 29.6, 29.4, 29.4, 29.4, 28.7, 22.8, 14.3.

The data is consistent with the literature.[13]

1,2-Bis(1-phenylethyl)disulfane (12) dr = 1:1



Following general procedure D, the title compound (26.2 mg, 93% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 100:1 to 80:1 hexane: Et_2O), starting from *S*-(1-phenylethyl) benzenesulfonothioate (55.7 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

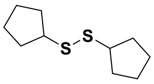
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.30 (m, 4H), 7.29 – 7.20 (m, 6H), 3.62 (q, *J* = 7.0 Hz, 1H), 3.54 (q, *J* = 7.0 Hz, 1H), 1.56 (dd, *J* = 7.0, 4.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.5, 127.9, 127.8, 127.6, 127.6, 77.5, 77.2, 76.8, 49.6, 49.6, 20.7, 20.6.

IR (ATR): ν 2961, 2923, 2857, 1492, 1450, 1371, 1182, 1026, 762, 694 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{16}H_{19}S_2^+$ $[M+H]^+$: 275.09227; found: 275.09267.

1,2-Dicyclopentyldisulfane (13)



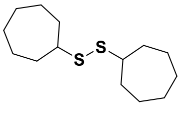
Following general procedure D, the title compound (17.3 mg, 86% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-cyclopentyl benzenesulfonothioate (48.5 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.31 – 3.27 (m, 2H), 2.01 – 1.94 (m, 4H), 1.79 – 1.71 (m, 4H), 1.70 – 1.63 (m, 4H), 1.59 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 77.4, 77.2, 77.0, 50.5, 33.3, 24.8.

The data is consistent with the literature.[14]

1,2-Dicycloheptyldisulfane (14)



Following general procedure D, the title compound (11.9 mg, 46% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-cycloheptyl benzenesulfonothioate (54.1 mg, 0.2 mmol, 1.0 equiv.), $NiCl_2$·glyme (2.2 mg, 0.01 mmol, 5 mol%), 6,6'-dimethyl-2,2'-bipyridine (1.9 mg, 0.01 mmol, 5 mol%), Mn (11.0 mg, 0.2 mmol, 1.0 equiv.) in DMF (1 mL) at rt for 16 h.

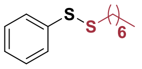
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.91 – 2.86 (m, 2H), 2.11 – 2.06 (m, 4H), 1.76 – 1.70 (m, 4H), 1.55 (m, 12H), 1.48 – 1.41 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 77.2, 76.8, 51.6, 34.4, 29.9, 28.5, 26.1.

IR (ATR): ν 2921, 2852, 1453, 1348, 1213, 1054, 947, 815 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{14}H_{27}S_2^+$ $[M+H]^+$: 259.15487; found: 259.15557.

1-Heptyl-2-phenyldisulfane (15)



Following general procedure E, the title compound (18.4 mg, 77% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2\cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-heptyl benzenesulfonothioate (49 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 16 h.

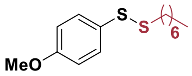
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.46 (m, 2H), 7.35 – 7.25 (m, 2H), 7.23 – 7.16 (m, 1H), 2.74 (t, *J* = 8 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.35 – 1.21 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 129.1, 127.5, 126.8, 39.1, 31.8, 29.0, 29.0, 28.6, 22.7, 14.2.

IR (ATR): ν 2924, 2854, 1579, 1468, 1440, 1070, 1023, 737, 688 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{13}H_{21}S_2^+$ [M +H]$^+$: 241.10792; found: 241.10804.

1-Heptyl-2-(4-methoxyphenyl)disulfane (16)



Following general procedure E, the title compound (16.0 mg, 60% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (eluent: 400:1 to 20:1 hexane: Et_2O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (28.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2\cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-heptyl benzenesulfonothioate (49 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 36 h.

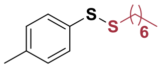
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.72 (d, *J* = 6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.38 – 1.21 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 131.8, 128.7, 114.7, 55.5, 39.0, 31.8, 29.0, 28.8, 28.6, 22.7, 14.2.

IR (ATR): ν 2924, 2854, 1590, 1489, 1459, 1287, 1243, 1173, 1031, 823, 722 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{14}H_{22}S_2^+$ [M]$^+$: 270.11066; found: 270.11050.

1-Heptyl-2-(p-tolyl)disulfane (17)



Following general procedure E, the title compound (21.3 mg, 83% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-(p-tolyl) benzenesulfonothioate (26.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2\cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-heptyl benzenesulfonothioate (49 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 24 h.

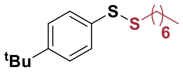
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 1.70 – 1.62 (m, 2H), 1.38 – 1.23 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 134.4, 129.9, 128.5, 39.1, 31.8, 29.0, 28.9, 28.6, 22.7, 21.2, 14.2.

IR (ATR): ν 3020, 2924, 2855, 1488, 1457, 1377, 1112, 1077, 1016, 803, 722 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{15}H_{23}S_2^+$ [M +H]$^+$: 255.12357; found: 255.12428.

1-(4-(Tert-butyl)phenyl)-2-heptyldisulfane (18)



Following general procedure F, the title compound (17.7 mg, 60% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (30.6 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2\cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-heptyl benzenesulfonothioate (49 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

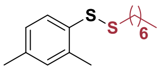
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 – 7.44 (m, 2H), 7.37 – 7.33 (m, 2H), 2.74 (t, *J* = 8 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.39 – 1.25 (m, 17H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 134.4, 128.0, 126.2, 39.1, 34.7, 31.8, 31.4, 29.0, 28.9, 28.6, 22.7, 14.2.

IR (ATR): ν 2956, 2925, 2858, 1487, 1460, 1396, 1365, 1268, 1114, 1012, 822, 724 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{17}H_{29}S_2^+$ [M +H]$^+$: 297.17052; found: 297.17056.

1-(2,4-Dimethylphenyl)-2-heptyldisulfane (19)



Following general procedure F, the title compound (20.0 mg, 75% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-(2,4-dimethylphenyl) benzenesulfonothioate (27.8 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2{\cdot}6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-heptyl benzenesulfonothioate (49 μL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

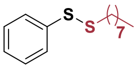
^{1}H NMR (600 MHz, CDCl$_3$) δ = 7.56 (d, *J* = 6 Hz, 1H), 7.01 (d, *J* = 6 Hz, 2H), 2.70 (t, *J* = 9 Hz, 2H), 2.40 (s, 3H), 2.31 (s, 3H), 1.69 – 1.64 (m, 2H), 1.37 – 1.32 (m, 2H), 1.30 – 1.22 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 137.8, 137.4, 132.8, 131.5, 129.5, 127.4, 38.7, 31.8, 29.0, 28.9, 28.6, 22.7, 21.1, 20.2, 14.2.

IR (ATR): ν 2923, 2855, 1601, 1465, 1376, 1276, 1231, 1044, 873, 810, 722 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{15}H_{25}S_2^+$ [M +H]$^+$: 269.13922; found: 269.13923.

1-Octyl-2-phenyldisulfane (20)



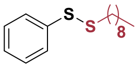
Following general procedure E, the title compound (17.5 mg, 69% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2{\cdot}6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-octyl benzenesulfonothioate (53 μL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 36 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.54 (d, *J* = 8 Hz, 2H), 7.32 (m, 2H), 7.22 (m, 1H), 2.74 (t, *J* = 8 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.39 – 1.33 (m, 2H), 1.31 – 1.25 (m, 8H), 0.88 (t, *J* = 8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.8, 129.1, 127.5, 126.8, 39.1, 31.9, 29.3, 29.0, 28.6, 22.8, 14.2.

The data is consistent with the literature.[15]

1-Nonyl-2-phenyldisulfane (21)



Following general procedure F, the title compound (16.4 mg, 61% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), *S*-nonyl benzenesulfonothioate (60 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2{\cdot}6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

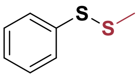
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.55 – 7.52 (m, 2H), 7.34 – 7.30 (m, 2H), 7.24 – 7.19 (m, 1H), 2.74 (t, *J* = 8.0 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.39 – 1.33 (m, 2H), 1.24 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.8, 129.1, 127.5, 126.8, 39.1, 32.0, 29.6, 29.4, 29.3, 28.9, 28.6, 22.8, 14.3.

IR (ATR): ν 3061, 2923, 2853, 1734, 1579, 1467, 1440, 1070, 1023, 737, 688 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{15}H_{24}S_2^+$ [M +H]$^+$: 269.13922; found: 269.13967.

1-Methyl-2-phenyldisulfane (22)



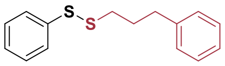
Following general procedure F, the title compound (9 mg, 58% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2{\cdot}6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.01 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-methyl benzenesulfonothioate (29 μL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.47 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.18 – 7.16 (m, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.1, 129.2, 127.8, 127.0, 23.1.

The data is consistent with the literature.[16]

1-Phenyl-2-(3-phenylpropyl)disulfane (23)



Following general procedure F, the title compound (16.7 mg, 65% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et$_2$O), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(3-phenylpropyl) benzenesulfonothioate (48 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 39 h.

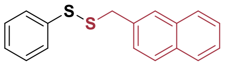
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.58 – 7.48 (m, 2H), 7.32 (m 2H), 7.29 – 7.16 (m, 4H), 7.15 – 7.09 (m, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.05 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.3, 137.7, 129.1, 128.6, 128.5, 127.8, 126.9, 126.1, 38.2, 34.4, 30.3.

IR (ATR): ν 3060, 3025, 2926, 2853, 1579, 1475, 1440, 1070, 1024, 738, 693 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{15}H_{16}S_2^+$ [M]$^+$: 260.06880; found: 260.06889.

1-(Naphthalen-2-ylmethyl)-2-phenyldisulfan (24)



Following general procedure E, the title compound (13.6 mg, 48% yield) was isolated as a white solid after flash chromatography on silica gel (eluent: 400:1 to 20:1 hexane: Et$_2$O), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(naphthalen-2-ylmethyl) benzenesulfonothioate (60.0 mg, 0.2 mmol, 2.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 36 h.

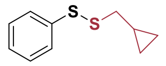
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.91 – 7.84 (m, 3H), 7.79 (s, 1H), 7.61 – 7.53 (m, 4H), 7.50 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 4.20 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.8, 129.1, 127.5, 126.8, 39.1, 32.0, 29.6, 29.4, 29.3, 28.9, 28.6, 22.8, 14.3.

IR (ATR): ν 3053, 2925, 1575, 1471, 1434, 900, 867, 827, 736, 686 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{17}H_{14}S_2^+$ [M]$^+$: 282.05315; found: 282.05356.

1-(Cyclopropylmethyl)-2-phenyldisulfane (25)



Following general procedure F, the title compound (14.9 mg, 79% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(cyclopropylmethyl) benzenesulfonothioate (35 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

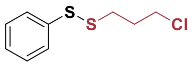
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.62 – 7.47 (m, 2H), 7.35 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 2.70 (d, 2H), 1.15 – 0.91 (m, 1H), 0.58 – 0.49 (m, 2H), 0.28 – 0.19 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.0, 129.0, 127.3, 126.7, 45.3, 10.9, 5.8.

IR (ATR): ν 3398, 2325, 2258, 2117, 1649, 1150, 998, 824, 763 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{10}H_{13}S_2^+$ [M +H]$^+$: 197.04532; found: 197.04587.

1-(3-Chloropropyl)-2-phenyldisulfane (26)



Following general procedure G, the title compound (13.5 mg, 62% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(3-chloropropyl) benzenesulfonothioate (50 mg, 0.2 mmol, 2 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (0.8 mg, 0.005 mmol, 5 mol%), 4'-(p-tolyl)-2,2':6',2''-terpyridine (1.7 mg, 0.005 mmol, 5 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

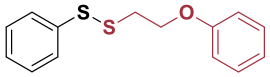
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.64 – 7.53 (m, 2H), 7.41 – 7.34 (m, 2H), 7.31 – 7.25 (m, 1H), 3.65 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.19 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 129.2, 128.0, 127.2, 43.2, 35.5, 31.3.

IR (ATR): v 2955, 2916, 1579, 1475,1437, 1303, 1263, 1069, 1022, 739, 688 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_9H_{12}S_2^+$ [M +H]$^+$: 219.00767; found: 219.00720.

1-(2-Phenoxyethyl)-2-phenyldisulfane (27)



Following general procedure E, the title compound (18.0 mg, 70% yield) was isolated as awhite solide after flash chromatography on silica gel (eluent: 80:1 to 50:1 hexane: Et_2O), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(2-phenoxyethyl) benzenesulfonothioate (58.8 mg, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 39 h.

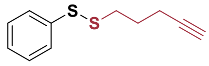
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ = 7.57 – 7.55 (m, 2H), 7.35 – 7.32 (m, 2H), 7.29 – 7.23 (m, 3H), 6.95 – 6.92 (m, 1H), 6.91 – 6.87 (m, 2H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.17 (t, *J* = 6.0 Hz, 2H).

^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 158.0, 136.4, 129.5, 129.3, 127.1, 127.1, 120.9, 114.5, 65.2, 37.6.

IR (ATR): v 3395, 1652, 996, 824, 762 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{14}H_{14}S_2^+$ [M]$^+$: 262.04806; found: 262.04852.

1-(Pent-4-yn-1-yl)-2-phenyldisulfane (28)



Following general procedure F, the title compound (11.6 mg, 56% yield) was isolated as a brown oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(pent-4-yn-1-yl) benzenesulfonothioate (39 μL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

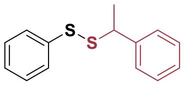
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.48 (m, 2H), 7.35 – 7.31 (m, 2H), 7.25 – 7.21 (m,1H), 2.85 (d, *J* = 8.0 Hz, 2H), 2.30 (td, *J* = 8.0, 4.0 Hz, 2H), 1.96 (t, *J* = 2.0 Hz, 1H), 1.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 129.1, 127.8, 127.0, 83.3, 69.3, 37.4, 27.4, 17.3.

IR (ATR): v 3297, 2922, 2853, 1715, 1579, 1473, 1438, 1253, 1068, 1023, 739, 689 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{11}H_{12}S_2^+$ [M]$^+$: 208.03750; found: 208.03821.

1-Phenyl-2-(1-phenylethyl)disulfane (29)



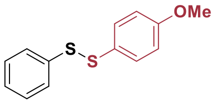
Following general procedure E, the title compound (16.5 mg, 67% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 100:1 to 50:1 hexane: Et_2O), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (1.6 mg, 0.01 mmol, 10 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(1-phenylethyl) benzenesulfonothioate (45 μL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 36 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 7.7 Hz, 2H), 7.26 – 7.15 (m, 7H), 7.14 – 7.10 (m, 1H), 4.05 (q, *J* = 7.0 Hz, 1H), 1.62 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.78, 129.0, 128.7, 127.8, 127.8, 127.6, 126.7, 50.4, 20.7.

The data is consistent with the literature.[17]

1-(4-Methoxyphenyl)-2-phenyldisulfane (30)



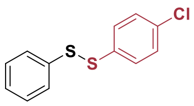
Following general procedure F, the title compound (15.5 mg, 63% yield) was isolated as a yellow oil after flash chromatography on silica gel (eluent: 100:1 to 50:1 hexane: Et_2O), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2·6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

^1H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 7.47 (m, 2H), 7.46 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.19 (m, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 137.6, 131.9, 129.1, 128.4, 128.2, 127.4, 114.8, 55.5.

The data is consistent with the literature.[18]

1-(4-Chlorophenyl)-2-phenyldisulfane (31)



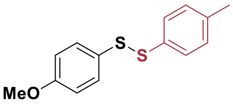
Following general procedure F, the title compound (16.4 mg, 65% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (eluent: hexane), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(4-chlorophenyl) benzenesulfonothioate (56.7 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2·6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

^1H NMR (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, Chloroform-*d*) δ = 7.47 – 7.40 (m, 2H), 7.40 – 7.35 (m, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.18 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 135.8, 133.4, 129.3, 129.3, 129.2, 127.9, 127.6.

The data is consistent with the literature.[18]

1-(4-Methoxyphenyl)-2-(p-tolyl)disulfane (32)



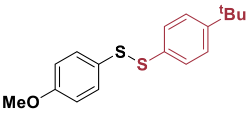
Following general procedure F, the title compound (13.0 mg, 50% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (400:1 to 200:1 hexane: Et_2O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (28.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(p-tolyl) benzenesulfonothioate (52.8 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2·6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

^1H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.33 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.86 – 6.81 (m, 2H), 3.79 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 137.7, 134.2, 132.1, 129.9, 129.3, 128.4, 114.8, 55.5, 21.2.

The data is consistent with the literature.[19]

1-(4-(Tert-butyl)phenyl)-2-(4-methoxyphenyl)disulfane (33)



Following general procedure F, the title compound (14.0 mg, 46% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (400:1 to 200:1 hexane: Et_2O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (28.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (71.2 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2·6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

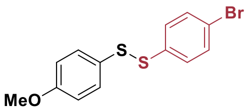
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.44 (dd, *J* = 8.8, 6.8 Hz, 4H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.9, 150.9, 134.2, 131.8, 128.6, 128.5, 126.2, 114.8, 55.5, 34.7, 31.4.

IR (ATR): ν 2958, 2867, 1589, 1488, 1460, 1397, 1365, 1288, 1244, 1173, 1111, 1030, 822 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{17}H_{20}OS_2^+$ [M]$^+$: 304.09501; found: 304.09510.

1-(4-Bromophenyl)-2-(4-methoxyphenyl)disulfane (34)



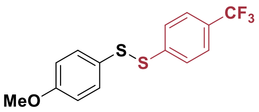
Following general procedure F, the title compound (18.7 mg, 57% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (400:1 to 200:1 hexane: Et$_2$O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (28.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(4-bromophenyl) benzenesulfonothioate (65.8 mg, 0.2 mmol, 2.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.51 – 7.28 (m, 6H), 6.85 – 6.81 (m, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 160.2, 136.9, 132.2, 132.2, 130.0, 127.6, 121.4, 114.9, 55.5.

The data is consistent with the literature.[18]

1-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)disulfane (35)



Following general procedure F, the title compound (17.4 mg, 55% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (400:1 to 200:1 hexane: Et$_2$O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (28.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(4-(trifluoromethyl)phenyl) benzenesulfonothioate (63.7 mg, 0.2 mmol, 2.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

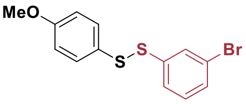
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 160.3, 142.5, 132.0, 129.0 (q, *J* = 30.3 Hz), 127.2, 127.1, 126.0 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 272.7 Hz), 115.03, 55.52.

^{19}F NMR (376 MHz, CDCl$_3$) δ -62.48 (3F).

The data is consistent with the literature.[18]

1-(3-Bromophenyl)-2-(4-methoxyphenyl)disulfane (36)



Following general procedure F, the title compound (21.2 mg, 65% yield) was isolated as a pale yellow oil after flash chromatography on silica gel (eluent: 400:1 to 200:1 hexane: Et$_2$O), starting from *S*-(4-methoxyphenyl) benzenesulfonothioate (28.0 mg, 0.1 mmol, 1.0 equiv.), *S*-(3-bromophenyl) benzenesulfonothioate (65.8 mg, 0.2 mmol, 2.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

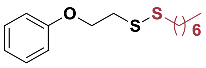
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.68 – 7.67 (m, 1H), 7.42 (m, 3H), 7.35 (m, 1H), 7.19 – 7.14 (m, 1H), 6.86 – 6.83 (m, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 160.2, 139.9, 132.2, 130.4, 130.2, 127.5, 126.4, 123.1, 115.0, 55.5.

IR (ATR): ν 2936, 1566, 1399, 1289, 1245, 1173, 1029, 822, 744, 675 cm^{-1}.

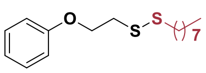
HRMS (EI) *m/z* Calcd for $C_{13}H_{11}BrOS_2^+$ [M]$^+$: 325.9473; found: 325.94406.

1-Heptyl-2-(2-phenoxyethyl)disulfane (37)



Following general procedure F, the title compound (16 mg, 55% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-heptyl benzenesulfonothioate (49 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h. **^{1}H NMR (400 MHz, DMSO-d_6)** δ = 7.31 – 7.27 (m, 2H), 6.98 – 6.91 (m, 3H), 4.21 (t, *J* = 6.2 Hz , 2H), 3.08 (t, *J* = 6.2 Hz, 2H), 2.76 – 2.67 (m, 2H), 1.64 – 1.57 (m, 2H), 1.34 – 1.16 (m, 8H), 0.88 – 0.81 (m, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 130.0, 120.8, 114.5, 65.5, 37.9, 37.2, 31.1, 28.5, 28.2, 27.7, 22.0, 13.9.
IR (ATR): ν 2924, 2855, 1596, 1493, 1462, 1378, 1296, 1238, 1171, 1075, 1031, 878, 751, 690 cm^{-1}.
HRMS (EI) *m/z* Calcd for $C_{15}H_{24}OS_2^+$ [M]$^+$: 284.12631; found: 284.12646.

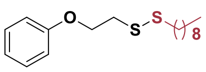
1-Octyl-2-(2-phenoxyethyl)disulfane (38)



Following general procedure F, the title compound (16.7 mg, 57% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-octyl benzenesulfonothioate (53 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

^{1}H NMR (400 MHz, DMSO-d_6) δ = δ = 7.31 – 7.27 (m, 2H), 6.96 – 6.93 (m, 3H), 4.20 (t, *J* = 6.0 Hz, 2H), 3.07 (d, *J* = 6.0 Hz, 2H), 2.74 – 2.69 (m, 2H), 1.64 – 1.57 (m, 2H), 1.33 – 1.21 (m, 10H), 0.85 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 129.6, 120.8, 114.5, 65.5, 37.9, 37.2, 31.2, 28.6, 28.5, 28.5, 27.8, 22.1, 14.0.
IR (ATR): ν 2923, 2854, 1596, 1494, 1463, 1378, 1296, 1238, 1172, 1074, 1031, 877, 750, 689 cm^{-1}.
HRMS (EI) *m/z* Calcd for $C_{16}H_{26}OS_2^+$ [M]$^+$: 298.14196; found: 298.14208.

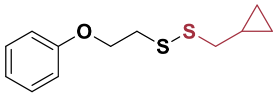
1-Nonyl-2-(2-phenoxyethyl)disulfane (39)



Following general procedure F, the title compound (14.3 mg, 46% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), *S*-nonyl benzenesulfonothioate (60 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 2H), 6.99 – 6.91 (m, 3H), 4.24 (t, *J* = 7.5 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H), 2.74 – 2.68 (m, 2H), 1.68 (m, 2H), 1.42 – 1.24 (m, 14H), 0.91 – 0.86 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 129.7, 121.2, 114.8, 66.4, 39.5, 37.7, 32.0, 29.6, 29.4 (2C), 29.3, 28.7, 22.8, 14.3.
IR (ATR): ν 2923, 2854, 1596, 1494, 1462, 1378, 1297, 1238, 1171, 1074, 1032, 877, 751, 690 cm^{-1}.
HRMS (EI) *m/z* Calcd for $C_{17}H_{28}OS_2^+$ [M]$^+$: 312.15761; found: 312.15783.

1-(Cyclopropylmethyl)-2-(2-phenoxyethyl)disulfane (40)



Following general procedure F, the title compound (10.9 mg, 45% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(cyclopropylmethyl) benzenesulfonothioate (35 µL, 0.2 mmol, 2 equiv.) in THF at 60 °C for 48 h.

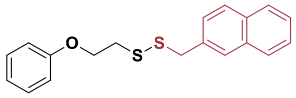
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.31 – 7.26 (m, 2H), 6.98 – 6.92 (m, 3H), 4.26 (t, *J* = 6.0 Hz, 2H), 3.09 (t, *J* = 6.0 Hz, 2H), 2.70 (d, *J* = 8 Hz, 2H), 1.19 – 1.00 (m, 1H), 0.67 – 0.53 (m, 2H), 0.34 – 0.23 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.6, 129.7, 121.2, 114.8, 66.4, 45.6, 37.9, 11.1, 5.7.

IR (ATR) : v 3073, 3004, 2922, 2867, 1595, 1493, 1464, 1418, 1381, 1296, 1237, 1172, 1075, 1017, 827, 752, 690 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{12}H_{17}OS_2^+$ [M +H]$^+$: 241.07154; found: 241.07243.

1-(Naphthalen-2-ylmethyl)-2-(2-phenoxyethyl)disulfane (41)



Following general procedure F, the title compound (15.6 mg, 48% yield) was isolated as a white solid after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et$_2$O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), *S*-(naphthalen-2-ylmethyl) benzenesulfonothioate (60.0 mg, 0.2 mmol, 2.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

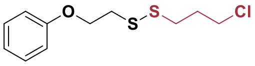
^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.83 – 7.80 (m, 3H), 7.74 (s, 1H), 7.51 – 7.45 (m, 3H), 7.26 – 7.22 (m , 2H), 6.96 – 6.92 (m, 1H), 6.81 – 6.79 (m, 2H), 4.07 (s, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 2.77 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.5, 134.7, 133.4, 132.8, 129.6, 128.6, 128.3, 127.9, 127.9, 127.3, 126.5, 126.2, 121.1, 114.7, 66.2, 44.2, 37.6.

IR (ATR) : v 3055, 2922, 2866, 1692, 1593, 1493, 1460, 1379, 1294, 1241, 1170, 1076, 1015, 865, 824, 749, 689 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{19}H_{18}OS_2^+$ [M +H]$^+$:326.07936 ; found:326.07946.

1-(3-Chloropropyl)-2-(2-phenoxyethyl)disulfane (42)



Following general procedure F, the title compound (12.3 mg, 47% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et$_2$O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), *S*-(3-chloropropyl) benzenesulfonothioate (50 mg, 0.2 mmol, 2.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

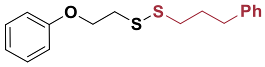
^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.33 – 7.26 (m, 2H), 7.00 – 6.90 (m, 3H), 4.25 (t, *J* = 7.5 Hz, 2H), 3.63 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.22 – 2.13 (m, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 158.5, 129.7, 121.3, 114.8, 66.2, 43.2, 37.8, 35.6, 31.6.

IR (ATR) : v 2922, 2865, 1595, 1493, 1463, 1299, 1237, 1172, 1073, 1029, 877, 753, 690 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{11}H_{15}ClOS_2^+$ [M]$^+$: 262.02474; found: 262.02484.

1-(2-Phenoxyethyl)-2-(3-phenylpropyl)disulfane (43)

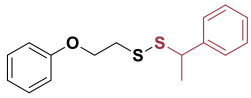


Following general procedure F, the title compound (15.1 mg, 50% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et$_2$O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), Ni(BF$_4$)$_2$·6H$_2$O (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(3-phenylpropyl) benzenesulfonothioate (48 μL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.37 – 7.26 (m, 4H), 7.23 – 7.17 (m, 3H), 7.00 – 6.90 (m, 3H), 4.23 (t, *J* = 6.0 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 4H), 2.09 – 1.99 (m, 2H). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 158.5, 141.3, 129.7, 128.6, 128.6, 126.1, 121.2, 114.8, 66.3, 38.4, 37.7, 34.5, 30.6. **IR (ATR) :** v 3062, 3027, 2924, 2857, 1595, 1493, 1459, 1381, 1295, 1238, 1172, 1074, 1029, 877, 748, 694 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{17}H_{20}OS_2^+$ [M]$^+$: 304.09501; found: 304.09444.

1-(2-Phenoxyethyl)-2-(1-phenylethyl)disulfane (44)



Following general procedure F, the title compound (14.5 mg, 50% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-(1-phenylethyl) benzenesulfonothioate (45 µL, 0.2 mmol, 2 equiv.) in THF at 60 °C for 48 h.

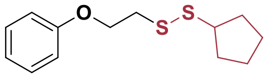
^{1}H NMR (400 MHz, CDCl₃) δ = 7.39 – 7.22 (m, 7H), 6.98 – 6.94 (m,1H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.11 – 4.04 (m, 3H), 2.69 – 2.65 (m, 2H), 1.69 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl₃) δ 158.5, 142.2, 129.6, 128.7, 127.8, 121.1, 114.8, 66.2, 50.4, 37.5, 20.7.

IR (ATR) : ν 3061, 3030, 2967, 2923, 2866, 1595, 1492, 1456, 1374, 1297, 1238, 1172, 1077, 1028, 878, 754, 693 cm^{-1}.

HRMS (APCI) *m/z* Calcd for $C_{16}H_{19}OS_2^+$ $[M+H]^+$: 291.08719; found: 291.08779.

1-Cyclopentyl-2-(2-phenoxyethyl)disulfane (45)



Following general procedure F, the title compound (16.5 mg, 65% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl)benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-cyclopentyl benzenesulfonothioate (38 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

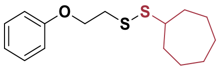
^{1}H NMR (600 MHz, CDCl₃) δ = 7.33 – 7.27 (m, 2H), 6.98 – 6.95 (m, 1H), 6.95 – 6.91 (m, 2H), 4.25 (td, *J* = 6.9, 0.8 Hz, 2H), 3.34 – 3.29 (m, 1H), 3.07 (td, *J* = 6.9, 0.8 Hz, 2H), 2.02 – 1.96 (m, 2H), 1.79 – 1.73 (m, 2H), 1.71 – 1.66 (m, 2H), 1.63 – 1.57 (m, 2H).

^{13}C NMR (151 MHz, CDCl₃) δ 158.6, 129.6, 121.2, 114.8, 66.5, 50.5, 37.9, 33.1, 24.8.

IR (ATR) : ν 3034, 2951, 2863, 2325, 2091, 2000, 1595, 1493, 1465, 1379, 1298, 1238, 1171, 1075, 1031, 879, 830, 753, 689 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{13}H_{18}OS_2^+$ $[M]^+$: 254.07936; found: 254.07944.

1-Cycloheptyl-2-(2-phenoxyethyl)disulfane (46)



Following general procedure F, the title compound (19.4 mg, 69% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 200:1 to 100:1 hexane: Et_2O), starting from *S*-(2-phenoxyethyl) benzenesulfonothioate (29.4 mg, 0.1 mmol, 1.0 equiv.), $Ni(BF_4)_2 \cdot 6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) and *S*-cycloheptyl benzenesulfonothioate (44 µL, 0.2 mmol, 2.0 equiv.) in THF at 60 °C for 48 h.

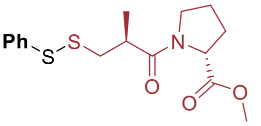
^{1}H NMR (600 MHz, CDCl₃) δ = 7.31 – 7.28 (m, 2H), 6.98 – 6.96 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.93 (dq, *J* = 9.3, 4.6 Hz, 1H), 2.10 (m, 2H), 1.73 (m, 2H), 1.57 (m, 6H), 1.47 – 1.41 (m, 2H).

^{13}C NMR (151 MHz, CDCl₃) δ 158.6, 129.6, 121.1, 114.7, 66.4, 51.4, 38.1, 34.3, 28.3, 26.0.

IR (ATR) : ν 3036, 2922, 2853, 2083, 1595, 1493, 1459, 1297, 1238, 1172, 1031, 877, 827, 751, 690 cm^{-1}.

HRMS (EI) *m/z* Calcd for $C_{15}H_{22}OS_2^+$ $[M]^+$: 282.11066; found: 282.11076.

Methyl ((S)-2-methyl-3-(phenyldisulfaneyl)propanoyl)-D-prolinate (47)



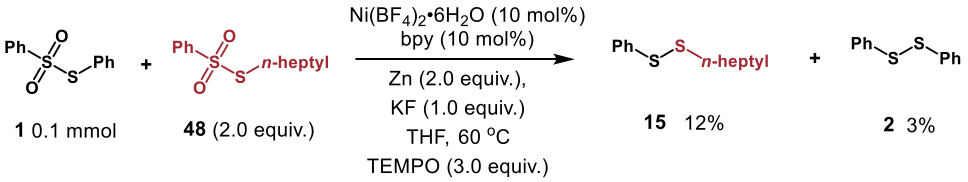
Following general procedure F, the title compound (20.4 mg, 60% yield) was isolated as a colorless oil after flash chromatography on silica gel (eluent: 2:1 to 1:1 hexane: Et_2O), starting from *S*-phenyl benzenesulfonothioate (25.0 mg, 0.1 mmol, 1.0 equiv.), methyl ((*S*)-2-methyl-3-(tosylthio)propanoyl)-D-prolinate (61.0 mg, 0.2 mmol, 2.0 equiv.), $Ni(BF_4)_2{\cdot}6H_2O$ (3.5 mg, 0.01 mmol, 10 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 15 mol%), Zn (13 mg, 0.2 mmol, 2.0 equiv.), KF (5.8 mg, 0.1 mmol, 1.0 equiv.) in THF at 60 °C for 48 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 4.49 (dd, *J* = 8.5, 3.4 Hz, 1H), 3.71 (s, 3H), 3.57 – 3.48 (m, 1H), 3.31 – 3.25 (m, 1H), 3.13 (dd, *J* = 13.2, 8.5 Hz, 1H), 3.10 – 2.93 (m, 1H), 2.69 (dd, *J* = 13.4, 5.4 Hz, 1H), 2.19 – 2.10 (m, 1H), 2.03 – 1.86 (m, 3H), 1.20 (d, *J* = 6.9 Hz, 3H).

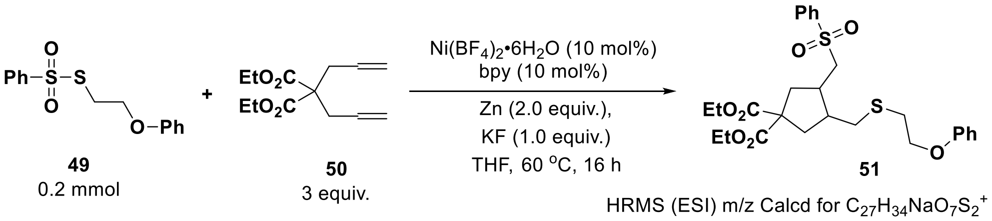
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 172.9, 137.6, 129.1, 127.7, 127.0, 58.7, 52.3, 46.7, 42.0, 37.6, 29.1, 24.9, 16.9.

The data is consistent with the literature.[15]

8. Control experiments

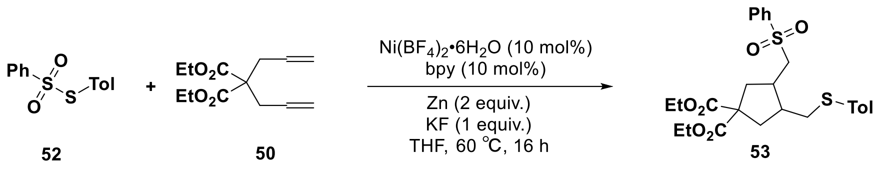


A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-phenyl benzenesulfonothioate **1** (0.1 mmol, 1.0 equiv), $Ni(BF_4)_2{\cdot}6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.), TEMPO (0.3 mmol, 3.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL), *S*-heptyl benzenesulfonothioate **48** (0.2 mmol, 2.0 equiv.,) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 16 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, **15** and **2** were obtained in 12%, 3% assay yield, respectively, (determined by GC analysis of the crude reaction mixtures using 0.1 mmol n-decane as internal standard).



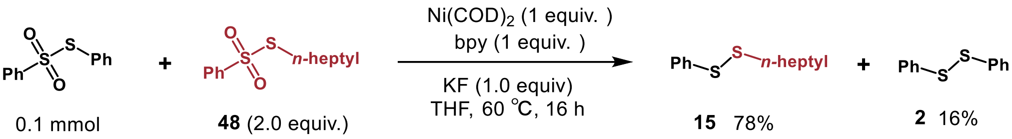
HRMS (ESI) m/z Calcd for $C_{27}H_{34}NaO_7S_2^+$ [M+Na]+: 557.1649 ; found: 557.1638

A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-(2-phenoxyethyl) benzenesulfonothioate (58.8 mg, 0.2 mmol,), $Ni(BF_4)_2{\cdot}6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.).The vial was close with a rubber septum, was introduced to a glovebox which with Argon atmosphere. Then anhydrous THF (1.0 mL), diethyl 2,2-diallylmalonate (0.6 mmol, 3 equiv.) were added via syringe, sequentially. The vial was close with a rubber septum and removed from the glovebox. The vial then was stirred at 60 °C for 16 h. Upon completion, the reaction mixture was analyzed by HRMS.

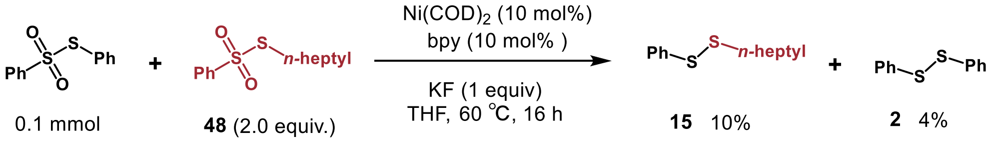


HRMS (ESI) m/z Calcd for $C_{26}H_{32}NaO_6S_2^+$ [M+Na]+: 527.1533 ; found: 527.1536

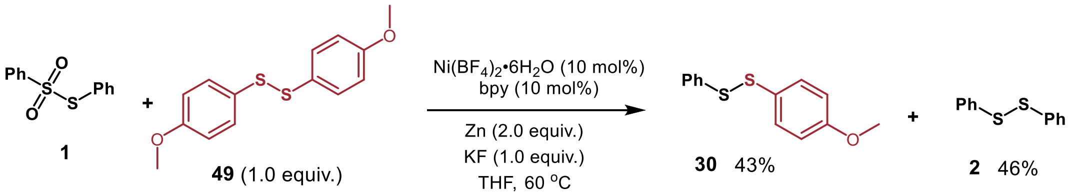
A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-(p-tolyl) benzenesulfonothioate (52.8 mg, 0.2 mmol), $Ni(BF_4)_2{\cdot}6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, was introduced to a glovebox which with Argon atmosphere. Then anhydrous THF (1.0 mL), diethyl 2,2-diallylmalonate (0.6 mmol, 3 equiv.) were added via syringe, sequentially. The vial was close with a rubber septum and removed from the glovebox. The vial then was stirred at 60 °C for 16 h. Upon completion, the reaction mixture was analyzed by HRMS.



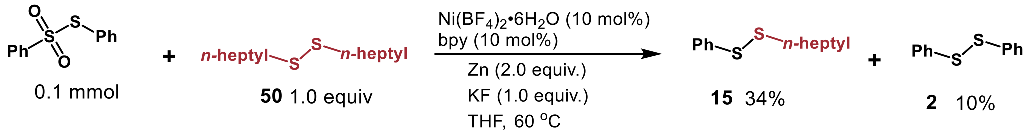
A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-phenyl benzenesulfonothioate **1** (0.1 mmol, 1.0 equiv), $Ni(COD)_2$ (0.1 mmol, 1.0 equiv.), 2,2'-bipyridine (0.1 mmol, 1.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL), *S*-heptyl benzenesulfonothioate **48** (0.2 mmol, 2.0 equiv.,) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 16 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, **15** and **2** were obtained in 78%, 16% assay yield, respectively, (determined by GC analysis of the crude reaction mixtures using 0.1 mmol n-decane as internal standard).



A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-phenyl benzenesulfonothioate **1** (0.1 mmol, 1.0 equiv), $Ni(COD)_2$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL), *S*-heptyl benzenesulfonothioate **48** (0.2 mmol, 2.0 equiv.,) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 16 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, **15** and **2** were obtained in 10%, 4% assay yield, respectively, (determined by GC analysis of the crude reaction mixtures using 0.1 mmol n-decane as internal standard).



A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-phenyl benzenesulfonothioate **1** (0.1 mmol, 1.0 equiv), 1,2-bis(4-methoxyphenyl)disulfane **49** (0.1 mmol, 1.0 equiv), $Ni(BF_4)_2·6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL) was added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 16 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, **30** and **2** were obtained in 43%, 46% assay yield, respectively, (determined by GC analysis of the crude reaction mixtures using 0.1 mmol n-decane as internal standard).



