

Ring-opening S-alkylation of sulfenamides with sulfonium salts

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Supporting Information

Table of contents

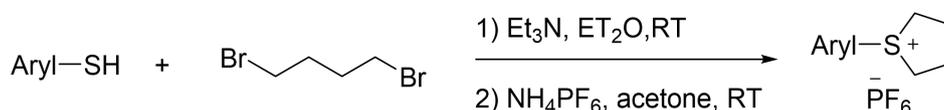
1. General Information	2
2. General procedures	2
2.1 Synthesis of sulfonium salts and sulfenamides	2
2.2 Synthesis of products 3	5
2.3 Synthetic transformations of 3aa	5
3. Characterization data of products	7
4. Reference	23
5. ¹ H, ¹³ C, and ¹⁹ F NMR Spectra	25

1. General Information

Unless stated otherwise, all reagents and solvents were purchased from Adamas-beta, Energy Chemical, Sigma-Aldrich or Aladdin and used without purification. Anhydrous solvents were purchased from Energy Chemical and used as received. Flash chromatography was performed on silica gel (200–300 mesh) with petroleum ether/ethyl acetate as the eluent. NMR spectra were recorded at ambient temperature using Bruker Avance III 400/600 MHz NMR spectrometers. Chemical shifts (ppm) are given relative to solvent: references for CDCl₃ were 7.26 ppm (¹H NMR) and 77.0 ppm (¹³C NMR). HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI). The products were isolated from the reaction mixture by column chromatography on silica gel 200-300 mesh. Starting materials of sulfonium salts **1** and sulfenamides **2** were synthesized according to literature procedures.¹⁻²

2. General procedures

2.1 Synthesis of sulfonium salts and sulfenamides

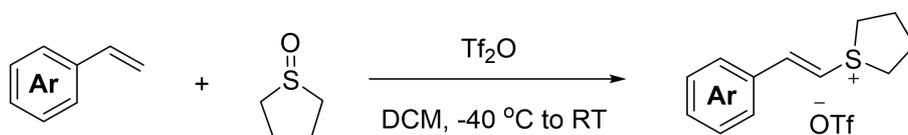


According to the literature methods^[1a]: To a stirred solution of thiophenol (5 mmol) and 1,4-dibromobutane (2.16 g, 10 mmol, 2.0 equiv.) in Et₂O (0.5 M) was slowly added Et₃N (759 mg, 7.5 mmol, 1.5 equiv.) at room temperature. After 2 h, the reaction was diluted with ethyl acetate and washed with 1 N HCl (and brine. The organic layer was dried (Na₂SO₄), the solvents were evaporated, and the crude material was dissolved in acetone (10 mL) and treated with NH₄PF₆ (1.23 g, 7.5 mmol, 1.5 equiv.). After stirring overnight at room temperature, the reaction mixture was filtered through a medium porosity fritted-glass funnel, Then the organic phase was filtered, concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography eluting with DCM/MeOH to give the corresponding sulfonium salts **1a-1i**, **1m** in 38-86% yields.

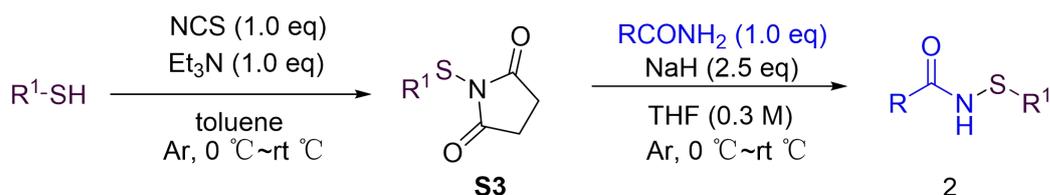


Method A^[1b-1c]: Tetrahydrothiophene (882 mg, 10 mmol, 1.1 equiv.), alkyl bromides (1.54 g, 9 mmol, 1.0 equiv.) was dissolved in acetone (10 mL) and stirred at 25 °C for 16 hours. The formed precipitate was filtered and washed with acetone. The filtrate was reduced to half its volume and excess diethyl ether was added. The formed precipitate was filtered and washed with diethyl ether then dried in-vacuo to get sulfonium salts **1l** and **1u** in 38% and 62%, respectively.

Method B^[1d]: A flame-dried flask was successively charged with tetrahydrothiophene (882 mg, 10 mmol, 1.1 equiv.), alkyl iodides (9 mmol, 1.0 equiv.) and acetonitrile (8 mL) was stirred at 70 °C for 2 days. The acetonitrile was removed under reduced pressure and the resulting yellow solid was triturated in ether. The resulting solid was concentrated in vacuo to afford sulfonium salts **1j** and **1k** in 35% and 31%, respectively.



According to the literature methods^[1e]: To a solution of sulfoxide (955 μL , 11 mmol, 1.1 equiv.) in anhydrous DCM (30 mL) at -40 °C, Tf₂O (1.85 mL, 11 mmol, 1.1 equiv.) was added dropwise under N₂, then styrene derivative (1.16 mL, 10 mmol, 1.0 equiv.) was added gradually. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. Upon completion monitored by the TLC, the solvent was removed by concentration under reduced pressure. The product was then precipitated by the addition of Et₂O. The pure products **1n-1t** were obtained by recrystallisation (DCM/Et₂O, 42-76% yields).



According to the literature methods^[2]: Under an argon atmosphere, a solution of the

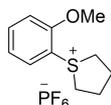
thiol (5 mmol, 1.0 equiv.) in toluene (0.25 M) was added to a flame-dried three-neck round-bottom flask. The mixture was stirred at 0 °C, and *N*-chlorosuccinimide (6 mmol, 1.0 equiv.) was added slowly. Upon completion of the addition, the reaction mixture was stirred at room temperature for 1 h. Subsequently, a solution of triethylamine (1.0 equiv.) in toluene (0.7 M) was added dropwise over 30 min. The resulting mixture was then heated to 40 °C and stirred overnight. After cooling to room temperature, the reaction mixture was diluted with diethyl ether and filtered through a pad of celite. The filtrate was concentrated under reduced pressure, and the crude residue was purified by the appropriate chromatographic method to afford the target product **S3**.

Under an argon atmosphere, the amide (5 mmol, 1.0 equiv) was added to a flame-dried three-neck round-bottom flask equipped with an addition funnel and a stir bar. THF was added to give a 0.15 M solution, and the mixture was cooled to 0 °C. Sodium hydride (12.5 mmol, 2.5 equiv) was added, and the mixture was allowed to warm to room temperature and stirred for 30 min. The corresponding thiosuccinimide (1.0 equiv) was dissolved in THF to give a 0.3 M solution, transferred to the addition funnel, and added dropwise to the reaction mixture over 1 h. After the addition was complete, the mixture was stirred at room temperature for an additional 30 min. The reaction was quenched with saturated aqueous ammonium chloride, and dichloromethane (10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give the crude product. Purification by column chromatography afforded target products **2** in 46-62% yields.

product was further purified through flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA 1:1) to obtain the expected oxidative product **4** (85.0 mg) in 98% yield.^[3]

3. Characterization data of products

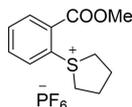
1-(2-methoxyphenyl)tetrahydro-1H-thiophen-1-ium hexafluorophosphate (**1b**)



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.78 (d, $J = 7.9$ Hz, 1H), 7.76 – 7.68 (m, 1H), 7.38 (d, $J = 8.3$ Hz, 1H), 7.28 – 7.17 (m, 1H), 4.00 (s, 3H), 3.87 – 3.75 (m, 4H), 2.35 – 2.15 (m, 4H).

$^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 157.3, 135.0, 129.2, 122.0, 113.4, 57.0, 44.8, 28.2.

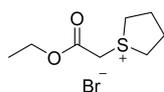
1-(2-(methoxycarbonyl)phenyl)tetrahydro-1H-thiophen-1-ium hexafluorophosphate (**1c**)



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.49 (dd, $J = 7.6, 1.5$ Hz, 1H), 8.26 (d, $J = 7.5$ Hz, 1H), 8.16 (td, $J = 7.8, 1.6$ Hz, 1H), 8.12 – 8.06 (m, 1H), 4.19 (s, 3H), 4.15 – 4.03 (m, 4H), 2.49 (m, 4H).

$^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 165.6, 134.8, 132.9, 132.5, 129.3, 128.6, 128.3, 53.5, 46.0, 28.1.

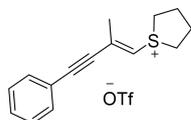
1-(2-methoxyphenyl)tetrahydro-1H-thiophen-1-ium bromide (**1l**)



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 4.90 (s, 2H), 4.48 (q, $J = 7.1$ Hz, 2H), 3.93 – 3.84 (m, 4H), 2.59 – 2.51 (m, 2H), 2.48 – 2.41 (m, 2H), 1.50 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 165.5, 62.6, 44.1, 43.5, 28.2, 13.9.

1-(2-methyl-4-phenylbut-1-en-3-yn-1-yl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**1t**)

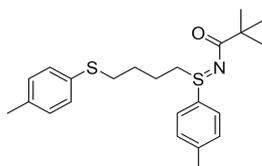


$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.66 – 7.58 (m, 2H), 7.55 – 7.47 (m, 3H), 7.00 –

6.83 (m, 1H), 3.82 – 3.71 (m, 2H), 3.63 – 3.51 (m, 2H), 3.37 (s, 2H), 2.31 – 2.25 (m, 2H), 2.19 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 136.9, 131.8, 130.5, 129.0, 122.7, 120.3, 101.2, 85.2, 47.7, 28.7, 23.2.

N-(*p*-tolyl(4-(*p*-tolylthio)butyl)-λ⁴-sulfaneylidene) pivalamide (**3aa**)



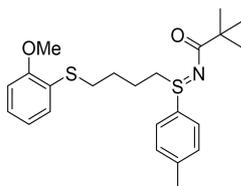
79.0 mg, light yellow oil, yield: 98%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.12 – 3.00 (m, 1H), 2.99 – 2.88 (m, 1H), 2.89 – 2.77 (m, 2H), 2.39 (s, 3H), 2.31 (s, 3H), 1.75 – 1.62 (m, 4H), 1.24 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.0, 142.3, 136.2, 131.8, 131.1, 130.2, 129.5, 126.8, 48.6, 39.8, 33.7, 28.5, 27.6, 21.8, 21.3, 20.8.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₃H₃₁NNaOS₂⁺ 424.1745, found 424.1743.

N-((4-((2-methoxyphenyl)thio)butyl) (*p*-tolyl)-λ⁴-sulfaneylidene) pivalamide (**3ba**)



75.0 mg, light yellow oil, yield: 90%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

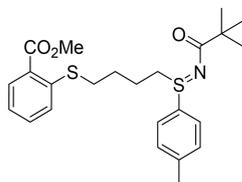
¹H NMR (600 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.15 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 3.07 – 3.03 (m, 1H), 2.94 – 2.90 (m, 1H), 2.85 – 2.80 (m, 2H), 2.37 (s, 3H), 1.72 – 1.67 (m, 4H), 1.21 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.1, 157.4, 142.4, 131.1, 130.3, 129.9, 127.4, 126.9, 123.6, 120.9, 110.4, 55.6, 48.7, 39.9, 31.3, 28.6, 27.5, 22.1, 21.3.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₃H₃₁NNaO₂S₂⁺ 440.1694, found

440.1701.

Methyl-2-((4-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)butyl)thio) benzoate (**3ca**)



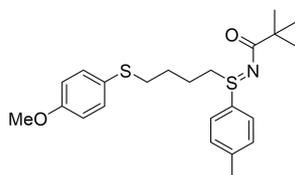
55.6 mg, light yellow oil, yield: 62%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 3.91 (s, 3H), 3.17 – 3.09 (m, 1H), 3.02 – 2.88 (m, 3H), 2.41 (s, 3H), 1.86 – 1.79 (m, 4H), 1.24 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.3, 166.8, 142.5, 141.1, 132.3, 131.3, 131.1, 130.4, 127.7, 127.0, 125.6, 124.0, 52.1, 48.8, 40.0, 31.3, 28.6, 26.9, 22.5, 21.4.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₄H₃₁NNaO₃S₂⁺ 468.1643, found 468.1643.

N-((4-((4-methoxyphenyl)thio)butyl) (p-tolyl)-λ⁴-sulfaneylidene) pivalamide (**3da**)



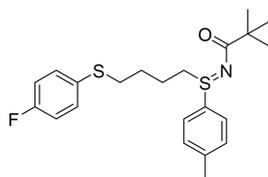
76.3 mg, light yellow oil, yield: 91%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 4H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.10 – 3.01 (m, 1H), 2.96 – 2.88 (m, 1H), 2.80 – 2.71 (m, 2H), 2.39 (s, 3H), 1.72 – 1.60 (m, 4H), 1.23 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.0, 158.9, 142.4, 133.4, 131.1, 130.3, 126.9, 125.6, 114.5, 55.2, 48.6, 39.9, 35.1, 28.5, 27.8, 21.8, 21.3.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₃H₃₁NNaO₂S₂⁺ 440.1688, found 440.1689.

N-((4-((4-fluorophenyl)thio)butyl) (p-tolyl)-λ⁴-sulfaneylidene) pivalamide (**3ea**)



72.0 mg, light yellow oil, yield: 89%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

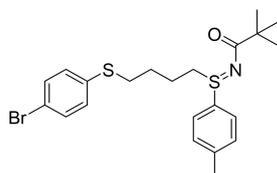
¹H NMR (600 MHz, CDCl₃) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.26 (m, 4H), 6.97 (t, *J* = 8.7 Hz, 2H), 3.07 – 3.03 (m, 1H), 2.95 – 2.90 (m, 1H), 2.84 – 2.78 (m, 2H), 2.39 (s, 3H), 1.72 – 1.63 (m, 4H), 1.22 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.2, 161.8 (d, *J* = 246.7 Hz), 142.5, 132.6 (d, *J* = 8.0 Hz), 131.2, 130.6 (d, *J* = 3.2 Hz), 130.3, 127.0, 116.0 (d, *J* = 21.9 Hz), 48.7, 40.0, 34.4, 28.6, 27.7, 21.9, 21.4.

¹⁹F NMR (565 MHz, CDCl₃) δ -115.18.

HR-MS(ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₂H₂₈FNNaOS₂⁺ 428.1494, found 428.1491.

N-((4-((4-bromophenyl)thio)butyl)(*p*-tolyl)-λ⁴-sulfaneylidene)pivalamide (**3fa**)



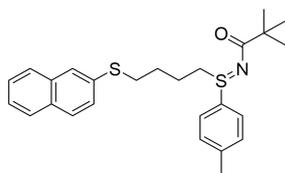
80.3 mg, light yellow oil, yield: 86%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 3.11 – 3.04 (m, 1H), 3.00 – 2.94 (m, 1H), 2.90 – 2.85 (m, 2H), 2.42 (s, 3H), 1.75 – 1.69 (m, 4H), 1.25 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.3, 142.5, 135.1, 132.0, 131.1, 130.9, 130.4, 127.0, 120.0, 48.7, 40.0, 33.2, 28.6, 27.6, 22.0, 21.4.

HR-MS(ESI-TOF)*m/z*: [M+Na]⁺ calcd. for C₂₂H₂₈BrNNaOS₂⁺ 488.0693, found 488.0699.

N-((4-(naphthalen-2-ylthio)butyl) (*p*-tolyl)-λ⁴-sulfaneylidene) pivalamide (**3ga**)



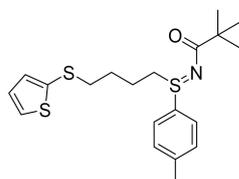
83.1 mg, light yellow oil, yield: 95%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (600 MHz, CDCl₃) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.71 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.46 – 7.43 (m, 1H), 7.40 – 7.37 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.10 – 3.06 (m, 1H), 3.03 – 2.95 (m, 3H), 2.39 (s, 3H), 1.79 – 1.74 (m, 4H), 1.26 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.2, 142.4, 133.6, 133.3, 131.7, 131.1, 130.3, 128.4, 127.6, 127.3, 127.1, 126.9, 126.9, 126.5, 125.7, 48.7, 39.9, 32.9, 28.6, 27.7, 22.0, 21.3.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₆H₃₁NNaOS₂⁺ 460.1745, found 460.1755.

N-((4-(thiophen-2-ylthio)butyl)(*p*-tolyl)-λ⁴-sulfaneylidene) pivalamide (**3ha**)



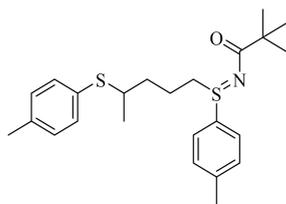
76.6 mg, light yellow oil, yield: 97%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.06 – 6.99 (m, 1H), 6.96 – 6.89 (m, 1H), 3.08 – 2.99 (m, 1H), 2.96 – 2.88 (m, 1H), 2.73 – 2.66 (m, 2H), 2.37 (s, 3H), 1.70 – 1.61 (m, 4H), 1.21 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.1, 142.4, 133.7, 133.6, 131.1, 130.3, 129.3, 127.4, 126.9, 48.6, 39.9, 37.9, 28.5, 27.4, 21.6, 21.3.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₀H₂₇NNaOS₃⁺ 416.1147, found 416.1143.

N-(*p*-tolyl(5-(*p*-tolylthio)pentan-2-yl)-λ⁴-sulfaneylidene) pivalamide (**3ia**)



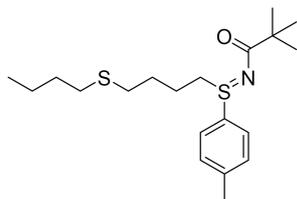
43.3 mg, light yellow oil, yield: 52%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.08 – 3.00 (m, 3H), 3.02 – 2.91 (m, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.03 (s, 1H), 1.82 – 1.75 (m, 2H), 1.74 – 1.64 (m, 2H), 1.19 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.5, 144.9, 142.8, 135.8, 130.6, 130.5, 130.0, 128.0, 127.0, 55.5, 48.4, 40.0, 28.5, 21.9, 21.7, 21.6, 21.4, 20.7.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₄H₃₃NNaOS₂⁺ 438.1901, found 438.1902.

N-((4-(butylthio)butyl)(p-tolyl)-λ⁴-sulfaneylidene)pivalamide (**3ja**)



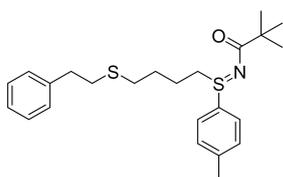
63.8 mg, light yellow oil, yield: 87%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 3.11 – 3.00 (m, 1H), 2.97 – 2.87 (m, 1H), 2.49 – 2.37 (m, 4H), 2.34 (s, 3H), 1.72 – 1.56 (m, 4H), 1.51 – 1.43 (m, 2H), 1.37 – 1.29 (m, 2H), 1.18 (s, 9H), 0.85 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.1, 142.3, 131.2, 130.2, 126.9, 48.8, 39.9, 31.6, 31.5, 31.2, 28.5, 28.1, 22.1, 21.8, 21.3, 13.5.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₀H₃₃NNaOS₂⁺ 390.1896, found 390.1899.

N-((4-(phenethylthio)butyl)(p-tolyl)-λ⁴-sulfaneylidene)pivalamide (**3ka**)



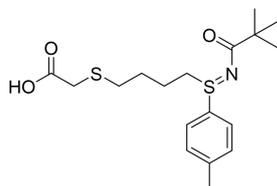
78.9 mg, light yellow oil, yield: 95%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.23 – 7.13 (m, 3H), 3.12 – 3.02 (m, 1H), 2.98 – 2.90 (m, 1H), 2.84 (dd, *J* = 9.0, 6.4 Hz, 2H), 2.76 – 2.66 (m, 2H), 2.53 – 2.43 (m, 2H), 2.38 (s, 3H), 1.74 – 1.60 (m, 4H), 1.24 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.1, 142.4, 140.3, 131.2, 130.3, 128.3, 126.9, 126.2, 48.8, 39.9, 36.1, 33.5, 31.4, 28.6, 28.0, 22.1, 21.3.

HR-MS(ESI-TOF) *m/z*: [M+H]⁺ calcd. for C₂₄H₃₄NOS₂⁺ 416.2077, found 416.2073.

2-((4-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)butyl)thio)acetic acid (**3la**)



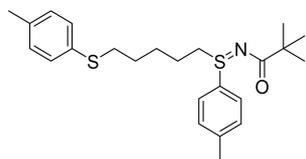
53.9 mg, light yellow oil, yield: 73%. Eluent: pentane/ethyl acetate = 3:1 to 0:1.

¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 5.72 (s, 1H), 4.16 – 4.08 (m, 2H), 3.09 (s, 4H), 2.40 – 2.31 (m, 2H), 2.26 (s, 3H), 1.86 – 1.77 (m, 2H), 1.19 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 181.3, 170.4, 139.0, 134.3, 129.3, 124.3, 59.4, 43.7, 38.5, 31.7, 30.9, 27.5, 20.8, 15.0.

