Supporting Information

Synthesis of *S*-alkyl sulfilimines via ring-opening sulfilimination of sulfonium salts

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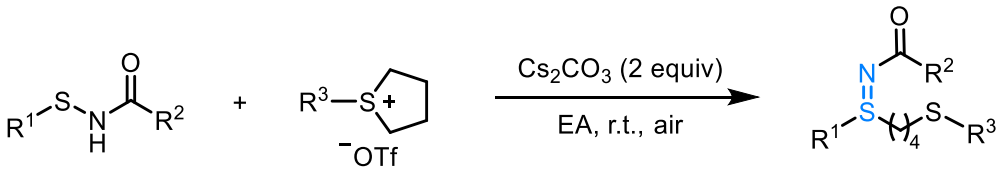
1. General Information

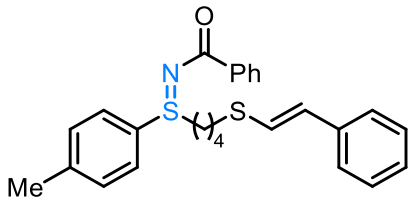
Unless otherwise stated, all commercial reagents were used as received. All solvents were purchased as analytical grade. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 100 MHz and 376 MHz respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument. Sulfonamides **1**[1] and sulfonium salts **2**[2] were prepared according to the reported literature procedures.

2. General Procedures and Characterization

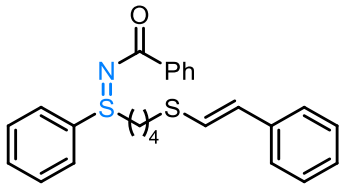


1 **2** **3-37**

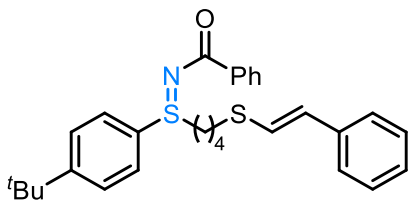
To a solution of sulfenamides **1** (0.2 mmol, 1.0 equiv) in EA (2 mL) was added sulfonium salts **2** (0.3 mmol, 1.5 equiv), and Cs_2CO_3 (0.4 mmol, 2.0 equiv) under air atmosphere. The reaction mixture was stirred at room temperature for 6 hours. After completion of reaction monitored by TLC analysis, the reaction mixture was evaporated under reduced pressure and the residue was purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding products **3-37**.



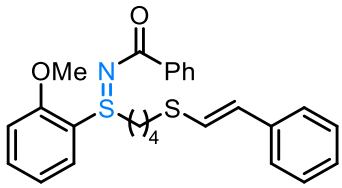
***N*-((4-((styryl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (3):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.28 (m, 3H), 7.28 – 7.25 (m, 3H), 7.22 – 7.16 (m, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 3.33 – 3.23 (m, 1H), 3.15 – 3.05 (m, 1H), 2.85 – 2.71 (m, 2H), 2.40 (s, 3H), 1.88 – 1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.0, 136.8, 136.6, 130.72, 130.67, 130.6, 128.8, 128.7, 127.9, 127.8, 127.3, 127.1, 125.6, 124.3, 49.4, 32.0, 28.2, 22.4, 21.5; HRMS (ESI) calcd for $C_{26}H_{28}NOS_2^+$ ($M+H^+$): 434.1612, found: 434.1611.



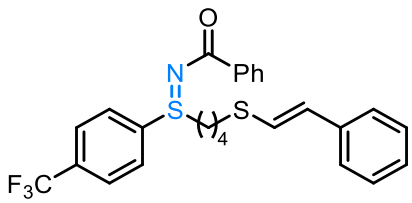
***N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzamide (4):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 89% yield. ^{1}1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.34 (m, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.16 (m, 4H), 7.15 – 7.08 (m, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 3.26 – 3.15 (m, 1H), 3.09 – 2.99 (m, 1H), 2.79 – 2.63 (m, 2H), 1.81 – 1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 136.8, 136.5, 134.1, 132.2, 130.8, 129.9, 128.8, 128.7, 127.91, 127.86, 127.2, 127.1, 125.6, 124.3, 49.3, 32.0, 28.2, 22.3; HRMS (ESI) calcd for $C_{25}H_{26}NOS_2^+$($M+H^+$): 420.1456, found: 420.1458.



***N*-((4-(*tert*-butyl)phenyl)(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzamide (5):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.0 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.22 – 7.15 (m, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.34 – 3.25 (m, 1H), 3.15 – 3.05 (m, 1H), 2.86 – 2.74 (m, 2H), 1.91 – 1.79 (m, 4H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 156.0, 136.8, 136.6, 130.72, 130.65, 128.77, 128.69, 127.86, 127.82, 127.11, 127.08, 127.0, 125.6, 124.3, 49.3, 35.1, 32.0, 31.1, 28.2, 22.5; HRMS (ESI) calcd for $C_{29}H_{34}NOS_2^+$ ($M+H^+$): 476.2076, found: 476.2072.

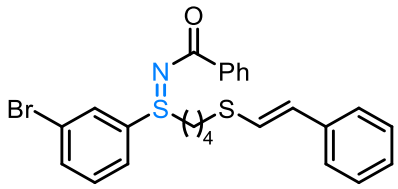


***N*-((2-methoxyphenyl)(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzamide (6):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.20 (m, 2H), 7.81 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.52 – 7.35 (m, 5H), 7.31 – 7.23 (m, 3H), 7.20 – 7.15 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 3.93 (s, 3H), 3.32 – 3.23 (m, 1H), 3.20 – 3.11 (m, 1H), 2.86 – 2.72 (m, 2H), 2.06 – 1.94 (m, 1H), 1.90 – 1.73 (m, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 156.7, 136.9, 136.8, 133.1, 130.8, 128.9, 128.7, 127.8, 127.6, 127.5, 127.0, 125.6, 124.5, 122.0, 120.9, 111.6, 56.3, 46.6, 32.0, 28.2, 22.2; HRMS (ESI) calcd for $C_{26}H_{28}NO_2S_2^+$ ($M+H^+$): 450.1556, found: 450.1553.

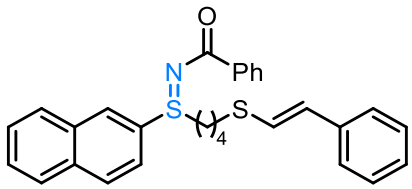


***N*-((4-((styryl)thio)butyl)(4-(trifluoromethyl)phenyl)-λ^4-sulfaneylidene)benzamide (7)**: prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2

Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.12 (d, J = 6.4 Hz, 1H), 6.56 (d, J = 15.5 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 3.25 – 3.13 (m, 1H), 3.13 – 3.00 (m, 1H), 2.79 – 2.63 (m, 2H), 1.89 – 1.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 136.8, 136.0, 134.0 (q, J = 33.0 Hz), 128.9, 128.7, 128.1, 127.9, 127.6, 127.2, 126.9 (q, J = 273 Hz), 126.8 (q, J = 3.0 Hz), 49.1, 31.9, 28.2, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; HRMS (ESI) calcd for $C_{26}H_{25}F_3NOS_2^+$ ($M+H^+$): 488.1324, found: 488.1318.

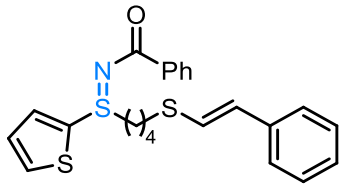


***N*-((3-bromophenyl)(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzamide (8):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.0 Hz, 2H), 7.96 – 7.92 (m, 1H), 7.72 – 7.64 (m, 2H), 7.52 – 7.34 (m, 5H), 7.30 – 7.27 (m, 3H), 7.23 – 7.16 (m, 1H), 6.64 (d, J = 15.6 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 3.32 – 3.22 (m, 1H), 3.18 – 3.07 (m, 1H), 2.87 – 2.72 (m, 2H), 1.93 – 1.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 136.8, 136.5, 136.2, 135.4, 131.3, 131.1, 129.7, 128.9, 128.7, 128.0, 127.9, 127.1, 125.8, 125.6, 124.3, 123.9, 49.4, 31.9, 28.2, 22.4; HRMS (ESI) calcd for $C_{25}H_{24}BrNNaOS_2^+$ ($M+Na^+$): 520.0375, found: 520.0374.

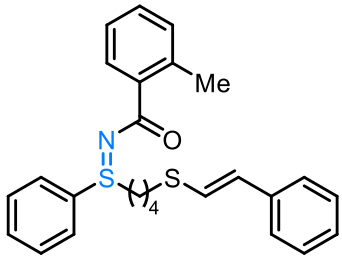


***N*-(naphthalen-2-yl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzamide (9):** prepared according to the general procedure A and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.22 (d, J = 7.0 Hz, 2H), 7.96 (d, J = 8.6 Hz, 1H), 7.87 (t, J = 7.8 Hz, 2H), 7.79 (dd, J = 8.7, 1.5 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.47 – 7.36 (m, 3H), 7.30 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 6.61 (d, J = 15.6 Hz, 1H), 6.42 (d, J = 15.6 Hz, 1H), 3.40 – 3.29 (m, 1H), 3.24 – 3.14 (m, 1H), 2.83 – 2.69 (m, 2H), 1.89 – 1.75 (m,

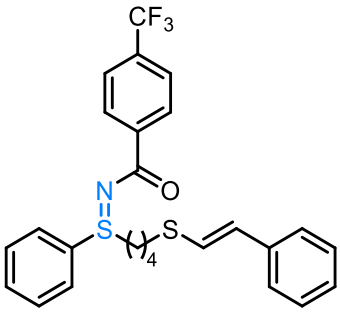
4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ177.0, 136.8, 136.6, 134.9, 132.9, 130.9, 130.4, 128.9, 128.7, 128.1, 127.91, 127.87, 127.6, 127.1, 125.6, 124.3, 122.0, 49.1, 32.0, 28.2, 22.4; HRMS (ESI) calcd for $C_{29}H_{28}NOS_2^+$ ($M+H^+$): 470.1607, found: 470.1604.



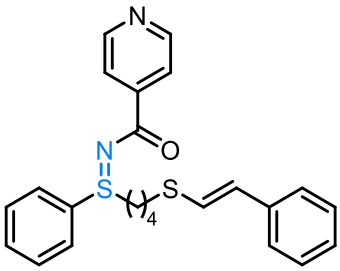
***N*-((4-((styryl)thio)butyl)(thiophen-2-yl)-λ^4-sulfaneylidene)benzamide (10):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 7.69 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.60 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.22 – 7.16 (m, 1H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.57 – 3.45 (m, 1H), 3.30 – 3.19 (m, 1H), 2.86 – 2.72 (m, 2H), 1.88 – 1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 136.8, 136.2, 133.7, 133.2, 132.9, 131.0, 128.9, 128.7, 128.0, 127.9, 127.7, 127.1, 125.6, 124.3, 51.3, 31.9, 28.1, 22.3; HRMS (ESI) calcd for $C_{23}H_{23}NNaOS_3^+$ ($M+Na^+$): 448.0834, found: 448.0837.



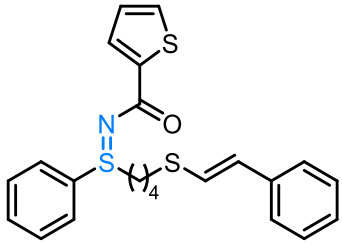
2-methyl-*N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzamide (11): prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.83 – 7.76 (m, 2H), 7.59 – 7.48 (m, 3H), 7.33 – 7.23 (m, 6H), 7.23 – 7.16 (m, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 15.5 Hz, 1H), 3.41 – 3.22 (m, 1H), 3.20 – 3.06 (m, 1H), 2.92 – 2.66 (m, 2H), 2.39 (s, 3H), 1.91 – 1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 141.0, 136.9, 134.2, 133.8, 132.2, 129.9, 128.9, 128.7, 128.6, 127.8, 127.2, 127.1, 125.6, 124.4, 49.3, 32.0, 28.2, 22.3, 21.6; HRMS (ESI) calcd for $C_{26}H_{28}NOS_2^+$ ($M+H^+$): 434.1607, found: 434.1605.



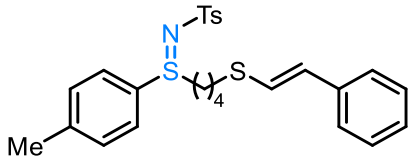
***N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)-4-(trifluoromethyl)benzamide (12):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.86 – 7.75 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.50 (m, 3H), 7.33 – 7.24 (m, 4H), 7.24 – 7.17 (m, 1H), 6.64 (d, *J* = 15.5 Hz, 1H), 6.46 (d, *J* = 15.5 Hz, 1H), 3.39 – 3.24 (m, 1H), 3.19 – 3.10 (m, 1H), 2.88 – 2.73 (m, 2H), 1.95 – 1.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 139.8, 136.8, 133.6, 132.5, 132.1, 130.0, 129.1, 128.7, 128.0, 127.1, 125.6, 124.8 (q, *J* = 3.6 Hz), 124.2, 122.8, 49.4, 31.9, 28.2, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; HRMS (ESI) calcd for $C_{26}H_{25}F_3NOS_2^+$ ($M+H^+$): 488.1324, found: 488.1320.



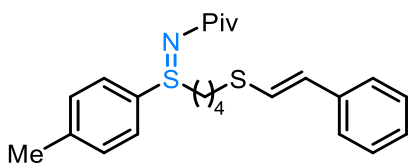
***N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)isonicotinamide (13):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 8.68 (d, *J* = 4.6 Hz, 2H), 7.97 (d, *J* = 4.7 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 2H), 7.62 – 7.50 (m, 3H), 7.33 – 7.24 (m, 4H), 7.24 – 7.16 (m, 1H), 6.64 (d, *J* = 15.5 Hz, 1H), 6.46 (d, *J* = 15.5 Hz, 1H), 3.39 – 3.25 (m, 1H), 3.20 – 3.09 (m, 1H), 2.87 – 2.75 (m, 2H), 1.92 – 1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 149.9, 143.7, 136.8, 133.2, 132.6, 130.4, 130.1, 128.7, 128.1, 127.4, 127.2, 125.7, 124.1, 122.7, 49.4, 31.9, 28.1, 22.3; HRMS (ESI) calcd for $C_{24}H_{25}N_2OS_2^+$ ($M+H^+$): 421.1403, found: 421.1408.



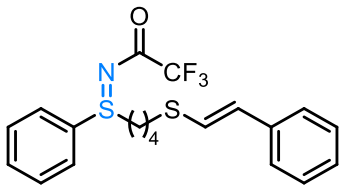
***N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)thiophene-2-carboxamide (14):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 3H), 7.55 – 7.45 (m, 3H), 7.35 (s, 1H), 7.32 – 7.21 (m, 4H), 7.21 – 7.13 (m, 1H), 7.05 – 6.99 (m, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.5 Hz, 1H), 3.32 – 3.18 (m, 1H), 3.15 – 3.01 (m, 1H), 2.83 – 2.69 (m, 2H), 1.86 – 1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 141.6, 136.8, 133.9, 132.3, 130.1 129.9, 129.4, 128.7, 127.9, 127.3, 127.2, 127.1 125., 124.3, 49.6, 31.9, 28.1, 22.3; HRMS (ESI) calcd for $C_{23}H_{24}NOS_3^+$ ($M+H^+$): 426.1015, found: 426.1009.



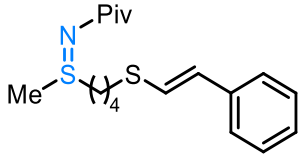
4-methyl-*N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)benzenesulfonamide (15): prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.21 (m, 6H), 7.19 – 7.16 (m, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 3.18 – 3.07 (m, 2H), 2.66 – 2.51 (m, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.82 – 1.60 (m, 2H), 1.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 141.5, 138.4, 137.1, 132.6, 129.8, 129.7, 129.6, 128.7, 127.1, 126.9, 125.6, 125.5, 124.9, 49.1, 32.0, 27.0, 26.3, 21.5, 21.3; HRMS (ESI) calcd for $C_{26}H_{29}NO_2S_3Na^+$ ($M+Na^+$): 506.1253, found: 506.1249.



***N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)pivalamide (16):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.24 – 7.19 (m, 6H), 7.15 – 7.09 (m, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 3.09 – 2.99 (m, 1H), 2.97 – 2.87 (m, 1H), 2.74 – 2.66 (m, 2H), 2.32 (s, 3H), 1.74 – 1.65 (m, 4H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 136.9, 131.2, 130.5, 128.7, 127.8, 127.07, 127.05, 125.5, 124.4, 48.8, 40.1, 32.0, 28.7, 28.2, 22.1, 21.5; HRMS (ESI) calcd for $C_{24}H_{31}NNaOS_2^+$ ($M+Na^+$): 436.1739 found: 436.1732.

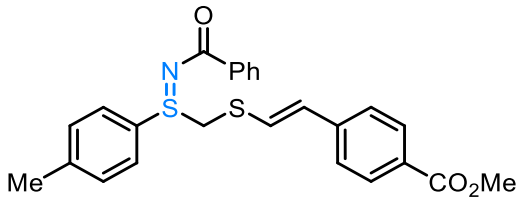


2,2,2-Trifluoro-*N*-(phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)acetamide (17): prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.0 Hz, 2H), 7.65 – 7.51 (m, 3H), 7.33 – 7.24 (m, 4H), 7.23 – 7.14 (m, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 3.37 – 3.26 (m, 1H), 3.21 – 3.09 (m, 1H), 2.88 – 2.68 (m, 2H), 1.84 – 1.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 (q, *J* = 35.1 Hz) ,136.7, 133.2, 131.3, 130.3, 128.7, 128.2, 127.5, 127.2, 125.6, 124.0, 117.1 (q, *J* = 287.7 Hz), 49.6, 31.8, 28.0, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.3; HRMS (ESI) calcd for $C_{20}H_{21}F_3NOS_2^+$($M+H^+$): 428.0960, found: 428.0959.

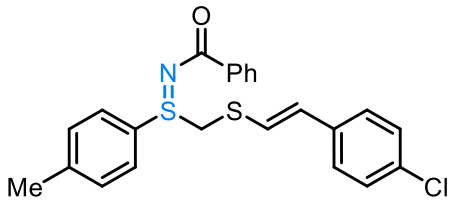


***N*-(methyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)pivalamide (18):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 6.67 (d, *J* = 15.5 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 3.10 – 3.03 (m, 1H), 2.92 – 2.80 (m, 3H), 2.61 (s, 3H), 1.91 – 1.84 (m, 4H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 136.8, 128.7, 127.9, 127.1, 125.6, 124.2,

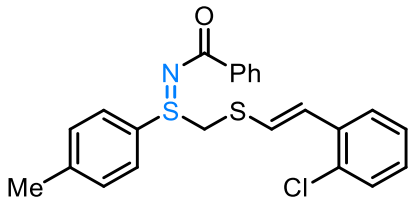
45.6, 39.8, 32.0, 29.6, 28.6, 28.1, 22.1; HRMS (ESI) calcd for $C_{18}H_{27}NNaOS_2^+$ ($M+Na^+$): 360.1426, found: 360.1422.



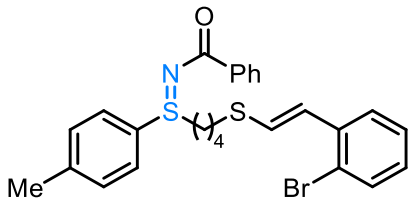
Methyl-4-(2-((4-(*N*-benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)butyl)thio)vinyl)benzoate (19): prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.14 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 2.9 Hz, 2H), 7.29 (d, *J* = 3.0 Hz, 2H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 3.89 (s, 3H), 3.32 – 3.23 (m, 1H), 3.15 – 3.05 (m, 1H), 2.87 – 2.75 (m, 2H), 2.38 (s, 3H), 1.87 – 1.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 166.9, 143.1, 141.2, 136.5, 130.8, 130.6, 130.1, 128.8, 128.1, 127.8, 127.3, 125.7, 125.2, 52.1, 49.3, 31.8, 28.1, 22.4, 21.5; HRMS (ESI) calcd for $C_{28}H_{30}NO_3S_2^+$ ($M+H^+$): 492.1662, found: 492.1654.



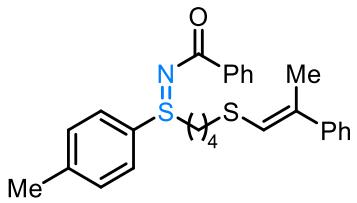
***N*-*N*-((4-((4-chlorostyryl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (20):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 6.9 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.29 (m, 5H), 7.25 (d, *J* = 10.2 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 3.35 – 3.20 (m, 1H), 3.18 – 3.03 (m, 1H), 2.86 – 2.71 (m, 2H), 2.41 (s, 3H), 1.87 – 1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.0, 136.6, 134.9, 131.9, 130.7, 130.6, 129.8, 128.8, 127.9, 127.8, 127.6, 127.3, 126.9, 126.0, 122.8, 49.3, 31.7, 28.0, 22.4, 21.5; HRMS (ESI) calcd for $C_{26}H_{27}ClNOS_2^+$ ($M+H^+$): 468.1217, found: 468.1212.



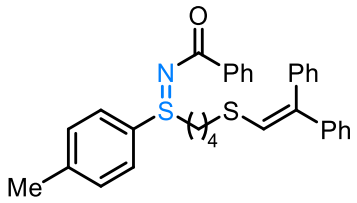
***N*-((4-((2-chlorostyryl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (21):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 7.73 – 7.65 (m, 2H), 7.46 – 7.29 (m, 7H), 7.21 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 6.80 – 6.73 (m, 1H), 6.71 – 6.65 (m, 1H), 3.36 – 3.23 (m, 1H), 3.16 – 3.05 (m, 1H), 2.89 – 2.74 (m, 2H), 2.39 (s, 3H), 1.89 – 1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.0, 136.6, 134.9, 131.9, 130.7, 130.6, 129.8, 128.8, 127.9, 127.8, 127.6, 127.3, 126.9, 126.0, 122.8, 49.3, 31.7, 28.0, 22.4, 21.5; HRMS (ESI) calcd for $C_{26}H_{27}ClNOS_2^+$ ($M+H^+$): 468.1217, found: 468.1212.



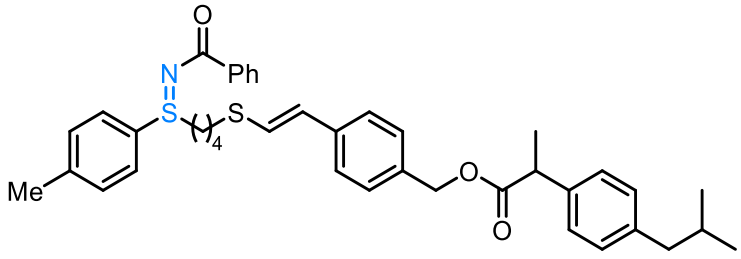
***N*-((4-((2-bromostyryl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (22):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.42 (dd, J = 8.0, 0.8 Hz, 1H), 7.37 – 7.25 (m, 4H), 7.22 (d, J = 8.1 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.98 – 6.89 (m, 1H), 6.63 (d, J = 15.5 Hz, 1H), 6.55 (d, J = 15.5 Hz, 1H), 3.25 – 3.14 (m, 1H), 3.07 – 2.97 (m, 1H), 2.79 – 2.67 (m, 2H), 2.30 (s, 3H), 1.82 – 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.0, 136.6, 136.57, 133.0, 130.7, 130.6, 130.6, 128.8, 128.2, 127.8, 127.7, 127.6, 127.3, 126.2, 125.2, 122.7, 49.3, 31.6, 27.9, 22.4, 21.5; HRMS (ESI) calcd for $C_{26}H_{27}BrNOS_2^+$ ($M+H^+$): 512.0712, found: 512.0706.



***N*-((4-((2-phenylprop-1-en-1-yl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (23):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 6.7 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.34 – 7.27 (m, 6H), 7.24 – 7.18 (m, 1H), 6.21 (d, *J* = 1.2 Hz, 1H), 3.35 – 3.23 (m, 1H), 3.15 – 3.04 (m, 1H), 2.83 – 2.69 (m, 2H), 2.39 (s, 3H), 2.09 (s, 3H), 1.84 – 1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 142.9, 141.8, 136.6, 134.4, 130.7, 130.65, 130.6, 128.8, 128.4, 127.8, 127.3, 126.8, 125.1, 122.8, 49.3, 33.5, 29.1, 22.1, 21.5, 17.7; HRMS (ESI) calcd for $C_{27}H_{30}NOS_2^+$ ($M+H^+$): 448.1763, found: 448.1759.

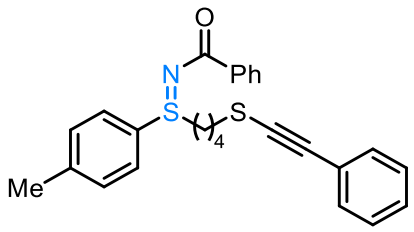


***N*-((4-((2,2-diphenylvinyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (24)**: prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.33 (m, 5H), 7.33 – 7.20 (m, 8H), 7.18 (d, *J* = 7.1 Hz, 2H), 6.49 (s, 1H), 3.30 – 3.18 (m, 1H), 3.11 – 3.01 (m, 1H), 2.81 – 2.65 (m, 2H), 2.36 (s, 3H), 1.84 – 1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.0, 141.7, 139.5, 139.3, 136.6, 130.8, 130.6, 129.7, 128.8, 128.4, 128.3, 127.8, 127.6, 127.4, 127.0, 125.3, 49.3, 34.1, 28.9, 22.2, 21.5; HRMS (ESI) calcd for $C_{32}H_{32}NOS_2^+$ ($M+H^+$): 510.1920, found: 510.1915.

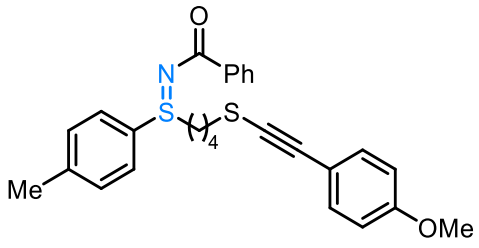


4-((*E*)-2-((4-(*N*-benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)butyl)thio)vinyl)benzyl 2-(4-isobutylphenyl)propanoate (25): prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.3 Hz, 2H), 7.69 (d, *J* = 7.9 Hz,

2H), 7.46 – 7.40 (m, 1H), 7.40 – 7.35 (m, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.22 – 7.11 (m, 6H), 7.08 (d, J = 7.7 Hz, 2H), 6.63 (d, J = 15.5 Hz, 1H), 6.42 (d, J = 15.5 Hz, 1H), 5.12 – 4.99 (m, 2H), 3.73 (q, J = 7.0 Hz, 1H), 3.34 – 3.22 (m, 1H), 3.16 – 3.04 (m, 1H), 2.85 – 2.72 (m, 2H), 2.44 (d, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.88 – 1.80 (m, 5H), 1.49 (d, J = 7.1 Hz, 3H), 0.89 (d, J = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 174.7, 143.2, 140.7, 137.7, 136.8, 136.7, 134.9, 130.9, 130.7, 129.4, 128.9, 128.4, 127.9, 127.4, 127.33, 127.30, 125.7, 124.9, 66.2, 49.5, 45.3, 45.1, 32.1, 30.3, 28.3, 22.51, 22.48, 21.6, 18.5; HRMS (ESI) calcd for $C_{22}H_{21}N_2O_2S^+$ ($M+H^+$): 652.2914, found: 652.2910.

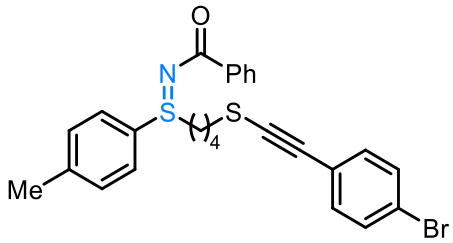


***N*-((4-((phenylethynyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (27):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.0 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.32 – 7.24 (m, 5H), 3.35 – 3.25 (m, 1H), 3.16 – 3.06 (m, 1H), 2.84 – 2.69 (m, 2H), 2.38 (s, 3H), 1.99 – 1.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.0, 136.6, 131.5, 130.8, 130.6, 128.8, 128.4, 128.2, 127.8, 127.3, 123.2, 93.5, 78.7, 49.3, 34.9, 28.1, 21.9, 21.5; HRMS (ESI) calcd for $C_{26}H_{26}NONaS_2^+$ ($M+H^+$): 432.1450, found: 432.1454.

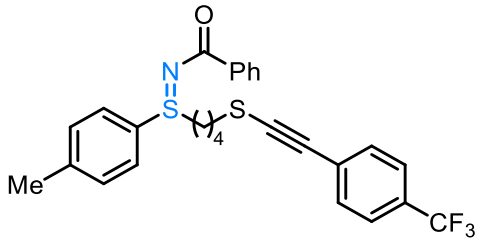


***N*-((4-(((4-methoxyphenyl)ethynyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (28):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.40 – 7.28 (m, 6H), 6.80 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 3.36 – 3.26 (m, 1H), 3.16 – 3.07 (m, 1H), 2.82 – 2.68 (m, 2H), 2.39 (s, 3H), 1.98 – 1.82 (m, 4H); ^{13}C NMR (100

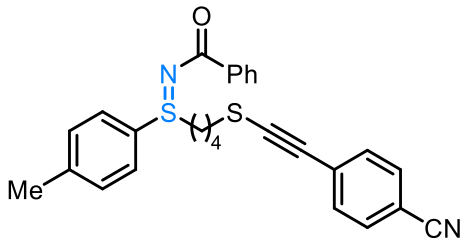
MHz, $CDCl_3$) δ 176.7, 159.7, 143.0, 136.6, 133.5, 130.72, 130.67, 130.6, 128.8, 127.8, 127.3, 115.3, 114.0, 93.3, 76.7, 55.3, 49.3, 35.0, 28.1, 22.0, 21.5; HRMS (ESI) calcd for $C_{27}H_{28}NO_2S_2^+$ ($M+H^+$): 462.1556, found: 462.1551.



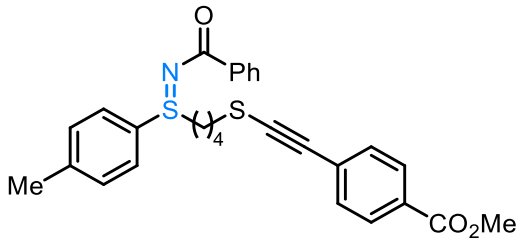
***N*-((4-(((4-bromophenyl)ethynyl)thio)butyl)(*p*-tolyl)-λ⁴-sulfaneylidene)benzamide (29):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 72% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 6.9 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.49 – 7.35 (m, 5H), 7.32 (d, J = 8.0 Hz, 2H), 7.27 – 7.22 (m, 2H), 3.42 – 3.25 (m, 1H), 3.23 – 3.06 (m, 1H), 2.92 – 2.68 (m, 2H), 2.41 (s, 3H), 2.03 – 1.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.1, 136.6, 132.9, 131.6, 130.8, 130.62, 130.60, 128.8, 127.8, 127.3, 122.4, 122.2, 92.4, 80.3, 49.3, 34.9, 28.1, 22.0, 21.5; HRMS (ESI) calcd for $C_{26}H_{25}BrNOS_2^+$ ($M+H^+$): 510.0555, found: 510.0552.



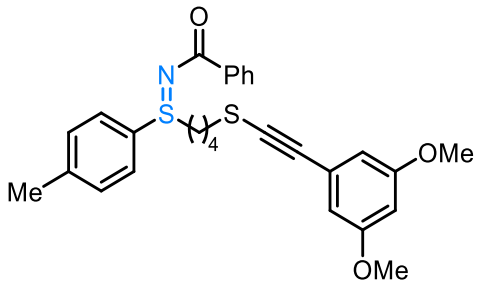
***N*-(*p*-tolyl(4-(((4-(trifluoromethyl)phenyl)ethynyl)thio)butyl)-λ⁴-sulfaneylidene)benzamide (30):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 56% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.1 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 (t, J = 7.3 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.30 – 3.18 (m, 1H), 3.10 – 2.99 (m, 1H), 2.80 – 2.66 (m, 2H), 2.31 (s, 3H), 1.94 – 1.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.1, 136.5, 131.3, 130.8, 130.6, 129.6 (q, J = 32.7 Hz), 128.8, 127.3, 127.0, 125.3 (q, J = 3.8 Hz), 122.6, 92.4, 82.2, 49.3, 34.9, 28.1, 22.0, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; HRMS (ESI) calcd for $C_{27}H_{25}F_3NOS_2^+$ ($M+H^+$): 500.1324, found: 500.1320.



