Directed, Nickel-Catalyzed 1,2-Alkylsulfenylation of Alkenyl Carbonyl Compounds

Zi-Qi Li,[a] Wen-Ji He,[a] Hui-Qi Ni,[a] and Keary M. Engle[a*]

[a] Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037, United States

*keary@scripps.edu

Table of Contents

General Information

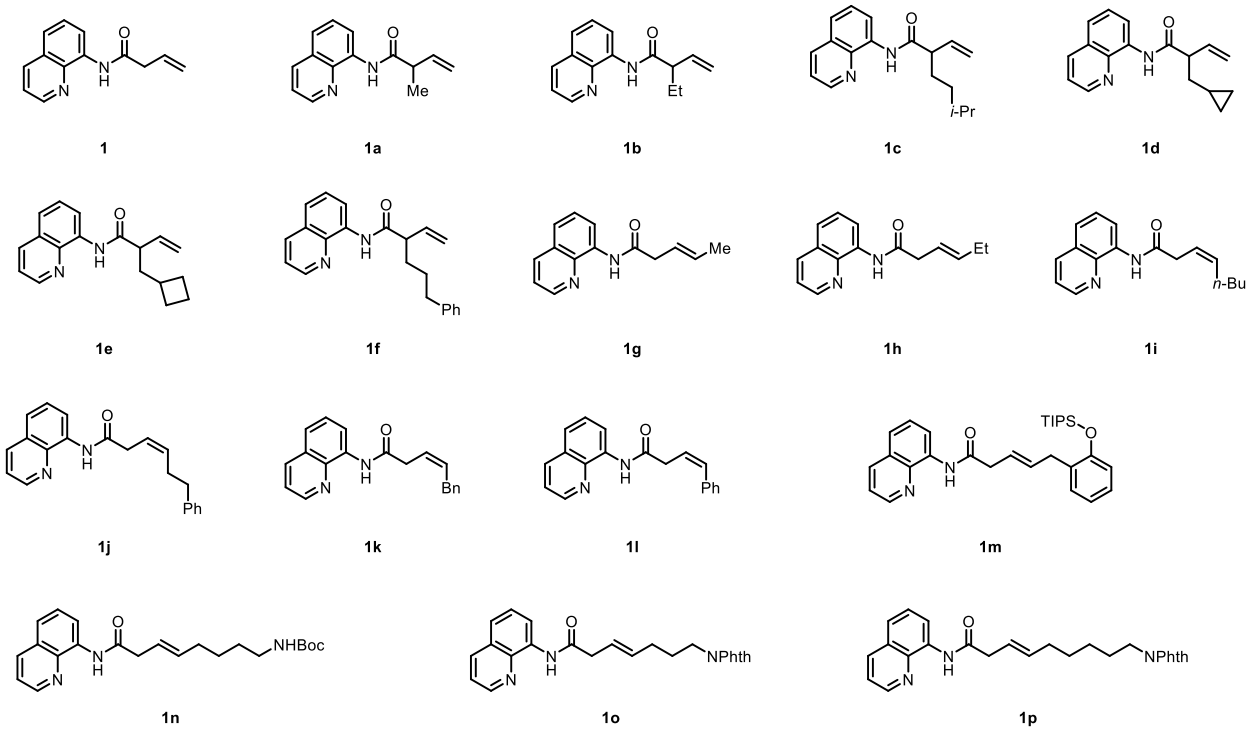
Unless otherwise stated, all materials were used as received from commercial sources without further purification. All glassware and magnetic stir bars were dried in an oven at 100 °C overnight unless otherwise stated. All solvents were purchased from MilliporeSigma (Sure/Seal^{TM}) and used as received. 2-Dram (8-mL) reaction tubes were purchased from Fisher (Cat#: 50976409). Caps with TFE septa were purchased from Chemglass (Cat#: CG-4910-16). Ambient (room) temperature refers to 21–24 °C. Elevated temperatures were maintained by an IKA heating block for 2-dram vials or a silicone oil bath for larger vessels. Thin-layer chromatography (TLC) was performed using EMD Millipore 250 mm silica gel F-254 plates (250 μm) with F-254 fluorescent indicator and visualized by UV fluorescence quenching, iodine, Seebach's stain, or potassium permanganate stain. SiliCycle SiliaFlash P60 silica gel (particle size 40–63 μm) was used for flash chromatography. Analtech thin layer chromatography products (20 cm × 20 cm, 1000 micron) were used for preparative TLC. ^{1}H,^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX equipped with a 5 mm DCH cryoprobe (600 MHz, 150 MHz, and 376 MHz, respectively). ^{1}H NMR spectra were reported relative to Me_4Si (δ 0.0) unless otherwise stated. ^{13}C NMR spectra were calibrated to residual solvent signals ($CDCl_3$ at 77.16 ppm). High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time of flight experiments or atmospheric-pressure chemical ionization time of flight experiments.

Commercial Suppliers of Chemicals:

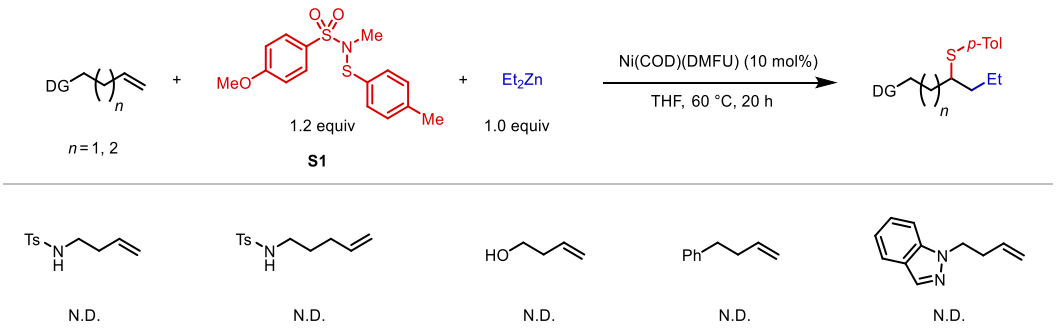
The following chemicals were purchased from the suppliers indicated:

$Ni(COD)_2$: Strem (1295-35-8)
Tetrahydrofuran: MilliporeSigma (401757-100ML)
All commercial reagents were purchased from MilliporeSigma, Alfa Aesar, Oakwood, TCI or Strem and used as received.

Table of Substrates



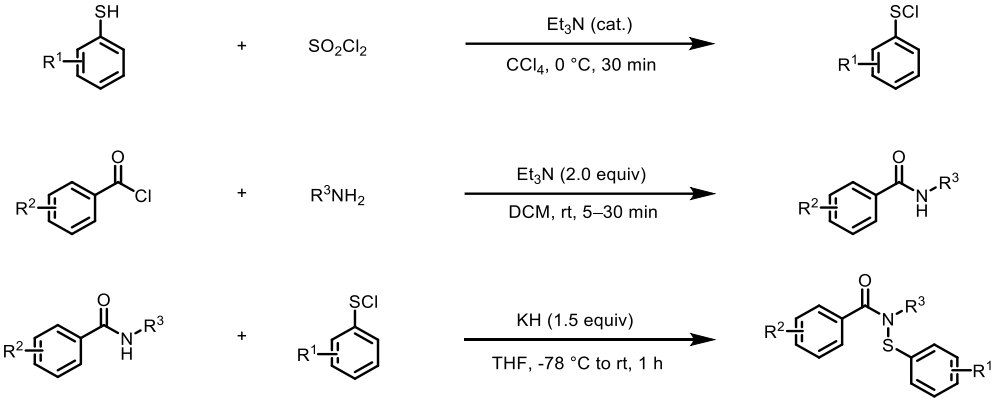
Scheme S1. List of alkene substrates used in this study.[1–2]



Scheme S2. Limitations. N.D. = product not detected.

Experimental Procedures

General Procedure A for the Synthesis of N–S Reagents

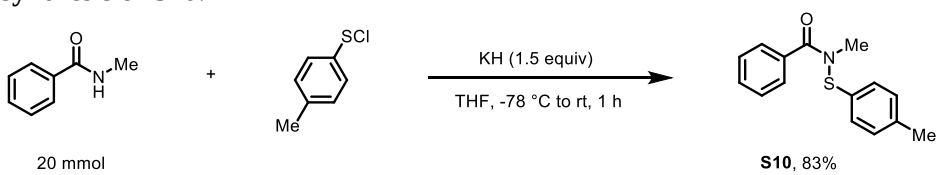


Synthesis of sulfenyl chlorides: The reaction was carried out according to a modified literature procedure.[3] To a solution of thiol (100 mmol) in CCl_4 (100 mL) was added triethylamine (3 drops). The solution was cooled to 0 °C. Sulfuryl chloride (110 mmol) was added dropwise. The reaction was kept stirring at 0 °C for an additional 30 min. After this time, the solvent was removed, and the residue was used without further purification.

Synthesis of *N*-alkylbenzamides: To a solution of the appropriate benzoyl chloride (1.0 equiv) in DCM (0.7 M) were added triethylamine (2.0 equiv) and the appropriate alkyl amine (1.2 equiv) under 0 °C. The reaction was warmed to room temperature and stirred for an additional 5−30 min, and reaction progress was monitored by TLC. After this time, the reaction was quenched with water. The aqueous solution was extracted with DCM (×3). The combined organic layers were dried over Na_2SO_4. The organic solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexanes/ethyl acetate as the eluent to afford the product. For the synthesis of *N*-methybenzamides, an aqueous solution of methylamine was used; in this case, no purification was required before subjecting the residue to the next step.

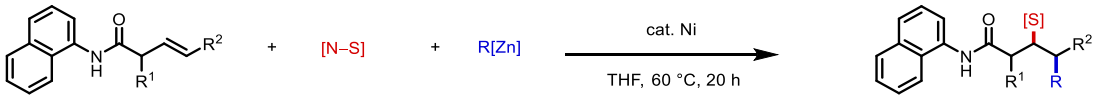
Synthesis of N–S reagents: The reaction was carried out according to a modified literature procedure.[4] To a solution of *N*-alkylbenzamide (5 mmol) in THF (10 mL) was added KH (1.5 equiv). The reaction mixture was stirred at room temperature for 1 h. After this time, solution of ArSCl in THF (5 mL) was added dropwise at –78 °C until a light-yellow color persisted, suggesting the reaction had reached completion. The reaction was allowed to warm to room temperature and continue stirring for an additional 1 h, and reaction progress was monitored by TLC. After this time, the reaction was quenched with water. The aqueous solution was extracted with DCM (×3). The combined organic layers were dried over Na_2SO_4. The organic solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexanes/ethyl acetate as the eluent to afford the product.

Large-scale synthesis of S10:



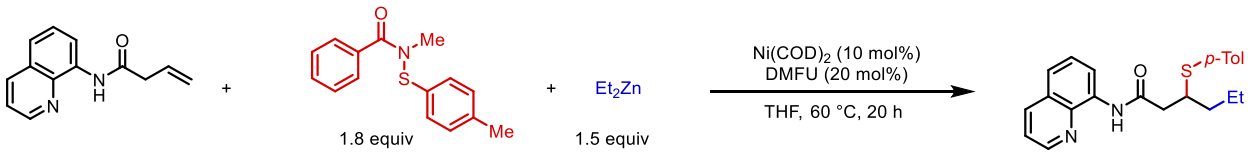
Following General Procedure A, **S10** was prepared on 20 mmol scale with 83% isolated yield.

General Procedure B for Nickel-catalyzed Carbosulfenylation



Outside of the glovebox, to an oven-dried 1-dram (4-mL) reaction tube equipped with a magnetic stir bar were added the appropriate alkene (0.1 mmol) and N–S reagent (0.12 mmol). The vial was then introduced into an argon-filled glovebox antechamber. Once transferred inside the glovebox, Ni(COD)(DMFU)[5] (3.1 mg, 10 mol%) or $Ni(COD)_2$ (2.8 mg, 10 mol%) was added to the vial, followed by THF (1.0 mL). The vial was sealed with a screw-top septum cap and removed from the glovebox. The dialkylzinc reagent (0.1 mmol, 1 M in THF) or alkylzinc bromide (0.1 mmol, 0.5 M in THF) was added dropwise over the course of 15 min as the reaction vessel was heated to 60 °C while stirring. The reaction was left to stir at 60 °C for 30 min. After this time, N–S reagent (0.06 mmol, 0.6 M in THF) was added in one portion followed by dropwise addition of dialkylzinc reagent (0.05 mmol, 1 M in THF) or alkylzinc bromide (0.05 mmol, 0.5 M in THF) over the course of 10 min. Following addition of the reagents, the septum cap was sealed with grease. The reaction was left to stir at 60 °C for 20 h. After this time, the reaction was diluted with saturated $NaHCO_3$ solution (10 mL). The aqueous solution was then extracted with ethyl acetate (3 × 2 mL). The combined organic layers were dried by passage through a pad of silica gel with ethyl acetate as eluent. The filtrate was concentrated and purified by preparative thin-layer chromatography (PTLC) to furnish the desired product.

Large-Scale Experiment



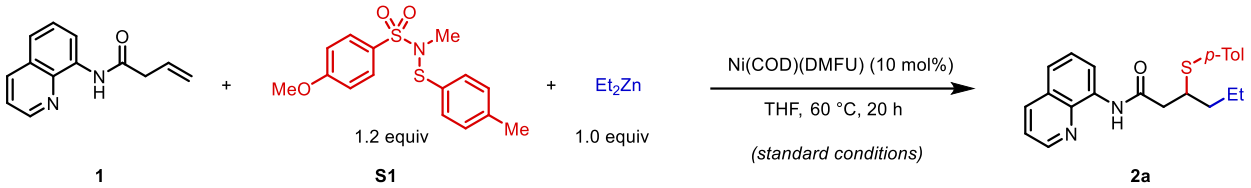
Outside of the glovebox, to an oven-dried 100-mL round-bottom flask equipped with a magnetic stir bar were added alkene **1** (530 mg, 2.5 mmol), N–S reagent (770 mg, 3.0 mmol), and DMFU (72 mg, 0.5 mmol). The vial was then introduced into an argon-filled glovebox antechamber. Once transferred inside the glovebox, $Ni(COD)_2$ (69 mg, 0.25 mmol) and THF (20 mL) were added to the flask. The flask was sealed with a septum cap, removed from the glovebox and then equipped with a nitrogen-filled balloon. The dialkylzinc reagent (2.5 mmol, 1 M in THF) was added dropwise over the course of 20 min as the reaction vessel was heated to 60 °C while stirring. The reaction was left to stir at 60 °C for 30 min. After this time, the N–S reagent (1.5 mmol, 0.6 M in THF) was added in one portion followed by dropwise addition of dialkylzinc reagent (1.25 mmol, 1 M in THF) over the course of 15 min. The reaction was left to stir at 60 °C for 20 h. After this time, the reaction was concentrated, and the crude residue was purified by column chromatography to furnish the desired product **2a** in 70% yield (639 mg).

Optimization of Reaction Conditions for Carbosulfenylation Using Et_2Zn as Nucleophile

Using **S1** as a benchmark, the reaction conditions were optimized under the following standard conditions:

Outside of the glovebox, to an oven-dried 1-dram (4-mL) reaction tube equipped with a magnetic stir bar were added alkene **1** (21.2 mg, 0.1 mmol) and **S1** (40 mg, 0.12 mmol). The vial was then introduced into an argon-filled glovebox antechamber. Once transferred inside the glovebox, the appropriate nickel catalyst[6] (0.01 mmol) and solvent (1.0 mL) were added to the vial. The vial was sealed with a screw-top septum cap and removed from the glovebox. Diethylzinc (0.1 mL, 0.1 mmol) was added dropwise over the course of 15 min at 60 °C while stirring. After the addition, the septum cap was sealed with grease. The reaction was left to stir at 60 °C for 20 h.

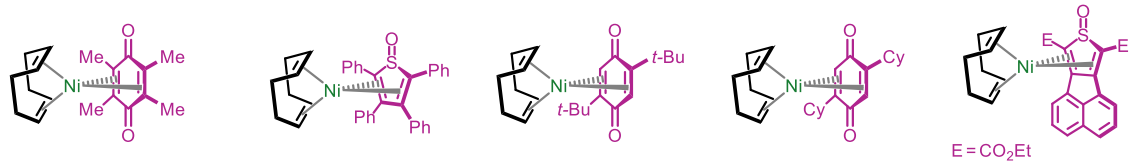
Table S1: Optimization of Reaction Conditions for Carbosulfenylation Using Et_2Zn as Nucleophile[a]



1 **S1** **2a**

Entry	Deviation from Standard Condition	Yield (%) (**1**/**2a**)[b]
1	None	22/76
2	Adding Et_2Zn at room temperature dropwise then heating to 60°C	40/56
3	$Ni(COD)_2$ + DMFU (20 mol%) in place of Ni(COD)(DMFU)	24/72
4	Other Ni precatalysts	See below
5	2.0 equiv **S1** in place of 1.2 equiv	27/72
6	1.2 equiv Et_2Zn in place of 1.0 equiv	12/76
7	2-MeTHF in place of THF	12/26
8	Dioxane in place of THF	26/74
9	DMF in place of THF	25/48
10	Toluene in place of THF	32/66
11	Portionwise (General Procedure B): **S1** (1.2 + 0.6), Et_2Zn (1.0 + 0.5)	8/82

[a]The reactions were performed on 0.1 mmol scale. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as internal standard.

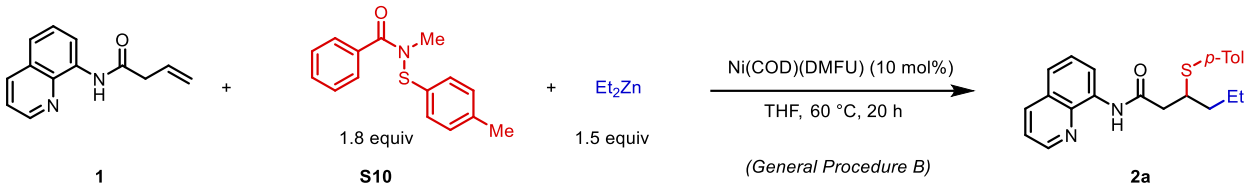


Yield (%) **1**/**2a**: 35/66 | 61/36 | 24/70 | 22/68 | 17/68

Comparison Between Batchwise and Single-batch Addition with S10 as Electrophile

Using General Procedure B, a series of sulfenylating agents were evaluated (see manuscript Table 1), with **S10** giving the best yield.[7] The following experiments were performed with **S10** to test the importance of portionwise addition. In all cases diethylzinc solution was added in a dropwise fashion.

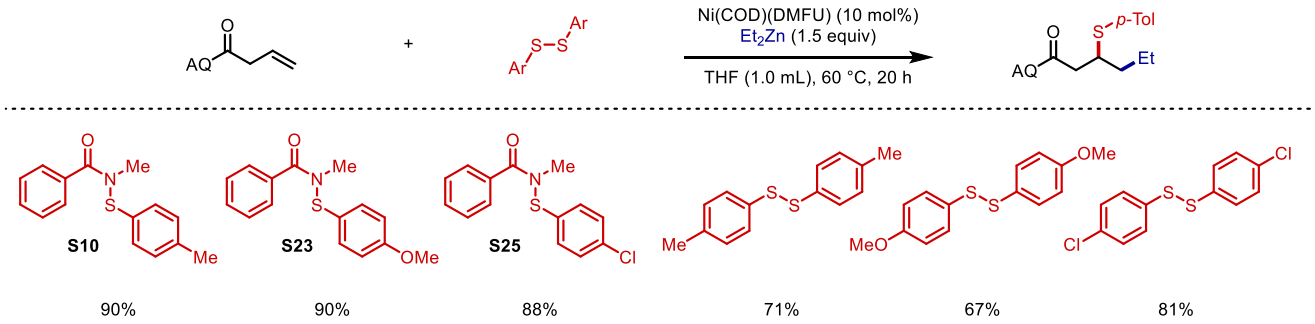
Table S2: Comparison Between Batchwise and Single-batch Addition with S10 as Electrophile[a]



Entry	Deviation from General Procedure B	Yield (%) (**1**/**2a**)[b]
1	None (batchwise): **S10** (1.2 + 0.6), Et_2Zn (1.0 + 0.5)	2/90
2	Single-batch: **S10** (1.8), Et_2Zn (1.5)	12/78
3	Single-batch: **S10** (1.8), Et_2Zn (1.2)	6/80
4	Single-batch: **S10** (1.8), Et_2Zn (1.0)	10/80
5	Single-batch: **S10** (1.5), Et_2Zn (1.0)	10/78

[a]The reactions were performed on 0.1 mmol scale. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as internal standard.

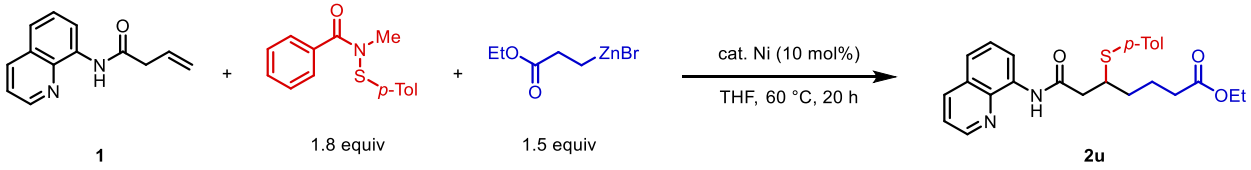
Comparison between S10, S23, S25, and Corresponding Aryldisulfides



Optimization of Reaction Conditions for Carbosulfenylation Using Alkylzinc Bromide as Nucleophile

Using (3-ethoxy-3-oxopropyl)zinc bromide or cyclohexylzinc bromide as nucleophile, we briefly optimized the reaction condition according to General Procedure B.

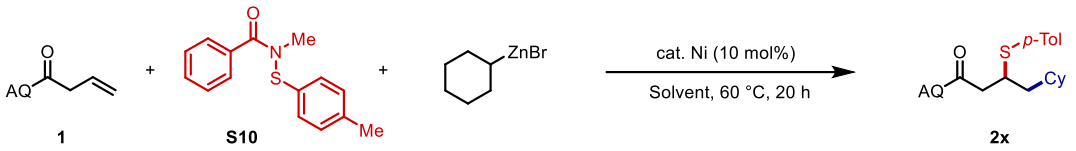
Table S3: Optimization of Reaction Conditions for Carbosulfenylation Using Alkylzinc Bromide as Nucleophile[a]



Entry	Ni catalysts	Yield% (**1**/**2u**)[b]
1	Ni(COD)(DMFU)	46/18
2	$Ni(COD)_2$	26/32
3	$NiBr_2$	32/18
4	$NiBr_2$·glyme	25/26
5	$Ni(acac)_2$	41/16

[a]The reactions were performed on 0.1 mmol scale. [b]Yields were determined by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as internal standard.

Table S4: Optimization of Reaction Conditions for Carbosulfenylation Using Alkylzinc Bromide as Nucleophile[a]



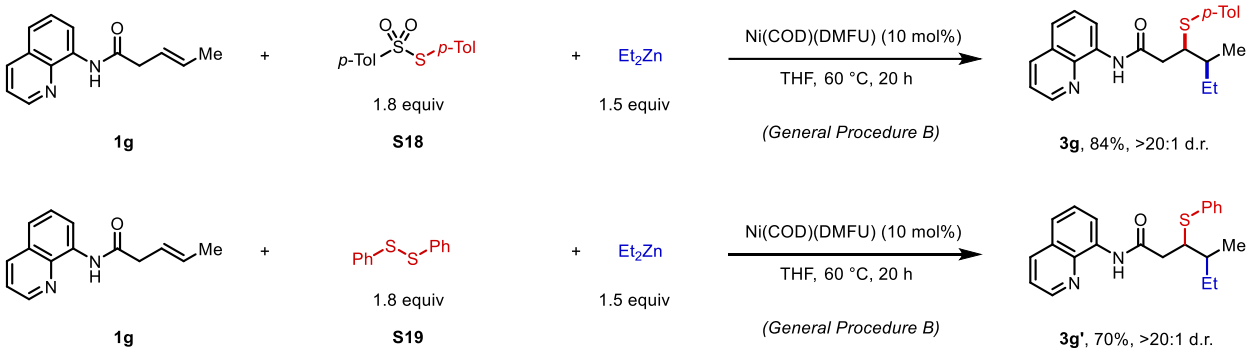
1 S10 2x

Entry	cat. Ni	Solvent	Yield (%) (**1**/**2x**)[c]
1	$Ni(COD)_2$	THF (1.0 mL)	47/18
2[b]	$Ni(COD)_2$	THF (1.0 mL)	trace/trace
3	Ni(COD)(DQ)	THF (1.0 mL)	59/10
4	Ni(COD)(DMFU)	THF (1.0 mL)	55/14
5	$Ni(COD)_2$	THF (1.0 mL) + MeCN (0.1 mL)	70/6
6	$Ni(COD)_2$	THF (0.6 mL)	53/14
7	$Ni(COD)_2$	THF (1.5 mL)	42/20

[a]The reactions were performed on 0.1 mmol scale. [b]Cy_2Zn in place of CyZnBr. [c]Yields were determined by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as internal standard.

Reactions of Internal Alkene 1g with S18 and S19 as Electrophiles

Using **1g** as alkene substrate and **S18** or **S19** as the electrophile, the following experiments were carried out following General Procedure B. Yields and diastereoselectivities were determined by ^1H NMR analysis of the crude reaction mixture with CH_2Br_2 as internal standard.

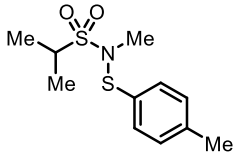


1g **S18** **3g**, 84%, >20:1 d.r.

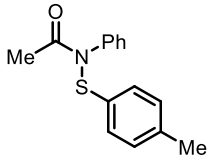
1g **S19** **3g'**, 70%, >20:1 d.r.

Scheme S3. Reactions of Internal Alkene **1g** with **S18** and **S19** as Electrophiles

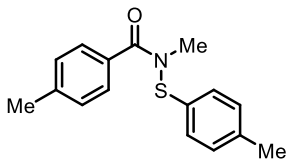
Representative Procedures and Analytical Data



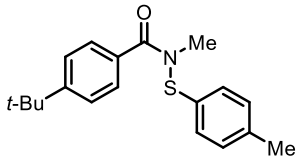
***N*-methyl-*N*-(*p*-tolylthio)propane-2-sulfonamide (S6):** The reaction was carried out following a literature procedure[8] using *N*-methylpropane-2-sulfonamide (685 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, triethylamine (1.4 mL, 10 mmol), and CCl_4 (10 mL). The reaction was run for 30 min at room temperature, and the product was purified by column chromatography using silica gel to afford **S6** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.20–7.17 (m, 2H), 3.52 (hept, *J* = 6.9 Hz, 1H), 3.30 (s, 3H), 2.35 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 6H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.91, 132.56, 130.04, 128.91, 53.45, 42.78, 21.31, 16.72. **HRMS** (ESI-TOF) Calcd for $C_{11}H_{18}NO_2S_2^+$ [M+H] 260.0779, found 260.0770.



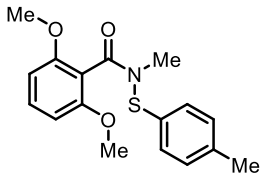
***N*-phenyl-*N*-(*p*-tolylthio)acetamide (S8):** The reaction was carried out following General Procedure A using *N*-phenylacetamide (675 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S8** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.28–7.24 (m, 3H), 7.18–7.11 (m, 4H), 2.35–2.18 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.10, 145.17, 138.41, 133.75, 130.00, 129.25, 128.27, 127.54, 126.99, 22.97, 21.19. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{16}NOS^+$ [M+H] 258.0953, found 258.0949.



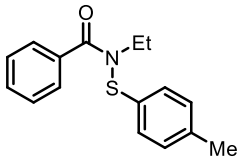
***N*,4-dimethyl-*N*-(*p*-tolylthio)benzamide (S11):** The reaction was carried out following General Procedure A using *N*,4-dimethyl-benzamide (745 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S11** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.17–7.12 (m, 4H), 7.03 (d, *J* = 7.8 Hz, 2H), 3.38 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.66, 140.68, 137.56, 133.84, 132.36, 130.20, 128.59, 128.03, 125.79, 40.65, 21.61, 21.19. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{18}NOS^+$ [M+H] 272.1109, found 272.1104.



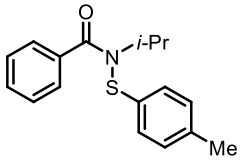
4-(*tert*-butyl)-*N*-methyl-*N*-(*p*-tolylthio)benzamide (S12): The reaction was carried out following General Procedure A using 4-(*tert*-butyl)-*N*-methylbenzamide (955 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S12** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50–7.45 (m, 2H), 7.38–7.33 (m, 2H), 7.17–7.12 (m, 2H), 7.06–7.01 (m, 2H), 3.38 (s, 3H), 2.32 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.52, 153.72, 137.45, 133.91, 132.23, 130.17, 127.86, 125.69, 124.85, 40.58, 34.94, 31.28, 21.16. **HRMS** (ESI-TOF) Calcd for $C_{19}H_{24}NOS^+$ [M+H] 314.1579, found 314.1577.



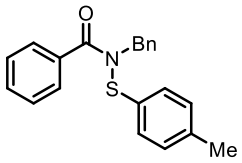
2,6-dimethoxy-*N*-methyl-*N*-(*p*-tolylthio)benzamide (S14): The reaction was carried out following General Procedure A using 2,6-dimethoxy-N-methylbenzamide (975 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S14** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.4 Hz, 1H), 7.09 (s, 4H), 6.50 (d, *J* = 8.4 Hz, 2H), 3.74 (s, 6H), 3.41 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.45, 156.77, 136.93, 133.76, 130.26, 129.69, 129.55, 126.19, 103.62, 55.62, 38.74, 21.05. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{20}NO_3S^+$ [M+H] 318.1164, found 318.1163.



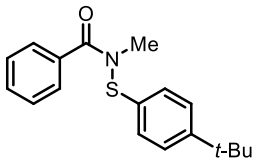
***N*-ethyl-*N*-(*p*-tolylthio)benzamide (S15):** The reaction was carried out following General Procedure A using *N*-ethylbenzamide (745 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S15** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.35–7.31 (m, 1H), 7.30–7.24 (m, 2H), 6.80 (qd, *J* = 1.5, 0.9 Hz, 2H), 6.68 (s, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.20, 138.99, 136.97, 135.10, 130.07, 128.73, 127.63, 127.45, 121.73, 40.39, 21.21. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{18}NOS^+$ [M+H] 272.1109, found 272.1107.



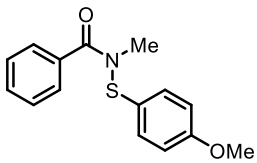
***N*-isopropyl-*N*-(*p*-tolylthio)benzamide (S16):** The reaction was carried out following General Procedure A using *N*-isopropylbenzamide (815 mg, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S16** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.39–7.33 (m, 1H), 7.33–7.29 (m, 2H), 7.07 (t, *J* = 7.2 Hz, 4H), 4.89 (s, 1H), 2.29 (s, 3H), 1.23 (d, *J* = 6.6 Hz, 6H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.83, 136.77, 136.71, 136.49, 129.87, 129.77, 127.94, 127.30, 124.88, 51.76, 21.20, 21.12. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{20}NOS^+$ [M+H] 286.1266, found 286.1268.



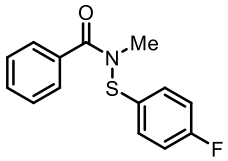
***N*-benzyl-*N*-(*p*-tolylthio)benzamide (S17):** The reaction was carried out following General Procedure A using *N*-benzylbenzamide (1.1 g, 5 mmol), 4-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S17** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.42–7.38 (m, 1H), 7.38–7.29 (m, 7H), 7.14–7.10 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 4.90 (s, 2H), 2.33 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.43, 137.71, 137.42, 135.48, 133.64, 130.36, 130.18, 128.86, 128.67, 127.97, 127.83, 127.80, 126.17, 54.10, 21.22. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{20}NOS^+$ [M+H] 334.1266, found 334.1263.



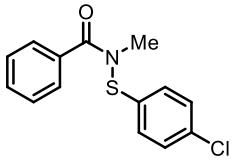
***N*-((4-(*tert*-butyl)phenyl)thio)-*N*-methylbenzamide (S22):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 4-(*tert*-butyl)-benzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S22** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55–7.50 (m, 2H), 7.42–7.38 (m, 1H), 7.37–7.32 (m, 4H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.40 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.57, 150.90, 135.39, 133.67, 130.33, 127.93, 127.89, 126.51, 125.62, 40.53, 34.70, 31.35. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{22}NOS^+$ [M+H] 300.1422, found 300.1414.



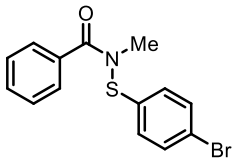
***N*-((4-methoxyphenyl)thio)-*N*-methylbenzamide (S23):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 4-methoxybenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S23** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.45–7.41 (m, 1H), 7.40–7.36 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.88–6.82 (m, 2H), 3.79 (s, 3H), 3.35 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.46, 160.45, 135.76, 131.48, 130.26, 128.15, 127.96, 127.08, 114.96, 55.52, 40.35. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{16}NO2S^+$ [M+H] 274.0902, found 274.0901.



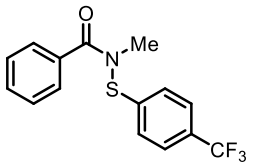
***N*-((4-fluorophenyl)thio)-*N*-methylbenzamide (S24):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 4-fluorobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S24** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.46–7.41 (m, 1H), 7.40–7.34 (m, 2H), 7.13 (t, J = 6.9 Hz, 2H), 7.08–7.01 (m, 2H), 3.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.43, 163.40, 135.22, 132.20 (d, J_{C-F} = 3.4 Hz), 130.51, 128.85, 128.04, 127.89, 116.71 (d, J_{C-F} = 22.4 Hz), 40.64. **^{19}F NMR** (471 MHz, $CDCl_3$) δ –113.56. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{13}FNOS^+$ [M+H] 262.0702, found 262.0703.



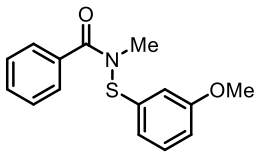
***N*-((4-chlorophenyl)thio)-*N*-methylbenzamide (S25):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 4-chlorobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S25** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50–7.45 (m, 2H), 7.42–7.36 (m, 1H), 7.35–7.26 (m, 4H), 7.01 (d, J = 8.2 Hz, 2H), 3.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.21, 135.98, 134.85, 133.00, 130.46, 129.56, 127.92, 127.54, 125.88, 40.56. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{13}ClNOS^+$ [M+H] 278.0406, found 278.0406.



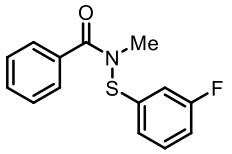
***N*-((4-bromophenyl)thio)-*N*-methylbenzamide (S26):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 4-bromobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S26** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50–7.45 (m, 4H), 7.44–7.39 (m, 1H), 7.36–7.32 (m, 2H), 6.97 (d, J = 8.3 Hz, 2H), 3.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.41, 136.82, 134.90, 132.58, 130.59, 128.04, 127.61, 125.97, 120.89, 40.65. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{13}BrNOS^+$ [M+H] 321.9901, found 321.9898.



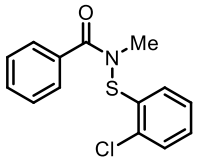
***N*-methyl-*N*-((4-(trifluoromethyl)phenyl)thio)benzamide (S27):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 4-trifluoromethylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S27** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H), 7.51–7.45 (m, 2H), 7.45–7.39 (m, 1H), 7.33 (dd, J = 8.3, 6.9 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 3.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.35, 143.12, 134.60 (d, J_{C-F} = 2.2 Hz), 130.76 (d, J_{C-F} = 2.1 Hz), 128.63 (q, J_{C-F} = 32.6 Hz), 128.11 (d, J_{C-F} = 2.2 Hz), 127.46 (d, J_{C-F} = 2.1 Hz), 126.44 (q, J_{C-F} = 4.2, 3.6 Hz), 124.02 (q, J_{C-F} = 271.7 Hz), 122.68, 40.70. **^{19}F NMR** (471 MHz, $CDCl_3$) δ –62.74. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{13}F_3NOS^+$ [M+H] 312.0670, found 312.0670.



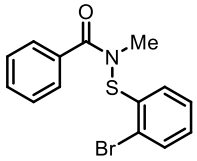
***N*-((3-methoxyphenyl)thio)-*N*-methylbenzamide (S28):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 3-methoxybenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S28** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52–7.46 (m, 2H), 7.39–7.34 (m, 1H), 7.32–7.27 (m, 2H), 7.23 (t, J = 8.0 Hz, 1H), 6.72 (ddd, J = 8.3, 2.5, 0.9 Hz, 1H), 6.67 (dd, J = 7.8, 1.8 Hz, 1H), 6.60 (d, J = 2.4 Hz, 1H), 3.73 (s, 3H), 3.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.28, 160.33, 138.92, 135.01, 130.30, 130.28, 127.79, 127.51, 116.06, 112.46, 109.29, 55.23, 40.56. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{16}NO_2S^+$ [M+H] 274.0902, found 274.0906.



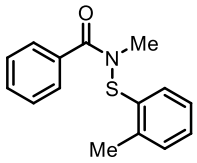
***N*-((3-fluorophenyl)thio)-*N*-methylbenzamide (S29):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 3-fluorobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S29** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.44–7.40 (m, 1H), 7.37–7.28 (m, 3H), 6.90 (tdd, J = 8.4, 2.5, 0.9 Hz, 1H), 6.85 (dt, J = 7.9, 1.3 Hz, 1H), 6.80 (dt, J = 9.1, 2.1 Hz, 1H), 3.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.39, 163.41 (d, J_{C-F} = 249.9 Hz), 140.37 (d, J_{C-F} = 7.2 Hz), 134.83, 131.00 (d, J_{C-F} = 8.7 Hz), 130.61, 128.04, 127.55, 119.14, 113.78 (d, J_{C-F} = 21.5 Hz), 110.73 (d, J_{C-F} = 24.6 Hz), 40.76. **^{19}F NMR** (471 MHz, $CDCl_3$) δ –110.99. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{13}FNOS^+$ [M+H] 262.0702, found 262.0702.



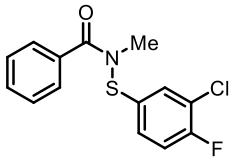
***N*-((2-chlorophenyl)thio)-*N*-methylbenzamide (S30):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 2-chlorobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S30** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.40 (ddt, J = 8.8, 7.1, 1.3 Hz, 1H), 7.37–7.28 (m, 4H), 7.15 (ddd, J = 8.0, 7.4, 1.5 Hz, 1H), 7.07 (dd, J = 7.9, 1.5 Hz, 1H), 3.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.54, 137.13, 134.57, 130.69, 130.11, 128.02, 127.80, 127.45, 126.96, 122.88, 40.45. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{13}ClNOS^+$ [M+H] 278.0406, found 278.0407.



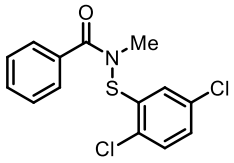
***N*-((2-bromophenyl)thio)-*N*-methylbenzamide (S31):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 2-bromobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S31** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50–7.44 (m, 3H), 7.43–7.37 (m, 2H), 7.31 (dd, J = 8.4, 7.0 Hz, 2H), 7.10–7.02 (m, 2H), 3.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.51, 138.97, 134.55, 133.28, 130.72, 128.39, 128.04, 127.46, 127.13, 122.86, 116.34, 40.41. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{13}BrNOS^+$ [M+H] 321.9901, found 321.9897.



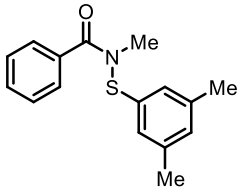
***N*-methyl-*N*-(o-tolylthio)benzamide (S32):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 2-methylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S32** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51–7.46 (m, 2H), 7.39 (ddt, J = 8.0, 6.9, 1.3 Hz, 1H), 7.32–7.29 (m, 2H), 7.28–7.26 (m, 1H), 7.14–7.08 (m, 3H), 3.43 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.59, 136.65, 135.06, 132.82, 130.76, 130.39, 127.89, 127.49, 127.02, 126.16, 122.36, 40.55, 18.68. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{16}NOS^+$ [M+H] 258.0953, found 258.0954.



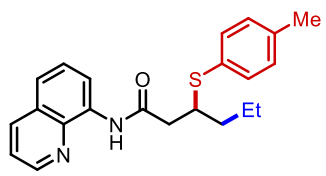
***N*-((3-chloro-4-fluorophenyl)thio)-*N*-methylbenzamide (S33):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 3-chloro-4-fluorobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S33** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.14–7.11 (m, 1H), 7.08 (t, J = 8.6 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 3.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.92, 157.39 (d, J_{C-F} = 250.3 Hz), 134.75, 133.79 (d, J_{C-F} = 3.8 Hz), 130.53, 127.98, 127.71, 127.65, 125.62 (d, J_{C-F} = 7.0 Hz), 122.23 (d, J_{C-F} = 18.6 Hz), 117.62 (d, J_{C-F} = 22.0 Hz), 40.66. **^{19}F NMR** (471 MHz, $CDCl_3$) δ –116.23. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{12}ClFNOS^+$ [M+H] 296.0312, found 296.0310.



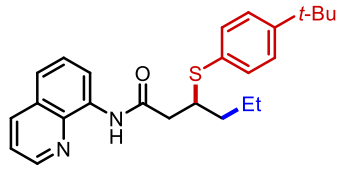
***N*-((2,5-dichlorophenyl)thio)-*N*-methylbenzamide (S34):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 2,5-dichlorobenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S34** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.43–7.38 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.09 (ddd, *J* = 8.3, 2.4, 1.1 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 3.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.00, 139.04, 134.24, 134.15, 131.05, 130.80, 128.10, 127.30, 126.98, 125.75, 122.38, 40.55. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{12}Cl_2NOS^+$ [M+H] 312.0017, found 312.0013.



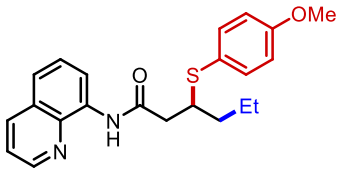
***N*-((3,5-dimethylphenyl)thio)-*N*-methylbenzamide (S35):** The reaction was carried out following General Procedure A using *N*-methylbenzamide (675 mg, 5 mmol), 3,5-dimethylbenzenesulfenyl chloride, KH (300 mg, 7.5 mmol), and THF (10 mL). The reaction was run for 1 h at room temperature, and the product was purified by column chromatography using silica gel to afford **S35** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52–7.47 (m, 2H), 7.35–7.31 (m, 1H), 7.30–7.24 (m, 2H), 6.80 (qd, *J* = 1.5, 0.9 Hz, 1H), 6.68 (s, 2H), 3.40 (s, 3H), 2.24 (s, 6H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.20, 138.99, 136.97, 135.10, 130.07, 128.73, 127.63, 127.45, 121.73, 40.39, 21.21. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{18}NOS^+$ [M+H] 272.1109, found 272.1109.



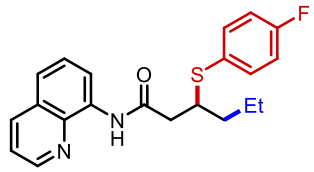
***N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (2a):** The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S10** (53.8 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 30.9 mg (85%) of **2a** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.55–7.47 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.42–7.39 (m, 2H), 7.10–7.05 (m, 2H), 3.69–3.64 (m, 1H), 2.80 (dd, *J* = 14.9, 6.8 Hz, 1H), 2.72 (dd, *J* = 14.9, 6.9 Hz, 1H), 2.28 (s, 3H), 1.75–1.68 (m, 1H), 1.68–1.61 (m, 2H), 1.60–1.52 (m, 1H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.63, 148.25, 138.47, 137.58, 136.44, 134.52, 133.57, 130.38, 129.83, 128.04, 127.50, 121.72, 121.65, 116.68, 45.77, 44.15, 36.94, 21.20, 20.36, 13.98. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{25}N_2OS^+$ [M+H] 365.1688, found 365.1680.



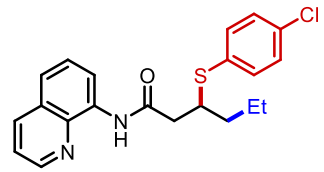
3-((4-(*tert*-butyl)phenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2b): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S22** (53.8 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 36.1 mg (89%) of **2b** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.53–7.48 (m, 2H), 7.46–7.42 (m, 3H), 7.30–7.27 (m, 2H), 3.70 (dtd, *J* = 7.8, 6.7, 5.2 Hz, 1H), 2.83 (dd, *J* = 14.9, 6.6 Hz, 1H), 2.73 (dd, *J* = 15.0, 7.1 Hz, 1H), 1.78–1.71 (m, 1H), 1.70–1.63 (m, 2H), 1.62–1.53 (m, 1H), 1.27 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.67, 150.62, 148.26, 138.49, 136.46, 134.53, 132.94, 130.58, 128.05, 127.52, 126.10, 121.73, 121.65, 116.69, 45.51, 44.30, 36.95, 34.63, 31.36, 20.39, 14.00. **HRMS** (ESI-TOF) Calcd for $C_{25}H_{31}N_2OS^+$ [M+H] 407.2157, found 407.2155.



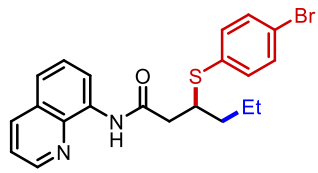
3-((4-methoxyphenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2c): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S23** (49.1 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 34.2 mg (90%) of **2c** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.76 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.54–7.49 (m, 2H), 7.48–7.47 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.83–6.79 (m, 2H), 3.75 (s, 3H), 3.59–3.53 (m, 1H), 2.76 (dd, *J* = 14.9, 7.1 Hz, 1H), 2.70 (dd, *J* = 14.9, 6.7 Hz, 1H), 1.72–1.52 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.67, 159.74, 148.26, 138.48, 136.46, 136.26, 134.53, 128.05, 127.52, 124.08, 121.73, 121.64, 116.70, 114.62, 55.38, 46.46, 44.12, 36.88, 20.35, 13.98. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{25}N_2O_2S^+$ [M+H] 381.1637, found 381.1632.



3-((4-fluorophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2d): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S24** (47.0 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 31.3 mg (85%) of **2d** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.74 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55–7.47 (m, 4H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.00–6.92 (m, 2H), 3.67–3.61 (m, 1H), 2.81–2.71 (m, 2H), 1.75–1.68 (m, 1H), 1.68–1.60 (m, 2H), 1.60–1.52 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.43, 162.59 (d, J_{C-F} = 247.7 Hz), 148.29, 138.44, 136.52, 135.67 (d, J_{C-F} = 8.3 Hz), 134.39, 129.20 (d, J_{C-F} = 3.3 Hz), 128.06, 127.51, 121.79, 121.77, 116.74, 116.13 (d, J_{C-F} = 21.5 Hz), 46.42, 44.12, 37.05, 20.32, 13.95. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –116.72. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}FN_2OS^+$ [M+H] 369.1437, found 369.1431.

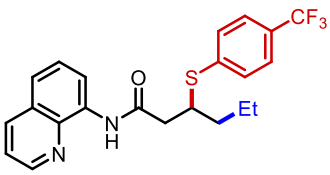


3-((4-chlorophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2e): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S25** (50.0 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 30.3 mg (79%) of **2e** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.55–7.48 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.44–7.38 (m, 2H), 7.24–7.18 (m, 2H), 3.72 (dtd, *J* = 7.9, 6.8, 5.4 Hz, 1H), 2.83–2.71 (m, 2H), 1.79–1.70 (m, 1H), 1.70–1.59 (m, 2H), 1.59–1.50 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.29, 148.30, 138.43, 136.51, 134.36, 134.00, 133.42, 133.08, 129.19, 128.06, 127.51, 121.81, 121.77, 116.71, 45.85, 44.17, 37.13, 20.35, 13.96. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}ClN_2OS^+$ [M+H] 385.1141, found 385.1134.

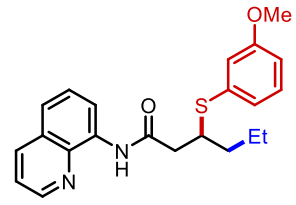


3-((4-bromophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2f): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S26** (57.8 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 33.4 mg (78%) of **2f** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.61–7.49 (m, 1H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.35 (d, *J* = 1.5 Hz, 3H), 3.74 (dtd, *J* = 7.9, 6.9, 5.4 Hz, 1H), 2.83–2.71 (m, 2H), 1.80–1.69 (m, 1H), 1.70–1.59 (m, 2H), 1.58–1.49 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.27, 148.30, 138.43, 136.51, 134.35,

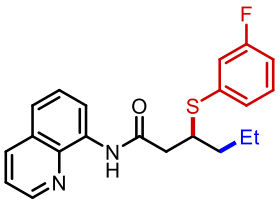
134.11, 133.81, 132.11, 128.06, 127.52, 121.82, 121.77, 121.39, 116.72, 45.70, 44.18, 37.14, 20.36, 13.97. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}BrN_2OS^+$ [M+H] 429.0636, found 429.0632.



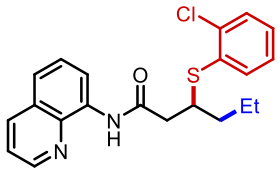
***N*-(quinolin-8-yl)-3-((4-(trifluoromethyl)phenyl)thio)hexanamide (2g):** The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S27** (56.0 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 25.1 mg (60%) of **2g** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.71 (dd, *J* = 6.1, 2.9 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.54–7.50 (m, 4H), 7.48–7.44 (m, 3H), 3.91 (dtd, *J* = 8.1, 6.8, 5.3 Hz, 1H), 2.89–2.79 (m, 2H), 1.81 (ddt, *J* = 14.0, 10.1, 5.7 Hz, 1H), 1.75–1.67 (m, 1H), 1.63 (dddd, *J* = 13.1, 10.2, 7.6, 3.9 Hz, 1H), 1.56 (dddd, *J* = 13.2, 10.2, 7.3, 5.9 Hz, 1H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.10, 148.32, 140.65 (d, J_{C-F} = 1.4 Hz), 138.42, 136.53, 134.29, 130.54, 128.47 (q, J_{C-F} = 32.5 Hz), 128.06, 127.49, 125.80 (q, J_{C-F} = 3.9 Hz), 124.20 (q, J_{C-F} = 271.8 Hz), 121.88, 121.80, 116.71, 44.68, 44.25, 37.23, 20.39, 13.97. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –65.19. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{22}F_3N_2OS^+$ [M+H] 419.1405, found 419.1402.



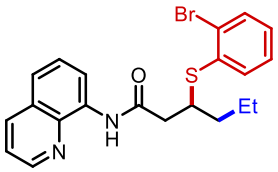
3-((3-methoxyphenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2h): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S28** (49.1 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 23.9 mg (63%) of **2h** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55–7.48 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.18 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.08 (ddd, *J* = 7.6, 1.6, 0.9 Hz, 1H), 7.04 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.75 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 3.78 (dtd, *J* = 8.0, 6.8, 5.2 Hz, 1H), 3.75 (s, 3H), 2.85 (dd, *J* = 14.9, 6.6 Hz, 1H), 2.77 (dd, *J* = 15.0, 7.1 Hz, 1H), 1.81–1.73 (m, 1H), 1.72–1.61 (m, 2H), 1.59–1.53 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.54, 159.89, 148.30, 138.49, 136.47, 135.83, 134.50, 129.86, 128.06, 127.52, 124.55, 121.76, 121.71, 117.48, 116.70, 113.20, 55.38, 45.28, 44.20, 37.05, 20.39, 14.02. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{25}N_2O_2S^+$ [M+H] 381.1637, found 381.1628.



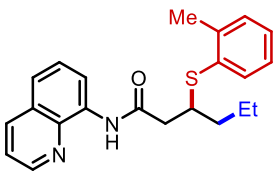
3-((3-fluorophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2i): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S29** (47.0 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 25.0 mg (68%) of **2i** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.0, 2.0 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.54–7.49 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.27–7.24 (m, 1H), 7.24–7.19 (m, 2H), 6.91–6.86 (m, 1H), 3.80 (dtd, *J* = 8.0, 6.8, 5.4 Hz, 1H), 2.83 (dd, *J* = 15.0, 6.7 Hz, 1H), 2.79 (dd, *J* = 15.0, 6.9 Hz, 1H), 1.78 (ddt, *J* = 13.7, 9.9, 5.6 Hz, 1H), 1.72–1.59 (m, 2H), 1.59–1.52 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.15, 162.71 (d, J_{C-F} = 248.7 Hz), 148.23, 138.35, 137.12 (d, J_{C-F} = 7.7 Hz), 136.39, 134.28, 130.18 (d, J_{C-F} = 8.8 Hz), 127.96, 127.40, 127.35 (d, J_{C-F} = 3.2 Hz), 121.70, 121.68, 118.57 (d, J_{C-F} = 22.5 Hz), 116.61, 113.94 (d, J_{C-F} = 21.0 Hz), 45.28, 43.99, 36.97, 20.26, 13.87. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –112.10. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}FN_2OS^+$ [M+H] 369.1437, found 369.1433.



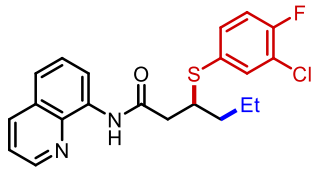
3-((2-chlorophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2j): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S30** (50.0 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 22.7 mg (59%) of **2j** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.72 (dd, *J* = 6.6, 2.4 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.55 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.53–7.49 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.34 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.18 (td, *J* = 7.6, 1.4 Hz, 1H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 3.95 (tt, *J* = 7.9, 5.5 Hz, 1H), 2.91 (dd, *J* = 15.1, 5.8 Hz, 1H), 2.81 (dd, *J* = 15.1, 7.7 Hz, 1H), 1.83 (ddt, *J* = 13.9, 10.2, 5.5 Hz, 1H), 1.77–1.70 (m, 1H), 1.69–1.62 (m, 1H), 1.58 (dddd, *J* = 13.3, 10.2, 7.3, 5.9 Hz, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.33, 148.33, 138.45, 136.46, 135.50, 134.61, 134.39, 131.67, 130.02, 128.03, 127.56, 127.46, 127.36, 121.79, 121.77, 116.68, 44.11, 43.94, 36.94, 20.35, 14.03. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}ClN_2OS^+$ [M+H] 385.1141, found 385.1140.



3-((2-bromophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2k): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S31** (57.8 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 20.5 mg (48%) of **2k** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 6.7, 2.3 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55–7.49 (m, 4H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.24 (td, *J* = 7.6, 1.4 Hz, 1H), 7.01 (td, *J* = 7.6, 1.6 Hz, 1H), 3.95 (tt, *J* = 7.9, 5.4 Hz, 1H), 2.93 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.81 (dd, *J* = 15.2, 7.8 Hz, 1H), 1.84 (ddt, *J* = 14.0, 10.7, 5.6 Hz, 1H), 1.78–1.71 (m, 1H), 1.66 (dddd, *J* = 15.2, 10.3, 7.4, 5.1 Hz, 1H), 1.60–1.54 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.34, 148.34, 138.45, 136.79, 136.47, 134.39, 133.32, 131.12, 128.04, 128.03, 127.54, 127.46, 125.72, 121.81, 121.78, 116.69, 44.22, 44.01, 36.87, 20.37, 14.05. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}BrN_2OS^+$ [M+H] 429.0636, found 429.0631.

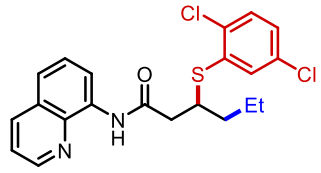


***N*-(quinolin-8-yl)-3-(o-tolylthio)hexanamide (2l):** The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S32** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 26.2 mg (72%) of **2l** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.74 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.54–7.48 (m, 4H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.17–7.11 (m, 2H), 7.09 (td, *J* = 7.3, 1.5 Hz, 1H), 3.81 (tt, *J* = 7.7, 5.6 Hz, 1H), 2.86 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.77 (dd, *J* = 15.0, 7.6 Hz, 1H), 2.42 (s, 3H), 1.81 (ddt, *J* = 13.7, 10.0, 5.6 Hz, 1H), 1.74–1.66 (m, 1H), 1.66–1.54 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.59, 148.27, 139.65, 138.47, 136.46, 134.48, 134.34, 131.58, 130.46, 128.04, 127.51, 126.87, 126.61, 121.74, 121.70, 116.67, 44.32, 44.06, 37.06, 20.91, 20.36, 14.08. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{25}N_2OS^+$ [M+H] 365.1688, found 365.1682.

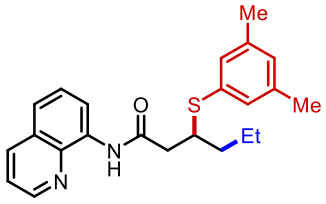


3-((3-chloro-4-fluorophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2m): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S33** (53.1 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 30.2 mg (75%) of **2m** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.82 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 6.6, 2.4 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.56 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.53–7.50 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.37 (ddd, *J* = 8.5, 4.5, 2.3 Hz, 1H), 7.01 (t, *J* = 8.7 Hz,

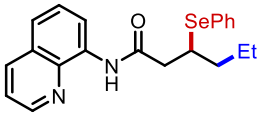
1H), 3.71–3.66 (m, 1H), 2.79 (dd, J = 14.3, 5.8 Hz, 1H), 2.76 (dd, J = 14.4, 6.8 Hz, 1H), 1.77–1.70 (m, 1H), 1.69–1.59 (m, 2H), 1.59–1.52 (m, 1H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.13, 158.61, 148.36, 138.43, 136.53, 135.20, 134.30, 133.21 (d, J_{C-F} = 7.1 Hz), 130.99 (d, J_{C-F} = 4.3 Hz), 128.08, 127.50, 121.86, 121.80, 121.41 (d, J_{C-F} = 18.1 Hz), 117.08 (d, J_{C-F} = 21.4 Hz), 116.71, 46.65, 44.23, 37.16, 20.33, 13.96. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –116.38. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{21}ClFN_2OS^+$ [M+H] 403.1047, found 403.1031.



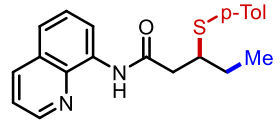
3-((2,5-dichlorophenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2n): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S34** (56.0 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 20.9 mg (50%) of **2n** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.81 (dd, J = 4.2, 1.7 Hz, 1H), 8.72 (dd, J = 6.4, 2.6 Hz, 1H), 8.16 (dd, J = 8.2, 1.7 Hz, 1H), 7.55–7.50 (m, 3H), 7.46 (dd, J = 8.2, 4.2 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.04 (dd, J = 8.5, 2.4 Hz, 1H), 3.98–3.91 (m, 1H), 2.89 (dd, J = 15.1, 6.4 Hz, 1H), 2.84 (dd, J = 15.1, 7.1 Hz, 1H), 1.84 (ddt, J = 14.0, 10.2, 5.7 Hz, 1H), 1.74 (dddd, J = 14.1, 10.2, 7.8, 5.1 Hz, 1H), 1.64 (dddd, J = 14.4, 7.0, 5.1, 3.5 Hz, 1H), 1.61–1.53 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.94, 148.36, 138.45, 136.67, 136.48, 134.31, 133.52, 133.08, 130.87, 130.76, 128.04, 127.49, 127.48, 121.85, 121.79, 116.75, 44.18, 44.10, 36.99, 20.30, 14.03. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{21}Cl_2N_2OS^+$ [M+H] 419.0752, found 419.0741.



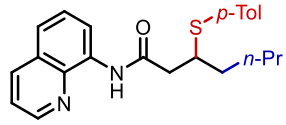
3-((3,5-dimethylphenyl)thio)-*N*-(quinolin-8-yl)hexanamide (2o): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S35** (48.8 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 24.2 mg (64%) of **2o** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, J = 4.2, 1.7 Hz, 1H), 8.76 (dd, J = 7.2, 1.8 Hz, 1H), 8.15 (dd, J = 8.2, 1.7 Hz, 1H), 7.54–7.48 (m, 2H), 7.45 (dd, J = 8.2, 4.2 Hz, 1H), 7.11 (dd, J = 1.5, 0.8 Hz, 2H), 6.81 (dt, J = 1.6, 0.8 Hz, 1H), 3.76–3.70 (m, 1H), 2.82 (dd, J = 14.9, 6.7 Hz, 1H), 2.74 (dd, J = 14.9, 7.0 Hz, 1H), 2.23 (d, J = 0.8 Hz, 6H), 1.79–1.72 (m, 1H), 1.70–1.62 (m, 2H), 1.61–1.52 (m, 1H), 0.95 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.67, 148.26, 138.59, 138.48, 136.45, 134.53, 133.77, 130.40, 129.15, 128.05, 127.50, 121.71, 121.65, 116.66, 45.33, 44.31, 36.96, 21.27, 20.36, 14.01. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{27}N_2OS^+$ [M+H] 379.1844, found 379.1836.



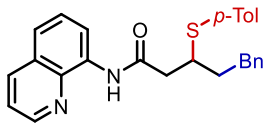
3-(phenylselanyl)-*N*-(quinolin-8-yl)hexanamide (2p): The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), diphenyldiselenide (56.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 20.2 mg (51%) of **2p** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.83 (s, 1H), 8.81 (dd, J = 4.2, 1.7 Hz, 1H), 8.76–8.66 (m, 1H), 8.16 (dd, J = 8.2, 1.7 Hz, 1H), 7.81–7.58 (m, 2H), 7.55–7.48 (m, 2H), 7.45 (dd, J = 8.2, 4.2 Hz, 1H), 7.30–7.20 (m, 3H), 3.94–3.66 (m, 1H), 2.88 (d, J = 7.1 Hz, 2H), 1.87–1.69 (m, 2H), 1.69–1.61 (m, 1H), 1.59–1.49 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.79, 148.26, 138.49, 136.49, 135.60, 134.47, 129.15, 128.50, 128.06, 127.85, 127.54, 121.75, 121.68, 116.71, 45.07, 41.15, 37.76, 21.27, 13.90. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{23}N_2OSe^+$ [M+H] 393.1035, found 393.1021.



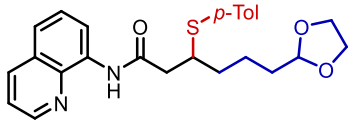
***N*-(quinolin-8-yl)-3-(p-tolylthio)pentanamide (2q):** The reaction was carried out following General Procedure B using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), dimethylzinc (0.15 mmol, 1.0 M in THF), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 28.4 mg (81%) of **2q** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.54–7.48 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.43–7.39 (m, 2H), 7.10–7.06 (m, 2H), 3.62 (qd, *J* = 7.1, 5.3 Hz, 1H), 2.79 (dd, *J* = 14.9, 6.9 Hz, 1H), 2.74 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.29 (s, 3H), 1.79 (dqd, *J* = 14.7, 7.4, 5.3 Hz, 1H), 1.73–1.65 (m, 1H), 1.12 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.63, 148.26, 138.48, 137.60, 136.46, 134.51, 133.59, 130.39, 129.84, 128.05, 127.51, 121.73, 121.67, 116.69, 47.62, 43.68, 27.71, 21.20, 11.62. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{23}N_2OS^+$ [M+H] 351.1531, found 351.1529.



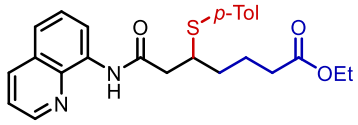
***N*-(quinolin-8-yl)-3-(*p*-tolylthio)heptanamide (2r):** The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), *n*-propylzinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 18.1 mg (48%) of **2r** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.56–7.48 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 3.66 (dtd, *J* = 8.0, 6.8, 5.3 Hz, 1H), 2.99–2.58 (m, 2H), 2.29 (s, 3H), 1.88–1.70 (m, 1H), 1.70–1.50 (m, 3H), 1.41–1.29 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.65, 148.27, 138.51, 137.61, 136.47, 134.55, 133.60, 130.41, 129.86, 128.07, 127.54, 121.74, 121.66, 116.71, 46.01, 44.15, 34.48, 29.28, 22.64, 21.22, 14.15. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{27}N_2OS^+$ [M+H] 379.1844, found 379.1832.



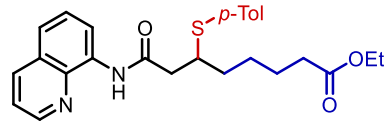
5-phenyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)pentanamide (2s): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), benzylzinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 29.0 mg (68%) of **2s** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.3, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.54–7.48 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.29–7.22 (m, 2H), 7.22–7.17 (m, 2H), 7.17–7.12 (m, 1H), 7.11–7.04 (m, 2H), 3.77–3.61 (m, 1H), 3.07–2.93 (m, 1H), 2.92–2.81 (m, 2H), 2.76 (dd, *J* = 14.9, 6.8 Hz, 1H), 2.29 (s, 3H), 2.12–2.02 (m, 1H), 2.00–1.91 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.36, 148.26, 141.65, 138.49, 137.82, 136.47, 134.48, 133.77, 129.99, 129.92, 128.62, 128.52, 128.06, 127.52, 126.04, 121.74, 121.71, 116.74, 45.64, 44.12, 36.43, 33.36, 21.23. **HRMS** (ESI-TOF) Calcd for $C_{27}H_{27}N_2OS^+$ [M+H] 427.1844, found 427.1842.



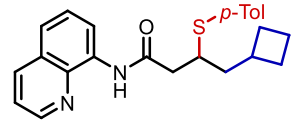
6-(1,3-dioxolan-2-yl)-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (2t): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 10.9 mg (25%) of **2t** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.74 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.59–7.49 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 5.02–4.74 (m, 1H), 4.10–3.90 (m, 2H), 3.87–3.74 (m, 2H), 3.68–3.61 (m, 1H), 2.91–2.57 (m, 2H), 2.29 (s, 3H), 1.89–1.75 (m, 2H), 1.76–1.65 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.49, 148.27, 138.50, 137.71, 136.46, 134.53, 133.75, 130.22, 129.87, 128.06, 127.53, 121.74, 121.67, 116.72, 104.50, 65.00, 64.99, 46.03, 44.03, 34.57, 33.66, 21.60, 21.23. **HRMS** (ESI-TOF) Calcd for $C_{25}H_{29}N_2O_3S^+$ [M+H] 437.1899, found 437.1883.



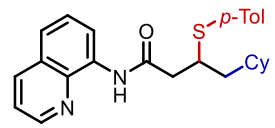
ethyl 7-oxo-7-(quinolin-8-ylamino)-5-(*p*-tolylthio)heptanoate (2u): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), (3-ethoxy-3-oxopropyl)zinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 8.3 mg (19%) of **2u** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.74 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.58–7.49 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.74–3.52 (m, 1H), 3.01–2.65 (m, 2H), 2.43–2.31 (m, 2H), 2.29 (s, 3H), 2.04–1.94 (m, 1H), 1.92–1.83 (m, 1H), 1.81–1.73 (m, 1H), 1.72–1.64 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.46, 169.38, 148.29, 138.49, 137.83, 136.48, 134.48, 133.80, 130.04, 129.91, 128.07, 127.52, 121.76, 121.73, 116.73, 60.44, 45.74, 43.96, 34.15, 34.12, 22.59, 21.23, 14.36. **HRMS** (ESI-TOF) Calcd for $C_{25}H_{29}N_2O_3S^+$ [M+H] 437.1899, found 437.1897.



ethyl 8-oxo-8-(quinolin-8-ylamino)-6-(*p*-tolylthio)octanoate (2v): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), (4-ethoxy-4-oxobutyl)zinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 8.1 mg (18%) of **2v** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.74 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.81–7.48 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.24–4.02 (m, 2H), 3.81–3.51 (m, 1H), 2.93–2.61 (m, 2H), 2.36–2.19 (m, 5H), 1.95–1.71 (m, 1H), 1.71–1.60 (m, 3H), 1.24 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.74, 169.48, 148.29, 138.50, 137.78, 136.48, 134.50, 133.74, 130.13, 129.90, 128.07, 127.54, 121.76, 121.71, 116.73, 60.37, 45.87, 44.08, 34.37, 26.66, 24.89, 21.23, 14.39. **HRMS** (ESI-TOF) Calcd for $C_{26}H_{31}N_2O_3S^+$ [M+H] 451.2055, found 451.2055.

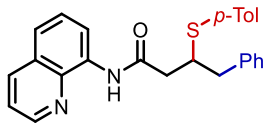


4-cyclobutyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)butanamide (2w): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), cyclobutylzinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 19.5 mg (50%) of **2w** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.58–7.48 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.14–7.01 (m, 2H), 3.72–3.47 (m, 1H), 3.01–2.56 (m, 3H), 2.28 (s, 3H), 2.15–2.03 (m, 2H), 1.92–1.75 (m, 4H), 1.73–1.61 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.59, 148.26, 137.55, 136.46, 134.55, 133.47, 130.50, 129.84, 128.07, 127.54, 121.73, 121.65, 116.71, 44.34, 44.13, 42.06, 33.94, 28.80, 28.62, 21.22, 18.69. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{27}N_2OS^+$ [M+H] 391.1844, found 391.1842.

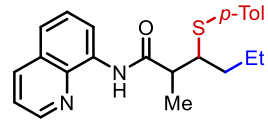


4-cyclohexyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)butanamide (2x): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), cyclohexylzinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 7.5 mg (18%) of **2x** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.75 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.60–7.48 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.10–7.01 (m, 2H), 3.80–3.70 (m, 1H), 3.04–2.59 (m, 2H), 2.29 (s, 3H), 1.85 (d, *J* = 12.9 Hz, 1H), 1.83–1.61 (m, 4H), 1.59–1.51 (m, 2H), 1.30–1.20 (m, 3H), 1.19–1.04 (m, 1H), 1.01–0.69 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.66, 148.26, 138.52, 137.62, 136.47, 134.56, 133.67, 130.24, 129.85, 128.07, 127.55, 121.74, 121.64, 116.73, 44.64,

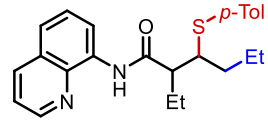
43.18, 42.58, 35.09, 33.80, 32.76, 26.71, 26.44, 26.28, 21.23. **HRMS** (ESI-TOF) Calcd for $C_{26}H_{31}N_2OS^+$ [M+H] 419.2157, found 419.2147.



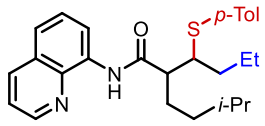
4-phenyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)butanamide (2y): The reaction was carried out following General Procedure C using **1** (21.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), phenylzinc bromide (0.15 mmol, 0.5 M in THF), $Ni(COD)_2$ (2.8 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 11.5 mg (28%) of **2y** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.74 (dd, *J* = 7.1, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.71–7.49 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30–7.24 (m, 3H), 7.23–7.17 (m, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 4.10–3.85 (m, 1H), 3.35–2.90 (m, 2H), 2.86–2.66 (m, 2H), 2.48–2.08 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.35, 148.25, 138.68, 138.49, 137.77, 136.48, 134.49, 133.63, 130.33, 129.90, 129.64, 128.53, 128.06, 127.54, 126.73, 121.74, 121.68, 116.75, 47.09, 42.61, 41.18, 21.24. **HRMS** (ESI-TOF) Calcd for $C_{26}H_{25}N_2OS^+$ [M+H] 413.1688, found 413.1682.



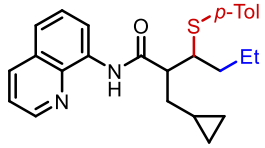
2-methyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (3a): The reaction was carried out following General Procedure B using **1a** (22.6 mg, 0.1 mmol), **S1** (58.9 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 28.4 mg (75%, 1.3:1 d.r.) of **3a** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) (major) δ 9.94 (s, 1H), 8.85–8.79 (m, 1H), 8.76 (d, *J* = 7.3 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.57–7.48 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.64–3.54 (m, 1H), 2.87–2.74 (m, 1H), 2.31 (s, 3H), 1.87–1.66 (m, 2H), 1.60–1.49 (m, 2H), 1.41 (d, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H); (minor) δ 10.1 (s, 1H), 8.85–8.79 (m, 1H), 8.76 (d, *J* = 7.3 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.57–7.48 (m, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 3.41–3.37 (m, 1H), 2.87–2.74 (m, 1H), 2.28 (s, 3H), 1.87–1.66 (m, 2H), 1.60–1.49 (m, 2H), 1.45 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) (major) δ 173.26, 148.26, 138.65, 137.09, 136.44, 134.55, 132.63, 131.89, 129.88, 128.05, 127.54, 121.70, 121.55, 116.64, 52.44, 46.48, 33.01, 21.23, 20.45, 14.09, 13.63; (minor) δ 173.00, 148.25, 138.70, 137.27, 136.39, 134.65, 133.00, 131.54, 129.83, 128.07, 127.52, 121.69, 121.56, 116.67, 53.92, 46.82, 34.62, 21.20, 20.93, 15.74, 13.95. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{27}N_2OS^+$ [M+H] 379.1844, found 379.1830.



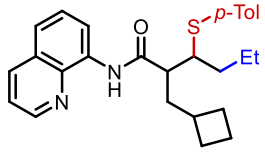
2-ethyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (3b): The reaction was carried out following General Procedure B using **1b** (24.0 mg, 0.1 mmol), **S1** (58.9 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 24.3 mg (62%, 3.1:1 d.r.) of **3b** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) (major) δ 9.90 (s, 1H), 8.85–8.77 (m, 2H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.60–7.32 (m, 5H), 7.13 (dt, *J* = 7.9, 0.7 Hz, 2H), 3.34–3.30 (m, 1H), 2.54 (ddd, *J* = 9.2, 6.7, 5.1 Hz, 1H), 2.34 (s, 3H), 2.00–1.75 (m, 3H), 1.57–1.50 (m, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); (minor) δ 10.02 (s, 1H), 8.85–8.77 (m, 2H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.60–7.32 (m, 5H), 7.15–7.00 (m, 2H), 3.45 (ddd, *J* = 8.7, 6.7, 3.9 Hz, 1H), 2.59 (ddd, *J* = 10.0, 6.7, 4.3 Hz, 1H), 2.32 (s, 3H), 2.00–1.75 (m, 3H), 1.57–1.50 (m, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) (major) δ 172.53, 148.25, 138.64, 137.13, 136.42, 134.54, 132.89, 132.08, 129.84, 128.06, 127.57, 121.69, 121.52, 116.70, 54.79, 52.56, 33.79, 22.46, 21.26, 20.25, 14.08, 12.55; (minor) δ 172.42, 148.27, 138.66, 137.33, 136.41, 134.58, 132.96, 131.64, 129.93, 128.11, 127.56, 121.71, 121.61, 116.67, 54.87, 52.84, 34.10, 24.34, 21.26, 20.87, 13.97, 12.31. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{29}N_2OS^+$ [M+H] 393.2001, found 393.2011.



2-isopentyl-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (3c): The reaction was carried out following General Procedure B using **1c** (28.2 mg, 0.1 mmol), **S1** (58.9 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 22.6 mg (52%, 1.8:1 d.r.) of **3c** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) (major) δ 9.89 (s, 1H), 8.84–8.76 (m, 2H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.56–7.48 (m, 2H), 7.48–7.44 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 3.49–3.43 (m, 1H), 2.64–2.60 (m, 1H), 2.33 (s, 3H), 1.96–1.64 (m, 4H), 1.58–1.49 (m, 3H), 1.33–1.15 (m, 2H), 0.96–0.82 (m, 9H); (minor) δ 10.02 (s, 1H), 8.84–8.76 (m, 2H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.56–7.48 (m, 2H), 7.48–7.44 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 3.33–3.29 (m, 1H), 2.60–2.55 (m, 1H), 2.34 (s, 3H), 1.96–1.64 (m, 4H), 1.58–1.49 (m, 3H), 1.33–1.15 (m, 2H), 0.96–0.82 (m, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) (major) δ 172.61, 148.24, 138.65, 137.10, 136.41, 134.57, 132.79, 132.17, 129.86, 128.07, 127.58, 121.70, 121.51, 116.69, 53.31, 52.86, 37.15, 33.75, 28.36, 26.87, 22.85, 22.46, 21.27, 20.41, 14.09; (minor) δ 172.49, 148.26, 138.69, 137.34, 136.40, 134.61, 133.04, 131.67, 129.92, 128.11, 127.57, 121.71, 121.57, 116.67, 53.27, 52.85, 36.82, 34.06, 28.96, 26.87, 22.74, 22.52, 20.93, 20.41, 13.98. **HRMS** (ESI-TOF) Calcd for $C_{27}H_{35}N_2OS^+$ [M+H] 435.2470, found 435.2463.

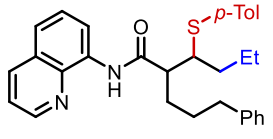


2-(cyclopropylmethyl)-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (3d): The reaction was carried out following General Procedure B using **1d** (26.6 mg, 0.1 mmol), **S1** (58.9 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 21.7 mg (52%, 2.9:1 d.r.) of **3d** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) (major) δ 9.93 (s, 1H), 9.05–8.60 (m, 2H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55–7.49 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.14–7.05 (m, 2H), 3.64–3.36 (m, 1H), 2.96–2.66 (m, 1H), 2.33 (s, 3H), 1.99–1.90 (m, 1H), 1.87–1.77 (m, 1H), 1.68–1.61 (m, 1H), 1.56–1.44 (m, 3H), 1.01–0.84 (m, 3H), 0.80–0.71 (m, 1H), 0.51–0.32 (m, 2H), 0.20–0.10 (m, 1H), 0.08–0.01 (m, 1H); (minor) δ 10.09 (s, 1H), 9.05–8.60 (m, 2H), 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.55–7.49 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.17–7.11 (m, 2H), 3.42–3.32 (m, 1H), 2.76–2.67 (m, 1H), 2.34 (s, 3H), 1.92–1.87 (m, 1H), 1.87–1.77 (m, 1H), 1.68–1.61 (m, 1H), 1.56–1.44 (m, 3H), 1.01–0.84 (m, 3H), 0.71–0.66 (m, 1H), 0.36–0.28 (m, 2H), 0.13–0.07 (m, 1H), 0.08–0.01 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) (major) δ 172.77, 148.26, 138.66, 137.11, 136.42, 134.64, 132.82, 132.13, 129.86, 128.08, 127.60, 121.69, 121.49, 116.71, 53.38, 52.49, 34.20, 33.76, 21.28, 20.23, 14.09, 9.74, 5.37, 4.30; (minor) δ 172.70, 148.28, 138.68, 137.29, 136.40, 134.68, 132.87, 131.58, 129.91, 128.11, 127.57, 121.71, 121.57, 116.67, 53.55, 52.48, 36.14, 34.08, 21.26, 20.82, 13.98, 9.47, 4.98, 4.51. **HRMS** (ESI-TOF) Calcd for $C_{26}H_{31}N_2OS^+$ [M+H] 419.2157, found 419.2153.

