Supporting Information

Synthesis of functionalized sulfilimines via iron-catalyzed sulfur alkylation of sulfenamides with diazo compounds

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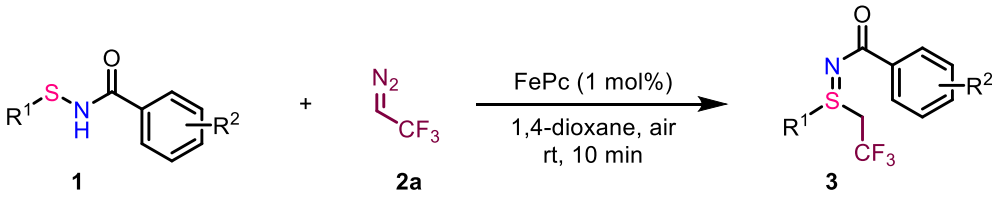
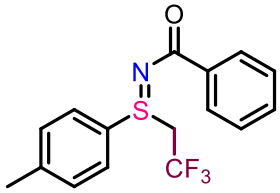
1. General Information

Unless otherwise stated, all commercial reagents were used as received. 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 precoated 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, ^{19}F and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 100 MHz, 376 MHz and 162 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 diazo compounds **2a**-**2c**[2] were prepared according to the reported procedures. Ethyl diazoacetate **2d** was commercially available and used as received.

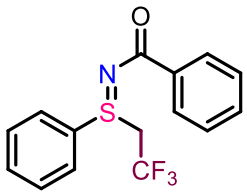
2. General Experimental Procedure and Characterization Data



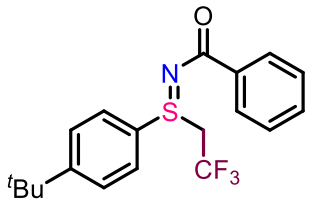
To a solution of sulfenamide **1** (0.2 mmol, 1.0 equiv) and FePc (0.002 mmol, 1 mol%) in analytical 1,4-dioxane (1 mL) was added 2,2,2-trifluorodiazoethane **2a** (0.22 mmol, 1.1 equiv, 0.17 M in DCM). The reaction mixture was stirred at room temperature for 10 minutes under an air atmosphere. After completion of reaction as monitored by TLC analysis, the mixture was evaporated 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**.



***N*-(*p*-tolyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3aa):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.09 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.42 – 7.33 (m, 4H), 4.26 (dq, *J* = 14.2, 9.6 Hz, 1H), 3.69 (dq, *J* = 14.2, 9.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 144.4, 135.6, 131.2, 130.9, 129.9, 128.8, 127.9, 127.6, 122.5 (q, *J* = 278.1 Hz), 52.4 (q, *J* = 30.9 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.87 (t, *J* = 9.4 Hz); HRMS (ESI) calcd for $C_{16}H_{14}NOF_3NaS^+$ ($M+Na^+$): 348.0646, found: 348.0653.

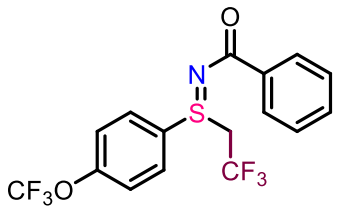


***N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ab):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 2H), 7.93 – 7.86 (m, 2H), 7.66 – 7.54 (m, 3H), 7.51 – 7.44 (m, 1H), 7.42 – 7.36 (m, 2H), 4.27 (dq, *J* = 14.2, 9.6 Hz, 1H), 3.72 (dq, *J* = 14.2, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 135.5, 133.4, 133.3, 131.3, 130.3, 128.9, 128.0, 127.6, 122.5 (q, *J* = 278.2 Hz), 52.5 (q, *J* = 31.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.86 (t, *J* = 9.4 Hz); HRMS (ESI) calcd for $C_{15}H_{12}NOF_3NaS^+$ ($M+Na^+$): 334.0489, found: 334.0492.

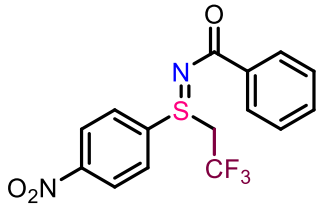


***N*-((4-(*tert*-butyl)phenyl)(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ac):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* =

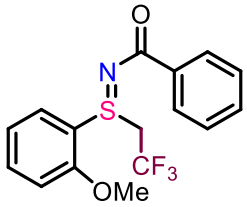
8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 4.25 (dq, *J* = 14.2, 9.6 Hz, 1H), 3.70 (dq, *J* = 14.2, 9.2 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 157.3, 135.7, 131.2, 129.9, 128.8, 127.9, 127.4, 127.4, 122.5 (q, *J* = 278.1 Hz), 52.4 (q, *J* = 30.8 Hz), 35.2, 31.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.97 (t, *J* = 9.4 Hz); HRMS (ESI) calcd for $C_{19}H_{20}F_3NONaS^+$ ($M+Na^+$): 390.1115, found: 390.1110.



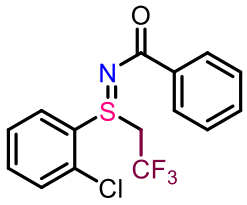
***N*-((2,2,2-trifluoroethyl)(4-(trifluoromethoxy)phenyl)-λ^4-sulfaneylidene)benzamide (3ad):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.44 – 7.37 (m, 4H), 4.26 (dq, *J* = 14.3, 9.5 Hz, 1H), 3.74 (dq, *J* = 14.3, 9.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 152.68, 152.66, 135.1, 131.5, 129.6, 128.9, 128.0, 122.4 (q, *J* = 278.2 Hz), 122.2, 120.2 (q, *J* = 259.8 Hz), 52.4 (q, *J* = 31.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.77 (s), -60.75 (t, *J* = 9.3 Hz); HRMS (ESI) calcd for $C_{16}H_{11}NO_2F_6NaS^+$ ($M+Na^+$): 418.0312, found: 418.0320.



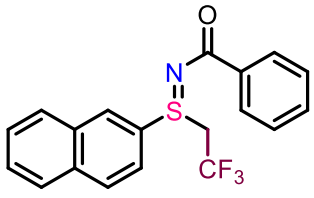
***N*-((4-nitrophenyl)(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ae):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.17 – 8.04 (m, 4H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 4.28 (dq, *J* = 14.4, 9.5 Hz, 1H), 3.86 (dq, *J* = 14.4, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 150.6, 140.6, 134.7, 131.8, 128.9, 128.6, 128.1, 125.2, 122.3 (q, *J* = 278.3 Hz), 51.9 (q, *J* = 31.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.49 (t, *J* = 9.3 Hz); HRMS (ESI) calcd for $C_{15}H_{11}N_2O_3F_3NaS^+$ ($M+Na^+$): 379.0340, found: 379.0348.



***N*-((2-methoxyphenyl)(2,2,2-trifluoroethyl)-λ⁴-sulfaneylidene)benzamide (3af):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 2H), 7.82 – 7.76 (m, 1H), 7.55 – 7.44 (m, 2H), 7.44 – 7.37 (m, 2H), 7.17 – 7.10 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 4.03 – 3.86 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 156.6, 135.9, 134.1, 131.2, 129.0, 127.9, 127.5, 122.84 (q, *J* = 278.7 Hz), 122.2, 119.5, 111.8, 56.4, 49.64 (q, *J* = 31.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.18 (t, *J* = 9.3 Hz); HRMS (ESI) calcd for $C_{16}H_{14}NO_2F_3NaS^+$ ($M+Na^+$): 364.0595, found: 364.0595.

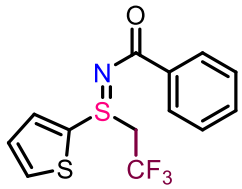


***N*-(2-chlorophenyl)(2,2,2-trifluoroethyl)-λ⁴-sulfaneylidene)benzamide (3ag):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.15 (m, 2H), 7.95 – 7.88 (m, 1H), 7.58 – 7.45 (m, 4H), 7.44 – 7.37 (m, 2H), 4.06 (dq, *J* = 14.3, 9.2 Hz, 1H), 3.88 (dq, *J* = 14.3, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 135.3, 133.9, 133.1, 131.5, 131.4, 130.8, 129.0, 128.7, 128.0, 127.9, 122.6 (q, *J* = 278.9 Hz), 50.2 (q, *J* = 31.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.03 (t, *J* = 9.1 Hz); HRMS (ESI) calcd for $C_{15}H_{11}NONaF_3SCl^+$ ($M+Na^+$): 368.0100, found: 368.0108.

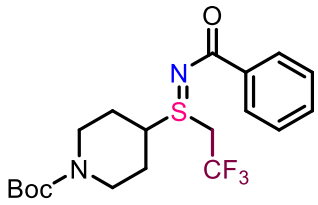


***N*-(naphthalen-2-yl(phenyl)-λ⁴-sulfaneylidene)benzamide (3ah):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.18 (d, *J* = 7.6 Hz, 2H), 8.04 – 7.97 (m,

1H), 7.94 – 7.84 (m, 3H), 7.66 – 7.55 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 4.30 (dq, *J* = 14.3, 9.6 Hz, 1H), 3.81 (dq, *J* = 14.3, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 135.6, 135.3, 132.7, 131.3, 130.9, 130.0, 129.6, 129.1, 128.9, 128.9, 128.2, 128.0, 127.9, 122.5 (q, *J* = 278.2 Hz), 121.6, 52.2 (q, *J* = 30.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) -60.78 (t, *J* = 9.3 Hz); HRMS (ESI) calcd for $C_{19}H_{14}NOF_3NaS^+$ ($M+Na^+$): 384.0646, found: 384.0646.

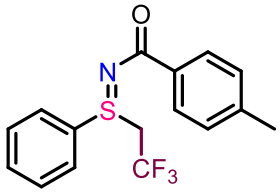


***N*-(thiophen-2-yl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ai):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 2H), 7.80 (dd, *J* = 5.2, 1.3 Hz, 1H), 7.74 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 7.15 (dd, *J* = 5.2, 3.8 Hz, 1H), 4.48 (dq, *J* = 14.2, 9.6 Hz, 1H), 3.96 (dq, *J* = 14.2, 9.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 135.4, 135.3, 135.0, 132.0, 131.5, 128.9, 128.0, 127.6, 122.4 (q, *J* = 278.2 Hz), 53.8 (q, *J* = 30.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) -61.33 (t, *J* = 9.5 Hz); HRMS (ESI) calcd for $C_{13}H_{10}NOF_3NaS_2^+$ ($M+Na^+$): 340.0054, found: 340.0063.

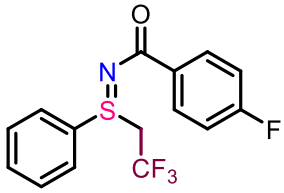


***Tert*-butyl -4-*(N*-benzoyl-*S*-(2,2,2-trifluoroethyl)sulfinimidoyl)piperidine-1-carb-oxylate (3aj):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.49 – 7.43 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 4.37 – 4.06 (m, 3H), 3.87 – 3.68 (m, 2H), 2.97 – 2.75 (m, 2H), 2.06 – 1.98 (m, 2H), 1.89 – 1.70 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 154.3, 135.8, 131.4, 128.8, 128.0, 123.0 (q, *J* = 277.7 Hz), 80.4, 53.9, 45.0 (q, *J* = 31.5 Hz), 42.7, 28.3, 26.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.11 (t,

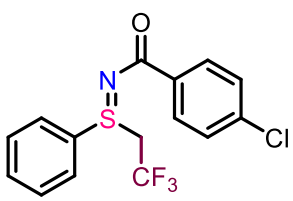
J = 9.7 Hz); HRMS (ESI) calcd for $C_{19}H_{25}NO_3F_3NaS^+$ ($M+Na^+$): 441.1436, found: 441.1440.



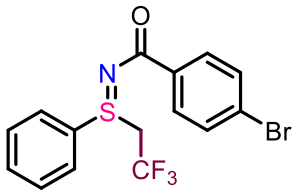
4-Methyl-*N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ba): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.50 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.24 (dq, *J* = 14.3, 9.6 Hz, 1H), 3.71 (dq, *J* = 14.3, 9.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 141.6, 133.5, 133.2, 132.8, 130.2, 128.9, 128.7, 127.5, 122.5 (q, *J* = 278.1 Hz), 52.4 (q, *J* = 31.1 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.86 (t, *J* = 9.4 Hz).HRMS (ESI) calcd for $C_{16}H_{14}NOF_3NaS^+$ ($M+Na^+$): 348.0646, found: 348.0651.



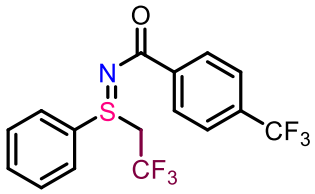
4-Fluoro-*N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ca): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 2H), 7.93 – 7.87 (m, 2H), 7.67 – 7.55 (m, 3H), 7.09 – 7.01 (m, 2H), 4.24 (dq, *J* = 14.2, 9.6 Hz, 1H), 3.72 (dq, *J* = 14.2, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 164.9 (d, *J* = 250.7 Hz), 133.4, 133.2, 131.8 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 8.9 Hz), 130.3, 127.5, 122.4 (q, *J* = 278.2 Hz), 114.8 (d, *J* = 21.6 Hz), 52.5 (q, *J* = 31.1 Hz); ^{19}F NMR (376 MHz, CDCl3) δ -60.87 (t, *J* = 9.1 Hz), -109.06 – -109.21 (m); HRMS (ESI) calcd for $C_{15}H_{11}NOF_4NaS^+$ ($M+Na^+$): 352.0395, found: 352.0404.



4-Chloro-*N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3da): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 7.93 – 7.84 (m, 2H), 7.67 – 7.55 (m, 3H), 7.38 – 7.31 (m, 2H), 4.25 (dq, *J* = 14.2, 9.5 Hz, 1H), 3.72 (dq, *J* = 14.2, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 137.5, 134.0, 133.5, 133.1, 130.3, 130.3, 128.1, 127.5, 122.4 (q, *J* = 278.3 Hz), 52.5 (q, *J* = 31.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) -60.85 (t, *J* = 9.4 Hz); HRMS (ESI) calcd for $C_{15}H_{11}NOF_3NaSCl^+$ ($M+Na^+$): 368.0100, found: 368.0106.

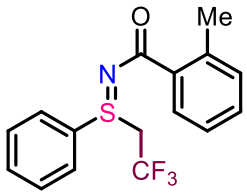


4-Bromo-*N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)benzamide (3ea): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.67 – 7.55 (m, 3H), 7.51 (d, *J* = 8.5 Hz, 2H), 4.24 (dq, *J* = 14.2, 9.5 Hz, 1H), 3.72 (dq, *J* = 14.2, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 134.4, 133.5, 133.0, 131.1, 130.5, 130.3, 127.5, 122.4 (q, *J* = 278.2 Hz), 126.1, 52.5 (q, *J* = 31.1 Hz); ^{19}F NMR (376 MHz, CDCl3) -60.84 (t, *J* = 9.3 Hz); HRMS (ESI) calcd for $C_{15}H_{11}NOF_3NaSBr^+$ ($M+Na^+$): 411.9595, found: 411.9602.

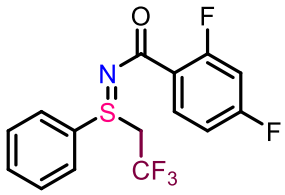


***N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)-4-(trifluoromethyl)benzamide (3fa):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 2H), 7.93 – 7.87 (m, 2H), 7.68 – 7.57 (m, 5H), 4.27 (dq, *J* = 14.2, 9.5 Hz, 1H), 3.75 (dq, *J* = 14.2, 9.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 138.7, 133.6, 132.9, 132.8 (q, *J* = 32.2 Hz), 130.4, 129.2, 127.6, 124.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.4 Hz), 122.4 (q, *J* = 278.2 Hz), 52.5 (q, *J* = 31.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.87 (t, *J* = 9.3

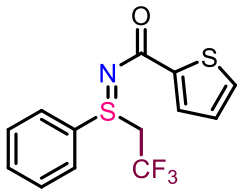
Hz), -62.76 (s); HRMS (ESI) calcd for $C_{16}H_{12}NOF_6S^+$ ($M+H^+$): 380.0544, found: 380.0549.



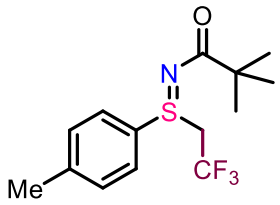
2-Methyl-*N*-(phenyl(2,2,2-trifluoroethyl)-λ⁴-sulfaneylidene)benzamide (3ga): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 3H), 7.65 – 7.55 (m, 3H), 7.31 – 7.25 (m, 1H), 7.22 – 7.16 (m, 2H), 4.22 (dq, *J* = 14.3, 9.5 Hz, 1H), 3.71 (dq, *J* = 14.3, 9.2 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 137.7, 136.0, 133.3, 133.3, 131.1, 130.3, 130.0, 129.6, 127.5, 125.4, 122.5 (q, *J* = 278.2 Hz), 52.2 (q, *J* = 31.1 Hz), 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.86 (t, *J* = 9.3 Hz); HRMS (ESI) calcd for $C_{16}H_{14}NOF_3NaS^+$ ($M+Na^+$): 348.0646, found: 348.0655.



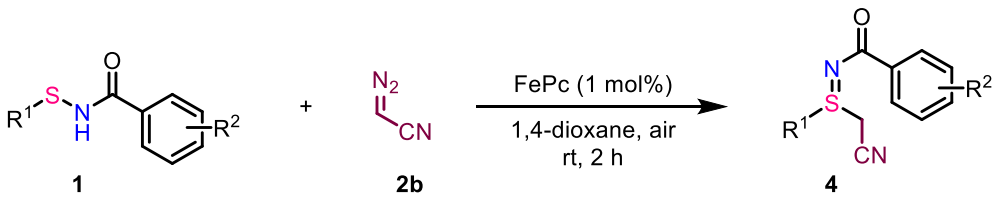
2,4-Difluoro-*N*-(phenyl(2,2,2-trifluoroethyl)-λ⁴-sulfaneylidene)benzamide (3ha): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.95 – 7.85 (m, 2H), 7.69 – 7.52 (m, 3H), 6.93 – 6.76 (m, 2H), 4.26 (dq, *J* = 14.3, 9.5 Hz, 1H), 3.75 (dq, *J* = 14.3, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2 (d, *J* = 4.4 Hz), 164.4 (dd, *J* = 250.4, 13.5 Hz), 162.0 (dd, *J* = 259.7, 17.2 Hz), 133.5, 133.2 (dd, *J* = 10.1, 3.2 Hz), 132.7, 130.3, 127.6, 122.4 (q, *J* = 278.2 Hz), 120.7 (dd, *J* = 11.0, 3.7 Hz), 111.0 (dd, *J* = 21.1, 3.8 Hz), 104.7 (dd, *J* = 26.6, 25.2 Hz), 52.3 (q, *J* = 31.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.88 (t, *J* = 9.4 Hz), -105.39 – -105.56 (m), -105.84 – -105.98 (m); HRMS (ESI) calcd for $C_{15}H_{10}NOF_5NaS^+$ ($M+Na^+$): 370.0301, found: 370.0304.



***N*-(phenyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)thiophene-2-carboxamide (3ia):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.66 – 7.53 (m, 3H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.08 – 7.00 (m, 1H), 4.24 (dq, *J* = 14.3, 9.6 Hz, 1H), 3.76 (dq, *J* = 14.3, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 140.4, 133.4, 133.2, 130.7, 130.3, 130.1, 127.6, 127.4, 122.4 (q, *J* = 278.3 Hz), 52.7 (q, *J* = 31.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.92 (t, *J* = 9.4 Hz). HRMS (ESI) calcd for $C_{13}H_{10}NOF_3NaS_2^+$ ($M+Na^+$): 340.0054, found: 340.0062.



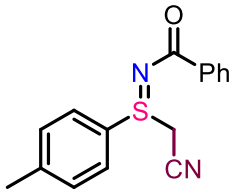
***N*-(*p*-tolyl(2,2,2-trifluoroethyl)-λ^4-sulfaneylidene)pivalamide (3ja):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.08 (dq, *J* = 14.2, 9.7 Hz, 1H), 3.57 (dq, *J* = 14.2, 9.3 Hz, 1H), 2.42 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 144.0, 130.8, 130.4, 127.3, 122.6 (q, *J* = 278.0 Hz), 51.9 (q, *J* = 30.7 Hz), 39.9, 28.4, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.04 (t, *J* = 9.5 Hz); HRMS (ESI) calcd for $C_{14}H_{18}NOF_3NaS^+$ ($M+Na^+$): 328.0959, found: 328.0962.



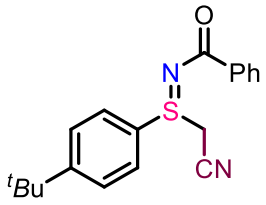
1 **2b** **4**

To a solution of sulfenamide **1** (0.2 mmol, 1.0 equiv) and FePc (0.002 mmol, 1 mol%) in analytical 1,4-dioxane (1 mL) was added diazoacetonitrile **2b** (0.22 mmol, 1.1 equiv, 1.3 M in DCM). The reaction mixture was stirred at room temperature for 2 hours under

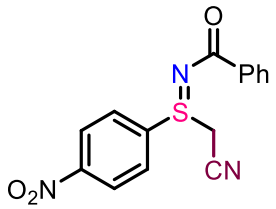
an air atmosphere. After completion of reaction as monitored by TLC analysis, the mixture was evaporated and the residue was purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding product **4**.



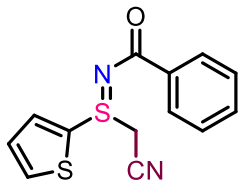
***N*-((cyanomethyl)(*p*-tolyl)-λ⁴-sulfaneylidene)benzamide (4a):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 2H), 7.89 – 7.83 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 4H), 4.24 (d, *J* = 15.9 Hz, 1H), 4.07 (d, *J* = 15.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 145.0, 135.4, 131.5, 131.0, 128.9, 128.1, 128.0, 127.2, 110.7, 38.0, 21.7; HRMS (ESI) calcd for $C_{16}H_{14}N_2ONaS^+$ ($M+Na^+$): 305.0725, found: 305.0734.



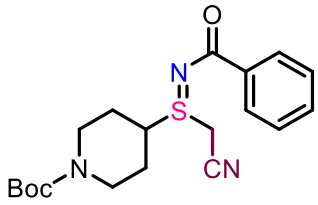
***N*-((4-(*tert*-butyl)phenyl)(cyanomethyl)-λ⁴-sulfaneylidene)benzamide (4b):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), brown solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 2H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 4.22 (d, *J* = 15.8 Hz, 1H), 4.11 (d, *J* = 15.8 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 158.0, 135.3, 131.5, 128.9, 128.0, 127.9, 127.5, 127.1, 110.6, 38.0, 35.4, 31.1; HRMS (ESI) calcd for $C_{19}H_{20}N_2ONaS^+$ ($M+Na^+$): 347.1194, found: 347.1203.



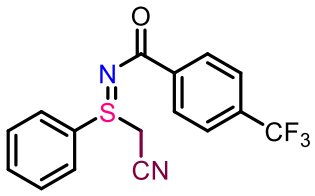
***N*-((cyanomethyl)(4-nitrophenyl)-λ^4-sulfaneylidene)benzamide (4c):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), brown solid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.8 Hz, 2H), 8.25 (d, *J* = 8.8 Hz, 2H), 8.21 – 8.13 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.17 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 151.0, 137.6, 134.4, 132.1, 129.3, 129.0, 128.2, 125.3, 109.9, 37.9; HRMS (ESI) calcd for $C_{15}H_{11}N_3O_3NaS^+$ ($M+Na^+$): 336.0419, found: 336.0426.



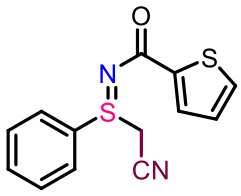
***N*-((cyanomethyl)(thiophen-2-yl)-λ^4-sulfaneylidene)benzamide (4d):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.09 (m, 2H), 7.87 (d, *J* = 5.1 Hz, 1H), 7.79 (d, *J* = 3.7 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 4.37 (d, *J* = 15.7 Hz, 1H), 4.22 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 135.6, 134.8, 134.5, 131.8, 129.7, 129.0, 128.3, 128.1, 110.7, 40.3; HRMS (ESI) calcd for $C_{13}H_{10}N_2ONaS_2^+$ ($M+Na^+$): 297.0132, found: 297.0140.