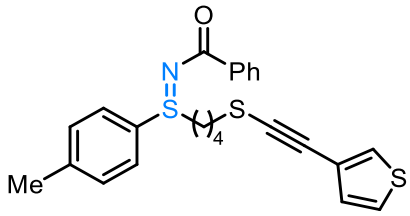
***N*-((4-(((4-cyanophenyl)ethynyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (31):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.0 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.30 (m, 7H), 3.39 – 3.23 (m, 1H), 3.20 – 3.05 (m, 1H), 2.90 – 2.74 (m, 2H), 2.41 (s, 3H), 2.07 – 1.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.1, 136.5, 132.0, 131.4, 130.8, 130.61, 130.58, 128.7, 128.1, 127.8, 127.3, 118.5, 111.0, 92.4, 84.9, 49.3, 35.0, 28.1, 22.0, 21.5; HRMS (ESI) calcd for $C_{27}H_{25}N_2OS_2^+$ ($M+H^+$): 457.1403, found: 457.1400.



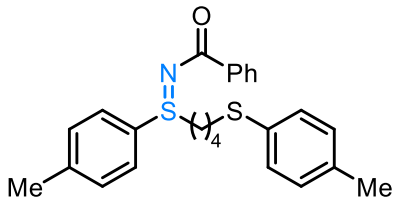
Methyl-4-(((4-(*N*-benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)butyl)thio)ethynyl)benzoate (32): prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.97 – 7.92 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.34 (m, 5H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 3.36 – 3.25 (m, 1H), 3.17 – 3.07 (m, 1H), 2.88 – 2.73 (m, 2H), 2.39 (s, 3H), 2.00 – 1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 166.5, 143.1, 130.9, 130.8, 130.6, 129.5, 129.2, 128.8, 127.8, 127.3, 93.1, 82.9, 52.2, 49.3, 34.9, 28.1, 21.9, 21.5; HRMS (ESI) calcd for $C_{28}H_{28}NO_3S_2^+$ ($M+H^+$): 490.1505, found: 490.1502.



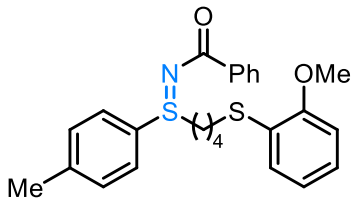
***N*-((4-(((3,5-dimethoxyphenyl)ethynyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (33):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.15 (m, 6H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.45 (d, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.27 – 3.19 (m, 1H), 3.10 – 3.00 (m, 1H), 2.86 – 2.73 (m, 2H), 2.39 (s, 3H), 1.91 – 1.75 (m, 2H), 1.66 – 1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 161.3, 160.6, 142.9, 136.7, 130.9, 130.6, 130.5, 129.6, 128.7, 127.8, 127.3, 116.0, 109.4, 100.4, 82.6, 81.6, 56.1, 55.5, 49.4, 34.1, 28.1, 22.3, 21.5; HRMS (ESI) calcd for $C_{28}H_{30}NO_3S_2^+$ ($M+H^+$): 492.1662, found: 492.1656.



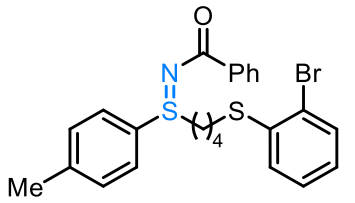
***N*-((4-((thiophen-3-ylethynyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (34):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 6.7 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.48 – 7.35 (m, 4H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.08 (d, *J* = 5.0 Hz, 1H), 3.37 – 3.21 (m, 1H), 3.21 – 3.04 (m, 1H), 2.85 – 2.66 (m, 2H), 2.40 (s, 3H), 1.97 – 1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.0, 136.6, 130.8, 130.6, 130.0, 129.4, 128.8, 127.8, 127.3, 125.4, 122.2, 88.4, 78.1, 49.3, 34.9, 28.1, 22.0, 21.5; HRMS (ESI) calcd for $C_{24}H_{23}NNaOS_3^+$ ($M+Na^+$): 460.0834, found: 460.0829.



***N*-(*p*-tolyl(4-(*p*-tolylthio)butyl)-λ^4-sulfaneylidene)benzamide (35):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.8 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.47 – 7.30 (m, 5H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.29 – 3.18 (m, 1H), 3.10 – 2.99 (m, 1H), 2.90 – 2.81 (m, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.82 – 1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.0, 136.62, 136.56, 131.9, 130.7, 130.6, 130.5, 129.8, 128.8, 127.8, 127.3, 49.3, 33.9, 27.9, 22.3, 21.5, 21.1; HRMS (ESI) calcd for $C_{25}H_{28}NOS_2^+$(M+H$^+$): 422.1607, found: 422.1605.

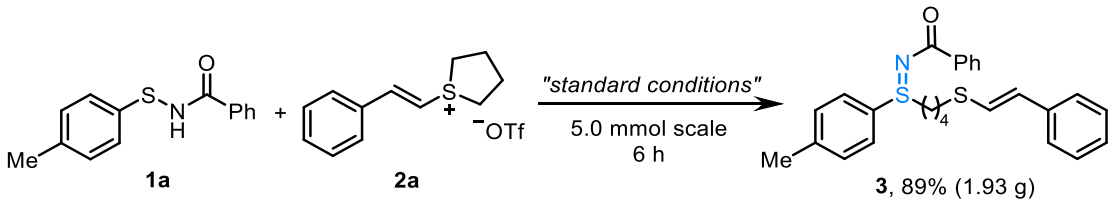


***N*-((4-((3-methoxyphenyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (36):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), yellow oil, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.0 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.14 (m, 2H), 6.93 – 6.79 (m, 2H), 3.85 (s, 3H), 3.32 – 3.18 (m, 1H), 3.12 – 3.00 (m, 1H), 2.93 – 2.79 (m, 2H), 2.39 (s, 3H), 1.86 – 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 157.6, 142.9, 136.6, 130.7, 130.6, 130.2, 128.8, 127.8, 127.6, 127.3, 123.7, 121.1, 110.7, 55.8, 49.3, 31.5, 27.8, 22.4, 21.5; HRMS (ESI) calcd for $C_{25}H_{28}NO_2S_2^+$ (M+H$^+$): 438.1556, found: 438.1553.



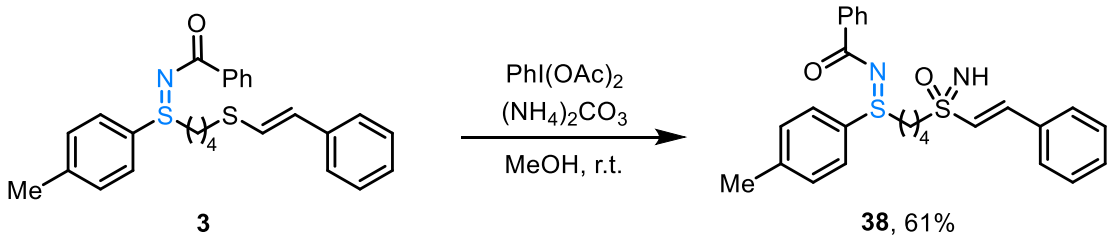
***N*-((4-((2-bromophenyl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (37):** prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.17 (m, 2H), 7.06 – 7.00 (m, 1H), 3.37 – 3.20 (m, 1H), 3.17 – 3.03 (m, 1H), 3.01 – 2.84 (m, 2H), 2.41 (s, 3H), 1.90 – 1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.0, 137.3, 136.6, 133.1, 130.7, 130.60, 130.57, 128.8, 128.5, 127.84, 127.81, 127.3, 126.9, 123.9, 49.3, 32.4, 27.2, 22.5, 21.5. HRMS (ESI) calcd for $C_{24}H_{24}BrNNaOS_2^+$ ($M+Na^+$): 508.0375, found: 508.0380.

3. Scale-Up Experiment



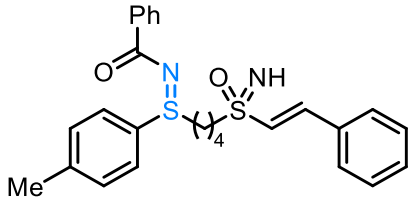
To a solution of of sulfenamides **1** (5 mmol, 1.0 equiv) in EA (2 mL) was added sulfonium salts **2** (7.5 mmol, 1.5 equiv), and Cs_2CO_3 (0.4 mmol, 2.0 equiv) under air atmosphere. The reaction mixture was stirred at room temperature for 6 hours. After completion of reaction monitored by TLC analysis, the reaction mixture was evaporated under reduced pressure and the residue was purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding product **3** (1.93 g, 89%).

4. Synthetic Applications

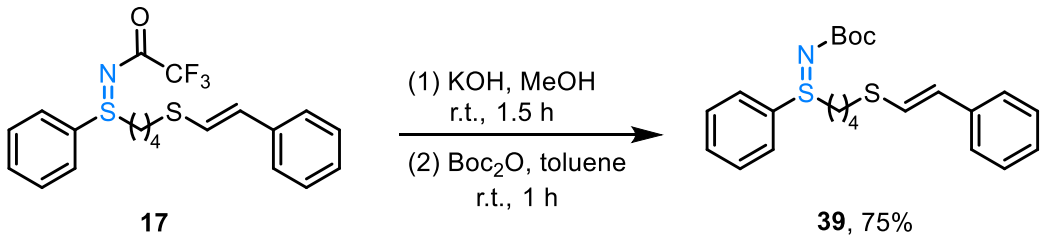


To a solution of **3** (0.1 mmol) in MeOH (5 mL) was added $(NH_4)_2CO_3$ (0.15 mmol) and $PhI(OAc)_2$ (0.2 mmol). The mixture was stirred at room temperature for overnight. After completion of reaction as monitored by TLC analysis, the reaction mixture was

evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to give the corresponding product **34**.

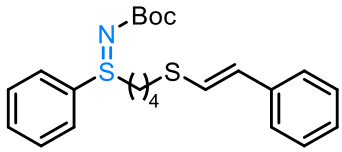


((4-(2-phenylvinylsulfonimidoyl)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (38): purified by column chromatography (petroleum ether/ethyl acetate = 4:1), colorless oil, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.46 (m, 3H), 7.45 – 7.30 (m, 4H), 6.89 (d, *J* = 15.3 Hz, 1H), 3.30 – 3.19 (m, 1H), 3.18 – 3.03 (m, 3H), 2.40 (s, 3H), 2.05 – 1.93 (m, 2H), 1.91 – 1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 144.0, 143.1, 136.5, 132.4, 131.2, 130.8, 130.6, 130.4, 129.2, 128.8, 128.6, 127.8, 127.7, 127.2, 55.6, 49.2 22.2 22.1, 21.5; HRMS (ESI) calcd for $C_{26}H_{29}N_2O_2S_2^+$ ($M+H^+$): 465.1665, found: 465.1663.

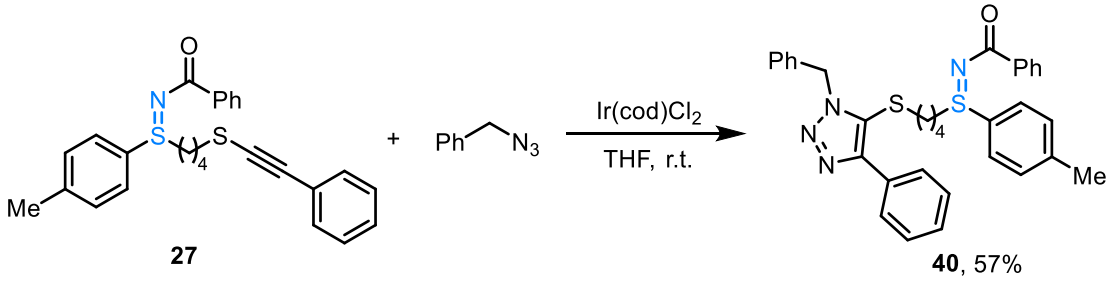


To a solution of **17** (0.1 mmol, 1 equiv) in methanol (2 mL) in a room temperature water bath was added 1 M KOH (1 mL). After 1.5 hour at room temperature, the reaction mixture was extracted with CH_2Cl_2 for three times. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated under reduced pressure to give the crude *NH*-free sulfilimine, which was used for next step immediately without any purification.

To a solution of the crude *NH*-free sulfilimine in anhydrous toluene (1 mL), di-tert-butyl dicarbonate (1.5 equiv) was added and the mixture was stirred at room temperature. After 1 hour, the reaction mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product **39**.

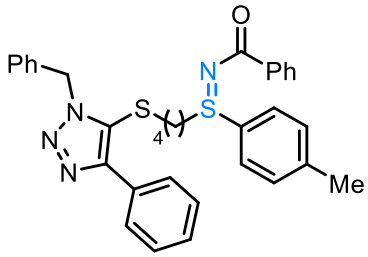


***tert*-Butyl (phenyl(4-((styryl)thio)butyl)-λ^4-sulfaneylidene)carbamate (39):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.1 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 3H), 7.25 – 7.16 (m, 4H), 7.15 – 7.08 (m, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.37 (d, *J* = 15.5 Hz, 1H), 3.14 – 2.97 (m, 1H), 2.93 – 2.80 (m, 1H), 2.77 – 2.59 (m, 2H), 1.83 – 1.64 (m, 4H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 136.8, 135.3, 132.2, 129.8, 128.7, 127.8, 127.1, 126.7, 125.6, 124.3, 79.0, 50.7, 31.9, 28.5, 28.2, 22.6; HRMS (ESI) calcd for $C_{23}H_{29}NNaO_2S_2^+$ ($M+Na^+$): 438.1532, found: 438.1541.



27 40, 57%

Under an argon atmosphere, an oven-dried round bottom flask equipped with a magnetic stir bar was charged with **27** (0.1 mmol), $PhCH_2N_3$ (0.2 mmol), $Ir(cod)Cl_2$ (3 mol%) and anhydrous THF (2 mL). The mixture was stirred at room temperature for 12 hours. After completion of reaction as monitored by TLC analysis, the reaction mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding product **40**.



***N*-((4-((1-benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)thio)butyl)(*p*-tolyl)-λ^4-sulfaneylidene)benzamide (40):** purified by column chromatography (petroleum

ether/ethyl acetate = 2:1), colorless oil, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.1 Hz, 2H), 8.09 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.32 (m, 6H), 7.31 – 7.25 (m, 6H), 7.24 – 7.18 (m, 1H), 5.62 (s, 2H), 2.89 – 2.79 (m, 1H), 2.70 – 2.60 (m, 1H), 2.38 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 1.52 – 1.39 (m, 2H), 1.29 – 1.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 149.5, 143.0, 136.6, 135.3, 130.8, 130.61, 130.59, 130.56, 128.9, 128.8, 128.7, 128.6, 128.4, 127.8, 127.7, 127.1, 127.0, 124.9, 52.1, 48.8, 35.0, 27.7, 22.0, 21.5; HRMS (ESI) calcd for $C_{33}H_{33}N_4OS_2^+$ ($M+H^+$): 565.2090, found: 565.2090.

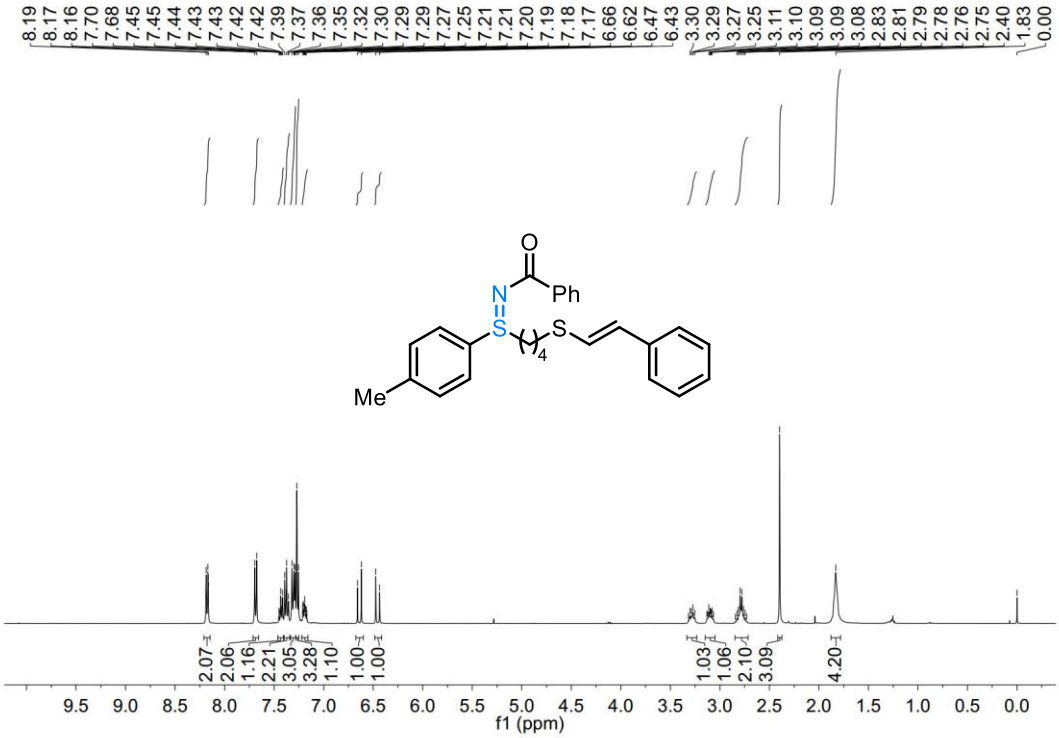
5. References

(1) (a) Greenwood, N. S.; Champlin, A. T.; Ellman, J. A. *J. Am. Chem. Soc.* **2022**, *144*, 17808-17814. (b) Yang, G.-F.; Yuan, Y.; Tian, Y.; Zhang, S.-Q.; Cui, X.; Xia, B.; Li, G.-X.; Tang, Z. *J. Am. Chem. Soc*. **2023**, *145*, 5439-5446. (c) Liang, Q.; Wells, L. A.; Han, K. S.; Chen, M.; Kozlowski, C.; Jia, T. *J. Am. Chem. Soc*. **2023**, *145*, 6310-6318. (d) Wu, X.; Li, Y.; Chen, M.; He, F.-S.; Wu, J. *J. Org. Chem*. **2023**, *88*, 9352-9359. (e) Greenwood, N. S.; Ellman, J. A. *Org. Lett.* **2023**, *25*, 4759-4764. (f) Chen, Y.; Fang, D.-M.; Huang, H.-S.; Nie, X.-K.; Zhang, S.-Q.; Cui, X.; Tang, Z.; Li, G.-X. *Org. Lett.* **2023**, *25*, 2134-2138.

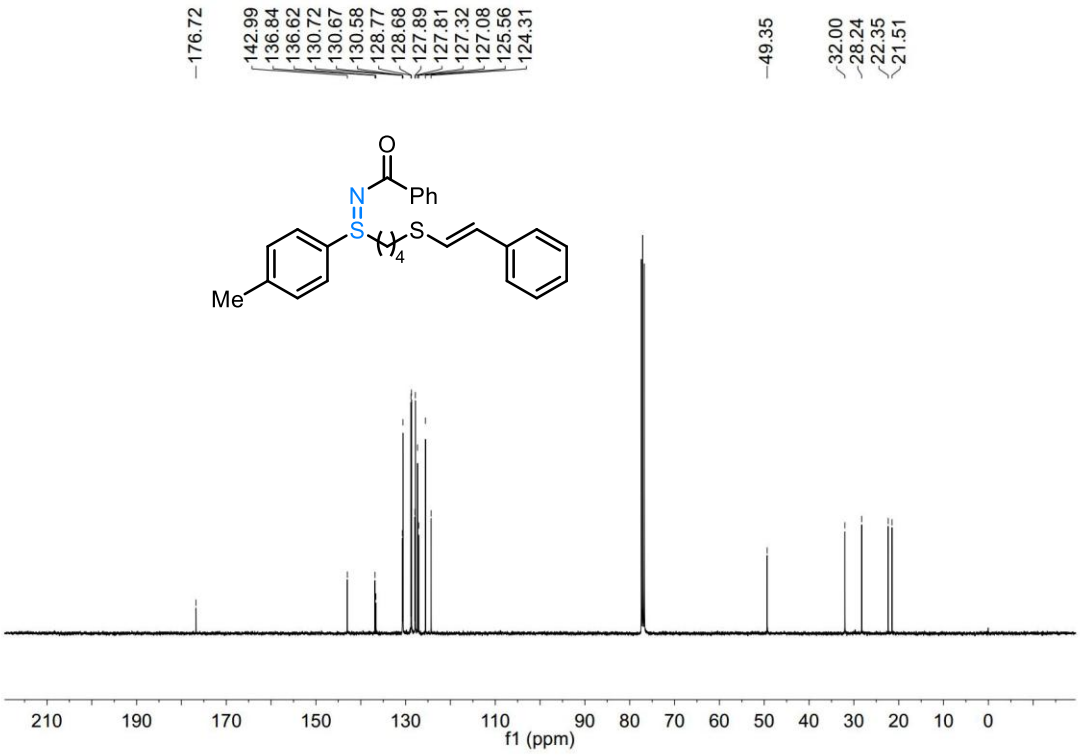
(2) (a) Wang, C.; Liu, B.; Shao, Z.; Zhou, J.; Shao, A.; Zou, L.-H.; Wen, J. *Org. Lett.* **2022**, *24*, 6455-6459; (b) Gao, P.; Zhang, Q.; Chen, F. *Org. Lett.* **2022**, *24*, 7769-7773.

6. Copies of ^{1}H ,^{13}C NMR and ^{19}F NMR Spectra

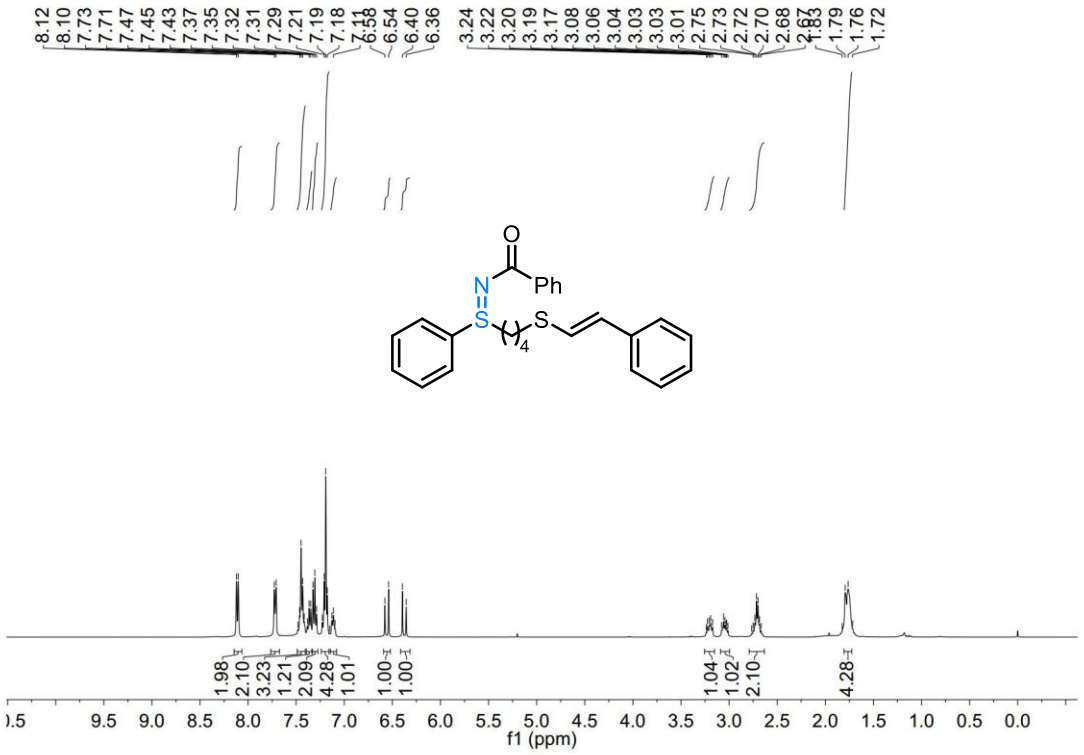
^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$)



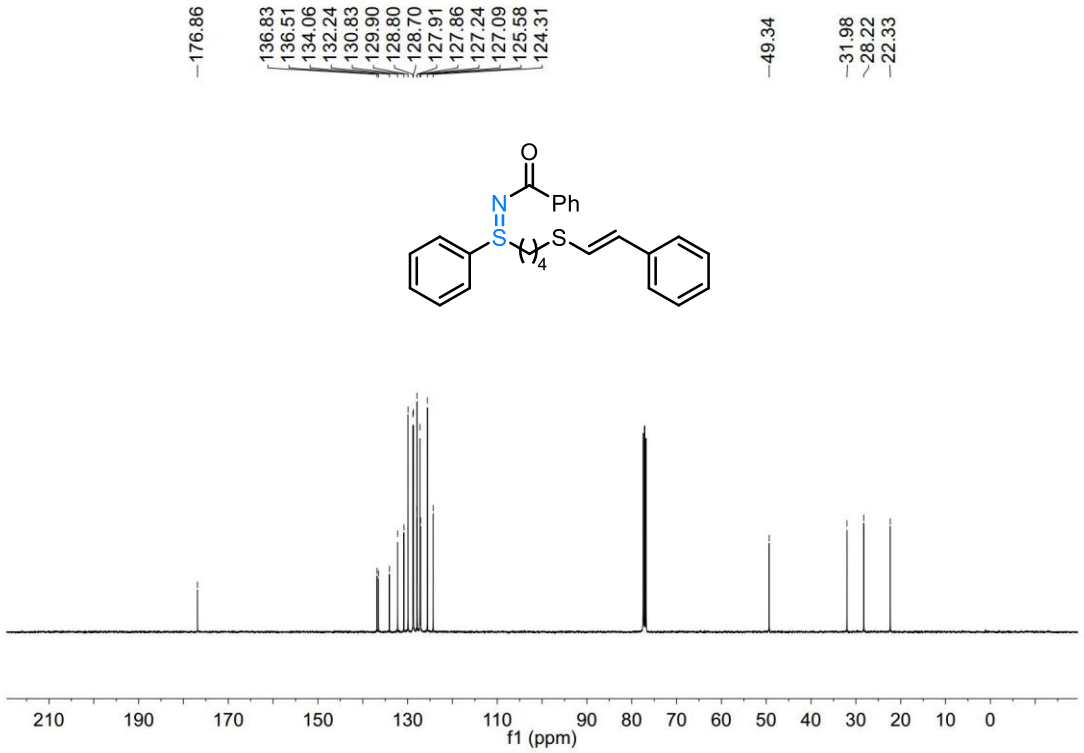
^{13}C NMR spectrum of compound **3** (100 MHz, $CDCl_3$)



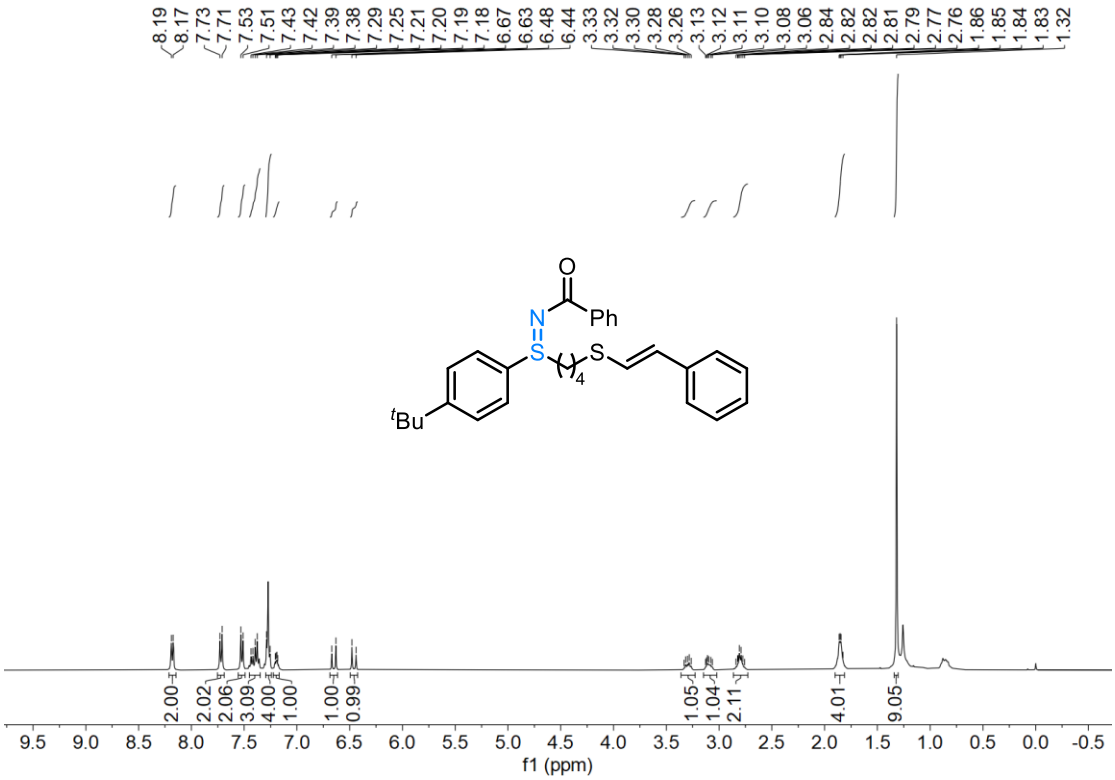
^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$)



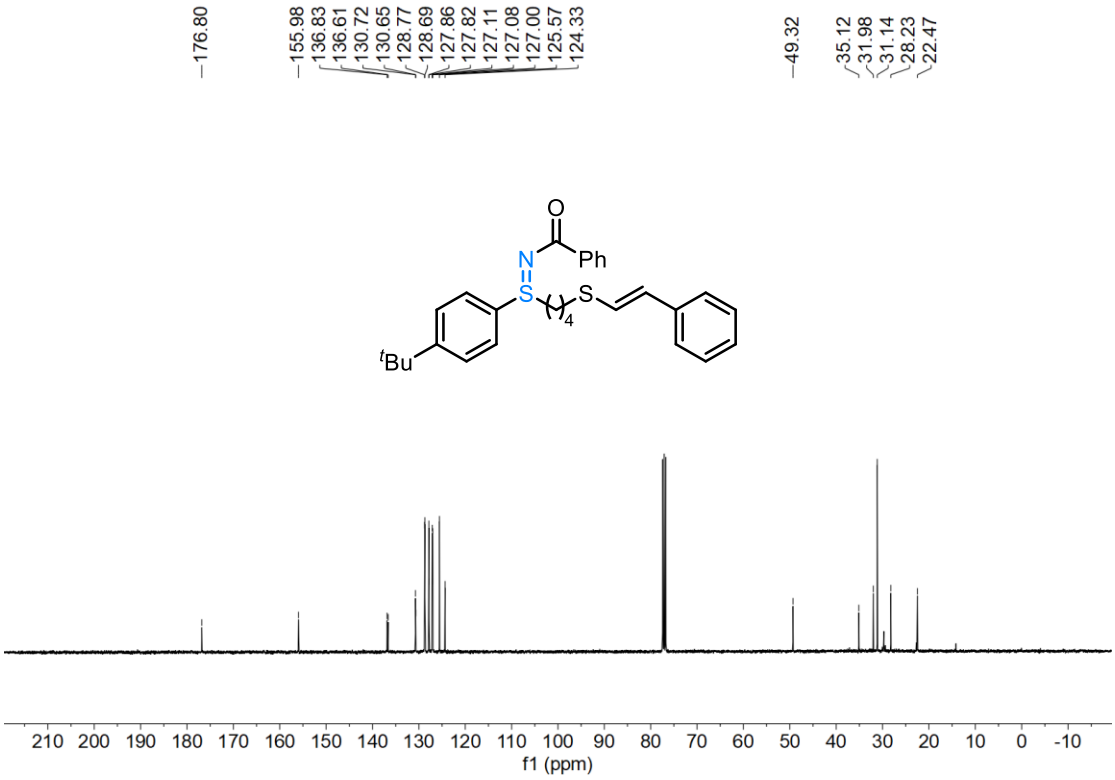
^{13}C NMR spectrum of compound **4** (100 MHz, $CDCl_3$)



