

Supporting Information

Photoredox catalyzed difunctionalization of alkenes with oxime esters and *NH*-Sulfoximines

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Table of Contents

1. General information	S2
2. Experimental procedures	S3
3. Mechanistic studies	S9
4. Characterization data for products	S13
5. NMR copies of product	S26
6. References	S61

1. General information

All commercial reagents were directly used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz in CDCl_3 at room temperature ($20 \pm 3 \text{ }^\circ\text{C}$), by using tetramethylsilane as the internal standard. High-resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Waters Q-ToF MS/MS system with the ESI technique. A Kessil PR160L-456 nm lamp was placed 5-6 cm away from the reaction vessel for light irradiation.

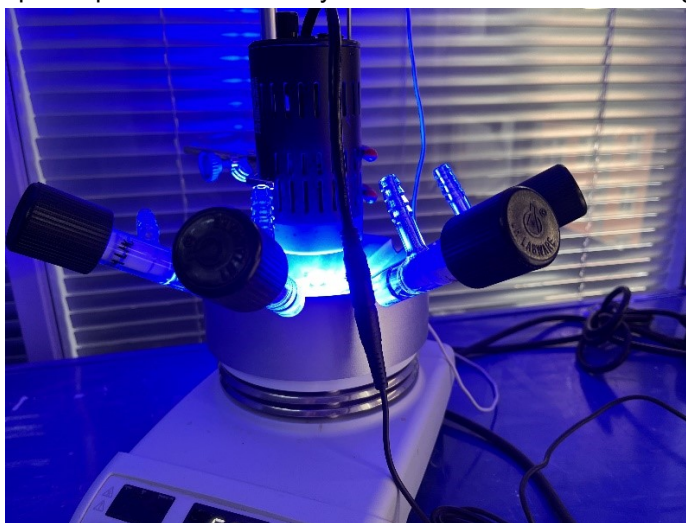


Figure S1. The visible-light irradiation instrument

2. Experimental procedures

2.1 Optimization of reaction conditions

Table S1. Optimizations of photocatalysts^a

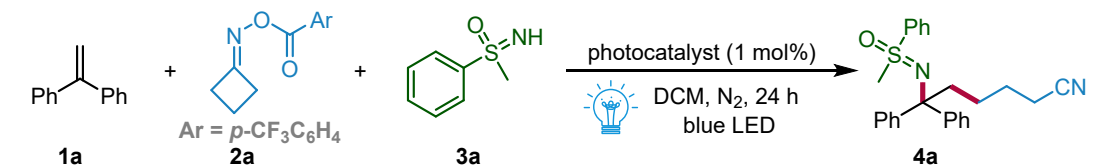


Table S1. Optimizations of photocatalysts^a

Entry	Photocatalyst	Yield (%)
1	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	55
2	Ir(dFppy) ₂ (bpy)PF ₆	67
3	Ir(dFppy) ₃	60
4	Ir(p-Fppy) ₂ (bpy)PF ₆	75
5	Ir(ppy) ₃	70
6	Eosin Y	trace
7	Eosin B	trace
8	Rose Bengal	trace

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), **3a** (0.3 mmol), photocatalyst (1 mol%), DCM (1 mL), 40 W blue Kessil LED lamp (456 nm), under N₂ for 24 h. Isolated yields were given.

Table S2. Optimizations of solvents^a

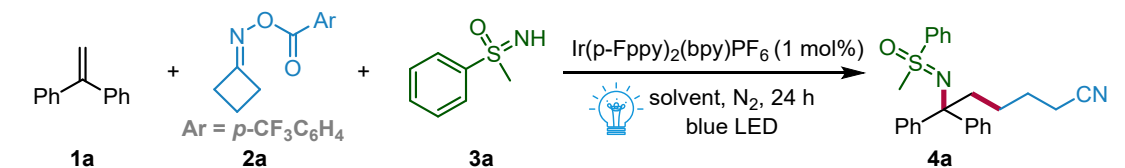


Table S2. Optimizations of solvents^a

Entry	Solvent	Yield (%)
1	DCE	66
2	THF	40
3	CH ₃ CN	55
4	DMC	20
5	Toluene	trace
6	DMF	trace
7	1,4-Dioxane	trace
8	DMSO	N.D.
9	DMA	N.D.
10	DCM	75

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), **3a** (0.3 mmol), Ir(p-Fppy)₂(bpy)PF₆ (1 mol%), solvent (1 mL), 40 W blue Kessil LED lamp (456 nm), under N₂ for 24 h. Isolated yields were given.

Table S3. Optimizations of reaction time^a

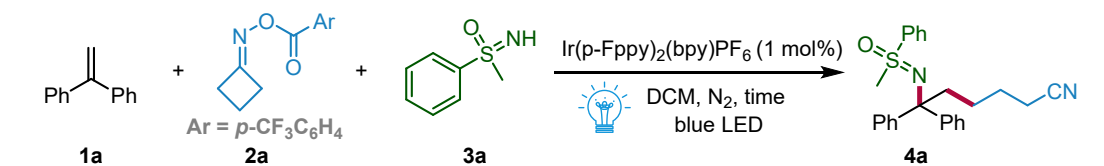
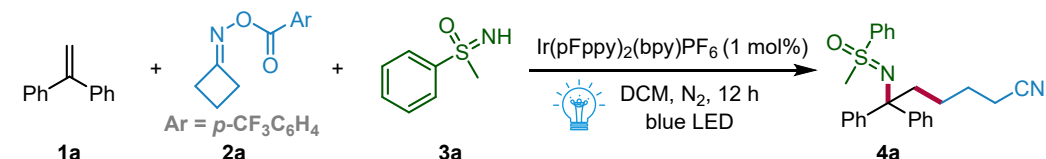


Table S3. Optimizations of reaction time^a

Entry	Time	Yield (%)
1	12 h	77
2	8 h	65
3	4 h	32

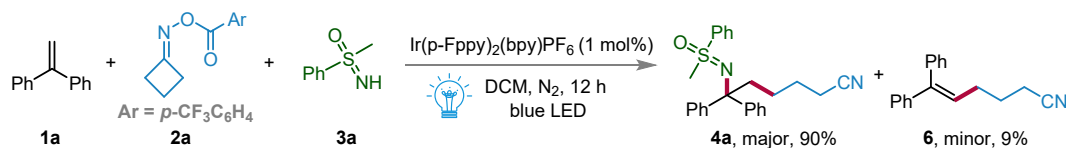
^aReaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), **3a** (0.3 mmol), Ir(p-Fppy)₂(bpy)PF₆ (1 mol%), DCM (1 mL), 40 W blue Kessil LED lamp (456 nm), under N₂. Isolated yields were given.

Table S4. Optimizations of substrate ratio^a



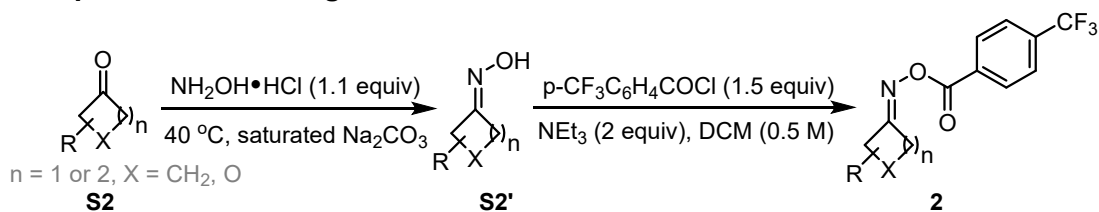
Entry	Substrate ratio (1a:2a:3a)	Yield (%)
1	1:1:3	60
2	2:1:3	66
3	4:1:3	82
4	4:1:1	71
5	4:1:2	75
6	4:1:4	90

^aReaction conditions: the ratio of **1a:2a:3a** as shown in Table (0.1 mmol scale), Ir(p-Fppy)₂(bpy)PF₆ (1 mol%), DCM (1 mL), 40 W blue Kessil LED lamp (456 nm), under N₂ for 12 h. Isolated yields were given.

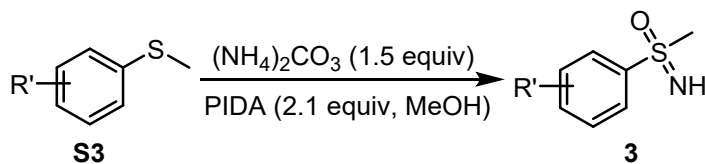


The photocatalytic reactions had a byproduct. It is assumed that excessive alkenes and sulfoximines might inhibit the generation of the byproduct, promoting the yield of the major product **4a**.

2.2 Preparation of starting materials **2** and **3**

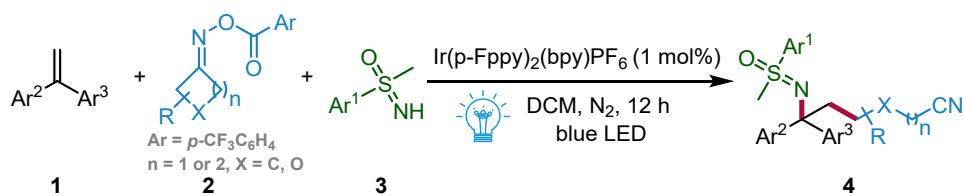


According to a modified literature procedure,¹ the ketone **S2** (10 mmol, 1 equiv) and hydroxylamine hydrochloride (11 mmol, 1.1 equiv) were placed in a 50 mL round-bottom flask equipped with stirrer. The pH of the solution was maintained at 7–8 by adding saturated aq. sodium carbonate (20 mL), and the mixture was stirred at $40\text{ }^\circ\text{C}$. After the reaction, the mixture was extracted with ether and water. The aqueous layer was extracted with ether (10 mL \times 3 times). The combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated in vacuo, providing the crude products **S2'** which were used in the next step without further purification. Then the oximes **S2'** (5 mmol, 1 equiv) and triethylamine (1.5 equiv) were dissolved in DCM (10 mL). The $p\text{-CF}_3\text{benzoyl}$ chloride (1.5 equiv) was slowly added at $0\text{ }^\circ\text{C}$ and the mixture was stirred overnight at room temperature. After the reaction, sodium bicarbonate solution (20 mL) was added to the reaction system. Then the mixture was diluted with water and ethyl acetate, the aqueous layer was extracted with ethyl acetate (20 mL \times 3 times). The combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography to obtain the desired products **2**.



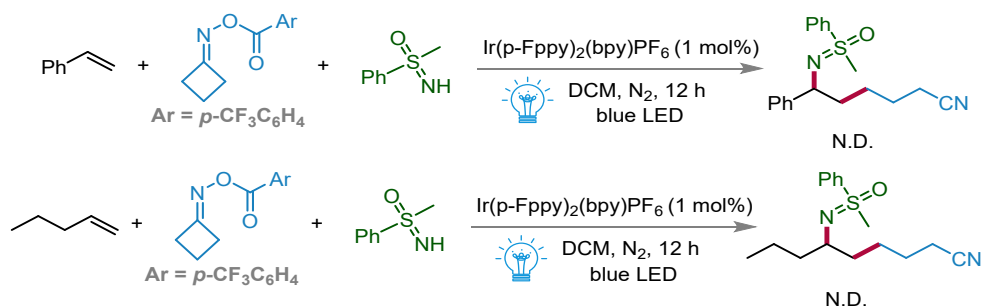
According to a modified literature procedure,² in a 50 mL round-bottom flask, sulfides **S3** (10 mmol, 1 equiv) and ammonium carbonate (15 mmol, 1.5 equiv) were dissolved in MeOH (20 mL), which was stirred at room temperature. Then PIDA (21 mmol, 2.1 equiv) was added in one portion. After the reaction, the mixture was extracted with DCM and water, the aqueous layer was extracted with DCM (20 mL \times 3 times). The combined organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatography to obtain the desired products **3**.

2.3 General experimental procedures for the desired products

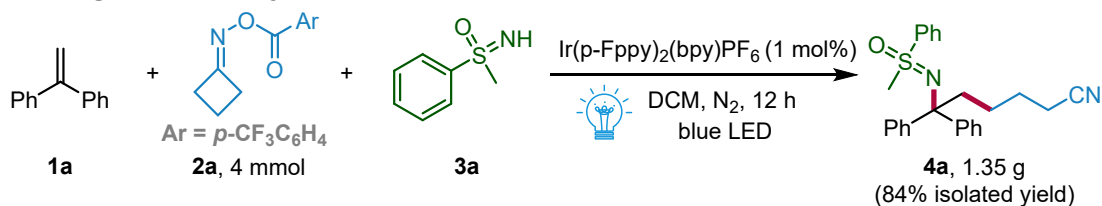


In a 10 mL Schlenk tube, **1** (4.0 equiv, 0.4 mmol), **2** (1.0 equiv, 0.1 mmol), **3** (4.0 equiv, 0.4 mmol), Ir(p-Fppy)₂(bpy)PF₆ (1 mol%) were dissolved in DCM (1 mL), and then charging with nitrogen more than three times. The tube was stirred for 12 h with the irradiation of 40 W blue LED ($\lambda = 456 \text{ nm}$). After the reaction, the mixture was extracted with water and ethyl acetate, and the organic layer was washed with saturated brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired products **4**.

Unsuccessful substrates:

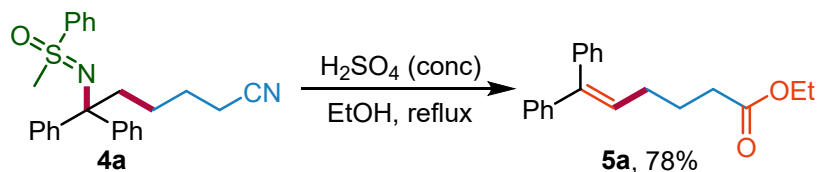


2.4 The gram-scale synthesis of **4a**

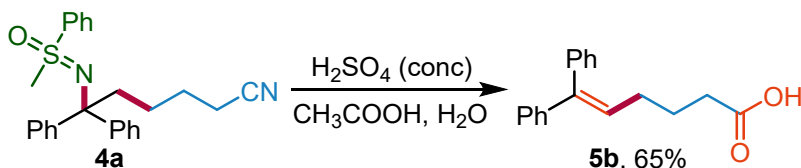


In a 100 mL three-neck flask, **1a** (16.0 mmol, 4.0 equiv), **2a** (4.0 mmol, 1.0 equiv), **3a** (16.0 mmol, 4.0 equiv) and Ir(p-Fppy)₂(bpy)PF₆ (1 mol%) were dissolved in DCM (40 mL), and then the tube was stirred for 12 h with the irradiation of blue LED. After the reaction, the mixture was extracted with water and ethyl acetate, and the organic layer was washed with saturated brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product **4a** in 84% yield (1.35 g).

2.5 The synthetic transformation of **4a**

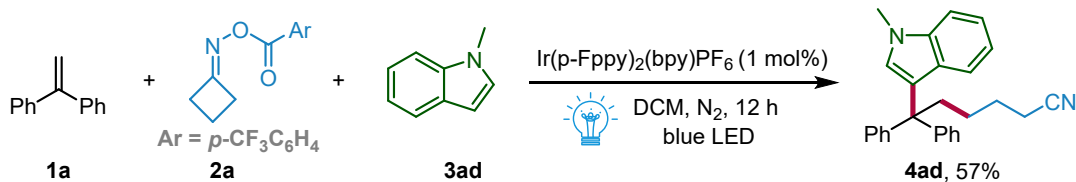


4a (0.1 mmol) was added into a 25 mL round bottom flask. Concentrated H_2SO_4 (0.2 mL) and EtOH (1 mL) were then added sequentially via syringe. The resulting mixture was heated to reflux for 12 hours. After the reaction, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to afford the desired product **5a** in 78% yield.

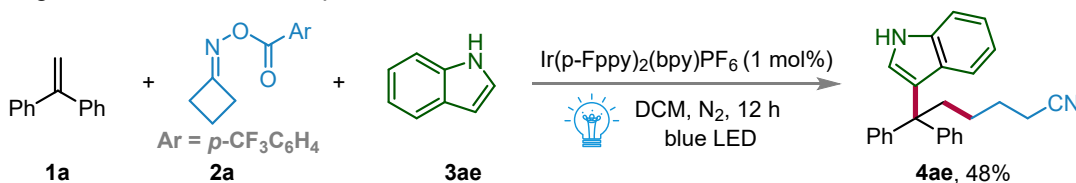


4a (0.5 mmol) was added into a 25 mL round bottom flask. Concentrated H_2SO_4 (0.3 mL), CH_3COOH (0.5 mL), and H_2O (0.5 mL) were then added sequentially via syringe. The resulting mixture was heated to reflux for 24 hours. After the reaction, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to give **5b** as white solid in 65% yield.

2.6 The photocatalyzed synthetic applications



In a 10 mL Schlenk tube, **1a** (4.0 equiv, 0.4 mmol), **2a** (1.0 equiv, 0.1 mmol), **3ad** (4.0 equiv, 0.4 mmol), $\text{Ir}(\text{p-Fppy})_2(\text{bpy})\text{PF}_6$ (1 mol%) were dissolved in DCM (1 mL), and then charging with nitrogen more than three times. The tube was stirred for 12 h with the irradiation of 40 W blue LED ($\lambda = 456 \text{ nm}$). After the reaction, the mixture was extracted with water and ethyl acetate, and the organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4 . After filtration, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product **4ad**.



In a 10 mL Schlenk tube, **1a** (4.0 equiv, 0.4 mmol), **2a** (1.0 equiv, 0.1 mmol), **3ae** (4.0 equiv, 0.4

mmol), Ir(p-Fppy)₂(bpy)PF₆ (1 mol%) were dissolved in DCM (1 mL), and then charging with nitrogen more than three times. The tube was stirred for 12 h with the irradiation of 40 W blue LED ($\lambda = 456$ nm). After the reaction, the mixture was extracted with water and ethyl acetate, and the organic layer was washed with saturated brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired product **4ae**.

2.7 Assessment of the sensitivity of the transformation

A set of experiments that employed **1a** with **2a** and **3a** were performed to evaluate the reaction-condition-based sensitivity of this conversion, which will be valuable in increasing the insight of this new synthetic method and reproducibility. Various parameters including concentration, water level, air atmosphere, photocatalyst level, light intensity, and scale were chosen with positive and negative direction relative to the standard reaction conditions. Each experiment only deliberately changed one parameter, while keeping others at standard levels.

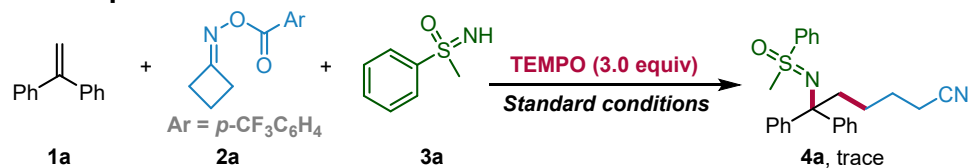
Table S5. Assessment of the sensitivity of the transformation^a

Parameter	Variation		Description	Yield (%) ^b
Concentration (c)	High c	c + 10% c	0.9 mL DCM	74
	Low c	c - 10% c	1.1 mL DCM	86
H ₂ O level	High H ₂ O	+ H ₂ O; V _{H₂O} = 1% V _{rxn}	10 μ L H ₂ O in 1.0 mL DCM	70
Air atmosphere	Air	Air	Air instead of N ₂	0
Photocatalyst (x mol%)	Low photocatalyst	x/2	0.5 mol%	75
	High photocatalyst	3·x	3 mol%	71
Light intensity (W)	Low W	W/16	2.5 W	67
Scale	Big scale	n·10	1.0 mmol of 2a	85

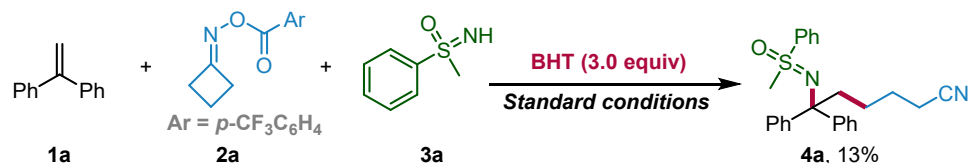
^aReaction conditions: **1a** (0.4 mmol), **2a** (0.1 mmol), **3a** (0.4 mmol), Ir(p-Fppy)₂(bpy)PF₆ (1 mol%), DCM (1 mL), 40 W blue Kessil LED lamp (456 nm), under N₂ for 12 h. ^bThe average yield of three parallel reactions.

3. Mechanistic studies

3.1 Control experiments



In a 10 mL Schlenk tube, **1a** (4.0 equiv, 0.4 mmol), **2a** (1.0 equiv, 0.1 mmol), **3a** (4.0 equiv, 0.4 mmol), Ir(*p*-Fppy)₂(bpy)PF₆ (1 mol%) were dissolved in DCM (1 mL). Afterward, (2,6-ditert-butyl-4-methyl-phenol) (TEMPO, 3.0 equiv) was added in the mixture, and then charging with nitrogen more than three times. The tube was stirred for 12 h with the irradiation of 40 W blue LED ($\lambda = 456$ nm). After the reaction, the yield of **4a** was detected by column chromatography on silica gel.



In a 10 mL Schlenk tube, **1a** (4.0 equiv, 0.4 mmol), **2a** (1.0 equiv, 0.1 mmol), **3a** (4.0 equiv, 0.4 mmol), Ir(*p*-Fppy)₂(bpy)PF₆ (1 mol%) were dissolved in DCM (1 mL). Afterward, (2,6-ditert-butyl-4-methyl-phenol) (BHT, 3.0 equiv) was added in the mixture, and then charging with nitrogen more than three times. The tube was stirred for 12 h with the irradiation of 40 W blue LED ($\lambda = 456$ nm). After the reaction, the yield of **4a** was detected by column chromatography on silica gel.

3.2 HRMS analysis of model reaction solution

To understand the reaction mechanism more deeply, we employed high-resolution mass spectrometry (HRMS) to analyze the reaction solution of the model reaction. The *m/z* 247.1778 obviously corresponds to the molecular ion [C₁₃H₂₄N₂NaO]⁺ as shown in Figure S2. The *m/z* 310.2146 obviously corresponds to the molecular ion [C₁₉H₂₉NNaO]⁺ as shown in Figure S3. The *m/z* 333.1611 obviously corresponds to the molecular ion [C₁₆H₂₆N₂NaO₂S]⁺ as shown in Figure S4.

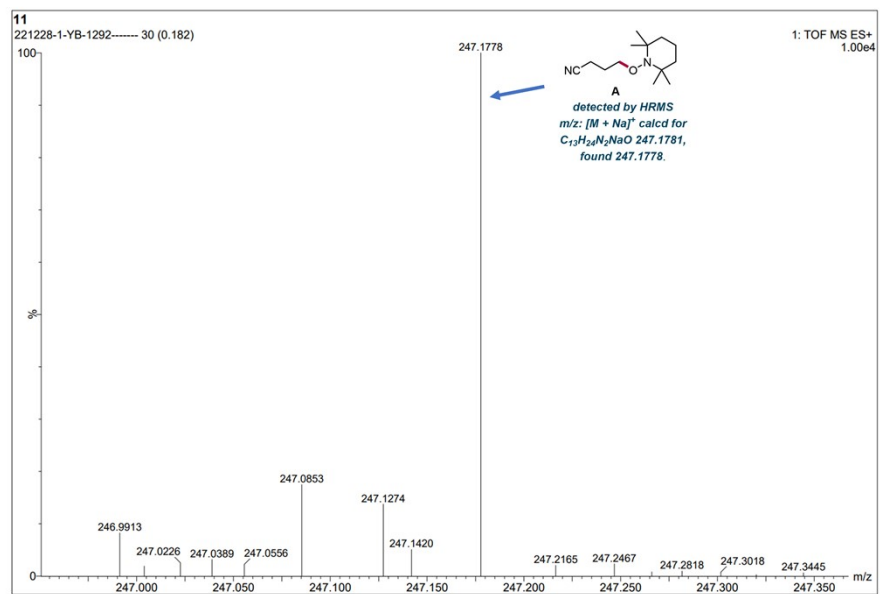


Figure S2. The HRMS analysis of reaction in the presence of TEMPO

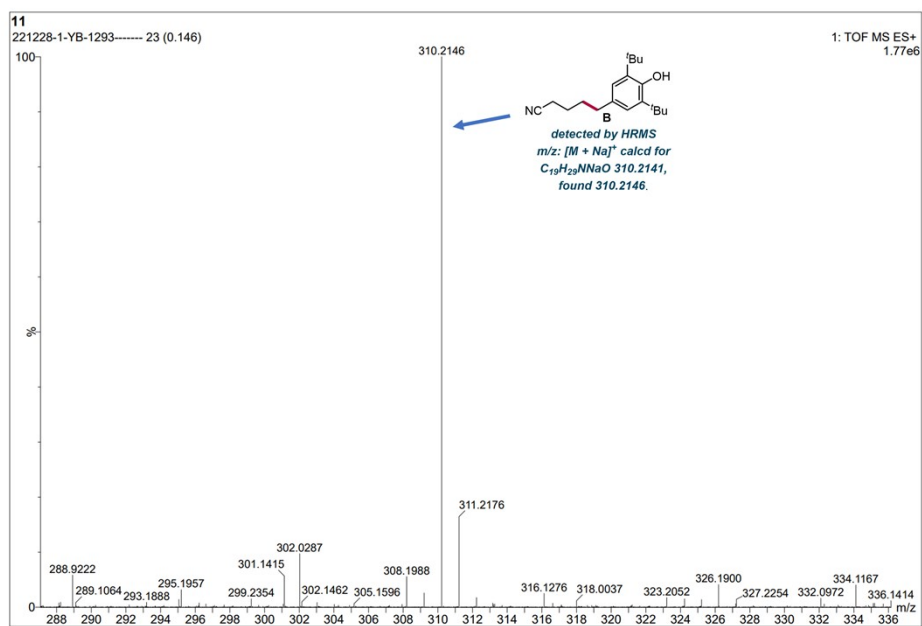


Figure S3. The HRMS analysis of reaction in the presence of BHT

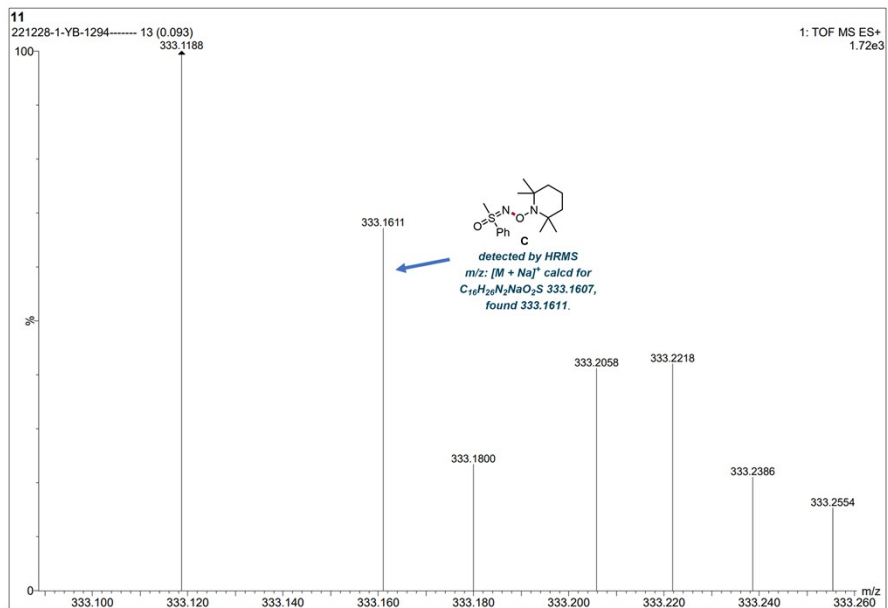


Figure S4. The HRMS analysis of reaction in the presence of TEMPO

3.3 Procedure for fluorescence quenching experiments

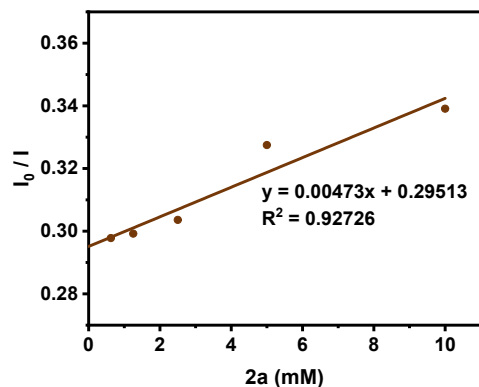
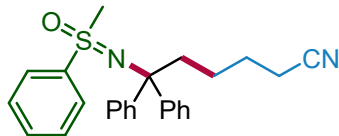


Figure S5 Fluorescence quenching experiments.

Stern-Volmer fluorescence quenching experiments were run with a freshly prepared solution of 5×10^{-5} M solution of $\text{Ir}(\text{p-Fppy})_2(\text{bpy})\text{PF}_6$ in dry DCM added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature (Figure S5). Emission intensities were recorded using an F-4600 FL Spectrophotometer. The fluorescence emission spectrum was measured from 380 nm to 750 nm. After degassing the sample with a stream of N_2 for 10 minutes, the emission of the sample was collected.

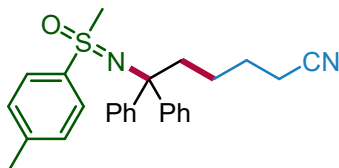
4. Characterization data for products

6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4a)



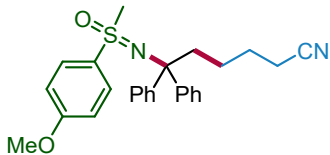
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (36.2 mg, 90%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.48 – 7.41 (m, 3H), 7.39 – 7.33 (m, 2H), 7.29 – 7.23 (m, 4H), 7.21 – 7.16 (m, 1H), 7.09 – 6.99 (m, 3H), 2.57 (s, 3H), 2.55 – 2.42 (m, 2H), 2.31 – 2.18 (m, 2H), 1.67 – 1.58 (m, 2H), 1.42 – 1.26 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.3, 147.5, 143.0, 131.8, 128.7, 127.9, 127.73, 127.65, 127.4, 127.1, 126.5, 126.1, 120.1, 67.3, 46.6, 41.8, 25.9, 23.7, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{NaOS}$, 425.1658; found, 425.1661.

6-((methyl(oxo)(*p*-tolyl)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4b)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (40.8 mg, 98%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 2H), 7.49 – 7.42 (m, 2H), 7.29 – 7.24 (m, 4H), 7.22 – 7.16 (m, 3H), 7.12 – 7.01 (m, 3H), 2.50 (s, 3H), 2.50 – 2.43 (m, 2H), 2.38 (s, 3H), 2.32 – 2.18 (m, 2H), 1.65 – 1.60 (m, 2H), 1.49 – 1.37 (m, 1H), 1.31 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 147.8, 142.4, 140.3, 129.3, 127.9, 127.8, 127.6, 127.4, 127.2, 126.5, 125.9, 120.1, 67.2, 46.4, 41.7, 25.9, 23.7, 21.4, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaOS}$, 439.1815; found, 439.1819.

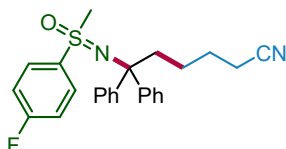
6-(((4-methoxyphenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4c)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (41.0 mg, 95%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.65 (m, 2H), 7.49 – 7.42 (m, 2H), 7.30 – 7.25 (m, 4H), 7.23 – 7.16 (m, 1H), 7.14 – 7.02 (m, 3H), 6.90 – 6.80 (m, 2H), 3.83 (s, 3H), 2.52 (s, 3H), 2.50 – 2.43 (m, 2H), 2.33 – 2.17 (m, 2H), 1.66 – 1.60 (m, 2H), 1.47 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 148.4, 147.8, 134.8,

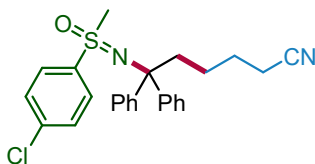
129.2, 127.9, 127.7, 127.6, 127.4, 126.5, 126.0, 120.1, 113.9, 67.2, 55.6, 46.7, 41.7, 25.9, 23.7, 17.0. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{26}H_{28}N_2NaO_2S$, 455.1764; found, 455.1765.

6-(((4-fluorophenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4d)



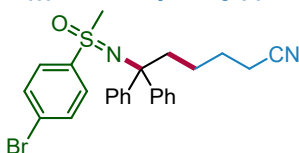
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (34.4 mg, 82%), 1H NMR (400 MHz, Chloroform- d) δ 7.72 – 7.65 (m, 2H), 7.46 – 7.41 (m, 2H), 7.29 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 7.08 – 6.95 (m, 5H), 2.65 (s, 3H), 2.59 – 2.50 (m, 1H), 2.45 – 2.35 (m, 1H), 2.32 – 2.18 (m, 2H), 1.68 – 1.58 (m, 2H), 1.42 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 164.6 (d, $J = 253.2$ Hz), 148.1, 147.1, 138.8 (d, $J = 3.0$ Hz), 129.9, 129.8, 127.9, 127.8, 127.7, 127.4, 126.5, 126.2, 120.1, 115.7 (d, $J = 22.5$ Hz), 67.4, 47.0, 41.8, 25.8, 23.7, 17.0. ^{19}F NMR (376 MHz, Chloroform- d) δ -107.38. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{25}H_{25}FN_2NaOS$, 443.1564; found, 443.1564.