HR-MS(ESI-TOF) *m/z*: [M-H]⁻ calcd. for C₁₈H₂₆NO₃S₂⁻ 368.1360, found 368.1538.

N-(*p*-tolyl(5-(*p*-tolylthio)pentyl)-λ⁴-sulfaneylidene) pivalamide (**3ma**)



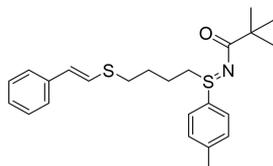
75.3 mg, light yellow oil, yield: 90%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.10 – 3.01 (m, 1H), 2.95 – 2.88 (m, 1H), 2.81 (t, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H), 1.61 – 1.48 (m, 6H), 1.23 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.3, 142.5, 136.2, 132.5, 131.5, 130.4, 130.1, 129.7, 127.0, 49.1, 40.0, 33.0, 28.7, 28.6, 27.3, 22.6, 21.5, 21.0.

HR-MS (ESI-TOF) m/z : $[M+Na]^+$ calcd. for $C_{24}H_{33}NNaOS_2^+$ 438.1901, found 438.1905.

((4-((styryl)thio)butyl) (p-tolyl)- λ^4 -sulfaneylidene) pivalamide (**3na**)



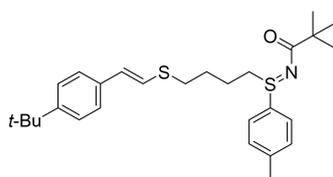
72.0 mg, light yellow oil, yield: 87%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.31 – 7.26 (m, 6H), 7.23 – 7.16 (m, 1H), 6.64 (d, $J = 15.6$ Hz, 1H), 6.45 (d, $J = 15.6$ Hz, 1H), 3.15 – 3.07 (m, 1H), 3.02 – 2.94 (m, 1H), 2.82 – 2.72 (m, 2H), 2.39 (s, 3H), 1.82 – 1.71 (m, 4H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 142.5, 136.8, 131.1, 130.4, 128.6, 127.7, 126.99, 126.97, 125.5, 124.3, 48.8, 40.0, 32.0, 28.6, 28.1, 22.1, 21.4.

HR-MS (ESI-TOF) m/z : $[M+Na]^+$ calcd. for $C_{24}H_{31}NNaOS_2^+$ 436.1739, found 436.1735.

((4-((4-(tert-butyl)styryl)thio)butyl) (p-tolyl)- λ^4 -sulfaneylidene)pivalamide (**3oa**)



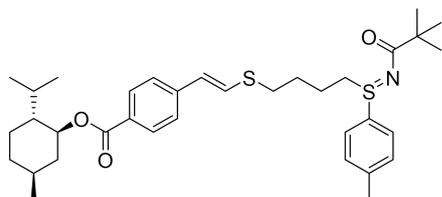
87.5 mg, light yellow oil, yield: 93%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

1H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.58 (d, $J = 15.5$ Hz, 1H), 6.45 (d, $J = 15.5$ Hz, 1H), 3.11 – 3.07 (m, 1H), 2.99 – 2.96 (m, 1H), 2.77 – 2.73 (m, 2H), 2.38 (s, 3H), 1.78 – 1.72 (m, 4H), 1.30 (s, 9H), 1.24 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2, 150.1, 142.5, 134.0, 131.1, 130.4, 128.0, 127.0, 125.5, 125.2, 123.2, 48.7, 40.0, 34.5, 32.0, 31.2, 28.6, 28.1, 22.0, 21.4.

HR-MS (ESI-TOF) m/z : $[M+Na]^+$ calcd. for $C_{28}H_{39}NNaOS_2^+$ 492.2365, found 492.2367.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl-4-(2-((4-(N-pivaloyl-S-(p-tolyl)sulfonimidoyl)butyl)thio)vinyl)benzoate (**3pa**)



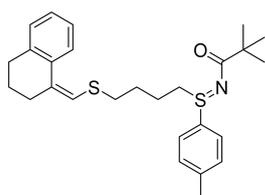
65.5 mg, light yellow oil, yield: 55%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.28 (m, 4H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 4.95 – 4.88 (m, 1H), 3.16 – 3.08 (m, 1H), 3.03 – 2.96 (m, 1H), 2.86 – 2.77 (m, 2H), 2.40 (s, 3H), 2.12 (d, *J* = 11.7 Hz, 1H), 2.03 – 1.87 (m, 2H), 1.84 – 1.70 (m, 6H), 1.60 – 1.51 (m, 2H), 1.24 (s, 9H), 1.15 – 1.05 (m, 2H), 0.92 (dd, *J* = 6.7, 4.8 Hz, 6H), 0.79 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.3, 165.8, 142.5, 141.0, 131.1, 130.4, 130.0, 128.9, 127.8, 127.0, 125.7, 125.1, 74.7, 48.8, 47.2, 40.9, 40.0, 34.3, 31.8, 31.4, 28.6, 28.0, 26.5, 23.6, 22.1, 22.0, 21.4, 20.7, 16.5.

HR-MS (ESI-TOF) *m/z*: [M+H]⁺ calcd. for C₃₅H₅₀NO₃S₂⁺ 596.3227, found 596.3220.

((4-(((3,4-dihydronaphthalen-1(2H)-ylidene)methyl)thio)butyl) (p-tolyl)-λ⁴-sulfaneylidene) pivalamide (**3qa**)



46.3 mg, light yellow oil, yield: 51%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

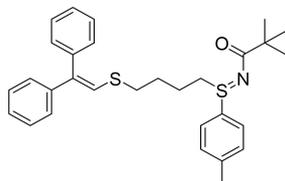
¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.57 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.23 (m, 1H), 7.21 – 7.06 (m, 3H), 3.14 – 3.06 (m, 1H), 3.02 – 2.95 (m, 1H), 2.80 – 2.72 (m, 4H), 2.51 – 2.43 (m, 2H), 2.40 (s, 3H), 2.21 (t, *J* = 1.7 Hz, 2H), 1.82 – 1.69 (m, 4H), 1.25 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.2, 142.4, 136.7, 136.0, 135.0, 130.3, 129.6, 128.8, 127.0, 126.5, 126.1, 123.3, 119.6, 48.7, 39.9, 33.5, 31.2, 30.4, 28.9, 28.6, 22.5, 21.8,

21.4, 16.2.

HR-MS (ESI-TOF) m/z : $[M+Na]^+$ calcd. for $C_{27}H_{35}NNaOS_2^+$ 476.2058, found 476.2057.

N-((4-((2,2-diphenylvinyl)thio)butyl)(*p*-tolyl)- λ^4 -sulfaneylidene)pivalamide (**3ra**)



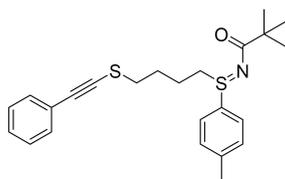
66.7 mg, light yellow oil, yield: 68%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 8.2$ Hz, 2H), 7.42 – 7.37 (m, 2H), 7.35 – 7.33 (m, 1H), 7.32 – 7.25 (m, 7H), 7.22 (d, $J = 1.7$ Hz, 1H), 7.21 – 7.19 (m, 1H), 6.51 (s, 1H), 3.16 – 3.06 (m, 1H), 3.03 – 2.95 (m, 1H), 2.79 – 2.69 (m, 2H), 2.40 (s, 3H), 1.81 – 1.68 (m, 4H), 1.26 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 190.2, 142.5, 141.6, 139.3, 139.0, 131.1, 130.4, 129.6, 128.2, 128.2, 127.5, 127.0, 126.9, 125.2, 48.8, 40.0, 34.1, 28.8, 28.6, 21.9, 21.4.

HR-MS (ESI-TOF) m/z : $[M+Na]^+$ calcd. for $C_{30}H_{35}NNaOS_2^+$ 512.2058, found 512.2068.

N-((4-((phenylethynyl)thio)butyl) (*p*-tolyl)- λ^4 -sulfaneylidene) pivalamide (**3sa**)



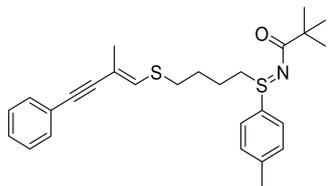
37.3 mg, light yellow oil, yield: 45%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.33 (m, 2H), 7.29 – 7.25 (m, 4H), 7.25 – 7.23 (m, 1H), 3.14 – 3.06 (m, 1H), 3.01 – 2.94 (m, 1H), 2.78 – 2.69 (m, 2H), 2.35 (s, 3H), 1.91 – 1.84 (m, 2H), 1.78 – 1.71 (m, 2H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 142.5, 131.4, 131.1, 130.4, 128.2, 128.1, 127.0, 123.1, 93.3, 78.6, 48.7, 40.0, 34.8, 28.6, 27.9, 21.6, 21.4.

HR-MS (ESI-TOF) m/z : $[M+Na]^+$ calcd. for $C_{24}H_{29}NNaOS_2^+$ 434.1588, found 434.1587.

((4-((2-methyl-4-phenylbut-1-en-3-yn-1-yl)thio)butyl) (p-tolyl)- λ^4 -sulfaneylidene) pivalamide (**3ta**)



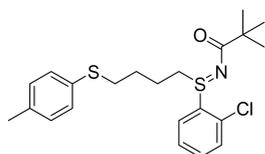
68.1 mg, brown oil, yield: 75%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 7.9 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.29 – 7.24 (m, 5H), 6.12 (s, 1H), 3.11 – 3.04 (m, 1H), 2.97 – 2.91 (m, 1H), 2.74 – 2.64 (m, 2H), 2.33 (s, 3H), 1.93 (s, 3H), 1.76 – 1.66 (m, 4H), 1.20 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.3, 142.5, 132.6, 131.4, 131.1, 130.4, 128.2, 128.1, 127.0, 123.3, 115.5, 96.4, 88.1, 48.9, 40.0, 33.0, 29.0, 28.6, 22.9, 21.9, 21.4.

HR-MS (ESI-TOF) m/z : [M+Na]⁺ calcd. for C₂₇H₃₃NNaOS₂⁺ 474.1901, found 474.1904.

N-((2-chlorophenyl) (4-(p-tolylthio)butyl)- λ^4 -sulfaneylidene) pivalamide (**3ab**)



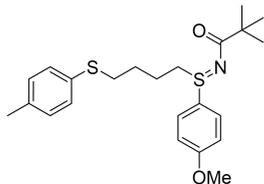
80.5 mg, light yellow oil, yield: 95%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (600 MHz, CDCl₃) δ 7.78 – 7.76 (m, 1H), 7.45 (d, J = 1.8 Hz, 3H), 7.23 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.17 – 3.11 (m, 1H), 3.04 – 2.99 (m, 1H), 2.86 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 1.96 – 1.78 (m, 2H), 1.76 – 1.72 (m, 2H), 1.28 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.6, 136.4, 133.0, 133.0, 132.5, 131.9, 130.4, 130.3, 129.7, 128.1, 127.5, 46.6, 40.1, 33.8, 28.6, 27.7, 22.0, 21.0.

HR-MS(ESI-TOF) m/z : [M+Na]⁺ calcd. for C₂₂H₂₈ClNNaOS₂⁺ 444.1199, found 444.1207.

N-((4-methoxyphenyl) (4-(p-tolylthio)butyl)- λ^4 -sulfaneylidene) pivalamide (**3ac**)



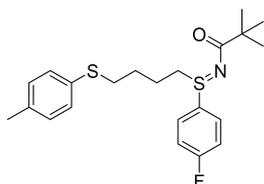
82.1 mg, light yellow oil, yield: 98%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.12 – 3.03 (m, 1H), 2.93 – 2.87 (m, 1H), 2.86 – 2.78 (m, 2H), 2.31 (s, 3H), 1.71 – 1.63 (m, 4H), 1.21 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.1, 162.4, 136.4, 131.9, 130.3, 129.7, 128.9, 125.0, 115.1, 55.5, 48.8, 39.9, 33.8, 28.6, 27.8, 27.6, 22.0, 20.9.

HR-MS(ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₃H₃₁NNaO₂S₂⁺ 440.1694, found 440.1690.

N-((4-fluorophenyl) (4-(*p*-tolylthio)butyl)-λ⁴-sulfaneylidene) pivalamide (**3ad**)



58.6 mg, light yellow oil, yield: 72%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

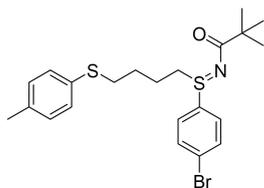
¹H NMR (600 MHz, CDCl₃) δ 7.70 – 7.65 (m, 2H), 7.22 – 7.16 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.09 – 3.03 (m, 1H), 2.97 – 2.90 (m, 1H), 2.88 – 2.79 (m, 2H), 2.31 (s, 3H), 1.74 – 1.65 (m, 4H), 1.22 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.4, 164.7 (d, *J* = 253.2 Hz), 136.5, 131.8, 130.4, 130.0 (d, *J* = 3.2 Hz), 129.7, 129.3 (d, *J* = 9.0 Hz), 117.0 (d, *J* = 22.7 Hz), 48.8, 40.0, 33.8, 28.6, 27.7, 21.9, 21.0.

¹⁹F NMR (565 MHz, CDCl₃) δ -106.69.

HR-MS(ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₂H₂₈FNNaOS₂⁺ 428.1494, found 428.1494.

N-((4-bromophenyl) (4-(*p*-tolylthio)butyl)-λ⁴-sulfaneylidene) pivalamide (**3ae**)



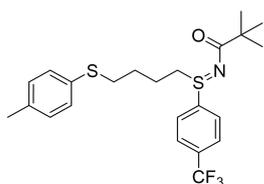
71.3 mg, light yellow oil, yield: 76%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (600 MHz, CDCl₃) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.07 – 3.02 (m, 1H), 2.98 – 2.92 (m, 1H), 2.88 – 2.80 (m, 2H), 2.31 (s, 3H), 1.74 – 1.64 (m, 4H), 1.22 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 190.5, 136.5, 133.8, 132.9, 131.8, 130.4, 129.7, 128.4, 126.5, 48.6, 40.0, 33.8, 28.6, 27.7, 21.9, 21.0.

HR-MS(ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₂H₂₈BrNNaOS₂⁺ 488.0693, found 488.0687.

N-(4-(*p*-tolylthio)butyl)(4-(trifluoromethyl)phenyl)-λ⁴-sulfaneylidene)pivalamide (**3af**)



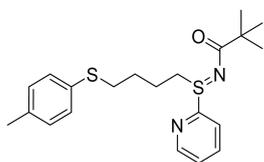
73.9 mg, light yellow oil, yield: 81%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.73 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.11 – 2.96 (m, 2H), 2.89 – 2.79 (m, 2H), 2.31 (s, 3H), 1.81 – 1.66 (m, 4H), 1.24 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.8, 139.3, 136.5, δ 133.7 (q, *J* = 33.1 Hz), 131.8, 130.4, 129.7, 127.3, 126.6 (q, *J* = 3.7 Hz), 123.24 (q, *J* = 272.9 Hz), 48.6, 40.0, 33.8, 28.5, 27.7, 21.9, 21.0.

HR-MS(ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₃H₂₈F₃NNaOS₂⁺ 478.1462, found 478.1470.

N-(pyridin-2-yl(4-(*p*-tolylthio)butyl)-λ⁴-sulfaneylidene) pivalamide (**3ag**)



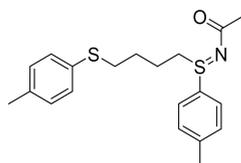
48.4 mg, light yellow oil, yield: 62%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (600 MHz, CDCl₃) δ 8.60 (s, 1H), 7.88 – 7.83 (m, 2H), 7.41 – 7.36 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 3.45 – 3.40 (m, 1H), 3.22 – 3.16 (m, 1H), 2.82 (t, *J* = 6.9 Hz, 2H), 2.29 (s, 3H), 1.90 – 1.84 (m, 1H), 1.71 – 1.62 (m, 3H), 1.27 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 191.0, 155.8, 149.9, 138.1, 136.3, 131.9, 130.3, 129.6, 125.0, 122.7, 45.9, 40.1, 33.8, 28.6, 27.7, 21.5, 20.9.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₁H₂₈N₂NaOS₂⁺ 411.1541, found 411.1543.

N-(*p*-tolyl(4-(*p*-tolylthio)butyl)-λ⁴-sulfaneylidene) acetamide (**3ah**)



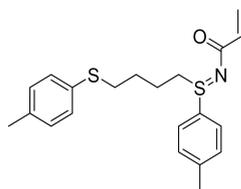
48.6 mg, light yellow oil, yield: 67%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.23 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.62 (t, *J* = 7.3 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 6H), 2.33 (s, 3H), 1.80 – 1.73 (m, 2H), 1.63 – 1.57 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 176.4, 136.8, 136.0, 134.1, 132.5, 130.1, 130.1, 129.6, 123.6, 50.3, 34.1, 27.3, 26.2, 22.1, 20.97, 20.95.

HR-MS (ESI-TOF) *m/z*: [M+Na]⁺ calcd. for C₂₀H₂₅NNaOS₂⁺ 382.1275, found 382.1275.

N-(*p*-tolyl(4-(*p*-tolylthio)butyl)-λ⁴-sulfaneylidene) acrylamide(**3ai**)



58.2 mg, light yellow oil, yield: 78%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

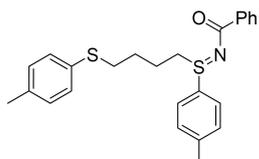
¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.45 (dd, *J* = 17.2, 10.1 Hz, 1H), 6.28 (dd, *J* = 17.2, 2.2 Hz, 1H), 5.58 (dd, *J* = 10.1, 2.2 Hz, 1H), 3.30 – 3.19 (m, 1H), 3.07 –

2.97 (m, 1H), 2.93 – 2.83 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 1.83 – 1.71 (m, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 175.6, 142.3, 135.8, 133.2, 131.0, 129.8, 129.7, 129.5, 129.0, 126.6, 124.0, 48.1, 33.0, 27.1, 21.5, 20.7, 20.2.

HR-MS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{21}\text{H}_{25}\text{NNaOS}_2^+$ 394.1275, found 394.1266.

N-(*p*-tolyl(4-(*p*-tolylthio)butyl)- λ^4 -sulfaneylidene) benzamide (**3aj**)



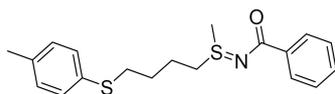
57.4 mg, light yellow oil, yield: 68%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, 2H), 7.70 (d, 2H), 7.47 – 7.38 (m, 3H), 7.34 (d, 2H), 7.22 (d, 2H), 7.09 (d, 2H), 3.30 – 3.23 (m, 1H), 3.11 – 3.03 (m, 1H), 2.92 – 2.83 (m, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 1.85 – 1.72 (m, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 176.6, 142.9, 136.5, 136.4, 131.8, 130.6, 130.6, 130.5, 130.4, 129.7, 128.7, 127.7, 127.2, 49.2, 33.8, 27.8, 22.2, 21.4, 21.0.

HR-MS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{25}\text{H}_{27}\text{NNaOS}_2^+$ 444.1432, found 444.1432.

N-(methyl(4-(*p*-tolylthio)butyl)- λ^4 -sulfaneylidene)benzamide (**3ak**)



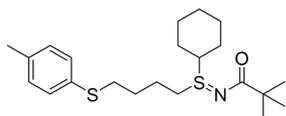
67.6 mg, light yellow oil, yield: 98%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.03 (m, 2H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.37 – 7.32 (m, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 3.14 – 3.06 (m, 1H), 2.92 – 2.85 (m, 3H), 2.67 (s, 3H), 2.29 (s, 3H), 1.95 – 1.86 (m, 2H), 1.79 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 136.4, 136.2, 131.6, 130.6, 130.3, 129.6, 128.3, 127.7, 45.8, 33.6, 29.7, 27.7, 21.9, 20.9.

HR-MS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{19}\text{H}_{24}\text{NOS}_2^+$ 346.1294, found 346.1288.

N-(cyclohexyl(4-(*p*-tolylthio)butyl)- λ^4 -sulfaneylidene)pivalamide (**3al**)



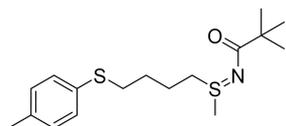
77.1 mg, light yellow oil, yield: 98%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.09 – 3.02 (m, 1H), 2.91 – 2.84 (m, 3H), 2.81 – 2.74 (m, 1H), 2.30 (s, 3H), 2.04 – 1.99 (m, 1H), 1.94 – 1.89 (m, 1H), 1.88 – 1.79 (m, 4H), 1.75 – 1.64 (m, 3H), 1.48 – 1.39 (m, 2H), 1.32 – 1.22 (m, 3H), 1.18 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 191.1, 136.3, 132.0, 130.3, 129.7, 54.5, 40.9, 40.2, 33.8, 28.7, 27.9, 27.1, 26.5, 25.4, 25.3, 22.3, 20.9.