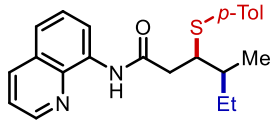


2-(cyclobutylmethyl)-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (3e): The reaction was carried out following General Procedure B using **1e** (28.0 mg, 0.1 mmol), **S1** (58.9 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 22.5 mg (52%, 3.7 d.r.) of **3e** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) (major) δ 9.83 (s, 1H), 8.98–8.68 (m, 2H), 8.16 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.56–7.48 (m, 2H), 7.48–7.43 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.43 (ddd, *J* = 8.5, 6.5, 3.8 Hz, 1H), 2.60–2.55 (m, 1H), 2.32 (s, 3H), 2.40–2.27 (m, 1H), 2.11–1.94 (m, 3H), 1.86–1.71 (m, 4H), 1.69–1.59 (m, 2H), 1.57–1.49 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); (minor) δ 10.00 (s, 1H), 8.98–8.68 (m, 2H), 8.16 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.56–7.48 (m, 2H), 7.48–7.43 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 0H), 3.30–3.26 (m, 1H), 2.57–2.51 (m, 1H), 2.34 (s, 3H), 2.40–2.27 (m, 1H), 2.11–1.94 (m, 3H), 1.86–1.71 (m, 4H), 1.69–1.59 (m, 2H), 1.57–1.49 (m, 2H), 0.88 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) (major) δ 172.59, 148.28, 138.64, 137.08, 136.41, 134.56, 132.82, 132.15, 129.83, 128.07, 127.58, 121.70, 121.51, 116.68, 52.79, 51.03, 36.32, 34.62, 33.70, 28.78, 28.22, 21.27, 20.18,

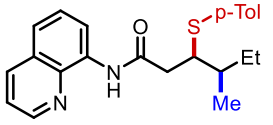
18.49, 14.12; (minor) δ 172.53, 148.31, 138.67, 137.34, 136.41, 134.62, 133.00, 131.62, 129.91, 128.12, 127.58, 121.72, 121.60, 116.67, 53.07, 51.14, 38.38, 34.48, 34.12, 28.63, 28.31, 20.88, 20.18, 18.54, 13.98. **HRMS** (ESI-TOF) Calcd for $C_{27}H_{33}N_2OS^+$ [M+H] 433.2314, found 433.2307.



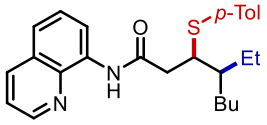
2-(3-phenylpropyl)-*N*-(quinolin-8-yl)-3-(*p*-tolylthio)hexanamide (3f): The reaction was carried out following General Procedure B using **1f** (33.0 mg, 0.1 mmol), **S1** (58.9 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 24.6 mg (51%, 1.7:1 d.r.) of **3f** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) (major) δ 9.93 (s, 1H), 8.92–8.70 (m, 2H), 8.23–8.14 (m, 1H), 7.60–7.51 (m, 2H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.26–7.20 (m, 2H), 7.18–7.14 (m, 3H), 7.13–7.10 (m, 2H), 3.50–3.44 (m, 1H), 2.72–2.56 (m, 3H), 2.36 (s, 3H), 2.05–1.63 (m, 6H), 1.58–1.51 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); (minor) 10.06 (s, 1H), 8.92–8.70 (m, 2H), 8.23–8.14 (m, 1H), 7.60–7.51 (m, 2H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.26–7.20 (m, 2H), 7.18–7.14 (m, 3H), 7.13–7.10 (m, 2H), 3.34–3.27 (m, 1H), 2.72–2.56 (m, 3H), 2.38 (s, 3H), 2.05–1.63 (m, 6H), 1.58–1.51 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) (major) δ 172.42, 148.26, 142.23, 138.62, 137.16, 136.42, 134.50, 132.85, 132.07, 129.88, 128.52, 128.37, 128.06, 127.55, 125.84, 121.70, 121.58, 116.71, 52.97, 52.74, 36.12, 33.74, 29.89, 28.88, 21.27, 20.35, 14.06; (minor) δ 172.29, 148.28, 142.23, 138.65, 137.45, 136.41, 134.54, 133.19, 131.53, 129.97, 128.54, 128.36, 128.11, 127.55, 125.82, 121.72, 121.65, 116.69, 53.26, 52.96, 35.95, 33.98, 30.84, 29.54, 21.28, 20.94, 13.96. **HRMS** (ESI-TOF) Calcd for $C_{31}H_{35}N_2OS^+$ [M+H] 483.2470, found 483.2465.



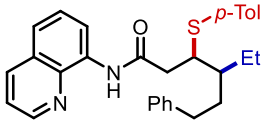
4-methyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)hexanamide (3g): The reaction was carried out following General Procedure B using **1g** (22.6 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 33.6 mg (89%) of **3g** as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.53–7.47 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40–7.36 (m, 2H), 7.02–6.98 (m, 2H), 3.79 (ddd, *J* = 8.8, 5.0, 3.8 Hz, 1H), 2.84 (dd, *J* = 15.1, 4.9 Hz, 1H), 2.67 (dd, *J* = 15.1, 8.8 Hz, 1H), 2.21 (s, 3H), 1.81 (dddd, *J* = 13.4, 6.6, 4.8, 3.3 Hz, 1H), 1.63–1.53 (m, 1H), 1.38–1.31 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.99, 148.24, 138.49, 137.10, 136.42, 134.58, 132.72, 131.71, 129.75, 128.03, 127.49, 121.70, 121.59, 116.68, 51.83, 40.52, 38.82, 26.68, 21.12, 16.00, 12.15. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{27}N_2OS^+$ [M+H] 379.1844, found 379.1838. **X-ray** (single-crystal) Colorless crystals of X-ray diffraction quality were obtained by vapor diffusion of hexane to a saturated solution of **4g** in ethyl acetate (CCDC 2154909).[7]



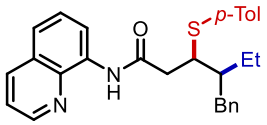
4-methyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)hexanamide (3h): The reaction was carried out following General Procedure B using **1h** (24.0 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), dimethylzinc (0.15 mmol, 1.0 M in THF), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 29.1 mg (77%) of **3h** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.72 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.53–7.47 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41–7.36 (m, 2H), 7.01–6.99 (m, 2H), 3.82 (ddd, *J* = 7.8, 6.3, 3.4 Hz, 1H), 2.85 (dd, *J* = 15.0, 6.4 Hz, 1H), 2.79 (dd, *J* = 15.0, 7.8 Hz, 1H), 2.22 (s, 3H), 1.87–1.78 (m, 1H), 1.73 (dqd, *J* = 12.8, 7.4, 5.3 Hz, 1H), 1.36 (ddq, *J* = 13.4, 8.4, 7.3 Hz, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.91, 148.26, 138.46, 137.05, 136.43, 134.54, 132.72, 131.80, 129.78, 128.03, 127.48, 121.71, 121.61, 116.65, 52.17, 42.39, 39.00, 27.18, 21.12, 15.71, 12.15. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{27}N_2OS^+$ [M+H] 379.1844, found 379.1834.



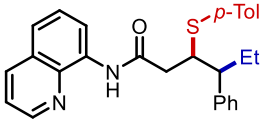
4-ethyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)octanamide (3i): The reaction was carried out following General Procedure B using **1i** (26.8 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 31.1 mg (74%) of **3i** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.72 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.52–7.47 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40–7.36 (m, 2H), 7.01–6.97 (m, 2H), 3.91 (ddd, *J* = 8.5, 5.7, 3.1 Hz, 1H), 2.85 (dd, *J* = 15.0, 5.7 Hz, 1H), 2.73 (dd, *J* = 15.0, 8.3 Hz, 1H), 2.21 (s, 3H), 1.74 (tt, *J* = 13.6, 7.3 Hz, 1H), 1.60 (pd, *J* = 6.5, 3.1 Hz, 1H), 1.50–1.22 (m, 7H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.98, 148.22, 138.47, 137.07, 136.41, 134.55, 132.72, 131.75, 129.75, 128.03, 127.48, 121.69, 121.58, 116.66, 49.86, 43.94, 41.48, 30.44, 30.09, 24.00, 23.07, 21.11, 14.18, 12.43. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{21}ClN_2OS^+$ [M+H] 421.2314, found 421.2305.



4-ethyl-6-phenyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)hexanamide (3j): The reaction was carried out following General Procedure B using **1j** (31.6 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 34.6 mg (74%) of **3j** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.71 (dd, *J* = 7.1, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.54–7.47 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.38–7.35 (m, 2H), 7.18 (tt, *J* = 7.6, 1.7 Hz, 2H), 7.14–7.11 (m, 2H), 7.09–7.05 (m, 1H), 7.01–6.98 (m, 2H), 3.96 (ddd, *J* = 8.1, 5.9, 3.3 Hz, 1H), 2.82 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.73 (dd, *J* = 15.1, 8.1 Hz, 1H), 2.63 (t, *J* = 7.9 Hz, 2H), 2.22 (s, 3H), 1.84–1.71 (m, 3H), 1.71–1.65 (m, 1H), 1.49–1.41 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.81, 148.23, 142.41, 138.45, 137.21, 136.42, 134.51, 132.90, 131.54, 129.81, 128.53, 128.39, 128.02, 127.47, 125.79, 121.71, 121.61, 116.67, 49.68, 43.31, 41.47, 34.01, 32.70, 23.86, 21.13, 12.29. **HRMS** (ESI-TOF) Calcd for $C_{30}H_{33}N_2OS^+$ [M+H] 469.2314, found 469.2310.

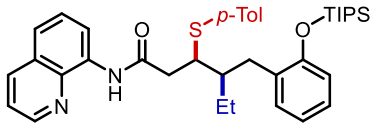


4-benzyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)hexanamide (3k): The reaction was carried out following General Procedure B using **1k** (30.2 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 23.2 mg (51%) of **3k** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.0, 2.0 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.53–7.48 (m, 2H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.24–7.20 (m, 4H), 7.18–7.14 (m, 3H), 6.98–6.90 (m, 2H), 3.90 (ddd, *J* = 8.6, 5.9, 2.8 Hz, 1H), 2.89 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.81–2.72 (m, 2H), 2.69 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.22 (s, 3H), 1.98 (pd, *J* = 6.9, 2.8 Hz, 1H), 1.77 (ddd, *J* = 13.7, 7.4, 6.3 Hz, 1H), 1.35 (dp, *J* = 14.3, 7.2 Hz, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.70, 148.22, 140.84, 138.48, 136.89, 136.41, 134.52, 132.16, 131.54, 129.75, 129.36, 128.47, 128.03, 127.49, 126.04, 121.71, 121.64, 116.72, 48.62, 46.16, 41.35, 37.12, 23.56, 21.11, 12.27. **HRMS** (ESI-TOF) Calcd for $C_{29}H_{31}N_2OS^+$ [M+H] 455.2157, found 455.2151.

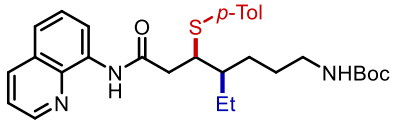


4-phenyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)hexanamide (3l): The reaction was carried out following General Procedure B using **1l** (28.8 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 15.4 mg (35%) of **3l** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.72 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.53–7.48 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40–7.37 (m, 2H), 7.34–7.29 (m, 4H), 7.28–7.24 (m, 1H), 7.05–7.00 (m, 2H), 4.03 (td, *J* = 7.0, 4.5 Hz, 1H), 2.98 (dt, *J* = 9.8, 4.9 Hz, 1H), 2.75 (dd, *J* = 15.2, 6.8

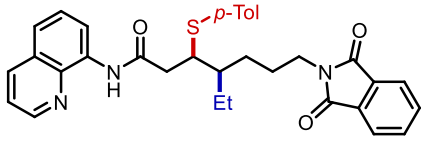
Hz, 1H), 2.66 (dd, *J* = 15.2, 7.3 Hz, 1H), 2.25 (s, 3H), 2.11–2.01 (m, 1H), 2.03–1.93 (m, 1H), 0.83 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.77, 148.25, 141.11, 138.49, 137.19, 136.43, 134.52, 132.69, 131.91, 129.87, 129.31, 128.38, 128.05, 127.49, 126.95, 121.73, 121.66, 116.71, 52.32, 51.20, 42.47, 25.64, 21.17, 12.52. **HRMS** (ESI-TOF) Calcd for $C_{28}H_{29}ClN_2OS^+$ [M+H] 441.2001, found 441.1989.



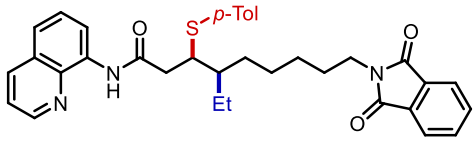
***N*-(quinolin-8-yl)-3-(p-tolylthio)-4-(2-((triisopropylsilyl)oxy)benzyl)hexanamide (3m):** The reaction was carried out following General Procedure B using **1m** (47.4 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 35.1 mg (56%) of **3m** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.67 (dd, *J* = 6.7, 2.2 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.50–7.46 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.35–7.32 (m, 2H), 7.15 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.00 (td, *J* = 7.7, 1.8 Hz, 1H), 6.96–6.93 (m, 2H), 6.80 (td, *J* = 7.4, 1.2 Hz, 1H), 6.75 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.91 (ddd, *J* = 8.5, 5.5, 2.9 Hz, 1H), 2.94–2.83 (m, 3H), 2.73 (dd, *J* = 14.8, 8.5 Hz, 1H), 2.18 (s, 3H), 2.16–2.09 (m, 1H), 1.55 (dp, *J* = 14.4, 7.2 Hz, 1H), 1.46 (ddd, *J* = 14.1, 7.5, 6.5 Hz, 1H), 1.28 (dq, *J* = 14.9, 7.4 Hz, 3H), 1.07 (dd, *J* = 7.5, 4.6 Hz, 18H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.74, 154.45, 148.18, 138.48, 136.87, 136.35, 134.60, 132.32, 131.66, 131.01, 130.81, 129.71, 127.98, 127.45, 126.85, 121.63, 121.47, 120.70, 118.05, 116.65, 49.41, 44.52, 41.56, 31.52, 23.56, 21.09, 18.26, 18.23, 13.32, 12.50. **HRMS** (ESI-TOF) Calcd for $C_{38}H_{51}N_2O_2SSi^+$ [M+H] 627.3441, found 627.3432.



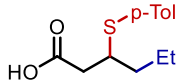
***tert*-butyl (4-ethyl-7-oxo-7-(quinolin-8-ylamino)-5-(p-tolylthio)heptyl)carbamate (3n):** The reaction was carried out following General Procedure B using **1n** (36.9 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 14.1 mg (27%) of **3n** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.72 (dd, *J* = 7.0, 2.0 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.55–7.47 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41–7.35 (m, 2H), 7.04–6.99 (m, 2H), 4.53 (s, 1H), 3.91 (ddd, *J* = 8.5, 5.6, 3.1 Hz, 1H), 3.11 (s, 2H), 2.84 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.72 (dd, *J* = 15.2, 8.3 Hz, 1H), 2.22 (s, 3H), 1.71 (ddd, *J* = 12.9, 10.3, 6.0 Hz, 1H), 1.61–1.40 (m, 13H), 1.37–1.24 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.83, 156.13, 148.29, 138.48, 137.24, 136.45, 134.52, 132.71, 131.64, 129.86, 128.05, 127.50, 121.74, 121.67, 116.70, 79.15, 49.62, 43.77, 41.14, 40.83, 28.60, 28.25, 28.01, 23.79, 12.40. **HRMS** (ESI-TOF) Calcd for $C_{30}H_{40}N_3O_3S^+$ [M+H] 522.2790, found 522.2791.



7-(1,3-dioxoisoindolin-2-yl)-4-ethyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)heptanamide (3o): The reaction was carried out following General Procedure B using **1o** (39.9 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 39.7 mg (72%) of **3o** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.80 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.70 (dd, *J* = 6.9, 2.0 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.83 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.53–7.47 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.37–7.34 (m, 2H), 7.01–6.97 (m, 2H), 3.90 (ddd, *J* = 8.5, 5.5, 3.1 Hz, 1H), 3.76–3.64 (m, 2H), 2.83 (dd, *J* = 15.2, 5.5 Hz, 1H), 2.70 (dd, *J* = 15.1, 8.4 Hz, 1H), 2.21 (s, 3H), 1.83–1.70 (m, 3H), 1.68–1.60 (m, 1H), 1.52–1.41 (m, 2H), 1.42–1.34 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.73, 168.51, 148.24, 138.44, 137.22, 136.39, 134.50, 133.94, 132.83, 132.29, 131.45, 129.81, 128.00, 127.46, 123.28, 121.68, 121.59, 116.68, 49.59, 43.71, 41.02, 38.36, 28.09, 27.05, 23.76, 21.12, 12.39. **HRMS** (ESI-TOF) Calcd for $C_{33}H_{34}N_3O_3S^+$ [M+H] 552.2321, found 552.2325.

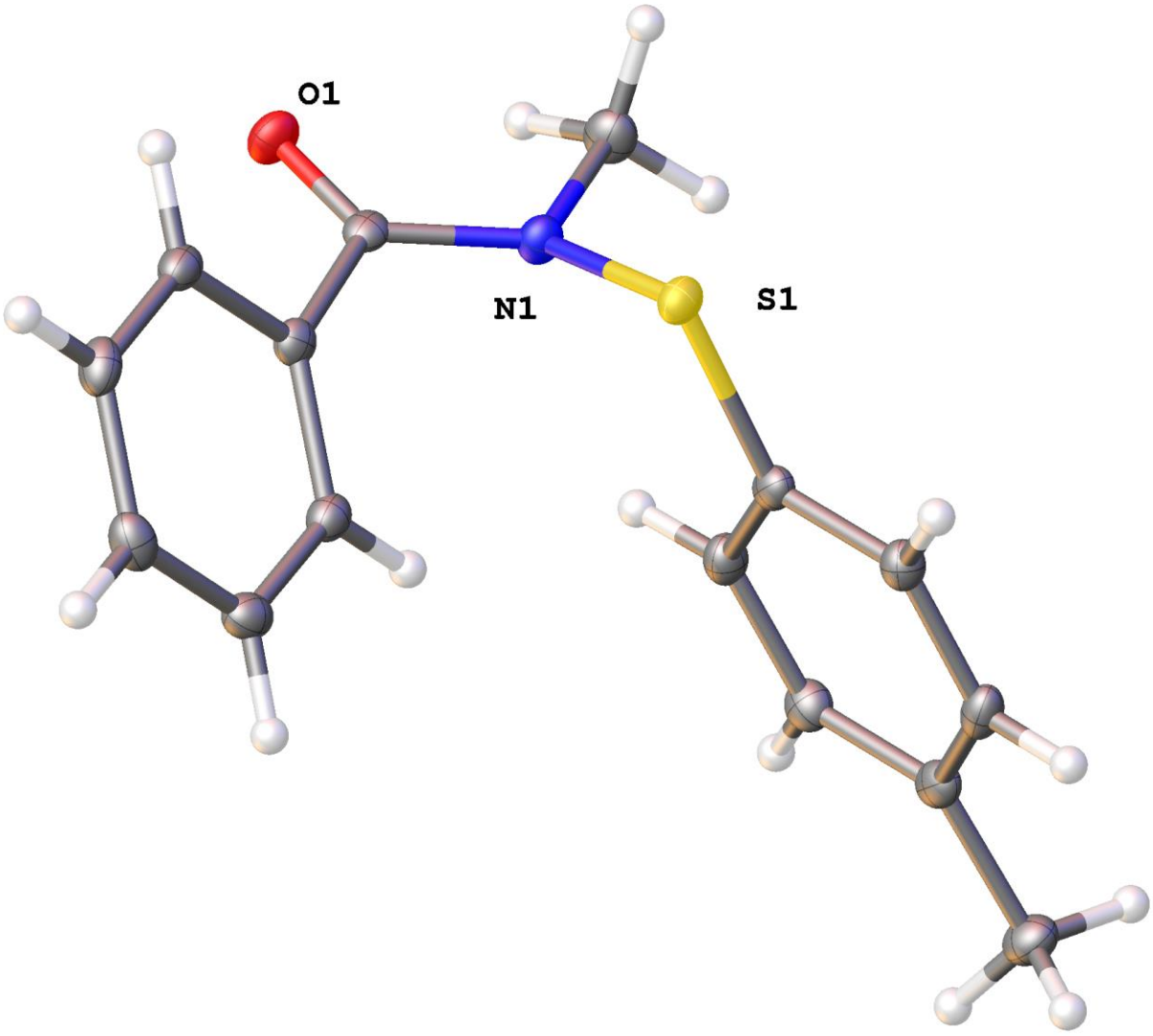


9-(1,3-dioxoisoindolin-2-yl)-4-ethyl-*N*-(quinolin-8-yl)-3-(p-tolylthio)nonanamide (3p): The reaction was carried out following General Procedure B using **1p** (42.7 mg, 0.1 mmol), **S10** (46.3 mg, 1.8 mmol), diethylzinc (0.15 mmol, 1.0 M in toluene), Ni(COD)(DMFU) (3.1 mg, 0.01 mmol), and THF (1.0 mL). The reaction was run for 20 h at 60 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 35.9 mg (62%) of **3p** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.71 (dd, *J* = 7.3, 1.7 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.53–7.45 (m, 2H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.40–7.35 (m, 2H), 7.02–6.94 (m, 2H), 3.91 (ddd, *J* = 8.5, 5.3, 3.1 Hz, 1H), 3.69–3.64 (m, 2H), 2.82 (dd, *J* = 15.1, 5.3 Hz, 1H), 2.69 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.20 (s, 3H), 1.74–1.63 (m, 3H), 1.59 (pd, *J* = 6.4, 3.0 Hz, 1H), 1.49–1.42 (m, 2H), 1.42–1.24 (m, 5H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.91, 168.55, 148.22, 138.44, 137.08, 136.38, 134.54, 133.93, 132.72, 132.31, 131.69, 129.74, 128.00, 127.47, 123.26, 121.67, 121.55, 116.65, 49.66, 43.99, 41.09, 38.16, 30.67, 28.66, 27.44, 27.31, 23.82, 21.09, 12.39. **HRMS** (ESI-TOF) Calcd for $C_{35}H_{38}N_3O_3S^+$ [M+H] 580.2634, found 580.2643.



3-(*p*-tolylthio)hexanoic acid (4): The reaction was carried out following a modified literature procedure[1] using **2a** (36.4 mg, 0.1 mmol) and HCl (6 M, 1 mL). The reaction was run for 40 h at 70 °C, and the product was purified by preparative thin-layer chromatography (PTLC) to afford 20.0 mg (84%) of **4** as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.59–3.19 (m, 1H), 2.90–2.44 (m, 2H), 2.33 (s, 3H), 1.75–1.42 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.81, 138.01, 134.07, 129.88, 129.67, 44.97, 40.36, 36.67, 21.27, 20.23, 13.90. **HRMS** (ESI-TOF) Calcd for $C_{13}H_{17}O_2S^-$ [M−H] 237.0949, found 237.0941.

X-Ray Crystallography



Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker APEX II Ultra diffractometer equipped with Mo K radiation (λ = 0.71073). Crystals of the subject compound were used as received (grown from Hexane). A 0.200 × 0.035 × 0.035 mm colorless crystal was mounted on a Cryoloop with Paratone oil.
Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 45 mm using exposure time 2.0 s (depending on the detector 2 position) with a scan width of 0.70°. Data collection was 99.7% complete to 25.242° in *θ*. A total of 13350 reflections were collected. 2508 reflections were found to be symmetry independent, with a R_{int} of 0.0422. Indexing and unit cell refinement indicated a **Primitive**, **Monoclinic** lattice. The space group was found to be ***P2₁/n***. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.
All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.
Crystallographic data are summarized in **Table S5**.

Notes: Excellent data and refinement.

Table S5: Crystal data and structure refinement for **S10** (CCDC 2149662).

Report date	2022-02-01	
Identification code	Engle389	
Empirical formula	C15 H15 N O S	
Molecular formula	C15 H15 N O S	
Formula weight	257.34	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 15.7788(18) Å	α= 90°.
	b = 5.6659(7) Å	β= 116.848(3)°.
	c = 16.0675(19) Å	γ = 90°.
Volume	1281.6(3) $Å^3$	
Z	4	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	0.239 mm^{-1}	
F(000)	544	
Crystal size	0.2 x 0.035 x 0.035 mm^3	
Crystal color, habit	colorless plank	
Theta range for data collection	1.501 to 26.029°.	
Index ranges	-19<=h<=14, -7<=k<=7, -19<=l<=19	
Reflections collected	13350	
Independent reflections	2508 [R(int) = 0.0422]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6465 and 0.6136	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2508 / 0 / 165	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0912	
R indices (all data)	R1 = 0.0456, wR2 = 0.0935	
Largest diff. peak and hole	0.314 and -0.276 e.$Å^{-3}$	

Table S6: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **S10**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6197(1)	5994(1)	8282(1)	14(1)
O(1)	4514(1)	7166(3)	9317(1)	18(1)
N(1)	5587(1)	7492(3)	8749(1)	15(1)
C(1)	6124(2)	9283(4)	9456(1)	19(1)
C(2)	4773(1)	6564(3)	8742(1)	13(1)
C(3)	4212(1)	4804(4)	7997(1)	13(1)
C(4)	3937(1)	5214(4)	7053(1)	15(1)
C(5)	3348(1)	3619(4)	6391(1)	17(1)
C(6)	3037(1)	1598(4)	6658(1)	18(1)
C(7)	3316(1)	1173(4)	7599(1)	18(1)
C(8)	3898(1)	2775(4)	8264(1)	16(1)
C(9)	6134(1)	7901(4)	7381(1)	14(1)
C(10)	5638(1)	10024(4)	7156(1)	16(1)
C(11)	5642(1)	11417(4)	6446(1)	16(1)
C(12)	6125(1)	10733(4)	5942(1)	16(1)
C(13)	6604(1)	8576(4)	6170(1)	17(1)
C(14)	6619(1)	7175(4)	6883(1)	15(1)
C(15)	6146(2)	12275(4)	5188(1)	20(1)

Table S7: Bond lengths [Å] and angles [°] for **S10**.

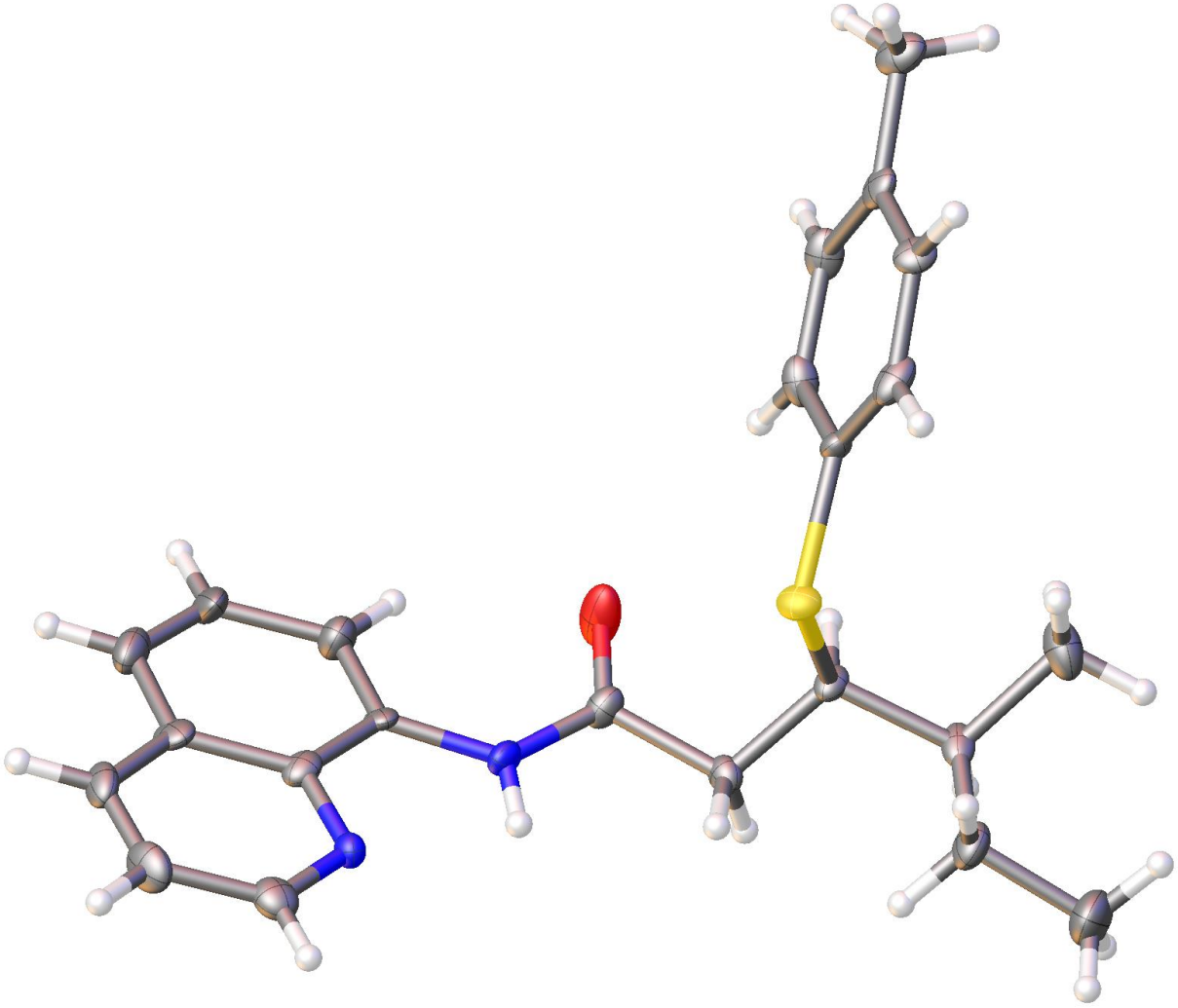
S(1)-N(1)	1.6924(17)	C(4)-C(3)-C(2)	122.54(18)
S(1)-C(9)	1.771(2)	C(8)-C(3)-C(2)	117.76(17)
O(1)-C(2)	1.217(2)	C(8)-C(3)-C(4)	119.52(18)
N(1)-C(1)	1.472(3)	C(3)-C(4)-H(4)	120.1
N(1)-C(2)	1.383(3)	C(5)-C(4)-C(3)	119.85(19)
C(1)-H(1A)	0.9800	C(5)-C(4)-H(4)	120.1
C(1)-H(1B)	0.9800	C(4)-C(5)-H(5)	119.7
C(1)-H(1C)	0.9800	C(4)-C(5)-C(6)	120.58(19)
C(2)-C(3)	1.502(3)	C(6)-C(5)-H(5)	119.7
C(3)-C(4)	1.395(3)	C(5)-C(6)-H(6)	120.1
C(3)-C(8)	1.394(3)	C(5)-C(6)-C(7)	119.73(19)
C(4)-H(4)	0.9500	C(7)-C(6)-H(6)	120.1
C(4)-C(5)	1.385(3)	C(6)-C(7)-H(7)	120.1
C(5)-H(5)	0.9500	C(8)-C(7)-C(6)	119.89(19)
C(5)-C(6)	1.389(3)	C(8)-C(7)-H(7)	120.1
C(6)-H(6)	0.9500	C(3)-C(8)-H(8)	119.8
C(6)-C(7)	1.392(3)	C(7)-C(8)-C(3)	120.43(18)
C(7)-H(7)	0.9500	C(7)-C(8)-H(8)	119.8
C(7)-C(8)	1.386(3)	C(10)-C(9)-S(1)	123.91(15)
C(8)-H(8)	0.9500	C(10)-C(9)-C(14)	119.67(18)
C(9)-C(10)	1.391(3)	C(14)-C(9)-S(1)	116.42(16)
C(9)-C(14)	1.396(3)	C(9)-C(10)-H(10)	120.2
C(10)-H(10)	0.9500	C(11)-C(10)-C(9)	119.59(19)
C(10)-C(11)	1.390(3)	C(11)-C(10)-H(10)	120.2
C(11)-H(11)	0.9500	C(10)-C(11)-H(11)	119.1
C(11)-C(12)	1.393(3)	C(10)-C(11)-C(12)	121.72(19)
C(12)-C(13)	1.396(3)	C(12)-C(11)-H(11)	119.1
C(12)-C(15)	1.506(3)	C(11)-C(12)-C(13)	117.65(19)
C(13)-H(13)	0.9500	C(11)-C(12)-C(15)	121.46(19)
C(13)-C(14)	1.385(3)	C(13)-C(12)-C(15)	120.89(19)
C(14)-H(14)	0.9500	C(12)-C(13)-H(13)	119.2
C(15)-H(15A)	0.9800	C(14)-C(13)-C(12)	121.61(19)
C(15)-H(15B)	0.9800	C(14)-C(13)-H(13)	119.2
C(15)-H(15C)	0.9800	C(9)-C(14)-H(14)	120.1
		C(13)-C(14)-C(9)	119.75(19)
N(1)-S(1)-C(9)	102.88(9)	C(13)-C(14)-H(14)	120.1
C(1)-N(1)-S(1)	116.34(13)	C(12)-C(15)-H(15A)	109.5
C(2)-N(1)-S(1)	121.20(14)	C(12)-C(15)-H(15B)	109.5
C(2)-N(1)-C(1)	118.48(16)	C(12)-C(15)-H(15C)	109.5
N(1)-C(1)-H(1A)	109.5	H(15A)-C(15)-H(15B)	109.5
N(1)-C(1)-H(1B)	109.5	H(15A)-C(15)-H(15C)	109.5
N(1)-C(1)-H(1C)	109.5	H(15B)-C(15)-H(15C)	109.5
H(1A)-C(1)-H(1B)	109.5		
H(1A)-C(1)-H(1C)	109.5		
H(1B)-C(1)-H(1C)	109.5		
O(1)-C(2)-N(1)	121.13(18)		
O(1)-C(2)-C(3)	120.82(18)		
N(1)-C(2)-C(3)	118.05(16)		

Table S8: Anisotropic displacement parameters ($Å^2 \times 10^3$) for **S10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	15(1)	14(1)	16(1)	1(1)	9(1)	2(1)
O(1)	22(1)	19(1)	18(1)	-3(1)	13(1)	-1(1)
N(1)	16(1)	15(1)	15(1)	-3(1)	9(1)	-2(1)
C(1)	20(1)	19(1)	18(1)	-6(1)	9(1)	-5(1)
C(2)	14(1)	12(1)	13(1)	4(1)	6(1)	3(1)
C(3)	13(1)	13(1)	16(1)	-1(1)	8(1)	2(1)
C(4)	15(1)	15(1)	17(1)	2(1)	9(1)	2(1)
C(5)	16(1)	20(1)	15(1)	1(1)	7(1)	3(1)
C(6)	15(1)	17(1)	22(1)	-5(1)	8(1)	-1(1)
C(7)	16(1)	14(1)	25(1)	3(1)	12(1)	0(1)
C(8)	15(1)	18(1)	16(1)	4(1)	8(1)	3(1)
C(9)	13(1)	15(1)	13(1)	-2(1)	6(1)	-5(1)
C(10)	15(1)	18(1)	17(1)	-3(1)	8(1)	-1(1)
C(11)	16(1)	13(1)	19(1)	0(1)	7(1)	-2(1)
C(12)	15(1)	17(1)	15(1)	-2(1)	6(1)	-6(1)
C(13)	17(1)	18(1)	18(1)	-5(1)	11(1)	-5(1)
C(14)	15(1)	14(1)	17(1)	-2(1)	8(1)	-1(1)
C(15)	24(1)	21(1)	18(1)	1(1)	11(1)	-4(1)

Table S9: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **S10**.

	x	y	z	U(eq)
H(1A)	6604	8504	10015	29
H(1B)	5688	10176	9619	29
H(1C)	6437	10361	9205	29
H(4)	4153	6584	6866	18
H(5)	3156	3911	5749	21
H(6)	2635	509	6200	22
H(7)	3108	-213	7786	21
H(8)	4083	2488	8906	19
H(10)	5298	10520	7485	19
H(11)	5308	12872	6300	20
H(13)	6926	8056	5828	20
H(14)	6959	5727	7033	18
H(15A)	5560	13208	4901	31
H(15B)	6196	11283	4713	31
H(15C)	6694	13337	5460	31



Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker ApexII-Ultra CCD diffractometer equipped with Mo Kα radiation (λ =0.7107 Å).

Crystals of the subject compound were used as received. A 0.21 × 0.18 × 0.17 mm piece of a colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ω scans. Crystal-to-detector distance was 50 mm and exposure time was 5 seconds per frame using a scan width of 0.70°. Data collection was 100 % complete to 25.242° in θ. A total of 44094 reflections were collected covering the indices, −9<=h<=9, −13<=k<=13, −31<=l<=31. 8011 reflections were found to be symmetry independent, with a R_{int} of 0.0445. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be $\boldsymbol{P_n}$. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in **Table S10**.

Notes: Great data! Absolute stereochemistry was conclusively assigned (Flack = -0.03(4)). There are two copies of the compound in the asymmetric unit. The crystal was a pseudomerohedral twin. There is excess electron density near the H17 hydrogen that could not be modeled. The chemical formula of the compound is: $C_{23}H_{26}N2OS$

Table S10: Crystal data and structure refinement for **3a** (CCDC 2154909).

Identification code	pn	
Empirical formula	C23 H26 N2 O S	
Formula weight	378.52	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 n 1	
Unit cell dimensions	a = 7.7413(14) Å	α= 90°.
	b = 10.5757(19) Å	β= 98.727(5)°.
	c = 25.507(5) Å	γ = 90°.
Volume	2064.1(7) $Å^3$	
Z	4	
Density (calculated)	1.218 Mg/m^3	
Absorption coefficient	0.171 mm^{-1}	
F(000)	808	
Crystal size	0.21 x 0.18 x 0.17 mm^3	
Theta range for data collection	1.615 to 26.066°.	
Index ranges	-9<=h<=9, -13<=k<=13, -31<=l<=31	
Reflections collected	19359	
Independent reflections	8011 [R(int) = 0.0445]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.5793	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8011 / 2 / 494	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1285	
R indices (all data)	R1 = 0.0541, wR2 = 0.1298	
Absolute structure parameter	-0.03(4)	
Largest diff. peak and hole	1.357 and -0.293 e.$Å^{-3}$	

Table S11: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1A)	4789(2)	2278(1)	6091(1)	20(1)
O(1A)	6362(6)	2606(5)	7445(2)	37(1)
N(1A)	3533(6)	2154(4)	7512(2)	19(1)
N(2A)	712(6)	771(4)	7605(2)	18(1)
C(9A)	4843(9)	4930(5)	6073(2)	22(1)
C(6A)	6874(10)	1174(5)	5454(2)	25(1)
C(19A)	2276(8)	-508(5)	8324(2)	22(1)
C(20A)	746(10)	-1201(5)	8329(2)	26(1)
C(16A)	5240(9)	953(6)	8226(2)	27(1)
C(14A)	4799(7)	2790(6)	7311(2)	20(1)
C(7A)	6833(7)	1745(5)	5947(2)	16(1)
C(23A)	2207(8)	478(5)	7936(2)	19(1)
C(15A)	3718(7)	1201(5)	7901(2)	16(1)
C(21A)	-753(9)	-908(6)	8001(3)	30(1)
C(8A)	5231(8)	3791(5)	6443(2)	17(1)
C(18A)	3881(10)	-733(6)	8661(2)	29(2)
C(11A)	2920(9)	5026(6)	5823(2)	28(1)
C(4A)	11496(8)	-16(6)	5549(3)	27(1)
C(22A)	-715(9)	111(6)	7644(2)	26(1)
C(13A)	4125(8)	3780(5)	6894(2)	18(1)
C(3A)	9907(8)	596(5)	5684(2)	21(1)
C(1A)	8361(8)	1753(6)	6309(2)	22(1)
C(10A)	6112(10)	4995(7)	5662(3)	33(2)
C(17A)	5330(10)	1(7)	8626(3)	40(2)
C(5A)	8367(8)	612(5)	5327(2)	19(1)
C(12A)	2477(13)	6230(8)	5505(3)	45(2)
C(2A)	9877(8)	1208(6)	6172(2)	23(1)
S(1)	5986(2)	4725(1)	3886(1)	23(1)
O(1)	6070(9)	5504(7)	2472(2)	69(2)
N(2)	573(6)	3238(4)	2451(2)	18(1)
N(1)	3441(6)	4653(4)	2542(2)	19(1)

C(6)	8664(8)	3696(5)	4560(2)	19(1)
C(8)	6139(8)	6278(5)	3579(2)	19(1)
C(22)	-839(8)	2529(6)	2418(2)	24(1)
C(15)	3311(8)	3703(5)	2155(2)	19(1)
C(23)	1758(7)	2949(5)	2122(2)	17(1)
C(16)	4532(8)	3450(6)	1824(2)	28(1)
C(13)	4555(9)	6356(5)	3131(2)	21(1)
C(3)	11493(7)	3168(5)	4347(2)	18(1)
C(9)	6231(8)	7389(5)	3972(2)	22(1)
C(2)	11029(8)	3694(5)	3853(2)	23(1)
C(7)	8173(8)	4220(5)	4056(2)	20(1)
C(11)	4596(10)	7497(6)	4239(2)	29(1)
C(1)	9379(8)	4206(5)	3698(2)	20(1)
C(5)	10268(8)	3174(6)	4695(2)	22(1)
C(18)	2783(10)	1701(6)	1420(2)	32(2)
C(21)	-1203(9)	1516(6)	2062(2)	28(1)
C(19)	1502(8)	1934(5)	1752(2)	23(1)
C(17)	4226(9)	2462(7)	1458(2)	31(2)
C(4)	13232(8)	2536(7)	4497(3)	27(1)
C(14)	4772(8)	5475(6)	2686(2)	25(1)
C(20)	-18(10)	1211(5)	1742(2)	30(1)
C(10)	7920(9)	7311(7)	4382(3)	30(2)
C(12)	4593(16)	8631(8)	4605(3)	53(2)

Table S12: Bond lengths [Å] and angles [°] for **3a**.

S(1A)-C(7A)	1.770(5)	C(11A)-C(12A)	1.521(9)
S(1A)-C(8A)	1.840(5)	C(4A)-H(4AA)	0.9800
O(1A)-C(14A)	1.222(7)	C(4A)-H(4AB)	0.9800
N(1A)-H(1A)	0.8800	C(4A)-H(4AC)	0.9800
N(1A)-C(14A)	1.352(7)	C(4A)-C(3A)	1.477(9)
N(1A)-C(15A)	1.405(7)	C(22A)-H(22A)	0.9500
N(2A)-C(23A)	1.360(8)	C(13A)-H(13A)	0.9900
N(2A)-C(22A)	1.323(8)	C(13A)-H(13B)	0.9900
C(9A)-H(9A)	1.0000	C(3A)-C(5A)	1.386(8)
C(9A)-C(8A)	1.531(7)	C(3A)-C(2A)	1.406(8)
C(9A)-C(11A)	1.532(10)	C(1A)-H(1AA)	0.9500
C(9A)-C(10A)	1.543(9)	C(1A)-C(2A)	1.398(9)
C(6A)-H(6A)	0.9500	C(10A)-H(10A)	0.9800
C(6A)-C(7A)	1.398(8)	C(10A)-H(10B)	0.9800
C(6A)-C(5A)	1.381(9)	C(10A)-H(10C)	0.9800
C(19A)-C(20A)	1.394(9)	C(17A)-H(17A)	0.9500
C(19A)-C(23A)	1.432(8)	C(5A)-H(5A)	0.9500
C(19A)-C(18A)	1.419(9)	C(12A)-H(12A)	0.9800
C(20A)-H(20A)	0.9500	C(12A)-H(12B)	0.9800
C(20A)-C(21A)	1.360(10)	C(12A)-H(12C)	0.9800
C(16A)-H(16A)	0.9500	C(2A)-H(2A)	0.9500
C(16A)-C(15A)	1.360(8)	S(1)-C(8)	1.832(6)
C(16A)-C(17A)	1.426(8)	S(1)-C(7)	1.766(6)
C(14A)-C(13A)	1.528(7)	O(1)-C(14)	1.215(8)
C(7A)-C(1A)	1.387(8)	N(2)-C(22)	1.317(7)
C(23A)-C(15A)	1.412(8)	N(2)-C(23)	1.369(7)
C(21A)-H(21A)	0.9500	N(1)-H(1)	0.8800
C(21A)-C(22A)	1.414(9)	N(1)-C(15)	1.401(7)
C(8A)-H(8A)	1.0000	N(1)-C(14)	1.355(7)
C(8A)-C(13A)	1.534(7)	C(6)-H(6)	0.9500
C(18A)-H(18A)	0.9500	C(6)-C(7)	1.400(8)
C(18A)-C(17A)	1.378(10)	C(6)-C(5)	1.355(9)
C(11A)-H(11A)	0.9900	C(8)-H(8)	1.0000
C(11A)-H(11B)	0.9900	C(8)-C(13)	1.546(8)

C(8)-C(9)	1.540(7)	C(10)-H(10D)	0.9800
C(22)-H(22)	0.9500	C(10)-H(10E)	0.9800
C(22)-C(21)	1.405(9)	C(10)-H(10F)	0.9800
C(15)-C(23)	1.435(8)	C(12)-H(12D)	0.9800
C(15)-C(16)	1.385(8)	C(12)-H(12E)	0.9800
C(23)-C(19)	1.424(7)	C(12)-H(12F)	0.9800
C(16)-H(16)	0.9500		
C(16)-C(17)	1.398(9)	C(7A)-S(1A)-C(8A)	105.8(3)
C(13)-H(13C)	0.9900	C(14A)-N(1A)-H(1A)	115.8
C(13)-H(13D)	0.9900	C(14A)-N(1A)-C(15A)	128.4(5)
C(13)-C(14)	1.497(8)	C(15A)-N(1A)-H(1A)	115.8
C(3)-C(2)	1.373(8)	C(22A)-N(2A)-C(23A)	118.4(5)
C(3)-C(5)	1.395(8)	C(8A)-C(9A)-H(9A)	106.1
C(3)-C(4)	1.500(8)	C(8A)-C(9A)-C(11A)	113.3(5)
C(9)-H(9)	1.0000	C(8A)-C(9A)-C(10A)	111.6(5)
C(9)-C(11)	1.530(9)	C(11A)-C(9A)-H(9A)	106.1
C(9)-C(10)	1.547(9)	C(11A)-C(9A)-C(10A)	113.1(5)
C(2)-H(2)	0.9500	C(10A)-C(9A)-H(9A)	106.1
C(2)-C(1)	1.389(9)	C(7A)-C(6A)-H(6A)	119.0
C(7)-C(1)	1.400(8)	C(5A)-C(6A)-H(6A)	119.0
C(11)-H(11C)	0.9900	C(5A)-C(6A)-C(7A)	122.0(6)
C(11)-H(11D)	0.9900	C(20A)-C(19A)-C(23A)	116.5(5)
C(11)-C(12)	1.519(9)	C(20A)-C(19A)-C(18A)	124.9(5)
C(1)-H(1B)	0.9500	C(18A)-C(19A)-C(23A)	118.5(5)
C(5)-H(5)	0.9500	C(19A)-C(20A)-H(20A)	119.3
C(18)-H(18)	0.9500	C(21A)-C(20A)-C(19A)	121.4(5)
C(18)-C(19)	1.419(9)	C(21A)-C(20A)-H(20A)	119.3
C(18)-C(17)	1.368(10)	C(15A)-C(16A)-H(16A)	119.5
C(21)-H(21)	0.9500	C(15A)-C(16A)-C(17A)	121.1(6)
C(21)-C(20)	1.357(10)	C(17A)-C(16A)-H(16A)	119.5
C(19)-C(20)	1.400(9)	O(1A)-C(14A)-N(1A)	124.0(5)
C(17)-H(17)	0.9500	O(1A)-C(14A)-C(13A)	121.5(5)
C(4)-H(4A)	0.9800	N(1A)-C(14A)-C(13A)	114.5(5)
C(4)-H(4B)	0.9800	C(6A)-C(7A)-S(1A)	117.9(5)
C(4)-H(4C)	0.9800	C(1A)-C(7A)-S(1A)	123.9(4)
C(20)-H(20)	0.9500	C(1A)-C(7A)-C(6A)	117.9(5)

N(2A)-C(23A)-C(19A)	122.2(5)	C(8A)-C(13A)-H(13A)	109.5
N(2A)-C(23A)-C(15A)	118.2(5)	C(8A)-C(13A)-H(13B)	109.5
C(15A)-C(23A)-C(19A)	119.6(5)	H(13A)-C(13A)-H(13B)	108.0
N(1A)-C(15A)-C(23A)	115.9(5)	C(5A)-C(3A)-C(4A)	121.0(5)
C(16A)-C(15A)-N(1A)	123.7(5)	C(5A)-C(3A)-C(2A)	116.6(6)
C(16A)-C(15A)-C(23A)	120.4(5)	C(2A)-C(3A)-C(4A)	122.4(5)
C(20A)-C(21A)-H(21A)	120.9	C(7A)-C(1A)-H(1AA)	120.1
C(20A)-C(21A)-C(22A)	118.1(6)	C(7A)-C(1A)-C(2A)	119.7(5)
C(22A)-C(21A)-H(21A)	120.9	C(2A)-C(1A)-H(1AA)	120.1
S(1A)-C(8A)-H(8A)	108.5	C(9A)-C(10A)-H(10A)	109.5
C(9A)-C(8A)-S(1A)	112.3(3)	C(9A)-C(10A)-H(10B)	109.5
C(9A)-C(8A)-H(8A)	108.5	C(9A)-C(10A)-H(10C)	109.5
C(9A)-C(8A)-C(13A)	112.8(5)	H(10A)-C(10A)-H(10B)	109.5
C(13A)-C(8A)-S(1A)	106.0(4)	H(10A)-C(10A)-H(10C)	109.5
C(13A)-C(8A)-H(8A)	108.5	H(10B)-C(10A)-H(10C)	109.5
C(19A)-C(18A)-H(18A)	119.6	C(16A)-C(17A)-H(17A)	120.3
C(17A)-C(18A)-C(19A)	120.8(6)	C(18A)-C(17A)-C(16A)	119.4(7)
C(17A)-C(18A)-H(18A)	119.6	C(18A)-C(17A)-H(17A)	120.3
C(9A)-C(11A)-H(11A)	108.8	C(6A)-C(5A)-C(3A)	121.2(5)
C(9A)-C(11A)-H(11B)	108.8	C(6A)-C(5A)-H(5A)	119.4
H(11A)-C(11A)-H(11B)	107.7	C(3A)-C(5A)-H(5A)	119.4
C(12A)-C(11A)-C(9A)	113.8(6)	C(11A)-C(12A)-H(12A)	109.5
C(12A)-C(11A)-H(11A)	108.8	C(11A)-C(12A)-H(12B)	109.5
C(12A)-C(11A)-H(11B)	108.8	C(11A)-C(12A)-H(12C)	109.5
H(4AA)-C(4A)-H(4AB)	109.5	H(12A)-C(12A)-H(12B)	109.5
H(4AA)-C(4A)-H(4AC)	109.5	H(12A)-C(12A)-H(12C)	109.5
H(4AB)-C(4A)-H(4AC)	109.5	H(12B)-C(12A)-H(12C)	109.5
C(3A)-C(4A)-H(4AA)	109.5	C(3A)-C(2A)-H(2A)	118.8
C(3A)-C(4A)-H(4AB)	109.5	C(1A)-C(2A)-C(3A)	122.5(5)
C(3A)-C(4A)-H(4AC)	109.5	C(1A)-C(2A)-H(2A)	118.8
N(2A)-C(22A)-C(21A)	123.3(6)	C(7)-S(1)-C(8)	104.7(3)
N(2A)-C(22A)-H(22A)	118.4	C(22)-N(2)-C(23)	117.4(5)
C(21A)-C(22A)-H(22A)	118.4	C(15)-N(1)-H(1)	115.8
C(14A)-C(13A)-C(8A)	110.9(5)	C(14)-N(1)-H(1)	115.8
C(14A)-C(13A)-H(13A)	109.5	C(14)-N(1)-C(15)	128.4(5)
C(14A)-C(13A)-H(13B)	109.5	C(7)-C(6)-H(6)	119.8

C(5)-C(6)-H(6)	119.8	C(3)-C(2)-C(1)	121.3(5)
C(5)-C(6)-C(7)	120.4(5)	C(1)-C(2)-H(2)	119.3
S(1)-C(8)-H(8)	108.0	C(6)-C(7)-S(1)	117.5(4)
C(13)-C(8)-S(1)	105.5(4)	C(6)-C(7)-C(1)	118.7(5)
C(13)-C(8)-H(8)	108.0	C(1)-C(7)-S(1)	123.5(4)
C(9)-C(8)-S(1)	113.9(4)	C(9)-C(11)-H(11C)	108.7
C(9)-C(8)-H(8)	108.0	C(9)-C(11)-H(11D)	108.7
C(9)-C(8)-C(13)	113.2(5)	H(11C)-C(11)-H(11D)	107.6
N(2)-C(22)-H(22)	118.0	C(12)-C(11)-C(9)	114.3(7)
N(2)-C(22)-C(21)	124.0(6)	C(12)-C(11)-H(11C)	108.7
C(21)-C(22)-H(22)	118.0	C(12)-C(11)-H(11D)	108.7
N(1)-C(15)-C(23)	114.2(5)	C(2)-C(1)-C(7)	119.6(5)
C(16)-C(15)-N(1)	125.8(5)	C(2)-C(1)-H(1B)	120.2
C(16)-C(15)-C(23)	120.0(5)	C(7)-C(1)-H(1B)	120.2
N(2)-C(23)-C(15)	118.3(5)	C(6)-C(5)-C(3)	121.7(5)
N(2)-C(23)-C(19)	122.5(5)	C(6)-C(5)-H(5)	119.2
C(19)-C(23)-C(15)	119.3(5)	C(3)-C(5)-H(5)	119.2
C(15)-C(16)-H(16)	120.3	C(19)-C(18)-H(18)	120.3
C(15)-C(16)-C(17)	119.3(6)	C(17)-C(18)-H(18)	120.3
C(17)-C(16)-H(16)	120.3	C(17)-C(18)-C(19)	119.5(5)
C(8)-C(13)-H(13C)	109.4	C(22)-C(21)-H(21)	120.6
C(8)-C(13)-H(13D)	109.4	C(20)-C(21)-C(22)	118.8(6)
H(13C)-C(13)-H(13D)	108.0	C(20)-C(21)-H(21)	120.6
C(14)-C(13)-C(8)	111.0(6)	C(18)-C(19)-C(23)	119.2(5)
C(14)-C(13)-H(13C)	109.4	C(20)-C(19)-C(23)	117.1(5)
C(14)-C(13)-H(13D)	109.4	C(20)-C(19)-C(18)	123.8(5)
C(2)-C(3)-C(5)	118.3(5)	C(16)-C(17)-H(17)	118.6
C(2)-C(3)-C(4)	121.0(5)	C(18)-C(17)-C(16)	122.8(6)
C(5)-C(3)-C(4)	120.7(5)	C(18)-C(17)-H(17)	118.6
C(8)-C(9)-H(9)	107.0	C(3)-C(4)-H(4A)	109.5
C(8)-C(9)-C(10)	110.5(5)	C(3)-C(4)-H(4B)	109.5
C(11)-C(9)-C(8)	112.8(5)	C(3)-C(4)-H(4C)	109.5
C(11)-C(9)-H(9)	107.0	H(4A)-C(4)-H(4B)	109.5
C(11)-C(9)-C(10)	112.0(5)	H(4A)-C(4)-H(4C)	109.5
C(10)-C(9)-H(9)	107.0	H(4B)-C(4)-H(4C)	109.5
C(3)-C(2)-H(2)	119.3	O(1)-C(14)-N(1)	122.8(5)

O(1)-C(14)-C(13)	121.4(6)
N(1)-C(14)-C(13)	115.9(5)
C(21)-C(20)-C(19)	120.2(5)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(9)-C(10)-H(10D)	109.5
C(9)-C(10)-H(10E)	109.5
C(9)-C(10)-H(10F)	109.5
H(10D)-C(10)-H(10E)	109.5
H(10D)-C(10)-H(10F)	109.5
H(10E)-C(10)-H(10F)	109.5
C(11)-C(12)-H(12D)	109.5
C(11)-C(12)-H(12E)	109.5
C(11)-C(12)-H(12F)	109.5
H(12D)-C(12)-H(12E)	109.5
H(12D)-C(12)-H(12F)	109.5
H(12E)-C(12)-H(12F)	109.5

Symmetry transformations used to generate equivalent atoms

Table S13: Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1A)	20(1)	15(1)	27(1)	-5(1)	4(1)	-1(1)
O(1A)	21(2)	44(3)	43(2)	21(2)	-3(2)	-11(2)
N(1A)	22(2)	21(2)	16(2)	5(2)	2(2)	7(2)
N(2A)	19(2)	16(2)	19(2)	4(2)	7(2)	1(2)
C(9A)	39(3)	11(2)	16(2)	-3(2)	11(2)	-1(3)
C(6A)	37(4)	12(3)	22(2)	0(2)	-4(3)	0(3)
C(19A)	25(3)	10(2)	32(3)	0(2)	9(2)	6(2)
C(20A)	42(4)	12(2)	26(3)	3(2)	15(3)	1(3)
C(16A)	28(4)	25(3)	28(3)	9(2)	5(3)	4(3)
C(14A)	21(3)	17(3)	21(2)	2(2)	-2(2)	-1(2)
C(7A)	13(3)	15(2)	19(2)	5(2)	3(2)	4(2)
C(23A)	27(3)	13(3)	19(2)	-3(2)	3(2)	4(2)
C(15A)	17(3)	10(2)	22(2)	2(2)	8(2)	6(2)
C(21A)	33(4)	21(3)	40(3)	-2(3)	15(3)	-11(3)
C(8A)	25(3)	11(2)	14(2)	-2(2)	3(2)	2(2)
C(18A)	44(4)	24(3)	21(3)	7(2)	9(3)	9(3)
C(11A)	38(3)	16(3)	29(3)	6(2)	6(3)	2(3)
C(4A)	24(3)	15(3)	42(4)	0(2)	2(3)	-1(2)
C(22A)	31(4)	24(3)	25(3)	-6(2)	10(3)	0(3)
C(13A)	21(3)	15(3)	20(3)	0(2)	7(2)	-3(2)
C(3A)	22(3)	12(2)	29(3)	8(2)	3(2)	-2(2)
C(1A)	26(3)	23(3)	17(2)	0(2)	1(2)	-10(2)
C(10A)	41(4)	34(4)	26(3)	2(3)	10(3)	-13(3)
C(17A)	39(4)	31(4)	57(4)	28(3)	28(3)	21(3)
C(5A)	23(3)	12(2)	22(3)	-6(2)	2(2)	0(2)
C(12A)	54(5)	41(4)	40(4)	20(3)	12(4)	14(4)
C(2A)	20(3)	24(3)	21(3)	2(2)	-5(2)	-10(3)
S(1)	19(1)	12(1)	39(1)	5(1)	8(1)	-2(1)
O(1)	66(4)	94(5)	59(3)	-55(4)	47(3)	-56(4)
N(2)	17(2)	17(2)	19(2)	3(2)	-1(2)	-2(2)

N(1)	18(2)	20(2)	19(2)	-10(2)	5(2)	-9(2)
C(6)	23(3)	19(3)	16(2)	0(2)	9(2)	-2(2)
C(8)	19(3)	14(3)	26(3)	1(2)	5(2)	-1(2)
C(22)	25(3)	23(3)	24(3)	4(2)	5(2)	-8(3)
C(15)	27(3)	14(2)	16(2)	0(2)	1(2)	1(2)
C(23)	23(3)	9(2)	18(2)	4(2)	-3(2)	4(2)
C(16)	23(3)	35(3)	27(3)	-11(3)	9(3)	-4(3)
C(13)	35(4)	11(2)	16(2)	3(2)	-3(2)	-5(2)
C(3)	18(3)	15(3)	20(2)	-1(2)	-2(2)	-4(2)
C(9)	27(3)	12(2)	25(3)	-5(2)	1(2)	-3(2)
C(2)	22(3)	24(3)	23(2)	0(2)	6(2)	-7(3)
C(7)	21(3)	12(3)	27(3)	1(2)	5(2)	-1(2)
C(11)	44(4)	24(3)	22(3)	-5(2)	11(3)	3(3)
C(1)	31(3)	15(2)	14(2)	3(2)	7(2)	7(2)
C(5)	28(3)	25(3)	15(2)	0(2)	4(2)	-7(3)
C(18)	40(4)	24(3)	30(3)	-9(2)	1(3)	8(3)
C(21)	35(4)	20(3)	29(3)	6(2)	4(3)	-15(3)
C(19)	26(3)	17(3)	21(3)	-4(2)	-5(2)	6(2)
C(17)	31(3)	48(4)	18(3)	-4(3)	15(2)	-1(3)
C(4)	20(3)	31(3)	29(3)	11(3)	4(2)	7(3)
C(14)	30(3)	21(3)	23(3)	-7(2)	6(3)	-13(3)
C(20)	45(4)	11(3)	31(3)	-4(2)	-3(3)	-3(3)
C(10)	35(4)	20(3)	36(3)	0(3)	3(3)	3(3)
C(12)	91(7)	40(4)	33(3)	-17(3)	27(4)	-11(4)

Table 14. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2×10^3) for **3a**.

	x	y	z	U(eq)
H(1A)	2452	2365	7383	23
H(9A)	5089	5697	6302	26
H(6A)	5843	1172	5199	29
H(20A)	752	-1893	8567	31
H(16A)	6259	1422	8187	32
H(21A)	-1796	-1374	8011	36
H(8A)	6493	3815	6602	20
H(18A)	3957	-1398	8914	35
H(11A)	2623	4289	5588	33
H(11B)	2184	4983	6108	33
H(4AA)	12085	563	5333	41
H(4AB)	11172	-792	5348	41
H(4AC)	12285	-223	5875	41
H(22A)	-1767	332	7420	31
H(13A)	4165	4626	7061	22
H(13B)	2893	3593	6747	22
H(1AA)	8378	2126	6648	27
H(10A)	5972	4236	5439	50
H(10B)	7317	5041	5847	50
H(10C)	5853	5747	5440	50
H(17A)	6381	-126	8865	48
H(5A)	8338	230	4989	23
H(12A)	3021	6203	5183	67
H(12B)	2919	6963	5719	67
H(12C)	1207	6300	5408	67
H(2A)	10927	1252	6419	27
H(1)	2543	4725	2714	23
H(6)	7868	3706	4809	23
H(8)	7226	6292	3411	23
H(22)	-1661	2714	2648	29

H(16)	5566	3944	1846	33
H(13C)	3476	6136	3275	26
H(13D)	4432	7233	2995	26
H(9)	6306	8182	3764	26
H(2)	11854	3708	3613	27
H(11C)	3559	7549	3961	35
H(11D)	4484	6718	4447	35
H(1B)	9070	4545	3352	23
H(5)	10566	2802	5036	27
H(18)	2639	1021	1174	38
H(21)	-2261	1052	2046	34
H(17)	5055	2312	1226	38
H(4A)	13443	1957	4214	40
H(4B)	13235	2060	4827	40
H(4C)	14154	3179	4549	40
H(20)	-219	506	1510	36
H(10D)	8141	8131	4558	46
H(10E)	8907	7089	4201	46
H(10F)	7781	6663	4647	46
H(12D)	4874	9397	4418	79
H(12E)	5468	8507	4921	79
H(12F)	3434	8722	4711	79

DFT Calculations

Computational Details

All calculations were performed with Gaussian 16, Revision B.01. The M052X density functional and a basis set of 6-31+G* were used in geometry optimizations. Single-point energies were calculated with M052X and a mixed basis set of 6-311+G**. For bond dissociation energy calculation, all structures have been optimized considering solvent effects using the SMD model for acetonitrile. The reported Gibbs free energies and enthalpies include zero-point vibrational energies and thermal corrections at 298 K.

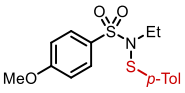
Complete Citation for Gaussian 16

Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

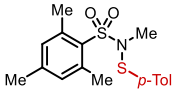
Data Analysis for DFT Calculation

Table S15: Calculated BDE (kcal/mol) of Sulfenylating Agents[a]

S1, R^1 = OMe, 50.8
S2, R^1 = Me, 50.8
S3, R^1 = Cl, 51.2

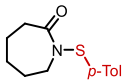


S4, 50.6

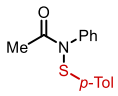


S5, 49.1

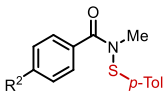
S6, 49.8



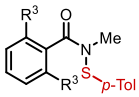
S7, 55.3



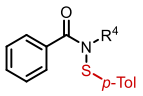
S8, 43.4



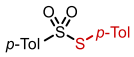
S9, R^2 = F, 52.2
S10, R^2 = H, 52.4
S11, R^2 = Me, 51.9
S12, R^2 = *t*-Bu, 52.7
S13, R^2 = OMe, 51.0



S14, R^3 = OMe, 58.4

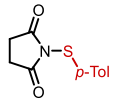


S15, R^4 = Et, 52.8
S16, R^4 = *i*-Pr, 51.8
S17, R^4 = Bn, 53.2

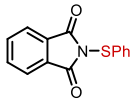


S18, 39.8

S19, 53.7



S20, 73.6



S21, 79.2

[a]Solution phase BDE (kcal/mol) calculated at SMD(acetonitrile)//M05-2X/6-311+G(d,p), SMD(acetonitrile)//M05-2X/6-31+G(d) level of theory.[8]

Cartesian Coordinates (Å) and Energies of Optimized Structures

S6

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1431.044826 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.227144 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1430.81768 a.u.

0 1

S	2.35239500	0.08345700	-0.11006000
O	3.06017000	0.11881900	-1.39823600
O	3.16679100	-0.10109400	1.10104300
N	1.19441100	-1.14793500	-0.26217300
S	0.24080100	-1.41915300	1.16257000
C	-1.32166900	-0.75440000	0.62165800
C	-1.90790600	0.27910600	1.34916700
C	-1.96845400	-1.27361600	-0.50469500
C	-3.14358600	0.79205200	0.94992100
H	-1.40376200	0.68937000	2.21695900
C	-3.18495700	-0.73692600	-0.90628100
H	-1.51683700	-2.08313300	-1.06686600
C	-3.79359900	0.29973100	-0.18289600
H	-3.59710300	1.59530900	1.51992800
H	-3.67925400	-1.13382300	-1.78652700
C	-5.12211700	0.85532700	-0.62423700
H	-5.42918000	1.68621800	0.01195600
H	-5.07117500	1.21024300	-1.65634400
H	-5.89630800	0.08470300	-0.58171400
C	1.69192600	-2.36901400	-0.93156800
H	2.41494600	-2.91149900	-0.31783800
H	2.14502300	-2.08765300	-1.87934100
H	0.82835000	-3.00197900	-1.12348100
C	1.35368400	1.57279900	0.08096800
H	0.74883000	1.38752000	0.97014000
C	2.31506100	2.73284400	0.33260600
H	2.97914500	2.88173000	-0.52150200
H	1.71896600	3.63786100	0.46301600
H	2.91137800	2.57839800	1.23155400
C	0.48090100	1.79177400	-1.14689500
H	-0.16857100	0.93915300	-1.34653600
H	-0.14545700	2.66695100	-0.96125000
H	1.09761700	1.98745100	-2.02604600

S8

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1108.932349 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.221796 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1108.710553 a.u.

0 1

N	1.26682200	0.95803800	0.19418800
S	0.10637500	1.18079700	1.43644400
C	-1.35656100	0.47191300	0.69821600
C	-2.24703800	-0.19672800	1.54208300
C	-1.64772100	0.60318800	-0.65854800
C	-3.43160100	-0.71362900	1.02505000
H	-2.01591800	-0.32064800	2.59436100
C	-2.82520000	0.05618800	-1.16588900
H	-0.96258900	1.11612500	-1.32332500
C	-3.73738300	-0.60154600	-0.33570800
H	-4.12008300	-1.22894200	1.68646200
H	-3.04025500	0.15190000	-2.22451900
C	-5.01501100	-1.18281100	-0.88299900
H	-5.09340700	-1.01065100	-1.95721900
H	-5.06085400	-2.25975000	-0.70299700
H	-5.88552900	-0.73299100	-0.39909300
C	1.68056100	1.98294400	-0.64235700
O	2.56281000	1.78266600	-1.46672300
C	1.83576400	-0.35327700	0.04631700
C	1.52348000	-1.11771300	-1.07650700
C	2.66960700	-0.85772900	1.04201300
C	2.05906800	-2.39822200	-1.20398900
H	0.87650200	-0.70658200	-1.84150900
C	3.19545200	-2.14158000	0.91242700
H	2.89884800	-0.24796600	1.90841700
C	2.89209700	-2.91251100	-0.21038400
H	1.82082000	-2.99375500	-2.07698200
H	3.84423400	-2.53602200	1.68502700
H	3.30330000	-3.90973900	-0.31003700
C	1.02720200	3.33062000	-0.47770600
H	-0.05962000	3.26525200	-0.54099700
H	1.28277300	3.76387600	0.49123400
H	1.40325900	3.97490000	-1.26956900

S11

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1148.249908 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.247741 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1148.002167 a.u.

0 1

C	-3.44971200	0.48136600	0.10157500
C	-4.13526900	-0.72531300	0.22339600
C	-3.49929000	-1.94160200	-0.04122200
C	-2.15438300	-1.91850200	-0.43209100
C	-1.45716600	-0.72013700	-0.53443900
C	-2.10225200	0.48985500	-0.26032900
H	-3.95810700	1.41900000	0.29178700
H	-5.17882600	-0.72123500	0.51840400
H	-1.64905400	-2.85091800	-0.65968000
H	-0.41955800	-0.73023300	-0.84568600
N	-0.16121600	2.00762400	0.02924800
S	0.44440100	1.12510600	1.36097300
C	1.81546400	0.25233700	0.62925600
C	2.62993400	-0.47790900	1.50194600
C	2.10475700	0.28033900	-0.73210700
C	3.71848800	-1.18227400	1.00155400
H	2.41772700	-0.49827500	2.56600200
C	3.20608500	-0.42938000	-1.21593600
H	1.48276500	0.84605100	-1.41565400
C	4.02757700	-1.16971000	-0.36508800
H	4.34260600	-1.74847300	1.68493600
H	3.42392800	-0.40154500	-2.27805400
C	0.47710500	3.29659800	-0.26239400
H	0.04591200	4.09213700	0.34849000
H	1.54074000	3.20658000	-0.05207000
H	0.33529600	3.53158900	-1.31522100
C	5.21601200	-1.93430300	-0.88837700
H	5.31026100	-1.81559400	-1.96869500
H	6.14100500	-1.58373200	-0.42375700
H	5.12288200	-3.00065600	-0.66765400
C	-1.43748700	1.81552500	-0.45248500
O	-2.00815300	2.72102400	-1.05448600
C	-4.23148300	-3.24993300	0.10102900
H	-3.92157800	-3.76487800	1.01474900
H	-5.30962200	-3.09200400	0.15072100
H	-4.01333400	-3.91281900	-0.73875900

S12

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1266.205428 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.332122 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1265.873306 a.u.

0 1

C	-2.28757100	1.86199600	0.08666700
C	-3.31954900	0.93730200	0.19346700
C	-3.11721000	-0.42125700	-0.09687100
C	-1.83456400	-0.81460900	-0.49572700
C	-0.78834300	0.10292500	-0.58329900
C	-1.00649700	1.44703800	-0.28644300
H	-2.46993300	2.90846500	0.30057900
H	-4.29868700	1.28490100	0.50059100
H	-1.63080100	-1.84702500	-0.74520200
H	0.18998100	-0.23747500	-0.90074600
N	1.31046200	2.26834700	0.04475800
S	1.57968300	1.22745300	1.37162100
C	2.58127800	-0.05305100	0.63853900
C	3.05117700	-1.05279400	1.49761000
C	2.91178600	-0.08718700	-0.71329600
C	3.83768400	-2.08164700	0.99277200
H	2.80485300	-1.03330300	2.55446700
C	3.70686500	-1.12650300	-1.20148900
H	2.55491700	0.68253300	-1.38722000
C	4.17964700	-2.13825100	-0.36486600
H	4.19341300	-2.85440500	1.66603900
H	3.95914400	-1.14409200	-2.25629000
C	2.32980900	3.29115900	-0.21955500
H	2.16428900	4.17475000	0.40019000
H	3.30653200	2.86511500	-0.00030600
H	2.28534000	3.57240300	-1.26971900
C	5.02771900	-3.26531300	-0.89573300
H	5.24865200	-3.12122500	-1.95418100
H	5.97369700	-3.33231200	-0.35296800
H	4.51633800	-4.22463000	-0.78116400
C	0.04838700	2.49237800	-0.46022800
O	-0.19532200	3.53166800	-1.06662600
C	-4.28357000	-1.40199300	0.01954100
C	-3.87481800	-2.83642200	-0.32714800
H	-3.52100800	-2.91996200	-1.35821200
H	-3.09210500	-3.20635300	0.34056200
H	-4.74483600	-3.48921900	-0.21810900
C	-4.82020200	-1.38914800	1.46037600
H	-5.17867400	-0.39876300	1.74933800
H	-5.65639100	-2.08920200	1.54697900
H	-4.04332100	-1.69354900	2.16738400
C	-5.40495100	-0.97284800	-0.94131500
H	-6.23919400	-1.67697300	-0.87094300
H	-5.78202400	0.02351000	-0.70026900
H	-5.04822700	-0.96487400	-1.97504000

S14

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1338.016432 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.285951 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1337.730481 a.u.

0 1

C	-1.44189200	1.72977300	0.19886300
C	-1.94203600	2.53006200	-0.83319300
C	-2.85866400	1.97440300	-1.72234700
C	-3.28642600	0.65188800	-1.61674800
C	-2.76820800	-0.13615900	-0.58649300
C	-1.84257100	0.39663600	0.31501200
H	-1.63231900	3.55930400	-0.94417700
H	-3.99944000	0.25392900	-2.32433400
N	-0.30867000	-1.30525100	1.20014000
S	0.21227100	-1.66149500	-0.39028800
C	1.84067400	-0.93002800	-0.38866400
C	2.84274000	-1.57024100	-1.11641000
C	2.11449600	0.27085400	0.27069200
C	4.11277400	-0.99733000	-1.19692200
H	2.64283600	-2.51284400	-1.61406300
C	3.39229600	0.81571700	0.20107600
H	1.33778400	0.77295600	0.83530000
C	4.40967600	0.19727700	-0.53788200
H	4.88627500	-1.49973500	-1.76733400
H	3.60112600	1.74426600	0.72250500
C	0.18514800	-2.14046600	2.29778700
H	-0.48654200	-2.98364100	2.47207400
H	1.17504500	-2.50695300	2.03457300
H	0.25134100	-1.53790900	3.20130200
C	5.78509000	0.80887500	-0.60622600
H	6.22966000	0.88086000	0.38956700
H	6.44682600	0.21118300	-1.23441800
H	5.74114600	1.82025800	-1.01793500
C	-1.33576800	-0.43863100	1.45611600
O	-1.81660800	-0.34467700	2.58060500
H	-3.25329500	2.59045900	-2.52146900
O	-0.55041300	2.15507100	1.13003100
O	-3.08276500	-1.44033800	-0.38423600
C	0.02451700	3.45249800	0.96378700
H	0.73936400	3.56210400	1.77527000
H	0.54029600	3.52501400	0.00408700
H	-0.73872500	4.22846500	1.04132700
C	-3.98275200	-2.05824500	-1.30628600
H	-4.95615000	-1.56543800	-1.28303600
H	-3.57292200	-2.03604300	-2.31763700
H	-4.08421600	-3.08728700	-0.97215000

S15

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1148.249608 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.250117 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1147.999491 a.u.

0 1

C	-3.57974700	-0.76418600	0.10194100
C	-3.99915300	-2.06725800	0.36137100
C	-3.11051100	-3.12991100	0.20095300
C	-1.80110700	-2.88738900	-0.21627500
C	-1.37261400	-1.58405300	-0.45534500
C	-2.26197000	-0.51921600	-0.28997500
H	-4.26848800	0.06549400	0.20730600
H	-5.01788300	-2.25187200	0.68021400
H	-1.11264500	-3.71212700	-0.35516500
H	-0.35569600	-1.40263100	-0.78179700
N	-0.74996800	1.44072500	-0.09787600
S	0.02237300	0.79826700	1.28273100
C	1.56225400	0.21625500	0.59657500
C	2.53020900	-0.22056600	1.50500200
C	1.83149400	0.19163000	-0.77090500
C	3.75408600	-0.69092100	1.03789300
H	2.33737900	-0.19210800	2.57246900
C	3.06671000	-0.27523600	-1.22019200
H	1.09130800	0.53596500	-1.48342600
C	4.04426400	-0.72756200	-0.33047800
H	4.49841500	-1.02805700	1.75111800

H	3.26930200	-0.28436000	-2.28585400
C	-0.39749600	2.82257200	-0.47724600
H	0.68030400	2.91995100	-0.34613900
H	-0.62442700	2.93294200	-1.53617200
C	5.36273300	-1.25922800	-0.83067300
H	5.66459100	-0.75460500	-1.75012600
H	6.14774400	-1.12310300	-0.08488900
H	5.29185700	-2.32931200	-1.04691100
C	-1.89415100	0.89382400	-0.62946200
O	-2.60571200	1.55210600	-1.38329200
H	-3.43773400	-4.14452500	0.39423600
C	-1.14339500	3.85679600	0.35313500
H	-0.91996600	3.73466200	1.41565800
H	-0.83588000	4.86140200	0.05427300
H	-2.22031500	3.76478500	0.20505500

S16

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1187.566341 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.27579 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1187.290551 a.u.