6-(((4-chlorophenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4e)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: white oil (42.3 mg, 97%), 1H NMR (400 MHz, Chloroform- d) δ 7.62 – 7.57 (m, 2H), 7.46 – 7.40 (m, 2H), 7.30 – 7.25 (m, 4H), 7.22 – 7.16 (m, 3H), 7.08 – 7.01 (m, 3H), 2.67 (s, 3H), 2.59 – 2.49 (m, 1H), 2.44 – 2.34 (m, 1H), 2.33 – 2.21 (m, 2H), 1.67 – 1.62 (m, 2H), 1.43 – 1.27 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 148.0, 147.0, 141.4, 138.2, 128.8, 128.7, 127.9, 127.8, 127.6, 127.4, 126.5, 126.2, 120.1, 67.4, 46.8, 41.8, 25.8, 23.6, 17.0. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{25}H_{25}ClN_2NaOS$, 459.1268; found, 459.1268.

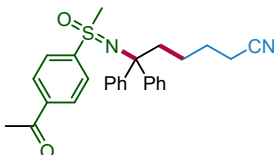
6-(((4-bromophenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4f)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (35.5 mg, 74%), 1H NMR (400 MHz, Chloroform- d) δ 7.55 – 7.49 (m, 2H), 7.47 – 7.39 (m, 4H), 7.28 – 7.23 (m, 2H), 7.23 – 7.15 (m, 3H), 7.08 – 6.99 (m, 3H),

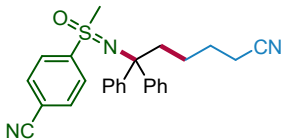
2.67 (s, 3H), 2.59 – 2.49 (m, 1H), 2.42 – 2.22 (m, 3H), 1.65 – 1.61 (m, 2H), 1.40 – 1.27 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 148.0, 147.0, 141.9, 131.8, 128.8, 127.9, 127.8, 127.6, 127.4, 126.6, 126.5, 126.2, 120.1, 67.4, 46.8, 41.8, 25.8, 23.6, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₅H₂₅BrN₂NaOS, 503.0763; found, 503.0768.

6-(((4-acetylphenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4g)



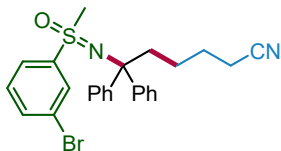
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: white oil (40.0 mg, 90%), ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.77 – 7.72 (m, 2H), 7.45 – 7.41 (m, 2H), 7.29 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 7.03 – 6.94 (m, 3H), 2.72 (s, 3H), 2.61 (s, 3H), 2.59 – 2.51 (m, 1H), 2.43 – 2.34 (m, 1H), 2.32 – 2.23 (m, 2H), 1.68 – 1.61 (m, 2H), 1.45 – 1.29 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 197.0, 147.9, 146.90, 146.87, 139.1, 128.5, 127.9, 127.8, 127.6, 127.5, 127.4, 126.5, 126.2, 120.1, 67.5, 46.6, 41.8, 26.9, 25.8, 23.6, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₇H₂₈N₂NaO₂S, 467.1764; found, 467.1767.

4-(N-(5-cyano-1,1-diphenylpentyl)-methylsulfonimidoyl)benzonitrile (4h)



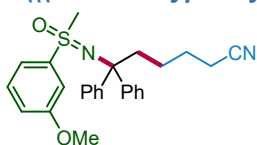
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: lightyellow oil (38.9 mg, 91%), ¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.58 – 7.52 (m, 2H), 7.42 – 7.37 (m, 2H), 7.28 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.13 – 7.08 (m, 2H), 7.00 – 6.93 (m, 3H), 2.84 (s, 3H), 2.65 – 2.56 (m, 1H), 2.37 – 2.22 (m, 3H), 1.67 – 1.61 (m, 2H), 1.32 – 1.13 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.6, 147.1, 146.3, 132.3, 128.0, 127.93, 127.85, 127.5, 127.4, 126.6, 126.4, 120.0, 117.6, 115.1, 67.7, 46.9, 41.8, 25.7, 23.6, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₆H₂₅N₃NaOS, 450.1611; found, 450.1612.

6-(((3-bromophenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4i)



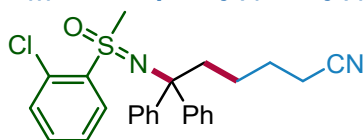
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: lightyellow oil (24 mg, 50%), ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.62 (m, 1H), 7.60 – 7.55 (m, 1H), 7.51 – 7.47 (m, 1H), 7.43 – 7.40 (m, 2H), 7.34 – 7.28 (m, 1H), 7.26 – 7.24 (m, 1H), 7.22 – 7.13 (m, 4H), 7.04 – 6.97 (m, 3H), 2.78 (s, 3H), 2.65 – 2.53 (m, 1H), 2.36 – 2.26 (m, 3H), 1.69 – 1.62 (m, 2H), 1.30 – 1.23 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.9, 146.4, 144.5, 134.5, 130.3, 130.1, 127.9, 127.8, 127.6, 127.3, 126.5, 126.4, 126.0, 125.7, 122.7, 120.1, 67.5, 47.1, 41.8, 25.8, 23.7, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₅H₂₅BrN₂NaOS, 503.0763; found, 503.0766.

6-(((3-methoxyphenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4j)



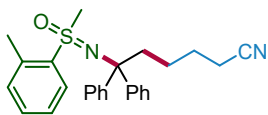
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: white oil (30.7 mg, 71%), ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.29 – 7.17 (m, 7H), 7.09 – 6.93 (m, 4H), 3.79 (s, 3H), 2.62 (s, 3H), 2.58 – 2.39 (m, 2H), 2.34 – 2.20 (m, 2H), 1.67 – 1.61 (m, 2H), 1.40 – 1.29 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.5, 148.3, 147.3, 144.3, 129.7, 127.9, 127.73, 127.71, 127.3, 126.5, 126.0, 120.1, 119.3, 118.1, 112.0, 67.3, 55.5, 46.6, 41.8, 25.9, 23.7, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₆H₂₈N₂NaO₂S, 455.1764; found, 455.1767.

6-(((2-chlorophenyl)(methyl)(oxo)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4k)



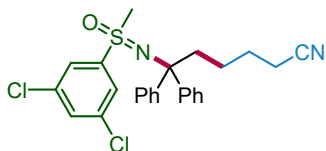
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (30.1 mg, 69%), ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 1H), 7.43 – 7.38 (m, 2H), 7.24 – 7.18 (m, 4H), 7.18 – 7.11 (m, 3H), 7.09 – 7.02 (m, 1H), 6.91 – 6.79 (m, 3H), 3.16 (s, 3H), 2.72 – 2.59 (m, 1H), 2.38 – 2.23 (m, 3H), 1.70 – 1.57 (m, 3H), 1.27 – 1.18 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 147.7, 145.6, 139.8, 132.4, 131.3, 131.1, 130.9, 127.7, 127.6, 127.5, 127.11, 127.07, 126.3, 126.2, 120.1, 67.6, 45.8, 41.8, 25.9, 23.6, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₅H₂₅ClN₂NaOS, 459.1268; found, 459.1269.

6-(((methyl)(oxo)(*o*-tolyl)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4l)



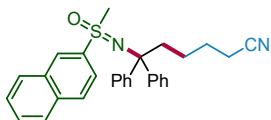
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (29.1 mg, 70%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 1H), 7.47 – 7.41 (m, 2H), 7.30 – 7.25 (m, 3H), 7.22 – 7.09 (m, 5H), 7.01 – 6.92 (m, 3H), 2.70 (s, 3H), 2.65 (s, 3H), 2.61 – 2.52 (m, 1H), 2.49 – 2.39 (m, 1H), 2.32 – 2.23 (m, 2H), 1.66 – 1.62 (m, 2H), 1.37 – 1.26 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.2, 146.8, 141.0, 136.2, 132.3, 131.7, 128.7, 127.83, 127.80, 127.6, 127.2, 126.4, 126.2, 126.1, 120.1, 67.7, 45.6, 41.9, 25.9, 23.6, 20.5, 17.0. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaOS}$, 439.1815; found, 439.1816.

6-(((3,5-dichlorophenyl)(methyl)oxo)sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4m)



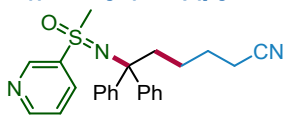
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (30.6 mg, 65%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.22 – 7.17 (m, 1H), 7.12 – 7.08 (m, 2H), 7.05 – 6.89 (m, 3H), 2.92 (s, 3H), 2.70 – 2.57 (m, 1H), 2.35 – 2.21 (m, 3H), 1.68 – 1.55 (m, 3H), 1.23 – 1.12 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 145.7, 145.1, 135.3, 131.3, 128.0, 127.8, 127.5, 127.3, 126.7, 126.4, 125.7, 120.0, 67.8, 47.2, 41.7, 25.8, 23.6, 17.0. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{N}_2\text{NaOS}$, 493.0879; found, 493.0881.

6-(((methyl(naphthalen-2-yl)oxo)sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4n)



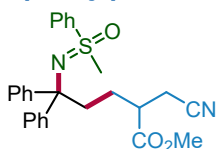
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (28.0 mg, 62%), ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.16 (m, 1H), 7.89 – 7.83 (m, 2H), 7.82 – 7.78 (m, 1H), 7.77 – 7.72 (m, 1H), 7.62 – 7.54 (m, 2H), 7.50 – 7.45 (m, 2H), 7.29 – 7.19 (m, 5H), 6.98 – 6.93 (m, 2H), 6.88 – 6.83 (m, 1H), 2.69 (s, 3H), 2.60 – 2.41 (m, 2H), 2.32 – 2.22 (m, 2H), 1.67 – 1.62 (m, 2H), 1.41 – 1.36 (m, 1H), 1.28 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.3, 147.3, 139.8, 134.4, 132.3, 129.1, 128.8, 128.4, 128.2, 127.9, 127.73, 127.70, 127.3, 127.1, 126.5, 126.0, 122.8, 120.1, 67.4, 46.6, 41.8, 25.9, 23.7, 17.0. HRMS (ESI-TOF) *m/z*: $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{NaOS}$, 475.1815; found, 475.1819.

6-((methyl(oxo)(pyridin-3-yl)-sulfaneylidene)amino)-6,6-diphenylhexanenitrile (4o)



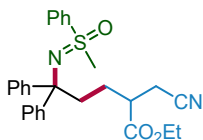
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (32.2 mg, 80%), ^1H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H), 7.39 – 7.34 (m, 2H), 7.24 – 7.19 (m, 3H), 7.16 – 7.10 (m, 3H), 6.95 – 6.88 (m, 3H), 3.07 (s, 3H), 2.66 – 2.58 (m, 1H), 2.38 – 2.28 (m, 3H), 1.69 – 1.62 (m, 2H), 1.33 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 149.0, 148.1, 146.9, 137.3, 127.9, 127.6, 127.4, 127.2, 126.1, 126.0, 125.2, 121.6, 120.1, 67.2, 43.3, 41.8, 25.9, 23.7, 17.0. HRMS (ESI-TOF) *m/z*: [M + Na] $^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{N}_3\text{NaOS}$, 426.1611; found, 426.1613.

methyl 2-(cyanomethyl)-5-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-5,5-diphenylpentanoate (4p)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (30.8 mg, 67%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.66 (m, 2H), 7.46 – 7.40 (m, 3H), 7.37 – 7.26 (m, 4H), 7.23 – 7.17 (m, 3H), 7.08 – 6.98 (m, 3H), 3.69 (d, *J* = 1.8 Hz, 3H), 2.76 – 2.44 (m, 8H), 1.71 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 173.3, 147.84, 147.79, 146.9, 146.8, 142.9, 142.8, 131.8, 131.7, 128.71, 128.67, 128.3, 128.0, 127.9, 127.7, 127.63, 127.60, 127.5, 127.4, 127.10, 127.08, 126.7, 126.6, 126.2, 125.9, 118.3, 67.0, 66.9, 52.2, 46.7, 46.6, 41.9, 41.8, 39.2, 39.1, 26.6, 26.5, 19.13, 19.11. HRMS (ESI-TOF) *m/z*: [M + Na] $^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{NaO}_3\text{S}$, 483.1713; found, 483.1719.

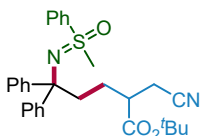
ethyl 2-(cyanomethyl)-5-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-5,5-diphenylpentanoate (4q)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (33.2 mg, 70%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.60 (m, 2H), 7.48 – 7.39 (m, 3H), 7.39 – 7.31 (m, 2H), 7.30 – 7.16 (m, 5H), 7.09 – 6.96 (m, 3H), 4.26 – 4.03 (m, 2H), 2.83 – 2.34 (m, 8H), 1.77 – 1.53 (m, 2H), 1.31 – 1.09 (m, 3H). ^{13}C NMR (101

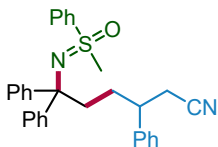
MHz, Chloroform-*d*) δ 172.9, 172.8, 147.9, 147.8, 146.90, 146.86, 142.9, 142.8, 131.8, 131.7, 128.72, 128.69, 128.0, 127.9, 127.7, 127.64, 127.62, 127.5, 127.4, 127.1, 126.64, 126.60, 126.2, 118.4, 66.99, 66.95, 61.1, 46.7, 46.6, 41.91, 41.87, 39.12, 39.08, 26.58, 26.56, 19.1, 14.2. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{28}H_{30}N_2NaO_3S$, 497.1869; found, 497.1873.

***tert*-butyl 2-(cyanomethyl)-5-((methyl(oxo)(phenyl)-*l*6-sulfaneylidene)amino)-5,5-diphenylpentanoate (4r)**



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (40.2 mg, 80%), 1H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.68 (m, 2H), 7.47 – 7.39 (m, 3H), 7.39 – 7.30 (m, 2H), 7.29 – 7.19 (m, 5H), 7.08 – 6.98 (m, 3H), 2.64 – 2.59 (m, 4H), 2.55 – 2.41 (m, 3H), 1.97 – 1.77 (m, 1H), 1.68 – 1.55 (m, 2H), 1.42 (d, $J = 2.1$ Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.03, 172.02, 147.94, 147.89, 147.0, 146.9, 143.0, 142.8, 132.2, 132.1, 131.73, 131.65, 128.69, 128.66, 128.0, 127.9, 127.72, 127.67, 127.6, 127.5, 127.4, 127.1, 126.6, 126.5, 126.2, 118.5, 81.6, 67.04, 67.01, 46.8, 46.6, 42.71, 42.65, 39.2, 39.1, 28.0, 26.6, 19.24, 19.20. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{30}H_{34}N_2NaO_3S$, 525.2182; found, 525.2183.

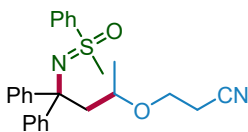
6-((methyl(oxo)(phenyl)-*l*6-sulfaneylidene)amino)-3,6,6-triphenylhexanenitrile (4s)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (24.9 mg, 52%), 1H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 1H), 7.60 – 7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.44 – 7.34 (m, 3H), 7.34 – 7.18 (m, 8H), 7.17 – 7.03 (m, 5H), 7.00 – 6.92 (m, 1H), 2.94 – 2.79 (m, 1H), 2.75 – 2.36 (m, 6H), 2.33 – 2.16 (m, 1H), 1.98 – 1.83 (m, 1H), 1.71 – 1.45 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 148.0, 147.7, 146.9, 143.2, 142.8, 142.0, 141.9, 132.0, 131.5, 128.9, 128.7, 128.6, 128.0, 127.9, 127.79, 127.76, 127.7, 127.52, 127.49, 127.47, 127.45, 127.4, 127.2, 127.1, 126.7, 126.4, 126.14, 126.07, 118.8, 67.2, 67.1, 47.1, 46.2, 42.63, 42.56, 40.3, 40.2, 29.6, 29.5, 25.4. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{31}H_{30}N_2NaOS$, 501.1971; found, 501.1976.

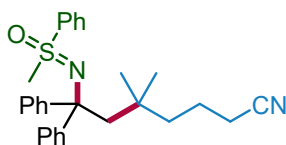
4-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-4,4-diphenylbutan-2-yl)oxypropanenitrile

(4t)



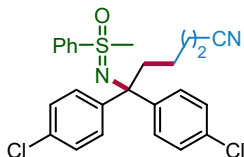
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (23.3 mg, 54%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.86 (m, 1H), 7.61 – 7.35 (m, 6H), 7.32 – 7.08 (m, 7H), 6.97 – 6.91 (m, 1H), 3.77 – 3.60 (m, 1H), 3.48 – 3.27 (m, 1H), 3.17 – 2.88 (m, 1H), 2.83 – 2.31 (m, 5H), 2.12 – 1.82 (m, 2H), 1.06 (dd, J = 23.1, 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 148.2, 146.7, 142.7, 132.1, 131.5, 128.9, 128.6, 128.14, 128.11, 128.04, 127.96, 127.7, 127.5, 127.3, 127.2, 127.13, 127.06, 126.8, 126.2, 125.8, 118.1, 73.6, 73.4, 66.34, 66.28, 62.7, 62.6, 49.9, 49.8, 47.3, 45.9, 21.3, 20.9, 18.5, 18.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaO}_2\text{S}$, 455.1764; found, 455.1766.

5,5-dimethyl-7-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-7,7-diphenylheptanenitrile (4u)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (20.4 mg, 46%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.65 (m, 2H), 7.47 – 7.37 (m, 3H), 7.37 – 7.14 (m, 7H), 7.06 – 6.94 (m, 3H), 2.68 – 2.56 (m, 2H), 2.53 (s, 3H), 2.09 – 1.96 (m, 2H), 1.66 – 1.49 (m, 2H), 1.27 – 1.10 (m, 2H), 0.76 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1, 148.0, 143.6, 131.4, 128.6, 128.43, 128.36, 127.6, 127.0, 126.9, 126.4, 126.0, 120.1, 66.8, 51.4, 46.9, 43.2, 34.4, 29.1, 28.9, 20.5, 17.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{NaOS}$, 467.2128; found, 467.2129.

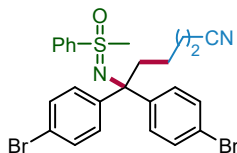
6,6-bis(4-chlorophenyl)-6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)hexanenitrile (4v)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (39.5 mg, 84%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.47 – 7.42 (m, 1H), 7.36 – 7.30 (m, 4H), 7.25 – 7.20 (m, 2H), 7.07 – 7.01 (m, 2H), 6.95 – 6.87 (m, 2H), 2.83 (s, 3H), 2.58 – 2.46 (m, 1H), 2.34 – 2.22 (m, 3H), 1.66 – 1.63 (m, 2H), 1.50 – 1.41 (m, 1H), 1.30 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.5, 145.1, 142.4, 132.3, 132.1, 131.7, 129.3, 129.0, 128.7, 128.0, 127.4, 127.1, 120.0, 66.6, 47.1, 41.7, 25.7, 23.6,

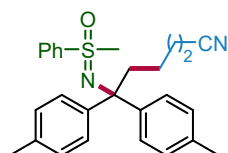
17.0. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{25}H_{24}Cl_2N_2NaOS$, 493.0879; found, 493.0881.

6,6-bis(4-bromophenyl)-6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)hexanenitrile (4w)



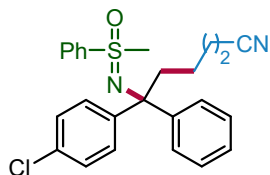
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (45.8 mg, 82%), 1H NMR (400 MHz, Chloroform- d) δ 7.57 – 7.52 (m, 2H), 7.48 – 7.43 (m, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.26 (m, 4H), 7.08 – 7.03 (m, 2H), 6.97 (d, J = 8.6 Hz, 2H), 2.85 (s, 3H), 2.58 – 2.46 (m, 1H), 2.34 – 2.20 (m, 3H), 1.68 – 1.63 (m, 2H), 1.52 – 1.43 (m, 1H), 1.29 – 1.21 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 146.9, 145.5, 142.3, 131.7, 130.9, 130.4, 129.7, 129.4, 128.7, 127.1, 120.5, 120.4, 120.0, 66.7, 47.1, 41.6, 25.7, 23.5, 17.0. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{25}H_{24}Br_2N_2NaOS$, 580.9868; found, 580.9875.

6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-6,6-di-*p*-tolylhexanenitrile (4x)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (36.6 mg, 85%), 1H NMR (400 MHz, Chloroform- d) δ 7.80 – 7.67 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.30 (m, 4H), 7.13 – 7.05 (m, 4H), 6.87 – 6.82 (m, 2H), 2.58 (s, 3H), 2.53 – 2.38 (m, 2H), 2.31 (s, 3H), 2.30 – 2.23 (m, 2H), 2.20 (s, 3H), 1.65 – 1.62 (m, 2H), 1.43 – 1.28 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 145.4, 144.7, 143.2, 135.9, 135.4, 131.5, 128.5, 128.0, 127.6, 127.6, 127.2, 120.2, 66.9, 46.5, 41.9, 25.9, 23.8, 21.0, 20.9, 17.0. HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{27}H_{30}N_2NaOS$, 453.1971; found, 453.1972.

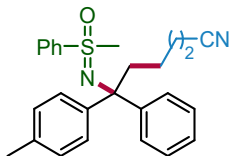
6-(4-chlorophenyl)-6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-6-phenylhexanenitrile (4y)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (32.7 mg, 75%), 1H NMR (400 MHz, Chloroform- d) δ 7.69 – 7.62 (m, 2H), 7.49 – 7.25 (m, 7H), 7.23 – 7.11 (m, 3H), 7.03 – 6.95 (m, 2H), 2.70 (d, J = 28.5 Hz, 3H), 2.57 – 2.47 (m, 1H), 2.43 – 2.32 (m, 1H), 2.31 – 2.25 (m, 2H), 1.67 – 1.60 (m, 2H), 1.39 – 1.28

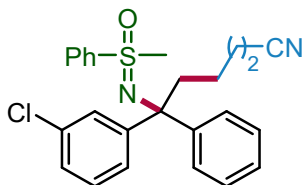
(m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.8, 147.0, 146.6, 146.0, 142.8, 142.6, 132.1, 131.8, 131.74, 131.68, 129.2, 129.1, 128.70, 128.67, 128.3, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.13, 127.10, 126.7, 126.3, 120.0, 66.93, 66.90, 47.1, 46.6, 41.8, 41.7, 25.8, 23.7, 23.6, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_2\text{NaOS}$, 459.1268; found, 459.1270.

6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-6-phenyl-6-(*p*-tolyl)hexanenitrile (4z)



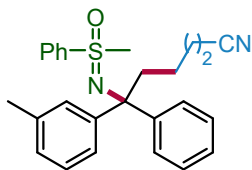
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (35.4 mg, 85%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.75 (m, 1H), 7.73 – 7.69 (m, 1H), 7.48 – 7.30 (m, 5H), 7.29 – 7.25 (m, 2H), 7.22 – 7.00 (m, 4H), 6.86 – 6.80 (m, 1H), 2.58 (d, $J = 23.8$ Hz, 3H), 2.52 – 2.36 (m, 2H), 2.33 – 2.18 (m, 5H), 1.67 – 1.60 (m, 2H), 1.47 – 1.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 147.7, 145.3, 144.4, 143.14, 143.10, 136.1, 135.5, 131.7, 131.5, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 127.6, 127.4, 127.2, 127.1, 126.4, 126.0, 120.1, 67.09, 67.07, 46.6, 46.5, 41.83, 41.80, 25.9, 23.7, 21.0, 20.9, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaOS}$, 439.1815; found, 439.1817.

6-(3-chlorophenyl)-6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-6-phenylhexanenitrile (4aa)



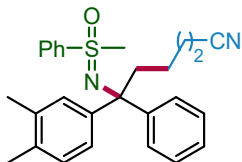
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (27.0 mg, 62%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 1H), 7.64 – 7.59 (m, 1H), 7.55 – 7.35 (m, 4H), 7.34 – 7.26 (m, 2H), 7.24 – 7.07 (m, 4H), 7.03 – 6.93 (m, 2H), 2.72 (d, $J = 51.8$ Hz, 3H), 2.61 – 2.21 (m, 4H), 1.69 – 1.62 (m, 2H), 1.40 – 1.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.7, 149.5, 147.6, 146.2, 142.4, 133.8, 133.4, 131.9, 131.6, 129.1, 128.74, 128.72, 128.65, 128.2, 128.0, 127.82, 127.75, 127.54, 127.46, 127.1, 127.0, 126.7, 126.5, 126.3, 126.2, 125.9, 125.7, 120.0, 67.1, 47.2, 46.7, 41.7, 41.5, 25.8, 23.59, 23.57, 16.98, 16.97. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_2\text{NaOS}$, 459.1268; found, 459.1270.

6-((methyl(oxo)(phenyl)-sulfaneylidene)amino)-6-phenyl-6-(*m*-tolyl)hexanenitrile (4ab)



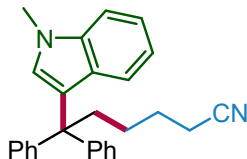
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: white oil (21.6 mg, 52%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.67 (m, 2H), 7.49 – 7.32 (m, 4H), 7.30 – 7.13 (m, 4H), 7.11 – 6.76 (m, 4H), 2.60 (d, J = 25.4 Hz, 3H), 2.55 – 2.35 (m, 2H), 2.35 – 2.10 (m, 5H), 1.69 – 1.58 (m, 2H), 1.49 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4, 148.1, 147.6, 147.1, 143.1, 142.9, 137.3, 136.7, 131.7, 131.6, 128.7, 128.6, 128.5, 128.3, 127.83, 127.79, 127.7, 127.6, 127.4, 127.31, 127.26, 127.14, 127.13, 126.8, 126.4, 126.0, 125.1, 124.8, 120.1, 67.28, 67.25, 46.8, 46.5, 41.8, 41.7, 25.9, 23.7, 21.7, 21.5, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaOS}$, 439.1815; found, 439.1816.

6-(3,4-dimethylphenyl)-6-((methyl(oxo)(phenyl)sulfaneylidene)amino)-6-phenylhexanenitrile (4ac)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 5:1, v/v) to give the desired product: colorless oil (26.2 mg, 61%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 1H), 7.69 – 7.61 (m, 1H), 7.49 – 7.35 (m, 3H), 7.33 – 7.25 (m, 3H), 7.21 – 6.94 (m, 4H), 6.86 – 6.74 (m, 1H), 2.71 – 2.40 (m, 5H), 2.39 – 2.24 (m, 2H), 2.21 (d, J = 3.2 Hz, 3H), 2.03 (d, J = 28.5 Hz, 3H), 1.71 – 1.58 (m, 2H), 1.51 – 1.39 (m, 1H), 1.35 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.5, 147.8, 145.6, 144.5, 143.2, 143.0, 135.8, 135.0, 134.7, 134.1, 131.7, 131.2, 129.4, 129.2, 128.9, 128.7, 128.6, 128.3, 127.8, 127.60, 127.55, 127.4, 127.23, 127.16, 126.2, 125.9, 125.3, 125.1, 120.2, 67.09, 67.05, 46.8, 46.4, 41.9, 41.7, 26.0, 25.9, 23.7, 20.0, 19.9, 19.4, 19.2, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{NaOS}$, 453.1971; found, 453.1972.

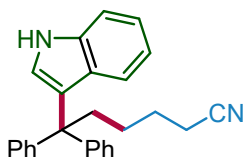
6-(1-methyl-1H-indol-3-yl)-6,6-diphenylhexanenitrile (4ad)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 30:1 to 20:1, v/v) to give the desired product: white oil (21.5 mg, 57%), ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 –

7.30 (m, 4H), 7.28 – 7.19 (m, 5H), 7.18 – 7.10 (m, 3H), 7.08 – 7.02 (m, 1H), 6.91 – 6.83 (m, 1H), 6.65 (s, 1H), 3.67 (s, 3H), 2.72 – 2.59 (m, 2H), 2.10 (t, $J = 7.2$ Hz, 2H), 1.65 – 1.50 (m, 2H), 1.33 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 147.1, 137.7, 129.0, 128.6, 128.0, 127.0, 125.9, 122.2, 121.4, 120.6, 119.8, 118.6, 109.4, 52.1, 39.5, 32.8, 26.2, 25.5, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{Na}$, 401.1988; found, 401.1992.

6-(1H-indol-3-yl)-6,6-diphenylhexanenitrile (4ae)



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 20:1 to 10:1, v/v) to give the desired product: white oil (17.5 mg, 48%), ^1H NMR (400 MHz, Chloroform- d) δ 7.98 (s, 1H), 7.37 – 7.30 (m, 5H), 7.26 – 7.20 (m, 4H), 7.19 – 7.03 (m, 4H), 6.93 – 6.85 (m, 1H), 6.83 – 6.78 (m, 1H), 2.74 – 2.60 (m, 2H), 2.22 – 2.07 (m, 2H), 1.66 – 1.53 (m, 2H), 1.34 – 1.19 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 146.9, 137.0, 128.5, 127.9, 126.5, 125.9, 124.2, 122.2, 122.1, 121.8, 119.1, 111.2, 52.1, 39.3, 26.1, 25.5, 17.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{Na}$, 387.1832; found, 387.1837.

ethyl 6,6-diphenylhex-5-enoate (5a)¹



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 100:1 to 50:1, v/v) to give the desired product: white solid (22.9 mg, 78%), ^1H NMR (400 MHz, Chloroform- d) δ 7.4 – 7.3 (m, 2H), 7.3 – 7.2 (m, 6H), 7.2 – 7.1 (m, 2H), 6.1 (t, $J = 7.4$ Hz, 1H), 4.1 (q, $J = 7.1$ Hz, 2H), 2.3 (t, $J = 7.5$ Hz, 2H), 2.2 (q, $J = 7.4$ Hz, 2H), 1.8 – 1.7 (m, 2H), 1.2 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 173.5, 142.6, 142.5, 140.0, 129.9, 128.7, 128.2, 128.1, 127.2, 127.0, 60.3, 33.9, 29.2, 25.2, 14.2.

6,6-diphenylhex-5-enoic acid (5b)¹



Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 3:1 to 1:2, v/v) to give the desired product: white solid (86.5 mg, 65%), ^1H NMR (400 MHz, Chloroform- d) δ 10.95 (s, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.13 (m, 8H), 6.04 (t, $J = 7.4$ Hz, 1H), 2.44 – 2.26 (m, 2H),

2.23 – 2.09 (m, 2H), 1.88 – 1.69 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.2, 142.8, 142.5, 140.0, 129.9, 128.4, 128.3, 128.2, 127.2, 127.0, 33.6, 29.1, 24.9.

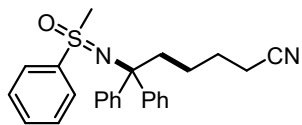
6,6-diphenylhex-5-enitrile (6)¹



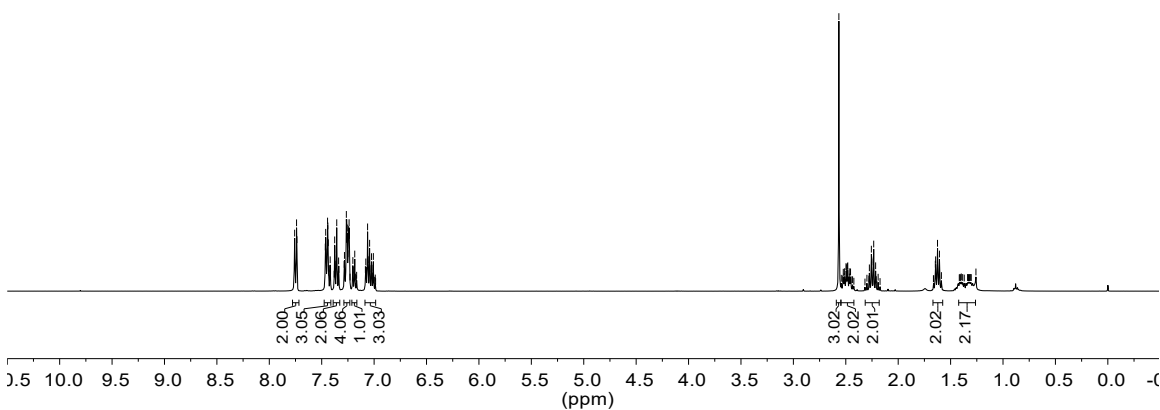
Purified by flash chromatography (silica gel, petroleum ether/ethyl acetate from 50:1 to 30:1, v/v) to give the desired product: colorless oil. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 7.28 – 7.25 (m, 2H), 7.25 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 6.01 (t, J = 7.4 Hz, 1H), 2.36 – 2.19 (m, 4H), 1.88 – 1.73 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.8, 142.1, 139.6, 129.7, 128.4, 128.2, 127.3, 127.24, 127.18, 126.6, 119.5, 28.7, 25.8, 16.7.