HR-MS (ESI-TOF) *m/z*: [M+H]⁺ calcd. for C₂₂H₃₆NOS₂⁺ 394.2234, found 394.2227.

N-(methyl(4-(*p*-tolylthio)butyl)-l4-sulfaneylidene)pivalamide (**3am**)



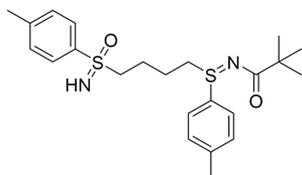
55.9 mg, light yellow oil, yield: 86%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.00 – 2.93 (m, 1H), 2.90 – 2.84 (m, 2H), 2.83 – 2.76 (m, 1H), 2.54 (s, 3H), 2.28 (s, 3H), 1.85 – 1.77 (m, 2H), 1.74 – 1.67 (m, 2H), 1.15 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 190.7, 136.4, 131.8, 130.3, 129.7, 45.3, 39.6, 33.7, 29.4, 28.5, 27.7, 21.8, 20.9.

HR-MS (ESI-TOF) *m/z*: [M+H]⁺ calcd. for C₁₇H₂₈NOS₂⁺ 326.1607, found 326.1601.

N-((4-(4-methylphenylsulfonimidoyl)butyl)(*p*-tolyl)-l4-sulfaneylidene)pivalamide (**4**)



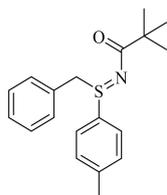
84.7 mg, light yellow oil, yield: 98%. Eluent: DCM/MeOH = 50:1.

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.05 – 2.82 (m, 5H), 2.36 (s, 3H), 2.31 (s, 3H), 1.76 – 1.64 (m, 2H), 1.62 – 1.50 (m, 2H), 1.12 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 190.1, 144.0, 142.5, 138.3, 130.6, 130.2, 129.7, 128.2, 126.7, 56.5, 48.2, 39.8, 28.4, 22.1, 21.5, 21.3, 21.2.

HR-MS(ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{32}\text{N}_2\text{NaO}_2\text{S}_2^+$ 455.1803, found 455.1801.

N-(benzyl(*p*-tolyl)- λ^4 -sulfaneylidene) pivalamide (**3ua**)^[4]



53.8 mg, light yellow oil, yield: 86%. Eluent: pentane/ethyl acetate = 3:1 to 1:1.

^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.1$ Hz, 2H), 7.30 – 7.26 (m, 1H), 7.21 (m, 4H), 6.90 (d, $J = 7.3$ Hz, 2H), 4.42 (d, $J = 12.3$ Hz, 1H), 4.15 (d, $J = 12.3$ Hz, 1H), 2.38 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 190.1, 142.5, 130.8, 129.9, 129.2, 128.5, 128.2, 127.9, 55.3, 40.0, 28.6, 21.4.

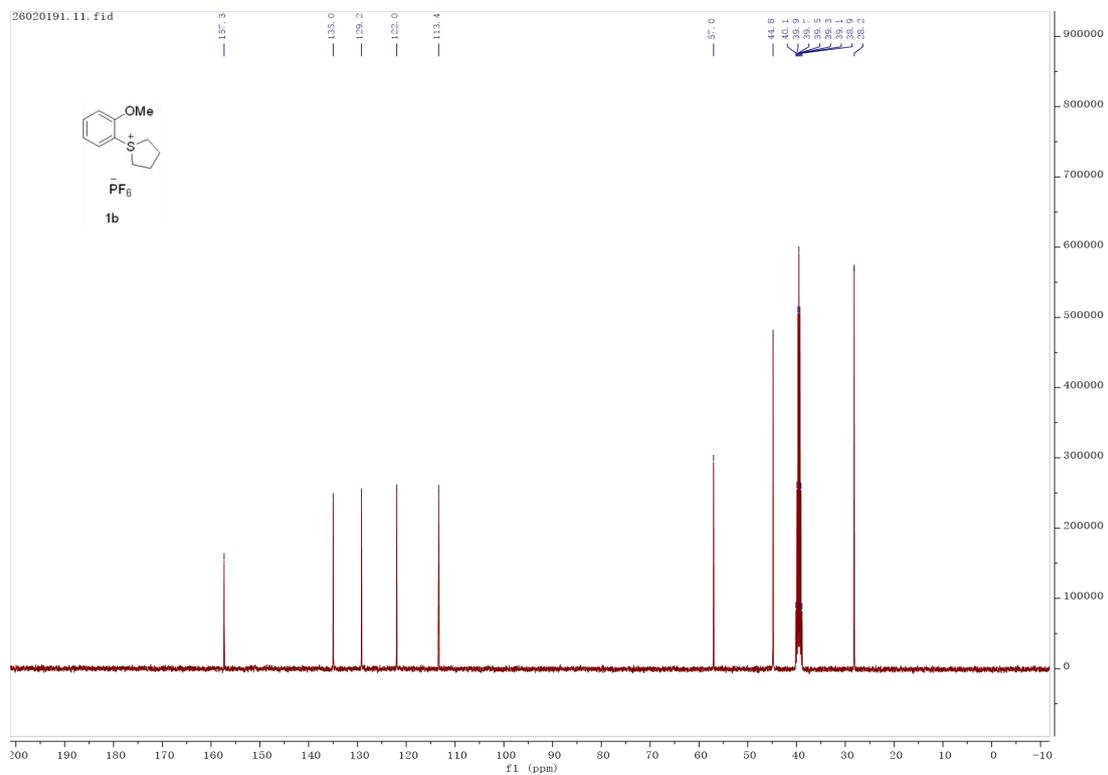
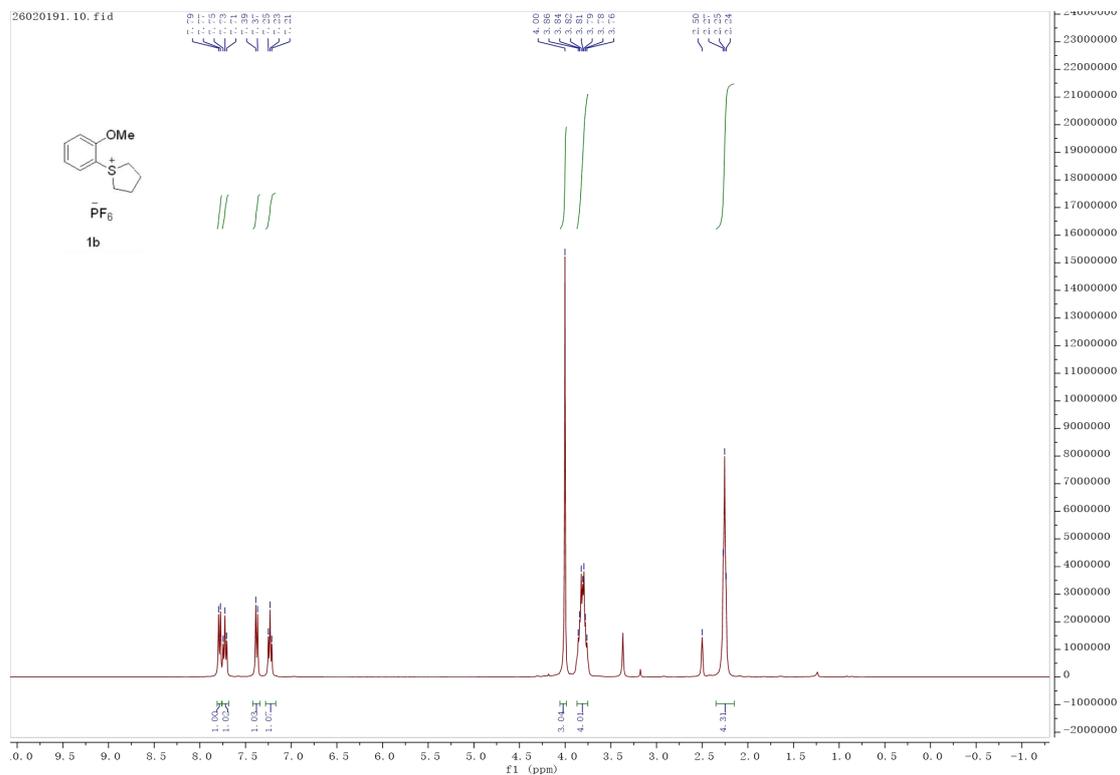
HR-MS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{19}\text{H}_{23}\text{NNaOS}^+$ 336.1398, found 336.1394.

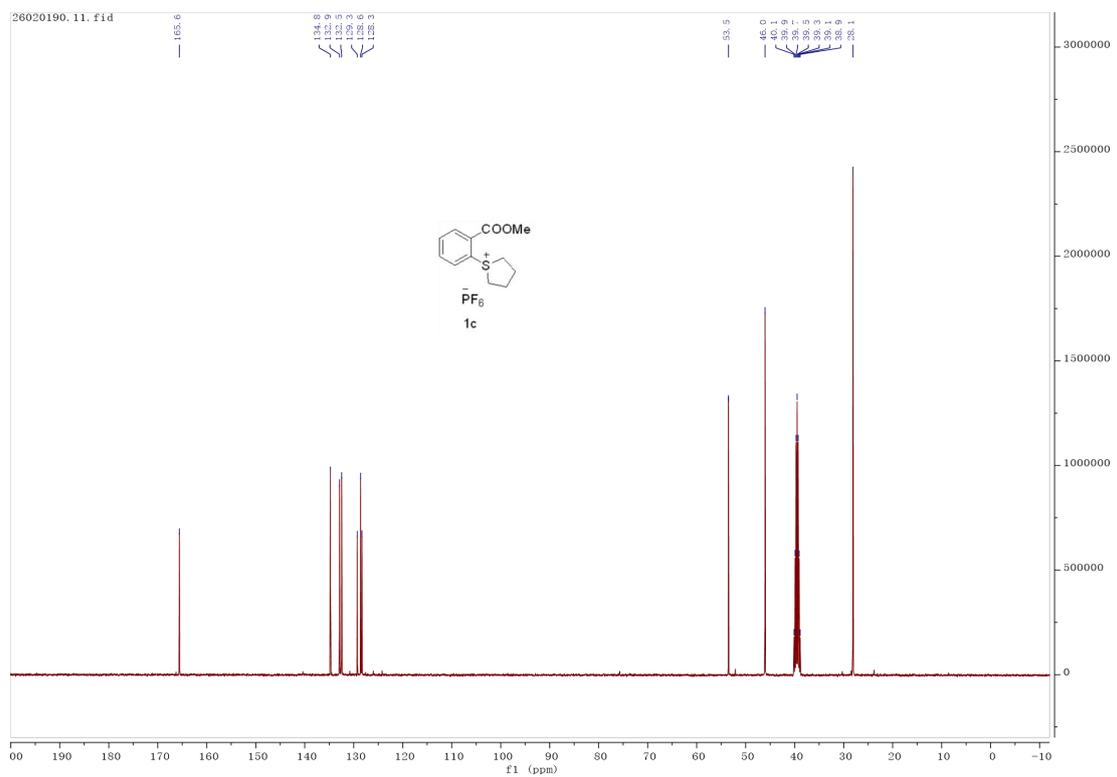
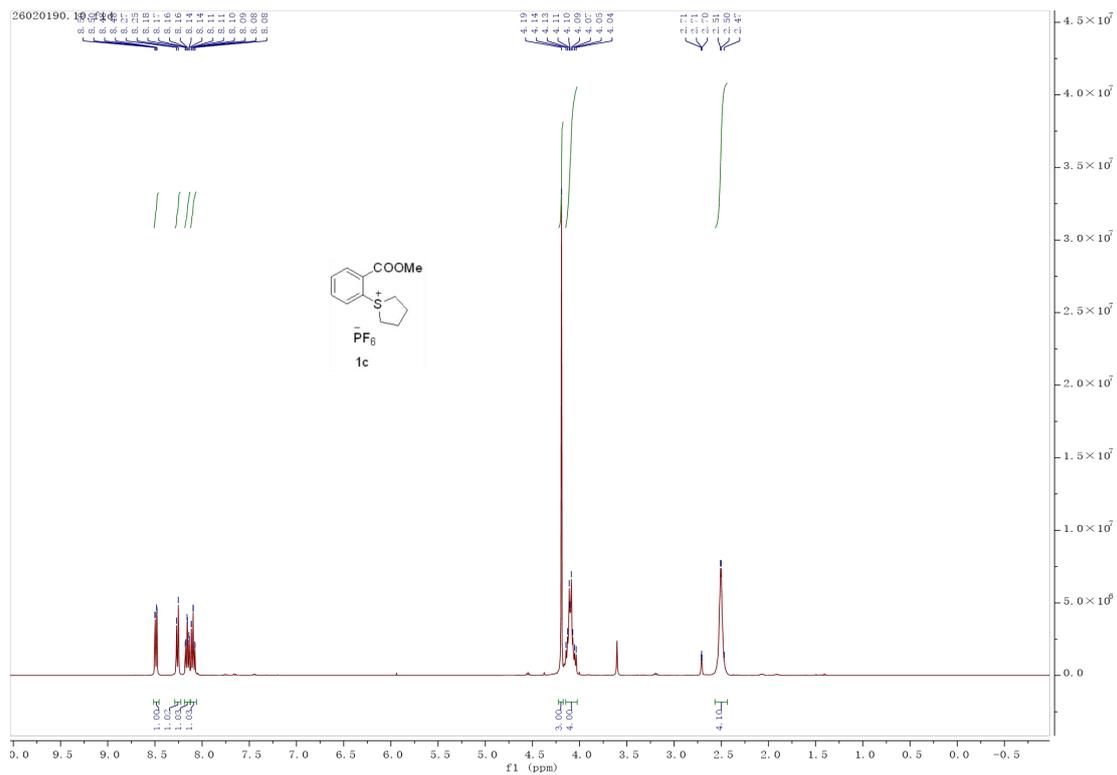
4. Reference

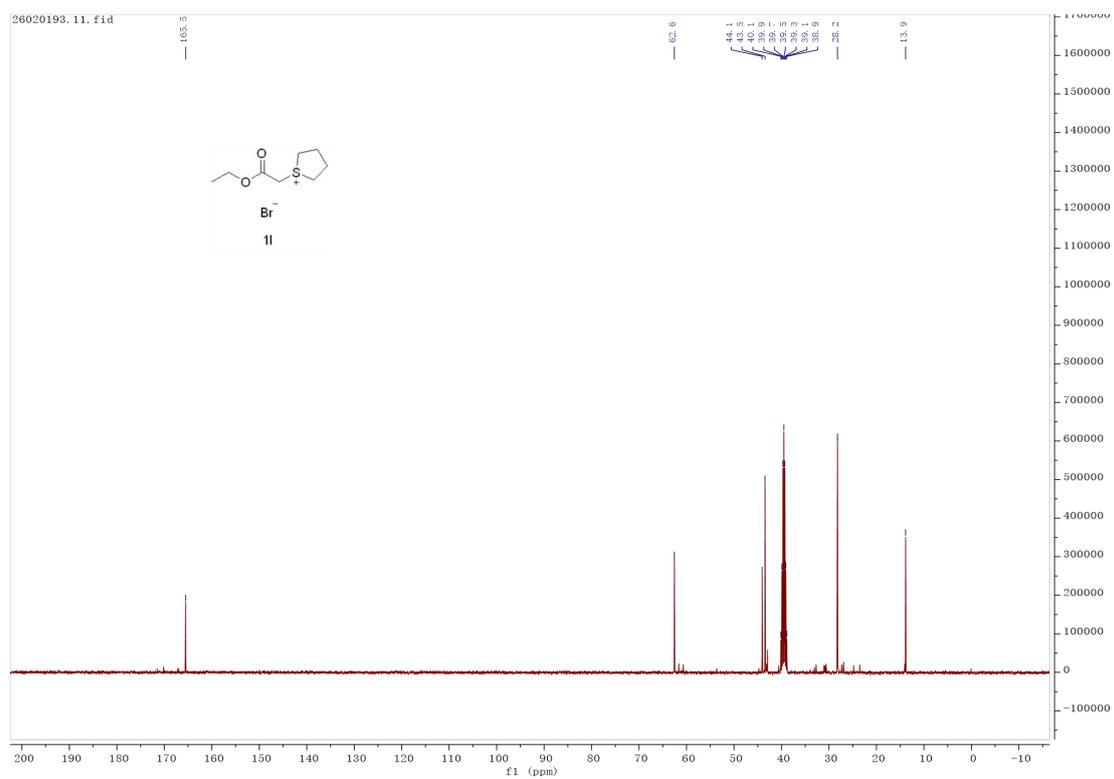
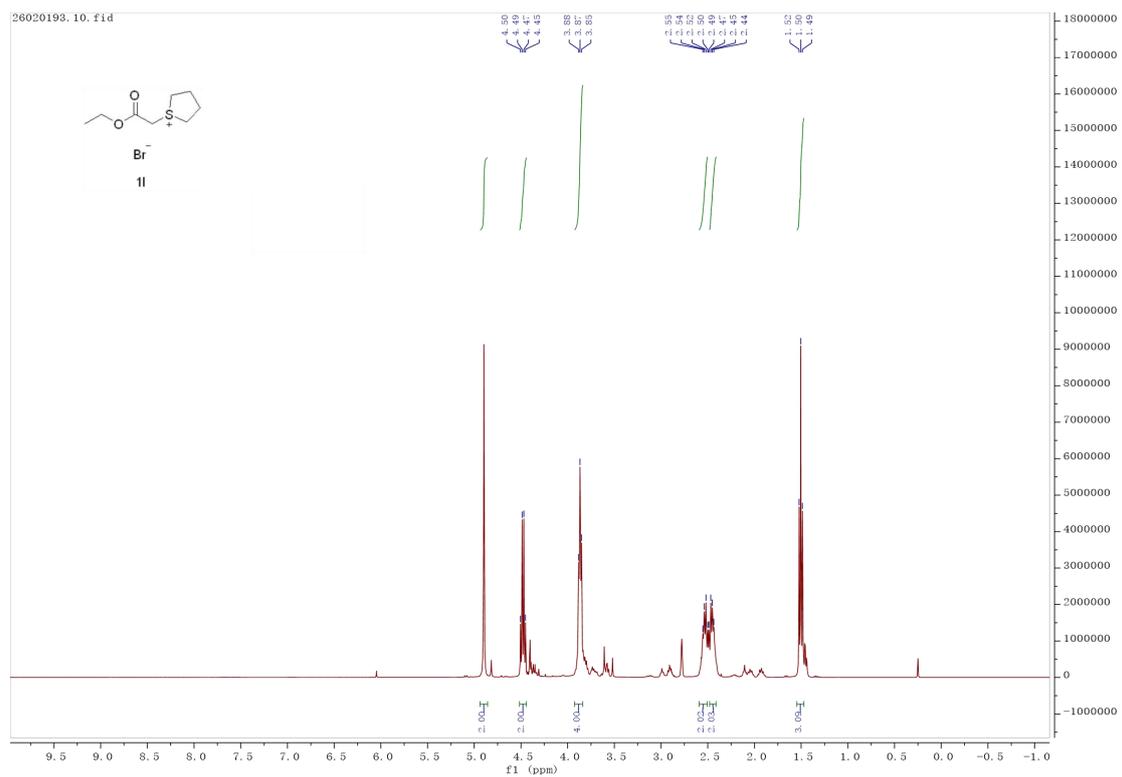
- [1] (a) W. Cui, X. Li, G. Guo, X. Song, J. Lv, and D. Yang, *Org. Lett.* **2022**, *24*, 5391-5396. (b) X. Zhu, M. Jiang, X. Li, E. Zhu, Q. Deng, X. Song, J. Lv, and D. Yang, *Org. Chem. Front.* **2022**, *9*, 386-393. (c) N. R. Lee, F. A. Moghadam, F. C. Braga, D. J. Lippincott, B. Zhu, F. Gallou, and B. H. Lipshutz, *Org. Lett.* **2020**, *22*, 4949-4954. (d) R. R. Hawker, R. S. Haines, and J. B. Harper, *Chem. Commun.* **2018**, *54*, 2296-2299. (e) Y.-L. Zhang, L. Yang, J. Wu, C. Zhu, and P. Wang, *Org. Lett.* **2020**, *22*, 7768-7772.
- [2] (a) Y. Han, Y. Yuan, S. Qi, Z.-K. Zhang, X. Kong, J. Yang, and J. Zhang, *Org. Lett.* **2024**, *26*, 3906–3910. (b) N. S. Greenwood, A. T. Champlin, and J. A. Ellman, *J. Am. Chem. Soc.* **2022**, *144*, 17808-17814.
- [3] C. Qian, W. Xiang, and M. Gu, *Chem. Eur. J.* **2025**, *31*, e202403990.