0 1

C	-3.43393700	-1.23031600	0.22042100
C	-3.69786700	-2.59728000	0.27679900
C	-2.73500900	-3.51126100	-0.15015000
C	-1.50633000	-3.05649000	-0.63146800
C	-1.23169800	-1.69189200	-0.66875200
C	-2.19435600	-0.77685500	-0.23503500
H	-4.18159000	-0.51276300	0.53684400
H	-4.65411000	-2.94671000	0.64681500
H	-0.76205900	-3.76340600	-0.97768000
H	-0.27731600	-1.34275400	-1.04388200
N	-0.81443400	1.24865800	0.12852300
S	0.00866500	0.49302200	1.42664400
C	1.57250200	0.05895200	0.69027700
C	2.53041300	-0.50200600	1.54146600
C	1.87481500	0.26578100	-0.65299800
C	3.77573200	-0.86156300	1.03741100
H	2.31053900	-0.65683400	2.59285000
C	3.13203700	-0.09545300	-1.14009600
H	1.14112500	0.70244600	-1.31886200
C	4.09890200	-0.66733800	-0.31140500
H	4.51065200	-1.29762900	1.70566300
H	3.35819600	0.07314200	-2.18746300
C	-0.52516600	2.70081700	-0.05958100
H	0.52093600	2.79305400	0.23592400
C	5.44252300	-1.08564000	-0.85067300
H	5.65694000	-0.58409500	-1.79563700
H	6.24043300	-0.85058800	-0.14350900
H	5.46834800	-2.16433100	-1.03029400
C	-1.99091500	0.70550600	-0.34261800
O	-2.85270300	1.40541800	-0.86332800
H	-2.94279400	-4.57400100	-0.11424400
C	-1.37551900	3.56332800	0.86712300
H	-1.25534700	3.25182600	1.90780200
H	-1.05846400	4.60585200	0.78549900
H	-2.42929200	3.49581400	0.59424100
C	-0.62737600	3.13646900	-1.51944100
H	-1.66061500	3.28156100	-1.82792900
H	-0.09268700	4.08292800	-1.62881800
H	-0.16137700	2.40563500	-2.18433100

S17

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1340.024412 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.297119 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1339.727293 a.u.

0 1

C	-0.66671100	3.59225800	-0.01146900
C	0.04265900	4.69258800	-0.48808200
C	1.43661600	4.66353900	-0.51612600
C	2.12050100	3.53176300	-0.07023100
C	1.41450200	2.42146500	0.38584000
C	0.01822500	2.45043800	0.40954400
H	-1.74954400	3.61146900	0.02717300
H	-0.49124900	5.57114600	-0.82947400
H	3.20359300	3.51235100	-0.07880600
H	1.94903700	1.54501300	0.73156600
N	-0.61338400	0.05226900	0.47381200
S	0.14138000	-0.25457900	-1.02750100
C	1.67163000	-1.02221800	-0.52524900
C	2.49736500	-1.49068700	-1.55291500
C	2.05855500	-1.17779300	0.80305600
C	3.70573200	-2.10309800	-1.24146700
H	2.20179600	-1.38095500	-2.59135800
C	3.27277200	-1.80243700	1.09672800
H	1.42805200	-0.81871500	1.60794800
C	4.11460400	-2.27199000	0.08766900
H	4.34026900	-2.46096200	-2.04533300
H	3.56431500	-1.92282800	2.13443800
C	-1.39906900	-1.03984000	1.05391700
H	-0.79851600	-1.94804400	0.99129600
C	5.42921200	-2.93628400	0.40645200
H	5.52566600	-3.11645300	1.47805100
H	5.51978000	-3.89254700	-0.11372000
H	6.26824200	-2.31068200	0.09012900
C	-0.79651400	1.32576100	0.97104300
O	-1.61907500	1.53477100	1.85592600
H	1.98923100	5.52206800	-0.87869300
H	-1.54448000	-0.80726900	2.10871500
C	-2.73848100	-1.26595700	0.38073000
C	-3.33906300	-0.31390100	-0.44387500
C	-3.40341300	-2.47329200	0.61843000
C	-4.58489800	-0.56437200	-1.02144300
H	-2.84321500	0.62883100	-0.64548700
C	-4.64928900	-2.72274700	0.04787300
H	-2.93853300	-3.22173500	1.25219500
C	-5.24493900	-1.76682000	-0.77639300
H	-5.03724800	0.18350100	-1.66203600
H	-5.15135100	-3.66337000	0.24124100
H	-6.21160600	-1.95986300	-1.22609800

S20

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -1029.336635 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.161871 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -1029.174764 a.u.

0 1

C	3.15916200	-0.76500100	-1.35343300
C	3.15906700	0.76507700	-1.35347900
H	2.80065700	-1.19416100	-2.28929000
H	4.13736400	-1.19437900	-1.13432000
H	2.80040600	1.19412200	-2.28932900
H	4.13723300	1.19460300	-1.13450200
C	2.20749700	-1.16690000	-0.25118700
C	2.20744400	1.16692700	-0.25117900
O	1.90068100	-2.28799000	0.08543900
O	1.90060600	2.28799800	0.08548300
N	1.70990400	-0.00000100	0.34312300

S	0.62557200	-0.00002800	1.67842700
C	-0.93900800	-0.00001600	0.82156300
C	-1.55639200	1.21058100	0.49802700
C	-1.55637200	-1.21060900	0.49796500
C	-2.78286300	1.20354800	-0.16100200
H	-1.07704500	2.14745000	0.75501100
C	-2.78284200	-1.20356200	-0.16106300
H	-1.07700400	-2.14748000	0.75489900
C	-3.41250400	-0.00000300	-0.49782000
H	-3.25799600	2.14414200	-0.41692800
H	-3.25796200	-2.14414900	-0.41703700
C	-4.75185800	0.00000000	-1.18607800
H	-5.55907300	0.00000600	-0.44767200
H	-4.87166600	0.88751100	-1.80939800
H	-4.87167100	-0.88751300	-1.80939300

N6

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -761.7852733 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.111984 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -761.6732893 a.u.

0 2

S	0.25507400	-0.35819700	0.08961000
O	0.35131800	-0.18972000	1.54681900
O	0.49851200	-1.69716600	-0.47045700
N	1.35594200	0.67813300	-0.67205400
C	2.69285500	0.52820600	-0.14648800
H	2.95432300	-0.51236800	0.06924900
H	2.75978900	1.09328500	0.79262000
H	3.39178700	0.95769900	-0.86067900
C	-1.31219400	0.28232800	-0.50600500
H	-1.18933700	0.28881700	-1.59136900
C	-2.41393400	-0.68802600	-0.09041300
H	-2.49770300	-0.73954000	0.99726800
H	-3.35868500	-0.31306300	-0.48757300
H	-2.24538100	-1.68898400	-0.48800200
C	-1.53008600	1.69030100	0.03385600
H	-0.70670400	2.35992600	-0.22010900
H	-2.44316700	2.08599100	-0.41475500
H	-1.65618200	1.67069000	1.11738400

N8

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -439.6814539 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.106526 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -439.5749279 a.u.

0 2

N	-1.01828600	-0.87294000	-0.14507800
C	-2.12083600	-0.02486200	-0.19636100
O	-2.32556100	0.70722800	-1.15335700
C	0.22433200	-0.39142200	-0.05901800
C	1.30181200	-1.32684500	-0.15009400
C	0.53727400	0.99106800	0.14523800
C	2.61070500	-0.90152400	-0.05678700
H	1.05582600	-2.37088200	-0.29805500
C	1.85319000	1.39465300	0.23936500
H	-0.26338700	1.71460700	0.22726000
C	2.89531700	0.45899200	0.13667400
H	3.41967200	-1.61728600	-0.13210700
H	2.08432200	2.44088100	0.39592700
H	3.92323400	0.78955800	0.21107900
C	-3.06963400	-0.17397600	0.95817100
H	-3.43538300	-1.20238100	0.99885900
H	-2.54084800	0.02625500	1.89357800
H	-3.90389900	0.51549700	0.84274400

N11

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -478.9844197 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.133837 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -478.8505827 a.u.

0 2

C	0.54083700	1.28942900	0.06433100
C	1.91739300	1.13667900	0.13867000
C	2.50755400	-0.13289400	0.04615700
C	1.67783000	-1.24499900	-0.12178500
C	0.29459700	-1.10212300	-0.19691000
C	-0.28133400	0.16863500	-0.10755100
H	0.09143200	2.27182900	0.14014900
H	2.54962500	2.00799200	0.27153900
H	2.11894900	-2.23214800	-0.20006400
H	-0.33230800	-1.97325600	-0.33850100
N	-2.51626700	-0.79382800	-0.21370600
C	-3.79449600	-0.72760400	0.43926200
H	-4.53377500	-0.41562400	-0.31120900
H	-4.07617800	-1.73120000	0.75920700
H	-3.82646400	-0.02199100	1.27142200
C	-1.75047900	0.36394200	-0.16916000
O	-2.27874600	1.47037300	-0.23957000
C	4.00267200	-0.28063800	0.13176500
H	4.49686400	0.36593100	-0.59718900
H	4.36101400	0.01077600	1.12262600
H	4.30723200	-1.31105700	-0.05415800

N12

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -596.9398151 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.215538 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -596.7242771 a.u.

0 2

C	0.58329200	-1.33338500	0.04337300
C	-0.79729400	-1.21975100	0.09897800
C	-1.43476100	0.02936900	-0.01211400
C	-0.62755600	1.16005700	-0.17794700
C	0.76151600	1.05597400	-0.23349600
C	1.37681400	-0.19262000	-0.12686900
H	1.05726900	-2.30291400	0.13440700
H	-1.38785400	-2.11808300	0.23308300
H	-1.07180200	2.14149800	-0.27147400
H	1.36036300	1.94692200	-0.37351300
N	3.58380700	0.83534200	-0.20023800
C	4.85443000	0.80437200	0.46988600
H	5.60895800	0.49497400	-0.26643500
H	5.11266700	1.81733500	0.77923600
H	4.88928000	0.11076800	1.31201400
C	2.85176600	-0.34462300	-0.16597700
O	3.41280500	-1.43536000	-0.22587800
C	-2.95939800	0.10471400	0.04877100
C	-3.47731700	1.53813000	-0.09713500
H	-3.11227200	2.18508900	0.70493700
H	-3.18832700	1.97601200	-1.05623800
H	-4.56927600	1.52748400	-0.04891600
C	-3.55819000	-0.74208000	-1.08713300
H	-3.27462500	-1.79327700	-1.00204800
H	-4.64991700	-0.68321100	-1.04986000

H	-3.22823900	-0.37486100	-2.06279600
C	-3.44270500	-0.44973200	1.40007700
H	-4.53443900	-0.39798500	1.44565600
H	-3.14829500	-1.49241500	1.53872500
H	-3.03617000	0.13559600	2.22942900

N14

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -668.7436483 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.168988 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -668.5746603 a.u.

0 2

C	0.65557200	1.07901600	0.05573700
C	0.08101900	2.34980600	-0.01031800
C	-1.30635200	2.44440400	-0.07860800
C	-2.12852100	1.32121300	-0.08270100
C	-1.54426100	0.05204800	-0.01065900
C	-0.14686700	-0.07240200	0.06489900
H	0.68703500	3.24404300	-0.00571500
H	-3.19988300	1.44095600	-0.14768500
N	1.47852500	-1.66407000	-0.79986000
C	2.71510500	-2.24291900	-0.34888600
H	3.05435800	-2.98963800	-1.06663300
H	3.46329900	-1.44007600	-0.32731400
H	2.63092900	-2.67110900	0.65264400
C	0.51110400	-1.40655900	0.16181800
O	0.18573300	-2.27129300	0.96374400
H	-1.76215500	3.42585000	-0.13175300
O	1.98946500	0.85542700	0.14562700
O	-2.25059600	-1.09824700	-0.04431600
C	2.86346800	1.98704000	0.12540300
H	3.86909300	1.58056300	0.19252600
H	2.75002400	2.54327200	-0.80628000
H	2.66986400	2.63559500	0.98104100
C	-3.67200800	-1.00856100	-0.15972700
H	-4.09729000	-0.48368200	0.69727600
H	-3.95414100	-0.50759200	-1.08749900
H	-4.02718500	-2.03530000	-0.17376000

N15

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -478.9837656 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.133678 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -478.8500876 a.u.

0 2

C	1.72040400	1.14580700	0.08526000
C	3.02701800	0.68501100	0.20294600
C	3.29311300	-0.68401800	0.12655300
C	2.25253900	-1.59232900	-0.06670900
C	0.94240100	-1.13521900	-0.18742900
C	0.67635100	0.23600600	-0.11171700
H	1.49834100	2.20381200	0.14586200
H	3.83667100	1.38827600	0.35417300
H	2.46091600	-2.65338500	-0.12739400
H	0.13411200	-1.83805400	-0.34670300
N	-1.71409200	-0.18637000	-0.39430300
C	-2.81401500	-0.13776900	0.53795500
H	-2.46261700	-0.59366400	1.47546200
H	-3.03443000	0.91097200	0.76942900
C	-0.71286200	0.75971800	-0.21129700
O	-0.97904100	1.95609900	-0.20704900
H	4.31176900	-1.04161600	0.21726800
C	-4.03363700	-0.87079500	0.00729800
H	-3.79353500	-1.91450000	-0.20407500
H	-4.83642900	-0.84261200	0.74660200
H	-4.39169600	-0.40190100	-0.91126400

N16

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -518.3026912 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.162384 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -518.1403072 a.u.

0 2

C	1.73797100	1.20237100	0.32864500
C	3.05552100	0.80746700	0.53381700
C	3.46131000	-0.48026000	0.17664900
C	2.55005500	-1.37332300	-0.38685200
C	1.22988200	-0.98169700	-0.59492100
C	0.82341100	0.30767900	-0.23585400
H	1.40776100	2.19607800	0.60398400
H	3.76510700	1.49886500	0.97145800
H	2.86665500	-2.37053200	-0.66637500
H	0.52395400	-1.67263600	-1.04041100
N	-1.46162400	-0.18007800	-0.96025600
C	-2.47815100	-0.76771000	-0.09586900
H	-2.82477200	-1.66332600	-0.61297200
C	-0.58749400	0.75283900	-0.41734300
O	-0.95999400	1.89602000	-0.18261000
H	4.48827300	-0.78617100	0.33695600
C	-3.66104300	0.21306300	-0.00210100
H	-4.00798300	0.50475900	-0.99456700
H	-4.47676100	-0.28795600	0.52316200
H	-3.37606500	1.10735900	0.55229200
C	-1.95578300	-1.13695100	1.29133100
H	-1.63677200	-0.24537700	1.83829600
H	-2.75581200	-1.61752100	1.85832800
H	-1.11633900	-1.83202500	1.22750700

N17

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -670.7581486 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.181717 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -670.5764316 a.u.

0 2

C	3.59527800	0.87592200	0.17134100
C	4.77565800	0.14351000	0.11588800
C	4.73607800	-1.22069400	-0.18137700
C	3.51664600	-1.85261700	-0.42388000
C	2.33144100	-1.12295900	-0.37124100
C	2.37185500	0.24357900	-0.07412600
H	3.60970700	1.93295300	0.40524500
H	5.72388500	0.63156400	0.30463900
H	3.48852800	-2.90998400	-0.65650600
H	1.38414000	-1.60969900	-0.56744000
N	-0.06563200	0.36238600	-0.18833100
C	-1.05979000	0.51652600	0.84410600
H	-0.75333800	-0.09206600	1.70641700
C	1.12691700	1.05104700	0.01741600
O	1.12201400	2.26284600	0.19454600
H	5.65679600	-1.79006000	-0.22481300
H	-1.04478300	1.56074200	1.18452400
C	-2.43646000	0.11760000	0.37718100
C	-2.96551900	0.67076900	-0.79318900
C	-3.20364400	-0.78689300	1.11200000

C	-4.24349500	0.32120500	-1.22272700
H	-2.37352300	1.37572900	-1.36748500
C	-4.48599600	-1.13598000	0.68537100
H	-2.79655000	-1.22205200	2.01824300
C	-5.00774800	-0.58349200	-0.48286000
H	-4.64467400	0.75488100	-2.13106500
H	-5.07203100	-1.84109400	1.26286300
H	-6.00216500	-0.85552000	-0.81607900

N20

SCF energy [M05-2X]/6-311+G**/SMD (acetonitrile): -360.0374169 a.u.
Thermal correction to Gibbs free energy at 298 K: 0.048217 a.u.
Gibbs free energy at 298 K [M05-2X]/6-311+G**/SMD (acetonitril)]: -359.9891999 a.u.

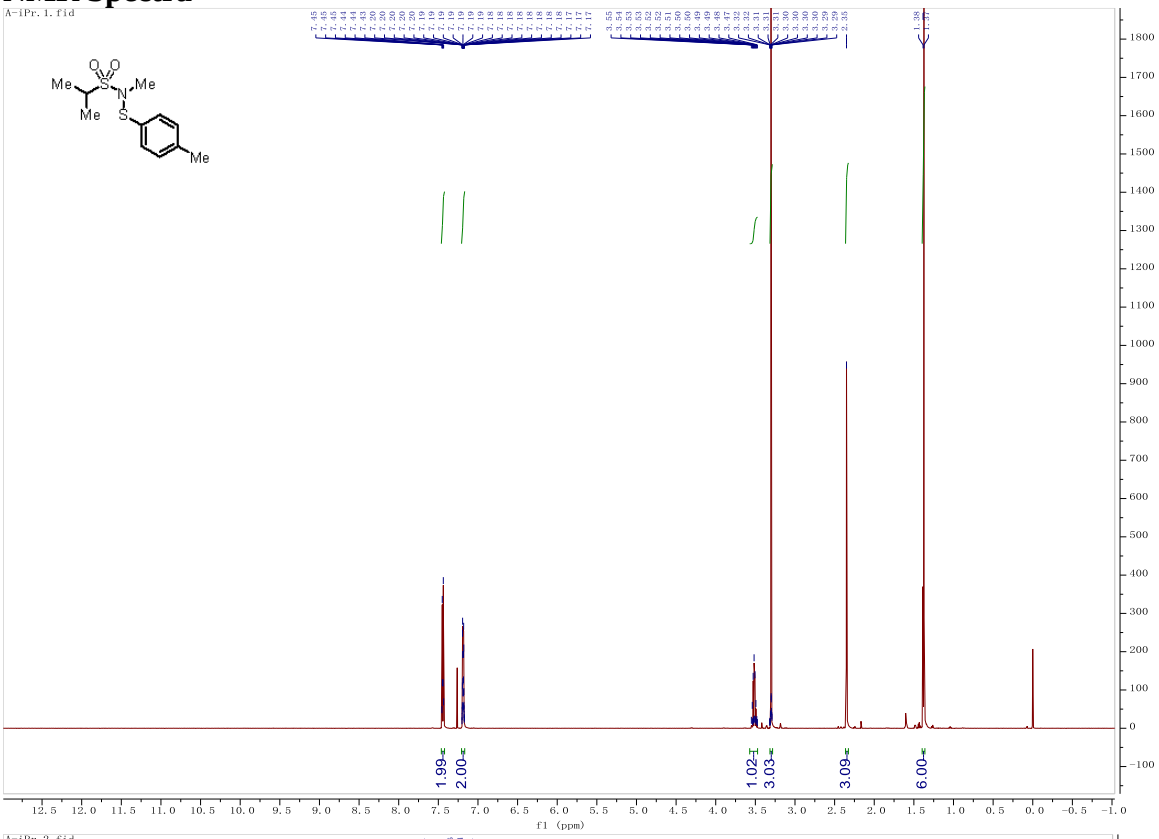
0 2

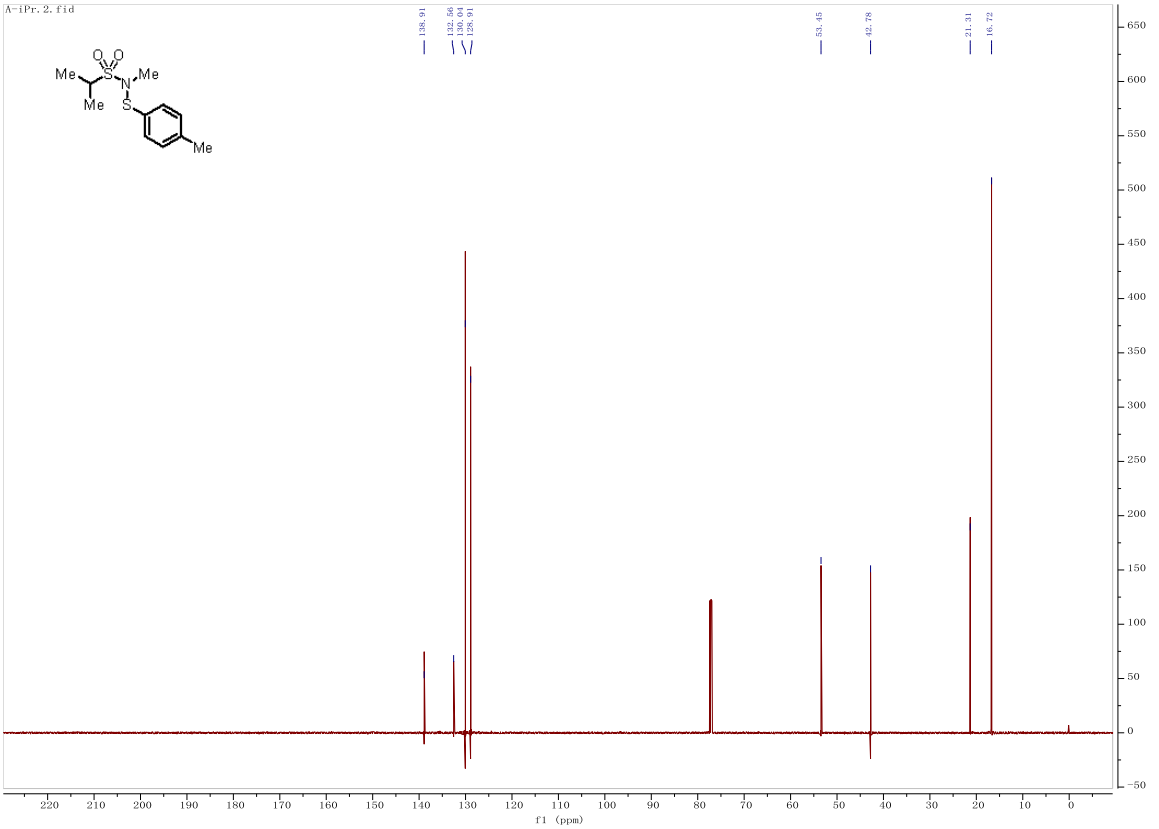
C	-0.76440700	1.23533900	-0.00003900
C	0.76442500	1.23533900	0.00006900
H	-1.19827600	1.70617000	0.88305600
H	-1.19817500	1.70608000	-0.88323300
H	1.19817200	1.70606400	0.88328600
H	1.19832700	1.70616300	-0.88301100
C	-1.13322400	-0.23129600	0.00001700
C	1.13322900	-0.23129900	0.00004000
O	-2.25282200	-0.70848600	-0.00013700
O	2.25280700	-0.70850400	-0.00019100
N	-0.00001100	-1.07672100	0.00028600

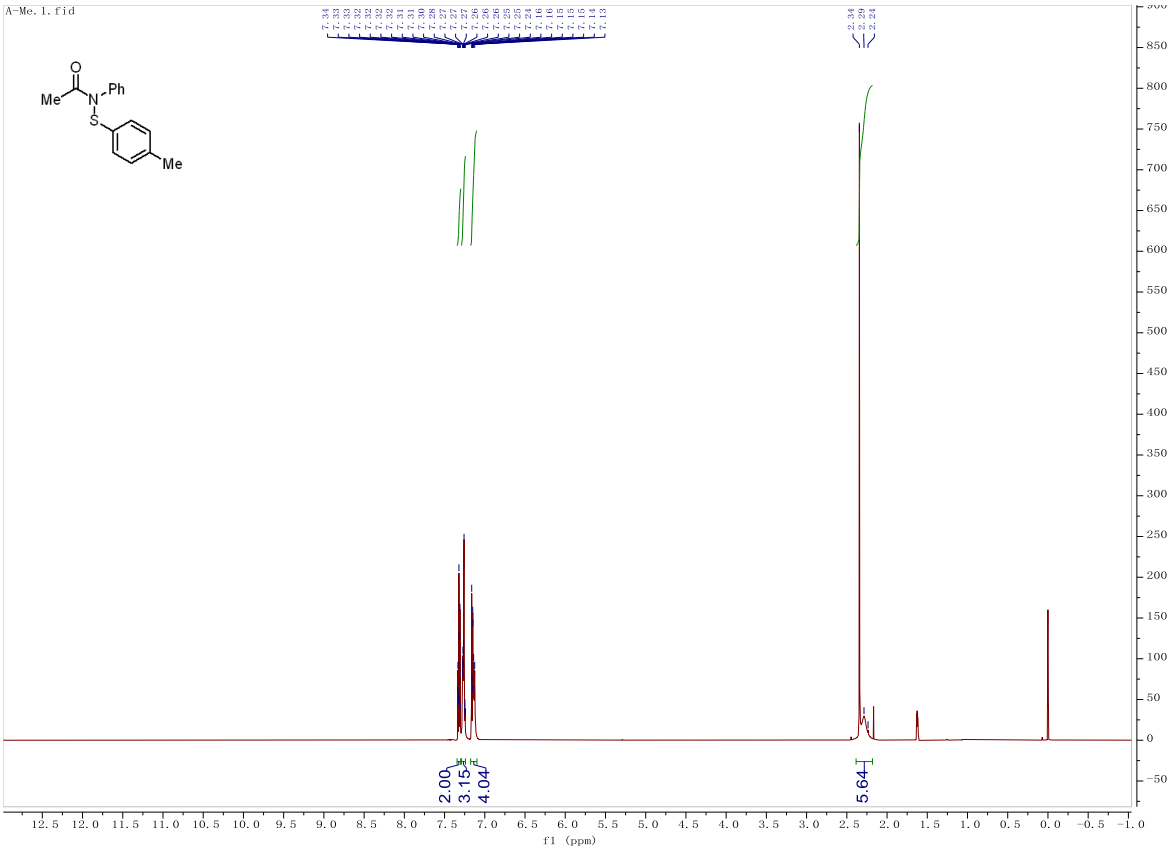
References

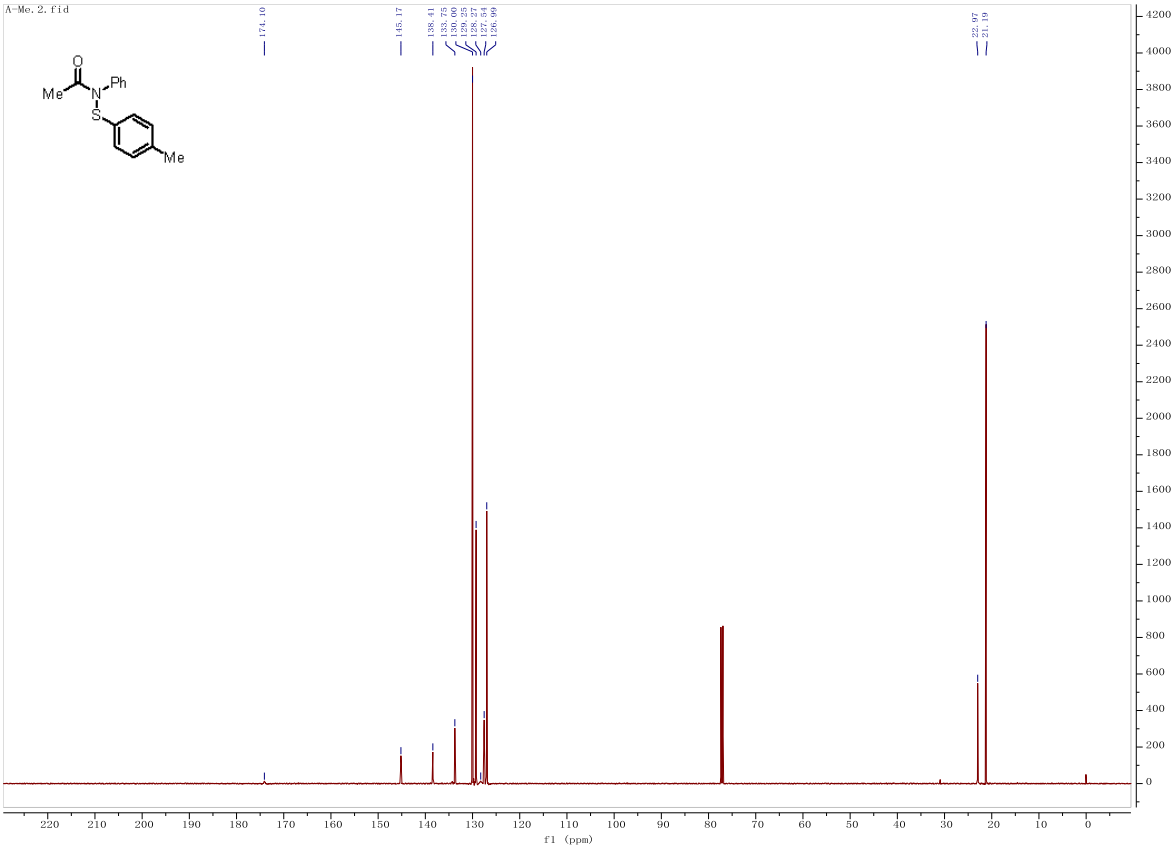
1. J. A., Gurak Jr., K. S. Yang, Z. Liu and K. M. Engle, *J. Am. Chem. Soc.* 2016, **138**, 5805–5808
2. X. Wang, Z.-Q. Li, B. K. Mai, J. A., Gurak Jr., J. E. Xu, V. T. Tran, H.-Q. Ni, Z. Liu, Z. Liu, K. S. Yang, R. Xiang, P. Liu and K. M. Engle, *Chem. Sci.* 2020, **11**, 11307–11314.
3. D. N. Harpp, B. T. Friedlander and R. A. Smith, *Synthesis* 1979, 181−182.
4. R. H. Li, Y. Zhou, K. Y. Yoon, Z. Dong and G. B. Dong, *Nat. Commun.* 2019, **10**, 8.
5. N. Kim, V. T. Tran, O. Apolinar, S. R. Wisniewski, M. D. Eastgate and K. M. Engle, *Synlett* 2021, **32**, 1570–1754.
6. V. T. Tran, N. Kim, C. Z. Rubel, X. Wu, T. Kang, T. C. Jankins, Z.-Q. Li, M. V. Joannou, S. Ayers, M. Gembicky, J. Bailey, E. J. Sturgell, B. B. Sanchez, J. S. Chen, S. Lin, M. D. Eastgate, S. R. Wisniewski and K. M. Engle, *ChemRxiv* 2022, DOI: 10.26434/chemrxiv-2022-7zjvh.
7. CCDC 2149662 **(S10)** and 2154909 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
8. Z.-Q. Li, Y. Cao, T. Kang and K. M. Engle, *ChemRxiv* **2021**, DOI: 10.26434/chemrxiv-2021-bj205.

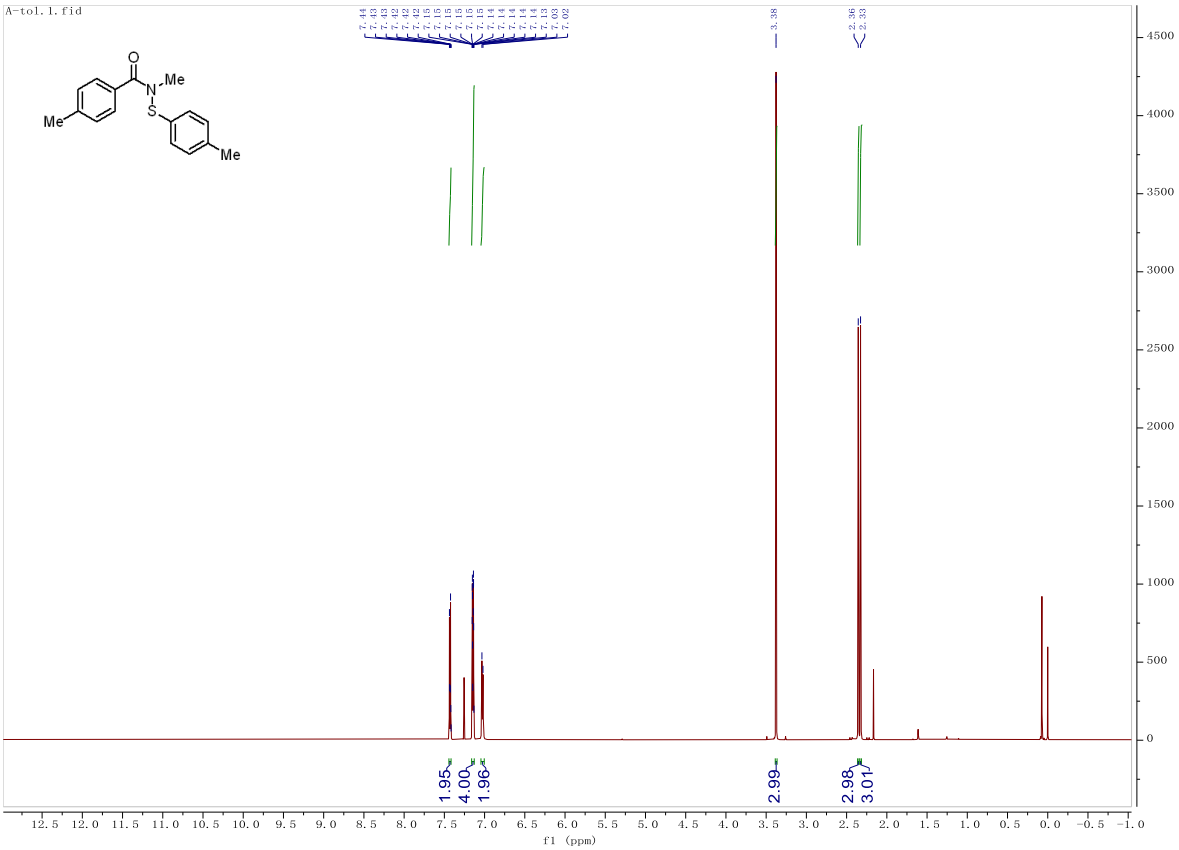
NMR Spectra

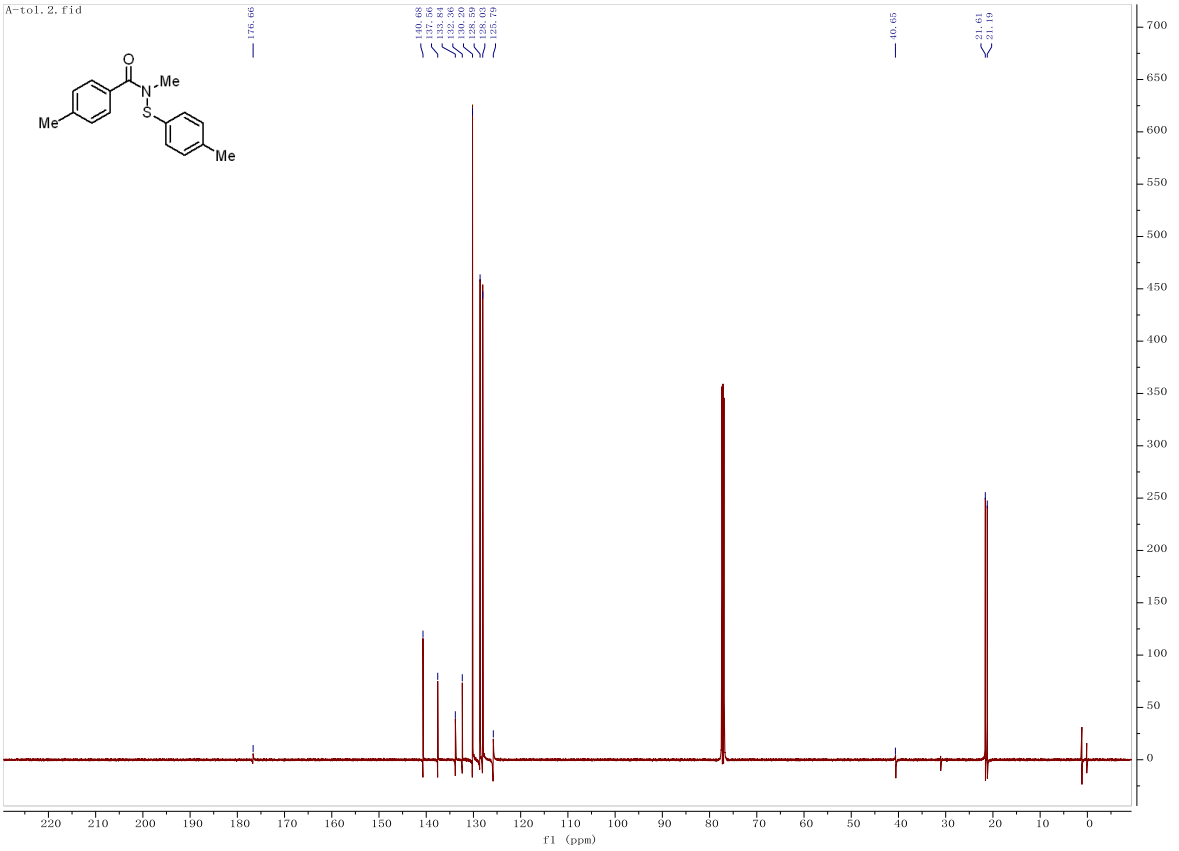

A-iPr.1.fid
Me
Me
Me
Me
1.99
2.00
1.02
3.03
3.09
6.00
f1 (ppm)

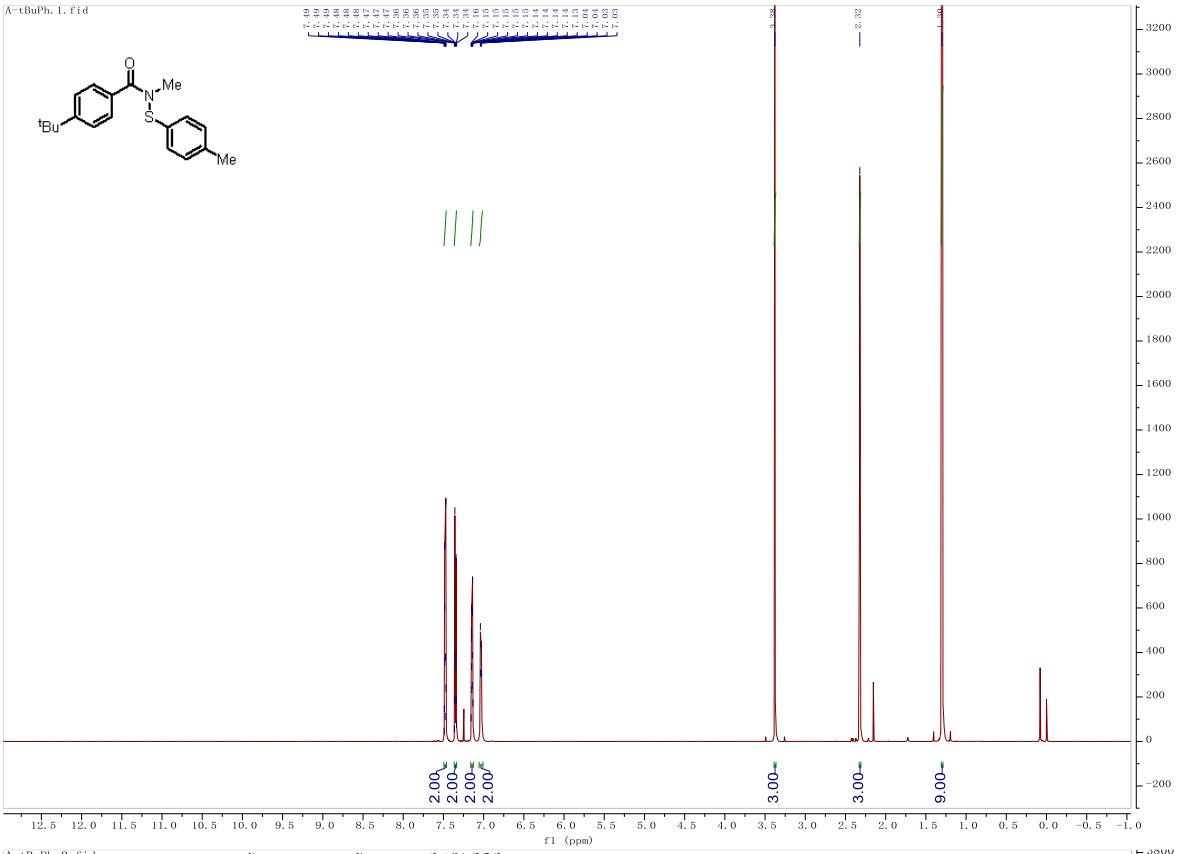

A-iPr.2.fid
Me
Me
Me
Me
138.91
132.56
130.04
128.91
53.45
42.78
21.31
16.72
f1 (ppm)

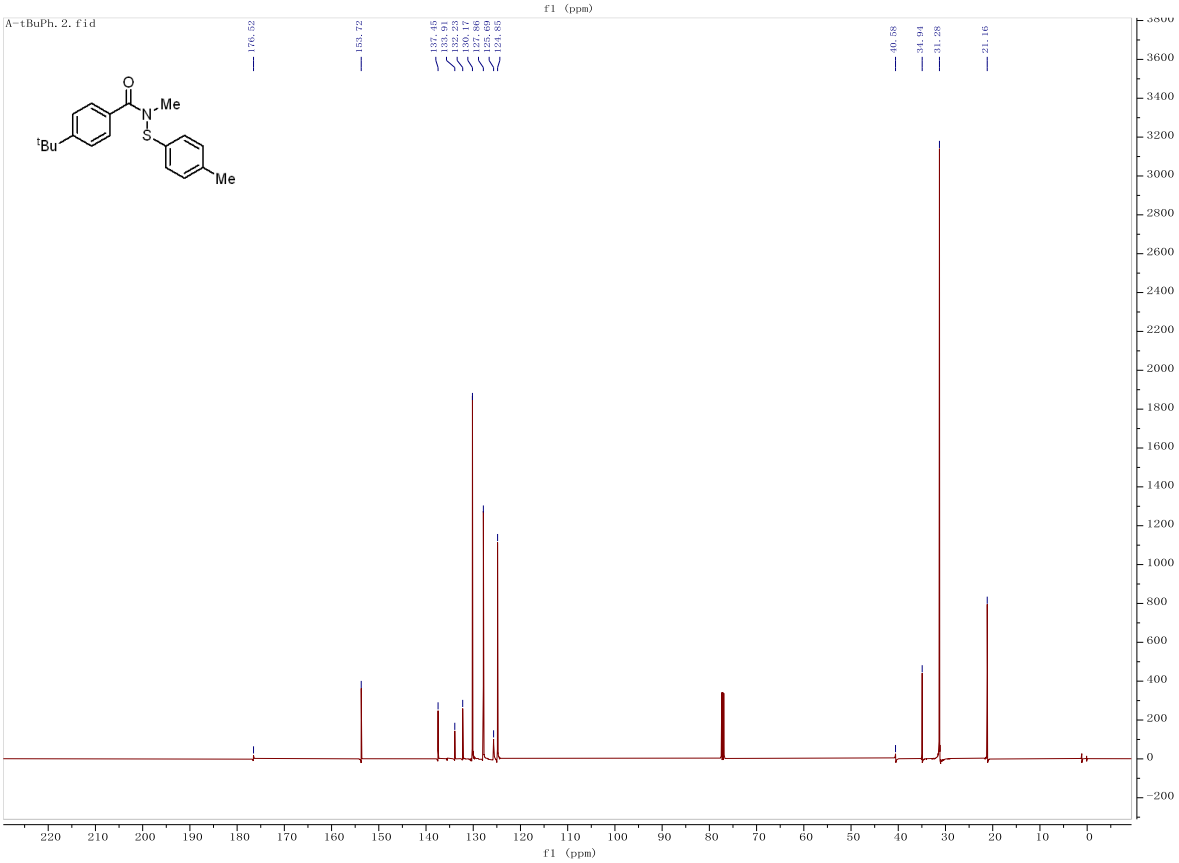

A-Me.1.fid
Me
O
N
Ph
S
Me
2.00
3.15
4.04
5.64
f1 (ppm)

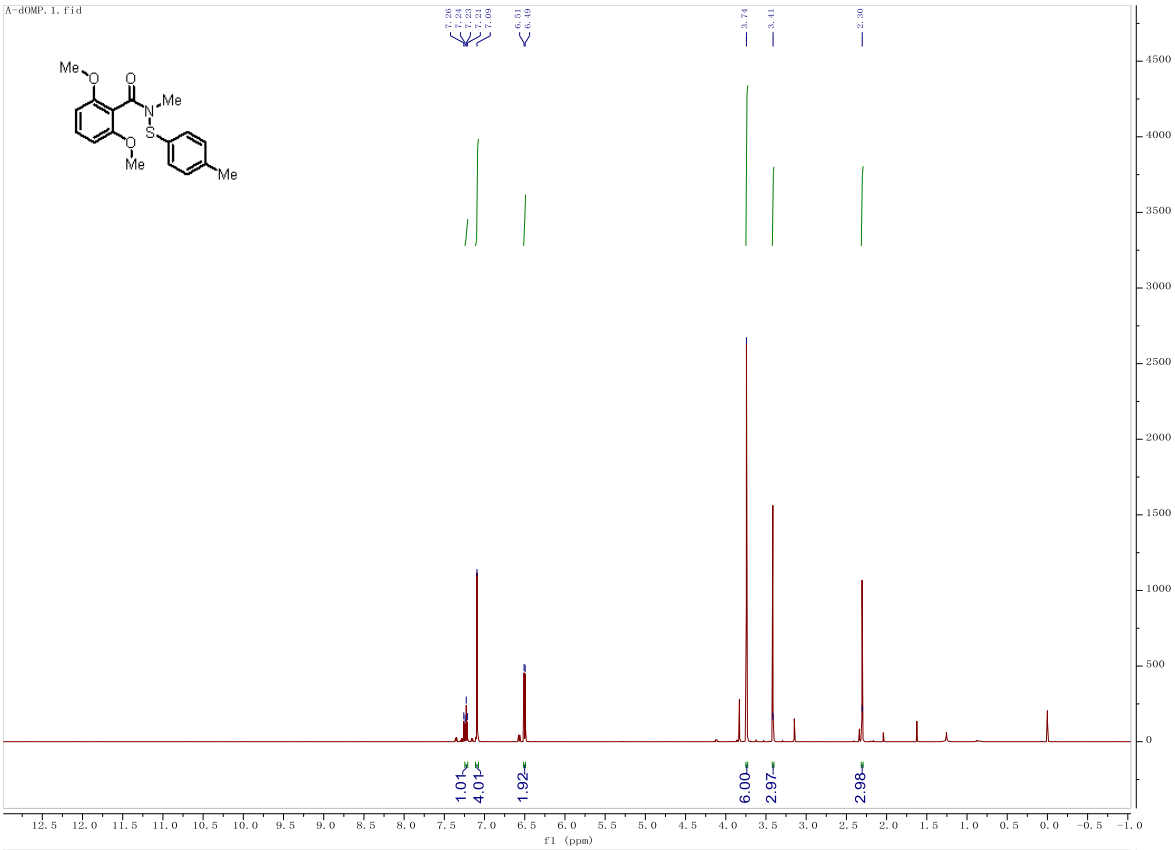

A-Me.2.fid
Me
O
N
Ph
S
Me
174.10
145.17
138.41
133.75
130.00
129.25
128.27
127.54
126.99
22.97
21.19
f1 (ppm)

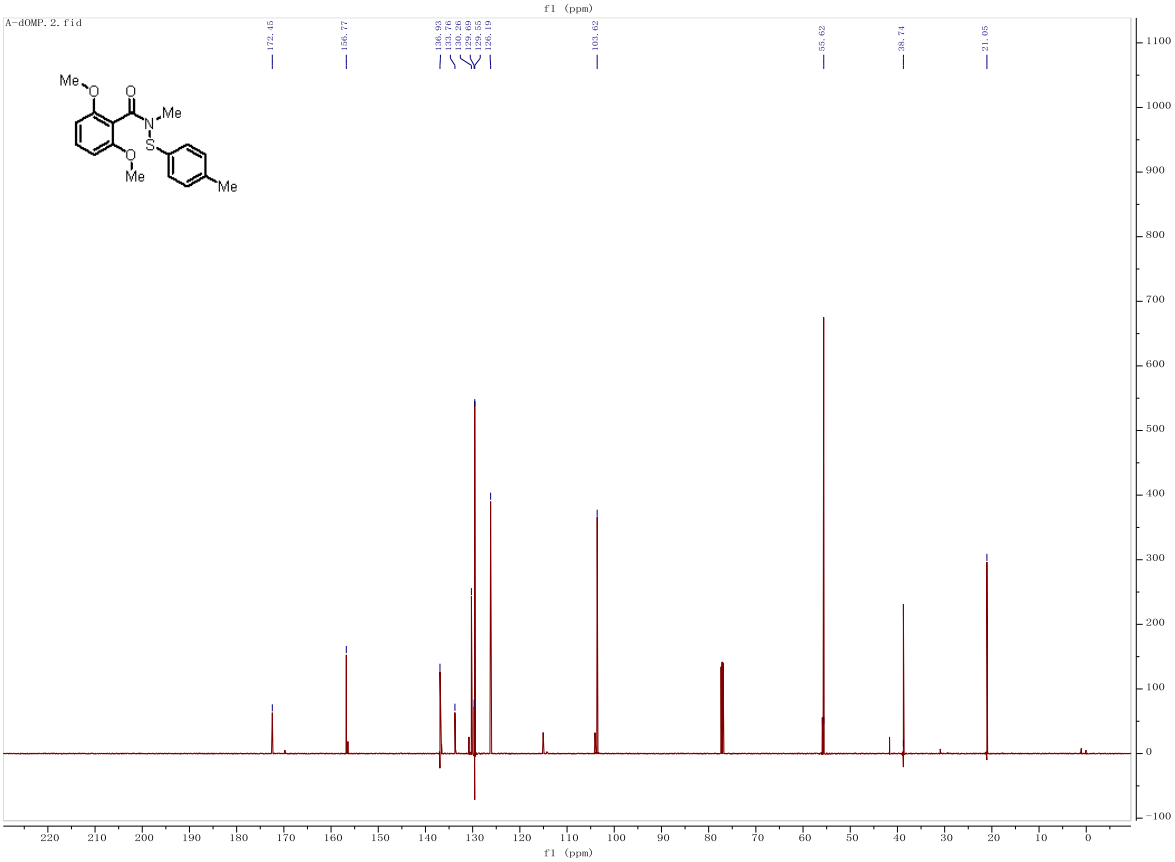

A-tol.1.fid
Me
N
Me
S
Me
1.95
4.00
1.96
2.99
2.98
3.01
f1 (ppm)

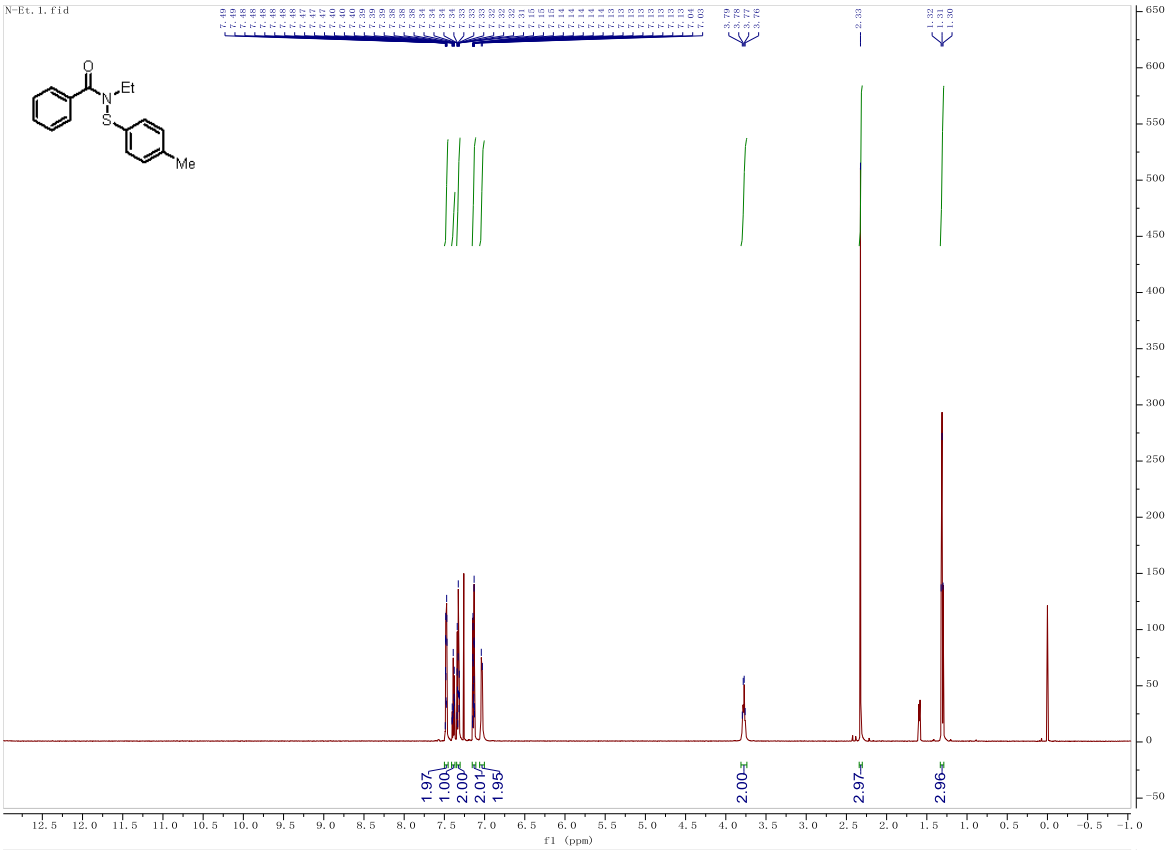

A-tol.2.fid
Me
N
Me
S
Me
f1 (ppm)

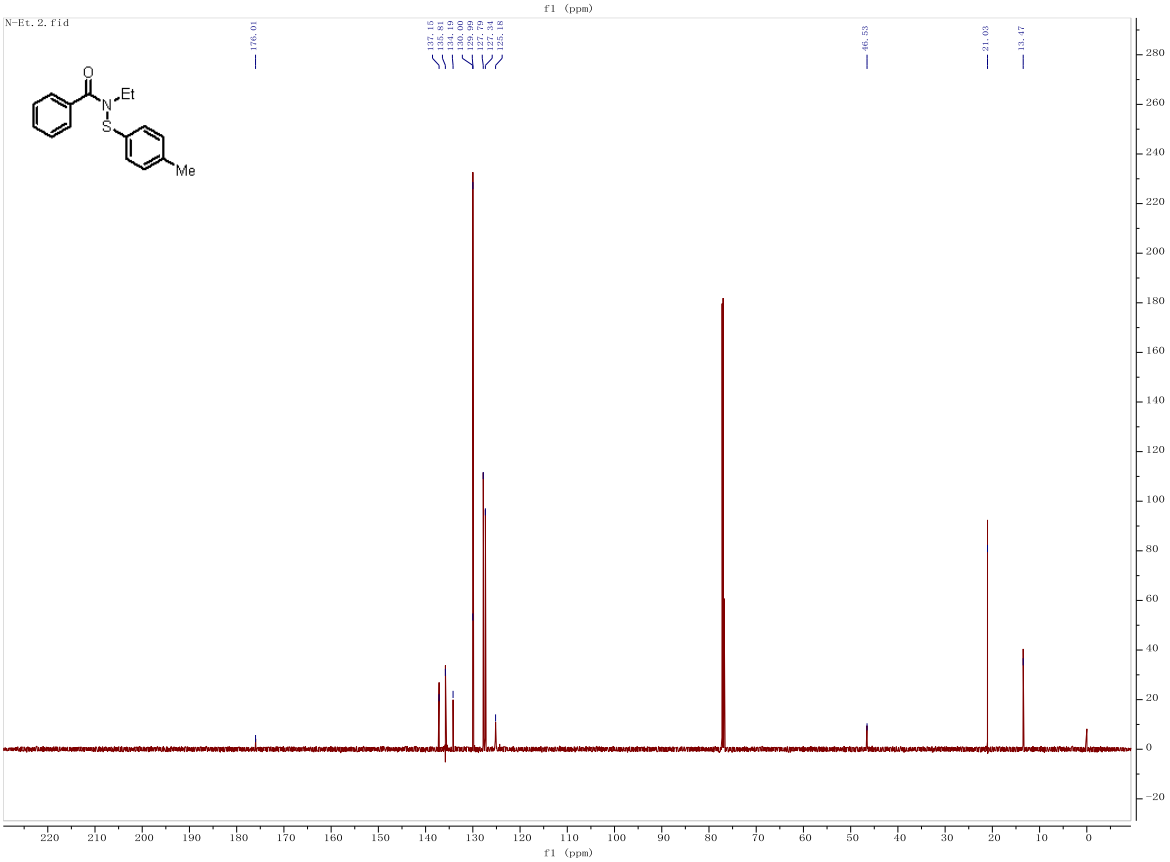

A-tBuPh. 1. fid
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.37
7.36
7.35
7.35
7.34
7.34
7.34
7.16
7.15
7.15
7.15
7.15
7.14
7.14
7.14
7.14
7.13
7.04
7.04
7.04
7.03
3.38
2.32
1.30
2.00
2.00
2.00
2.00
3.00
3.00
9.00
f1 (ppm)

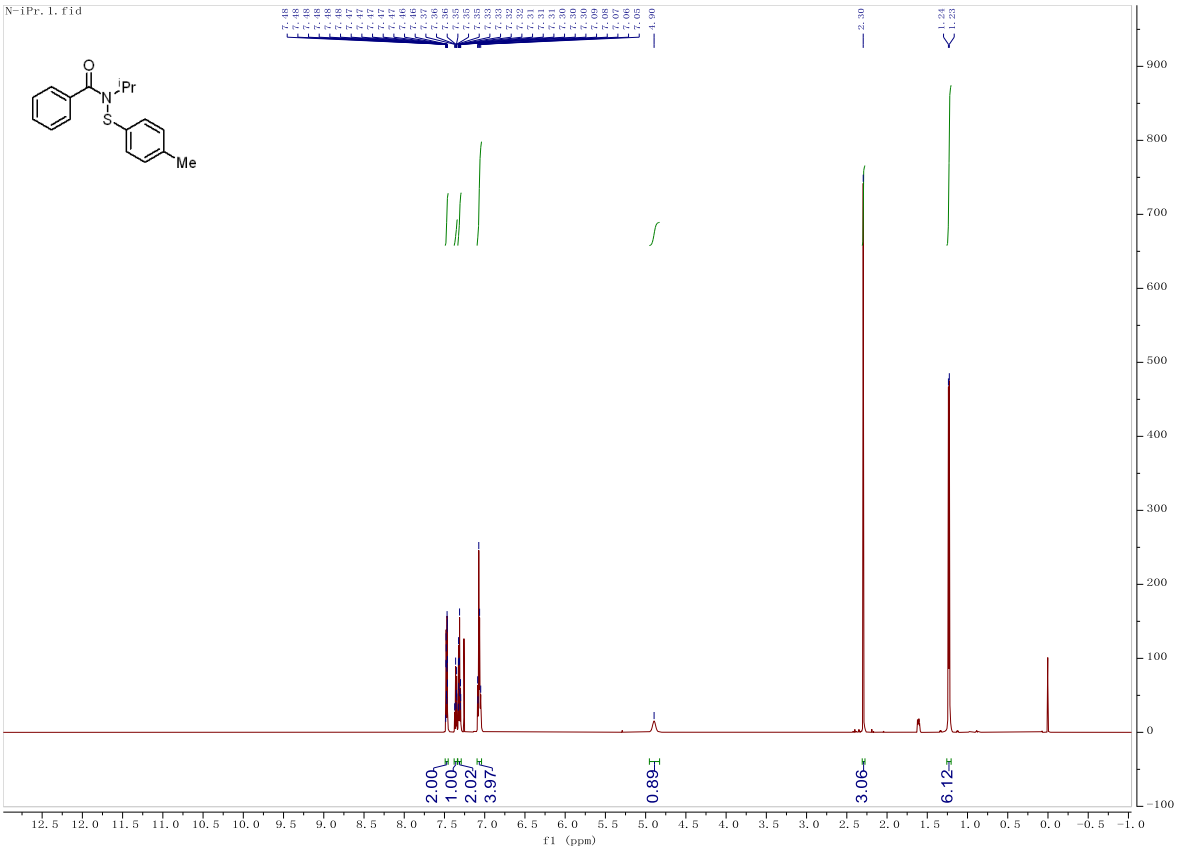

A-tBuPh. 2. fid
176.52
153.72
137.45
133.91
132.23
130.17
127.86
125.69
124.85
40.58
34.94
31.28
21.16
f1 (ppm)

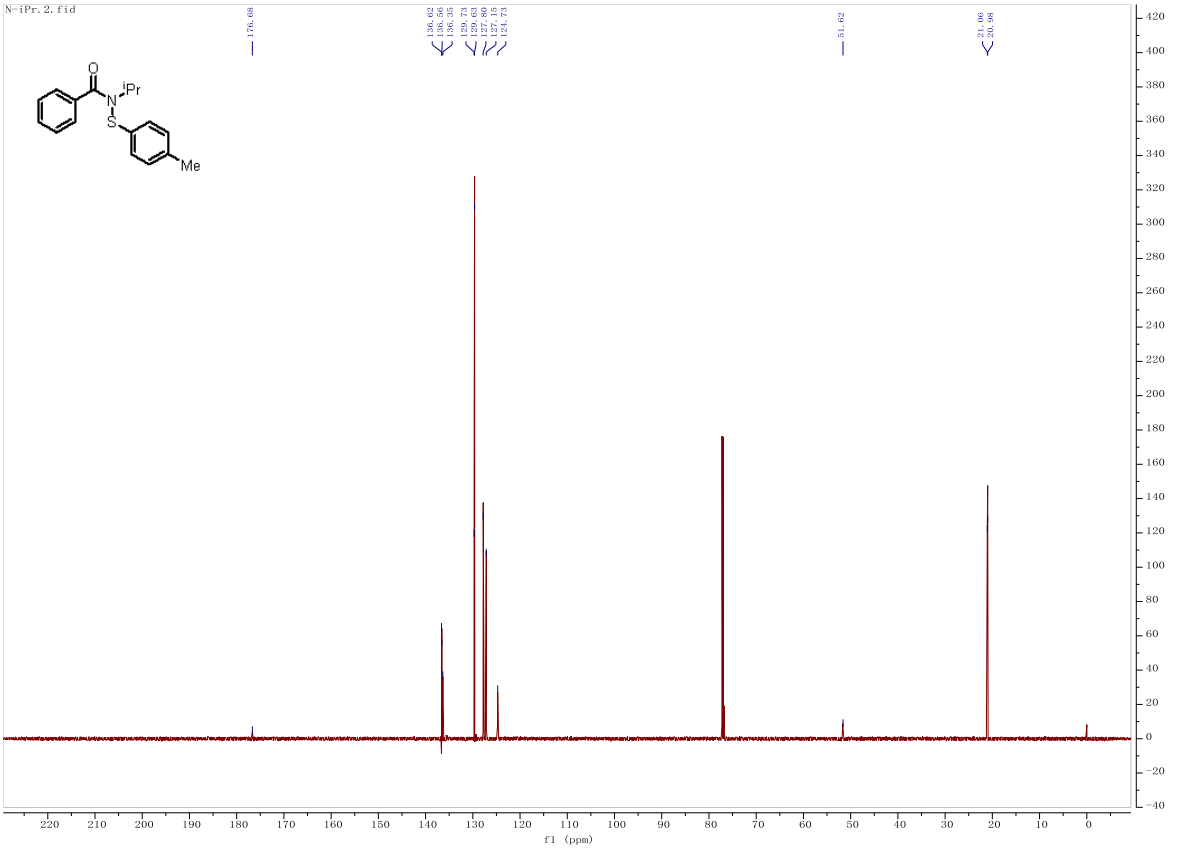

A-dOMP.1.fid
7.26
7.24
7.23
7.21
7.09
6.51
6.49
3.74
3.41
2.30
1.01
4.01
1.92
6.00
2.97
2.98
f1 (ppm)

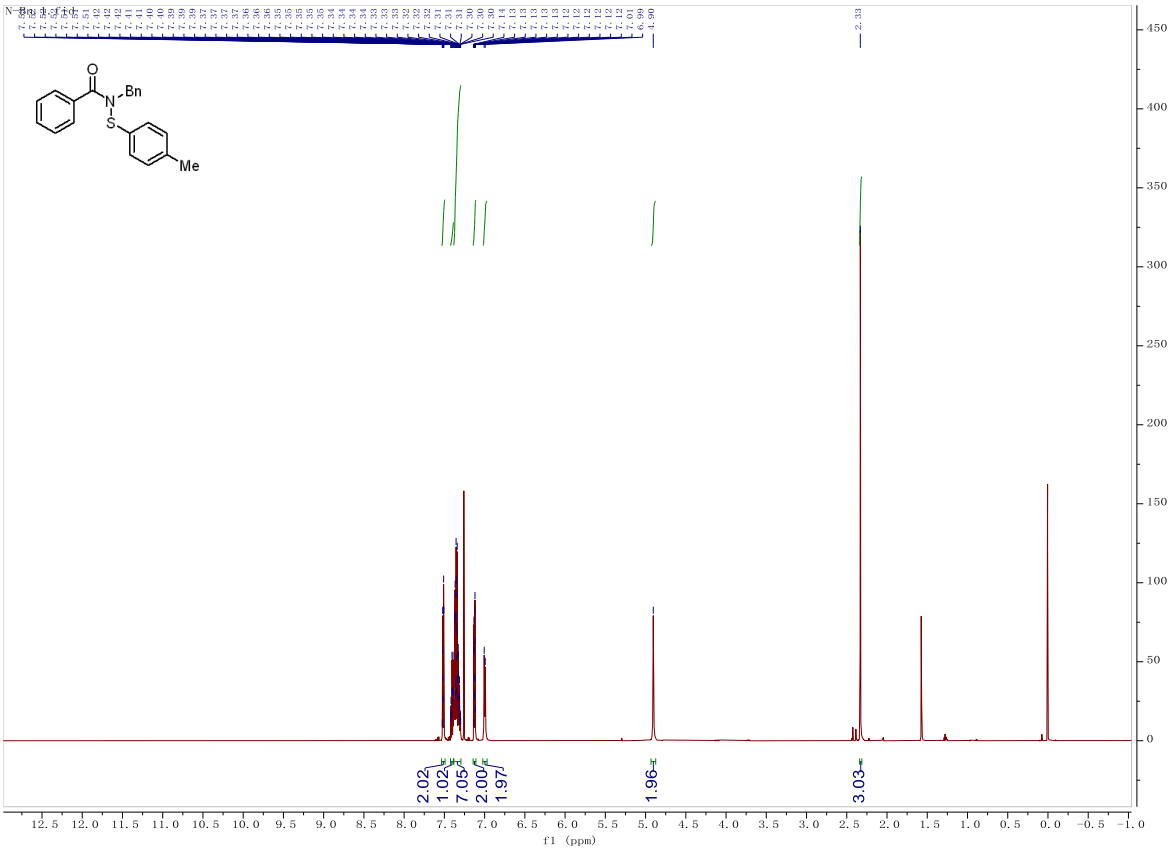

A-dOMP.2.fid
172.45
156.77
136.93
133.76
130.26
129.80
129.55
126.19
103.62
55.62
38.74
21.05
f1 (ppm)

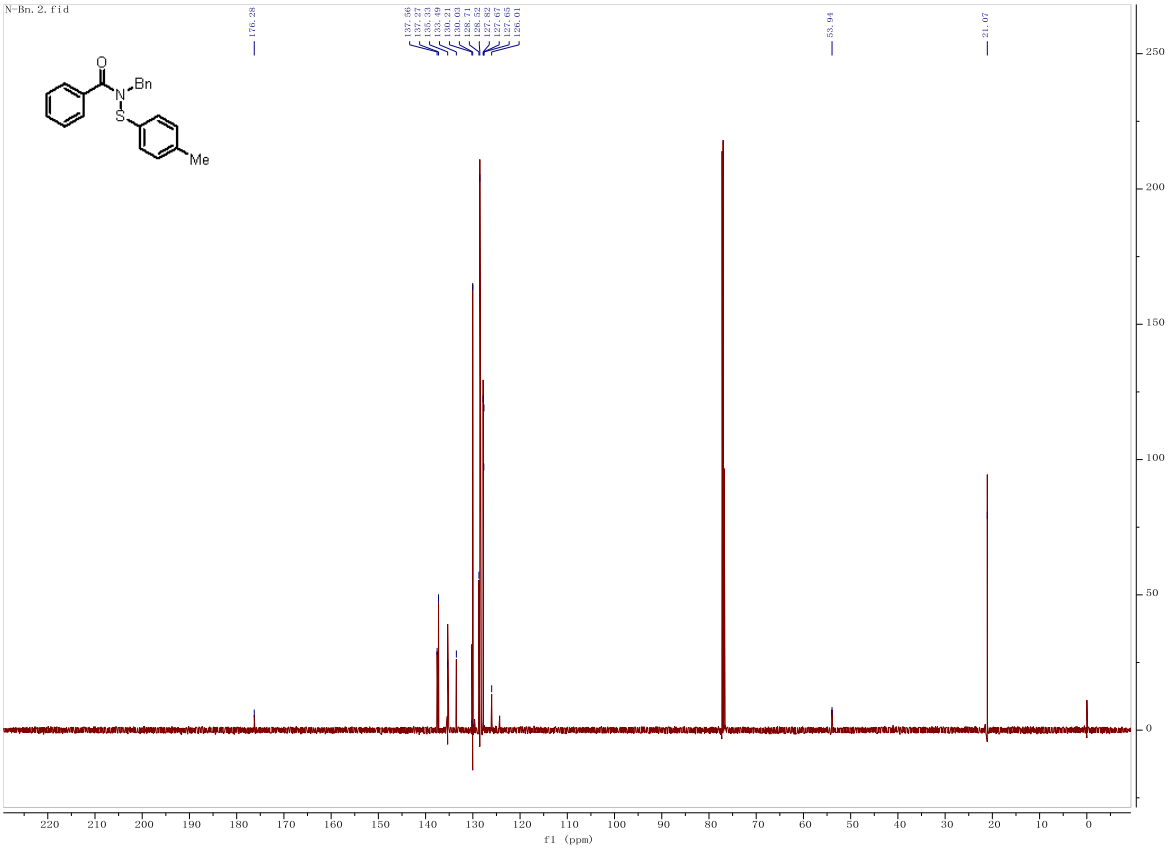

N-Et. 1. fid
Et
N
S
Me
1.97
1.00
2.00
2.01
1.95
2.00
2.97
2.96
f1 (ppm)

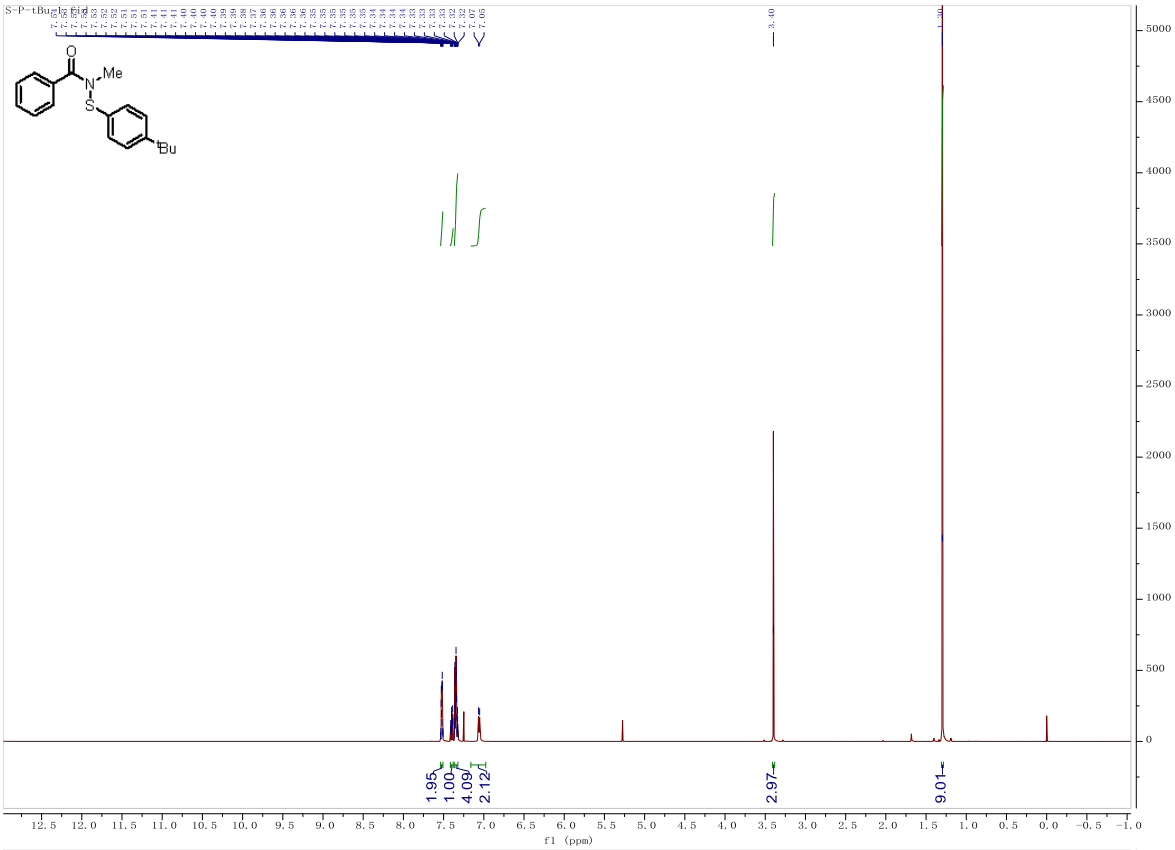

N-Et. 2. fid
Et
N
S
Me
176.01
137.15
136.84
134.19
130.60
129.99
127.79
127.34
125.18
46.53
21.03
13.47
f1 (ppm)

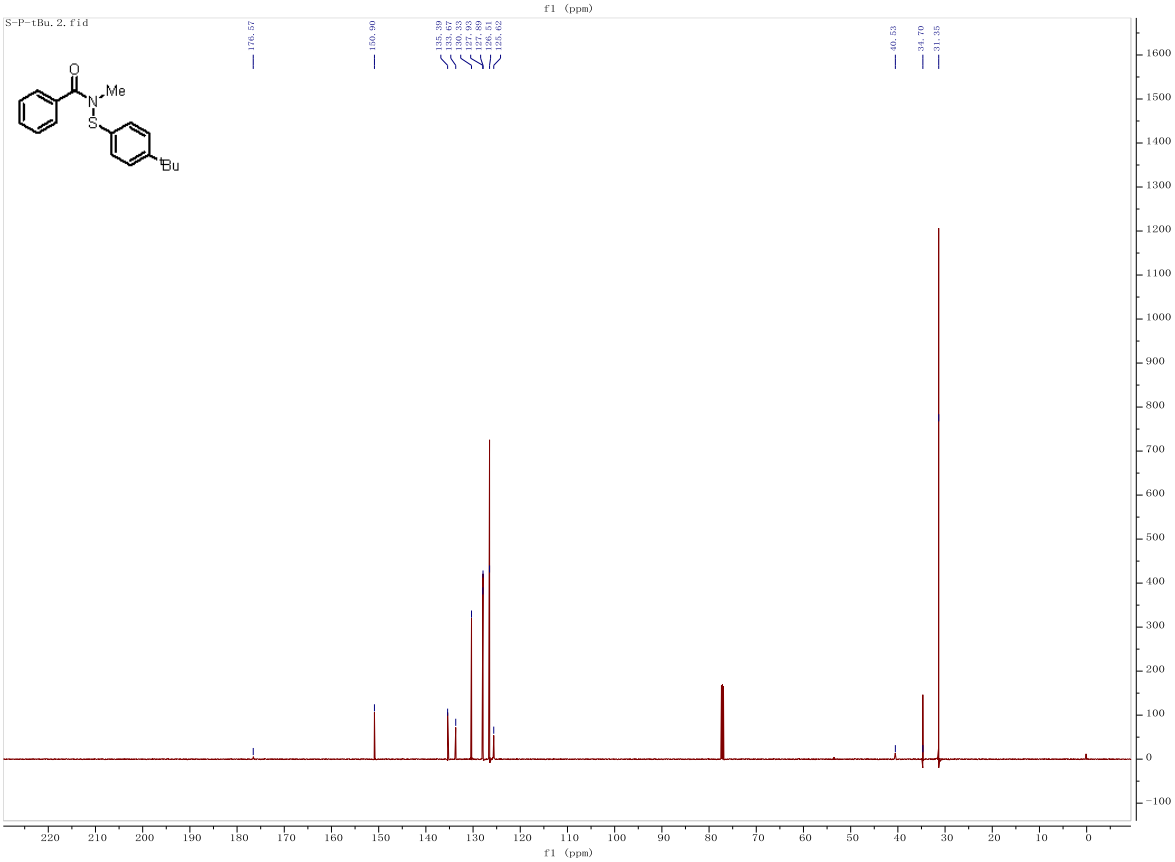

N-iPr.1.fid
iPr
N
S
Me
2.00
1.00
2.02
3.97
0.89
3.06
6.12
f1 (ppm)

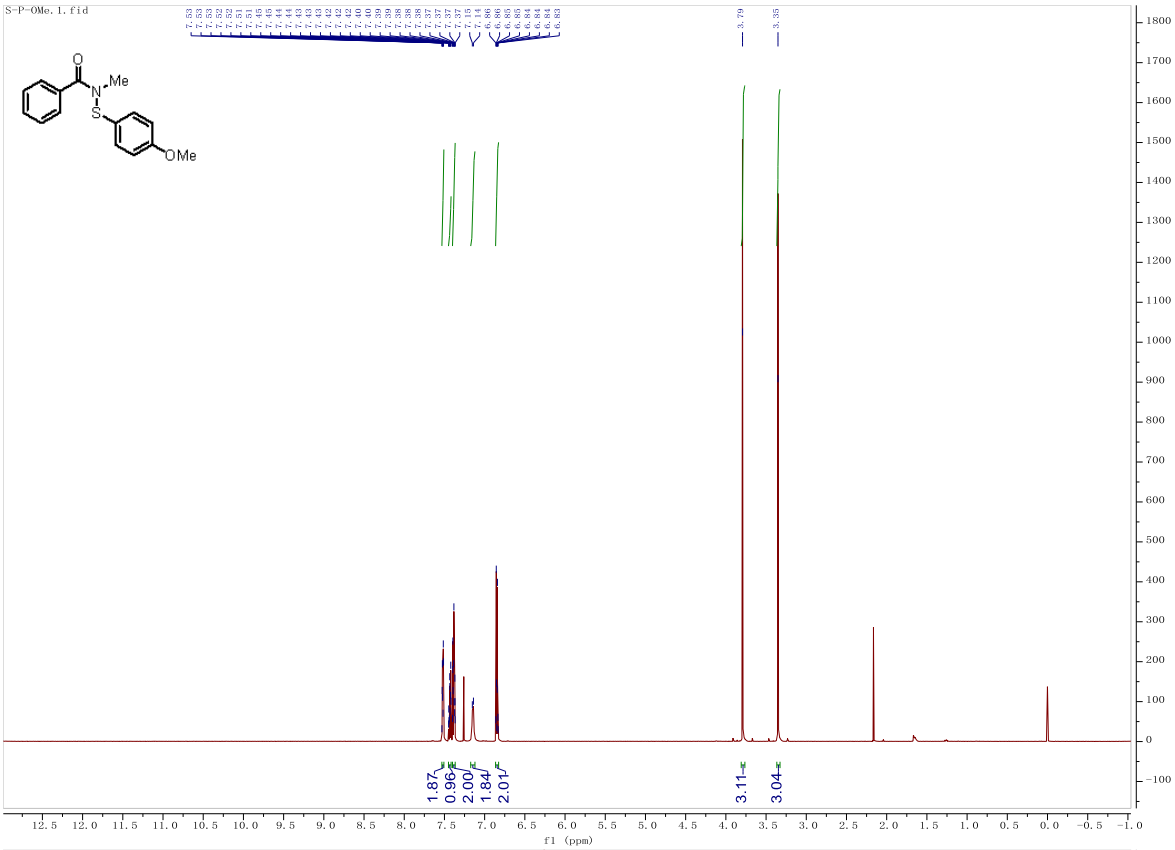

N-iPr.2.fid
iPr
N
S
Me
f1 (ppm)

