Supporting Information

Organo-photocatalyzed visible-light-driven multicomponent approach for carbothioaryl/alkylation of activated alkene *via* C(sp^3)–H bond functionalization

Debabrata Das,[†a] Krishna Gopal Ghosh,[†a] Sumit Garai[a], Palasetty Chandu[a] and Devarajulu Sureshkumar *[a]

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata Mohanpur-741246, West Bengal, India.

[a]*Department of Chemical Sciences*

Indian Institute of Science Education and Research Kolkata

Mohanpur 741246, West Bengal, India.

E-mail: suresh@iiserkol.ac.in

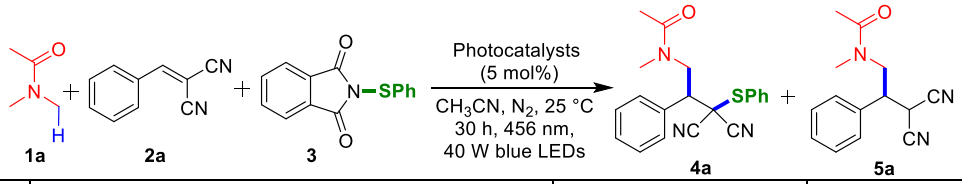
Group webpage: https://www.iiserkol.ac.in/~suresh/

1. General Information:

All solvents were dried, and commercial reagents were purified following the guidelines of L. L Chai and Armarego Purification of Laboratory Chemicals. Acr-mes$^+$ClO$_4^-$ was purchased from Tokyo Chemical Industries Chemicals (TCI); Eosin-Y and all-metal and other photocatalysts were either prepared as per literature procedures or purchased (Sigma-Aldrich) and used without purification unless otherwise specified. Other reagents were obtained from commercial suppliers (Alfa Aesar and Spectrochem). All reactions were conducted in dried glassware with magnetic stirring under a nitrogen atmosphere unless otherwise stated. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 and visualized under ultraviolet light or in iodine stain. Flash column chromatography was performed using silica gel (230−400 μm, Merck) using the eluent system described for each experiment. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Kessil blue LEDs, 456 nm (40 W), were used as a visible-light source. Details of the photoreaction setup are described. All NMR spectra were recorded on 400 MHz Jeol or 500 MHz Bruker spectrometers. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectral data are reported as chemical shifts (δ) in parts per million (ppm), and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, br = broad, m = multiplet. NMR spectra were processed in MestReNova, keeping the $CDCl_3$ residual peak at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. High-resolution mass spectra (HRMS, m/z) were recorded on a Micro-TOF spectrometer (Bruker). All fluorescence spectra and UV−vis spectra were recorded in a HORIBA FluoroMax Plus spectrofluorometer and a Hitachi UV−vis spectrophotometer, respectively. X-ray diffraction data for the crystal was collected at 100 K on a SuperNova, Eos diffractometer using monochromatic Cu Kα radiation (λ = 1.54184 Å). Diastereomeric ratio and rotameric ratio are abbreviated as dr and rr respectively.

2. Optimization of reaction conditions:

Table S1. Optimization of photocatalysts[a]:



Entry	Photocatalysts	Yield 4a (%)[b]	Yield 5a (%)[b]
1	Acr-Mes$^+$ClO$_4^-$	43	56
2	Ph-Acr-Mes$^+$ BF$_4^-$	86	13
3	Eosin-Y	17	24
4	T(*p*-CH$_3$)PPT	53	43
5	T(*p*-Cl)PPT	17	44
6	T(*p*-F)PPT	52	36
7	T(*p*-OMe)PPT	12	83
8	(Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$	0	11

.

[a]Reaction conditions: **1a** (1.0 mmol, 5 equiv.), **2a** (0.2 mmol, 1 equiv.), **3** (0.3 mmol, 1.5 equiv.), photocatalyst (5 mol%), CH$_3$CN (2.0 mL), irradiation with 40 W 456 nm blue LED under N$_2$, 25 °C, 30 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard.

Table S2. Optimization of solvent[a]:

Entry	Solvent	Yield 4a(%)[b]	Yield 5a(%)[b]
1	DCM	78	17
2	CH_3CN	86	13
3	DCE	68	31
4	$CHCl_3$	79	16
5	EtOAc	56	38
6	Acetone	51	33

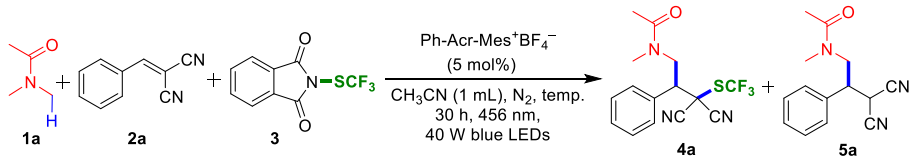
[a]Reaction conditions: **1a** (1.0 mmol, 5 equiv.), **2a** (0.2 mmol, 1 equiv.), **3** (0.3 mmol, 1.5 equiv.), Ph-Acr-Mes⁺BF₄⁻ (**PC-II,** 5 mol%), Solvent (1.0 mL), irradiation with 40 W 456 nm blue LED under N_2, 25 °C, 30 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard.

Table S3. Optimization of solvent amount[a]:

Entry	CH_3CN (x mL)	Yield 4a (%)[b]	Yield 5a (%)[b]
1	0.5	75	6
2	1	86	13
3	2	72	25

[a]Reaction conditions: **1a** (1.0 mmol, 5 equiv.), **2a** (0.2 mmol, 1 equiv.), **3** (0.3 mmol, 1.5 equiv.), Ph-Acr-Mes⁺BF₄⁻ (**PC-II**, 5 mol%), CH_3CN (x mL), irradiation with 40 W 456 nm blue LED under N_2, 25 °C, 30 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard.

Table S4. Optimization of temperature[a]:



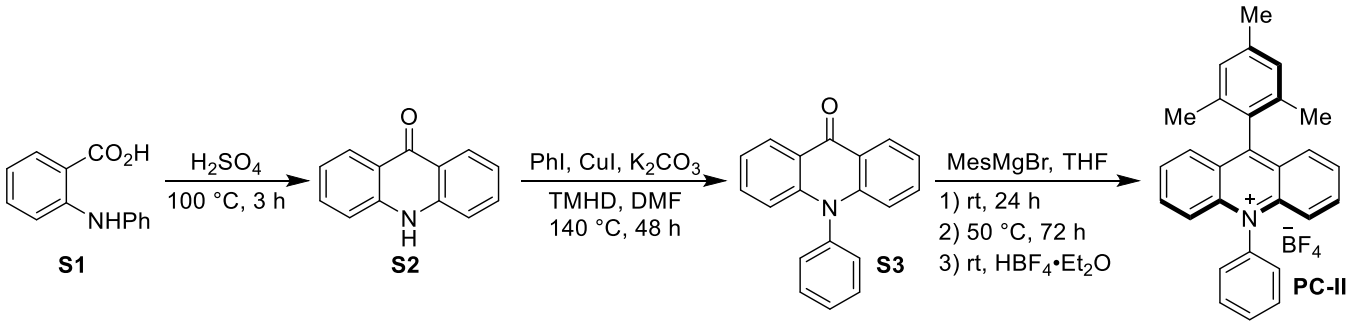
Entry	Temperature	Yield 4a (%)[b]	Yield 5a (%)[b]
1	25 °C	86	6
2	40 °C	92	3
3	50 °C	93	0
4[c]	40 °C	97	0

[a]Reaction conditions: **1a** (1.0 mmol, 5 equiv.), **2a** (0.2 mmol, 1 equiv.), **3** (0.3 mmol, 1.5 equiv.), Ph-Acr-Mes⁺BF₄⁻ (**PC-II**, 5 mol%), CH_3CN (1 mL), irradiation with 40 W 456 nm blue LED under N_2, temp., 30 h, [b]^{1}H NMR Yield using tetrachloroethane as internal standard, [c]2.5 equiv. (0.5 mmol) of **3**.

3. Synthesis of photocatalyst:

The photocatalyst Acr-Mes⁺ClO_4^- (**PC-I**) was purchased from the TCI, Eosin-Y (**PC-III**), and (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (**PC-VIII**) were purchased from Sigma Aldrich, and were used without any further purification. Other Acridinium photocatalysts **PC-II** and Pyrylium salt (**PC-IV** to **VII**) based organo-photocatalysts were synthesized from commercially available chemicals using the reported synthetic procedure with slight modification. The elaborate synthetic procedure for photocatalyst **PC-II** is discussed below.

3.1. Preparation of *9-mesityl-10-phenylacridin-10-ium tetrafluoroborate* (Ph-Acr-Mes⁺BF_4^-), PC-II:



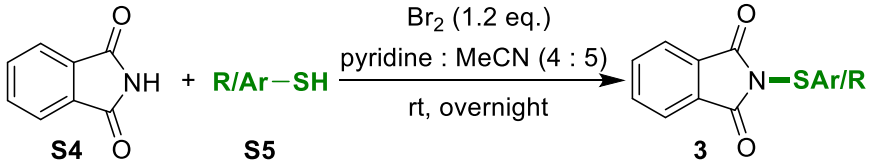
According to the reported procedure, in a flame-dried 250 mL, round bottom flask with a magnetic stirring bar, N-phenyl anthranilic acid (**S1**, 15 g, 70.4 mmol, 1 equiv.) was dissolved in 60 mL concentrated sulphuric acid, and the reaction mixture was heated at 100 °C with continuous stirring. After 3 hours, the reaction became a hot dark green colored mixture that was cooled to room temperature and poured on crushed ice, and yellow-colored precipitation was observed immediately. Then the excess added acid was neutralized by ammonium hydroxide solution. The resulted yellow precipitated was isolated through filtration on a filter paper using a Büchner funnel setup. The residue was thoroughly washed with distilled water and dried in air for 24 hours. The yellow solid was further purified by

recrystallization from acetic acid, and 10.5 grams of acridin-9(10H)-one (**S2**) was collected with 76% yield after drying under vacuum.

N-Phenylation of acridin-9(10H)-one (**S2**) was obtained with a slightly modified version of the previously reported process. According to our modified procedure, acridin-9(10H)-one (**S2**, 4 g, 20.5 mmol, 1.0 equiv.), CuI (780 mg, 4.1 mmol, 0.2 equiv.) and K_2CO_3 (5.6 g, 41.0 mmol, 2.0 equiv.) were added in a 500 mL sealed tube under nitrogen atmosphere inside a glovebox. Then 100 mL of freshly dried DMF was added. Iodobenzene (2.8 mL, 24.6 mmol, 1.2 equiv.) and 2,2,6,6-tetramethylheptane-3,5-dione (TMHD) (1.7 mL, 8.2 mmol, 0.4 equiv.) were added. After closing the cap, the sealed tube was removed from the glove box, and the reaction mixture was heated at 140 °C using an oil bath under continuous stirring. After 48 h, the reaction mixture was cooled to room temperature and quenched with 3M HCl (aq.) until the bobbles of carbon dioxide were stopped. Then the aqueous solution was extracted with DCM (3×100 mL), and the combined organic layer was washed with sat. sodium bicarbonate (150 mL) followed by (150 mL) sat. ammonium chloride and brine, and collected through anhydrous sodium sulphate. After evaporation of the solvent, the crude was purified by column chromatography (5 : 1 hexane : ethyl acetate) and 4.7 g of 10-phenylacridin-9(10H)-one (**S3**) was obtained with 85% of yield.

To an oven-dried 500 mL, double neck round bottom flask equipped with a magnetic stir bar, 10-phenylacridin-9(10H)-one (**S3**, 3.0 g, 11.1 mmol, 1.0 equiv.) was dissolved in 250 mL dry THF under argon atmosphere. Then freshly prepared Mesityl magnesium bromide (7.4 g, 33.3 mmol, 3.0 equiv.) was added dropwise, and the mixture was stirred at room temperature for 24 h, and then the solution was heated at 50 °C with an oil bath. After 72 h, the red-colored solution was cooled to room temperature and quenched with saturated sodium bicarbonate solution (200 mL). The aqueous layer was extracted with DCM (3×150 mL), the combined organic layer was washed with brine and collected through anhydrous sodium sulphate and concentrated using a rotary evaporator, followed by drying the crude for 4 h under a high vacuum. Diethyl ether 75 mL was added to the red crude oil, and the solution was stirred for 30 minutes. The purple-colored solution was decanted to another round bottom flask, equipped with a magnetic stir bar, and tetrafluoroboric acid diethyl ether complex (0.5 mL diluted in 25 mL diethyl ether) was added dropwise with continuous stirring until the yellow-colored precipitation stopped. Again, the purple-colored diethyl ether solution was extracted and repeated the procedure two times. Then the combined yellow precipitate was collected by filtration. The residue was thoroughly washed with ether and dried under vacuum for 6 h, which afford 3.6 g of 9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (**PC-II**) with 70% yield.

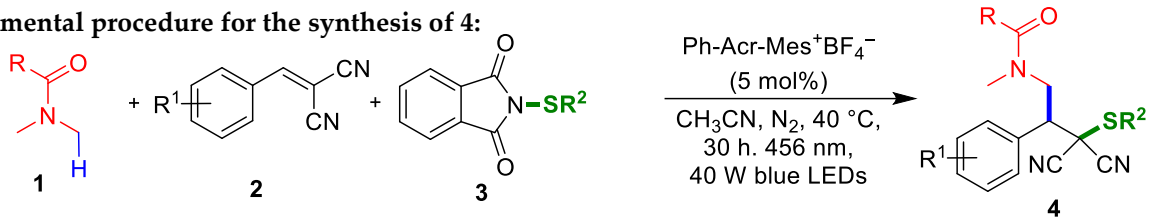
4. Synthesis of S-aryl/alkyl sources (3):



In a 100 mL round bottom flax equipped with a magnetic stir bar, phthalimide (**S4**, 20 mmol, 1.0 equiv.) and thiol derivatives (**S5**, 21 mmol, 1.05 equiv.) were dissolved in 18 mL pyridine/acetonitrile (4 : 5) upon heating in an oil bath. The resulting solution was cooled at room temperature, and a solution of bromine (24 mmol, 1.2 equiv.) in 10 mL

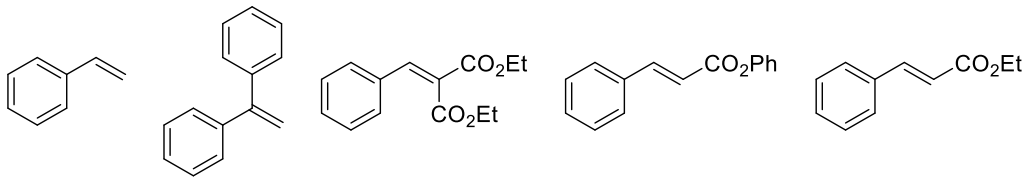
acetonitrile was added dropwise for half an hour. After addition, the resultant mixture was stirred for 30 minutes with continuous stirring. White-colored precipitation was observed after cooling the reaction mixture for 30 minutes at 0 °C. Then the product was filtered and purified by column chromatography using hexane/DCM as eluent to afford the products **3**.

5.1. Experimental procedure for the synthesis of 4:



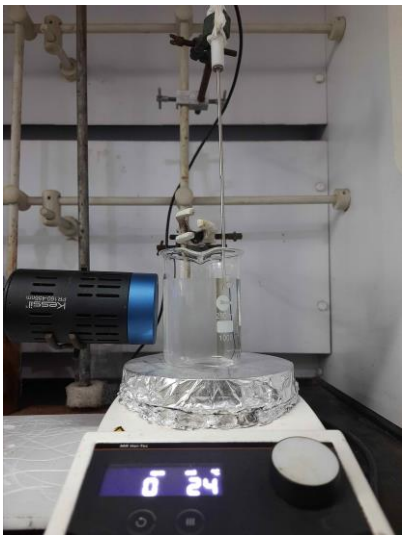
To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar **2** (0.2 mmol, 1 equiv.), Ph-Acr-Mes^{+}BF$_4^{-}$ (**PC-II**, 0.01 mmol, 0.05 equiv.), **3** (0.5 mmol, 2.5 equiv.) and **1** (1.0 mmol, 1.0 equiv.) were added. Then the reaction tube was applied to a vacuum for 5 minutes and backfilled with nitrogen. This cycle was repeated another four times, and a rubber septum was put on the top of the reaction tube tightly, with continuous nitrogen flow. A photo-reaction setup was previously prepared, a water-filled clean 250 mL glass beaker was placed on a heating stirrer, and 40 °C was maintained, and a Kessil 40 W, 456 nm blue LED lamp was fitted at a 1 cm distance from the glass wall of the beaker. After adding 1 mL of freshly dried acetonitrile solvent, the reaction tube was dipped into the water-filled beaker so that the distance of the reaction tube from the light source should be maintained at 3 cm overall. After 30 h of irradiation with blue LED, the reaction tube was removed from the setup, and the reaction mixture was diluted with 5 mL DCM followed by 10 mL brine solution and extracted with DCM (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using ethyl acetate and hexane as eluent to afford products **4**. In the case of liquid **1**, it was added to the reaction mixture after adding the solvent. To obtain the products **4i**, **4j**, **4n,** and **4o**, 20 mol% of 2,6-lutidine was added after the solvent.

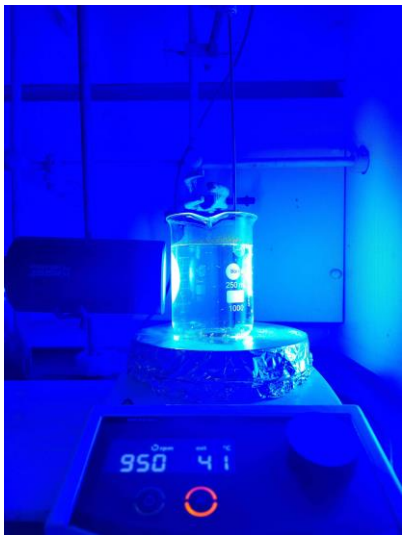
5.2. List of failed activated alkenes:

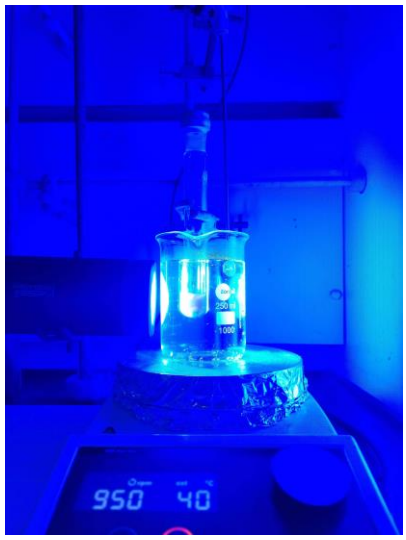


6. Reaction setup:

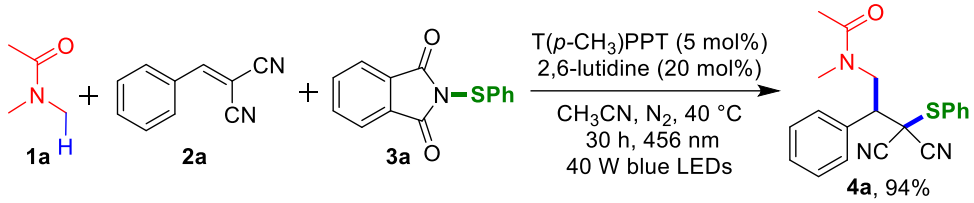
A photo-reaction setup was previously prepared, a water-filled crystal clean 250 mL glass beaker was placed on a heating stirrer, and 40 °C was maintained using a temperature sensor connected to the heating stirrer. A Kessil 40 W, 456 nm blue LED lamp was fitted at a 1 cm distance from the glass wall of the beaker. And the reaction tube was placed so that the distance of the reaction tube from the light source should be maintained at 3 cm overall.





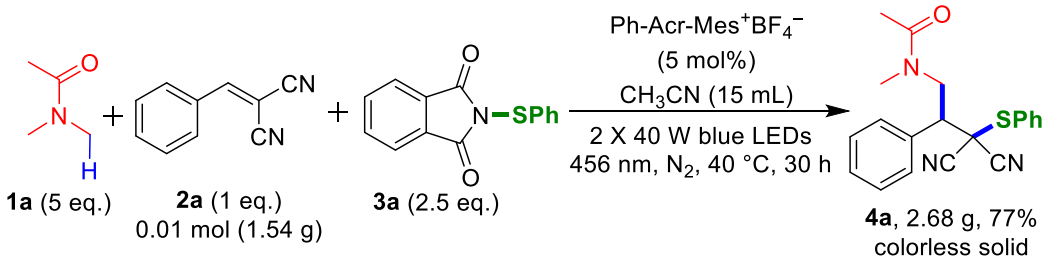


7. Pyrylium salt photocatalyzed synthesis of 4a:



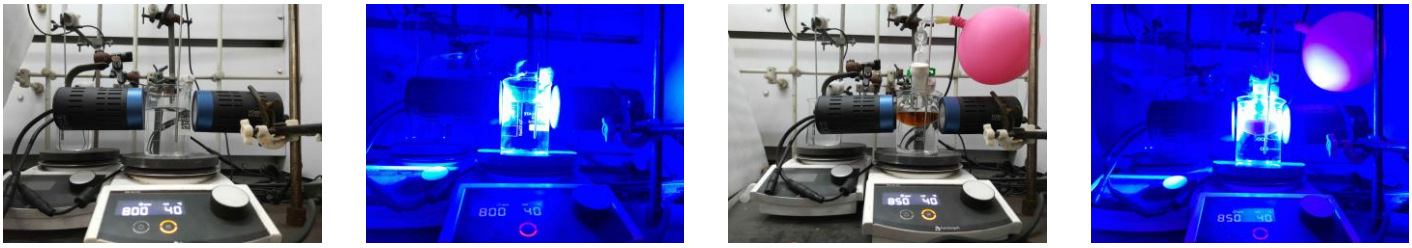
To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar **2** (0.2 mmol, 1 equiv.), T(*p*-CH_3)PPT (**PC-IV**, 0.01 mmol, 0.05 equiv.), **3** (0.5 mmol, 2.5 equiv.) and **1** (1.0 mmol, 1.0 equiv.) were added. Then the reaction tube was applied to vacuum for 5 minutes and backfilled with nitrogen. The cycle was repeated another four times, and a rubber septum was put on the top of the reaction tube tightly, with continuous nitrogen flow. A photo-reaction setup was previously prepared, a water-filled clean 250 mL glass beaker was placed on a heating stirrer, and 40 °C was maintained, and a Kessil 40 W, 456 nm blue LED lamp was fitted at a 1 cm distance from the glass wall of the beaker. After adding 1 mL of freshly dried acetonitrile solvent, the reaction tube was dipped into the water-filled beaker so that the distance of the reaction tube from the light source should be maintained at 3 cm overall. After 30 h of irradiation with blue LED, the reaction tube was removed from the setup, and the reaction mixture was diluted with 5 mL DCM, followed by a 10 mL brine solution, and extracted with DCM (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using ethyl acetate and hexane as eluent to afford products **4a**. The desired product **4a** has been isolated with 94% yield.

8.1. Gram-scale synthesis of 4a:



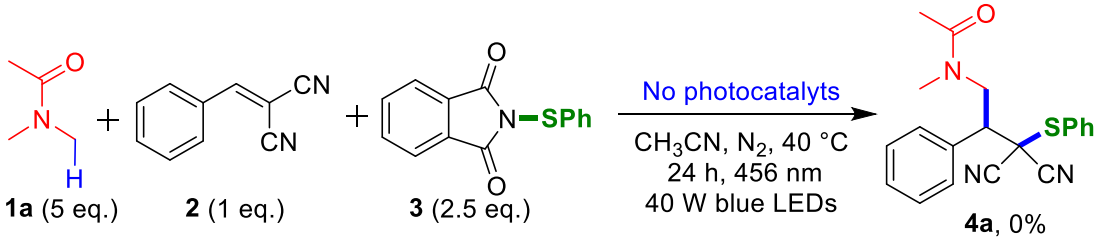
To an oven-dried 50 mL two-neck round bottom flask equipped with a magnetic stir bar, **2a** (1.54 g, 10 mmol, 1 equiv.), **3a** (6.37 g, 25 mmol, 2.5 equiv.), and Ph-Acr-Mes^{+}BF$_4^{-}$ (**PC-II**, 230 mg, 0.5 mmol, 0.05 equiv.) were added. After fitting a septum on one neck and an adapter with a stopcock on the other, the reaction flask was kept under a vacuum for 10 minutes and backfilled with nitrogen, which was repeated four times. A balloon filled with nitrogen was connected to the adapter. Then 15 mL of freshly dried acetonitrile was added and followed by **1a** (4.35 g, 50 mmol, 5 equiv.) using a syringe. Then the RB flask was placed in our photo-reaction setup using two Kessil, 40 W-456 nm blue LED lights at 40 °C, so the distance of the reaction tube from the light source should be maintained at 3 cm overall from both lights. After 30 h of irradiation, the reaction mixture was diluted with 25 mL of DCM, and 30 mL of brine solution was added, added, and extracted with DCM (3 × 50 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using ethyl acetate and hexane as eluent to afford 2.68 g of product **4a** in 77% yield.

8.2. Reaction setup for the gram-scale synthesis:



9. Control experiments:

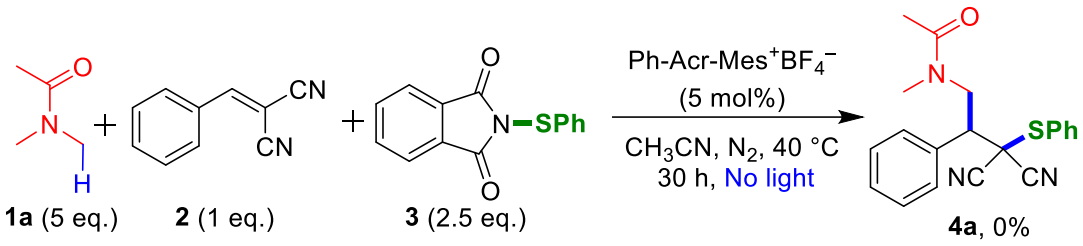
9.1. Reaction without photocatalyst:



An oven-dried 20 mL reaction tube equipped with a magnetic stir bar **2a** (0.2 mmol, 1 equiv.) and **3** (0.5 mmol, 2.5 equiv.) were added. Then the reaction tube was applied to vacuum for 5 minutes and then backfilled with nitrogen; this cycle was repeated another four times, and a rubber septum was placed on the top of the reaction tube tightly, with continuous nitrogen flow. After addition of 1 mL freshly dried acetonitrile solvent **1a** (1.0 mmol, 1.0 equiv.) was added to the reaction and subject to the irradiation of Kessil 40 W, 456 nm blue LED at 40 °C. After 24 h of irradiation of the reaction, the mixture was diluted with 5 mL DCM followed by adding 10 mL brine solution and extracted with DCM (3

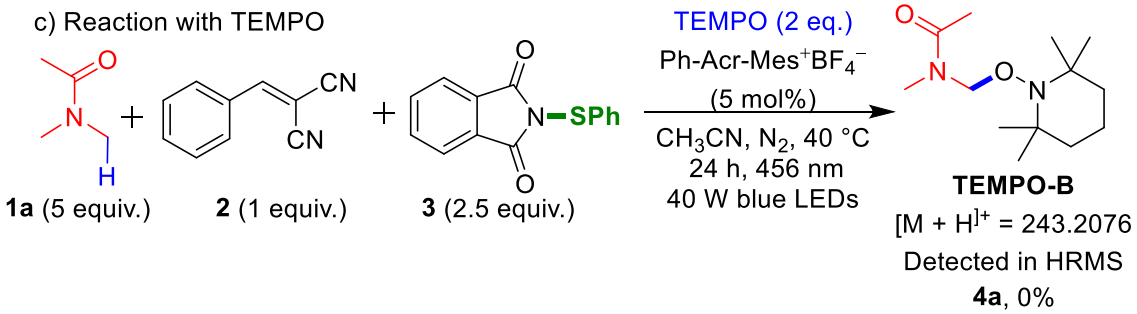
× 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. ^1H NMR shows no desired product formation, suggesting the photocatalysts' necessity for transformation.

9.2. Reaction without light:



To an oven-dried 20 mL reaction tube was equipped with a magnetic stir bar **2a** (0.2 mmol, 1 equiv.), Ph-Acr-Mes$^+$BF$_4^-$ (**PC-II**, 0.01 mmol, 0.05 equiv.) and **3** (0.5 mmol, 2.5 equiv.) were added. Then the reaction tube was applied to a vacuum for 5 minutes and backfilled with nitrogen. This cycle was repeated another four times, and a rubber septum was put on the top of the reaction tube tightly, with continuous nitrogen flow. After addition of 1 mL freshly dried acetonitrile solvent **1a** (1.0 mmol, 1.0 equiv.) was added to the reaction and subject to the irradiation of Kessil 40 W, 456 nm blue LED at 40 °C. After 24 h of irradiation of the reaction, the mixture was diluted with 5 mL DCM followed by adding 10 mL brine solution and extracted with DCM (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. ^1H NMR shows no desired product formation, suggesting the light's necessity for the transformation.

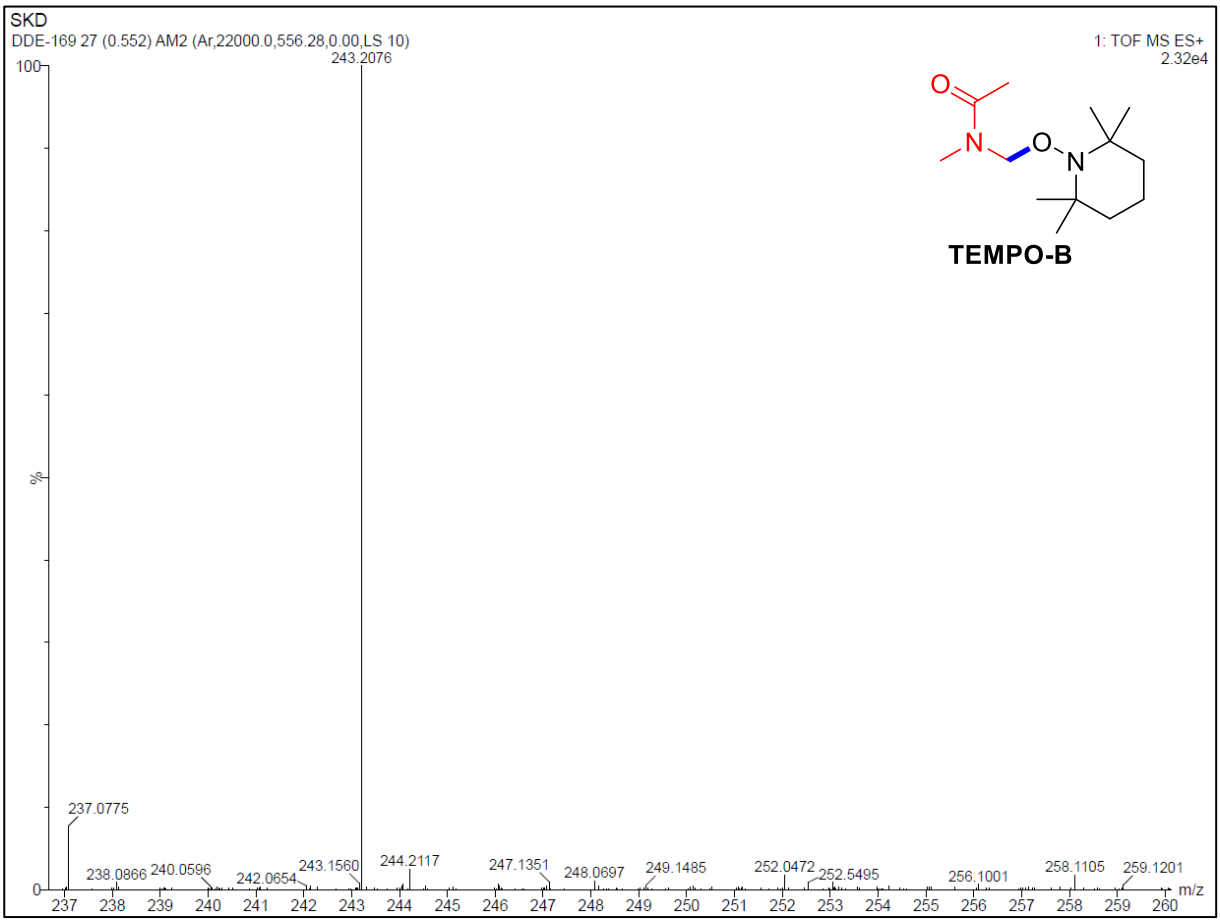
9.3.1. Reaction with TEMPO:



To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar **2a** (0.2 mmol, 1 equiv.), Ph-Acr-Mes$^+$BF$_4^-$ (**PC-II**, 0.01 mmol, 0.05 equiv.), TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv.), and **3** (0.5 mmol, 2.5 equiv.) were added. Then the reaction tube was applied to a vacuum for 5 minutes and backfilled with nitrogen; this cycle was repeated another four times. A rubber septum was tightly fitted on the reaction tube's top, with continuous nitrogen flow. After addition of 1 mL freshly dried acetonitrile solvent **1a** (1.0 mmol, 1.0 equiv.) was added to the reaction and subject to the irradiation of Kessil 40 W, 456 nm blue LED at 40 °C. After 24 h of irradiation of the reaction, the mixture was diluted with 5 mL DCM followed by adding 10 mL brine solution and extracted with DCM (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. ^1H NMR shows no desired product formation suggesting that the reaction proceeds through the radical mechanism.

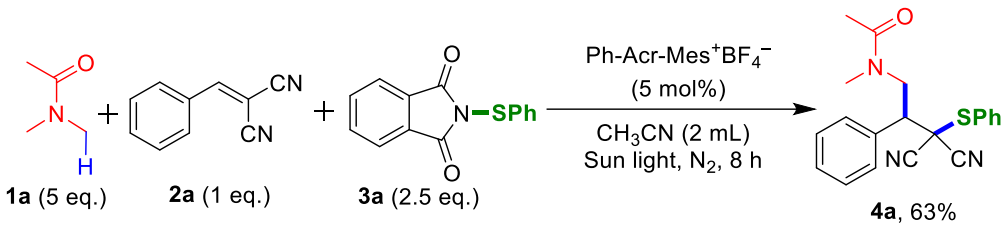
9.3.2. ESI-HRMS analysis to detect the TEMPO adduct with radical intermediate B:

The crude reaction mixture was also analysed by ESI-HRMS, and an adduct formation between TEMPO and the radical intermediate **B** has been confirmed. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{27}N_2O_2$ 243.2073, found 243.2076.



ESI-HRMS spectrum of the TEMPO adduct with radical intermediate **B**

10.1. Reaction with sunlight:



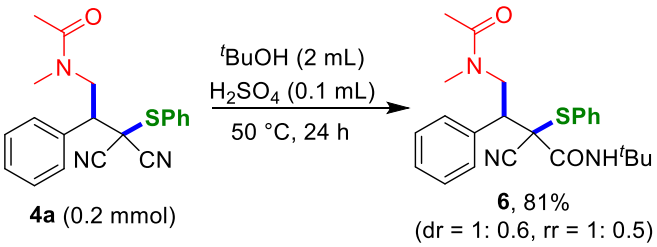
To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar **2a** (0.2 mmol, 1 equiv.), Ph-Acr-Mes⁺BF₄⁻ (**PC-II**, 0.01 mmol, 0.05 equiv.), **3a** (0.5 mmol, 2.5 equiv.) and **1a** (1.0 mmol, 1.0 equiv.) were added. Then the reaction tube was applied to a vacuum for 5 minutes and backfilled with nitrogen. This cycle was repeated another four times, and a rubber septum was put on the top of the reaction tube tightly, with continuous nitrogen flow. Then 2 mL of freshly dried acetonitrile solvent was added through the septum using a syringe, and the reaction tube was placed in the sunlight. After 8 h of irradiation under sunlight, the reaction mixture was diluted with 5 mL DCM followed by 10 mL brine solution and extracted with DCM (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. Then the product yield was measured by ^1H NMR, using tetrachloroethane as the internal standard.

10.2. Reaction set-up for sunlight synthesis:

Coordinates of the places: 27.2046° N, 77.4977° E, Time: 9 am to 5 pm.

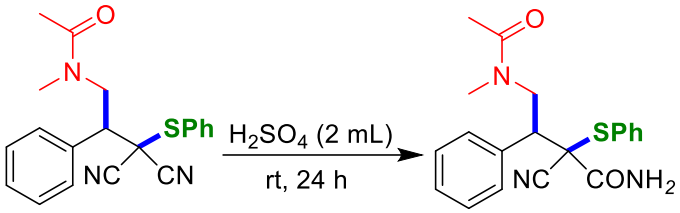
11. Functionalization of product 4a:

11.1. Synthesis of compound 6:



To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar were added 0.2 mmol **4a** (1 equiv.), 0.1 mL of concentrated H_2SO_4, and 2 mL of ^{t}BuOH. After sealing with a septum, the reaction tube was heated at 50 ° C for 24 h. Then, the reaction mixture was neutralized with saturated $NaHCO_3$ solution (added dropwise) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified *via* flash column chromatography on silica gel mesh 230–400 using ethyl acetate and hexane as the eluent to afford 68.5 mg of product **6** in 81% combined yield of both diastereomers.

11.2. Synthesis of compound 7:



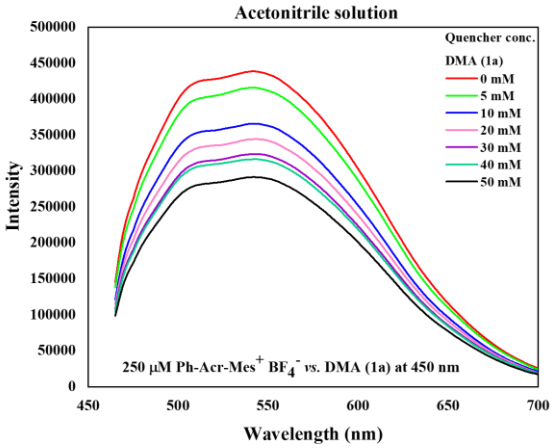
4a (0.2 mmol) **7**, 66% (dr = 1: 0.6)

To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar were added 0.2 mmol **4a** (1 equiv.) and 2 mL of concentrated H_2SO_4. After sealing with a septum, the reaction tube was stirred at room temperature for 24 h. Then, the reaction mixture was neutralized with saturated $NaHCO_3$ solution (added dropwise) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified *via* flash column chromatography on silica gel mesh 230–400 using ethyl acetate and hexane as the eluent to afford 48.4 mg of product **7** in 66% yield.

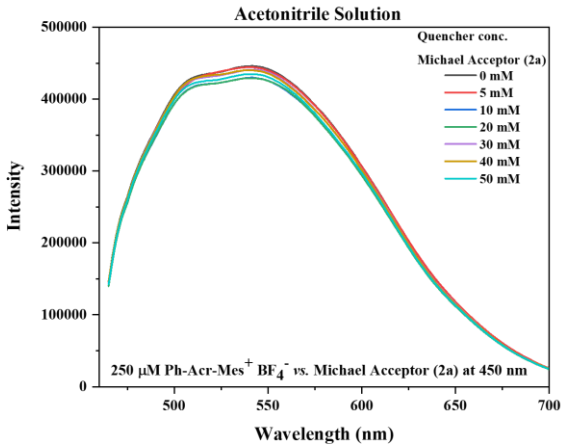
12. Fluorescence quenching studies of Ph-Acr-Mes⁺BF₄⁻ (PC-II) with substrates 1a, 2a, and 3a:

To perform luminescence quenching studies, 10 mM of commercially available Ph-Acr-Mes⁺BF₄⁻ **(PC-II)**, 1 M of **1a** (DMA), 1 M of Michael acceptor **2a,** and 1 M of **3a** (SPh Source) solution in spectroscopic grade acetonitrile were prepared as a stock solution. All other solutions with different concentrations were prepared by dilution.

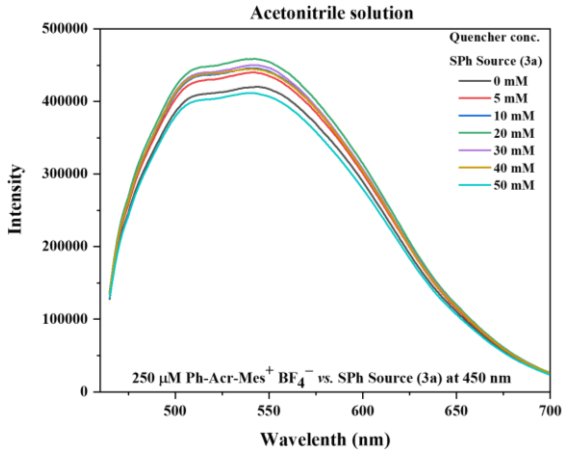
a)



b)



c)



d)

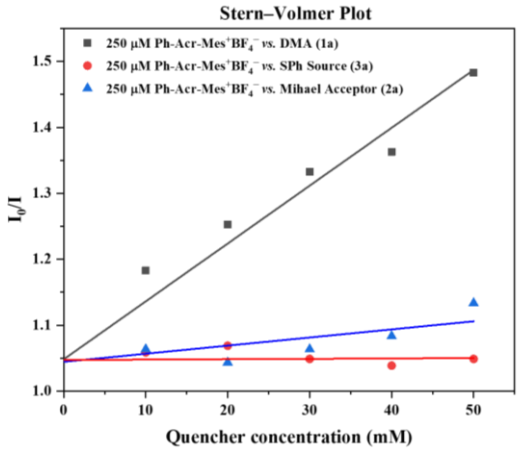
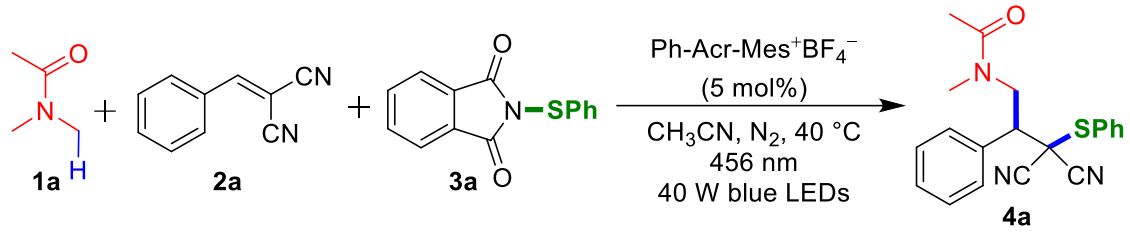


Figure S1. Luminescence quenching spectra of Ph-Acr-Mes⁺BF₄⁻ **(PC-II)** at λ_{ex} 450 nm.

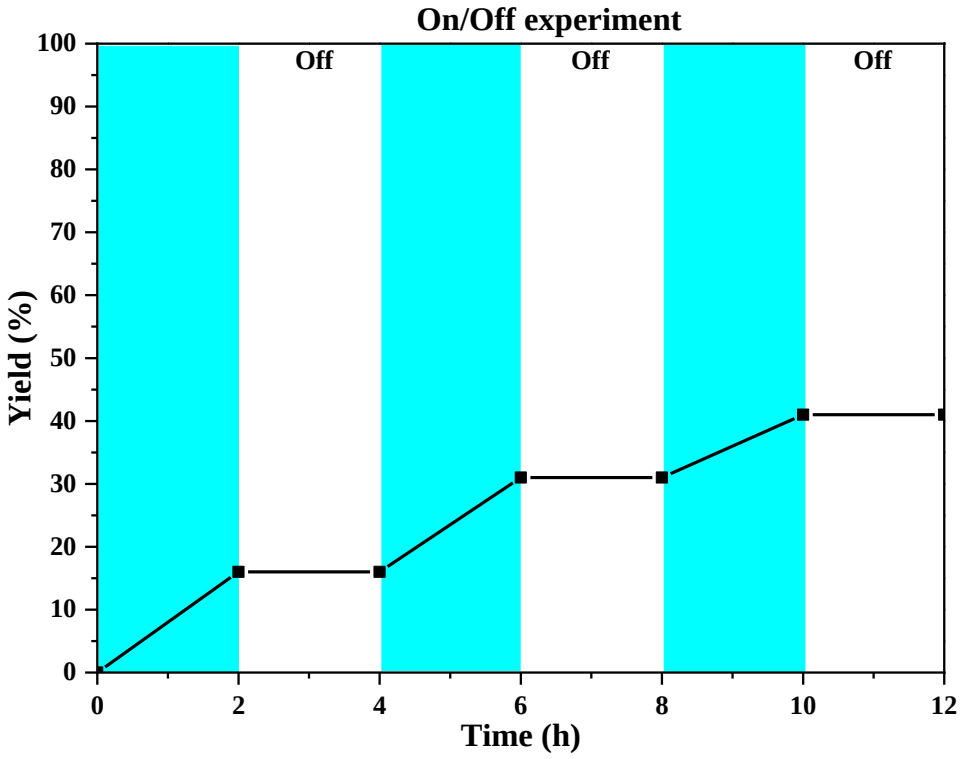
In acetonitrile solution: a) 250 µM Ph-Acr-mes⁺BF₄⁻ **(PC-II)**, *vs* **1a** at 450 nm; b) 250 µM Ph-Acr-Mes⁺BF₄⁻ **(PC-II)** *vs* **2a** at 450 nm; c) 250 µM Ph-Acr-Mes⁺BF₄⁻ **(PC-II)** *vs*. **3a** at 450 nm; d) Stern-Volmer plot of Fluorescence quenching of 250 µM Ph-Acr-Mes⁺BF₄⁻ **(PC-II)** *vs*. **1a**, **2a** and **3a**.

