Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Access to Chiral Sulfones with An All-Carbon Quaternary Stereocenter from Sulfur Dioxide

Chunxi Huang,[1†] Xuemei Zhang,[1†] Liping Luo,[1] Xiuwen Jia,[1] Jian Liao*[2] and Zhong Lian*[1]

[1] C. Huang, Dr. X. Zhang, Dr. Li Xue, L. Luo, X. Jia, Prof. Dr. Z. Lian

Department of Dermatology, State Key Laboratory of Biotherapy and Cancer Center

West China Hospital, Sichuan University

[2] Prof. Dr. J. Liao

Chengdu Institute of Biology, Chinese Academy of Sciences

†These authors contributed equally.

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1. General information

All reactions were carried out in oven dried two-chamber under argon atmosphere glovebox (Vigor, SGI800-750TS-F). Unless otherwise noted, all reactions or reagents were obtained from commercial suppliers and used as received. All work-up and purification procedures were carried out with reagent-grade solvents in air. Chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

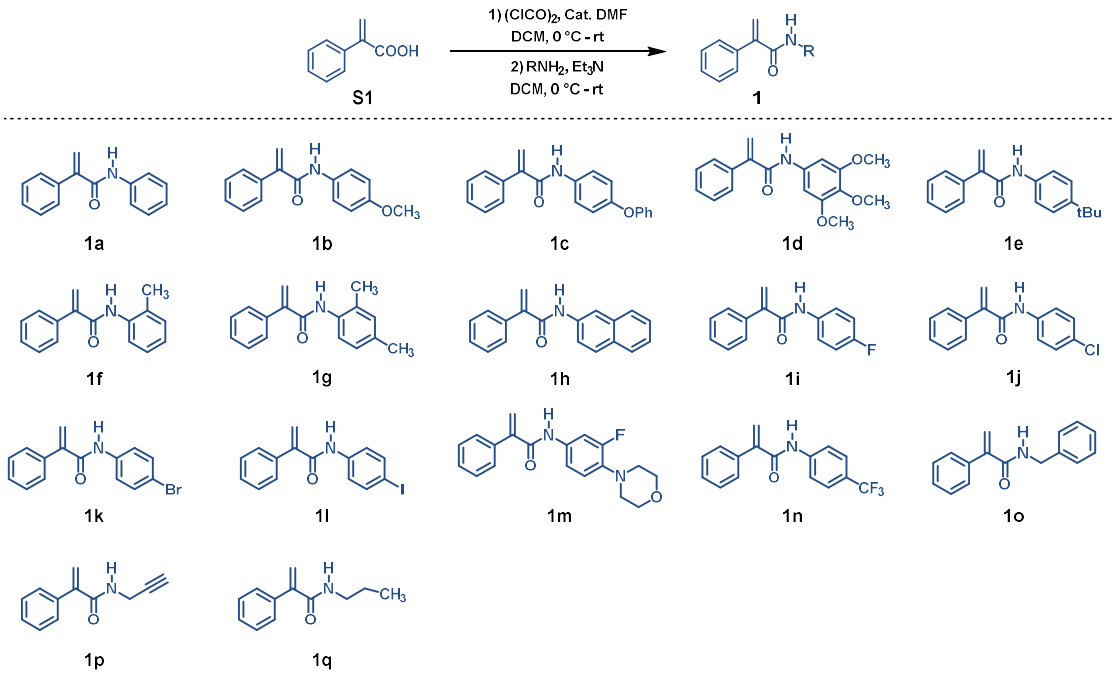
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz, respectively in $CDCl_3$ or $(CD_3)_2SO$ at room temperature. ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 2.50 ppm for $(CD_3)_2SO$ for ^{1}H NMR. The ^{13}C NMR spectra (^{1}H-broadband decoupled) were reported in ppm using the central peak of $(CD_3)_2SO$ at 39.52 ppm. The solvent residue peak of ethyl acetate in $(CD_3)_2SO$ was at 1.99 ppm, 4.03 ppm and 1.17 ppm for ^{1}H NMR and 20.68 ppm, 170.31 ppm, 59.74ppm and 14.40 ppm for ^{13}C NMR. The solvent residue peak for dichloromethane in $(CD_3)_2SO$ is at 5.76 ppm for ^{1}H NMR and 54.84 ppm for ^{13}C NMR.

High-resolution mass spectrometric measurements were provided by the Department of The State Key Laboratory of Biotherapy, Sichuan University. The molecular ion $[M+H]^+$ and $[M+Na]^+$ are given in m/z units.

Enantiomer ratios were determined by UHPLC (Chiralpak AD-H, OD-H, IA-H, IB-H, IC-H columns were purchased from Daicel Chemical Industries, LTD). Optical rotations were measured on an INESA SGW-1polarimeter, and reported as $[\alpha]_{\lambda}^{T}$ (concentration (c): g/100 mL, in $CHCl_3$).

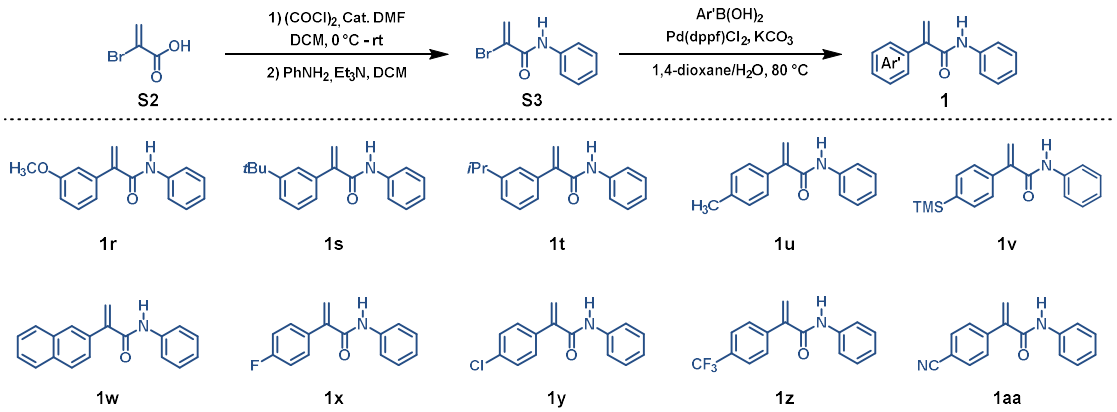
2. General procedure for the synthesis of starting material

A. General procedure for the synthesis of *α, β*-unsaturated amides[1-4]



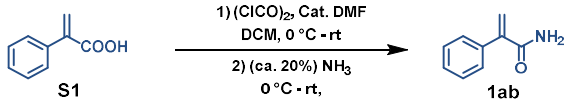
The procedure was based on a modified literature procedure. Oxalyl chloride (10.0 mmol, 2.0 equiv.) was added dropwise to a solution of 2-aryl acrylic acid (5.0 mmol, 1.0 equiv.) in dry DCM (20 mL) under N_2 at 0 °C, followed by the addition of a catalytic amount of dry DMF (3 drops). The reaction mixture was stirred at room temperature for 3 hours. Subsequently, the reaction was evaporated under reduced pressure and the resulting crude acyl chloride was used directly for the next reaction without further purification.

For the next step, a solution of aniline (5.0 mmol, 1.0 equiv.) and Et_3N (1.1 mL, 7.5 mmol, 1.5 equiv.) in DCM (30 mL) was prepared at 0 °C. To this solution, a solution of acyl chloride (5.0 mmol, 1.0 equiv.) in DCM was added dropwise, and the resulting mixture was stirred at room temperature for 3 hours. The mixture was then diluted with DCM (20 mL) and washed sequentially with saturated $NaHCO_3$ (aq. 30 mL) and brine (30 mL). The organic extracts were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the corresponding *α, β*-unsaturated amides. The product was purified by flash chromatography.

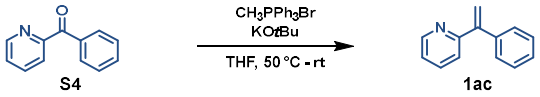


The procedure was based on a modified literature procedure. Oxalyl chloride (10.0 mmol, 2.0 equiv.) was added dropwise to a solution of 2-bromoacrylic acid (5.0 mmol, 1.0 equiv.) in dry dichloromethane (DCM, 20 mL) at 0 °C under a nitrogen atmosphere, followed by some dimethylformamide (DMF, 3 drops). The reaction mixture was stirred at room temperature for 2 hours. The volatiles were evaporated under reduced pressure and the resulting crude acyl chloride was used directly for the next reaction without further purification. To a solution of aniline (5.0 mmol, 1.0 equiv.) and Et_3N (7.5 mmol, 1.5 equiv.) in DCM (20.0 mL) at 0 °C was added dropwise a solution of acyl chloride (5.0 mmol, 1.0 equiv.) in DCM (5.0 mL), the resulting mixture was stirred at room temperature for 2 hours. The mixture was washed by H_2O, and the organic extracts were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Finally, the residue was purified by column chromatography to give the desired 2-bromoacrylic amide.

In glovebox, to a pressure bottle was added the 2-bromoacrylic amide (2.0 mmol, 1.0 equiv.), aryl boronic acid (2.4 mmol, 1.2 equiv.), $Pd(dppf)Cl_2$ (0.04 mmol, 0.02 equiv.), K_2CO_3 (2.4 mmol, 1.2 equiv.), dioxane (5.0 mL) and water (5.0 mL). The bottle was sealed and removed out of the glovebox and heated to 80 °C for 6 hours in an oil bath. After 6 hours, the bottle was cooled to room temperature. The mixture was washed by brine, dried, concentrated and purified by column chromatography to give the desired product.

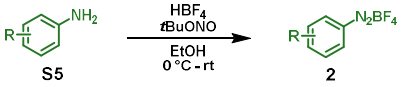


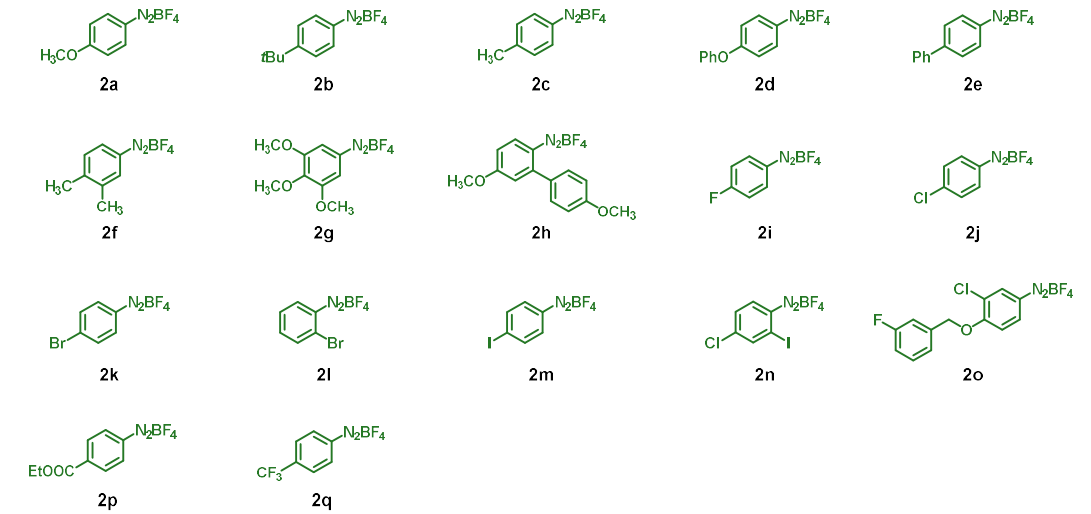
The procedure was based on a modified literature procedure. To a solution of atropic acid (3.37 mmol, 1.0 equiv.) and oxalyl chloride (4.1 mmol, 1.2 equiv.) in anhydrous DCM (6.7 mL), was added a drop of anhydrous DMF. The reaction was then stirred at room temperature for 3 h. The excess amount of solvent and oxalyl chloride were removed in vacuo, and (ca. 20%) aqueous solution of NH_3 (0.54 mL) was added to the residue under stirring at 0 °C. The reaction was stirred at room temperature for another 1 h. The reaction mixture was extracted with ethyl acetate (15 mL × 3), then combined organic layer was then washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The solid residue was purified through crystallization (10% EA/PE) to afford the product as a colorless crystalline solid (367 mg, 2.49 mmol, 74%).



The procedure was based on a modified literature procedure. A dry 100 mL round bottom flask equipped with a magnetic stir bar was charged with methyltriphenylphosphonium bromide (10 mmol, 2.0 equiv.) and KO*t*Bu (12 mmol, 1.2 equiv.) followed by THF (20 mL). The resulting yellow suspension was stirred at room temperature for 1 hour. A solution of 2-benzoylpyridine (5.0 mmol, 1.0 equiv.) in THF (10 mL) was added dropwise and the resulting mixture was stirred at 50 °C for 1 hour and allowed to cool down overnight. Next, a saturated solution of NH_4Cl (25 mL) followed by distilled water (25 mL) were added and the resulting mixture was extracted with ethyl acetate (3 x 50 mL). The organic phases were combined and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was further purified by flash chromatography on silica gel to afford the corresponding alkenes.

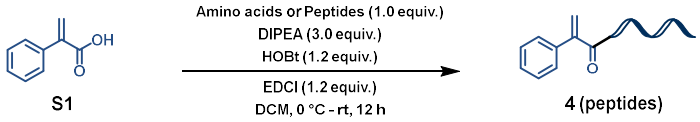
B. General procedure for the synthesis of diazonium salts[5-6]





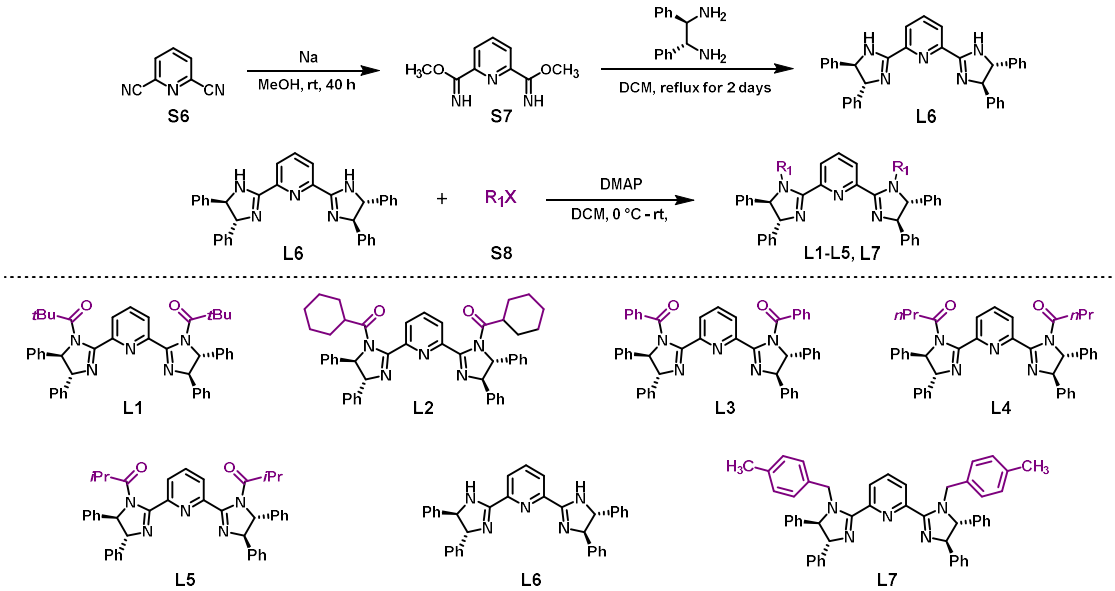
In a 100 mL round-bottom flask, the aniline (10.0 mmol, 1.0 equiv.) was dissolved in a mixture of absolute ethanol (3.0 mL) and an aqueous solution of HBF_4 (48% aq. 13.6 mmol, 1.36 equiv.), followed by dropwise addition of tert-butyl nitrite (23.0 mmol, 2.3 equiv.) at 0 °C. After stirring at room temperature for 2 hours, diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. The solids were filtered off and washed with diethyl ether (3×10 mL), dried in vacuo for 10 minutes, and stored in refrigerator under N_2 atmosphere.

C. sGeneral procedure for the synthesis of 4[7]



To a mixture of **1a** (0.44 g, 3.0 mmol), amino acids or peptides (3.0 mmol), and diisopropylethylamine (1.16 g, 9.0 mmol) in dry CH_2Cl_2 (20 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 0.69 g, 3.6 mmol) and 1-hydroxybenzotriazole (HOBt, 0.49 g, 3.6 mmol) in portions at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and stirred at 25 ºC for 12 h. The mixture was washed with sat. aq. $NaHCO_3$ (1 x 20 mL), citric acid (1 x 20 mL) and H_2O (1 x 20 mL), dried over anhydrous $MgSO_4$, filtrated, and concentrated. The resulting crude material was purified by column chromatography on silica gel to provide **4** as a white solid.

3. General procedure for the synthesis of pybim ligands[8]



To pyridine-2,6-carbodinitrile **S6** (41.5 mmol) in anhydrous MeOH (100 mL), Na (5.2 mmol) was added. After stirring for 40 h at room temperature, acetic acid (5.25 mmol) was added and the solvent was removed under reduced pressure. **S7** was obtained as a yellow powder (100 %) and was used directly for further reactions.

A 100 mL pressure tube was charged with **S7** (804 mg, 4.17 mmol), (*R, R*)-1,2-diphenyl ethylene diamine (8.75 mmol) and DCM (20 mL). After the resulting mixture was stirred at refluxing temperature for two days, water (20 mL) was added and the phases

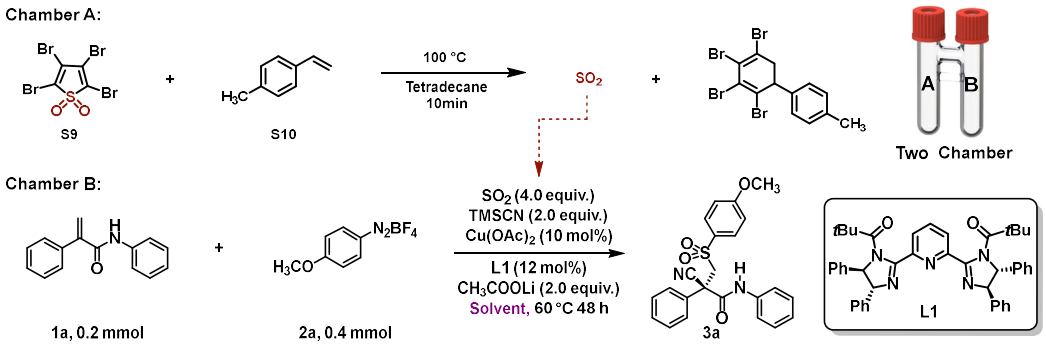
were separated. The aqueous phase was extracted with DCM (20 mL x 2). The combined organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo to give a yellow solid, which was purified by crystallization to give **L6** as a white solid.

To a stirring solution of **L6** (0.62 mmol) in anhydrous THF (15 mL), sodium hydride (2.47 mmol) was added at 0 °C. After 15 min, 4-Methylbenzyl bromide (1.85 mmol) was slowly added and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with water and the aqueous phase was extracted with DCM (20 mL x 2). The organic layer was dried over $MgSO_4$ and the solvents were removed in vacuo to give a yellow solid, which was purified by column chromatography on silica gel to give **L7** as a white solid.

A 100 mL round-bottom flask was charged with **L6** (1.0 mmol), DMAP (3.0 mmol) and DCM (15 mL). The resulting mixture was cooled to 0 °C, and acyl chloride (2.5 mmol) was added neat at once. The ice bath was removed, and the reaction mixture was stirred at room temperature for 5 hours. The solvent was removed under vacuo, the residue was partitioned between saturated NH_4Cl (25 mL) and ethyl acetate (25 mL), and the aqueous phase was re-extracted with ethyl acetate (25 mL x 2). The combined organic layer was dried (over $MgSO_4$), and the solvent was removed in vacuo to give **L1-L5** as a white solid, which was purified by column chromatography on silica gel.

4. Detailed Optimization of Reaction Conditions

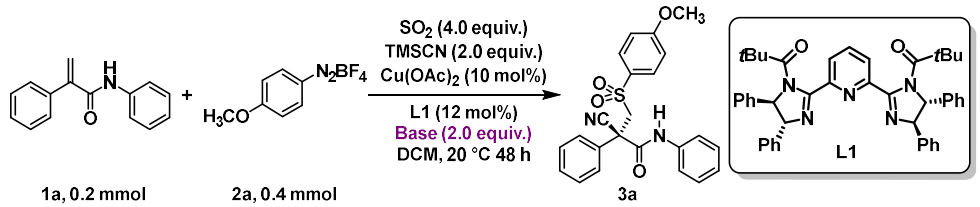
Supplementary Table S1. Reaction condition optimization: screening of solvent



Entry	**Solvent**	Yield (%)	Ee (%)
1	DCM (20 ℃)	62	>99
2	DMSO	n.d.	/
3	THF	trace	/
4	Anisole	26	>99
5	$CHCl_3$	n.d.	/

[a] Reaction conditions: The metal and ligand were stirred for 1h in advance. Chamber A, **S9** (0.88 mmol), **S10** (0.8 mmol), tetradecane (1 mL), at 100 °C for 10 min; Chamber B, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol), TMSCN (0.4 mmol), CH_3COOLi (0.4 mmol), $Cu(OAc)_2$ (10 mol%), **L1** (12 mol%), Solvent (x mL), at 60 °C for 48 h. Yields were determined by ^1H NMR (1,3,5-Trimethoxybenzene was the internal standard). Enantiomeric excess (*ee*) was determined by ultra-high-performance liquid chromatography with a chiral stationary phase.

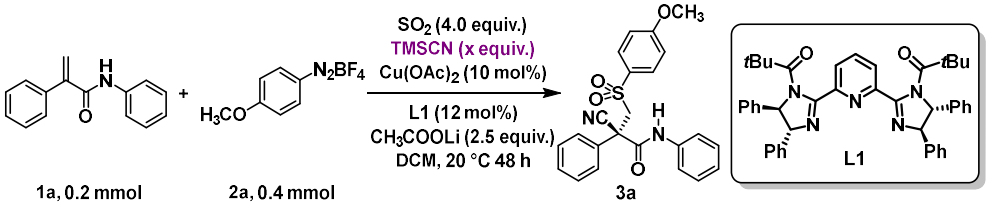
Supplementary Table S2. Reaction condition optimization: screening of base



Entry	**Base**	Yield (%)	Ee (%)
1	None	n.d.	/
2	CsF	40	>99
3	*t*BuOLi	21	>99
4	CH_3COONa	15	>99
5	CH_3COOK	17	>99
6	CH_3COOLi (2.0 equiv.)	62	>99
7	CH_3COOLi (2.5 equiv.)	66	>99
8	CH_3COOLi (3.0 equiv.)	59	>99

[a] Reaction conditions: The metal and ligand were stirred for 1h in advance. Chamber A, **S9** (0.88 mmol), **S10** (0.8 mmol), tetradecane (1 mL), at 100 °C for 10 min; Chamber B, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol), TMSCN (0.4 mmol), base (x mmol), $Cu(OAc)_2$ (10 mol%), **L1** (12 mol%), DCM (2.5 mL), at 20 °C for 48 h. Yields were determined by ^1H NMR (1,3,5-Trimethoxybenzene was the internal standard). Enantiomeric excess (*ee*) was determined by ultra-high-performance liquid chromatography with a chiral stationary phase.

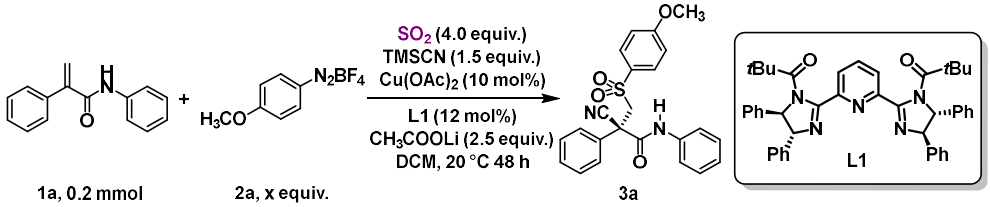
Supplementary Table S3. Reaction condition optimization: screening of TMSCN ratio



Entry	**TMSCN** (x equiv.)	Yield (%)	Ee (%)
1	2.0	66	>99
2	1.75	67	>99
3	1.5	71	>99
4	1.25	65	>99
5	1.0	61	>99

[a] Reaction conditions: The metal and ligand were stirred for 1h in advance. Chamber A, **S9** (0.88 mmol), **S10** (0.8 mmol), tetradecane (1 mL), at 100 °C for 10 min; Chamber B, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol), TMSCN (x mmol), CH_3COOLi (0.5 mmol), $Cu(OAc)_2$ (10 mol%), **L1** (12 mol%), DCM (2.5 mL), at 20 °C for 48 h. Yields were determined by ^1H NMR (1,3,5-Trimethoxybenzene was the internal standard). Enantiomeric excess (*ee*) was determined by ultra-high-performance liquid chromatography with a chiral stationary phase.

Supplementary Table S4. Reaction condition optimization: screening of aryldiazonium tetrafluoroborate ratio

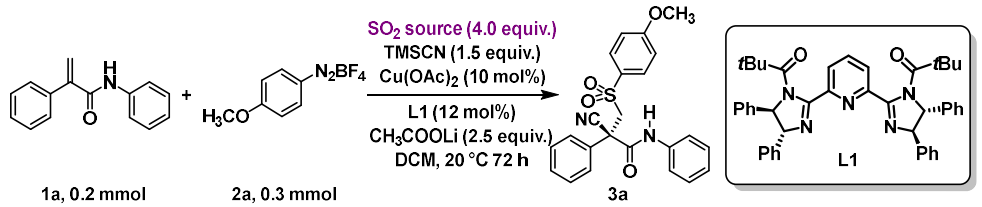


1a, 0.2 mmol 2a, x equiv. 3a

Entry	**2a** (x equiv.)	Yield (%)	Ee (%)
1	1.0	67	>99
2	1. 5 (48 h)	77	>99
3	1. 5 (72 h)	85	>99
4	2.0	71	>99
5	2.5	70	>99
6	3.0	57	>99

[a] Reaction conditions: The metal and ligand were stirred for 1h in advance. Chamber A, **S9** (0.88 mmol), **S10** (0.8 mmol), tetradecane (1 mL), at 100 °C for 10 min; Chamber B, **1a** (0.2 mmol, 1.0 equiv.), **2a** (x mmol), TMSCN (0.3 mmol), CH_3COOLi (0.5 mmol), $Cu(OAc)_2$ (10 mol%), L1 (12 mol%), DCM (2.5 mL), at 20 °C for 48 h. Yields were determined by ^1H NMR (1,3,5-Trimethoxybenzene was the internal standard). Enantiomeric excess (*ee*) was determined by ultra-high-performance liquid chromatography with a chiral stationary phase.

Supplementary Table S5. Reaction condition optimization: screening of SO_2 source and SO_2 ratio



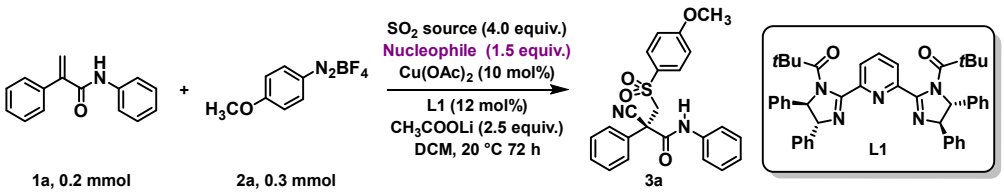
1a, 0.2 mmol 2a, 0.3 mmol 3a

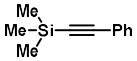
Entry	**SO_2**	Yield (%)	Ee (%)
1	$Na_2S_2O_5$	28	>99
2	$K_2S_2O_5$	23	>99
3	$Na_2S_2O_4$	25	>99
4	DABSO	35	>99
5	Rongalite	n.d.	>99
6[b]	TsCl	trace	/
7	SOgen (3.5 equiv.)	60	>99
8	SOgen (4.0 equiv.)	85	>99
9[c]	SOgen (4.0 equiv.)	trace	/

[a] Reaction conditions: The metal and ligand were stirred for 1h in advance. **SO_2 substitutes**, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol), TMSCN (0.3 mmol), CH_3COOLi (0.5 mmol), $Cu(OAc)_2$ (10 mol%), **L1** (12 mol%), DCM (2.5 mL), at 20 °C for 72 h. Yields were determined by ^1H NMR (1,3,5-Trimethoxybenzene was the internal standard). Enantiomeric excess (*ee*) was determined by ultra-high-performance liquid chromatography with a chiral stationary phase. [b] TsCl was substituted for **2a** and **SOgen** at 20 °C for 72 h. [c] The metal and ligand were stirred for 1h in advance. Then, a mixture of **S9** (0.88 mmol), **S10** (0.8

mmol), tetradecane (1 mL), **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol), TMSCN (0.3 mmol), CH_3COOLi (0.5 mmol), $Cu(OAc)_2$ (10 mol%), **L1** (12 mol%), and DCM (2.5 mL) was heated at 100 °C for 10 minutes followed by an additional 72 hours at 20 °C.

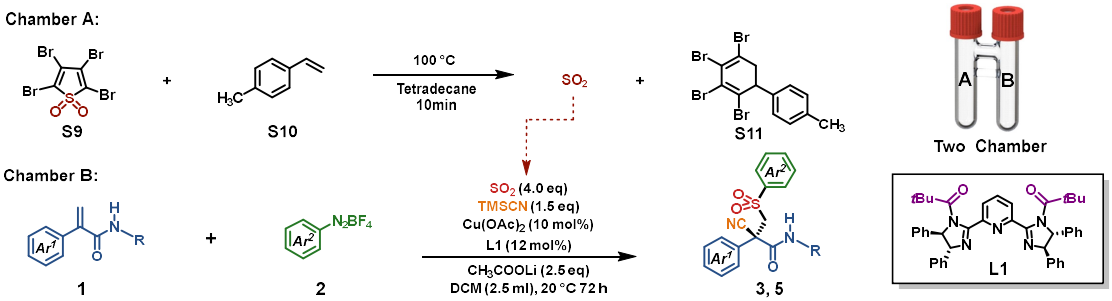
Supplementary Table S6. Reaction condition optimization: screening of other nucleophile



Entry	**Nucleophile**	Yield (%)	Ee (%)
1	$TMSCF_3$	n.d.	/
2	TMSCl	n.d.	/
3		n.d.	/

[a] Reaction conditions: The metal and ligand were stirred for 1h in advance. Chamber A, **S9** (0.88 mmol), **S10** (0.8 mmol), tetradecane (1 mL), at 100 °C for 10 min; Chamber B, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol), nucleophile (0.3 mmol), CH_3COOLi (0.5 mmol), $Cu(OAc)_2$ (10 mol%), **L1** (12 mol%), DCM (2.5 mL), at 20 °C for 48 h. Yields were determined by ^1H NMR (1,3,5-Trimethoxybenzene was the internal standard). Enantiomeric excess (*ee*) was determined by ultra-high-performance liquid chromatography with a chiral stationary phase.

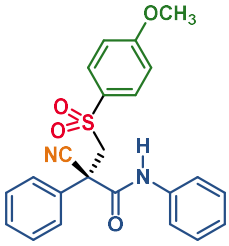
5. General procedure for the synthesis of compounds 3 and 5



In the argon glovebox, $Cu(OAc)_2$ (3.6 mg, 10.0 mol%) and **L1** (16.5 mg 12.0 mol%) were dissolved in DCM (2.5 mL) in a dried sealed vial under argon atmosphere, and the mixture was stirred for 30 minutes. Then **1** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CH_3COOLi (0.5 mmol, 2.5 equiv.) and the mixture were added to chamber B. Tetrabromothiophene S, S-dioxides (0.88 mmol, 380 mg) in tetradecane (1.0 mL) was added to chamber A, followed by addition of 4-methylphenylene (0.80 mmol, 105 μl). The chamber A was sealed and removed out of the glovebox and heated to 100 °C in heating mantle for 10 min. Then chamber B heated to 20 °C in low-temperature stirring reaction bath for 72 hours. After 72 hours, two chamber was cooled to room temperature. The filtrate was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography to give the desired product.

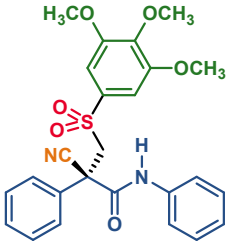
6. Characterization data of products 3 and 5

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*,2-diphenylpropanamide (3a)



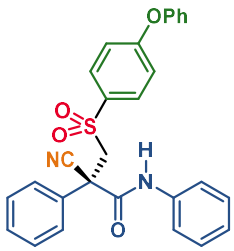
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (70 mg, 83% yield, >99% *ee*). $[\alpha]D^{19}$ = + 47.0 (c = 0.64, $CHCl_3$). According to the X-ray analysis, the "absolute stereochemistry" of the product is the *R* configuration. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.00 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.48 (m, 4H), 7.44 – 7.36 (m, 3H), 7.33 – 7.29 (m, 2H), 7.14 – 7.07 (m, 3H), 4.71 (d, *J* = 14.8 Hz, 1H), 4.52 (d, *J* = 14.8 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.8, 137.8, 133.3, 131.4, 130.2, 129.1, 128.6, 126.4, 124.7, 121.0, 117.2, 114.5, 59.4, 55.8, 51.0; **HRMS** *m/z* calculated for $C_{23}H_{20}N_2O_4S$ $[M+Na]^+$: 443.1036, found: 443.1038; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 45.28 min (minor) and 50.66 min (major).

(*R*)-2-cyano-*N*,2-diphenyl-3-((3,4,5-trimethoxyphenyl)sulfonyl)propenamide (3b)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (48 mg, 50% yield, >99% *ee*). $[\alpha]D^{16}$ = + 31.8 (c = 0.37, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.99 (s, 1H), 7.50 – 7.47 (m, 4H), 7.39 – 7.29 (m, 5H), 7.14 – 7.09 (m, 1H), 7.01 (s, 2H), 4.74 – 4.66 (m, 2H), 3.81 (s, 6H), 3.69 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 162.8, 152.7, 141.6, 137.8, 134.3, 132.6, 129.1, 128.9, 128.7, 126.6, 124.7, 120.9, 117.3, 105.3, 60.1, 59.3, 56.1, 51.0; **HRMS** *m/z* calculated for $C_{25}H_{24}N_2O_6S$ $[M+Na]^+$: 503.1247, found: 503.1249; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 70/30, flow 0.5 mL/min, detection at 214 nm) retention time = 73.61 min (minor) and 78.53 min(major).

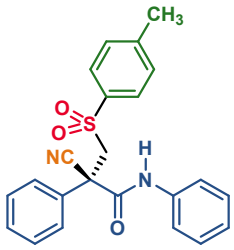
(*R*)-2-cyano-3-((4-phenoxyphenyl)sulfonyl)-*N*,2-diphenylpropanamide (3c)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (61 mg, 63% yield, >99% *ee*). $[\alpha]D^{19}$ = + 33.3 (c = 0.40, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.02 (s, 1H), 7.80 (d, *J* = 9.2 Hz, 2H), 7.53 – 7.46 (m, 6H), 7.44 – 7.38 (m, 3H), 7.34 – 7.25 (m, 3H), 7.15 – 7.09 (m, 3H), 7.06 (d, *J* = 9.2 Hz, 2H), 4.74 (d, *J* = 15.2 Hz, 1H), 4.60 (d, *J* =

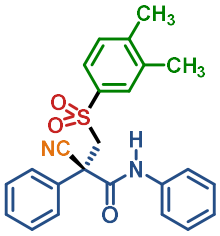
15.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.7, 161.7, 154.6, 137.7, 133.5, 133.0, 130.6, 130.5, 129.13, 129.11 , 128.6, 126.4, 125.1, 124.7, 121.0, 120.1, 117.5, 117.2, 59.2, 50.9; **HRMS** *m/z* calculated for $C_{28}H_{22}N_2O_4S$ $[M+Na]^+$: 505.1192, found: 505.1196; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 49.37 min (minor) and 54.81 min (major).

(*R*)-2-cyano-*N*,2-diphenyl-3-tosylpropanamide (3d)



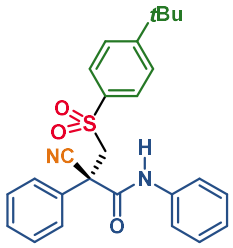
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (50 mg, 62% yield, 96% *ee*). $[\alpha]D^{19}$ = + 36.9 (c = 0.29, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.02 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.43 – 7.37 (m, 5H), 7.34 – 7.29 (m, 2H), 7.14 – 7.10 (m, 1H), 4.72 (d, *J* = 14.8 Hz, 1H), 4.54 (d, *J* = 14.8 Hz, 1H), 2.36 (s, 3H) ; **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.7, 144.6, 137.7, 137.1, 133.2, 129.7, 129.1, 128.6, 127.9, 126.4, 124.7, 121.0, 117.2, 59.3, 50.9, 21.1; **HRMS** *m/z* calculated for : $C_{23}H_{20}N_2O_3S$ $[M+Na]^+$: 427.1087, found: 427.1088; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 38.98 min (minor) and 44.59 min (major).

(*R*)-2-cyano-3-((3,4-dimethylphenyl)sulfonyl)-*N*,2-diphenylpropanamide (3e)



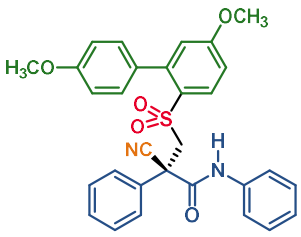
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (53 mg, 63% yield, >99% *ee*). $[\alpha]D^{19}$ = + 65.8 (c = 0.57, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.96 (s, 1H), 7.55 (d, *J* = 8.0, 1H), 7.51 – 7.45 (m, 5H), 7.41-7.37 (m, 3H), 7.33-7.29 (m, 3H), 7.13 – 7.09 (m, 1H), 4.70 (d, *J* = 15.2 Hz, 1H), 4.54 (d, *J* = 15.2 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.7, 143.4, 137.7, 137.6, 137.1, 133.1, 130.0, 129.1, 129.0, 128.6, 128.4, 126.4, 125.3, 124.6, 120.9, 117.2, 59.2, 51.0, 19.5, 19.3; **HRMS** *m/z* calculated for $C_{24}H_{22}N_2O_3S$ $[M+Na]^+$: 441.1243, found: 441.1245; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 33.79 min (minor) and 37.53 min (major).

(*R*)-3-((4-(*tert*-butyl)phenyl)sulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3f)



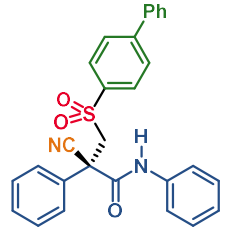
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (67 mg, 75% yield, >99% *ee*). $[\alpha]D^{18}$ = + 19.7 (c = 0.29, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.01 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.47 (m, 4H), 7.39 – 7.29 (m, 5H), 7.14 – 7.09 (m, 1H), 4.72 (d, *J* = 15.2 Hz, 1H), 4.57 (d, *J* = 15.2 Hz, 1H), 1.28 (s, 9H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 162.7, 157.0, 137.8, 137.0, 132.9, 129.12, 129.05, 128.6, 127.7, 126.4, 126.1, 124.7, 121.0, 117.3, 59.2, 50.9, 35.0, 30.7; **HRMS** *m/z* calculated for $C_{26}H_{26}N_2O_3S$ $[M+Na]^+$: 469.1556, found: 469.1557; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 70/30, flow 0.5 mL/min, detection at 214 nm) retention time = 77.25 min (minor) and 84.58 min (major).

(*R*)-2-cyano-3-((4',5-dimethoxy-[1,1'-biphenyl]-2-yl)sulfonyl)-*N*,2-diphenylpropanamide (3g)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (71 mg, 67% yield, >99% *ee*). $[\alpha]D^{16}$ = + 28.0 (c = 0.71, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.02 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.28 (m, 9H), 7.13 – 7.09 (m, 1H), , 7.03 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 2.4 Hz, 1H), 4.24 (d, *J* = 14.8 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.67 (d, *J* = 14.8 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 162.6, 162.5, 159.2, 143.0, 137.7, 132.7, 131.5, 131.1, 130.5, 130.3, 129.2, 129.1, 128.6, 126.2, 124.7, 121.1, 118.2, 117.1, 113.3, 112.8, 59.3, 55.9, 55.2, 50.6; **HRMS** *m/z* calculated for : $C_{30}H_{26}N_2O_5S$ $[M+Na]^+$: 549.1455, found: 549.1456; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 20.37 min (major) and 24.50 min (minor).

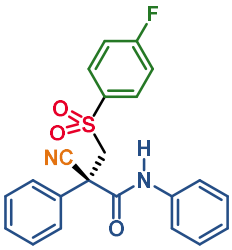
(*R*)-3-([1,1'-biphenyl]-4-ylsulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3h)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (75 mg, 80% yield, >99% *ee*). $[\alpha]D^{19}$ = + 33.5 (c = 0.20, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.07 (s, 1H), 7.88 (dd, *J* =

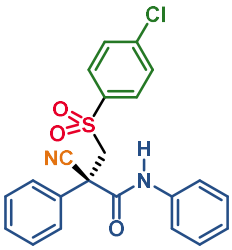
8.8 Hz, 18.4 Hz 4H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.44 (m, 7H), 7.42 – 7.36 (m, 3H), 7.32 – 7.28 (m, 2H), 7.13 – 7.09 (m, 1H), 4.80 (d, *J* = 15.2 Hz, 1H), 4.65 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 162.7, 145.4, 138.6, 138.3, 137.7, 133.0, 129.2, 129.1, 128.8, 128.6, 128.5, 127.4, 127.2, 126.4, 124.7, 121.0, 117.3, 59.3, 50.9; **HRMS** *m/z* calculated for : $C_{28}H_{22}N_2O_3S$ $[M+Na]^+$: 489.1243, found: 489.1244; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 29.78 min (minor) and 32.39 min (major).

(*R*)-2-cyano-3-((4-fluorophenyl)sulfonyl)-*N*,2-diphenylpropanamide (3i)



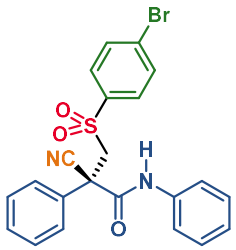
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (53 mg, 65% yield, >99% *ee*). $[\alpha]D^{18}$ = + 69.6 (c = 0.73, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.06 (s, 1H), 7.92 – 7.87 (m, 2H), 7.52 – 7.49 (m, 4H), 7.44 – 7.39 (m, 5H), 7.34 – 7.30 (m, 2H), 7.15 – 7.10 (m, 1H), 4.77 (d, *J* = 15.2 Hz, 1H), 4.66 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 165.1 (d, *J* = 251), 162.7, 137.7, 136.2 (d, *J* = 3), 132.9, 131.2 (d, *J* = 10), 129.2, 129.1, 128.6, 126.4, 124.7, 121.0, 117.2, 116.4 (d, *J* = 23), 59.2, 50.9; **^{19}F NMR (376 Hz, DMSO-d6)** δ -104.5; **HRMS** *m/z* calculated for : $C_{22}H_{17}FN_2O_3S$ $[M+Na]^+$: 431.0836, found: 431.0838; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 30.91 min (minor) and 35.01 min (major).

(*R*)-3-((4-chlorophenyl)sulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3j)



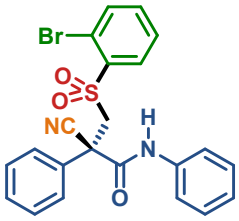
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (56 mg, 66% yield, >99% *ee*). $[\alpha]D^{18}$ = + 50.8 (c = 0.44, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.06 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.51-7.47 (m, 4H), 7.42 – 7.37 (m, 3H), 7.34-7.30 (m, 2H), 7.15 – 7.10 (m, 1H), 4.78 (d, *J* = 15.2 Hz, 1H), 4.67 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 162.6, 139.1, 138.6, 137.7, 132.9, 129.8, 129.4, 129.17, 129.12, 128.6, 126.4, 124.7, 121.0, 117.1, 59.1, 50.8; **HRMS** *m/z* calculated for $C_{22}H_{17}ClN_2O_3S$ $[M+Na]^+$: 447.0541, found: 447.0541; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 27.06 min (minor) and 29.44 min (major).

(*R*)-3-((4-bromophenyl)sulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3k)



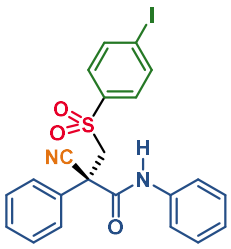
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (60 mg, 64% yield, >99% *ee*). $[\alpha]D^{19}$ = + 69.0 (c = 0.58, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.07 (s, 1H), 7.81 – 7.74 (m, 4H), 7.52-7.47 (m, 4H), 7.42-7.37 (m, 3H), 7.34-7.30 (m, 2H), 7.14 – 7.10 (m, 1H), 4.78 (d, *J* = 15.2 Hz, 1H), 4.66 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.6, 139.0, 137.7, 132.9, 132.3, 129.9, 129.2, 129.1, 128.6, 128.3, 126.4, 124.7, 121.0, 117.1, 59.1, 50.8; **HRMS** *m/z* calculated for $C_{22}H_{17}BrN_2O_3S$ $[M+Na]^+$: 491.0035, found: 491.0041; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 35.52 min (minor) and 38.99 min (major).

(*R*)-3-((2-bromophenyl)sulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3l)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (59 mg, 63% yield, >99% *ee*). $[\alpha]D^{16}$ = + 3.6 (c = 0.41, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.2 (s, 1H), 7.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.55 (td, *J* = 7.6, 1.6 Hz, 1H), 7.51 – 7.46 (m, 5H), 7.37 – 7.29 (m, 5H), 7.14 – 7.10 (m, 1H), 4.86 – 4.76 (m, 2H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.7, 139.0, 137.8, 135.5, 135.3, 132.2, 131.2, 129.4, 129.2 128.7, 128.4, 126.4, 124.8, 121.1, 120.0, 117.3, 58.6, 50.9; **HRMS** *m/z* calculated for : $C_{22}H_{17}BrN_2O_3S$ $[M+Na]^+$: 491.0035, found: 491.0039; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 85/15, flow 0.5 mL/min, detection at 214 nm) retention time = 58.26 min (major) and 66.27 min (minor).

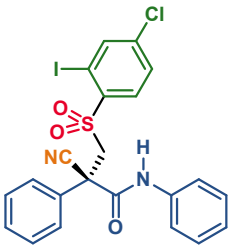
(*R*)-2-cyano-3-((4-iodophenyl)sulfonyl)-*N*,2-diphenylpropanamide (3m)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (62 mg, 60% yield, >99% *ee*). $[\alpha]D^{19}$ = + 65.6 (c = 0.75, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.05 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.42 – 7.37 (m, 3H), 7.34-7.30 (m, 2H), 7.14 – 7.10 (m, 1H), 4.76 (d, *J* = 15.2 Hz, 1H), 4.63 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.6, 139.4, 138.1, 137.7, 132.9, 129.4, 129.1,

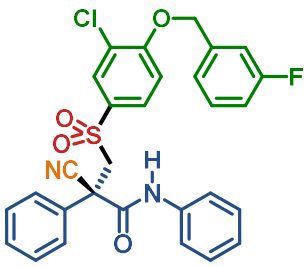
128.7, 126.4, 124.7, 121.0, 117.1, 103.0, 59.1, 50.8; **HRMS** *m/z* calculated for $C_{22}H_{17}IN_2O_3S$ $[M+Na]^+$: 538.9897, found: 538.9900; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 40.11 min (minor) and 43.96 min (major).

(*R*)-3-((4-chloro-2-iodophenyl)sulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3n)



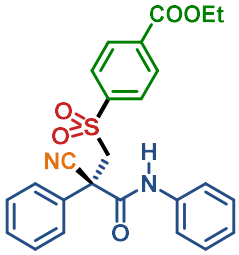
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (47 mg, 43% yield, 99% *ee*). $[\alpha]D^{19}$ = + 21.1 (c = 0.37, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.18 (s, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.37 – 7.29 (m, 5H), 7.14 – 7.10 (m, 1H), 4.86 – 4.76 (m, 2H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.6, 141.0, 140.9, 138.7, 137.6, 132.1, 132.0, 129.2, 129.1, 128.6, 126.3, 124.8, 121.0, 117.1, 96.2, 57.8, 50.8; **HRMS** *m/z* calculated for : $C_{22}H_{16}ClIN_2O_3S$ $[M+H]^+$: 572.9507, found: 572.9507; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 27.26 min (minor) and 30.68 min (major).

(*R*)-3-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)sulfonyl)-2-cyano-*N*,2-diphenylpropanamide (3o)



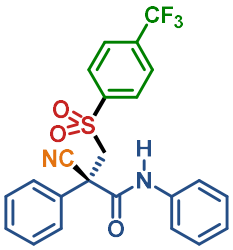
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (77 mg, 70% yield, >99% *ee*). $[\alpha]D^{18}$ = + 30.7 (c = 0.48, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.02 (s, 1H), 7.76 – 7.74 (m, 2H), 7.52 – 7.46 (m, 5H), 7.39 – 7.29 (m, 8H), 7.21 (td, *J* = 8.4, 2.4 Hz, 1H), 7.13 – 7.09 (m, 1H), 5.31 (s, 2H), 4.79 – 4.69 (m, 2H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 162.7, 162.2 (d, *J* = 243 Hz), 157.5, 138.6 (d, *J* = 7 Hz),137.7, 132.8, 132.4, 130.7 (d, *J* = 8 Hz), 129.7, 129.2, 129.0, 128.9, 128.6, 126.5, 124.7, 123.4 (d, *J* = 3 Hz), 122.1, 120.9, 117.2, 115.0 (d, *J* = 20 Hz), 114.2 (d, *J* = 22 Hz), 114.0, 69.7, 59.2, 51.0; **^{19}F NMR (376 Hz, DMSO-d6)** δ -112.8; **HRMS** *m/z* calculated for : $C_{29}H_{22}ClFN_2O_4S$ $[M+Na]^+$: 571.0865, found: 571.0864; **HPLC** (Daicel Chirapak IB column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 40.05 min (minor) and 44.73 min (major).

Ethyl (*R*)-4-((2-cyano-3-oxo-2-phenyl-3-(phenylamino)propyl)sulfonyl)benzoate (3p)



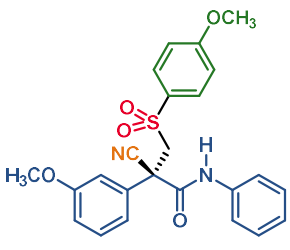
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (40 mg, 43% yield, 99% *ee*). $[\alpha]D^{15}$ = + 52.7 (c = 0.89, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d6)** δ 10.06 (s, 1H), 8.08 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.52 – 7.45 (m, 4H), 7.40 – 7.36 (m, 3H), 7.32 – 7.28 (m, 2H), 7.13 – 7.09 (m, 1H), 4.83 (d, J = 15.2 Hz, 2H), 4.74 (d, J = 15.2 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d6)** δ 164.6, 162.6, 143.5, 137.7, 134.3, 132.9, 129.9, 129.3, 129.2, 128.7, 128.4, 126.5, 124.8, 120.9, 117.2, 61.6, 59.0, 50.9, 14.1. **HRMS** *m/z* calculated for: $C_{25}H_{22}N_2O_5S$ $[M+H]^+$: 463.1322, found: 463.1320; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 70/30, flow 1.0 mL/min, detection at 210 nm) retention time = 27.56 min (minor) and 31.08 min (major).

(*R*)-2-cyano-*N*,2-diphenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)propenamide (3q)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (32 mg, 35% yield, 98% *ee*). $[\alpha]D^{15}$ = + 10.1 (c = 1.39, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d6)** δ 10.09 (s, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.50 – 7.46 (m, 4H), 7.38 – 7.29 (m, 5H), 7.14 – 7.10 (m, 1H), 4.81 (dd, J = 15.2 Hz, 2H). **^{13}C NMR (101 MHz, DMSO-d6)** δ 162.6, 143.6, 137.7, 133.4 (q, J = 32.2 Hz), 132.6, 129.2, 129.1, 129.0, 128.7, 126.5, 126.4 (q, J = 3.7 Hz) , 124.8, 120.9, 117.1, 59.0, 50.8. **^{19}F NMR (376 Hz, DMSO-d6)** δ -61.8; **HRMS** *m/z* calculated for: $C_{23}H_{17}F_3N_2O_3S$ $[M+H]^+$: 459.0985, found: 459.0988; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 70/30, flow 0.5 mL/min, detection at 210 nm) retention time = 24.68 min (minor) and 25.93 min (major).

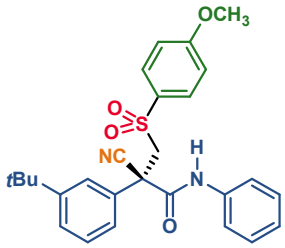
(*R*)-2-cyano-2-(3-methoxyphenyl)-3-((4-methoxyphenyl)sulfonyl)-*N*-phenylpropanamide (3r)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (68 mg, 75% yield, >99% *ee*). $[\alpha]D^{18}$ = + 30.6 (c = 0.26, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.98 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 7.2 Hz,

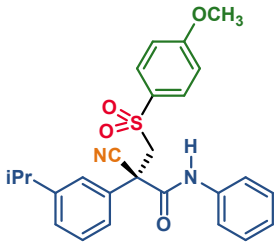
2H), 7.32 (td, *J* = 8.0, 3.2 Hz, 3H),, 7.14 – 7.04 (m, 4H), 6.99 – 6.93 (m, 2H), 4.67 (d, *J* = 15.2 Hz, 1H), 4.55 (d, *J* = 15.2 Hz, 1H) 3.81 (s, 3H), 3.73 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.7, 159.5, 137.8, 134.3, 131.3, 130.3, 130.2, 128.6, 124.7, 121.0, 118.5, 117.2, 114.4, 114.3, 112.6, 59.2, 55.8, 55.3, 50.9; **HRMS** *m/z* calculated for : $C_{24}H_{22}N_2O_5S$ $[M+Na]^+$: 473.1142, found: 473.1142; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 80/20, flow 0.5 mL/min, detection at 214 nm) retention time = 66.19 min (major) and 71.48 min (minor).

(*R*)-2-(3-(tert-butyl)phenyl)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-phenylpropanamide (3s)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (58 mg, 61% yield, >99% *ee*). $[\alpha]D^{19}$ = + 57.9 (c = 0.49, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.02 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.51 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.39 (m, 1H), 7.34 – 7.30 (m, 4H), 7.14 – 7.10 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.69 (d, *J* = 14.8 Hz, 1H), 4.57 (d, *J* = 14.8 Hz, 1H), 3.81 (s, 3H), 1.24 (s, 9H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.9, 151.6, 137.7, 132.9, 131.4, 130.2, 128.8, 128.6, 126.1, 124.7, 123.6, 123.1, 121.2, 117.4, 114.4, 59.6, 55.8, 51.2, 34.7, 31.0; **HRMS** *m/z* calculated for : $C_{27}H_{28}N_2O_4S$ $[M+Na]^+$: 499.1662, found: 499.1665; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 12.29 min (major) and 13.91 min (minor).

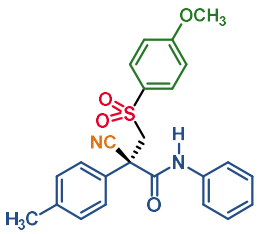
(*R*)-2-cyano-2-(3-isopropylphenyl)-3-((4-methoxyphenyl)sulfonyl)-*N*-phenylpropanamide (3t)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (60 mg, 65% yield, >99% *ee*). $[\alpha]D^{18}$ = + 64.3 (c = 0.85, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.00 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.37 (s, 1H), 7.34 – 7.24 (m, 5H), 7.14 – 7.10 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.54 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H), 2.86 (hept, *J* = 6.8 Hz, 1H), 1.17 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.8, 149.3, 137.8, 133.1, 131.4, 130.2, 129.1, 128.6, 127.0, 124.7, 124.5, 123.9, 121.1, 117.3, 114.4, 59.5 55.8, 51.0, 33.4, 23.6; **HRMS** *m/z* calculated for : $C_{26}H_{26}N_2O_4S$ $[M+Na]^+$: 485.1505, found:

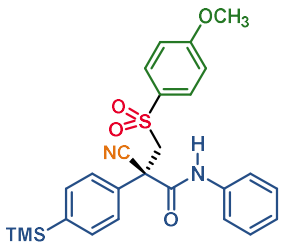
485.1506; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 13.37 min (major) and 15.09 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-phenyl-2-(*p*-tolyl)propenamide (3u)



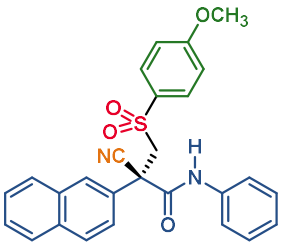
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (46 mg, 53% yield, >99% *ee*). $^{[\alpha]}D^{19}$ = + 32.6 (c = 0.28, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.95 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.09 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.66 (d, *J* = 15.2 Hz, 1H), 4.49 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H), 2.27 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.4, 162.9, 138.7, 137.8, 131.4, 130.21, 130.18, 129.6, 128.6, 126.2, 124.6, 121.0, 117.3, 114.4, 59.4, 55.8, 50.7, 20.5; **HRMS** *m/z* calculated for : $C_{24}H_{22}N_2O_4S$ $[M+Na]^+$: 457.1192, found: 457.1192; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 34.34 min (major) and 40.55 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-phenyl-2-(4-(trimethylsilyl)phenyl)propenamide (3v)



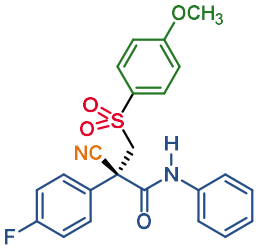
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (66 mg, 67% yield, >99% *ee*). $^{[\alpha]}D^{16}$ = + 3.3 (c = 0.31, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.99 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.46 (m, 6H), 7.33 – 7.29 (m, 2H), 7.14 – 7.09 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.55 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H), 0.23 (s, 9H); **^{13}C NMR (100 MHz, DMSO-d_6)** 163.3, 162.7, 141.2, 137.8, 133.9, 133.6, 131.3, 130.2, 128.6, 125.7, 124.7, 120.9, 117.1, 114.4, 59.3, 55.8, 51.0, -1.3; **HRMS** *m/z* calculated for : $C_{26}H_{28}N_2O_4SSi$ $[M+Na]^+$: 515.1431, found: 515.1432; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 16.67 min (major) and 18.65 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-(naphthalen-2-yl)-*N*-phenylpropanamide (3w)



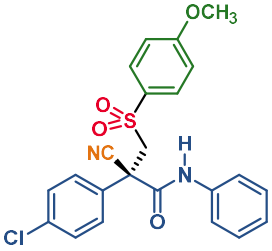
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (66 mg, 70% yield, >99% *ee*). $[\alpha]D^{18}$ = + 66.6 (c = 0.49, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.05 (s, 1H), 8.06 (d, *J* = 2.4 Hz, 1H), 7.96 – 7.86 (m, 3H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.51 – 7.46 (m, 3H), 7.32 – 7.28 (m, 2H), 7.13 – 7.08 (m, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.76 (d, *J* = 15.2 Hz, 1H), 4.66 (d, *J* = 15.2 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.2, 162.8, 137.8, 132.7, 132.4, 131.1, 130.1, 130.0, 128.9, 128.6, 128.2, 127.4, 127.2, 127.0, 126.3, 124.7, 123.3, 121.0, 117.2, 114.2, 59.2, 55.6, 51.0; **HRMS** *m/z* calculated for : $C_{27}H_{22}N_2O_4S$ $[M+Na]^+$: 493.1192, found: 493.1193; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 27.61 min (major) and 31.90 min (minor).

(*R*)-2-cyano-2-(4-fluorophenyl)-3-((4-methoxyphenyl)sulfonyl)-*N*-phenylpropanamide (3x)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (55 mg, 63% yield, >99% *ee*). $[\alpha]D^{19}$ = + 50.1 (c = 0.41, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.03 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.46 (m, 4H), 7.34 – 7.30 (m, 2H), 7.24 – 7.20 (m, 2H), 7.14 – 7.10 (m, 1H), 7.06 (d, *J* = 9.2 Hz, 2H), 4.67 (d, *J* = 15.2 Hz, 1H), 4.57 (d, *J* = 15.2 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.7, 162.2 (d, *J* = 245 Hz), 137.7, 131.3, 130.2, 129.1 (d, *J* = 4 Hz), 128.9 (d, *J* = 9 Hz), 128.6, 124.8, 121.0, 117.2, 115.9 (d, *J* = 22 Hz), 114.4, 59.3, 55.8, 50.4; **^{19}F NMR (376 Hz, DMSO-d6)** δ -112.9; **HRMS** *m/z* calculated for : $C_{23}H_{19}FN_2O_4S$ $[M+Na]^+$: 461.0942, found: 461.0941; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 28.15 min (major) and 31.98 min (minor).

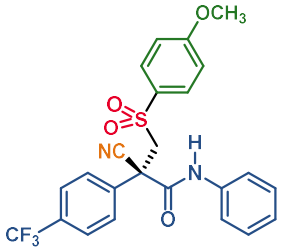
(*R*)-2-(4-chlorophenyl)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-phenylpropanamide (3y)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (57 mg, 63% yield, >99% *ee*). $[\alpha]D^{16}$ = + 90.8 (c = 0.90, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.06 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.41 (m, 6H),

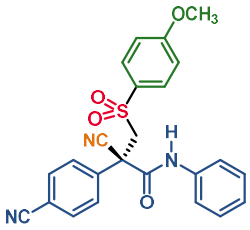
7.34 – 7.30 (m, 2H), 7.15 – 7.10 (m, 1H), 7.04 (d, *J* =9.2 Hz, 2H), 4.66 (d, *J* = 15.2 Hz, 1H), 4.59 (d, *J* = 15.2 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.4, 137.7, 134.0, 131.6, 131.2, 130.1, 128.9, 128.7, 128.6, 124.8, 121.0, 117.0, 114.4, 59.1, 55.8, 50.4; **HRMS** *m/z* calculated for : $C_{23}H_{19}ClN_2O_4S$ $[M+Na]^+$: 477.0646, found: 477.0647; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 25.10 min (major) and 30.88 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-phenyl-2-(4-(trifluoromethyl)phenyl)propenamide (3z)



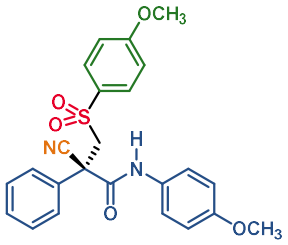
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (62 mg, 63% yield, >99% *ee*). $[\alpha]D^{19}$ = + 61.1 (c = 0.84, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.14 (s, 1H), 7.74 – 7.64 (m, 6H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.15 – 7.11 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.74 – 4.66 (m, 2H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.2, 137.6, 136.7, 131.1, 130.1, 129.5 (q, *J* = 32 Hz), 128.7, 127.9, 125.9 (q, *J* = 4 Hz), 124.9, 123.9 (q, *J* = 271 Hz), 121.1, 116.8, 114.4, 59.0, 55.7, 50.8. ; **^{19}F NMR (376 Hz, DMSO-d6)** δ -61.4; **HRMS** *m/z* calculated for : $C_{24}H_{19}F_3N_2O_4S$ $[M+Na]^+$: 511.0910, found: 511.0915; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 23.94 min (major) and 33.06 min (minor).

(*R*)-2-cyano-2-(4-cyanophenyl)-3-((4-methoxyphenyl)sulfonyl)-*N*-phenylpropanamide (3aa)



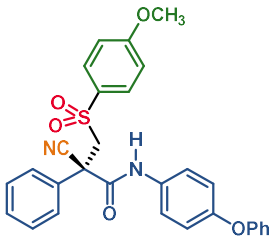
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (42 mg, 47% yield, >99% *ee*). $[\alpha]D^{15}$ = + 41.6 (c = 0.51, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.14 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 8.8, 1.2 Hz, 4H), 7.47 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.15 – 7.11 (m, 1H), 7.04 (d, *J* = 9.2 Hz, 2H), 4.69 (dd, *J* = 15.2, 17.2 Hz, 2H), 3.83 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 161.9, 137.6, 137.4, 132.8, 131.0, 130.1, 128.7, 127.9, 124.9, 121.0, 118.1, 116.6, 114.4, 112.0, 58.7, 55.8, 50.9; **HRMS** *m/z* calculated for : $C_{24}H_{19}N_3O_4S$ $[M+Na]^+$: 468.0988, found: 468.0990; **HPLC** (Daicel Chirapak IB column, hexane/isopropanol = 35/65, flow 0.7 mL/min, detection at 214 nm) retention time = 26.52 min (major) and 46.78 min (minor).

(*R*)-2-cyano-*N*-(4-methoxyphenyl)-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ab)



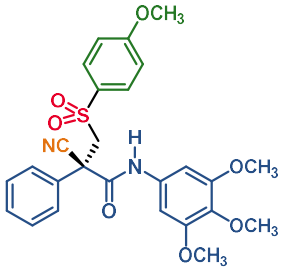
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (63 mg, 70% yield, >99% *ee*). $[\alpha]D^{19}$ = + 67.6 (c = 0.60, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.88 (s, 1H), 7.75 (d, *J* = 9.2 Hz, 2H), 7.50 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.43-7.35 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.67 (d, *J* = 14.8 Hz, 1H), 4.49 (d, *J* = 14.8 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H).; **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.4, 162.5, 156.2, 133.4, 131.4, 130.7, 130.2, 129.12, 129.09, 126.3, 122.7, 117.3, 114.4, 113.7, 59.5, 55.8, 55.2, 50.7; **HRMS** *m/z* calculated for: $C_{24}H_{22}N_2O_5S$ $[M+Na]^+$: 473.1142, found: 473.1144; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 28.81 min (major) and 36.40 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-(4-phenoxyphenyl)-2-phenylpropanamide (3ac)



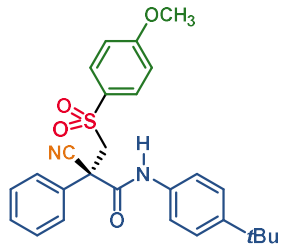
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (74 mg, 72% yield, >99% *ee*). $[\alpha]D^{19}$ = + 51.5 (c = 0.28, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.03 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.48 (m, 4H), 7.44 – 7.34 (m, 5H), 7.14 – 7.07 (m, 3H), 6.99 – 6.96 (m, 4H), 4.70 (d, *J* = 14.8 Hz, 1H), 4.51 (d, *J* = 14.8 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.5, 162.7, 157.0, 153.0, 133.4, 133.3, 131.4, 130.3, 130.0, 129.2, 126.3, 123.3, 122.7, 119.0, 118.2, 117.3, 114.5, 59.4, 55.8, 50.9; **HRMS** *m/z* calculated for : $C_{29}H_{24}N_2O_5S$ $[M+Na]^+$: 535.1298, found: 535.1299; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 41.04 min (major) and 46.42 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenyl-*N*-(3,4,5-trimethoxyphenyl)propenamide (3ad)



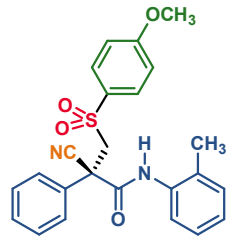
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (70 mg, 69% yield, 99% *ee*). $[\alpha]D^{19}$ = + 29.0 (c = 0.31, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.74 (d, *J* = 9.2 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.43 – 7.36 (m, 3H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.94 (s, 2H), 4.69 (d, *J* = 14.8 Hz, 1H), 4.52 (d, *J* = 14.8 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 6H), 3.61 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.4, 162.5, 152.5, 134.3, 134.0, 133.2, 131.3, 130.2, 129.2, 126.4, 117.2, 114.4, 98.1, 60.1, 59.3, 55.8, 55.7, 51.1; **HRMS** *m/z* calculated for $C_{26}H_{26}N_2O_7S$ $[M+Na]^+$: 533.1353, found: 533.1356; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 20.90 min (minor) and 44.24 min (major).

(*R*)-*N*-(4-(tert-butyl)phenyl)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ae)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (46 mg, 48% yield, >99% *ee*). $[\alpha]D^{16}$ = + 48.7 (c = 1.03, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.93 (s, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.43 – 7.37 (m, 5H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.50 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H), 1.24 (s, 9H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.5, 162.6, 147.1, 135.3, 133.4, 131.4, 130.3, 129.1, 126.4, 125.2, 120.6, 117.3, 114.5, 59.4, 55.8, 51.0, 34.1, 31.2; **HRMS** *m/z* calculated for : $C_{27}H_{28}N_2O_4S$ $[M+Na]^+$: 499.1662, found: 499.1662; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 26.23 min (major) and 37.70 min (minor).

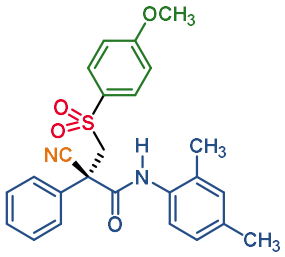
(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenyl-*N*-(o-tolyl)propanamid (3af)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (53 mg, 61% yield, 99% *ee*). $[\alpha]D^{15}$ = + 18.5 (c = 0.37, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.71 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.55 – 7.53 (m, 2H), 7.45 – 7.38 (m, 3H), 7.21 – 7.13 (m, 3H), 7.10 (d, *J* = 9.2 Hz, 2H), 7.07 – 7.05 (m, 1H), 4.64 (d, *J* = 15.2 Hz, 1H), 4.49 (d, *J* = 15.2 Hz, 1H), 3.84 (s, 3H), 1.95 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.44, 163.35, 135.1,

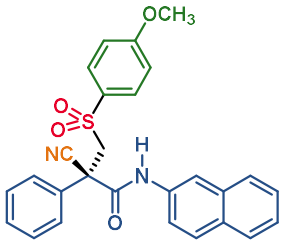
134.3, 133.4, 131.6, 130.4, 130.2, 129.11, 129.07, 126.82, 126.76, 126.3, 126.1, 117.4, 114.5, 59.3, 55.9, 50.3, 17.1; **HRMS** *m/z* calculated for : $C_{24}H_{22}N_2O_4S$ $[M+Na]^+$: 457.1192, found: 457.1190; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 17.70 min (major) and 21.01 min (minor).

(*R*)-2-cyano-*N*-(2,4-dimethylphenyl)-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ag)



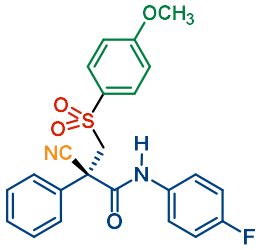
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolate as white solid using ethyl acetate/petroleum ether (1:3) as eluent (65 mg, 72% yield, >99% *ee*). $[\alpha]D^{19}$ = + 58.0 (c = 0.60, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.63 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.53 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.99 – 6.96 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.62 (d, *J* = 15.2 Hz, 1H), 4.47 (d, *J* = 15.2 Hz, 1H), 3.84 (s, 3H), 2.24 (s, 3H), 1.90 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.41, 163.35, 136.0, 134.0, 133.4, 132.5, 131.6, 130.9, 130.2, 129.04, 129.01, 126.6, 126.5, 126.3, 117.4, 114.4, 59.3, 55.8, 50.2, 20.5, 17.0; **HRMS** *m/z* calculated for : $C_{25}H_{24}N_2O_4S$ $[M+Na]^+$: 471.1349, found: 471.1349; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 24.89 min (major) and 45.82 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-*N*-(naphthalen-2-yl)-2-phenylpropanamide (3ah)



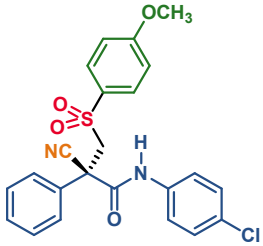
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (52 mg, 55% yield, >99% *ee*). $[\alpha]D^{10}$ = + 68.3 (c = 1.0, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.20 (s, 1H), 8.08 (d, *J* = 2.0 Hz, 1H), 7.87 – 7.83 (m, 3H), 7.77 (d, *J* = 9.2 Hz, 2H), 7.58 – 7.54 (m, 3H), 7.51 – 7.39 (m, 5H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.76 (d, *J* = 15.2 Hz, 1H), 4.57 (d, *J* = 15.2 Hz, 1H), 3.76 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.5, 163.0, 135.4, 133.3, 133.0, 131.3, 130.4, 130.3, 129.2, 128.2, 127.49, 127.46, 126.6, 126.4, 125.3, 121.0, 117.8, 117.2, 114.5, 59.3, 55.7, 51.1; **HRMS** *m/z* calculated for : $C_{27}H_{22}N_2O_4S$ $[M+Na]^+$: 493.1192, found: 493.1195; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 27.59 min (major) and 32.24 min (minor).

(*R*)-2-cyano-*N*-(4-fluorophenyl)-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ai)



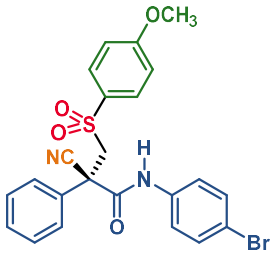
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (53 mg, 60% yield, >99% *ee*). $[\alpha]D^{20}$ = + 43.0 (c = 0.30, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.07 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.47 (m, 4H), 7.44 – 7.37 (m, 3H), 7.18 – 7.14 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.68 (d, *J* = 14.8 Hz, 1H), 4.52 (d, *J* = 14.8 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.5, 162.8, 158.9 (d, *J* = 240 Hz), 134.1 (d, *J* = 3 Hz), 133.2, 131.3, 130.2, 129.2, 126.3, 123.0 (d, *J* = 8 Hz), 117.2, 115.3 (d, *J* = 23 Hz), 114.5, 59.4, 55.8, 50.8; **^{19}F NMR (376 Hz, DMSO-d6)** δ -117.6; **HRMS** *m/z* calculated for : $C_{23}H_{19}FN_2O_4S$ $[M+Na]^+$: 461.0942, found: 461.0938; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 29.12 min (minor) and 32.23 min (major).

(*R*)-*N*-(4-chlorophenyl)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3aj)



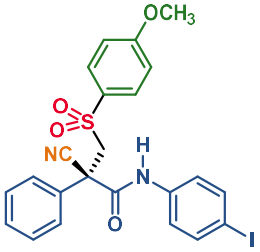
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (65 mg, 71% yield, >99% *ee*). $[\alpha]D^{15}$ = + 72.0 (c = 0.45, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.13 (s, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.50 (m, 4H), 7.44 – 7.36 (m, 5H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.70 (d, *J* = 15.2 Hz, 1H), 4.54 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.4, 162.9, 136.7, 133.1, 131.3, 130.2, 129.22, 129.20, 128.5, 128.4, 126.3, 122.5, 117.1, 114.5, 59.3, 55.8, 51.0; **HRMS** *m/z* calculated for : $C_{23}H_{19}ClN_2O_4S$ $[M+Na]^+$: 477.0646, found: 477.0648; **HPLC** (Daicel Chirapak IC column, hexane/isopropanol = 60/40, flow 0.5 mL/min, detection at 214 nm) retention time = 58.48 min (minor) and 62.34 min (major).

(*R*)-*N*-(4-bromophenyl)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ak)



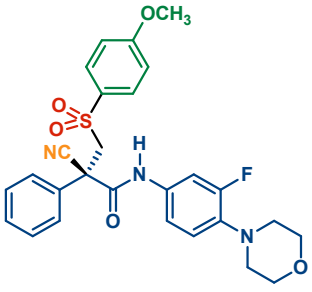
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (59 mg, 59% yield, >99% *ee*). $[\alpha]D^{19}$ = + 48.7 (c = 0.32, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.11 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.38 (m, 9H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.53 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.5, 162.9, 137.1, 133.1, 131.5, 131.3, 130.2, 129.24, 129.22, 126.3, 122.9, 117.1, 116.6, 114.5, 59.2, 55.8, 51.0; **HRMS** *m/z* calculated for : $C_{23}H_{19}BrN_2O_4S$ $[M+Na]^+$: 521.0141, found: 521.0145; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 33.89 min (major) and 37.80 min (minor).

(*R*)-2-cyano-*N*-(4-iodophenyl)-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3al)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (65 mg, 60% yield, >99% *ee*). $[\alpha]D^{16}$ = + 59.3 (c = 0.48, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.07 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.43 – 7.36 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.53 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.4, 162.9, 137.6, 137.3, 133.1, 131.2, 130.2, 129.2, 126.3, 123.0, 117.1, 114.5, 88.8, 59.2, 55.8, 51.1; **HRMS** *m/z* calculated for : $C_{23}H_{19}IN_2O_4S$ $[M+Na]^+$: 569.0002, found: 569.0004; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 28.76 min (major) and 31.78 min (minor).

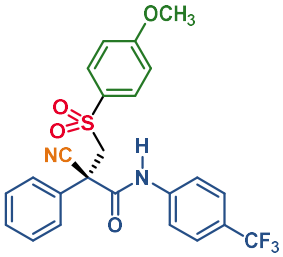
(*R*)-2-cyano-*N*-(3-fluoro-4-morpholinophenyl)-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3am)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (48 mg, 46% yield, 99% *ee*). $[\alpha]D^{18}$ = + 59.2 (c = 0.50, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.02 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.20 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.95 (m, 1H), 4.67 (d, *J* = 15.2 Hz, 1H), 4.51 (d, *J*

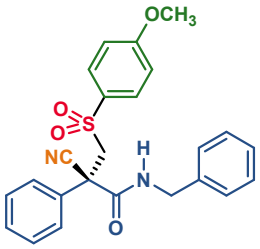
= 15.2 Hz, 1H), 3.81 (s, 3H), 3.72 (t, *J* = 4.4 Hz, 4H), 2.94 (t, *J* = 4.4 Hz, 4H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.5, 162.6, 154.1 (d, *J* = 242 Hz), 136.4 (d, *J* = 8 Hz), 133.3, 132.6 (d, *J* = 11 Hz), 131.3, 130.3, 129.2, 126.3, 118.8 (d, *J* = 4 Hz), 117.2, 117.0 (d, *J* = 3 Hz), 114.5, 109.08 (d, *J* = 25 Hz), 66.2, 59.3, 55.8, 50.9, 50.6 (d, *J* = 3 Hz); **^{19}F NMR (376 Hz, DMSO-d6)** δ -121.7; **HRMS** *m/z* calculated for : $C_{27}H_{26}FN_3O_5S$ $[M+Na]^+$: 546.1469, found: 546.1473; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 32.36 min (major) and 45.96 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenyl-*N*-(4-(trifluoromethyl)phenyl)propenamide (3an)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (43 mg, 44% yield, 99% *ee*). $[\alpha]D^{18}$ = + 25.7 (c = 0.32, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.31 (s, 1H), 7.77 – 7.68 (m, 6H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.74 (d, *J* = 15.2 Hz, 1H), 4.59 (d, *J* = 15.2 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.5, 163.3, 141.4, 133.0, 131.2, 130.3, 129.33, 129.28, 126.4, 125.9 (q, *J* = 3 Hz), 124.6 (q, *J* = 32 Hz), 124.2 (q, *J* = 270 Hz), 120.8, 117.0, 114.5, 59.1, 55.8, 51.2; **^{19}F NMR (376 Hz, DMSO-d6)** δ -60.6; **HRMS** *m/z* calculated for : $C_{24}H_{19}F_3N_2O_4S$ $[M+Na]^+$: 511.0910, found: 511.0912; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 25.89 min (major) and 29.76 min (minor).

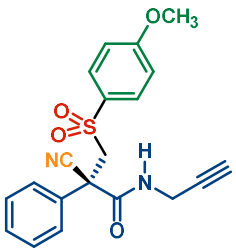
(*R*)-*N*-benzyl-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ao)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (52 mg, 60% yield, >99% *ee*). $[\alpha]D^{16}$ = + 17.7 (c = 0.30, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.83 (t, *J* = 6.0 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.36 – 7.35 (m, 3H), 7.25 – 7.17 (m, 3H), 7.10 – 7.06 (m, 4H), 4.52 (d, *J* = 14.8 Hz, 1H), 4.38 (d, *J* = 14.8 Hz, 1H), 4.30 (dd, *J* = 15.2, 6.0 Hz, 1H), 4.18 (dd, *J* = 15.2, 5.6 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 164.3, 163.4, 138.5, 133.3, 130.1, 128.9, 128.14, 128.11, 126.9, 126.8, 126.2, 117.5, 114.4, 59.4, 55.8, 49.8, 43.3; **HRMS** *m/z* calculated for : $C_{24}H_{22}N_2O_4S$ $[M+Na]^+$: 457.1192, found: 457.1192; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 17.09

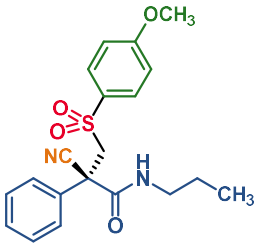
min (major) and 22.69 min (minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenyl-*N*-(prop-2-yn-1-yl)propenamide (3ap)



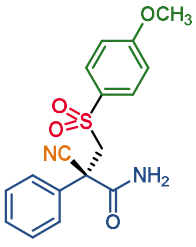
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:2) as eluent (41 mg, 53% yield, >99% *ee*). $^{[\alpha]}D^{16}$ = + 16.1 (c = 0.27, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.76 (t, *J* = 5.2 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.35 (m, 5H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.46 (d, *J* = 14.8 Hz, 1H), 4.37 (d, *J* = 14.8 Hz, 1H), 3.85 – 3.73 (m, 5H), 3.09 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 164.0, 163.4, 133.1, 131.4, 130.1, 128.9, 126.2, 117.2, 114.4, 79.9, 73.4, 59.4, 55.8, 49.7 29.5; **HRMS** *m/z* calculated for $C_{20}H_{18}N_2O_4S$ $[M+Na]^+$: 405.0879, found: 405.0880; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 16.22 min (major) and 19.19 min(minor).

(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenyl-*N*-propylpropanamide (3aq)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (34 mg, 44% yield, 98% *ee*). $^{[\alpha]}D^{18}$ = + 39.4 (c = 0.33, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.22 (t, *J* = 5.6 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.43 – 7.33 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.47 (d, *J* = 14.8 Hz, 1H), 4.32 (d, *J* = 14.8 Hz, 1H), 3.84 (s, 3H), 3.04 – 2.90 (m, *J* = 6.4 Hz 2H), 1.39 – 1.30 (m, *J* = 7.2 Hz, 2H), 0.70 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 164.0, 163.3, 133.6, 131.5, 130.2, 128.9, 128.8, 126.1, 117.6, 114.4, 59.6, 55.8, 49.7, 41.7, 21.7, 11.0; **HRMS** *m/z* calculated for : $C_{20}H_{22}N_2O_4S$ $[M+Na]^+$: 409.1192, found: 409.1193; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 17.04 min (major) and 22.47 min (minor).

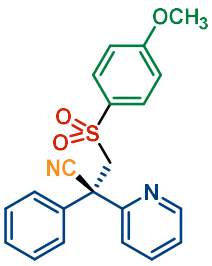
(*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamide (3ar)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (30 mg, 44% yield, 97% *ee*). $^{[\alpha]}D^{18}$ = + 4.9 (c = 0.43, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.74 – 7.68 (m, 4H), 7.44 – 7.41 (m, 2H), 7.37 – 7.33 (m, 3H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.45 (d, *J* = 14.8 Hz, 1H),

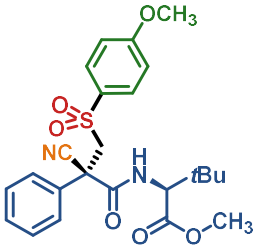
4.33 (d, *J* = 14.8 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 165.7, 163.3, 133.4, 131.6, 130.1, 128.9, 128.8, 126.2, 117.6, 114.4, 59.4, 55.8, 49.8; **HRMS** *m/z* calculated for : $C_{17}H_{16}N_2O_4S$ $[M+Na]^+$: 367.0723, found: 367.0719; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 35/65, flow 0.5 mL/min, detection at 214 nm) retention time = 15.94 min (major) and 18.17 min (minor).

(*S*)-3-((4-methoxyphenyl)sulfonyl)-2-phenyl-2-(pyridin-2-yl)propanenitrile (3as)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (44 mg, 58% yield, 92% *ee*). $[\alpha]D^{18}$ = + 53.2 (c = 0.36, $CHCl_3$). According to the X-ray analysis, the "absolute stereochemistry" of the product is the *S* configuration. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.47 (d, *J* = 4.4 Hz, 1H), 7.80 (td, *J* = 7.6, 1.6 Hz, 1H), 7.58 (d, *J* = 9.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.34 – 7.25 (m, 4H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.87 (d, *J* = 15.2 Hz, 1H), 4.70 (d, *J* = 15.2 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 163.2, 155.8, 149.0, 138.0, 136.9, 131.4, 130.0, 128.9, 128.4, 126.5, 123.5, 121.7, 119.4, 114.3, 60.3, 55.8, 49.9; **HRMS** *m/z* calculated for : $C_{21}H_{18}N_2O_3S$ $[M+Na]^+$: 401.0930, found: 401.0934; **HPLC** (Daicel Chirapak OD-H column, hexane/isopropanol = 55/45, flow 0.5 mL/min, detection at 214 nm) retention time = 22.84 min (major) and 25.94 min (minor).

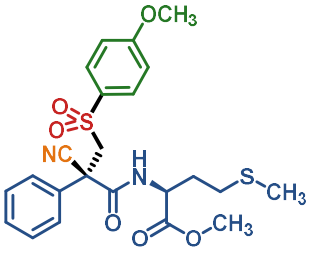
Methyl (*S*)-2-((*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanamido)-3,3-dimethylbutanoate (5a)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (20 mg, 21% yield, >99% *de*). $[\alpha]D^{16}$ = + 8.7 (c = 0.30, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.37 – 7.35 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.65 (d, *J* = 14.8 Hz, 1H), 4.48 (d, *J* = 14.8 Hz, 1H), 4.21 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 3.58 (s, 3H), 0.84 (s, 9H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 170.2, 164. 6, 163. 5, 132.9, 131.6, 130.3, 129.0, 128.9, 126.6, 117.4, 114.4, 61.2, 58.7, 55.9, 51.7, 50.7, 34.5, 26.4; **HRMS** *m/z* calculated for: $C_{24}H_{28}N_2O_6S$ $[M+Na]^+$: 495.1560, found: 495.1561; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 85/15, flow 0.5 mL/min, detection at 214 nm) retention time = 55.26 min (major) and 108.27 min (minor). Our reactions can also be applied to chiral substrates, but may be affected by the chirality of

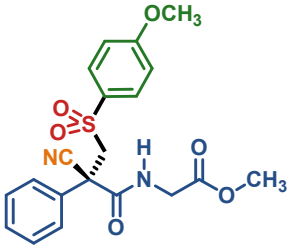
the substrate, and the product of the reaction is not racemic.

Methyl ((*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanoyl)-*L*-methioninate (5b)



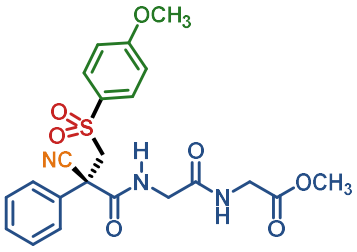
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:1) as eluent (31 mg, 32% yield, >99% *de*). $[\alpha]D^{10}$ = + 30.6 (c = 0.61, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.72 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.35 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.45 – 4.31 (m, 3H), 3.84 (s, 3H), 3.52 (s, 3H), 2.48 – 2.34 (m, 2H), 2.01 – 1.96 (m, 5H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 171.2, 164.5, 163.4, 132.9, 131.7, 130.1, 129.0, 128.8, 126.6, 117.3, 114.4, 59.9, 55.9, 52.1, 52.0, 49.6, 29.6, 14.6; **HRMS** *m/z* calculated for $C_{23}H_{26}N_2O_6S_2$ $[M+Na]^+$: 513.1124, found: 513.1126; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 20.82 min (major) and 24.10 min (minor).

Methyl (*R*)-(2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanoyl)glycinate (5c)



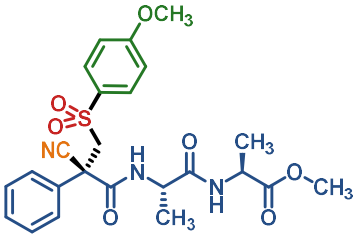
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (1:1) as eluent (41 mg, 49% yield, >99% *ee*). $[\alpha]D^{10}$ = + 45.6 (c = 0.48, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.72 (t, *J* =6.0 Hz, 1H), 7.69 (d, *J* = 9.2 Hz, 2H), 7.46 – 7.44 (m, 2H), 7.38 – 7.35 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.42 – 4.34 (m, 2H), 3.85 (s, 3H), 3.78 (t, *J* = 5.2 Hz, 2H), 3.55 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 169.2, 164.7, 163.4, 133.0, 131.4, 130.2, 129.0, 128.9, 126.5, 117.3, 114.4, 59.6, 55.8, 51.7, 49.5, 41.8; **HRMS** *m/z* calculated for $C_{20}H_{20}N_2O_6S$ $[M+Na]^+$: 439.0934, found: 439.0934; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 19.15 min (major) and 22.64 min(minor).

Methyl (*R*)-(*R*)-(2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanoyl)glycylglycinate (5d)



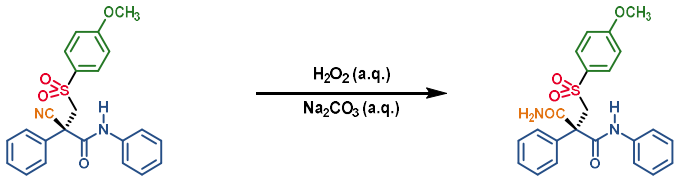
Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (2:1) as eluent (29 mg, 31% yield, >99% *ee*). $[\alpha]D^{10}$ = + 54.0 (c = 0.39, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.53 (t, *J* = 5.6 Hz, 1H), 8.23 (t, *J* = 6.0 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.35 – 7.34 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 4.48 – 4.40 (m, 2H), 3.87 – 3.85 (m, 5H), 3.70 (t, *J* = 5.6 Hz, 2H), 3.62 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 170.1, 168.3, 164.4, 163.4, 133.1, 131.2, 130.2, 128.93, 128.88, 126.5, 117.4, 114.4, 59.4, 55.8, 51.8, 49.8, 42.9, 40.5; **HRMS** *m/z* calculated for $C_{22}H_{23}N_3O_7S$ [M+Na]$^+$: 496.1149, found: 496.1150; **HPLC** (Daicel Chirapak ADH column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 24.32 min (major) and 37.48 min(minor).

