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理學碩士學位論文

가시광선 광촉매를 이용하여 알킬 실란 치환된
설파이드 또는 다이사이엔과 알켄의 Giese 반응
개발

Photocatalytic Giese Reaction of Alkylsilane Substituted sulfides
and dithianes

蔚山大學校大學院

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指導教授 이상국

이 論文을 理學碩士 學位論文으로 提出함


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영문 초록(ABSTRACT)

Visible-light mediated photoredox catalyzed Giese reaction of alkylsilane substituted sulfide and dithianes with alkenes is described. This reaction involves *in situ* generated methyl sulfide radicals or dithiane radicals by single electron oxidation of α -TMS alkylsilane substituted sulfide or dithianes, followed by subsequent conjugate addition to activated alkenes. Various functional groups were tolerated under developed conditions to provide good to excellent yields.

국문초록

가시광선 광촉매를 이용한 알켄과 알킬 실란 치환된 설파이드 또는 다이사이엔의 Giese반응을 개발하였다. 이 반응은 알파위치에 TMS 치환된 메틸설파이드와 다이사이엔의 산화를 통해 메틸설파이드라디칼과 다이사이엔라디칼을 형성하여 알켄과 반응시켜 진행된다. 좋은 수율으로 다양한 기질의 물질을 얻었다.

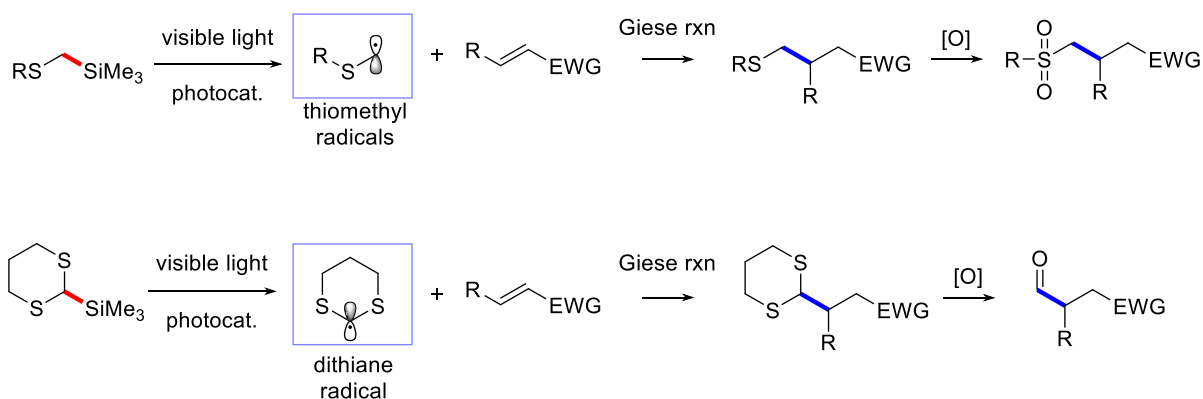
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I. 서론

I-1. Giese반응

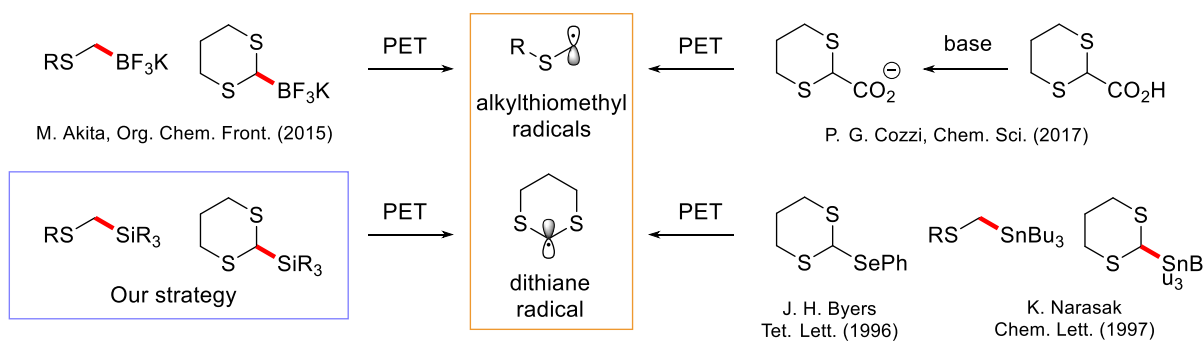
탄소라디칼은 친핵성이므로 다양한 친전자체와 반응할 수 있다. 특히 Giese반응은 전자결핍 알켄과 라디칼이 반응하여 탄소-탄소 결합을 형성하는 반응이다. 새로 형성된 탄소라디칼은 친전자체와 추가로 반응할 수 있다. 우리는 Giese반응을 통해 다이사이엔¹ 또는 메틸설파이드 라디칼²과 알켄의 탄소-탄소 결합을 형성하는 반응을 개발하였다. 1,3-다이사이엔은 Corey-Seebach 반응과 같은 음폴롱반응에 사용되어 다양한 합성에 사용되어 질 수 있고, 쉽게 산화되 케톤이나 알데하이드를 형성할 수 있는 매력적인 빌딩블럭(building block)으로써 활발히 연구되어지며, 설파이드는 천연물과 생물학적 분자, 유기촉매, 재료화학 등 다양한 물질에서 존재하여 다양한 분야에서 중요한 작용기로 높은 활용 가치가 있어 활발히 연구되어진다 (Scheme 1).



Scheme 1. Reaction concept

이전까지 다이사이엔과 메틸설파이드에 라디칼을 형성하는 반응에는 트리플루오로보레이트를 사용하거나, 카복실산, 주석을 사용하는 방법이 있었다. organotrifluoroborates^{2a}를 사용하는 경우 염상태이므로 정제가 어려워 다루기 어렵거고, 카복실산^{2b}을 쓰면 카르복시산염을 형성해 알켄과 반응해 주어야 하므로 염

기를 첨가해 주어야만 하고, 주석과 같은 물질을 사용할 경우 독성이 있다는 단점이 있다. 하지만 우리는 중성실리콘을 사용하였다. 실리콘은 지표의 28%를 차지할 정도로 많이 존재하므로 구하기 쉽다. 또 β -실리콘효과³를 통해 탄소와 실리콘의 시그마본드와 양이온라디칼사이의 오버랩이 일어나 안정화시켜주기 때문에 좋은 이탈성을 갖고있기 때문에 라디칼 중간체의 형성이 쉽게되고, 따라서 추가적인 첨가물없이 좋은 수율을 나타낸다. 우리는 TMS치환된 다이사이엔과 메틸셀파이드를 사용하여 환경친화적으로 짧은 시간에 효율적인 반응을 개발하였다 (Scheme 2).

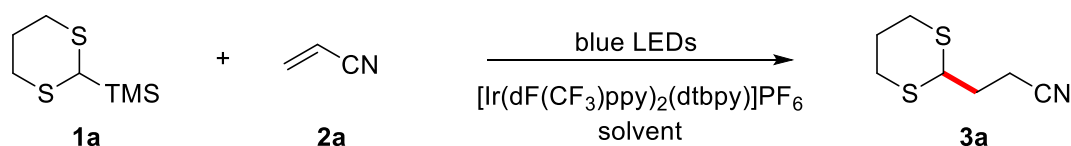


Scheme 2. Generation of alkylthiomethyl or dithiane radicals by PET

II. 결과 및 토의

II-1. 다이싸이엔의 Giese반응 최적화

Table 1. Optimization of the Reaction Conditions



Entry	catalyst	solvent (M)	Alkene	Time (h)	yield (%)
1	1mol%	MeCN (1.0)	2eq	14	16
2	1mol%	DMF (1.0)	2eq	14	30
3	1mol%	EtOH (1.0)	2eq	14	34
4	1mol%	MeOH (1.0)	2eq	14	60
5	1mol%	MeOH (0.1)	2eq	14	70
6	1mol%	MeOH:DMF (0.1)	2eq	14	43
7	1mol%	MeOH:MeCN (0.1)	2eq	14	76
8	2mol%	MeOH:MeCN (0.1)	2eq	14	76
9	4mol%	MeOH:MeCN (0.1)	2eq	14	73
10	1mol%	MeOH:MeCN (0.1)	3eq	14	76
11	1mol%	MeOH:MeCN (0.1)	2eq	7	75
12	1mol%	MeOH:MeCN (0.1)	2eq	3.5	76

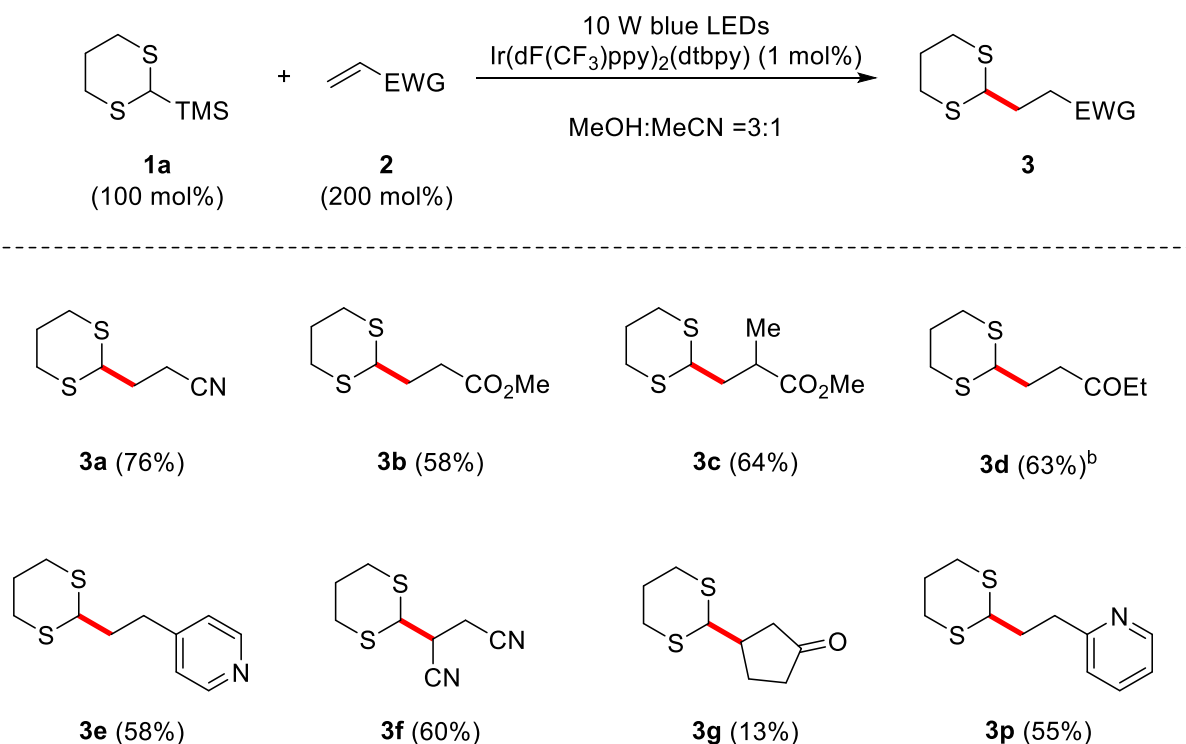
반응조건: **1a** (0.20 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]$, solvent (0.1 M) with 10 W blue LEDs irradiation at room temperature under an Ar balloon. Isolated yield by flash column chromatography.

출발물질인 **1a** 는 1.18 V 의 산화 포텐셜(oxidative potential)을 지니고, $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ 는 $(E_{1/2}^{\text{ox}}(\text{Ir}^*/\text{Ir}^{\cdot-})) = +1.21$ V 의 산화력을 가지고 있으므로 산화시키기 충분하기 때문에 초기 연구에서 $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ 를 광촉매로 선택하였다. 그 후 반응의 최적화를 위하여 **1a** (0.2 mmol)를 기준으로 파트너 물질인 **2a** 2 당량과 촉매 1 mol% 기준으로 용매조건을 바꿔보았다.(표 1. 항목 1~7). 항목 1~4 에서 아세토니트릴, 디메틸포름아마이드, 에탄올, 메탄올으로 실험해 본 결과 메탄올에서 60%로 수율이 가장 좋은 것을 확인하고, 항목 5 에서 농도를 조절해 본 결과 0.1 M 농도로 고정해 준 후 다른 용매와 섞어서 반응시켜 본 결과 항

목 7 에서 메탄올과 아세토니트릴을 섞어 준 조건을 고정하였다. 항목 8,9 에서 촉매 당량을 2 mol%, 4 mol%로 올려서 실험해 본 결과 반응 수율이 개선되지 않는 것을 확인하고 촉매는 1mol%로 고정하고, 항목 10에서 **2a**를 3당량으로 올려주었을 때도 수율이 개선되지 않아서 2 당량으로 고정해 주었다. 그 후 항목 11, 12 에서 앞의 모든 조건을 고정한 후 시간 최적화를 실시해주었고, 3.5 시간으로 고정하여 항목 12 를 최종 반응조건으로 고정하였다.

II-2. 알킬 실란 치환된 설파이드 또는 다이사이엔의 Giese반응 기질탐구

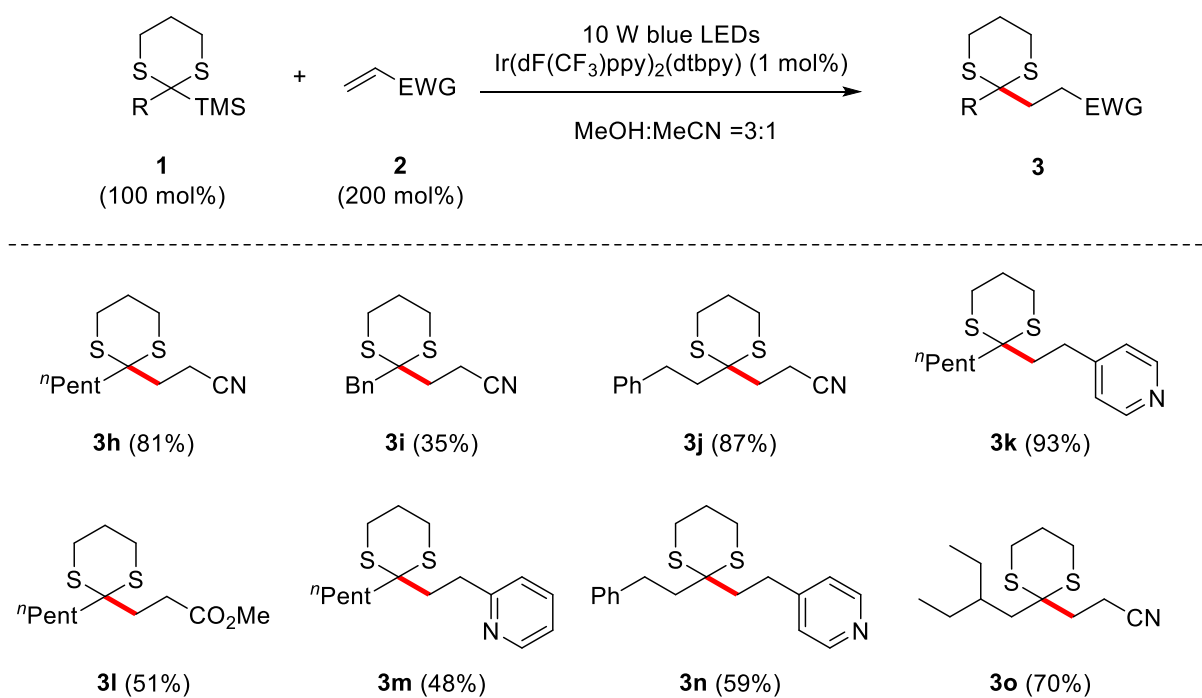
Table 2. Substrate scope of various alkenes



^aReaction conditions as given in Table 1, entry 12; reported yields are for isolated material. ^b $\text{MeOH}:\text{MeCN}=1:9$. See Experimental section for details.

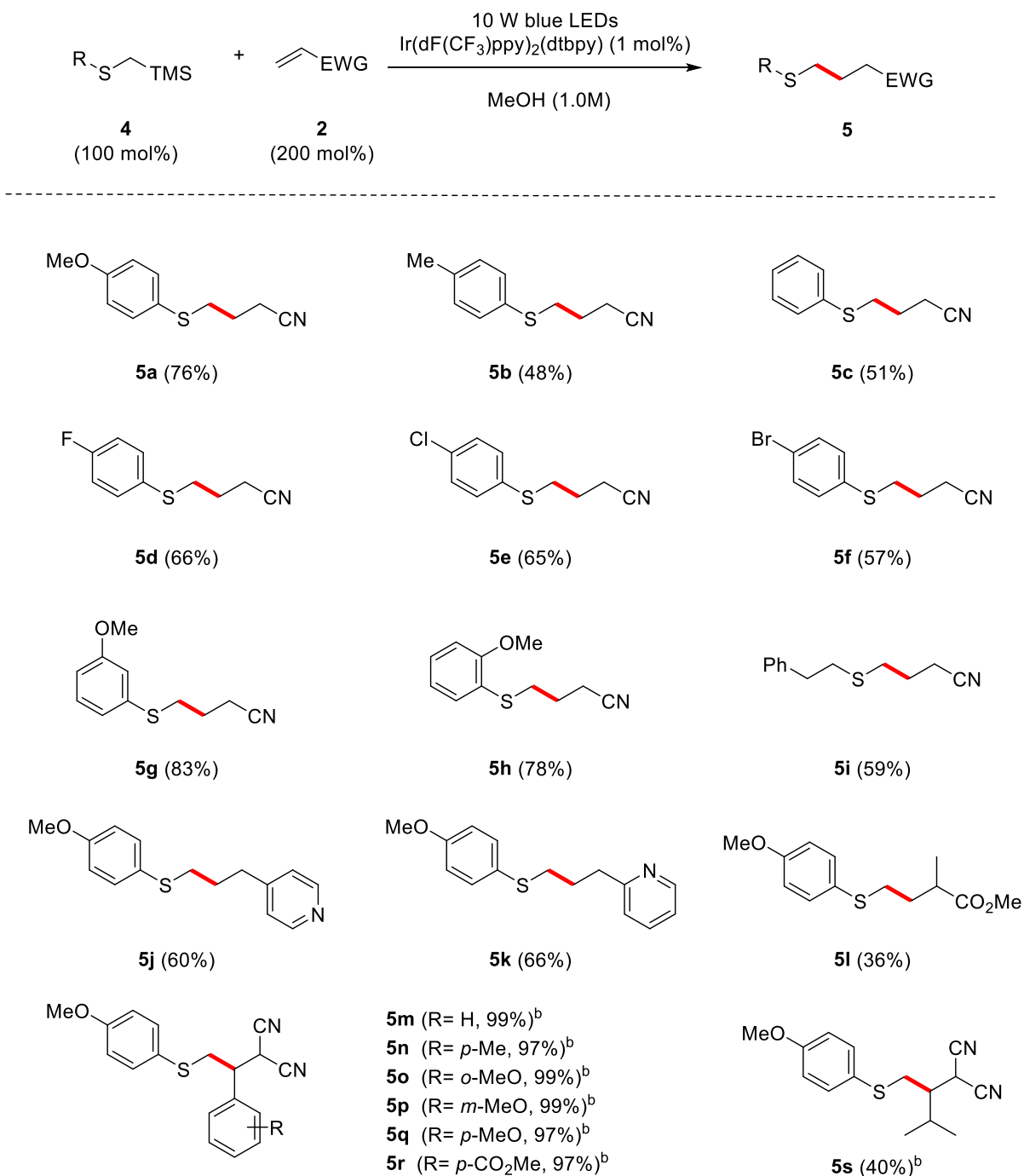
최적화된 조건이 설정됨에 따라, 다양한 기질확장을 위한 실험을 실시하였다. 다이사이엔과 전자를 끄는 그룹이 포함된 다양한 알켄을 사용하여 아크릴로나이트릴(acrylonitrile)뿐만 아니라 메틸아크릴산(methylacrylate), 메틸메타크릴레이트(methylmethacrylate), 케톤 및 헤테로아릴시스템에서 위와 같은 결과를 얻었다 (**3a** ~ **3p**).

Table 3. Substrate scope of alkyl substituted dithiane



^aReaction conditions as given in Table 1, entry 12; reported yields are for isolated material. See Experimental section for details.

다음으로, 출발물질인 다이사이엔의 확장성을 확인하는 실험을 실시하였다. 알킬기가 치환된 다이사이엔으로 펜틸, 벤질, 에틸페닐, 에틸부틸그룹이 붙은 출발 물질을 사용하여 아크릴로나이트릴과 반응시킨 결과 기본 1 차 시스템과 유사한 결과를 얻을 수 있었다(**3h** ~ **3j**, **3o**). 결과가 좋았던 펜틸그룹이 붙은 2 차다이사이엔의 경우 추가적으로 헤테로아릴, 메틸아크릴산시스템과 반응시켜 본 결과 위와 같이 1 차 시스템과 유사한 결과를 얻었다(**3k**~**3m**).

Table 4. Substrate scope of sulfides and alkenes

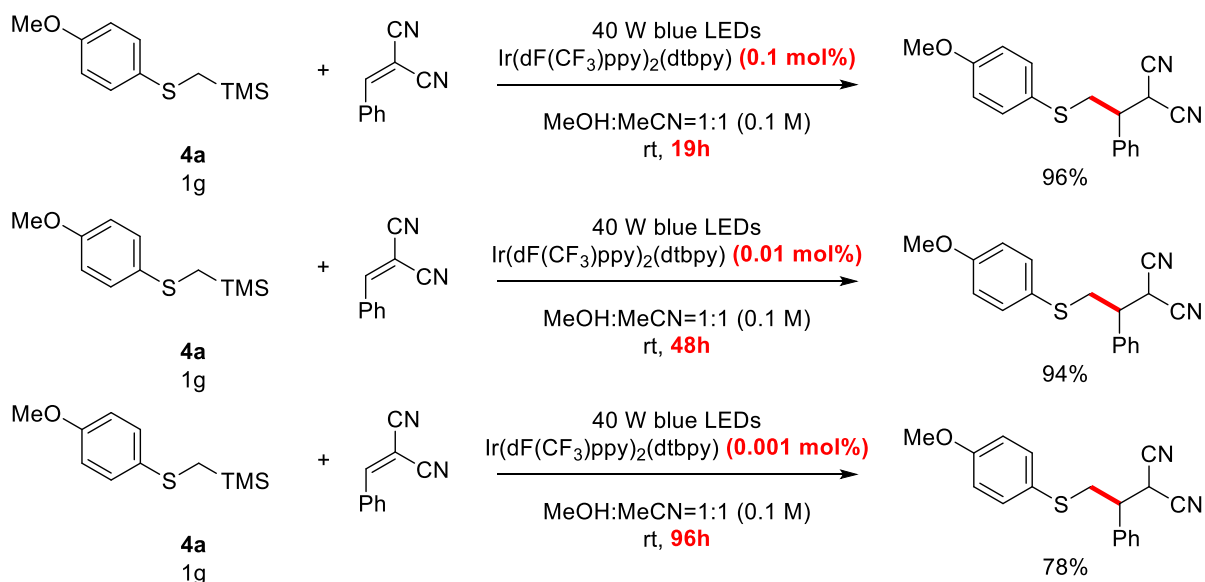
^aReaction conditions: **4** (0.20 mmol), Cat (1.0 mol %), MeOH (1.0 M) with 10 W blue LEDs irradiation at room temperature under an Ar balloon, reported yields are for isolated material. ^bMeOH:MeCN=1:1 (0.1M). See Experimental section for details.

다양한 설파이드그룹에 대해서 반응을 진행하였다. 아크릴로나이트릴을 알켄으로 사용하여 반응시킨 **5a~5i** 중 전자를 주는 그룹이 붙은 **5a, 5g~5h**의 경우에서 76~83% 수율을 얻을 수 있었고, 할로젠이 붙은 **5d~5f**의 경우에 57~66%의 결과를 얻었다. 메틸설파이드의 아릴기 파라위치에 메톡시가 붙은 경우를 기본으로 다양한 알켄을 반응시켜보았다(**5j~5s**). 바이닐피리딘을 사용한 경우 60~66%의 수율을 얻었다(**5j~5k**). 말로노나이트릴을 사용한 경우에 97%이상의 수율을 얻음을 확인하였다(**5m~5r**). 이는 전자를 끄는 그룹이 두 개 가 붙었기 때문에 생성된 라디칼과 더 잘 반응함을 알 수 있었다.

II-3. 알킬 실란 치환된 설파이드 또는 다이사이엔의 Giese반응 응용연구

A. Gram scale reaction

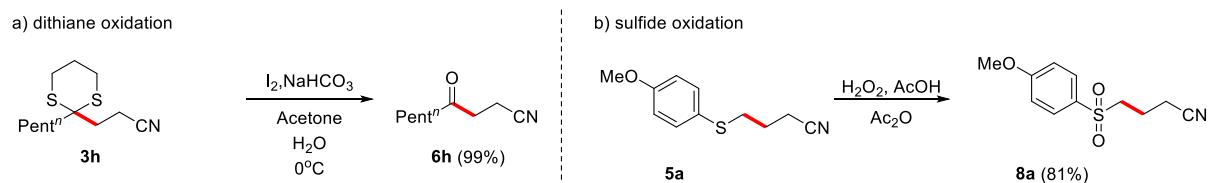
유기합성에서 유용한 사용을 위해 광원의 강도를 높여 **1g** 이상의 양으로 반응을 진행하였다. **4a** 와 벤잘말로노나이트릴을 사용하였다. 아래의 변형된 조건 하에 촉매량을 0.1 mol%부터 0.001 mol%로 줄여서 반응을 진행 한 결과 78%~96%의 수율을 얻었다. (Scheme 3).



Scheme 3. Gram scale reaction

B. 다이사이엔 또는 설파이드 산화

다이사이엔의 경우 산화반응을 통해 케톤으로 만들어 줄 수 있다. 반응의 확장성을 확인하기 위해 **3h** 를 사용하여 산화시켜 케톤을 형성해 본 결과 99%의 수율을 얻을 수 있었다 (Scheme 4a). 설파이드는 산화반응을 통해 설피온을 형성한다. **5a** 를 사용해 산화시켜 본 결과 81%의 수율을 얻을 수 있었다 (Scheme 4b).

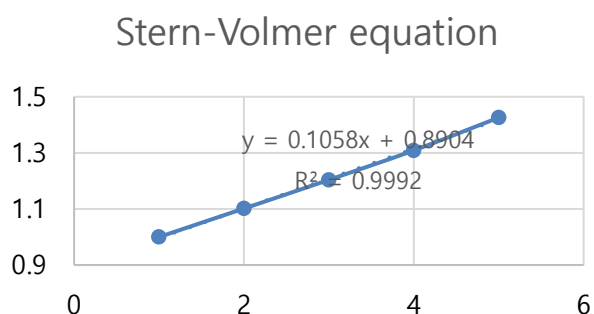
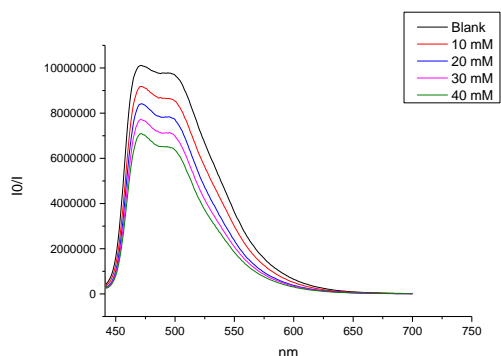


Scheme 4. Oxidation

II-4. Giese반응 메커니즘 연구

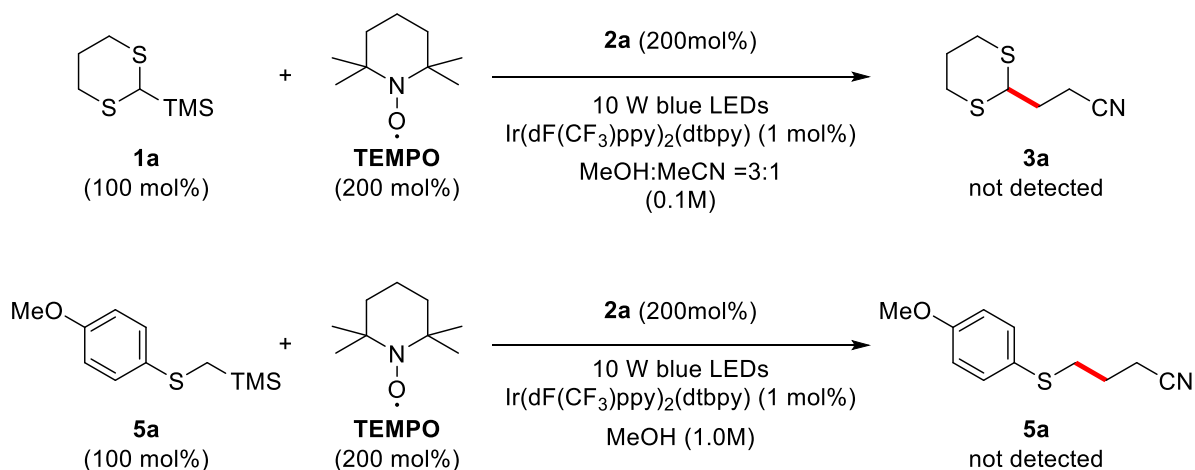
A. 형광 소광 실험(Luminescence quenching experiments)

형광소광실험은 첫번째 산화가 단일전자산화로 일어나는지 확인하기 위해 실시하였다. 촉매가 들뜬 후 떨어지면서 방출하는 형광이 출발물질인 **1a**의 농도가 높아짐에 따라 줄어드는 것을 확인하였고, 따라서 광촉매와 출발물질이 단일전자산화로 먼저 반응하여 진행됨을 확인할 수 있었다. 오른쪽의 그래프는 stern-volmer 식으로 출발물질의 농도가 높아지는 것에 따라 형광이 일정하게 줄어드는 것을 확인하였다.



B. 라디칼 트랩 실험(Radical trapping experiments)

2,2,6,6-테트라메틸피페리딘-1-옥실(TEMPO)은 $(CH_2)_3(CMe_2)_2NO$ 의 화학식을 갖는 물질로 안정화된 라디칼을 갖기 때문에 반응에서 라디칼 트랩핑 시약으로 사용될 수 있다. 우리는 이 2,2,6,6-테트라메틸피페리딘-1-옥실(TEMPO)을 기본 반응에 넣어줬을 때, 반응이 가지 않는 것을 확인하여 반응이 라디칼과정을 갖는다는 것을 보여주었다.

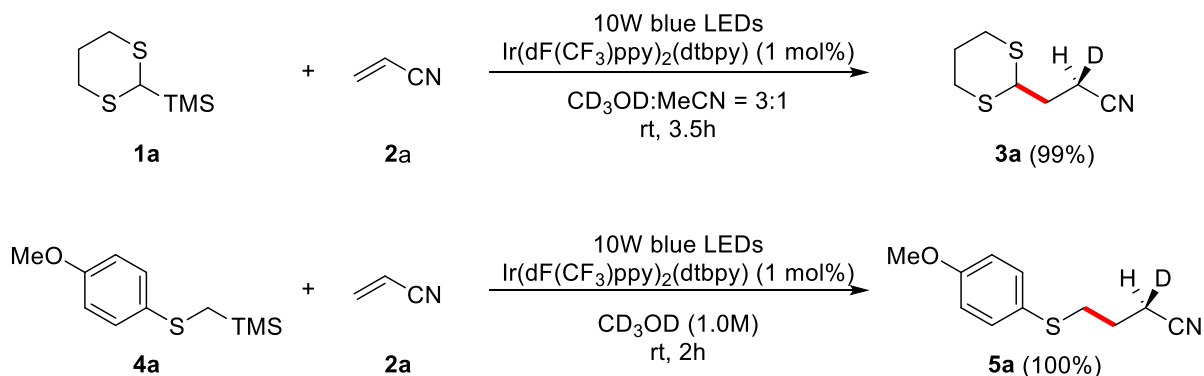


Scheme 4. TEMPO experiments

^aReaction conditions : **1a** (0.20 mmol), **2a** (2eq, 200 mol%), **TEMPO** (2eq, 200 mol%), [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (1.0 mol%), solvent (0.1 M) with 10 W blue LEDs irradiation at room temperature under an Ar balloon. ^bReaction conditions: **5a** (0.20 mmol), **2a** (2eq, 200 mol%) [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (1.0 mol %), **TEMPO** (2eq, 200mol%) MeOH (1.0 M) with 10 W blue LEDs irradiation at room temperature under an Ar balloon.

C. 중수소 치환실험

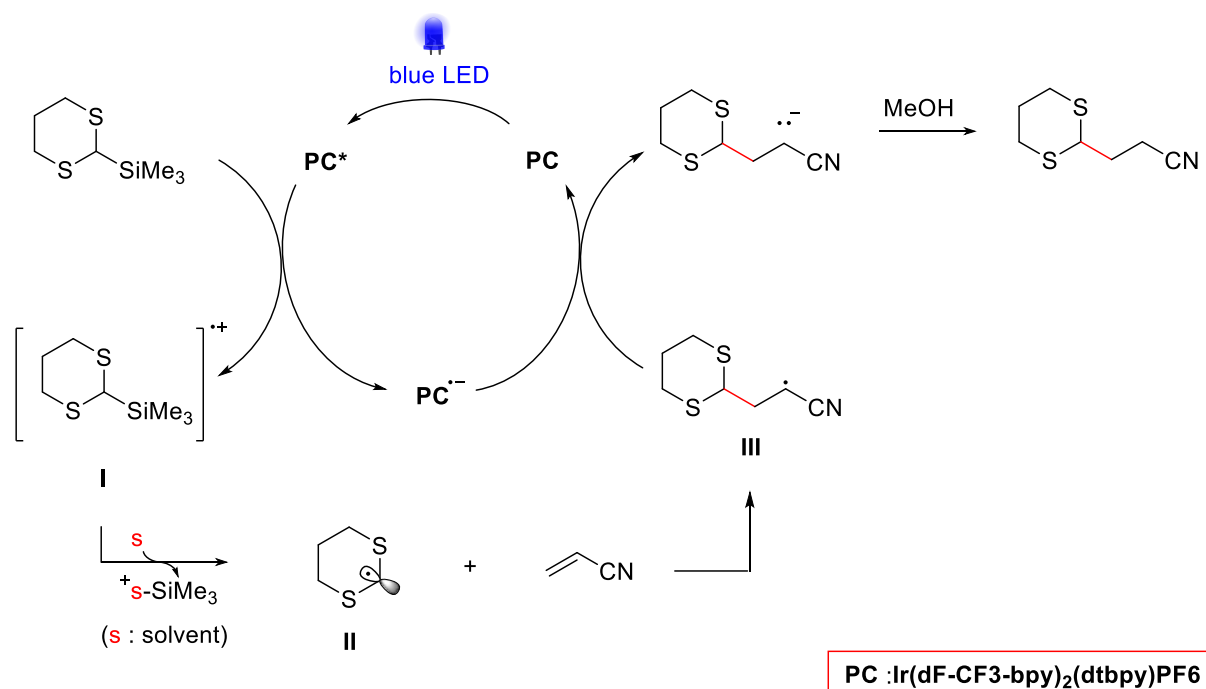
반응에서 수소가 어디서 오는지 확인하기 위해 중수소 치환된 메탄올을 사용하여서 반응을 진행시켜보았다. 반응 후 분리하여 NMR확인을 통해 반응 중 수소가 메탄올에서 오는 것을 확인하였다.