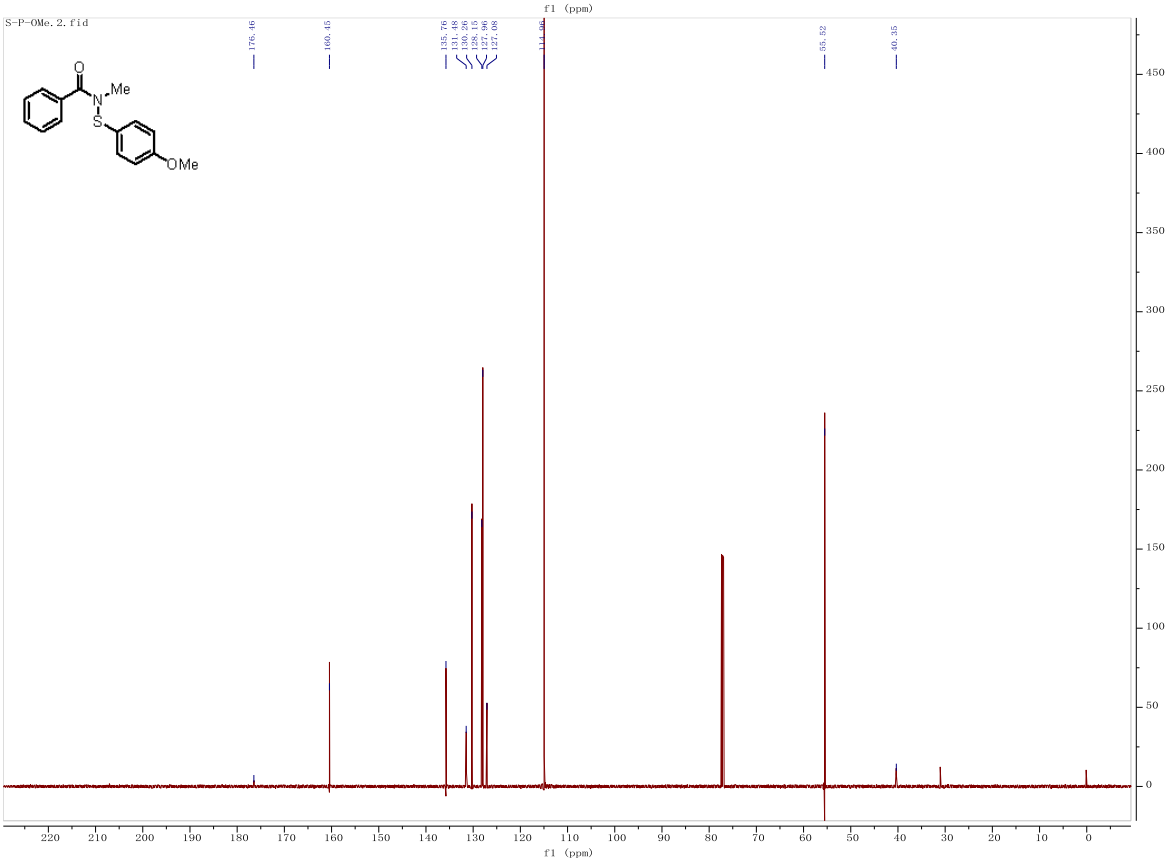

N-Bn.1.fid
Bn
N
S
Me
2.02
1.02
7.05
2.00
1.97
1.96
3.03
f1 (ppm)

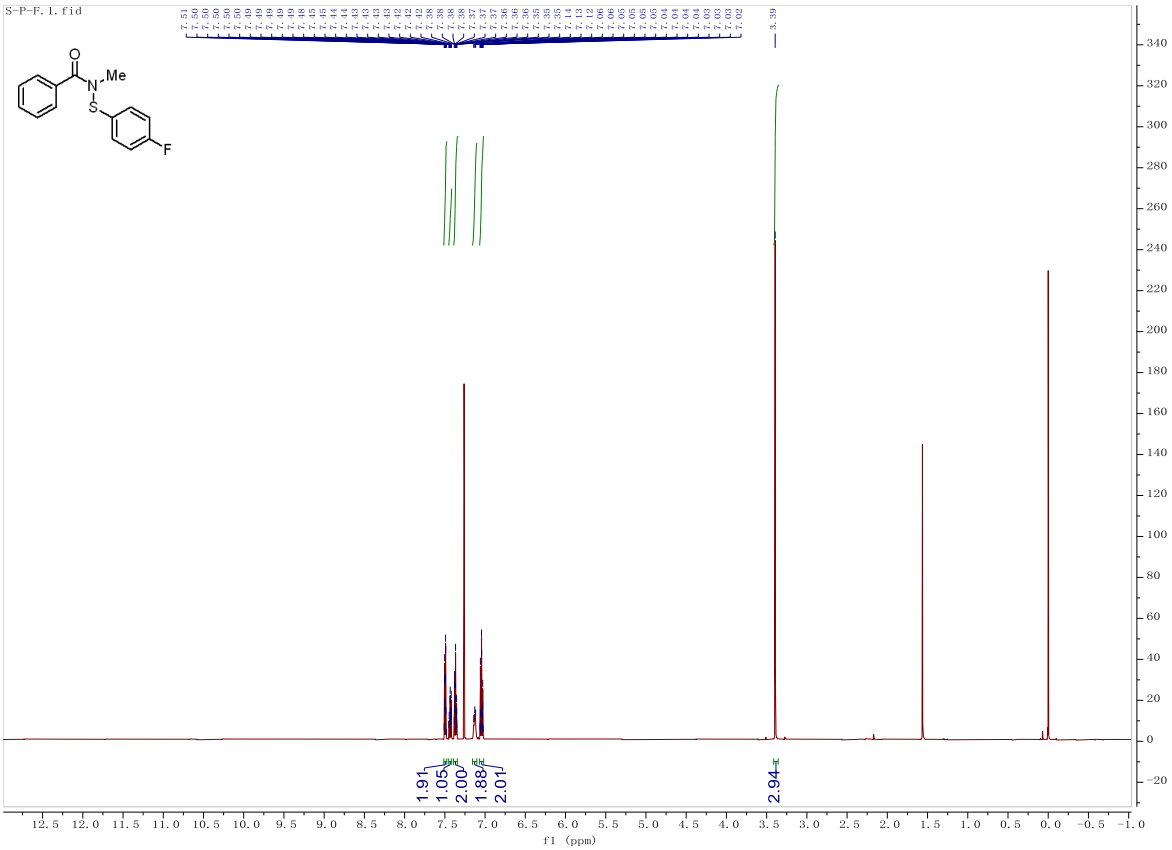

N-Bn. 2. fid
176.28
137.56
137.27
135.03
133.49
130.21
130.03
128.71
128.52
127.82
127.67
127.65
126.01
53.94
21.07
Bn
N
S
Me
f1 (ppm)

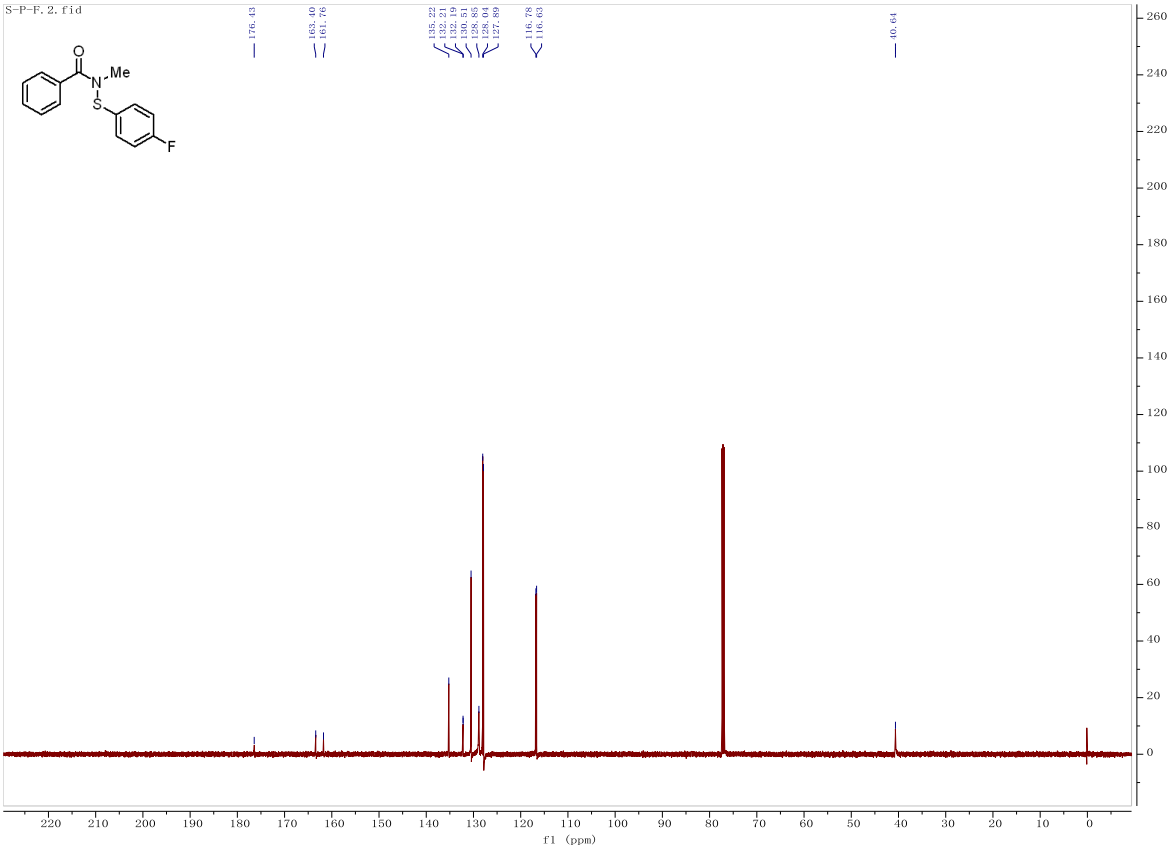

S-P-tBu.1.fid
Me
N
S
tBu
3.40
1.95
1.00
4.09
2.12
2.97
9.01
f1 (ppm)

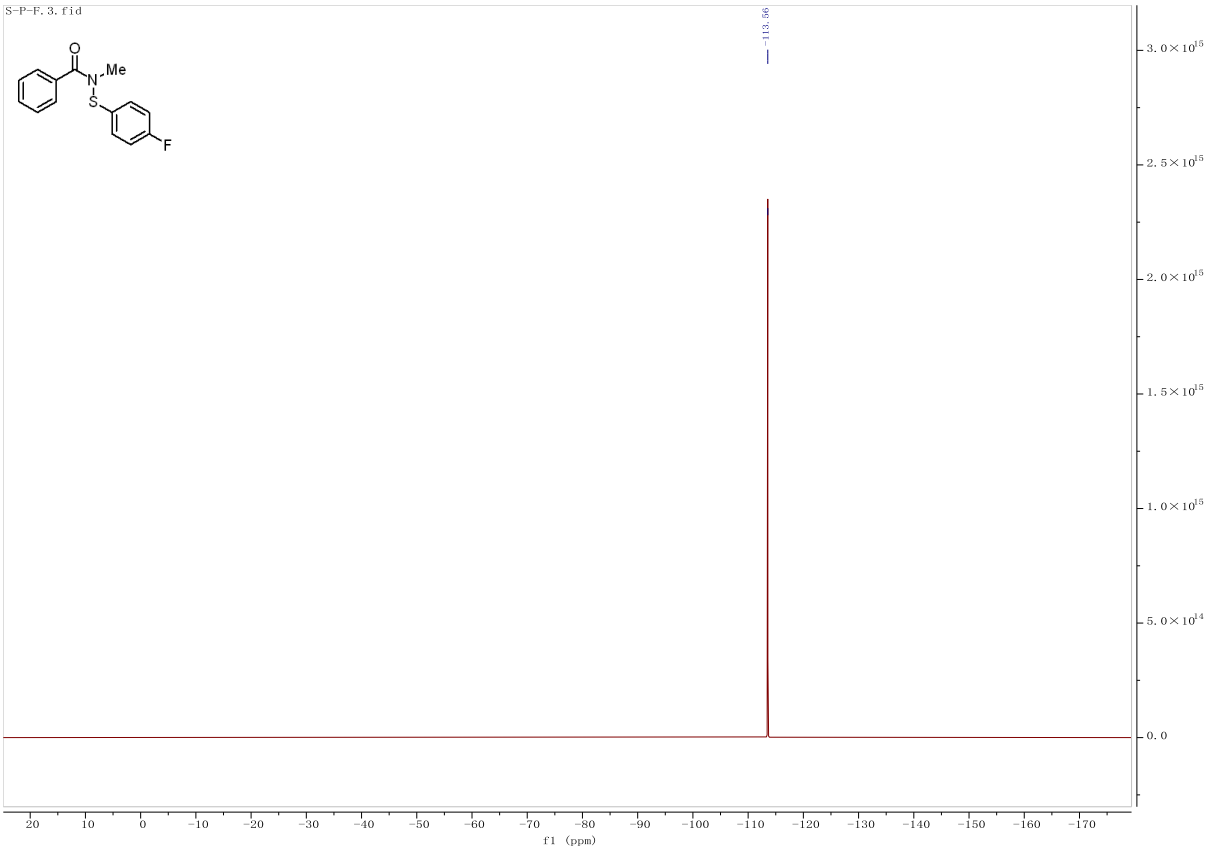

S-P-tBu.2.fid
Me
N
S
tBu
176.57
150.90
135.39
133.67
130.33
127.89
127.89
126.51
125.62
40.53
34.70
31.35
f1 (ppm)

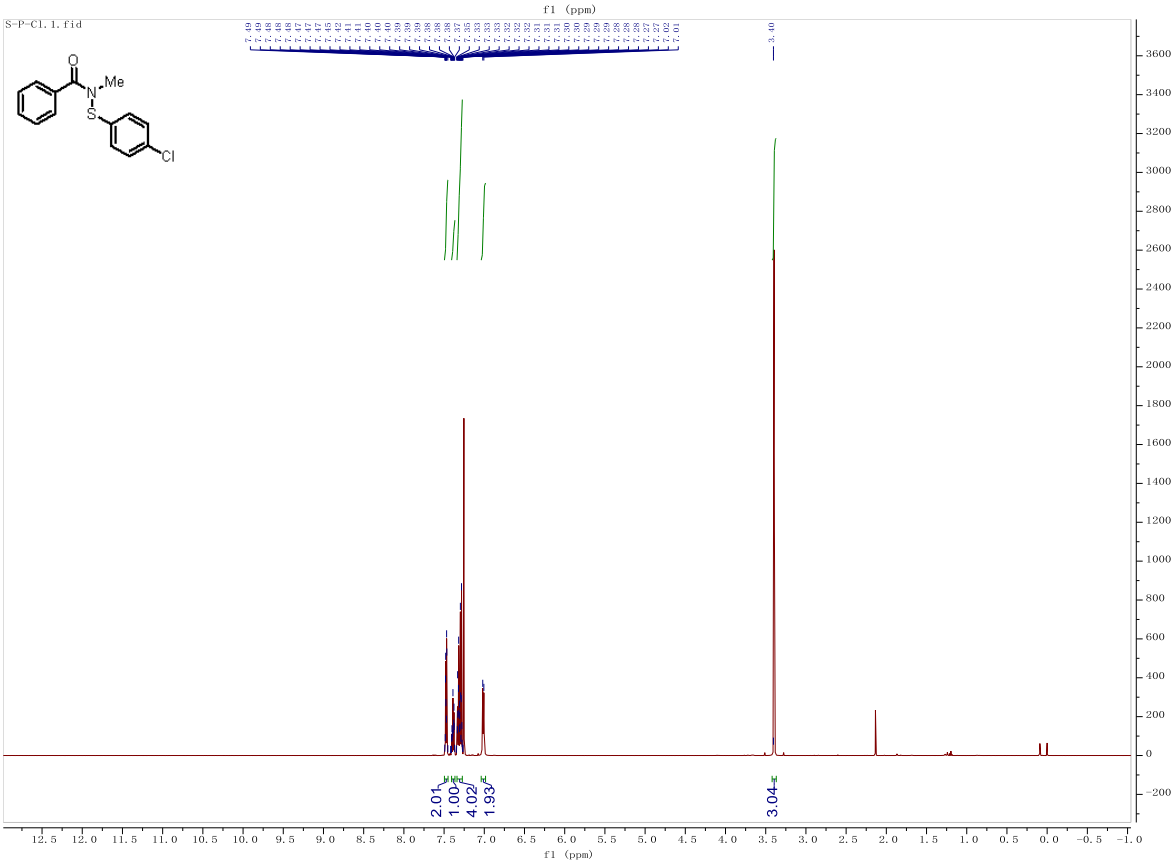

S-P-OMe.1.fid
Me
N
S
OMe
1.87
0.96
2.00
1.84
2.01
3.11
3.04
f1 (ppm)

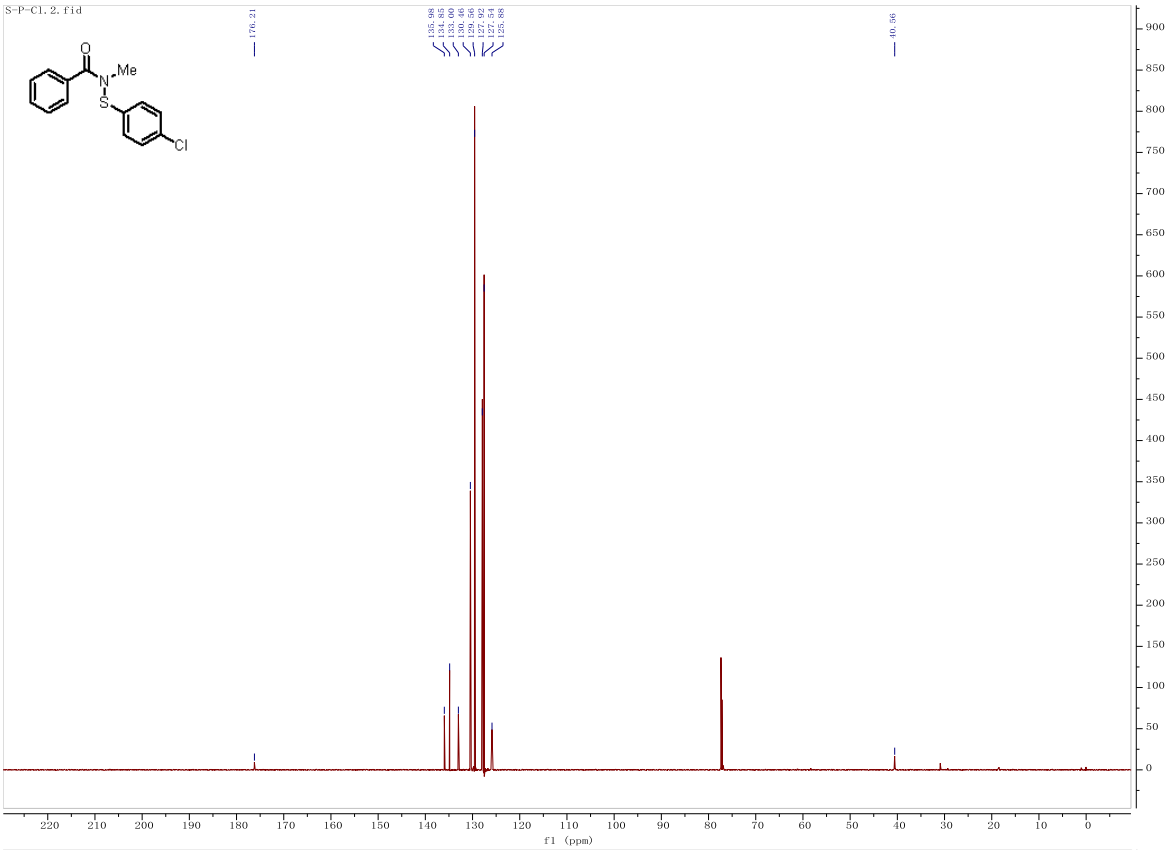

S-P-OMe.2.fid
Me
N
S
OMe
176.46
160.45
135.78
131.46
130.20
128.15
127.96
127.68
114.06
55.52
40.35
f1 (ppm)

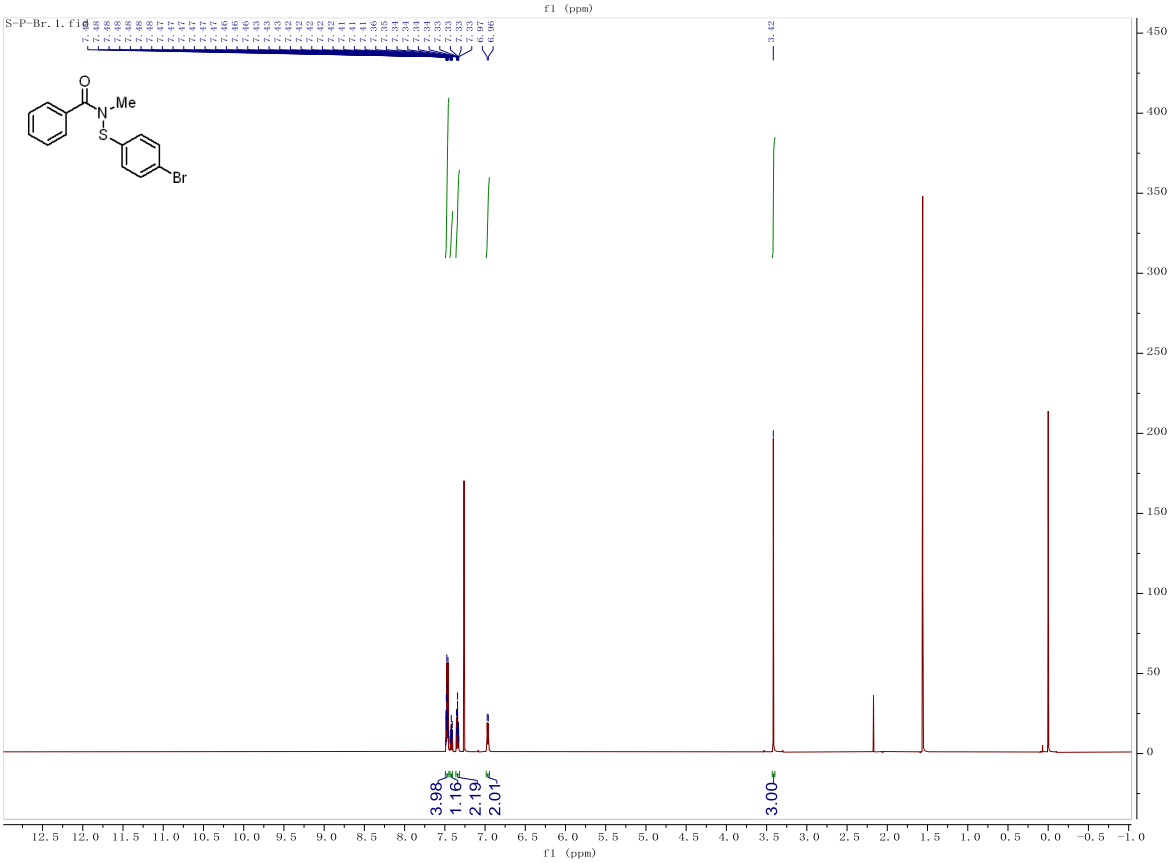

S-P-F.1.fid
Me
N
S
F
1.91
1.05
2.00
1.88
2.01
2.94
f1 (ppm)

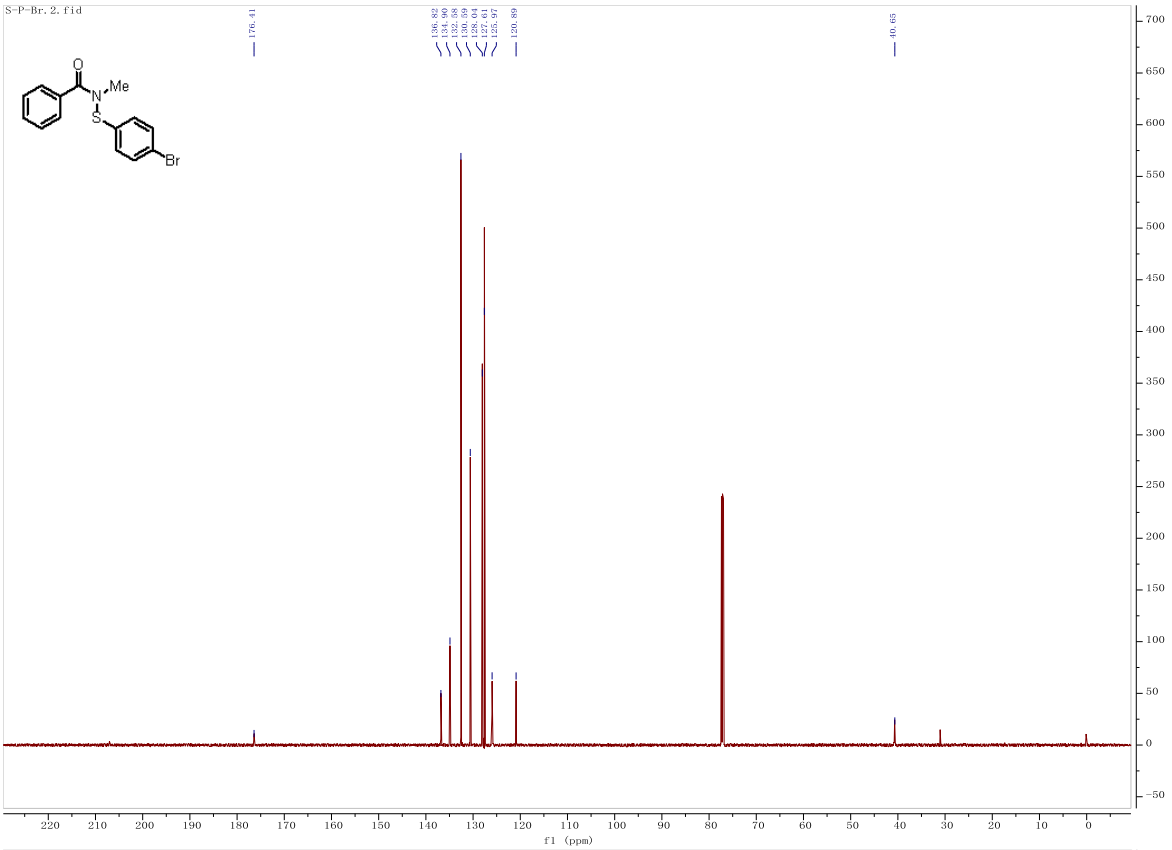

S-P-F.2.fid
Me
N
S
F
176.43
163.40
161.76
135.22
132.21
132.19
130.51
128.85
128.04
127.89
116.78
116.63
40.64
f1 (ppm)

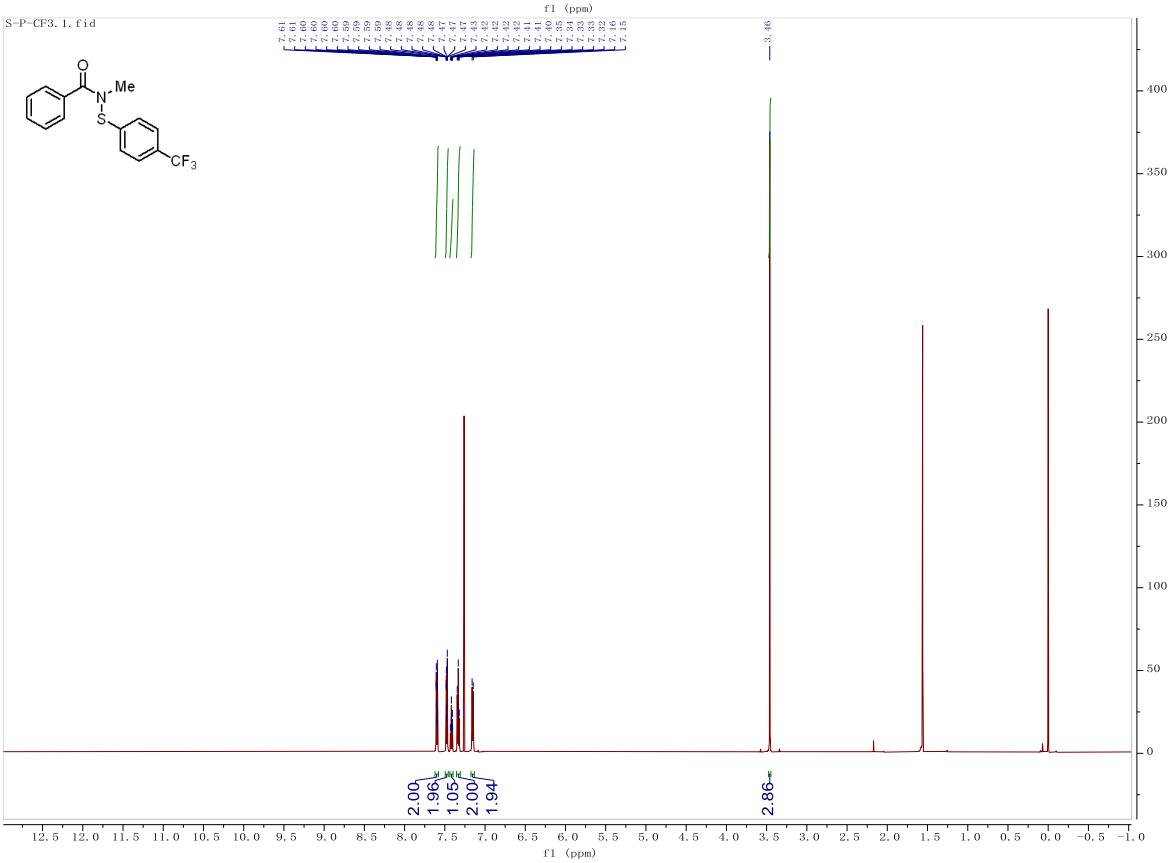

S-P-F.3.fid
Me
N
S
O
F
-113.56
f1 (ppm)

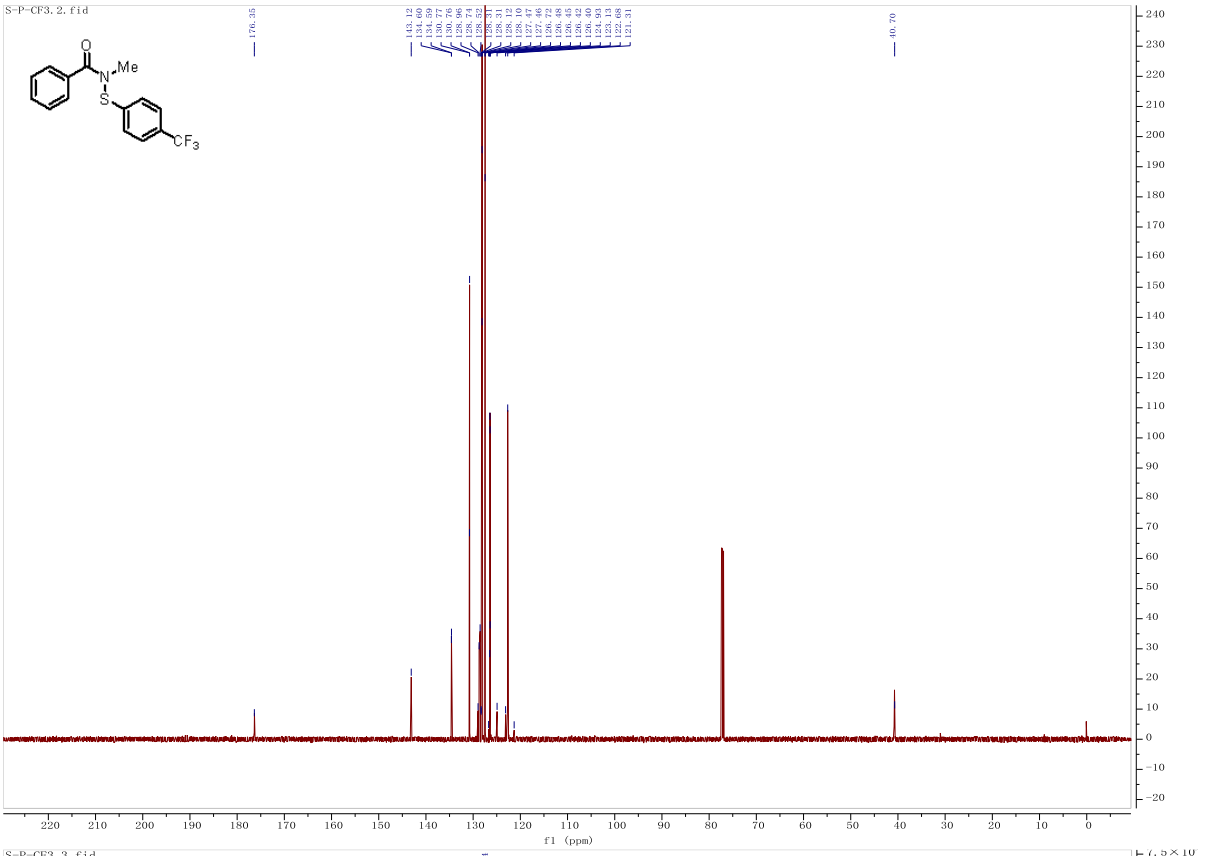

S-P-Cl.1.fid
Me
N
S
O
Cl
3.40
2.01
1.00
4.02
1.93
3.04
f1 (ppm)

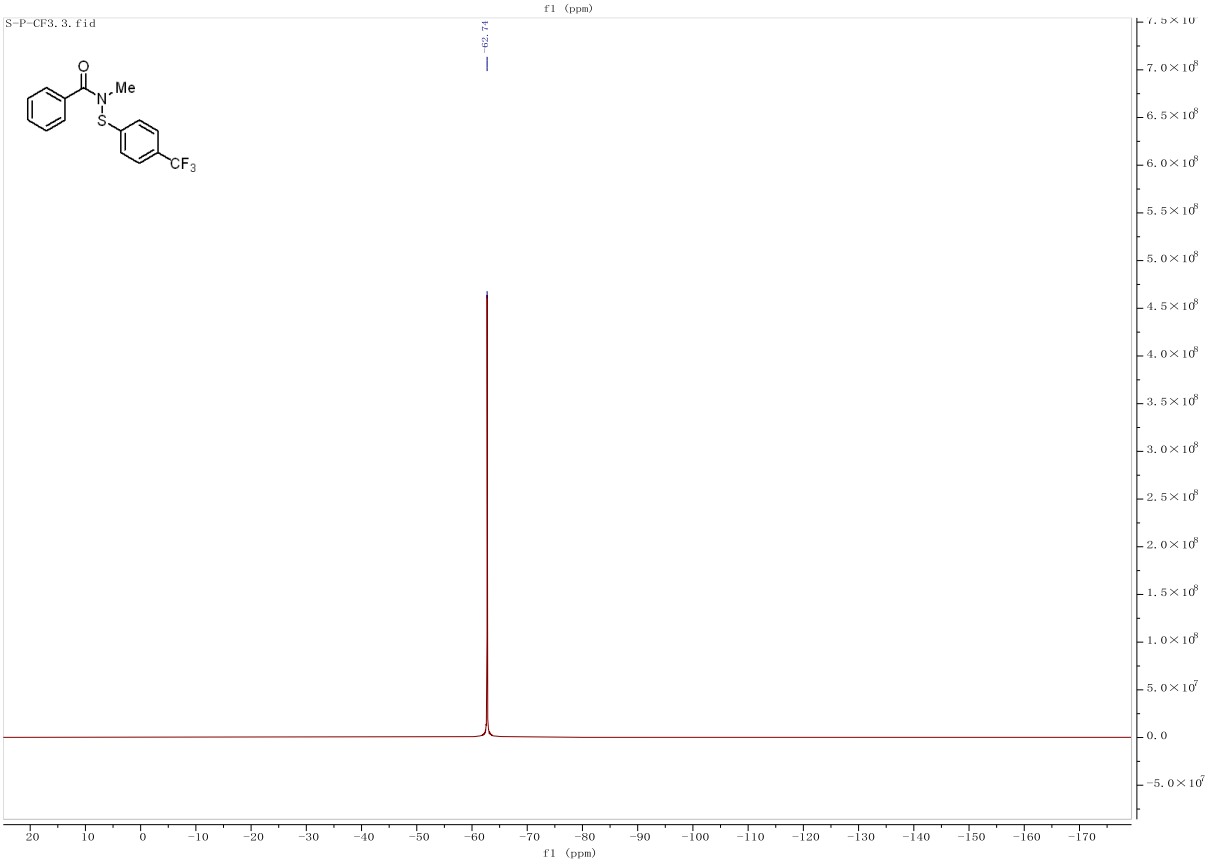

S-P-Cl.2.fid
Me
Cl
f1 (ppm)

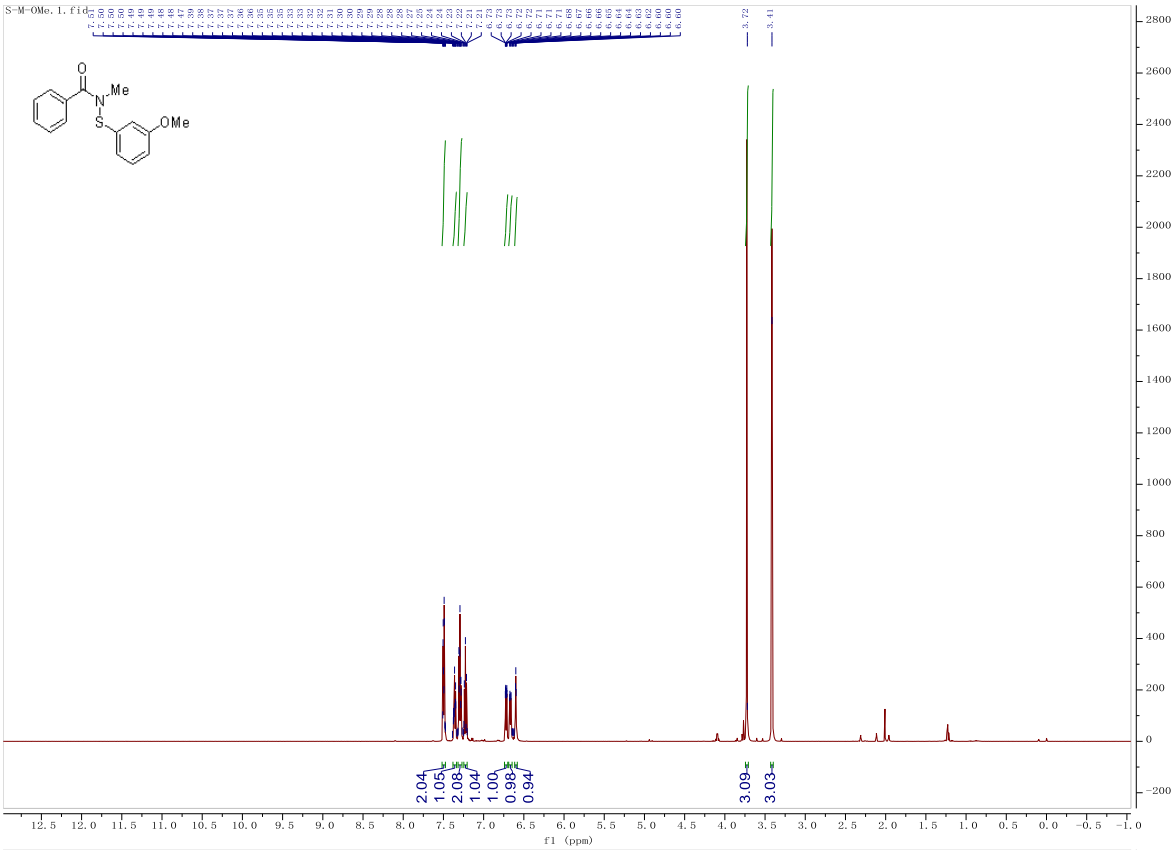

S-P-Br.1.fid
Me
Br
3.98
1.16
2.19
2.01
3.00
f1 (ppm)

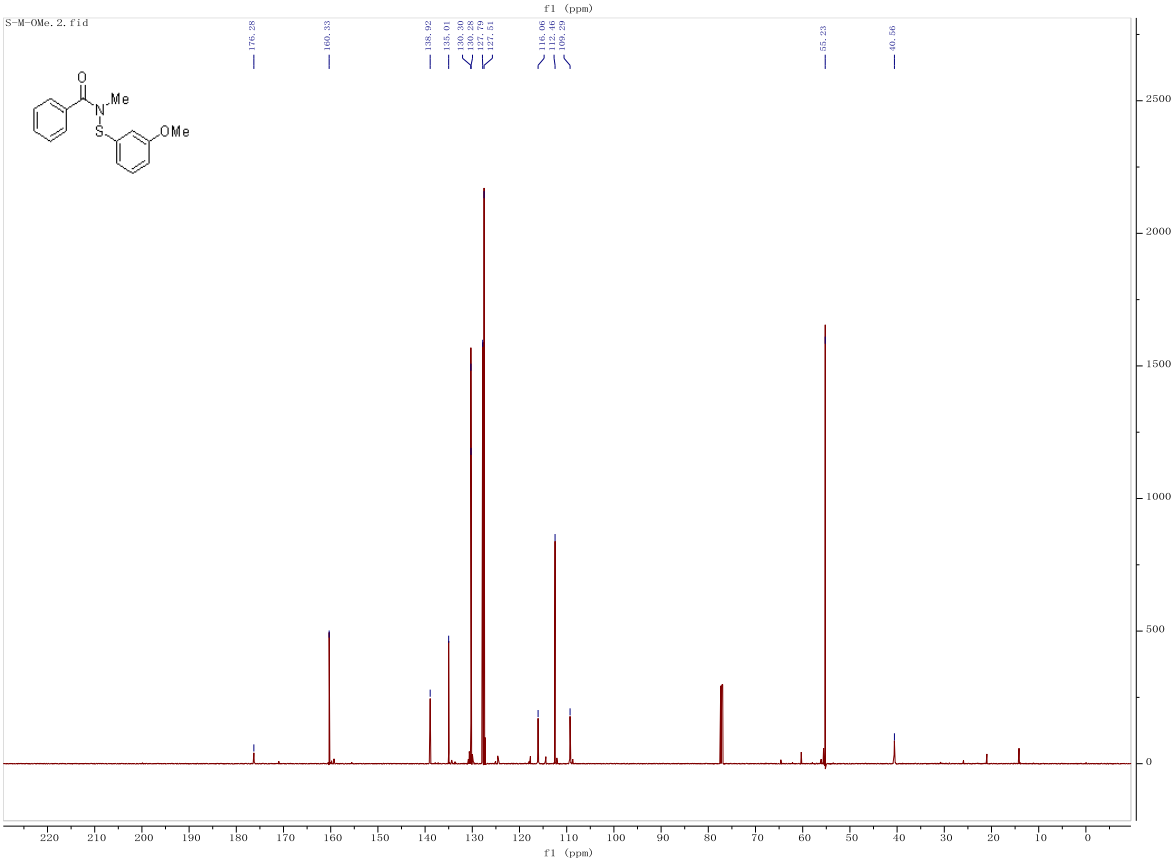

S-P-Br.2.fid
O
N
Me
S
Br
176.41
136.82
134.99
132.58
130.09
128.04
127.61
125.57
120.89
40.65
f1 (ppm)

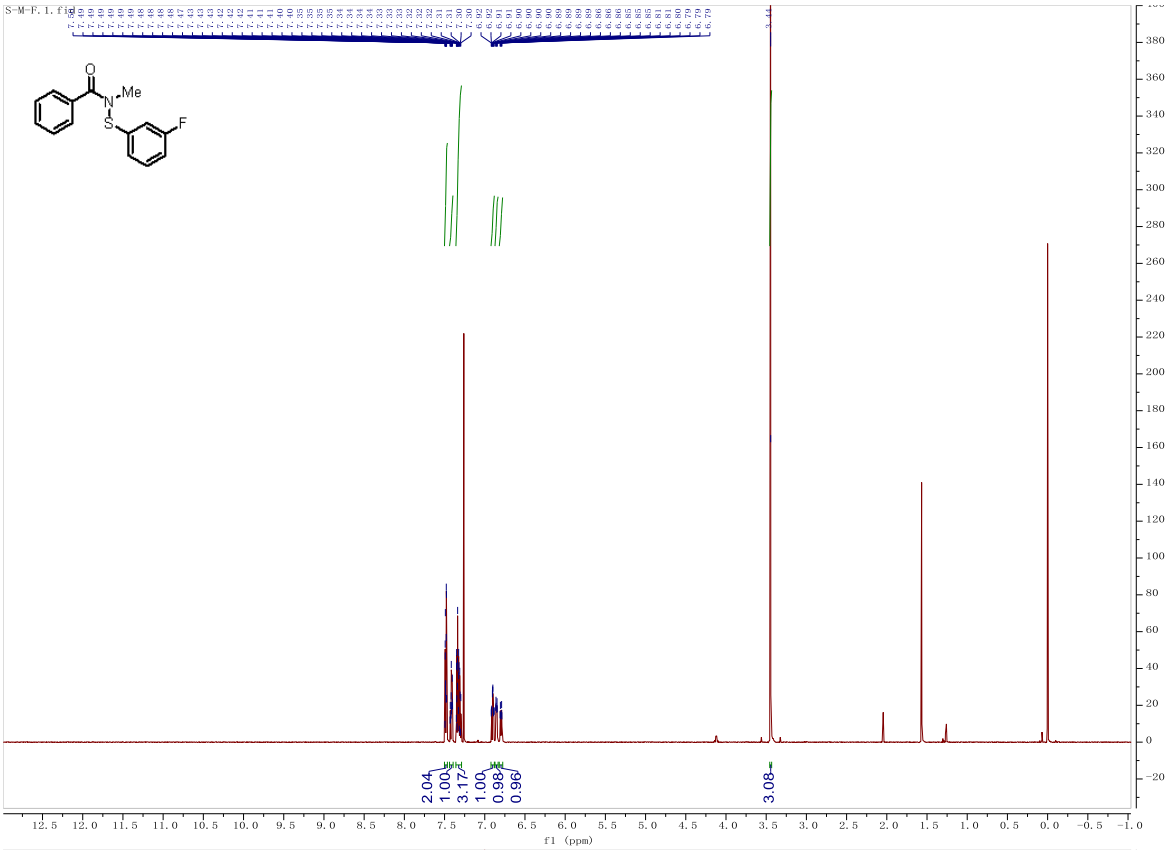

S-P-CF3.1.fid
O
N
Me
S
CF3
7.61
7.60
7.59
7.48
7.47
7.43
7.42
7.41
7.40
7.35
7.34
7.33
7.32
7.16
7.15
3.46
2.00
1.96
1.05
2.00
1.94
2.86
f1 (ppm)

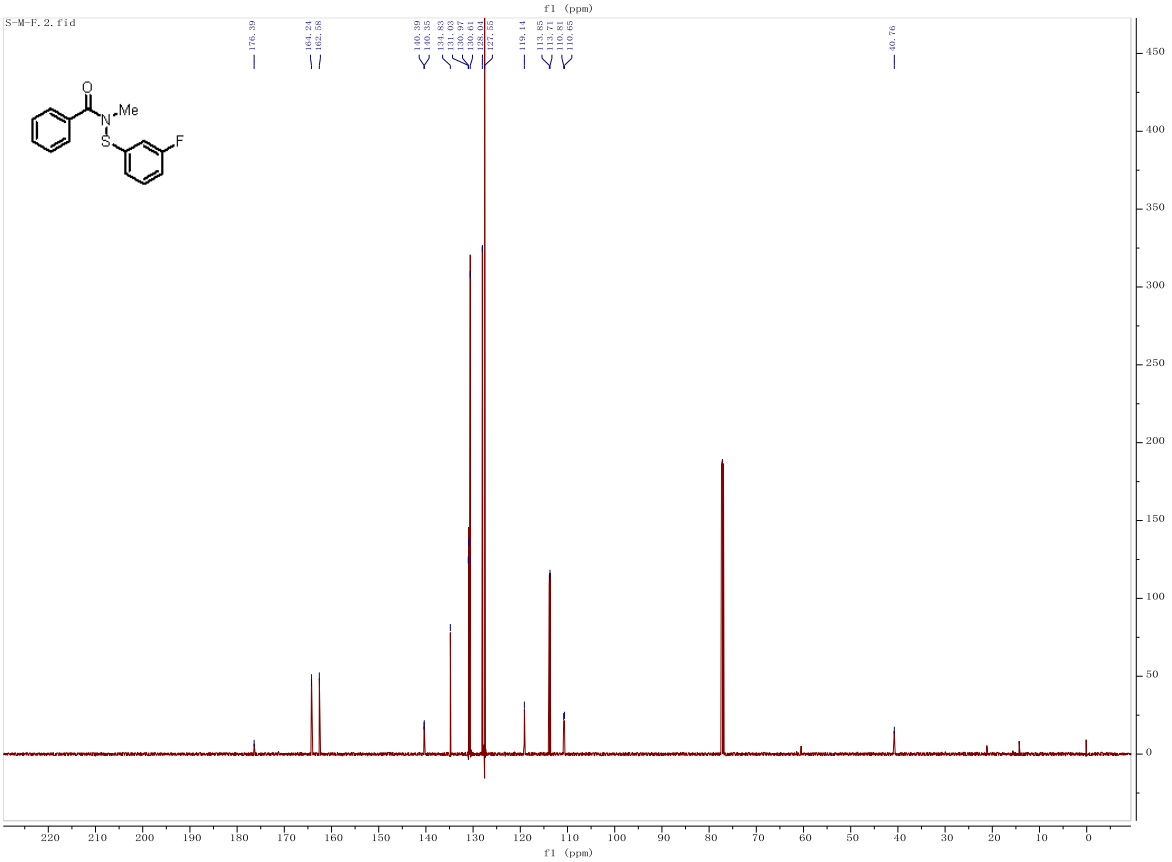

S-P-CF3.2.fid
f1 (ppm)

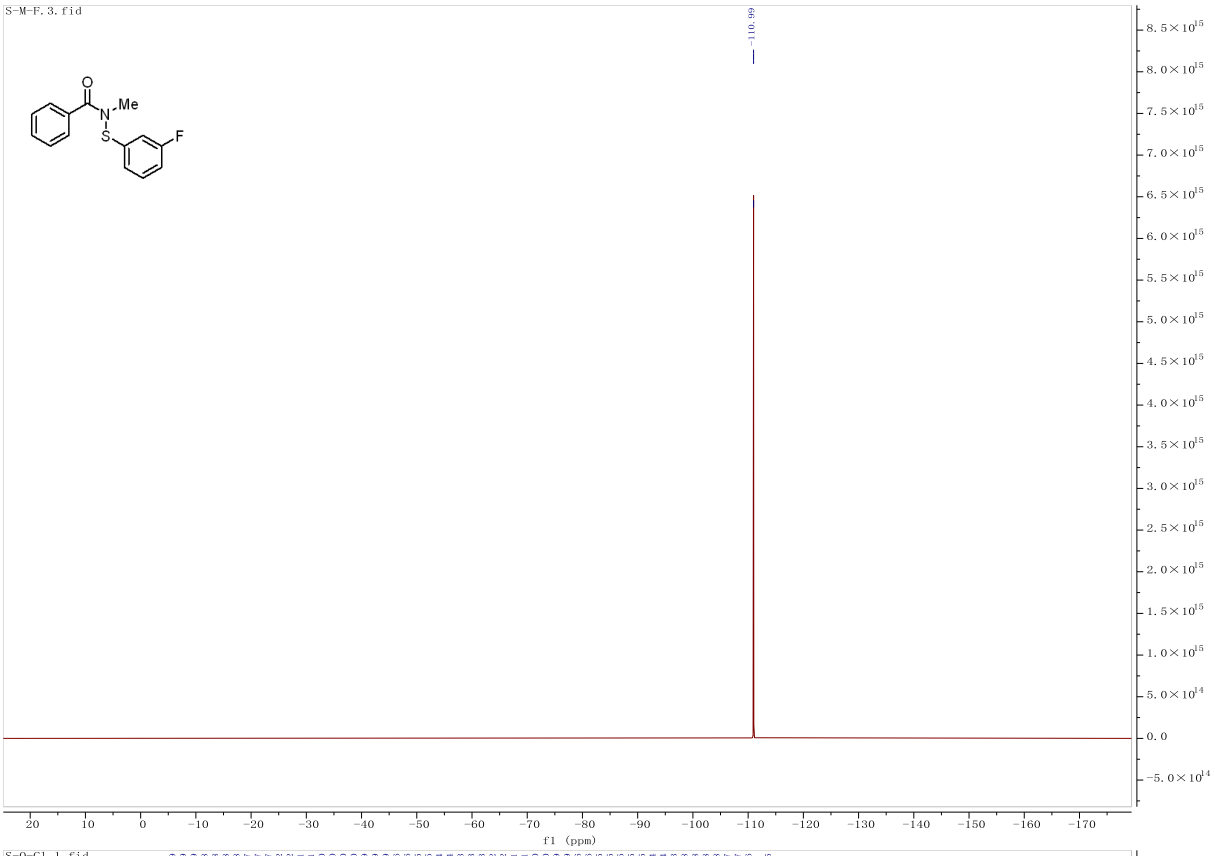

S-P-CF3.3.fid
f1 (ppm)

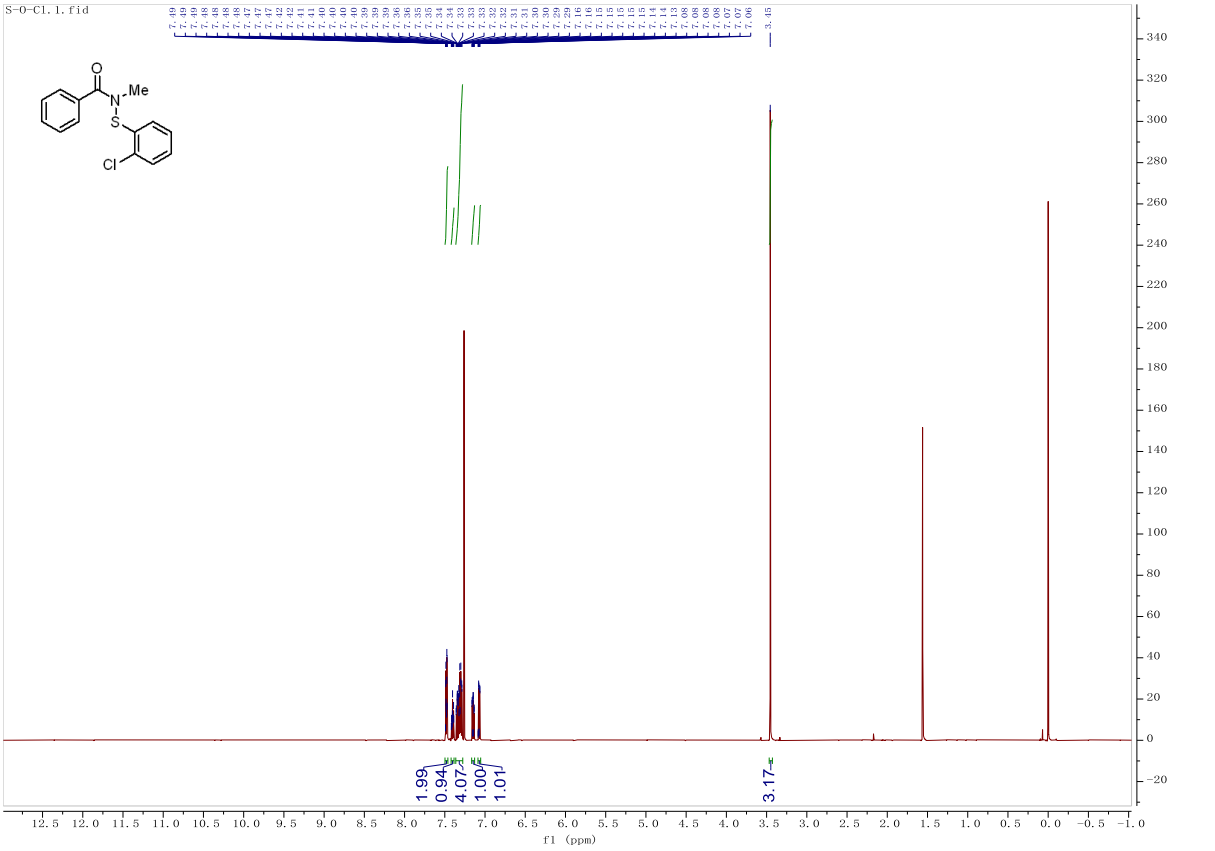

S-M-OMe.1.fid
Me
N
S
OMe
3.72
3.41
2.04
1.05
2.08
1.04
1.00
0.98
0.94
3.09
3.03
f1 (ppm)

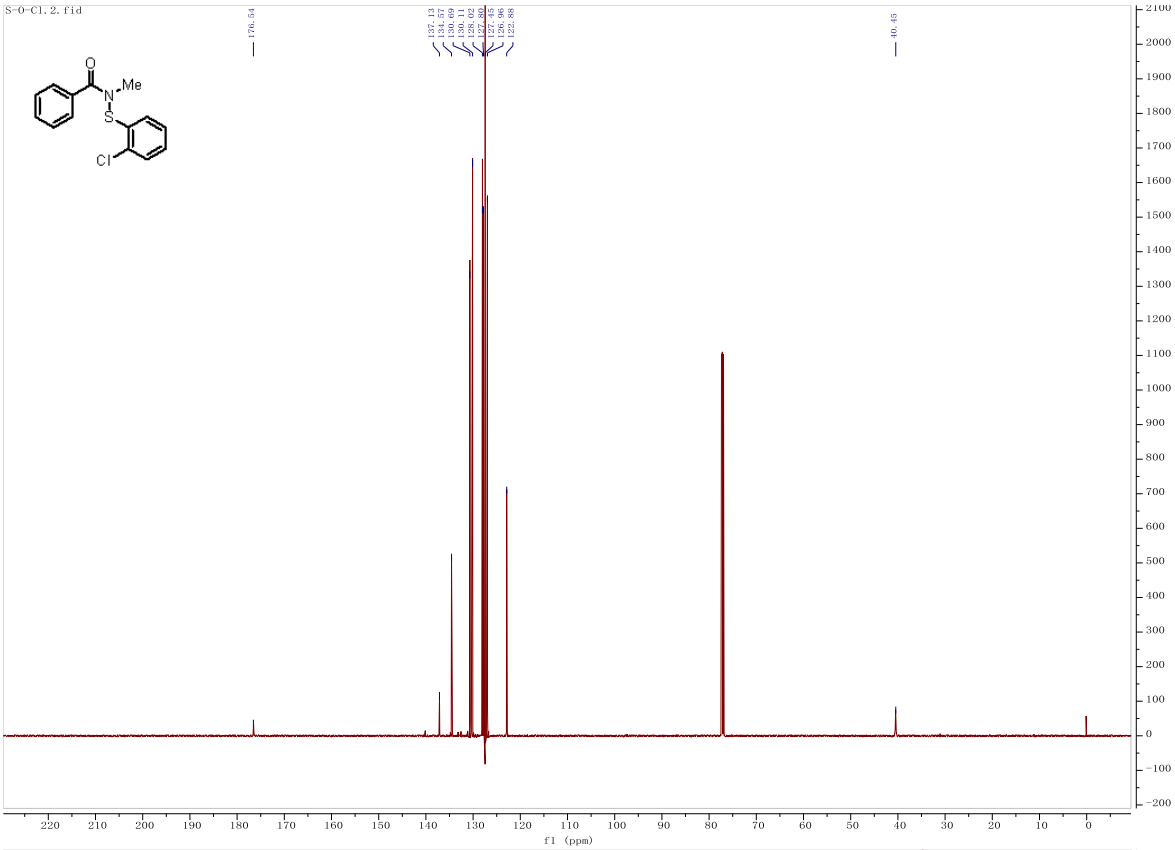

S-M-OMe.2.fid
Me
N
S
OMe
176.28
160.33
138.92
135.01
130.39
130.28
127.51
116.08
112.46
109.29
55.23
40.56
f1 (ppm)

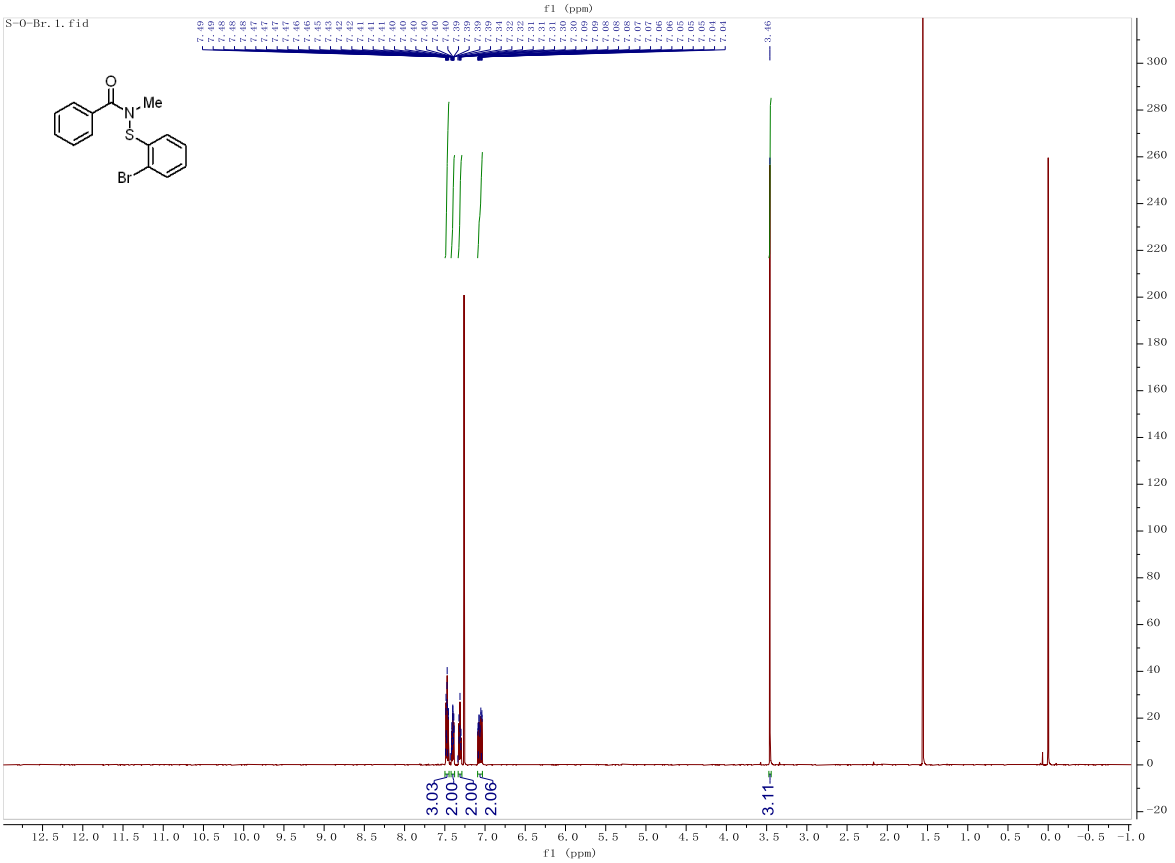

S-M-F.1.fid
Me
N
S
O
F
2.04
1.00
3.17
1.00
0.98
0.96
3.08
f1 (ppm)

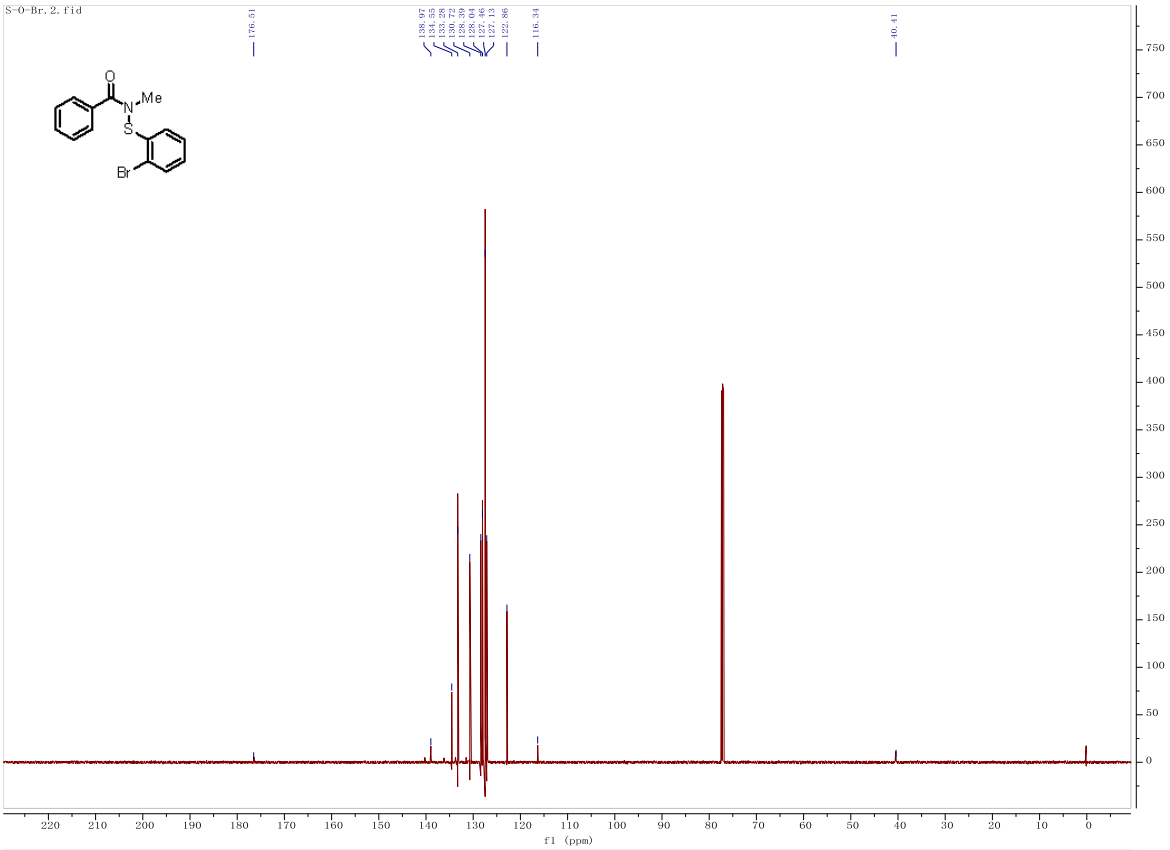

S-M-F.2.fid
176.39
164.24
162.68
140.39
140.35
134.55
131.03
130.97
130.61
129.44
127.56
119.14
113.95
113.71
110.81
110.65
40.76
Me
N
S
O
F
f1 (ppm)

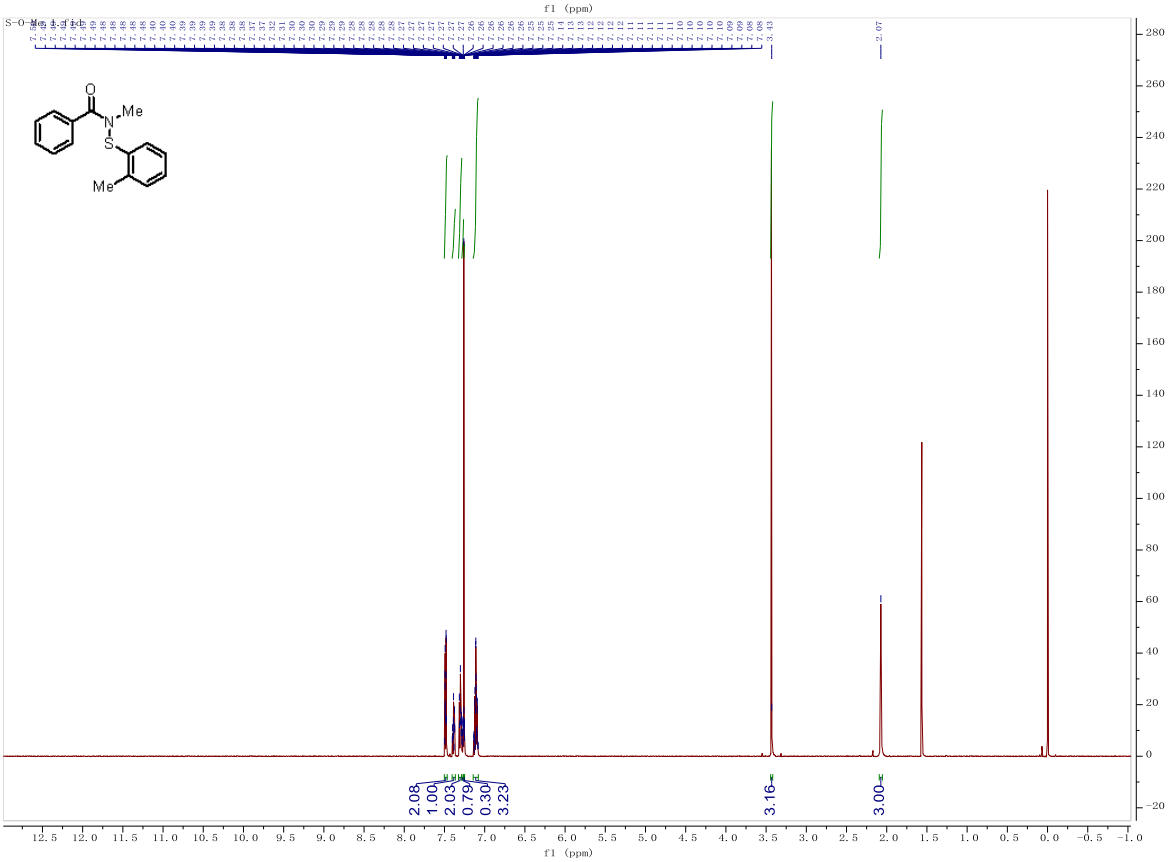

S-M-F.3.fid
-110.99
f1 (ppm)

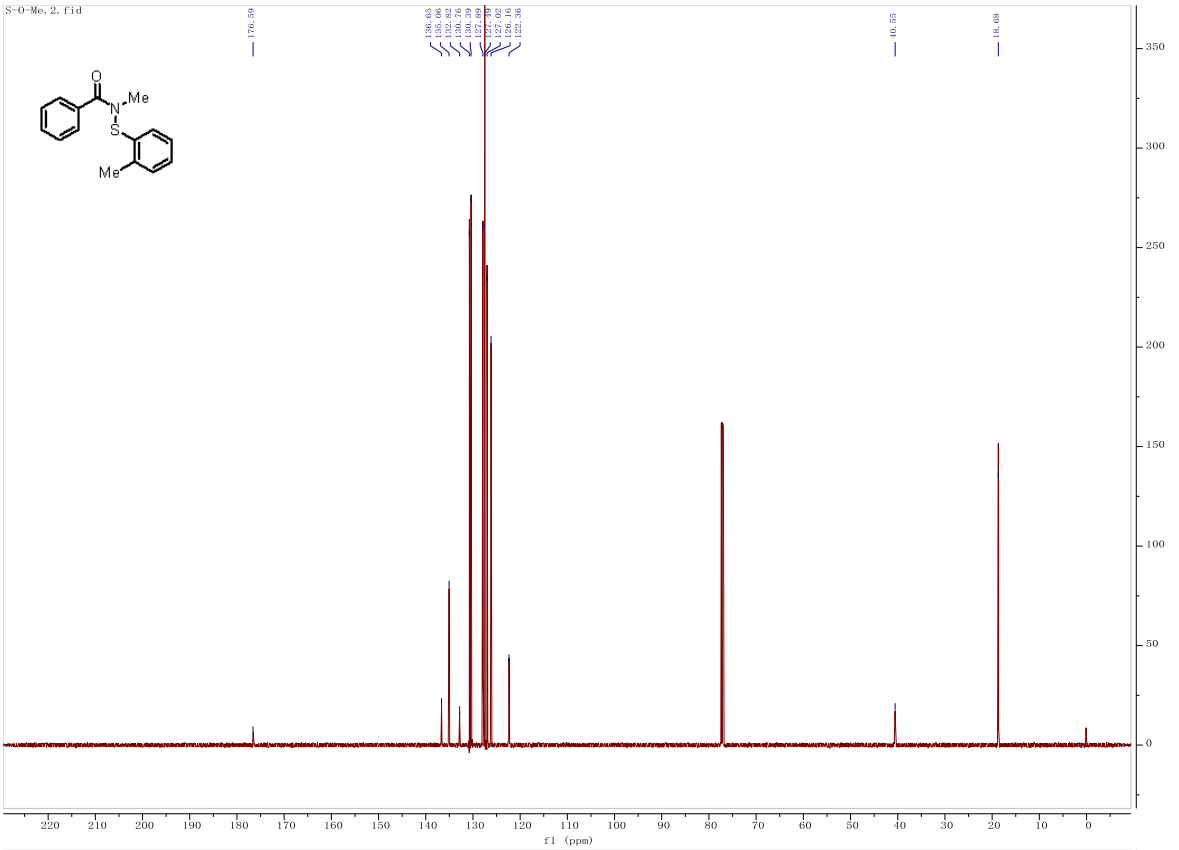

S-O-Cl.1.fid
1.99
0.94
4.07
1.00
1.01
3.17
f1 (ppm)

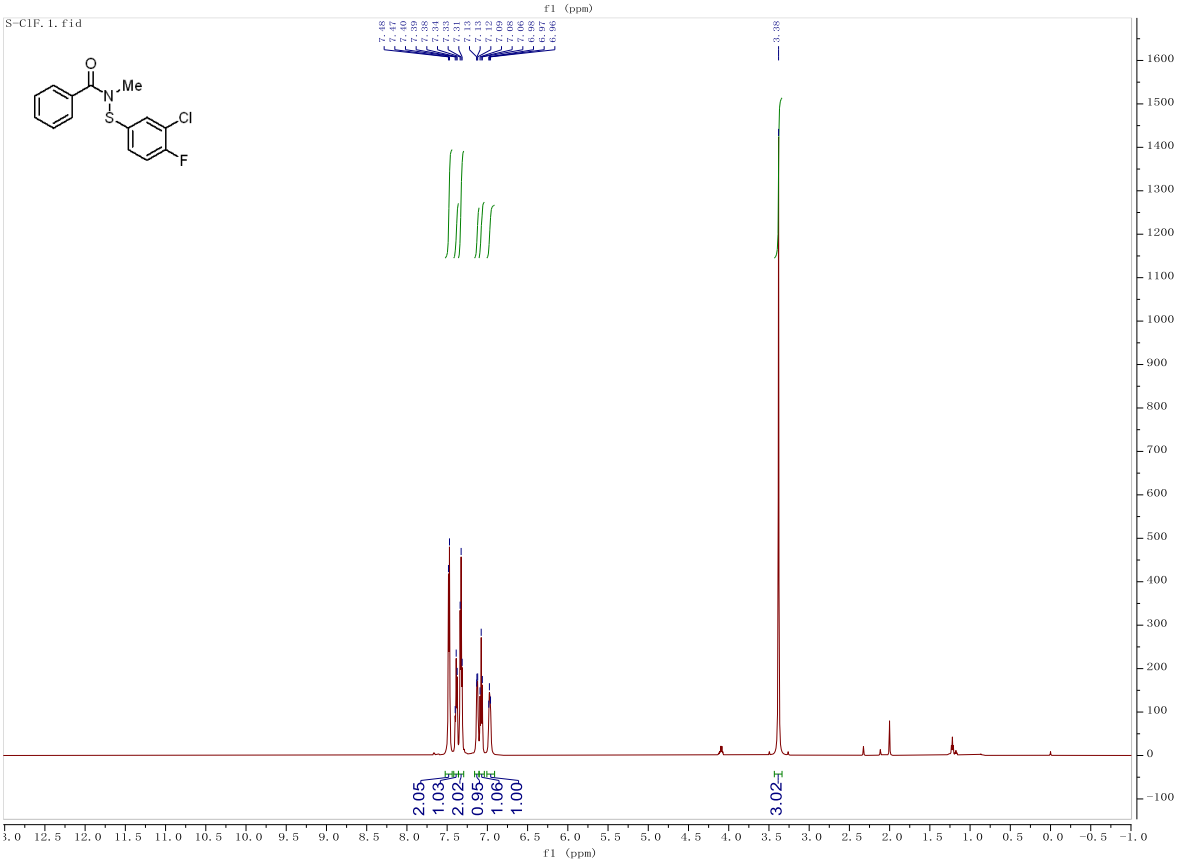

S-O-Cl.2.fid
Me
N
S
Cl
f1 (ppm)