Methyl ((*R*)-2-cyano-3-((4-methoxyphenyl)sulfonyl)-2-phenylpropanoyl)-*L*-alanyl-*L*-alaninate (5e)



Prepared by the general procedure in a 0.2 mmol scale at the 20 °C for 72 h; Isolated as white solid using ethyl acetate/petroleum ether (2:1) as eluent (40 mg, 40% yield, >99% *de*). $[\alpha]D^{10}$ = + 11.6 (c = 0.32, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.18 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.70 (d, *J* = 9.2 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.36 – 7.34 (m, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 4.49 – 4.40 (m, 2H), 4.27 – 4.19 (m, 2H), 3.85 (s, 3H), 3.60 (s, 3H), 1.24 (dd, *J* = 7.2, 5.2 Hz, 6H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 172.8, 171.1, 163.6, 163.4, 133.0, 131.3, 130.2, 128.9, 126.5, 117.5, 114.4, 59.3, 55.9, 51.9, 50.0, 49.3, 47.6, 17.5, 16.8; **HRMS** *m/z* calculated for $C_{24}H_{27}N_3O_7S$ [M+Na]$^+$: 524.1462, found: 524.1464; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 17.30 min (major) and 29.38 min(minor).

7. Transformations

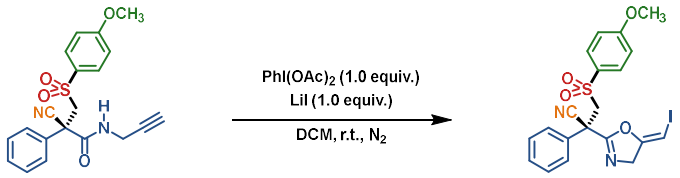


3a

6, 56% >99% ee

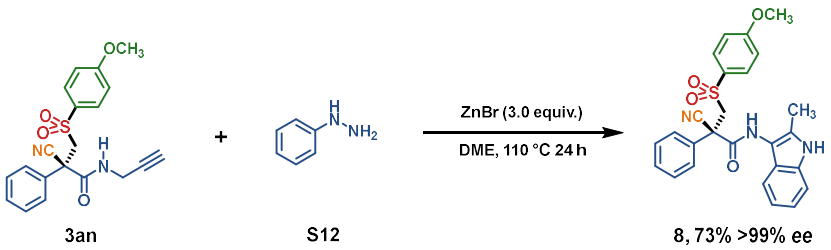
In a vial, **3a** (42.6 mg, 0.1 mmol, 1.0 equiv.) was dissolved in 1 mL of MeOH. Then H_2O_2 (0.15 mL, 30% aqueous solution) and 3 drops of sat. Na_2CO_3 solution were added

sequentially. The reaction mixture was stirred at room temperature for overnight. The aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were concentrated under reduced pressure. The residue was purified by column chromatography (PE/ EA = 2/1) to afford **6** (49 mg, 56%, >99% *ee*) as a white solid. $[\alpha]D^{16}$ = + 37.3 (c = 0.89, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 11.65 (s, 1H), 8.00 (s, 1H), 7.79 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.43 – 7.38 (m, 4H), 7.36 – 7.26 (m, 5H), 7.10 – 7.06 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.76 (d, *J* = 14.4 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 3.75 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 172.9, 167.4, 163.1, 139.2, 138.1, 132.3, 130.0, 128.71, 128.66, 127.8, 126.1, 123.9, 119.9, 114.2, 59.6, 56.7, 55.7; **HRMS** *m/z* calculated for $C_{23}H_{22}N_2O_5S$ $[M+Na]^+$: 461.1142, found: 461.1144; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 16.07 min (minor) and 20.49 min(major).



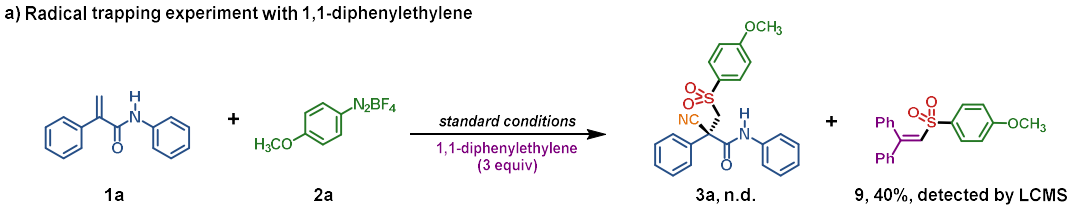
3an 7, 68% 99% *ee*

In a vial, **3an** (42.6 mg, 0.1 mmol, 1.0 equiv.), 0.1 mmol $PhI(OAc)_2$, 0.1 mmol LiI and 1 mL CH_2Cl_2 were added under argon atmosphere. The reaction mixture was stirred at room temperature until complete disappearance of the starting material as shown by TLC (usually 12 h). CH_2Cl_2 (10 mL) was then added, and the mixture was washed with aqueous $Na_2S_2O_3$. The organic layer was dried by Na_2SO_4 and concentrated to give crude residue, which was purified by flash column chromatography to give the corresponding products **7** (69 mg, 68%, 99% *ee*) as a white solid. $[\alpha]D^{10}$ = + 37.6 (c = 0.33, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.75 (d, *J* = 9.2 Hz, 2H), 7.52 – 7.50 (m, 2H), 7.44 – 7.41 (m, 3H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.85 (t, *J* = 3.2 Hz, 1H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.51 (d, *J* = 15.2 Hz, 1H), 4.47 – 4.30 (m, 2H), 3.86 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 163.7, 160.6, 156.1, 132.5, 130.4, 130.3, 129.6, 129.4, 126.4, 115.9, 114.4, 59.9, 57.8, 55.9, 51.3, 44.3; **HRMS** *m/z* calculated for $C_{20}H_{17}IN_2O_4S$ $[M+Na]^+$: 530.9846, found: 530.9846; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 18.86 min (minor) and 39.05 min(major).



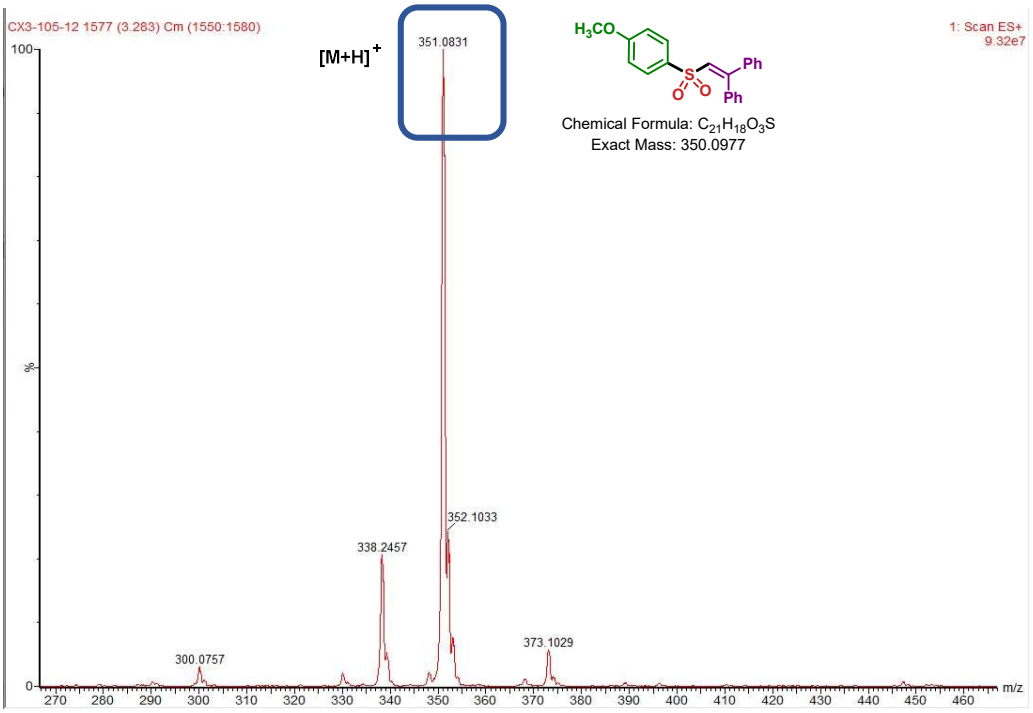
In a vial, a solution of **3an** (0.1 mmol) and arylhydrazine (0.15 mmol) in 1,2-dimethoxyethane (1 mL), zinc bromide (0.3 mmol) was added under argon atmosphere. The reaction mixture was heated at 110 °C for 24 h (TLC control). After removal of the solvent, the crude product was purified by column chromatography (PE/EA = 2/1) to afford **8** (69 mg, 73%, >99% *ee*) as a white solid. $[\alpha]D^{15}$ = + 30.8 (c = 0.34, $CHCl_3$); **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.92 (s, 1H), 9.59 (s, 1H), 7.78 (d, *J* = 9.2 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.47 – 7.41 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 9.2 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.91 – 6.87 (m, 1H), 4.69 (d, *J* = 14.8 Hz, 1H), 4.50 (d, *J* = 14.8 Hz, 1H), 3.85 (s, 3H), 2.11 (s, 3H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 164.2, 163.4, 133.9, 133.5, 131.8, 130.6, 130.1, 129.0, 126.3, 124.7, 120.4, 118.5, 117.6, 117.1, 114.4, 110.7, 108.9, 59.4, 55.8, 50.2, 10.8; **HRMS** *m/z* calculated for $C_{26}H_{23}N_3O_4S$ $[M+Na]^+$: 496.1301, found: 496.1302; **HPLC** (Daicel Chirapak IA column, hexane/isopropanol = 45/55, flow 0.5 mL/min, detection at 214 nm) retention time = 20.43 min (major) and 28.56 min(minor).

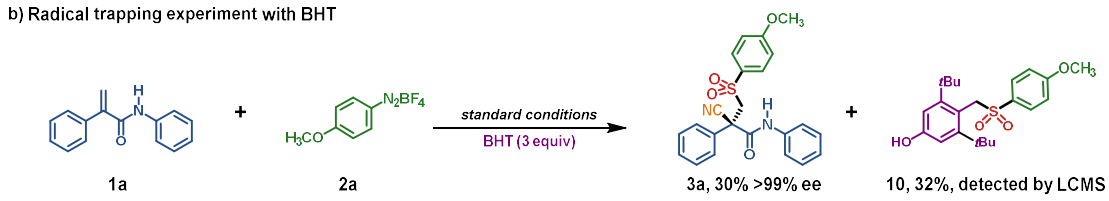
8. Mechanistic Experiments



In the argon glovebox, $Cu(OAc)_2$ (3.6 mg, 10.0 mol%) and **L6** (16.5 mg 12.0 mol%) were dissolved in DCM (2.5 mL) in a dried sealed vial under argon atmosphere, and the mixture was stirred for 30 minutes. Then **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CH_3COOLi (0.5 mmol, 2.5 equiv.), 1,1- diphenylethylene (0.6 mmol, 3.0 equiv.) and the mixture were added to chamber B. Tetrabromothiophene S,S-dioxides (0.88 mmol, 380 mg) in tetradecane (1.0 mL) was added to chamber A, followed by addition of 4-methylphenylene (0.80 mmol, 105 μl). The chamber A was sealed and removed out of the glovebox and heated to 100 °C in heating mantle for 10 min. Then chamber B heated to 20 °C in low-temperature stirring reaction bath for 72 hours. After 72 hours, two chamber was cooled to room temperature. TLC, GC and LC-MS analysis

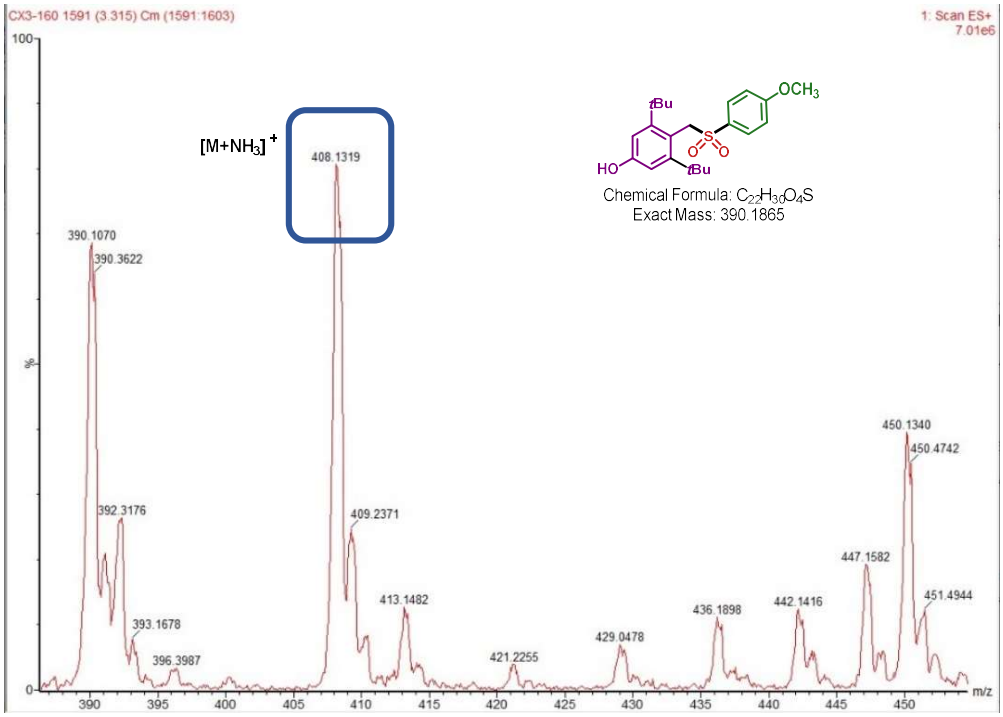
demonstrated the product **3a** was not detected. The arylsulfonyl radical combined with 1,1-diphenylethylene **9** was detected by LC-MS. **^{1}H NMR (400 MHz, DMSO-d6)** δ 7.55 – 7.51 (m, 2H), 7.43 – 7.33 (m, 6H), 7.31 (s, 1H), 7.24 – 7.22 (m, 2H), 7.04 – 7.00 (m, 4H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, DMSO-d6)** δ 162.9, 152.9, 138.6, 135.6, 133.0, 130.3, 129.5, 129.2, 129.0, 128.7, 128.6, 128.1, 127.9, 114.4, 55.8.





In the argon glovebox, $Cu(OAc)_2$ (3.6 mg, 10.0 mol%) and **L6** (16.5 mg 12.0 mol%) were dissolved in DCM (2.5 mL) in a dried sealed vial under argon atmosphere, and the mixture was stirred for 30 minutes. Then **1** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), TMSCN (0.3 mmol, 1.5 equiv.), CH_3COOLi (0.5 mmol, 2.5 equiv.), BHT (0.6 mmol, 3.0 equiv.) and the mixture were added to chamber B. Tetrabromothiophene S,S-dioxides (0.88 mmol, 380 mg) in tetradecane (1.0 mL) was added to chamber A, followed by addition of 4-methylphenylene (0.80 mmol, 105 μl). The chamber A was sealed and removed out of the glovebox and heated to 100 °C in heating mantle for 10 min. Then chamber B heated to 20 °C in low-temperature stirring reaction bath for 72 hours. After 72 hours, two chamber was cooled to room temperature. The mixture was purified by column chromatography on silica gel. Isolated as white solid using ethyl acetate/petroleum ether (1:3) as eluent (25

mg, 30% yield, >99% *ee*). The arylsulfonyl radical combined with BHT **10** was detected by LC-MS. **^{1}H NMR (400 MHz, DMSO-d6)** δ 7.50 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.00 (s, 1H), 6.72 (s, 2H), 4.40 (s, 2H), 3.82 (s, 3H), 1.26 (s, 18H). **^{13}C NMR (101 MHz, DMSO-d6)** δ 163.2, 154.0, 138.7, 130.6, 129.7, 127.4, 120.0, 114.2, 61.7, 55.8, 34.3, 30.2.



9. Reference

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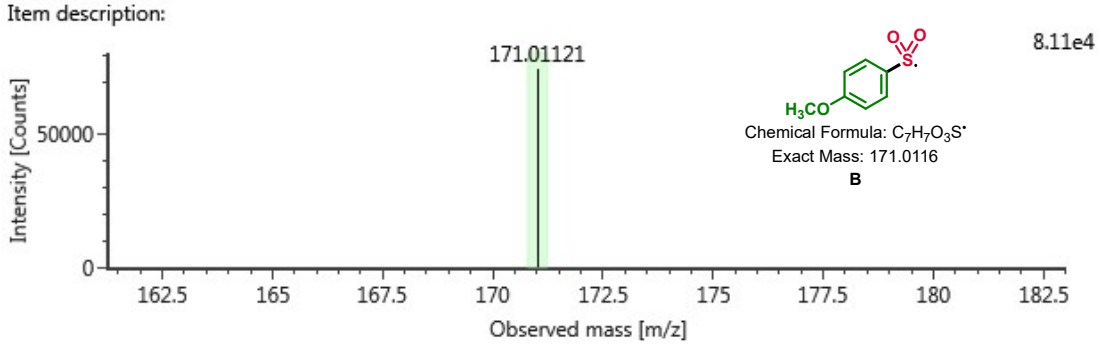
10. HRMS detection of intermediates

Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer. The reaction ran for 3 hours. After the 3 hours, 10 μL of reaction sample was extracted with a syringe, diluted into 1 mL of methanol, and transferred to a 0.5 mL syringe for immediate infusion into the mass spectrometer.

3-C7H7O3S	171.01159	171.01121	0.2	1.0	8938	-e	Identified

Item name: 20230209-CDLZ-CX3-3H
Item description:
Channel name: Time 0.2061 +/- 0.0500 minutes



4-C22H20NO4S	394.11130	394.11128	0.5	1.3	30647	-e, +H	Identified

Item name: 20230209-CDLZ-CX3-3H
Item description:
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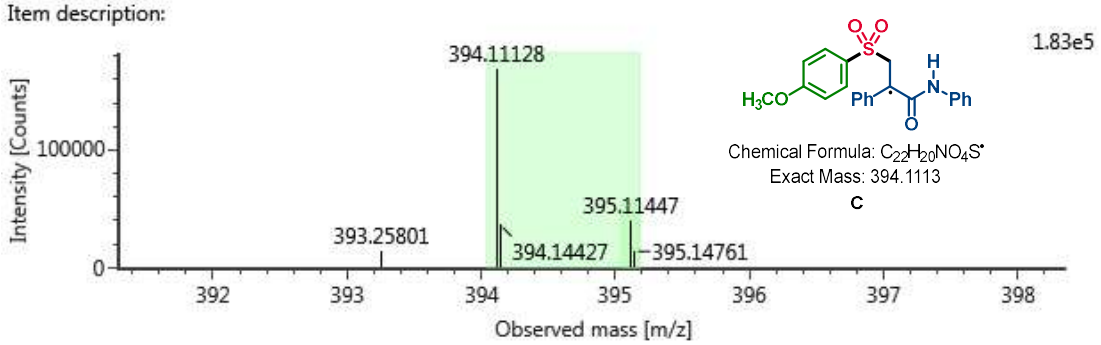
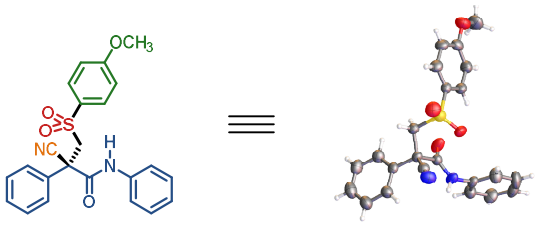


11. Single Crystal X-Ray Diffraction Data

Crystal data and structure refinement for **3a** (CCDC 2214049), Thermal ellipsoids are shown at 50% probability level.



3a

A suitable crystal of compound **3a** was obtained by slowly evaporating a mixture of petroleum ether and ethyl acetatec solution at ambient temperature. It was selected and analyzed on a Bruker APEX-II CCD diffractometer. The crystal was kept at 302.0 K during data collection. Using Olex2,[9] the structure was solved with the SHELXT[10] structure solution program using Charge Flipping and refined with the SHELXL[11] refinement package using Least Squares minimisation.

Crystal Data for $C_{23}H_{20}N_2O_4S$ (M =420.47 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.1780(12) Å, b = 10.3013(13) Å, c = 19.462(3) Å, V = 2040.6(5) $Å^3$, Z = 4, T = 302.0 K, μ(MoKα) = 0.192 mm^{-1}, Dcalc = 1.369 g/cm^3, 9227 reflections measured (4.186° ≤ 2Θ ≤ 55.03°), 4458 unique (R_{int} = 0.0556, R_{sigma} = 0.0847) which were used in all calculations. The final R_1 was 0.0559 (I > 2σ(I)) and wR_2 was 0.1171.

Table S6 Crystal data and structure refinement for 3a

Identification code	mo_lz_hcx_0622_3_0m_a
Empirical formula	$C_{23}H_{20}N_2O_4S$
Formula weight	420.47
Temperature/K	302.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.1780(12)
b/Å	10.3013(13)
c/Å	19.462(3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2040.6(5)
Z	4
$\rho_{calc}g/cm^3$	1.369
μ/mm^{-1}	0.192

F(000)	880.0
Crystal size/mm^3	0.13 × 0.13 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.186 to 55.03
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 9, -25 ≤ l ≤ 22
Reflections collected	9227
Independent reflections	4458 [R_{int} = 0.0556, R_{sigma} = 0.0847]
Data/restraints/parameters	4458/0/272
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.0943
Final R indexes [all data]	R_1 = 0.1123, wR_2 = 0.1171
Largest diff. peak/hole / e Å^{-3}	0.17/-0.24
Flack parameter	0.01(10)

Table S7 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
S1	5216.2(11)	4838.6(12)	3616.0(7)	48.1(3)
C5	-892(5)	3409(7)	4637(3)	79(2)
O2	4870(3)	7209(4)	4874.8(16)	61.5(10)
O3	5645(3)	4277(4)	2979.7(19)	64.4(11)
O4	5910(3)	4524(4)	4238.7(18)	57.6(10)
N1	7004(3)	6892(4)	5142.5(18)	47.0(11)
N2	8586(4)	6080(4)	3621(3)	64.3(13)
O1	-262(4)	3267(4)	3999(2)	69.1(11)
C2	1000(5)	3671(5)	3952(3)	51.2(13)
C3	1751(5)	4089(5)	4500(3)	54.6(14)
C4	3040(5)	4466(5)	4393(3)	49.8(13)
C1	3563(4)	4430(4)	3739(3)	43.7(11)
C6	5267(5)	6579(4)	3509(2)	46.5(12)
C7	6379(4)	7218(5)	3931(2)	38.4(11)
C8	6019(4)	7095(5)	4707(2)	41.7(11)
C9	6784(4)	6597(5)	5852(2)	41.8(12)
C10	6846(5)	5340(6)	6076(3)	65.8(16)
C11	6701(6)	5069(7)	6762(3)	73.6(17)
C12	6463(5)	6044(7)	7222(3)	65.0(17)
C13	2802(5)	4055(5)	3186(3)	53.6(14)
C14	1528(5)	3676(5)	3291(3)	56.7(14)
C15	6523(4)	8672(5)	3764(2)	42.6(11)
C16	5440(5)	9435(5)	3645(3)	53.9(13)
C17	5583(6)	10746(5)	3509(3)	64.3(15)
C18	6793(6)	11311(6)	3503(3)	68.3(16)

C19	7884(6)	10559(5)	3637(3)	66.0(15)
C20	7759(5)	9244(5)	3764(3)	51.1(13)
C21	6526(5)	7568(5)	6310(3)	55.2(13)
C22	6366(5)	7273(7)	6999(3)	64.3(16)
C23	7623(4)	6566(5)	3767(2)	43.8(12)

Table S8 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U11	U22	U33	U23	U13	U12
S1	41.2(6)	51.6(7)	51.4(8)	0.3(7)	-3.0(6)	0.3(6)
C5	52(3)	104(5)	80(5)	19(4)	11(3)	-18(3)
O2	35.1(17)	104(3)	45(2)	14(2)	4.4(15)	9.0(19)
O3	60(2)	73(3)	61(2)	-16(2)	13.4(18)	8(2)
O4	45.7(18)	61(3)	66(2)	11.8(19)	-16.6(17)	-1.5(17)
N1	31.1(18)	74(3)	36(2)	6(2)	2.5(17)	0(2)
N2	52(2)	66(3)	76(3)	-14(3)	9(3)	3(2)
O1	49.3(19)	75(3)	83(3)	3(2)	-2(2)	-20(2)
C2	45(3)	42(3)	66(4)	3(3)	-2(3)	-5(2)
C3	51(3)	67(4)	46(3)	10(3)	0(3)	-10(3)
C4	50(3)	58(3)	41(3)	2(2)	-7(2)	-9(2)
C1	44(2)	44(3)	43(3)	4(2)	-3(2)	0(2)
C6	45(2)	51(3)	44(3)	4(2)	-7(2)	-3(2)
C7	33(2)	47(3)	36(3)	2(2)	-0.7(19)	1(2)
C8	37(2)	46(3)	43(3)	7(2)	2(2)	0(2)
C9	34(2)	57(3)	34(3)	9(2)	-1(2)	2(2)
C10	84(4)	59(4)	55(4)	1(3)	10(3)	9(3)
C11	87(4)	61(4)	74(4)	29(4)	14(3)	10(4)
C12	55(3)	97(5)	43(3)	23(3)	-3(3)	8(3)
C13	52(3)	62(4)	47(3)	-8(3)	-5(3)	-4(3)
C14	54(3)	66(4)	50(3)	-8(3)	-12(3)	-12(3)
C15	48(3)	48(3)	31(3)	3(2)	0(2)	2(2)
C16	52(3)	58(3)	52(3)	4(3)	6(3)	3(3)
C17	77(4)	57(4)	59(4)	4(3)	-1(3)	18(3)
C18	90(4)	52(3)	63(4)	6(3)	8(3)	-1(3)
C19	74(3)	58(4)	66(4)	6(3)	4(3)	-11(3)
C20	49(3)	55(3)	50(3)	1(3)	3(2)	-5(3)
C21	59(3)	61(4)	45(3)	6(3)	4(3)	-1(3)
C22	73(4)	78(5)	42(3)	-7(3)	2(3)	4(3)
C23	44(3)	47(3)	40(3)	-4(2)	0(2)	-2(2)

Table S9 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O3	1.435(4)	C7	C8	1.559(6)
S1	O4	1.440(3)	C7	C15	1.540(6)

S1	C1	1.751(5)	C7	C23	1.469(6)
S1	C6	1.806(5)	C9	C10	1.368(7)
C5	O1	1.405(6)	C9	C21	1.366(7)
O2	C8	1.220(5)	C10	C11	1.372(7)
N1	C8	1.329(5)	C11	C12	1.368(8)
N1	C9	1.431(5)	C12	C22	1.342(8)
N2	C23	1.137(5)	C13	C14	1.369(7)
O1	C2	1.354(5)	C15	C16	1.374(6)
C2	C3	1.381(7)	C15	C20	1.389(6)
C2	C14	1.393(7)	C16	C17	1.385(7)
C3	C4	1.384(6)	C17	C18	1.363(8)
C4	C1	1.380(6)	C18	C19	1.378(7)
C1	C13	1.381(6)	C19	C20	1.382(6)
C6	C7	1.545(6)	C21	C22	1.384(7)

Table S10 Bond Angles for 3a.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O3	S1	O4	119.1(2)	O2	C8	N1	124.6(4)
O3	S1	C1	108.3(2)	O2	C8	C7	118.4(4)
O3	S1	C6	107.0(2)	N1	C8	C7	117.0(4)
O4	S1	C1	107.6(2)	C10	C9	N1	120.1(5)
O4	S1	C6	107.8(2)	C21	C9	N1	120.3(5)
C1	S1	C6	106.4(2)	C21	C9	C10	119.6(5)
C8	N1	C9	122.0(4)	C9	C10	C11	119.8(6)
C2	O1	C5	117.4(4)	C12	C11	C10	120.5(6)
O1	C2	C3	124.7(5)	C22	C12	C11	119.5(5)
O1	C2	C14	115.4(5)	C14	C13	C1	119.6(5)
C3	C2	C14	119.9(4)	C13	C14	C2	120.3(5)
C2	C3	C4	119.7(5)	C16	C15	C7	121.0(4)
C1	C4	C3	119.8(5)	C16	C15	C20	118.9(5)
C4	C1	S1	119.3(4)	C20	C15	C7	120.0(4)
C4	C1	C13	120.7(4)	C15	C16	C17	120.4(5)
C13	C1	S1	120.0(4)	C18	C17	C16	120.9(5)
C7	C6	S1	112.5(3)	C17	C18	C19	119.1(5)
C6	C7	C8	108.0(3)	C18	C19	C20	120.7(5)
C15	C7	C6	111.9(4)	C19	C20	C15	119.9(5)
C15	C7	C8	107.8(4)	C9	C21	C22	119.6(5)
C23	C7	C6	108.7(4)	C12	C22	C21	120.8(6)
C23	C7	C8	112.1(4)	N2	C23	C7	177.9(6)
C23	C7	C15	108.4(4)				

Table S11 Torsion Angles for 3a.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
S1	C1	C13	C14	176.9(4)	C6	C7	C15	C20	-144.9(5)

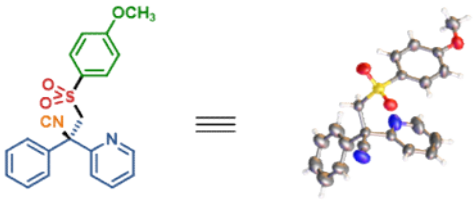
S1	C6	C7	C8	-68.8(4)	C7	C15	C16	C17	178.8(5)
S1	C6	C7	C15	172.7(3)	C7	C15	C20	C19	-177.8(5)
S1	C6	C7	C23	53.0(5)	C8	N1	C9	C10	99.5(6)
C5	O1	C2	C3	6.9(8)	C8	N1	C9	C21	-81.2(6)
C5	O1	C2	C14	-171.7(5)	C8	C7	C15	C16	-80.4(5)
O3	S1	C1	C4	158.6(4)	C8	C7	C15	C20	96.6(5)
O3	S1	C1	C13	-20.4(5)	C9	N1	C8	O2	9.4(8)
O3	S1	C6	C7	-109.6(3)	C9	N1	C8	C7	-171.8(4)
O4	S1	C1	C4	28.6(5)	C9	C10	C11	C12	1.6(9)
O4	S1	C1	C13	-150.3(4)	C9	C21	C22	C12	0.0(8)
O4	S1	C6	C7	19.7(4)	C10	C9	C21	C22	1.8(7)
N1	C9	C10	C11	176.7(5)	C10	C11	C12	C22	0.2(9)
N1	C9	C21	C22	-177.5(4)	C11	C12	C22	C21	-1.0(9)
O1	C2	C3	C4	179.2(5)	C14	C2	C3	C4	-2.3(8)
O1	C2	C14	C13	-179.3(5)	C15	C7	C8	O2	83.7(5)
C2	C3	C4	C1	0.4(8)	C15	C7	C8	N1	-95.2(5)
C3	C2	C14	C13	2.0(9)	C15	C16	C17	C18	-1.4(9)
C3	C4	C1	S1	-177.1(4)	C16	C15	C20	C19	-0.8(8)
C3	C4	C1	C13	1.8(8)	C16	C17	C18	C19	0.0(9)
C4	C1	C13	C14	-2.0(8)	C17	C18	C19	C20	1.0(10)
C1	S1	C6	C7	134.9(3)	C18	C19	C20	C15	-0.6(9)
C1	C13	C14	C2	0.1(8)	C20	C15	C16	C17	1.8(8)
C6	S1	C1	C4	-86.7(4)	C21	C9	C10	C11	-2.6(8)
C6	S1	C1	C13	94.4(4)	C23	C7	C8	O2	-157.0(5)
C6	C7	C8	O2	-37.3(6)	C23	C7	C8	N1	24.1(6)
C6	C7	C8	N1	143.8(4)	C23	C7	C15	C16	158.1(4)
C6	C7	C15	C16	38.2(6)	C23	C7	C15	C20	-25.0(6)

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	x	y	z	U(eq)
H5A	-1800	3172	4592	118
H5B	-828	4295	4785	118
H5C	-478	2855	4969	118
H1	7797	6940	4993	56
H3	1392	4116	4939	66
H4	3552	4742	4760	60
H6A	5393	6780	3027	56

H6B	4431	6944	3650	56
H10	6986	4670	5764	79
H11	6766	4217	6915	88
H12	6369	5857	7687	78
H13	3152	4059	2745	64
H14	1013	3422	2920	68
H16	4605	9068	3657	65
H17	4843	11248	3419	77
H18	6882	12192	3411	82
H19	8712	10940	3641	79
H20	8502	8744	3849	61
H21	6457	8422	6160	66
H22	6190	7934	7311	77

Crystal data and structure refinement for **3aq** (CCDC 2267265), Thermal ellipsoids are shown at 50% probability level.



3as

A suitable crystal of compound **3as** was obtained by slowly evaporating a mixture of petroleum ether and ethyl acetate solution at ambient temperature. It was selected and analyzed on a Xcalibur, Eos diffractometer. The crystal was kept at 293.15 K during data collection. Using Olex2, [9] the structure was solved with the ShelXT[10] structure solution program using Charge Flipping and refined with the ShelXL[11] refinement package using Least Squares minimisation.

Crystal Data for $C_{21}H_{18}N_2O_3S$ (M =378.43 g/mol): monoclinic, space group I2/a (no. 15), a = 16.5437(14) Å, b = 6.8832(5) Å, c = 33.016(3) Å, β = 97.208(9)°, V = 3729.9(5) Å^3, Z = 8, T = 293.15 K, μ(MoKα) = 0.198 mm^{-1}, Dcalc = 1.348 g/cm^3, 8138 reflections measured (6.048° ≤ 2Θ ≤ 52.734°), 3830 unique (Rint = 0.0428, Rsigma = 0.0783) which were used in all calculations. The final R_1 was 0.0918 (I > 2σ(I)) and wR_2 was 0.2422.

Table S13 Crystal data and structure refinement for 3aq.

Identification code	230602_s2_hcx_auto
Empirical formula	$C_{21}H_{18}N_2O_3S$
Formula weight	378.43

Temperature/K	293.15
Crystal system	monoclinic
Space group	I2/a
a/Å	16.5437(14)
b/Å	6.8832(5)
c/Å	33.016(3)
α/°	90
β/°	97.208(9)
γ/°	90
Volume/Å^3	3729.9(5)
Z	8
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.198
F(000)	1584.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.048 to 52.734
Index ranges	-13 ≤ h ≤ 20, -8 ≤ k ≤ 5, -40 ≤ l ≤ 41
Reflections collected	8138
Independent reflections	3830 [R_{int} = 0.0428, R_{sigma} = 0.0783]
Data/restraints/parameters	3830/1/233
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0918, wR_2 = 0.2070
Final R indexes [all data]	R_1 = 0.1444, wR_2 = 0.2422
Largest diff. peak/hole / e Å^{-3}	0.93/-0.91

Table S14 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aq. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2167.1(7)	7362.0(18)	3511.6(4)	43.2(4)
O1	2195(2)	9379(5)	3399.5(10)	52.2(9)
N1	4350(3)	6872(8)	3925.7(14)	67.9(14)
C1	3969(3)	8624(7)	3960.8(13)	42.6(11)
O2	1385.7(19)	6398(5)	3479.8(11)	60.0(10)
N2	2551(3)	11976(7)	4219.5(16)	76.1(15)
C2	4227(3)	10310(8)	3800.9(15)	56.9(14)
O3	4121(2)	3153(5)	2434.7(11)	59.4(10)
C3	4925(4)	10257(11)	3597.9(18)	75.1(19)
C4	5319(3)	8543(14)	3563.5(18)	81(2)

C5	5025(4)	6914(11)	3722.0(18)	76.7(19)
C6	3237(3)	8564(7)	4204.4(14)	40.4(11)
C7	3555(4)	8048(9)	4651.3(18)	76.9(11)
C8	3810(4)	9456(10)	4928.7(17)	79.8(19)
C9	4159(5)	8968(13)	5321(2)	93(2)
C10	4230(4)	7107(11)	5429(2)	80(2)
C11	3967(4)	5733(10)	5155.7(18)	76.9(11)
C12	3624(4)	6210(9)	4764.8(18)	76.9(11)
C13	2847(3)	10500(8)	4204.6(16)	52.8(13)
C14	2593(3)	7061(7)	4029.9(14)	43.6(11)
C15	2775(3)	6049(7)	3208.8(13)	37.6(10)
C16	2783(3)	4055(7)	3217.5(15)	48.2(12)
C17	3229(3)	3041(7)	2962.7(15)	49.8(13)
C18	3664(3)	4011(7)	2698.5(13)	42.6(11)
C19	3649(3)	6027(7)	2687.3(15)	56.9(14)
C20	3213(3)	7023(7)	2947.0(16)	53.8(13)
C21	4156(4)	1095(8)	2428.3(17)	62.4(15)

Table S15 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aq. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	37.4(6)	44.0(7)	48.5(7)	-6.4(6)	6.9(5)	1.1(5)
O1	61(2)	39.1(18)	56(2)	-2.7(16)	4.2(17)	7.7(16)
N1	57(3)	88(4)	61(3)	0(3)	16(2)	15(3)
C1	38(2)	53(3)	36(2)	-2(2)	4(2)	-3(2)
O2	36.3(18)	69(2)	76(2)	-19(2)	8.2(17)	-6.0(17)
N2	103(4)	54(3)	70(3)	-15(3)	7(3)	14(3)
C2	60(3)	60(3)	52(3)	1(3)	10(3)	-16(3)
O3	74(3)	50(2)	59(2)	-8.6(18)	28(2)	6.1(19)
C3	66(4)	106(5)	55(3)	1(4)	12(3)	-39(4)
C4	38(3)	149(7)	56(4)	-8(4)	9(3)	-17(4)
C5	64(4)	105(5)	64(4)	-6(4)	21(3)	29(4)
C6	42(3)	40(2)	41(2)	-2(2)	10(2)	-6(2)
C7	111(3)	64(2)	52.4(19)	-0.8(19)	1(2)	5(2)
C8	112(5)	71(4)	50(3)	-1(3)	-16(3)	-16(4)
C9	110(6)	110(6)	54(4)	-8(4)	-11(4)	-16(5)
C10	79(4)	108(6)	53(4)	11(4)	4(3)	14(4)
C11	111(3)	64(2)	52.4(19)	-0.8(19)	1(2)	5(2)
C12	111(3)	64(2)	52.4(19)	-0.8(19)	1(2)	5(2)
C13	59(3)	48(3)	52(3)	-14(3)	11(3)	-3(3)

C14	46(3)	44(3)	42(3)	-2(2)	13(2)	-4(2)
C15	33(2)	40(3)	39(2)	-5(2)	2.8(19)	-2(2)
C16	51(3)	41(3)	55(3)	3(2)	17(2)	-1(2)
C17	61(3)	32(2)	58(3)	2(2)	16(3)	0(2)
C18	47(3)	43(3)	39(2)	-7(2)	7(2)	4(2)
C19	78(4)	44(3)	56(3)	3(3)	36(3)	-3(3)
C20	67(3)	38(3)	59(3)	1(2)	20(3)	1(2)
C21	73(4)	53(3)	62(3)	-9(3)	12(3)	14(3)

Table S16 Bond Lengths for 3aq.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.439(3)	C6	C13	1.481(7)
S1	O2	1.445(3)	C6	C14	1.543(6)
S1	C14	1.779(5)	C7	C8	1.363(8)
S1	C15	1.755(4)	C7	C12	1.321(8)
N1	C1	1.372(6)	C8	C9	1.391(8)
N1	C5	1.374(7)	C9	C10	1.331(9)
C1	C2	1.366(7)	C10	C11	1.342(9)
C1	C6	1.536(6)	C11	C12	1.383(8)
N2	C13	1.131(6)	C15	C16	1.373(6)
C2	C3	1.406(8)	C15	C20	1.371(6)
O3	C18	1.358(5)	C16	C17	1.377(6)
O3	C21	1.418(6)	C17	C18	1.372(6)
C3	C4	1.360(9)	C18	C19	1.388(7)
C4	C5	1.353(9)	C19	C20	1.371(7)
C6	C7	1.544(7)			

Table S17 Bond Angles for 3aq.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	118.8(2)	C8	C7	C6	121.2(5)
O1	S1	C14	109.8(2)	C12	C7	C6	119.9(5)
O1	S1	C15	108.1(2)	C12	C7	C8	118.8(6)
O2	S1	C14	105.0(2)	C7	C8	C9	120.7(7)
O2	S1	C15	107.1(2)	C10	C9	C8	119.7(7)
C15	S1	C14	107.6(2)	C9	C10	C11	119.2(6)
C1	N1	C5	115.6(5)	C10	C11	C12	121.4(6)
N1	C1	C6	114.9(4)	C7	C12	C11	120.2(6)
C2	C1	N1	123.0(4)	N2	C13	C6	177.5(6)
C2	C1	C6	122.0(4)	C6	C14	S1	116.9(3)
C1	C2	C3	118.5(6)	C16	C15	S1	120.5(3)

C18	O3	C21	118.1(4)	C20	C15	S1	119.6(4)
C4	C3	C2	119.6(6)	C20	C15	C16	119.8(4)
C5	C4	C3	119.2(6)	C15	C16	C17	119.9(4)
C4	C5	N1	124.1(6)	C18	C17	C16	120.4(4)
C1	C6	C7	108.0(4)	O3	C18	C17	125.1(4)
C1	C6	C14	112.0(4)	O3	C18	C19	115.3(4)
C13	C6	C1	110.4(4)	C17	C18	C19	119.6(4)
C13	C6	C7	107.6(4)	C20	C19	C18	119.5(5)
C13	C6	C14	108.9(4)	C15	C20	C19	120.7(5)
C14	C6	C7	109.8(4)				

Table S18 Torsion Angles for 3aq.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C15	C16	C17	176.6(4)	C6	C7	C8	C9	-174.5(6)
S1	C15	C20	C19	-175.6(4)	C6	C7	C12	C11	175.1(6)
O1	S1	C14	C6	-27.1(4)	C7	C6	C14	S1	-178.5(4)
O1	S1	C15	C16	-172.3(4)	C7	C8	C9	C10	-1.5(12)
O1	S1	C15	C20	4.5(5)	C8	C7	C12	C11	-1.5(11)
N1	C1	C2	C3	-1.3(8)	C8	C9	C10	C11	0.5(11)
N1	C1	C6	C7	65.6(5)	C9	C10	C11	C12	0.0(11)
N1	C1	C6	C13	-177.0(4)	C10	C11	C12	C7	0.6(11)
N1	C1	C6	C14	-55.5(5)	C12	C7	C8	C9	2.0(11)
C1	N1	C5	C4	0.4(9)	C13	C6	C7	C8	-30.9(8)
C1	C2	C3	C4	0.4(8)	C13	C6	C7	C12	152.6(6)
C1	C6	C7	C8	88.3(7)	C13	C6	C14	S1	63.9(4)
C1	C6	C7	C12	-88.2(7)	C14	S1	C15	C16	69.2(4)
C1	C6	C14	S1	-58.5(5)	C14	S1	C15	C20	-114.0(4)
O2	S1	C14	C6	-155.9(3)	C14	C6	C7	C8	-149.3(6)
O2	S1	C15	C16	-43.2(5)	C14	C6	C7	C12	34.2(8)
O2	S1	C15	C20	133.5(4)	C15	S1	C14	C6	90.3(4)
C2	C1	C6	C7	-113.0(5)	C15	C16	C17	C18	-0.3(8)
C2	C1	C6	C13	4.5(6)	C16	C15	C20	C19	1.2(8)
C2	C1	C6	C14	126.0(5)	C16	C17	C18	O3	-179.9(5)
C2	C3	C4	C5	0.8(9)	C16	C17	C18	C19	-0.4(8)
O3	C18	C19	C20	-179.1(5)	C17	C18	C19	C20	1.4(8)
C3	C4	C5	N1	-1.2(10)	C18	C19	C20	C15	-1.8(8)
C5	N1	C1	C2	0.9(7)	C20	C15	C16	C17	-0.1(8)
C5	N1	C1	C6	-177.6(4)	C21	O3	C18	C17	0.1(7)
C6	C1	C2	C3	177.1(4)	C21	O3	C18	C19	-179.4(5)

Table S19 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aq.

Atom	*x*	*y*	*z*	U(eq)
H2	3947.94	11468.08	3825.83	68
H3	5114.99	11386.67	3487.74	90
H4	5784.51	8490.65	3432.81	97
H5	5296.34	5751.04	3691.07	92
H8	3748.76	10757.11	4855.02	96
H9	4342.72	9937.14	5506	112
H10	4459.33	6763.78	5691	96
H11	4015.5	4431.56	5230.8	92
H12	3441.35	5233.24	4581.17	92
H14A	2151.81	7082.57	4197.37	52
H14B	2840.33	5781.72	4058.39	52
H16	2487.37	3389.79	3395.23	58
H17	3235.95	1690.71	2969.72	60
H19	3932.35	6696.86	2505.09	68
H20	3214.61	8374.14	2945.42	65
H21A	4462.31	680.68	2215.51	94
H21B	3613.12	579.71	2378.46	94
H21C	4414.96	631	2686.66	94

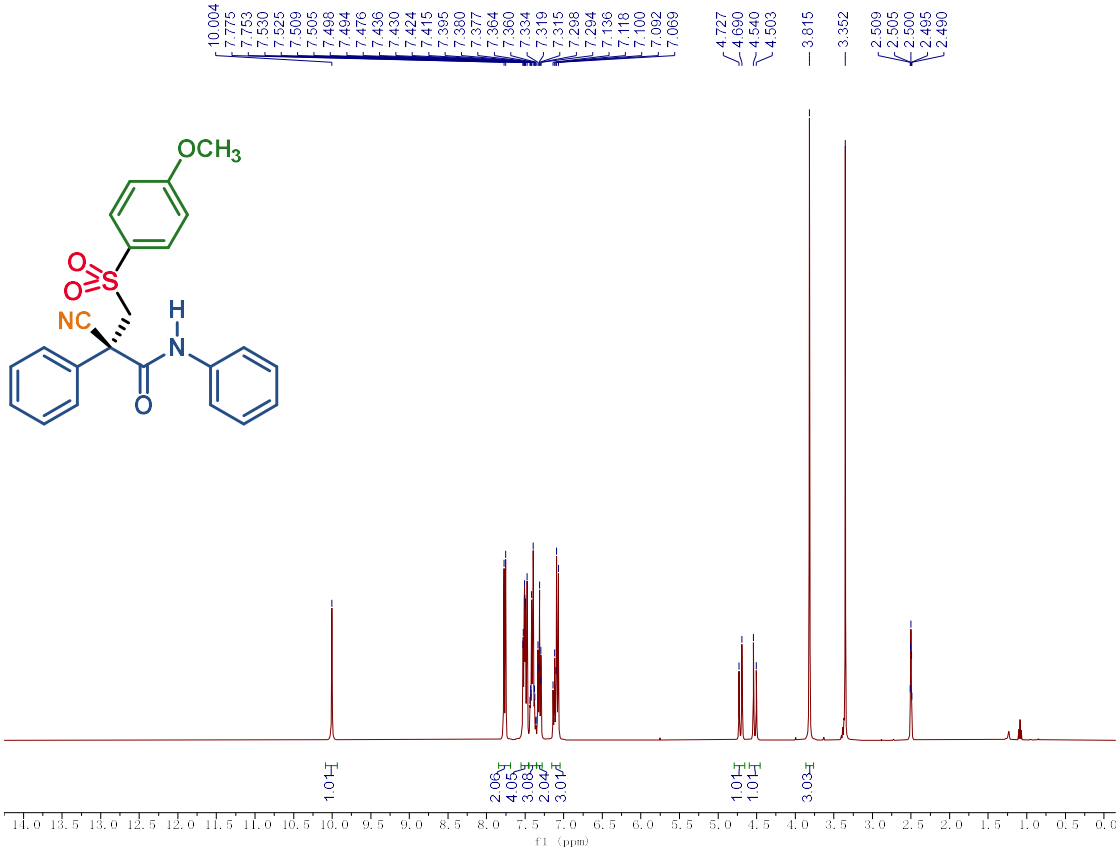
[9] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

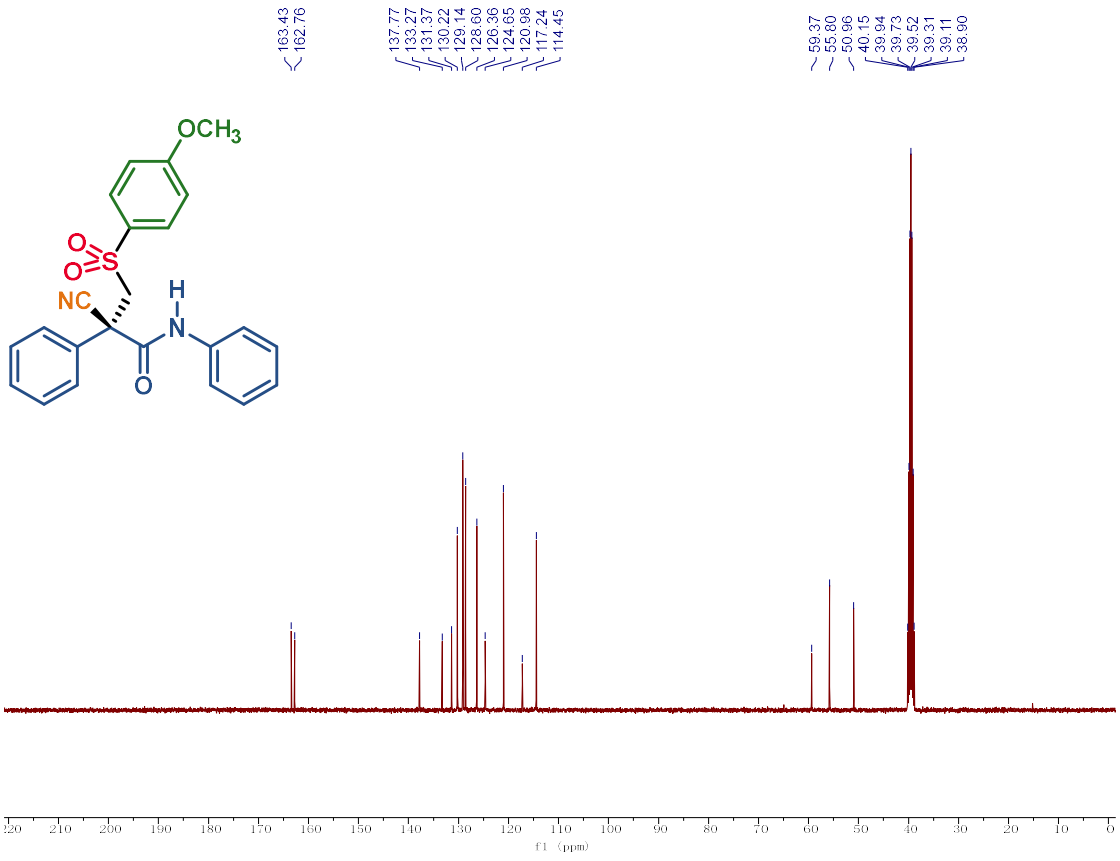
[10] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[11] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

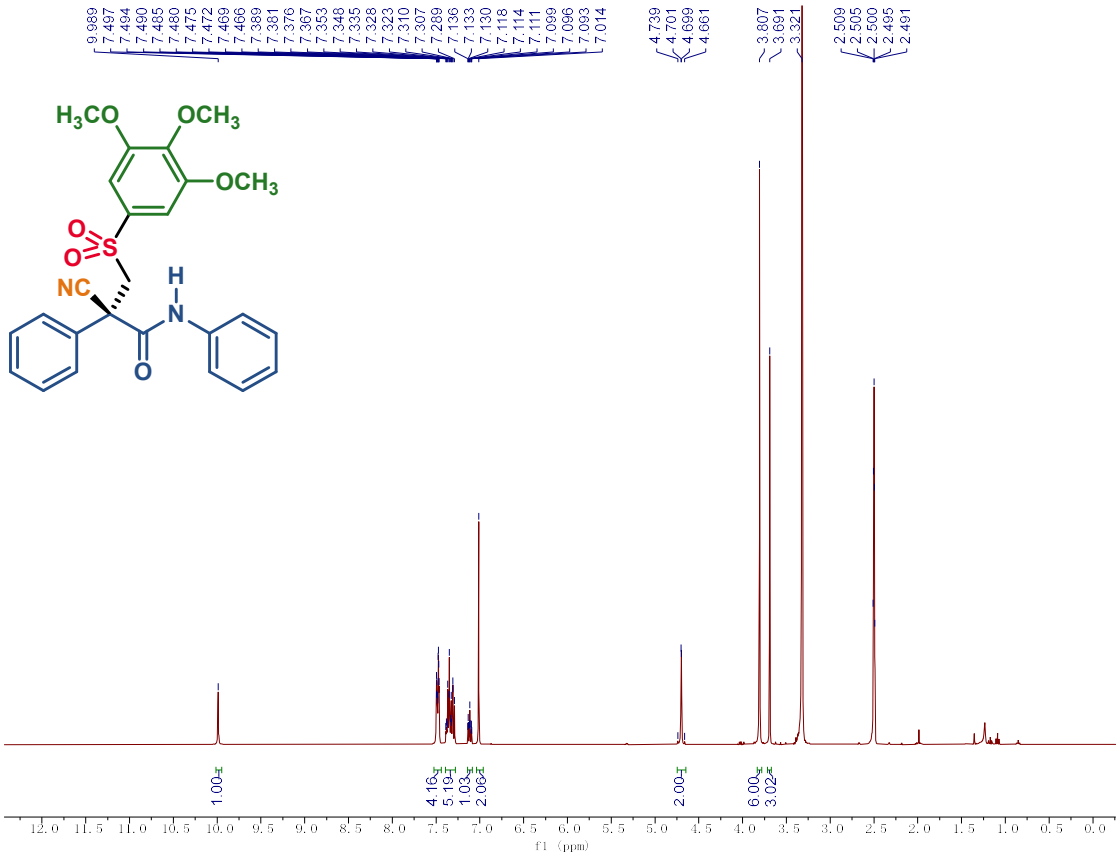
12. The spectrums of NMR and HPLC chromatograms