Scheme 5. Deuterium experiments

D. Giese Reaction 반응 메커니즘

메커니즘 선행연구를 통해 제안된 위와 같은 메커니즘을 제안했다. 먼저 빛에 의해 광촉매가 들뜨게 되고 출발물질(2a)을 산화시켜 라디칼을 형성하고 Giese 반응을 통해 III 중간체를 형성한 후 환원되었던 촉매가 III 중간체를 환원시켜주면서 음이온을 형성하고 용매인 메탄올에서 수소를 받아와서 최종 생성물을 형성한다.



Scheme 6. Proposed mechanism

III. 결론

본 연구에서 가시광선 광촉매를 사용하여 다이사이엔과 메틸설파이드 치환 된 물질을 생성하는 반응을 개발하였다. 이 반응을 통해 35 개의 물질을 합성하였고, 그램스케일 반응에서 조건을 확립하였다. 또한 전기화학적 실험과 중수소치환 실험등을 통해 합리적인 메커니즘을 제시하였다.

IV. 실험

IV-1. 시약

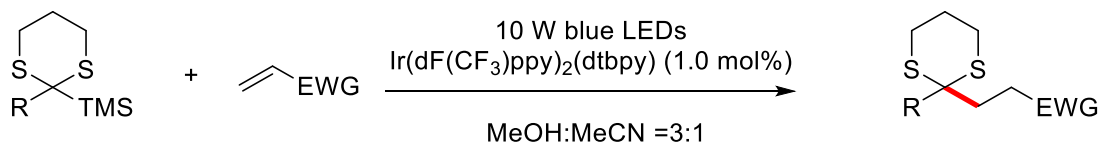
모든 광촉매 반응은 $Ar_{(g)}$ 하에서 진행하였다. 메탄올과 아세토니트릴은 Pure-Solv MD-5 Solvent Purification System (Innovative Technology)을 활용하여 사용하였다. 화합물의 합성에 사용된 대부분의 시약들은 Alfa, TCI, Aldrich, Across 사의 제품을 구입하고 정제하지 않고 그대로 사용하였다. 반응 진행의 확인은 TLC plates (Merck 5554 Kiesel gel 60 F254)를 사용하였으며, 관 크로마토그래피는 hexanes-EtOAc (v/v) 혹은 dichloromethane-methanol (v/v)과 silica gel (Merck 9385 Kiesel gel 60)로 수행하였다.

IV-2. 분석기기

고분해능 질량 스펙트럼은 대한민국 대구 한국기초과학지원연구원(KBSI)의 Jeol JMS700 HRMS(EI)를 사용하였다. 정확한 질량값은 분자 이온 $[M^+]$ 으로 기록하였다. 핵자기공명 스펙트럼은(1H NMR and ^{13}C NMR)은 Bruker AM-300(MHz)를 사용하였다. NMR 분석을 위해 사용한 용매는 chloroform-d ($CDCl_3$)를 사용하였다.

IV. 합성

IV -3-1. 다이싸이엔과 알켄의 giese 반응 방법 (3a – 3o)



Re-sealable pressure tube (13 x 100 mm)에 작은 마그네틱바를 넣고, [Ir(dF(CF₃)ppy)₂(dtbpy)]PF₆ (2.3mg, 0.0020 mmol, 1.0 mol%)를 넣어준다. 그 후 반응튜브를 캡핑한 후 튜브를 Ar으로 채워준다. 그 후 가스를 뺀 아세토니트릴(0.5ml)을 첨가한 후 **1** (0.20 mmol, 100mol%), **2** (2eq., 200mol%)를 넣어준다. 그 후 가스를 뺀 메탄올(1.5ml)을 넣어 준다. 반응 혼합물을 5W 블루 LED 두개로 조사하고 실온에서 반응을 돌려준다. 반응이 종결된 혼합물의 용매를 제거한 후 관 크로마토 그래피를 통해서 분리/정제해준다. (전개액: ethyl acetate/hexanes)

IV -3-2. 메틸설파이드와 알켄의 giese 반응 방법 (5a – 5s)

Re-sealable pressure tube (13 x 100 mm)에 작은 마그네틱바를 넣고, [Ir(dF(CF₃)ppy)₂(dtbpy)]PF₆ (2.3mg, 0.0020 mmol, 1.0 mol%)를 넣어준다. 그 후 반응튜브를 캡핑한 후 튜브를 Ar으로 채워준다. 그 후 가스를 뺀 메탄올(0.1ml)을 첨가한 후 **4** (0.20 mmol, 100mol%), **2** (2eq., 200mol%)를 넣어준다. 그 후 가스를 뺀 메탄올(0.1ml)을 넣어 준다. 반응 혼합물을 5W 블루 LED 두개로 조사하고 실온에서 반응을 돌려준다. 반응이 종결된 혼합물의 용매를 제거한 후 관 크로마토 그래피를 통해서 분리/정제해준다. (전개액: ethyl acetate/hexanes)

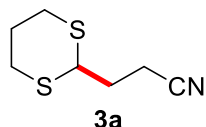
IV -3-2. 메틸설파이드와 알켄의 giese 반응 그램스케일 방법

마그네틱바를넣은 100ml 둥근플라스크에 [Ir(dF(CF₃)ppy)₂(dtbpy)]PF₆ (5.06mg, 0.1mol%)와 벤잘말로노니트릴(1.3596g, 2.0 equiv)을 넣고, 캡핑 후 플라스크를 아르

곤으로 채워준다. 그 후 가스를 뺀 메탄올(11ml)을 첨가한 후 **4a** (1.1g, 4.4mmol)를 넣어 준 후 가스를 뺀 아세토니트릴(11ml)를 넣어준다. 반응혼합물을 40WKessil 블루 LED 로조사하여실온에서 반응을 돌려준다. 후에 TLC 모니터링을 통해서 반응이 완료되면, 혼합물의 용매를 제거한 후 관 크로마토그래피를 통해 분리/정제해 준다.(전개액:ethyl acetate/hexane)

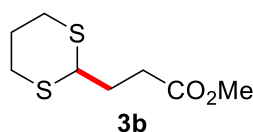
IV -3-3. ¹H-NMR, ¹³C-NMR 스펙트럼 분석 (3a-5s)

3-(1,3-dithian-2-yl)propanenitrile (3a)



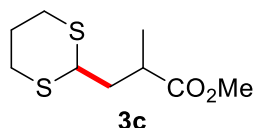
Following the general procedures, **3a** were obtained as a colourless liquid in the yield of 76% (26.3 mg) utilizing [Ir(dF(CF₃)ppy)₂(dtbpy)]PF₆ respectively. R_f = 0.20 (EtOAc:Hexane, 1:4); ¹H NMR (300 MHz, Chloroform-*d*) δ 4.10 (t, *J* = 7.2 Hz, 1H), 2.90 – 2.83 (m, 4H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.18 – 2.06 (m, 1H), 2.12 (td, *J* = 7.3 Hz, 2H), 1.99 – 1.79 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 118.7, 45.0, 30.9, 29.7, 25.6, 14.8.; Compound **3a** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

methyl 3-(1,3-dithian-2-yl)propanoate (3b)



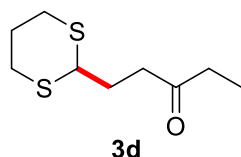
Following the general procedures, **3b** were obtained as a colourless liquid in the yield of 58% (24.1 mg) utilizing [Ir(dF(CF₃)ppy)₂(dtbpy)]PF₆ respectively. R_f = 0.20 (EtOAc:Hexane, 1:4); ¹H NMR (300 MHz, Chloroform-*d*) δ 4.04 (t, *J* = 7.1 Hz, 1H), 3.67 (s, 3H), 2.87 – 2.79 (m, 4H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.15 – 2.03 (m, 3H), 1.87 (dq, *J* = 14.4, 7.4 Hz, 1H).; ¹³C NMR (75 MHz, CDCl₃) δ 173.2, 51.9, 46.3, 31.1, 30.4, 30.0, 25.9.; Compound **3b** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

methyl 3-(1,3-dithian-2-yl)-2-methylpropanoate (3c)



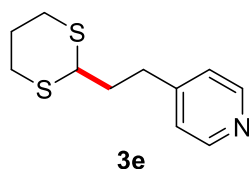
Following the general procedures, **3c** were obtained as a colourless liquid in the yield of 64% (28.3 mg) utilizing [Ir(dF(CF₃)ppy)₂(dtbpy)]PF₆ respectively. R_f = 0.20 (EtOAc:Hexane, 1:4); ¹H NMR (300 MHz, Chloroform-*d*) δ 4.08 – 3.97 (t, 1H), 3.68 (s, 3H), 2.88 – 2.72 (m, 5H), 2.29 – 2.02 (m, 2H), 1.94 – 1.71 (m, 2H), 1.19 (d, *J* = 7.1 Hz, 3H).; ¹³C NMR (75 MHz, CDCl₃) δ 176.3, 52.0, 45.0, 38.8, 36.7, 30.1, 26.0, 17.5.; Compound **3c** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

1-(1,3-dithian-2-yl)pentan-3-one (3d)



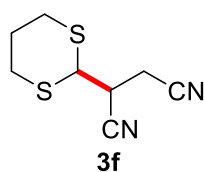
Following the general procedures, **3d** were obtained as a colourless liquid in the yield of 63% (25.9 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.30$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 4.05 (t, $J = 7.0$ Hz, 1H), 2.89 – 2.76 (m, 4H), 2.65 (t, $J = 7.3$ Hz, 2H), 2.45 (q, $J = 7.3$ Hz, 2H), 2.14 – 2.02 (m, 3H), 1.86 (dp, $J = 14.3, 7.2$ Hz, 1H), 1.06 (t, $J = 7.4$ Hz, 3H).; ^{13}C NMR (75 MHz, CDCl_3) δ 210.3, 46.6, 38.9, 36.2, 30.1, 29.2, 26.0, 7.9.; Compound **3d** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:20 ratio.

4-(2-(1,3-dithian-2-yl)ethyl)pyridine (3e)



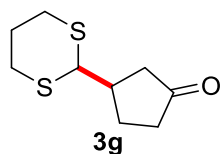
Following the general procedures, **3a** were obtained as a colourless liquid in the yield of 58% (26.3 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.10$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 4.10 (t, $J = 7.2$ Hz, 1H), 2.90 – 2.83 (m, 4H), 2.59 (t, $J = 7.3$ Hz, 2H), 2.18 – 2.06 (m, 1H), 2.12 (td, $J = 7.3$ Hz, 2H), 1.99 – 1.79 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 118.7, 45.0, 30.9, 29.7, 25.6, 14.8.; Compound **3a** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:5 ratio.

(S)-2-(1,3-dithian-2-yl)succinonitrile (3f)



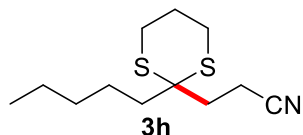
Following the general procedures, **3f** were obtained as a colourless liquid in the yield of 60% (24.0 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 4.13 (dd, $J = 9.6, 7.1$ Hz, 1H), 3.43 (td, $J = 7.1, 6.3$ Hz, 1H), 3.13 – 2.91 (m, 4H), 2.85 (ddt, $J = 14.4, 9.1, 3.1$ Hz, 2H), 2.21 – 1.91 (m, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 116.8, 115.3, 44.1, 34.9, 28.4, 28.3, 24.6, 20.0; Compound **3f** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

(R)-3-(1,3-dithian-2-yl)cyclopentan-1-one (**3g**)



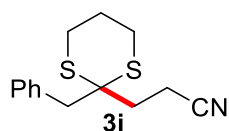
Following the general procedures, **3g** were obtained as a colourless liquid in the yield of 13% (5.4 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 4.11 (d, $J = 7.5$ Hz, 1H), 2.91 – 2.79 (m, 4H), 2.59 – 2.43 (m, 2H), 2.36 – 2.22 (m, 3H), 2.20 – 2.09 (m, 2H), 1.95 – 1.78 (m, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 217.5, 52.4, 42.9, 41.7, 38.8, 30.5, 29.8, 27.2, 26.0.; Compound **3g** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

3-(2-pentyl-1,3-dithian-2-yl)propanenitrile (**3h**)



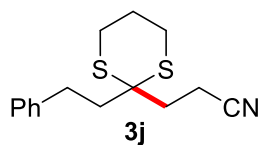
Following the general procedures, **3h** were obtained as a colourless liquid in the yield of 81% (39.6 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 2.85 (ddd, $J = 14.6, 9.7, 3.3$ Hz, 2H), 2.73 (ddd, $J = 14.5, 6.4, 3.5$ Hz, 2H), 2.57 – 2.42 (m, 2H), 2.35 – 2.27 (m, 2H), 2.08 – 1.80 (m, 2H), 1.80 – 1.67 (m, 2H), 1.52 – 1.38 (m, 2H), 1.36 – 1.23 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H).; ^{13}C NMR (75 MHz, CDCl_3) δ 119.7, 52.0, 38.9, 33.7, 31.9, 26.1, 25.0, 23.4, 22.5, 14.1, 13.3.; Compound **3h** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

3-(2-benzyl-1,3-dithian-2-yl)propanenitrile (**3i**)



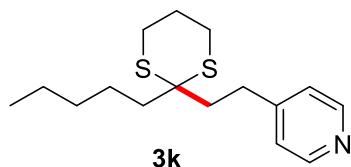
Following the general procedures, **3i** were obtained as a colourless liquid in the yield of 35% (18.3 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 5H), 7.28 – 7.23 (m, 2H), 3.16 (s, 2H), 2.92 – 2.76 (m, 4H), 2.64 – 2.54 (m, 2H), 2.24 – 2.13 (m, 2H), 2.04 – 1.87 (m, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 134.8, 130.9, 128.3, 127.6, 119.8, 52.4, 45.7, 33.6, 26.4, 24.5, 13.6.; Compound **3i** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

3-(2-phenethyl-1,3-dithian-2-yl)propanenitrile (**3j**)



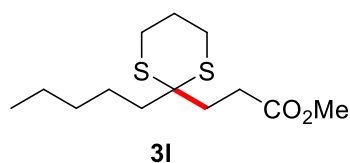
Following the general procedures, **3j** were obtained as a colourless liquid in the yield of 87% (48.3 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 7.21 (td, $J = 6.3, 1.6$ Hz, 3H), 2.95 – 2.75 (m, 6H), 2.62 – 2.53 (m, 2H), 2.41 – 2.33 (m, 2H), 2.13 – 2.05 (m, 2H), 2.05 – 1.87 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.2, 128.7, 128.5, 126.4, 119.7, 51.9, 41.1, 34.1, 30.6, 26.1, 24.8, 13.3.; Compound **3j** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-(2-(2-pentyl-1,3-dithian-2-yl)ethyl)pyridine (**3k**)



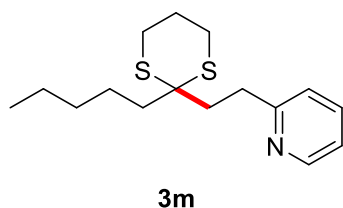
Following the general procedures, **3k** were obtained as a colourless liquid in the yield of 93% (55.0 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 8.56 – 8.43 (m, 2H), 7.21 – 7.08 (m, 2H), 2.91 – 2.79 (m, 4H), 2.79 – 2.71 (m, 2H), 2.23 – 2.12 (m, 2H), 2.07 – 1.82 (m, 4H), 1.55 – 1.41 (m, 2H), 1.41 – 1.25 (m, 4H), 0.96 – 0.84 (t, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.4, 149.6, 124.1, 53.0, 39.0, 38.7, 32.1, 30.5, 26.1, 25.5, 23.8, 22.7, 14.2.; Compound **3k** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

methyl 3-(2-pentyl-1,3-dithian-2-yl)propanoate (**3l**)



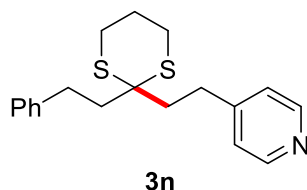
Following the general procedures, **3l** were obtained as a colourless liquid in the yield of 51% (28.2 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 3.68 (s, 3H), 2.92 (ddd, $J = 14.6, 9.9, 3.2$ Hz, 2H), 2.71 (ddd, $J = 14.5, 6.5, 3.3$ Hz, 2H), 2.52 – 2.41 (m, 2H), 2.35 – 2.23 (m, 2H), 2.09 – 1.80 (m, 2H), 1.80 – 1.69 (m, 2H), 1.53 – 1.38 (m, 2H), 1.29 (ddd, $J = 13.0, 10.7, 5.5$ Hz, 4H), 0.89 (t, $J = 6.9$ Hz, 3H).; ^{13}C NMR (75 MHz, CDCl_3) δ 173.9, 52.5, 51.8, 38.9, 32.6, 32.0, 29.8, 26.0, 25.3, 23.3, 22.5, 14.1.; Compound **3l** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

2-(2-(2-pentyl-1,3-dithian-2-yl)ethyl)pyridine (**3m**)



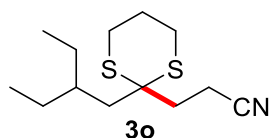
Following the general procedures, **3m** were obtained as a colourless liquid in the yield of 48% (28.5 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 8.53 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 7.60 (td, $J = 7.6, 1.9$ Hz, 1H), 7.18 (dt, $J = 7.8, 1.1$ Hz, 1H), 7.11 (ddd, $J = 7.6, 4.9, 1.2$ Hz, 1H), 3.01 – 2.85 (m, 4H), 2.77 (ddd, $J = 14.5, 6.7, 3.6$ Hz, 2H), 2.42 – 2.30 (m, 2H), 2.07 – 1.83 (m, 4H), 1.58 – 1.43 (m, 2H), 1.40 – 1.21 (m, 4H), 0.89 (t, $J = 6.9$ Hz, 3H).; ^{13}C NMR (75 MHz, CDCl_3) δ 161.6, 149.0, 137.0, 123.3, 121.4, 53.3, 38.9, 38.0, 33.5, 32.2, 26.2, 25.6, 23.7, 22.7, 14.2.; Compound **3m** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-(2-(2-phenethyl-1,3-dithian-2-yl)ethyl)pyridine (3n)



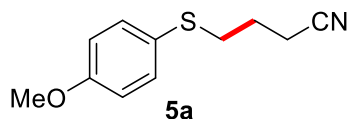
Following the general procedures, **3n** were obtained as a colourless liquid in the yield of 59% (38.9 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); $^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 8.50 (d, $J = 5.3$ Hz, 2H), 7.35 – 7.27 (m, 2H), 7.21 (dq, $J = 6.9, 4.1, 3.3$ Hz, 3H), 7.16 – 7.10 (m, 2H), 2.83 (ddd, $J = 17.2, 7.6, 4.0$ Hz, 8H), 2.30 – 2.16 (m, 4H), 1.98 (qd, $J = 7.1, 4.3$ Hz, 2H).; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 151.0, 149.7, 141.6, 128.6, 128.5, 126.2, 124.0, 52.9, 40.6, 39.4, 30.9, 30.4, 26.1, 25.2., CDCl_3 ; Compound **3n** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

3-(2-(2-ethylbutyl)-1,3-dithian-2-yl)propanenitrile (3o)



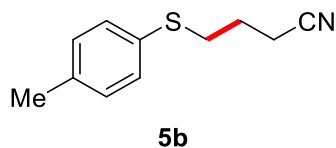
Following the general procedures, **3o** were obtained as a colourless liquid in the yield of 70% (35.9 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); $^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 2.88 (ddd, $J = 14.8, 10.3, 3.1$ Hz, 2H), 2.72 (ddd, $J = 14.5, 6.1, 3.3$ Hz, 2H), 2.58 – 2.47 (m, 2H), 2.39 – 2.27 (m, 2H), 2.07 – 1.80 (m, 2H), 1.69 – 1.54 (m, 3H), 1.48 – 1.28 (m, 4H), 0.86 (t, $J = 7.4$ Hz, 6H).; $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 119.9, 52.9, 43.0, 36.2, 34.5, 27.1, 26.3, 24.7, 13.6, 10.7.; Compound **3o** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-((4-methoxyphenyl)thio)butanenitrile (5a)



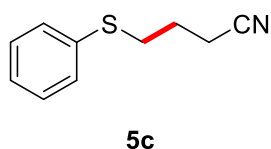
Following the general procedures, **5a** were obtained as a colourless liquid in the yield of 76% (31.6 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); $^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 2H), 6.93 – 6.79 (m, 2H), 3.80 (s, 3H), 2.91 (t, $J = 6.8$ Hz, 2H), 2.50 (t, $J = 7.1$ Hz, 2H), 1.88 (p, $J = 7.0$ Hz, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 159.5, 134.1, 124.8, 119.3, 114.9, 55.5, 34.7, 24.9, 15.9.; Compound **5a** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-(*p*-tolylthio)butanenitrile (**5b**)



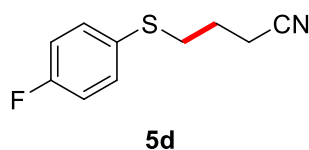
Following the general procedures, **5b** were obtained as a colourless liquid in the yield of 48% (18.3 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.23 (m, 2H), 7.17 – 7.06 (m, 2H), 2.98 (t, $J = 6.8$ Hz, 2H), 2.50 (t, $J = 7.1$ Hz, 2H), 2.33 (s, 3H), 1.92 (tt, $J = 7.1, 6.8$ Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 137.2, 131.1, 130.9, 130.1, 119.2, 33.4, 29.8, 24.9, 21.2, 16.0.; Compound **3b** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:25 ratio.

4-(phenylthio)butanenitrile (**5c**)



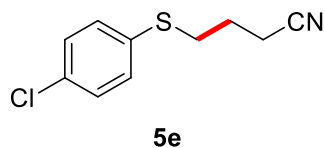
Following the general procedures, **5c** were obtained as a colourless liquid in the yield of 51% (18.1 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 4H), 7.26 – 7.19 (m, 1H), 3.04 (t, $J = 6.8$ Hz, 2H), 2.52 (t, $J = 7.1$ Hz, 2H), 1.96 (tt, $J = 7.1, 6.8$ Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 134.8, 130.3, 129.3, 126.9, 119.2, 32.7, 24.9, 16.0.; Compound **3a** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:25 ratio.

4-((4-fluorophenyl)thio)butanenitrile (**5d**)



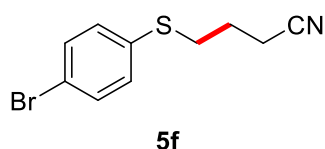
Following the general procedures, **5d** were obtained as a colourless liquid in the yield of 66% (25.8 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 2H), 7.08 – 6.95 (m, 2H), 2.98 (t, $J = 6.9$ Hz, 2H), 2.51 (t, $J = 7.0$ Hz, 2H), 1.92 (tt, $J = 6.9$ Hz, 7.0 Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 133.4, 133.3, 129.7, 119.1, 116.6, 116.3, 34.0, 29.8, 24.9, 16.0.; Compound **3a** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-((4-chlorophenyl)thio)butanenitrile (**5e**)



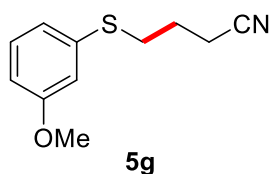
Following the general procedures, **5e** were obtained as a colourless liquid in the yield of 65% (27.6 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.29 (s, 4H), 3.02 (t, $J = 6.9$ Hz, 2H), 2.51 (t, $J = 7.0$ Hz, 2H), 1.95 (tt, $J = 7.0$ Hz, 6.9 Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 133.4, 133.0, 131.5, 129.4, 119.0, 32.9, 24.8, 16.0.; Compound **3a** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-((4-bromophenyl)thio)butanenitrile (**5f**)



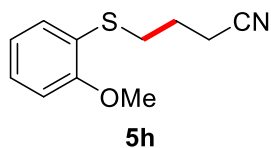
Following the general procedures, **5f** were obtained as a colourless liquid in the yield of 57% (29.2 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.48 – 7.38 (m, 2H), 7.25 – 7.19 (m, 2H), 3.02 (t, $J = 6.9$ Hz, 2H), 2.51 (t, $J = 7.0$ Hz, 2H), 1.95 (tt, $J = 7.0$, 6.9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.1, 132.4, 131.7, 120.8, 119.0, 32.7, 24.8, 16.1.; Compound **5f** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-((3-methoxyphenyl)thio)butanenitrile (**5g**)



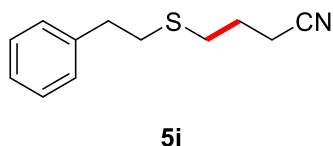
Following the general procedures, **5g** were obtained as a colourless liquid in the yield of 83% (34.4 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.22 (t, $J = 8.0$ Hz, 1H), 6.97 – 6.85 (m, 2H), 6.76 (ddd, $J = 8.3, 2.5, 0.9$ Hz, 1H), 3.80 (s, 3H), 3.04 (t, $J = 6.8$ Hz, 2H), 2.52 (t, $J = 7.1$ Hz, 2H), 1.97 (tt, $J = 7.1$ Hz, 6.8 Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 160.0, 136.1, 130.0, 121.9, 119.1, 115.3, 112.3, 55.4, 32.3, 24.9, 16.0.; Compound **5g** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-((2-methoxyphenyl)thio)butanenitrile (**5h**)



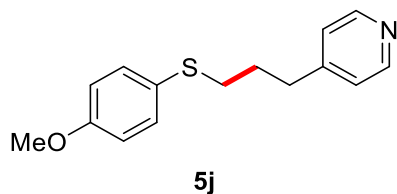
Following the general procedures, **5h** were obtained as a colourless liquid in the yield of 78% (32.4 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.32 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.25 (ddd, $J = 8.2, 7.5, 1.7$ Hz, 1H), 6.97 – 6.84 (m, 2H), 3.90 (s, 3H), 3.01 (t, $J = 6.8$ Hz, 2H), 2.54 (t, $J = 7.1$ Hz, 2H), 1.92 (tt, $J = 7.1, 6.8$ Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 158.3, 131.7, 128.6, 122.4, 121.2, 119.4, 110.9, 55.9, 31.3, 25.0, 16.1.; Compound **5h** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-(phenethylthio)butanenitrile (**5i**)



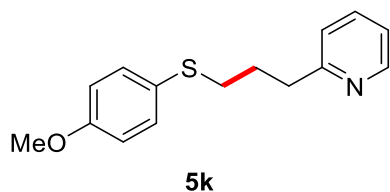
Following the general procedures, **5i** were obtained as a colourless liquid in the yield of 59% (24.3 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 2.94 – 2.84 (m, 2H), 2.82 – 2.74 (m, 2H), 2.65 (t, $J = 6.9$ Hz, 2H), 2.48 (t, $J = 7.1$ Hz, 2H), 1.92 (tt, $J = 7.1, 6.9$ Hz, 2H).; ^{13}C NMR (75 MHz, CDCl_3) δ 140.3, 128.7, 128.6, 126.6, 119.3, 36.3, 33.8, 30.9, 25.3, 16.1.; Compound **5i** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

4-(3-((4-methoxyphenyl)thio)propyl)pyridine (**5j**)



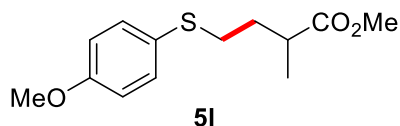
Following the general procedures, **5j** were obtained as a colourless liquid in the yield of 60% (31.2 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*); ^{13}C NMR (75 MHz, CDCl_3) δ 159.0, 150.4, 149.8, 133.5, 125.9, 123.9, 114.6, 55.3, 35.1, 33.7, 29.6.; Compound **5j** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:5 ratio.

2-(3-((4-methoxyphenyl)thio)propyl)pyridine (**5k**)



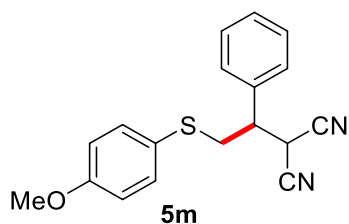
Following the general procedures, **5k** were obtained as a colourless liquid in the yield of 66% (34.4 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform- d) δ 7.44 – 7.28 (m, 2H), 6.89 – 6.79 (m, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 2.89 – 2.73 (m, 2H), 2.71 – 2.56 (m, 1H), 1.95 (dtd, $J = 13.8, 8.0, 6.8$ Hz, 1H), 1.73 – 1.58 (m, 1H), 1.15 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 161.3, 159.0, 149.4, 136.5, 133.3, 126.6, 123.1, 121.3, 114.7, 55.5, 37.1, 35.4, 29.3.; Compound **5k** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:5 ratio.

methyl 4-((4-methoxyphenyl)thio)-2-methylbutanoate (**5l**)



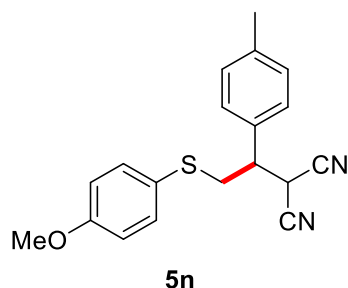
Following the general procedures, **5l** were obtained as a colourless liquid in the yield of 36% (18.3 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform- d) δ 7.40 – 7.28 (m, 2H), 6.89 – 6.79 (m, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 2.89 – 2.73 (m, 2H), 2.71 – 2.56 (m, 1H), 1.95 (dtd, $J = 13.8, 8.0, 6.8$ Hz, 1H), 1.73 – 1.58 (m, 1H), 1.15 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 176.7, 159.1, 133.4, 126.2, 114.7, 55.5, 51.8, 38.4, 33.6, 33.2, 17.1.; Compound **5l** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

(*R*)-2-(2-((4-methoxyphenyl)thio)-1-phenylethyl)malononitrile (**5m**)



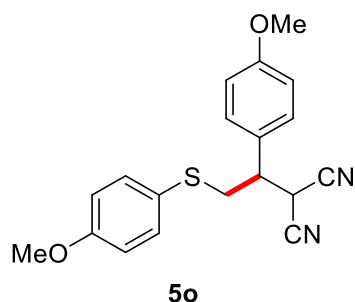
Following the general procedures, **5m** were obtained as a colourless liquid in the yield of 99% (61.1 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform- d) δ 7.44 – 7.28 (m, 7H), 6.94 – 6.85 (m, 2H), 4.63 (d, $J = 4.5$ Hz, 1H), 3.83 (s, 3H), 3.42 – 3.17 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.1, 135.6, 134.4, 129.4, 129.4, 128.1, 123.2, 115.3, 112.1, 111.3, 55.5, 45.6, 38.3, 27.9.; Compound **5m** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

(R)-2-(2-((4-methoxyphenyl)thio)-1-(p-tolyl)ethyl)malononitrile (5n)



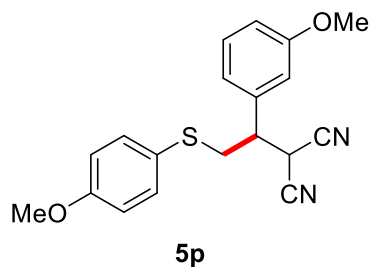
Following the general procedures, **5n** were obtained as a colourless liquid in the yield of 97% (62.6 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.41 – 7.31 (m, 2H), 7.24 – 7.15 (m, 4H), 6.93 – 6.84 (m, 2H), 4.60 (d, $J = 4.5$ Hz, 1H), 3.82 (s, 3H), 3.41 – 3.14 (m, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 159.9, 139.2, 134.2, 132.5, 129.9, 127.8, 123.2, 115.2, 112.2, 111.3, 55.4, 45.1, 38.2, 28.0, 21.2.; Compound **5n** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

(R)-2-(1-(4-methoxyphenyl)-2-((4-ethoxyphenyl)thio)ethyl)malononitrile (5o)



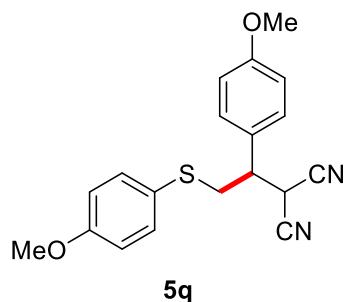
Following the general procedures, **5o** were obtained as a colourless liquid in the yield of 99% (67.1 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 2H), 7.25 – 7.20 (m, 2H), 6.94 – 6.86 (m, 4H), 4.60 (d, $J = 4.4$ Hz, 1H), 3.82 (s, 6H), 3.81 (s, 3H), 3.39 – 3.13 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.3, 160.0, 134.4, 129.3, 127.5, 123.3, 115.3, 114.7, 112.2, 111.3, 55.5, 55.4, 45.1, 38.4, 28.2; Compound **5o** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:10 ratio.