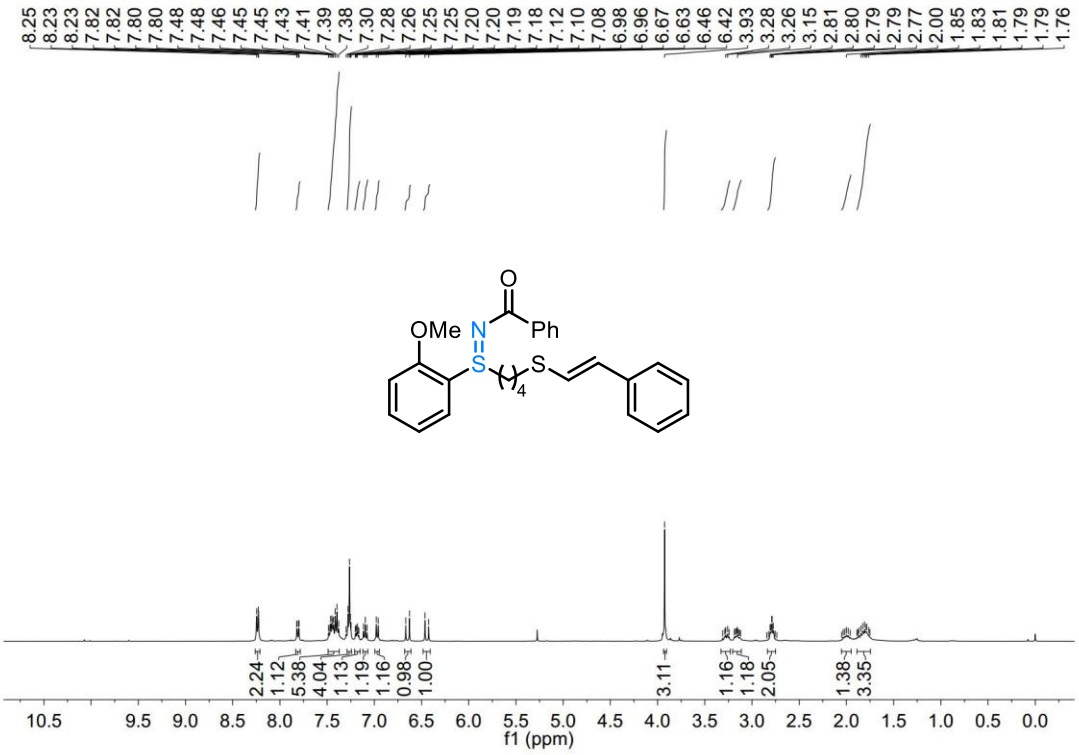
^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$)



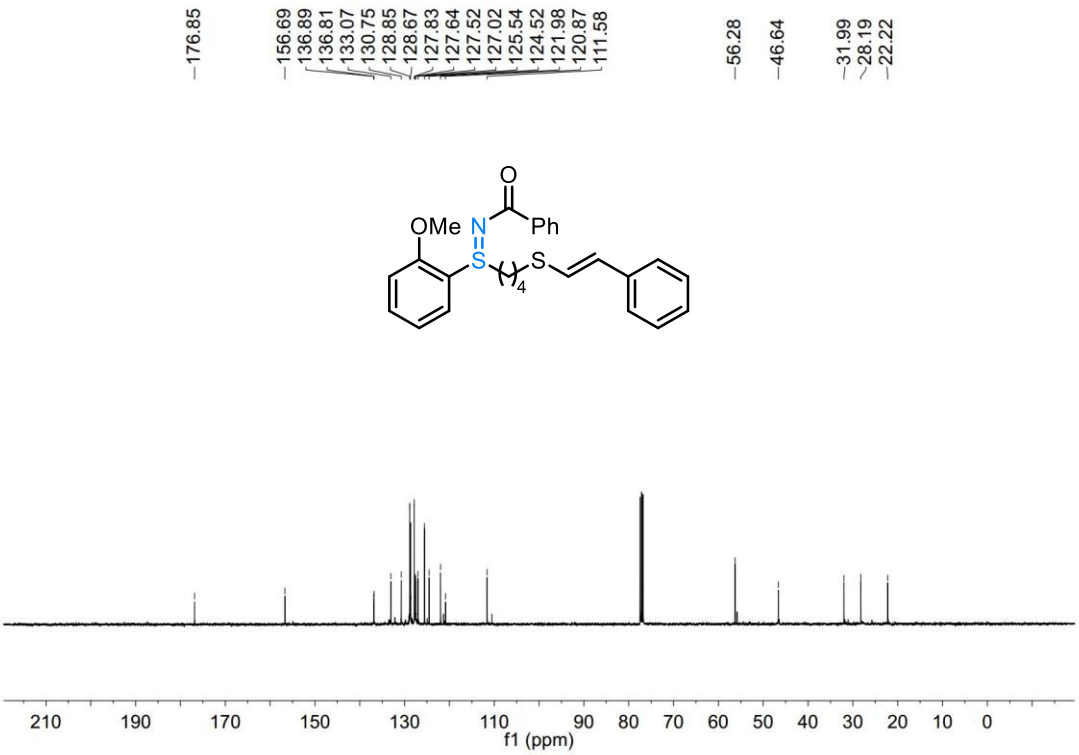
^{13}C NMR spectrum of compound **5** (100 MHz, $CDCl_3$)



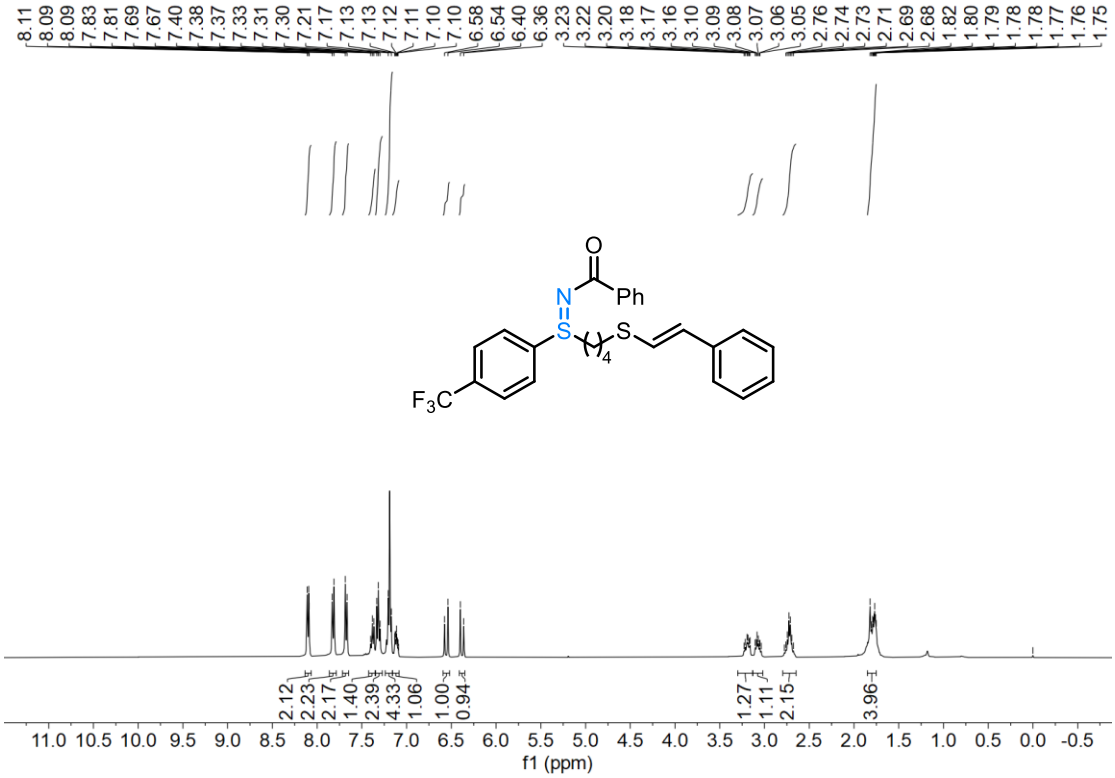
^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$)



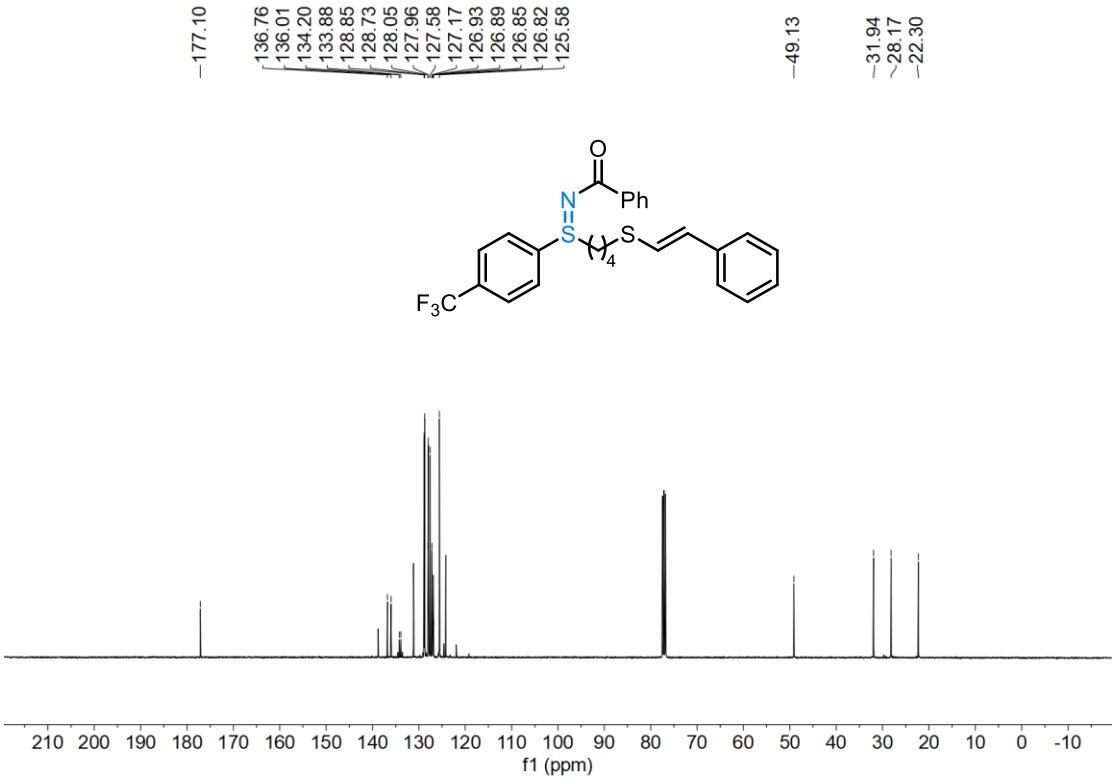
^{13}C NMR spectrum of compound **6** (100 MHz, $CDCl_3$)



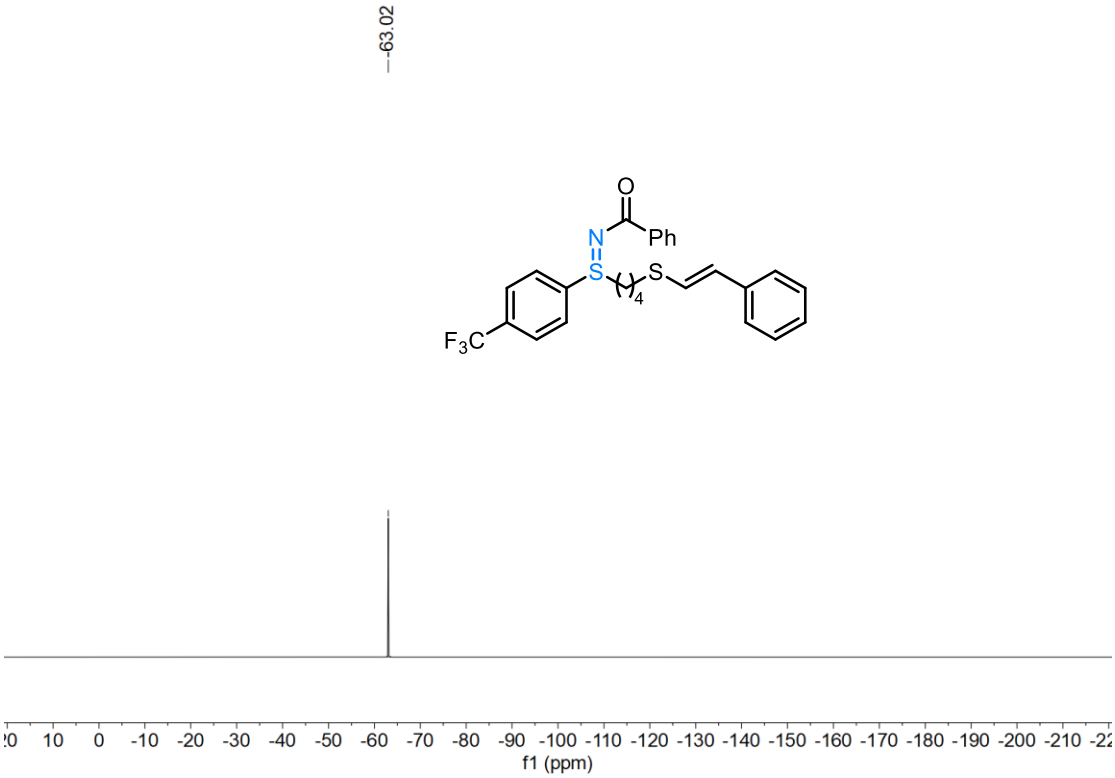
^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$)



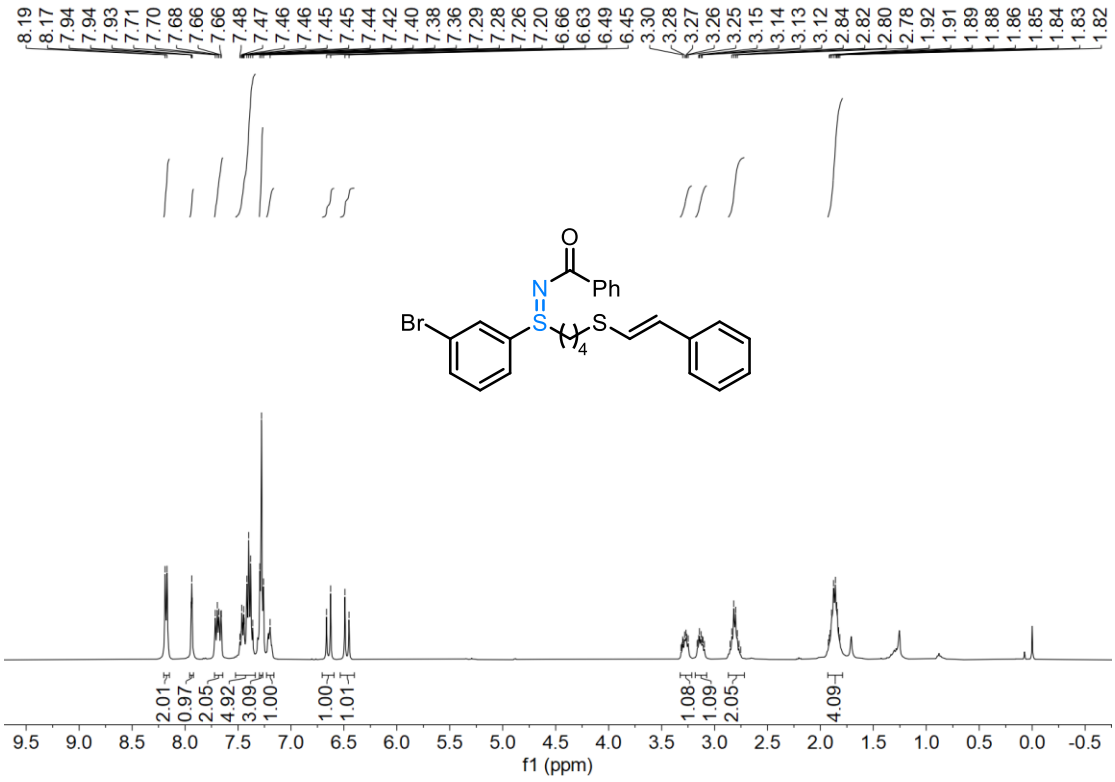
^{13}C NMR spectrum of compound **7** (100 MHz, $CDCl_3$)



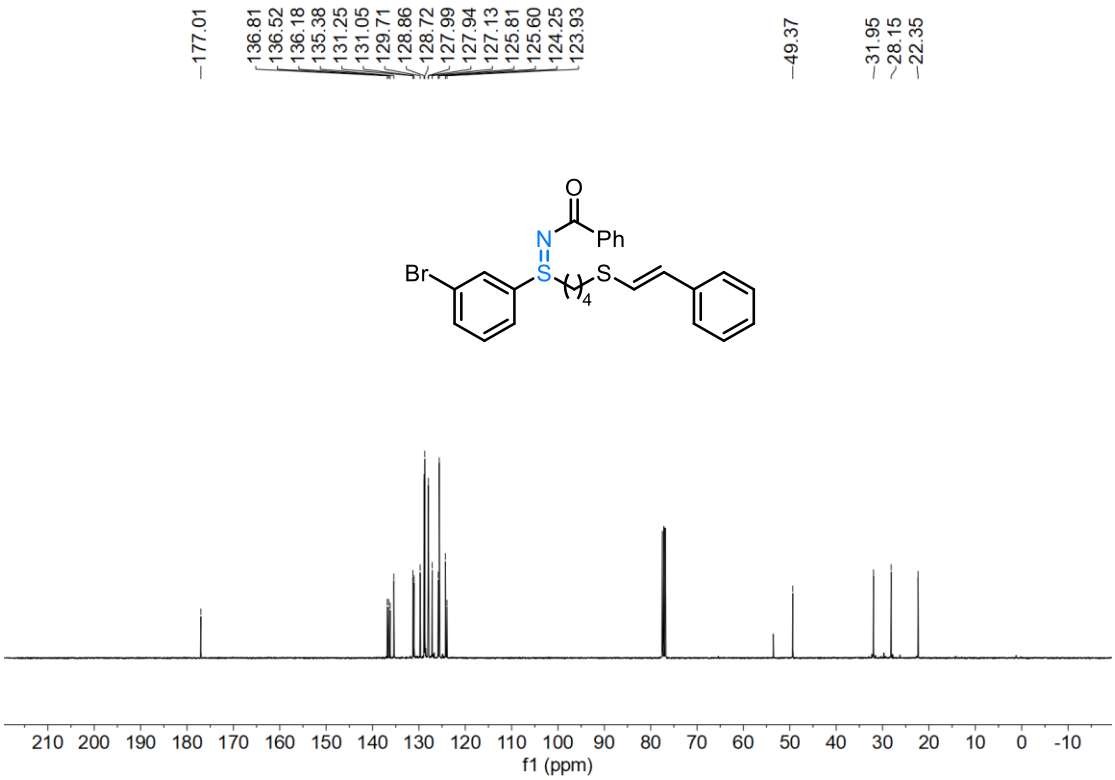
^{19}F NMR spectrum of compound **7** (376 MHz, $CDCl_3$)



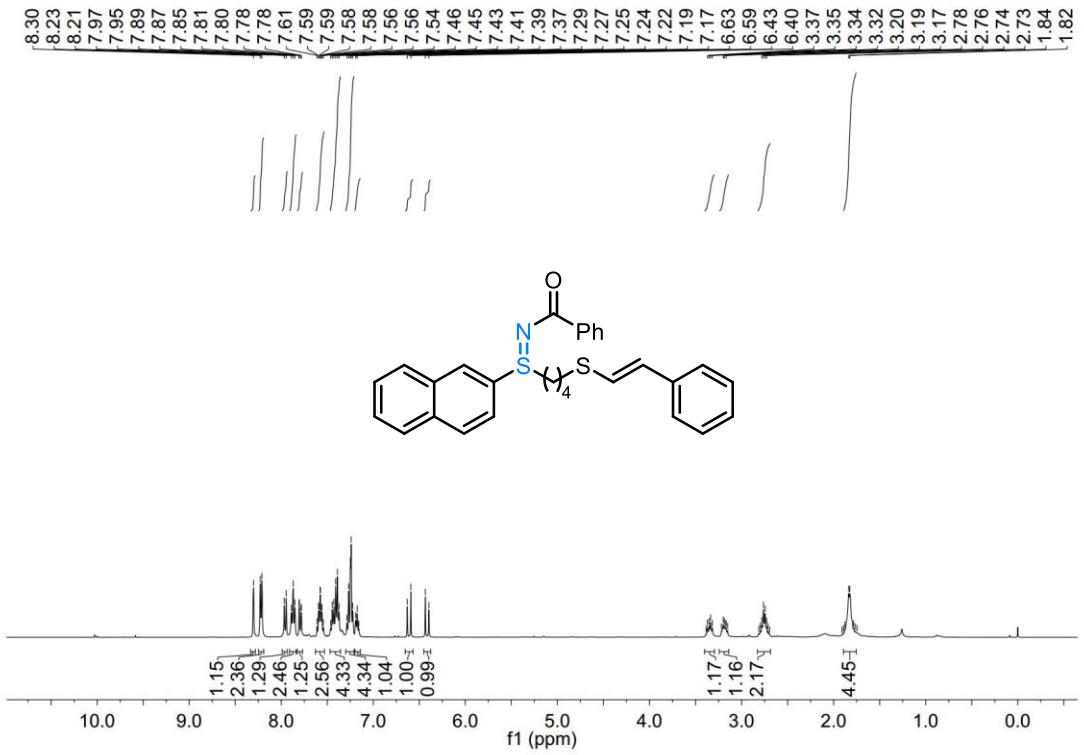
^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$)



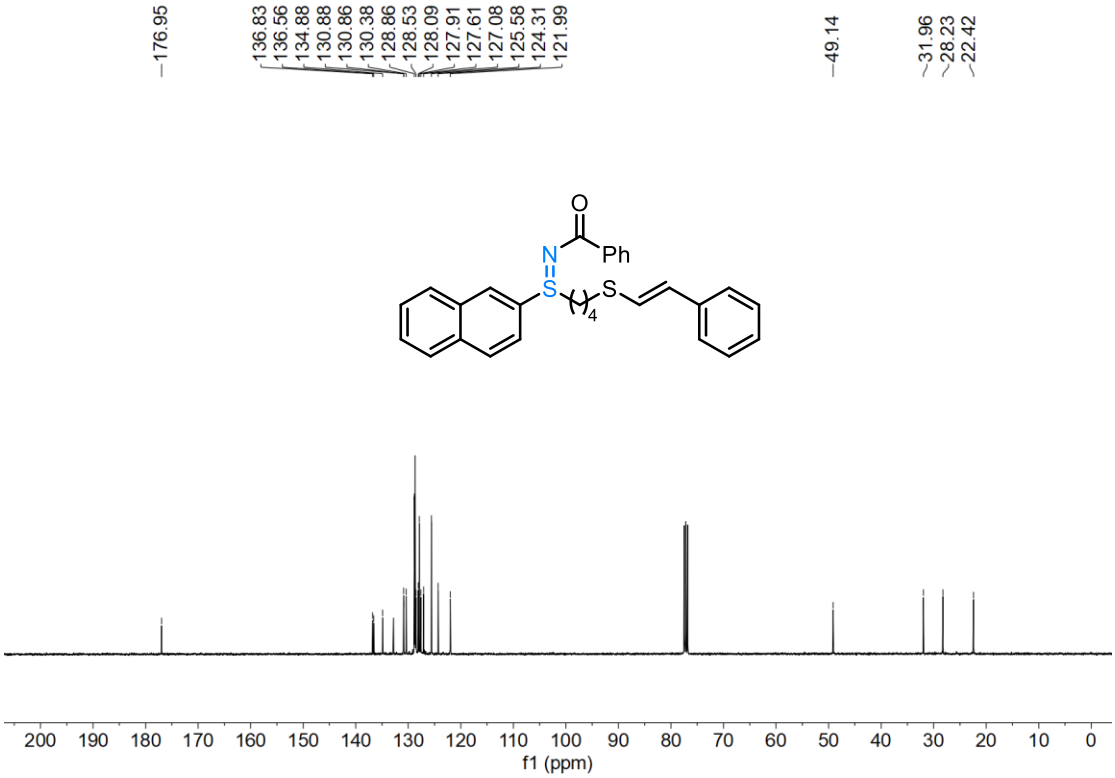
^{13}C NMR spectrum of compound **8** (100 MHz, $CDCl_3$)



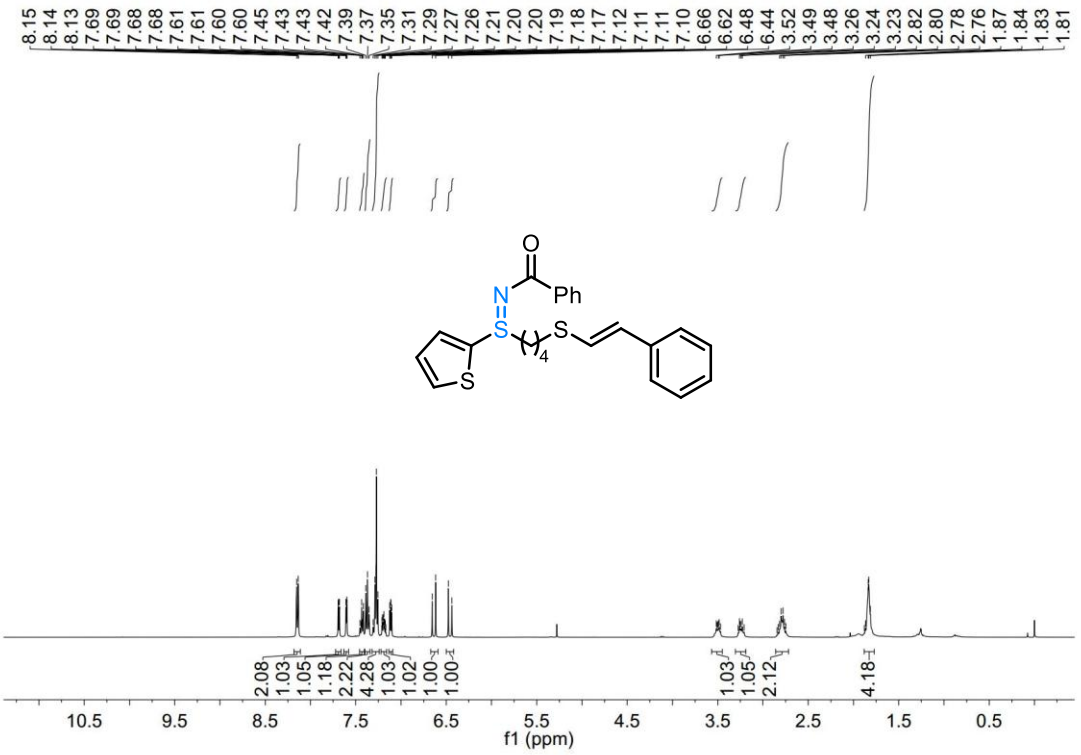
^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$)



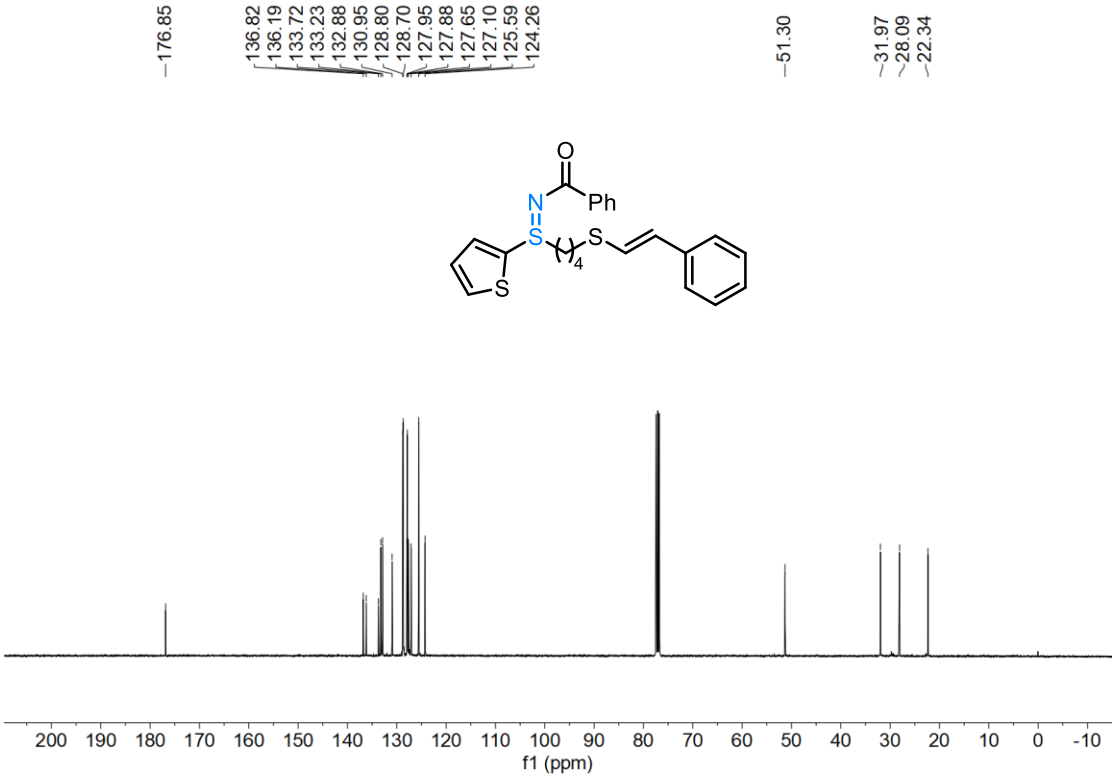
^{13}C NMR spectrum of compound **9** (100 MHz, $CDCl_3$)



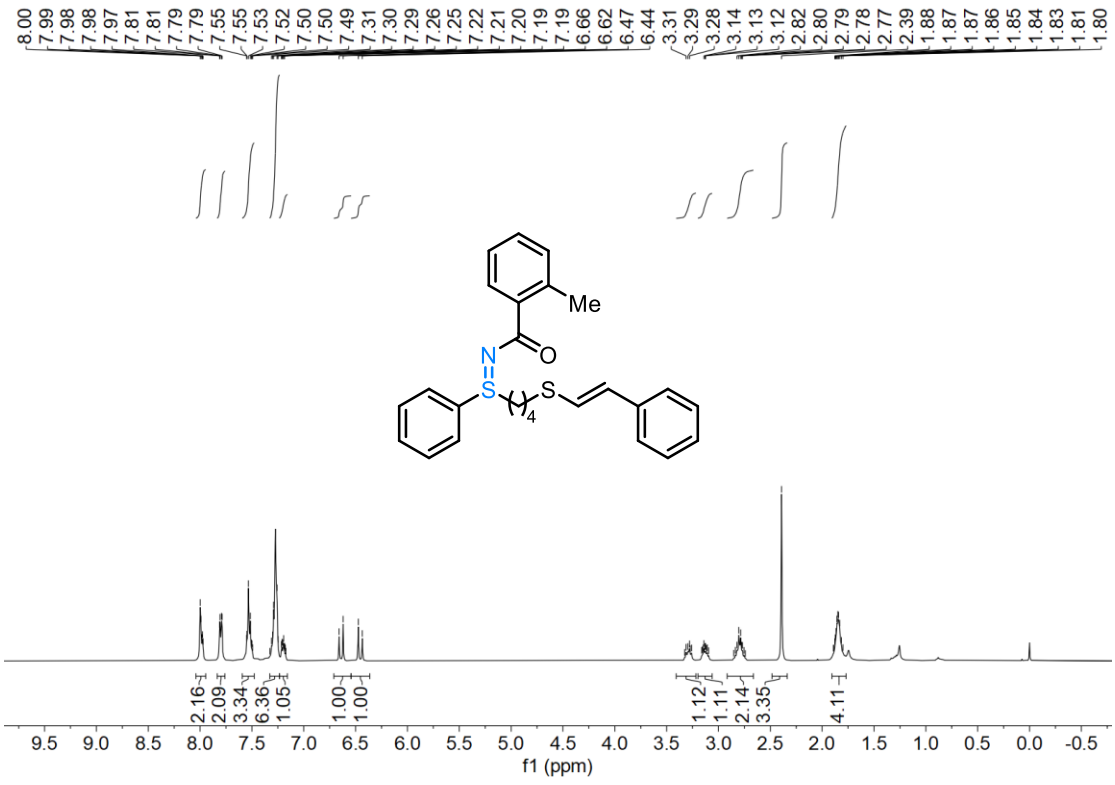
^{1}H NMR spectrum of compound **10** (400 MHz, $CDCl_3$)