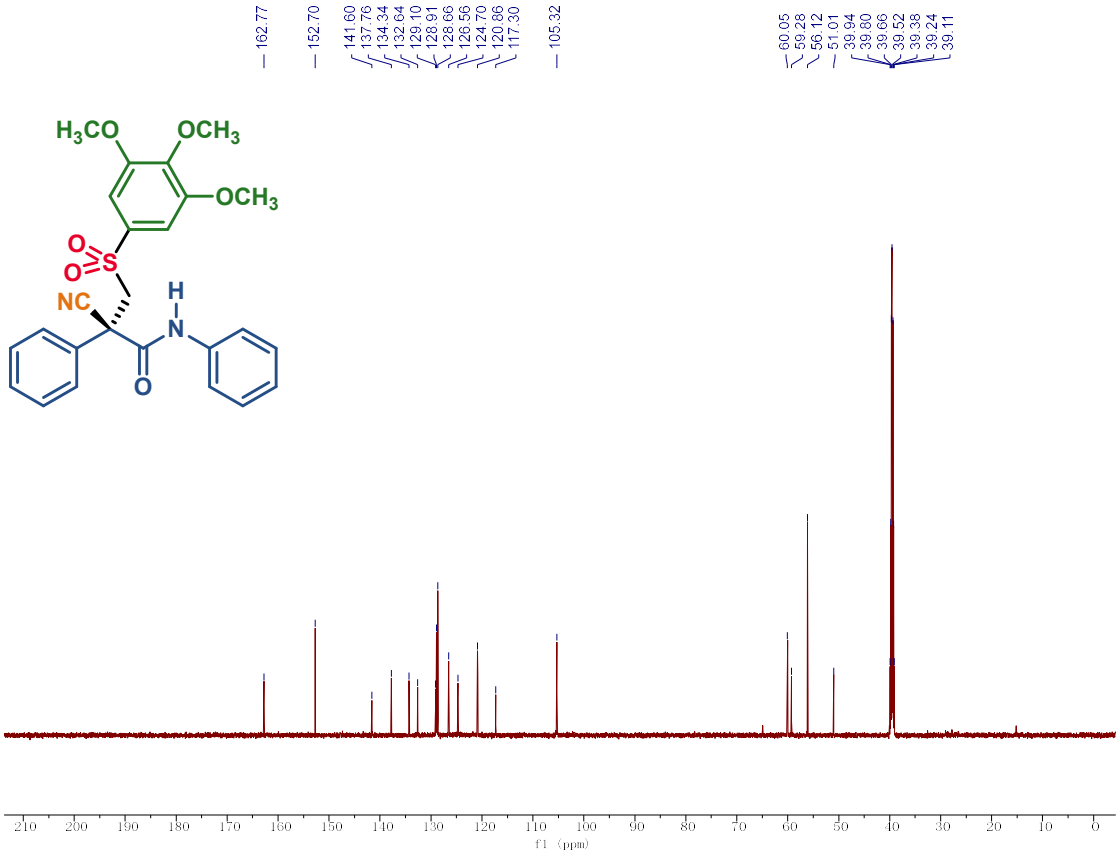
NMR of Compound of 3a



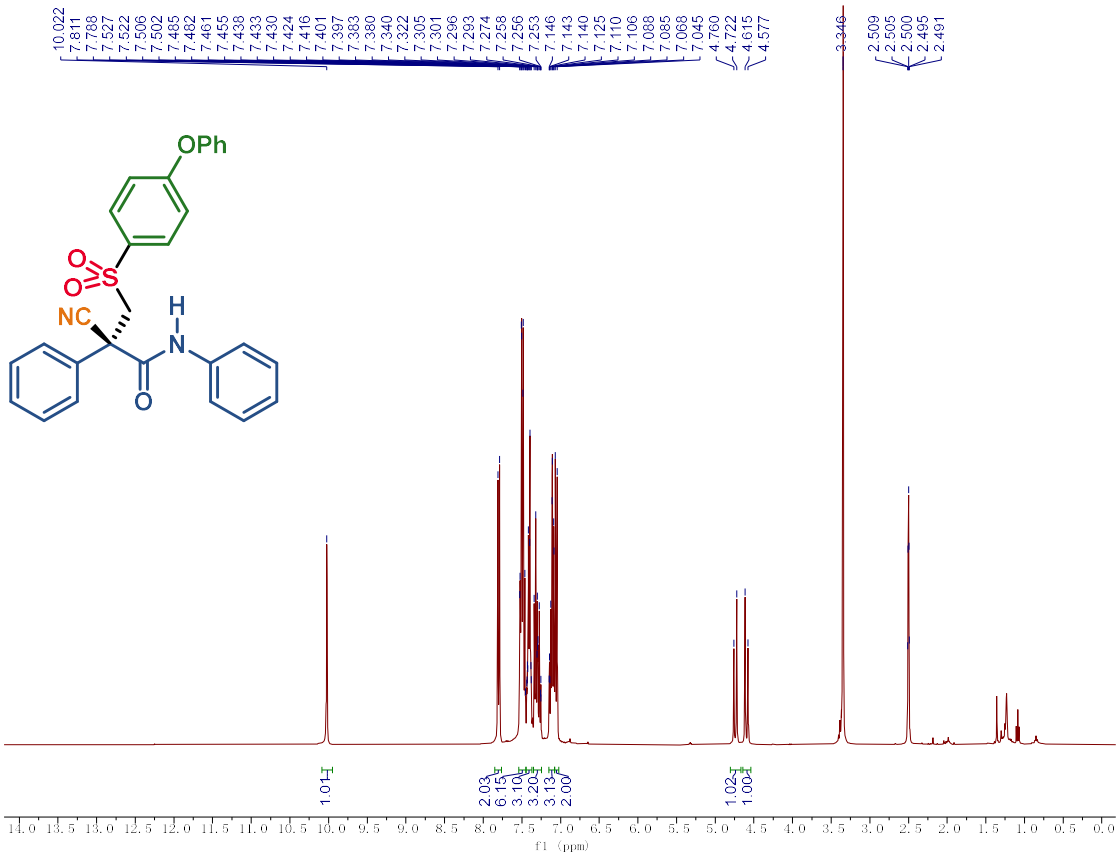


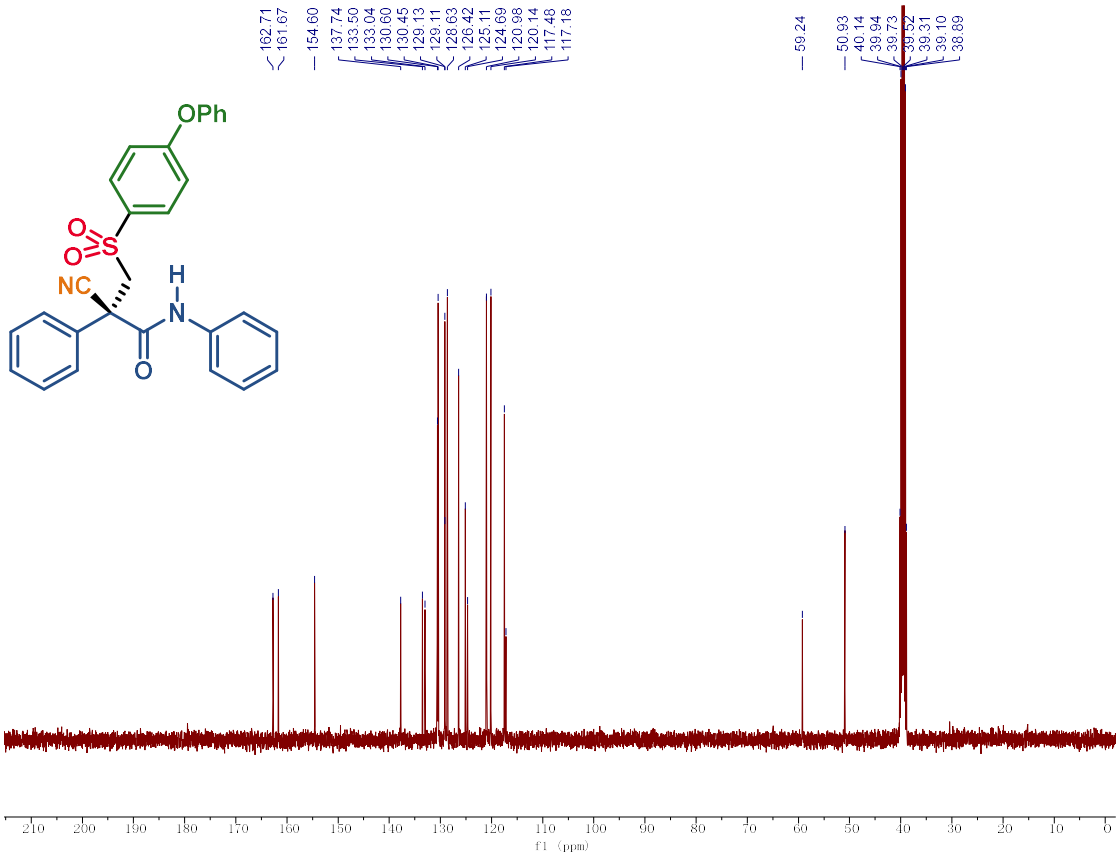
NMR of Compound of 3b



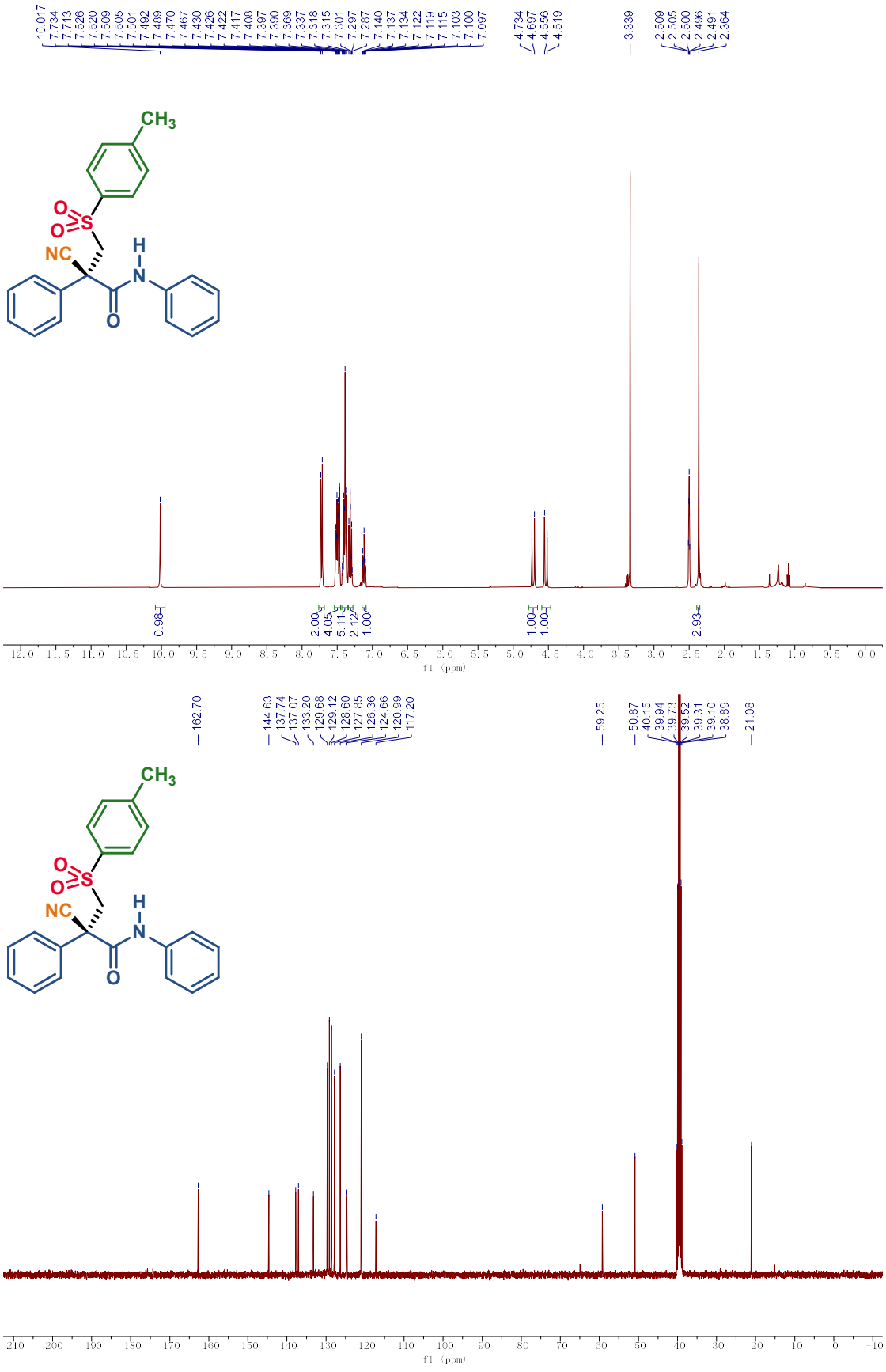


NMR of Compound of 3c

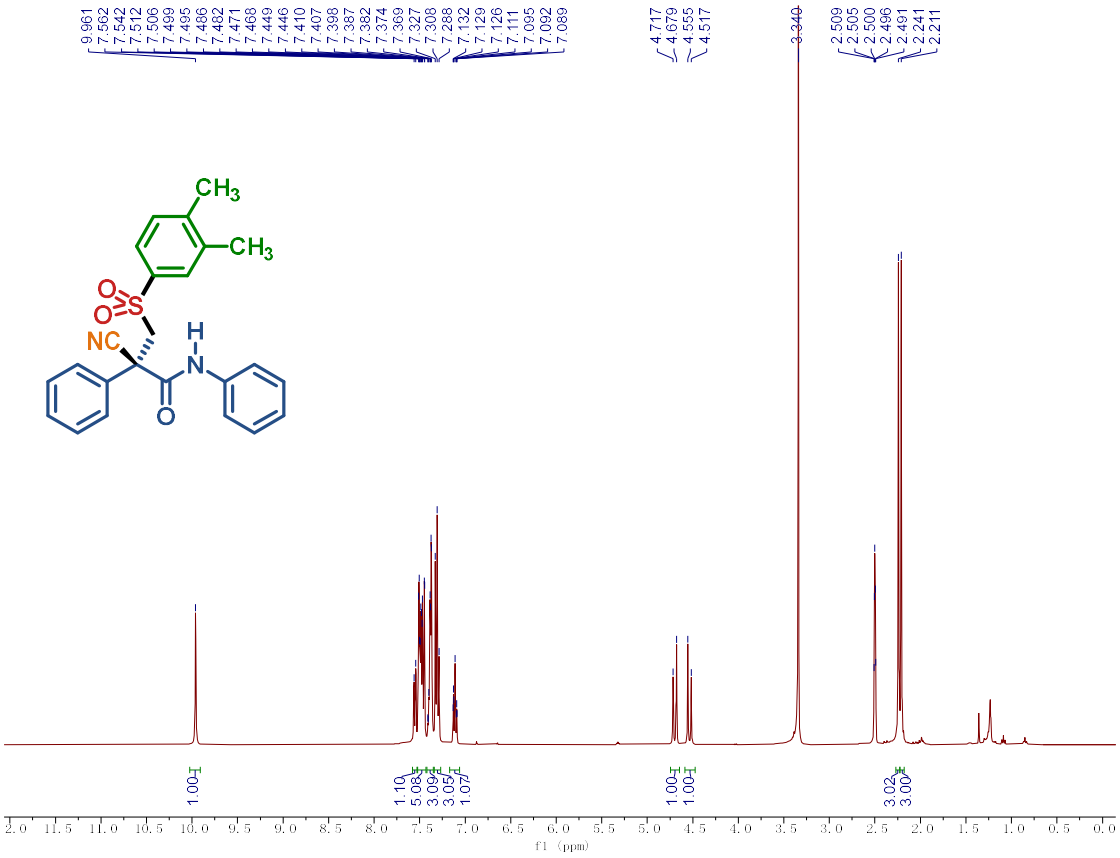


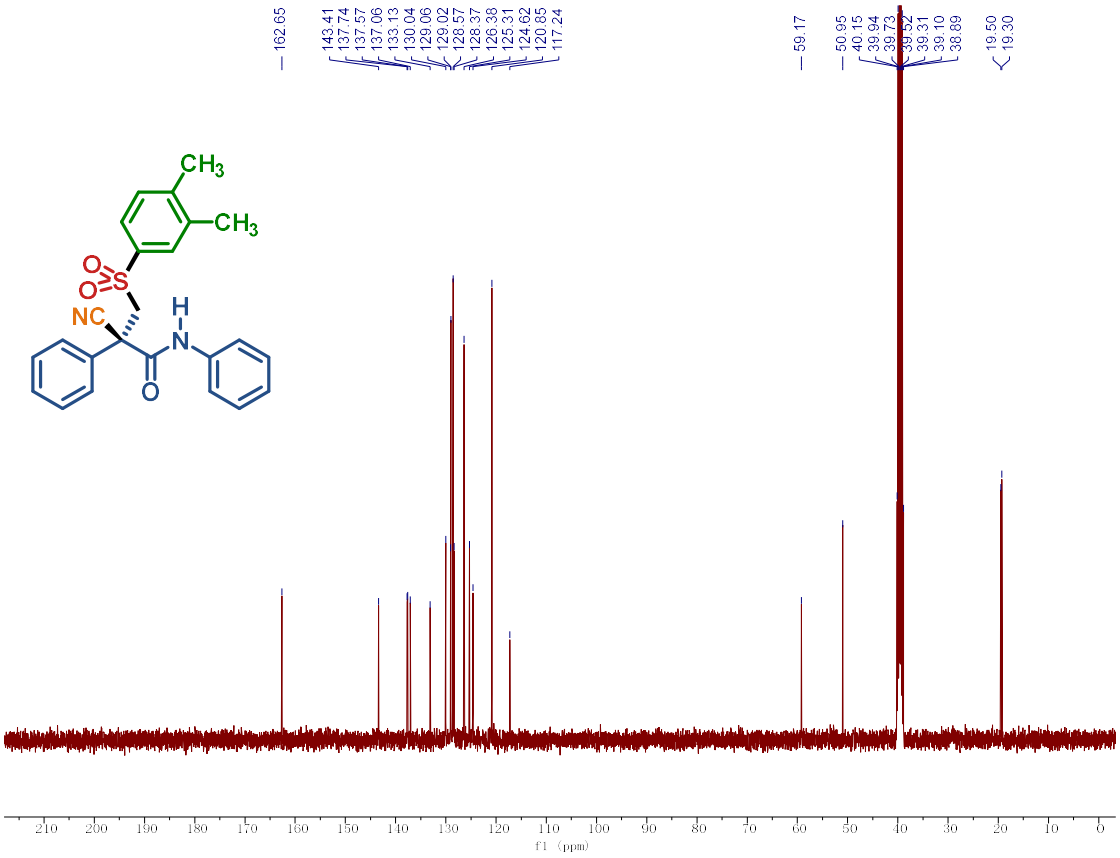


NMR of Compound of 3d

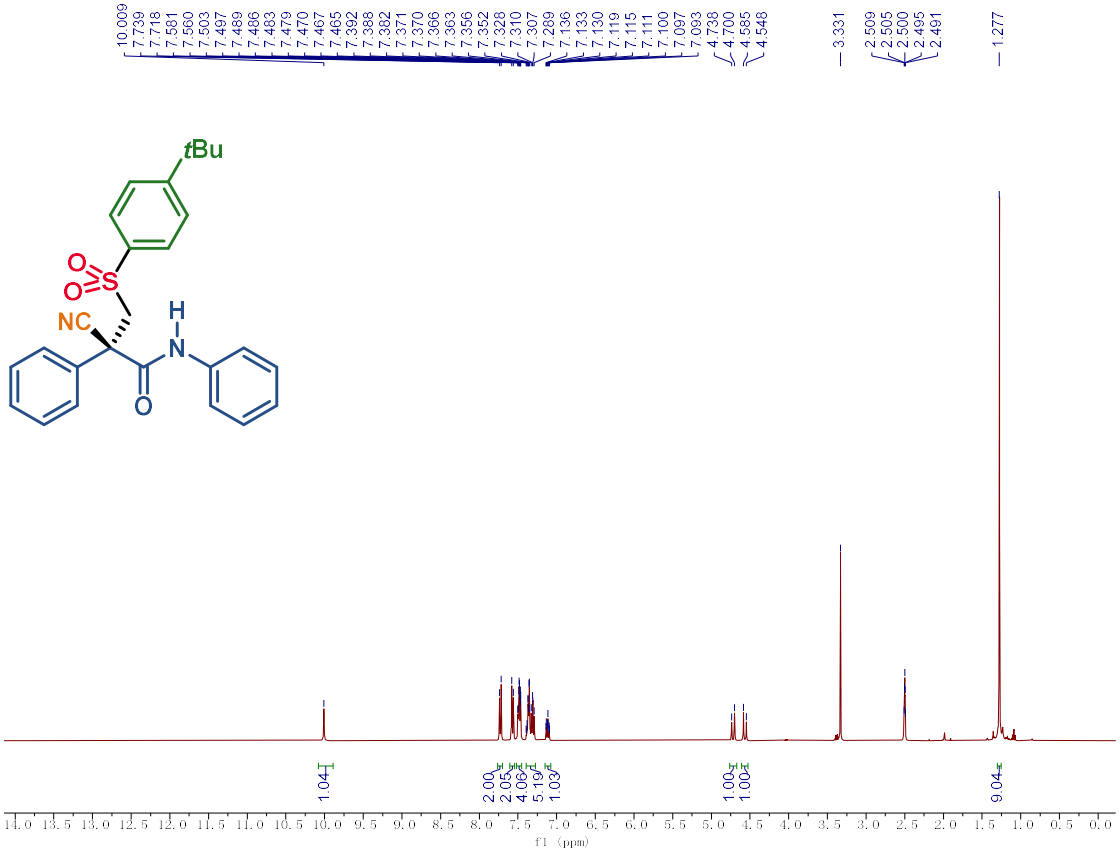


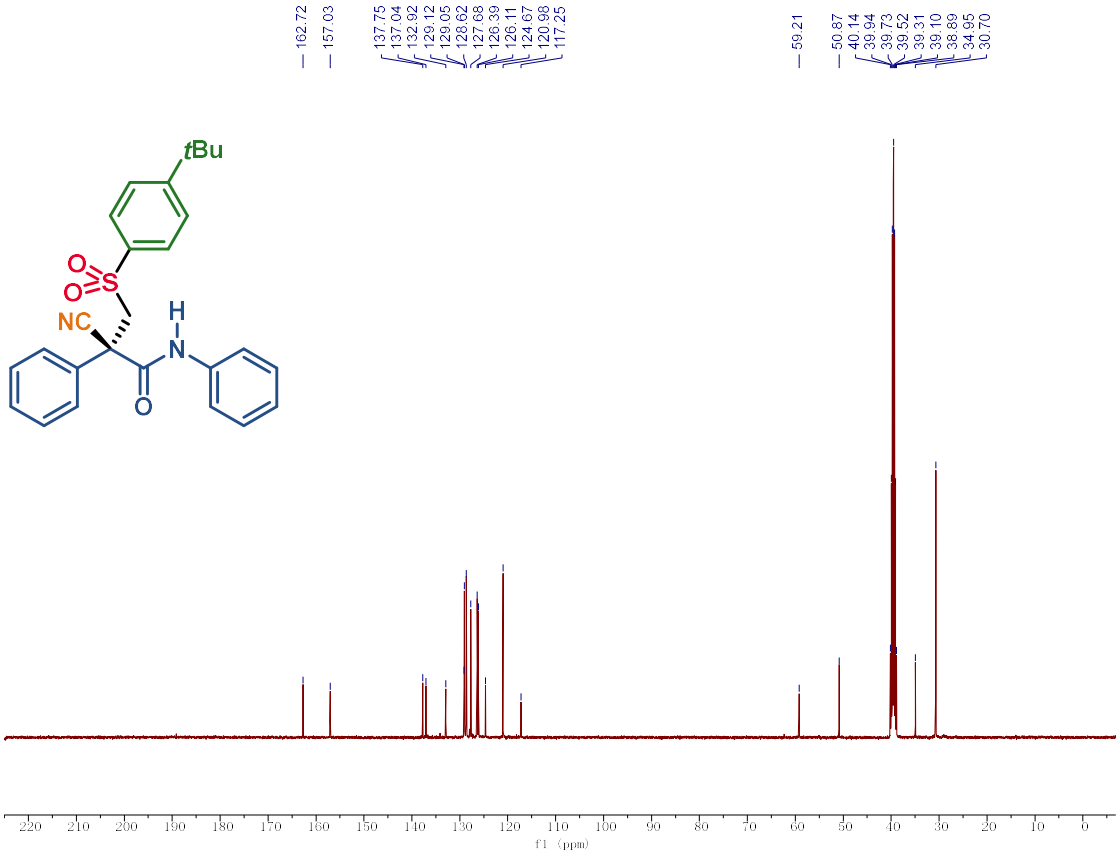
NMR of Compound of 3e



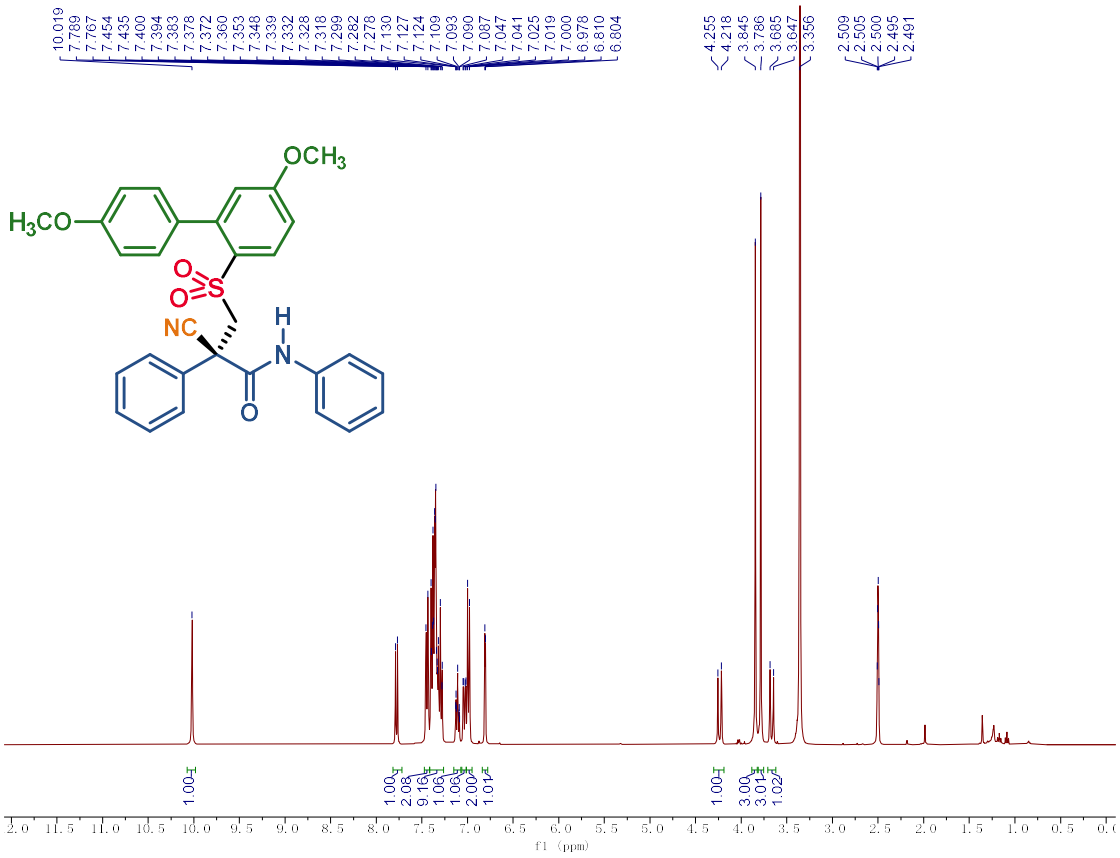


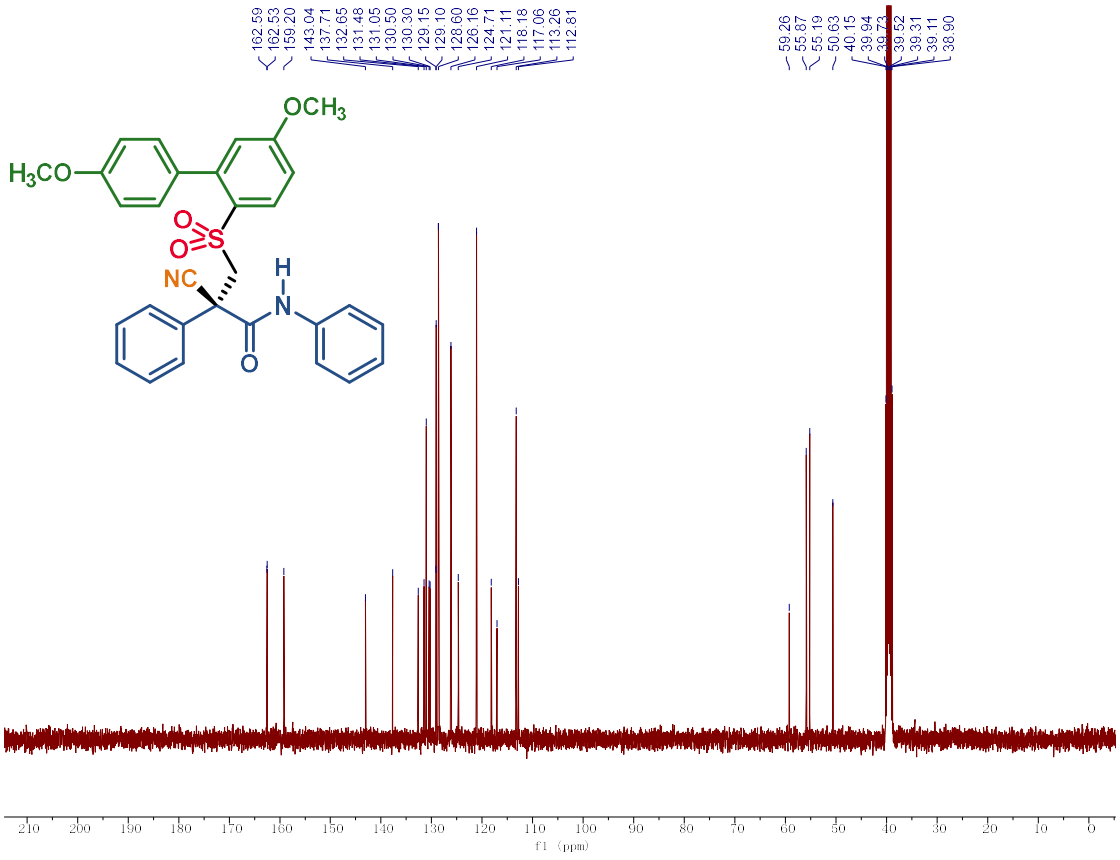
NMR of Compound of 3f



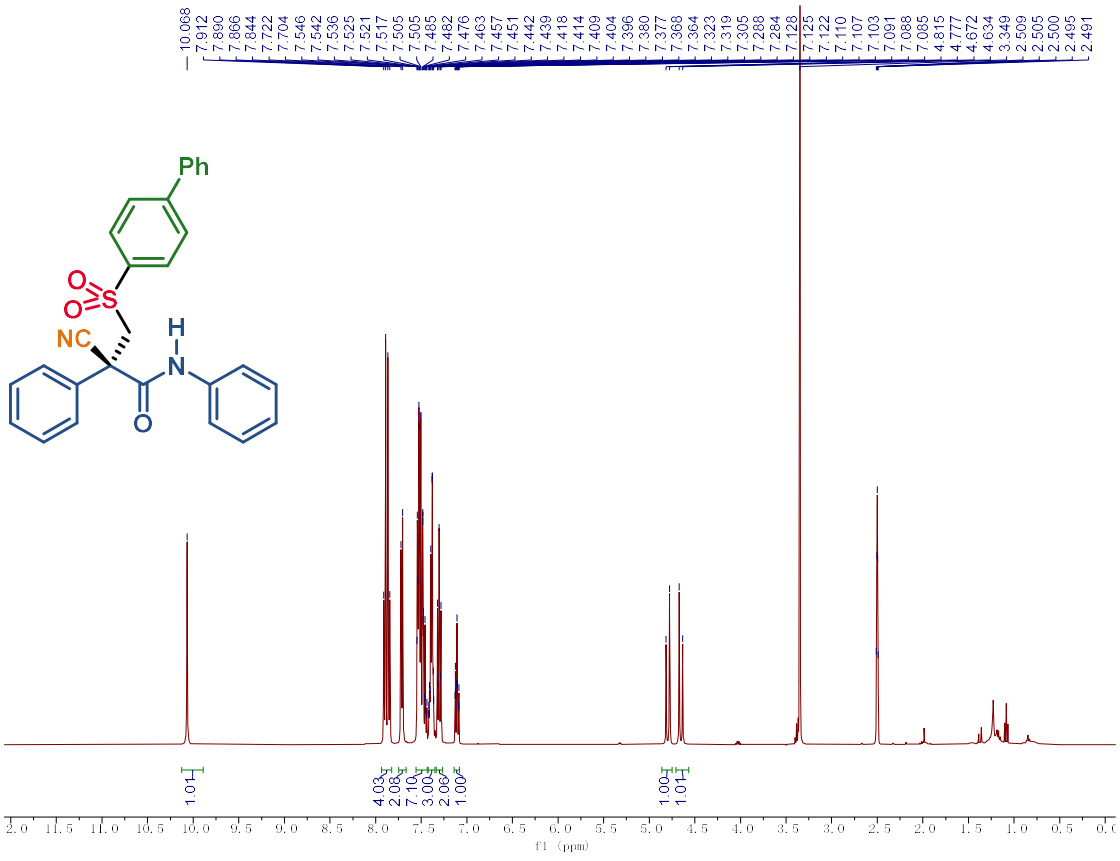


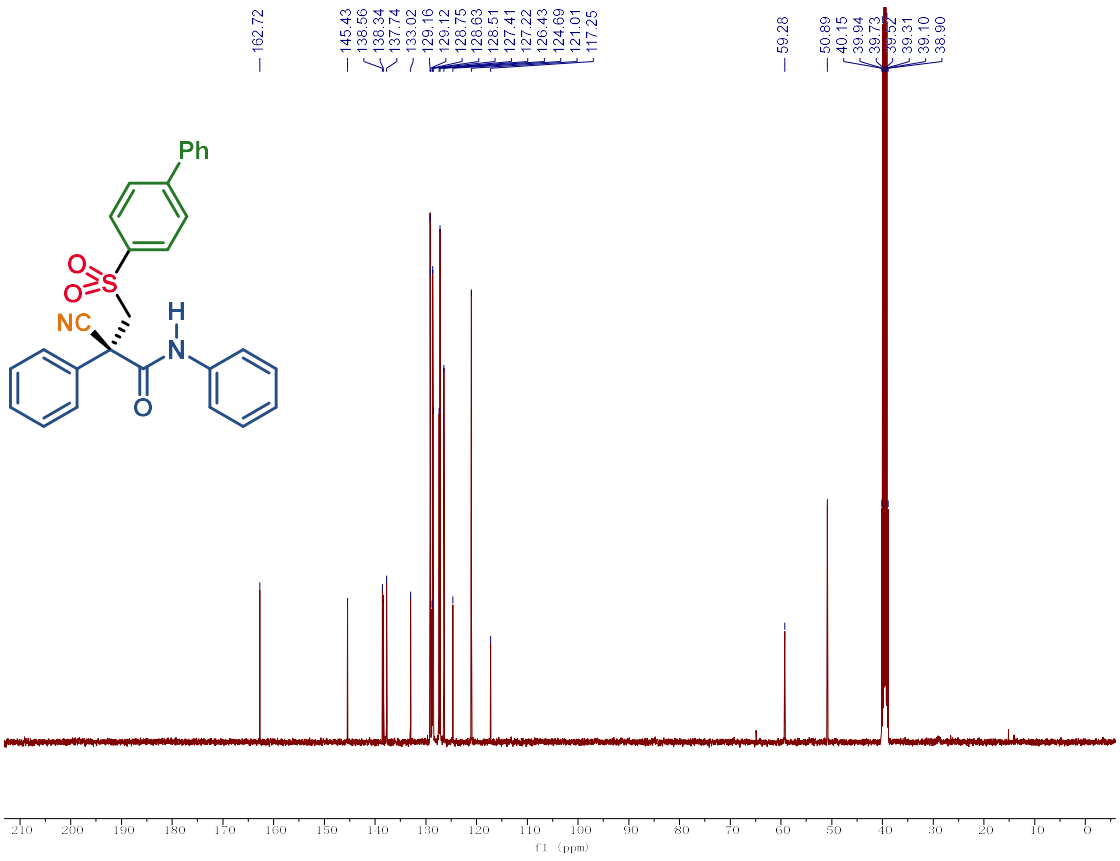
NMR of Compound of 3g



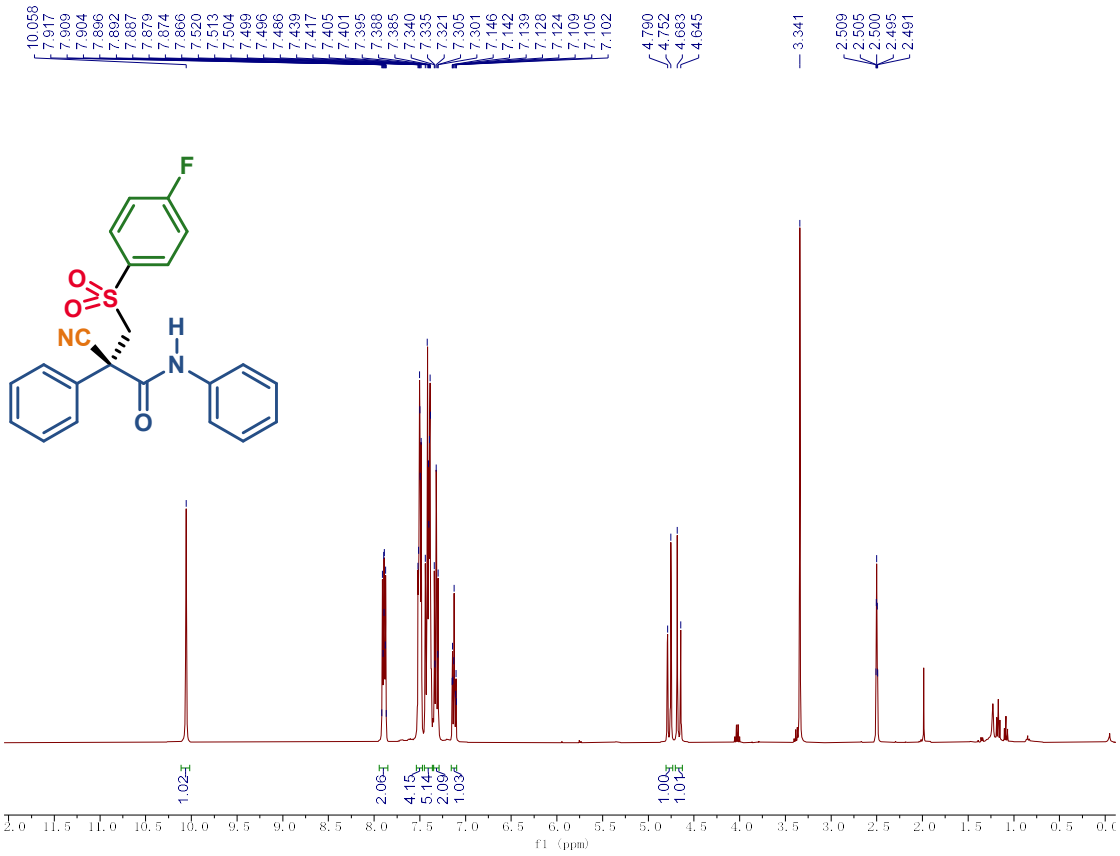


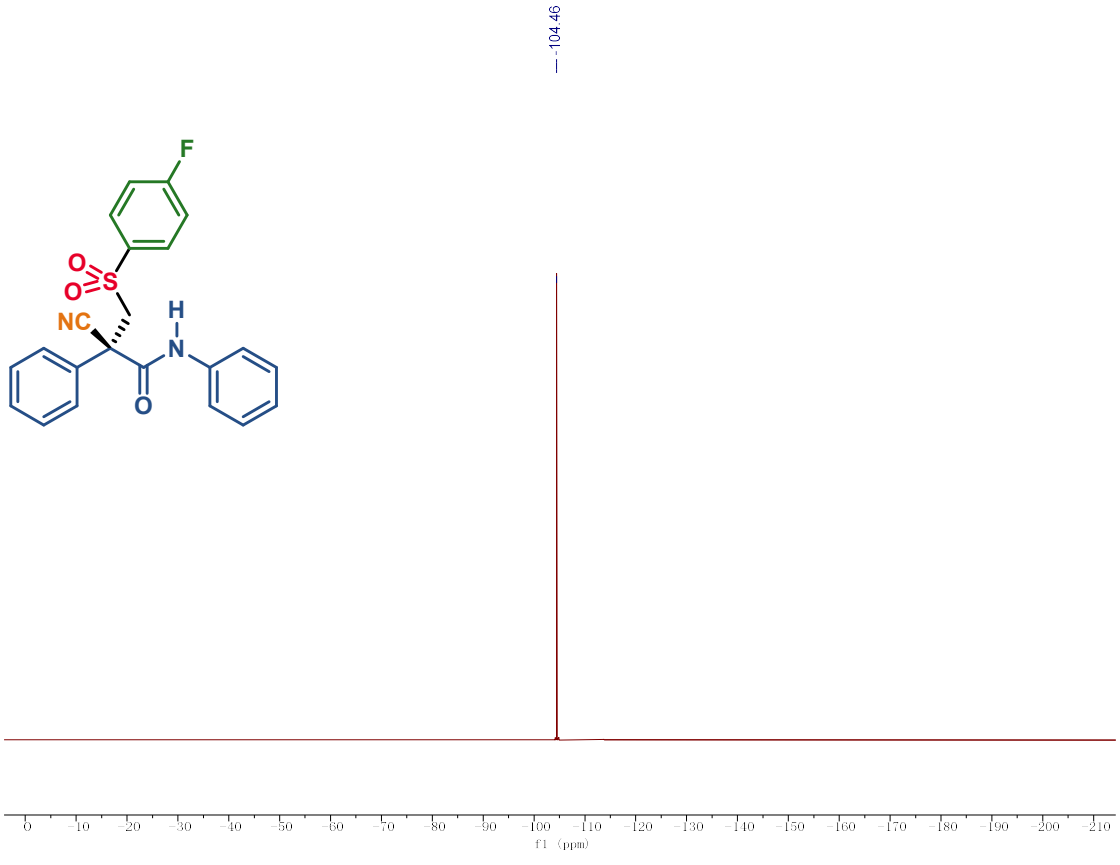
NMR of Compound of 3h

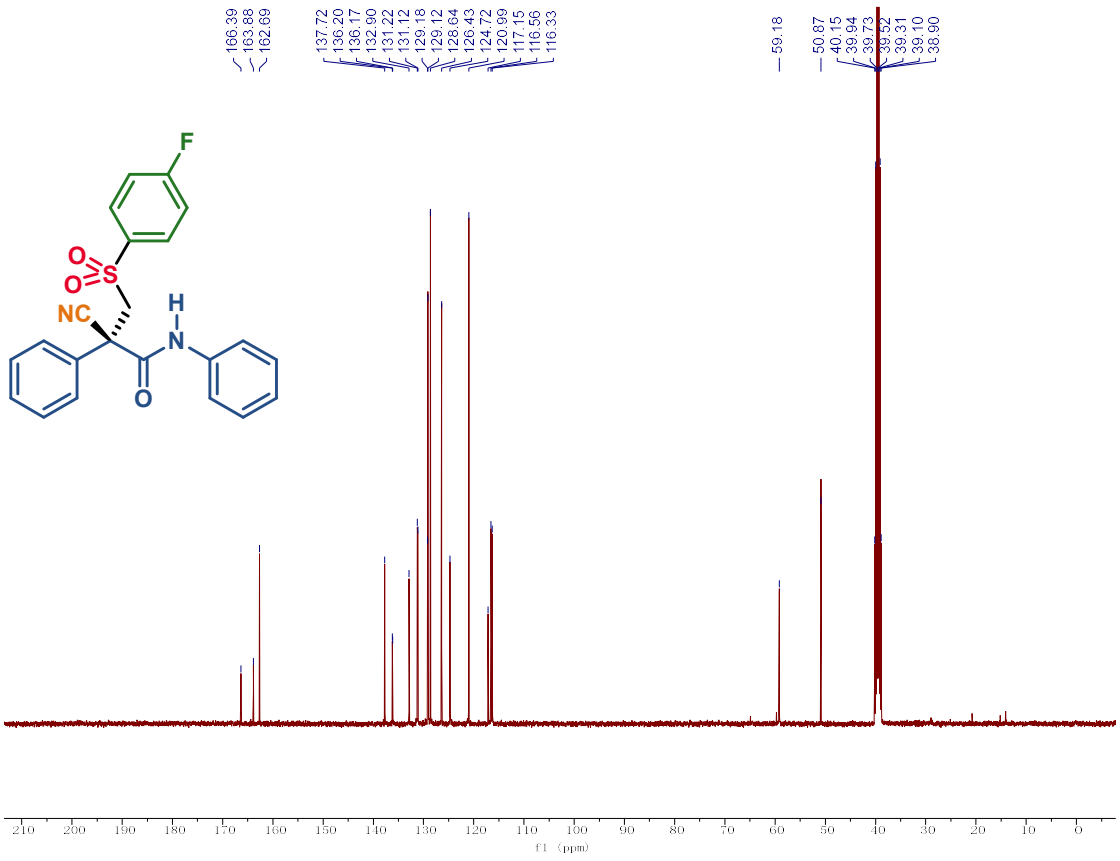




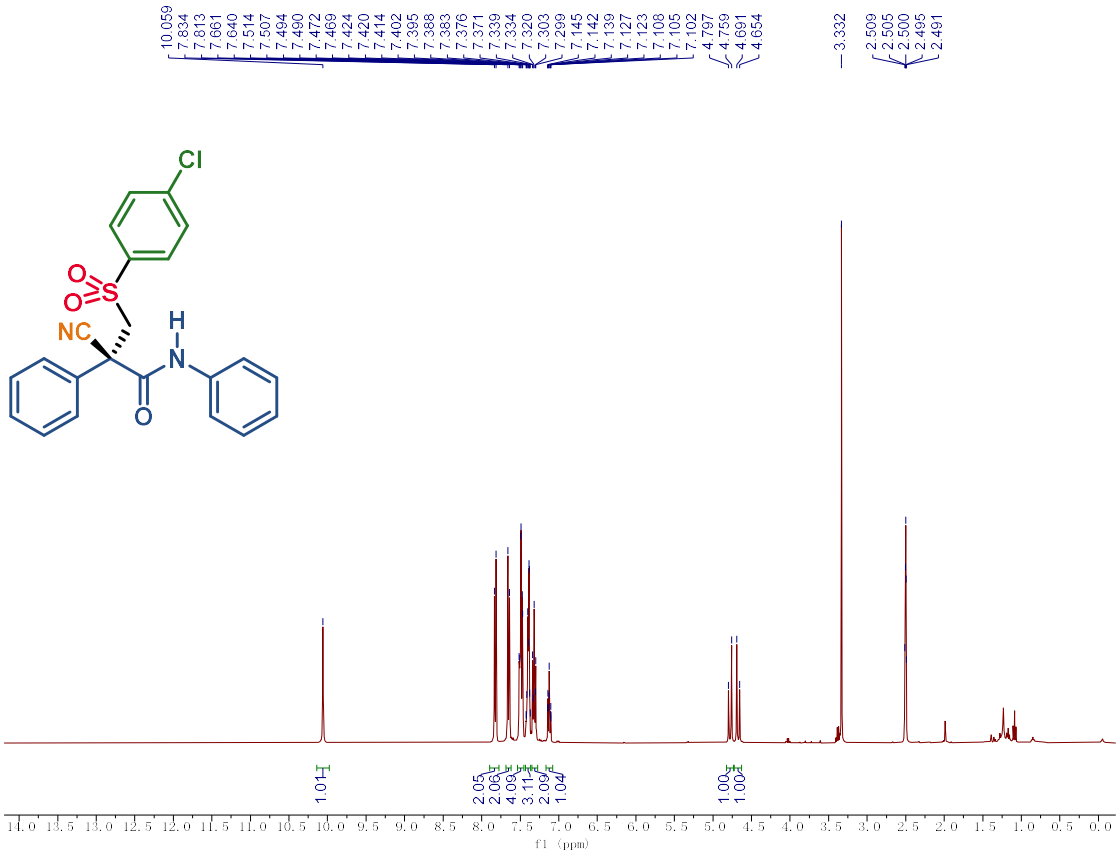
NMR of Compound of 3i

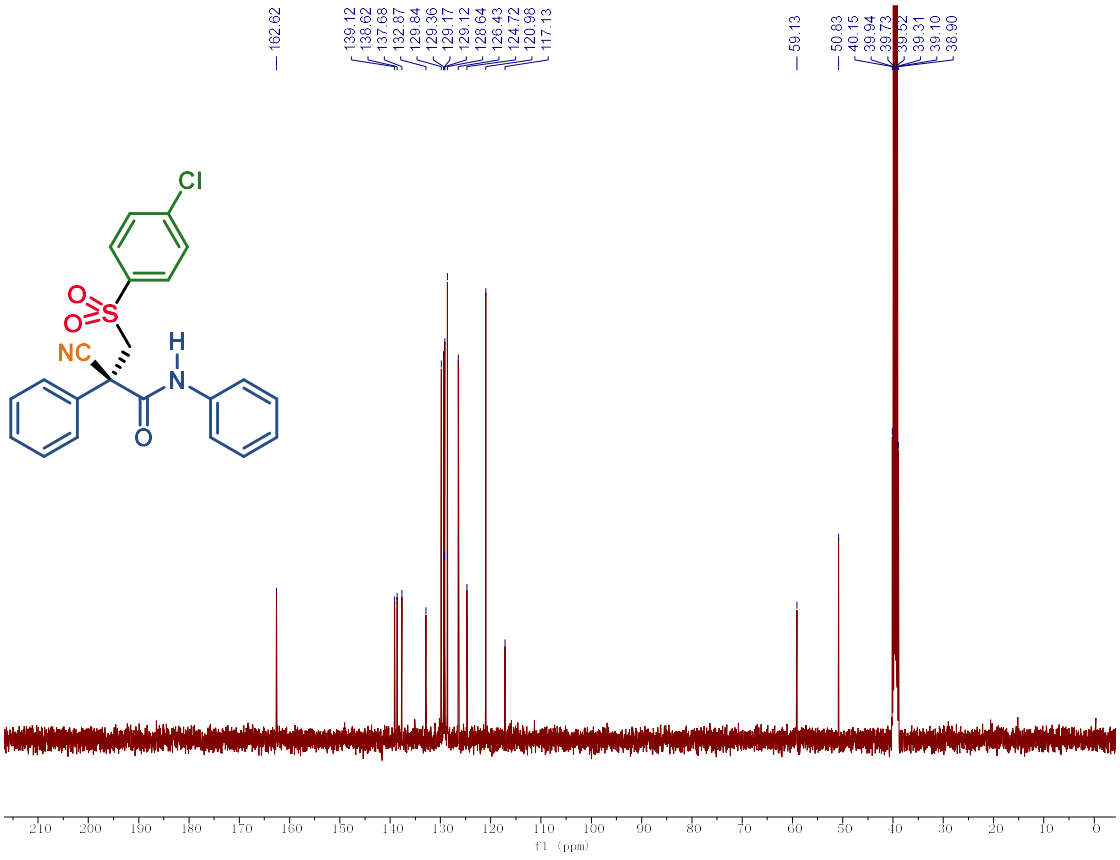




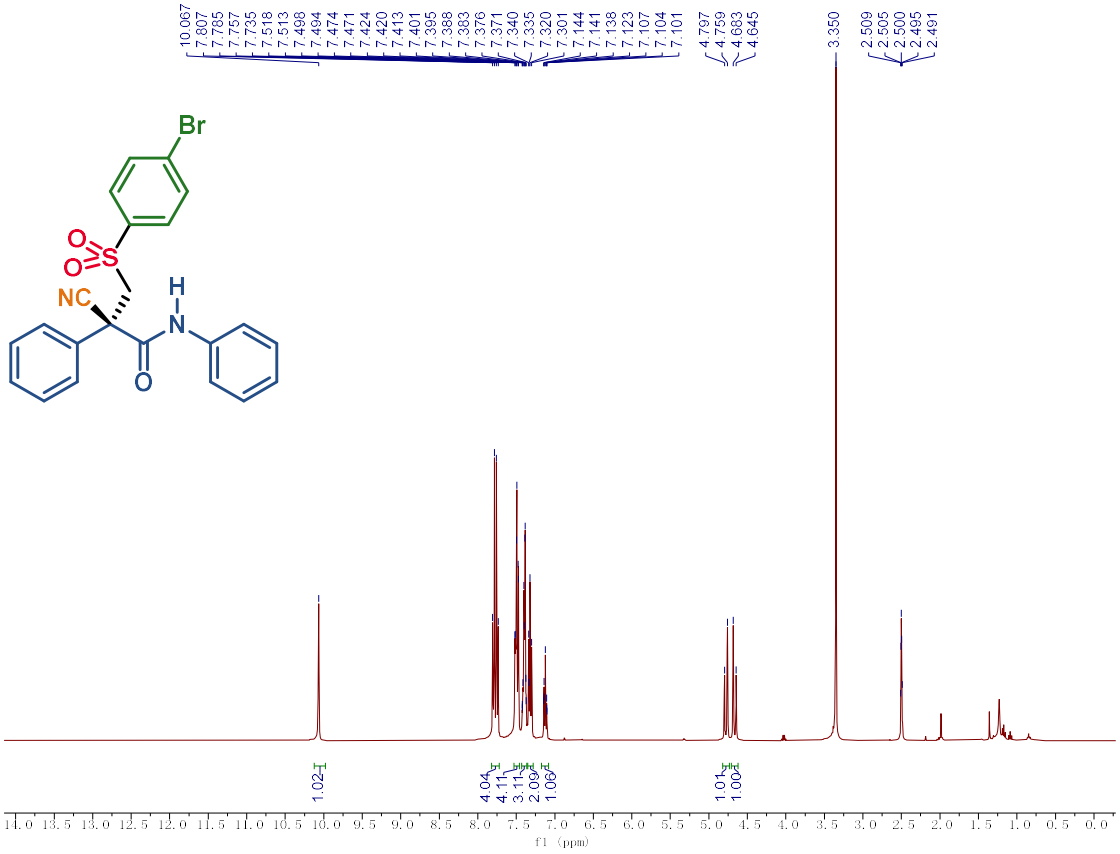

166.39
163.88
162.69
137.72
136.20
136.17
132.90
131.22
131.12
129.18
129.12
128.64
126.43
124.72
120.99
117.15
116.56
116.33
59.18
50.87
40.15
39.94
39.73
39.52
39.31
39.10
38.90
F
O
O
S
NC
H
N
O
f1 (ppm)

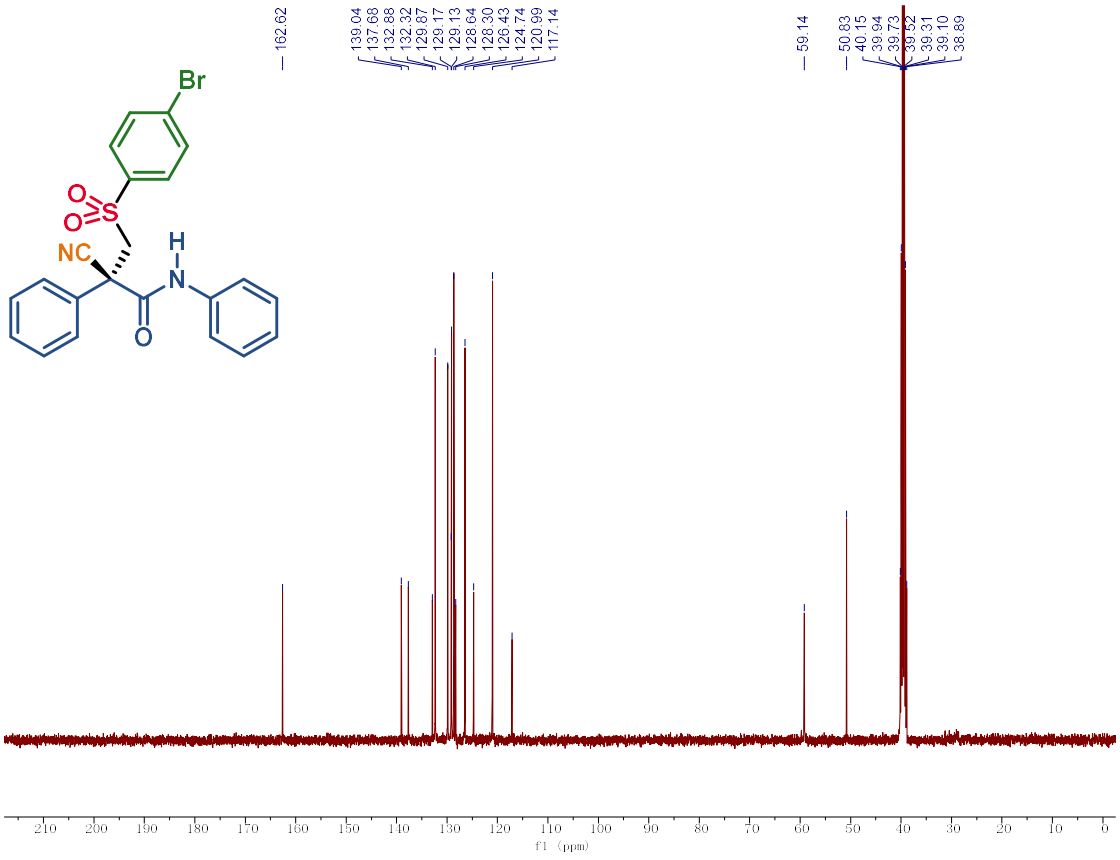
NMR of Compound of 3j



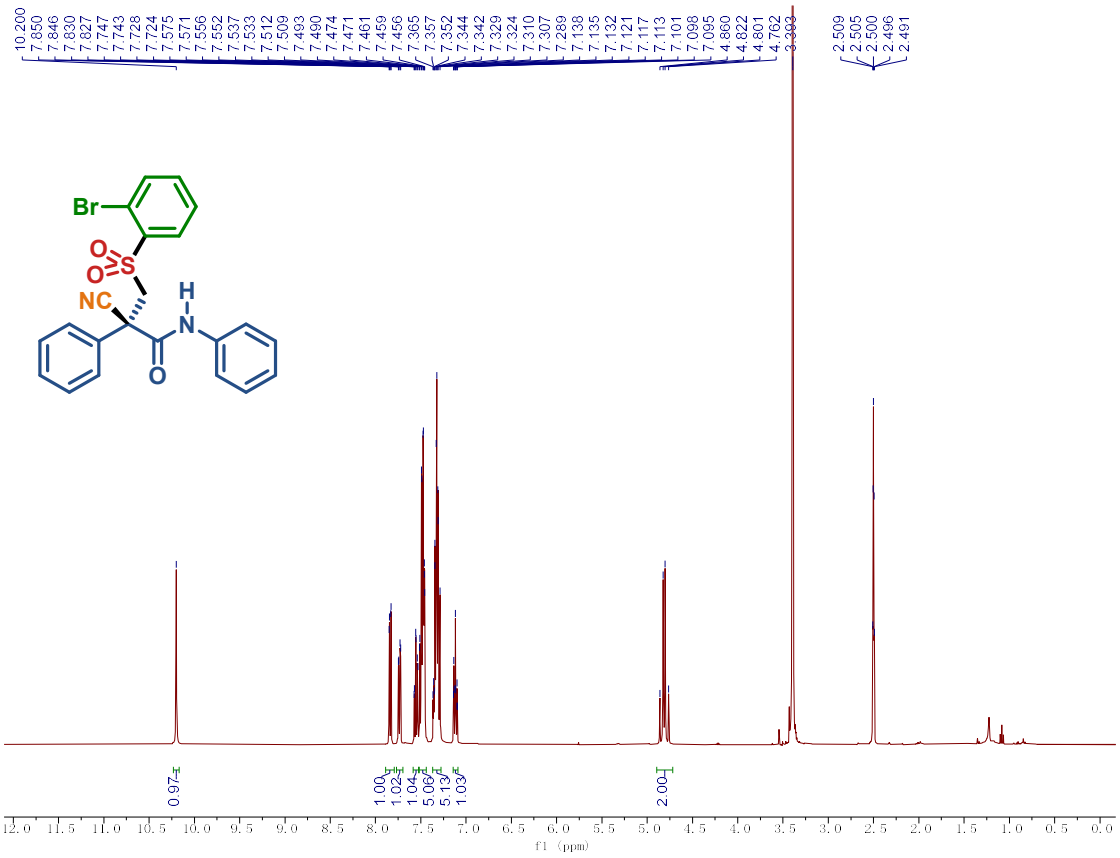


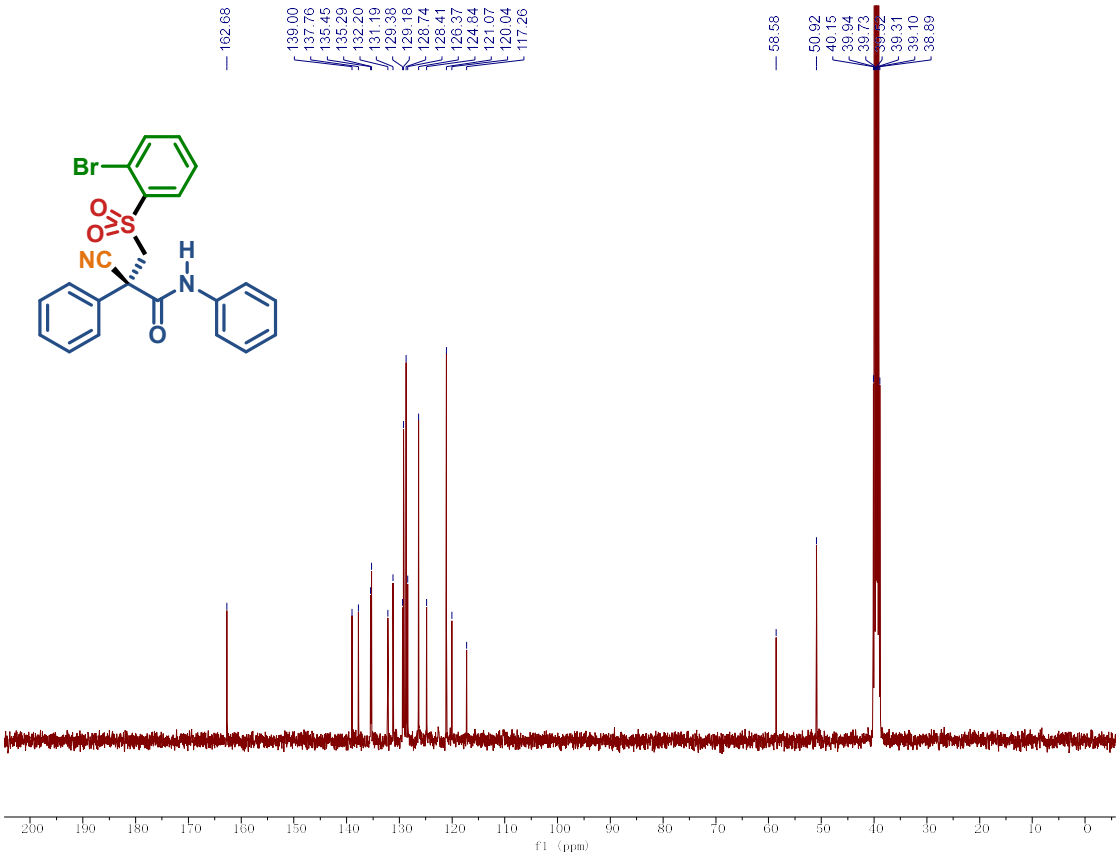
NMR of Compound of 3k



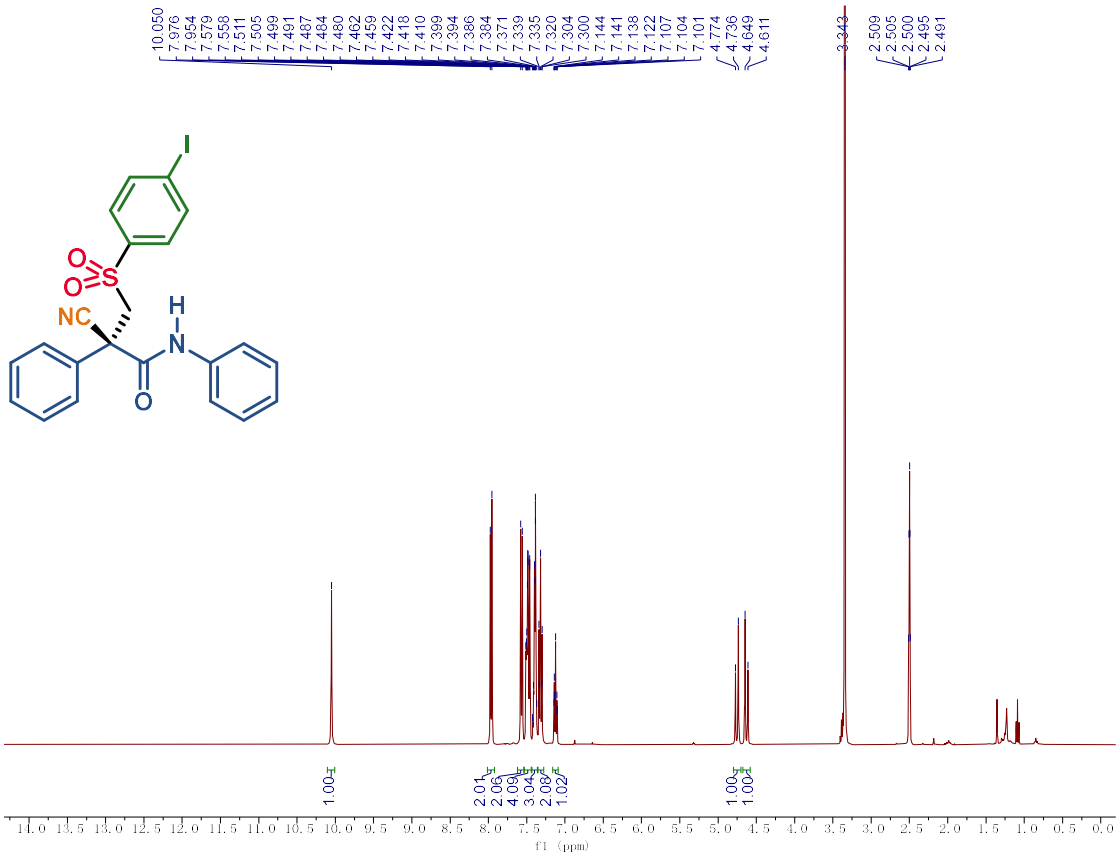


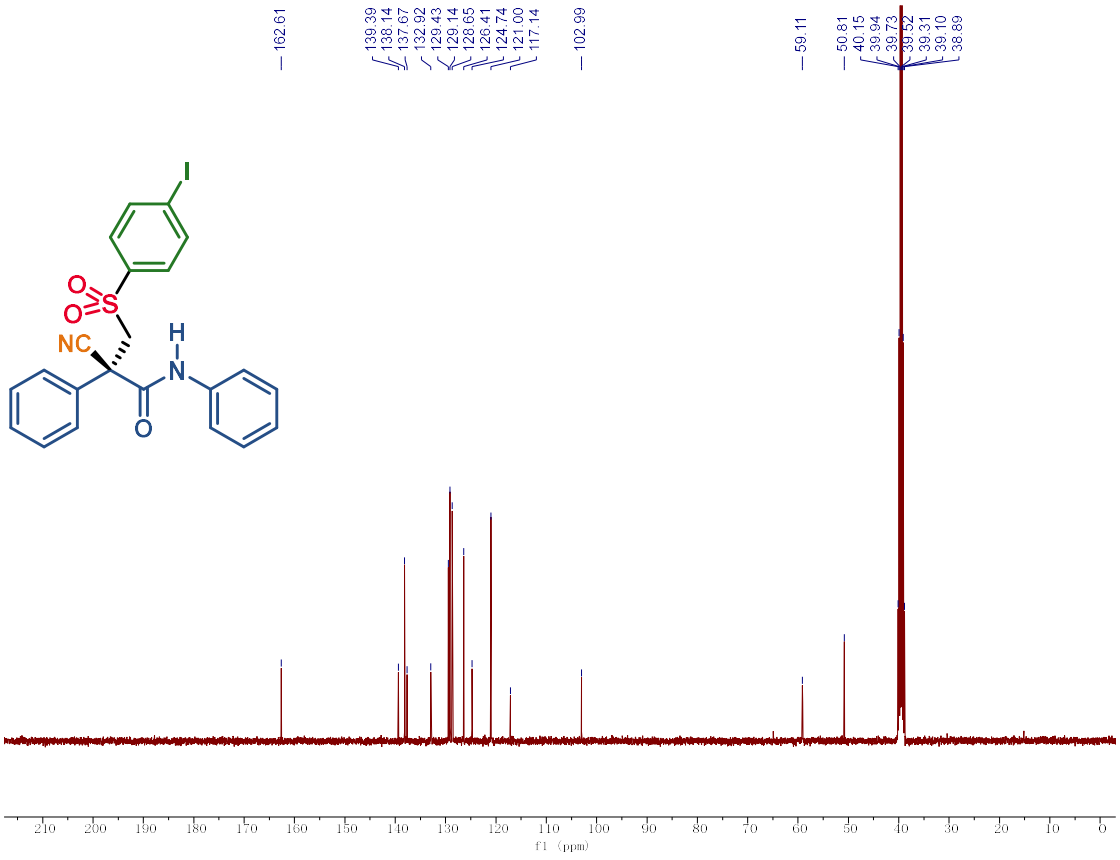
NMR of Compound of 3l



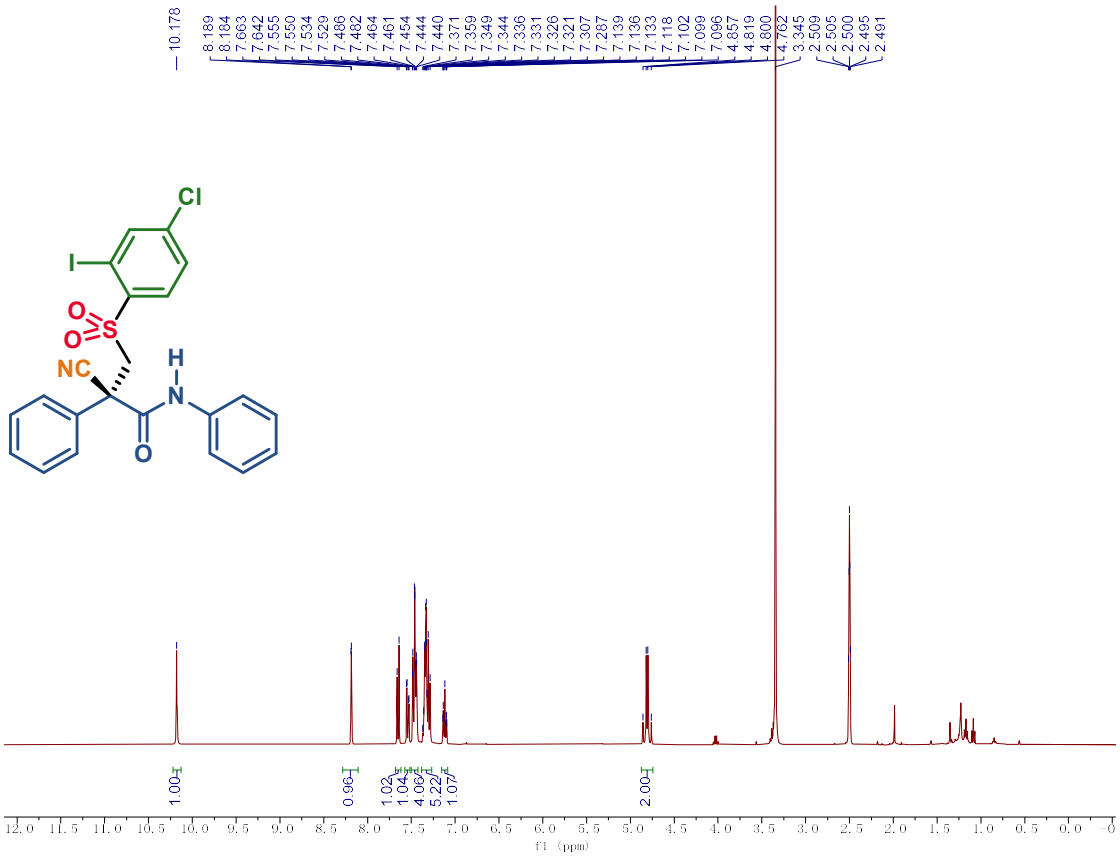


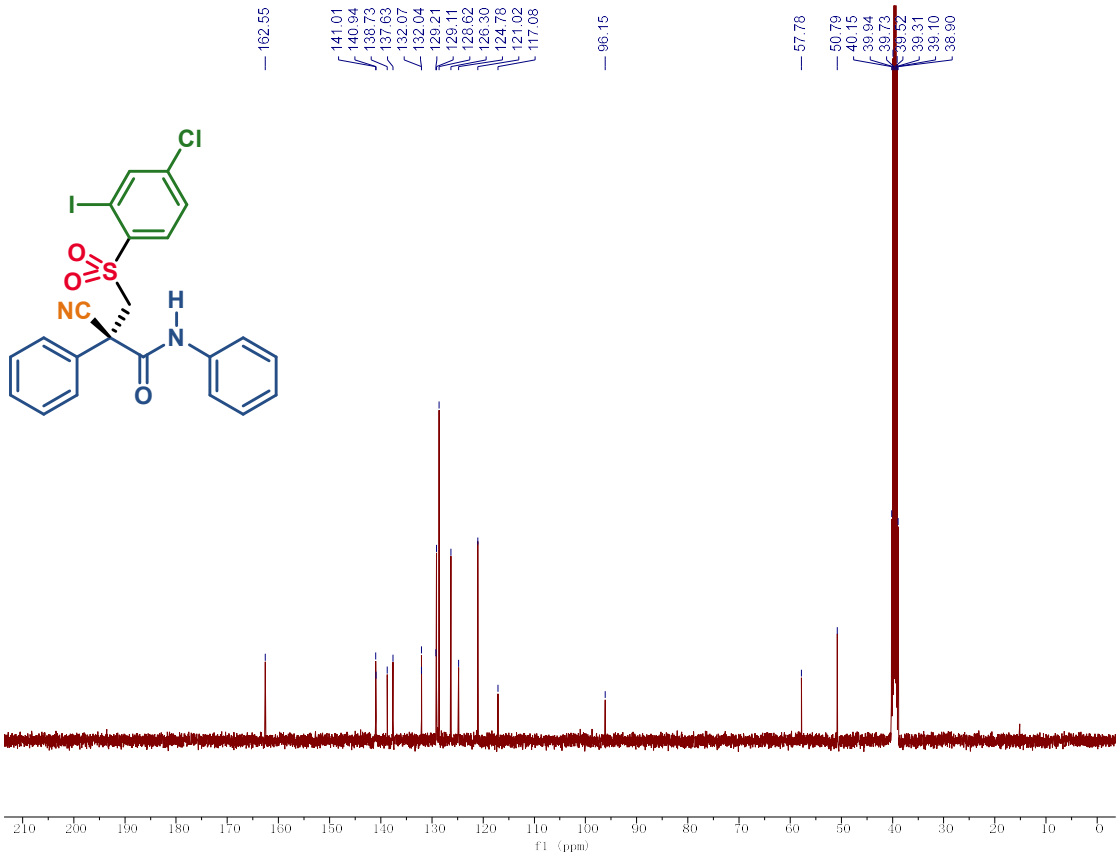
NMR of Compound of 3m



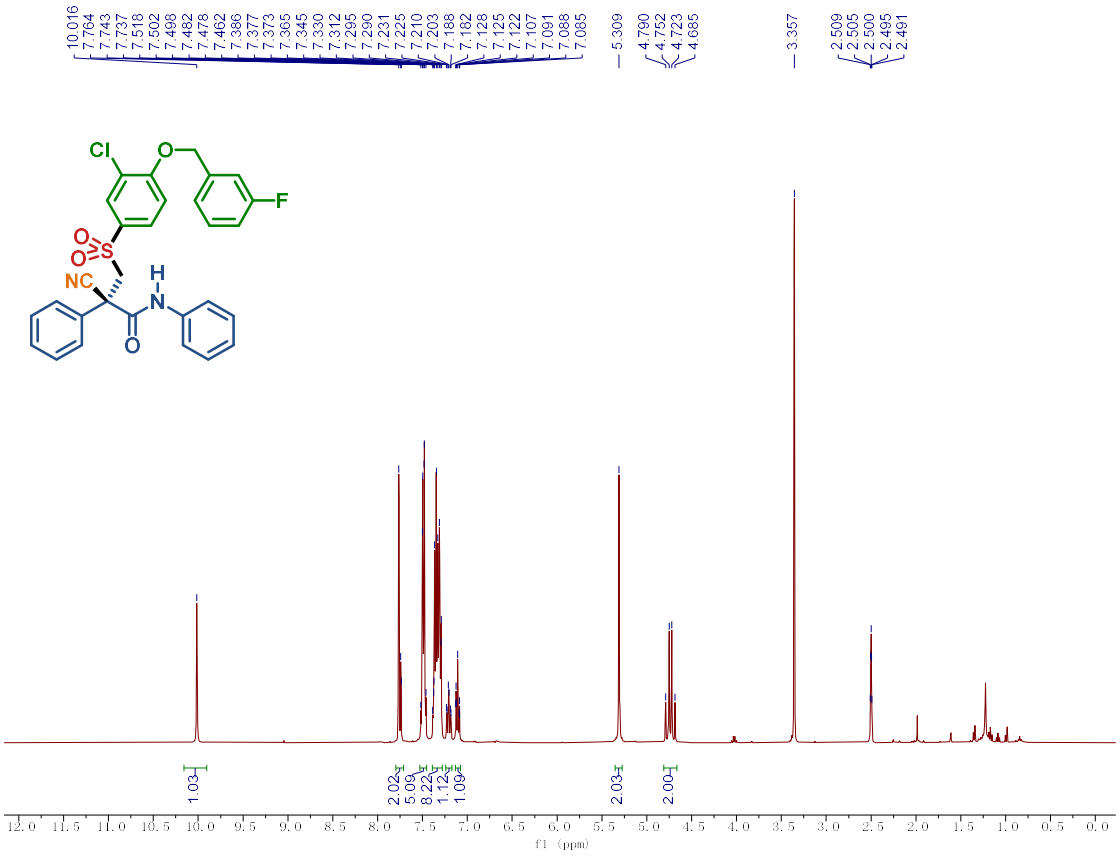


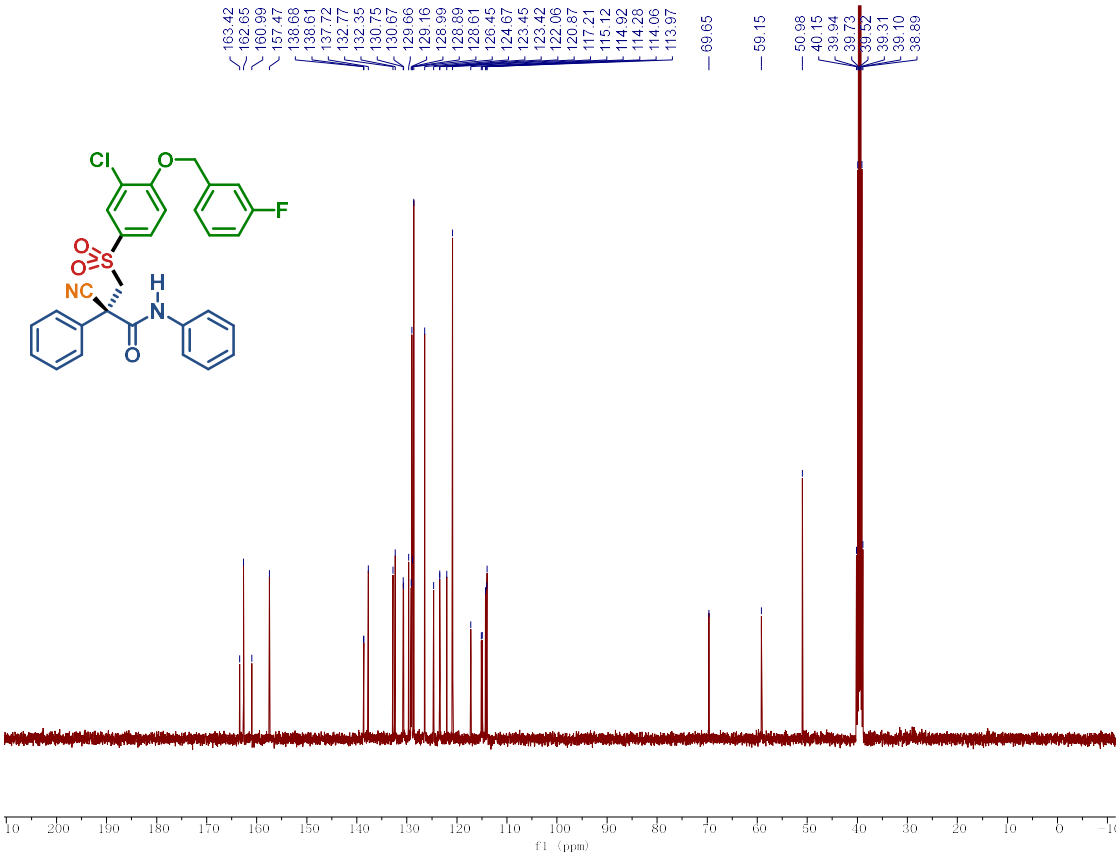
NMR of Compound of 3n

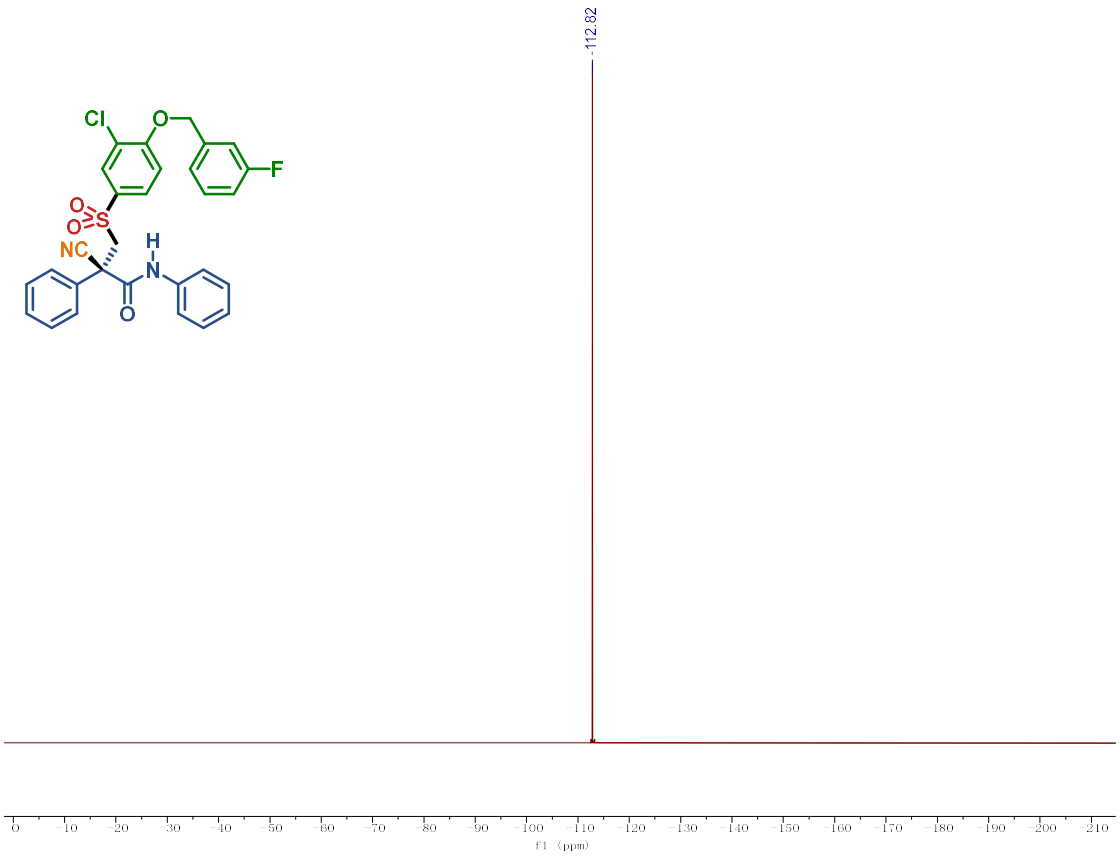




NMR of Compound of 3o

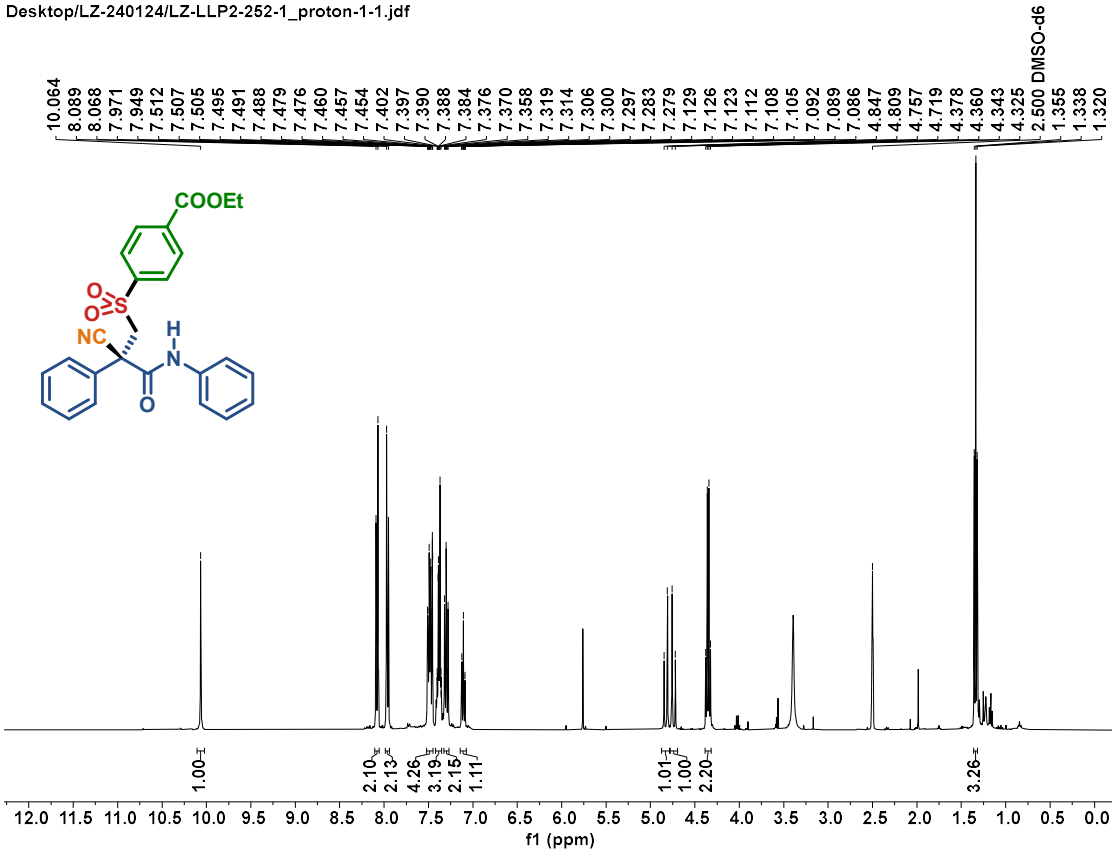




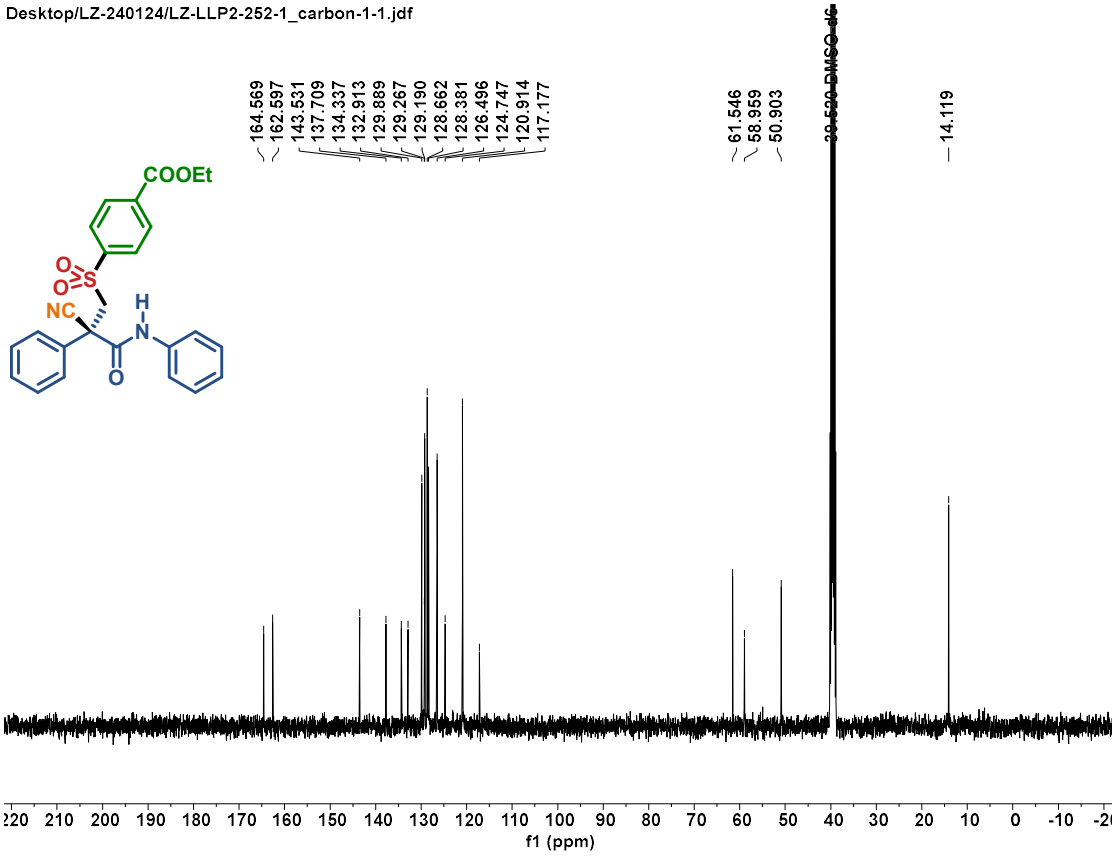

Cl
O
F
O
O
S
NC
H
N
O
-112.82
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

NMR of Compound of 3p

Desktop/LZ-240124/LZ-LLP2-252-1_proton-1-1.jdf

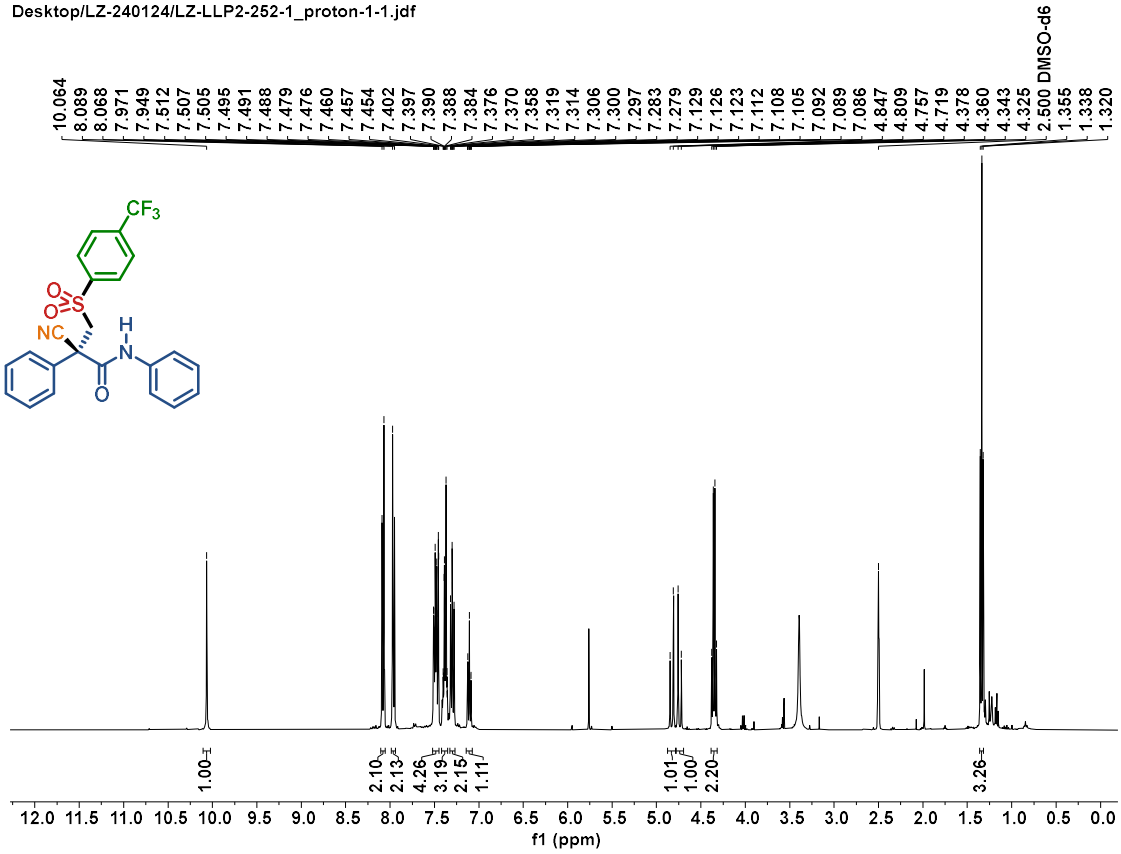


Desktop/LZ-240124/LZ-LLP2-252-1_carbon-1-1.jdf

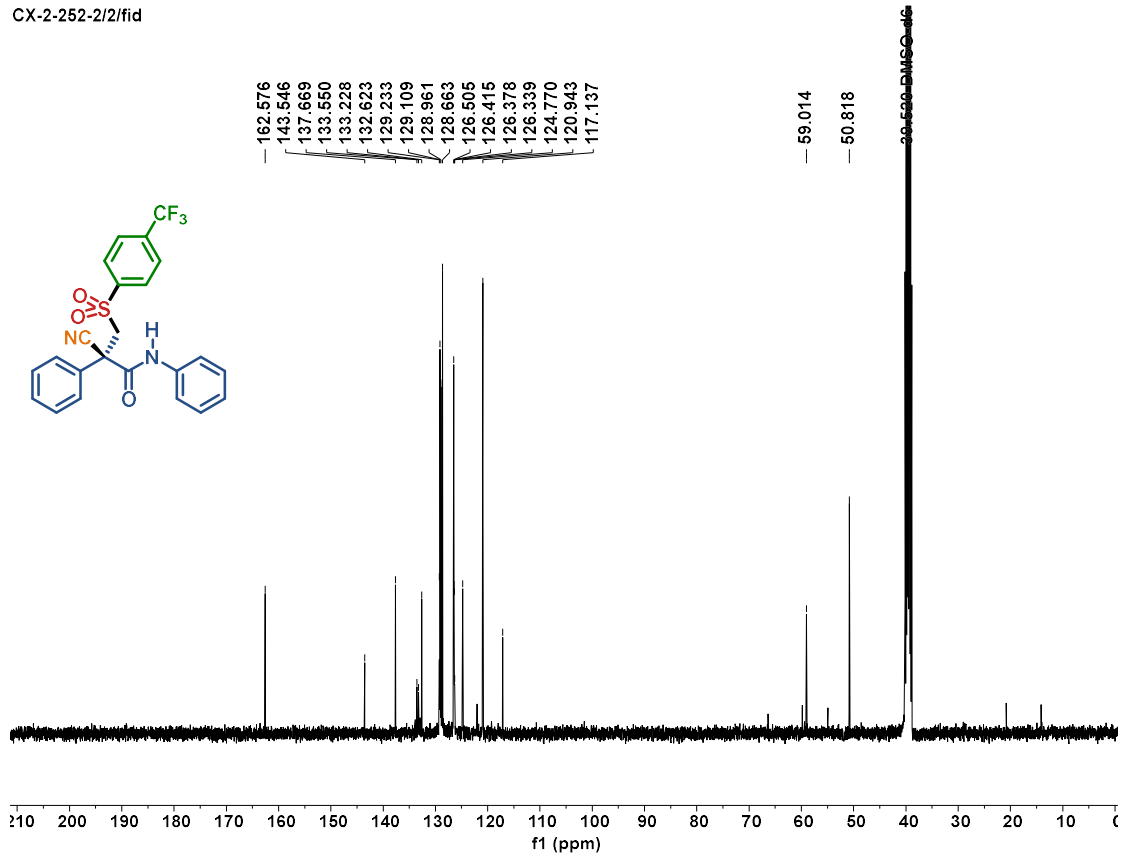


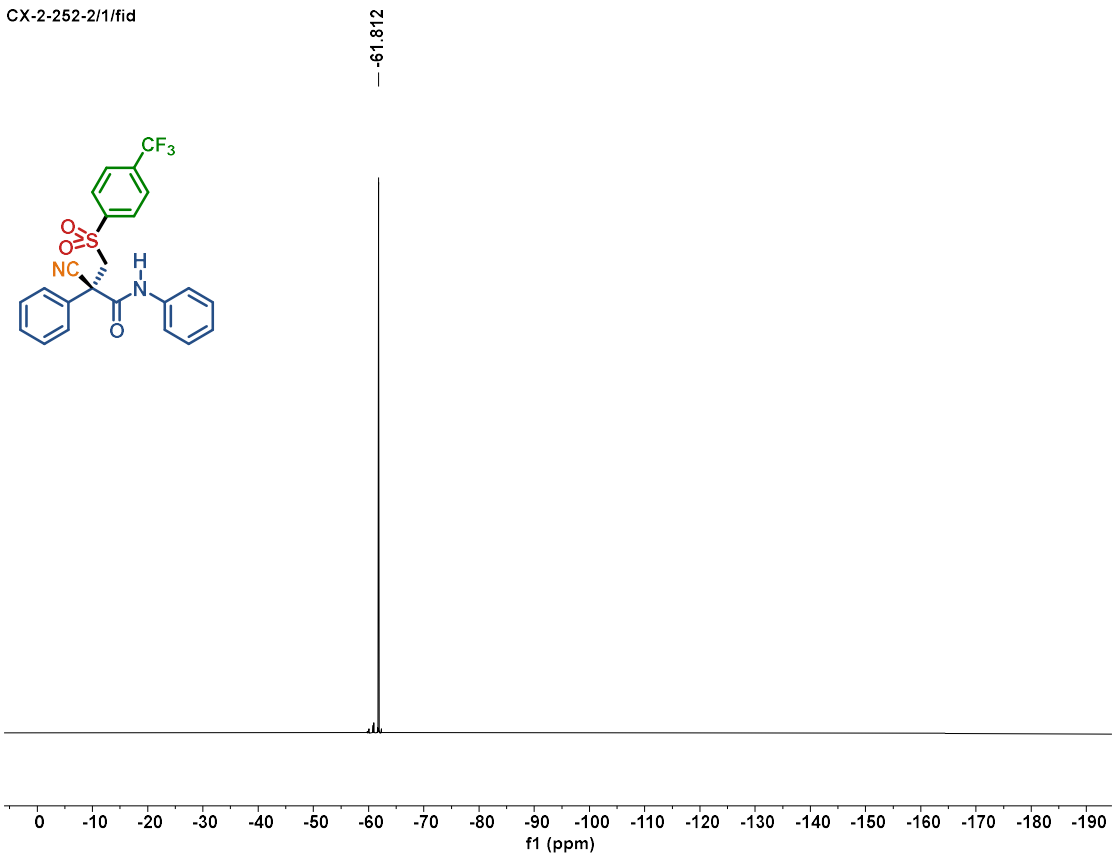
NMR of Compound of 3q

Desktop/LZ-240124/LZ-LLP2-252-1_proton-1-1.jdf

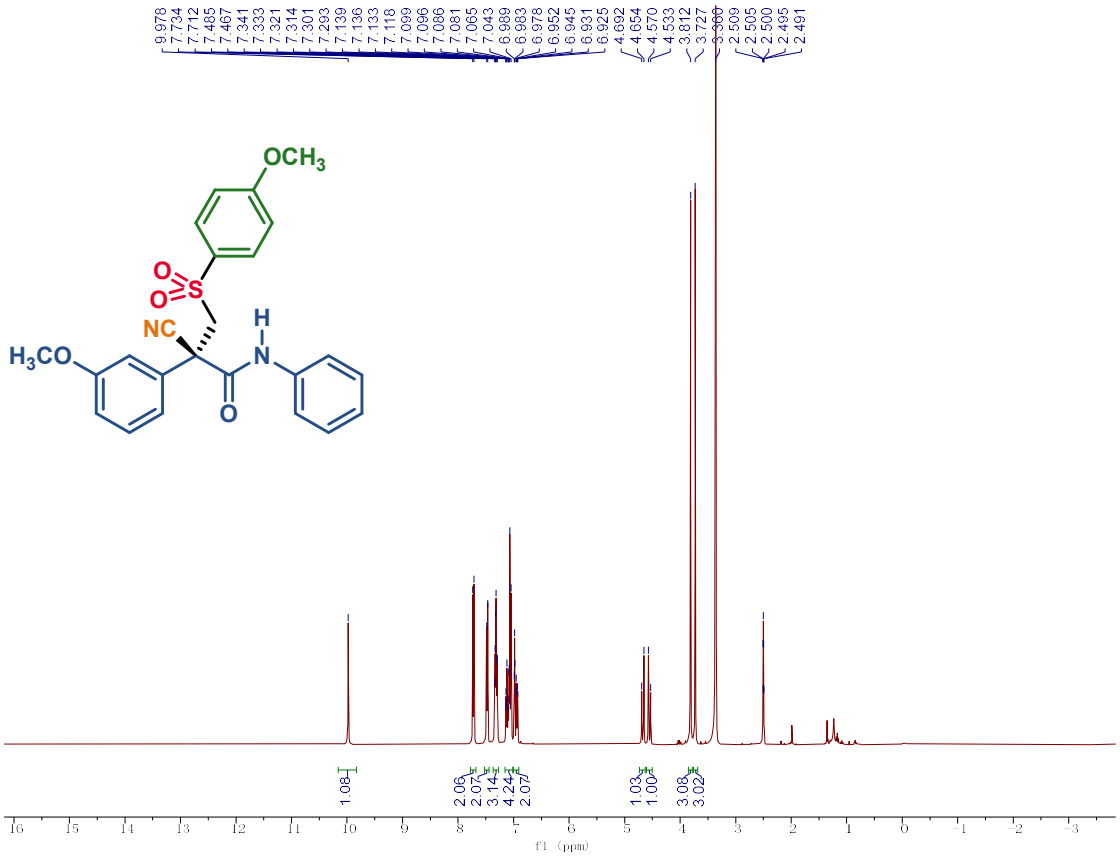


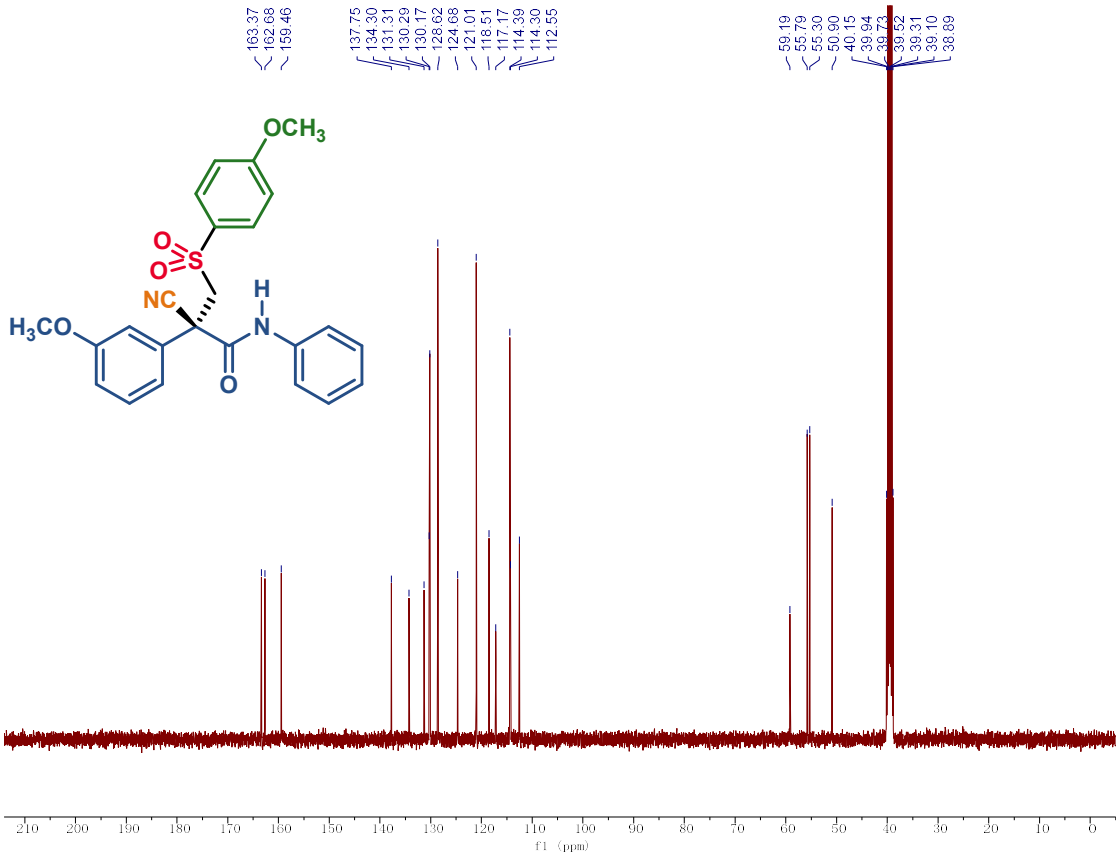
CX-2-252-2/2/fid



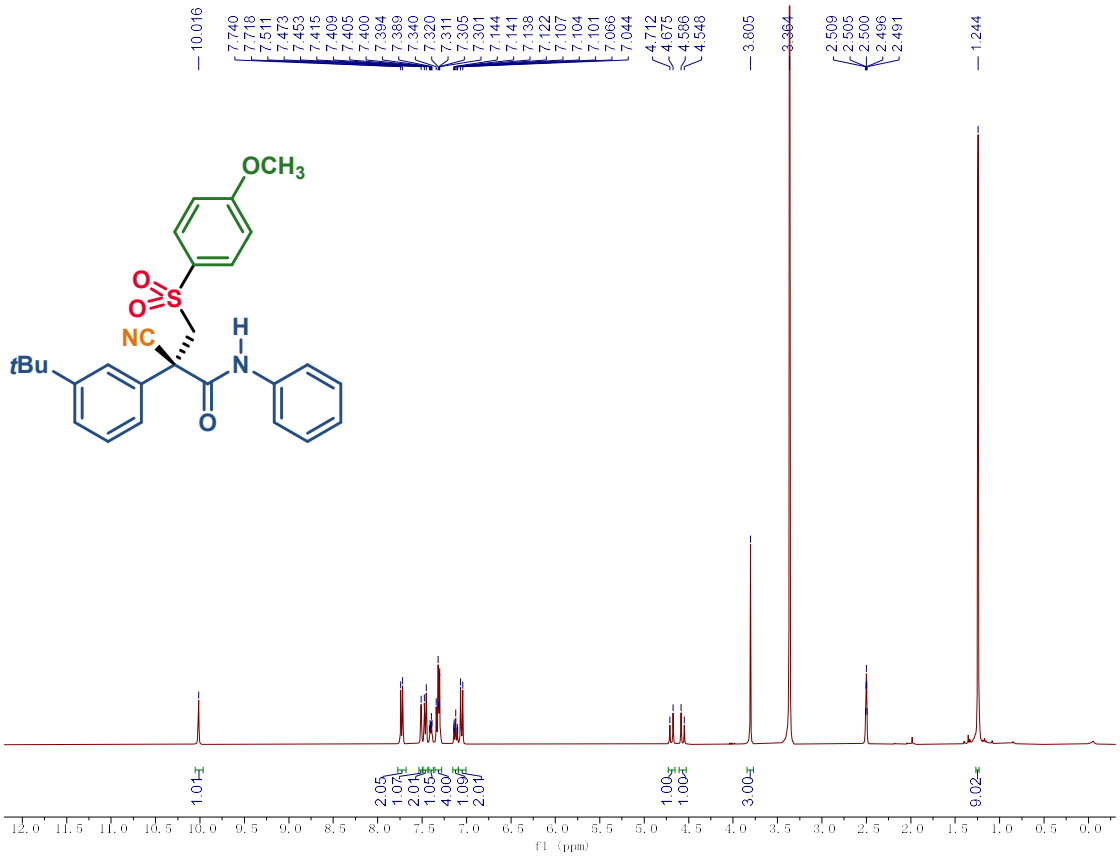

CX-2-252-2/1/fid
-61.812
CF3
O
O
S
NC
H
N
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