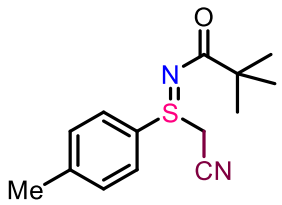
***Tert*-butyl-4-(*N*-benzoyl-*S*-(cyanomethyl)sulfinimidoyl)piperidine-1-carboxylate (4e):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), brown oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 4.41 – 4.13 (m, 3H), 4.07 (d, *J* = 16.6 Hz, 1H), 3.71 – 3.58 (m, 1H), 3.02 – 2.83 (m, 2H), 2.30 – 2.22 (m, 1H), 2.03 – 1.96 (m, 1H), 1.92 – 1.74 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 154.3, 135.4, 131.6, 128.8, 128.0, 110.8, 80.5, 52.9, 42.7, 29.6, 28.4, 26.4; HRMS (ESI) calcd for $C_{19}H_{25}N_3O_3NaS^+$ ($M+Na^+$): 398.1514, found: 398.1508.



***N*-((cyanomethyl)(phenyl)-λ⁴-sulfaneylidene)-4-(trifluoromethyl)benzamide (4f):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 2H), 8.06 – 8.00 (m, 2H), 7.76 – 7.64 (m, 5H), 4.31 (d, *J* = 15.9 Hz, 1H), 4.12 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 138.4, 134.2, 133.0 (q, *J* = 32.4 Hz), 130.5, 130.1, 129.3, 128.1, 125.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.5 Hz), 110.2, 38.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74 (s); HRMS (ESI) calcd for $C_{16}H_{11}N_2OF_3NaS^+$ ($M+Na^+$): 359.0442, found: 359.0451.

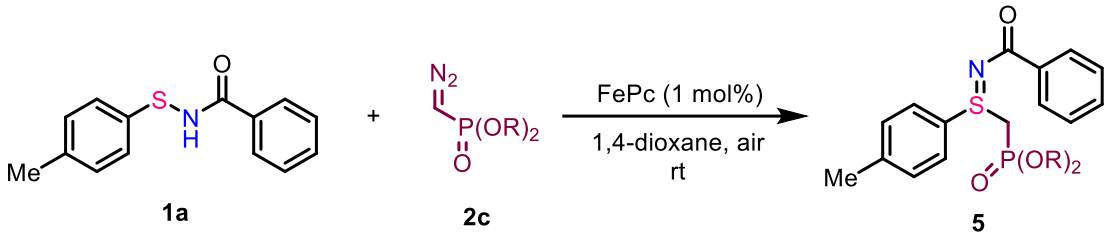


***N*-((cyanomethyl)(phenyl)-λ⁴-sulfaneylidene)thiophene-2-carboxamide (4g):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), brown solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.78 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.74 – 7.60 (m, 3H), 7.44 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.07 (dd, *J* = 4.9, 3.7 Hz, 1H), 4.24 (d, *J* = 15.9 Hz, 1H), 4.13 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ172.7, 140.2, 134.0, 131.1, 130.6, 130.4, 130.3, 128.0, 127.6, 110.4, 38.4; HRMS (ESI) calcd for $C_{13}H_{10}N_2ONaS_2^+$ ($M+Na^+$): 297.0132, found: 297.0140.

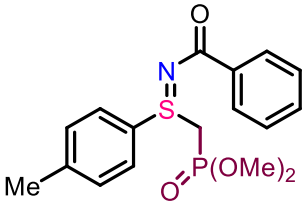


***N*-((cyanomethyl)(*p*-tolyl)-λ⁴-sulfaneylidene)pivalamide (4h):** purified by column chromatography (petroleum ether/ethyl acetate = 2:1), brown oil, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 4.27 (d, *J* = 15.8 Hz, 1H), 3.88 (d, *J* = 15.8 Hz, 1H), 2.45 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz,

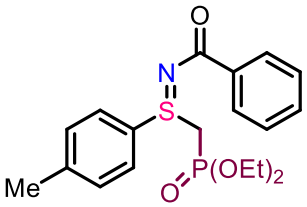
$CDCl_3$) δ 191.7, 144.8, 130.9, 128.0, 127.4, 110.4, 40.3, 37.8, 28.5, 21.6; HRMS (ESI) calcd for $C_{14}H_{18}N_2ONaS^+$ ($M+Na^+$): 285.1038, found: 285.1043.



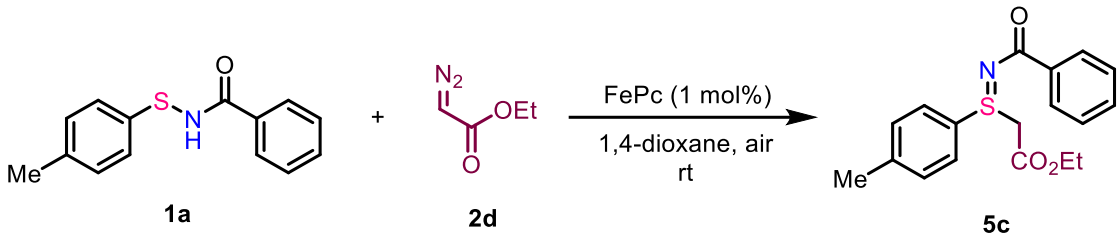
To a solution of sulfenamide **1a** (0.2 mmol, 1.0 equiv) and FePc (0.002 mmol, 1 mol%) in analytical 1,4-dioxane (2 mL) was added diazomethylphosphonate **2c** (0.3 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature under an air atmosphere. After completion of reaction as monitored by TLC analysis, the mixture was evaporated and the residue was purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give the corresponding product **5**.



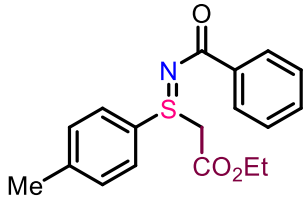
Dimethyl-((*N*-benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)methyl)phosphonate (5a): purified by column chromatography (petroleum ether/ethyl acetate = 1:1), colorless oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.10 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.33 (m, 5H), 4.12 – 4.00 (m, 1H), 3.73 (dd, *J* = 11.3, 5.7 Hz, 6H), 3.45 – 3.33 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 143.8, 136.0, 131.0, 130.8 (d, *J* = 3.8 Hz), 130.5, 128.7, 128.0, 127.9, 53.5 (d, *J* = 6.3 Hz), 44.3 (d, *J* = 140.1 Hz), 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.11 – 17.12 (m); HRMS (ESI) calcd for $C_{17}H_{20}NO_4NaSP^+$ ($M+Na^+$): 388.0748, found: 388.0747.



Diethyl-((*N*-benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)methyl)phosphonate (5b): purified by column chromatography (petroleum ether/ethyl acetate = 1:1), colorless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.12 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.40 – 7.32 (m, 4H), 4.18 – 3.99 (m, 5H), 3.38 (dd, *J* = 14.4, 13.7 Hz, 1H), 2.41 (s, 3H), 1.26 (dt, *J* = 7.1, 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.7, 136.1, 130.9, 130.4, 128.7, 128.1, 127.8, 63.24 (d, *J* = 6.3 Hz), 63.21 (d, *J* = 6.4 Hz), 45.0 (d, *J* = 139.6 Hz), 21.6, 16.2 (d, *J* = 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.09 – 14.31 (m); HRMS (ESI) calcd for $C_{19}H_{24}NO_4NaSP^+$ ($M+Na^+$): 416.1061, found: 416.1066.

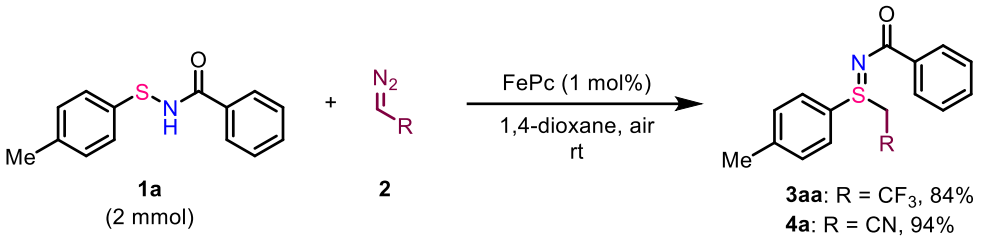


To a solution of sulfenamide **1a** (0.2 mmol, 1.0 equiv) and FePc (0.002 mmol, 1 mol%) in analytical 1,4-dioxane (2 mL) was added ethyl diazoacetate **2d** (0.22 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 10 minutes under an air atmosphere. After completion of reaction as monitored by TLC analysis, the mixture was evaporated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding product **5c**.



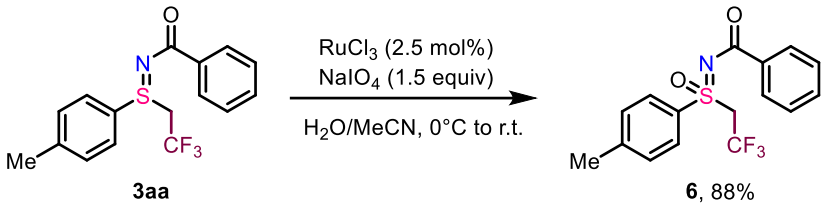
Ethyl-2-(*N*-benzoyl-*S*-(*p*-tolyl)sulfinimidoyl)acetate (5c): purified by column chromatography (petroleum ether/ethyl acetate = 2:1), colorless oil, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 2H), 7.83 – 7.76 (m, 2H), 7.47 – 7.42 (m, 1H), 7.41 – 7.31 (m, 4H), 4.39 (d, *J* = 14.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.87 (d, *J* = 14.4 Hz, 1H), 2.42 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 164.2, 143.7, 136.1, 130.9, 130.6, 130.1, 128.8, 127.8, 127.8, 62.4, 53.1, 21.6, 14.0; HRMS (ESI) calcd for $C_{18}H_{20}NO_3S^+$ ($M+H^+$): 330.1158, found: 330.1159.

3. Scale-Up Experiment



To a solution of *N*-(*p*-tolylthio)benzamide **1a** (2 mmol, 1.0 equiv) and FePc (0.02 mmol, 1 mol%) in analytical 1,4-dioxane (10 mL) was added diazo compound **2** (2.2 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature under an air atmosphere. After completion of reaction as monitored by TLC analysis, the mixture was purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the corresponding product.

4. Transformation of Sulfilimine



To a solution of **3aa** (1.6 mmol, 1.0 equiv) in MeCN (16 mL) was added a predissolved solution of $NaIO_4$ (2.4 mmol, 1.5 equiv) in H_2O (40 mL). This solution was cooled to 0 ℃, and then $RuCl_3$ (0.04 mmol, 2.5 mol%) was added. After the reaction mixture was stirred at room temperature for 2 hours. After completion of reaction as monitored by TLC analysis, the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated, and the residue was purified directly by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to give the corresponding product **6** in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.13 (m, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.38 (m, 4H), 4.69 – 4.52 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 146.3, 135.1, 133.2, 132.7, 130.4, 129.6, 128.6, 128.2, 121.2 (q, *J* = 278.1 Hz), 56.7 (q, *J* = 31.7 Hz), 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.88 (t, *J* = 8.9 Hz); HRMS (ESI) calcd for $C_{16}H_{14}NO_2F_3NaS^+$ ($M+Na^+$): 364.0595, found: 364.0595.

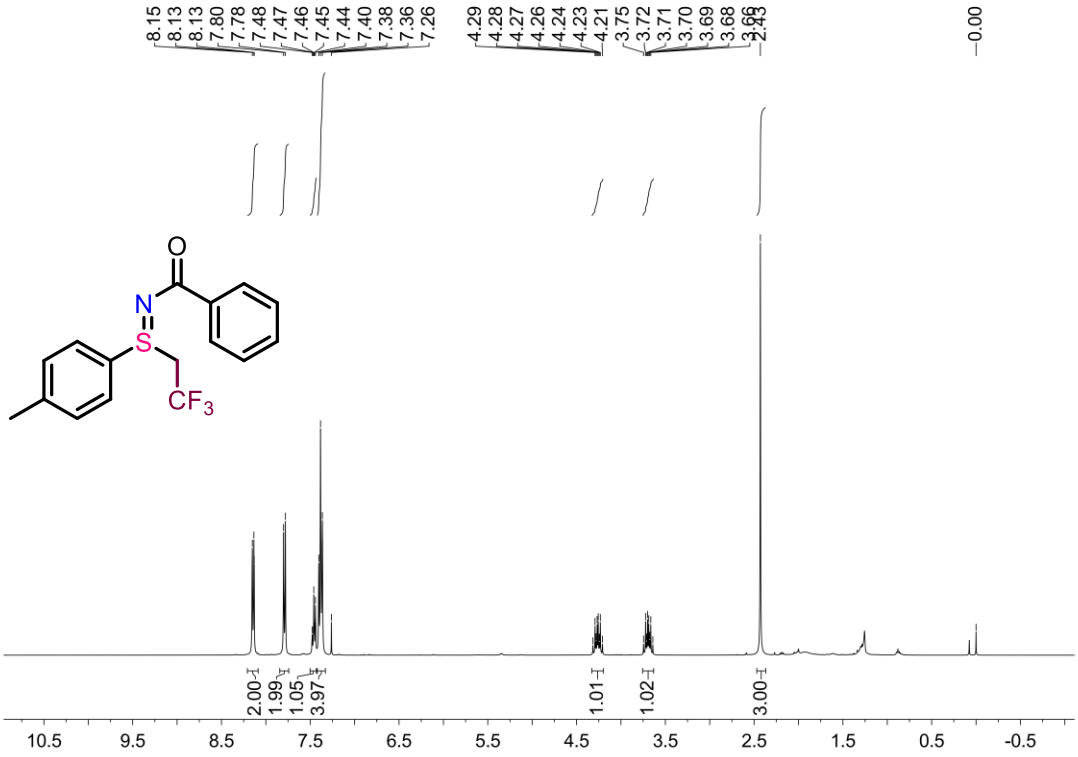
5. References

[1] (a) Liang, Q.; Wells, L. A.; Han, K. S.; Chen, M.; Kozlowski, C.; Jia, T. Synthesis of Sulfilimines Enabled by Copper-Catalyzed S-Arylation of Sulfenamides. *J. Am. Chem. Soc*. **2023**, *145*, 6310-6318. (b) Yang, G.-f.; Yuan, Y.; Tian, Y.; Zhang, S.-q.; Cui, X.; Xia, B.; Li, G.-x.; Tang, Z. Synthesis of Chiral Sulfonimidoyl Chloride via Desymmetrizing Enantioselective Hydrolysis. *J. Am. Chem. Soc.* **2023**, *145*, 5439-5446. (c) Zhou, Q.; Li, J.; Wang, T.; Yang, X. Base-Promoted S-Arylation of Sulfenamides for the Synthesis of Sulfilimines. *Org. Lett.* **2023**, *25*, 4335-4339.

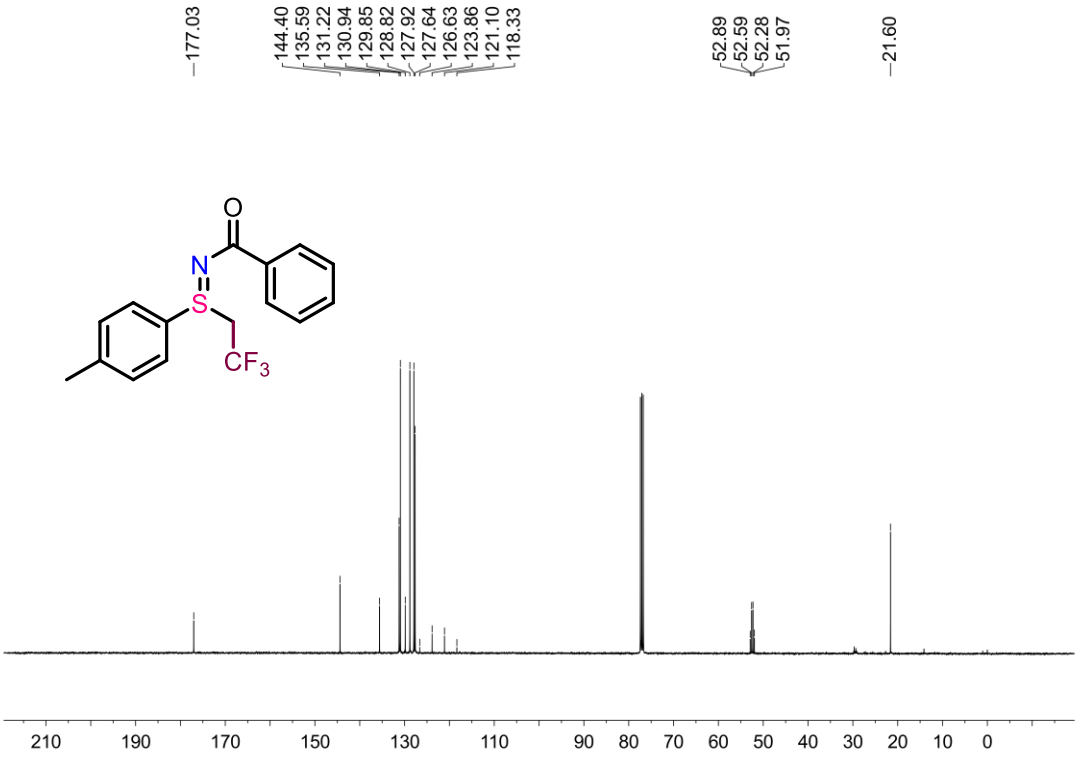
[2] (a) Hyde, S.; Veliks, J.; Liégault, B.; Grassi, D.; Taillefer, M.; Gouverneu, V. Copper-CatalyzedInsertioninto Heteroatom-Hydrogen Bonds with Trifluorodiazoalkanes, *Angew. Chem. Int. Ed.* **2016**, *55*, 3785-3789. (b) Xiao, M.; Zheng, M.; Peng, X.; Xue, X.; Zhang, F.; Ma, J. Catalytic Direct Construction of Cyano-tetrazoles. *Org. Lett*. **2020**, *22*, 7762-7767. (c) Chanthamath, S.; Ozaki, S.; Shibatomi, K.; Iwasa, S. Highly Stereoselective Synthesis of Cyclopropyl-phosphonates Catalyzed by Chiral Ru(II)-Pheox Complex. *Org. Lett.* **2014**, *16*, 3012-3015.

6. Copies of ^{1}H, ^{13}C, $^{19}F$and ^{31}P NMR Spectra

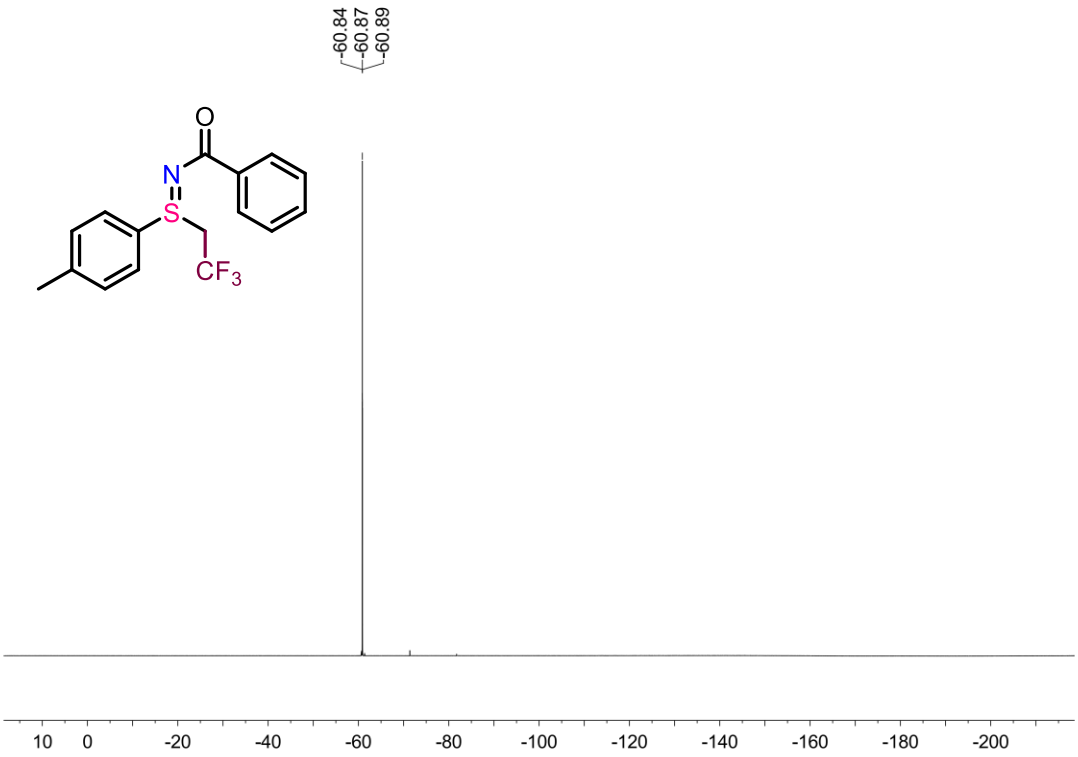
^{1}H NMR spectrum of compound **3aa** (400 MHz, $CDCl_3$)



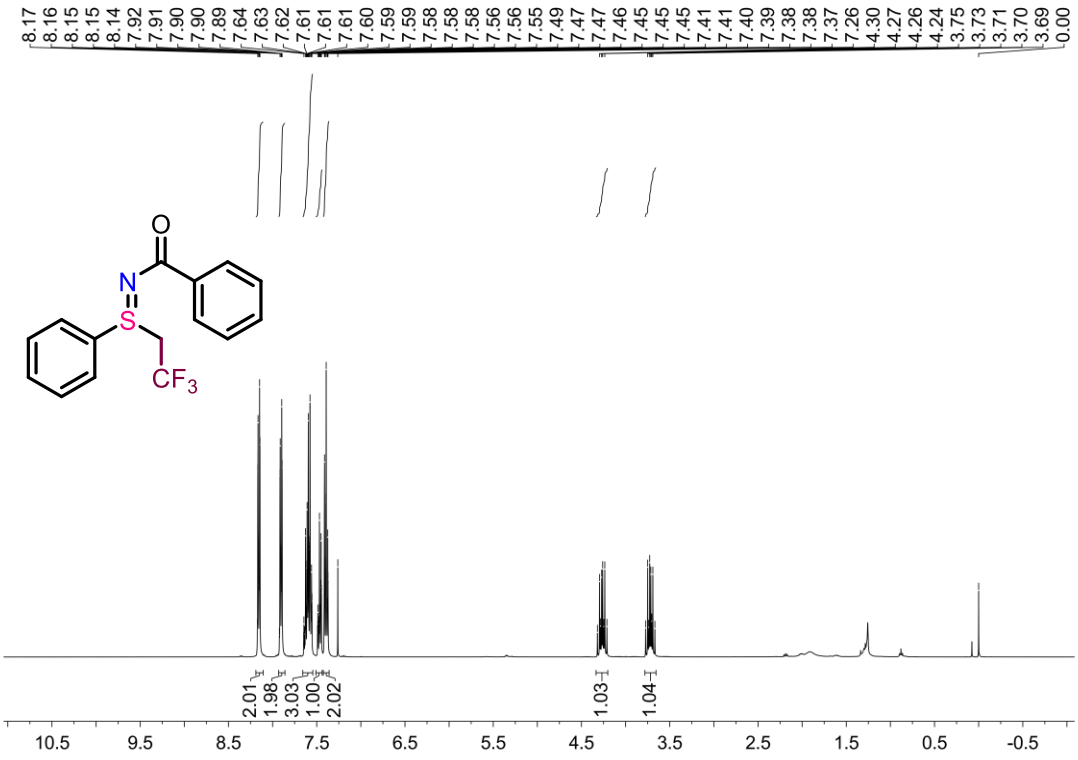
^{13}C NMR spectrum of compound **3aa** (100 MHz, $CDCl_3$)



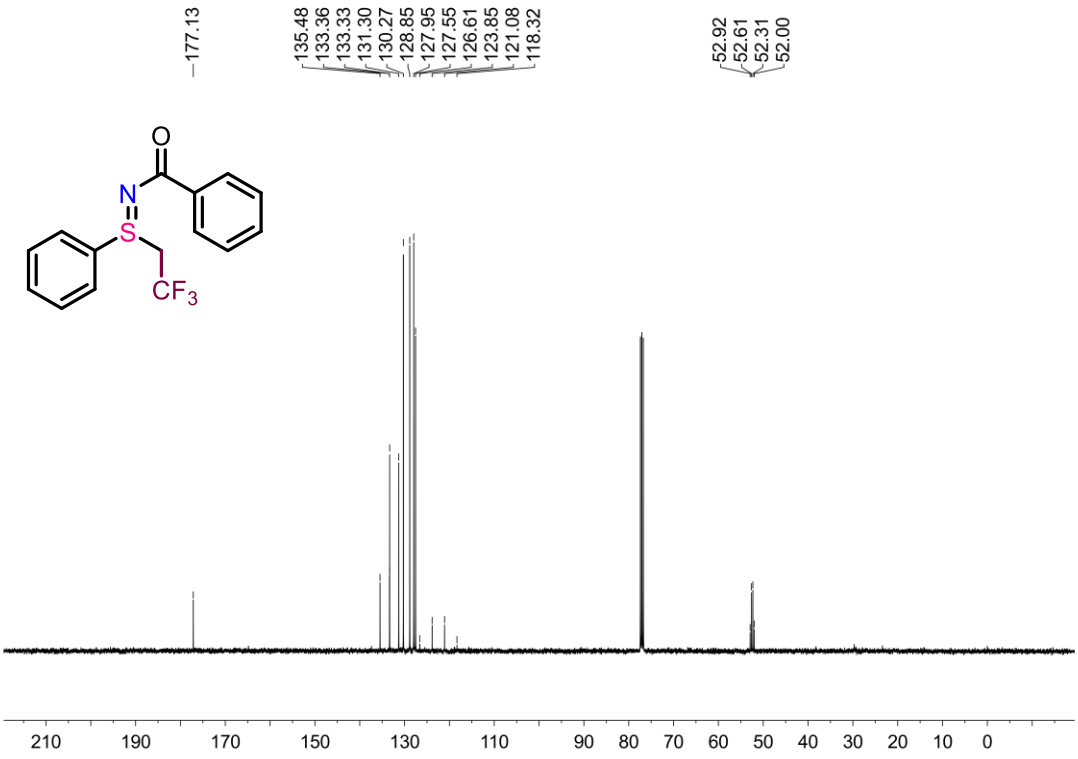
^{19}F NMR spectrum of compound **3aa** (376 MHz, $CDCl_3$)