(R)-2-(1-(3-methoxyphenyl)-2-((4-methoxyphenyl)thio)ethyl)malononitrile (5p)



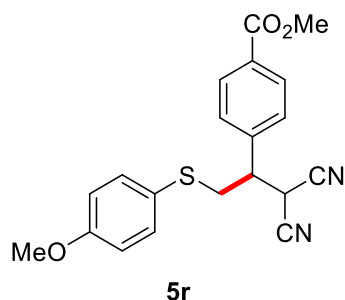
Following the general procedures, **5p** were obtained as a colourless liquid in the yield of 99% (67.2 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.28 (m, 3H), 6.90 (ddt, $J = 9.7, 7.6, 2.4$ Hz, 4H), 6.81 (t, $J = 2.1$ Hz, 1H), 4.61 (d, $J = 4.7$ Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.40 – 3.14 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.2, 160.1, 137.1, 134.4, 130.5, 123.2, 120.2, 115.3, 114.7, 114.0, 112.1, 111.3, 55.5, 55.5, 45.7, 38.3, 27.9.; Compound **5p** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:10 ratio.

(R)-2-(1-(4-methoxyphenyl)-2-((4-methoxyphenyl)thio)ethyl)malononitrile (5q)



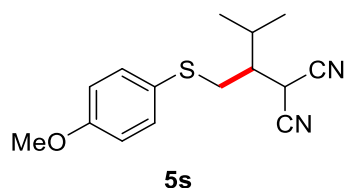
Following the general procedures, **5q** were obtained as a colourless liquid in the yield of 97% (65.7 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 2H), 7.25 – 7.20 (m, 2H), 6.94 – 6.86 (m, 4H), 4.60 (d, $J = 4.4$ Hz, 1H), 3.82 (s, 6H), 3.81 (s, 3H), 3.39 – 3.13 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 160.3, 160.0, 134.4, 129.3, 127.5, 123.3, 115.3, 114.7, 112.2, 111.3, 55.5, 55.4, 45.1, 38.4, 28.2.; Compound **5q** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:10 ratio.

methyl (R)-4-(1,1-dicyano-3-((4-methoxyphenyl)thio)propan-2-yl)benzoate (5r)



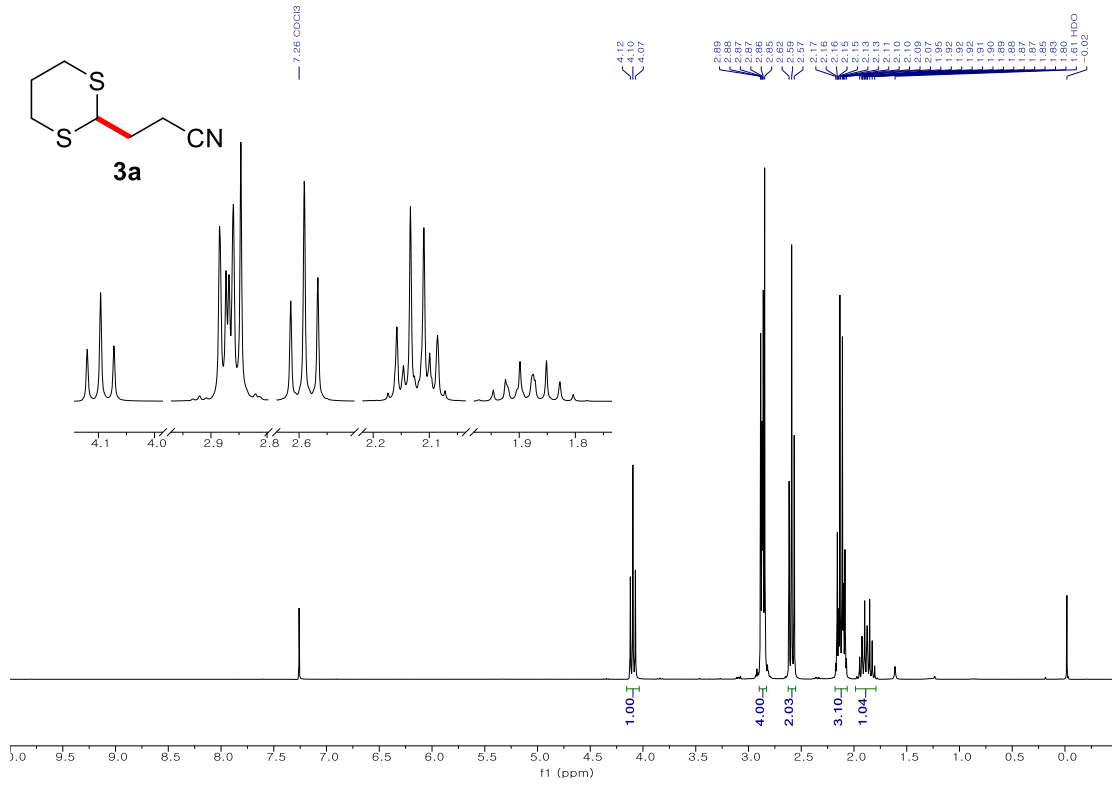
Following the general procedures, **5r** were obtained as a colourless liquid in the yield of 97% (71.1 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 8.11 – 8.02 (m, 2H), 7.41 – 7.29 (m, 4H), 6.93 – 6.83 (m, 2H), 4.63 (d, $J = 4.2$ Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.38 – 3.23 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.36, 160.15, 140.38, 134.49, 131.17, 130.52, 128.26, 122.82, 115.35, 111.78, 111.00, 55.50, 52.42, 45.52, 38.11, 27.65.; Compound **5r** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:15 ratio.

(S)-2-(1-((4-methoxyphenyl)thio)-3-methylbutan-2-yl)malononitrile (5s)

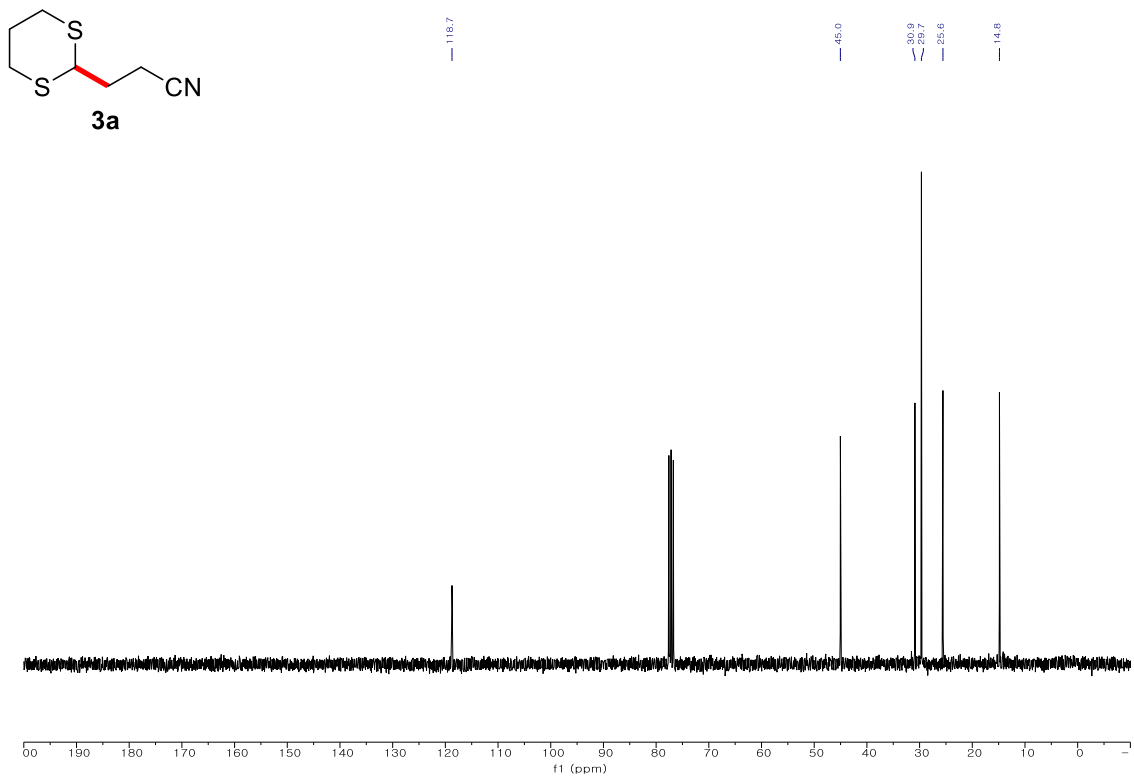


Following the general procedures, **5s** were obtained as a colourless liquid in the yield of 40% (22.0 mg) utilizing $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ respectively. $R_f = 0.20$ (EtOAc:Hexane, 1:4); ^1H NMR (300 MHz, Chloroform-*d*) δ 7.67 – 7.57 (m, 2H), 7.14 – 7.02 (m, 2H), 3.88 (s, 3H), 2.94 – 2.63 (m, 2H), 2.57 (dq, $J = 8.7, 4.2$ Hz, 1H), 2.37 – 2.22 (m, 1H), 1.14 (d, $J = 6.8$ Hz, 3H), 1.08 (d, $J = 6.8$ Hz, 3H), 0.96 (d, $J = 6.8$ Hz, 1H), 0.84 (d, $J = 6.8$ Hz, 1H).; ^{13}C NMR (75 MHz, CDCl_3) δ 162.9, 126.1, 125.9, 115.4, 115.4, 112.1, 55.8, 54.5, 42.4, 30.7, 25.7, 21.1, 18.3.; Compound **5s** was purified by flash chromatography on silica gel using eluent (EtOAc:Hexane) in 1:25 ratio.

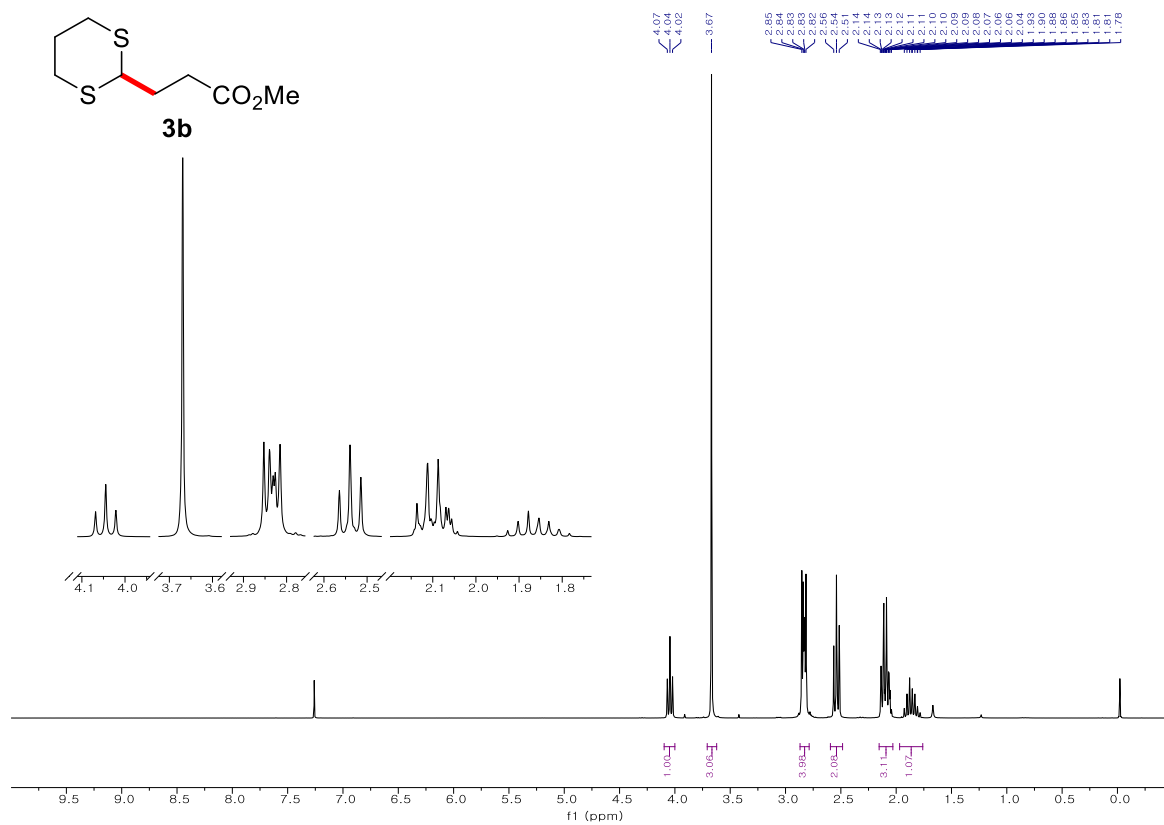
$^1\text{H-NMR}$, $^{13}\text{C-NMR}$ 스펙트럼



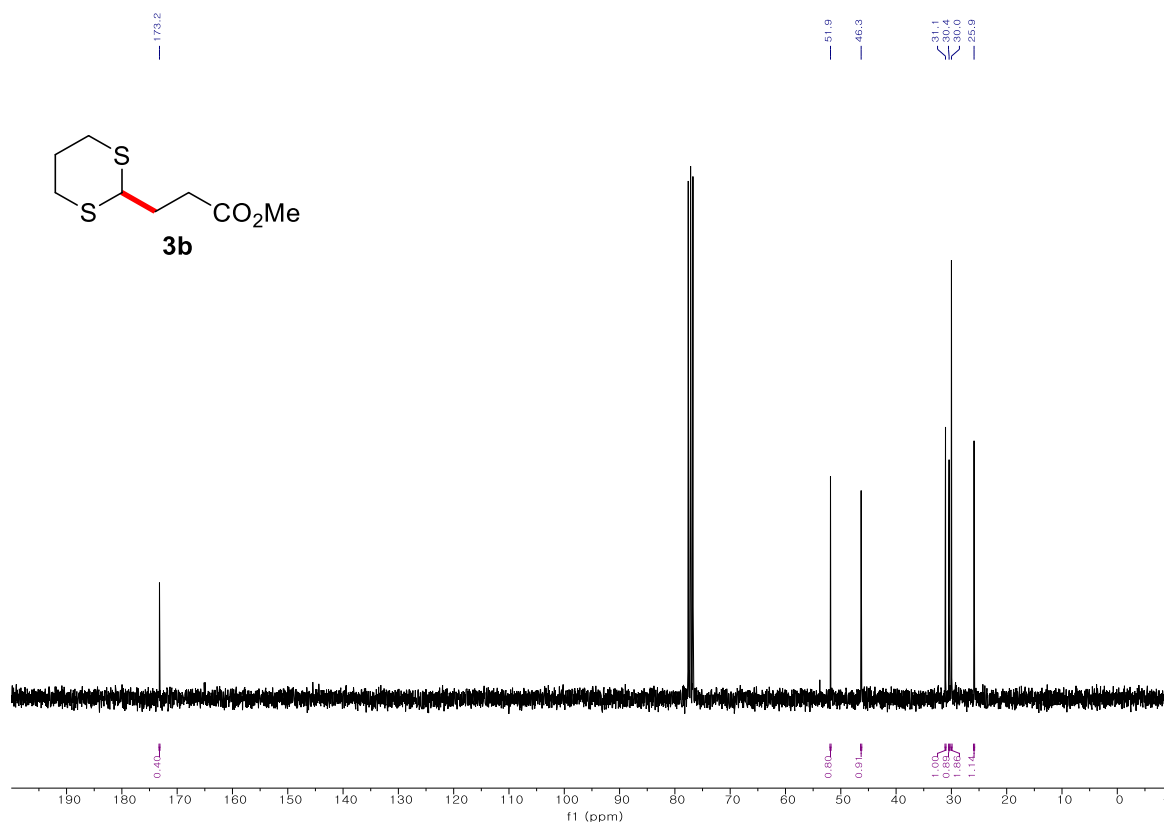
$^1\text{H-NMR}$ (300 MHz, CDCl_3) of **3a**



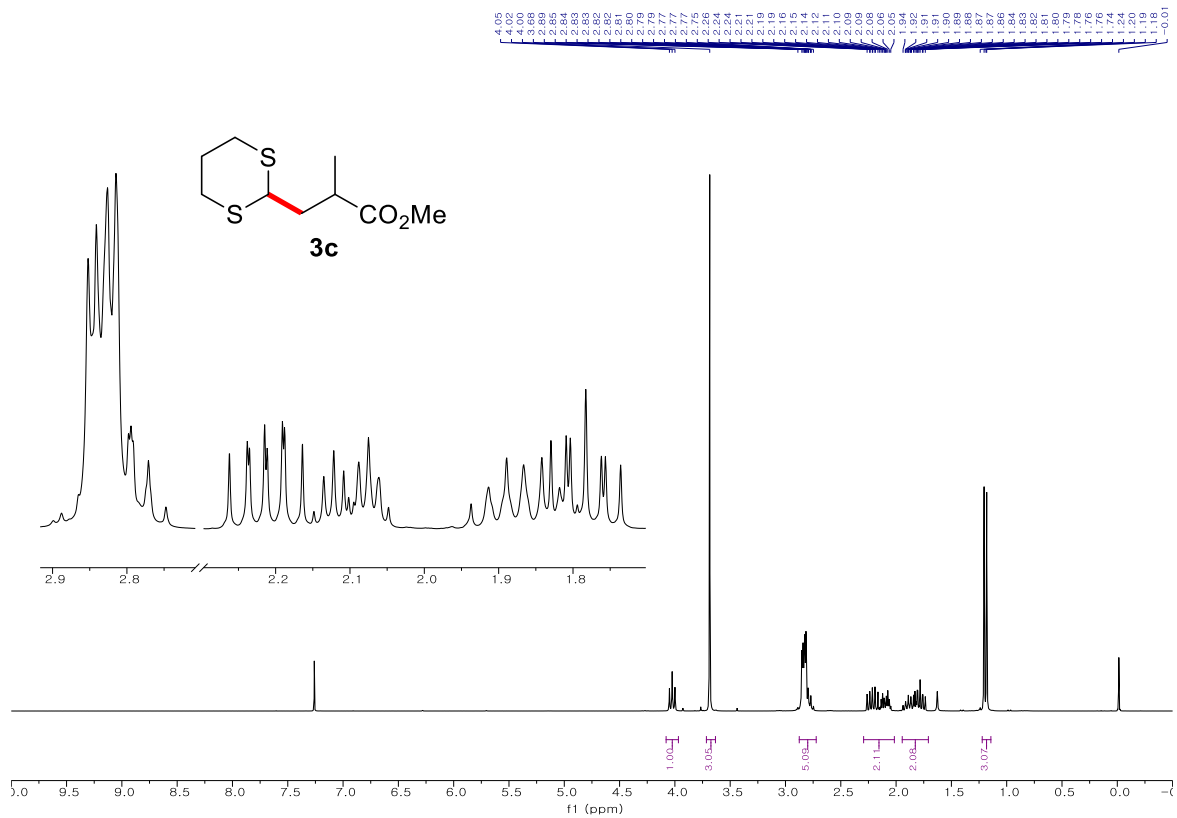
$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of **3a**