A oven-dried vial containing a teflon coated stirring bar was equipped with *S*-phenyl benzenesulfonothioate **1** (0.1 mmol, 1.0 equiv), $Ni(BF_4)_2·6H_2O$ (0.01 mmol, 10 mol%), 2,2'-bipyridine (0.01 mmol, 10 mol%), Zn (0.2 mmol, 2.0 equiv.), KF (0.1 mmol, 1.0 equiv.). The vial was close with a rubber septum, evacuated and backfilled with nitrogen three times. Then, degassed THF (1.0 mL), *S*-heptyl 1,2-diheptyldisulfane **50** (0.2 mmol, 2.0 equiv.,) were added via syringe. The septum and the vial were sealed with parafilm and then was stirred at 60 °C for 16 h. Upon completion, the crude reaction mixture was filtered and washed with EtOAc (10 mL), the mixture was concentrated by rotary evaporation. Then, **15** and **2** were obtained in 34%, 10% assay yield, respectively, (determined by GC analysis of the crude reaction mixtures using 0.1 mmol n-decane as internal standard).

9. References

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10. Copies of NMR Spectra

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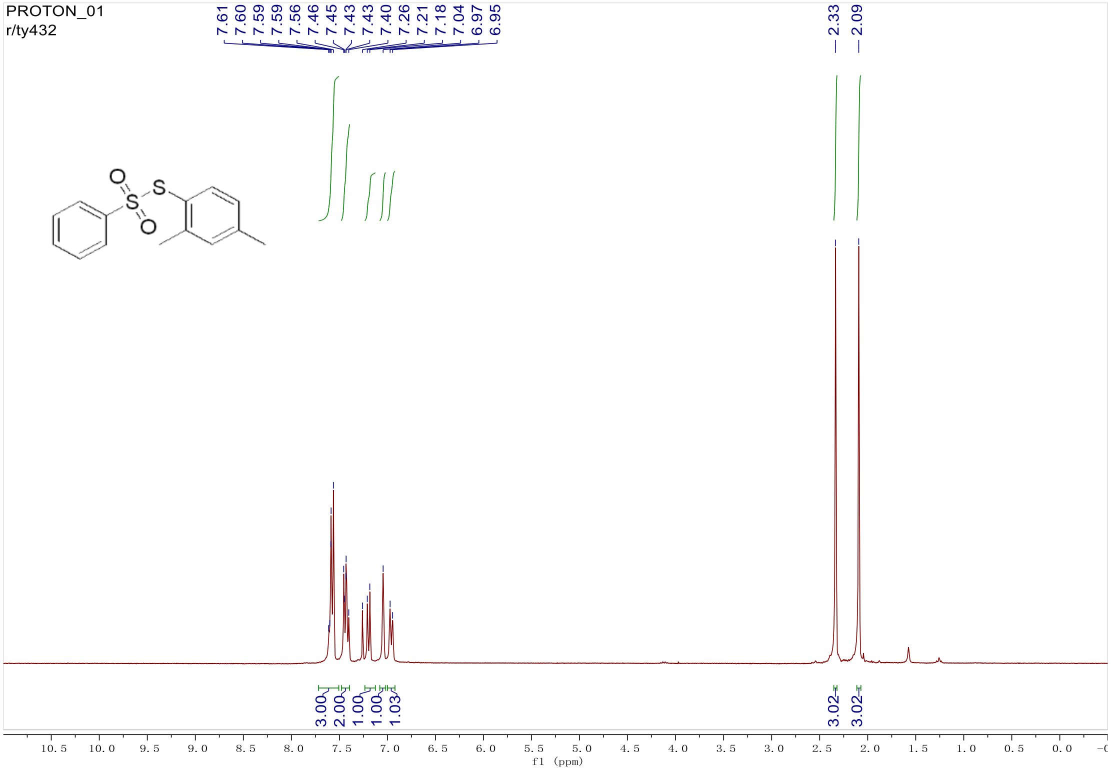

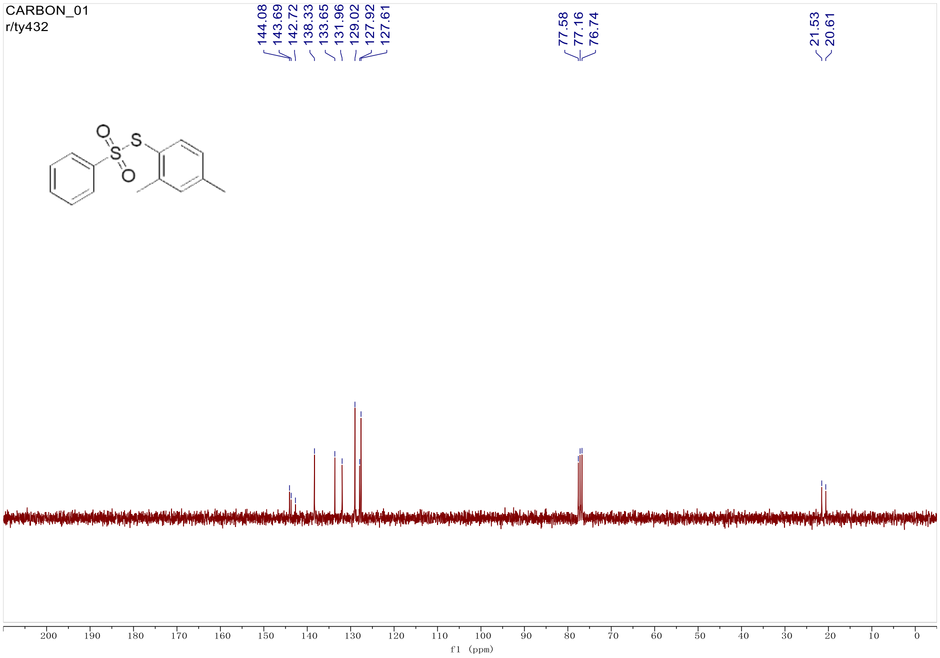

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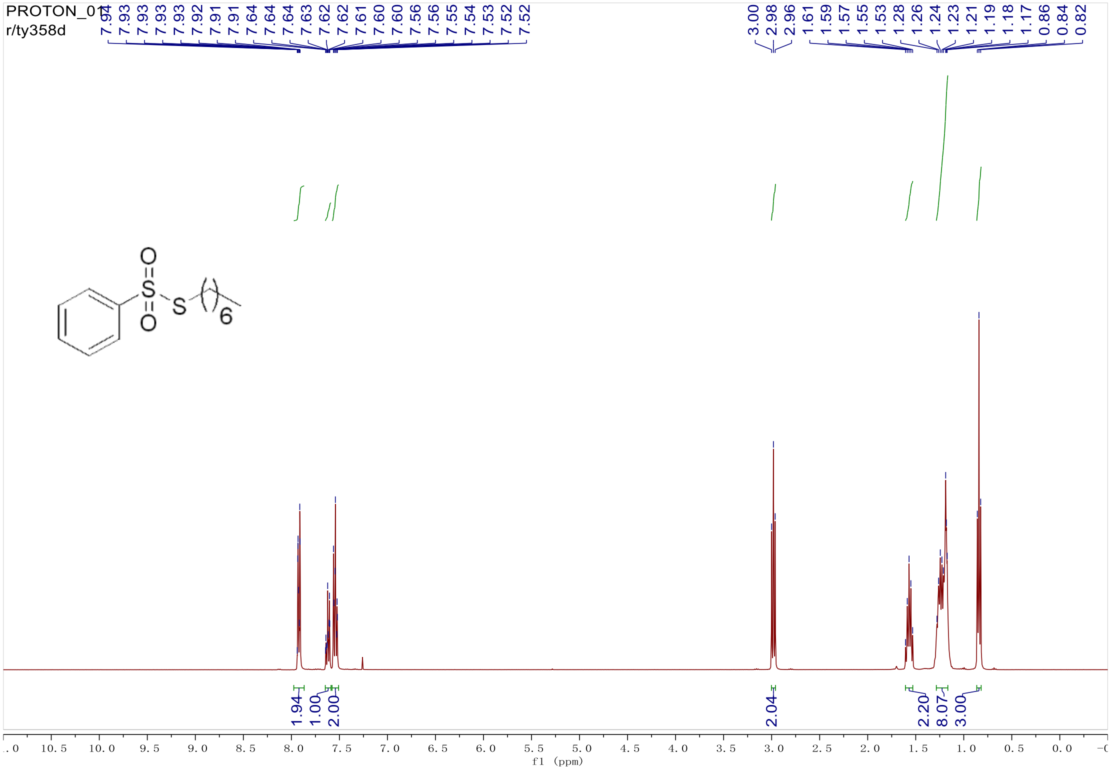

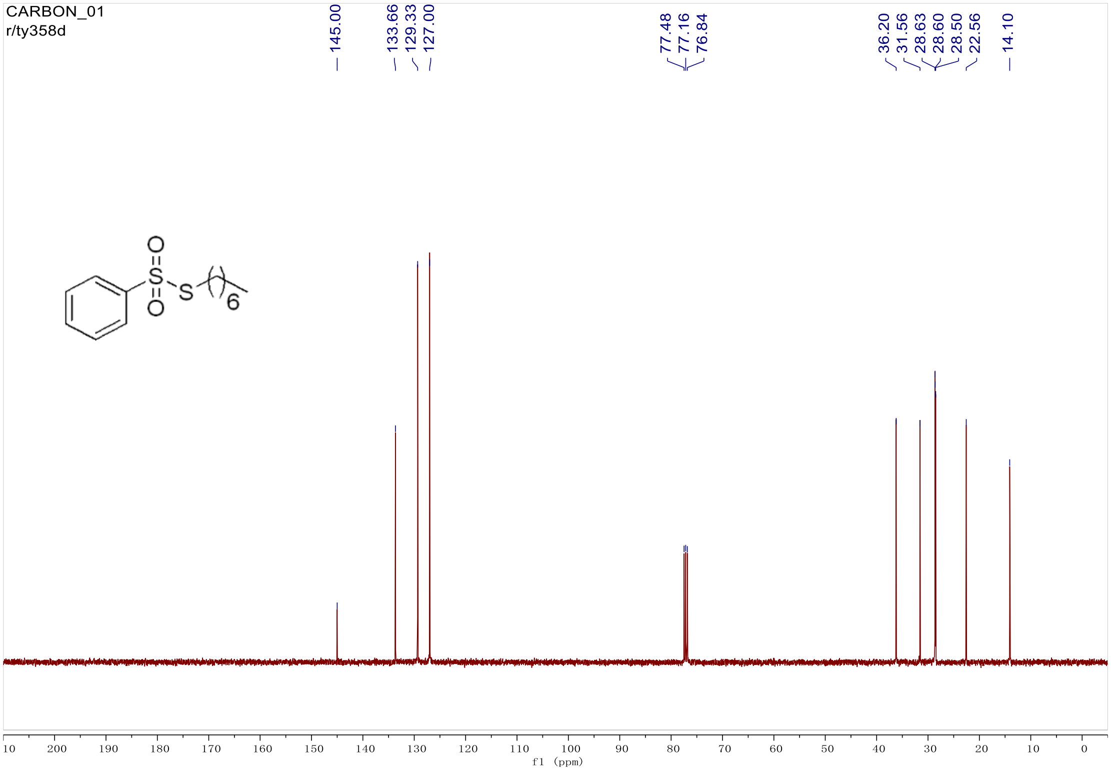

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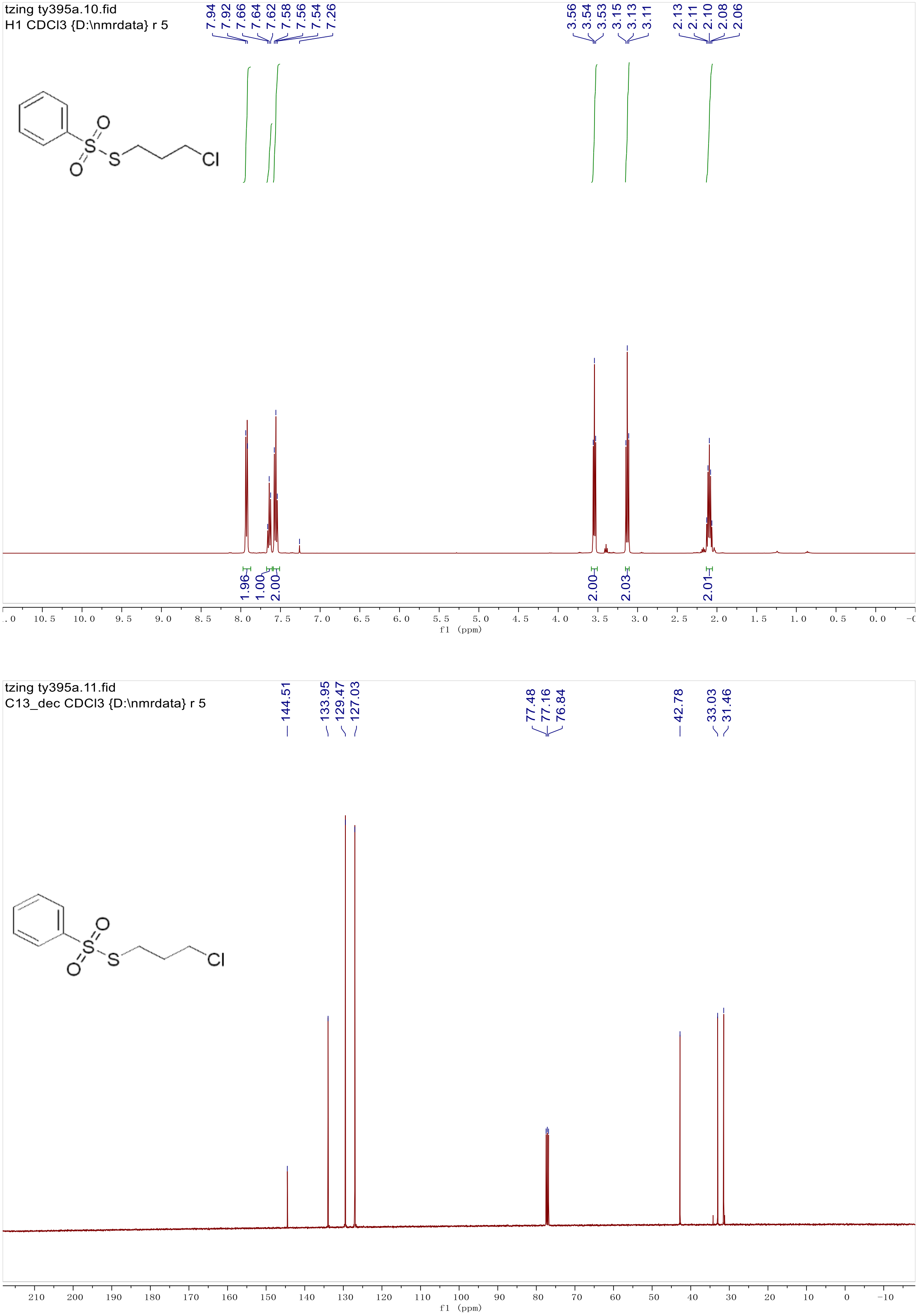

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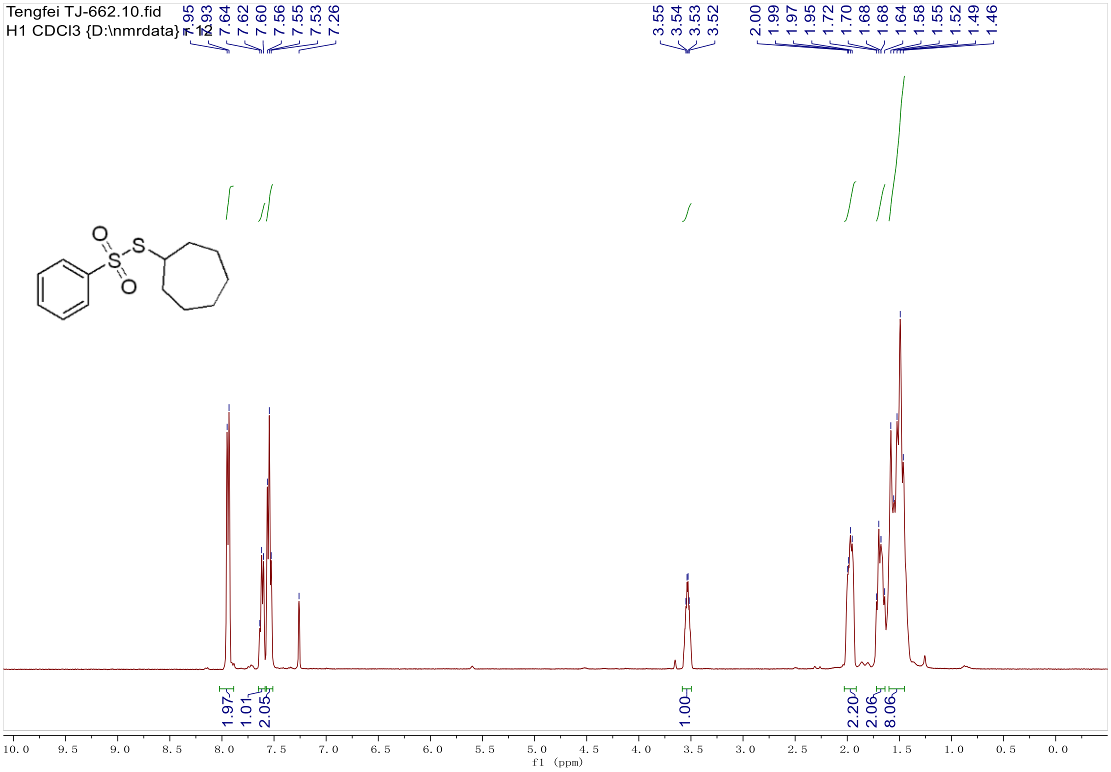

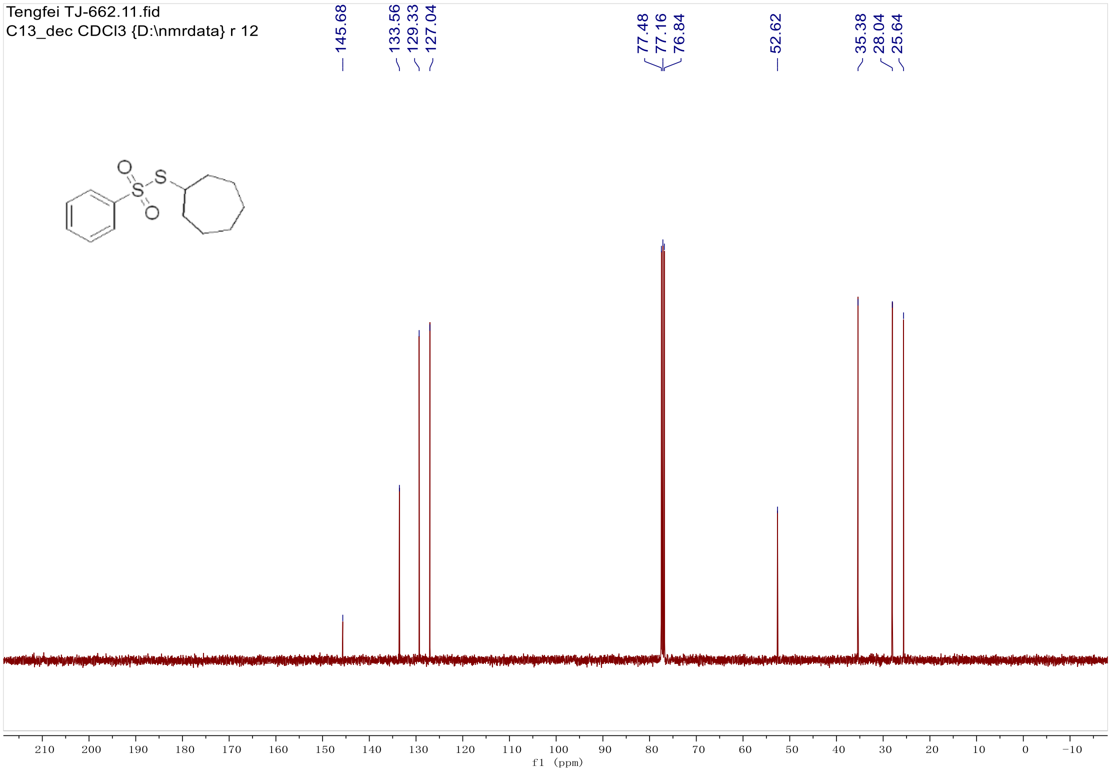

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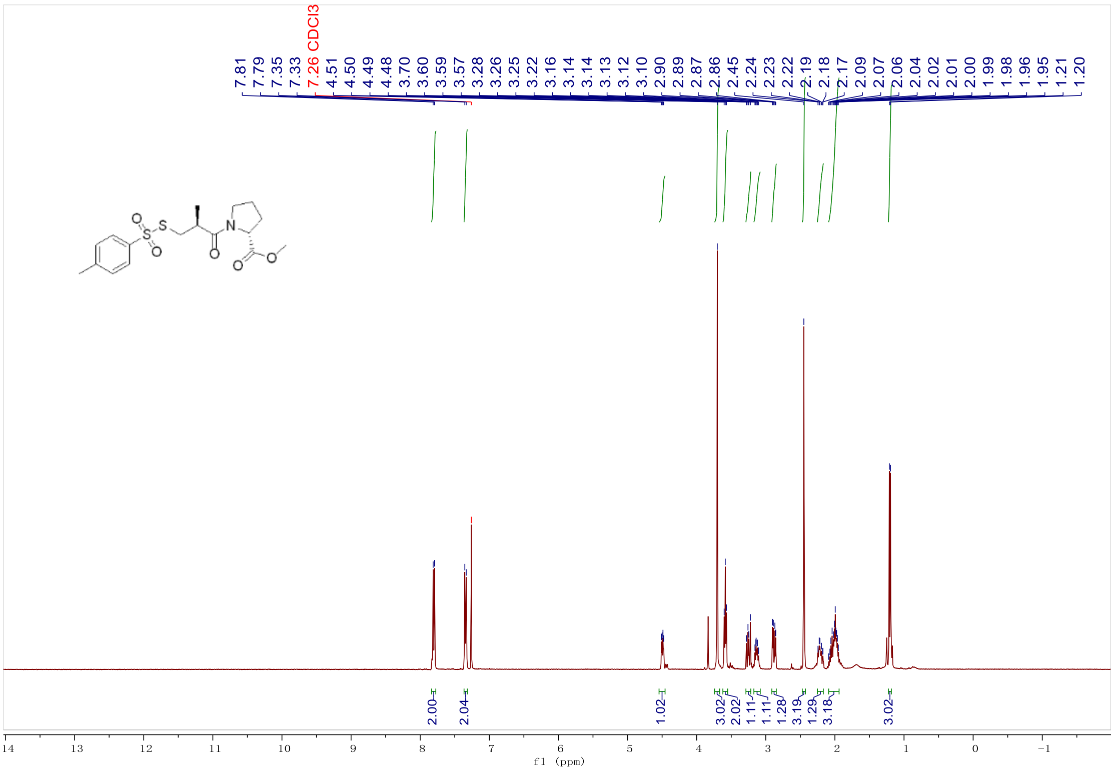

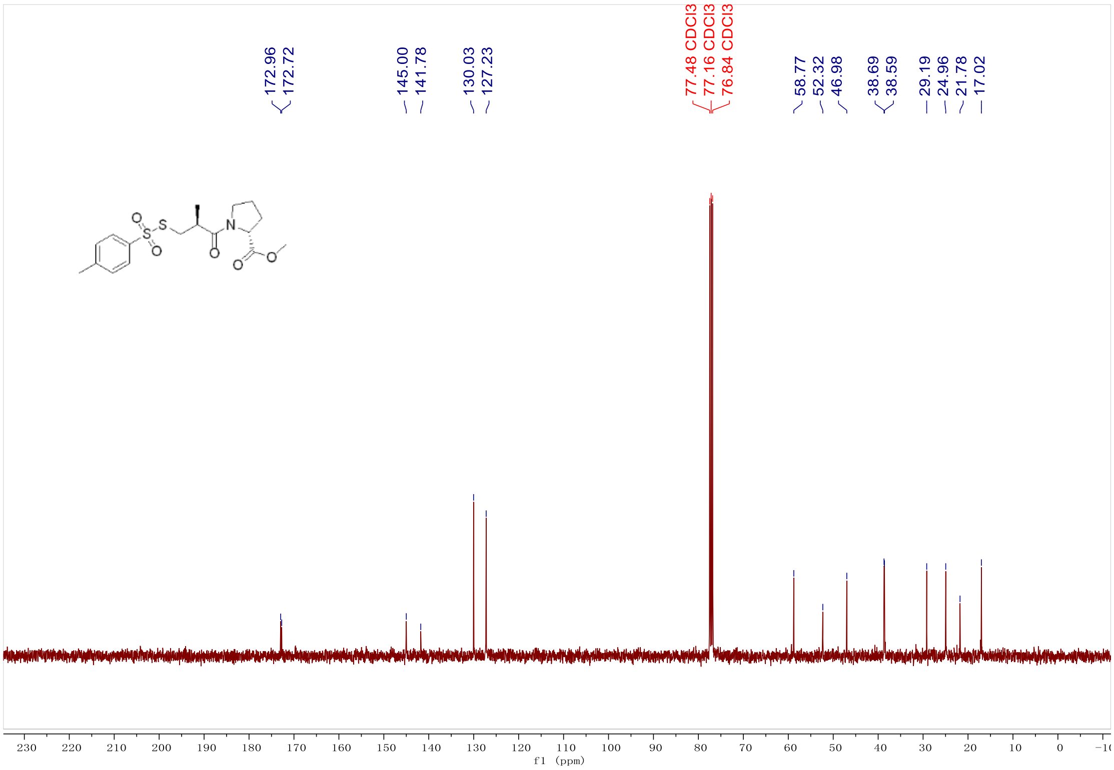

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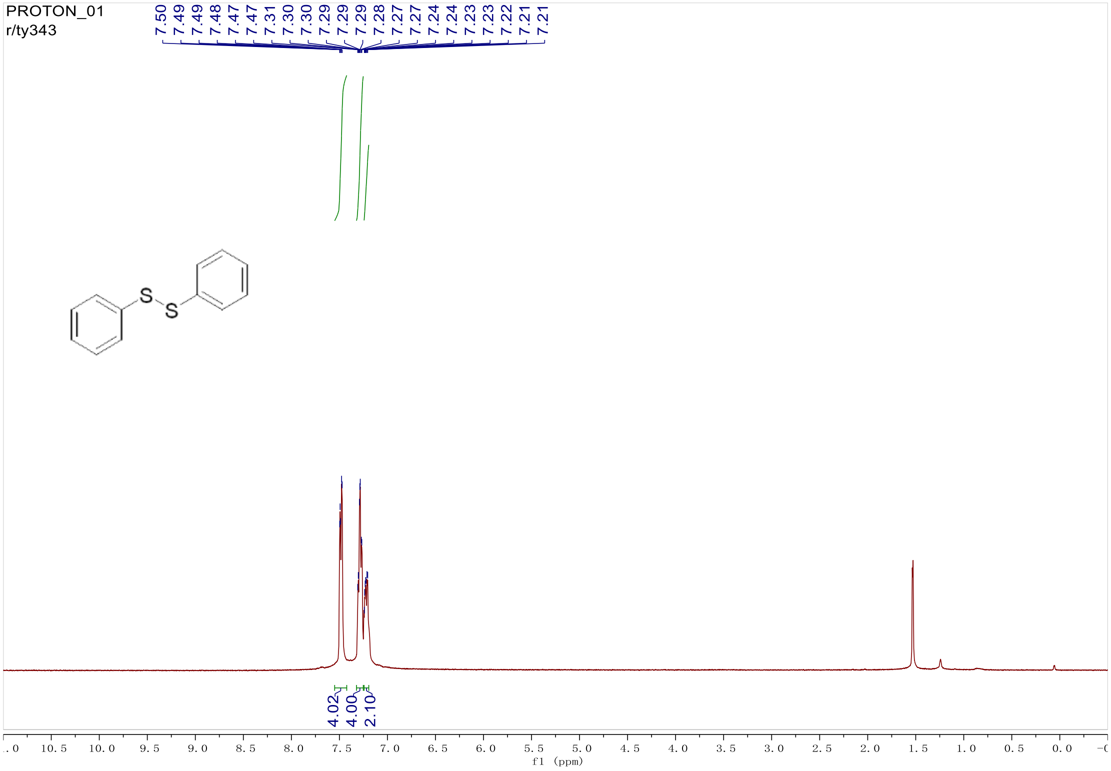
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7.49
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7.30
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.24
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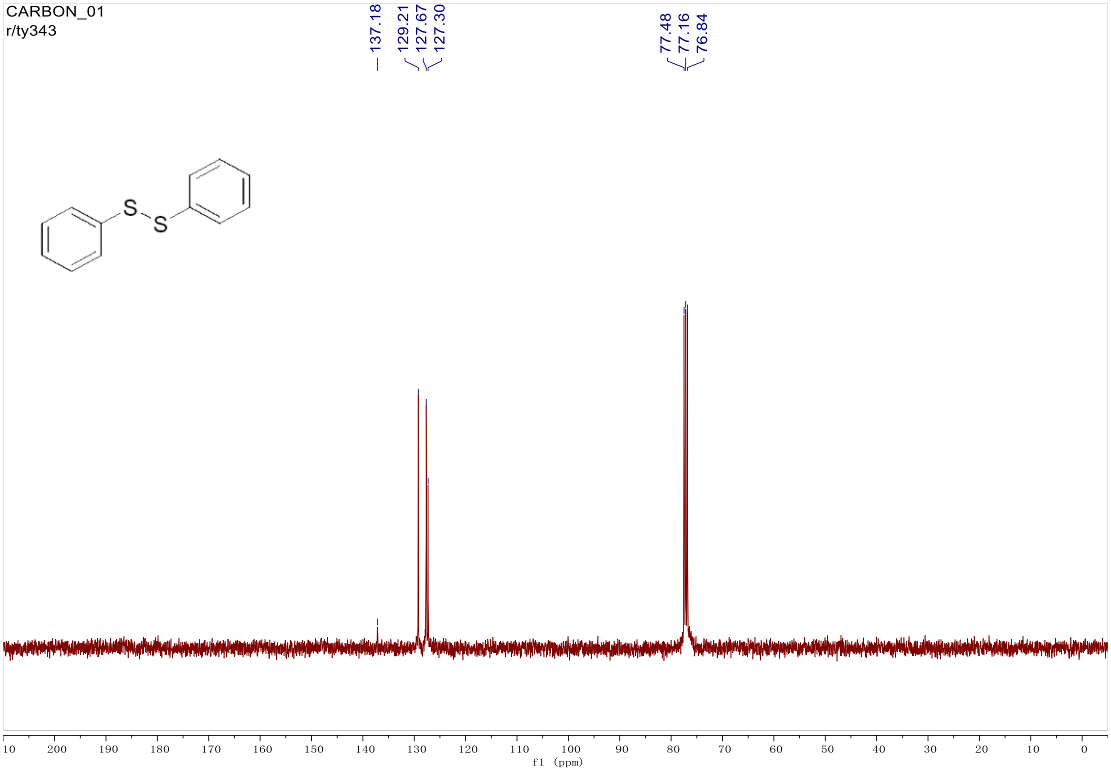
7.23
7.22
7.21
7.21
S
S
4.02
4.00
2.10
f1 (ppm)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r/ty343
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129.21
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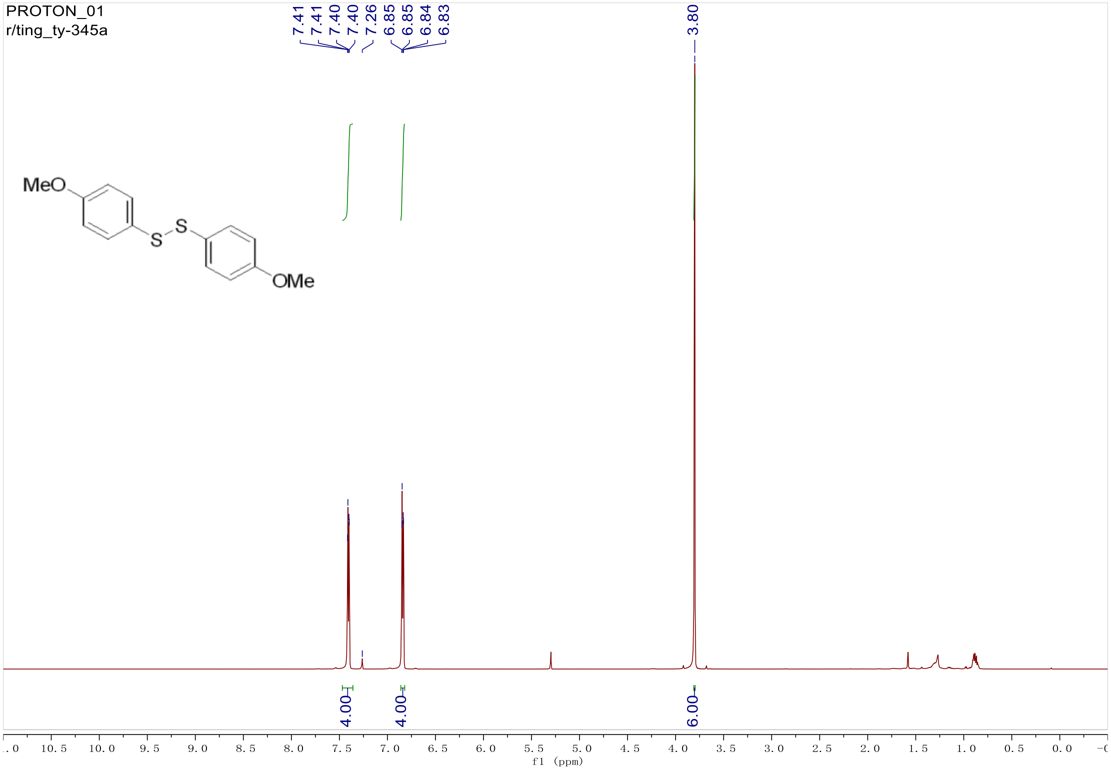
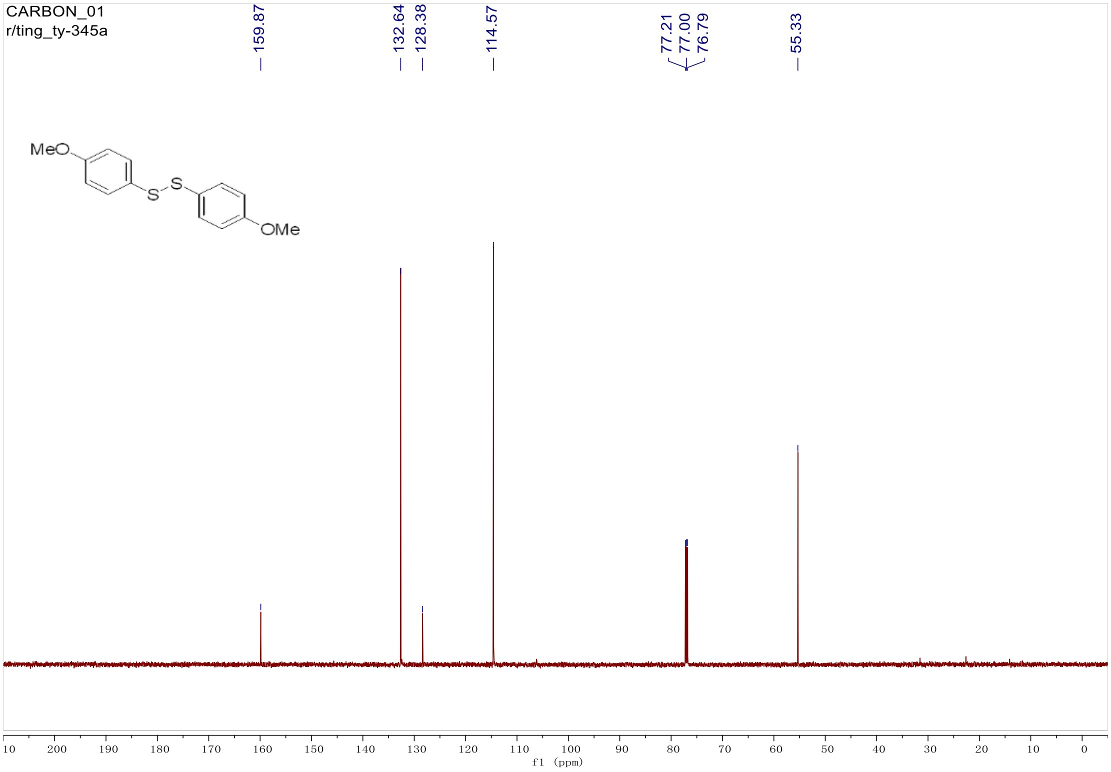
76.84
S
S
f1 (ppm)

^{1}H and ^{13}C of 3





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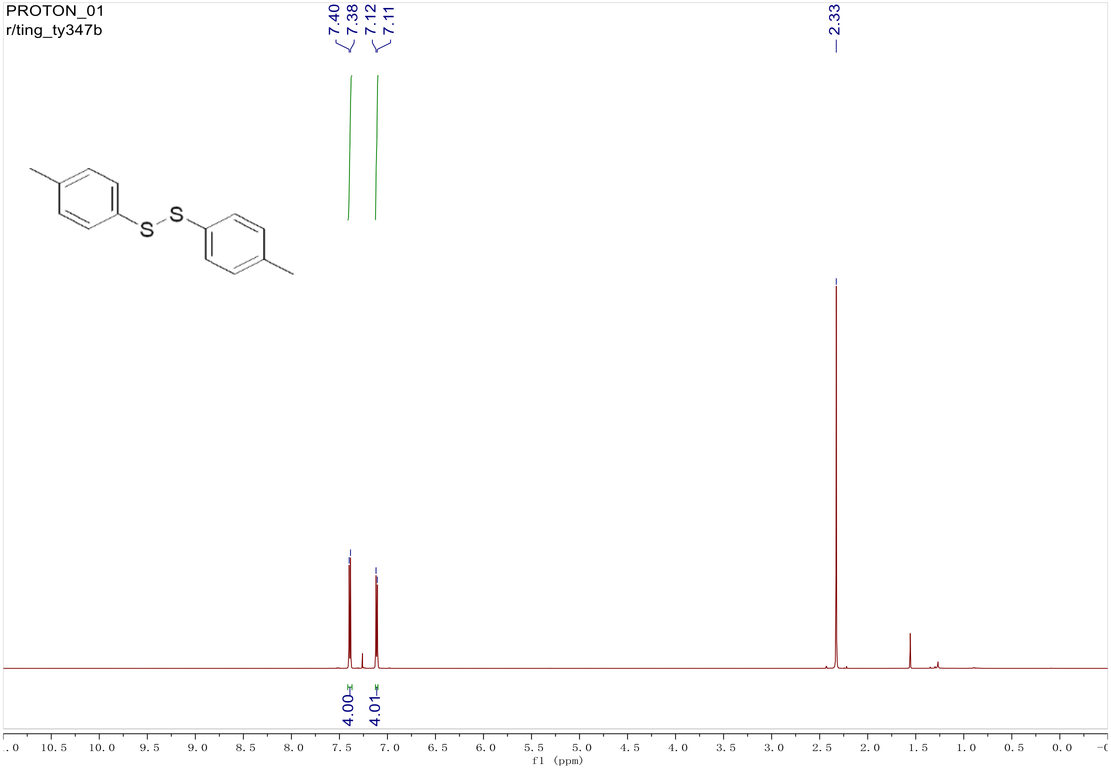