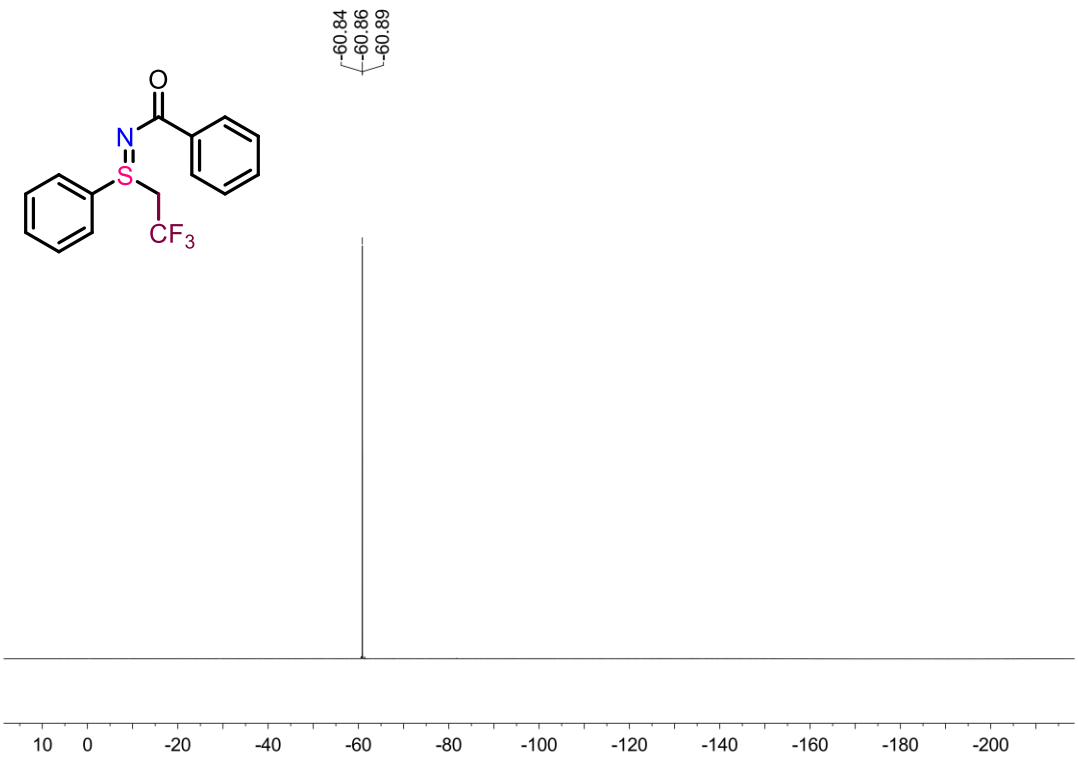
^{1}H NMR spectrum of compound **3ab** (400 MHz, $CDCl_3$)



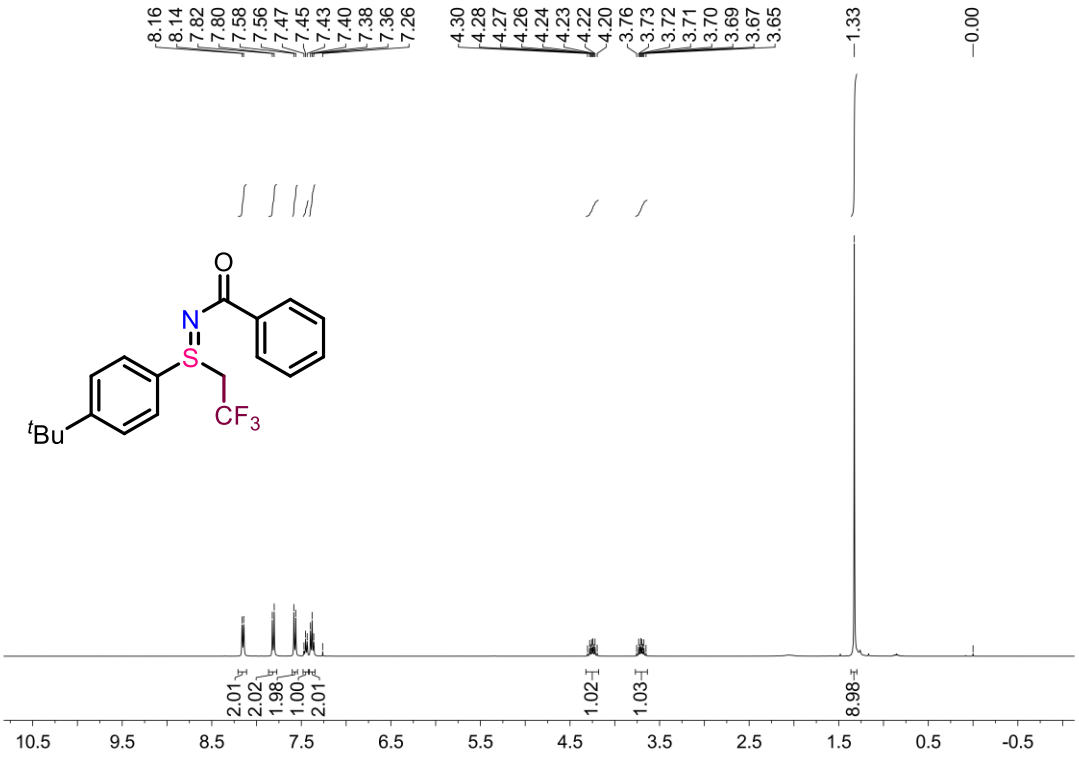
^{13}C NMR spectrum of compound **3ab** (100 MHz, $CDCl_3$)



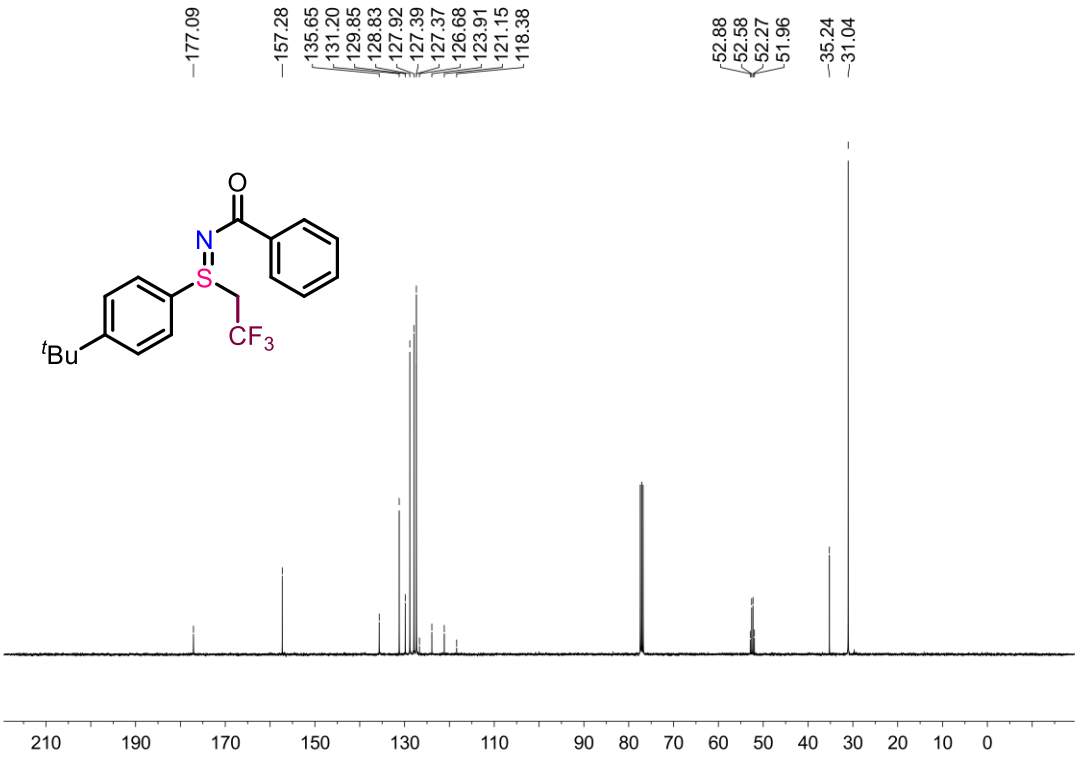
^{19}F NMR spectrum of compound **3ab** (376 MHz, $CDCl_3$)



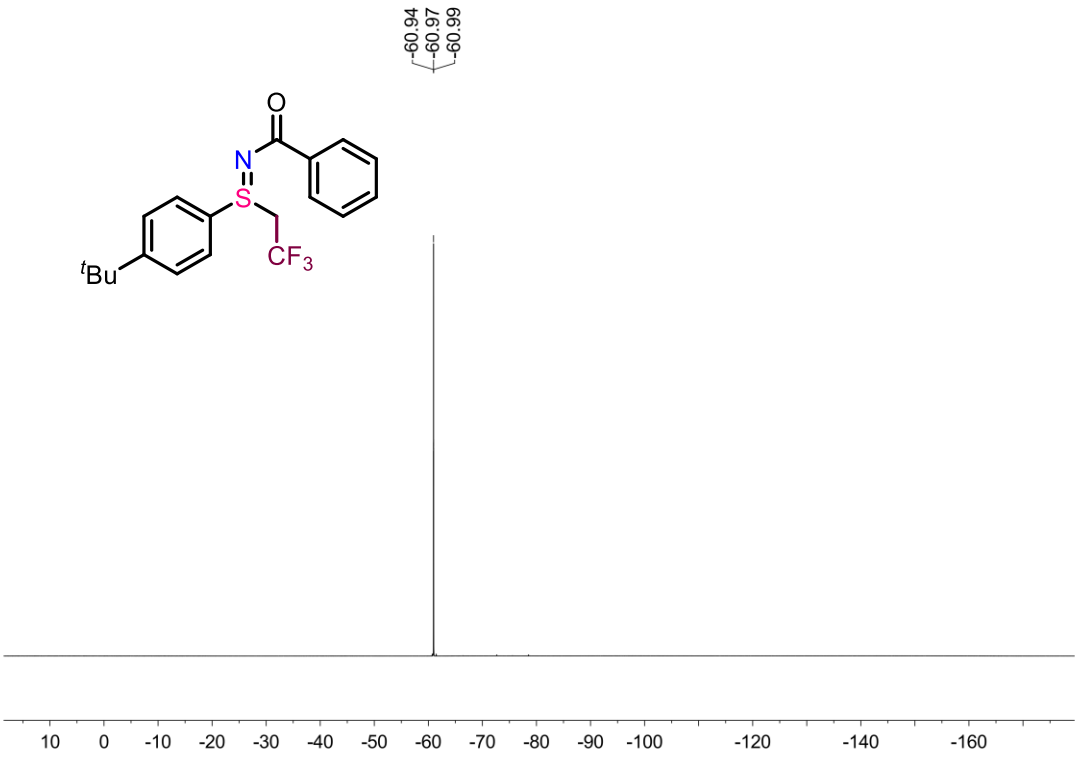
^{1}H NMR spectrum of compound **3ac** (400 MHz, $CDCl_3$)



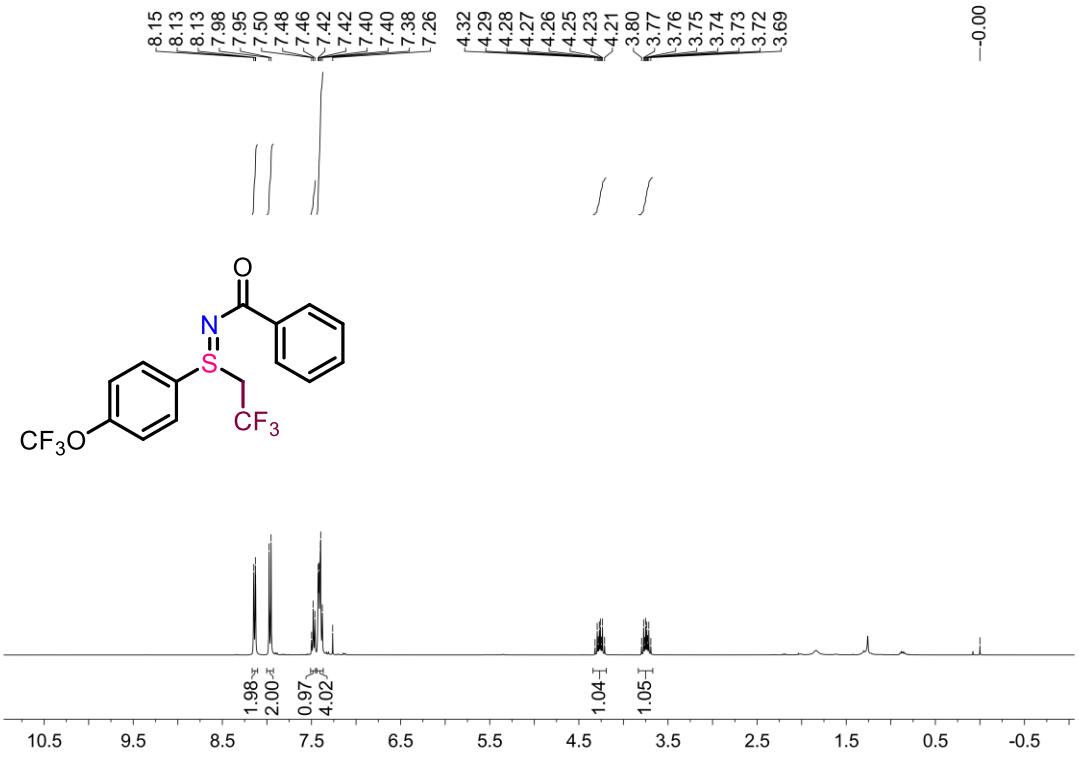
^{13}C NMR spectrum of compound **3ac** (100 MHz, $CDCl_3$)



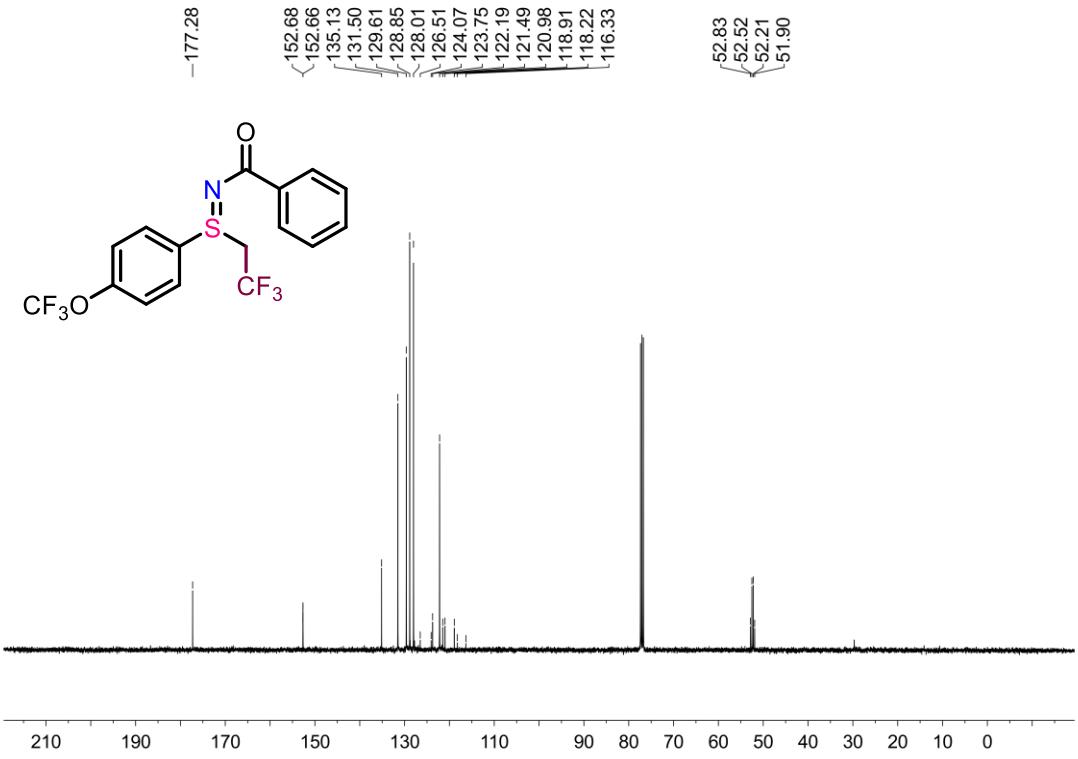
^{19}F NMR spectrum of compound **3ac** (376 MHz, $CDCl_3$)



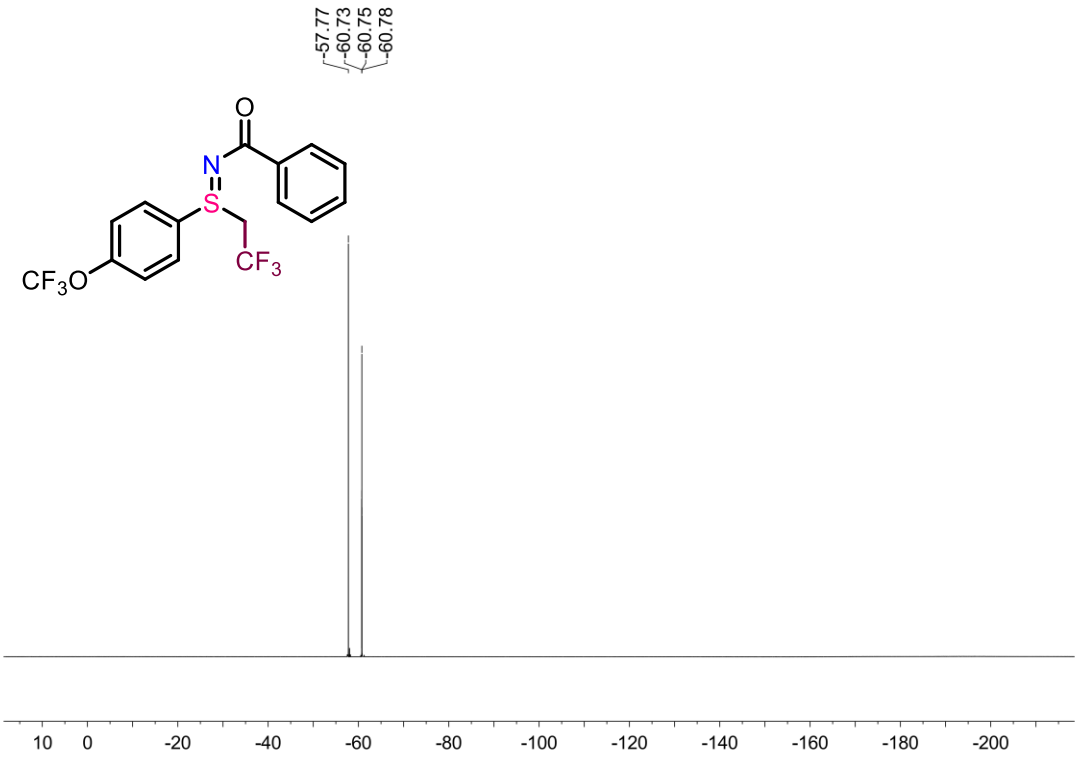
^{1}H NMR spectrum of compound **3ad** (400 MHz, $CDCl_3$)



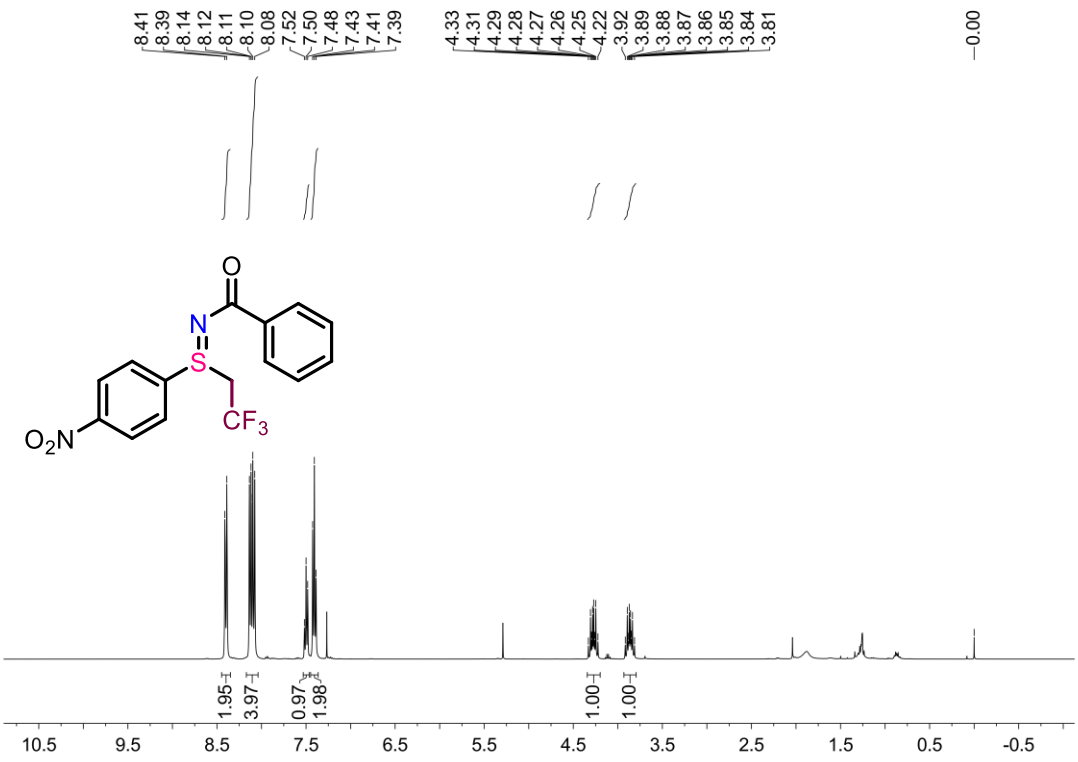
^{13}C NMR spectrum of compound **3ad** (100 MHz, $CDCl_3$)



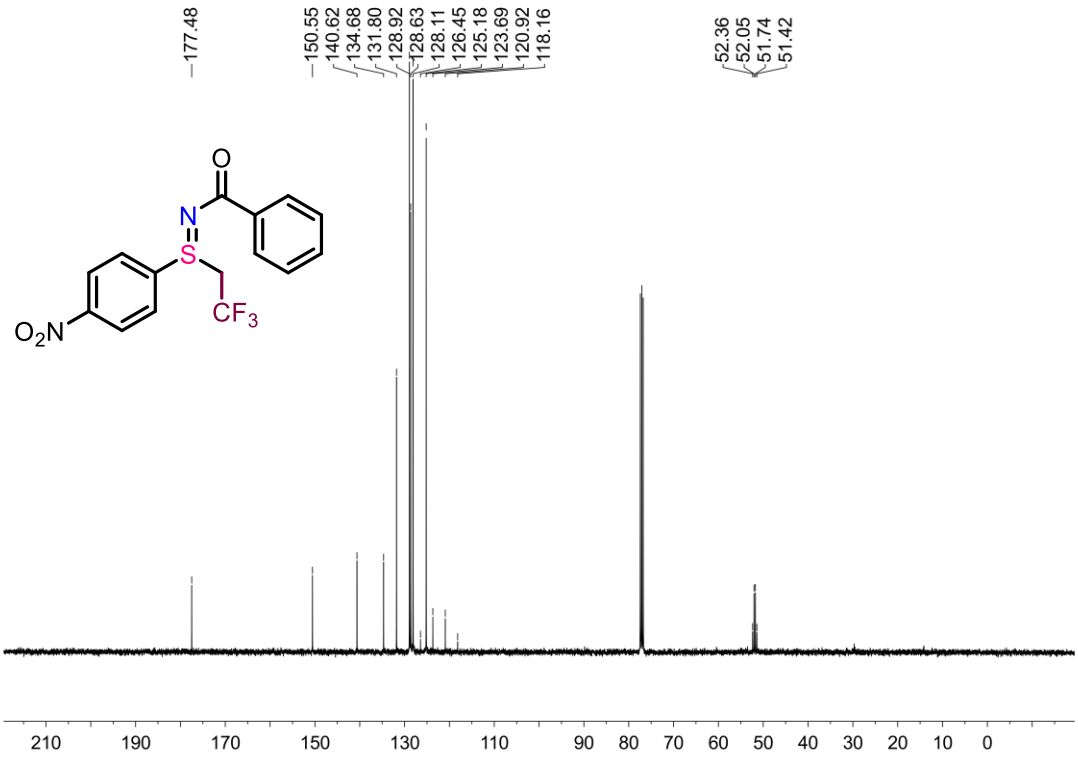
^{19}F NMR spectrum of compound **3ad** (376 MHz, $CDCl_3$)