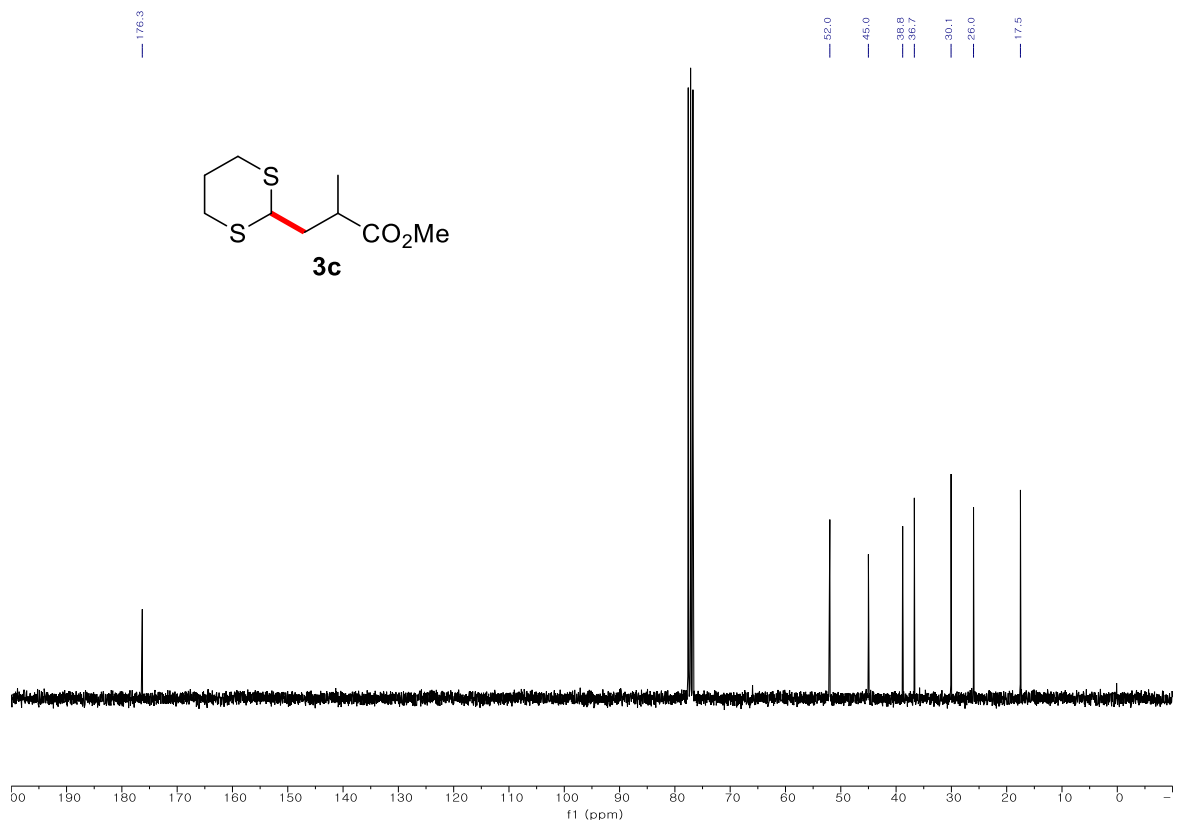
1H-NMR (300 MHz, CDCl₃) of **3b**



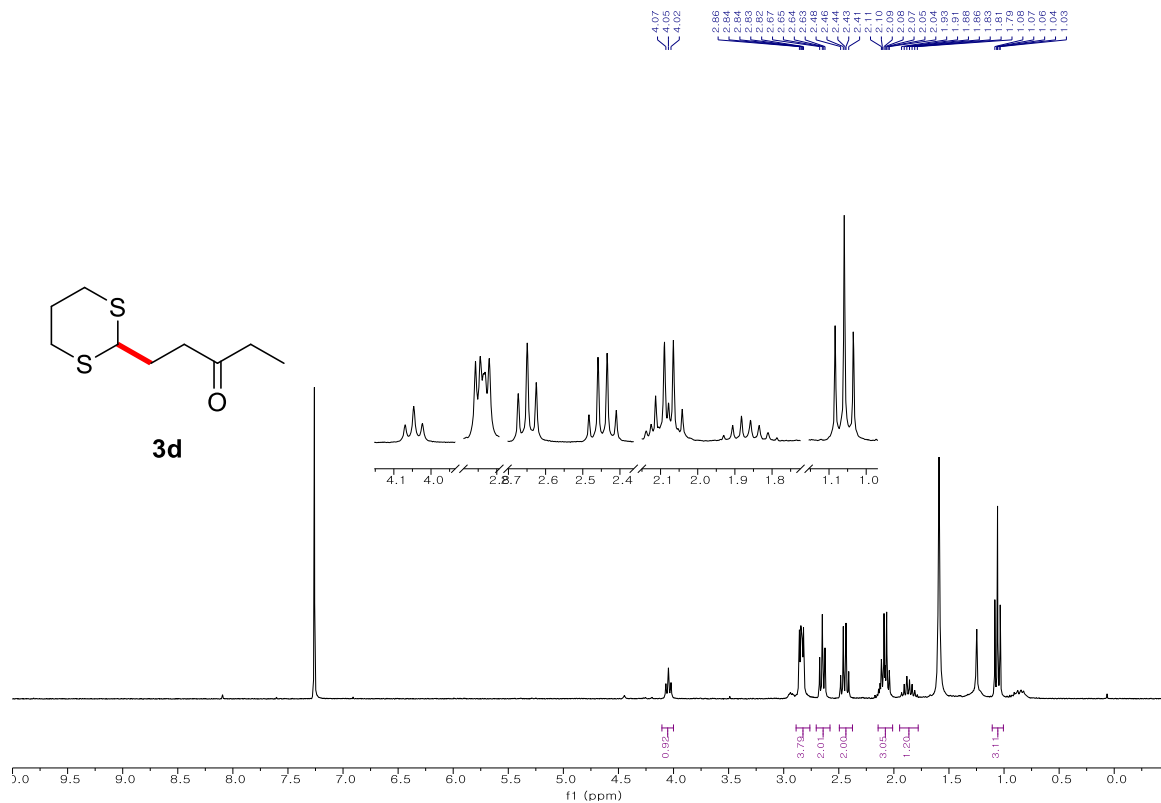
13C-NMR (75 MHz, CDCl₃) of **3b**



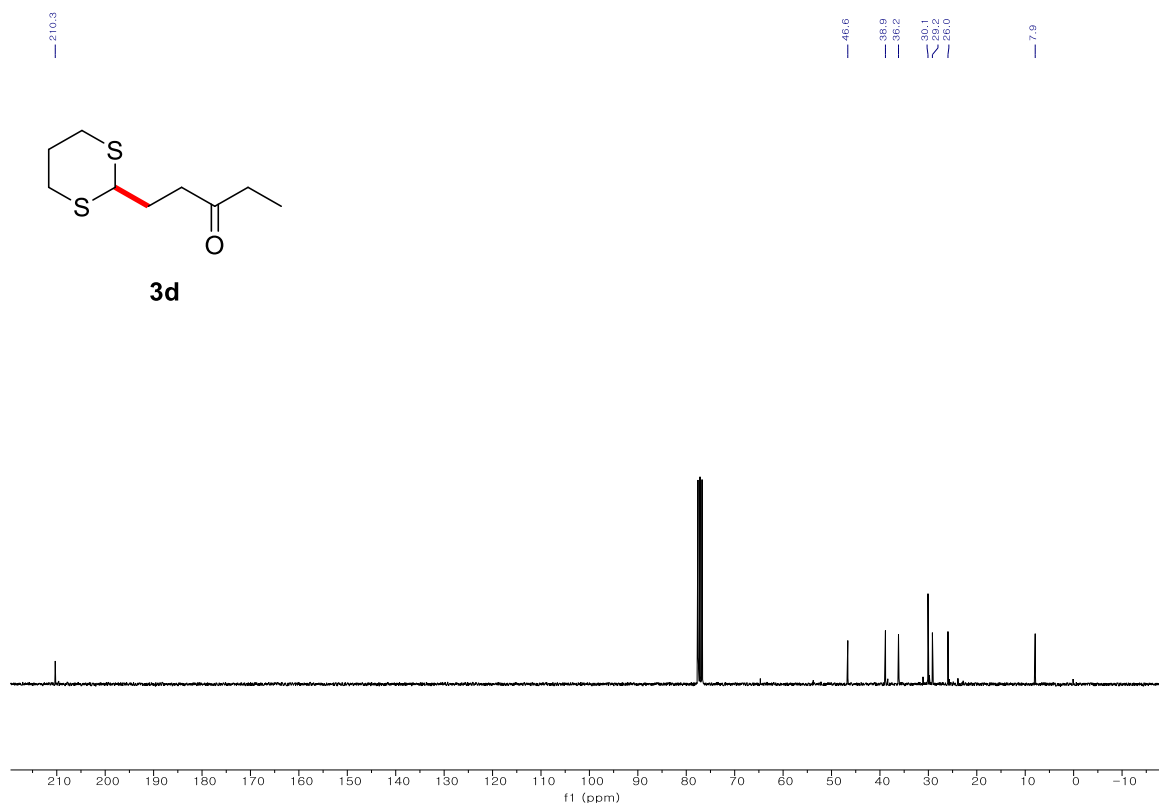
¹H-NMR (300 MHz, CDCl₃) of 3c



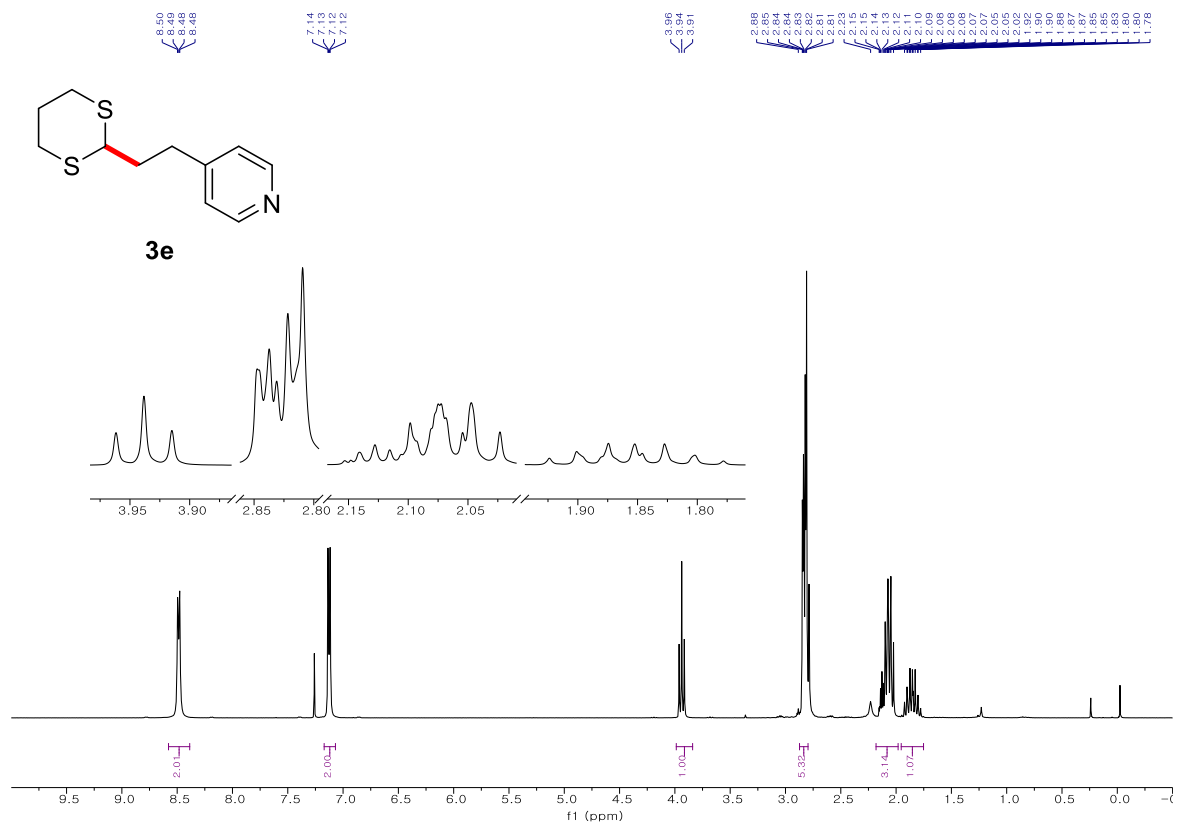
¹³C-NMR (75 MHz, CDCl₃) of 3c



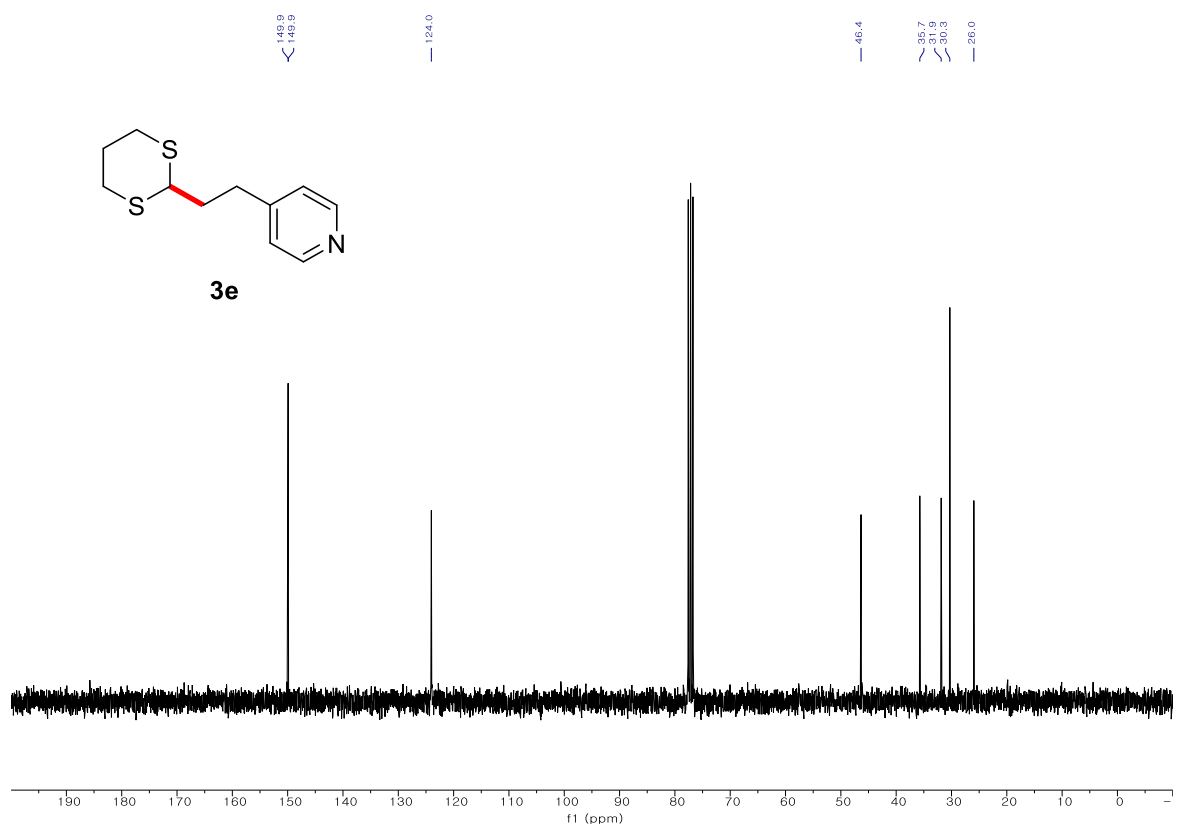
1H-NMR (300 MHz, CDCl₃) of 3d



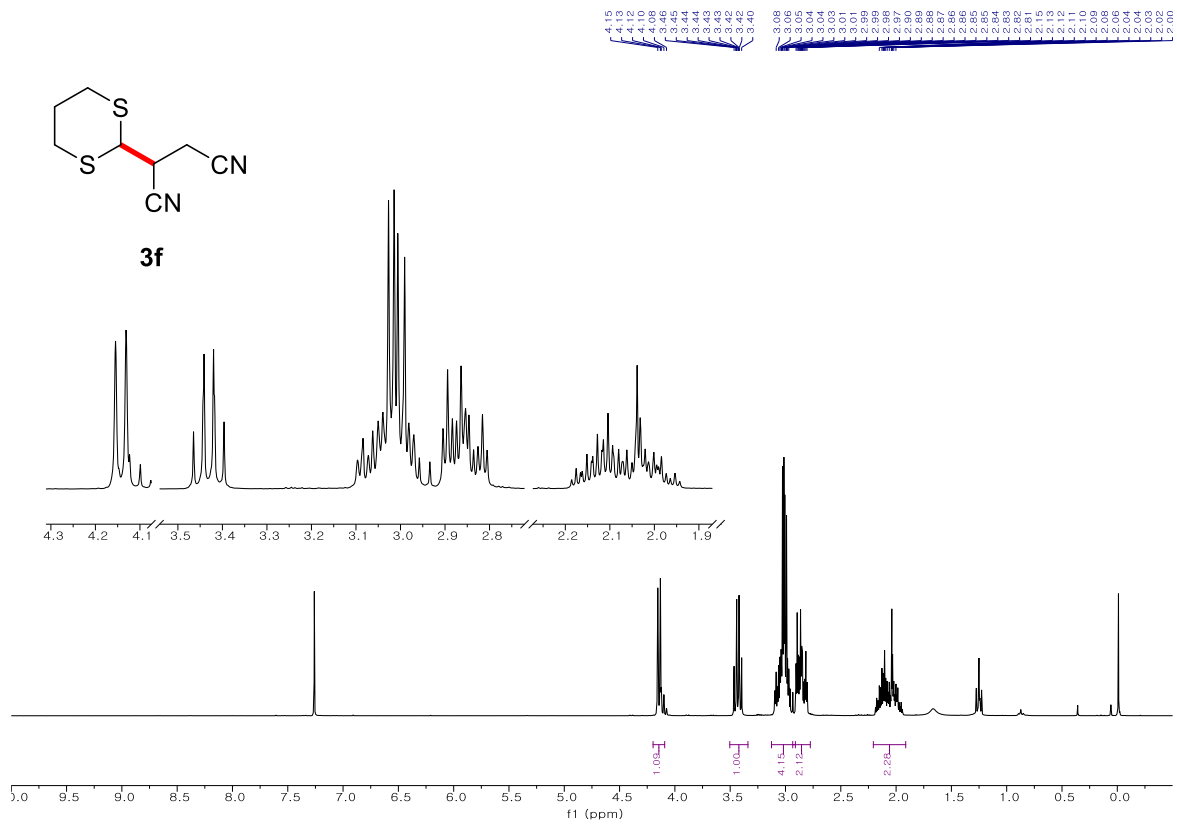
13C-NMR (75 MHz, CDCl₃) of 3d



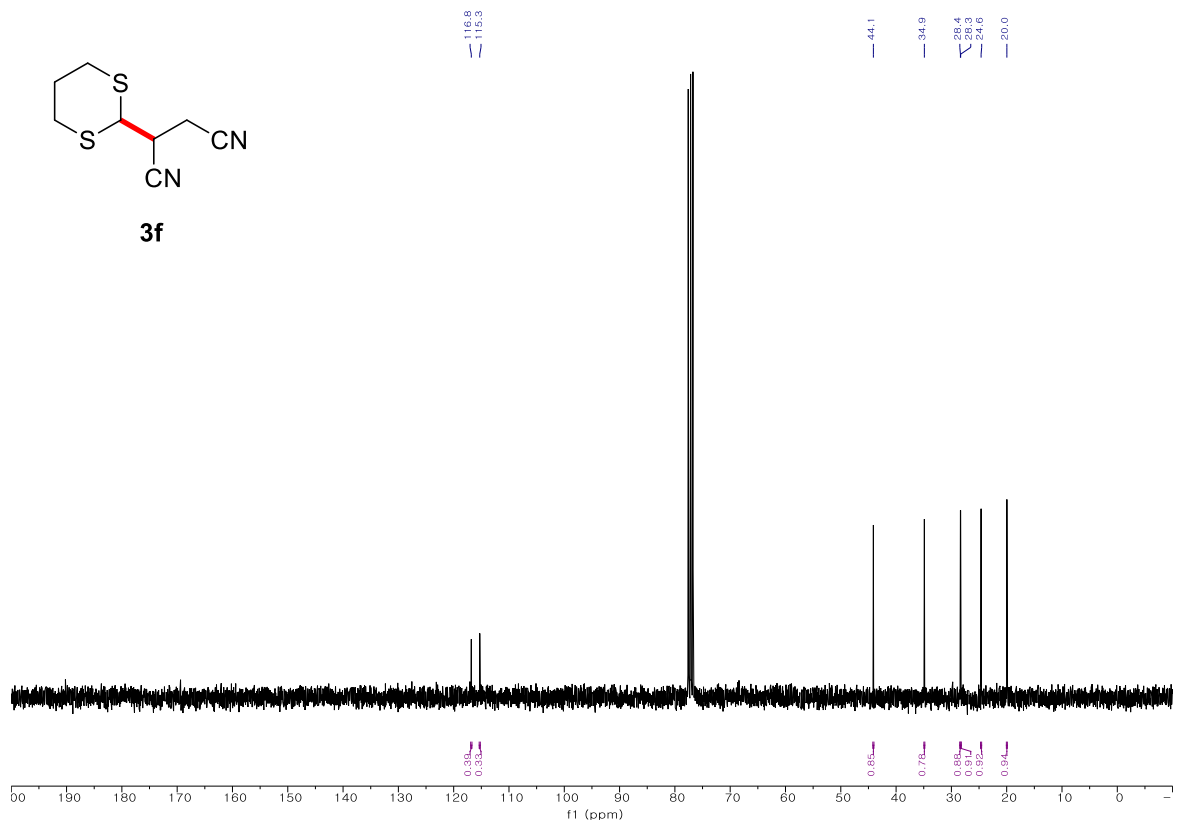
¹H-NMR (300 MHz, CDCl₃) of **3e**



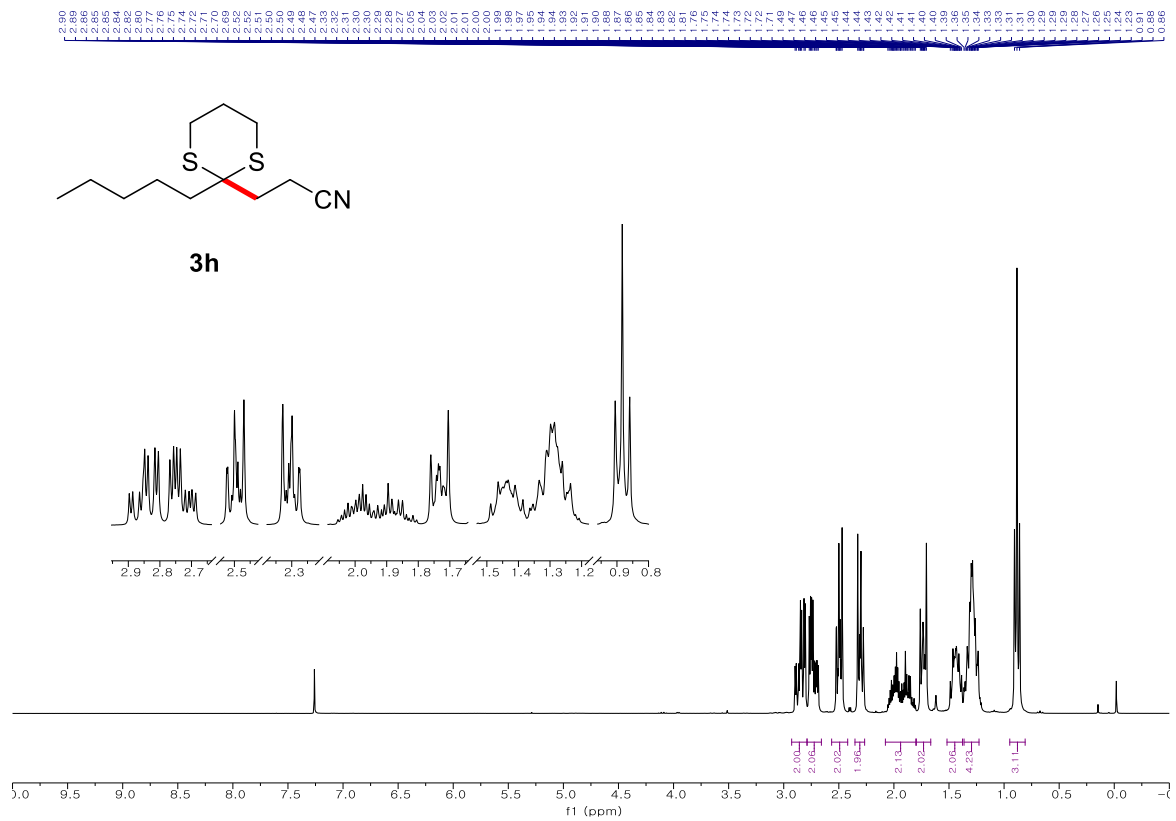
¹³C-NMR (75 MHz, CDCl₃) of **3e**



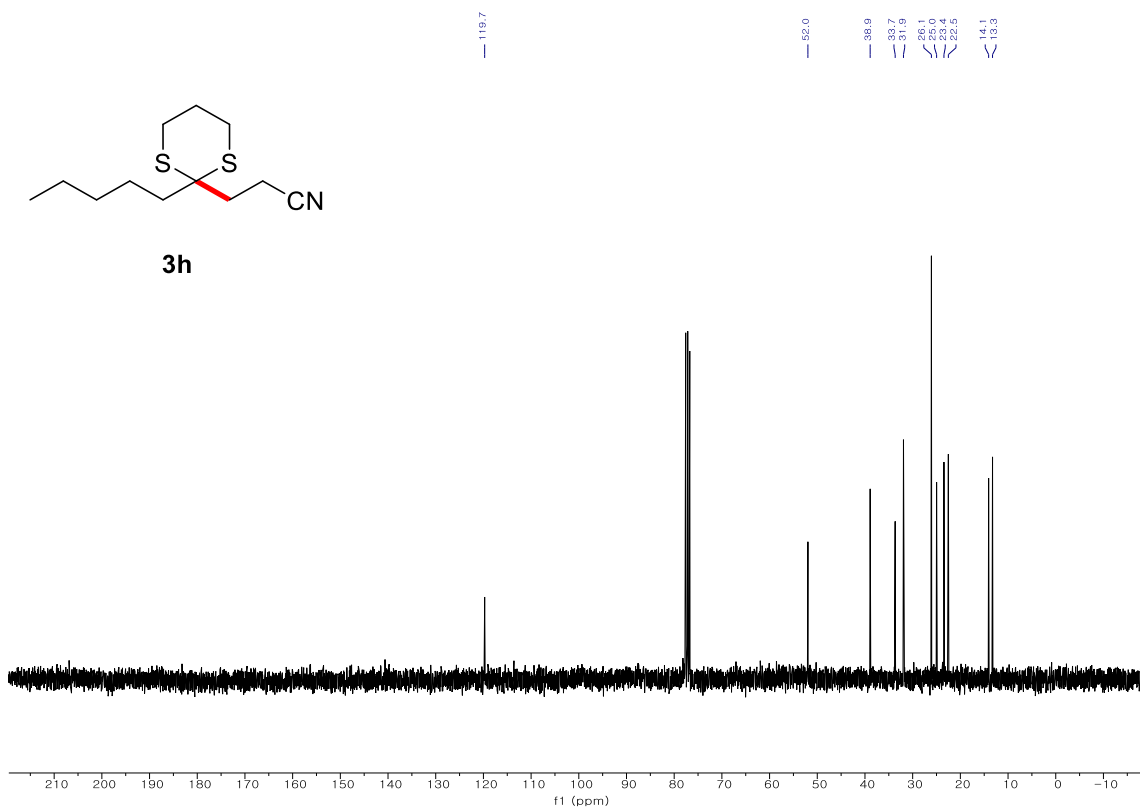
1H-NMR (300 MHz, CDCl₃) of 3f



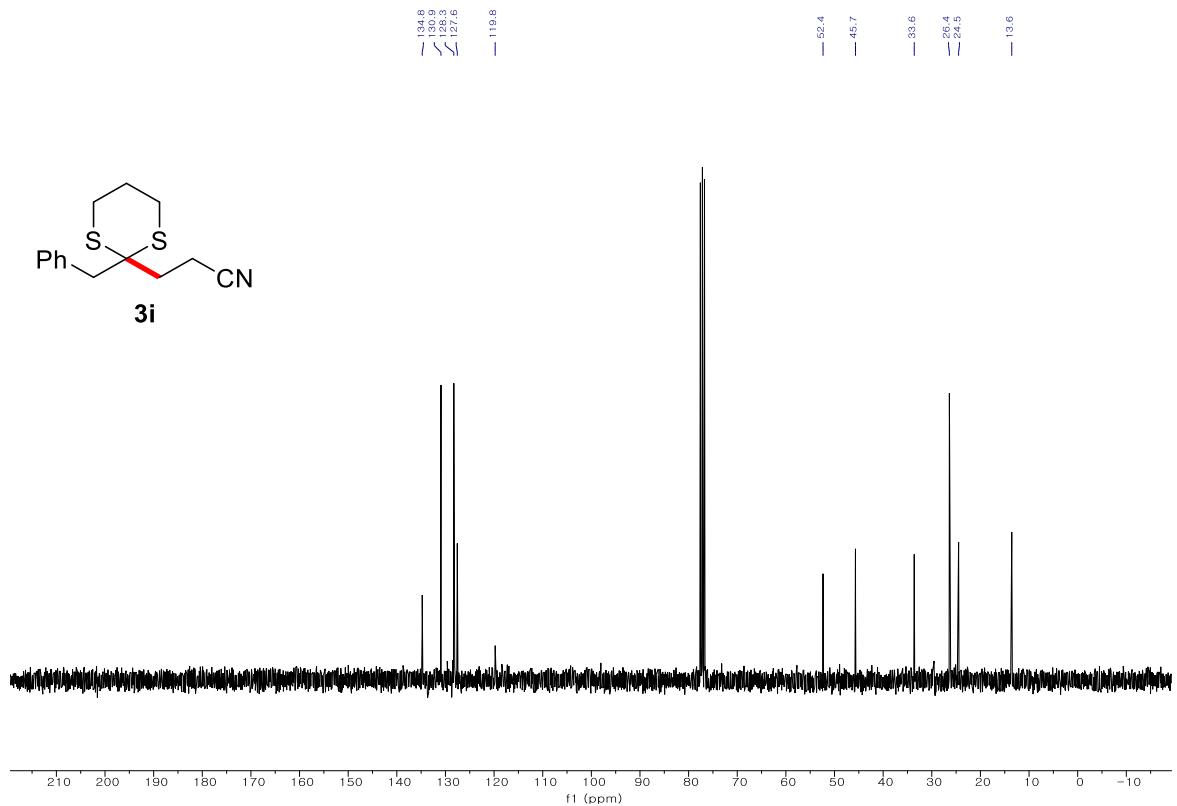
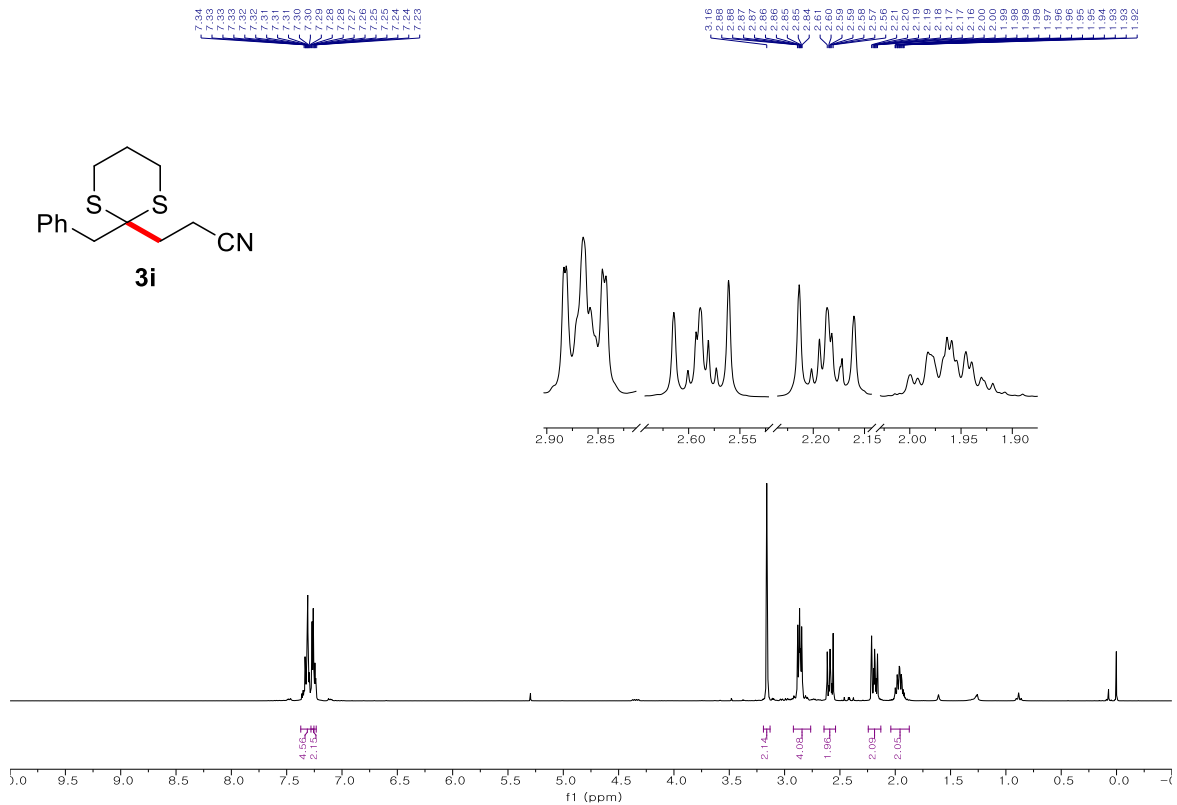
13C-NMR (75 MHz, CDCl₃) of 3f

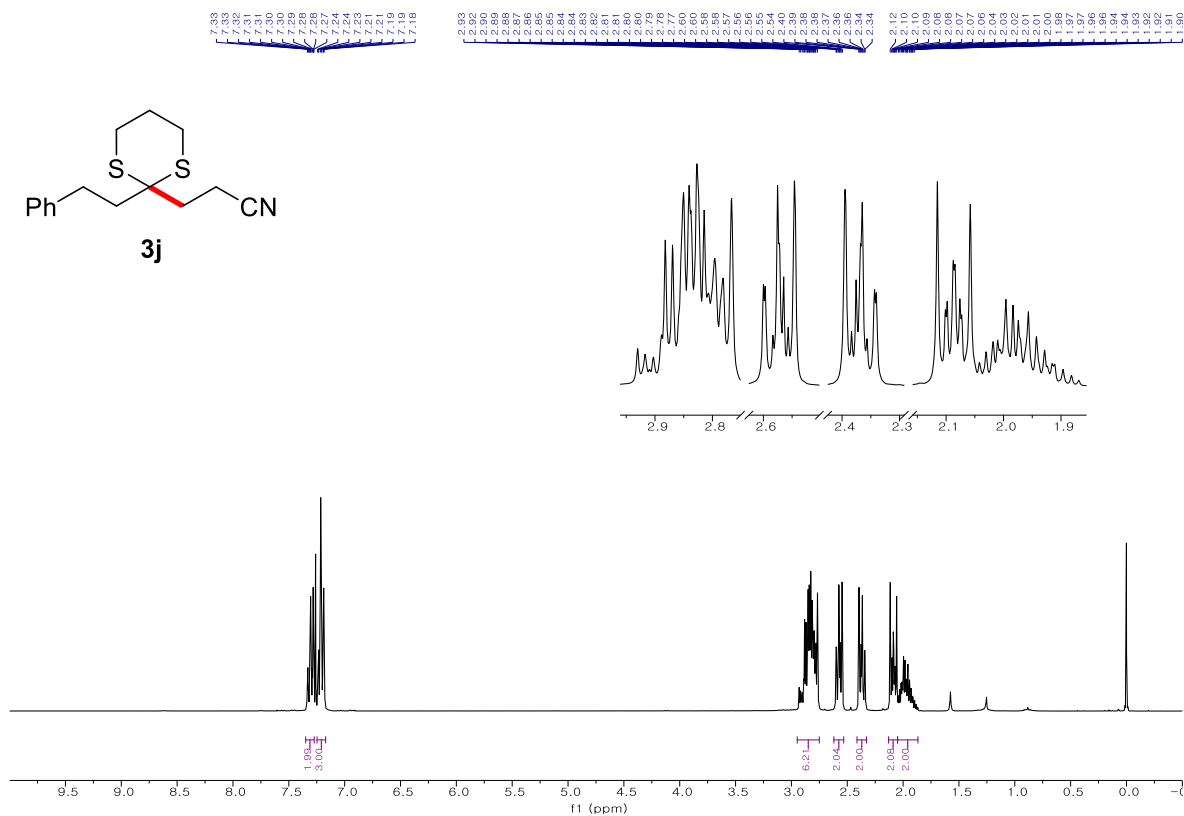


$^1\text{H-NMR}$ (300 MHz, CDCl_3) of **3h**

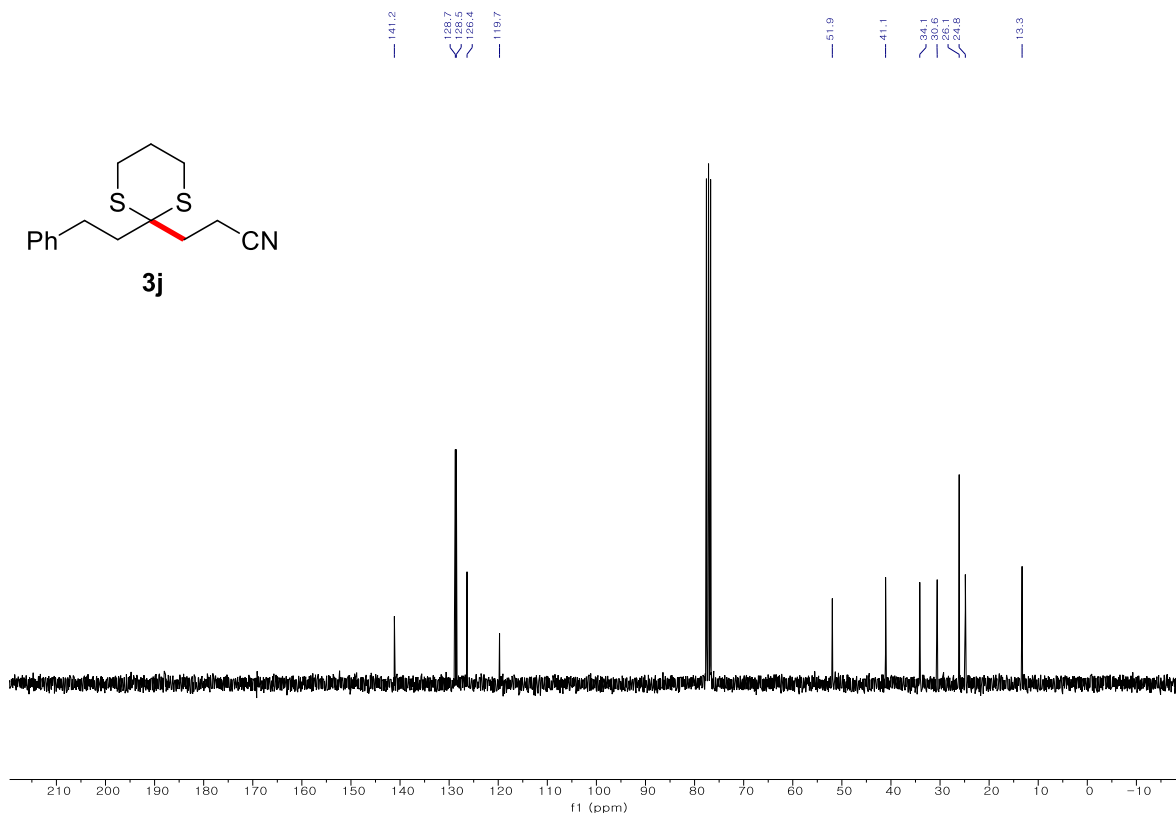


$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of **3h**

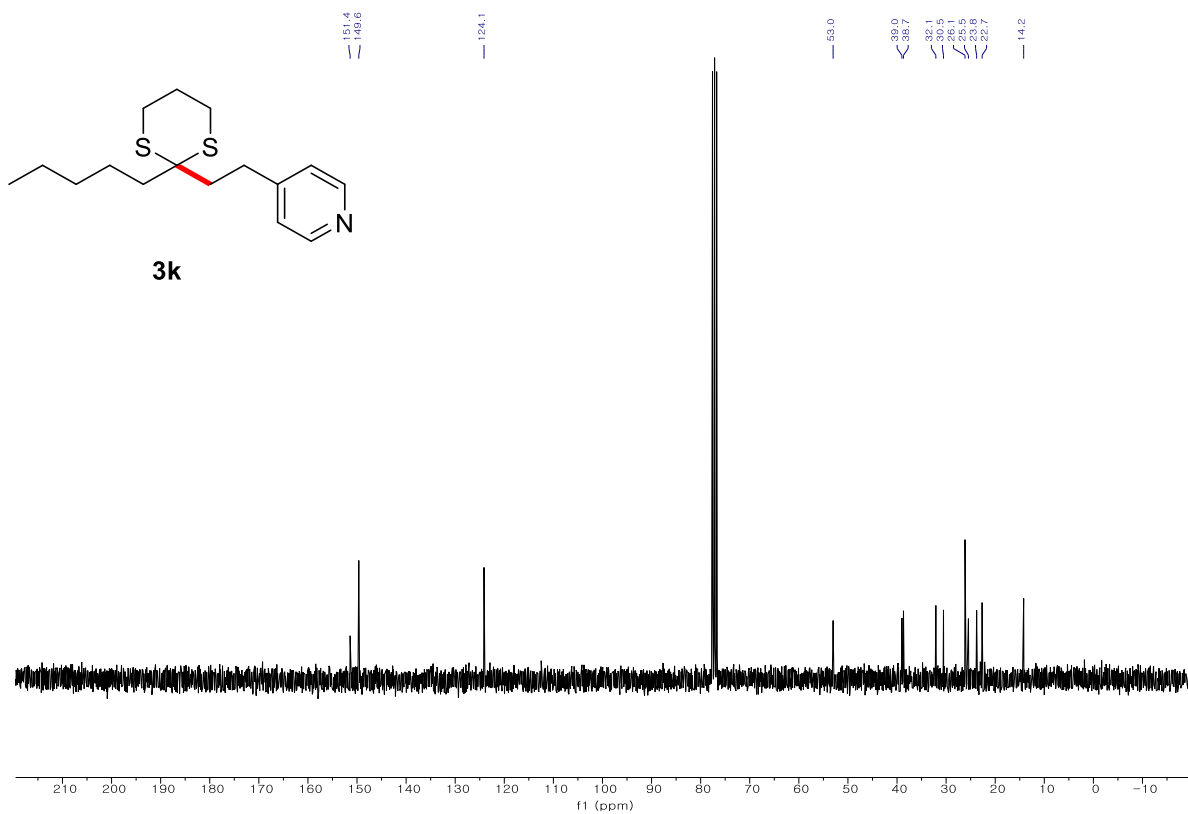
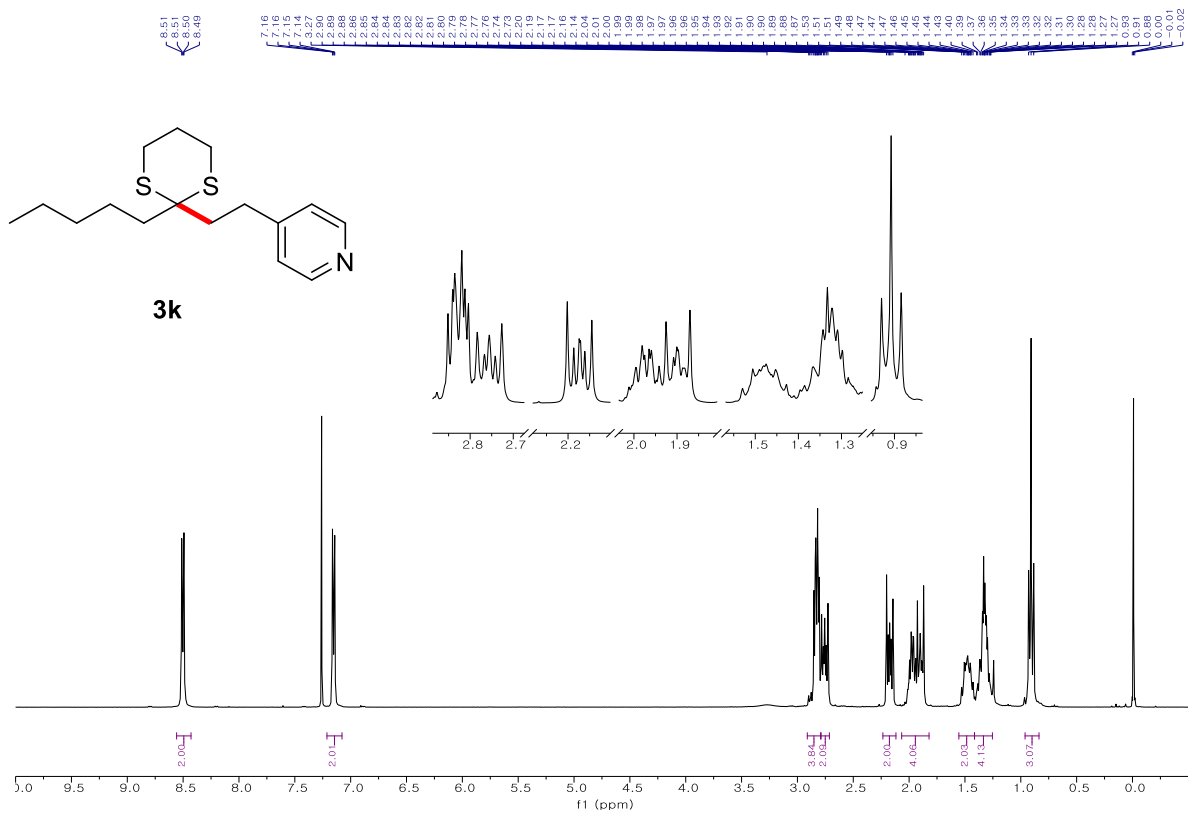