- [4] (a) W. Liu, S. Qiu, R. Jin, L. Huang, J. Huang, and H. Feng, *J. Org. Chem.* **2025**, *90*, 13761–13765.(b) N. S. Greenwood and J. A. Ellman, *Org. Lett.* 2023, *25*, 4759–4764.

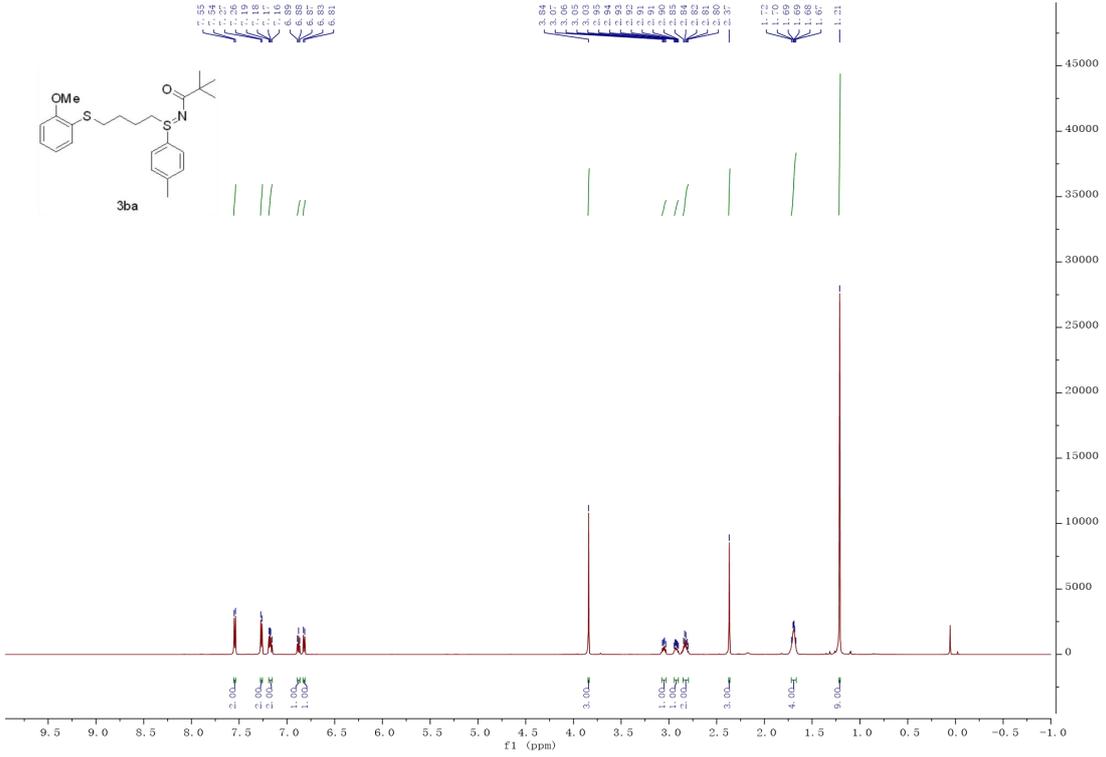
5. ^1H , ^{13}C , and ^{19}F NMR Spectra



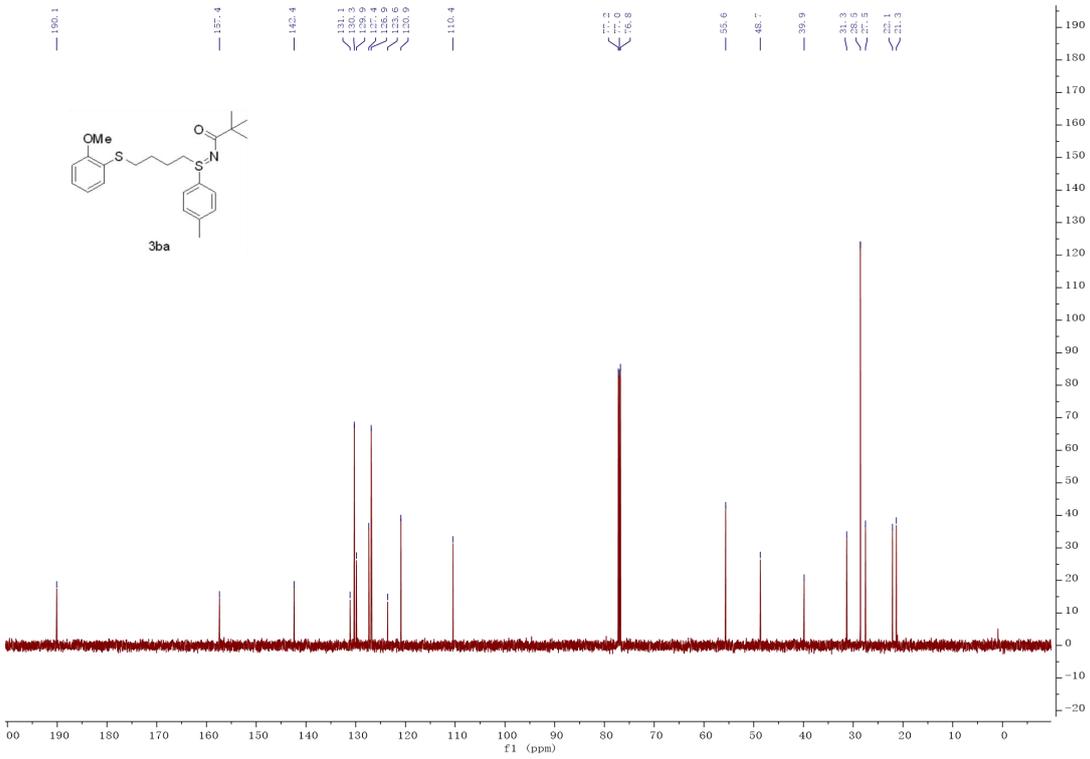


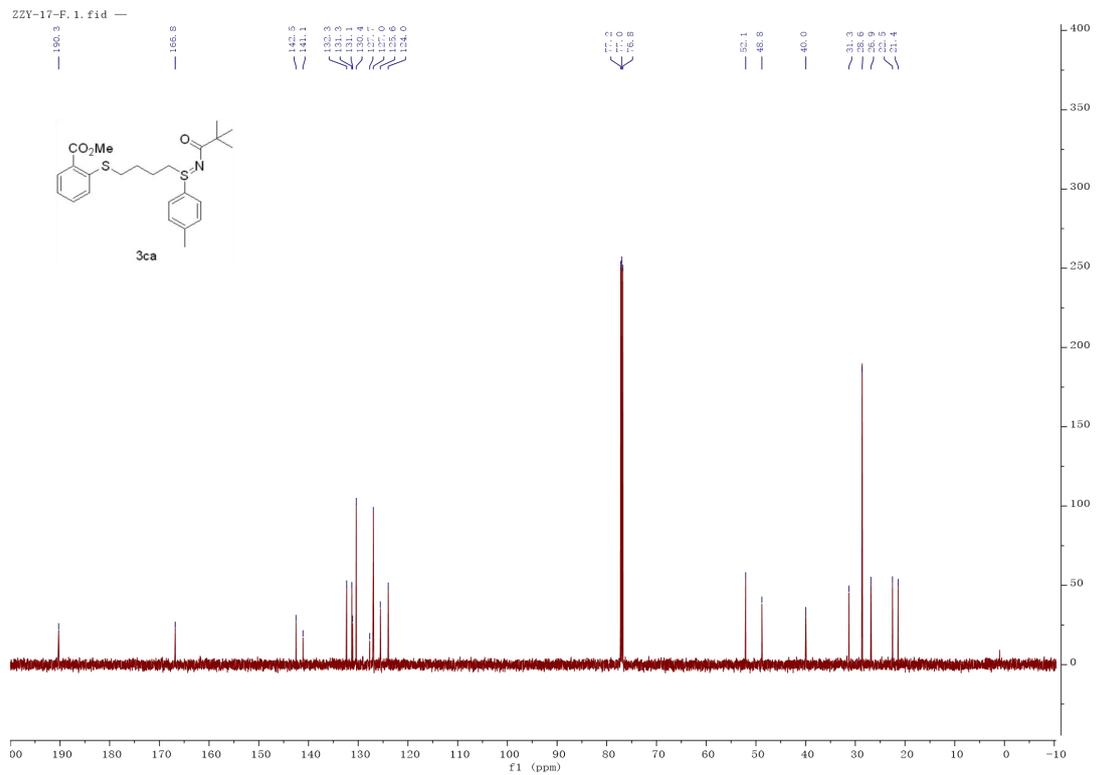
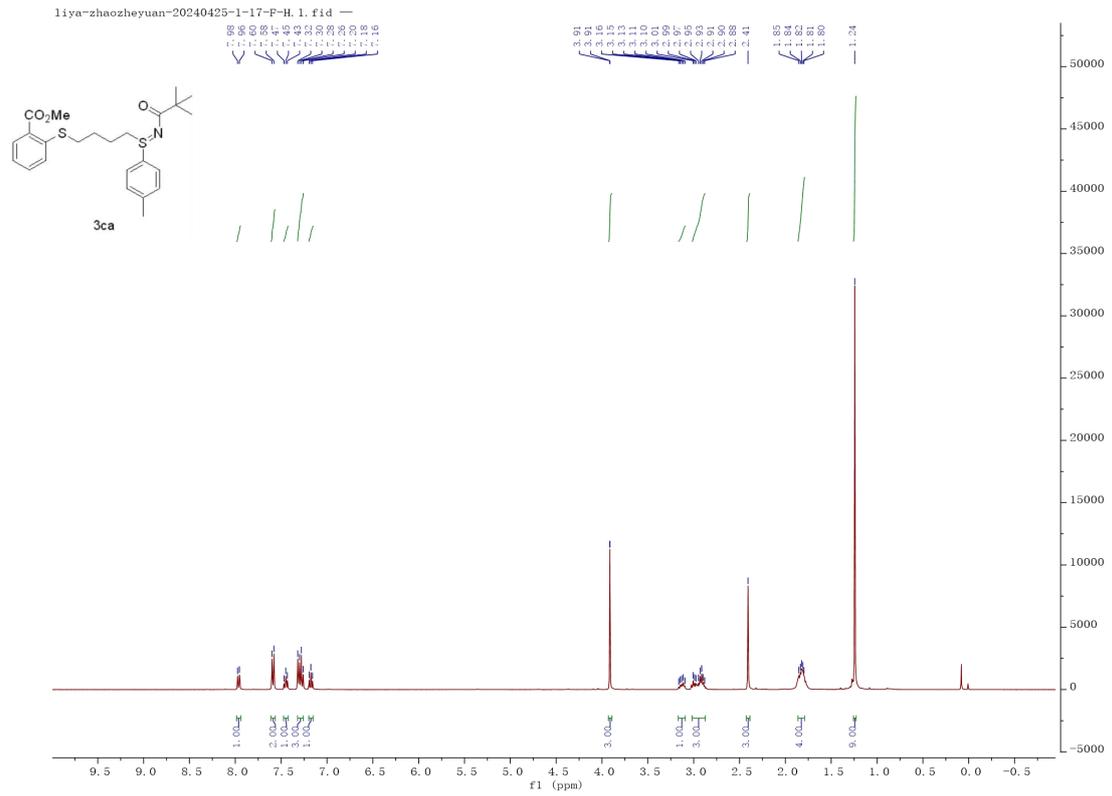


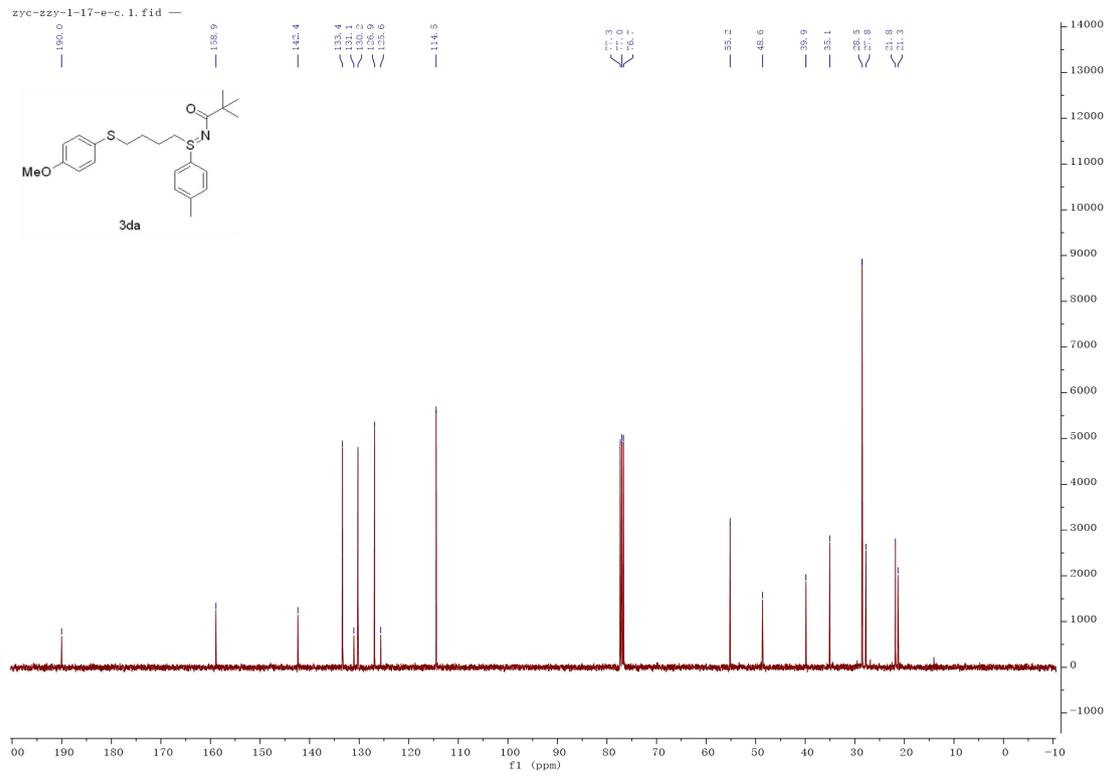
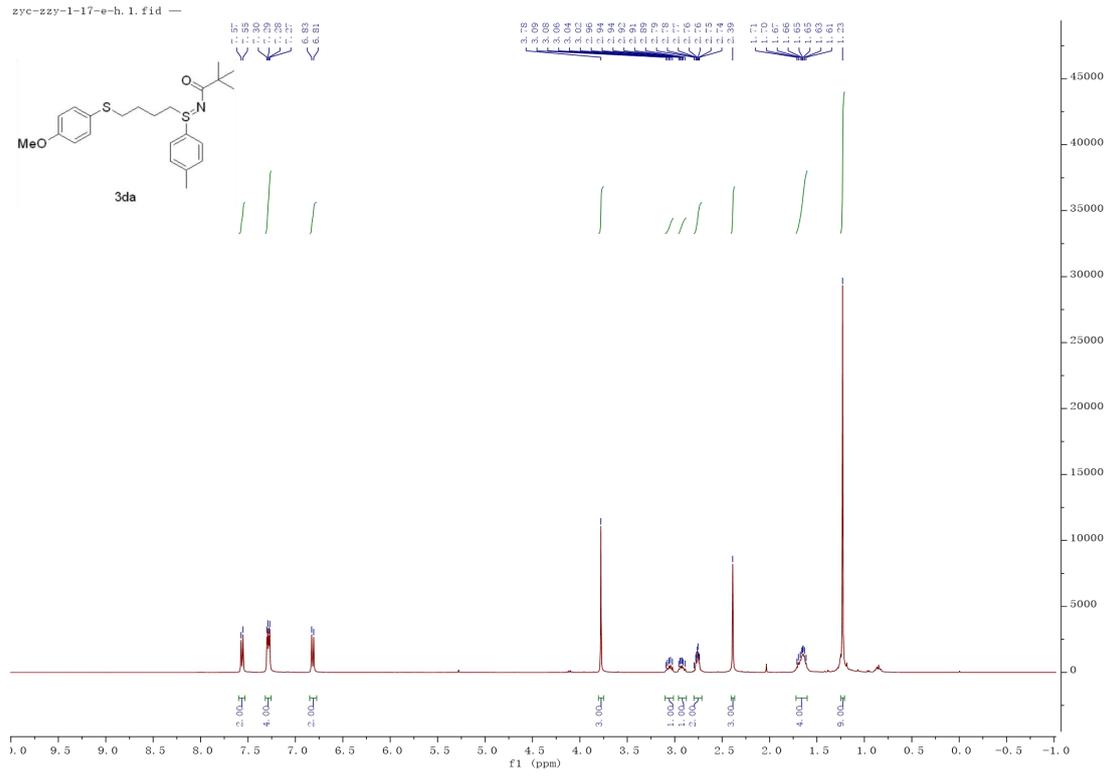
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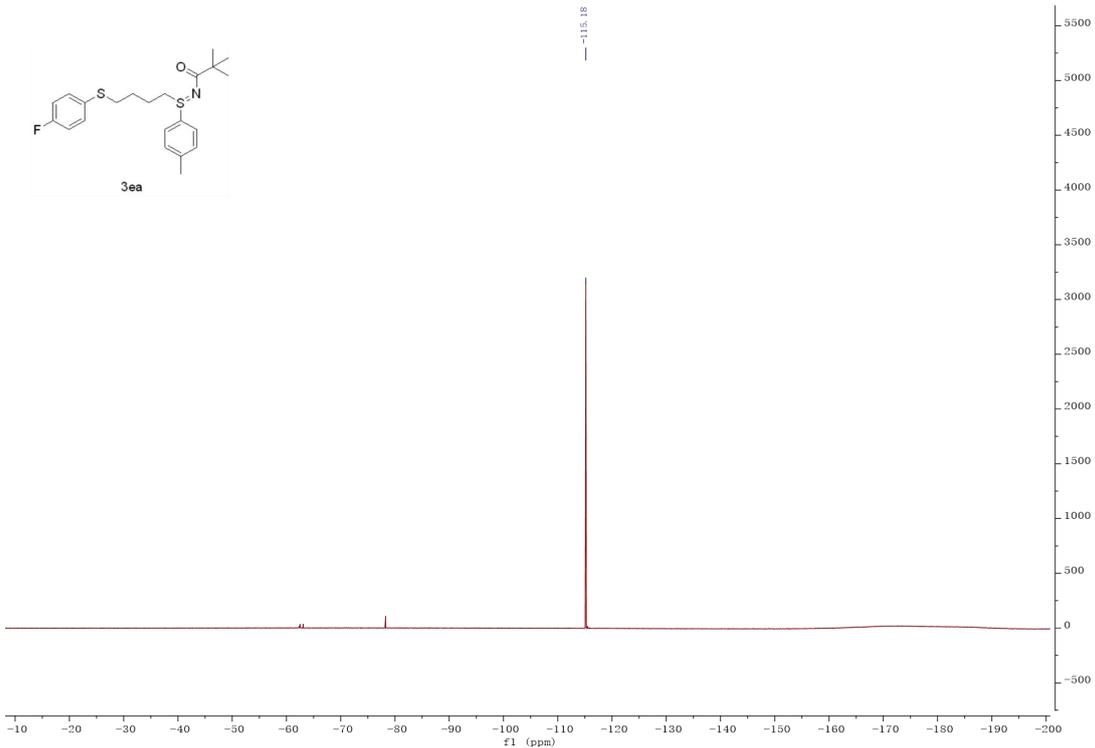
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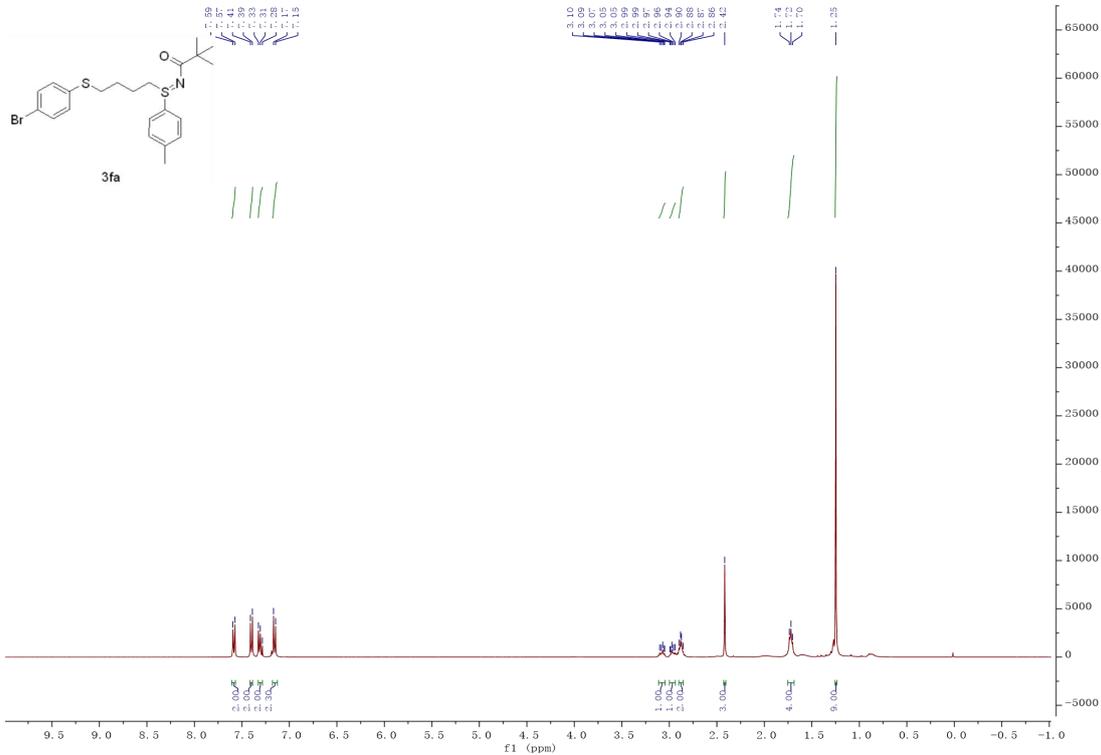


