Supporting Information

Photoredox Mediated Nickel Catalyzed C(sp^3)–H Thiocarbonylation of Ethers

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Complete list of authors of Gaussian 09

Gaussian 09, revision B.01; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K.; Burant, J. C.; Millam, J. M.; Iyengay, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Comperts, R.; Startmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenbuerg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chem, W.; Wong, M. W., Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford CT, 2010.

I. Experimental section

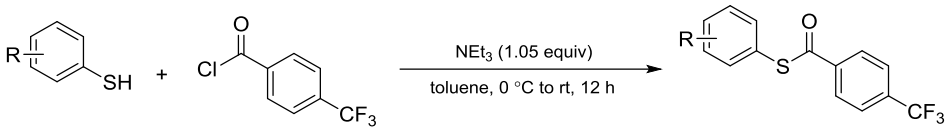
1. General information

Unless otherwise noted, all reactions were carried out using standard Schlenk techniques or in an argon-filled glove box. NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 on a Bruker DPX-300 (300 MHz) spectrometer or Varian 500-MR. Chemical shifts are reported in ppm and coupling constant are given in Hz. High-resolution mass spectrometry (HRMS) analysis was performed at the Organic Chemistry Research Center in Sogang University and Korea Basic Science Institute Daegu Center using either the ESI or EI method. GC analyses were carried out with a 7980A GC system from Agilent Technologies, equipped with an HP-5 column and a Beta DEX^{TM} 120 column using He as the mobile phase with FID detector. Single crystal X-ray crystallography was conducted at the Agilent Core Center in Research Institute of Pharmaceutical Science, Seoul National University. 34 W Blue LED lamp purchased from Kessil (Kessil H150 Grow light-Blue) was used for all the visible light photocatalytic reactions.

Unless otherwise noted, all commercially available chemicals were purchased from Sigma-Aldrich, Alfa Aesar, or Tokyo Chemical Industry (TCI), and directly used without purification. Nickel complexes were purchased from Strem Chemicals Inc. All photoredox catalysts except $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$[1] were purchased from Sigma-Aldrich. $PhCH_2CH_2{}^{13}CN$ was synthesized from 2-phenylethylbromide and $K^{13}CN$ (99 atom % ^{13}C, Cambridge Isotope Laboratories).[2] Ether was purified by distillation or purification column to remove the stabilizer, and directly used within 24 h to prevent side reactions. All thiols were purchased or synthesized from the corresponding aryl iodides following a reported procedure.[3] All thioesters were synthesized from corresponding thiols and acyl chlorides according to a modified literature procedure.[4]

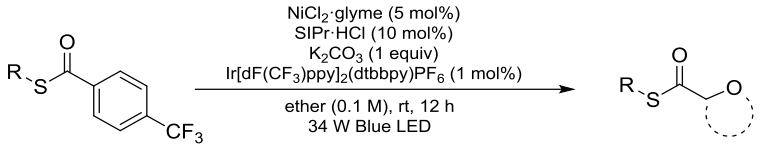
2. General reaction procedures

General procedure for reactant thioester synthesis



The thiol (5 mmol) and triethylamine (0.73 mL, 5.25 mmol) were dissolved in toluene (8 mL), and stirred at room temperature for 10 min. 4-(trifluoromethyl)benzoyl chloride (0.78 mL, 5.25 mmol) was added dropwise to the solution at 0 °C. The mixture was slowly warmed to the room temperature, and stirred for another 12 h. When the reaction was complete, dichloromethane (20 mL) and a 1 M HCl (aq) solution (20 mL) were added to the Schlenk tube. The organic phase was separated and the aqueous phase was washed with an additional 20 mL of dichloromethane. Evaporation of the volatile solvent gave a yellowish solid, that was further purified by silica column chromatography (hexane and ethyl acetate as eluent) to afford the desired product.

General procedure for thiocarbonylation of ether

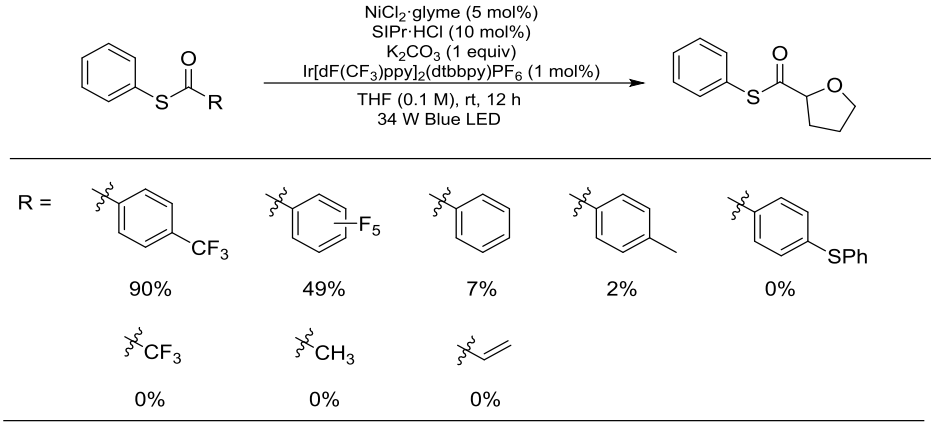


$NiCl_2$·glyme (2.7 mg, 0.0125 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (SIPr·HCl, 10.7 mg, 0.025 mmol), and K_2CO_3 (34.6 mg, 0.25 mmol) were placed in an 4 mL vial inside the glove box. 2.5 mL of ether was added to the vial, and the mixture stirred at room temperature for 10 min. The thioester (0.25 mmol) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.8 mg, 0.0025 mmol) were added to the vial. The vial was taken out of the glove box and stirred at room temperature for 4–18 h under irradiation from a Kessil H150 Blue light and fan (the vial was placed at least 5 cm away from the light to minimize heating). When the reaction was complete, the mixture was diluted with dichloromethane and directly purified with silica chromatography (hexane and ethyl acetate as eluent) to afford the desired product.

3. Reaction condition optimization

Initial reaction development with various thioester structure

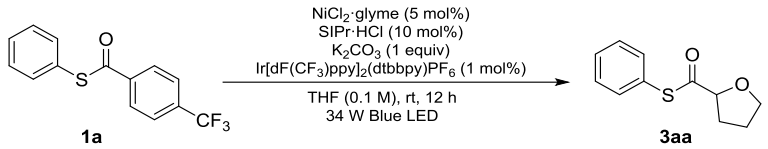
Table S1. Thioester screening results [a]



[a]Yield is measured by GC using dodecane as internal standard

Representative screening results

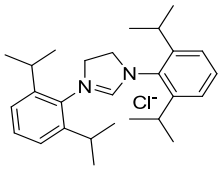
Table S2. Representative screening results



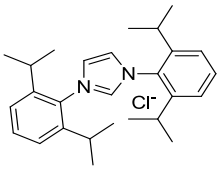
entry	variation	change	conversion (%)[a]	yield (%)[a]
1	No change	No change	100	90
2	Time	1 h	60	51
3	Time	2 h	87	74
4	Time	4 h	100	89
5	Ni complex	$NiBr_2$·glyme	58	33
6	Ni complex	$Ni(acac)_2$	28	28
7	Ni complex	$Ni(PPh_3)_2Cl_2$	0	0
8	Photocatalyst	$Ru(bpy)_3Cl_2$	0	0
9	Photocatalyst	$Ir(ppy)_3$	0	0
10	Photocatalyst	$Ru(1,10\text{-}phen)_3Cl_2$	0	0
11	Photocatalyst	$Ir(ppy)_2(dtbbpy)PF_6$	0	0
12	Ligand	PPh_3	37	0
13	Ligand	dppb	88	0
14	Ligand	dppBz	1	0
15	Ligand	bipyridyl	79	0

16	Ligand	biox	79	0
17	Ligand	dtbbpy (5 mol %)	40	10
18	Ligand	IPr-diimine (10 mol %)	89	0
19	Ligand	I*i*Pr·HCl (10 mol %)	53	18
20	Ligand	IPr·HCl (10 mol %)	100	86
21	Ligand	SIPr·HCl (5 mol %)	97	85
22	Solvent	THF (0.25 M)	25	17
23	Solvent	THF : DCM = 4 : 1 (0.1 M)	100	77
24	Base	$KHCO_3$	75	8
25	Base	NaOAc	51	0
26	Base	Na_2CO_3	79	8
27	Base	K_2HPO_4	100	90
28	Base	K_3PO_4	66	36
29	Base	NaOMe	100	0
30	Base	KOtBu	100	0
31	Base	K_2CO_3 (10 mol %)	29	29

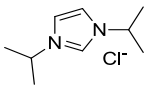
[a]Measured by GC using dodecane as internal standard



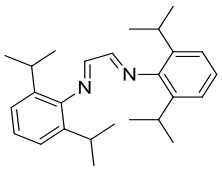
SIPr·HCl



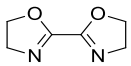
IPr·HCl



I*i*Pr·HCl

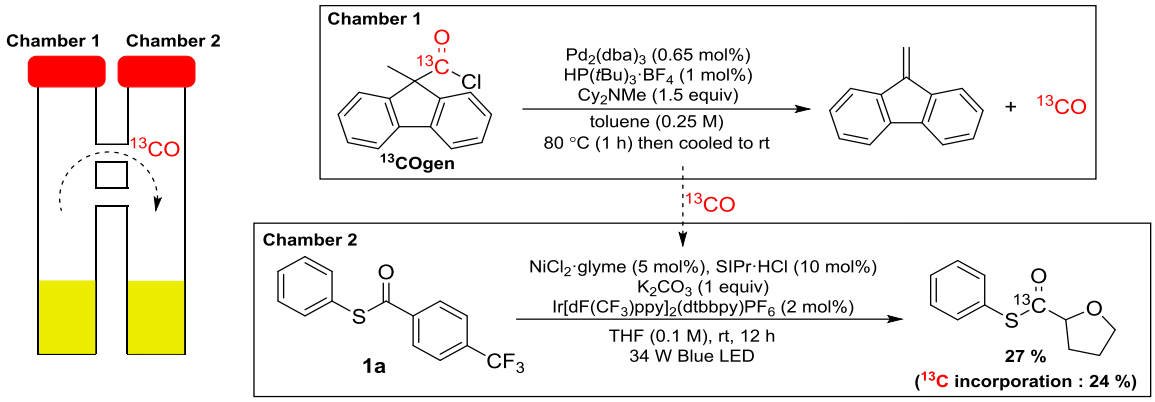


IPr-diimine



biox

4. ^{13}CO incorporation experiment



COware (two chamber reactor) [Product No. STW1] and ^{13}COgen [Product No. 745146] were purchased from Sigma-Aldrich. The COware was equipped with two stirring bars and was placed inside the glove box. In Chamber 1, ^{13}COgen (90.2 mg, 0.37 mmol), $Pd_2(dba)_3$ (2.2 mg, 0.0024 mmol), $[(tBu)_3PH]BF_4$ (1.1 mg, 0.0038 mmol), Cy_2NMe (0.12 mL, 0.56 mmol), and toluene (1.5 mL) were added. In Chamber 2, $NiCl_2$·glyme (2.7 mg, 0.0125 mmol), 1,3-bis(2,6-diisopropylphenyl)-imidazolinium chloride (SIPr·HCl, 10.7 mg, 0.025 mmol), K_2CO_3 (34.6 mg, 0.25 mmol), **1a** (70.6 mg, 0.25 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol) and THF (2.5 mL) were placed. COware was removed from the glovebox. Chamber 1 was placed inside the oil bath, while Chamber 2 was placed 5 cm away from the Kessil H150 Blue LED and fan (Figure S1). Chamber 1 was warmed to 80 °C for 10 min to generate ^{13}CO (the temperature of Chamber 2 was 32 °C) then cooled to room temperature. The reaction proceeded at room temperature for 12 h. The reaction mixture in Chamber 2 was diluted with dichloromethane, and filtered with celite to remove the insoluble solids. The volatile solvent was evaporated, and the crude product was purified with silica column chromatography using hexane and ethyl acetate as eluent. 14.1 mg (27%) of the desired product is obtained. The ^{13}CO incorporation ratio was analyzed with an inverse-gated ^{13}C NMR experiment. 6.7 mg (0.032 mmol) of product was mixed with independently-synthesized $PhCH_2CH_2{}^{13}CN$ (4.2 mg, 0.032 mmol). The mixture was dissolved in $CDCl_3$, and inverse-gated ^{13}C NMR analysis was performed. The direct integration comparison revealed that the ^{13}C incorporation ratio into the acyl carbon was 24% (Figure S2).

Figure S1. Two chamber reaction set-up for ^{13}CO incorporation experiment

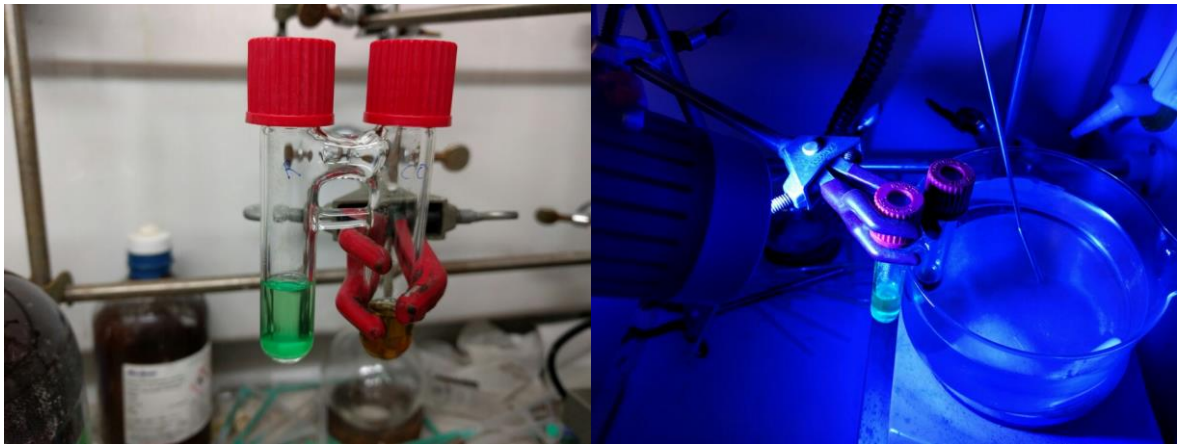
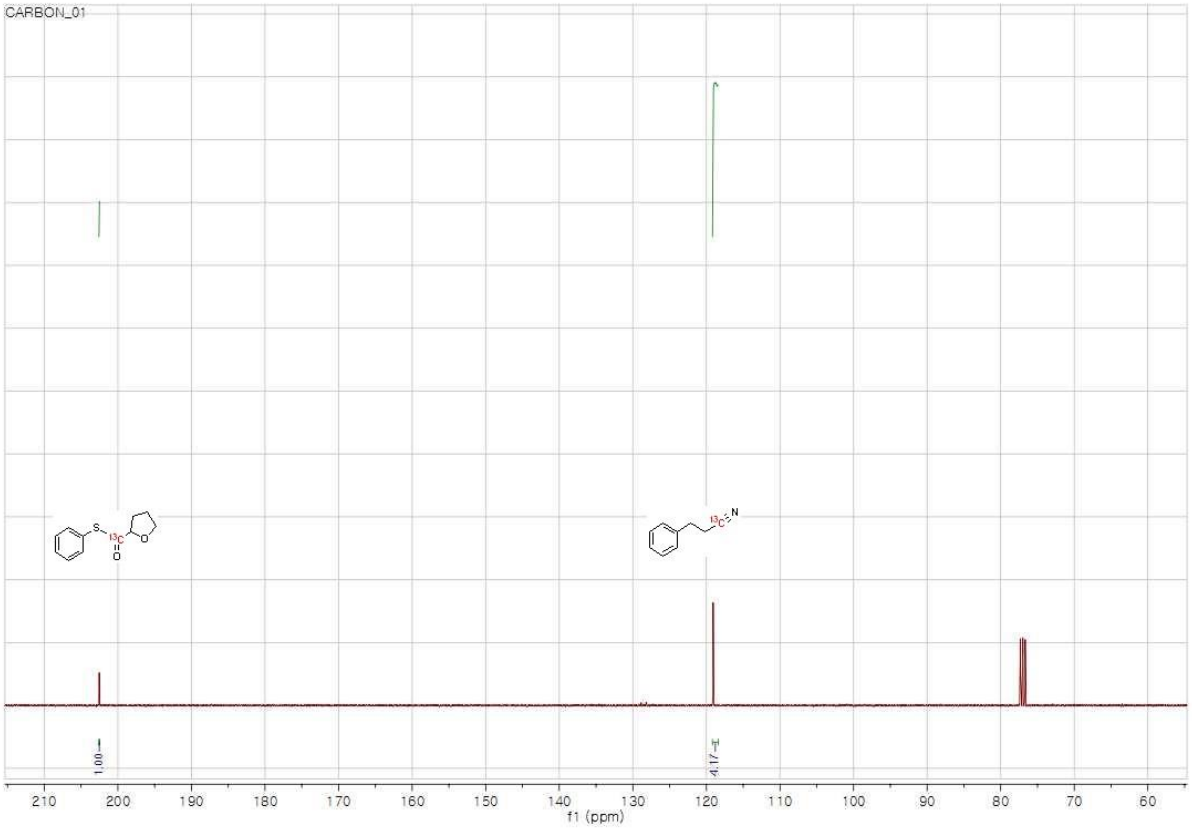
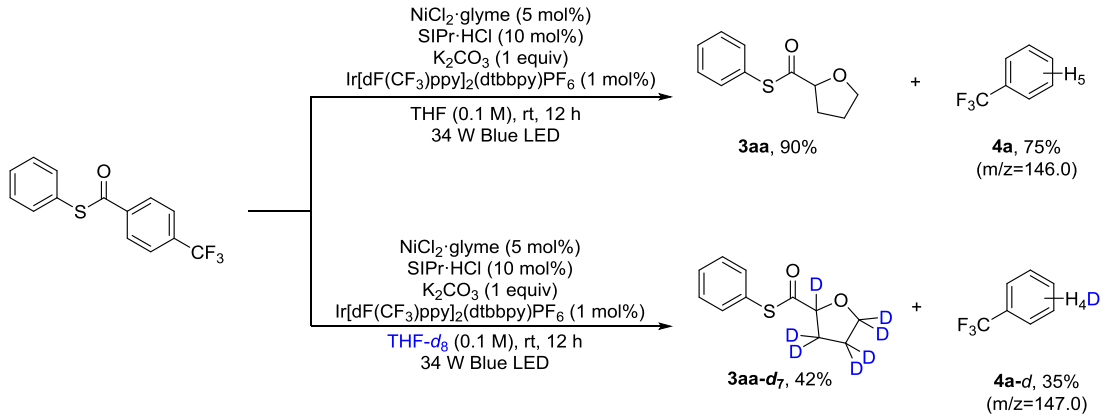


Figure S2. Inverse-gated ^{13}C NMR experiment

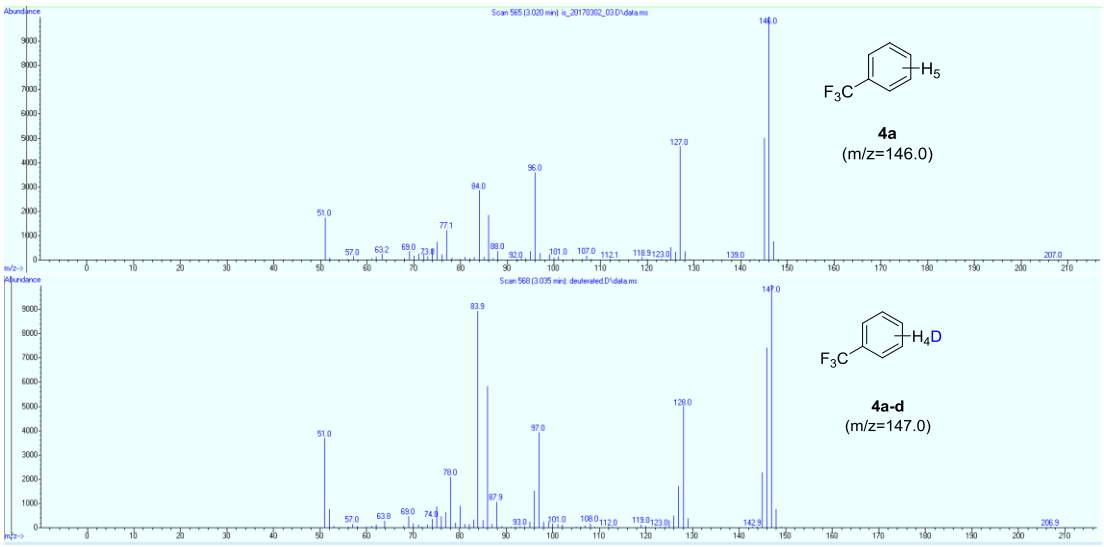


5. Deuterium incorporation experiment



$NiCl_2$·glyme (2.7 mg, 0.0125 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (SIPr·HCl, 10.7 mg, 0.025 mmol), and K_2CO_3 (34.6 mg, 0.25 mmol) were placed in an 4 mL vial inside the glove box. 2.5 mL of THF-d_8 was added to the vial, and the mixture stirred at room temperature for 10 min. **1a** (70.6 mg, 0.25 mmol) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.8 mg, 0.0025 mmol) were added to the vial. The vial was taken out of the glove box and stirred at room temperature for 12 h under irradiation from a Kessil H150 Blue light and fan (the vial was placed at least 5 cm away from the light to minimize heating). When the reaction was complete, the mixture was diluted with dichloromethane, and dodecane (28.4 μl, 0.125 mmol) was added as standard for quantitative GC analysis. Deuterium incorporation in α,α,α-trifluorotoluene (**4a-*d***) was confirmed by GC-MS analysis of crude reaction mixture (Figure S3). **3aa-d_7** was purified with silica chromatography to report the isolated yield.

Figure S3. GC-MS result of **4a** and **4a-*d***



6. Cyclic voltammetry (CV) studies

(a) Conversion constant calibration

<Electrode composition>

Working electrode: glassy carbon electrode.

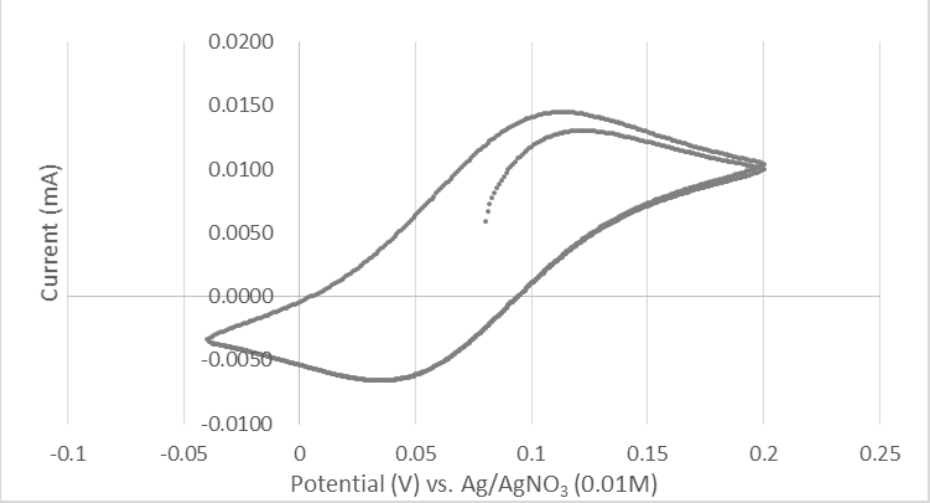
Reference electrode: $Ag/AgNO_3$ (0.01 M) in acetonitrile with TBAP 0.1 M.

Counter electrode: Pt wire electrode.

<Procedure>

Ferrocene (**Fc**, 0.001 M) and Tetrabutylammonium perchlorate (TBAP, 0.1 M) in acetonitrile were transferred to an electrochemical cell equipped with three electrode system. Scan rate: 0.01 V/s. Scan range: -0.04 to +0.2 V.

Figure S4. Cyclic voltammogram of **Fc/Fc$^+$**



$E_{1/2}$[**Fc$^+$/Fc**] = 0.074 V vs $Ag/AgNO_3$ (0.01 M) in acetonitrile.

$E_{1/2}$[**Fc$^+$/Fc**] = 0.380 V vs SCE in acetonitrile. (reference value)

The conversion constant between the reference electrode and SCE is calculated as +0.31 V.

(b) Thioester **1a**

<Electrode composition>

Working electrode: glassy carbon electrode.

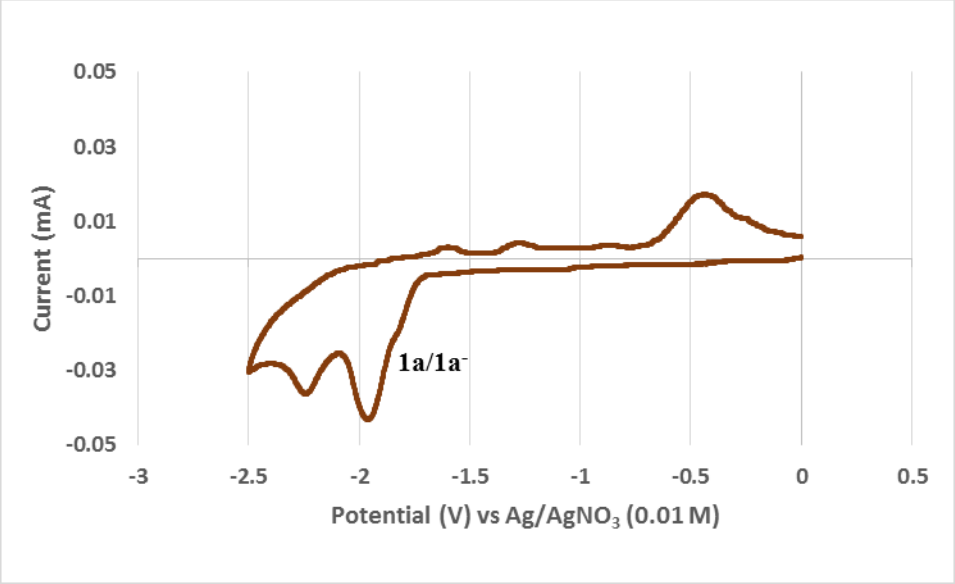
Reference electrode: Ag/$AgNO_3$ (0.01 M) in acetonitrile with TBAP 0.1 M.

Counter electrode: Pt wire electrode.

<Procedure>

The mixture of **1a** (0.001 M) and TBAP (0.1 M) in acetonitrile was transferred to an electrochemical cell equipped with a three electrode system. Scan rate: 0.1 V/s. Scan range: 0 to -2.5 V.

Figure S5. Cyclic voltammogram of thioester **1a**



E_P[**1a/1a**$^-$] = –1.96 V vs Ag/$AgNO_3$ (0.01M); –1.65 V vs SCE

$E_{P/2}$[**1a/1a**$^-$] = –1.84 V vs Ag/$AgNO_3$ (0.01M); –1.53 V vs SCE

(c) Thioester **1a** + $MgCl_2$

<Electrode composition>

Working electrode: glassy carbon electrode.

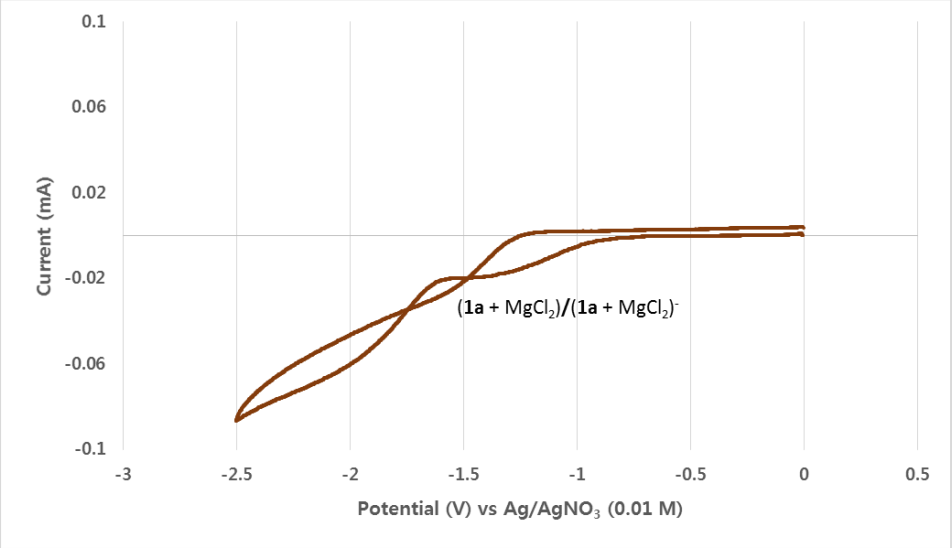
Reference electrode: $Ag/AgNO_3$ (0.01 M) in acetonitrile with TBAP 0.1 M.

Counter electrode: Pt wire electrode.

<Procedure>

The mixture of **1a** (0.001 M), $MgCl_2$ (0.001 M), and TBAP (0.1 M) in acetonitrile was stirred in room temperature for 3 h. Than the mixture is transferred to an electrochemical cell equipped with a three electrode system. Scan rate: 0.1 V/s. Scan range: 0 to -2.5 V.

Figure S6. Cyclic voltammogram of (**1a** + $MgCl_2$) mixture



E_P[(**1a** + $MgCl_2$)**/**(**1a** + $MgCl_2$)$^-$] = –1.52 V vs $Ag/AgNO_3$ (0.01M); –1.21 V vs SCE

$E_{P/2}$[(**1a** + $MgCl_2$)**/**(**1a** + $MgCl_2$)$^-$] = –1.18 V vs $Ag/AgNO_3$ (0.01M); –0.87 V vs SCE

(d) [(SIPr)NiCl]$_2$(μ-Cl)$_2$ (**[Ni-II]**)

<Electrode composition>

Working electrode: glassy carbon electrode.

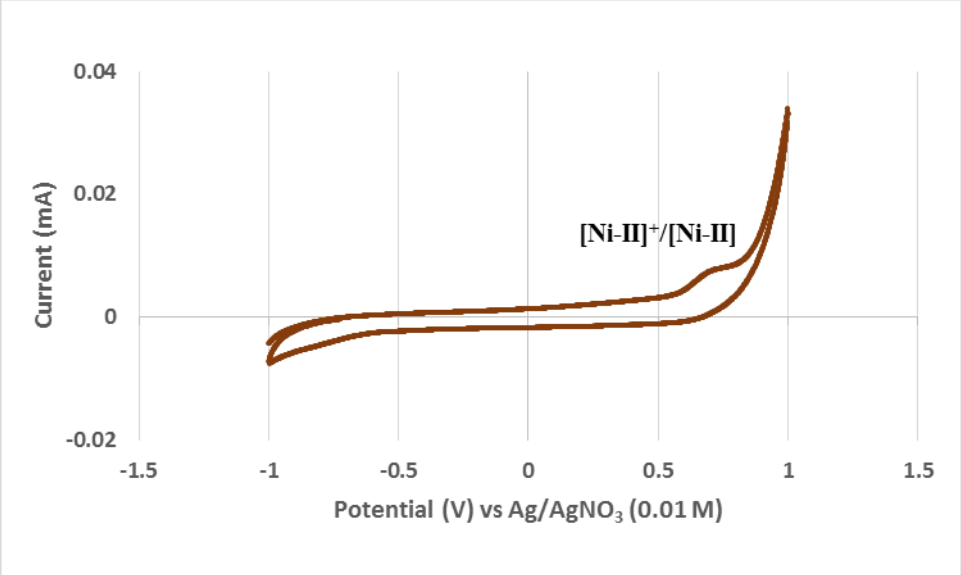
Reference electrode: Ag/$AgNO_3$ (0.01 M) in acetonitrile with TBAP 0.1 M.

Counter electrode: Pt wire electrode

<Procedure>

[(SIPr)NiCl]$_2$(μ-Cl)$_2$ (0.001 M) and TBAP (0.1 M) in acetonitrile were transferred to an electrochemical cell equipped with three electrode system under argon atmosphere. Scan rate: 0.1 V/s. Scan range: -1.0 to +1.0 V.

Figure S7. Cyclic voltammogram of [(SIPr)NiCl]$_2$(μ-Cl)$_2$ (**Ni-II**)



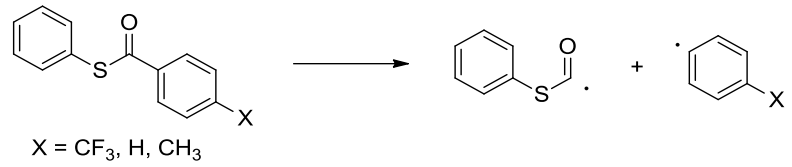
E_P[**[Ni-II]$^+$/ [Ni-II]**] = +0.70 V vs Ag/$AgNO_3$(0.01M); +1.01 V vs SCE

$E_{P/2}$[**[Ni-II]$^+$/ [Ni-II]**] = +0.64 V vs. Ag/$AgNO_3$(0.01M); +0.95 V vs SCE

7. DFT calculation results about bond dissociation energy (BDE) of thioesters

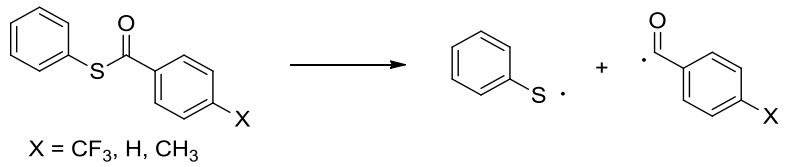
Bond dissociation energies were calculated as the change in the 'sum of electronic and thermal enthalpies' of the following reaction at 298 K in the gas-phase.

(1) C(acyl)-C cleavage



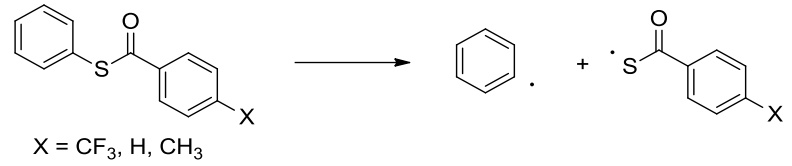
X = CF_3, H, CH_3

(2) S-C(acyl) cleavage



X = CF_3, H, CH_3

(3) C-S cleavage



X = CF_3, H, CH_3

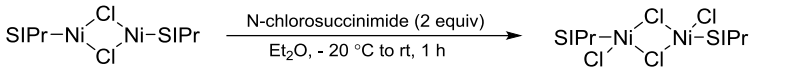
All calculations were performed with the Gaussian 09 program set. For all calculations, UB3LYP functional was used. Geometry optimization and frequency calculations were carried out using 6-311++g(d, p) level basis set in all atoms in the gas phase. No imaginary frequency was obtained in all cases.

Table S3. Bond dissociation energy (BDE) calculation results

BDE (kcal/mol)	X = CF_3	X = H	X = CH_3
(1)	85.1	85.0	86.7
(2)	64.4	64.0	63.6
(3)	76.2	75.5	75.3

8. Synthesis and characterization of nickel complexes

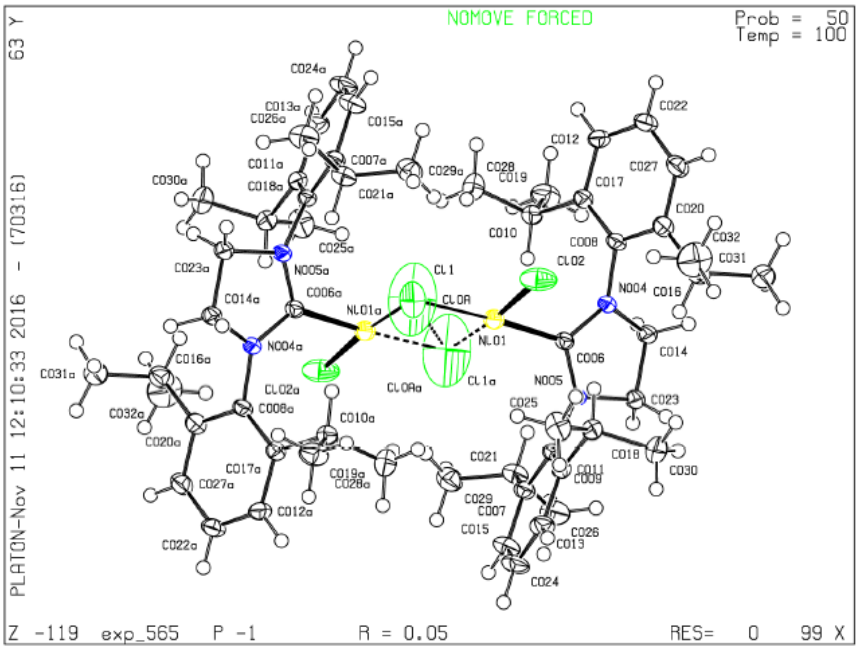
[(SIPr)NiCl]$_2$(μ-Cl)$_2$ ([Ni-II]) complex



[(SIPr)NiCl]$_2$ (**[Ni-I]**) [(SIPr)NiCl]$_2$(μ-Cl)$_2$ (**[Ni-II]**)

The complex was synthesized using a modified procedure of a similar N-heterocyclic carbene coordinated Ni(II) complex.[5] All experiments were performed under argon atmosphere. [(SIPr)NiCl]$_2$ was synthesized following literature procedure.[6] Synthesized [(SIPr)NiCl]$_2$ (35.8 mg, 0.037 mmol) and *N*-chlorosuccinimide (10.0 mg, 0.075 mmol) were separately dissolved in 5 mL of diethylether (Et_2O). Each solution was cooled to -20 °C. Then combined to give a purple solution. The solution was warmed to room temperature and stirred for an additional 1 h. Solvent was removed under vacuum to give a purple solid which was washed with pentane, and dried in vacuo. After collecting the purple solid, it was dissolved in a minimal amount of dichloromethane. Addition of 10 mL of pentane generated a white precipitate (within 1 h) that was removed by celite filter to give a clean purple solution. Evaporation of the solvent gave a lavender solid, which was again dissolved in a minimal amount of dichloromethane. Gradual evaporation of dichloromethane at -20 °C provided a lavender solid (5.1 mg, 0.0049 mmol) with purity suitable for single crystal X-ray analysis. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ = 1.03 (d, J = 6.8 Hz, 12 H), 1.29 (d, J = 6.8 Hz, 12 H), 2.95 (m, 4H), 3.00 (s, 4H), 7.21 (d, J = 7.6 Hz, 4 H), 7.42 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ = 224.2, 156.9, 146.5, 129.5, 124.9, 29.5, 26.4, 24.4;

Figure S8. Single crystal structure of $[(SIPr)NiCl]_2(\mu\text{-}Cl)_2$ (**[Ni-II]**)



The complete data for this structure is on file with the CCDC under entry 1516709.

Table S4. Crystal data and structure refinement for **[Ni-II]**

Identification code	exp_565
Empirical formula	$C_{54}H_{76}Cl_4N_4Ni_2$
Formula weight	1040.40
Temperature/K	99.9(5)
Crystal system	triclinic
Space group	P-1
a/Å	9.8953(4)
b/Å	12.1959(5)
c/Å	12.3731(5)
α/°	110.000(4)
β/°	107.743(3)
γ/°	96.007(3)
Volume/Å^3	1299.50(10)
Z	1
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	3.084
F(000)	552.0
Crystal size/mm^3	0.083 × 0.053 × 0.028
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.934 to 153.094
Index ranges	-12 ≤ h ≤ 11, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	21503

Independent reflections	5427 [R_{int} = 0.0336, R_{sigma} = 0.0295]
Data/restraints/parameters	5427/0/306
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0535, wR_2 = 0.1521
Final R indexes [all data]	R_1 = 0.0604, wR_2 = 0.1583
Largest diff. peak/hole / e $Å^{-3}$	0.51/-1.36

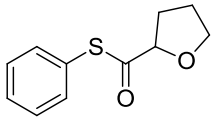
Table S5. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for **[Ni-II]**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	***x***	***Y***	***z***	**U(eq)**
Ni01	4440.2(5)	9106.1(4)	3692.4(4)	26.26(16)
Cl02	5511.7(8)	8389.4(8)	2430.7(8)	42.7(2)
N004	1879(2)	8377.8(17)	1495.7(18)	18.7(4)
N005	1608(2)	7569.0(18)	2759.9(18)	19.3(4)
C006	2568(3)	8273(2)	2557(2)	18.0(4)
C007	1261(3)	7222(2)	4492(2)	22.2(5)
C008	2447(3)	8952(2)	833(2)	20.5(5)
C009	1937(3)	6993(2)	3619(2)	19.4(5)
C010	2501(3)	11009(2)	2365(2)	25.8(5)
C011	2775(3)	6123(2)	3475(2)	21.1(5)
C012	3058(3)	10688(2)	435(2)	26.6(5)
C013	2926(3)	5495(2)	4240(3)	26.8(5)
C014	299(3)	7859(2)	1010(2)	22.8(5)
C015	1439(3)	6560(3)	5226(3)	29.3(6)
C016	2441(3)	6860(2)	-617(3)	31.5(6)
C017	2666(3)	10197(2)	1198(2)	22.1(5)
C018	3487(3)	5834(2)	2515(2)	23.4(5)
C019	1277(4)	11650(3)	2063(3)	35.6(6)
C020	2626(3)	8204(2)	-242(2)	24.0(5)
C021	312(3)	8125(2)	4649(2)	26.3(5)
C022	3216(3)	9977(3)	-638(3)	29.3(6)
C023	205(3)	7061(2)	1707(2)	24.2(5)
C024	2258(3)	5701(3)	5101(3)	31.3(6)
C025	5077(3)	5793(3)	3068(3)	35.7(6)
C026	-1288(3)	7474(3)	4234(3)	35.2(6)
C027	3003(3)	8741(3)	-971(2)	27.7(5)
C028	3942(4)	11914(3)	3250(3)	39.9(7)
C029	831(4)	9061(3)	5979(3)	35.7(6)
C030	2642(4)	4657(3)	1417(3)	36.3(6)
C031	1132(4)	6151(3)	-1818(3)	40.3(7)

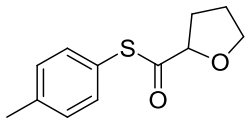
C032	3828(5)	6474(3)	-751(4)	54.2(9)
Cl1	6649(2)	9959.2(15)	5037.6(13)	62.8(4)
Cl0A	5984(6)	10287(8)	5097(7)	145(4)

9. Characterization of products

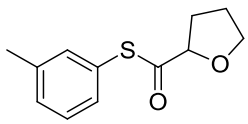
1a,[7] **4a,**[8] **5a,**[9] $[(SIPr)NiCl]_2$ (**[Ni-I]**),[6] are identified by spectral comparison with literature data.



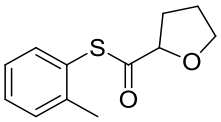
***S*-Phenyl tetrahydrofuran-2-carbothioate** (**3aa**)[10]: yellow oil (43.1 mg, 0.207 mmol, 83%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.97 (m, 1H), 2.04 (m, 1H), 2.15 (m, 1H), 2.30 (m, 1H), 4.02 (q, *J* = 6.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 4.59 (dd, *J* = 4.9, 8.9 Hz, 1H) 7.41 (s, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.5, 134.6, 129.2, 129.1, 127.7, 83.7, 70.1, 31.1, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}O_2SNa$: 231.0456. Found: 231.0450.