As expected in the acridinium photocatalyst **(PC-II)**, no quenching was observed concerning Michael acceptor (**2a**) and SPh source (**3a**), shown in Figures S1b and S1c, respectively. However, quenching of the acridinium photocatalyst **PC-II** was observed concerning DMA, as shown in Figure S1a and Stern-Volmer plot Figure S1d. Therefore, we can conclude that the reaction follows a single electron transfer (SET) pathway mechanism in the case of the acridinium photocatalyst **(PC-II)**.

13. Light on/off experiments

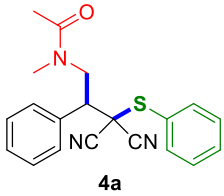


To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar **2a** (0.2 mmol, 1 equiv.), Ph-Acr-Mes⁺BF₄⁻ (**PC-II**, 0.01 mmol, 0.05 equiv.), **3a** (0.5 mmol, 2.5 equiv.) and **1a** (1.0 mmol, 1.0 equiv.) were added. Then the reaction tube was applied to a vacuum for 5 minutes and backfilled with nitrogen. This cycle was repeated another four times, and a rubber septum was put on the top of the reaction tube tightly, with continuous nitrogen flow. A photo-reaction setup was previously prepared, a water-filled clean 250 mL glass beaker was placed on a heating stirrer, and 40 °C was maintained, and a Kessil 40 W, 456 nm blue LED lamp was fitted at a 1 cm distance from the glass wall of the beaker. After adding 1 mL of freshly dried acetonitrile solvent, and 2 equiv. of internal standard, the reaction tube was dipped into the water-filled beaker so that the distance of the reaction tube from the light source should be maintained at 3 cm overall. The light on/off experiment was performed by altering light-dark conditions (light : dark; 2 : 2 h) for up to 12 h. At the end of each light/dark session, the reaction progress was monitored by measuring the yield based on ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The results in figure show the essential role of light, as the reaction progressed in the presence of light and stopped in the dark. From the experiment, we conclude that continuous light supply needed for reaction and conforms that reaction does not proceed through a chain propagation mechanism.



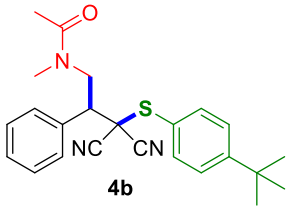
14. Characterisation data for 4:

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylacetamide (4a)*:** (rr = 1: 0.15); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 97% (67.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.1 Hz, 2.3H), 7.64 – 7.35 (m, 9.2H), 4.37 (dd, *J* = 13.6, 5.9 Hz, 1H), 4.19 (dd, *J* = 14.7, 3.5 Hz, 0.15H), 4.04 (dd, *J* = 14.6, 10.2 Hz, 0.15H), 3.96 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.79 (dd, *J* = 13.6, 9.0 Hz, 1H), 3.50 (dd, *J* = 10.2, 3.5 Hz, 0.15H), 2.79 (s, *J* = 14.8 Hz, 3H), 2.76 (s, 0.45H), 2.00 (s, 3H), 1.96 (s, 0.45H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.7, 137.4, 134.7, 134.5, 132.5, 132.2, 130.2, 130.0, 129.7, 129.3, 129.1, 127.2, 126.6, 113.3, 113.1, 112.8, 53.4, 51.4, 49.0, 45.0, 44.8, 38.4, 34.3, 22.0, 21.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{20}H_{19}N_3OSNa$ 372.1147, found 372.1151.



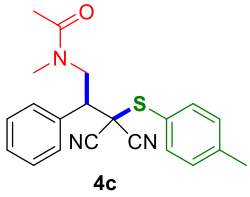
4a

***N-(3-((4-(tert-butyl)phenyl)thio)-3,3-dicyano-2-phenylpropyl)-N-methylacetamide (4b)*:** (rr = 1: 0.15); R_f = 0.2 (ethyl acetate/n-hexane, 2: 8); colorless solid; Yield 97% (78.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2.3H), 7.53 – 7.37 (m, 8.05H), 4.38 (dd, *J* = 13.5, 5.9 Hz, 1H), 4.20 (dd, *J* = 14.6, 3.5 Hz, 0.15H), 4.04 (dd, *J* = 14.6, 10.2 Hz, 0.15H), 3.95 (dd, *J* = 8.9, 5.9 Hz, 1H), 3.79 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.49 (dd, *J* = 10.3, 3.5 Hz, 0.15H), 2.79 (d, *J* = 0.9 Hz, 3H), 2.76 (s, 0.45H), 2.00 (d, *J* = 0.8 Hz, 3H), 1.95 (s, 0.45H), 1.32 (d, *J* = 5.5 Hz, 10.35H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 170.6, 156.2, 155.72, 137.3, 134.5, 133.8, 130.1, 129.6, 129.6, 129.2, 129.1, 127.3, 127.0, 123.7, 123.0, 113.3, 113.3, 113.2, 112.8, 53.4, 51.3, 51.2, 48.9, 44.96, 44.8, 38.3, 35.1, 35.1, 34.2, 31.2, 22.0, 21.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{24}H_{28}N_3OS$ 406.1953, found 406.1941.



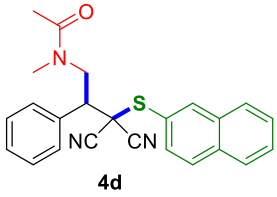
4b

***N-(3,3-dicyano-2-phenyl-3-(p-tolylthio)propyl)-N-methylacetamide (4c)*:** (rr = 1: 0.2); R_f = 0.2 (ethyl acetate/n-hexane, 2: 8); colorless solid; Yield 94% (68.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 2.4H), 7.51 – 7.38 (m, 6H), 7.32 – 7.23 (m, 2.4H), 4.36 (dd, J = 13.5, 5.9 Hz, 1H), 4.19 (dd, J = 14.6, 3.5 Hz, 0.2H), 4.03 (dd, J = 14.6, 10.3 Hz, 0.2H), 3.94 (dd, J = 9.0, 5.9 Hz, 1H), 3.79 (dd, J = 13.5, 9.1 Hz, 1H), 3.48 (dd, J = 10.2, 3.5 Hz, 0.2H), 2.78 (s, 3H), 2.75 (s, 0.6H), 2.41 (s, 0.6H), 2.39 (s, 3H), 1.99 (s, 3H), 1.95 (s, 0.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 142.9, 137.5, 137.3, 134.5, 131.0, 130.7, 1296, 129.2, 129.1, 123.7, 113.3, 113.2, 53.4, 51.3, 48.9, 45.1, 44.9, 38.4, 34.3, 22.0, 21.6, 21.6, 21.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{21}H_{21}N_3OSNa$ 386.1303, found 386.1293.



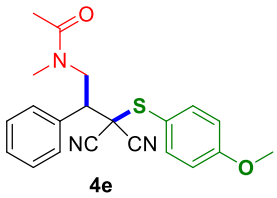
4c

***N-(3,3-dicyano-3-(naphthalen-2-ylthio)-2-phenylpropyl)-N-methylacetamide (4d)*:** (rr = 1: 0.2); R_f = 0.3 (ethyl acetate/n-hexane, 2: 8); colorless solid; Yield 82% (65.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.49 (m, 1.2H), 8.17 – 8.00 (m, 2.4H), 7.95 – 7.84 (m, 1.2H), 7.71 – 7.38 (m, 9.6H), 4.42 (dd, *J* = 13.6, 6.0 Hz, 1H), 4.25 (dd, *J* = 14.6, 3.4 Hz, 0.2H), 4.15 – 4.03 (m, 1.2H), 3.86 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.60 (dd, *J* = 10.3, 3.3 Hz, 0.2H), 2.81 (s, 3H), 2.79 (s, 0.6H), 2.02 (s, 3H), 1.98 (s, 0.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 170.8, 138.7, 138.7, 135.5, 135.4, 134.6, 134.5, 134.4, 133.8, 133.7, 133.4, 130.3, 129.7, 129.3, 129.2, 129.0, 128.8, 128.1, 127.8, 127.3, 127.1, 126.0, 125.9, 125.8, 125.4, 124.6, 113.2, 113.2, 112.8, 53.6, 51.9, 51.5, 49.6, 44.41, 44.2, 38.5, 34.4, 22.0, 14.2; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{24}H_{21}N_3OSNa$ 422.1303, found 422.1308.



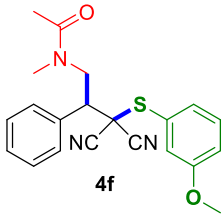
4d

N-(3,3-dicyano-3-((4-methoxyphenyl)thio)-2-phenylpropyl)-N-methylacetamide (4e): (rr = 1: 0.2); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless semisolid; Yield 40% (30.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2.4H), 7.52 – 7.33 (m, 6H), 7.01 – 6.89 (m, 2.4H), 4.36 (dd, *J* = 13.5, 5.9 Hz, 1H), 4.18 (dd, *J* = 14.6, 3.6 Hz, 0.2H), 4.01 (dd, *J* = 14.5, 10.0 Hz, 0.2H), 3.91 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.84 – 3.72 (m, 4.6H), 3.46 (dd, *J* = 10.2, 3.5 Hz, 0.2H), 2.76 (s, 3H), 2.74 (s, 0.6H), 1.98 (s, 3H), 1.94 (s, 0.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 127.8 (d, *J* = 313.5 Hz), 112.5, 111.9, 48.2, 47.1, 39.1, 38.2 (d, *J* = 1.9 Hz), 29.9, 29.8, 22.5, 22.0, 16.4; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{21}H_{21}N_3O_2SNa$ 402.1252, found 402.1253.



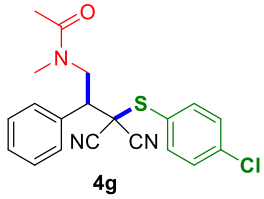
4e

***N-(3,3-dicyano-3-((3-methoxyphenyl)thio)-2-phenylpropyl)-N-methylacetamide (4f)*:** (rr = 1: 0.15); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless semisolid; Yield 74% (56.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.27 (m, 9.2H), 7.13 – 7.03 (m, 1.15H), 4.36 (dd, *J* = 13.5, 5.9 Hz, 1H), 4.19 (dd, *J* = 14.6, 3.5 Hz, 0.15H), 4.04 (dd, *J* = 14.6, 10.2 Hz, 0.15H), 3.95 (dd, *J* = 8.9, 5.9 Hz, 1H), 3.86 – 3.73 (m, 4.45H), 3.49 (dd, *J* = 10.2, 3.5 Hz, 0.15H), 2.79 (s, 3H), 2.75 (s, 0.45H), 2.00 (s, 3H), 1.95 (s, 0.45H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.7, 160.3, 160.2, 134.4, 133.6, 130.9, 130.6, 130.2, 129.7, 129.6, 129.3, 129.3, 129.1, 128.9, 128.0, 127.4, 121.7, 118.9, 118.8, 113.3, 113.2, 112.9, 55.6, 55.6, 53.4, 51.3, 49.1, 44.9, 44.7, 38.4, 34.3, 22.0, 21.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{21}H_{21}N_3O_2SNa$ 402.1252, found 402.1260.



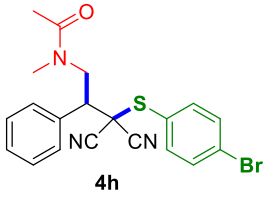
4f

***N-(3-((4-chlorophenyl)thio)-3,3-dicyano-2-phenylpropyl)-N-methylacetamide (4g)*:** (rr = 1: 0.15); R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 94% (72.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 2.3H), 7.53 – 7.37 (m, 8.05H), 4.38 (dd, *J* = 13.5, 5.9 Hz, 1H), 4.17 (dd, *J* = 14.6, 3.6 Hz, 0.15H), 4.04 (dd, *J* = 14.6, 10.1 Hz, 0.15H), 3.94 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.75 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.50 (dd, *J* = 10.1, 3.6 Hz, 0.15H), 2.78 (s, 3H), 2.75 (s, 0.45H), 2.01 (s, 3H), 1.96 (s, 0.45H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.6, 139.6, 139.2, 138.8, 138.6, 134.3, 133.4, 130.6, 130.3, 129.8, 129.7, 129.3, 129.1, 125.6, 124.9, 113.1, 112.9, 112.6, 53.4, 51.4, 51.3, 48.9, 45.0, 44.8, 38.5, 34.3, 22.0, 21.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{20}H_{18}ClN_3OSNa$ 406.0757, found 406.0763.



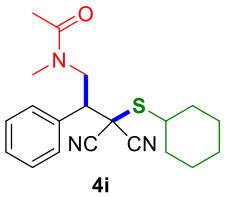
4g

***N-(3-((4-bromophenyl)thio)-3,3-dicyano-2-phenylpropyl)-N-methylacetamide (4h)*:** (rr = 1: 0.15); R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 89% (76.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4.6H), 7.50 – 7.36 (m, 5.75H), 4.36 (dd, *J* = 13.6, 5.9 Hz, 1H), 4.16 (dd, *J* = 14.6, 3.7 Hz, 0.15H), 4.02 (dd, *J* = 14.6, 10.2 Hz, 0.15H), 3.93 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.73 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.48 (dd, *J* = 10.1, 3.6 Hz, 0.15H), 2.77 (s, 3H), 2.74 (s, 0.45H), 1.99 (s, 3H), 1.94 (s, *J* = 8.8 Hz, 0.45H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.6, 138.90, 134.3, 133.4, 133.3, 130.3, 129.7, 129.7, 129.31, 129.0, 128.9, 128.1, 127.7, 126.2, 125.5, 113.1, 112.9, 112.6, 53.4, 51.4, 51.3, 48.9, 44.9, 44.7, 38.4, 34.3, 22.0, 21.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{19}BrN_3OS$ 428.0432, found 428.0437.



4h

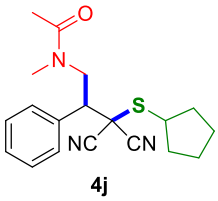
***N-(3,3-dicyano-3-(cyclohexylthio)-2-phenylpropyl)-N-methylacetamide (4i)*:** (rr = 1: 0.2); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 89% (67.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 6H), 4.26 (dd, *J* = 13.1, 5.2 Hz, 1H), 4.11 (dd, *J* = 14.6, 3.5 Hz, 0.2H), 3.96 (dd, *J* = 14.6, 10.3 Hz, 0.2H), 3.87 – 3.70 (m, 2H), 3.39 – 3.24 (m, 1.4H), 2.75 (s, 3H), 2.70 (s, 0.6H), 2.24 – 2.02 (m, 2.4H), 1.96 (s, 3H), 1.91 (s, 0.6H), 1.75 (dd, *J* = 19.6, 11.2 Hz, 2.4H), 1.66 – 1.31 (m, 6H), 1.30 – 1.11 (m, 1.2H); ^{13}C NMR (126 MHz,



4i

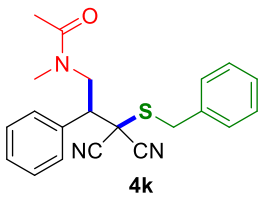
$CDCl_3$) δ 171.5, 170.6, 134.4, 133.8, 129.5, 129.2, 129.1, 128.9, 113.7, 113.5, 113.5, 113.3, 53.1, 52.1, 50.8, 49.73, 48.0, 47.4, 39.0, 38.2, 34.2, 33.5, 33.0, 25.8, 25.7, 25.3, 25.2, 21.9, 21.2; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{26}N_3OS$ 356.1797, found 356.1799.

N-(3,3-dicyano-3-(cyclopentylthio)-2-phenylpropyl)-N-methylacetamide (4j): (rr = 1: 0.2); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless semisolid; Yield 89% (67.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 6H), 4.26 (dd, *J* = 13.1, 5.3 Hz, 1H), 4.11 (dd, *J* = 14.6, 3.5 Hz, 0.2H), 3.96 (dd, *J* = 14.6, 10.2 Hz, 0.2H), 3.82 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.73 (dd, *J* = 13.1, 9.2 Hz, 1H), 3.66 – 3.50 (m, 1.2H), 3.36 (dd, *J* = 10.1, 3.5 Hz, 0.2H), 2.74 (s, 3H), 2.69 (s, 0.6H), 2.27 – 2.08 (m, 2.4H), 1.95 (s, 3H), 1.91 (s, 0.6H), 1.81 – 1.47 (m, 7.2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 170.6, 134.2, 134.1, 133.7, 130.0, 129.4, 129.1, 129.0, 128.8, 123.4, 113.7, 113.5, 113.4, 113.3, 53.0, 51.8, 50.8, 49.5, 46.6, 46.2, 39.8, 39.6, 38.1, 34.2, 33.6, 33.2, 33.2, 24.7, 24.6, 21.9; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{24}N_3OS$ 342.1640, found 342.1601.



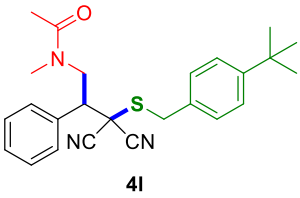
4j

***N-(3-(benzylthio)-3,3-dicyano-2-phenylpropyl)-N-methylacetamide (4k)*:** (rr = 1: 0.2); R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless semisolid; Yield 91% (66.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.27 (m, 12H), 4.33 – 4.23 (m, 1.4H), 4.21 (s, 2H), 4.11 (dd, *J* = 7.7, 5.3 Hz, 0.2H), 3.99 (dd, *J* = 14.7, 10.1 Hz, 0.2H); 3.89 (dd, *J* = 8.9, 5.9 Hz, 1H), 3.76 (dd, *J* = 13.5, 8.8 Hz, 1H), 3.38 (dd, *J* = 10.0, 3.6 Hz, 0.2H), 2.79 (s, 3H), 2.70 (s, 0.6H), 2.00 (s, 3H), 1.92 (s, 0.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.7, 134.4, 134.2, 133.5, 133.2, 130.2, 129.9, 129.8, 129.7, 129.7, 129.2, 129.1, 128.8, 128.5, 123.7, 113.0, 112.8, 53.2, 51.6, 51.1, 49.1, 40.5, 40.3, 38.4, 38.3, 37.9, 34.3, 22.0, 21.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{21}H_{21}N_3OSNa$ 386.1303, found 386.1286.



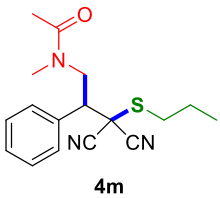
4k

***N-(3-((4-(tert-butyl)benzyl)thio)-3,3-dicyano-2-phenylpropyl)-N-methylacetamide (4l)*:** (rr = 1: 0.2); R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); yellow oil; Yield 76% (63.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 10.8H), 4.29 (dd, *J* = 13.4, 5.7 Hz, 1H), 4.24 – 4.15 (m, 2.4H), 4.12 (dd, *J* = 14.7, 3.6 Hz, 0.2H), 3.99 (dd, *J* = 14.6, 10.0 Hz, 0.2H), 3.88 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.78 (dd, *J* = 13.4, 9.0 Hz, 1H), 3.38 (dd, *J* = 10.2, 3.6 Hz, 0.2H), 2.79 (s, 3H), 2.69 (s, 0.6H), 1.99 (s, 3H), 1.92 (s, 0.6H), 1.29 (s, 10.8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 170.6, 151.9, 151.6, 134.1, 133.5, 130.1, 129.8, 129.5, 129.5, 129.4, 129.1, 129.0, 128.7, 126.1, 125.89, 113.0, 112.9, 112.8, 112.3, 53.1, 51.4, 50.9, 49.0, 40.4, 40.2, 38.2, 37.8, 37.4, 34.6, 34.1, 31.2, 21.9, 21.2; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{25}H_{29}N_3OSNa$ 442.1929, found 442.1932.



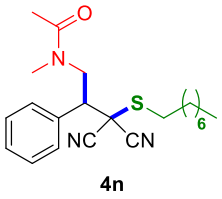
4l

***N-(3,3-dicyano-2-phenyl-3-(propylthio)propyl)-N-methylacetamide (4m)*:** (rr = 1: 0.2); R_f = 0.5 (ethyl acetate/n-hexane, 3: 7); colorless oil; Yield 74% (46.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.31 (m, 6H), 4.30 (dd, *J* = 13.3, 5.6 Hz, 1H), 4.13 (dd, *J* = 14.7, 3.6 Hz, 0.2H), 3.98 (dd, *J* = 14.6, 10.1 Hz, 0.2H), 3.84 (dd, *J* = 9.1, 5.6 Hz, 1H), 3.74 (dd, *J* = 13.3, 9.1 Hz, 1H), 3.37 (dd, *J* = 10.1, 3.5 Hz, 0.2H), 3.08 – 2.90 (m, 2.4H), 2.78 (s, 3H), 2.72 (s, 0.6H), 1.99 (s, 1H), 1.94 (s, 1H), 1.84 – 1.65 (m, 2.4H), 1.11 – 0.95 (m, 3.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.8, 134.4, 133.8, 130.2, 129.6, 129.2, 129.1, 128.8, 113.3, 113.2, 112.8, 53.2, 51.7, 51.0, 49.2, 40.4, 40.2, 38.3, 35.7, 35.3, 34.3, 22.0, 21.5, 21.4, 21.3, 13.5, 13.5; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{17}H_{21}N_3OSNa$ 338.1303, found 338.1303.



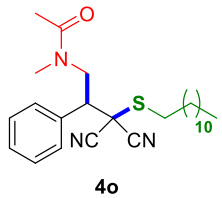
4m

***N-(3,3-dicyano-3-(octylthio)-2-phenylpropyl)-N-methylacetamide (4n)*:** (rr = 1: 0.2); R_f = 0.5 (ethyl acetate/n-hexane, 3: 7); yellow oil; Yield 62% (67.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.31 (m, 6H), 4.28 (dd, *J* = 13.3, 5.5 Hz, 1H), 4.12 (dd, *J* = 14.6, 3.5 Hz, 0.2H), 3.97 (dd, *J* = 14.6, 10.1 Hz, 0.2H), 3.83 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.74 (dd, *J* = 13.3, 9.1 Hz, 1H), 3.37 (dd, *J* = 10.0, 3.5 Hz, 0.2H), 3.10 – 2.91 (m, 2.4H), 2.77 (s, 3H), 2.71 (s, 0.6H), 1.97 (s, 3), 1.93 (s, 0.6H), 1.77 – 1.61 (m, 2.4H), 1.46 – 1.34 (m, 2.4H), 1.33 – 1.14 (m, 9.6H), 0.86 (t, *J* = 6.9 Hz, 3.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 170.6, 134.4, 133.8, 130.1, 129.5, 129.1, 129.0, 128.8, 113.2, 113.2, 112.8, 53.1, 51.6, 50.9, 49.2, 40.4, 40.2, 38.2, 34.2, 33.7, 33.3, 31.7, 29.0, 29.0, 28.9, 28.8, 28.8, 27.7, 27.7, 22.6, 21.9, 21.2, 14.1; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{22}H_{31}N_3OSNa$ 408.2086, found 408.2071.



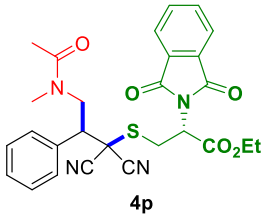
4n

***N-(3,3-dicyano-3-(dodecylthio)-2-phenylpropyl)-N-methylacetamide (4o)*:** (rr = 1: 0.2); R_f = 0.5 (ethyl acetate/n-hexane, 2: 8); yellow oil; Yield 86% (75.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.33 (m, 6H), 4.29 (dd, *J* = 13.2, 5.6 Hz, 1H), 4.13 (dd, *J* = 14.7, 3.6 Hz, 0.2H), 3.98 (dd, *J* = 14.7, 10.1 Hz, 0.2H), 3.84 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.74 (dd, *J* = 13.3, 9.1 Hz, 1H), 3.37 (dd, *J* = 10.2, 3.6 Hz, 0.2H), 3.08 – 2.92 (m, 2.4H), 2.78 (s, 3H), 2.72 (s, 0.6H), 1.98 (s, 3H), 1.93 (s, 0.6H), 1.78 – 1.60 (m, 2.4H), 1.46 – 1.34 (m, 2.4H), 1.33 – 1.15 (m, 19.2H), 0.87 (t, *J* = 6.8 Hz, 3.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 170.6, 134.4, 133.8, 130.1, 129.6, 129.1, 129.1, 128.8, 113.3, 113.2, 112.8, 53.2, 51.6, 51.0, 49.2, 40.4, 38.3, 34.3, 33.7, 33.4, 32.0, 29.8, 29.7, 29.6, 29.4, 29.1, 29.0, 28.9, 27.8, 27.7, 22.8, 22.0, 21.3, 14.2; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{26}H_{39}N_3OSNa$ 464.2712, found 464.2708.



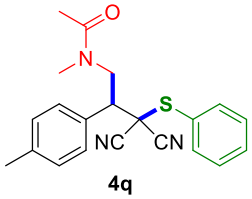
4o

***Ethyl-(2R)-3-((1,1-dicyano-3-(N-methylacetamido)-2-phenylpropyl)thio)-2-(1,3-dioxoisoindolin-2-yl)propanoate (4p)*:** (dr = 1: 0.5; rr = 1: 0.15); R_f = 0.3 (ethyl acetate/n-hexane, 4: 6); colourless solid; Yield 67% (69.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 3H), 7.80 – 7.72 (m, 3H), 7.42 – 7.31 (m, 7.5H), 5.23 (dd, *J* = 9.7, 5.4 Hz, 1H), 5.18 (dd, *J* = 9.8, 5.4 Hz, 0.5H), 4.30 – 4.13 (m, 4.5H), 3.91 – 3.67 (m, 6H), 2.75 (s, 4.5H), 1.94 (s, 4.5H), 1.22 (t, *J* = 7.2 Hz, 4.5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 171.6, 170.6, 167.2, 167.2, 167.1, 166.98, 134.6, 134.1, 134.0, 133.4, 131.7, 131.6, 130.2, 129.7, 129.6, 129.2, 129.0, 128.8, 124.0, 123.9, 113.2, 113.1, 113.0, 112.9, 112.9, 112.6, 63.0, 62.9, 53.1, 51.5, 51.5, 51.0, 50.9, 50.8, 49.2, 49.1, 40.7, 40.6, 40.4, 40.4, 38.32, 38.3, 34.2, 32.8, 32.8, 32.5, 32.4, 32.0, 29.8, 29.4, 22.8, 21.9, 21.2, 14.2, 14.1; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{27}H_{26}N_4O5SNa$ 541.1522, found 541.1490.



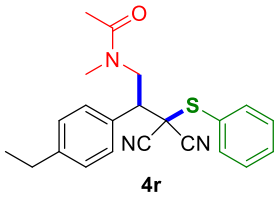
4p

***N-(3,3-dicyano-3-(phenylthio)-2-(p-tolyl)propyl)-N-methylacetamide (4q)*:** (rr = 1: 0.2); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 81% (58.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2.2H), 7.66 – 7.42 (m, 3.6H), 7.42 – 7.30 (m, 2.4H), 7.31 – 7.18 (m, 2.6H); 4.36 (dd, *J* = 13.5, 5.7 Hz, 1H), 4.17 (dd, *J* = 14.6, 3.3 Hz, 0.2H), 4.03 (dd, *J* = 14.6, 10.3 Hz, 0.2H), 3.92 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.77 (dd, *J* = 13.4, 9.1 Hz, 1H), 3.46 (dd, *J* = 10.2, 3.3 Hz, 0.2H), 2.80 (s, 3H), 2.76 (s, 0.45H), 2.37 (s, 3.45H), 2.01 (s, 3H), 1.97 (s, 0.45H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 170.7, 140.3, 139.6, 137.5, 137.4, 132.5, 132.1, 131.3, 130.5, 130.3, 130.2, 129., 128.9, 128.8, 127.3, 126.7, 113.3, 113.2, 112.8, 53.4, 51.3, 51.0, 48.72, 45.1, 44.9, 38.4, 34.3, 22.0, 21.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{22}N_3OS$ 364.1483, found 364.1482.



4q

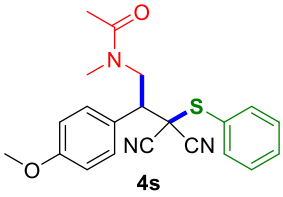
***N-(3,3-dicyano-2-(4-ethylphenyl)-3-(phenylthio)propyl)-N-methylacetamide (4r)*:** (rr = 1: 0.2);



4r

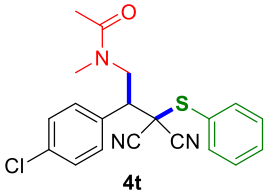
R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 84% (63.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2.2H), 7.62 – 7.43 (m, 3.6H), 7.39 (d, *J* = 8.2 Hz, 2.4H), 7.32 – 7.18 (m, 2.6H), 4.36 (dd, *J* = 13.5, 6.0 Hz, 1H), 4.17 (dd, *J* = 14.6, 3.6 Hz, 0.2H), 4.03 (dd, *J* = 14.6, 10.3 Hz, 0.2H), 3.93 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.76 (dd, *J* = 13.5, 8.9 Hz, 1H), 3.47 (dd, *J* = 10.2, 3.5 Hz, 0.2H), 2.80 (s, 3H), 2.76 (s, 0.6H), 2.73 – 2.61 (m, 2.4H), 2.01 (s, 3H), 1.96 (s, 0.6H), 1.25 (t, *J* = 7.6 Hz, 3.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 170.7, 146.4, 145.7, 137.5, 137.3, 132.1, 131.4, 130.6, 130.1, 129.9, 129.0, 129.0, 128.8, 128.6, 127.3, 126.7, 113.3, 113.2, 113.2, 112.8, 53.4, 51.2, 50.9, 48.7, 45.1, 44.9, 38.3, 34.2, 28.6, 22.0, 21.3, 15.2; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{22}H_{23}N_3OSNa$ 400.1460, found 400.1471.

***N-(3,3-dicyano-2-(4-methoxyphenyl)-3-(phenylthio)propyl)-N-methylacetamide (4s)*:** (rr = 1: 0.2); R_f = 0.3 (ethyl acetate/n-hexane, 4: 6); yellow oil; Yield 68% (51.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.66 (m, 2.4H), 7.69 – 7.29 (m, 6H), 6.95 (t, *J* = 8.7 Hz, 2.4H), 4.32 (dd, *J* = 13.4, 5.8 Hz, 1H), 4.16 (dd, *J* = 14.6, 3.5 Hz, 0.2H), 4.00 (dd, *J* = 14.5, 10.4 Hz, 0.2H), 3.91 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.88 – 3.72 (m, 4.6H), 3.46 (dd, *J* = 10.3, 3.4 Hz, 50.2H), 2.81 (s, 3H), 2.76 (s, 3H), 2.00 (s, 3H), 1.98 (s, 0.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 170.7, 160.8, 160.4, 137.5, 137.3, 132.4, 132.1, 130.3, 130.1, 129.9, 127.3, 126.7, 126.1, 125.2, 114.93, 114.5, 113.2, 113.2, 112.8, 55.4, 55.3, 53.3, 51.1, 50.8, 48.4, 45.3, 45.1, 38.3, 34.3, 22.0, 21.3; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{22}N_3O_2S$ 380.1433, found 380.1432.



4s

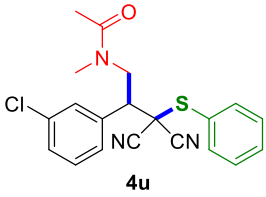
***N-(2-(4-chlorophenyl)-3,3-dicyano-3-(phenylthio)propyl)-N-methylacetamide (4t)*:** (rr = 1: 0.1);



4t

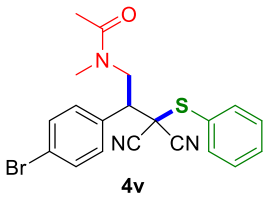
R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 97% (74.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2.1H), 7.59 – 7.35 (m, 7.8H), 4.27 (dd, *J* = 13.5, 5.8 Hz, 1H), 4.19 (dd, *J* = 14.7, 3.5 Hz, 0.1H), 4.03 – 3.91 (m, 1.1H), 3.83 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.51 (dd, *J* = 10.2, 3.5 Hz, 1H), 2.81 (s, 3H), 2.74 (s, 0.3H), 1.99 (s, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.6, 137.5, 136.4, 135.7, 132.8, 132.6, 132.3, 132.1, 130.4, 130.2, 130.0, 129.9, 129.5, 126.9, 126.3, 112.99, 113.0, 112.9, 112.6, 53.2, 51.0, 50.7, 48.4, 44.8, 44.6, 38.4, 34.4, 22.0, 21.4; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{19}ClN_3OS$ 384.0937, found 384.0915.

***N-(2-(3-chlorophenyl)-3,3-dicyano-3-(phenylthio)propyl)-N-methylacetamide (4u)*:** (rr = 1: 0.1); R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colourless solid; Yield 91% (70.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2.2H), 7.61 – 7.42 (m, 5.5H), 7.36 (d, *J* = 8.5 Hz, 2.2H), 4.26 (dd, *J* = 13.5, 5.8 Hz, 1H), 4.19 (dd, *J* = 14.8, 3.6 Hz,0.1H), 4.04 – 3.92 (m, 1.1H), 3.83 (dd, *J* = 13.5, 9.1 Hz, 1H), 3.49 (dd, *J* = 10.1, 3.6 Hz, 0.1H), 2.82 (s, 3H), 2.76 (d, *J* = 8.3 Hz, 0.3H), 1.99 (s, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 170.5, 137.5, 137.3, 133.3, 132.9, 132.6, 132.4, 132.3, 130.7, 130.2, 130.0, 126.9, 126.3, 124.5, 123.9, 113.0, 112.9, 112.9, 112.5, 53.1, 51.0, 50.8, 48.5, 44.7, 44.5, 38.4, 34.4, 22.0, 21.4; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{20}H_{18}ClN_3OS$ 407.0757, found 407.0756.



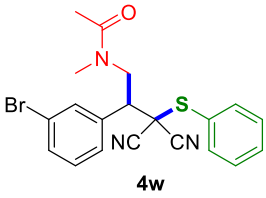
4u

***N-(2-(4-bromophenyl)-3,3-dicyano-3-(phenylthio)propyl)-N-methylacetamide (4v)*:** (rr = 1: 0.1); R_f = 0.5 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 93% (79.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2.1H), 7.63 – 7.31 (m, 7.8H), 4.29 (dd, *J* = 13.6, 6.1 Hz, 1H), 4.20 (dd, *J* = 14.8, 3.7 Hz, 0.1H), 4.06 – 3.91 (m, 1.1H), 3.79 (dd, *J* = 13.5, 8.7 Hz, 1H), 3.49 (dd, *J* = 10.2, 3.7 Hz, 0.1H), 2.84 (s, 3H), 2.76 (s, 0.3H), 2.01 (s, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 137.6, 137.4, 136.4, 135.6, 135.1, 132.7, 132.31, 130.9, 130.6, 130.5, 130.3, 130.0, 129.9, 129.4, 127.1, 126.9, 113.0, 112.9, 112.5, 53.2, 51.4, 50.9, 48.6, 44.6, 44.52, 38.5, 34.4, 22.0, 21.4; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{19}BrN_3OS$ 428.0432, found 428.0431.



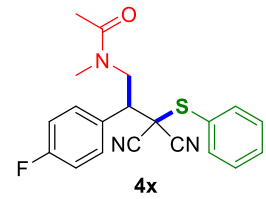
4v

***N-(2-(3-bromophenyl)-3,3-dicyano-3-(phenylthio)propyl)-N-methylacetamide (4w)*:** (rr = 1: 0.1); R_f = 0.5 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 74% (63.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.69 (m, 2.2H), 7.63 – 7.39 (m, 6.6H), 7.36 – 7.26 (m, 1.1H), 4.27 (dd, *J* = 13.7, 6.2 Hz, 1H), 4.18 (dd, *J* = 14.7, 3.6 Hz, 0.1H), 4.05 – 3.90 (m, 1.1H), 3.78 (dd, *J* = 13.6, 8.6 Hz, 1H), 3.46 (dd, *J* = 10.1, 3.6 Hz, 0.1H), 2.84 (s, 3H), 2.75 (s, 0.3H), 2.01 (s, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 170.6, 137.6, 137.41, 136.6, 135.8, 133.5, 132.9, 132.7, 132.3, 131.2, 130.8, 130.3, 130.0, 127.5, 126.9, 123.2, 113.0, 112.9, 53.2, 51.4, 50.9, 48.5, 44.6, 38.6, 34.4, 22.1, 21.4; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{19}BrN_3OS$ 428.0432, found 428.0430.



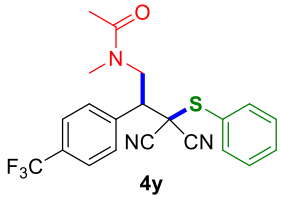
4w

***N-(3,3-dicyano-2-(4-fluorophenyl)-3-(phenylthio)propyl)-N-methylacetamide (4x)*:** (rr = 1: 0.1); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 89% (65.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.33 (m, 8.4H), 7.33 – 7.09 (m, 2.4H), 4.50 – 4.11 (m, 2.4H), 4.02 – 3.86 (m, 1.2H), 2.86 (s, 3H), 2.81 (s, 0.6H), 1.99 (s, *J* = 3.5 Hz, 3.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 170.6, 161.3 (d, *J* = 248.2 Hz), 137.6, 137.4, 132.6, 132.3, 131.2 (d, *J* = 7.8 Hz), 130.2, 130.0, 128.5, 126.9, 125.3 (d, *J* = 3.6 Hz), 125.0 (d, *J* = 3.6 Hz), 121.6 (d, *J* = 13.7 Hz), 116.7 (d, *J* = 23.0 Hz), 116.1 (d, *J* = 22.1 Hz), 113.0, 113.0, 112.7, 112.5, 52.8, 49.9, 44.49, 39.8, 37.7, 34.1, 32.0, 29.8, 21.9, 21.2; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{19}FN_3OS$ 368.1233, found 368.1232.



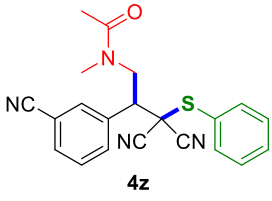
4x

***N-(3,3-dicyano-3-(phenylthio)-2-(4-(trifluoromethyl)phenyl)propyl)-N-methylacetamide (4y)*:** (rr = 1: 0.07); R_f = 0.5 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 96% (80.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.74 – 7.68 (m, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.44 (m, 2H), 4.28 (dd, *J* = 13.7, 6.1 Hz, 1H), 4.09 (dd, *J* = 8.7, 6.1 Hz, 1H), 3.90 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.85 (s, 3H), 2.01 (s, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 170.5, 138.3, 137.5, 137.4, 132.7, 131.8 (q, *J* = 32.9 Hz), 132.4, 130.3, 130.0, 129.6, 126.7, 126.6 (q, *J* = 3.8 Hz), 126.2 (q, *J* = 3.7 Hz), 126.1, 123.8 (d, *J* = 272.5 Hz), 112.9, 112.8, 53.2, 51.1, 50.9, 48.7, 44.5, 40.8, 38.4, 34.3, 29.2, 25.9, 21.9, 21.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{19}F_3N_3OS$ 418.1201, found 418.1200.



4y

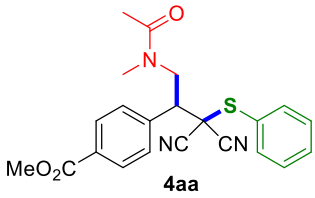
***N-(3,3-dicyano-2-(3-cyanophenyl)-3-(phenylthio)propyl)-N-methylacetamide (4z)*:** (rr = 1: 0.07); R_f = 0.2 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 86% (64.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.68 (m, 5H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.18 (dd, *J* = 13.3, 6.0 Hz, 1H), 4.05 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.95 (dd, *J* = 13.3, 8.4 Hz, 1H), 2.89 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 137.5, 135.9, 133.3, 132.8, 132.46, 130.2, 130.1, 126.5,



4z

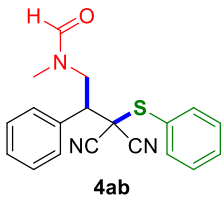
118.0, 113.5, 112.8, 112.7, 51.0, 48.5, 44.4, 38.4, 22.0; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{21}H_{18}N_4OSNa$ 397.1099, found 397.1112.

***Methyl 4-(1,1-dicyano-3-(N-methylacetamido)-1-(phenylthio)propan-2-yl)benzoate (4aa)*:** (rr = 1: 0.1); R_f = 0.3 (ethyl acetate/n-hexane, 3: 7); colorless solid; Yield 74% (60.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 2.2H), 7.77 (d, *J* = 7.3 Hz, 2.2H), 7.64 – 7.44 (m, 5.5H), 4.33 (dd, *J* = 13.6, 6.0 Hz, 1H), 4.23 (dd, *J* = 14.7, 3.5 Hz, 0.1H), 4.11 – 3.92 (m, 1.1H), 3.93 (s, 3.3H), 3.84 (dd, *J* = 13.6, 8.9 Hz, 1H), 3.57 (dd, *J* = 10.1, 3.5 Hz, 0.1H), 2.81 (s, 3H), 2.75 (s, 0.3H), 2.00 (s, 3H), 1.98 (s, 0.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 170.6, 166.4, 166.1, 139.3, 138.5, 137.5, 132.7, 132.3, 131.9, 131.4, 130.8, 130.4, 130.3, 130.0, 129.2, 126.8, 126.2, 113.0, 112.9, 112.8, 112.5, 53.2, 52.5, 52.4, 51.2, 51.1, 48.8, 44.5, 38.4, 34.4, 22.0, 21.3; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{22}N_3O_3S$ 408.1382, found 408.1369.



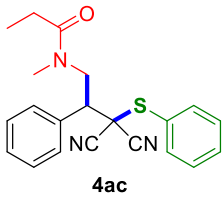
4aa

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylformamide (4ab)*:** (rr = 1: 0.7); R_f = 0.3 (ethyl acetate/n-hexane, 2: 8); yellow oil; Yield 76% (51.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.84 (s, 0.7H), 7.82 – 7.72 (m, 3.4H), 7.63 – 7.35 (m, 13.6H), 4.31 (dd, *J* = 13.1, 4.4 Hz, 1H), 4.12 – 3.99 (m, 1.4H), 3.94 (dd, *J* = 13.1, 10.6 Hz, 1H), 3.85 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.55 (dd, *J* = 9.2, 5.4 Hz, 0.7H), 2.82 (s, 2.1H), 2.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 162.7, 137.6, 137.4, 133.6, 132.7, 132.6, 132.3, 130.4, 130.2, 130.1, 129.9, 129.8, 129.3, 129.2, 128.9, 127.0, 126.5, 113.0, 113.0, 112.8, 112.6, 51.6, 50.4, 48.7, 46.9, 45.2, 44.9, 36.0, 30.3; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{19}H_{17}N_3OSNa$ 358.0990, found 358.1008.



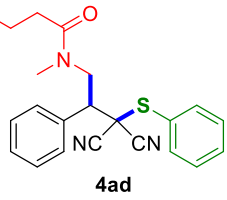
4ab

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylpropionamide (4ac)*:** (rr = 1: 0.1); R_f = 0.4 (ethyl acetate/n-hexane, 2: 8); colourless semisolid; Yield 82% (60.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2.2H), 7.62 – 7.34 (m, 8.8H), 4.39 (dd, *J* = 13.5, 5.7 Hz, 1H), 4.20 (dd, *J* = 14.6, 3.5 Hz, 0.1H), 4.08 – 3.93 (m, 1.1H), 3.77 (dd, *J* = 13.5, 9.0 Hz, 1H), 3.49 (dd, *J* = 10.2, 3.4 Hz, 0.1H), 2.76 (s, 3.3H), 2.32 – 2.13 (m, 2.2H), 1.12 – 0.98 (m, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 137.5, 134.6, 132.1, 129.9, 129.6, 129.2, 129.1, 127.3, 113.2, 113.1, 51.7, 49.0, 45.0, 37.6, 26.9, 9.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{22}N_3OS$ 364.1484, found 364.1471.