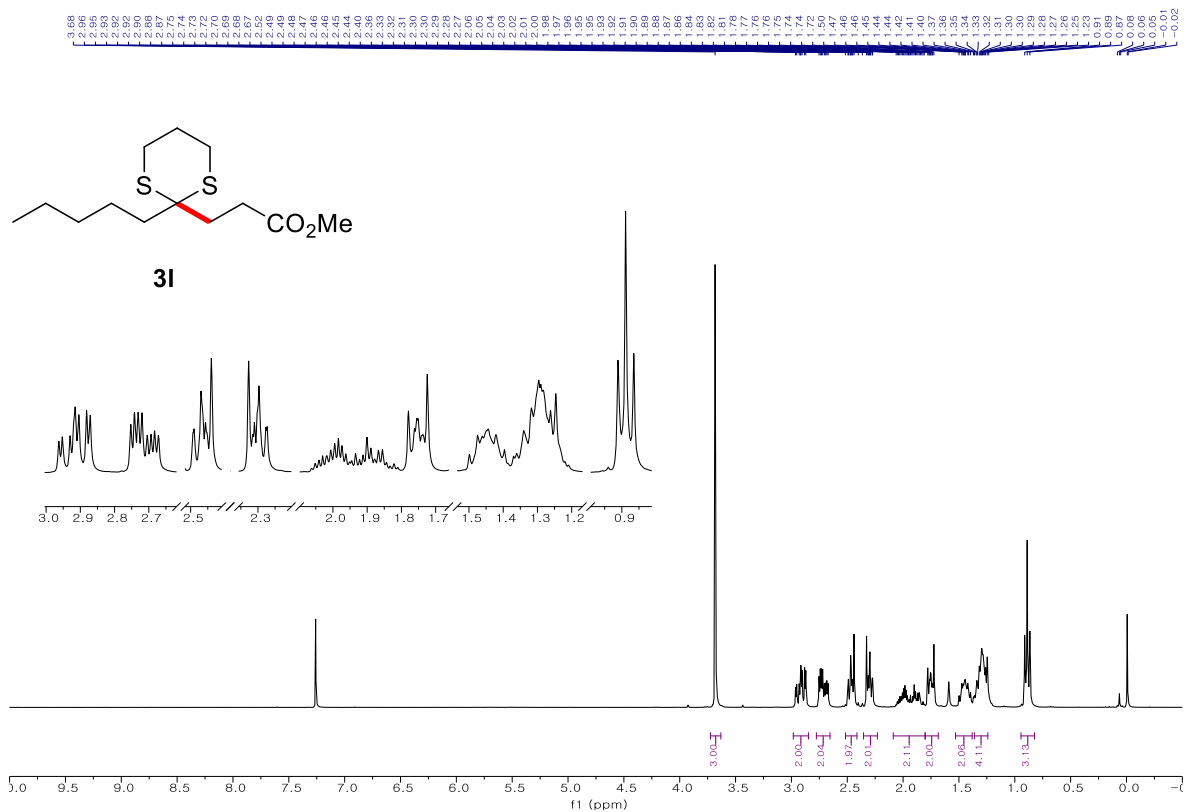


¹H-NMR (300 MHz, CDCl₃) of **3j**

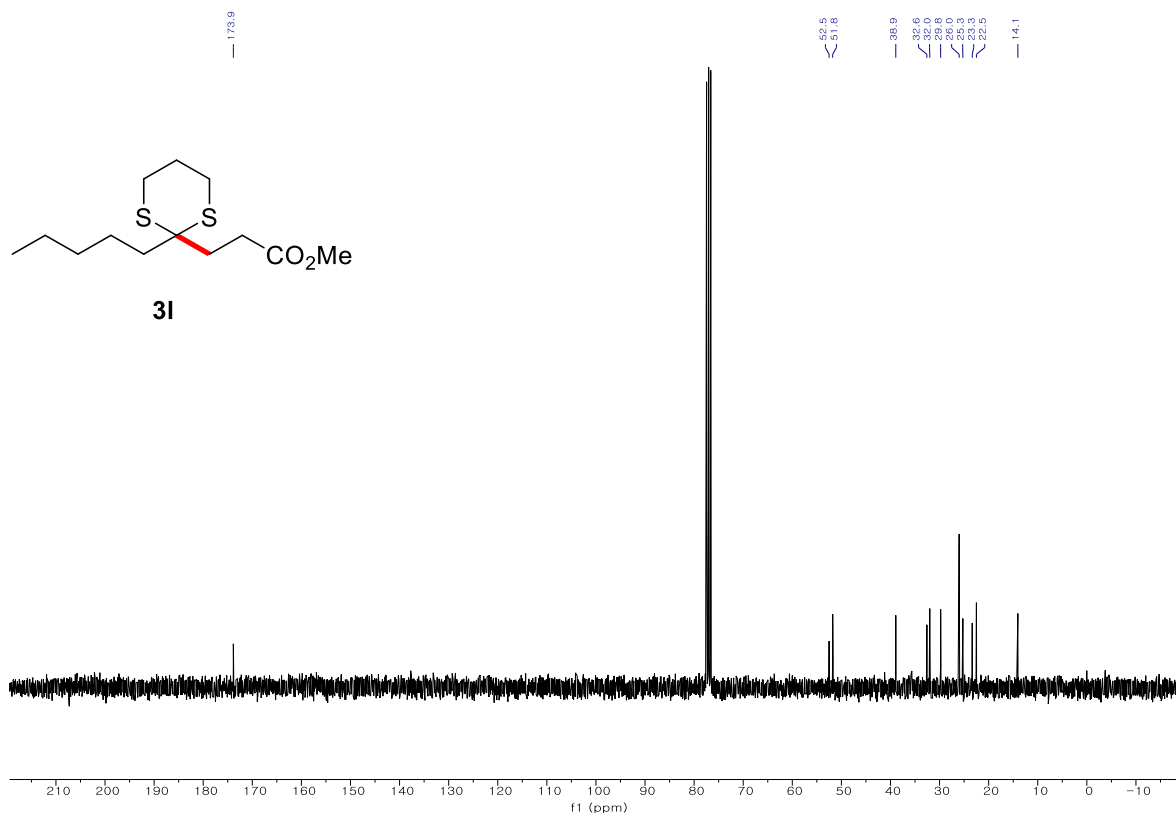


¹³C-NMR (75 MHz, CDCl₃) of **3j**

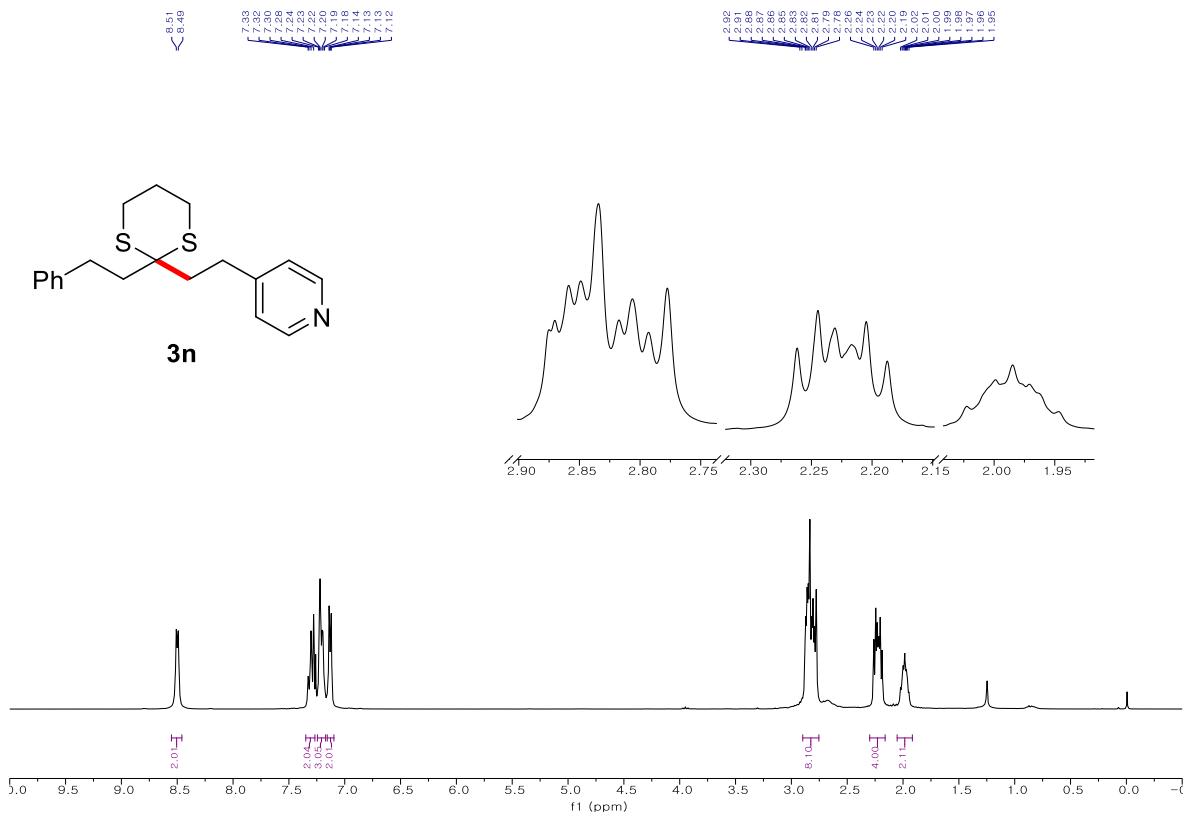




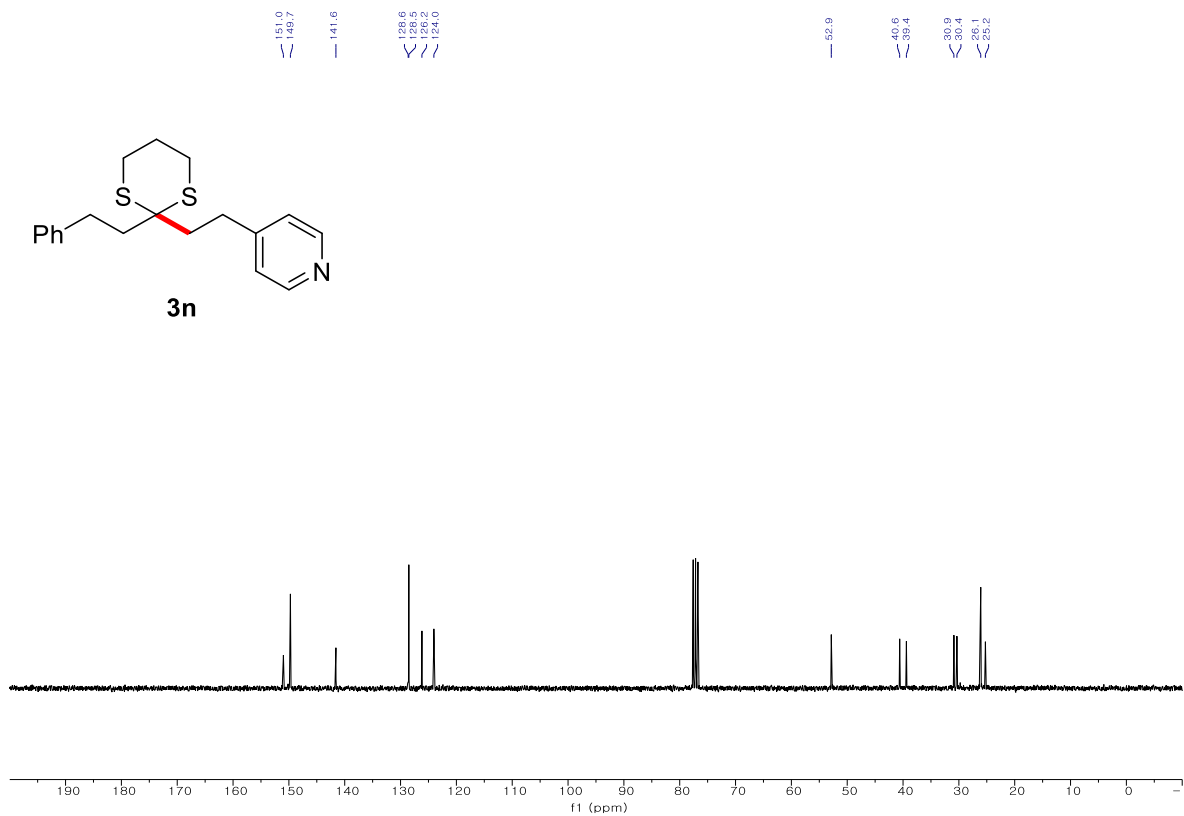
1H-NMR (300 MHz, CDCl₃) of **3I**



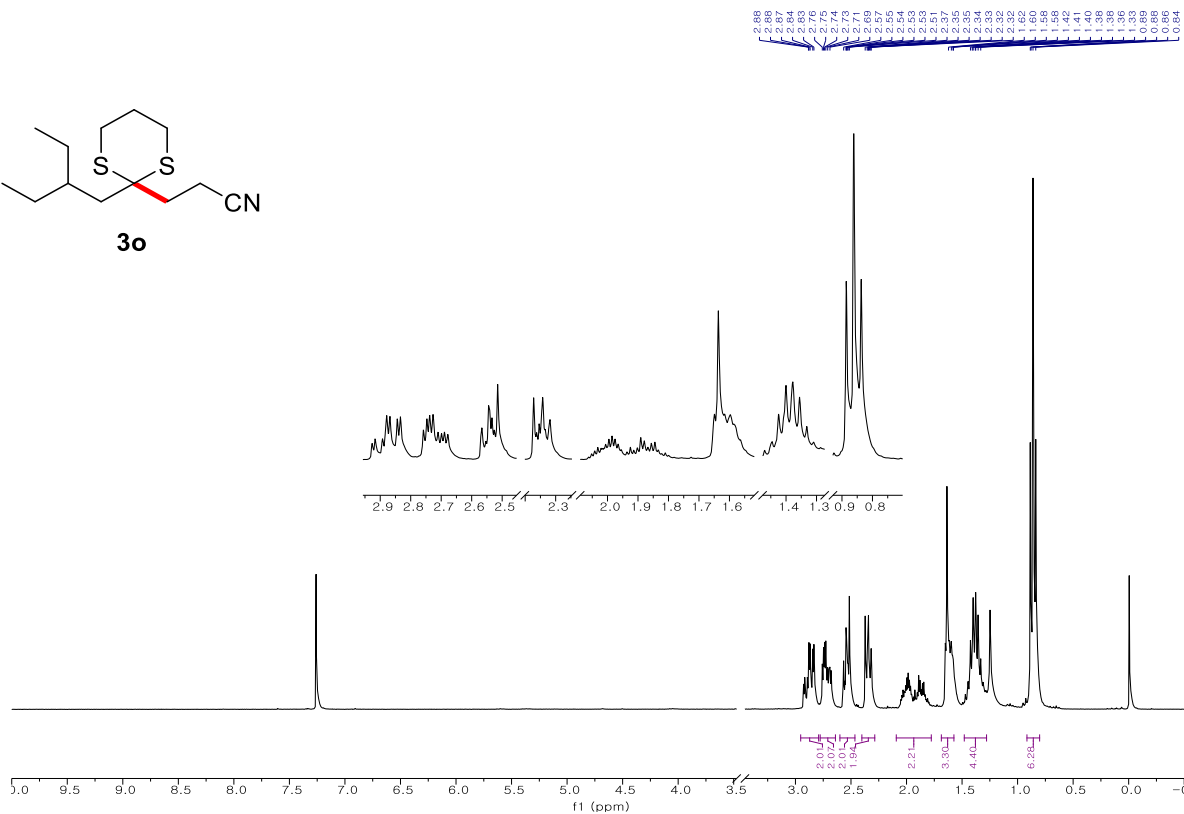
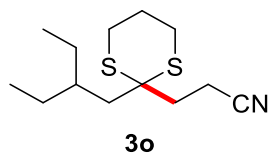
13C-NMR (75 MHz, CDCl₃) of **3I**



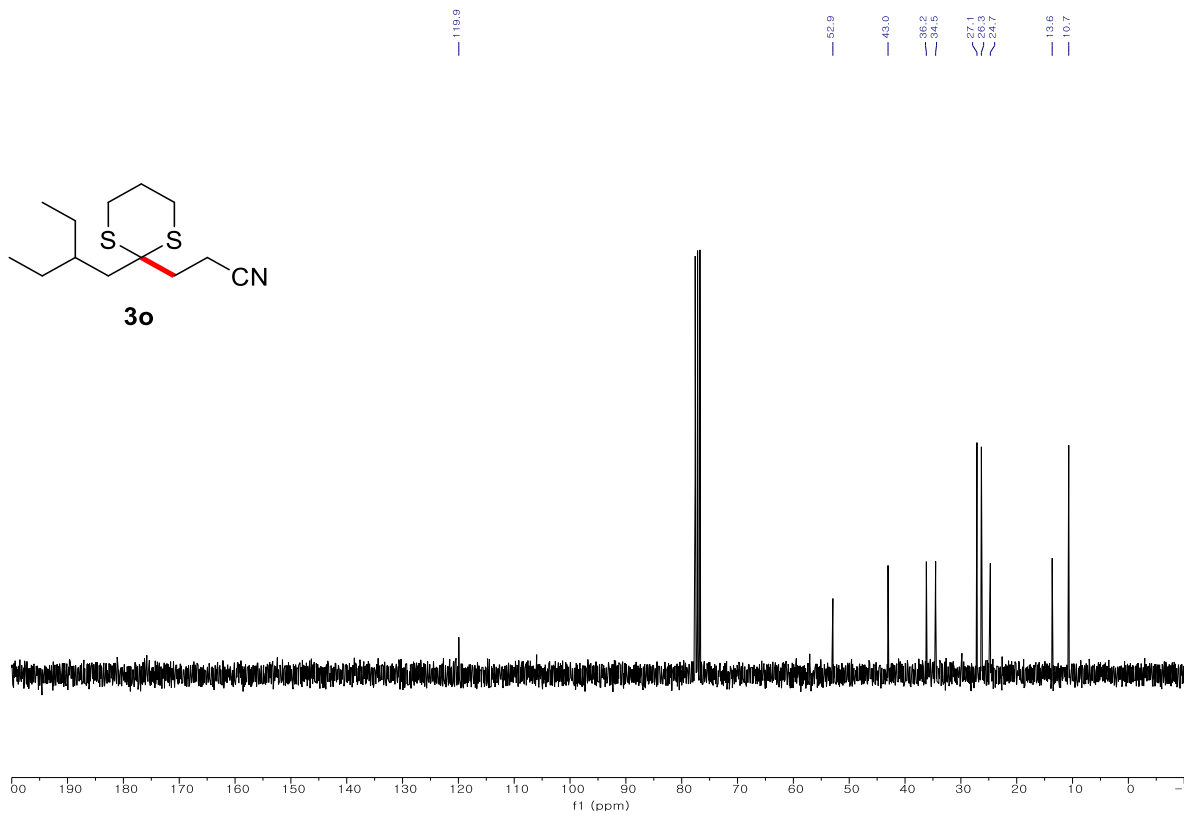
¹H-NMR (300 MHz, CDCl₃) of **3n**



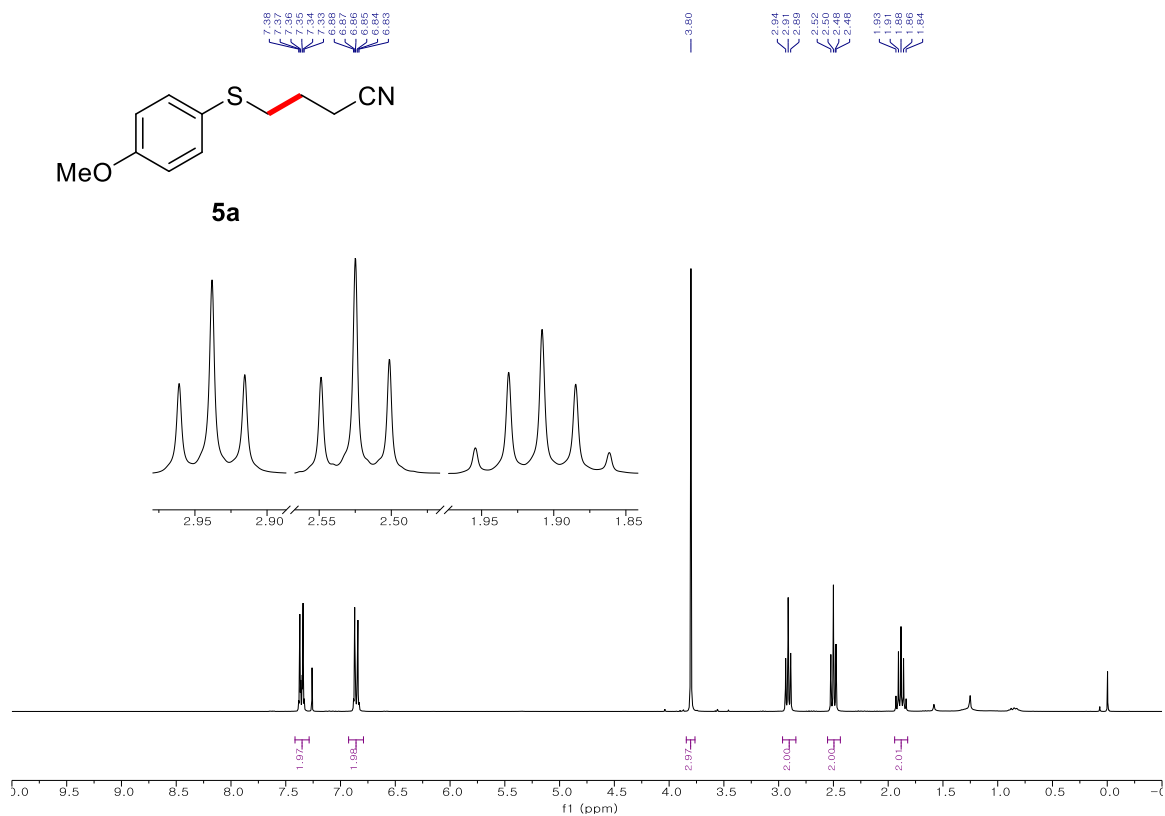
¹³C-NMR (75 MHz, CDCl₃) of **3n**



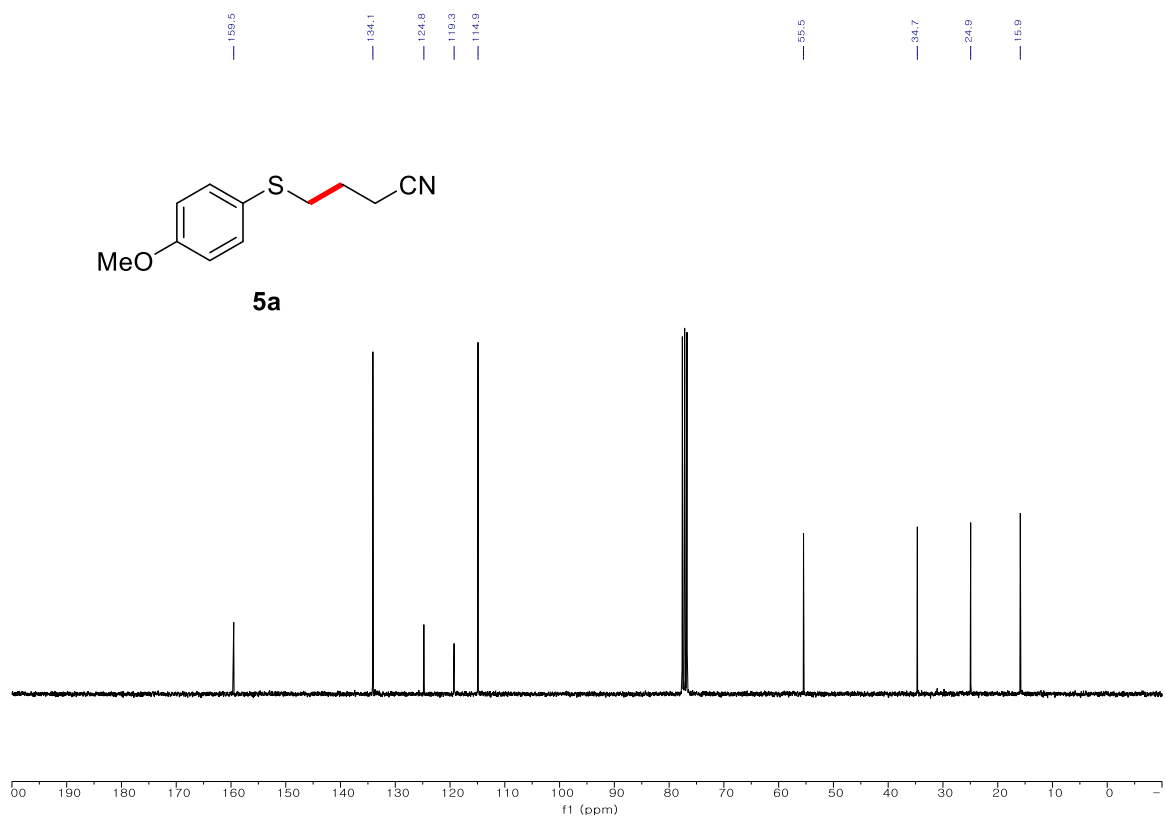
1H-NMR (300 MHz, CDCl₃) of **3o**



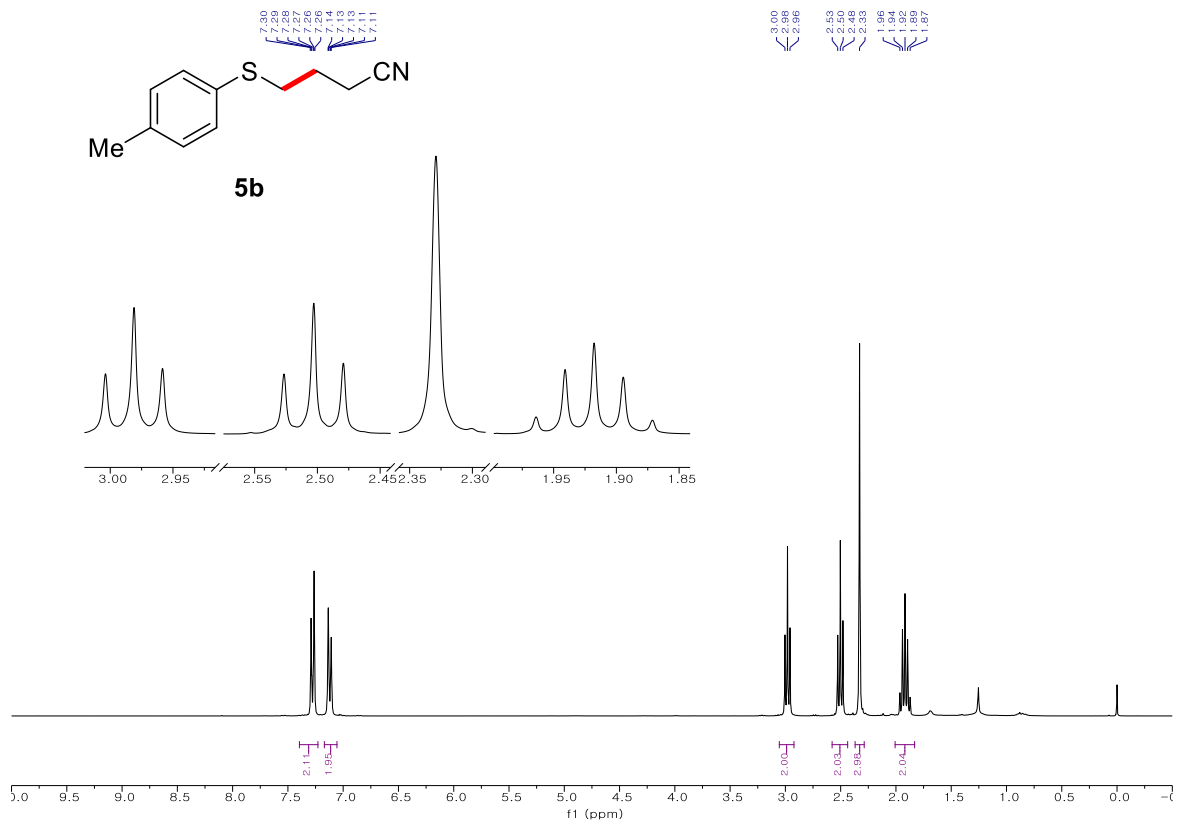
13C-NMR (75 MHz, CDCl₃) of **3o**



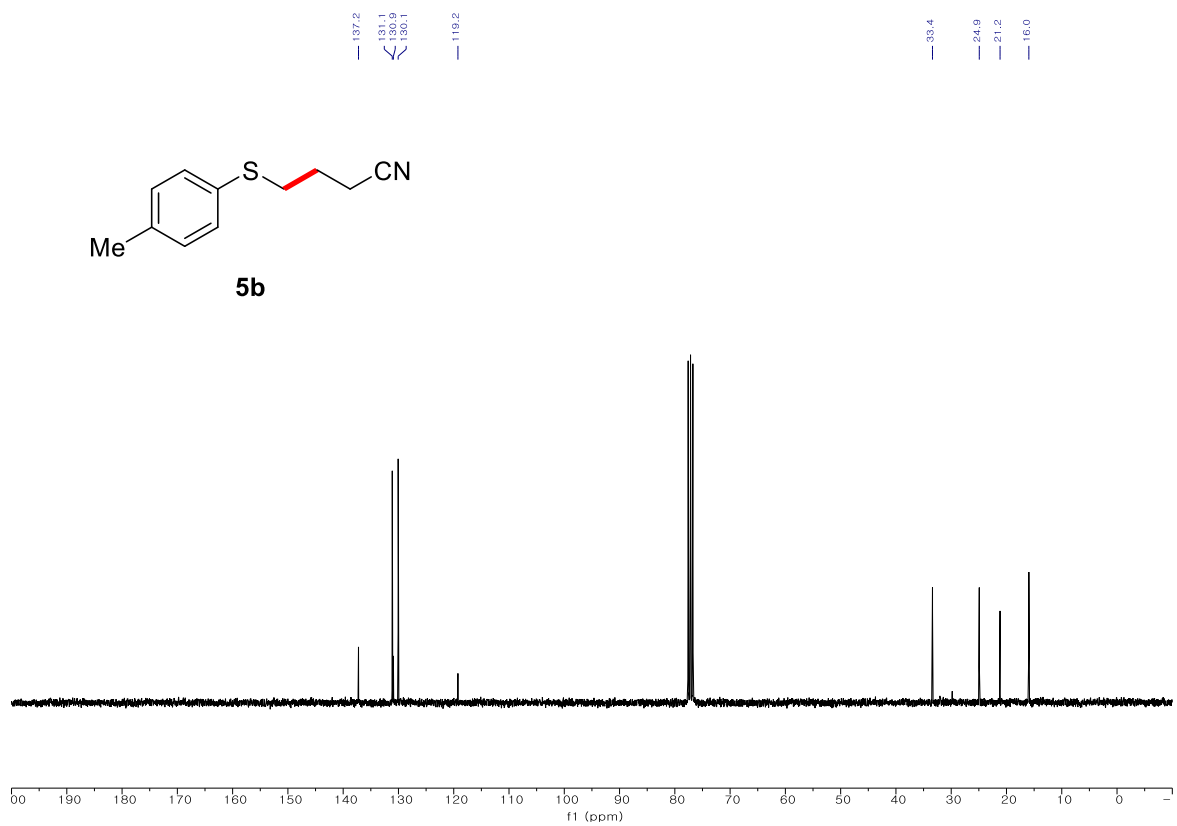
¹H-NMR (300 MHz, CDCl₃) of **5a**



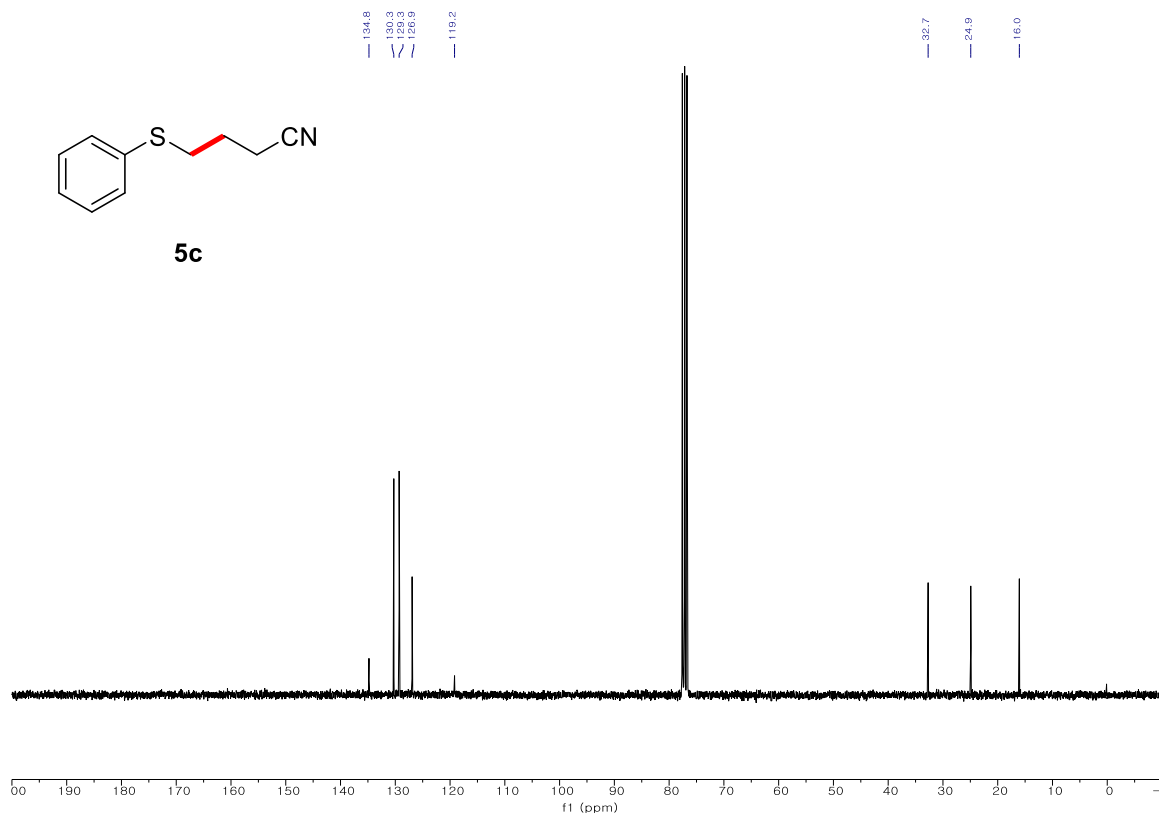
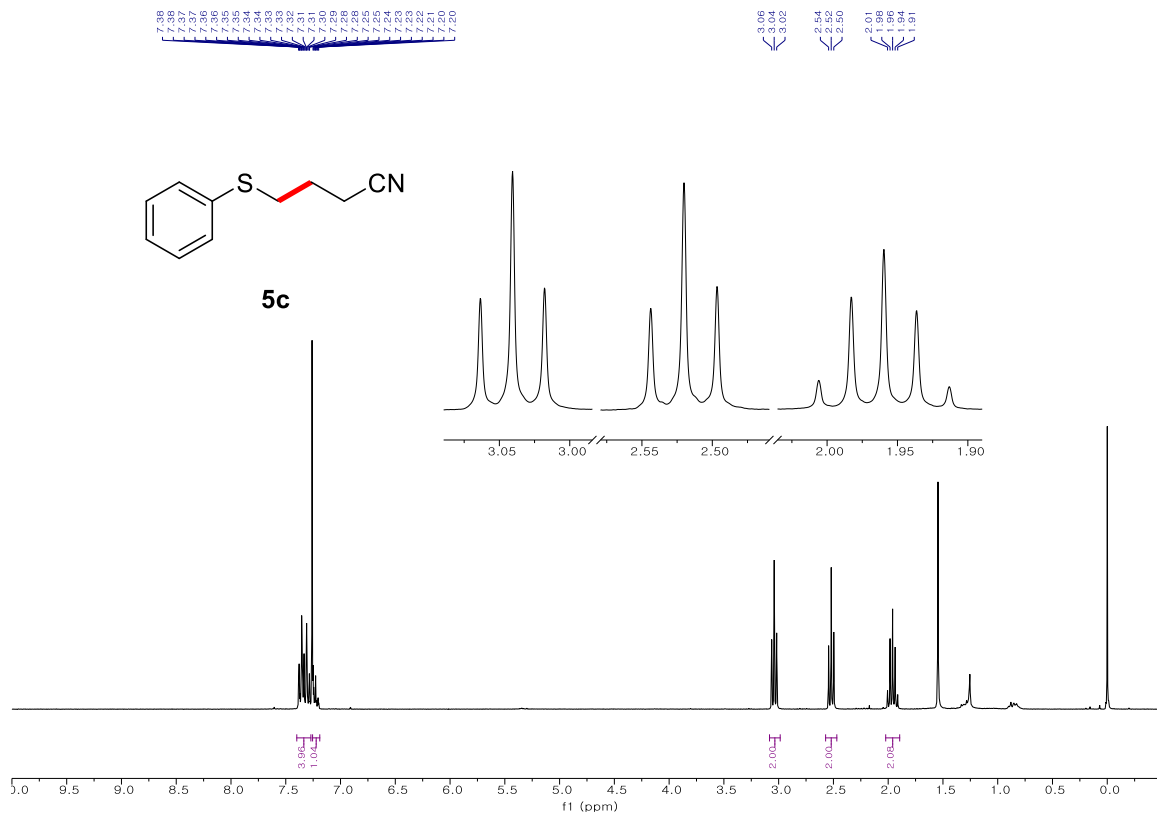
¹³C-NMR (75 MHz, CDCl₃) of **5a**