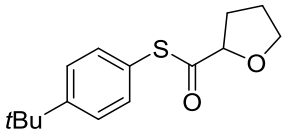
***S*-(*p*-Tolyl)-tetrahydrofuran-2-carbothioate** (**3ba**): yellow oil (44.5 mg, 0.200 mmol, 80%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.97 (m, 1H), 2.03 (m, 1H), 2.14 (m, 1H), 2.28 (m, 1H), 2.37 (s, 3H), 4.01 (q, *J* = 6.6 Hz, 1H), 4.16 (q, *J* = 6.6 Hz, 1H), 4.59 (m, 1H), 7.16-7.34 (dd, *J* = 7.5, 31.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.9, 139.5, 134.6, 130.0, 124.0, 83.7, 70.1, 31.2, 25.3, 21.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2SNa$: 245.0612. Found: 245.0609.



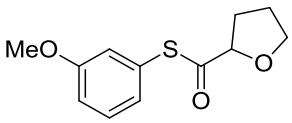
***S*-(*m*-Tolyl)-tetrahydrofuran-2-carbothioate** (**3ca**): yellow oil (49.8 mg, 0.224 mmol, 90%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.98 (m, 1H), 2.03 (m, 1H), 2.15 (m, 1H), 2.29 (m, 1H), 2.37 (s, 3H), 4.02 (q, *J* = 6.6 Hz, 1H), 4.16 (q, *J* = 6.6 Hz, 1H), 4.59 (m, 1H), 7.20 (m, 3H), 7.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.7, 139.0, 135.2, 131.7, 130.1, 129.0, 127.3, 83.7, 70.1, 31.2, 25.3, 21.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2SNa$: 245.0612. Found: 245.0609.



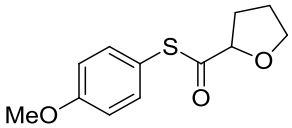
***S*-(*o*-Tolyl)-tetrahydrofuran-2-carbothioate** (**3da**): yellow oil (39.6 mg, 0.178 mmol, 71%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.98 (m, 1H), 2.05 (m, 1H), 2.14 (m, 1H), 2.29 (m, 1H), 2.33 (s, 3H), 4.03 (q, *J* = 6.9 Hz, 1H), 4.20 (q, *J* = 6.9 Hz, 1H), 4.59 (dd, *J* = 4.9, 8.6 Hz, 1H), 7.22 (m, 1H), 7.28-7.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.0, 142.2, 136.0, 130.7, 129.9, 127.0, 126.6, 83.8, 70.1, 31.2, 25.3, 20.6; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2SNa$: 245.0612. Found: 245.0607.



***S*-[4-(*tert*-butyl)-phenyl]-tetrahydrofuran-2-carbothioate** (**3ea**): yellow oil (53.9 mg, 0.204 mmol, 82%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.34 (s, 9H), 1.98 (m, 1H), 2.04 (m, 1H), 2.16 (m, 1H), 2.30 (m, 1H), 4.03 (q, *J* = 7.3 Hz, 1H), 4.17 (q, *J* = 7.3 Hz, 1H), 4.60 (dd, *J* = 4.9, 8.5 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.9, 152.4, 134.2, 126.3, 124.1, 83.7, 70.1, 34.7, 31.2(1), 31.1(6), 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{20}O_2SNa$: 287.1082. Found: 287.1077.

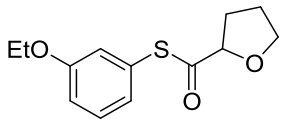


***S*-(3-Methoxyphenyl)-tetrahydrofuran-2-carbothioate** (**3fa**): yellow oil (53.6 mg, 0.225 mmol, 90%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.97 (m, 1H), 2.03 (m, 1H), 2.15 (m, 1H), 2.29 (m, 1H), 3.81 (s, 3H), 4.01 (q, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 1H), 4.59 (dd, *J* = 5.0, 8.8 Hz, 1H), 6.90-7.03 (m, 3H), 7.32 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 202.4, 159.8, 129.9, 128.6, 126.8, 119.7, 115.4, 83.7, 70.1, 55.3, 31.1, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_3SNa$: 261.0561. Found: 261.0555.

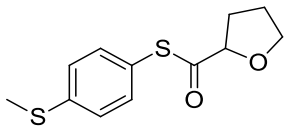


***S*-(4-Methoxyphenyl)-tetrahydrofuran-2-carbothioate** (**3ga**): yellow oil (42.7 mg, 0.179

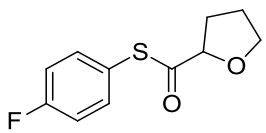
mmol, 72%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.97 (m, 1H), 2.02 (m, 1H), 2.13 (m, 1H), 2.28 (m, 1H), 3.82 (s, 3H), 4.01 (q, *J* = 7.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 4.58 (dd, *J* = 5.0, 8.7 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 203.3, 160.5, 136.1, 118.2, 114.9, 83.7, 70.0, 55.3, 31.1, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_3SNa$: 261.0561. Found: 261.0555.



S*-(3-Ethoxyphenyl)-tetrahydrofuran-2-carbothioate*e (**3ha**): yellow oil (40.0 mg, 0.158 mmol, 63%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.33 (t, *J* = 7.0 Hz, 3H), 2.03 (m, 2H), 2.07 (m, 1H), 2.20 (m, 1H), 3.95 (m, 3H), 4.08 (q, *J* = 7.0 Hz, 1H), 4.50 (dd, *J* = 5.0, 4.8 Hz, 1H), 6.87 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 202.5, 159.2, 129.9, 128.6, 126.6, 120.3, 115.8, 83.7, 70.1, 63.6, 31.2, 25.3, 14.8; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{16}O_3SNa$: 275.0718 Found: 275.0713.

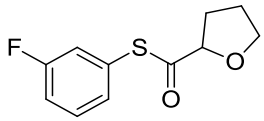


S*-[4-(methylthio)-phenyl]-tetrahydrofuran-2-carbothioate*e (**3ia**): yellow oil (51.3 mg, 0.202 mmol, 81%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.97 (m, 1H), 2.02 (m, 1H), 2.14 (m, 1H), 2.28 (m, 1H), 2.48 (d, *J* = 0.4 Hz, 3H), 4.01 (q, *J* = 7.0 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 1H), 4.58 (dd, *J* = 4.9, 8.8 Hz, 1H), 7.27 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.7, 140.7, 134.9, 126.6, 123.4, 83.7, 70.1, 31.2, 25.3, 15.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2S_2Na$: 277.0333. Found: 277.0325.

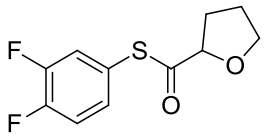


S*-(4-Fluorophenyl)-tetrahydrofuran-2-carbothioate*e (**3ja**): yellow oil (44.6 mg, 0.197 mmol, 79%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.98 (m, 1H), 2.03 (m, 1H), 2.13 (m, 1H), 2.29 (m, 1H), 4.01 (q, *J* = 7.6 Hz, 1H), 4.15 (q, *J* = 7.6 Hz, 1H), 4.58 (dd, *J* = 5.0, 8.5 Hz, 1H), 7.10 (m, 2H), 7.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.6, 163.4 (d, *J* = 250.0 Hz), 136.6 (d, *J* = 8.1 Hz), 123.0

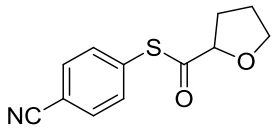
(d, *J* = 3.4 Hz), 116.4 (d, *J* = 22.0 Hz), 83.6, 70.1, 31.2, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_2SFNa$: 249.0361. Found: 249.0356.



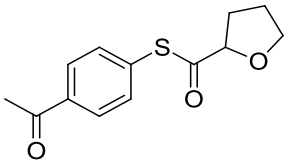
***S*-(3-Fluorophenyl)-tetrahydrofuran-2-carbothioate** (**3ka**): yellow oil (43.5 mg, 0.192 mmol, 77%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.98 (m, 1H), 2.03 (m, 1H), 2.15 (m, 1H), 2.30 (m, 1H), 4.02 (q, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 1H), 4.59 (dd, *J* = 4.9, 8.7 Hz, 1H), 7.05-7.21 (m, 3H), 7.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 201.9, 162.5 (d, *J* = 250.0 Hz), 130.3 (d, *J* = 8.1 Hz), 130.2 (d, *J* = 2.9 Hz), 129.7 (d, *J* = 7.7 Hz), 121.5 (d, *J* = 23.7 Hz), 116.3 (d, *J* = 22.0 Hz), 83.6, 70.1, 31.2, 25.3; HRMS-EI (*m/z*): $[M - (THF–CO)]^+$ calcd for C_6H_4SF: 127.0018. Found: 127.0021.



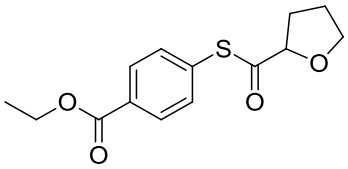
***S*-(3,4-Difluorophenyl)-tetrahydrofuran-2-carbothioate** (**3la**): yellow oil (50.9 mg, 0.208 mmol, 83%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.00 (m, 2H), 2.12 (m, 1H), 2.30 (m, 1H), 4.01 (q, *J* = 6.9 Hz, 1H), 4.14 (q, *J* = 6.9 Hz, 1H), 4.58 (dd, *J* = 4.9, 8.5 Hz, 1H), 7.09-7.14 (m, 1H), 7.16-7.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.0, 151.1 (dd, *J* = 250.0, 13.8 Hz), 150.3 (dd, 250.0. 15.1 Hz) 131.1 (m), 124.1 (m), 123.7 (dd, *J* = 17.6, 1.5 Hz), 117.9 (dd, *J* = 16.8, 1.9 Hz), 83.6, 70.1, 31.1, 25.3; HRMS-EI (*m/z*): $[M - (THF–CO)]^+$ calcd for $C_6H_3SF_2$: 144.9924. Found: 144.9926.



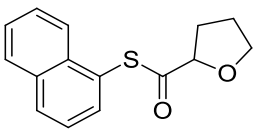
***S*-(4-Cyanophenyl)-tetrahydrofuran-2-carbothioate** (**3ma**): yellow oil (38.2 mg, 0.164 mmol, 66%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.01 (m, 2H), 2.14 (m, 1H), 2.32 (m, 1H), 4.03 (q, *J* = 6.8 Hz, 1H), 4.16 (q, *J* = 6.8 Hz, 1H), 4.60 (dd, *J* = 4.9, 8.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 201.0, 134.9, 134.6, 132.4, 118.2, 112.8, 83.6, 70.2, 31.2, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{11}O_2NSNa$: 256.0408. Found: 256.0407



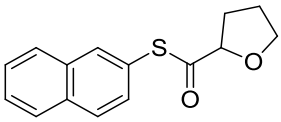
***S*-(4-Acetylphenyl)-tetrahydrofuran-2-carbothioate** (**3na**): yellow oil (38.5 mg, 0.154 mmol, 62%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.94 (m, 2H), 2.09 (m, 1H), 2.24 (m, 1H), 2.54 (s, 3H), 3.95 (q, *J* = 6.8 Hz, 1H), 4.09 (q, *J* = 6.8 Hz, 1H), 4.53 (dd, *J* = 4.8, 8.5 Hz, 1H), 7.44 (m, 2H), 7.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 201.6, 197.4, 137.3, 134.5, 134.0, 128.8, 83.7, 70.2, 31.2, 26.7, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{13}H_{14}O_3SNa$: 273.0561. Found: 273.0557.



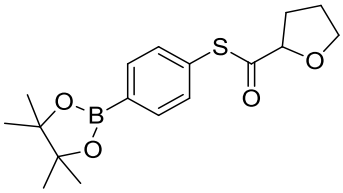
Ethyl-4-[(tetrahydrofuran-2-carbonyl)thio]benzoate (**3oa**): yellow oil (39.5 mg, 0.141 mmol, 56%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.38 (t, *J* = 7.0 Hz, 3H), 1.98 (m, 1H), 2.03 (m, 1H), 2.14 (m, 1H), 2.30 (m, 1H), 4.01 (q, *J* = 6.9 Hz, 1H), 4.16 (q, *J* = 6.9 Hz, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 4.59 (dd, *J* = 4.8, 8.4 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 201.6, 166.0, 134.3, 133.5, 131.0, 130.0, 83.7, 70.1, 61.2, 31.2, 25.3, 14.3; HRMS(ESI) calcd for $C_{14}H_{16}O_4SNa$: 303.0667 Found: 303.0665



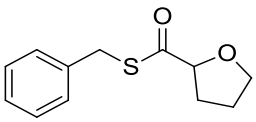
***S*-Naphthalen-1-yl-tetrahydrofuran-2-carbothioate** (**3pa**): yellow solid (26.7 mg, 0.103 mmol, 41%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.97 (m, 1H), 2.13 (m, 1H), 2.20 (m, 1H), 2.32 (m, 1H), 4.08 (q, *J* = 7.0 Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 1H), 4.65 (dd, *J* = 4.7, 8.4 Hz, 1H), 7.53 (m, 3H), 7.68 (m, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.0, 135.0, 134.5, 134.2, 130.7, 128.7, 127.0, 126.3, 125.6, 125.1, 125.0, 83.9, 70.2, 31.2, 25.4; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{14}O_2SNa$: 281.0612. Found: 281.0606.



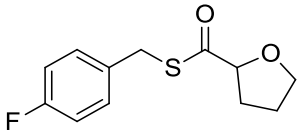
***S*-Naphthalen-2-yl-tetrahydrofuran-2-carbothioate** (**3qa**): yellow solid (45.3 mg, 0.175 mmol, 70%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.99 (m, 1H), 2.07 (m, 1H), 2.19 (m, 1H), 2.31 (m, 1H), 4.05(q, *J* = 7.1 Hz, 1H), 4.21(q, *J* = 7.1 Hz, 1H), 4.64(dd, *J* = 4.8, 8.7 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.52 (m, 2H), 7.85 (m, 3H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.8, 134.5, 133.6, 133.3, 131.1, 128.7, 127.9, 127.8, 127.0, 126.5, 125.0, 83.8, 70.1, 31.2, 25.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{14}O_2SNa$: 281.0612. Found: 281.0607.



***S*-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-tetrahydrofuran-2-carbothioate** (**3ra**): yellow oil (62.1 mg, 0.186 mmol, 74%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.26 (s, 12H), 1.91 (m, 2H), 2.07 (m, 1H), 2.20 (m, 1H), 3.92 (q, *J* = 7.0 Hz, 1H), 4.07 (q, *J* = 7.0 Hz, 1H), 4.50 (dd, *J* = 4.7, 8.5 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.1, 135.3, 133.7, 131.1, 84.0, 83.7, 70.1, 31.2, 25.3, 24.9; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{23}BO_4SNa$: 357.1308. Found: 357.1314.

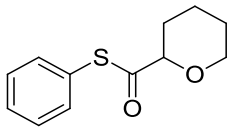


***S*-benzyl tetrahydrofuran-2-carbothioate** (**3sa**): yellow oil (34.2 mg, 0.154 mmol, 62%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.93 (m, 2H), 2.07 (m, 1H), 2.26 (m, 1H), 3.95 (q, *J* = 6.8 Hz, 1H), 4.05(q, *J* = 6.8 Hz, 1H), 4.08 (s, 2H), 4.52 (dd, *J* = 5.0, 8.5 Hz, 1H), 7.21-7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 203.9, 137.5, 128.9, 128.6, 127.2, 83.5, 69.9, 32.5, 31.1, 25.2; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{14}O_2SNa$: 245.0612. Found: 245.0605.

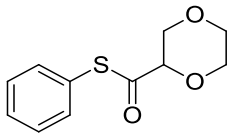


***S*-4-fluorobenzyl tetrahydrofuran-2-carbothioate** (**3ta**): yellow oil (28.0 mg, 0.117 mmol,

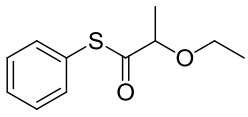
47%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.91 (m, 2H), 2.04 (m, 1H), 2.25 (m, 1H), 3.93 (q, *J* = 6.8 Hz, 1H), 4.03(s, 2H), 4.04 (m, 1H), 4.50 (dd, *J* = , 8.6 Hz, 1H), 6.96 (m, 2H), 7.24 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 203.8, 161.9 (d, *J* = 244.0 Hz), 133.4, 130.4 (d, *J* = 7.9 Hz), 115.4 (d, *J* = 20.6 Hz), 83.5, 69.9, 31.7, 31.0, 25.2; HRMS(ESI) calcd for $C_{12}H_{13}O_2SNa$: 263.0518. Found: 263.0515



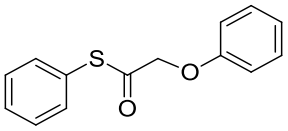
***S*-Phenyl tetrahydro-2H-pyran-2-carbothioate** (**3ab**): yellow oil (52.1 mg, 0.234 mmol, 94%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.51-1.74 (m, 4H), 1.93 (m, 1H), 2.0 (m, 1H), 3.58 (m, 1H), 4.07 (m, 1H), 4.18 (m, 1H) 7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 199.6, 134.9, 129.3, 128.1, 127.2, 82.7, 68.6, 29.2, 25.4, 22.8; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2SNa$: 245.0612. Found: 245.0606.



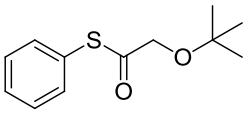
***S*-Phenyl-(1,4-dioxane)-2-carbothioate** (**3ac**): white solid (33.6 mg, 0.150 mmol, 60%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 3.61 (m, 3H), 3.75 (m, 1H), 3.95 (m, 2H), 4.28 (dd, *J* = 3.2, 9.2 Hz, 1H), 7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 196.8, 134.8, 129.6, 129.3, 126.4, 80.1, 67.9, 66.6, 66.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}O_3SNa$: 247.0405. Found: 247.0398.



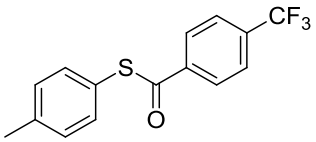
***S*-Phenyl-2-ethoxypropanethioate** (**3ad**): yellow oil (20.9 mg, 0.099 mmol, 40%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.33 (t, *J* = 7.0 Hz, 3H), 1.45 (t, *J* = 6.8 Hz, 3H) 3.63 (m, 1H), 3.77 (m, 1H), 4.03 (q, *J* = 6.8 Hz, 1H), 7.41 (s, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 202.5, 134.7, 129.2, 129.1, 127.6, 81.6, 66.8, 19.4, 15.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{14}O_2SNa$: 233.0612. Found: 233.0607.



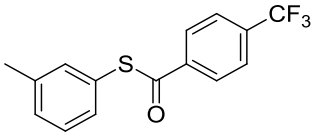
***S*-Phenyl-2-phenoxyethanethioate** (**3ae**): yellow oil (22.4 mg, 0.092 mmol, 37%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 4.79 (s, 2H), 7.00 (m, 2H), 7.06 (m, 1H), 7.35 (m, 2H), 7.43 (s, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 196.7, 157.7, 134.8, 129.7, 129.6, 129.3, 126.2, 122.2, 114.9, 72.9; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{12}O_2SNa$: 267.0456. Found: 267.0451.



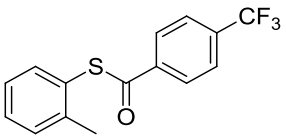
***S*-phenyl 2-(*tert*-butoxy)ethanethioate** (**3af**): white solid (12.0 mg, 0.053 mmol, 21%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.32 (s, 9H), 4.17 (s, 2H), 7.41 (s, 5H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 199.9, 134.8, 129.2, 129.1, 127.6, 75.5, 68.3, 27.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_{12}O_2SNa$: 247.0769. Found: 247.0765.



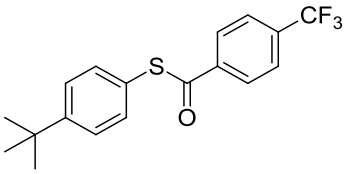
***S*-*p*-tolyl-4-(trifluoromethyl)benzothioate** (**1b**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.44 (s, 3H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 8.15 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.6, 140.1, 139.4 (d, *J* = 7.3 Hz), 134.8. 134.7 (m), 130.2, 127.7, 125.8 (m), 123.0, 123.5 (q, *J* = 270.0 Hz), 21.2; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}OF_3SNa$: 319.0380. Found: 319.0377.



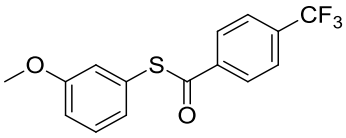
***S*-*m*-tolyl-4-(trifluoromethyl)benzothioate** (**1c**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.41 (s, 3H), 7.33 (m, 4H), 7.76 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.6, 139.5, 139.3, 135.5, 134.8 (m), 132.0, 130.7, 129.2, 127.8, 126.2, 125.8 (m), 123.5 (q, *J* = 270.0 Hz), 21.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}OF_3SNa$: 319.0380. Found: 319.0376.



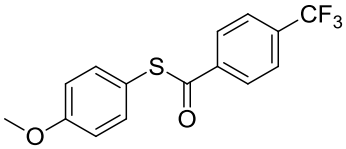
***S*-*o*-tolyl-4-(trifluoromethyl)benzothioate** (**1d**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.49 (s, 3H), 7.34 (m, 1H), 7.44 (m, 2H), 7.57 (m, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 8.21 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 188.6, 142.6, 139.6, 136.3, 134.7 (m), 131.0, 130.6, 127.9, 126.9, 126.2, 125.8 (m), 123.5 (q, *J* = 270.0 Hz), 20.7; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}OF_3SNa$: 319.0380. Found: 319.0377.



***S*-(4-(*tert*-butyl)phenyl)-4-(trifluoromethyl)benzothioate** (**1e**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.36 (s, 9H), 7.46 (m, 4H), 7.75 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.7, 153.2, 139.5, 134.7 (m), 134.6, 127.8, 126.6, 125.8 (m), 123.5 (q, *J* = 270.0 Hz), 123.1, 34.8, 31.2; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{17}OF_3SNa$: 361.0850. Found: 361.0846.

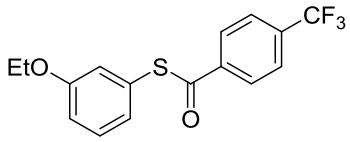


***S*-(3-methoxyphenyl)-4-(trifluoromethyl)benzothioate** (**1f**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 3.84 (s, 3H), 7.02 (m, 1H), 7.11 (m, 2H), 7.39 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.2, 160.0, 139.4, 134.8 (m), 130.1, 127.8, 127.4, 127.1, 125.8 (m), 123.5 (q, *J* = 270.0 Hz), 120.1, 116.0, 55.4; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}O_2F_3SNa$: 335.0330. Found: 335.0327.

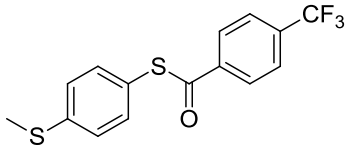


***S*-(4-methoxyphenyl)-4-(trifluoromethyl)benzothioate** (**1g**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ =

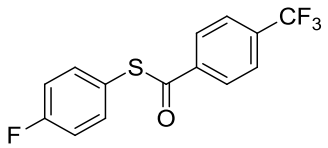
3.86 (s, 3H), 7.00 (m, 2H), 7.42 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 190.3, 161.0, 139.5, 136.5, 134.8 (m), 127.8, 125.7 (m), 123.5 (q, *J* = 270.0 Hz), 117.0, 115.1, 55.4; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}O_2F_3SNa$: 335.0330. Found: 335.0324.



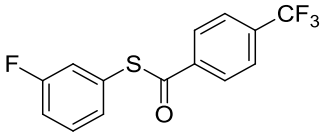
***S*-(3-ethoxyphenyl)-4-(trifluoromethyl)benzothioate** (**1h**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.43 (t, *J* = 7.0 Hz, 3H), 4.06 (q, *J* = 7.0 Hz, 2H), 7.01 (m, 1H), 7.10 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 8.13 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.2, 159.4, 139.5, 134.8 (m), 130.1, 127.8, 127.4, 126.9, 125.8 (m), 123.6 (q, *J* = 270.0 Hz), 120.6, 116.4, 63.7, 14.7; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{16}H_{13}O_2F_3SNa$: 349.0486. Found: 349.0483.



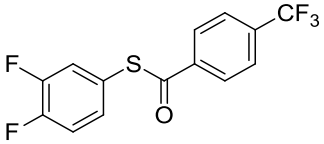
***S*-(4-thiomethoxyphenyl)-4-(trifluoromethyl)benzothioate** (**1i**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.50 (s, 3H), 7.31 (m, 2H), 7.41 (m, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 8.12 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.5, 141.8, 139.4, 135.2, 134.9 (m), 127.8, 126.6, 125.8 (m), 123.4 (q, *J* = 270.0 Hz), 122.2 15.2; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}OF_3S_2Na$: 351.0101. Found: 351.0095.



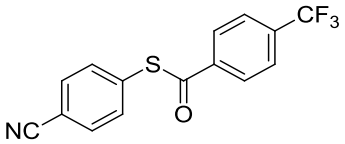
***S*-(4-fluorophenyl)-4-(trifluoromethyl)benzothioate** (**1j**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.17 (m, 2H), 7.49 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 189.3, 163.8 (d, *J* = 253.0 Hz), 139.2, 137.1, 135.0, 127.8, 125.9 (m), 123.4 (q, *J* = 270.0 Hz), 121.8 (d, *J* = 3.5 Hz), 116.7 (d, *J* = 21.6 Hz); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_8OF_4SNa$: 323.0130. Found: 323.0125.



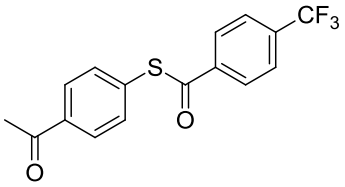
***S*-(3-fluorophenyl)-4-(trifluoromethyl)benzothioate** (**1k**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.18 (m, 1H), 7.29 (m, 2H), 7.45 (m, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 188.6, 162.5 (d, *J* = 261.0 Hz), 139.1, 135.1 (m), 130.6, 130.5 (d, *J* = 5.0 Hz), 128.3 (m), 127.8, 125.9 (m), 123.4 (q, *J* = 270.0 Hz), 121.9 (d, *J* = 21.5 Hz), 117.1 (d, *J* = 20.5 Hz); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_8OF_4SNa$: 323.0130. Found: 323.0126.



***S*-(3,4-difluorophenyl)-4-(trifluoromethyl)benzothioate** (**1l**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.26 (m, 2H), 7.38 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 188.6, 152.7 (dd, *J* = 150.0, 11.0 Hz), 149.3 (dd, *J* = 150.0, 11.0 Hz), 138.9, 135.2 (m), 131.6 (m), 127.8, 125.9 (m), 124.2 (d, *J* = 17.0 Hz), 123.4 (q, *J* = 270.0 Hz), 122.7 (m), 118.2 (d, *J* = 16.5 Hz); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{14}H_7OF_5SNa$: 341.0035. Found: 341.0032.

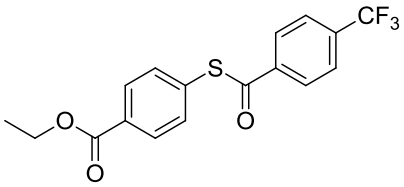


***S*-(4-cyanophenyl)-4-(trifluoromethyl)benzothioate** (**1m**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.66 (m, 2H), 7.77 (m, 4H), 8.12 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 187.5, 138.8, 135.5 (m), 135.3, 133.0, 132.7, 127.9, 126.0 (m), 123.3 (q, *J* = 270.0 Hz), 118.0, 113.5; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_8NOF_3SNa$: 330.0176. Found: 330.0174.

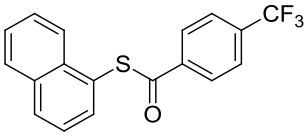


***S*-(4-acetylphenyl)-4-(trifluoromethyl)benzothioate** (**1n**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.64 (s, 3H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 197.3, 188.3, 139.1, 137.8, 135.2 (m), 134.9, 132.5, 129.0, 127.9, 125.9 (m), 123.4 (q, *J* = 270.0 Hz), 26.7; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for

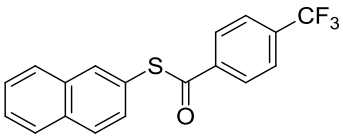
$C_{16}H_{11}O_2F_3SNa$: 347.0330. Found: 347.0326.



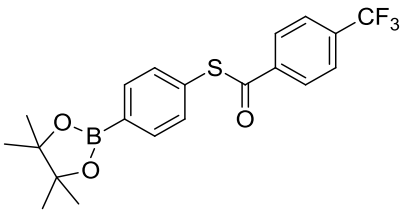
Ethyl 4-((4-(trifluoromethyl)benzoyl)thio)benzoate (**1o**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.41 (t, *J* = 6.8 Hz, 3H), 4.41 (q, *J* = 6.8 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 8.13 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 188.3, 165.8, 139.2, 134.9 (m), 134.6, 132.1, 131.6, 130.3, 127.9, 125.9 (m), 123.4 (q, *J* = 270.0 Hz), 61.3, 14.3; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{13}O_3F_3SNa$: 377.0435. Found: 377.0433.



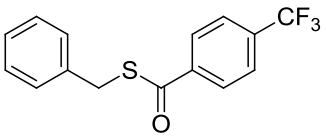
***S*-naphthalen-1-yl-4-(trifluoromethyl)benzothioate** (**1p**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.57 (m, 3H), 7.80 (t *J* = 6.5 Hz, 3H), 7.94 (m, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 8.21 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 188.9, 139.4, 135.5, 135.1 (m), 134.4, 134.3, 131.4, 128.8, 128.0, 127.4, 126.6, 125.8 (m), 125.7, 125.1, 124.0, 123.5 (q, *J* = 270.0 Hz); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{11}OF_3SNa$: 355.0380. Found: 355.0374.



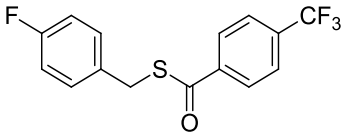
***S*-naphthalen-2-yl-4-(trifluoromethyl)benzothioate** (**1q**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.57 (m, 3H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.89 (m, 2H), 7.95 (d, *J* = 8.5 Hz, 1H), 8.08 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 189.5, 139.5, 135.0, 134.5 (m), 133.6, 133.5, 131.1, 129.1, 128.0, 127.9, 127.8, 127.4, 126.7, 125.8 (m), 123.9, 123.5 (d, *J* = 270.0 Hz); HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{11}OF_3SNa$: 355.0380. Found: 355.0376.



***S*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-(trifluoromethyl)-benzothioate** (**1r**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.37 (s, 12H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 8.12 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 188.9, 139.5, 135.6, 134.9 (m), 134.0, 129.8, 127.8, 125.8 (m), 123.5 (q, *J* = 270 Hz), 84.1, 24.8; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{22}H_{24}BOF_3SNa$: 431.1076. Found: 431.1082.



***S*-benzyl-4-(trifluoromethyl)benzothioate** (**1s**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 4.37 (s, 2H), 7.29 (m, 1H), 7.35 (m, 2H), 7.41 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 190.3, 139.6, 137.0, 134.6 (m), 129.1, 128.8, 127.7, 127.6, 125.7 (m), 123.5 (q, *J* = 270.0 Hz), 33.6; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{11}OF_3SNa$: 319.0380. Found: 319.0376.



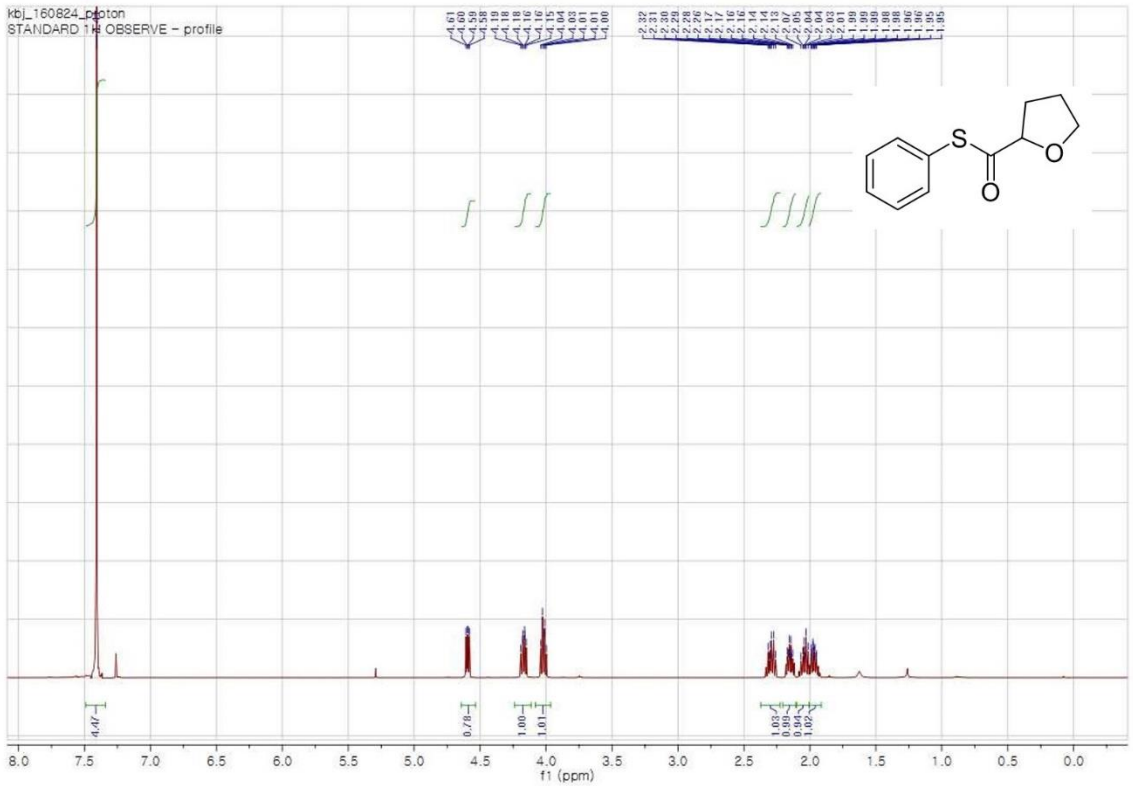
***S*-(4-fluorobenzyl)-4-(trifluoromethyl)benzothioate** (**1t**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 4.32 (s, 2H), 7.01 (t, *J* = 8.3 Hz, 2H), 7.35 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 8.06 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ = 190.2, 162.2 (d, *J* = 240.0 Hz), 139.4, 134.8 (m), 132.8 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 7.9 Hz), 127.6, 125.7 (m), 123.4 (q, *J* = 270.0 Hz), 115.6 (d), 32.8; HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{15}H_{10}OF_4SNa$: 337.0286. Found: 337.0280.

II. References

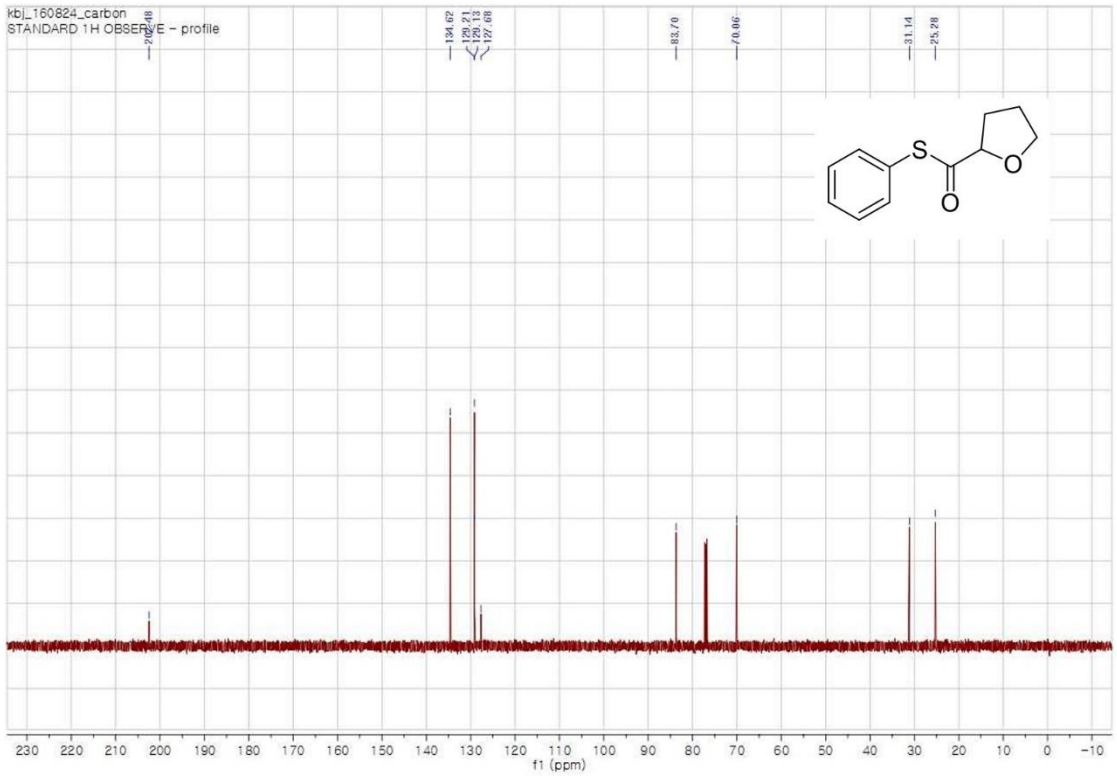
1. M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712.
2. D. L. Holmes and D. A. Lightner, *Tetrahedron*, 1995, **51**, 1607.
3. Y. J. Liu, J. Kim, H. Seo, S. Park and J. Chae, *Adv. Synth. Catal.*, 2015, **357**, 2205.
4. R. A. Aitken, M. J. Drysdale and B. M. Ryan, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3345.
5. C. A. Laskowski and G. L. Hillhouse, *Organometallics*, 2009, **28**, 6114.
6. B. R. Dible, M. S. Sigman and A. M. Arif, *Inorg. Chem.*, 2005, **44**, 3774.
7. C. H. He, X. W. Qian and P. P. Sun, *Org. Biomol. Chem.*, 2014, **12**, 6072.
8. Y. Lin, M. Z. Cai, Z. G. Fang and H. Zhao, *Tetrahedron*, 2016, **72**, 3335.
9. E. A. Jo and C. H. Jun, *Eur. J. Org. Chem.*, 2006, 2504.
10. A. G. M. Barrett, J. A. Flygare and C. D. Spilling, *J. Org. Chem.*, 1989, **54**, 4723.