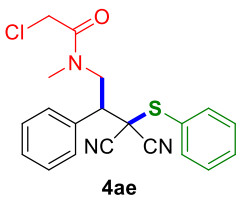
4ac

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylbutyramide (4ad)*:** (rr = 1: 0.1); R_f = 0.4 (ethyl acetate/n-hexane, 2: 8); yellow oil; Yield 55% (41.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2.2H), 7.61 – 7.37 (m, 8.8H), 4.38 (dd, *J* = 13.5, 5.6 Hz, 1H), 4.20 (dd, *J* = 14.6, 3.4 Hz, 0.1H), 4.05 (dd, *J* = 14.6, 10.3 Hz, 0.1H), 3.97 (dd, *J* = 9.2, 5.7 Hz, 1H), 3.79 (dd, *J* = 13.5, 9.2 Hz, 1H), 3.48 (dd, *J* = 10.2, 3.4 Hz, 0.1H), 2.76 (s, 3.3H), 2.28 – 2.11 (m, 2H), 2.10 – 1.97 (m, 0.2H), 1.68 – 1.51 (m, 2.3H), 0.96 – 0.82 (m, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 137.5, 134.5, 132.1, 129.9, 129.6, 129.2, 129.1, 127.2, 113.2, 113.1, 51.5, 49.0, 45.0, 37.7, 35.6, 18.2, 14.0; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{22}H_{23}N_3OSNa$ 400.1460, found 400.1452.



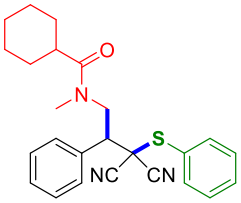
4ad

***2-chloro-N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylacetamide (4ae)*:** (rr = 1: 0.1); R_f = 0.3 (ethyl acetate/n-hexane, 2: 8); yellow oil; Yield 58% (44.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2.2H), 7.62 – 7.37 (m, 8.8H), 4.44 (dd, *J* = 13.4, 5.1 Hz, 1H), 4.26 (dd, *J* = 14.8, 3.4 Hz, 0.1H), 4.14 (dd, *J* = 15.7, 5.6 Hz, 0.1H), 4.02 – 3.90 (m, 3H), 3.88 – 3.74 (m, 1.2H), 3.55 (dd, *J* = 10.1, 3.3 Hz, 0.1H), 2.82 (s, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 137.6, 137.4, 134.4, 134.0, 132.3, 130.3, 130.0, 129.85, 129.4, 129.1, 127.1, 123.7, 113.137, 112.927, 51.917, 48.7, 44.9, 41.3, 37.9; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{20}H_{18}ClN_3OSNa$ 406.0757, found 406.0760.



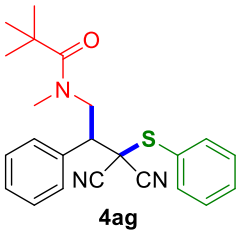
4ae

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylcyclohexanecarboxamide (4af)*:** (rr = 1: 0.1); R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless semisolid; Yield 88% (73.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 2.2H), 7.64 – 7.29 (m, 8.8H), 4.41 (dd, *J* = 13.4, 4.9 Hz, 1H), 4.20 (dd, *J* = 14.0, 2.2 Hz, 0.1H), 4.07 (dd, *J* = 14.5, 10.3 Hz, 0.1H), 3.96 (dd, *J* = 9.7, 5.1 Hz, 1H), 3.74 (dd, *J* = 13.3, 9.8 Hz, 1H), 3.45 (dd, *J* = 9.8, 2.4 Hz, 0.1H), 2.75 (d, *J* = 2.0 Hz, 3.3H), 2.38 – 2.26 (m, 1.1H), 1.87 – 1.07 (m, 11.8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 137.5, 134.6, 132.1, 129.9, 129.6, 129.2, 129.1, 127.3, 113.2, 113.1, 51.6, 48.9, 45.0, 40.9, 37.5, 29.12, 28.7, 25.9, 25.9, 25.7; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{28}N_3OS$ 418.1953, found 418.1960.



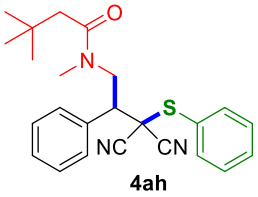
4af

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N-methylpivalamide (4ag)*:** R_f = 0.4 (ethyl acetate/n-hexane, 3: 7); colorless semisolid; Yield 35% (27.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.58 – 7.52 (m, 1H), 7.52 – 7.37 (m, 7H), 4.46 (dd, *J* = 13.3, 5.0 Hz, 1H), 4.01 (dd, *J* = 9.9, 4.9 Hz, 1H), 3.64 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.83 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.3, 137.5, 134.9, 132.1, 130.0, 129.6, 129.2, 127.4, 113.3, 113.2, 53.8, 48.7, 45.1, 39.3, 38.9, 27.9; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{23}H_{25}N_3OSNa$ 414.1616, found 414.1613.



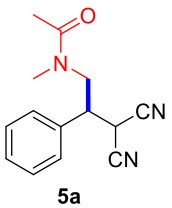
4ag

***N-(3,3-dicyano-2-phenyl-3-(phenylthio)propyl)-N,3,3-trimethylbutanamide (4ah)*:** (rr = 1: 0.1); R_f = 0.2 (ethyl acetate/n-hexane, 2: 8); yellow oil; Yield 27% (21.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2.2H), 7.58 – 7.39 (m, 8.8H), 4.37 (dd, *J* = 12.7, 4.4 Hz, 1H), 4.24 (dd, *J* = 14.7, 3.2 Hz, 0.1H), 4.04 (dd, *J* = 14.7, 10.4 Hz, 0.1H), 4.01 – 3.84 (m, 2H), 3.47 (dd, *J* = 10.3, 3.1 Hz, 0.1H), 2.79 (s, 1H), 2.71 (s, 0.H), 2.21 – 2.07 (m, 2.2H), 0.99 (s, 0.9H), 0.94 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.8, 137.6, 134.3, 132.2, 130.0, 129.7, 129.3, 129.2, 127.3, 113.2, 113.1, 51.1, 49.1, 45.2, 38.6, 31.5, 29.9; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{27}N_3OSNa$ 428.1773, found 428.1781.

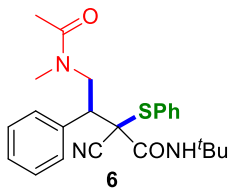


4ah

***N-(3,3-dicyano-2-phenylpropyl)-N-methylacetamide (5a)*:** R_f = 0.3 (ethyl acetate/n-hexane, 7: 3); yellow oil; Yield 56% (26.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 3H), 7.38 – 7.33 (m, 2H), 4.30 – 4.21 (m, 2H), 3.66 (dt, *J* = 8.7, 6.2 Hz, 1H), 3.46 (dd, *J* = 14.1, 5.9 Hz, 1H), 2.94 (s, 3H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.4, 135.2, 129.4, 129.2, 127.9, 112.2, 111.6, 51.2, 44.8, 37.6, 27.4, 21.8; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{16}N_3O$ 242.1293, found 242.1283.

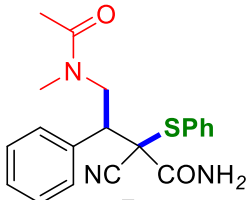


5a



6

***N-(tert-butyl)-2-cyano-4-(N-methylacetamido)-3-phenyl-2-(phenylthio)butanamide (6)*:** (dr = 1:0.6, rr = 1 : 0.5); R_f = 0.5 (ethyl acetate/n-hexane, 5: 5); white solid; Yield 81% (68.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 4.0, 1.5 Hz, 3H), 7.62 – 7.26 (m, 22H), 5.97 (s, 0.5H), 5.71 (s, 0.4H), 5.52 (s, 1H), 5.37 (s, 0.6H), 4.29 – 4.19 (m, 2.2H), 4.09 – 3.96 (m, 1.6H), 3.88 (dd, *J* = 10.8, 4.3 Hz, 0.8H), 3.80 (ddd, *J* = 10.8, 7.2, 3.9 Hz, 1.4H), 3.70 – 3.56 (m, 1.5H), 2.74 (s, 1.8H), 2.70 (s, 3H), 2.68 (s, 1.5H), 2.66 (s, 1.2H), 1.98 (s, 1.8H), 1.93 (s, 3H), 1.87 (s, 1.2H), 1.96 (s, 1.5H), 1.16 (s, 4.5H), 1.11 (s, 3.6H), 0.81 (s, 9H), 0.79 (s, 5.4H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.9, 170.8, 162.2, 161.4, 160.9, 137.0, 136.7, 136.5, 136.2, 135.9, 135.7, 134.8, 131.0, 130.8, 130.5, 130.4, 129.7, 129.5, 129.4, 129.4, 129.3, 129.3, 129.2, 129.0, 128.9, 128.8, 128.8, 128.7, 128.5, 128.4, 128.3, 127.9, 119.1, 118.5, 118.3, 118.2, 58.9, 58.3, 58.0, 56.7, 53.6, 53.0, 52.9, 52.6, 52.3, 52.0, 50.2, 49.9, 49.6, 49.1, 48.8, 48.6, 37.2, 36.7, 34.2, 34.1, 28.0, 28.0, 27.8, 27.7, 21.8, 21.7, 21.3, 21.0; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{24}H_{30}N_3O_2S$ 424.2059, found 424.2045.

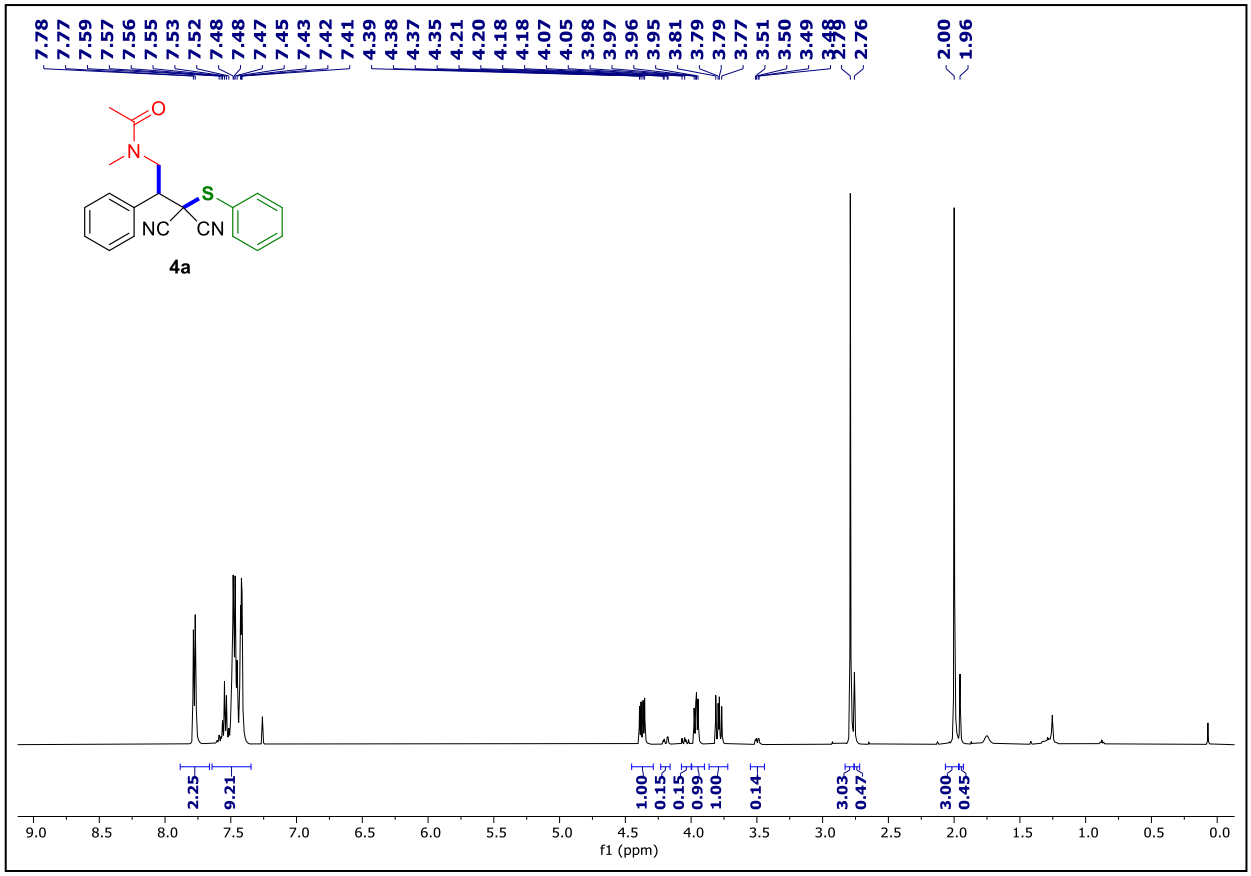


7

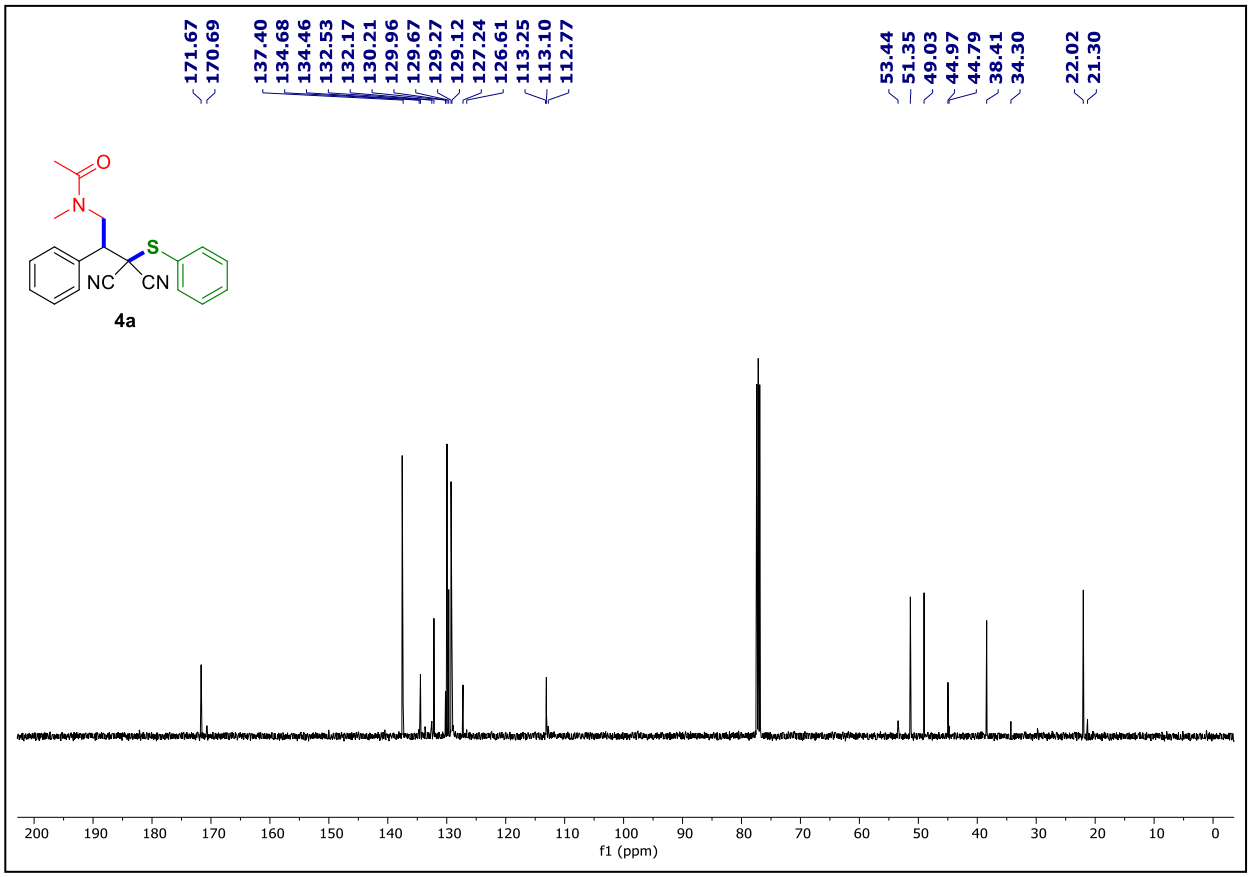
***2-cyano-4-(N-methylacetamido)-3-phenyl-2-(phenylthio)butanamide (7)*:** (dr = 1: 0.6); R_f = 0.2 (ethyl acetate/n-hexane, 8: 2); white solid; Yield 66% (48.4 mg); ^{1}H NMR (500 MHz, DMSO-D_6) δ 7.98 (d, *J* = 22.2 Hz, 1.2H), 7.71 – 7.29 (m, 14.8H), 4.23 (dd, *J* = 13.0, 1.8 Hz, 0.6H), 4.16 (dd, *J* = 12.8, 4.0 Hz, 1H), 4.05 – 3.86 (m, 3.2H), 2.64 (s, 3H), 2.64 (s, 1.8H), 1.85 (s, 3H), 1.81 (s, 1.8H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$-DMSO-D_6) δ 170.7, 170.6, 165.2, 164.9, 136.4, 136.2, 135.8, 135.7, 130.9, 130.5, 129.4, 129.2, 129.0, 128.7, 128.5, 128.4, 128.3, 128.1, 127.6, 117.3, 117.2, 60.1, 58.6, 57.5, 53.4, 50.6, 49.2, 47.8, 37.4, 33.9, 21.6, 21.0, 13.9; HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{22}N_3O_2S$ 368.1433, found 368.1420.

14. NMR spectra of the products:

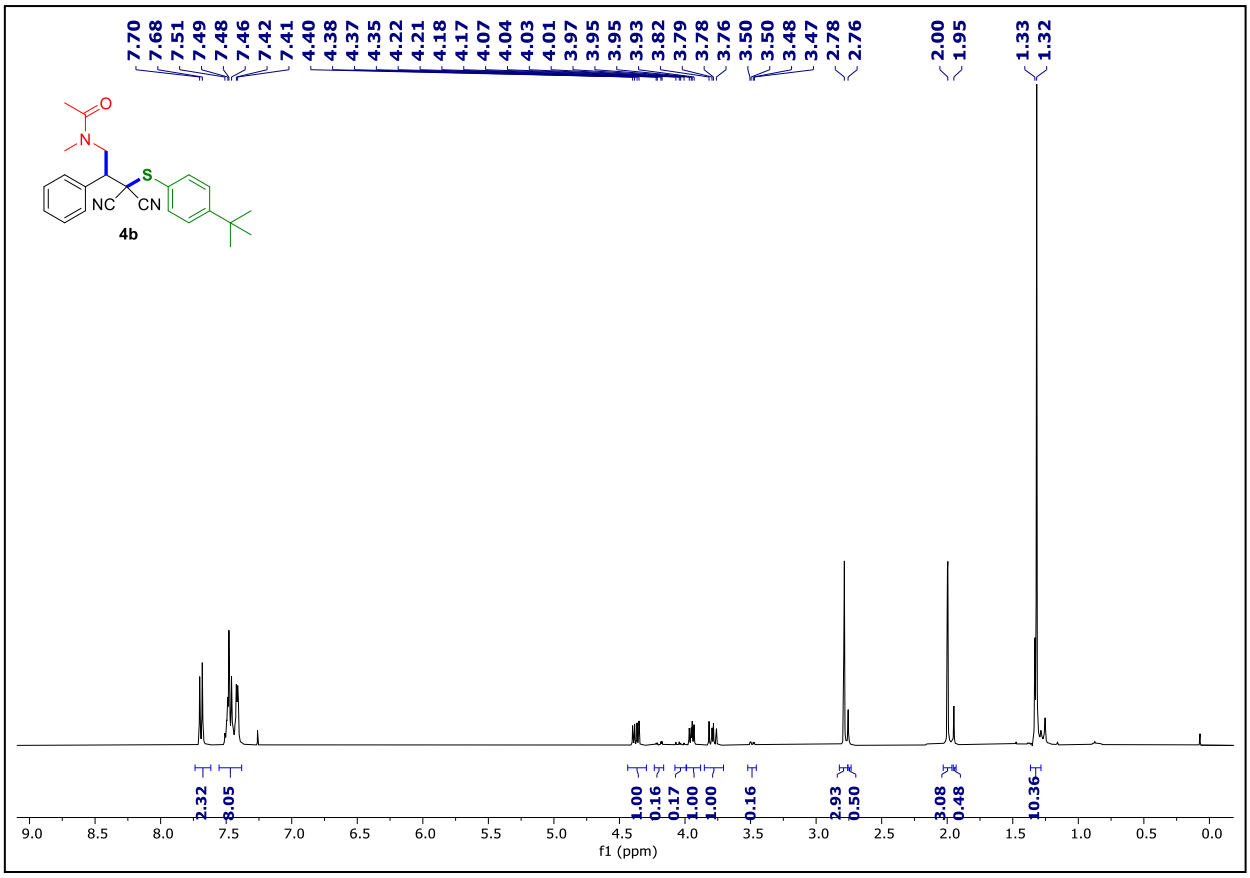
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a,** (rr = 1: 0.15)



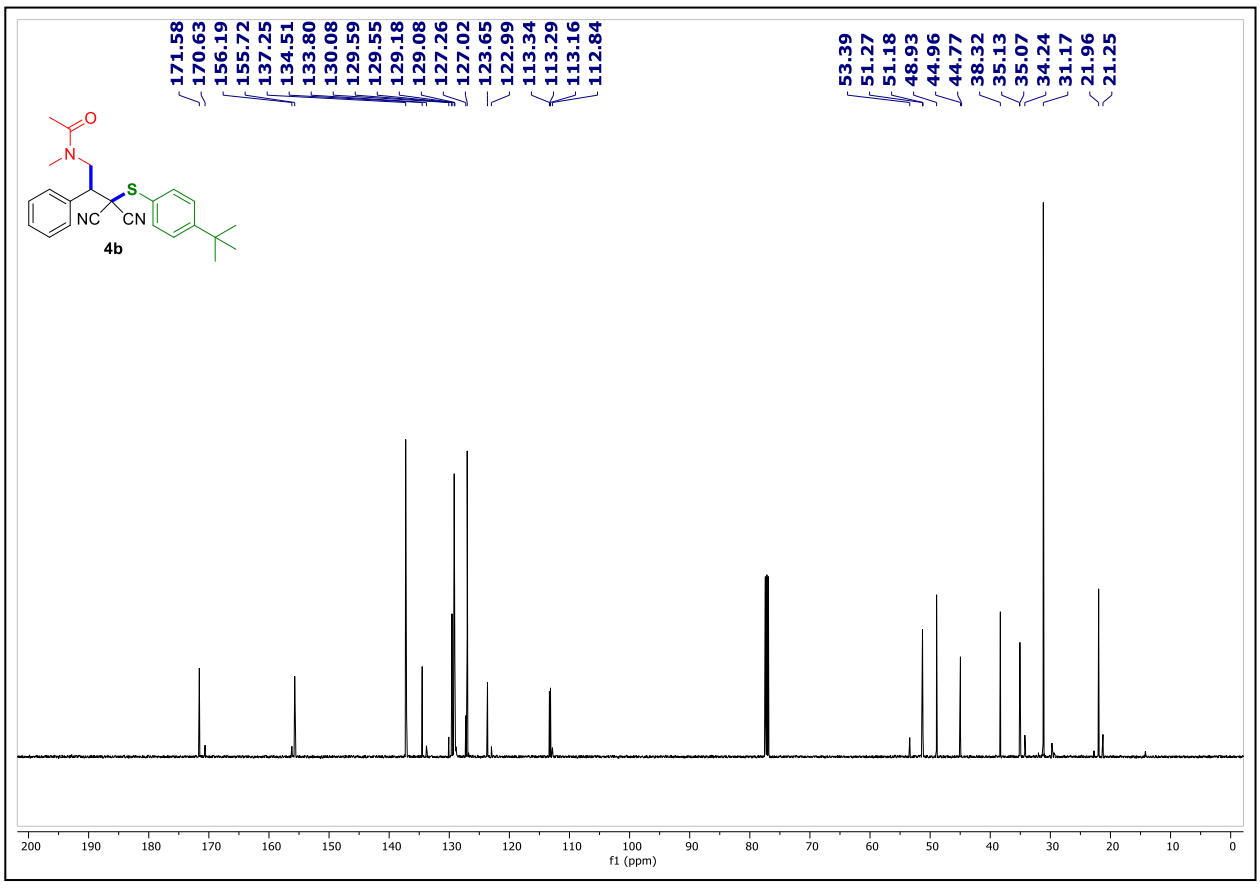
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4a,** (rr = 1: 0.15)



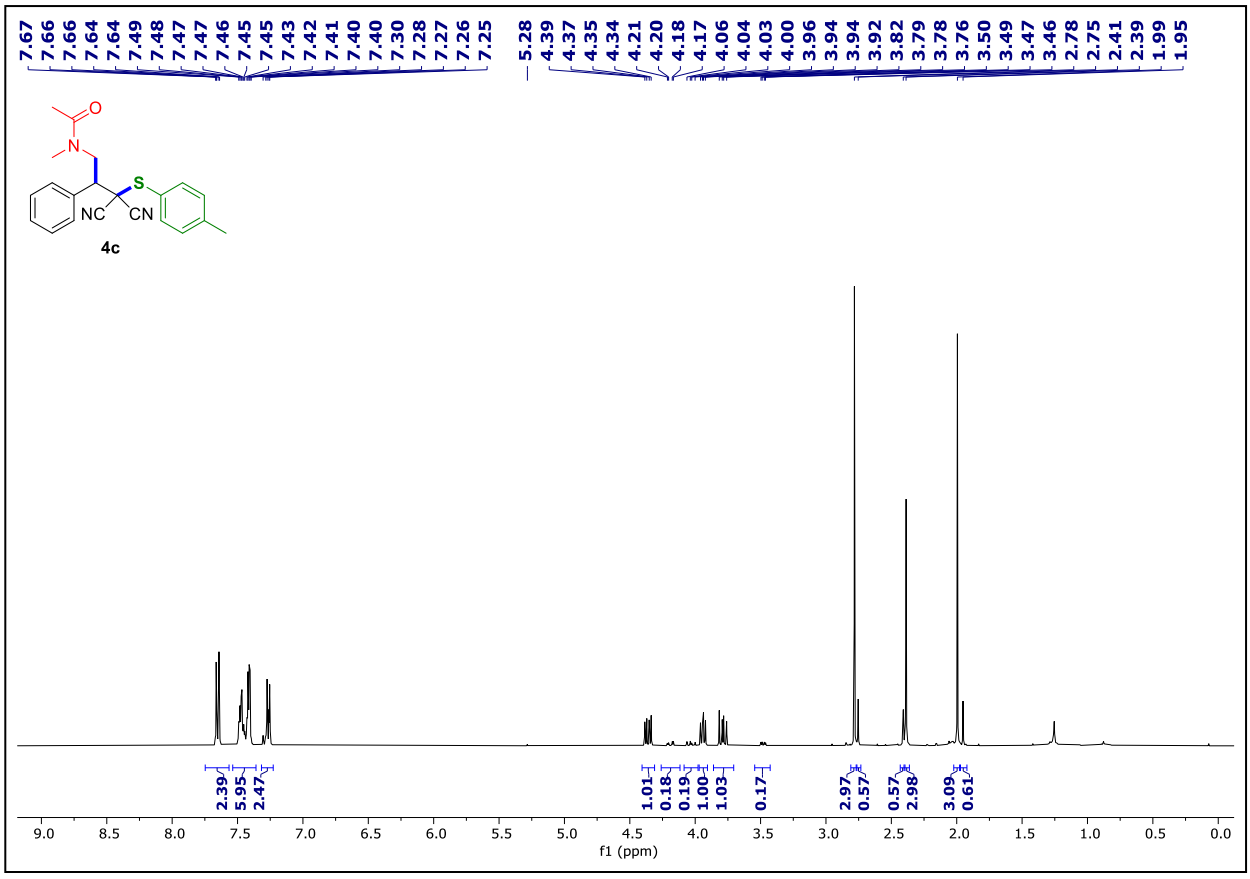
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b,** (rr = 1: 0.15)



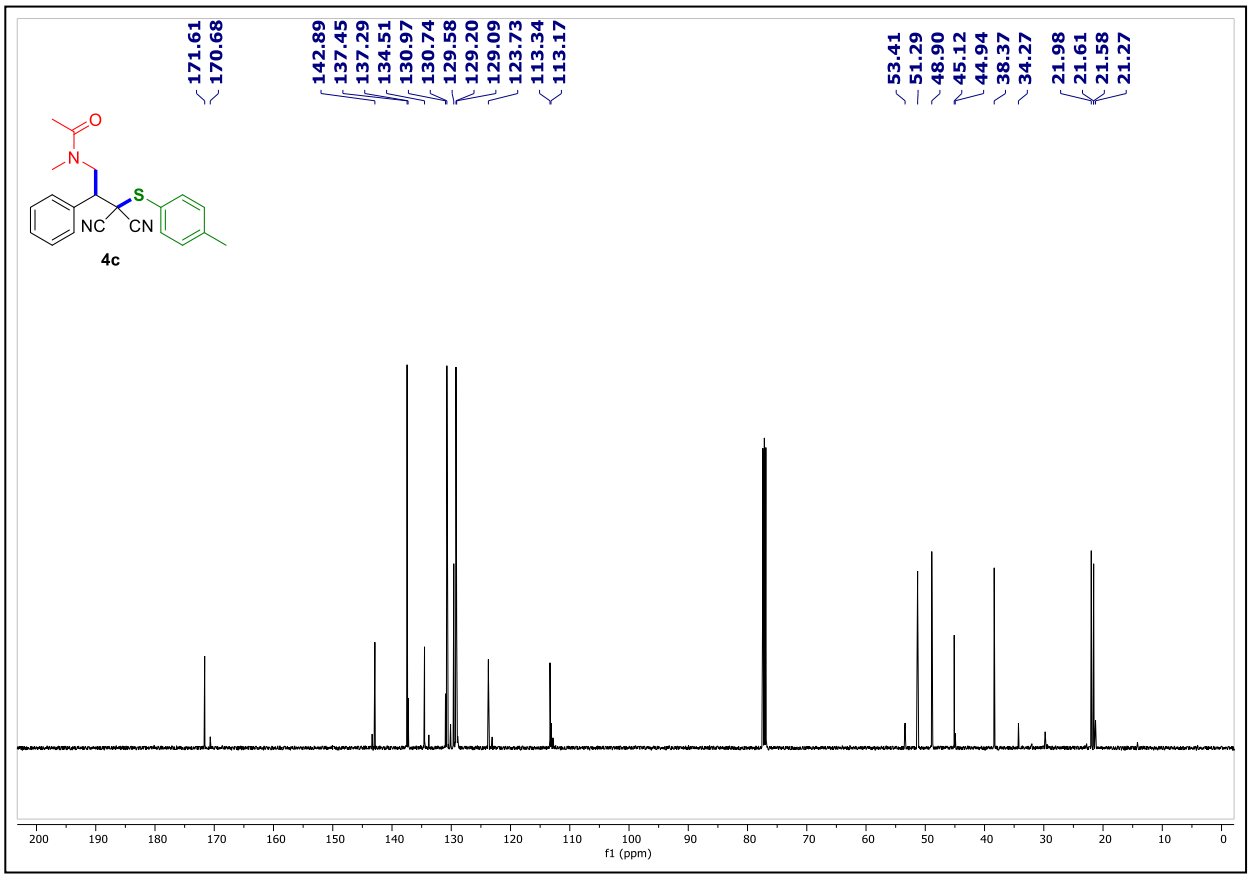
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4b,** (rr = 1: 0.15)



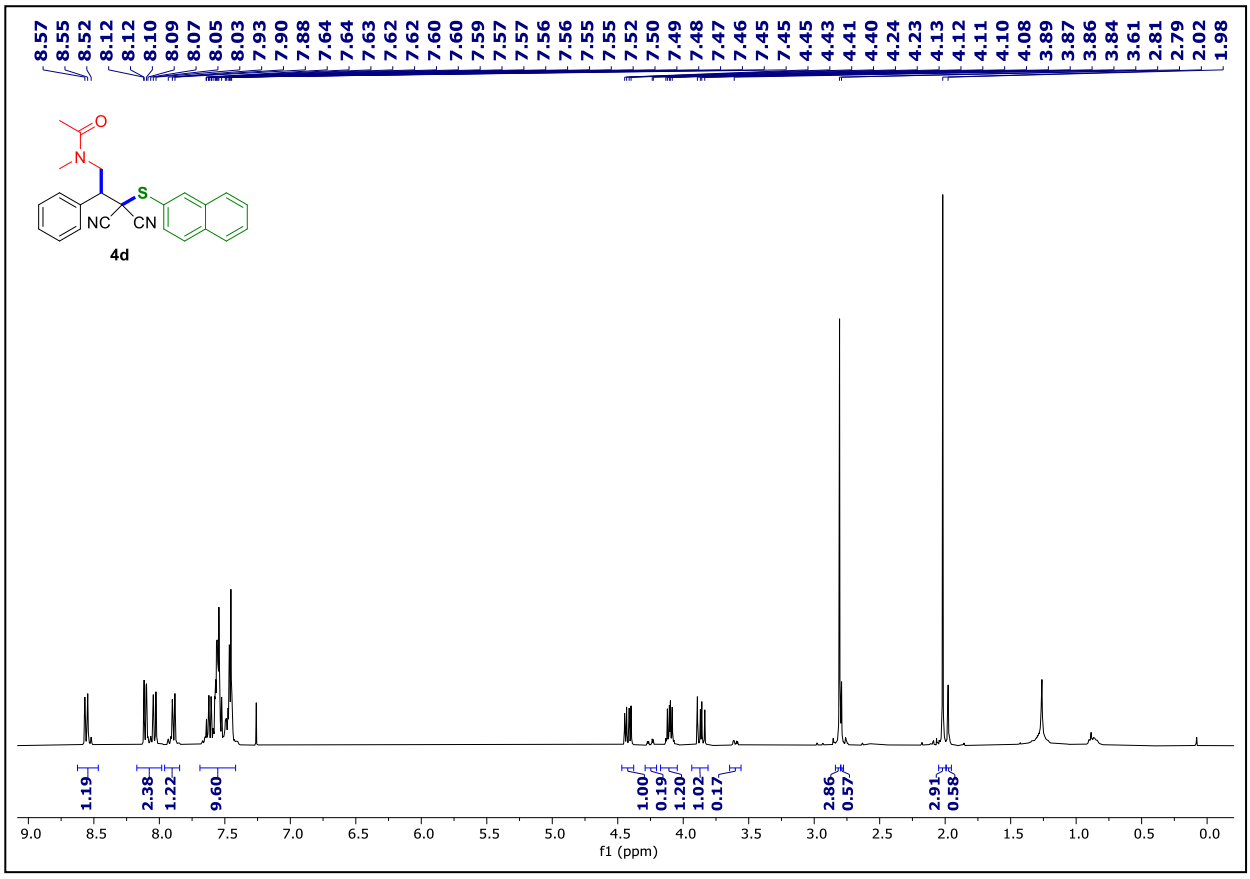
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**, (rr = 1: 0.2)



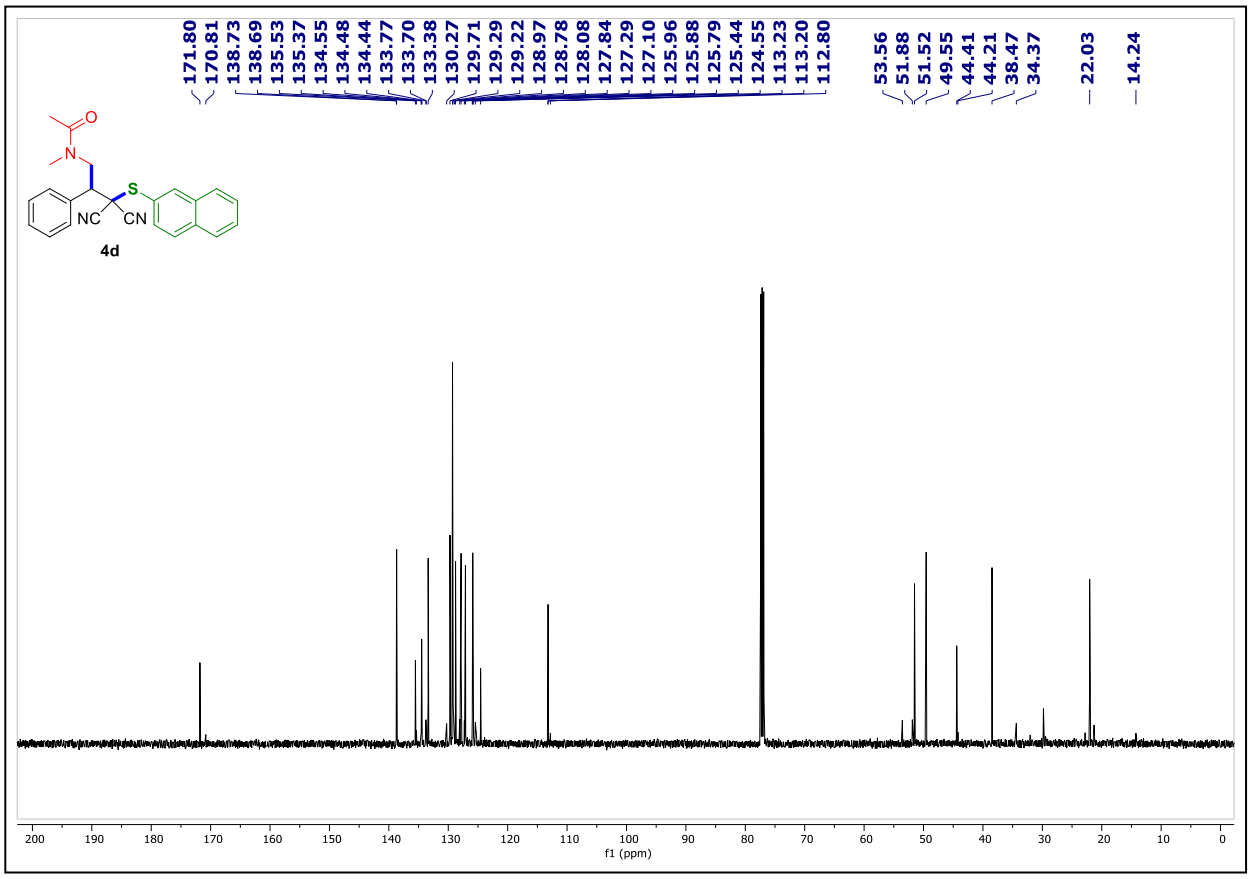
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4c**, (rr = 1: 0.2)



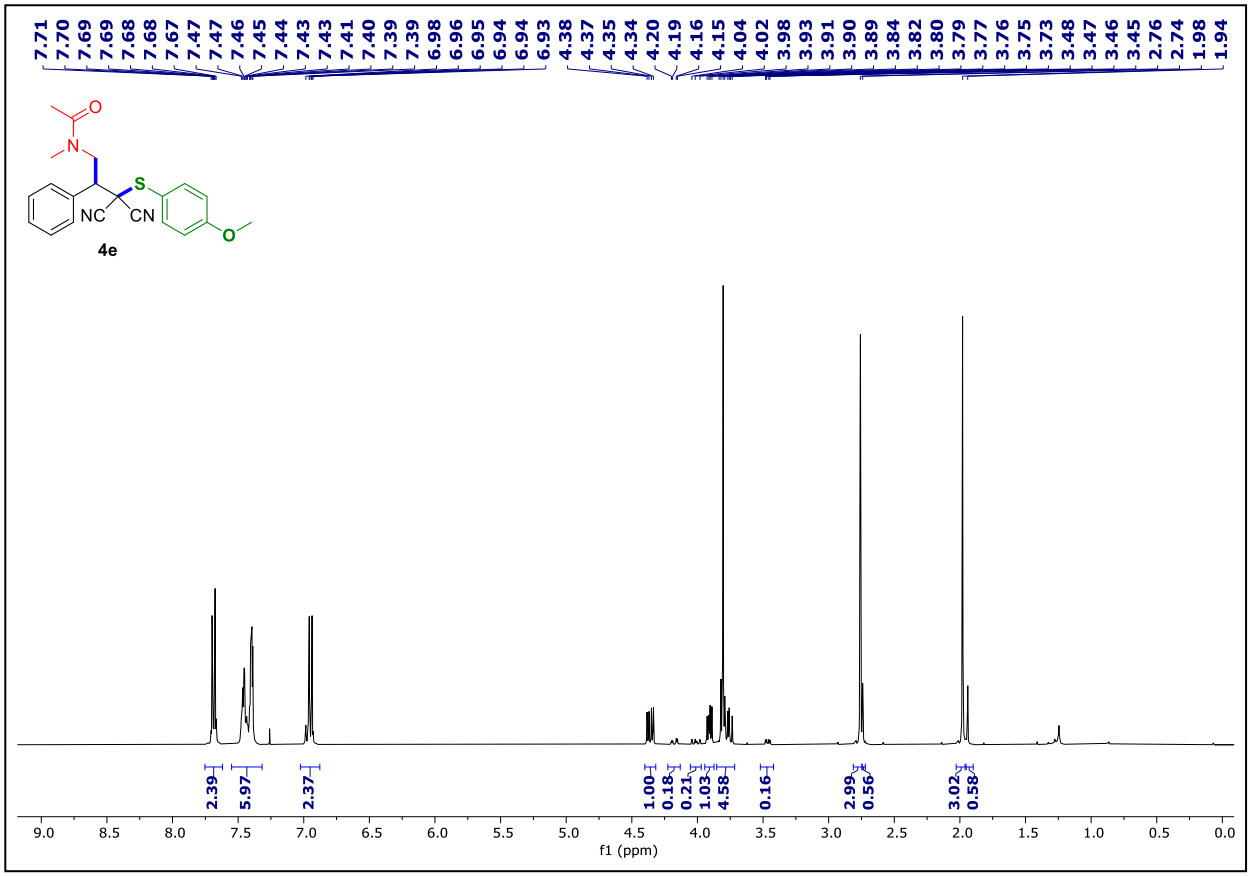
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**, (rr = 1: 0.2)



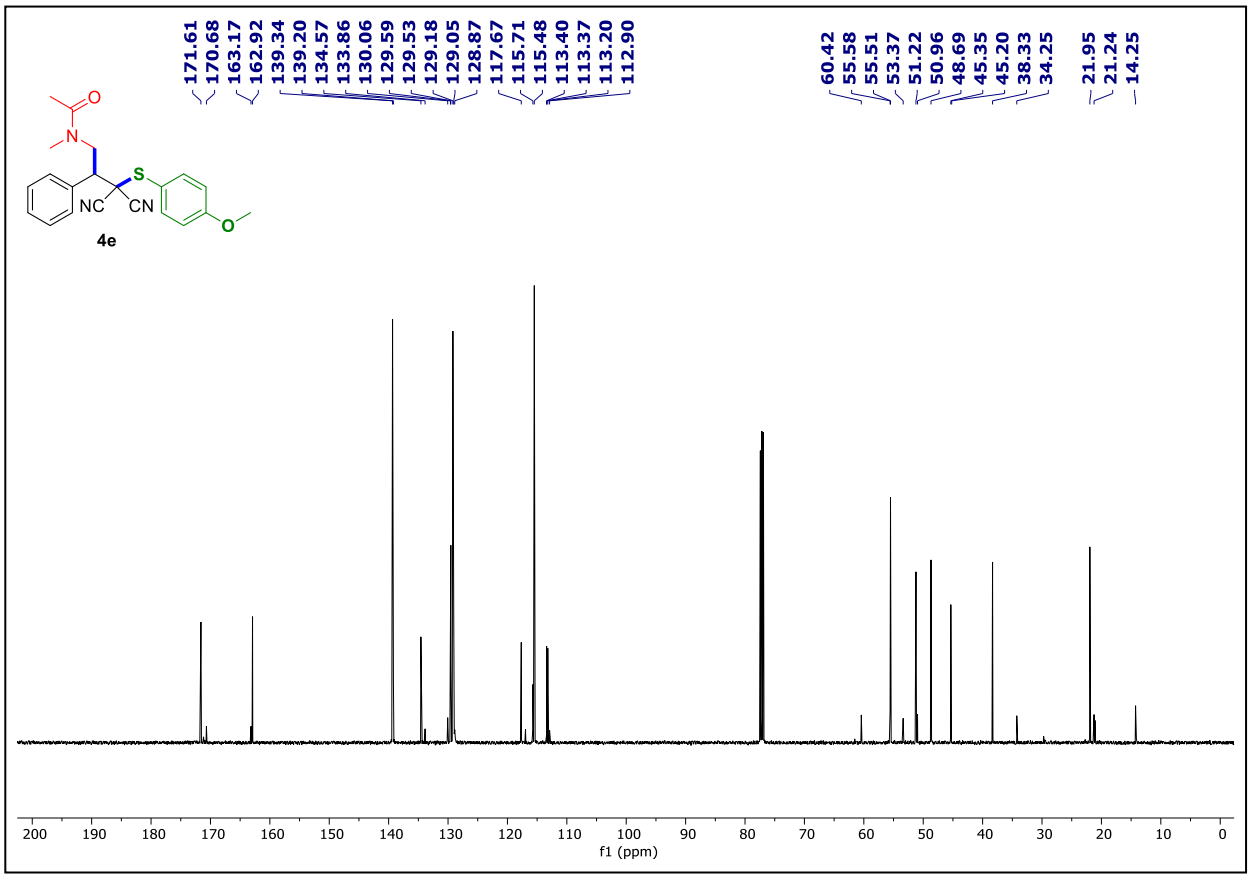
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4d**, (rr = 1: 0.2)