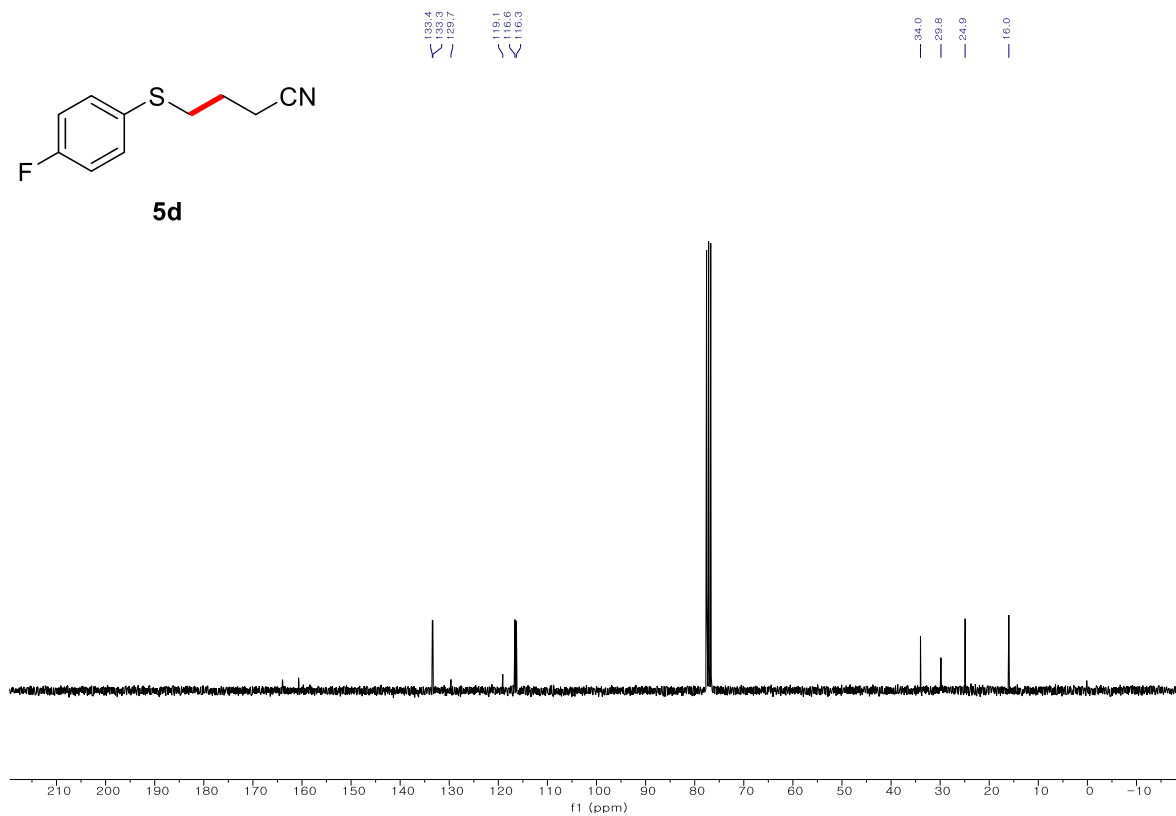
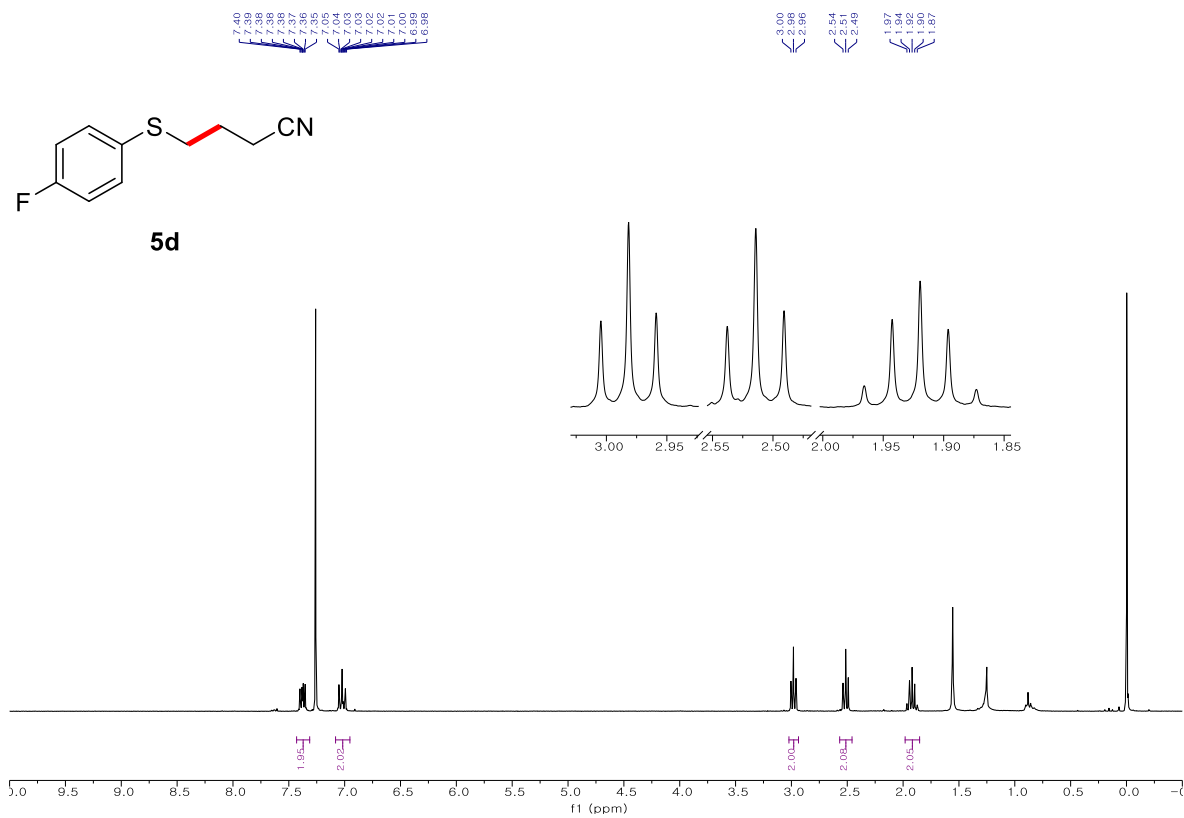


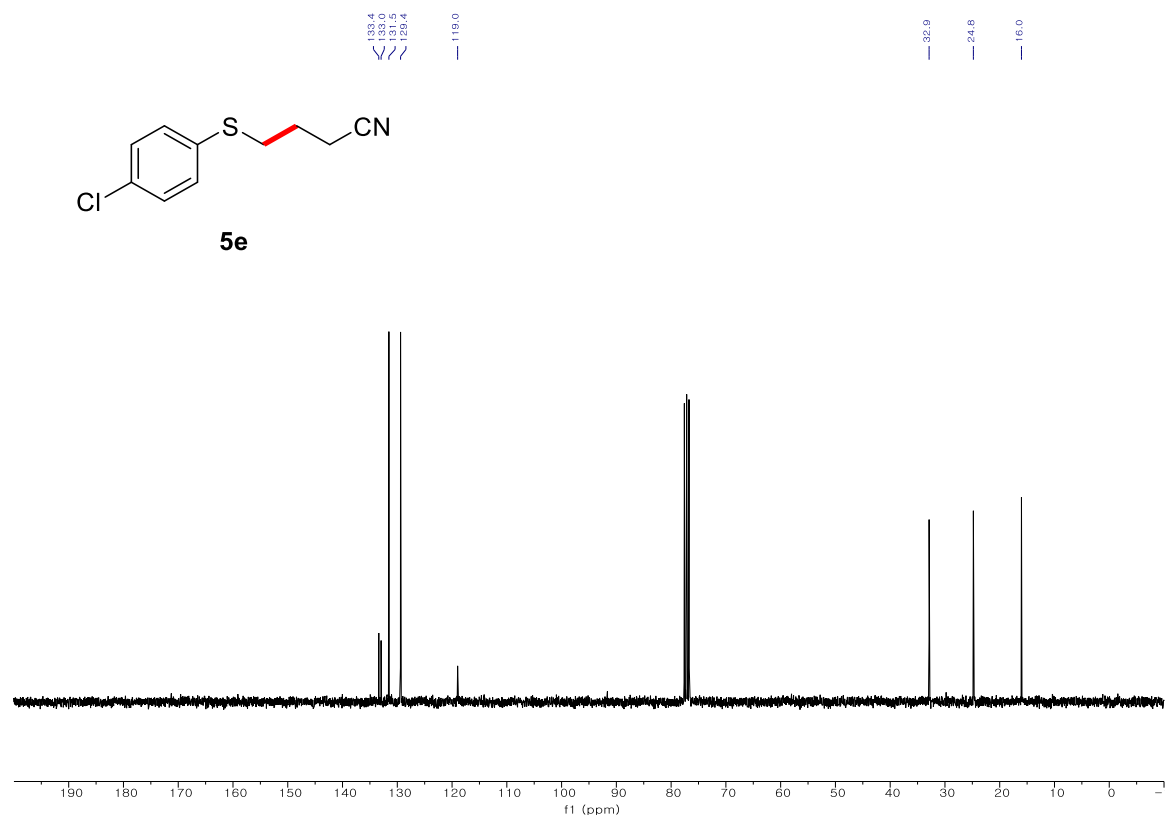
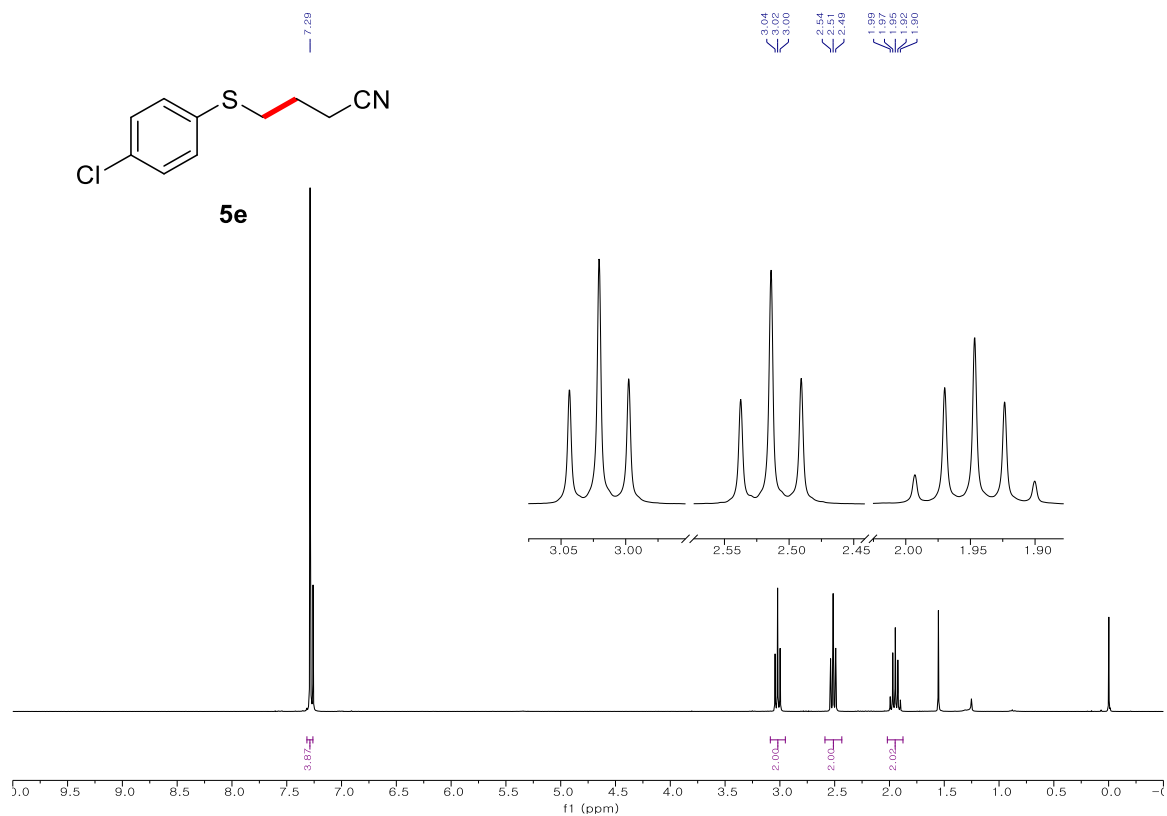
1H-NMR (300 MHz, CDCl₃) of **5b**