5. NMR copies of product

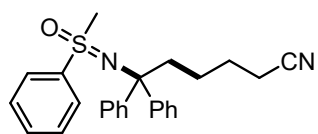
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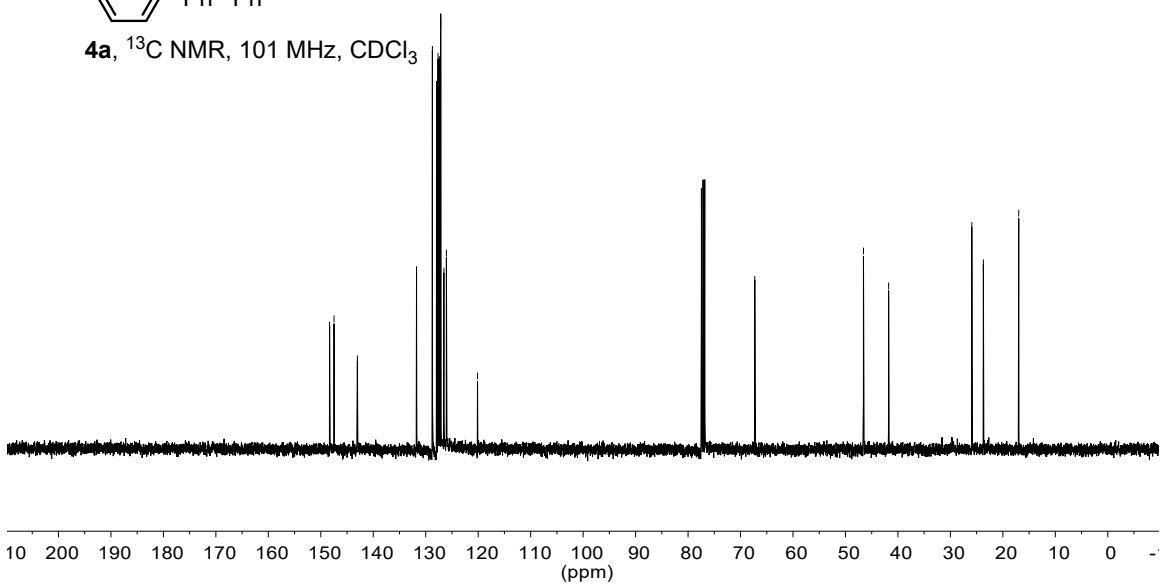
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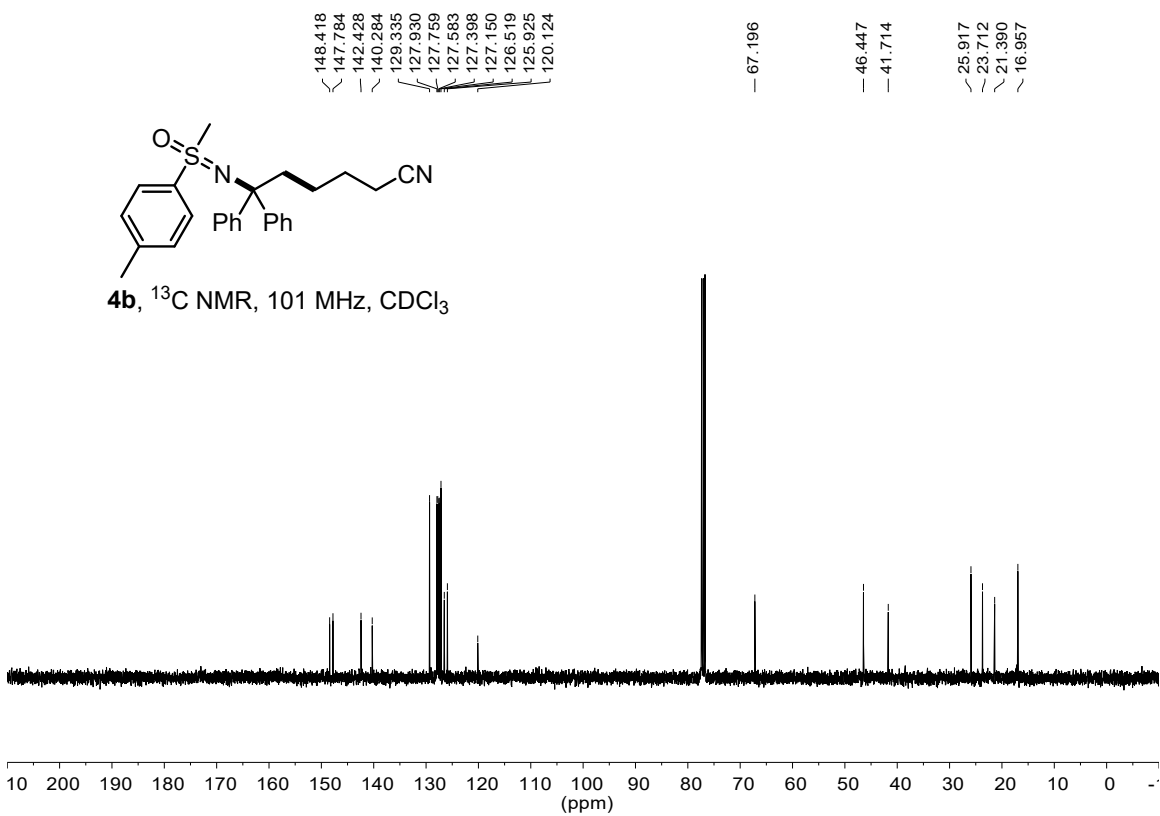
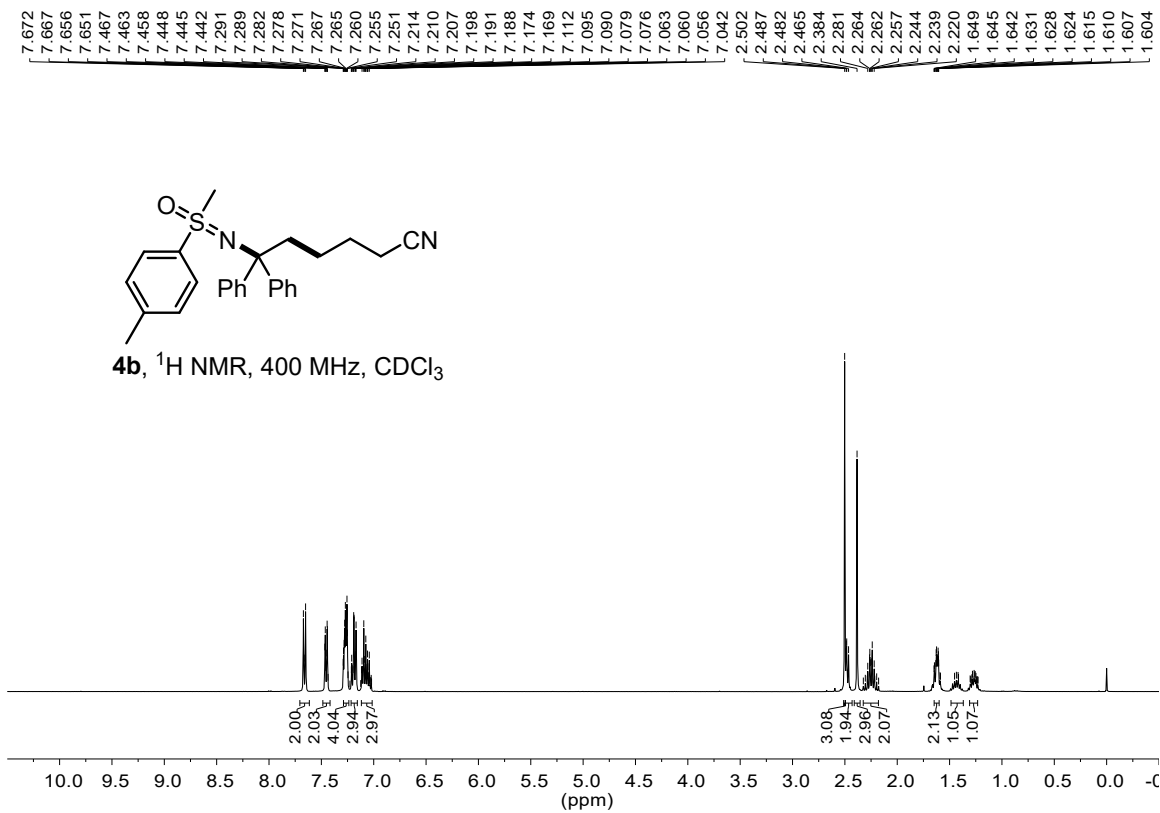


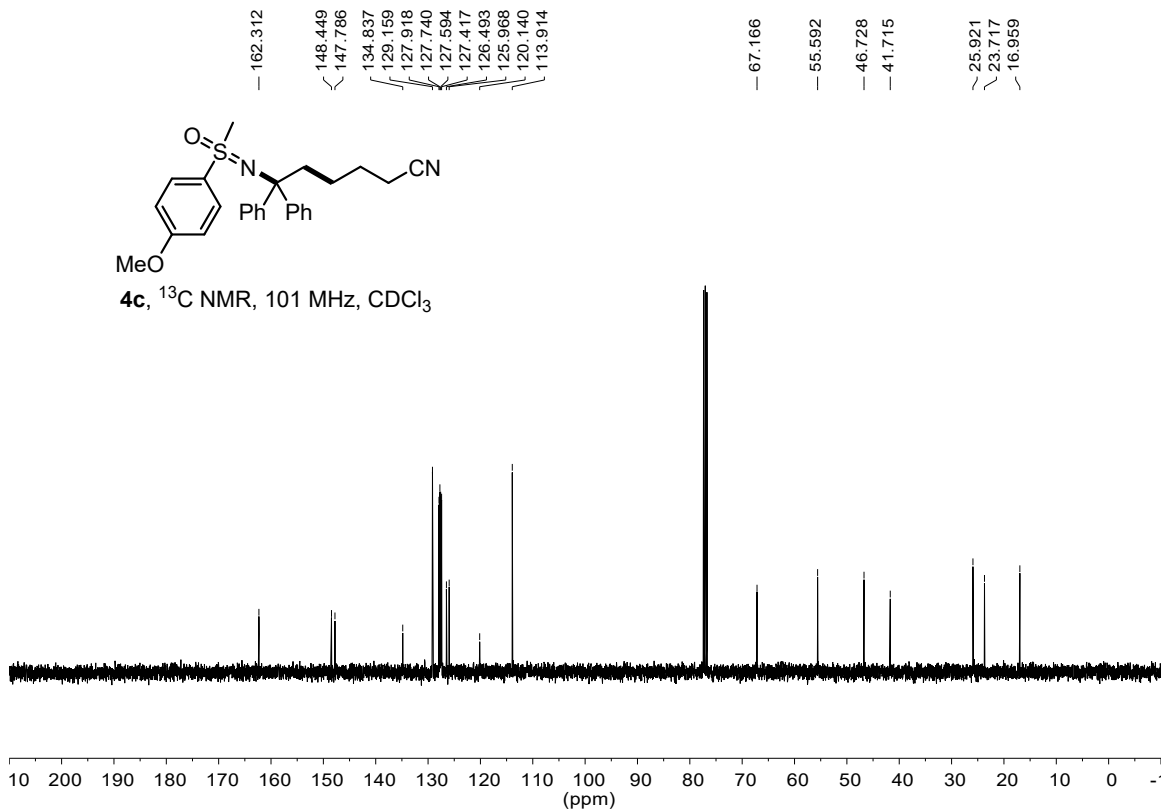
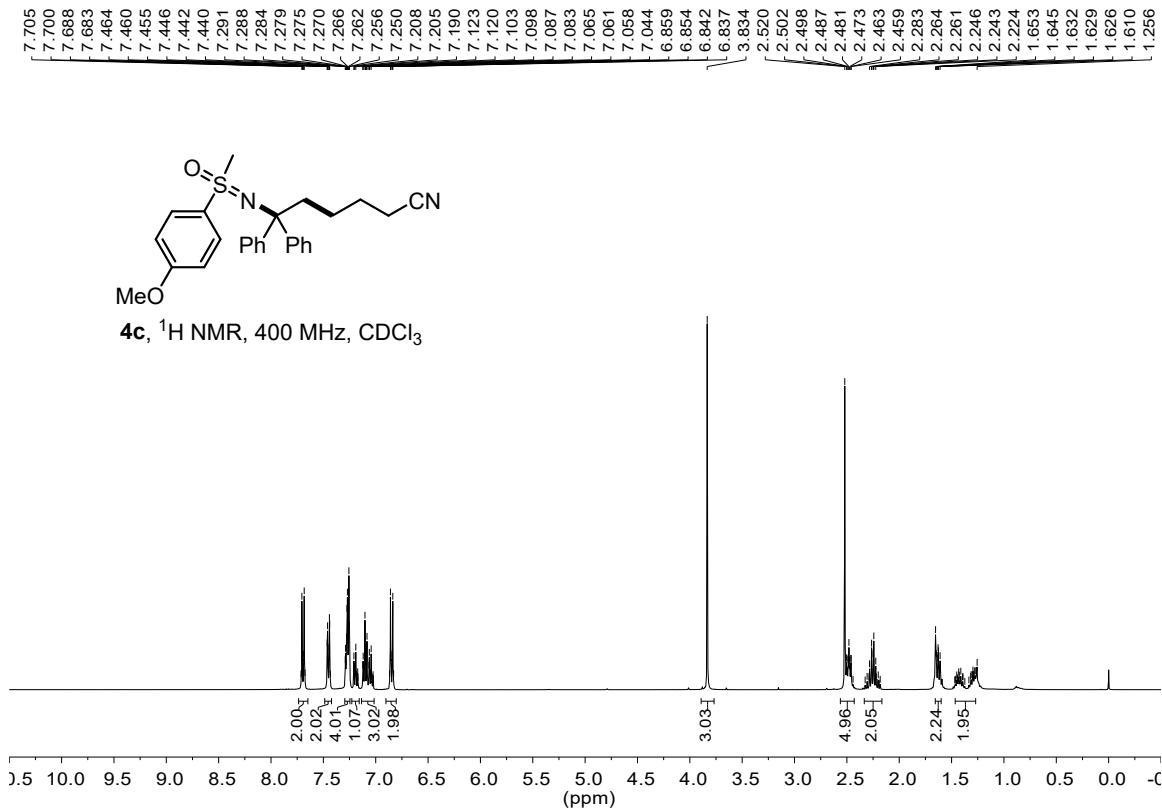
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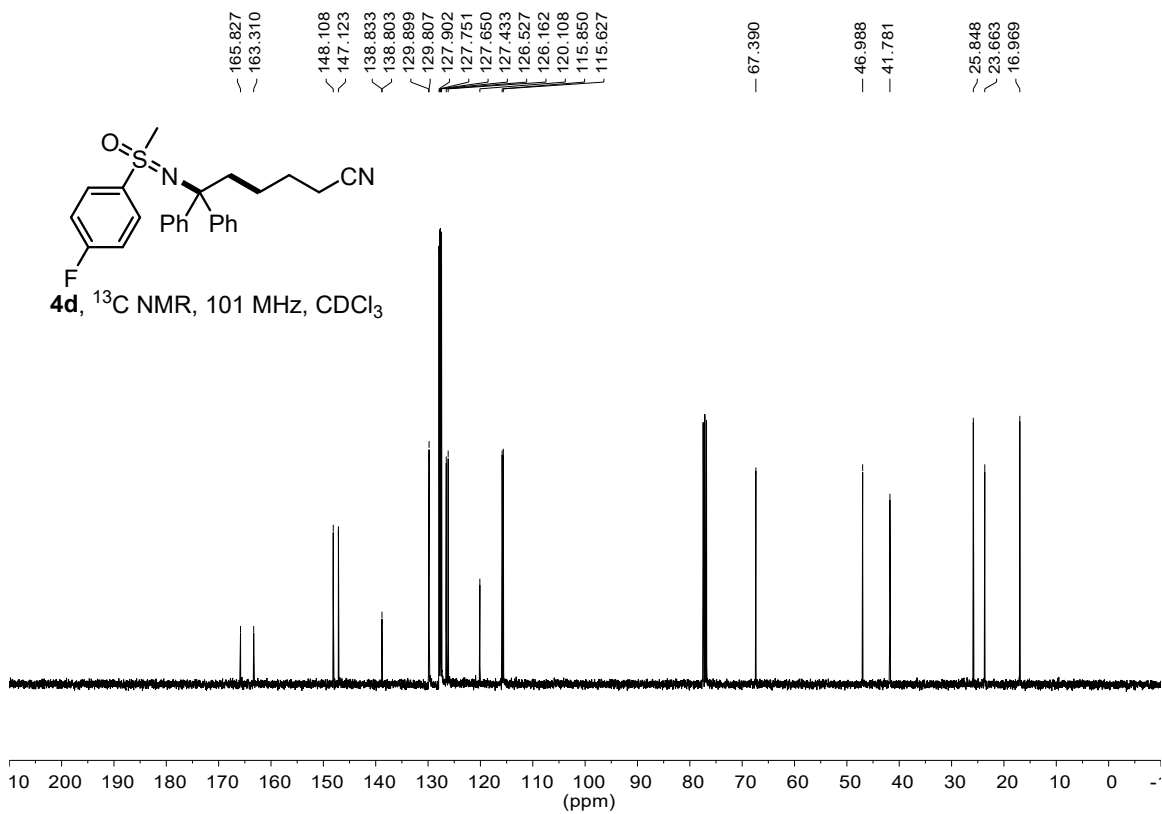
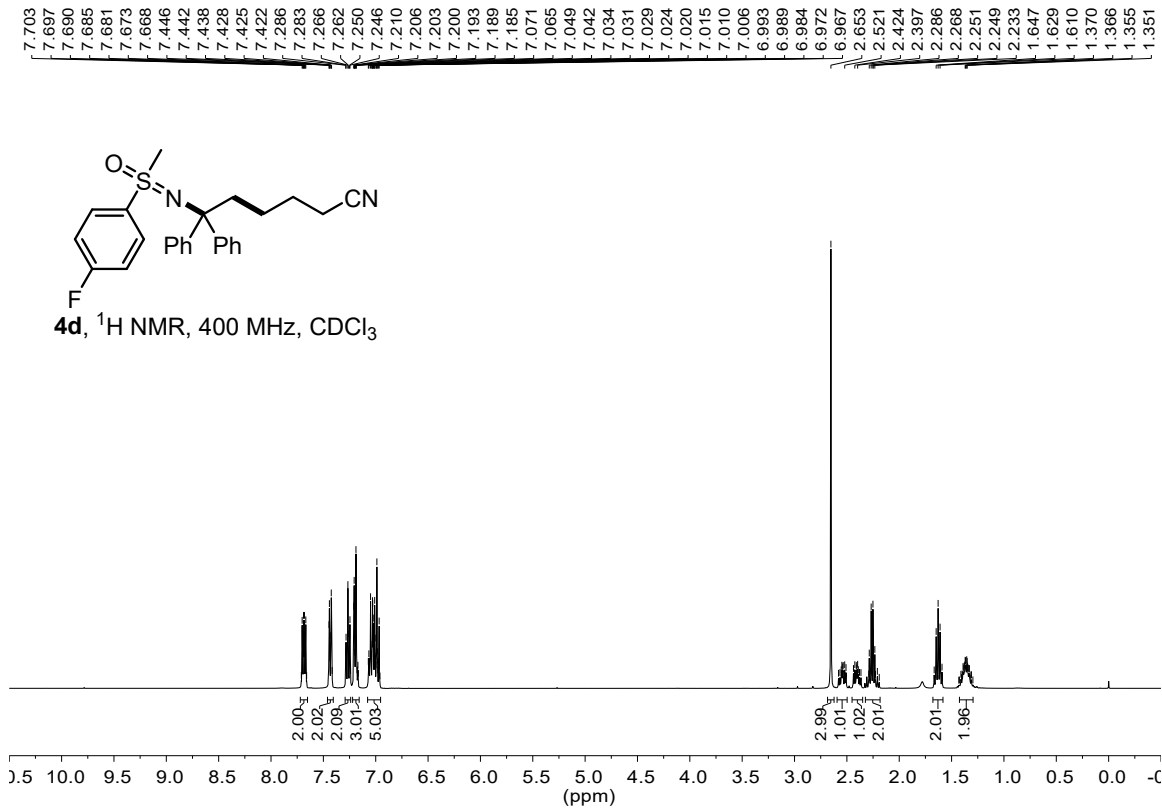


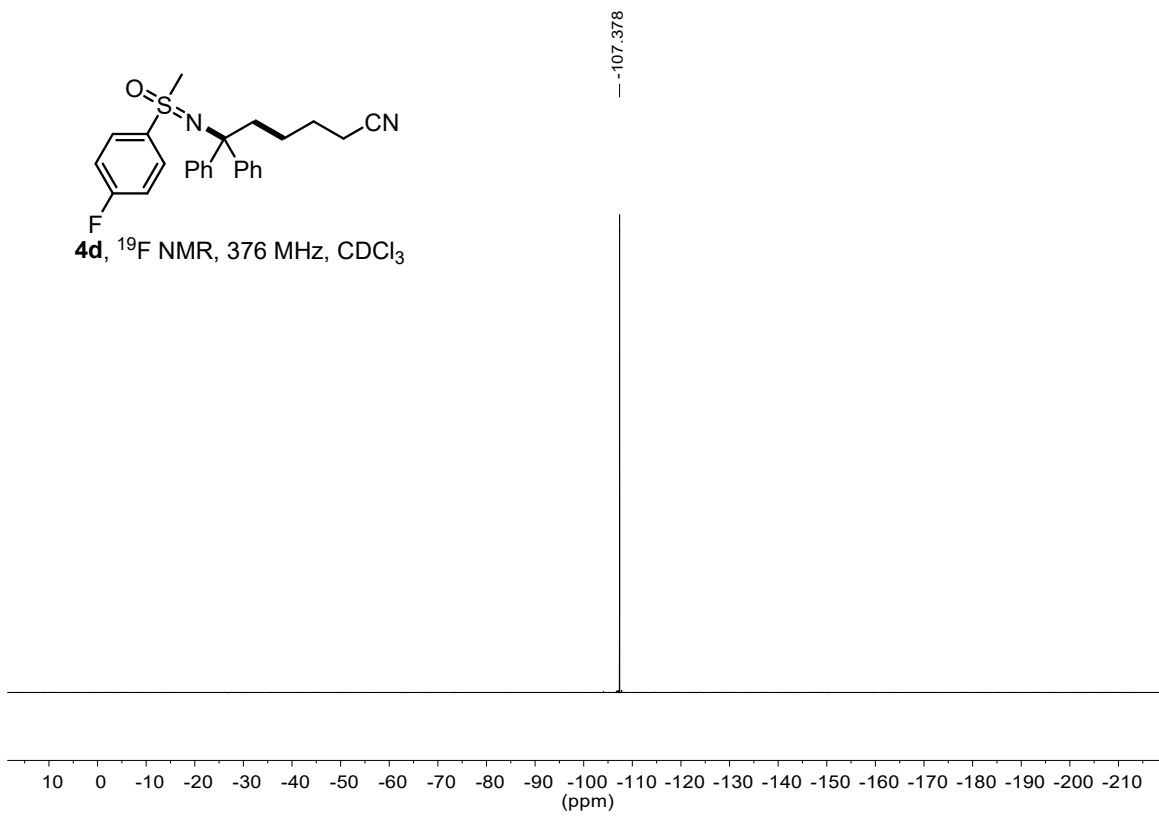
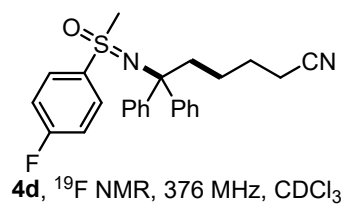
4a, ^{13}C NMR, 101 MHz, CDCl_3

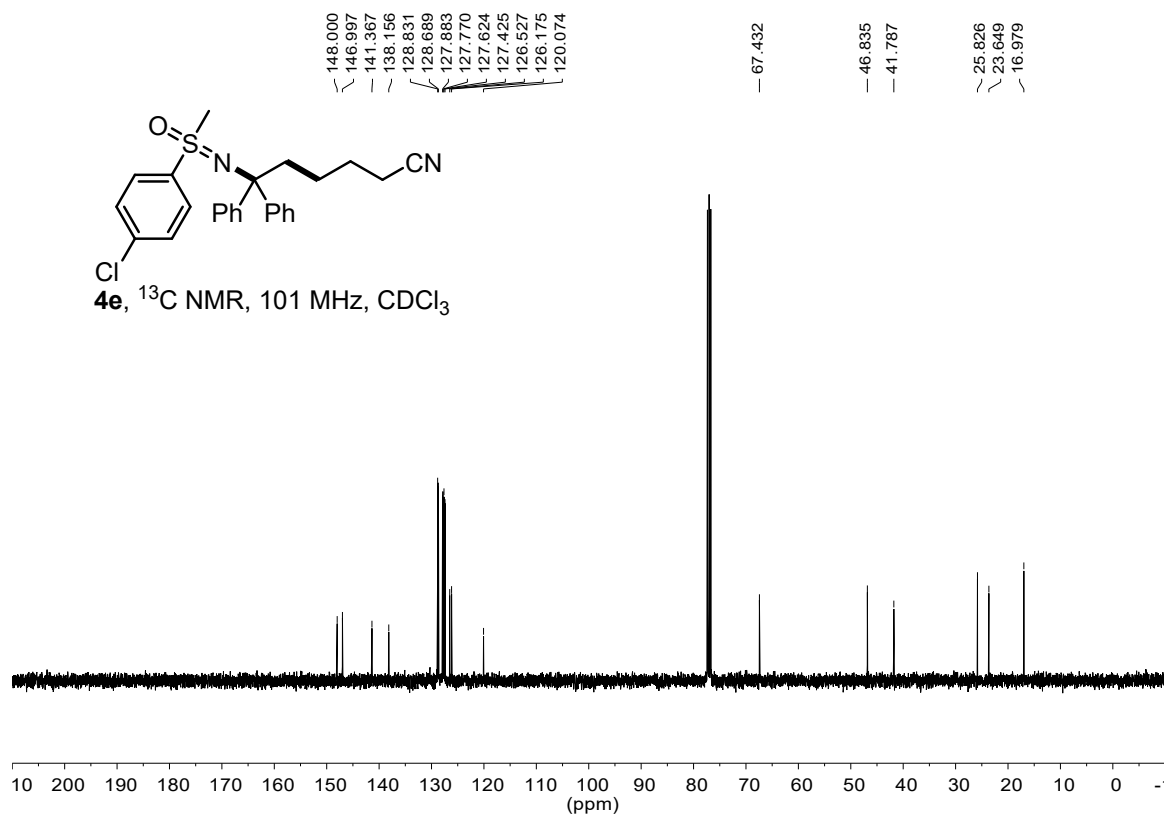
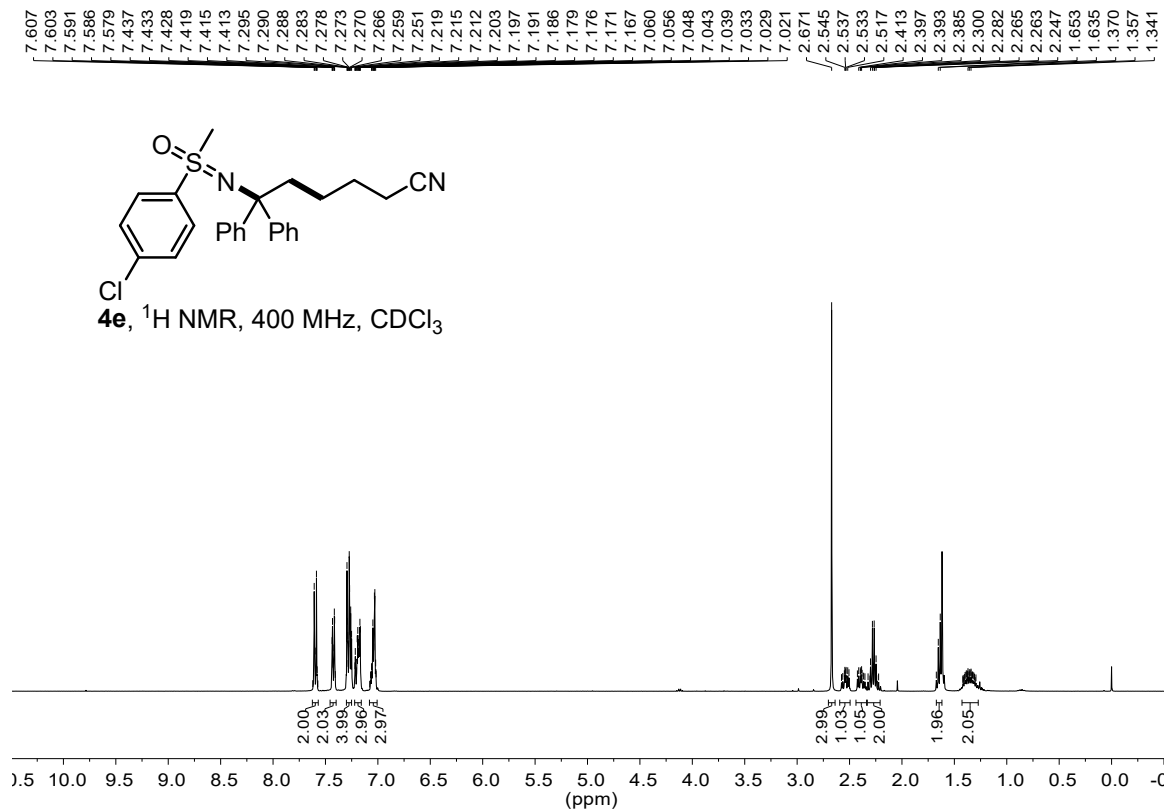


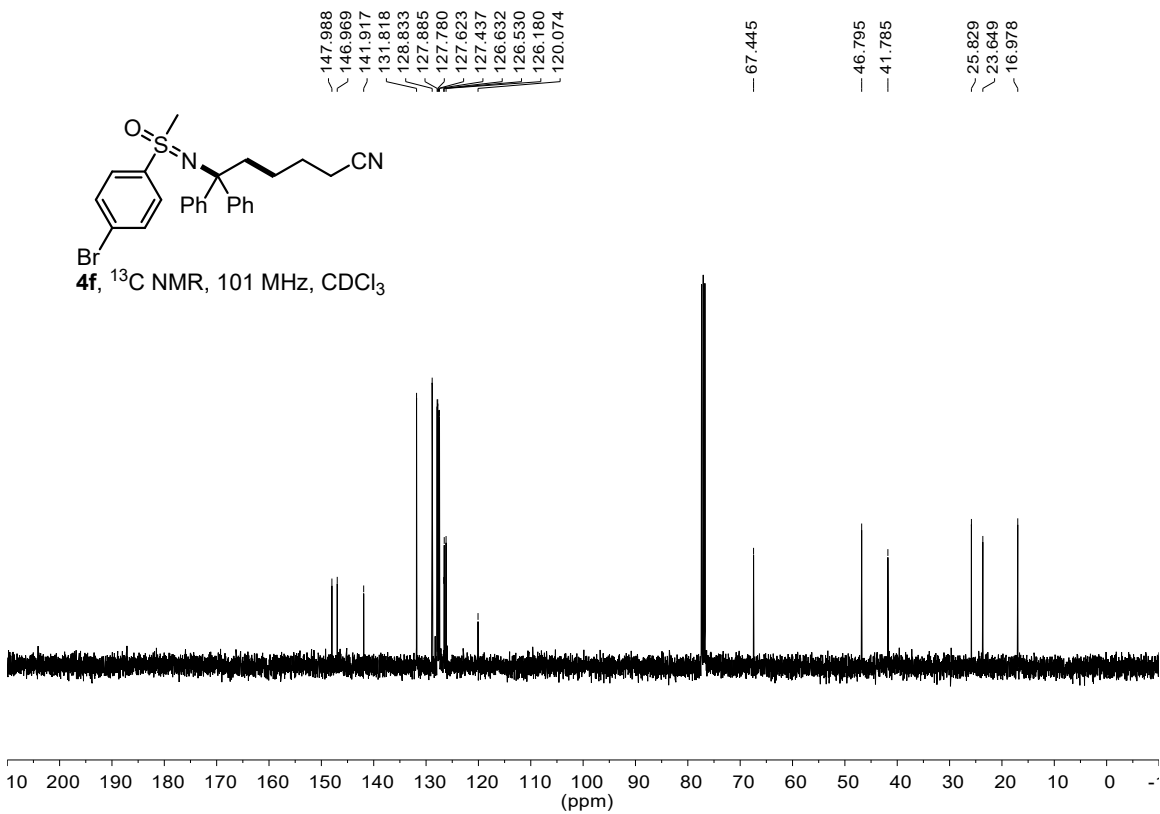
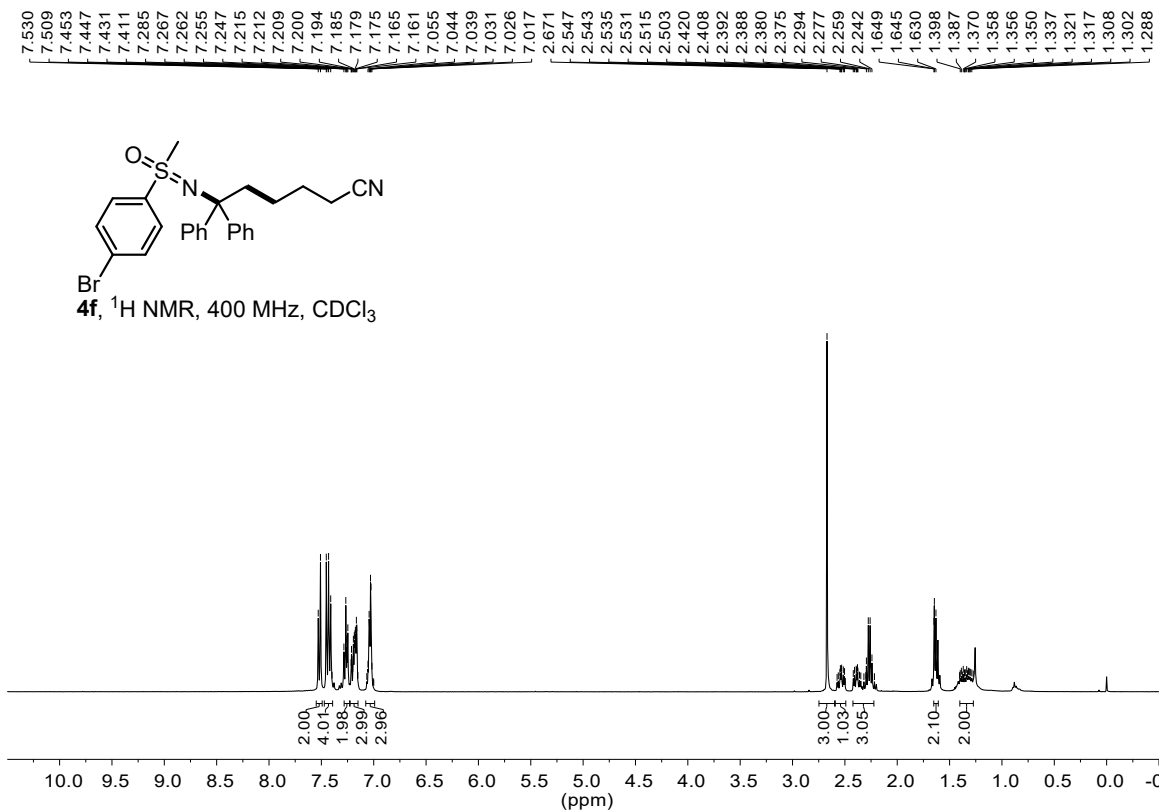