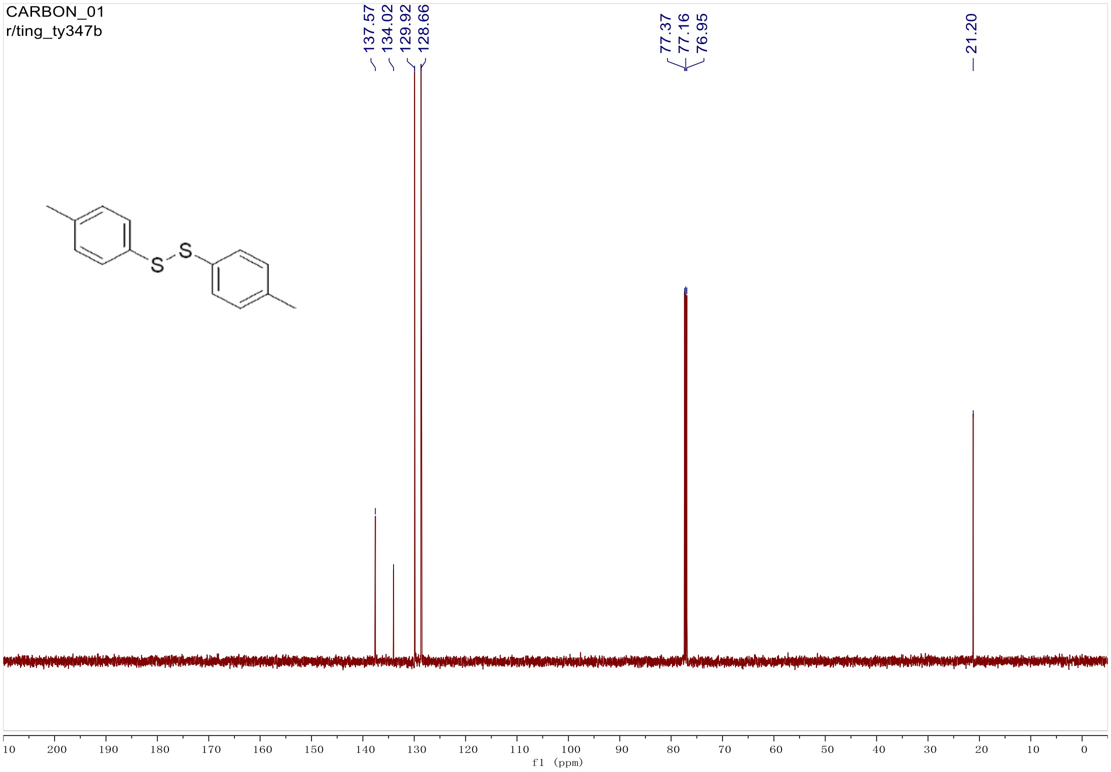

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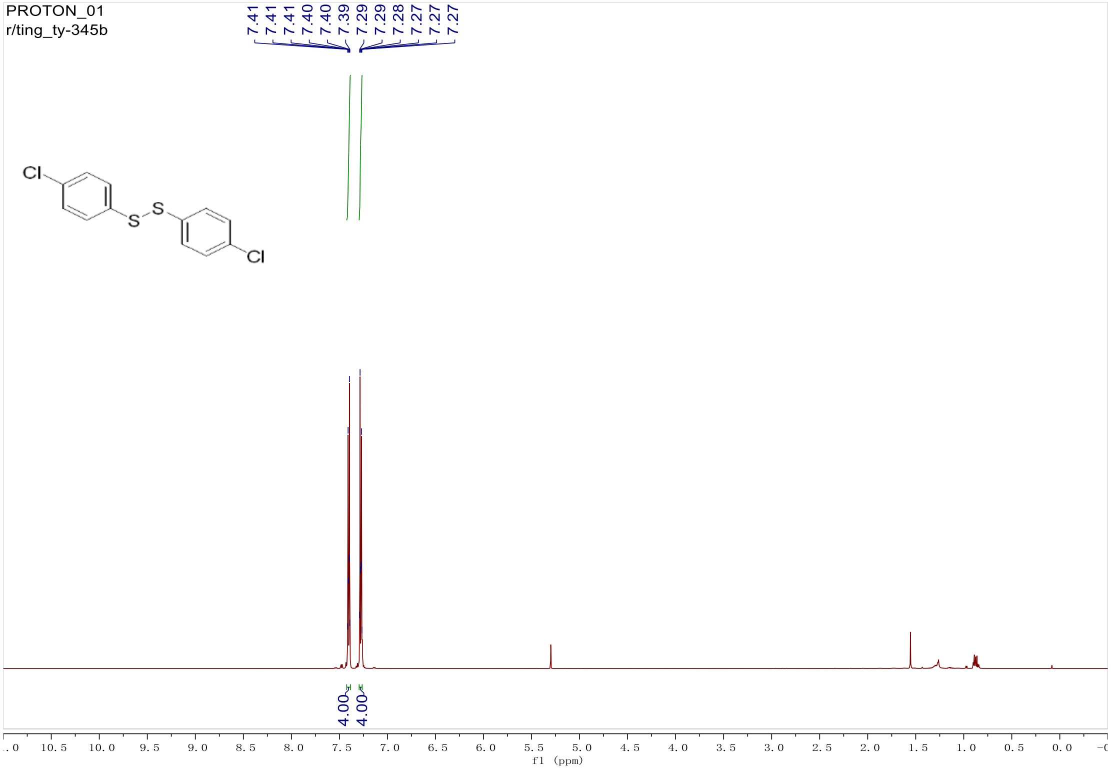

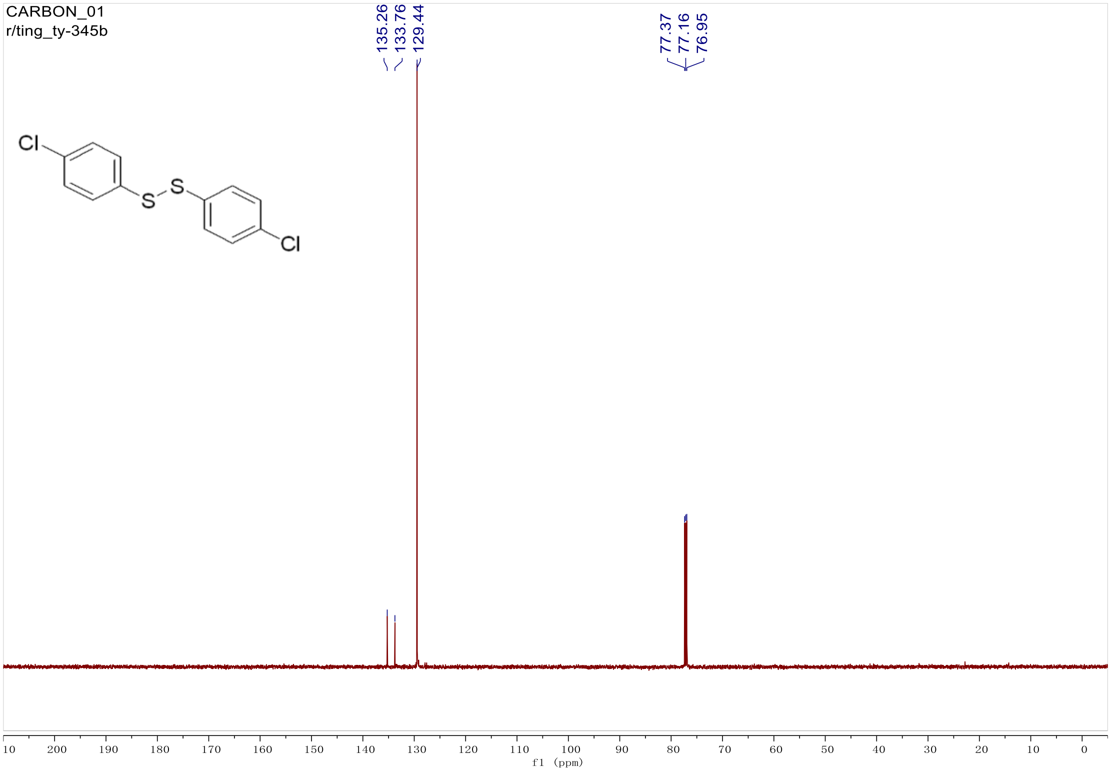

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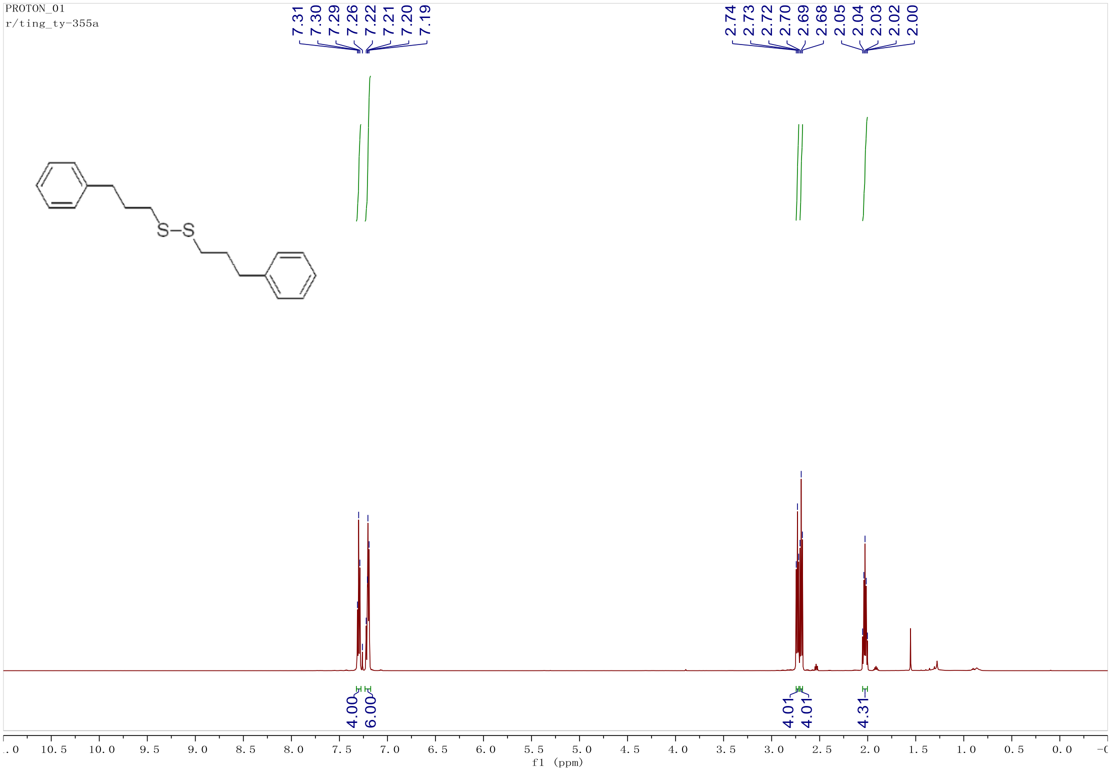

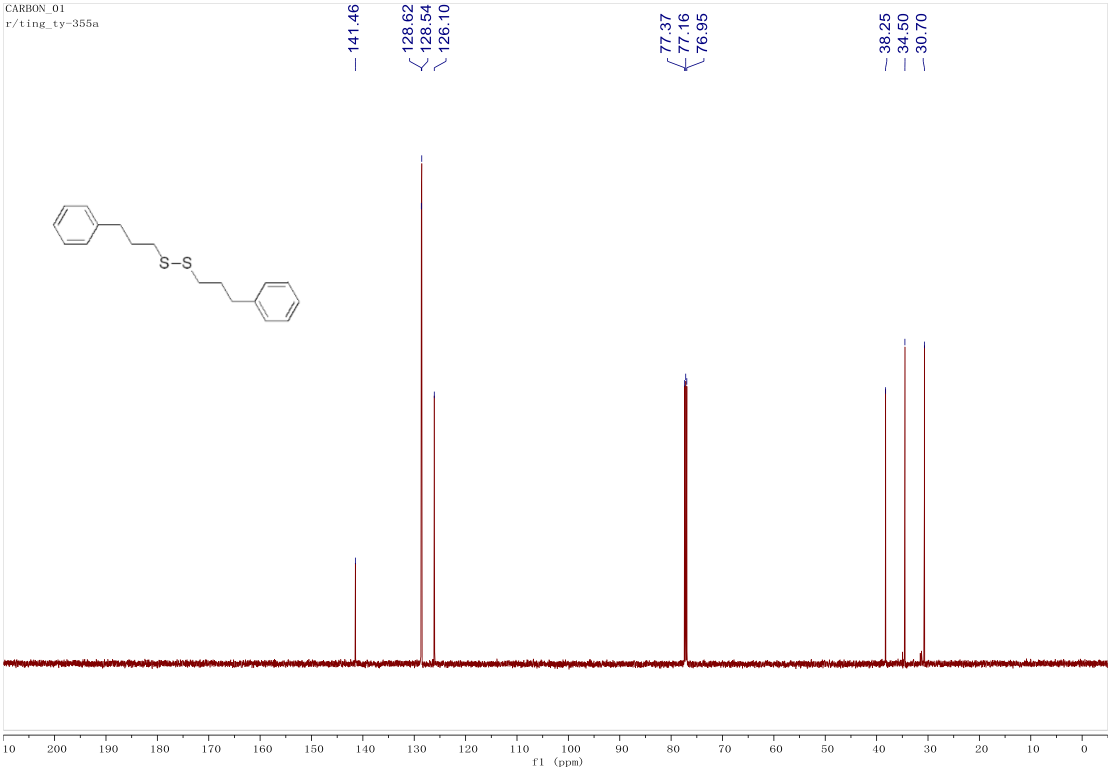

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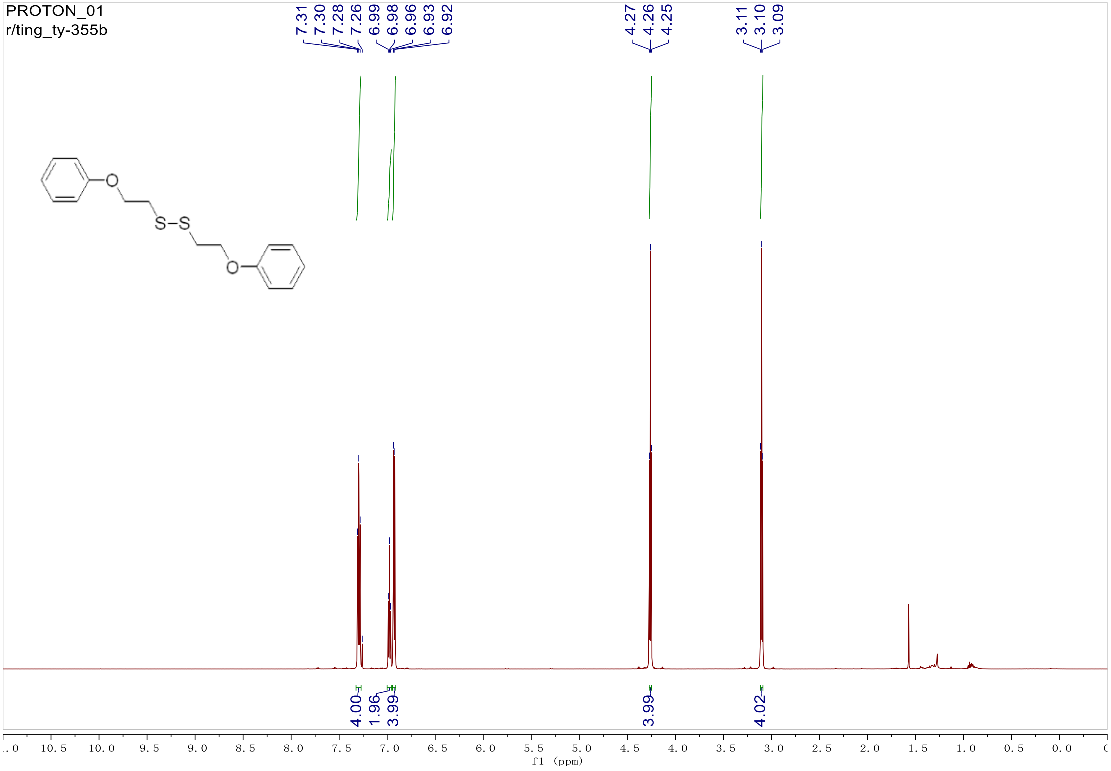

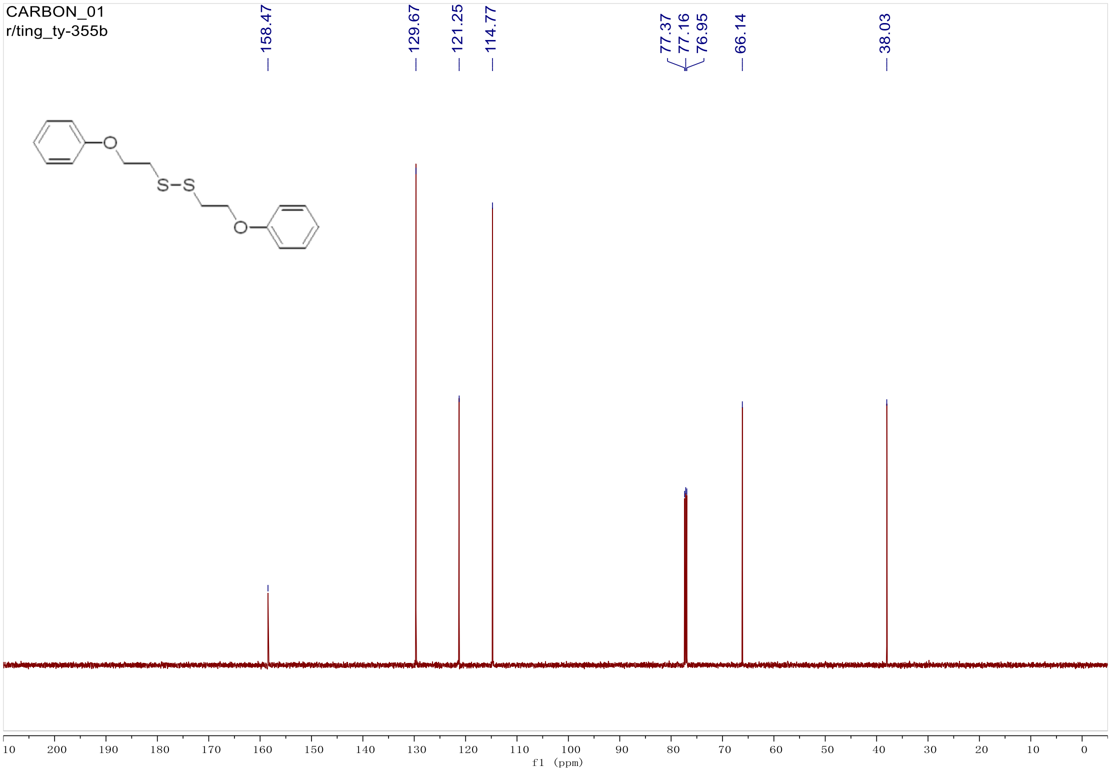

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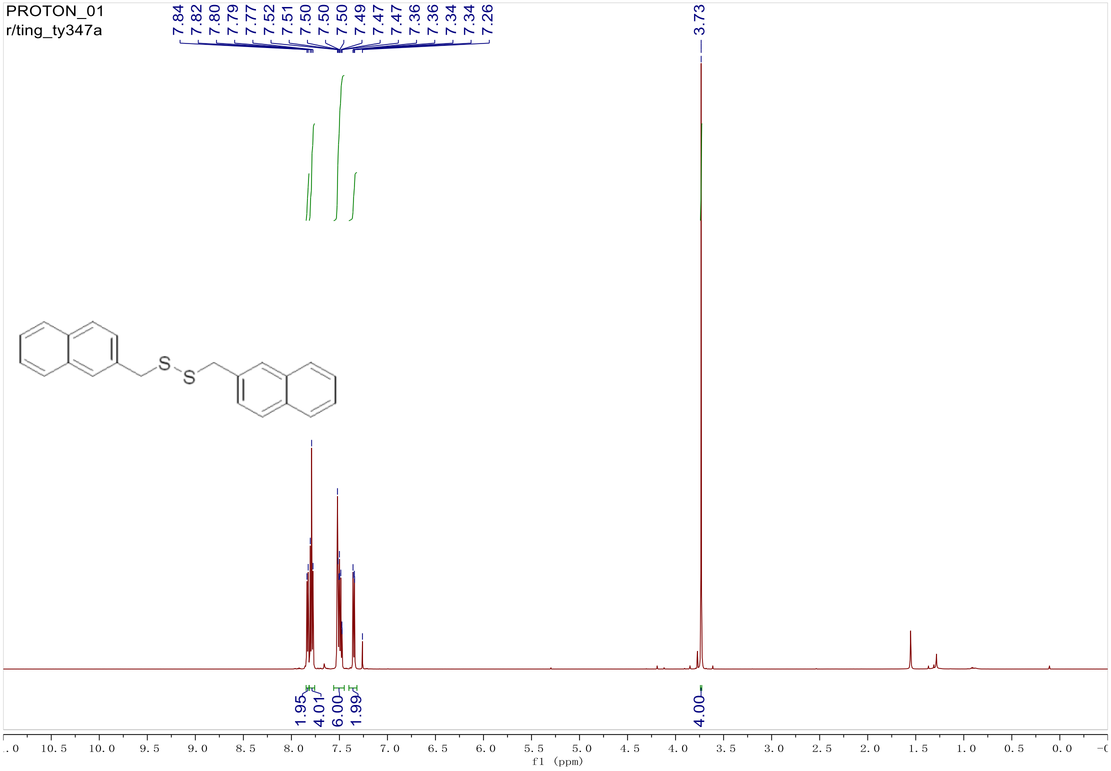

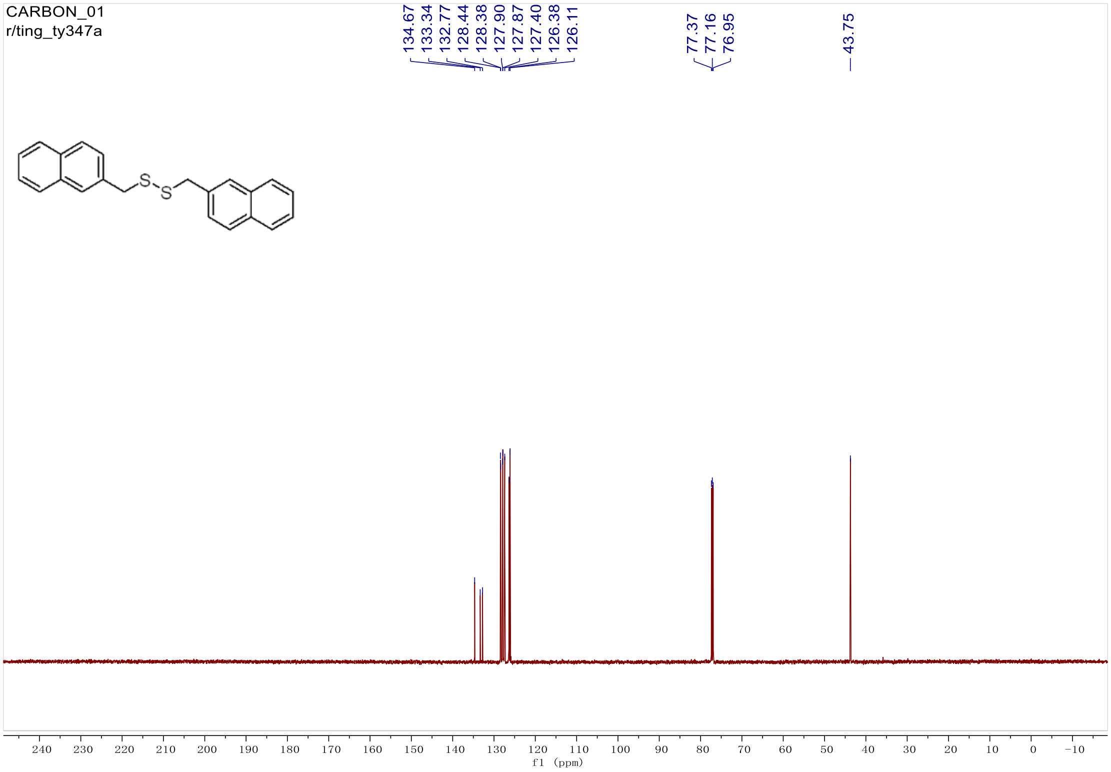

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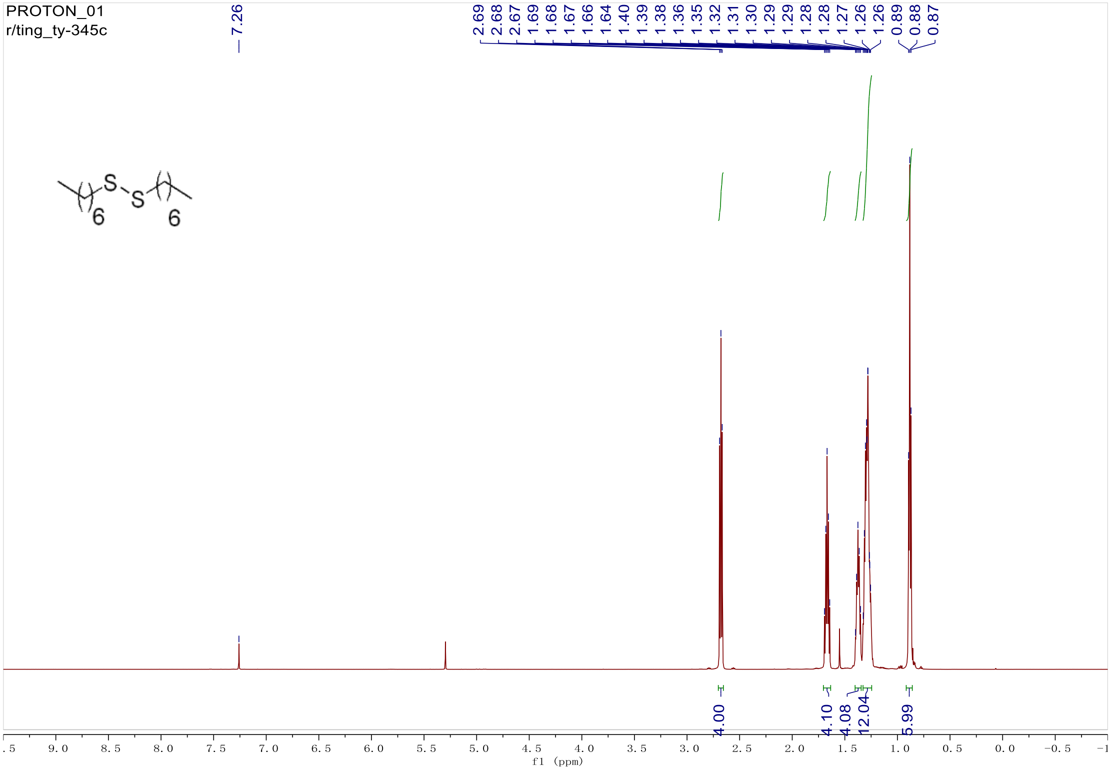

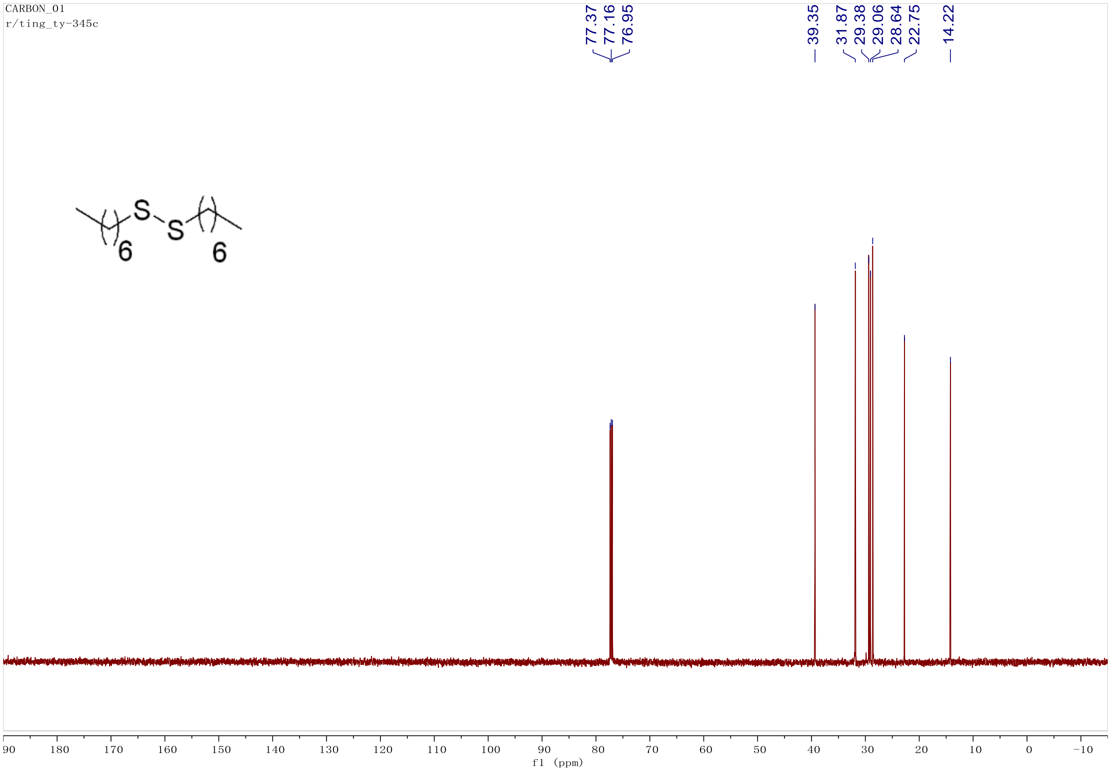

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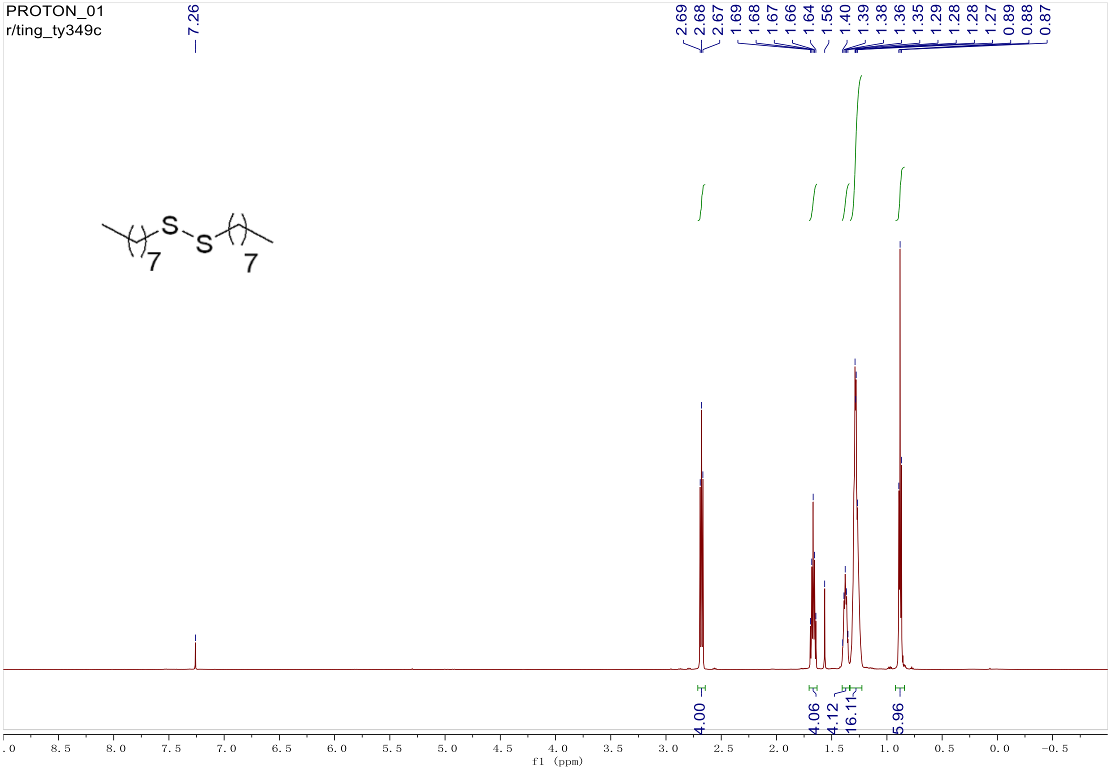

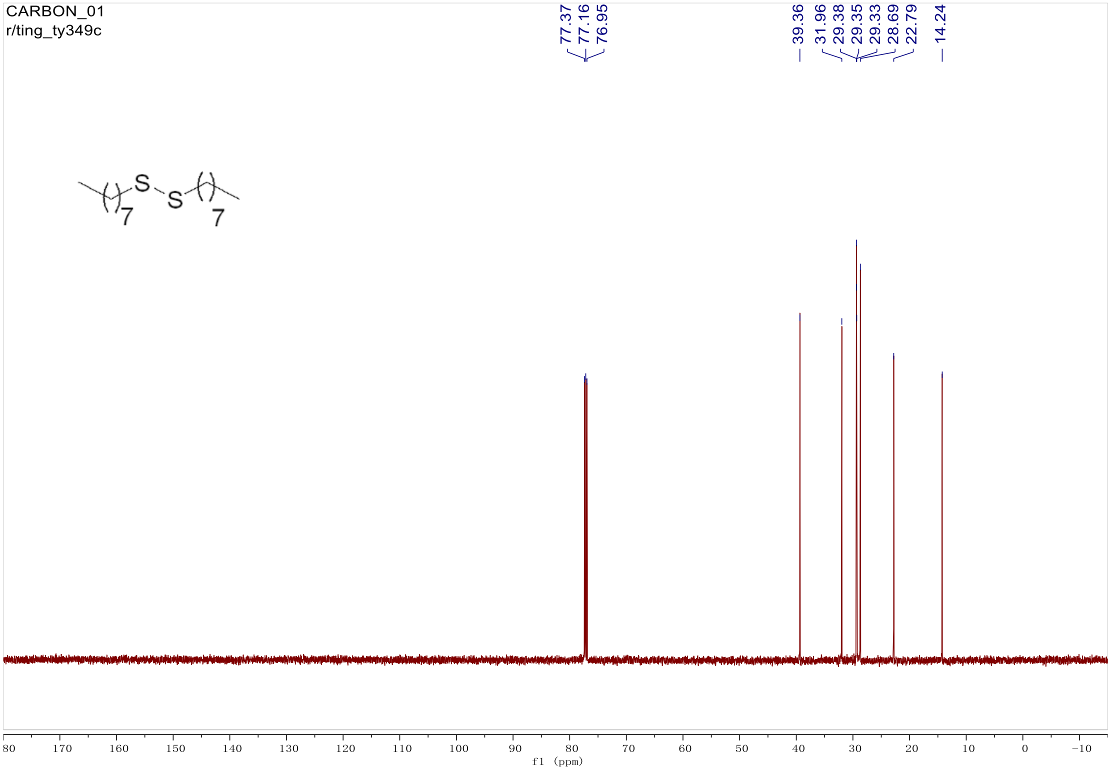

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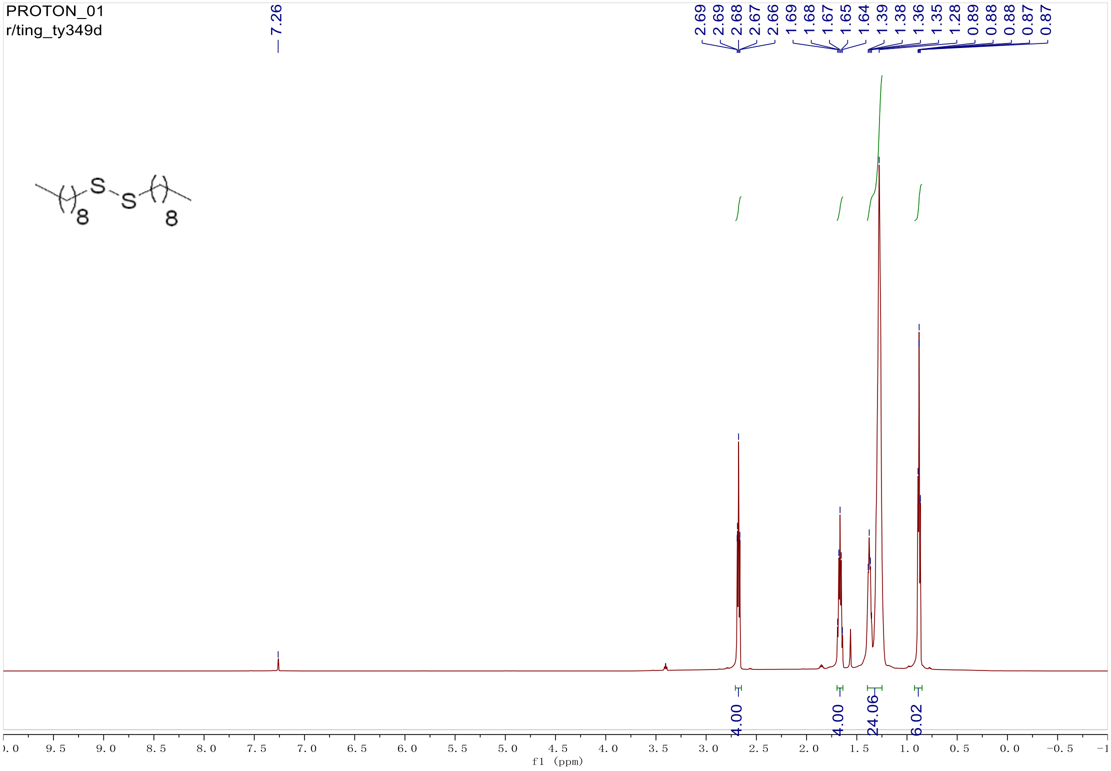