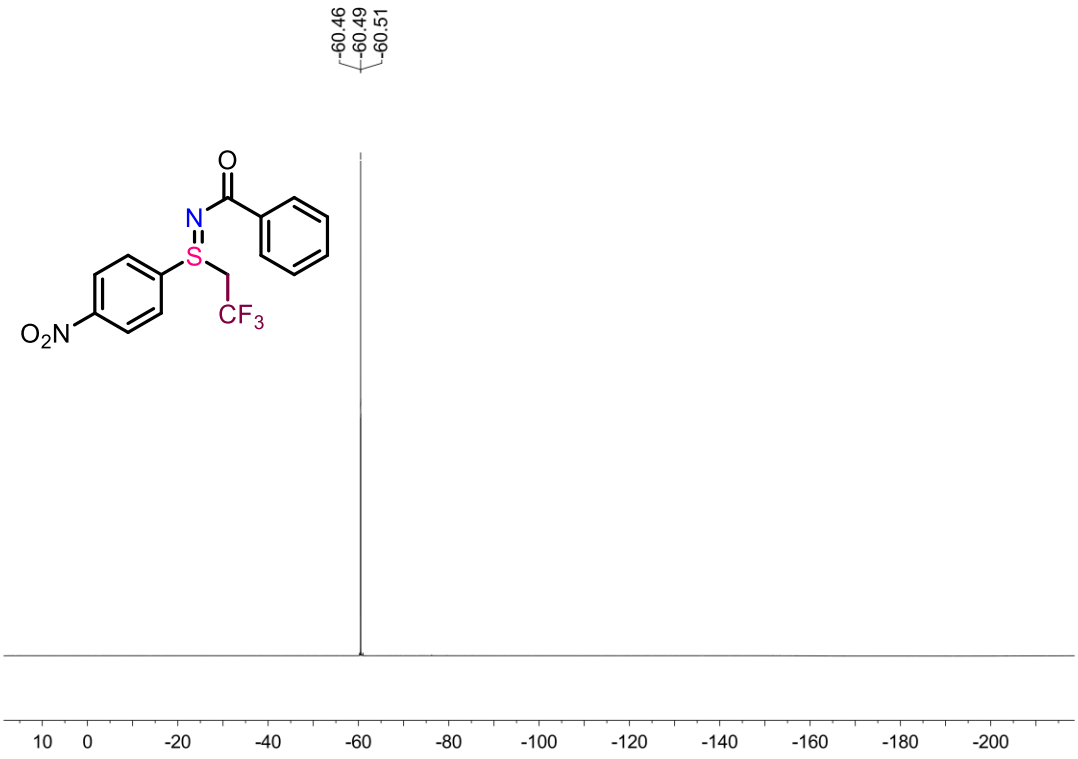
^{1}H NMR spectrum of compound **3ae** (400 MHz, $CDCl_3$)



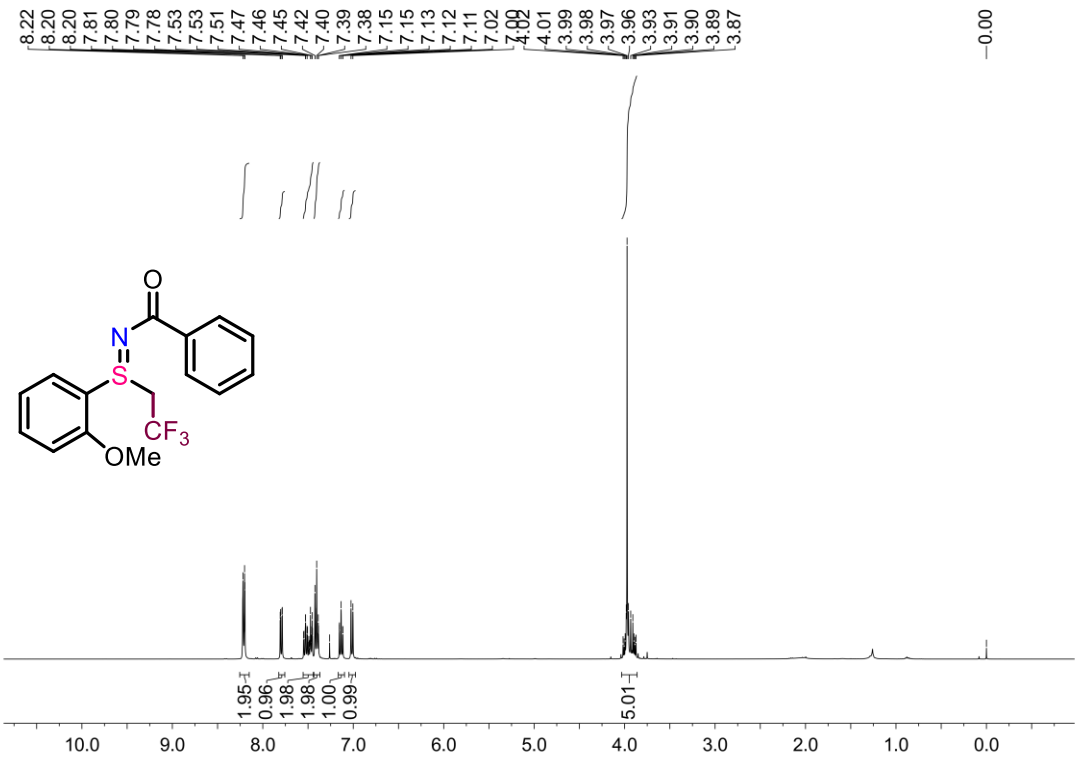
^{13}C NMR spectrum of compound **3ae** (100 MHz, $CDCl_3$)



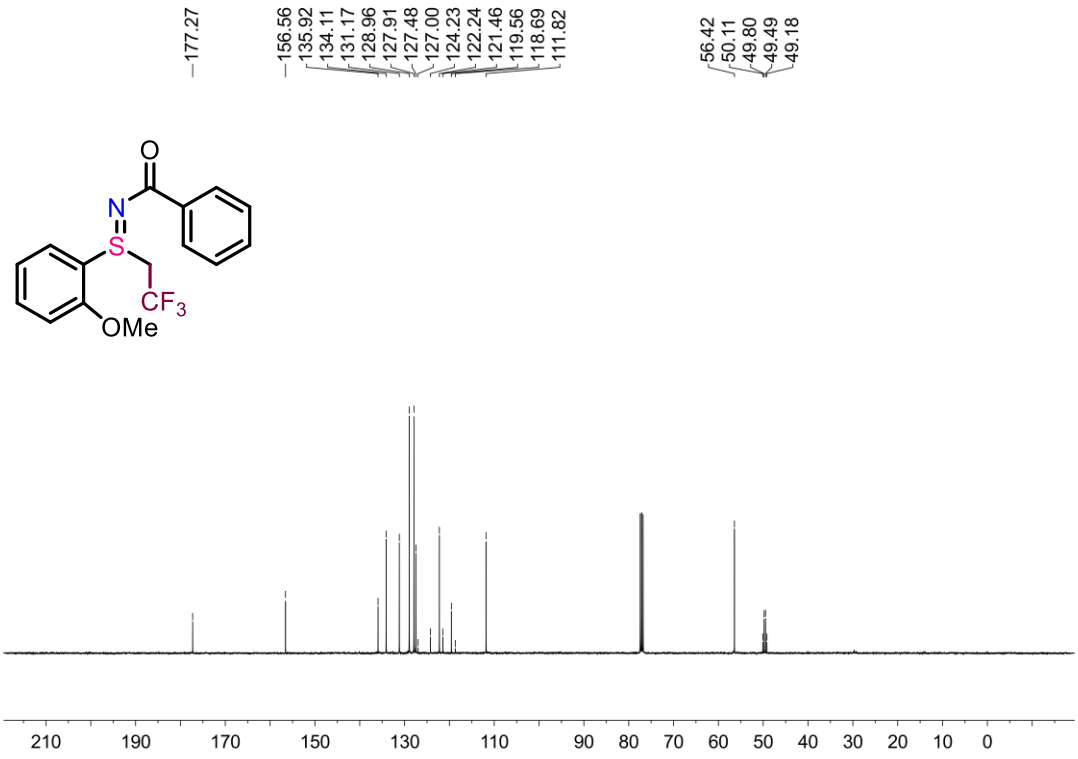
^{19}F NMR spectrum of compound **3ae** (376 MHz, $CDCl_3$)



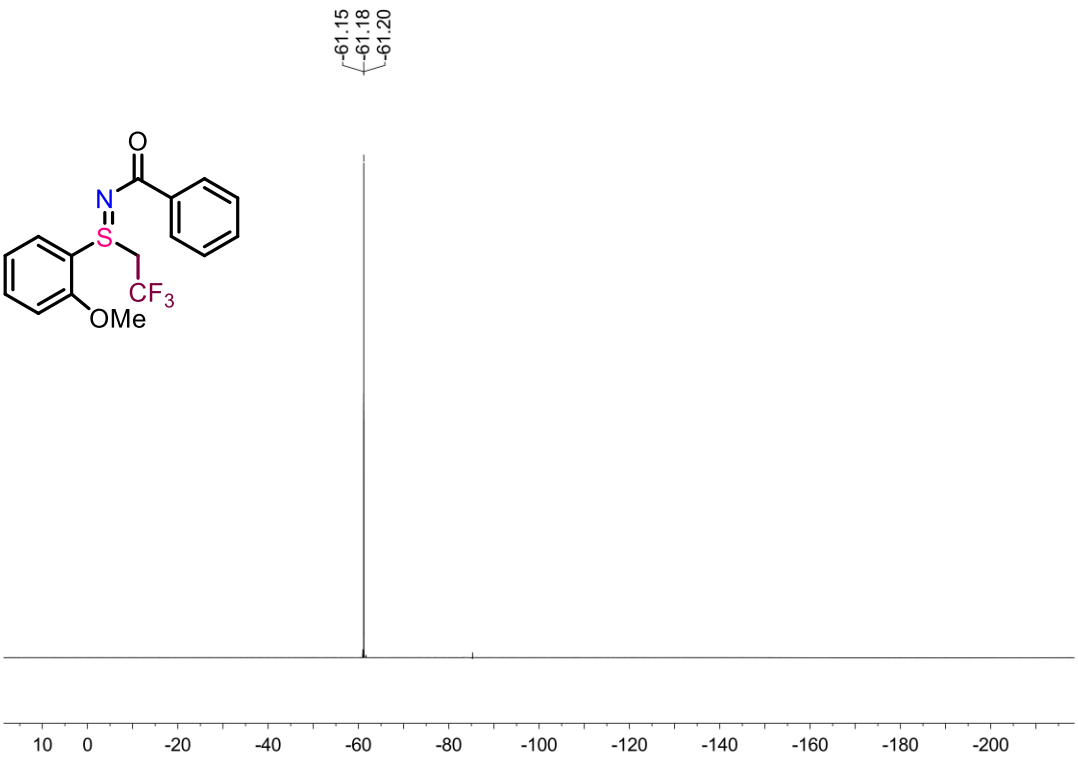
^{1}H NMR spectrum of compound **3af** (400 MHz, $CDCl_3$)



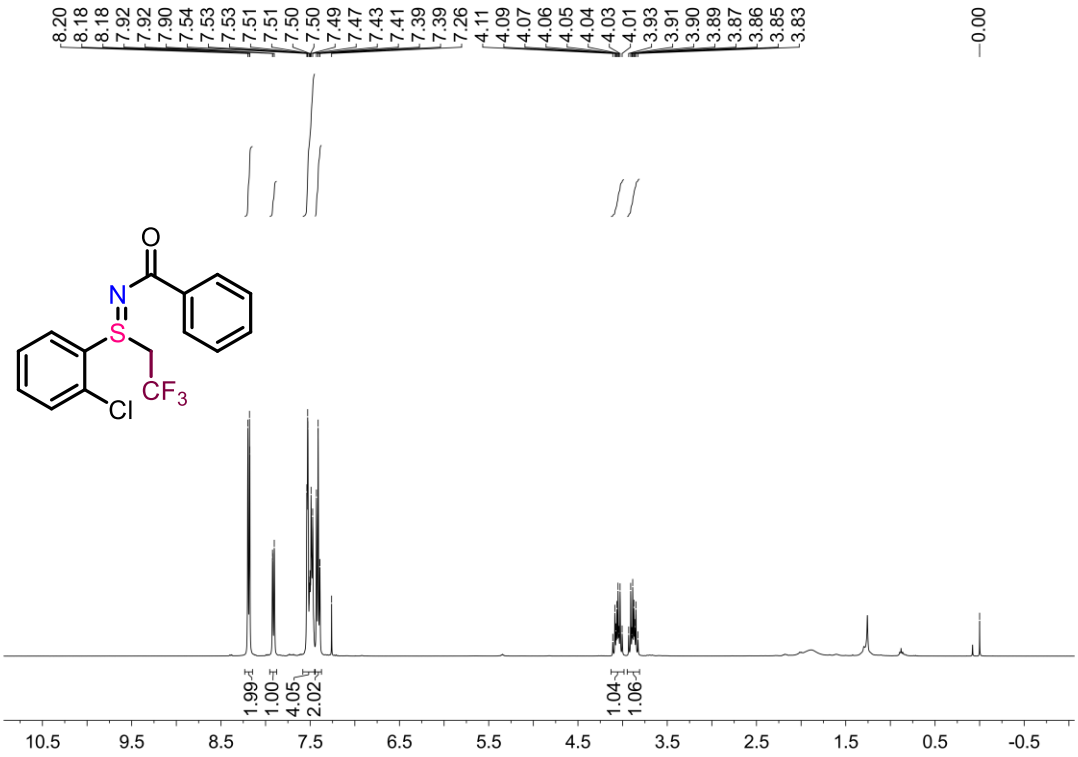
^{13}C NMR spectrum of compound **3af** (100 MHz, $CDCl_3$)



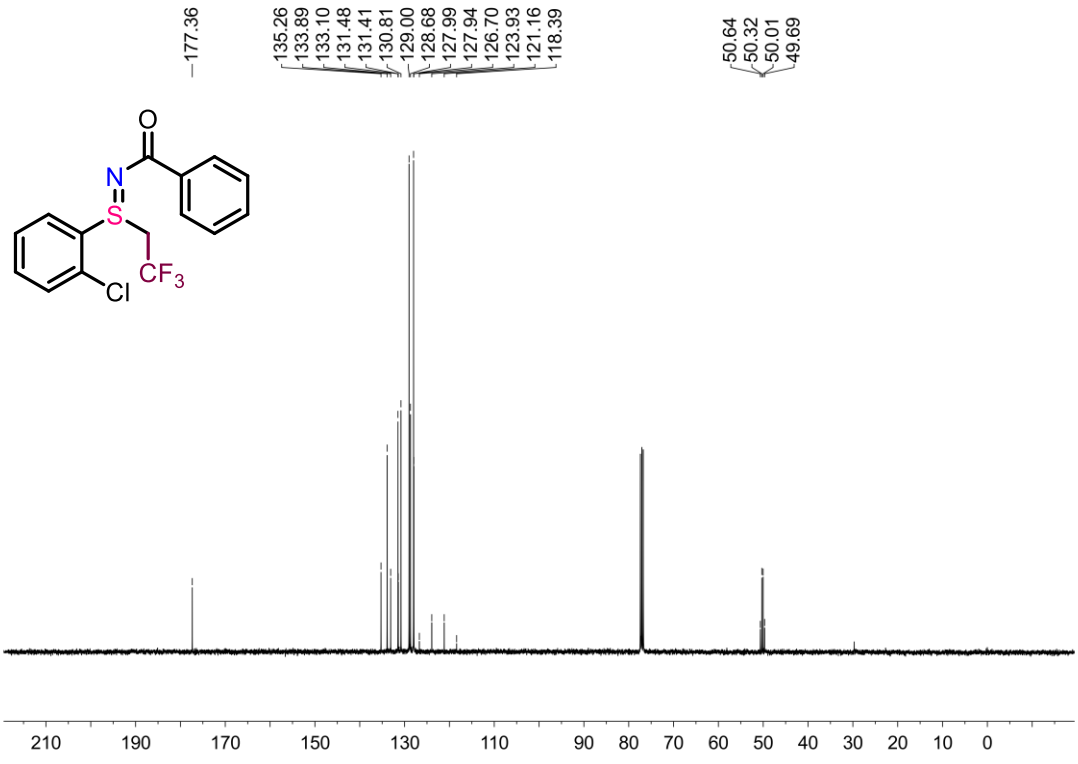
^{19}F NMR spectrum of compound **3af** (376 MHz, $CDCl_3$)



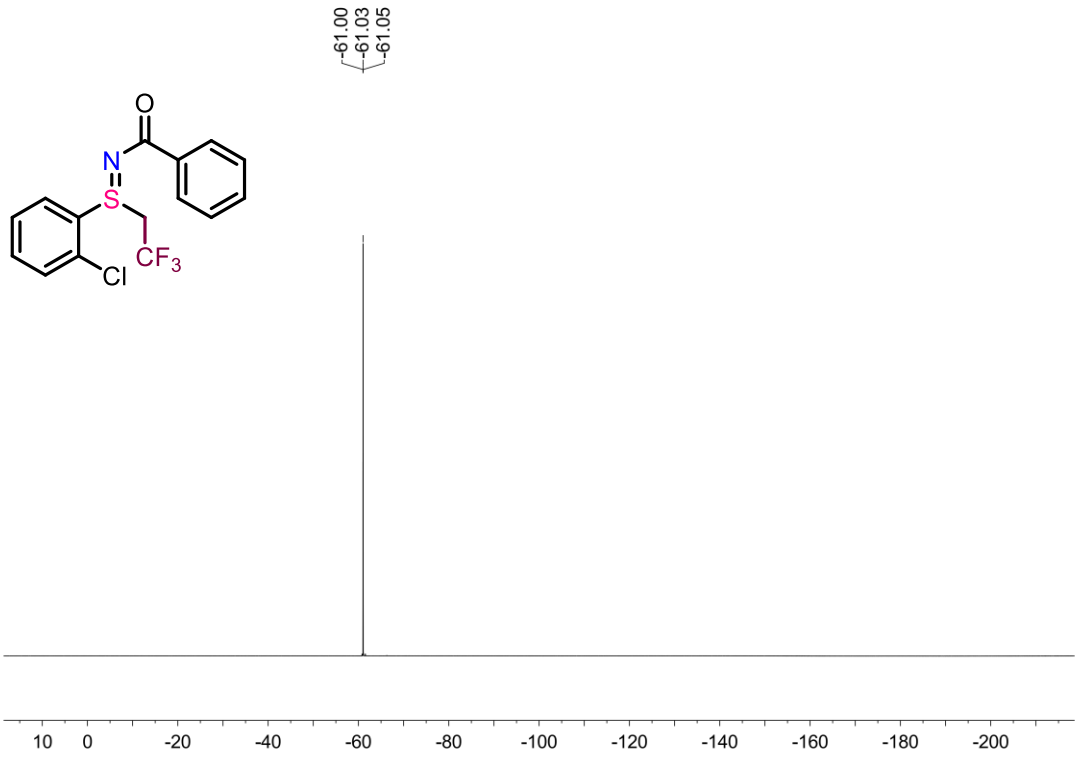
^{1}H NMR spectrum of compound **3ag** (400 MHz, $CDCl_3$)



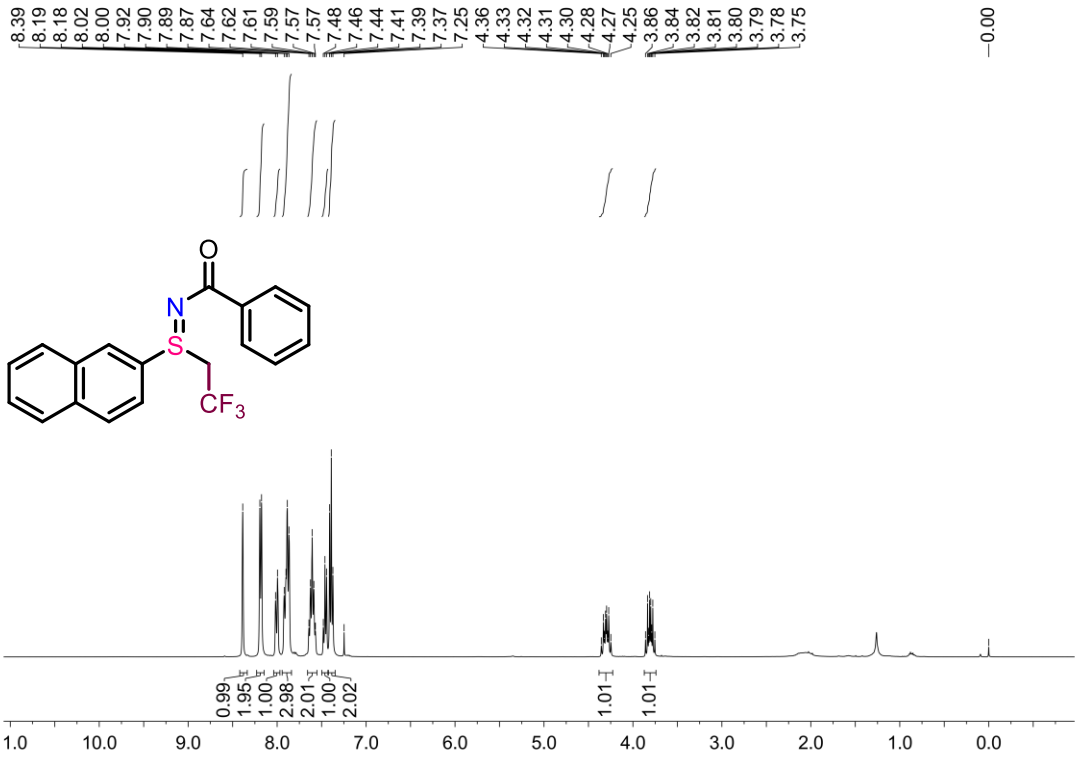
^{13}C NMR spectrum of compound **3ag** (100 MHz, $CDCl_3$)



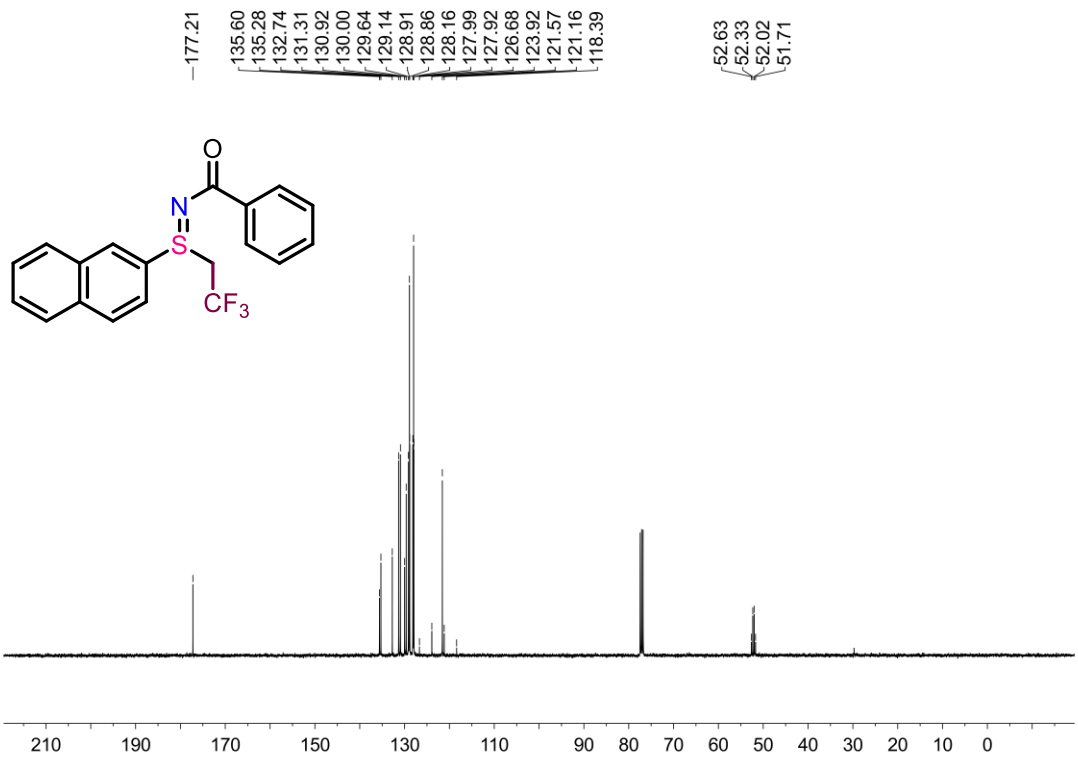
^{19}F NMR spectrum of compound **3ag** (376 MHz, $CDCl_3$)