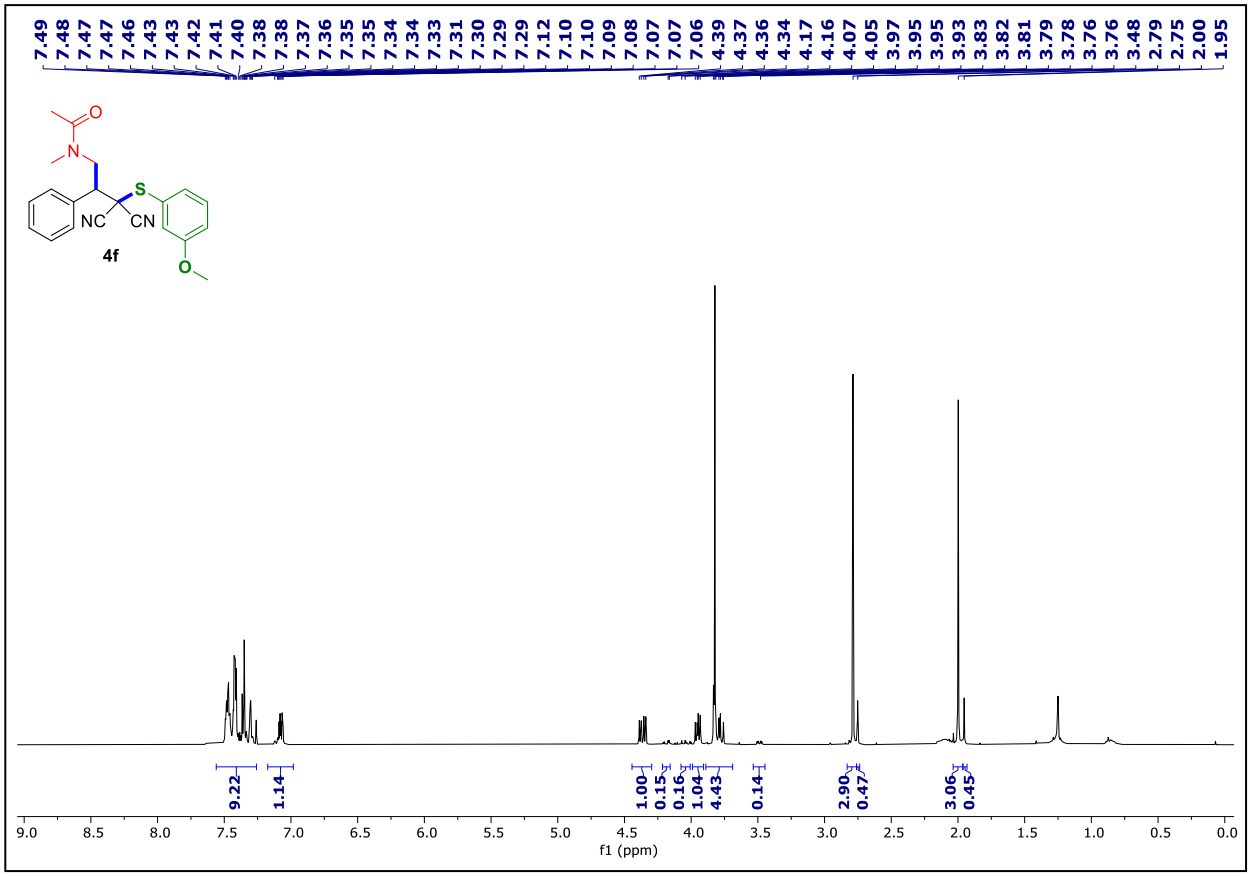
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**, (rr = 1: 0.2)



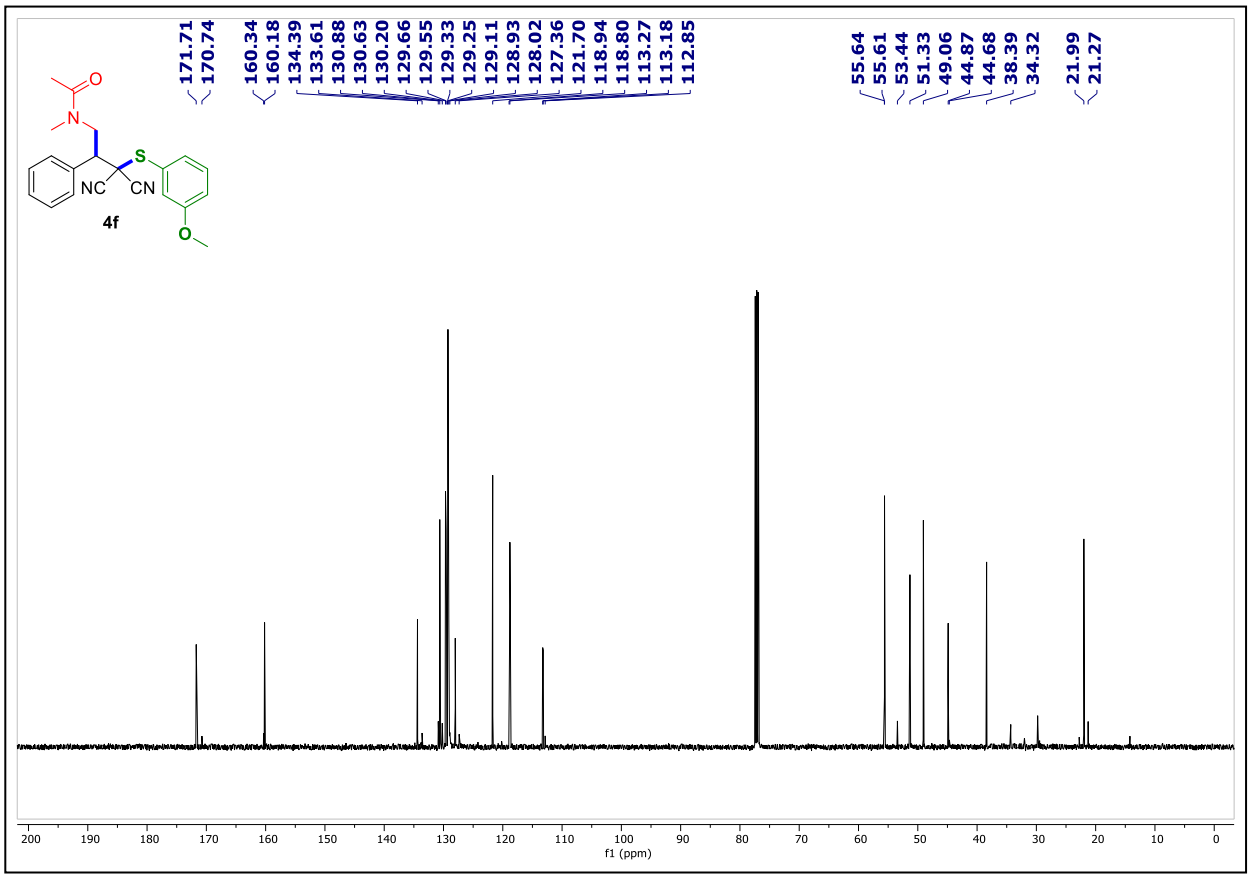
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4e**, (rr = 1: 0.2)



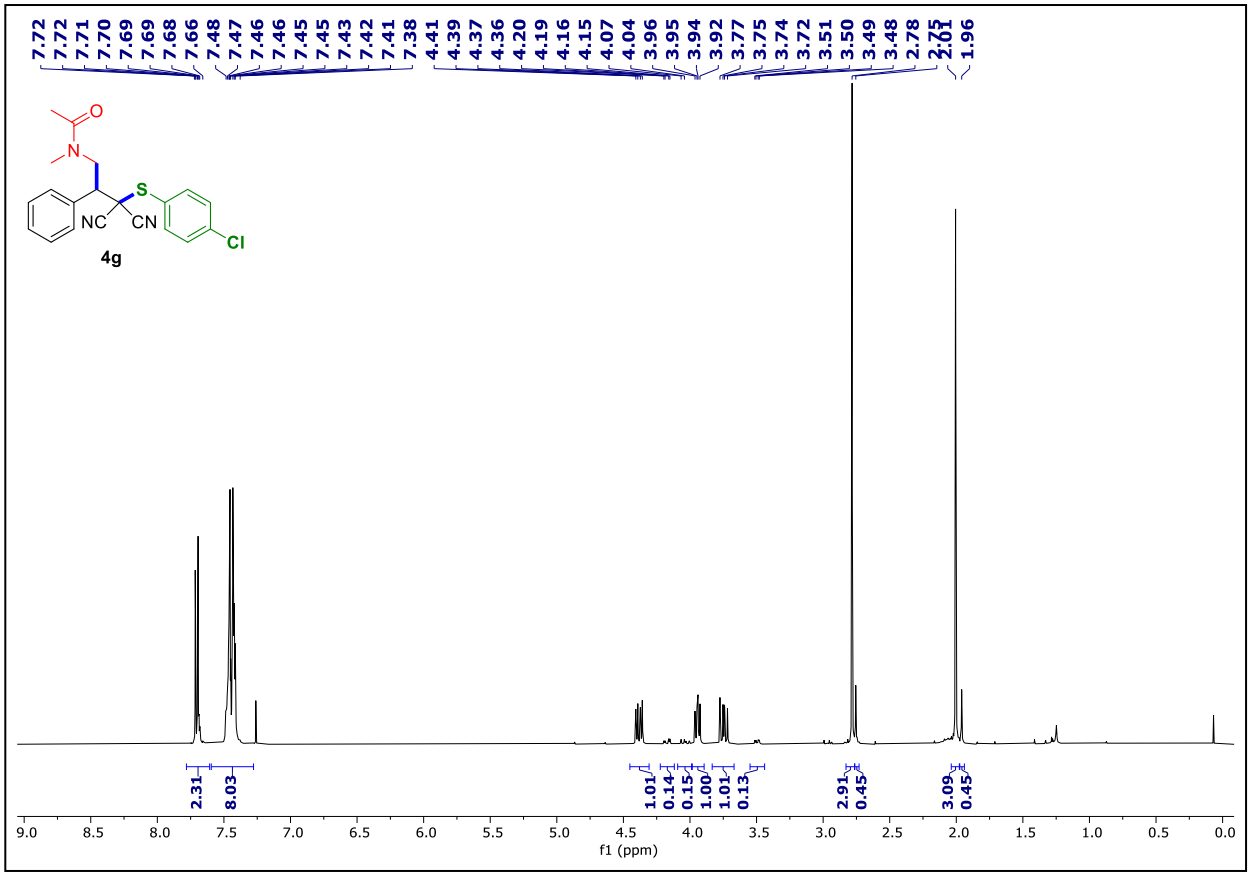
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4f**, (rr = 1: 0.15)



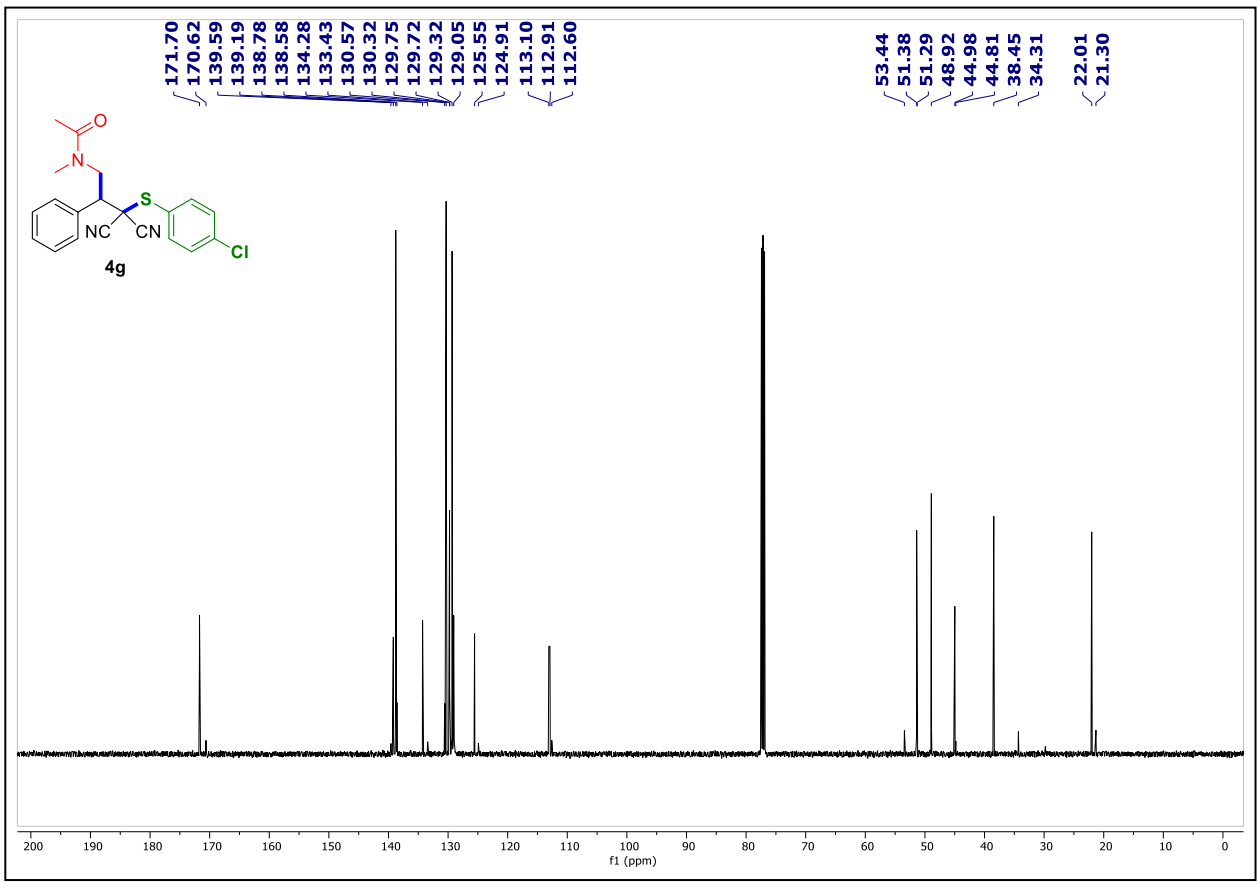
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4f**, (rr = 1: 0.15)



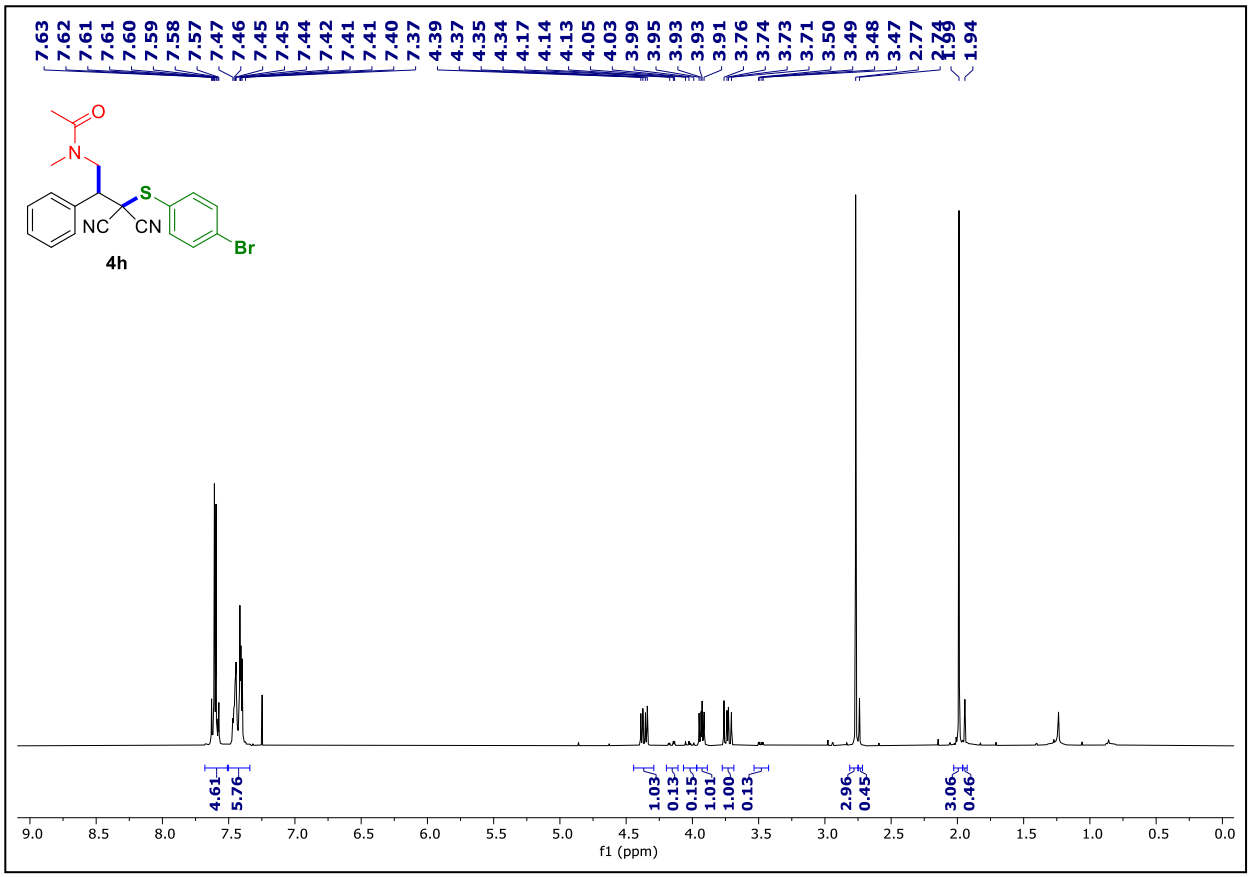
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4g**, (rr = 1: 0.15)



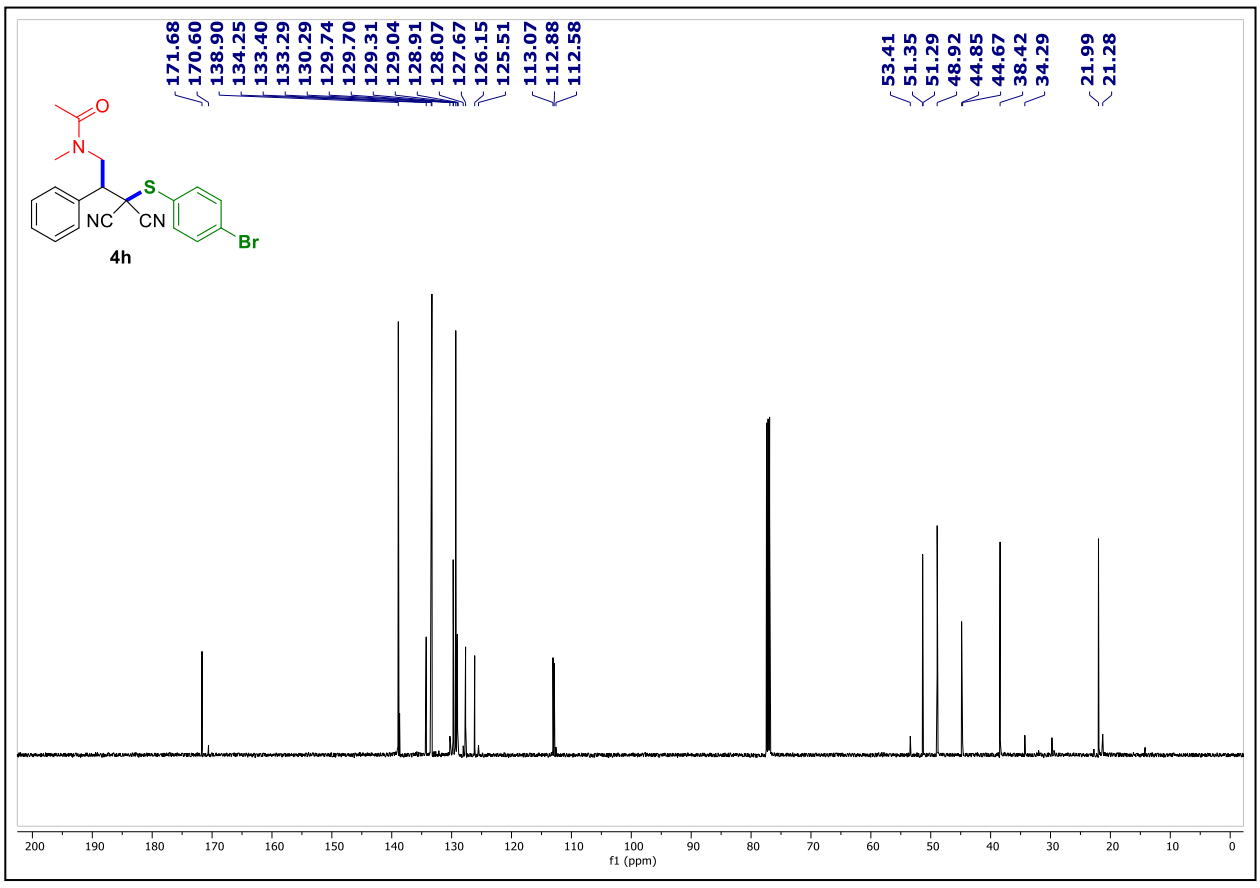
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4g**, (rr = 1: 0.15)



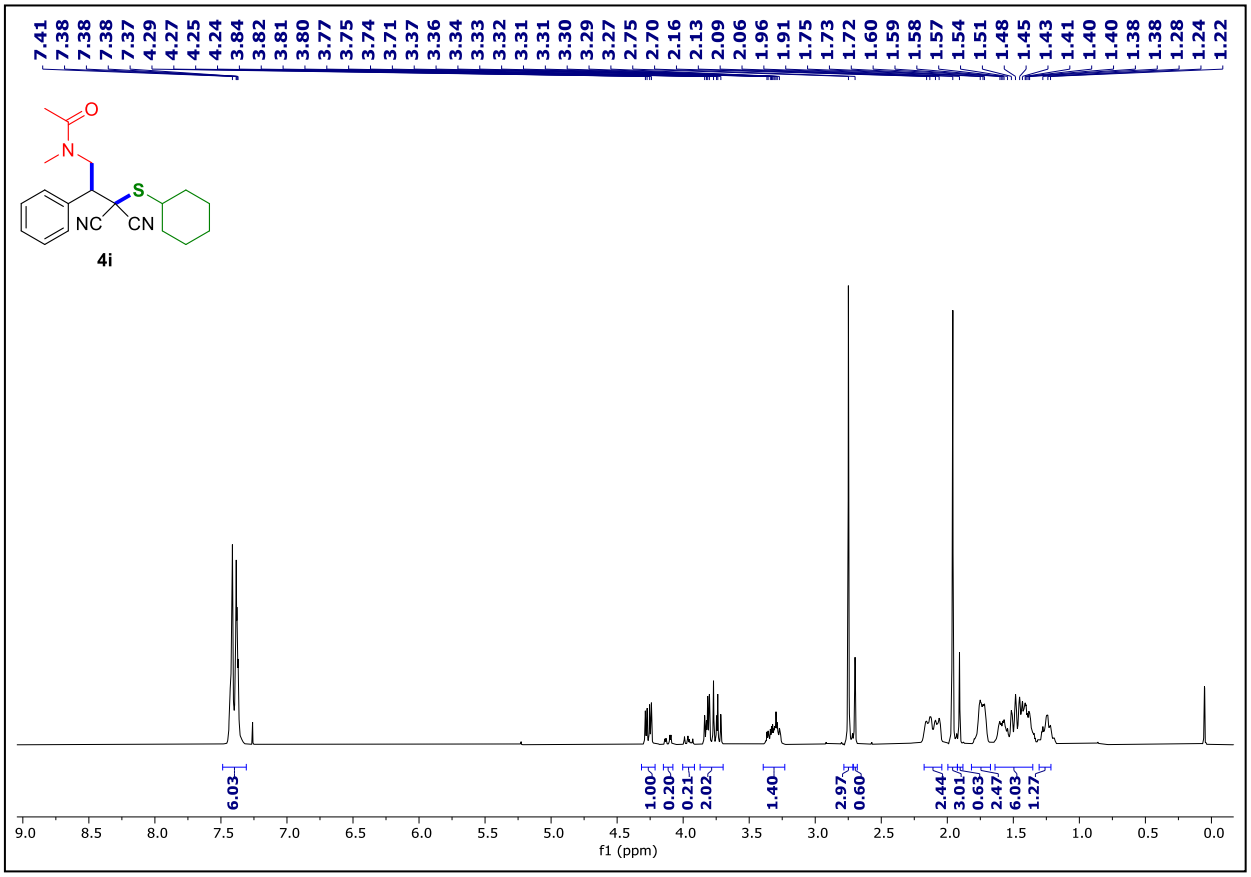
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**, (rr = 1: 0.15)



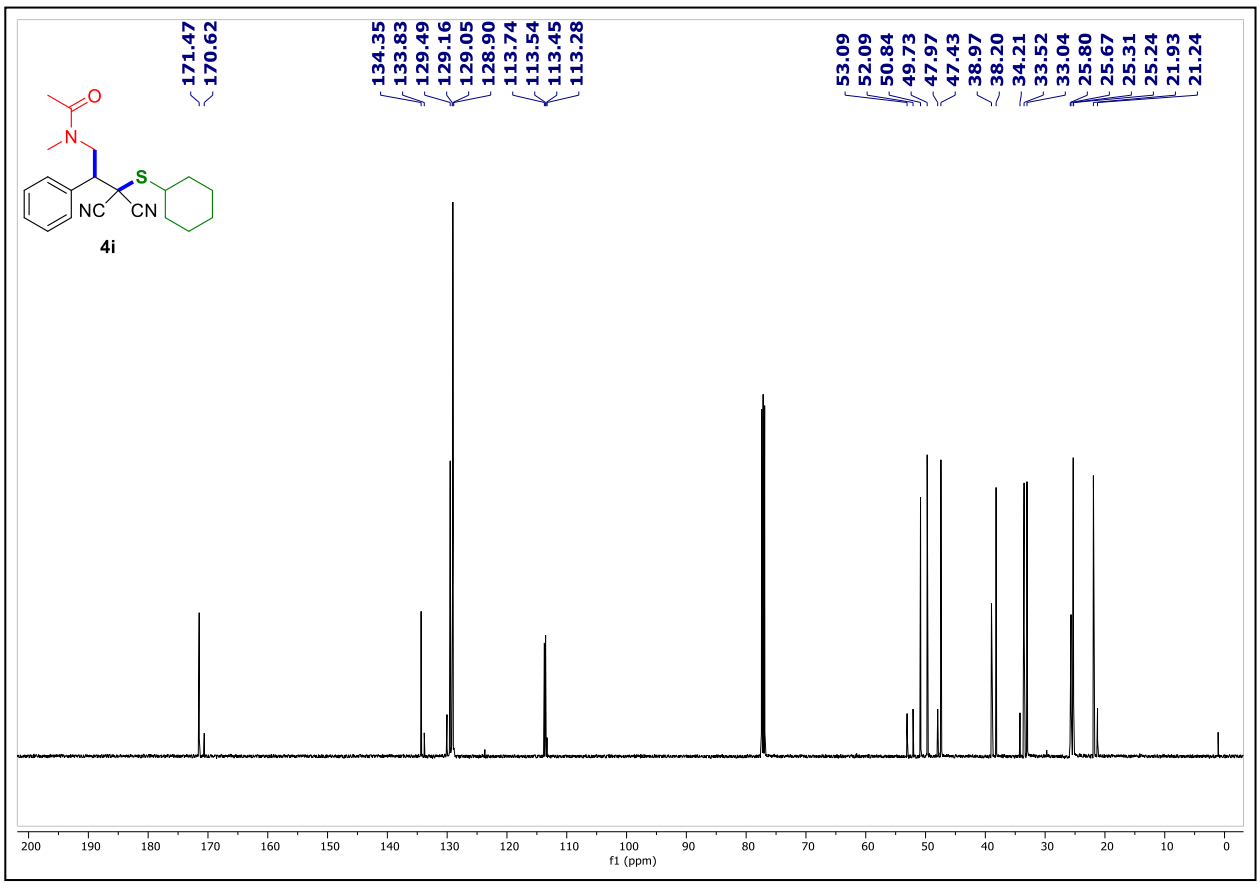
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h**, (rr = 1: 0.15)



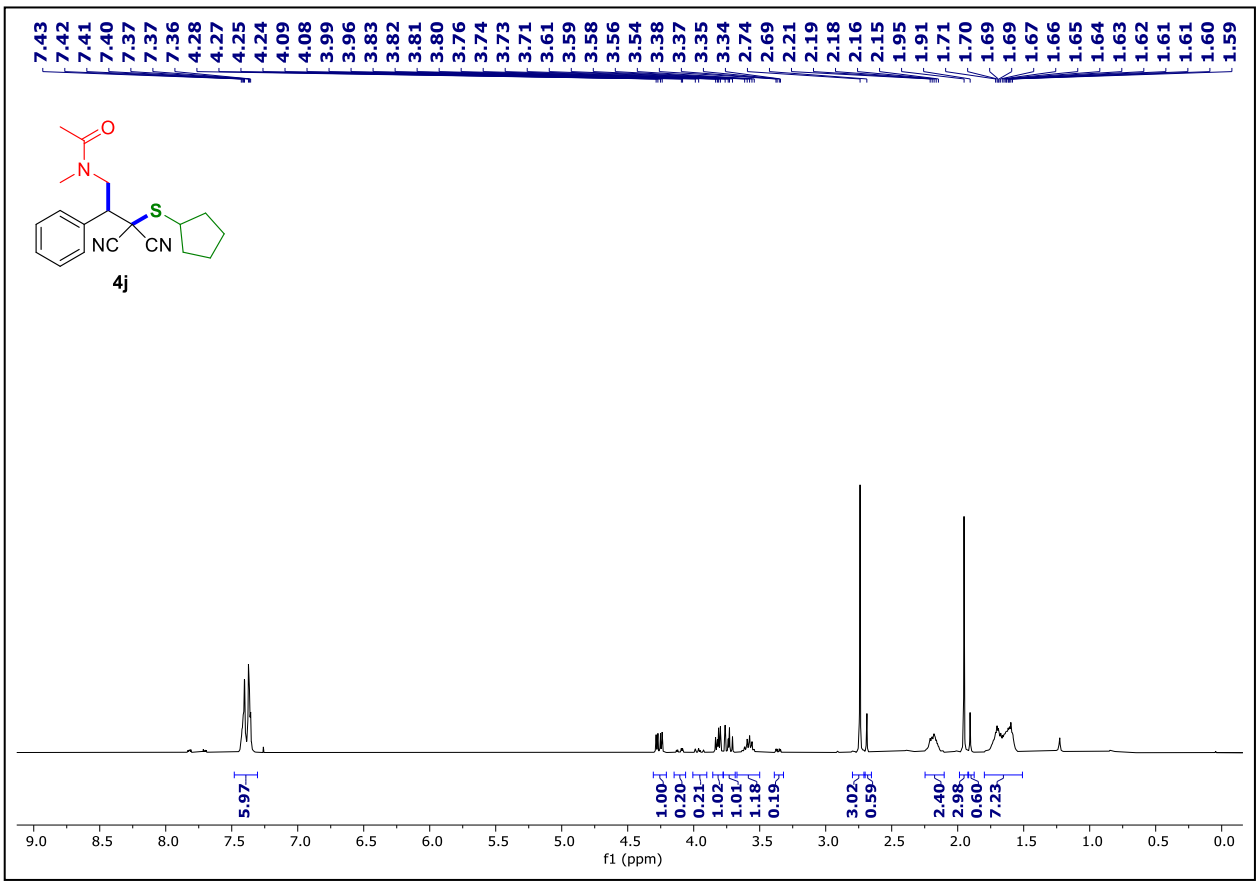
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4i**, (rr = 1: 0.2)



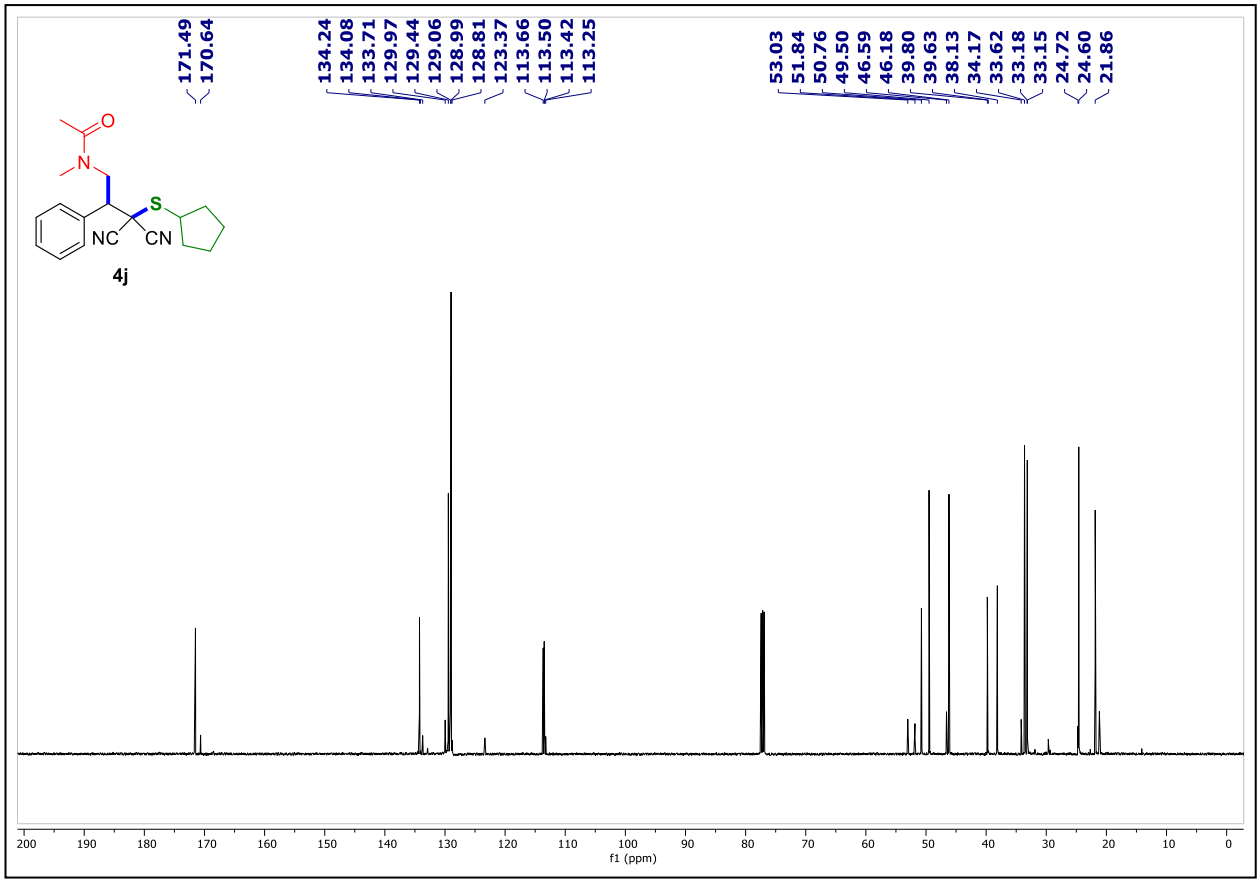
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4i**, (rr = 1: 0.2)



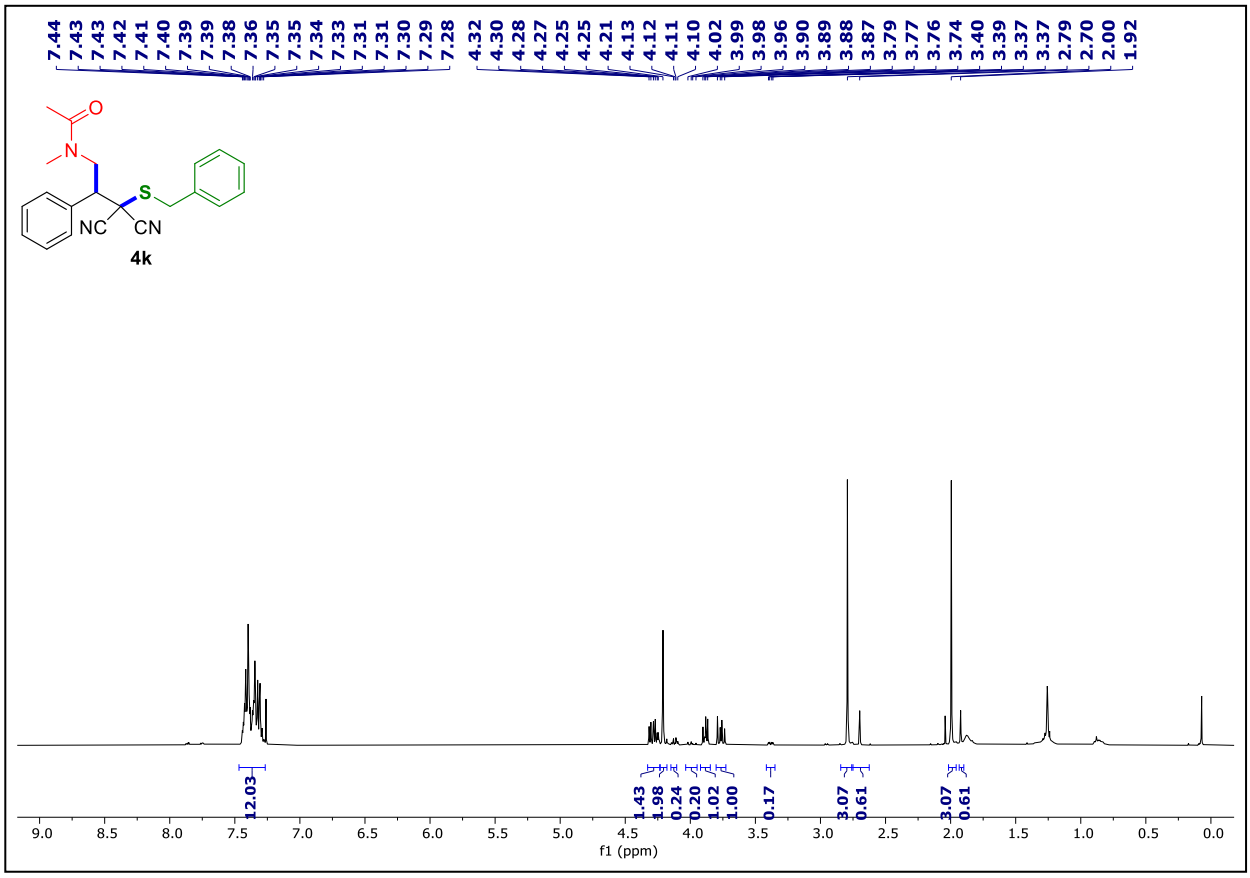
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4j**, (rr = 1: 0.2)



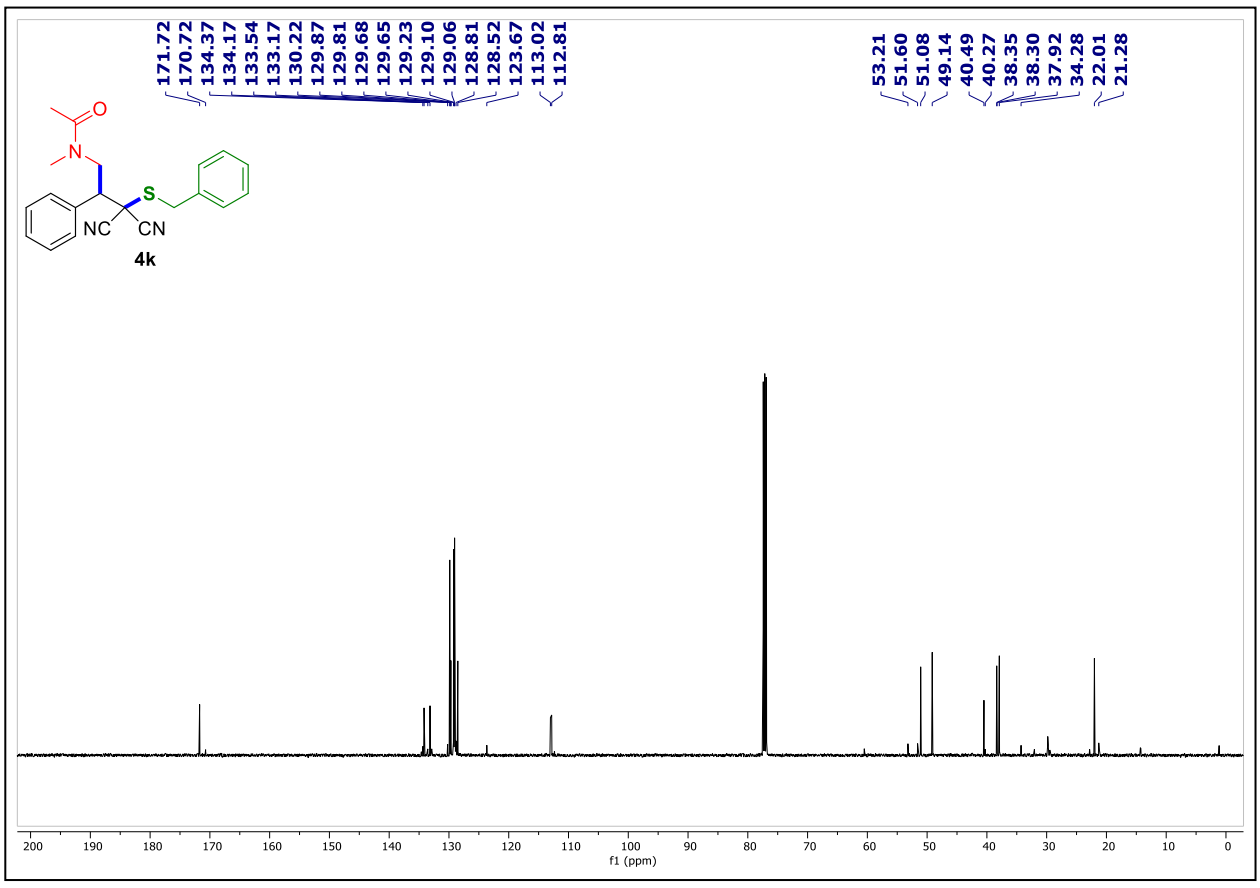
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4j**, (rr = 1: 0.2)