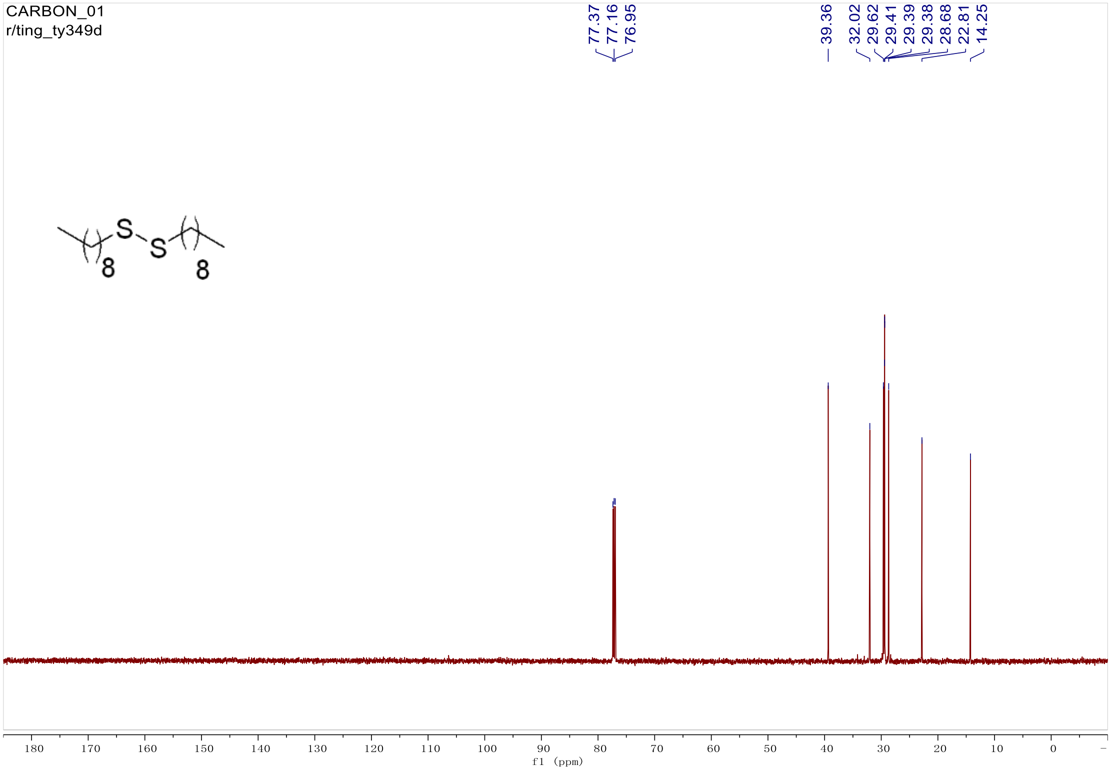

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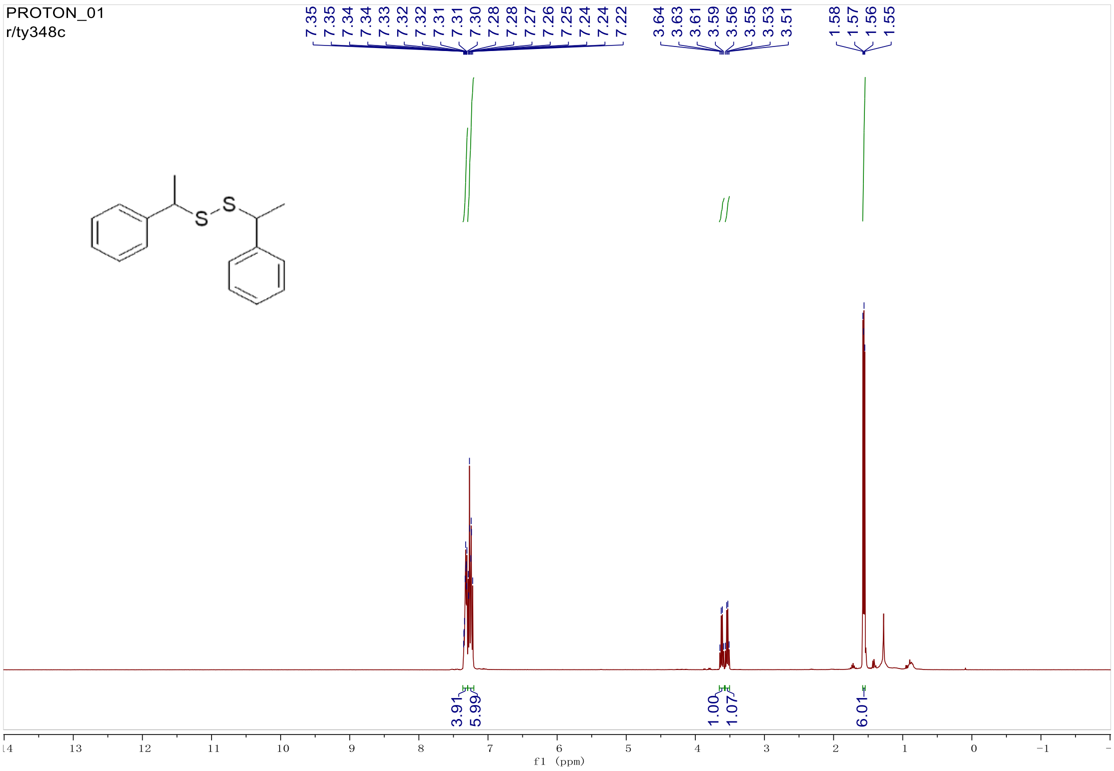

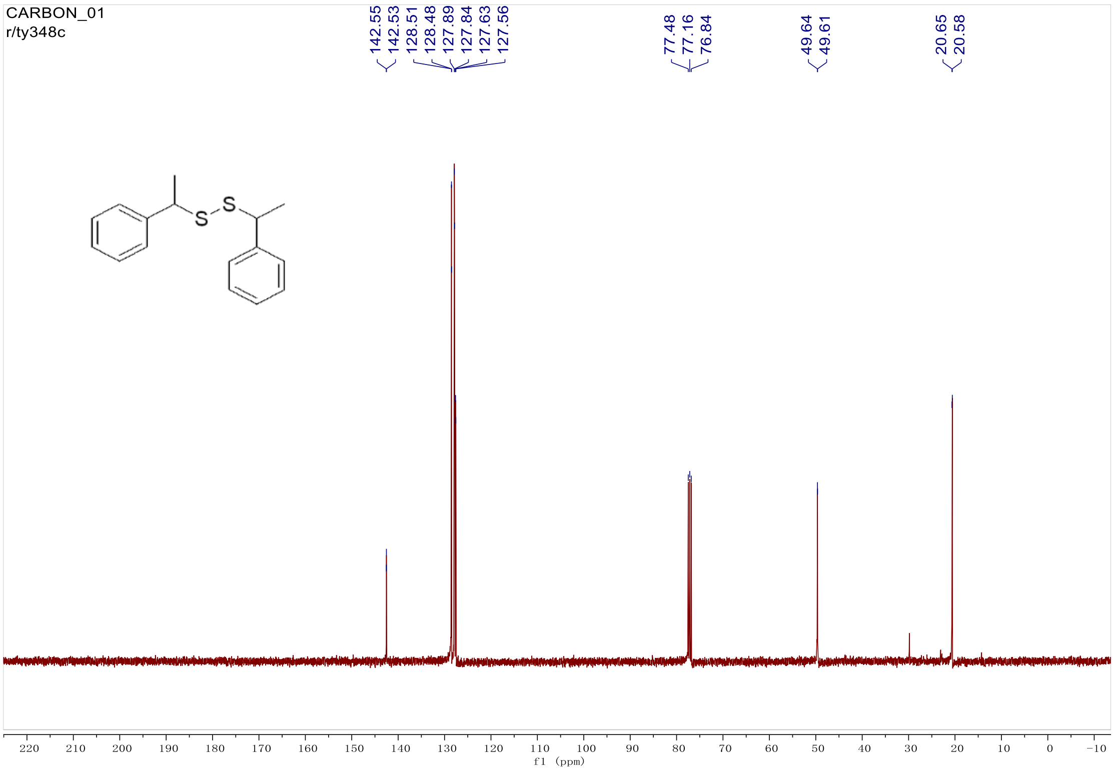

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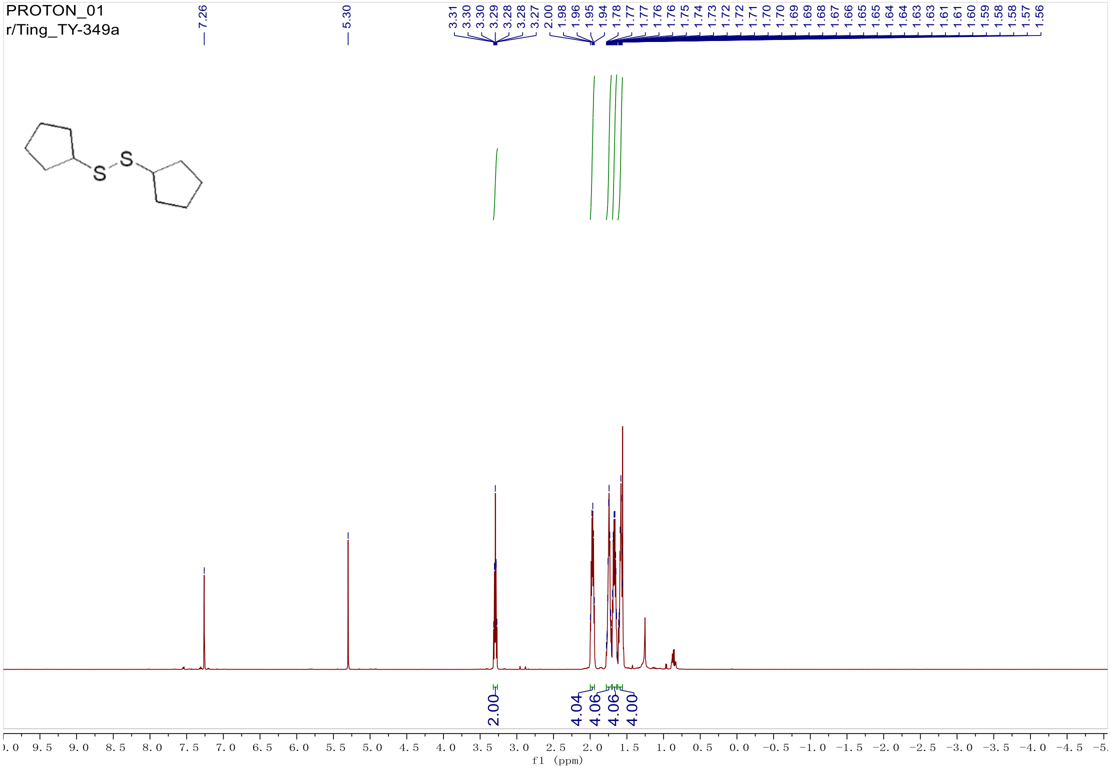

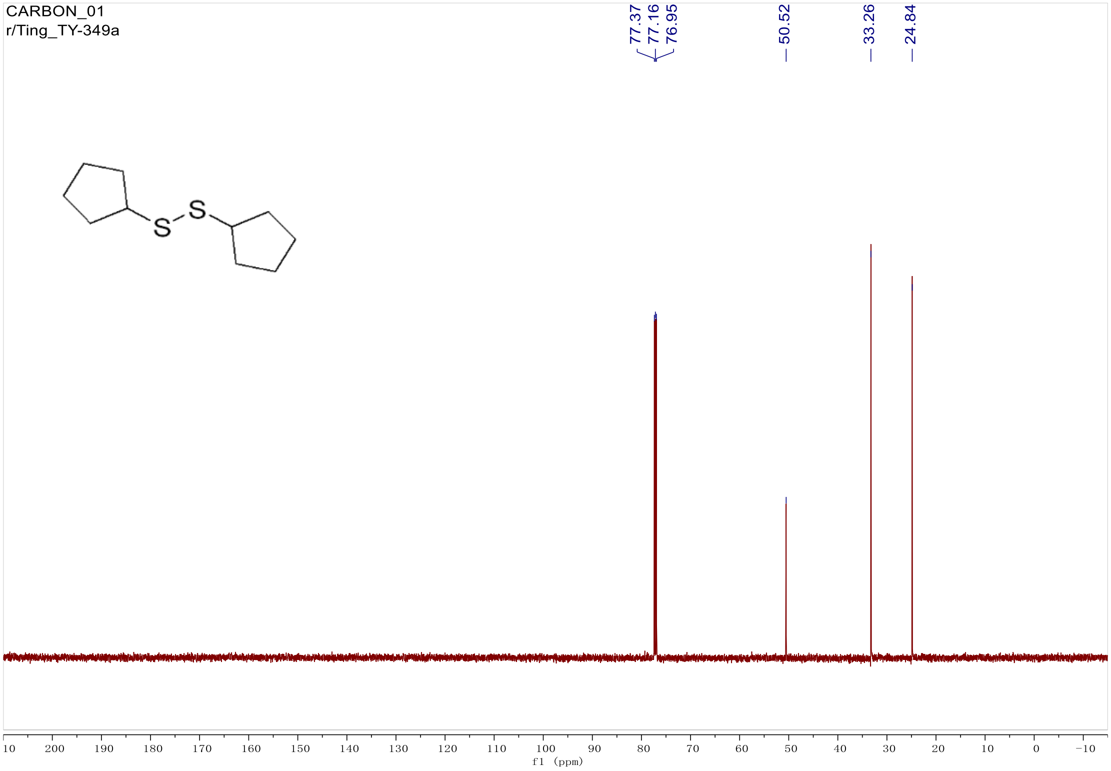

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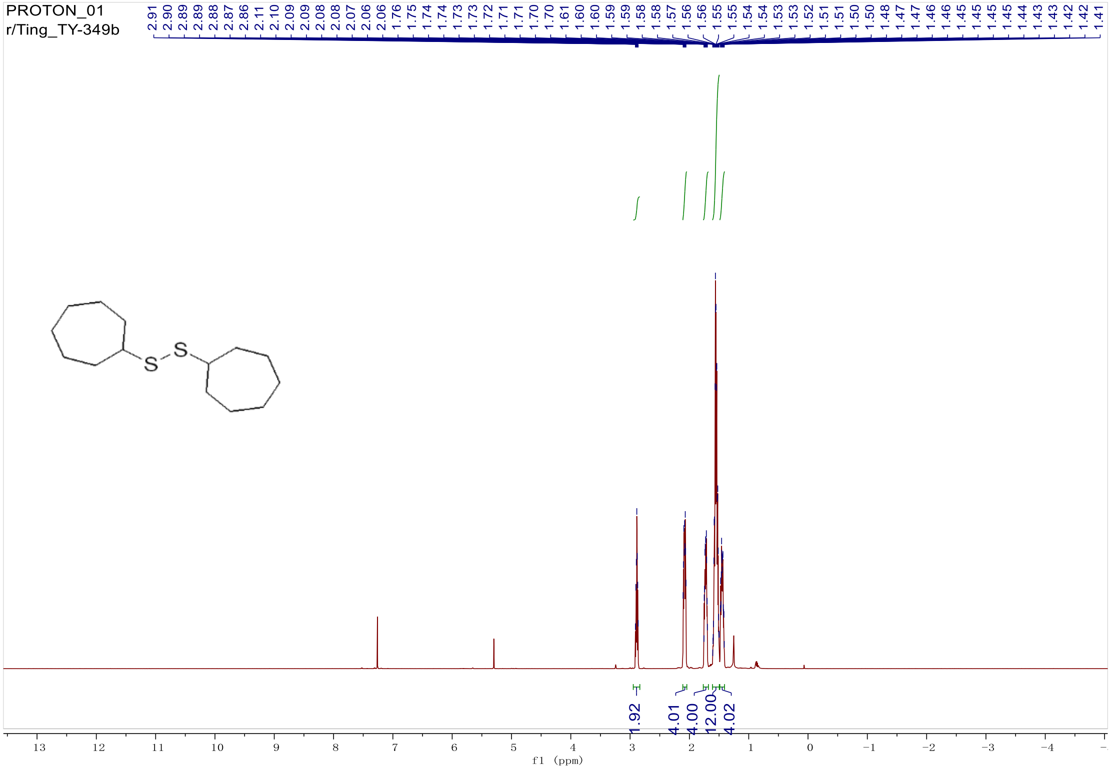

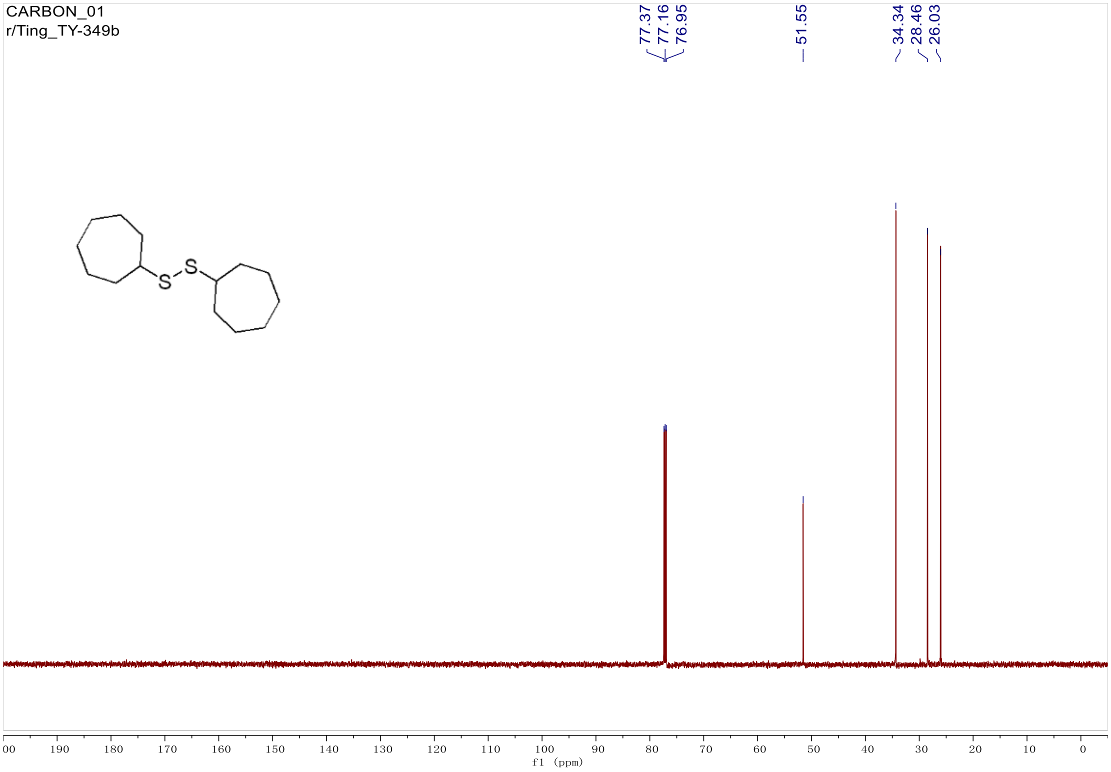

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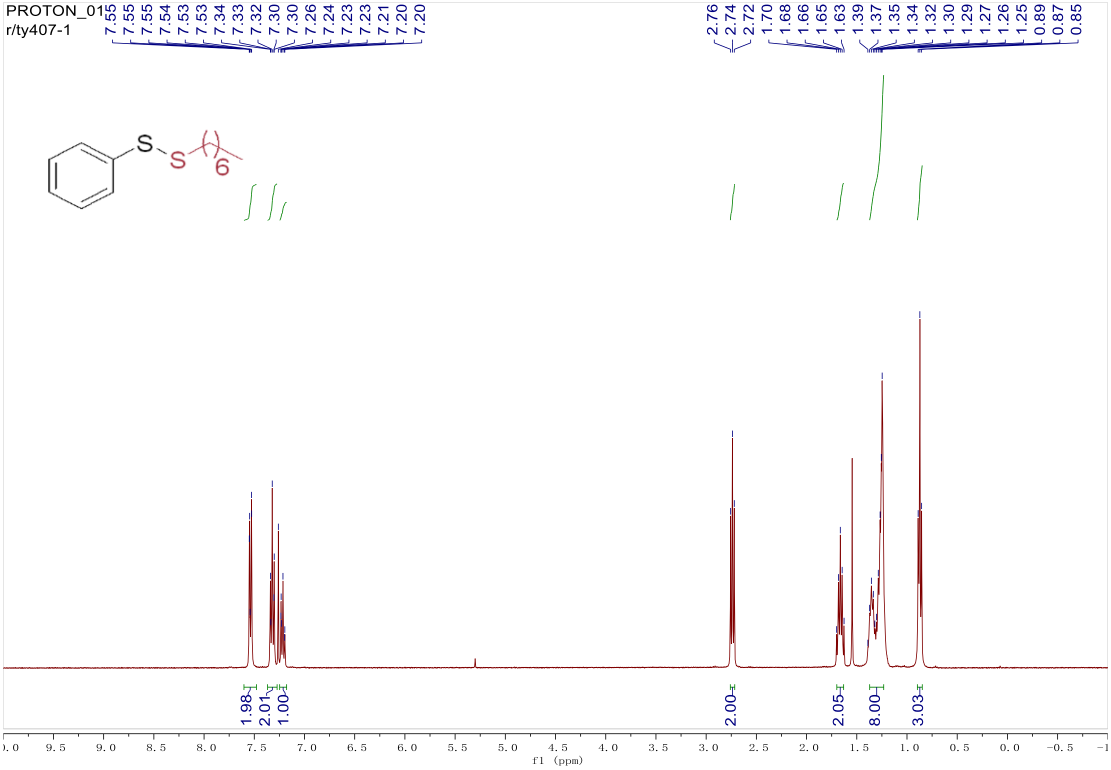

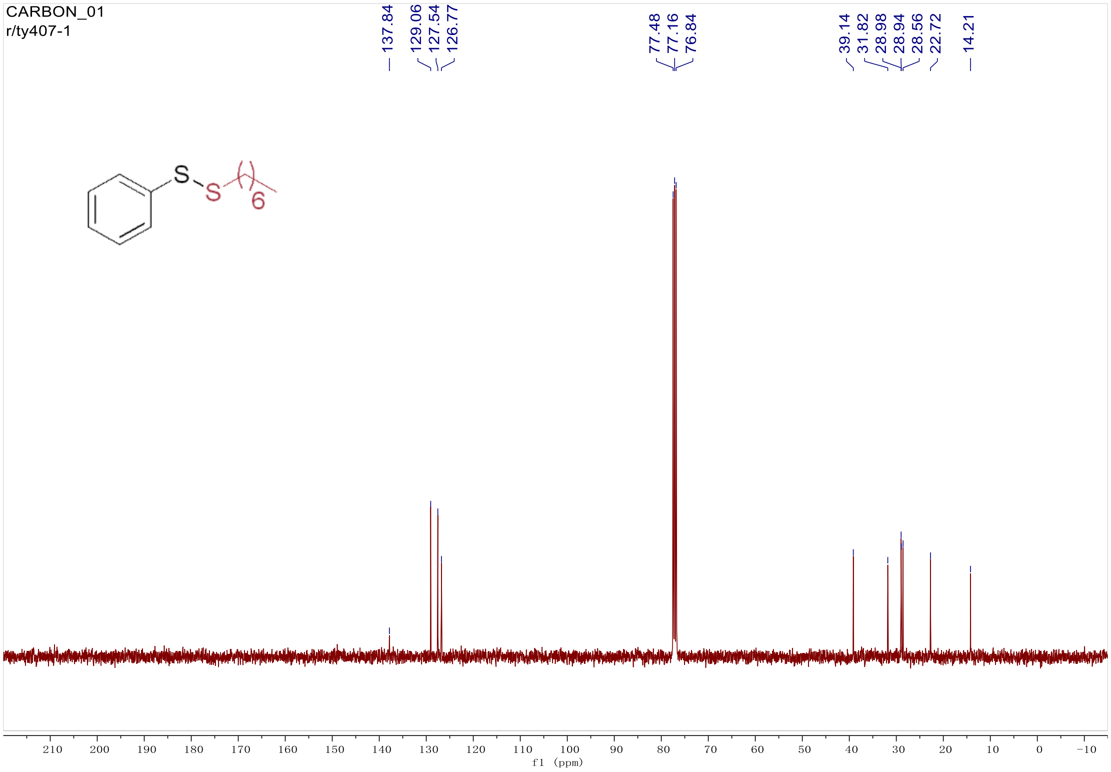

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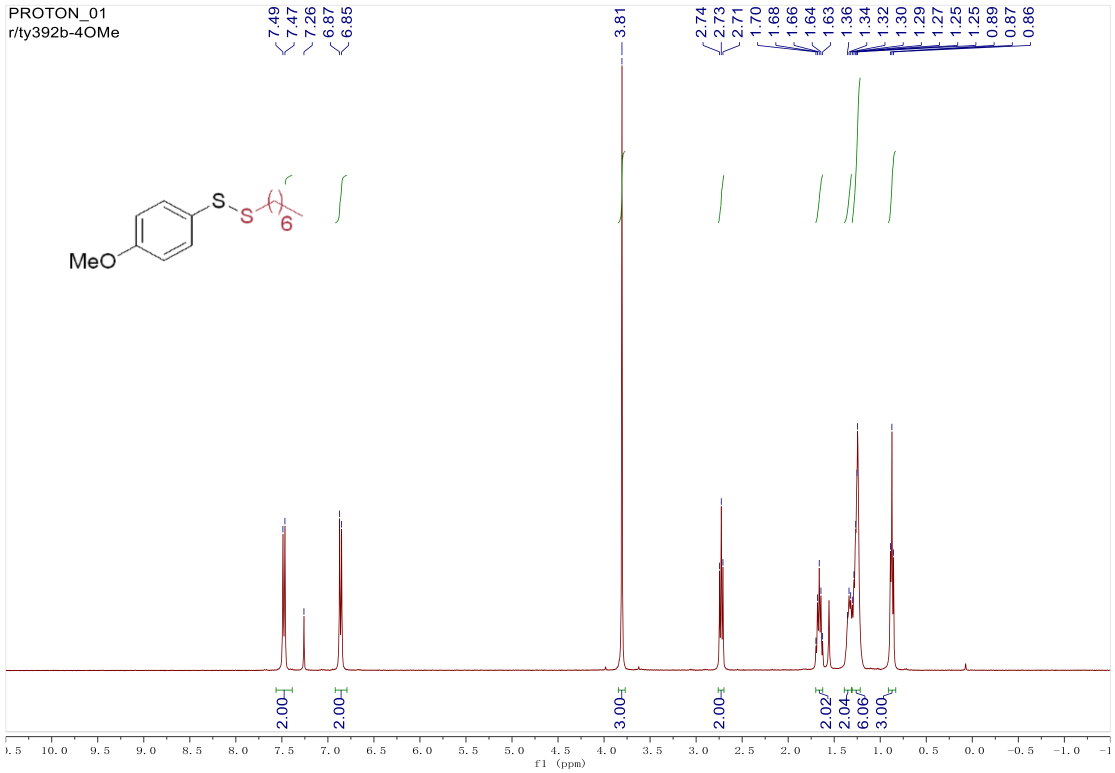

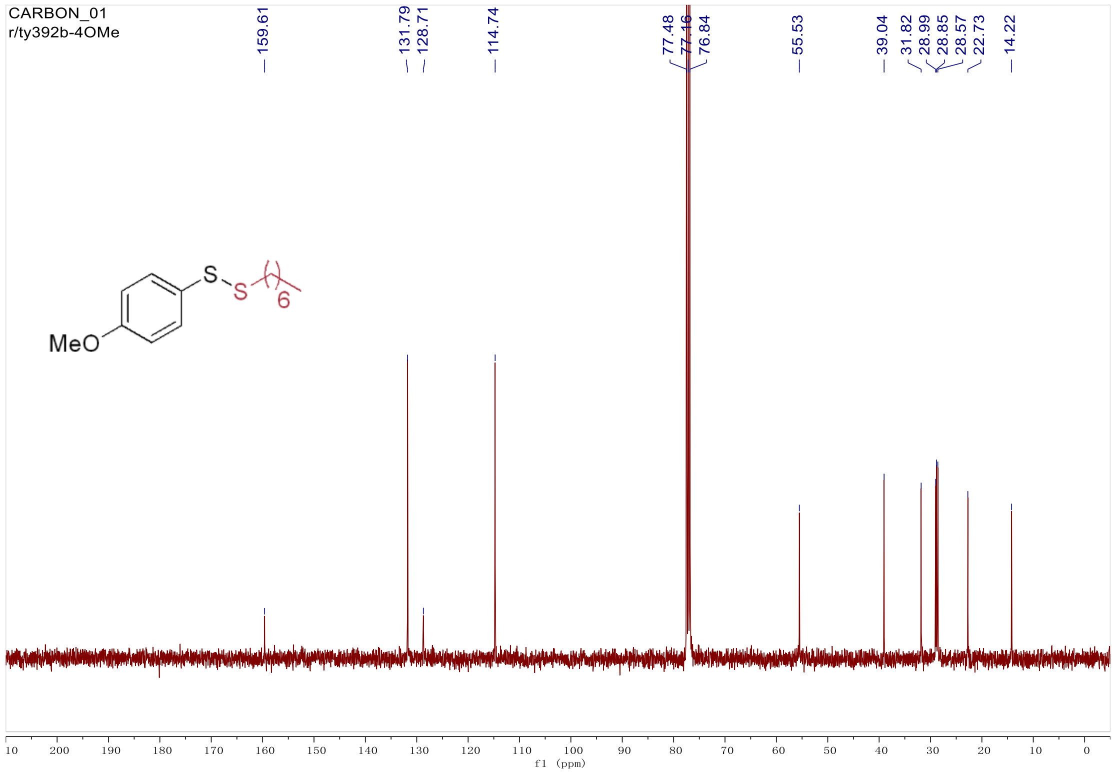

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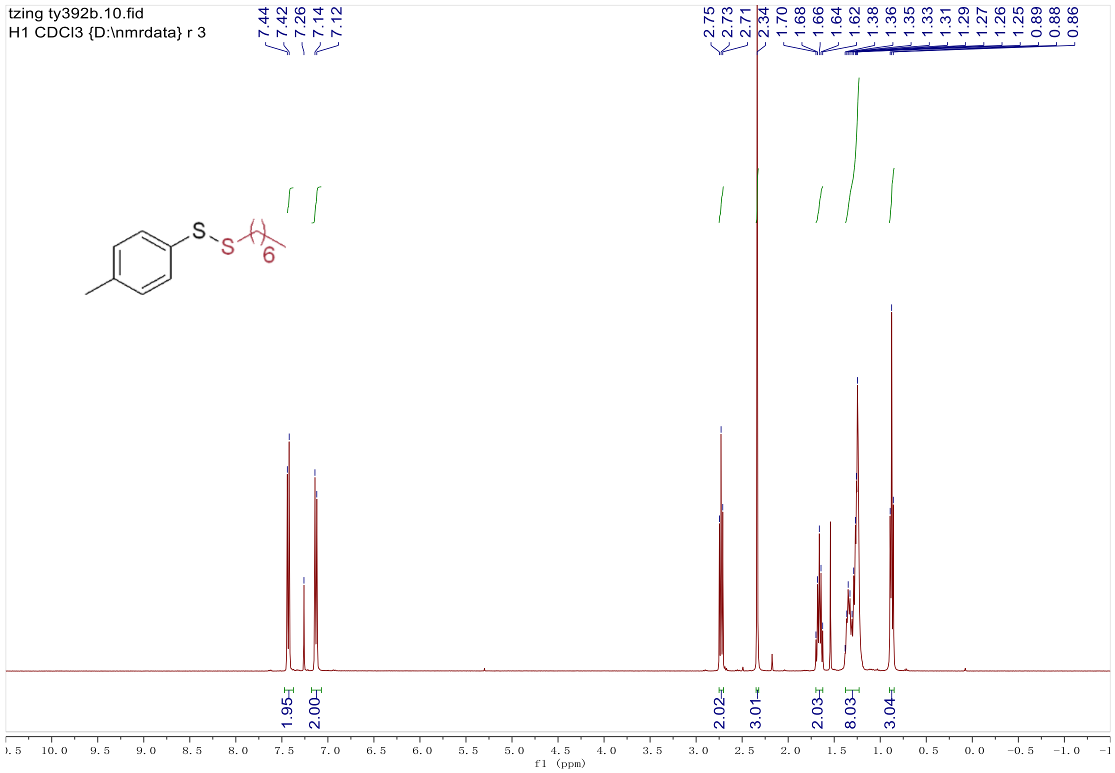

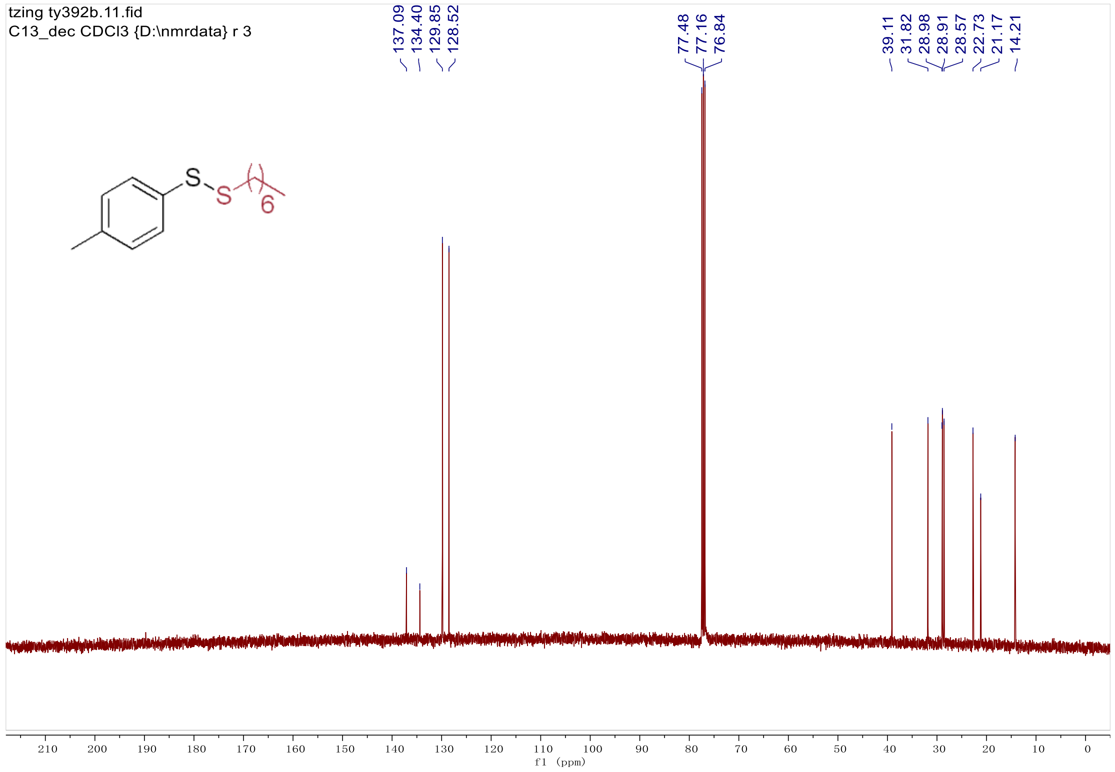

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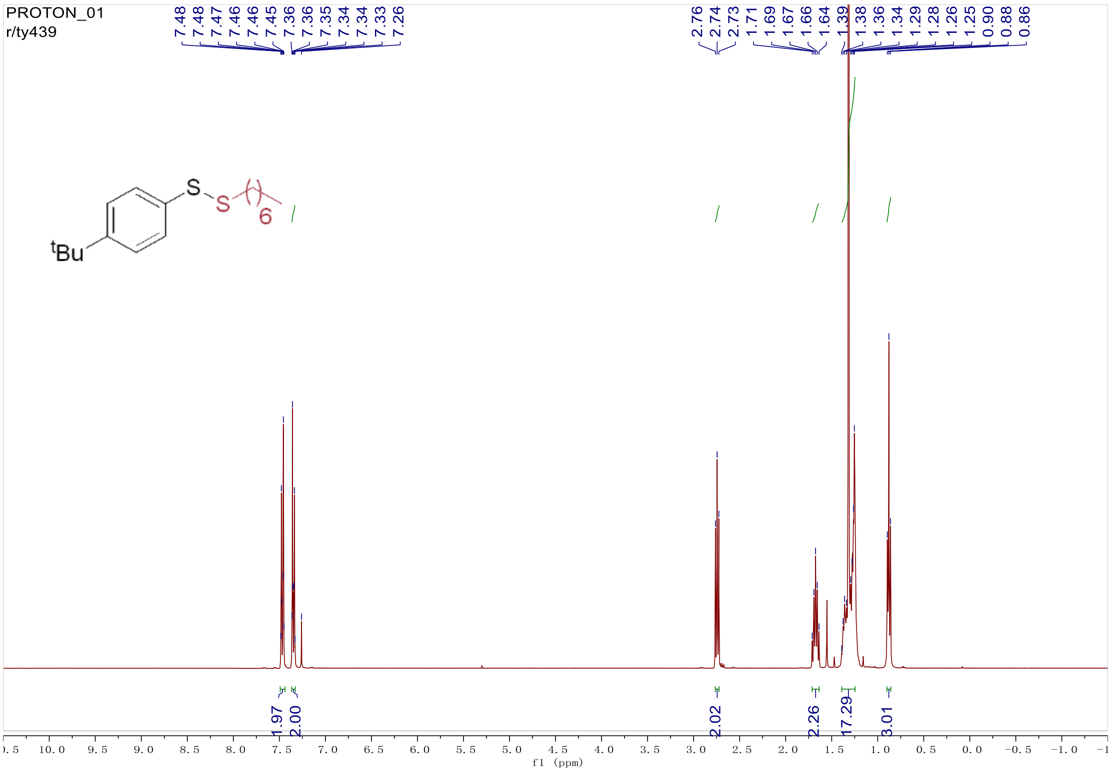

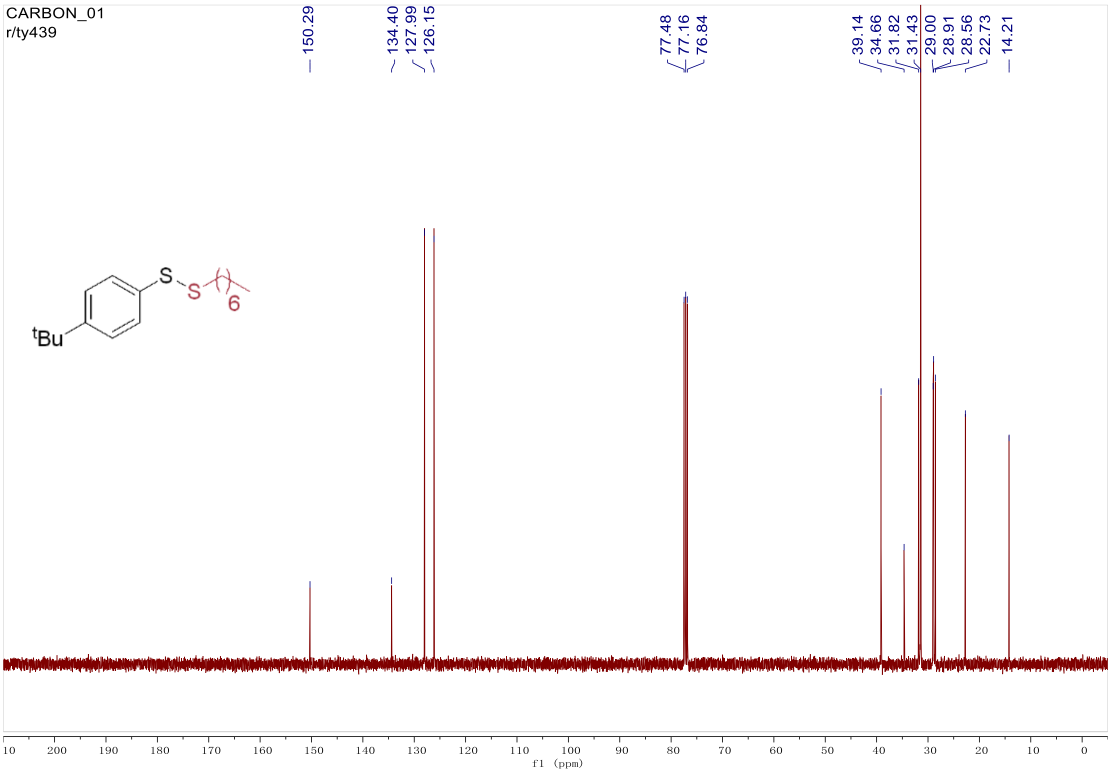

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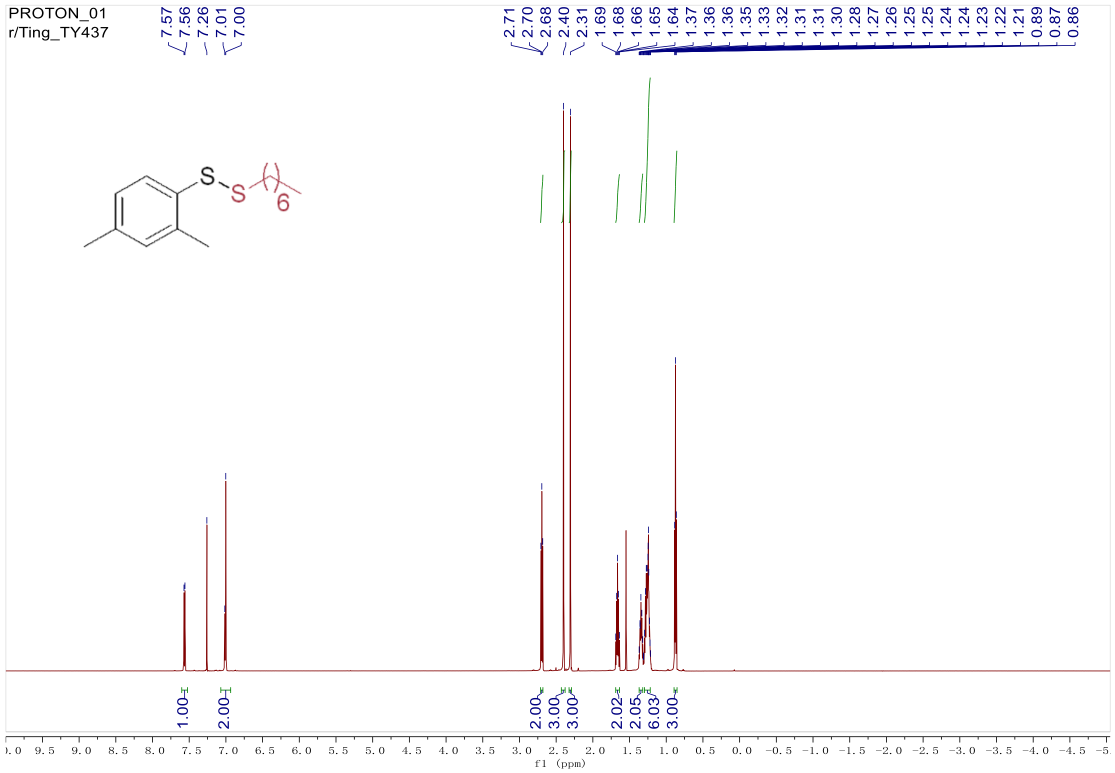