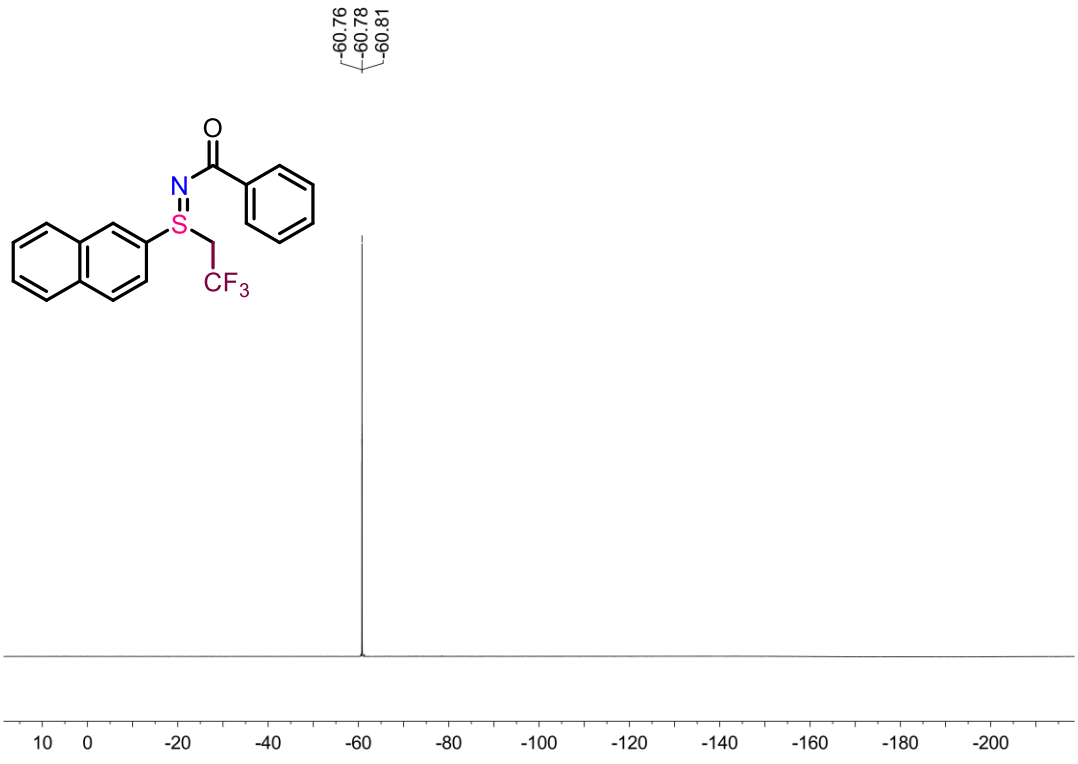
^{1}H NMR spectrum of compound **3ah** (100 MHz, $CDCl_3$)



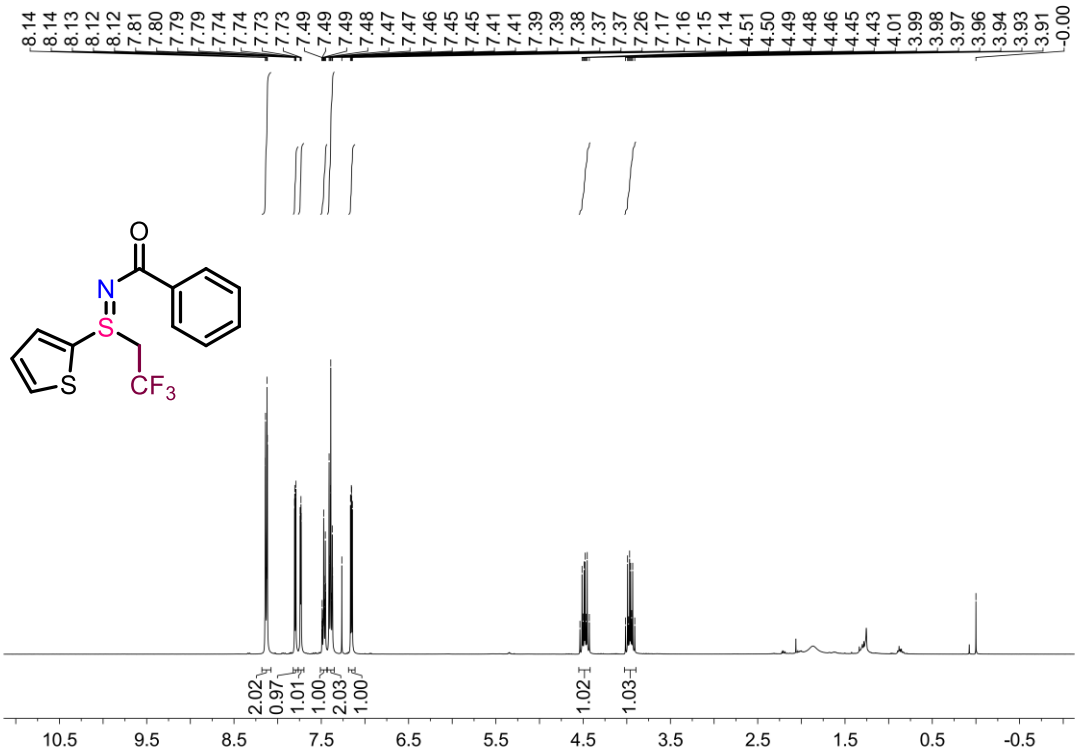
^{13}C NMR spectrum of compound **3ah** (376 MHz, $CDCl_3$)



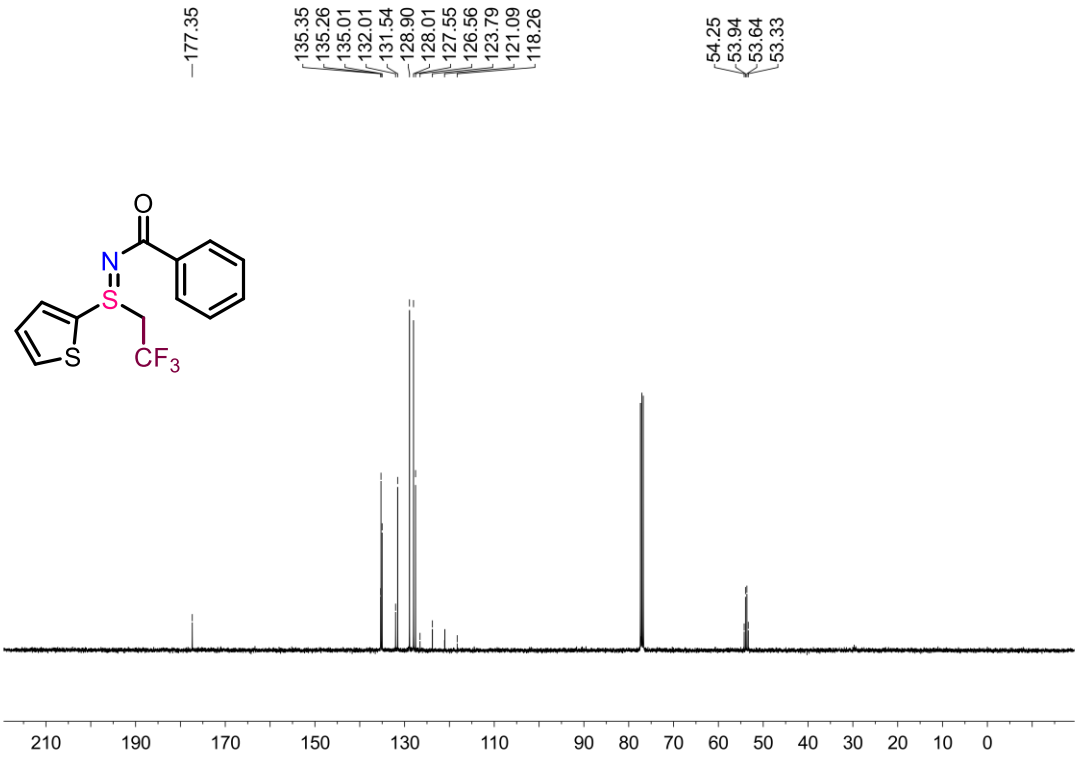
^{19}F NMR spectrum of compound **3ah** (376 MHz, $CDCl_3$)



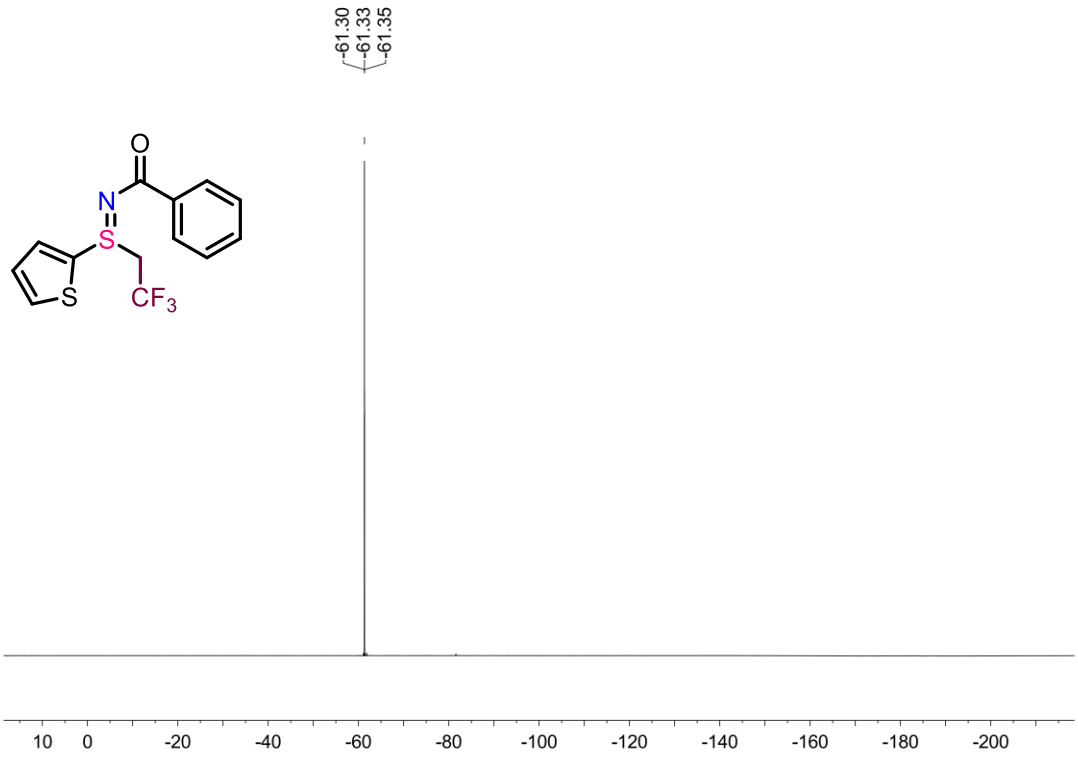
^{1}H NMR spectrum of compound **3ai** (400 MHz, $CDCl_3$)



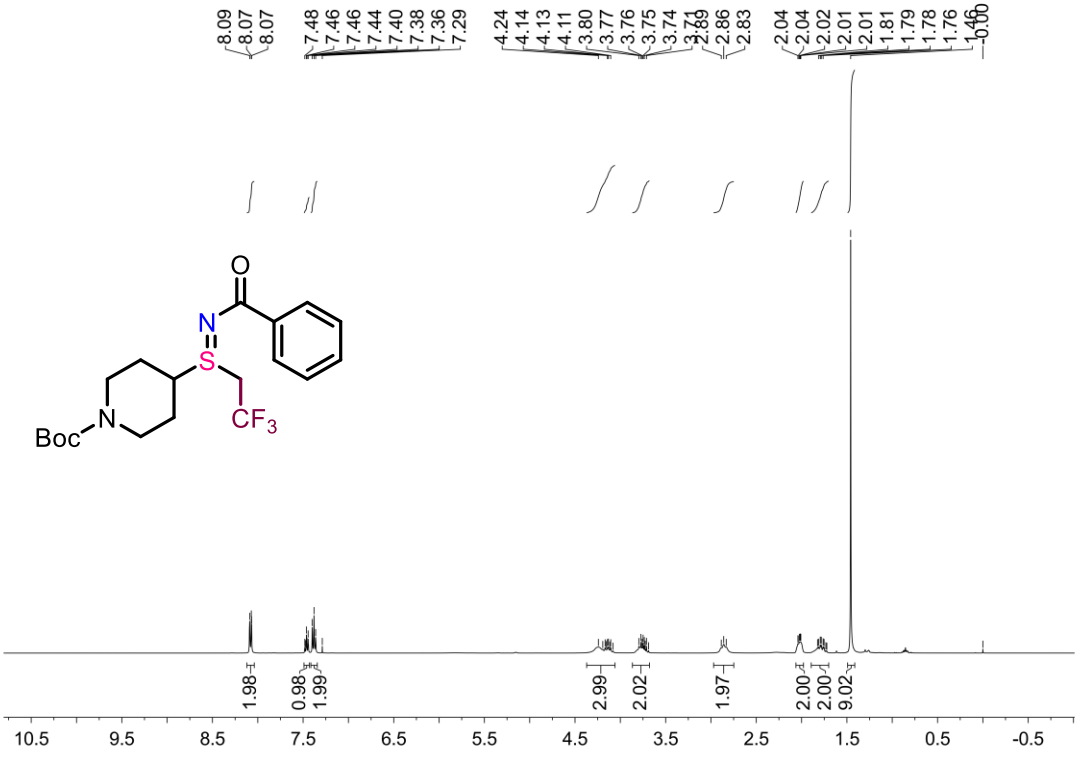
^{13}C NMR spectrum of compound **3ai** (100 MHz, $CDCl_3$)



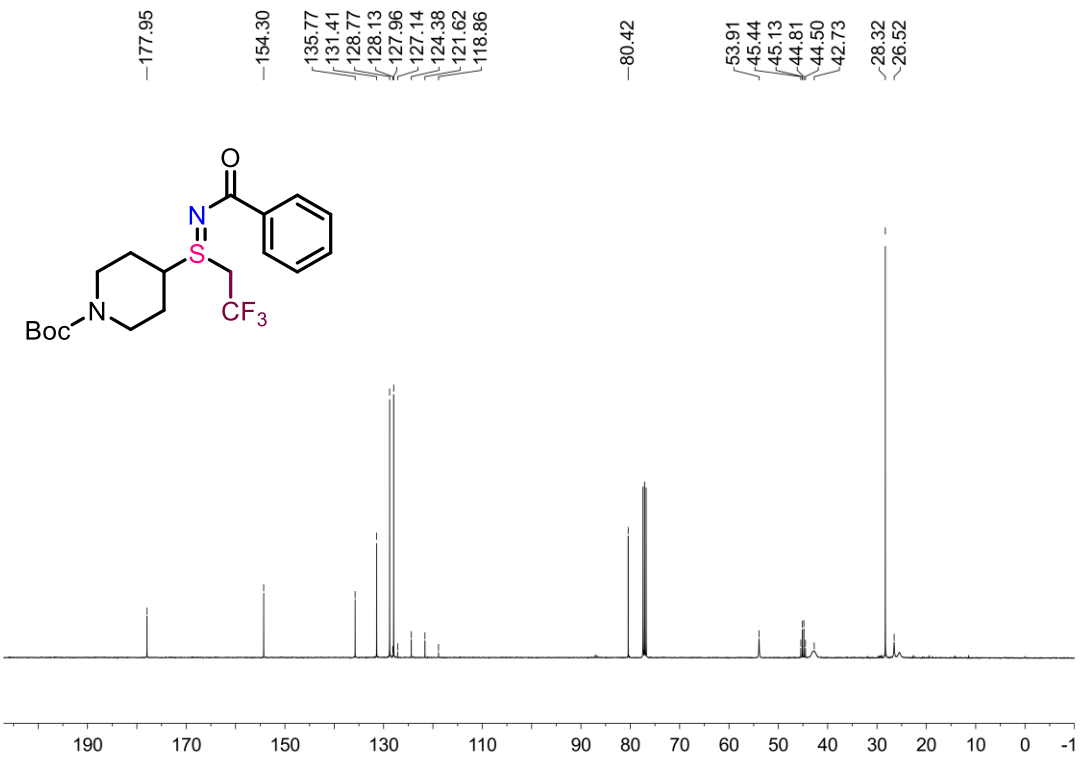
^{19}F NMR spectrum of compound **3ai** (376 MHz, $CDCl_3$)



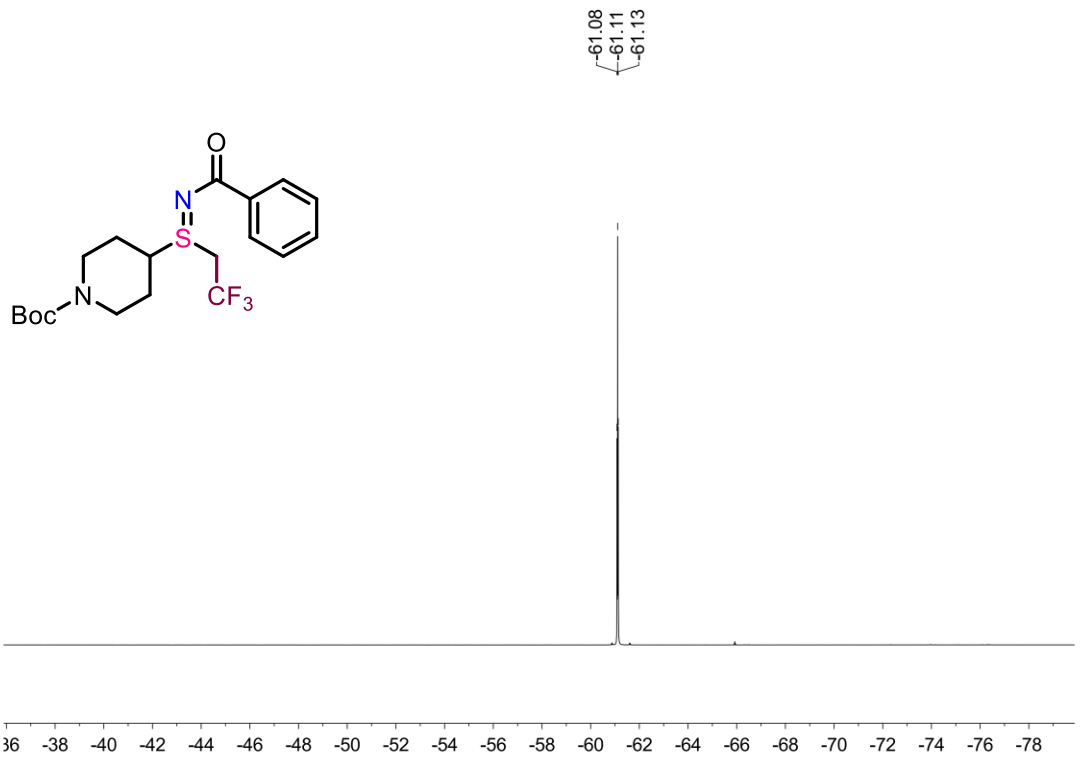
^{1}H NMR spectrum of compound **3aj** (400 MHz, $CDCl_3$)



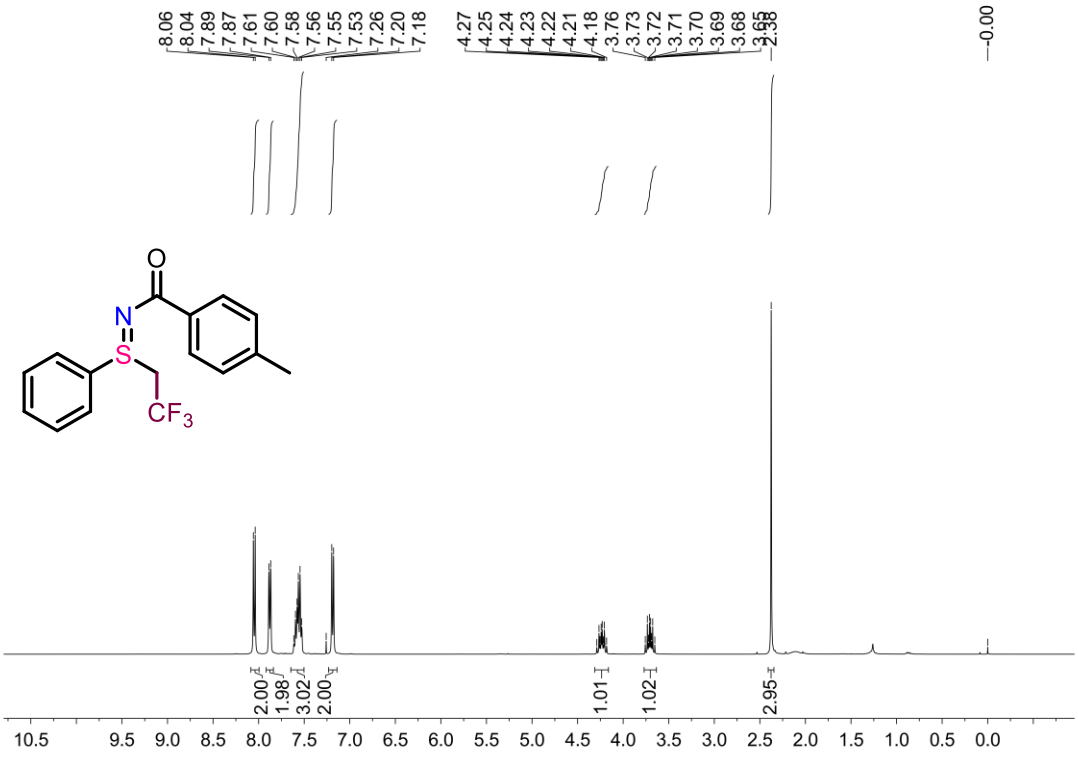
^{13}C NMR spectrum of compound **3aj** (100 MHz, $CDCl_3$)



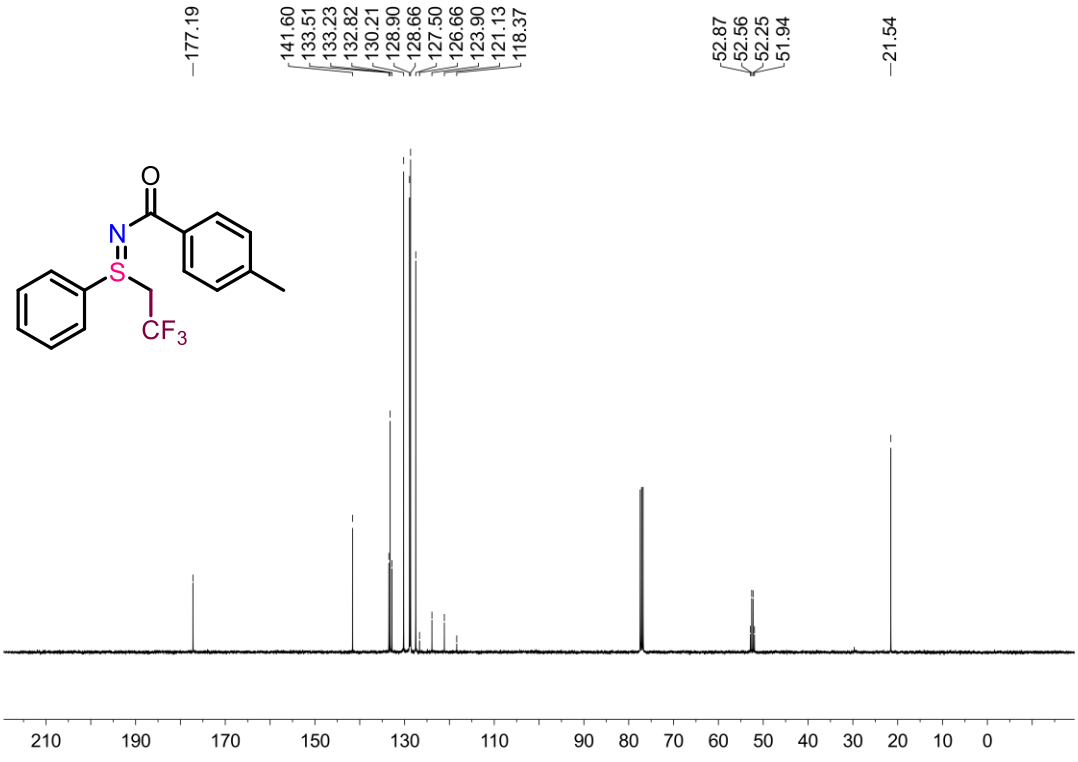
^{19}F NMR spectrum of compound **3aj** (376 MHz, $CDCl_3$)