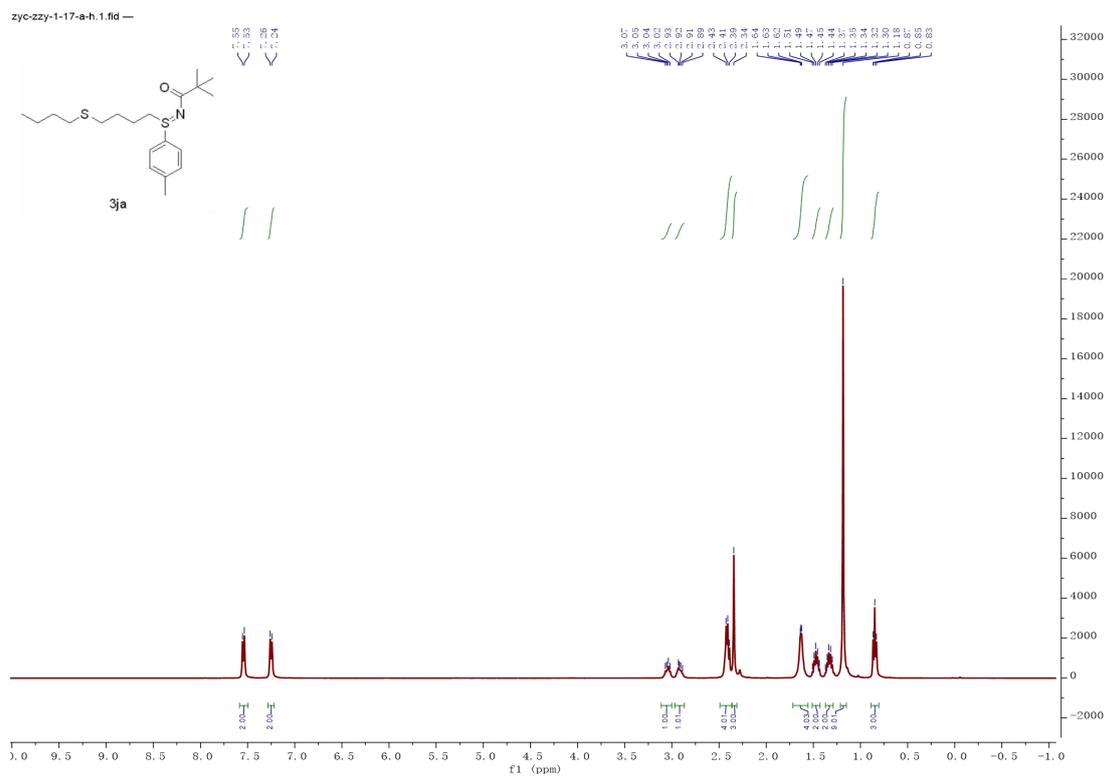
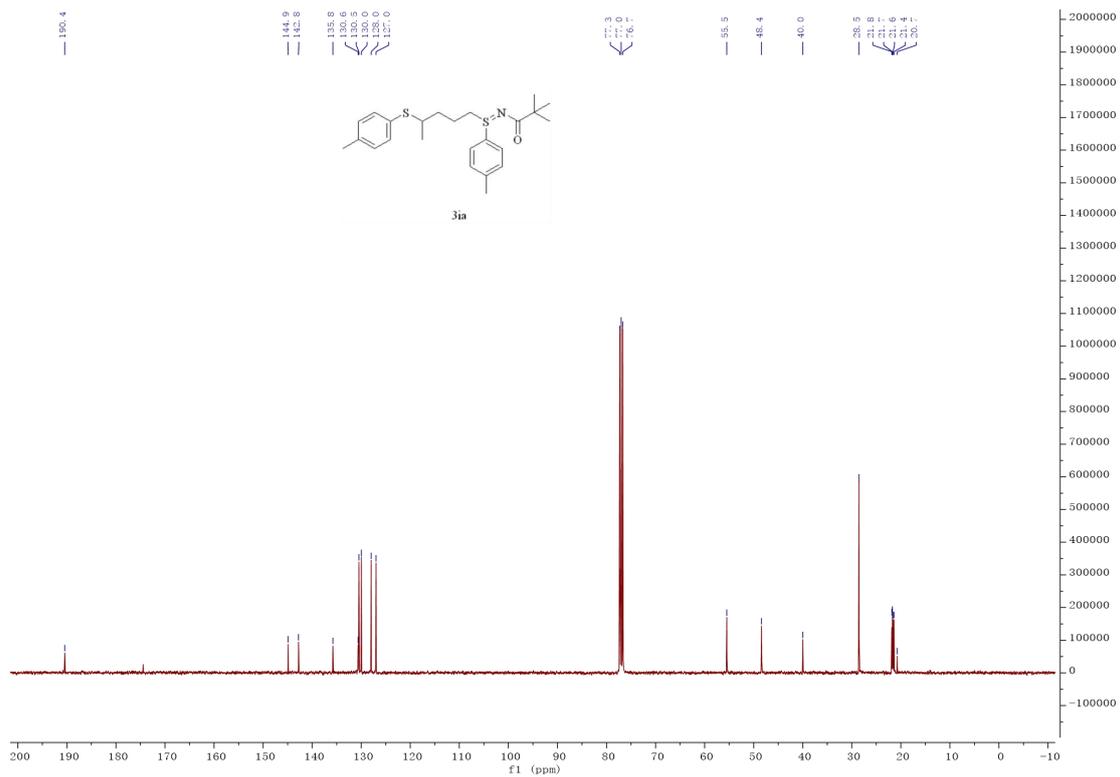


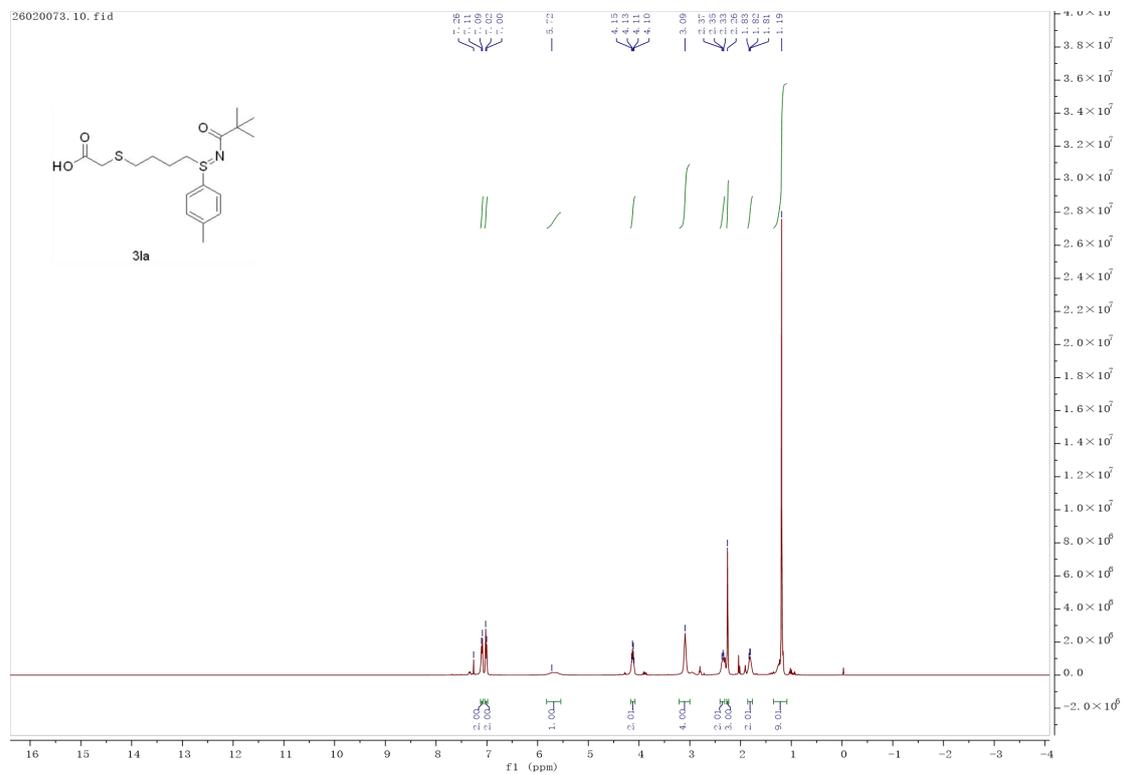
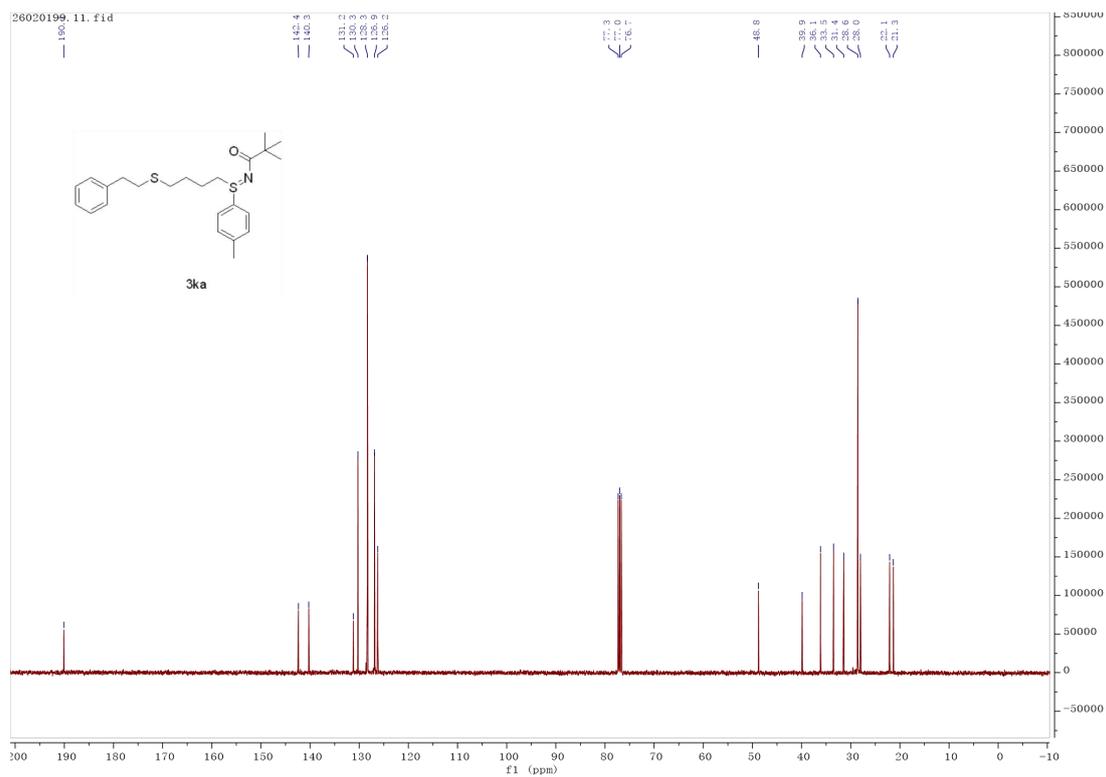
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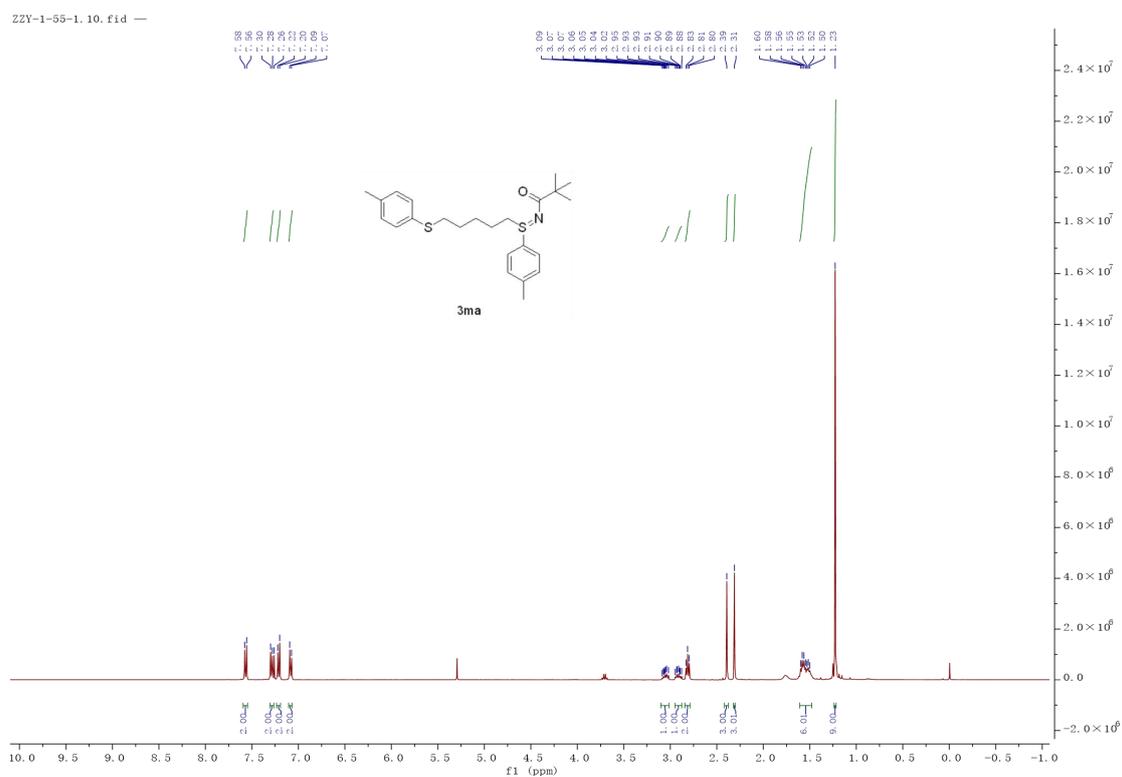
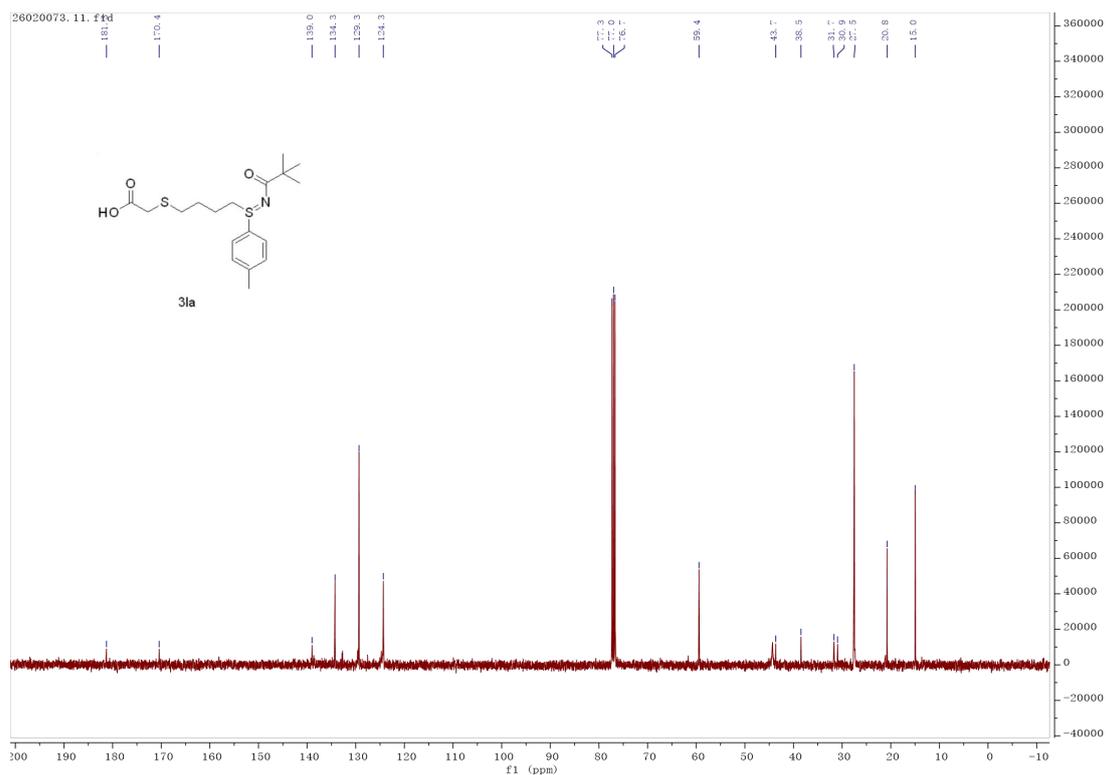