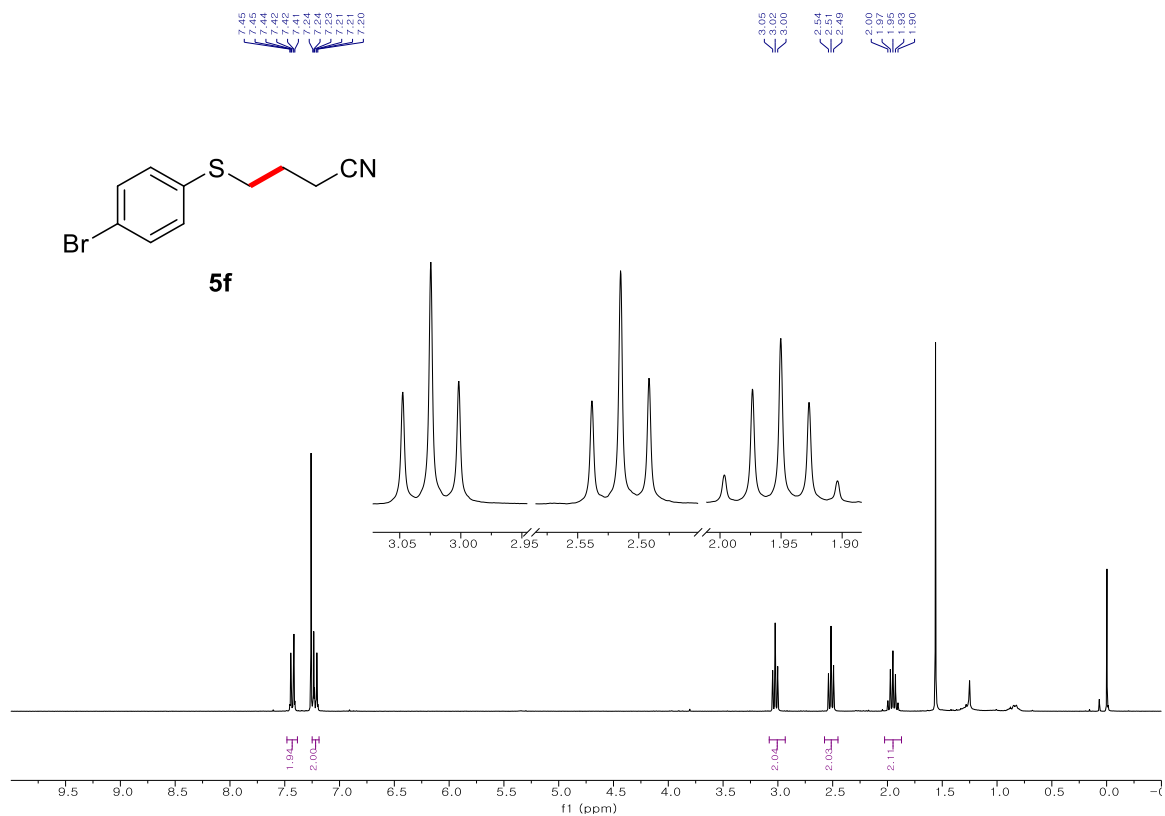


13C-NMR (75 MHz, CDCl₃) of **5b**

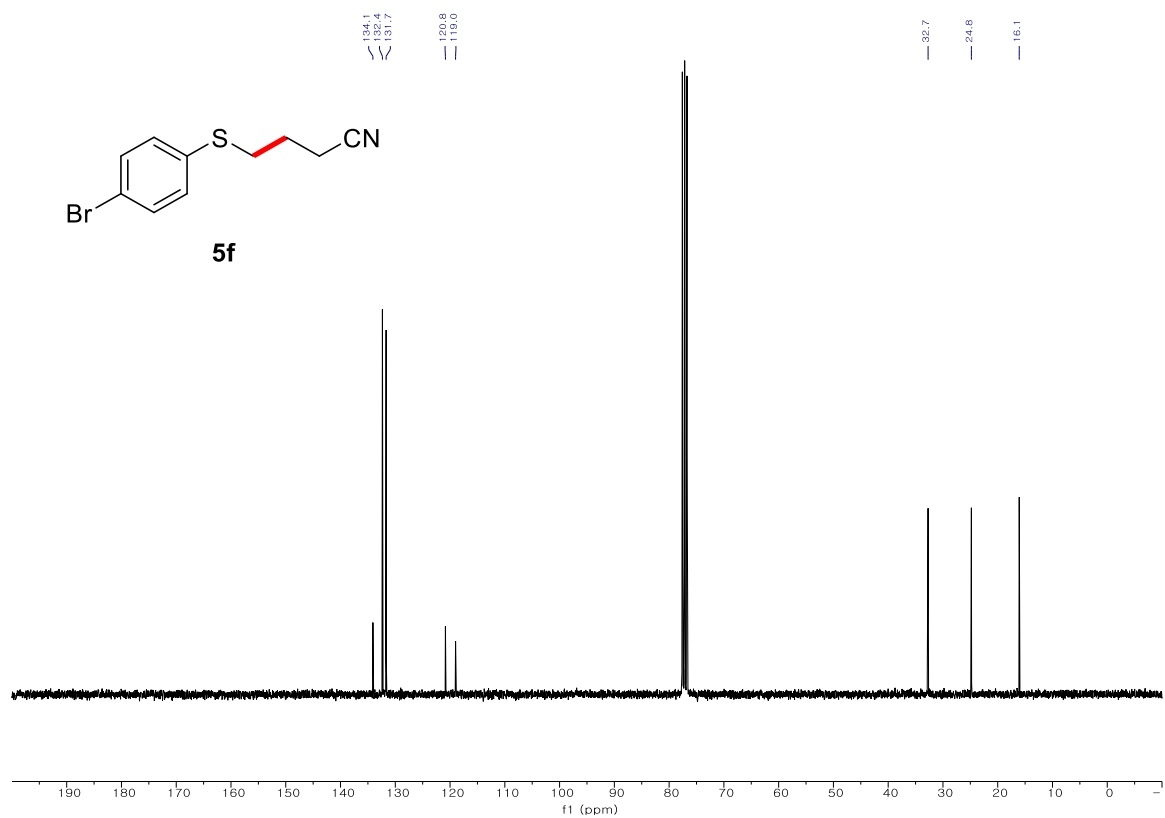




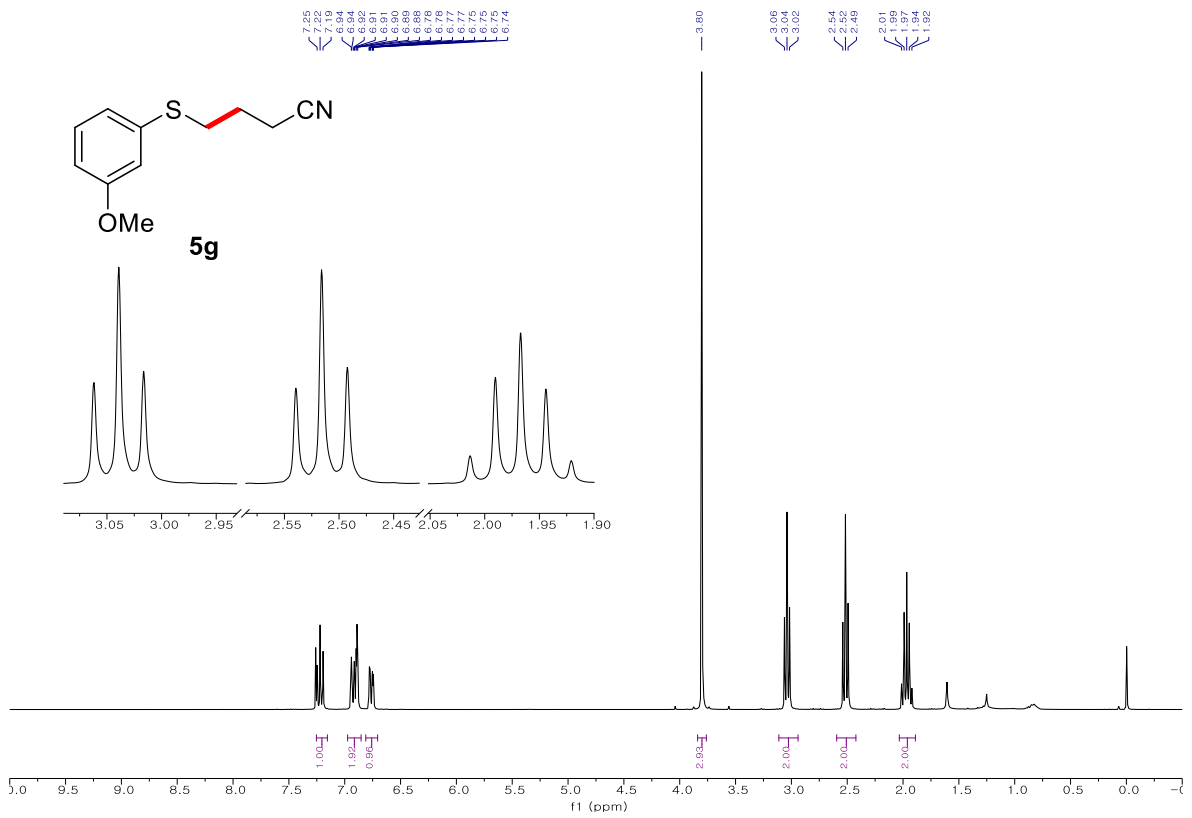




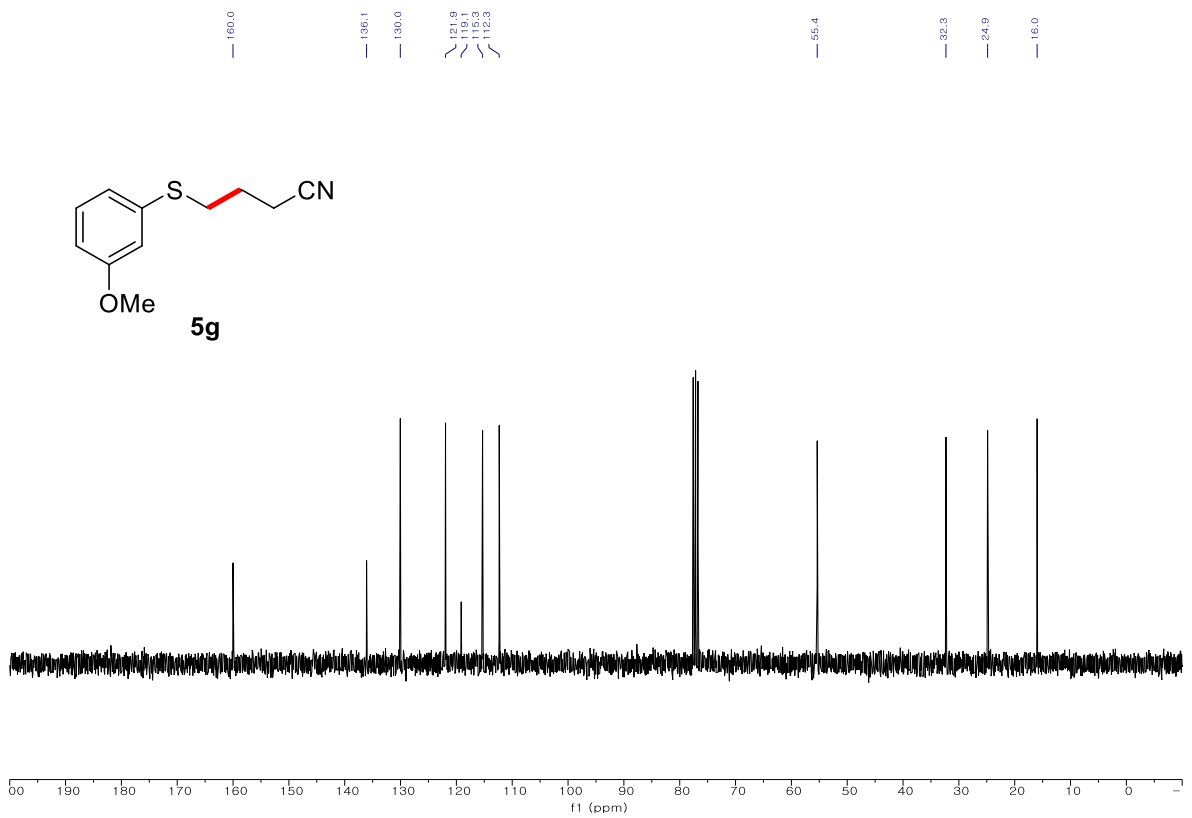
¹H-NMR (300 MHz, CDCl₃) of 5f



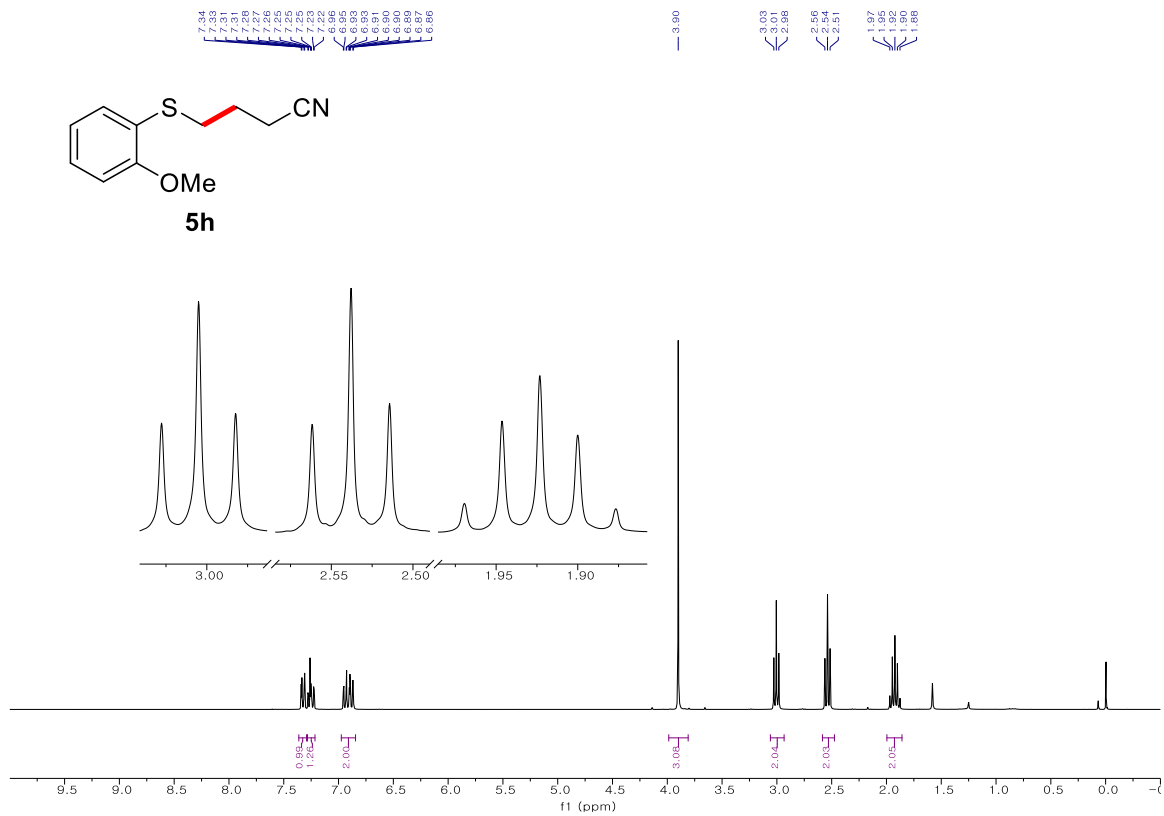
¹³C-NMR (75 MHz, CDCl₃) of 5f



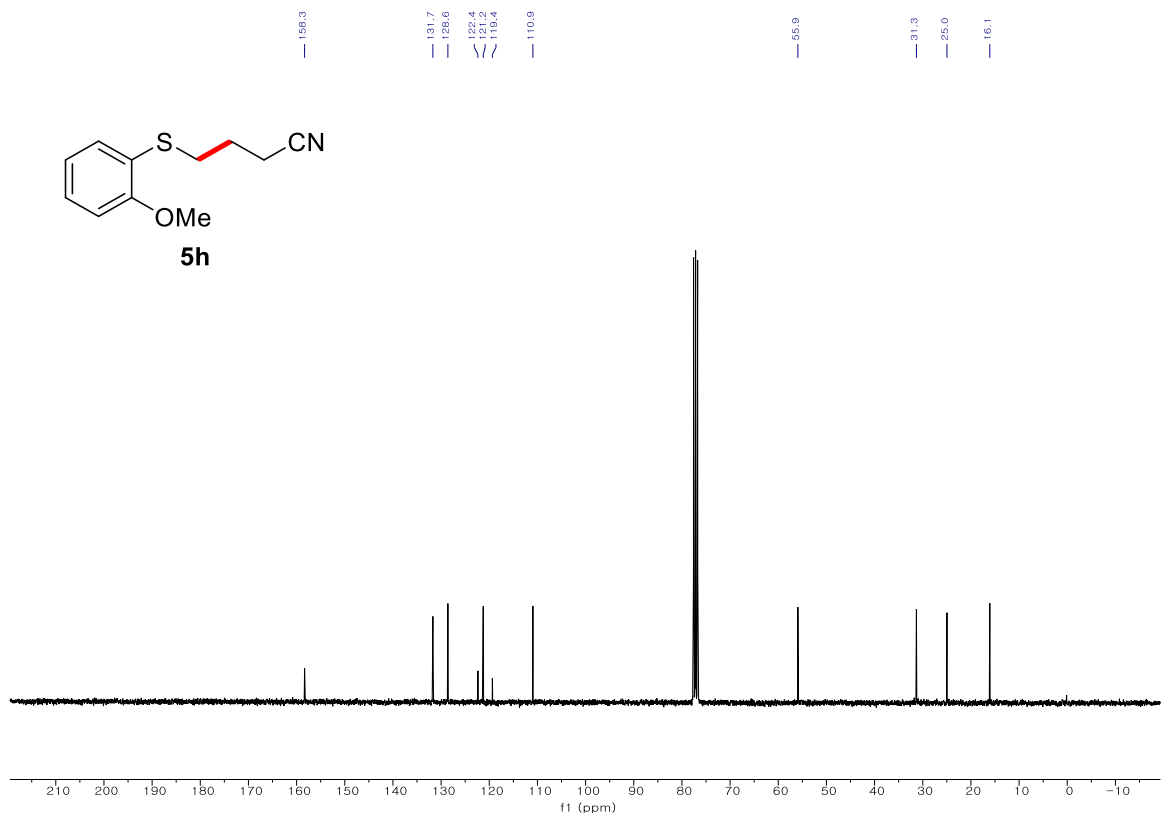
1H-NMR (300 MHz, CDCl₃) of **5g**



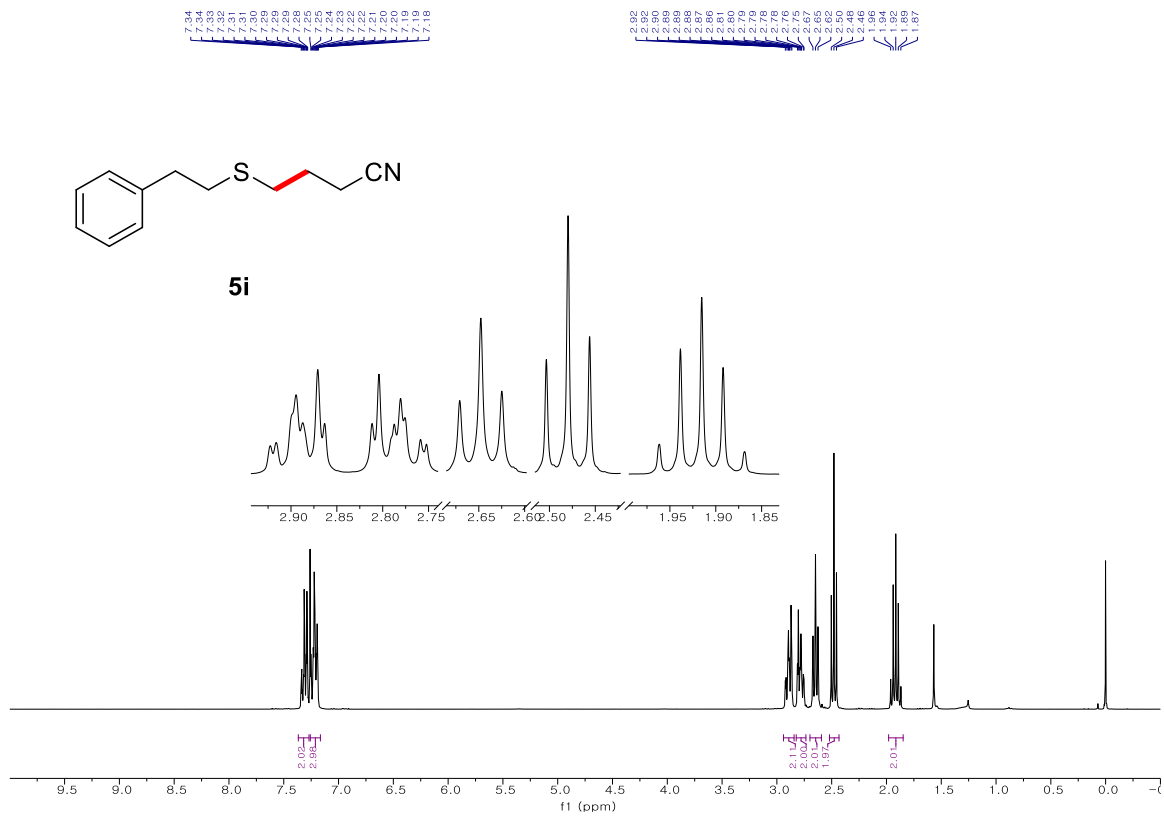
13C-NMR (75 MHz, CDCl₃) of **5g**



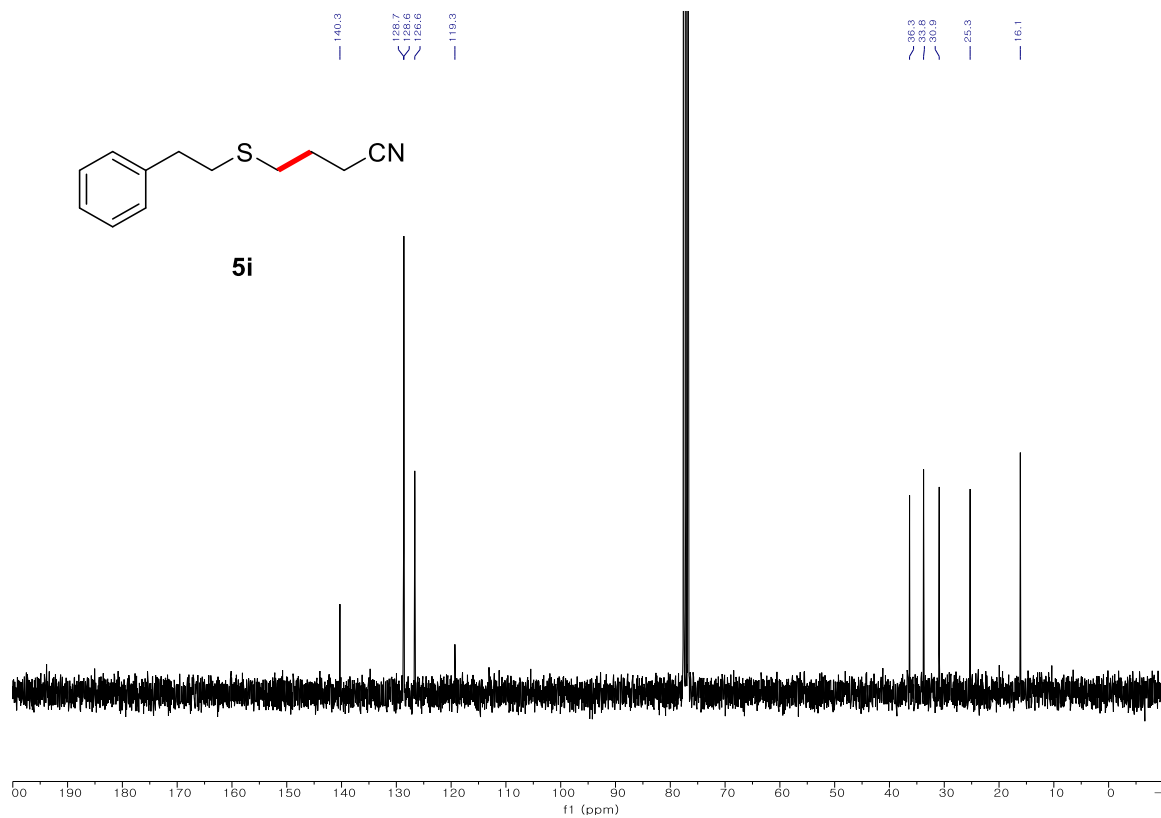
¹H-NMR (300 MHz, CDCl₃) of **5h**



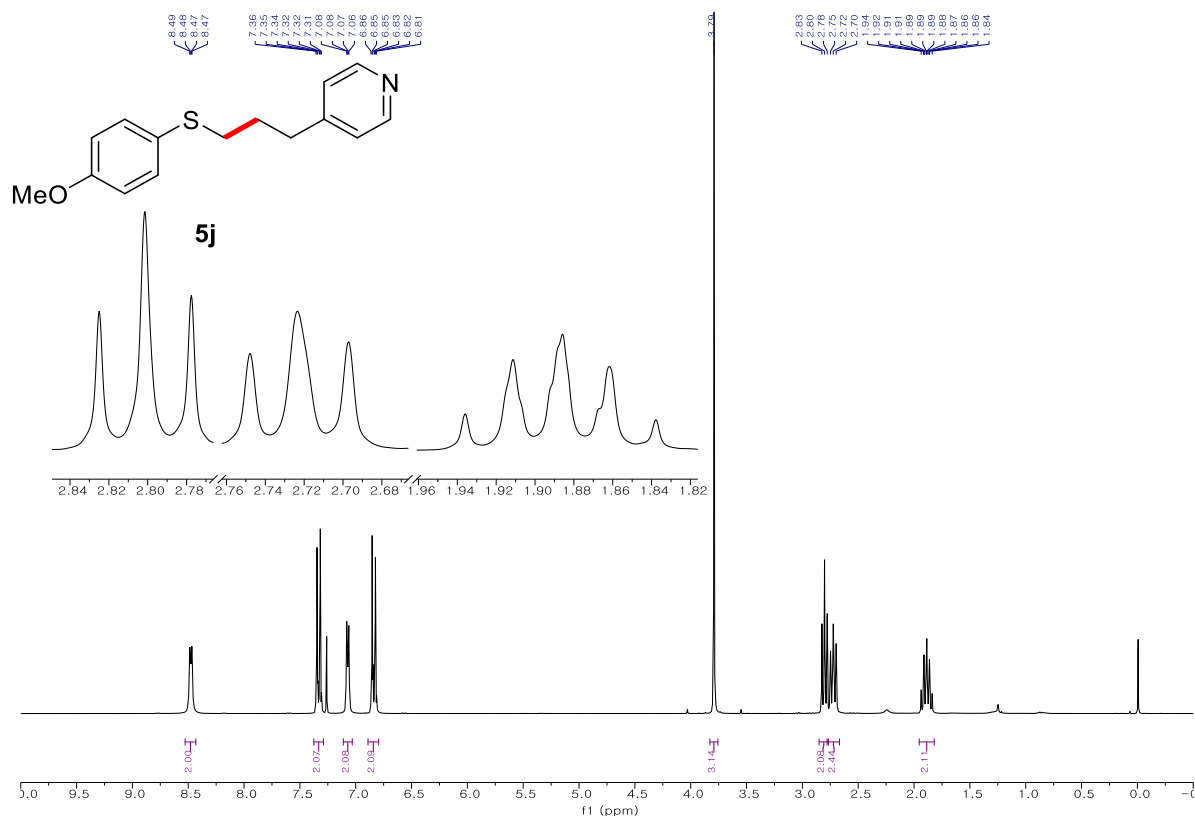
¹³C-NMR (75 MHz, CDCl₃) of **5h**



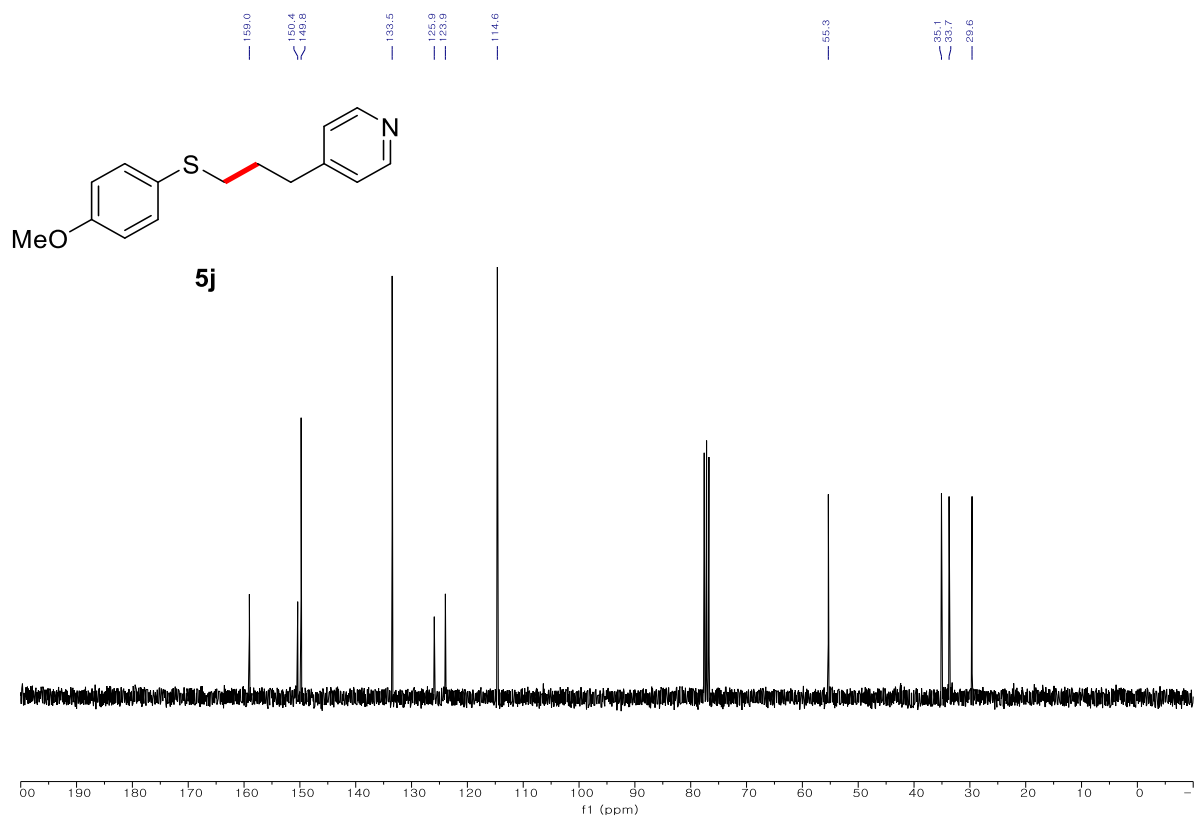
¹H-NMR (300 MHz, CDCl₃) of **5i**



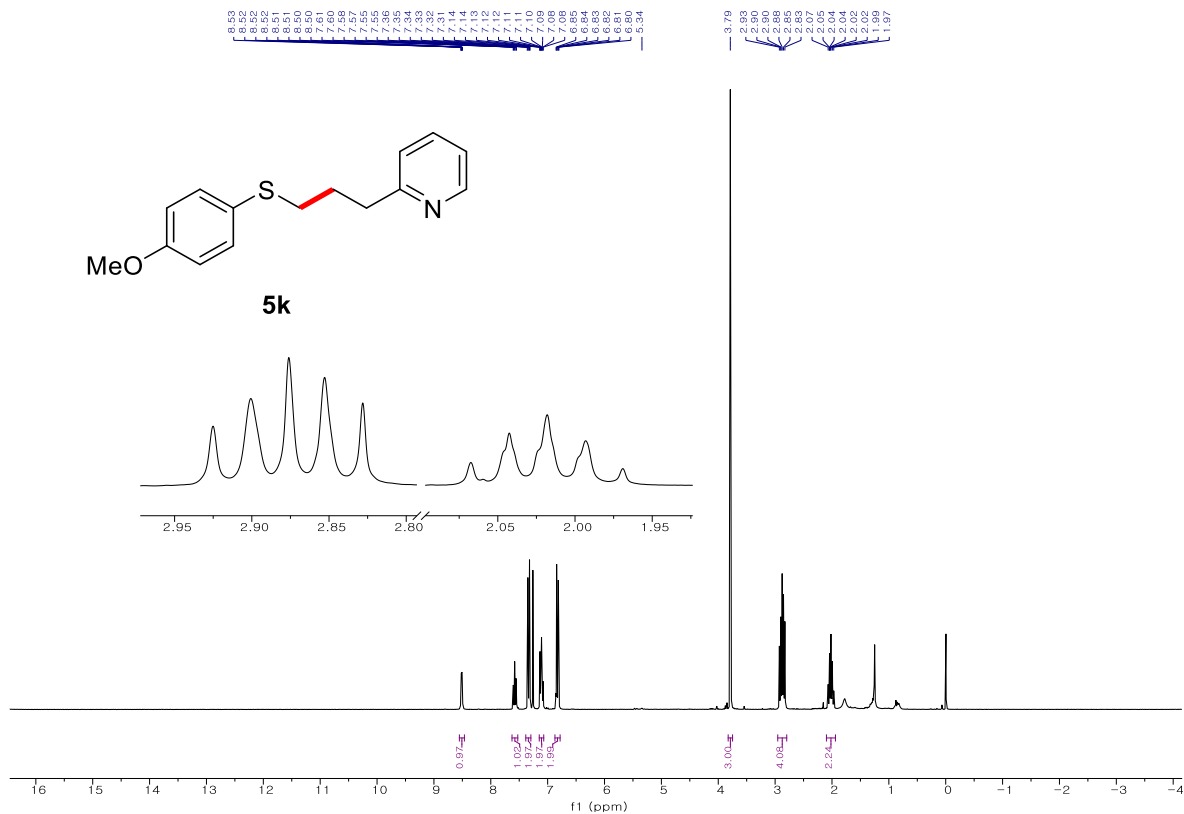
¹³C-NMR (75 MHz, CDCl₃) of **5i**



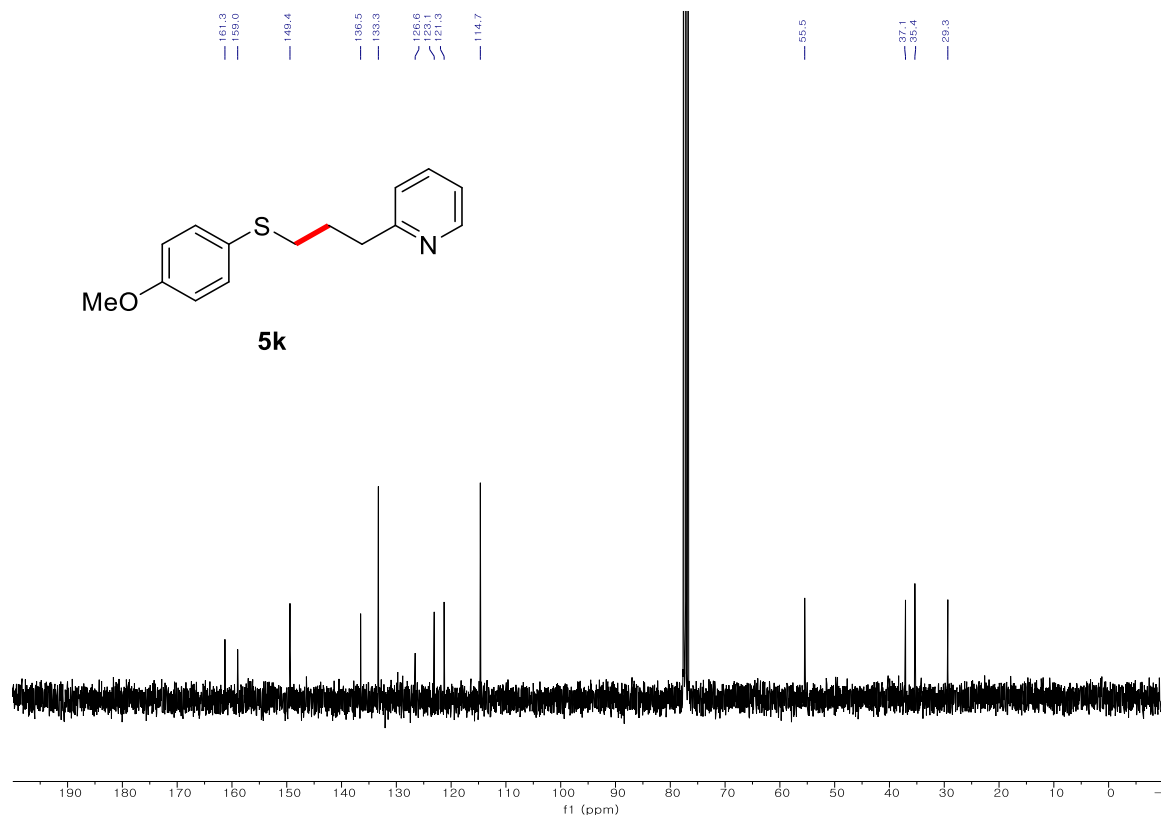
1H-NMR (300 MHz, CDCl₃) of 5j



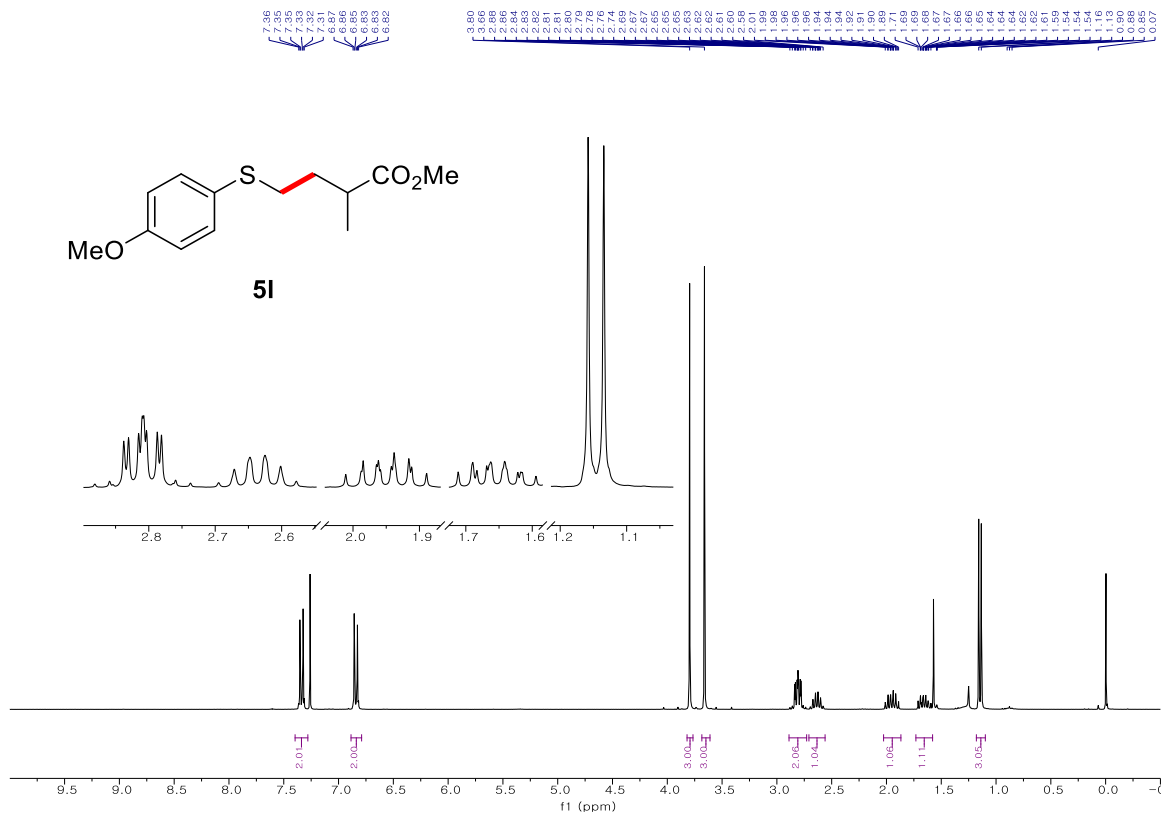
13C-NMR (75 MHz, CDCl₃) of 5j



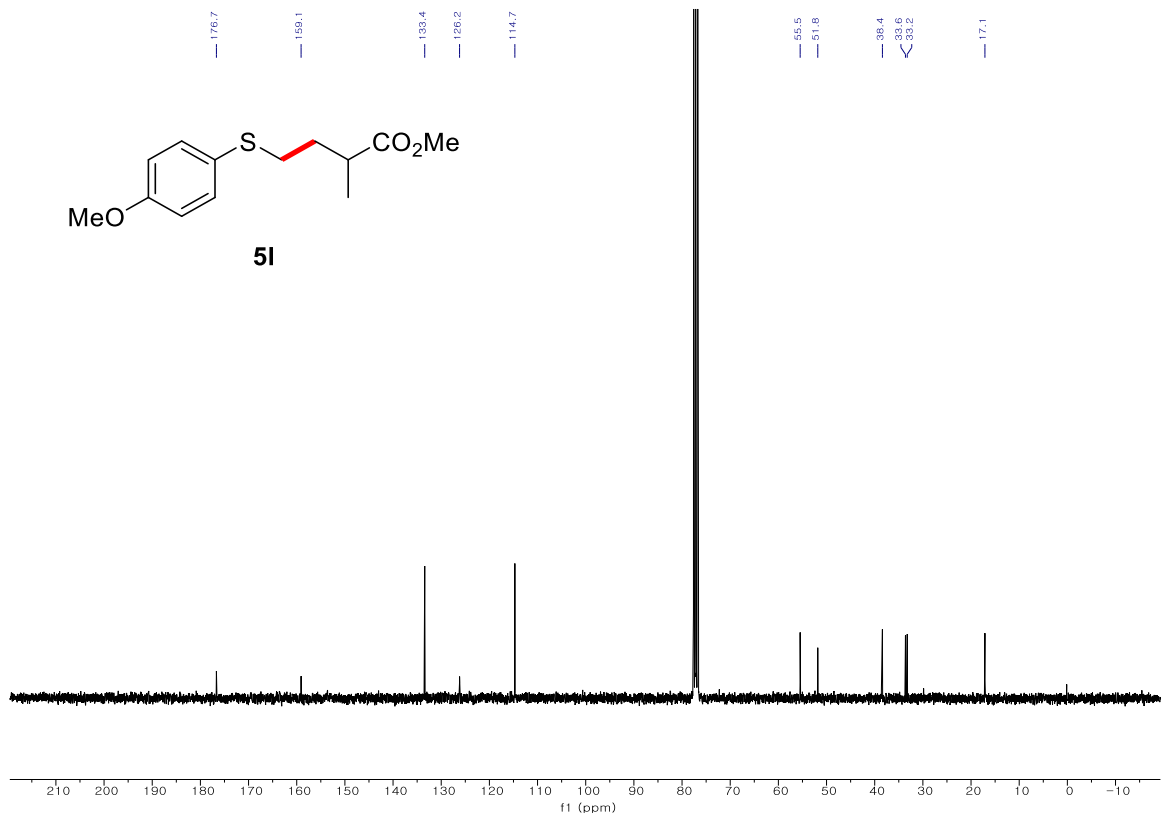
1H-NMR (300 MHz, CDCl₃) of **5k**



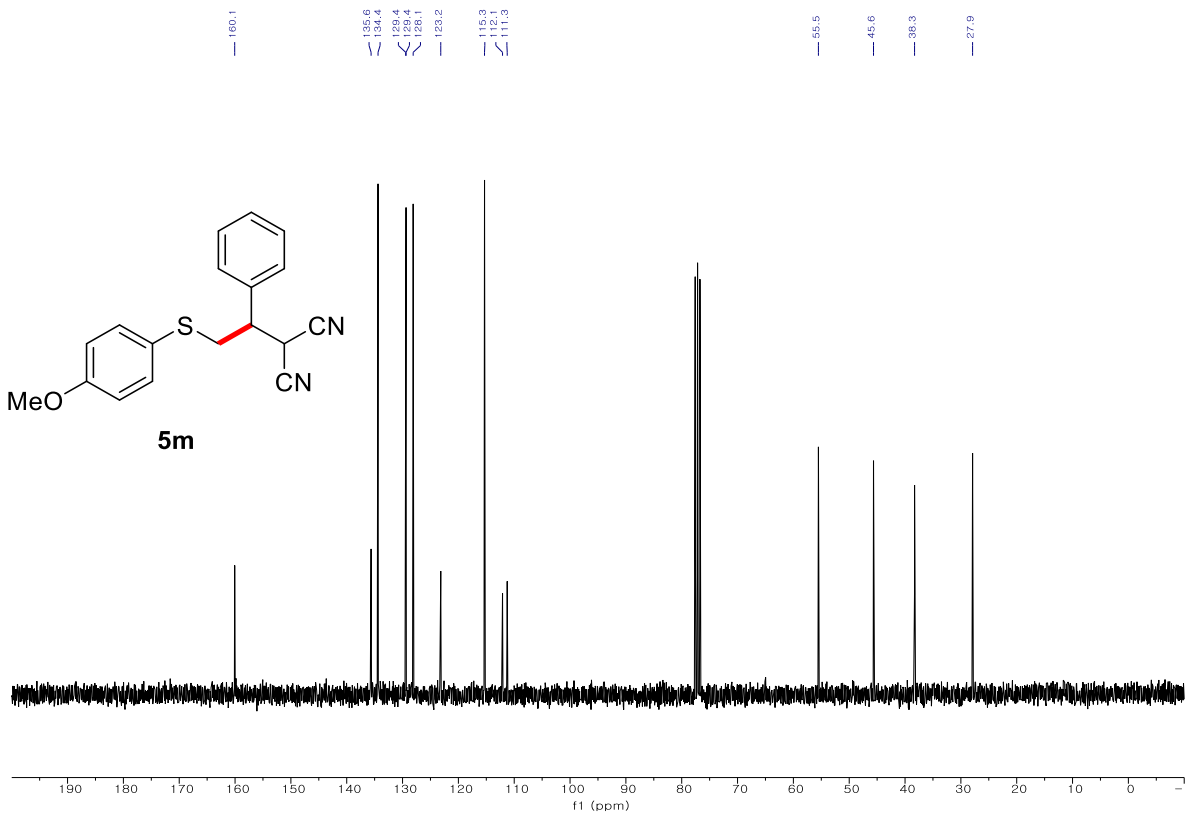
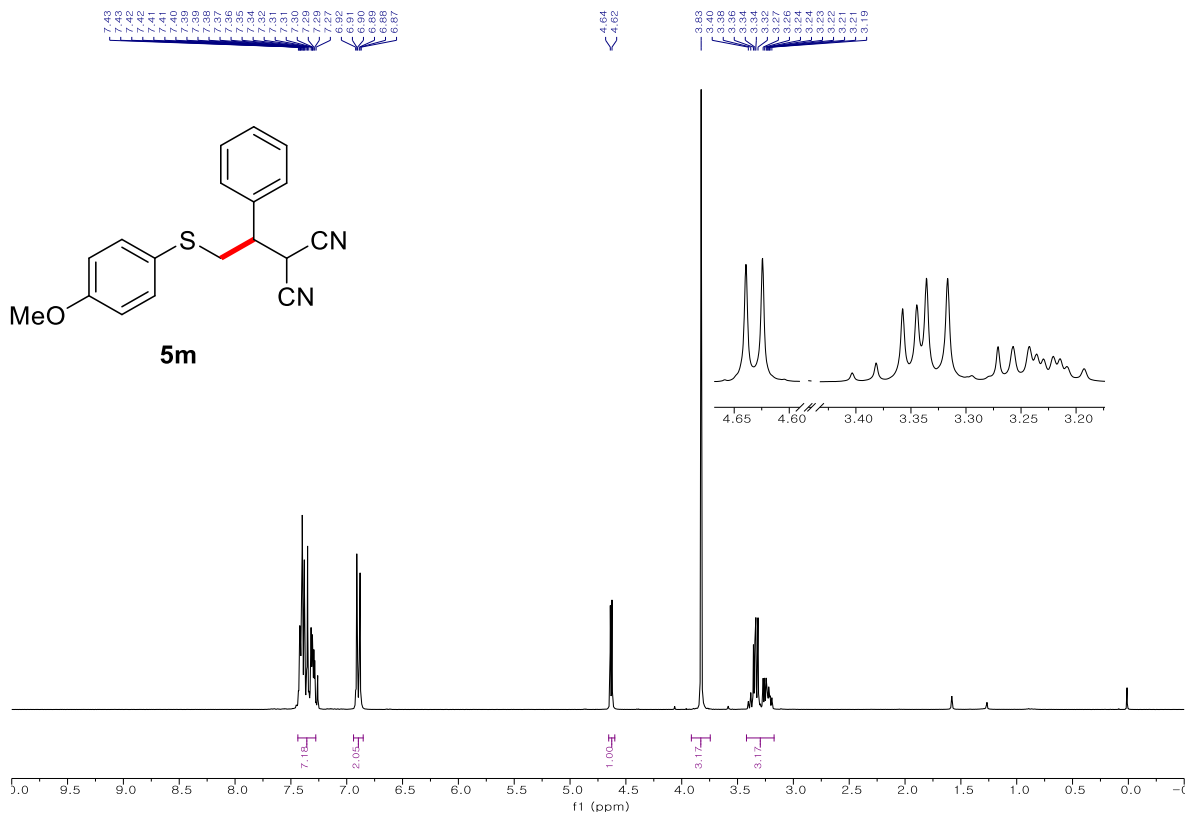
13C-NMR (75 MHz, CDCl₃) of **5k**