III. ^{1}H and ^{13}C NMR spectra

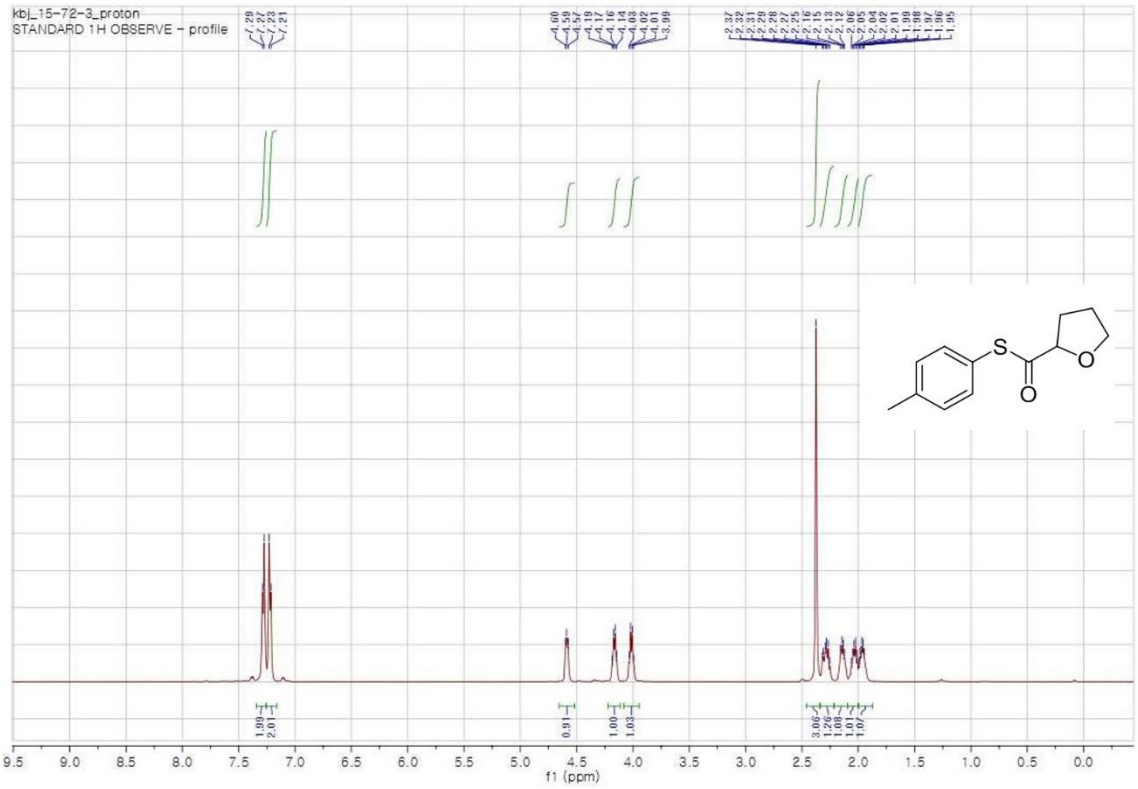
^{1}H NMR **(3aa)**



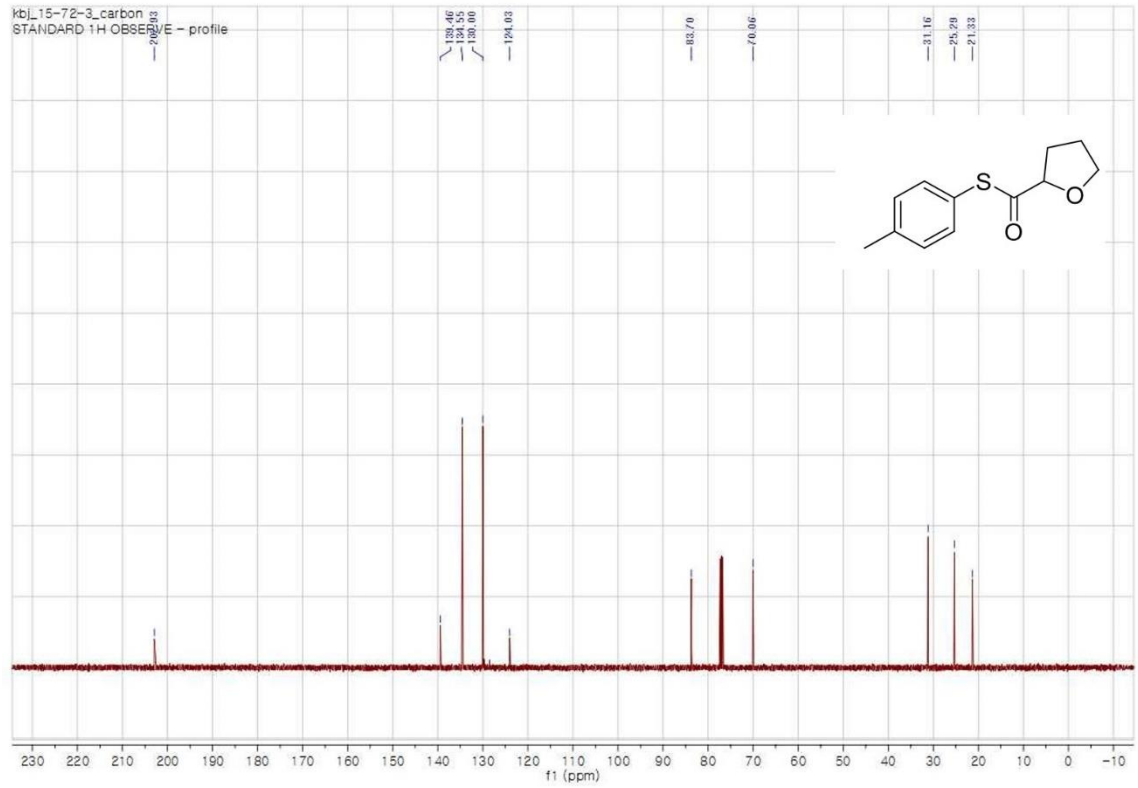
^{13}C NMR **(3aa)**



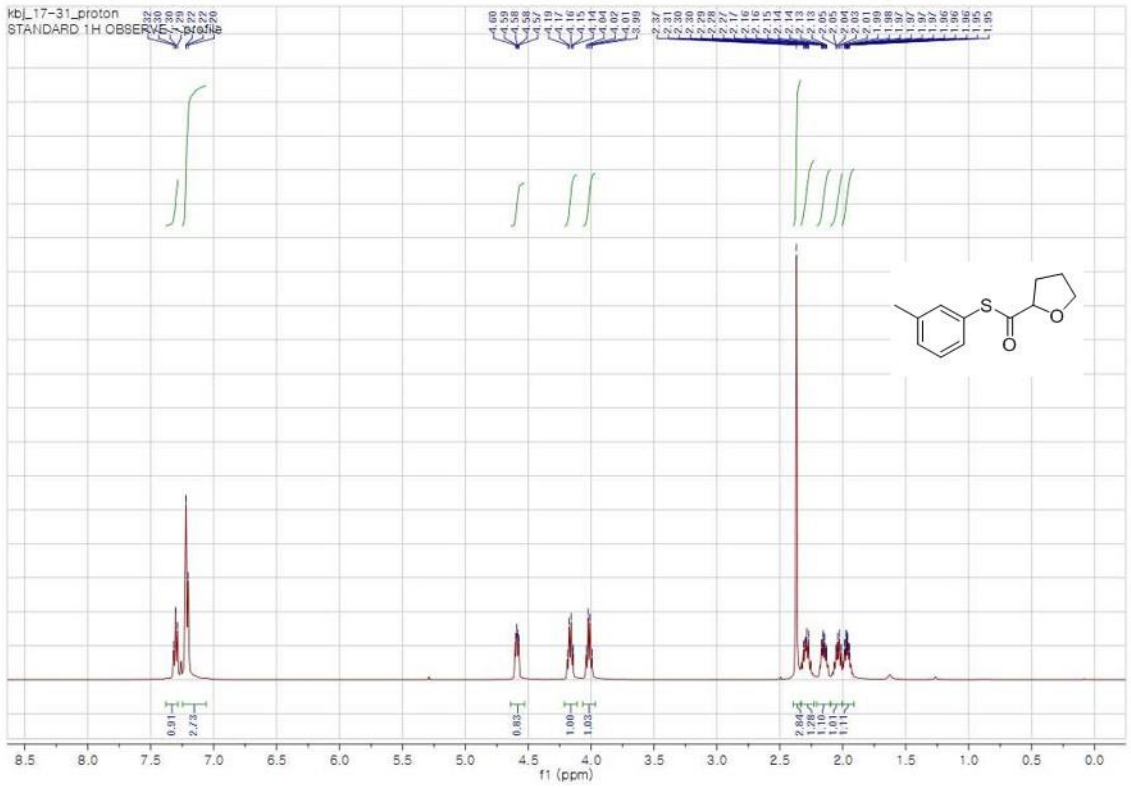
^{1}H NMR **(3ba)**



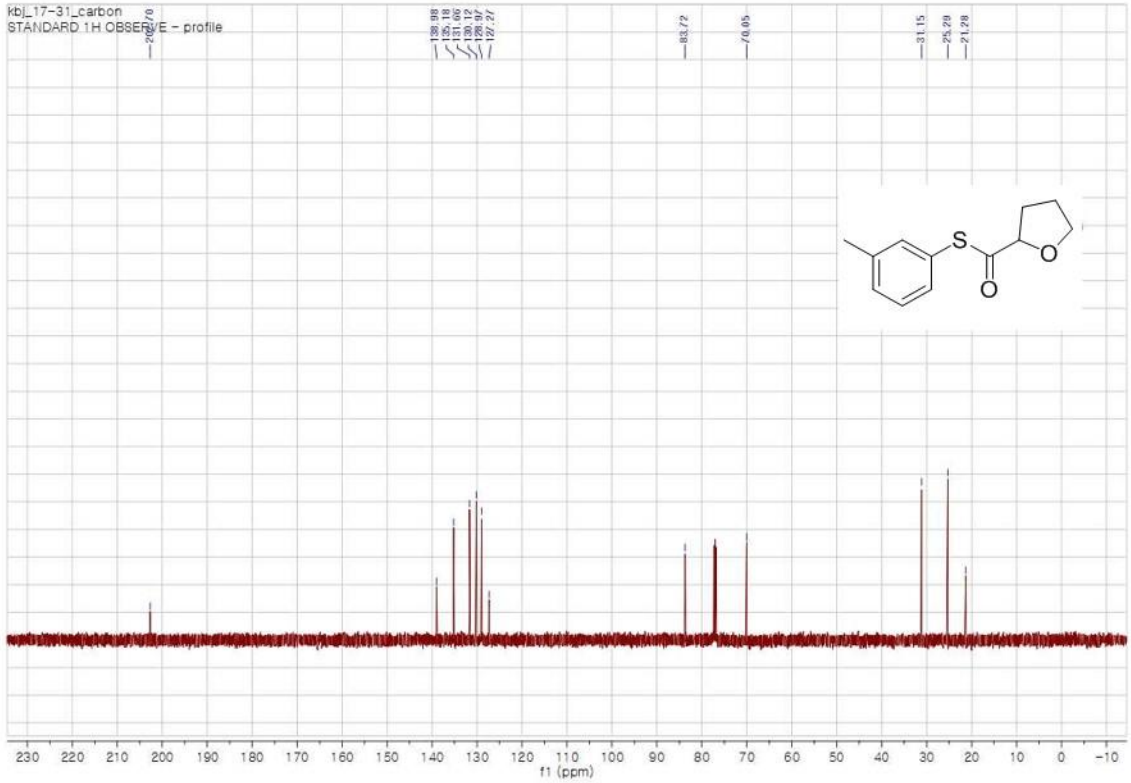
^{13}C NMR **(3ba)**



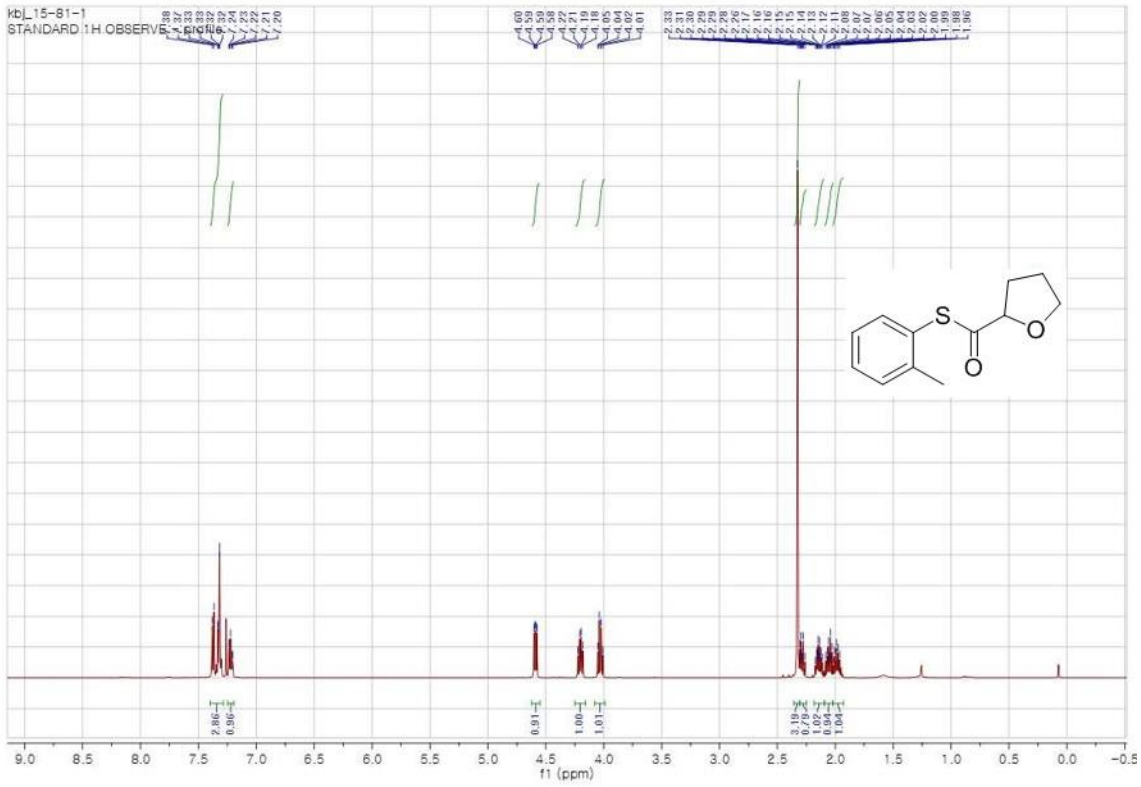
^{1}H NMR **(3ca)**



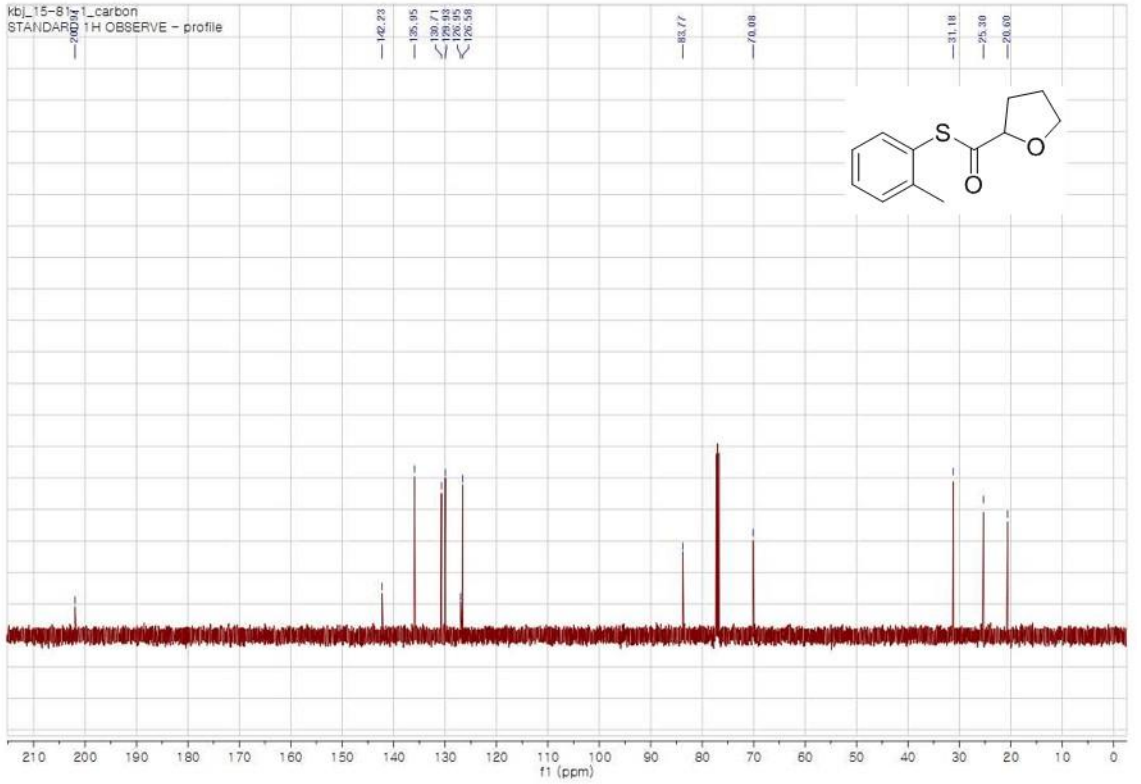
^{13}C NMR **(3ca)**



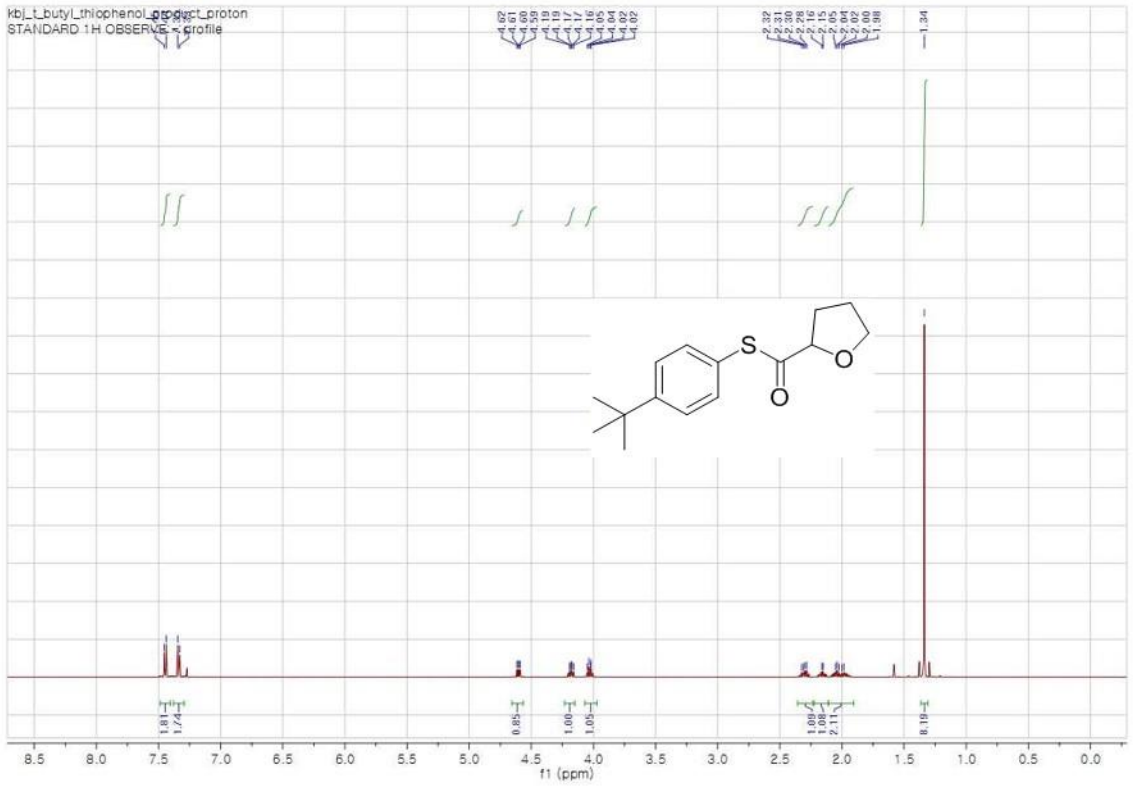
^{1}H NMR **(3da)**



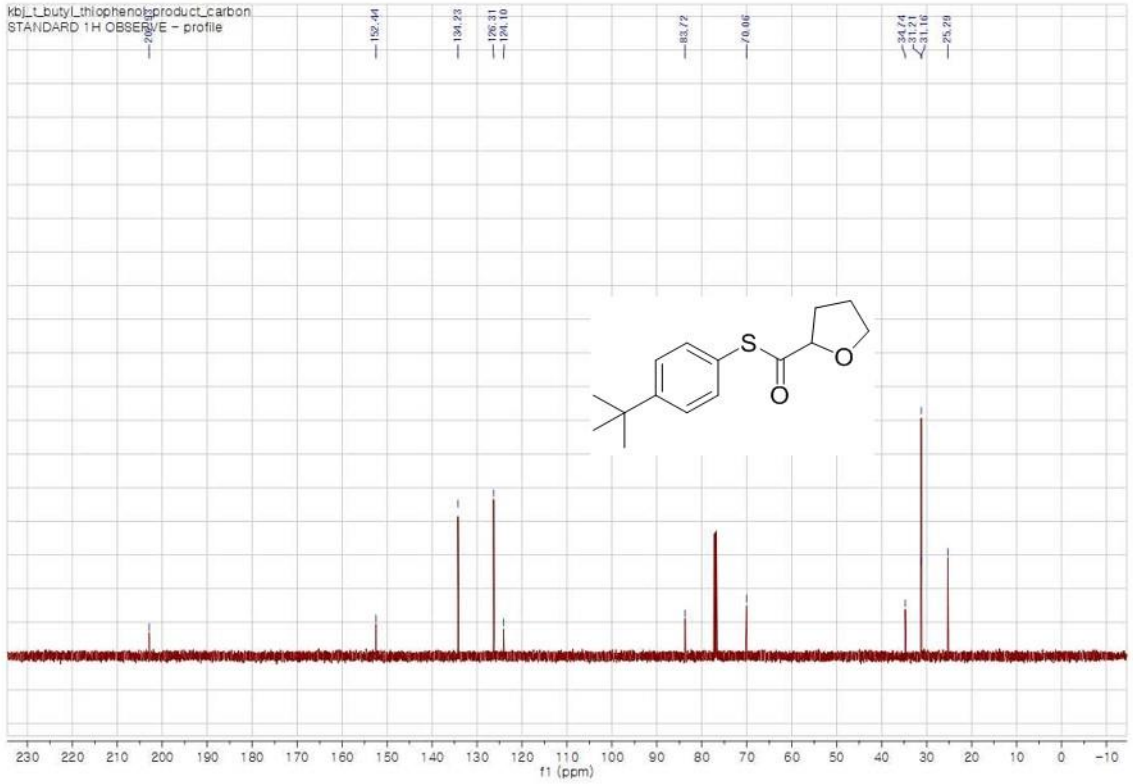
^{13}C NMR **(3da)**



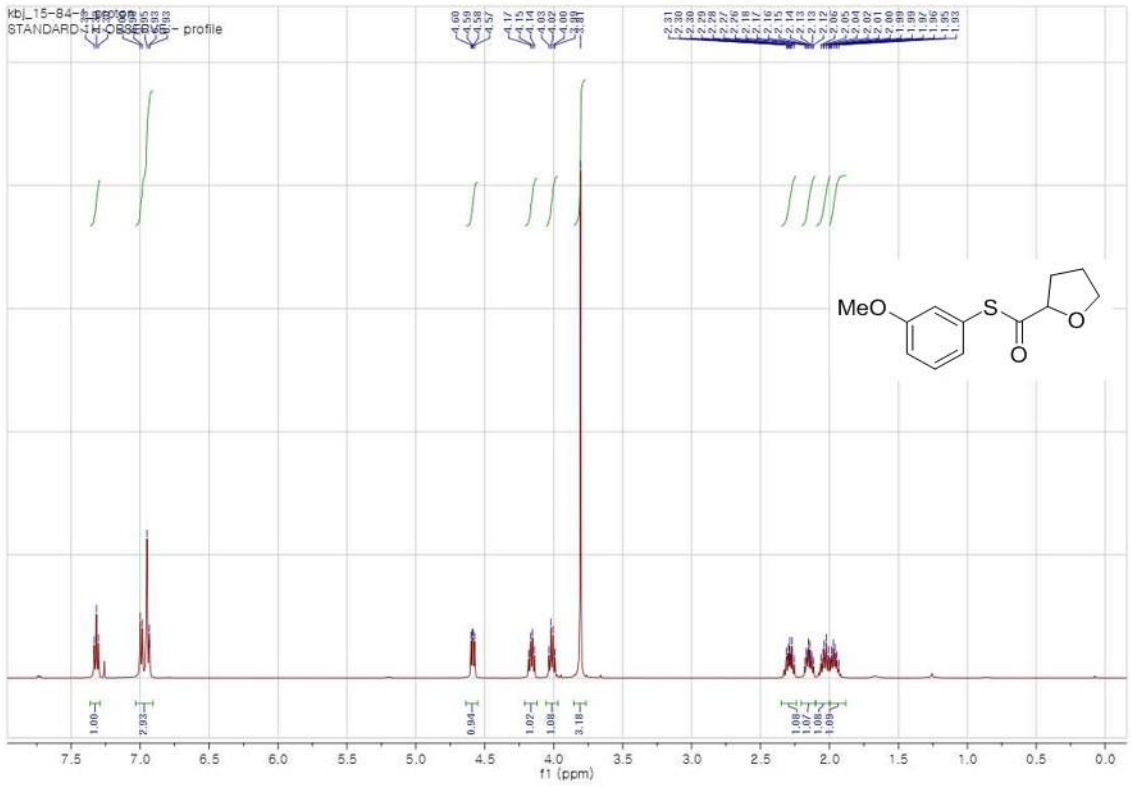
^{1}H NMR **(3ea)**



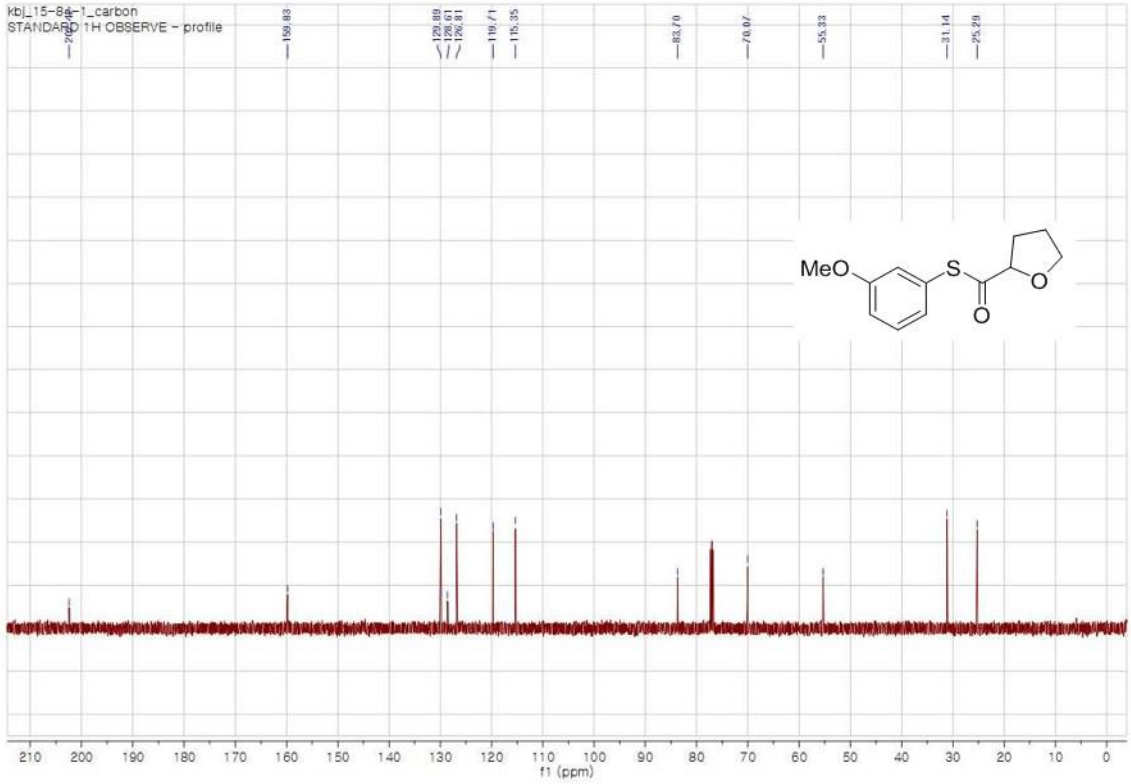
^{13}C NMR **(3ea)**



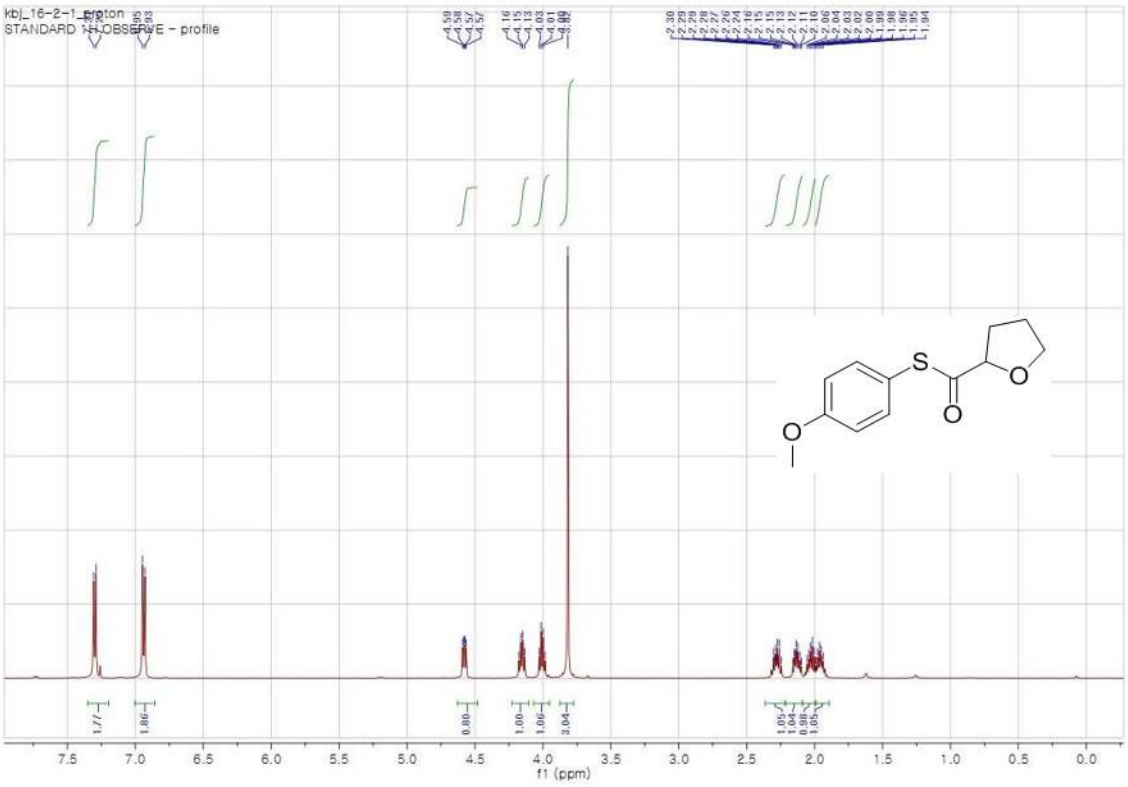
^{1}H NMR **(3fa)**



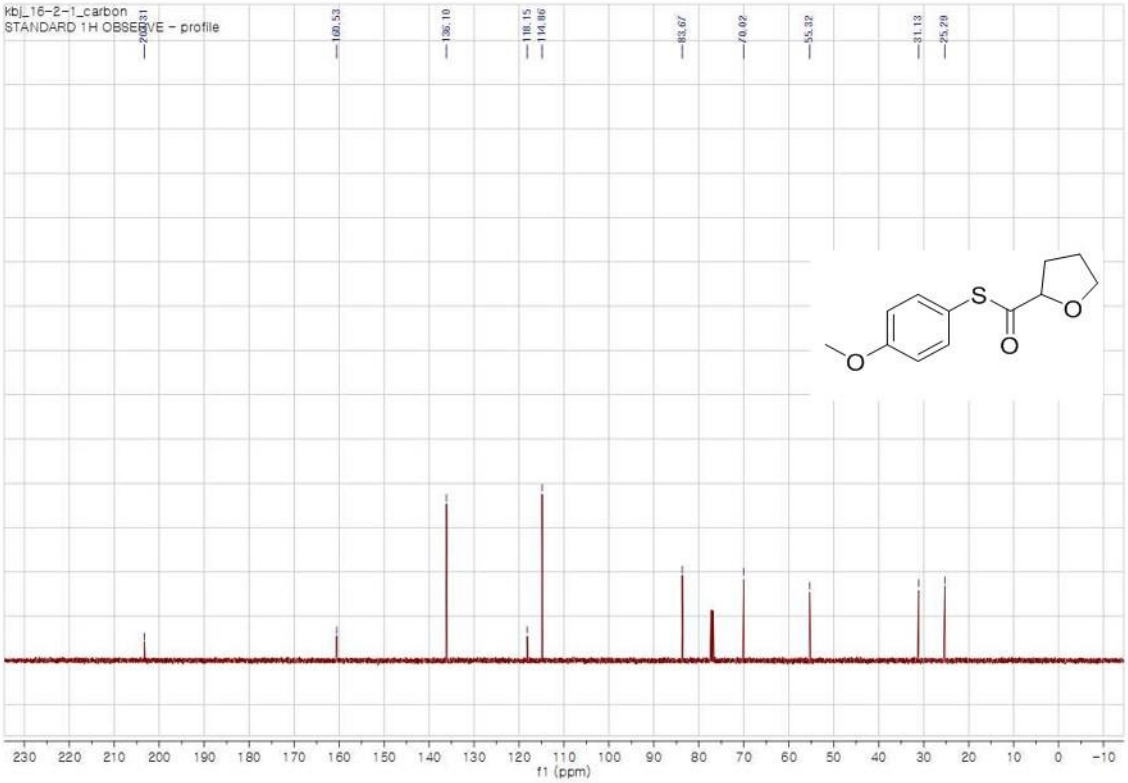
^{13}C NMR **(3fa)**



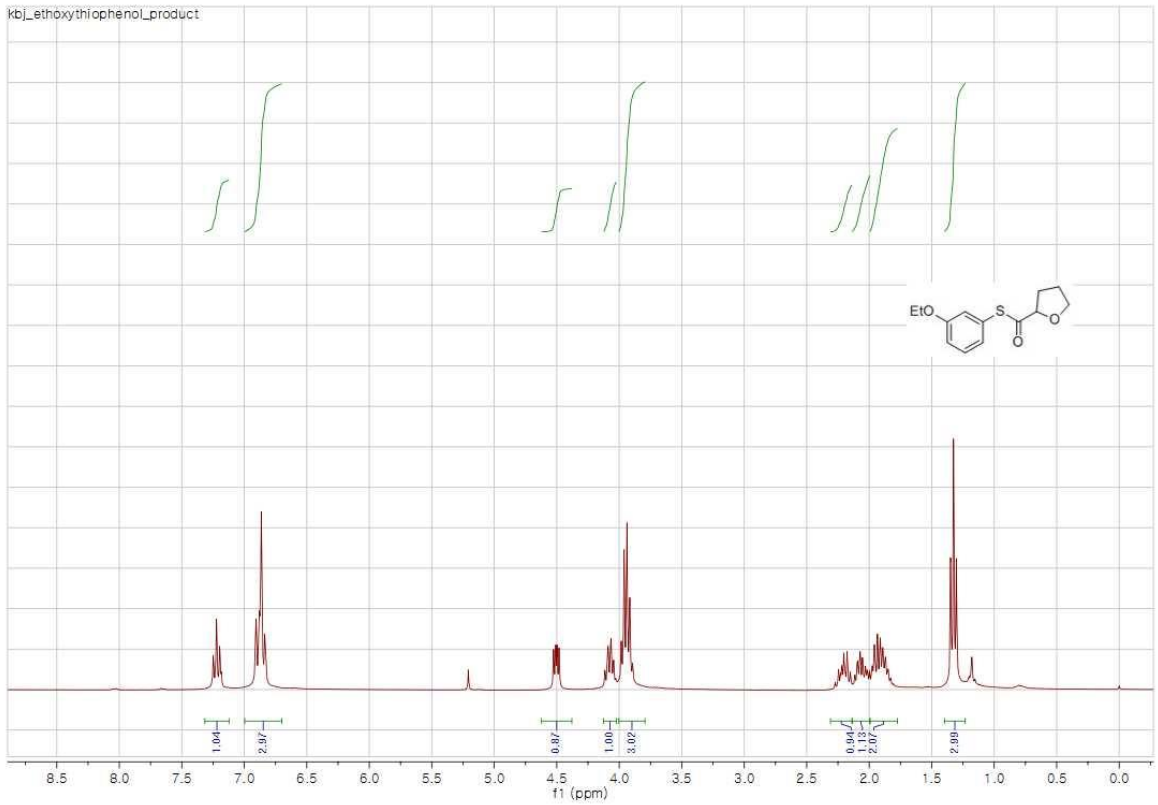
^{1}H NMR **(3ga)**