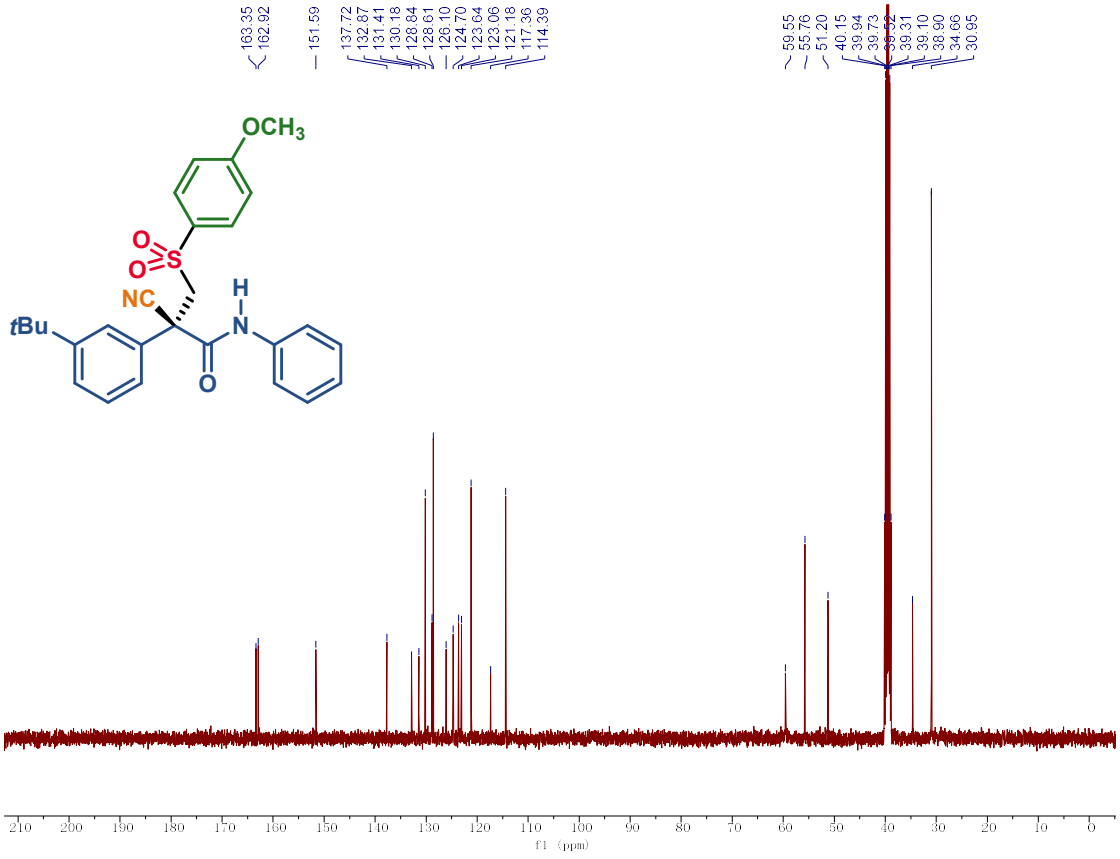
NMR of Compound of 3r



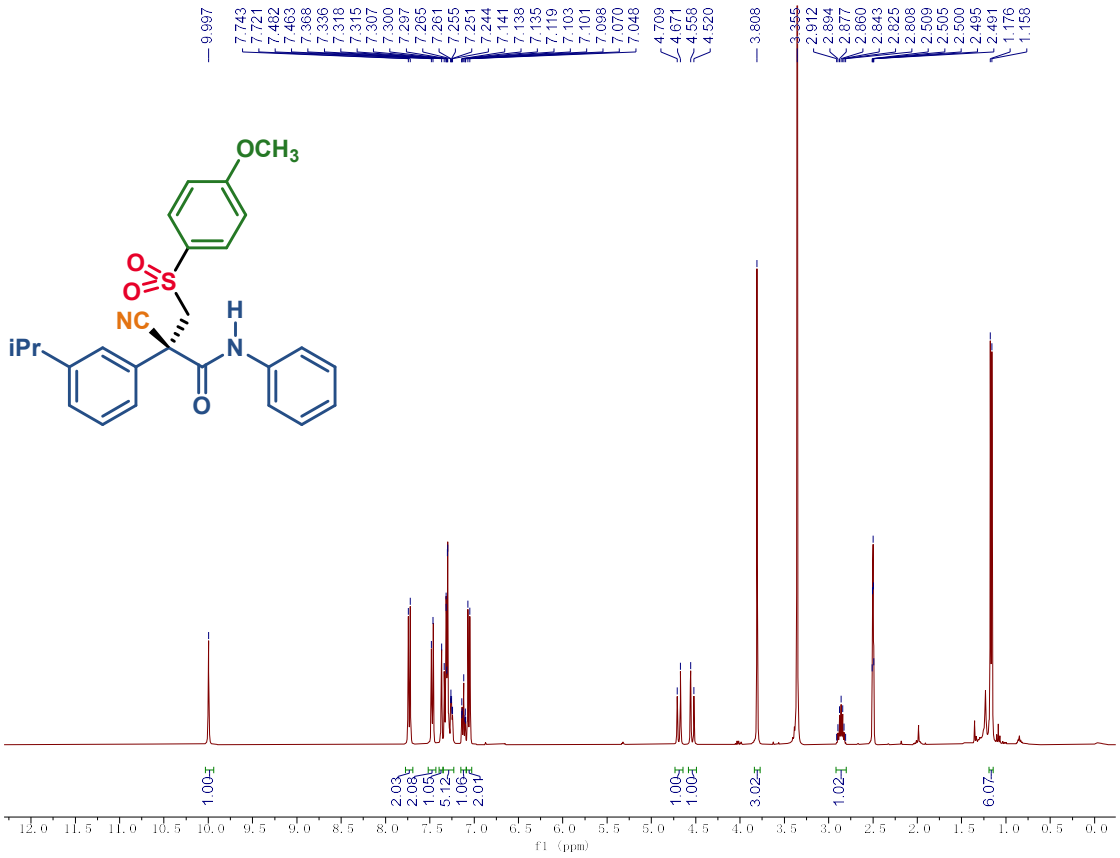


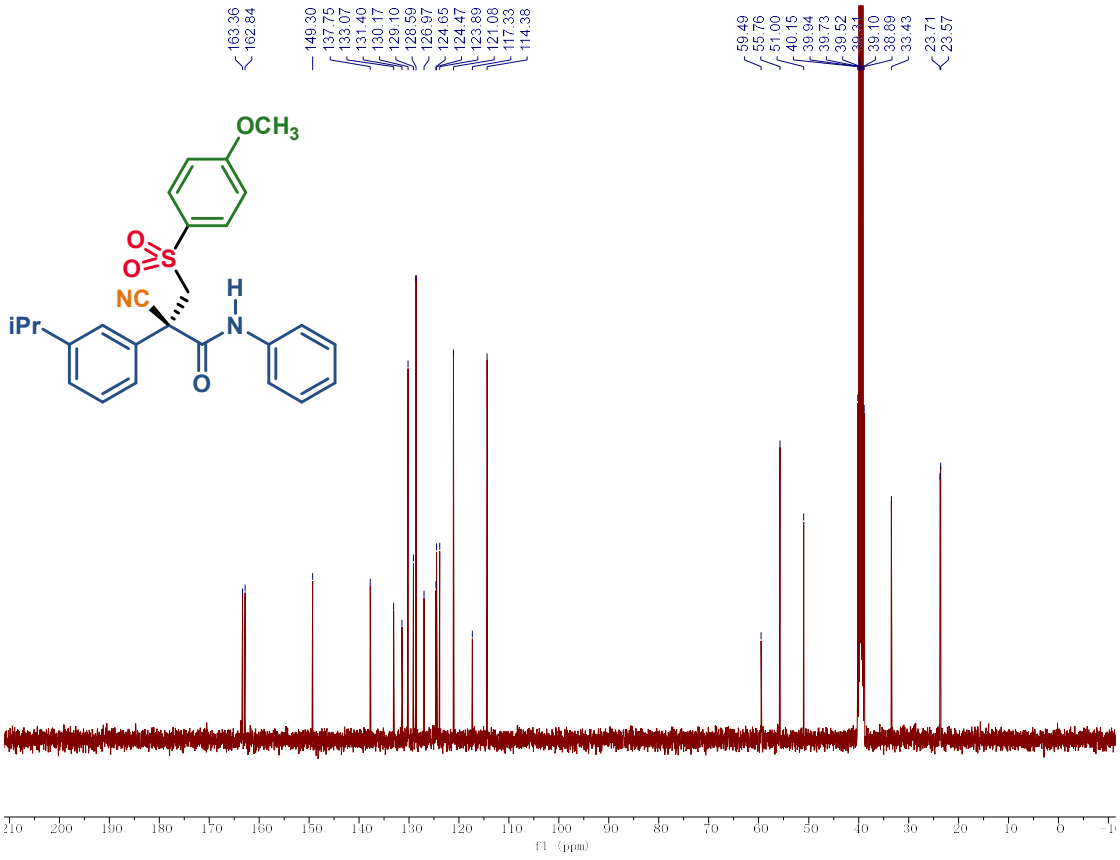
NMR of Compound of 3s



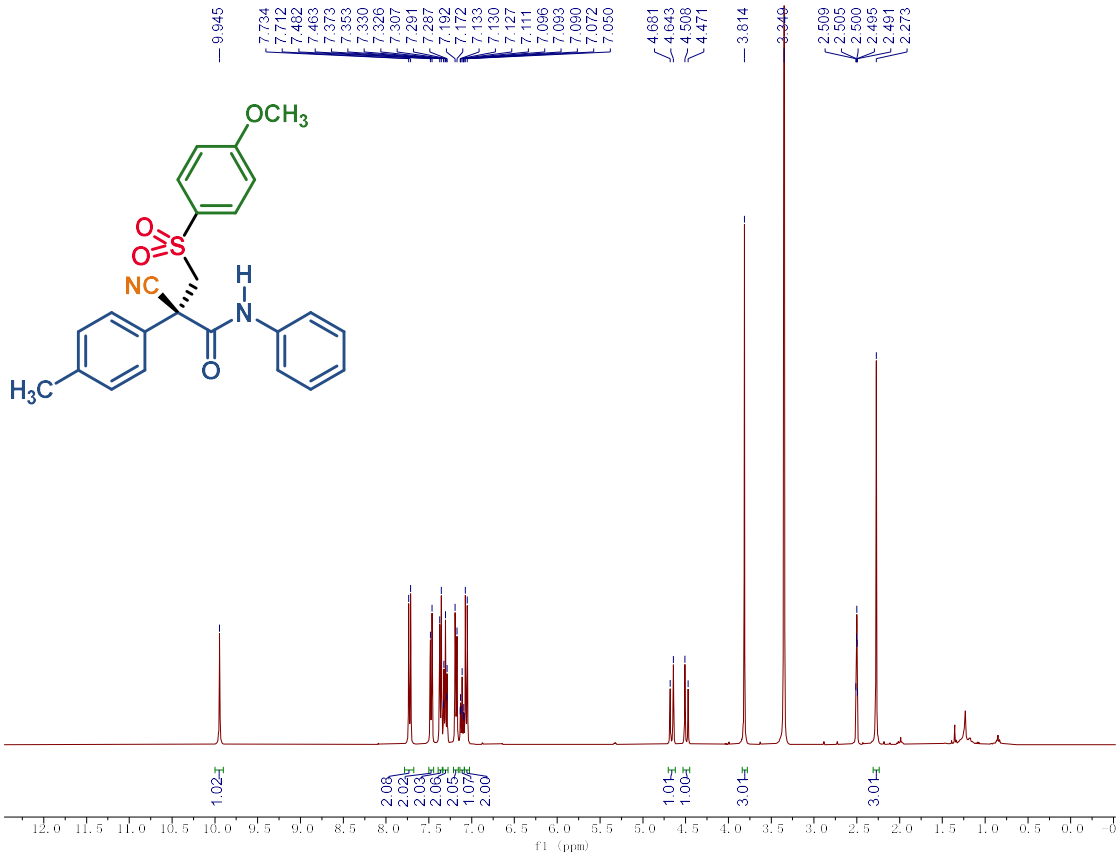


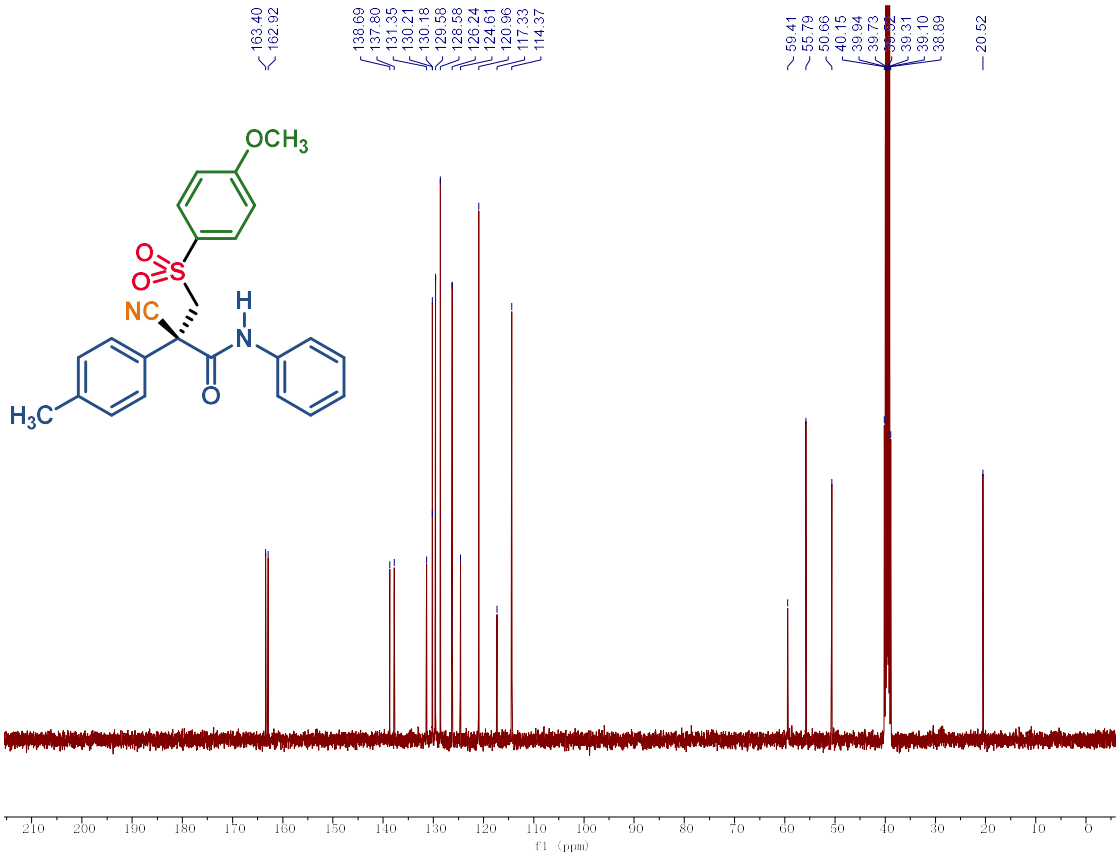
NMR of Compound of 3t



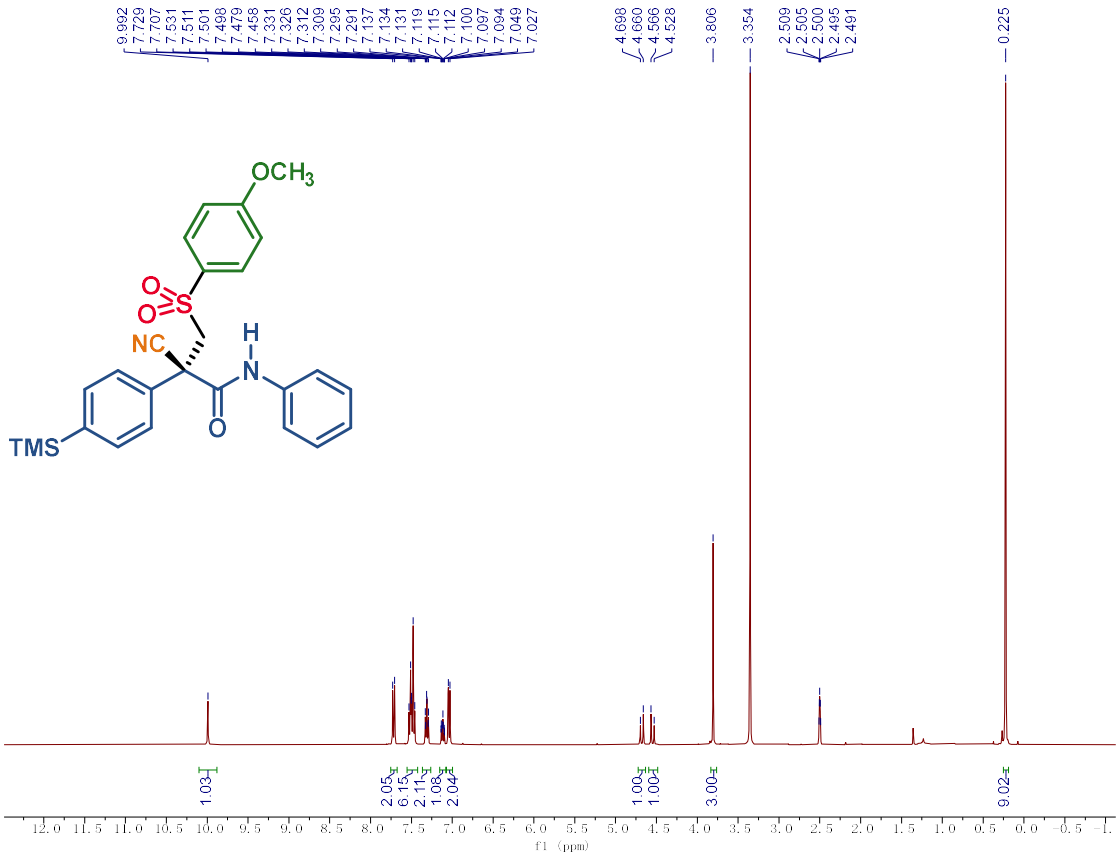


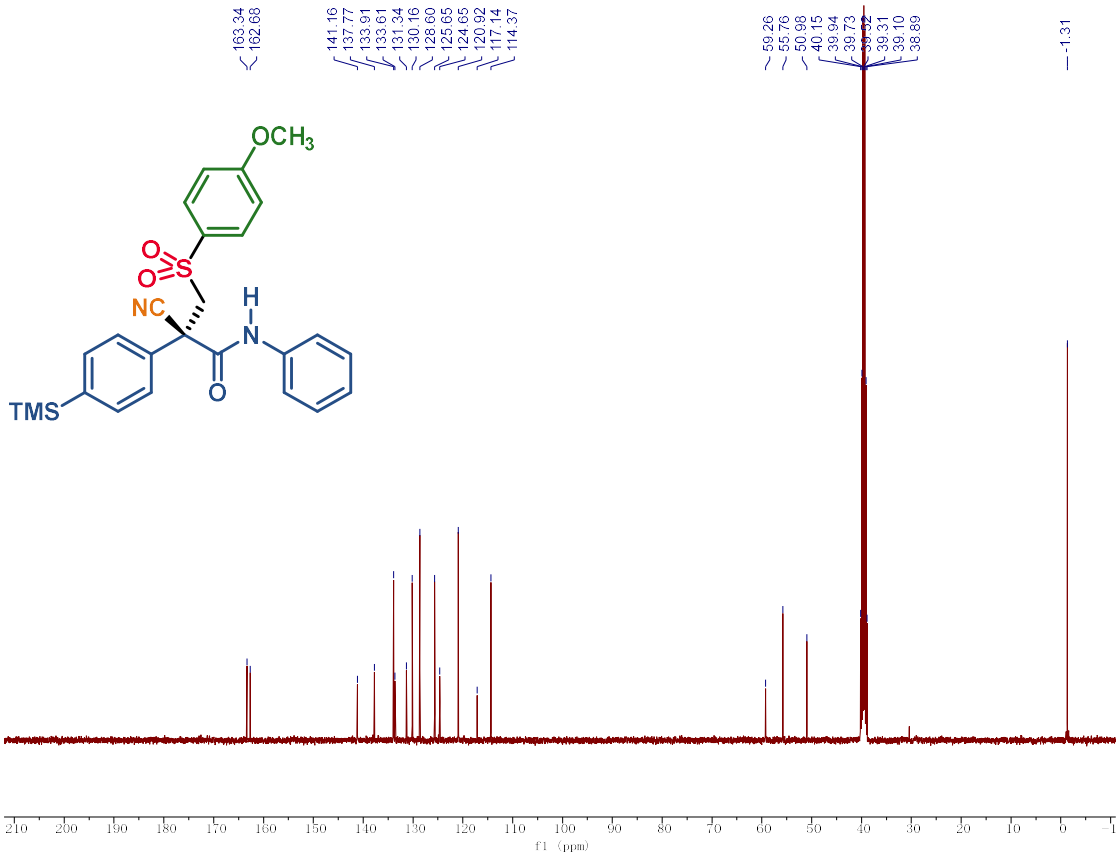
NMR of Compound of 3u



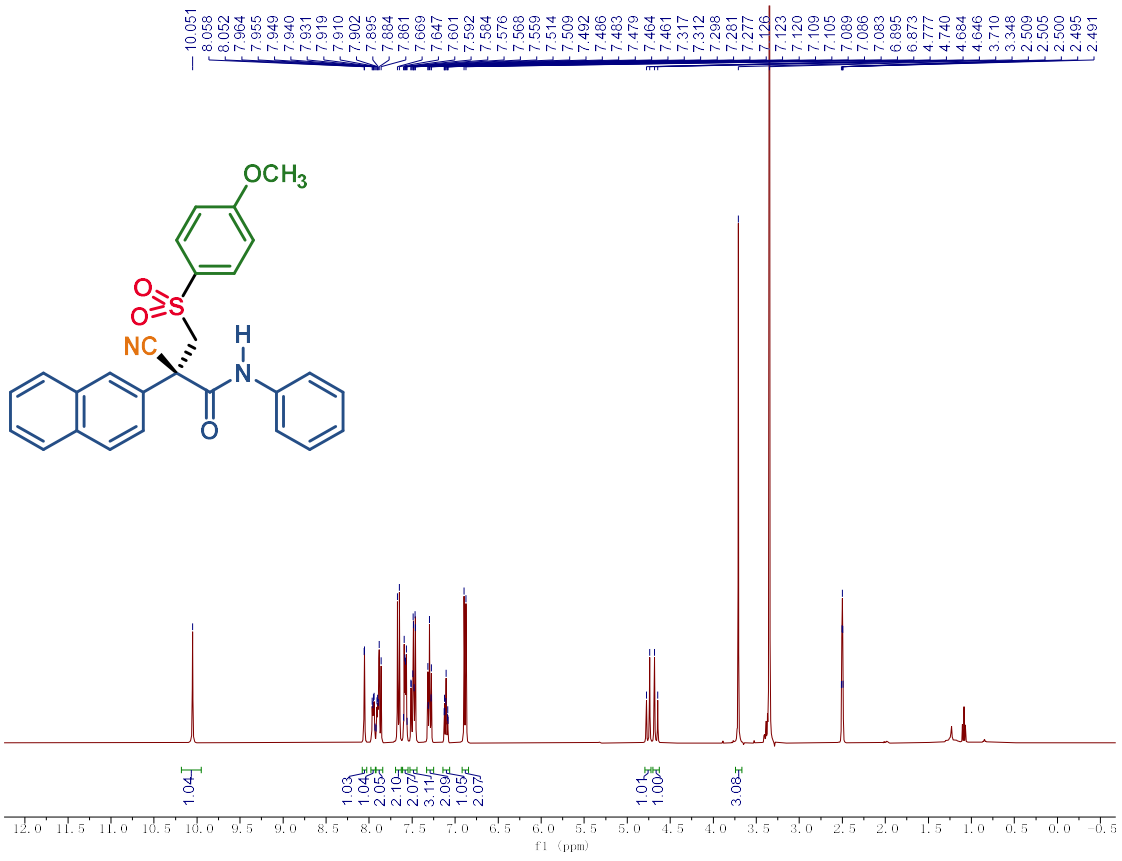


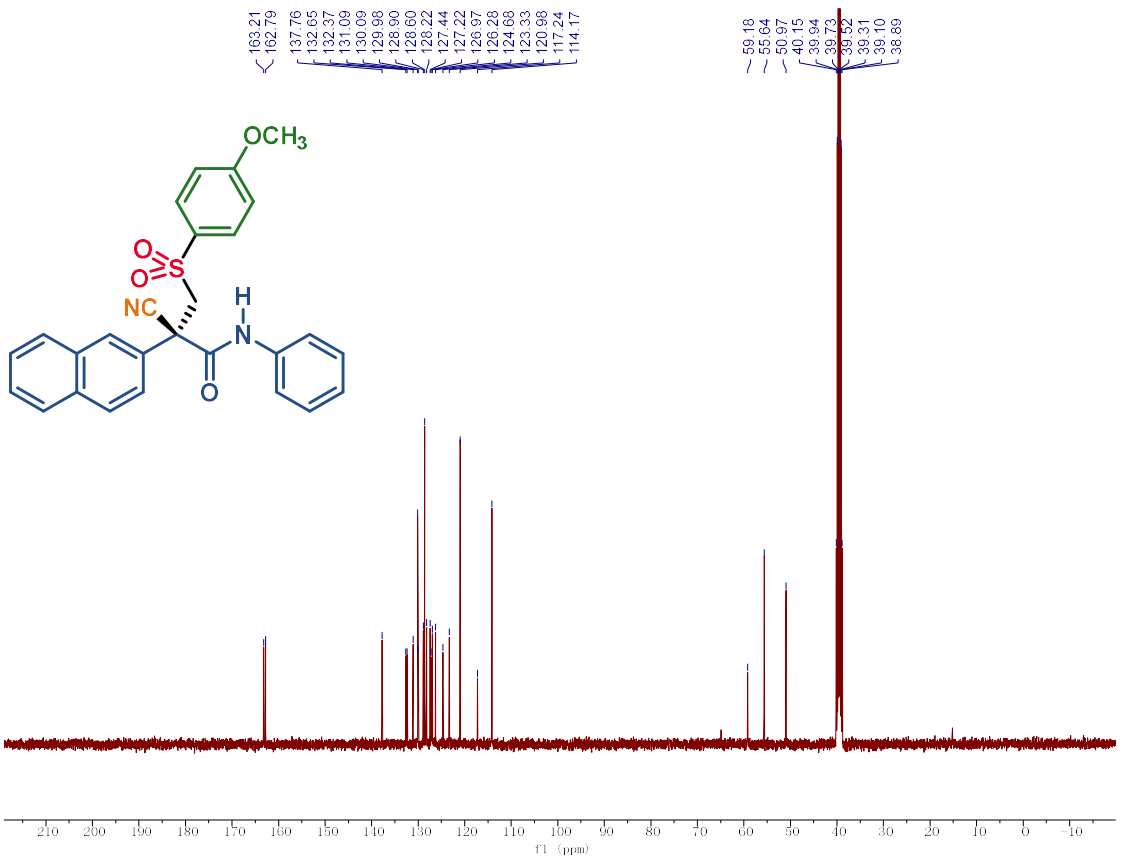
NMR of Compound of 3v



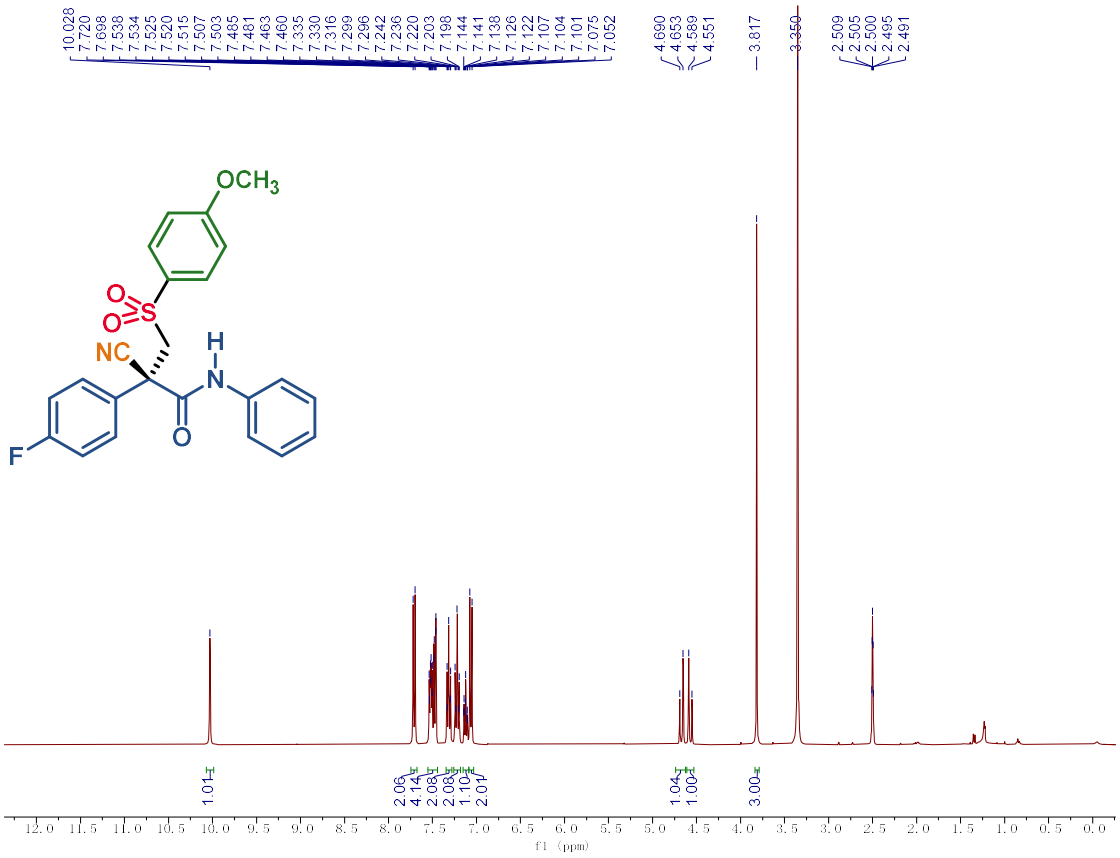


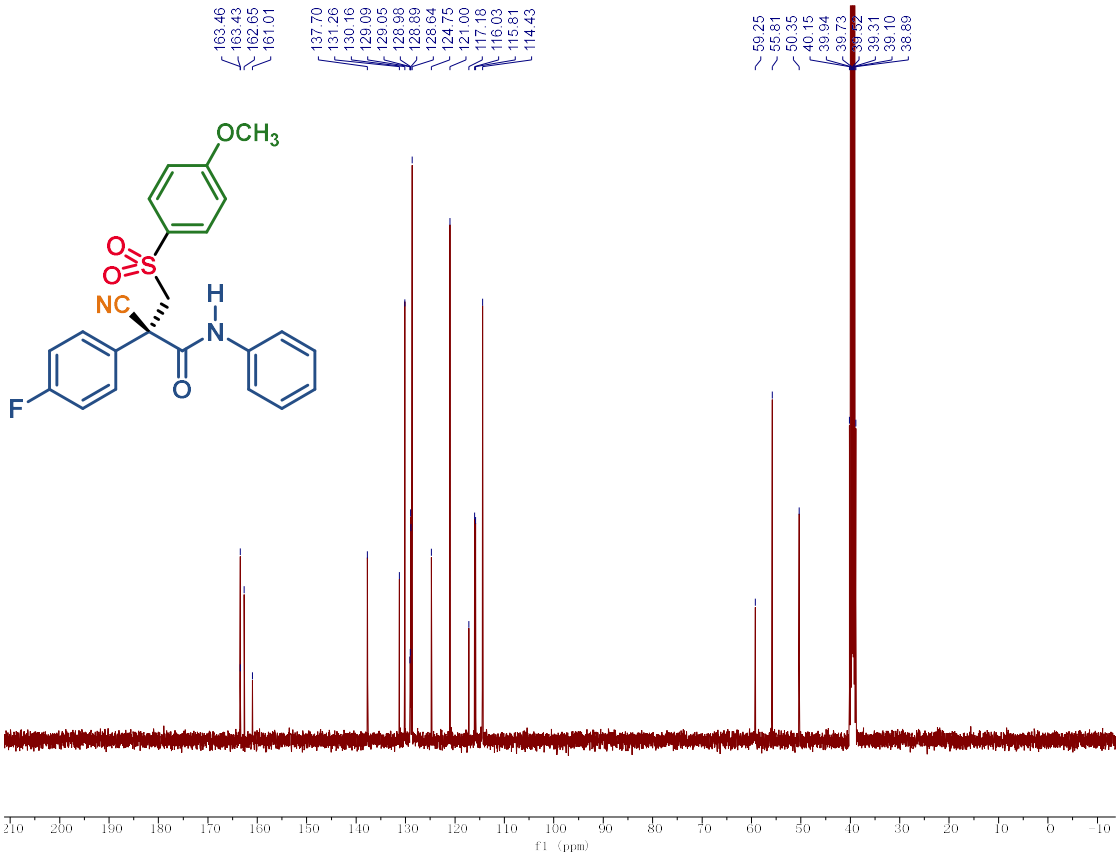
NMR of Compound of 3w

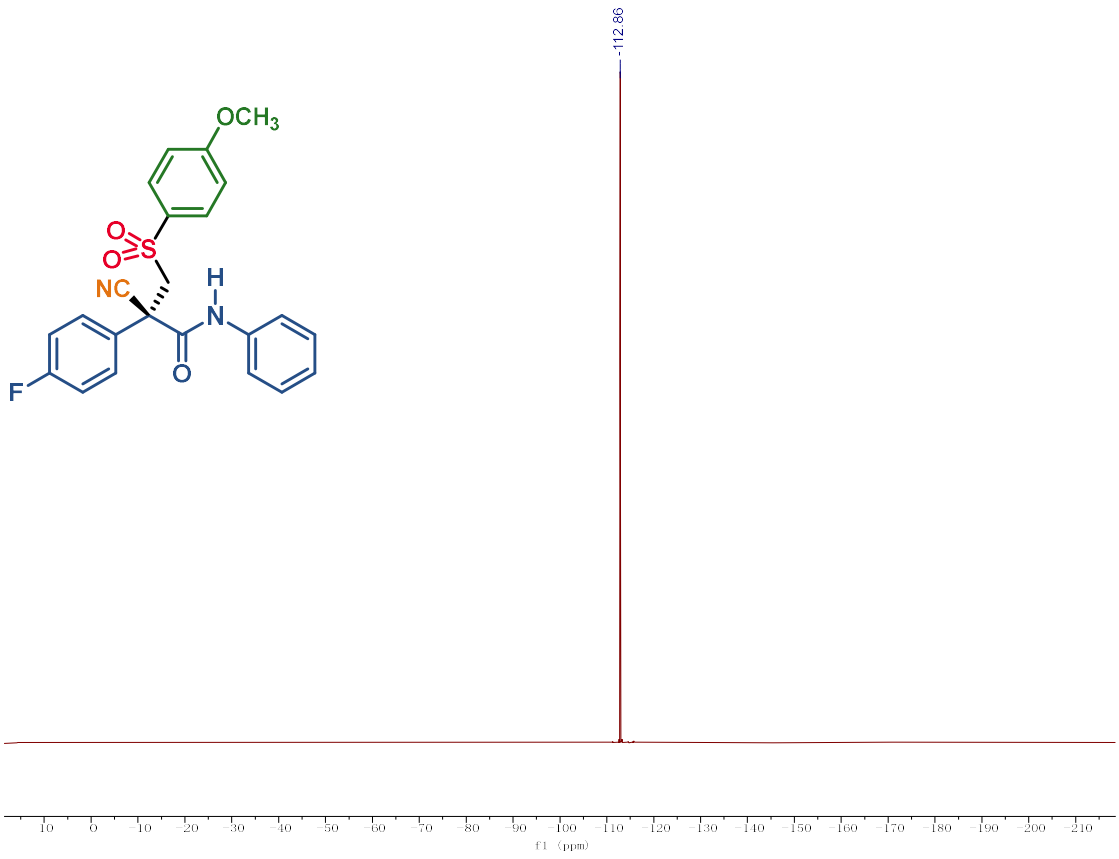




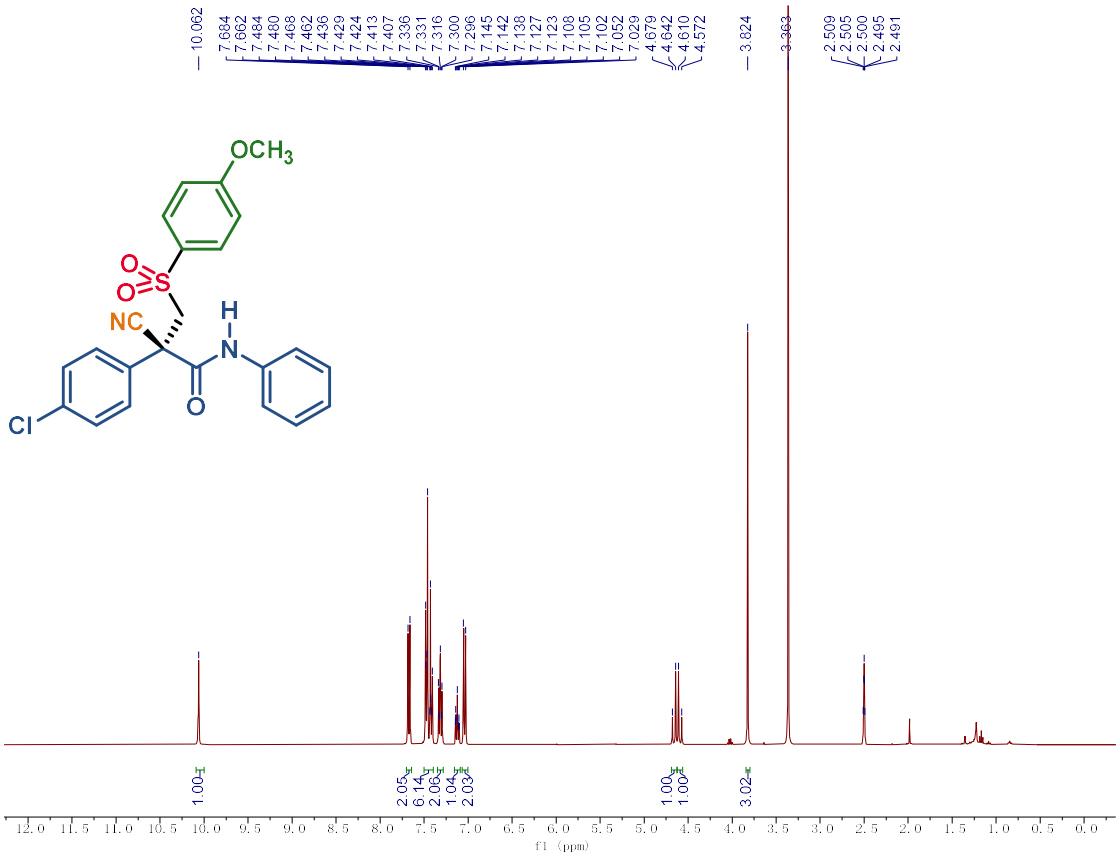
NMR of Compound of 3x

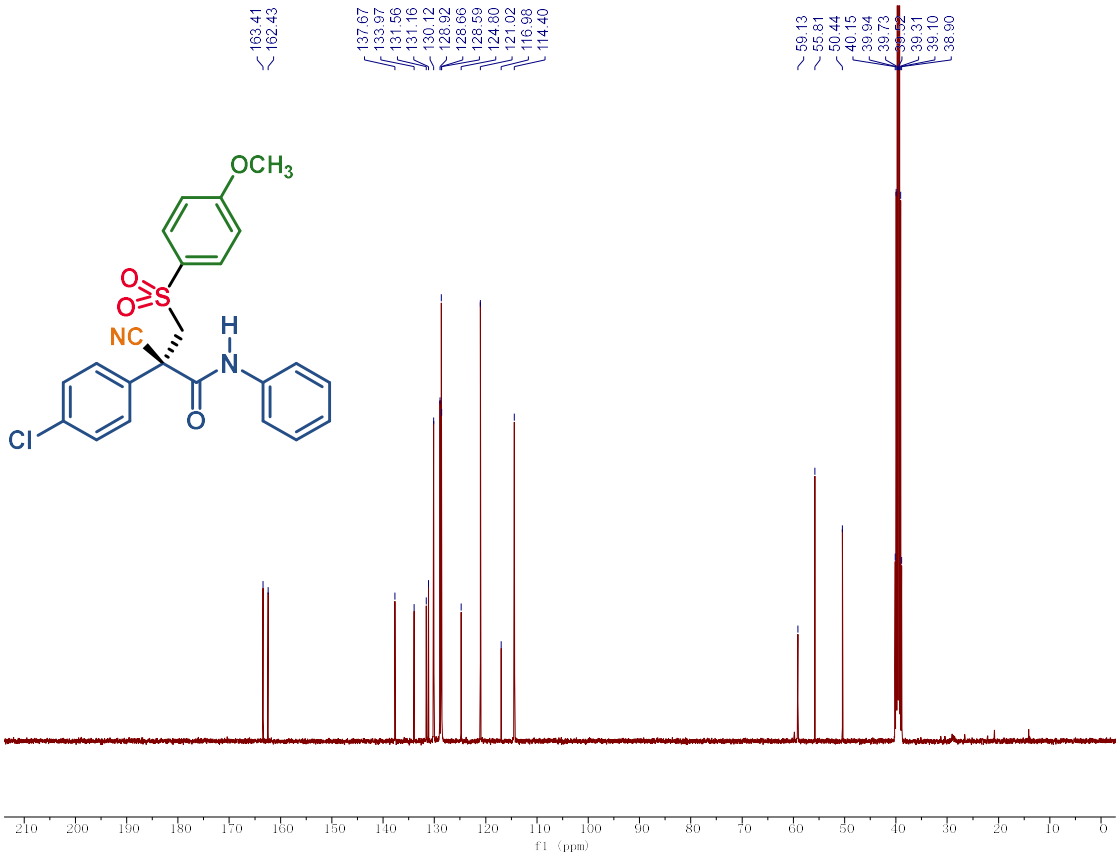




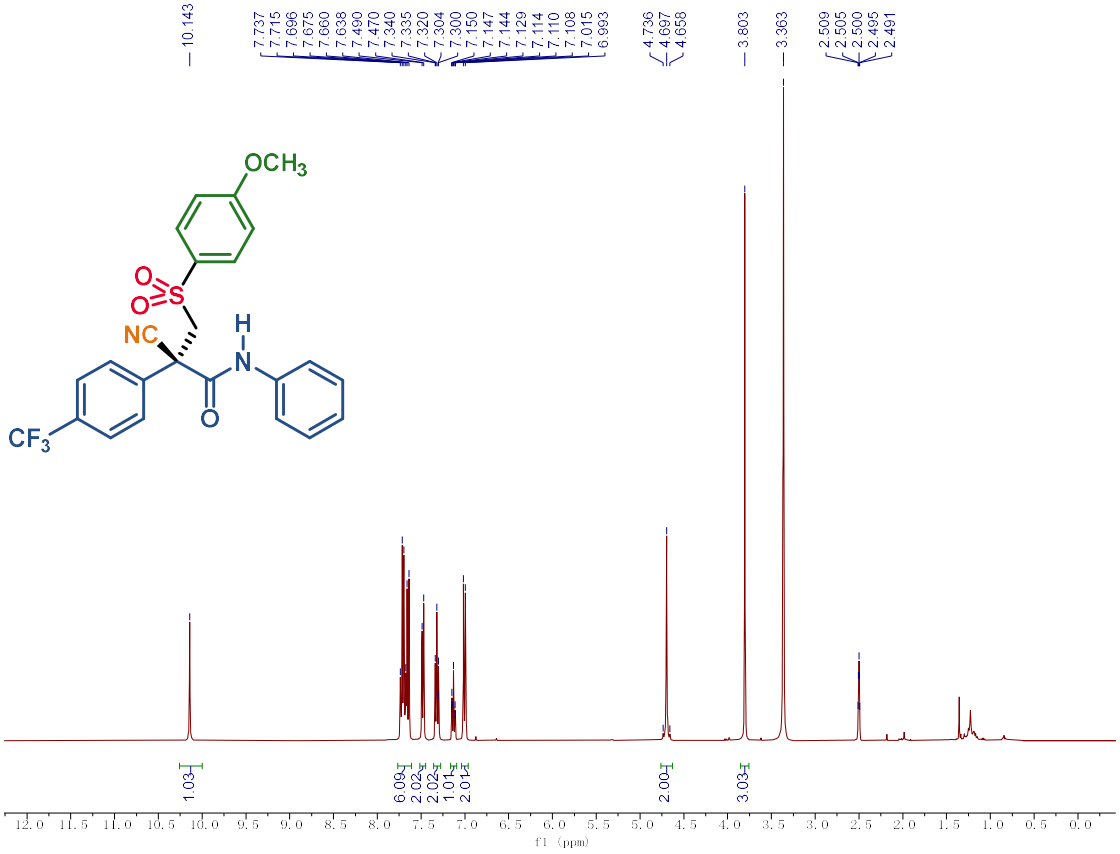

112.86
OCH3
O
S
O
NC
H
N
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

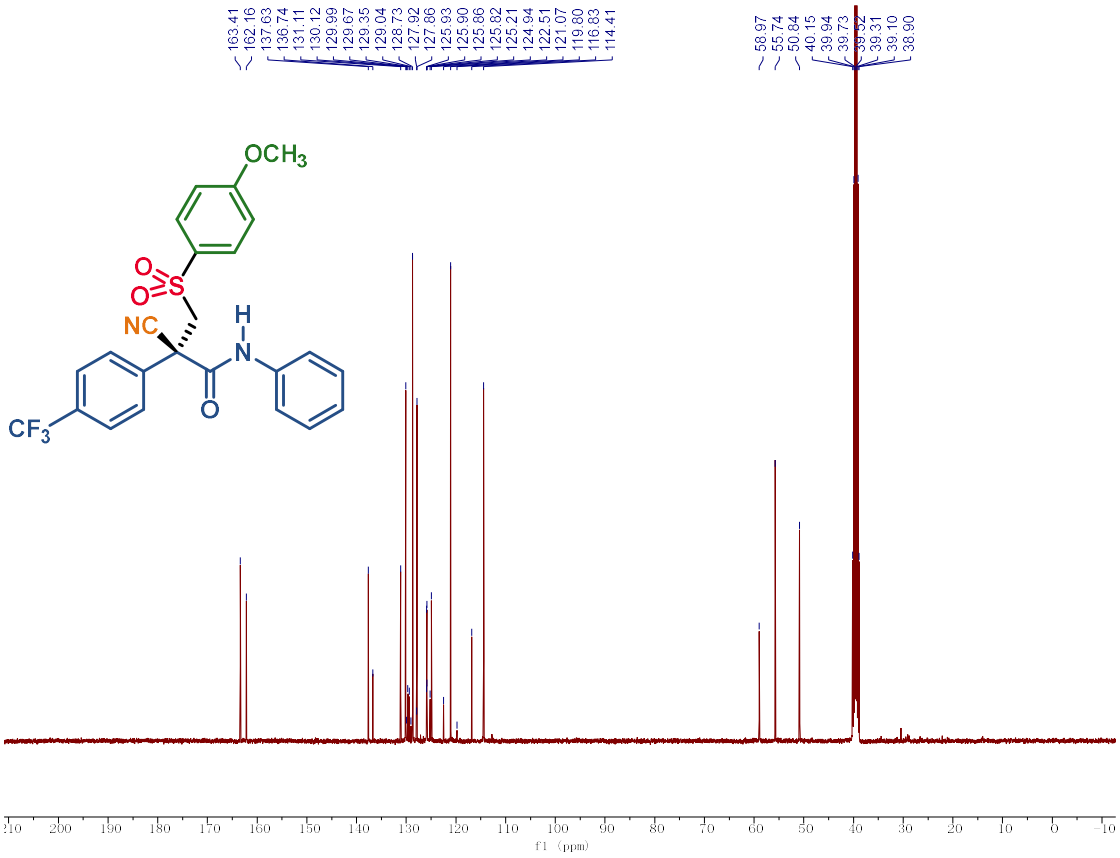
NMR of Compound of 3y

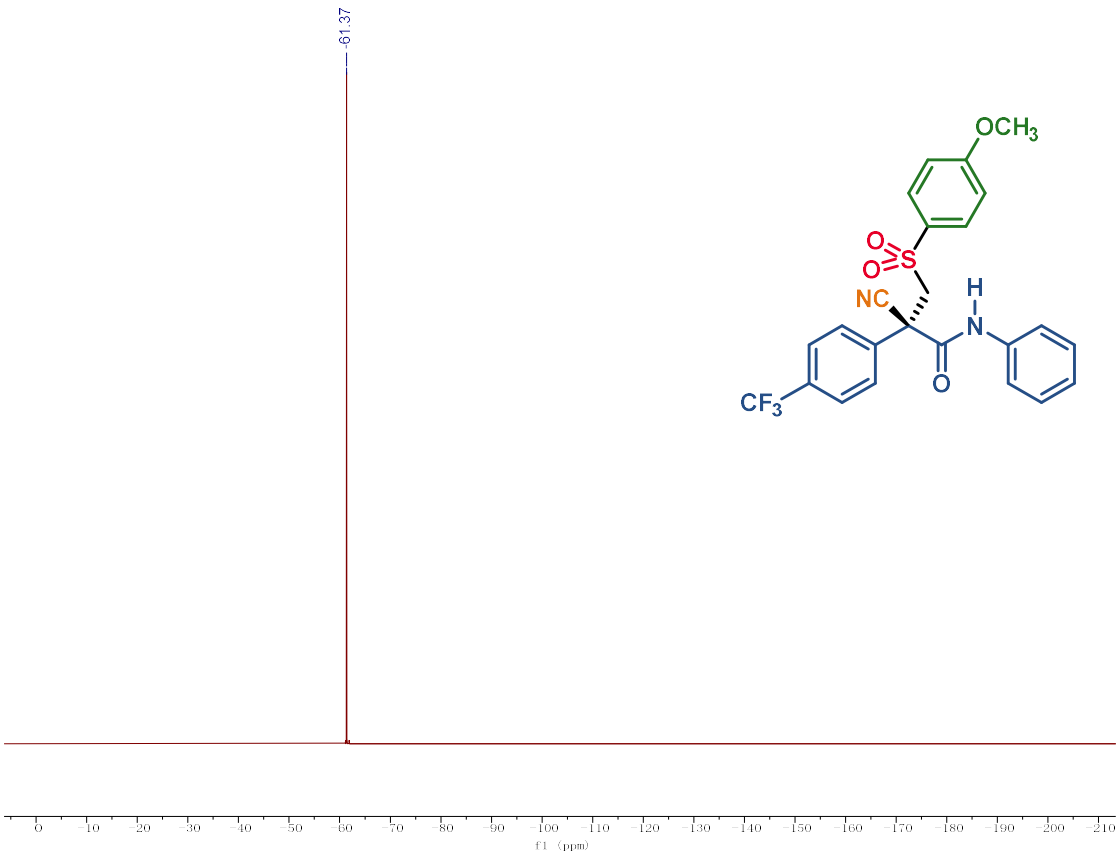




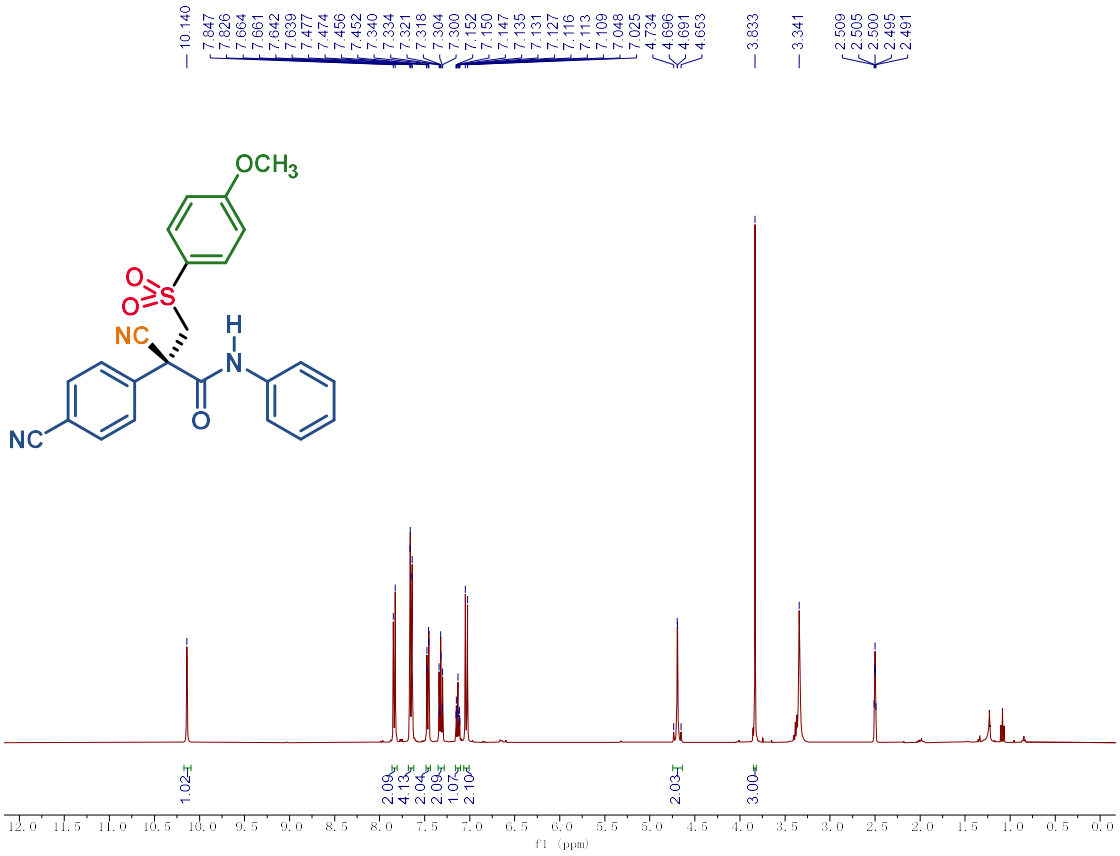
NMR of Compound of 3z

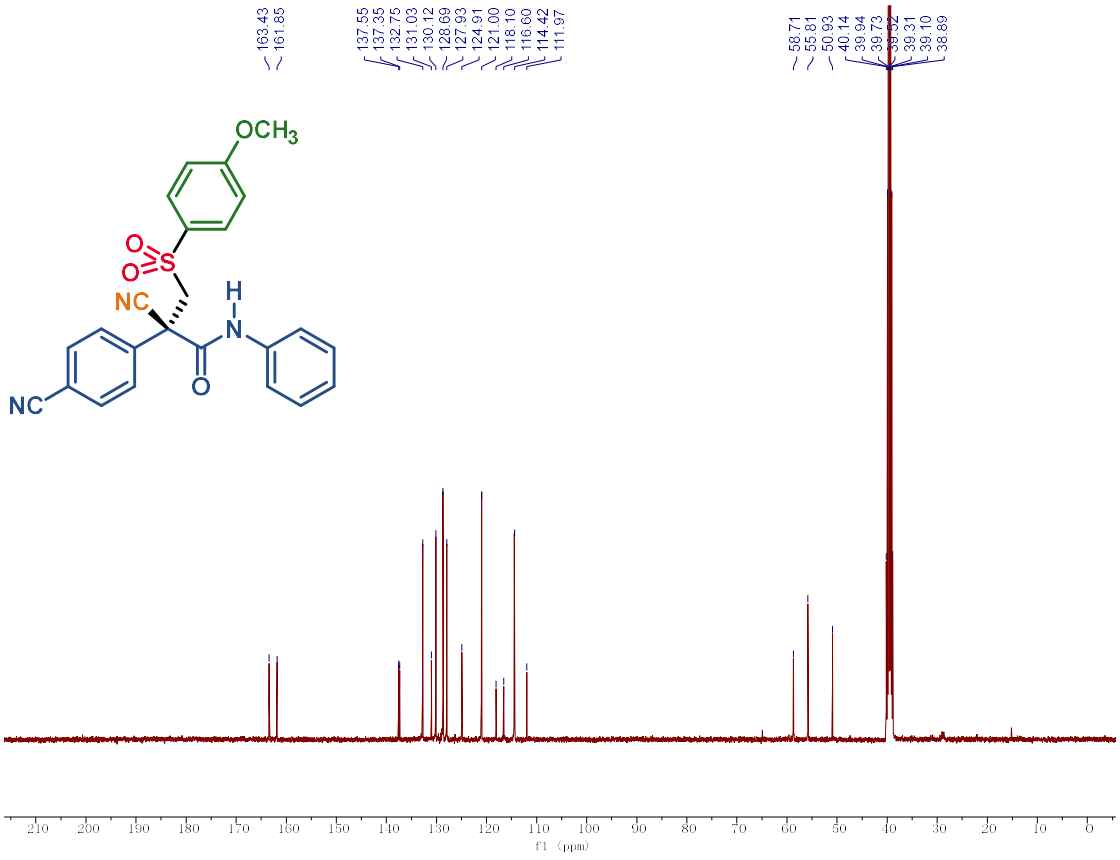




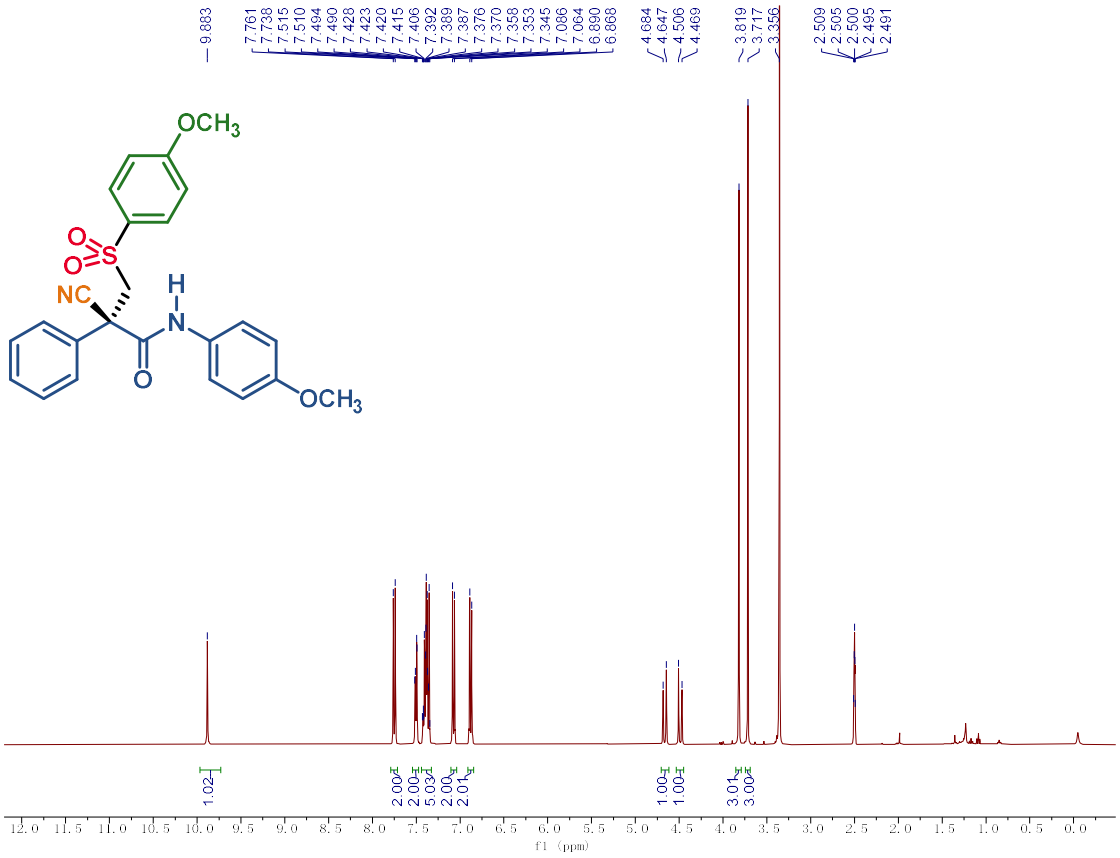

-61.37
OCH3
O
S
O
NC
H
N
O
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

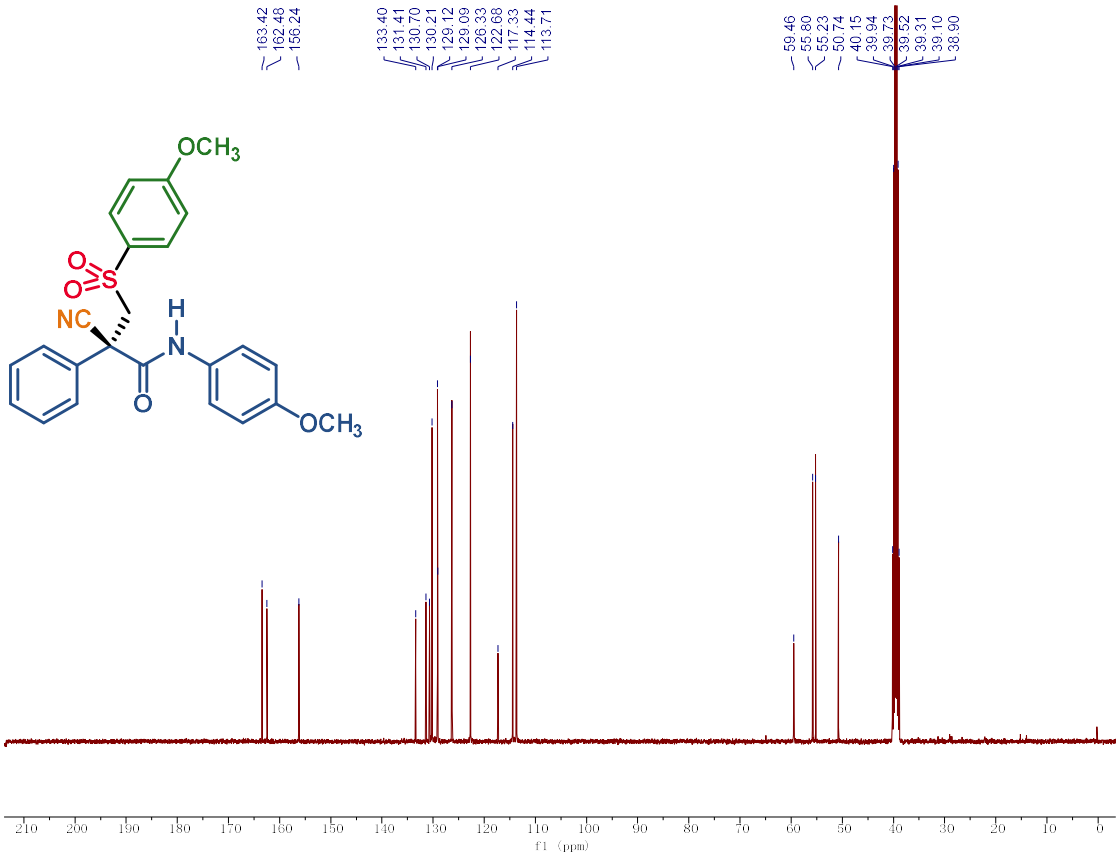
NMR of Compound of 3aa



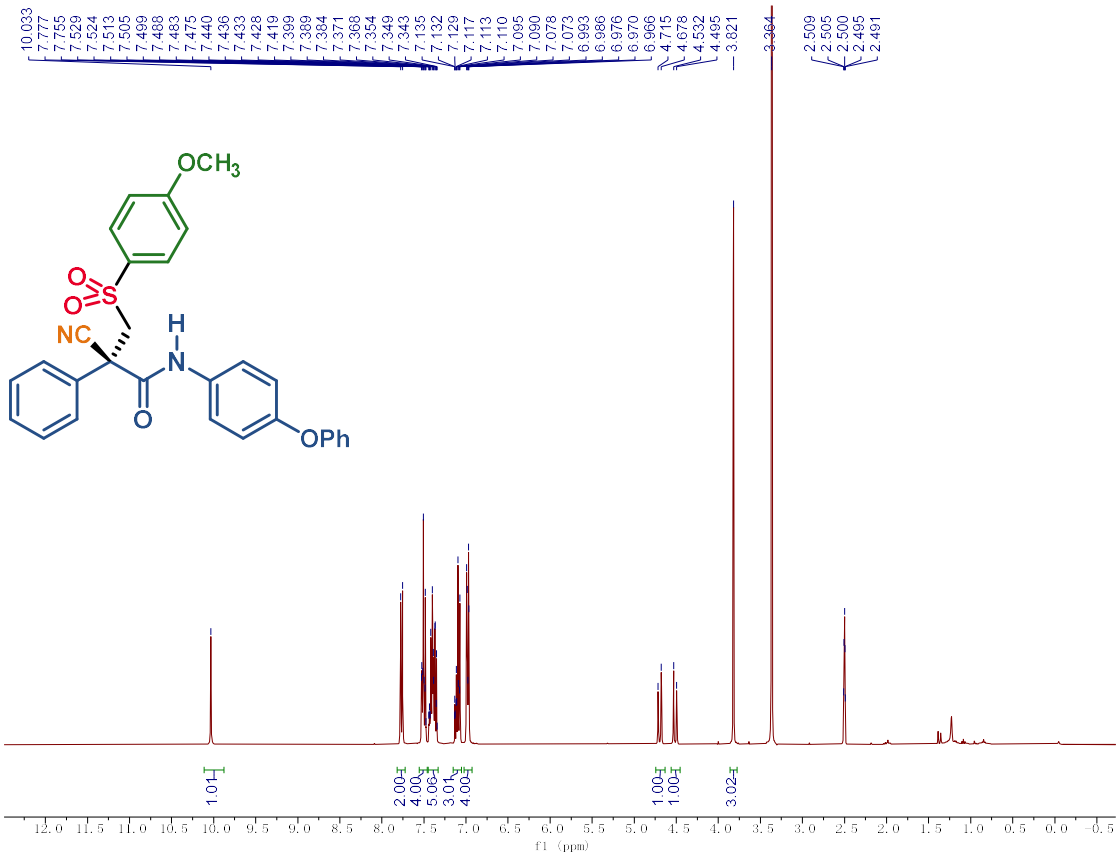


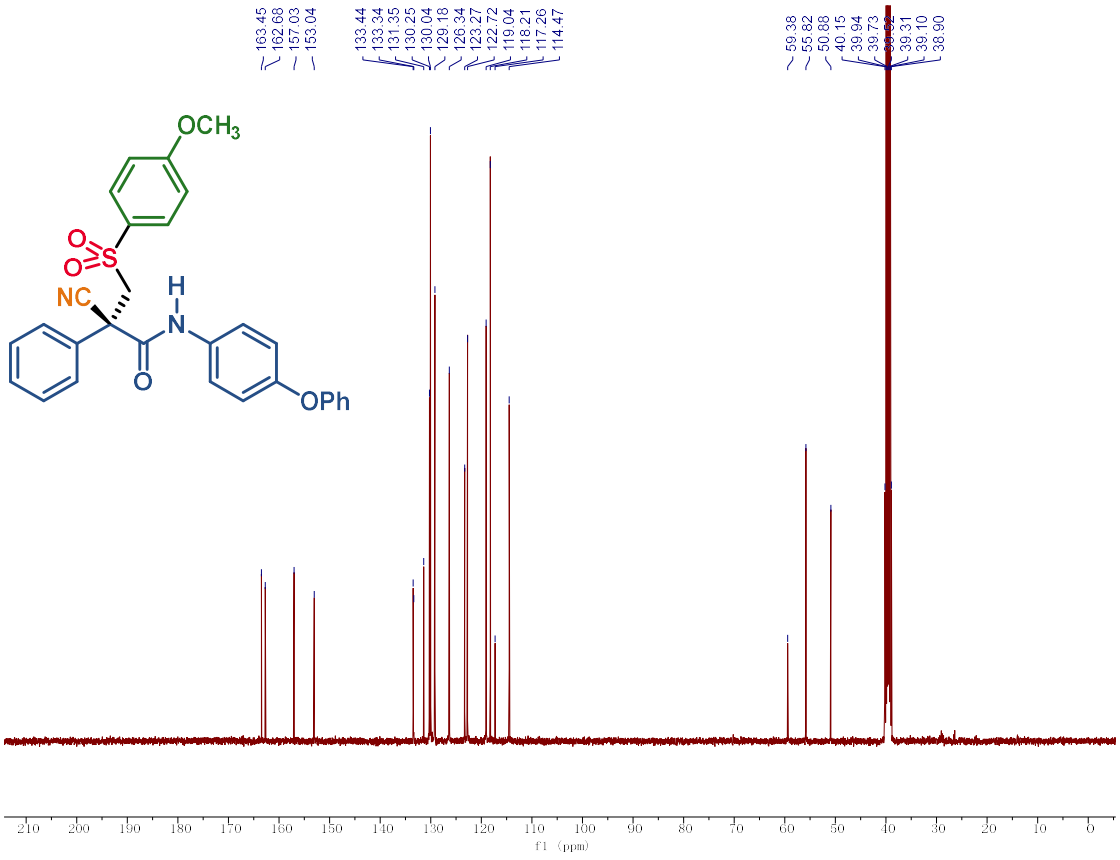
NMR of Compound of 3ab



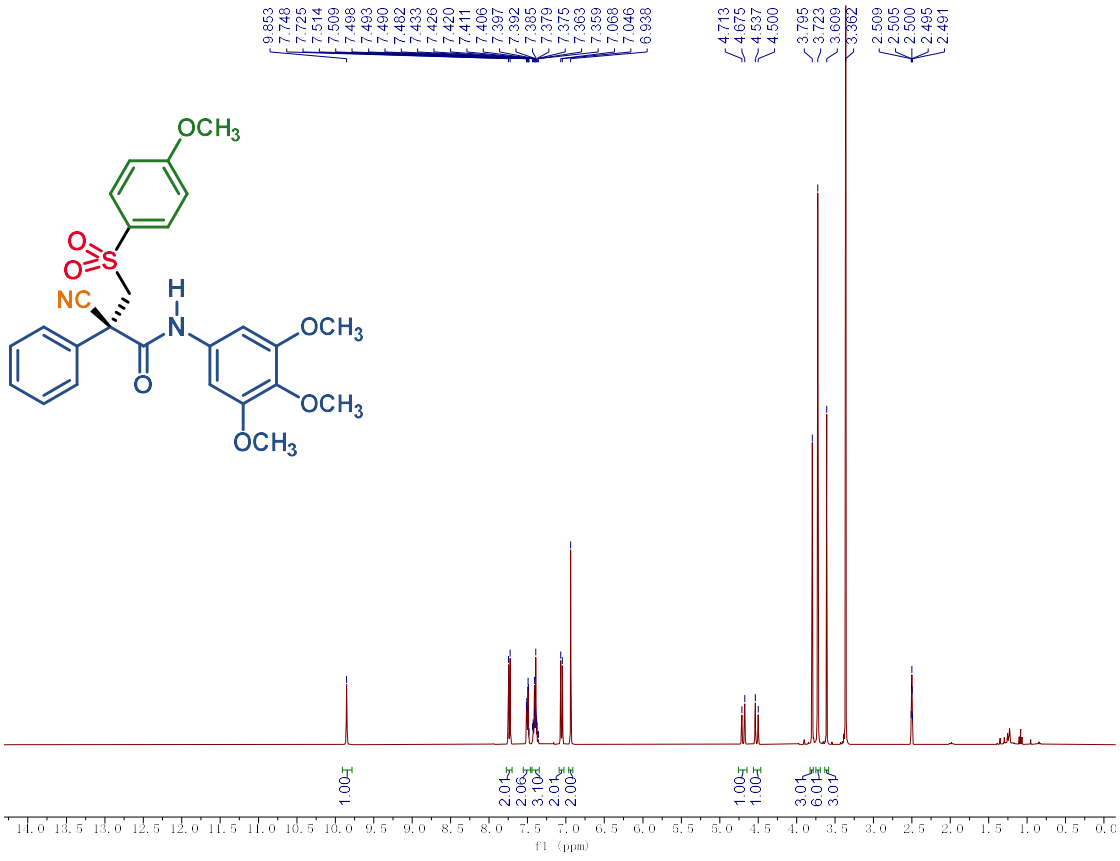


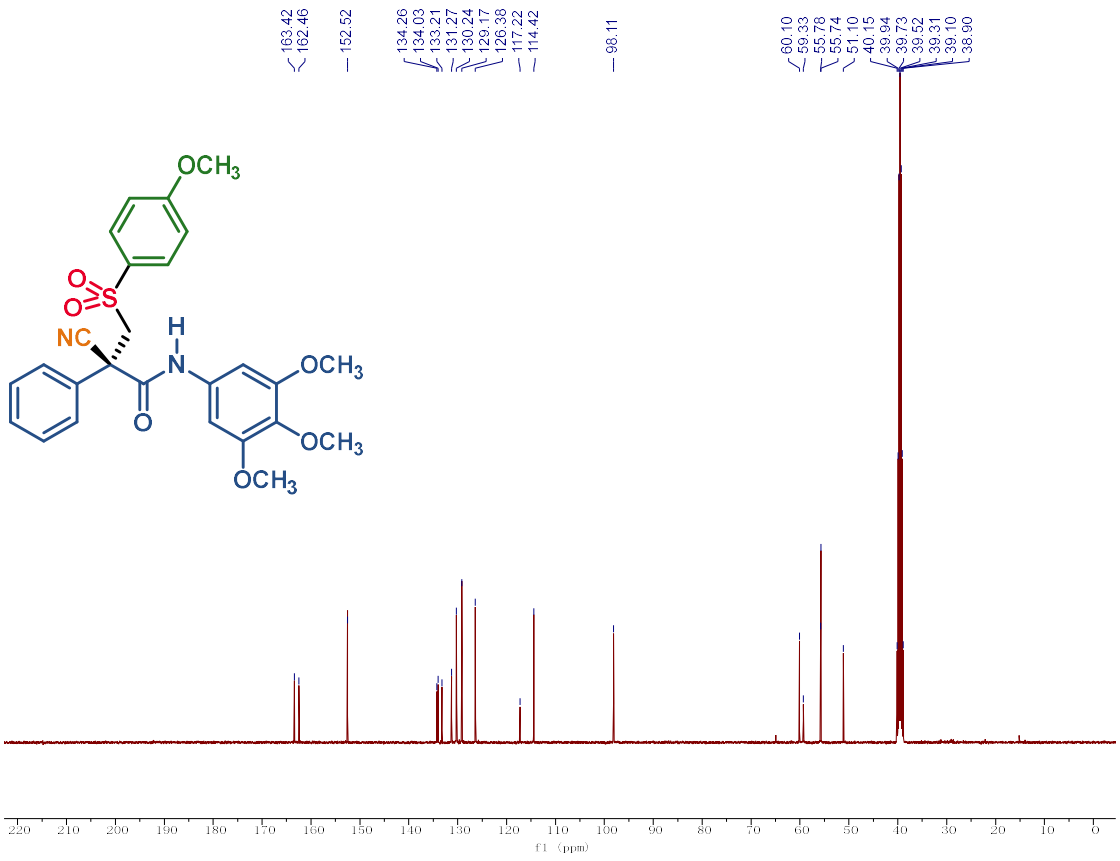
NMR of Compound of 3ac



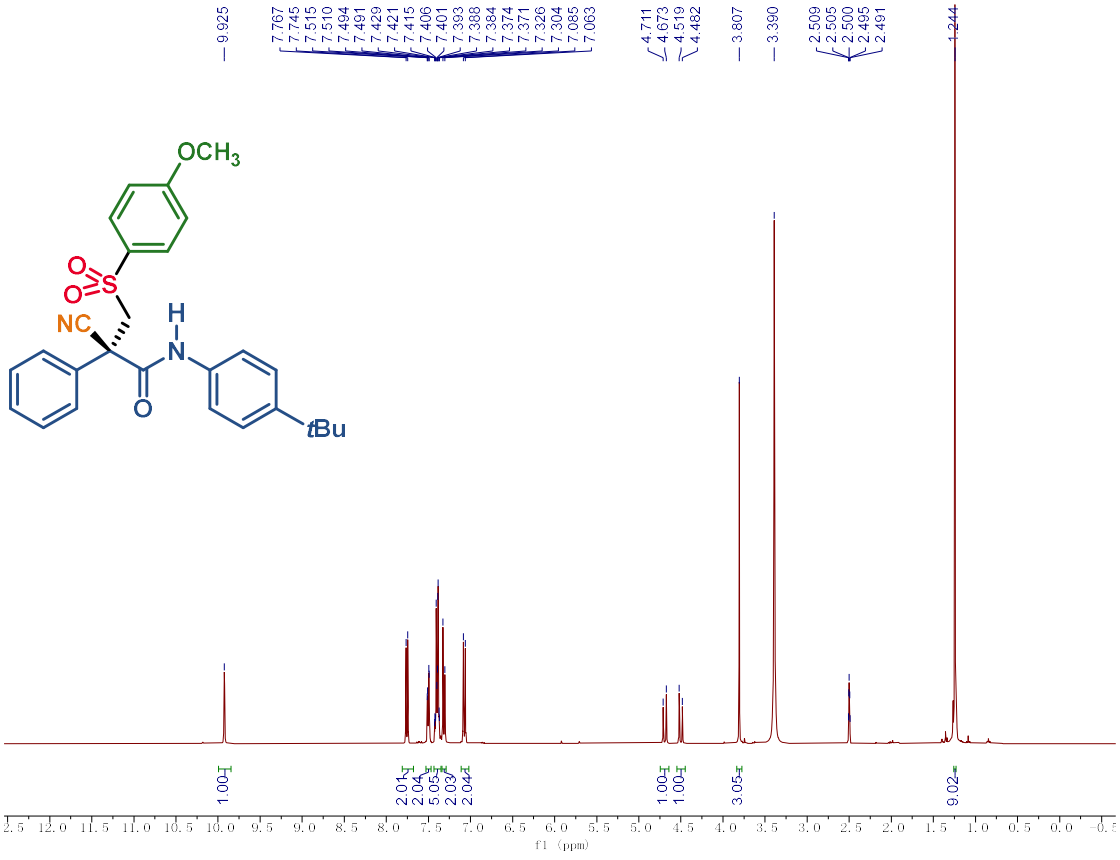


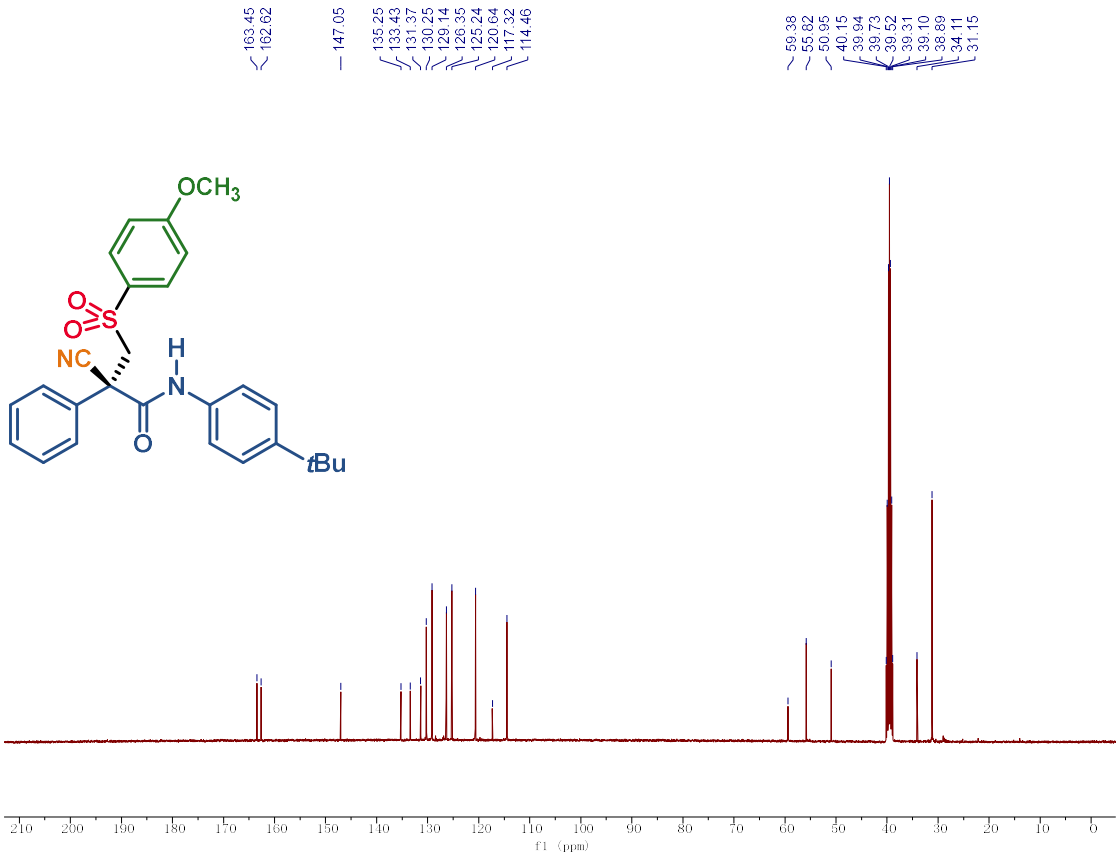
NMR of Compound of 3ad



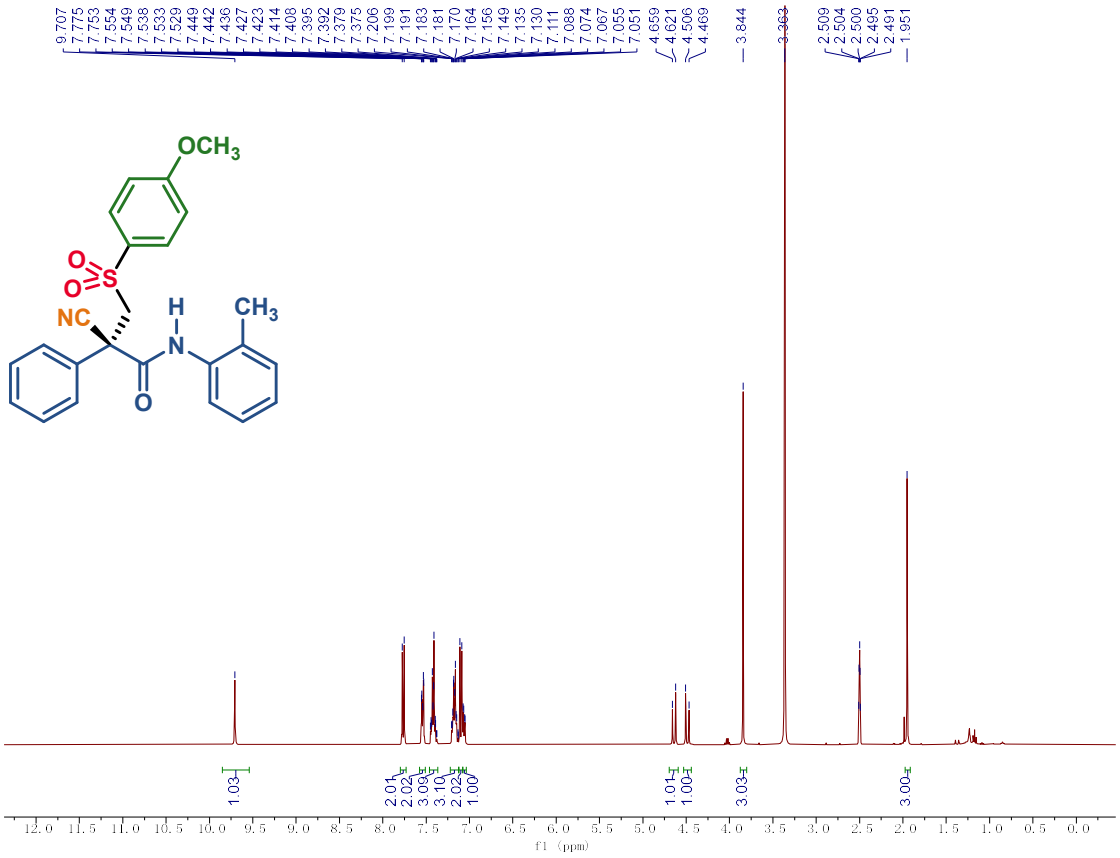


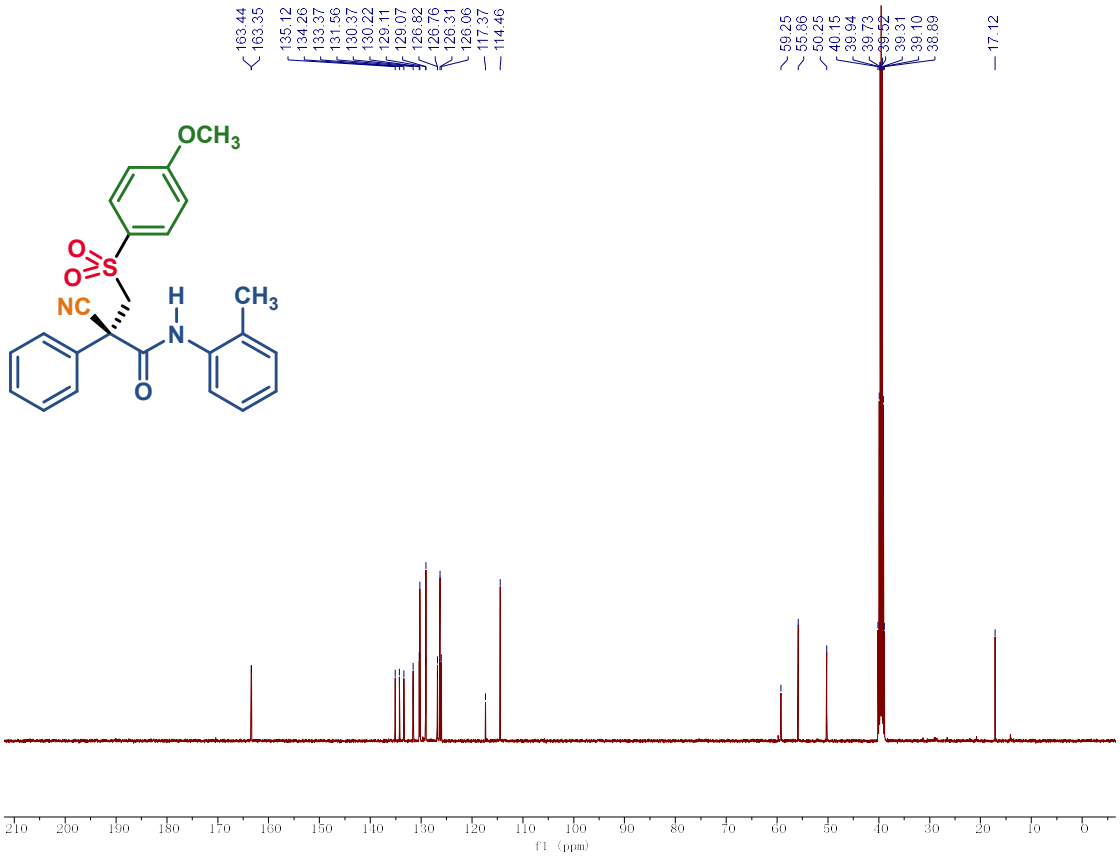
NMR of Compound of 3ae



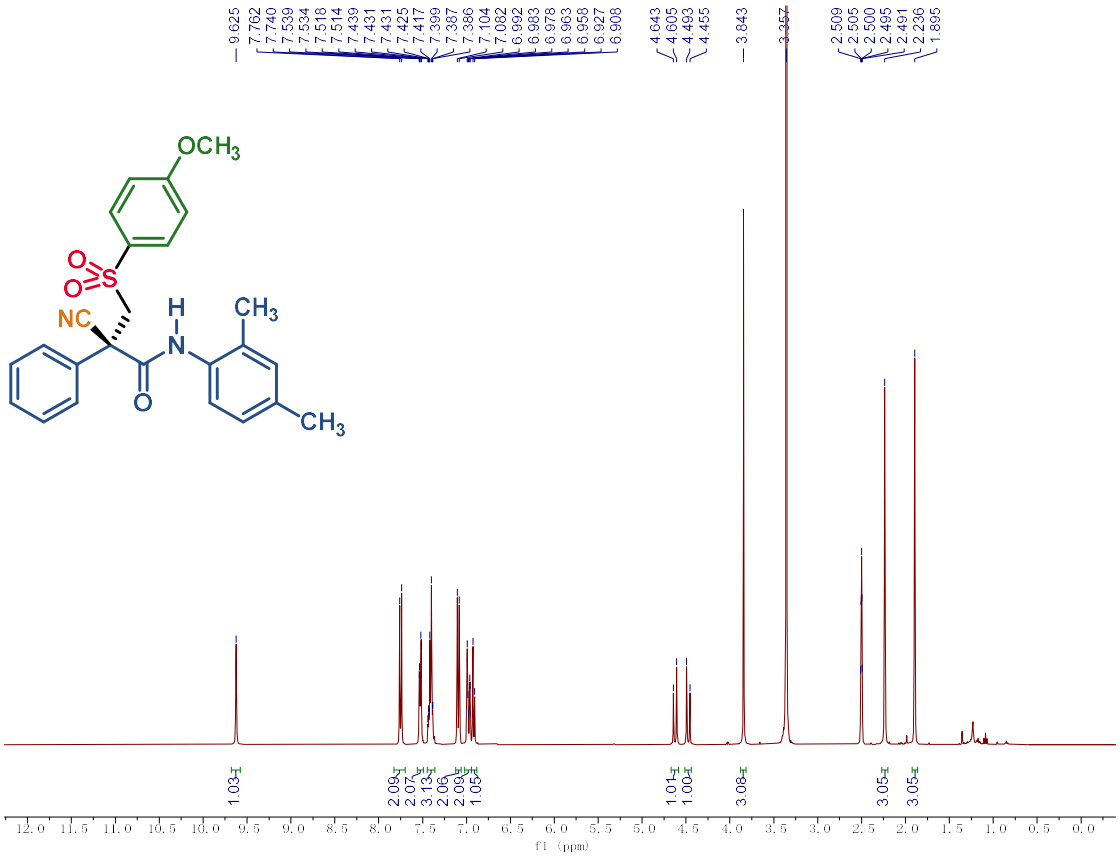


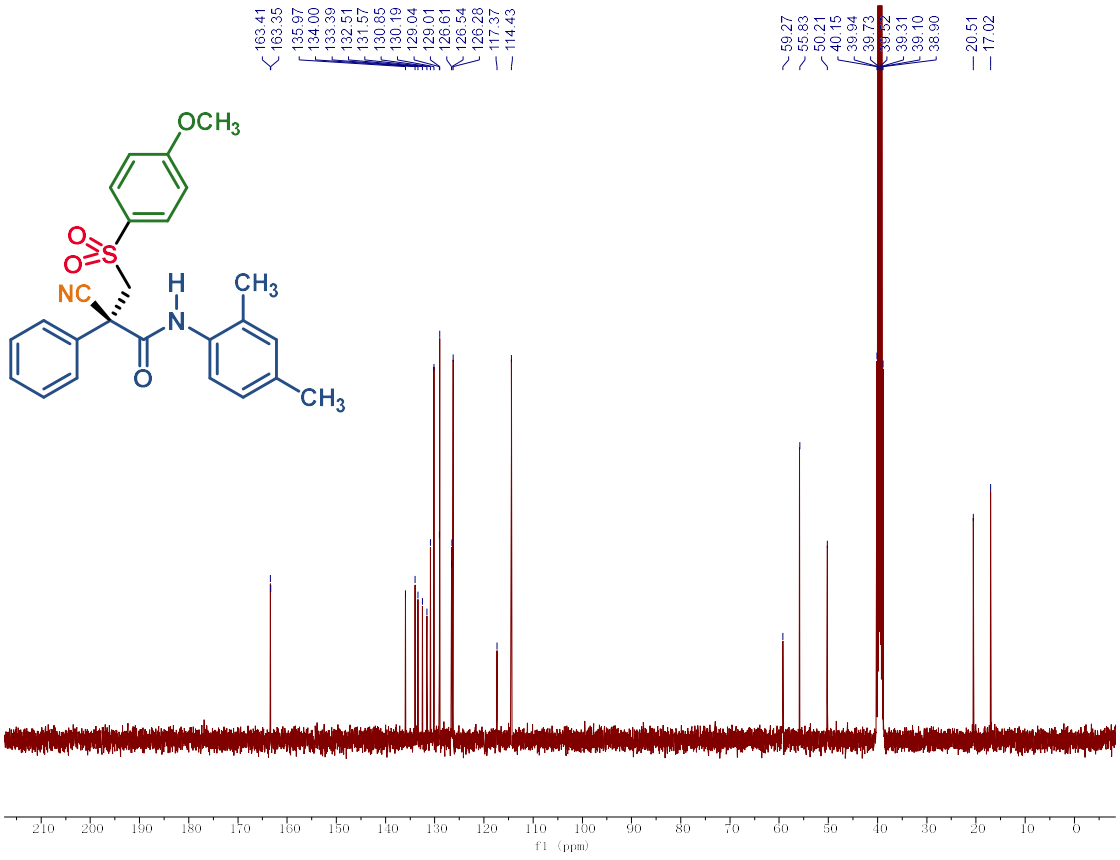
NMR of Compound of 3af



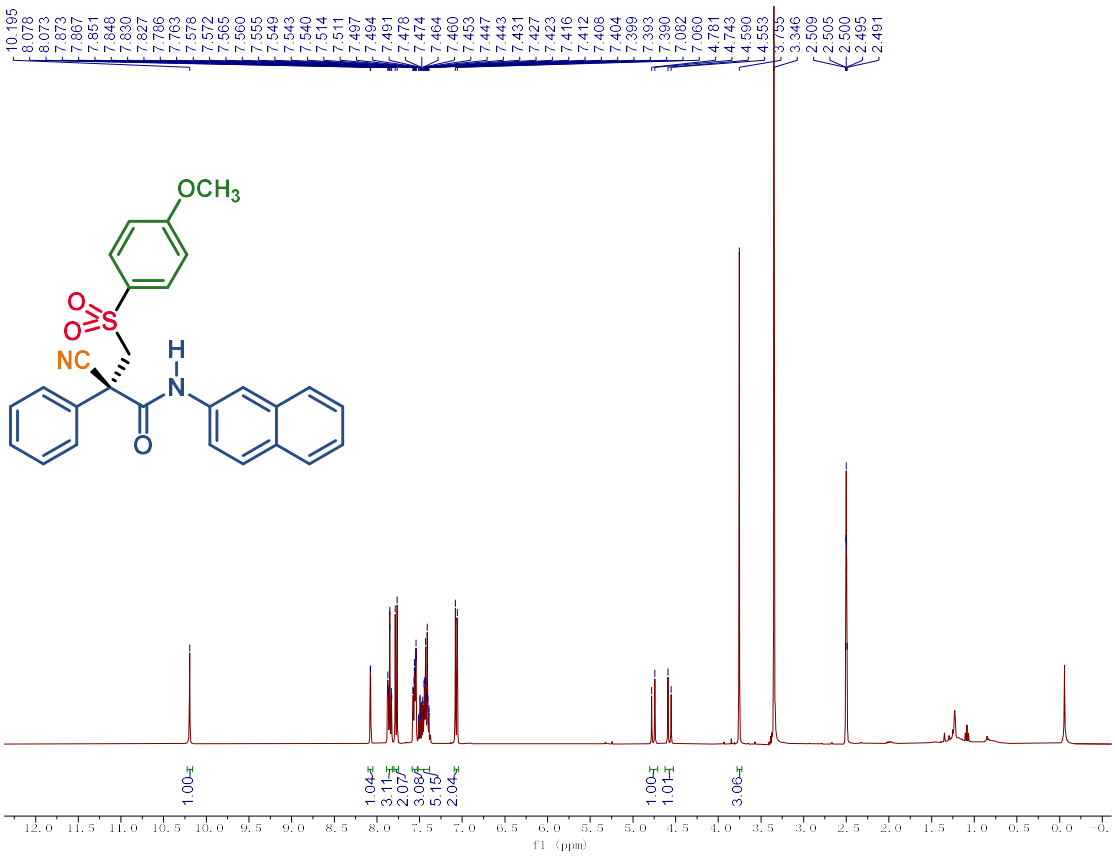


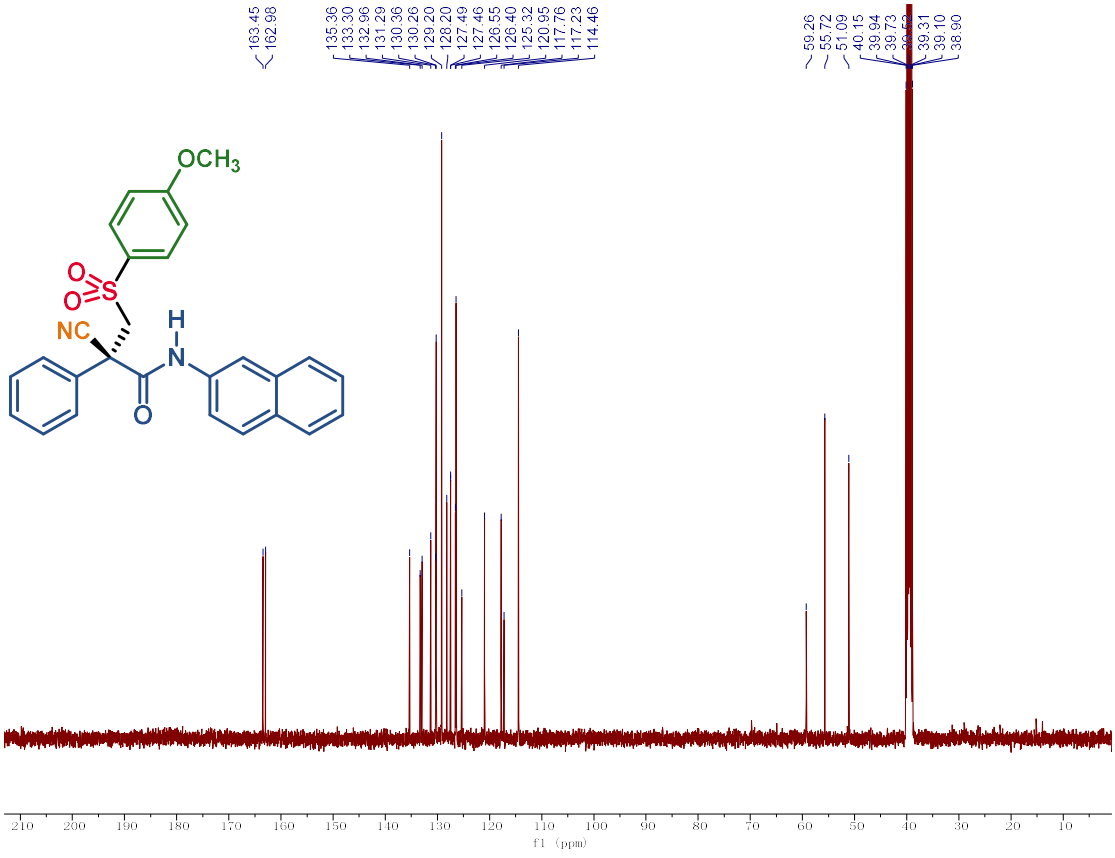
NMR of Compound of 3ag



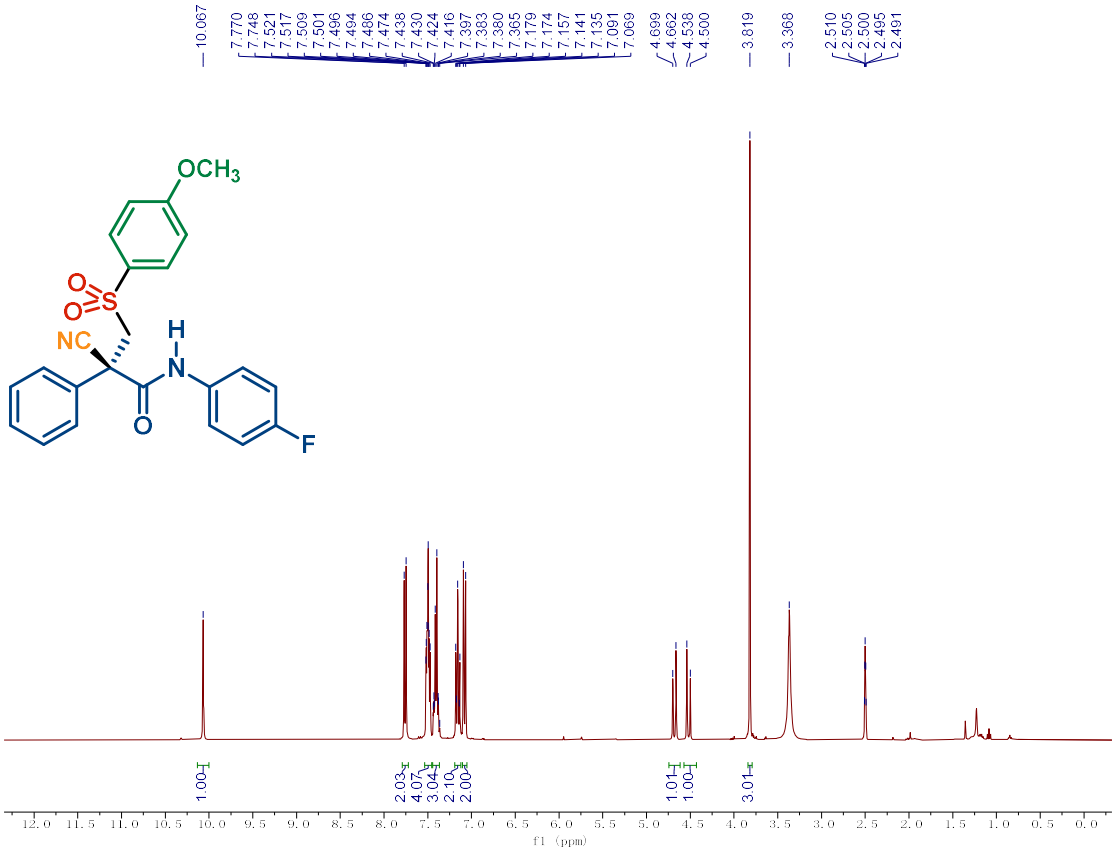


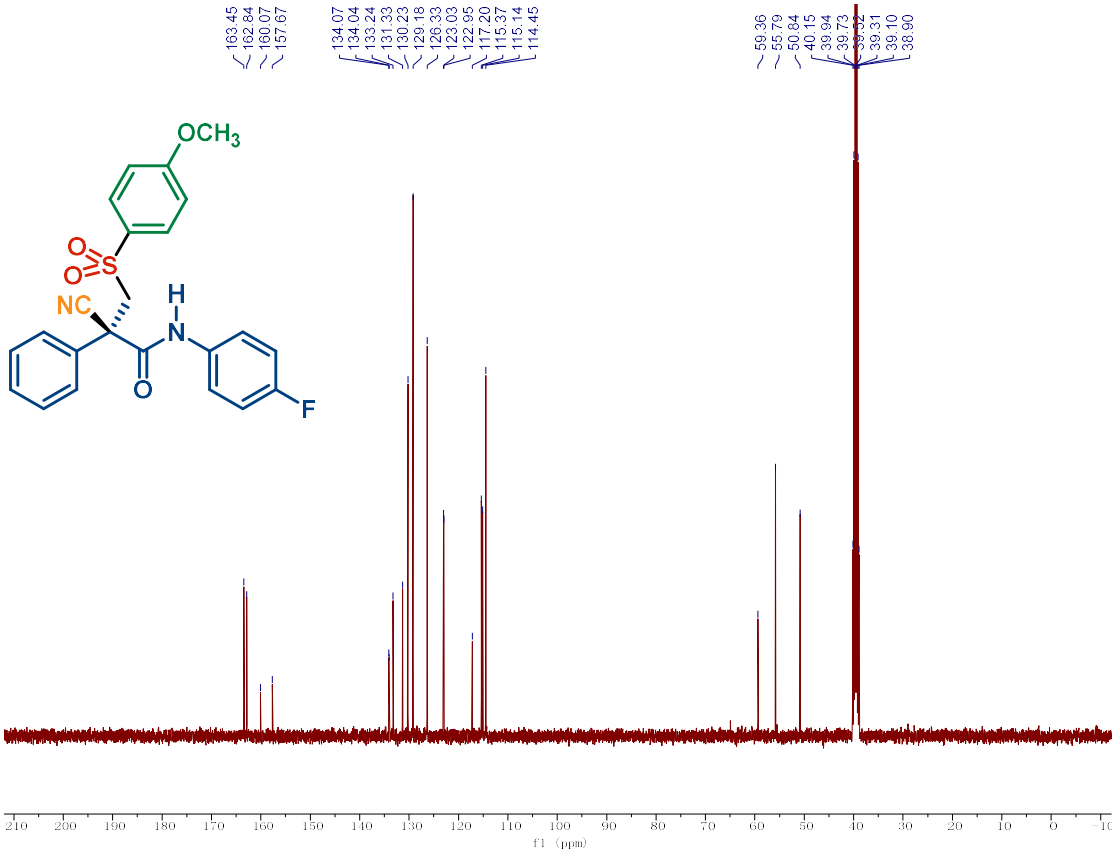
NMR of Compound of 3ah

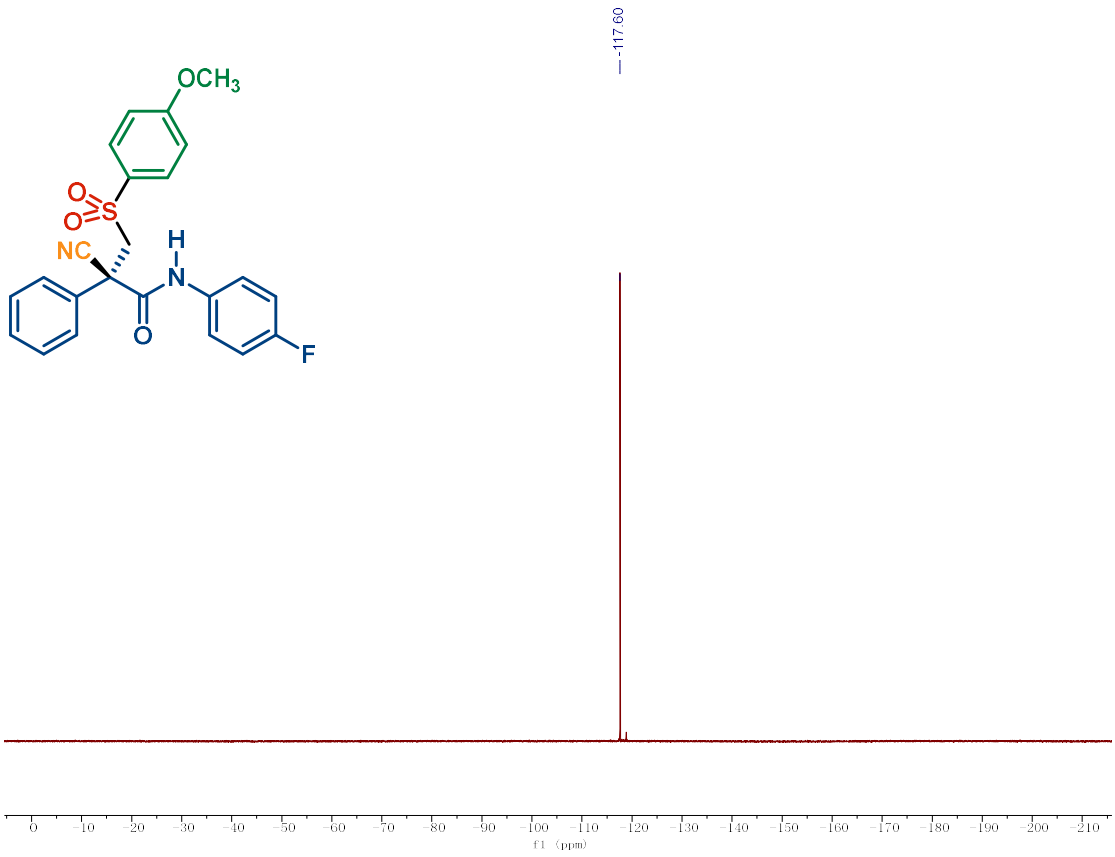




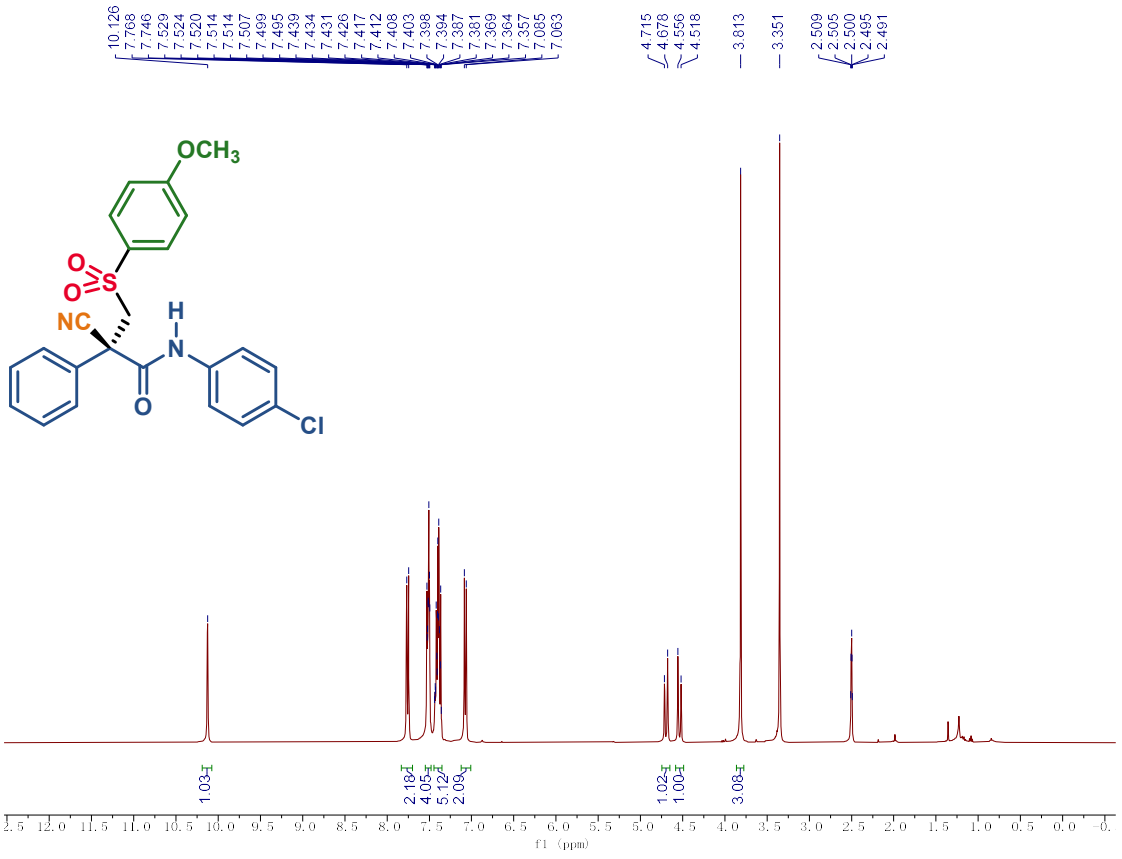
NMR of Compound of 3ai

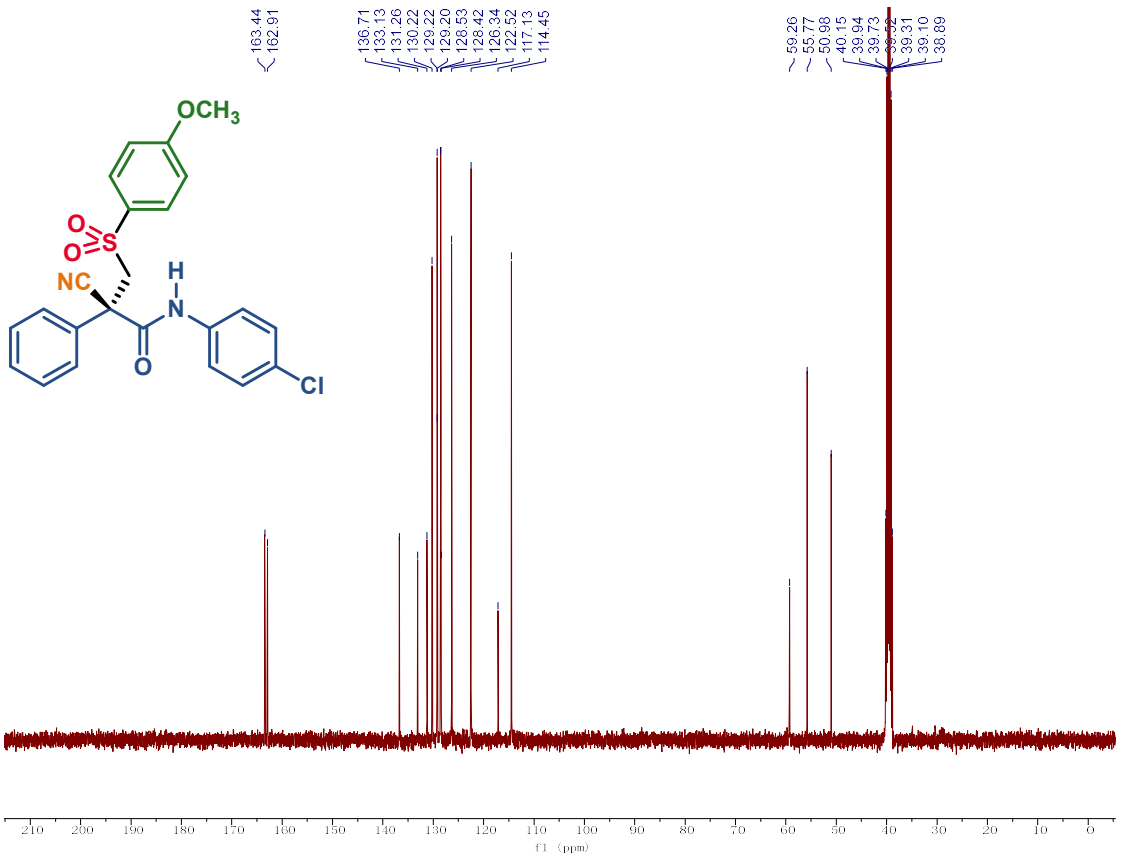




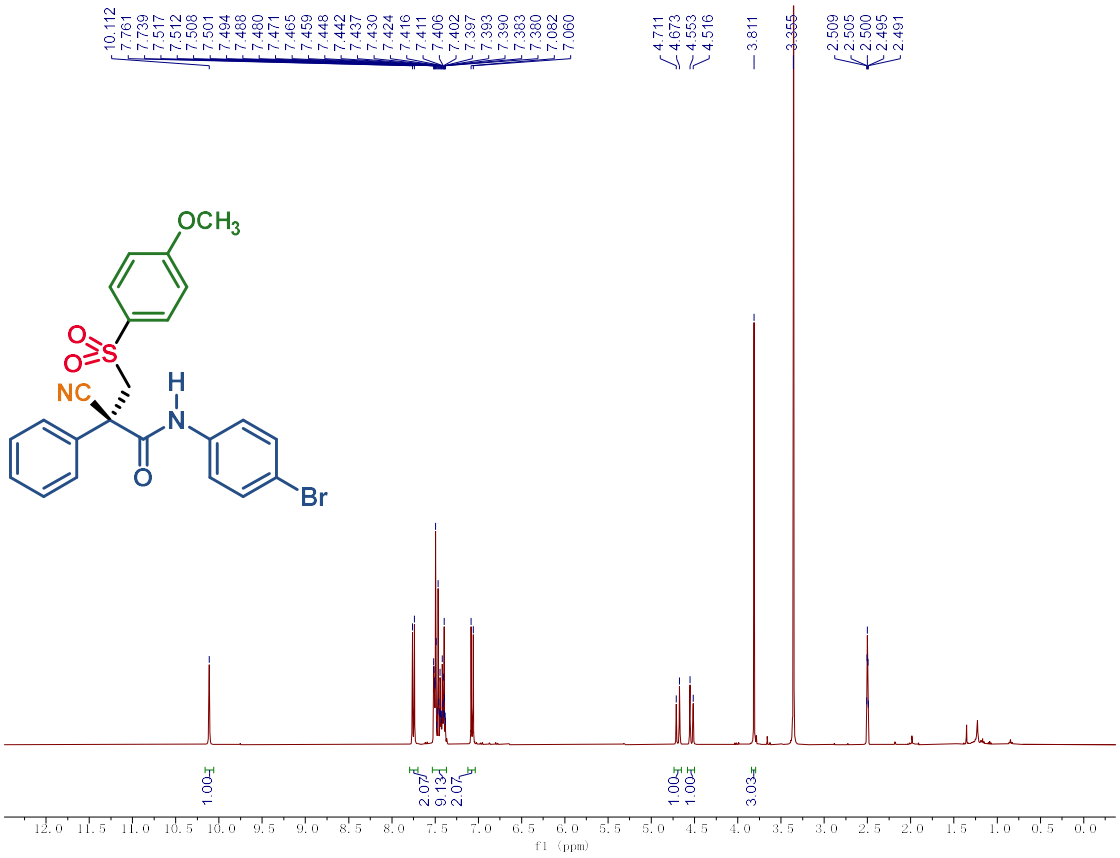

OCH3
O
O
S
NC
H
N
O
F
-117.60
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