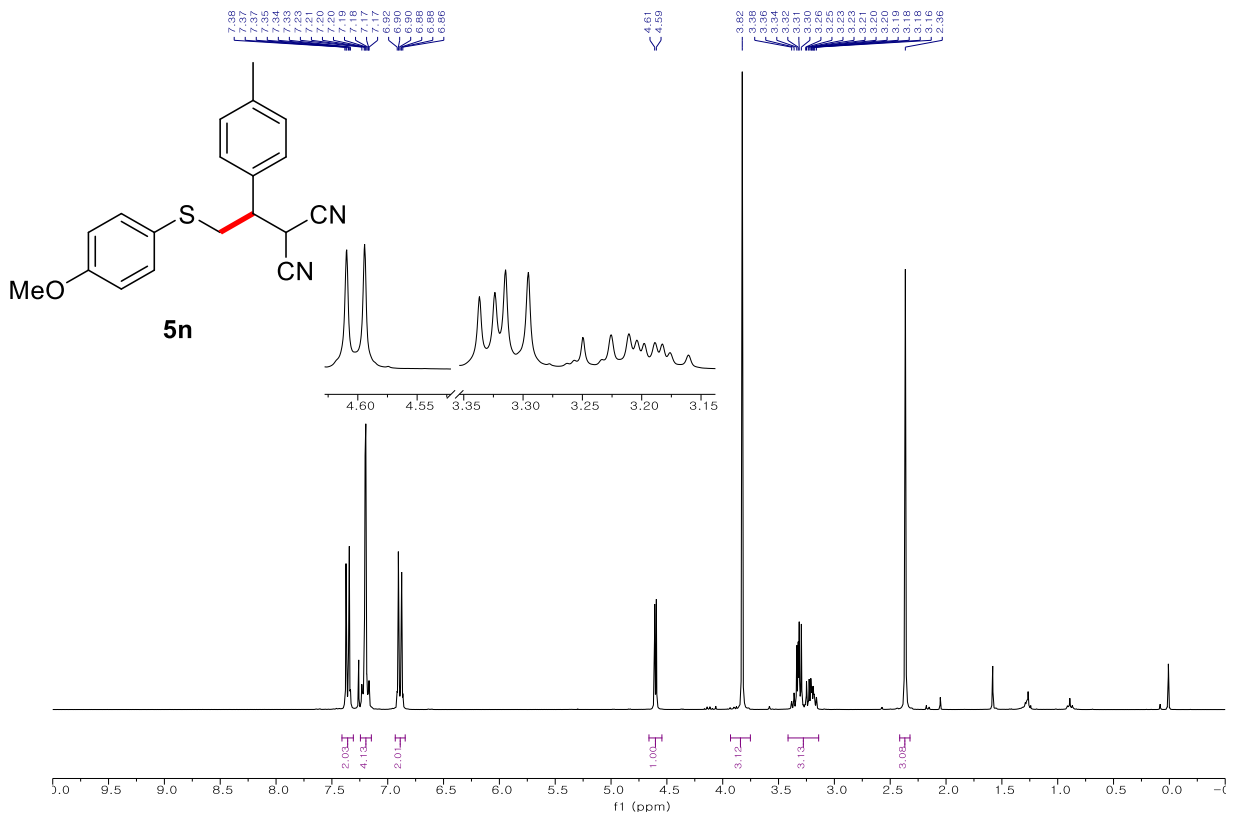


$^1\text{H-NMR}$ (300 MHz, CDCl_3) of **5I**

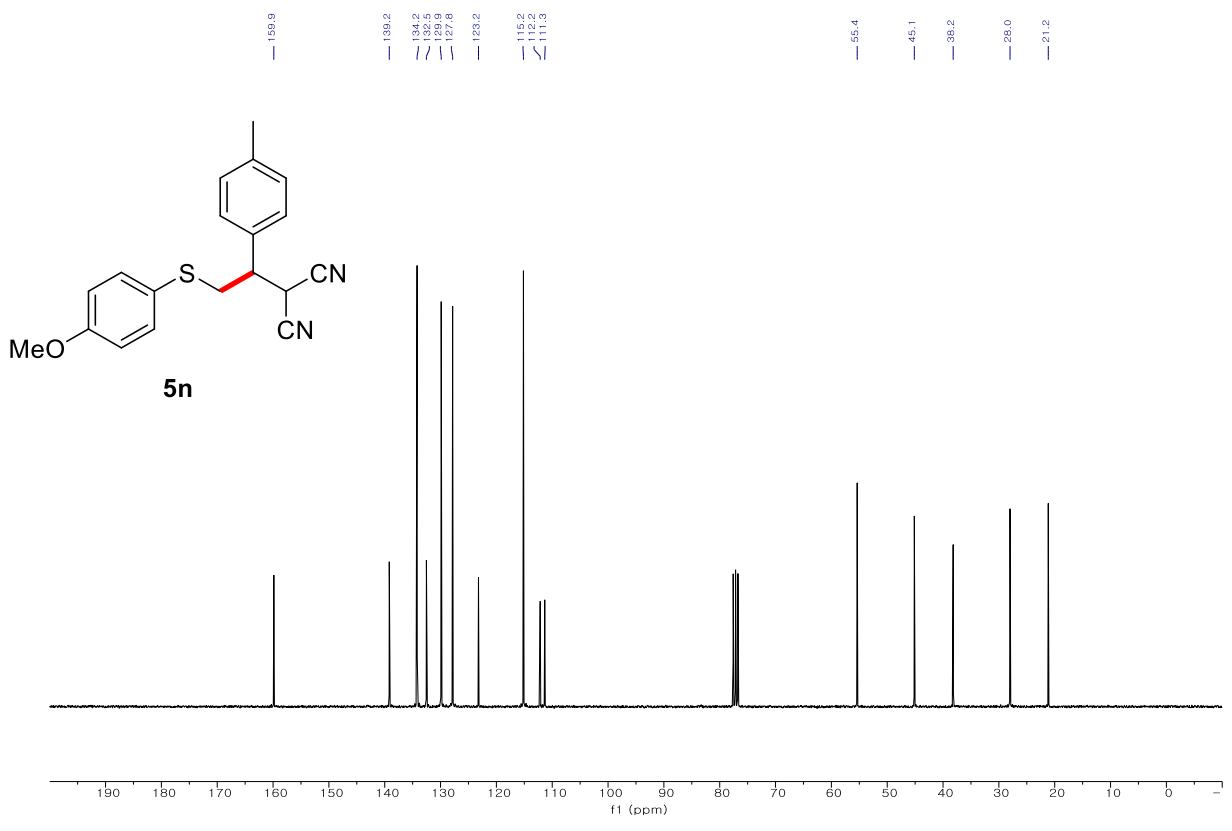


$^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of **5I**

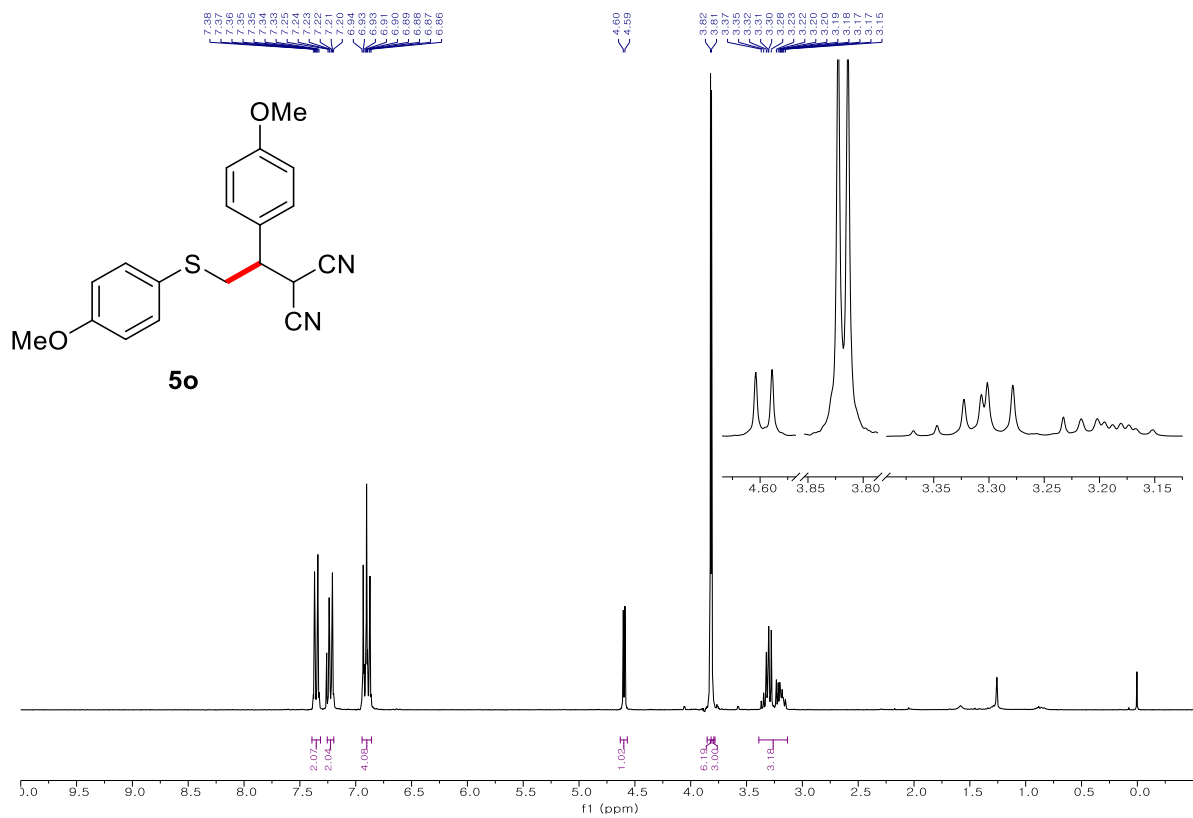




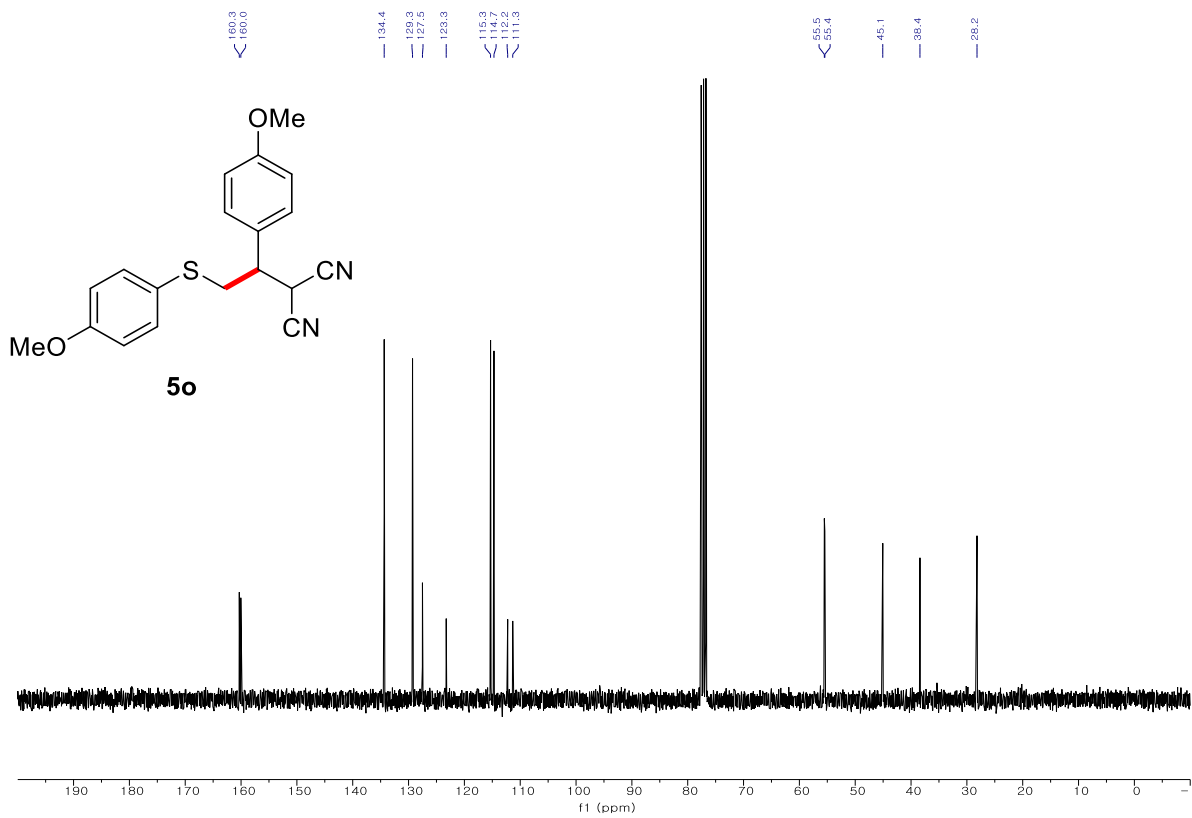
1H-NMR (300 MHz, CDCl₃) of 5n



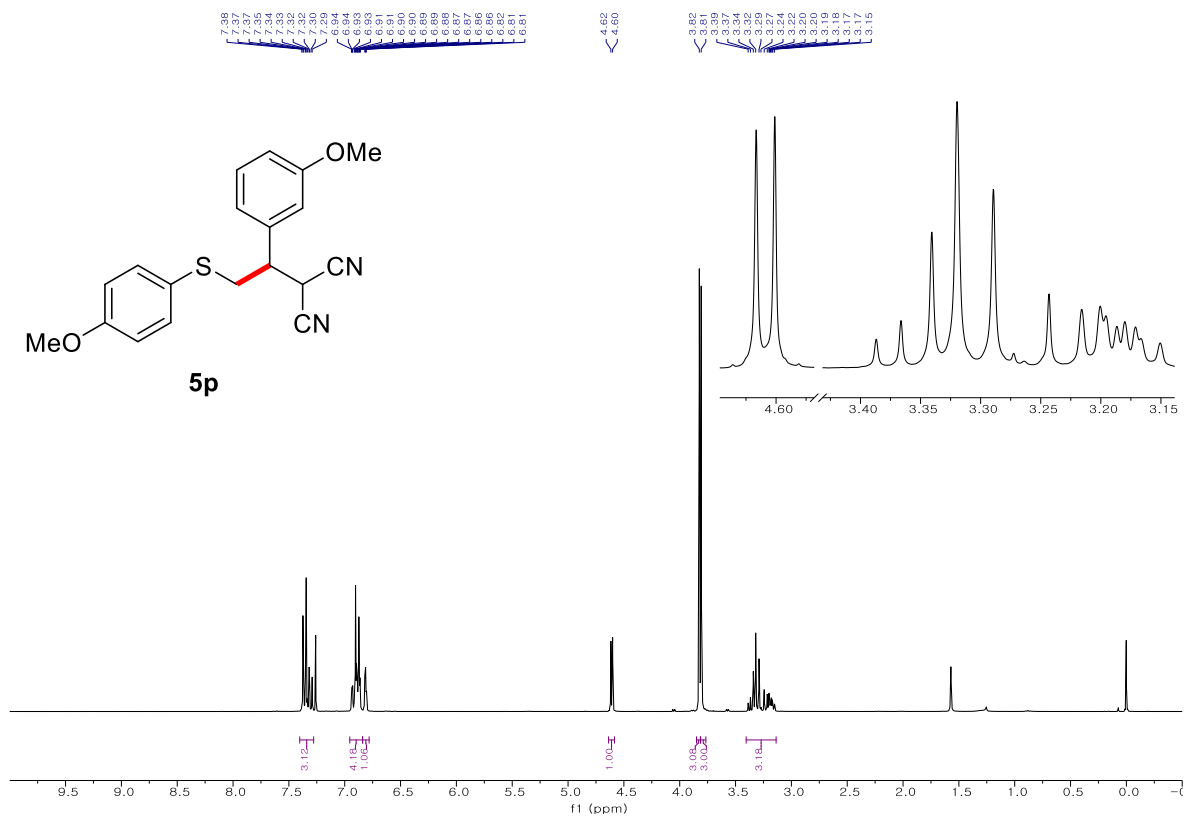
13C-NMR (75 MHz, CDCl₃) of 5n



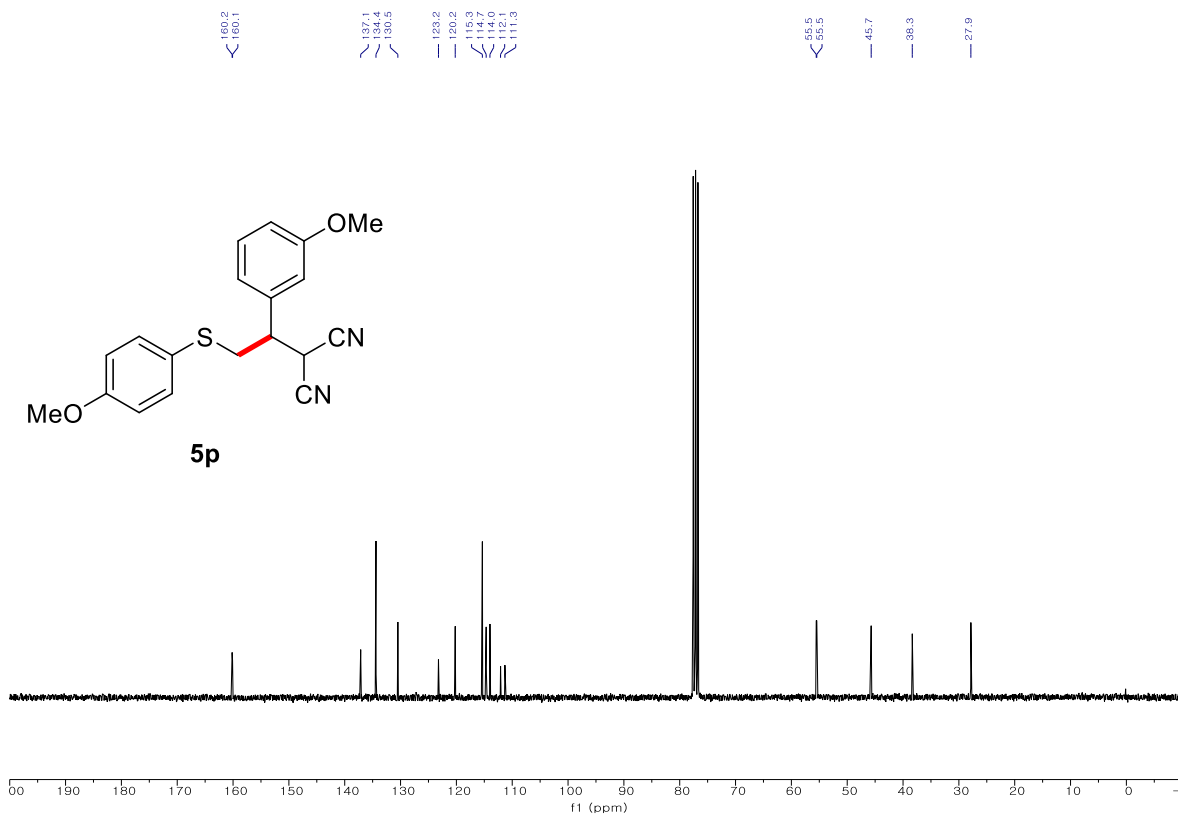
1H-NMR (300 MHz, CDCl₃) of **5o**



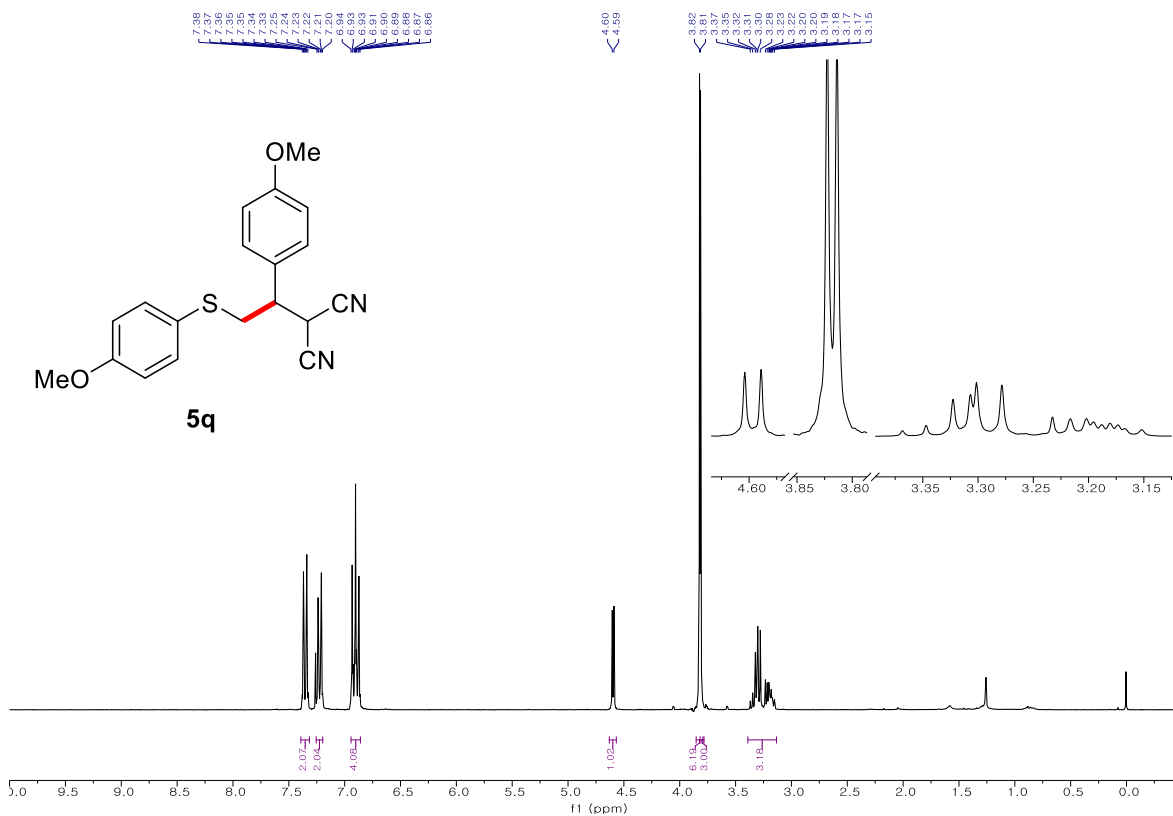
13C-NMR (75 MHz, CDCl₃) of **5o**



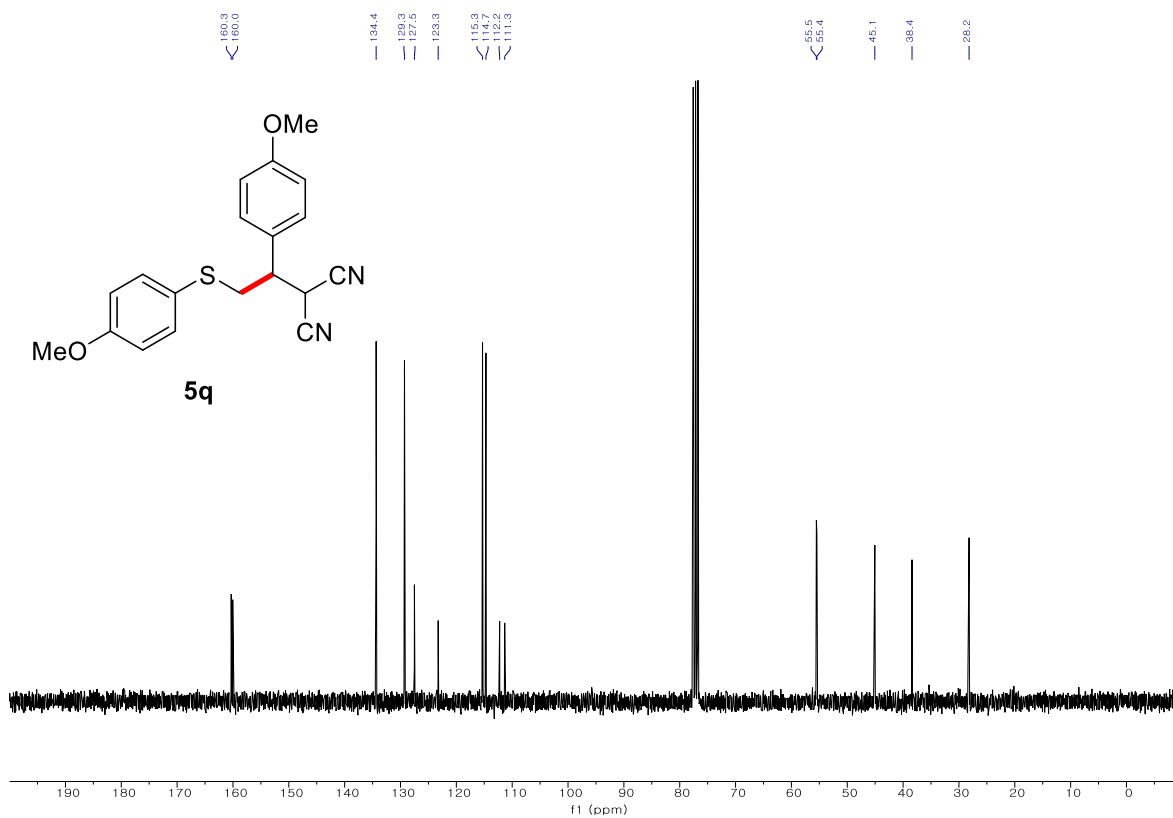
1H-NMR (300 MHz, CDCl₃) of **5p**



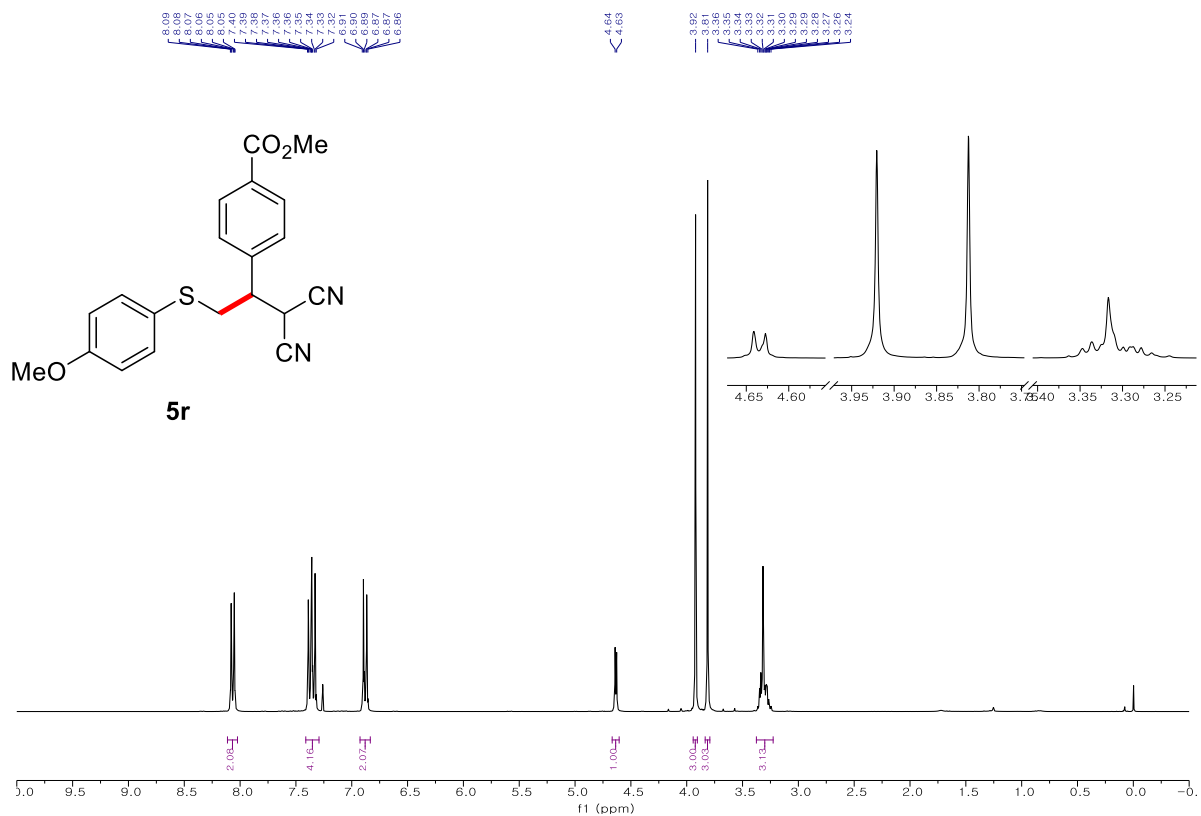
13C-NMR (75 MHz, CDCl₃) of **5p**



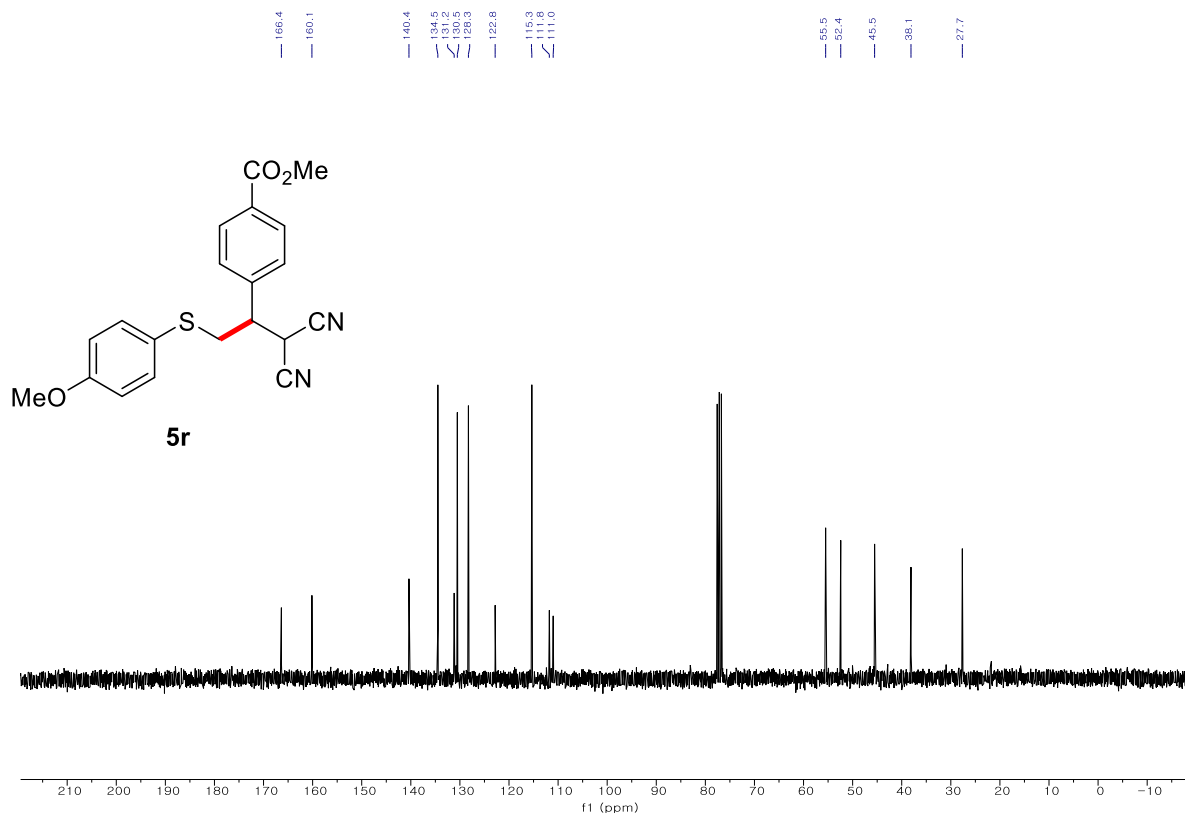
1H-NMR (300 MHz, CDCl₃) of **5q**



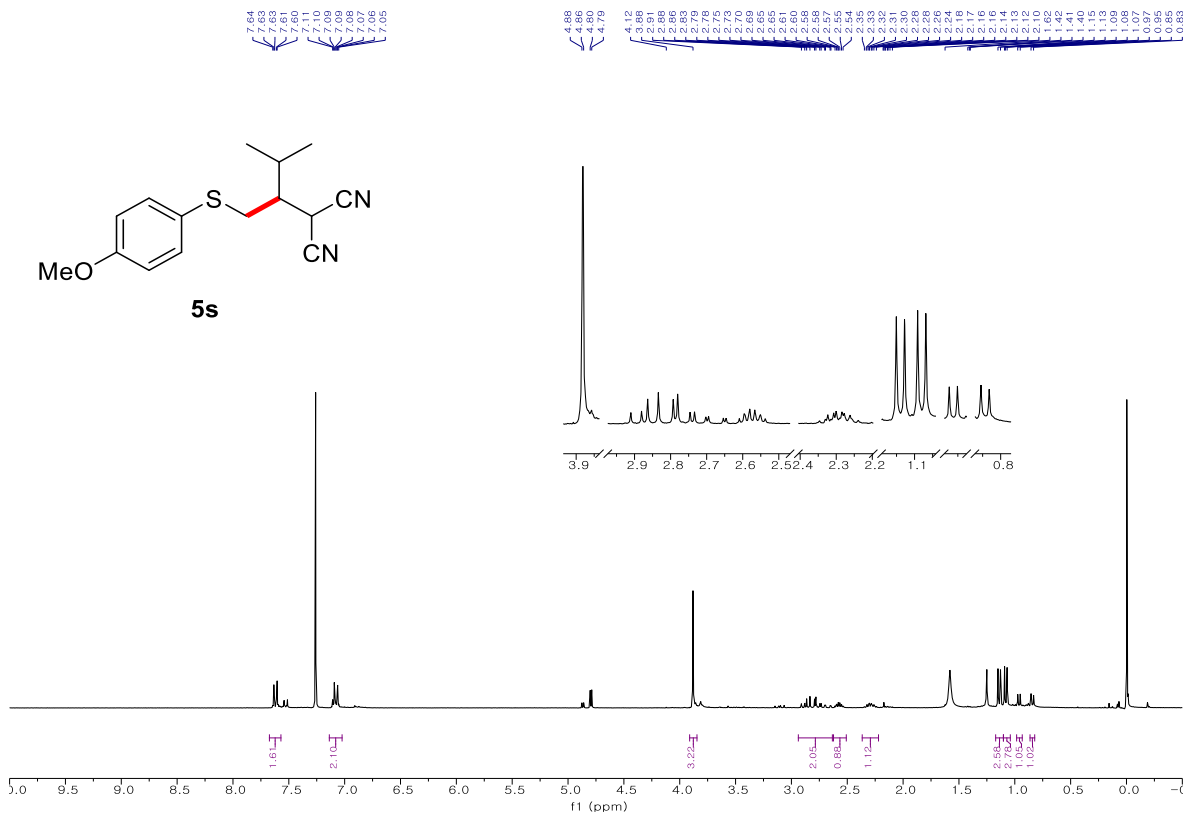
13C-NMR (75 MHz, CDCl₃) of **5q**



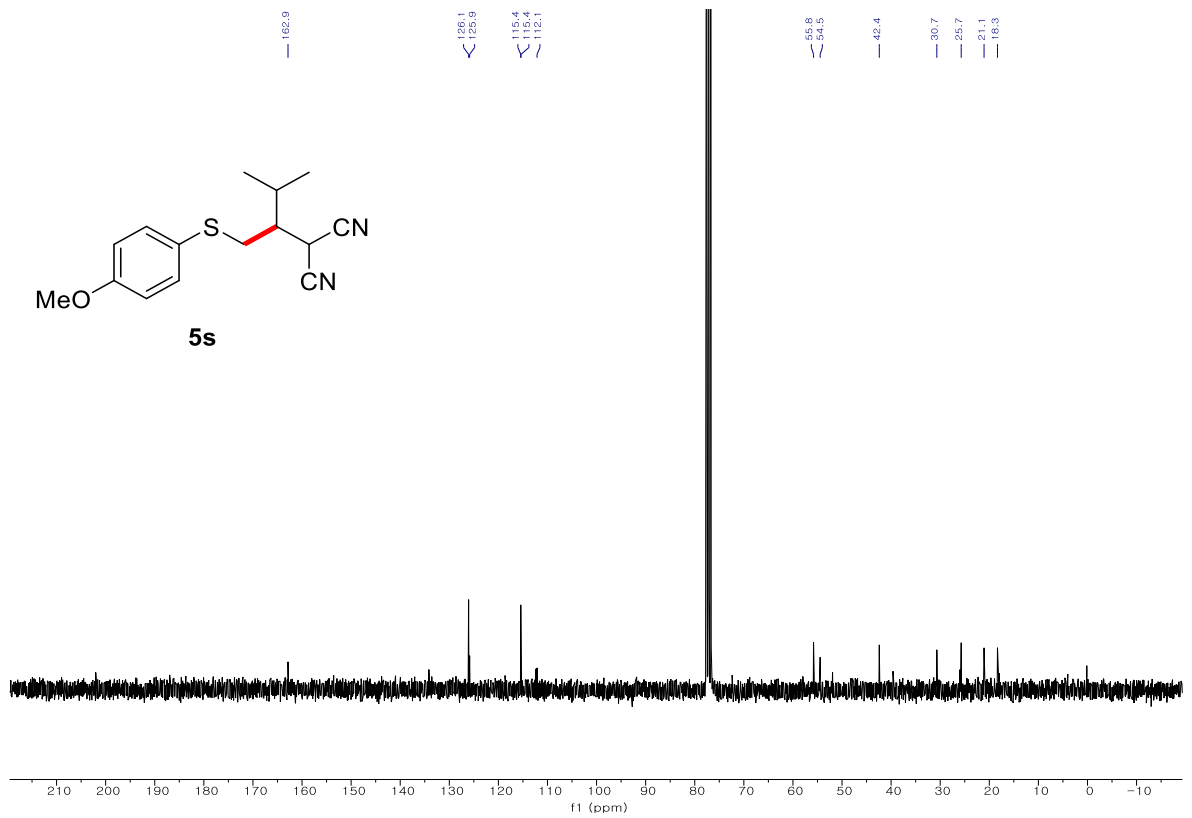
¹H-NMR (300 MHz, CDCl₃) of **5r**



¹³C-NMR (75 MHz, CDCl₃) of **5r**



¹H-NMR (300 MHz, CDCl₃) of **5s**



¹³C-NMR (75 MHz, CDCl₃) of **5s**

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