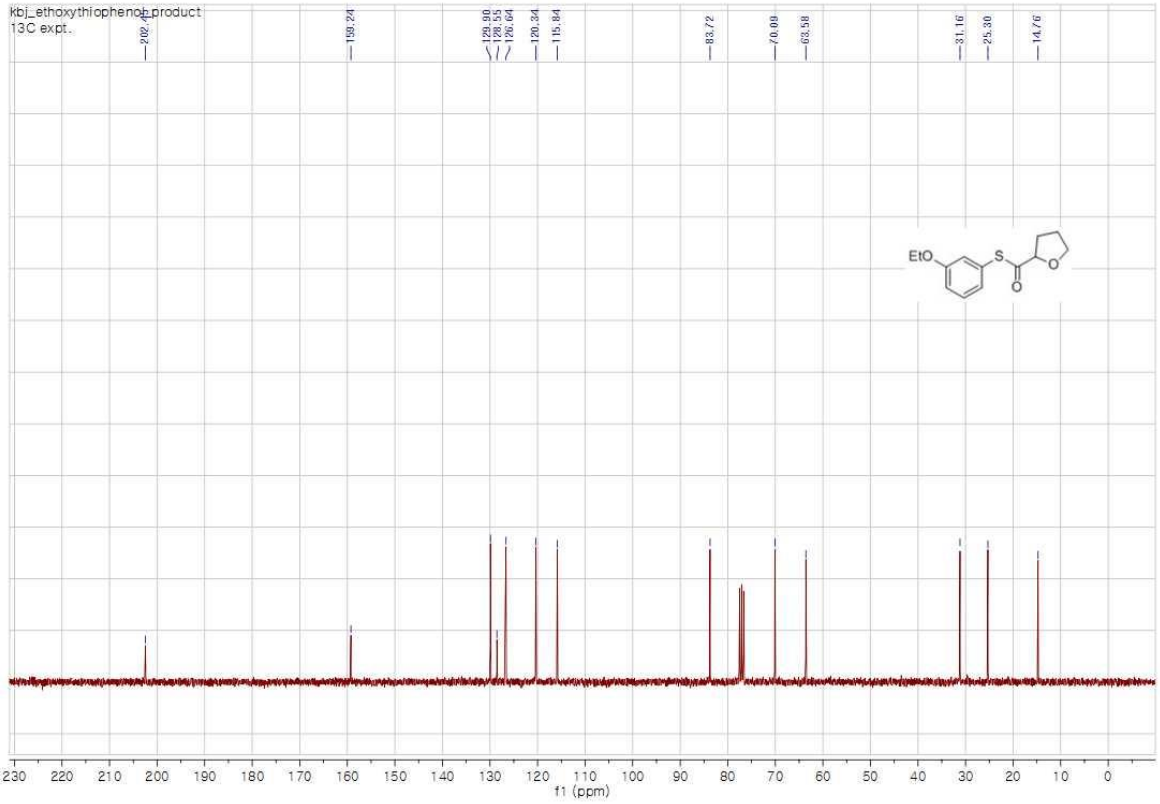
^{13}C NMR **(3ga)**



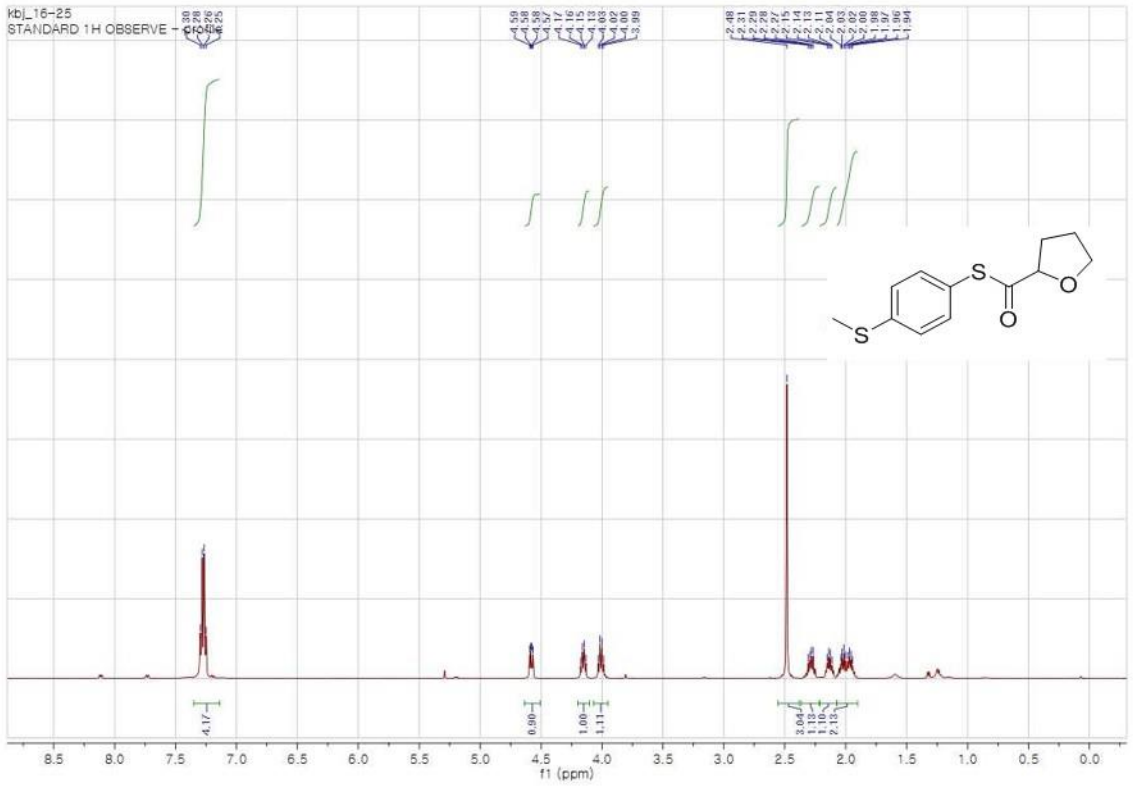
^{1}H NMR **(3ha)**



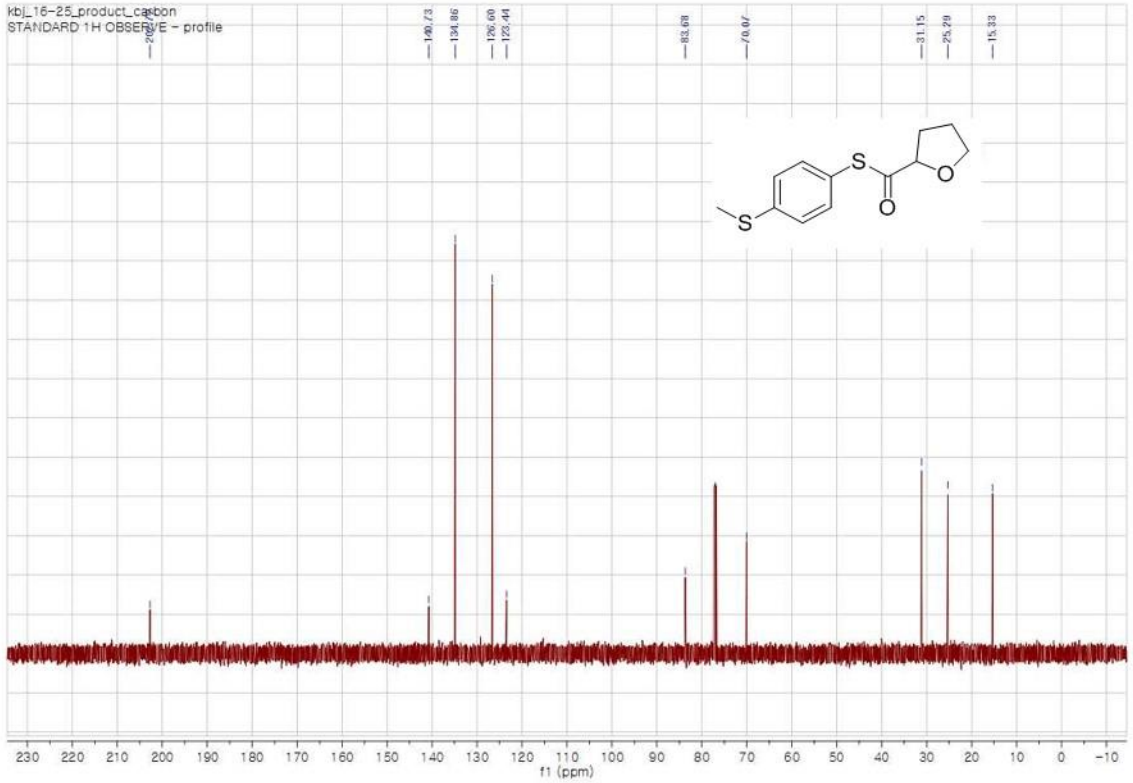
^{13}C NMR **(3ha)**



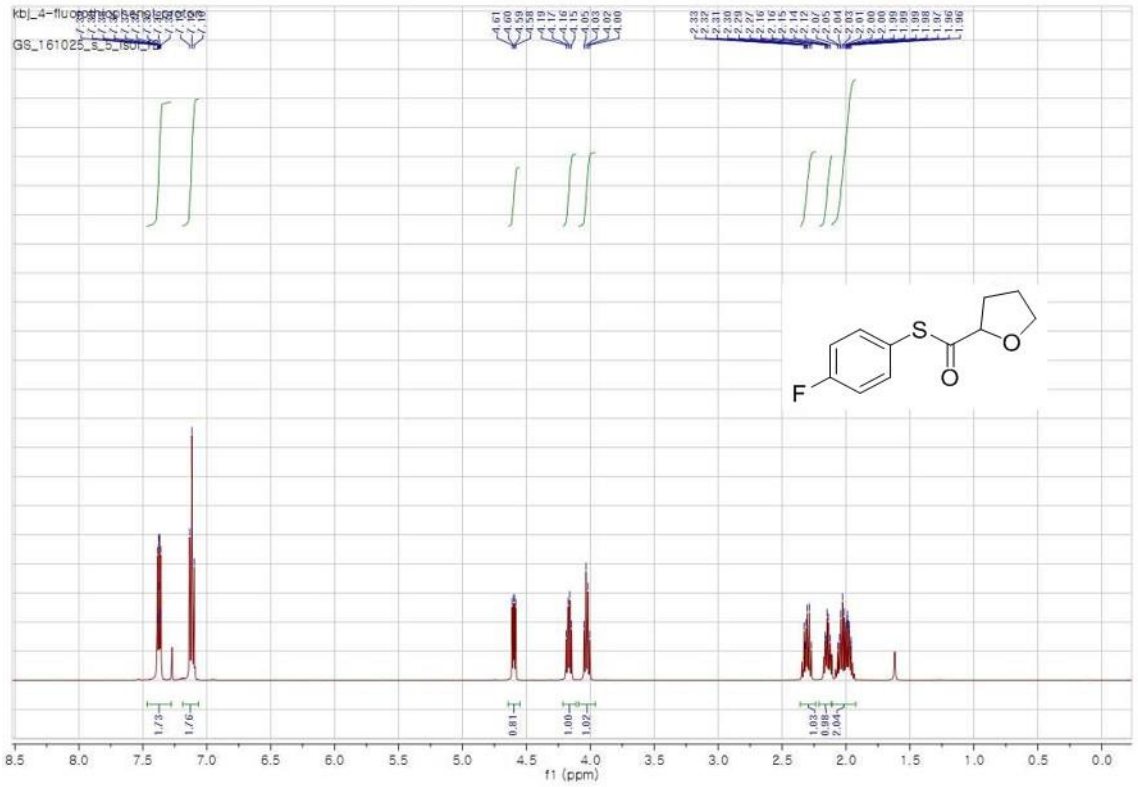
^{1}H NMR **(3ia)**



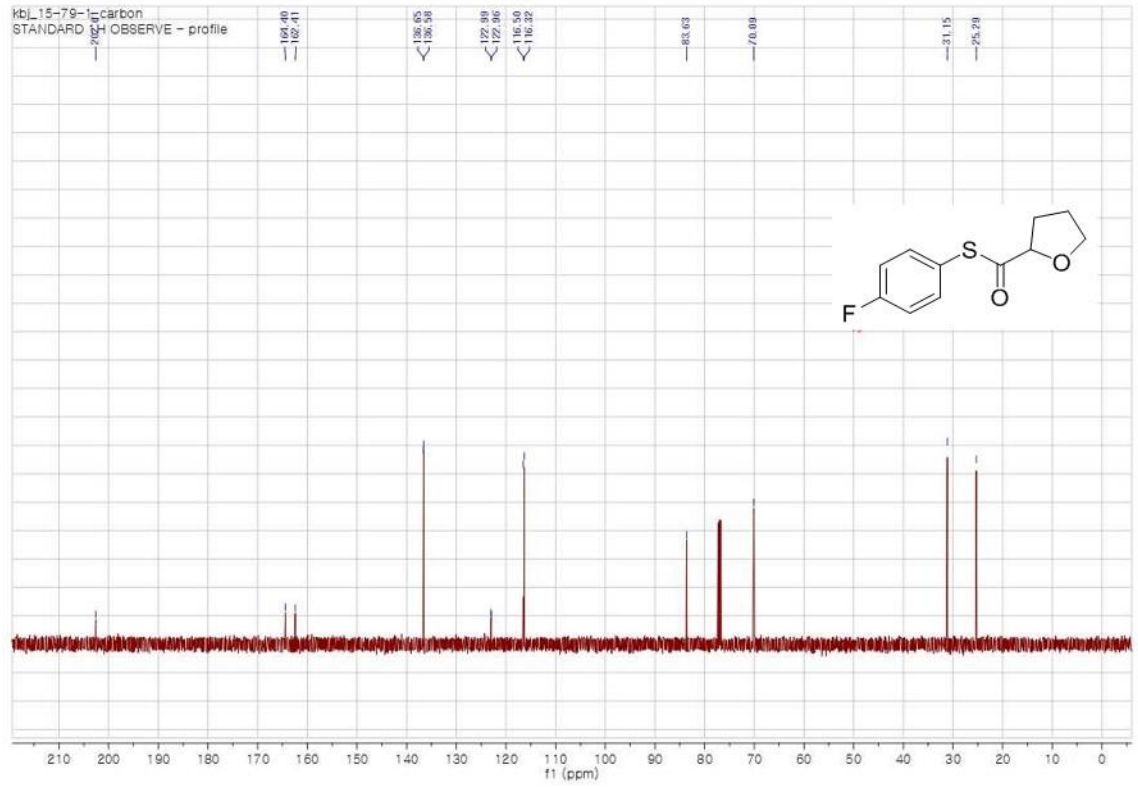
^{13}C NMR **(3ia)**



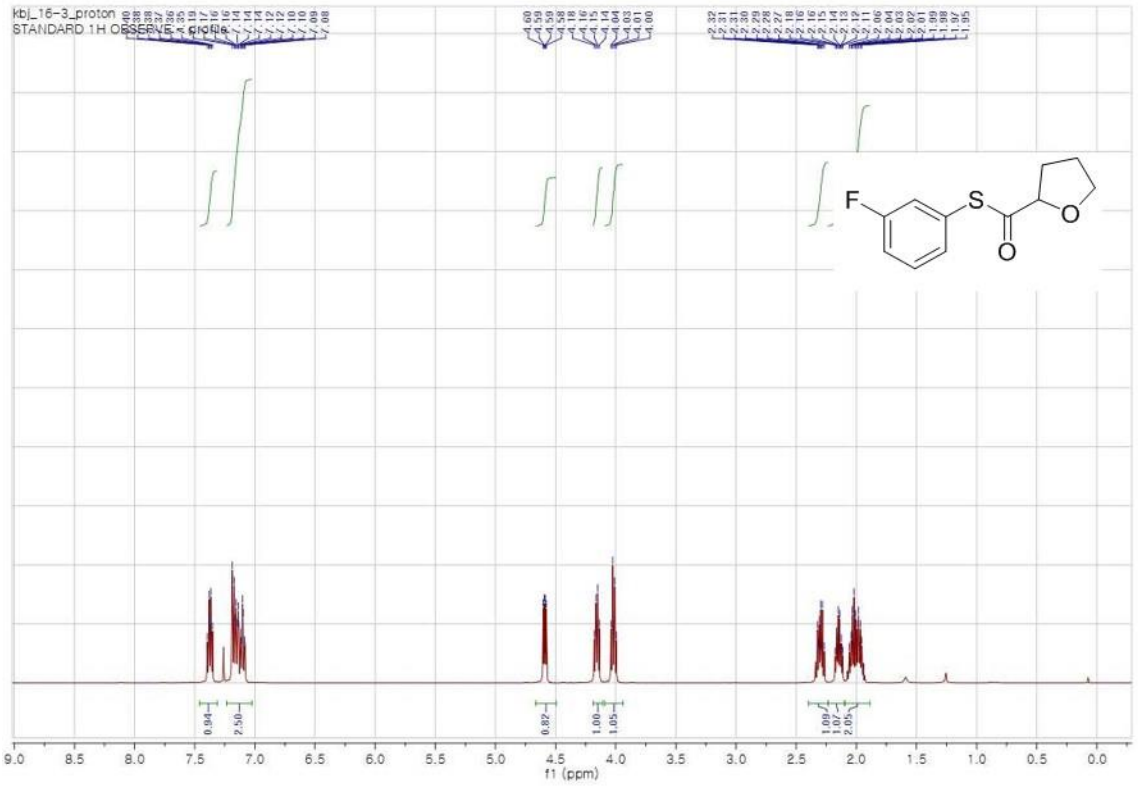
^{1}H NMR **(3ja)**



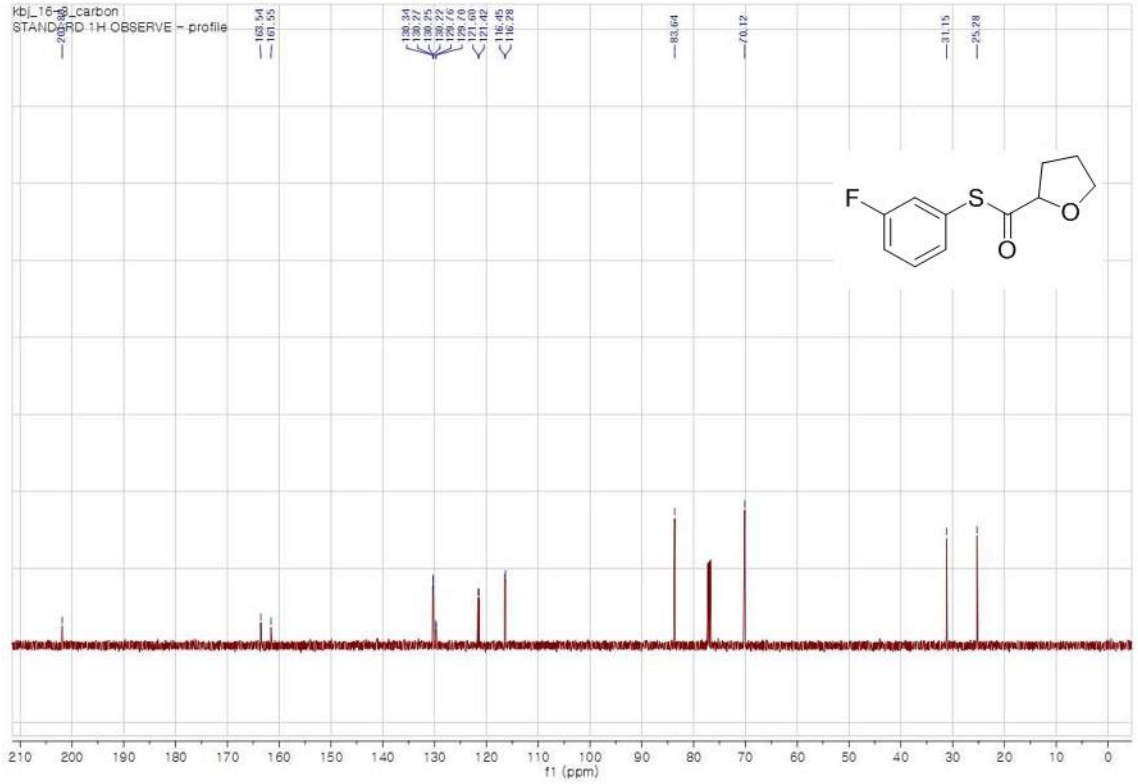
^{13}C NMR **(3ja)**



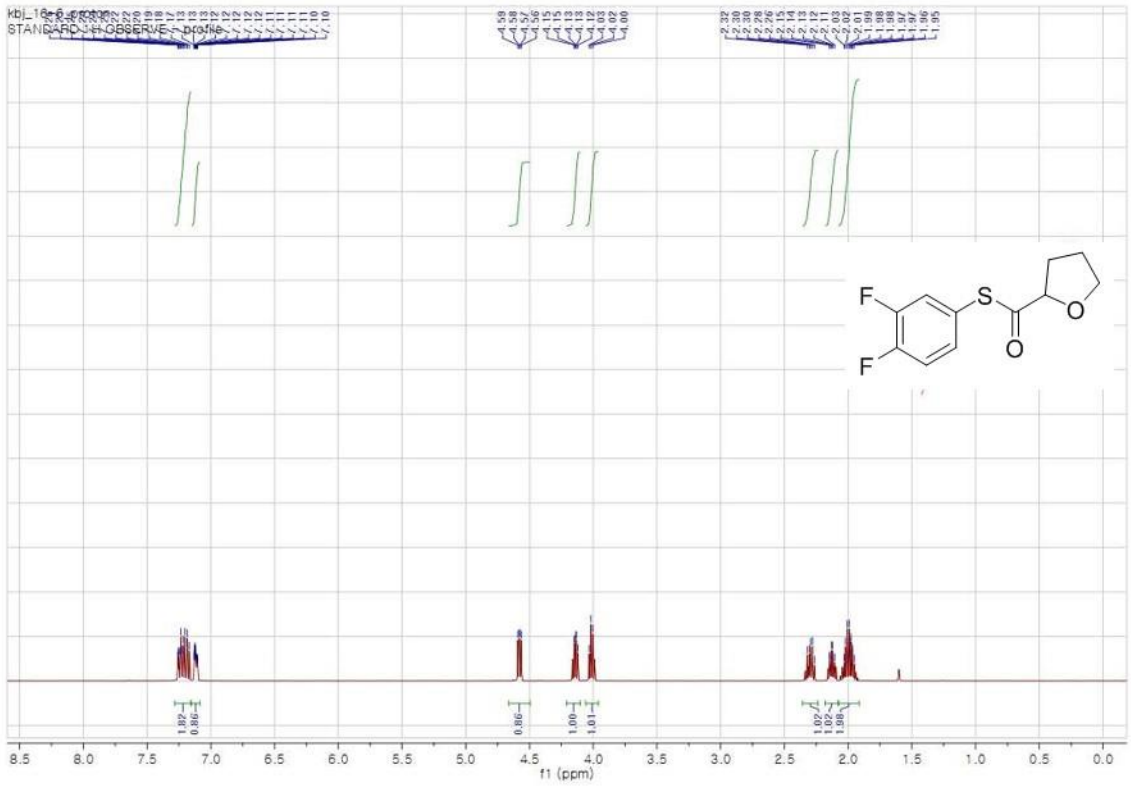
^{1}H NMR **(3ka)**



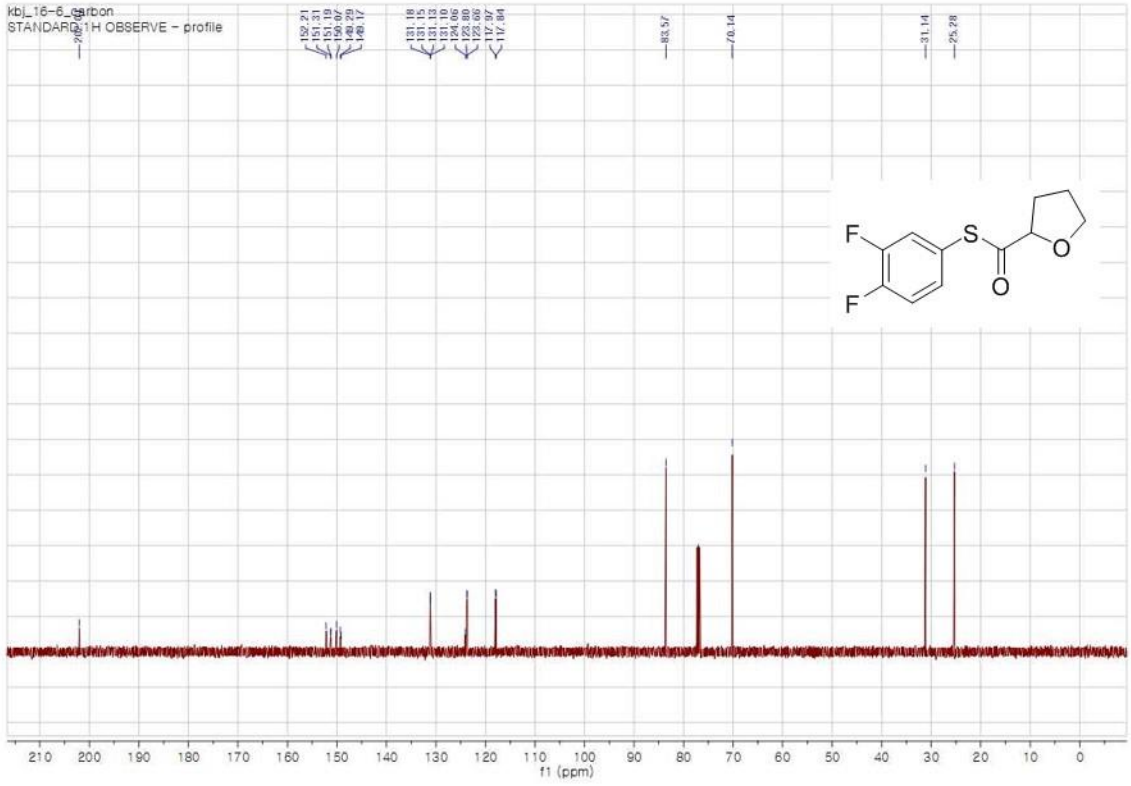
^{13}C NMR **(3ka)**



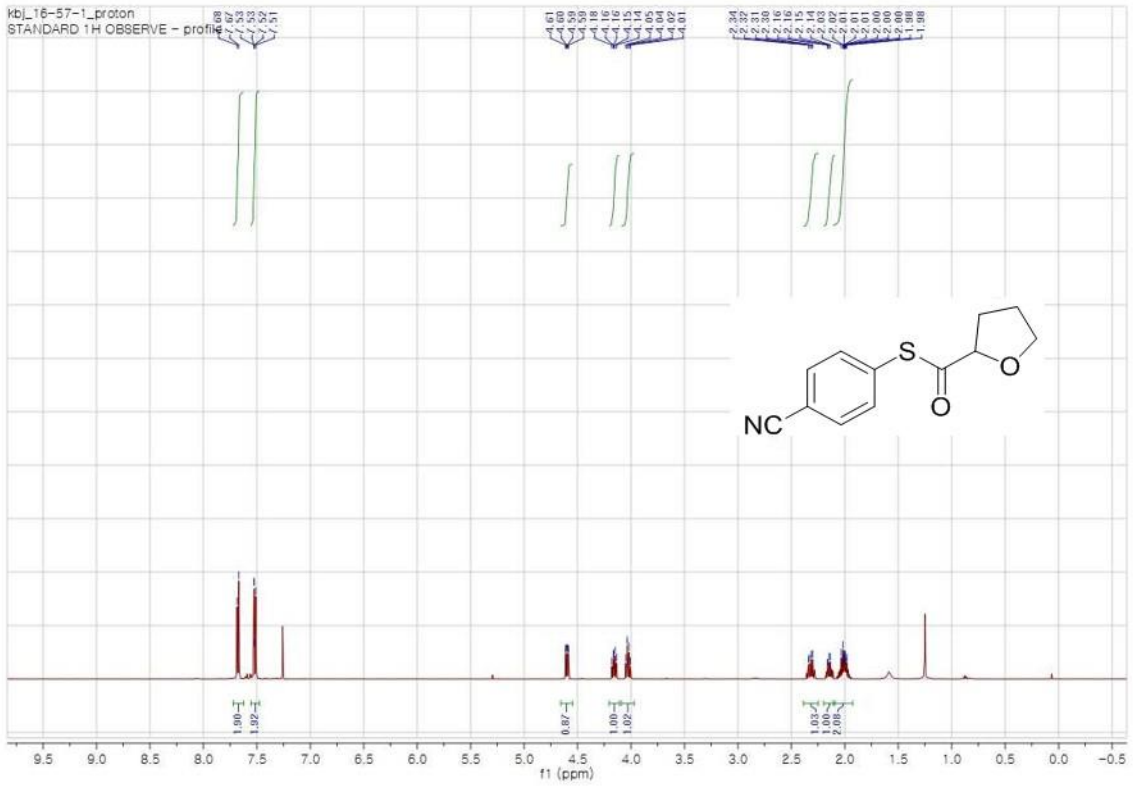
^{1}H NMR **(3la)**



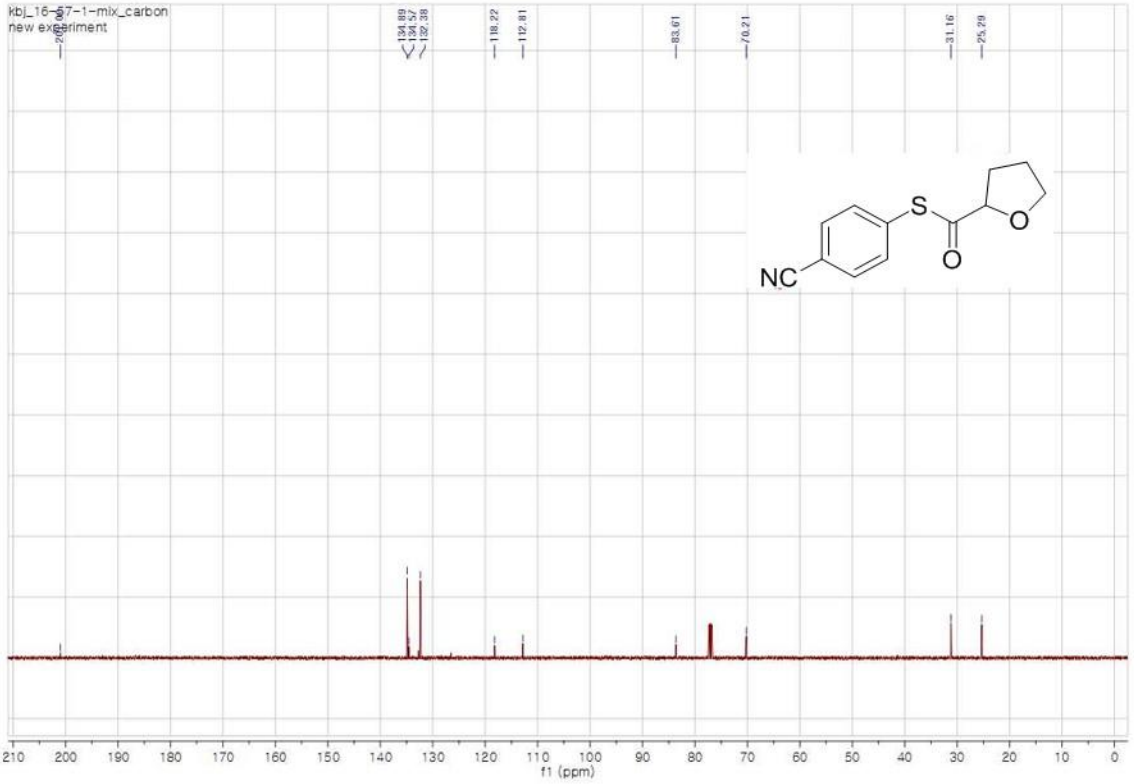
^{13}C NMR **(3la)**



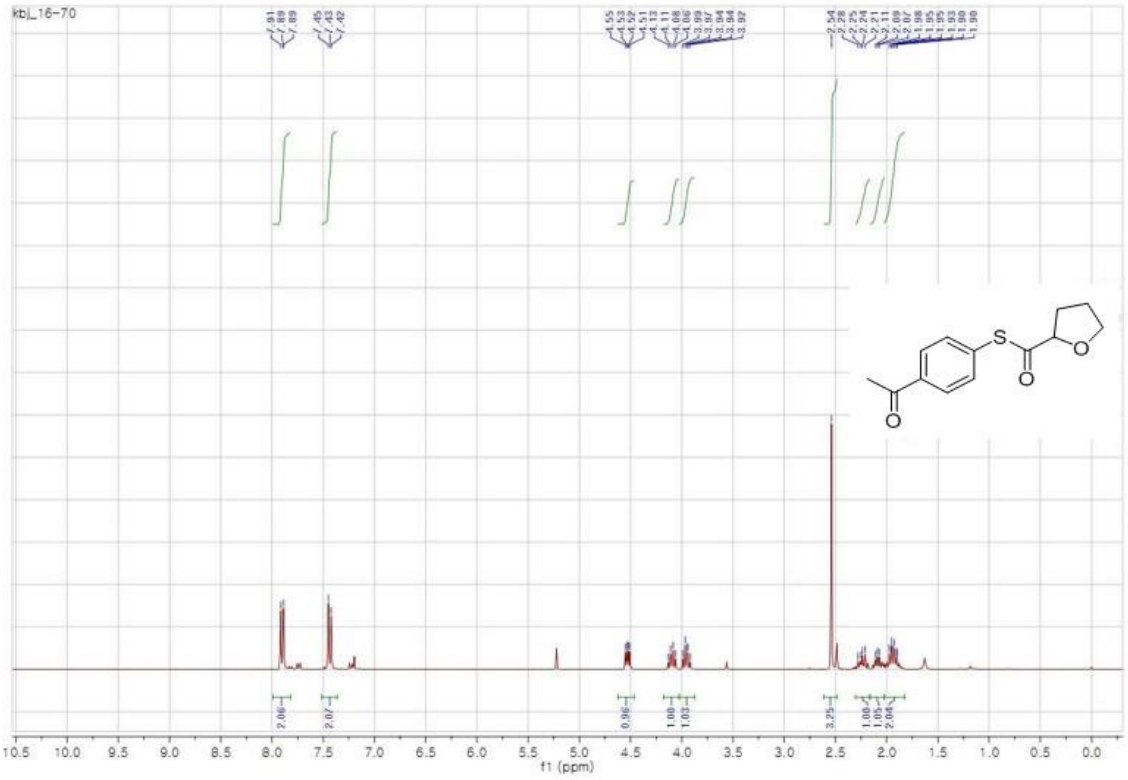
^{1}H NMR **(3ma)**



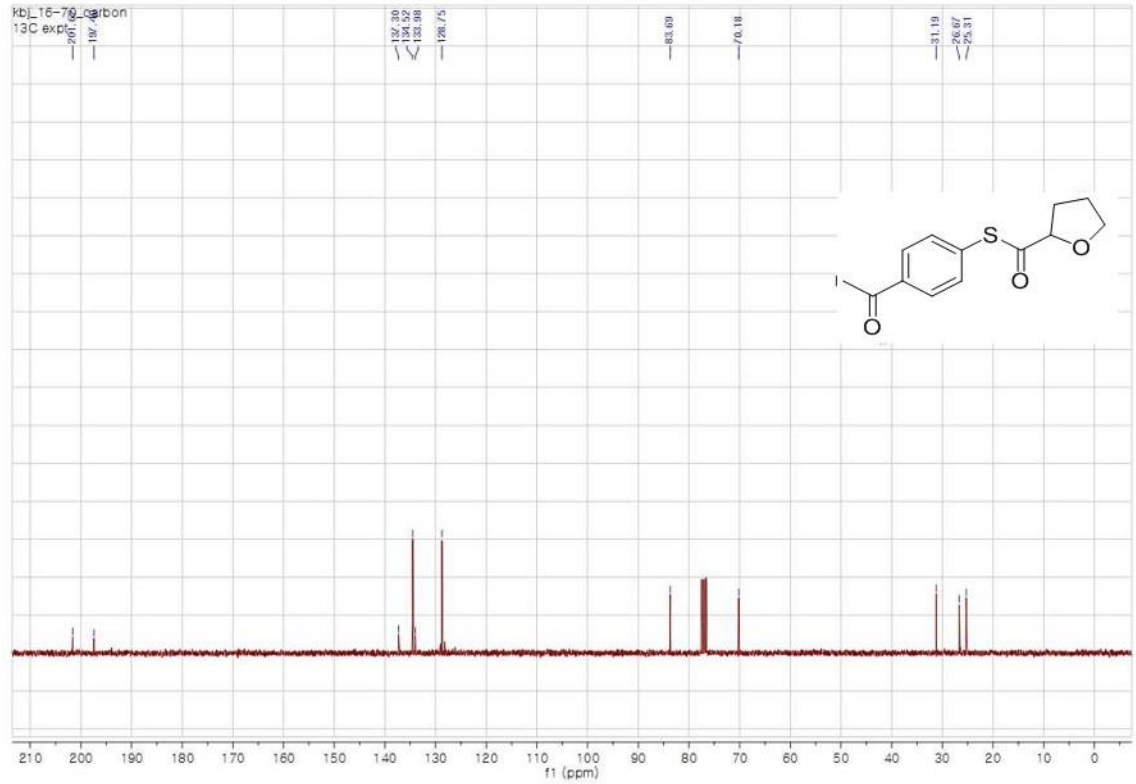
^{13}C NMR **(3ma)**