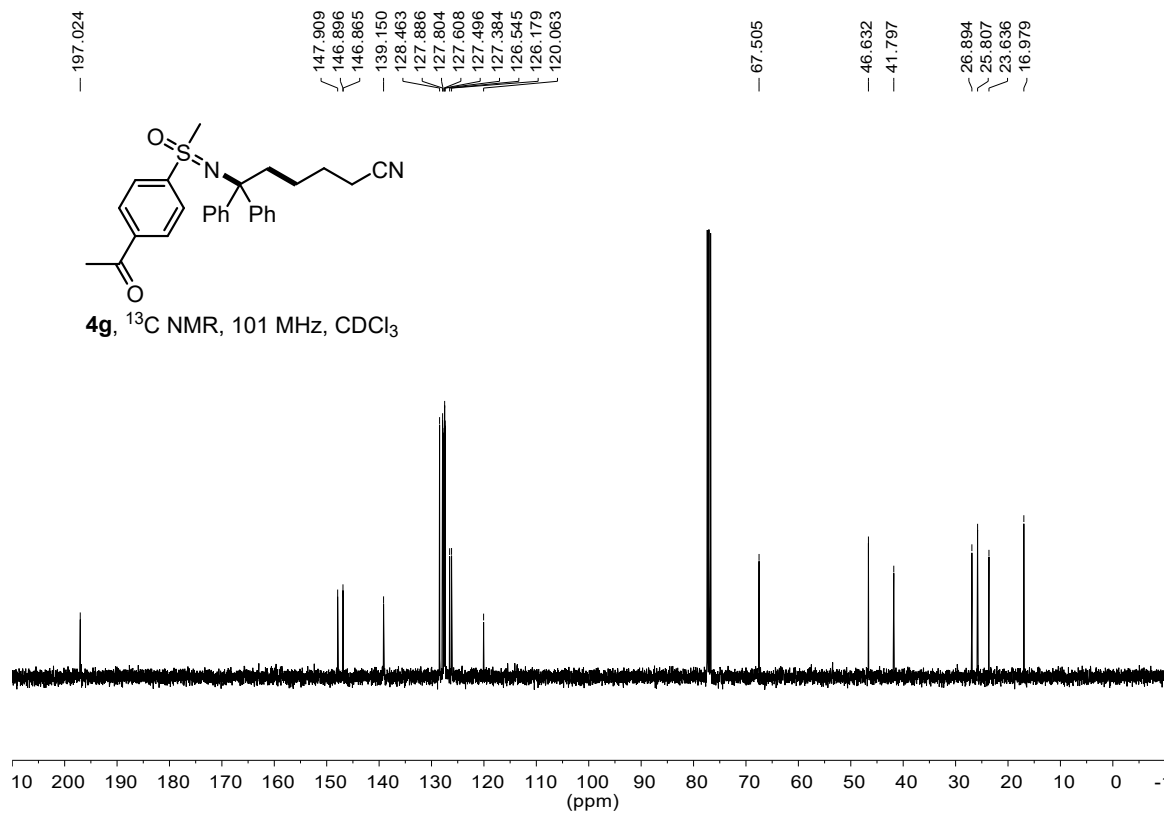
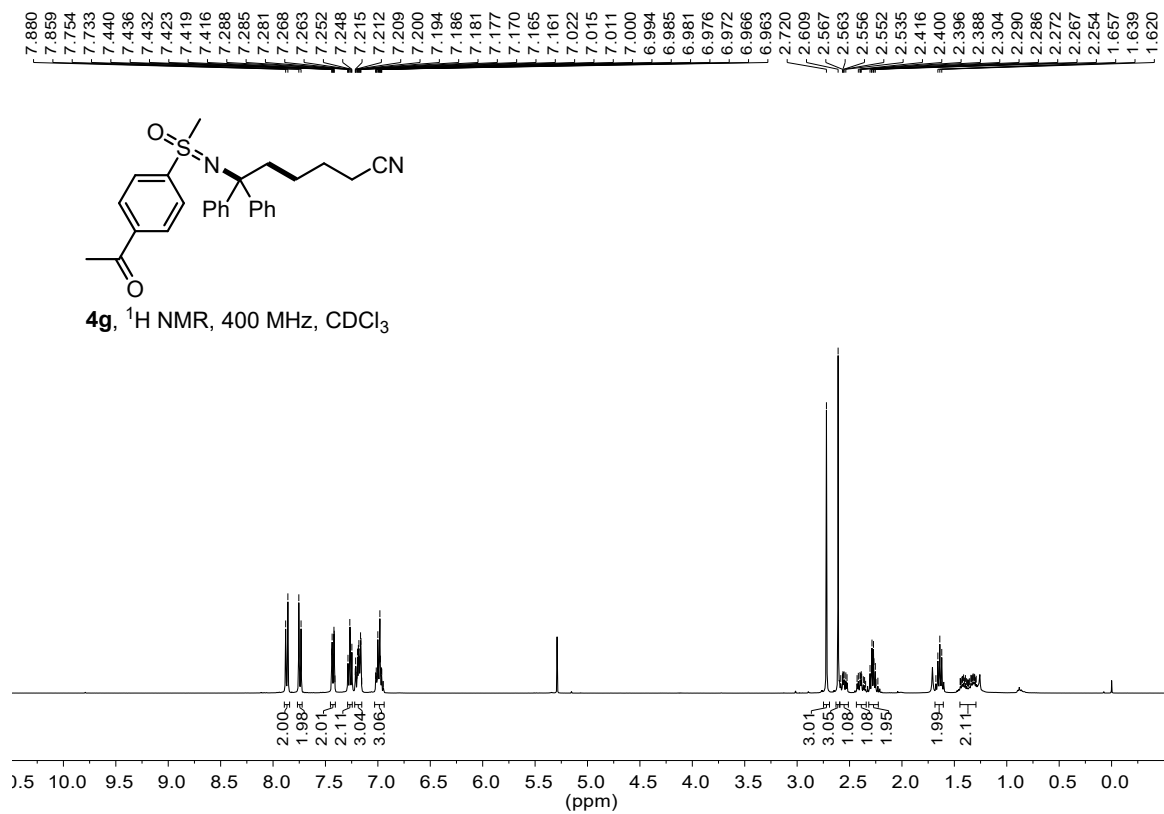


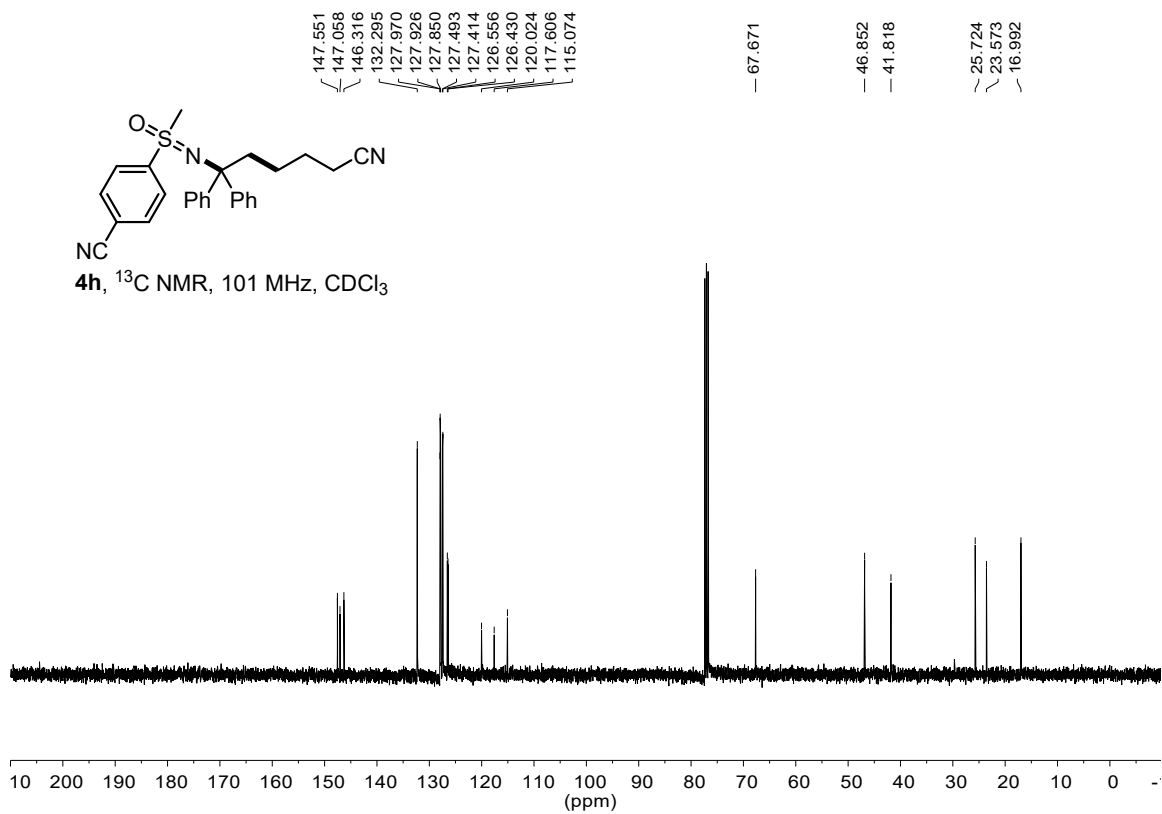
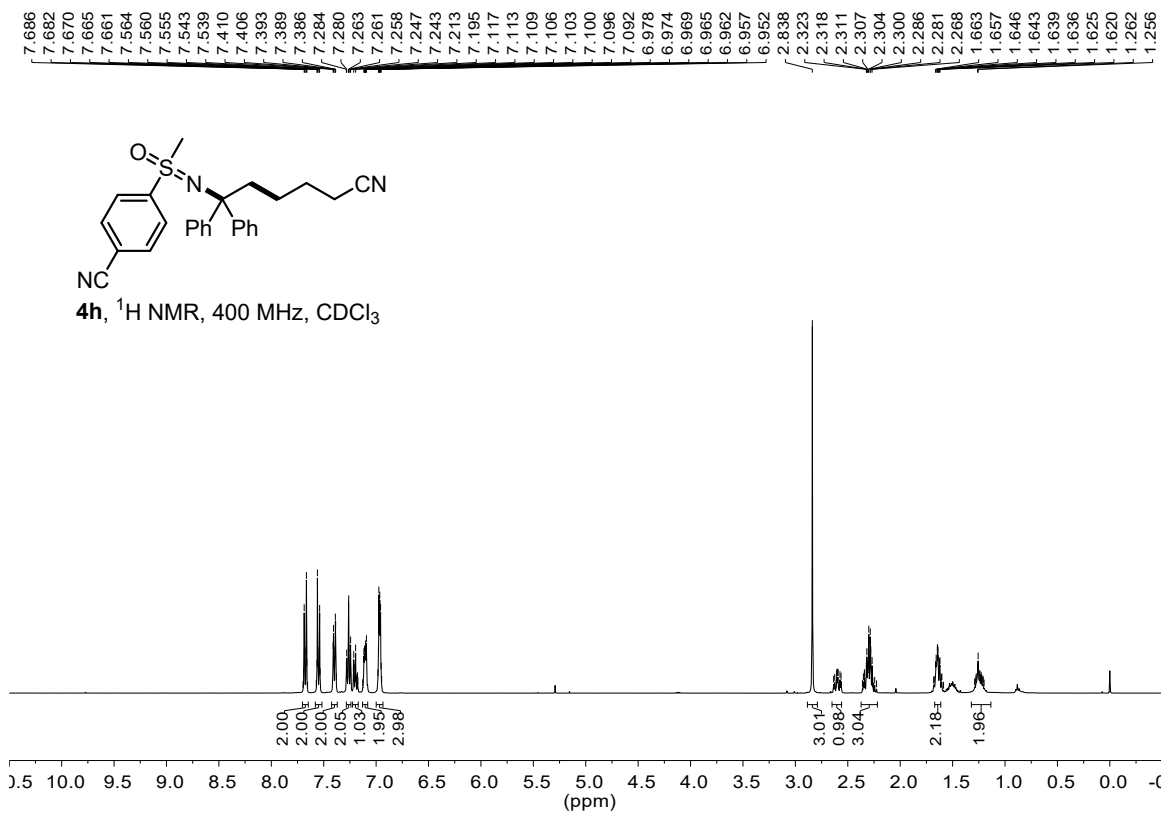


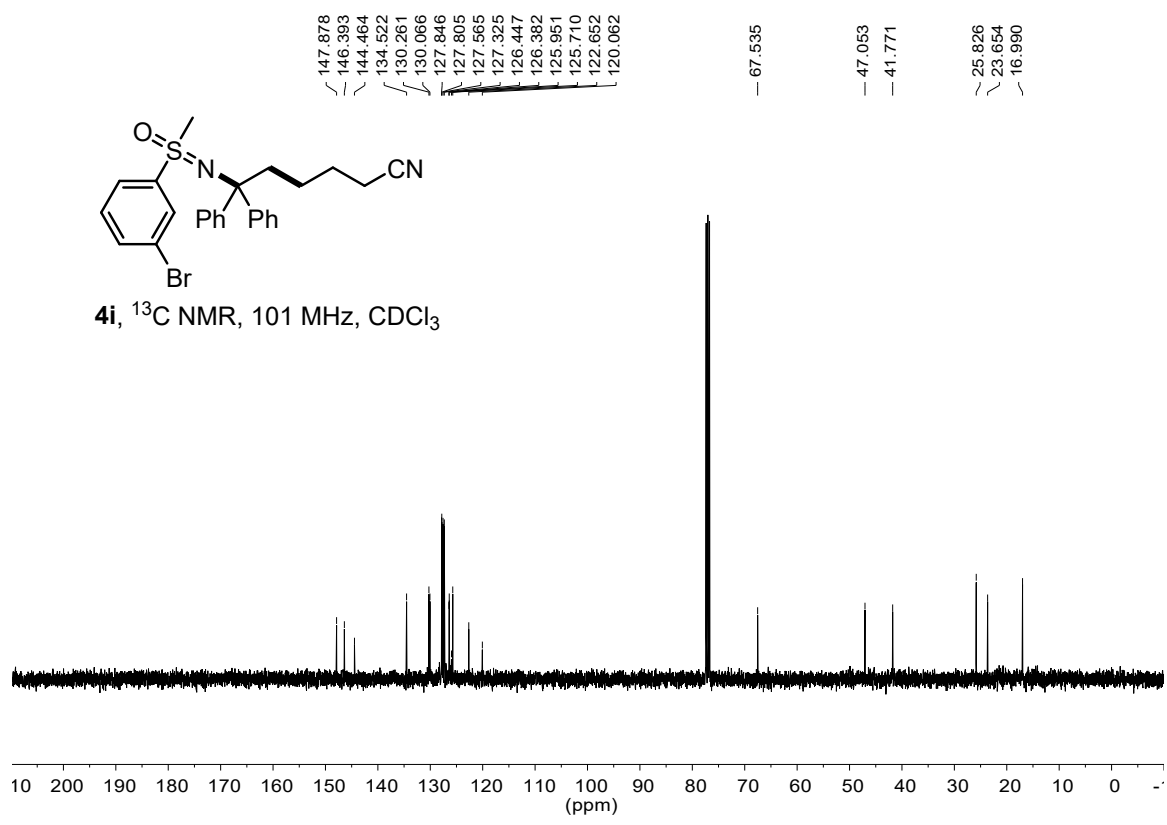
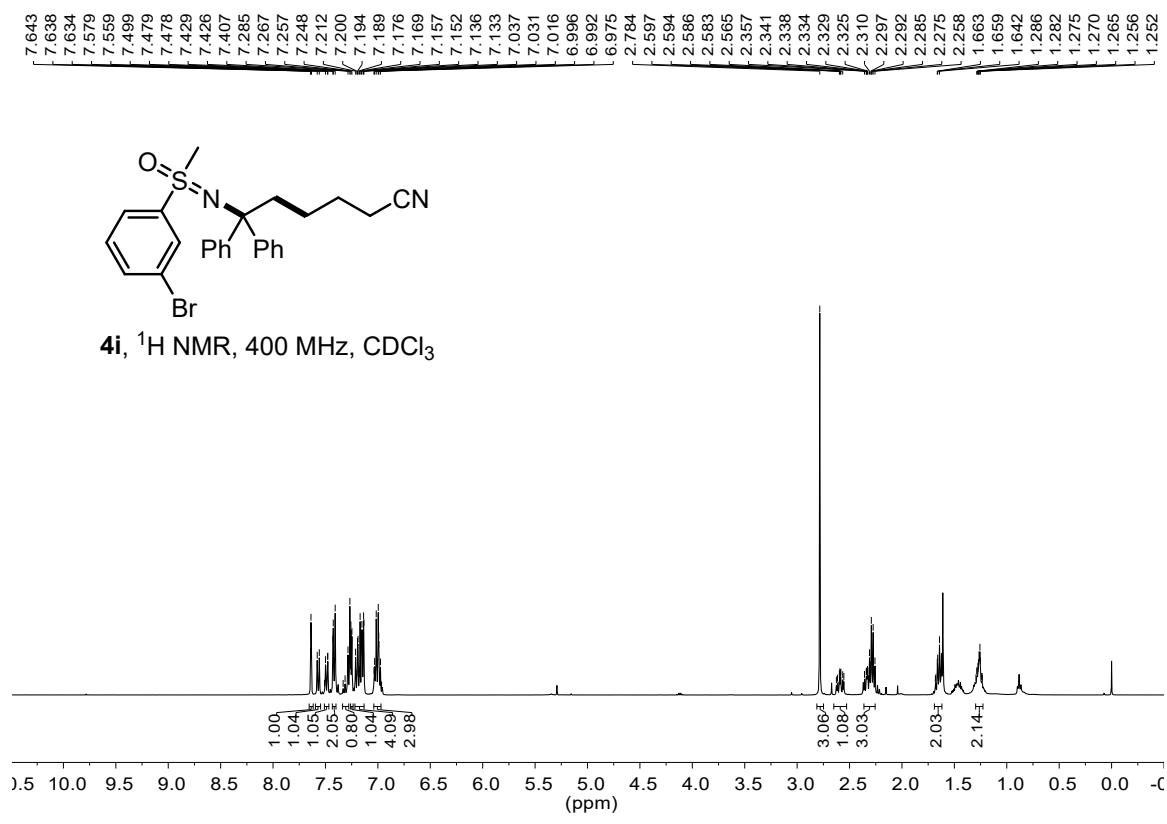


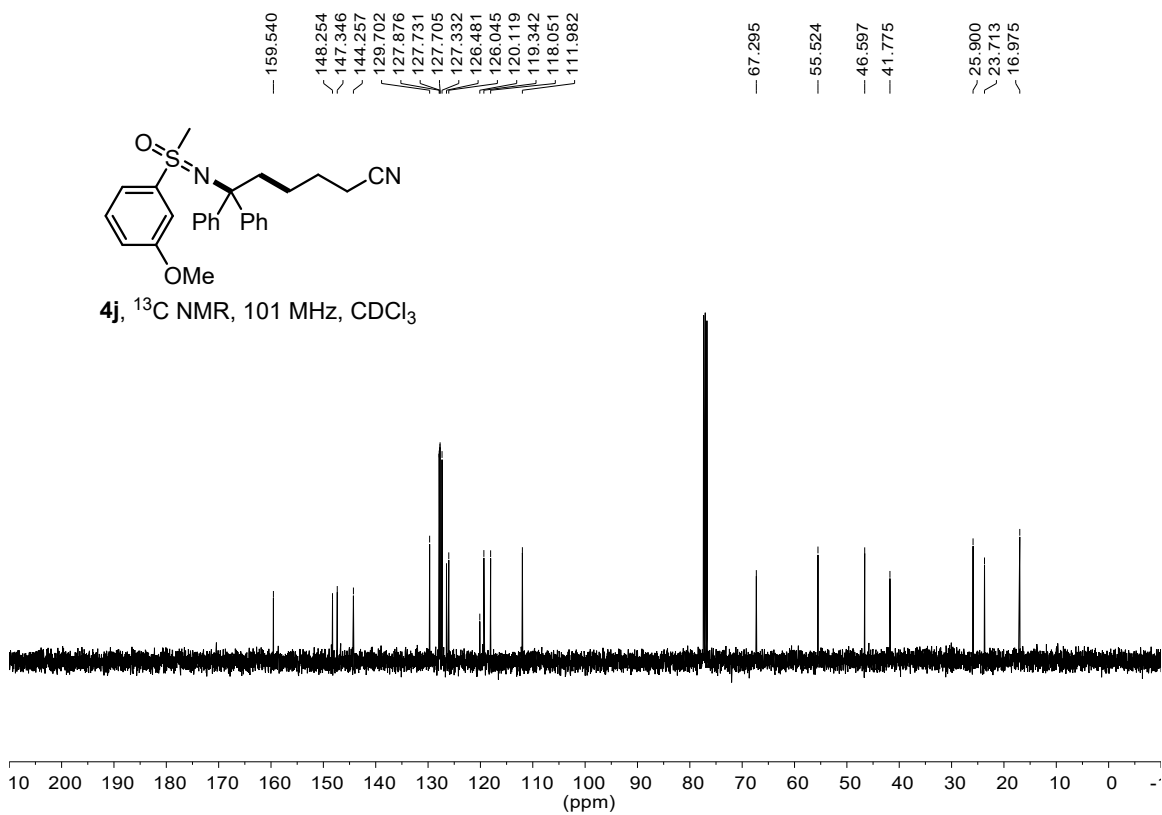
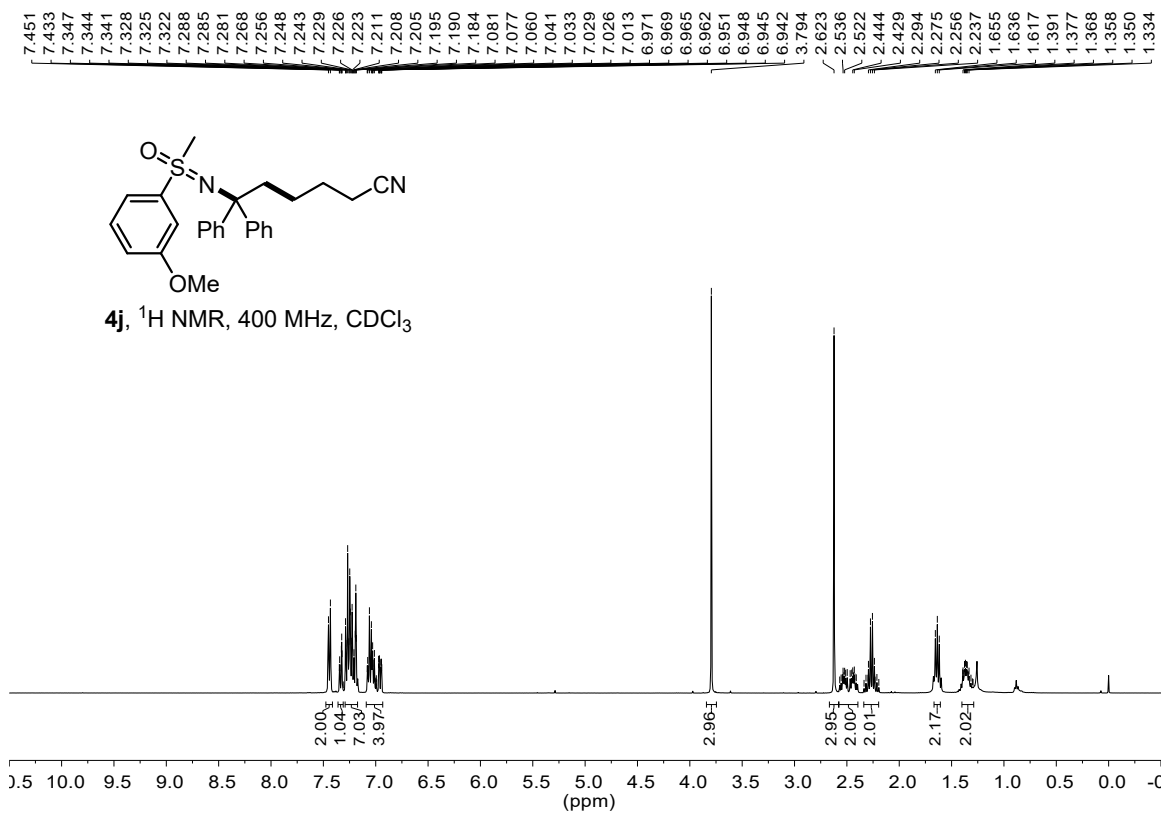


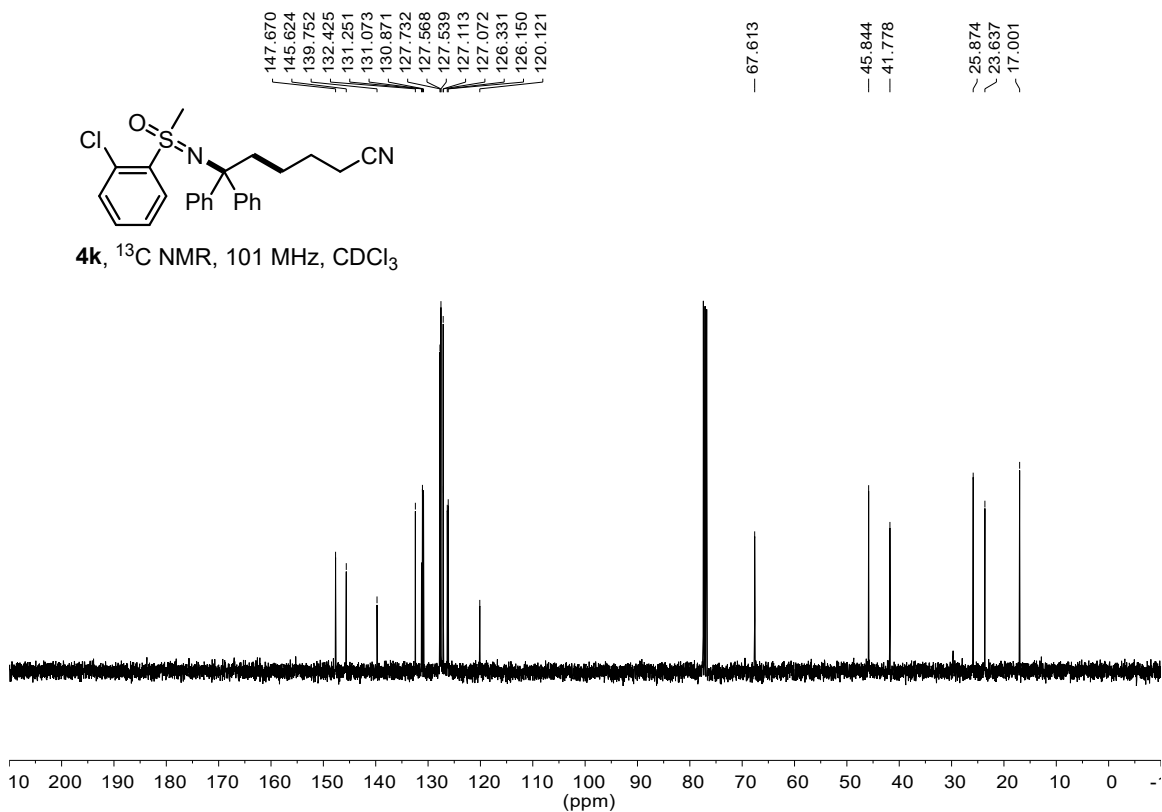
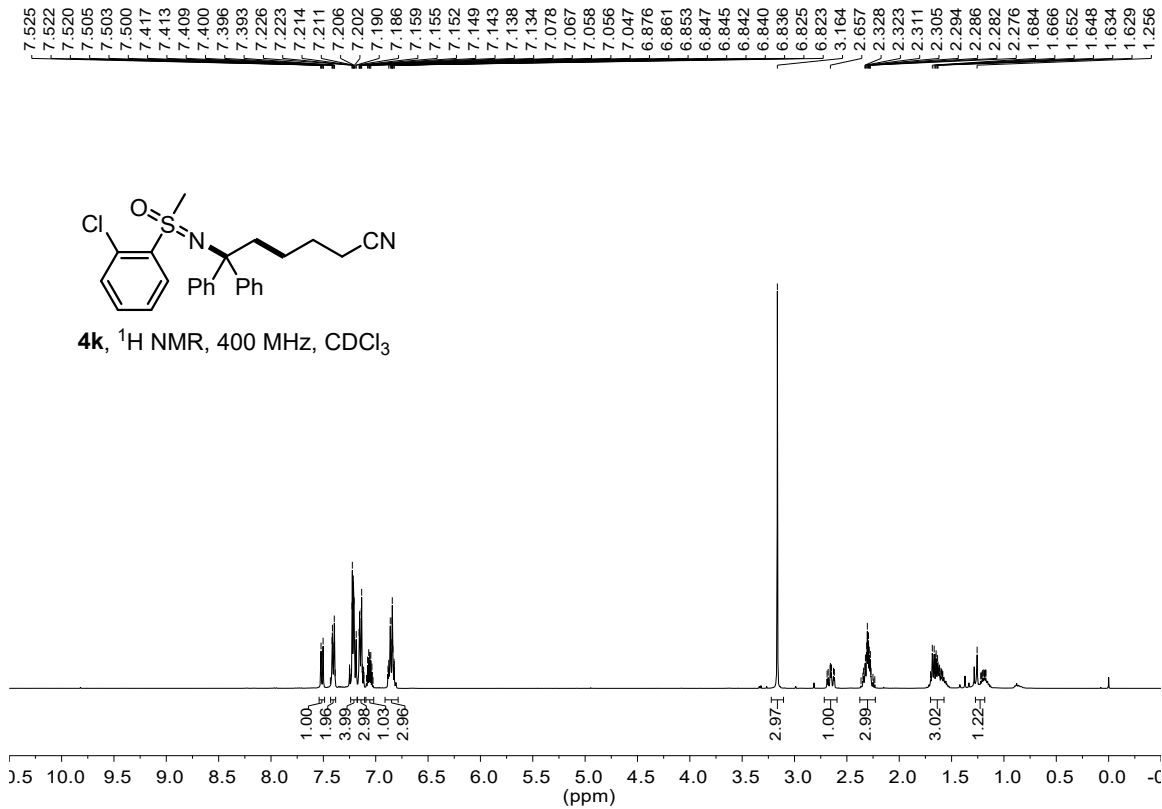


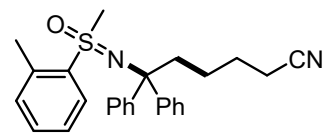
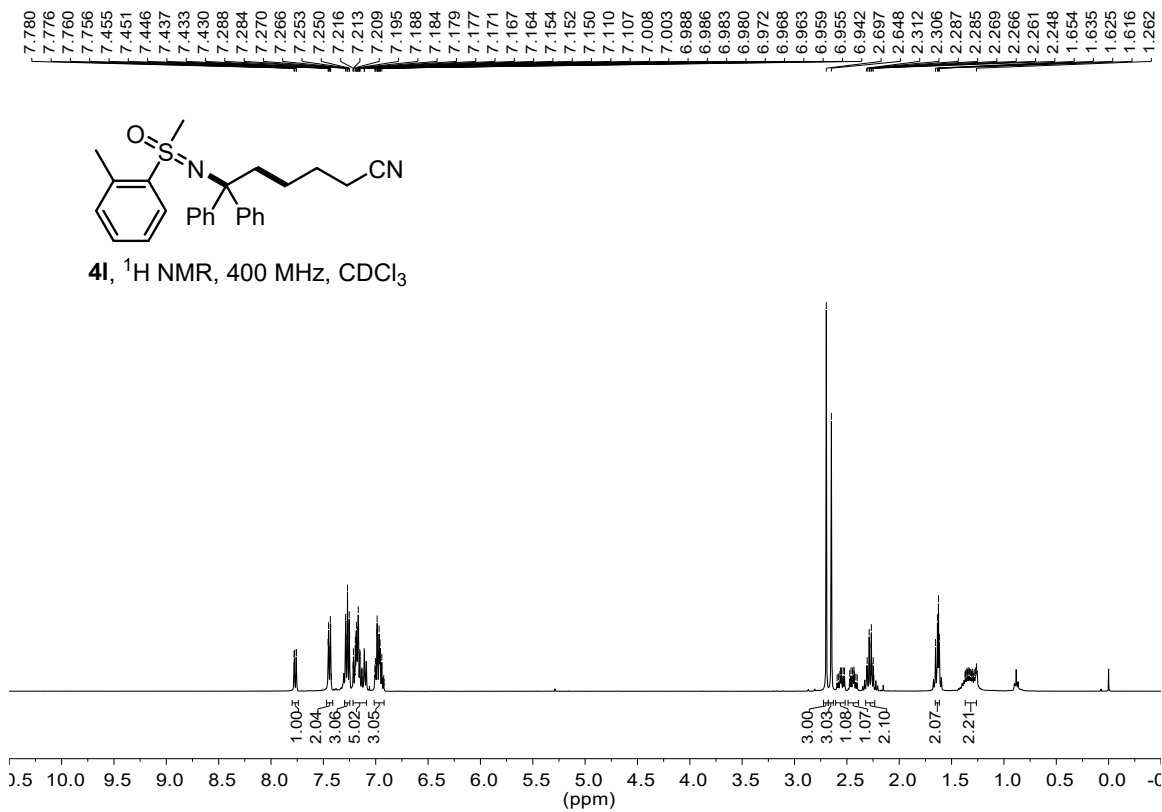