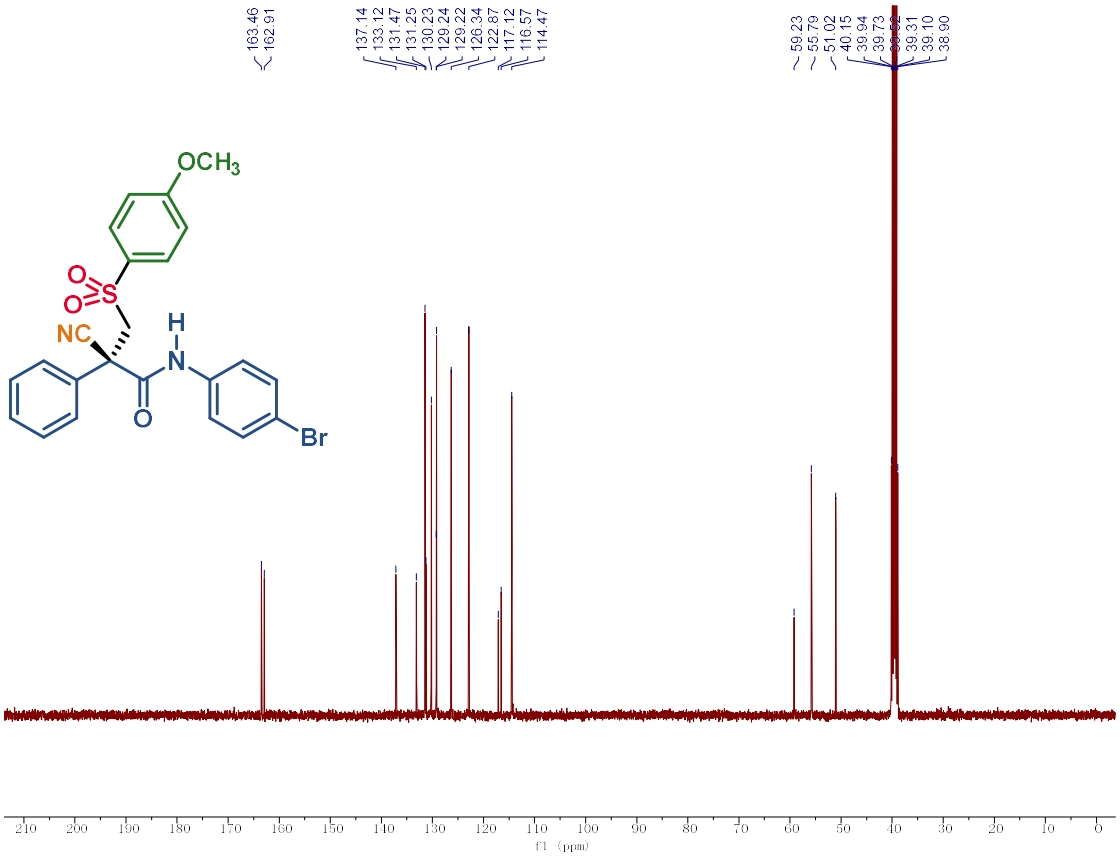
NMR of Compound of 3aj



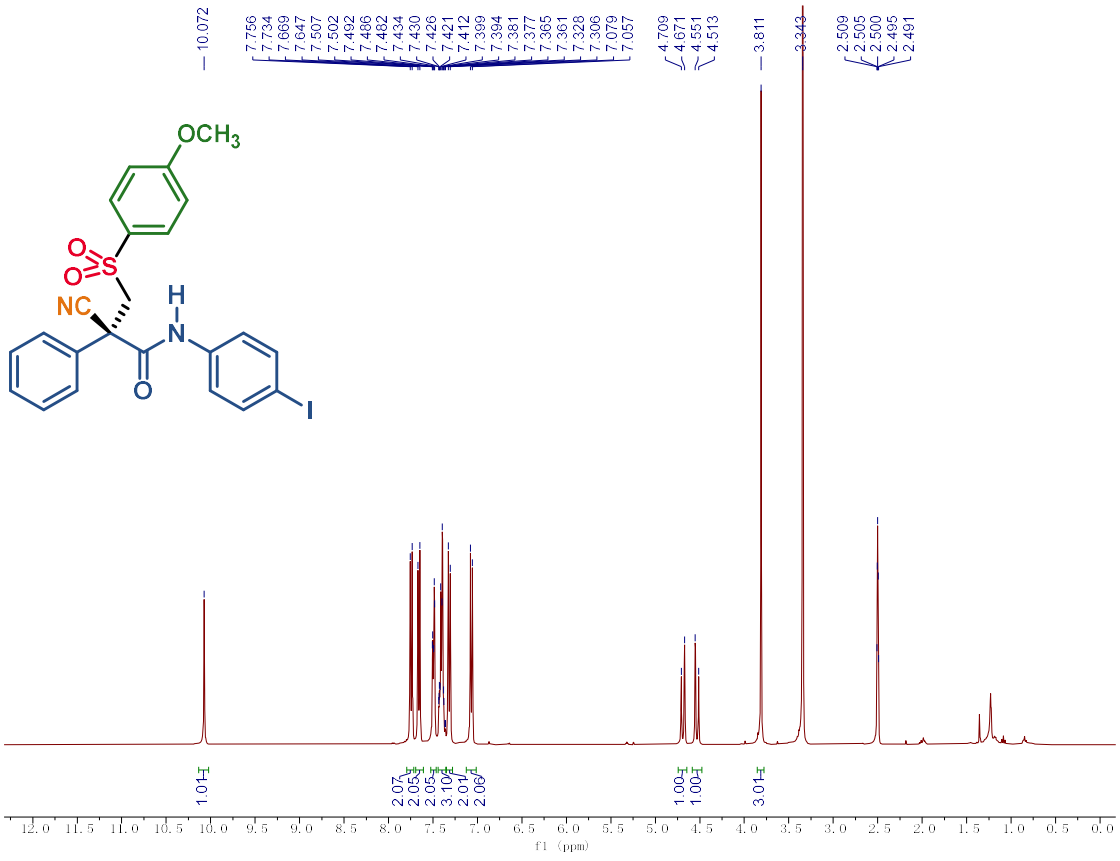


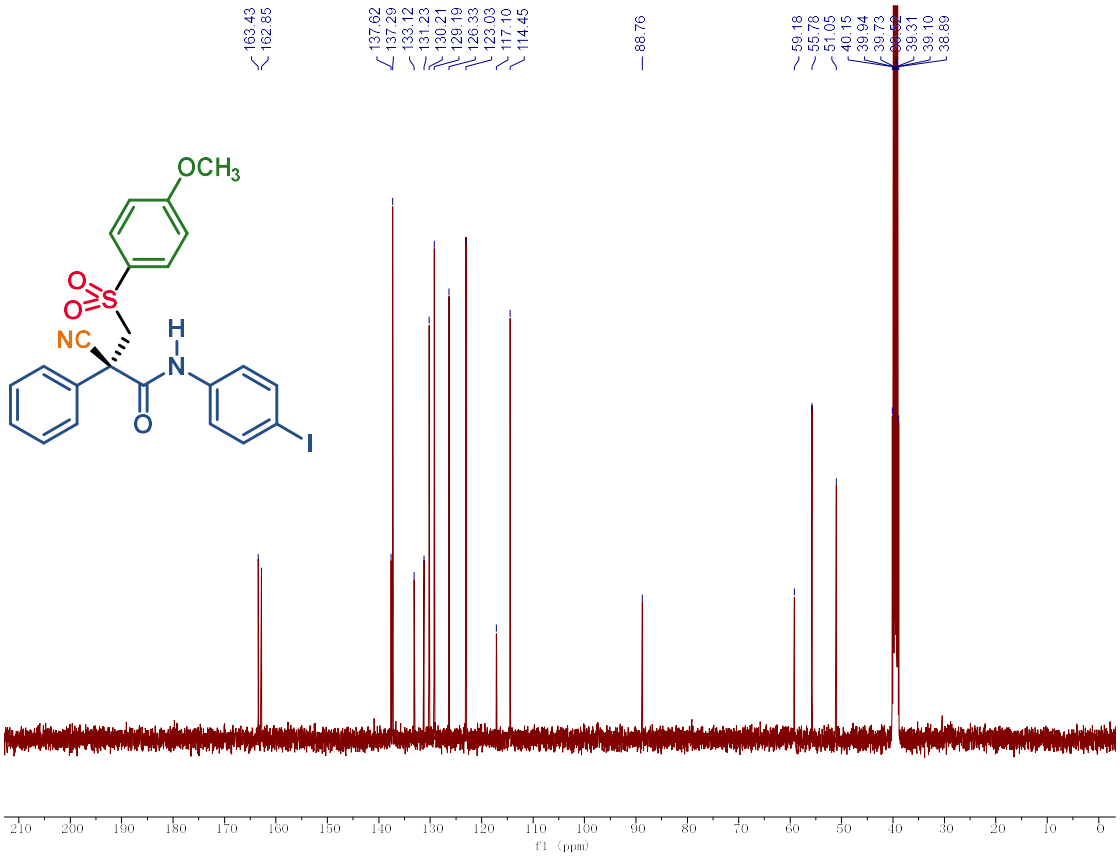
NMR of Compound of 3ak



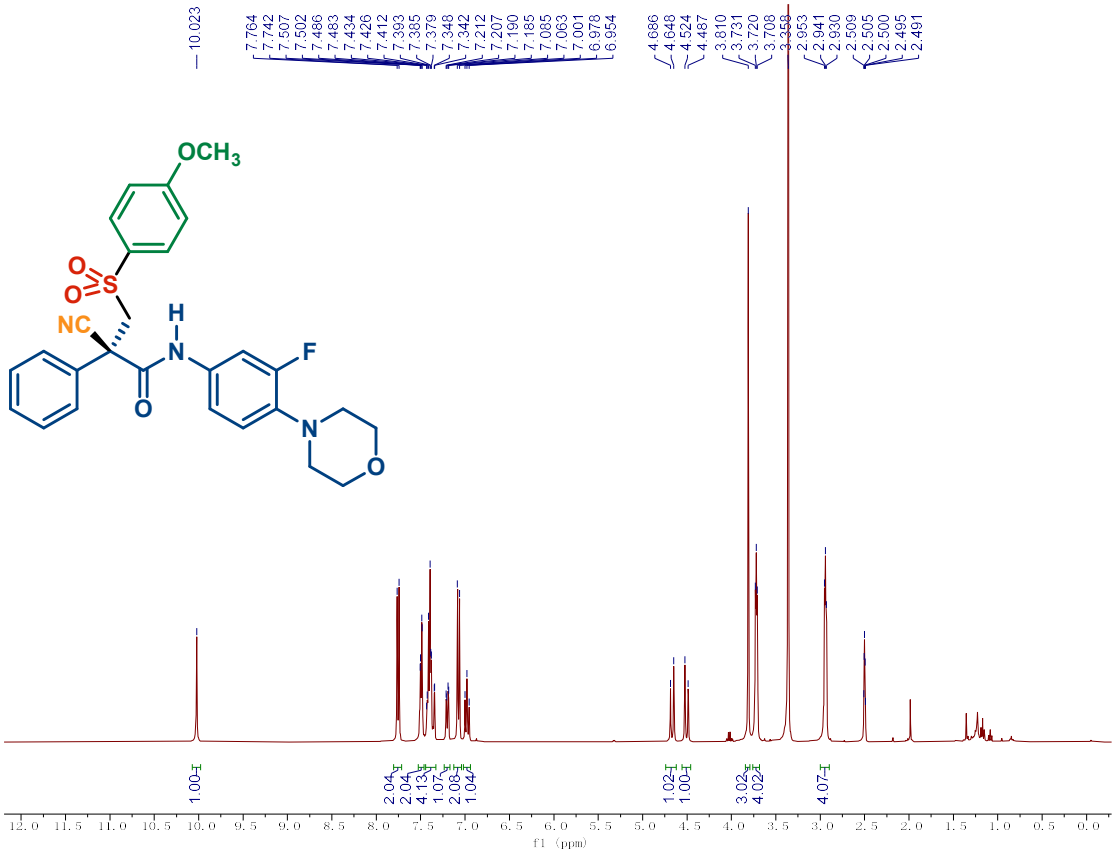


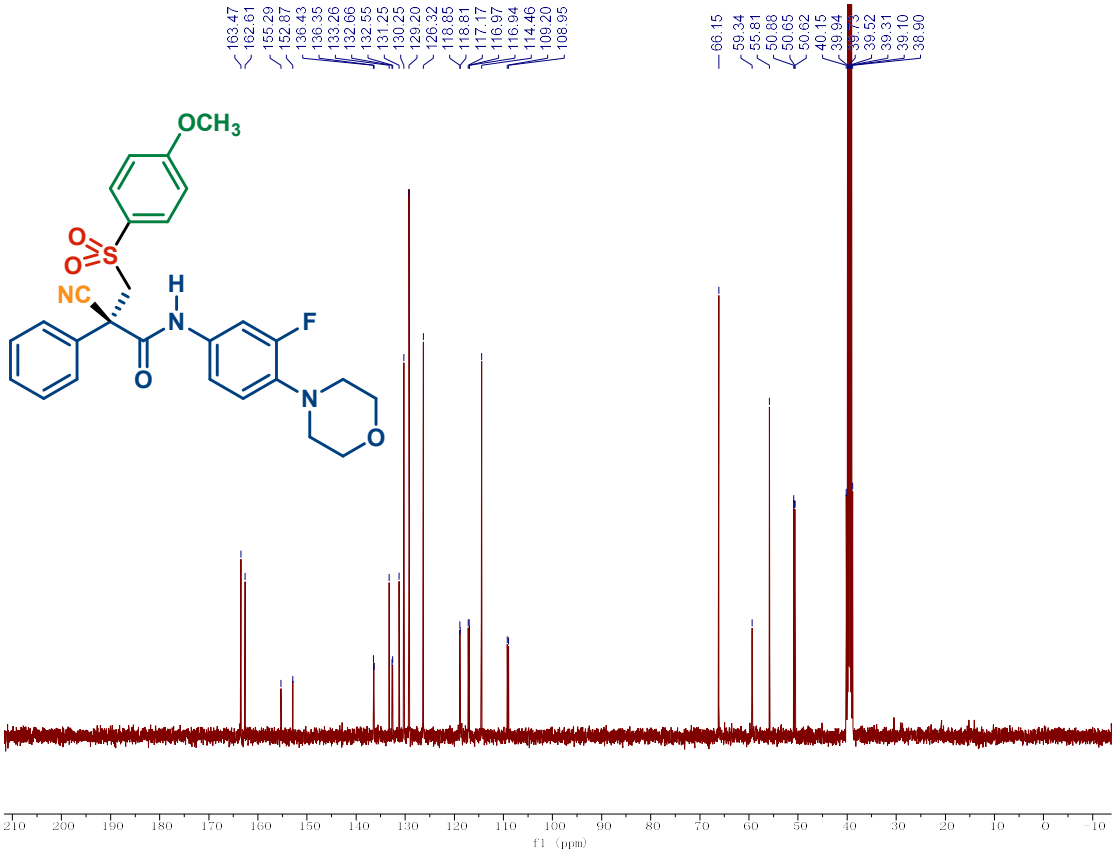
NMR of Compound of 3al

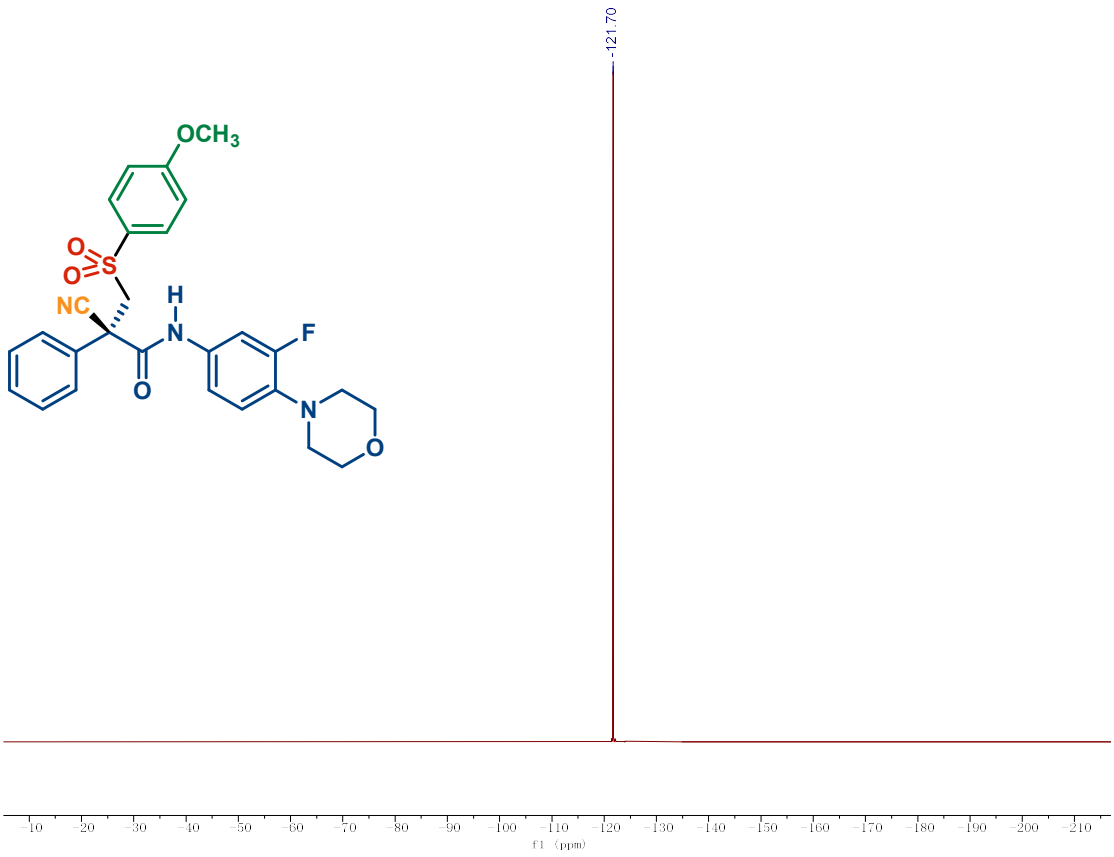




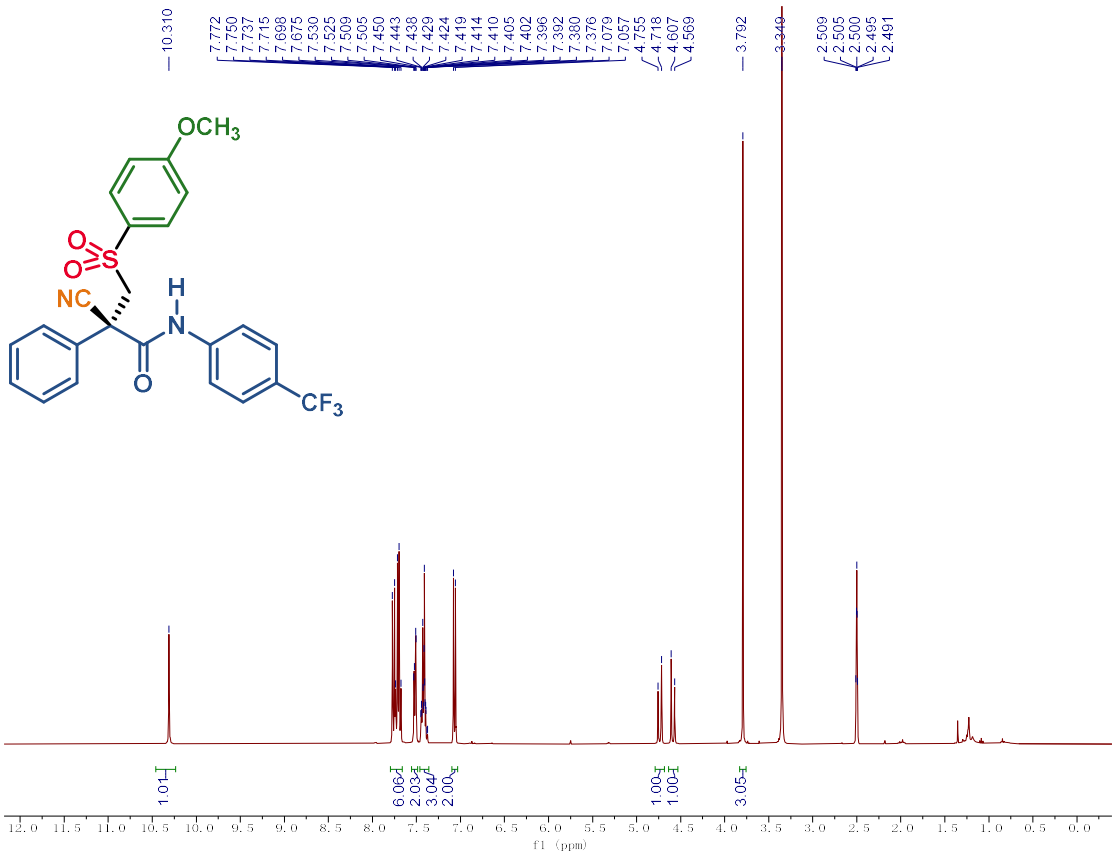
NMR of Compound of 3am

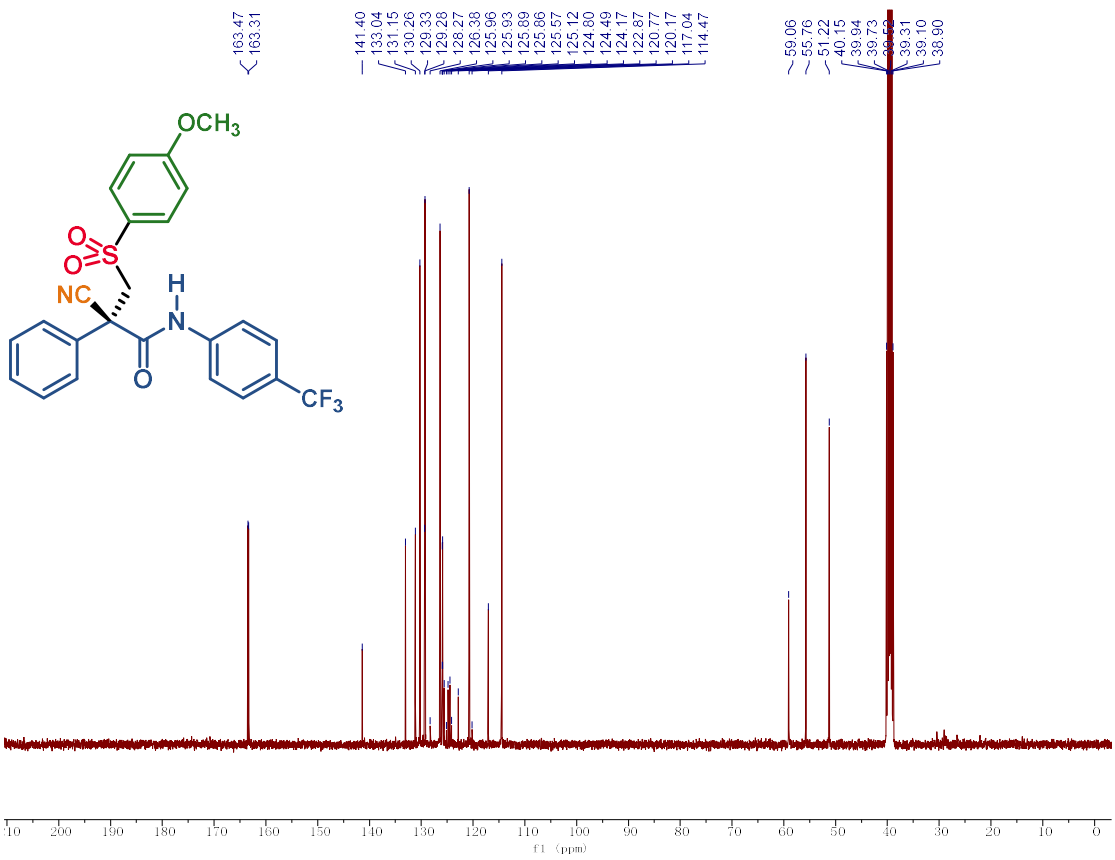


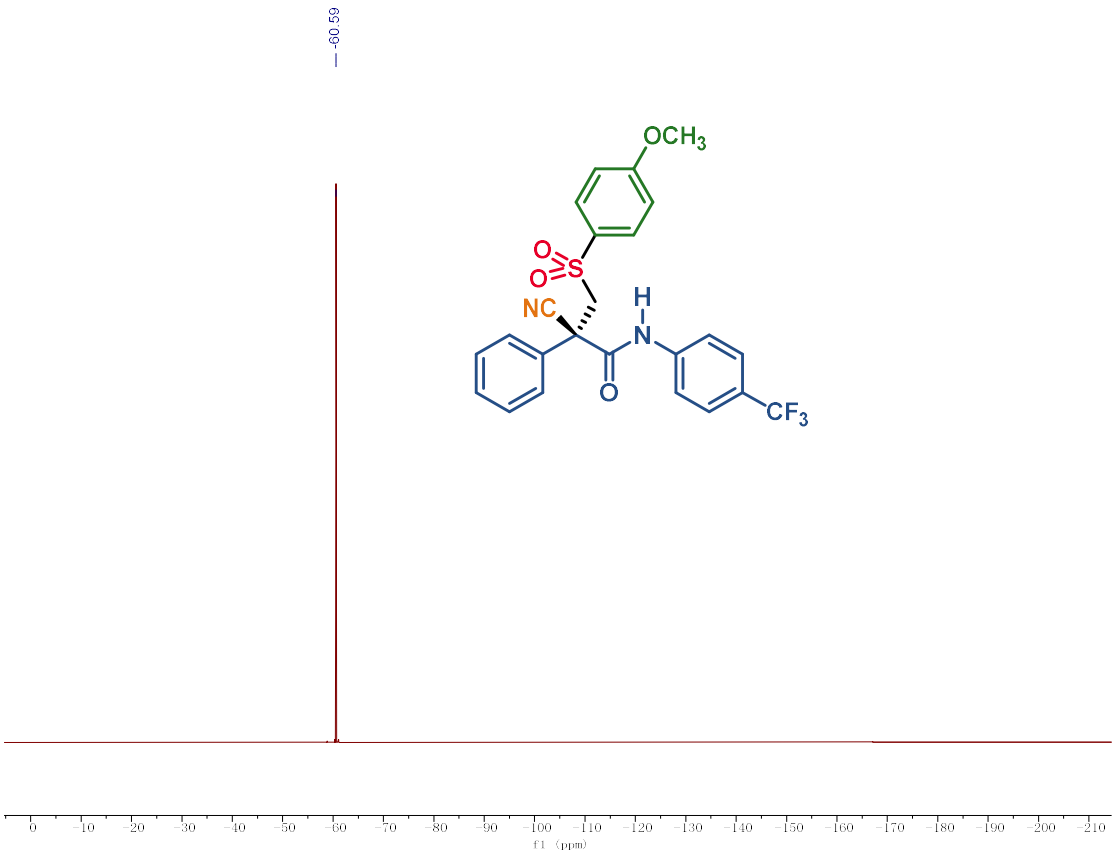



-121.70
OCH3
O
O
S
NC
H
N
O
F
N
O
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