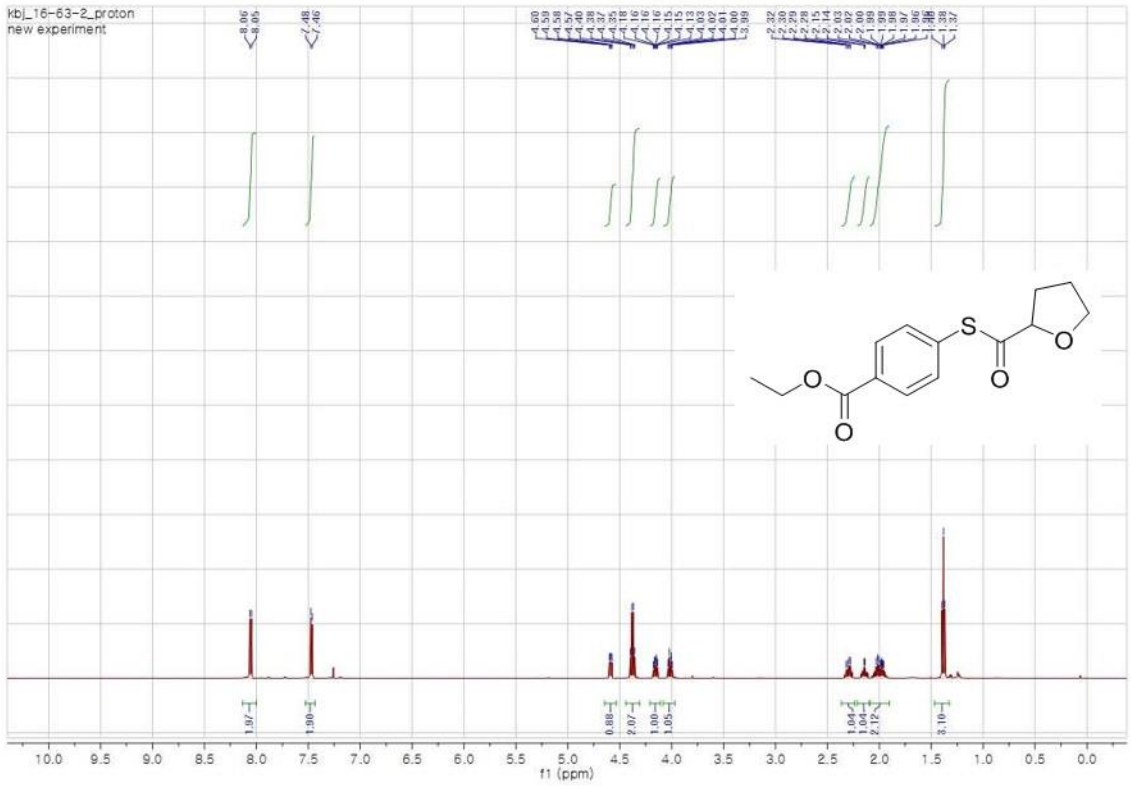
^{1}H NMR **(3na)**



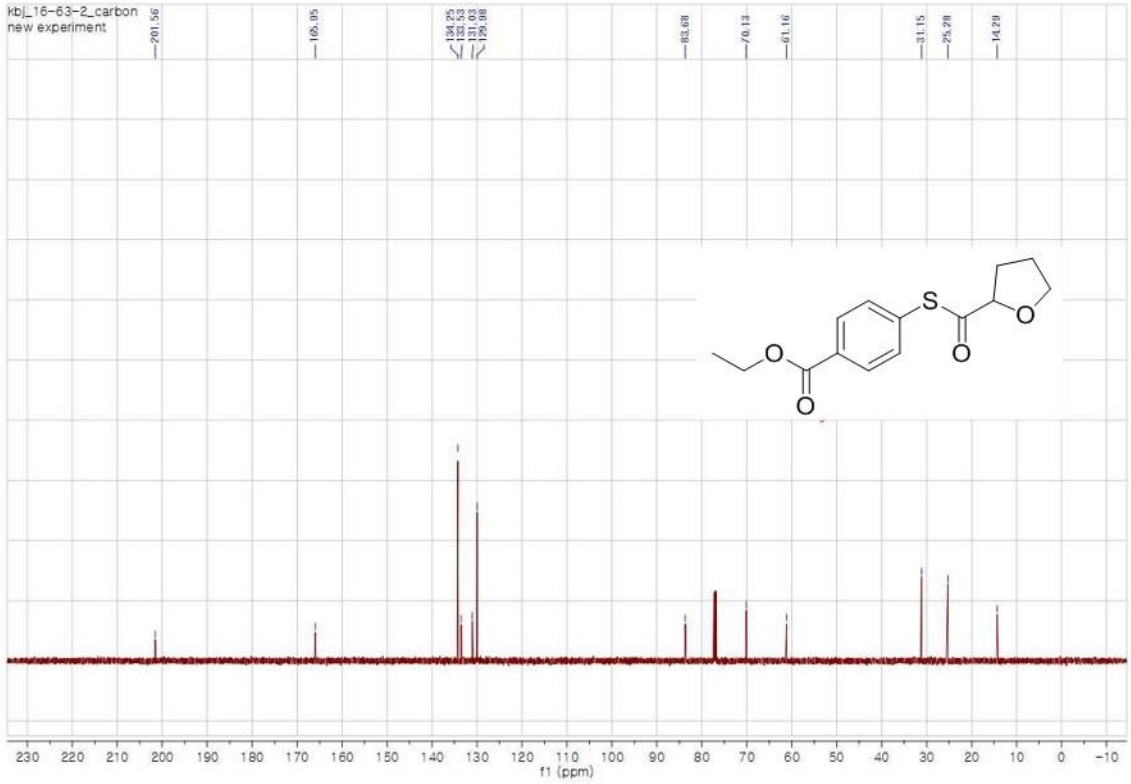
^{13}C NMR **(3na)**



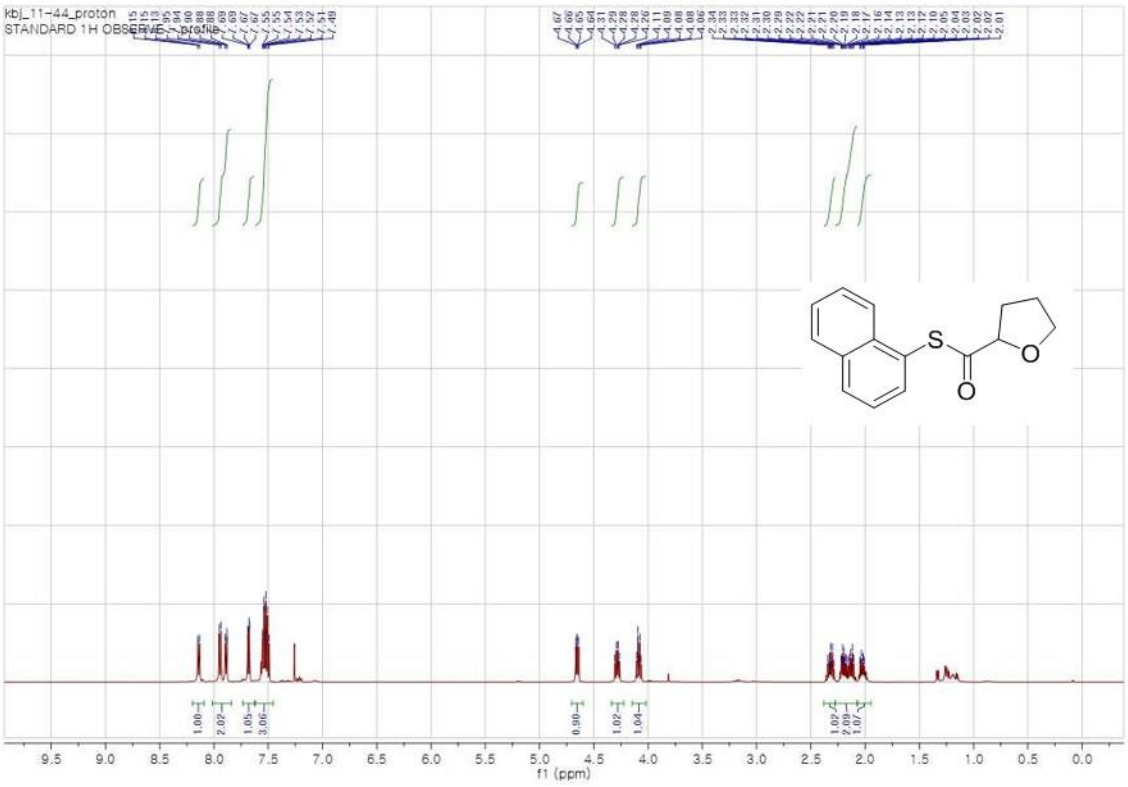
^{1}H NMR **(3oa)**



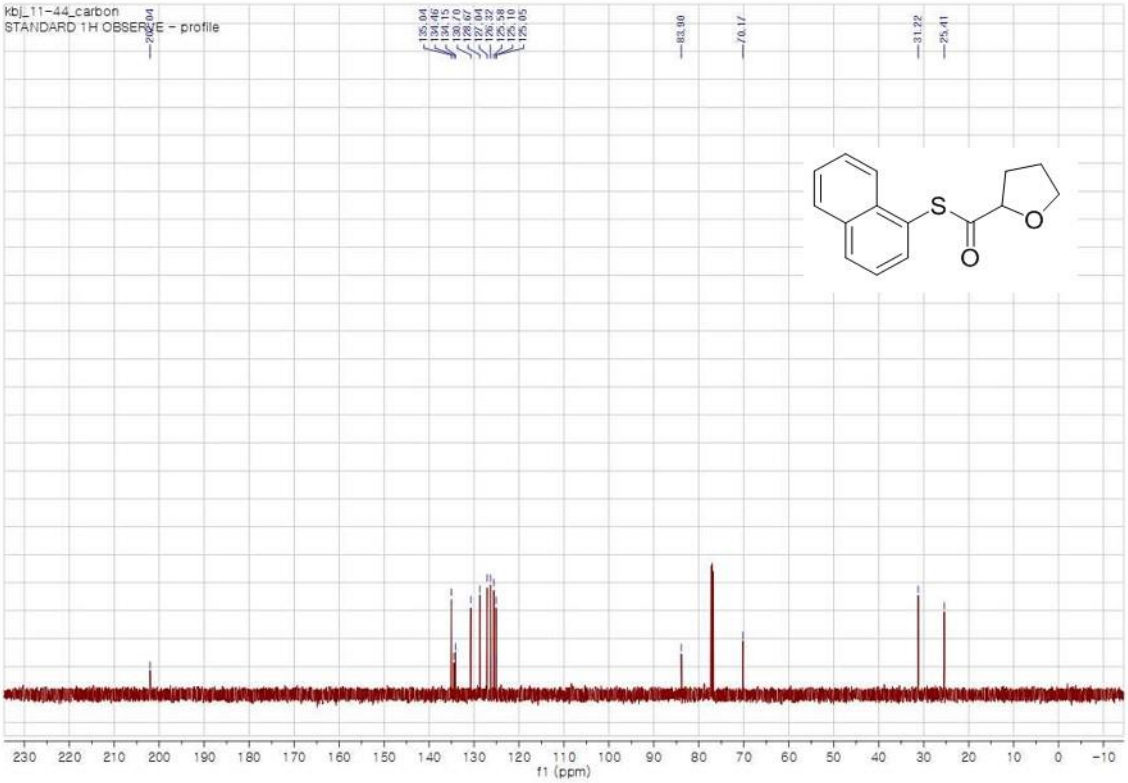
^{13}C NMR **(3oa)**



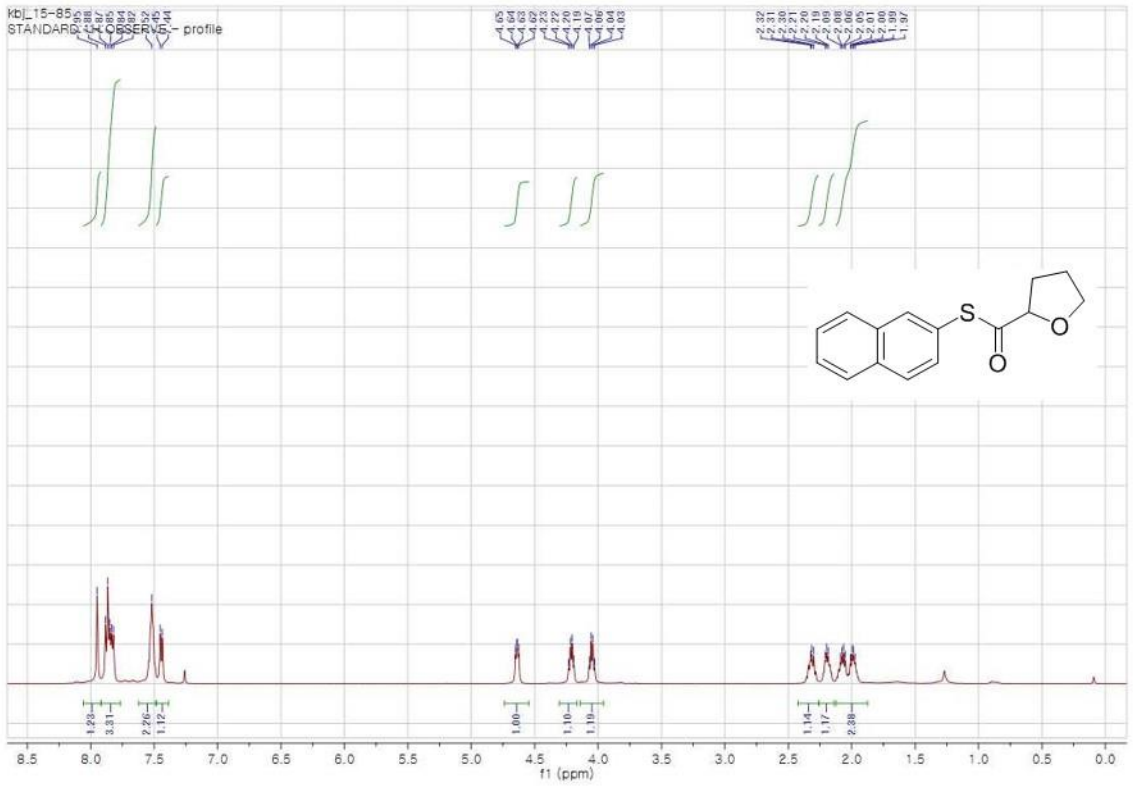
^{1}H NMR **(3pa)**



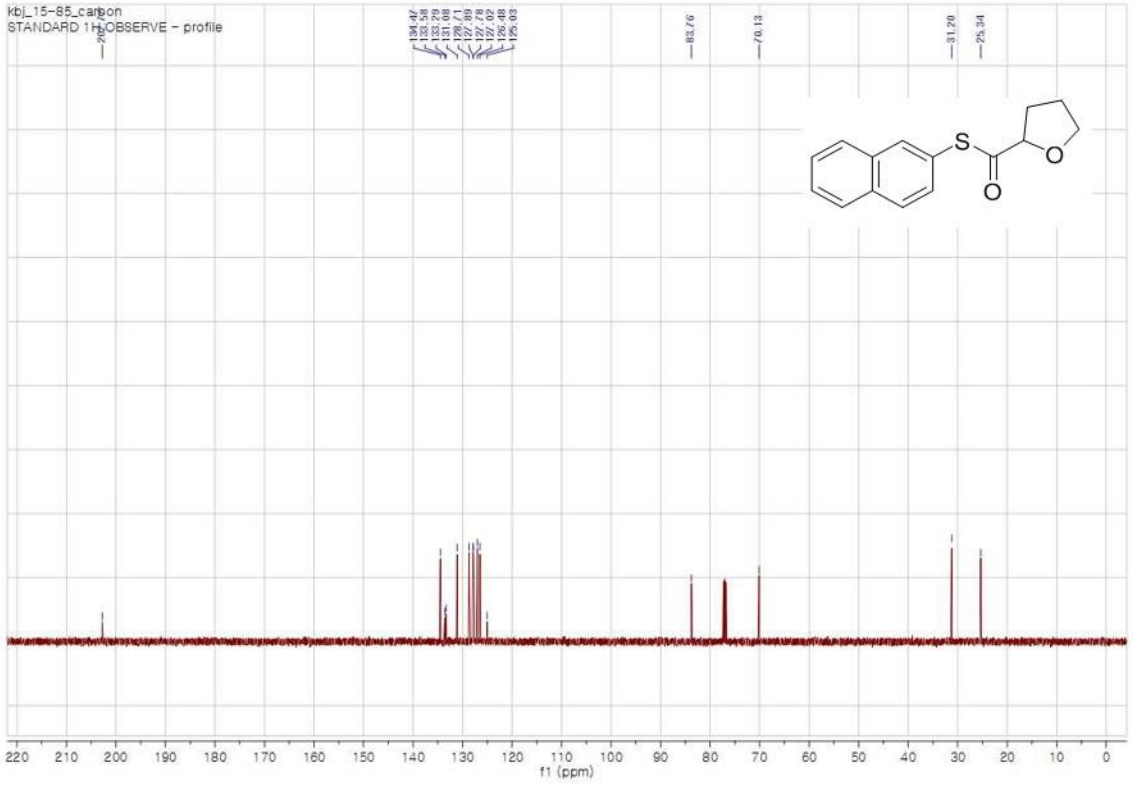
^{13}C NMR **(3pa)**



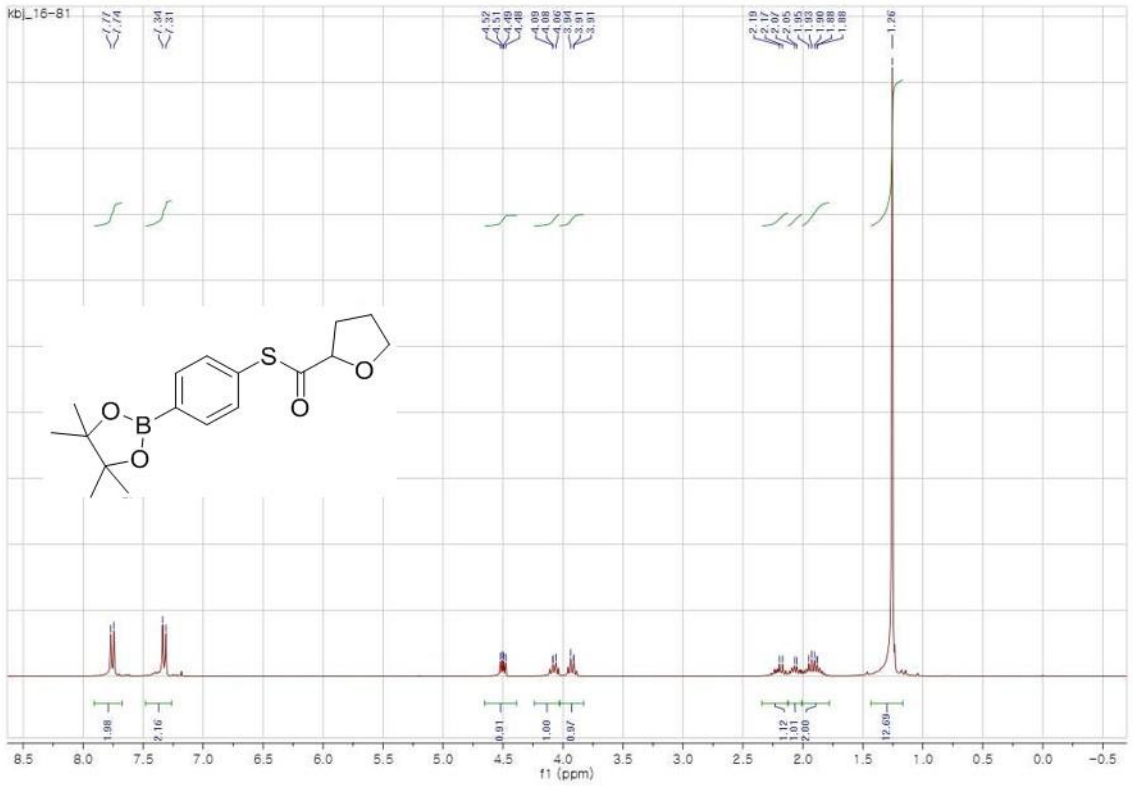
^{1}H NMR **(3qa)**



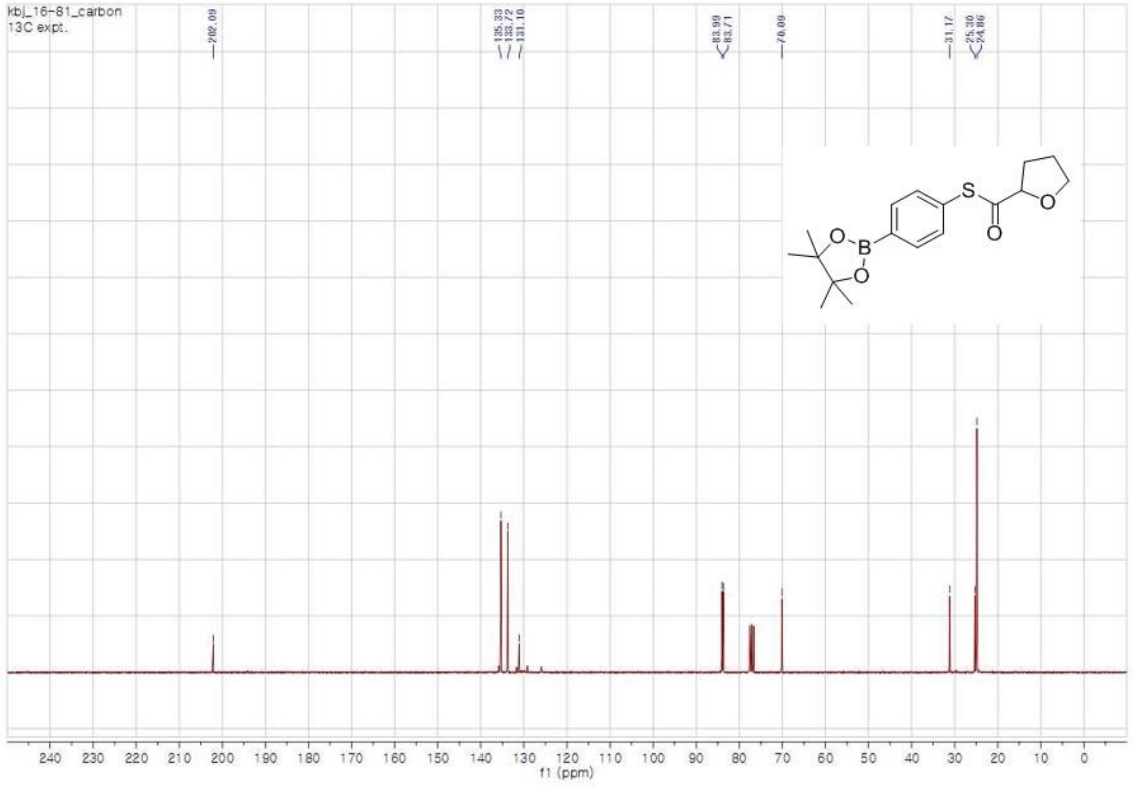
^{13}C NMR **(3qa)**



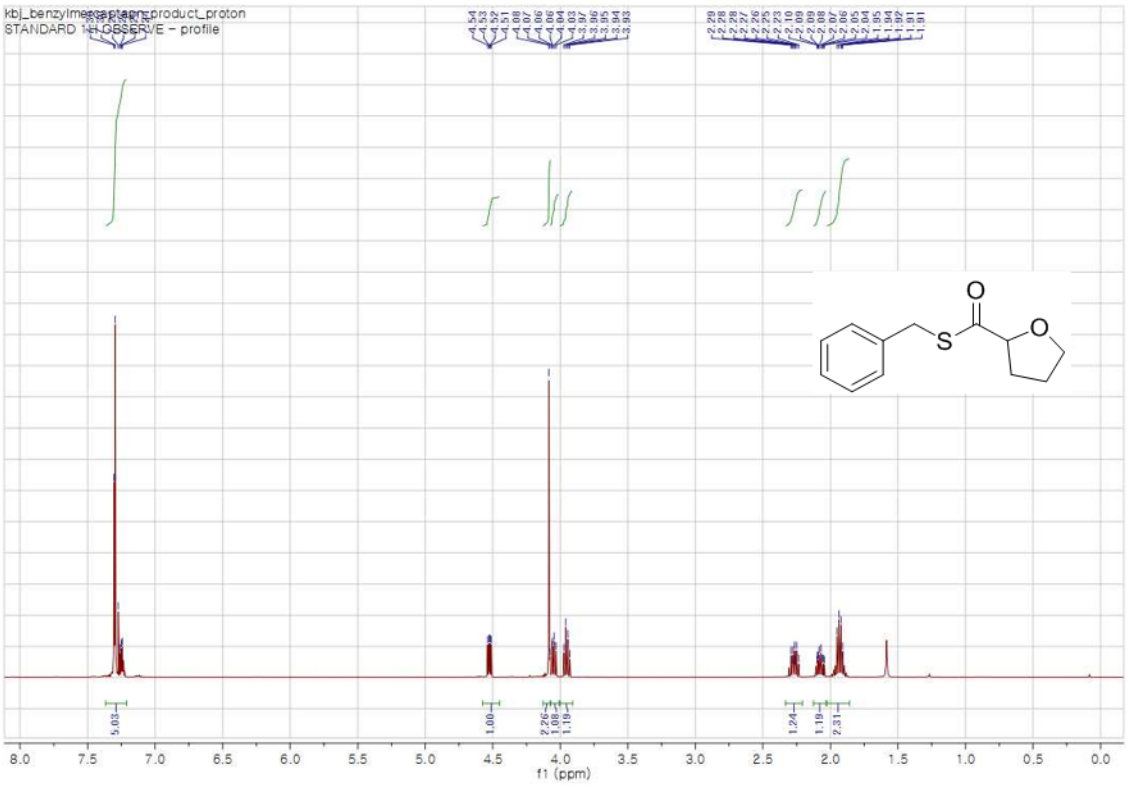
^{1}H NMR **(3ra)**



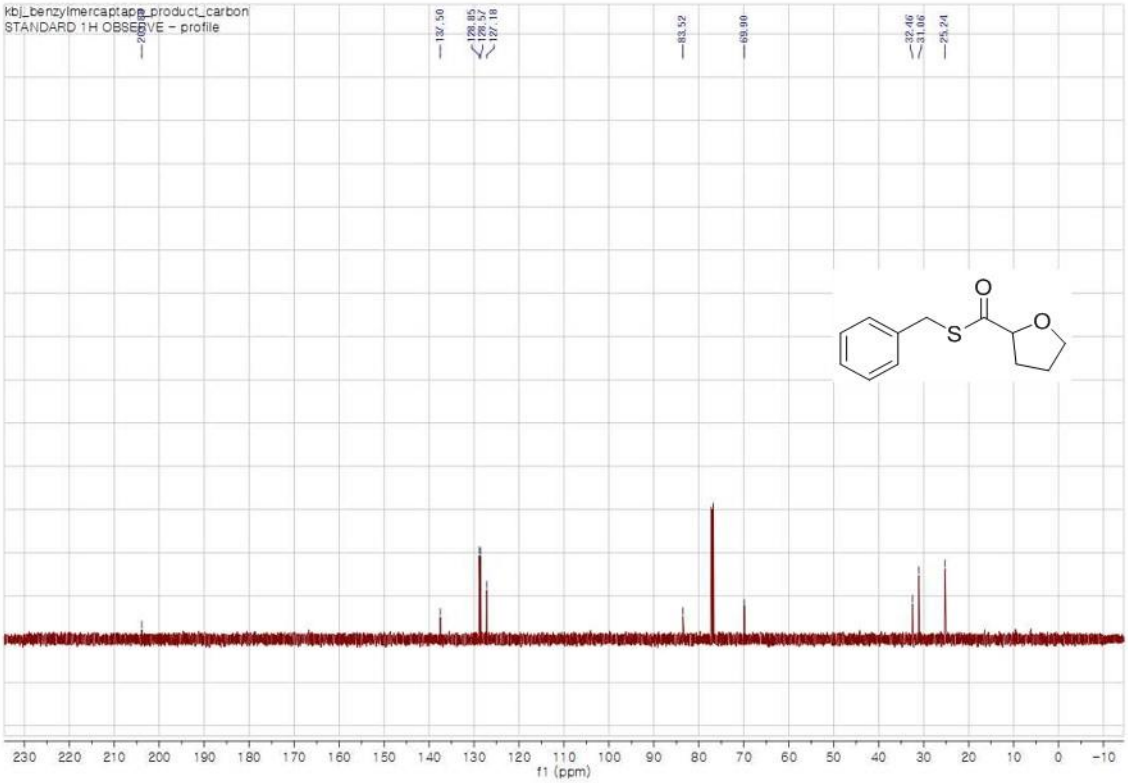
^{13}C NMR **(3ra)**



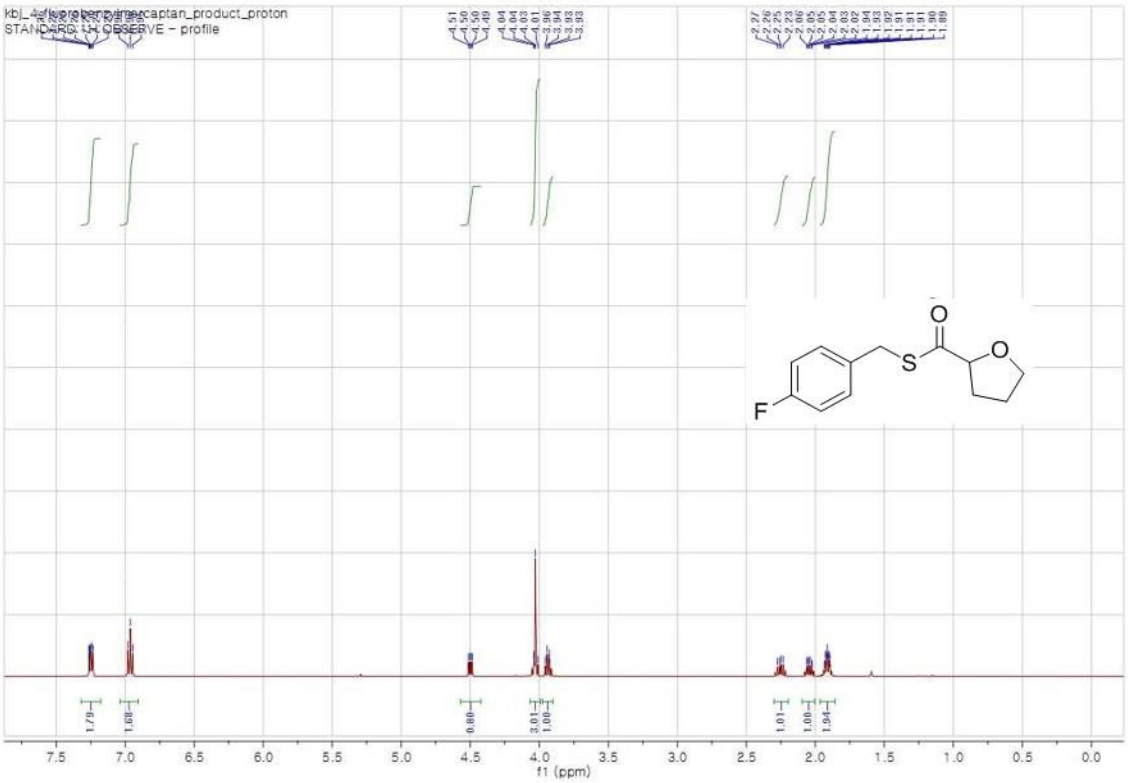
^{1}H NMR **(3sa)**



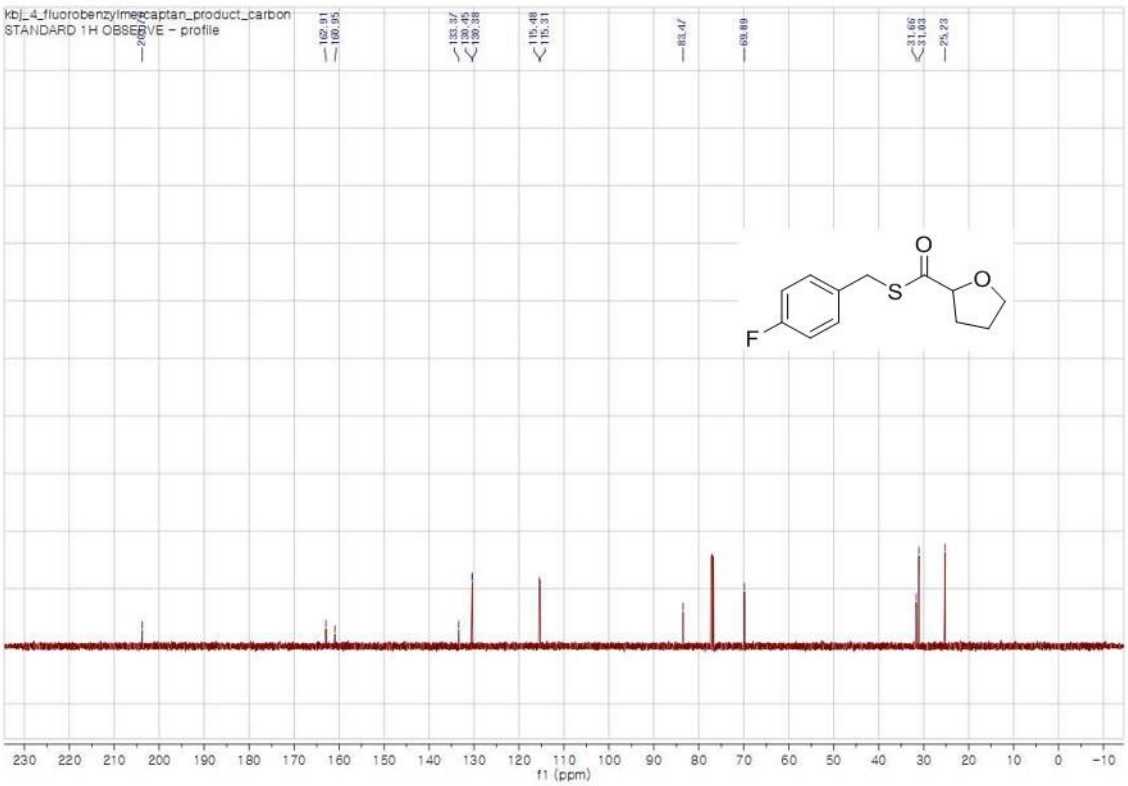
^{13}C NMR **(3sa)**



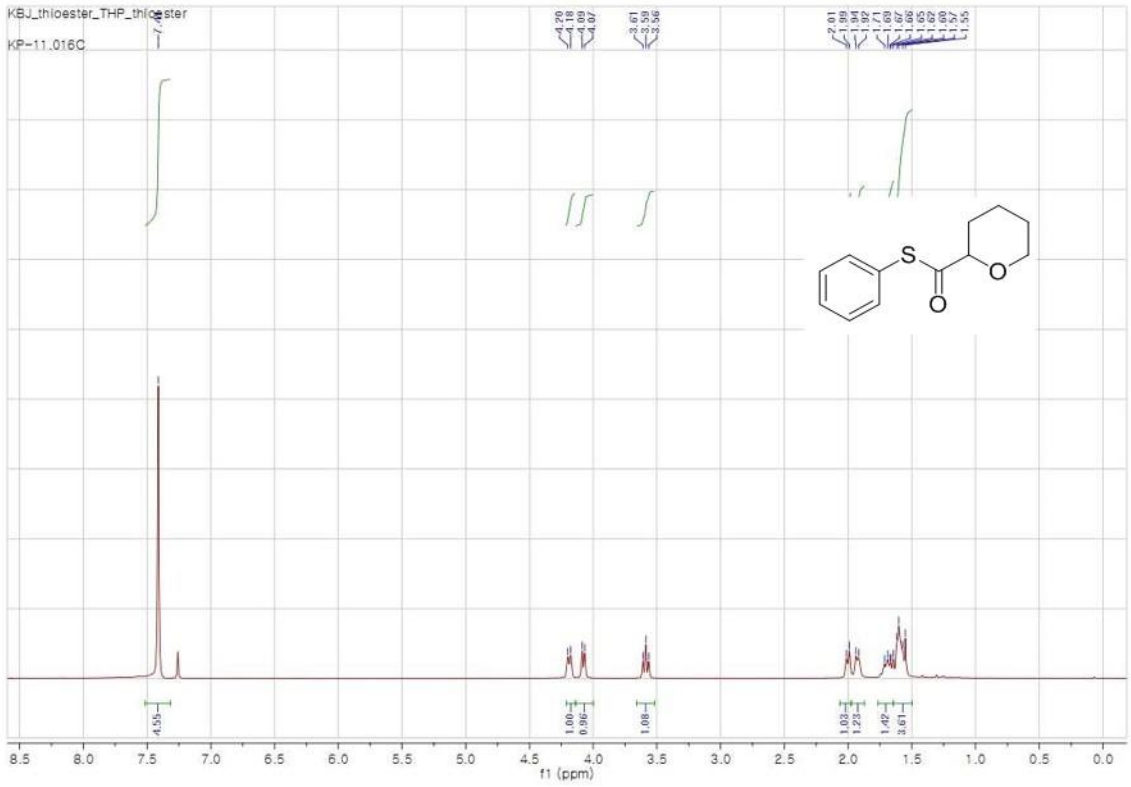
^{1}H NMR **(3ta)**



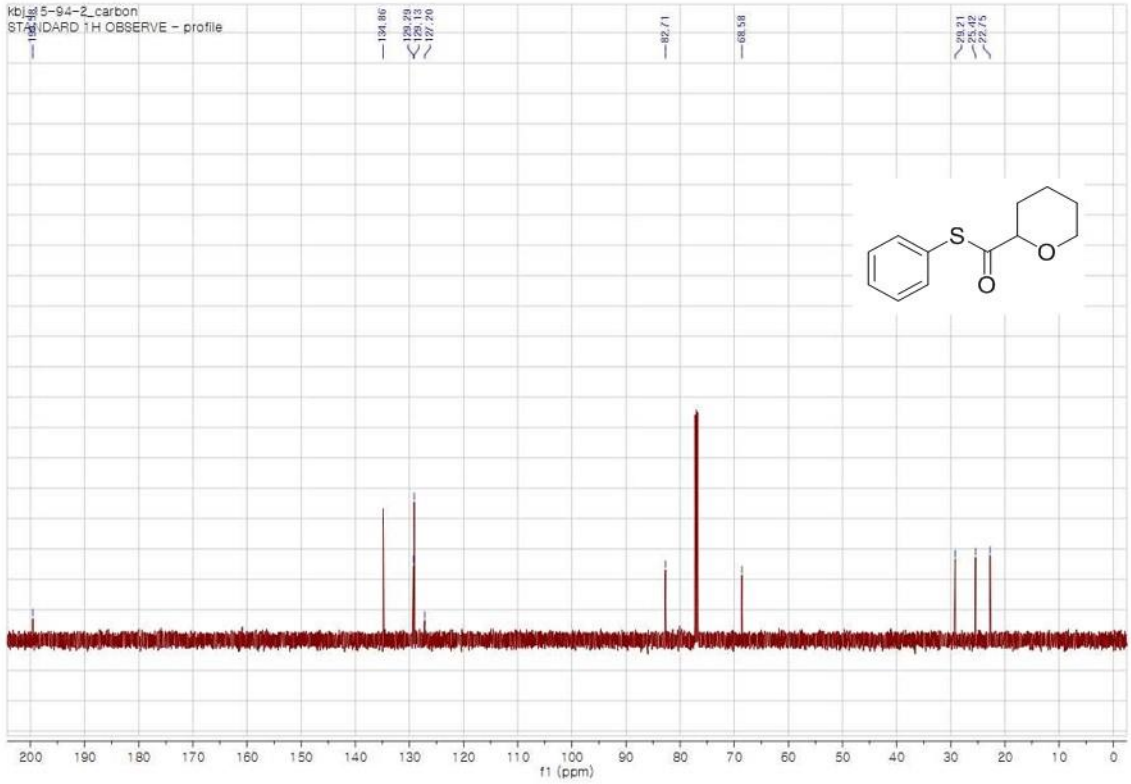