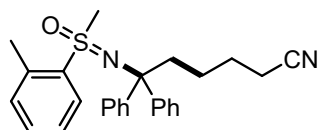
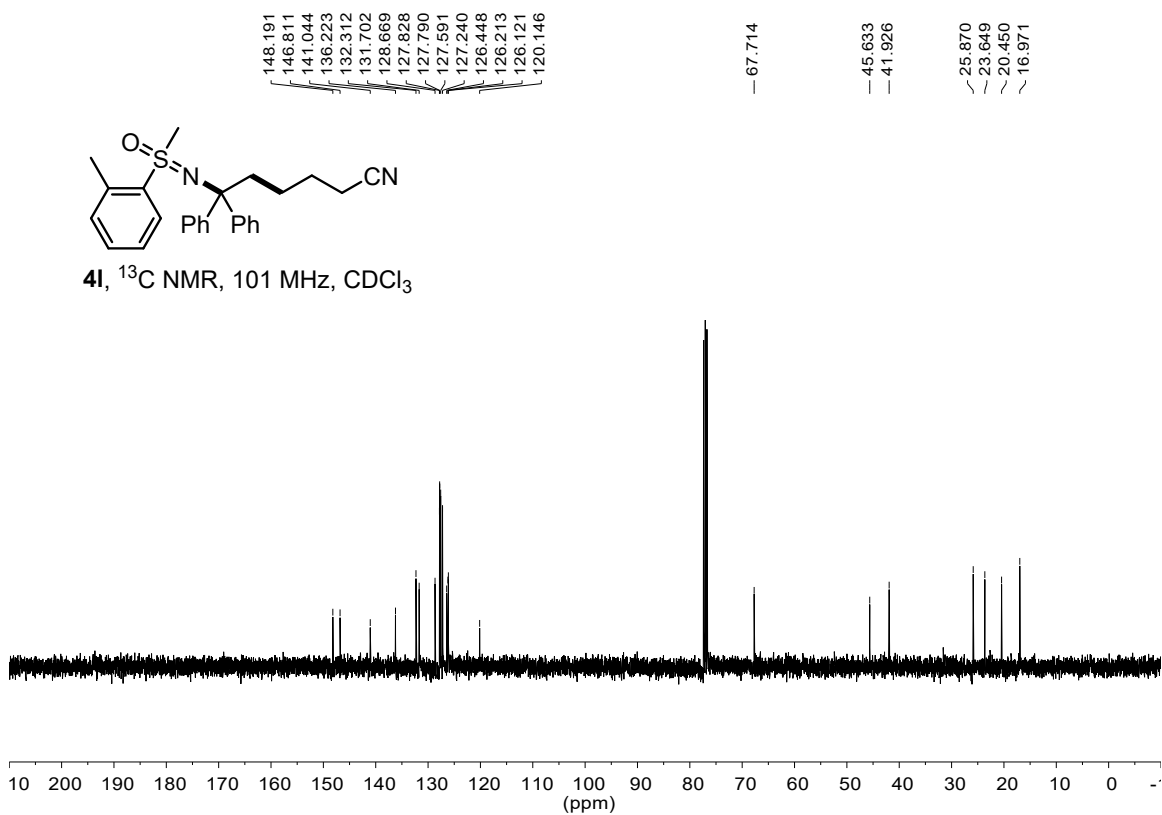




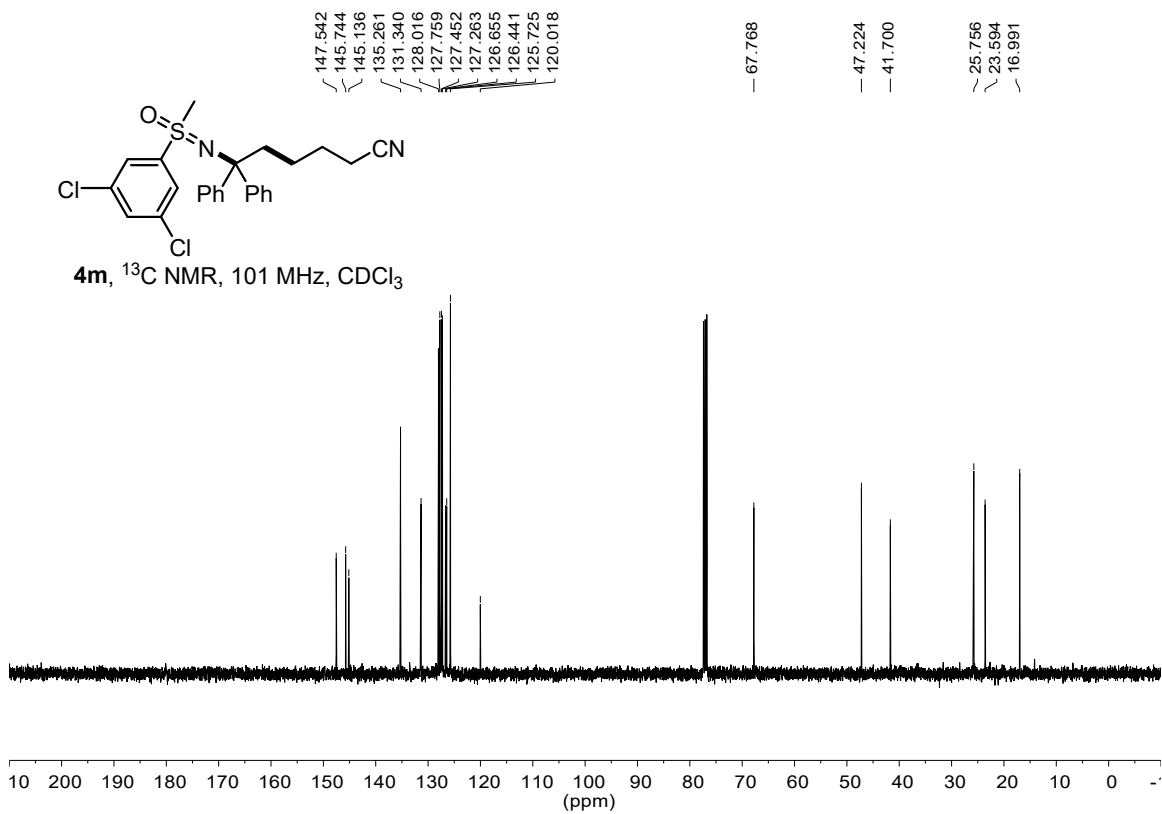
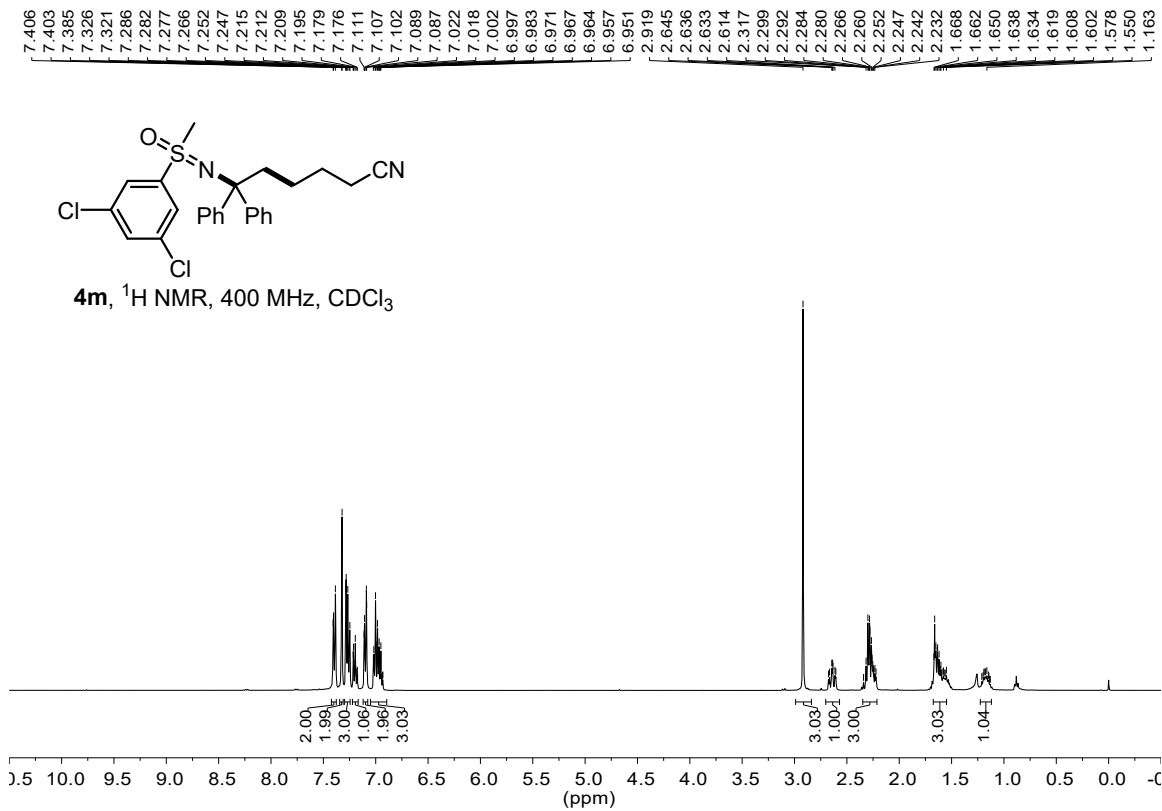




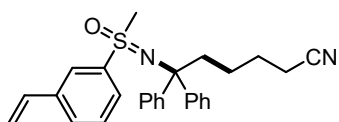
4i, ^1H NMR, 400 MHz, CDCl_3



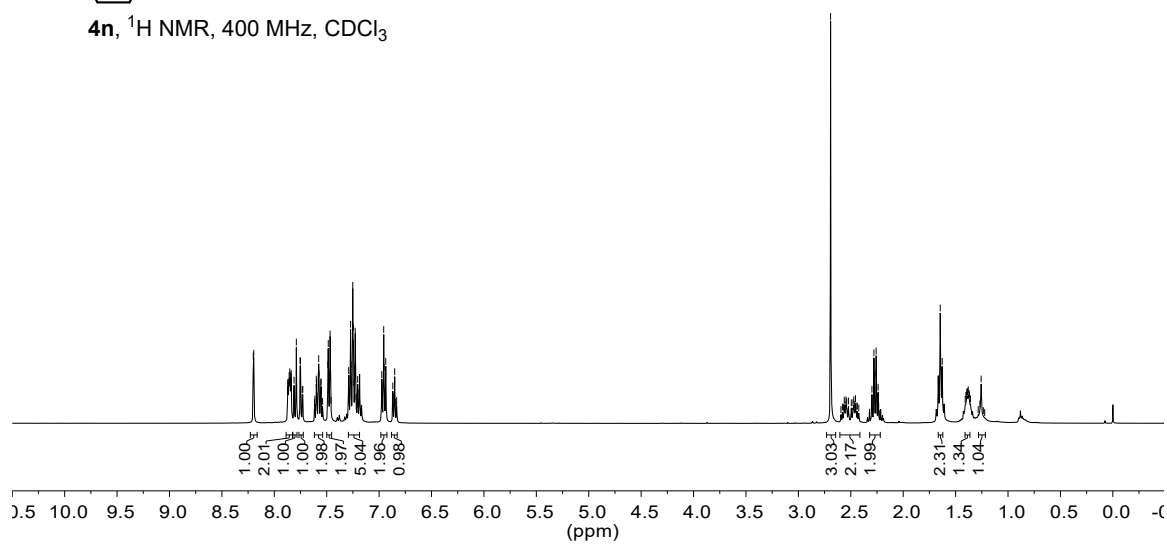
4i, ^{13}C NMR, 101 MHz, CDCl_3



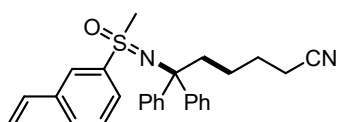
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7.754
7.750
7.733
7.728
7.599
7.596
7.580
7.576
7.573
7.557
7.554
7.489
7.485
7.480
7.471
7.468
7.465
7.292
7.290
7.272
7.268
7.252
7.246
7.241
7.232
7.229
7.226
7.204
6.975
6.956
6.953
6.937
6.869
6.851
2.693
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1.256



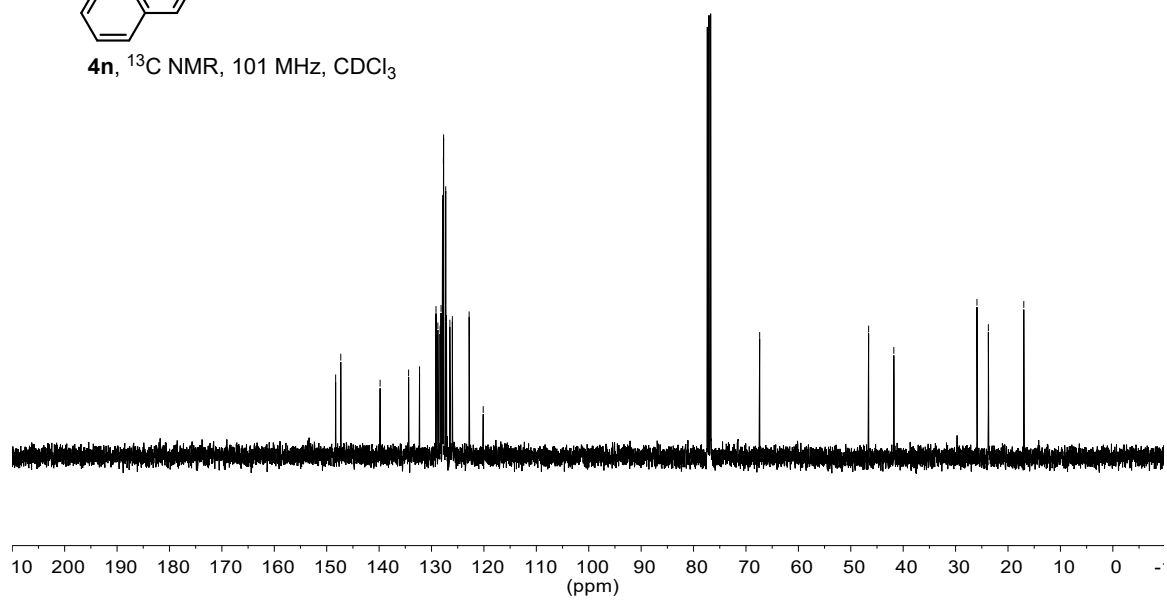
4n, ^1H NMR, 400 MHz, CDCl_3

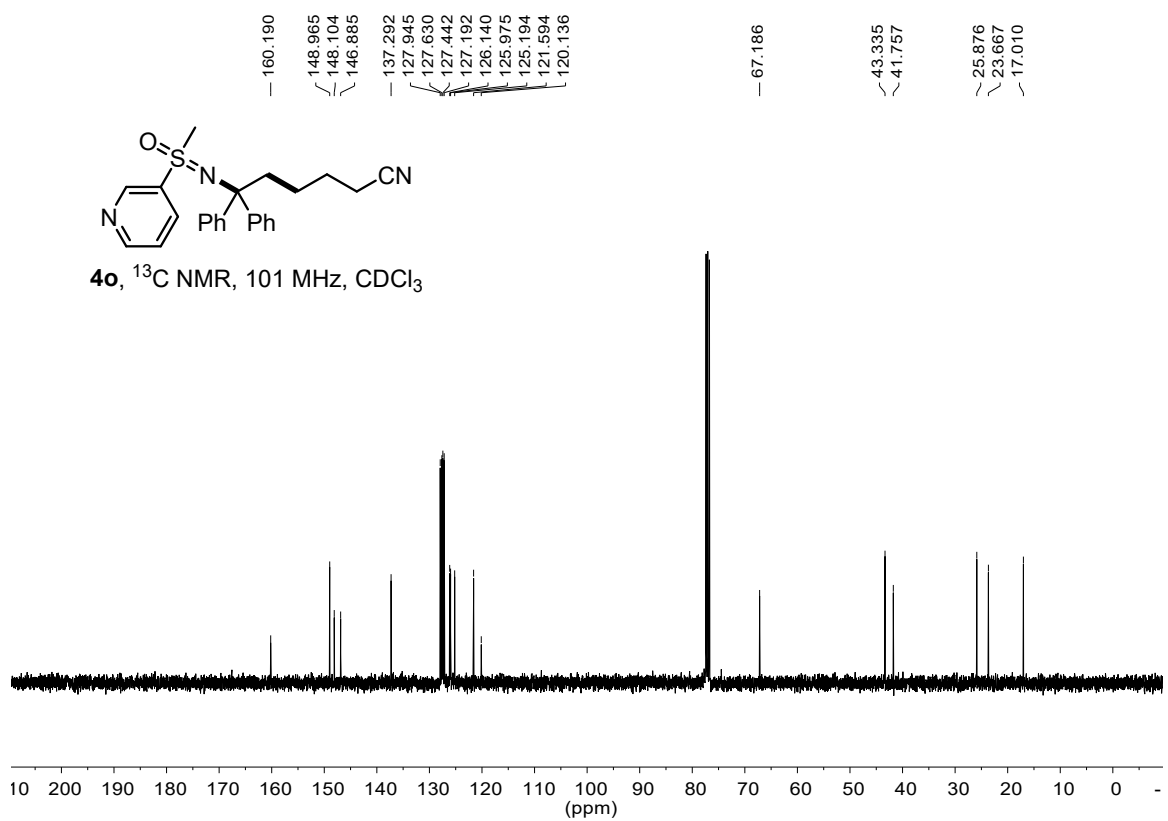
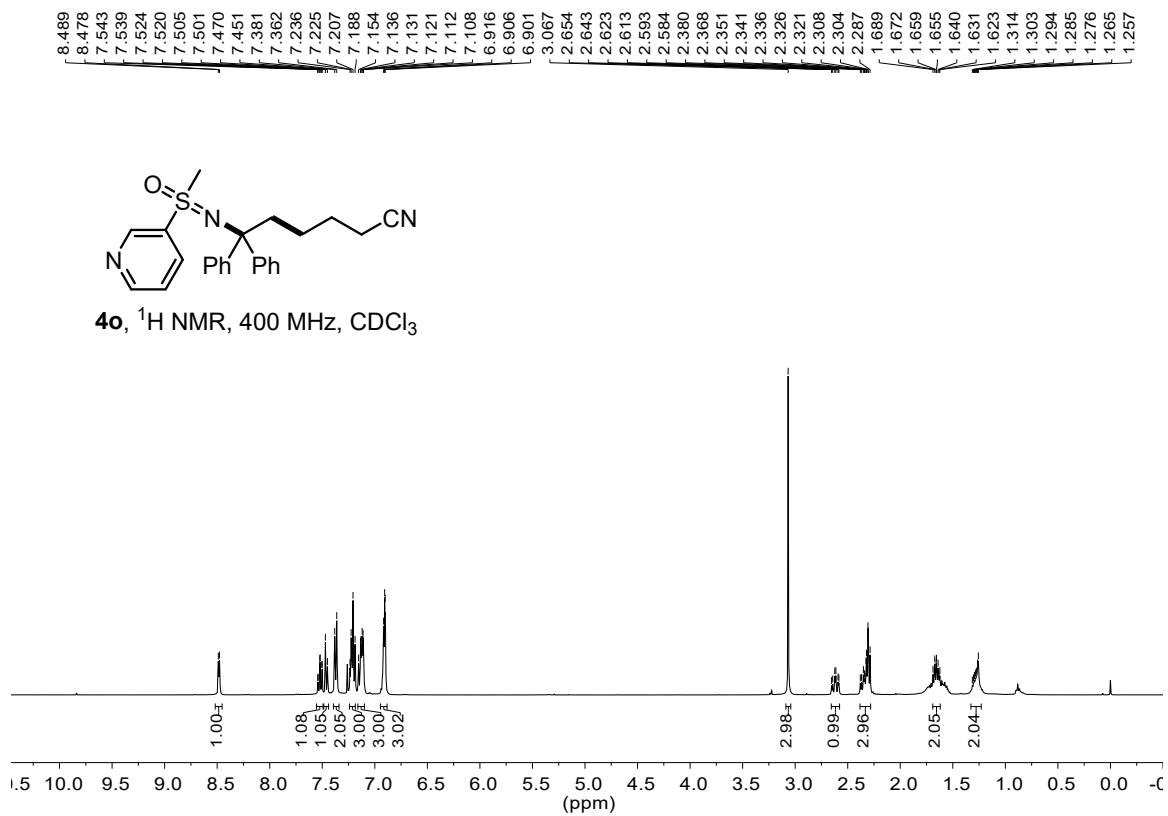


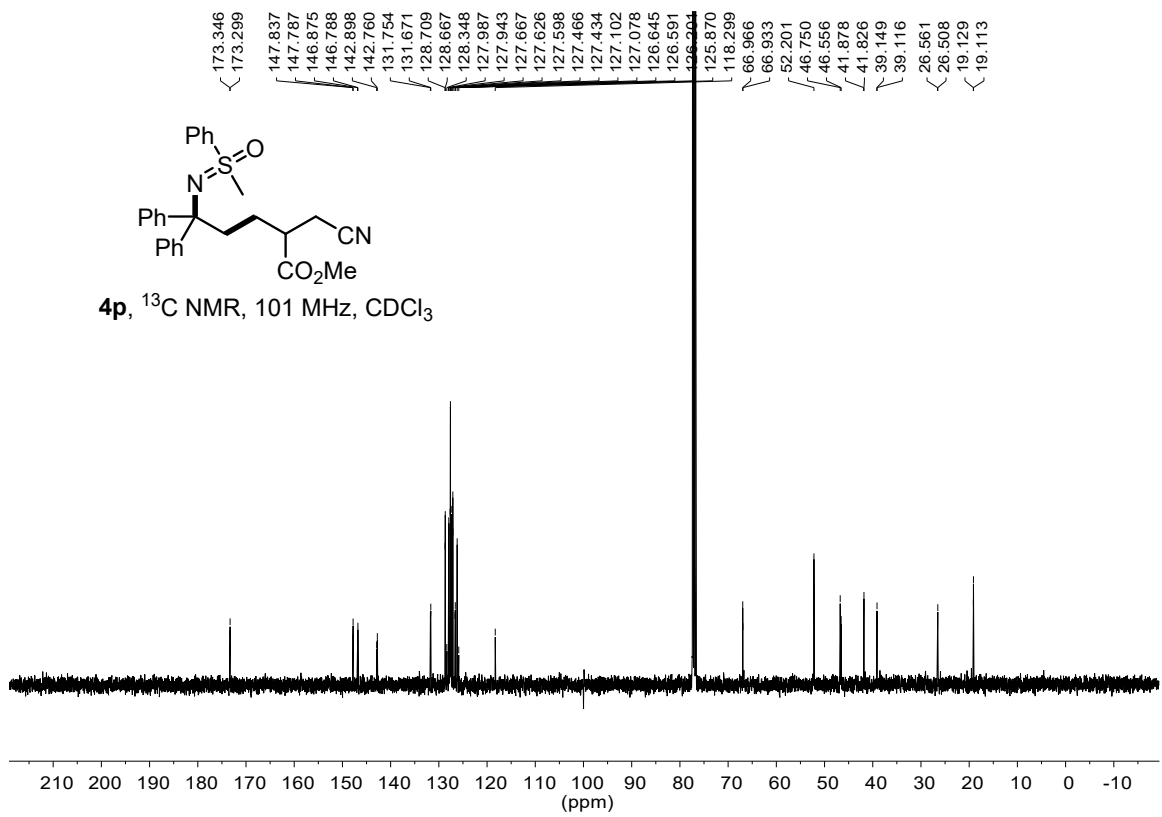
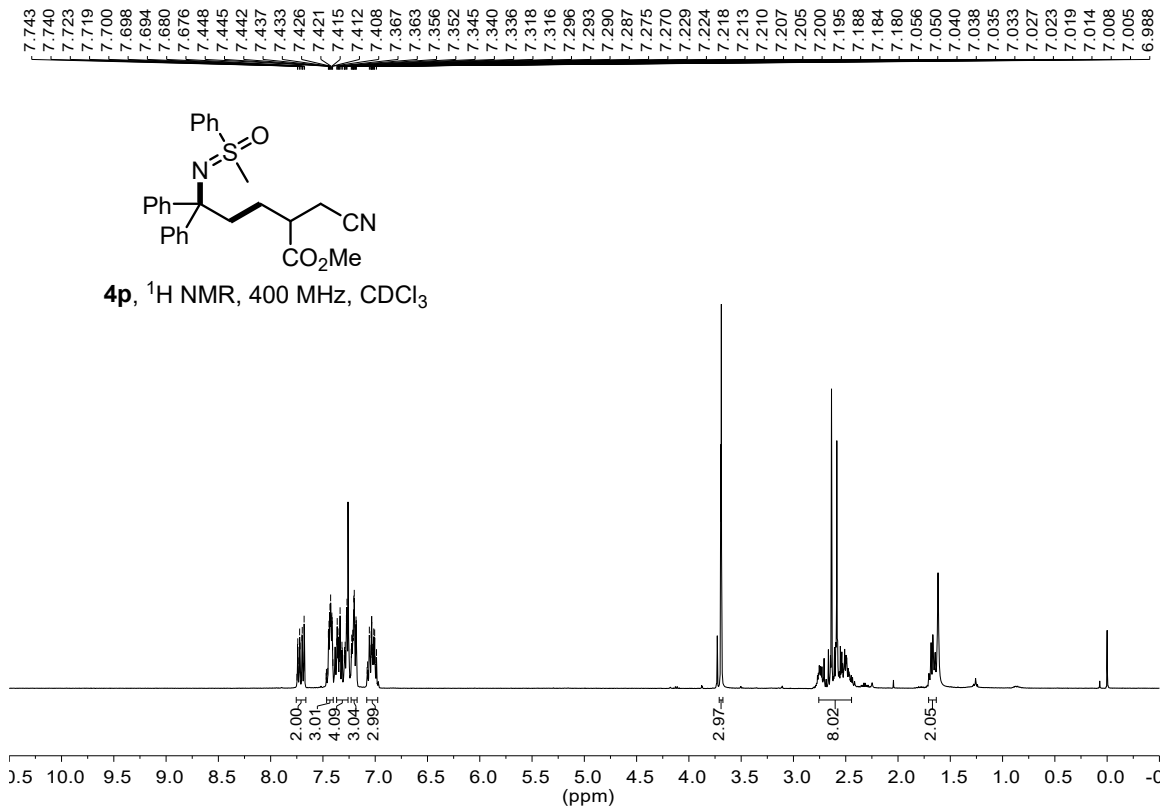
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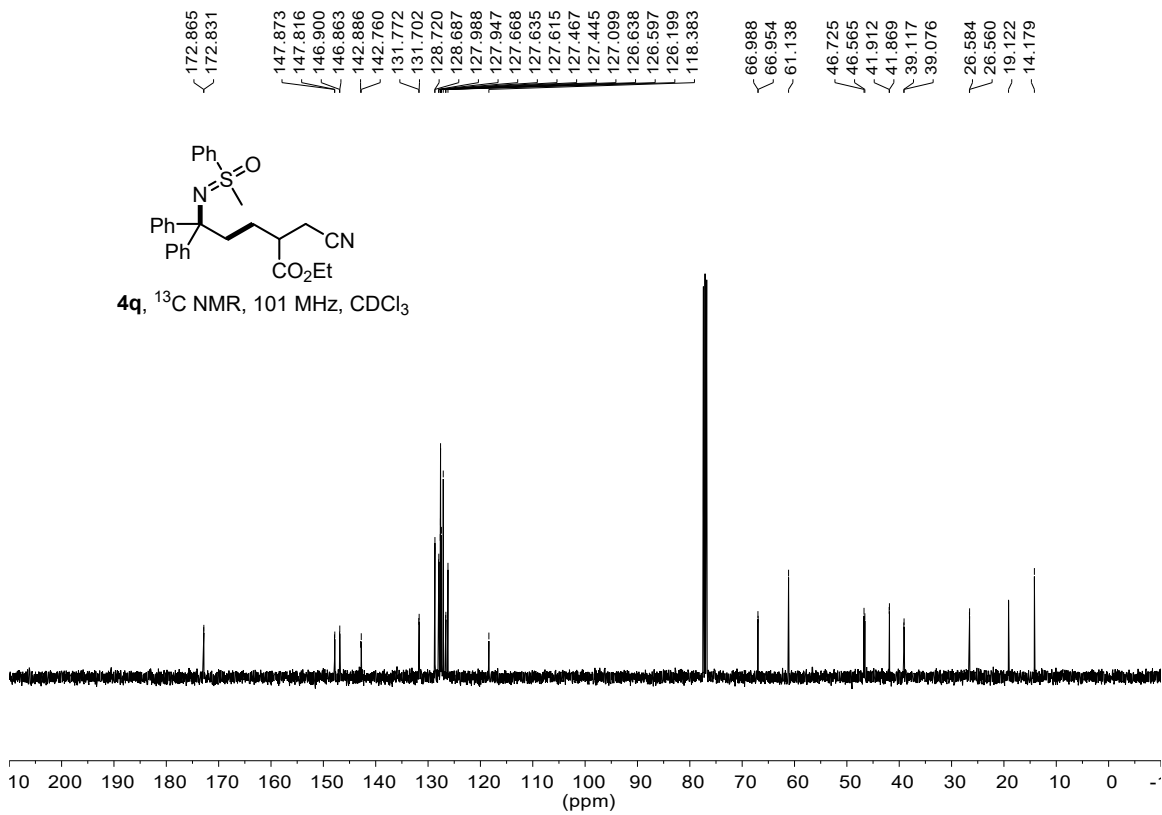
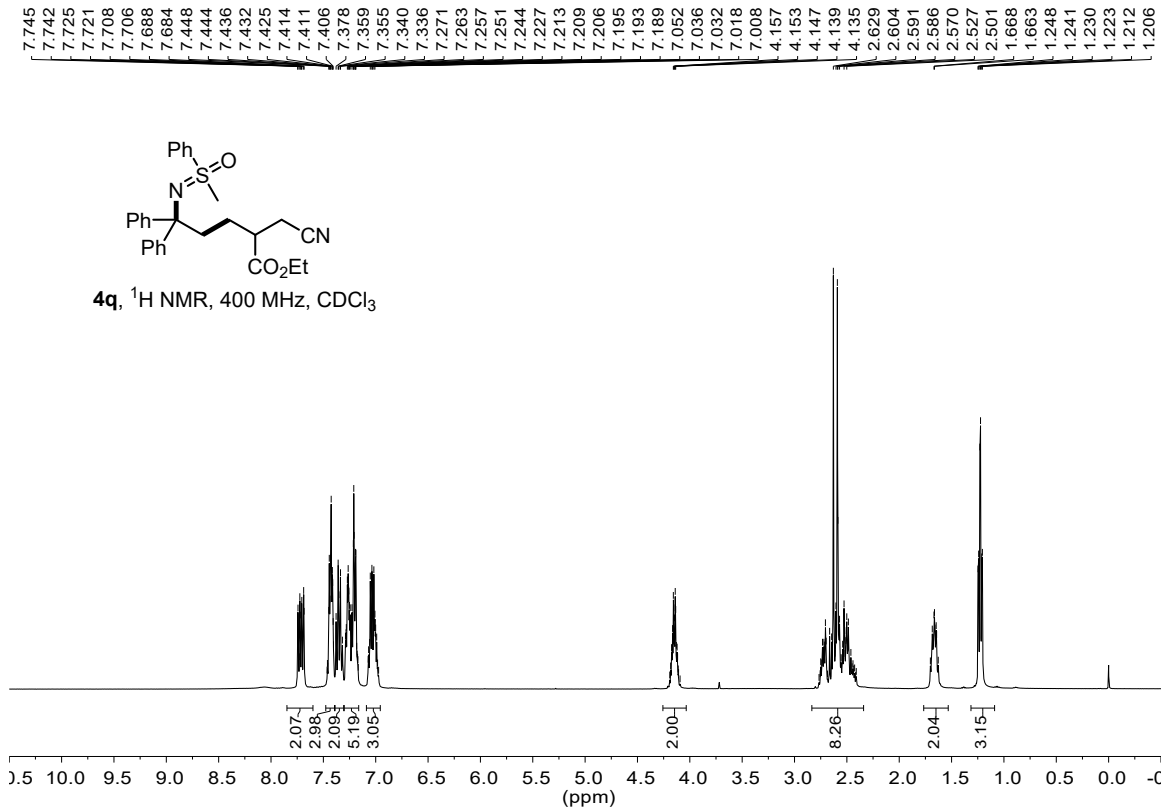