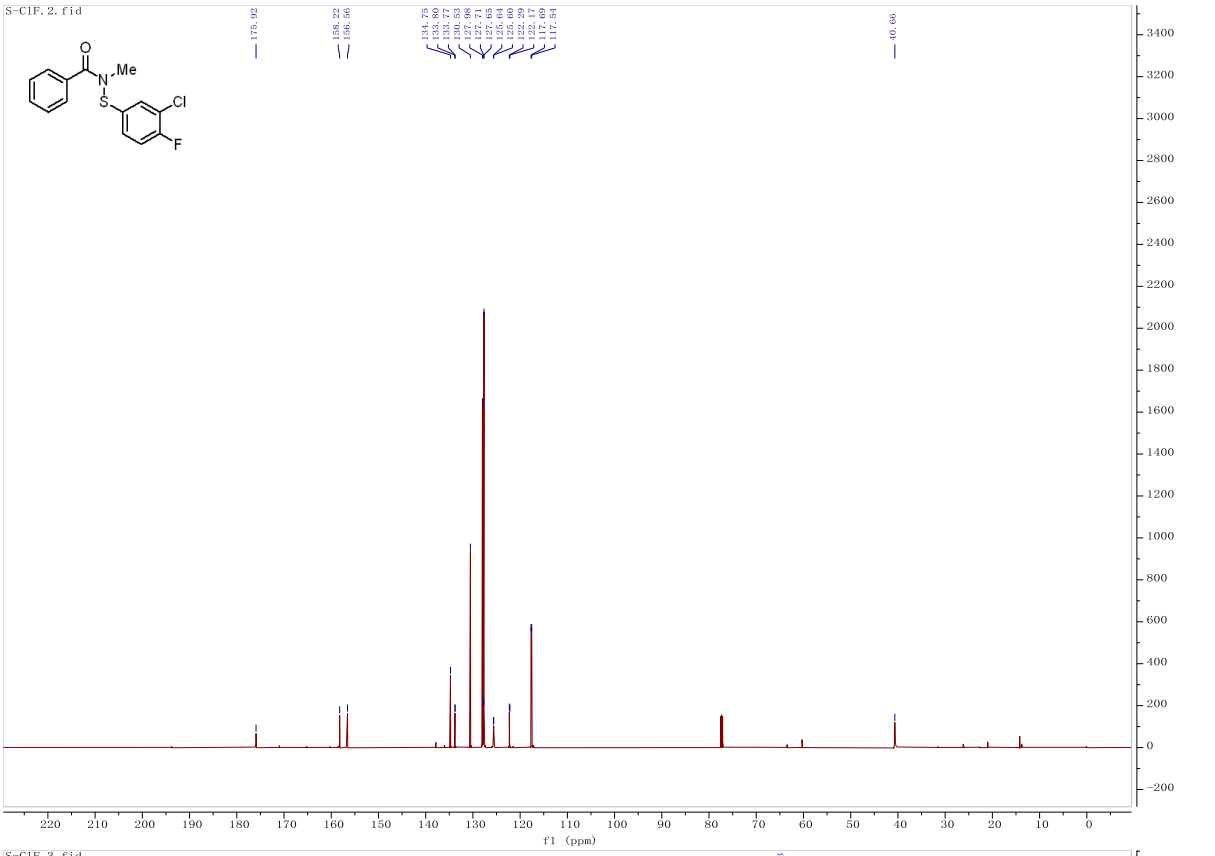

S-O-Br.1.fid
Me
N
S
Br
3.03
2.00
2.00
2.06
3.11
f1 (ppm)

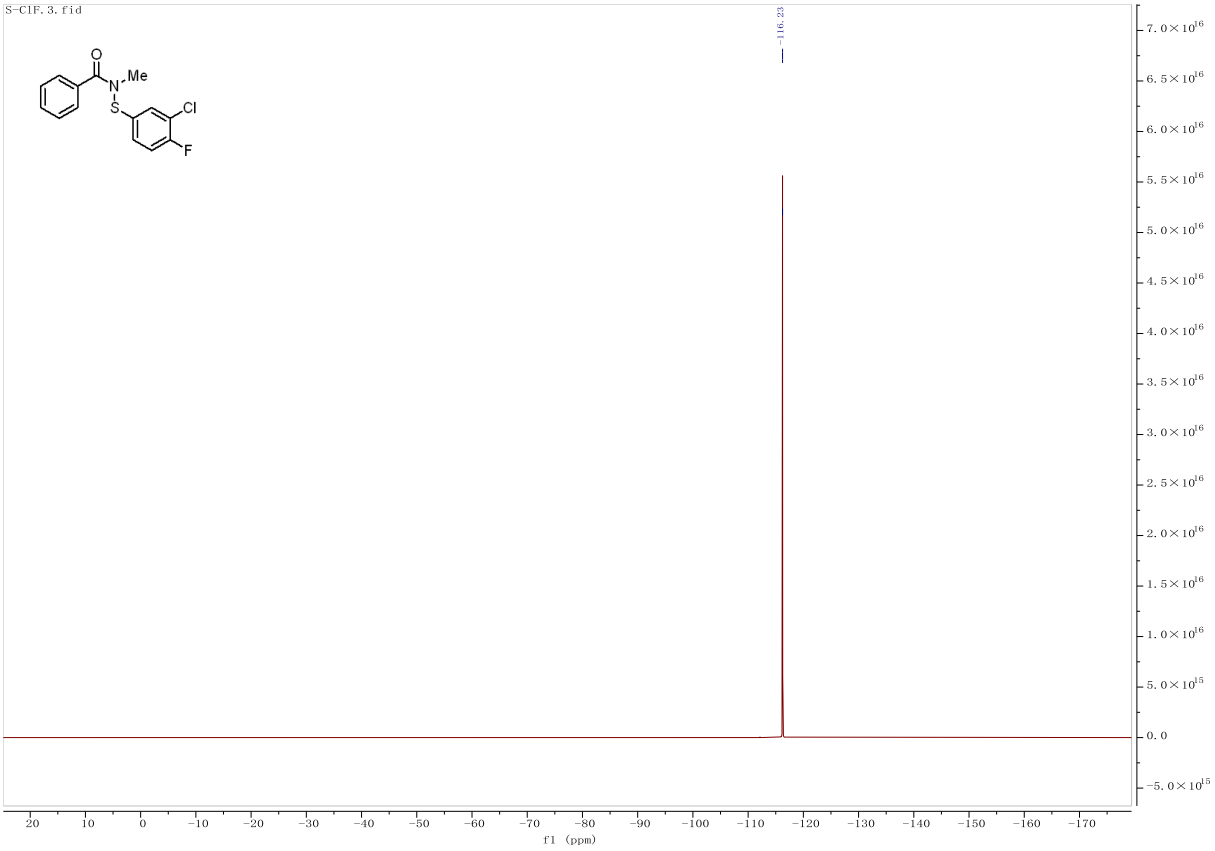

S-O-Br. 2. fid
O
N
Me
S
Br
176.51
138.97
134.55
133.38
130.72
128.39
128.04
127.46
127.13
122.86
116.34
40.41
f1 (ppm)

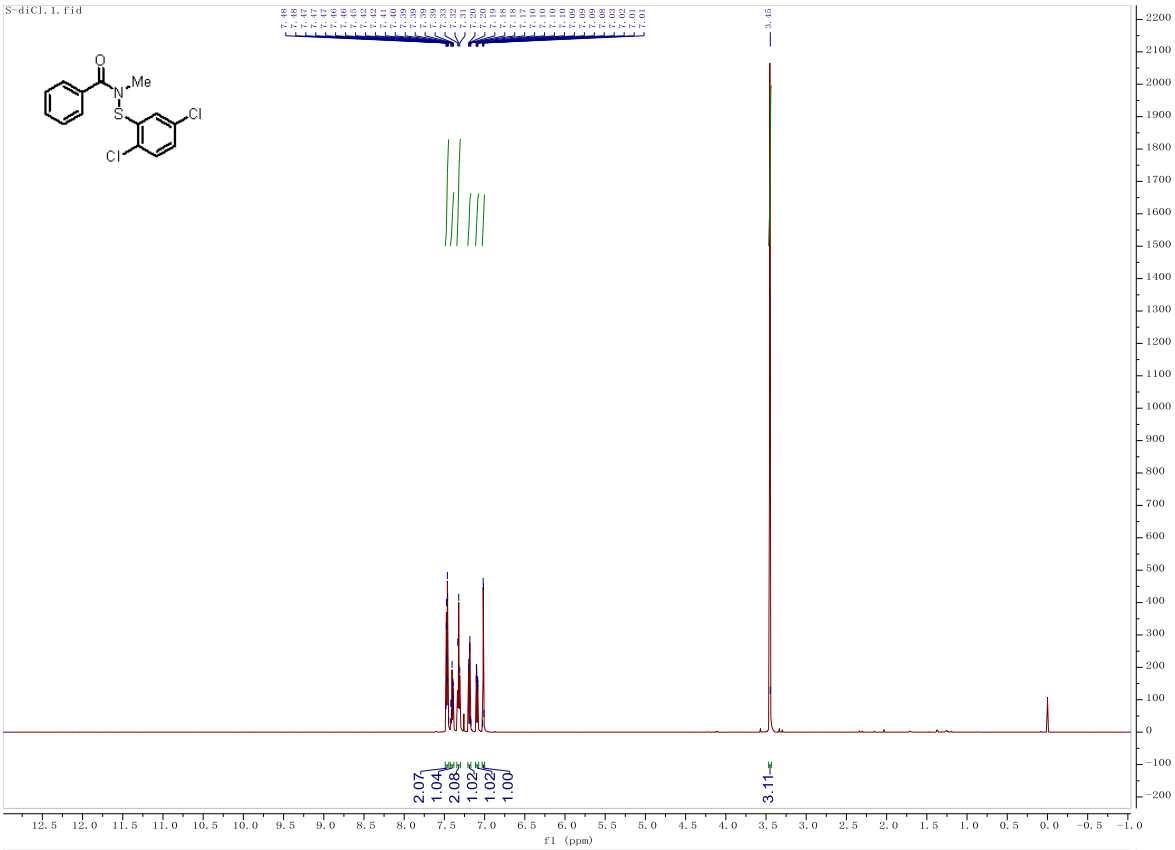

O
N
Me
S
Me
7.43
2.07
2.08
1.00
2.03
0.79
0.30
3.23
3.16
3.00
f1 (ppm)

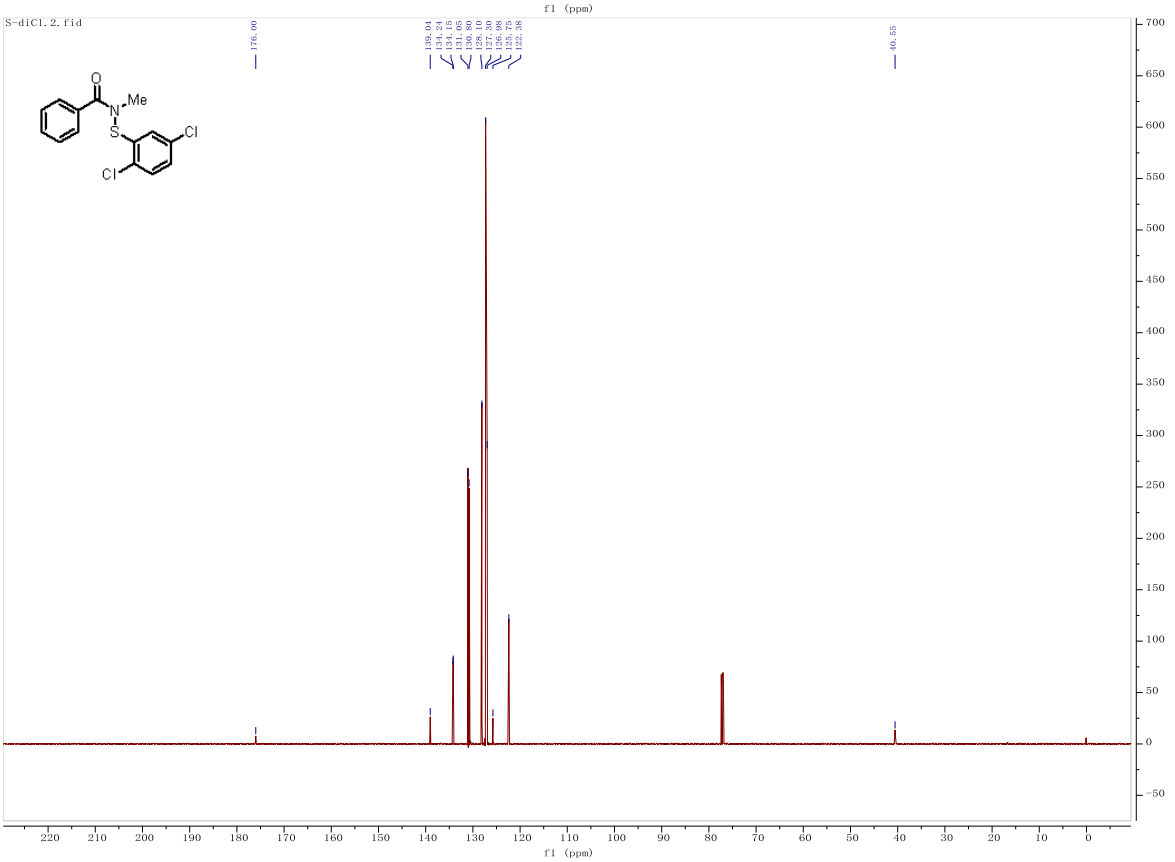

S-O-Me.2.fid
176.59
138.65
135.66
132.82
130.76
130.39
129.89
127.89
127.49
127.02
125.16
122.36
40.55
18.68
Me
N
S
Me
O
f1 (ppm)

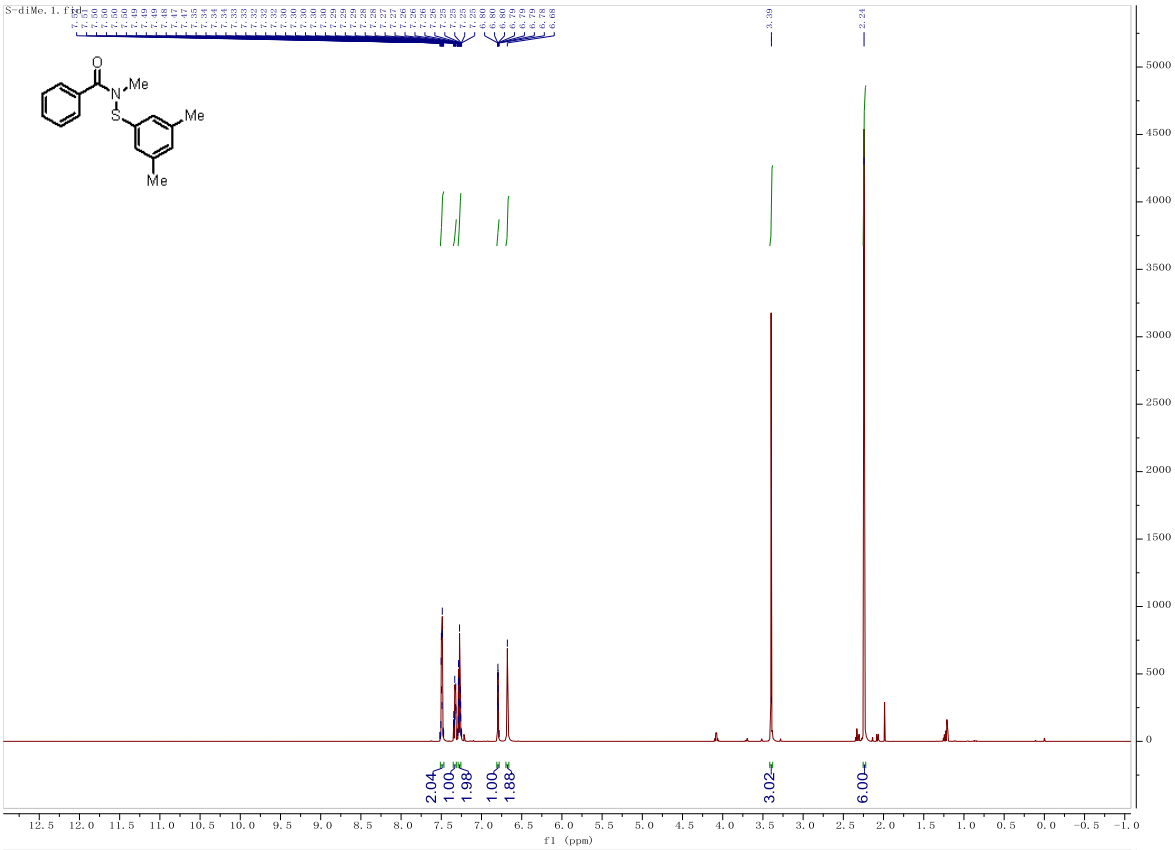

S-ClF.1.fid
7.48
7.47
7.40
7.39
7.36
7.34
7.33
7.31
7.15
7.13
7.12
7.09
7.08
7.06
6.98
6.97
6.96
3.38
2.05
1.03
2.02
0.95
1.06
1.00
3.02
Me
N
S
Cl
F
O
f1 (ppm)

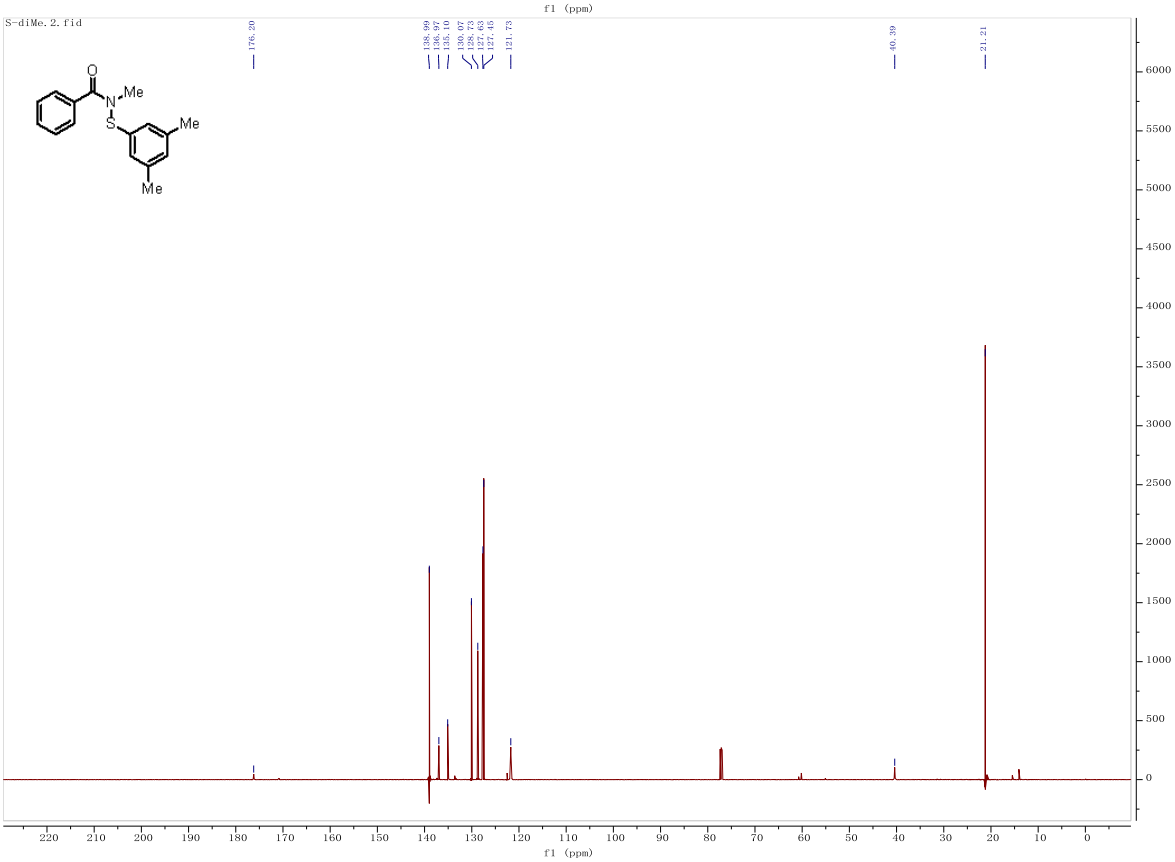

S-ClF.2.fid
175.92
158.22
156.56
134.75
133.80
133.77
130.53
127.96
127.71
127.65
125.64
125.60
122.29
122.17
117.69
117.54
40.66
f1 (ppm)

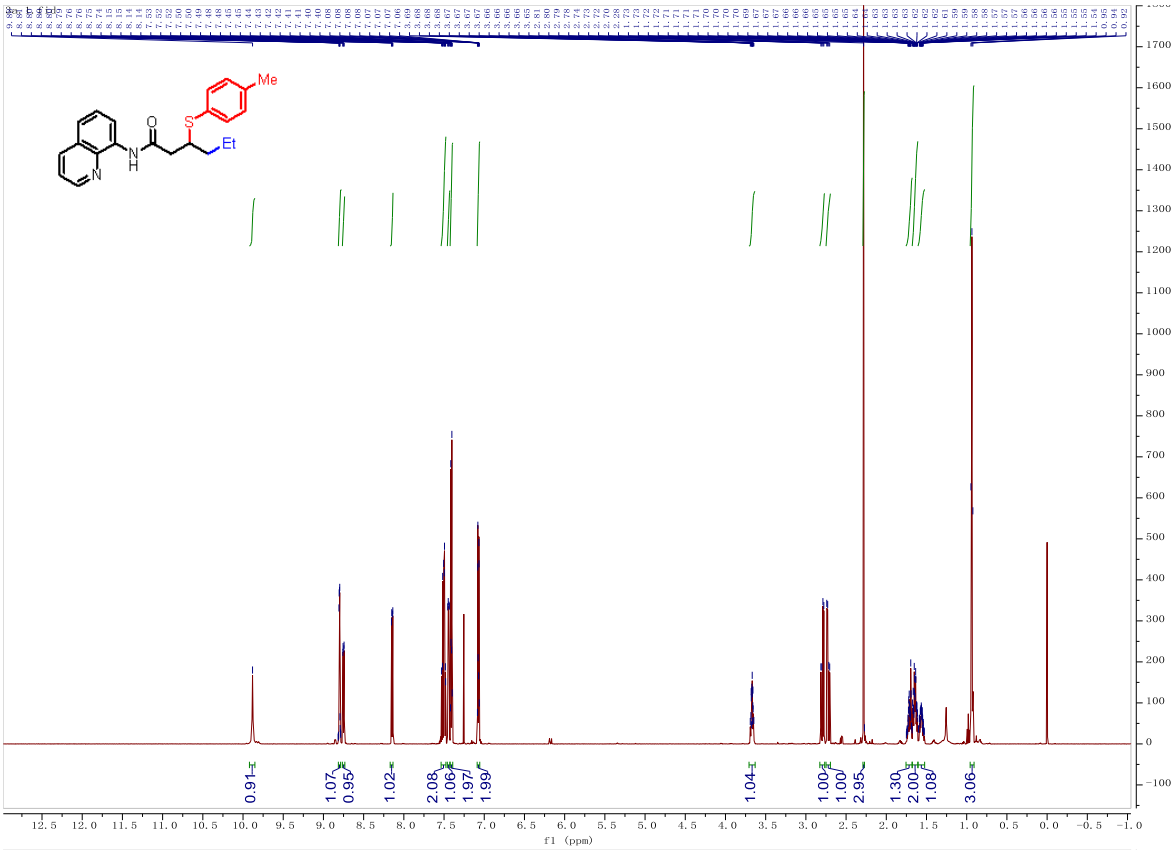

S-ClF.3.fid
-116.23
f1 (ppm)

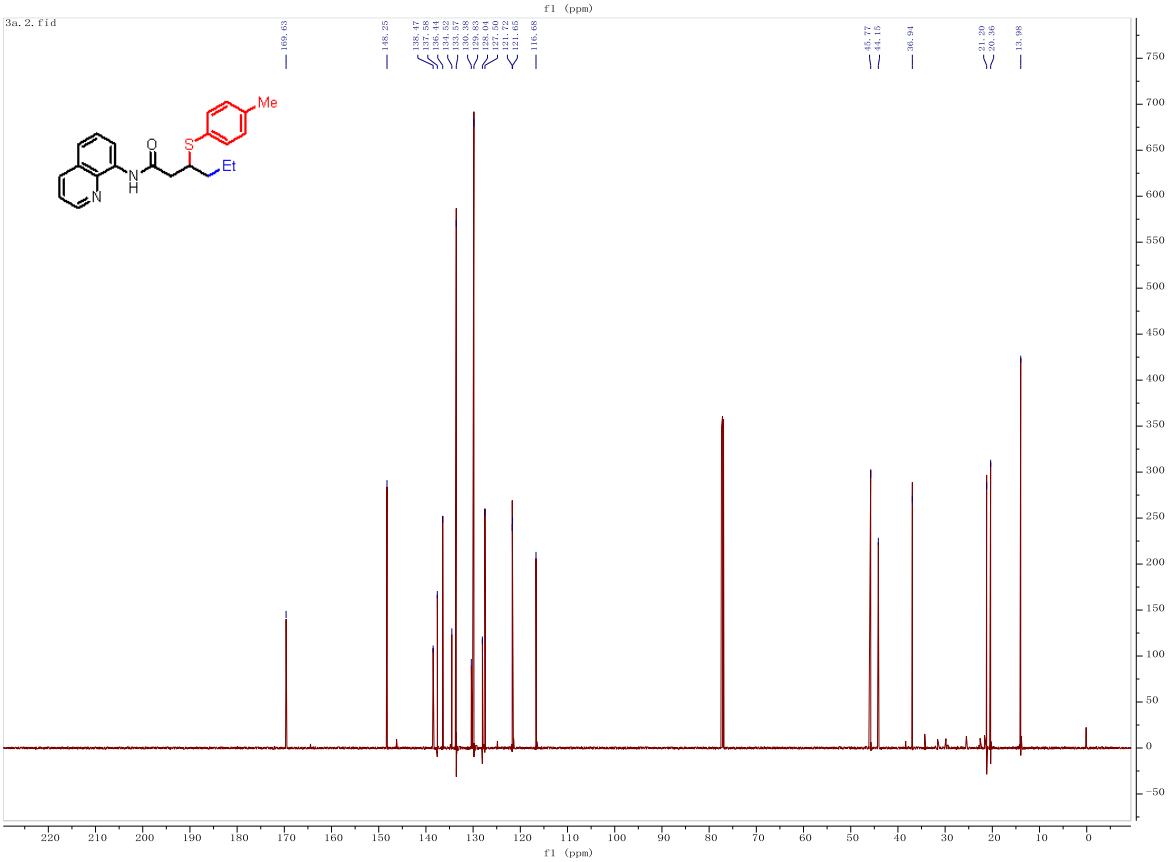

S-diCl.1.fid
Me
N
S
Cl
Cl
7.48
7.47
7.46
7.45
7.42
7.41
7.40
7.39
7.38
7.33
7.32
7.31
7.20
7.19
7.18
7.17
7.10
7.09
7.08
7.03
7.02
7.01
3.45
2.07
1.04
2.08
1.02
1.02
1.00
3.11
f1 (ppm)

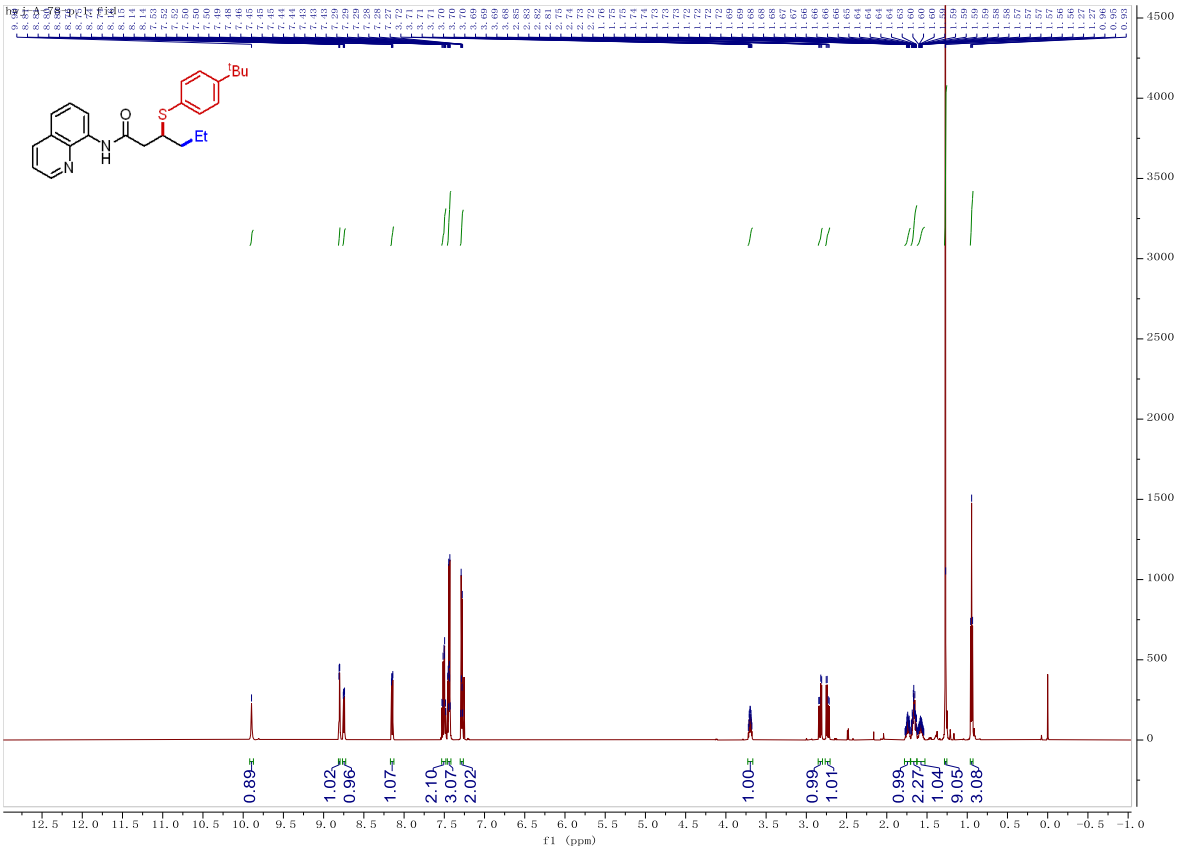

S-diCl.2.fid
Me
N
S
Cl
Cl
176.00
139.04
134.21
134.15
131.05
130.89
128.10
127.30
126.98
126.95
122.38
40.55
f1 (ppm)

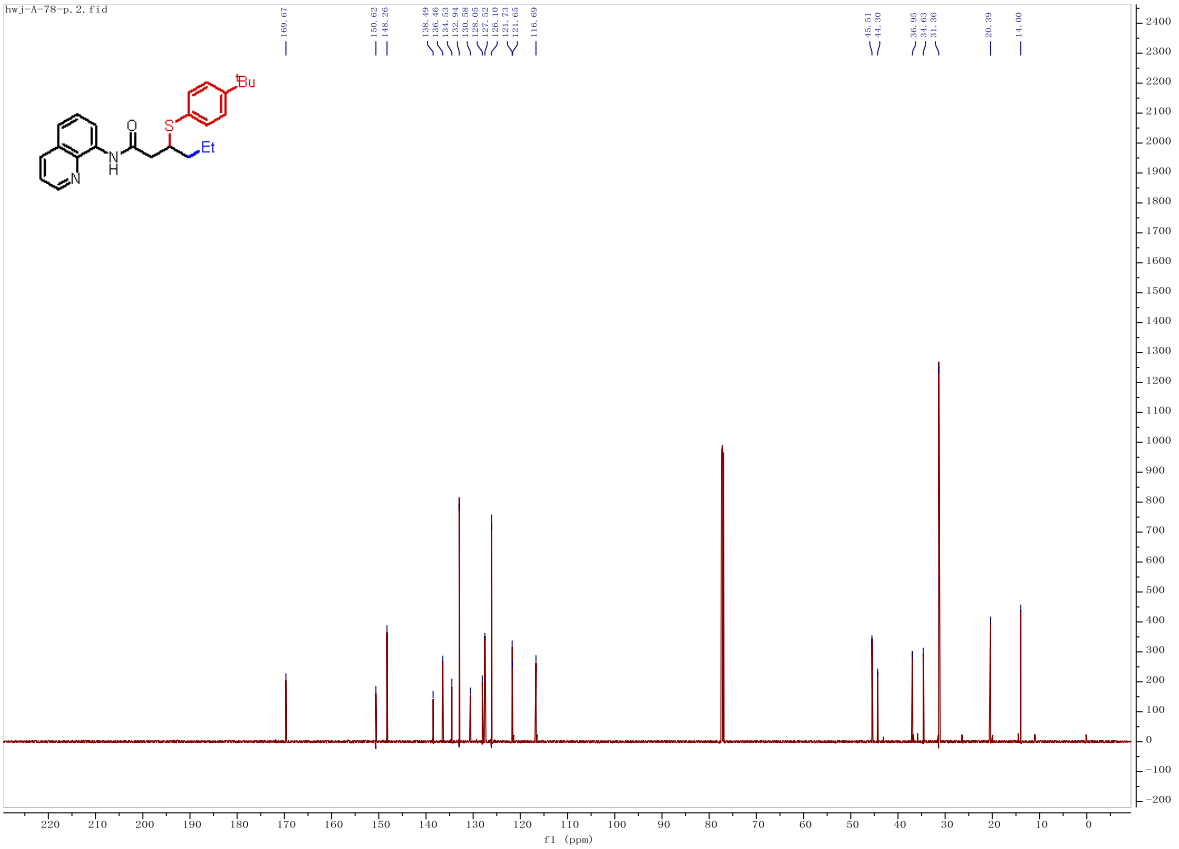

S-diMe.1.fid
3.39
2.24
2.04
1.00
1.98
1.00
1.88
3.02
6.00
f1 (ppm)

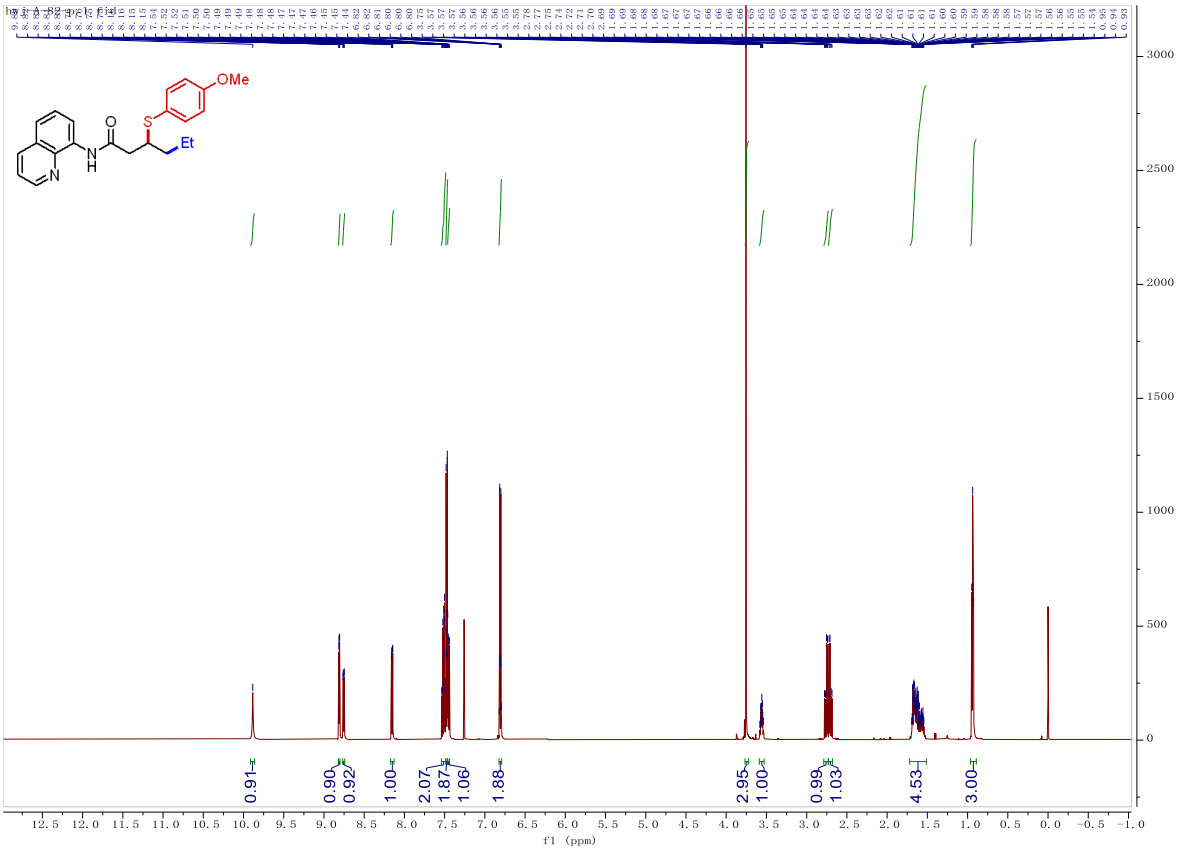

S-diMe.2.fid
176.20
138.99
136.97
135.10
130.07
128.73
127.45
127.45
121.73
40.39
21.21
f1 (ppm)

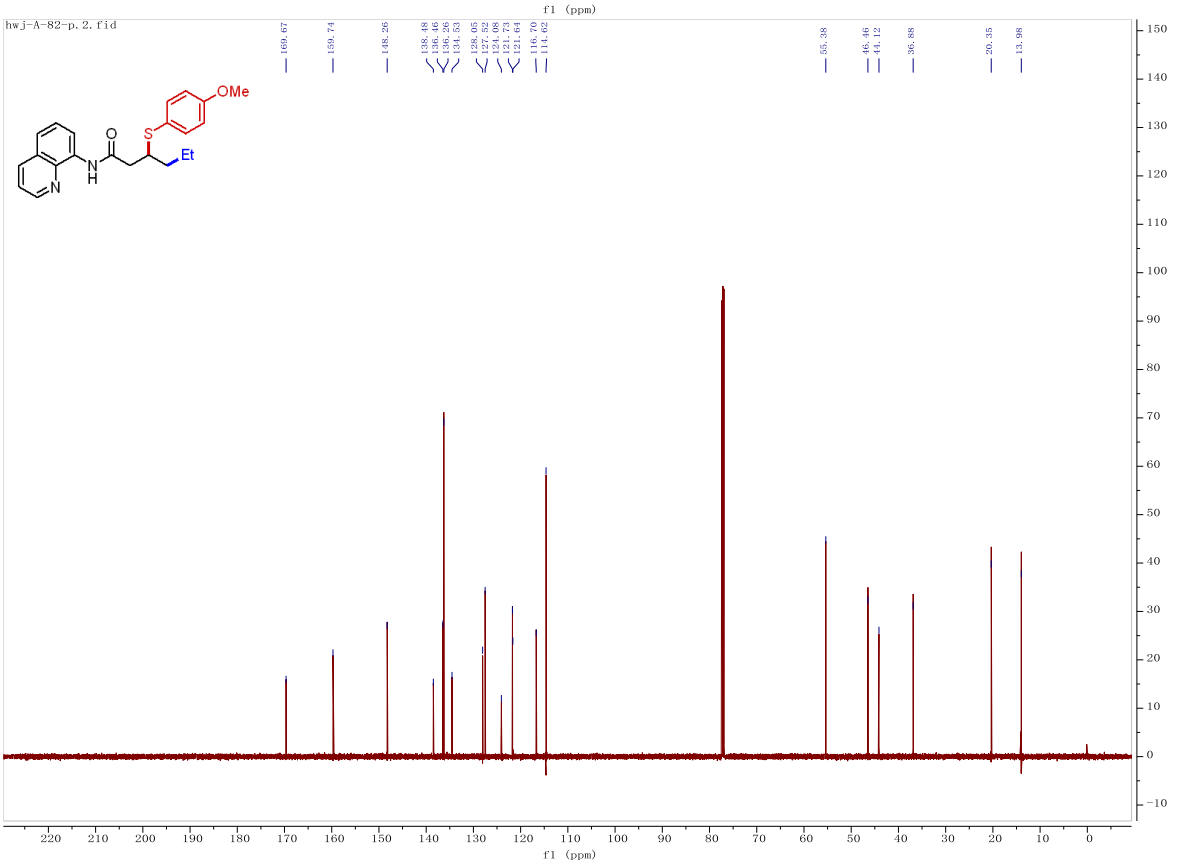

Me
S
O
N
H
N
Et
0.91
1.07
0.95
1.02
2.08
1.06
1.97
1.99
1.04
1.00
1.00
2.95
1.30
2.00
1.08
3.06
f1 (ppm)

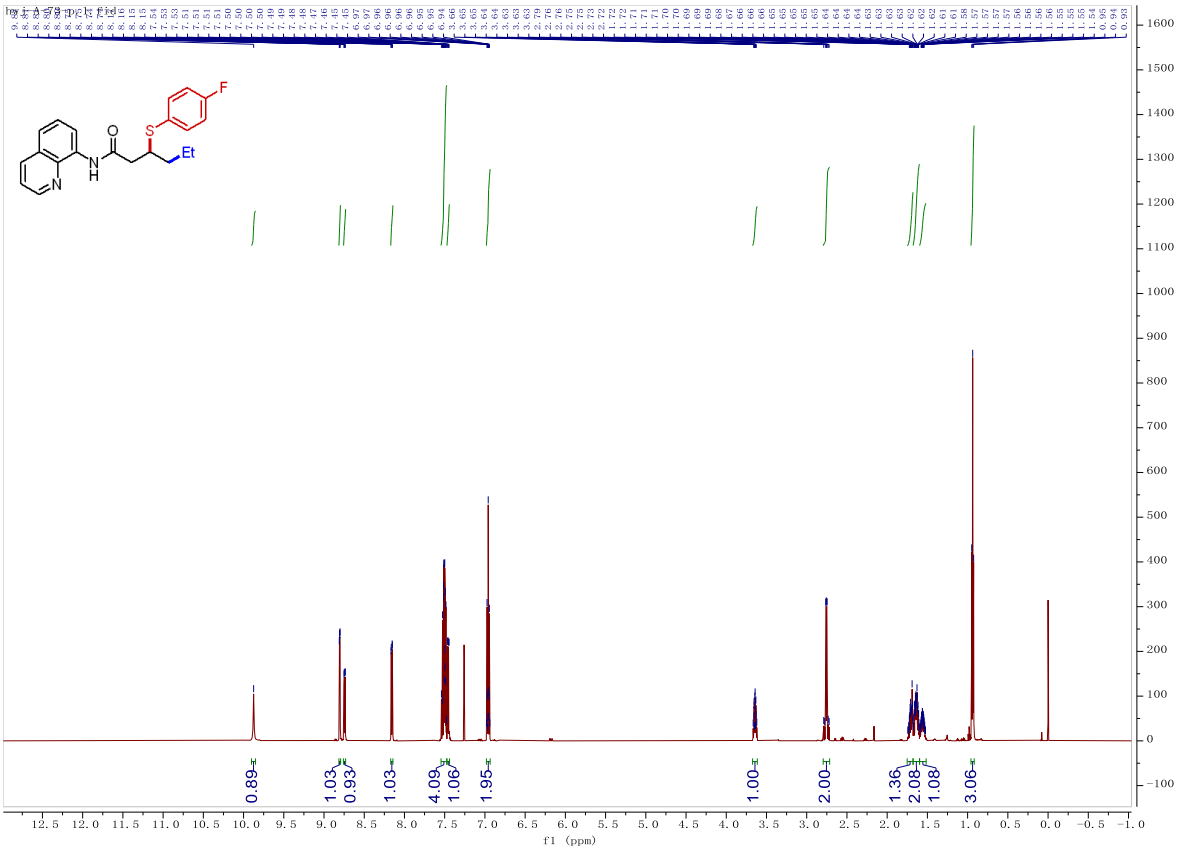

3a. 2. fid
169. 63
148. 25
138. 47
137. 98
136. 44
134. 52
133. 57
130. 38
129. 83
128. 04
125. 60
121. 72
121. 65
116. 68
45. 77
44. 15
36. 94
21. 20
20. 36
13. 98
Me
S
O
N
H
N
Et
f1 (ppm)

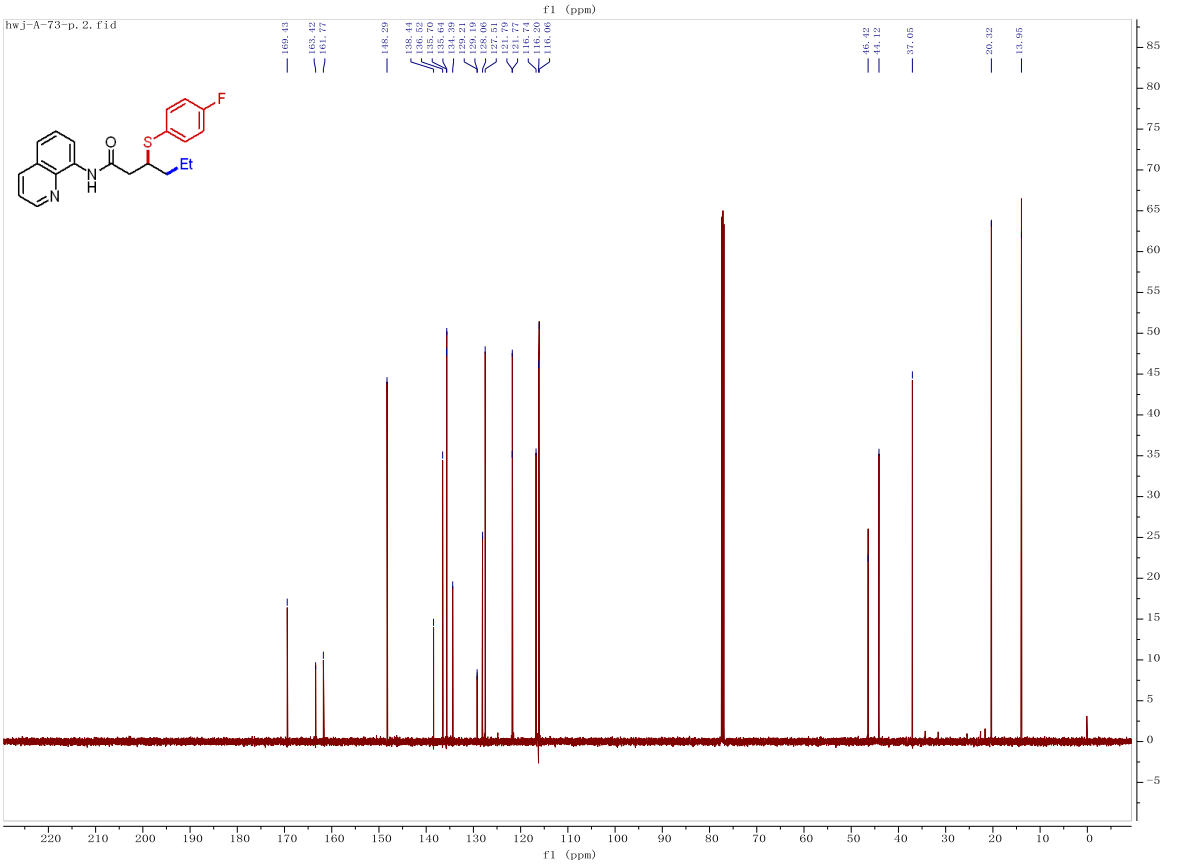

tBu
S
Et
O
N
H
N
0.89
1.02
0.96
1.07
2.10
3.07
2.02
1.00
0.99
1.01
0.99
2.27
1.04
9.05
3.08
f1 (ppm)

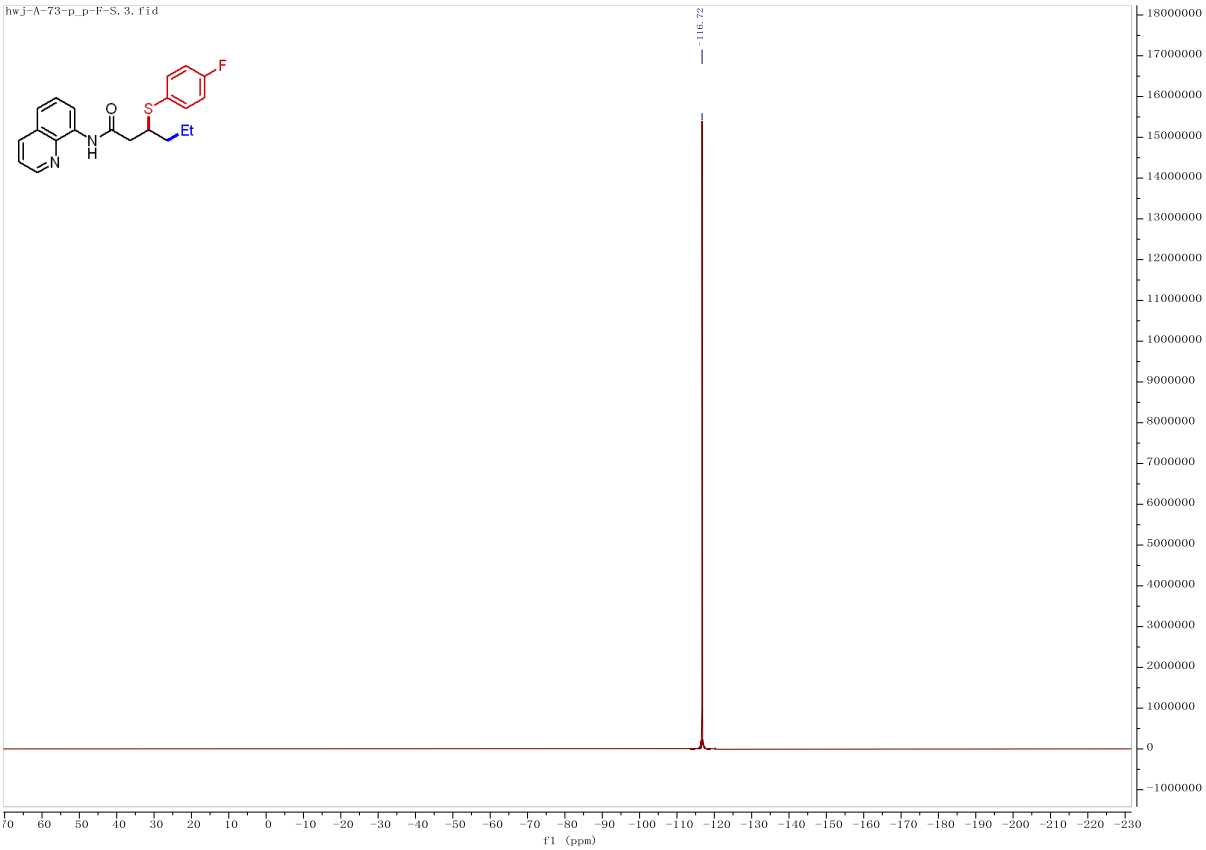

hwj-A-78-p.2.fid
169.67
150.62
146.26
138.49
136.46
134.53
132.84
130.58
128.05
127.52
125.10
121.73
121.65
116.69
45.51
44.30
36.95
34.63
31.36
20.39
14.00
tBu
S
Et
O
N
H
N
f1 (ppm)

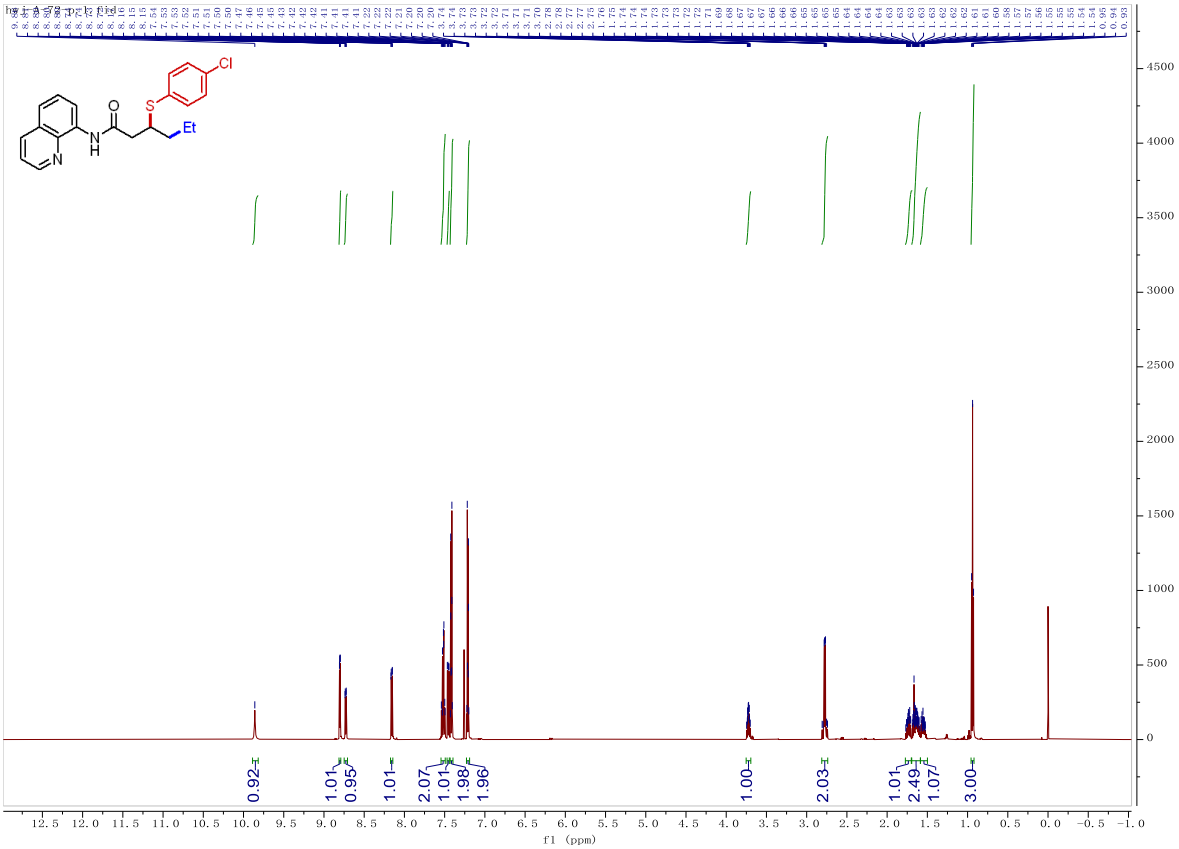

OMe
S
Et
O
N
H
N
0.91
0.90
0.92
1.00
2.07
1.87
1.06
1.88
2.95
1.00
0.99
1.03
4.53
3.00
f1 (ppm)

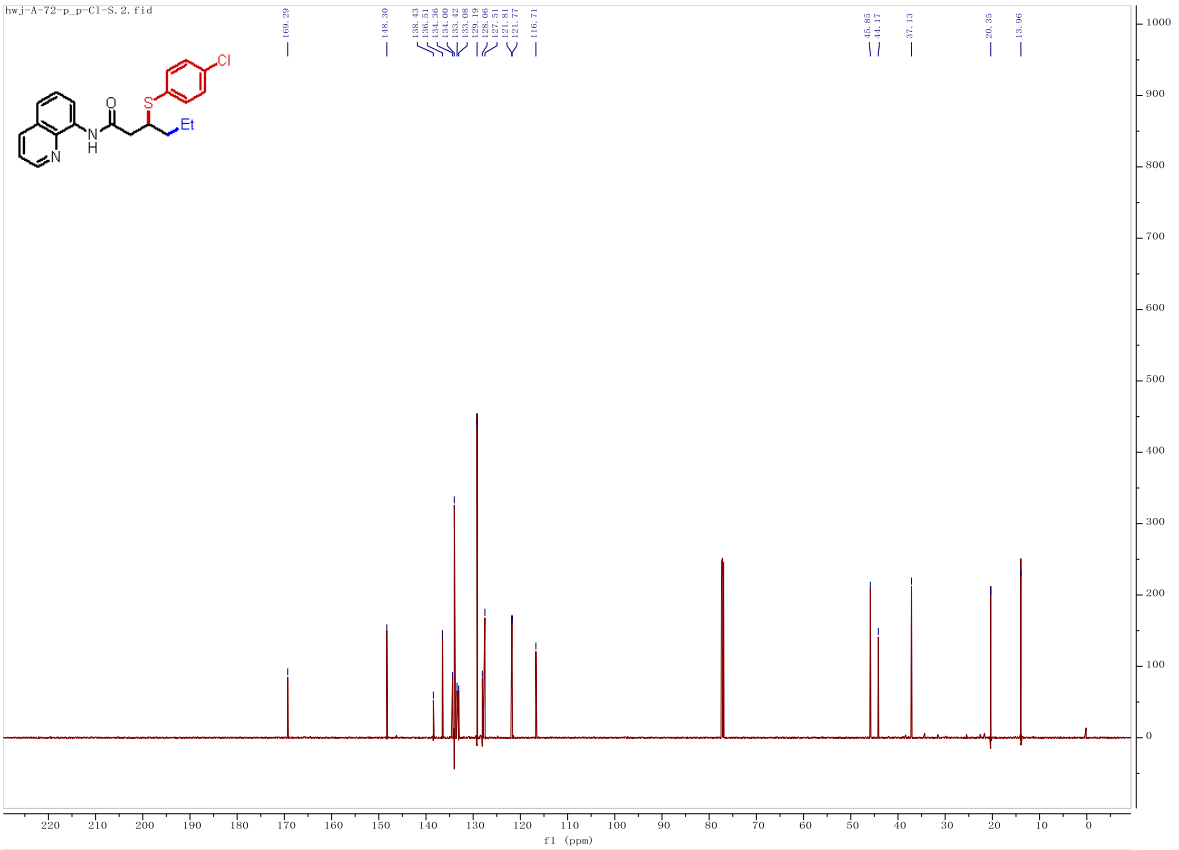

OMe
S
Et
O
N
H
N
169.67
159.74
148.26
138.48
136.46
136.26
134.53
128.05
127.82
124.86
121.73
121.64
116.70
114.62
55.38
46.46
44.12
36.88
26.35
13.98
f1 (ppm)

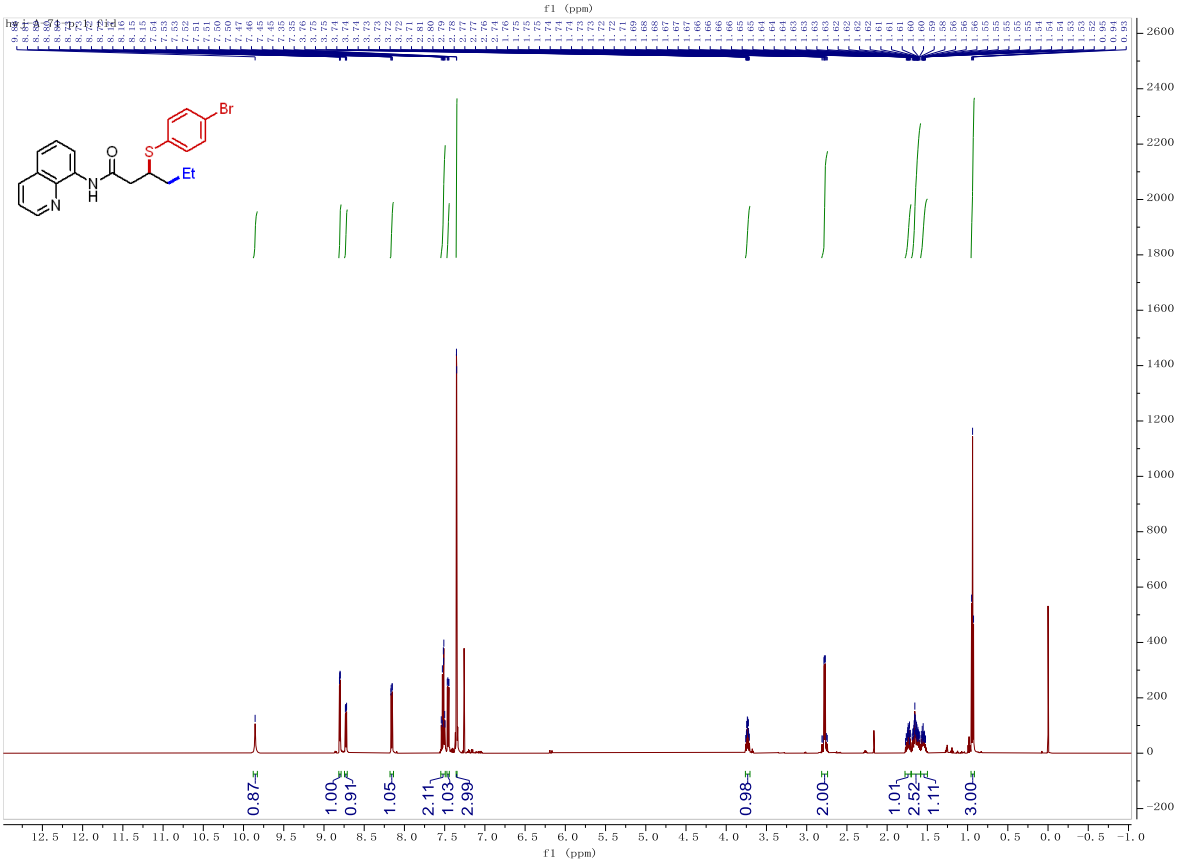

F
S
Et
O
N
H
N
0.89
1.03
0.93
1.03
4.09
1.06
1.95
1.00
2.00
1.36
2.08
1.08
3.06
f1 (ppm)

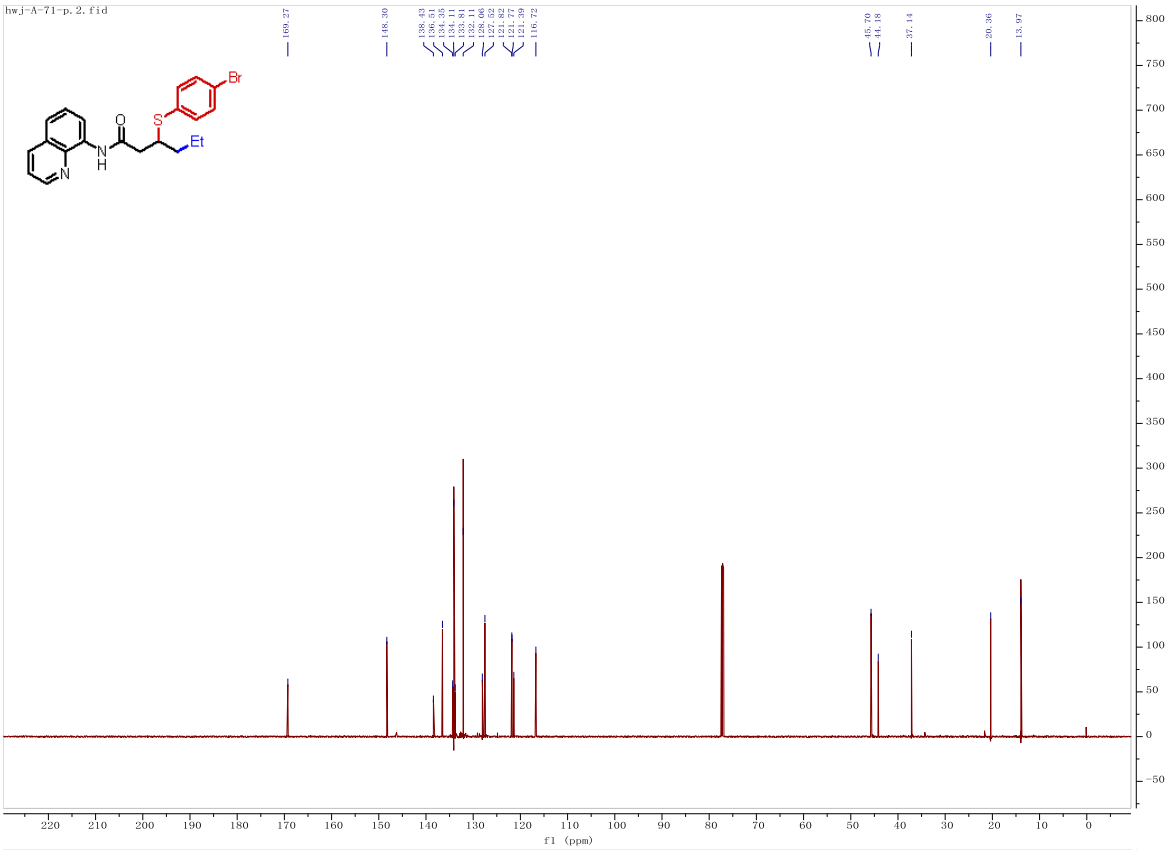

hwj-A-73-p.2.fid
169.43
163.42
161.77
148.29
138.44
136.52
135.70
135.64
134.59
129.21
129.19
128.96
127.51
121.79
121.77
116.74
116.50
116.06
46.42
44.12
37.05
26.32
13.95
F
S
Et
O
N
H
f1 (ppm)

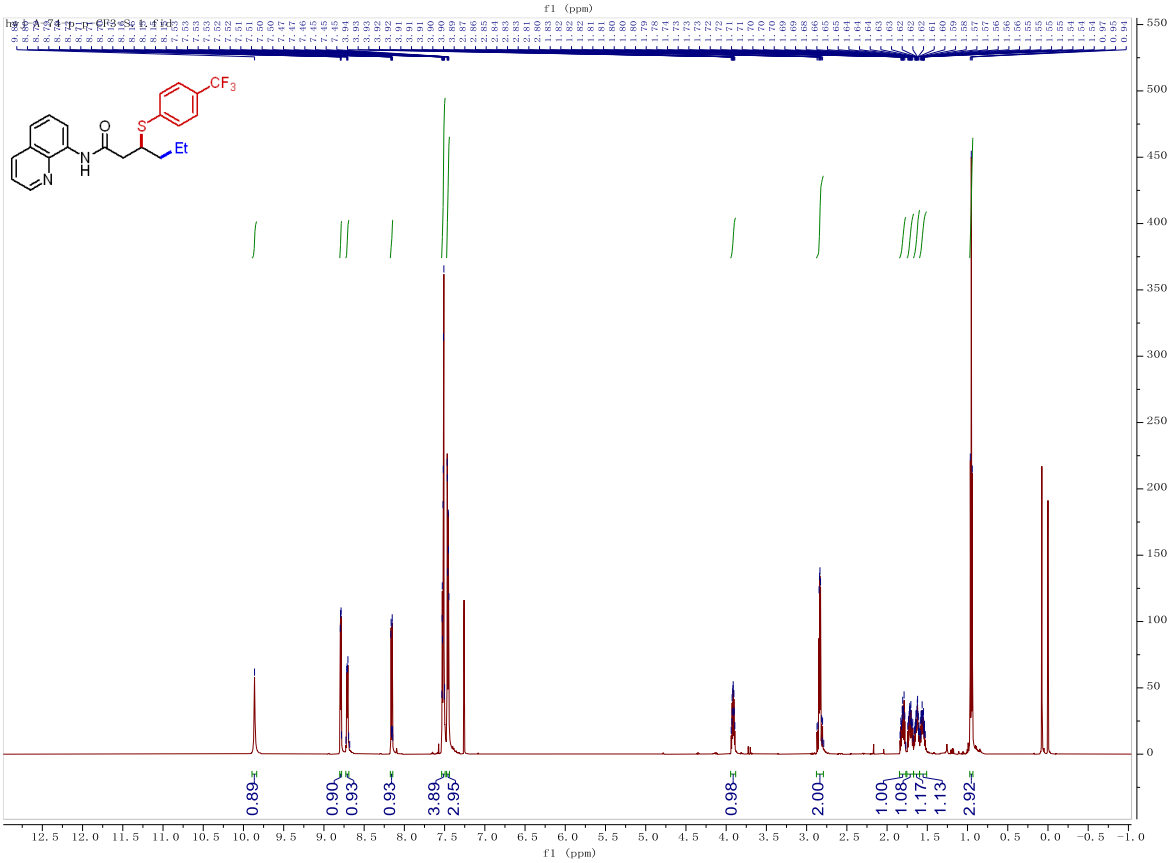

hwj-A-73-p_p-F-S.3.fid
-116.72
F
S
O
N
H
N
Et
f1 (ppm)

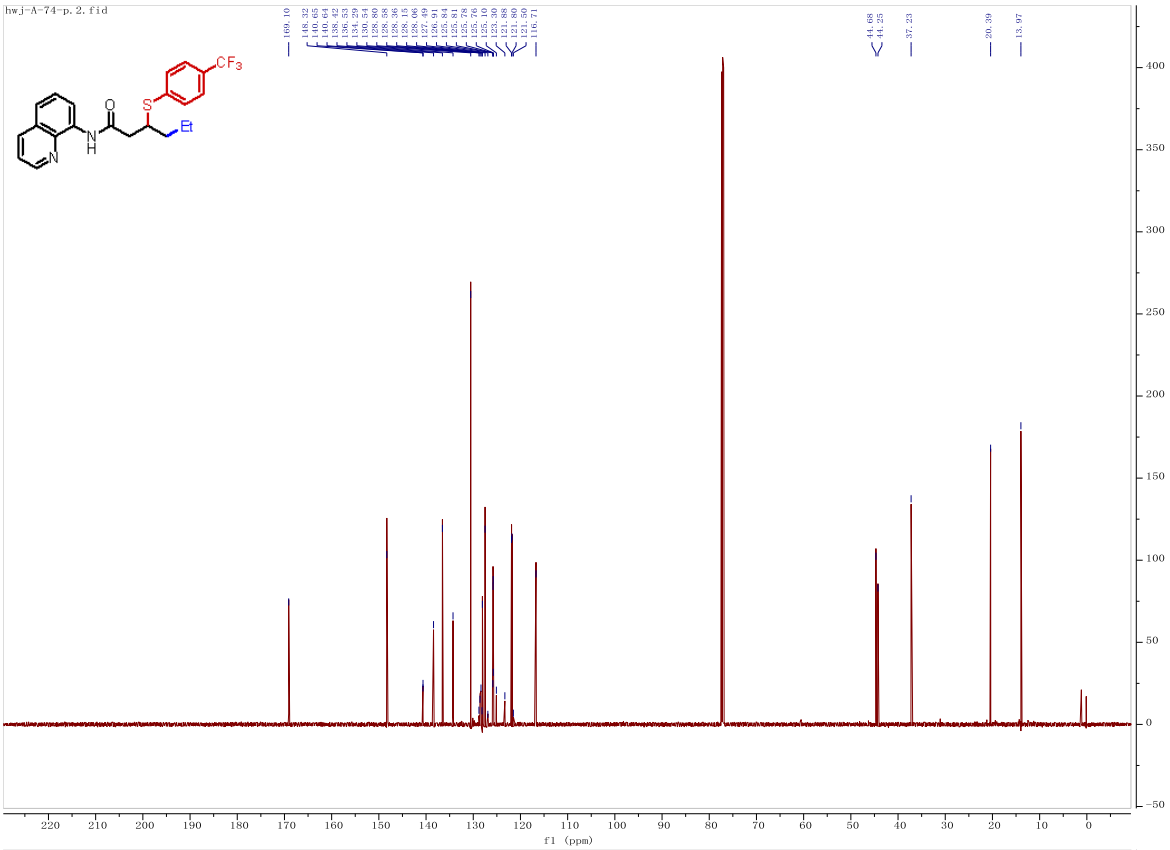

Cl
S
O
N
H
N
Et
0.92
1.01
0.95
1.01
2.07
1.01
1.98
1.96
1.00
2.03
1.01
2.49
1.07
3.00
f1 (ppm)

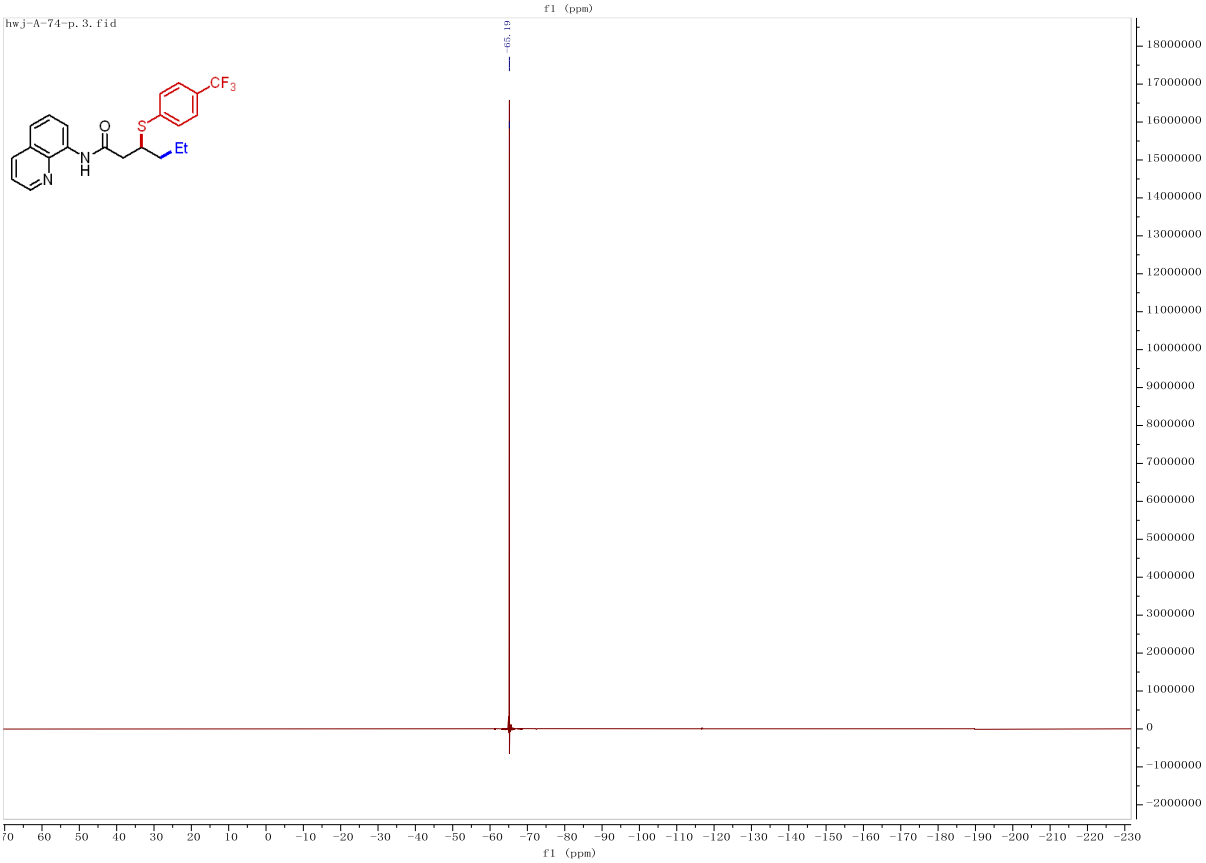

hwj-A-72-p_p-Cl-S.2.fid
169.29
148.30
138.43
136.51
134.36
134.00
133.42
133.08
129.19
128.06
127.51
121.81
121.77
116.71
45.85
44.17
37.13
20.35
13.96
Cl
S
O
N
H
N
Et
f1 (ppm)

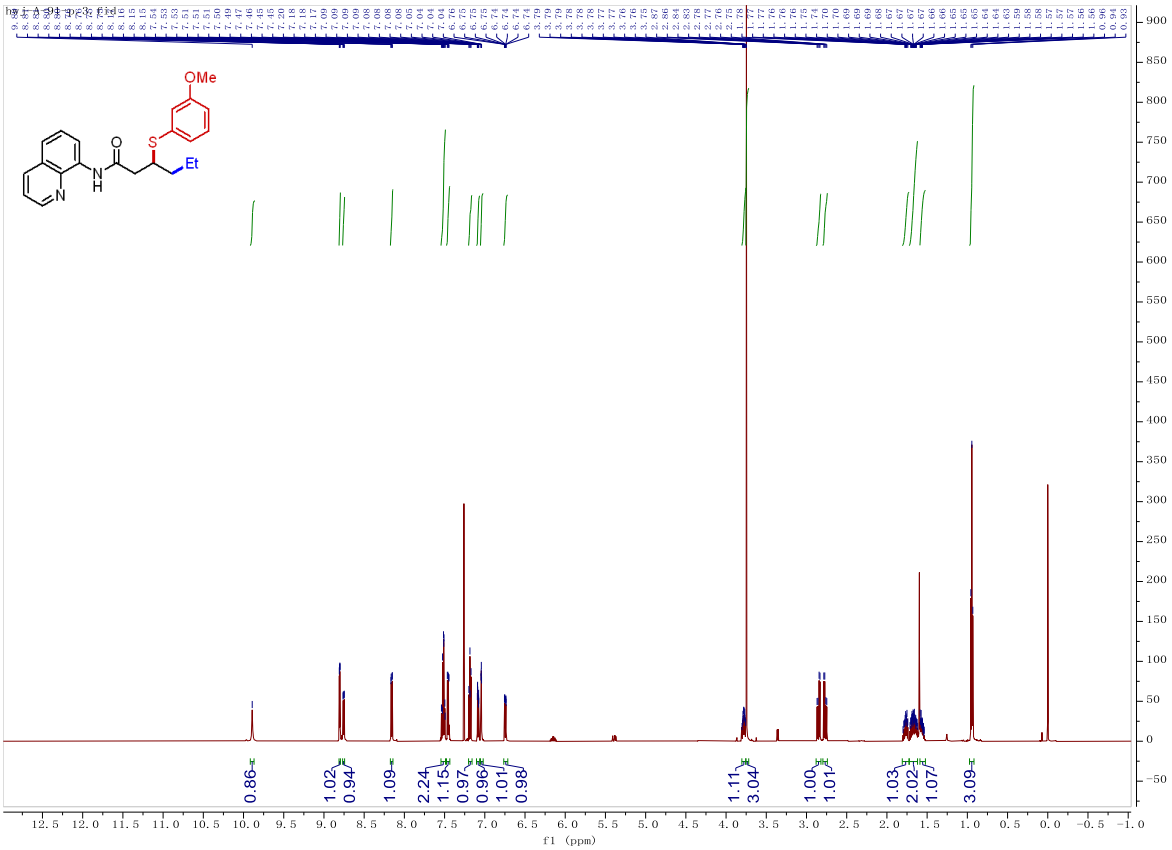

Br
S
O
N
H
N
Et
0.87
1.00
0.91
1.05
2.11
1.03
2.99
0.98
2.00
1.01
2.52
1.11
3.00
f1 (ppm)