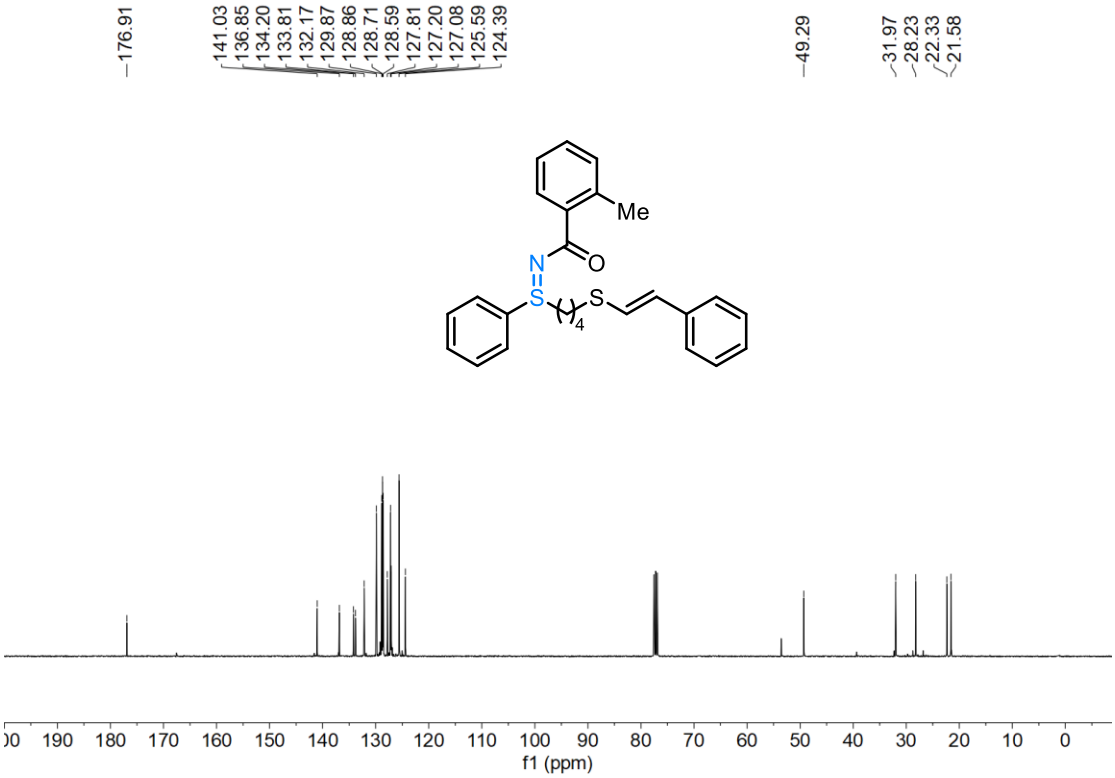
^{13}C NMR spectrum of compound **10** (100 MHz, $CDCl_3$)



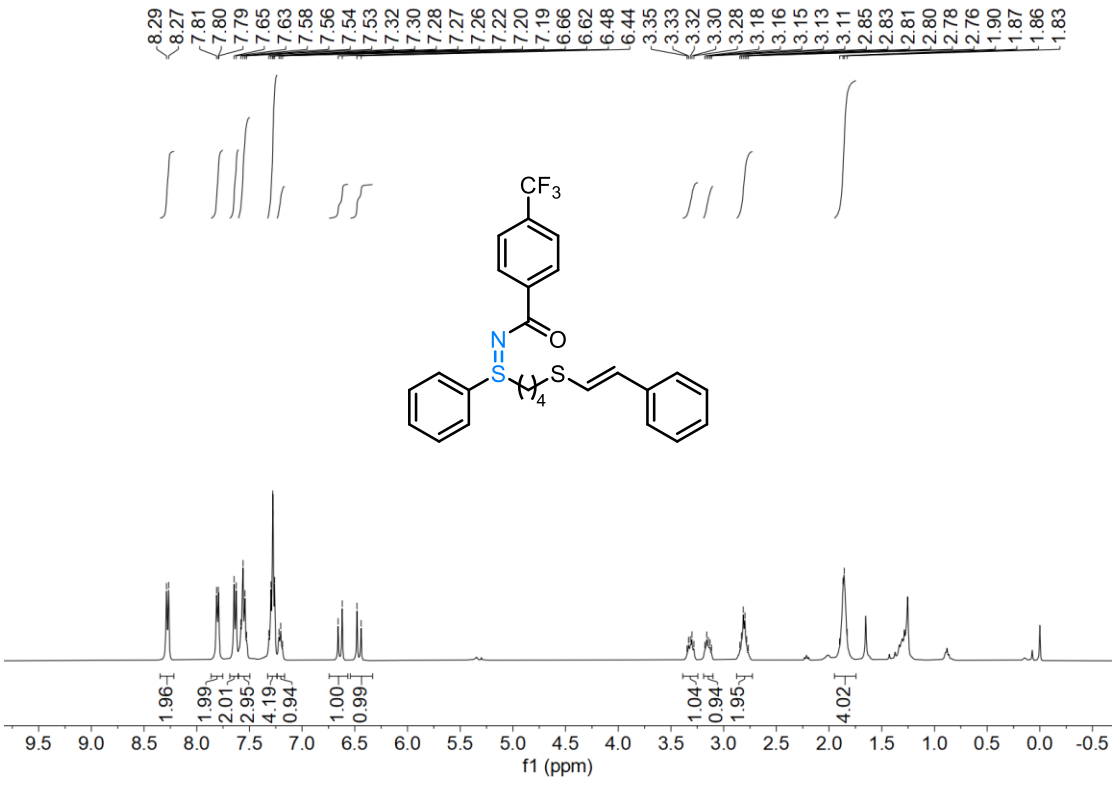
^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$)



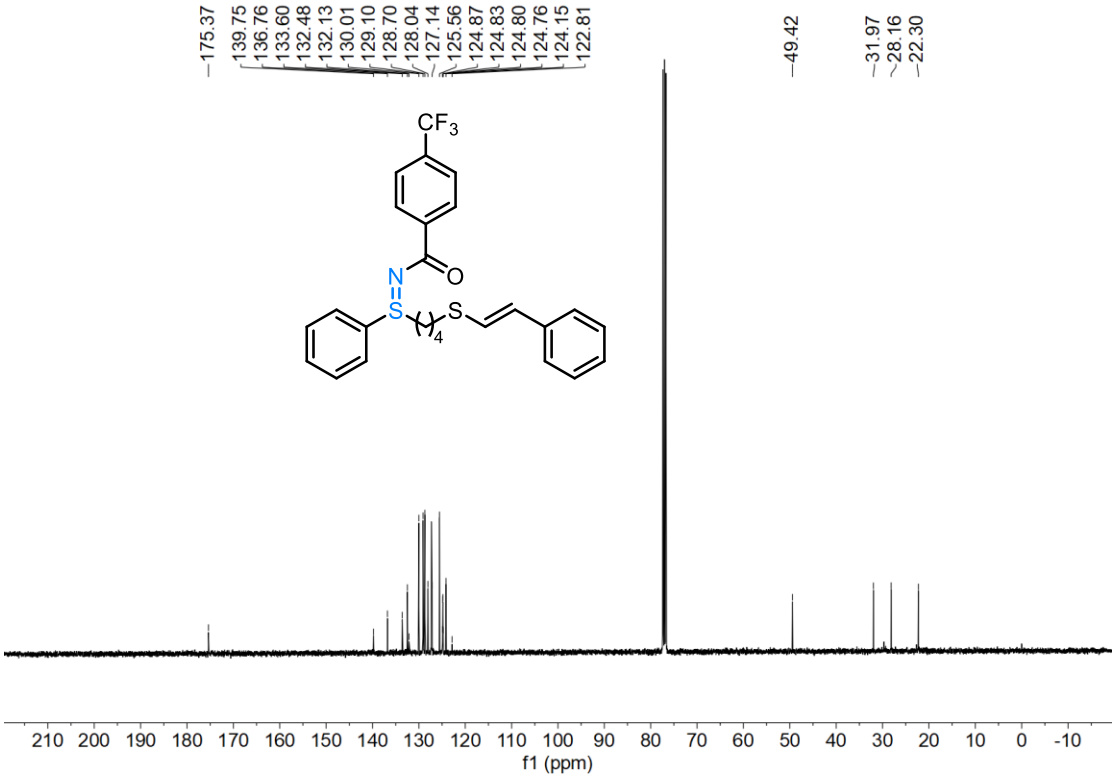
^{13}C NMR spectrum of compound **11** (100 MHz, $CDCl_3$)



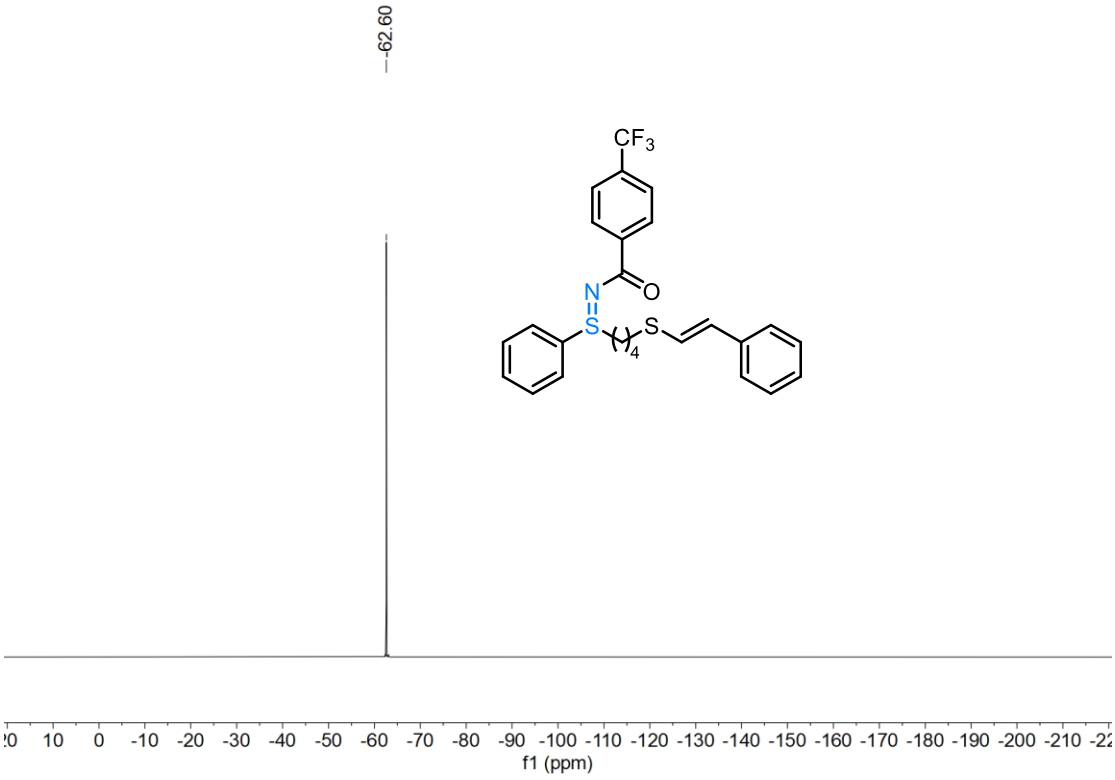
^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$)



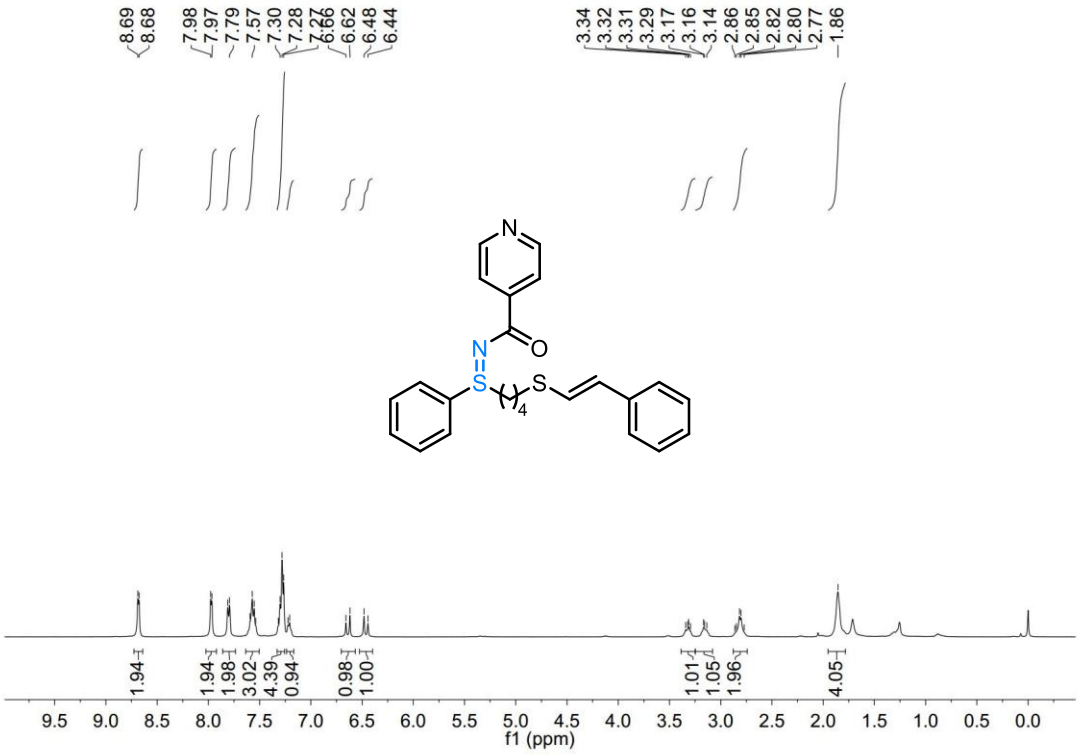
^{13}C NMR spectrum of compound **12** (100 MHz, $CDCl_3$)



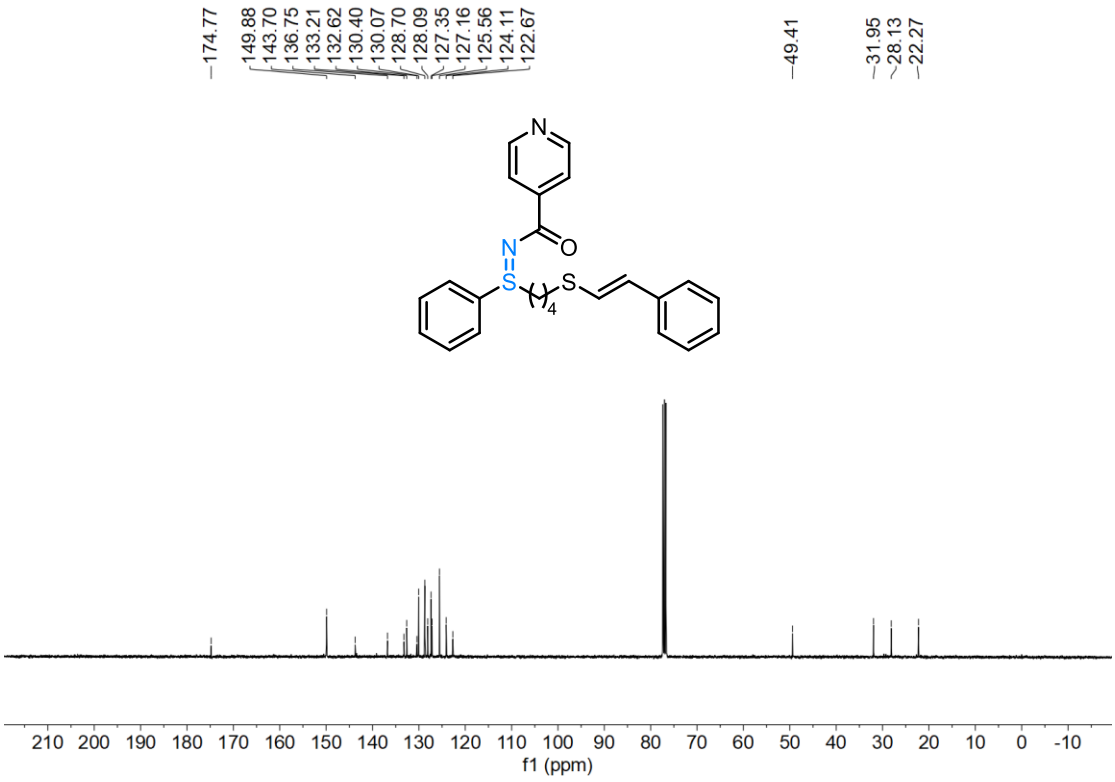
^{19}F NMR spectrum of compound **12** (376 MHz, $CDCl_3$)



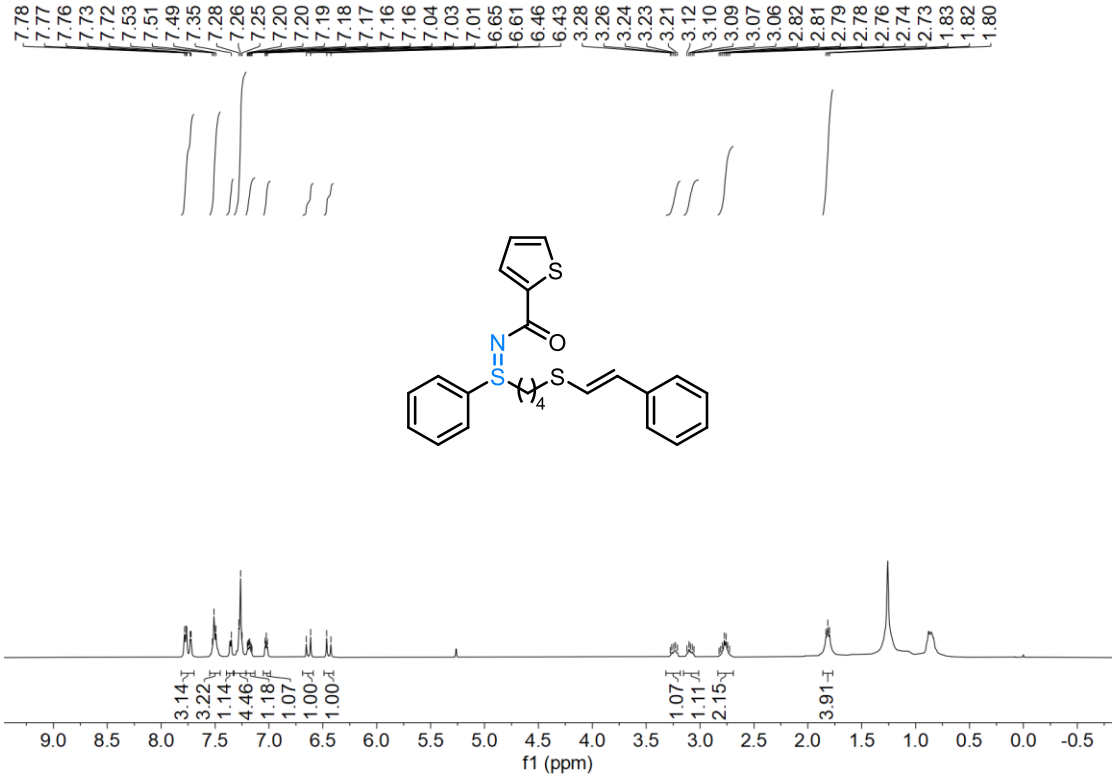
^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$)



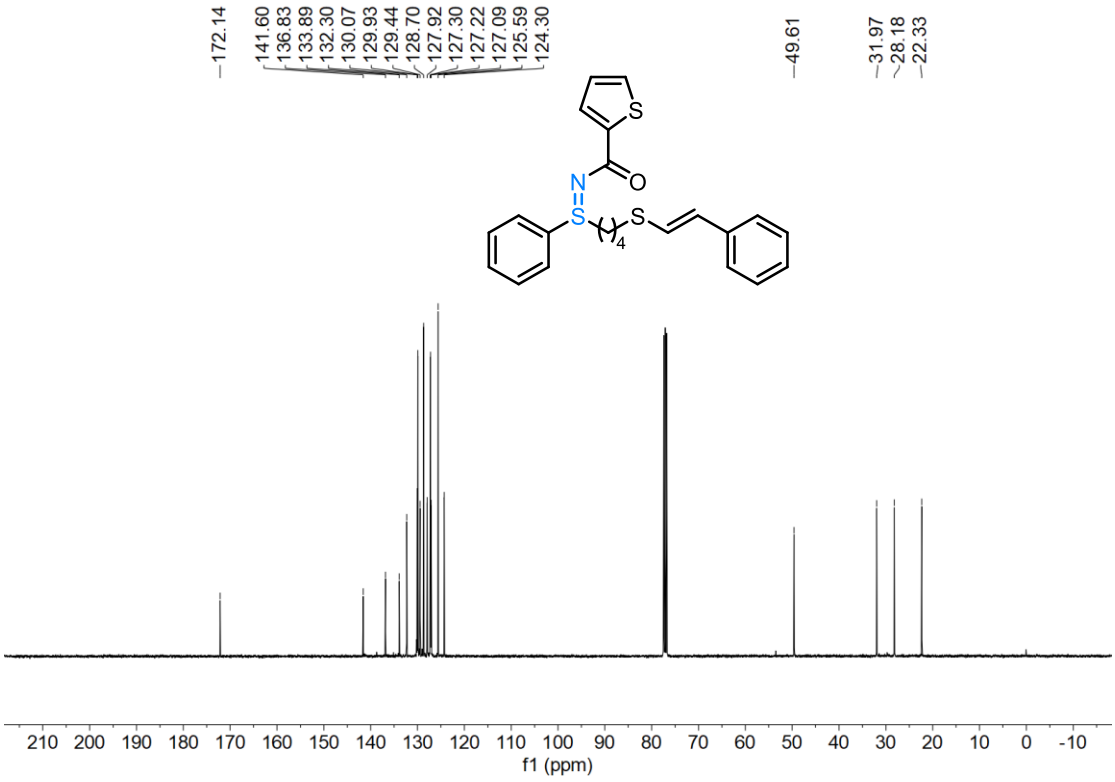
^{13}C NMR spectrum of compound **13** (100 MHz, $CDCl_3$)



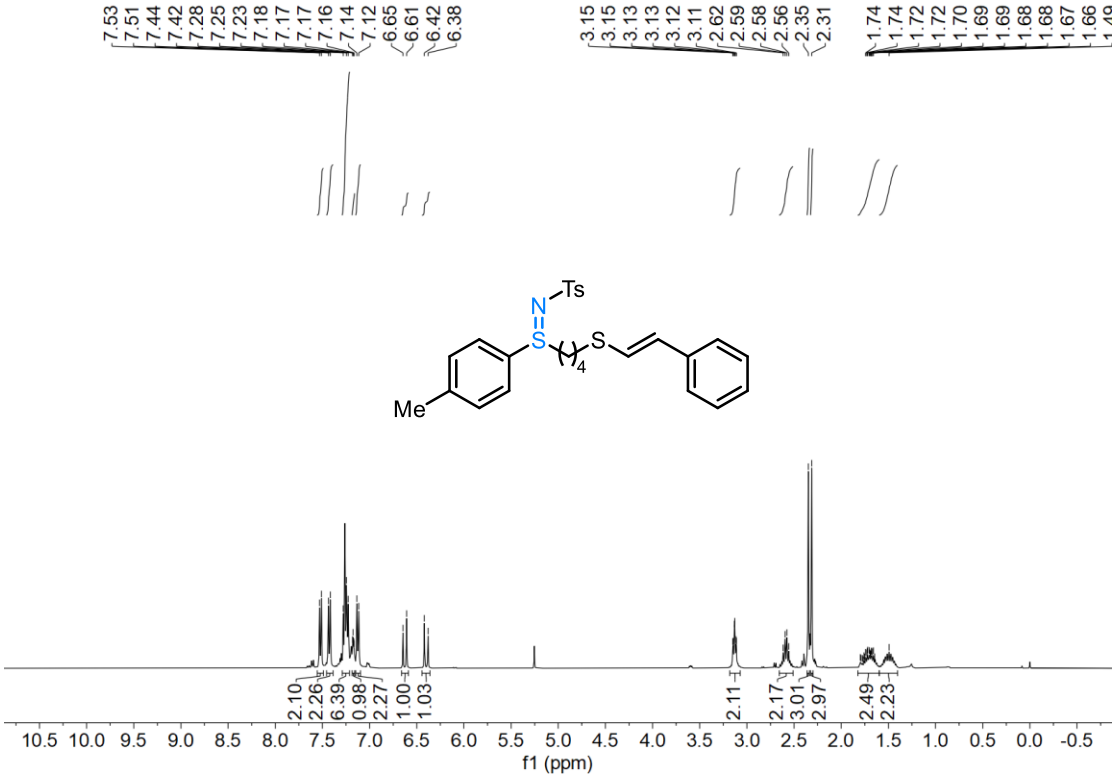
^{1}H NMR spectrum of compound **14** (400 MHz, $CDCl_3$)



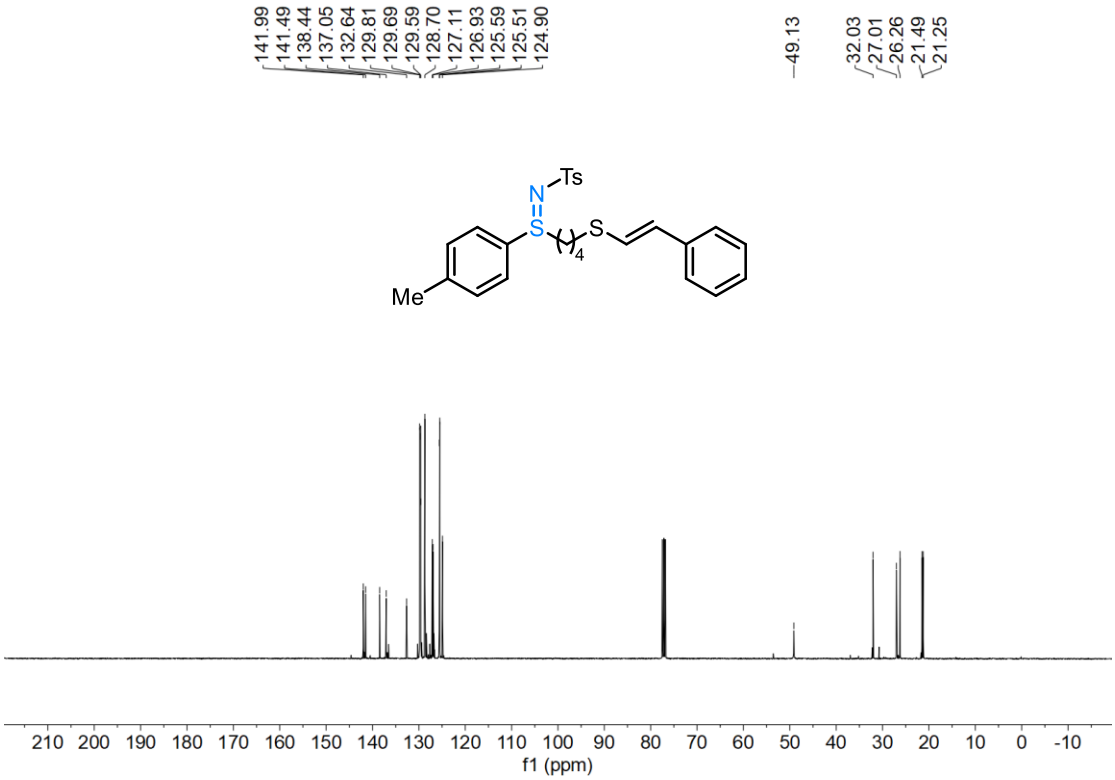
^{13}C NMR spectrum of compound **14** (100 MHz, $CDCl_3$)



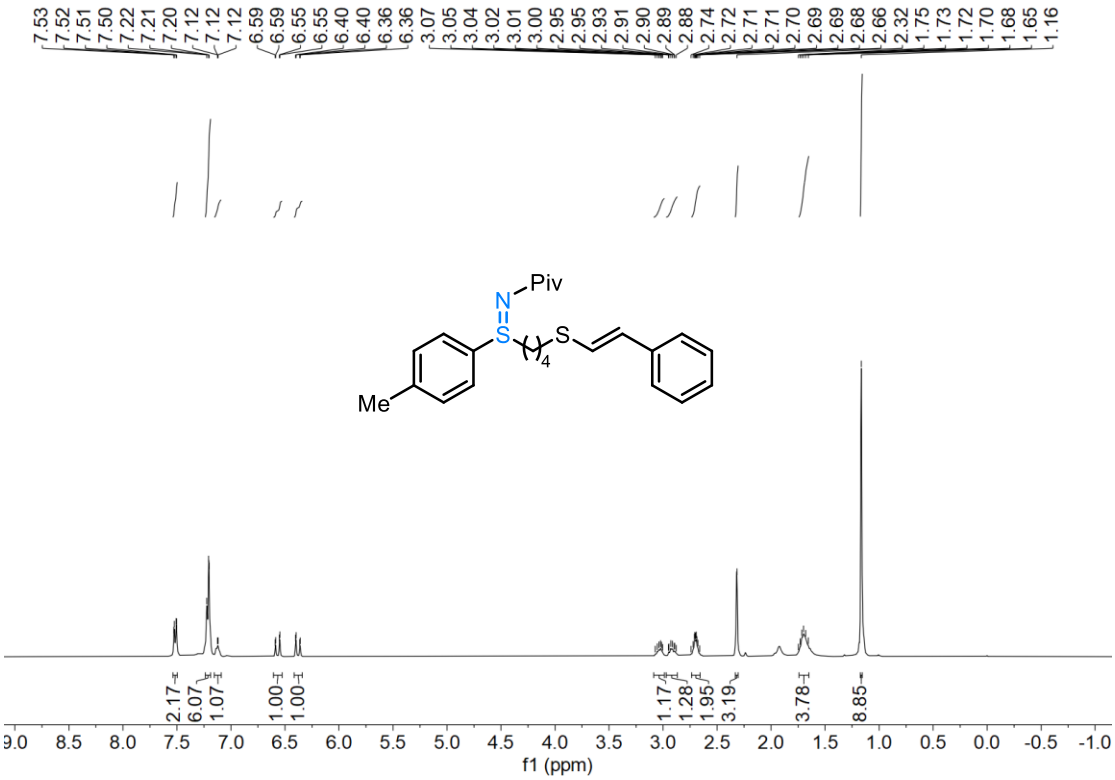
^{1}H NMR spectrum of compound **15** (400 MHz, $CDCl_3$)



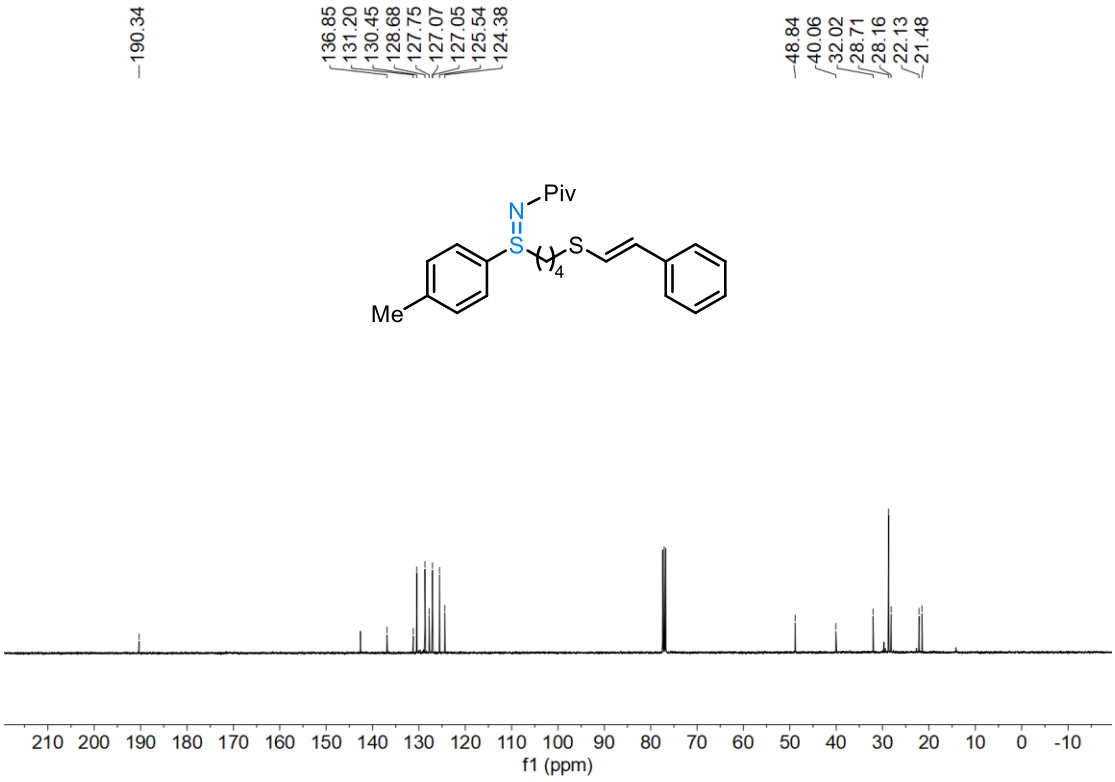
^{13}C NMR spectrum of compound **15** (100 MHz, $CDCl_3$)