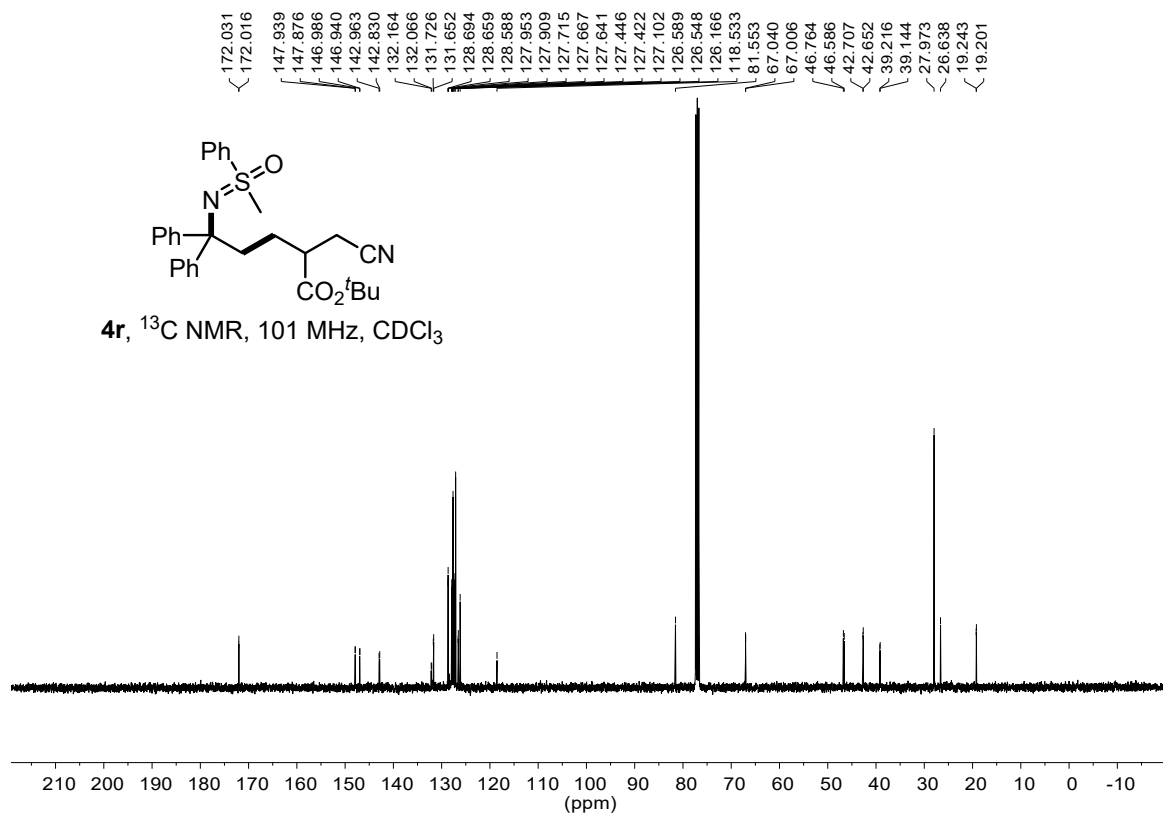
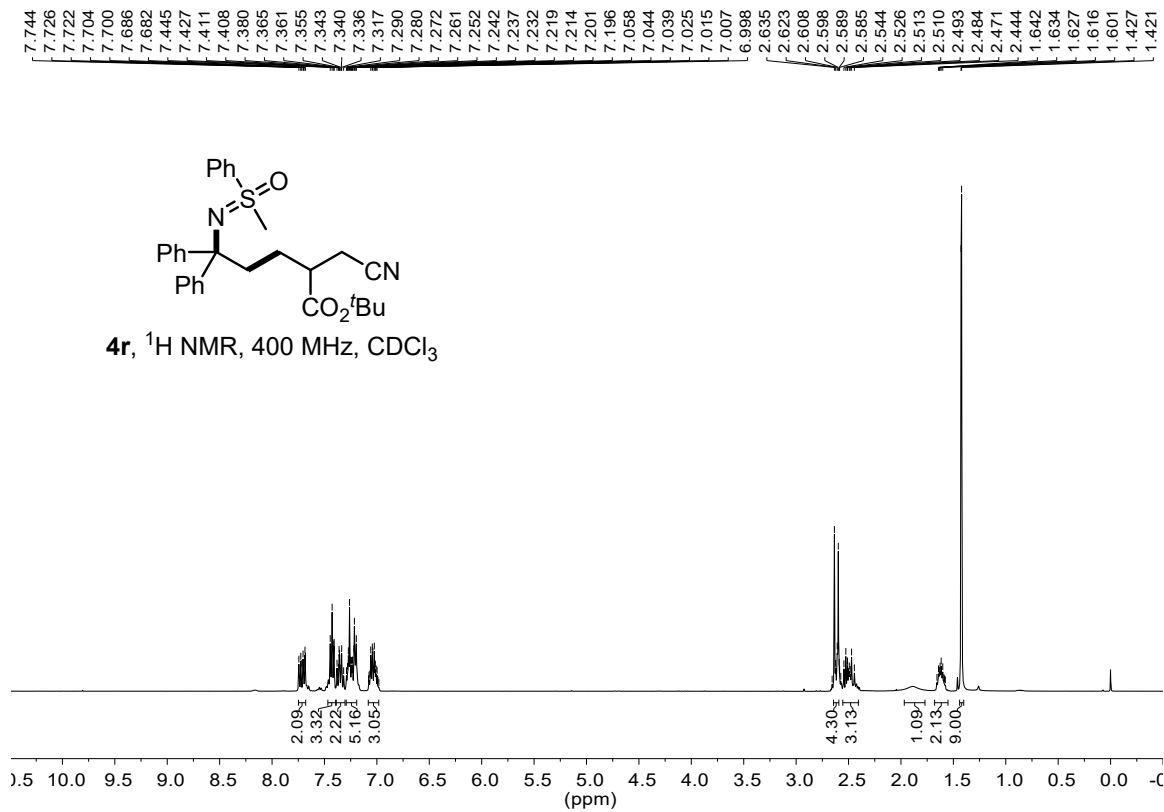
4n, ^{13}C NMR, 101 MHz, CDCl_3

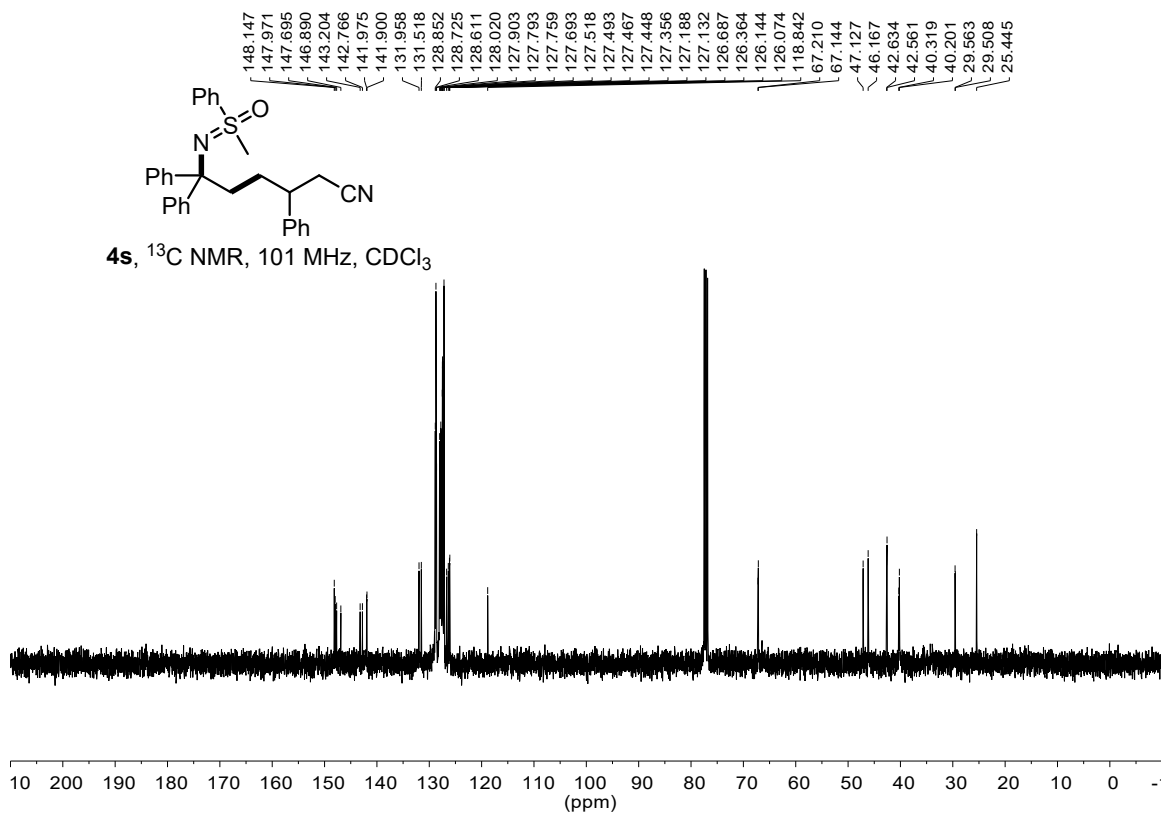
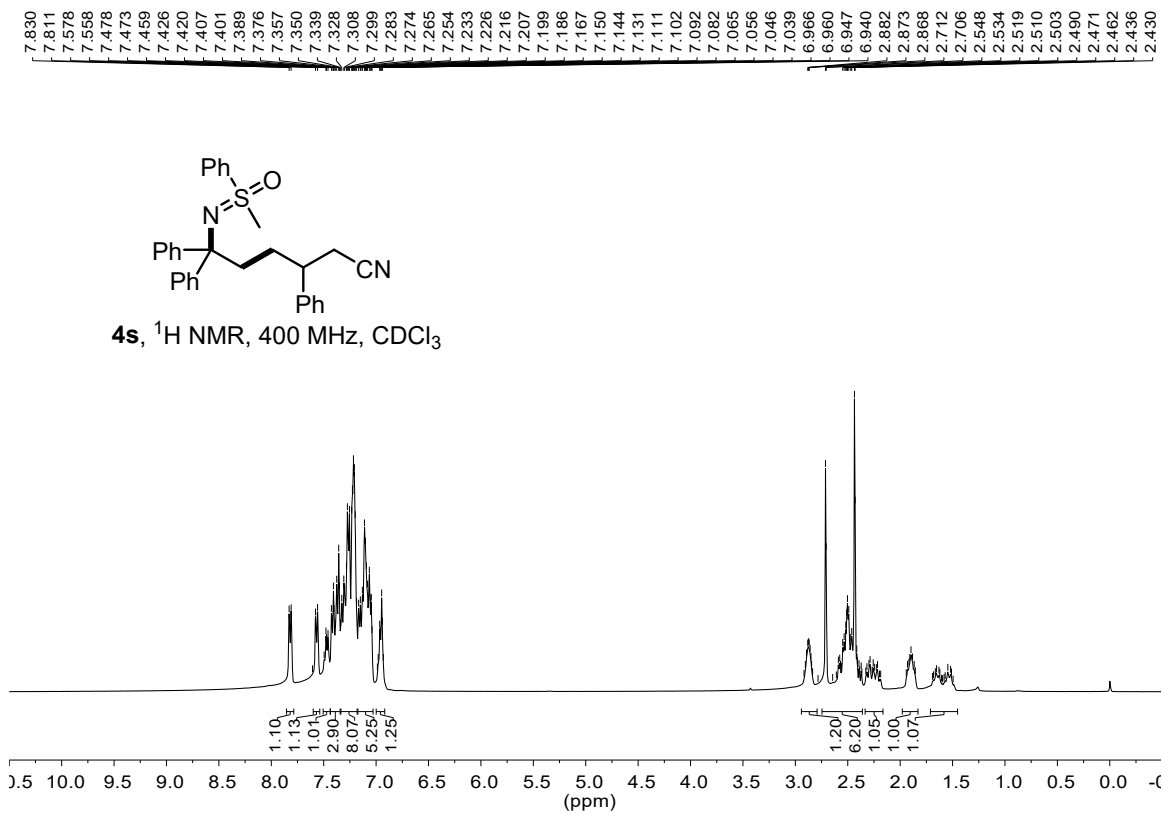


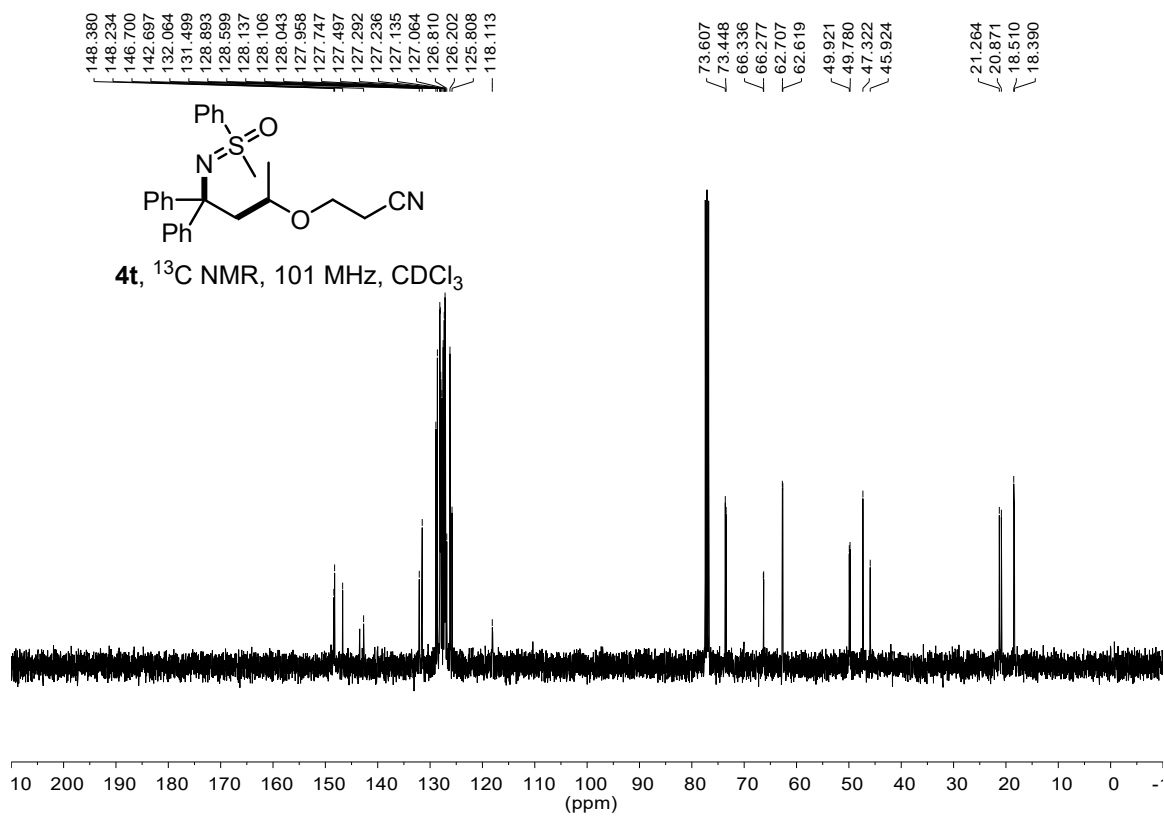
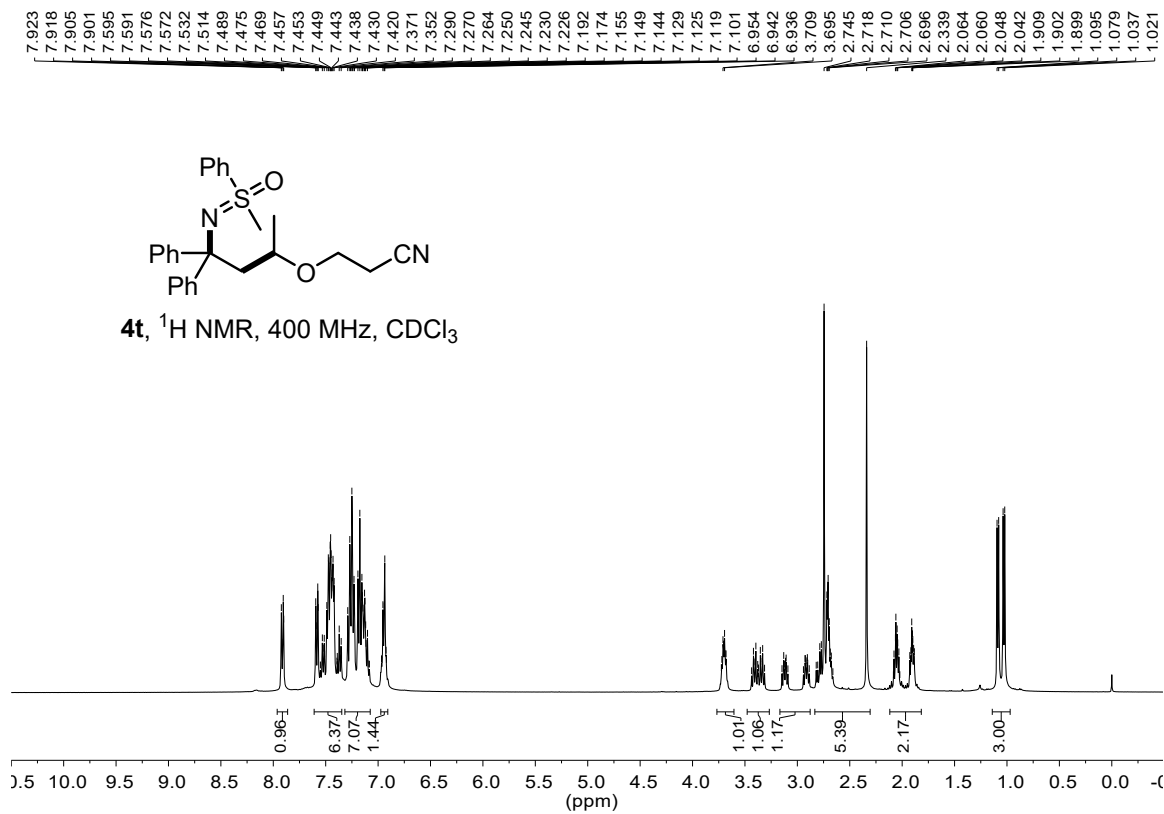


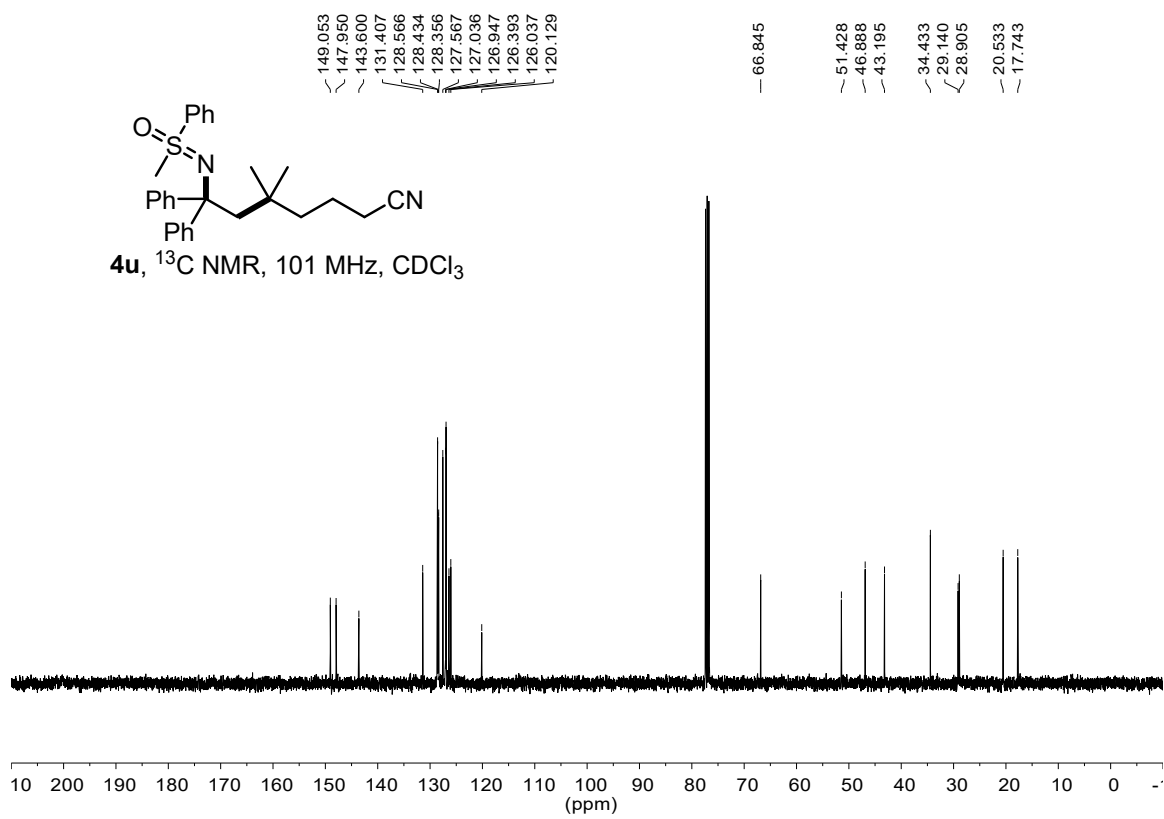
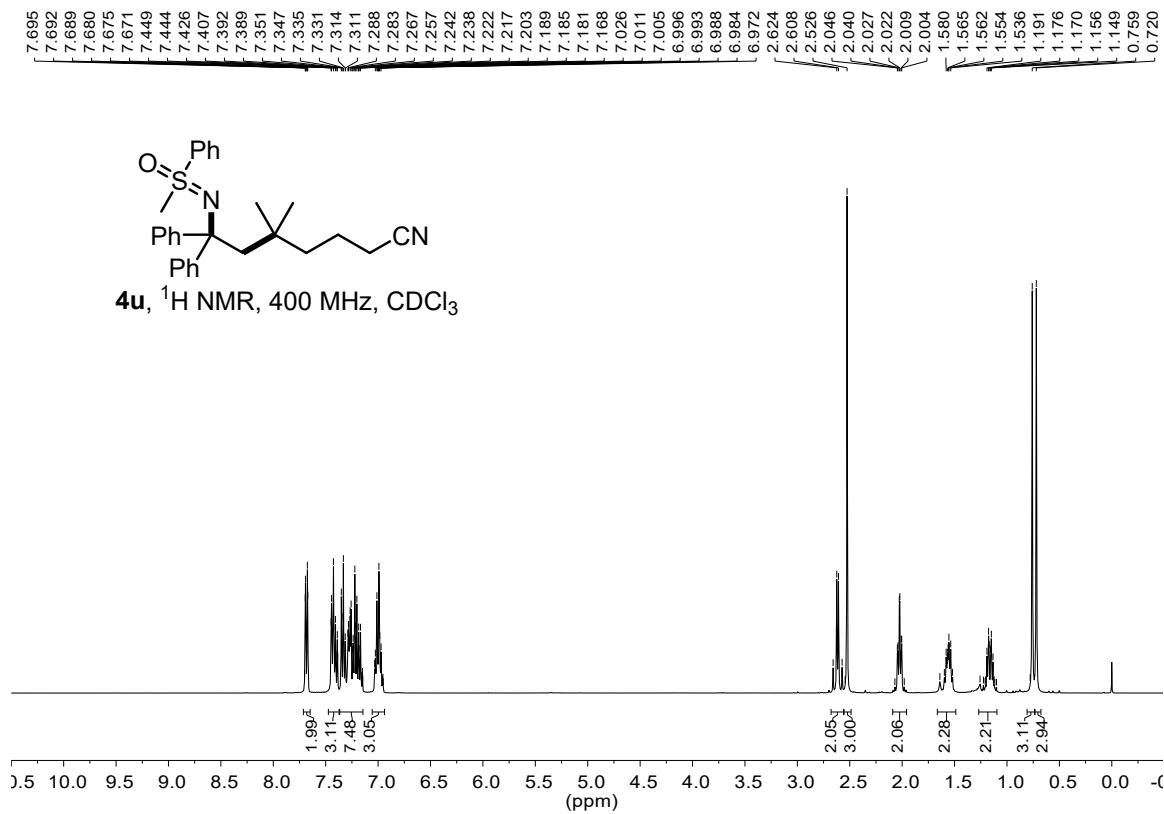


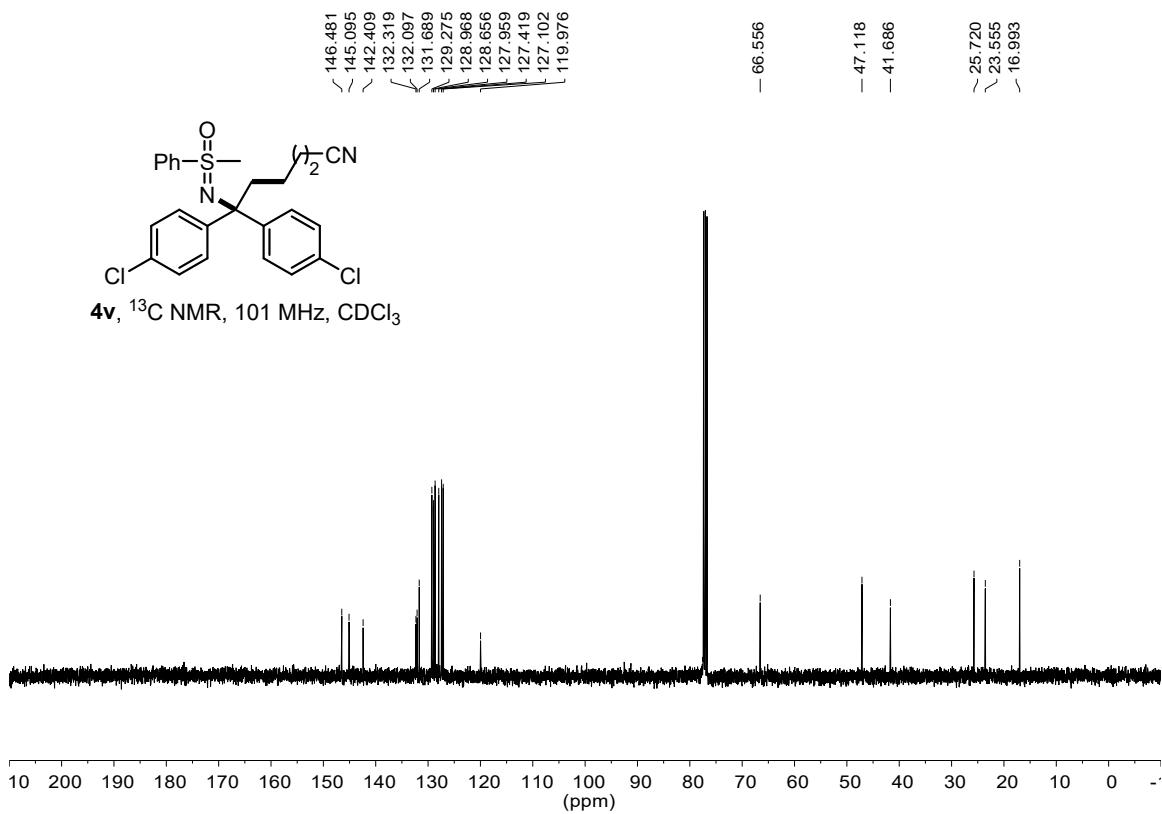
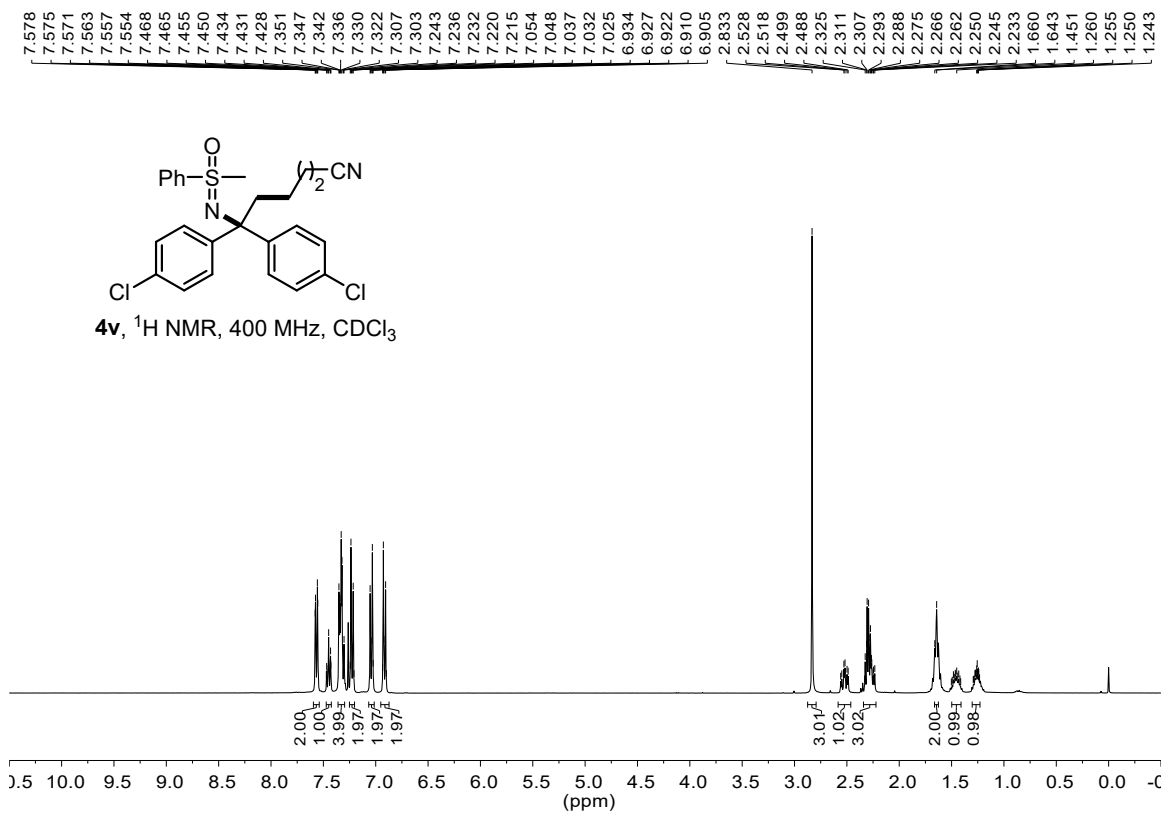


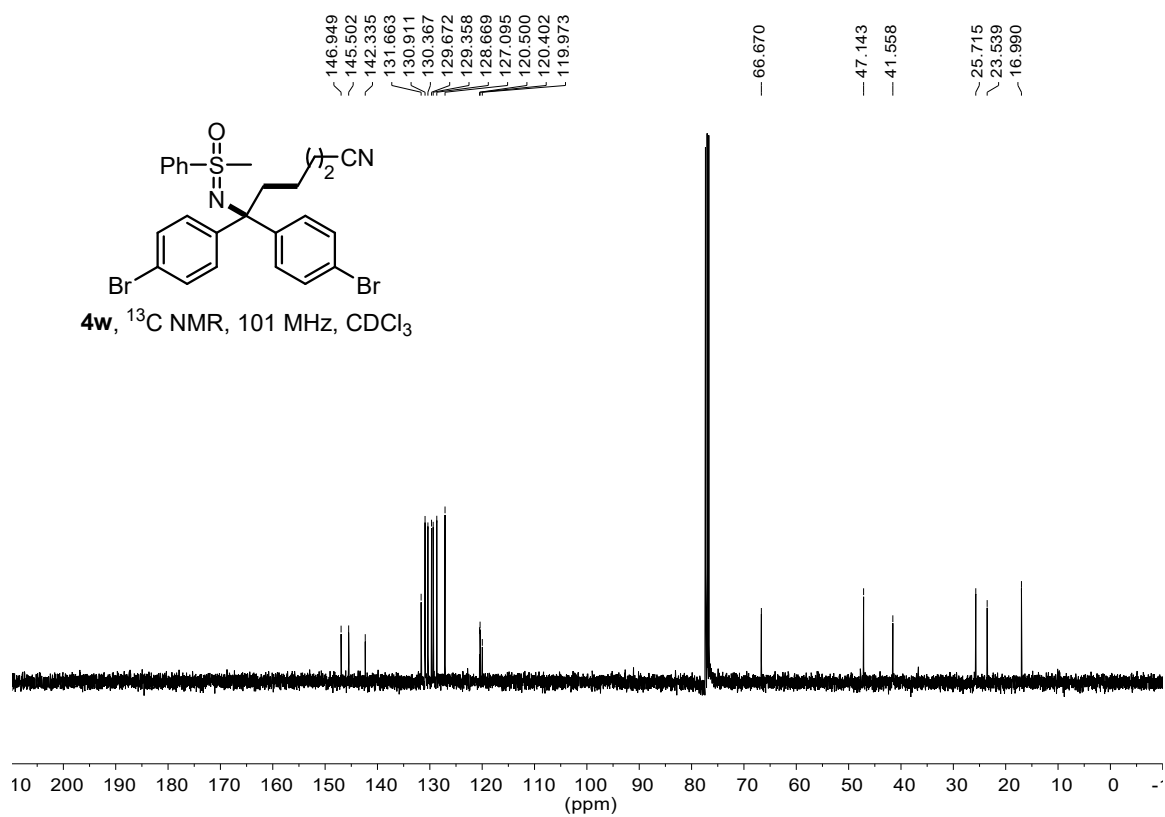
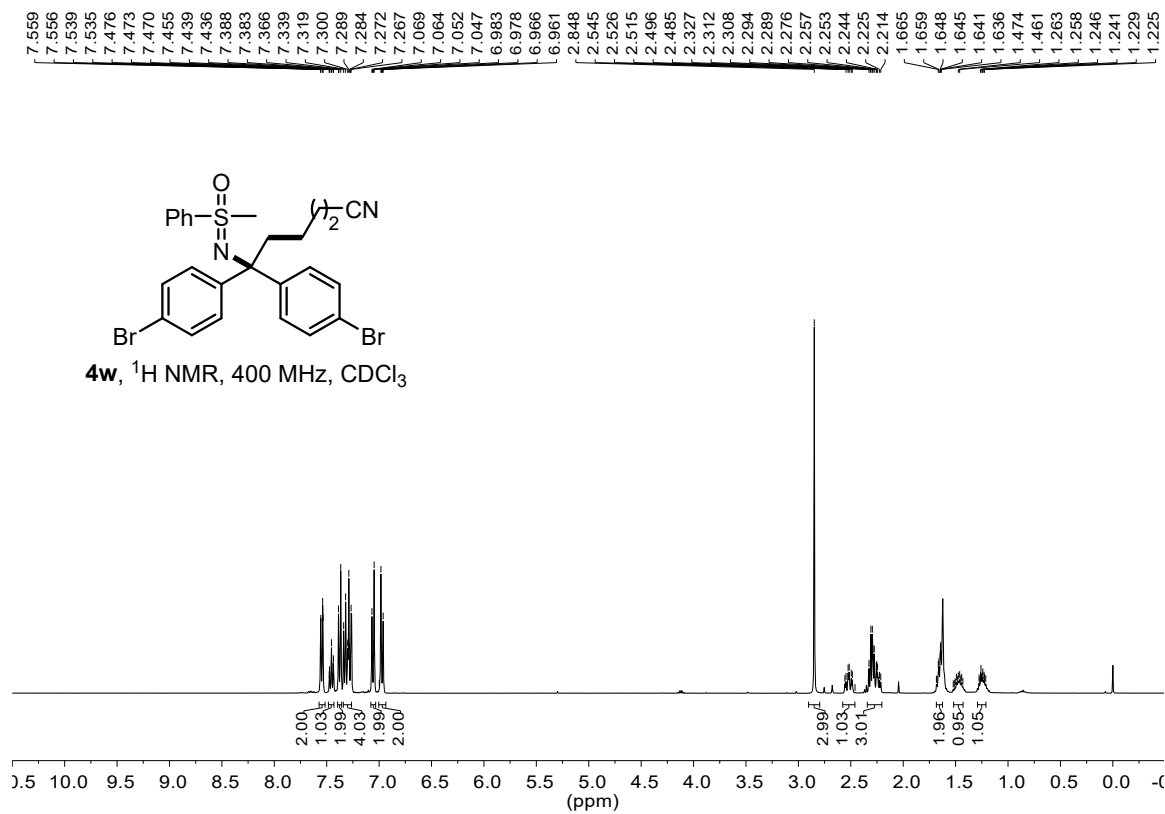