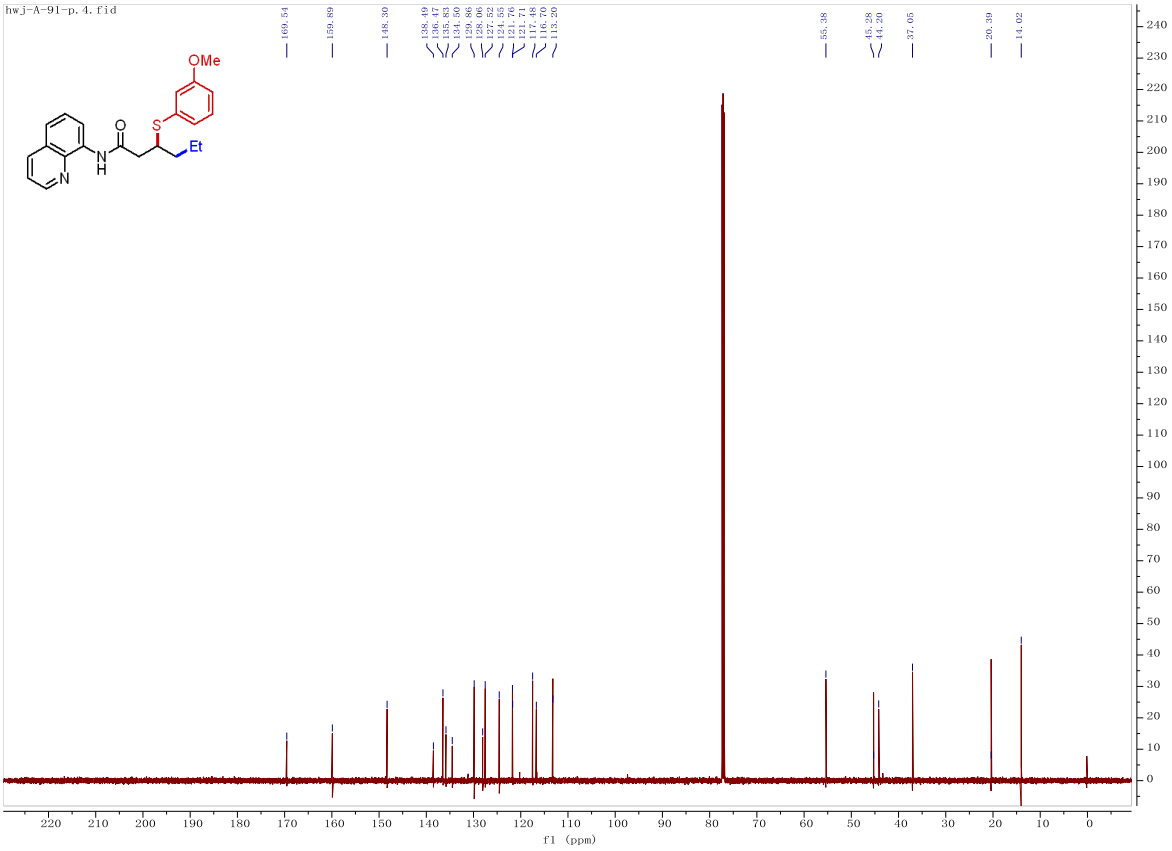

hwj-A-71-p.2.fid
169.27
148.30
138.43
136.51
134.35
134.11
133.81
132.11
130.86
127.52
121.82
121.77
121.39
116.72
45.70
44.18
37.14
20.36
13.97
Br
S
Et
O
N
H
f1 (ppm)

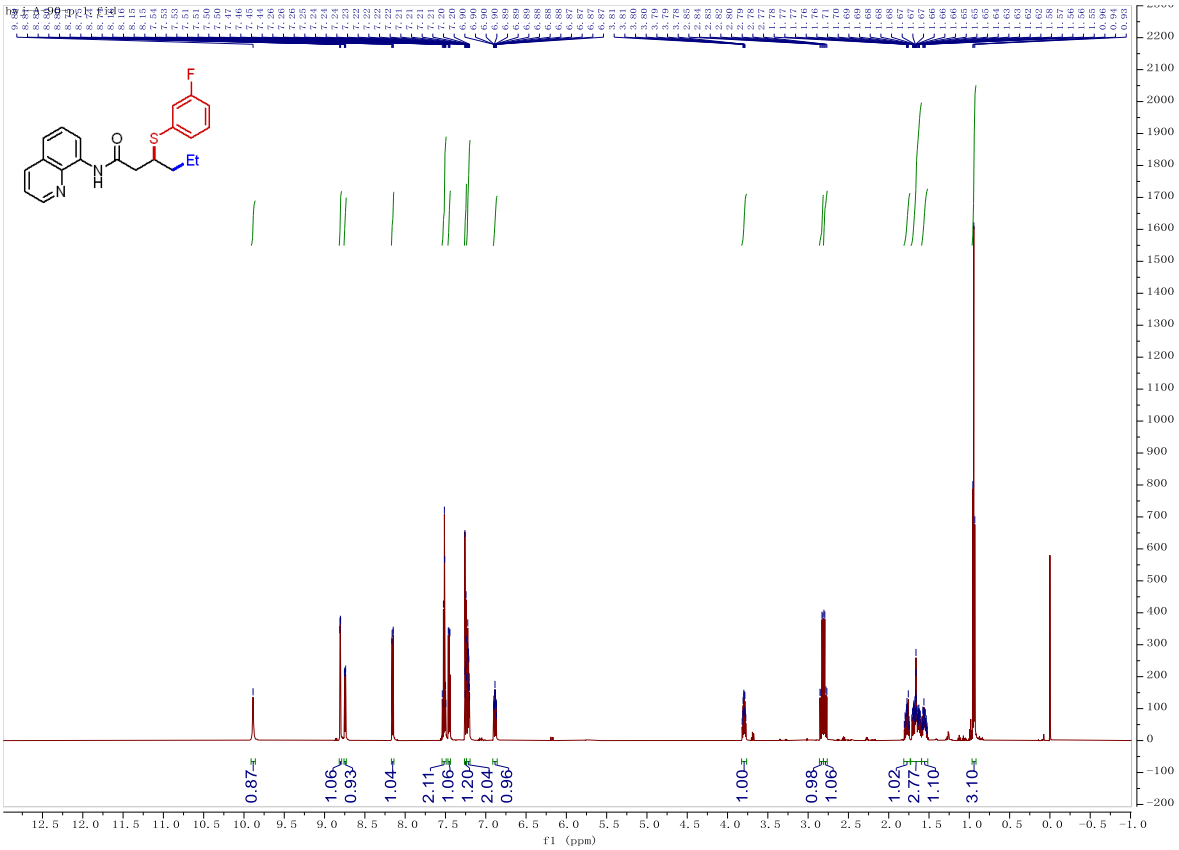

CF3
S
Et
O
N
H
0.89
0.90
0.93
0.93
3.89
2.95
0.98
2.00
1.00
1.08
1.17
1.13
2.92
f1 (ppm)

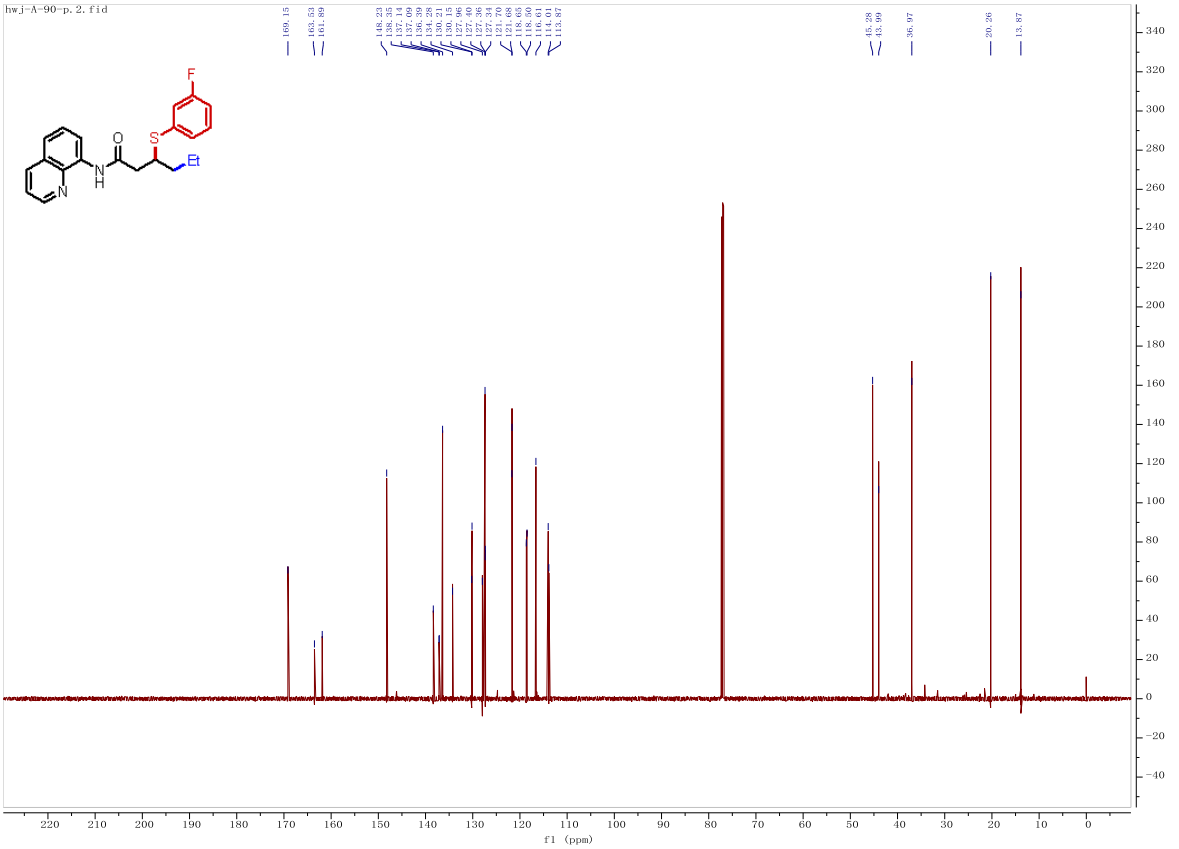

hwj-A-74-p.2.fid
169.10
148.32
140.65
140.64
138.42
136.53
134.29
130.54
128.89
128.58
128.36
128.15
128.06
127.40
126.91
125.84
125.81
125.78
125.76
125.10
123.30
121.88
121.80
121.69
116.71
44.68
44.25
37.23
20.39
13.97
CF3
S
Et
N
H
O
f1 (ppm)

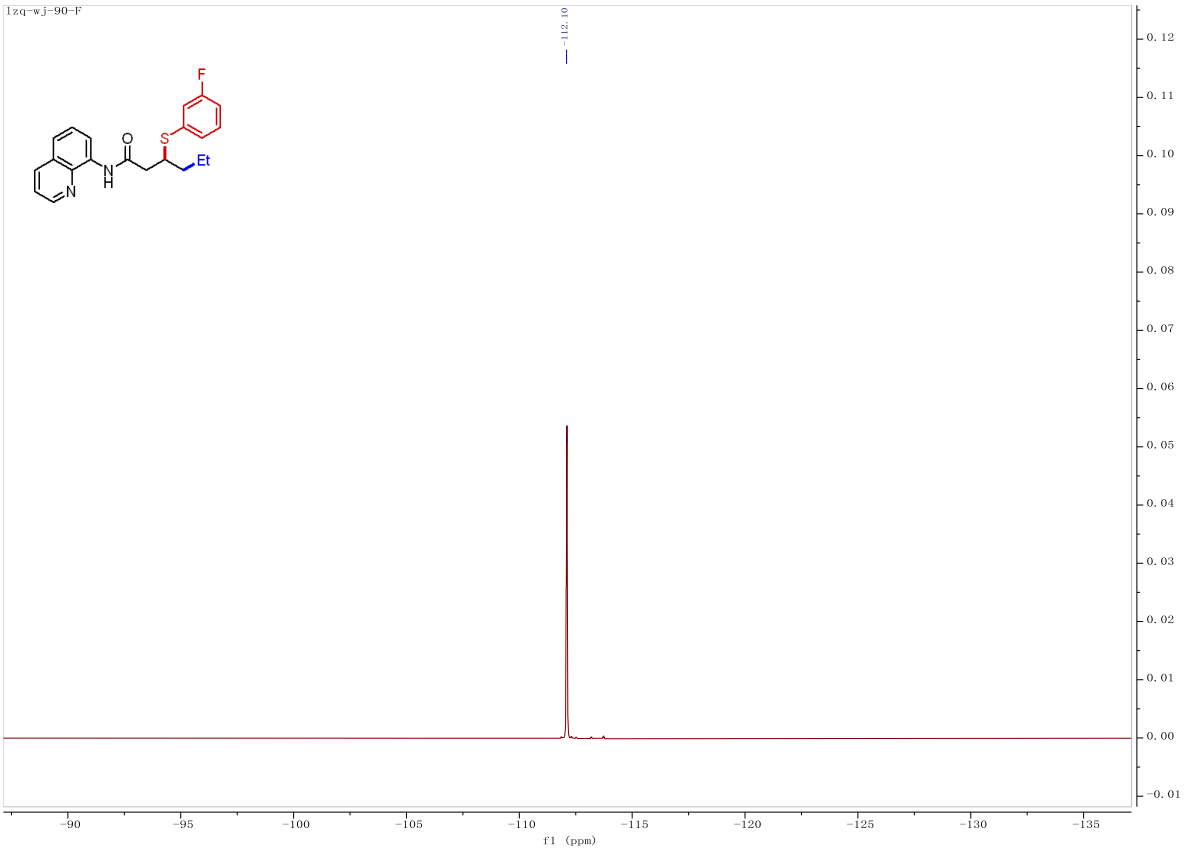

hwj-A-74-p.3.fid
-65.19
CF3
S
Et
N
H
O
f1 (ppm)

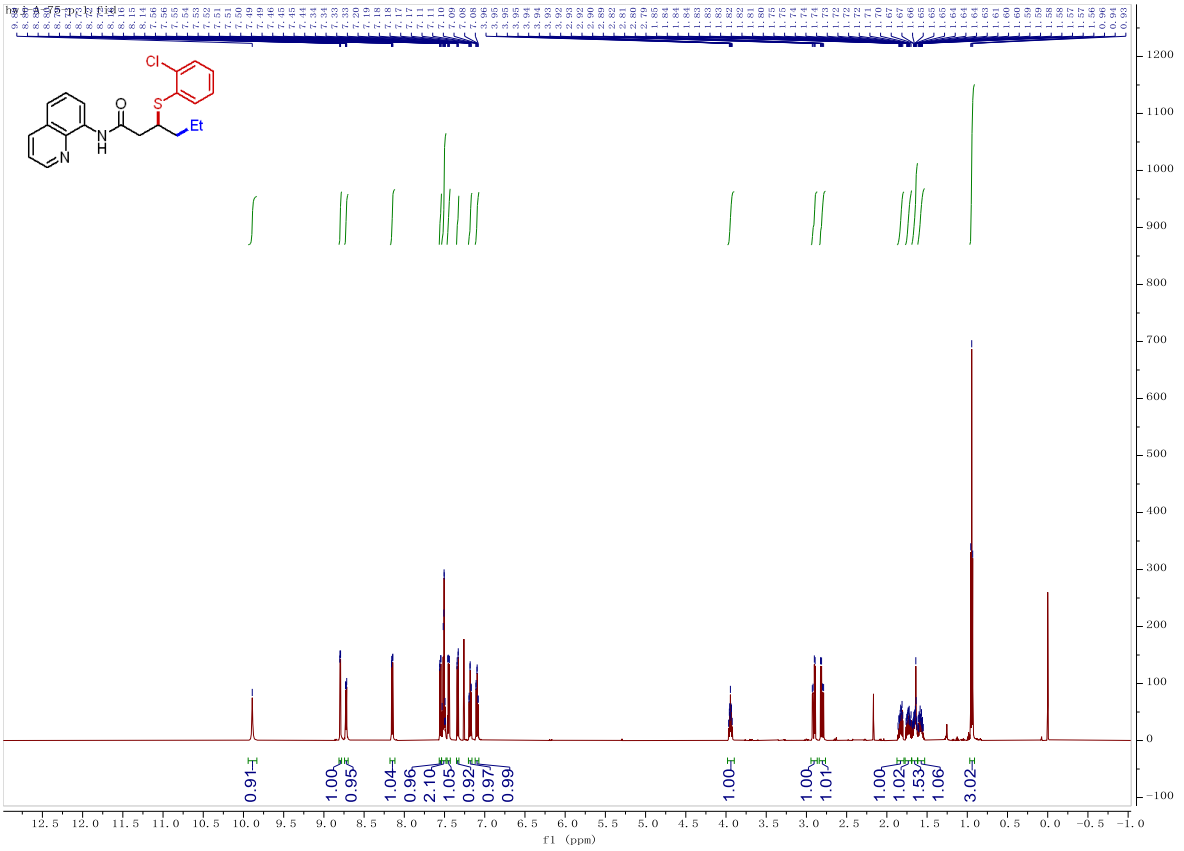

OMe
S
Et
O
N
H
N
0.86
1.02
0.94
1.09
2.24
1.15
0.97
0.96
1.01
0.98
1.11
3.04
1.00
1.01
1.03
2.02
1.07
3.09
f1 (ppm)

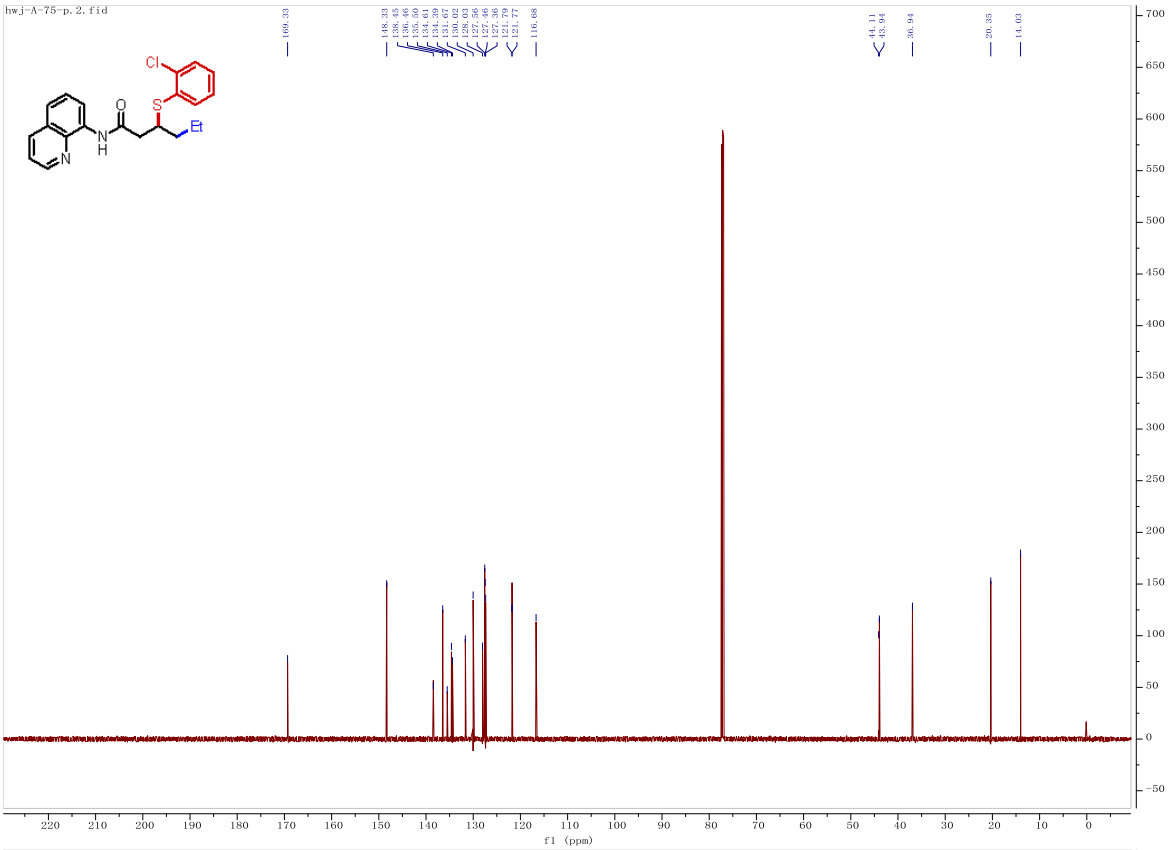

hwj-A-91-p.4.fid
OMe
S
Et
O
N
H
N
169.54
159.89
148.30
138.49
136.47
135.83
134.60
129.96
128.06
127.52
124.55
121.76
121.71
117.48
116.70
113.20
55.38
45.28
44.20
37.05
26.39
14.02
f1 (ppm)

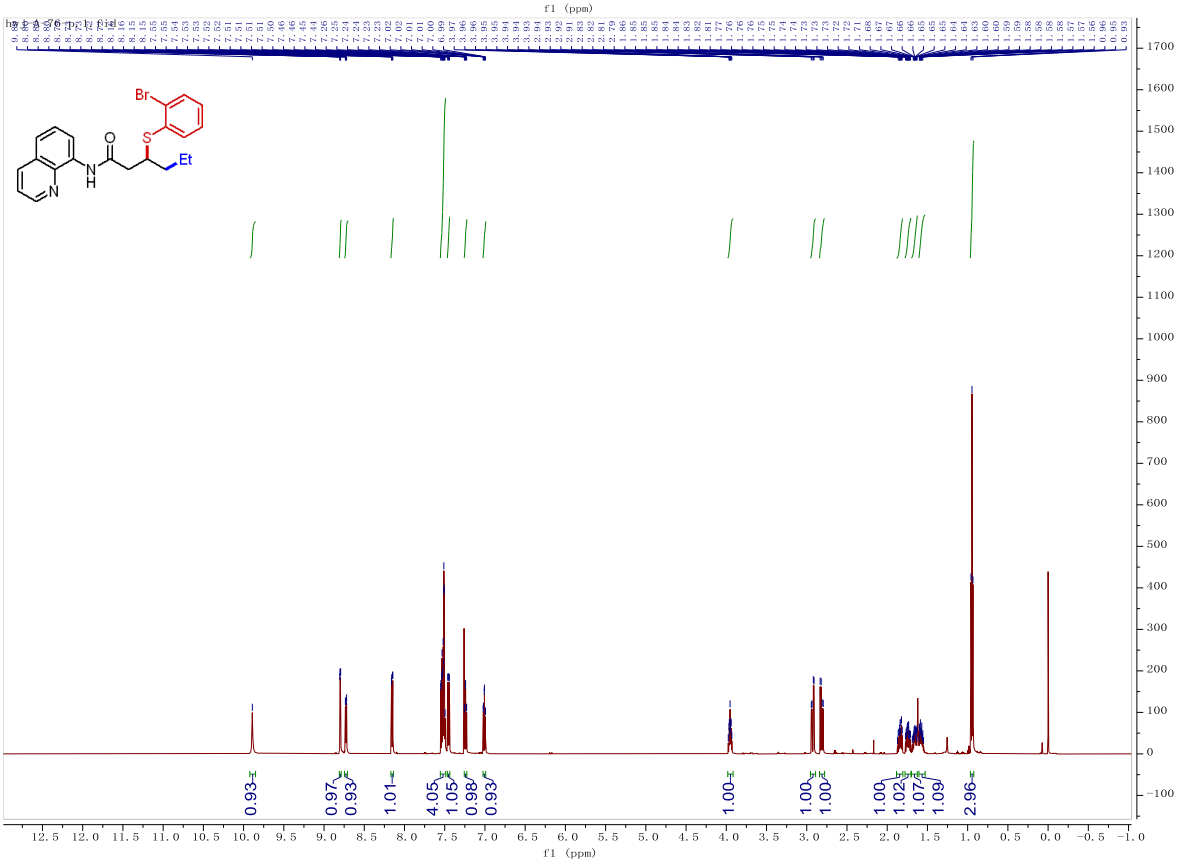

F
S
Et
O
N
H
N
0.87
1.06
0.93
1.04
2.11
1.06
1.20
2.04
0.96
1.00
0.98
1.06
1.02
2.77
1.10
3.10
f1 (ppm)

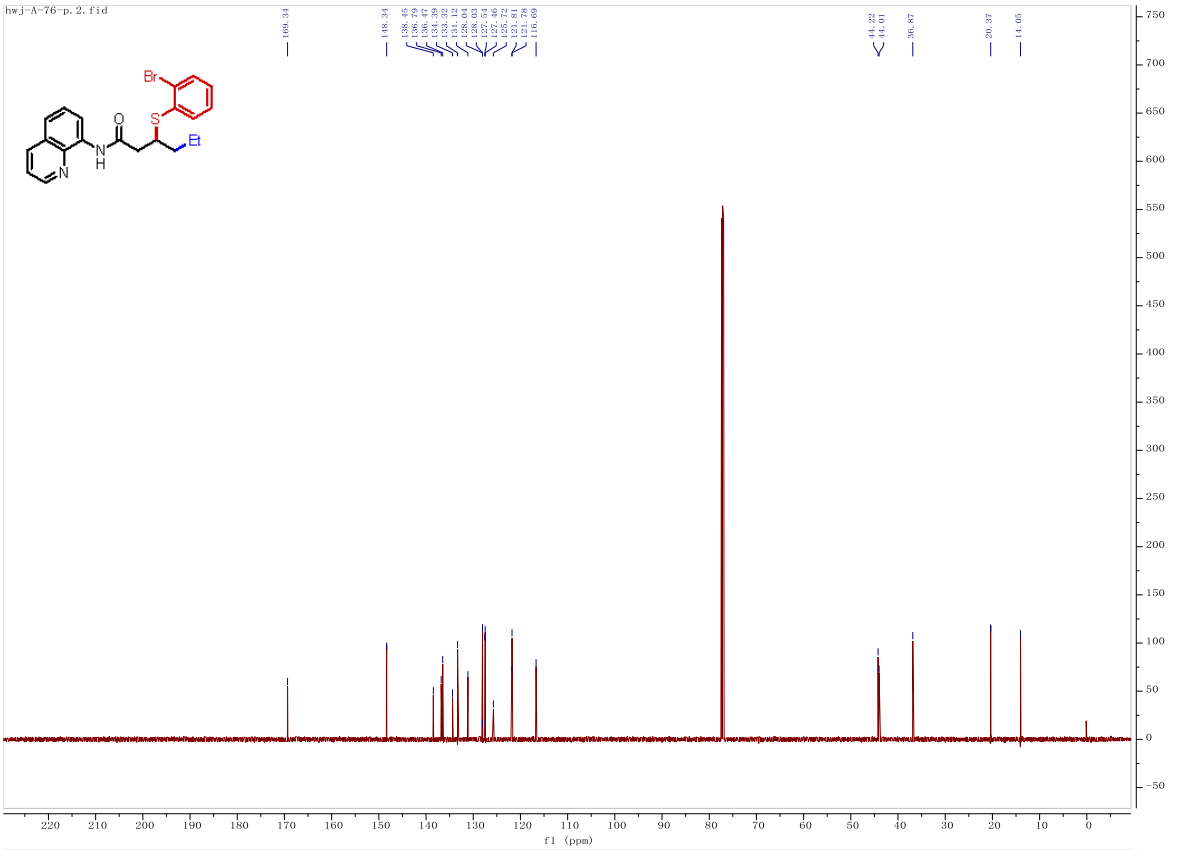

hwj-A-90-p.2.fid
F
S
Et
O
N
H
N
f1 (ppm)

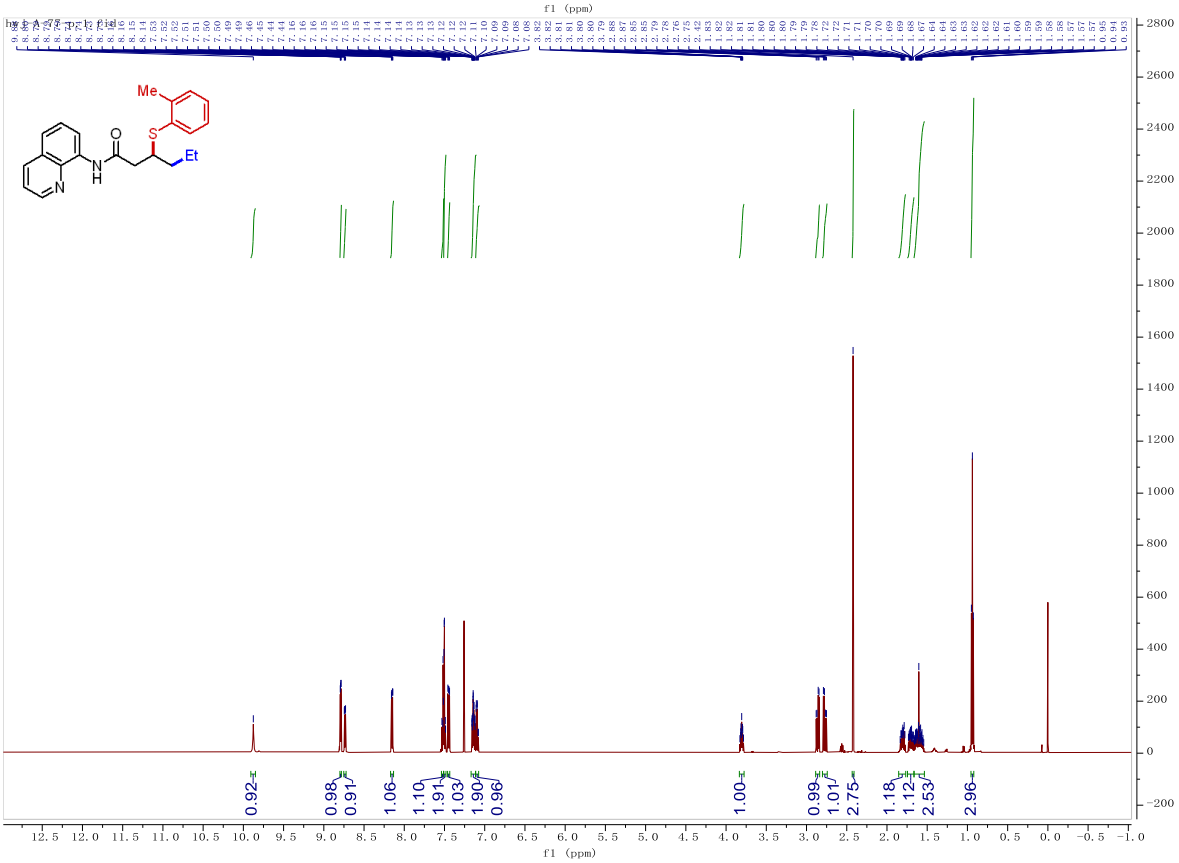

lzq-wj-90-F
-112.10
F
S
Et
N
H
O
f1 (ppm)

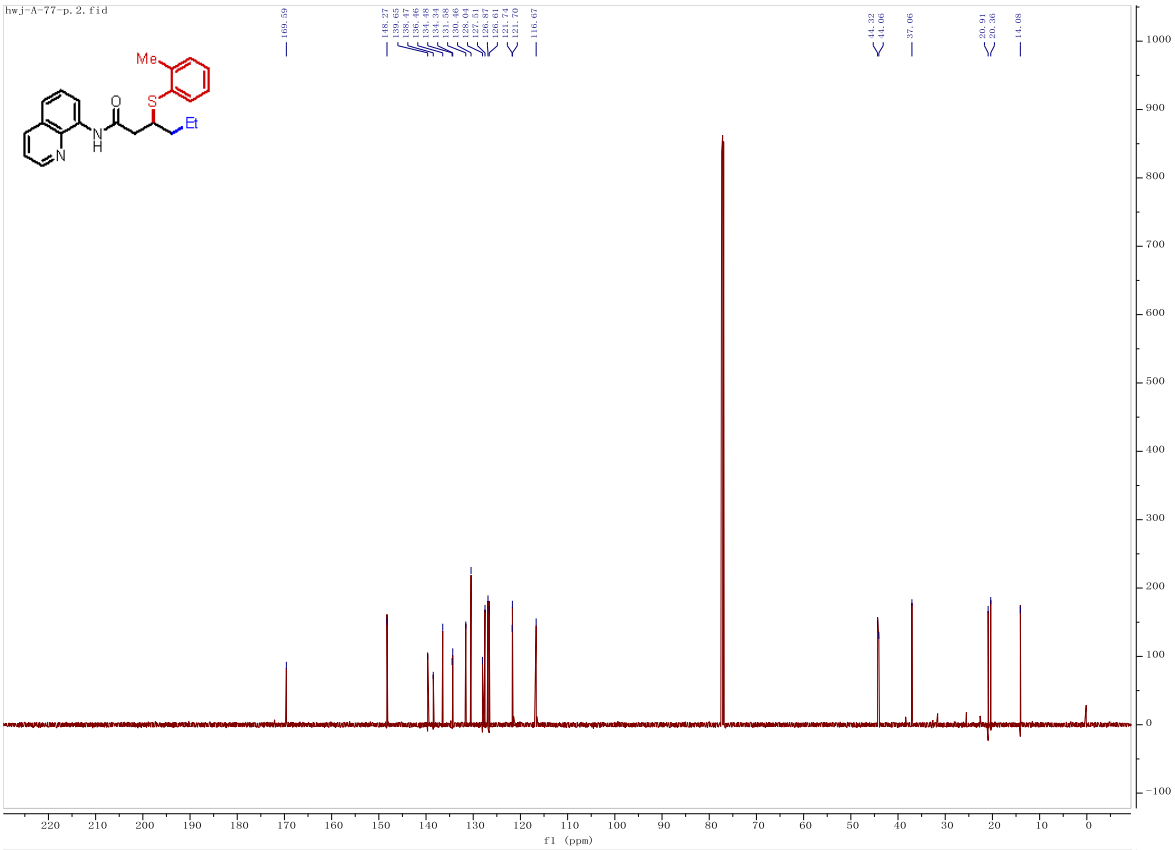

Cl
S
Et
N
H
O
0.91
1.00
0.95
1.04
0.96
2.10
1.05
0.92
0.97
0.99
1.00
1.00
1.01
1.00
1.02
1.53
1.06
3.02
f1 (ppm)

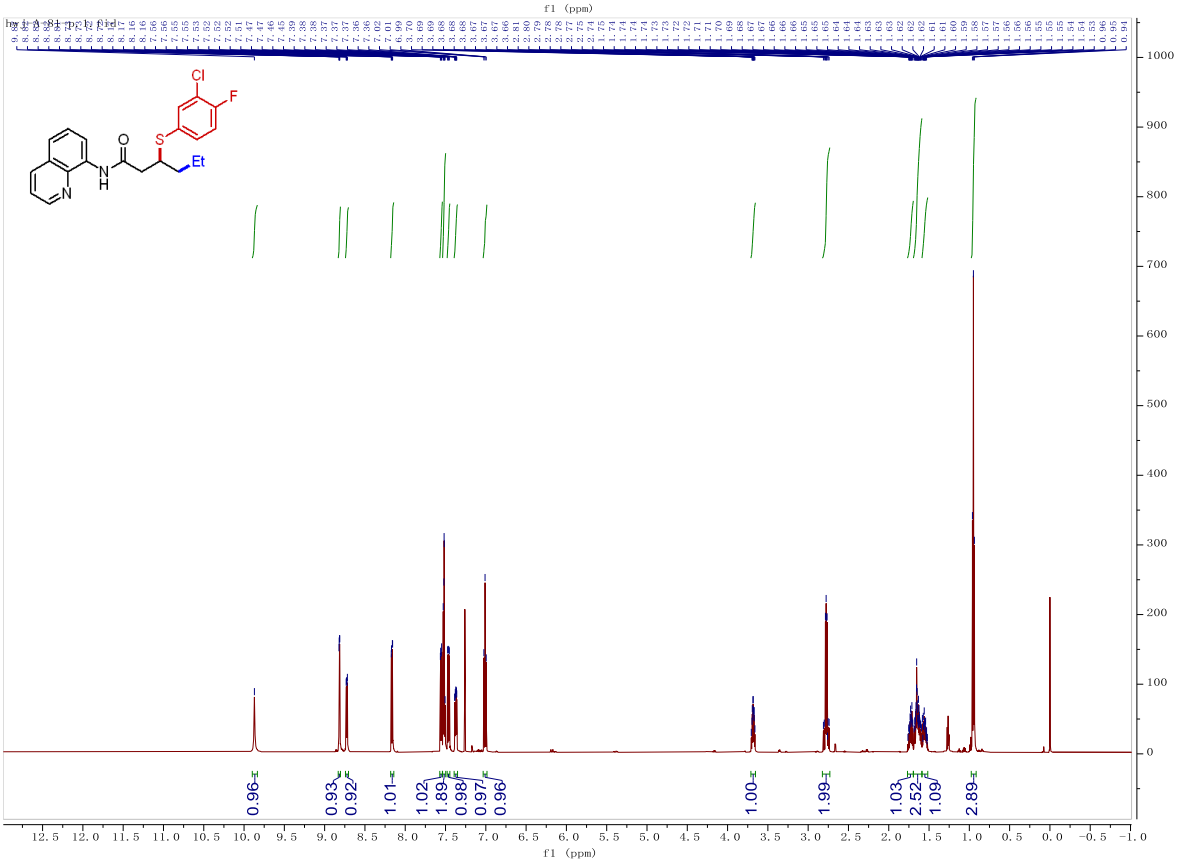

hwj-A-75-p.2.fid
Cl
S
Et
O
N
H
N
169.33
148.33
138.45
136.46
135.50
134.61
134.39
131.67
130.02
128.03
127.56
127.46
127.36
121.79
121.77
116.68
44.11
43.94
36.94
20.35
14.03
f1 (ppm)

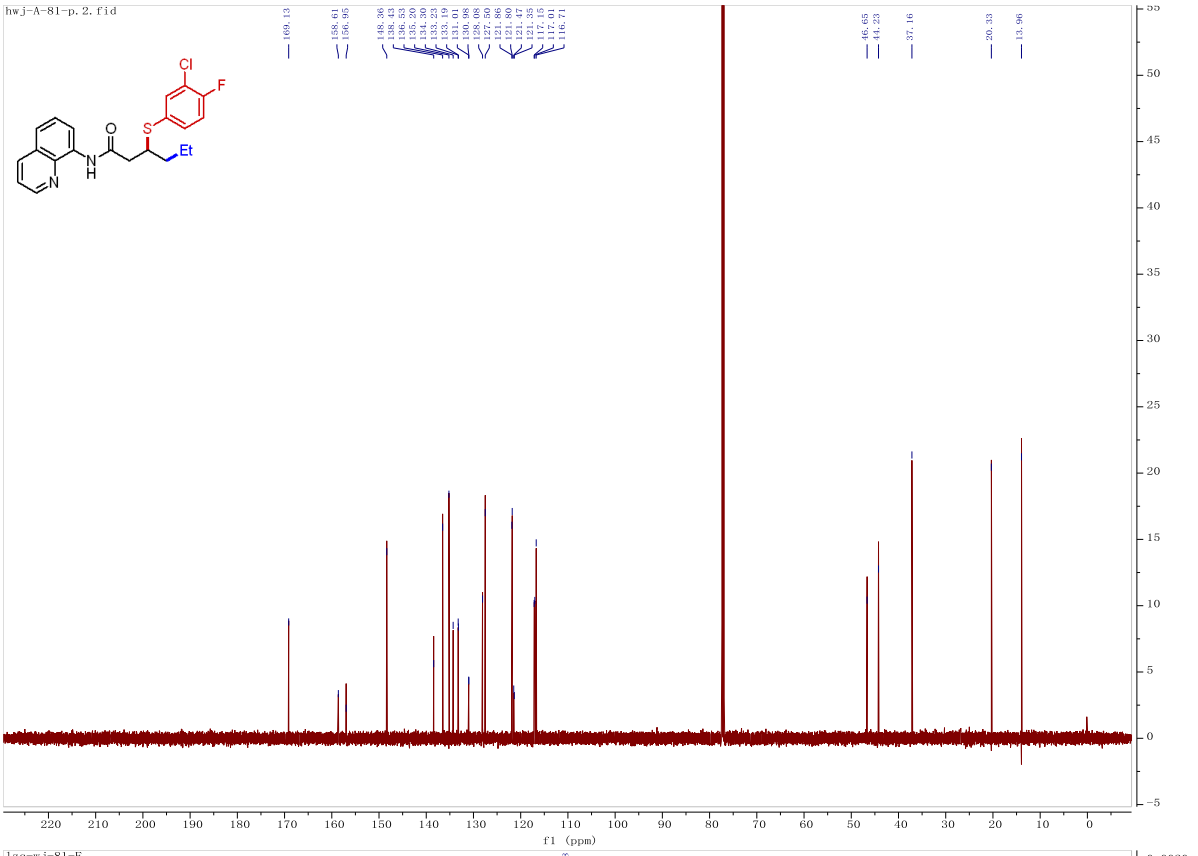

Br
S
Et
O
N
H
0.93
0.97
0.93
1.01
4.05
1.05
0.98
0.93
1.00
1.00
1.00
1.00
1.02
1.07
1.09
2.96
f1 (ppm)

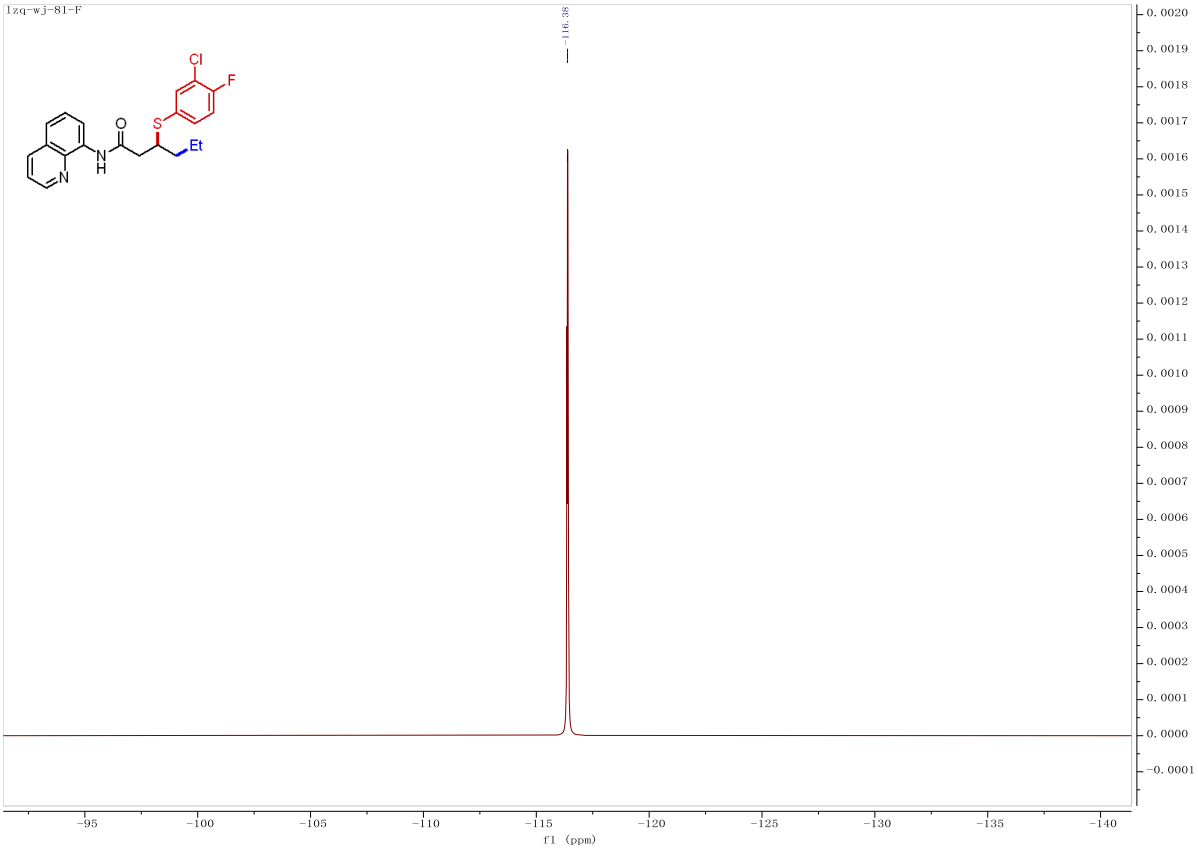

hwj-A-76-p.2.fid
Br
S
Et
O
N
H
N
169.34
148.34
138.45
136.79
134.67
134.39
133.32
131.12
128.04
128.03
127.54
125.40
125.72
121.81
121.78
116.69
44.22
44.01
36.87
20.37
14.05
f1 (ppm)

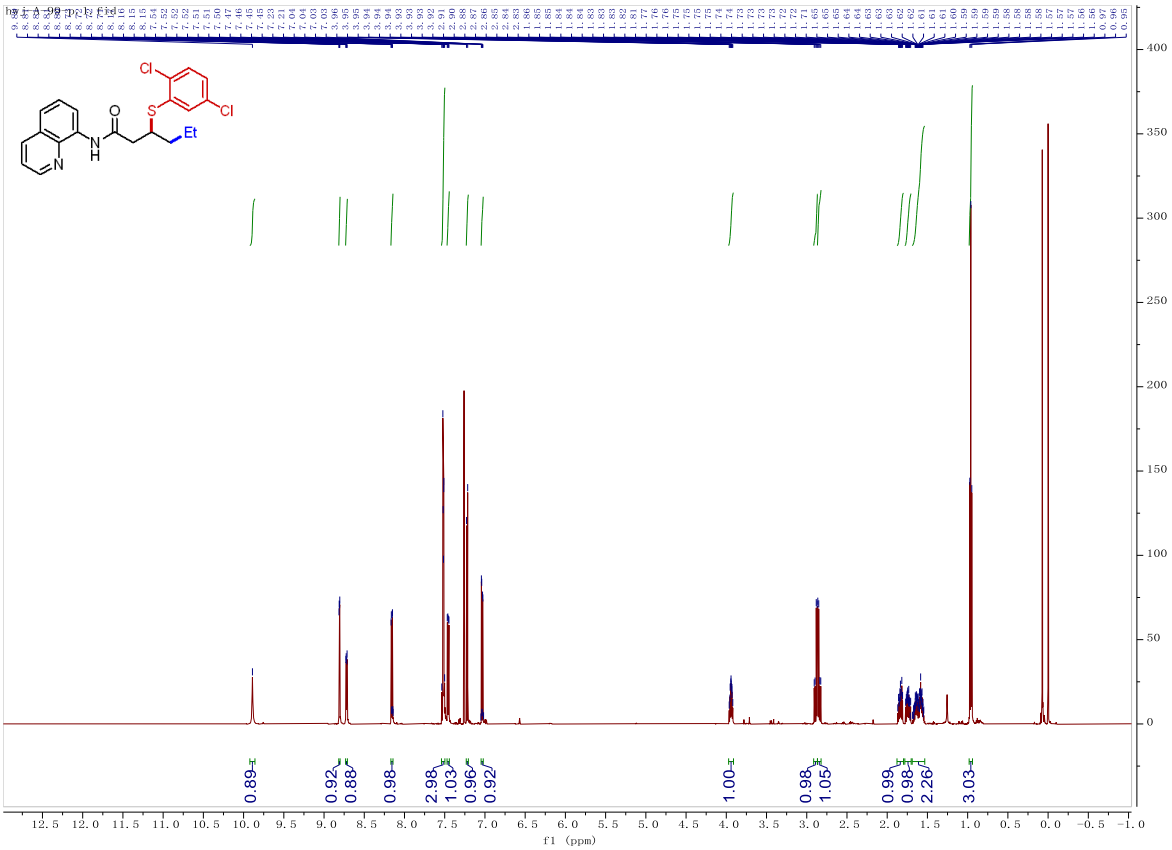

Me
S
Et
O
N
H
N
0.92
0.98
0.91
1.06
1.10
1.91
1.03
1.90
0.96
1.00
0.99
1.01
2.75
1.18
1.12
2.53
2.96
f1 (ppm)

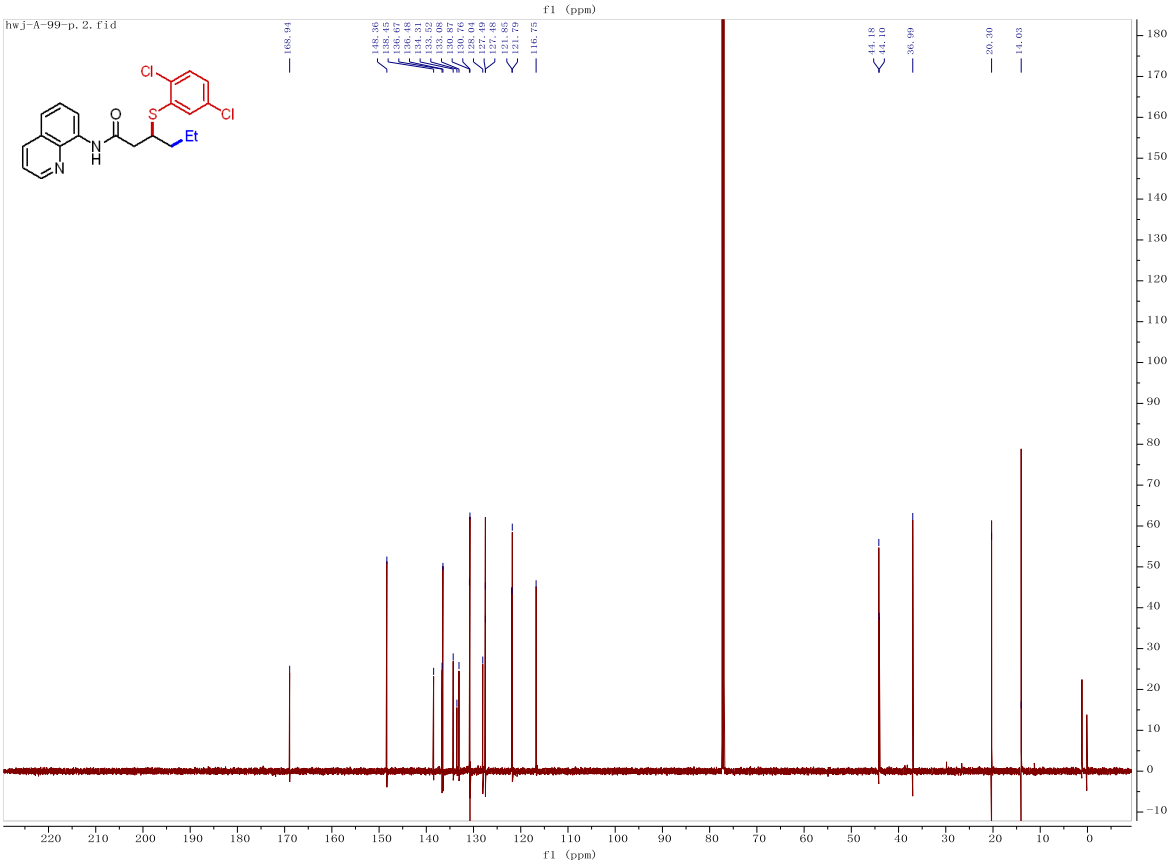

hwj-A-77-p.2.fid
Me
S
Et
O
N
H
N
169.59
148.27
139.65
138.47
136.46
134.68
134.34
131.08
130.66
128.04
127.51
126.87
126.61
121.74
121.70
116.67
44.32
44.06
37.06
20.91
20.36
14.08
f1 (ppm)

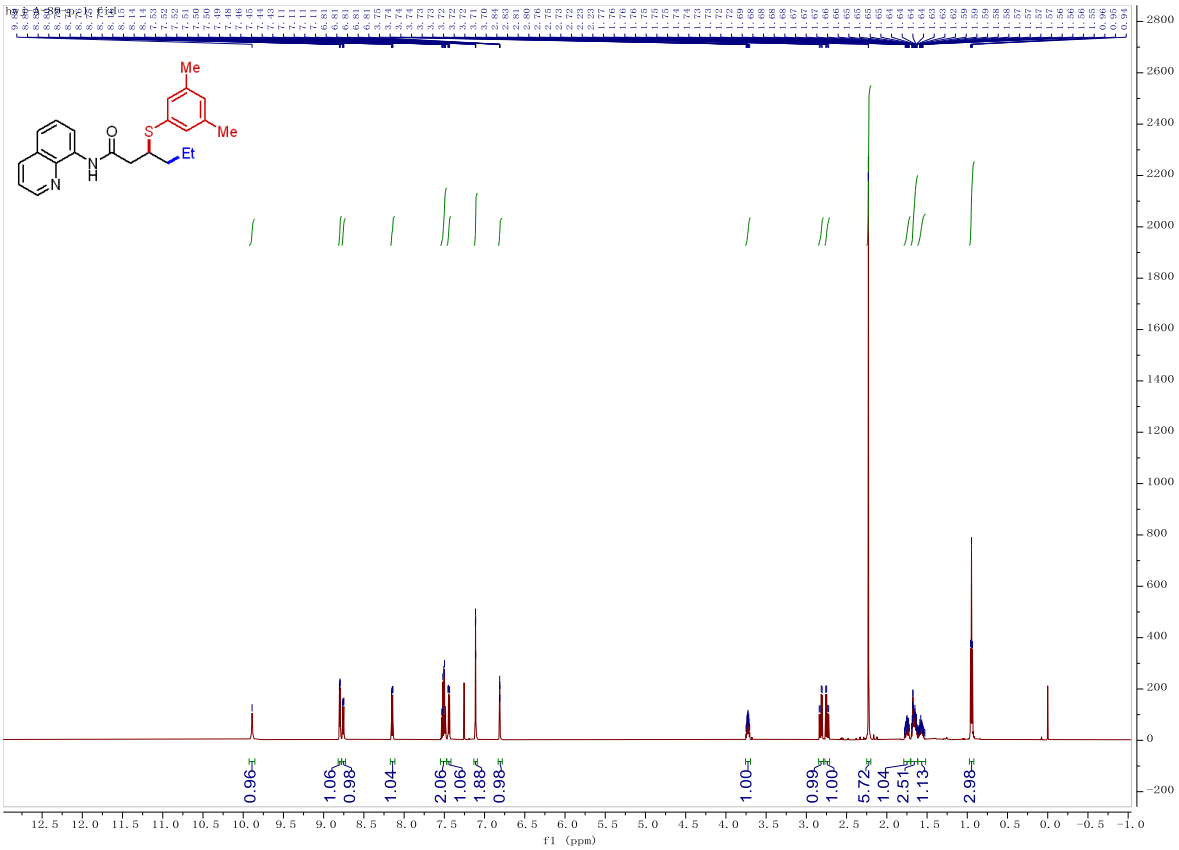

Cl
F
S
Et
O
N
H
0.96
0.93
0.92
1.01
1.02
1.89
0.98
0.97
0.96
1.00
1.99
1.03
2.52
1.09
2.89
f1 (ppm)

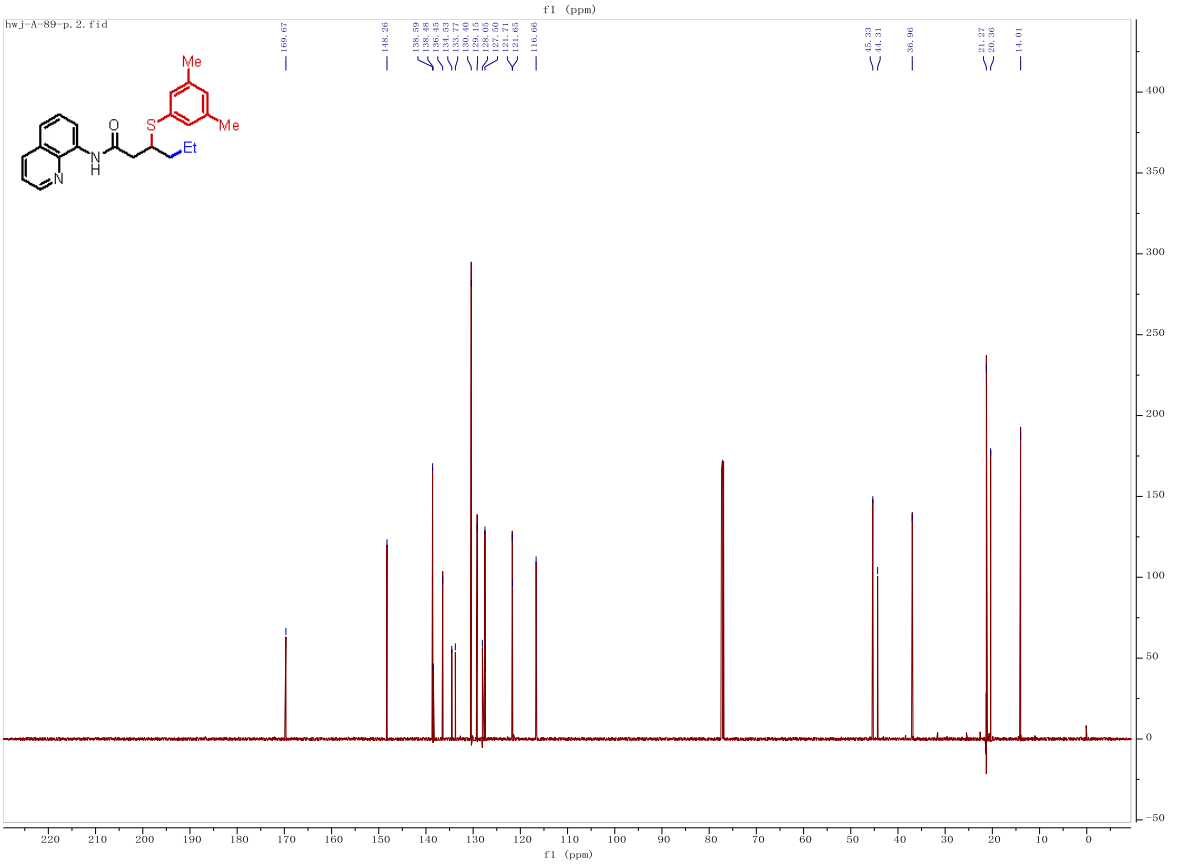

hwj-A-81-p.2.fid
169.13
158.61
156.95
148.36
138.43
136.53
135.00
134.30
133.23
133.19
131.01
130.98
128.08
127.59
121.86
121.60
121.47
121.35
117.15
117.01
116.71
46.65
44.23
37.16
20.33
13.96
Cl
F
S
Et
O
N
H
f1 (ppm)

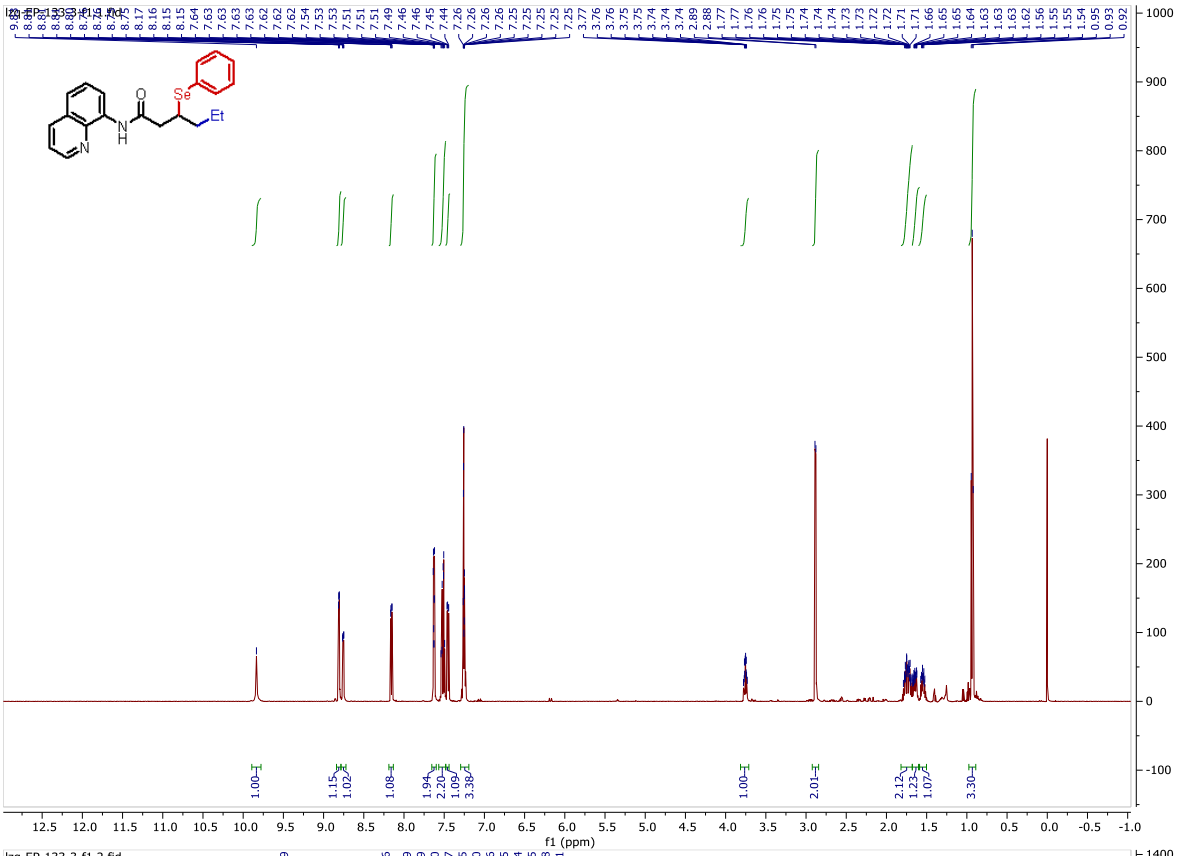

lzq-wj-81-F
-116.38
Cl
F
S
Et
O
N
H
f1 (ppm)

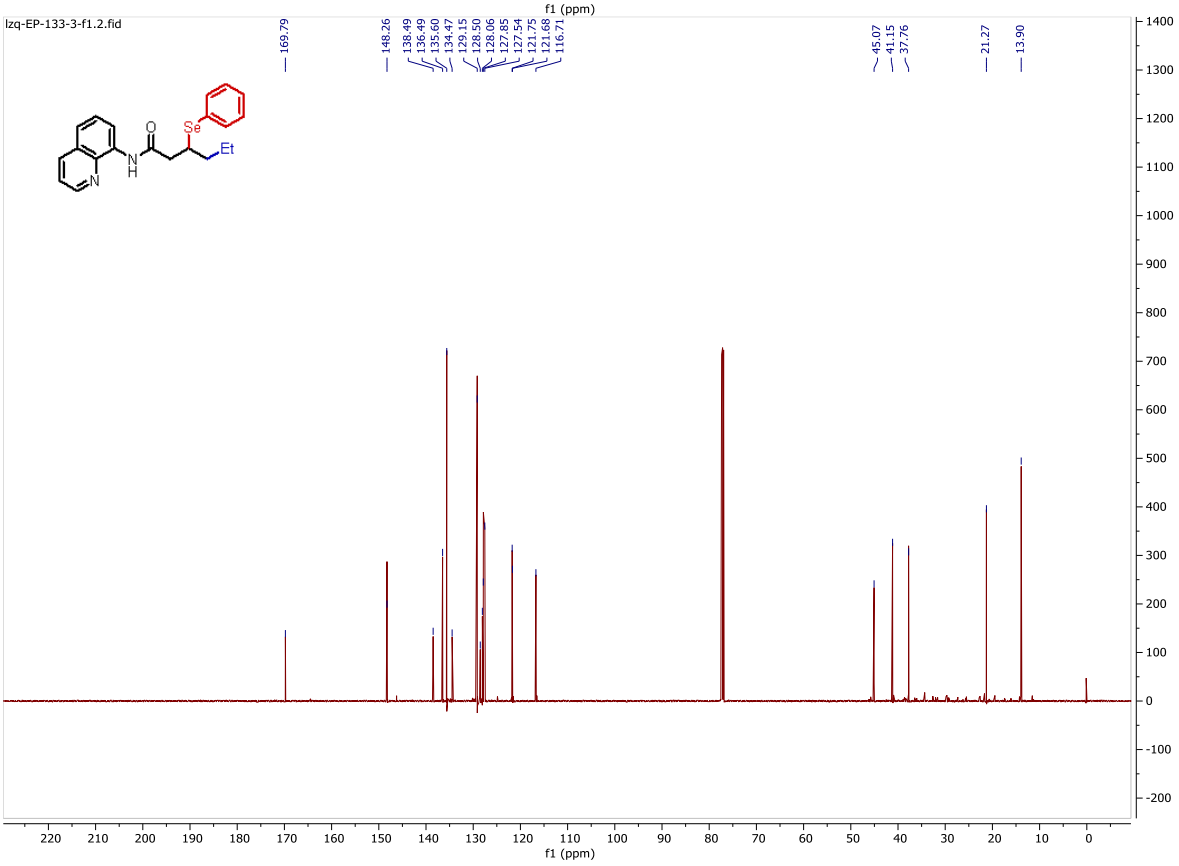

Cl
S
Cl
Et
O
N
H
N
0.89
0.92
0.88
0.98
2.98
1.03
0.96
0.92
1.00
0.98
1.05
0.99
0.98
2.26
3.03
f1 (ppm)

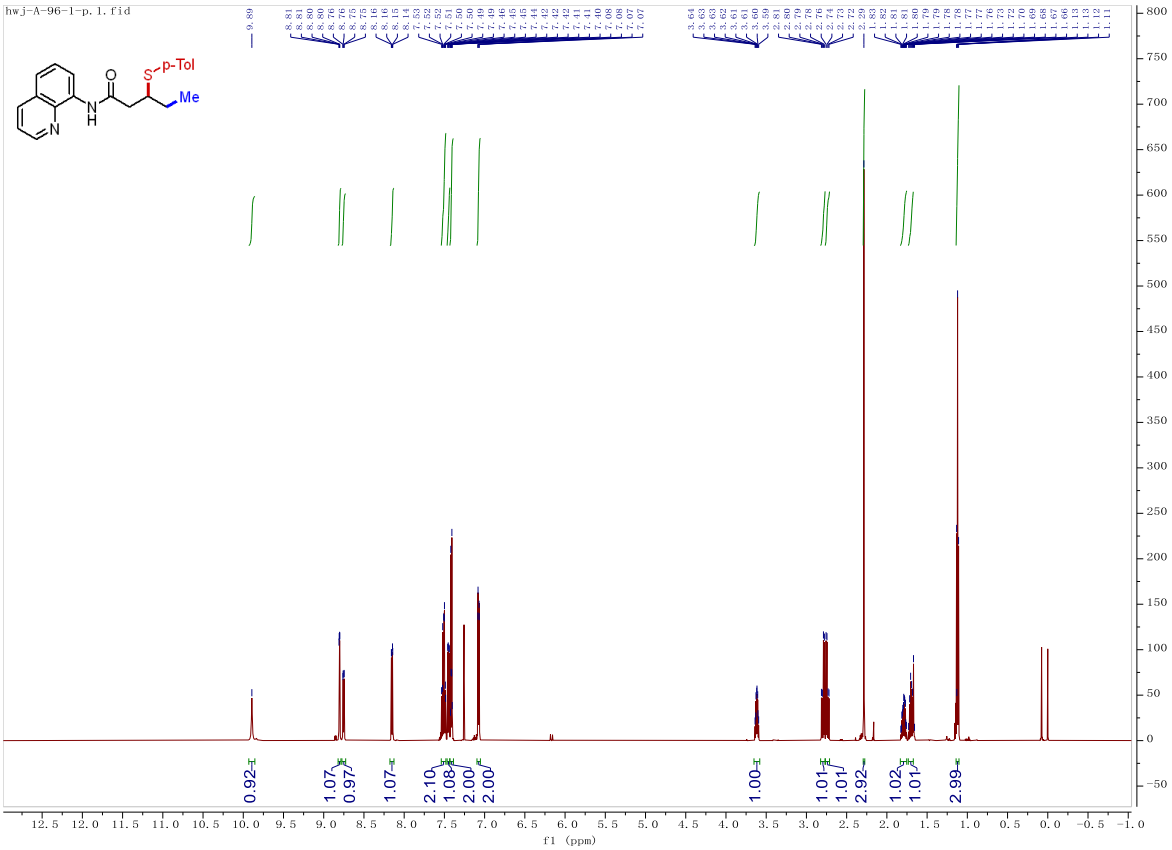

hwj-A-99-p.2.fid
168.94
148.36
138.45
136.67
136.48
134.31
133.82
133.06
130.87
130.76
128.04
127.49
127.48
121.85
121.79
116.75
44.18
44.10
36.99
20.30
14.03
Cl
S
Cl
Et
O
N
H
N
f1 (ppm)

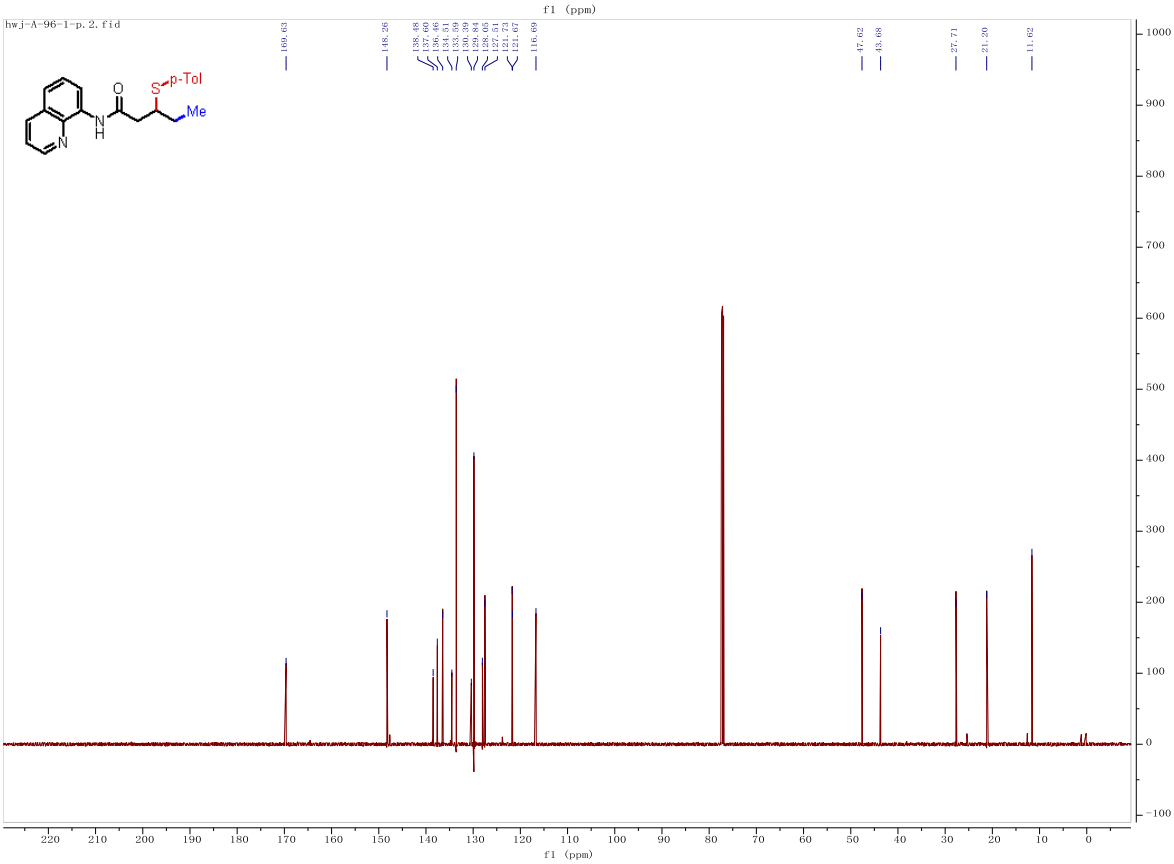

Me
Me
S
O
N
H
Et
N
0.96
1.06
0.98
1.04
2.06
1.06
1.88
0.98
1.00
0.99
1.00
5.72
1.04
2.51
1.13
2.98
f1 (ppm)

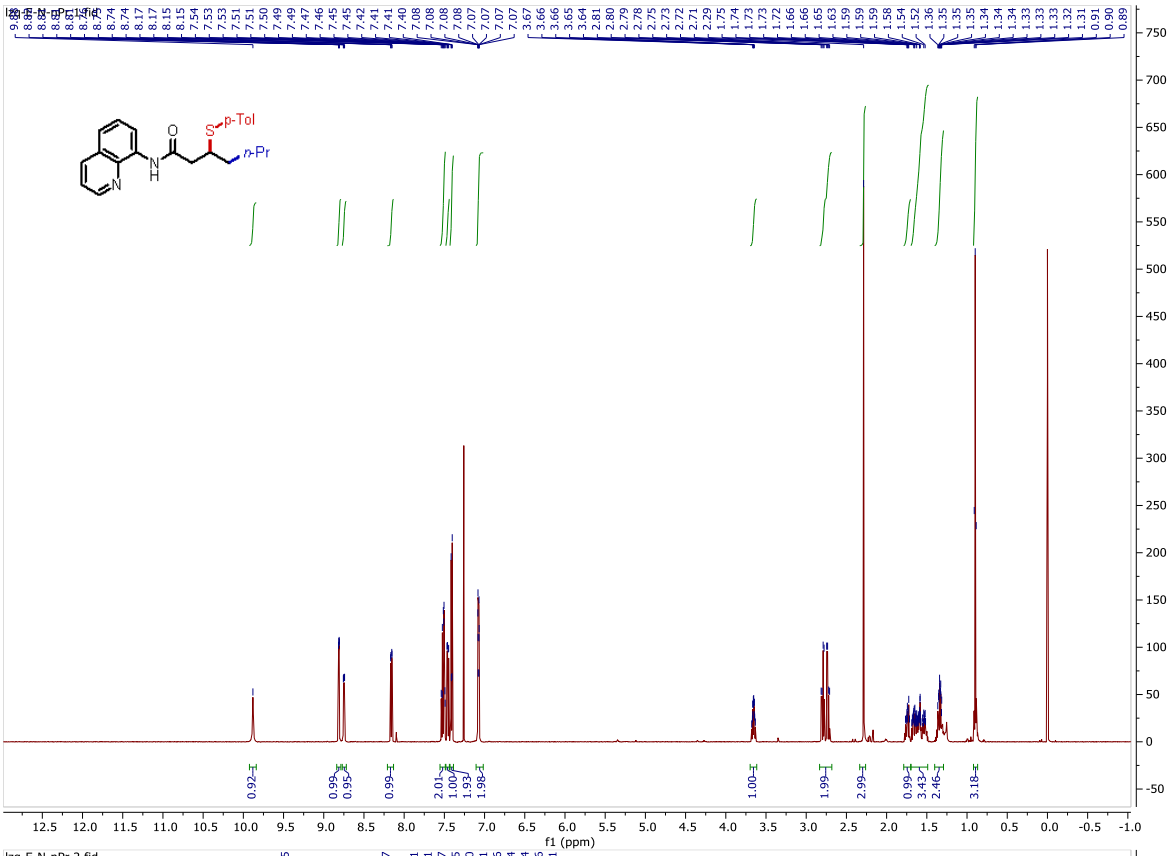

hwj-A-89-p.2.fid
Me
Me
S
O
N
H
Et
N
169.67
148.26
138.59
138.46
136.45
134.53
132.77
130.49
129.15
128.05
127.60
121.71
121.65
116.66
45.33
44.31
36.96
21.27
20.36
14.01
f1 (ppm)

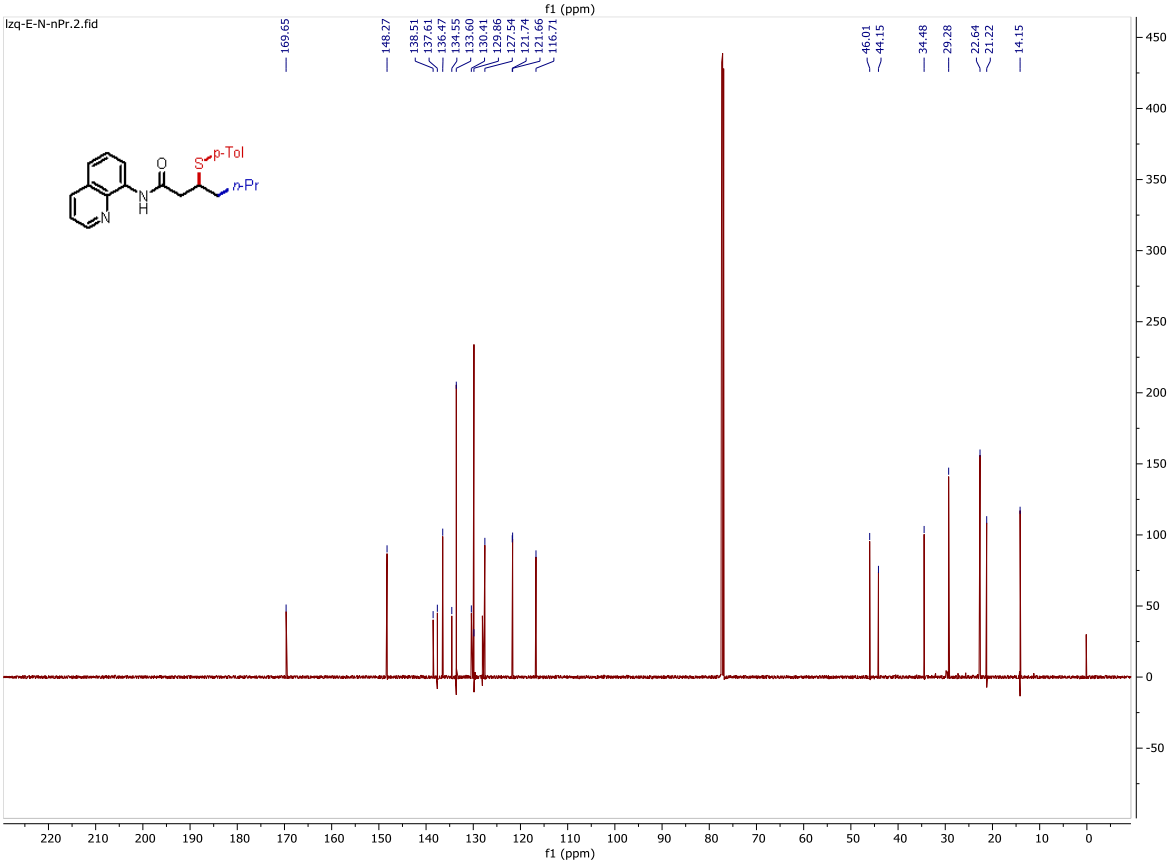

1.00
1.15
1.02
1.08
1.94
2.20
1.09
3.38
1.00
2.01
2.12
1.23
1.07
3.30
f1 (ppm)