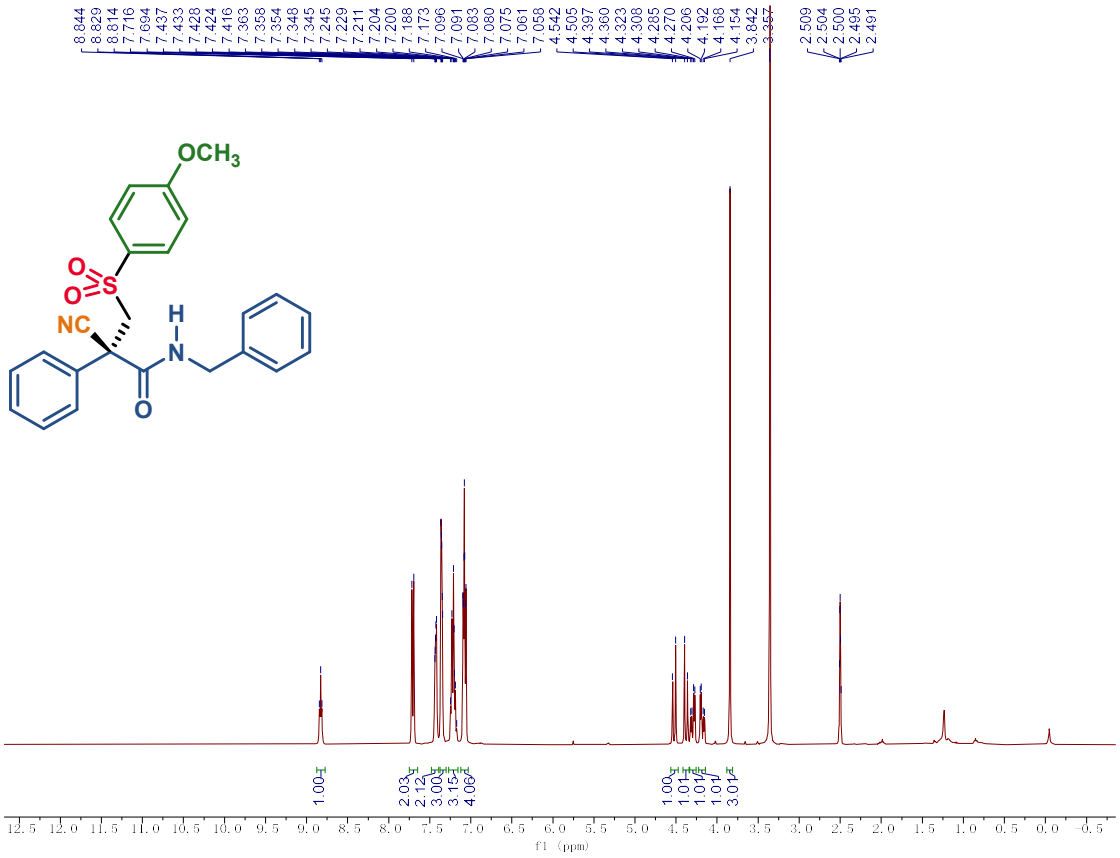
NMR of Compound of 3an

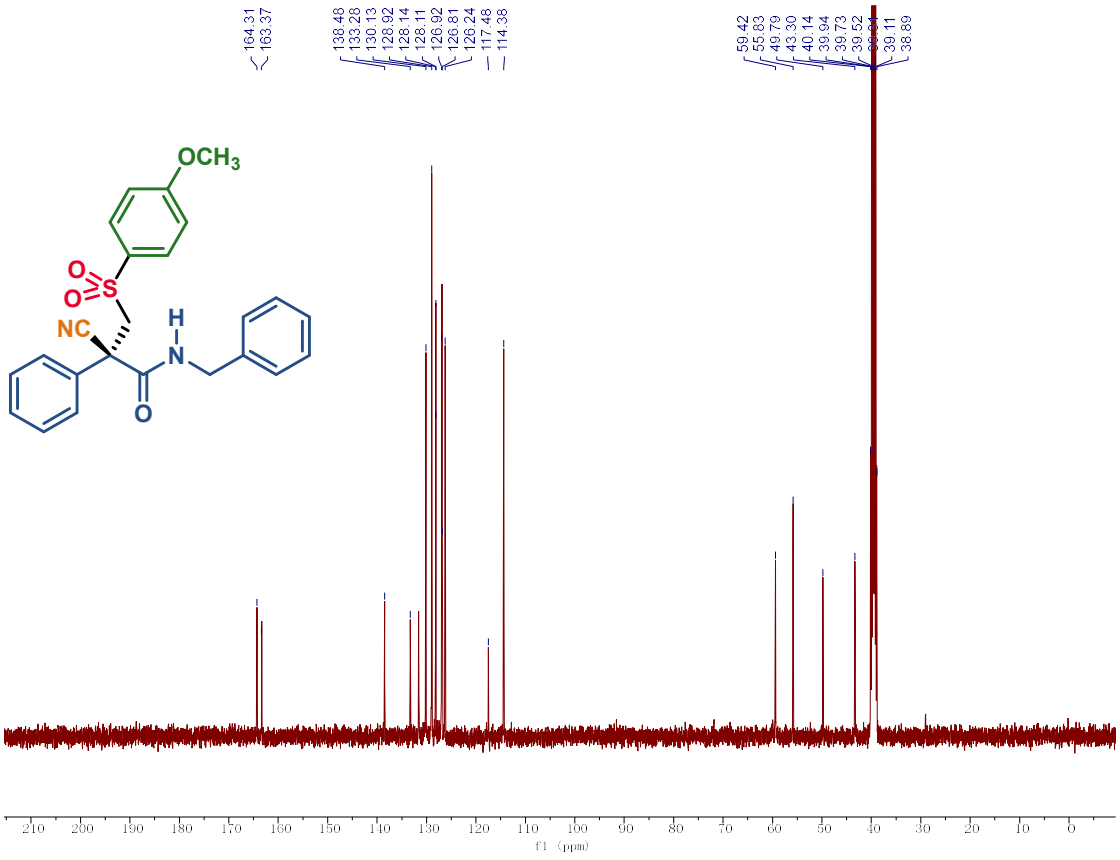




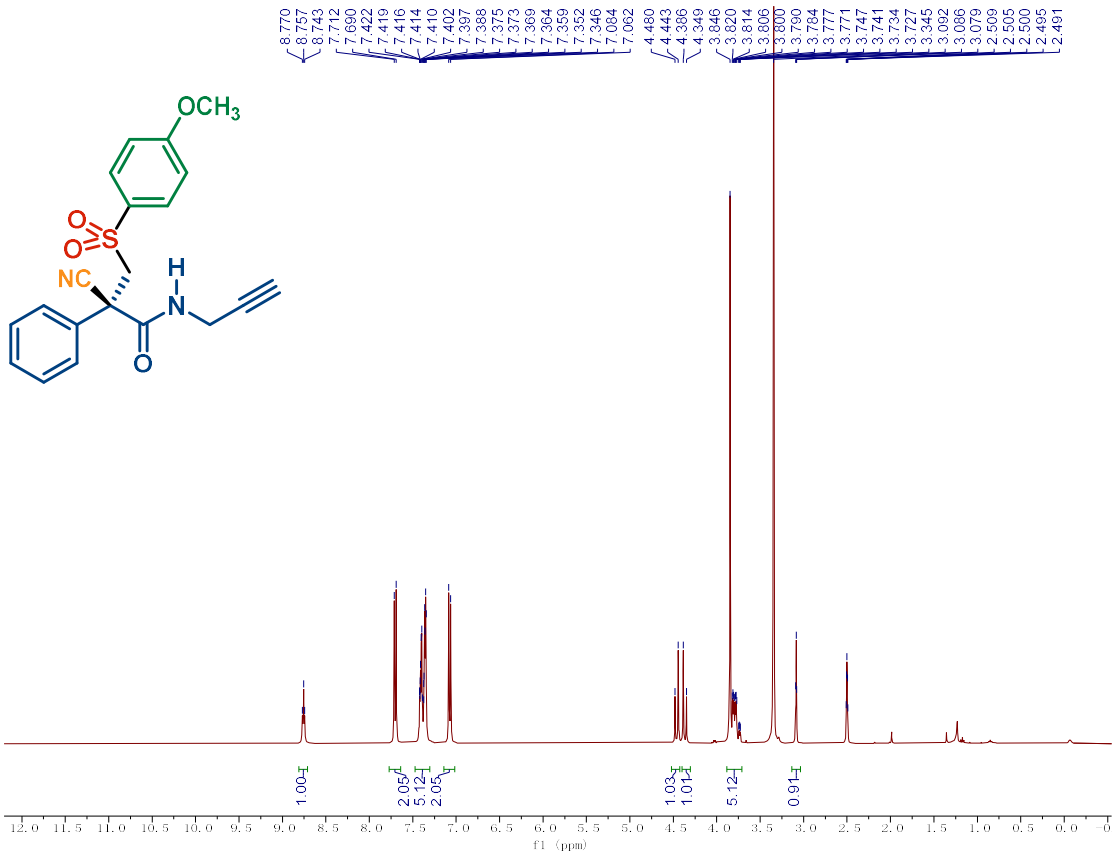

-60.59
OCH3
O
O
S
NC
H
N
O
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

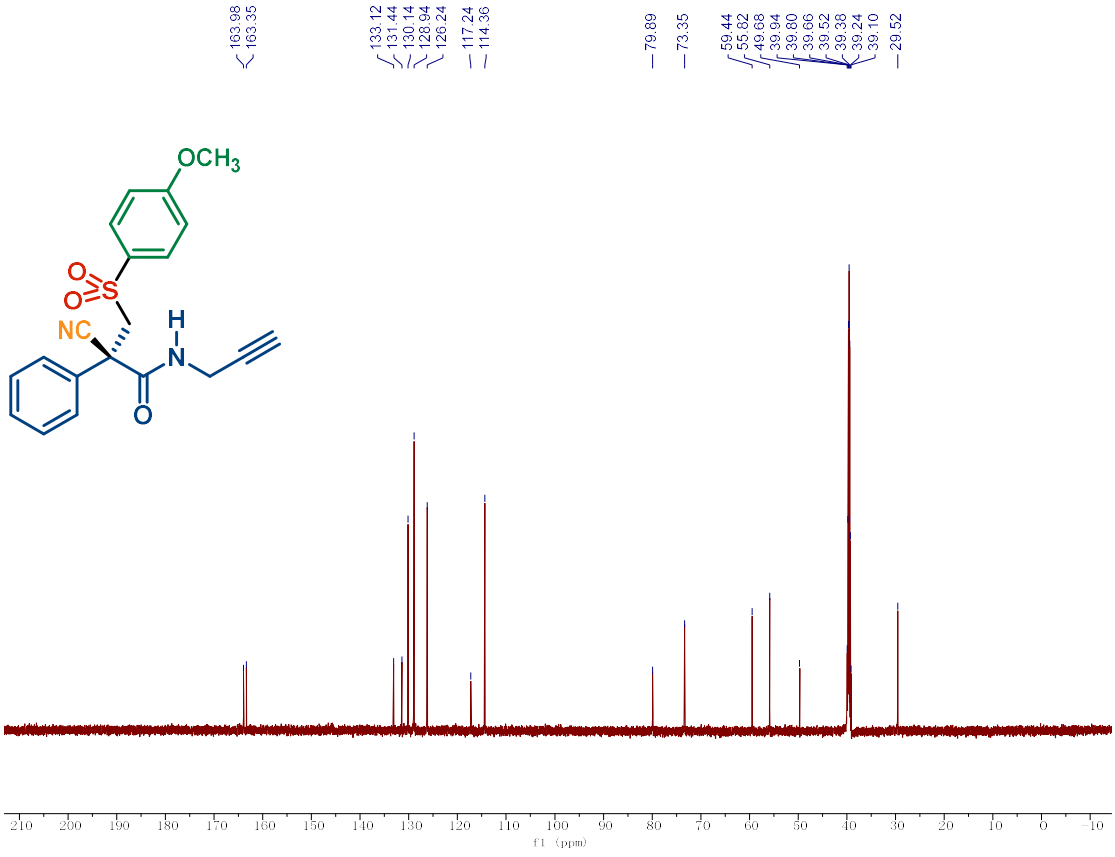
NMR of Compound of 3ao



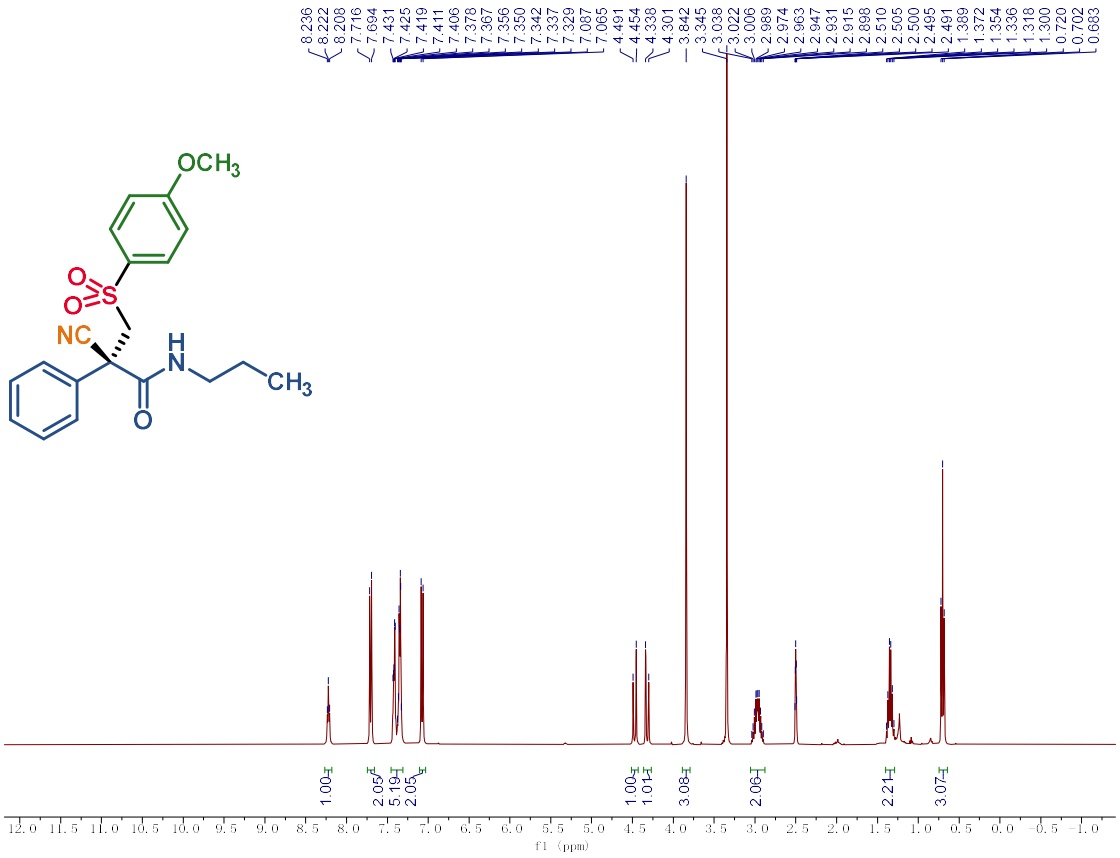


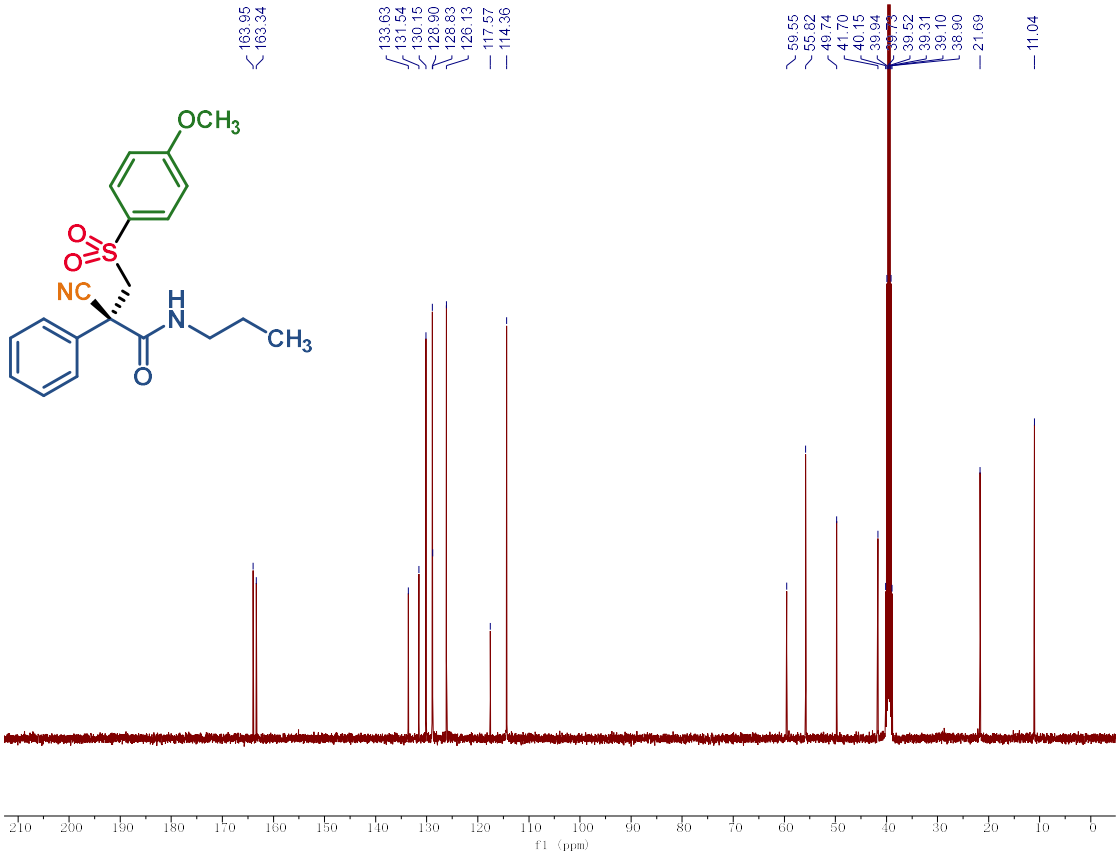
NMR of Compound of 3ap



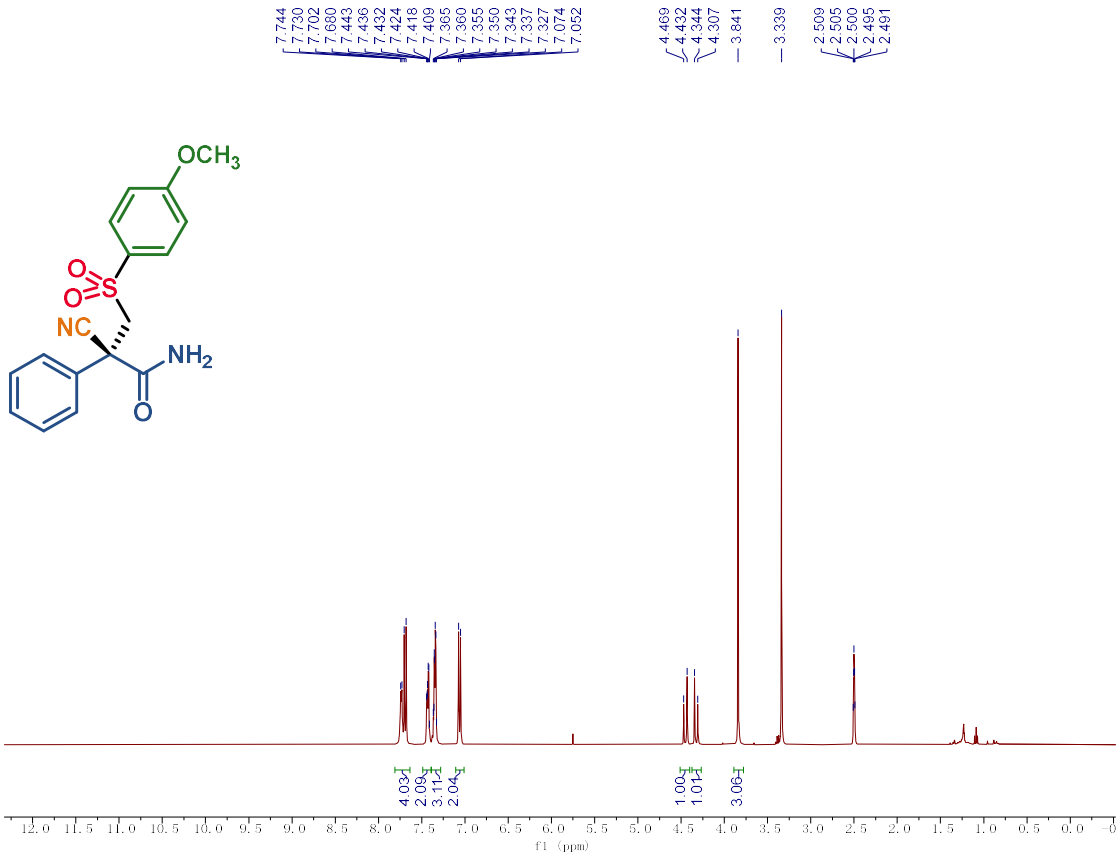


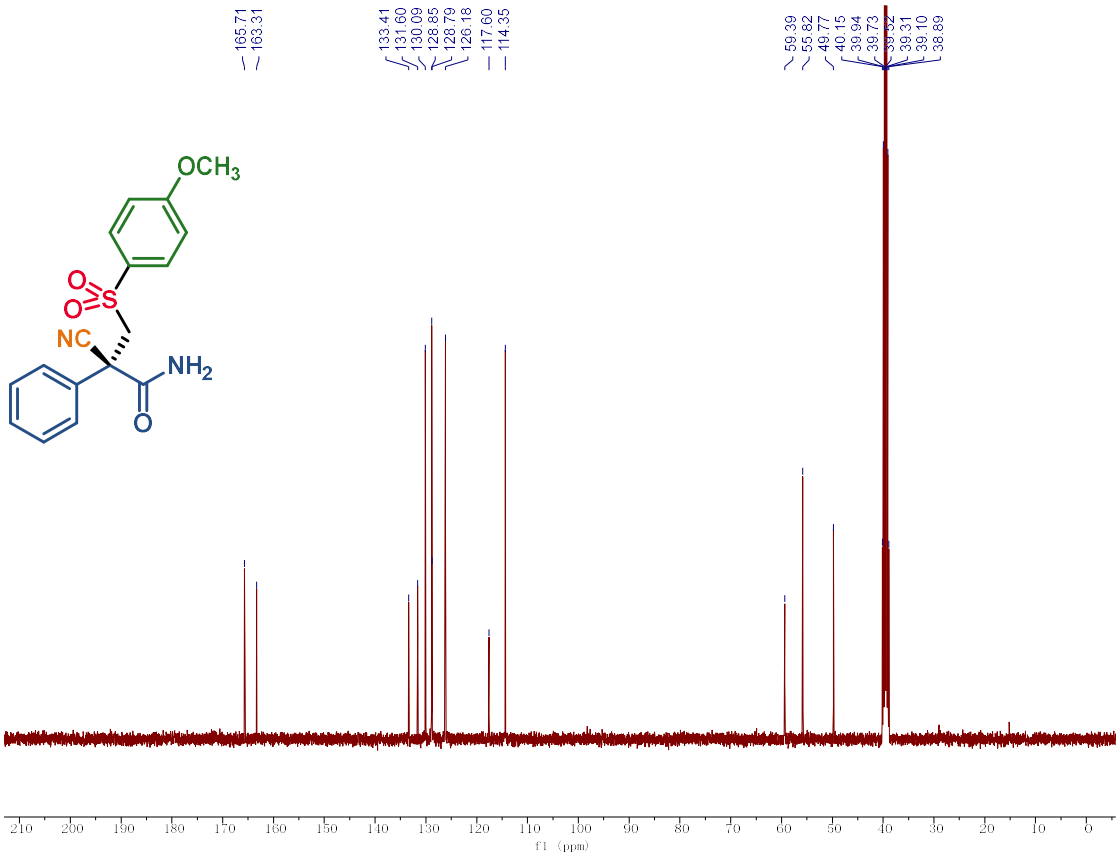
NMR of Compound of 3aq



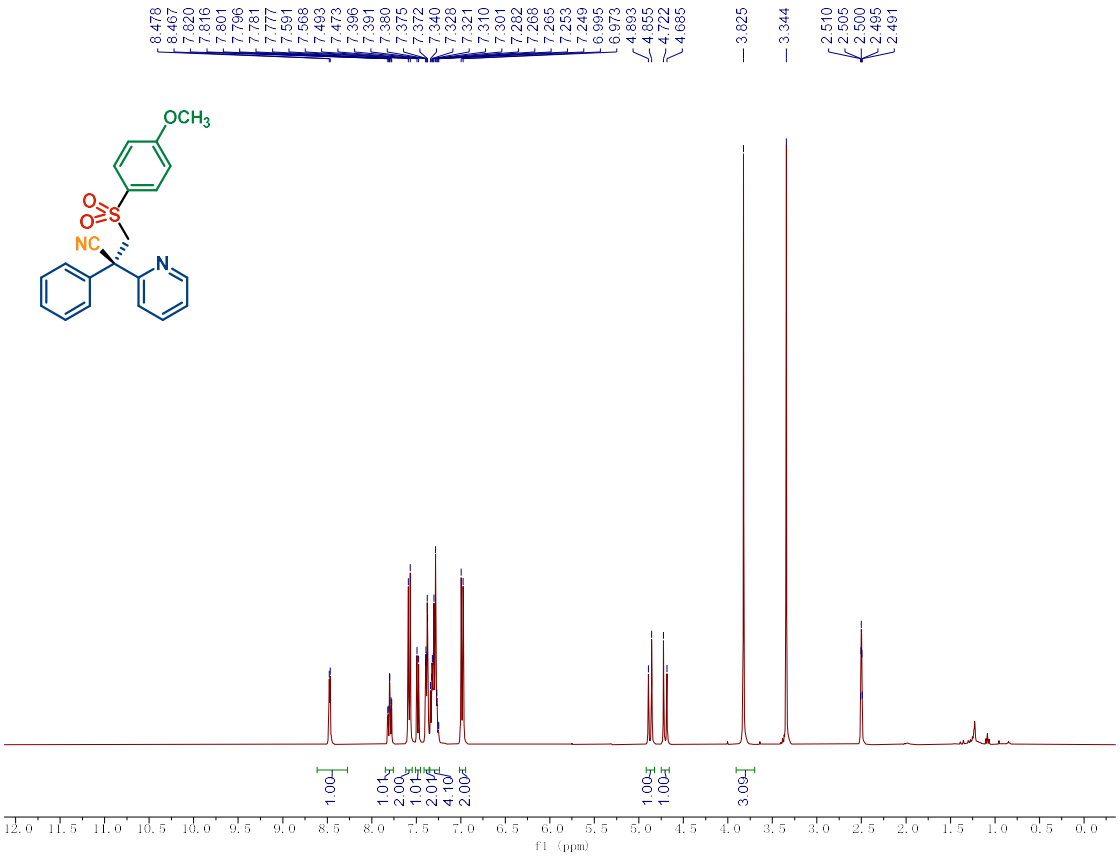


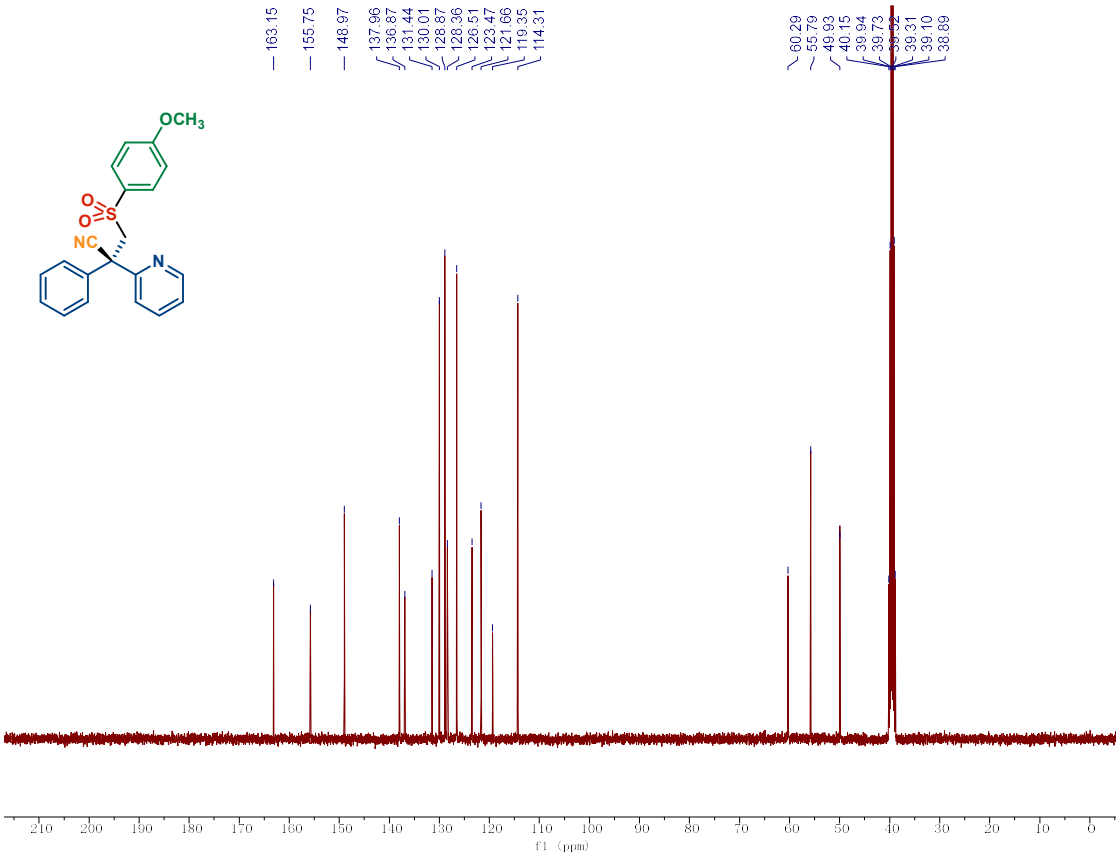
NMR of Compound of 3ar



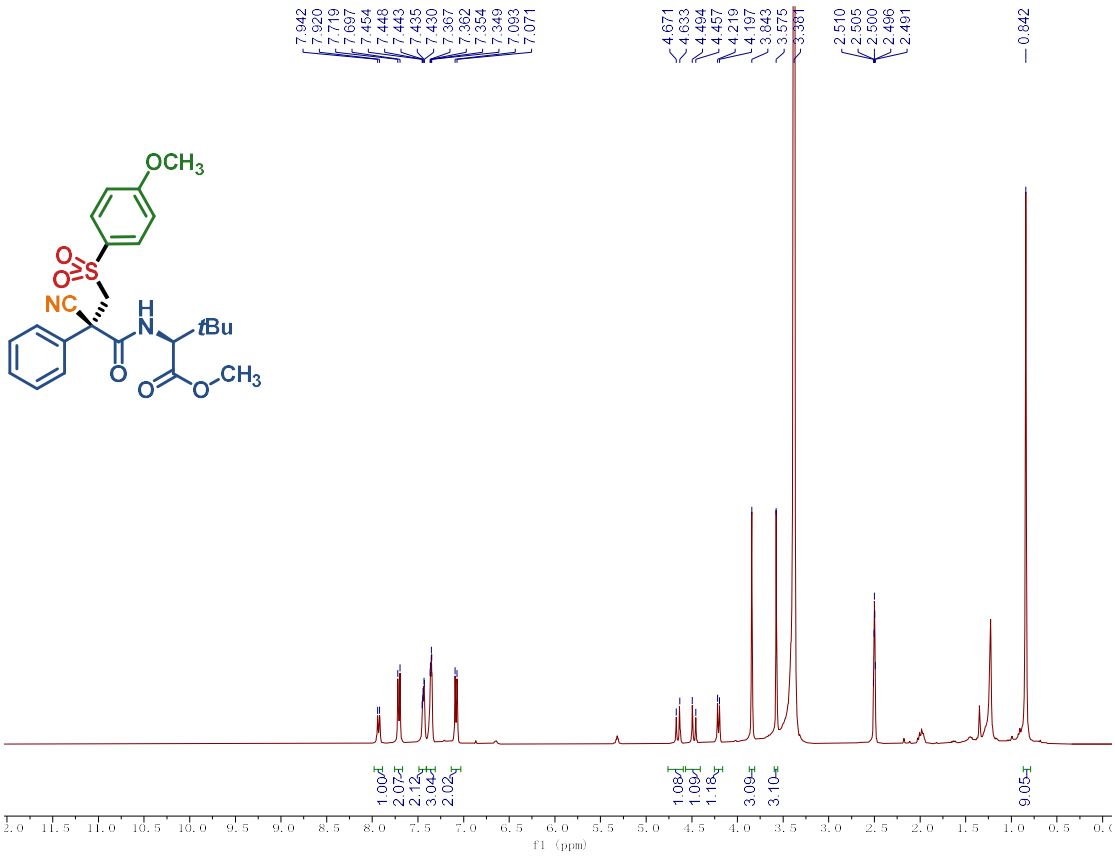


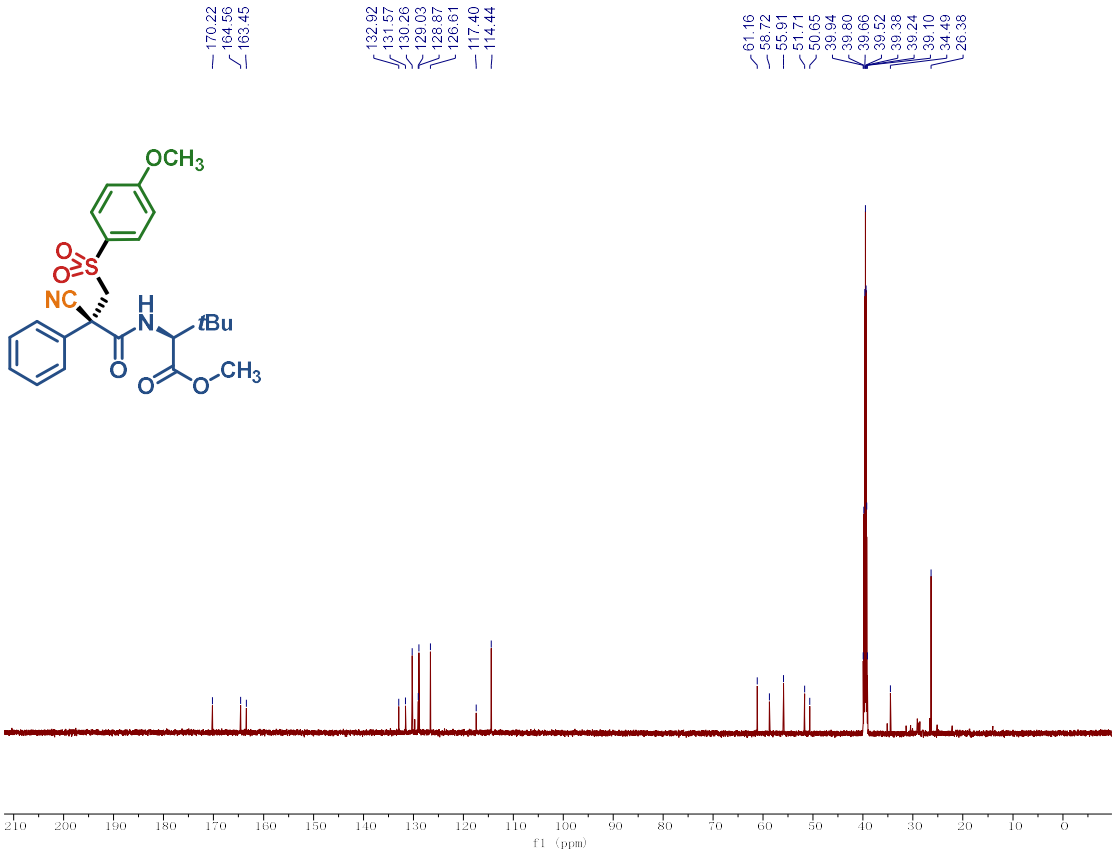
NMR of Compound of 3as



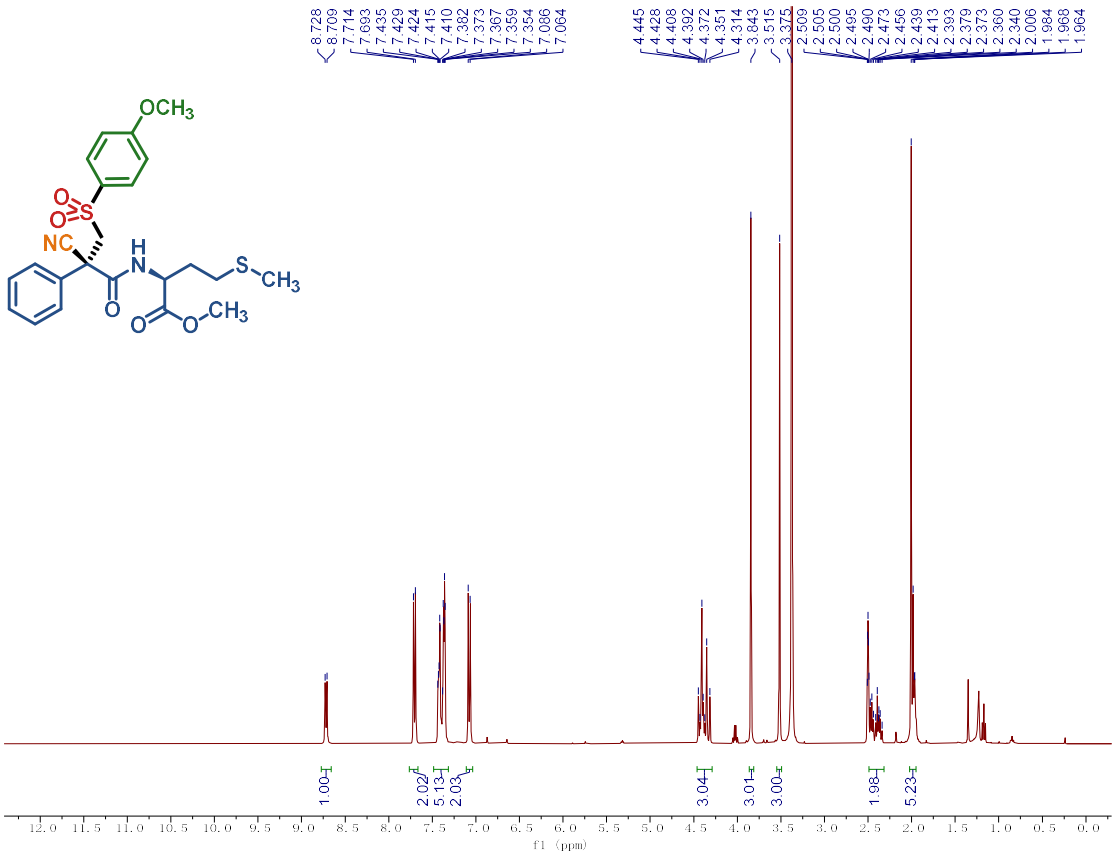


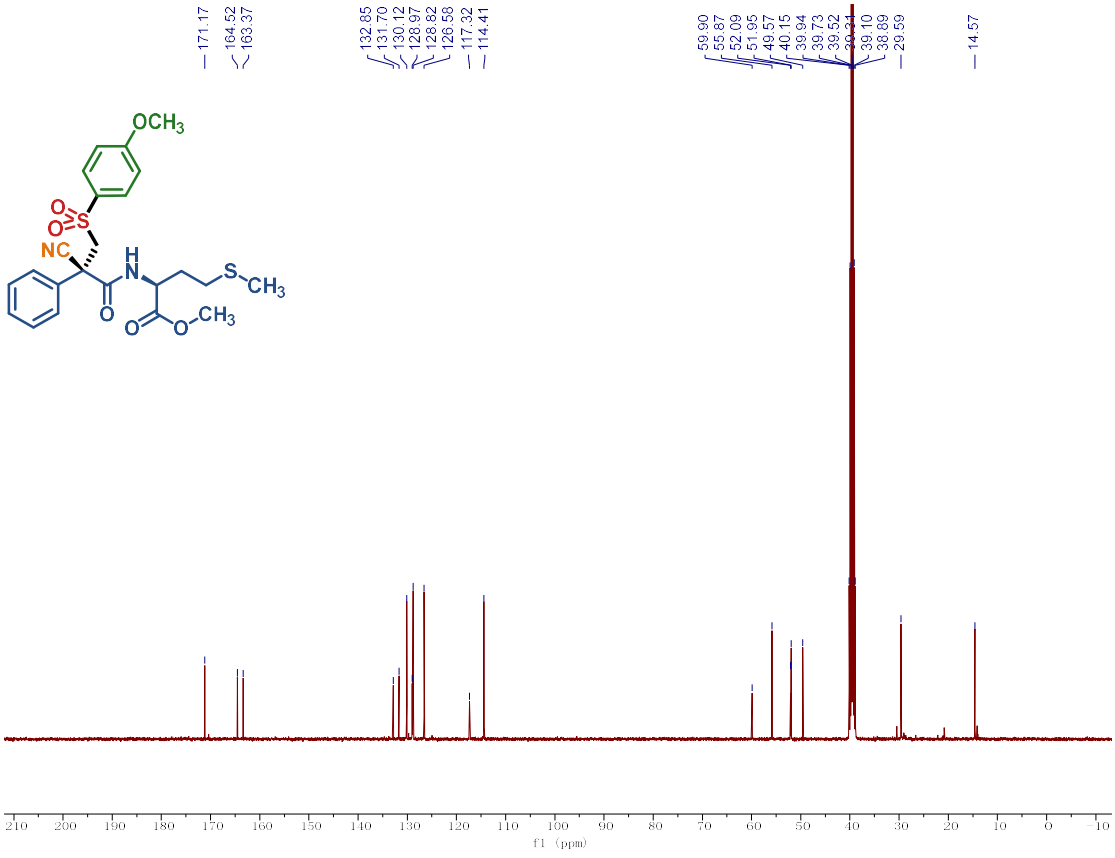
NMR of Compound of 5a



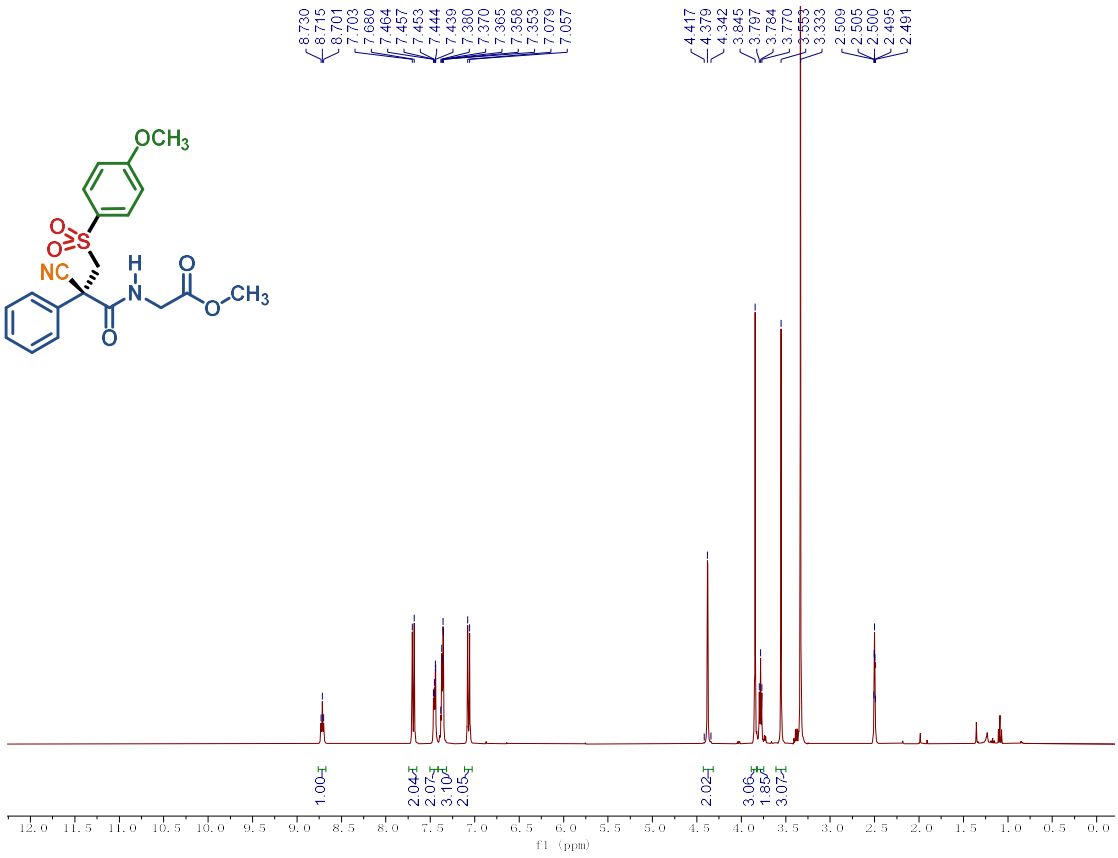


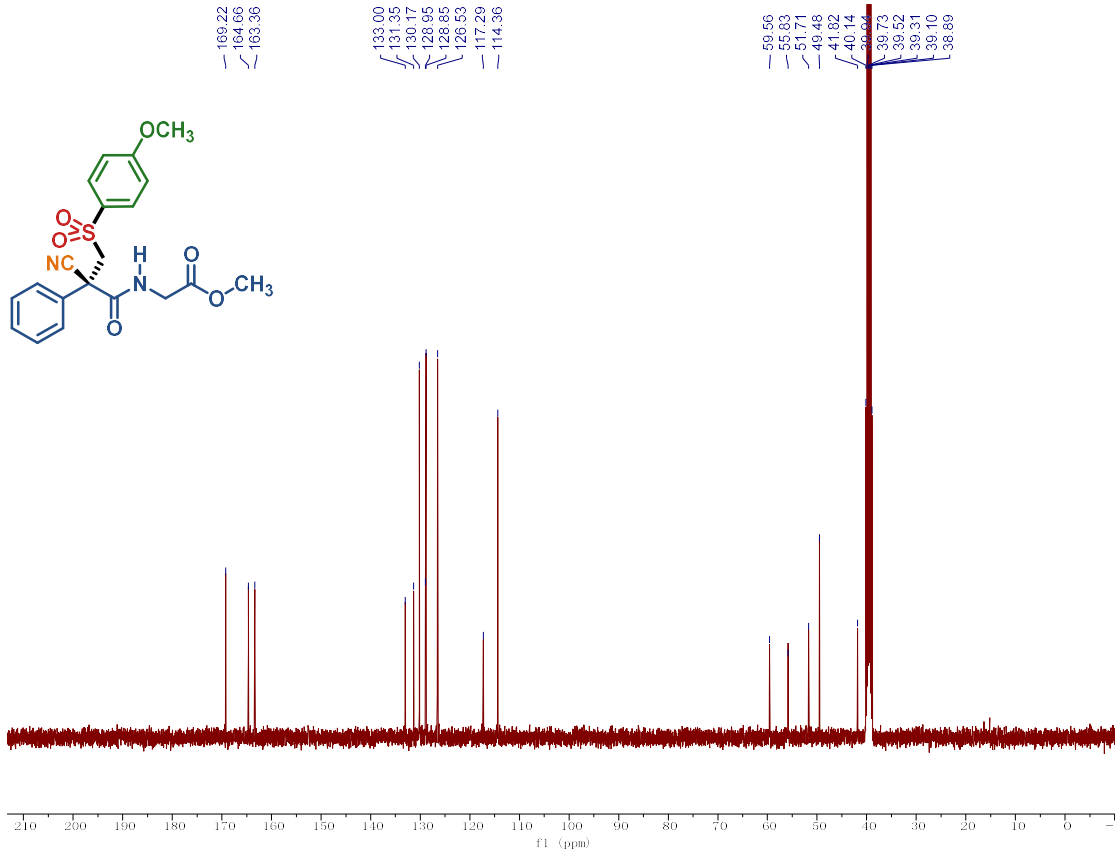
NMR of Compound of 5b



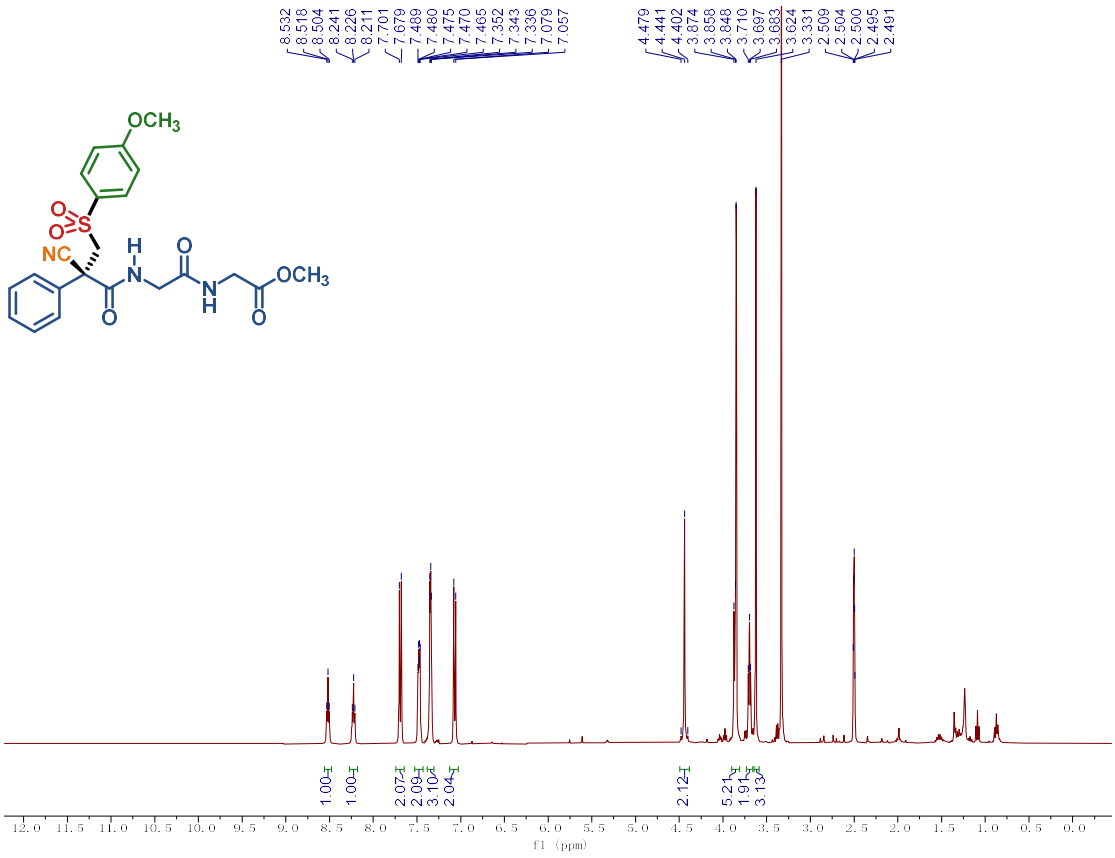


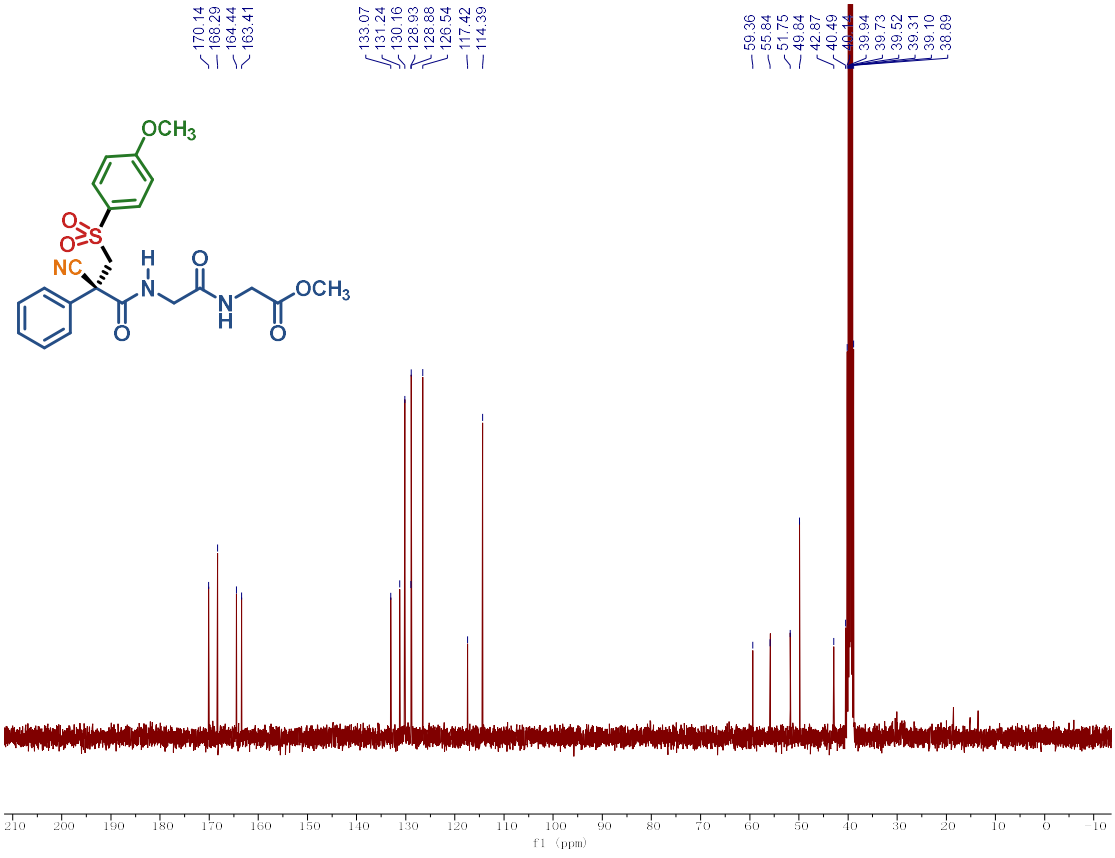
NMR of Compound of 5c



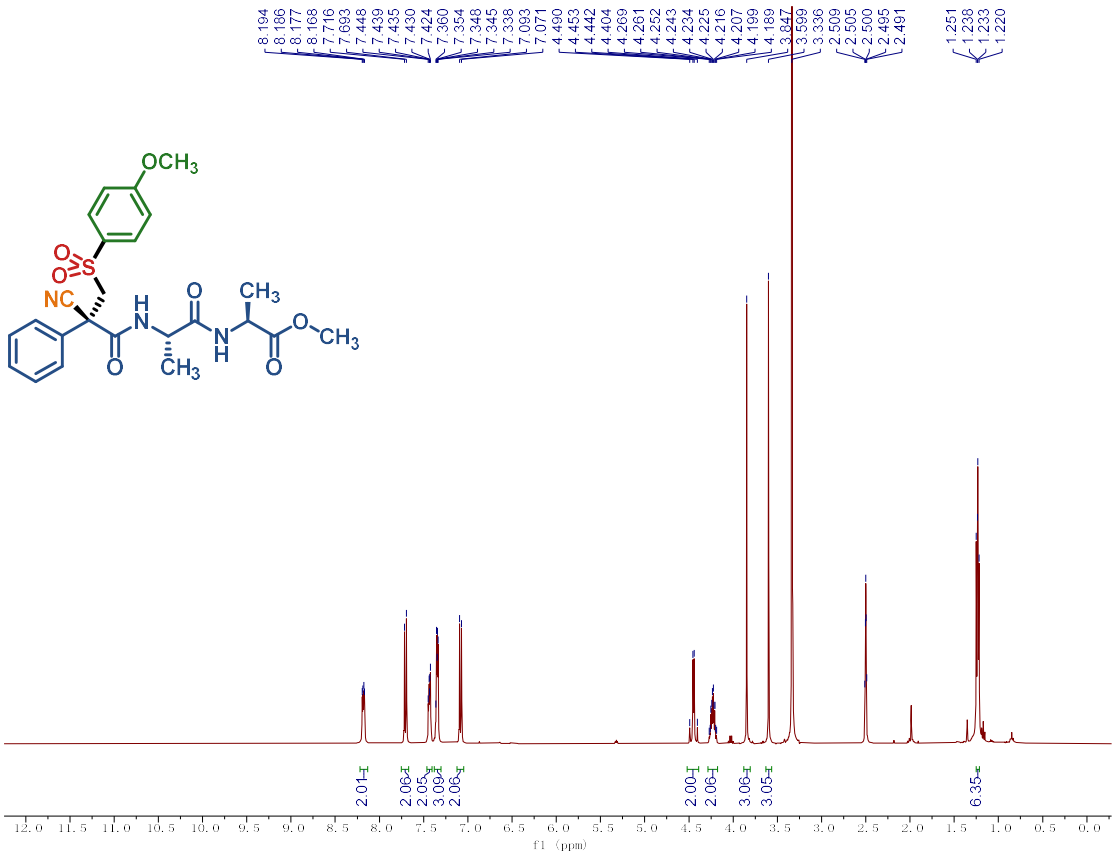


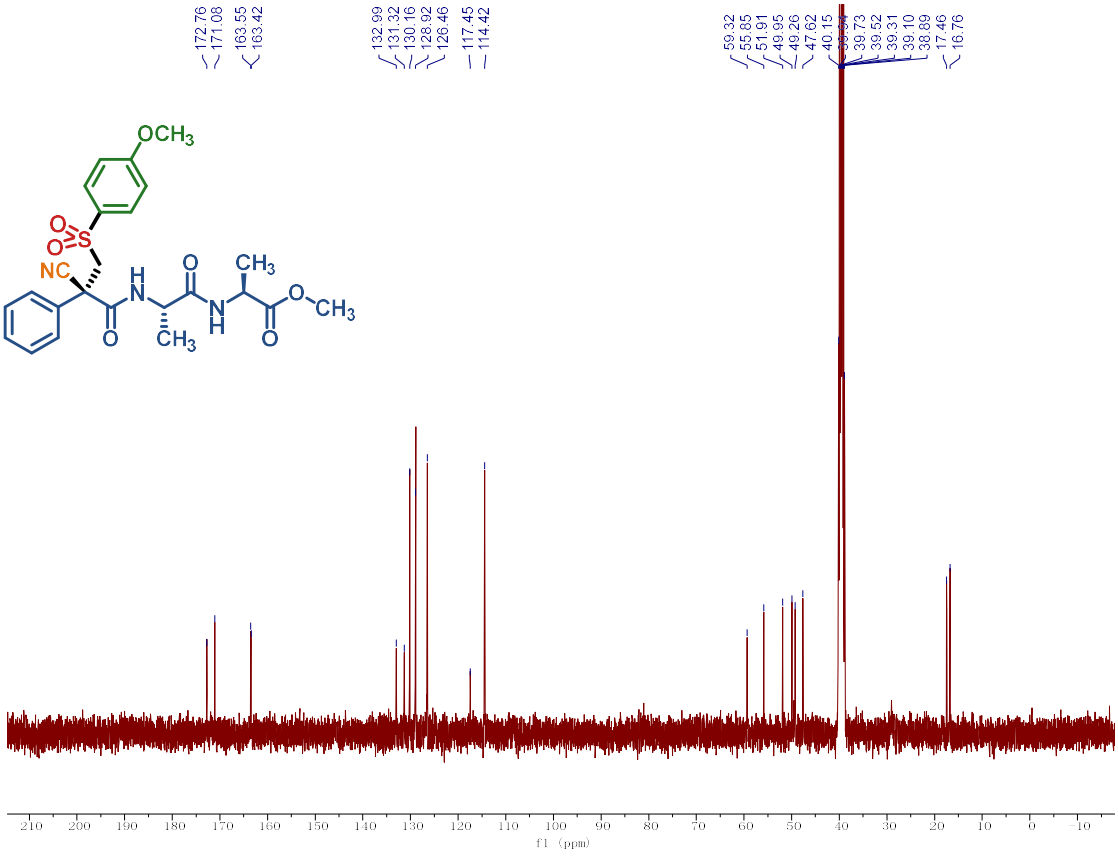
NMR of Compound of 5d



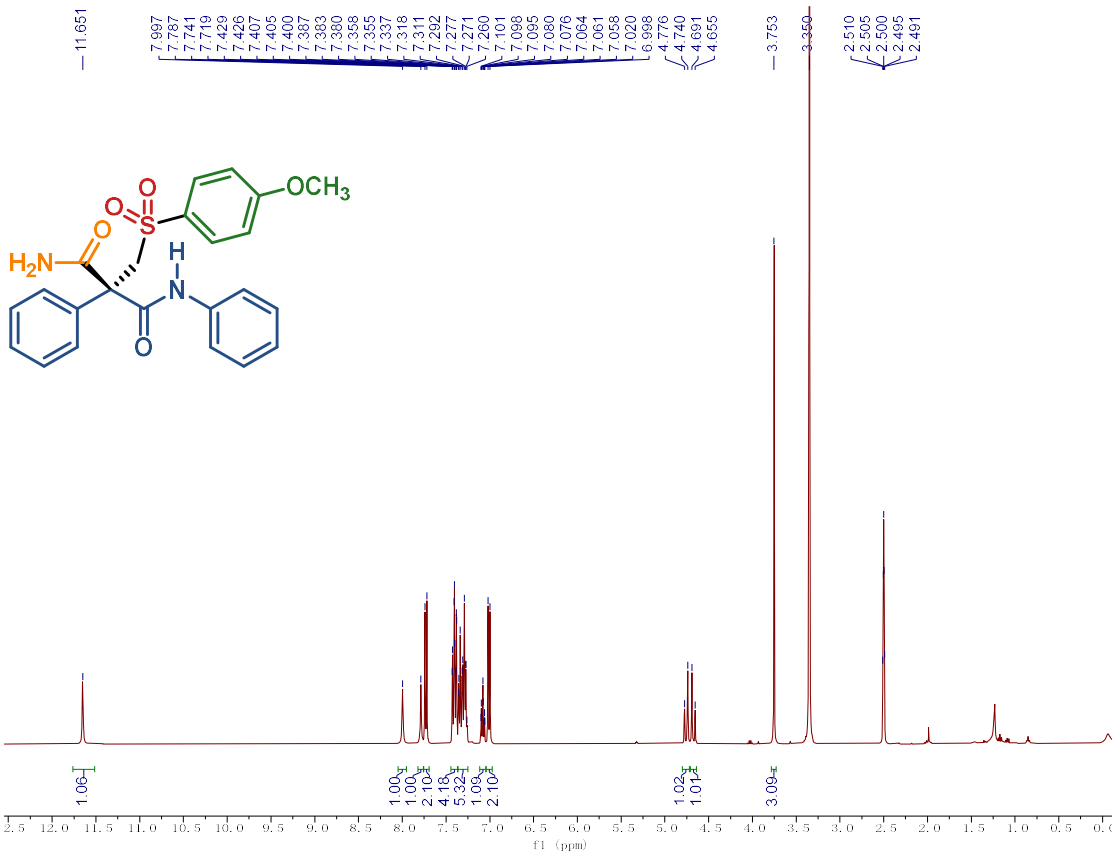


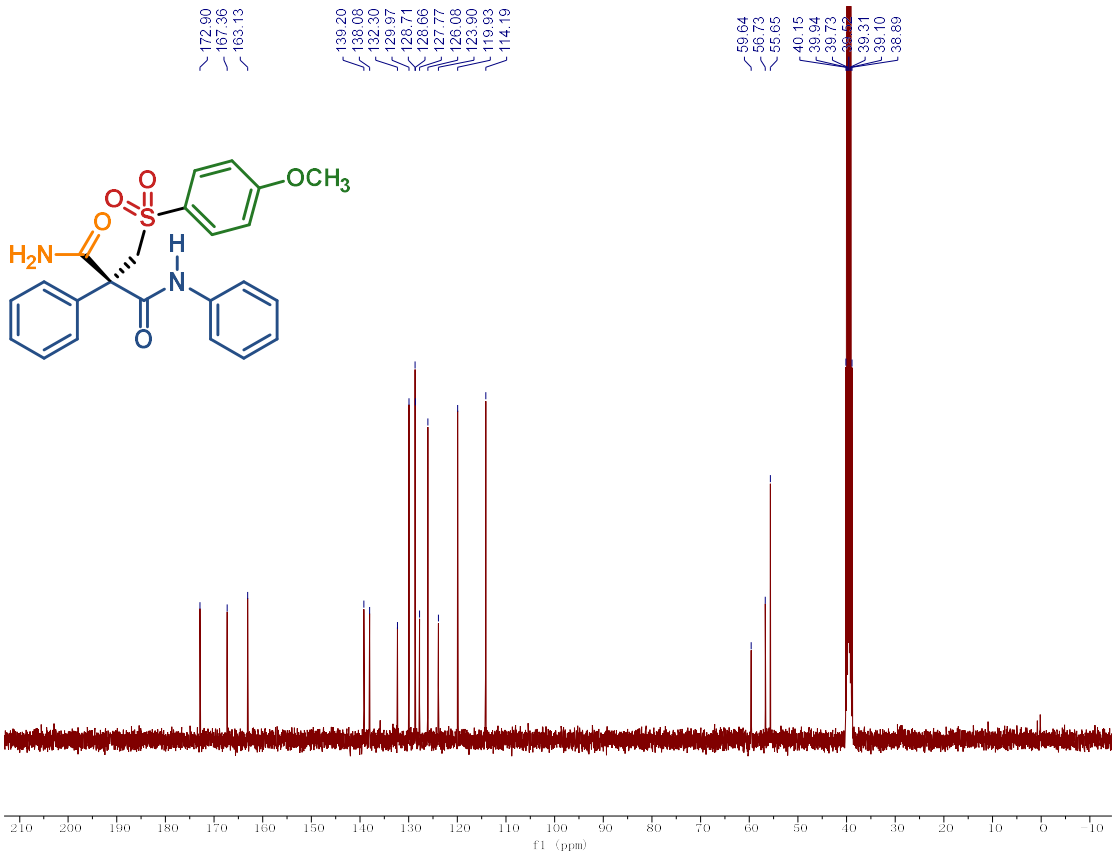
NMR of Compound of 5e



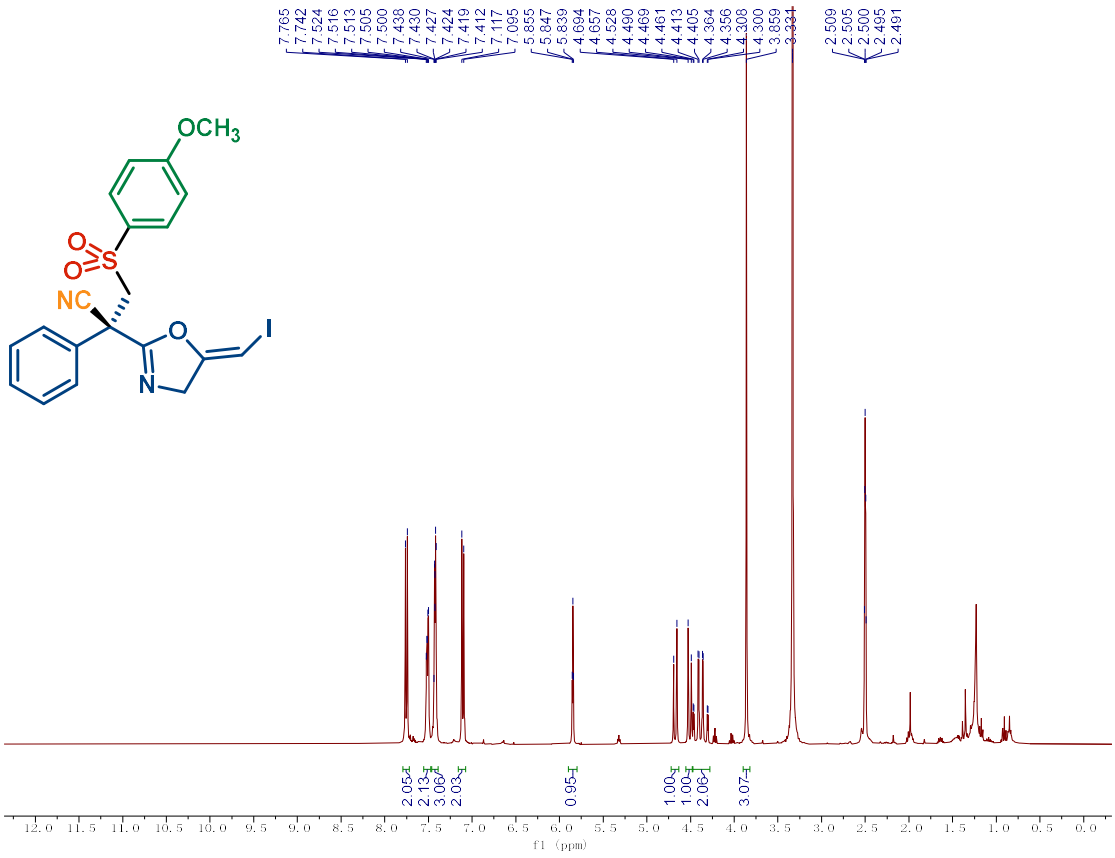


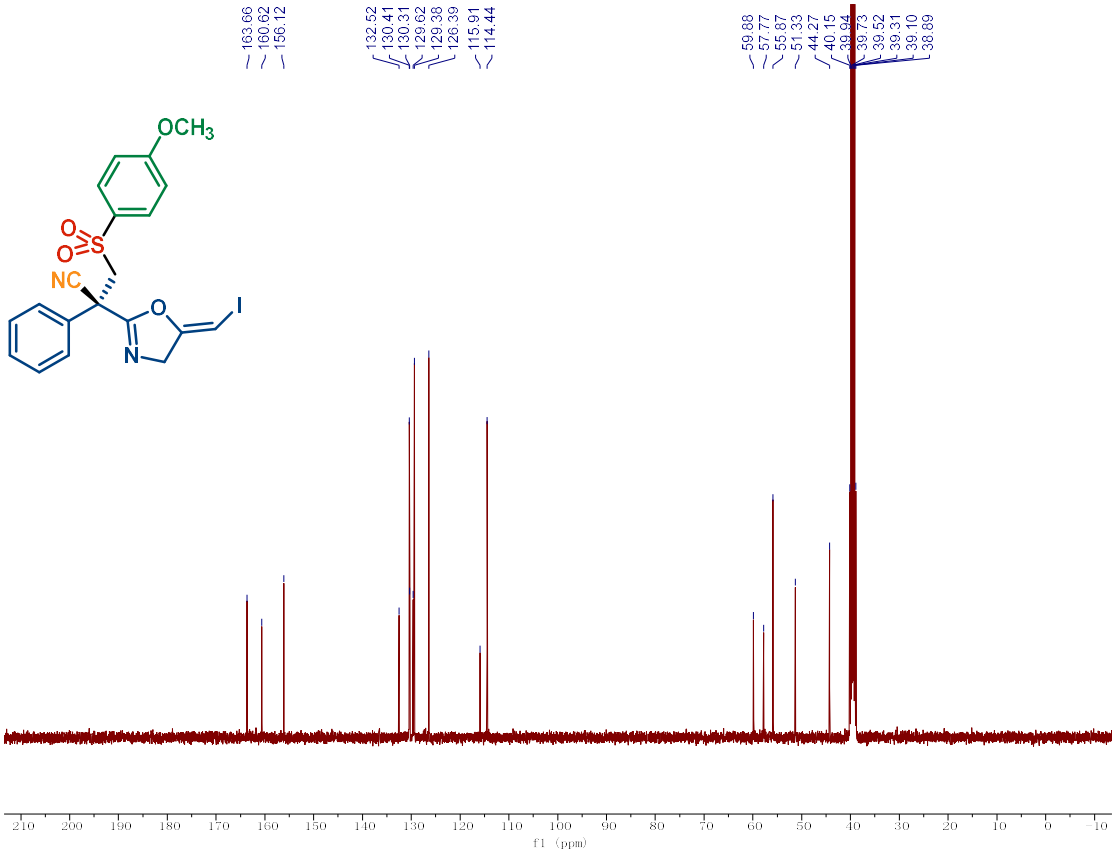
NMR of Compound of 6



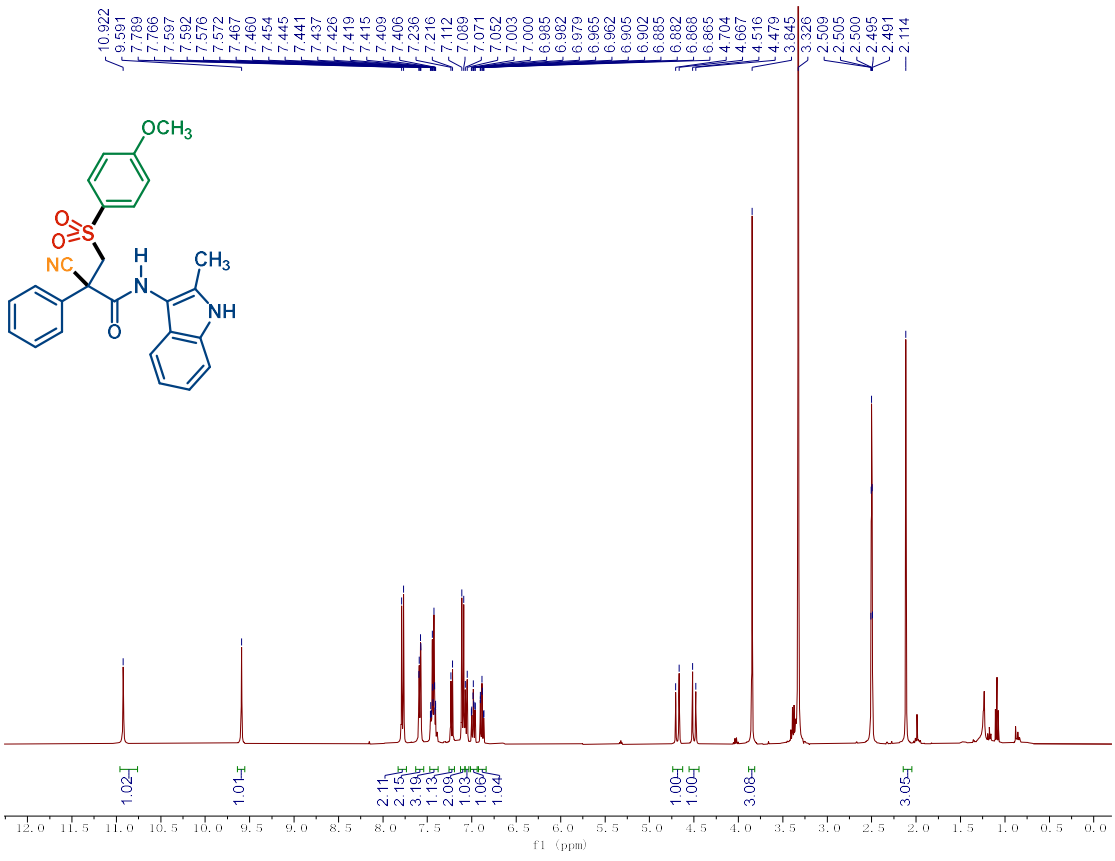


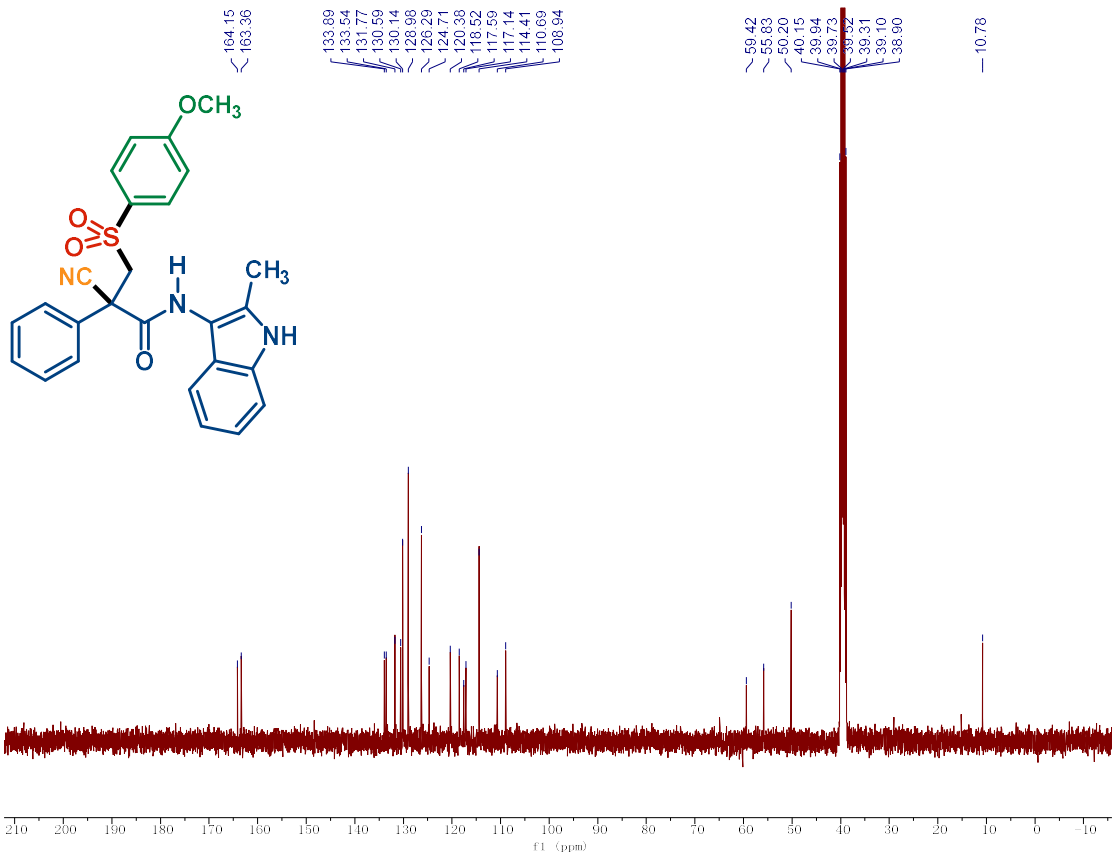
NMR of Compound of 7



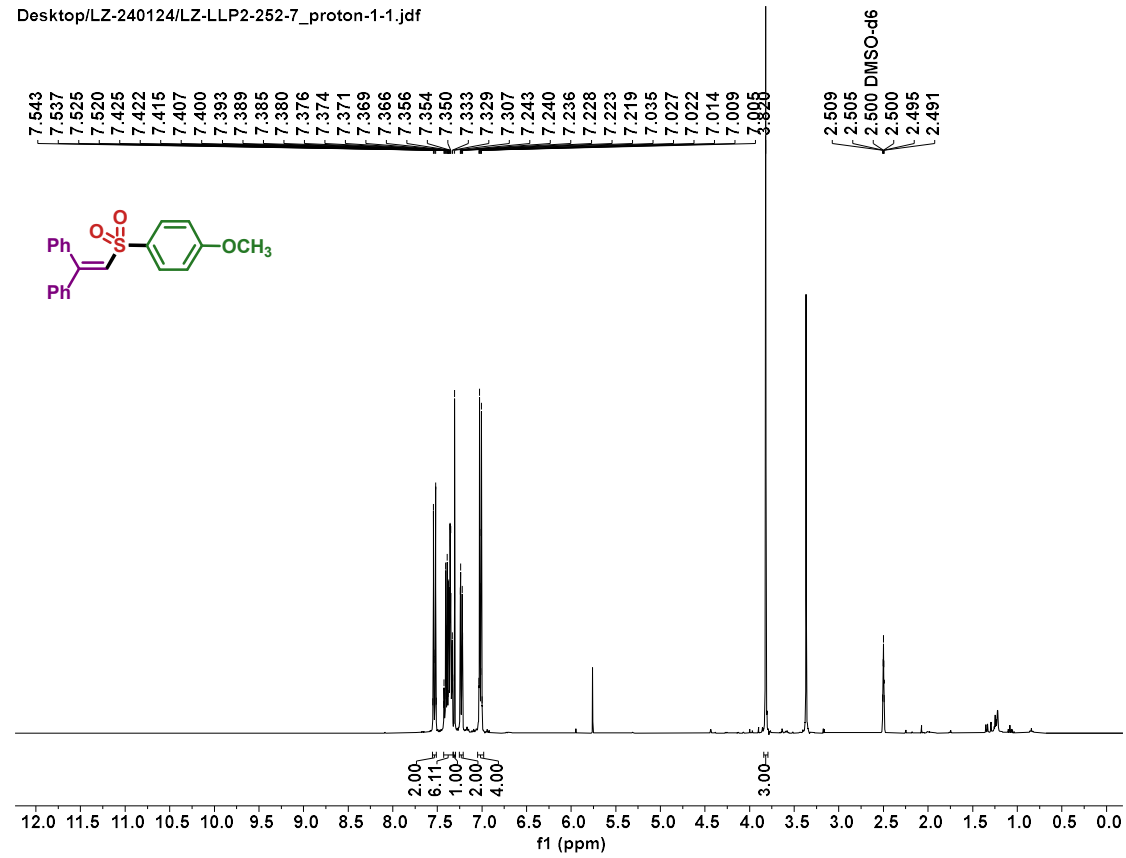


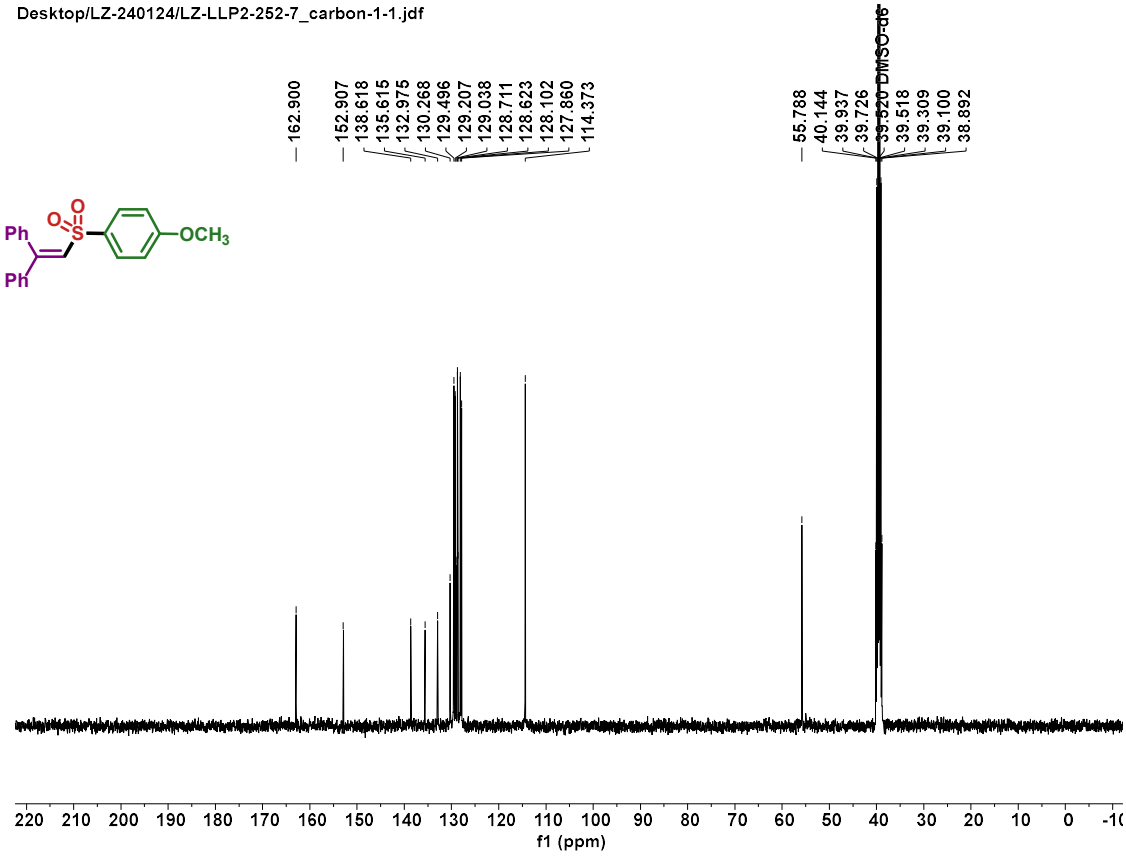
NMR of Compound of 8



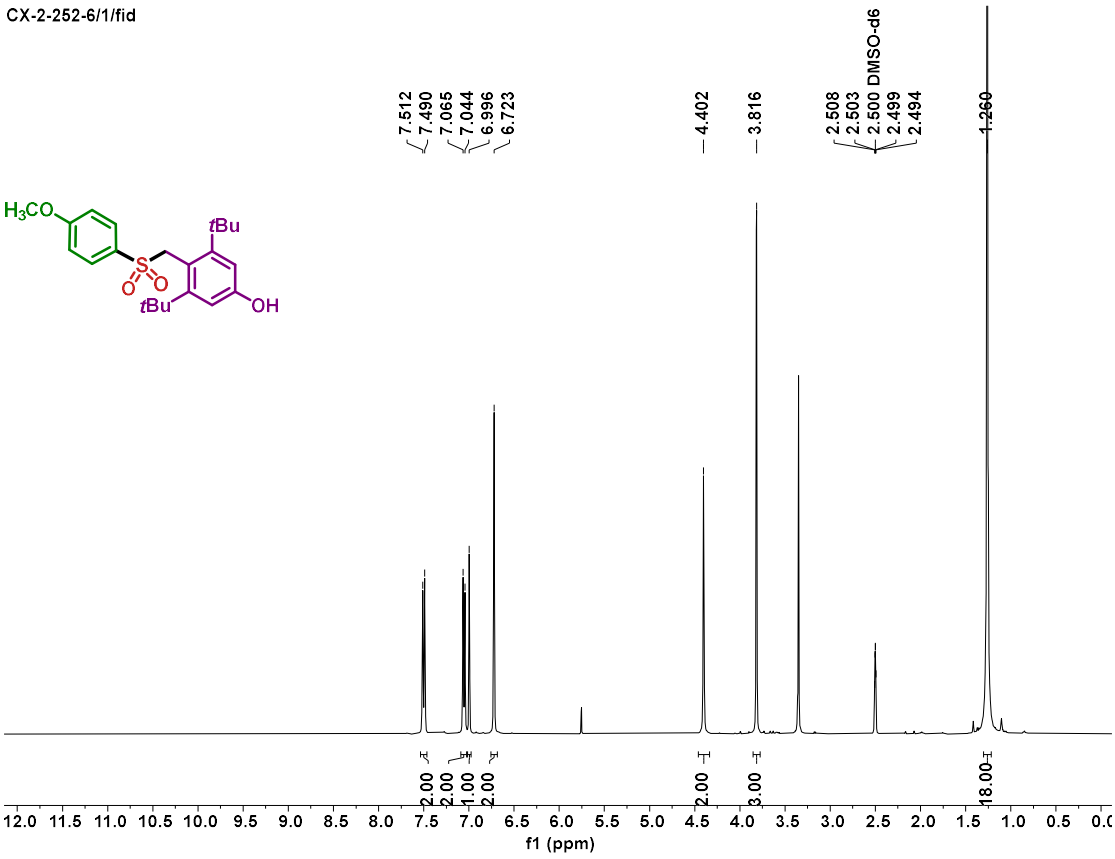


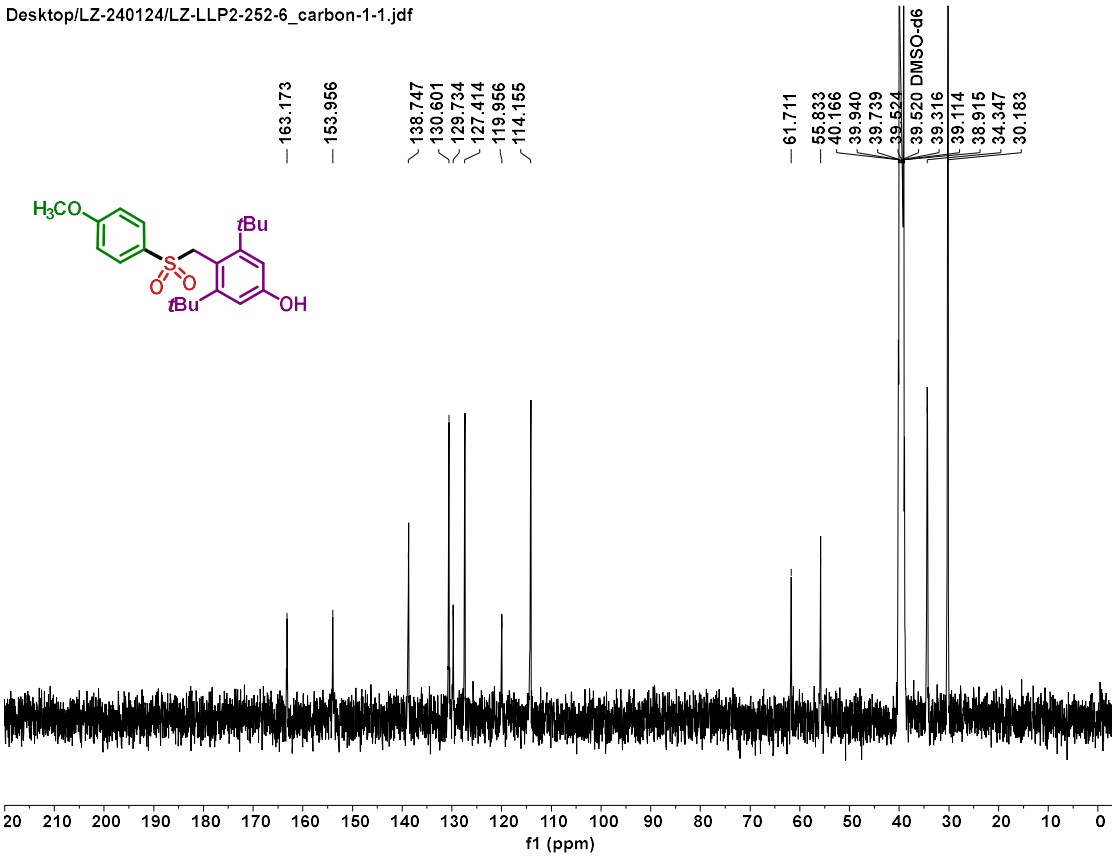
NMR of Compound of 9



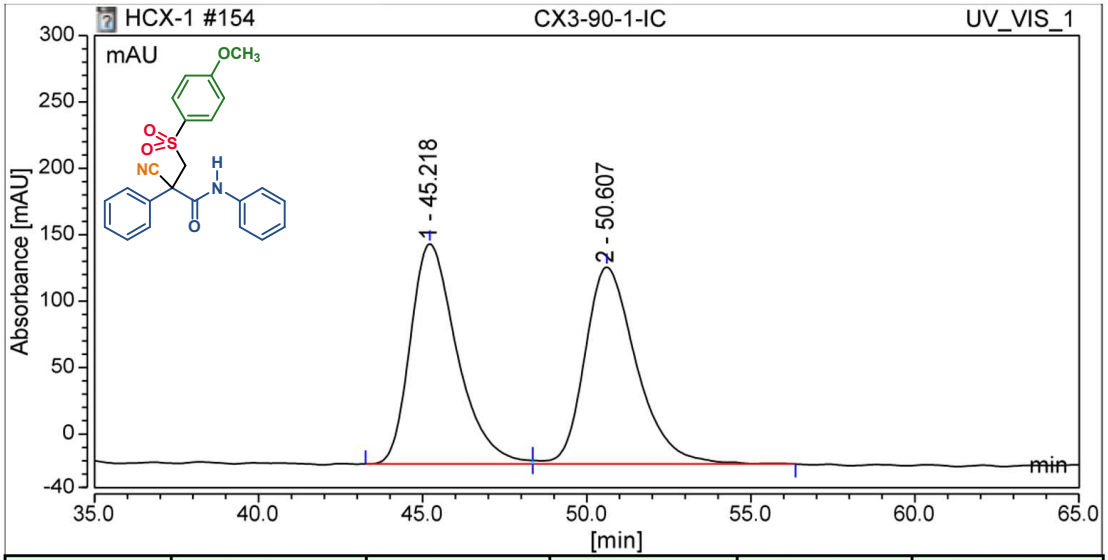


NMR of Compound of 10

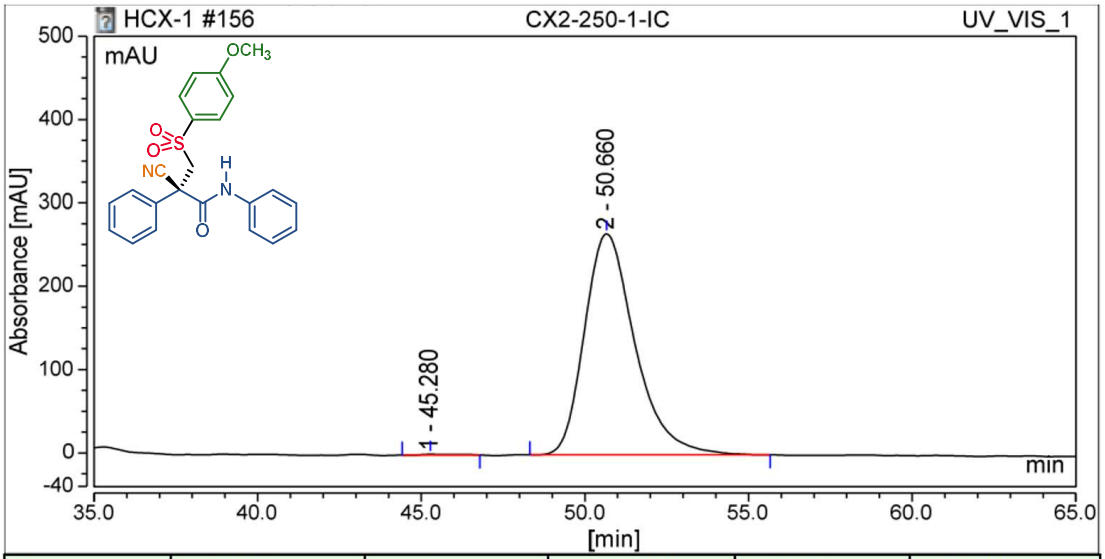




HPLC chromatograms of Compound of 3a

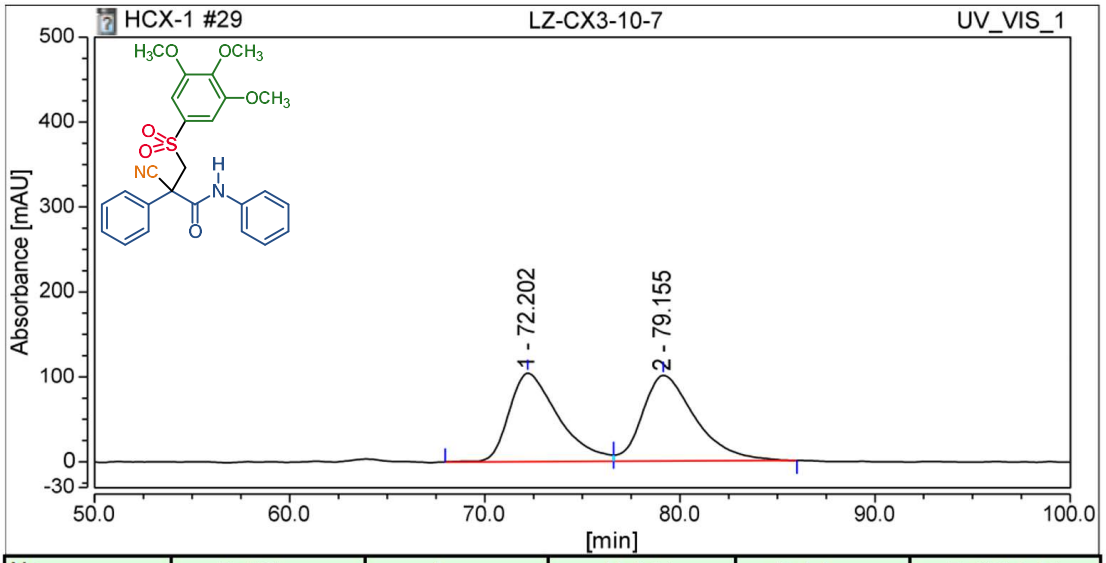


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	45.22	273.231	165.694	50.23	52.78
2	50.61	270.756	148.210	49.77	47.22
Total:		**543.987**	**313.904**	**100.00**	**100.00**

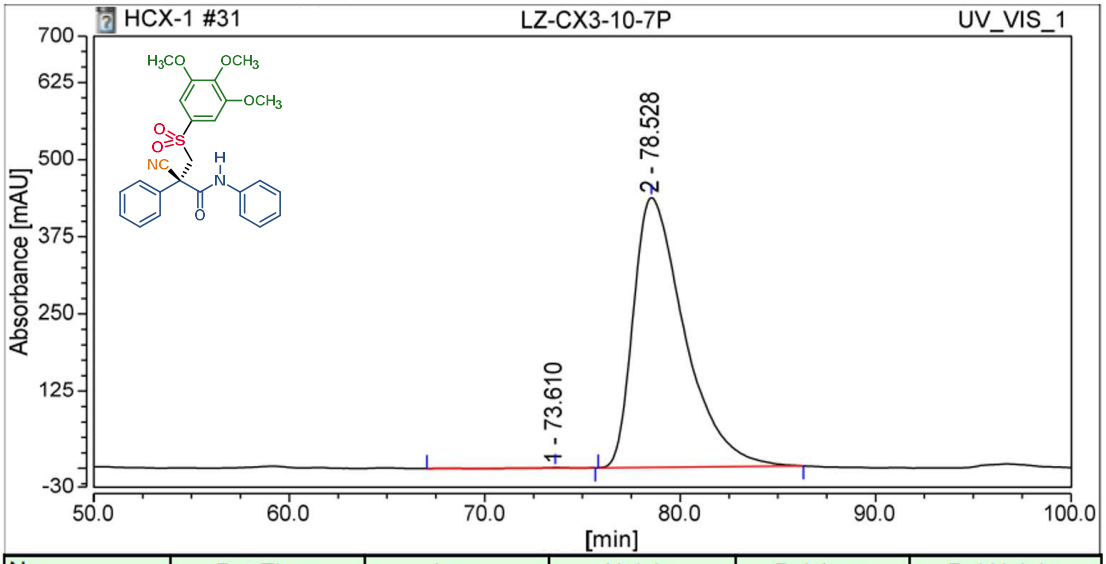


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	45.28	1.062	0.893	0.22	0.34
2	50.66	472.755	265.077	99.78	99.66
Total:		**473.817**	**265.970**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3b

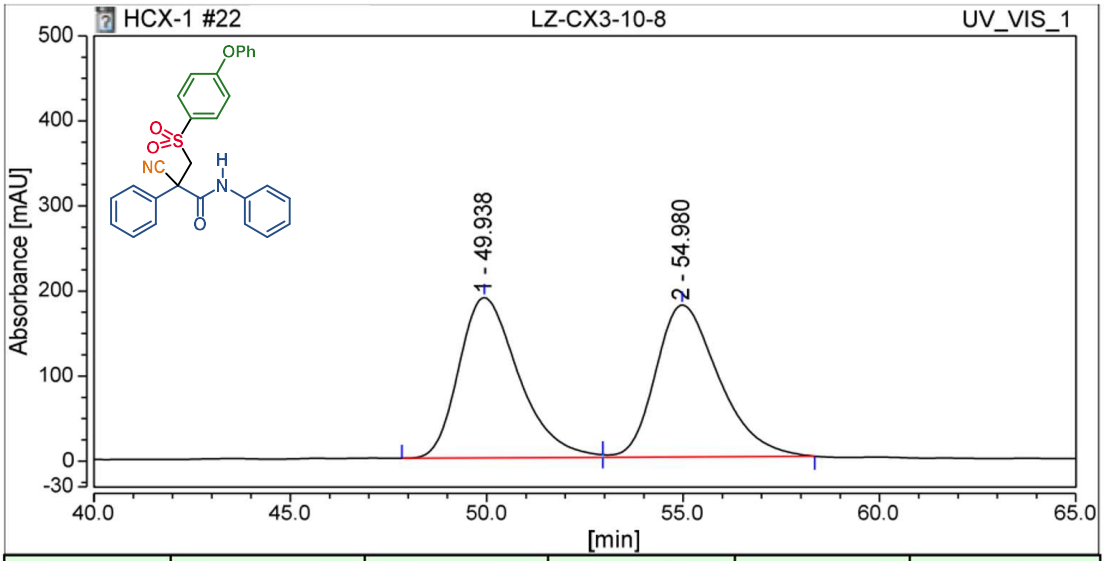


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	72.20	303.591	104.187	49.02	50.82
2	79.15	315.785	100.812	50.98	49.18
Total:		**619.376**	**205.000**	**100.00**	**100.00**

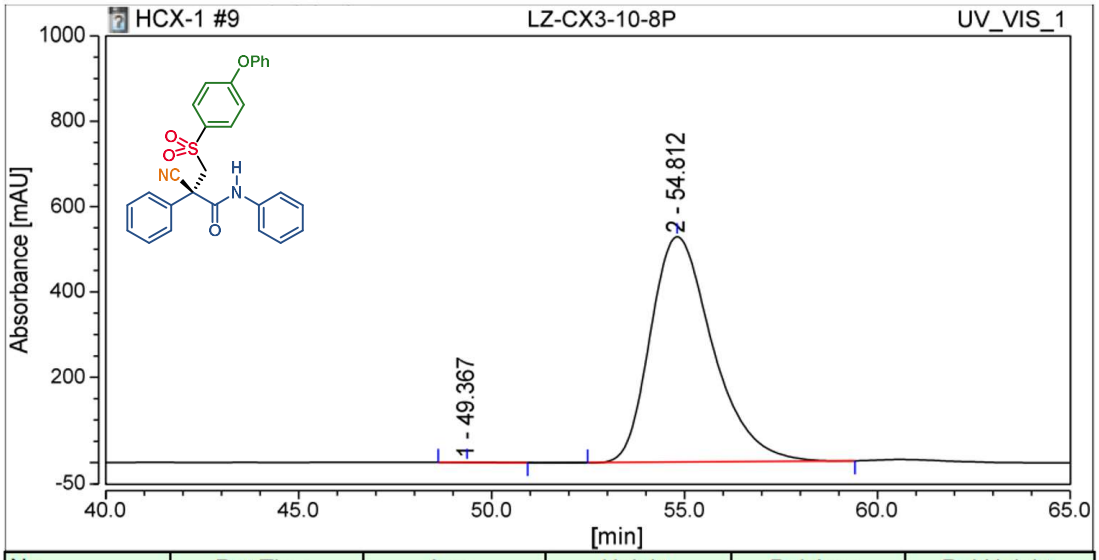


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	73.61	0.391	0.664	0.03	0.15
2	78.53	1322.190	436.807	99.97	99.85
Total:		**1322.580**	**437.472**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3c

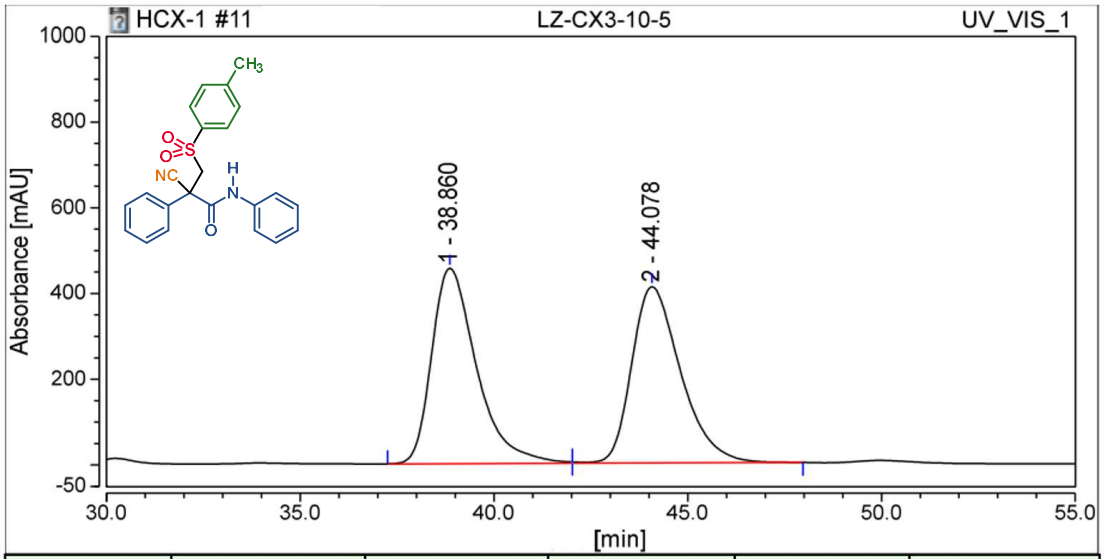


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	49.94	332.207	188.432	49.92	51.36
2	54.98	333.306	178.434	50.08	48.64
Total:		**665.513**	**366.866**	**100.00**	**100.00**

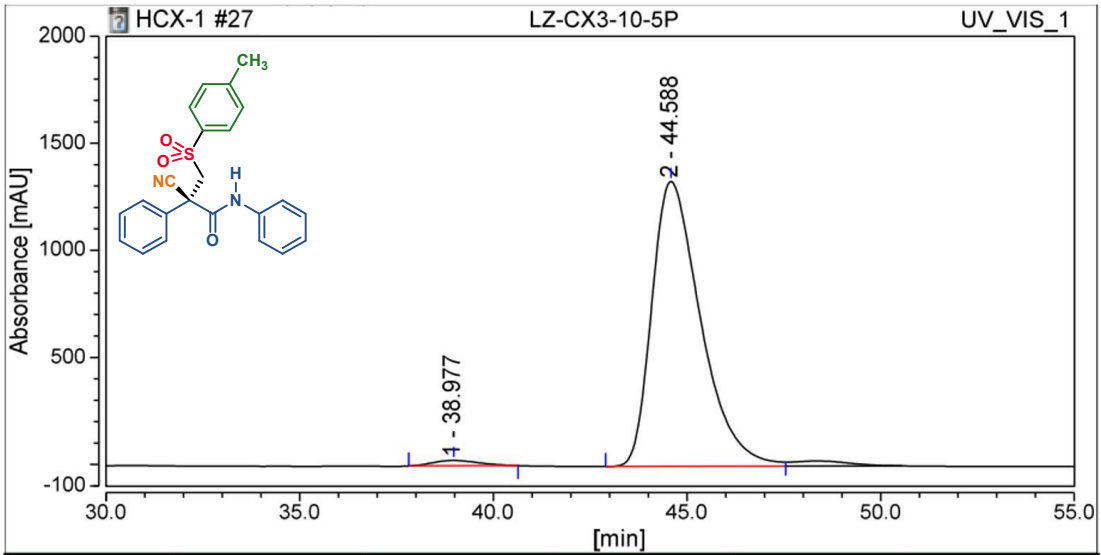


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	49.37	0.994	0.571	0.10	0.11
2	54.81	985.623	527.735	99.90	99.89
Total:		**986.617**	**528.306**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3d

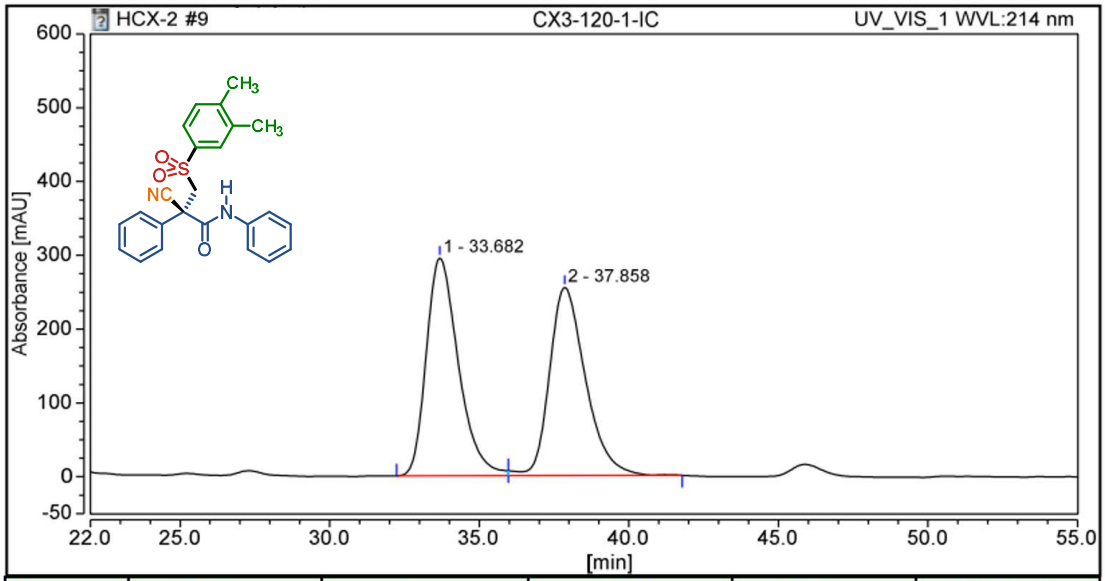


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	38.86	610.844	456.358	50.36	52.60
2	44.08	602.108	411.261	49.64	47.40
Total:		**1212.952**	**867.619**	**100.00**	**100.00**

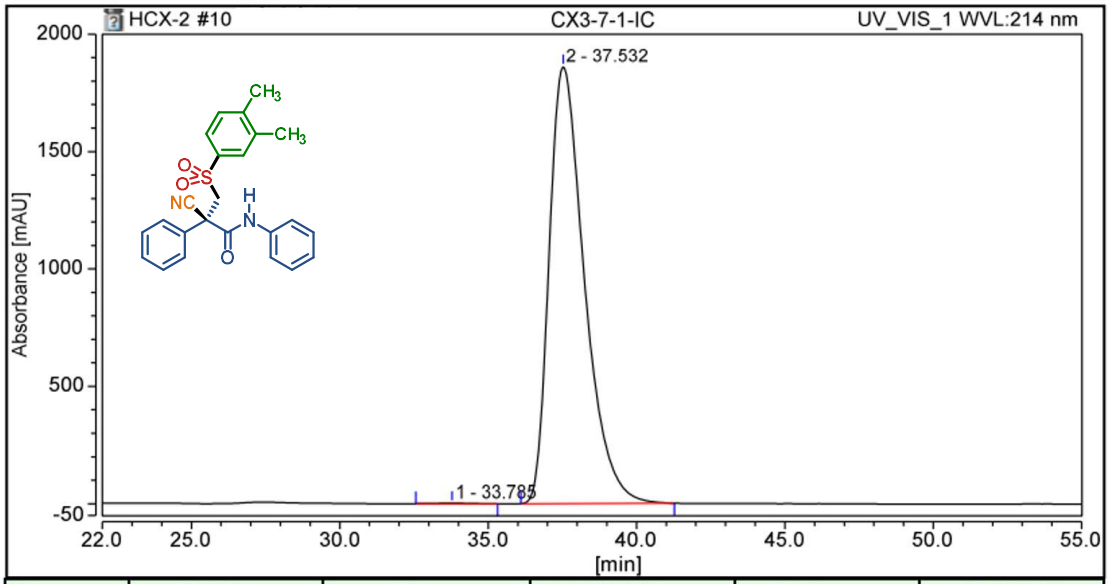


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	38.98	34.892	25.267	1.77	1.86
2	44.59	1941.647	1330.962	98.23	98.14
Total:		**1976.540**	**1356.229**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3e

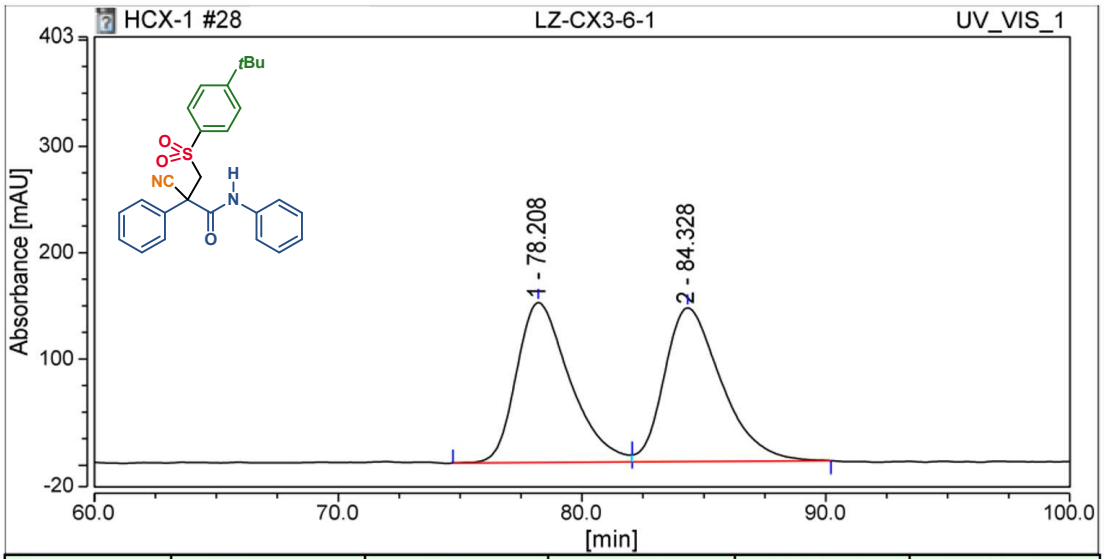


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	33.682	366.852	295.161	50.73	53.65
2	37.858	356.301	254.980	49.27	46.35
Total:		**723.153**	**550.142**	**100.00**	**100.00**

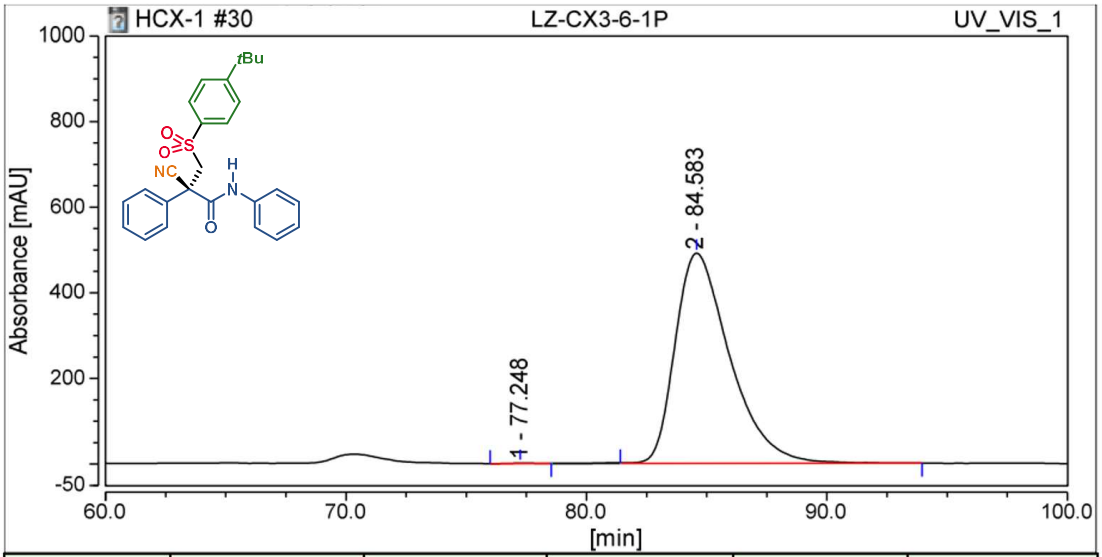


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	33.785	3.081	2.047	0.12	0.11
2	37.532	2561.965	1860.339	99.88	99.89
Total:		**2565.045**	**1862.386**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3f

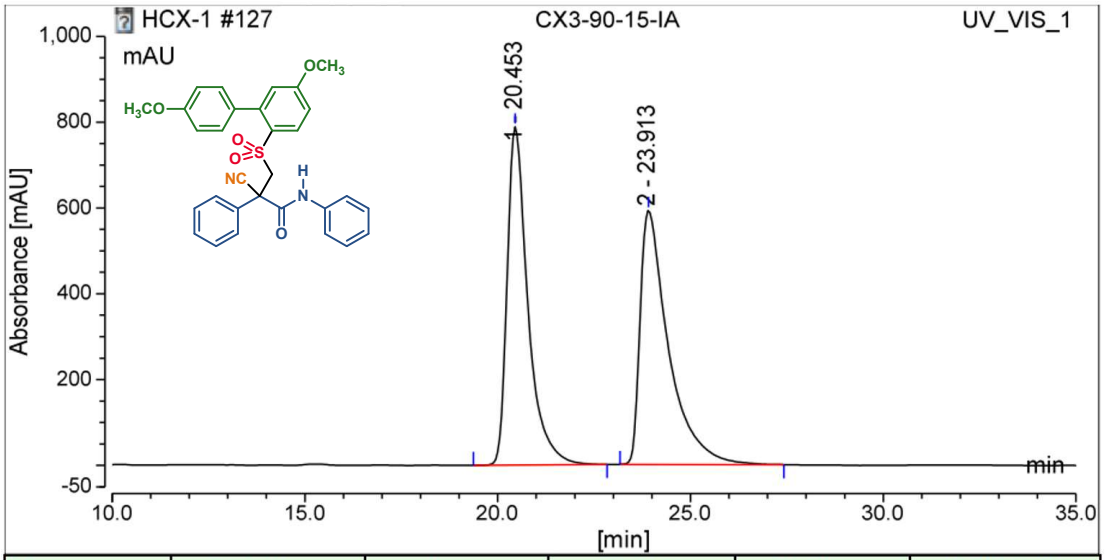


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	78.21	381.601	150.609	49.38	51.01
2	84.33	391.254	144.663	50.62	48.99
Total:		**772.856**	**295.272**	**100.00**	**100.00**

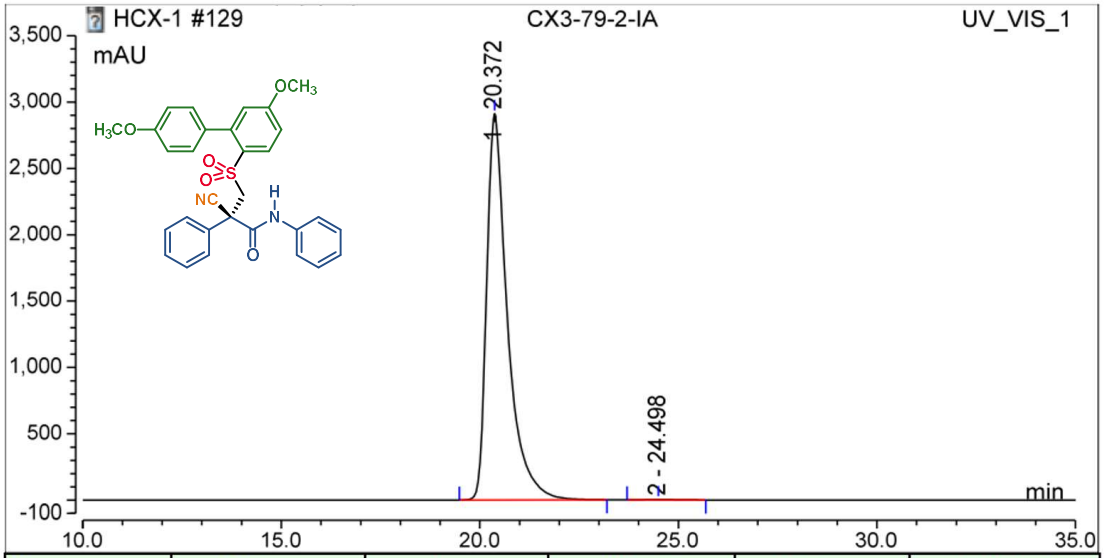


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	77.25	1.211	0.958	0.09	0.19
2	84.58	1291.952	491.396	99.91	99.81
Total:		**1293.163**	**492.354**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3g

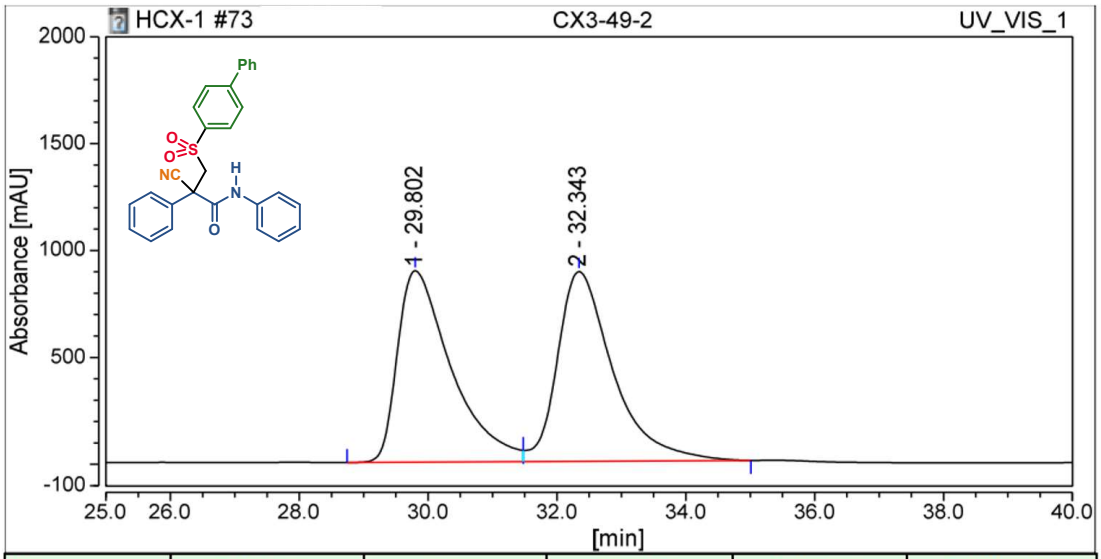


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.45	492.131	788.349	49.44	57.11
2	23.91	503.334	592.066	50.56	42.89
Total:		**995.465**	**1380.415**	**100.00**	**100.00**

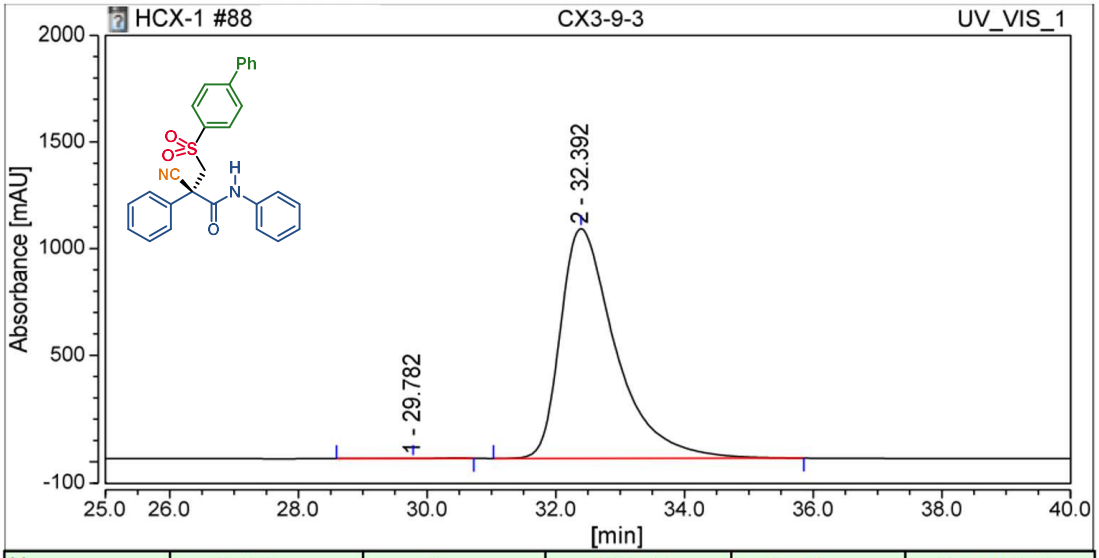


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.37	1760.082	2910.030	99.85	99.89
2	24.50	2.576	3.350	0.15	0.11
Total:		**1762.658**	**2913.380**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3h

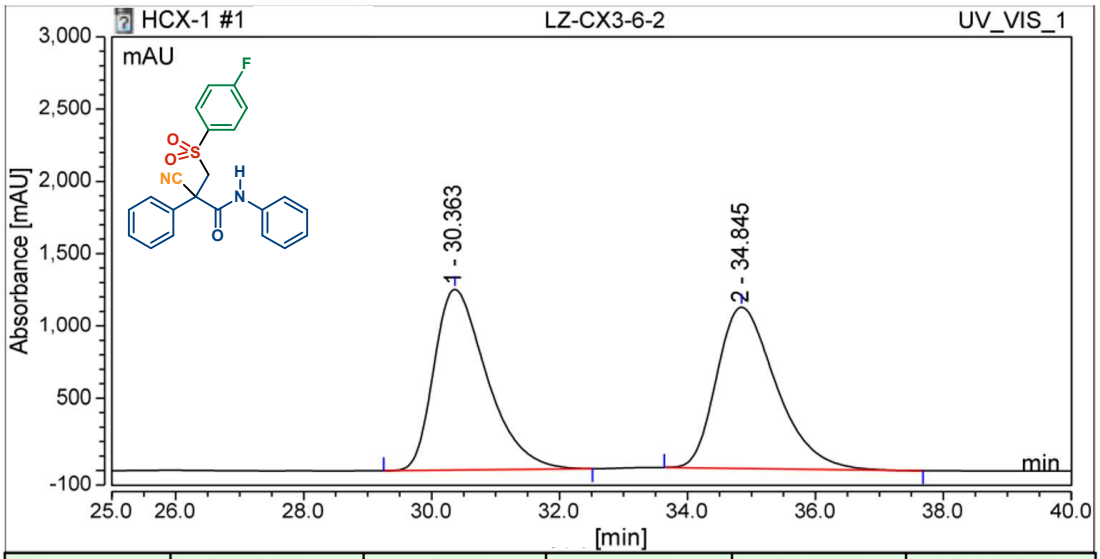


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	29.80	862.337	895.588	49.42	50.22
2	32.34	882.524	887.842	50.58	49.78
Total:		**1744.861**	**1783.430**	**100.00**	**100.00**

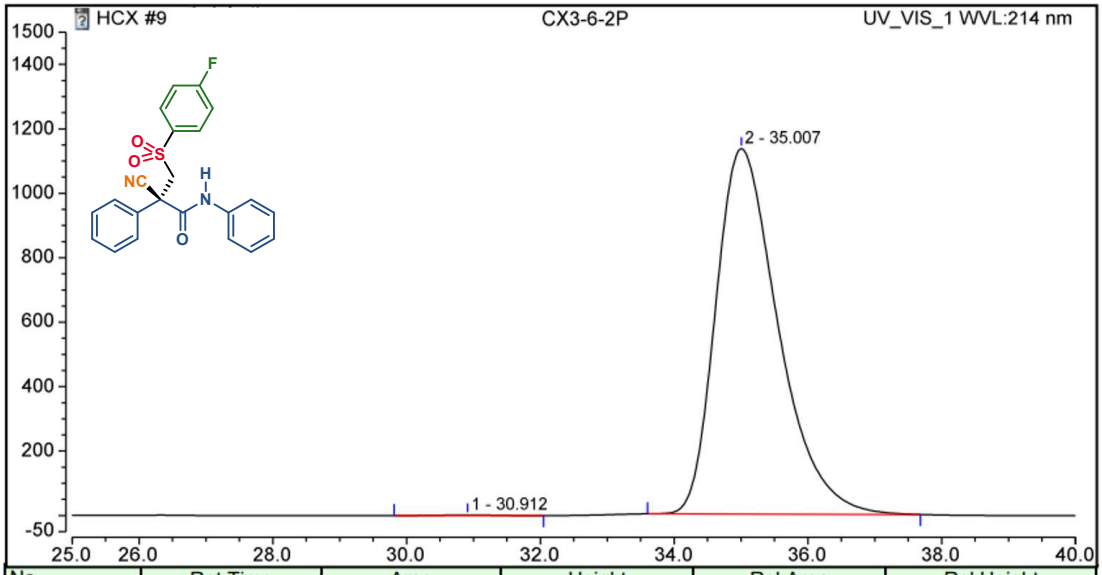


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	29.78	0.432	1.185	0.04	0.11
2	32.39	1072.544	1077.970	99.96	99.89
Total:		**1072.976**	**1079.156**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3i

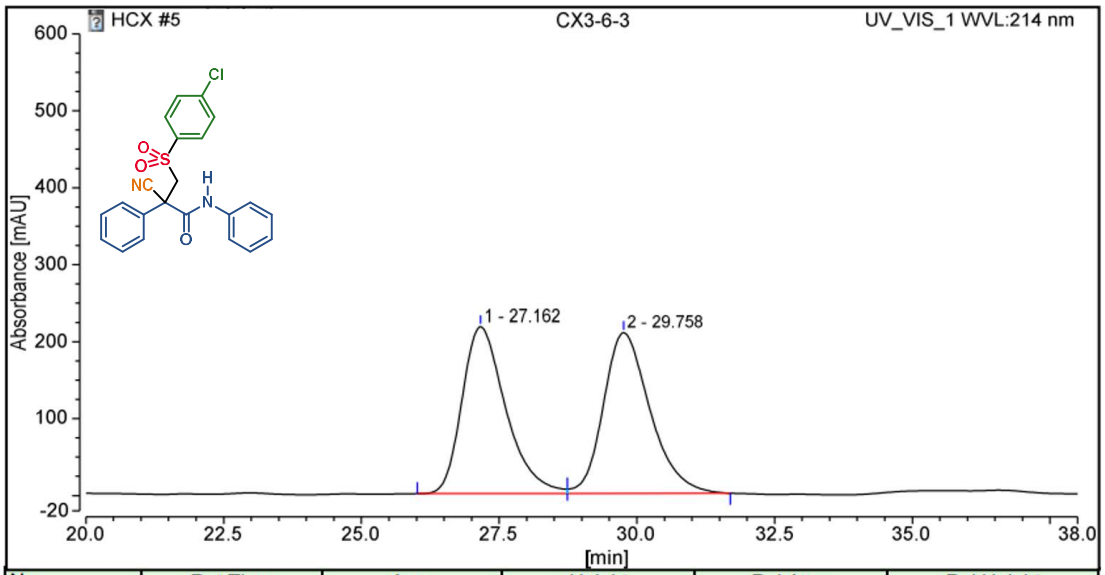


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	30.36	1196.568	1250.096	49.92	52.86
2	34.84	1200.532	1114.871	50.08	47.14
Total:		**2397.100**	**2364.967**	**100.00**	**100.00**

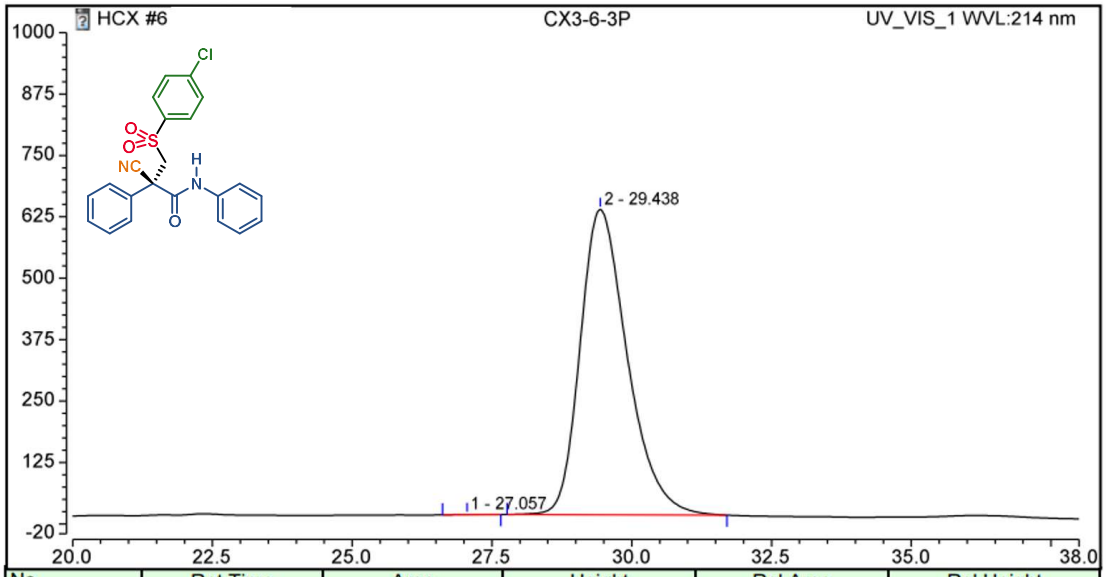


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	30.912	1.880	2.082	0.15	0.18
2	35.007	1225.551	1133.964	99.85	99.82
Total:		**1227.432**	**1136.046**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3j

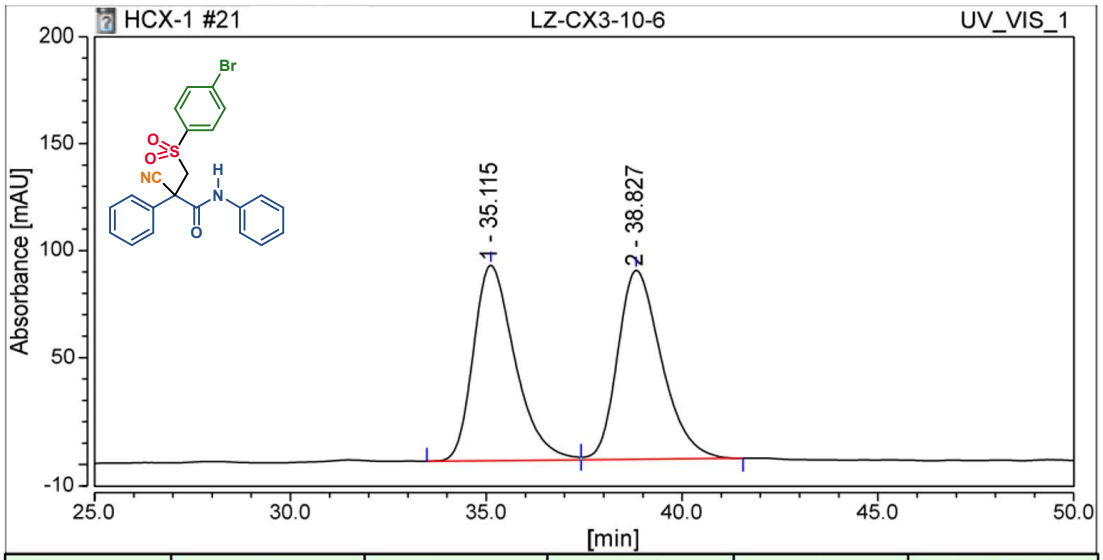


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.162	199.311	216.724	49.34	50.94
2	29.758	204.614	208.757	50.66	49.06
Total:		**403.925**	**425.481**	**100.00**	**100.00**

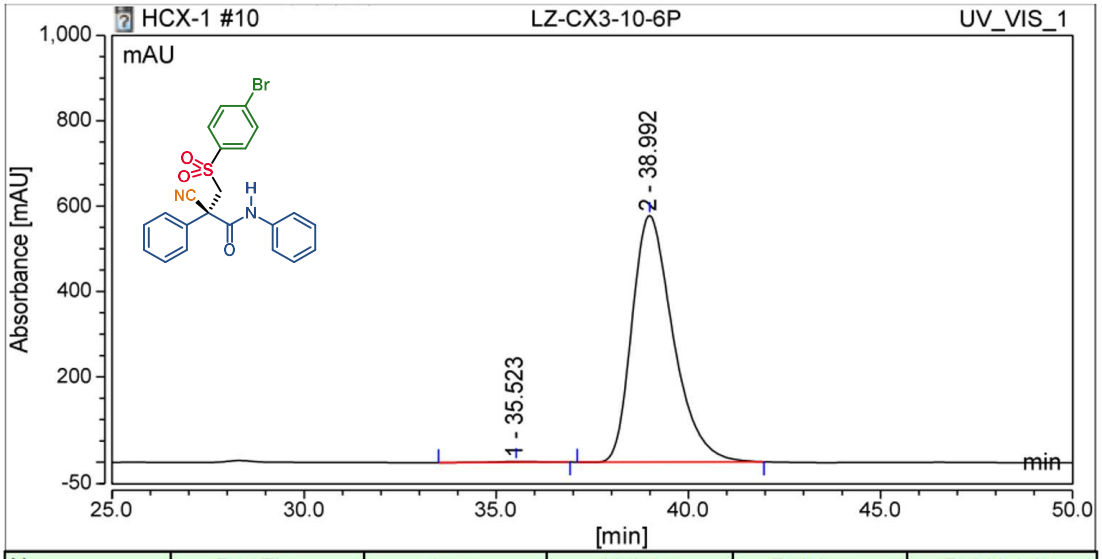


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.057	0.250	0.445	0.04	0.07
2	29.438	608.511	621.571	99.96	99.93
Total:		**608.761**	**622.016**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3k

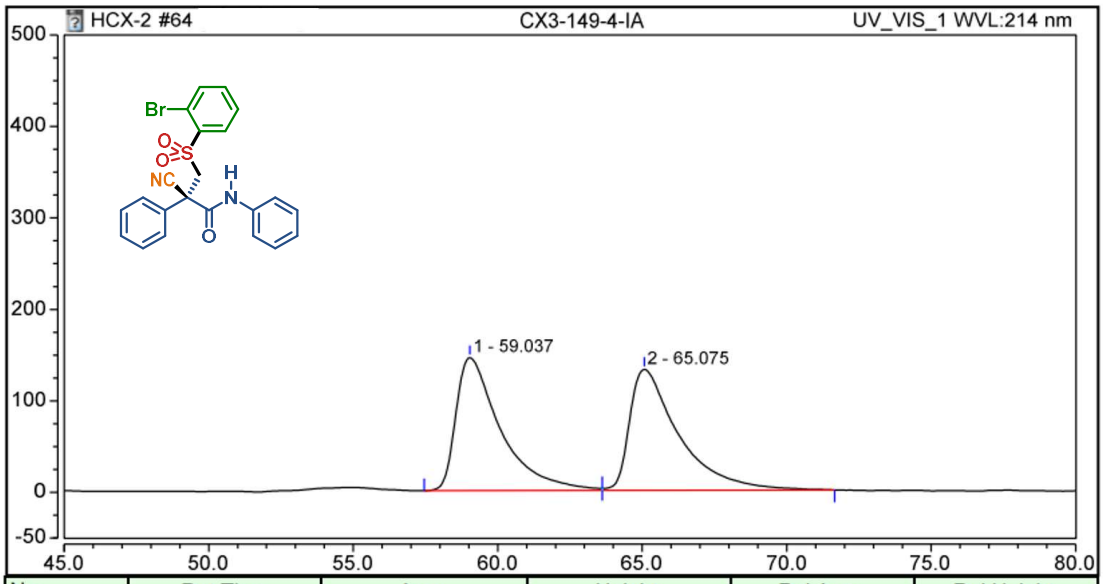


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	35.11	112.580	91.350	49.53	50.82
2	38.83	114.722	88.406	50.47	49.18
Total:		**227.302**	**179.756**	**100.00**	**100.00**