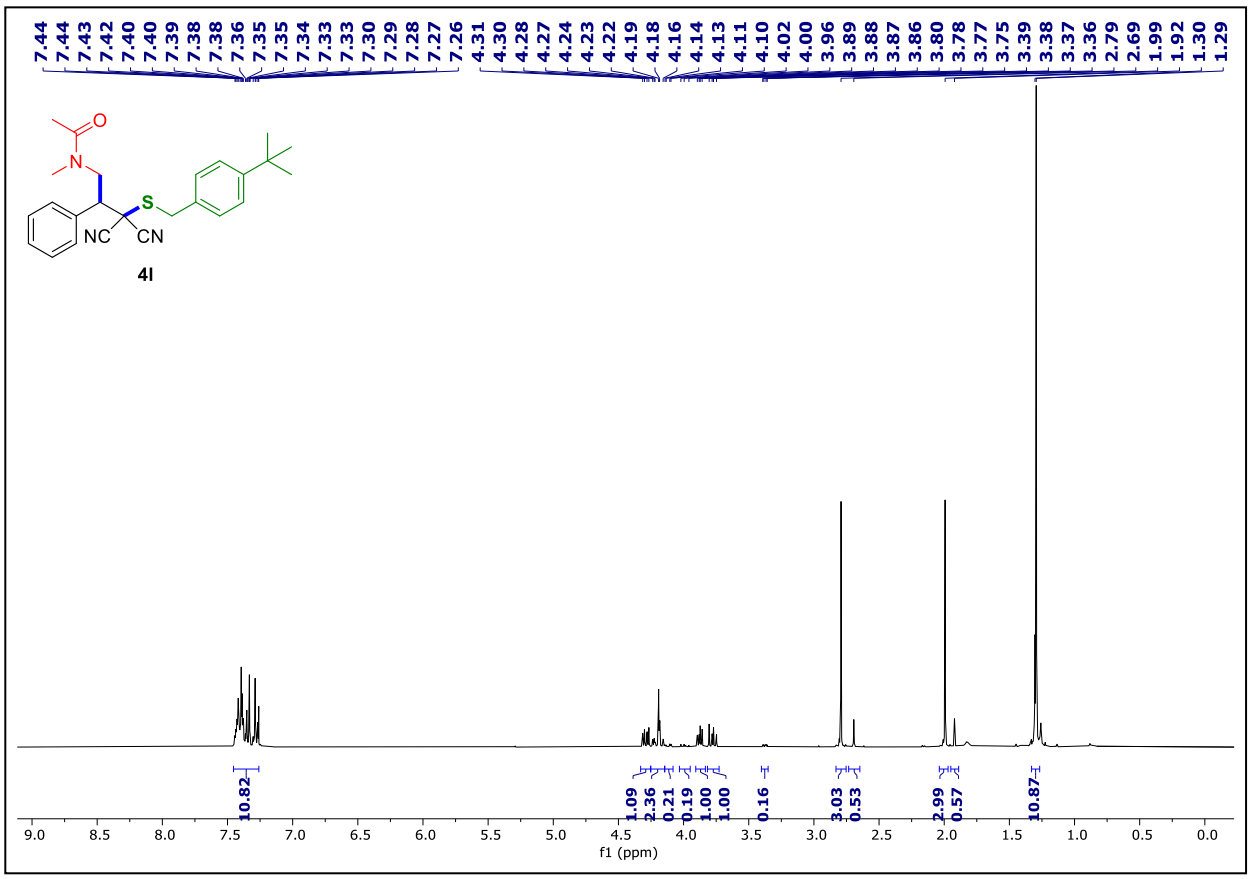
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4k**, (rr = 1: 0.2)



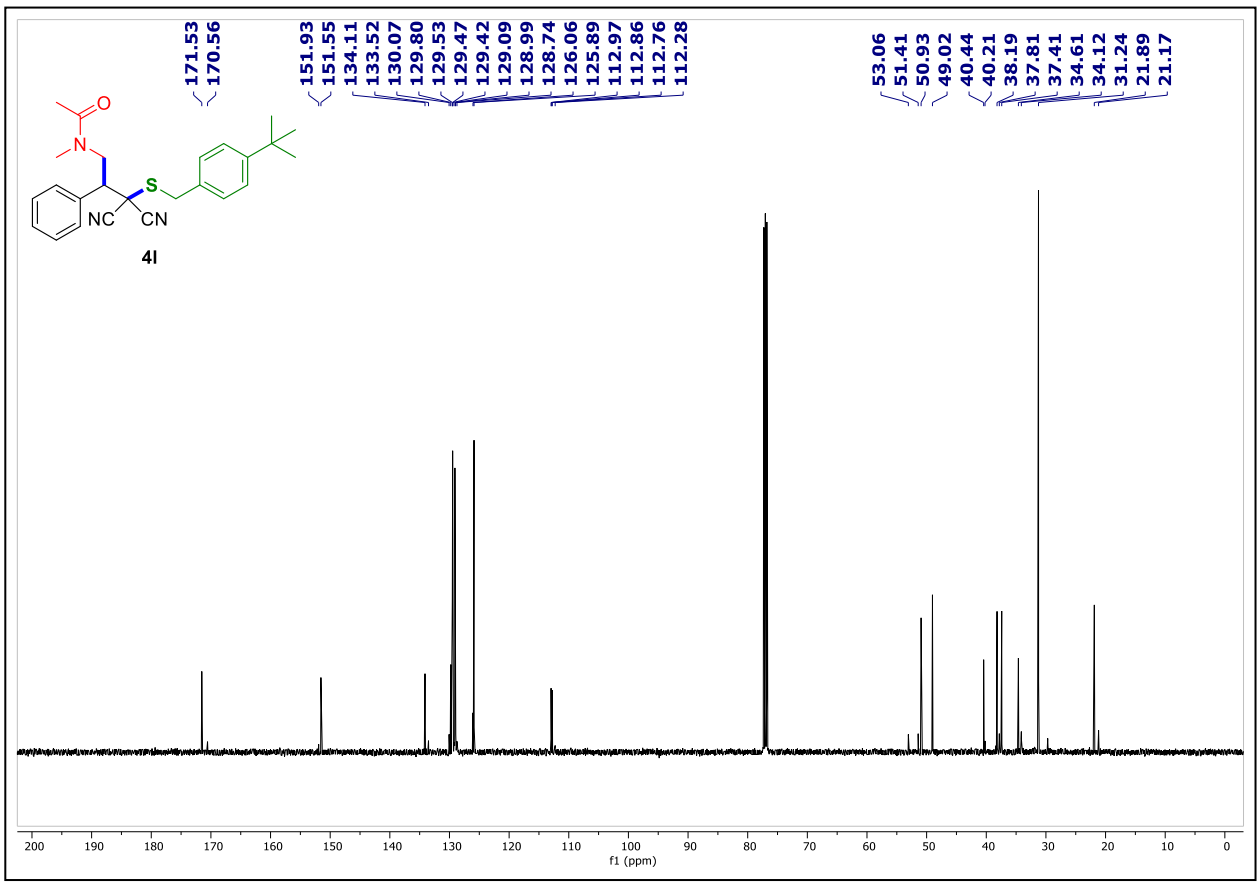
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4k**, (rr = 1: 0.2)



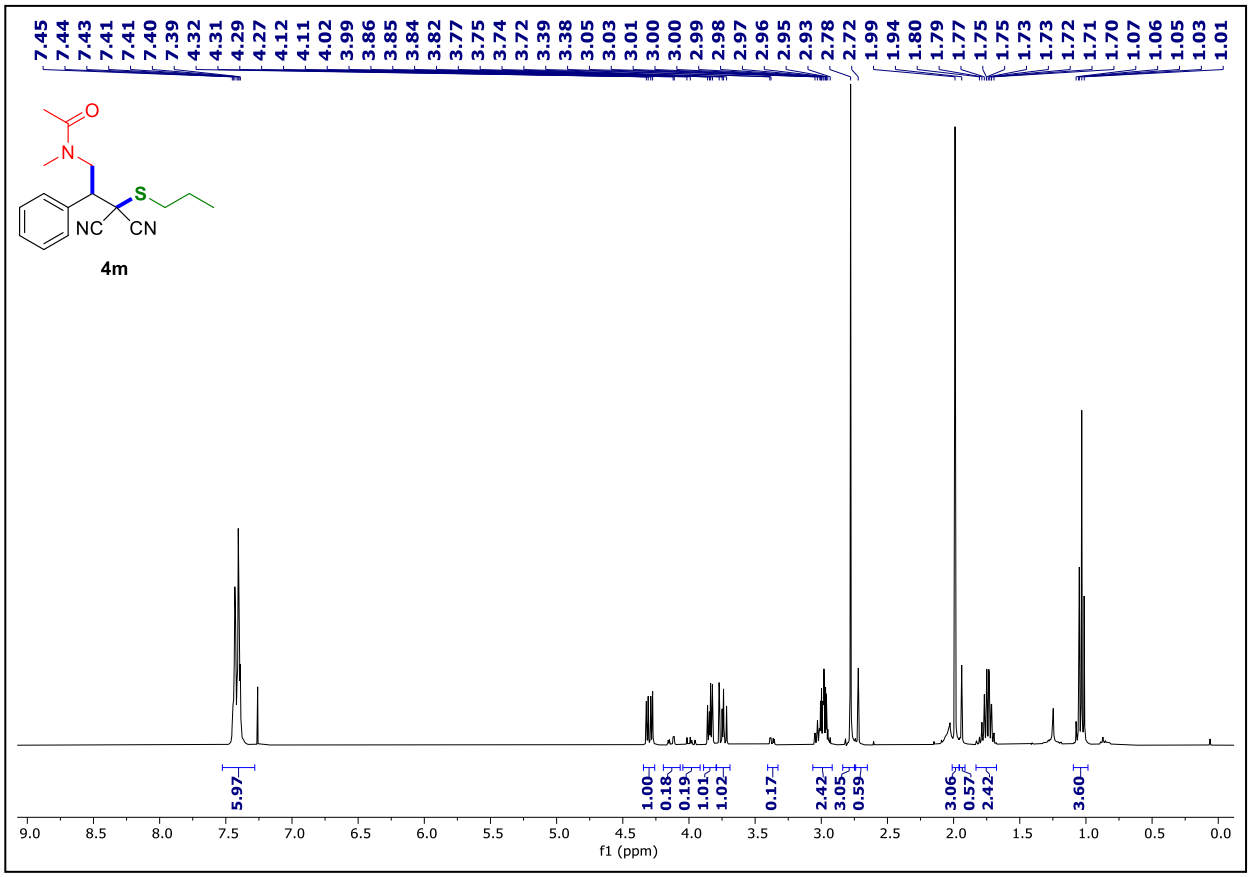
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4l**, (rr = 1: 0.2)



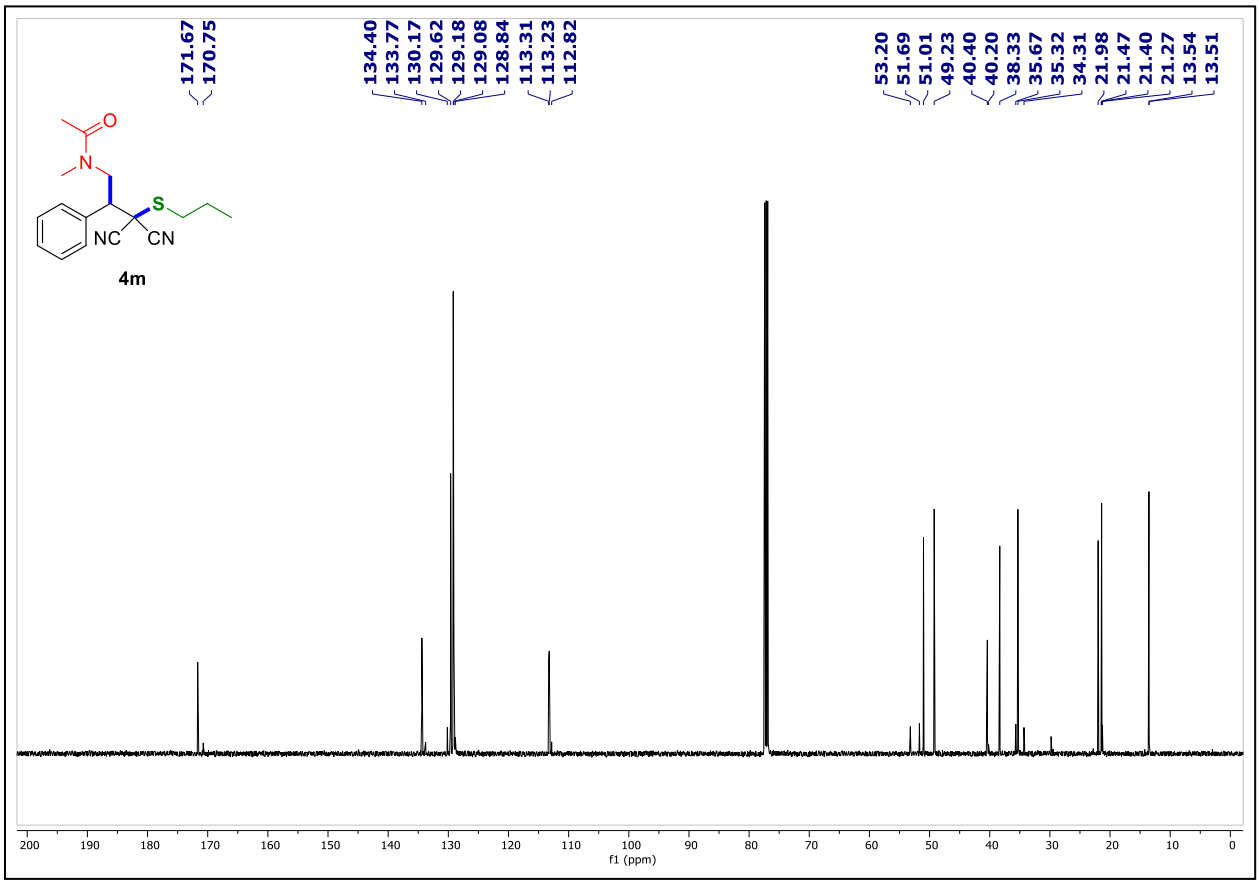
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4l**, (rr = 1: 0.2)



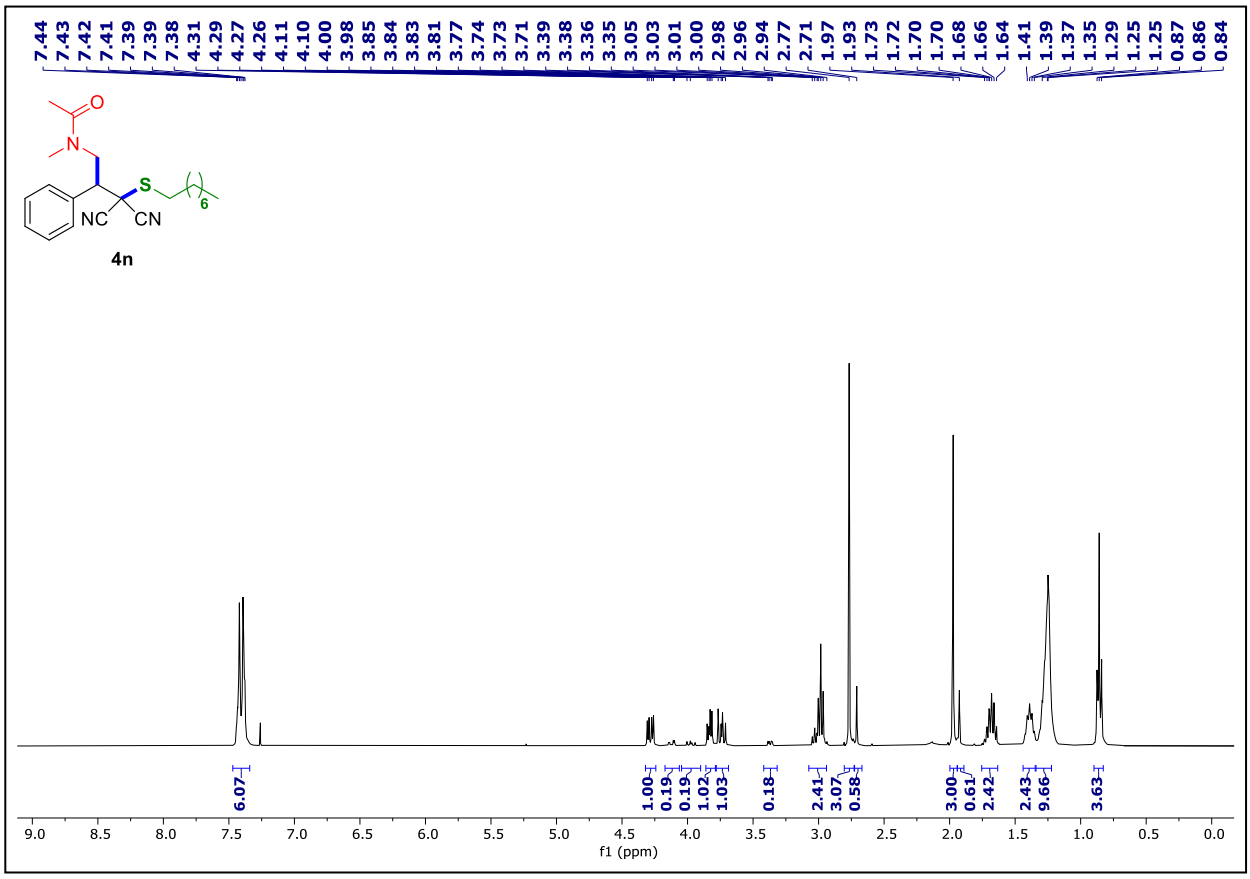
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4m**, (rr = 1: 0.2)



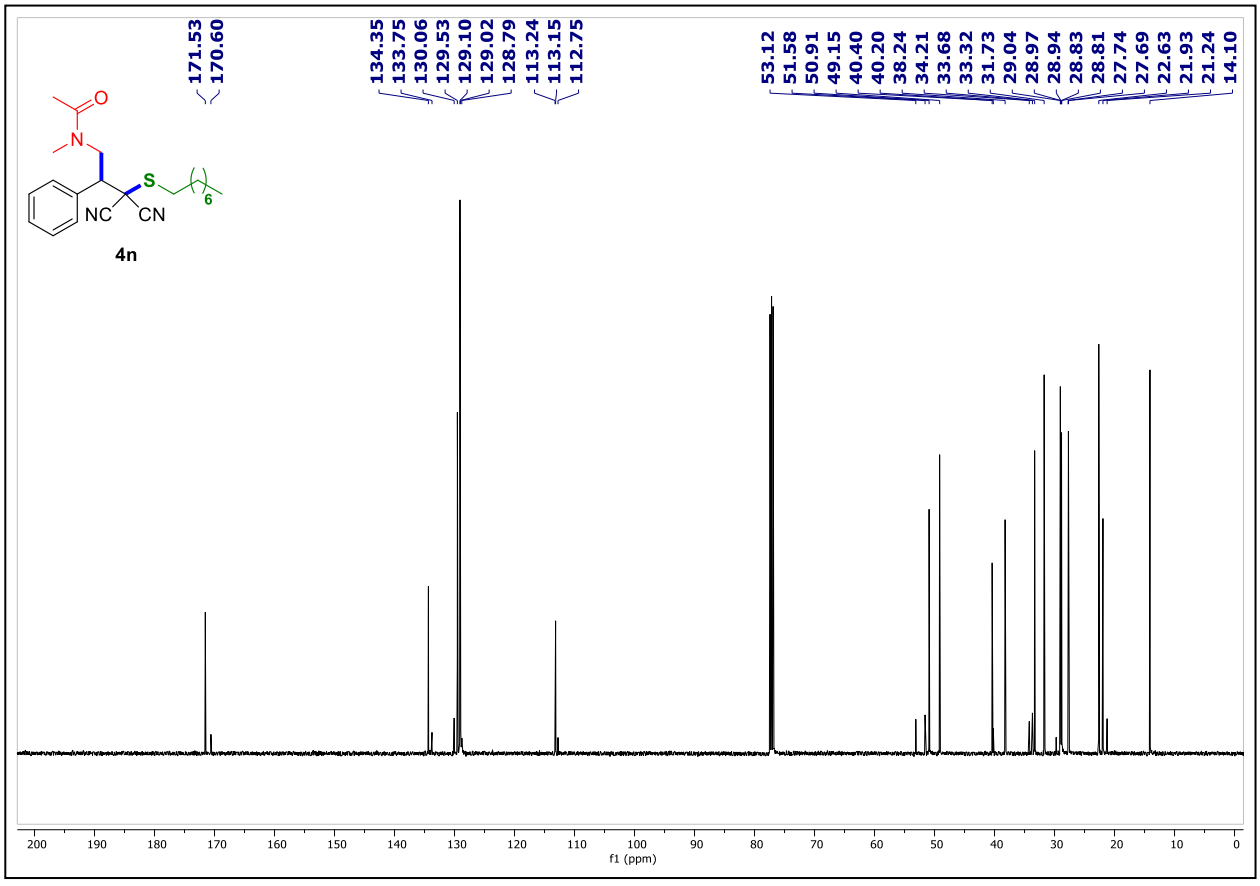
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4m**, (rr = 1: 0.2)



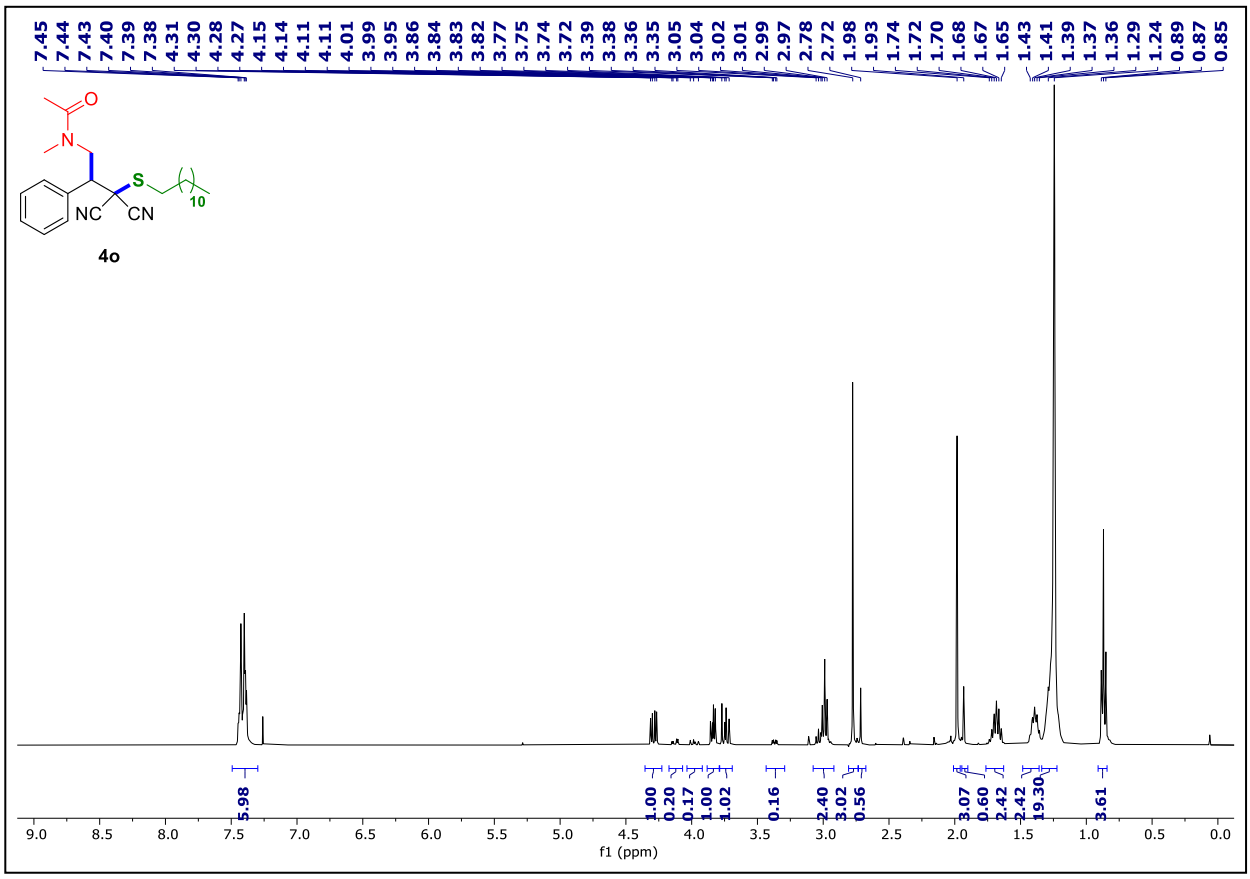
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4n**, (rr = 1: 0.2)



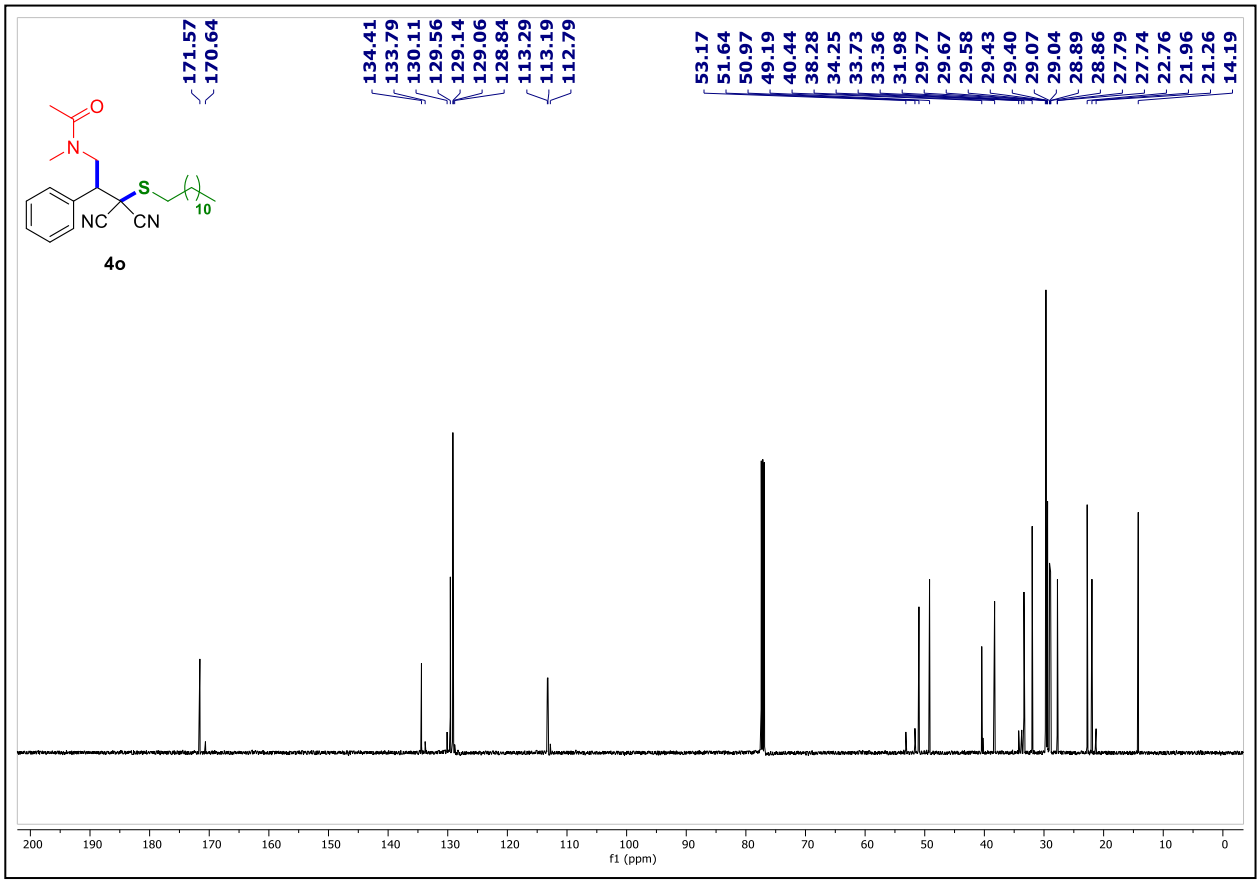
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4n**, (rr = 1: 0.2)



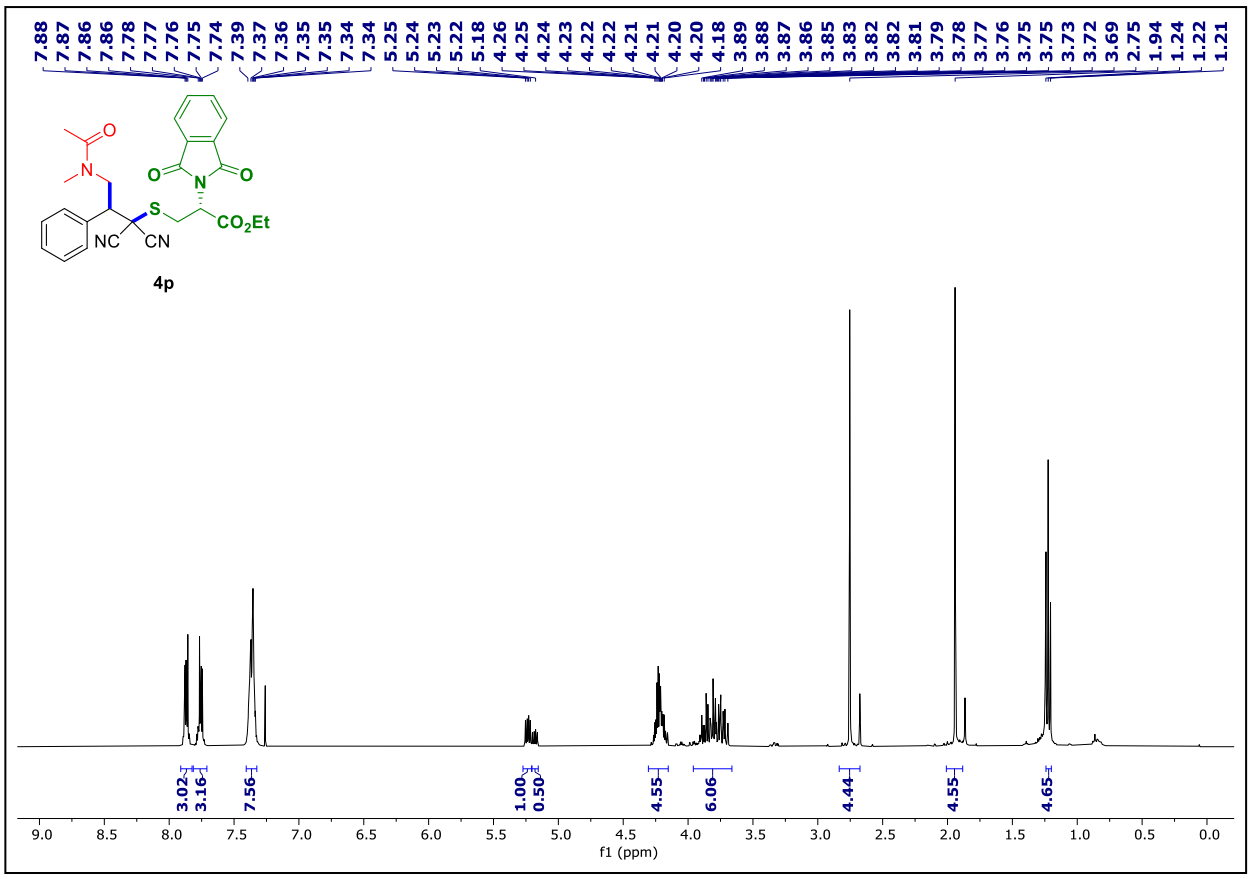
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4o**, (rr = 1: 0.2)



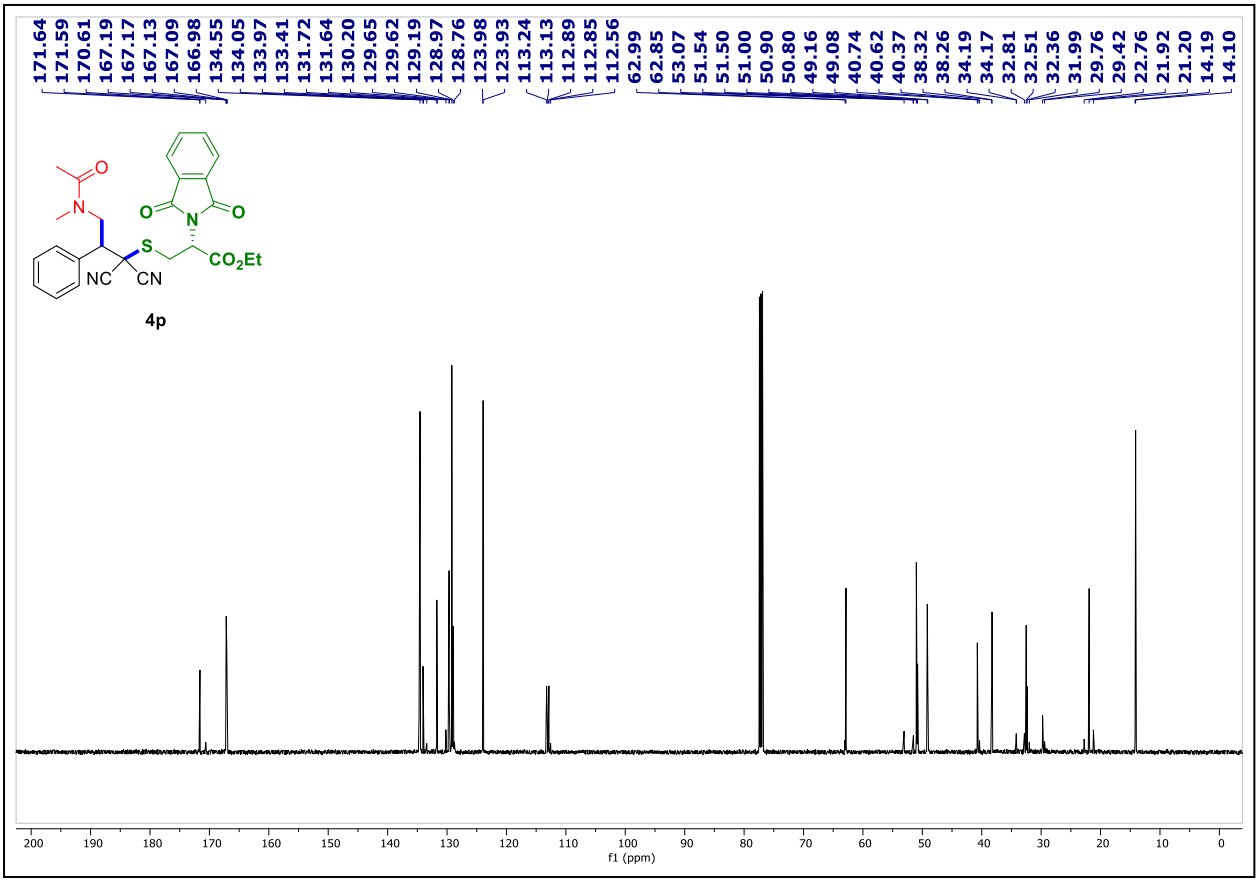
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4o**, (rr = 1: 0.2)



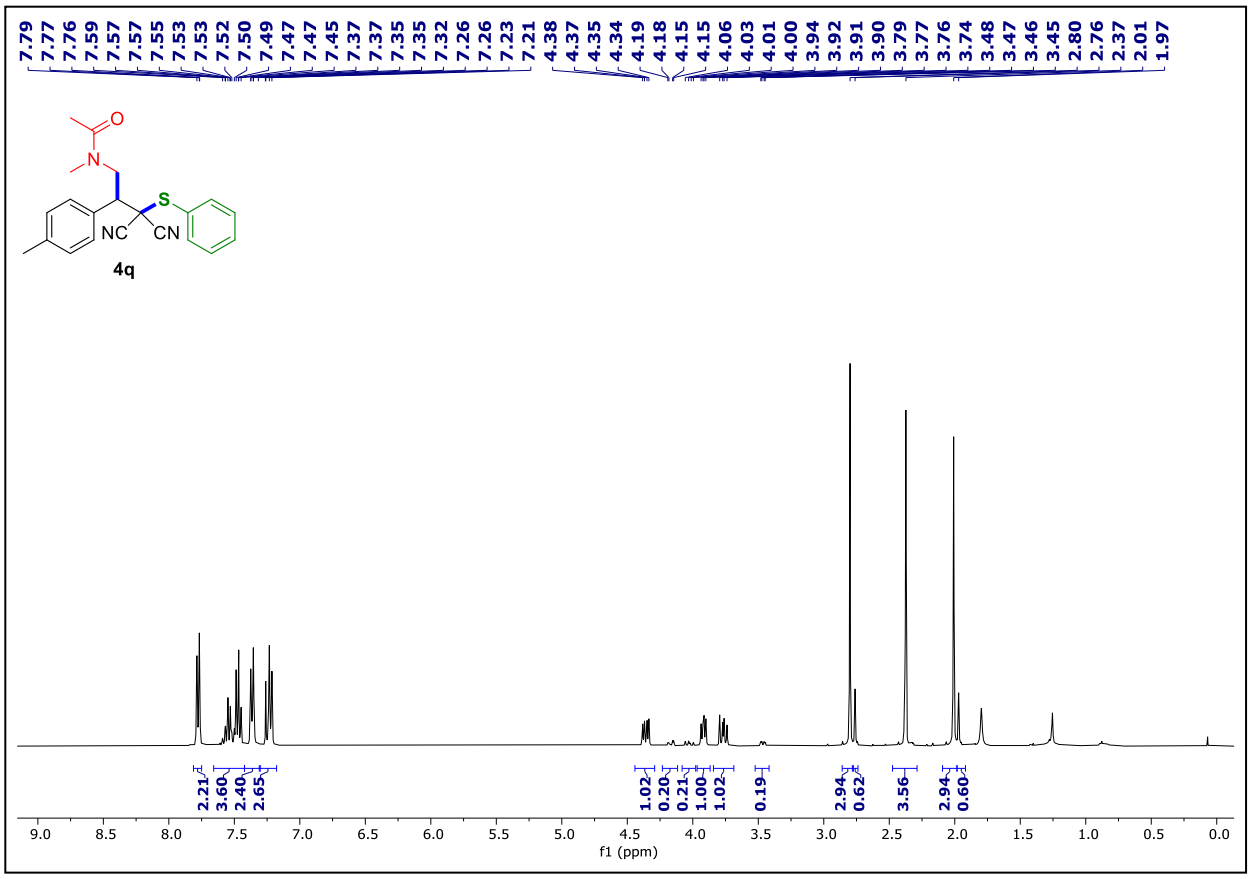
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4p**, (dr = 1: 0.5; rr = 1: 0.15)



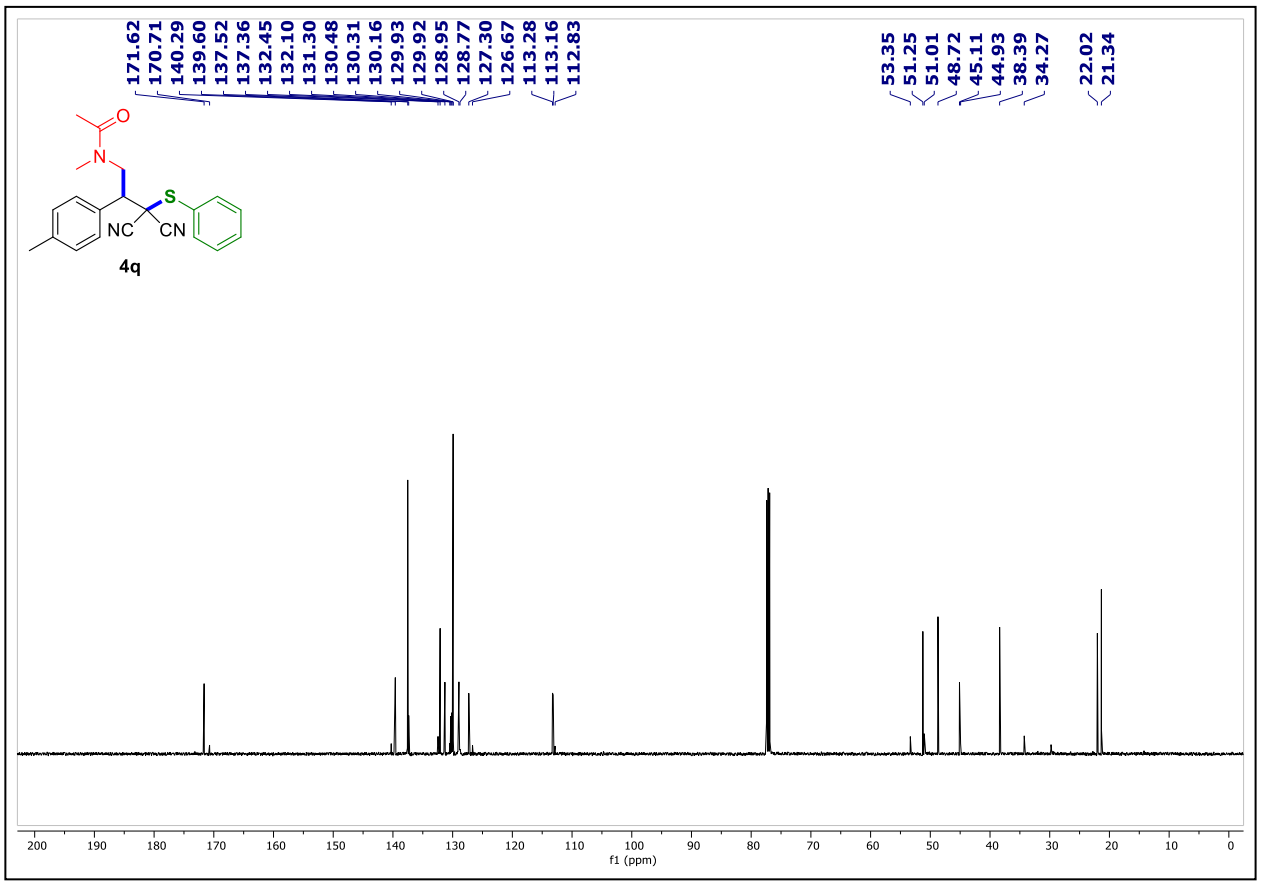
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4p**, (dr = 1: 0.5; rr = 1: 0.15)



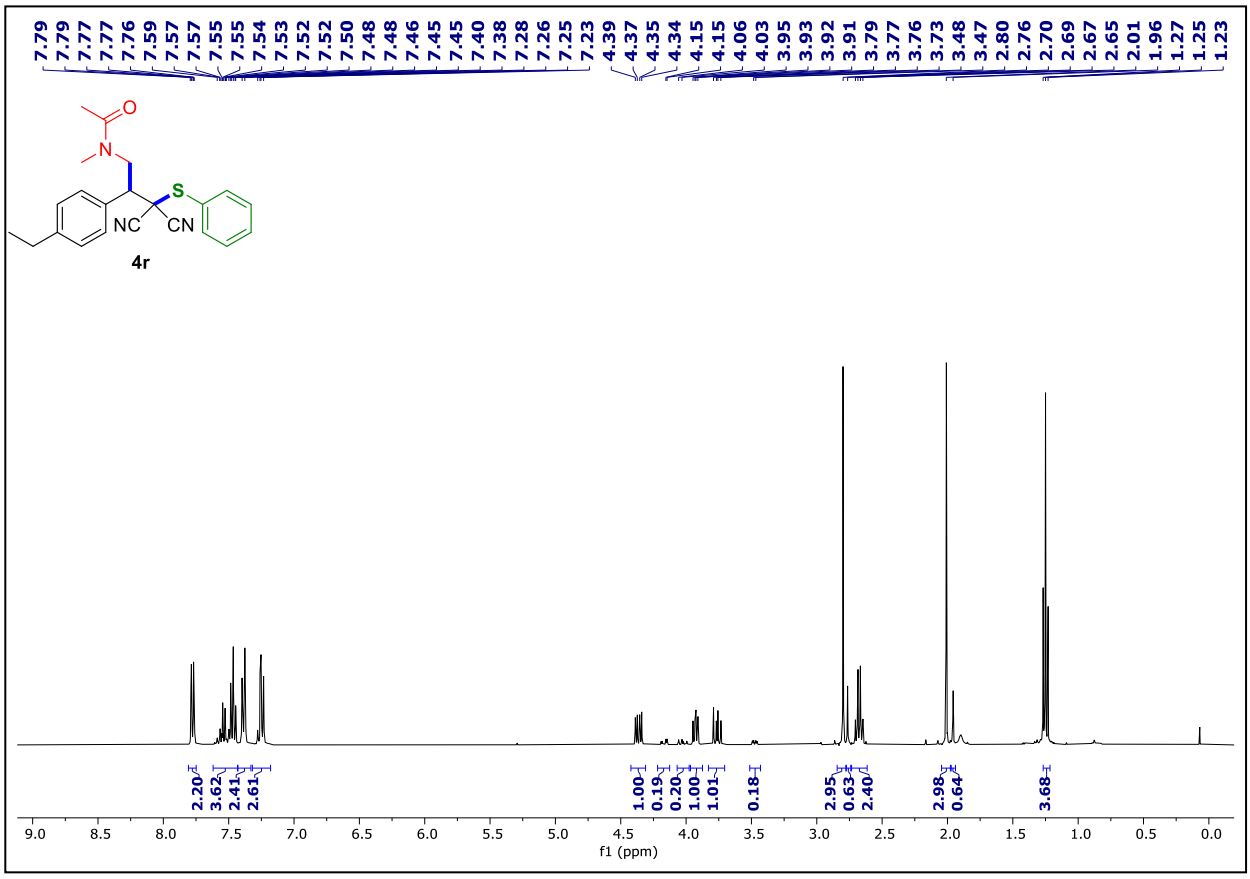
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4q**, (rr = 1: 0.2)