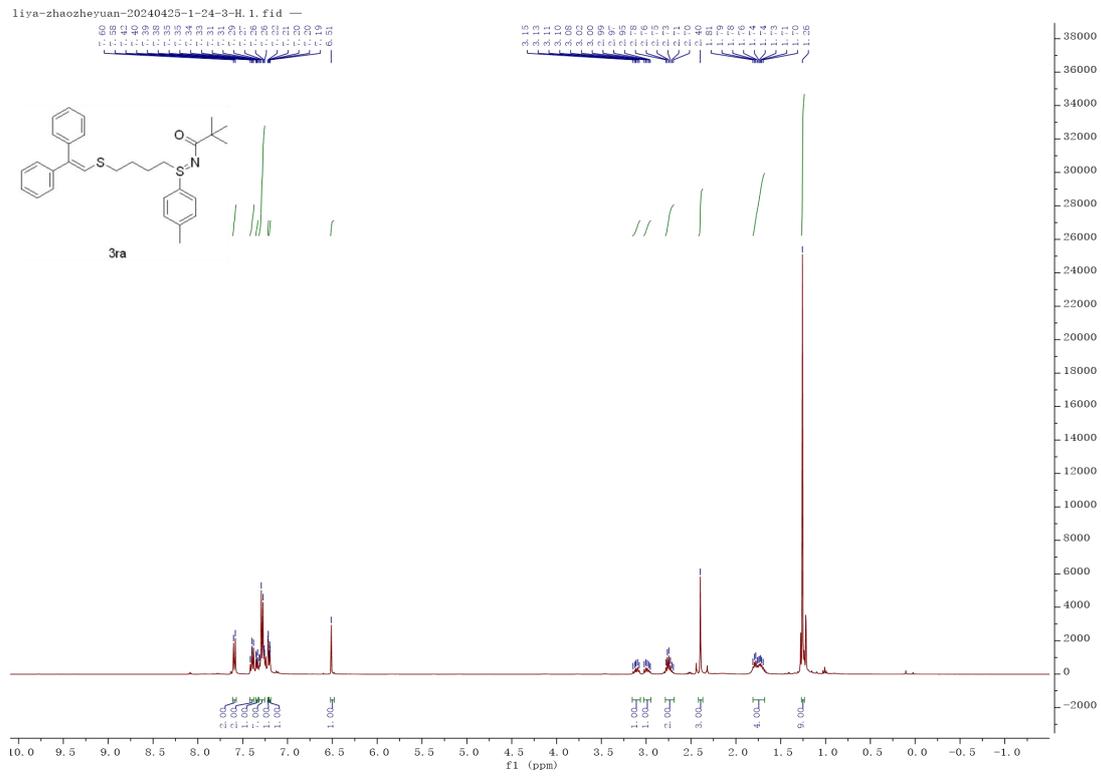
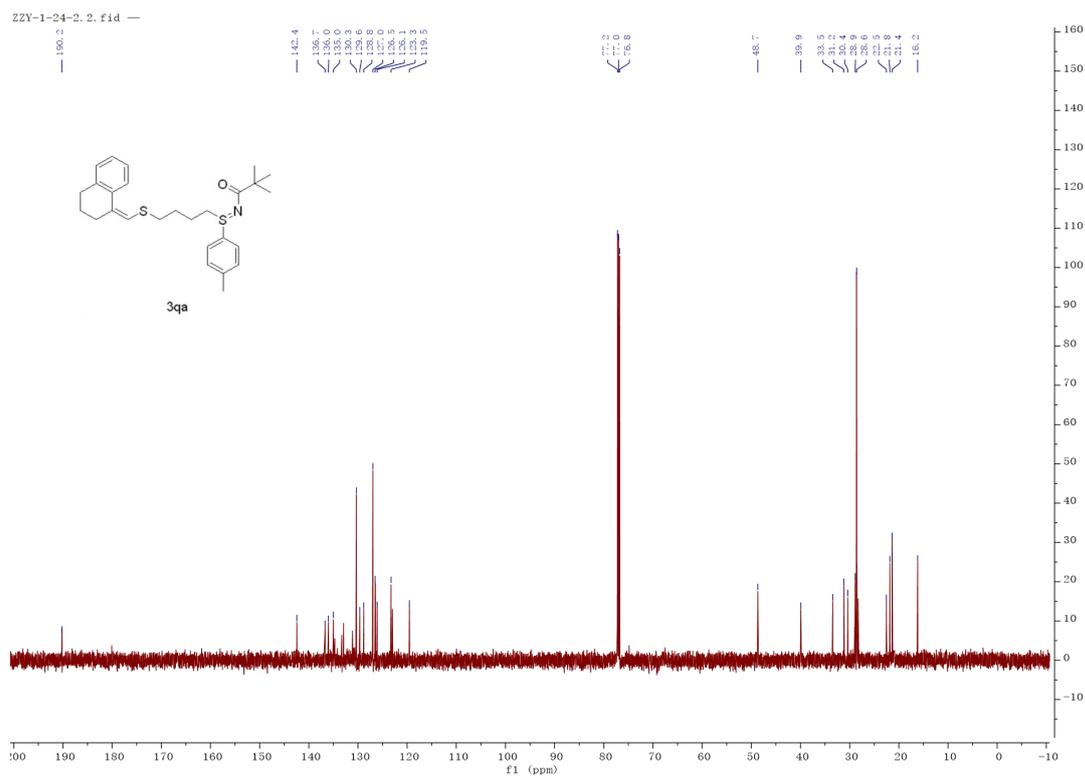
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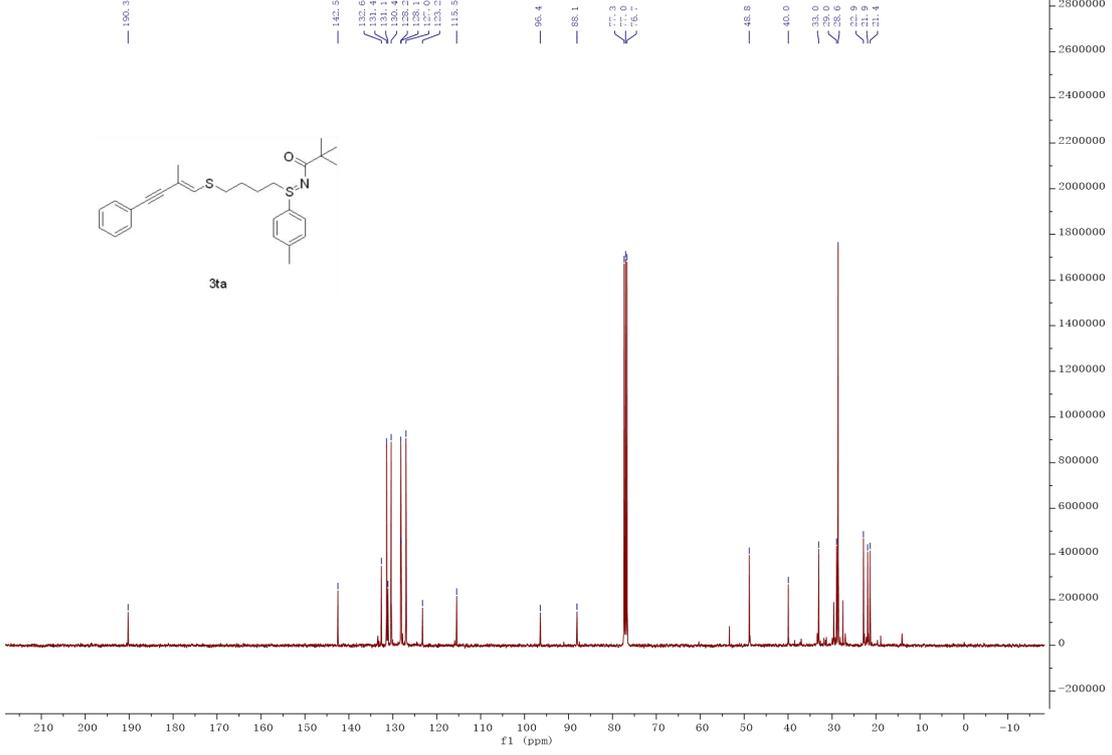




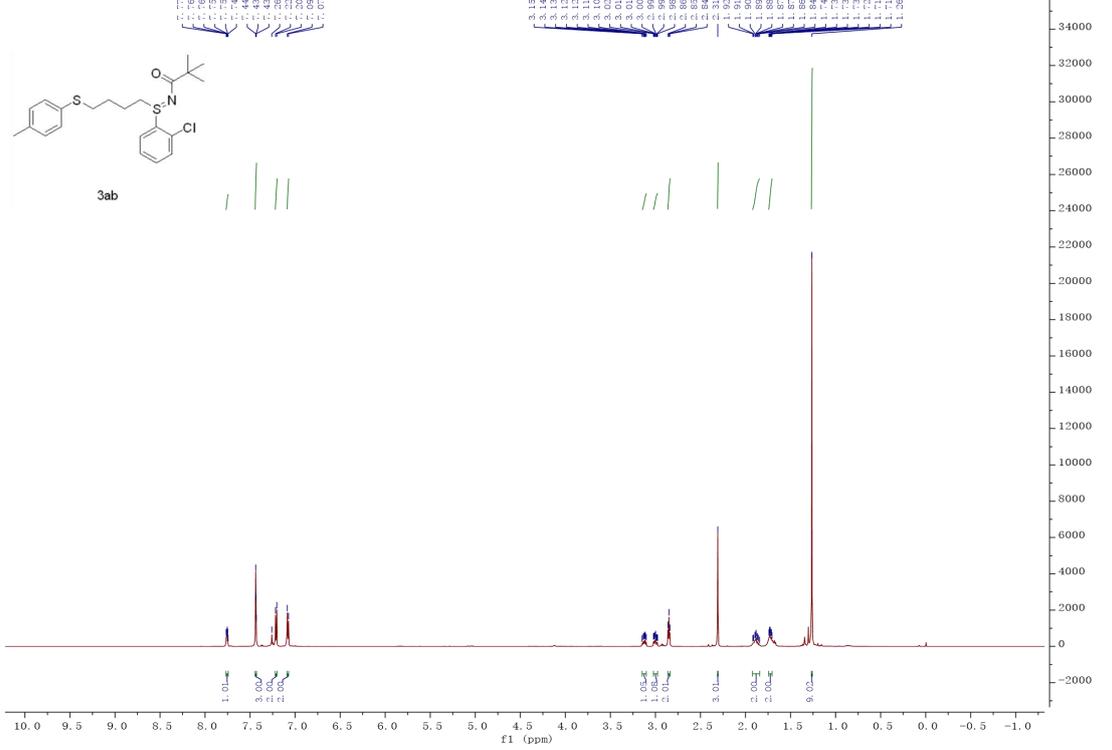




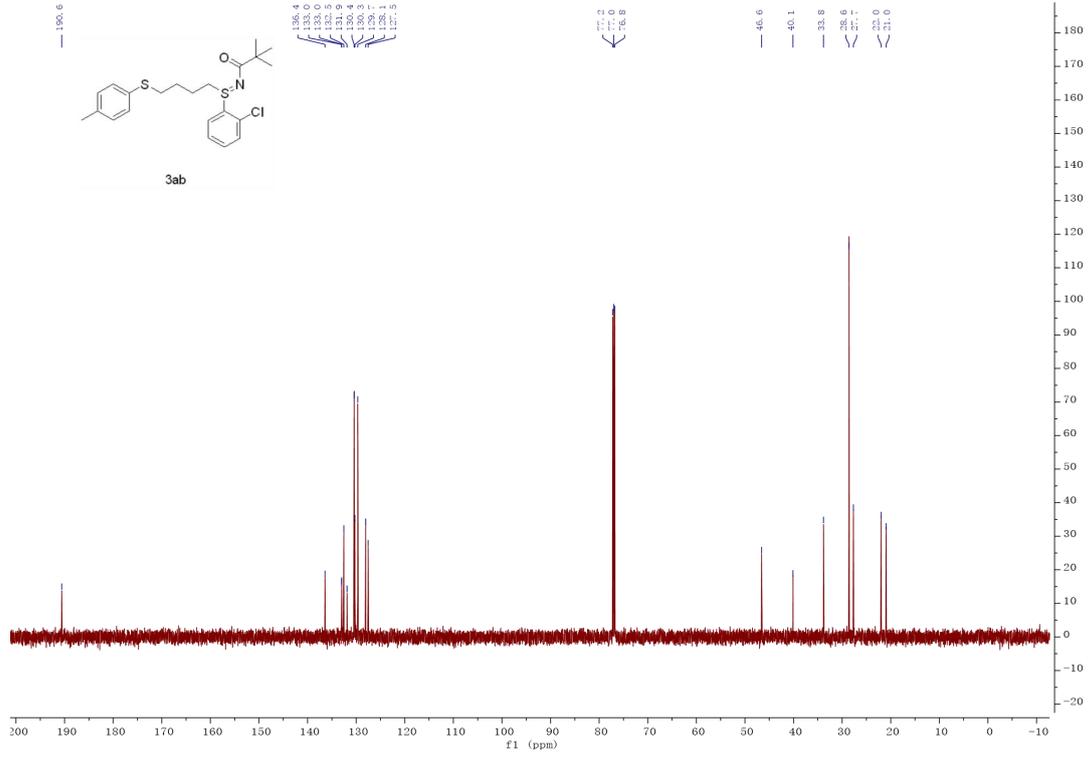
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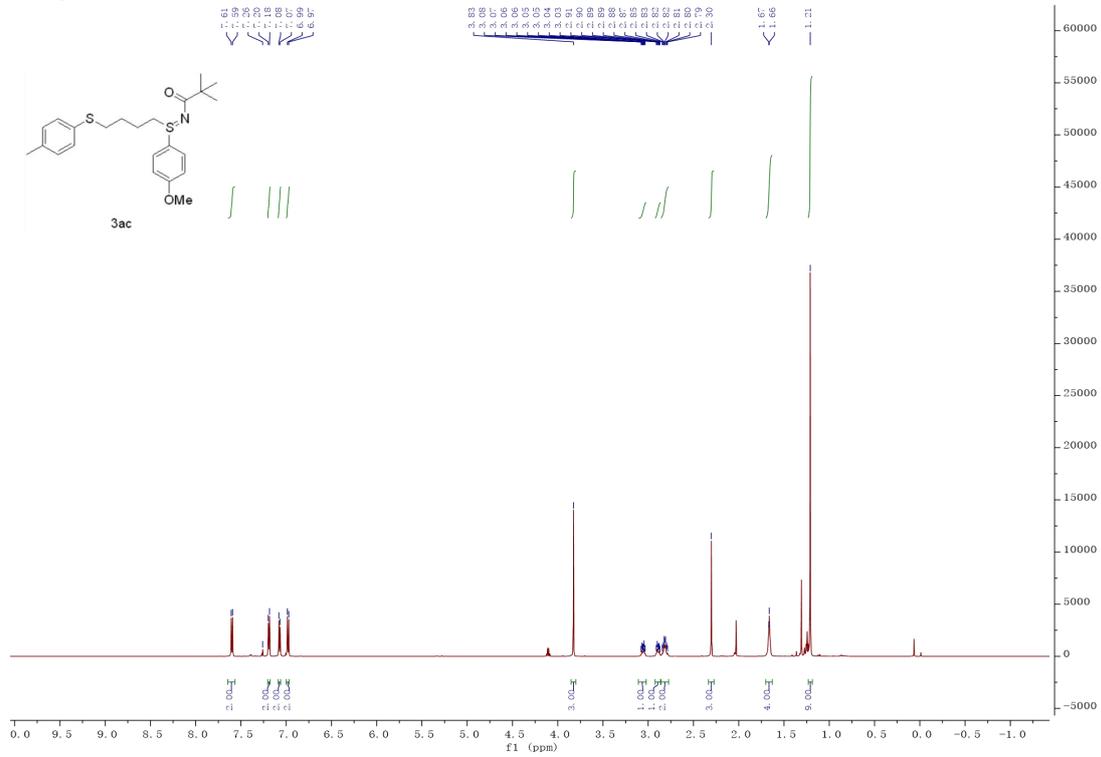
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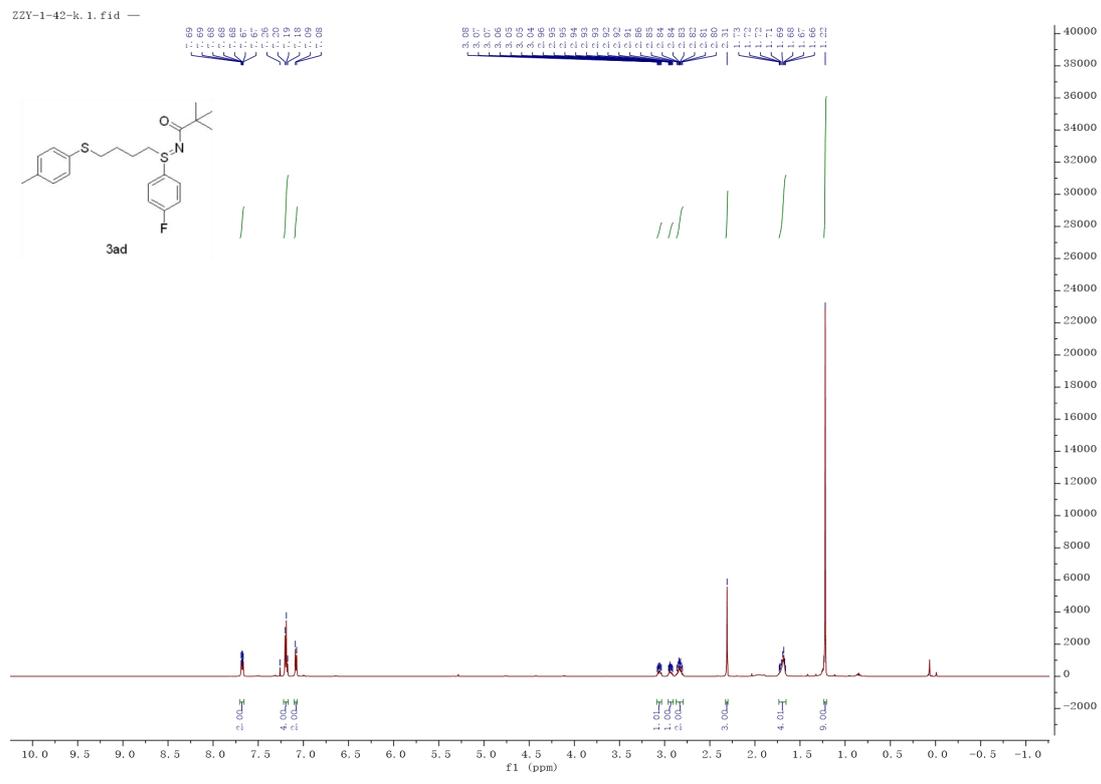
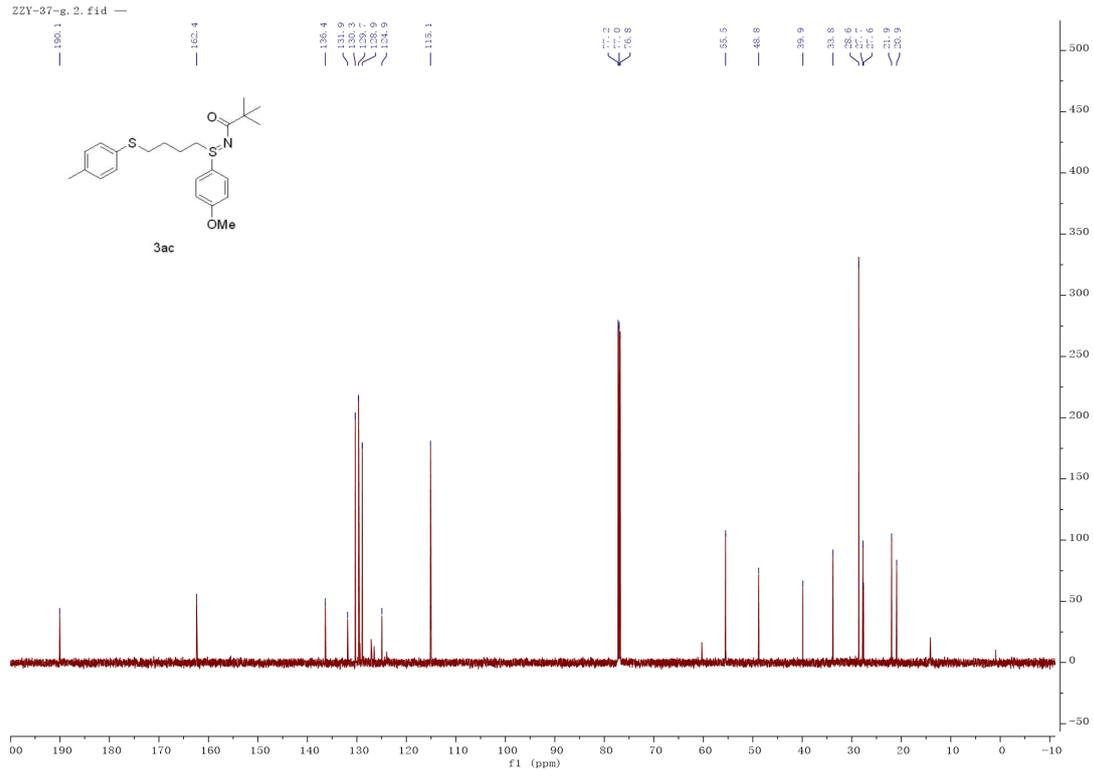