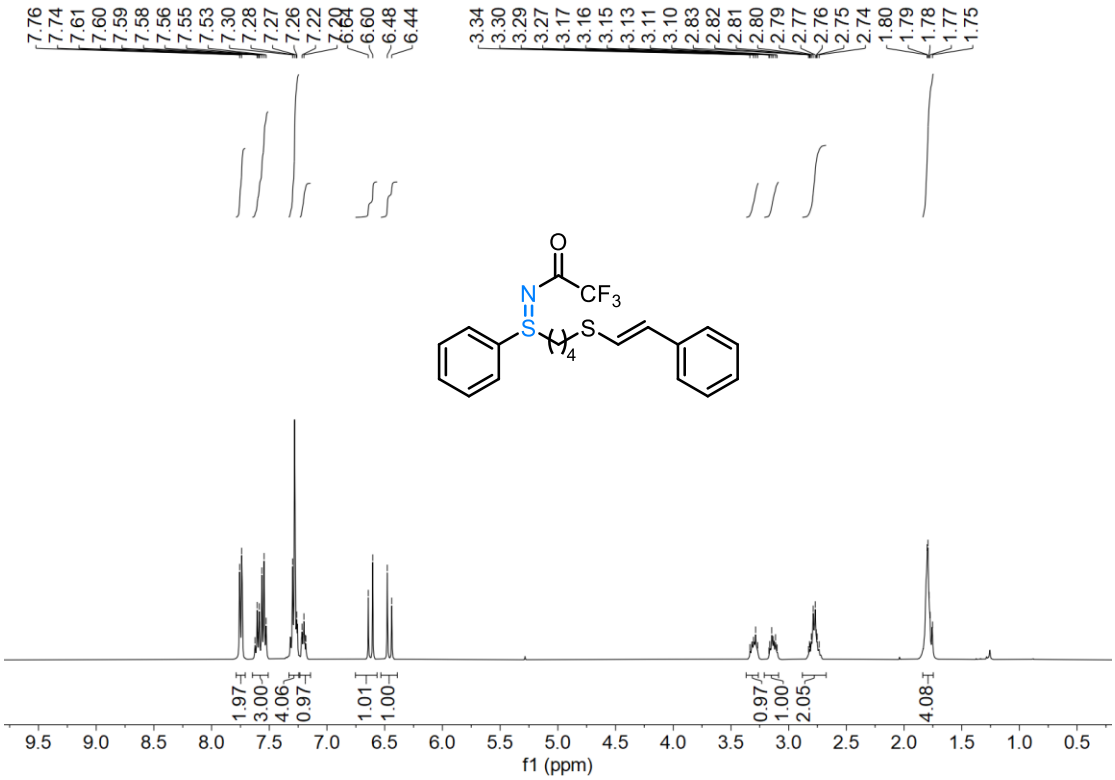
^{1}H NMR spectrum of compound **16** (400 MHz, $CDCl_3$)



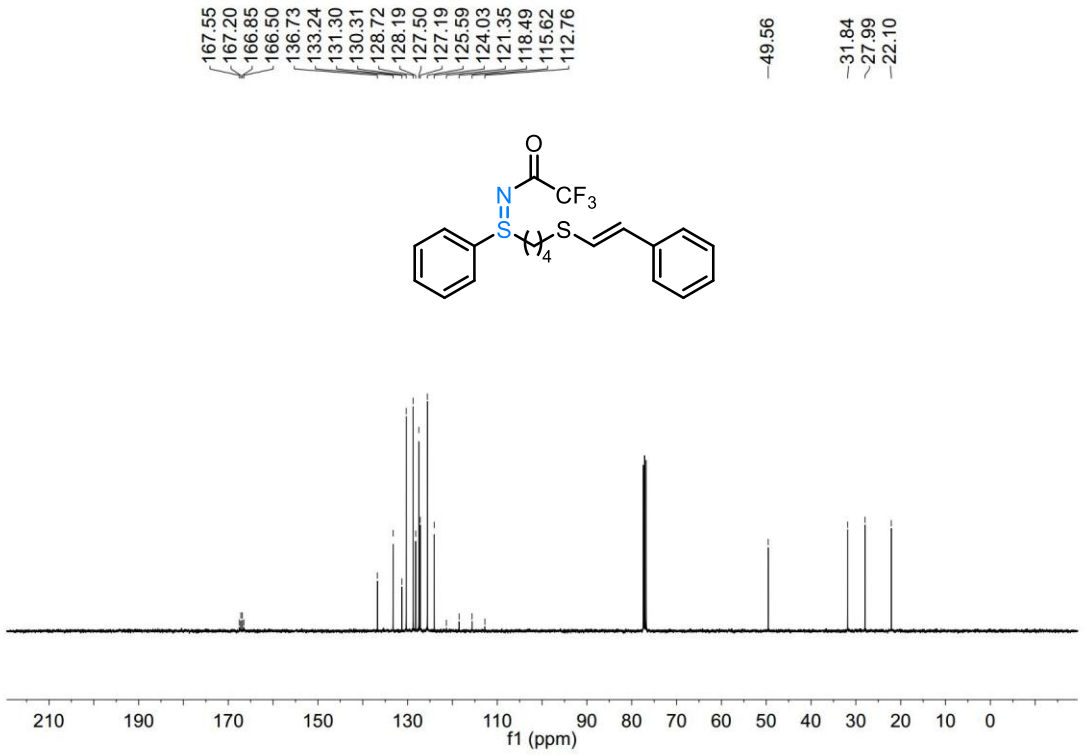
^{13}C NMR spectrum of compound **16** (100 MHz, $CDCl_3$)



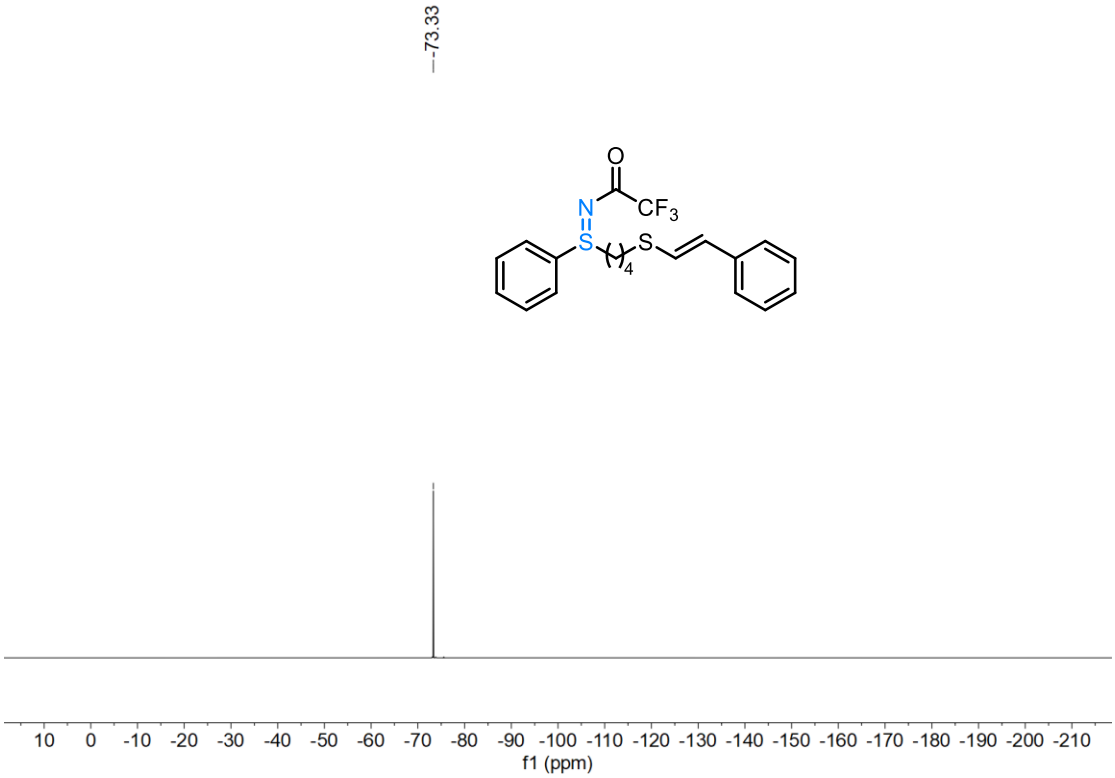
^{1}H NMR spectrum of compound **17** (400 MHz, $CDCl_3$)



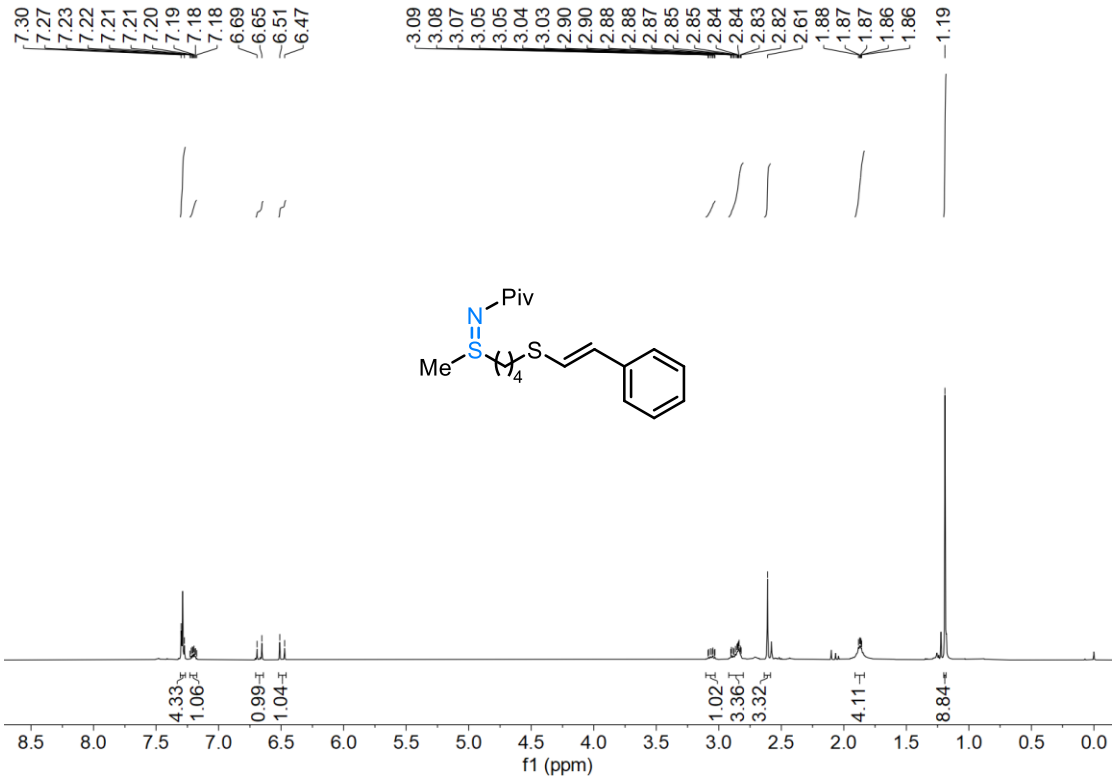
^{13}C NMR spectrum of compound **17** (100 MHz, $CDCl_3$)



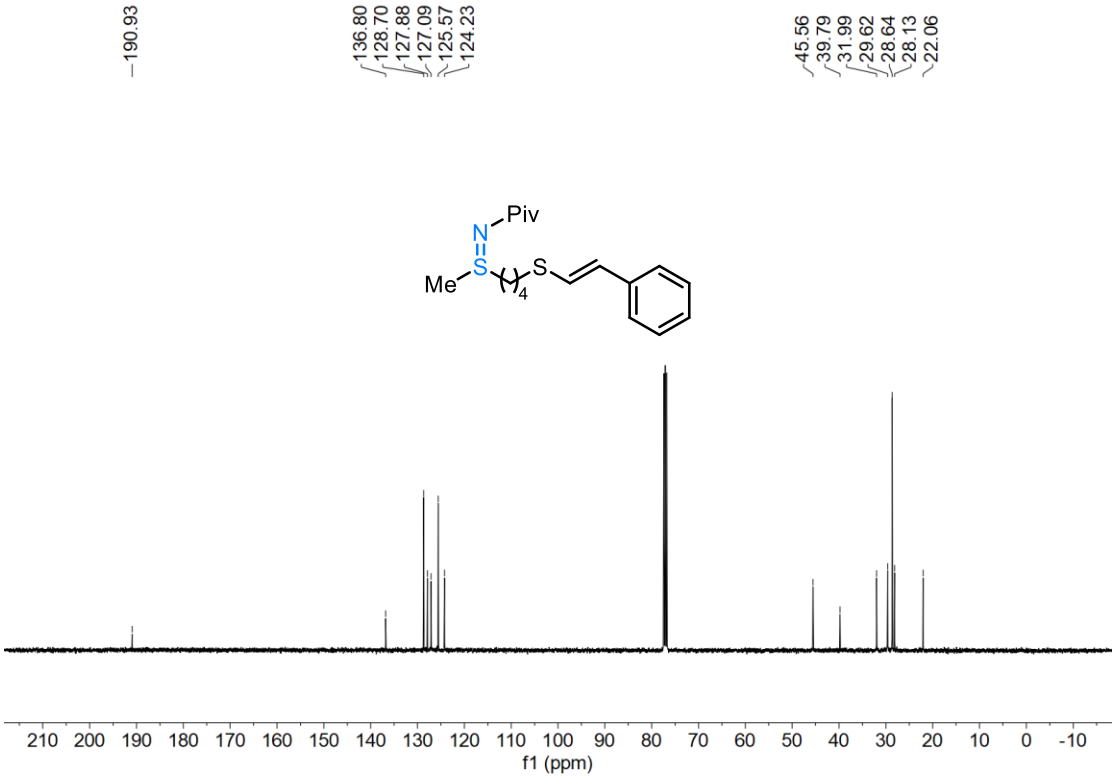
^{19}F NMR spectrum of compound **17** (376 MHz, $CDCl_3$)



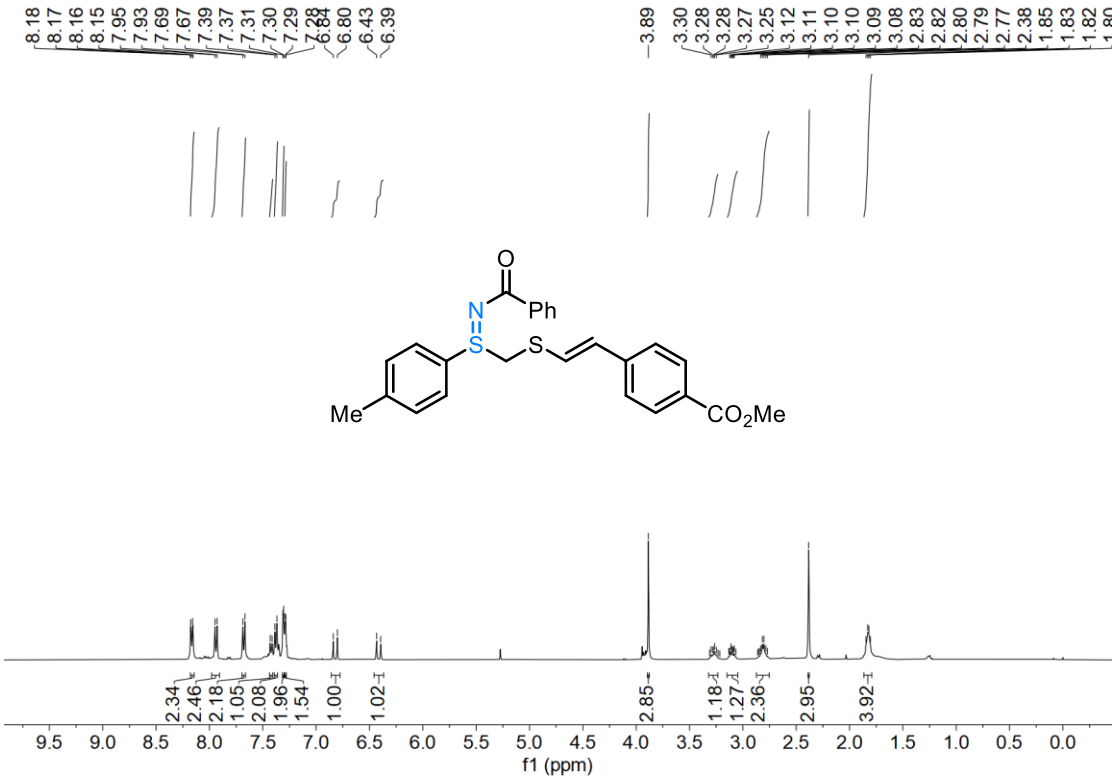
^{1}H NMR spectrum of compound **18** (400 MHz, $CDCl_3$)



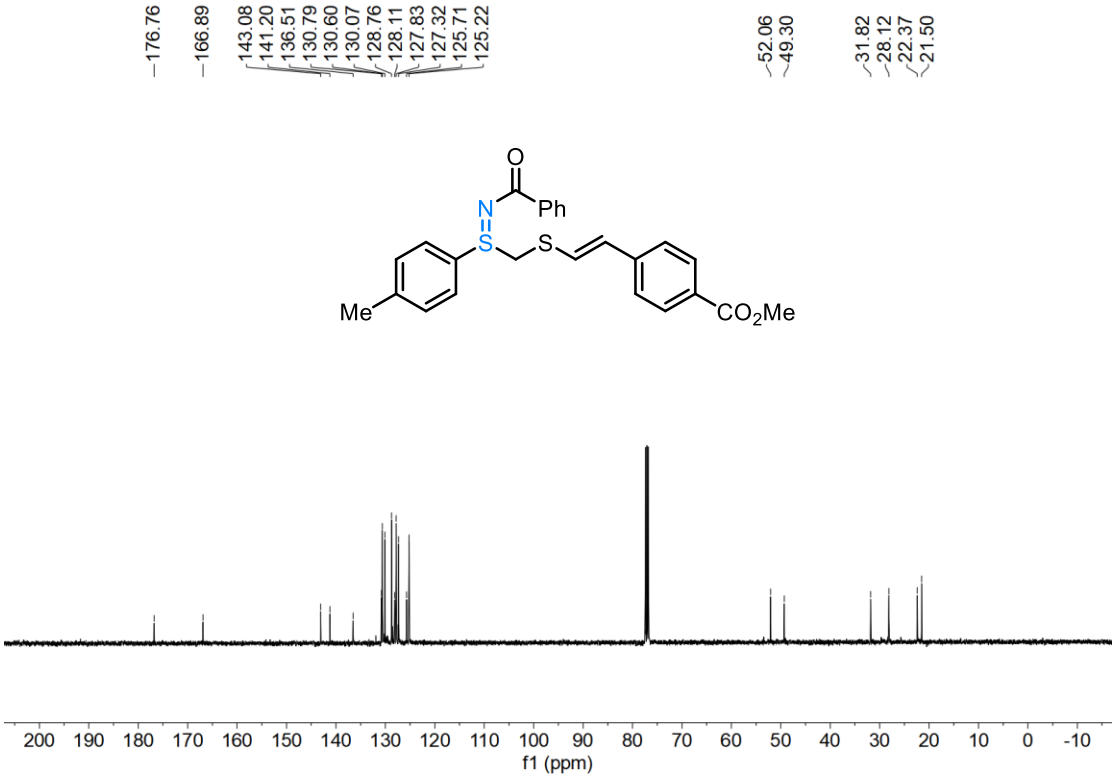
^{13}C NMR spectrum of compound **18** (100 MHz, $CDCl_3$)



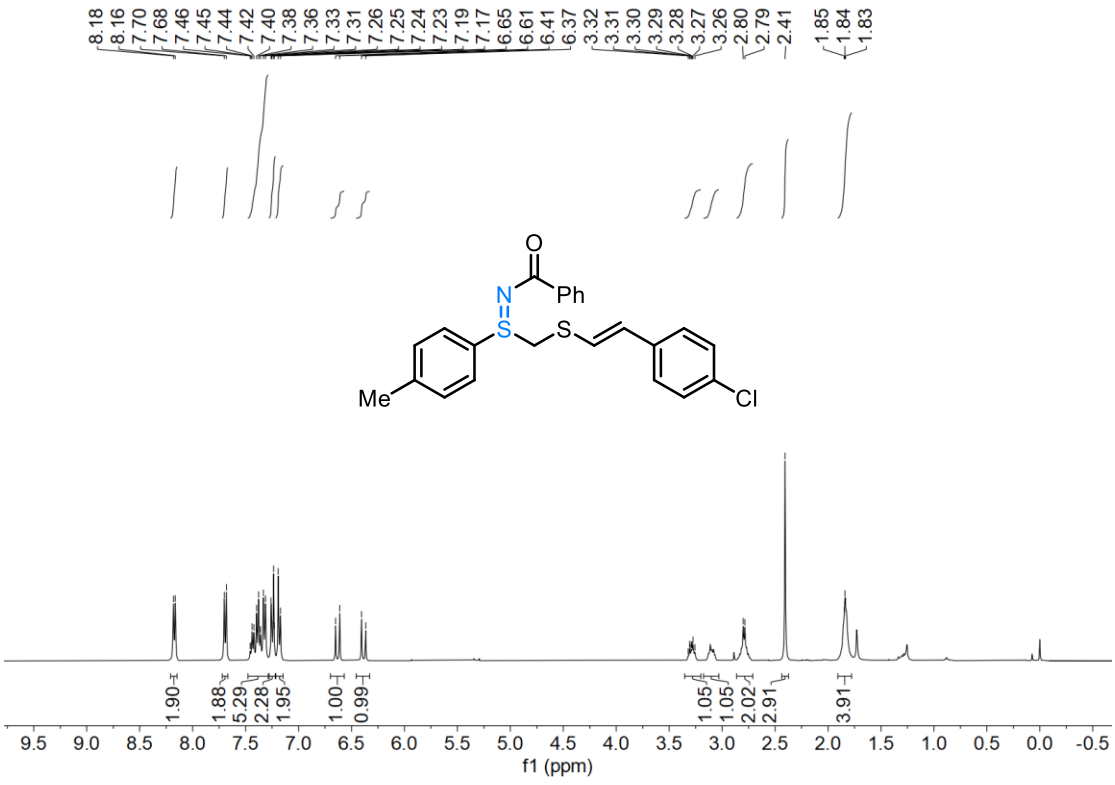
^{1}H NMR spectrum of compound **19** (400 MHz, $CDCl_3$)



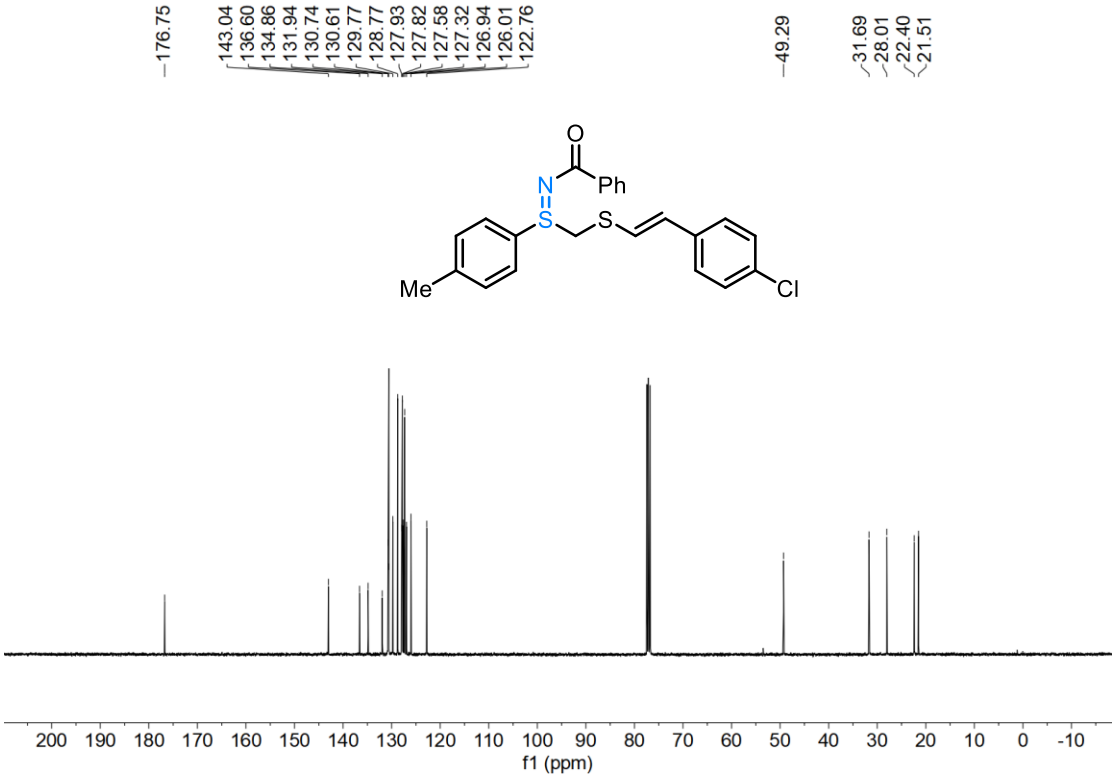
^{13}C NMR spectrum of compound **19** (100 MHz, $CDCl_3$)



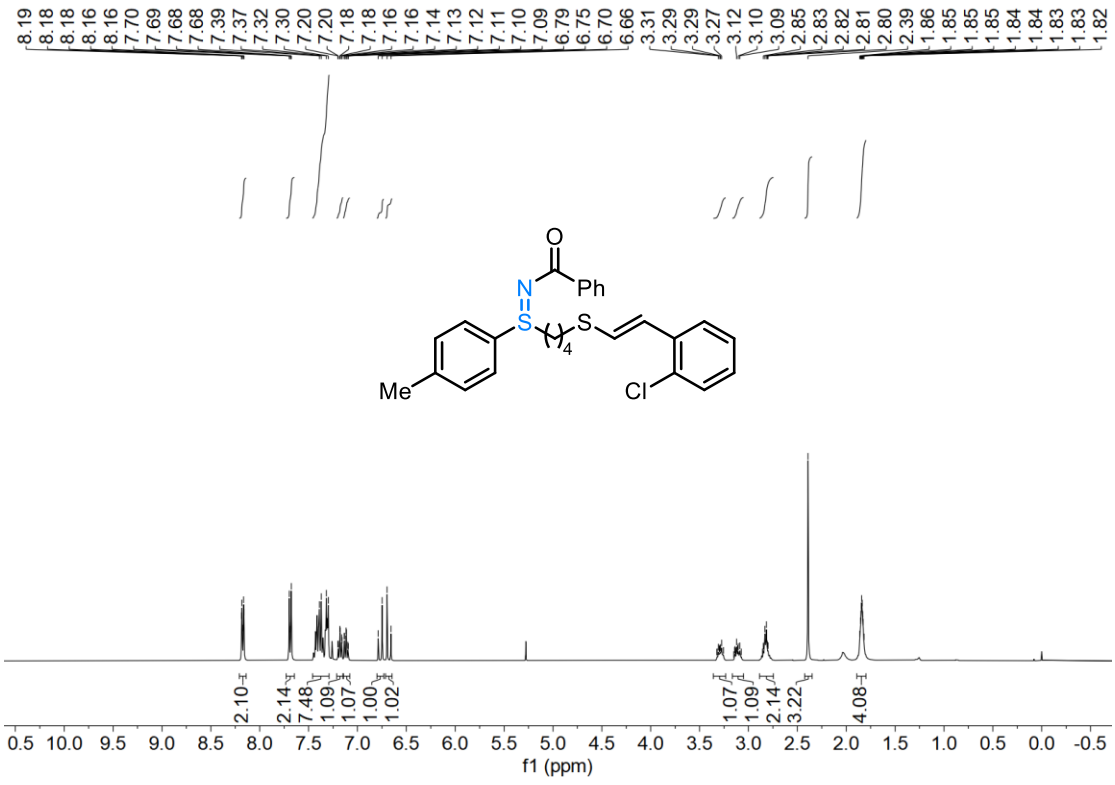
^{1}H NMR spectrum of compound **20** (400 MHz, $CDCl_3$)



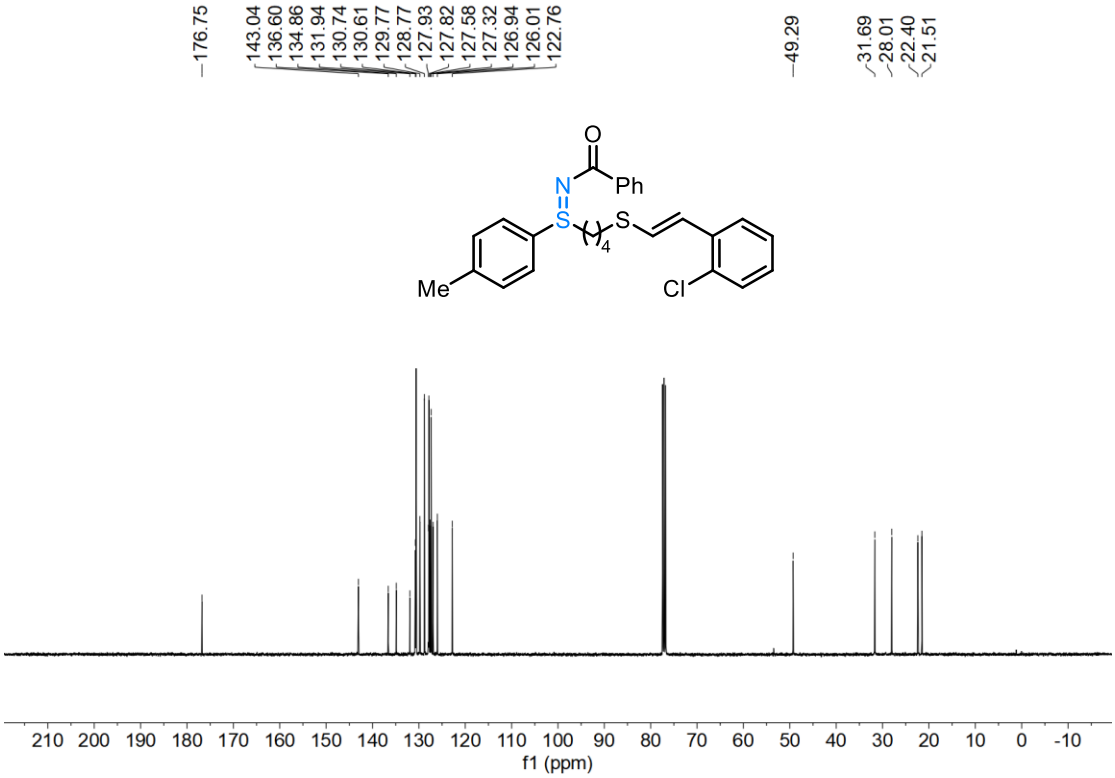
^{13}C NMR spectrum of compound **20** (100 MHz, $CDCl_3$)



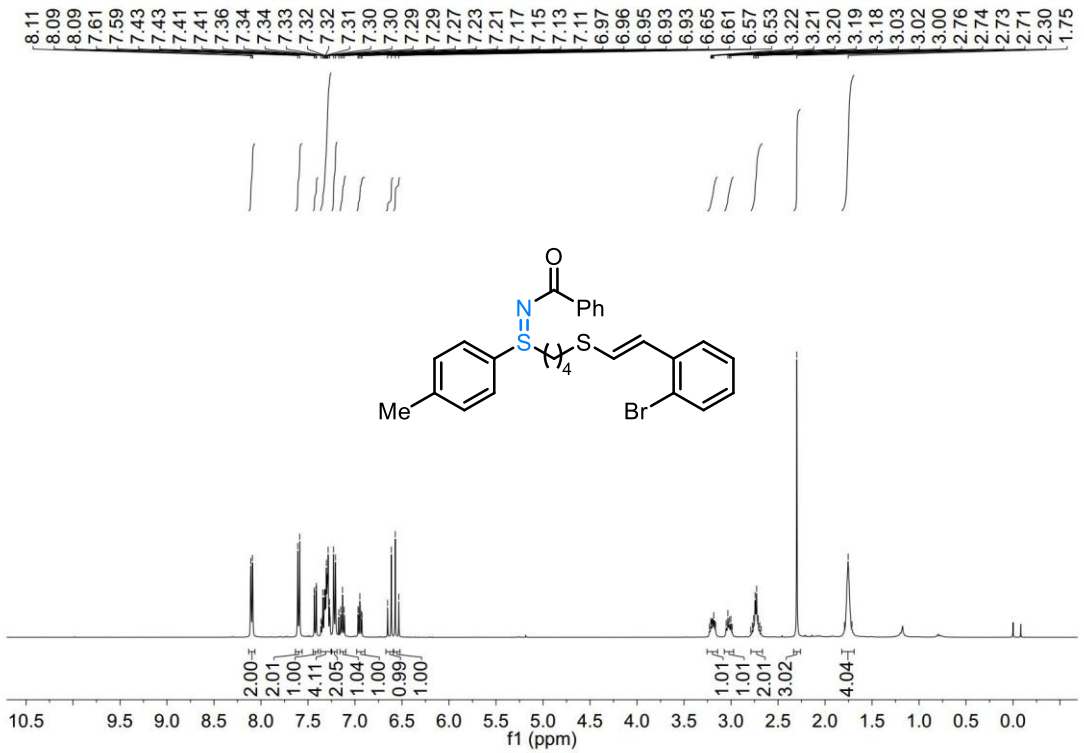
^{1}H NMR spectrum of compound **21** (400 MHz, $CDCl_3$)