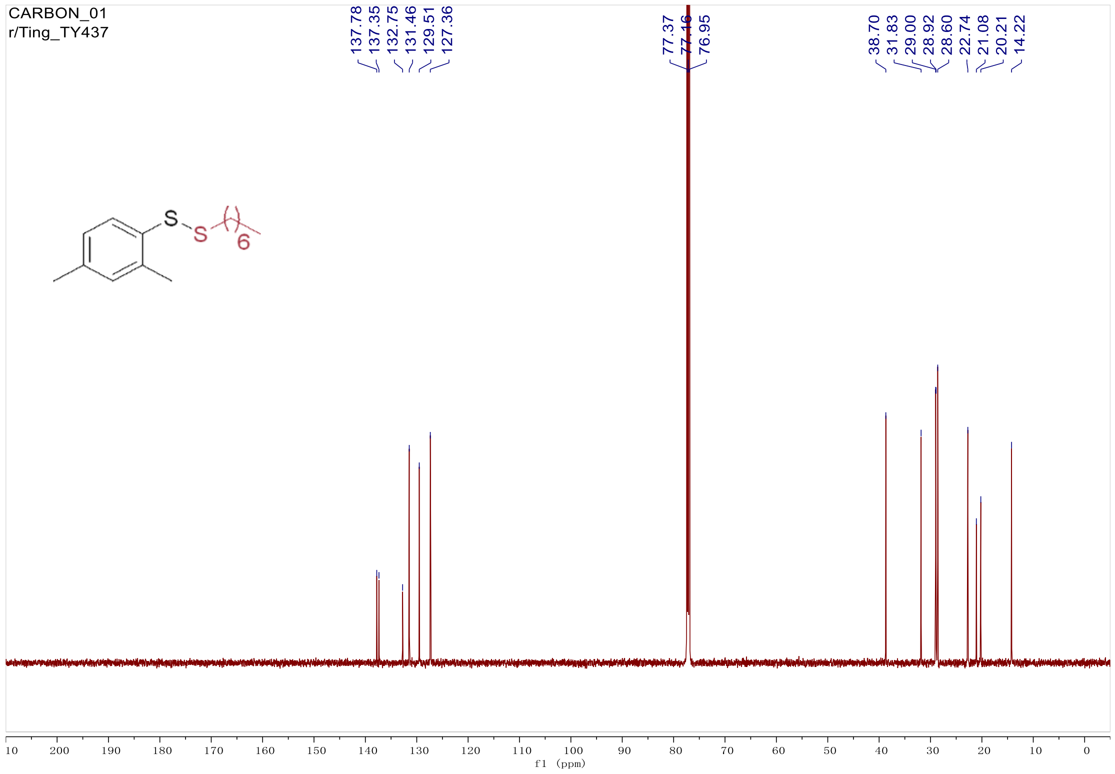

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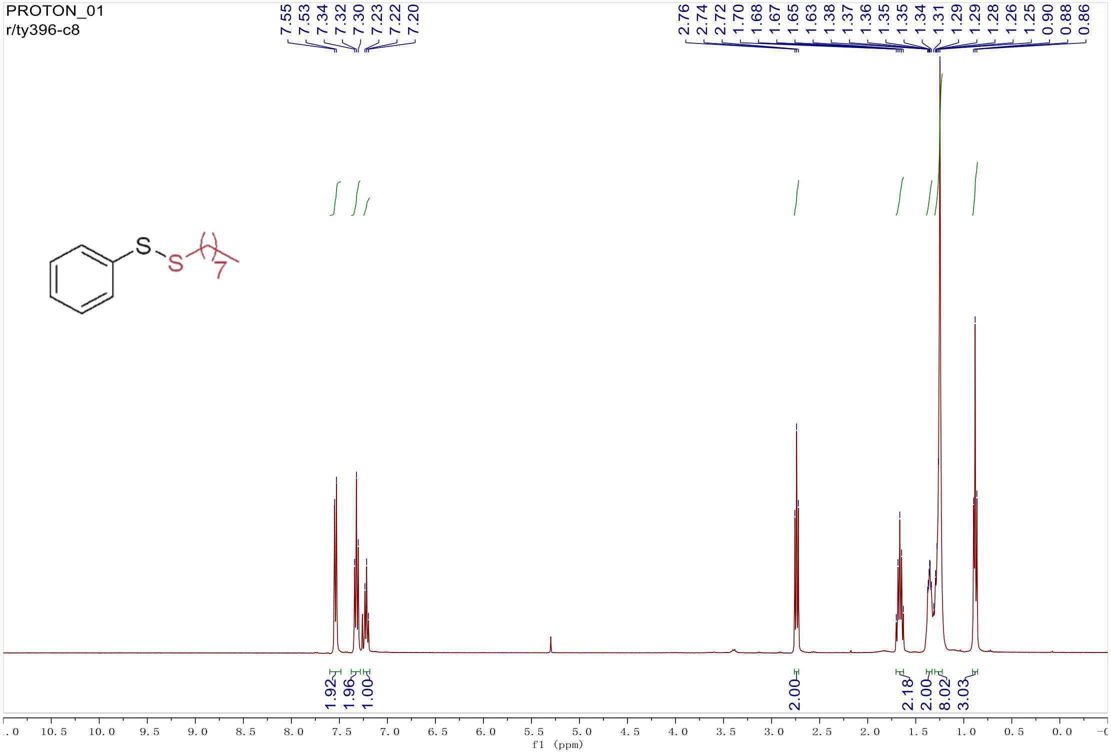

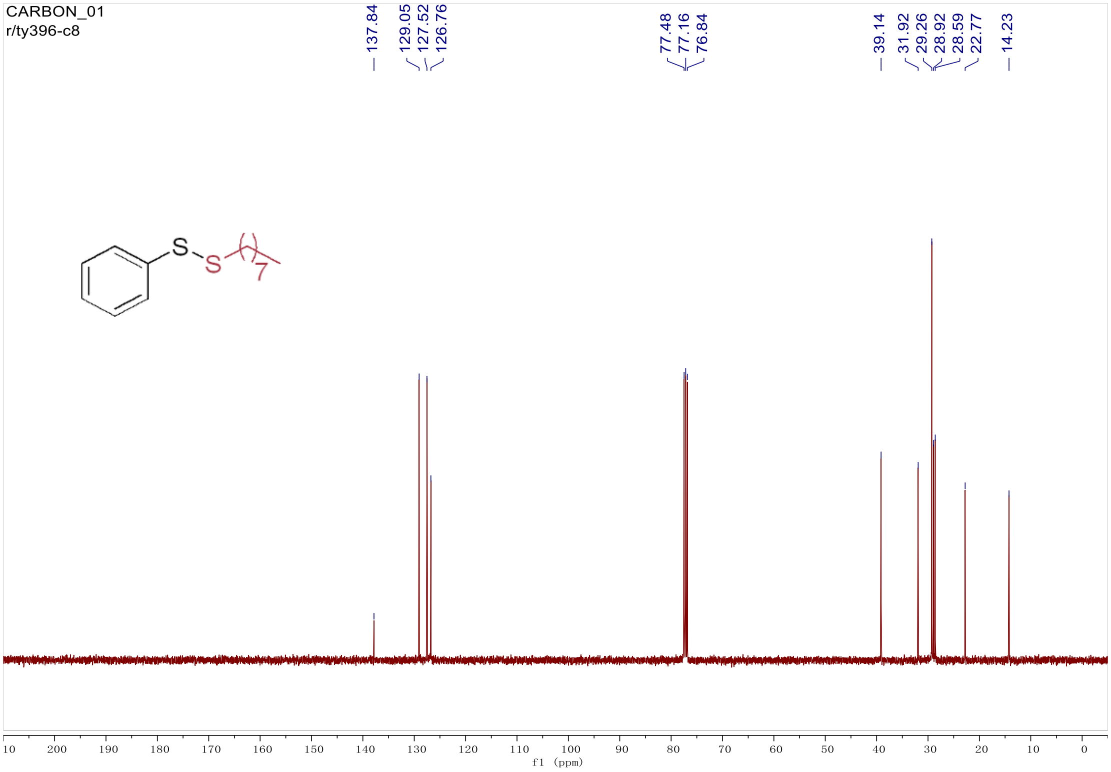

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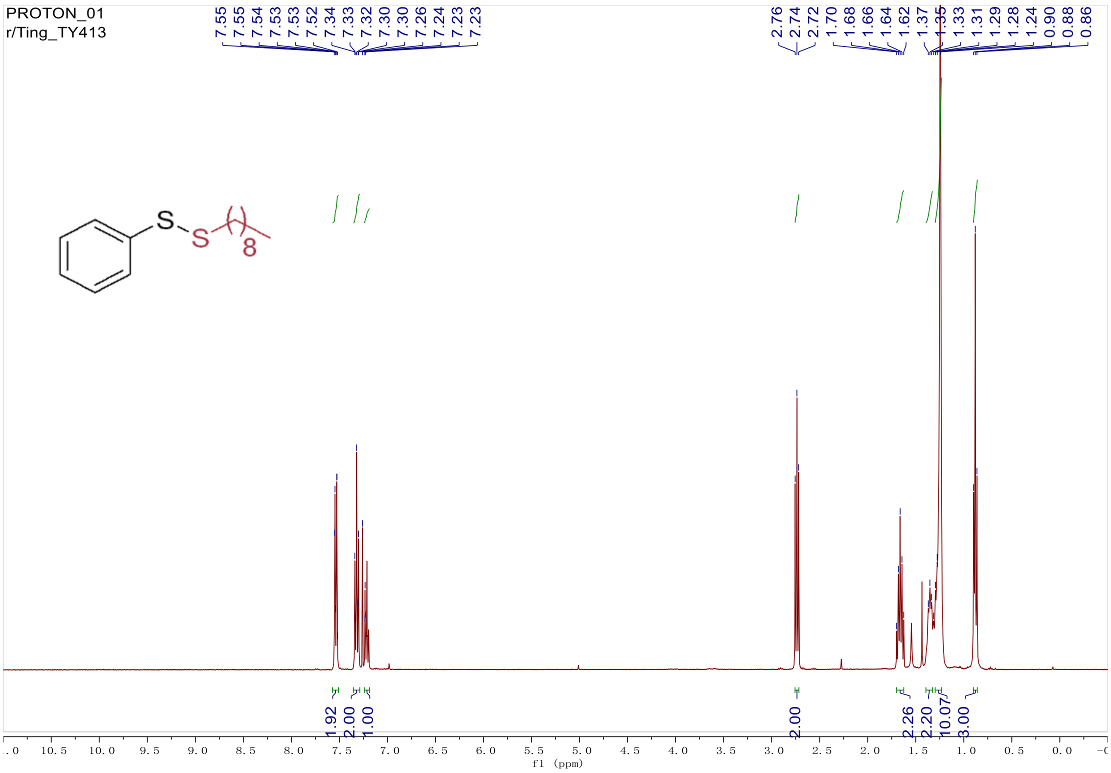

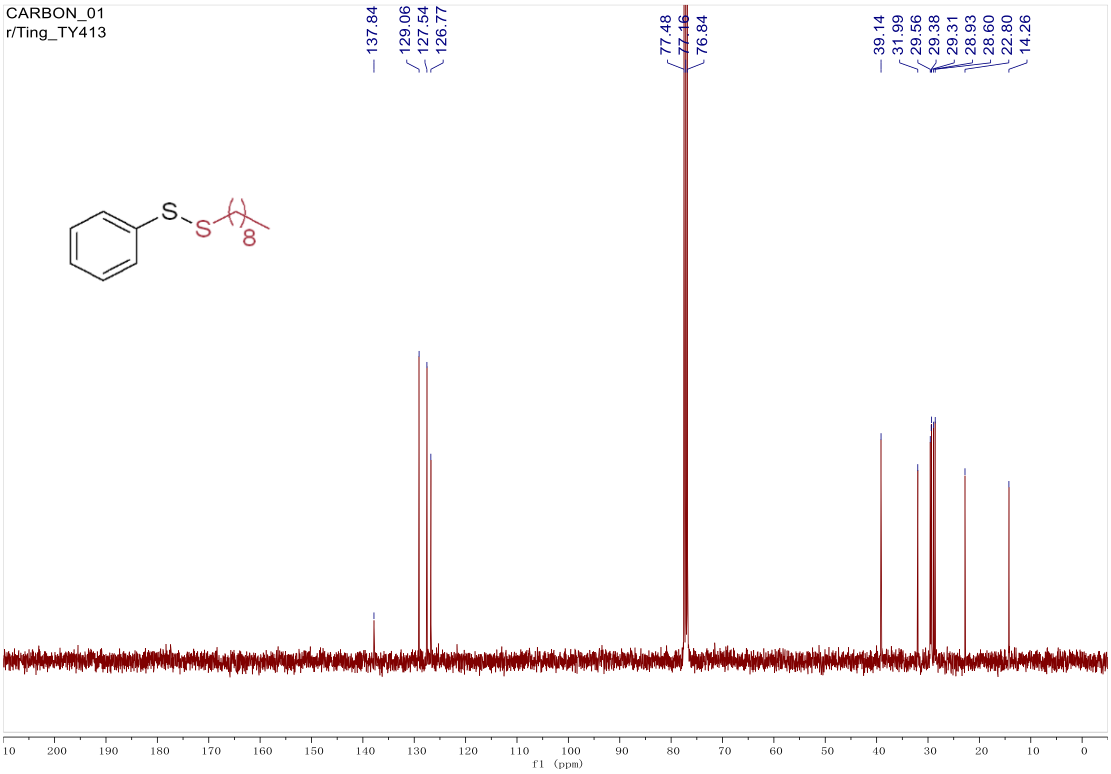

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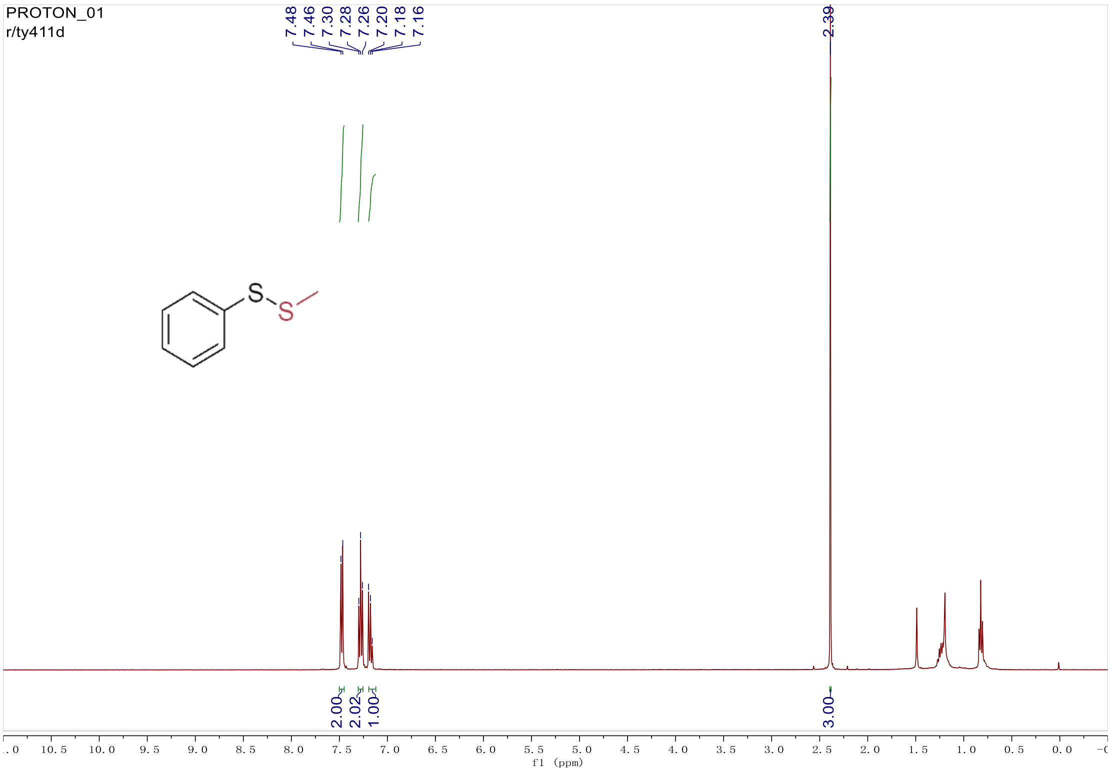

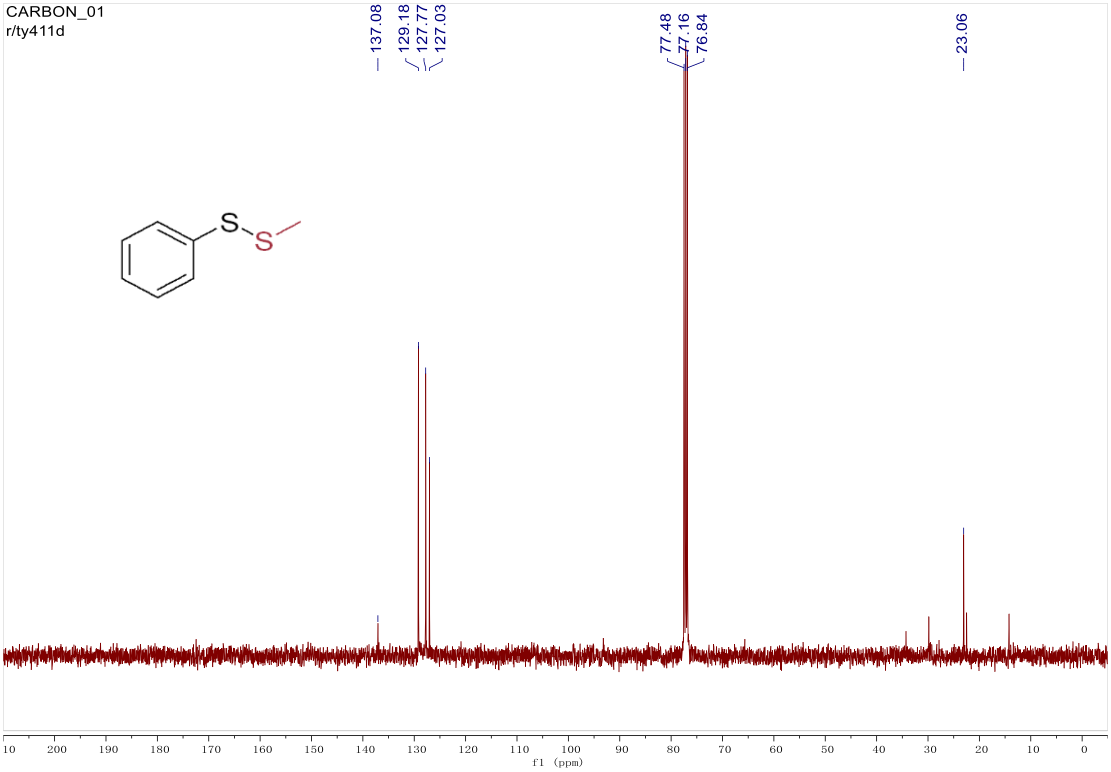

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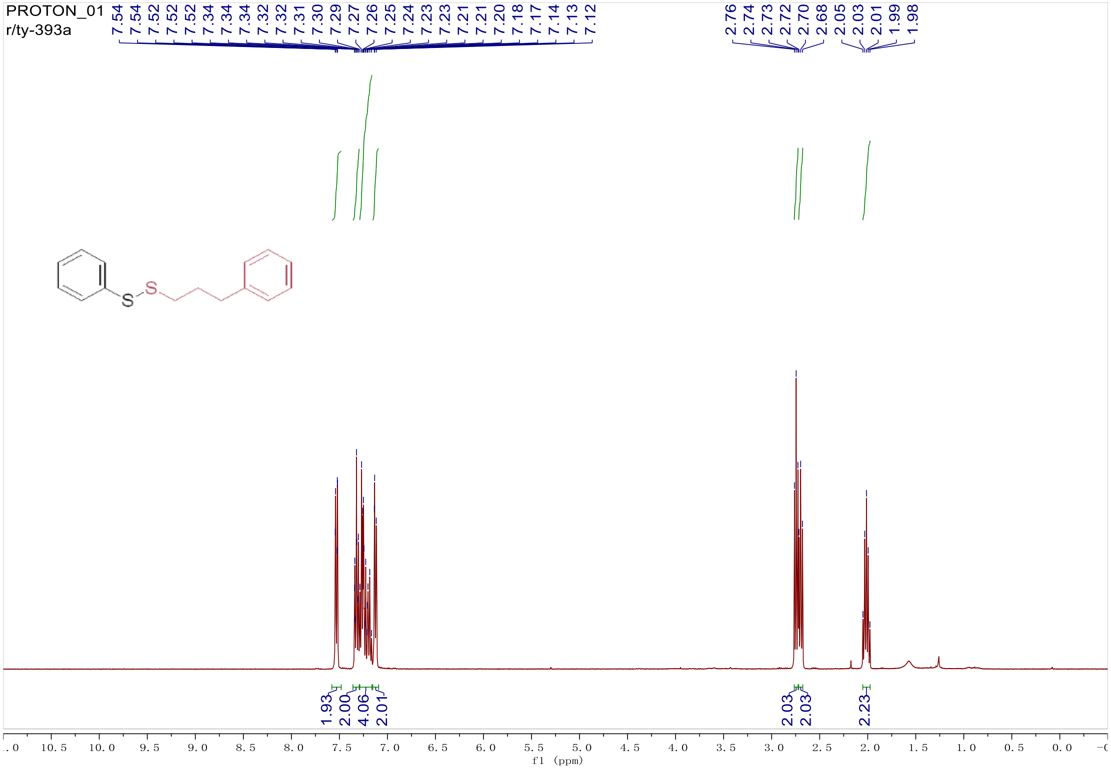

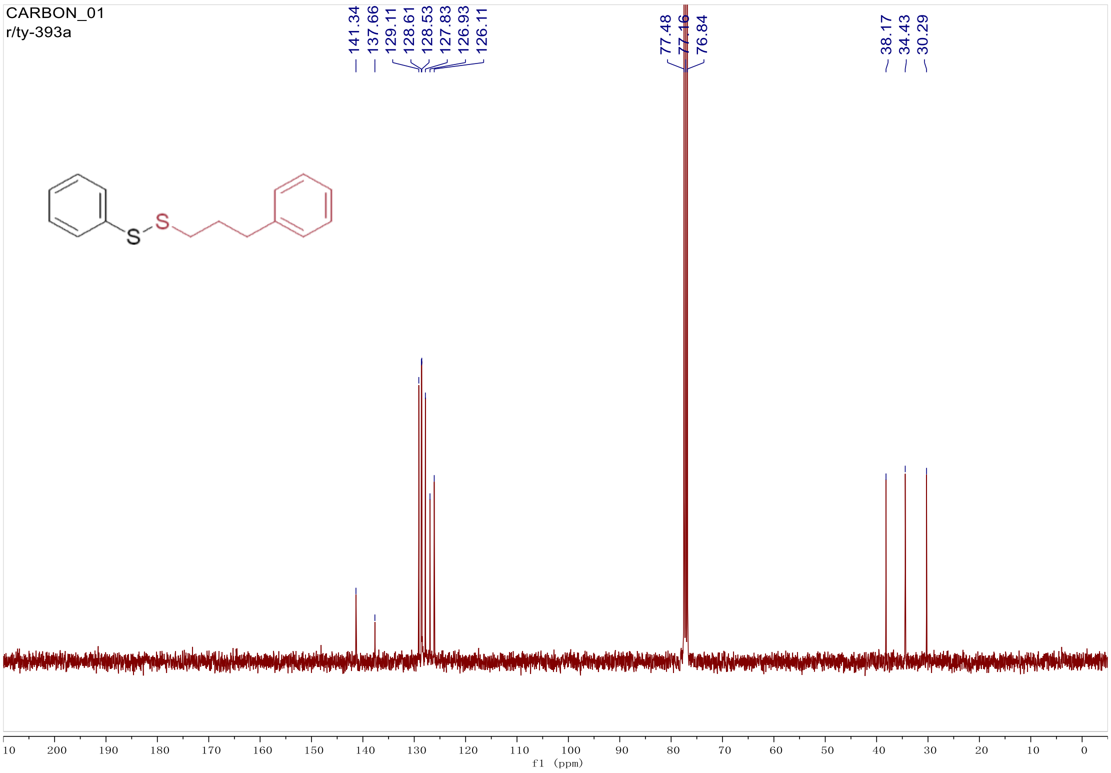

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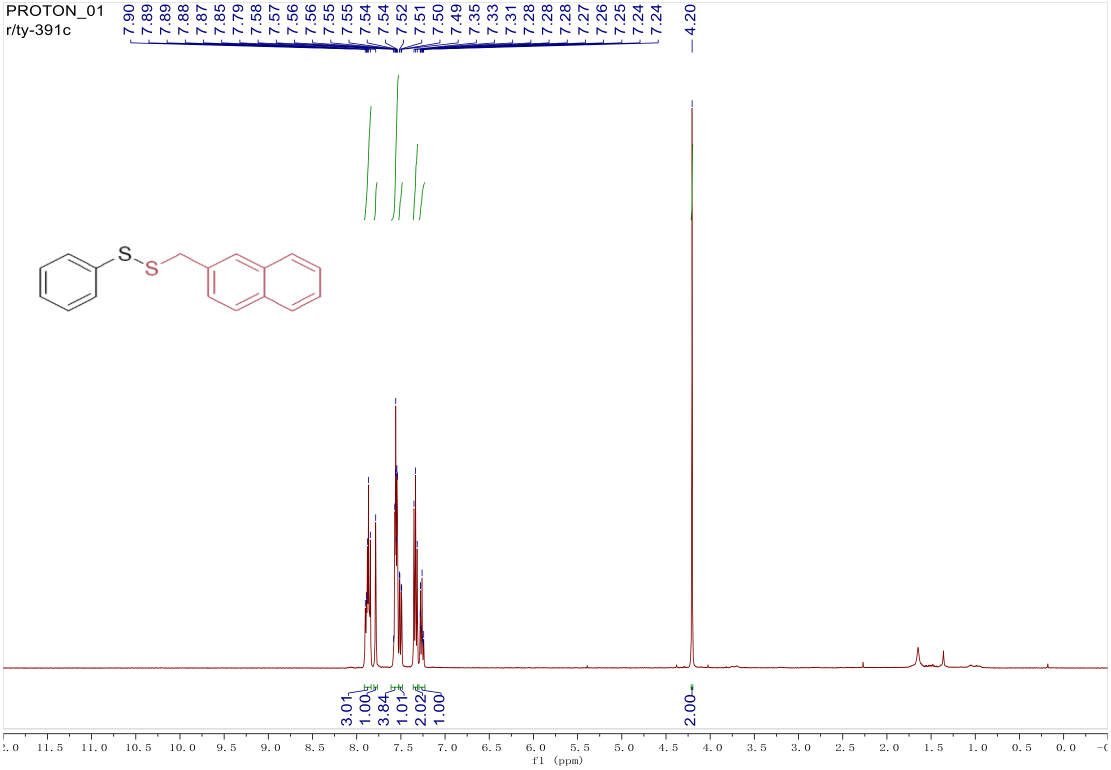
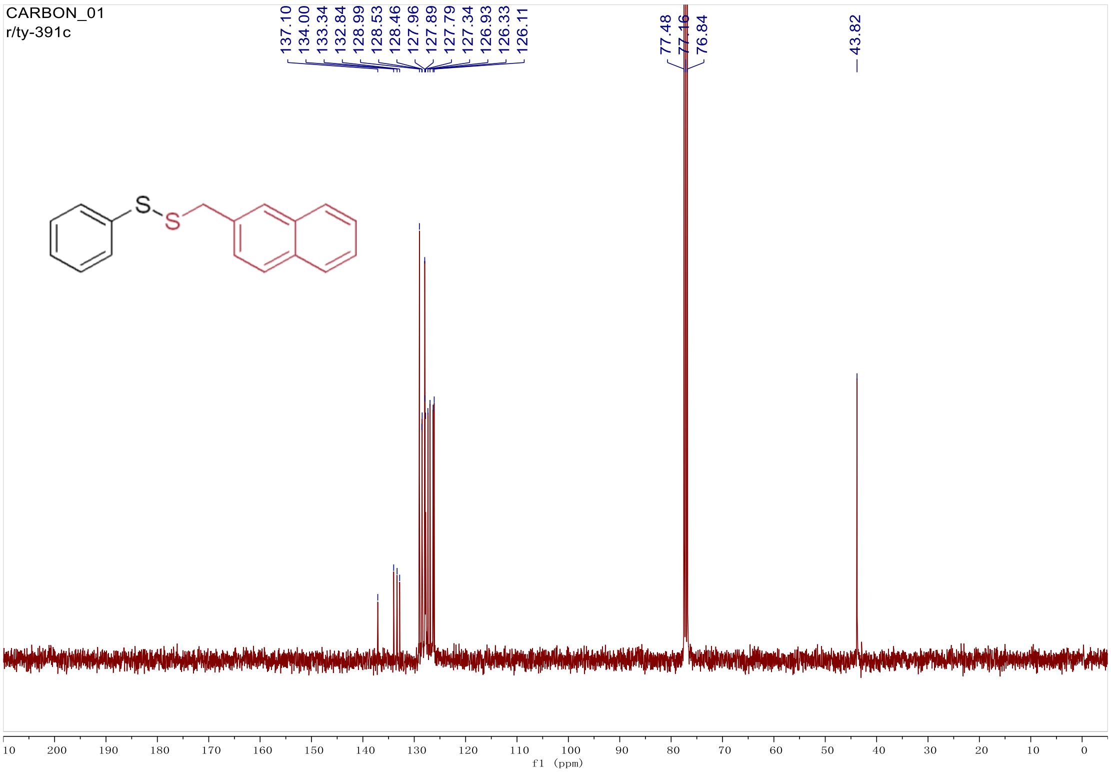
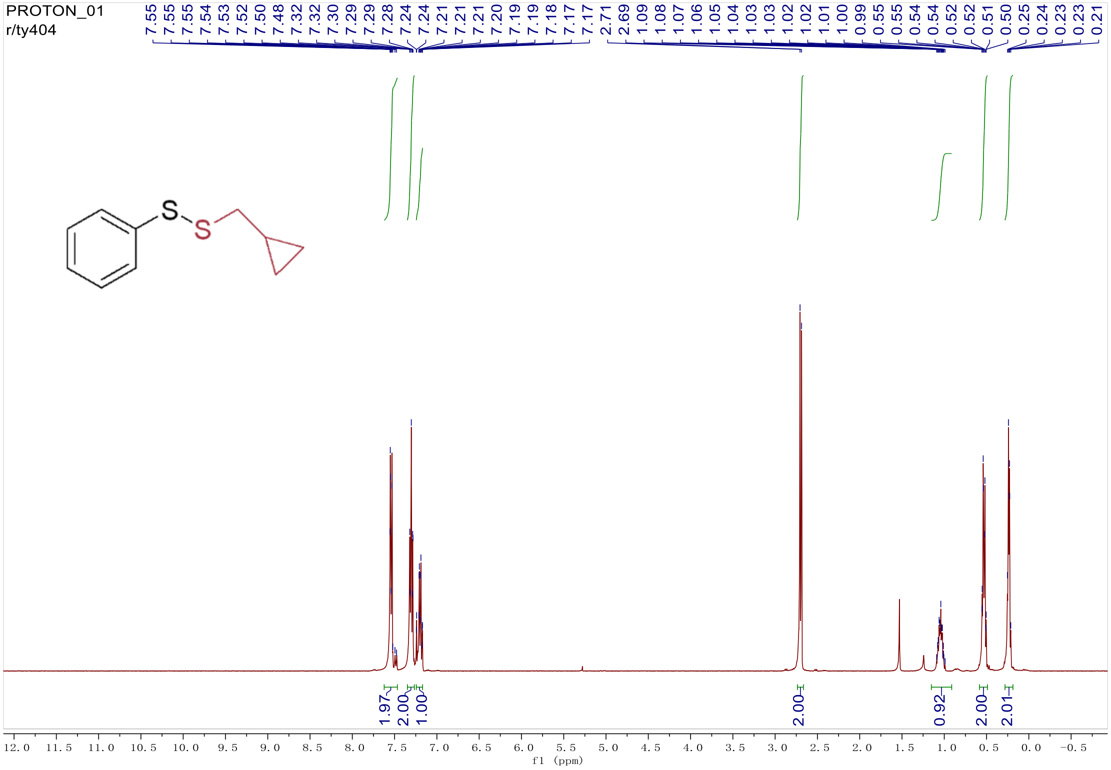
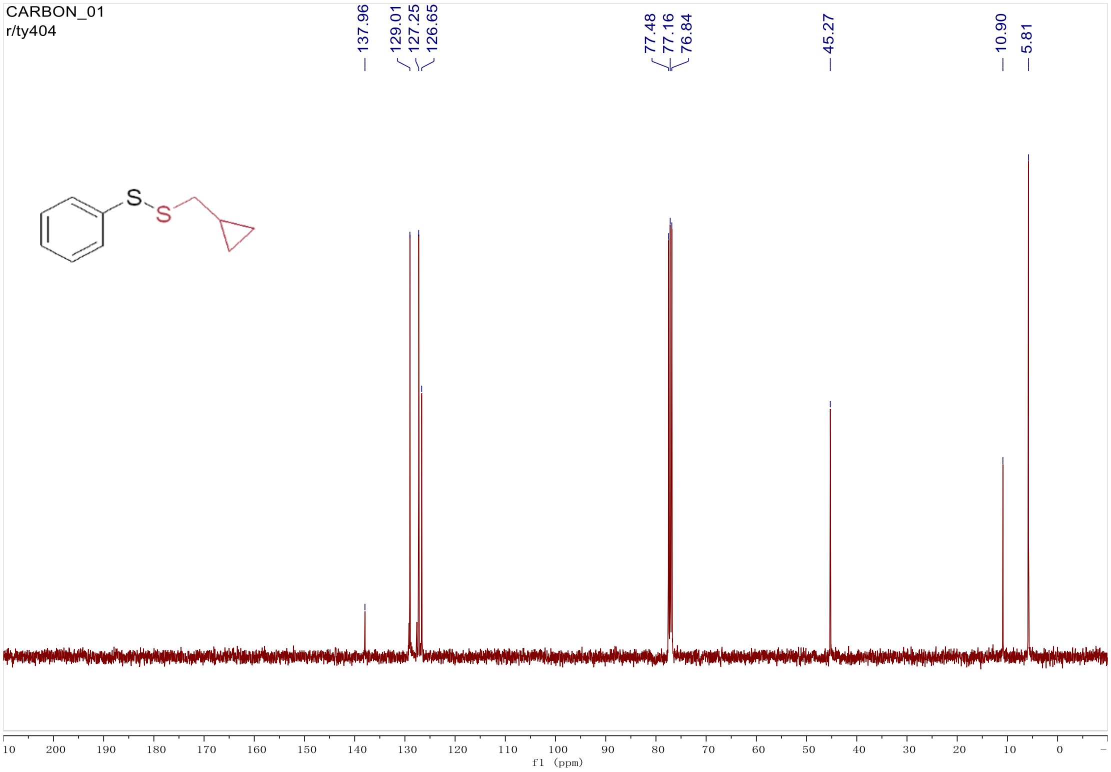