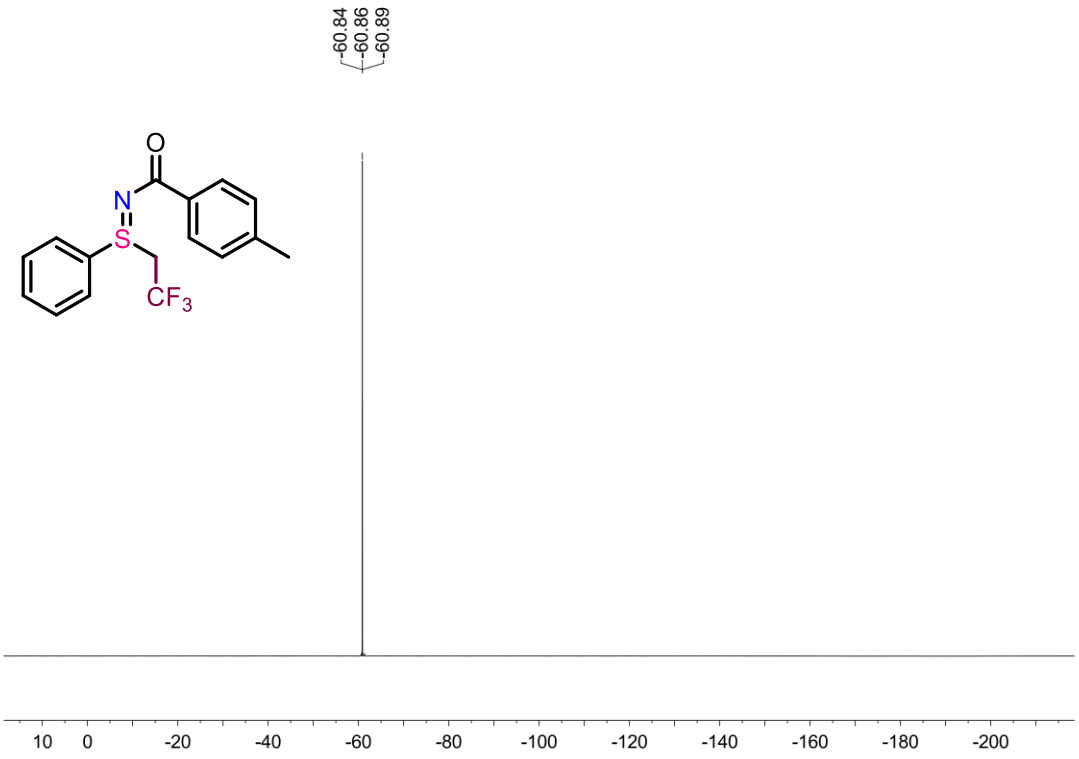
^{1}H NMR spectrum of compound **3ba** (400 MHz, $CDCl_3$)



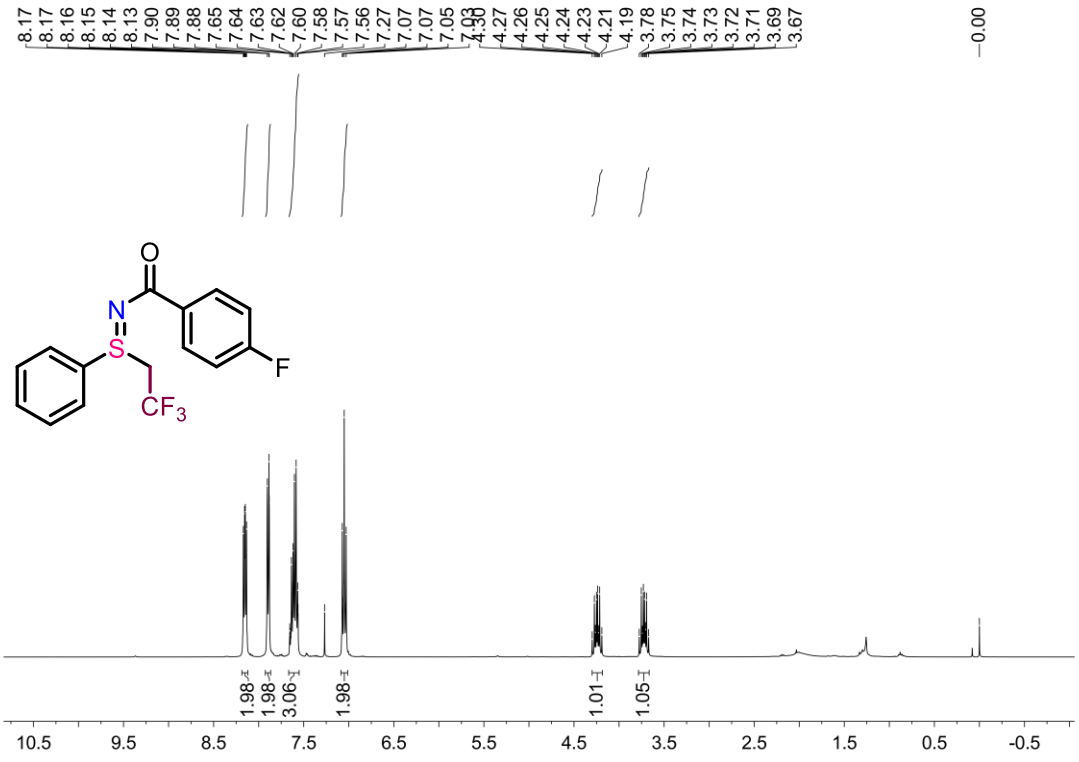
^{13}C NMR spectrum of compound **3ba** (100 MHz, $CDCl_3$)



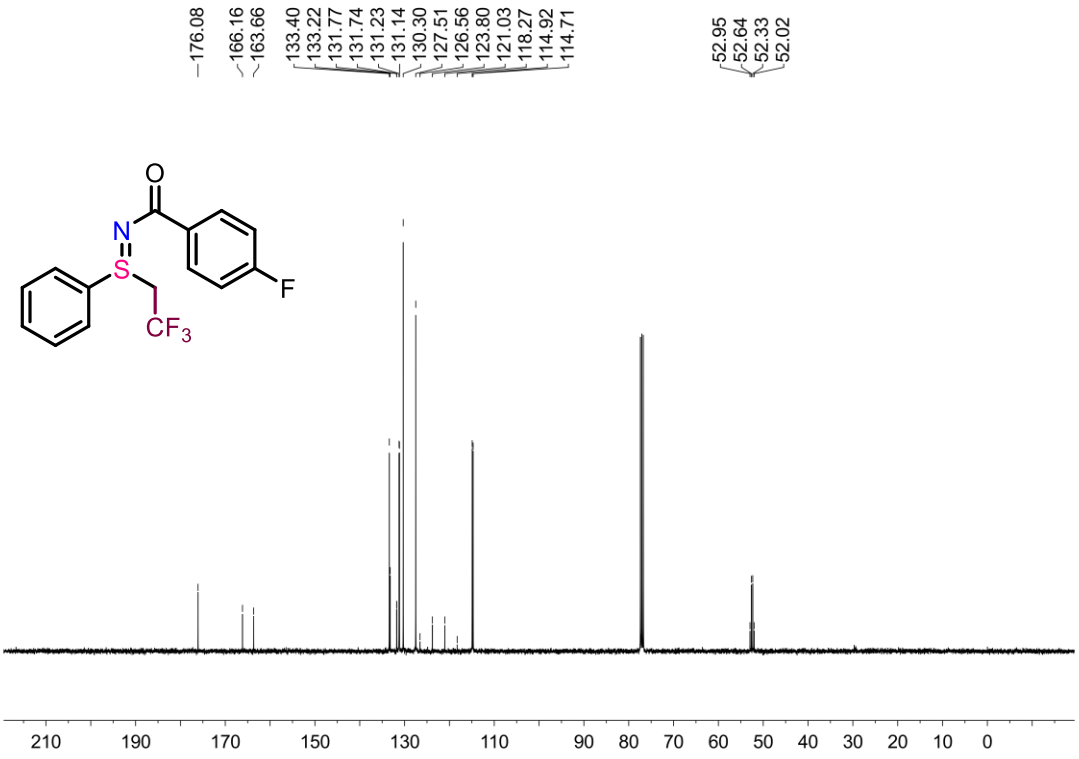
^{19}F NMR spectrum of compound **3ba** (376 MHz, $CDCl_3$)



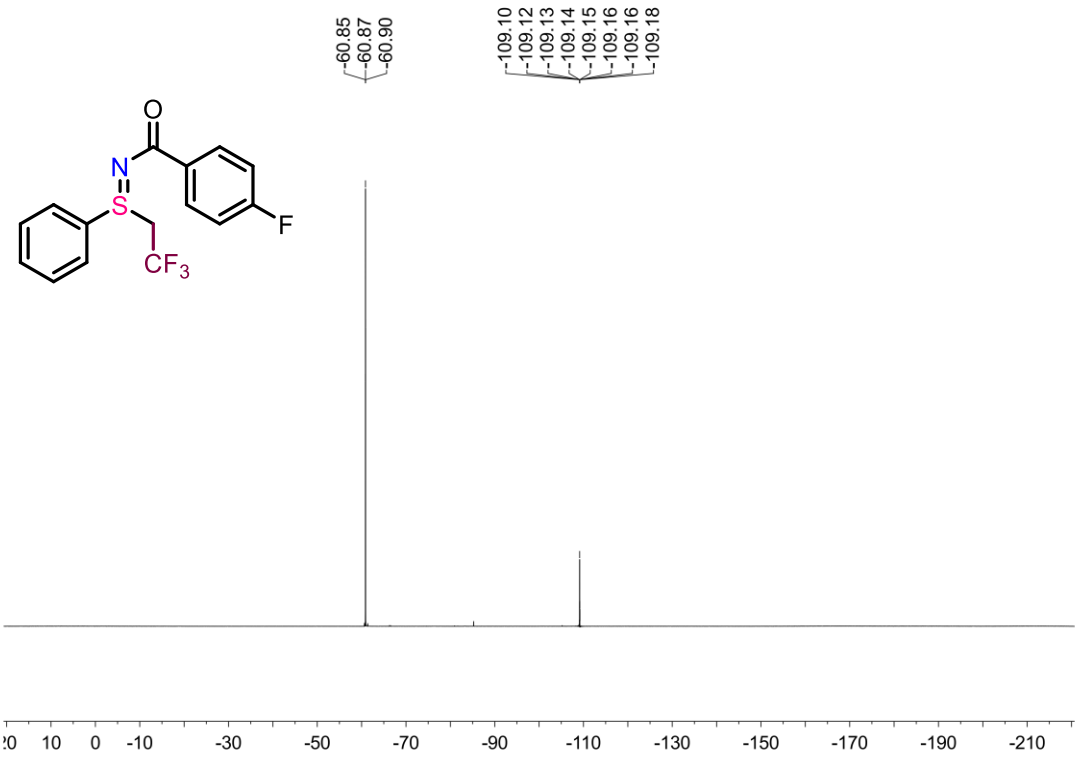
^{1}H NMR spectrum of compound **3ca** (400 MHz, $CDCl_3$)



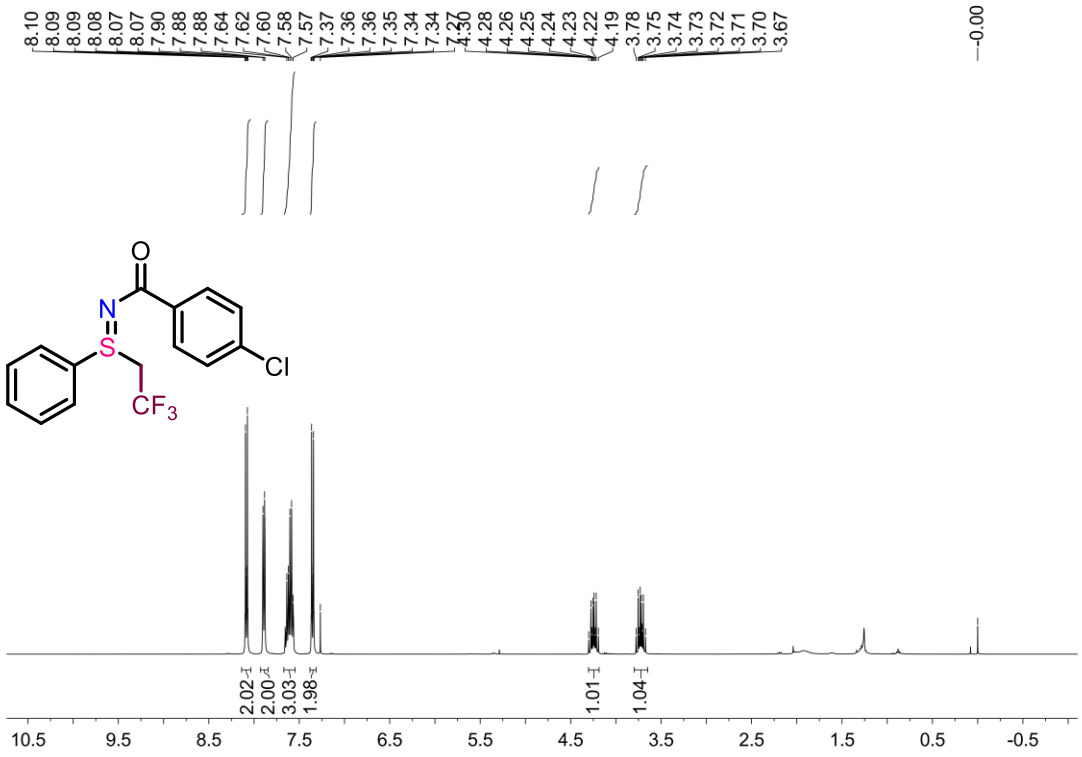
^{13}C NMR spectrum of compound **3ca** (100 MHz, $CDCl_3$)



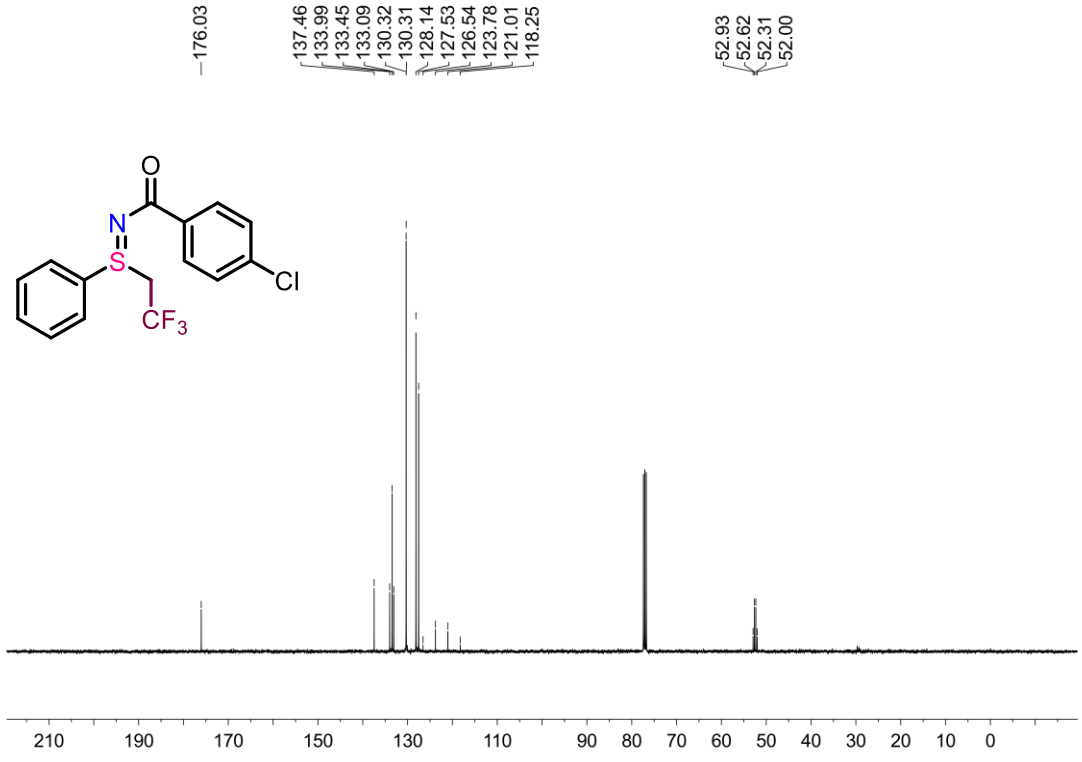
^{19}F NMR spectrum of compound **3ca** (376 MHz, $CDCl_3$)



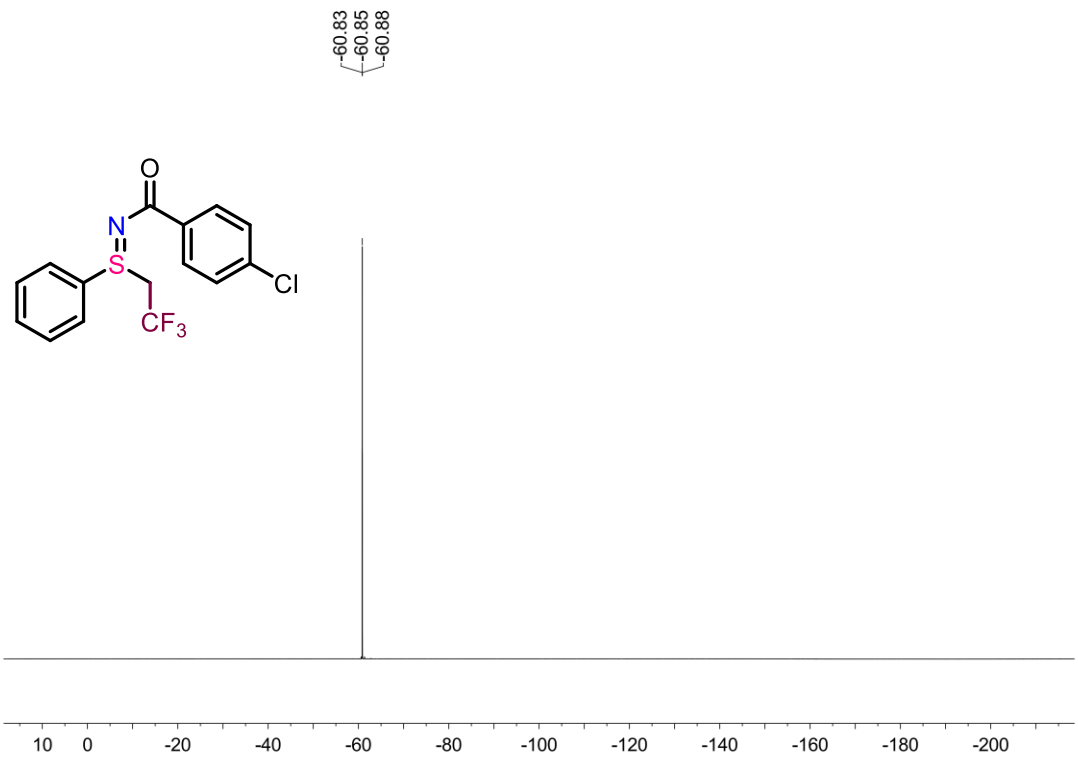
^{1}H NMR spectrum of compound **3da** (400 MHz, $CDCl_3$)



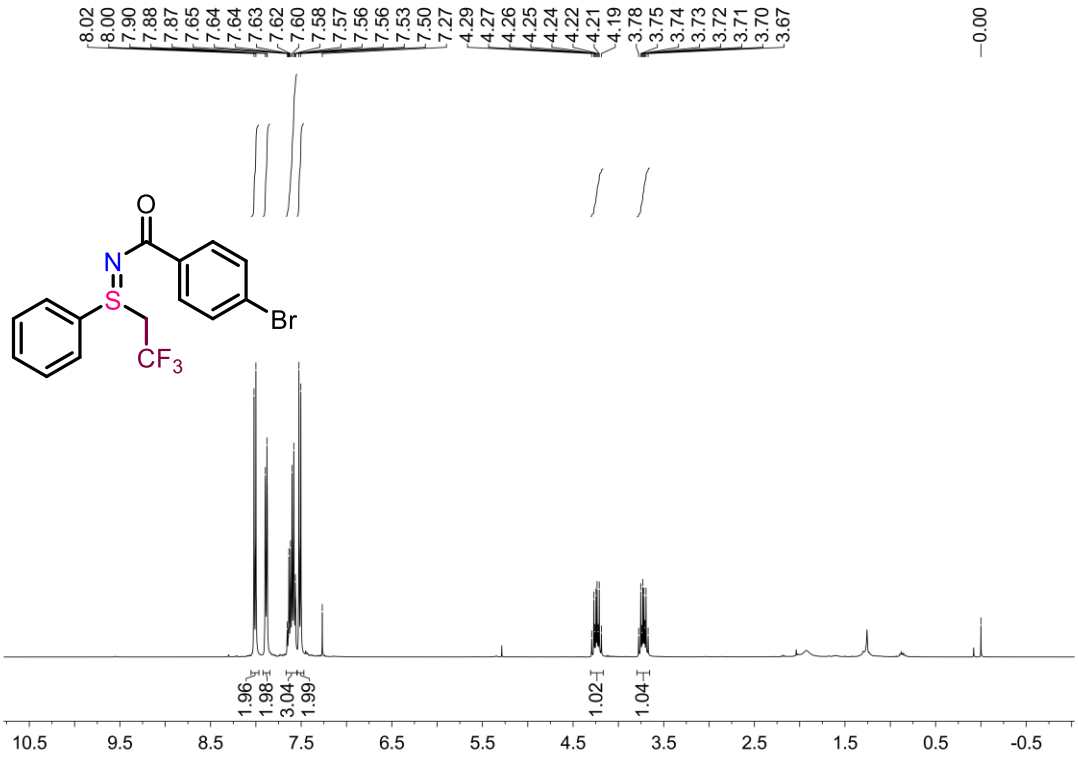
^{13}C NMR spectrum of compound **3da** (100 MHz, $CDCl_3$)



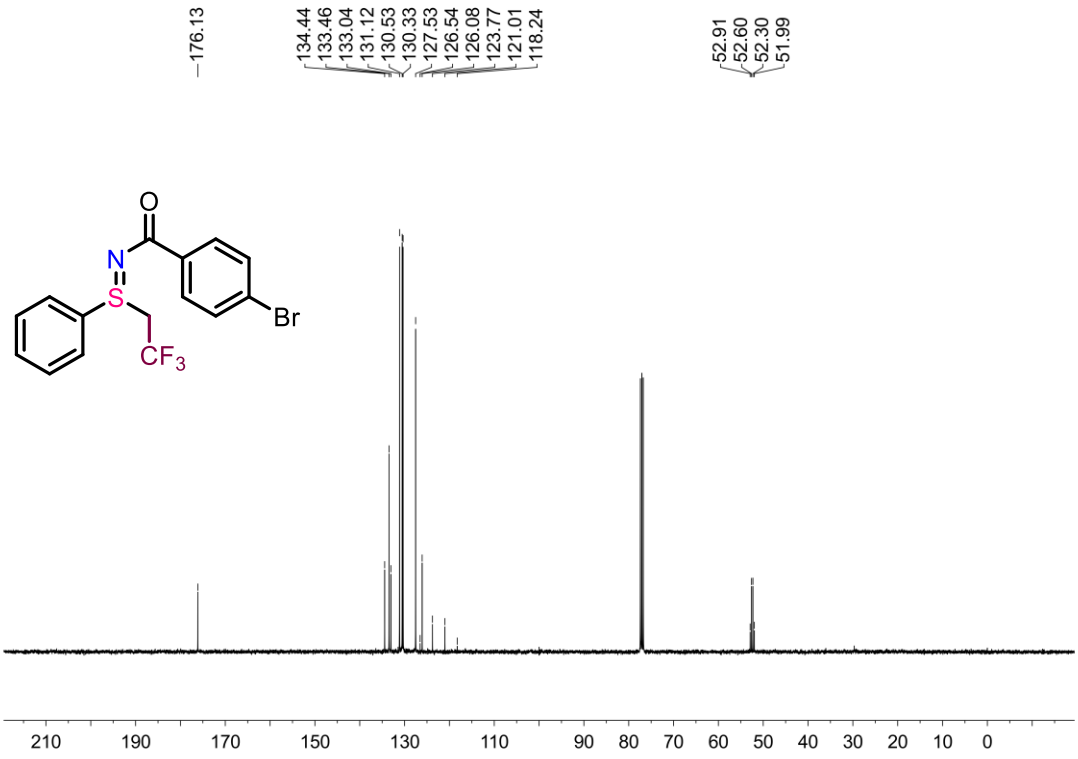
^{19}F NMR spectrum of compound **3da** (376 MHz, $CDCl_3$)