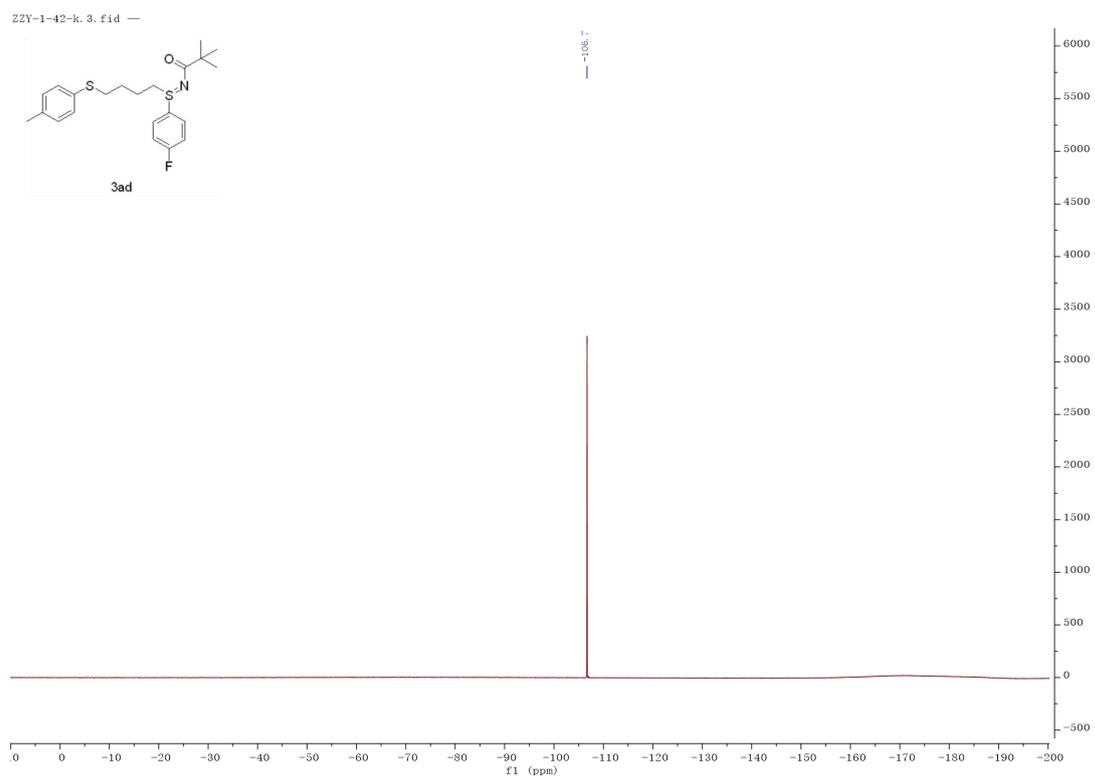
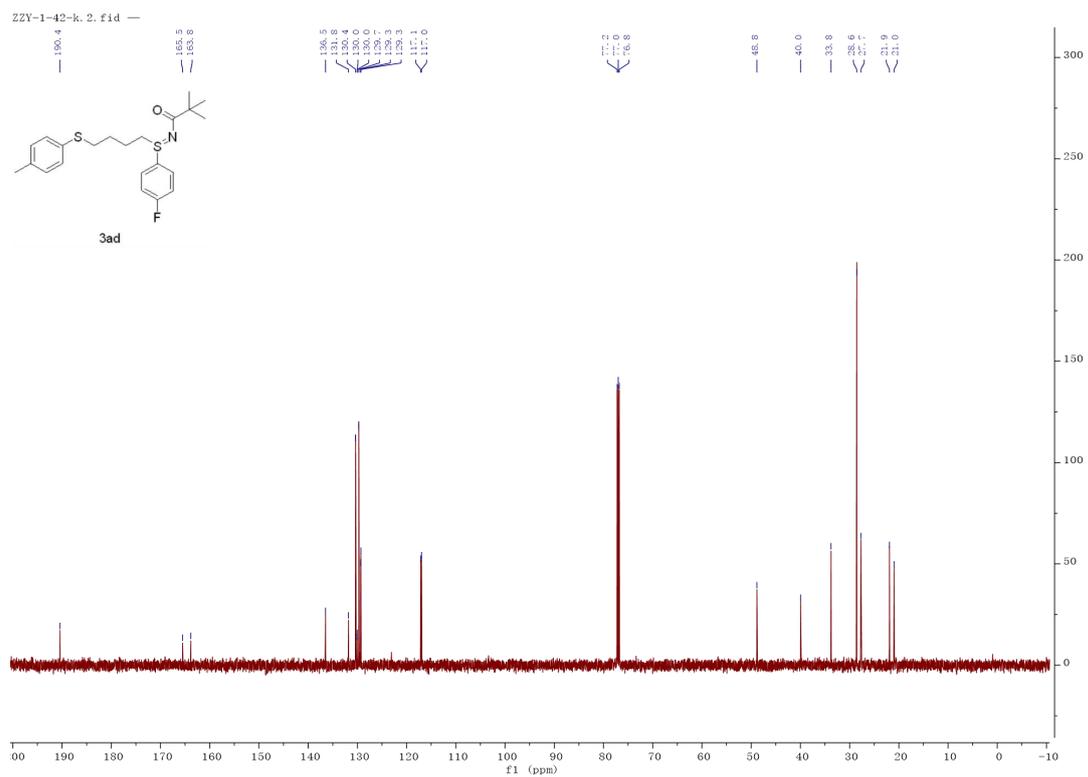
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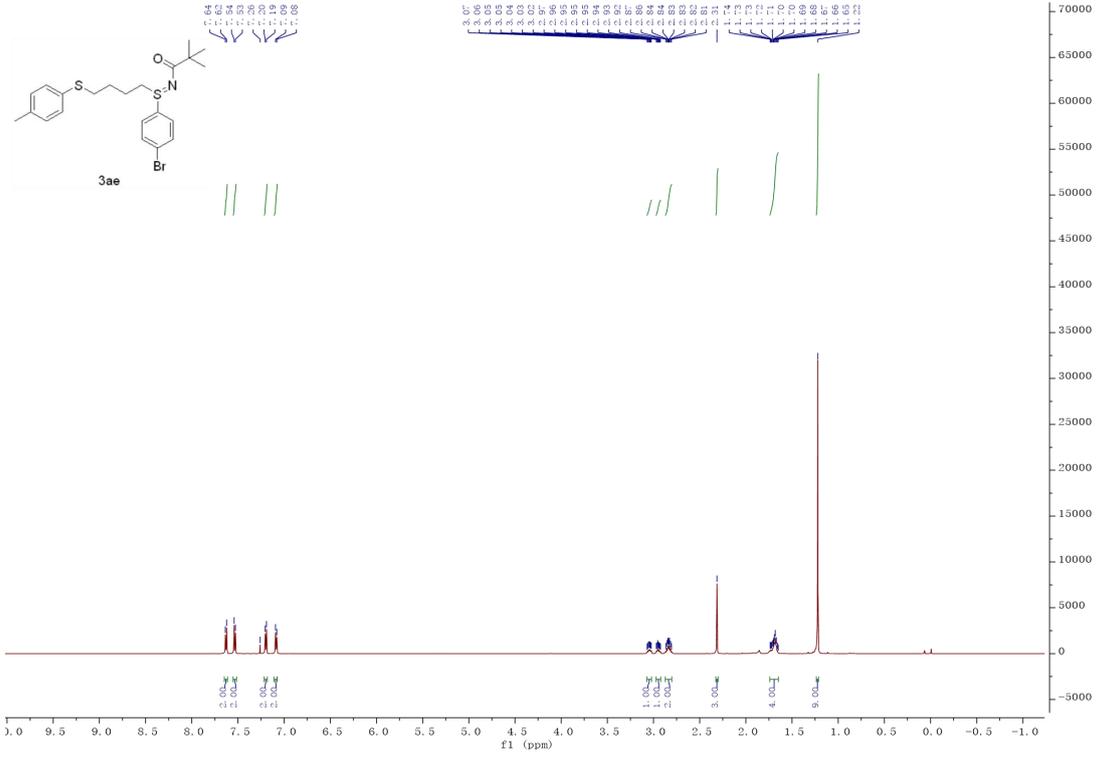
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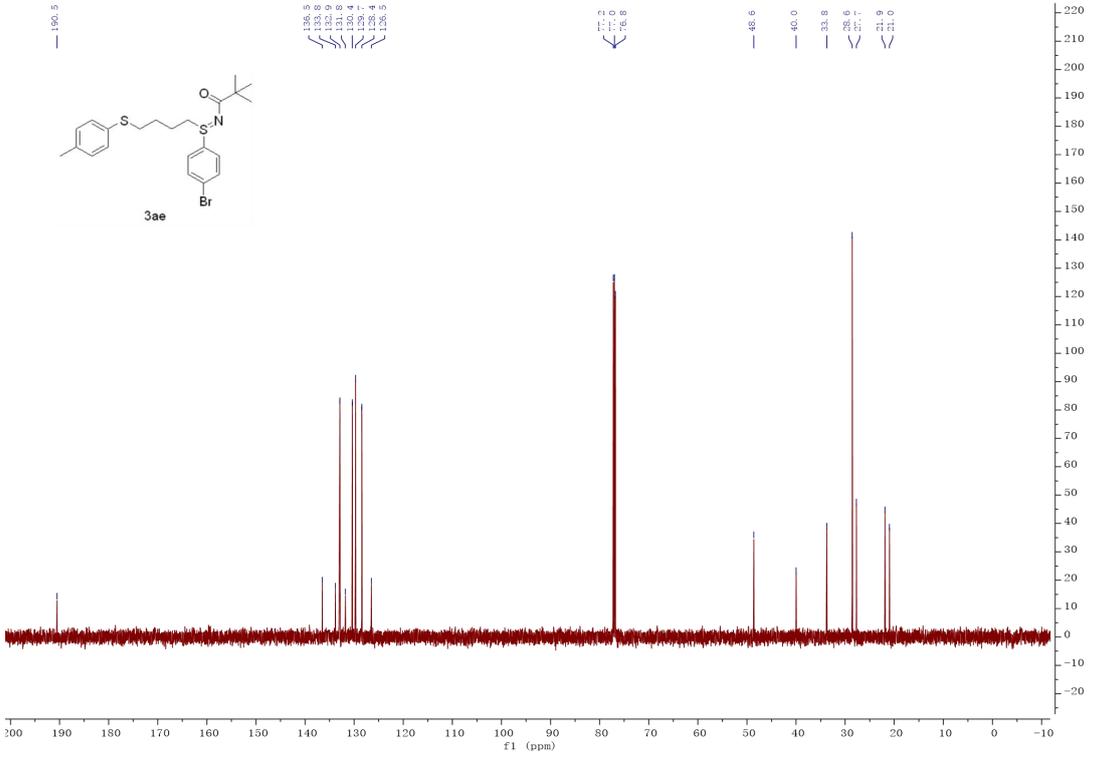




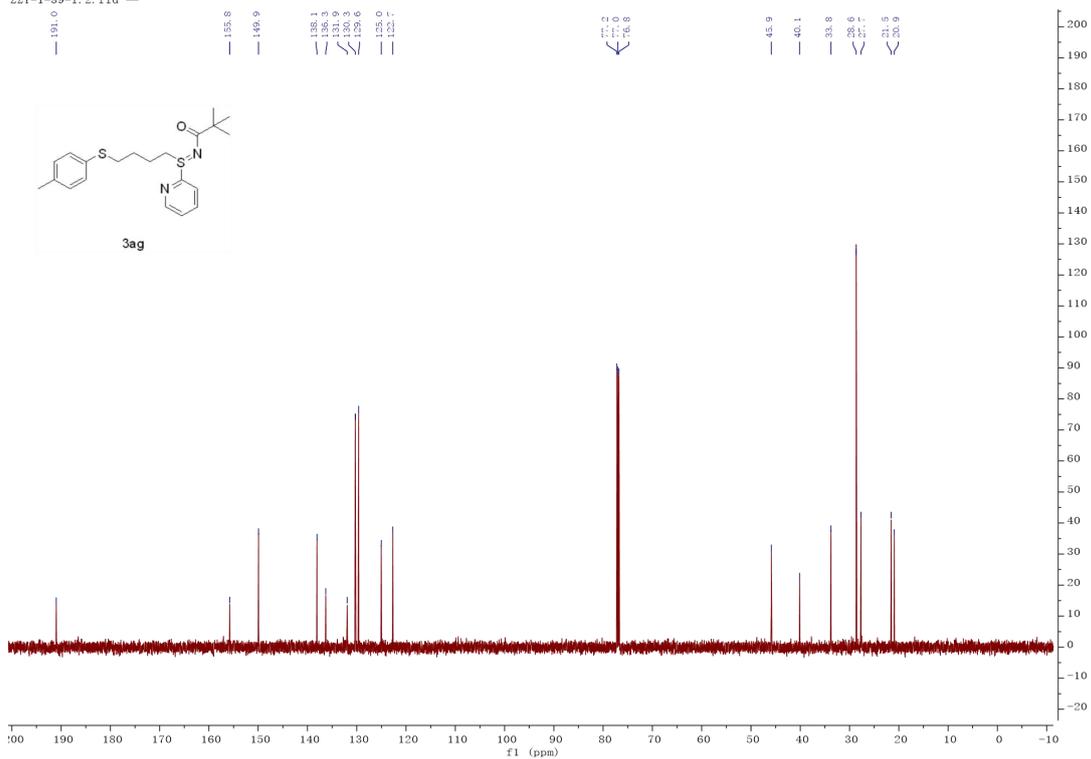
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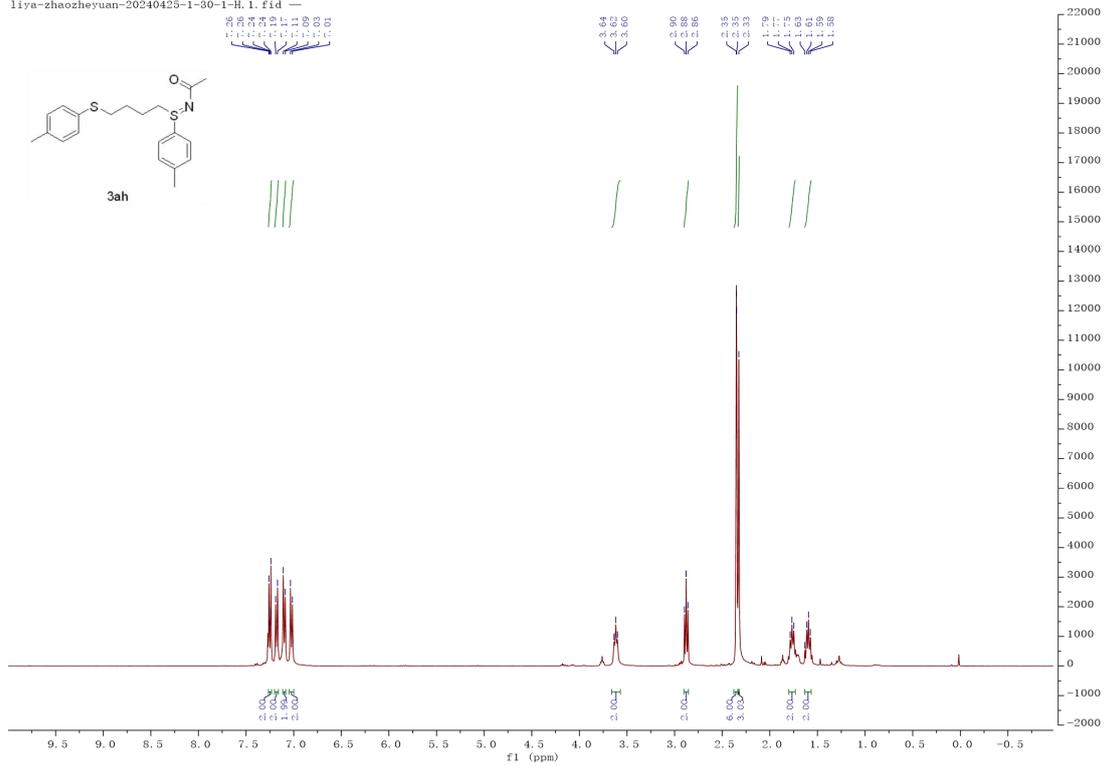
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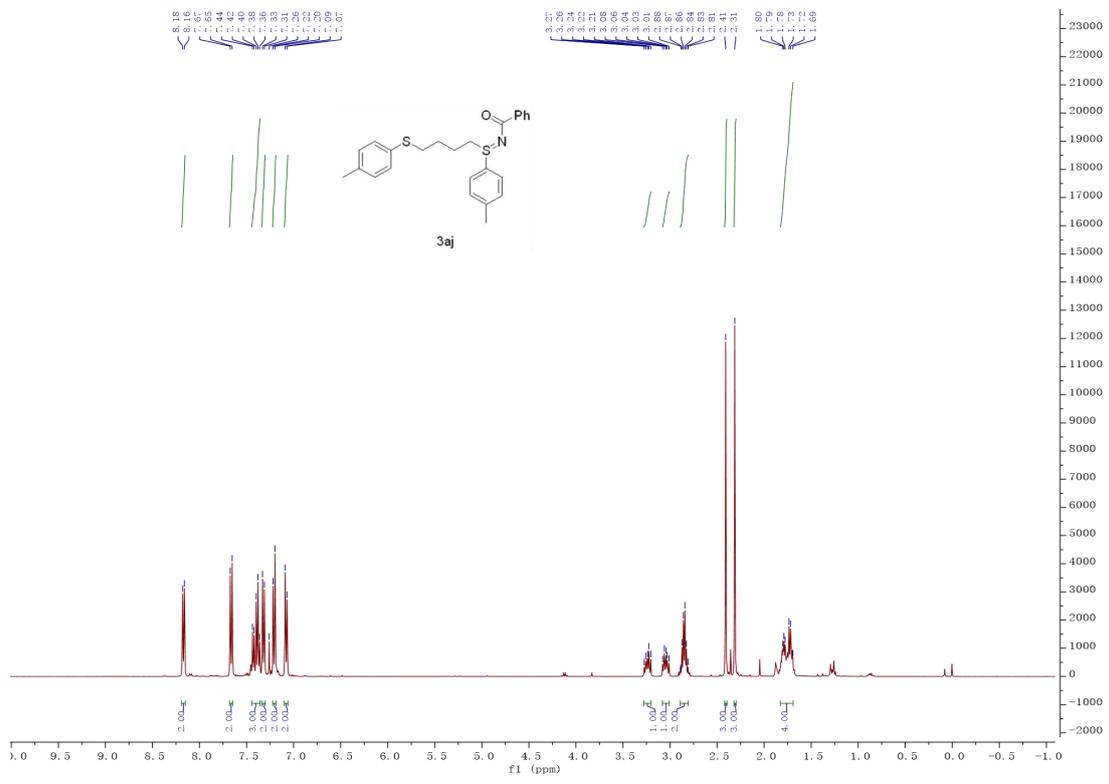
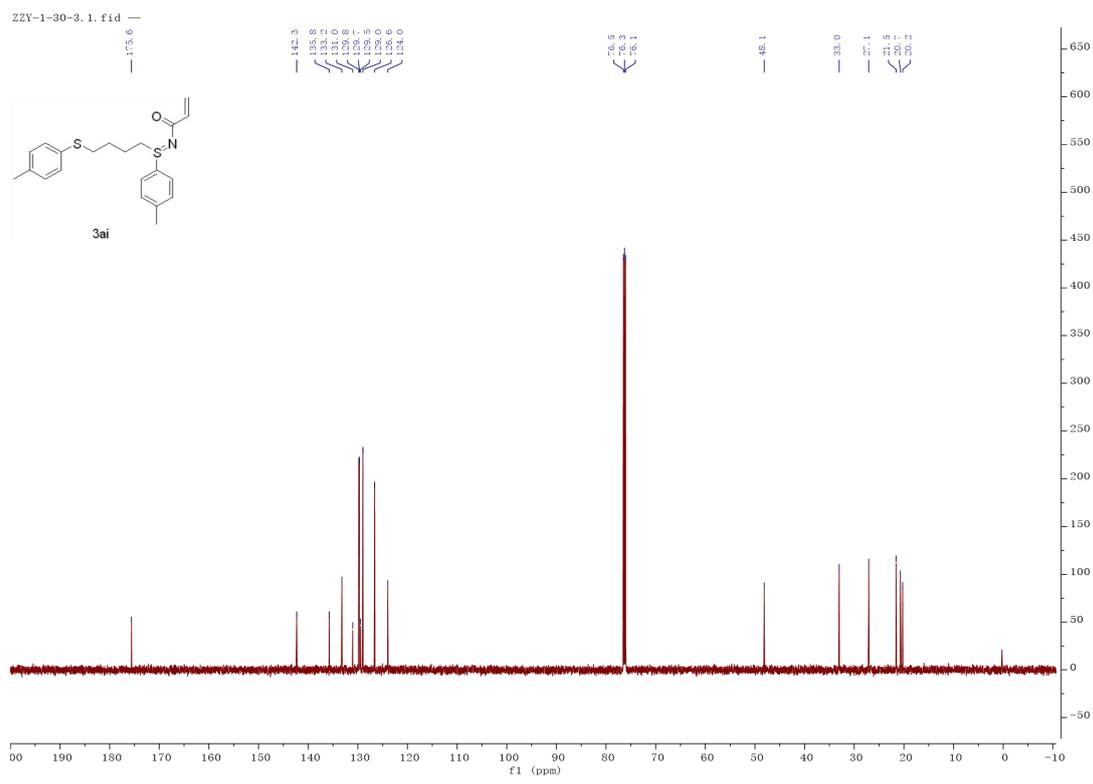