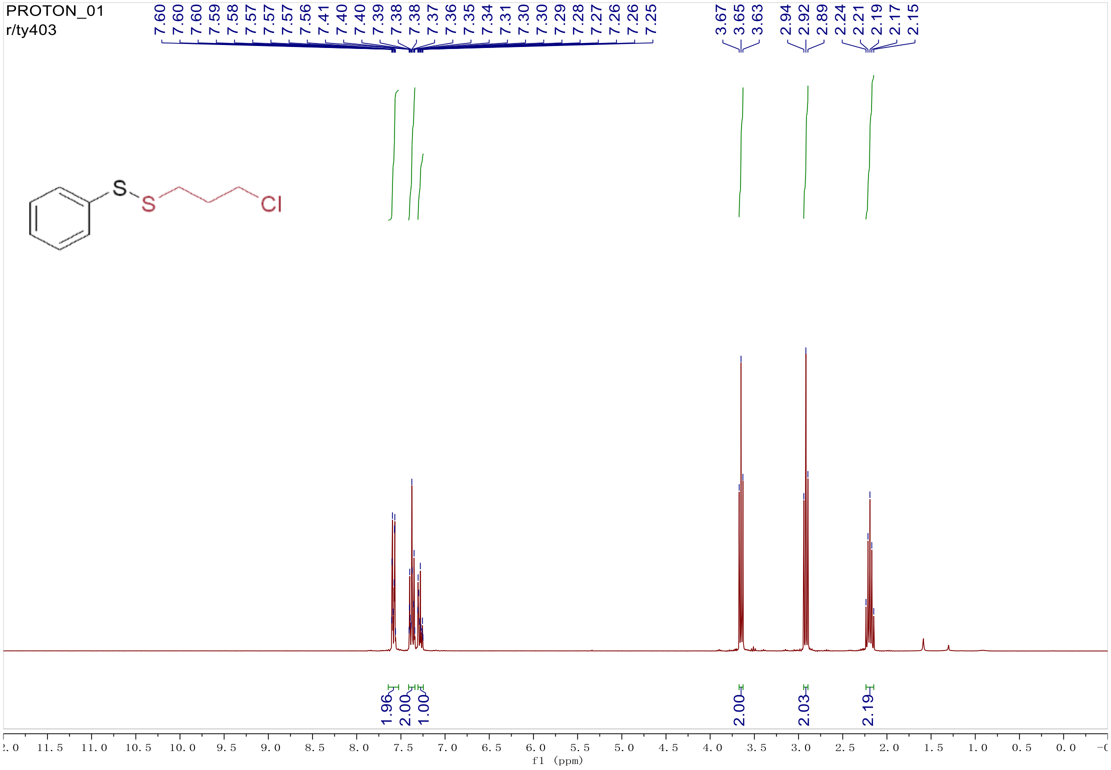


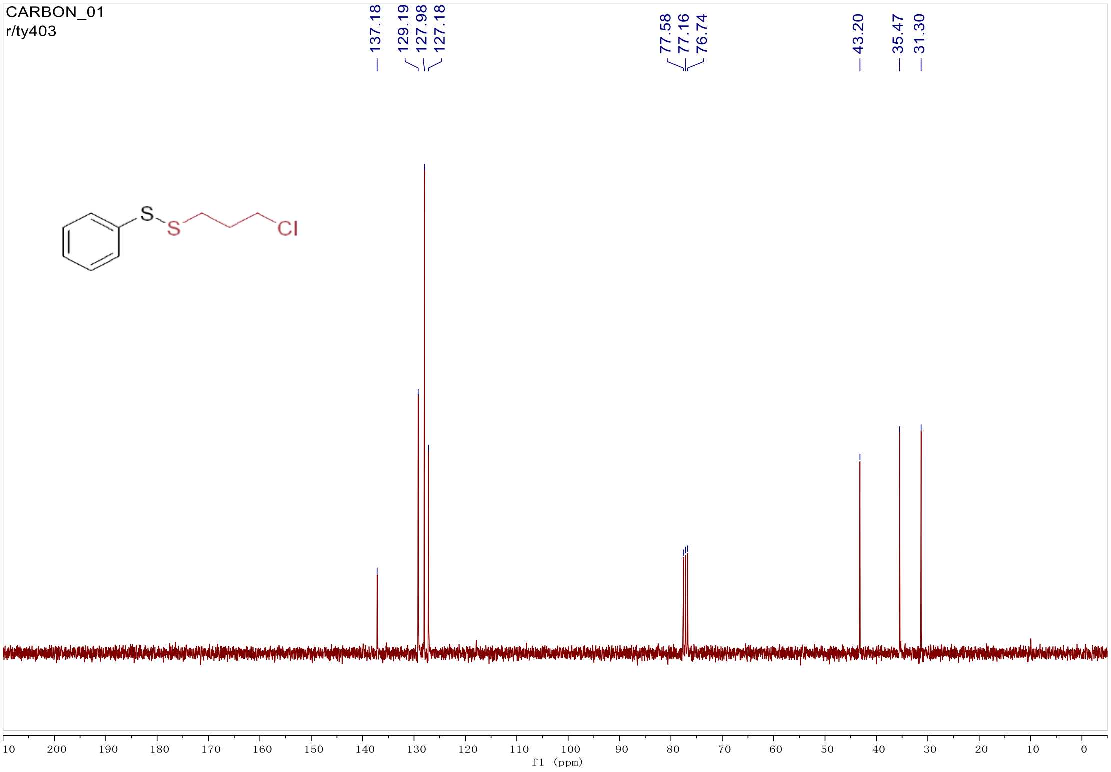
^{1}H and ^{13}C of 25



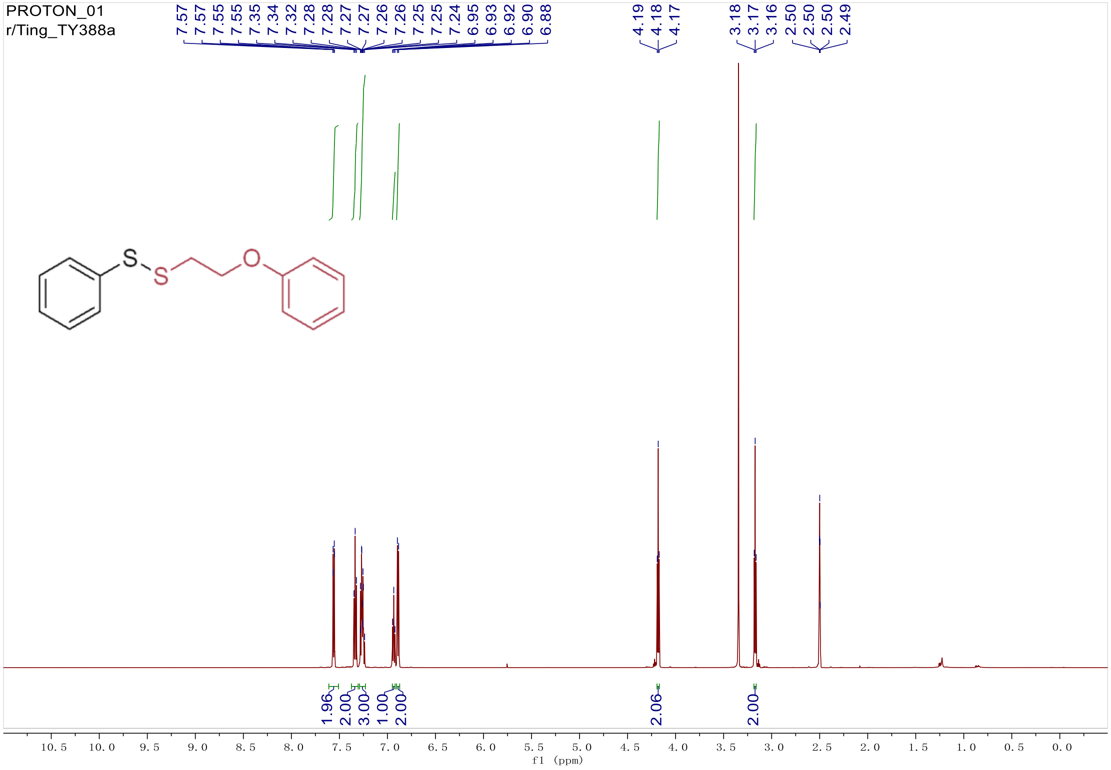


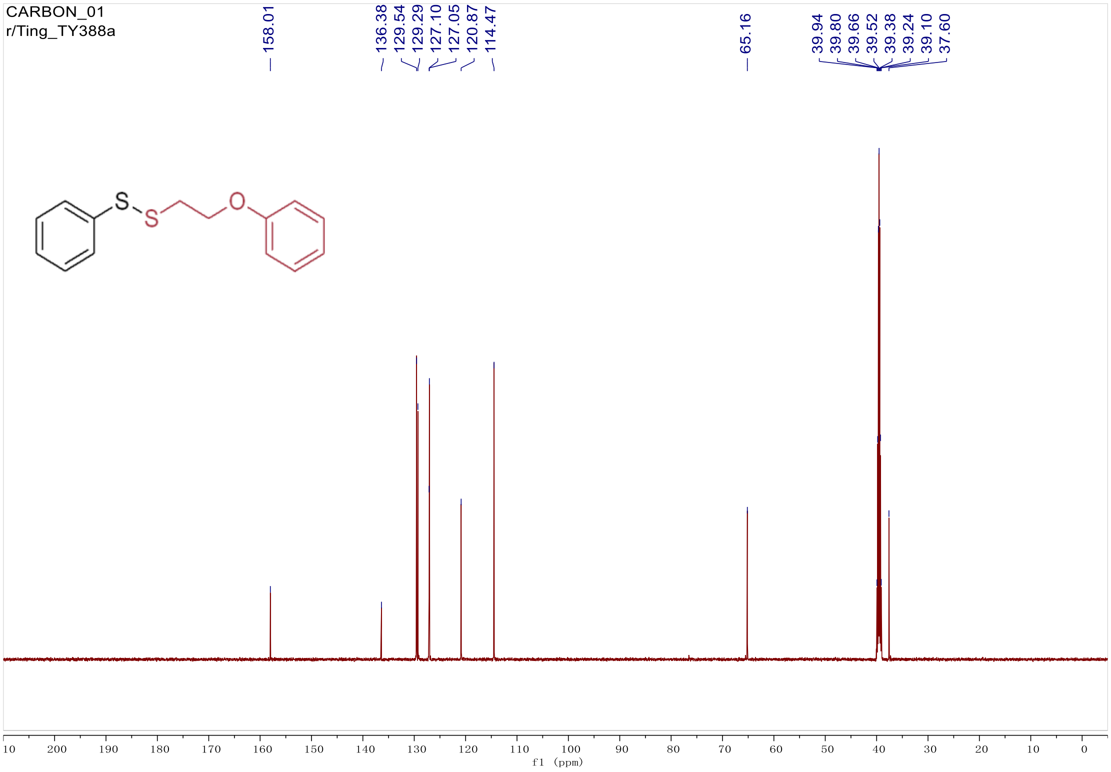
^{1}H and ^{13}C of 26



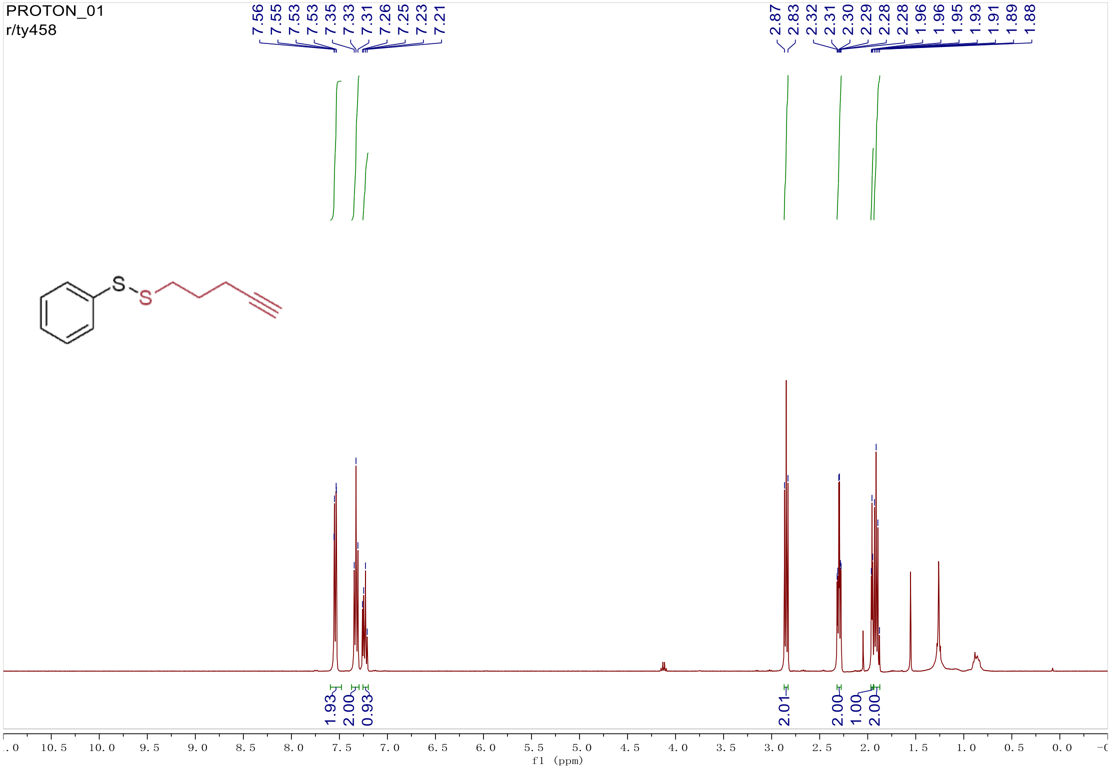


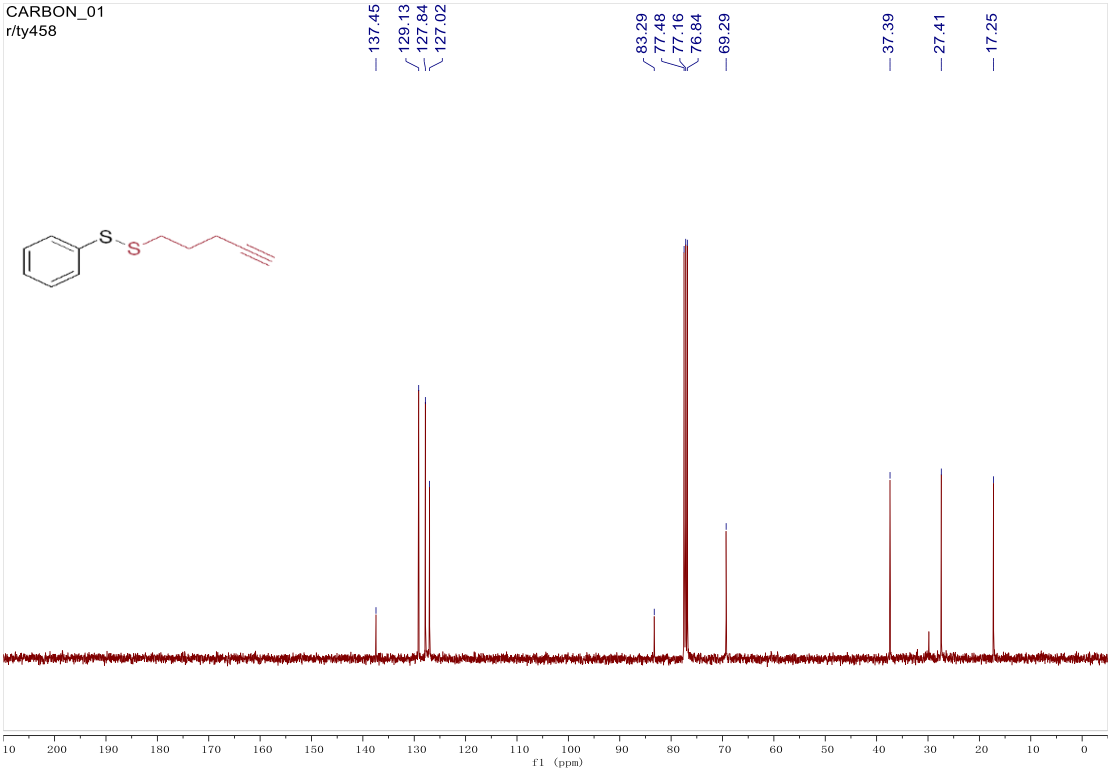
^{1}H and ^{13}C of 27



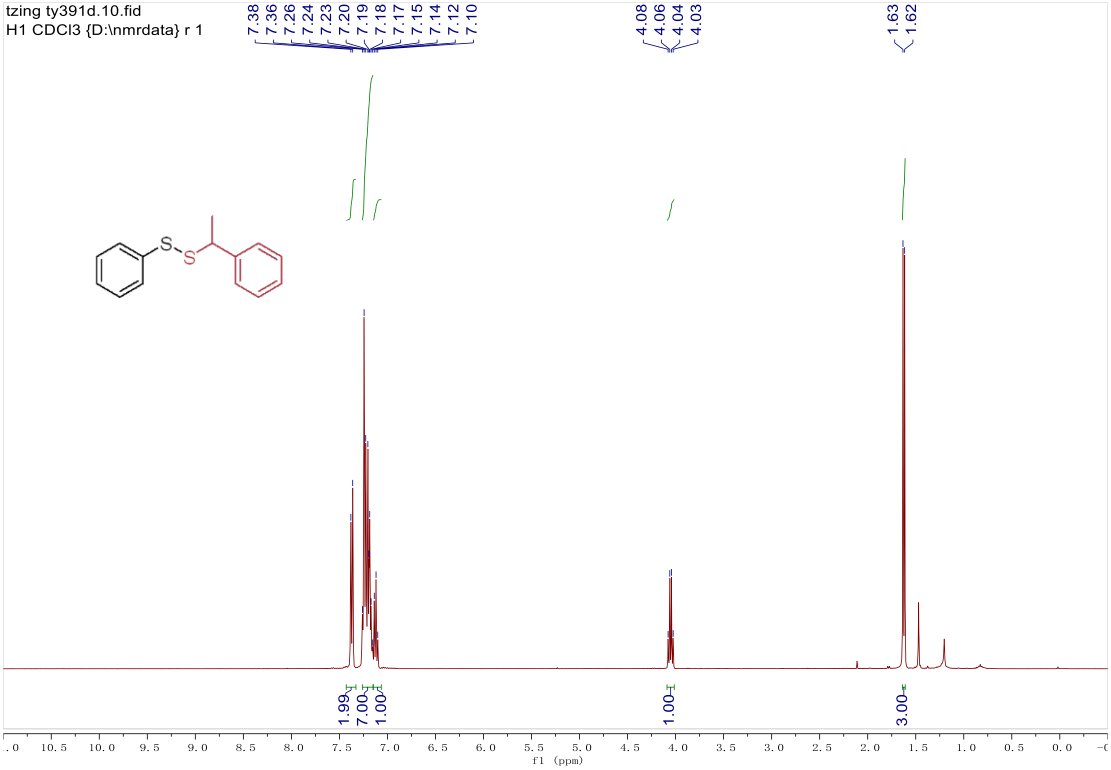


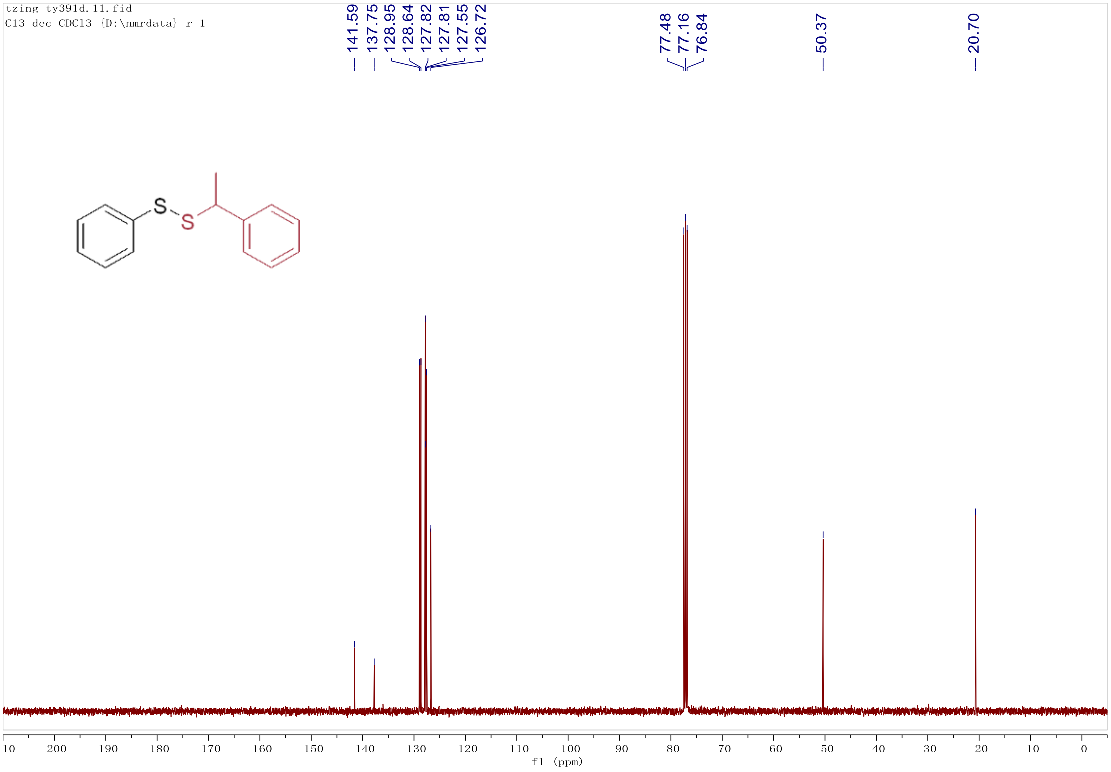
^{1}H and ^{13}C of 28



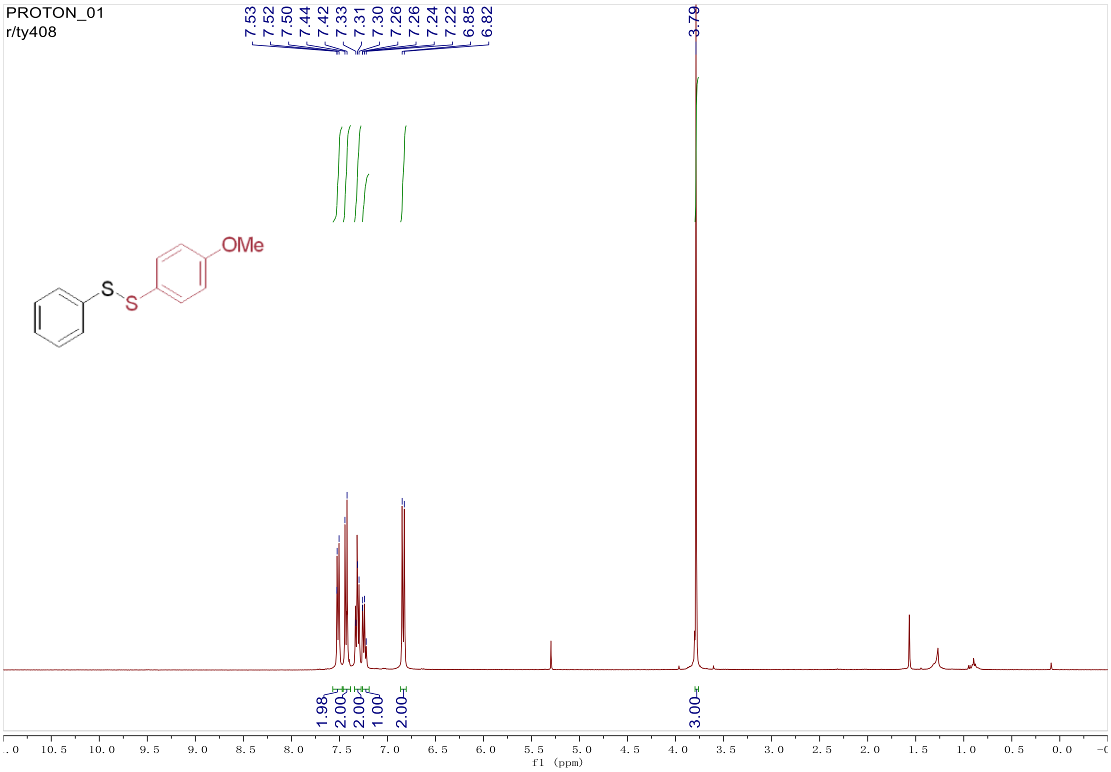


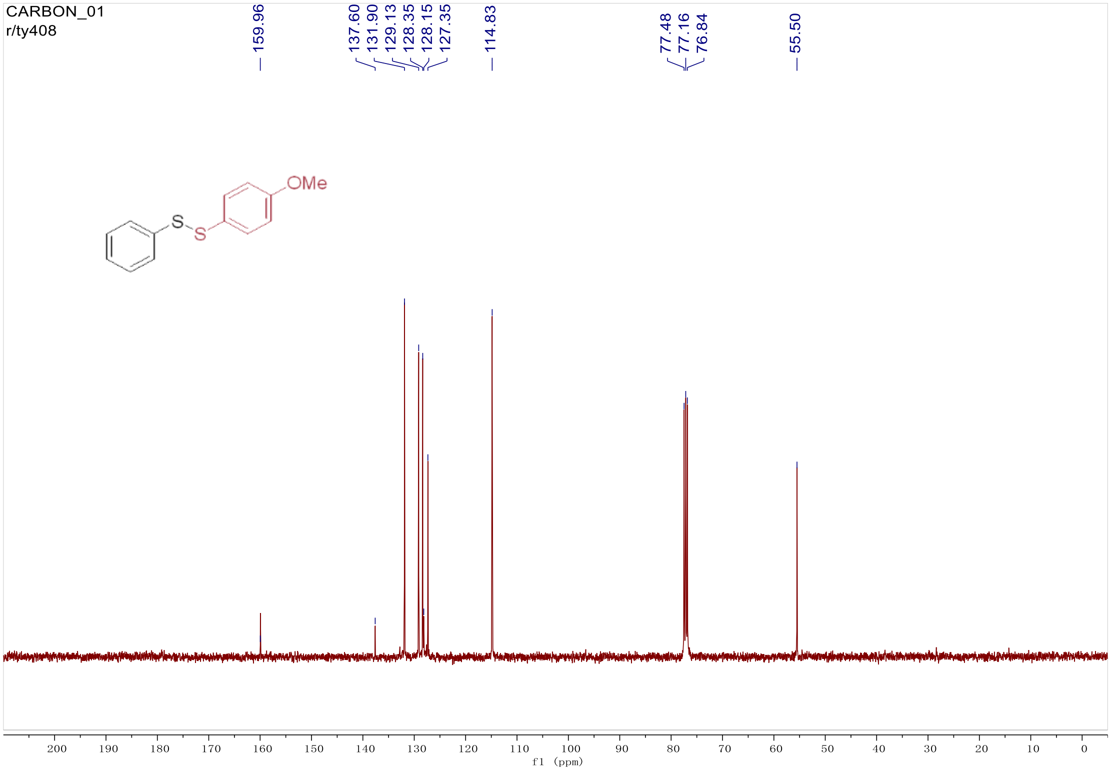
^{1}H and ^{13}C of 29



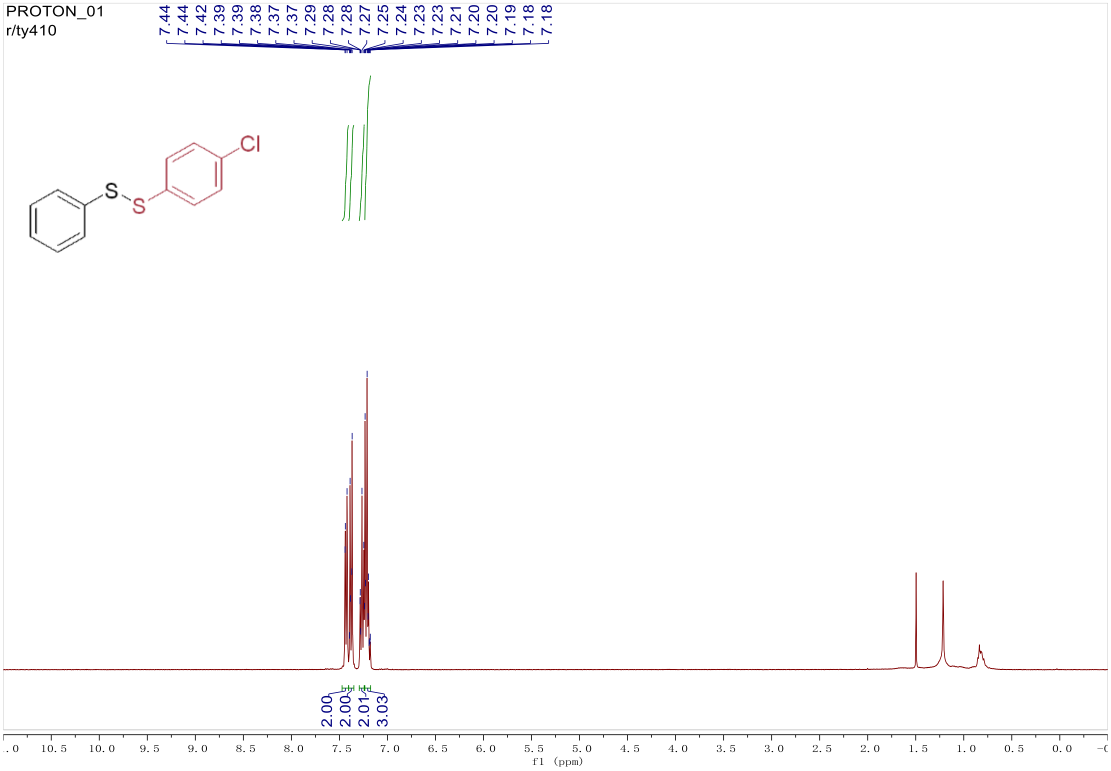


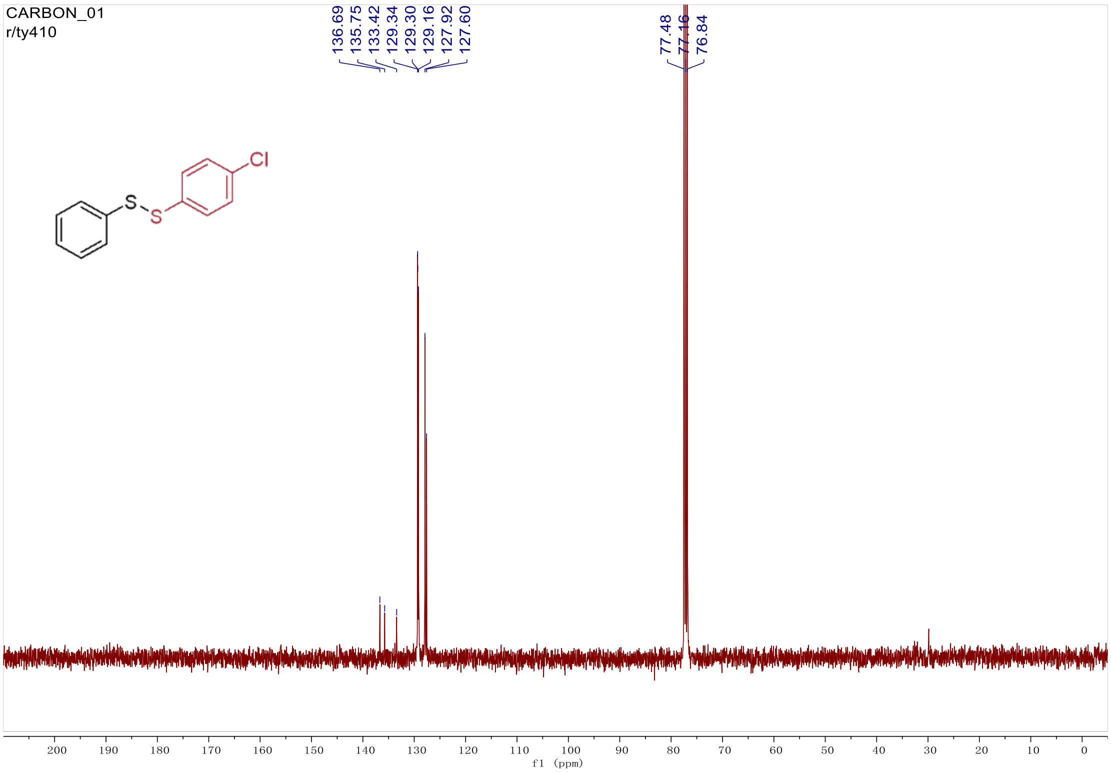
^{1}H and ^{13}C of 30



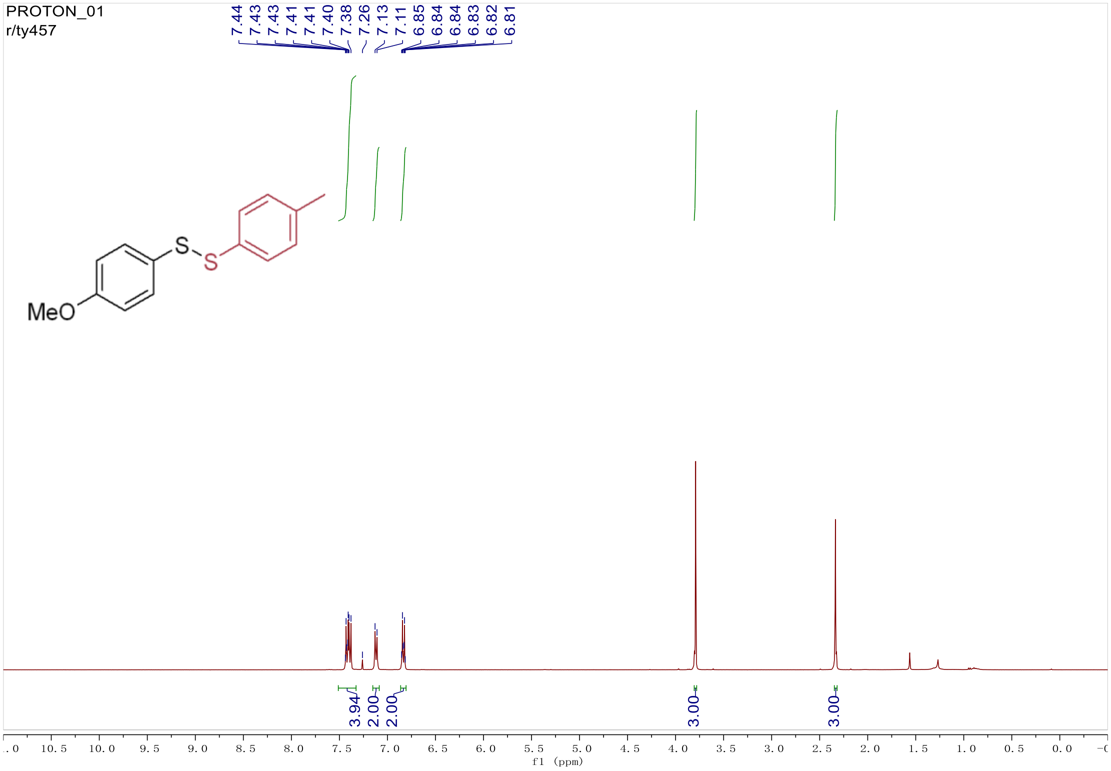


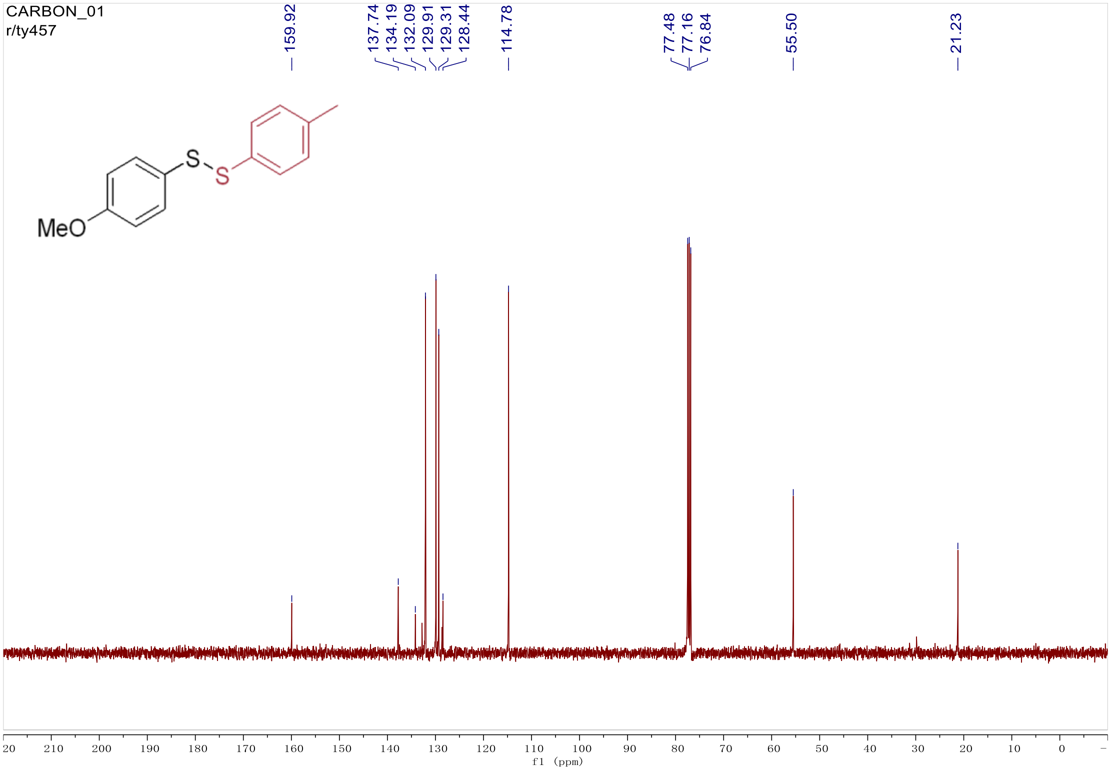
^{1}H and ^{13}C of 31



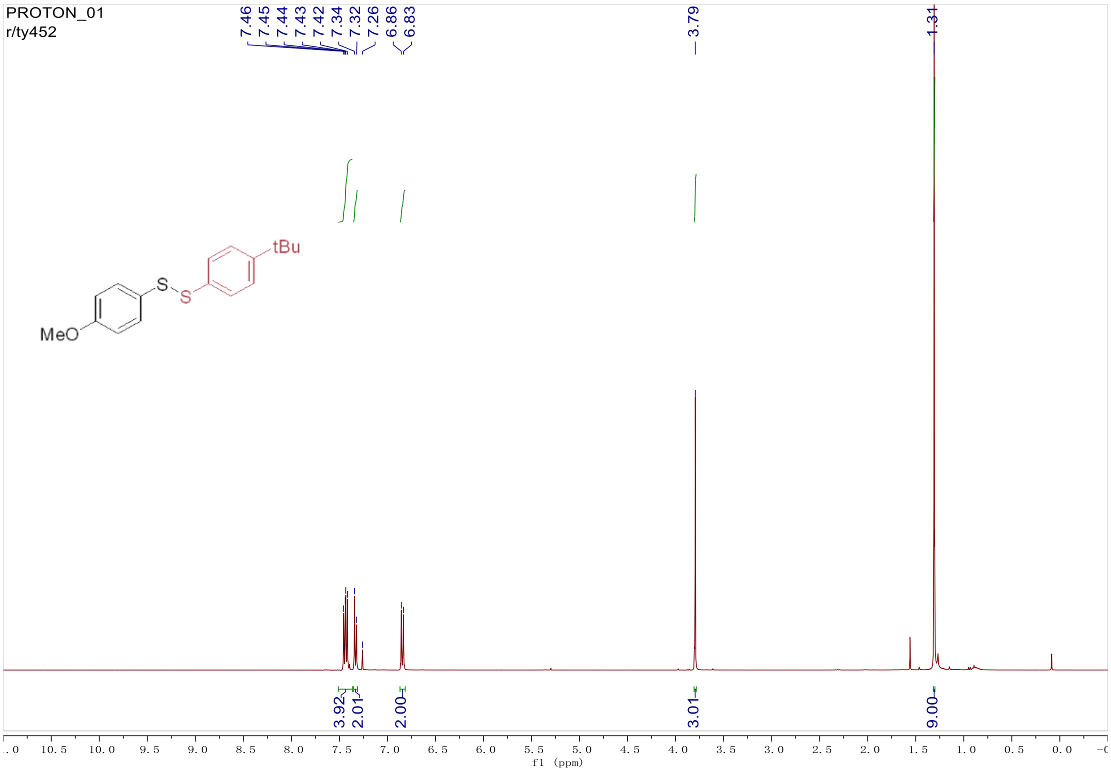


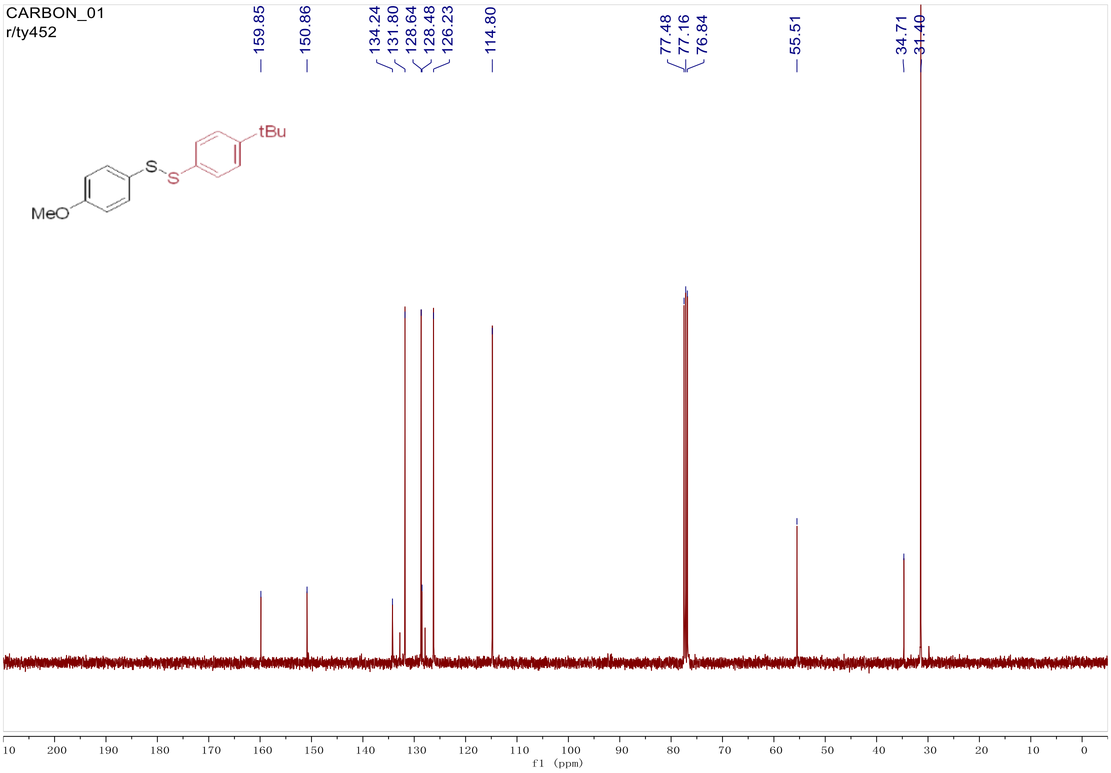