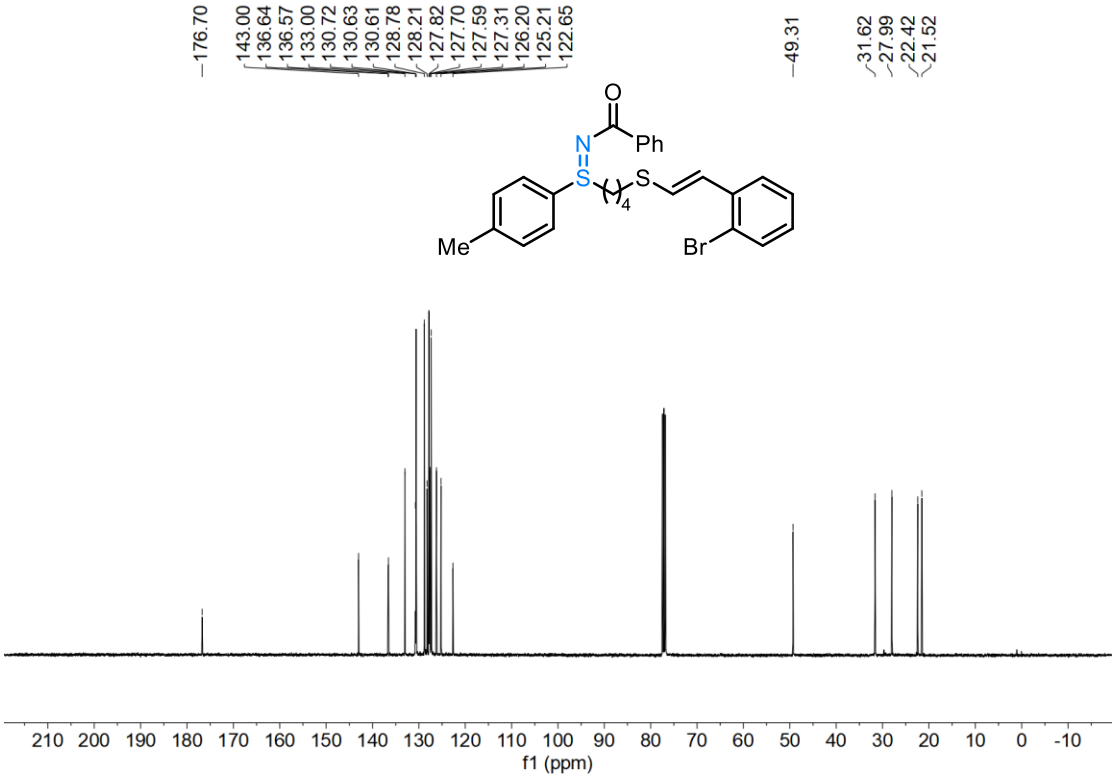
^{13}C NMR spectrum of compound **21** (100 MHz, $CDCl_3$)



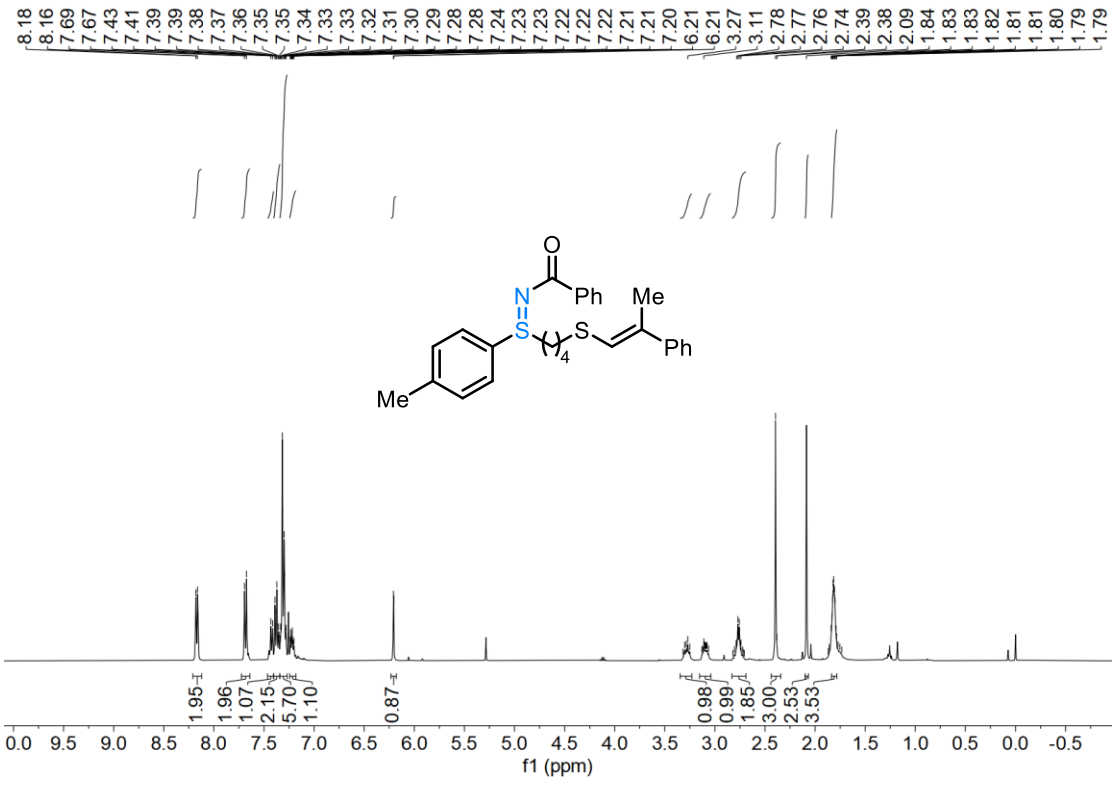
^{1}H NMR spectrum of compound **22** (400 MHz, $CDCl_3$)



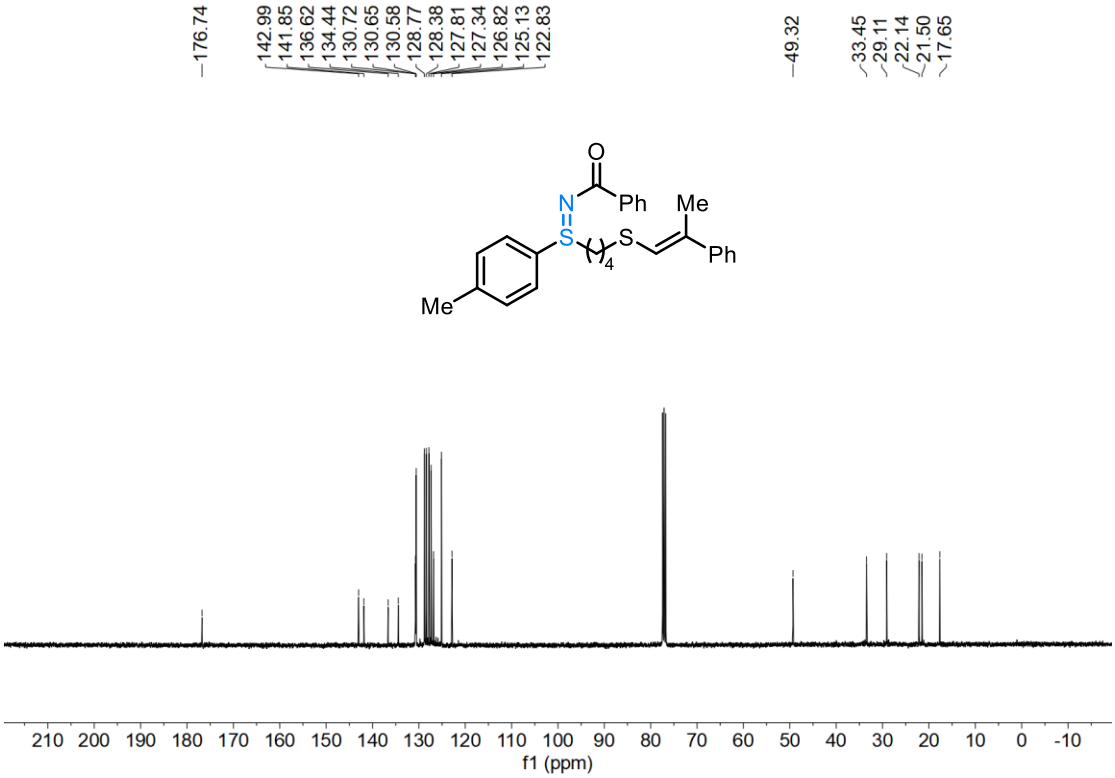
^{13}C NMR spectrum of compound **22** (100 MHz, $CDCl_3$)



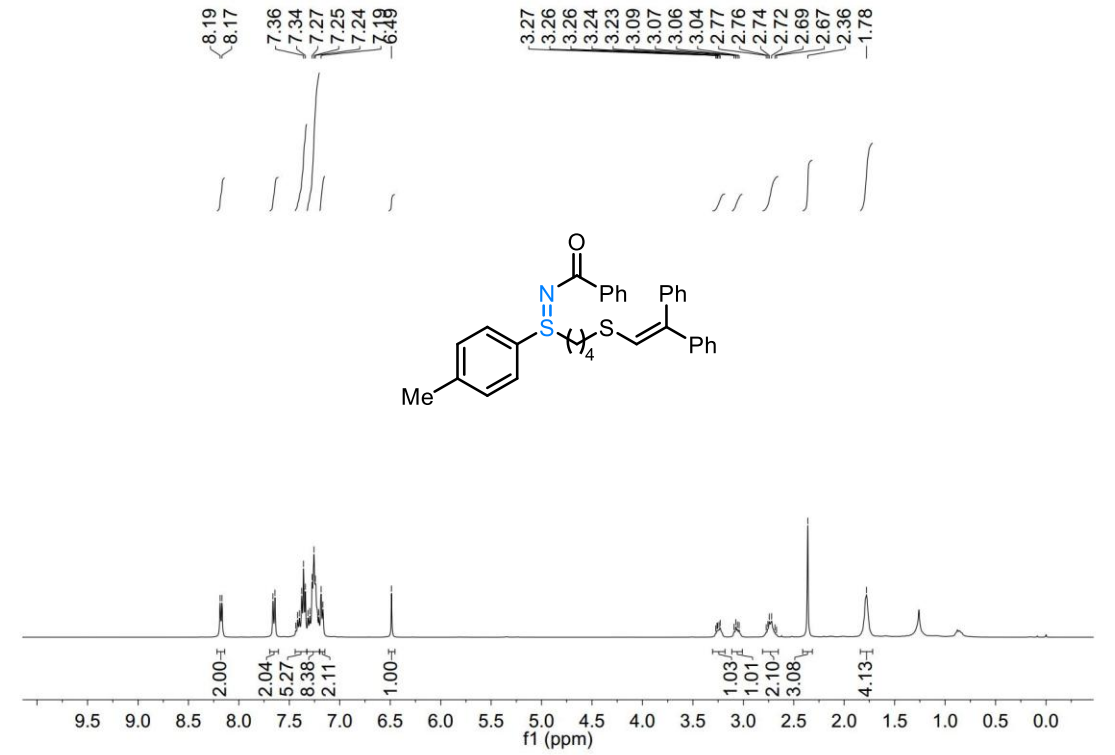
^{1}H NMR spectrum of compound **23** (400 MHz, $CDCl_3$)



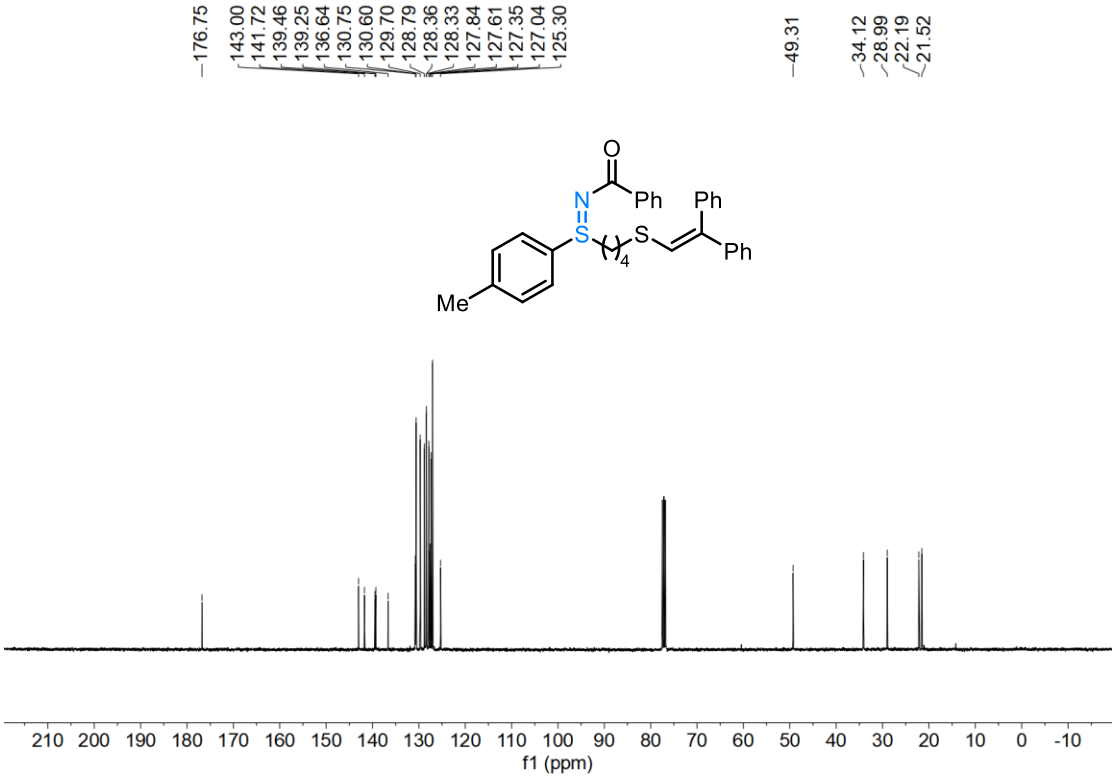
^{13}C NMR spectrum of compound **23** (100 MHz, $CDCl_3$)



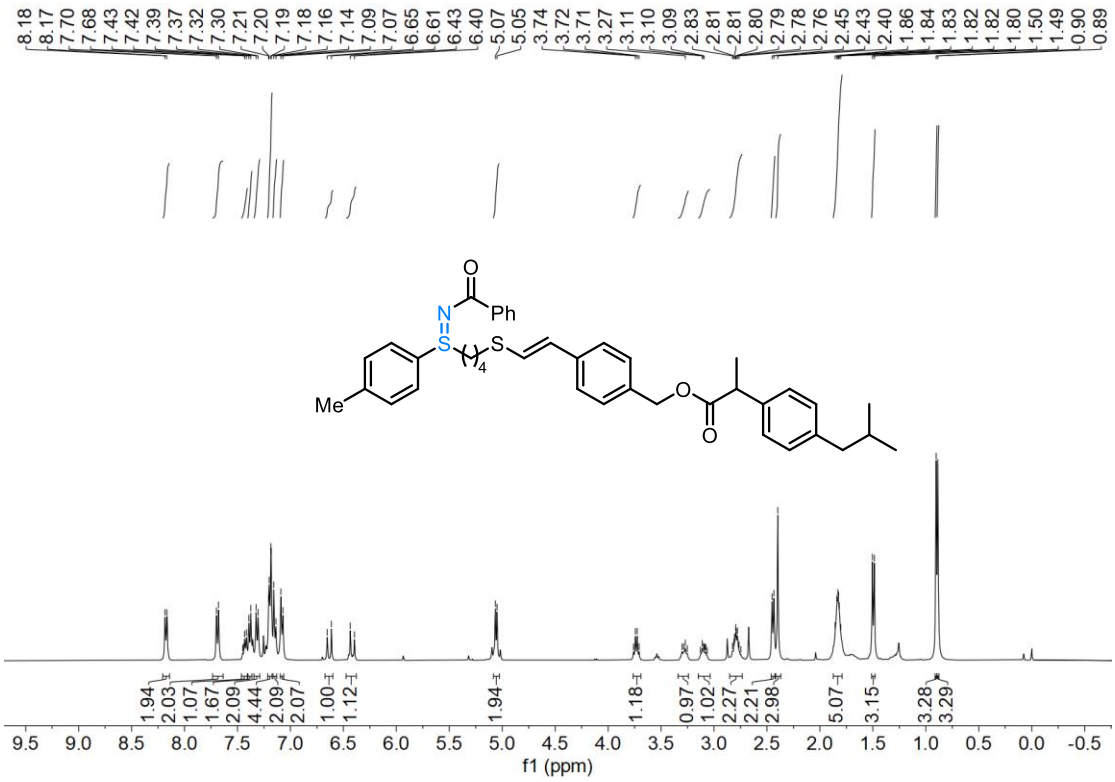
^{1}H NMR spectrum of compound **24** (400 MHz, $CDCl_3$)



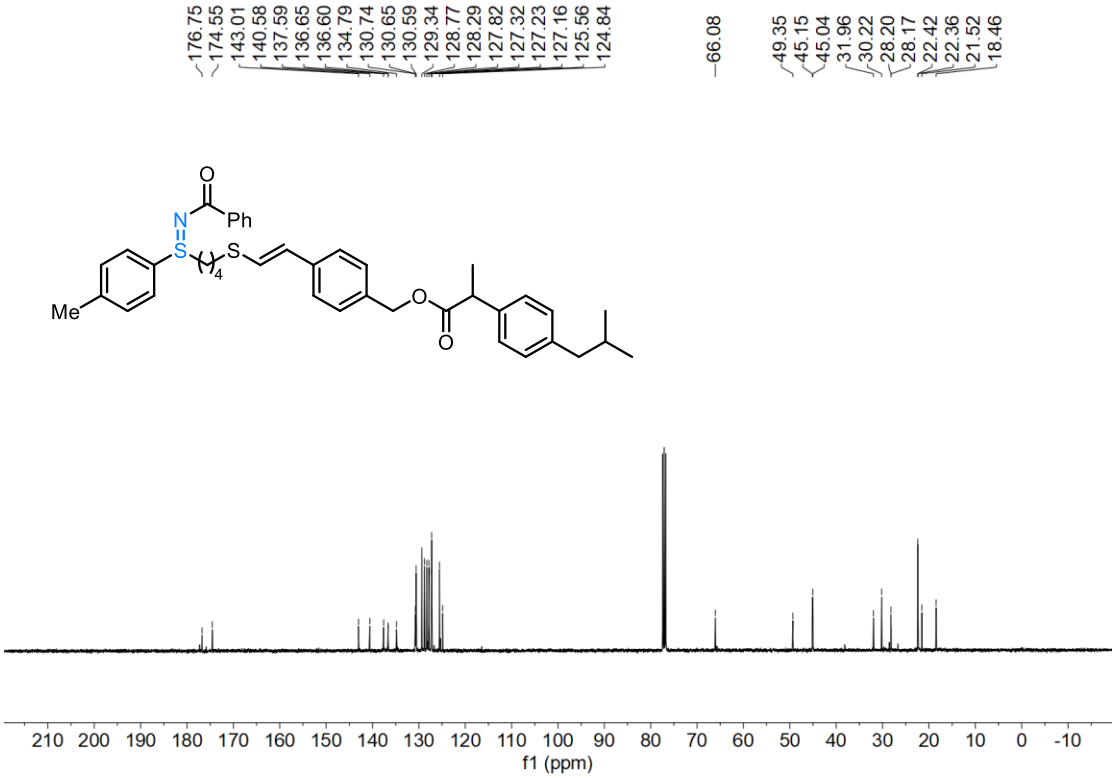
^{13}C NMR spectrum of compound **24** (100 MHz, $CDCl_3$)



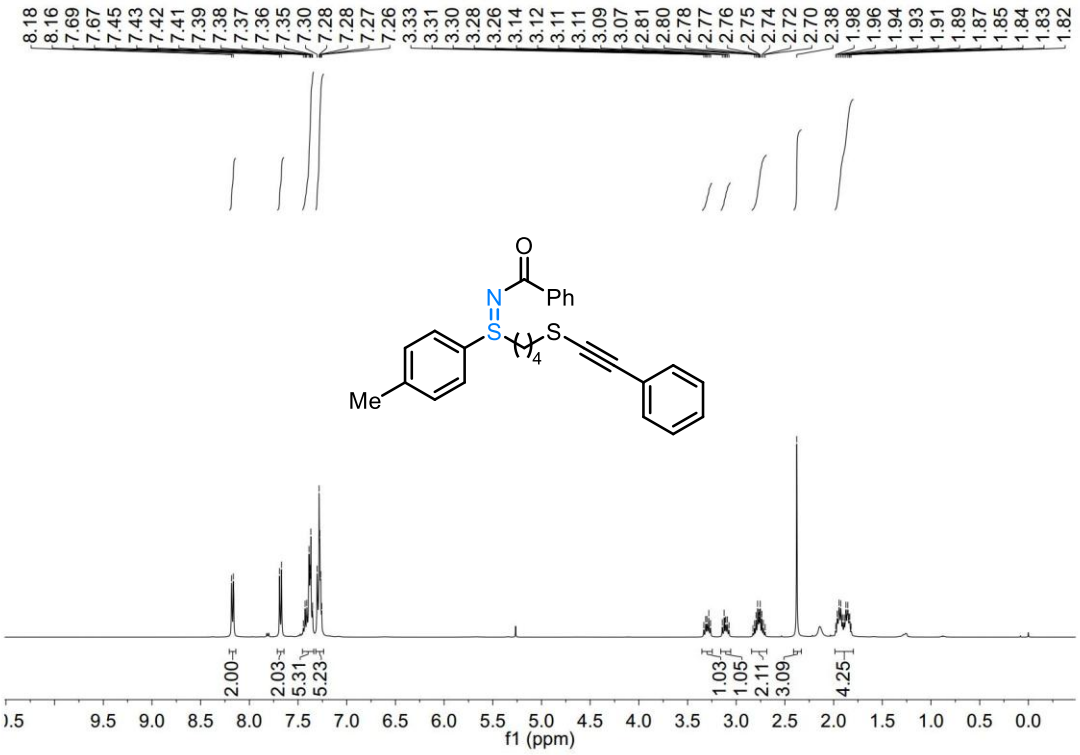
^{1}H NMR spectrum of compound **25** (400 MHz, $CDCl_3$)



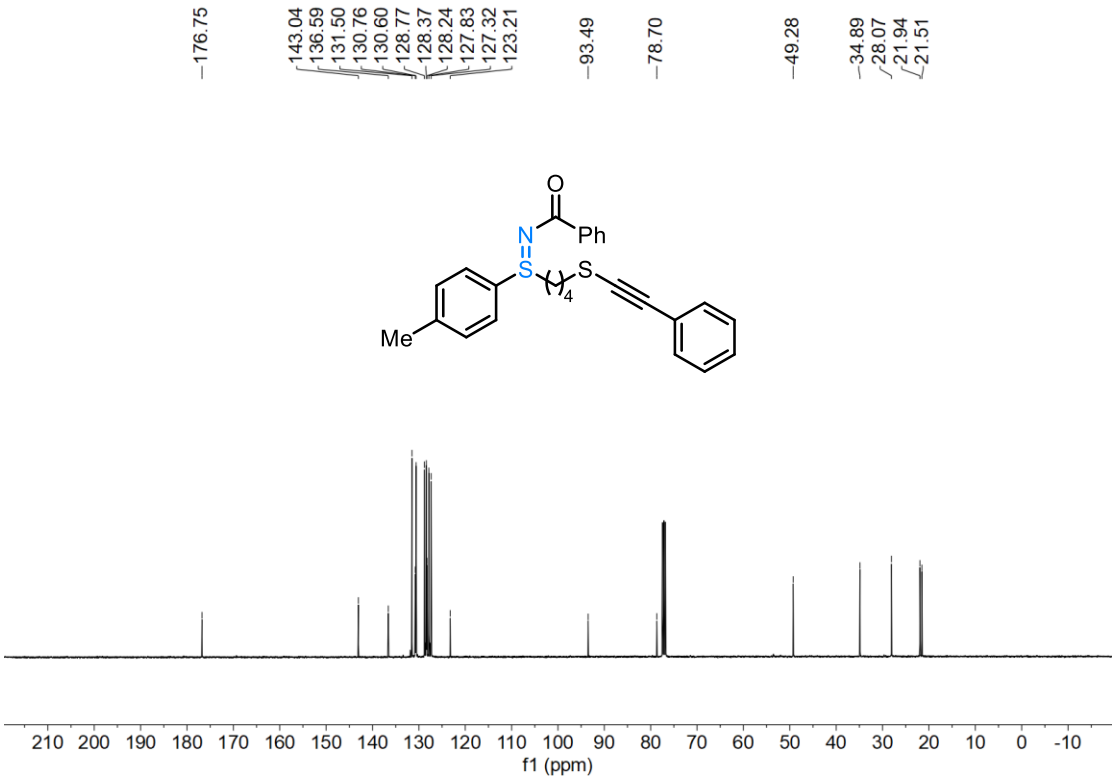
^{13}C NMR spectrum of compound **25** (100 MHz, $CDCl_3$)



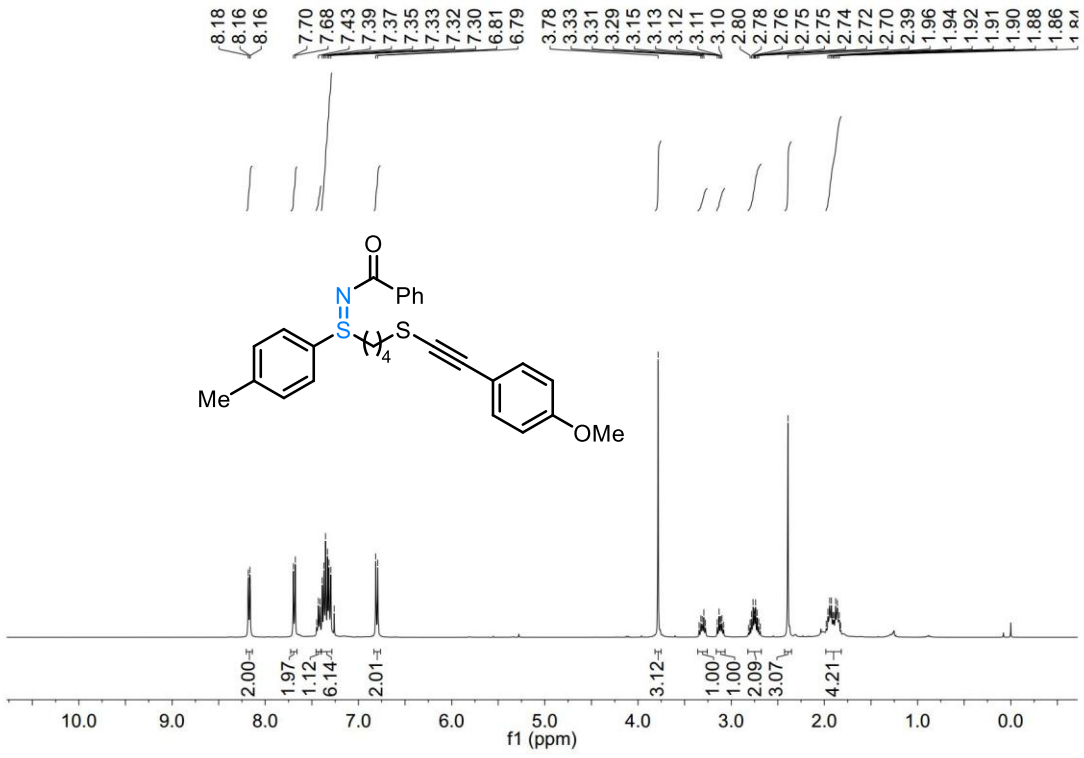
^{1}H NMR spectrum of compound **27** (400 MHz, $CDCl_3$)



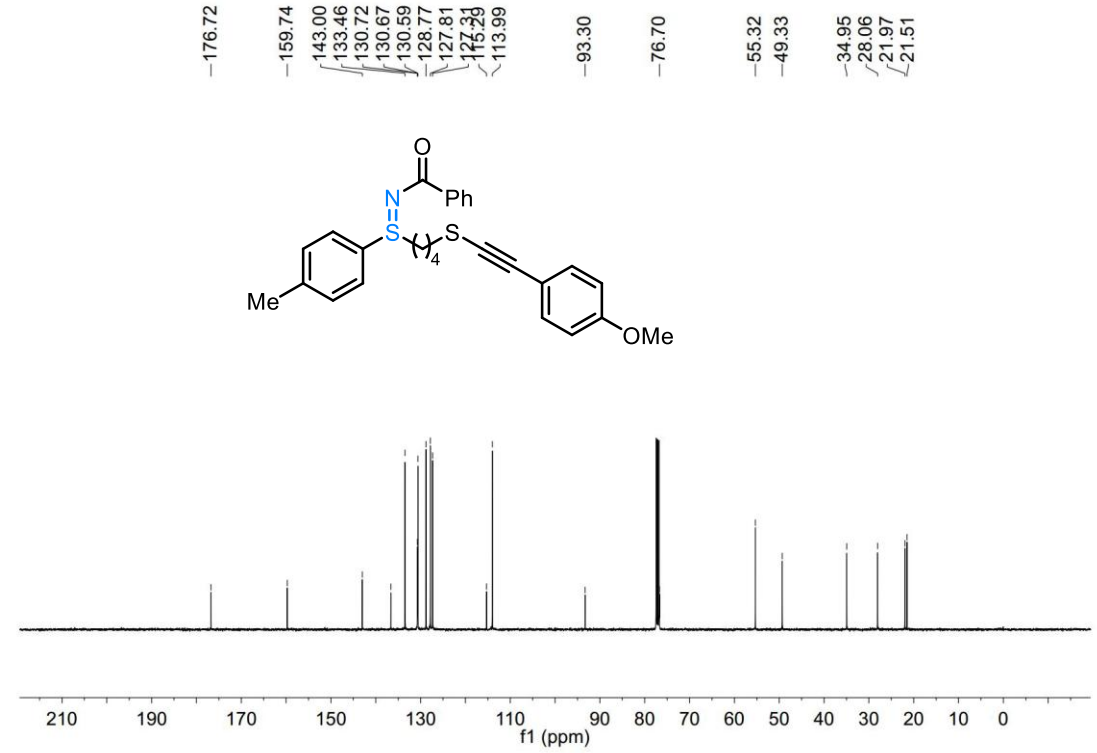
^{13}C NMR spectrum of compound **27** (100 MHz, $CDCl_3$)