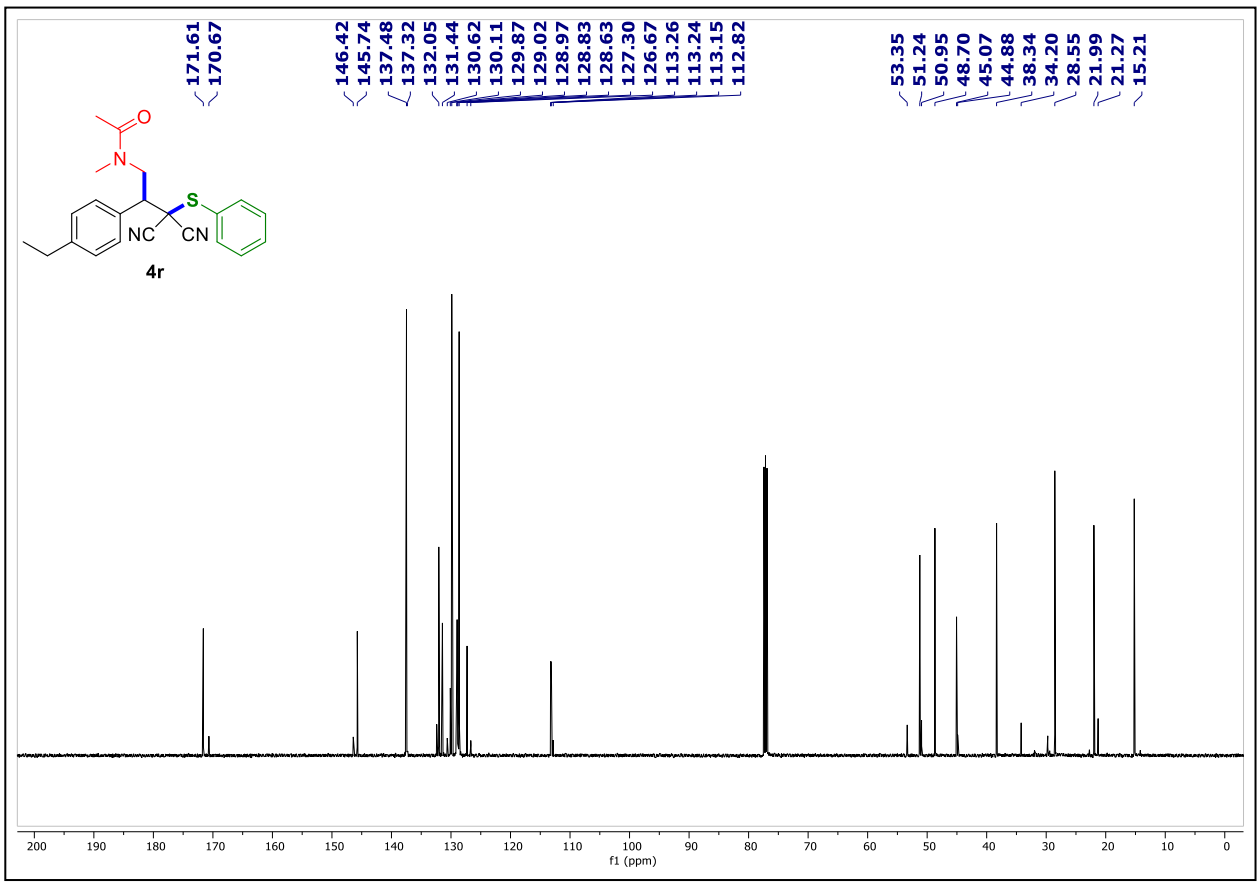
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4q**, (rr = 1: 0.2)



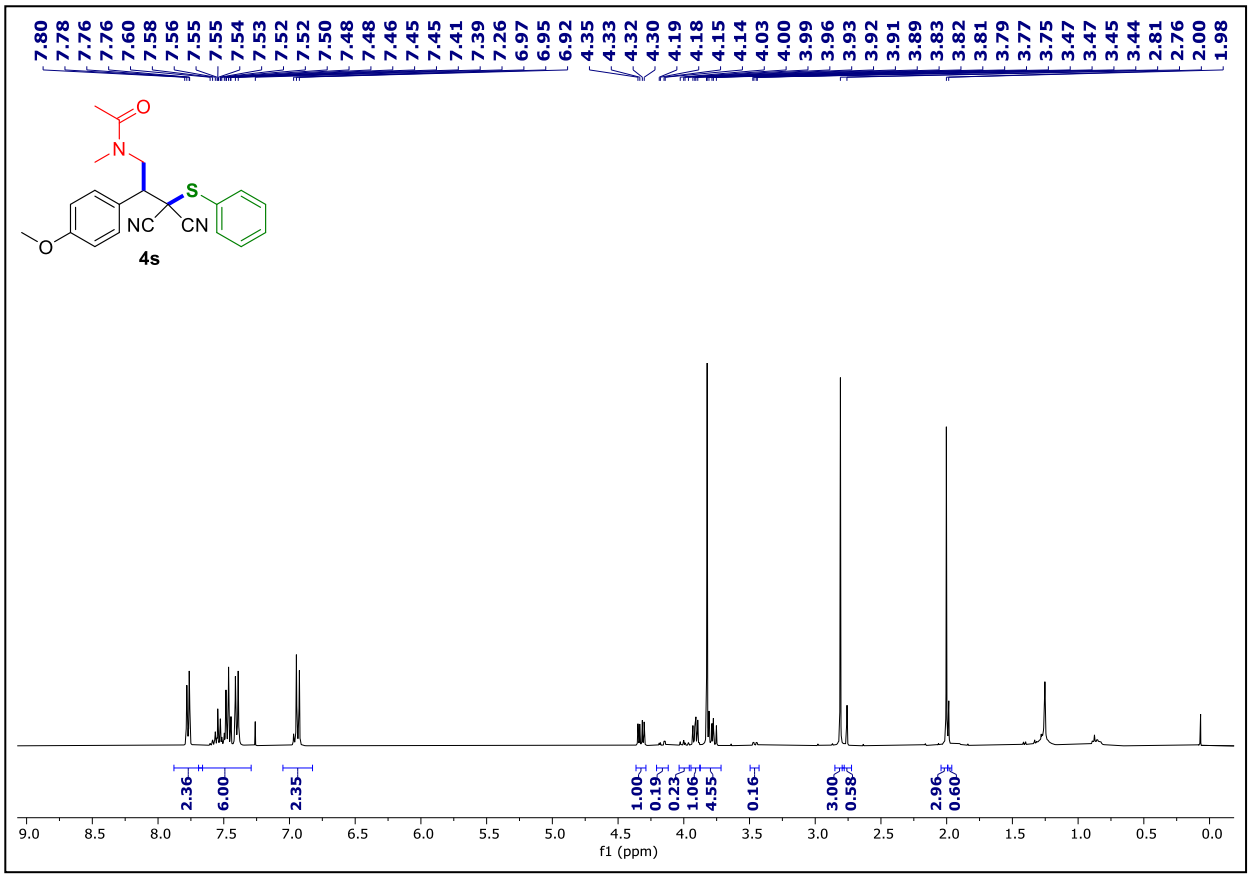
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4r**, (rr = 1: 0.2)



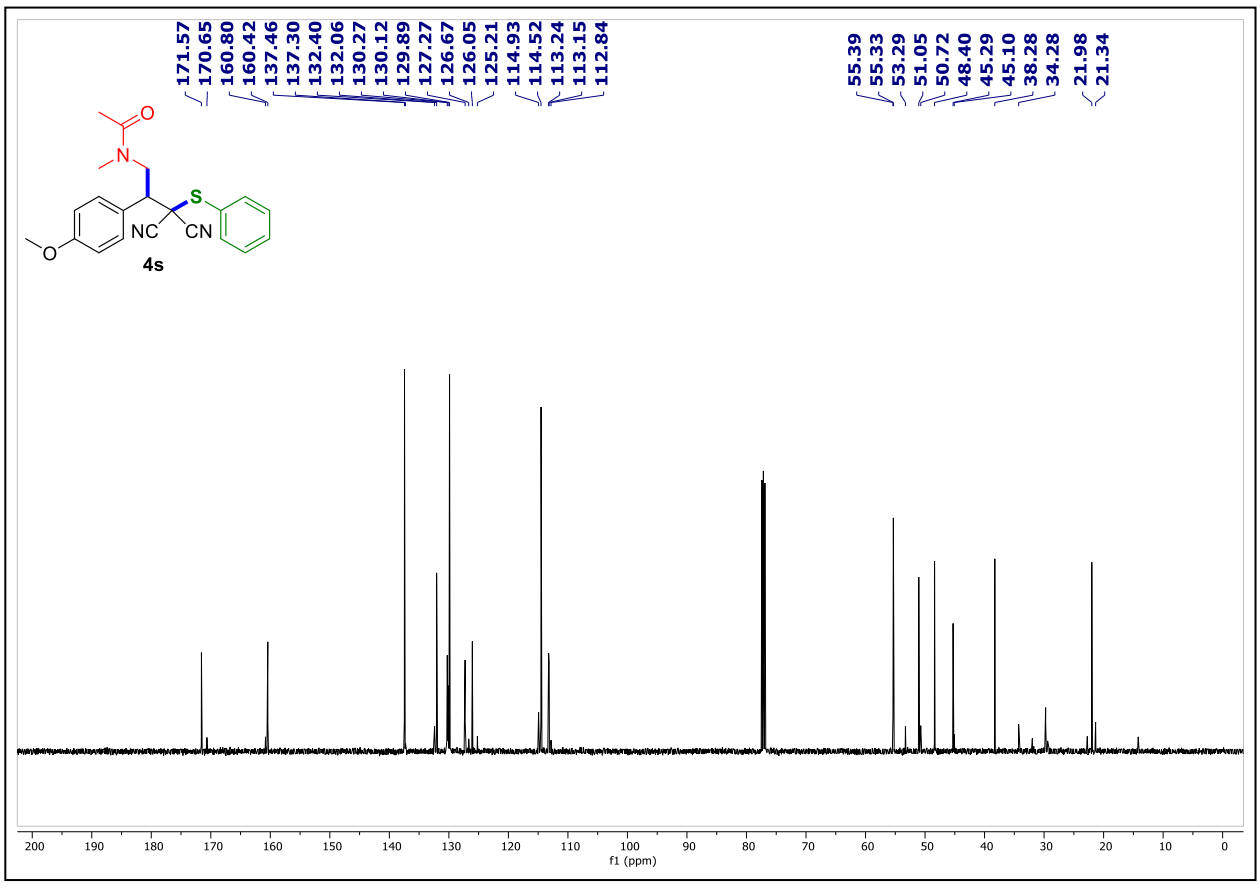
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4r**, (rr = 1: 0.2)



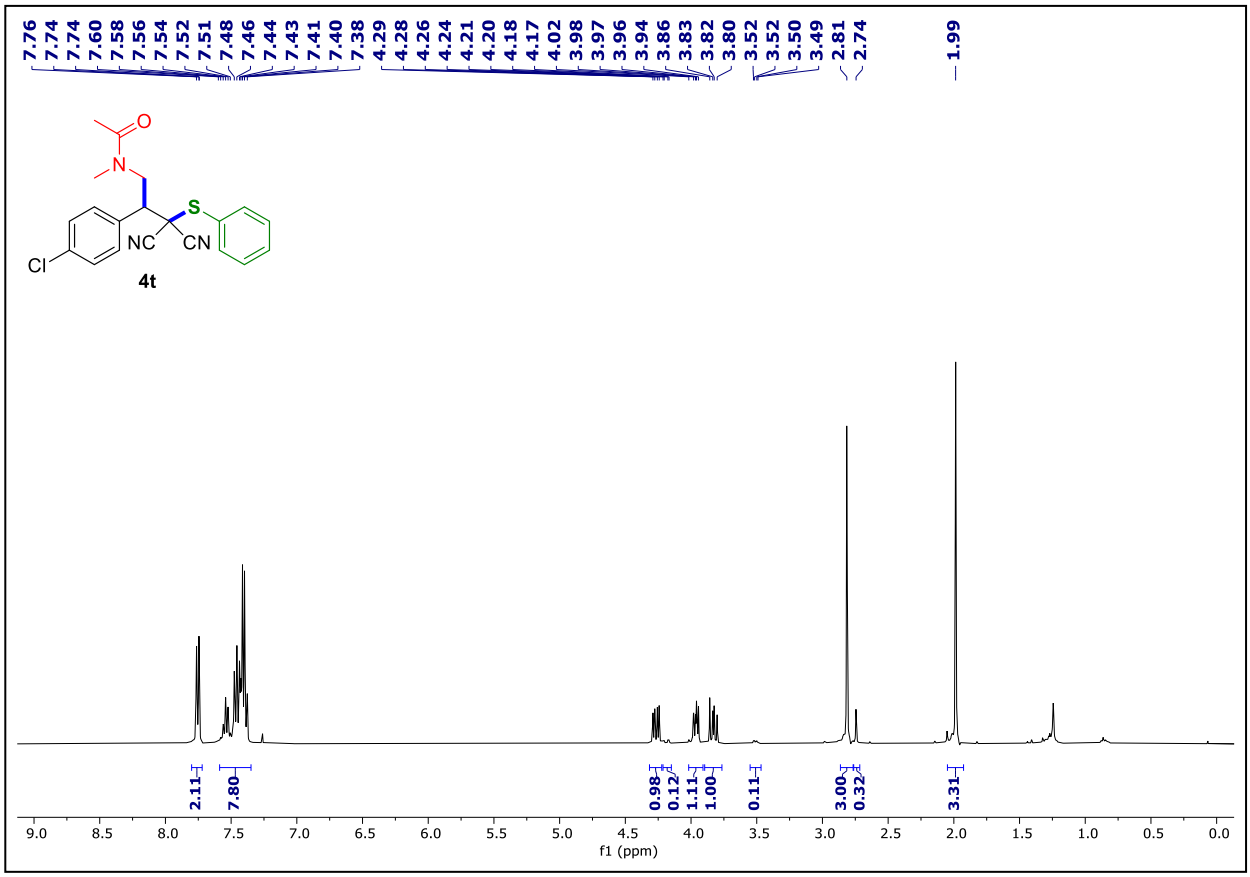
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4s**, (rr = 1: 0.2)



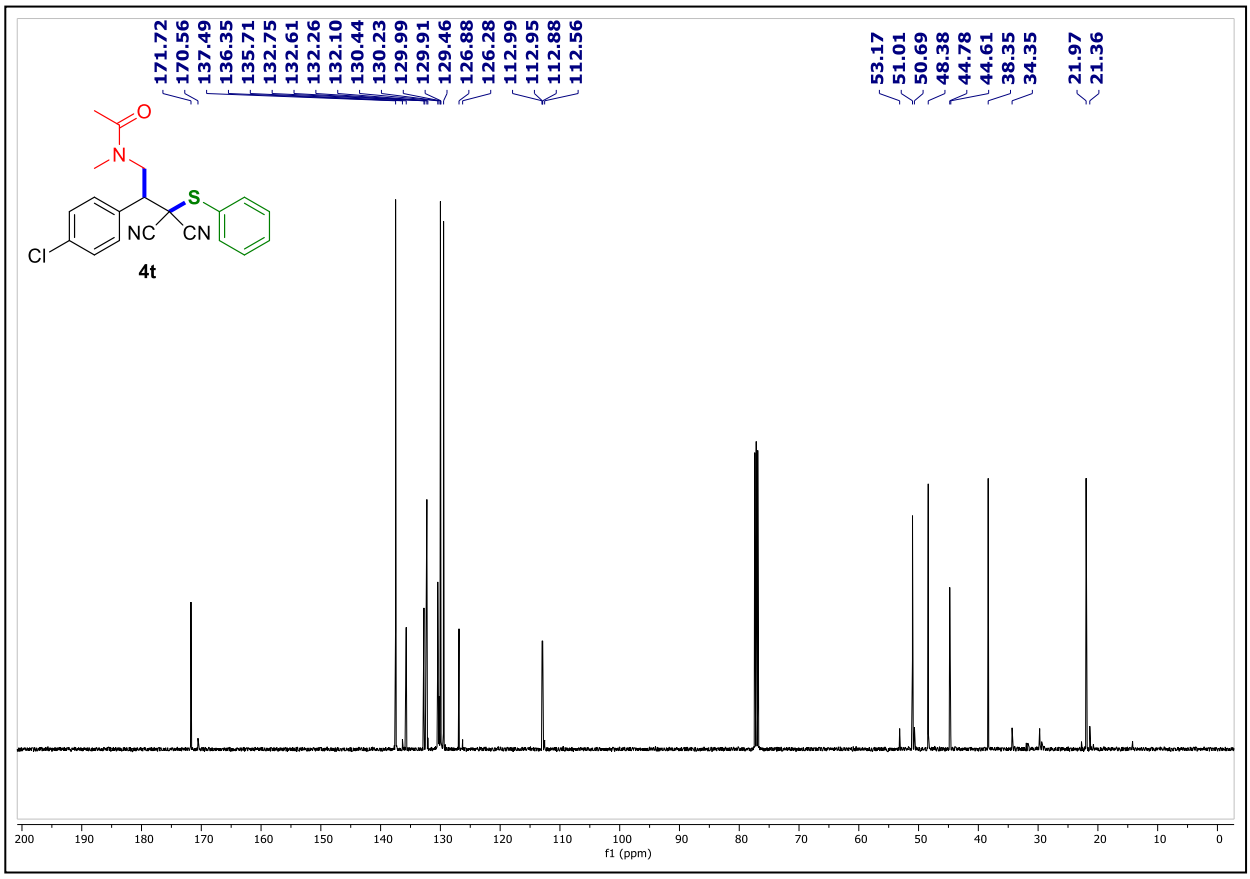
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4s**, (rr = 1: 0.2)



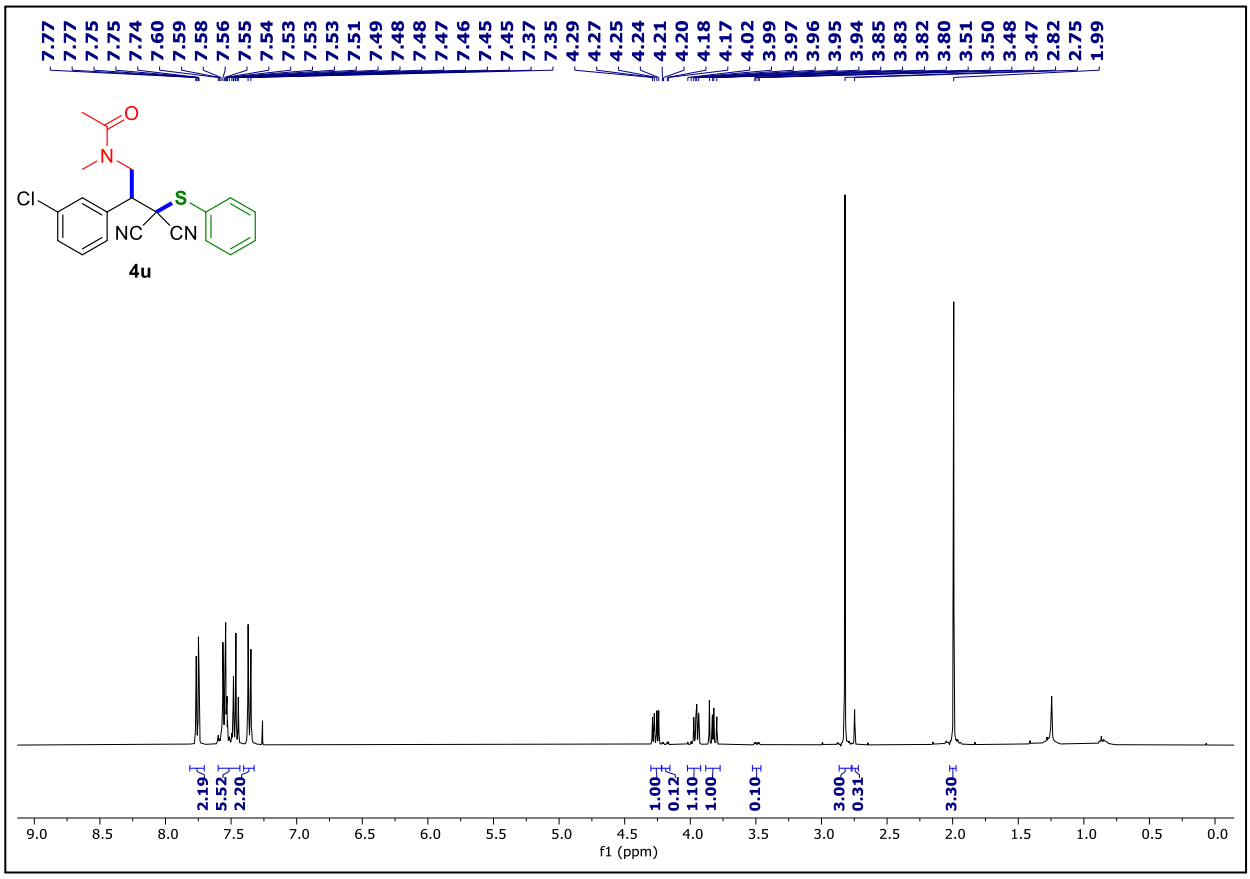
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4t**, (rr = 1: 0.1)



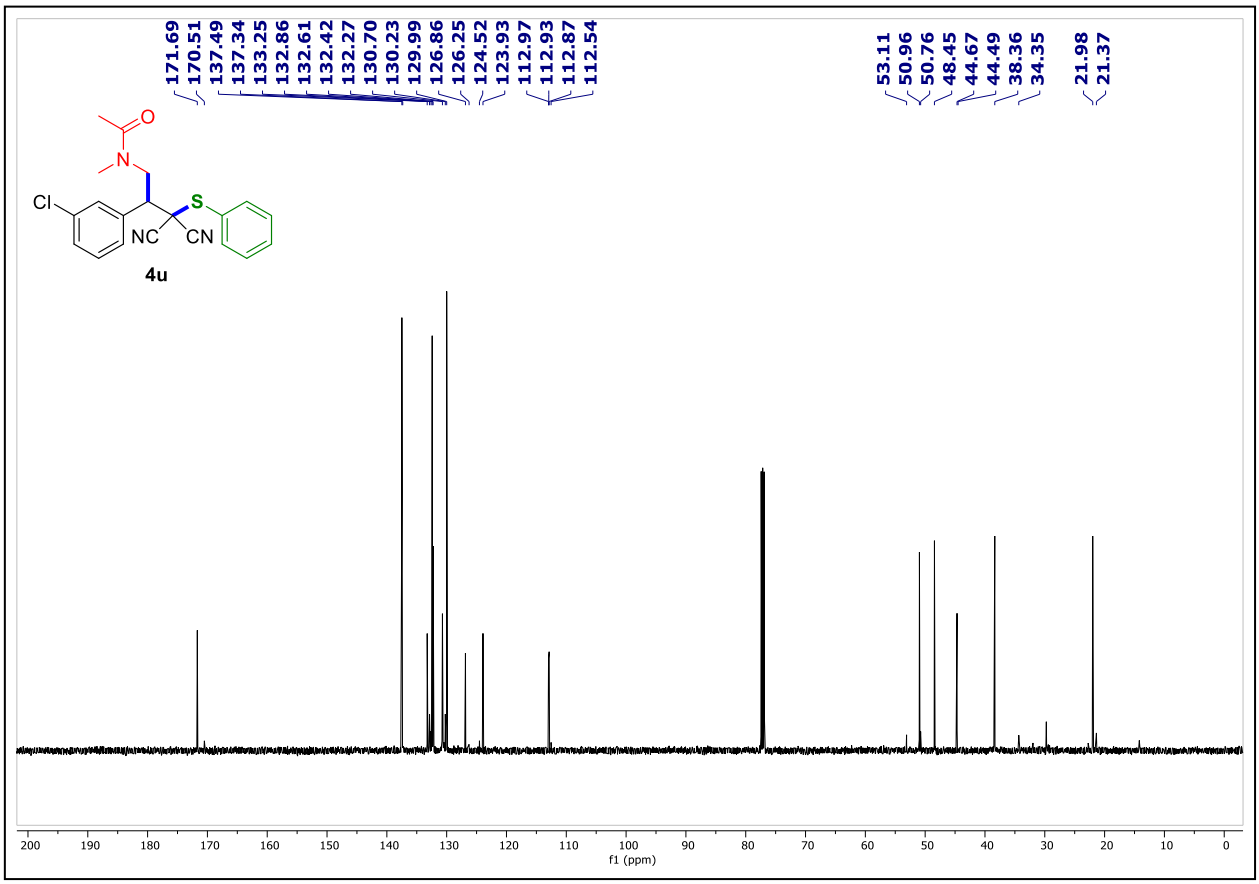
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4t**, (rr = 1: 0.1)



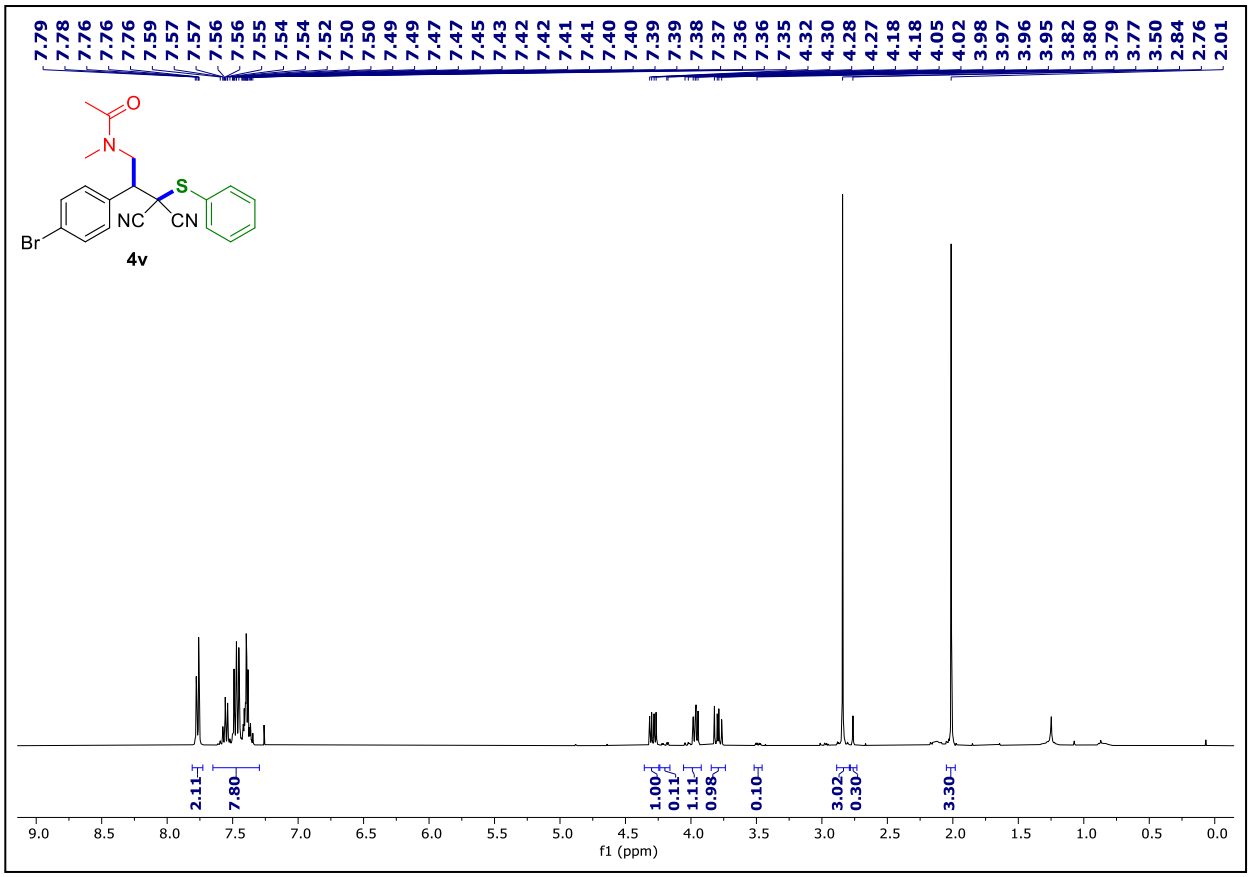
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4u**, (rr = 1: 0.1)



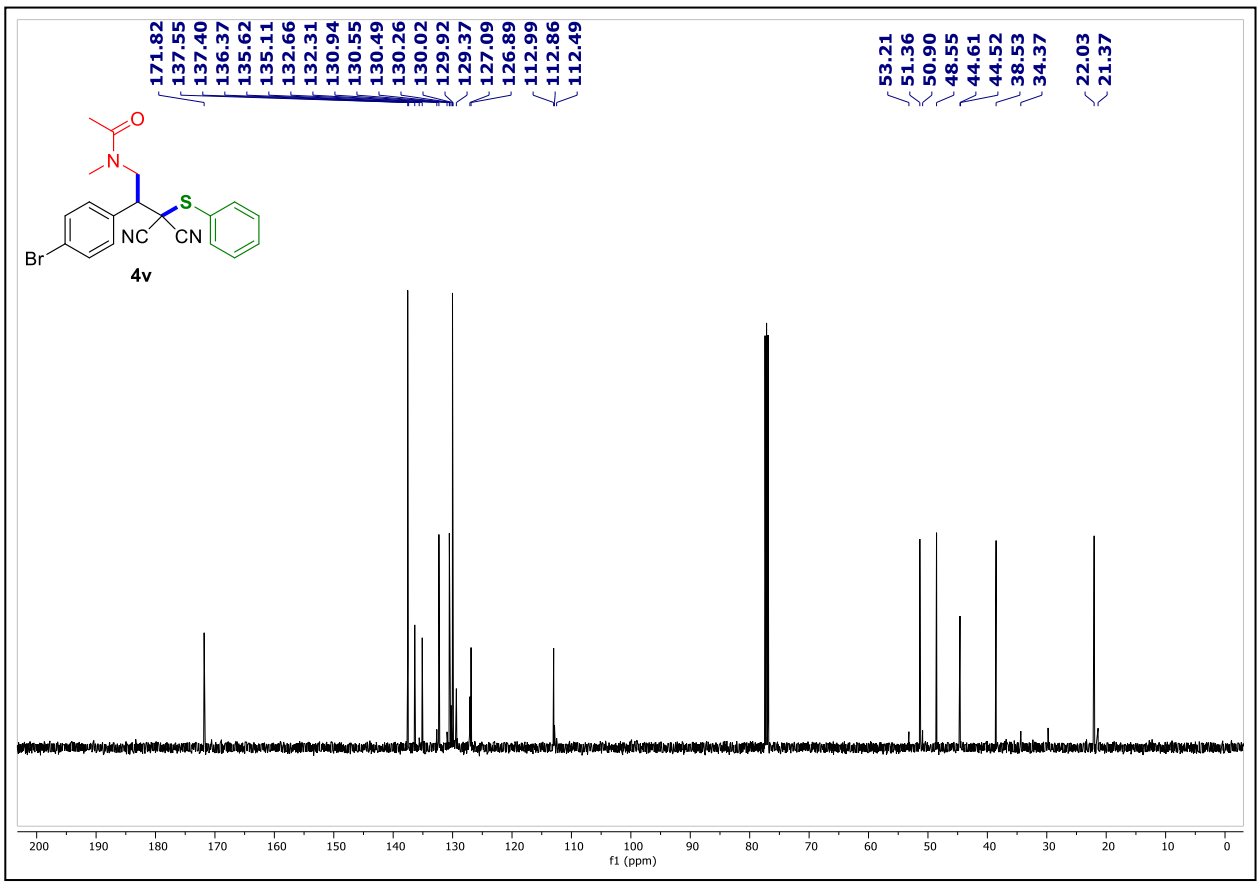
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4u**, (rr = 1: 0.1)



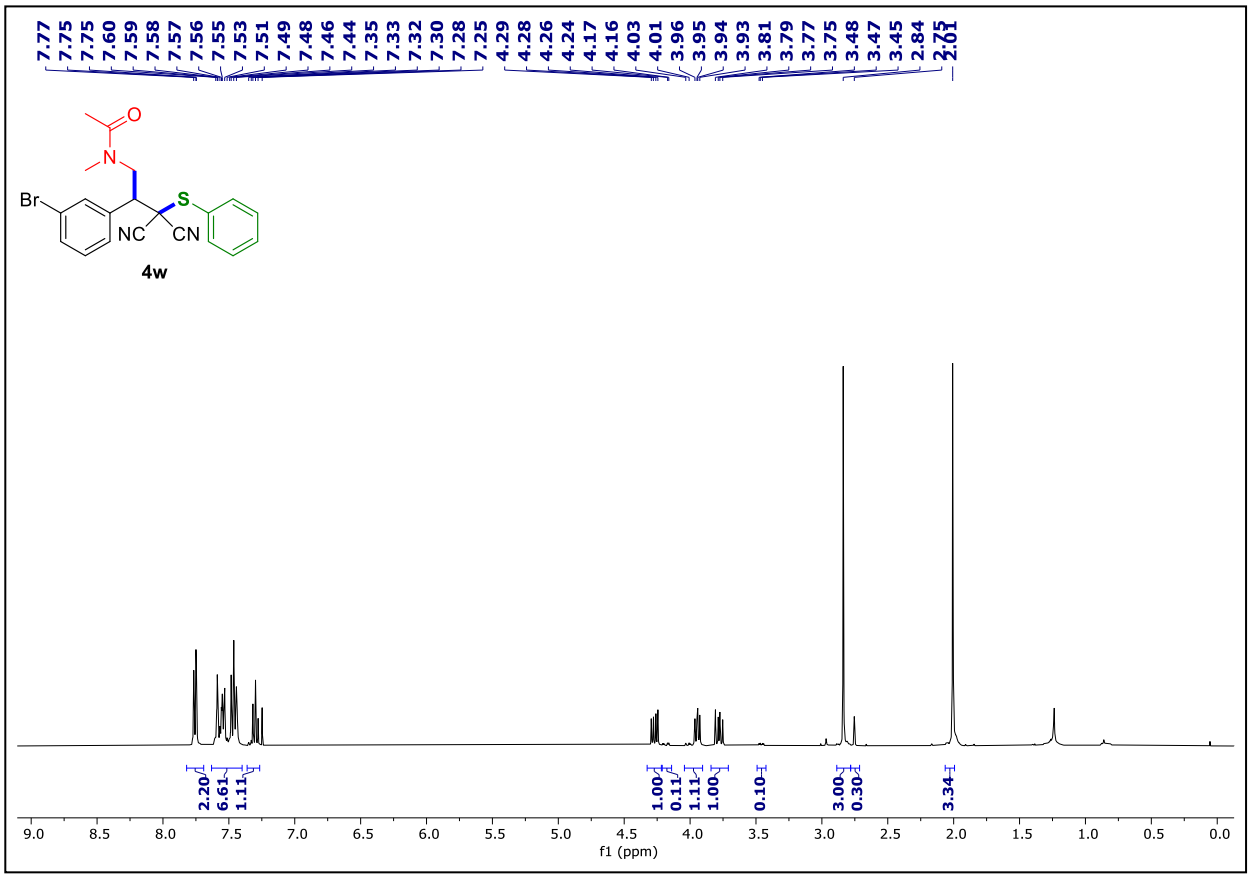
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4v**, (rr = 1: 0.1)



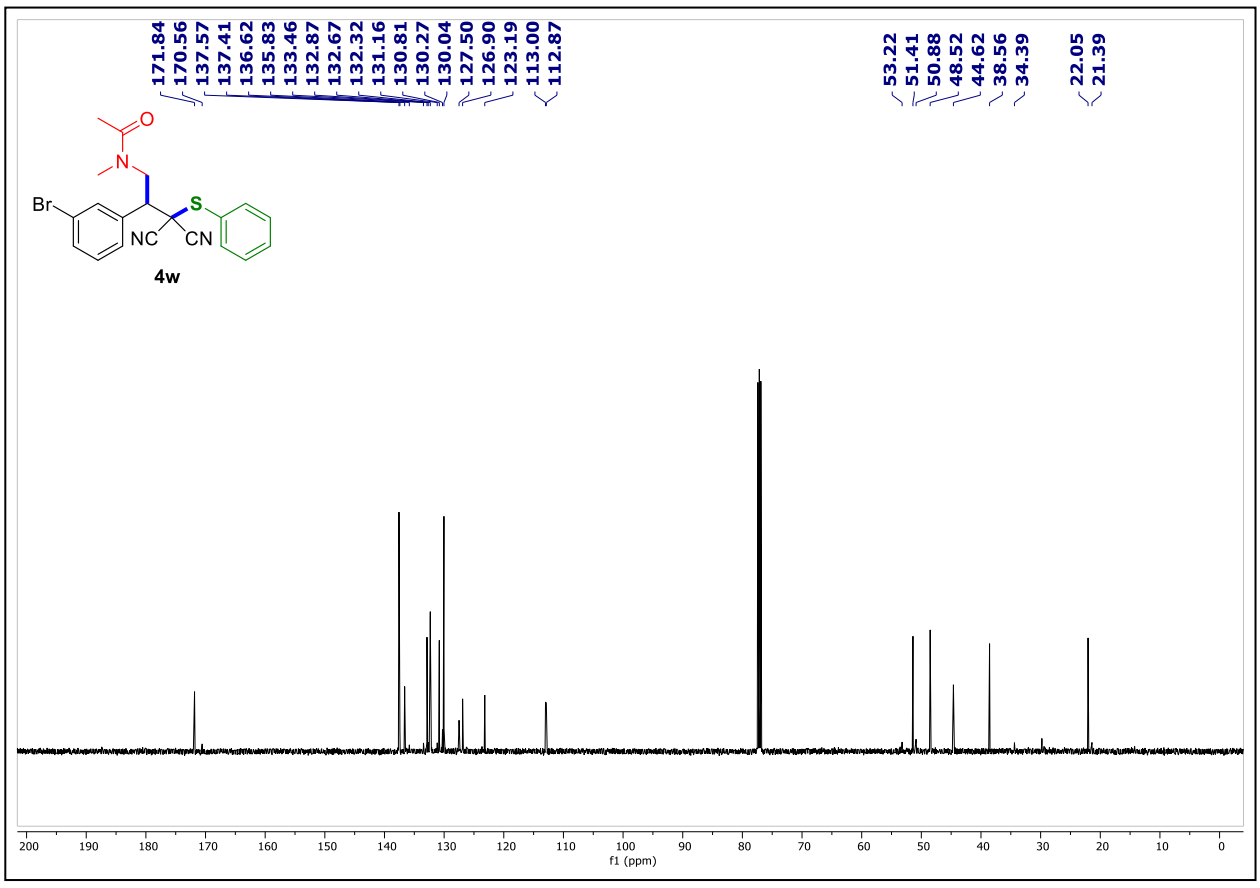
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4v**, (rr = 1: 0.1)



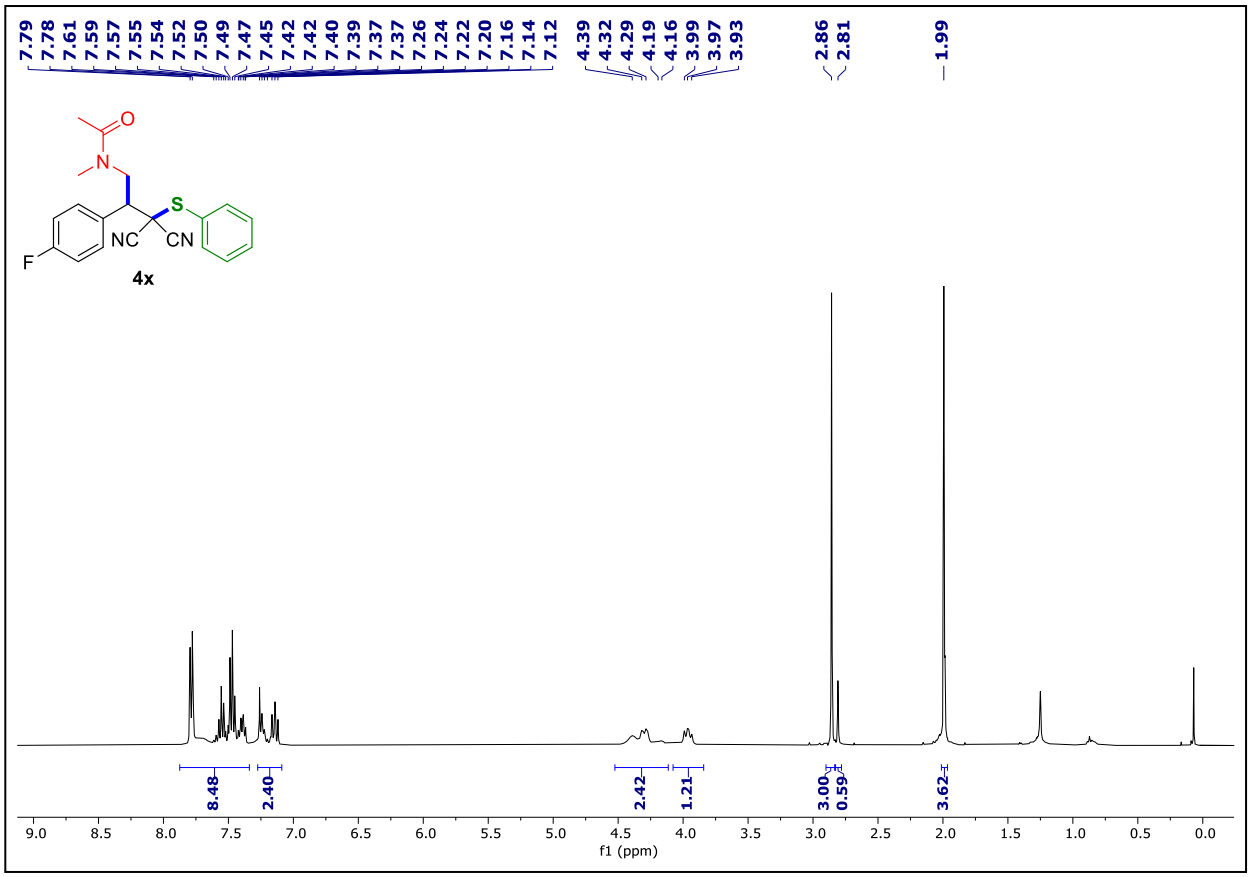
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4w**, (rr = 1: 0.1)



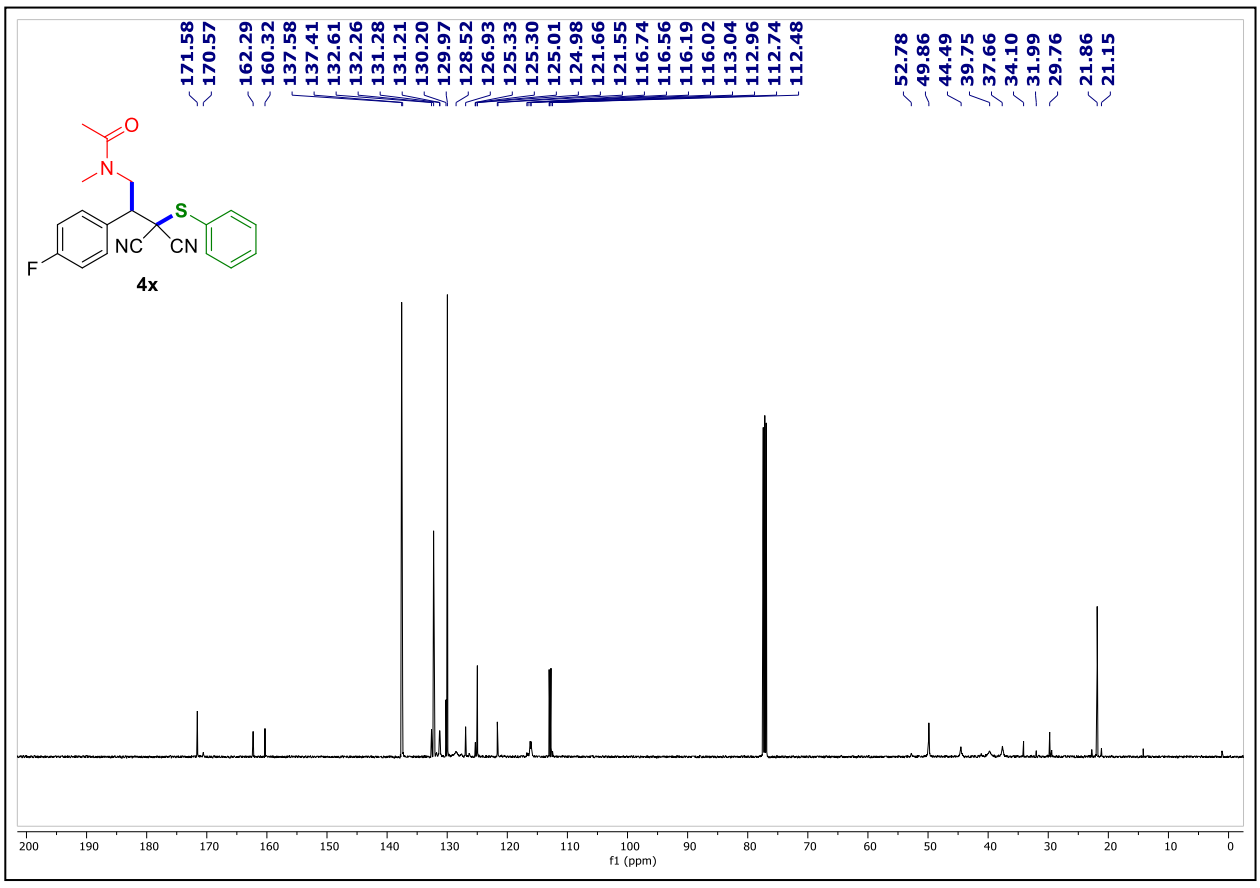
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4w**, (rr = 1: 0.1)