^{1}H and ^{13}C of 32



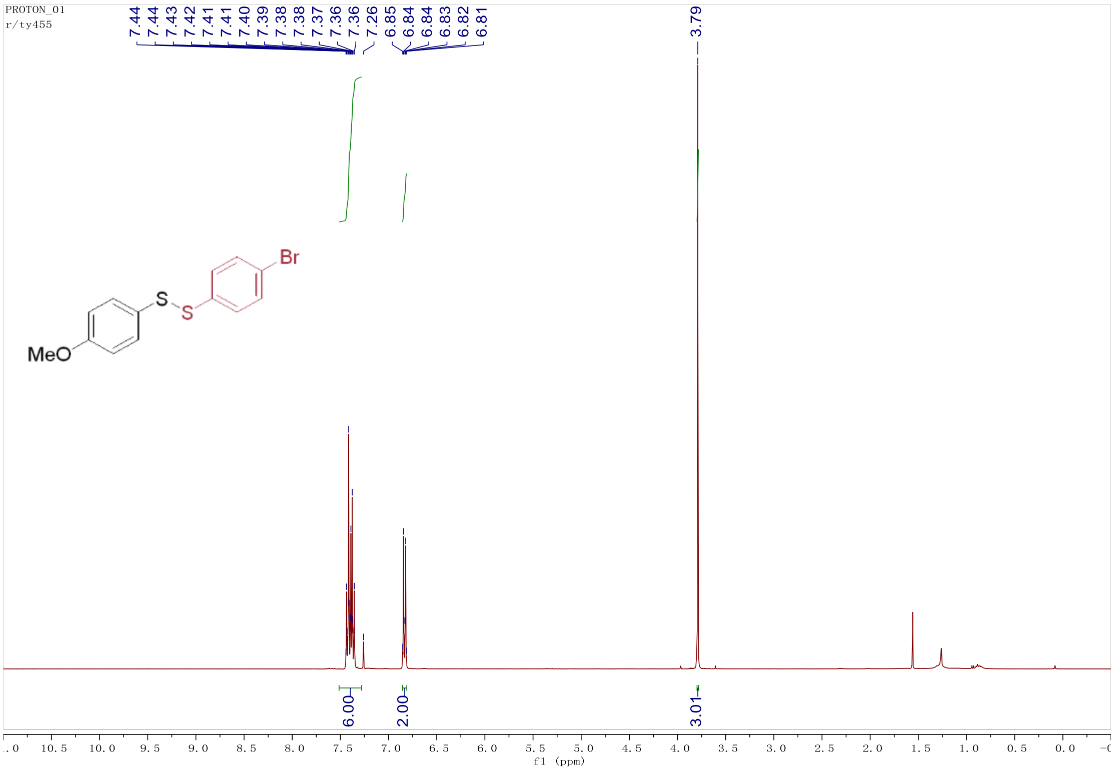


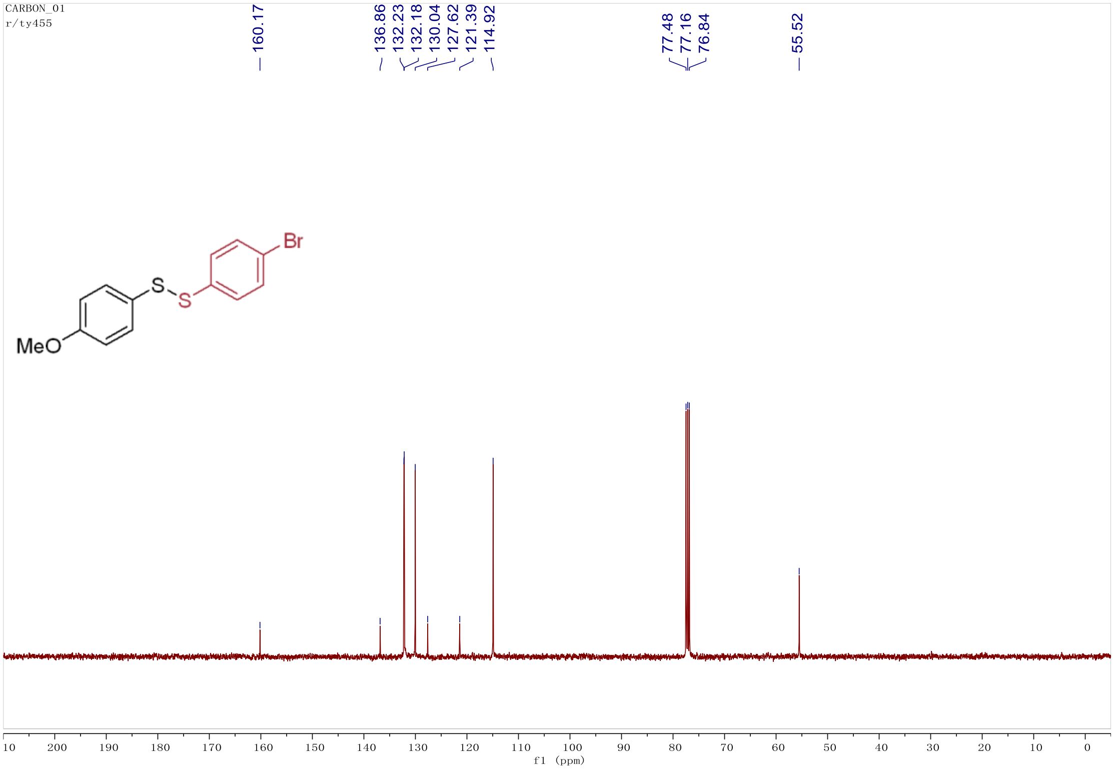
^{1}H and ^{13}C of 33



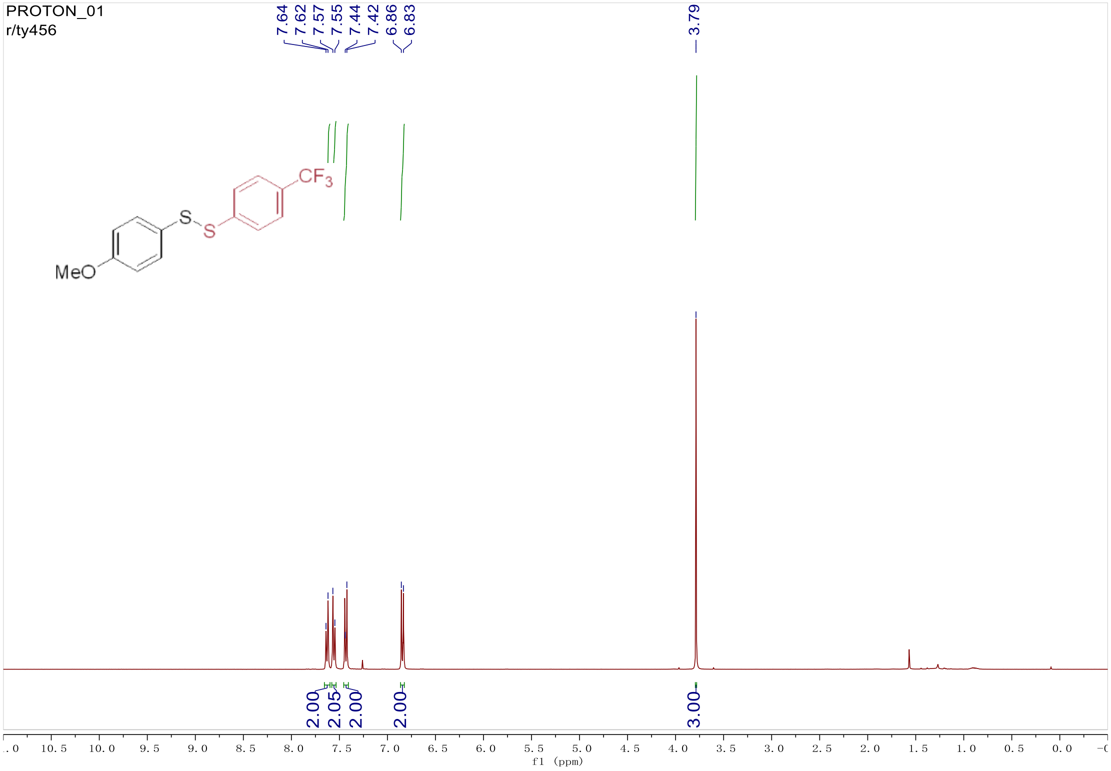


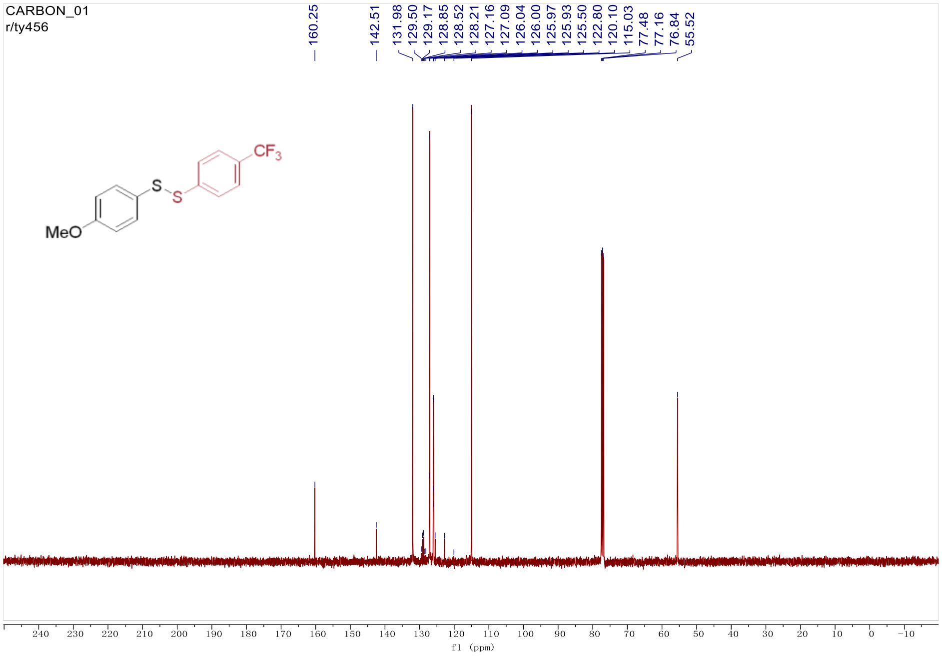
^{1}H and ^{13}C of 34

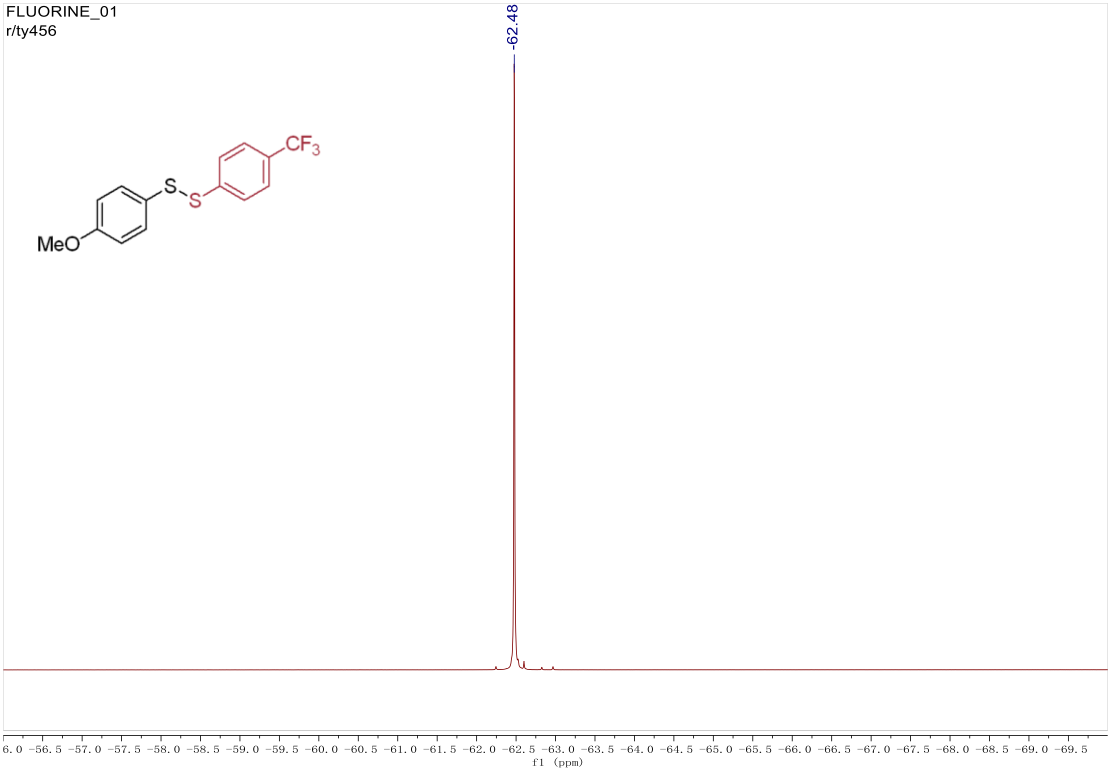




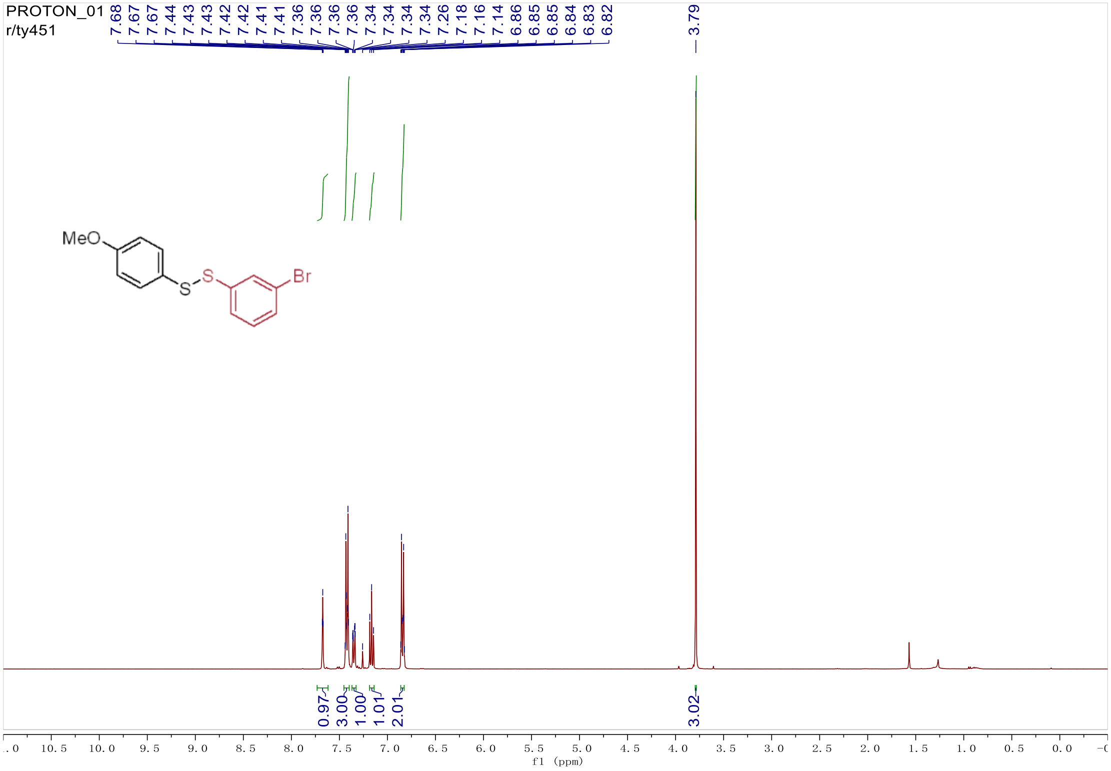
^{1}H and ^{13}C of 35

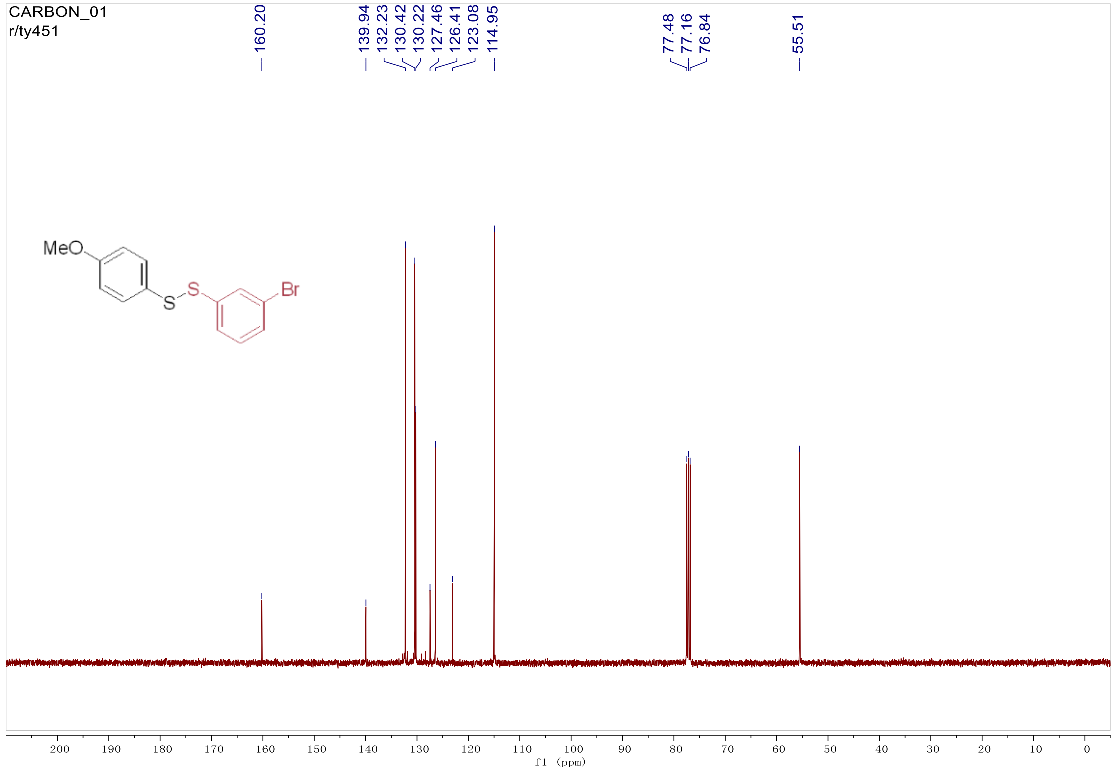




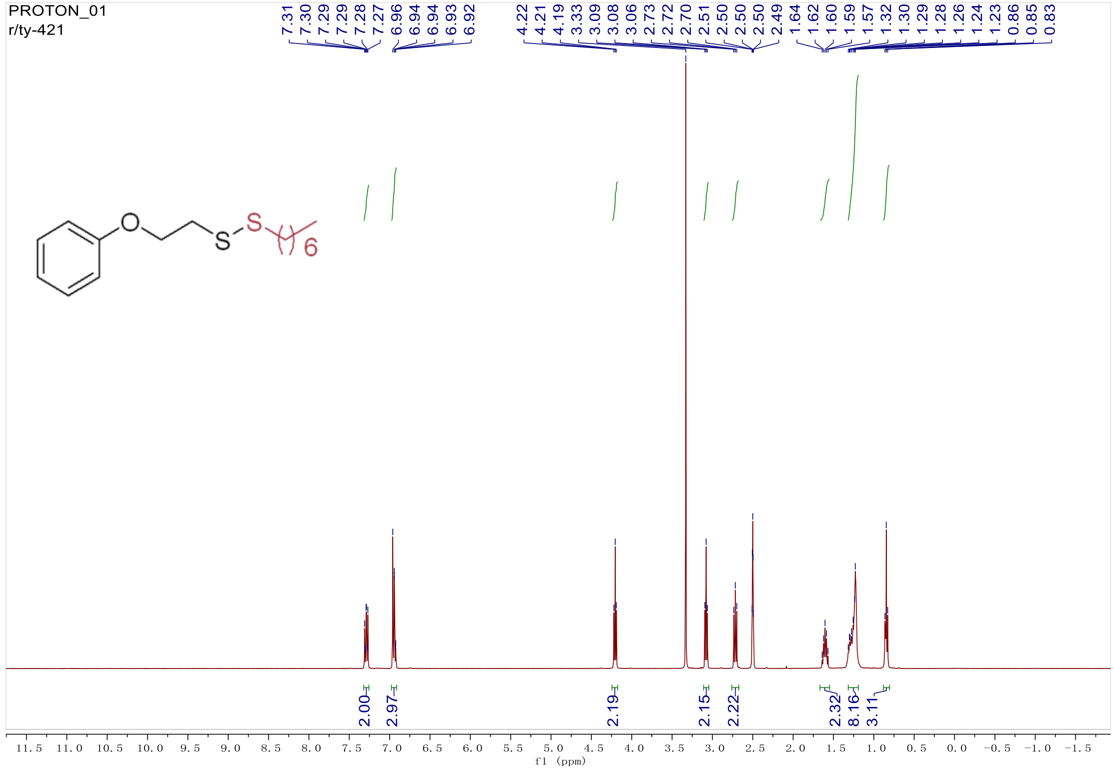


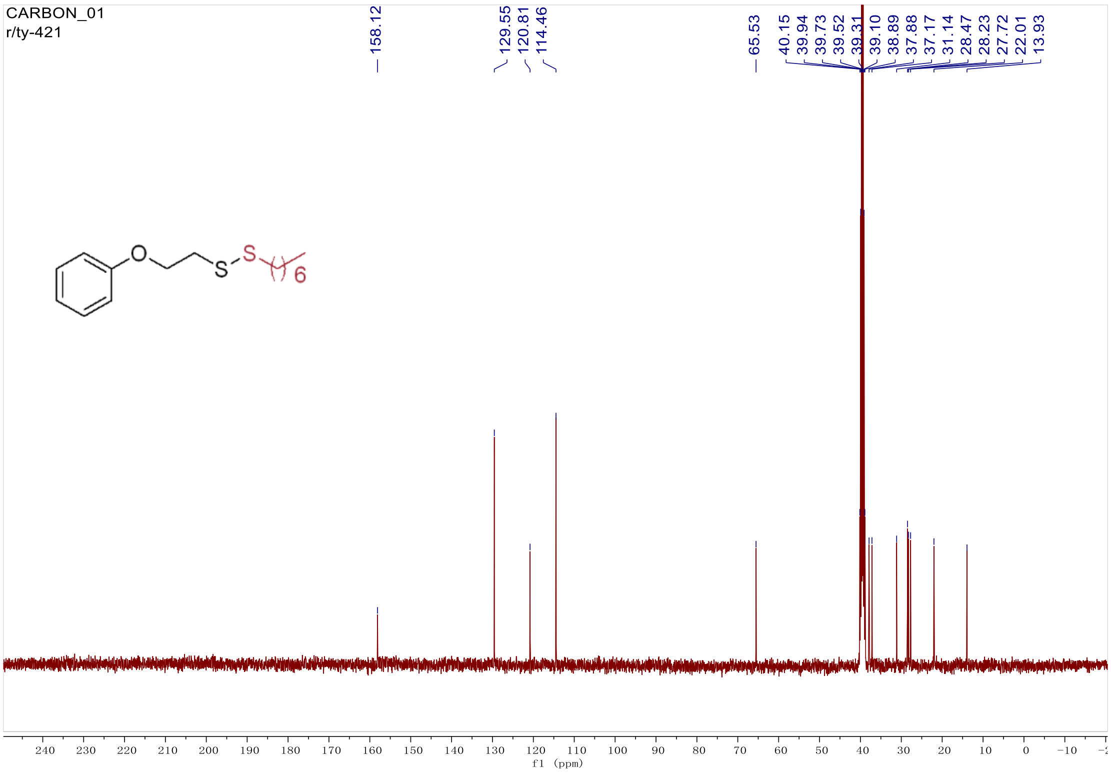
^{1}H and ^{13}C of 36



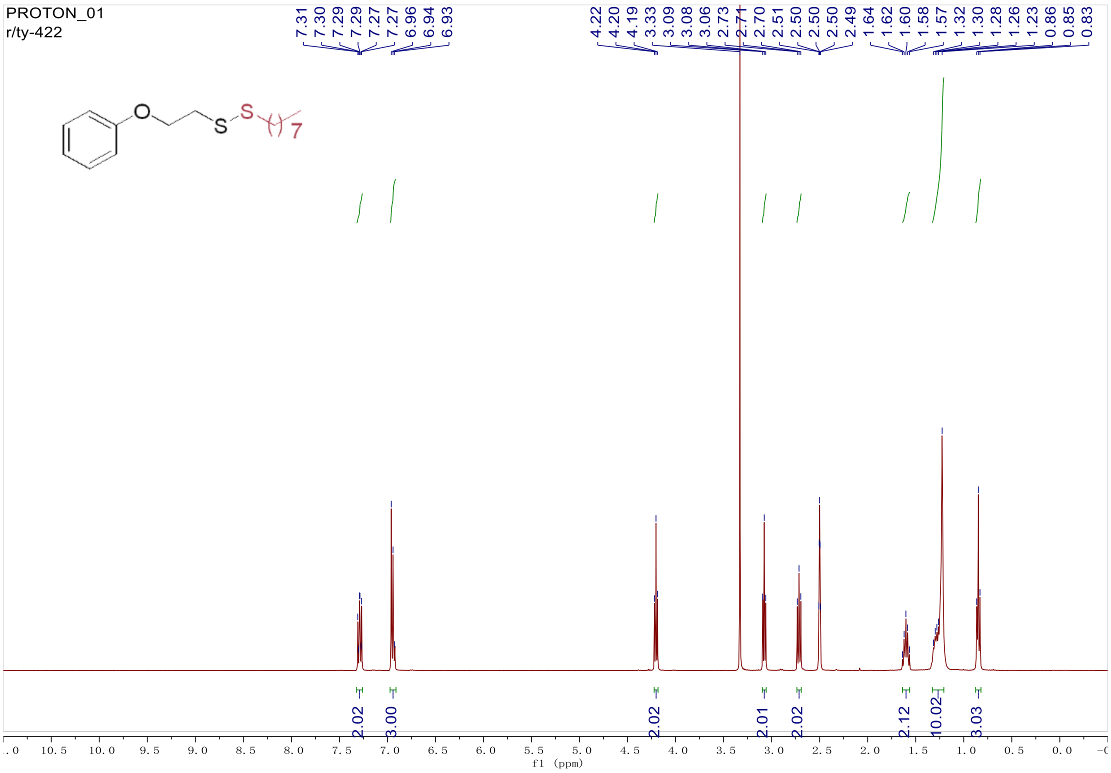


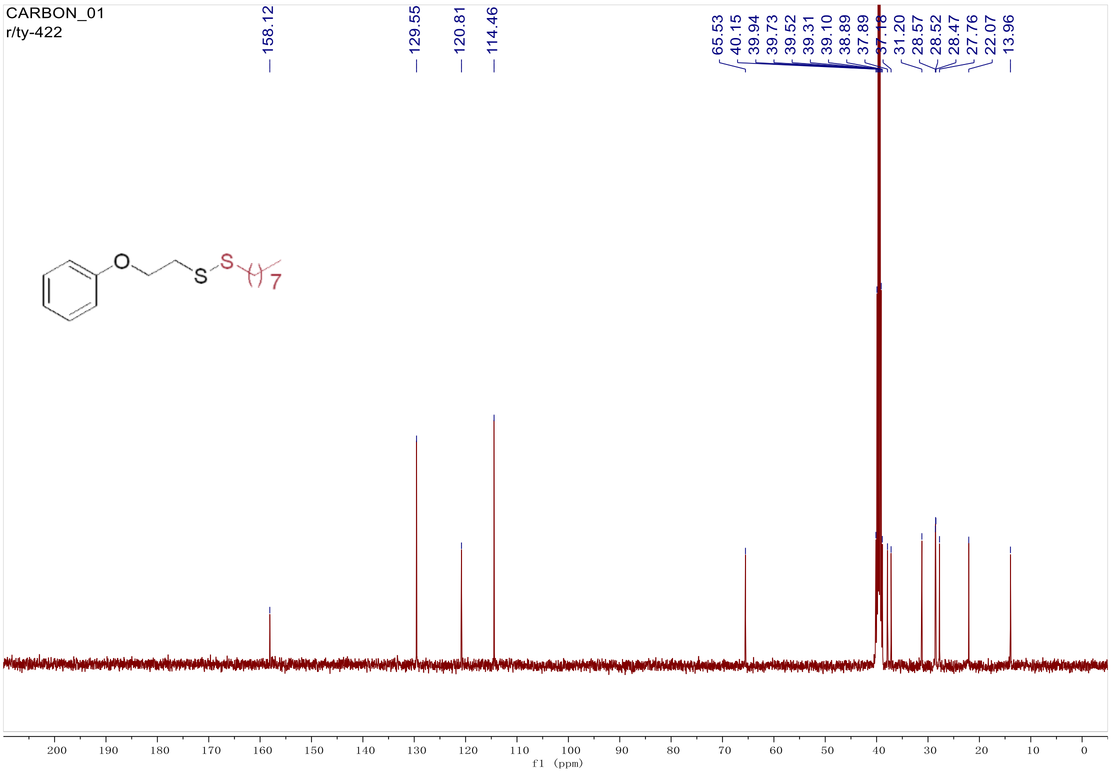
^{1}H and ^{13}C of 37



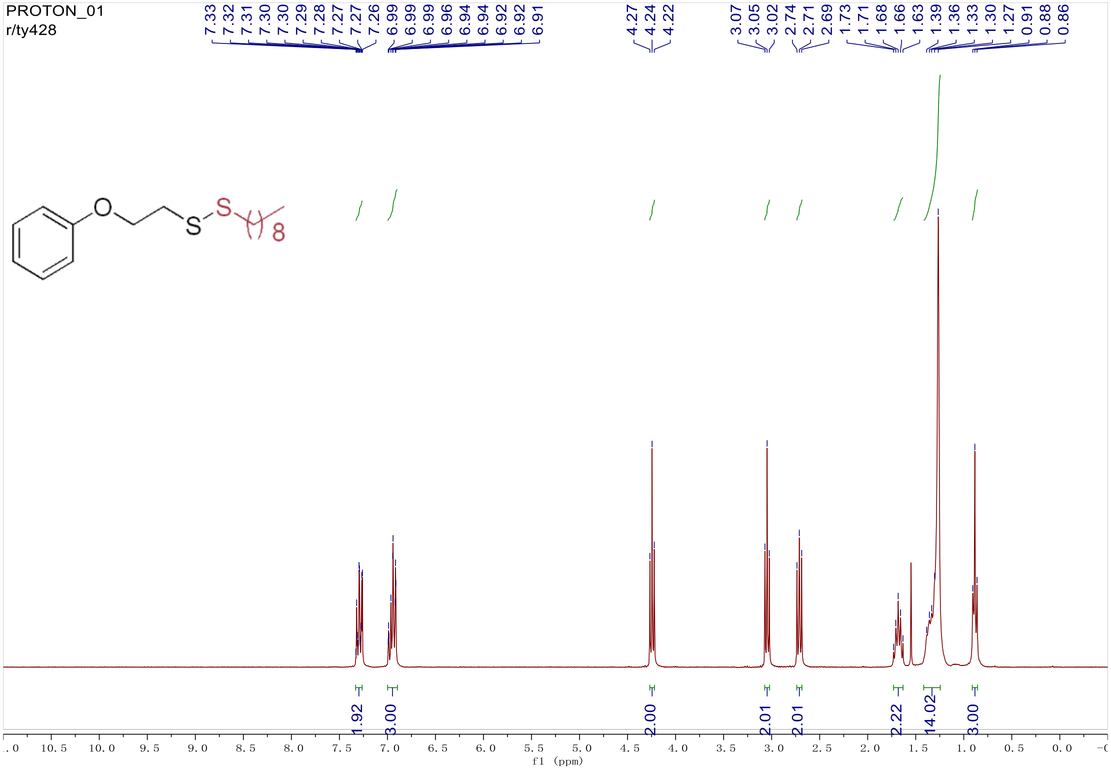


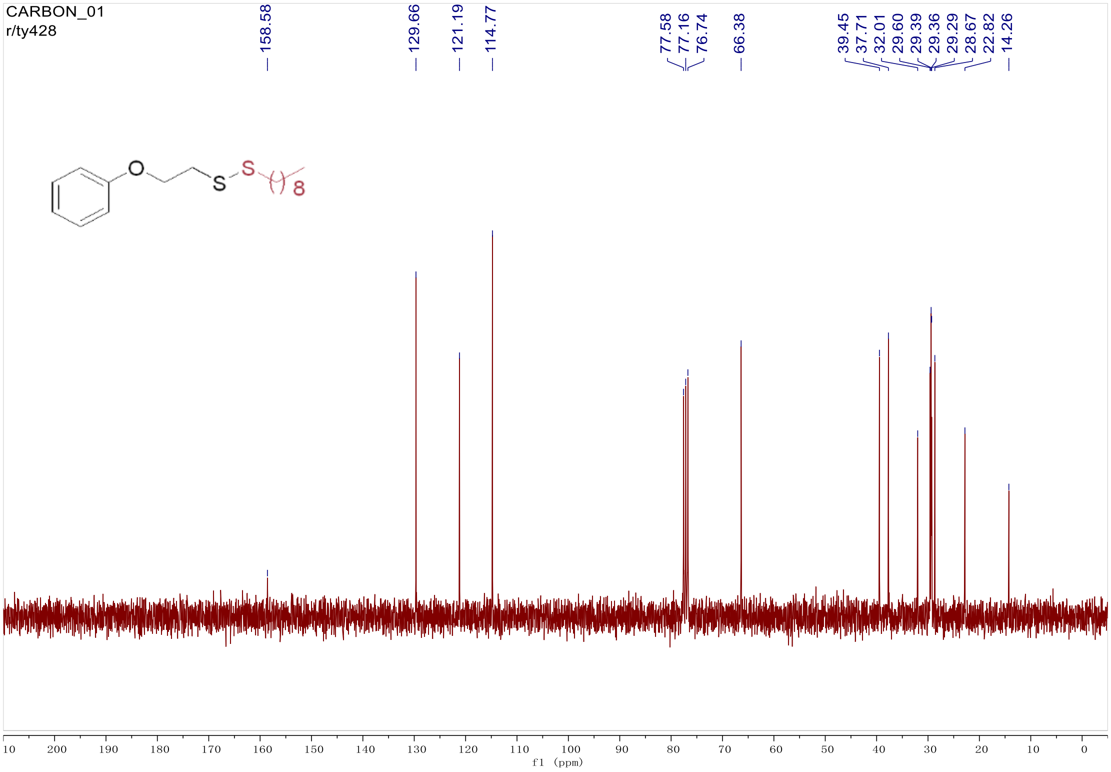
^{1}H and ^{13}C of 38



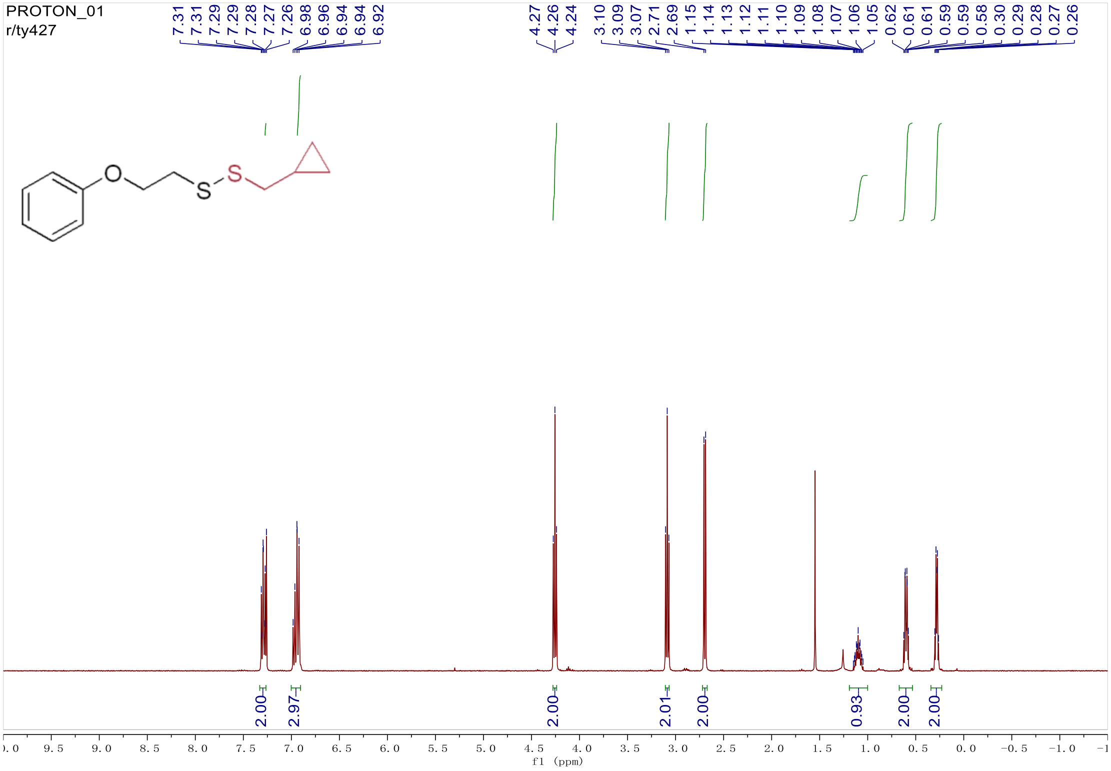


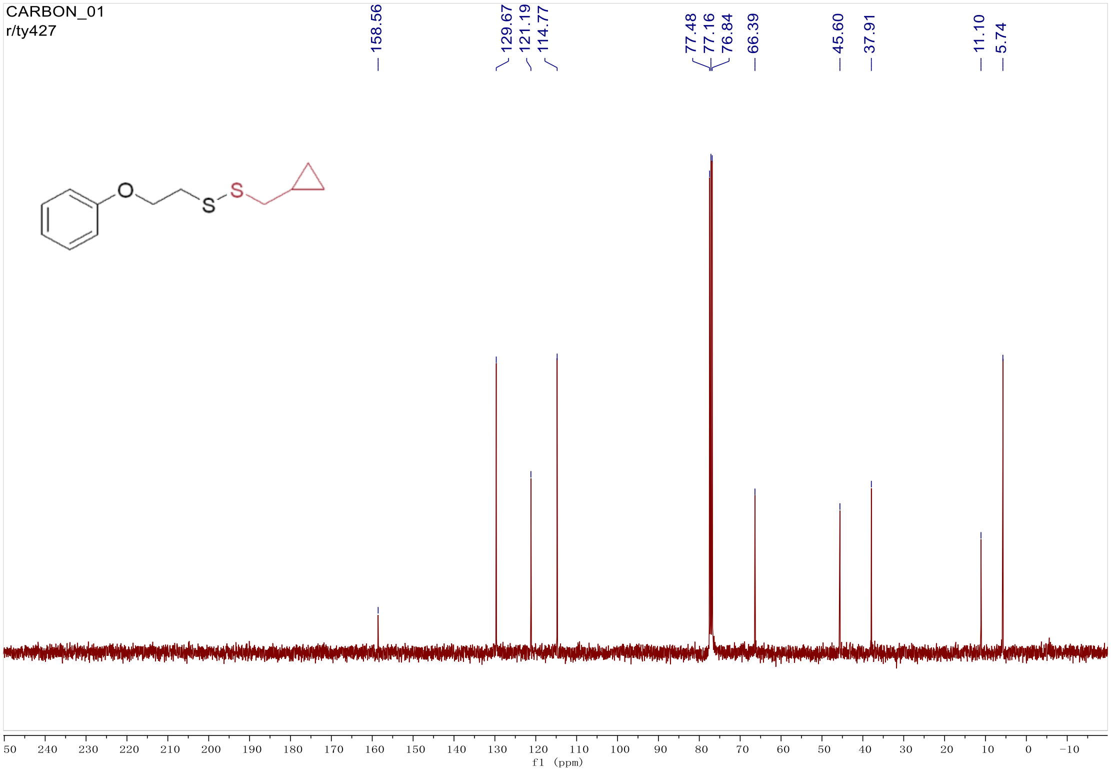
^{1}H and ^{13}C of 39