^{13}C NMR **(3ta)**



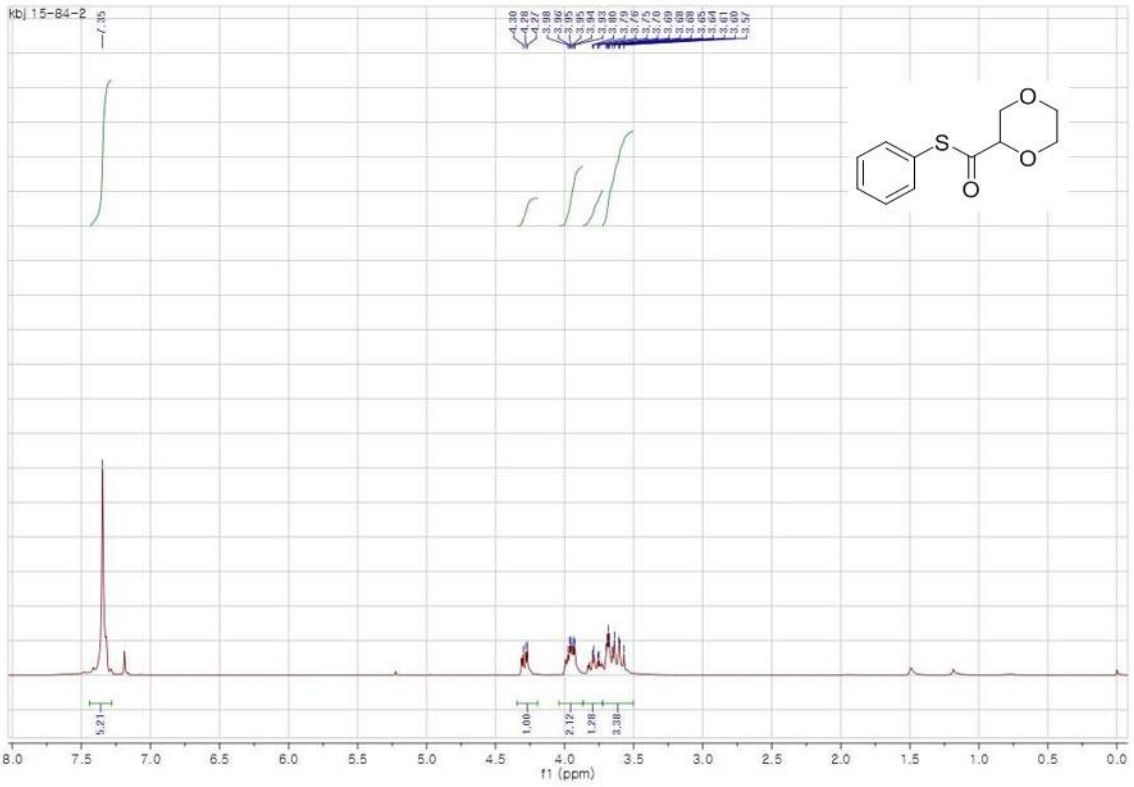
^{1}H NMR **(3ab)**



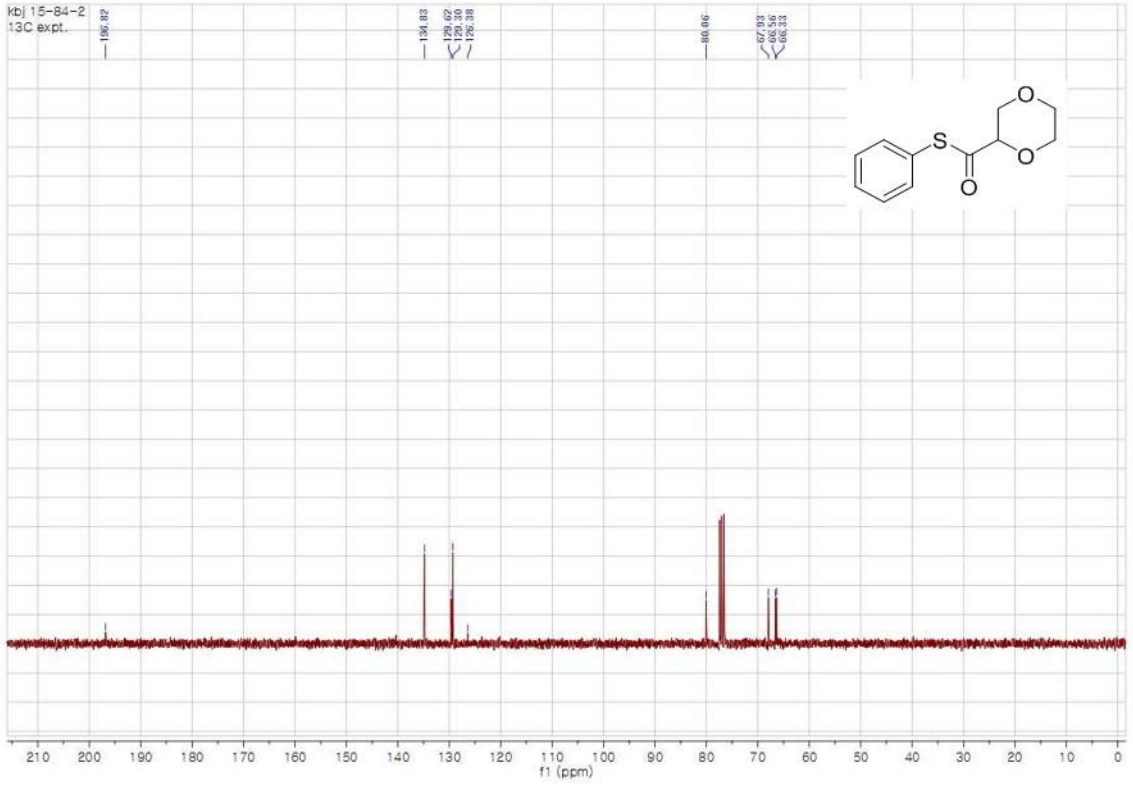
^{13}C NMR **(3ab)**



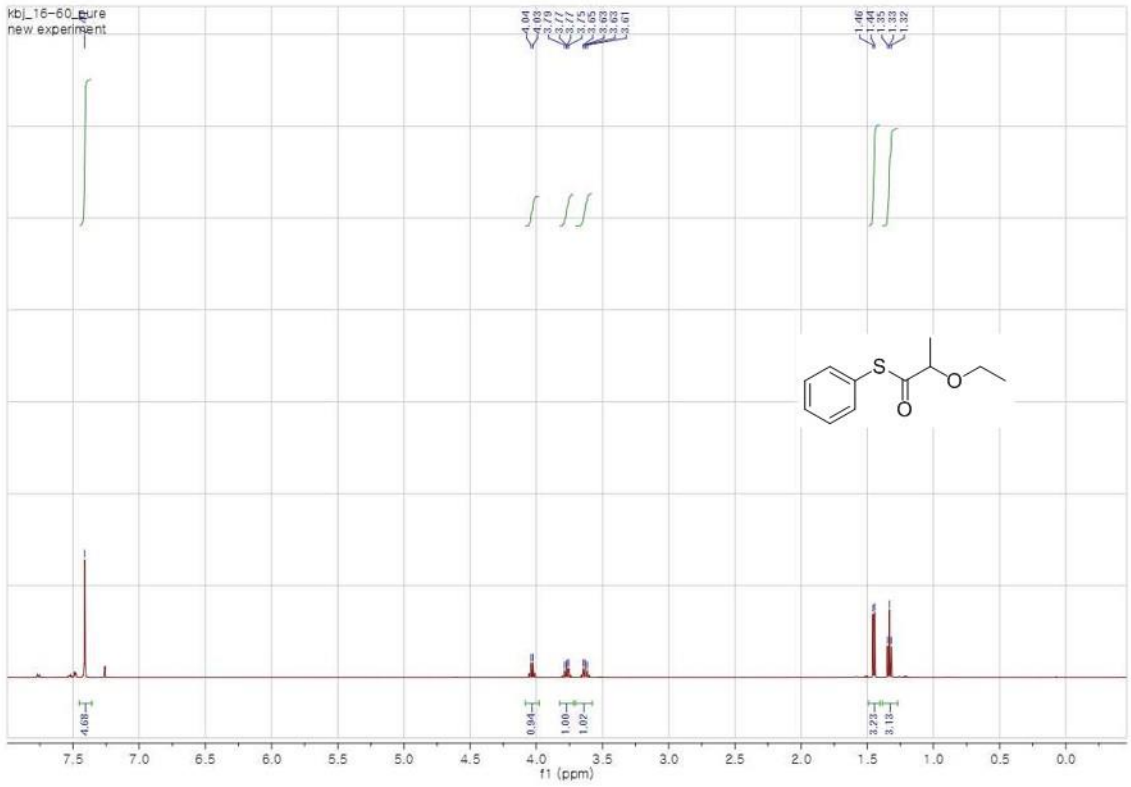
^{1}H NMR **(3ac)**



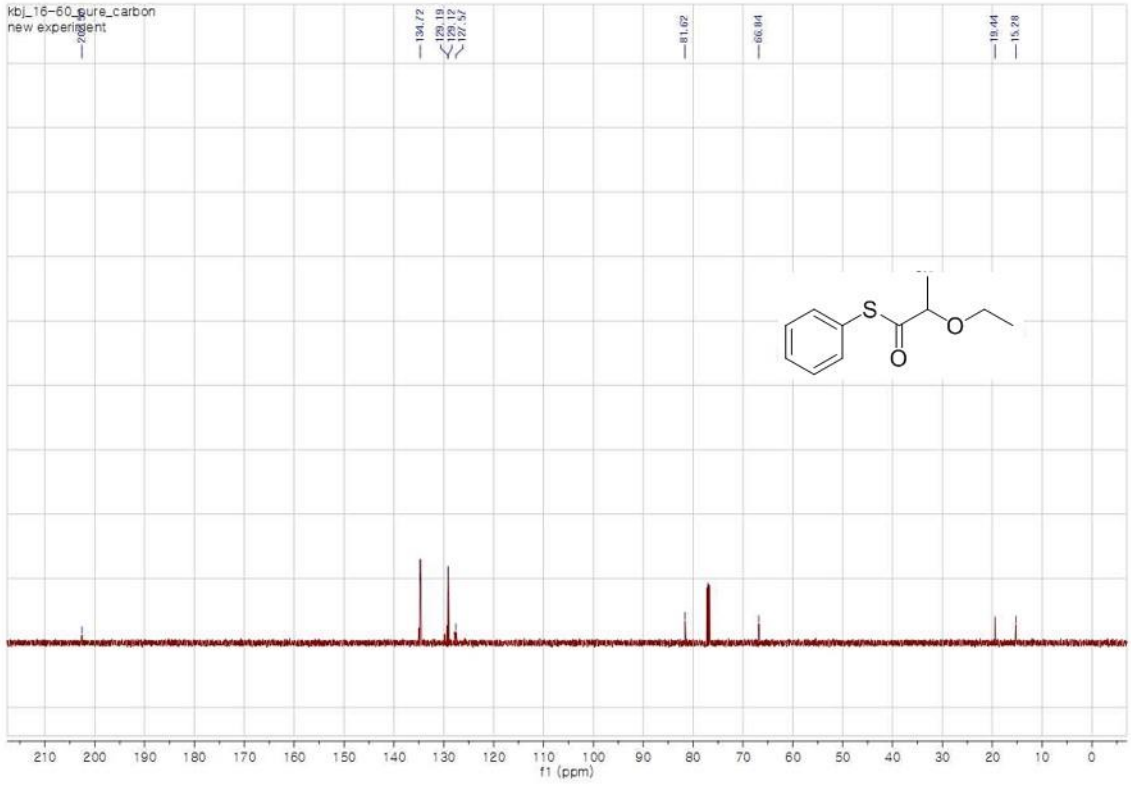
^{13}C NMR **(3ac)**



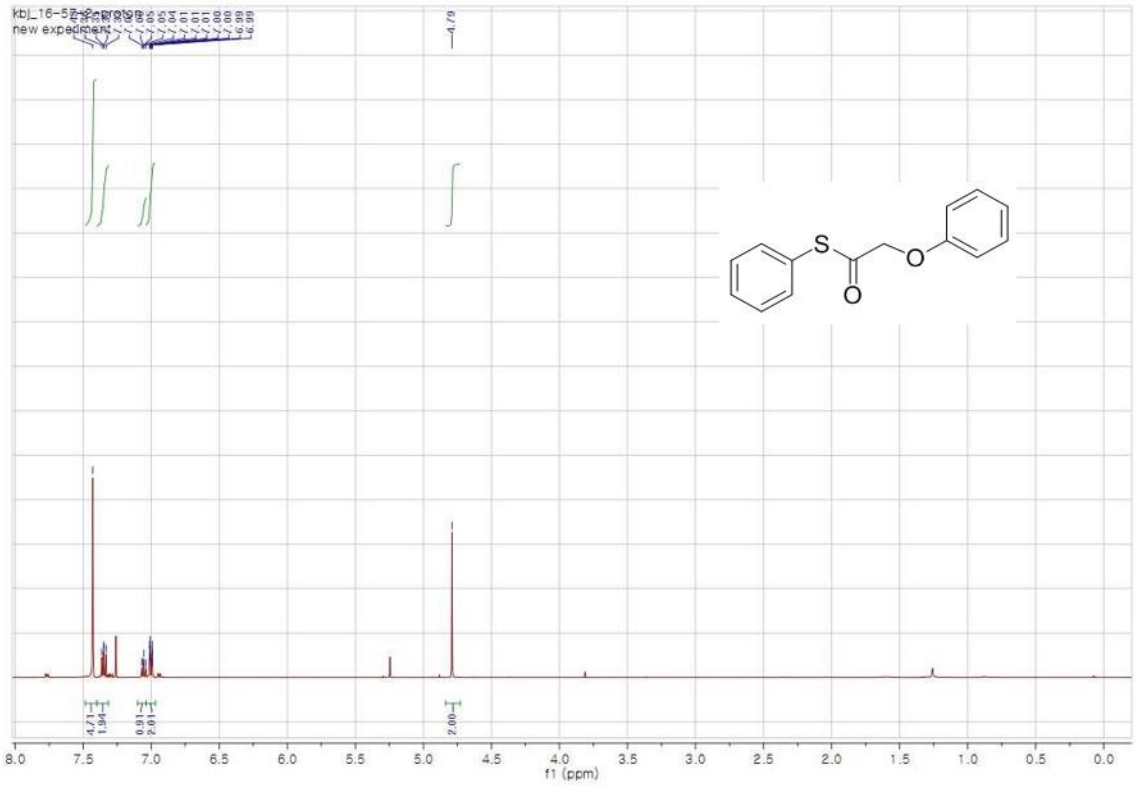
^{1}H NMR **(3ad)**



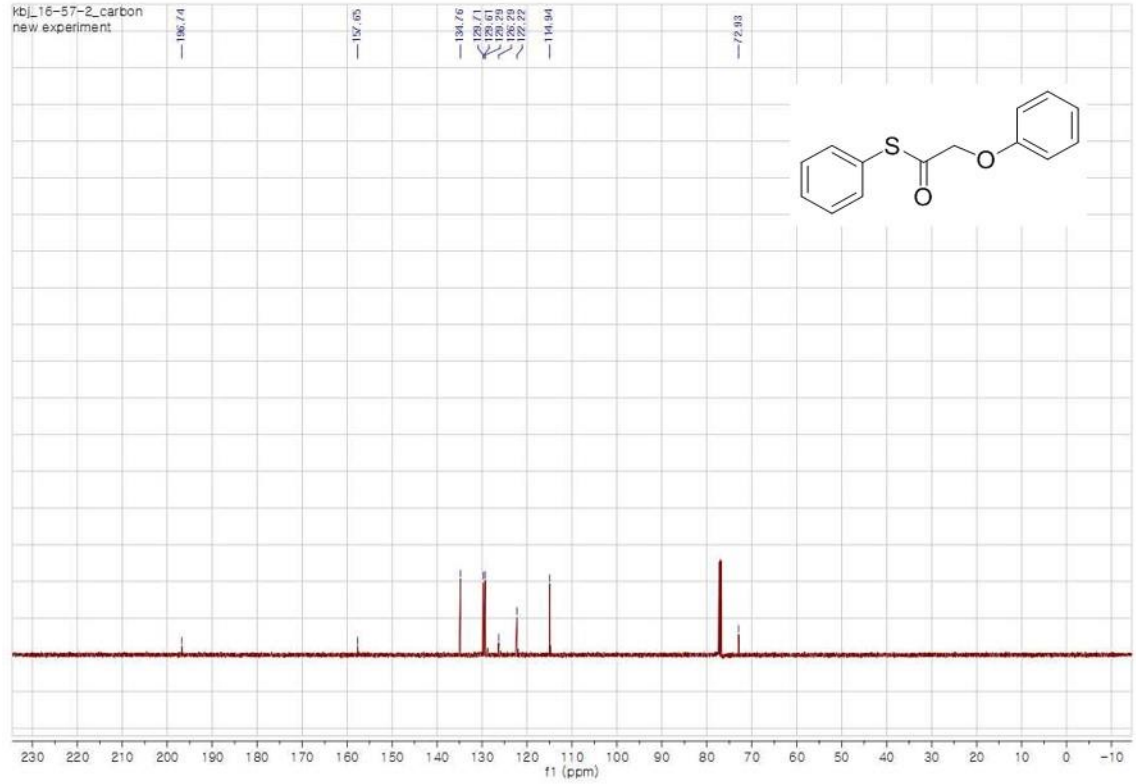
^{13}C NMR **(3ad)**



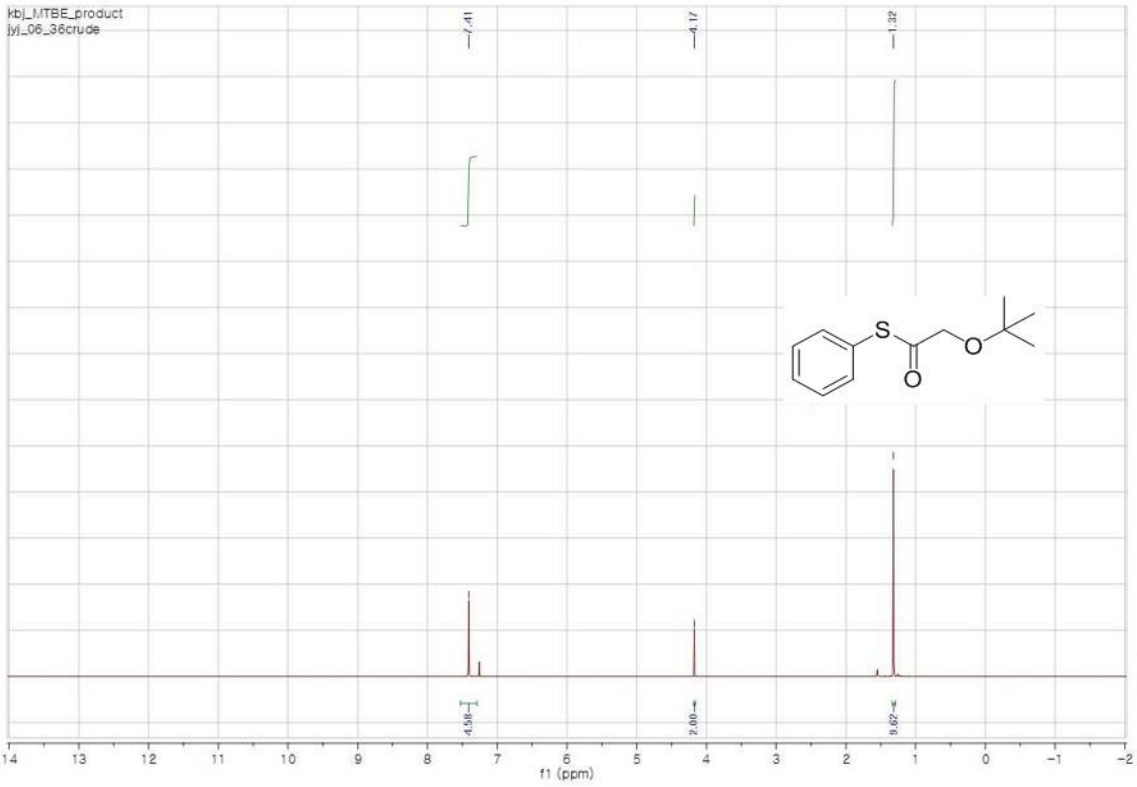
^{1}H NMR **(3ae)**



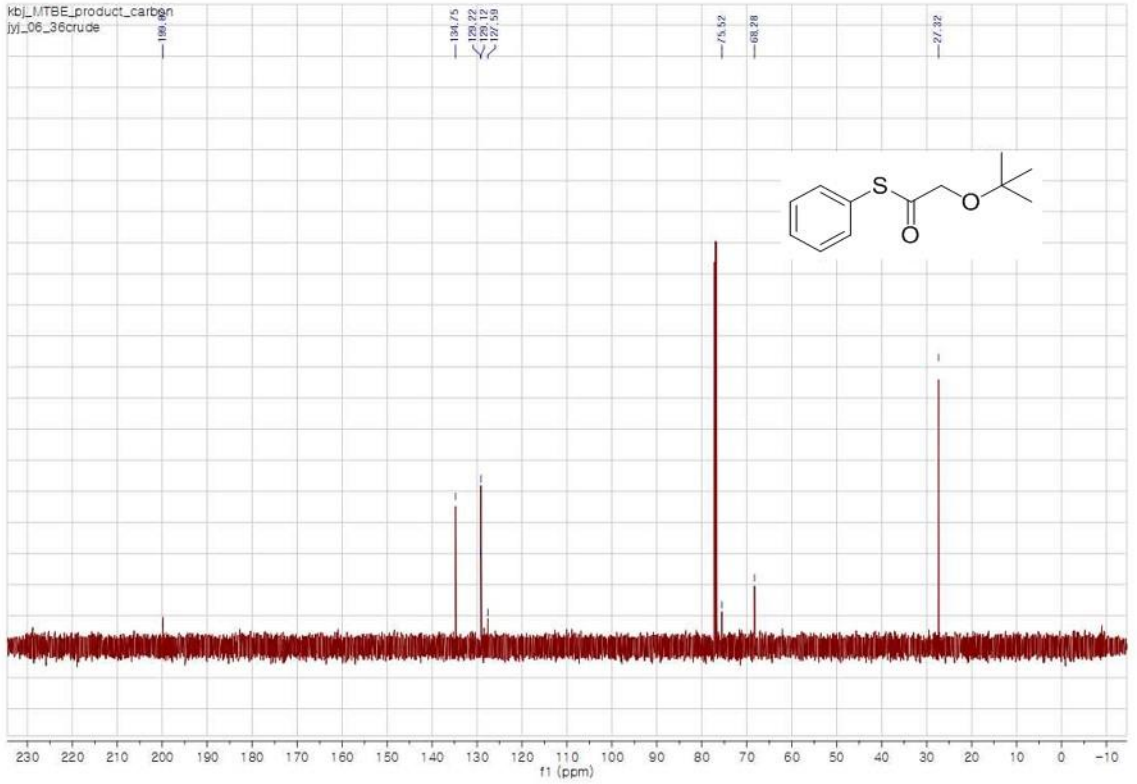
^{13}C NMR **(3ae)**



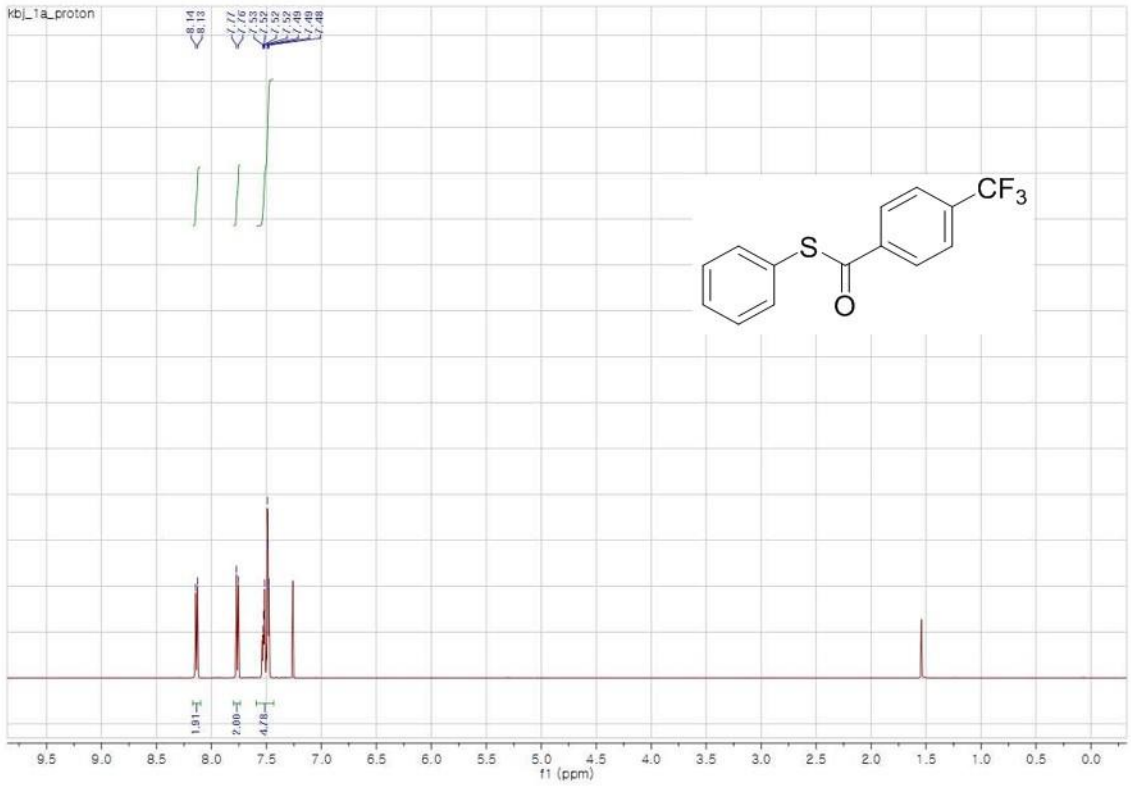
^{1}H NMR **(3af)**



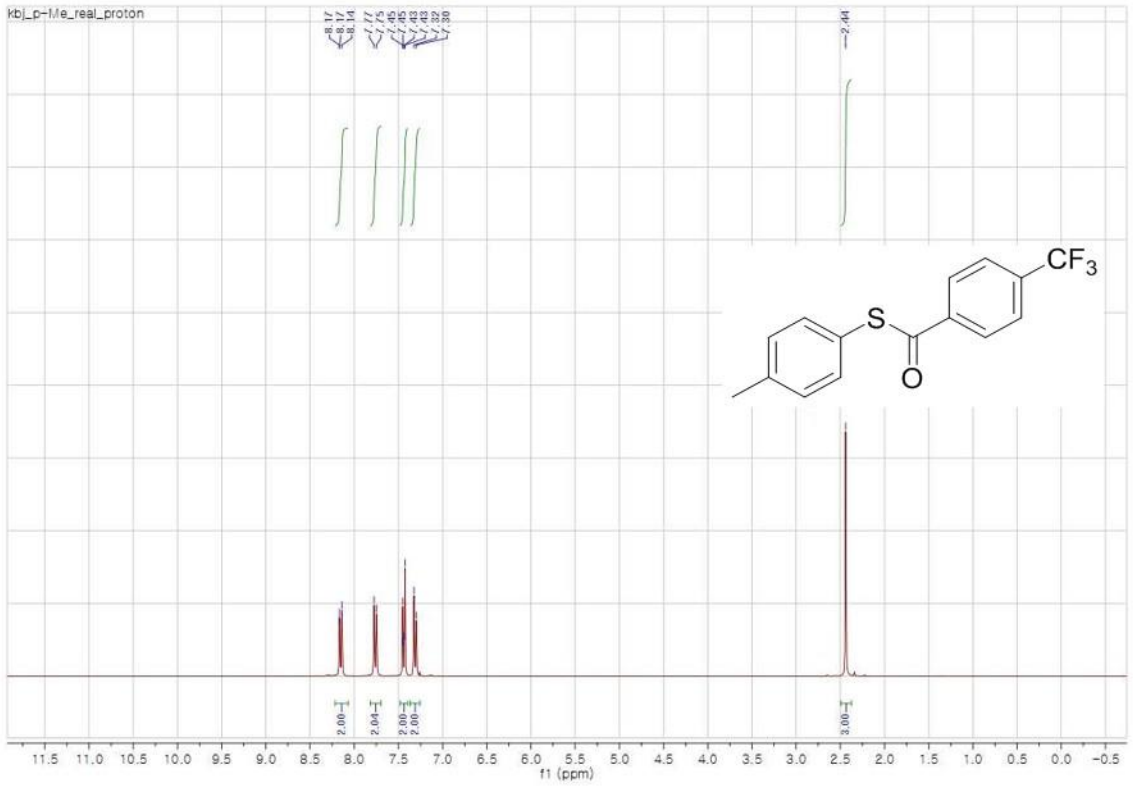
^{13}C NMR **(3af)**



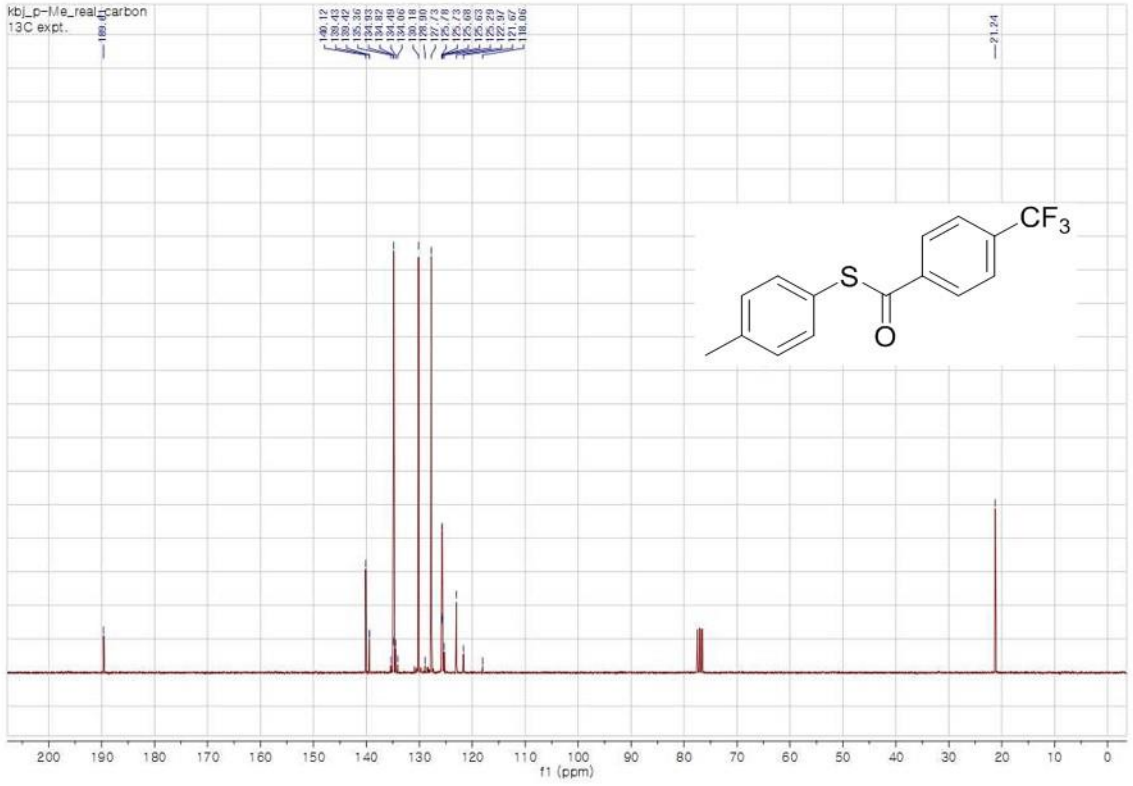
^{1}H NMR (**1a)**


kbj_1a_proton
8.14
8.13
7.77
7.76
7.53
7.52
7.52
7.49
7.49
7.48
CF3
S
O
1.91
2.00
4.78
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