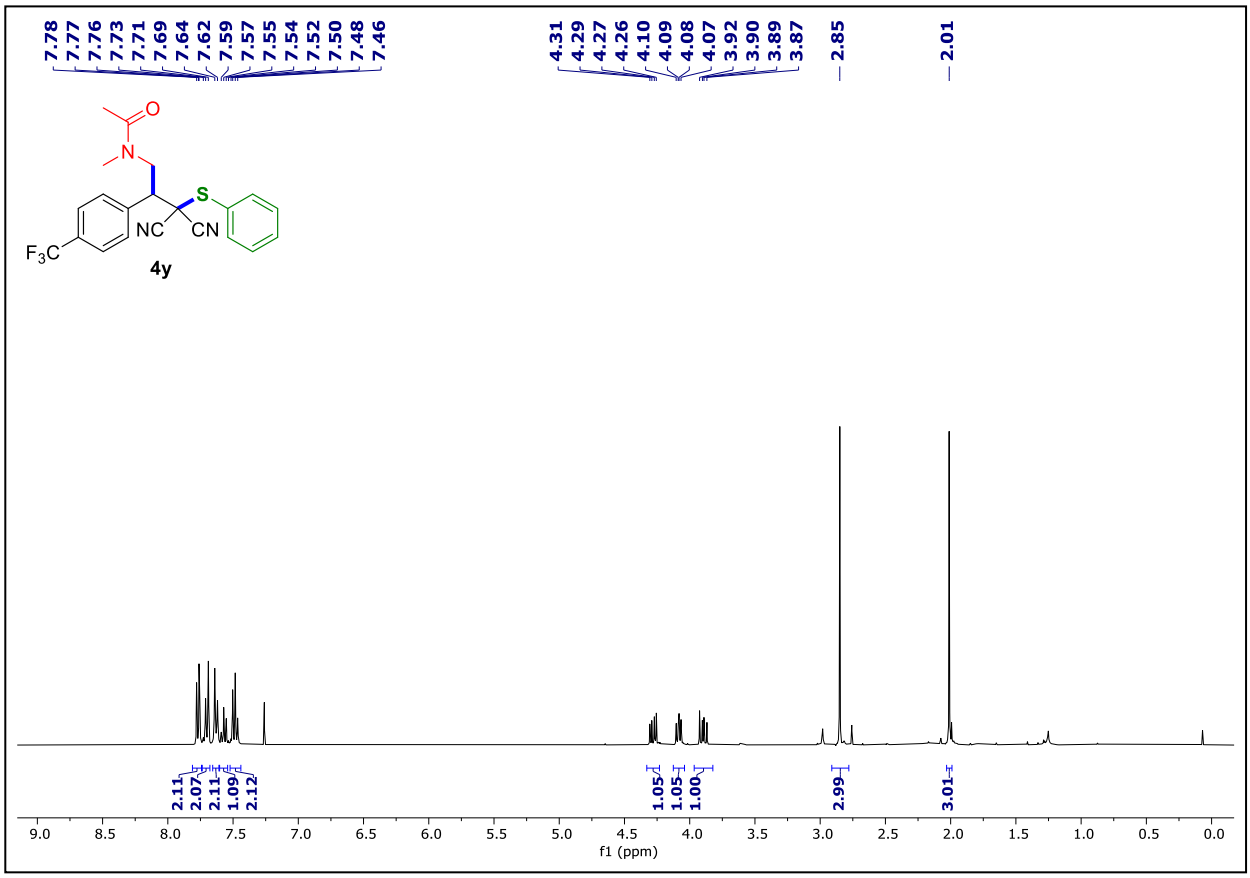
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4x**, (rr = 1: 0.1)



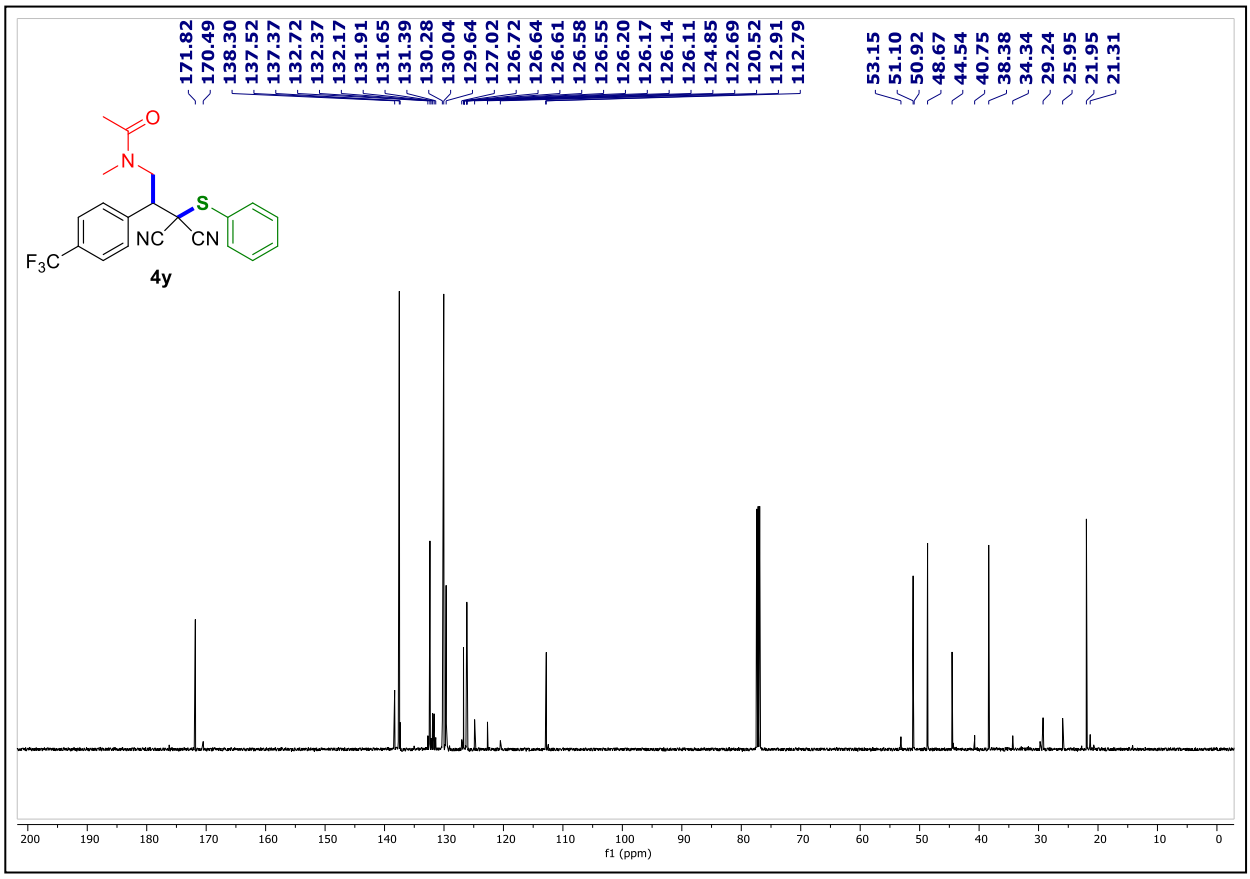
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4x**, (rr = 1: 0.1)



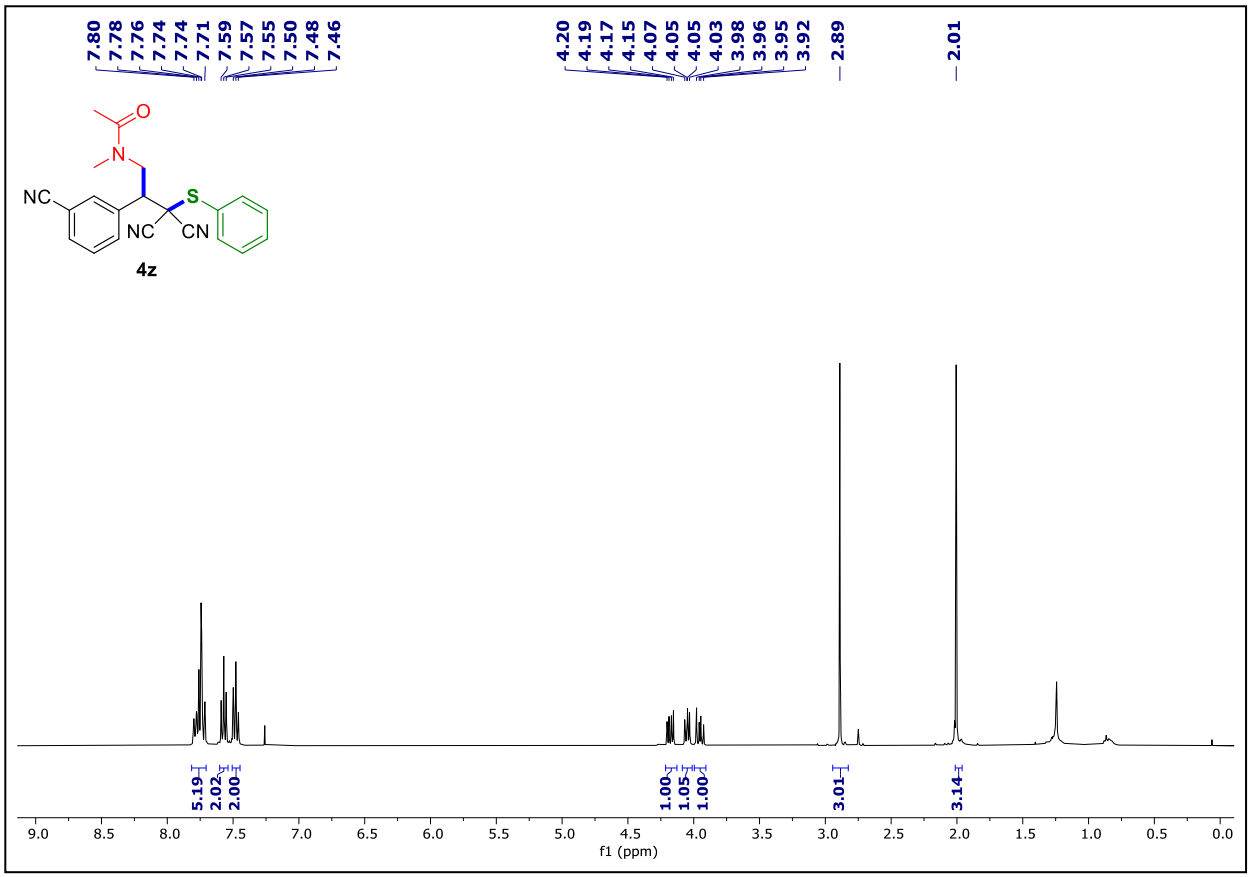
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4y**, (rr = 1: 0.07)



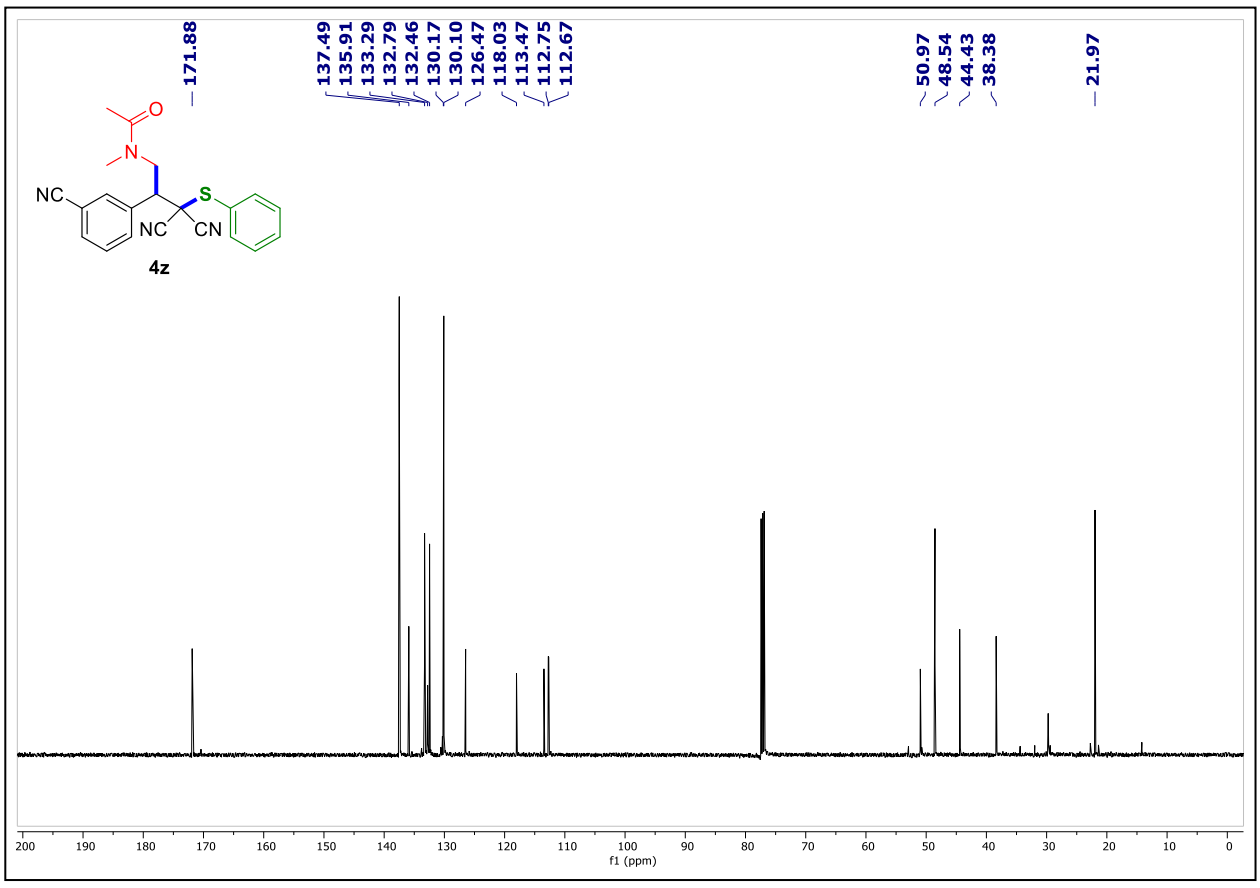
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4y**, (rr = 1: 0.07)



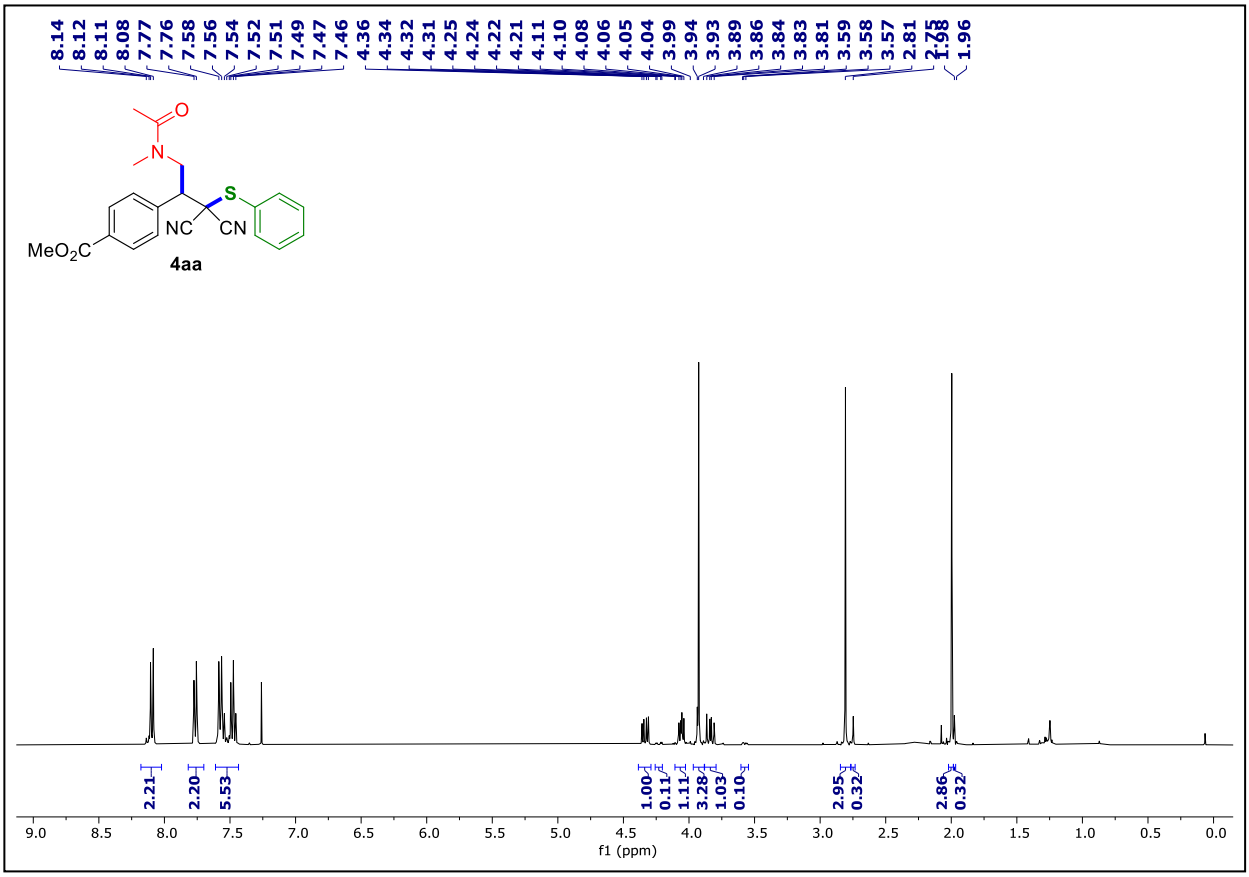
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4z**, (rr = 1: 0.07)



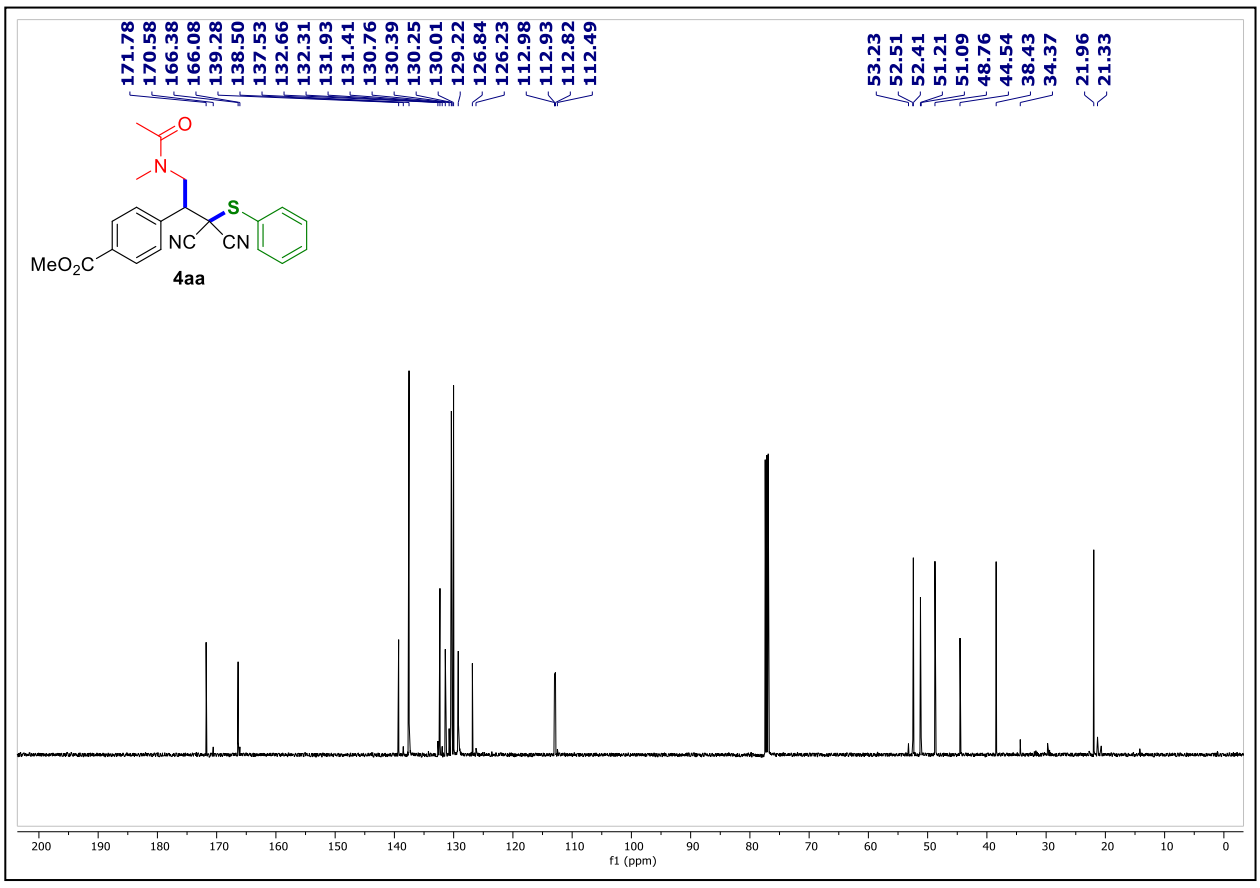
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4z**, (rr = 1: 0.07)



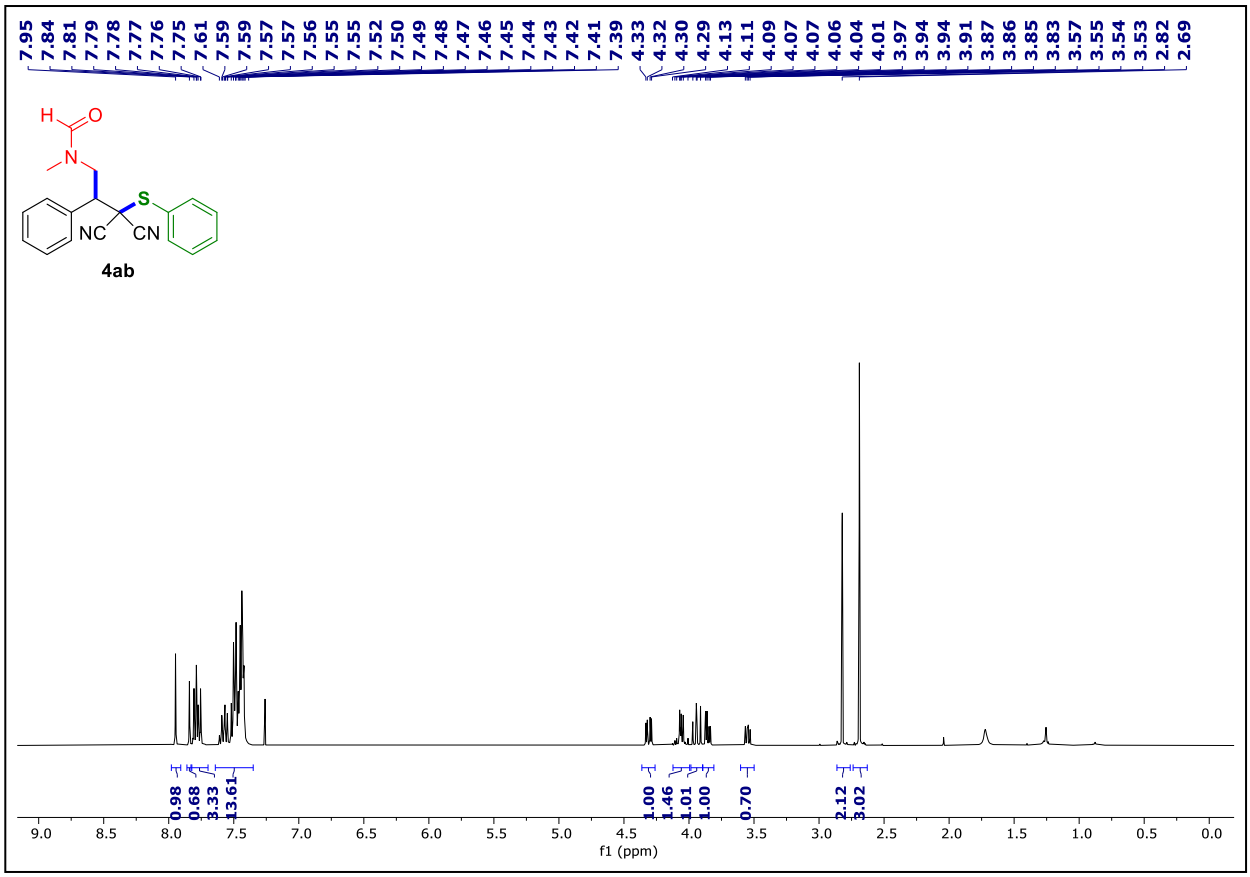
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4aa**, (rr = 1: 0.1)



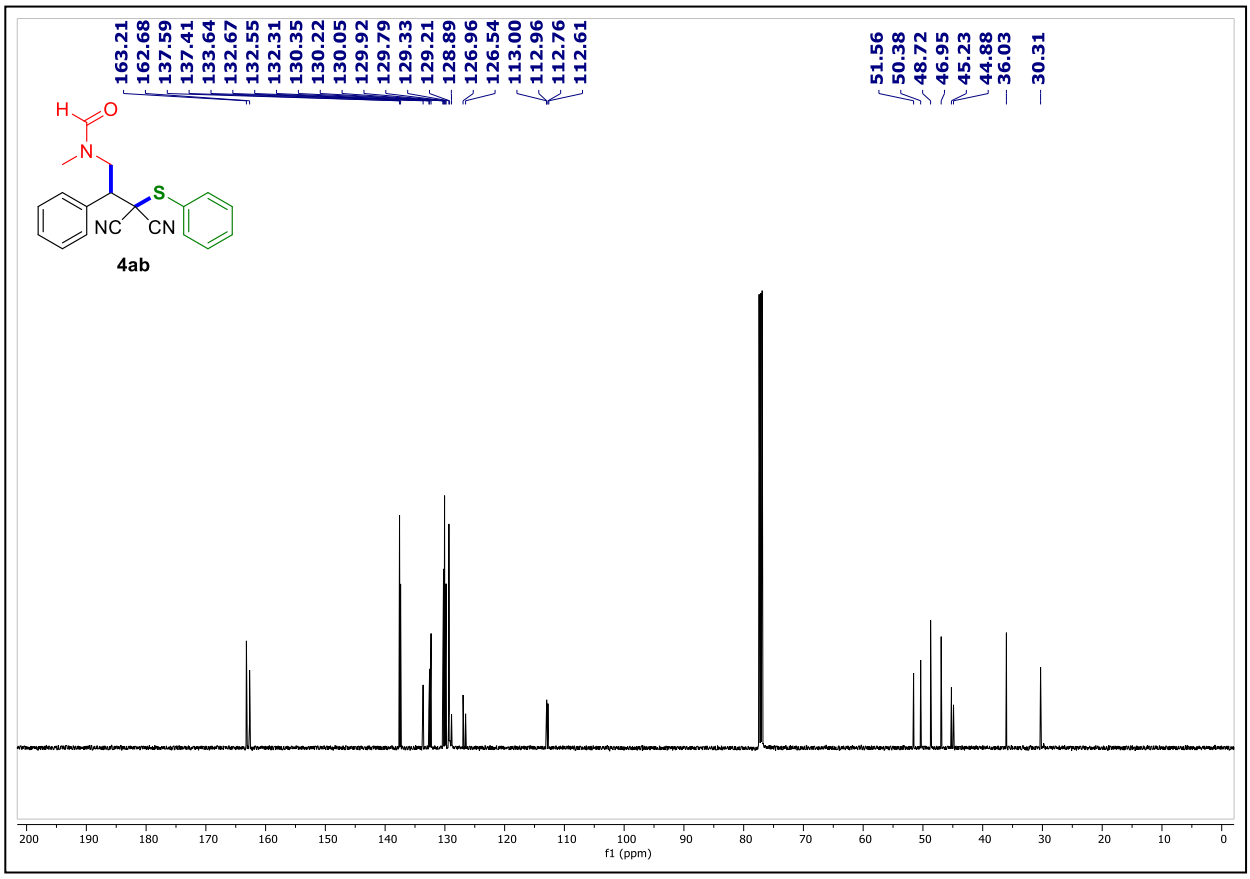
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4aa**, (rr = 1: 0.1)



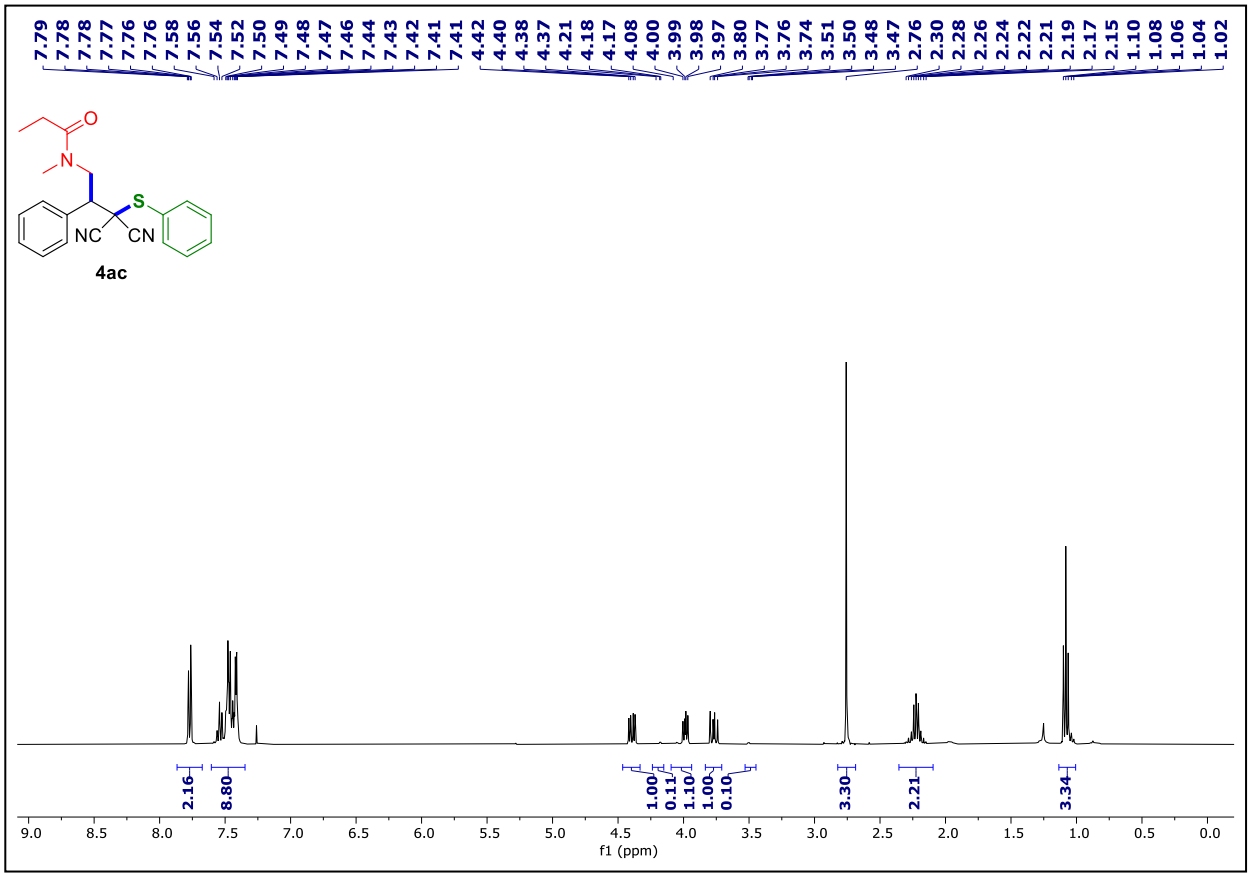
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ab**, (rr = 1: 0.7)



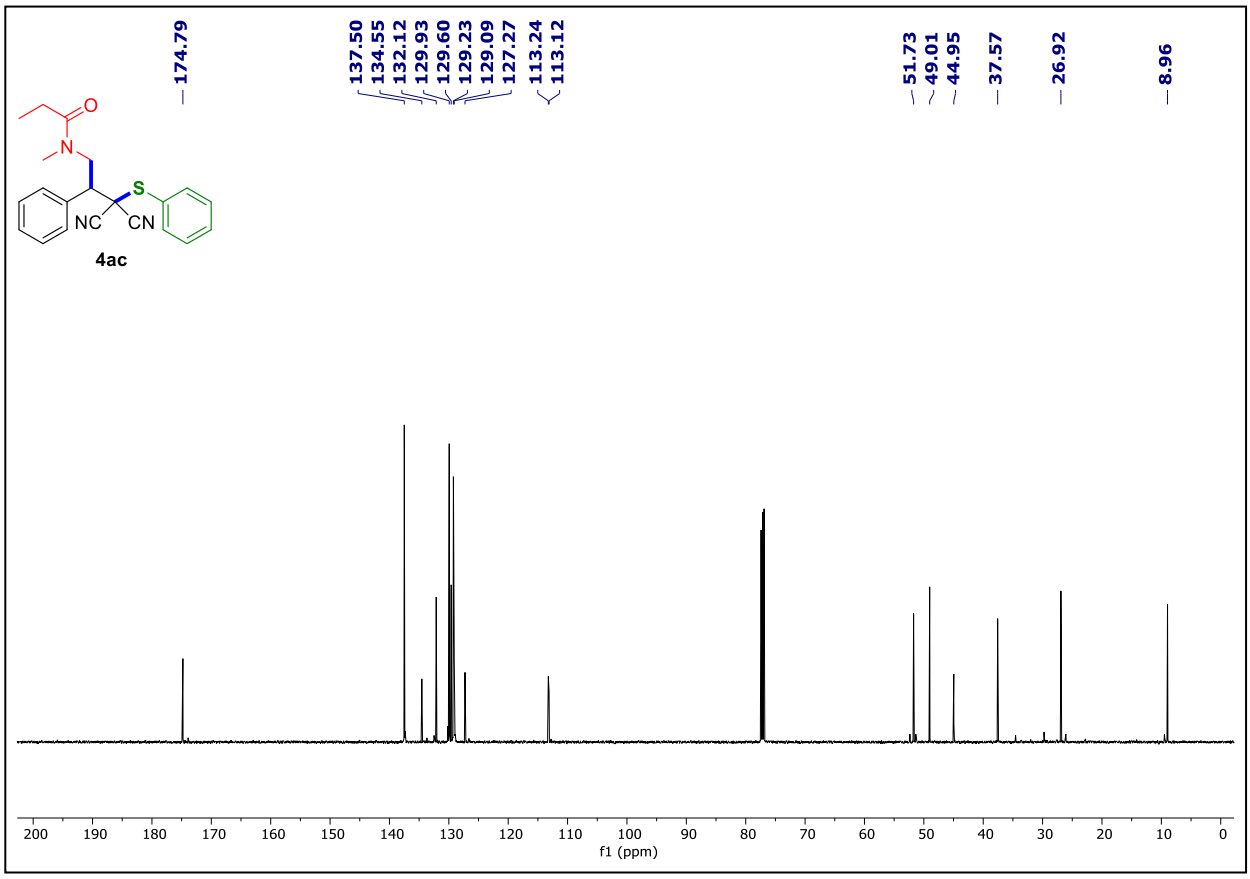
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4ab**, (rr = 1: 0.7)



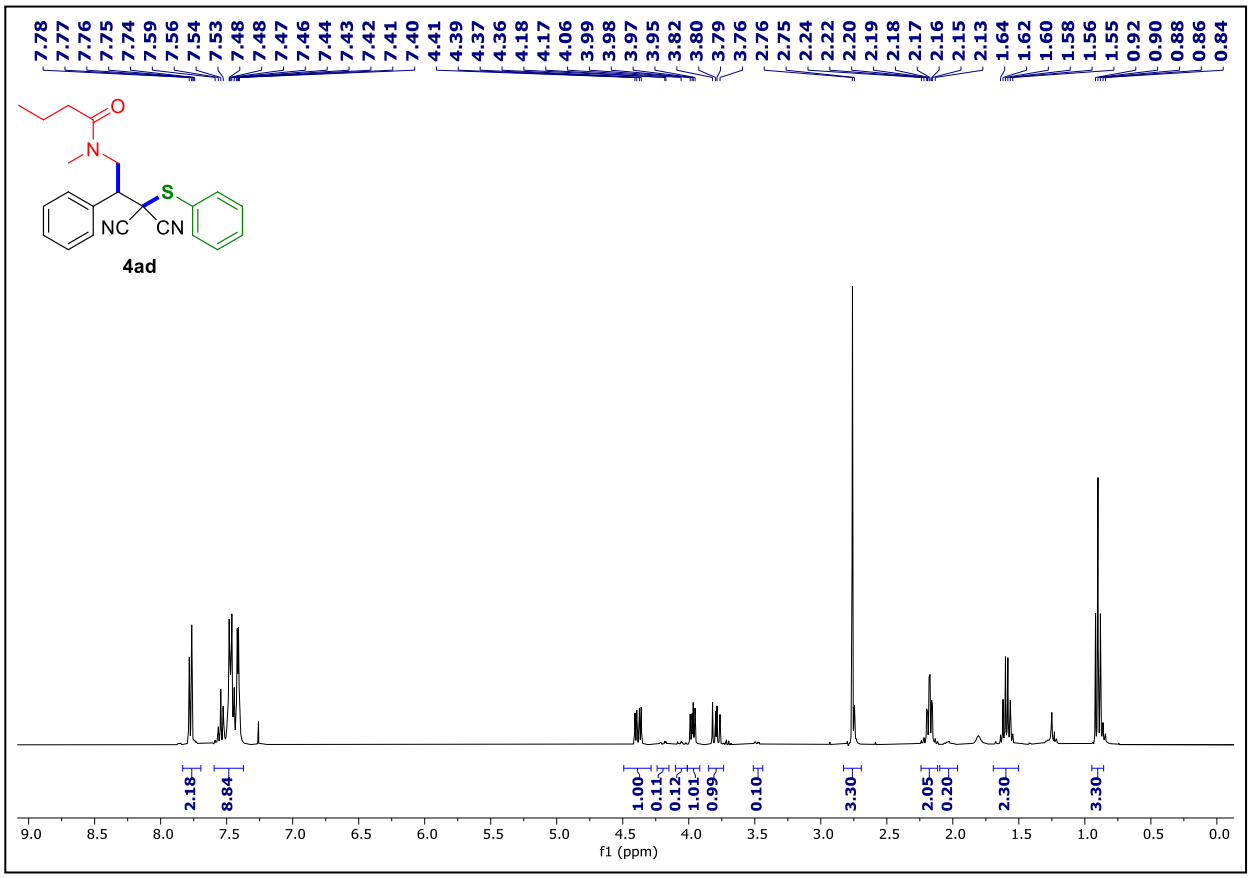
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ac**, (rr = 1: 0.1)



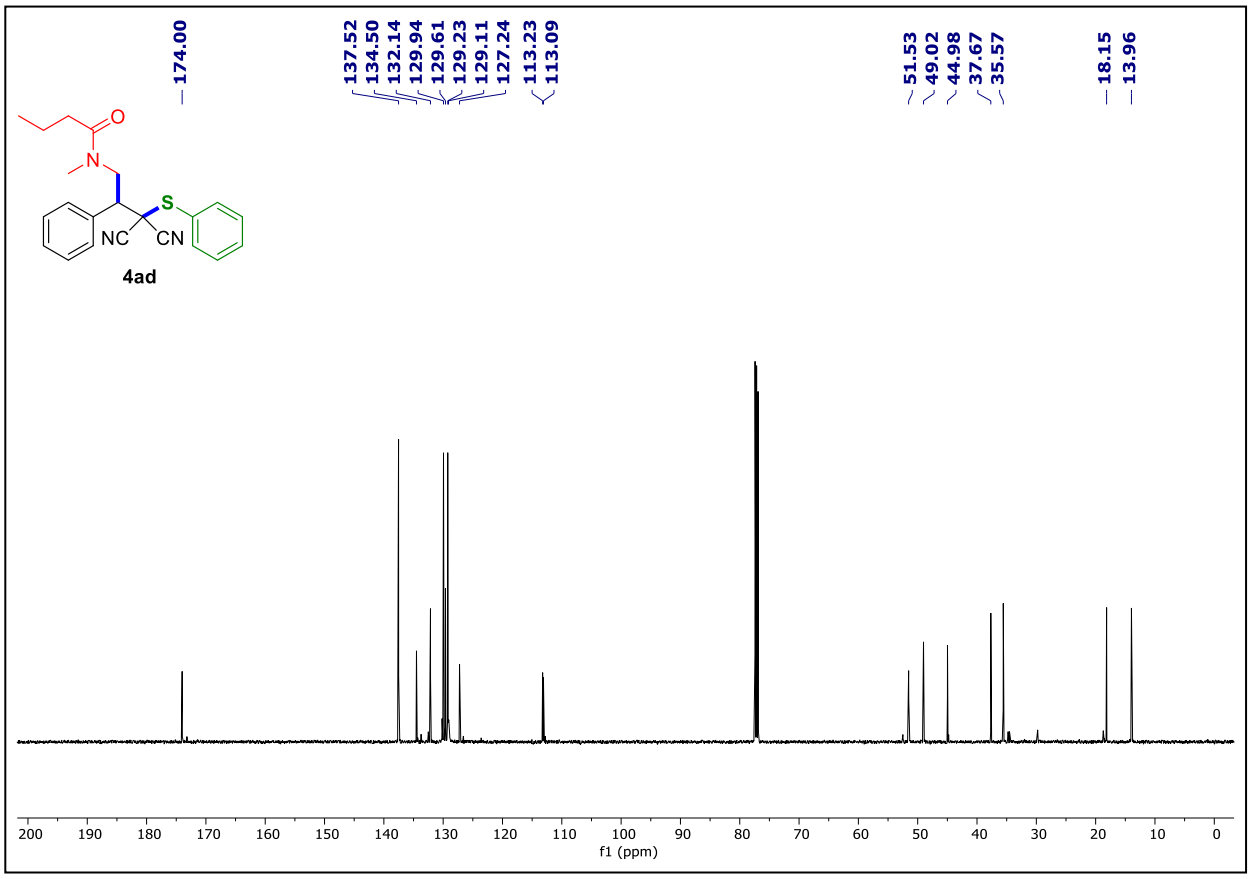
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4ac**, (rr = 1: 0.1)