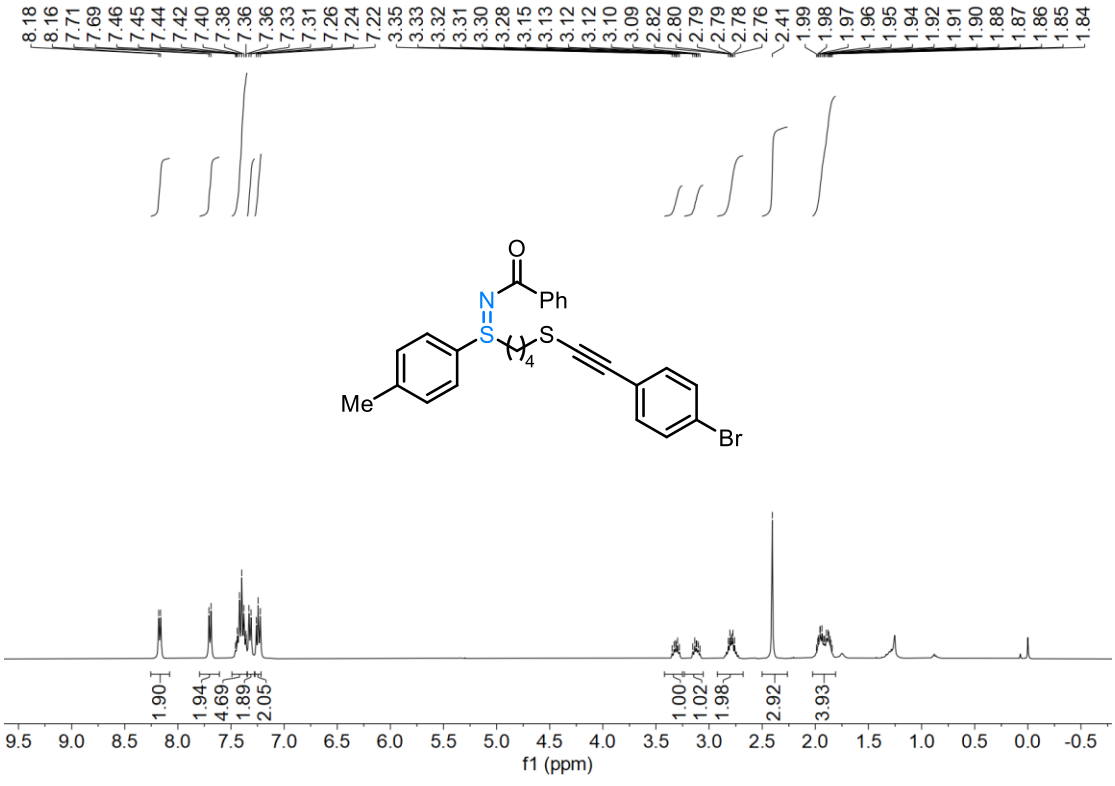
^{1}H NMR spectrum of compound **28** (400 MHz, $CDCl_3$)



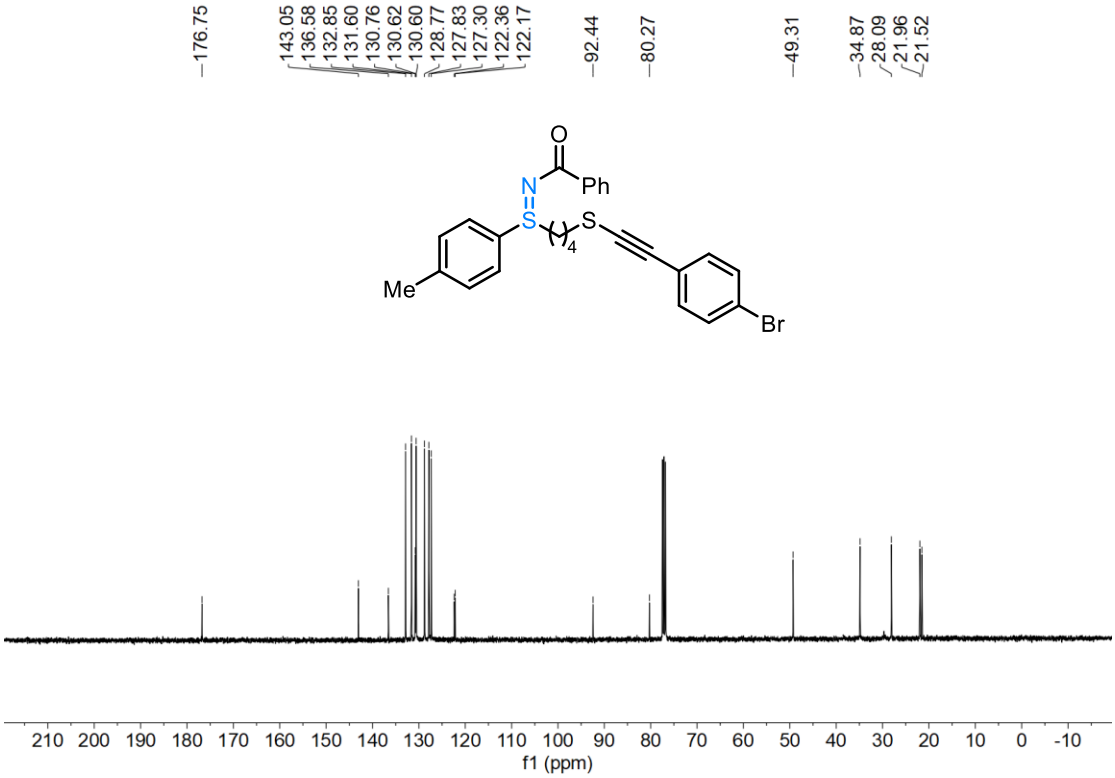
^{13}C NMR spectrum of compound **28** (100 MHz, $CDCl_3$)



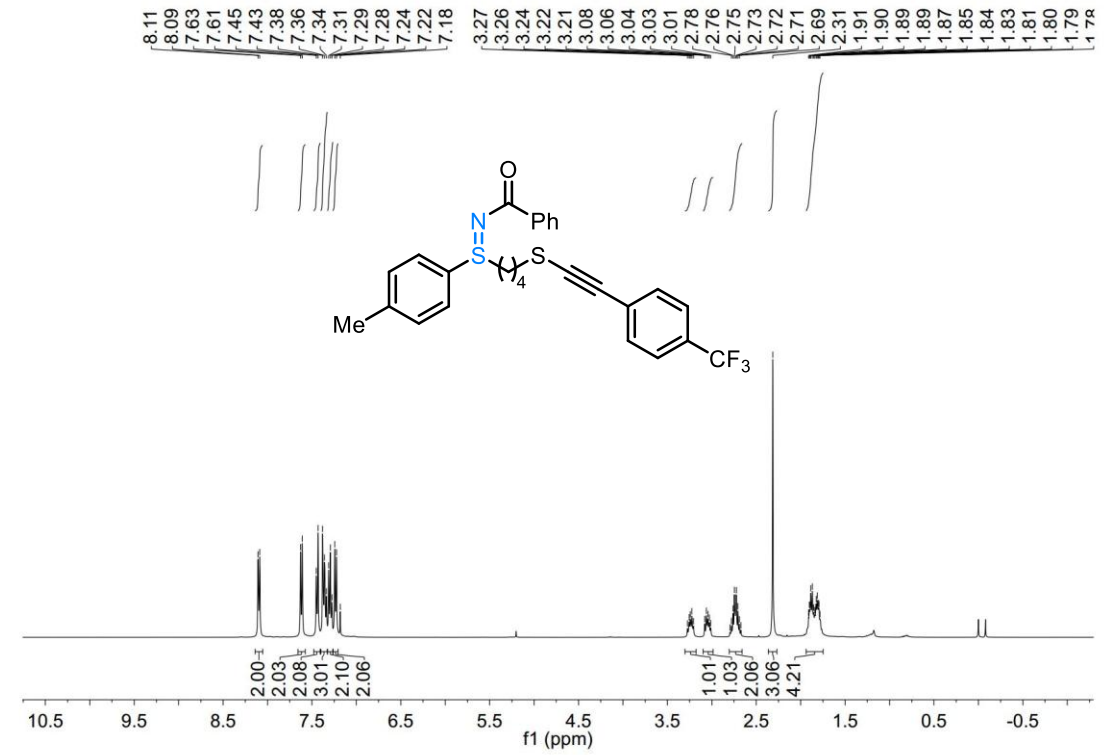
^{1}H NMR spectrum of compound **29** (400 MHz, $CDCl_3$)



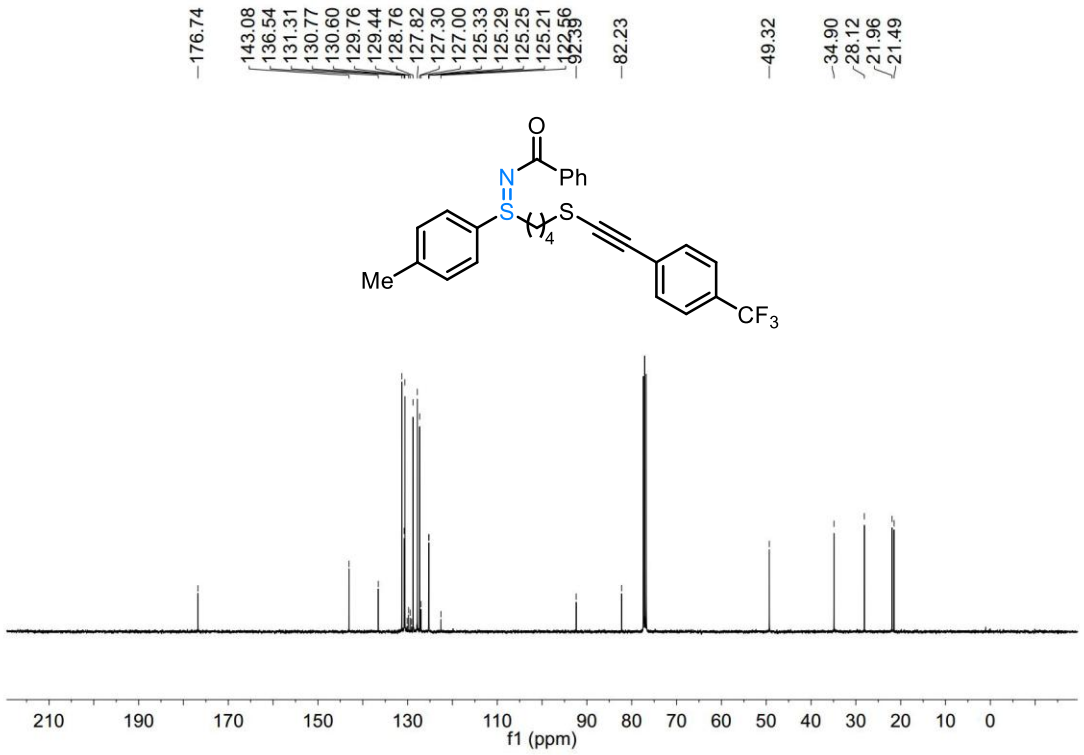
^{13}C NMR spectrum of compound **29** (100 MHz, $CDCl_3$)



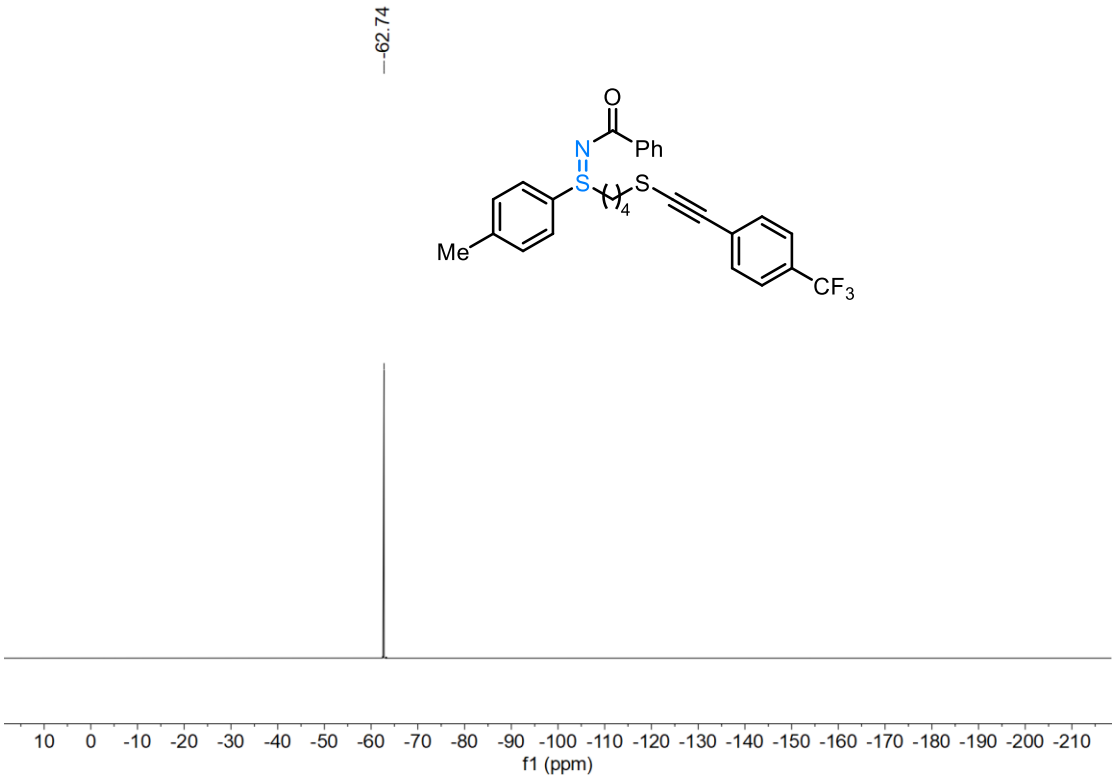
^{1}H NMR spectrum of compound **30** (400 MHz, $CDCl_3$)



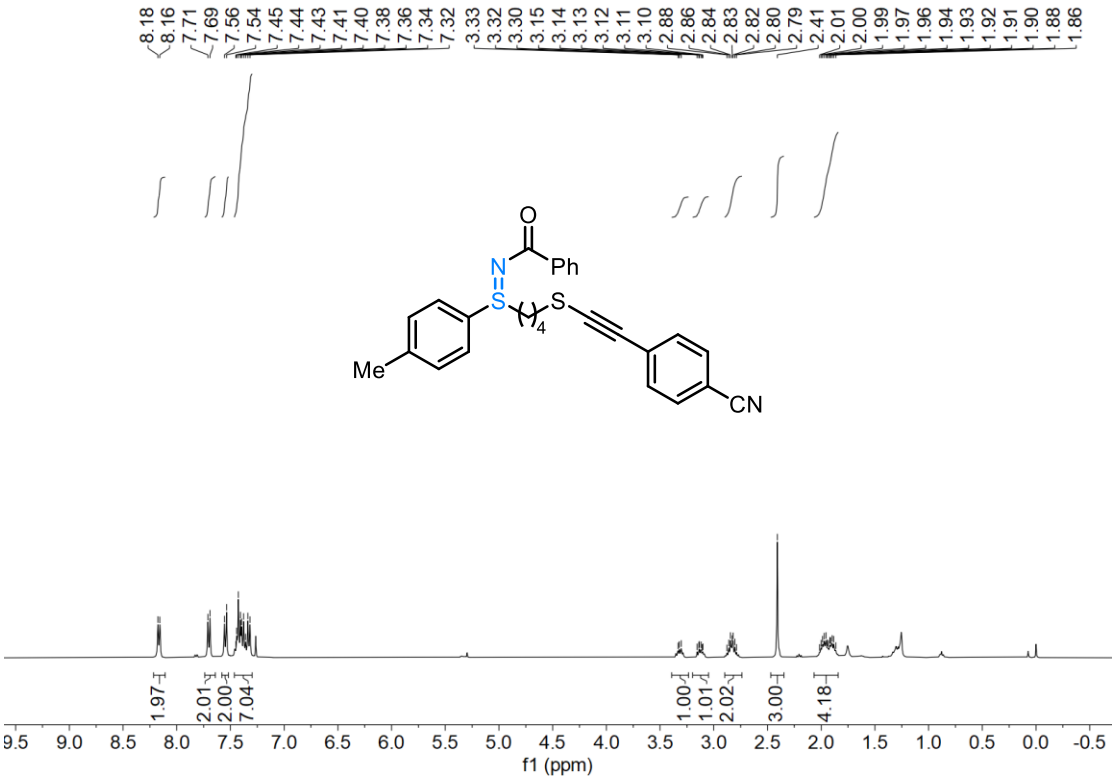
^{13}C NMR spectrum of compound **30** (100 MHz, $CDCl_3$)



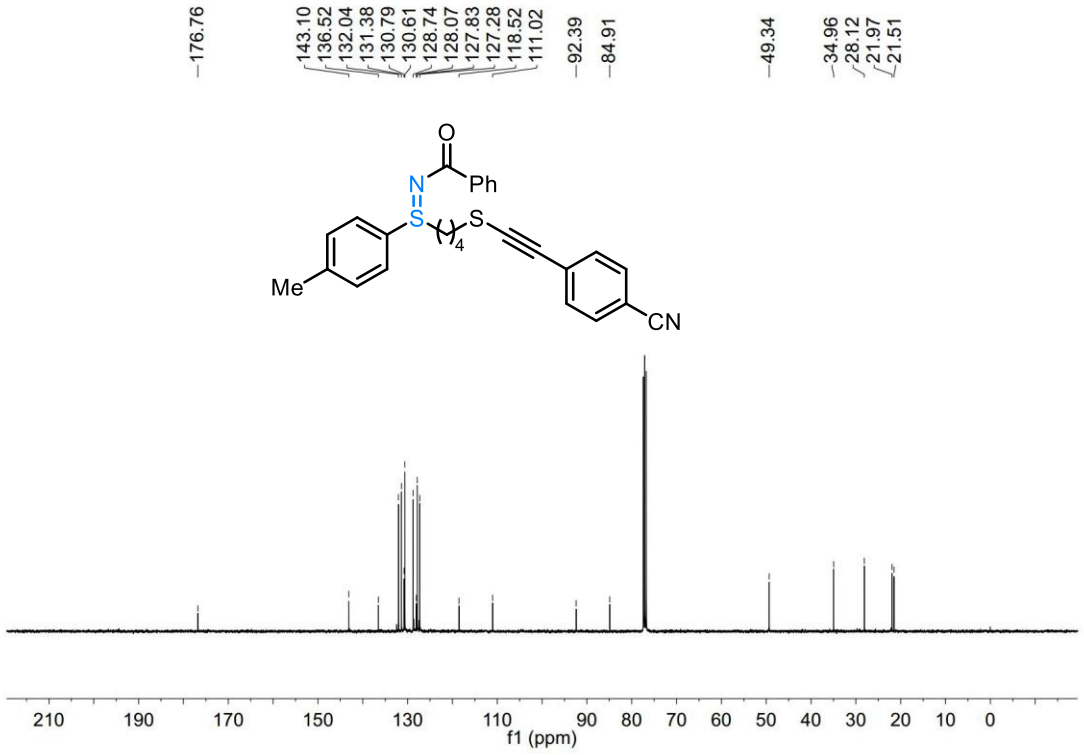
^{19}F NMR spectrum of compound **30** (376 MHz, $CDCl_3$)



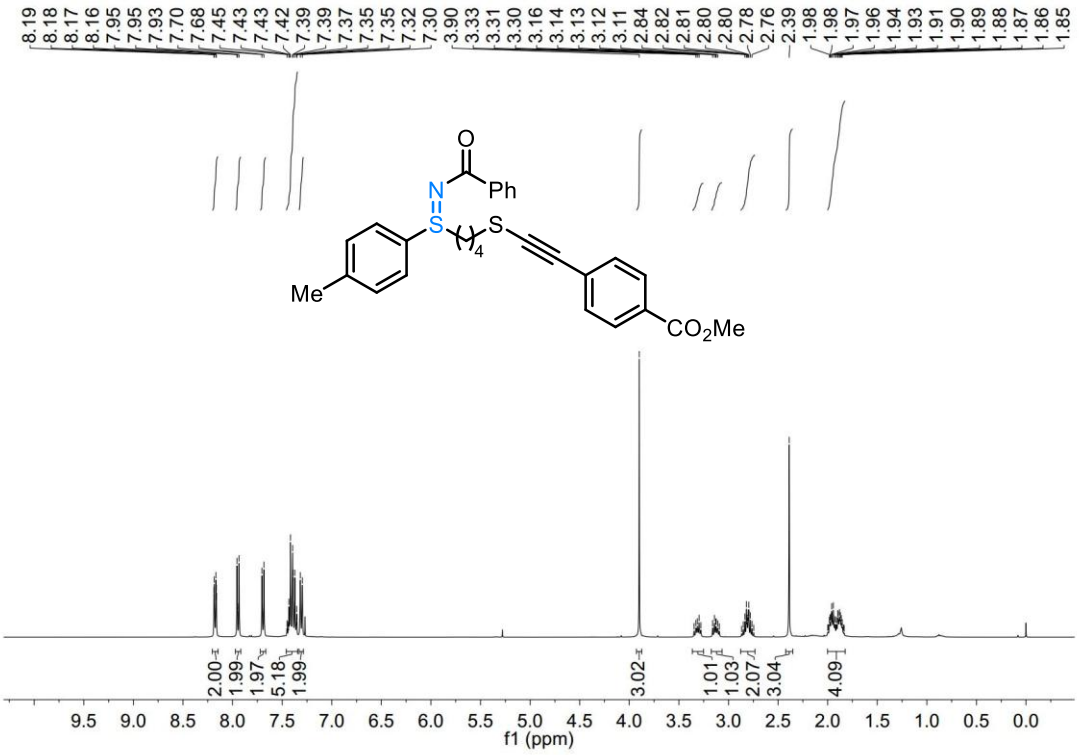
^{1}H NMR spectrum of compound **31** (400 MHz, $CDCl_3$)



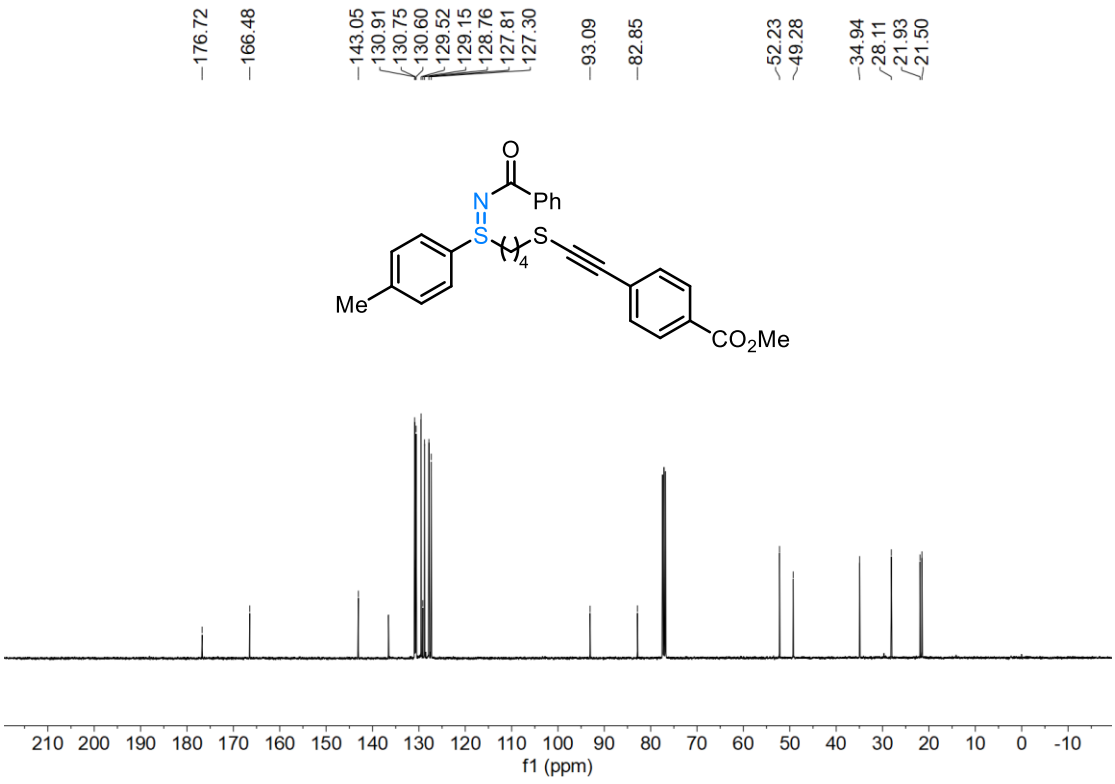
^{13}C NMR spectrum of compound **31** (100 MHz, $CDCl_3$)



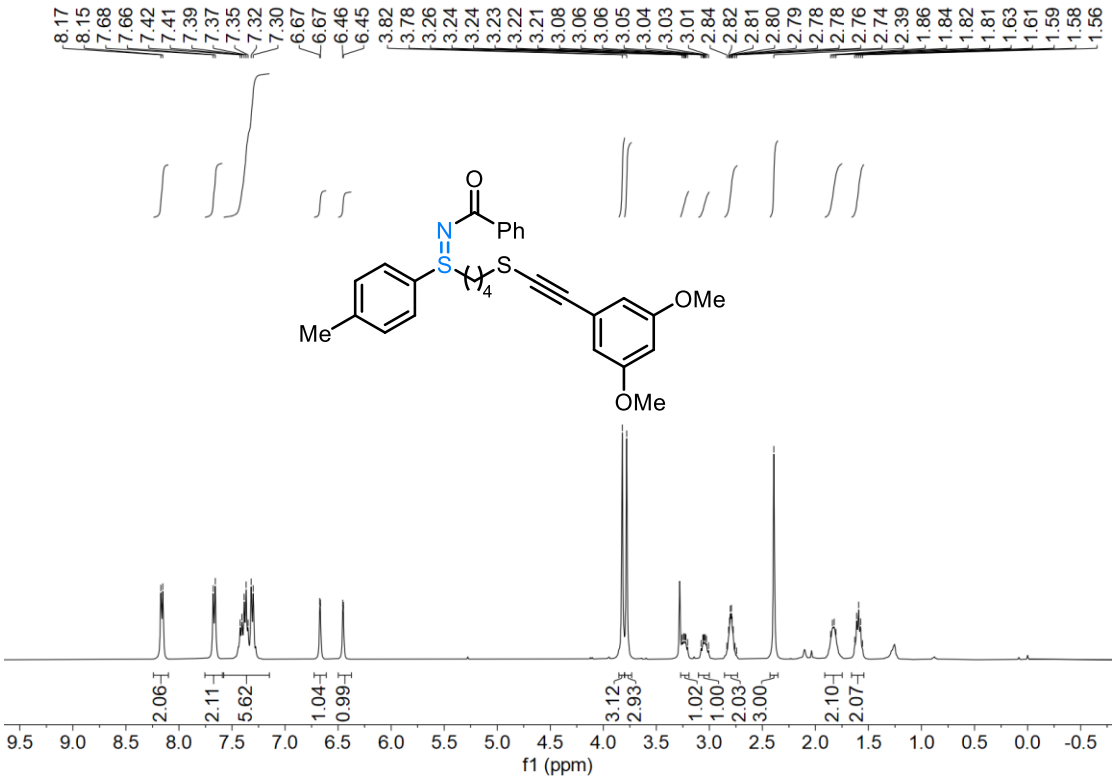
^{1}H NMR spectrum of compound **32** (400 MHz, $CDCl_3$)



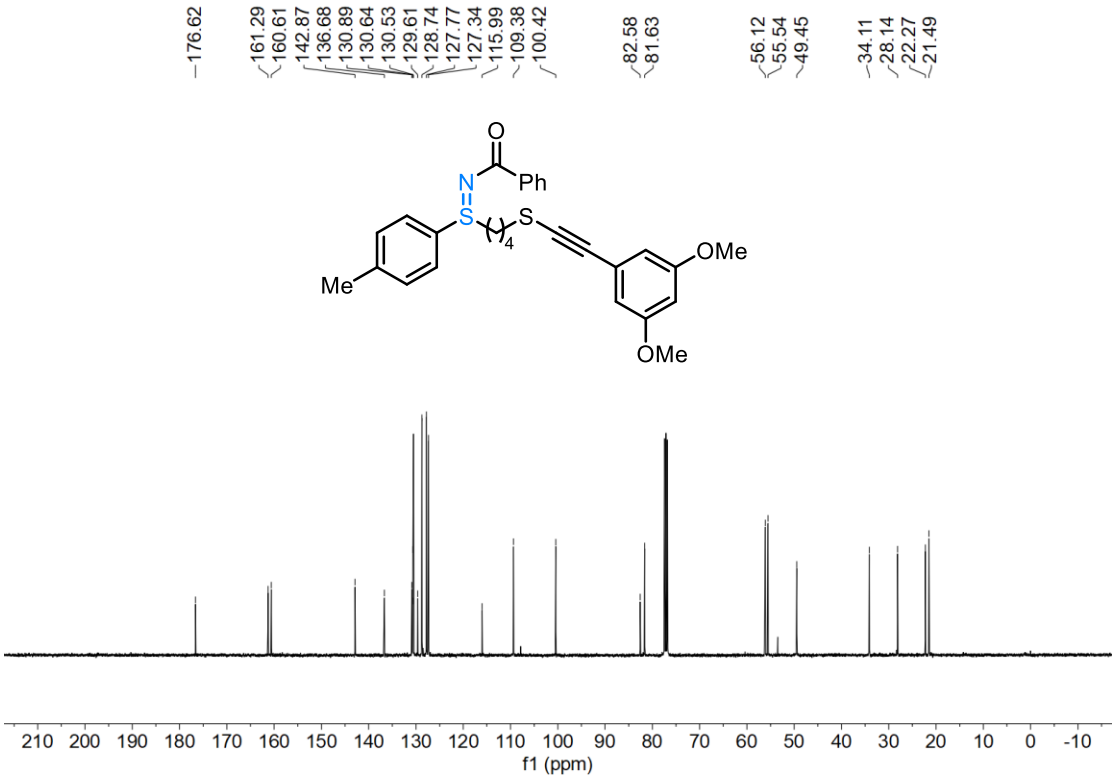
^{13}C NMR spectrum of compound **32** (100 MHz, $CDCl_3$)



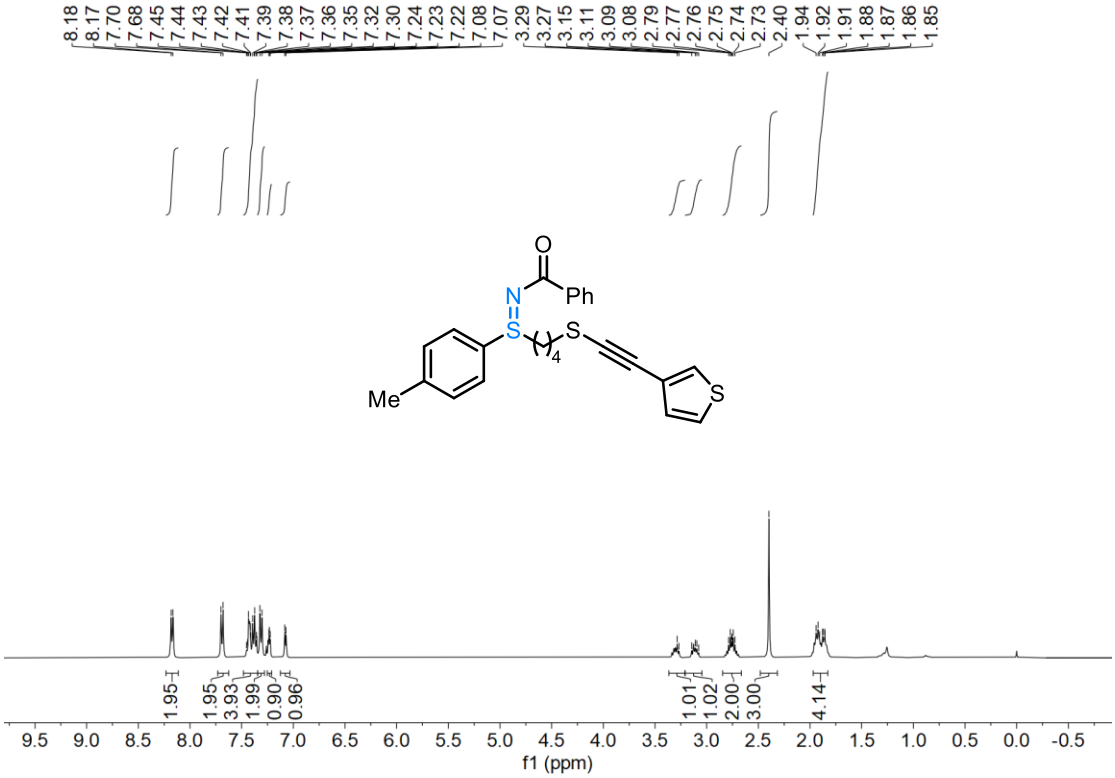
^{1}H NMR spectrum of compound **33** (400 MHz, $CDCl_3$)