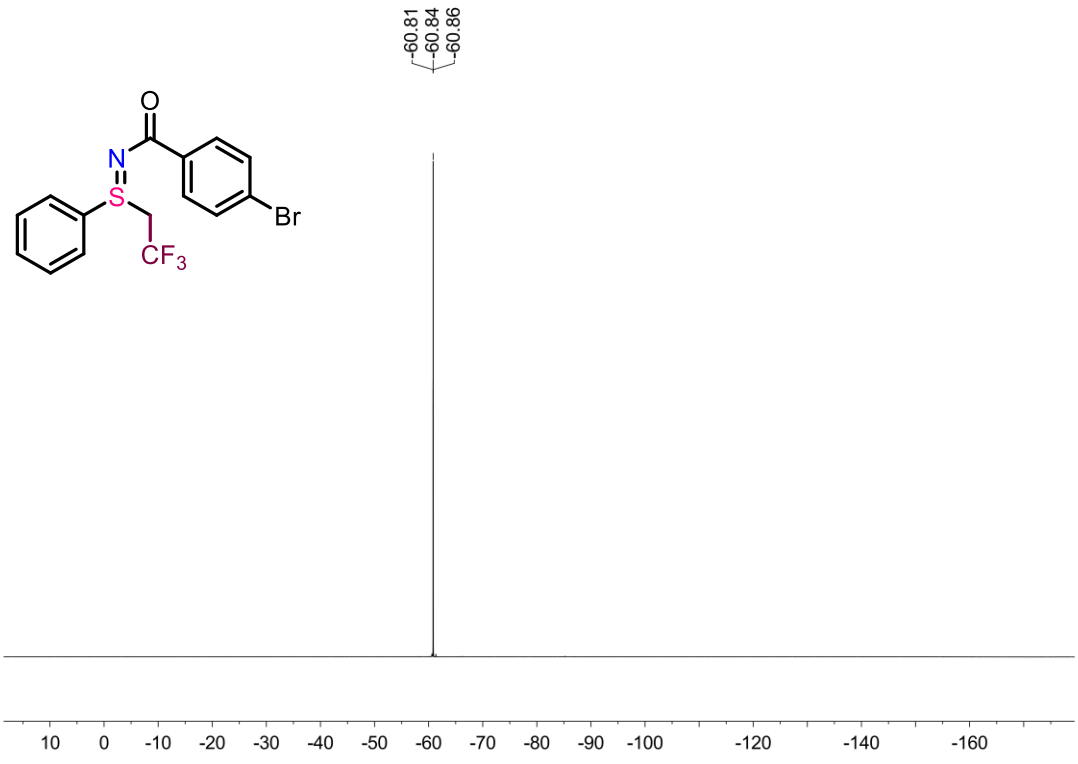
^{1}H NMR spectrum of compound **3ea** (400 MHz, $CDCl_3$)



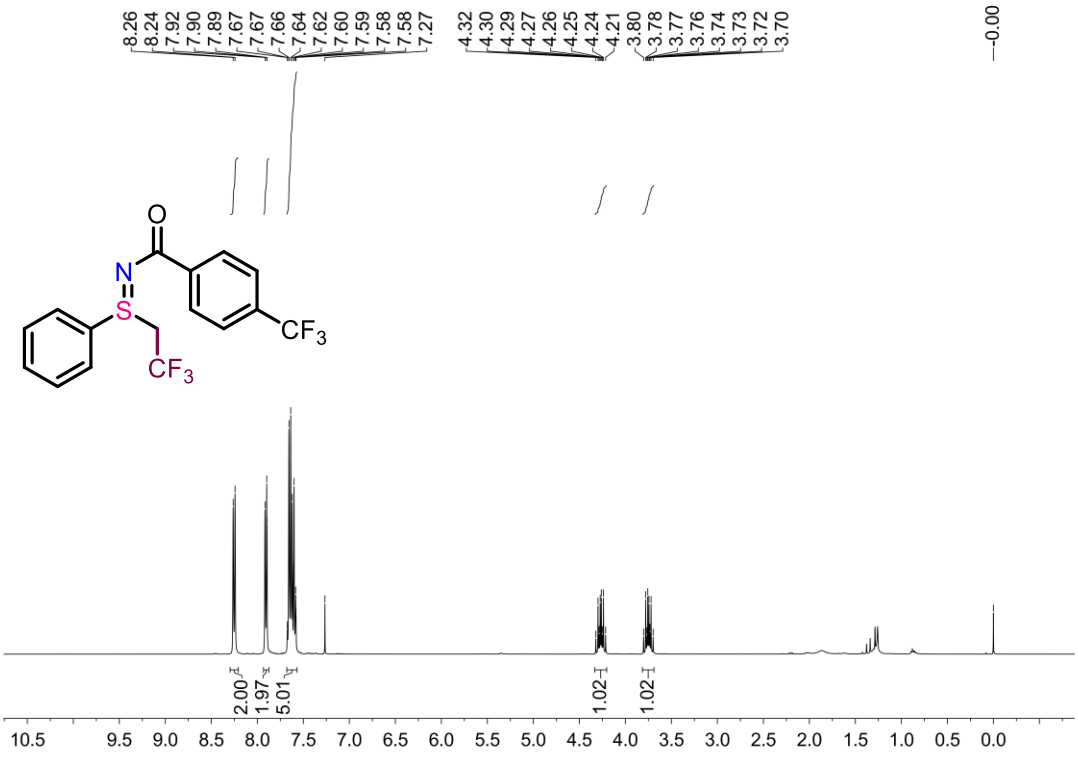
^{13}C NMR spectrum of compound **3ea** (100 MHz, $CDCl_3$)



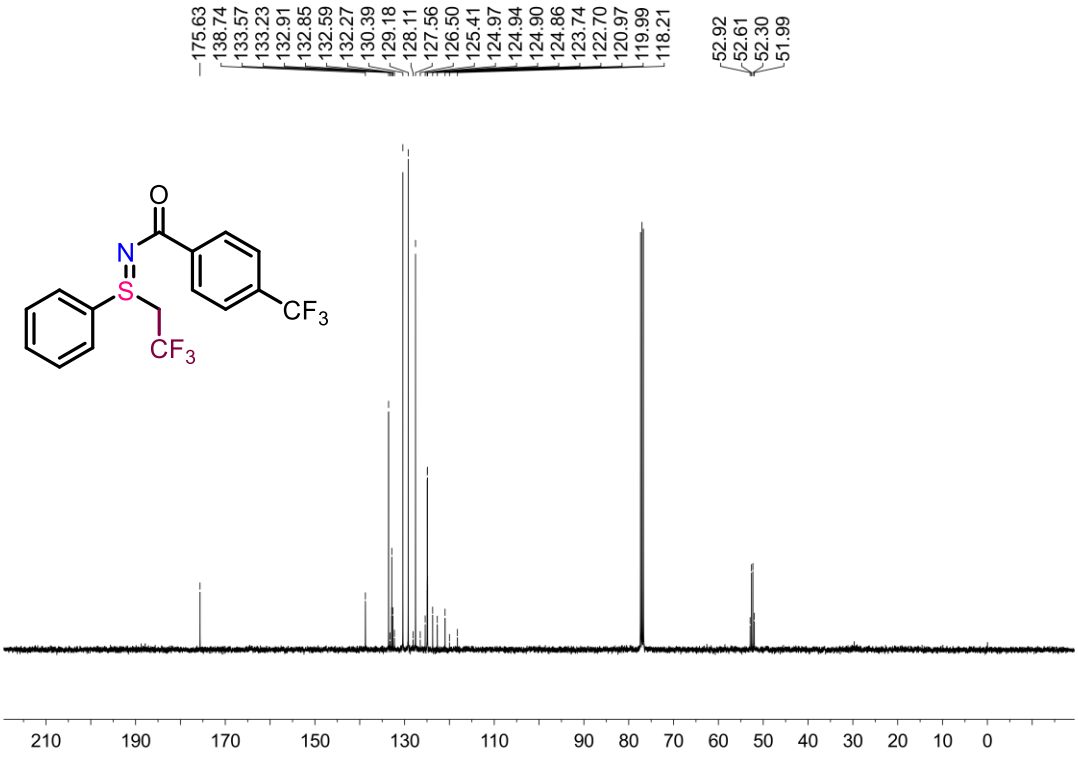
^{19}F NMR spectrum of compound **3ea** (376 MHz, $CDCl_3$)



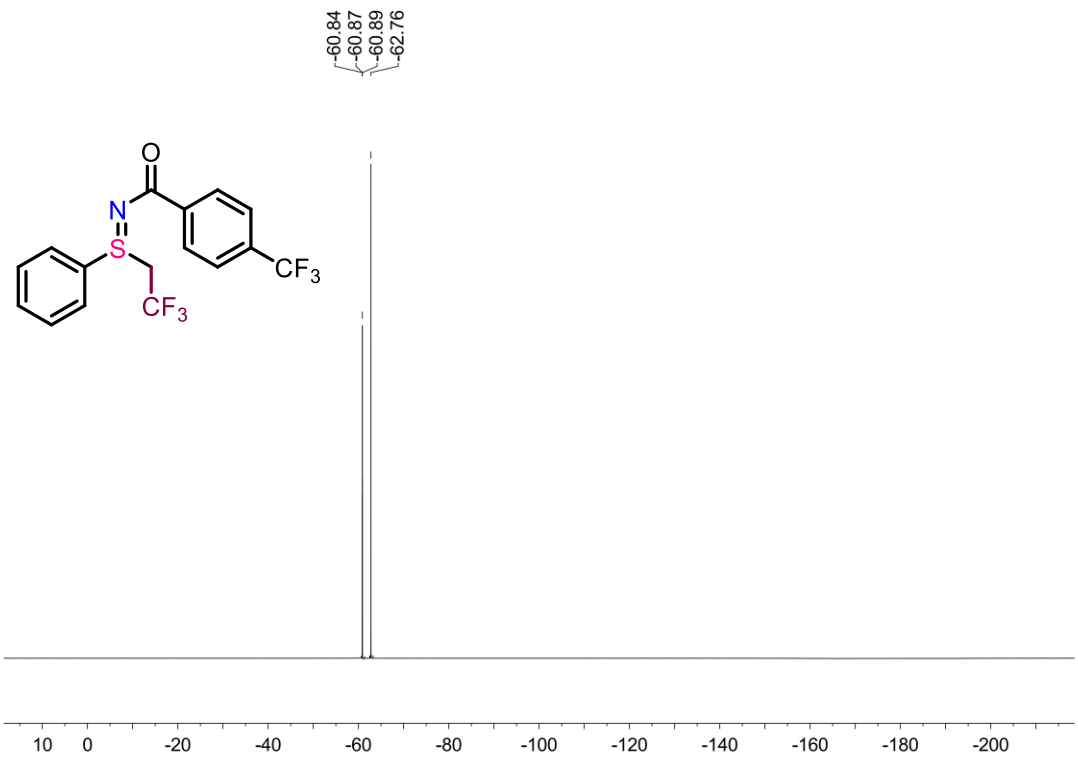
^{1}H NMR spectrum of compound **3fa** (400 MHz, $CDCl_3$)



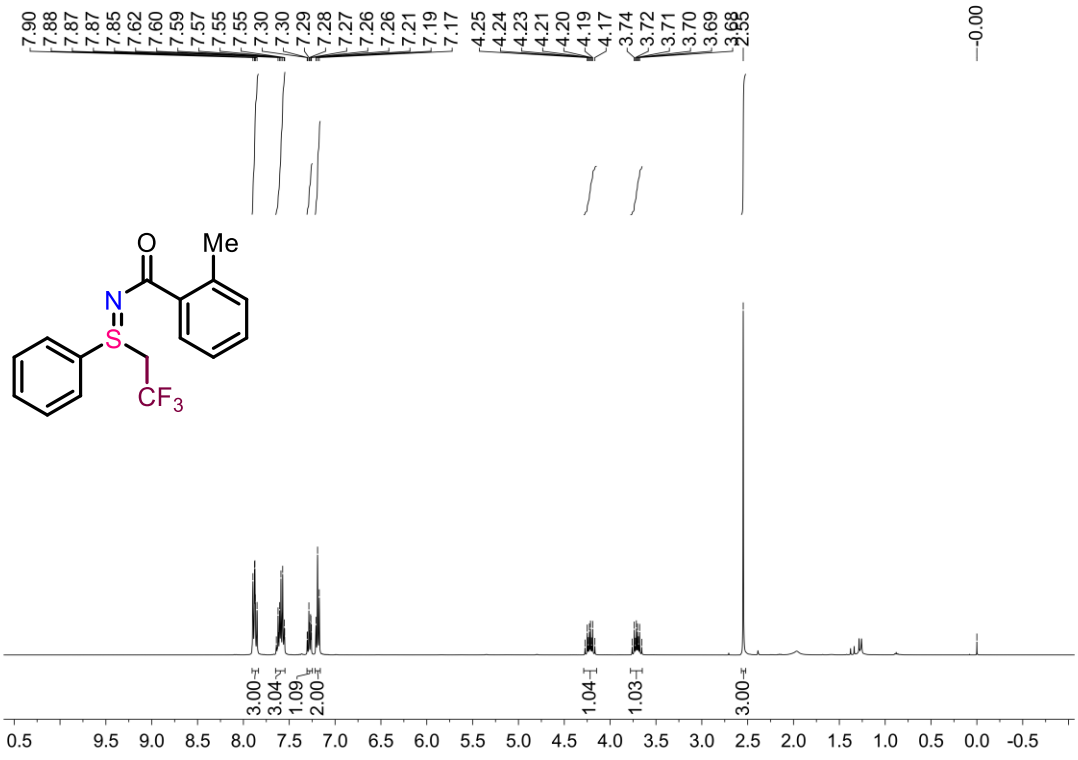
^{13}C NMR spectrum of compound **3fa** (100 MHz, $CDCl_3$)



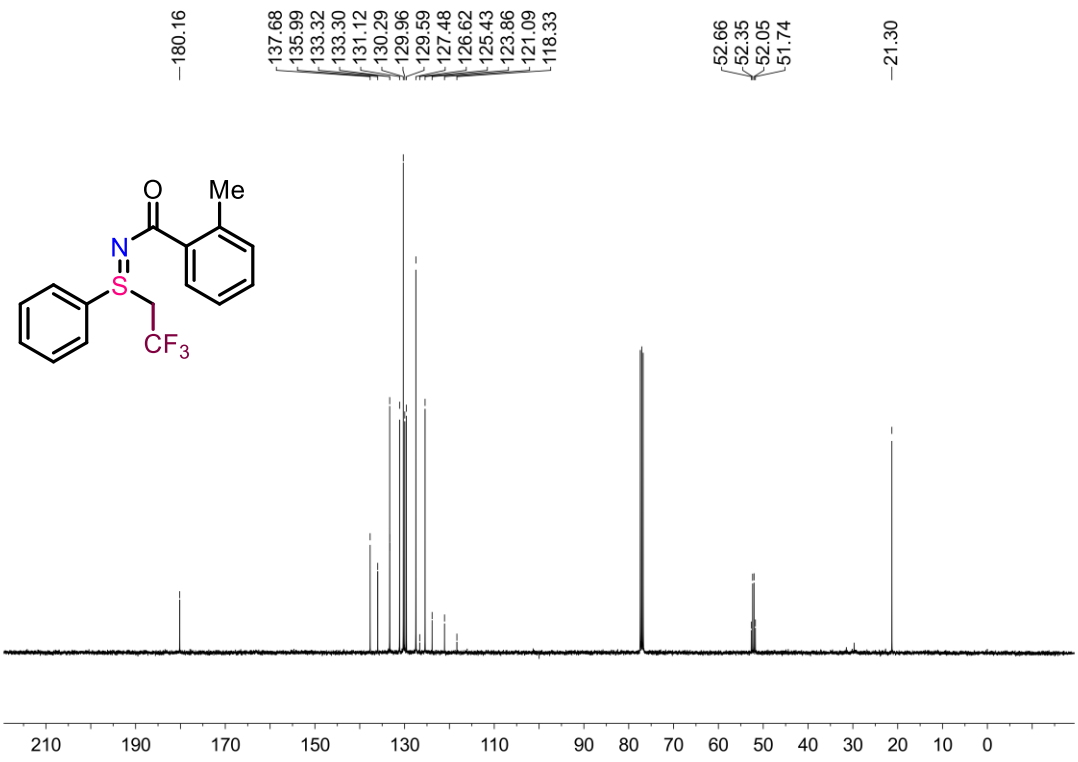
^{19}F NMR spectrum of compound **3fa** (376 MHz, $CDCl_3$)



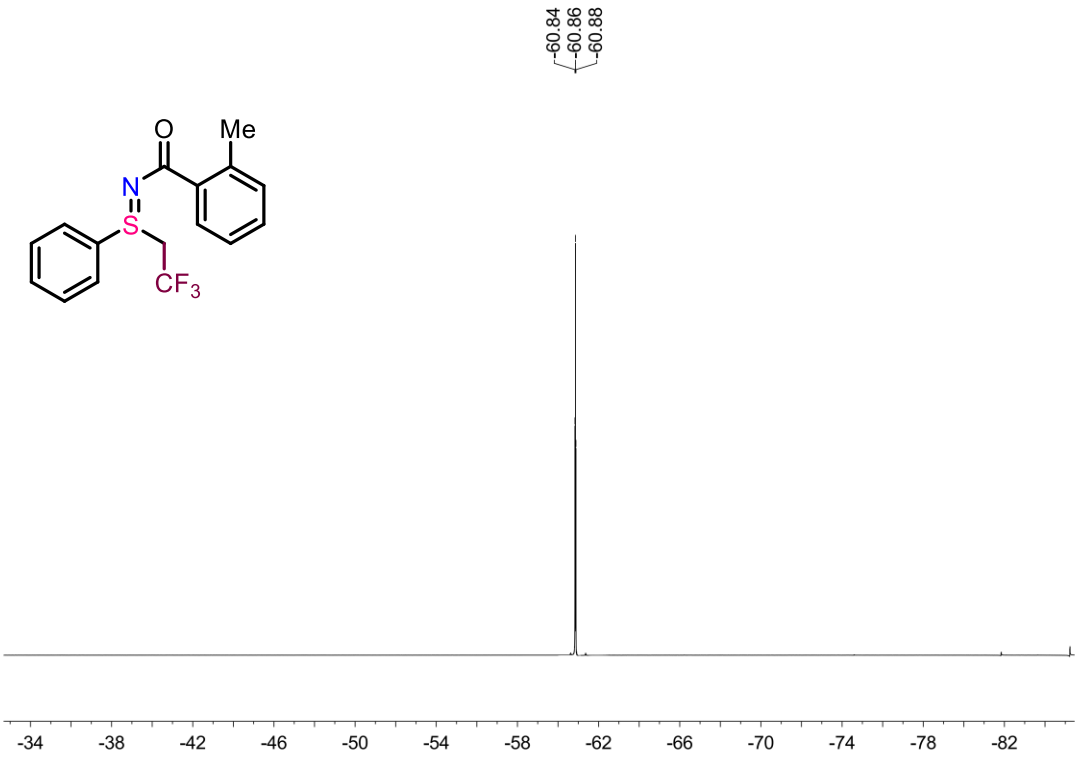
^{1}H NMR spectrum of compound **3ga** (400 MHz, $CDCl_3$)



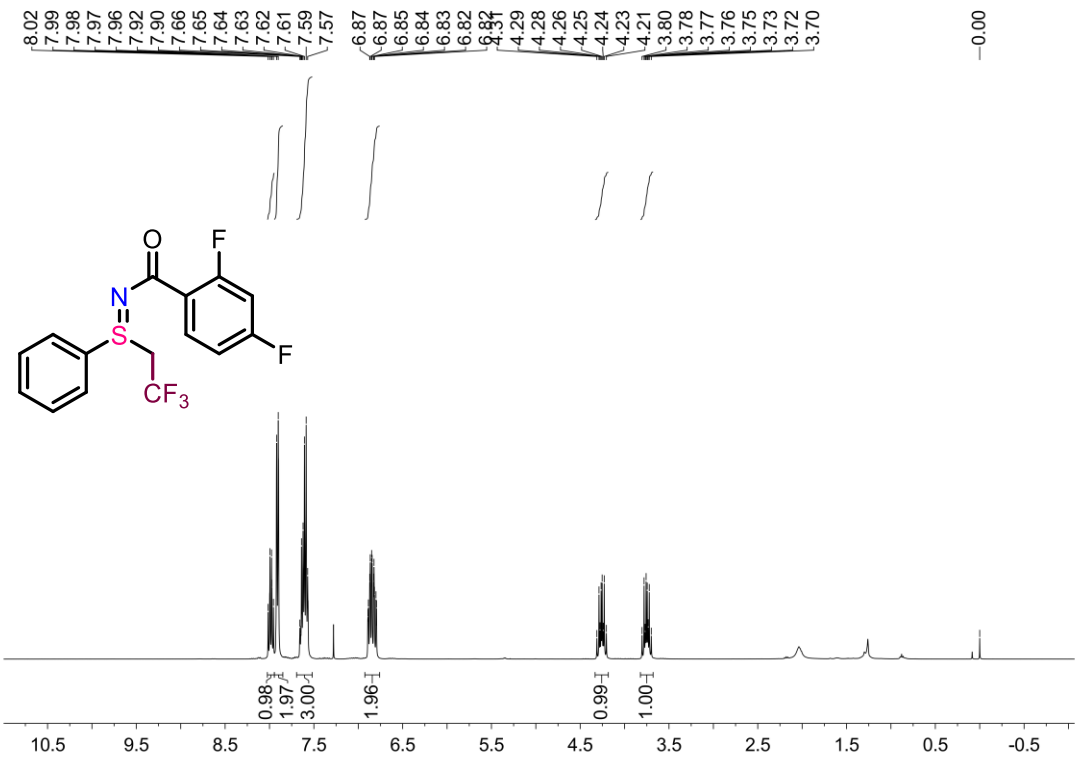
^{13}C NMR spectrum of compound **3ga** (100 MHz, $CDCl_3$)



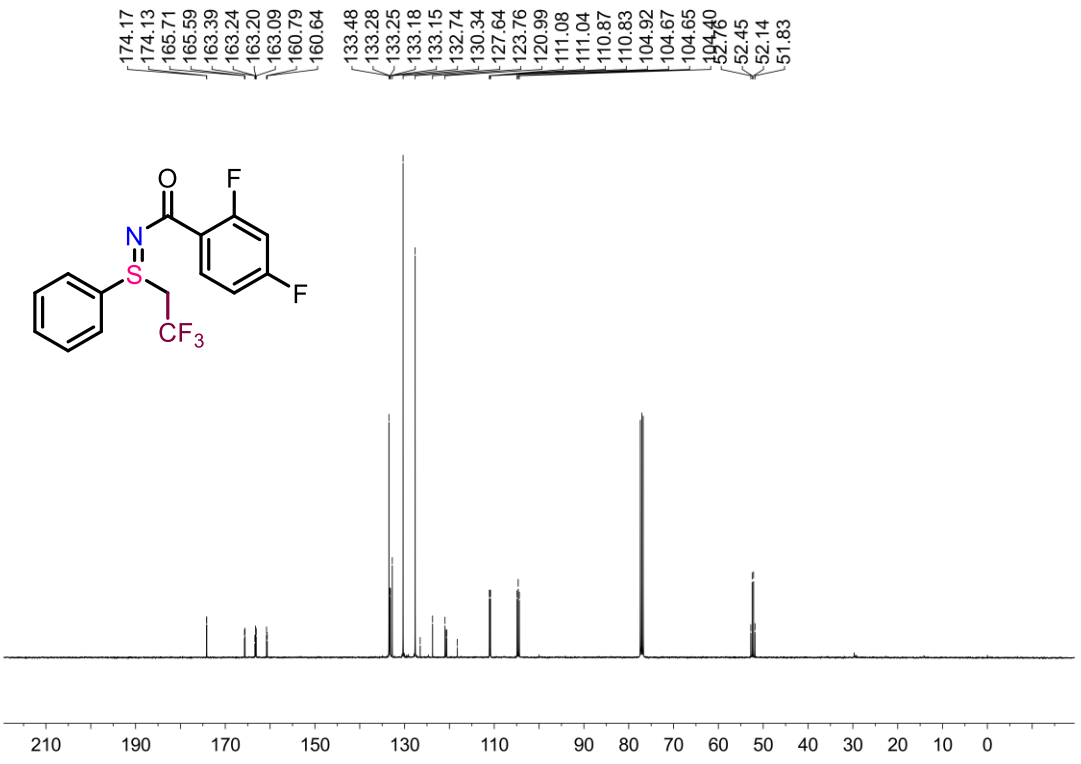
^{19}F NMR spectrum of compound **3ga** (376 MHz, $CDCl_3$)