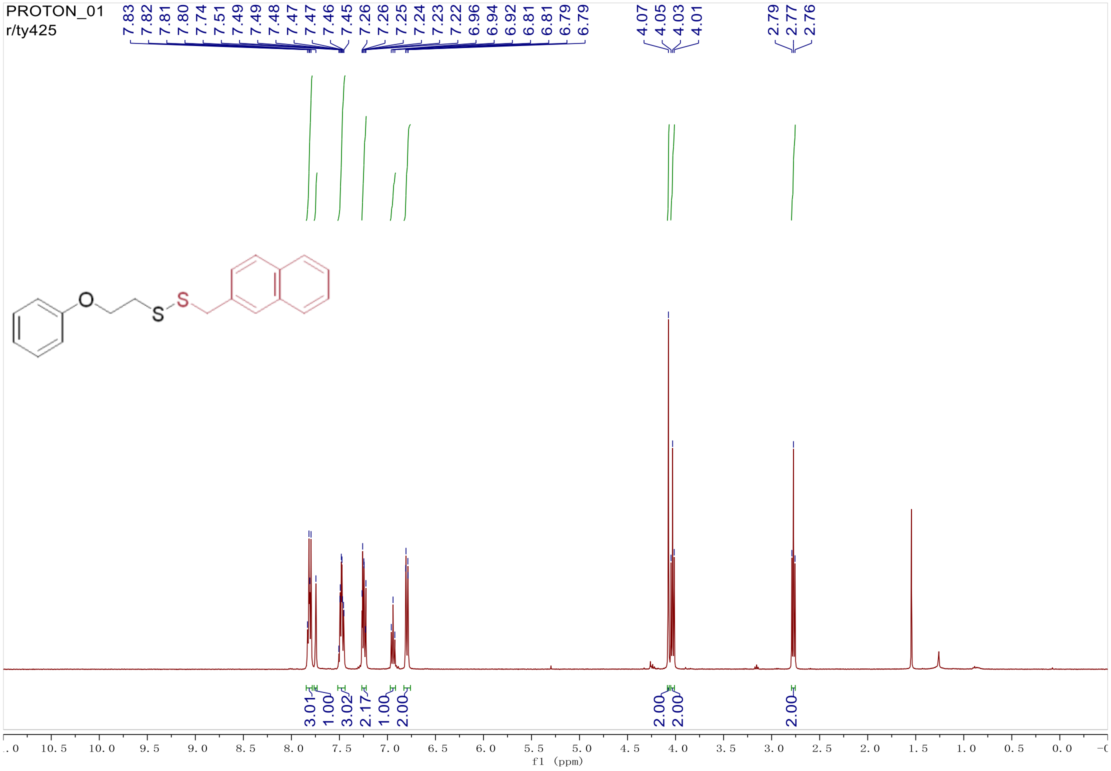


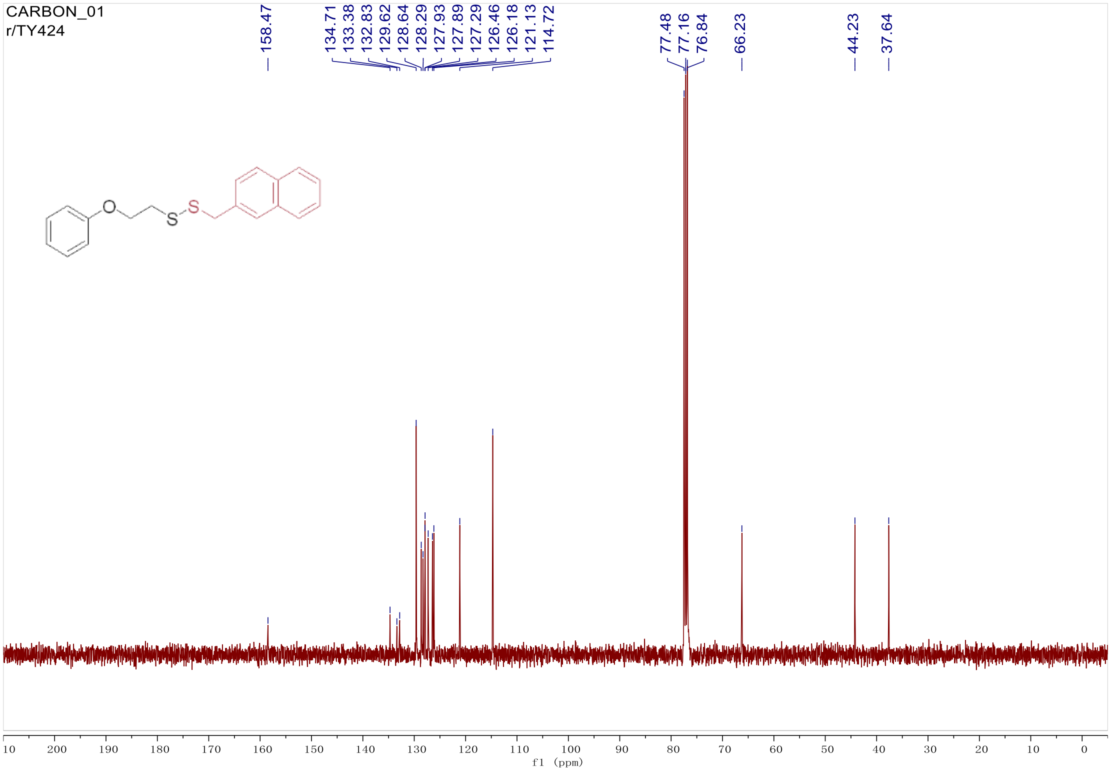
^{1}H and ^{13}C of 40



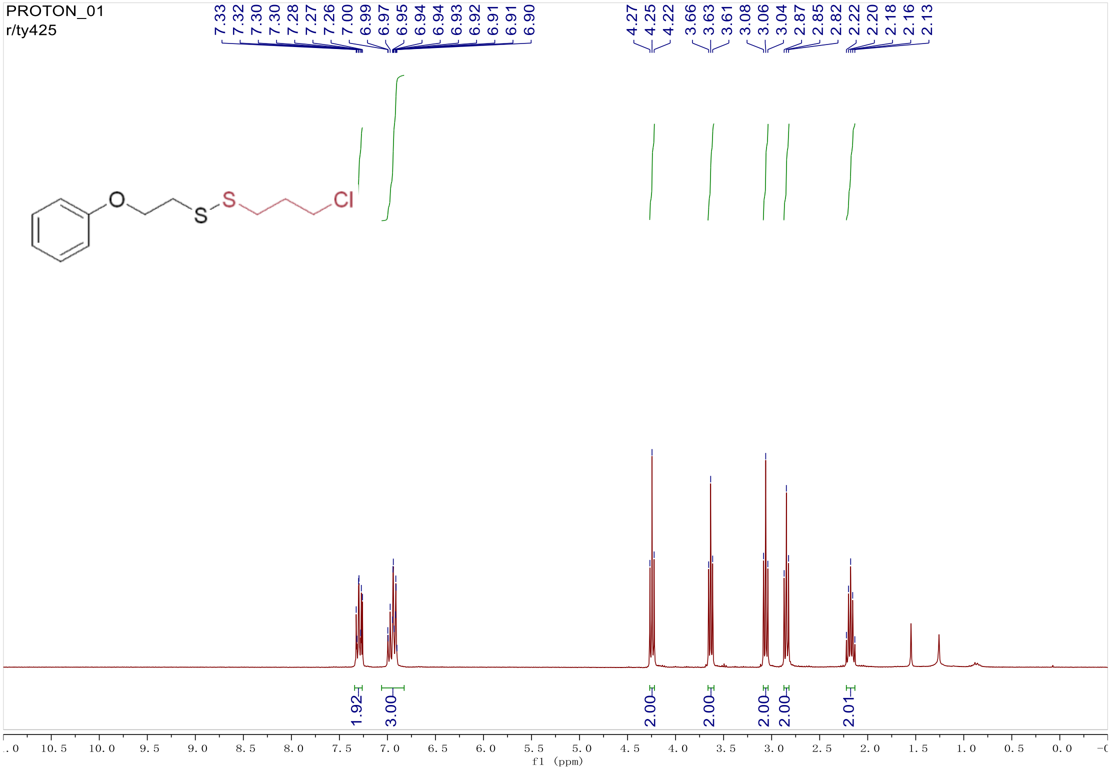


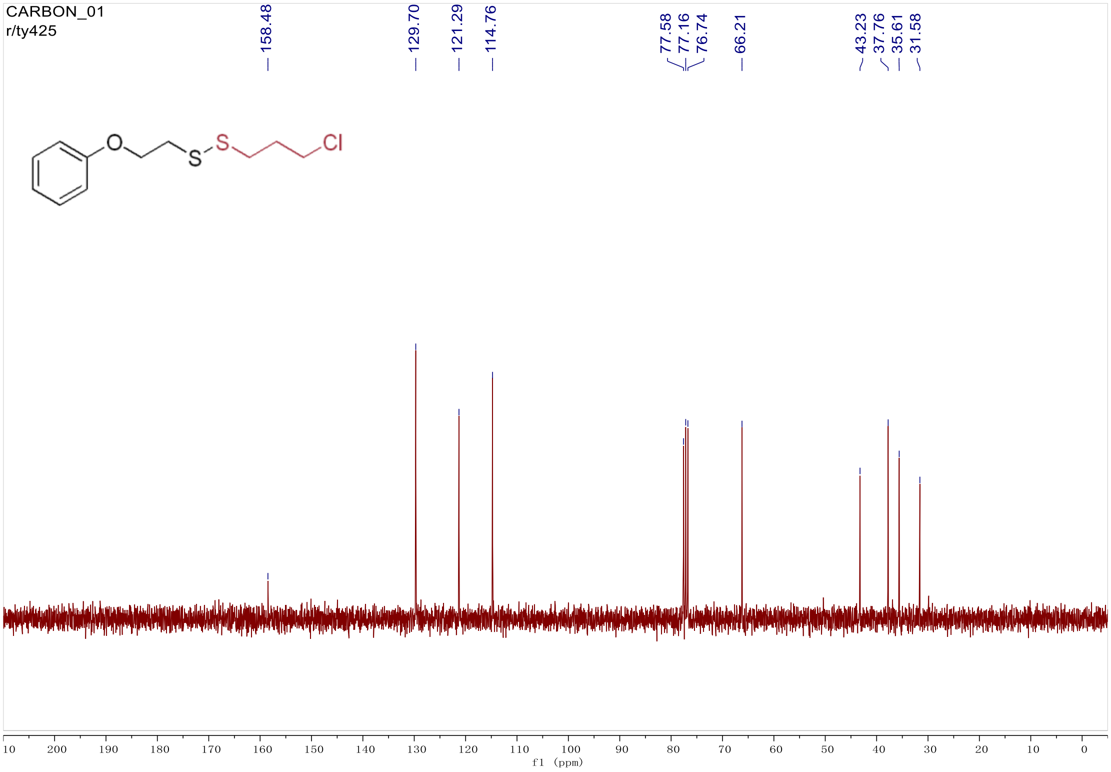
^{1}H and ^{13}C of 41



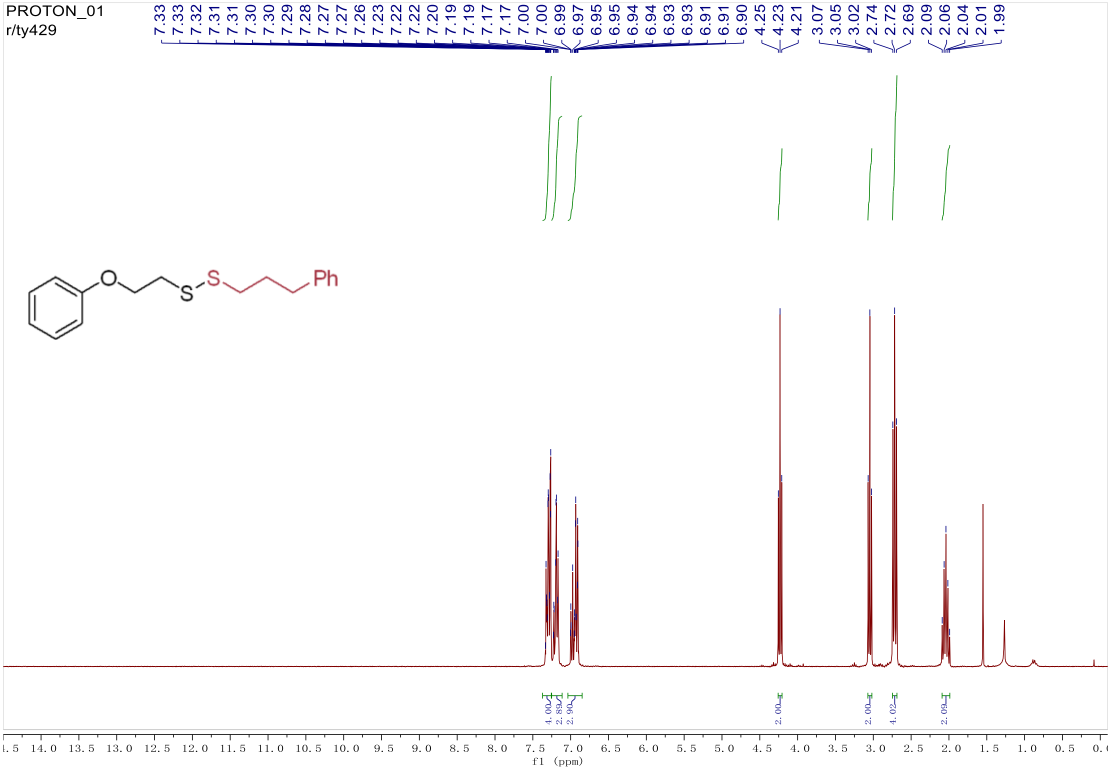


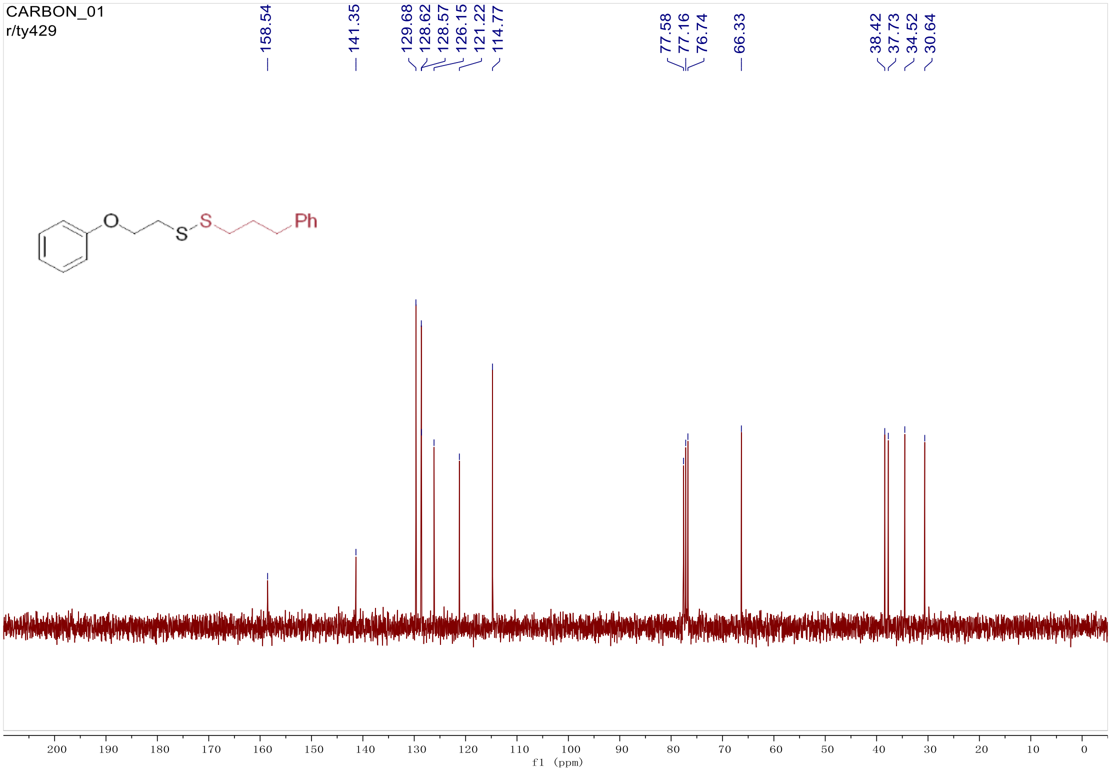
^{1}H and ^{13}C of 42



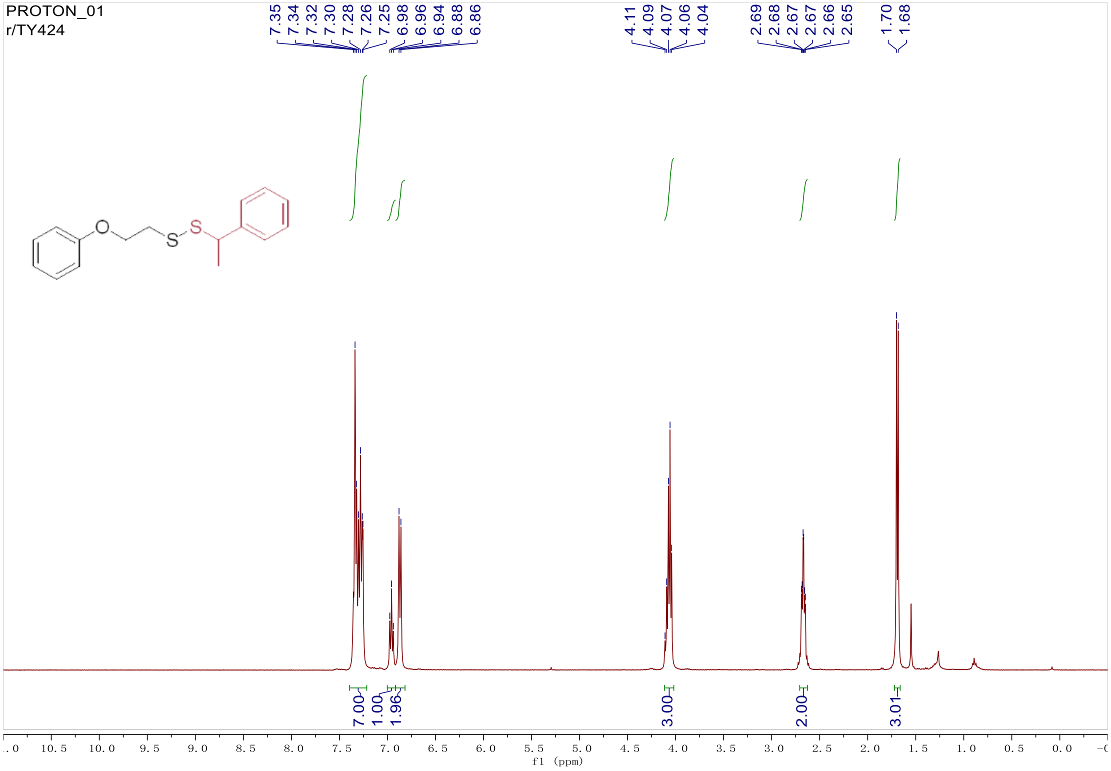


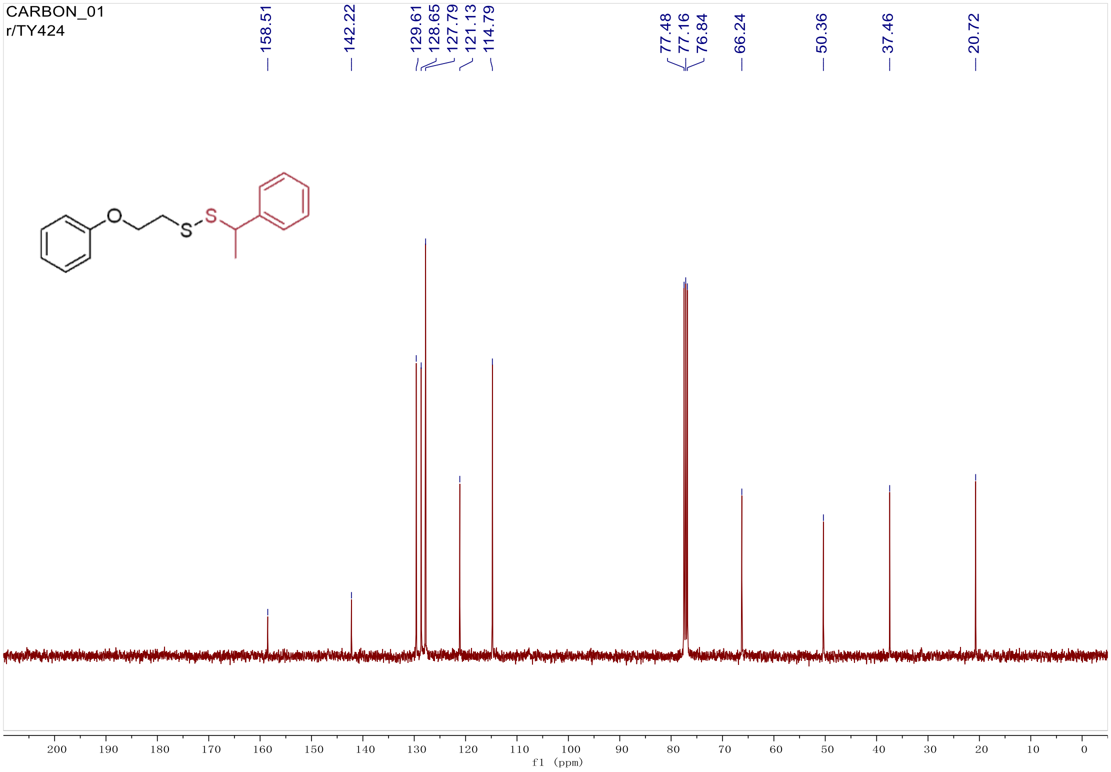
^{1}H and ^{13}C of 43



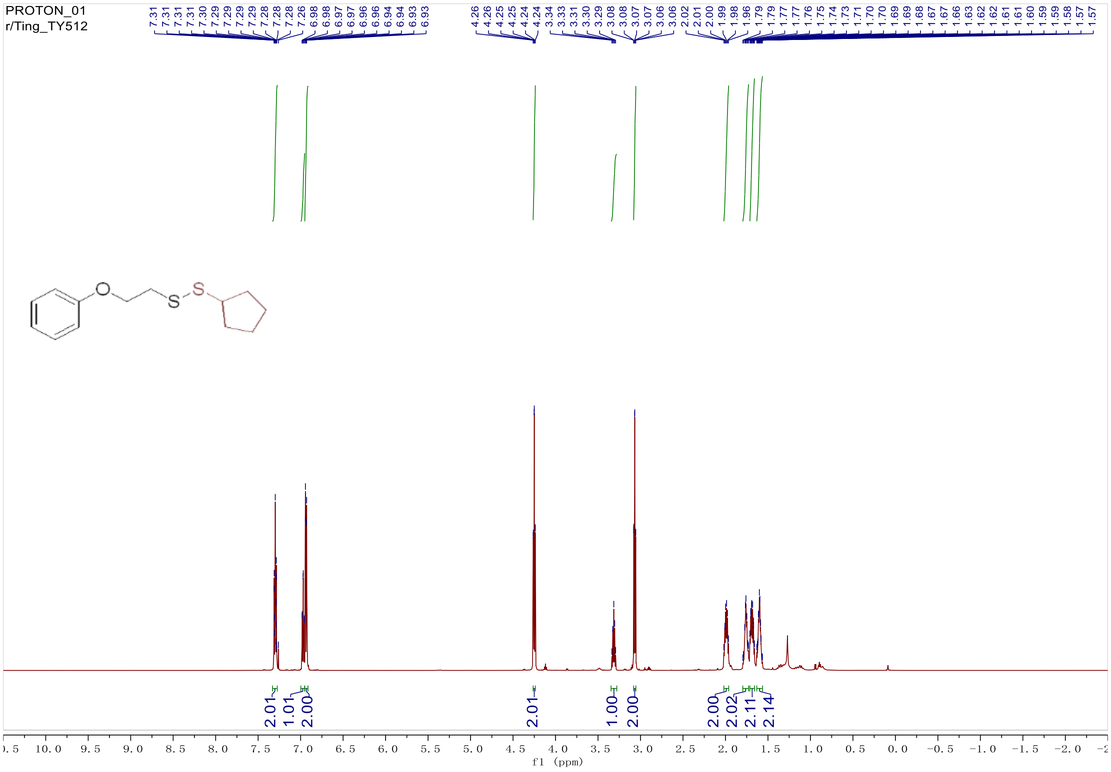


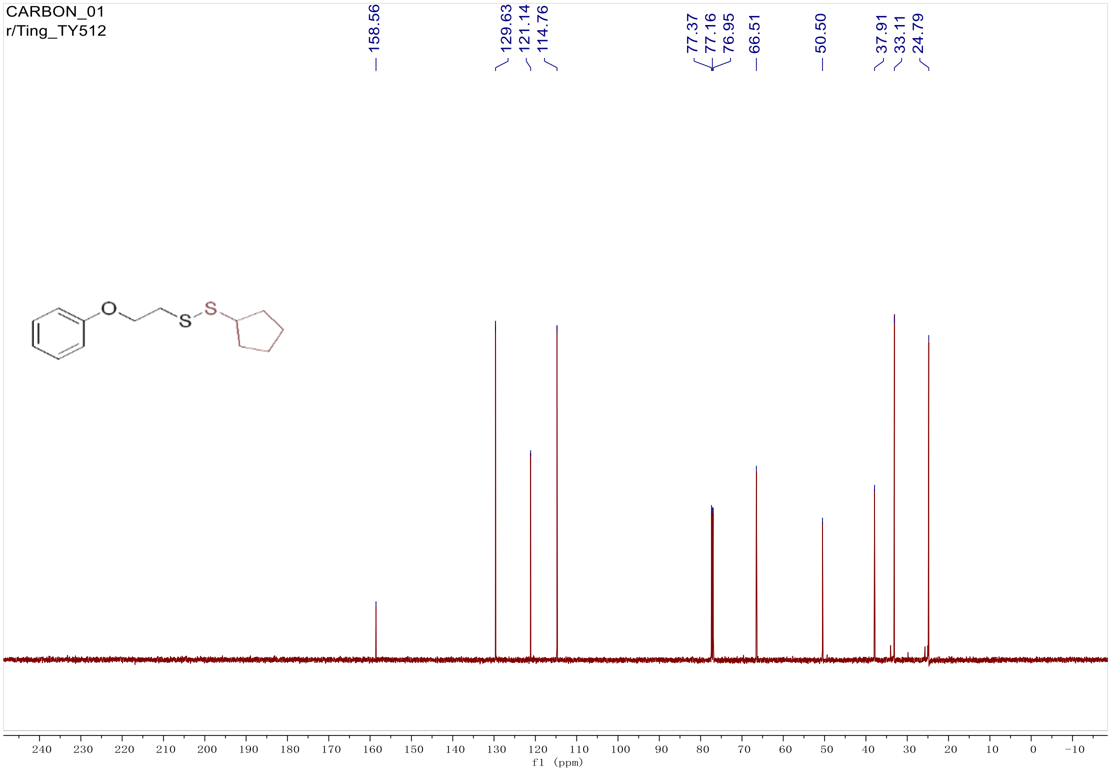
^{1}H and ^{13}C of 44



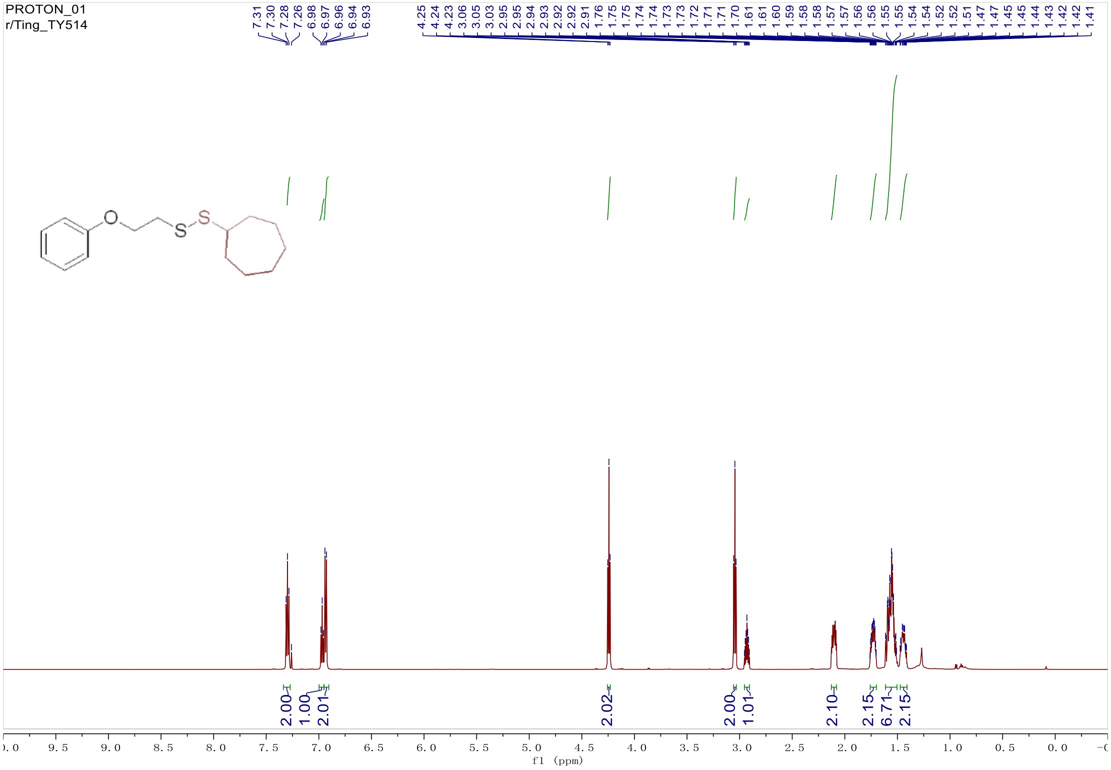


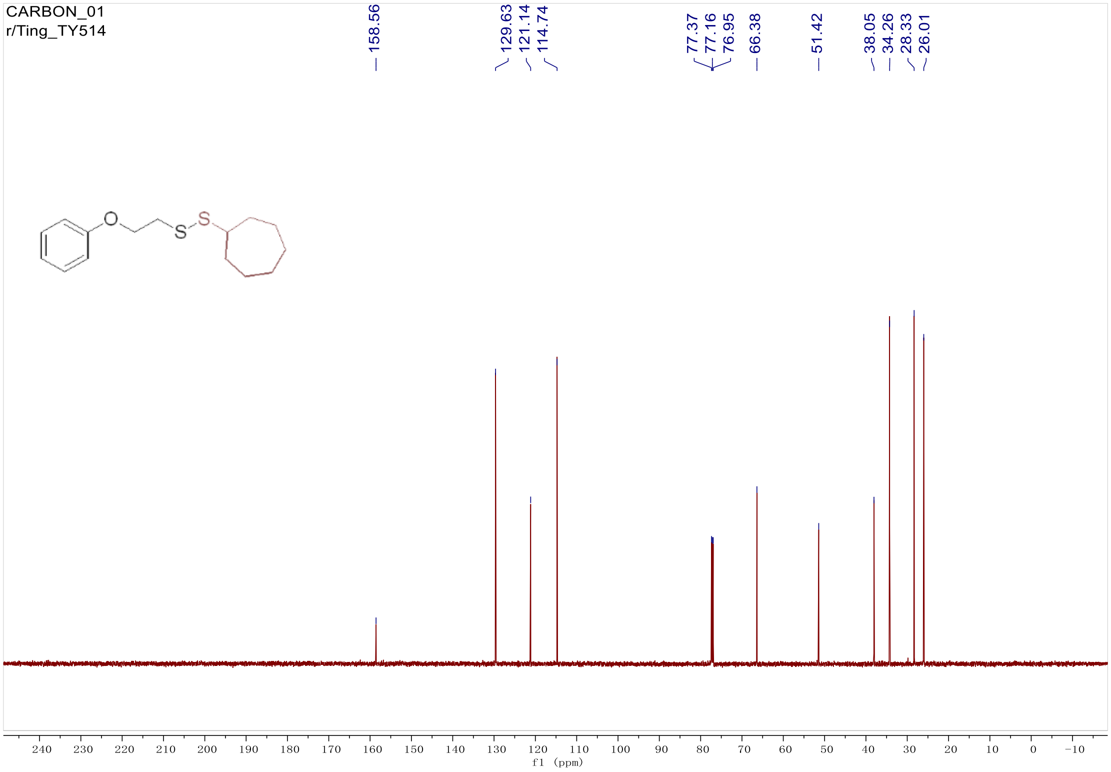
^{1}H and ^{13}C of 45



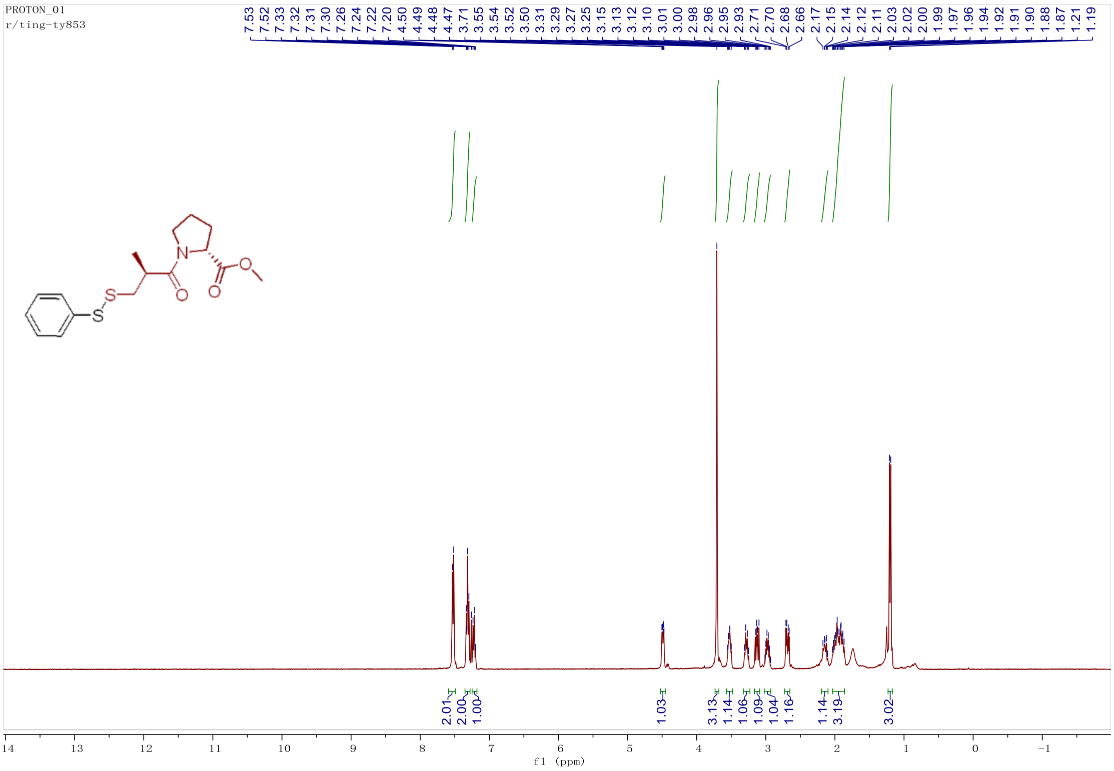


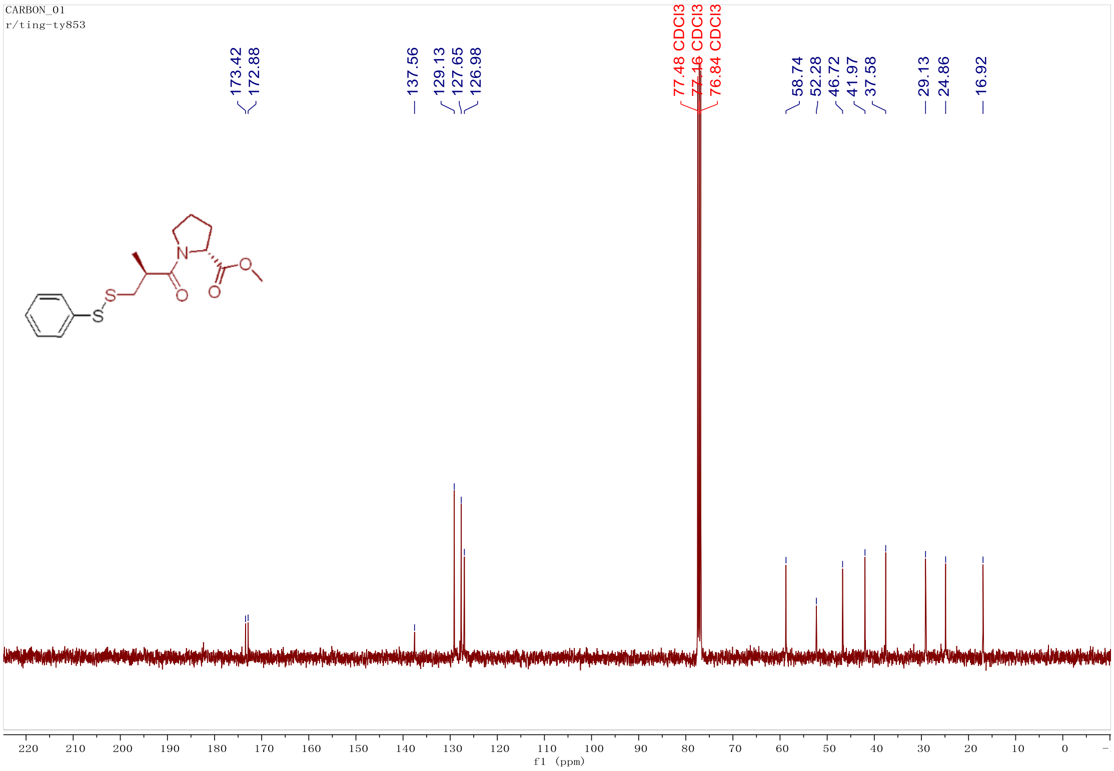
^{1}H and ^{13}C of 46





^{1}H and ^{13}C of 47

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