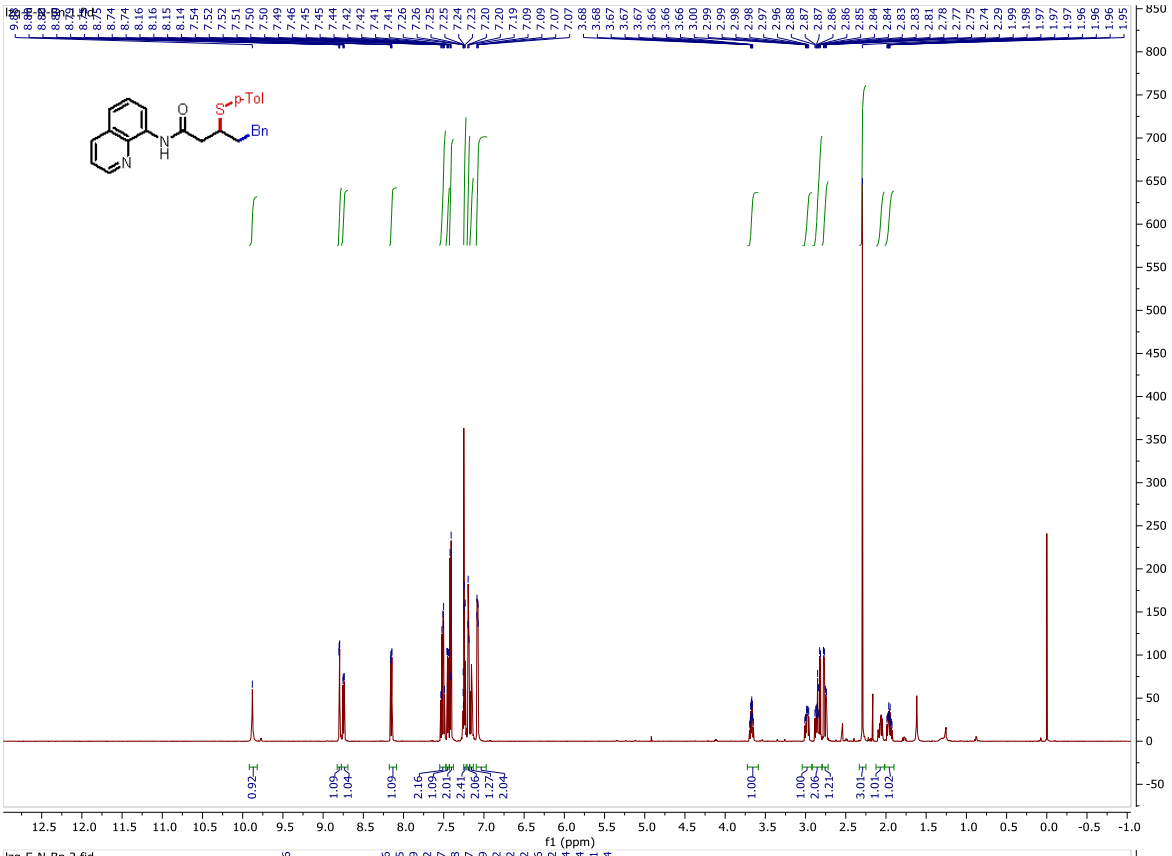

lzq-EP-133-3-f1.2.fid
169.79
148.26
138.49
136.49
135.60
134.47
129.15
128.50
128.06
127.85
127.54
121.75
121.68
116.71
45.07
41.15
37.76
21.27
13.90
f1 (ppm)

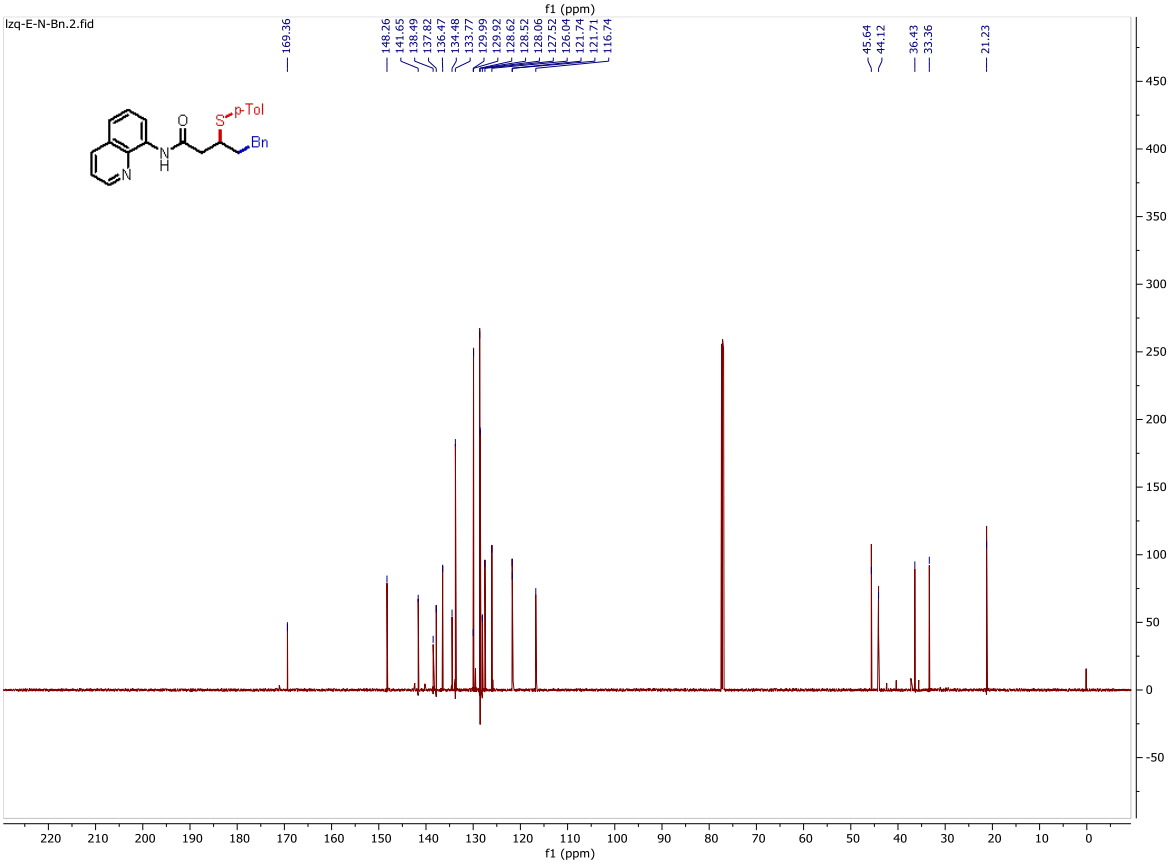

hwj-A-96-1-p.1.fid
p-Tol
Me
f1 (ppm)

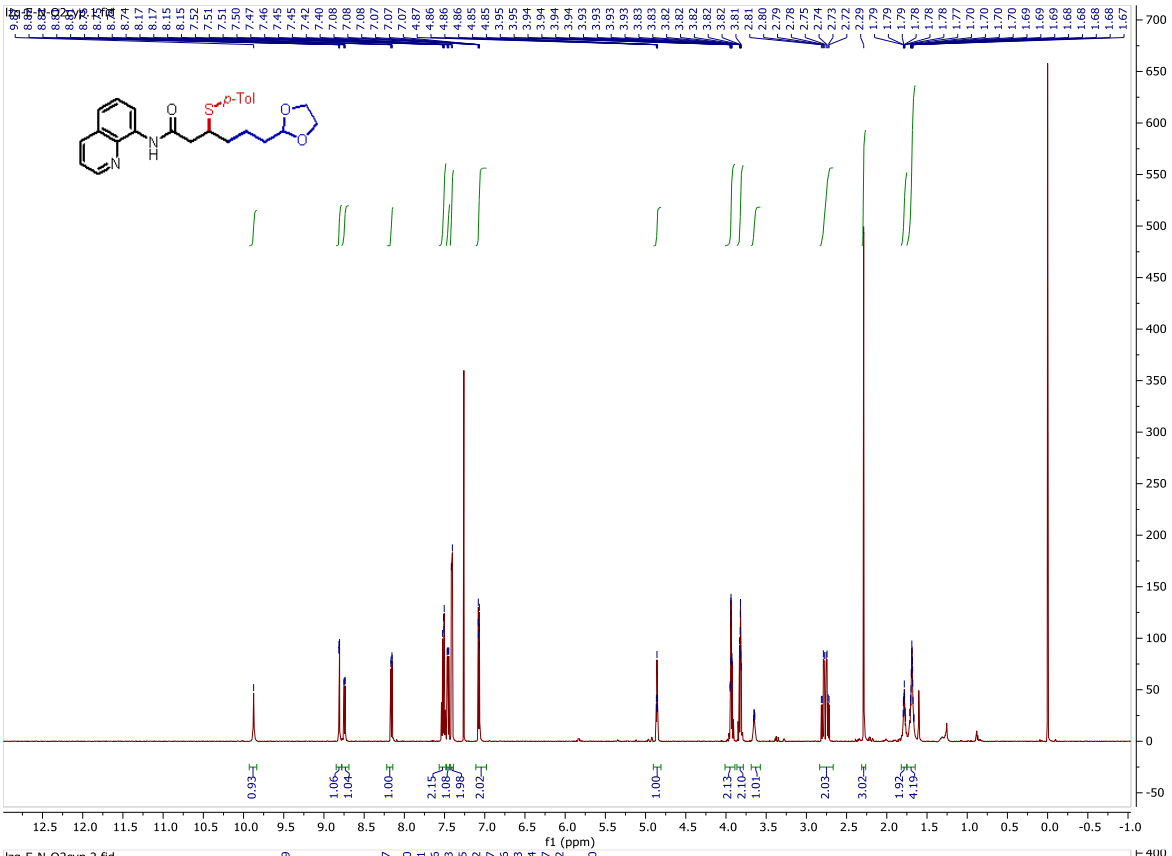

hwj-A-96-1-p.2.fid
p-Tol
Me
f1 (ppm)

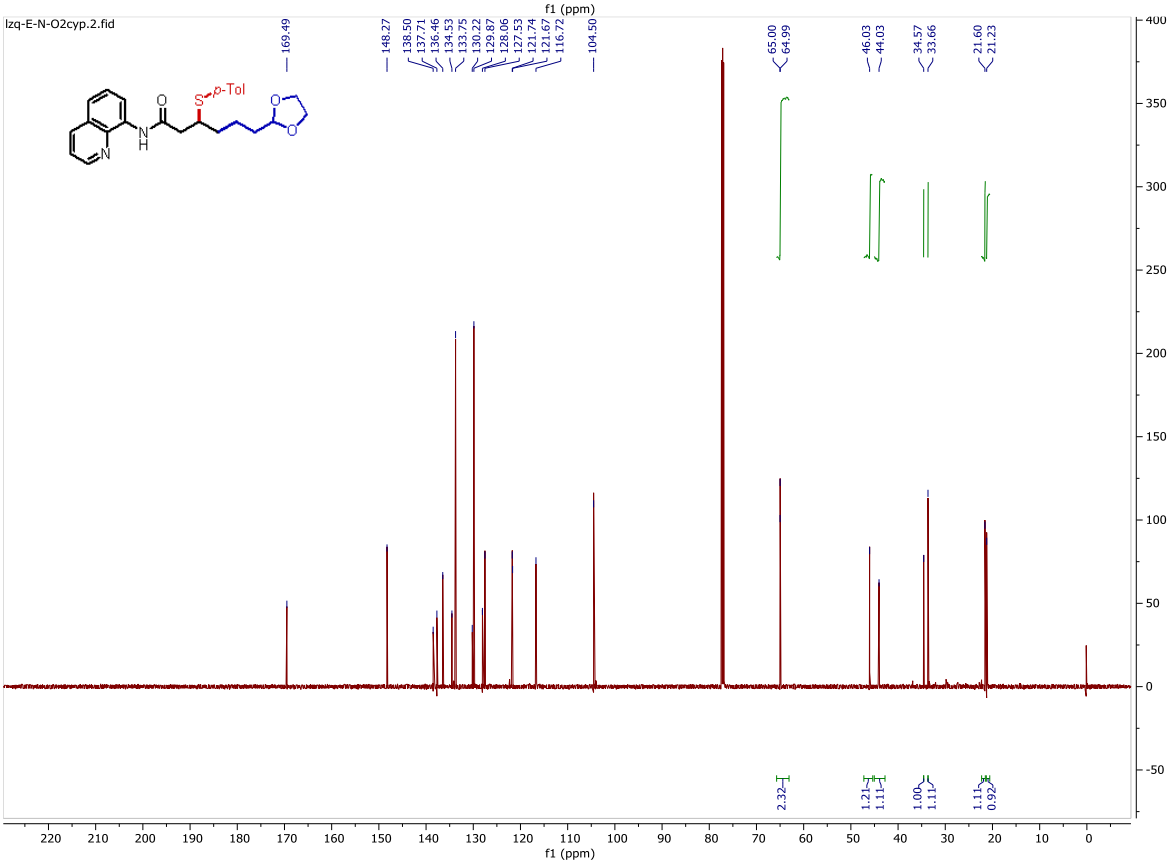

p-Tol
n-Pr
f1 (ppm)

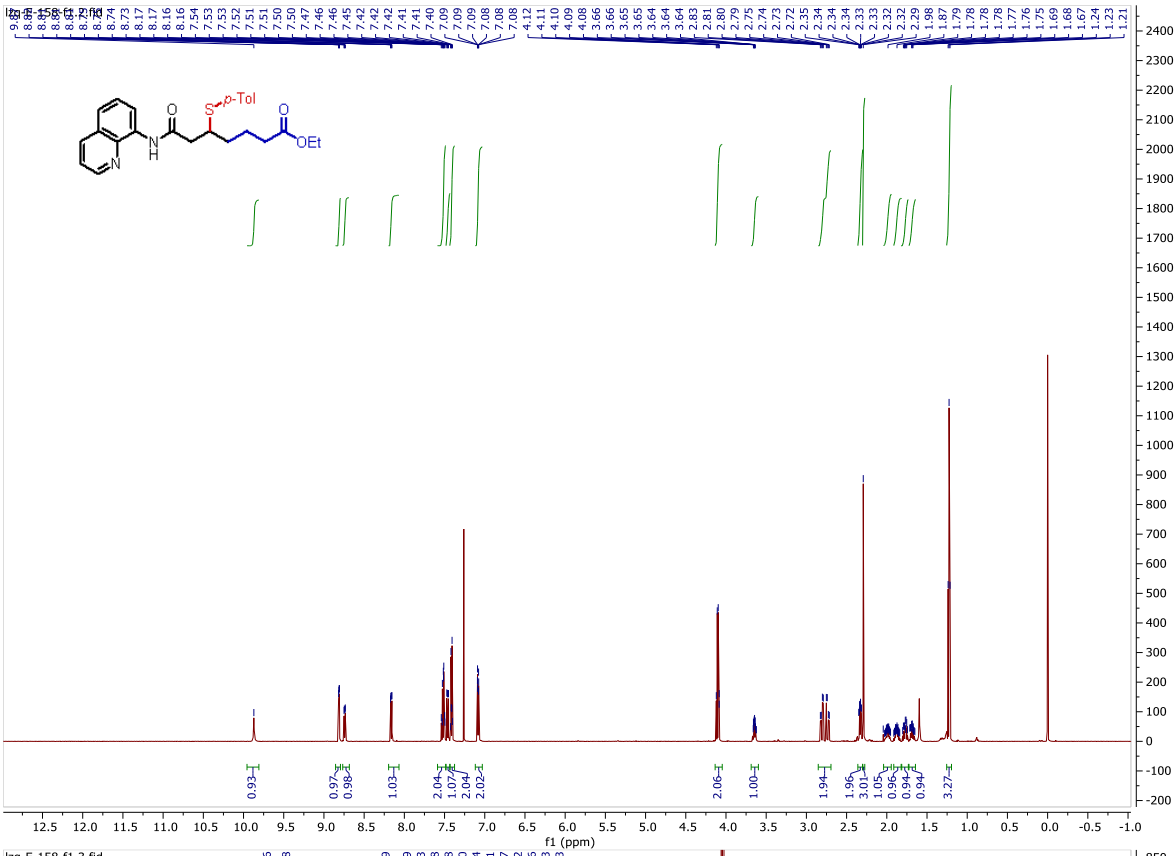

lzq-E-N-nPr.2.fid
169.65
148.27
138.51
137.61
136.47
134.55
133.60
130.41
129.86
127.54
121.74
121.66
116.71
46.01
44.15
34.48
29.28
22.64
21.22
14.15
p-Tol
n-Pr
f1 (ppm)

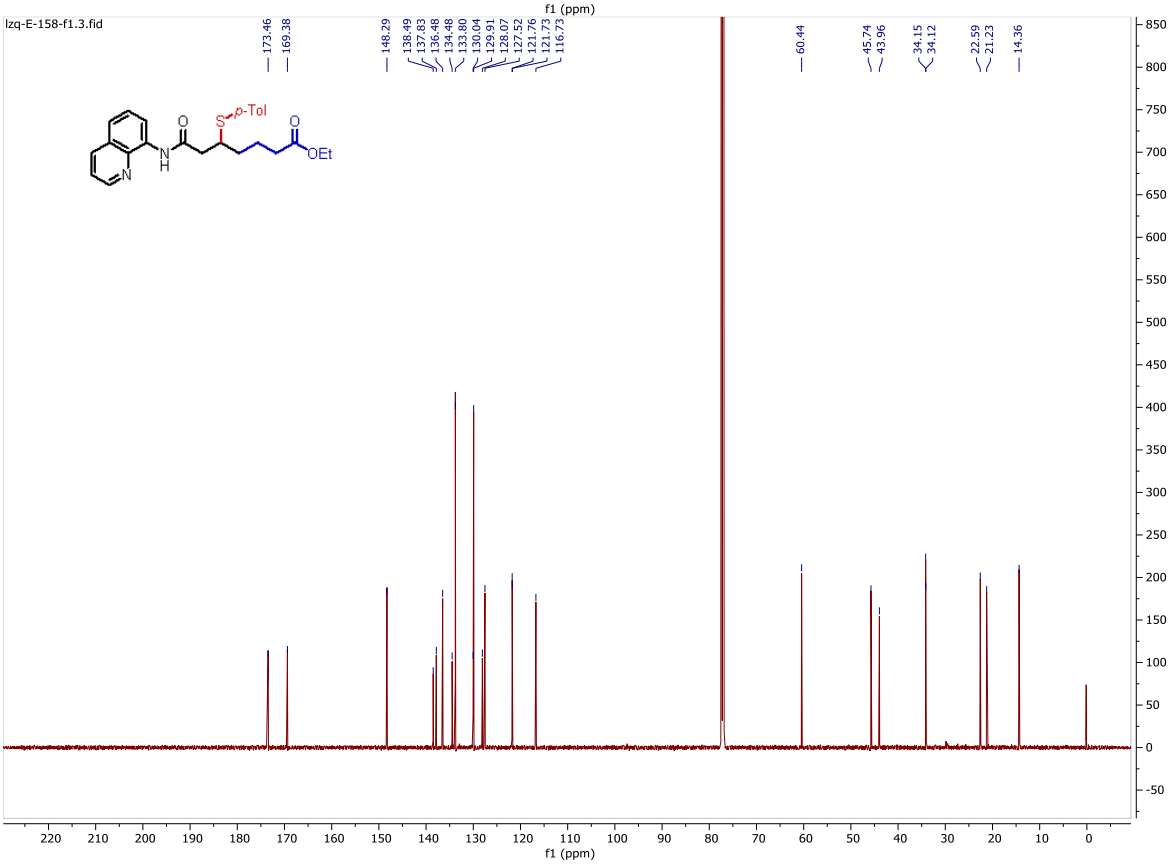

p-Tol
Bn
f1 (ppm)

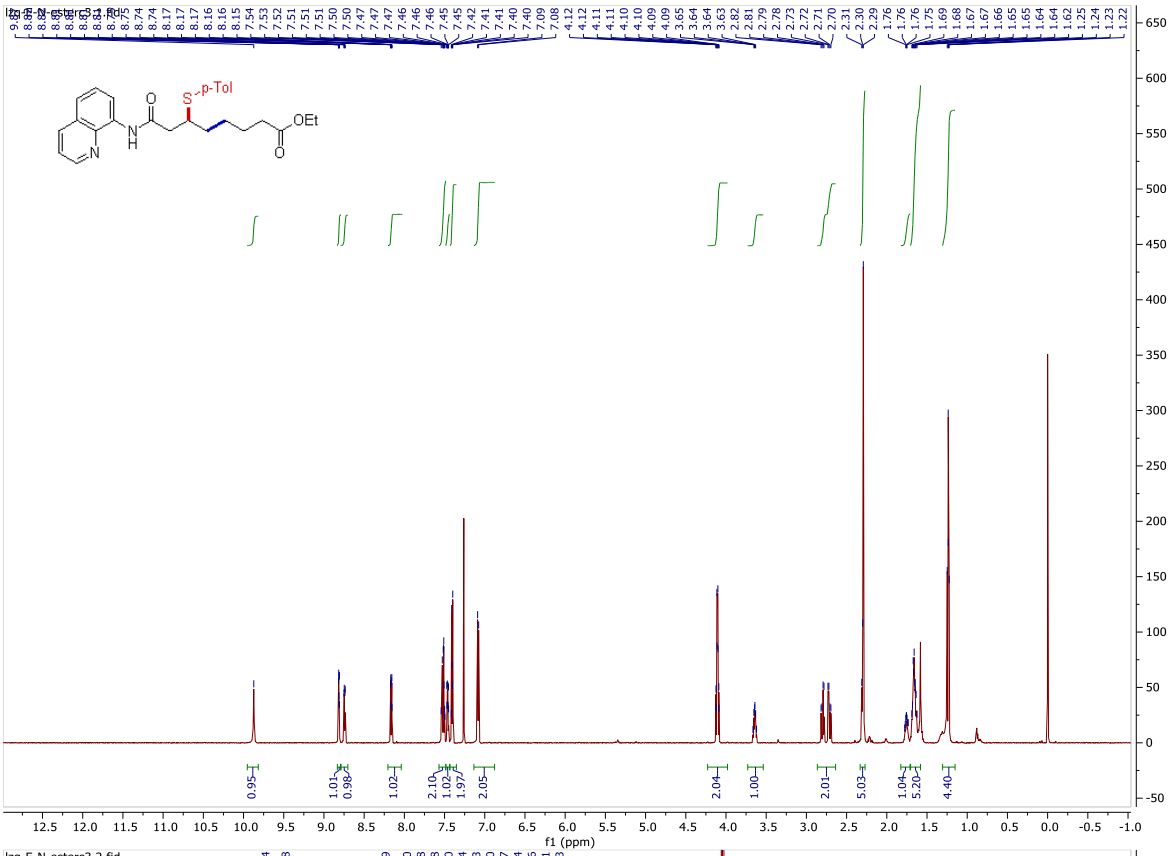

lzq-E-N-Bn.2.fid
169.36
148.26
141.65
138.49
137.82
136.47
134.48
133.77
129.99
129.82
128.52
128.06
127.52
126.04
121.74
121.71
116.74
45.64
44.12
36.43
33.36
21.23
p-Tol
Bn
f1 (ppm)

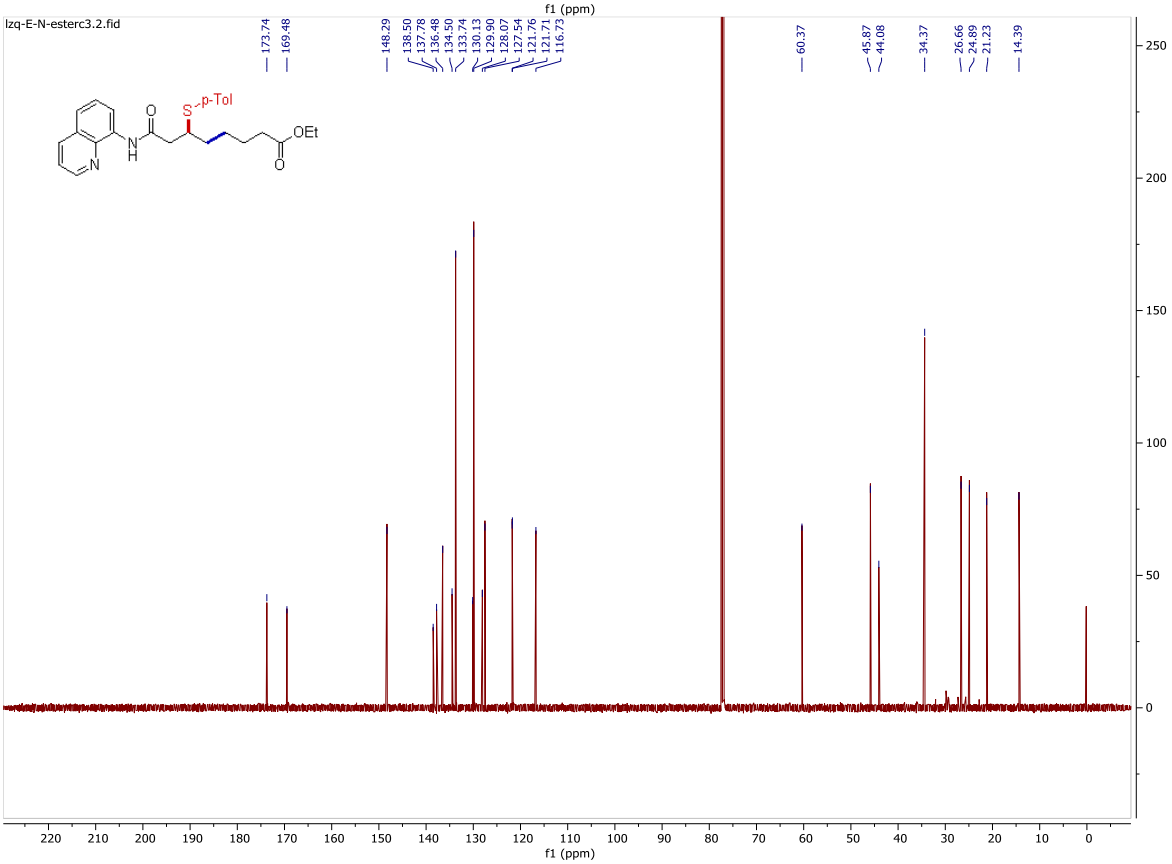

lzq-E-N-O2cyp.1.fid
p-Tol
f1 (ppm)

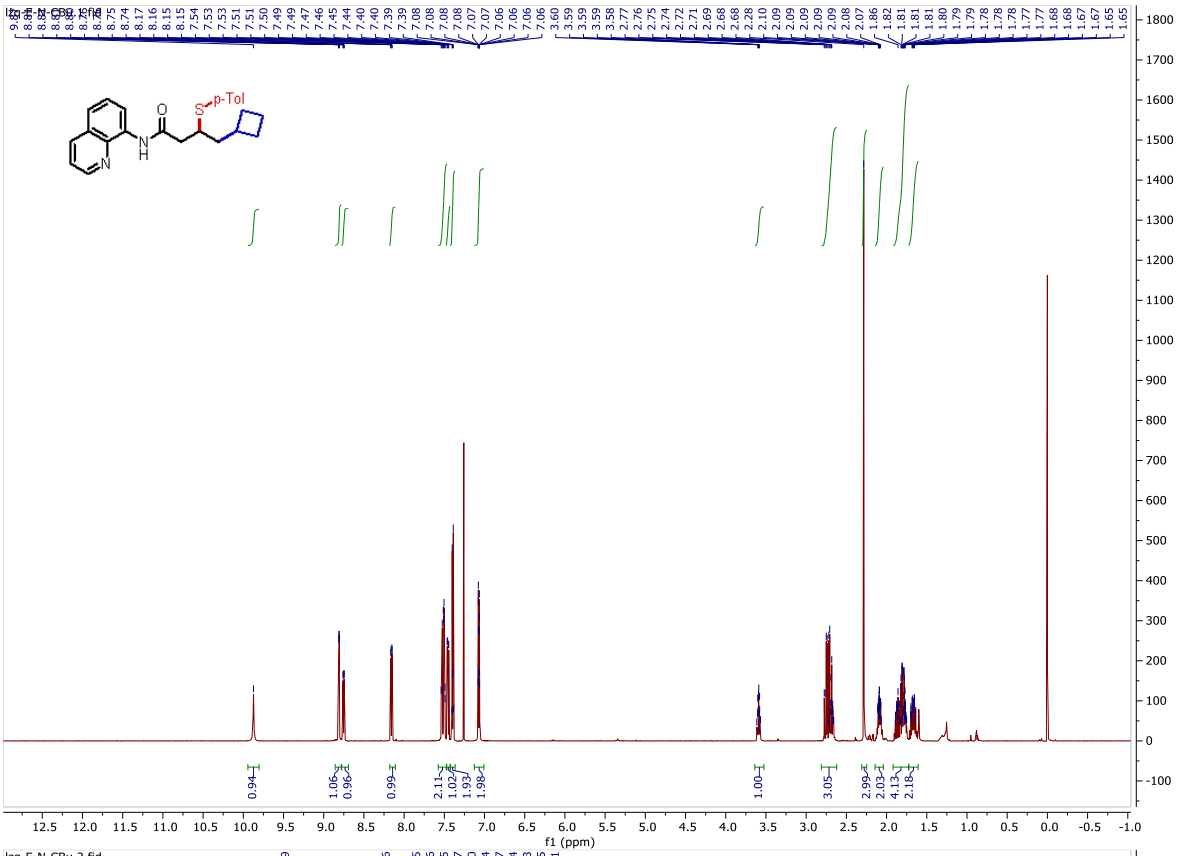

lzq-E-N-O2cyp.2.fid
169.49
148.27
138.50
137.71
136.46
134.53
133.75
130.22
129.87
128.06
127.53
121.74
121.67
116.72
104.50
65.00
64.99
46.03
44.03
34.57
33.66
21.60
21.23
p-Tol
f1 (ppm)

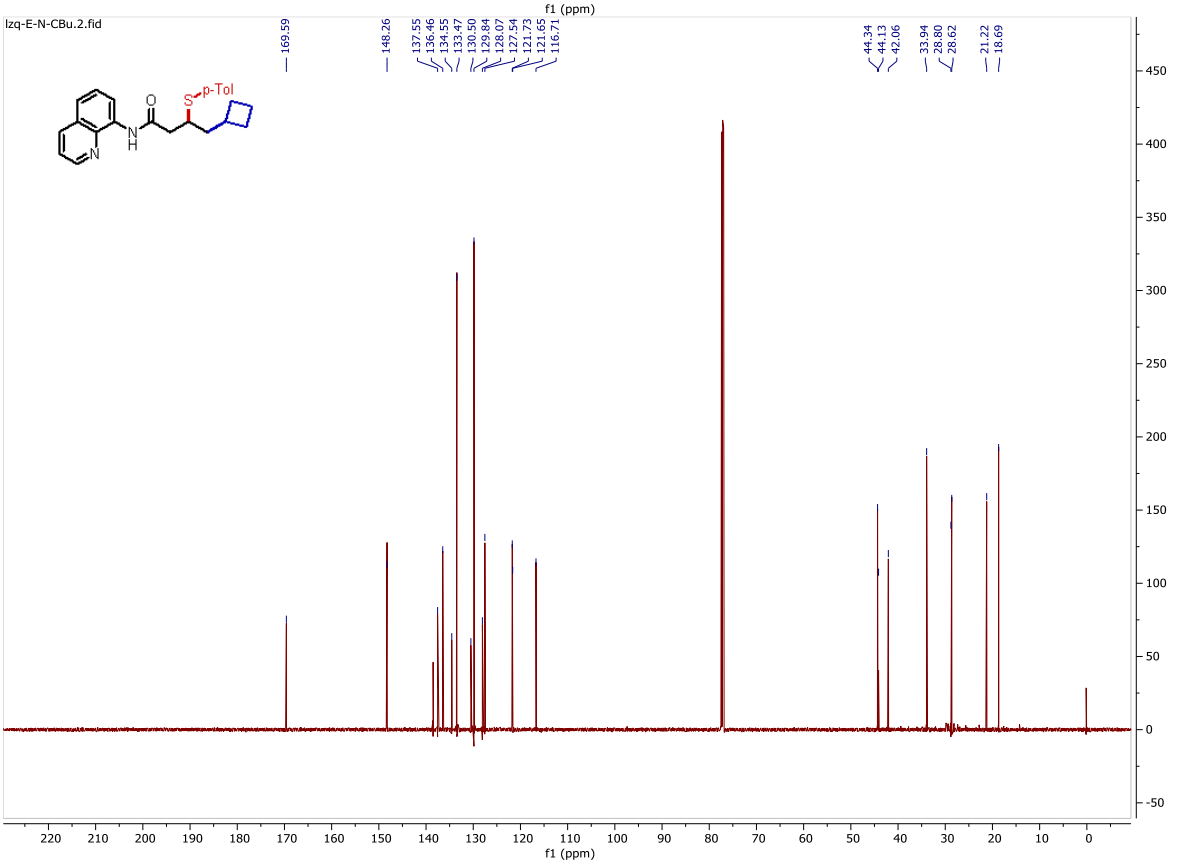

O
S
p-Tol
O
OEt
N
H
N
f1 (ppm)

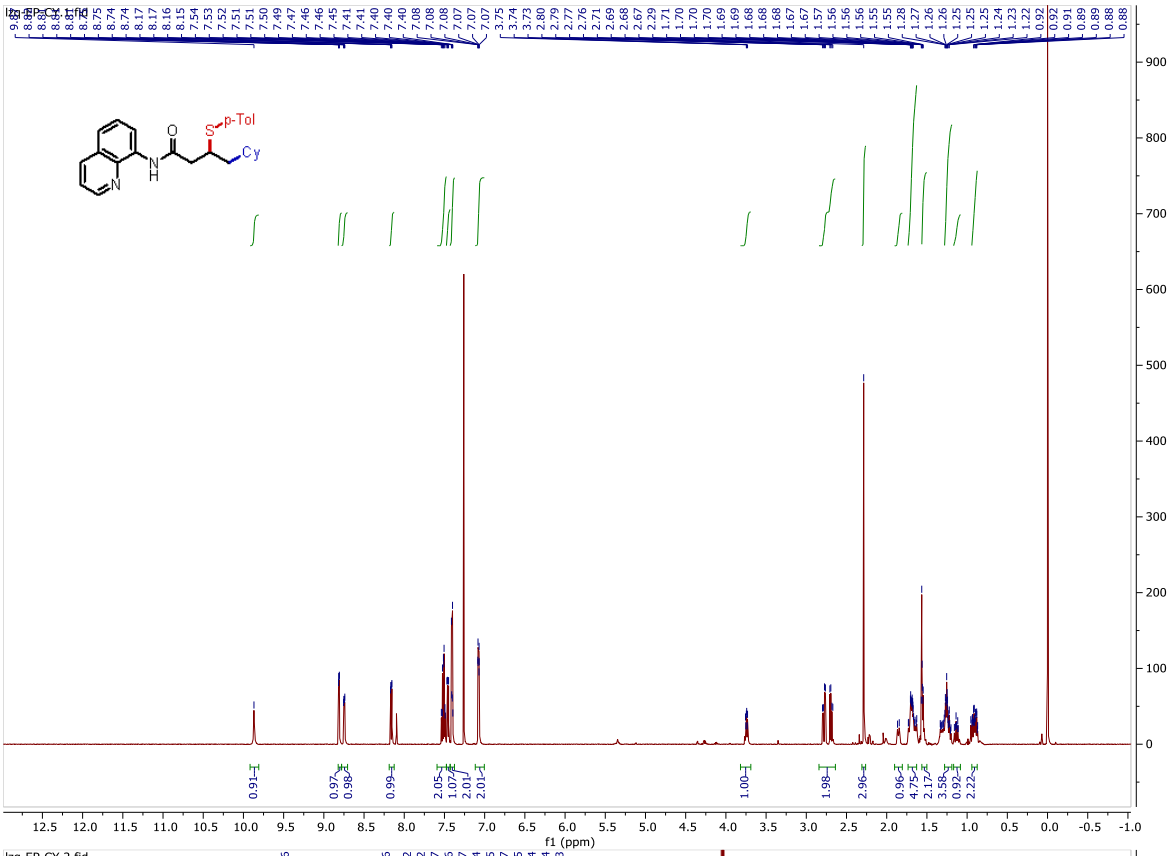

lzq-E-158-f1.3.fid
173.46
169.38
148.29
138.49
137.83
136.48
134.48
133.80
130.04
129.91
128.07
127.52
121.76
121.73
116.73
60.44
45.74
43.96
34.15
34.12
22.59
21.23
14.36
O
S
p-Tol
O
OEt
N
H
N
f1 (ppm)

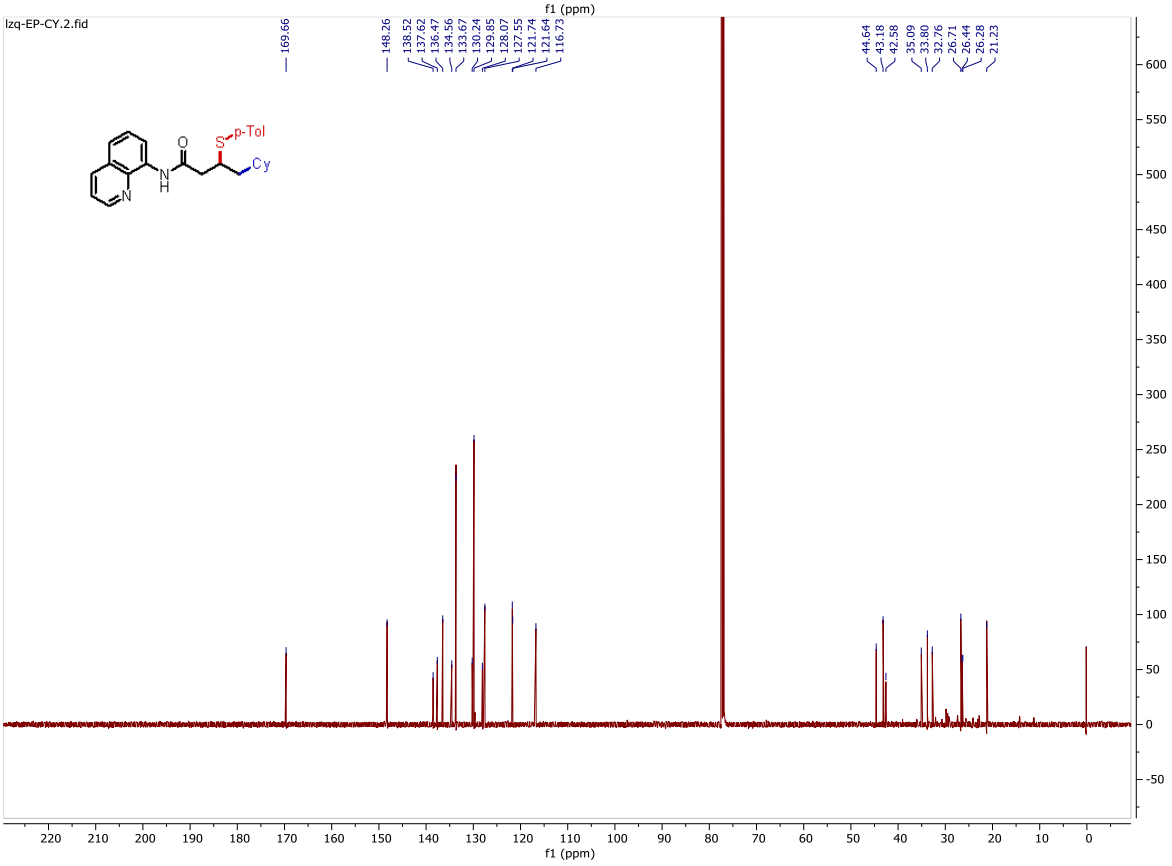

lzq-E-N-esterc3.1.fid
S
p-Tol
O
N
H
OEt
O
0.95
1.01
0.98
1.02
2.10
1.02
1.97
2.05
2.04
1.00
2.01
5.03
1.04
5.20
4.40
f1 (ppm)

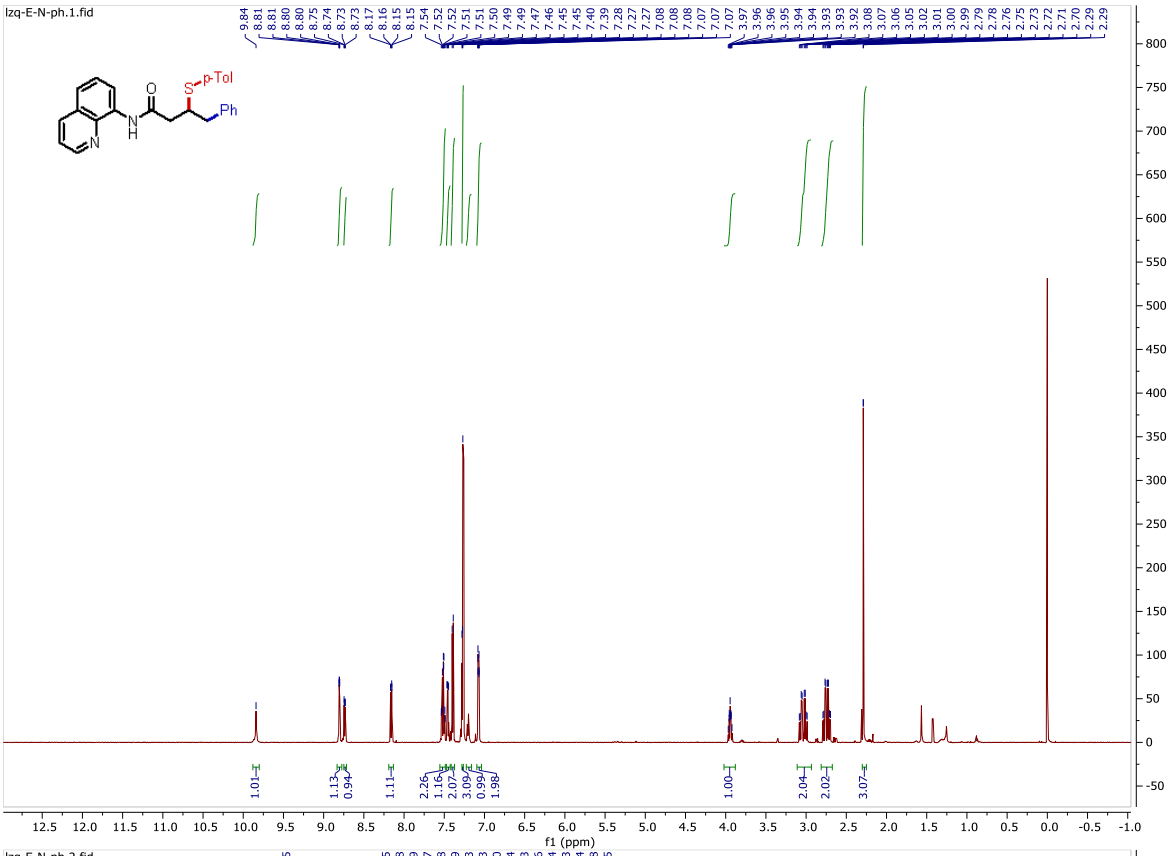

lzq-E-N-esterc3.2.fid
173.74
169.48
148.29
138.50
137.78
136.48
134.50
133.74
130.13
129.90
128.07
127.54
121.76
121.71
116.73
60.37
45.87
44.08
34.37
26.66
24.89
21.23
14.39
S
p-Tol
O
N
H
OEt
O
f1 (ppm)

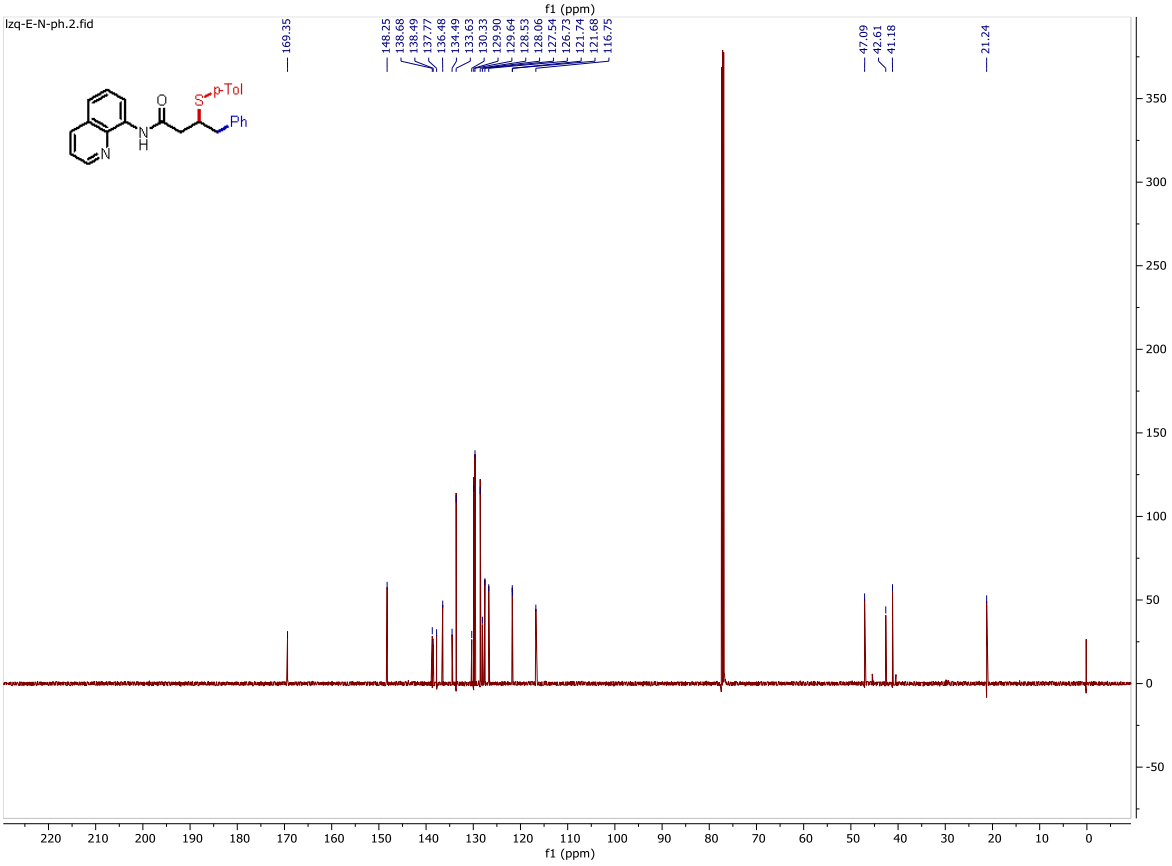

lzq-E-N-CBu.fid
p-Tol
f1 (ppm)

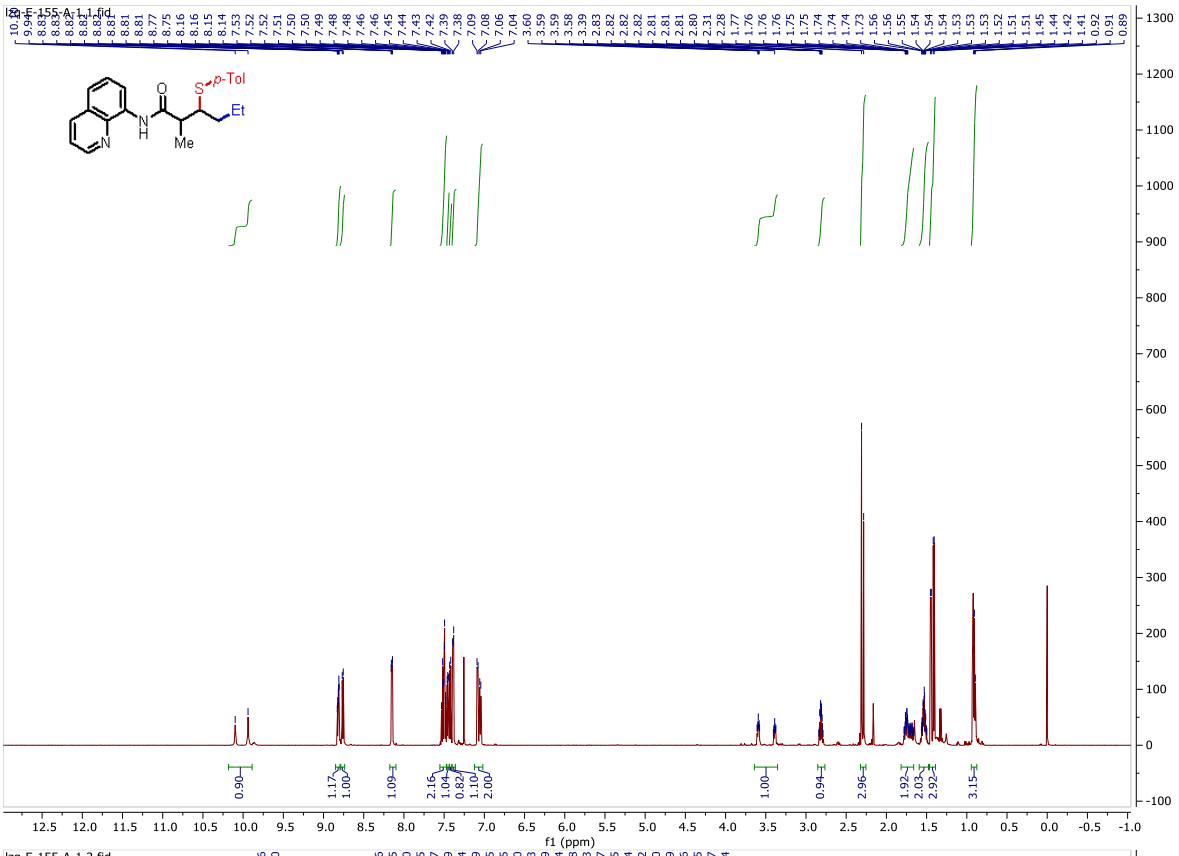

lzq-E-N-CBu.2.fid
169.59
148.26
137.55
136.46
134.55
133.47
130.50
129.84
128.07
127.54
121.73
121.65
116.71
44.34
44.13
42.06
33.94
28.80
28.62
21.22
18.69
p-Tol
f1 (ppm)

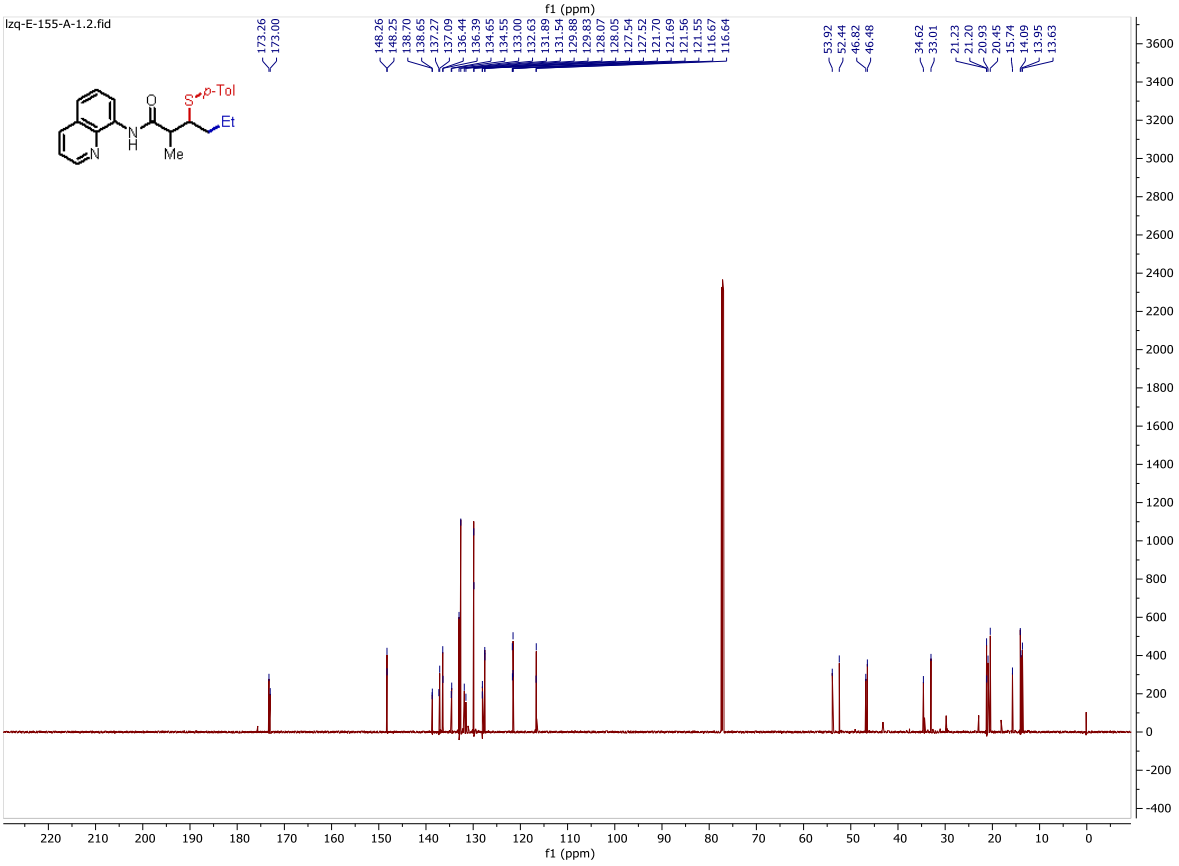

p-Tol
Cy
f1 (ppm)

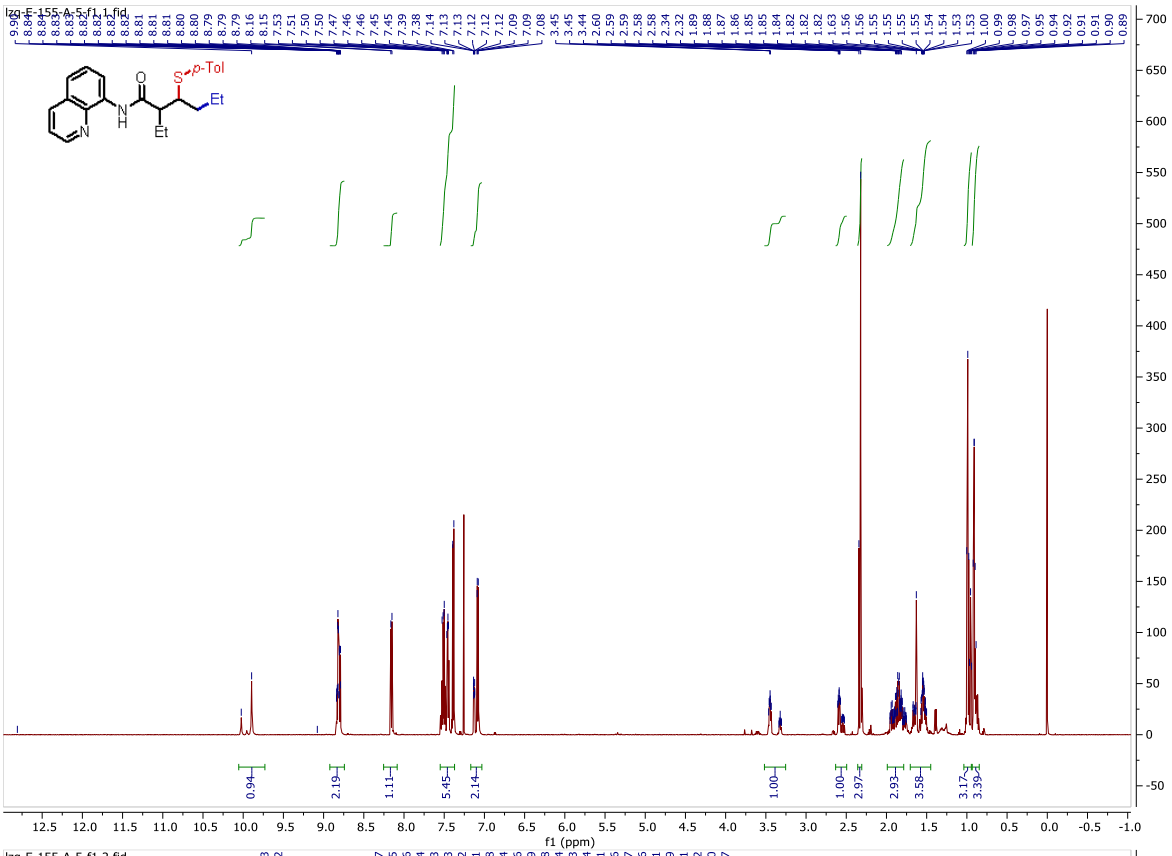

lzq-EP-CY.2.fid
p-Tol
Cy
f1 (ppm)

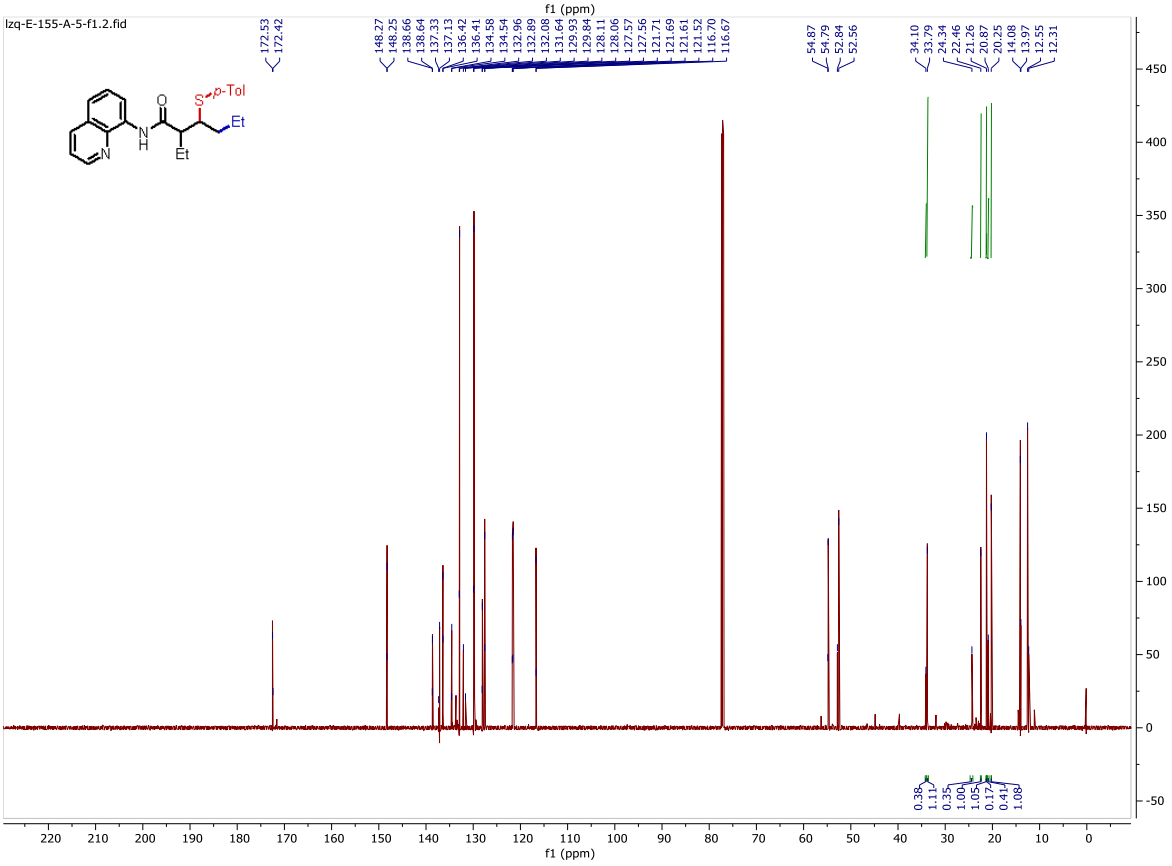

lzq-E-N-ph.1.fid
p-Tol
Ph
f1 (ppm)

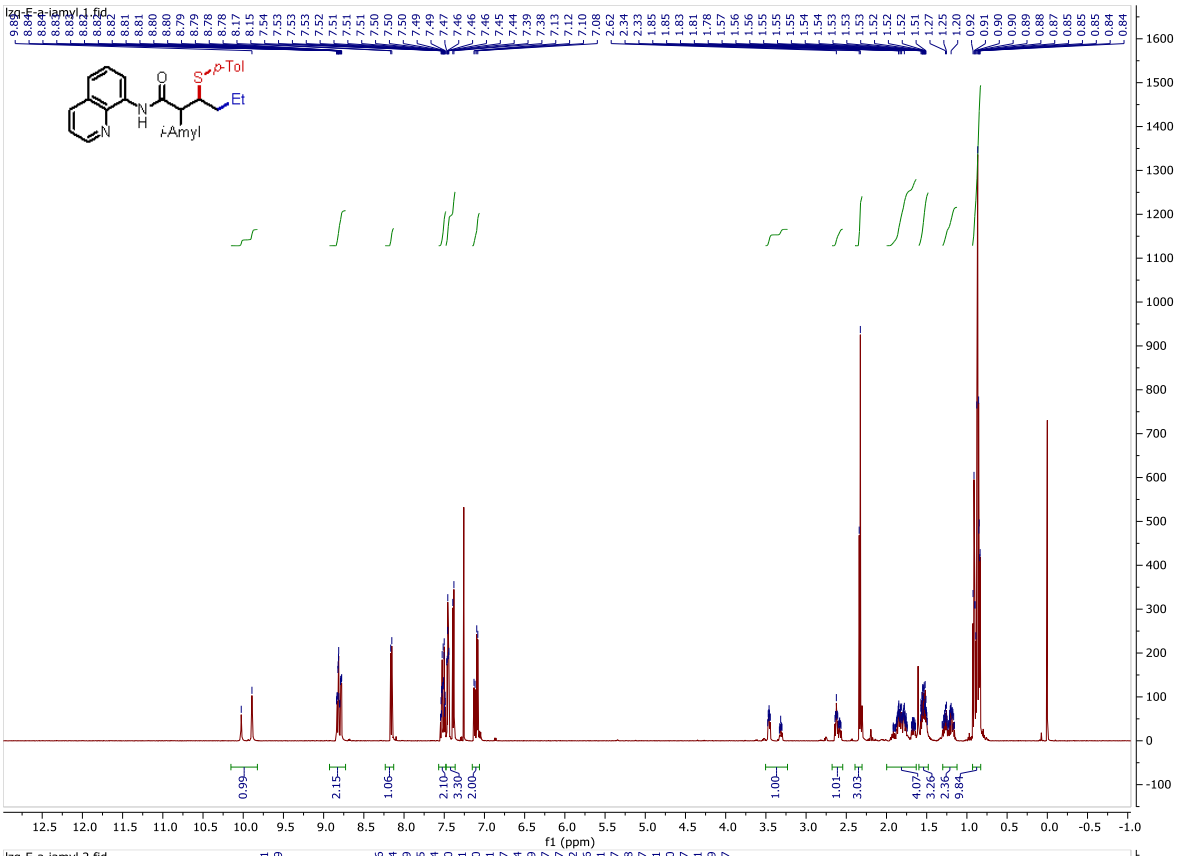

lzq-E-N-ph.2.fid
169.35
148.25
138.68
138.49
137.77
136.48
134.49
133.63
130.33
129.90
129.64
128.53
128.06
127.54
126.73
121.74
121.68
116.75
47.09
42.61
41.18
21.24
p-Tol
Ph
f1 (ppm)

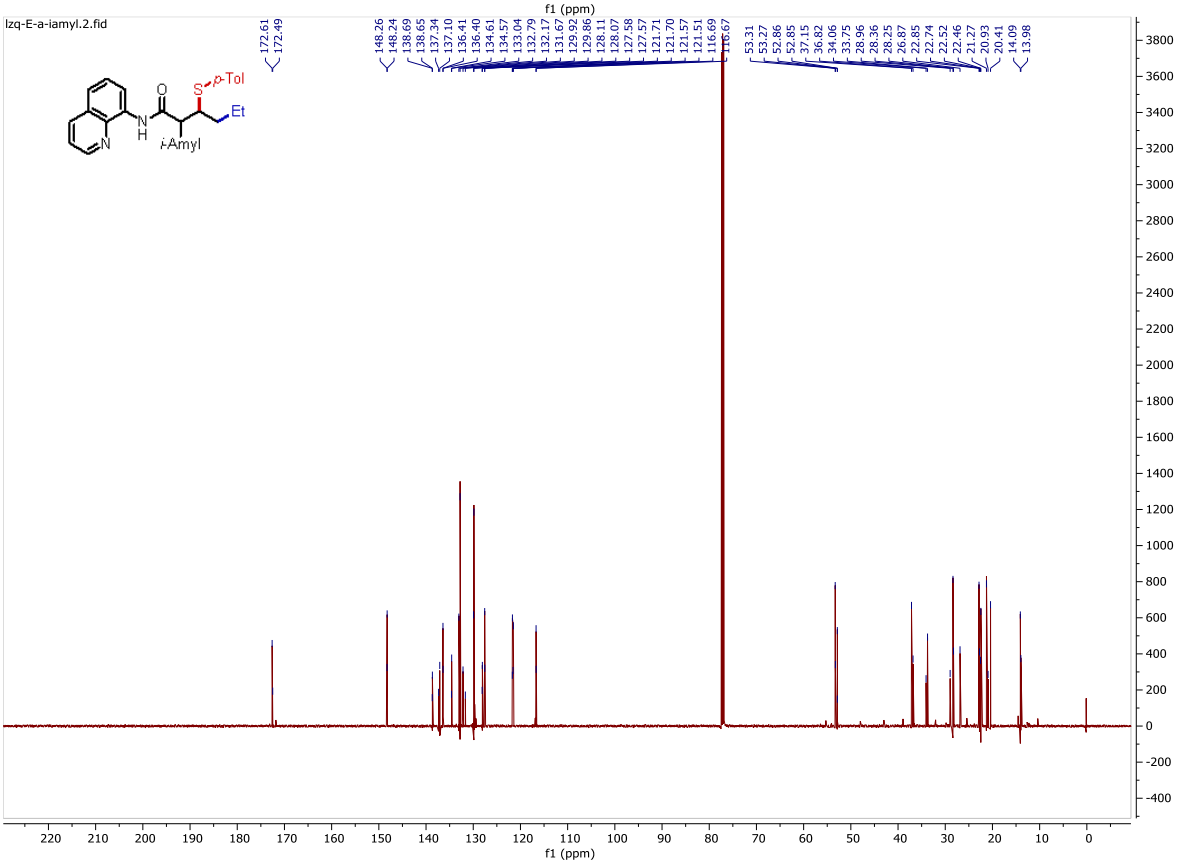

lzq-E-155-A-1.1.fid
p-Tol
Et
Me
N
H
O
S
f1 (ppm)

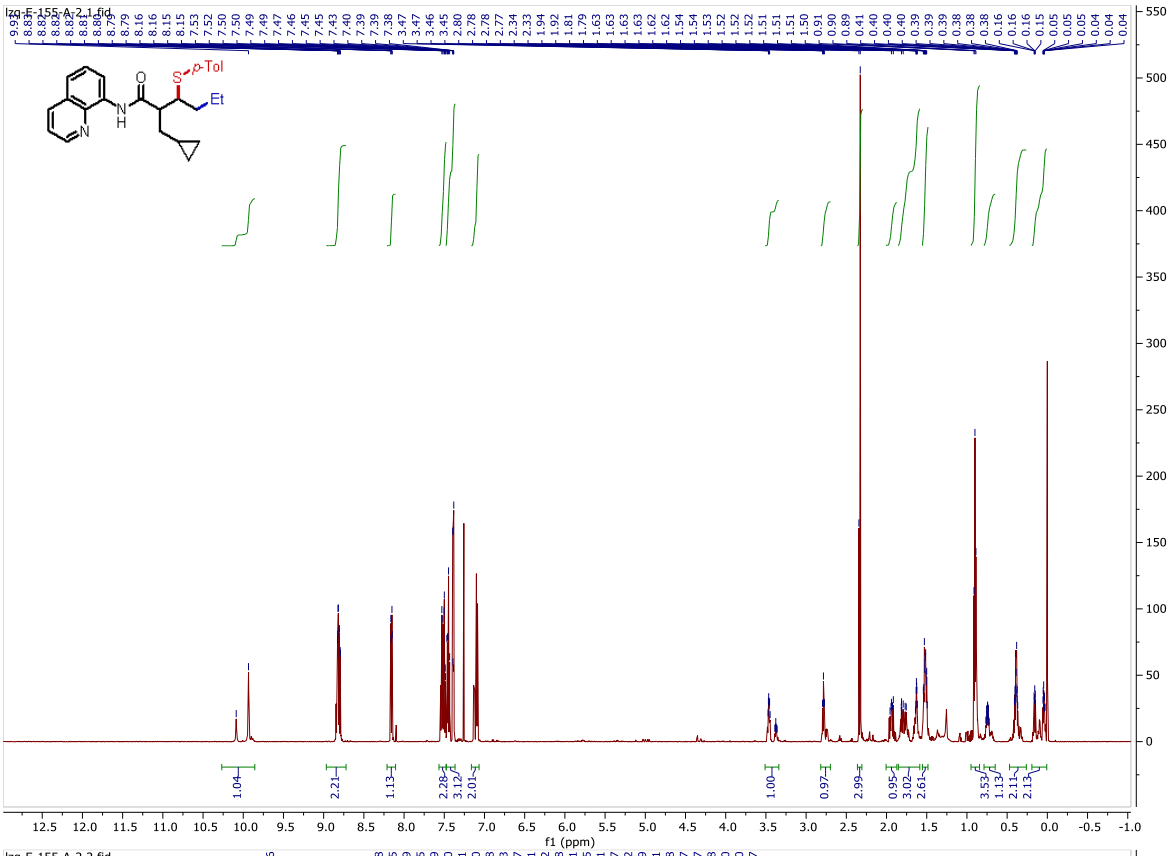

lzq-E-155-A-1.2.fid
p-Tol
Et
Me
N
H
O
S
f1 (ppm)

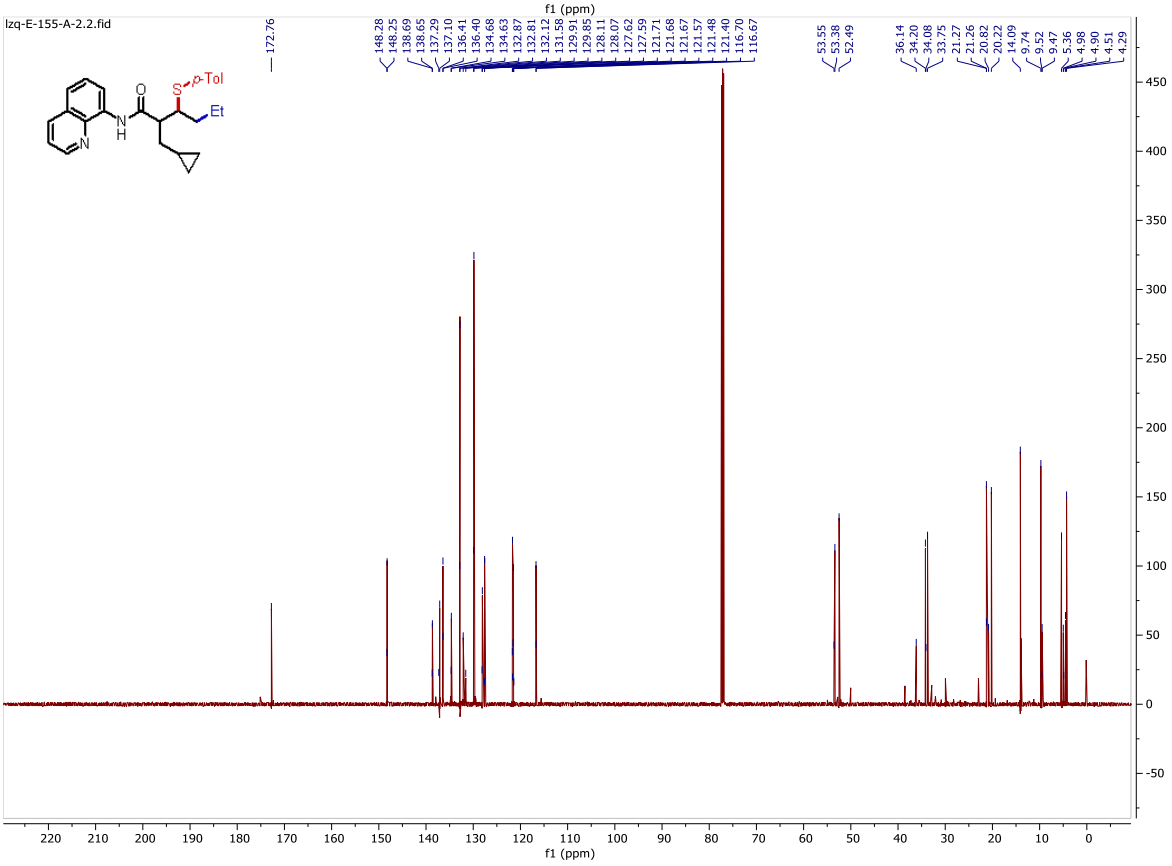

lzq-E-155-A-5-f1.1.fid
p-Tol
Et
Et
f1 (ppm)

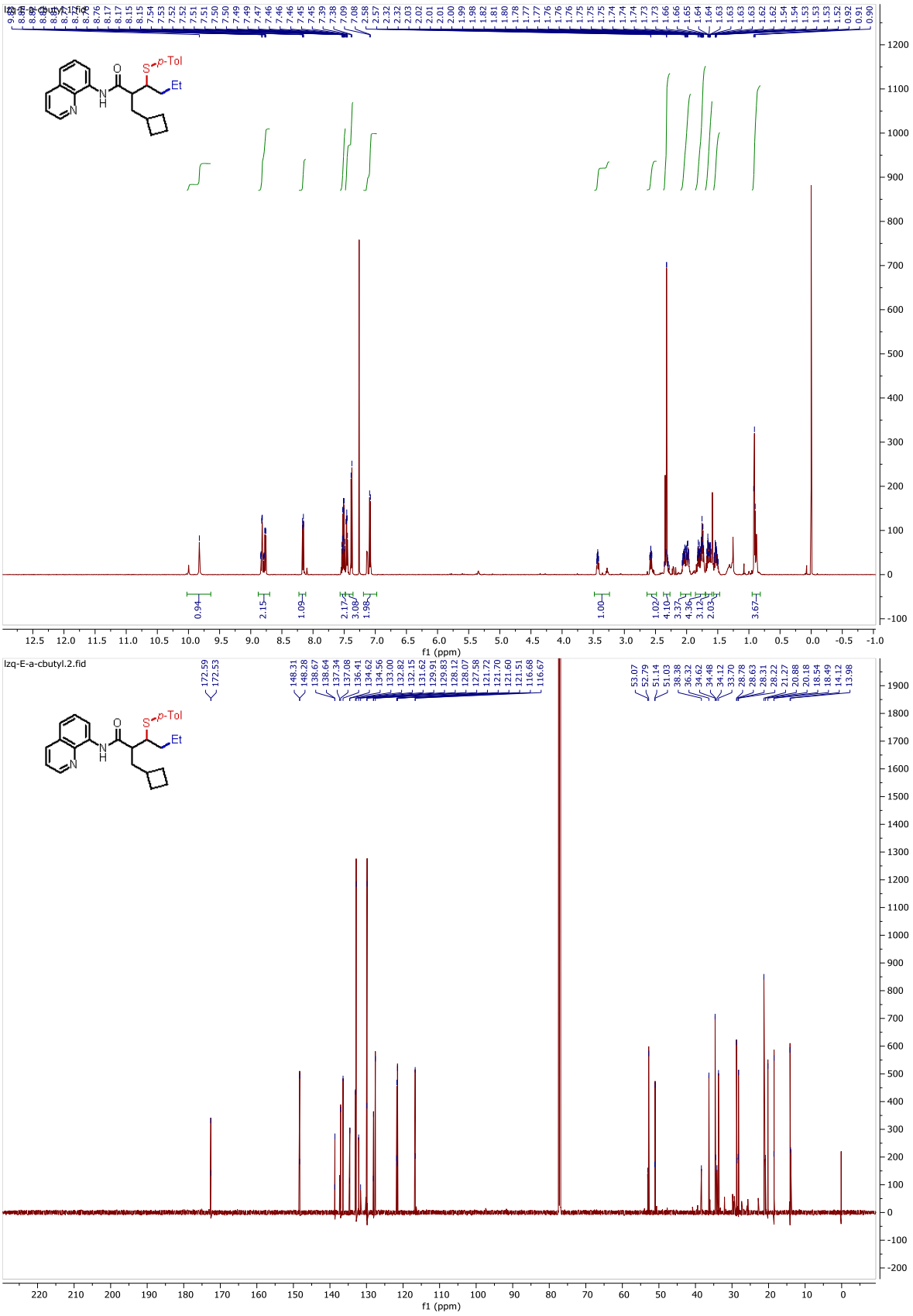

lzq-E-155-A-5-f1.2.fid
p-Tol
Et
Et
f1 (ppm)

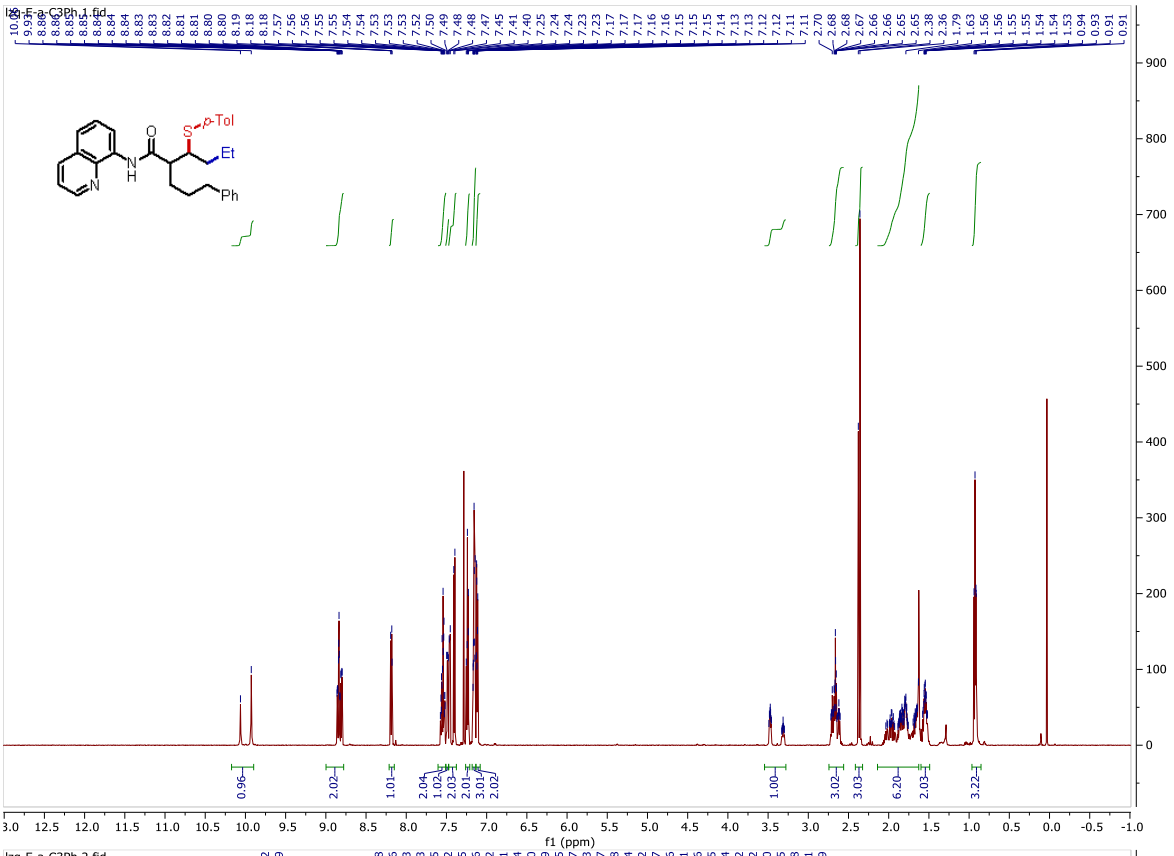

lzq-E-a-iamyl.1.fid
p-Tol
Et
i-Amyl
f1 (ppm)