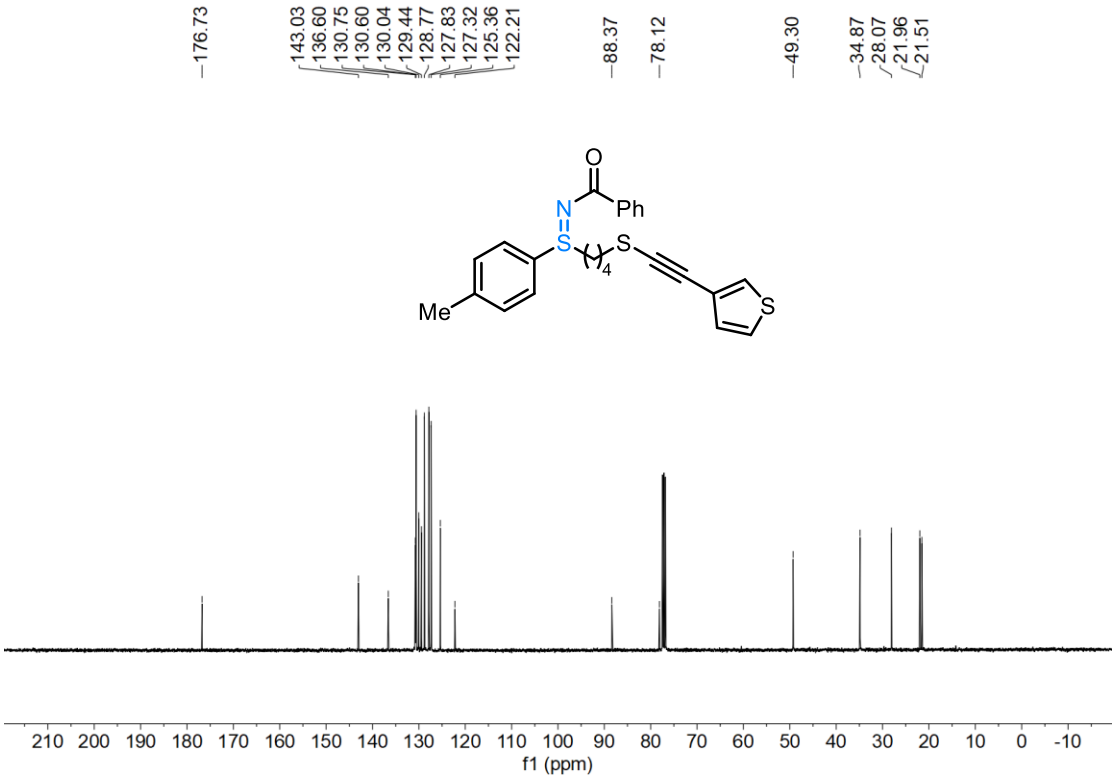
^{13}C NMR spectrum of compound **33** (100 MHz, $CDCl_3$)



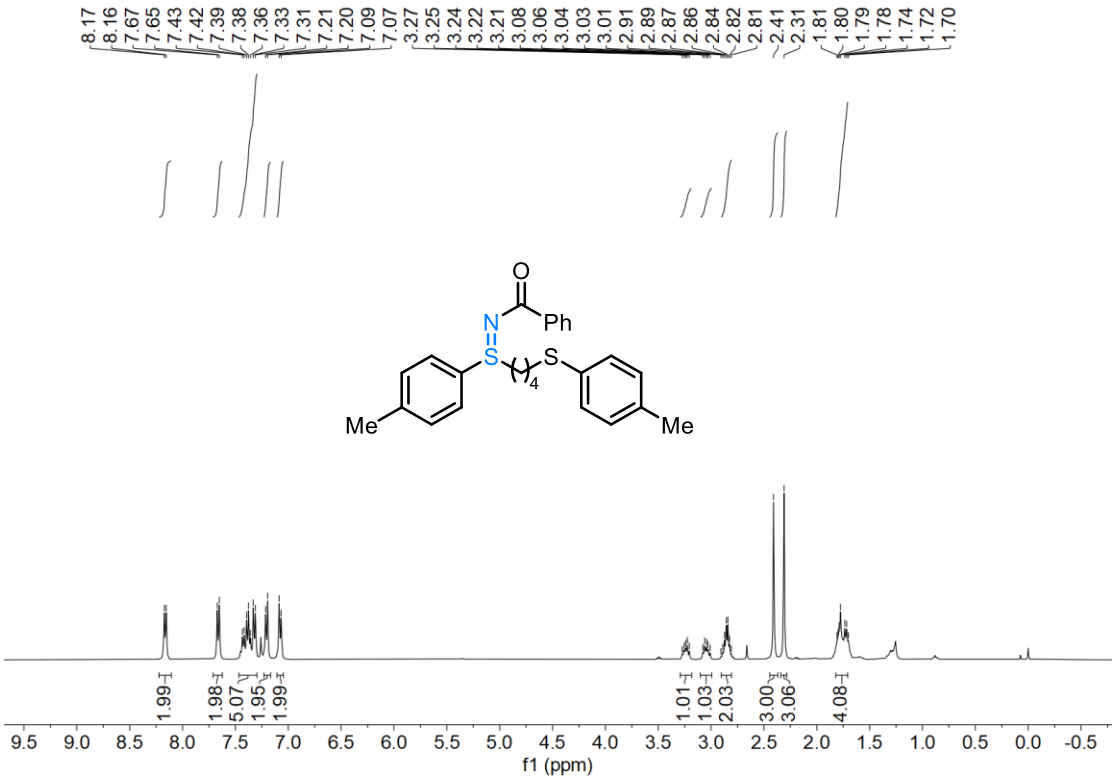
^{1}H NMR spectrum of compound **34** (400 MHz, $CDCl_3$)



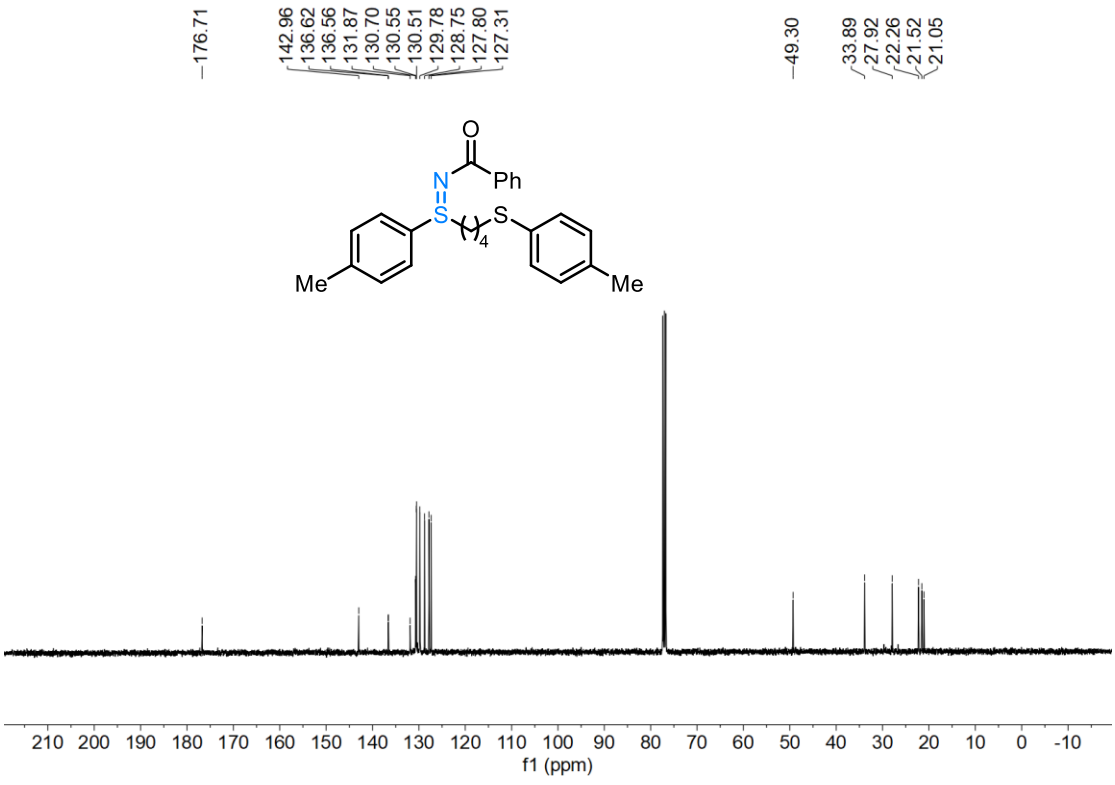
^{13}C NMR spectrum of compound **34** (100 MHz, $CDCl_3$)



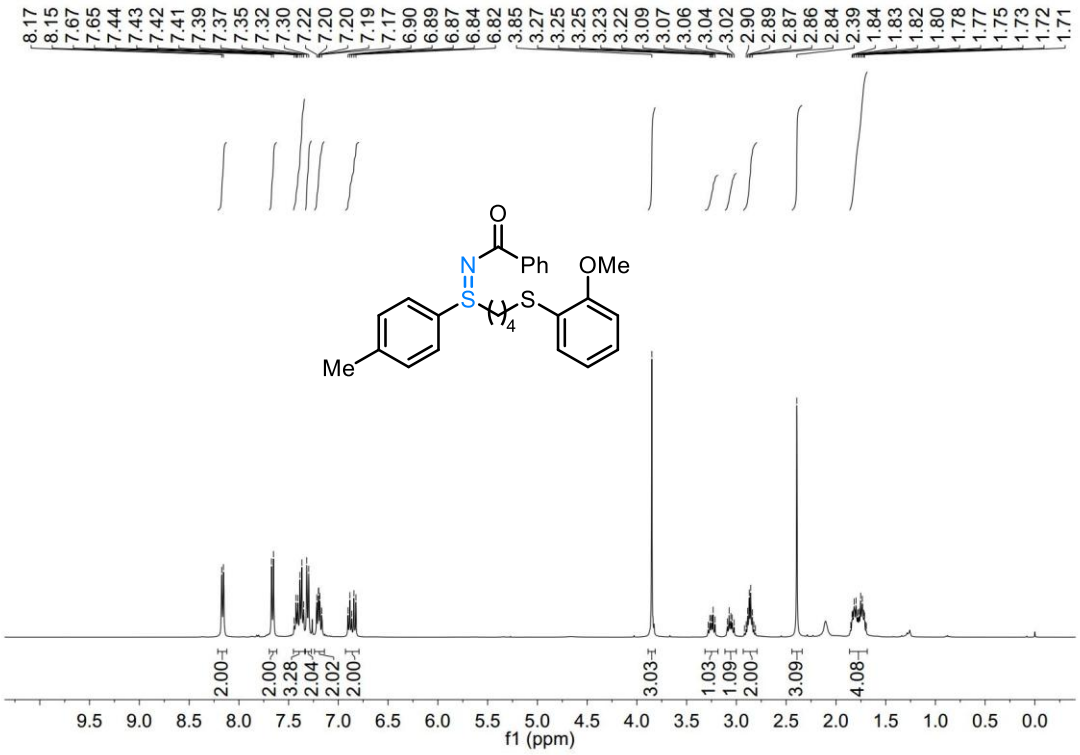
^{1}H NMR spectrum of compound **35** (400 MHz, $CDCl_3$)



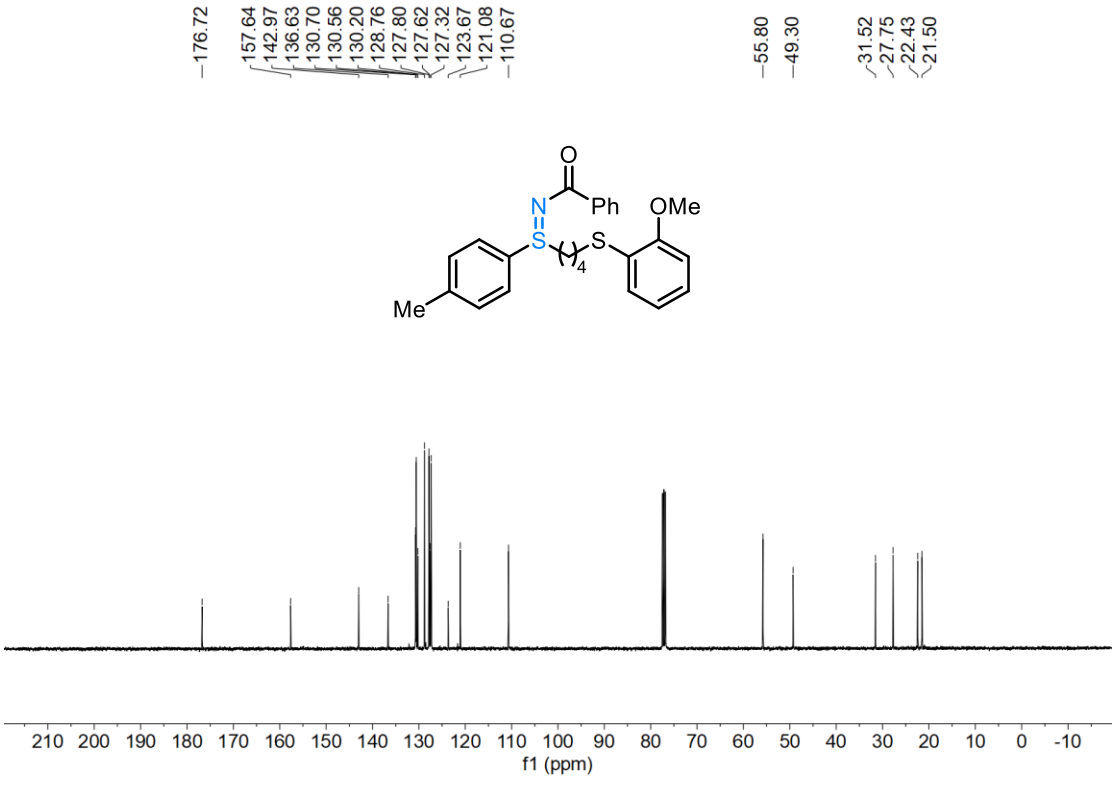
^{13}C NMR spectrum of compound **35** (100 MHz, $CDCl_3$)



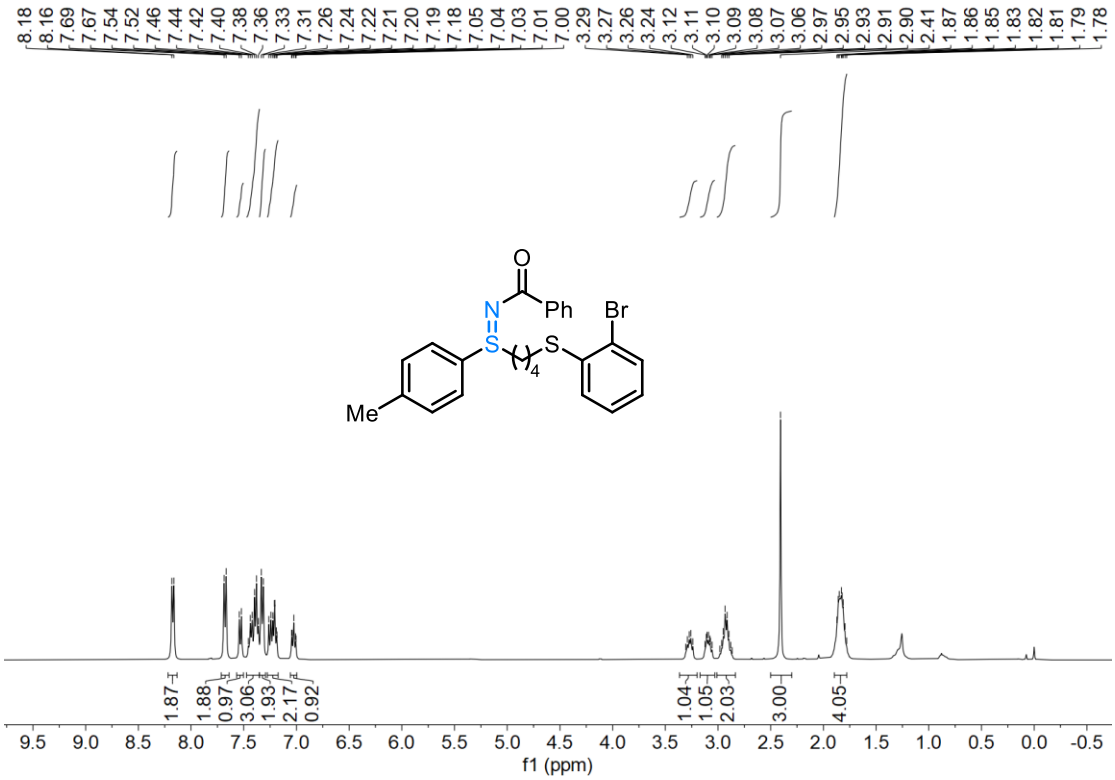
^{1}H NMR spectrum of compound **36** (400 MHz, $CDCl_3$)



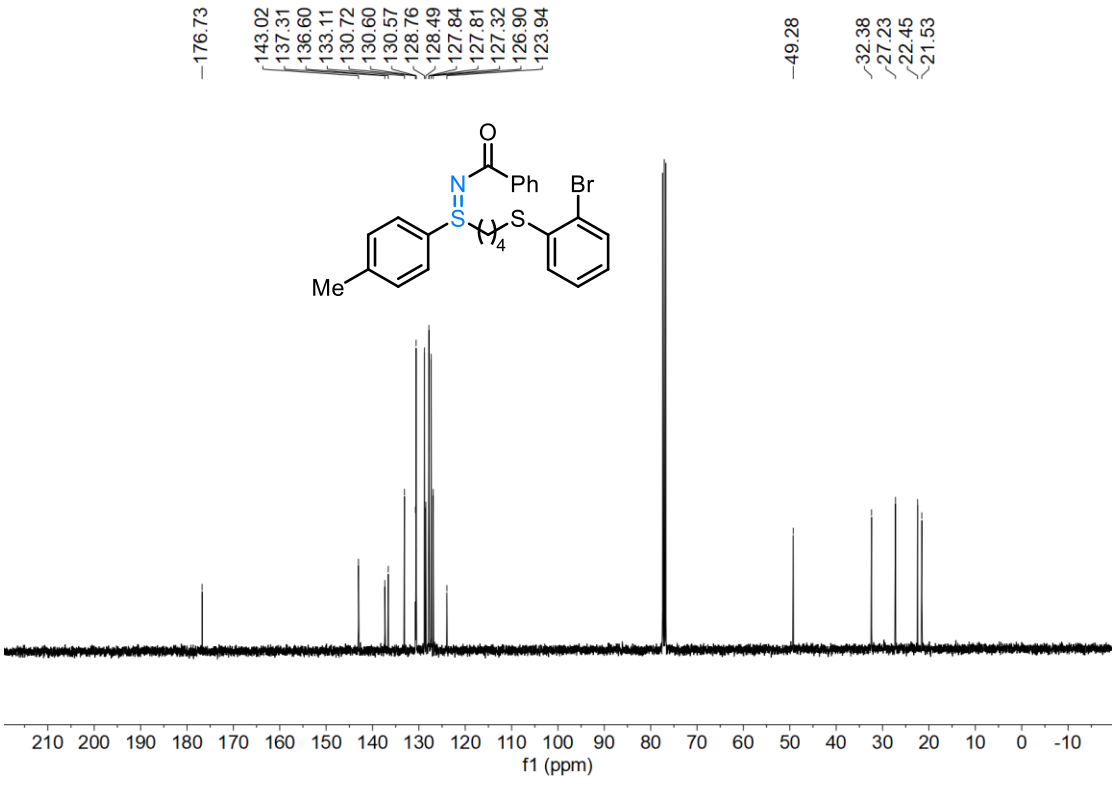
^{13}C NMR spectrum of compound **36** (100 MHz, $CDCl_3$)



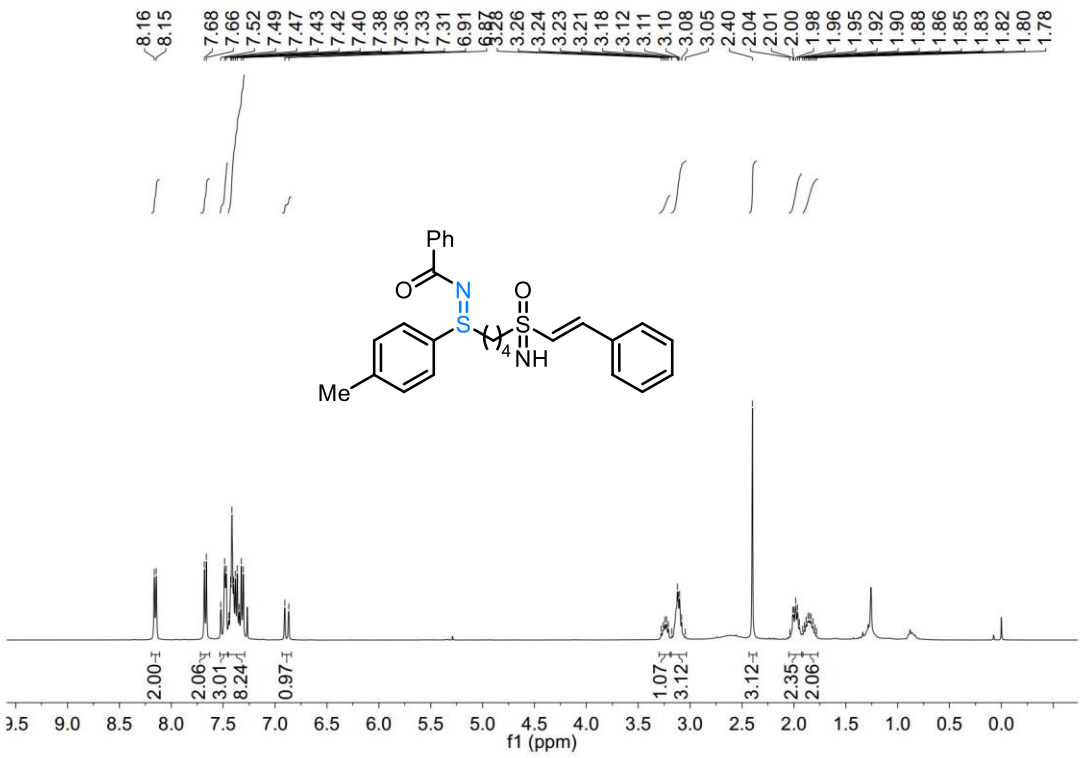
^{1}H NMR spectrum of compound **37** (400 MHz, $CDCl_3$)



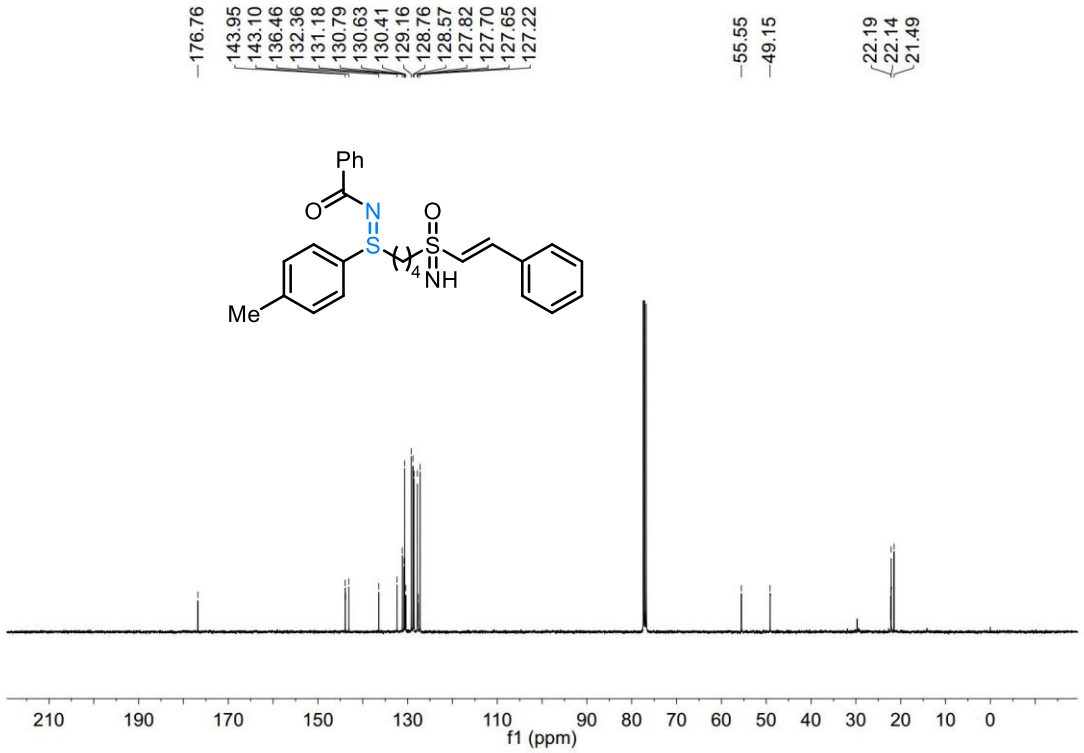
^{13}C NMR spectrum of compound **37** (100 MHz, $CDCl_3$)



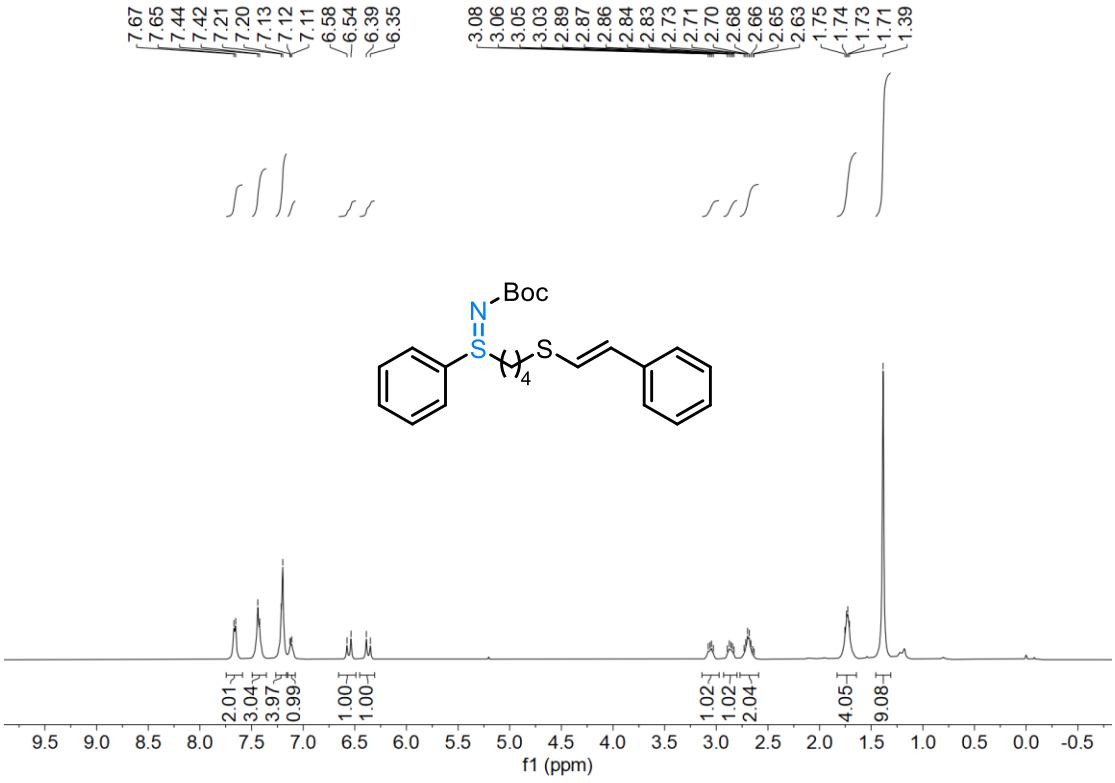
^{1}H NMR spectrum of compound **38** (400 MHz, $CDCl_3$)



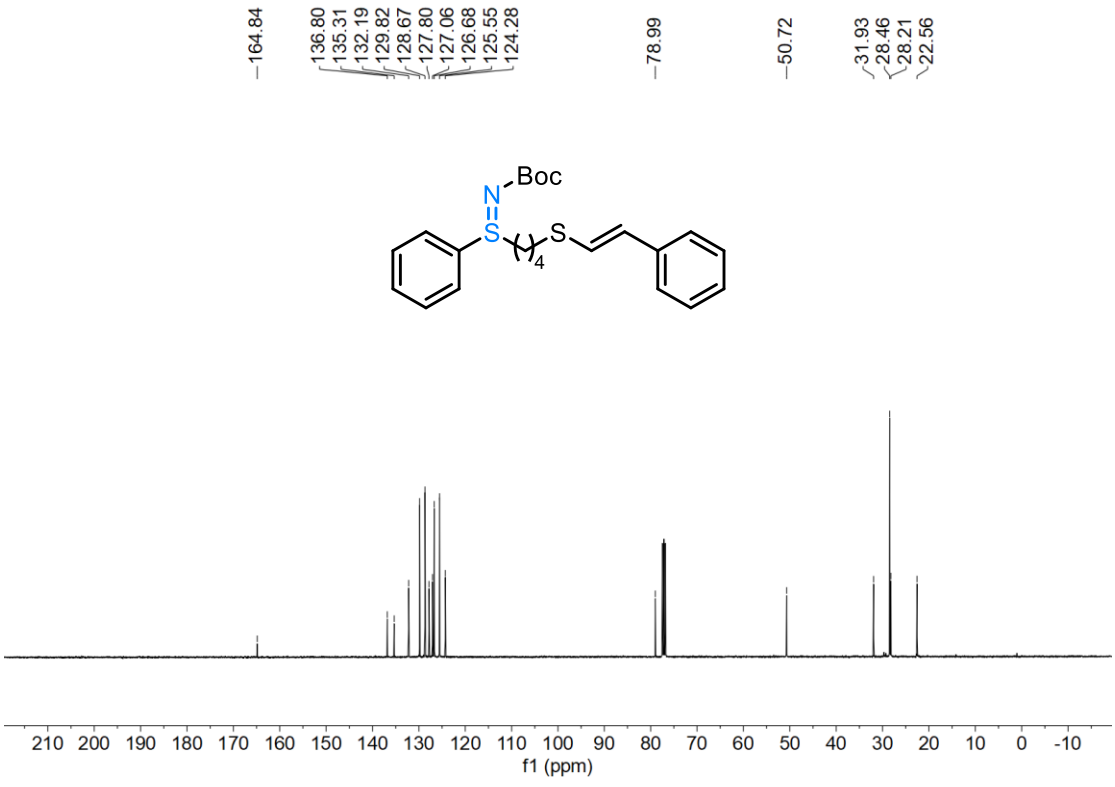
^{13}C NMR spectrum of compound **38** (100 MHz, $CDCl_3$)



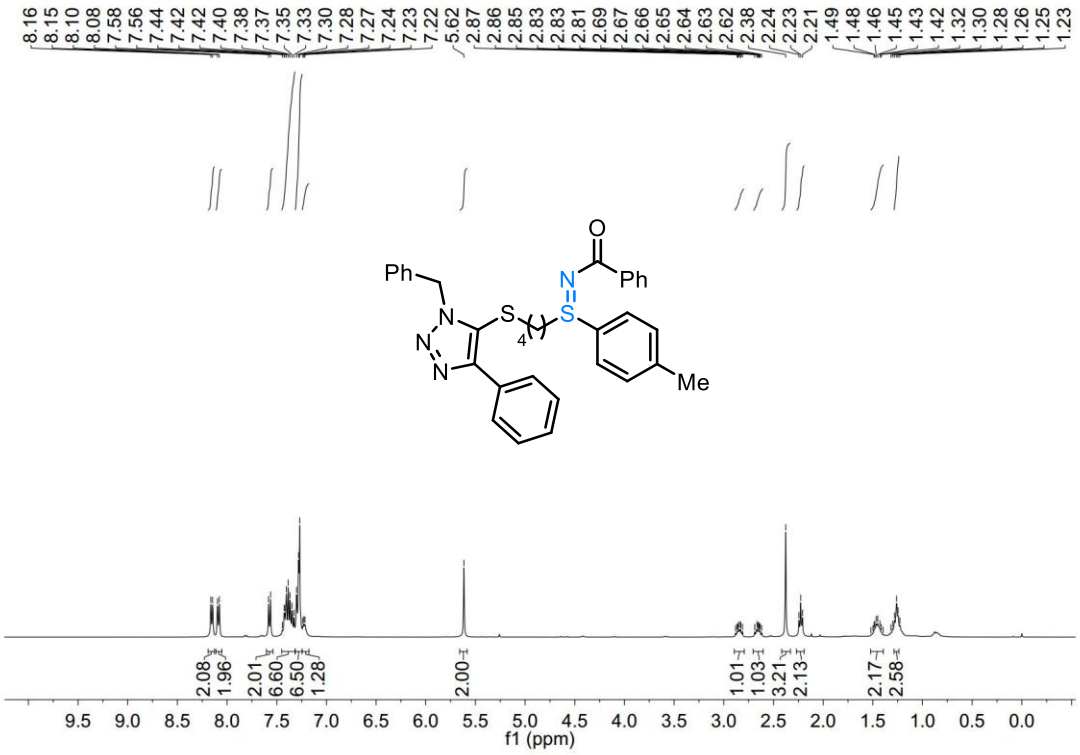
^{1}H NMR spectrum of compound **39** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **39** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **40** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **40** (100 MHz, $CDCl_3$)