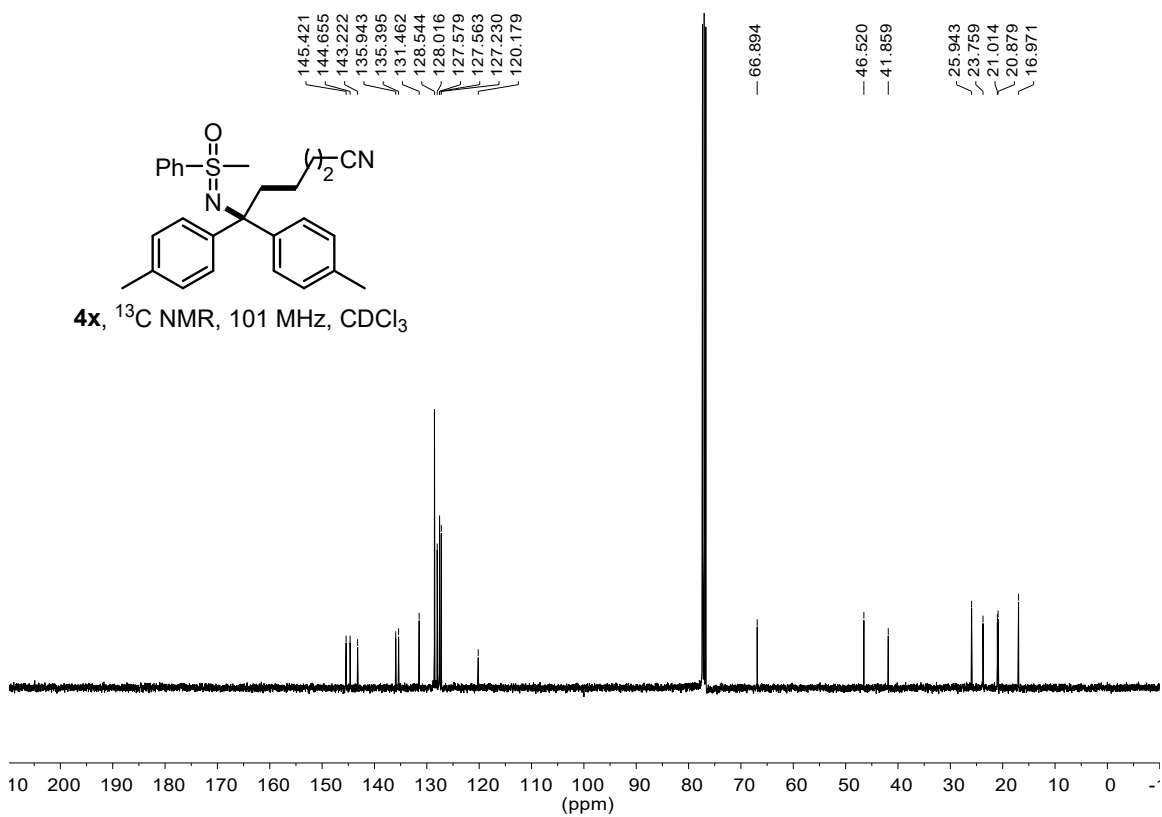
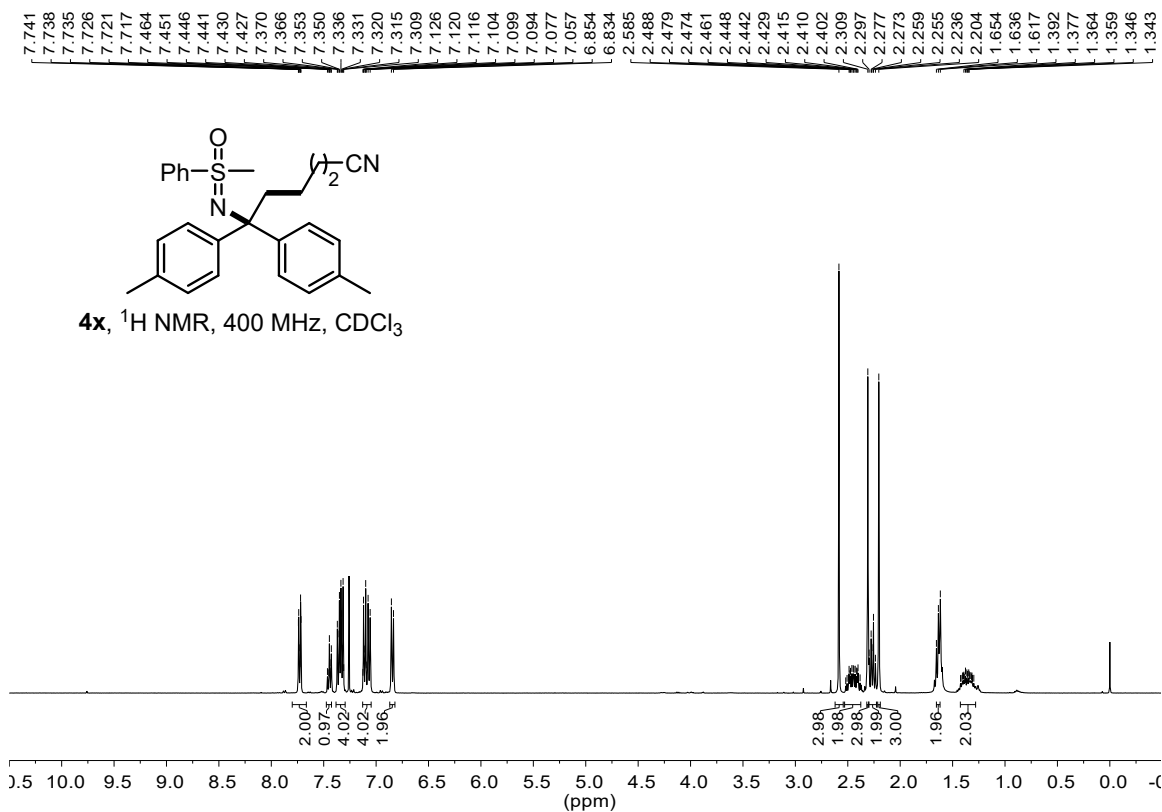


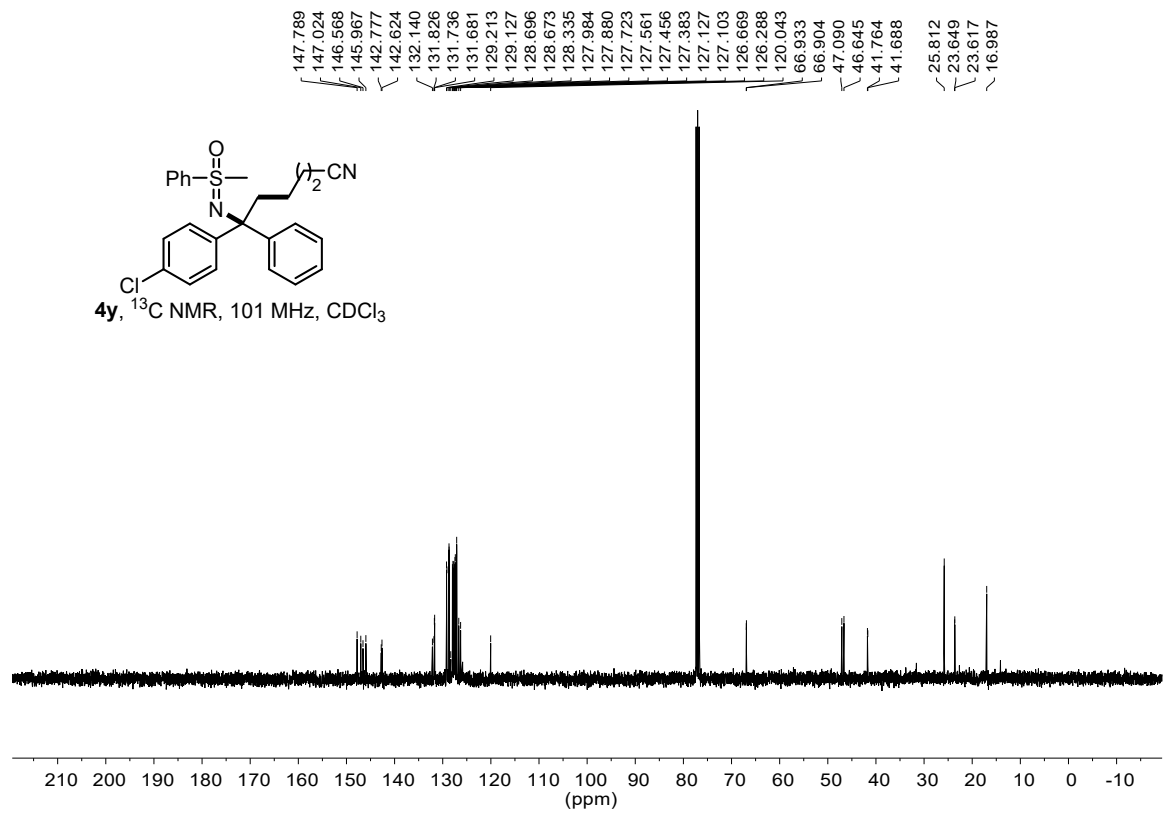
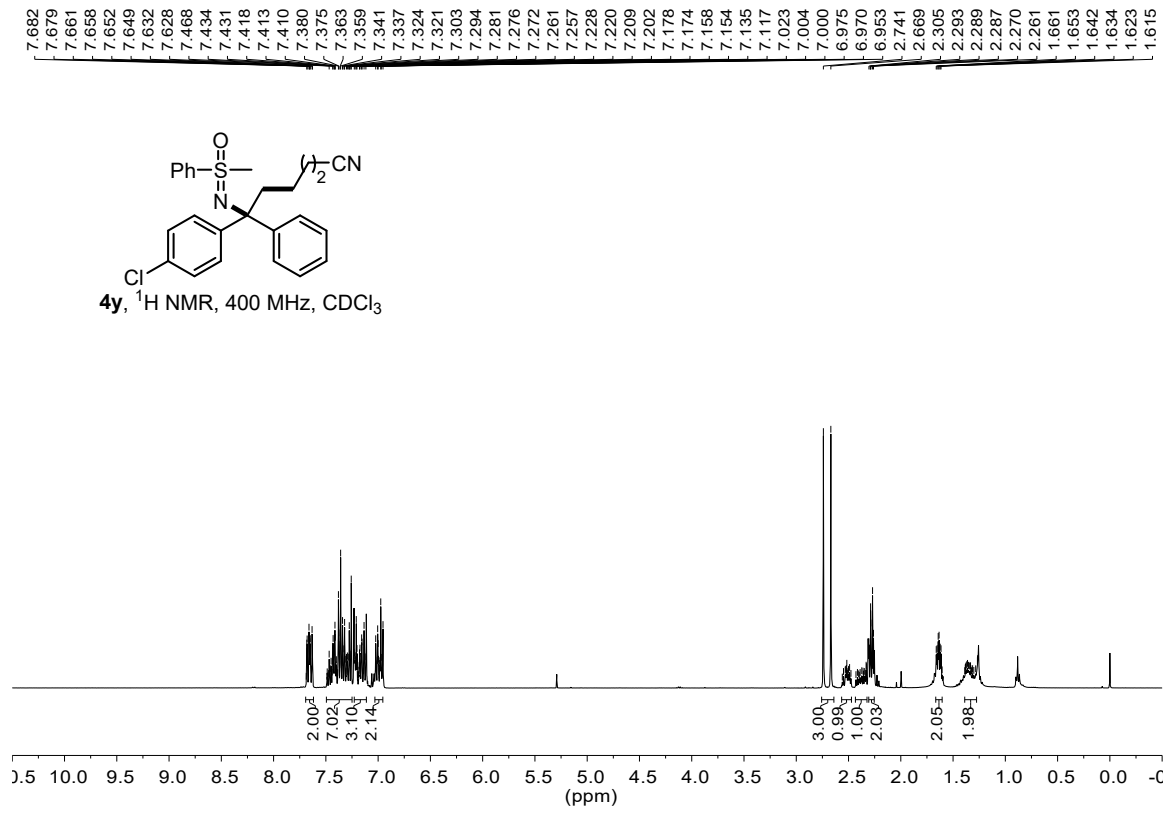


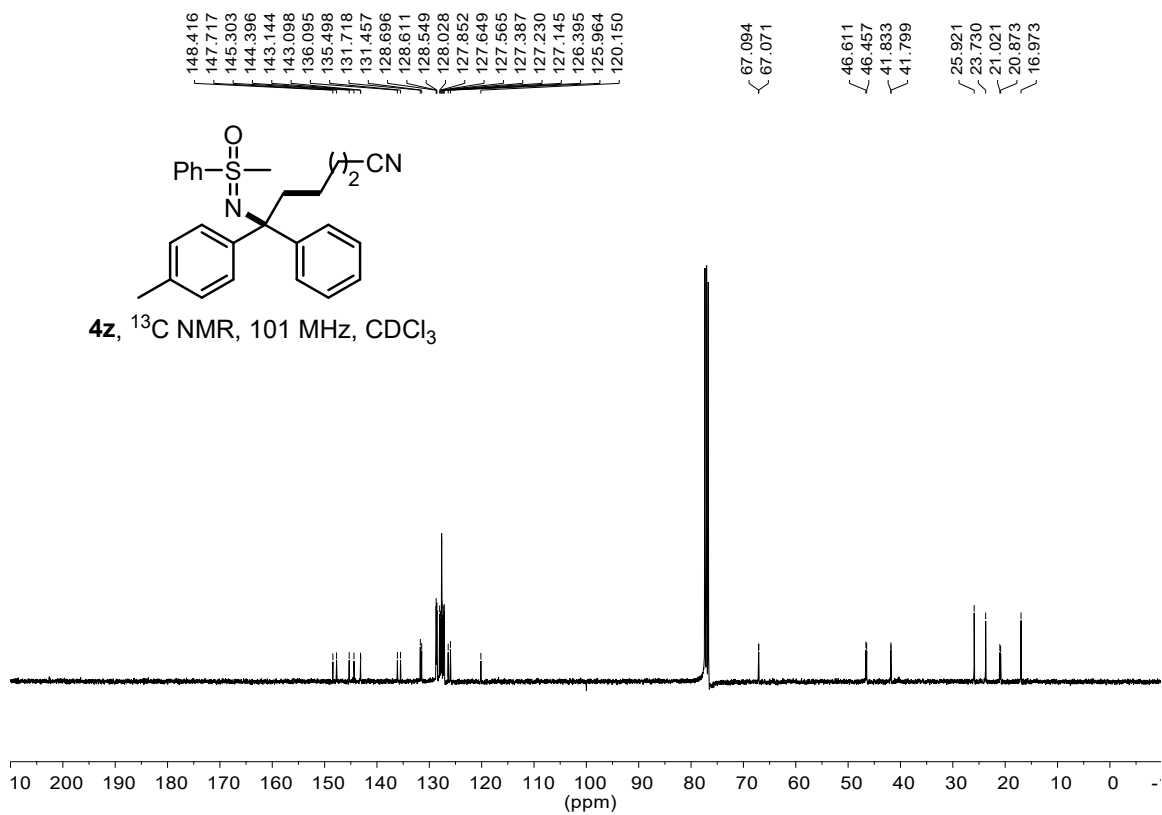
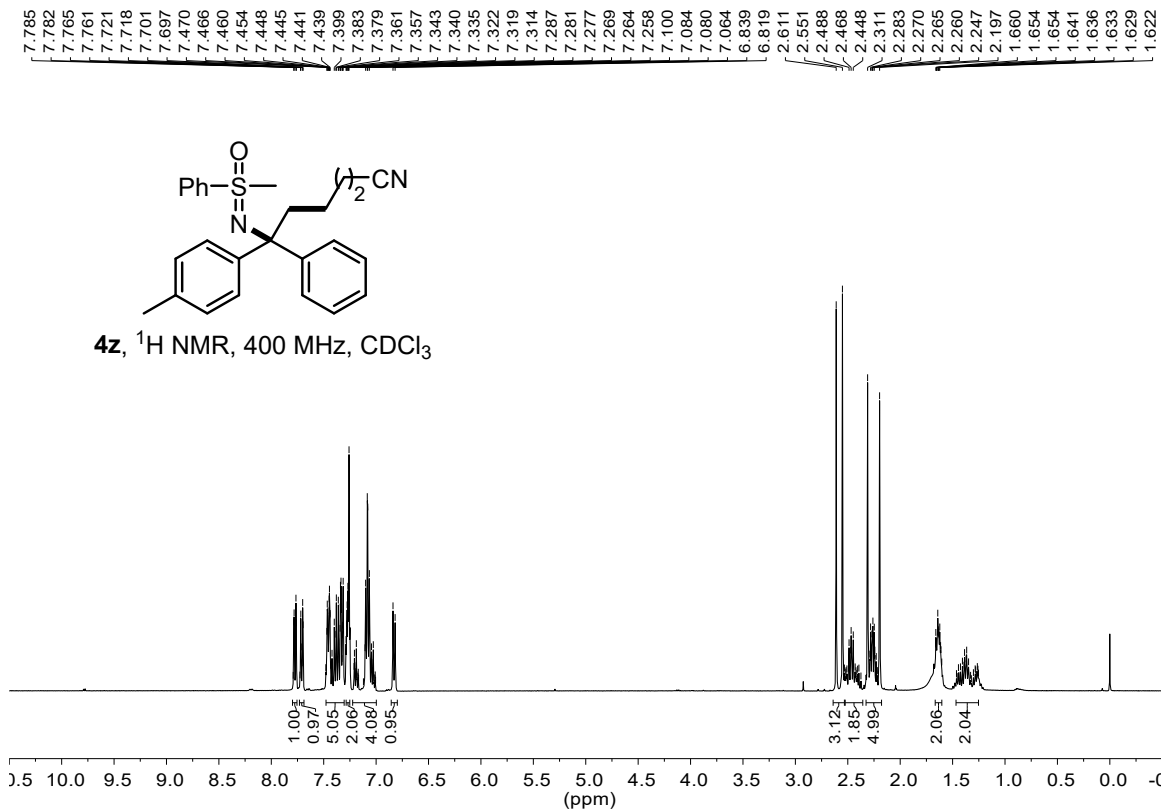


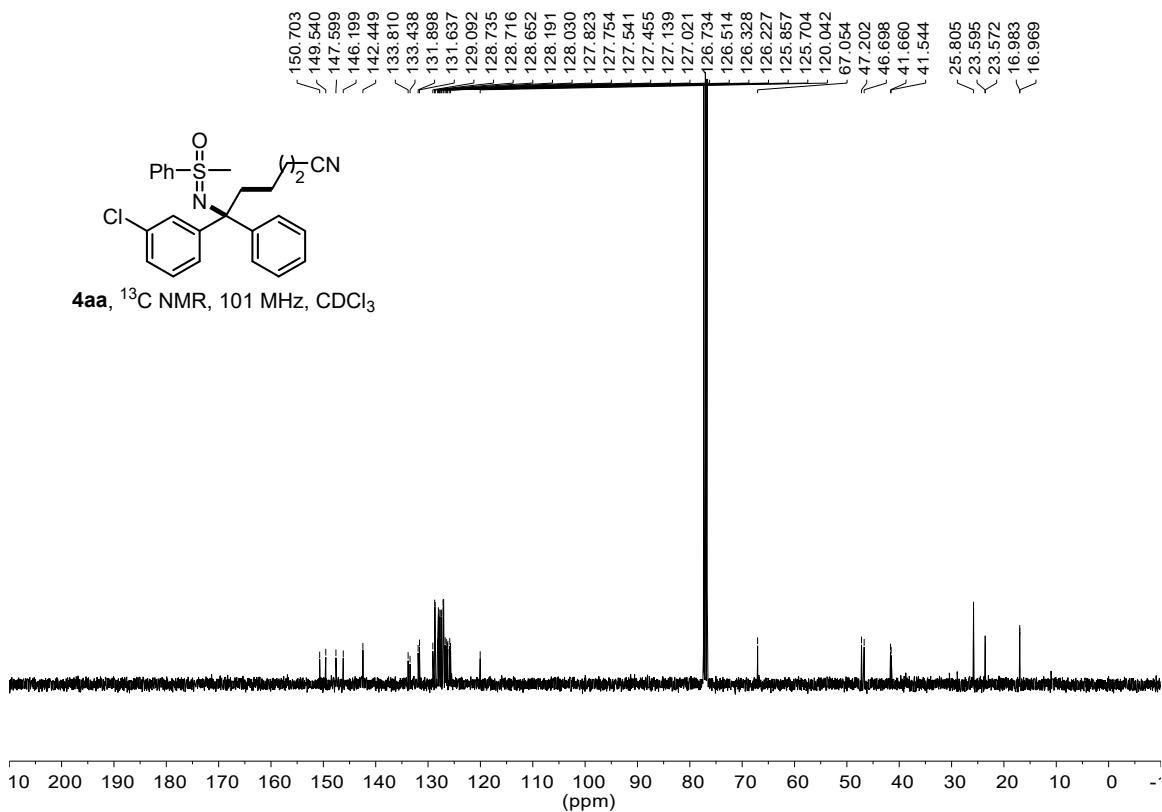
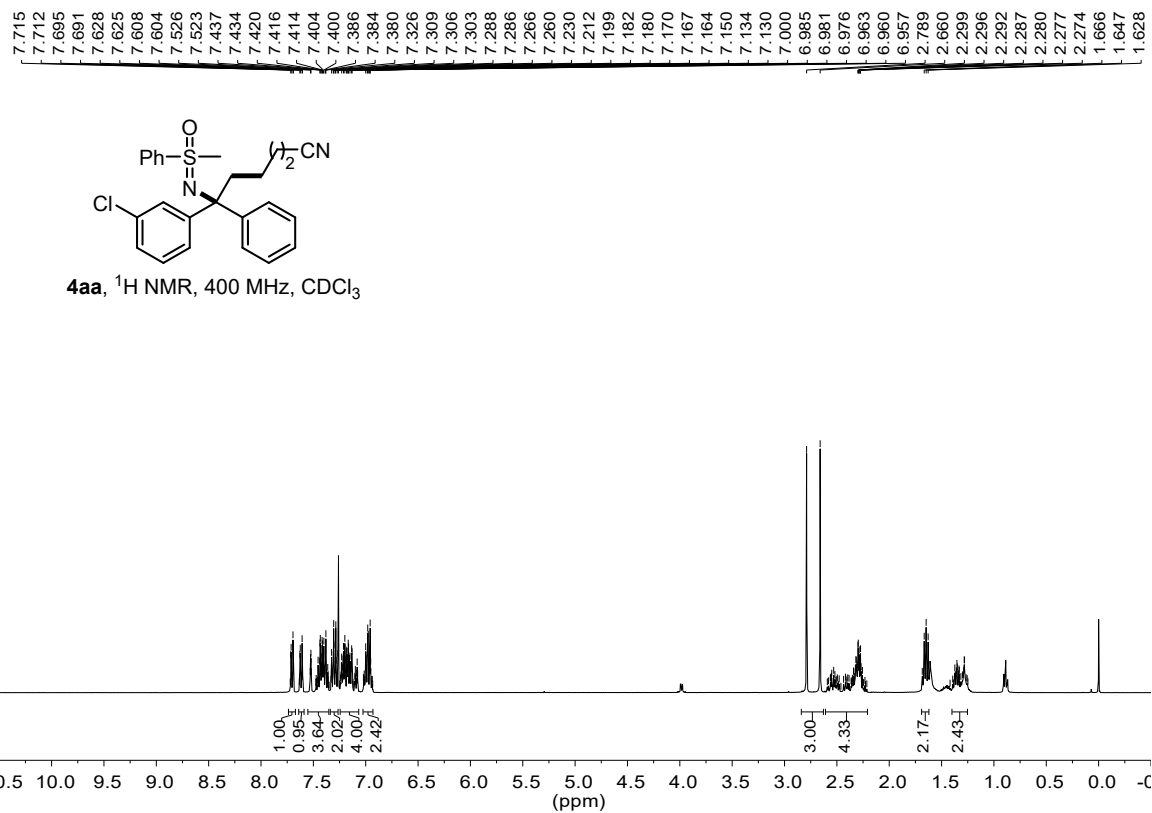


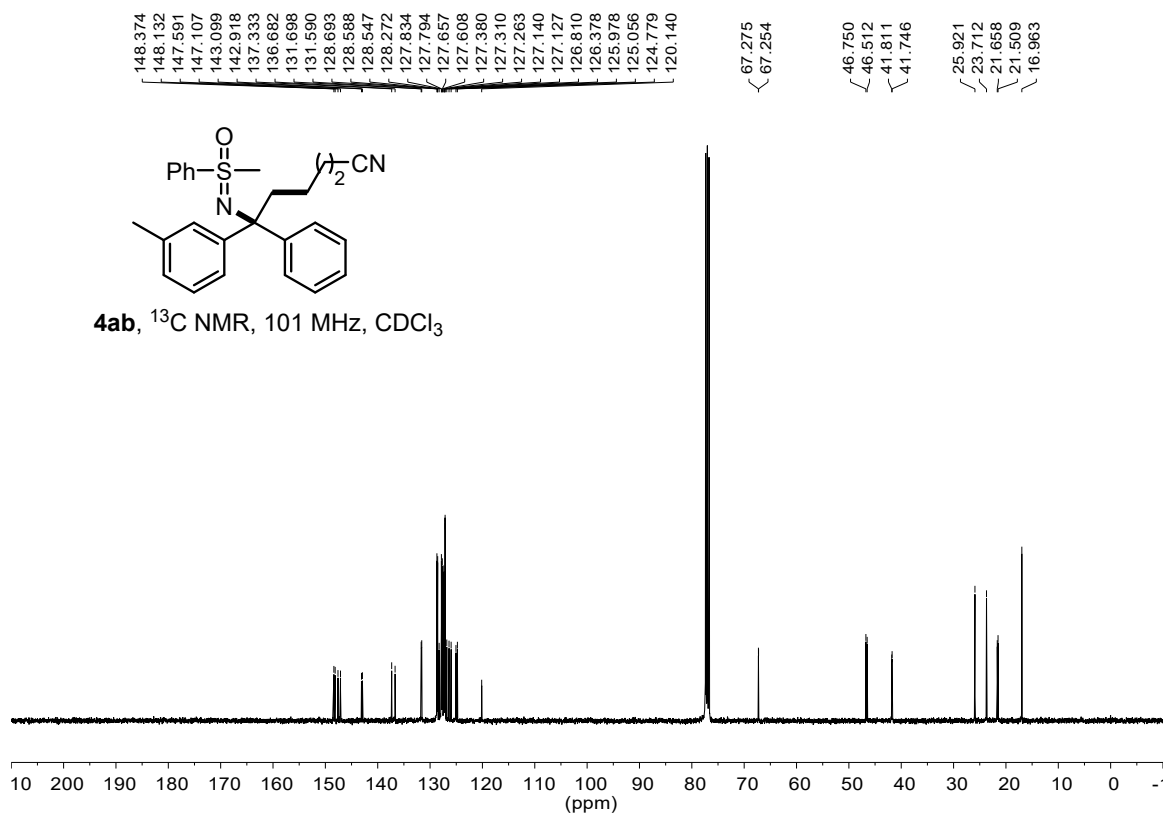
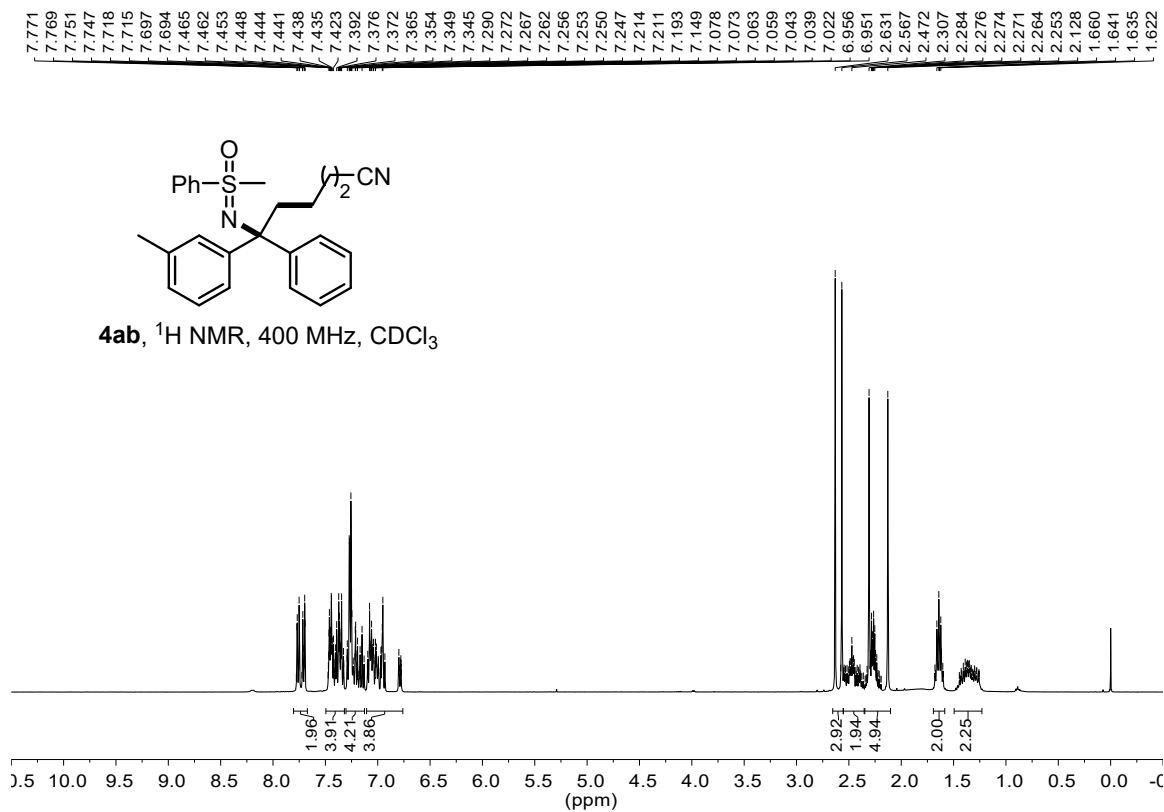