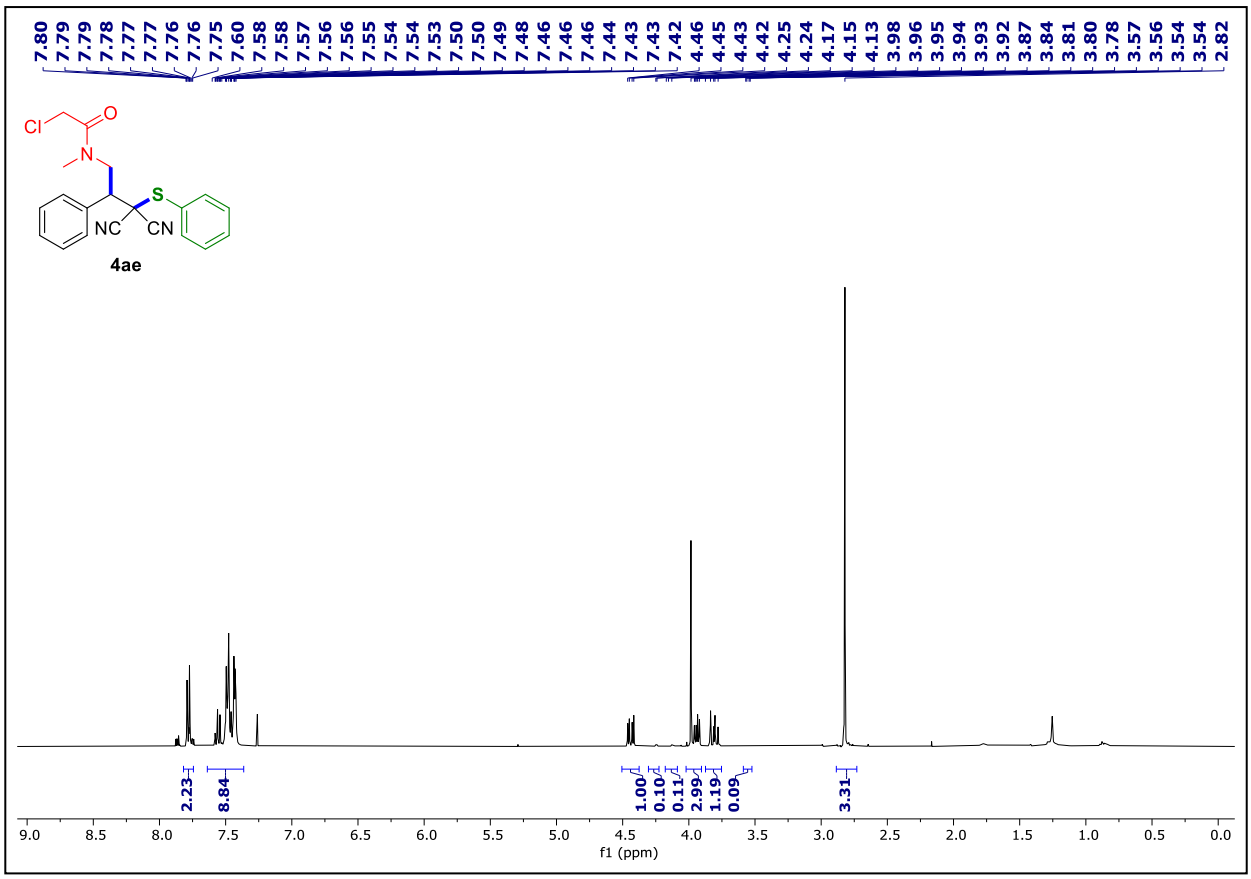
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ad**, (rr = 1: 0.1)



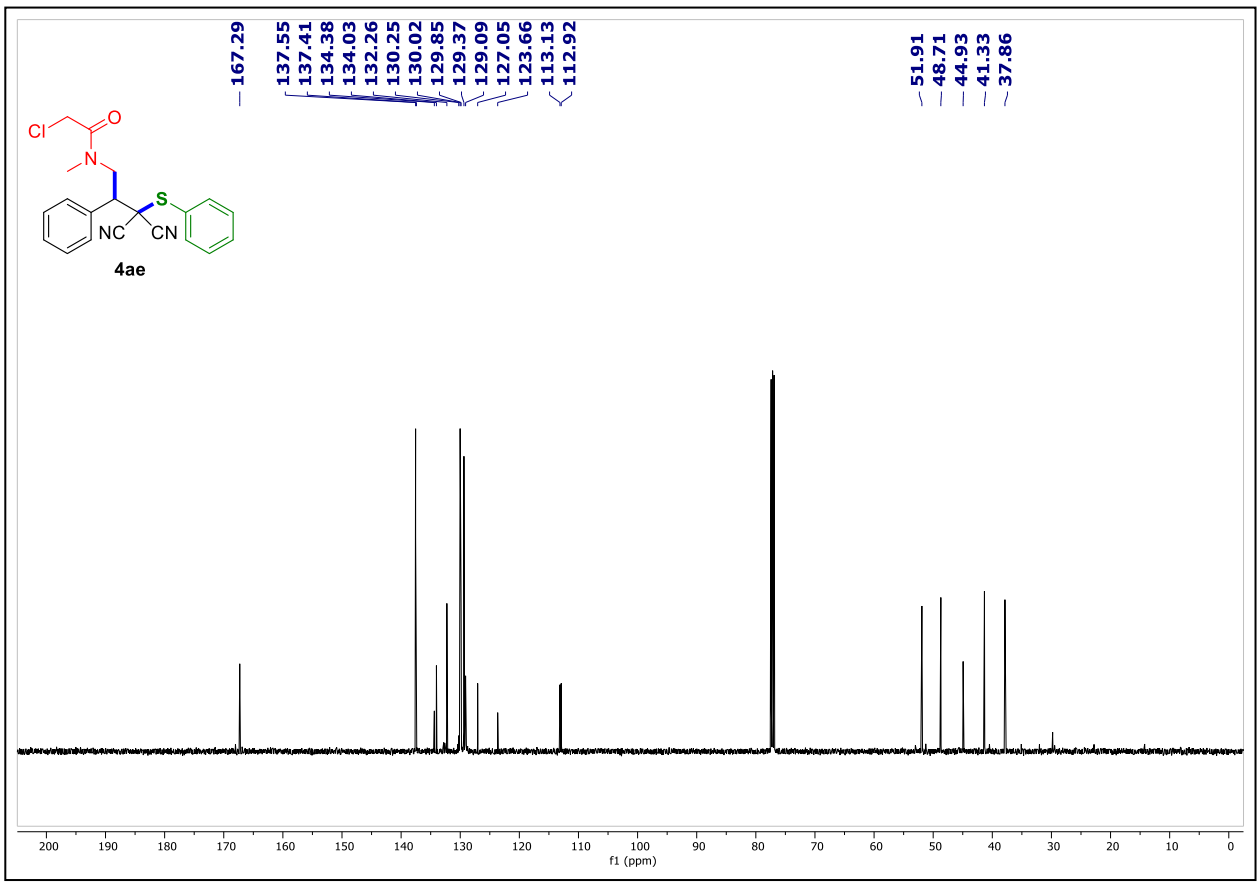
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4ad**, (rr = 1: 0.1)



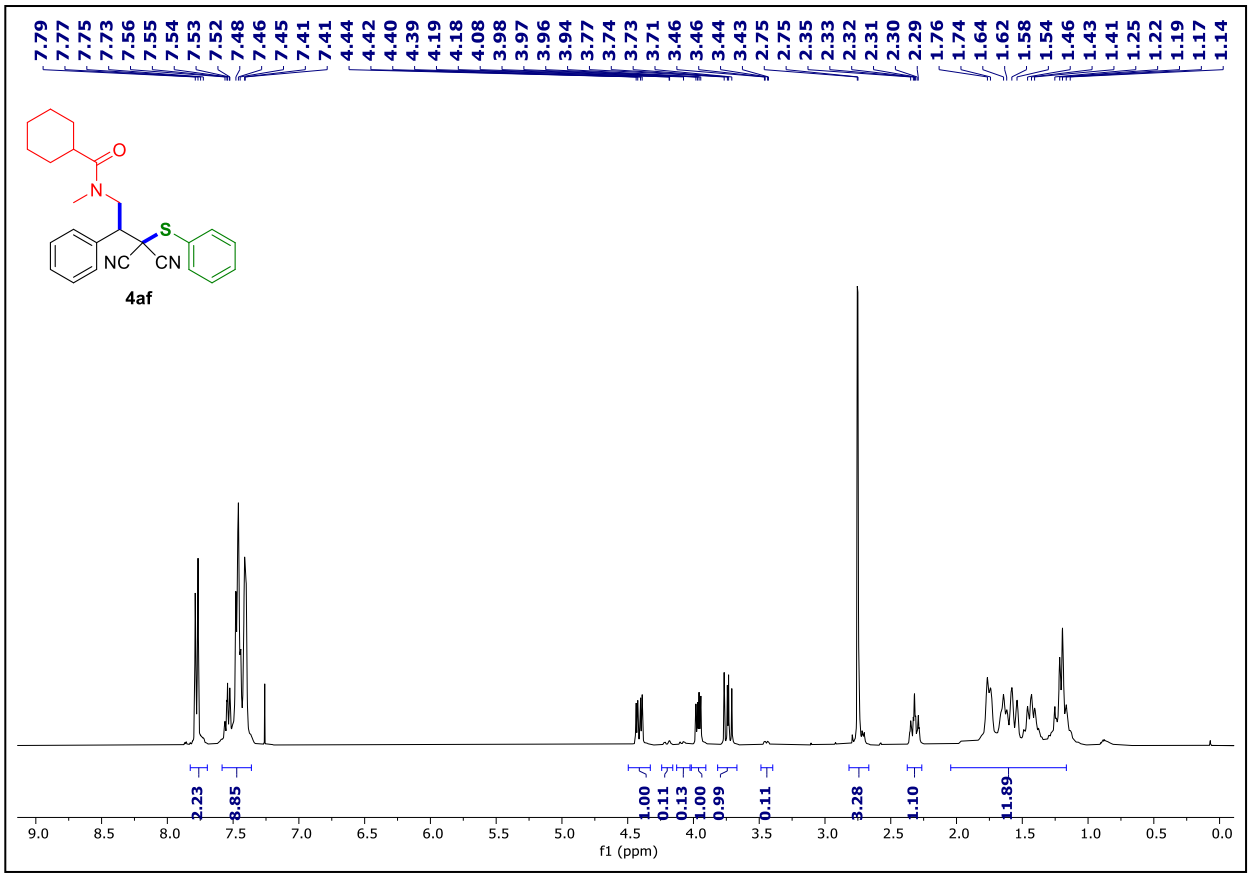
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ae**, (rr = 1: 0.1)



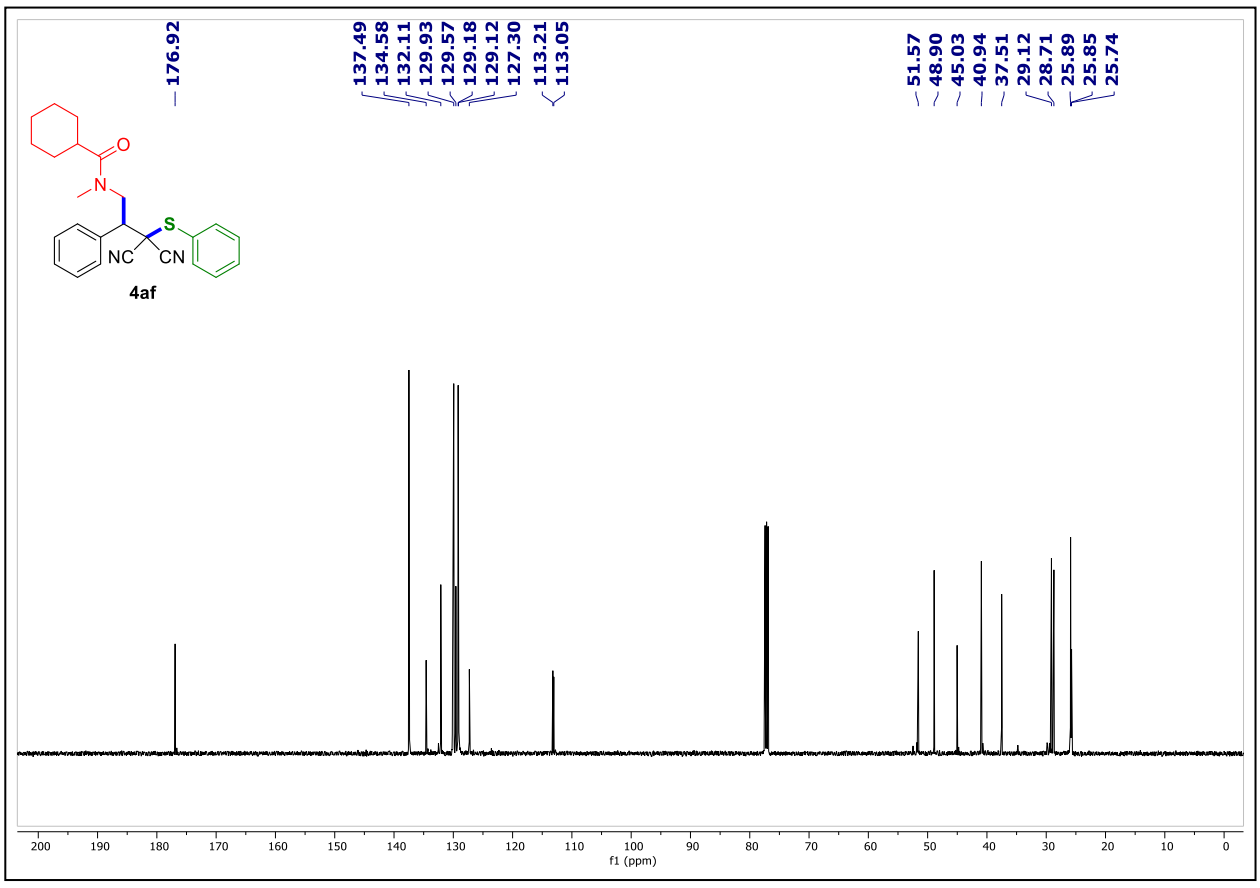
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4ae**, (rr = 1: 0.1)



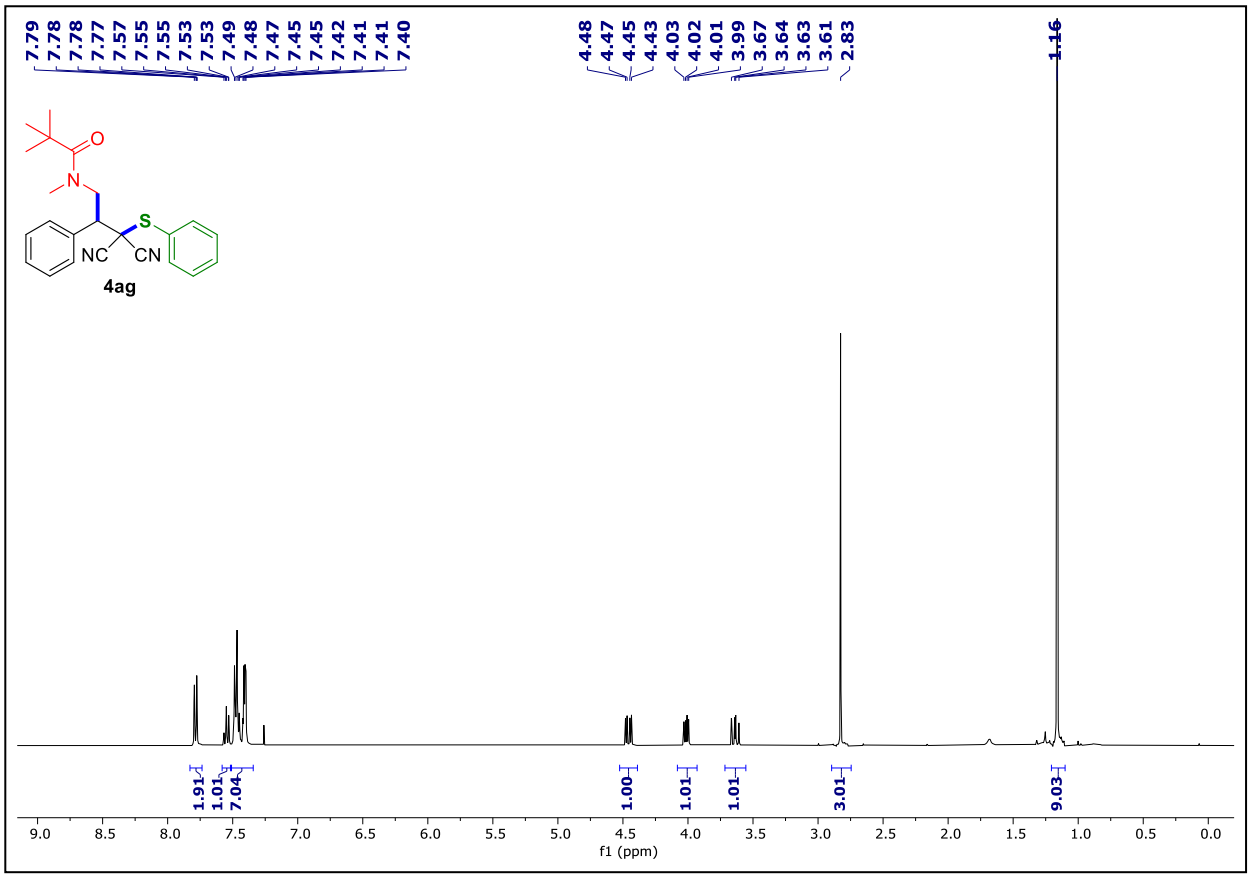
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4af**, (rr = 1: 0.1)



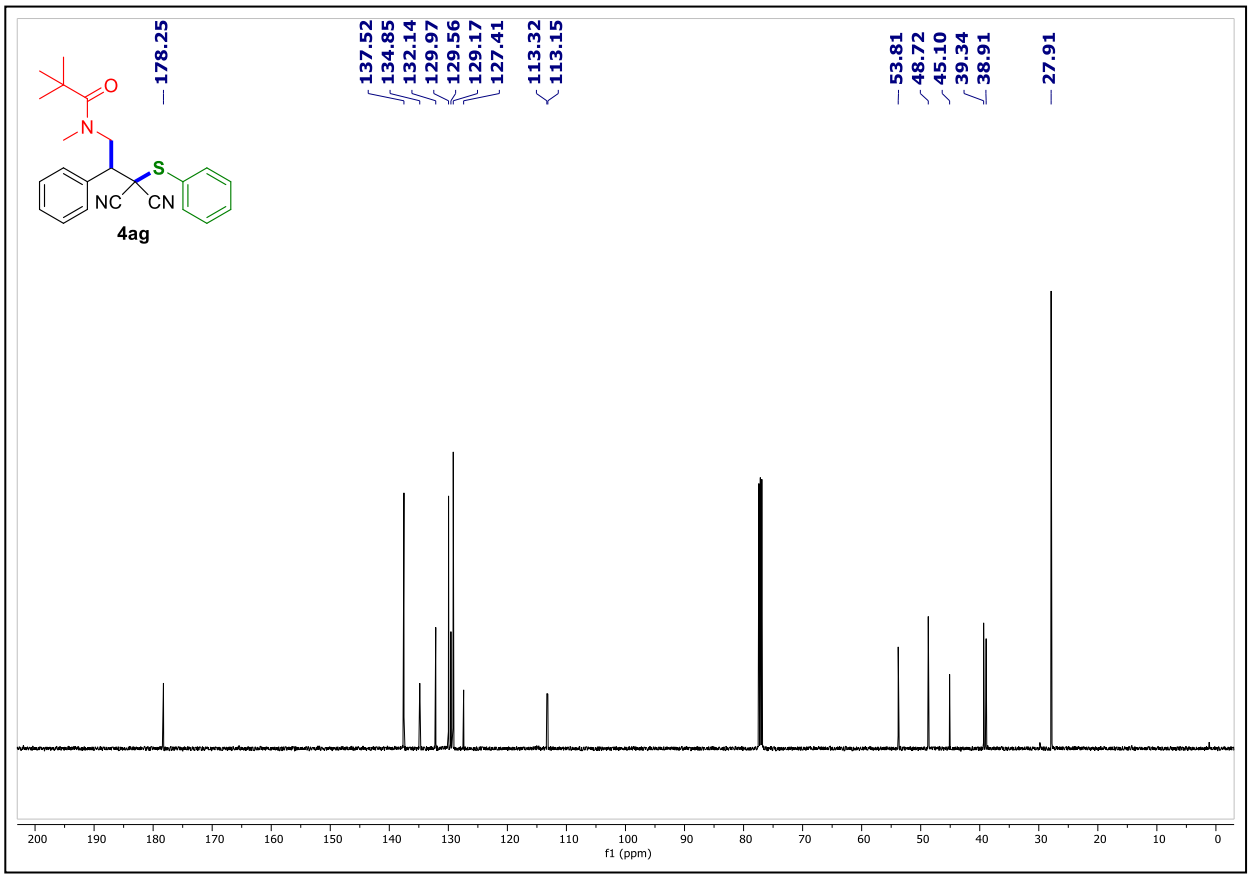
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4af**, (rr = 1: 0.1)



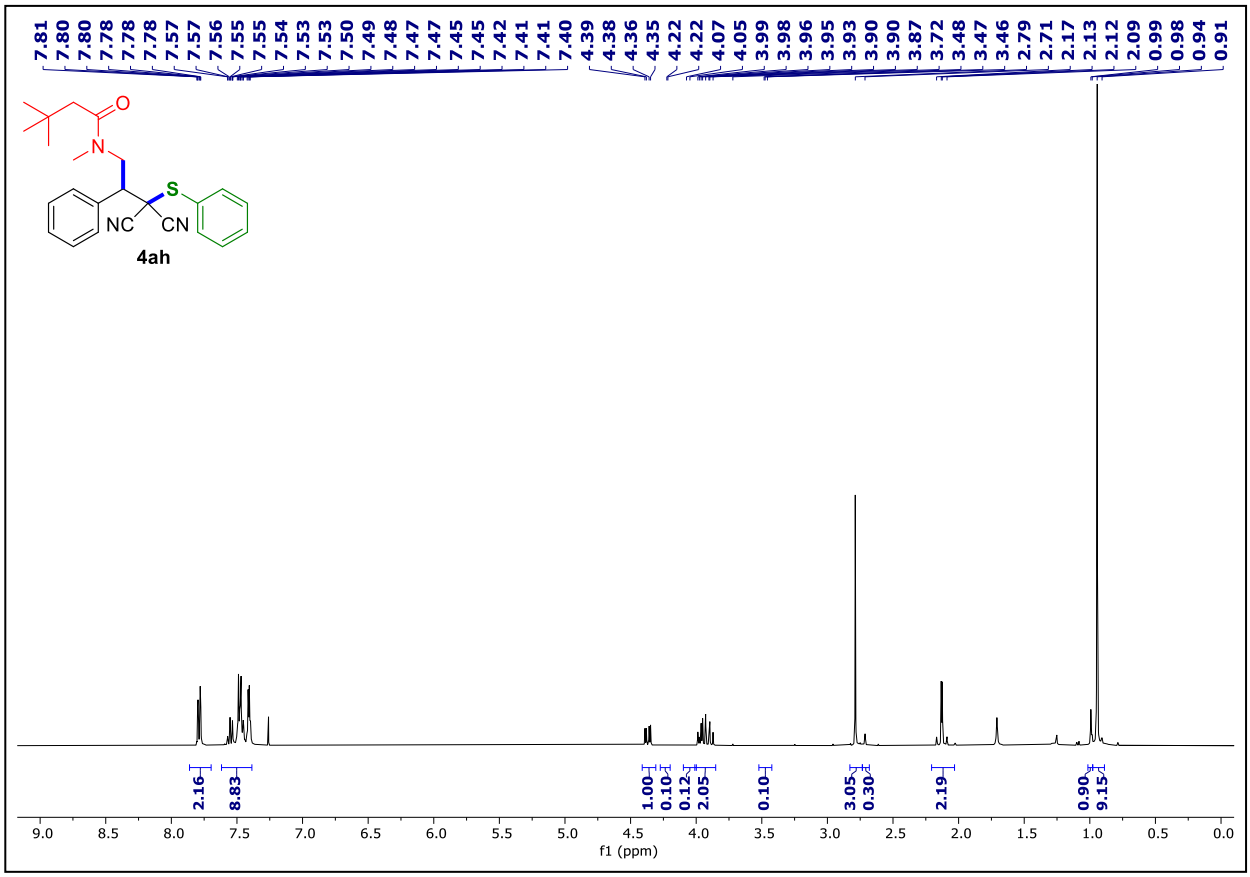
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ag**



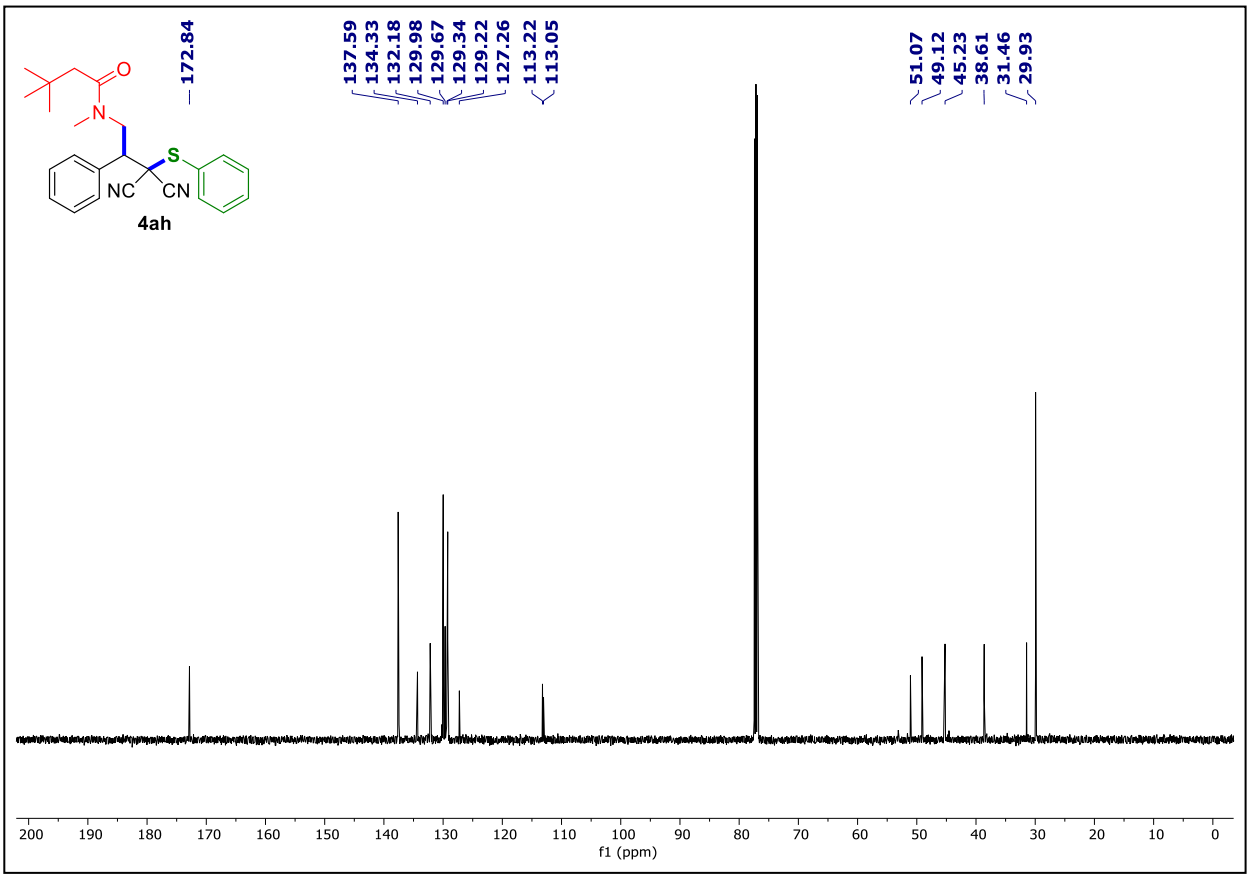
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4ag**



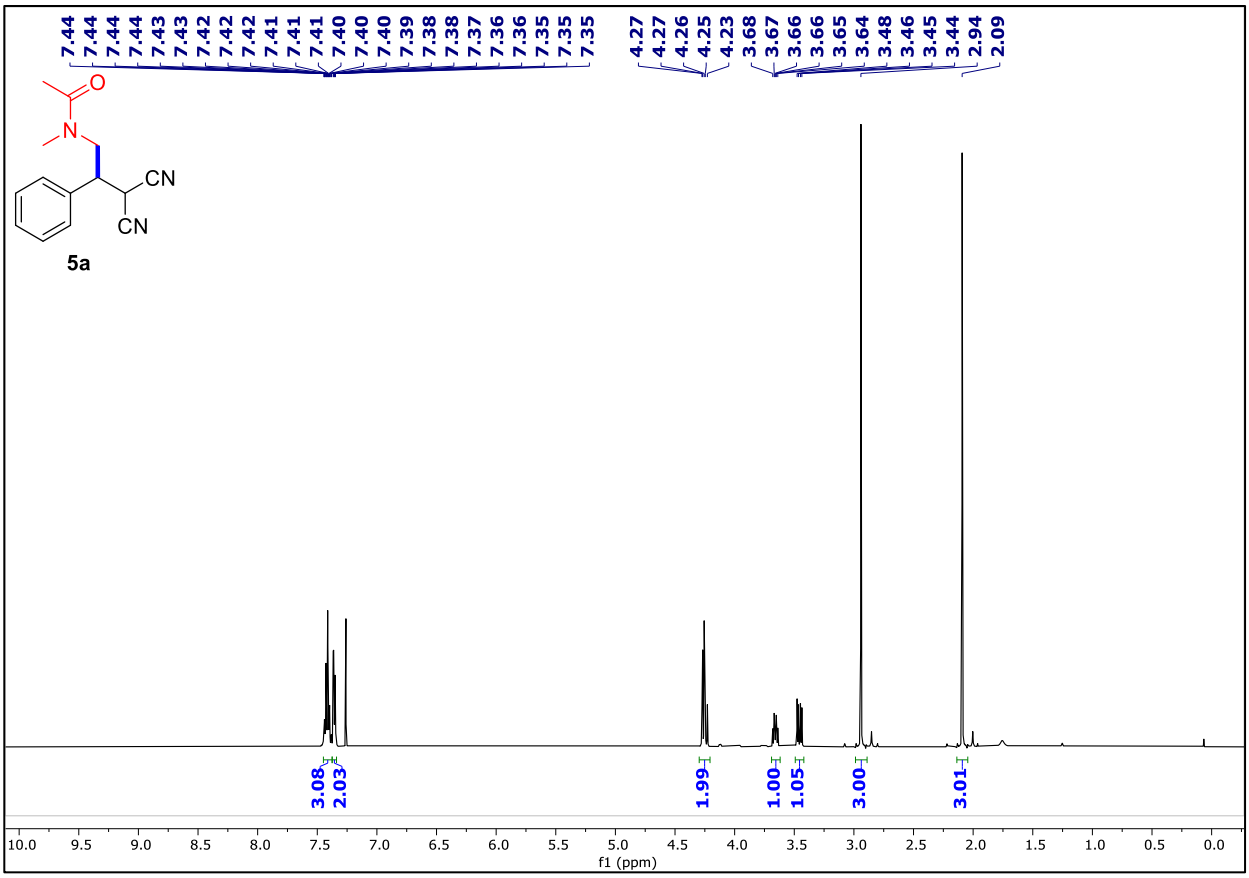
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4ah**, (rr = 1: 0.1)



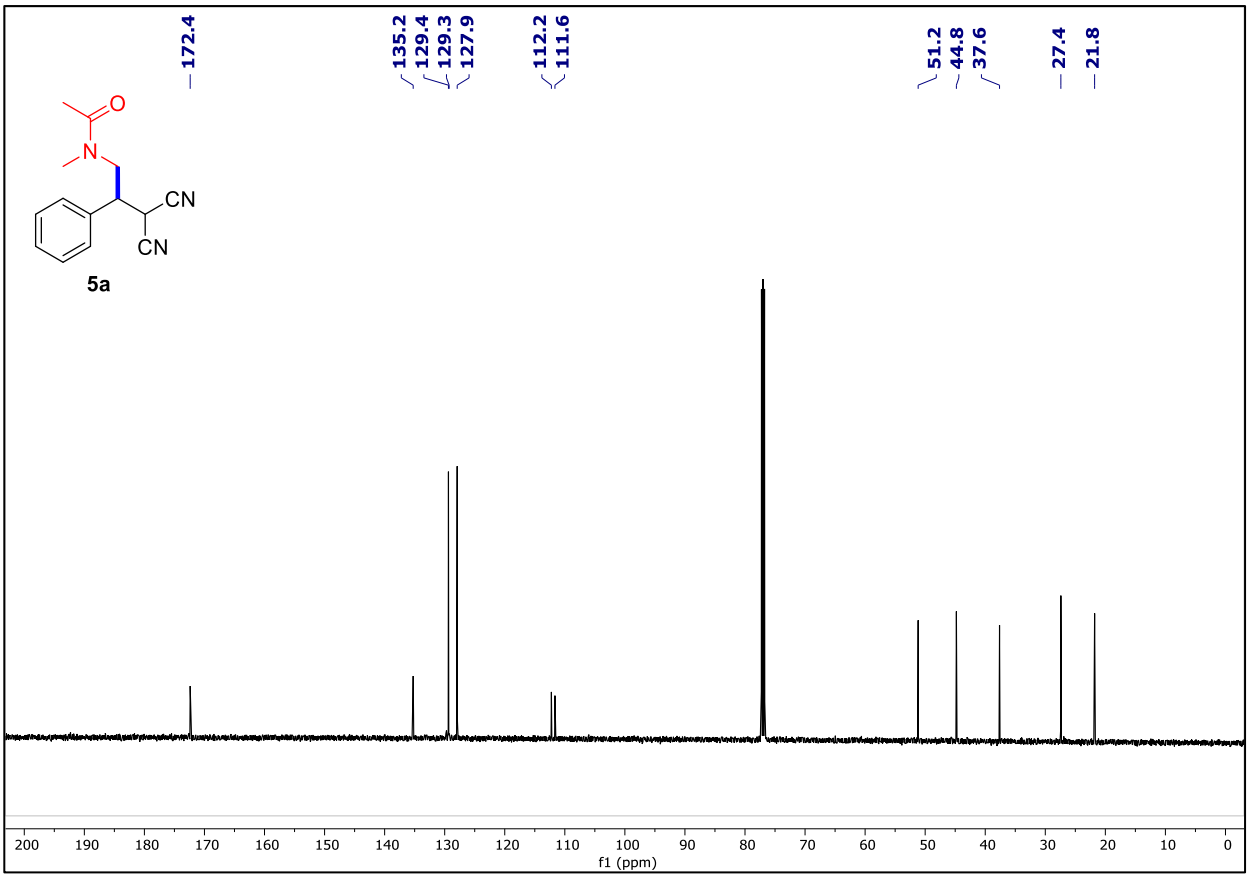
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4ah**, (rr = 1: 0.1)



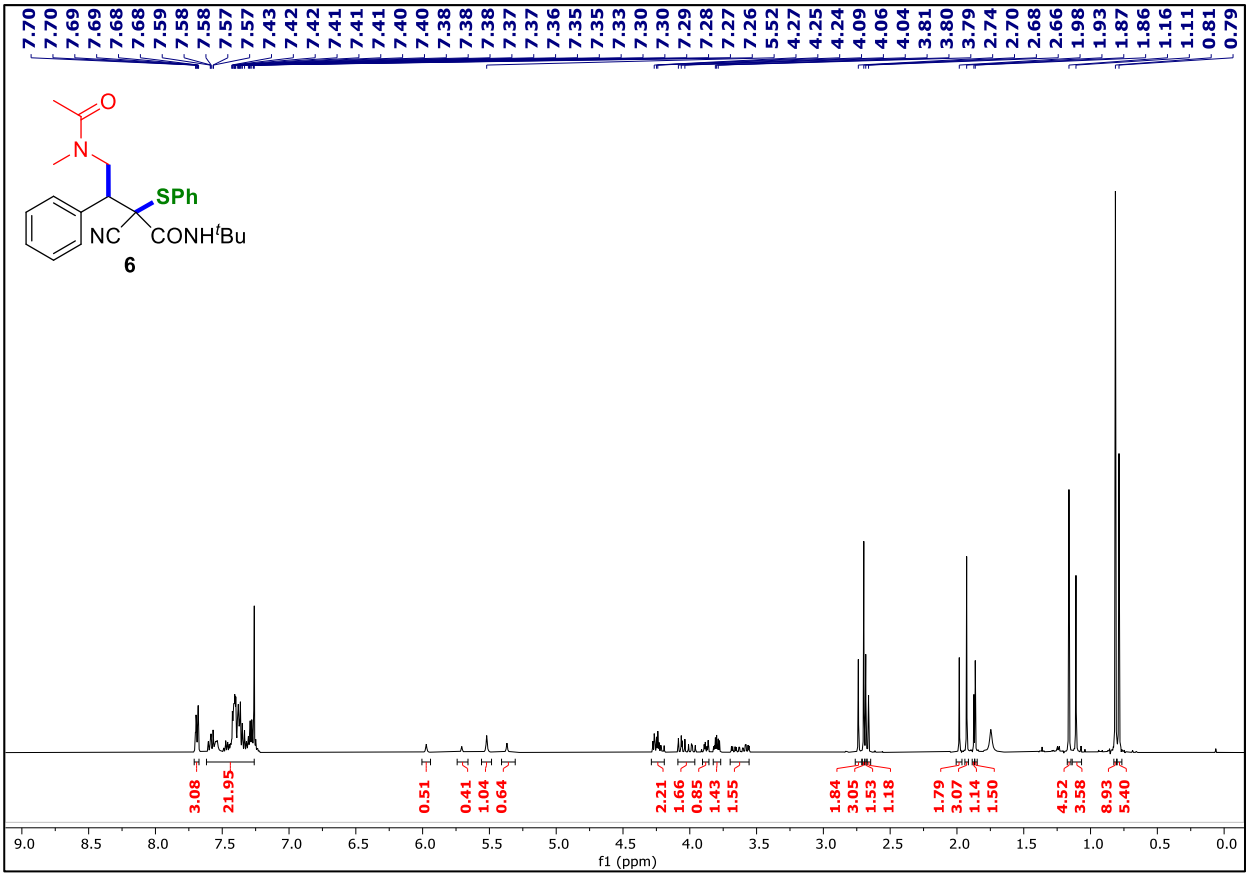
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a**



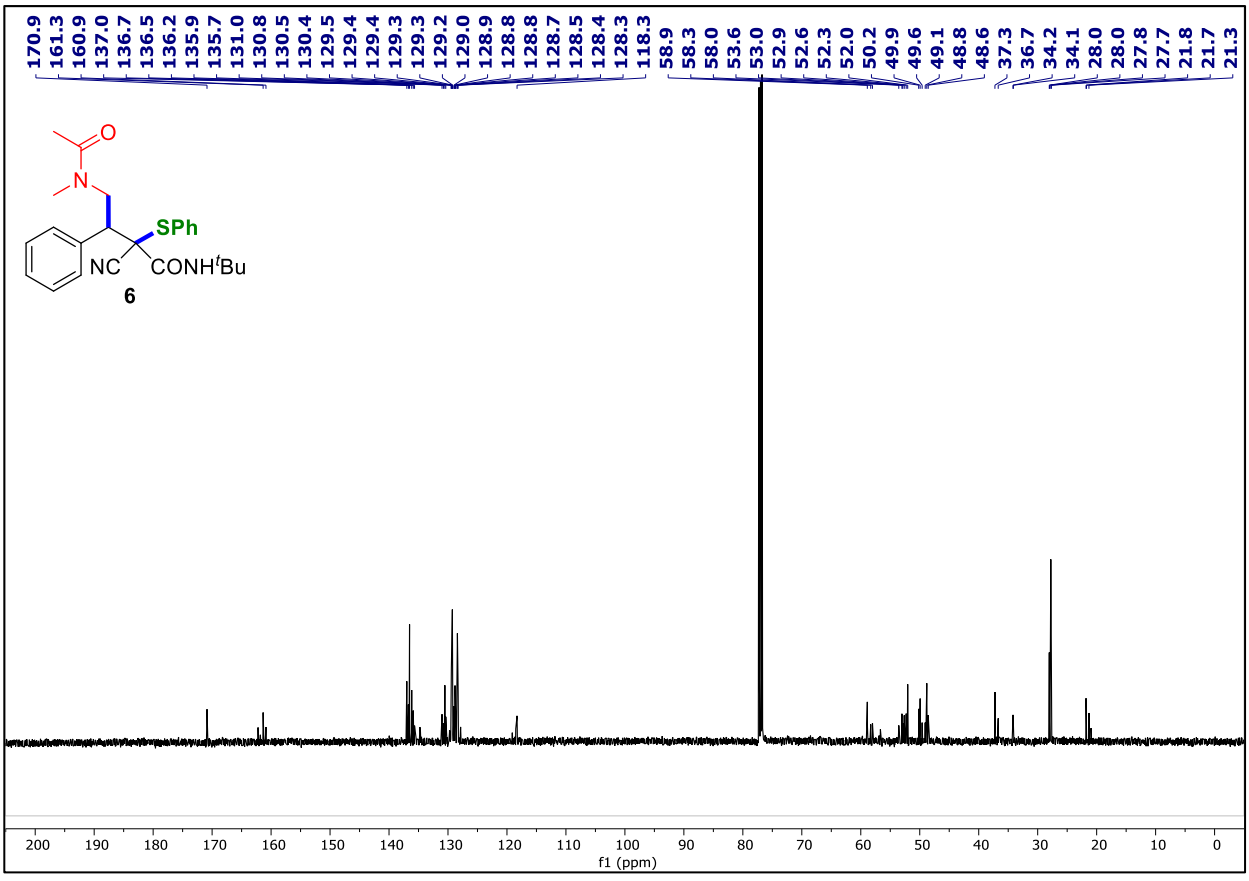
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5a**



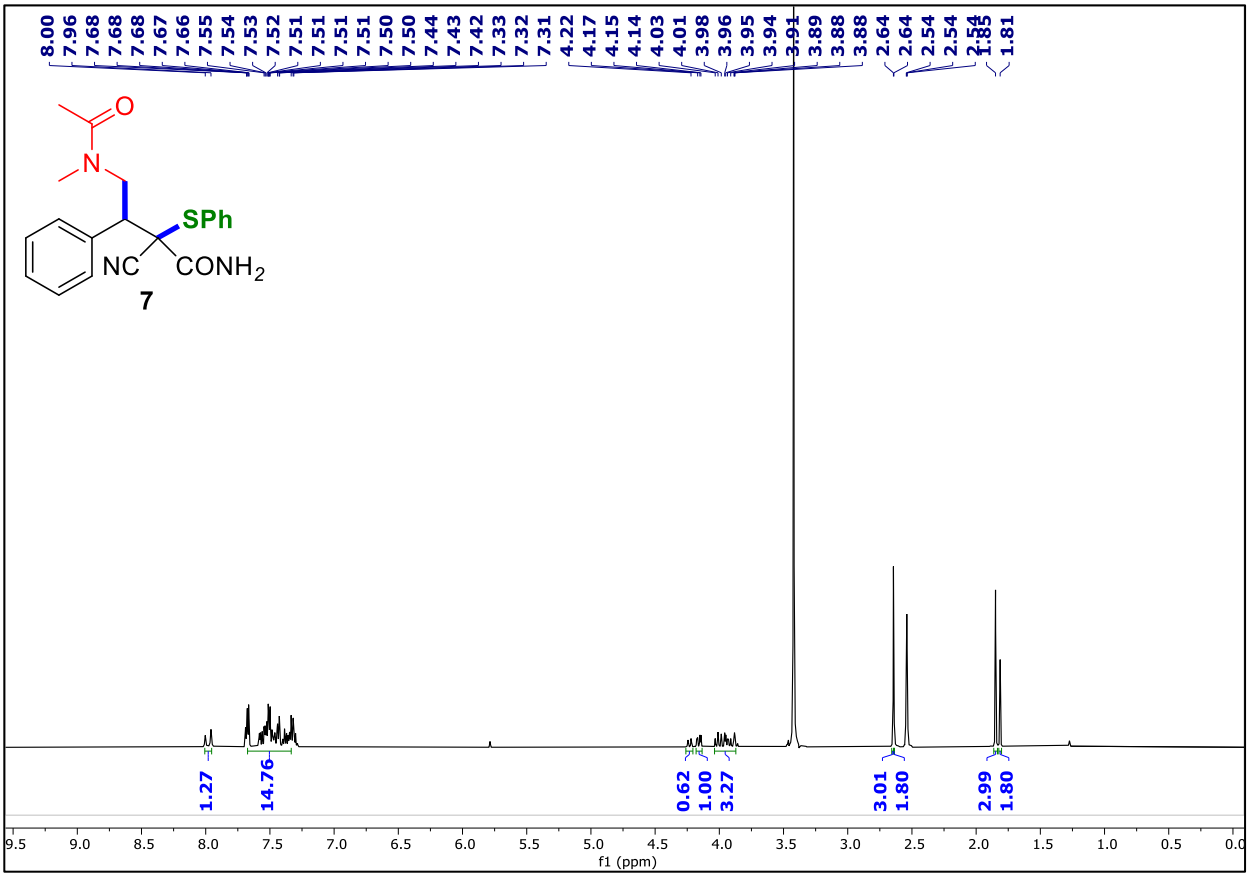
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6,** (dr = 1:0.6, rr = 1 : 0.5)



^{13}C NMR (126 MHz, $CDCl_3$) of compound **6,** (dr = 1:0.6, rr = 1 : 0.5)



^{1}H NMR (500 MHz, DMSO-D$_6$) of compound **7**, (dr = 1: 0.6)



^{13}C NMR (126 MHz, CDCl$_3$–DMSO-D$_6$) of compound **7**, (dr = 1: 0.6)