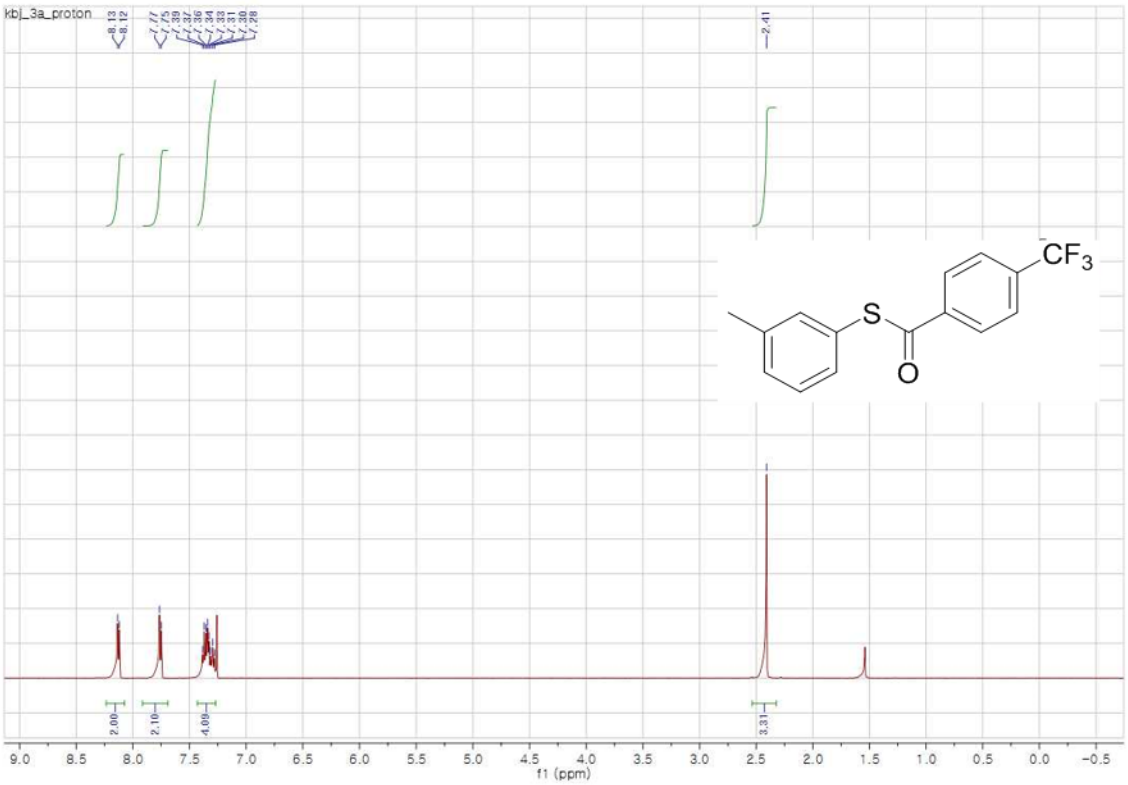
^{1}H NMR (**1b)**



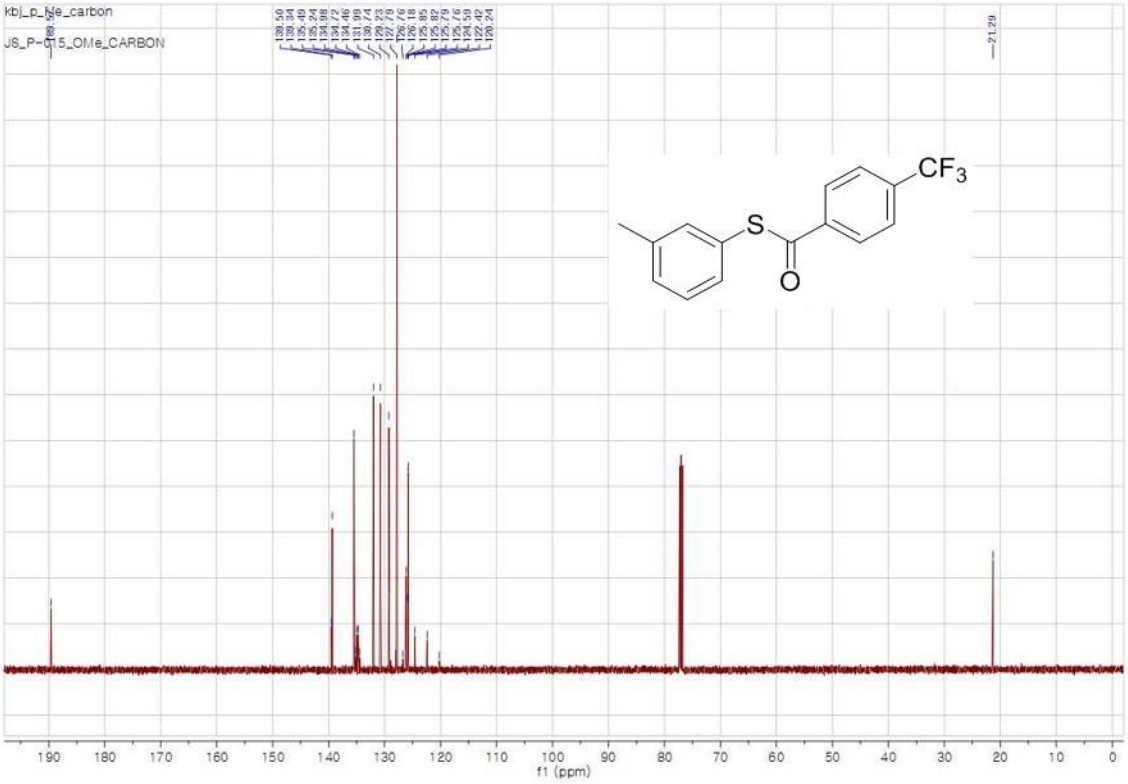
^{13}C NMR **(1b)**



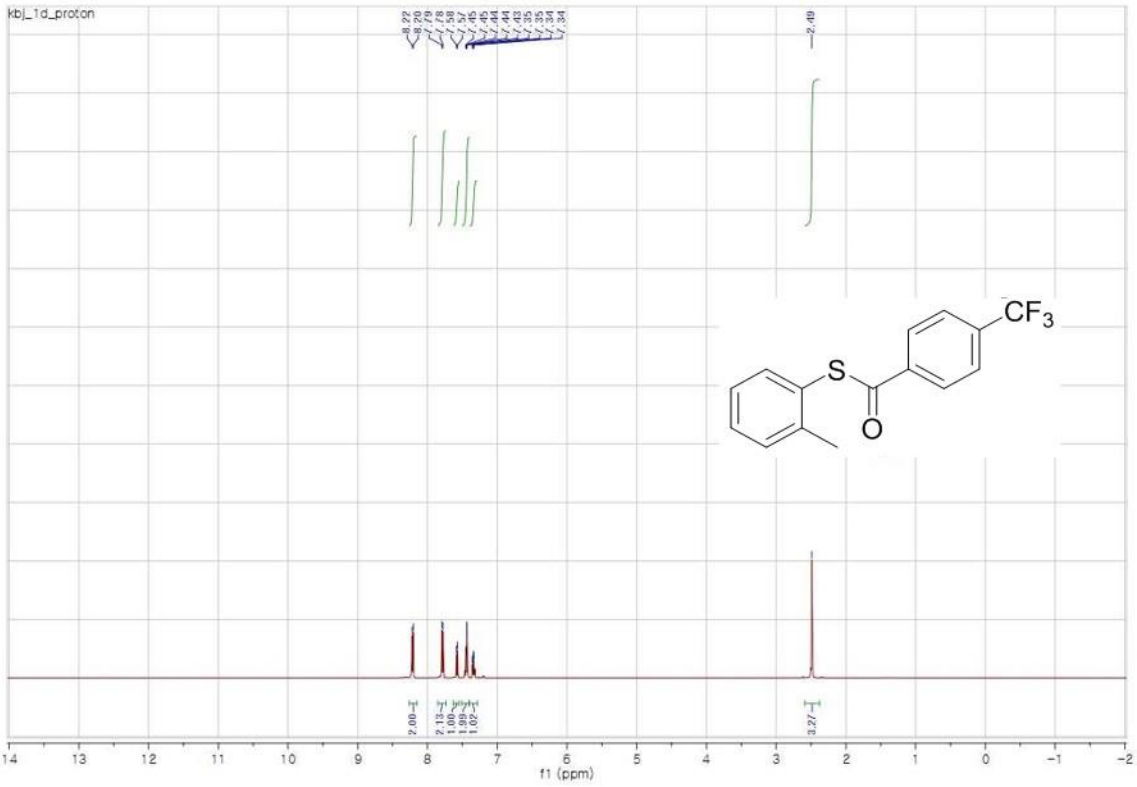
^{1}H NMR (**1c)**



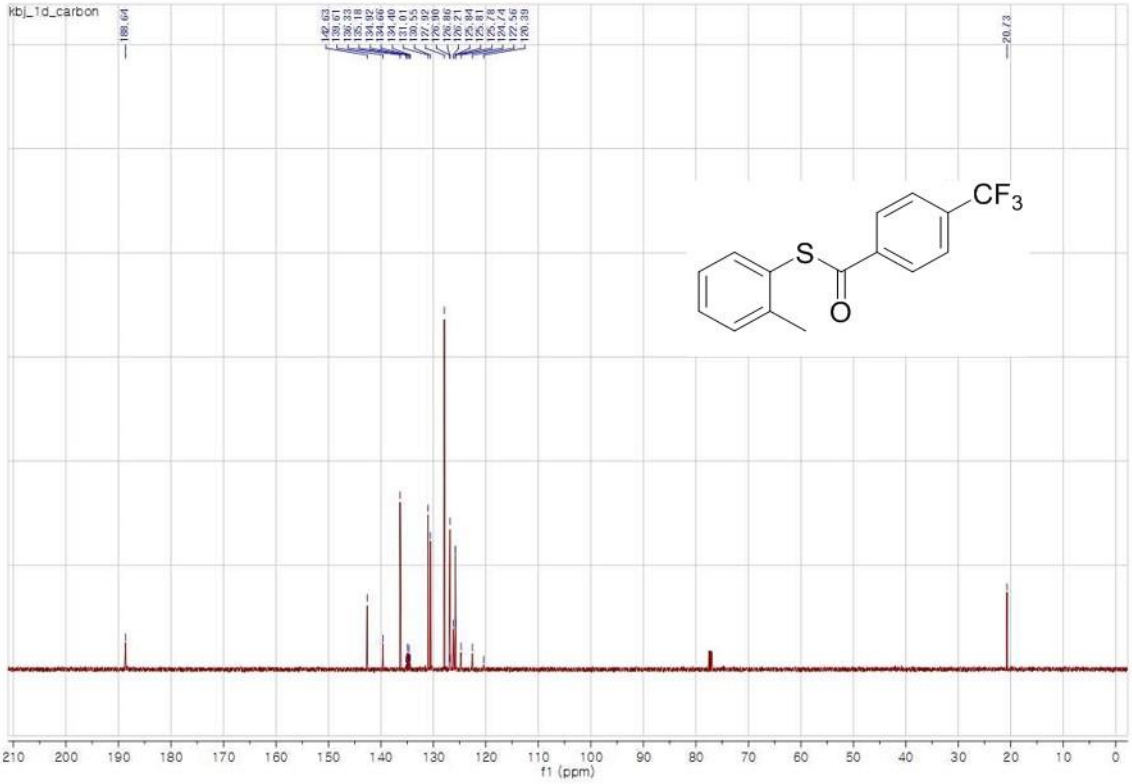
^{13}C NMR **(1c)**



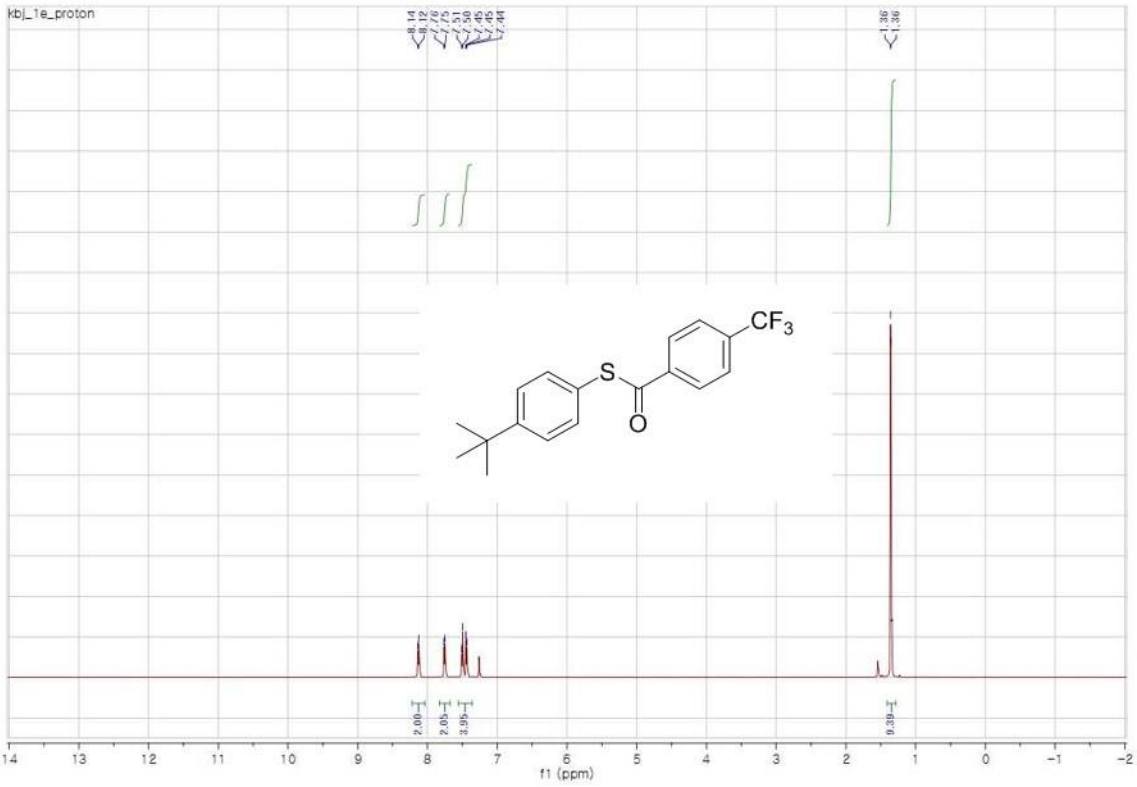
^{1}H NMR (**1d)**



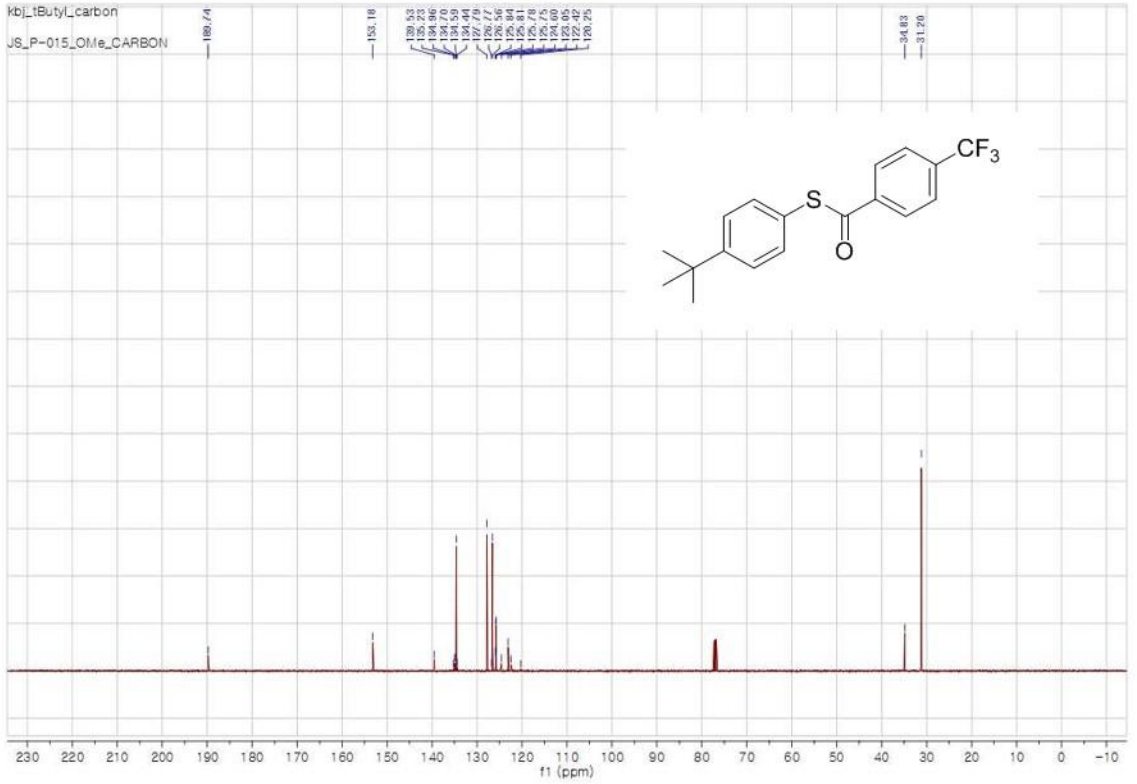
^{13}C NMR **(1d)**



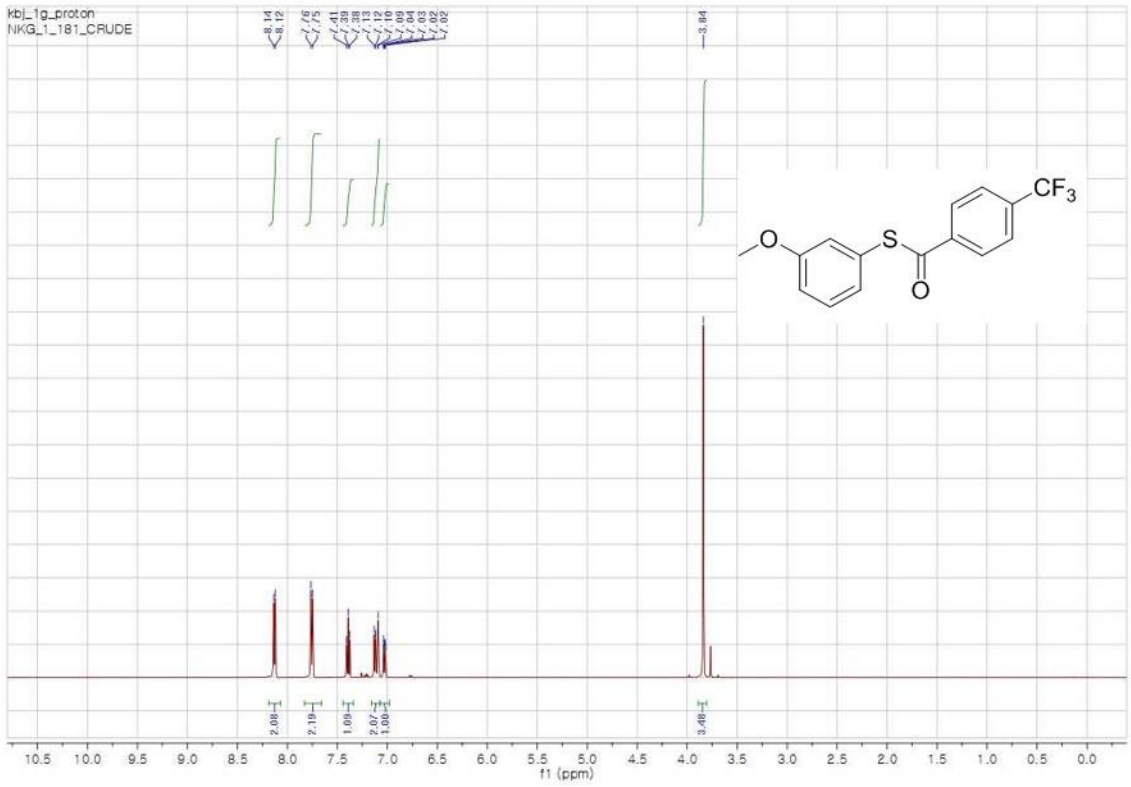
^{1}H NMR (**1e)**



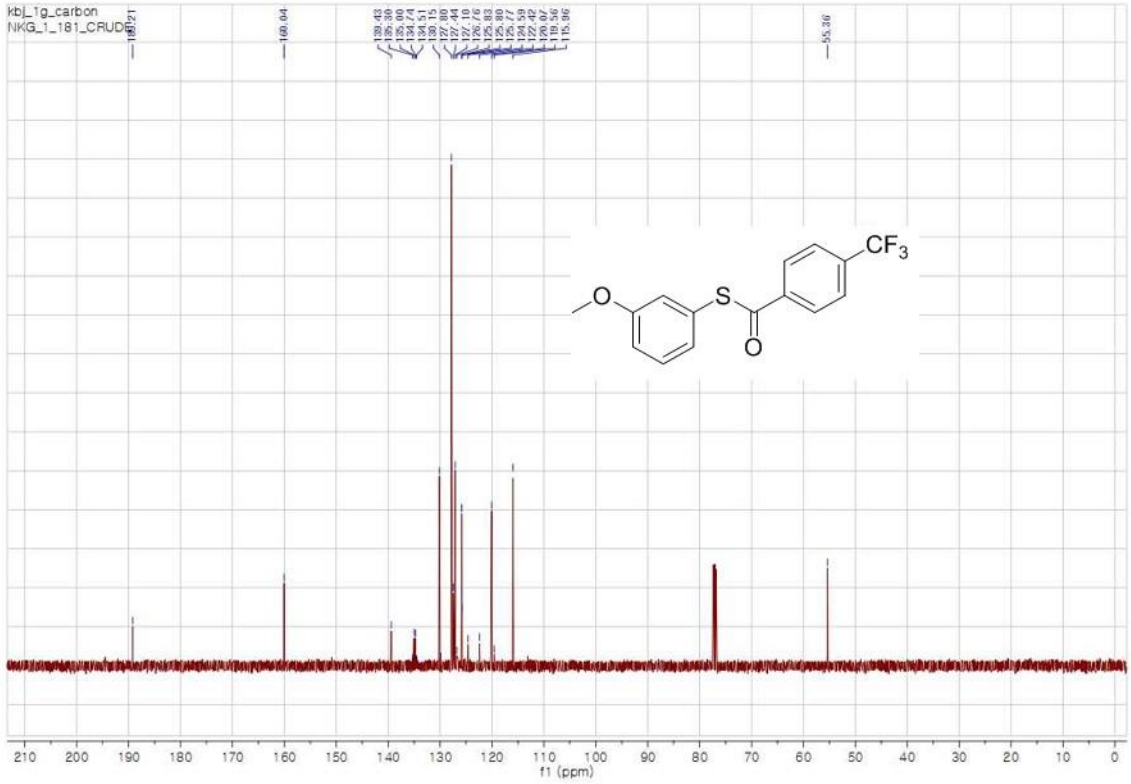
^{13}C NMR **(1e)**



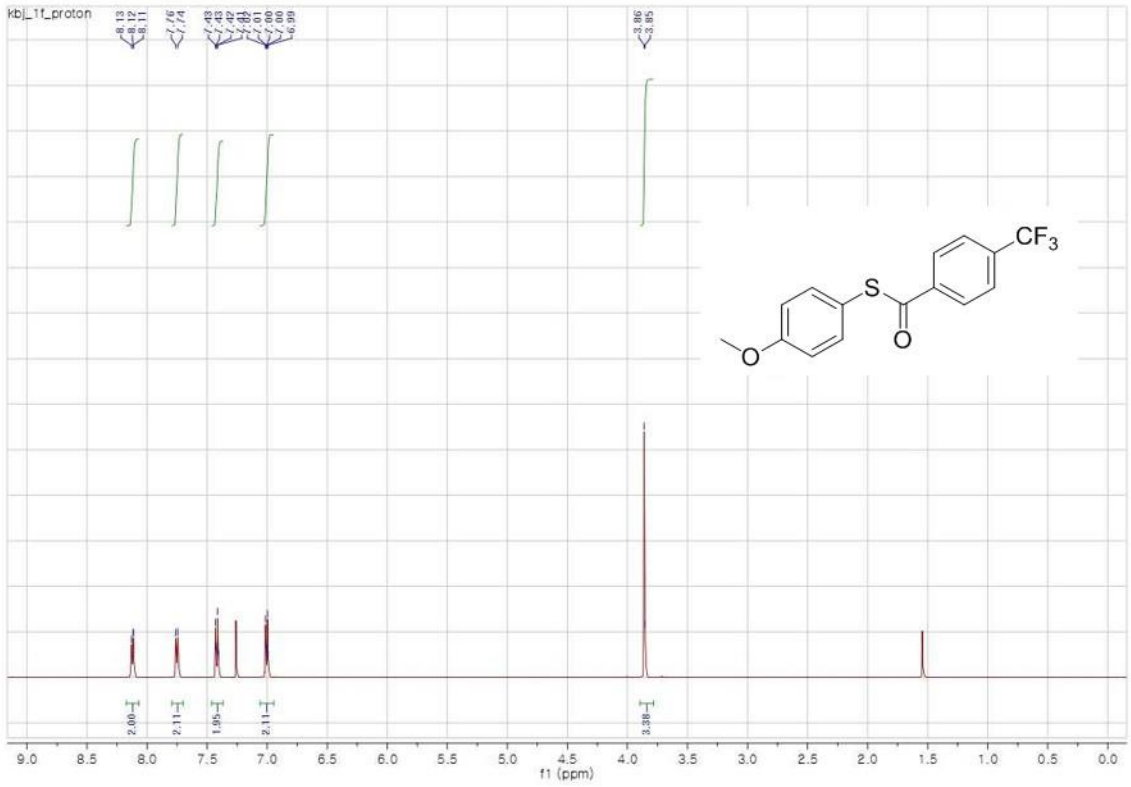
^{1}H NMR (**1f)**



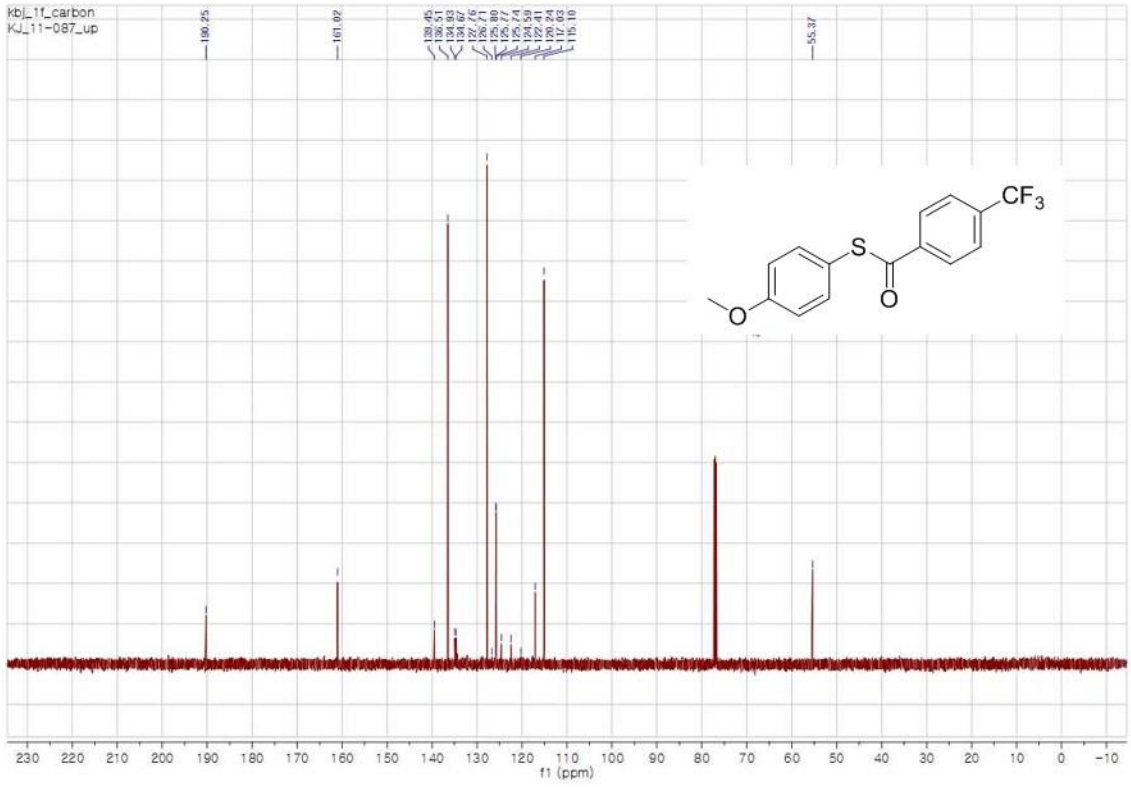
^{13}C NMR **(1f)**



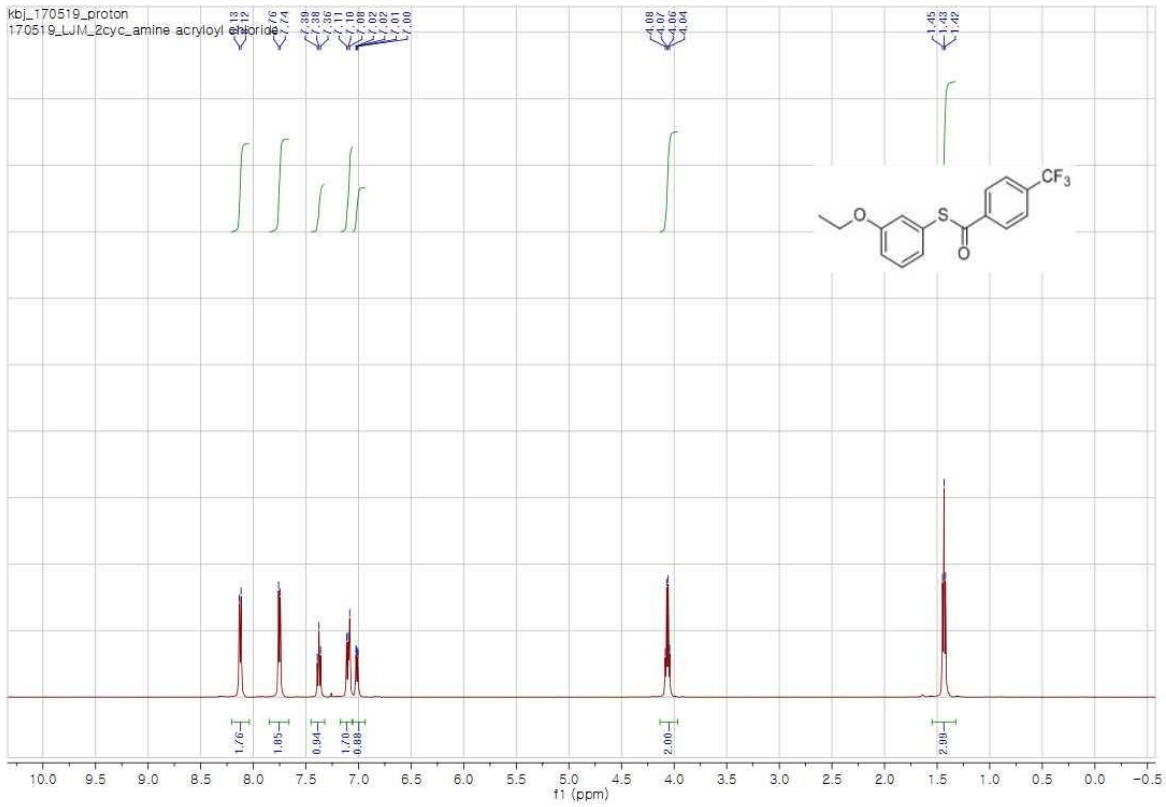
^{1}H NMR (**1g)**



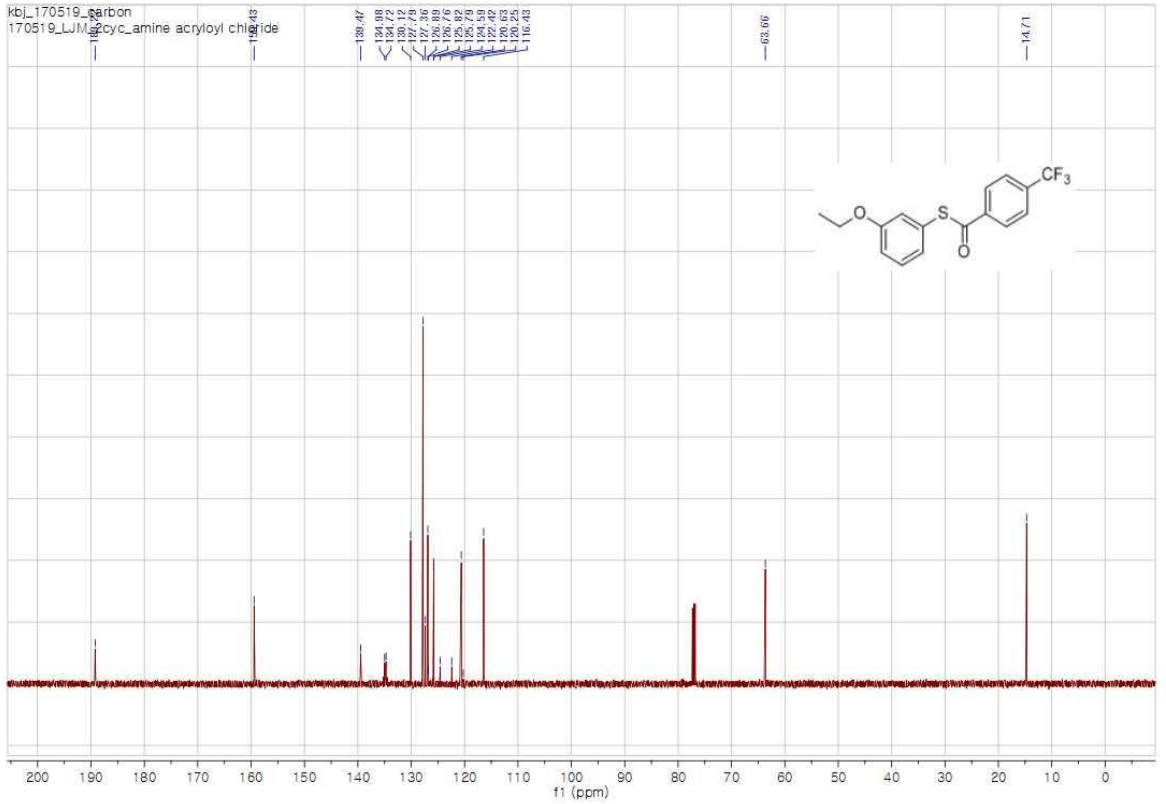
^{13}C NMR **(1g)**



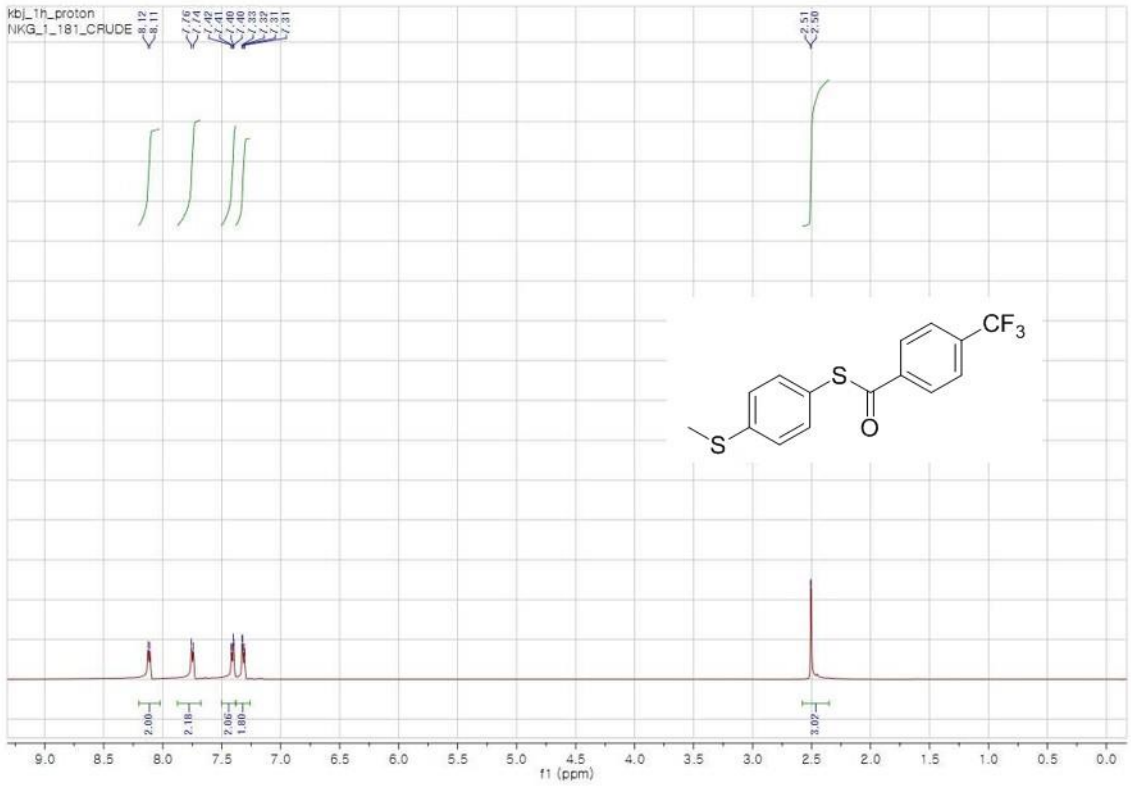
^{1}H NMR (**1h)**



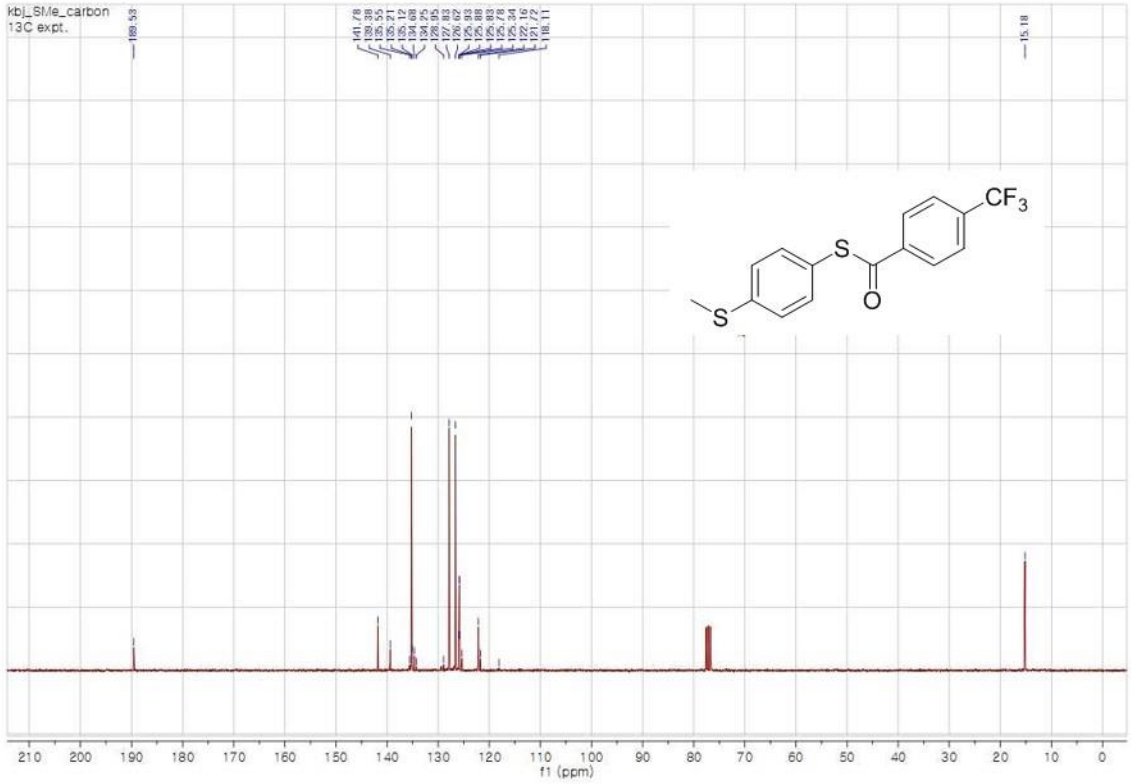
^{13}C NMR **(1h)**



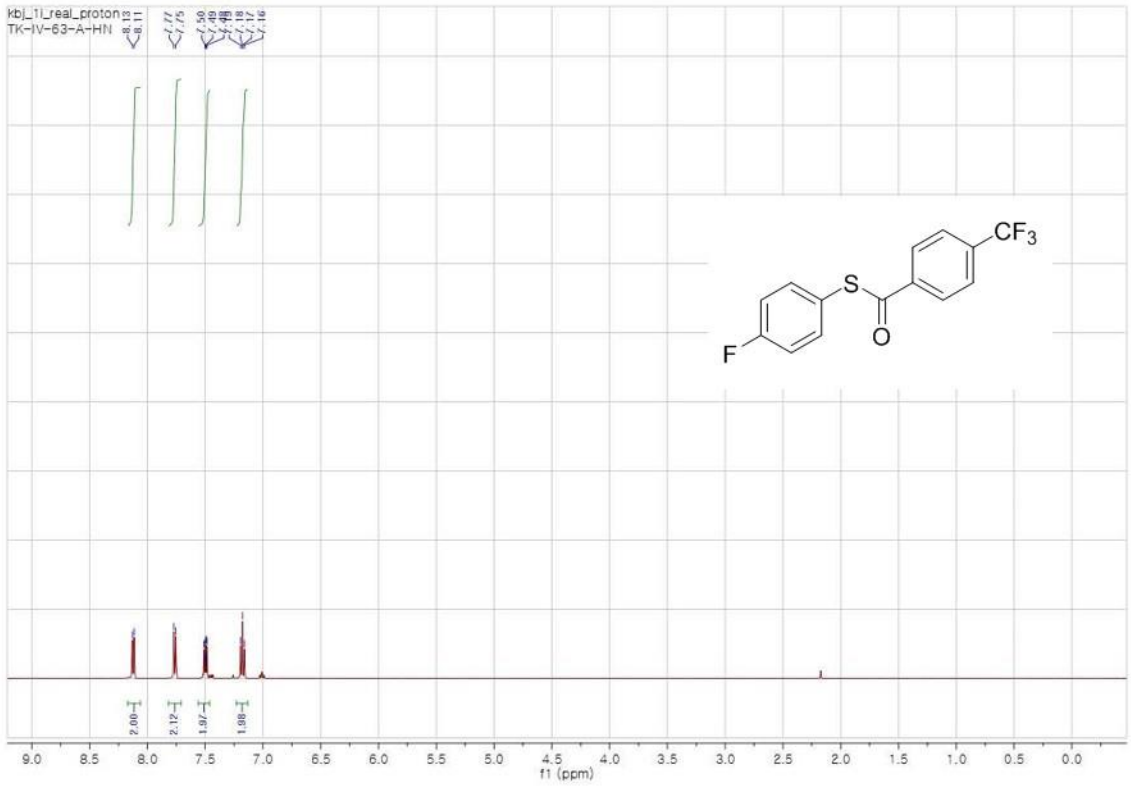
^{1}H NMR (**1i)**



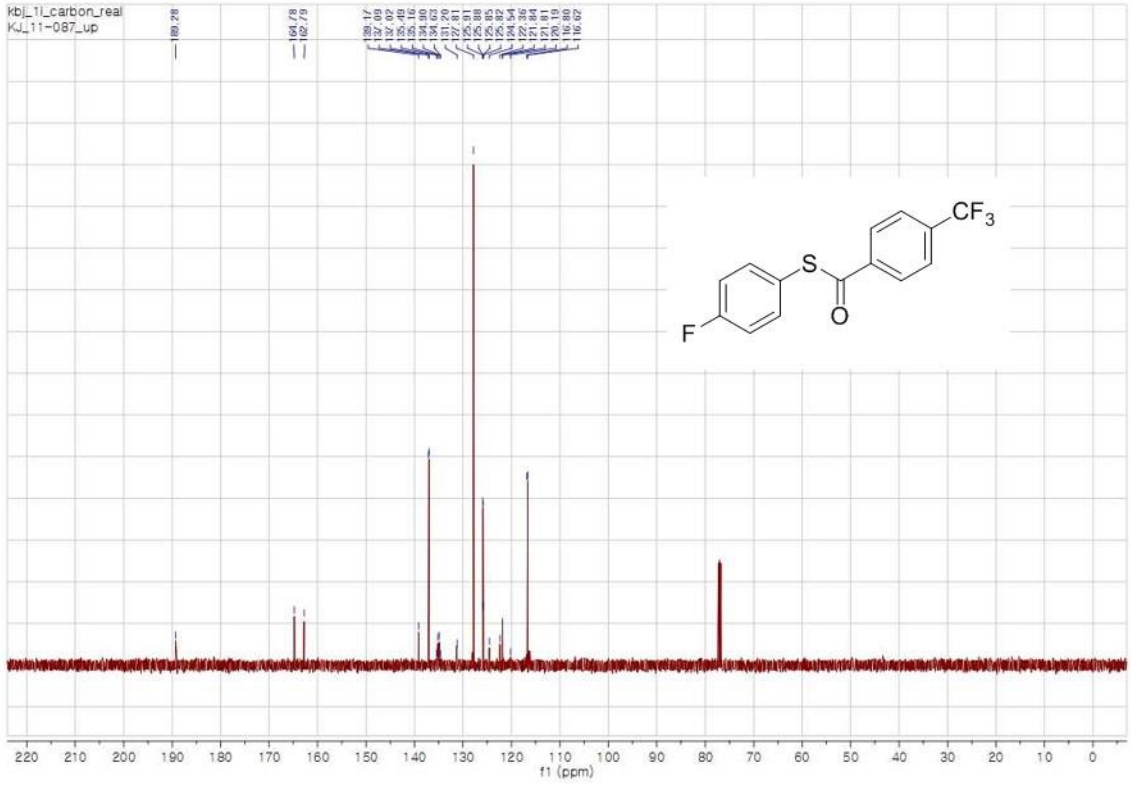
^{13}C NMR **(1i)**



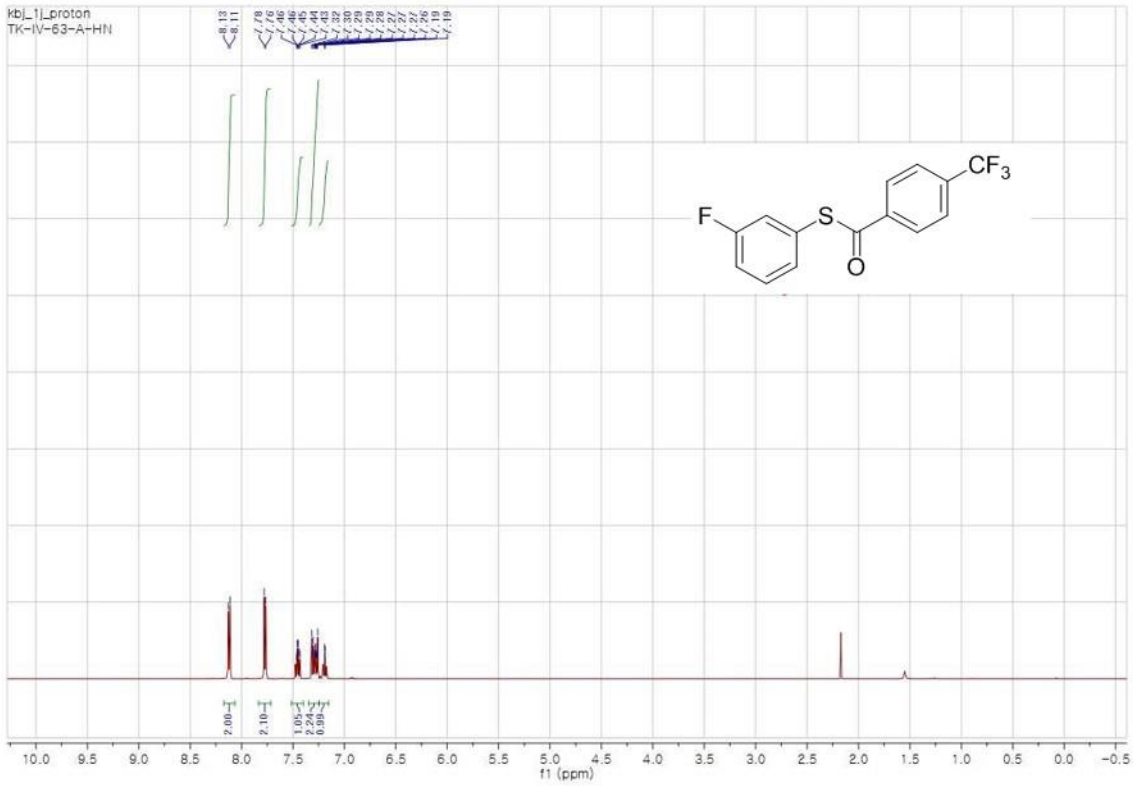
^{1}H NMR **(1j)**



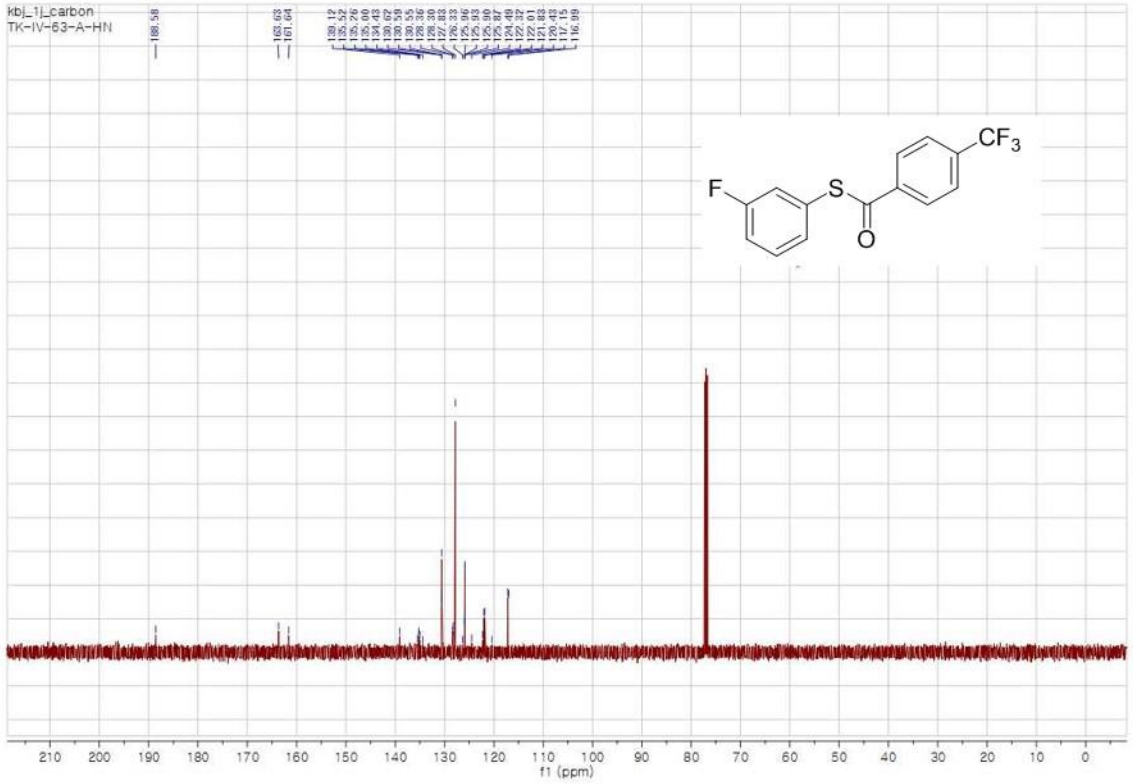
^{13}C NMR **(1j)**



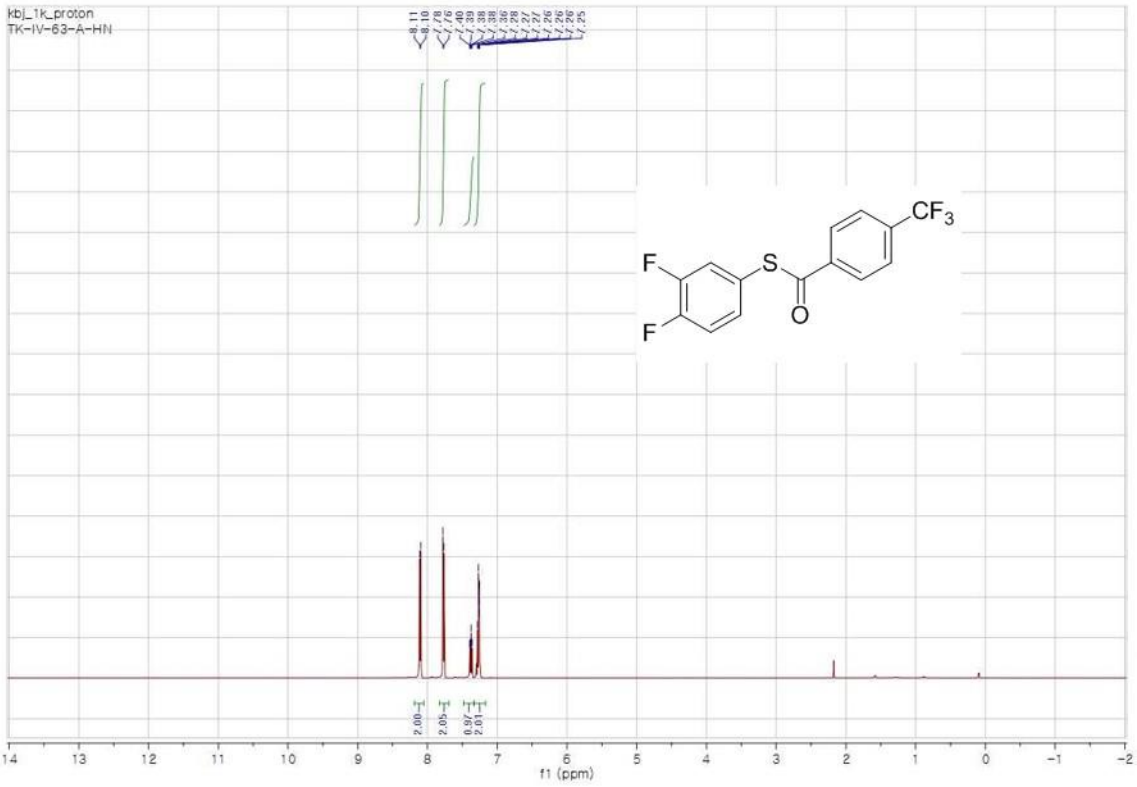
^{1}H NMR (**1k)**



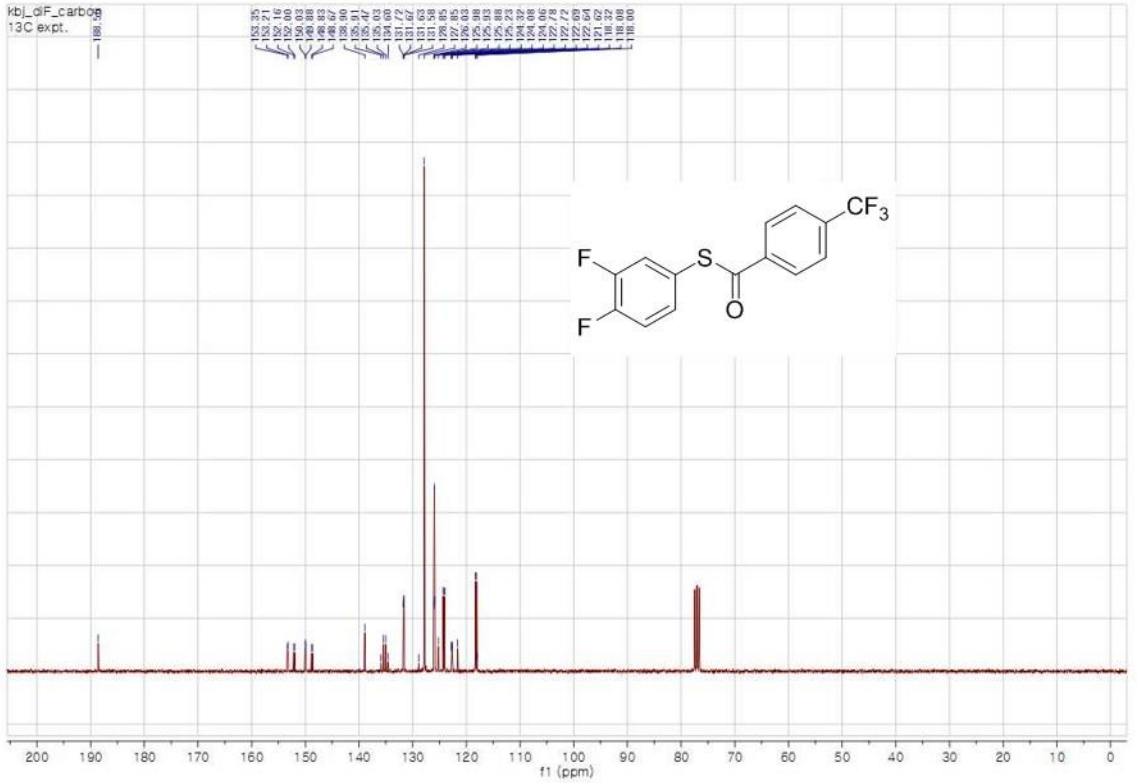
^{13}C NMR **(1k)**



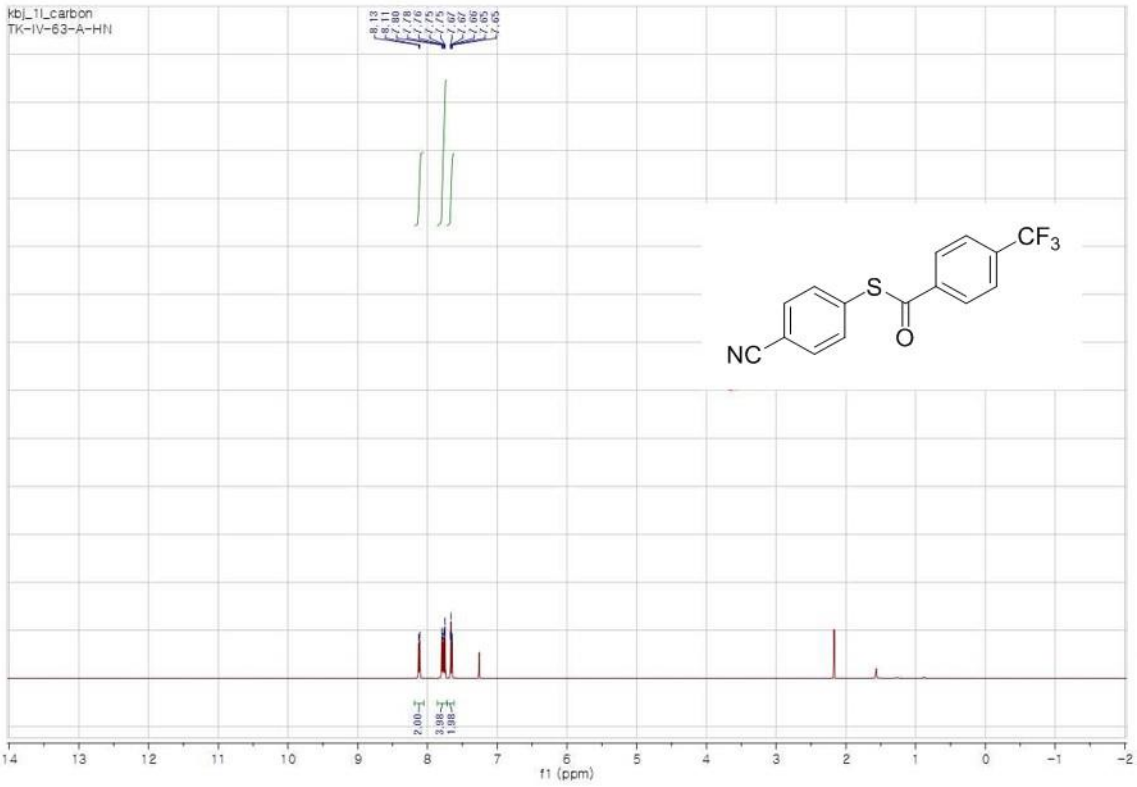
^{1}H NMR (**1l**)