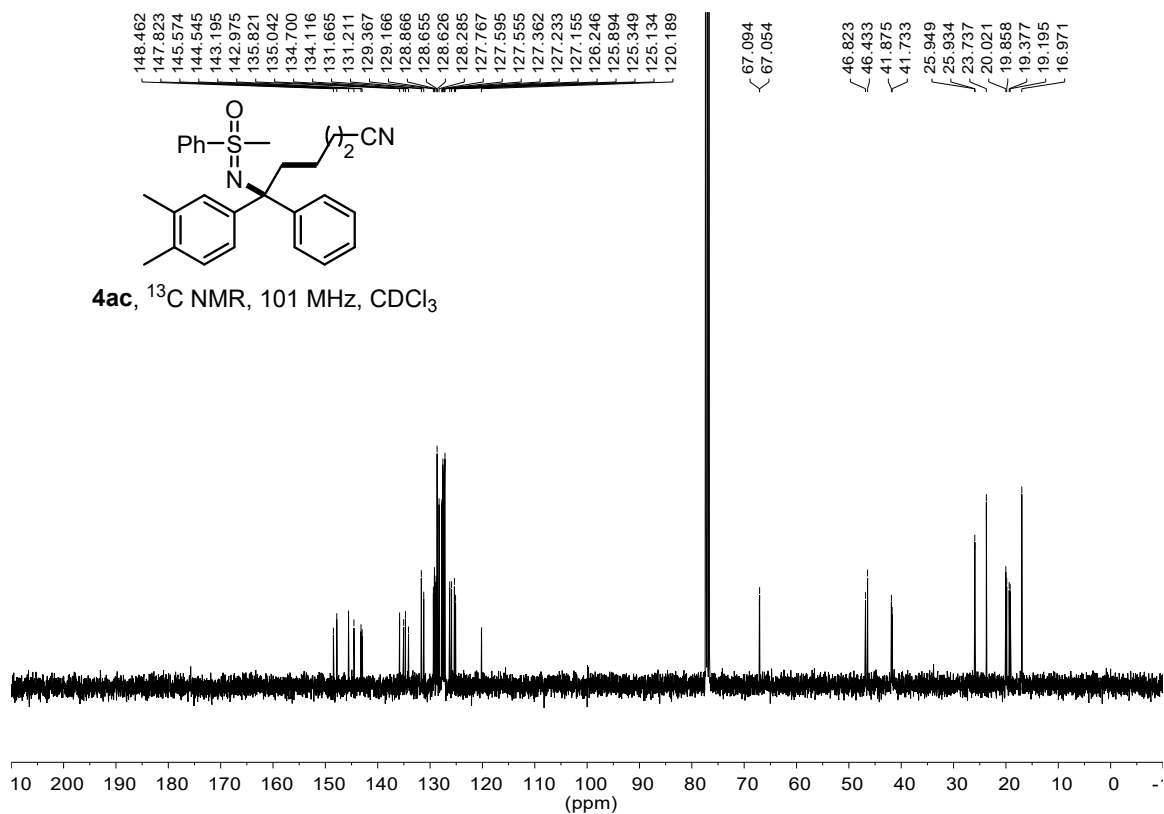
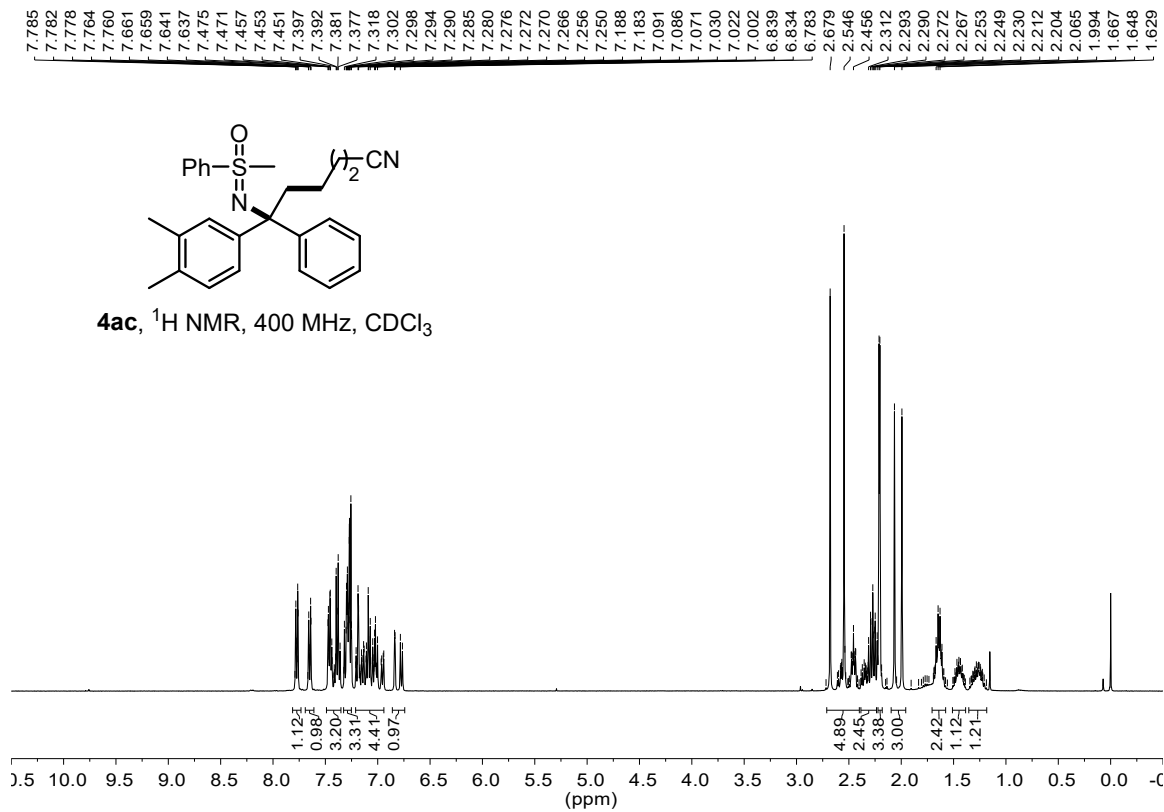


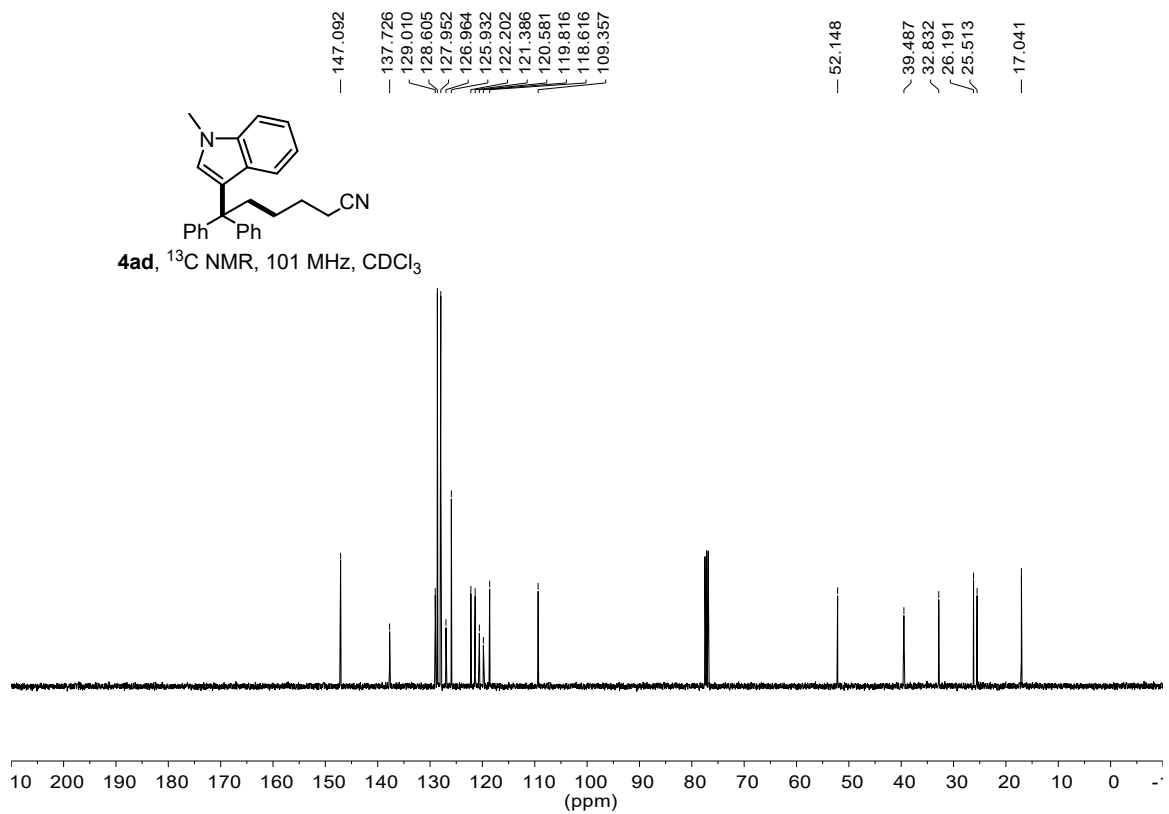
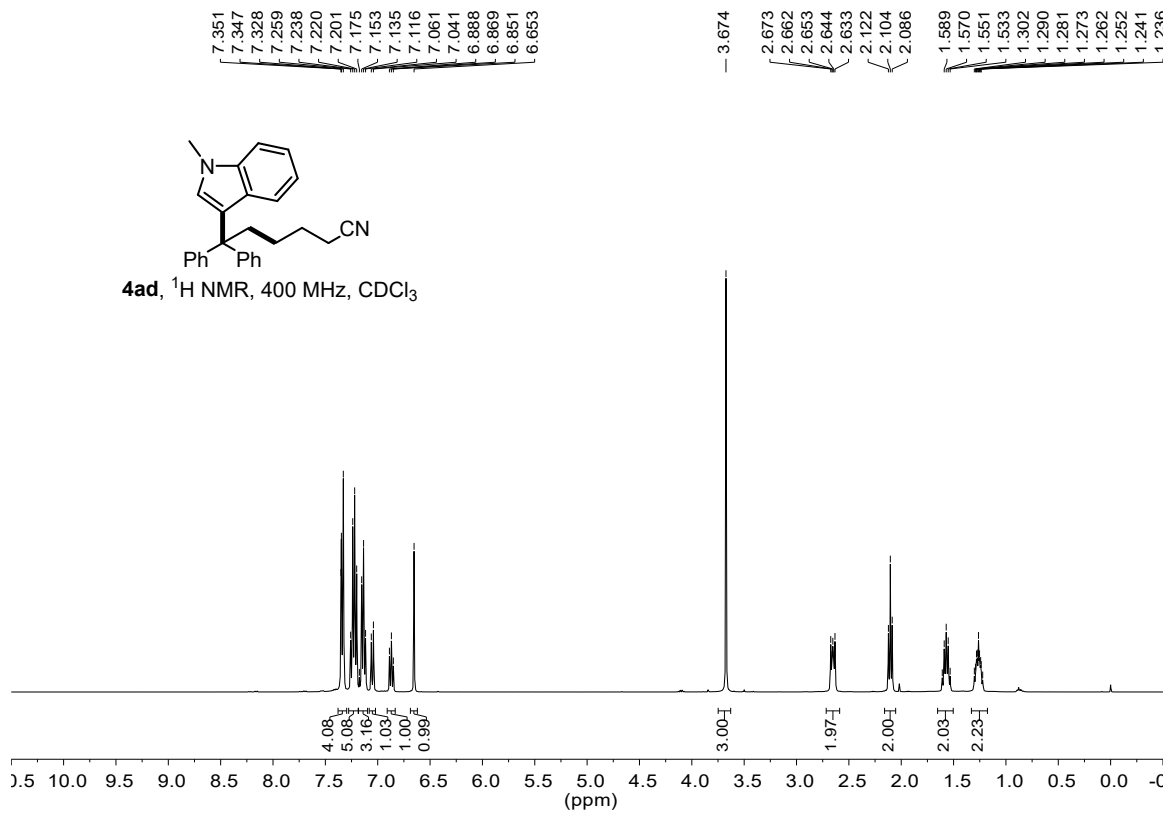


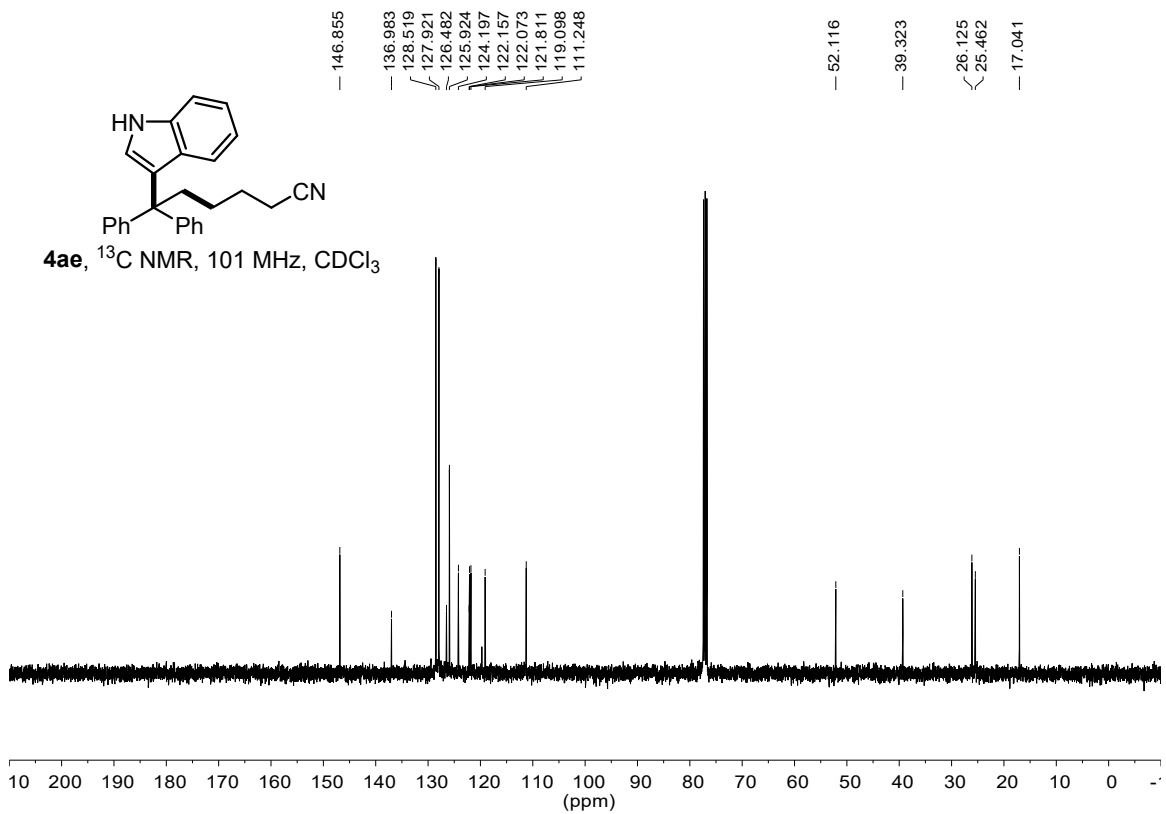
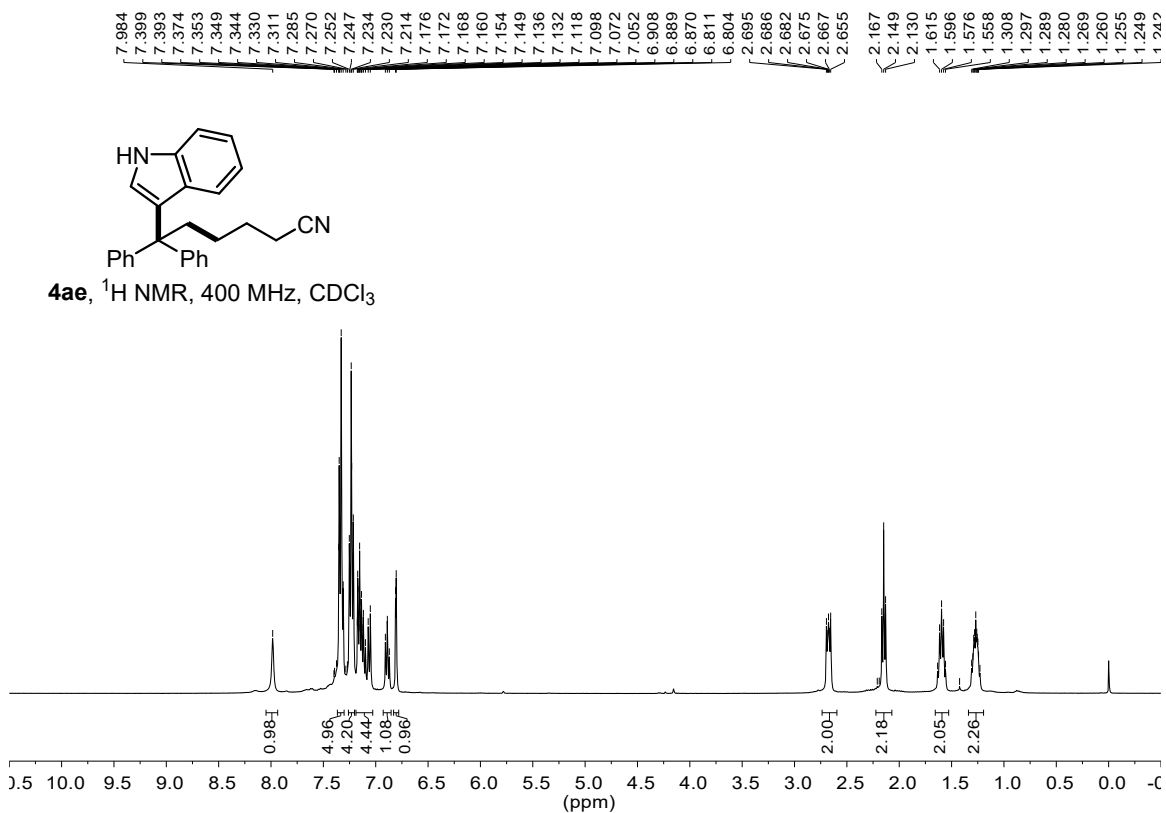


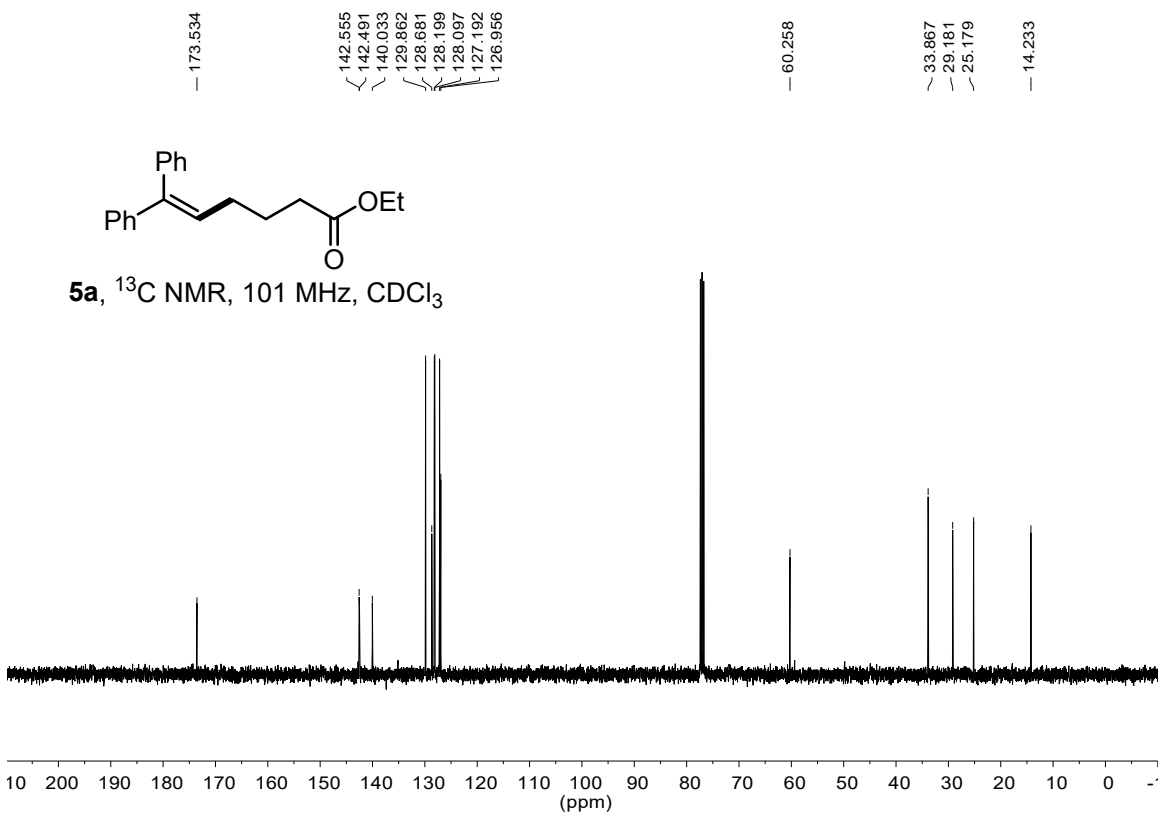
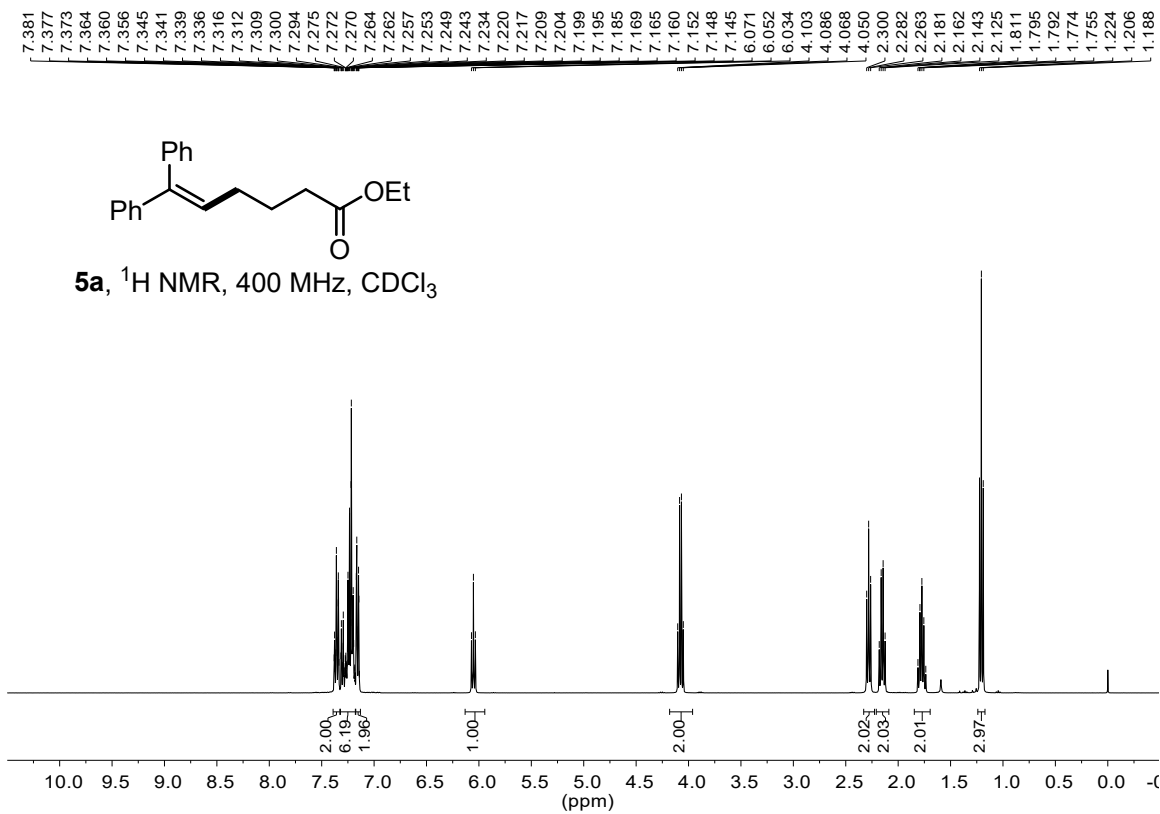


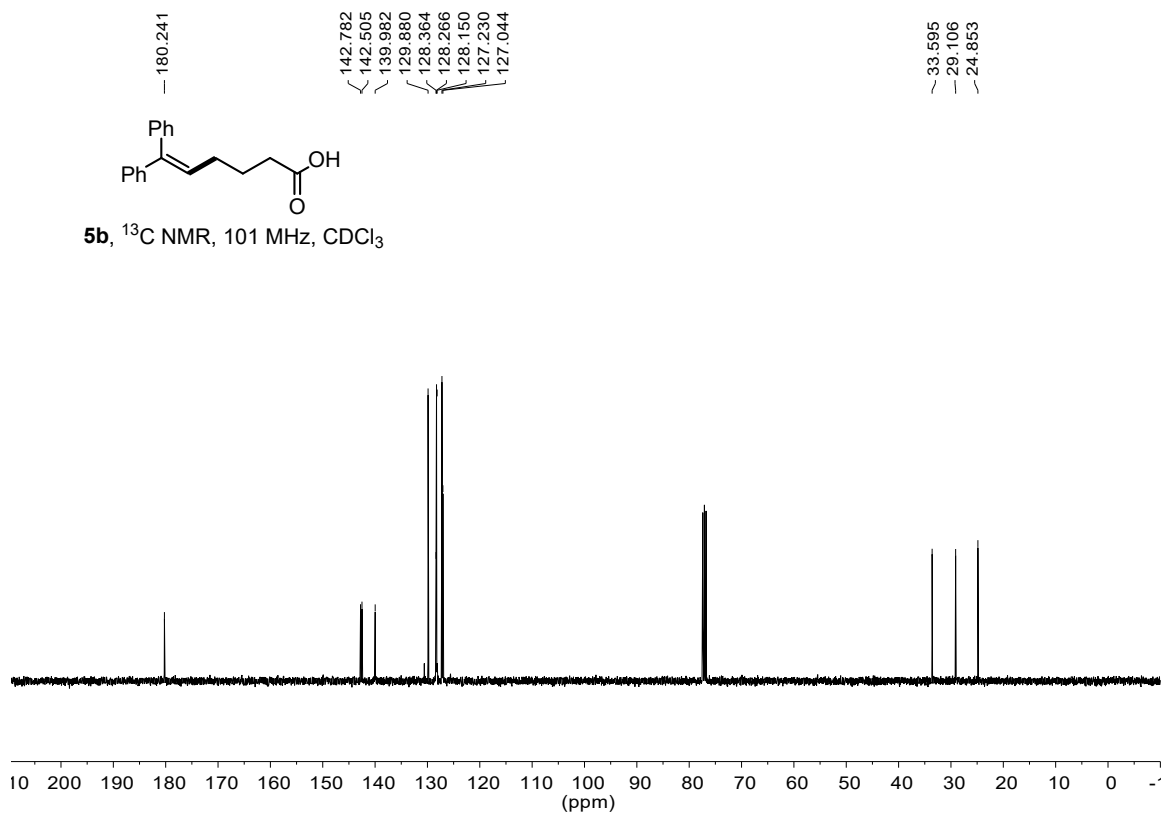
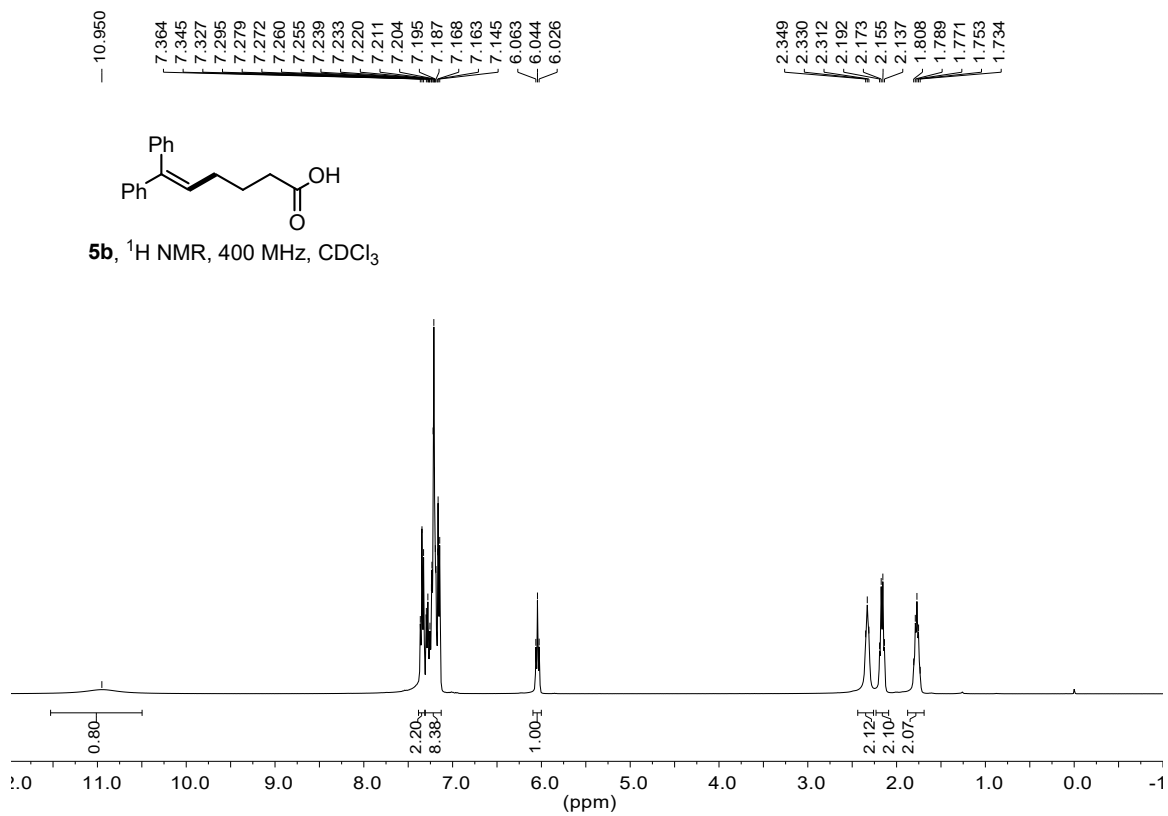








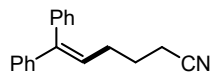




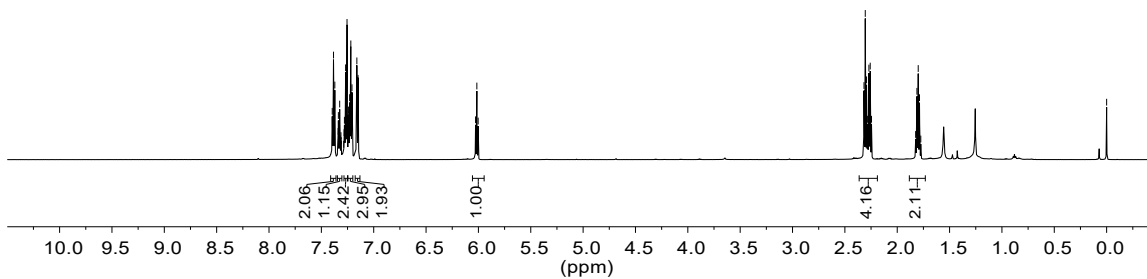
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7.222
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7.210
7.208
7.206
7.164
7.161
7.150
6.027
6.015
6.003

2.317
2.305
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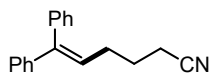


6, ^1H NMR, 600 MHz, CDCl_3

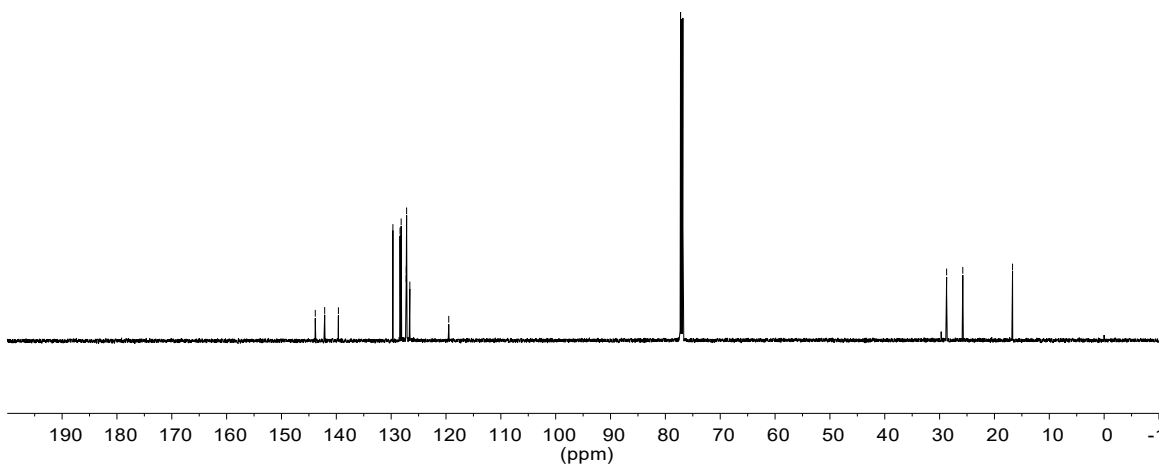


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127.245
127.182
126.598
119.501

28.721
25.772
16.702



6, ^{13}C NMR, 151 MHz, CDCl_3



6. References

1. X.-Y. Yu, J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang and W.-J. Xiao, *A Visible-Light-Driven Iminyl Radical-Mediated C–C Single Bond Cleavage/Radical Addition Cascade of Oxime Esters*, *Angew. Chem. Int. Ed.*, 2018, **57**, 738-743.
2. G. Zhang, H. Tan, W. Chen, H. C. Shen, Y. Lu, C. Zheng and H. Xu, *Synthesis of NH-Sulfoximines by Using Recyclable Hypervalent Iodine(III) Reagents under Aqueous Micellar Conditions*, *ChemSusChem*, 2020, **13**, 922-928.