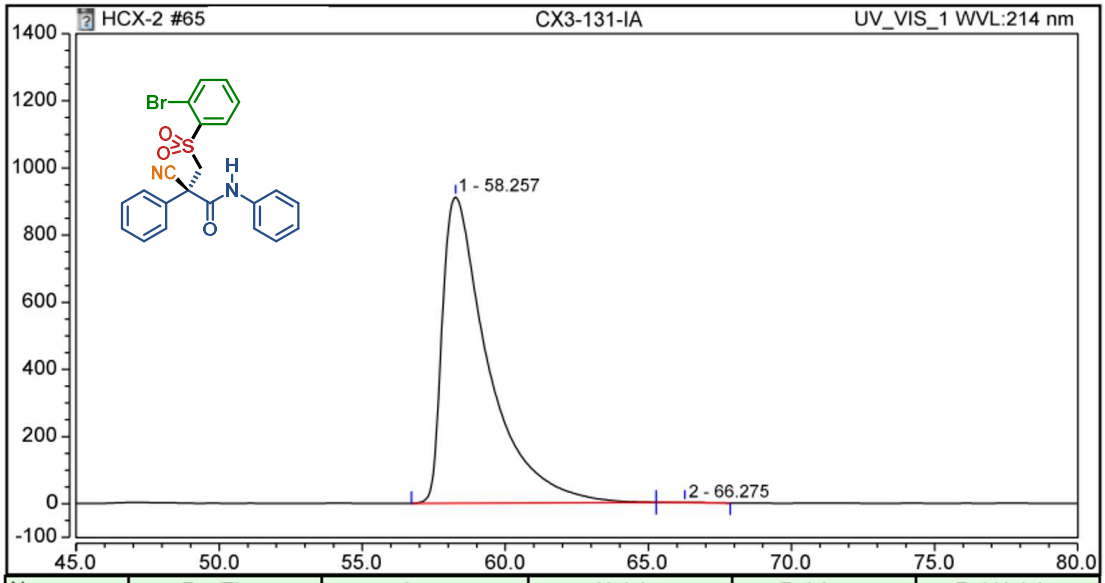


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	35.52	1.863	1.761	0.26	0.30
2	38.99	713.065	577.174	99.74	99.70
Total:		**714.928**	**578.935**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3l

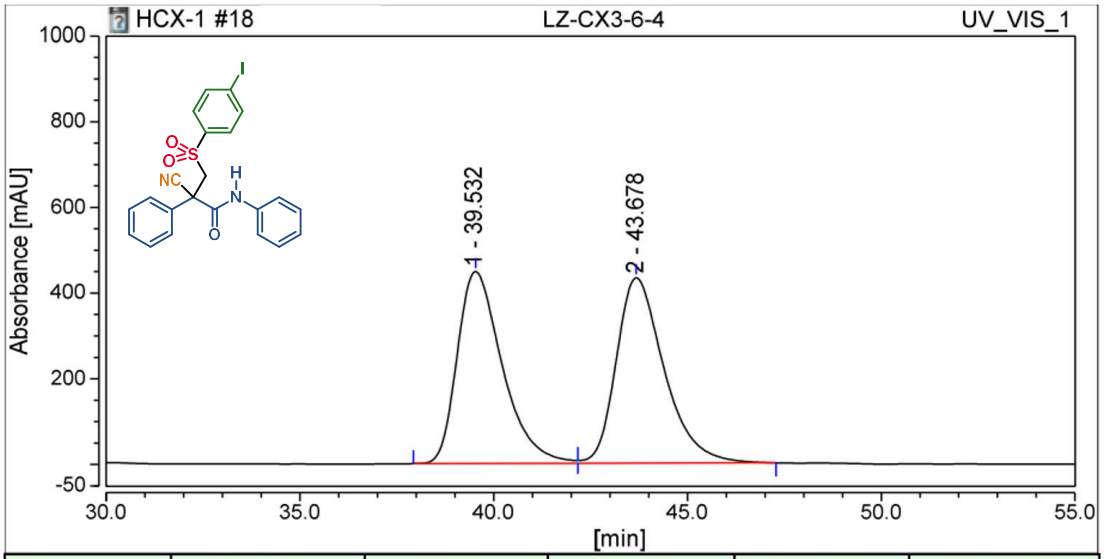


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	59.04	259.398	145.290	49.85	52.36
2	65.07	260.960	132.172	50.15	47.64
Total:		**520.358**	**277.461**	**100.00**	**100.00**

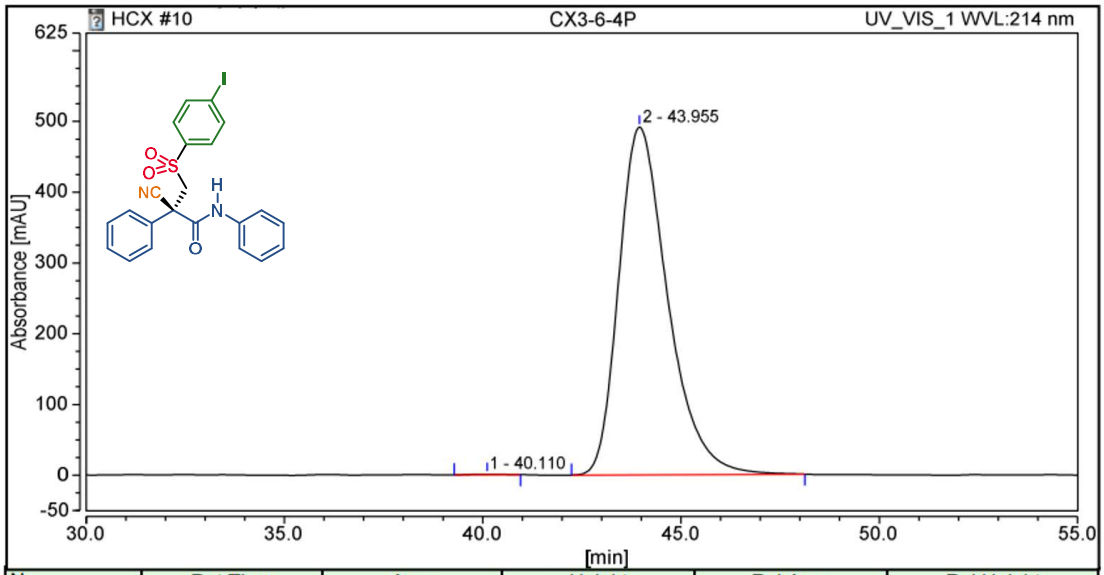


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	58.26	1696.142	911.886	99.95	99.91
2	66.27	0.882	0.810	0.05	0.09
Total:		**1697.024**	**912.697**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3m

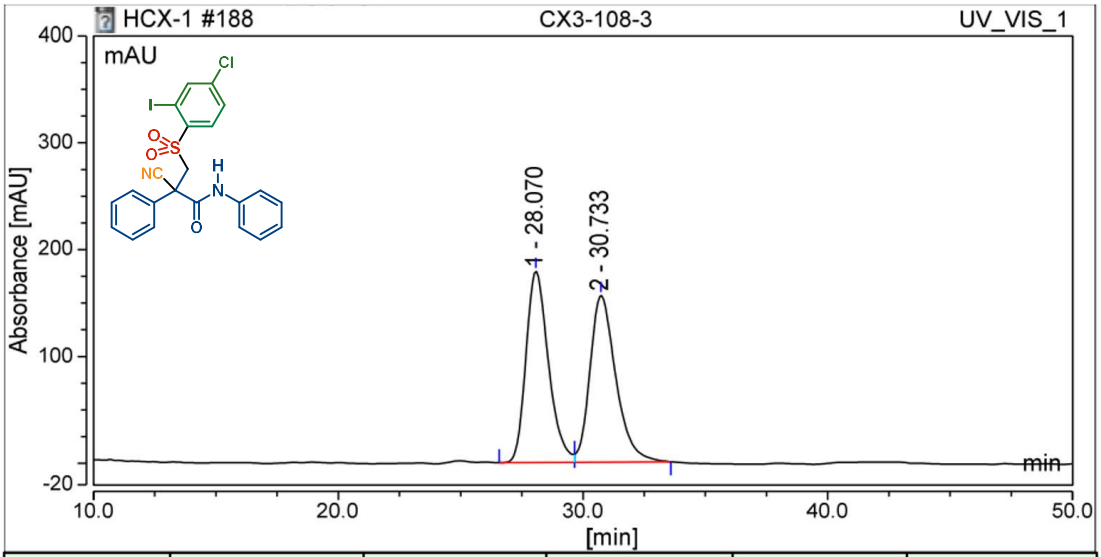


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	39.53	603.078	448.453	49.32	50.87
2	43.68	619.783	433.035	50.68	49.13
Total:		**1222.861**	**881.488**	**100.00**	**100.00**

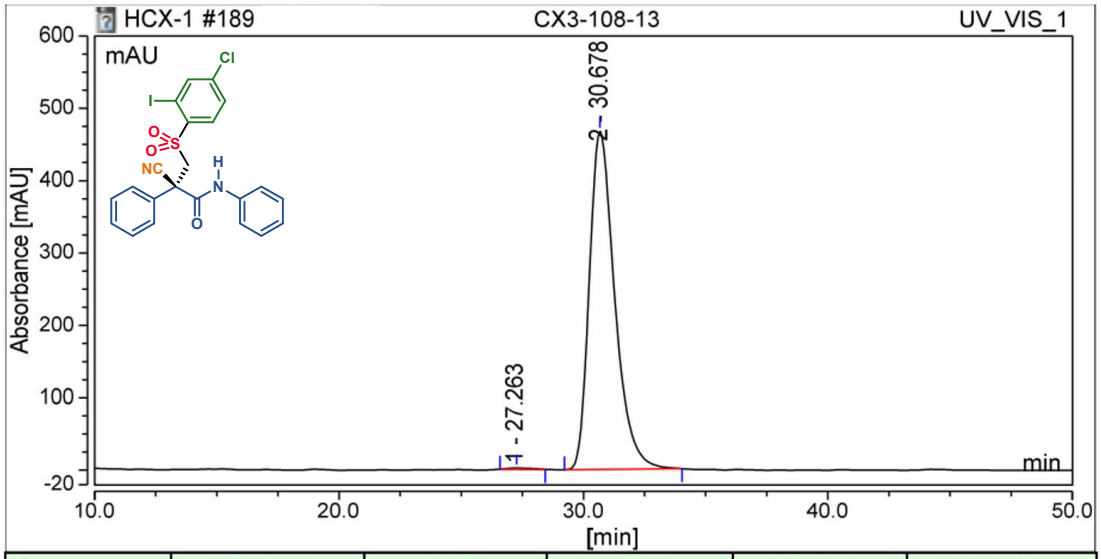


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	40.110	0.862	0.919	0.12	0.19
2	43.955	702.704	491.679	99.88	99.81
Total:		**703.566**	**492.598**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3n

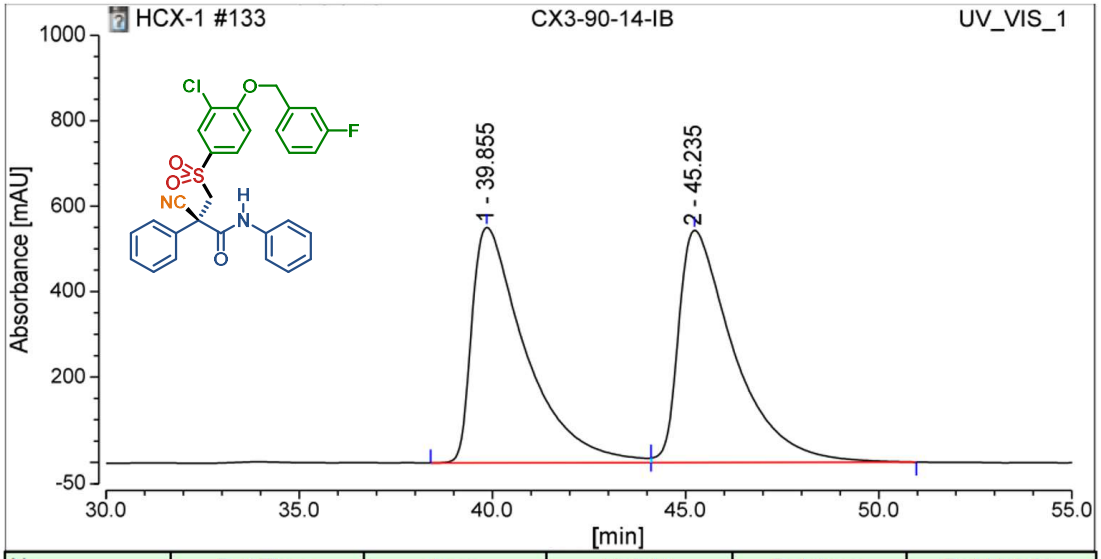


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.07	190.421	179.033	49.92	53.42
2	30.73	191.000	156.091	50.08	46.58
Total:		**381.421**	**335.125**	**100.00**	**100.00**

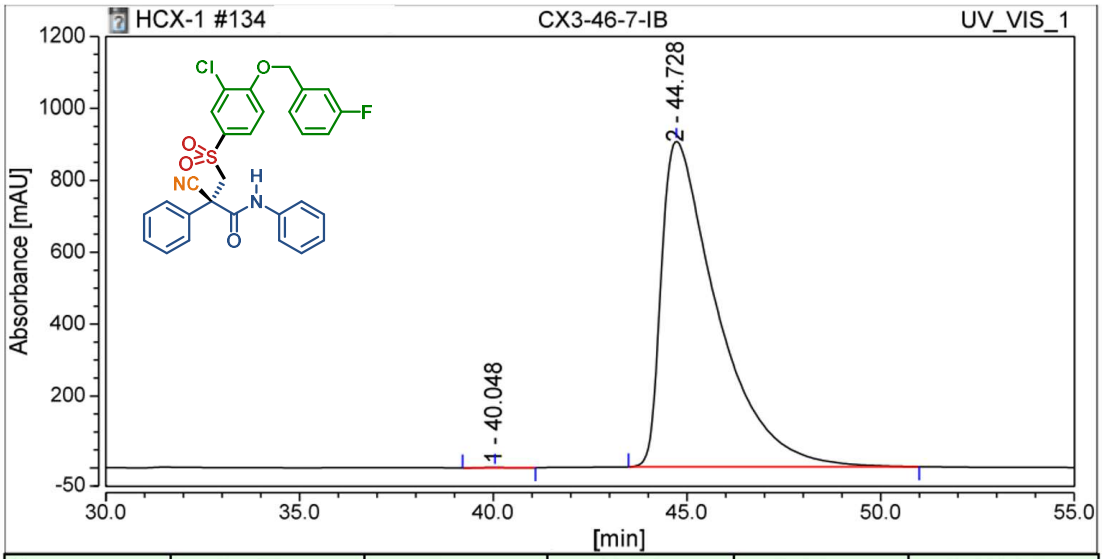


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.26	1.932	1.723	0.34	0.37
2	30.68	562.639	467.602	99.66	99.63
Total:		**564.571**	**469.325**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3o

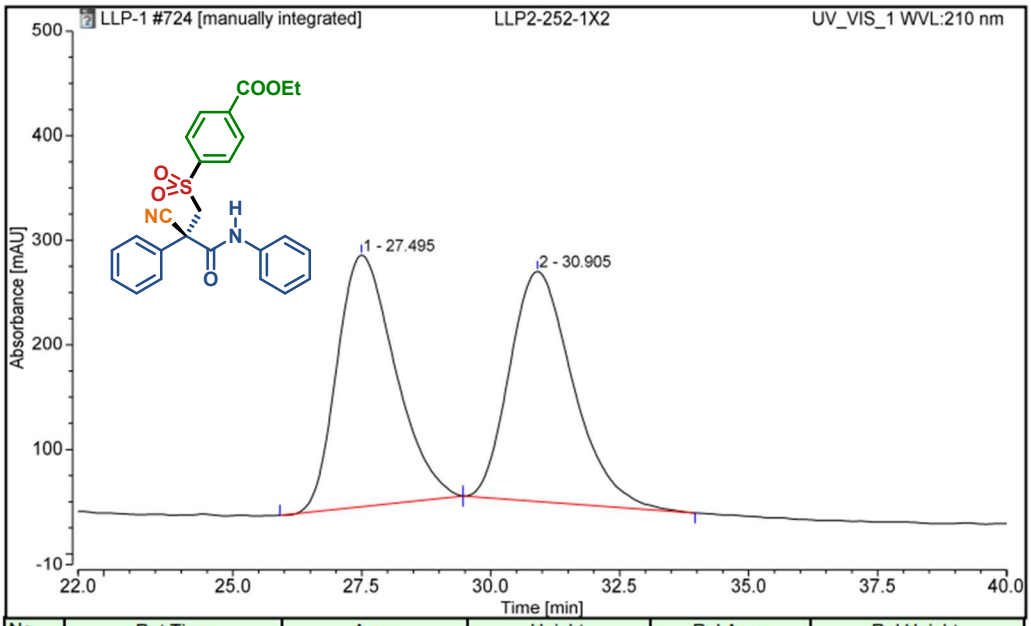


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	39.85	890.300	551.456	49.72	50.35
2	45.23	900.202	543.694	50.28	49.65
Total:		**1790.502**	**1095.150**	**100.00**	**100.00**

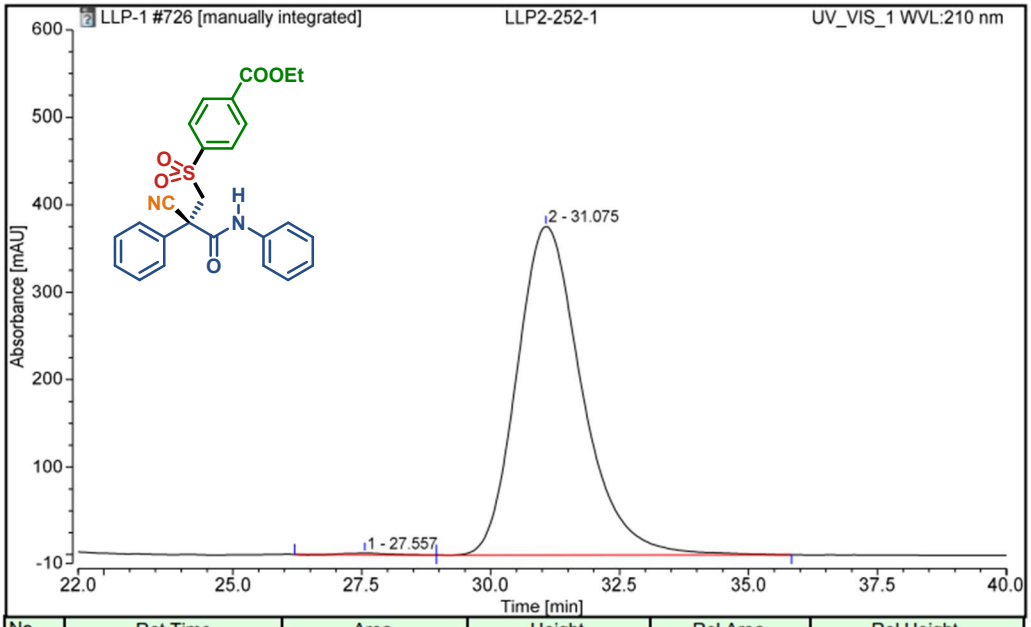


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	40.05	0.669	0.879	0.04	0.10
2	44.73	1516.238	905.214	99.96	99.90
Total:		**1516.907**	**906.093**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3p

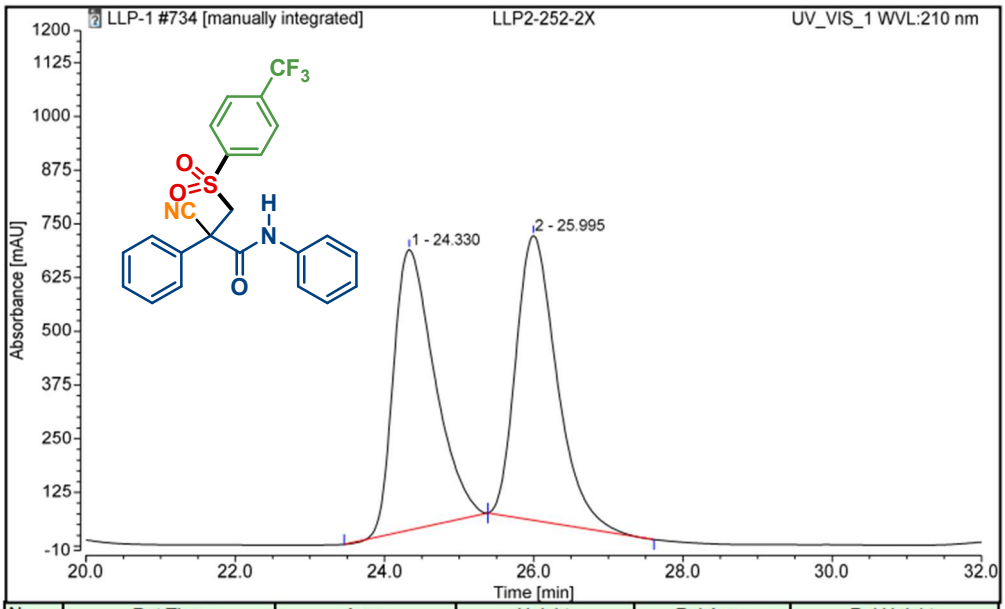


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.495	313.464	240.418	50.00	52.23
2	30.905	313.445	219.869	50.00	47.77
Total:		**626.910**	**460.287**	**100.00**	**100.00**

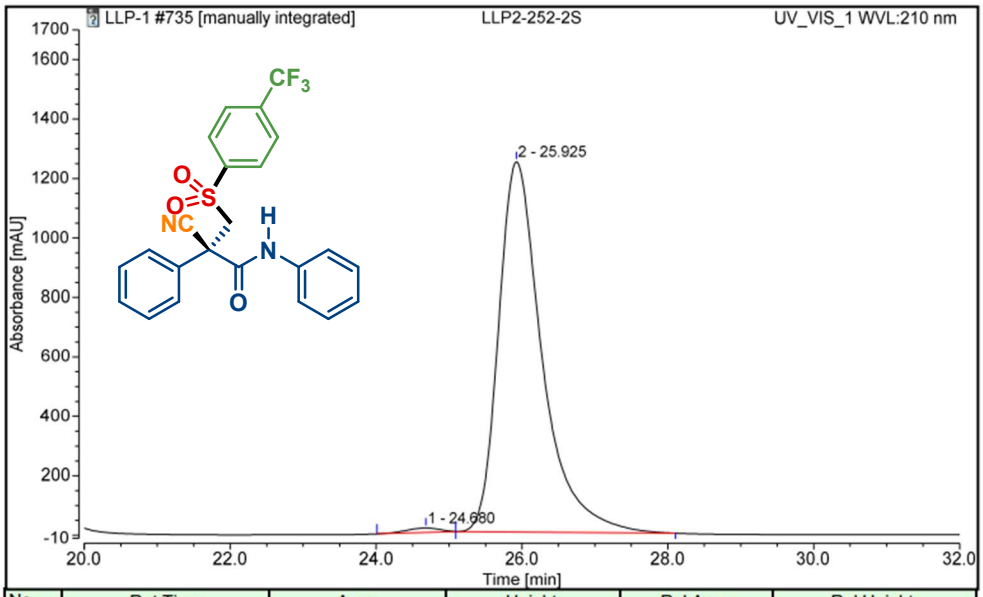


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.557	1.611	1.884	0.29	0.50
2	31.075	548.796	375.771	99.71	99.50
Total:		**550.407**	**377.655**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3q

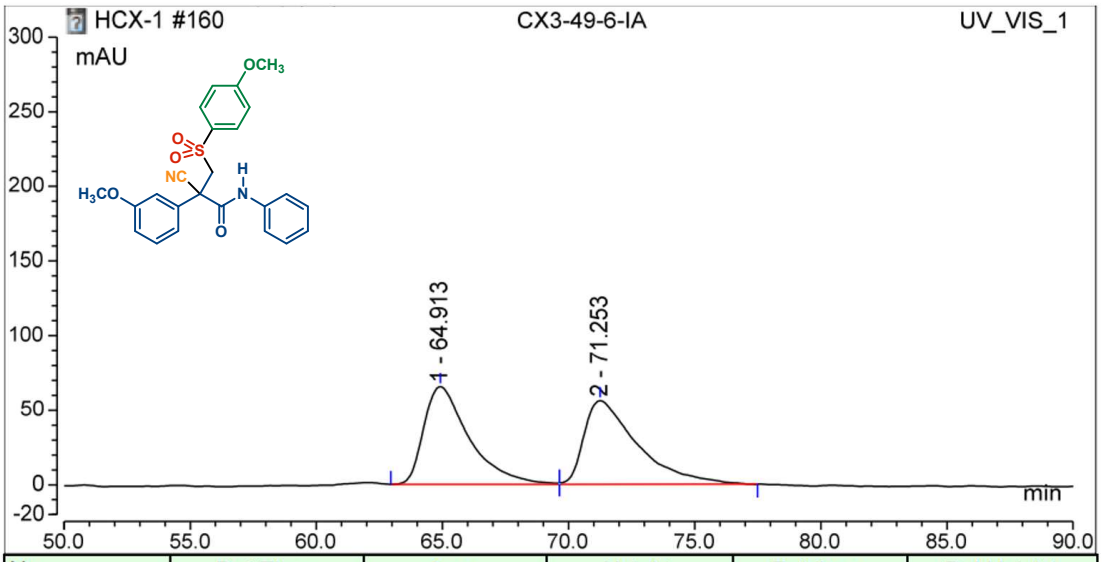


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	24.330	415.876	652.994	49.69	49.64
2	25.995	420.994	662.503	50.31	50.36
Total:		**836.870**	**1315.497**	**100.00**	**100.00**

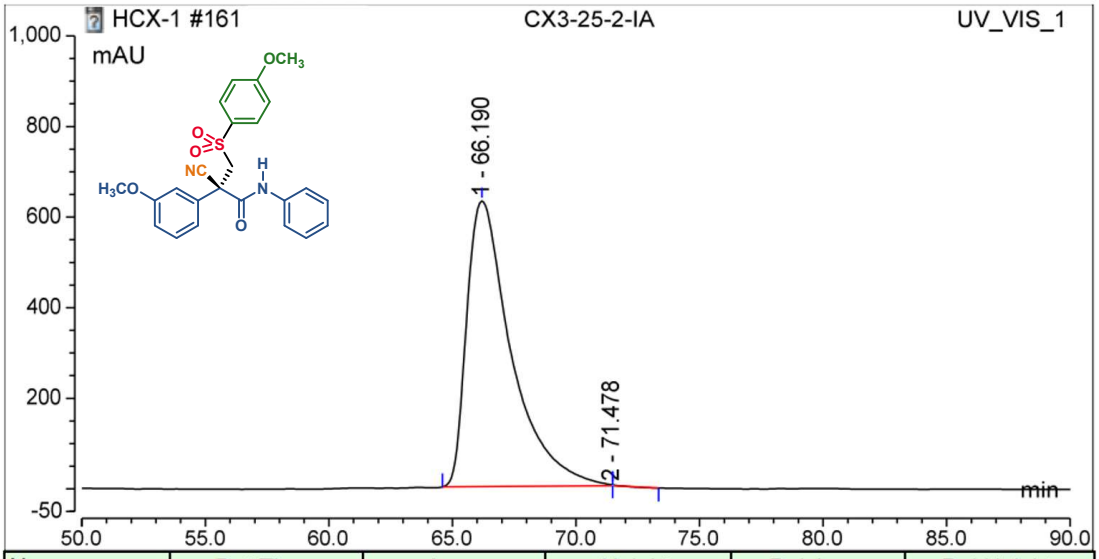


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	24.680	7.923	14.910	0.91	1.18
2	25.925	860.465	1245.692	99.09	98.82
Total:		**868.388**	**1260.602**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3r

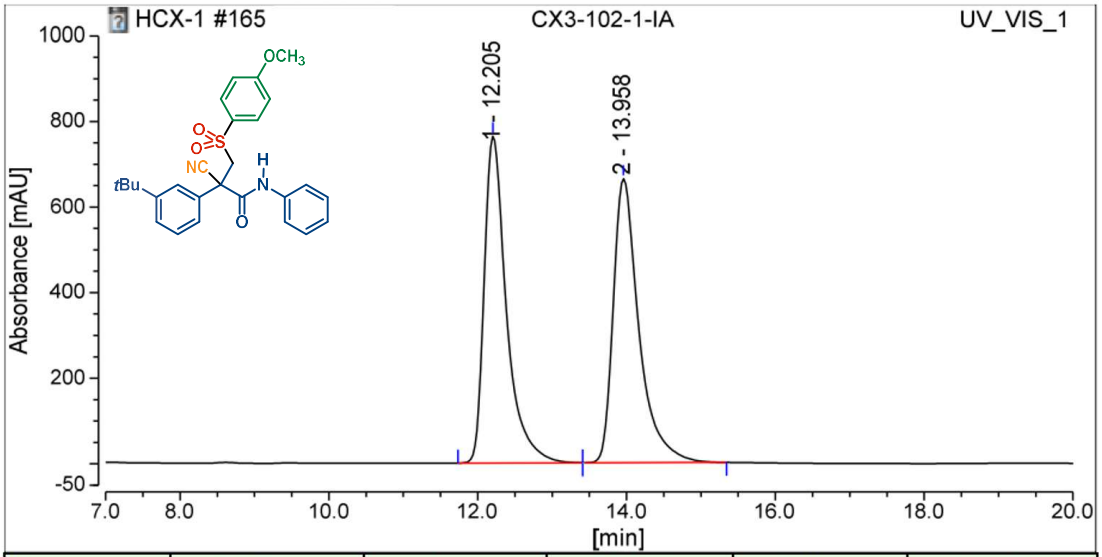


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	64.91	136.183	65.488	49.79	53.89
2	71.25	137.324	56.031	50.21	46.11
Total:		**273.507**	**121.520**	**100.00**	**100.00**

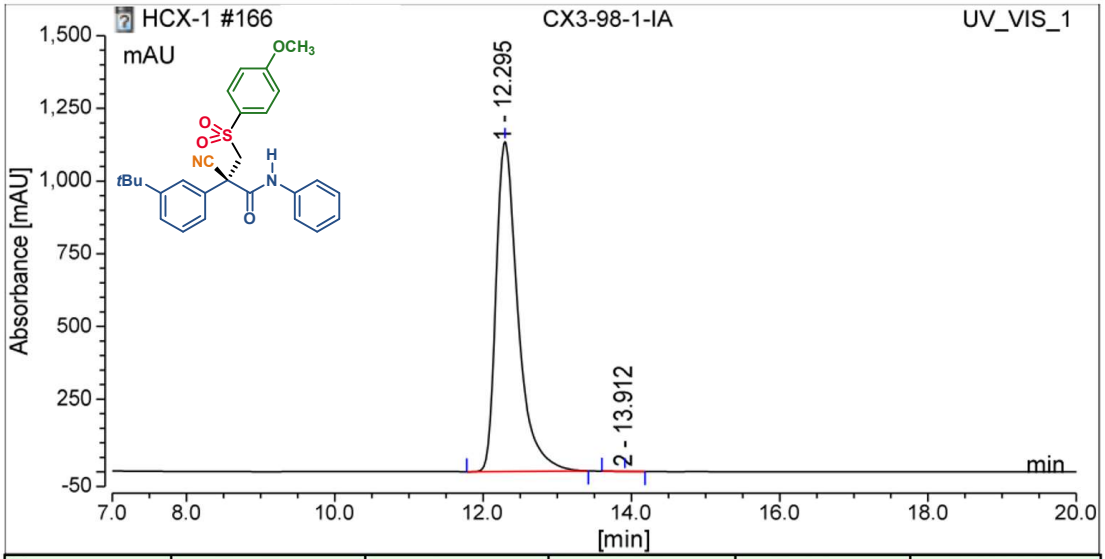


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	66.19	1312.963	630.297	99.97	99.77
2	71.48	0.383	1.462	0.03	0.23
Total:		**1313.347**	**631.759**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3s

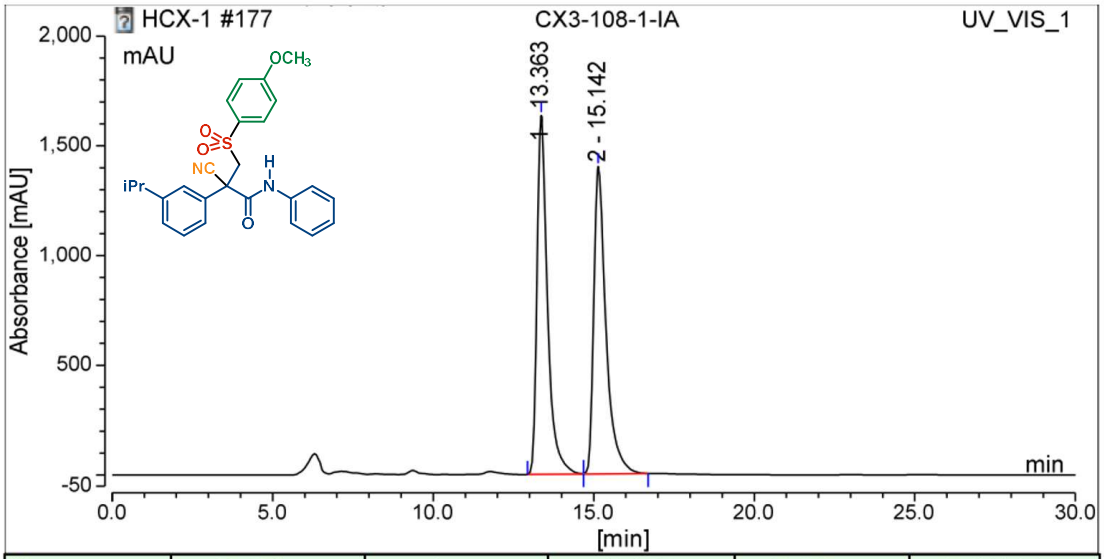


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	12.20	264.213	765.048	49.95	53.53
2	13.96	264.696	664.048	50.05	46.47
Total:		**528.909**	**1429.096**	**100.00**	**100.00**

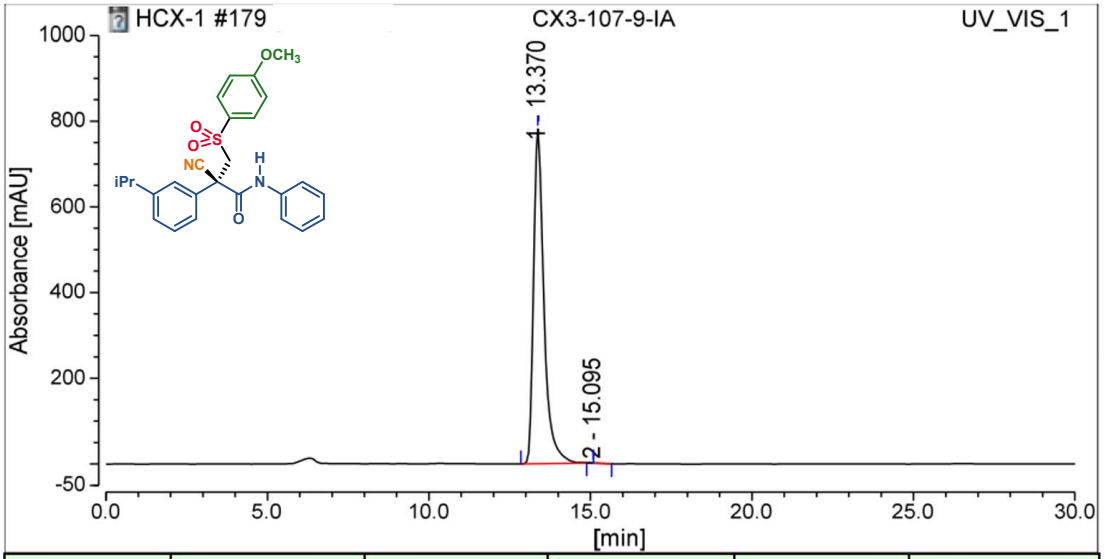


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	12.29	387.894	1134.396	99.97	99.97
2	13.91	0.114	0.349	0.03	0.03
Total:		**388.009**	**1134.746**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3t

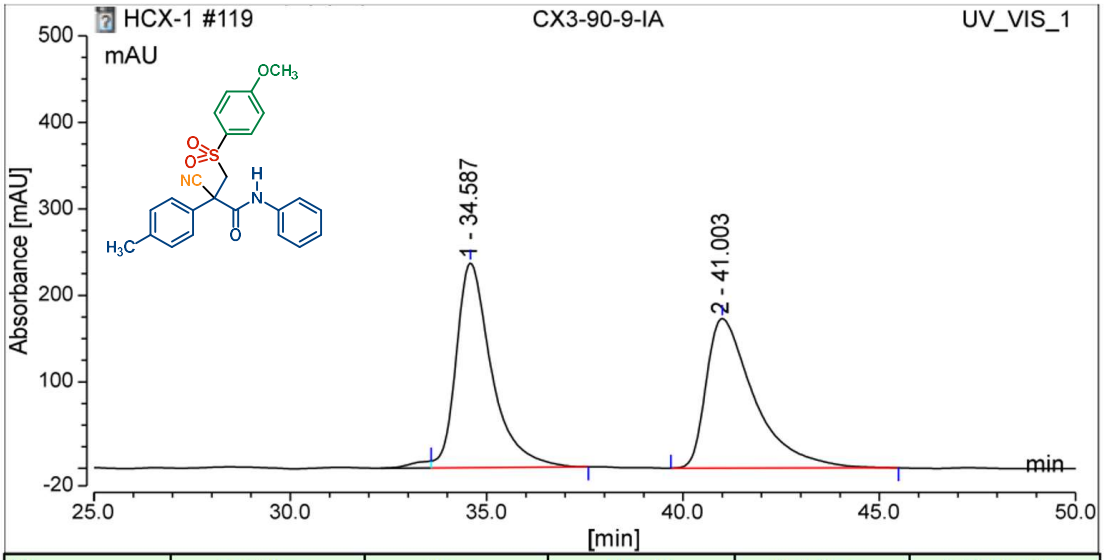


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	13.36	618.847	1635.400	50.00	53.87
2	15.14	618.803	1400.429	50.00	46.13
Total:		**1237.650**	**3035.830**	**100.00**	**100.00**

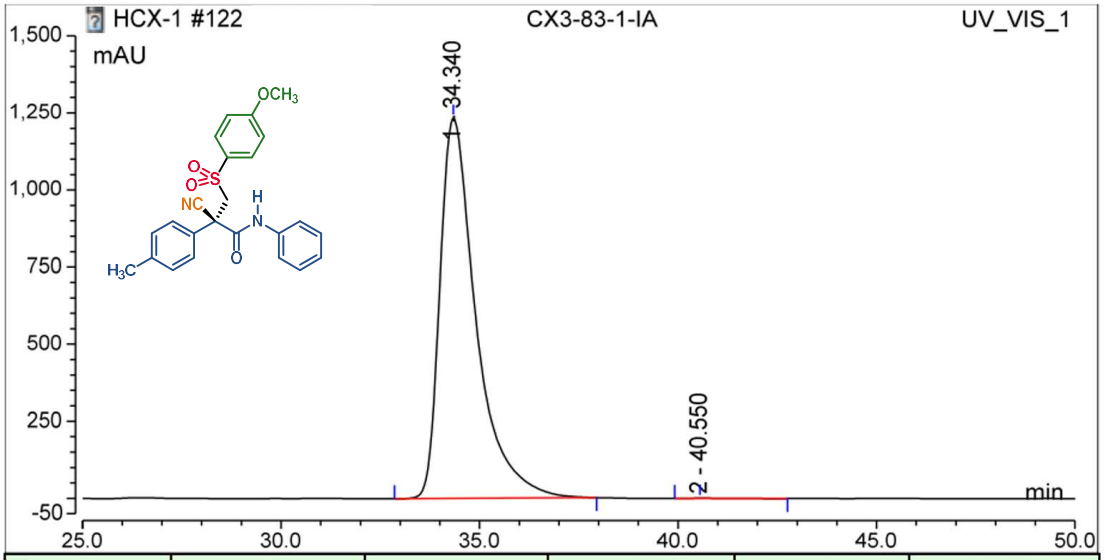


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	13.37	291.180	781.392	99.96	99.95
2	15.09	0.115	0.367	0.04	0.05
Total:		**291.295**	**781.759**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3u

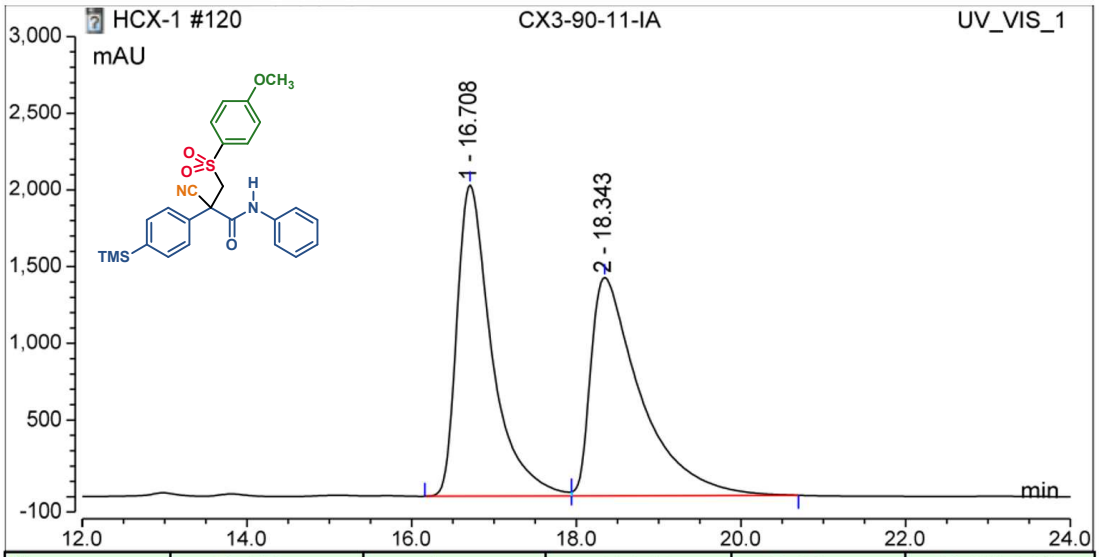


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	34.59	246.681	236.492	50.16	57.78
2	41.00	245.128	172.800	49.84	42.22
Total:		**491.809**	**409.292**	**100.00**	**100.00**

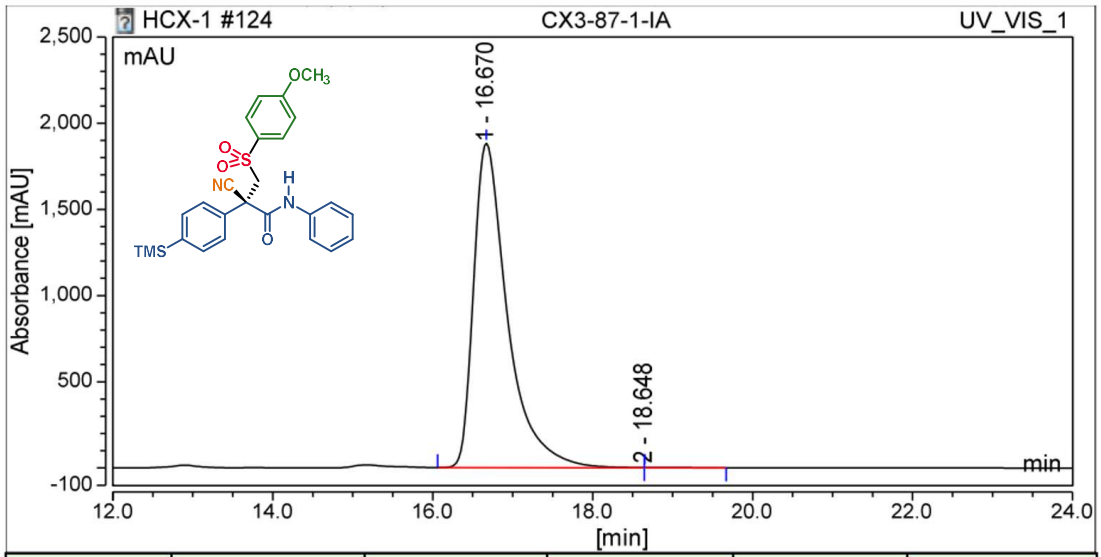


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	34.34	1300.110	1232.997	99.95	99.94
2	40.55	0.683	0.759	0.05	0.06
Total:		**1300.793**	**1233.756**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3v

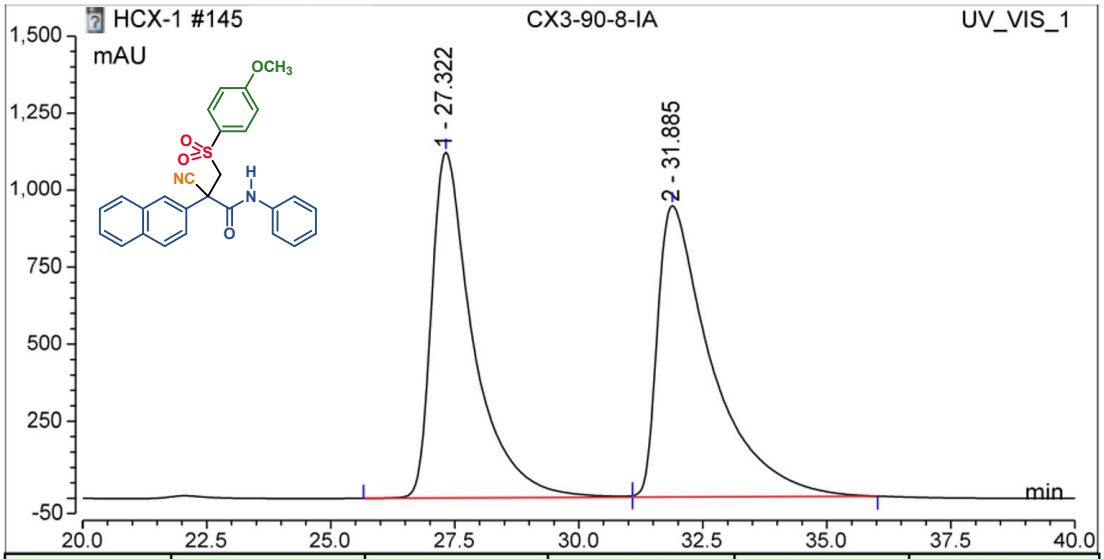


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	16.71	995.247	2030.348	49.98	58.78
2	18.34	996.225	1423.525	50.02	41.22
Total:		**1991.472**	**3453.874**	**100.00**	**100.00**

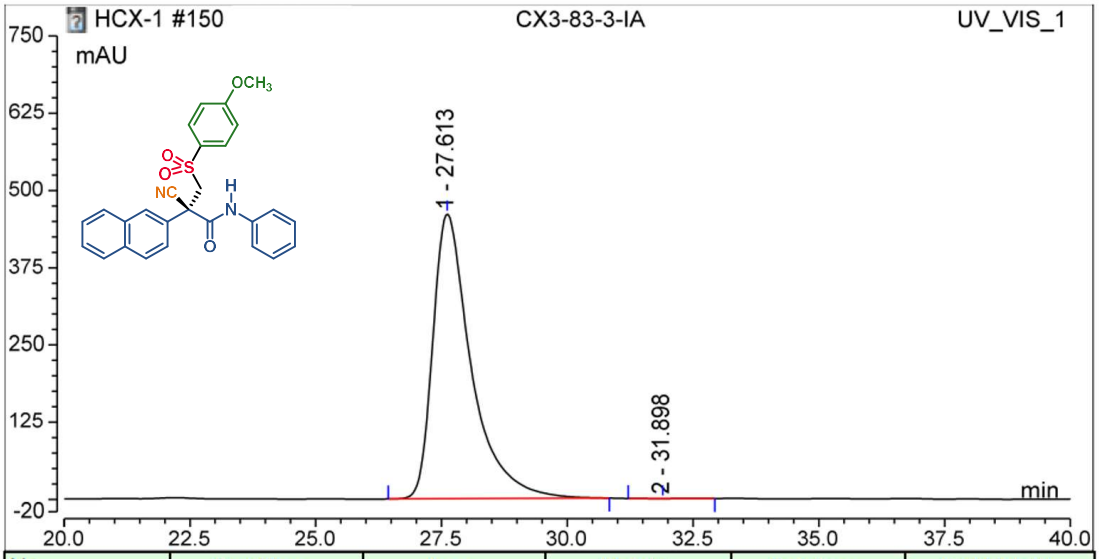


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	16.67	921.466	1882.272	99.94	99.95
2	18.65	0.565	1.015	0.06	0.05
Total:		**922.031**	**1883.288**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3w

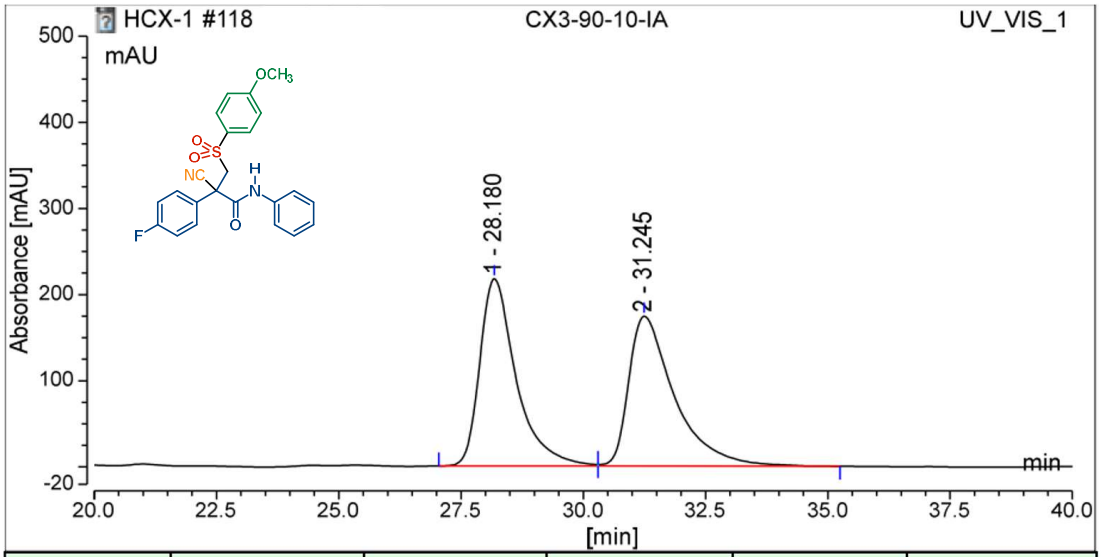


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.32	1096.109	1122.021	47.89	54.26
2	31.88	1192.684	945.862	52.11	45.74
Total:		**2288.793**	**2067.883**	**100.00**	**100.00**

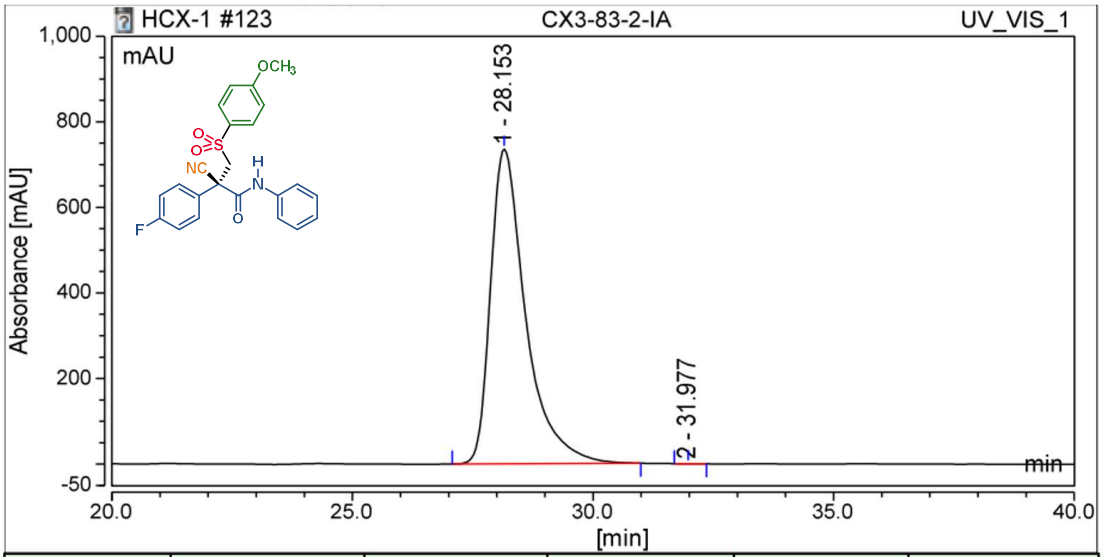


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.61	407.613	460.742	99.91	99.89
2	31.90	0.363	0.504	0.09	0.11
Total:		**407.976**	**461.246**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3x

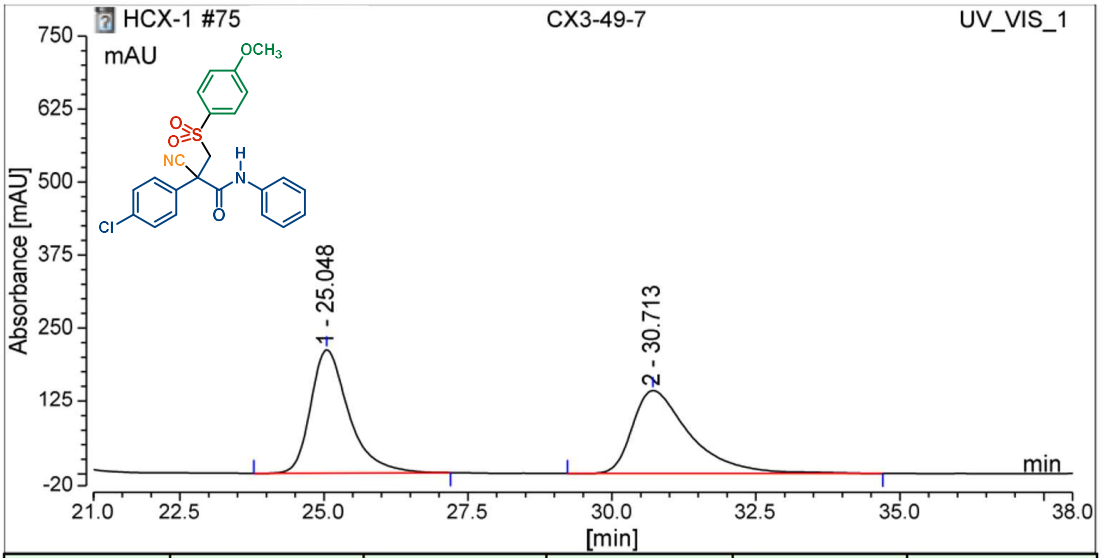


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.18	187.017	217.461	49.82	55.54
2	31.24	188.347	174.094	50.18	44.46
Total:		**375.364**	**391.555**	**100.00**	**100.00**

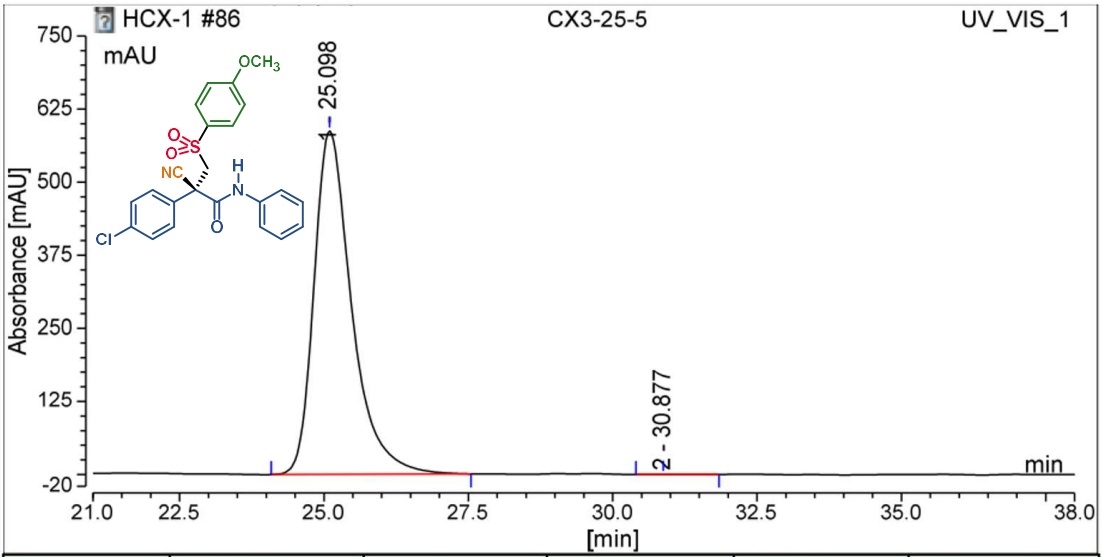


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.15	622.122	735.782	99.98	99.97
2	31.98	0.110	0.253	0.02	0.03
Total:		**622.232**	**736.035**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3y

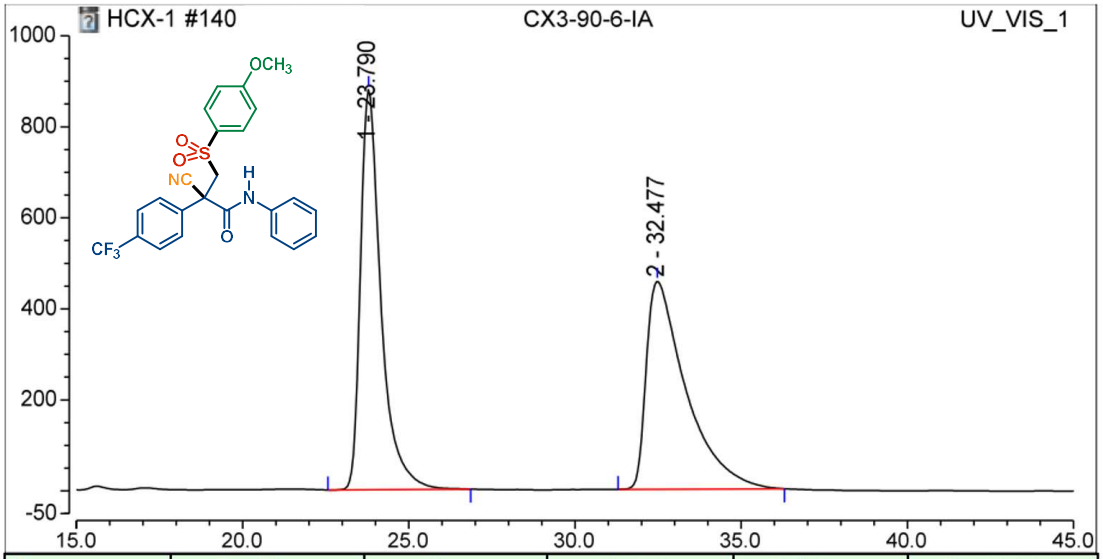


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	25.05	162.272	211.285	49.77	59.83
2	30.71	163.756	141.853	50.23	40.17
Total:		**326.028**	**353.138**	**100.00**	**100.00**

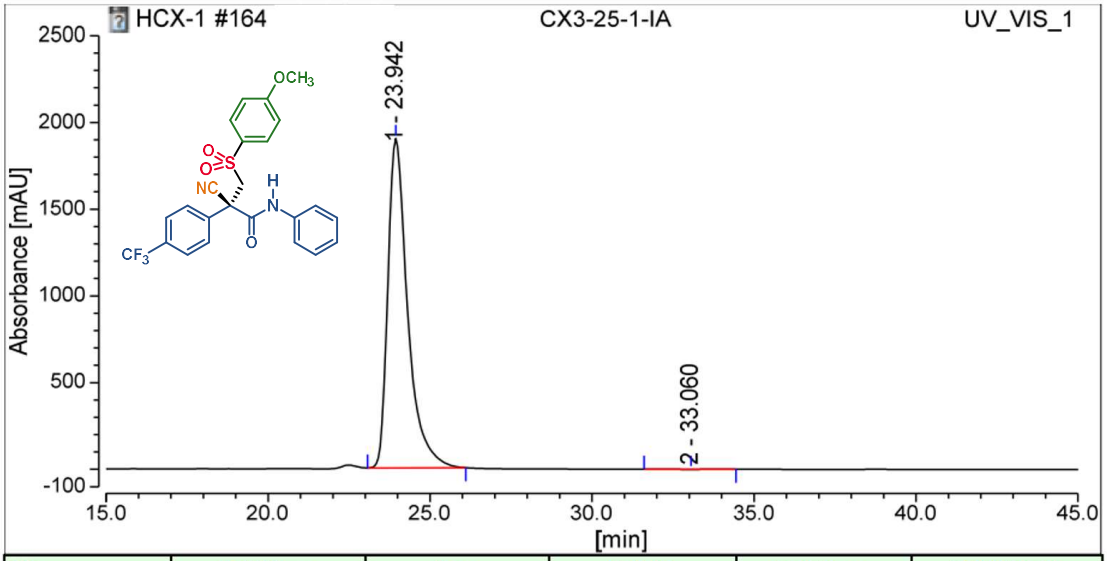


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	25.10	443.822	587.336	99.96	99.94
2	30.88	0.168	0.341	0.04	0.06
Total:		**443.990**	**587.677**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3z

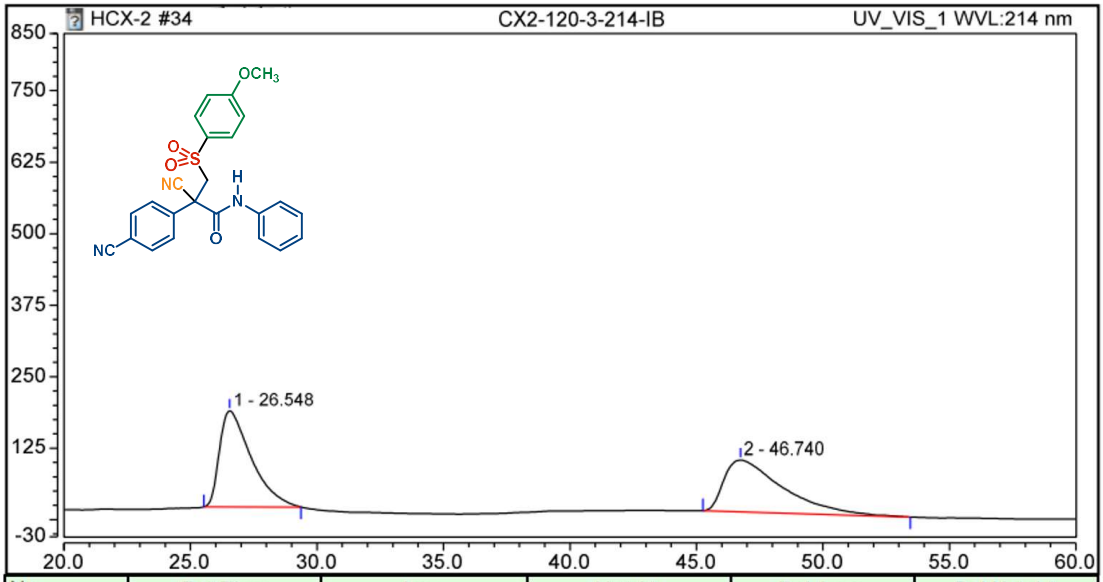


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	23.79	629.269	879.227	49.90	65.81
2	32.48	631.861	456.840	50.10	34.19
Total:		**1261.130**	**1336.067**	**100.00**	**100.00**

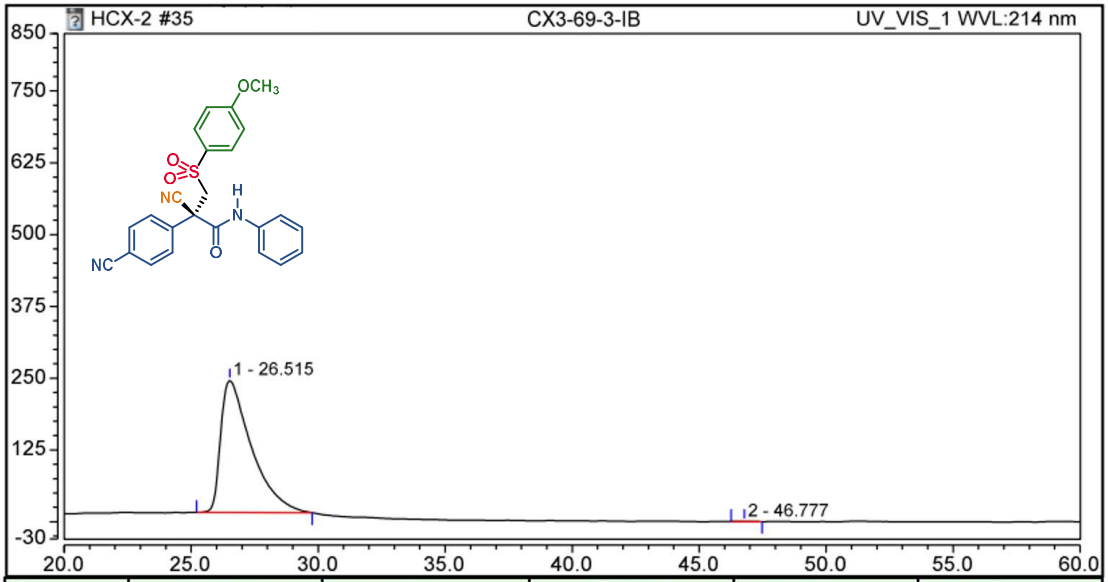


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	23.94	1344.419	1900.253	99.90	99.94
2	33.06	1.404	1.094	0.10	0.06
Total:		**1345.823**	**1901.347**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3aa

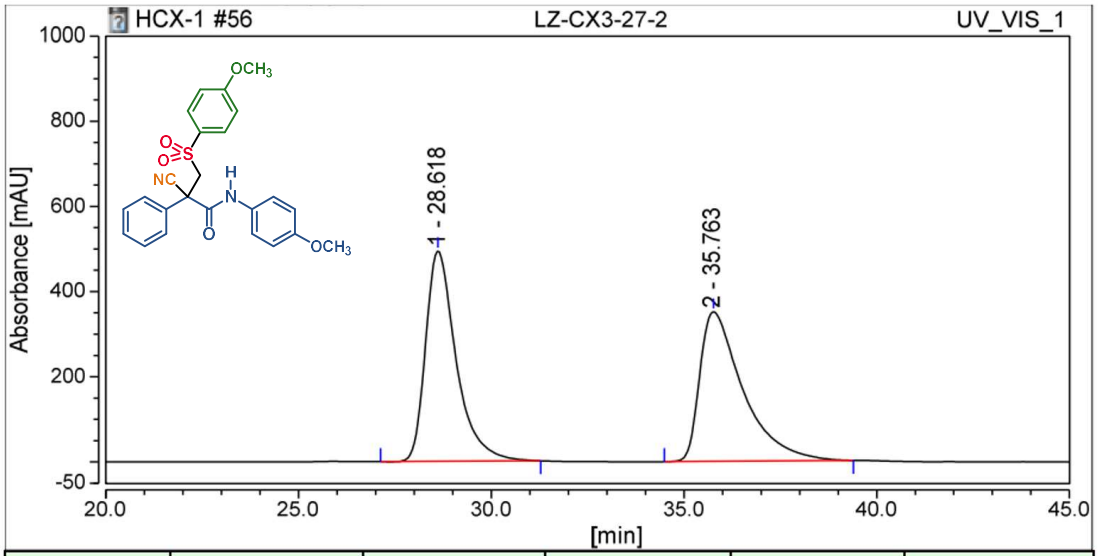


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	26.548	244.350	167.697	50.06	65.02
2	46.740	243.794	90.236	49.94	34.98
Total:		**488.144**	**257.933**	**100.00**	**100.00**

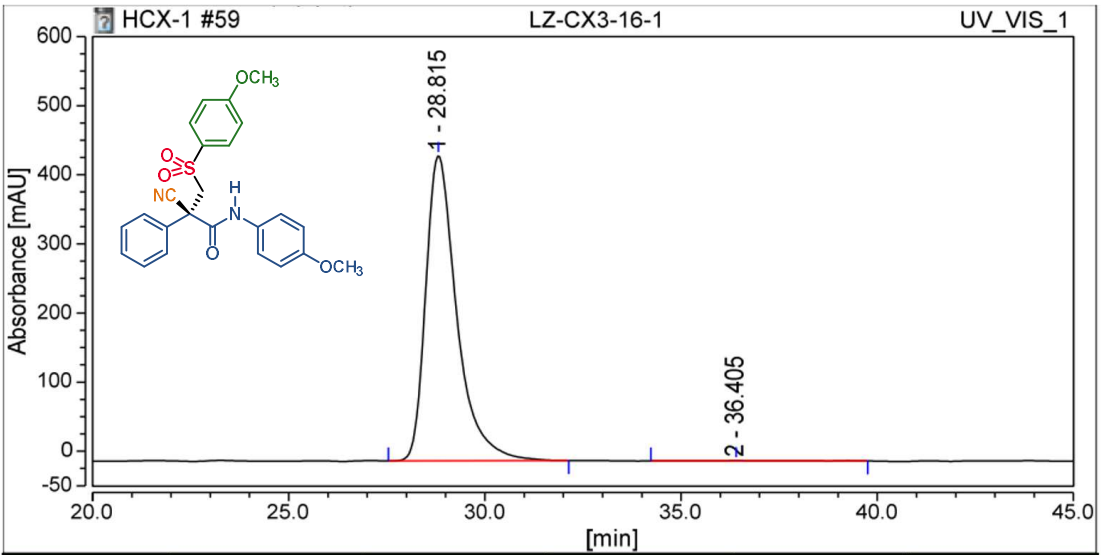


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	26.515	322.717	229.321	99.97	99.94
2	46.777	0.109	0.146	0.03	0.06
Total:		**322.826**	**229.467**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ab

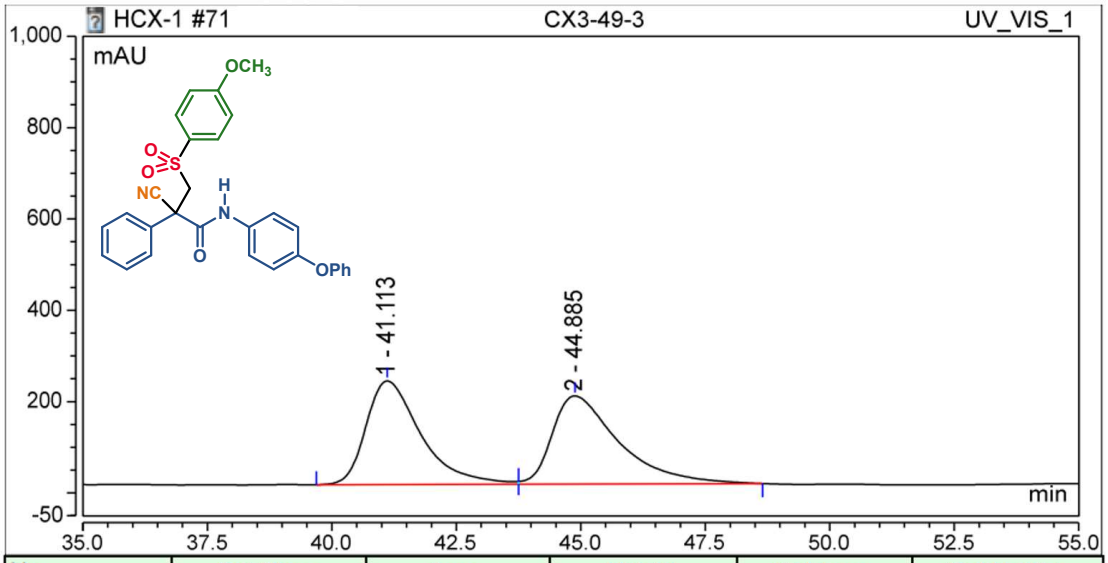


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.62	453.284	494.418	49.88	58.46
2	35.76	455.534	351.295	50.12	41.54
Total:		**908.819**	**845.712**	**100.00**	**100.00**

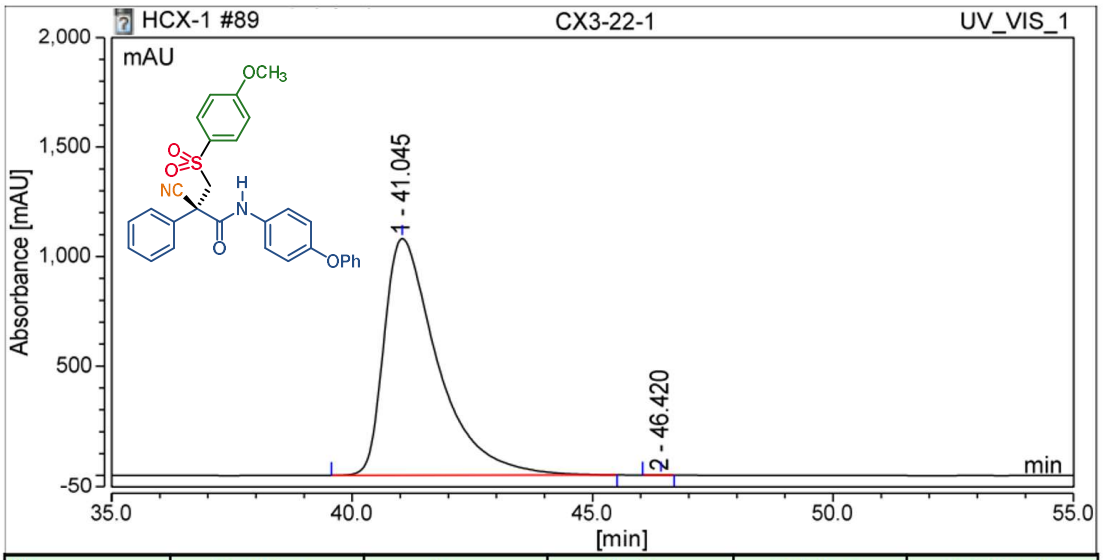


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.81	403.941	441.753	99.98	99.94
2	36.40	0.086	0.265	0.02	0.06
Total:		**404.027**	**442.018**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ac

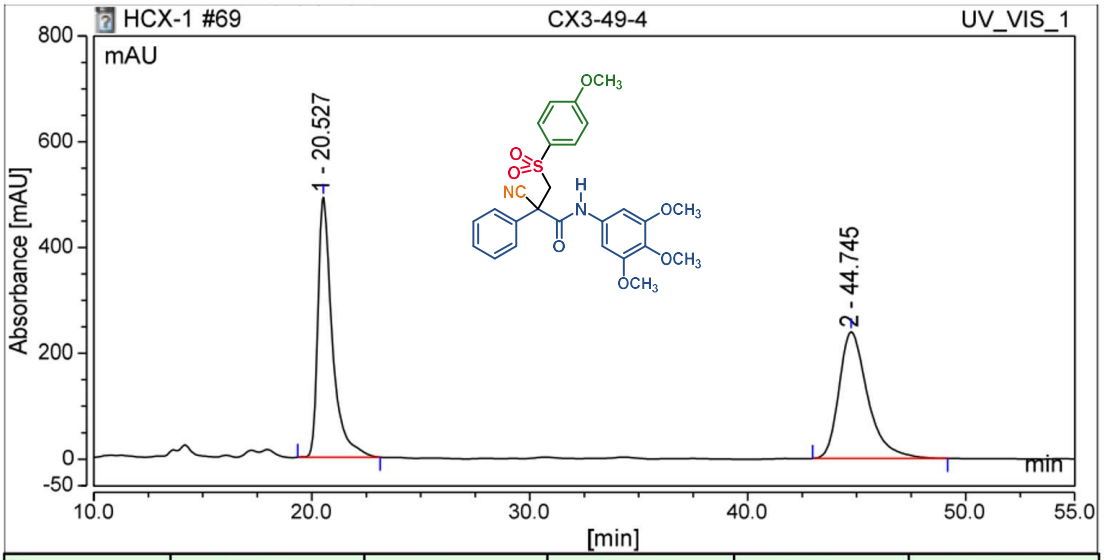


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	41.11	289.302	226.865	49.22	54.04
2	44.88	298.509	192.973	50.78	45.96
Total:		**587.811**	**419.838**	**100.00**	**100.00**

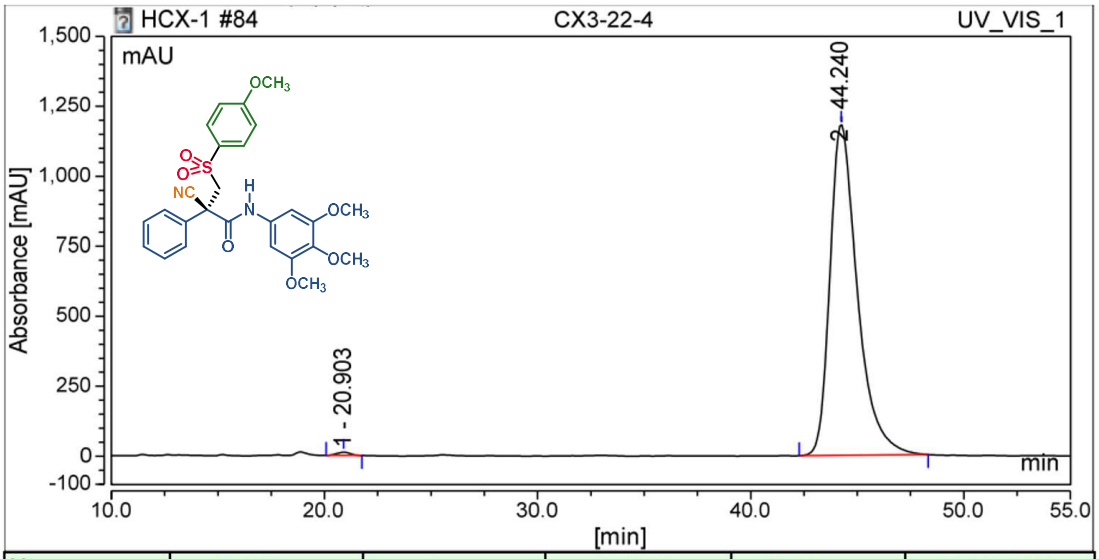


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	41.04	1397.583	1081.727	99.99	99.97
2	46.42	0.087	0.274	0.01	0.03
Total:		**1397.670**	**1082.000**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ad

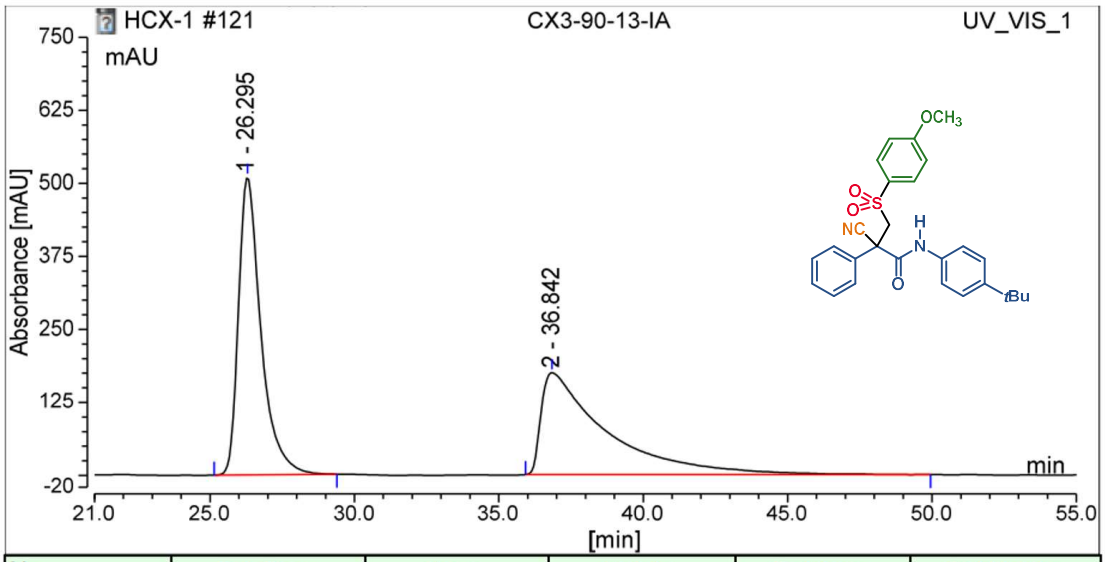


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.53	375.739	491.769	50.59	67.23
2	44.74	366.911	239.747	49.41	32.77
Total:		**742.650**	**731.515**	**100.00**	**100.00**

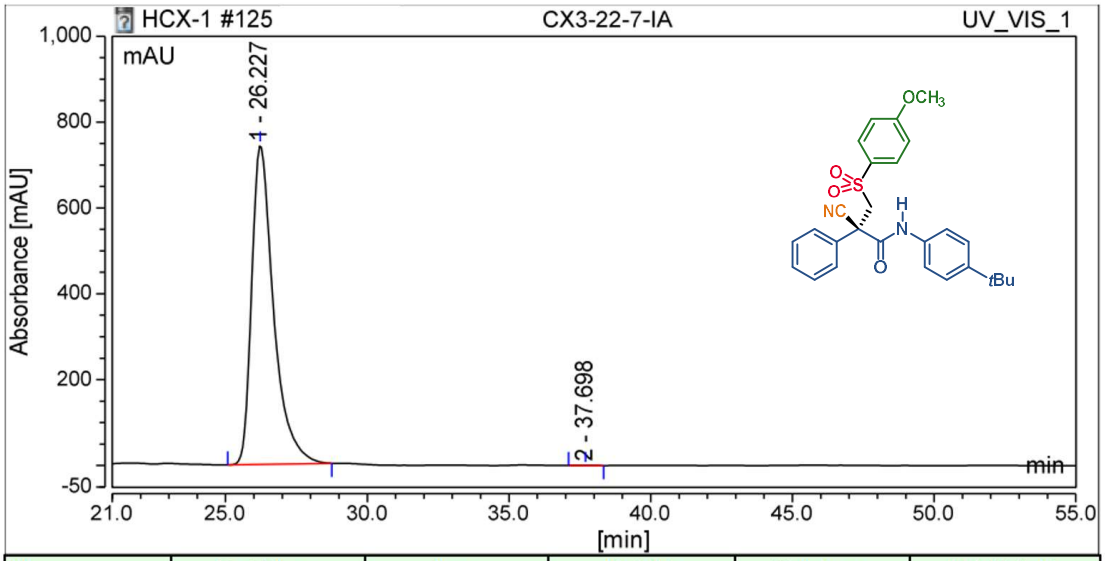


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.90	8.398	11.502	0.47	0.96
2	44.24	1763.459	1183.022	99.53	99.04
Total:		**1771.857**	**1194.524**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ae

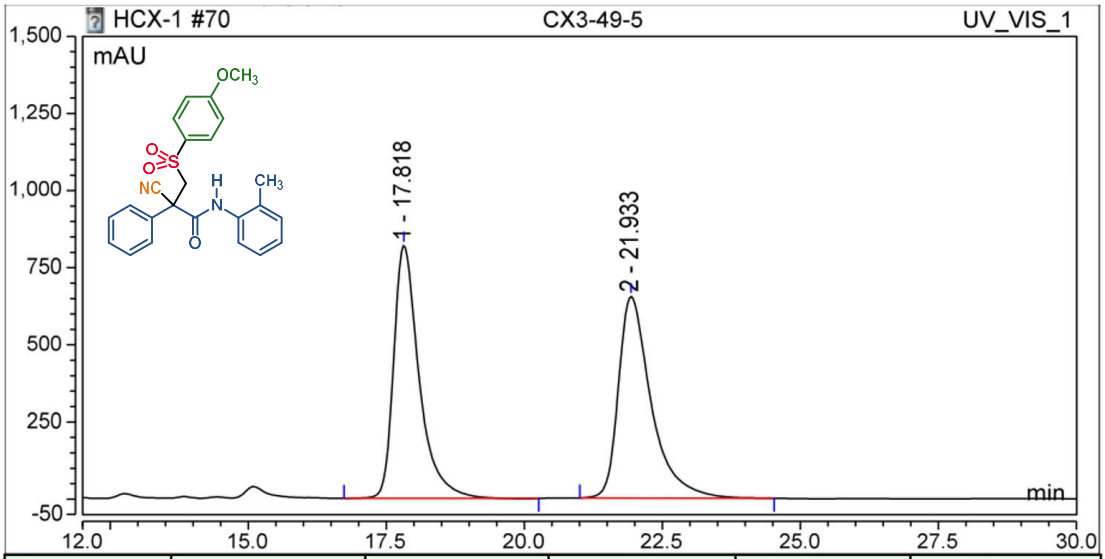


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	26.29	458.886	509.774	50.29	74.49
2	36.84	453.671	174.598	49.71	25.51
Total:		**912.556**	**684.372**	**100.00**	**100.00**

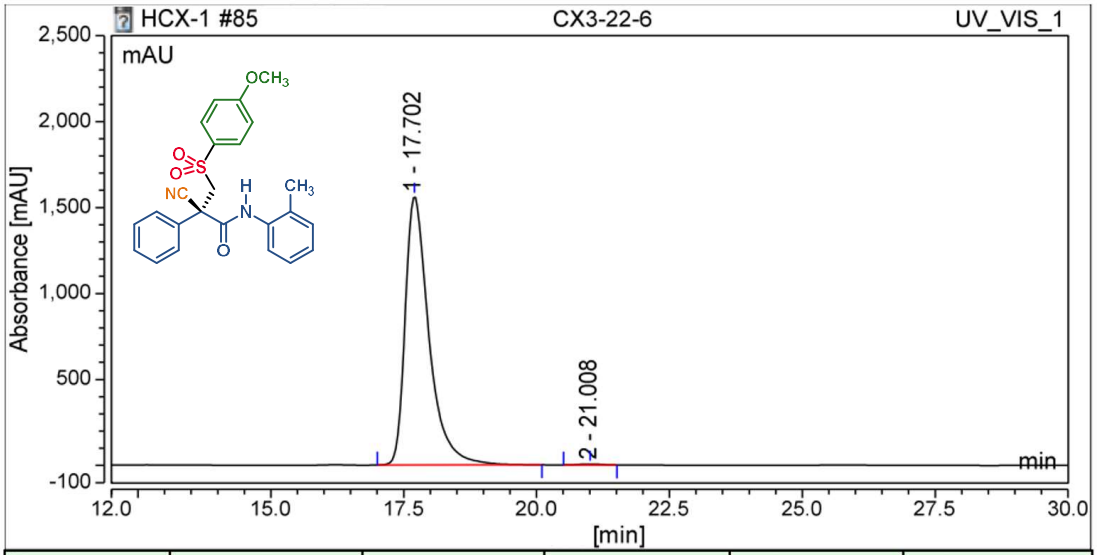


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	26.23	665.224	744.572	99.97	99.95
2	37.70	0.199	0.369	0.03	0.05
Total:		**665.422**	**744.941**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3af

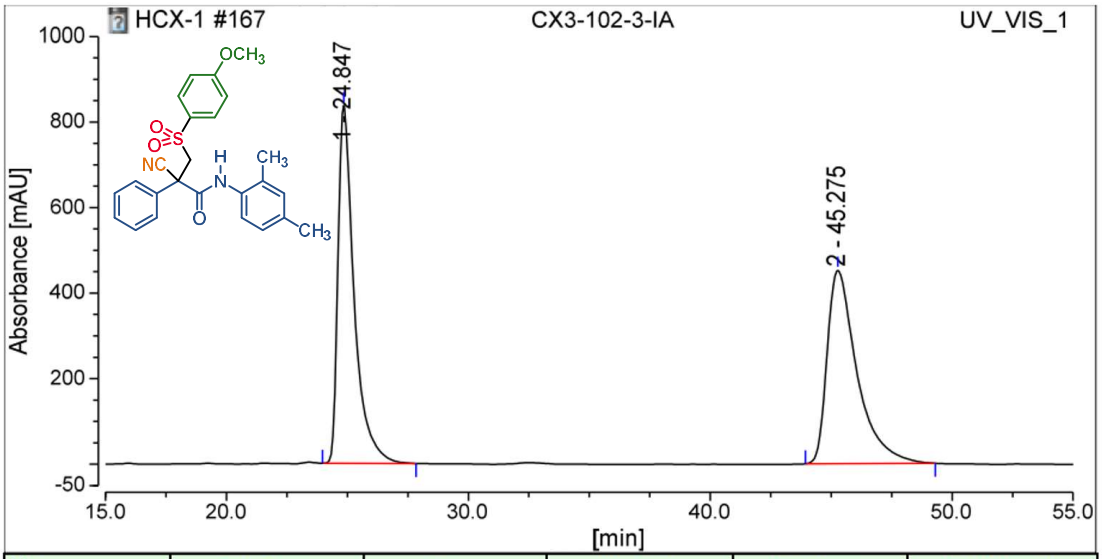


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.82	438.372	820.543	49.40	55.65
2	21.93	449.079	653.892	50.60	44.35
Total:		**887.451**	**1474.435**	**100.00**	**100.00**

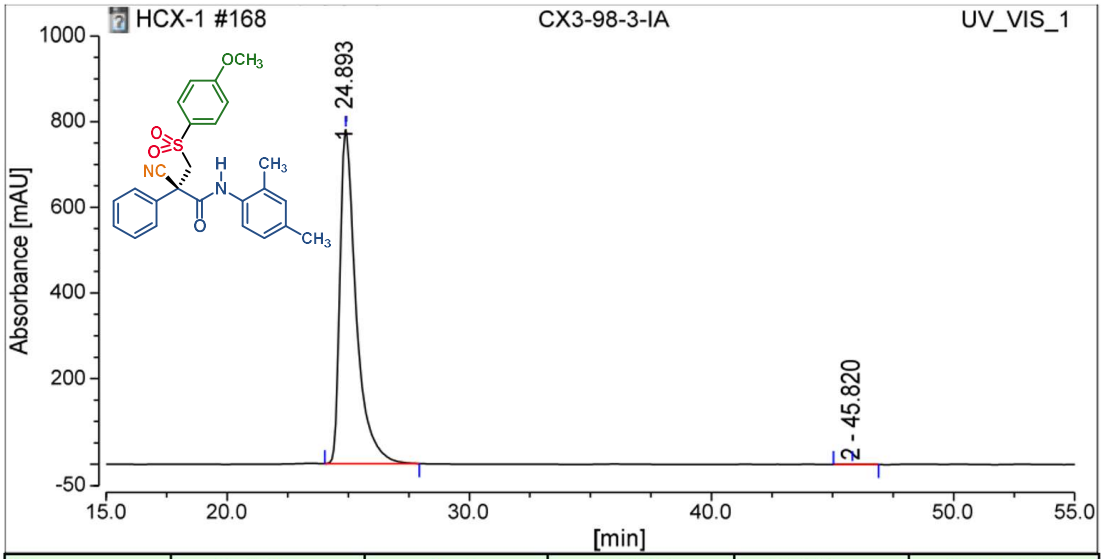


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.70	811.611	1563.463	99.69	99.68
2	21.01	2.536	4.977	0.31	0.32
Total:		**814.147**	**1568.440**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ag