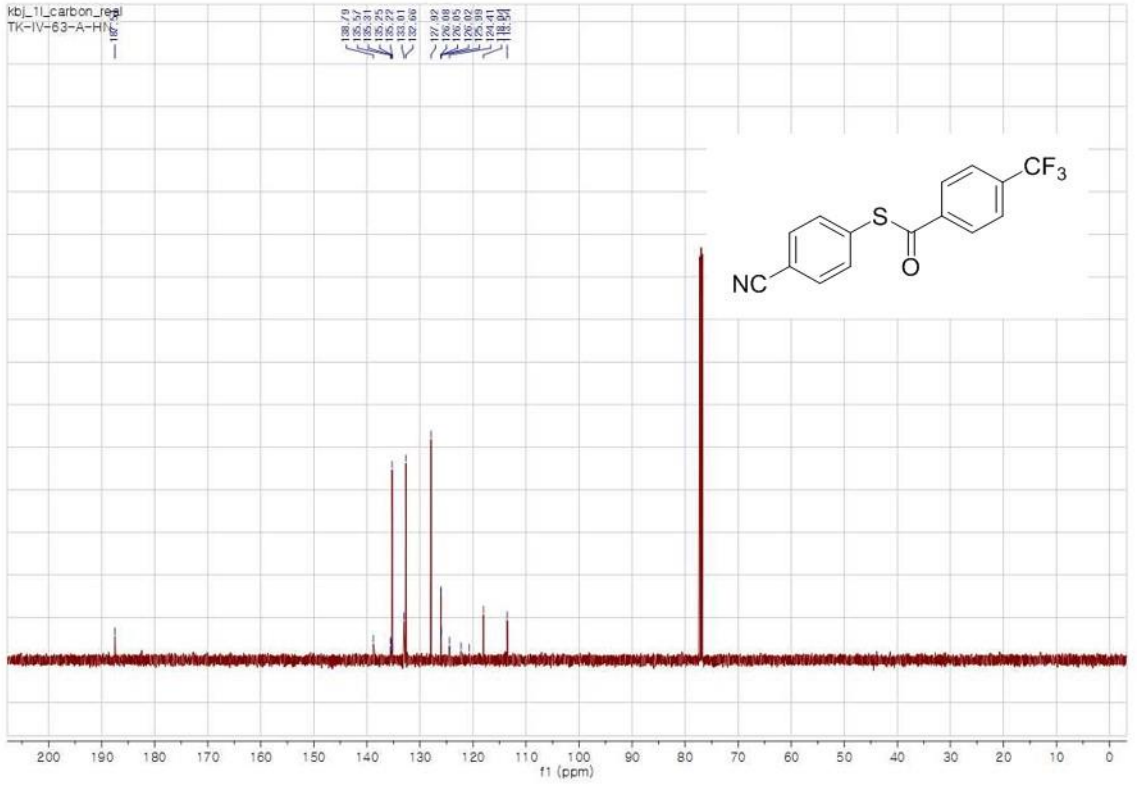
^{13}C NMR **(1l)**



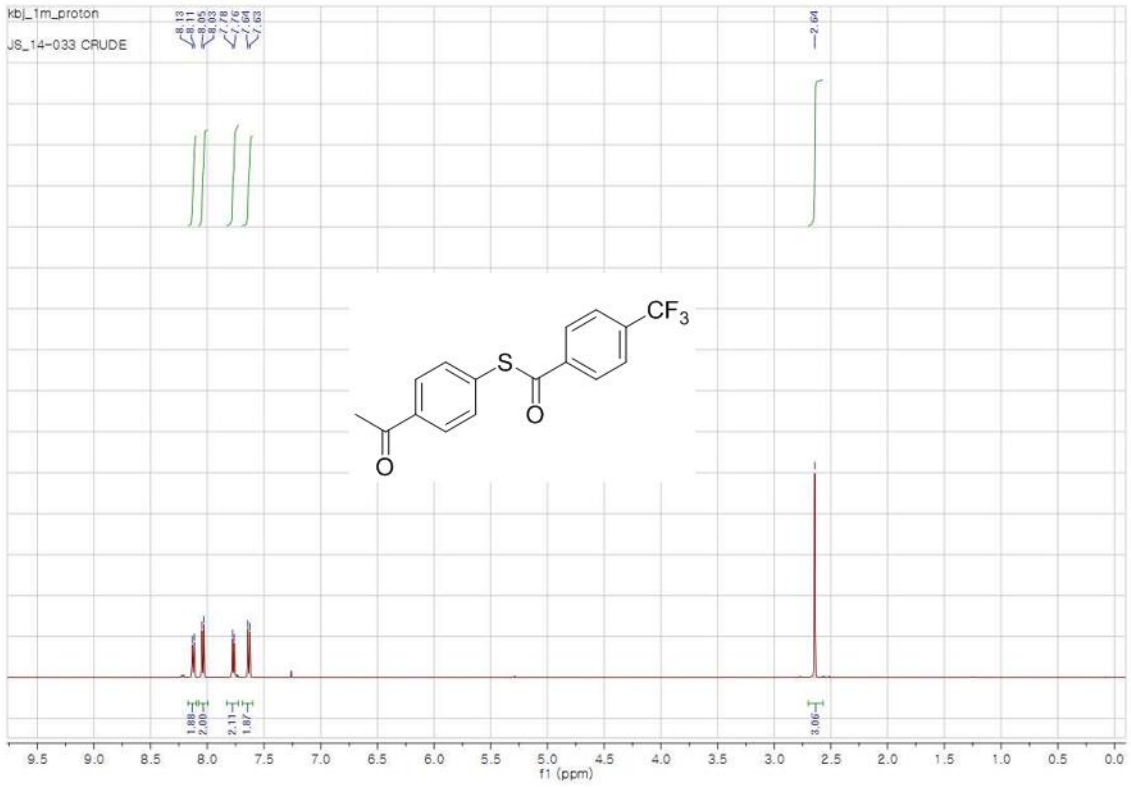
^{1}H NMR (**1m)**



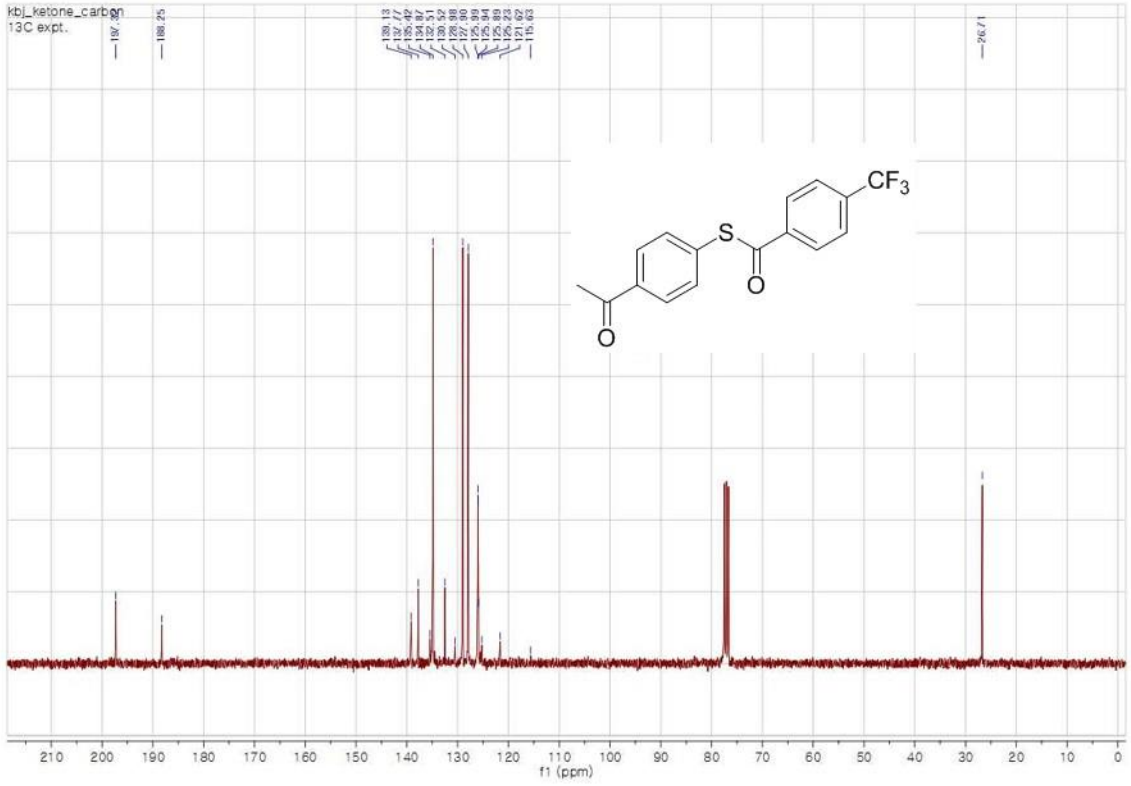
^{13}C NMR **(1m)**



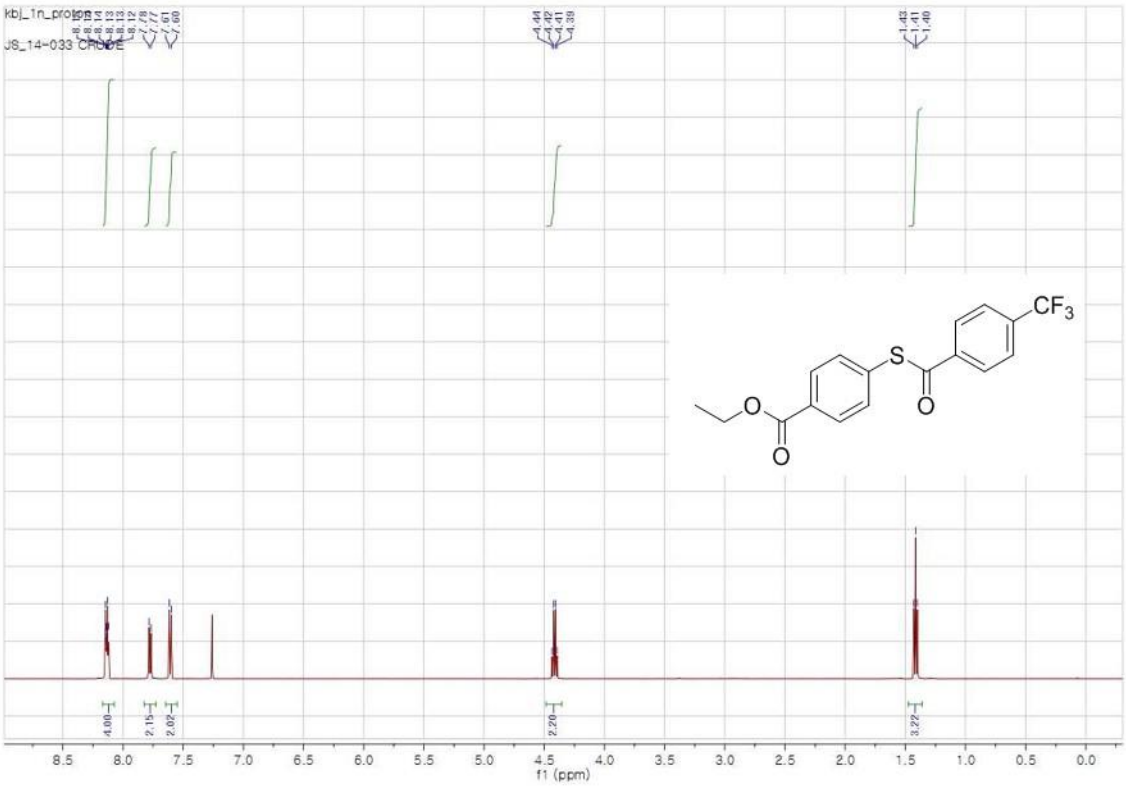
^{1}H NMR (**1n)**



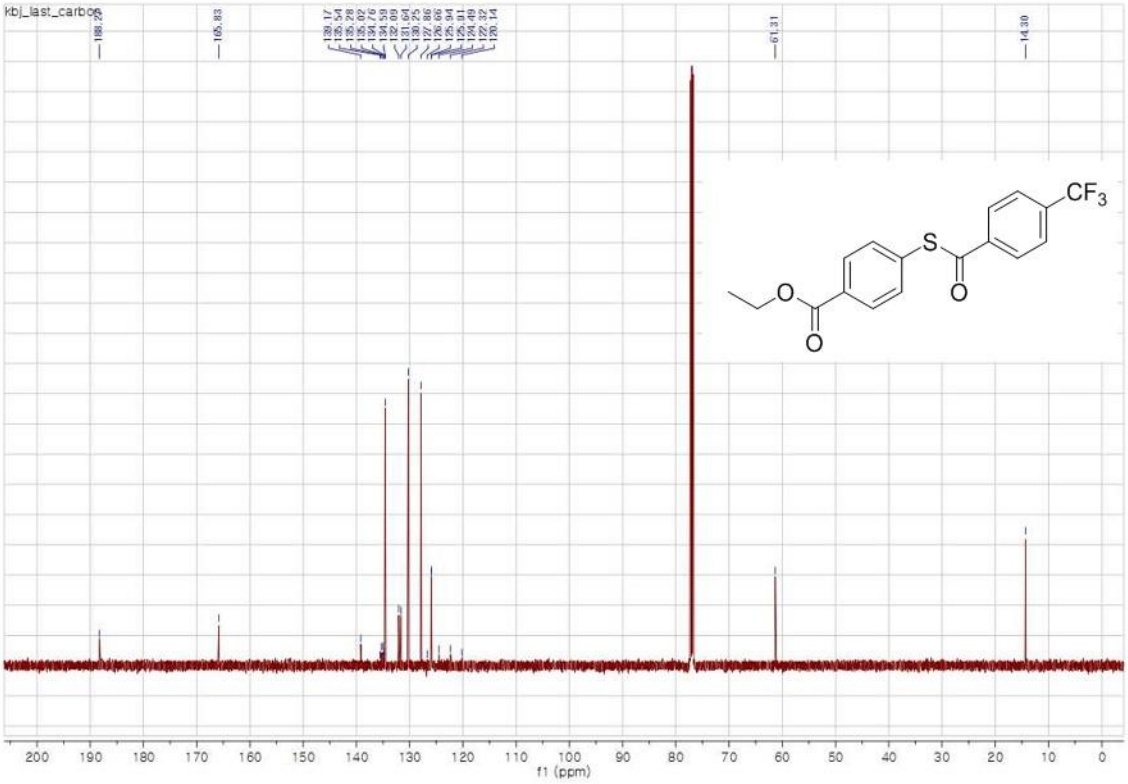
^{13}C NMR **(1n)**



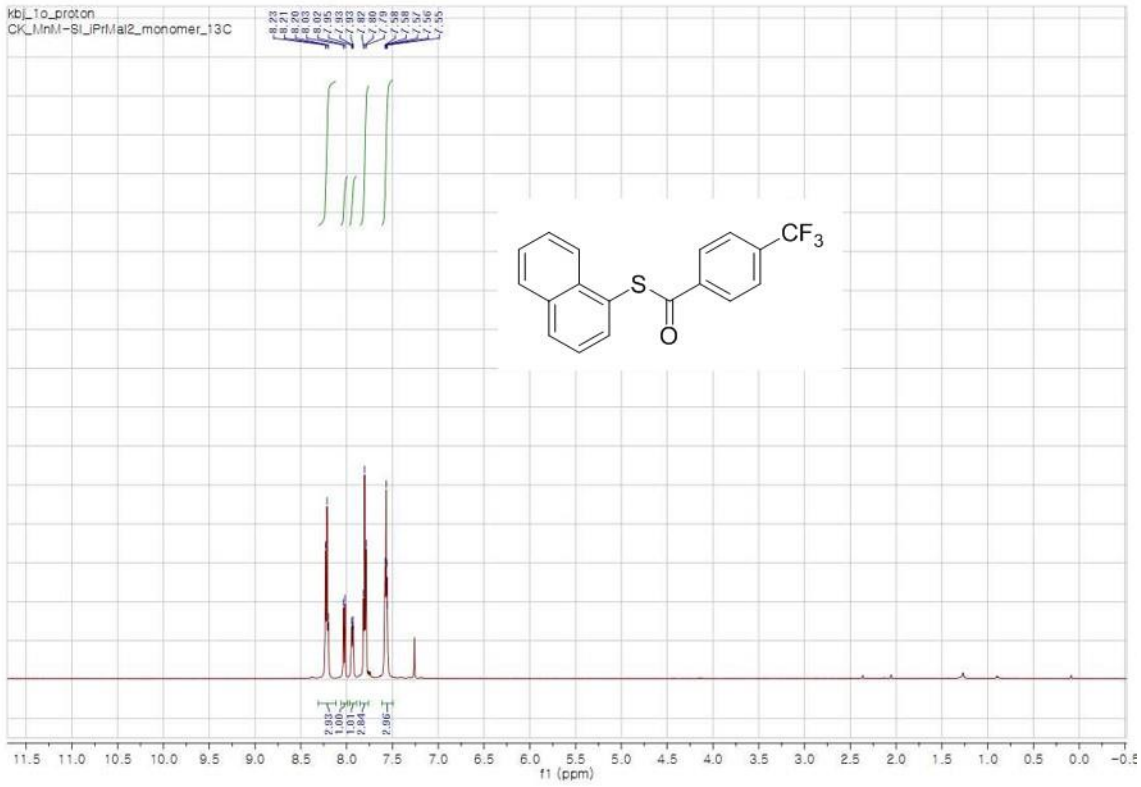
^{1}H NMR (**1o)**



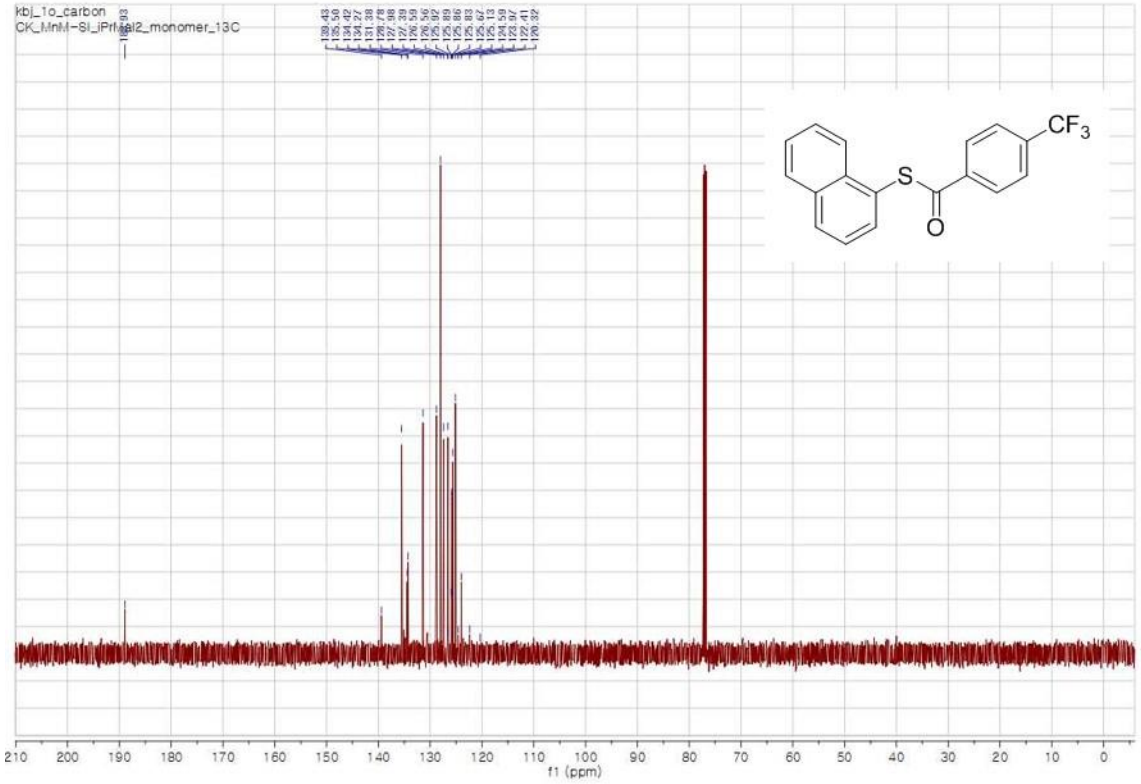
^{13}C NMR **(1o)**



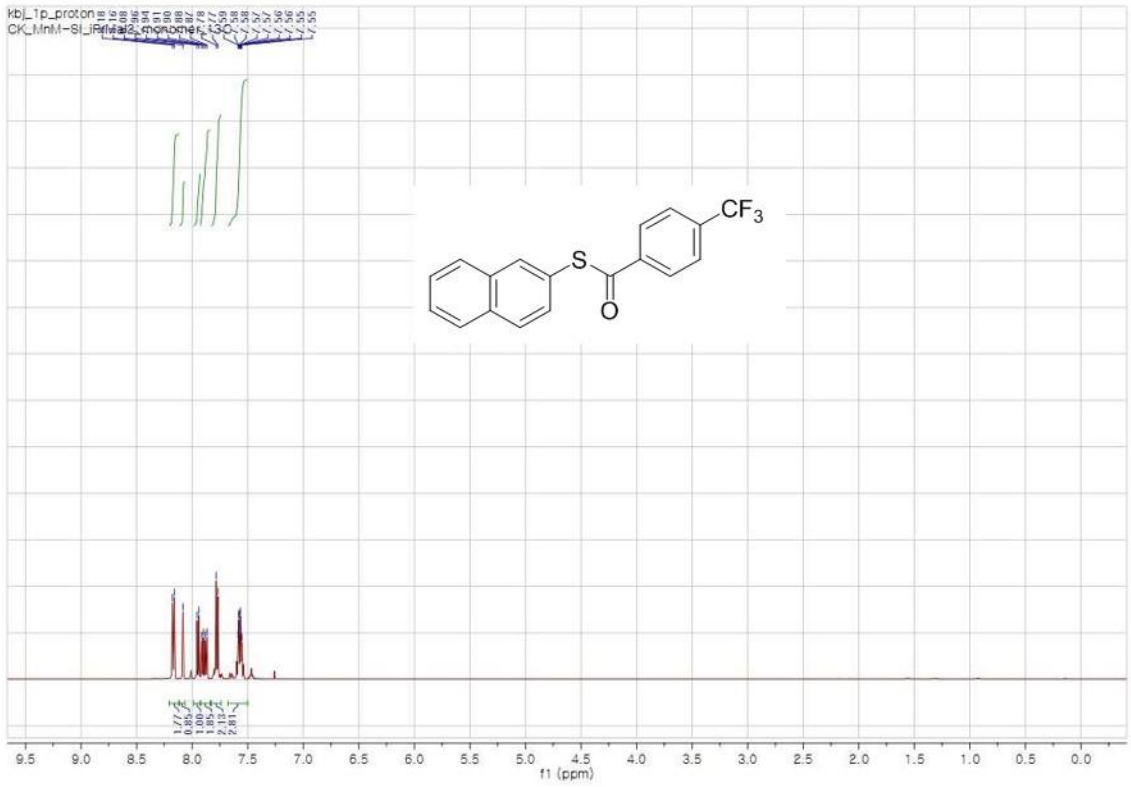
^{1}H NMR (**1p)**



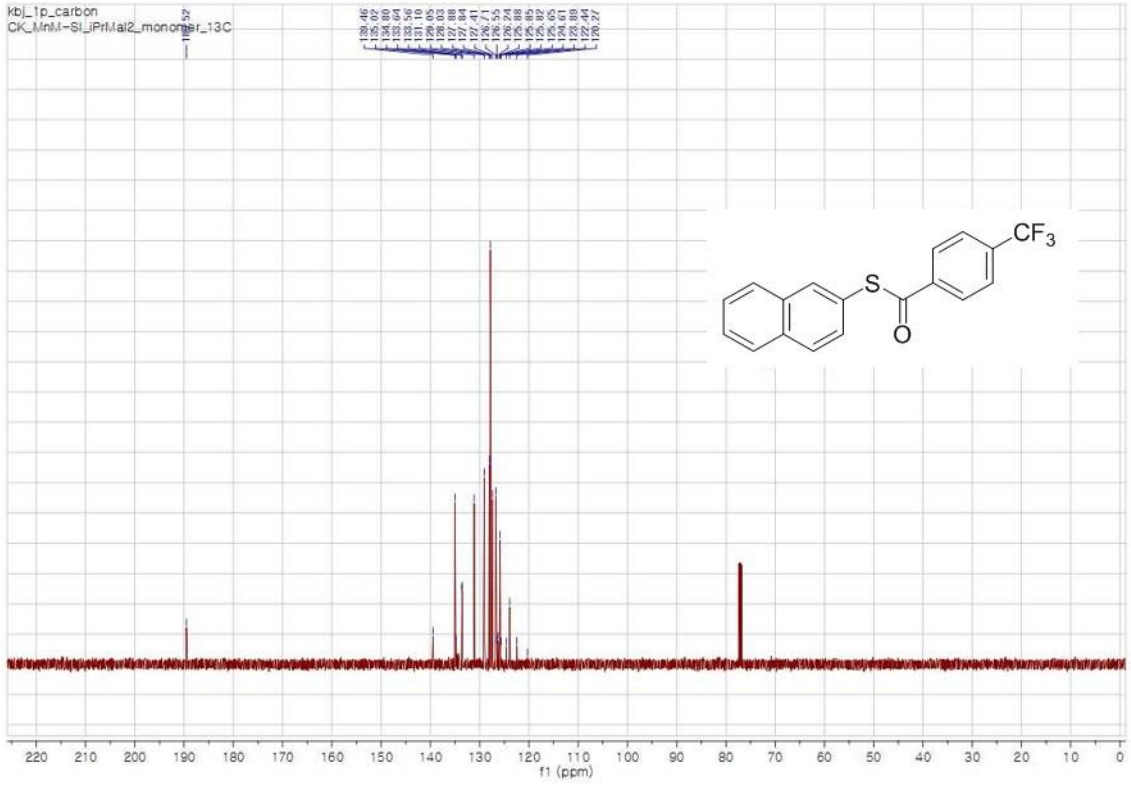
^{13}C NMR **(1p)**



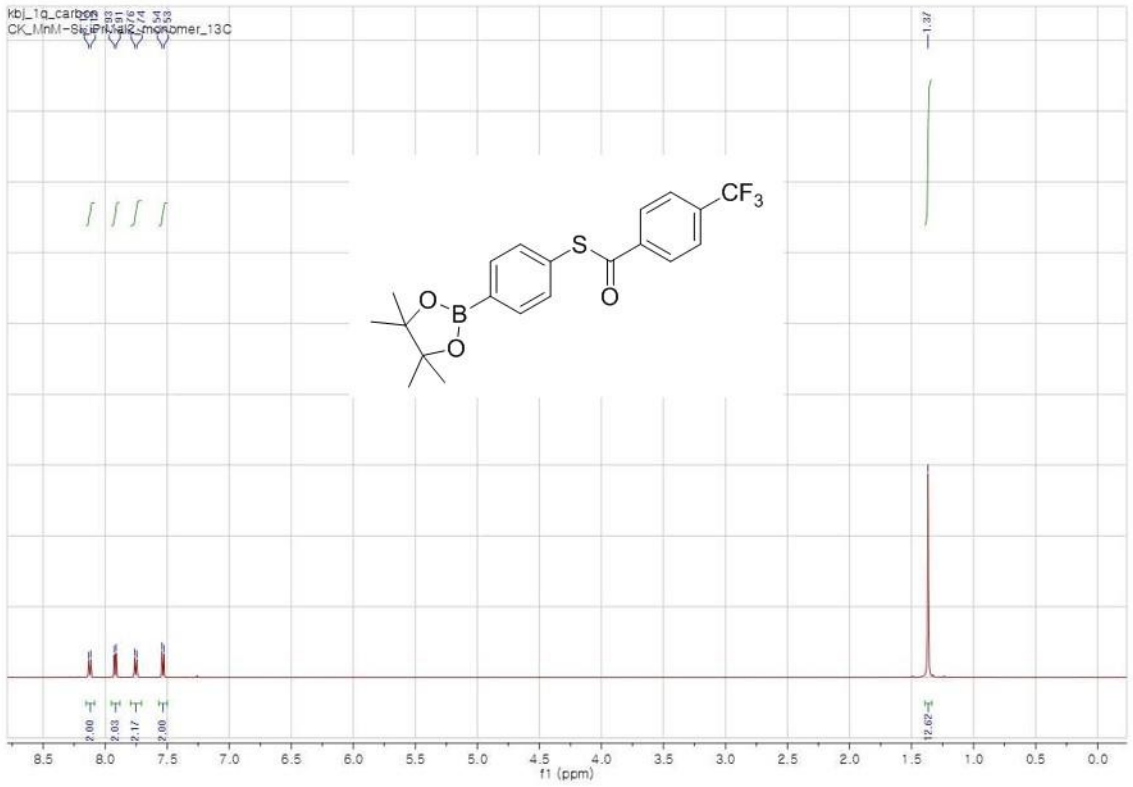
^{1}H NMR (**1q)**



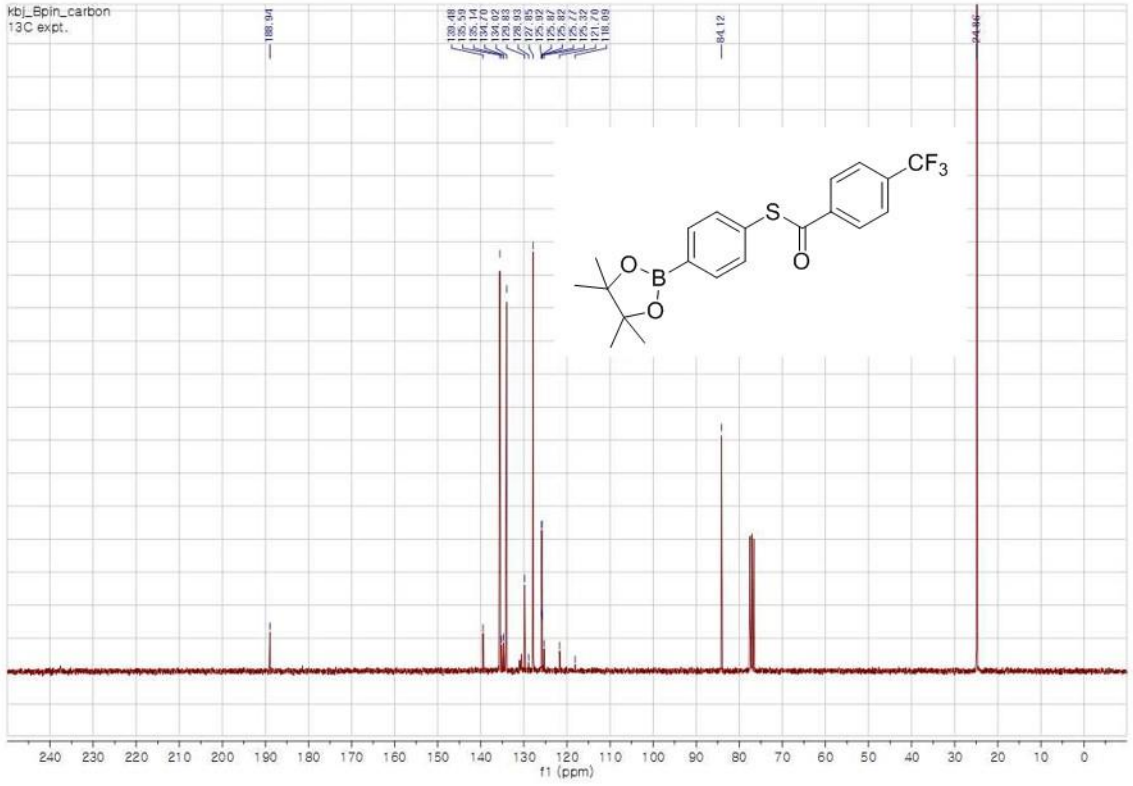
^{13}C NMR **(1q)**



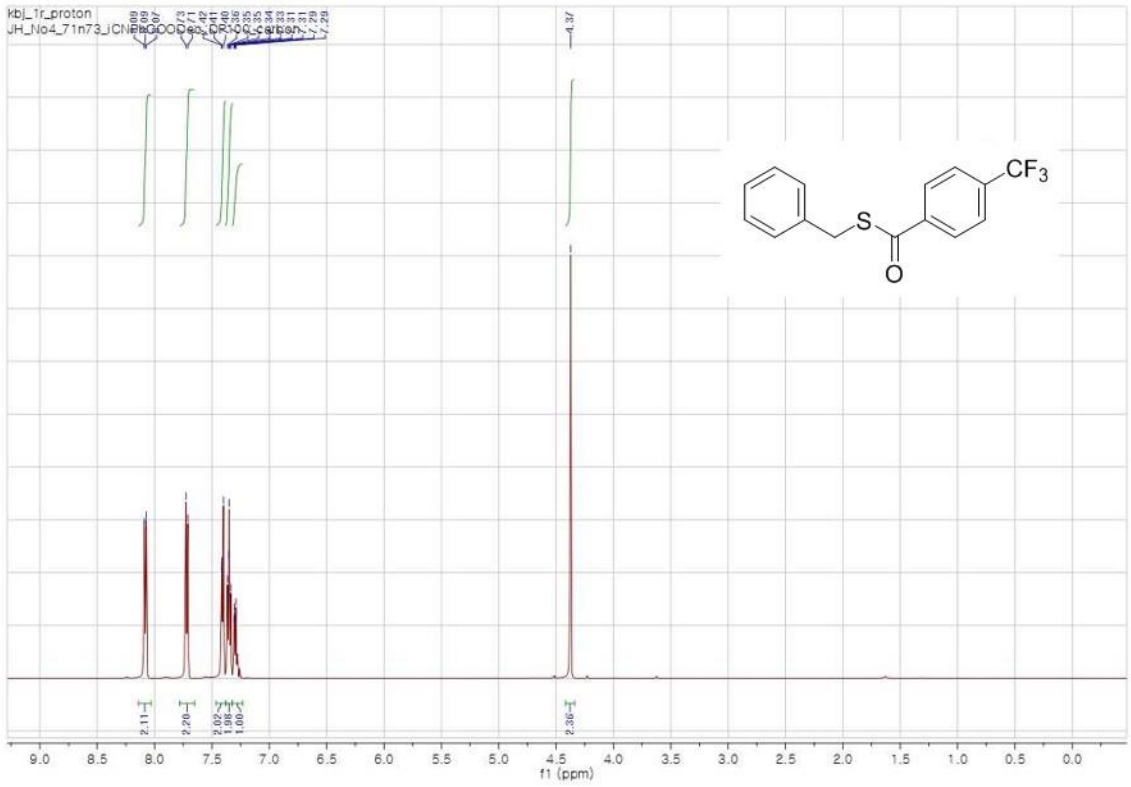
^{1}H NMR (**1r)**



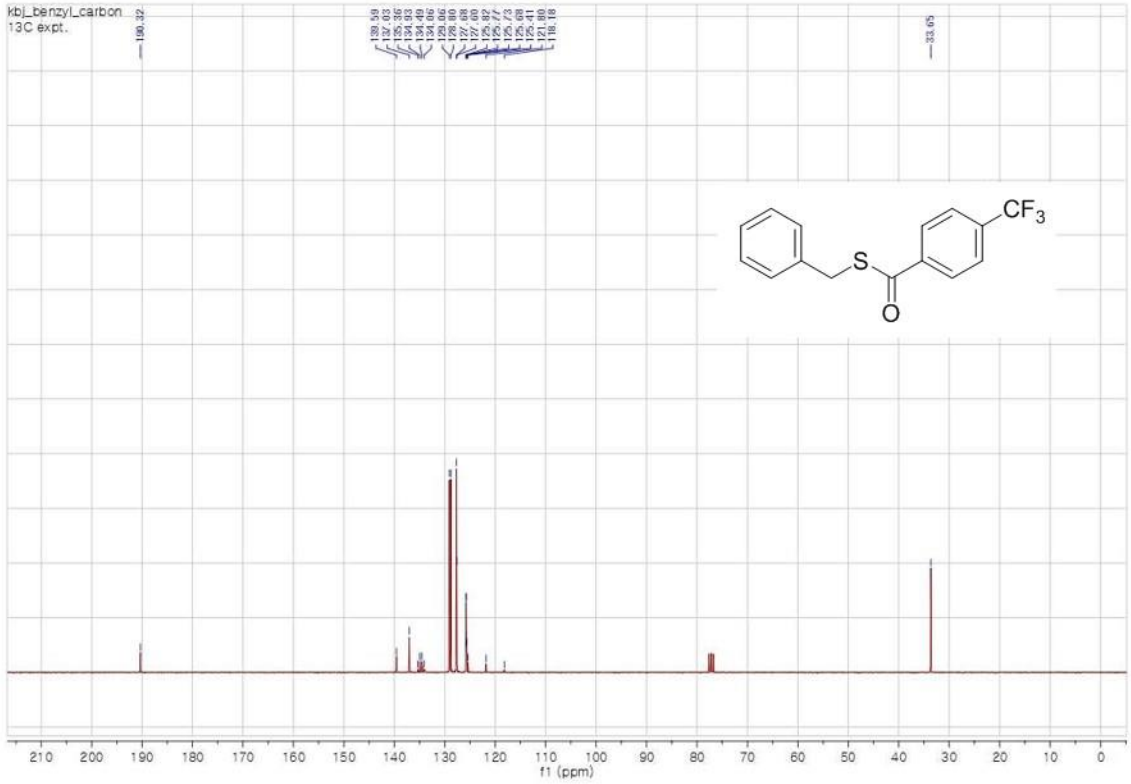
^{13}C NMR **(1r)**



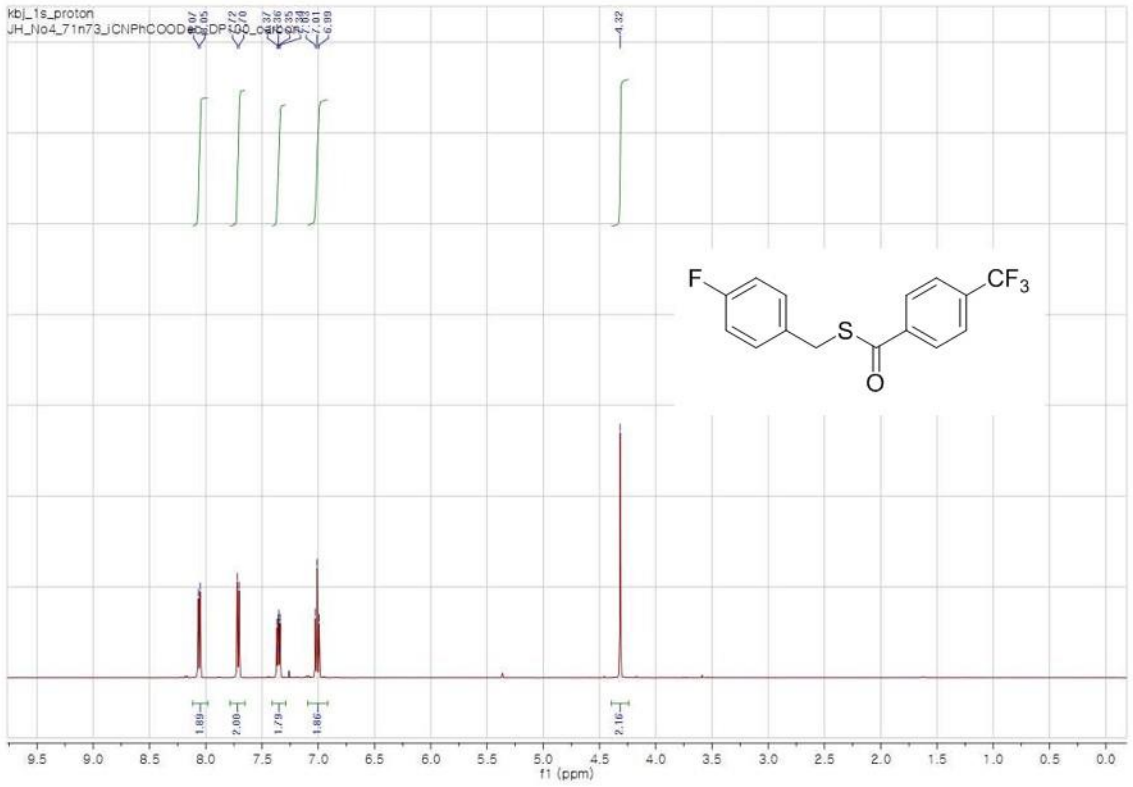
^{1}H NMR (**1s)**



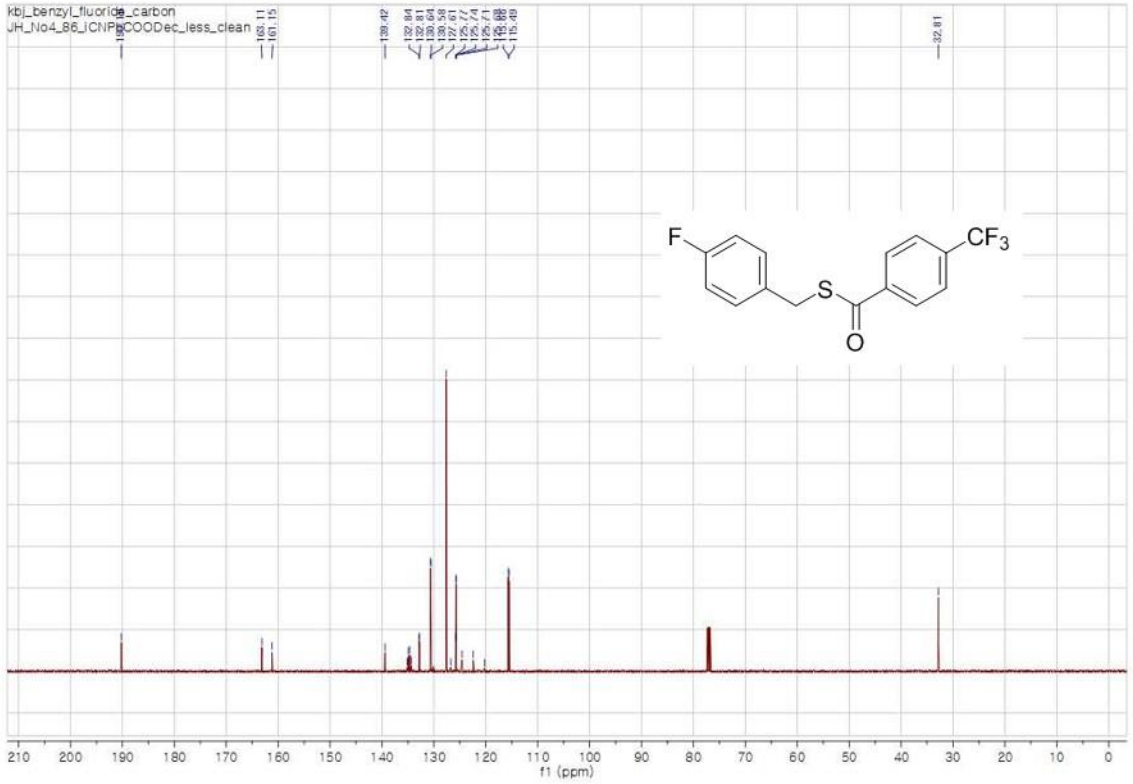
^{13}C NMR **(1s)**



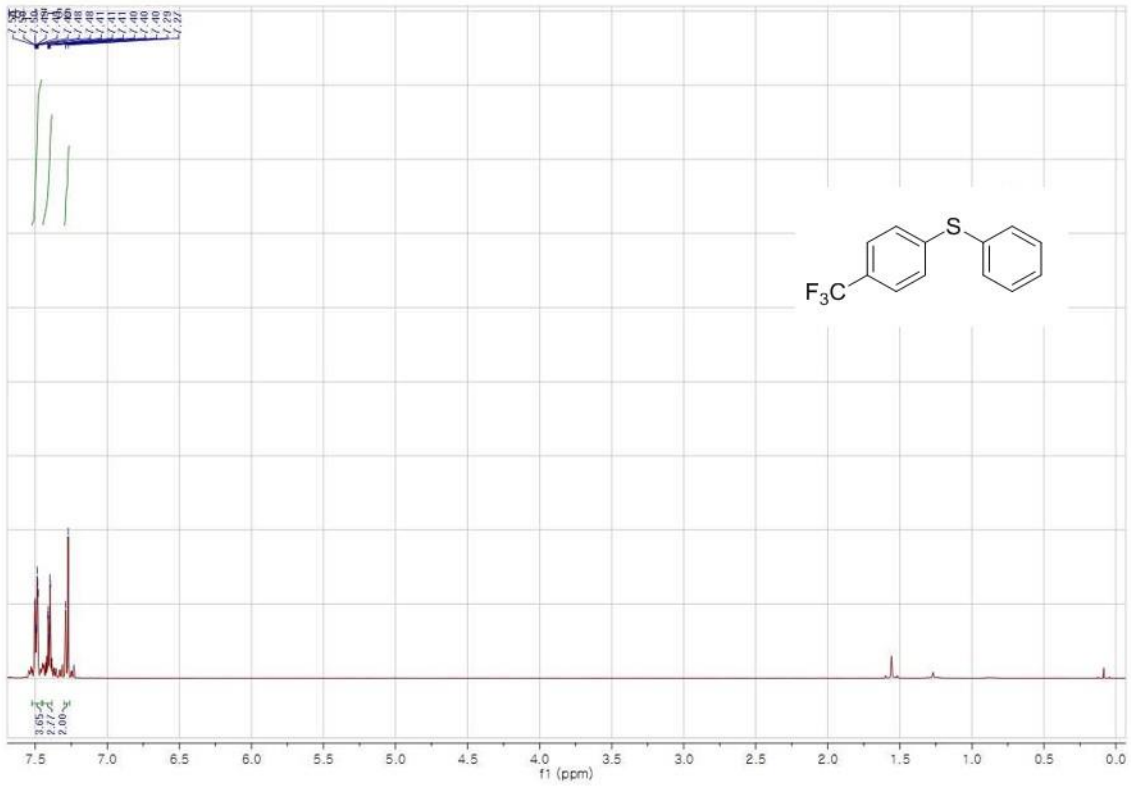
^{1}H NMR (**1t)**



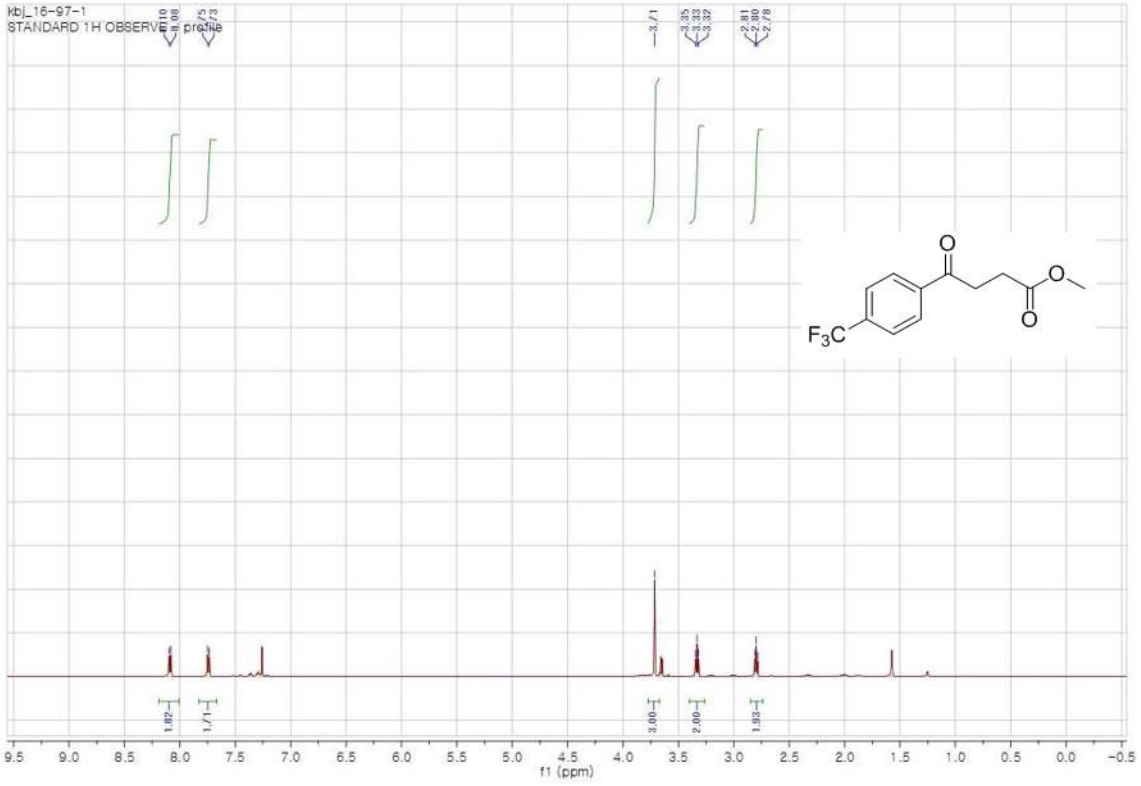
^{13}C NMR **(1t)**



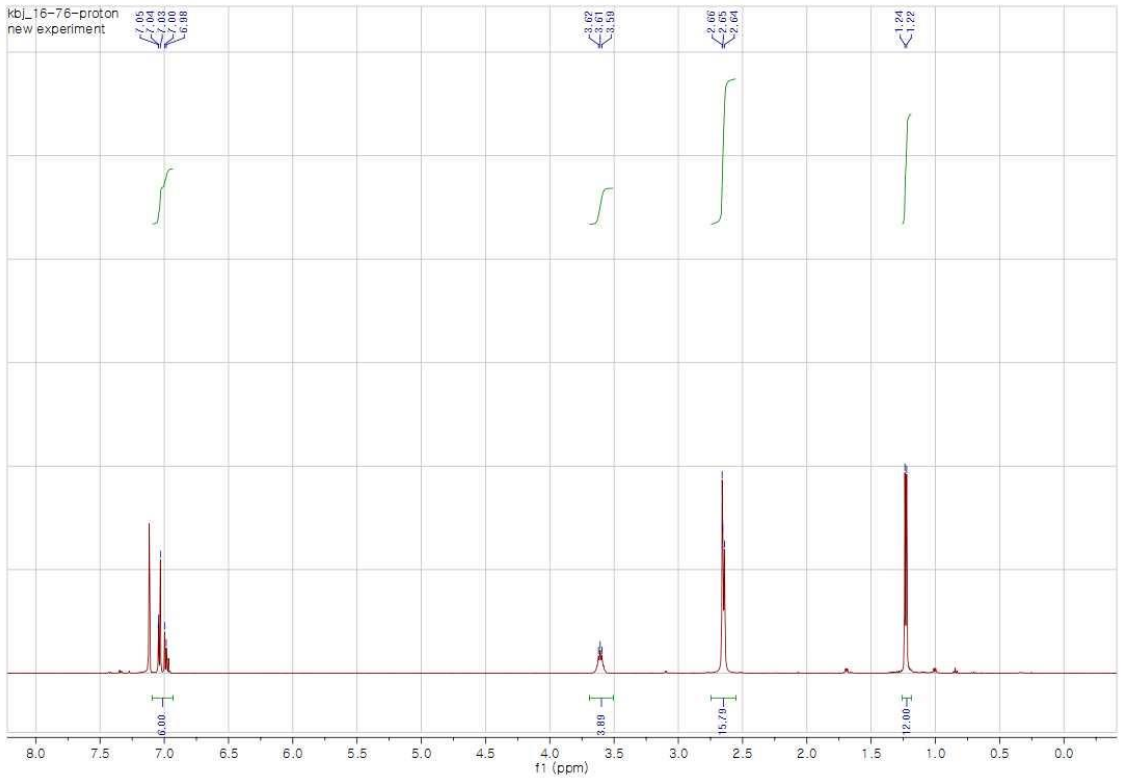
^{1}H NMR **(4a)**



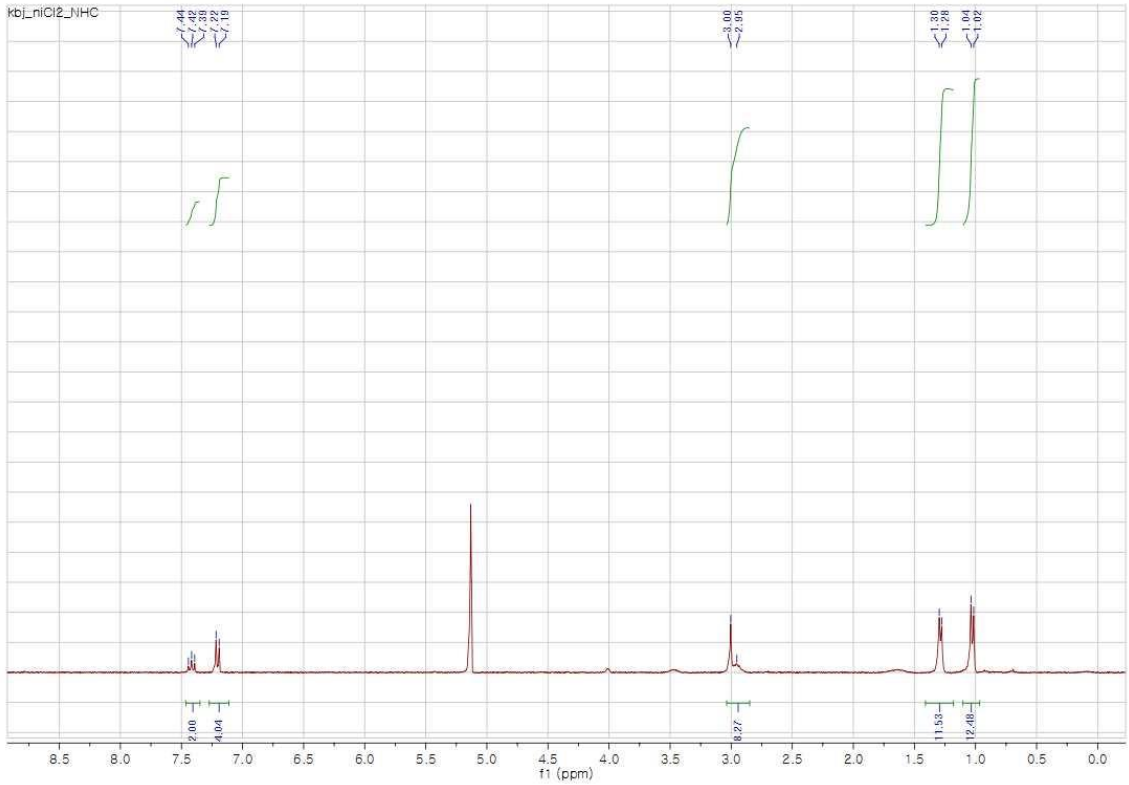
^{1}H NMR **(5a)**



^{1}H NMR of [(SIPr)NiCl]$_2$ (**[Ni-I]**) in $CDCl_3$



^{1}H NMR of [(SIPr)NiCl]$_2$(μ-Cl)$_2$ (**[Ni-II]**) in CD_2Cl_2



^{13}C NMR of $[(SIPr)NiCl]_2(\mu\text{-}Cl)_2$ (**[Ni-II]**) in CD_2Cl_2