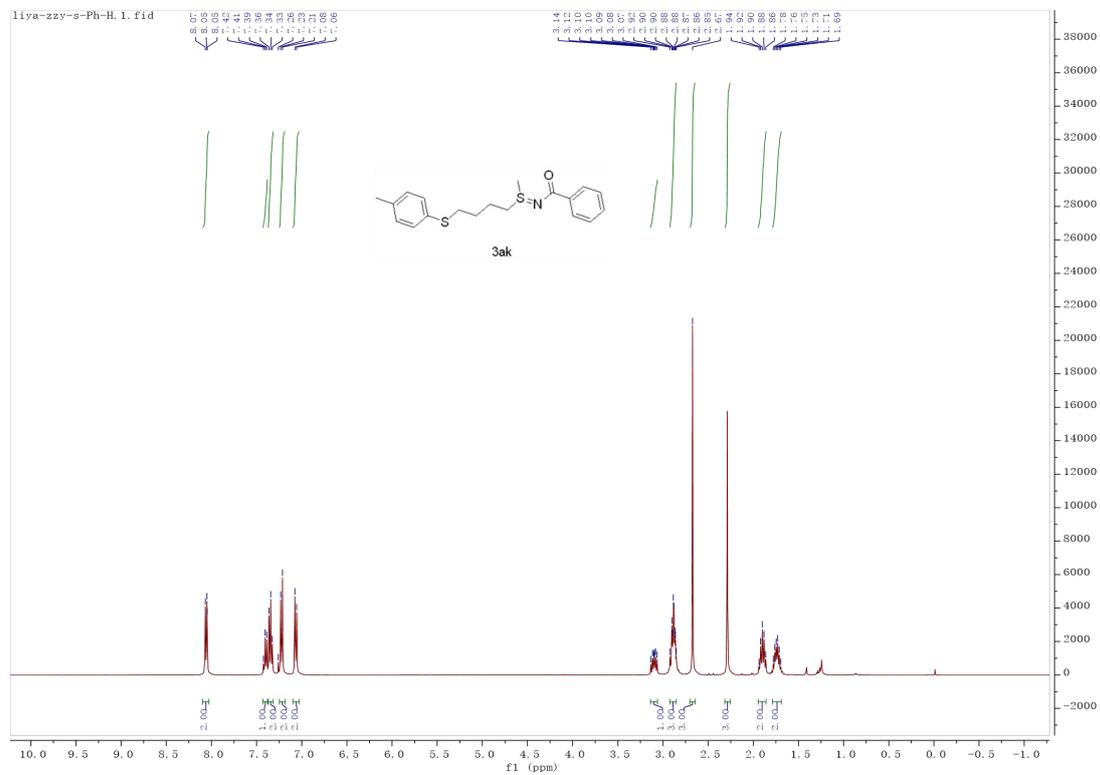
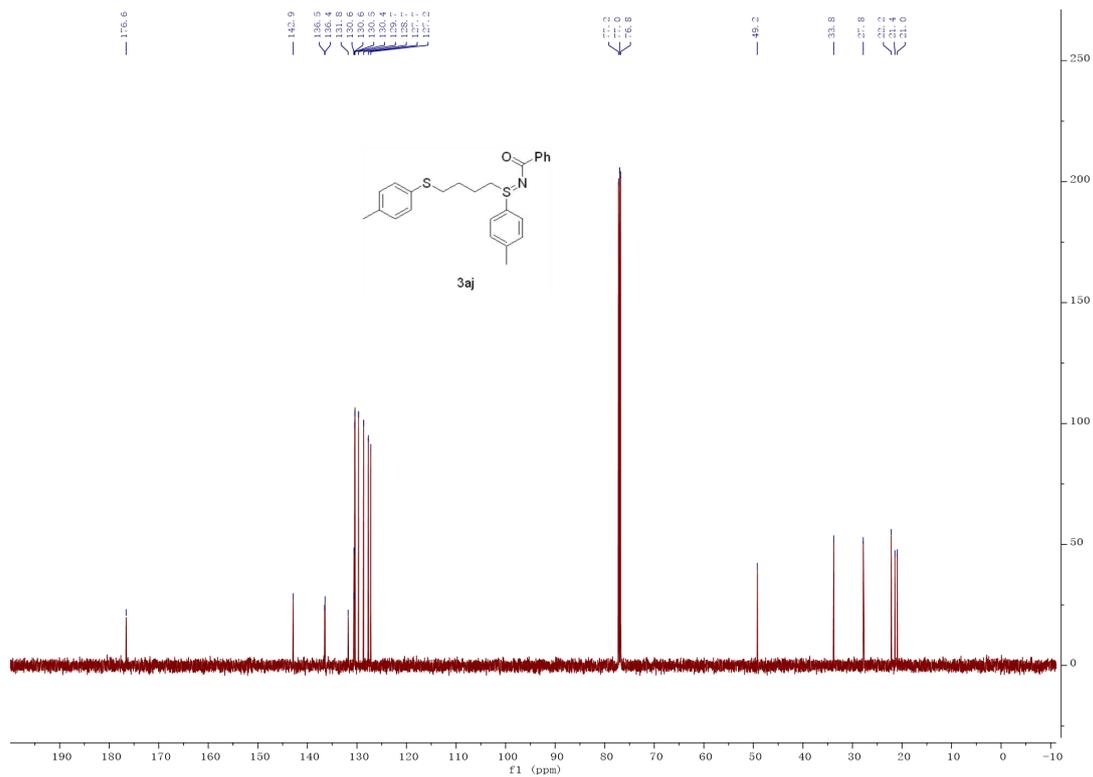
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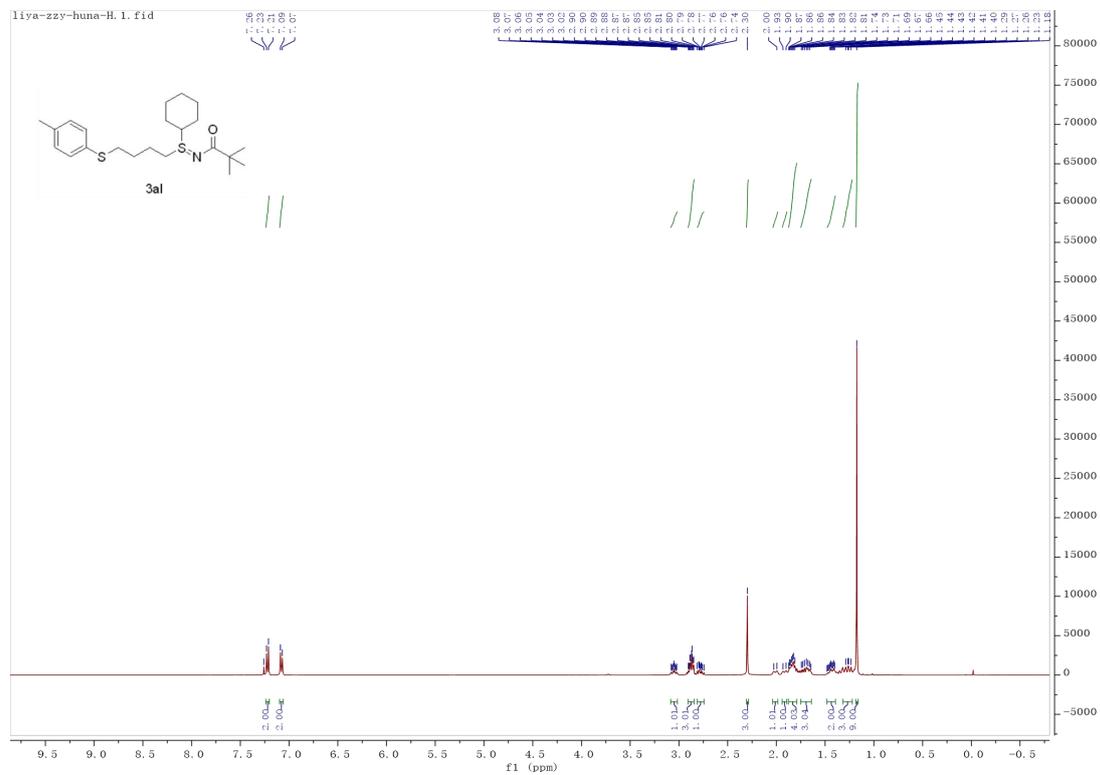
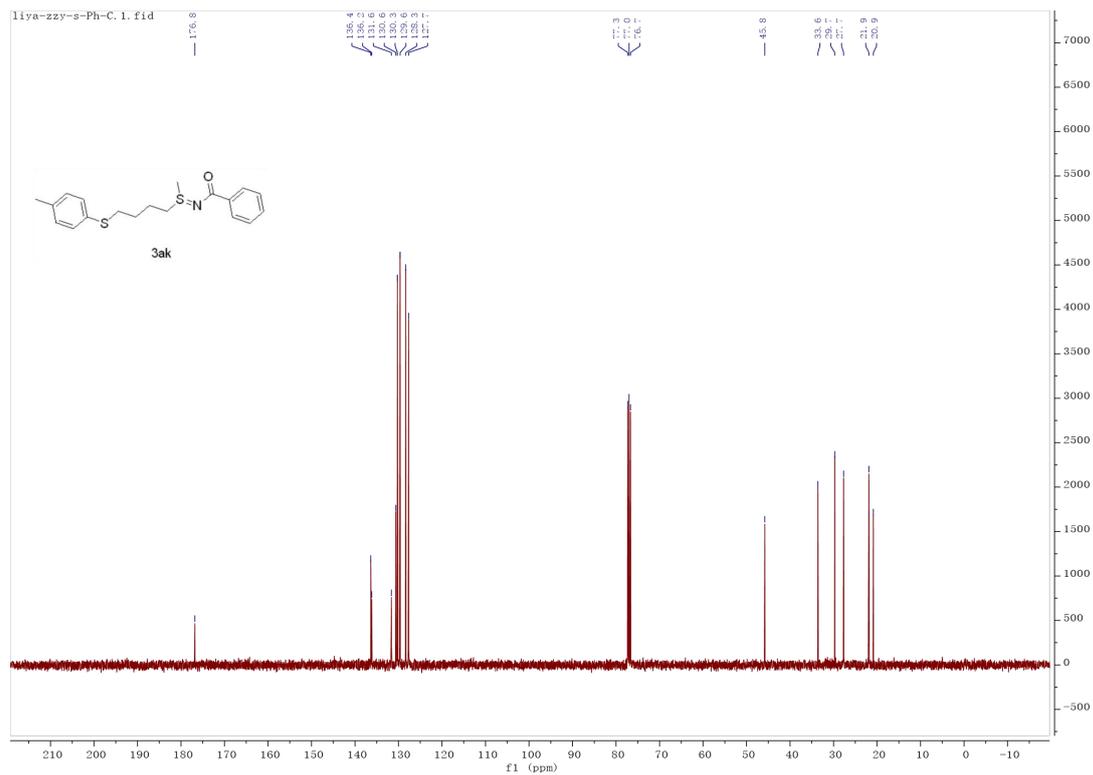


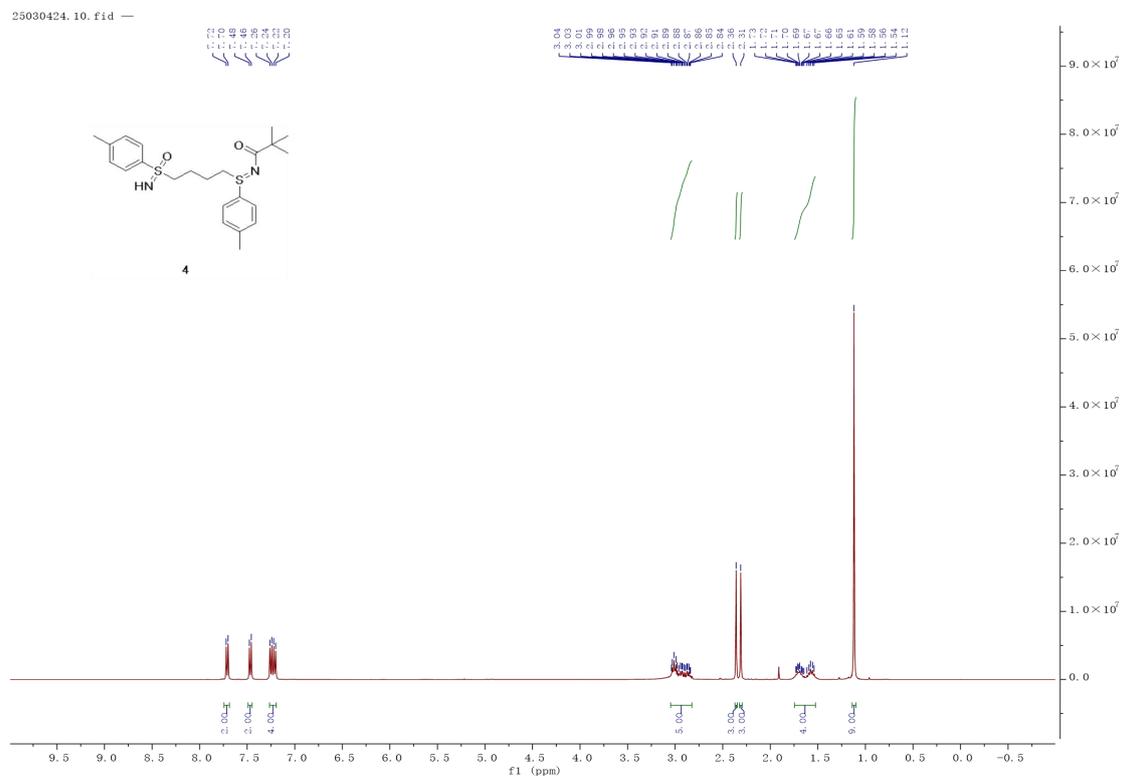
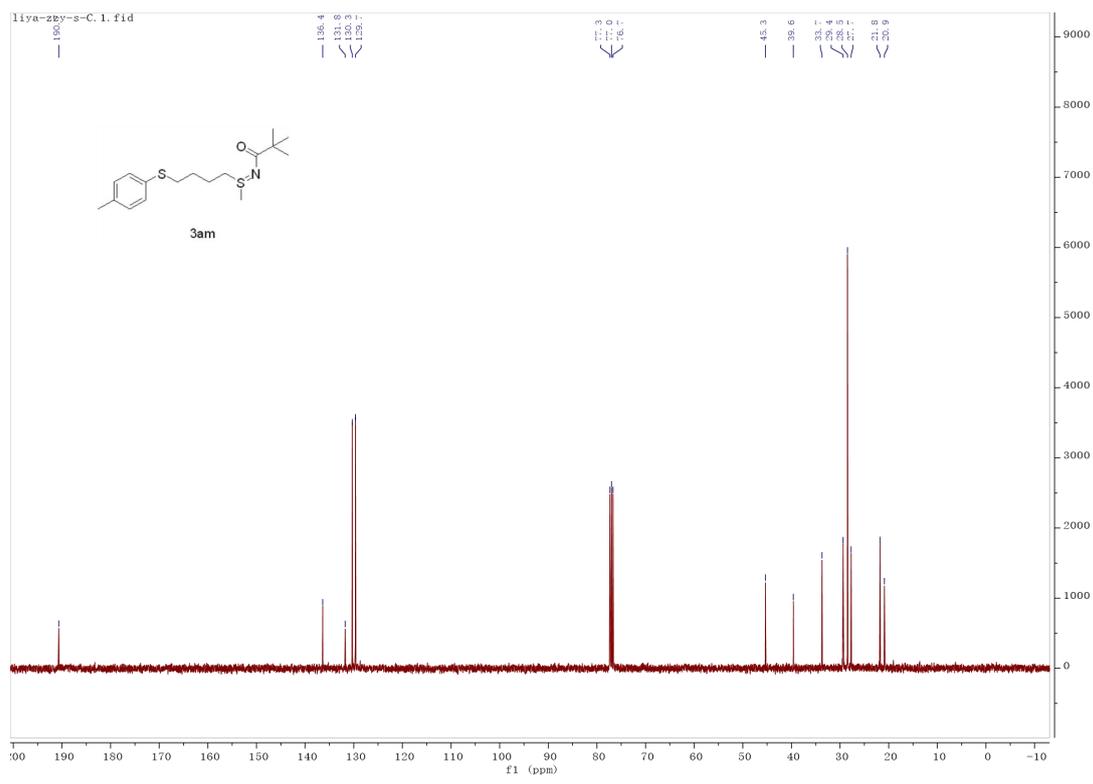
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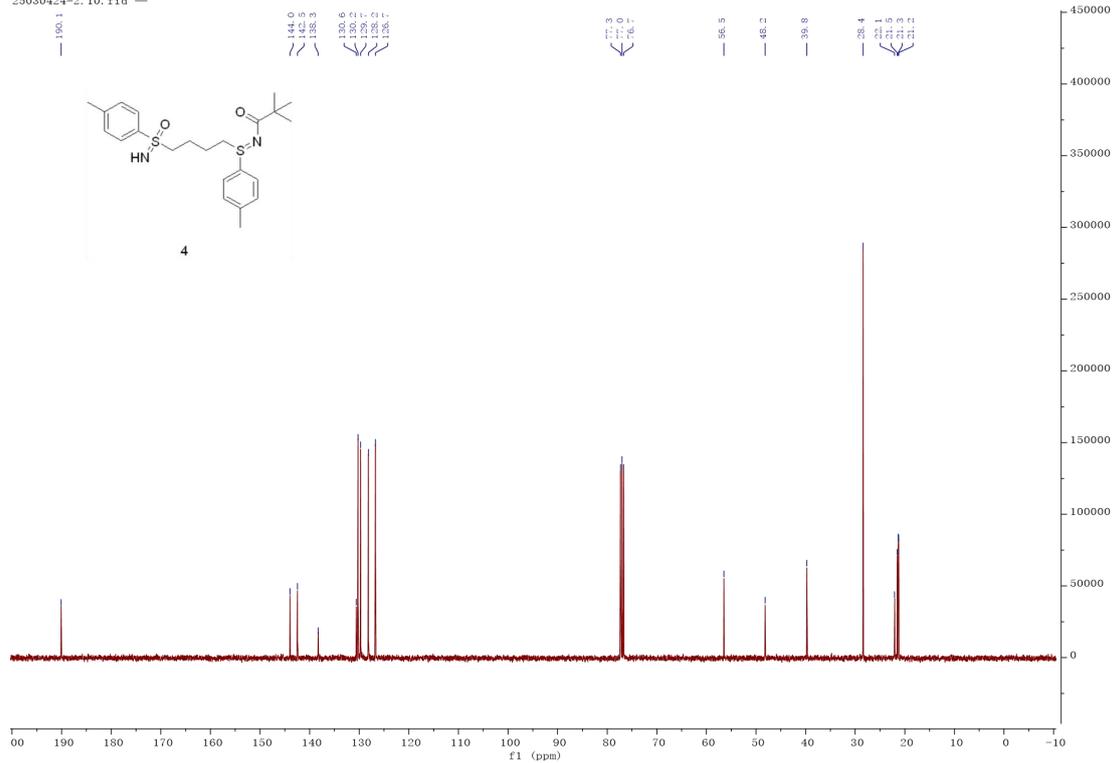




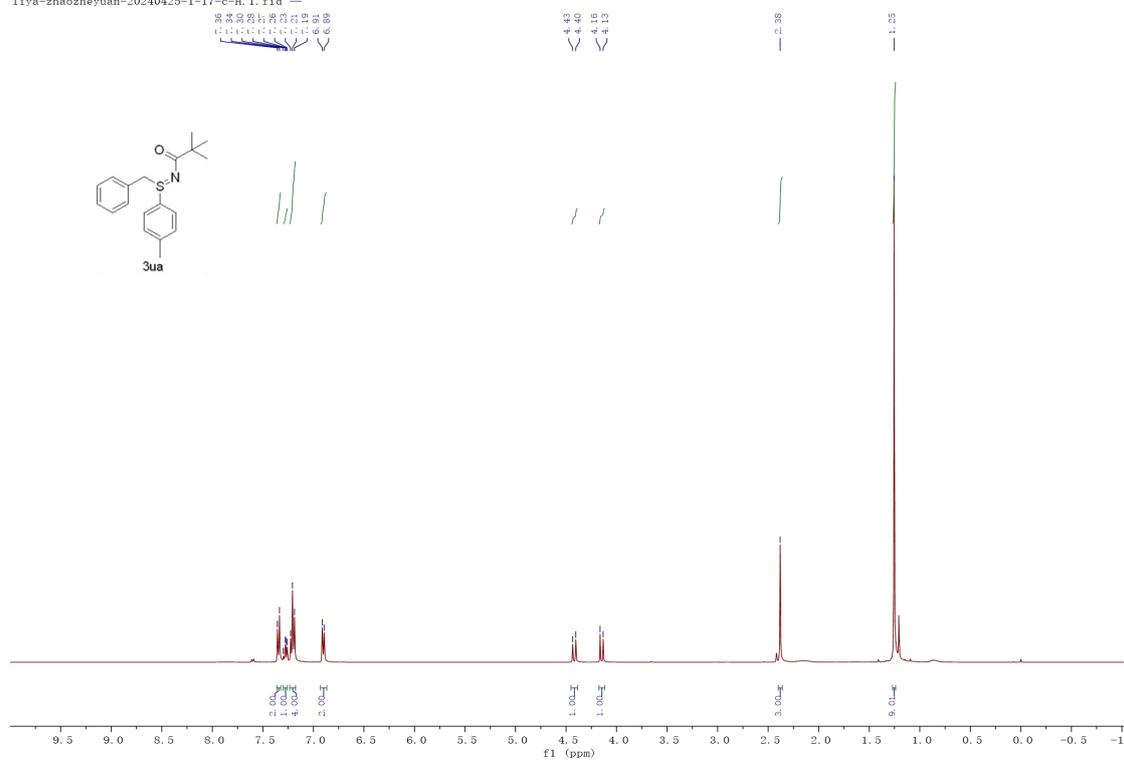




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