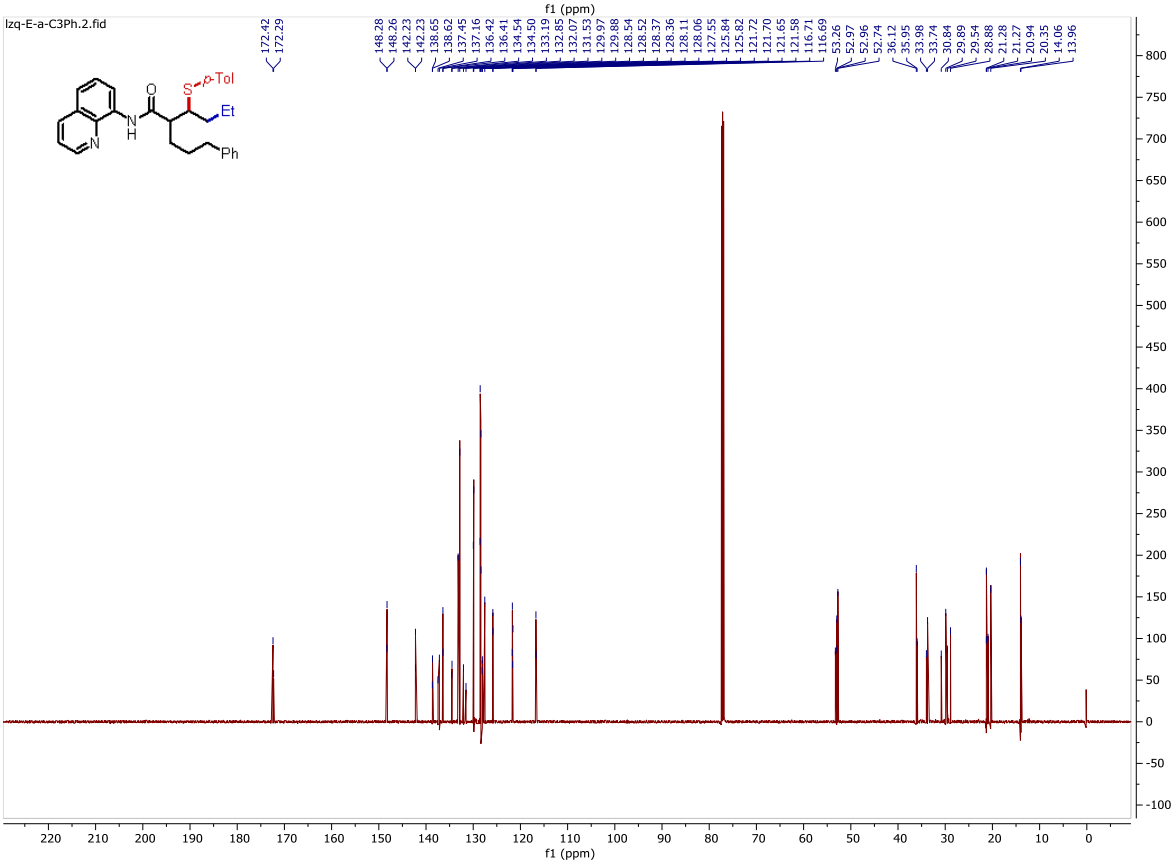

lzq-E-a-iamyl.2.fid
p-Tol
Et
i-Amyl
f1 (ppm)

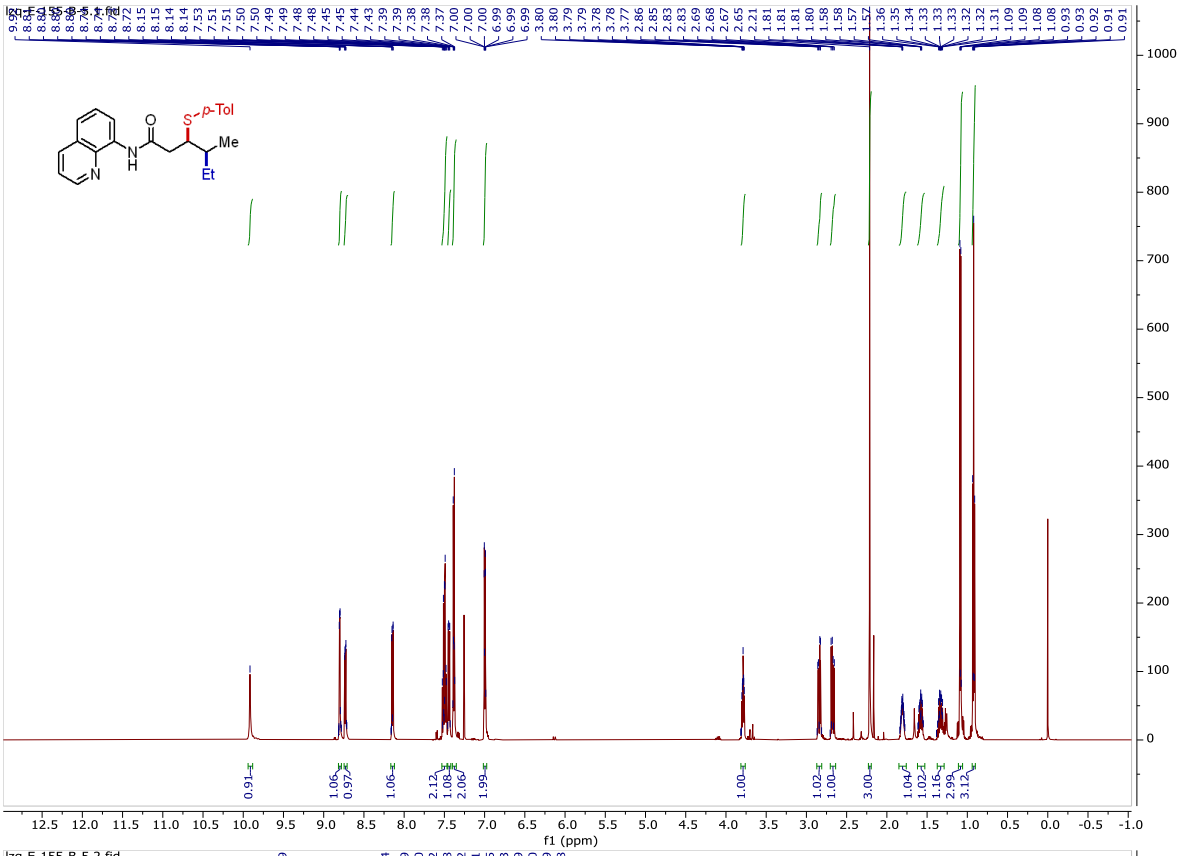

lzq-E-155-A-2.1.fid
p-Tol
Et
f1 (ppm)

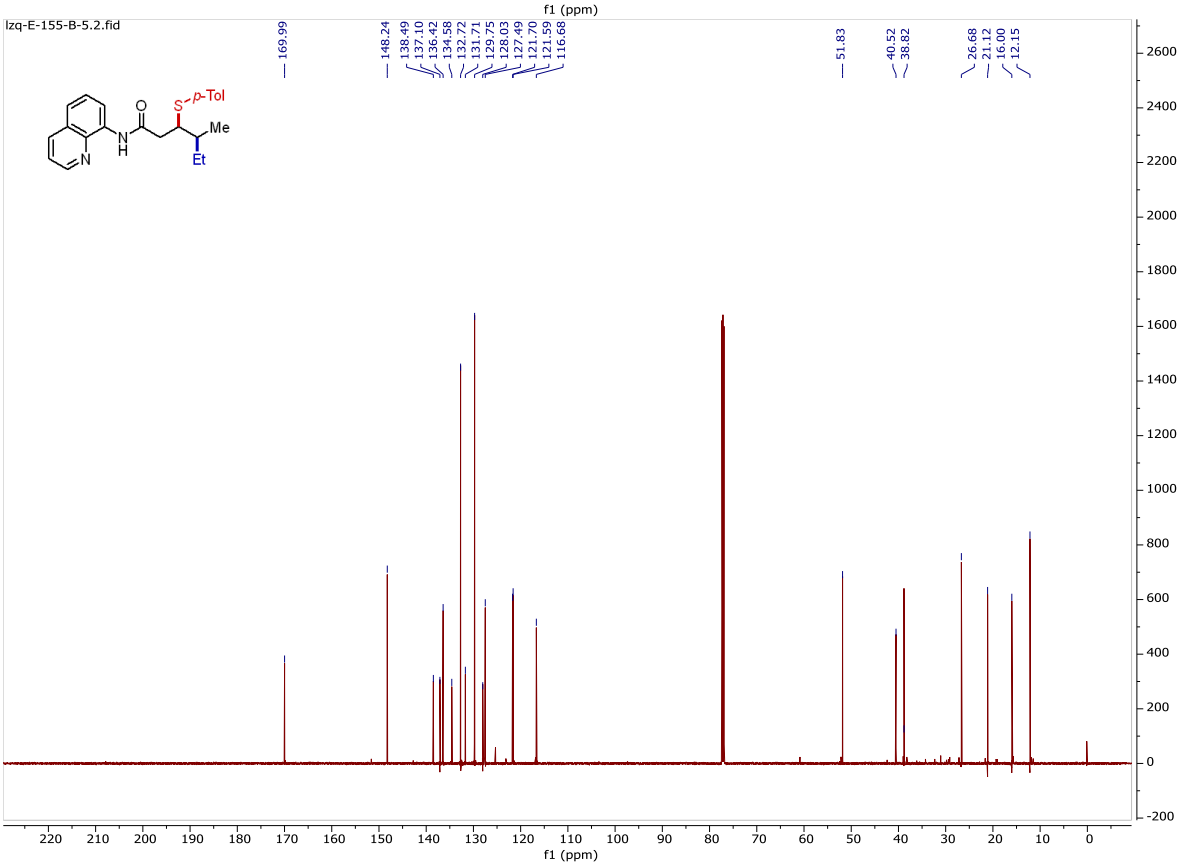

lzq-E-155-A-2.2.fid
p-Tol
Et
f1 (ppm)

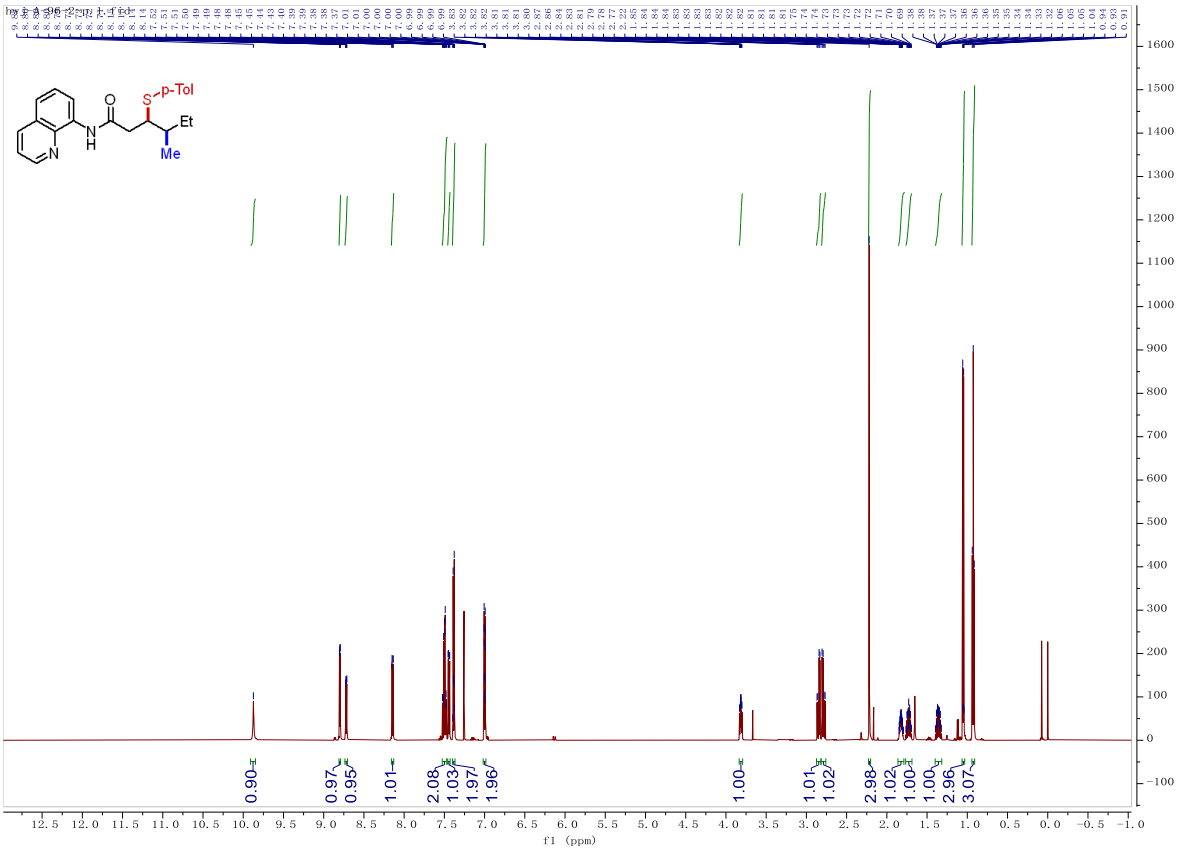

lzq-E-a-cbutyl.1.fid
p-Tol
Et
f1 (ppm)
lzq-E-a-cbutyl.2.fid
p-Tol
Et
f1 (ppm)

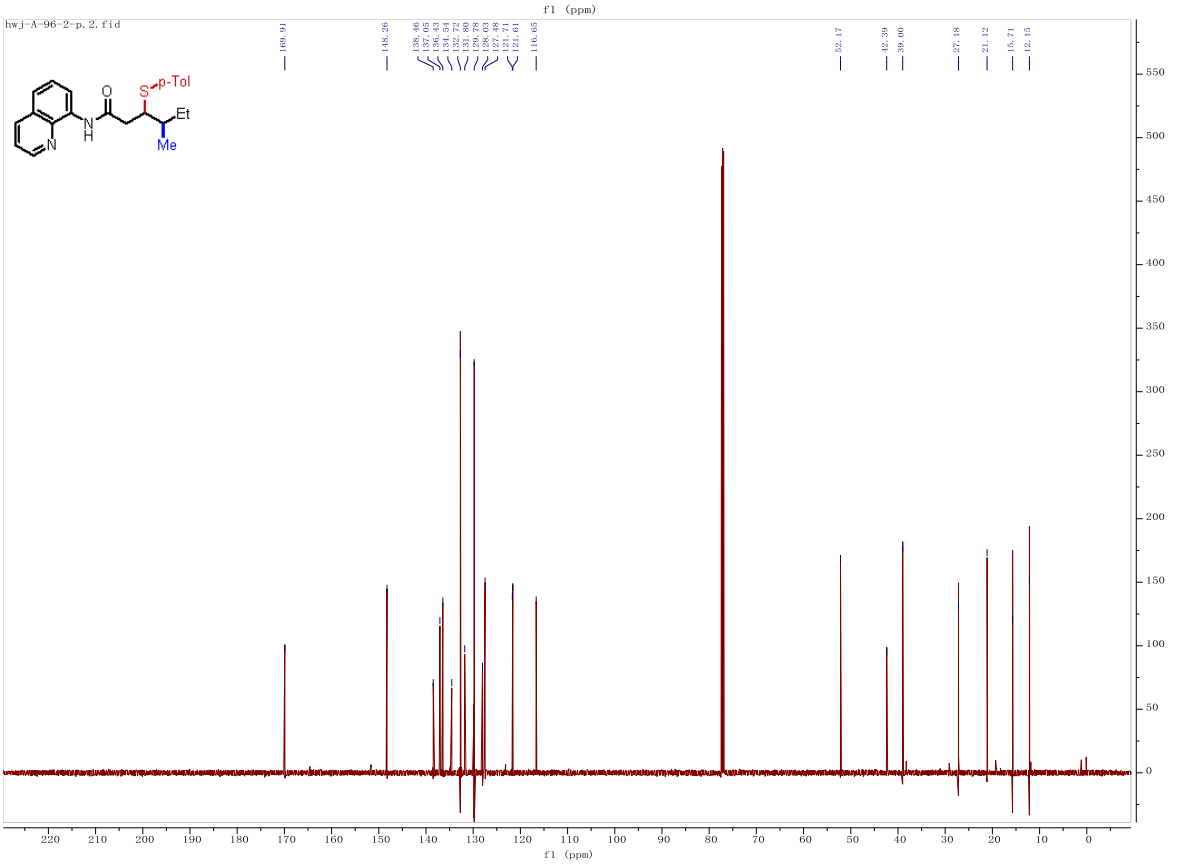

lzq-E-a-C3Ph.1.fid
p-Tol
Et
Ph
f1 (ppm)

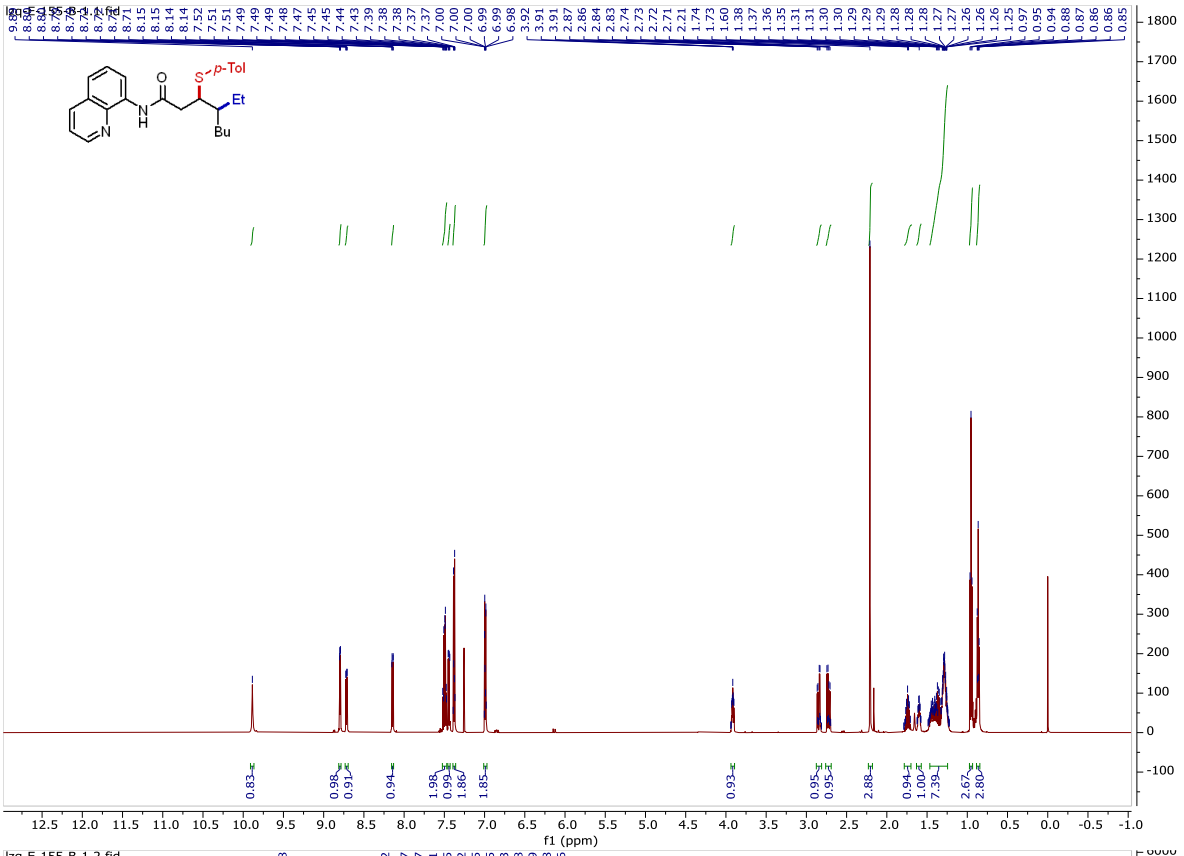

lzq-E-a-C3Ph.2.fid
p-Tol
Et
Ph
f1 (ppm)

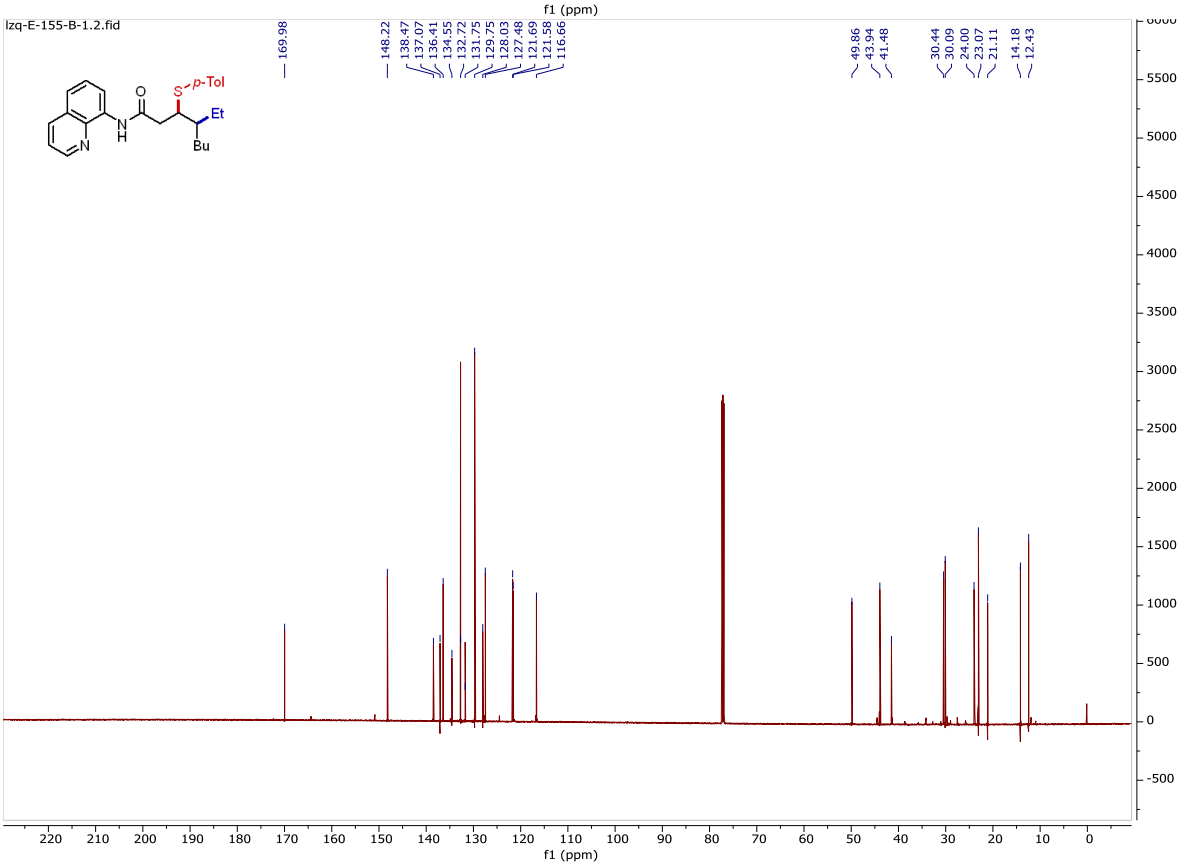

lzq-E-155-B-5.1.fid
p-Tol
Me
Et
f1 (ppm)

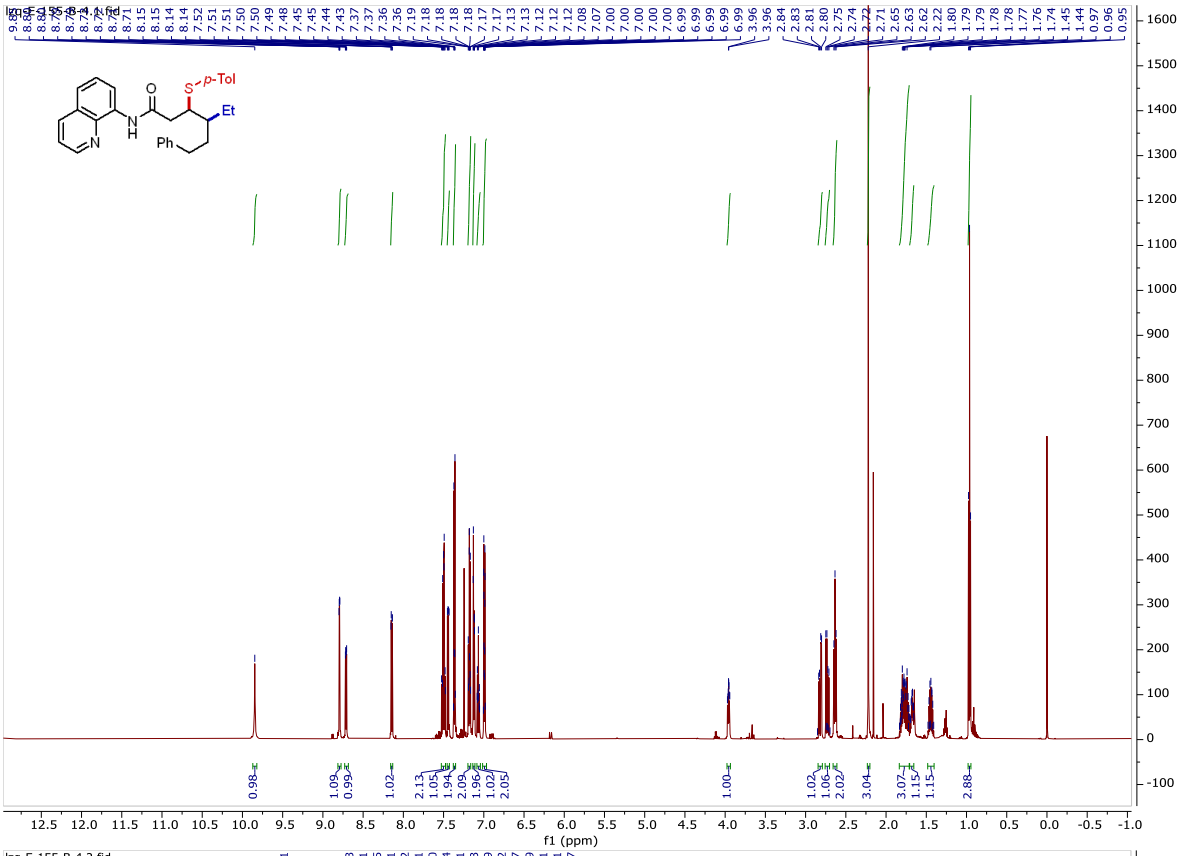

lzq-E-155-B-5.2.fid
169.99
148.24
138.49
137.10
136.42
134.58
132.72
131.71
129.75
128.03
127.49
121.70
121.59
116.68
51.83
40.52
38.82
26.68
21.12
16.00
12.15
p-Tol
Me
Et
f1 (ppm)

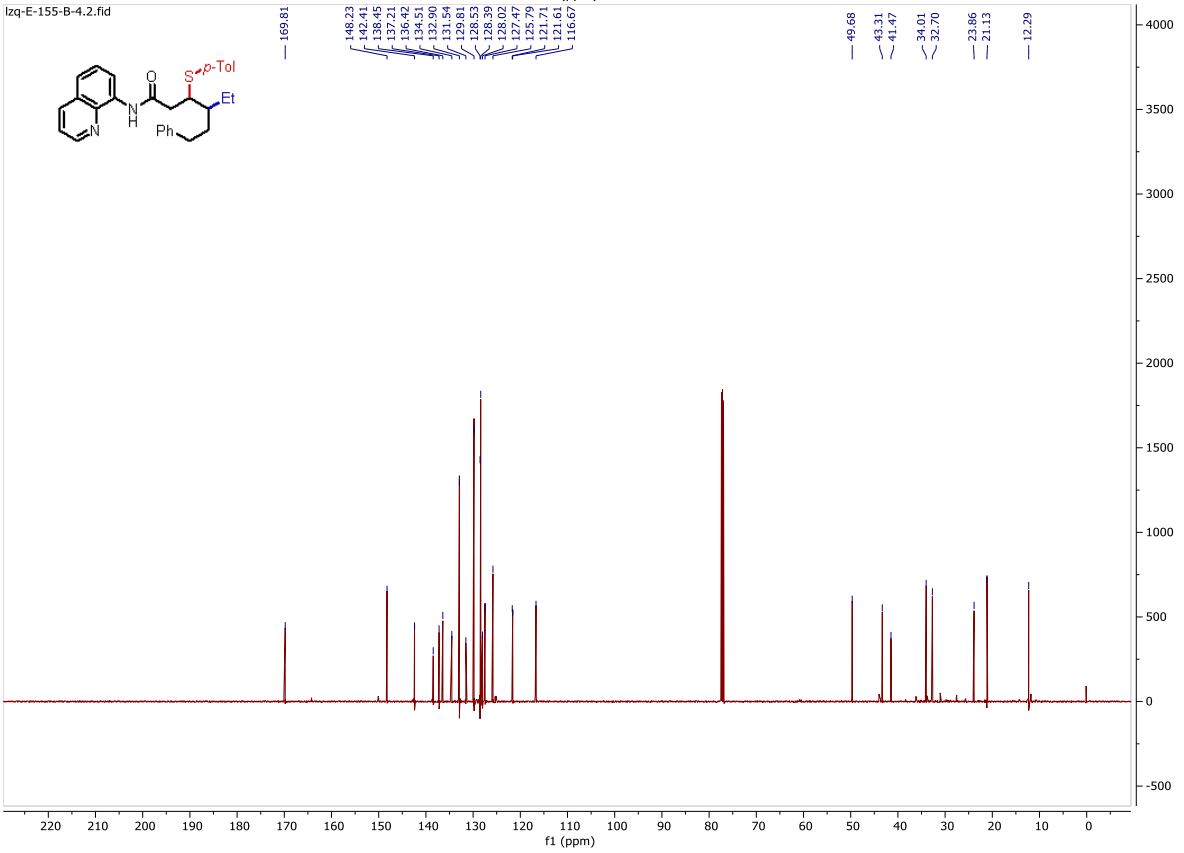

p-Tol
Et
Me
0.90
0.97
0.95
1.01
2.08
1.03
1.97
1.96
1.00
1.01
1.02
2.98
1.02
1.00
1.00
2.96
3.07
f1 (ppm)

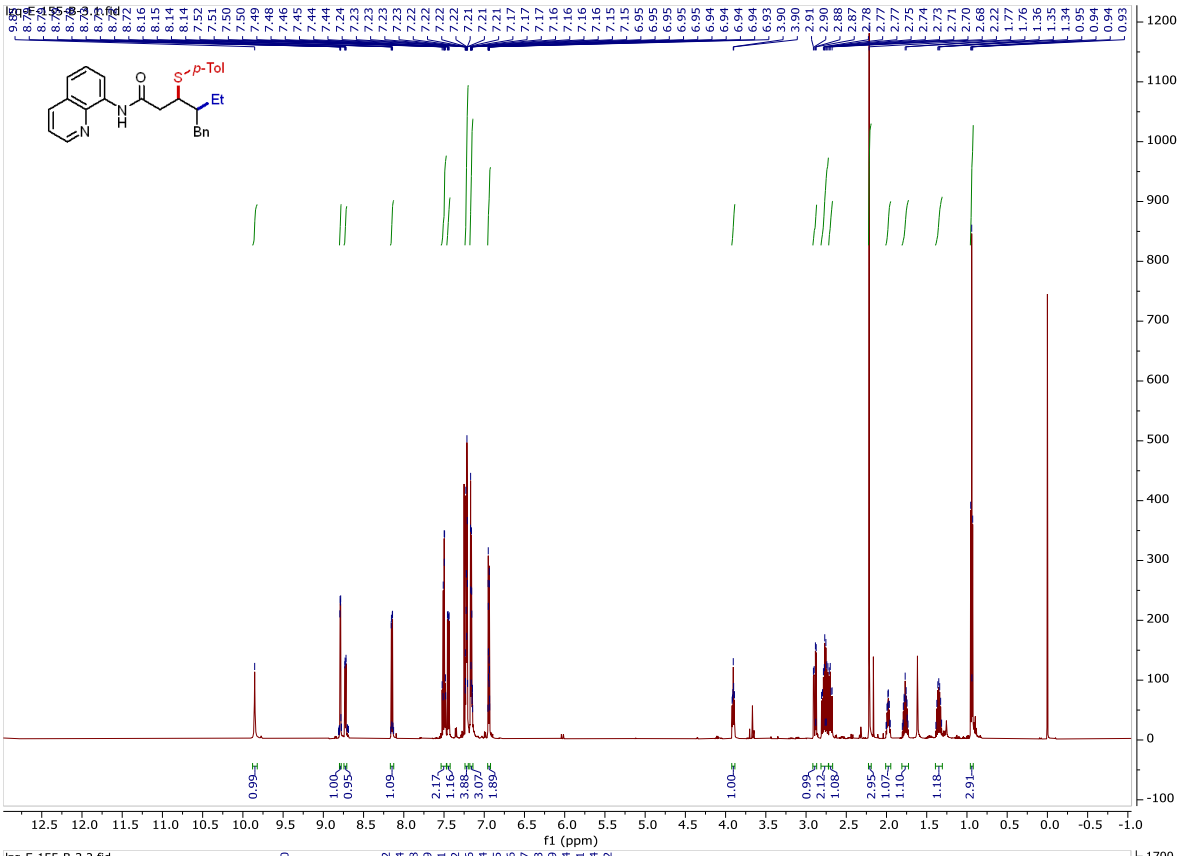

hwj-A-96-2-p.2.fid
p-Tol
Et
Me
169.91
148.26
138.46
137.45
136.43
134.54
132.72
131.88
129.78
128.63
125.68
121.71
121.61
116.65
62.17
42.39
39.00
27.18
21.12
15.71
12.15
f1 (ppm)

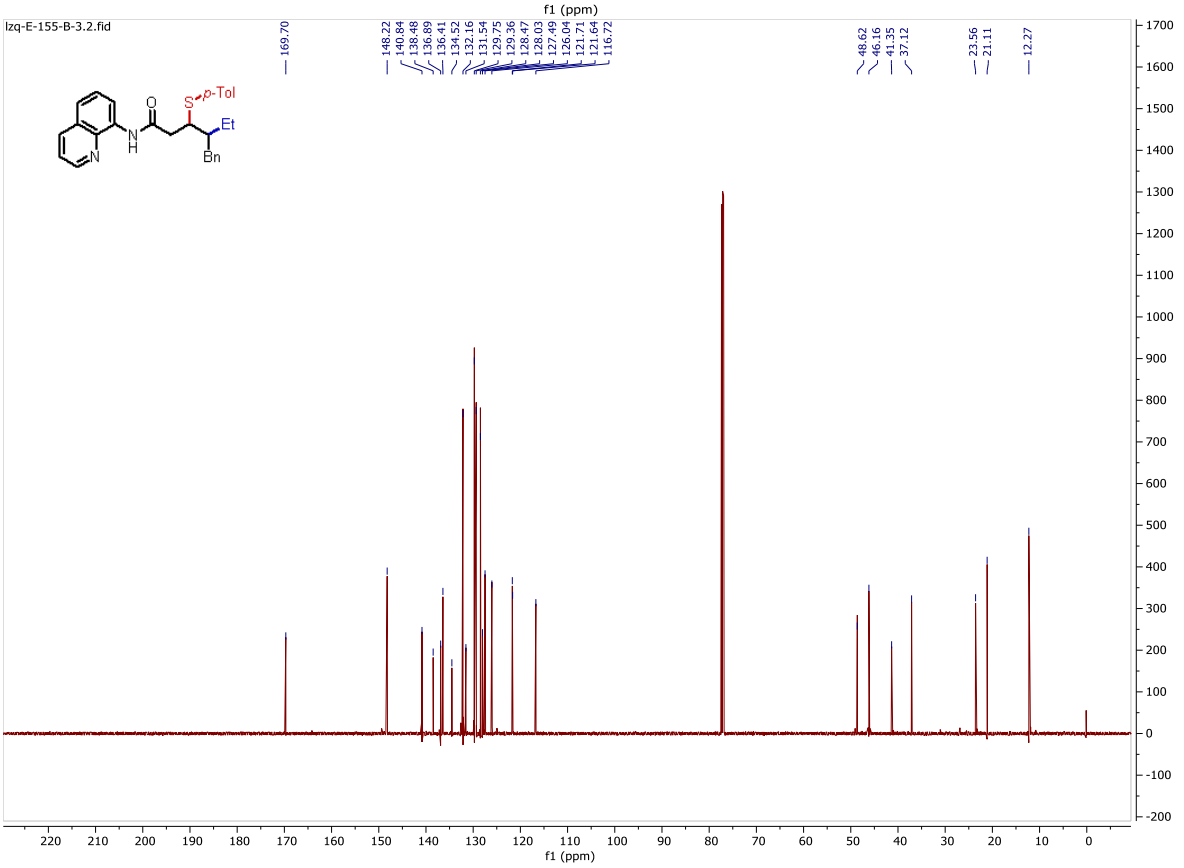

lzq-E-155-B-1.1.fid
p-Tol
Et
Bu
f1 (ppm)

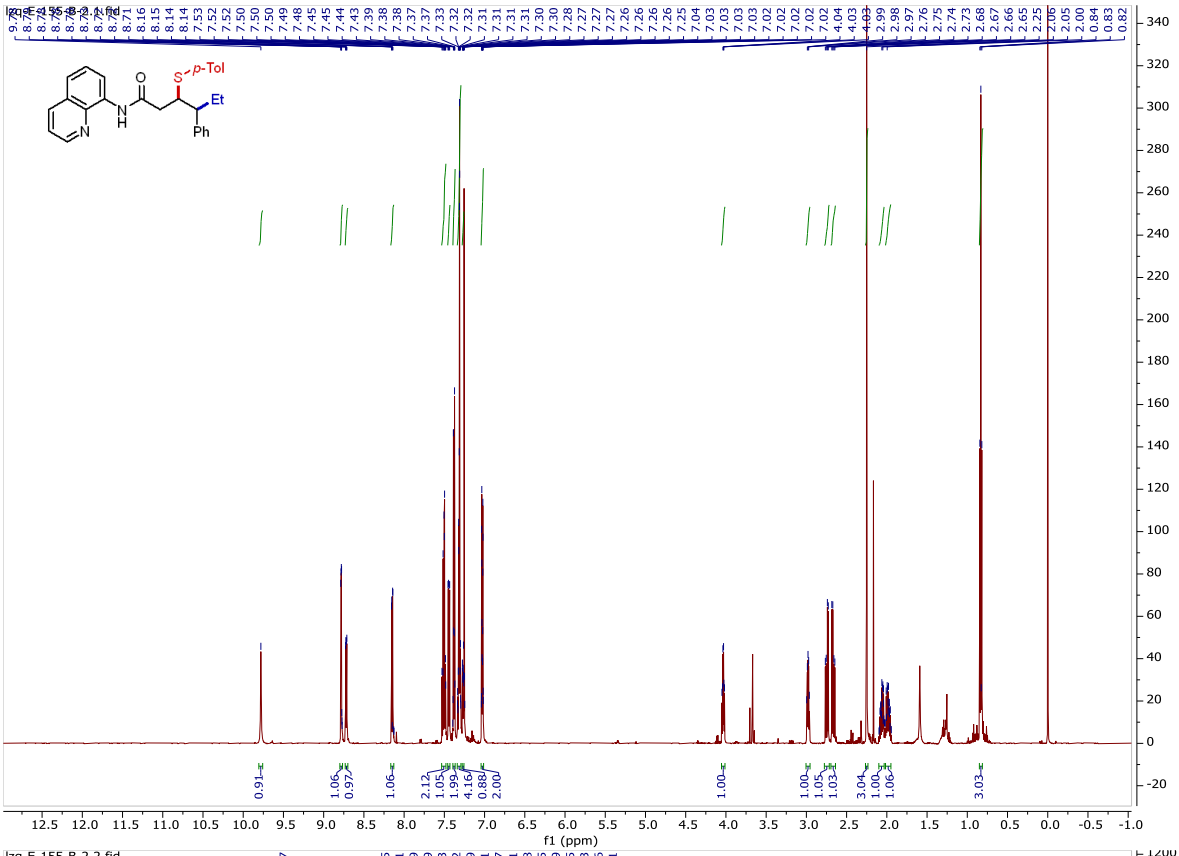

lzq-E-155-B-1.2.fid
169.98
148.22
138.47
137.07
136.41
134.55
132.72
131.75
129.75
128.03
127.48
121.69
121.58
116.66
49.86
43.94
41.48
30.44
30.09
24.00
23.07
21.11
14.18
12.43
p-Tol
Et
Bu
f1 (ppm)

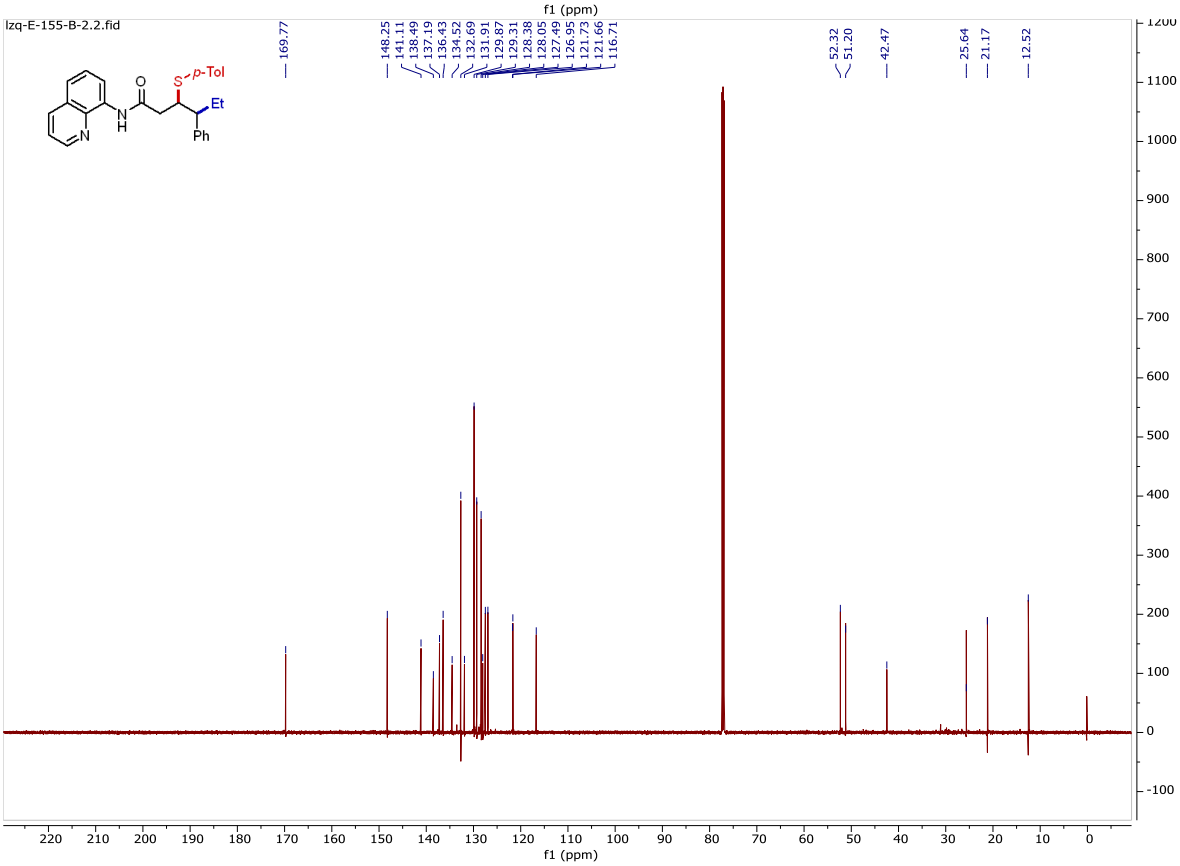

lzq-E-155-B-4.1.fid
p-Tol
Et
Ph
f1 (ppm)

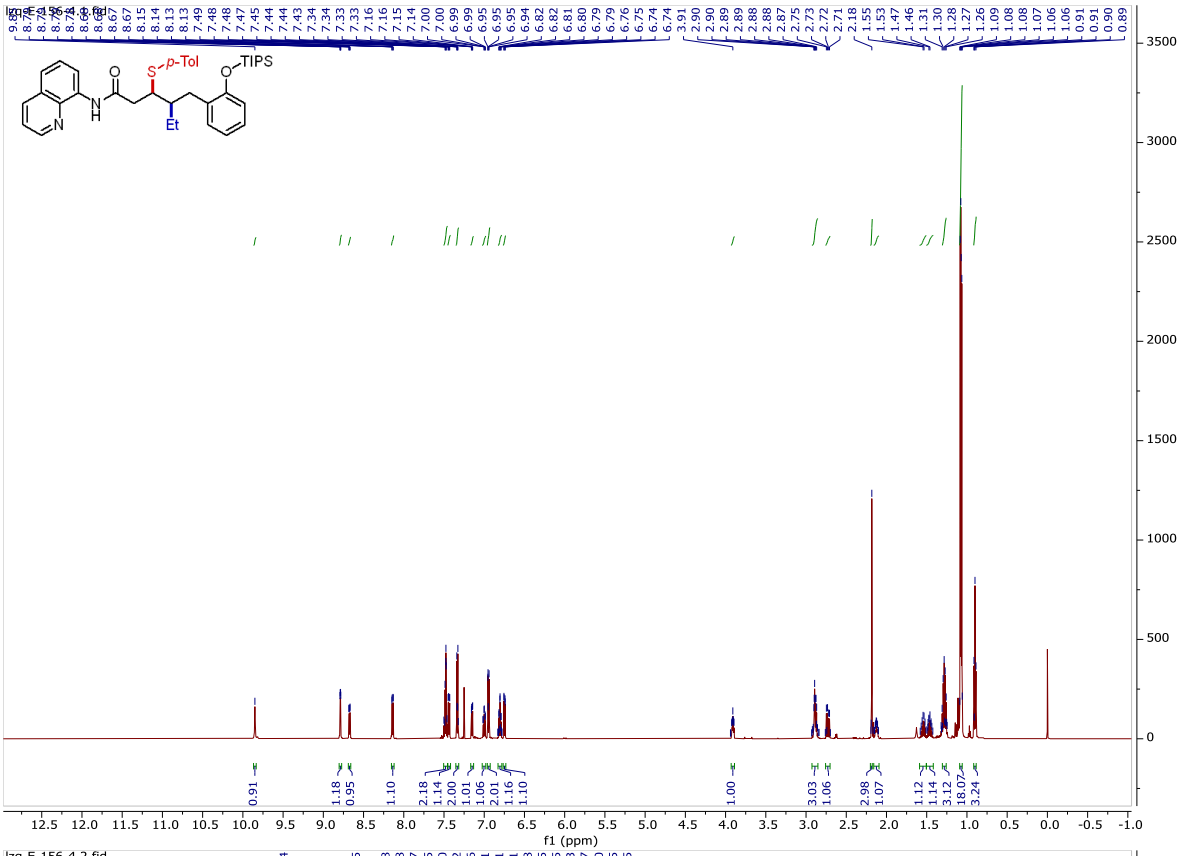

lzq-E-155-B-4.2.fid
169.81
148.23
142.41
138.45
137.21
136.42
134.51
132.90
131.54
129.81
128.53
128.39
128.02
127.47
125.79
121.71
121.61
116.67
49.68
43.31
41.47
34.01
32.70
23.86
21.13
12.29
p-Tol
Et
Ph
f1 (ppm)

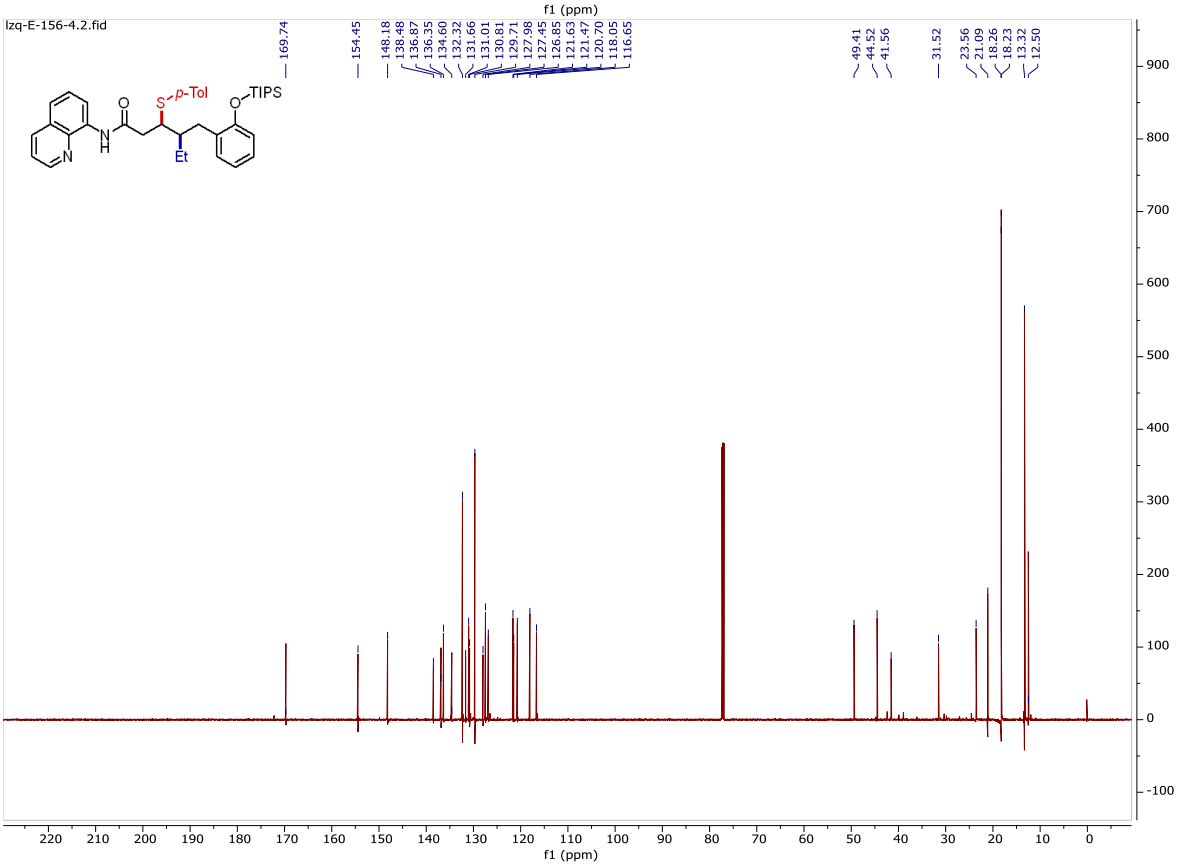

lzq-E-155-B-3.1.fid
p-Tol
Et
Bn
f1 (ppm)

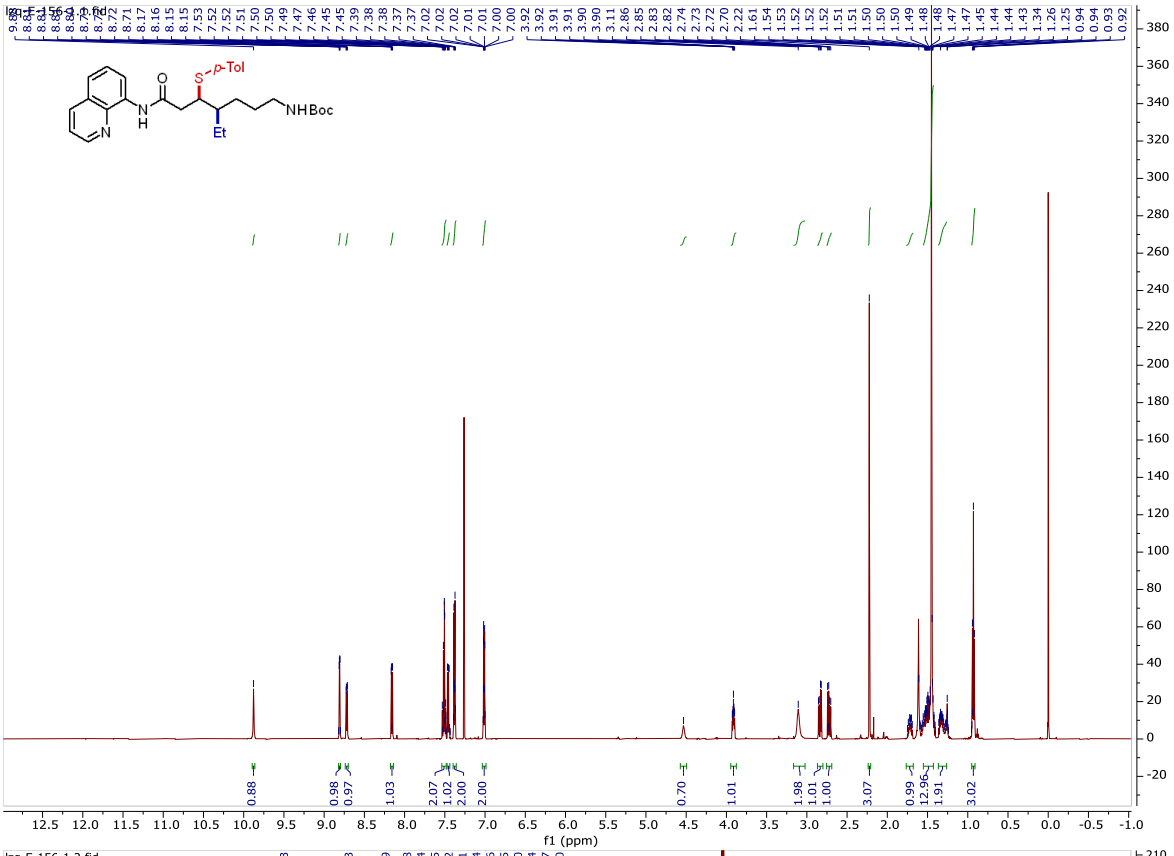

lzq-E-155-B-3.2.fid
169.70
148.22
140.84
138.48
136.89
136.41
134.52
132.16
131.54
129.75
129.36
128.47
128.03
127.49
126.04
121.71
121.64
116.72
48.62
46.16
41.35
37.12
23.56
21.11
12.27
p-Tol
Et
Bn
f1 (ppm)

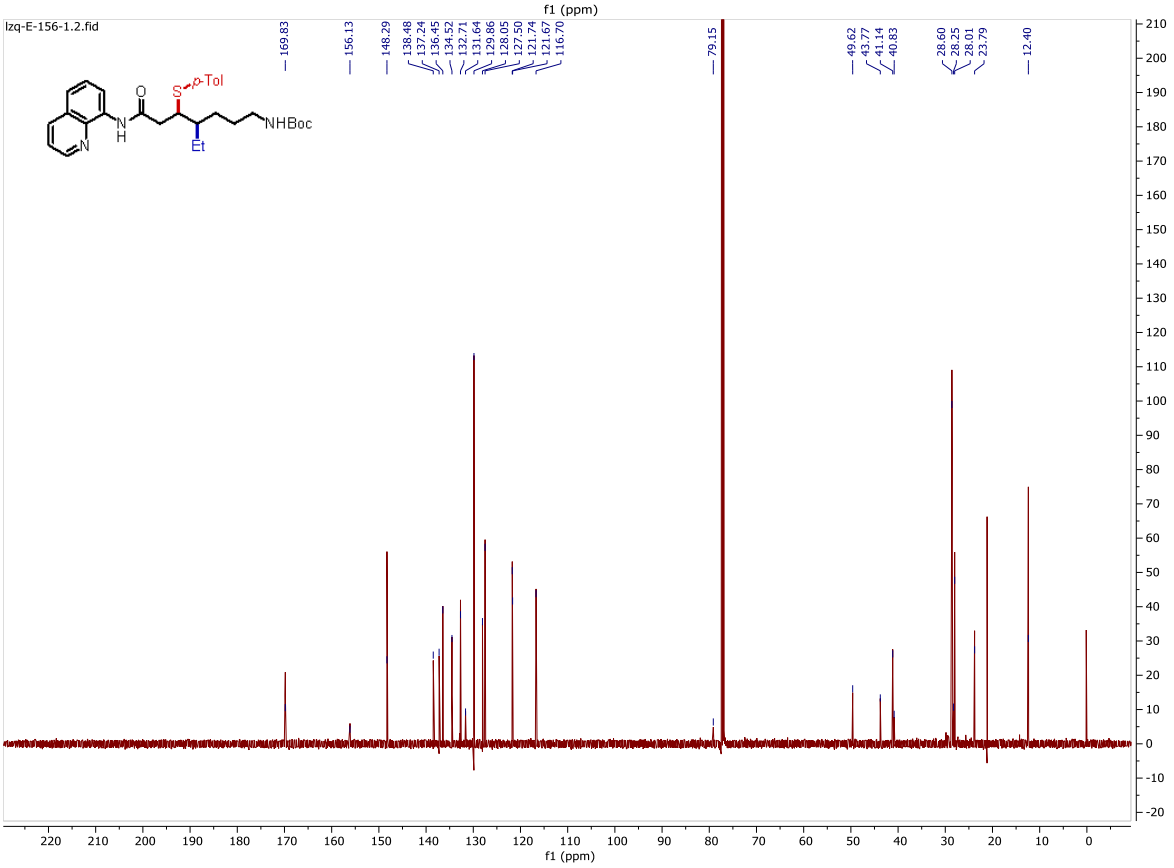

lzq-E-155-B-2.1.fid
p-Tol
Et
Ph
f1 (ppm)

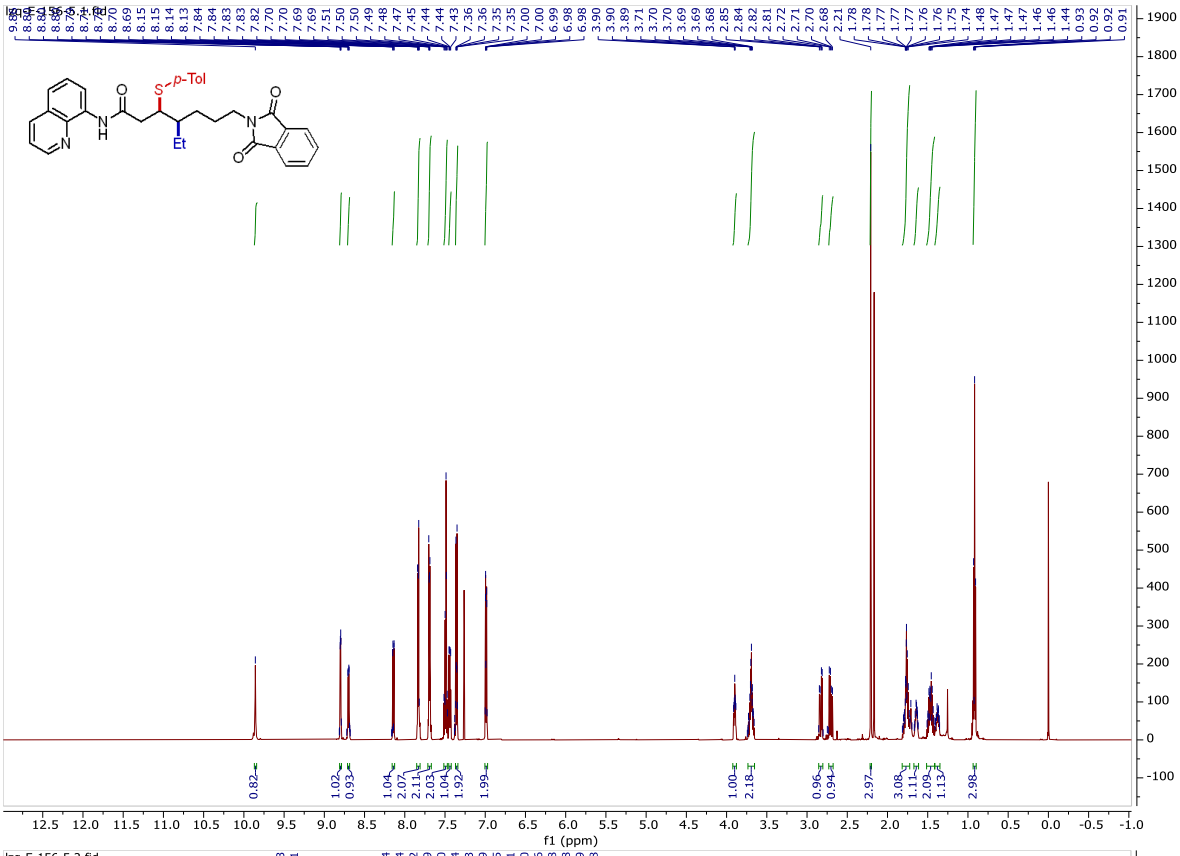

lzq-E-155-B-2.2.fid
p-Tol
Et
Ph
f1 (ppm)

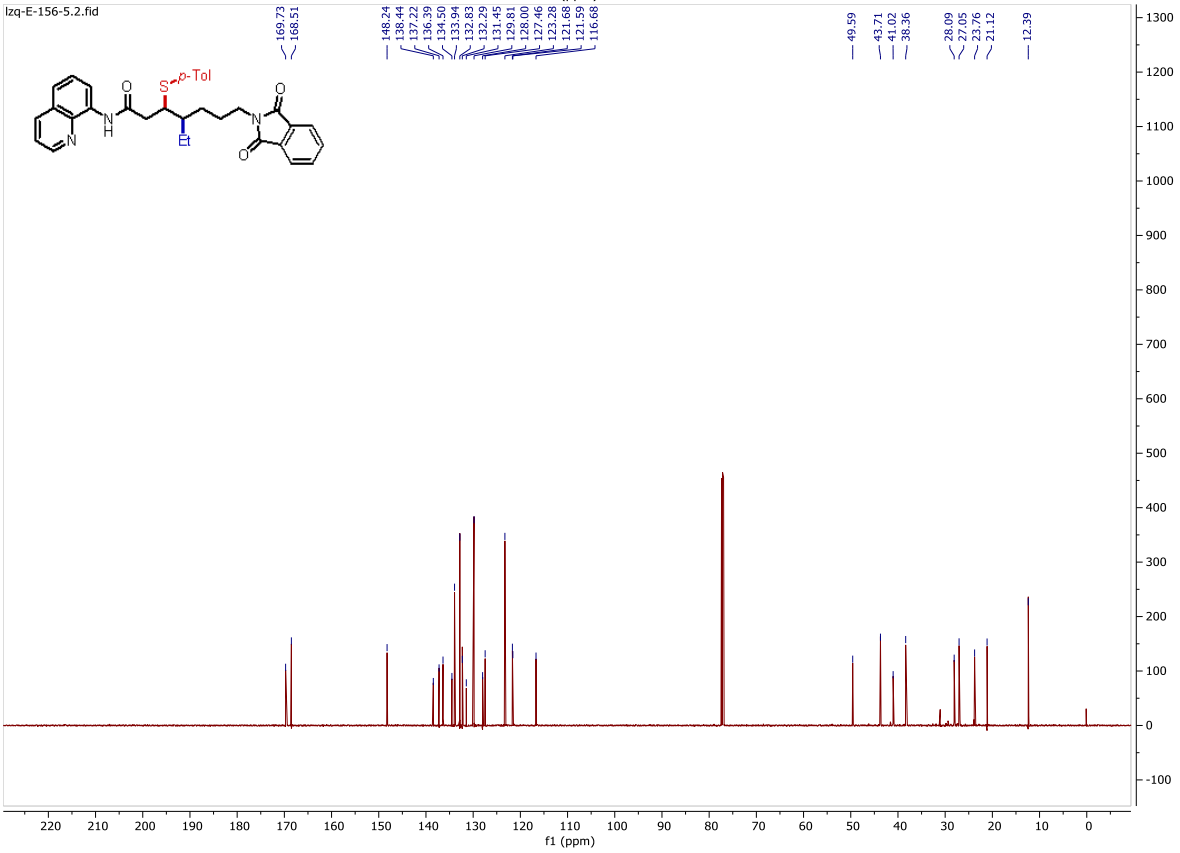

lzq-E-156-4.1.fid
p-Tol
TIPS
Et
f1 (ppm)

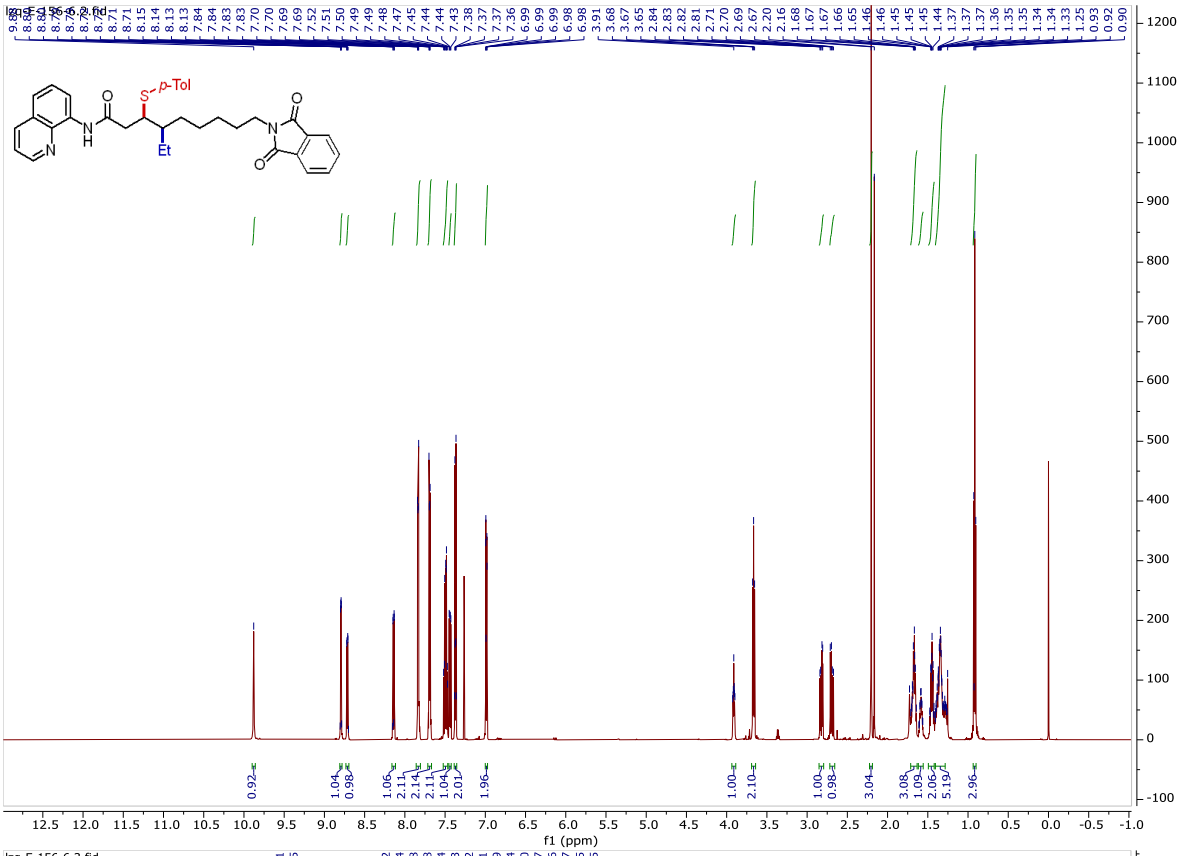

lzq-E-156-4.2.fid
p-Tol
TIPS
Et
f1 (ppm)

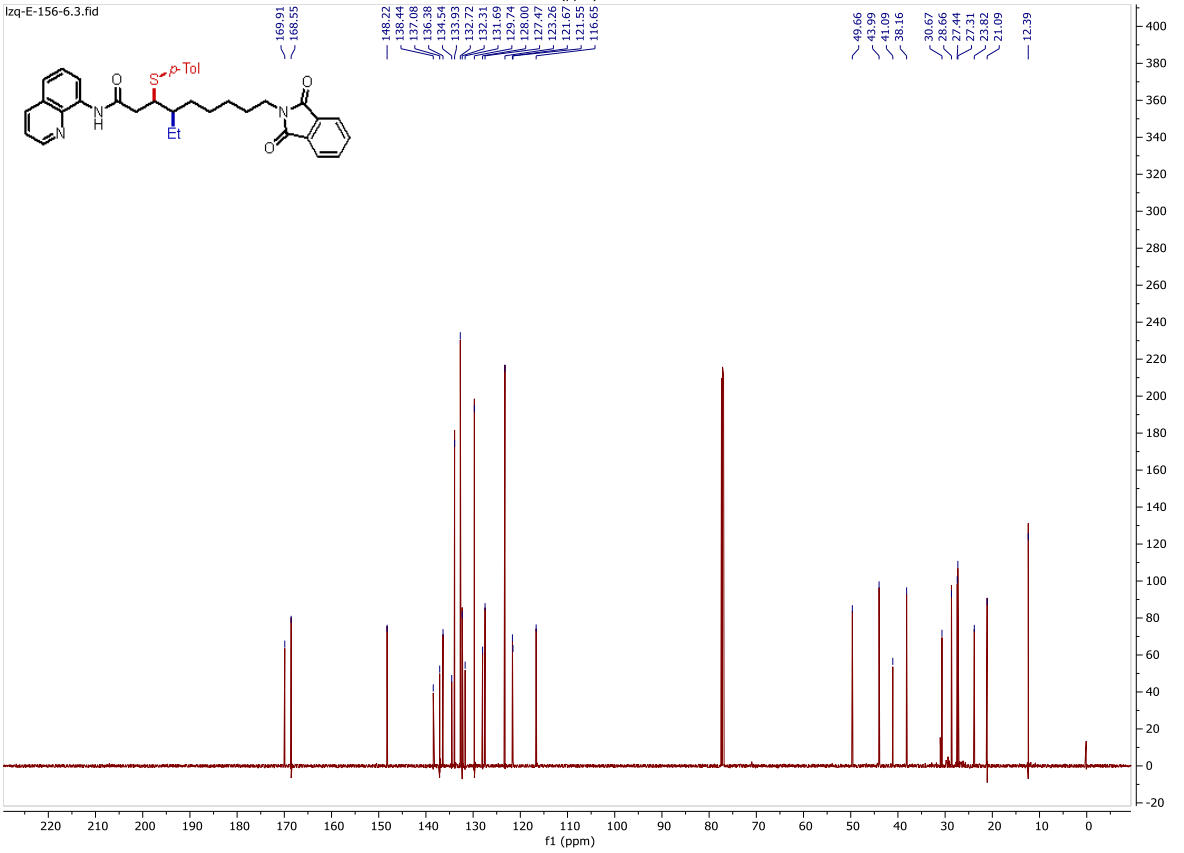

lzq-E-156-1.1.fid
p-Tol
NHBoc
Et
f1 (ppm)

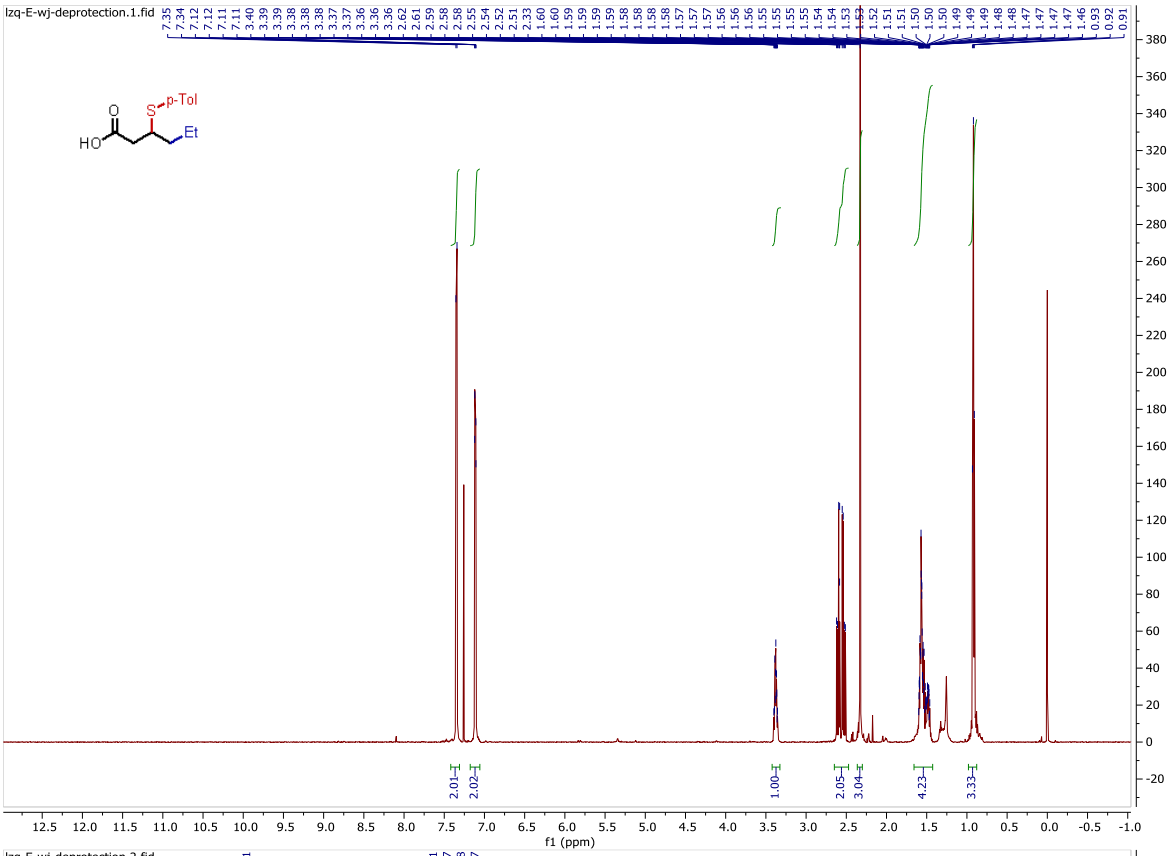

lzq-E-156-1.2.fid
169.83
156.13
148.29
138.48
137.24
136.45
134.52
132.71
131.64
129.86
128.05
127.50
121.74
121.67
116.70
79.15
49.62
43.77
41.14
40.83
28.60
28.25
28.01
23.79
12.40
p-Tol
NHBoc
Et
f1 (ppm)

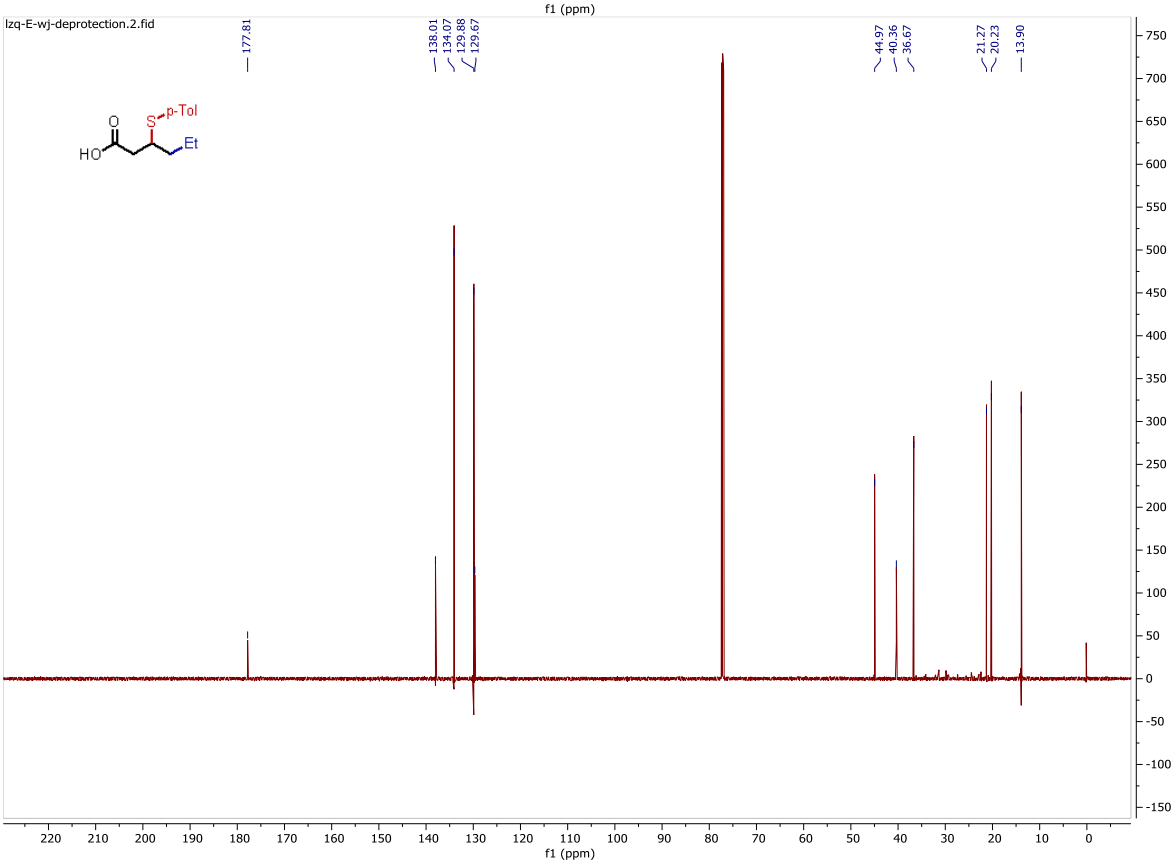

lzq-E-156-5.1.fid
p-Tol
Et
f1 (ppm)


lzq-E-156-5.2.fid
169.73
168.51
148.24
138.44
137.22
136.39
134.50
133.94
132.83
132.29
131.45
131.01
128.00
127.46
123.28
121.68
121.59
116.68
49.59
43.71
41.02
38.36
28.09
27.05
23.76
21.12
12.39
p-Tol
Et
f1 (ppm)


lzq-E-156-6.2.fid
p-Tol
Et
f1 (ppm)


lzq-E-156-6.3.fid
p-Tol
Et
f1 (ppm)


lzq-E-wj-deprotection.1.fid
p-Tol
Et
HO
O
S
2.01
2.02
1.00
2.05
3.04
4.23
3.33
f1 (ppm)


lzq-E-wj-deprotection.2.fid
177.81
138.01
134.07
129.88
129.67
44.97
40.36
36.67
21.27
20.23
13.90
p-Tol
Et
HO
O
S
f1 (ppm)