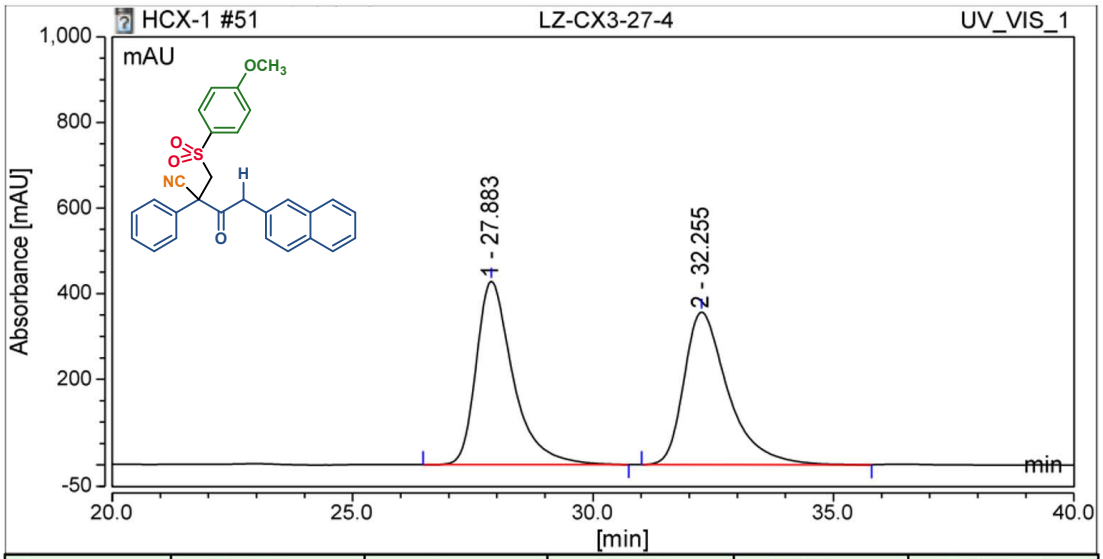


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	24.85	647.429	837.092	50.02	64.91
2	45.27	646.930	452.489	49.98	35.09
Total:		**1294.358**	**1289.581**	**100.00**	**100.00**

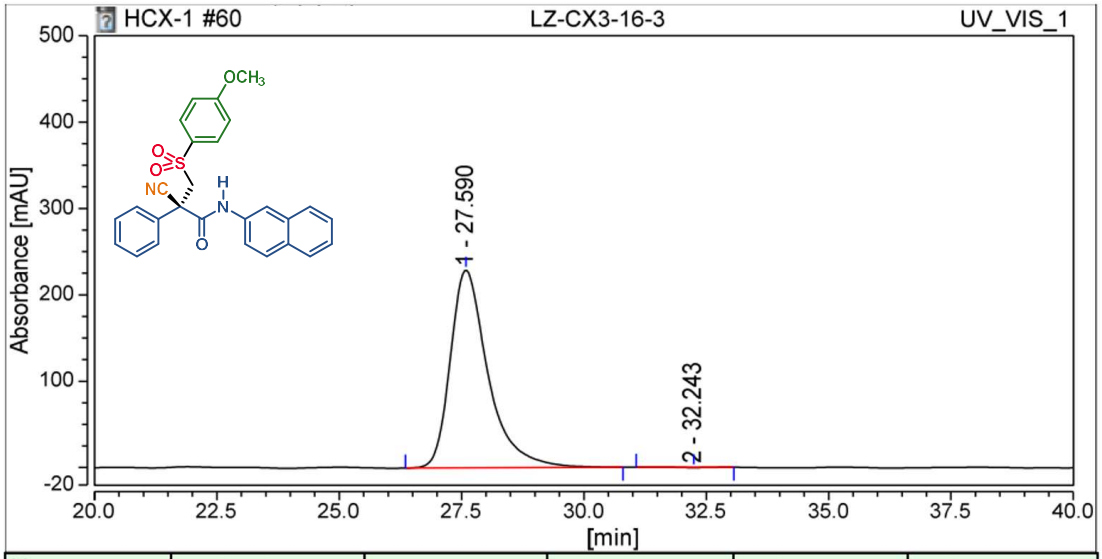


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	24.89	604.721	779.582	99.96	99.96
2	45.82	0.260	0.298	0.04	0.04
Total:		**604.980**	**779.879**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ah

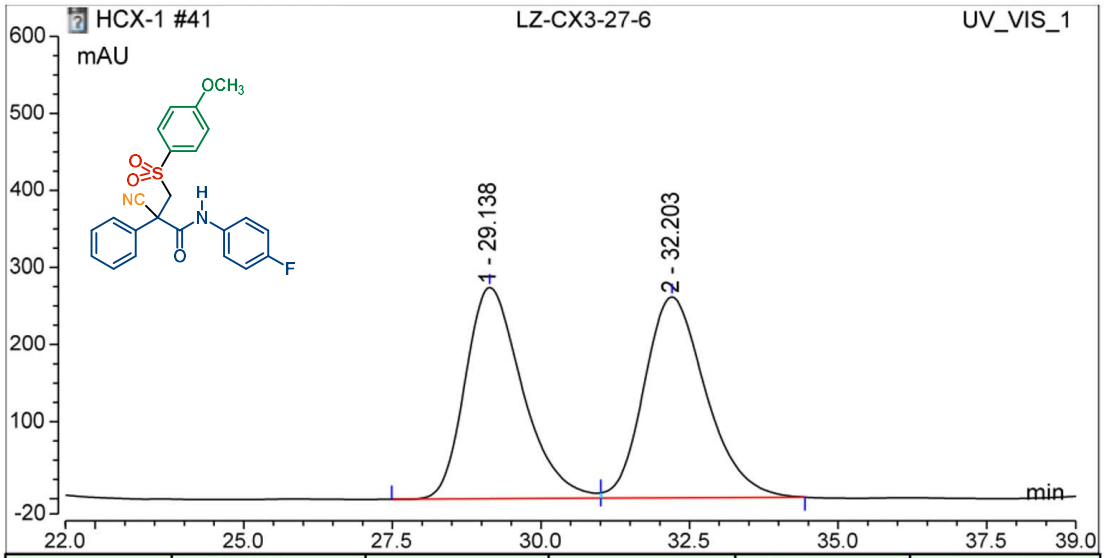


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.88	379.607	428.045	50.11	54.57
2	32.25	377.867	356.302	49.89	45.43
Total:		**757.474**	**784.347**	**100.00**	**100.00**

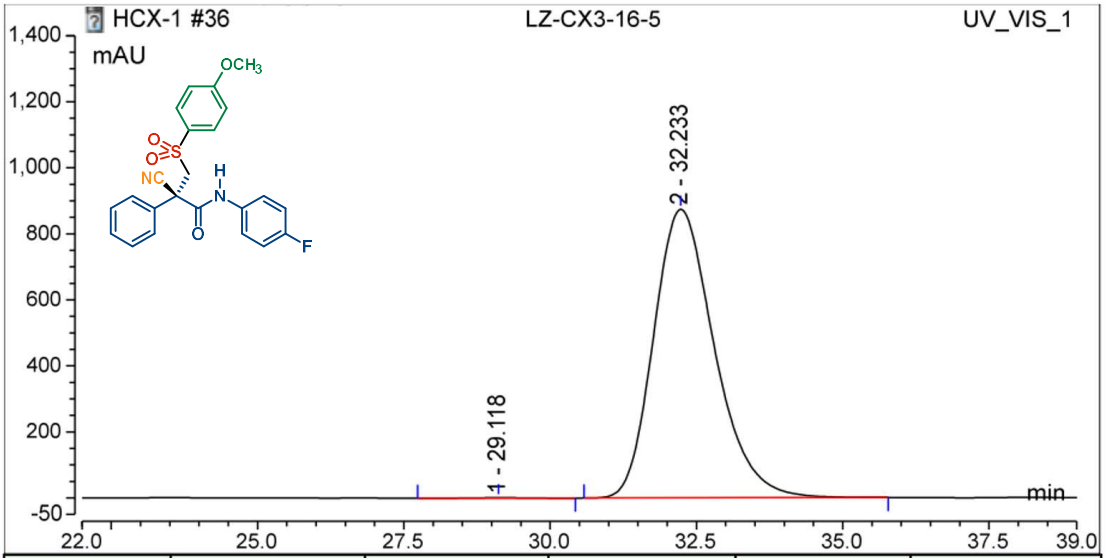


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	27.59	204.730	228.789	99.88	99.78
2	32.24	0.239	0.513	0.12	0.22
Total:		**204.969**	**229.302**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ai

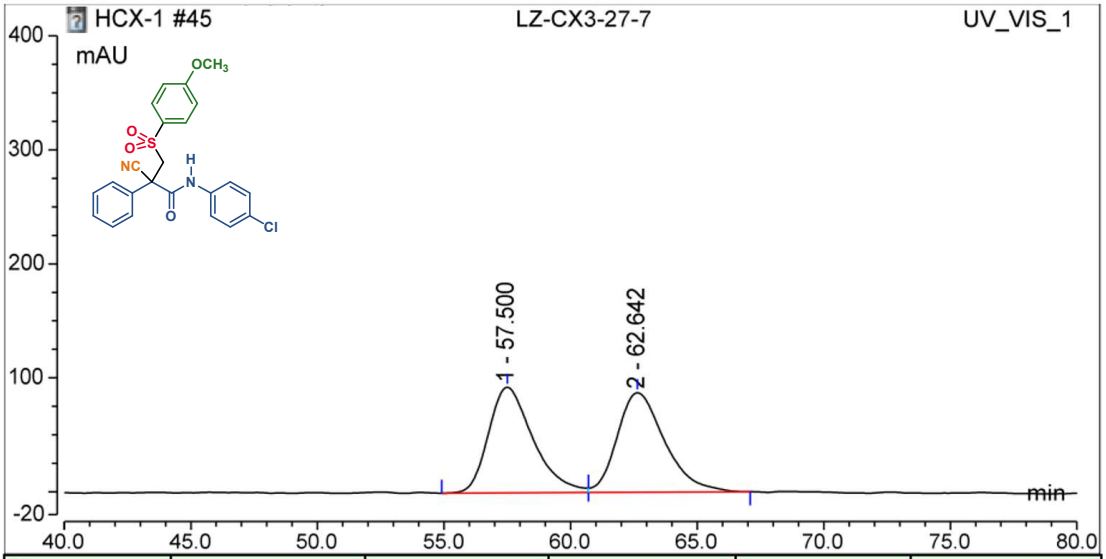


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	29.14	305.440	274.016	49.31	51.24
2	32.20	313.943	260.751	50.69	48.76
Total:		**619.383**	**534.767**	**100.00**	**100.00**

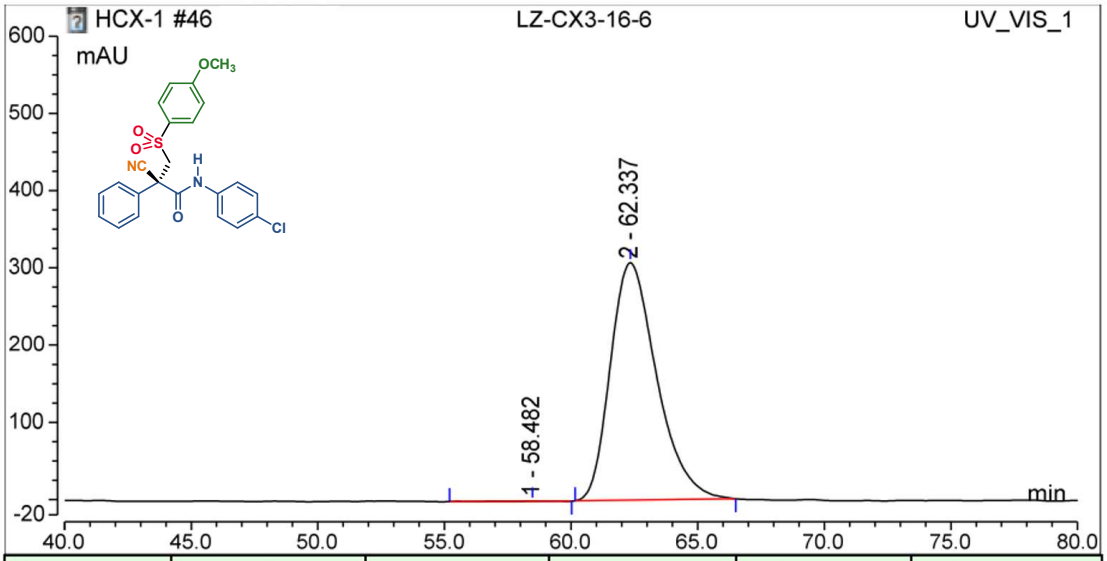


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	29.12	1.455	1.449	0.14	0.17
2	32.23	1052.359	874.432	99.86	99.83
Total:		**1053.813**	**875.881**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3aj

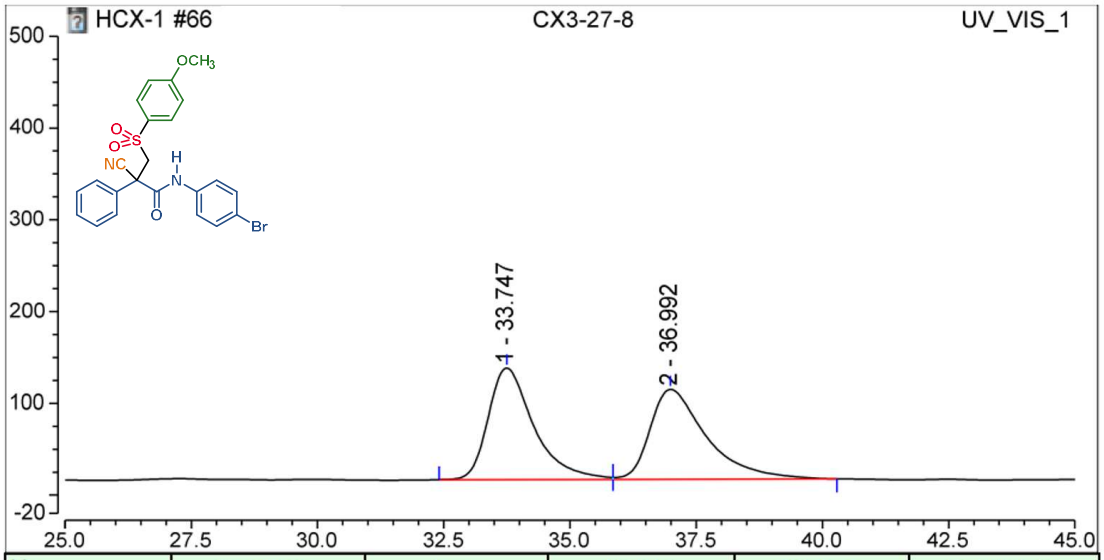


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	57.50	189.055	92.667	49.97	51.50
2	62.64	189.286	87.257	50.03	48.50
Total:		**378.341**	**179.924**	**100.00**	**100.00**

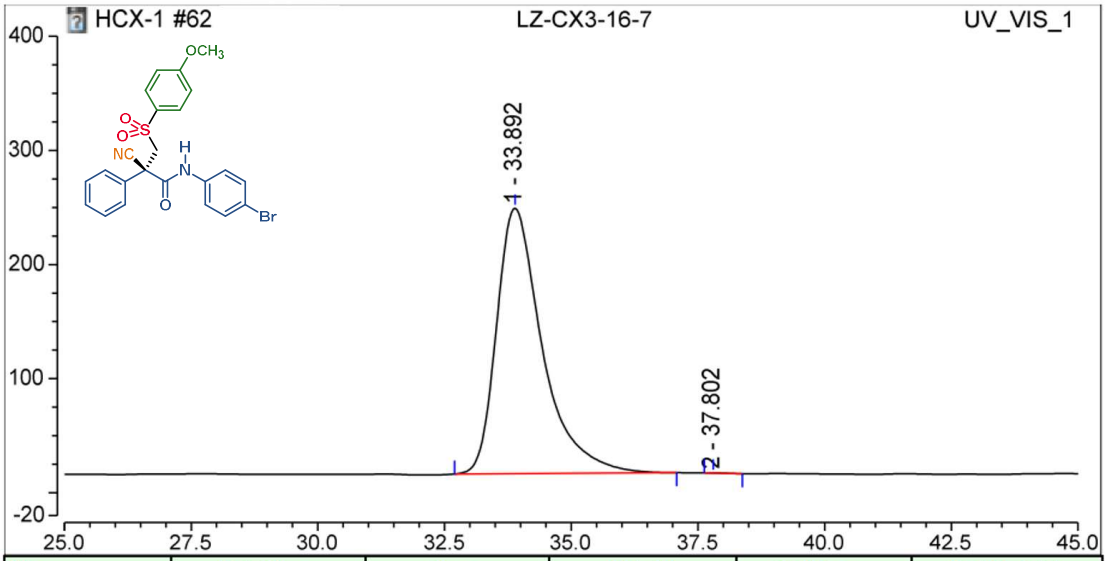


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	58.48	0.394	0.374	0.06	0.12
2	62.34	651.171	307.549	99.94	99.88
Total:		**651.565**	**307.923**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ak

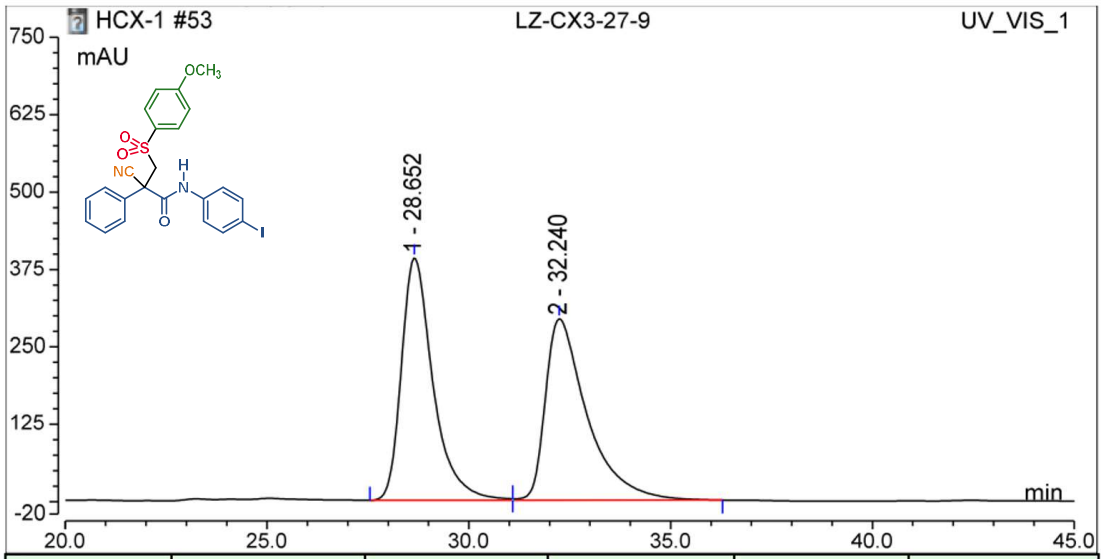


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	33.75	126.962	121.599	50.09	55.36
2	36.99	126.486	98.042	49.91	44.64
Total:		**253.448**	**219.641**	**100.00**	**100.00**

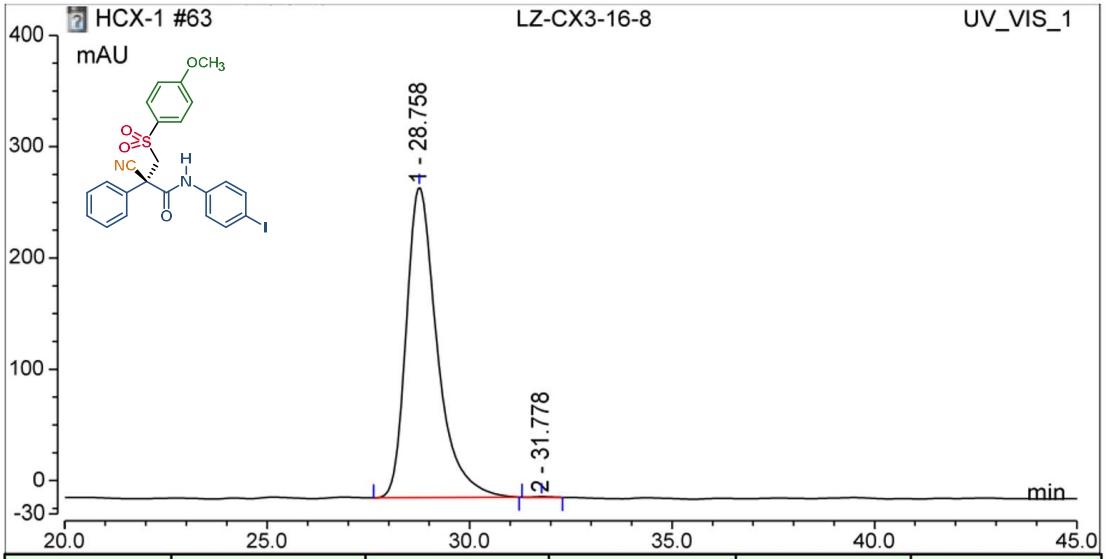


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	33.89	242.963	232.536	99.96	99.92
2	37.80	0.106	0.193	0.04	0.08
Total:		**243.069**	**232.729**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3al

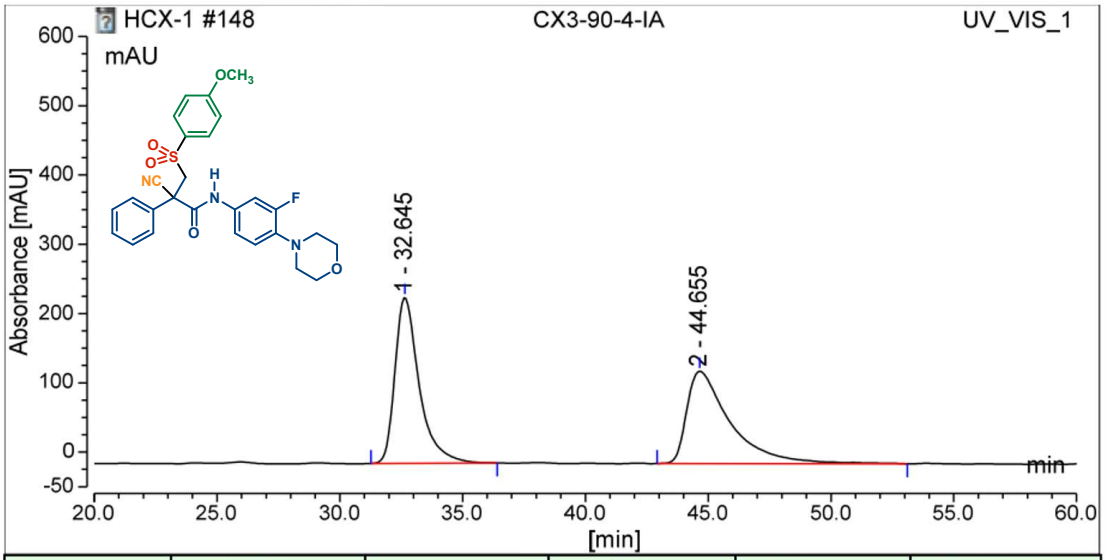


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.65	355.307	391.397	50.37	57.20
2	32.24	350.119	292.805	49.63	42.80
Total:		**705.426**	**684.202**	**100.00**	**100.00**

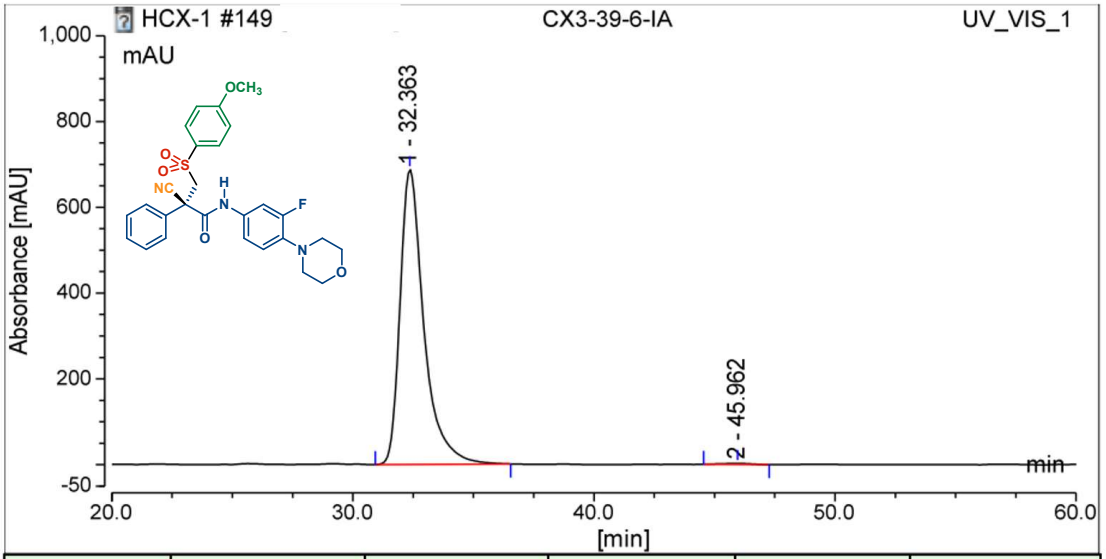


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	28.76	247.086	278.851	99.88	99.79
2	31.78	0.301	0.593	0.12	0.21
Total:		**247.387**	**279.444**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3am

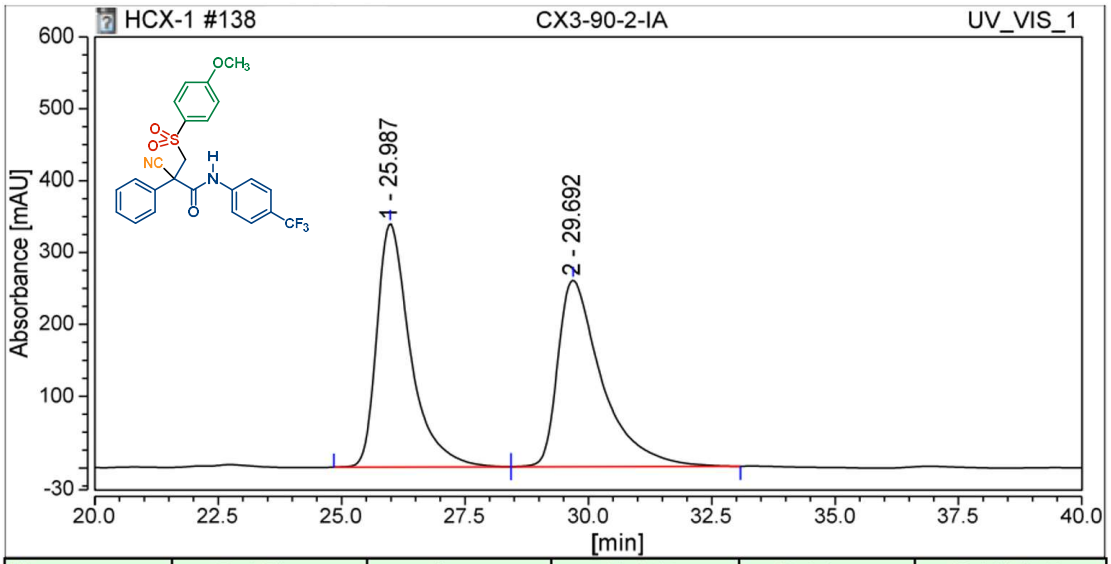


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	32.64	273.407	239.588	50.00	64.26
2	44.65	273.423	133.251	50.00	35.74
Total:		**546.830**	**372.839**	**100.00**	**100.00**

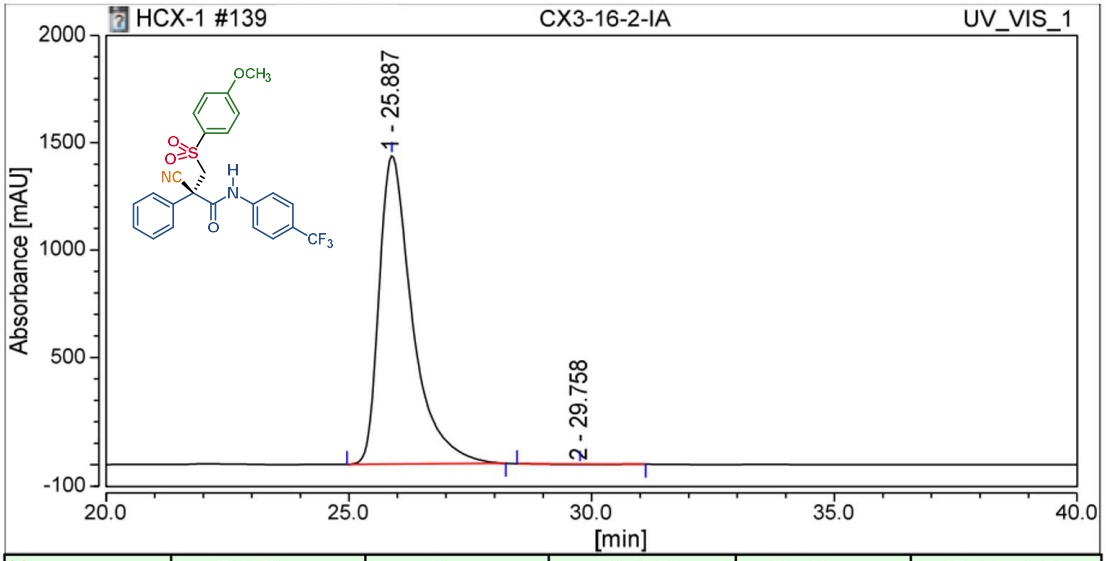


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	32.36	785.967	687.419	99.56	99.63
2	45.96	3.507	2.523	0.44	0.37
Total:		**789.473**	**689.941**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3an

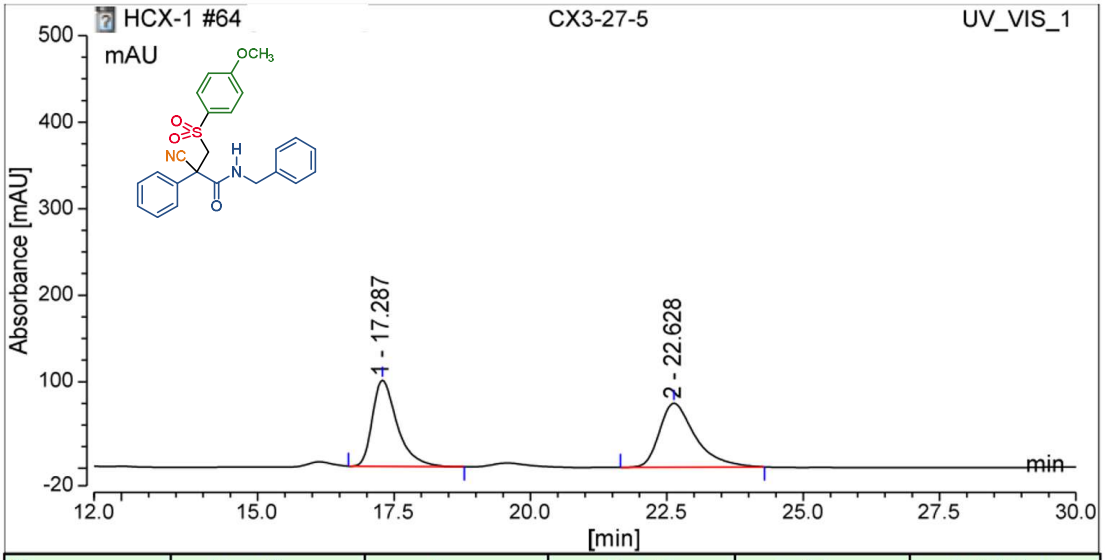


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	25.99	267.208	338.762	49.95	56.65
2	29.69	267.726	259.221	50.05	43.35
Total:		**534.934**	**597.983**	**100.00**	**100.00**

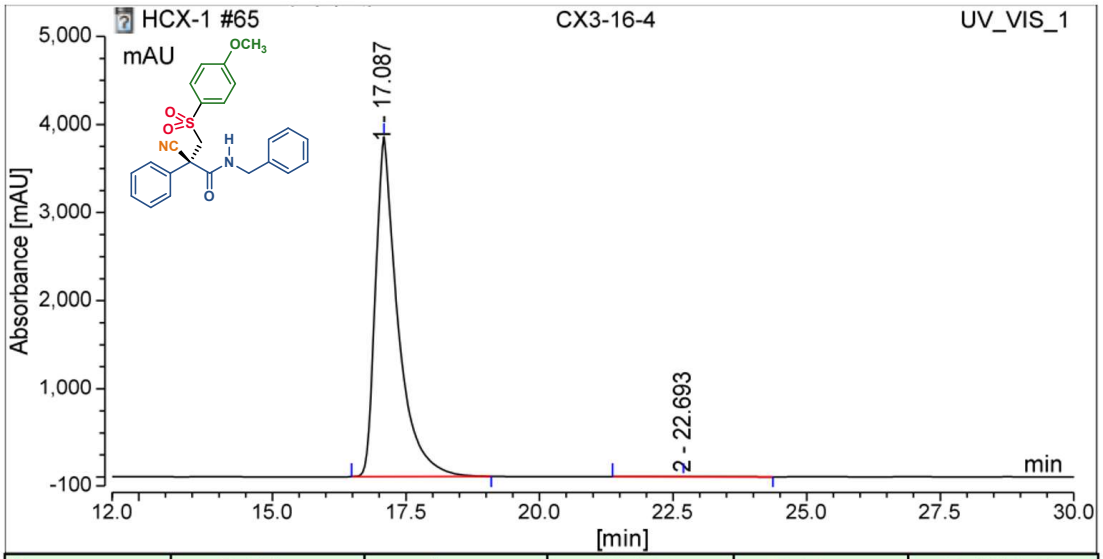


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	25.89	1139.932	1436.962	99.69	99.83
2	29.76	3.521	2.447	0.31	0.17
Total:		**1143.453**	**1439.410**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ao

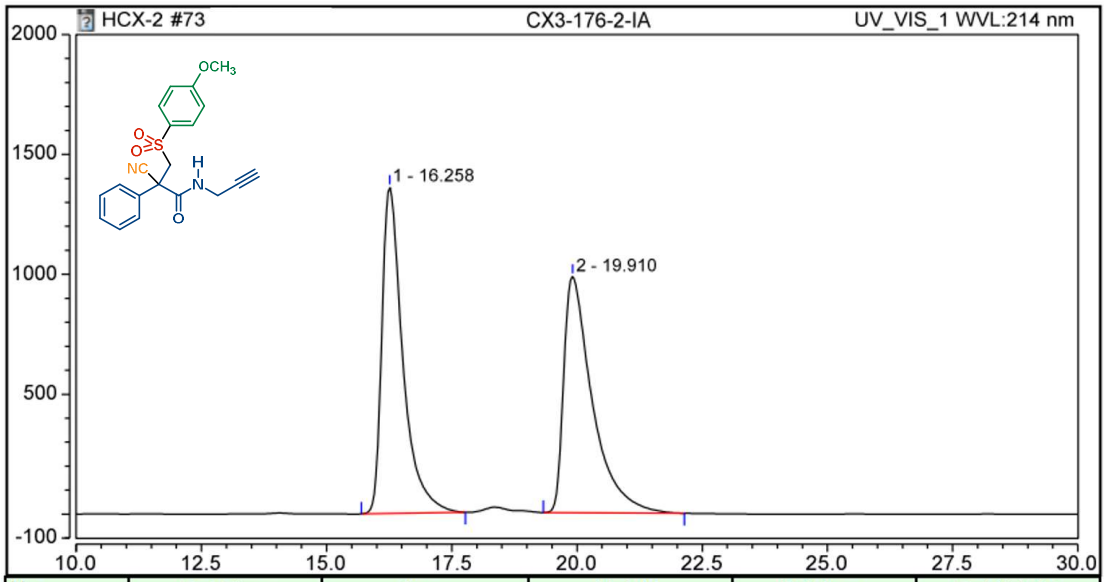


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.29	52.470	99.515	48.31	57.41
2	22.63	56.151	73.836	51.69	42.59
Total:		**108.621**	**173.352**	**100.00**	**100.00**

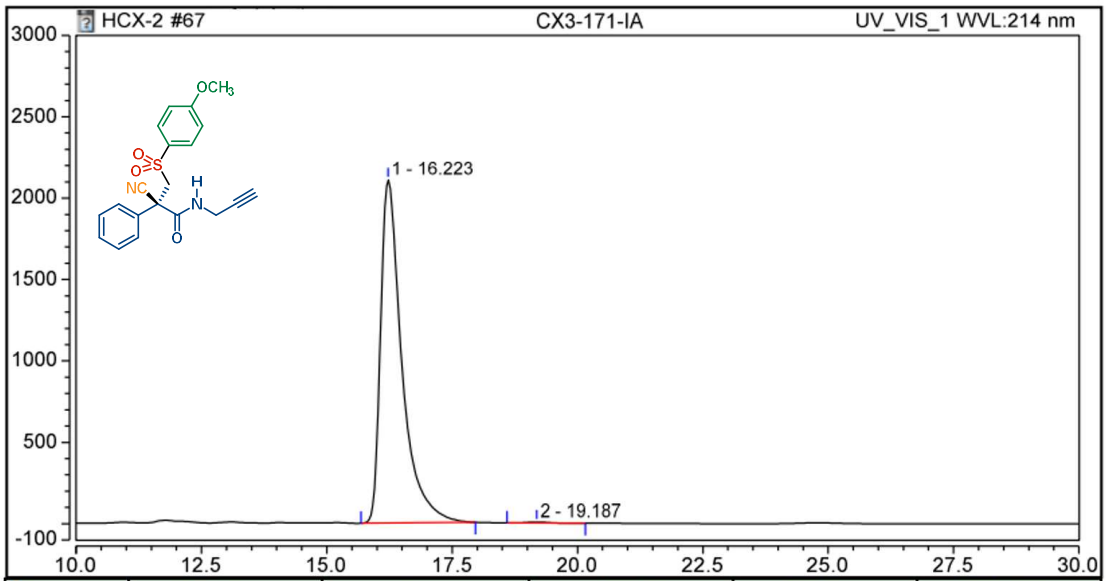


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.09	1870.779	3859.999	99.85	99.95
2	22.69	2.814	2.071	0.15	0.05
Total:		**1873.594**	**3862.070**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ap

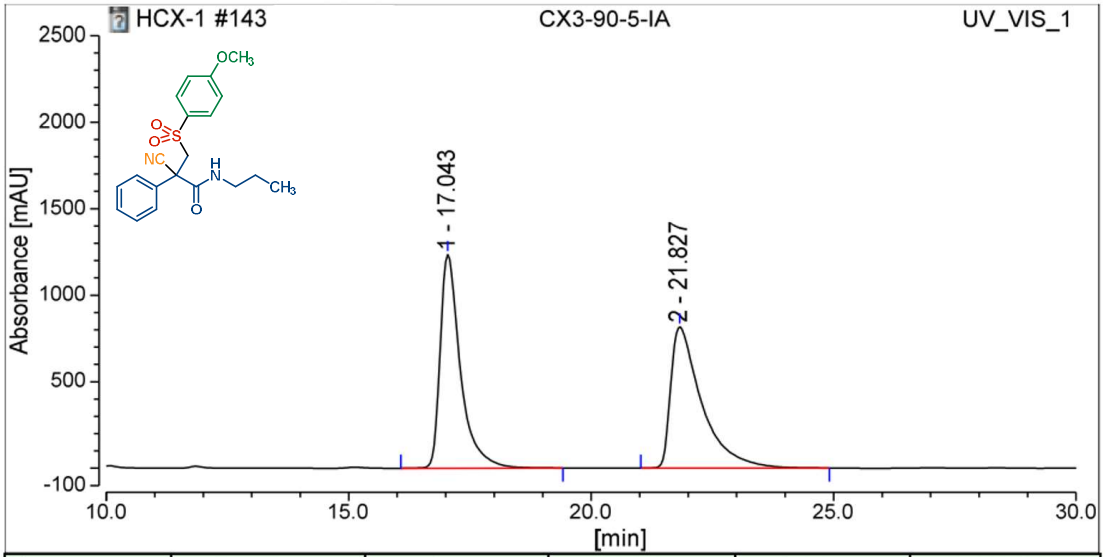


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	16.26	660.193	1360.211	50.26	57.99
2	19.91	653.234	985.300	49.74	42.01
Total:		**1313.427**	**2345.510**	**100.00**	**100.00**

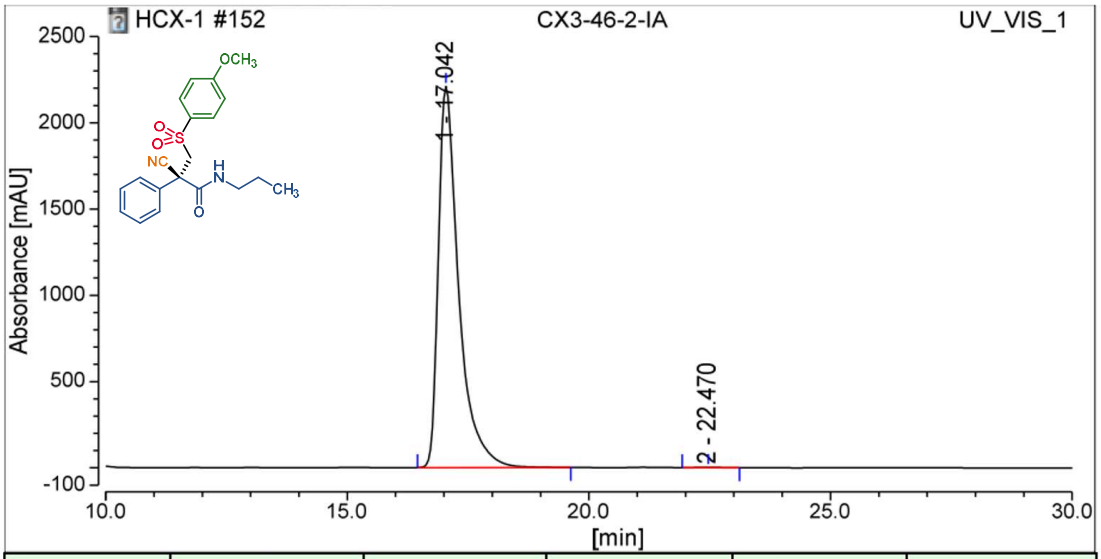


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	16.22	1042.055	2108.026	99.75	99.72
2	19.19	2.607	5.899	0.25	0.28
Total:		**1044.662**	**2113.925**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3aq

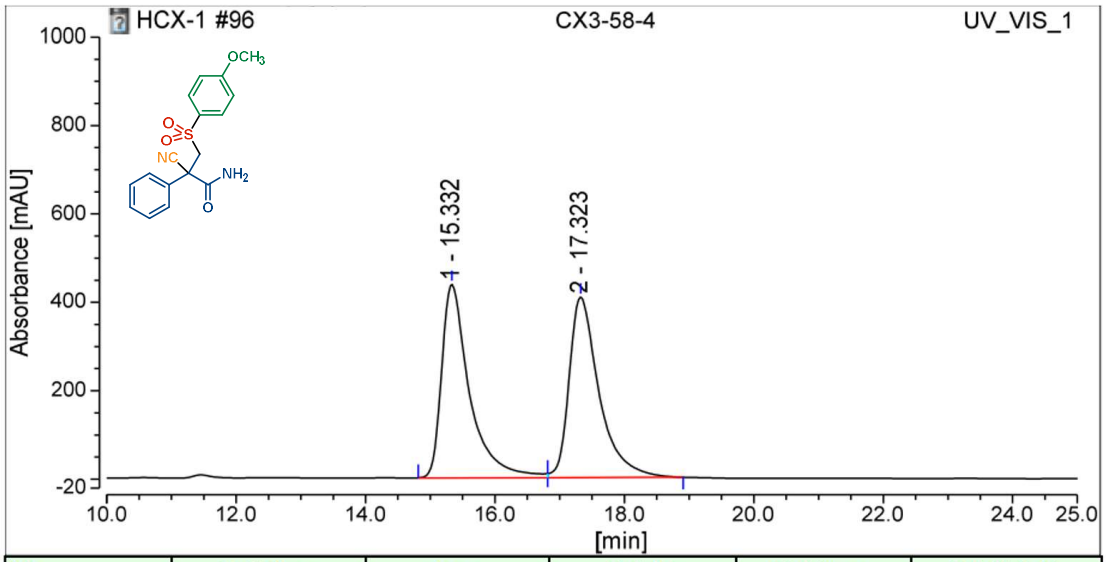


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.04	596.293	1234.775	49.67	60.19
2	21.83	604.192	816.751	50.33	39.81
Total:		**1200.485**	**2051.527**	**100.00**	**100.00**

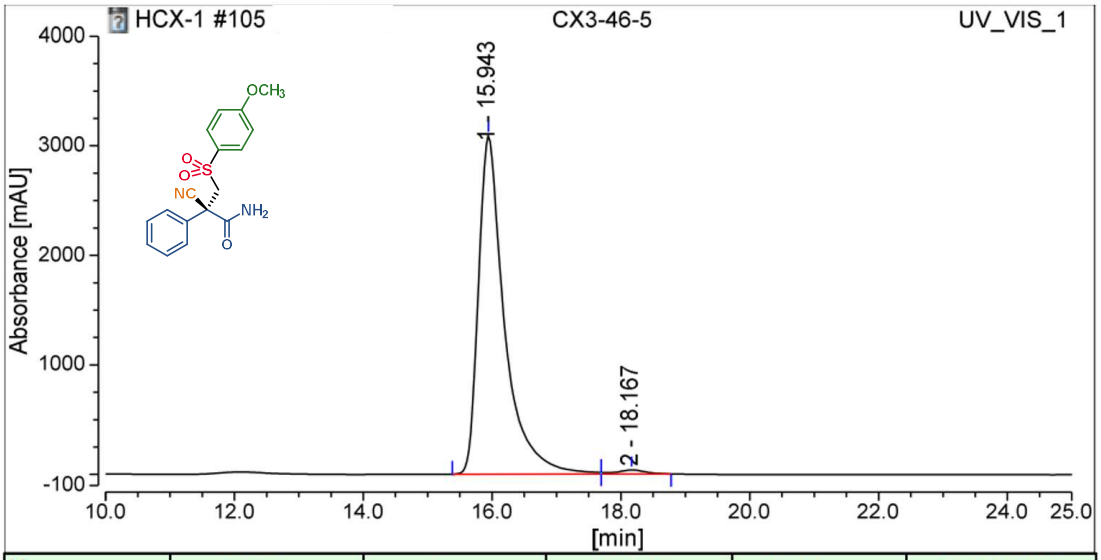


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.04	1077.561	2209.073	99.94	99.95
2	22.47	0.669	1.180	0.06	0.05
Total:		**1078.231**	**2210.253**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3ar

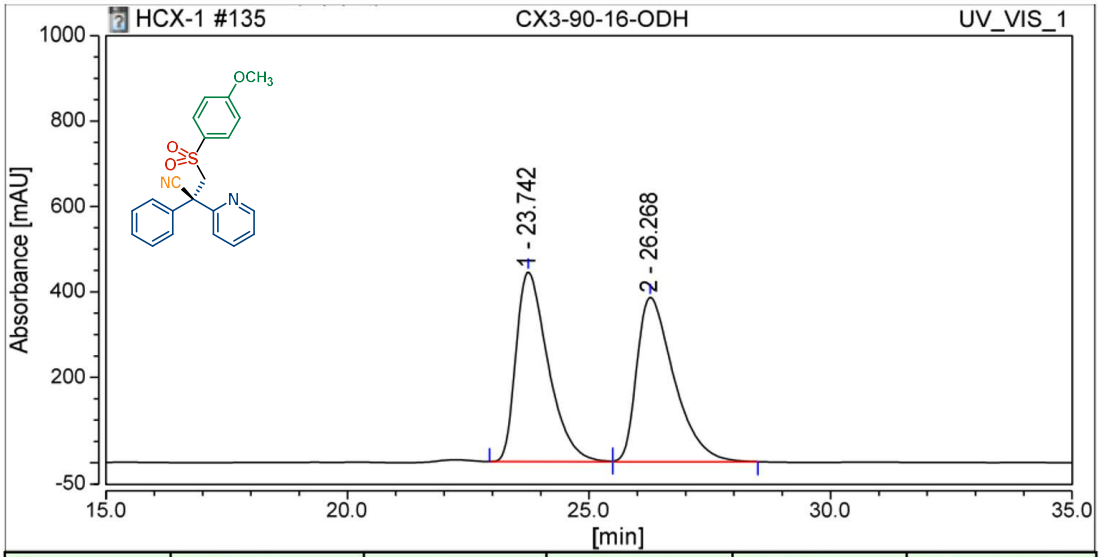


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	15.33	217.925	438.179	49.94	51.75
2	17.32	218.433	408.542	50.06	48.25
Total:		**436.358**	**846.721**	**100.00**	**100.00**

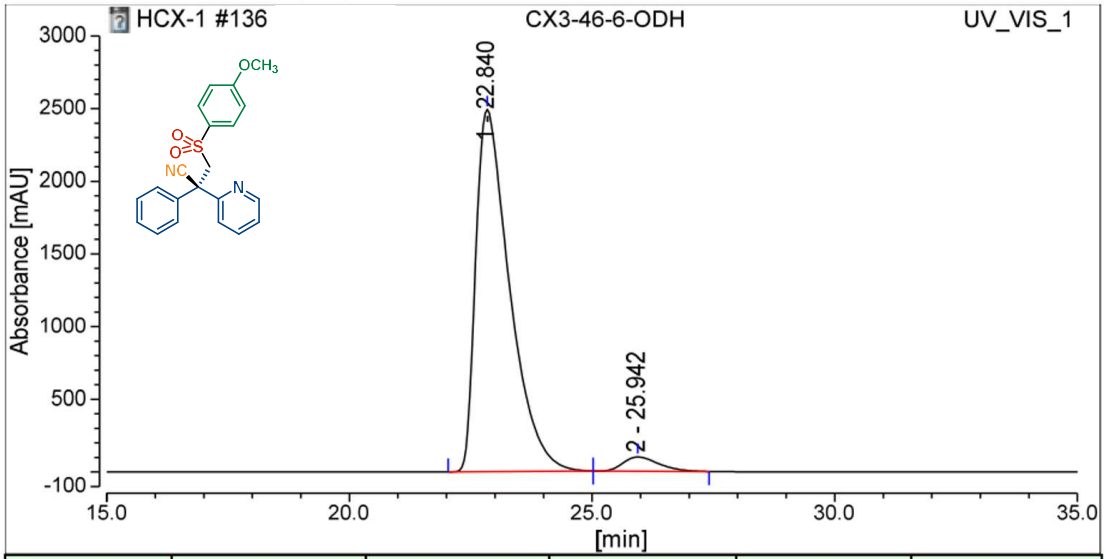


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	15.94	1447.091	3092.943	98.69	98.79
2	18.17	19.200	37.752	1.31	1.21
Total:		**1466.291**	**3130.694**	**100.00**	**100.00**

HPLC chromatograms of Compound of 3as

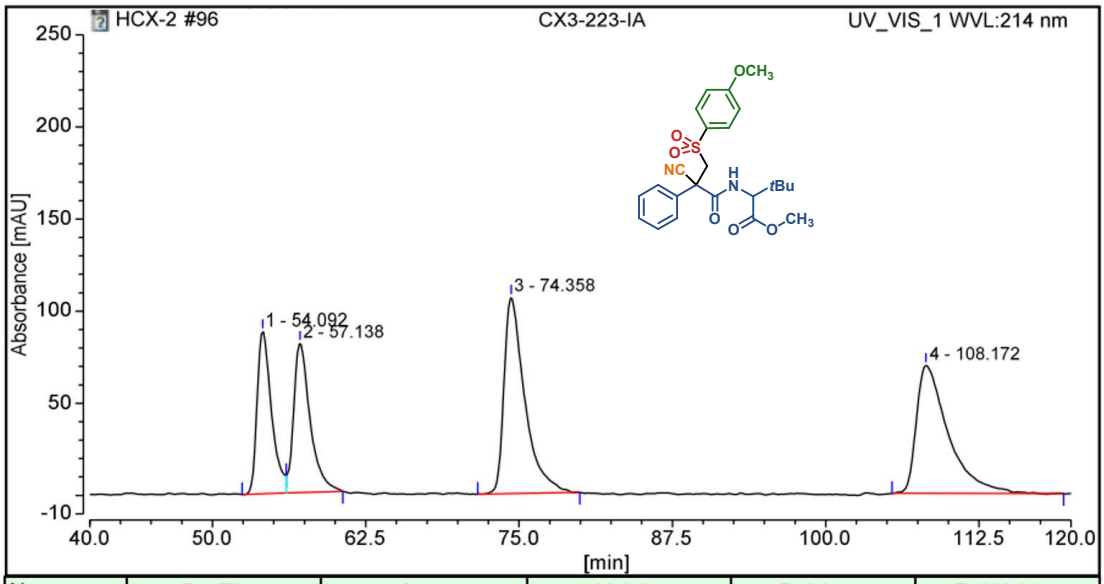


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	23.74	342.328	444.209	49.90	53.57
2	26.27	343.661	384.929	50.10	46.43
Total:		**685.989**	**829.139**	**100.00**	**100.00**

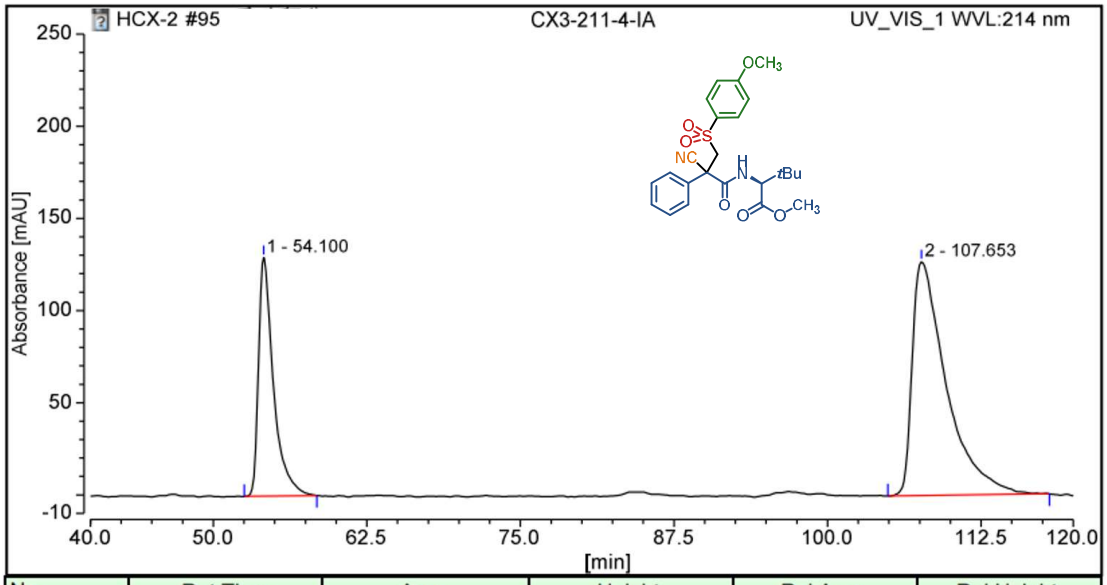


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	22.84	2011.040	2491.526	96.02	96.21
2	25.94	83.308	98.128	3.98	3.79
Total:		**2094.348**	**2589.654**	**100.00**	**100.00**

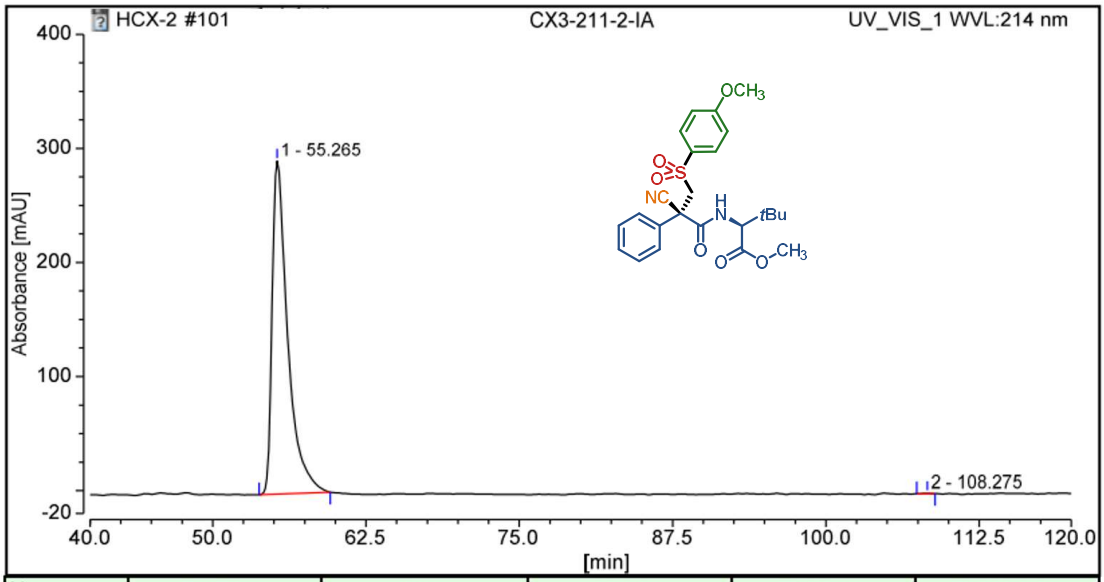
HPLC chromatograms of Compound of 5a



No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	54.09	120.448	88.222	18.08	25.53
2	57.14	126.714	81.231	19.02	23.51
3	74.36	209.565	106.608	31.45	30.85
4	108.17	209.595	69.521	31.46	20.12
Total:		**666.322**	**345.581**	**100.00**	**100.00**

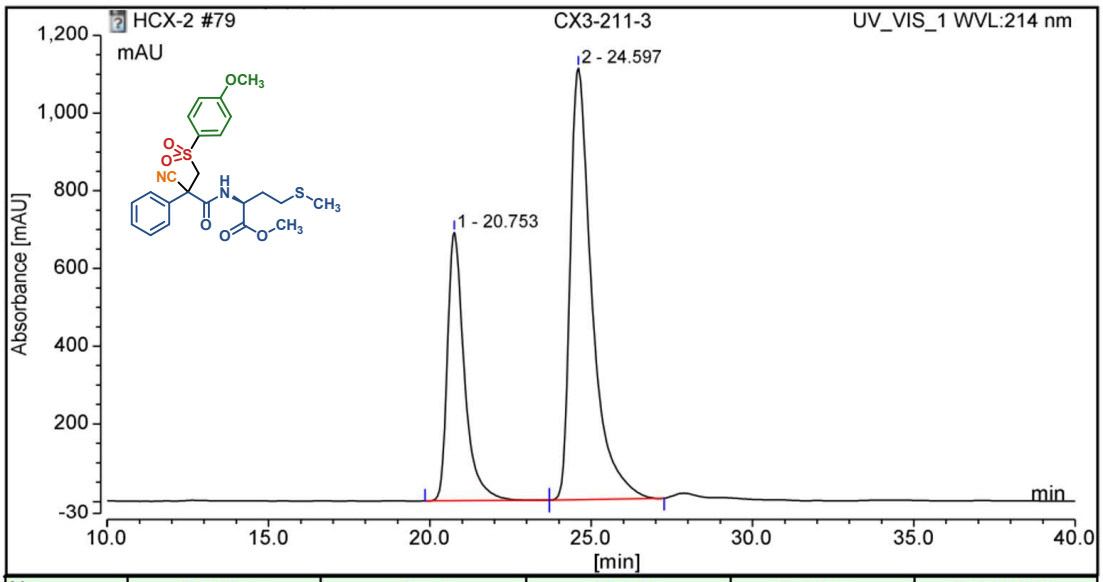


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	54.10	182.314	129.445	30.93	50.53
2	107.65	407.194	126.720	69.07	49.47
Total:		**589.509**	**256.165**	**100.00**	**100.00**

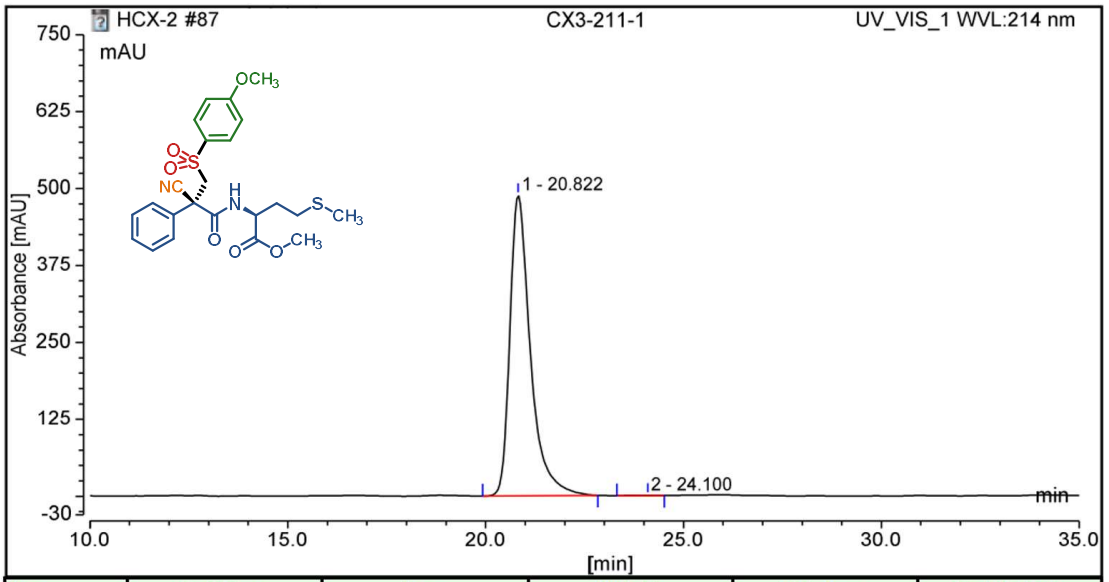


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	55.26	430.444	292.019	99.99	99.93
2	108.27	0.058	0.218	0.01	0.07
Total:		**430.501**	**292.237**	**100.00**	**100.00**

HPLC chromatograms of Compound of 5b

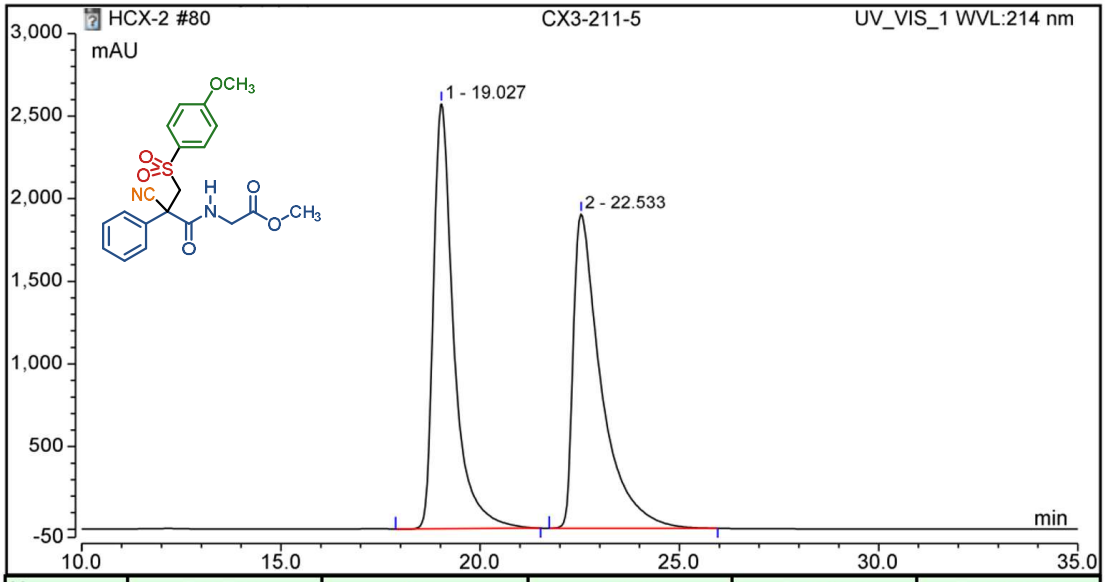


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.75	419.633	690.203	32.56	38.33
2	24.60	869.230	1110.650	67.44	61.67
Total:		**1288.863**	**1800.853**	**100.00**	**100.00**

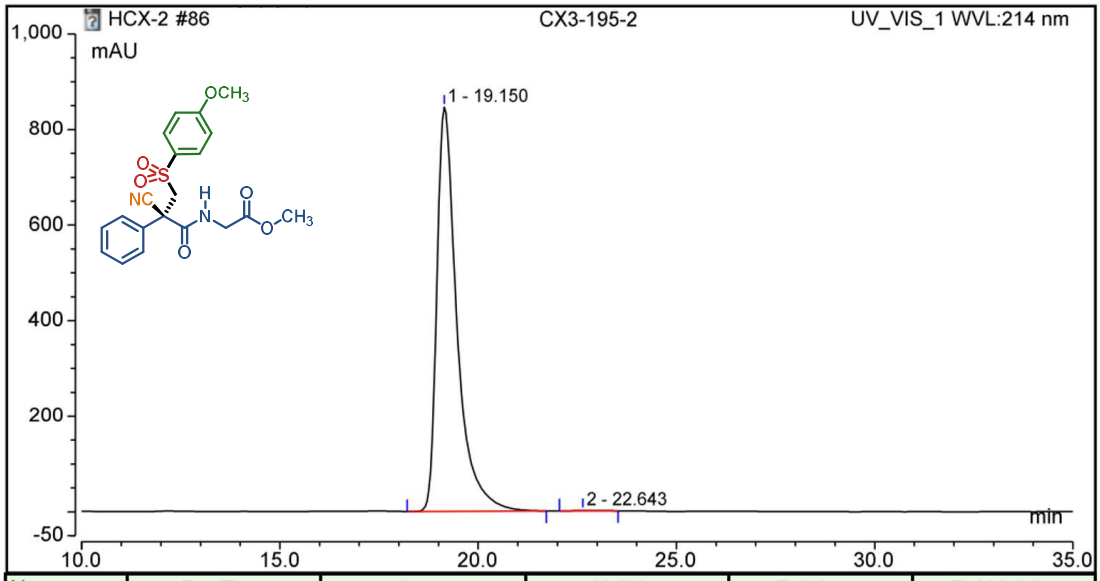


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.82	294.334	488.061	99.89	99.90
2	24.10	0.318	0.496	0.11	0.10
Total:		**294.652**	**488.558**	**100.00**	**100.00**

HPLC chromatograms of Compound of 5c

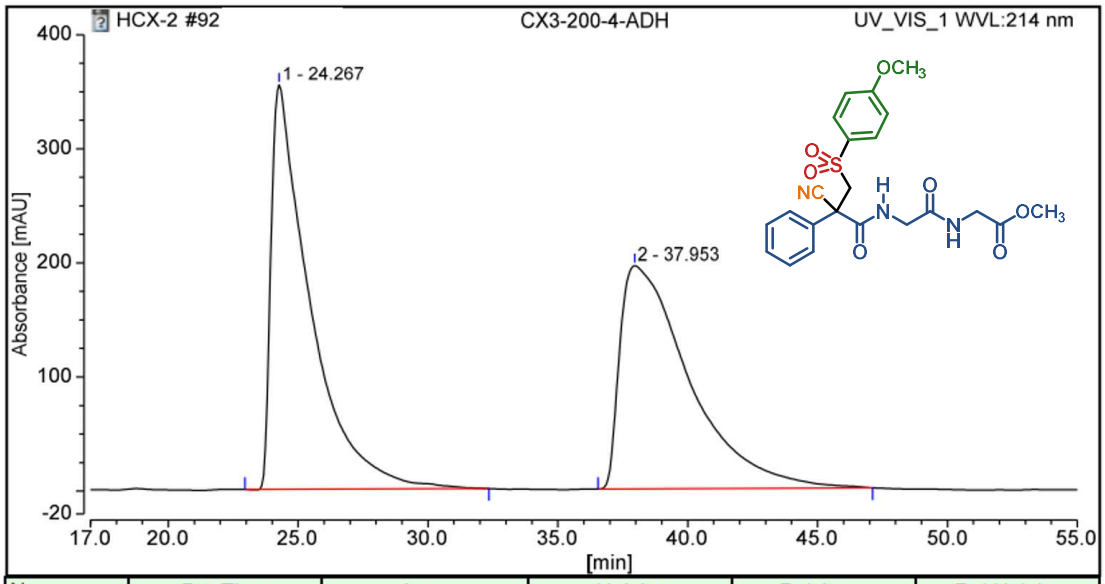


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	19.03	1519.273	2572.285	49.55	57.47
2	22.53	1546.736	1903.201	50.45	42.53
Total:		**3066.009**	**4475.486**	**100.00**	**100.00**

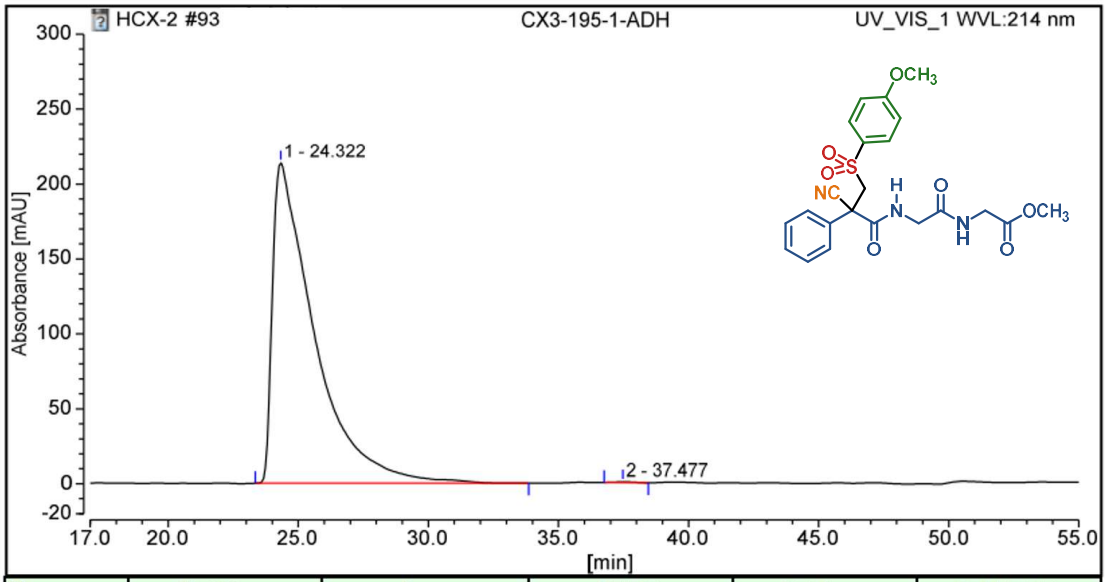


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	19.15	498.787	845.993	99.87	99.89
2	22.64	0.656	0.935	0.13	0.11
Total:		**499.443**	**846.928**	**100.00**	**100.00**

HPLC chromatograms of Compound of 5d

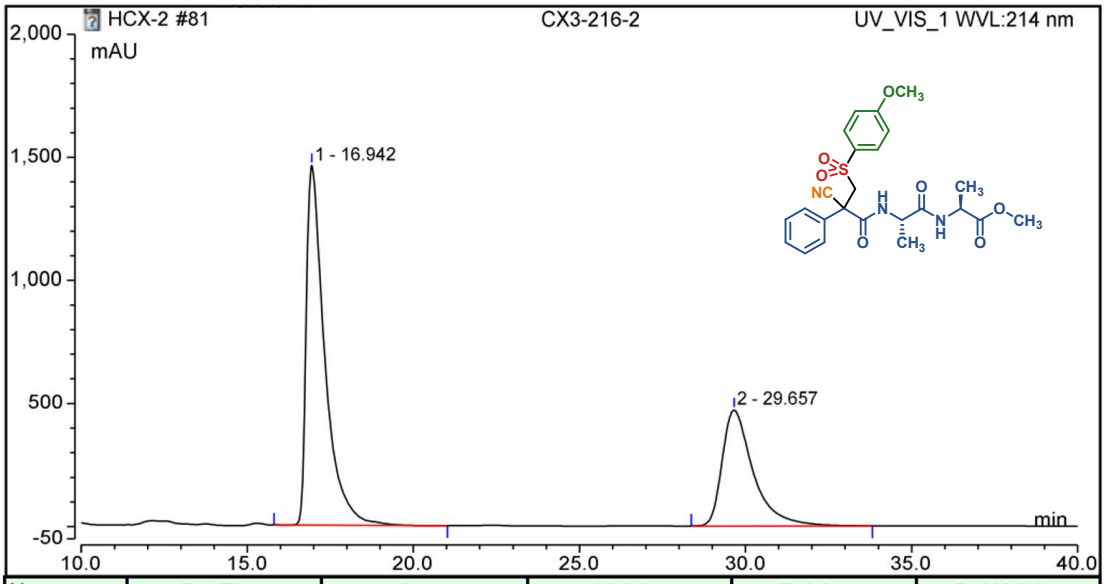


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	24.27	617.069	354.571	50.43	64.42
2	37.95	606.446	195.792	49.57	35.58
Total:		**1223.514**	**550.363**	**100.00**	**100.00**

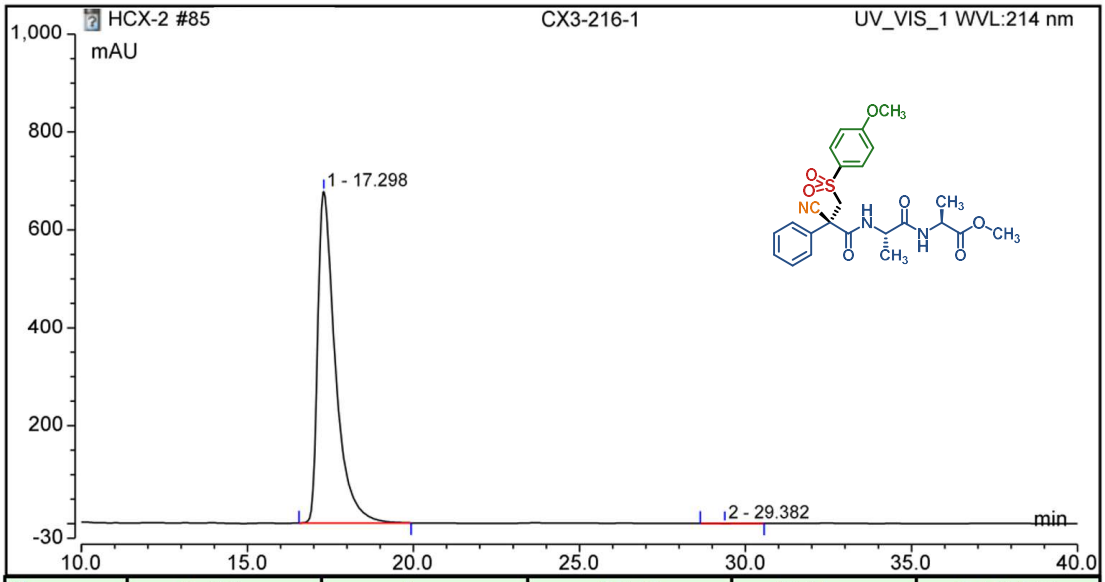


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	24.32	398.313	213.925	99.89	99.78
2	37.48	0.434	0.465	0.11	0.22
Total:		**398.747**	**214.391**	**100.00**	**100.00**

HPLC chromatograms of Compound of 5e

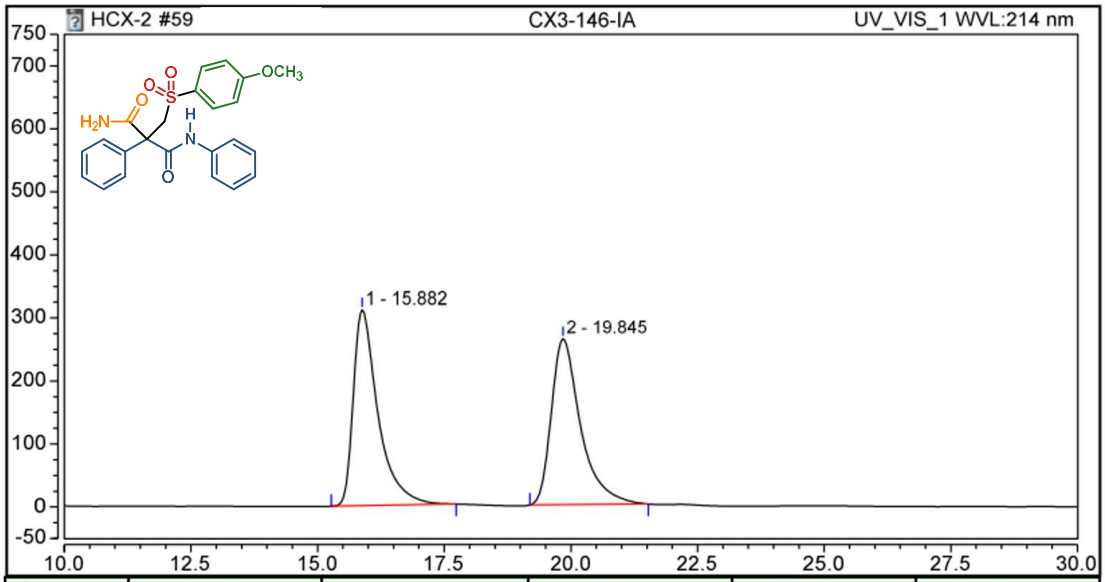


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	16.94	943.285	1461.210	64.83	75.62
2	29.66	511.774	471.105	35.17	24.38
Total:		**1455.059**	**1932.315**	**100.00**	**100.00**

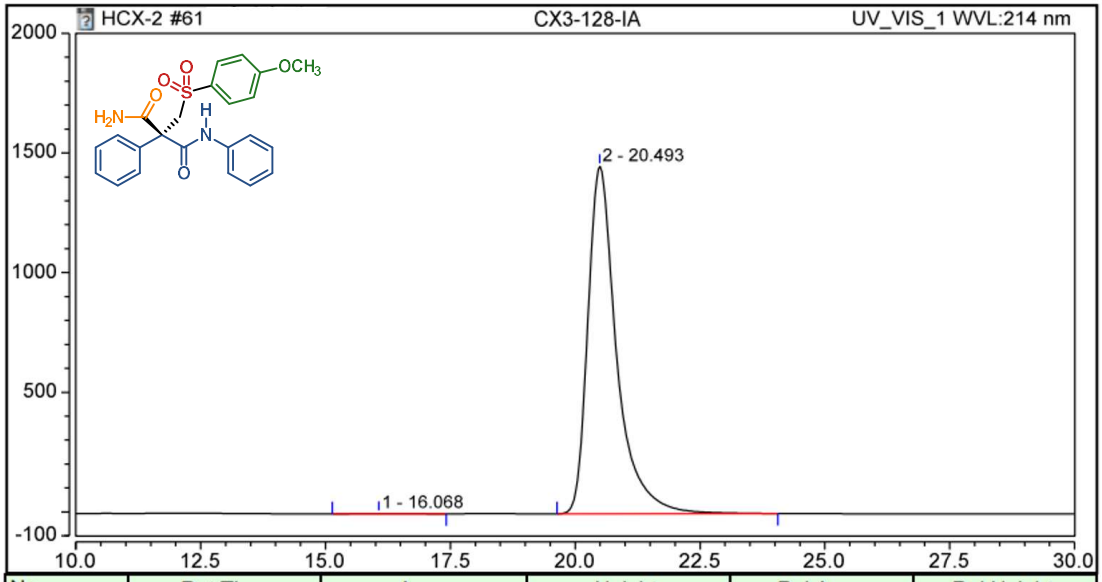


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	17.30	416.804	676.890	99.90	99.93
2	29.38	0.397	0.502	0.10	0.07
Total:		**417.201**	**677.391**	**100.00**	**100.00**

HPLC chromatograms of Compound of 6

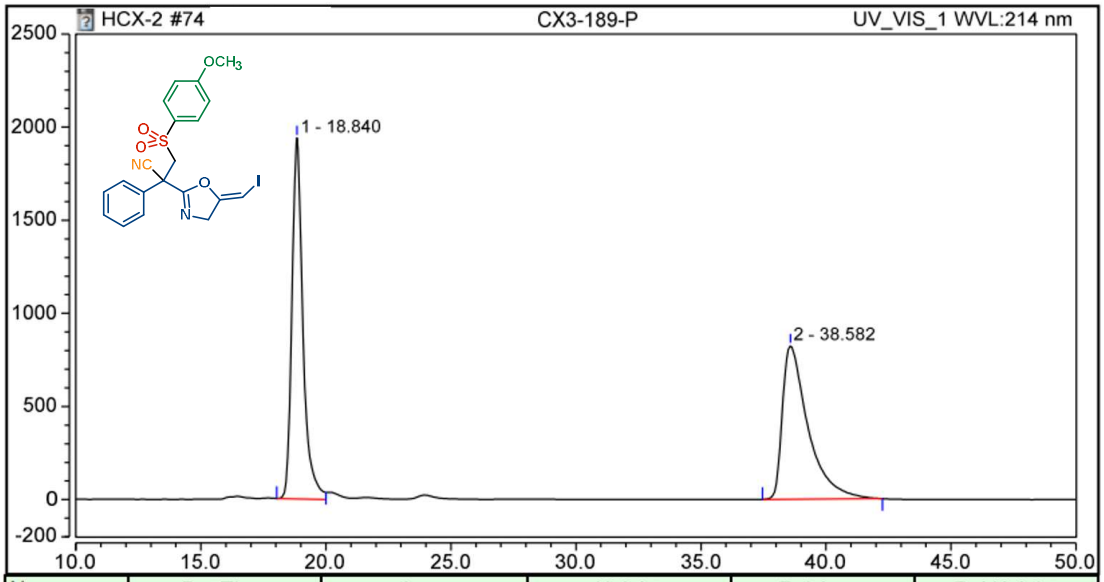


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	15.88	176.098	310.862	49.97	54.14
2	19.84	176.330	263.292	50.03	45.86
Total:		**352.427**	**574.153**	**100.00**	**100.00**

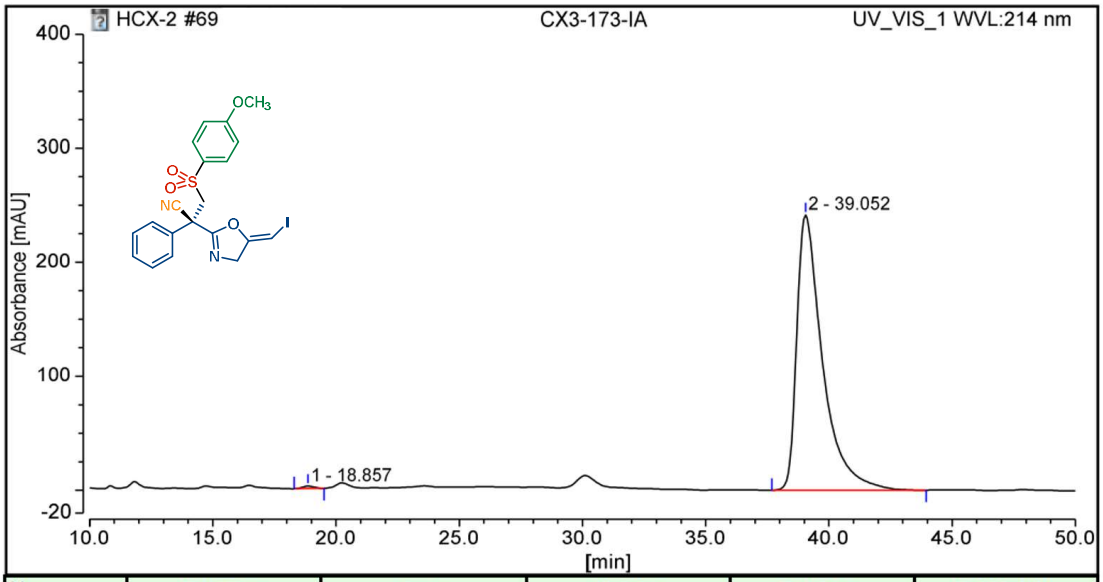


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	16.07	1.785	1.589	0.18	0.11
2	20.49	973.081	1451.929	99.82	99.89
Total:		**974.866**	**1453.518**	**100.00**	**100.00**

HPLC chromatograms of Compound of 7

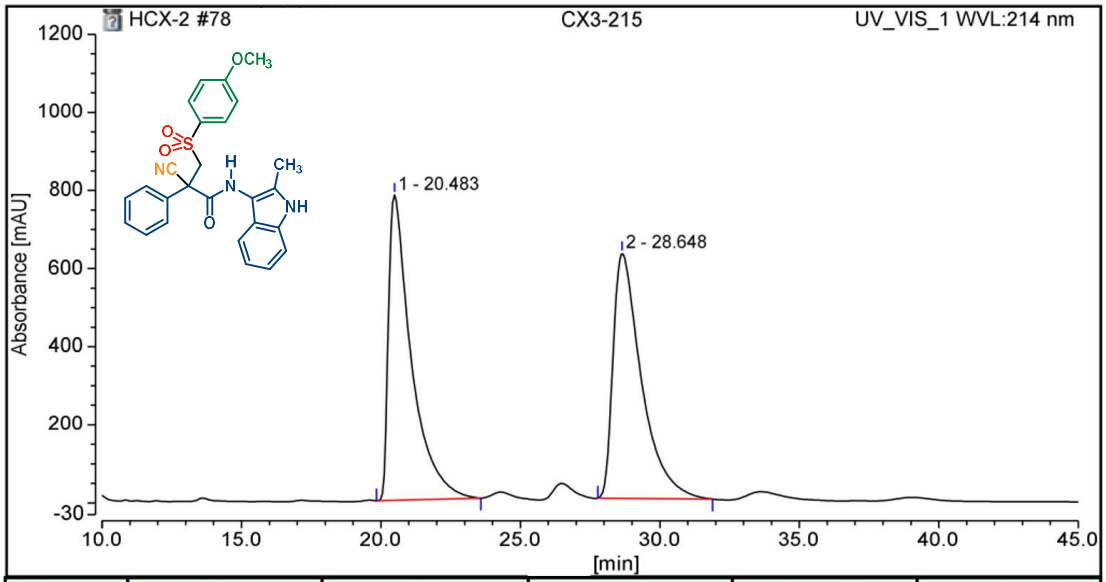


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	18.84	992.673	1937.503	50.28	70.17
2	38.58	981.468	823.629	49.72	29.83
Total:		**1974.140**	**2761.132**	**100.00**	**100.00**

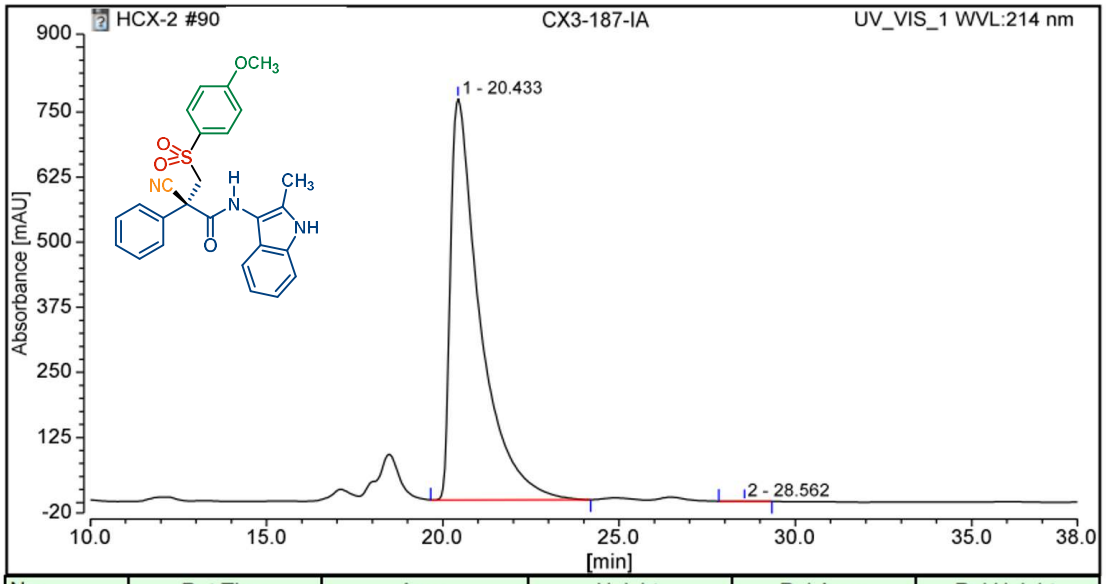


No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	18.86	1.127	2.089	0.38	0.86
2	39.05	292.945	241.551	99.62	99.14
Total:		**294.072**	**243.640**	**100.00**	**100.00**

HPLC chromatograms of Compound of 8



No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.48	739.414	781.618	50.00	55.49
2	28.65	739.555	626.924	50.00	44.51
Total:		**1478.969**	**1408.542**	**100.00**	**100.00**



No.	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %	Rel.Height %
1	20.43	744.827	770.715	99.97	99.96
2	28.56	0.260	0.293	0.03	0.04
Total:		**745.087**	**771.009**	**100.00**	**100.00**