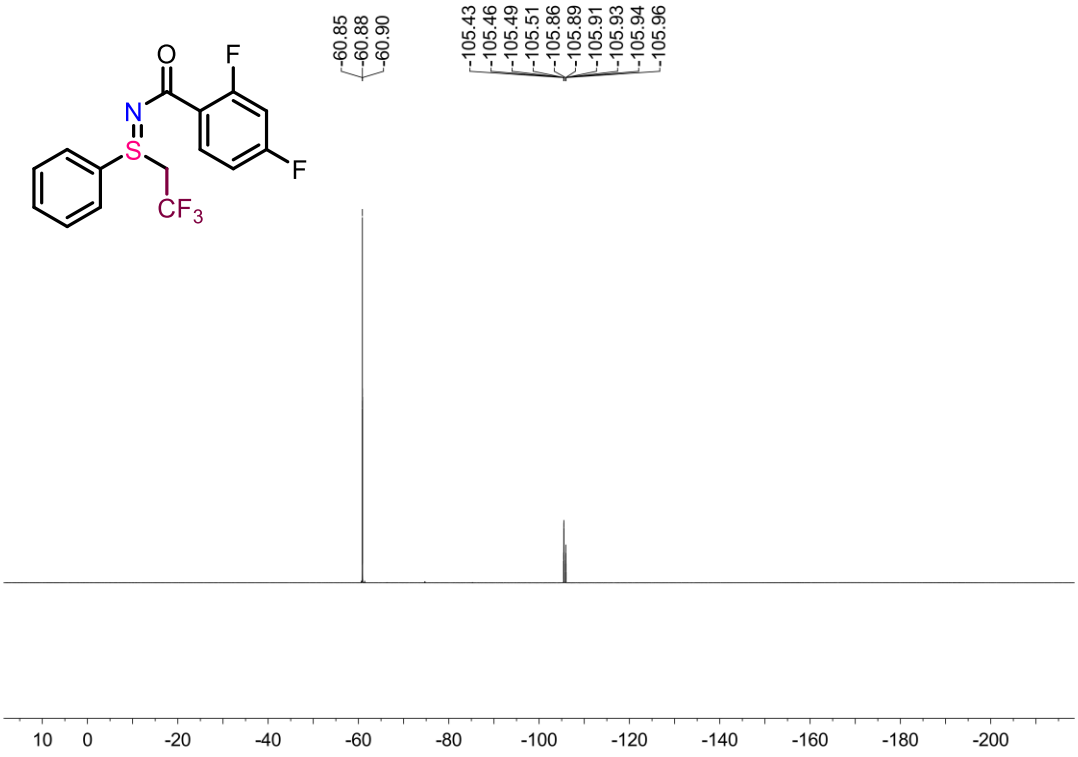
^{1}H NMR spectrum of compound **3ha** (400 MHz, $CDCl_3$)



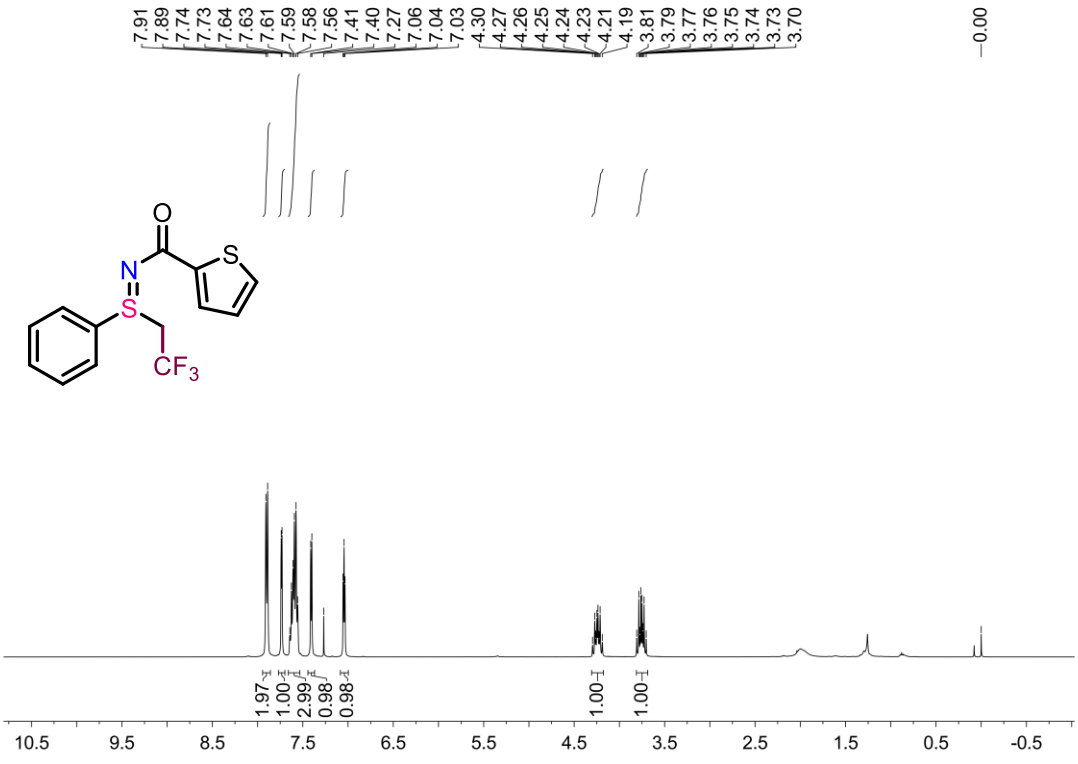
^{13}C NMR spectrum of compound **3ha** (100 MHz, $CDCl_3$)



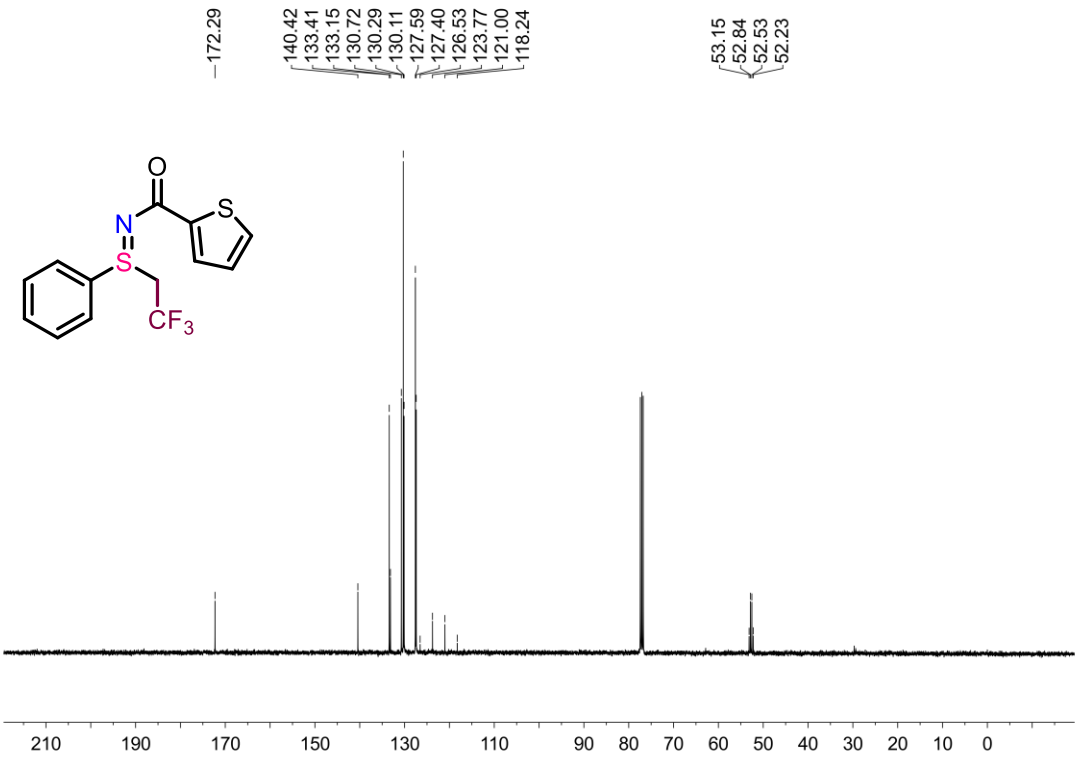
^{19}F NMR spectrum of compound **3ha** (376 MHz, $CDCl_3$)



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

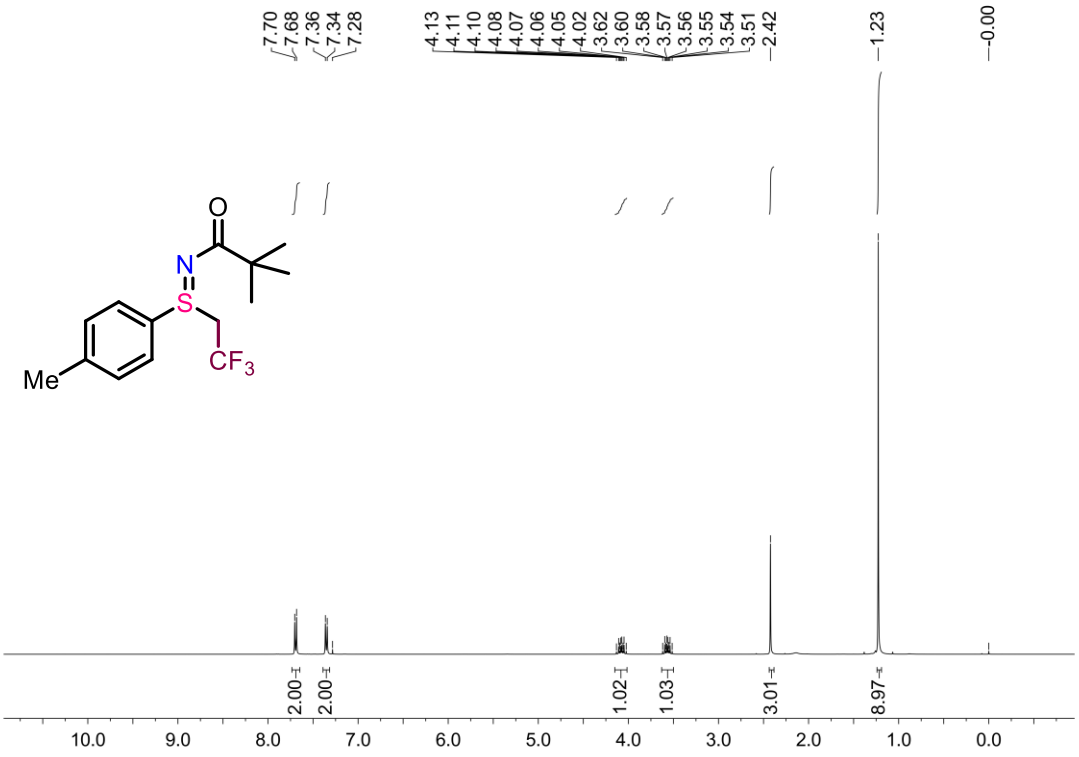


^{13}C NMR spectrum of compound **3ia** (100 MHz, $CDCl_3$)

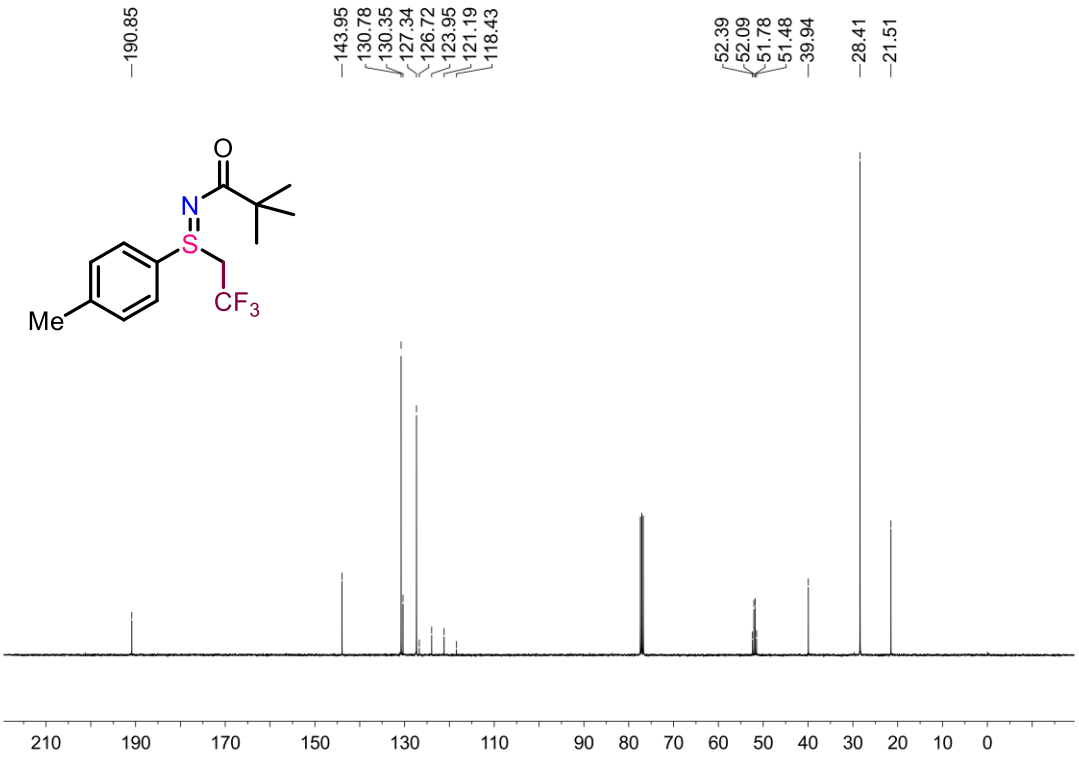


^{19}F NMR spectrum of compound **3ia** (376 MHz, $CDCl_3$)

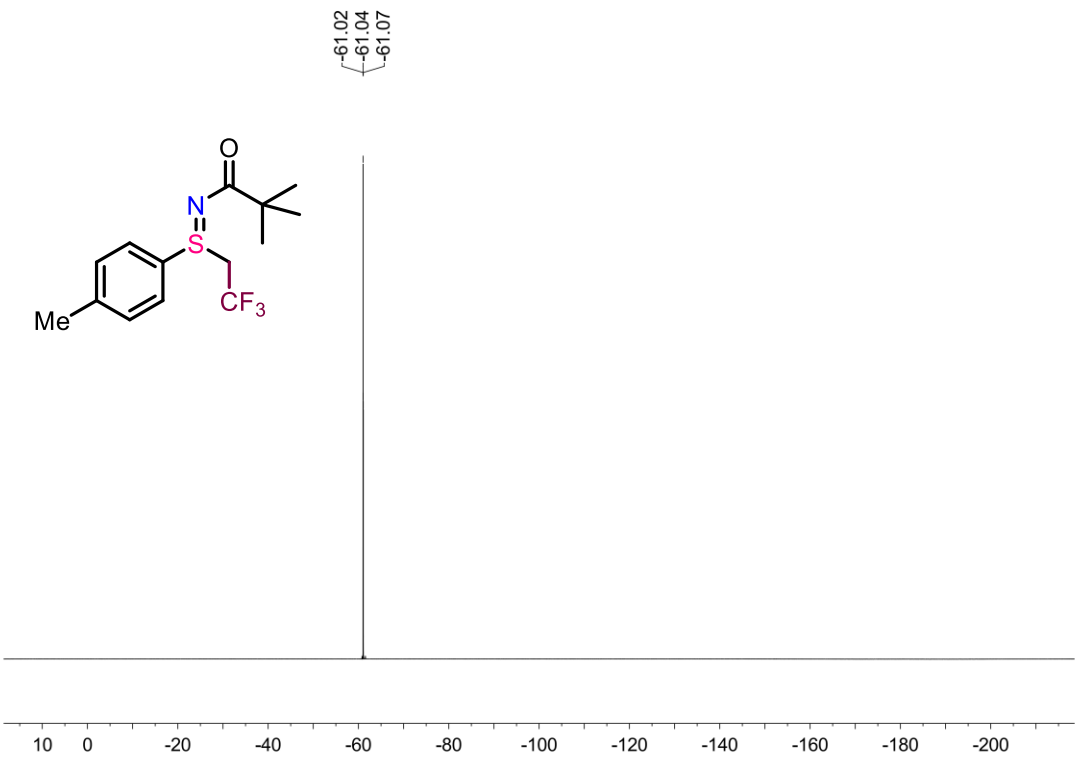
^{1}H NMR spectrum of compound **3ja** (400 MHz, $CDCl_3$)



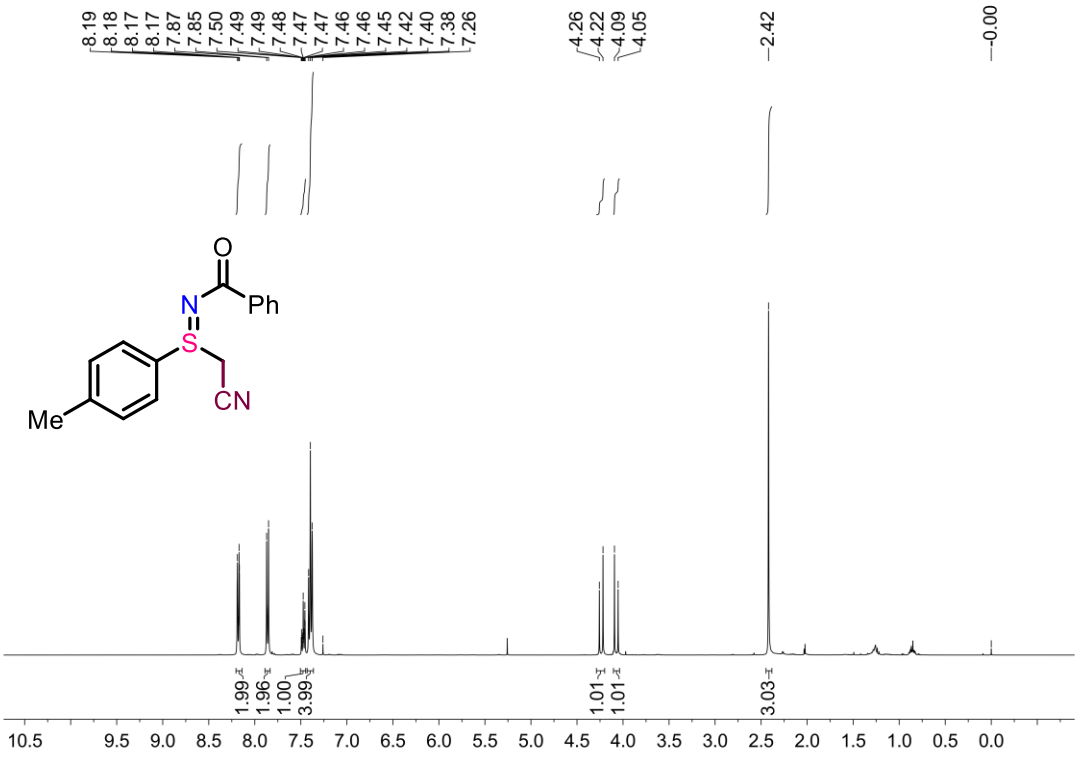
^{13}C NMR spectrum of compound **3ja** (100 MHz, $CDCl_3$)



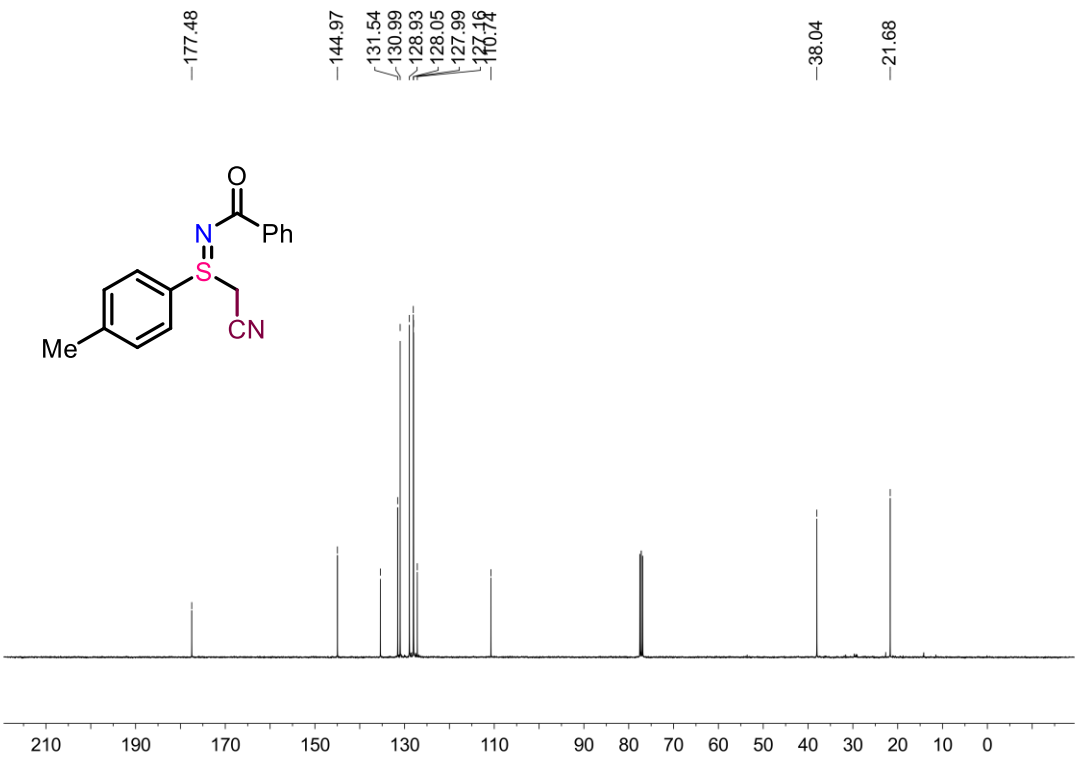
^{19}F NMR spectrum of compound **3ja** (376 MHz, $CDCl_3$)



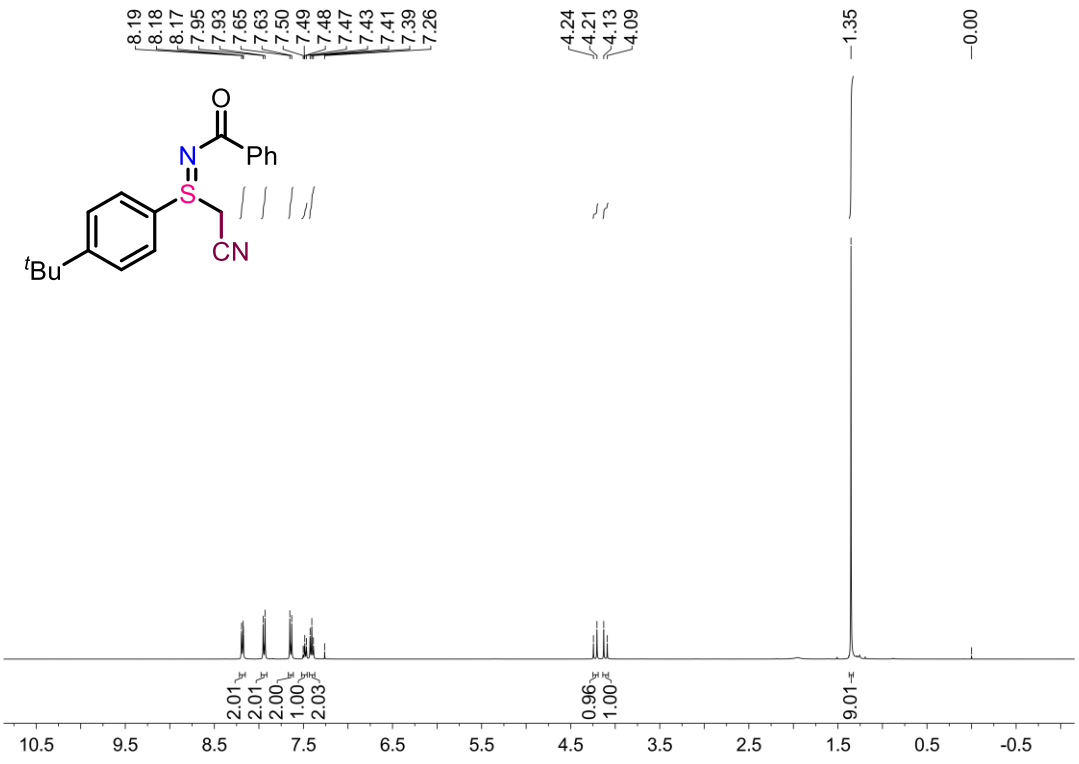
^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$)



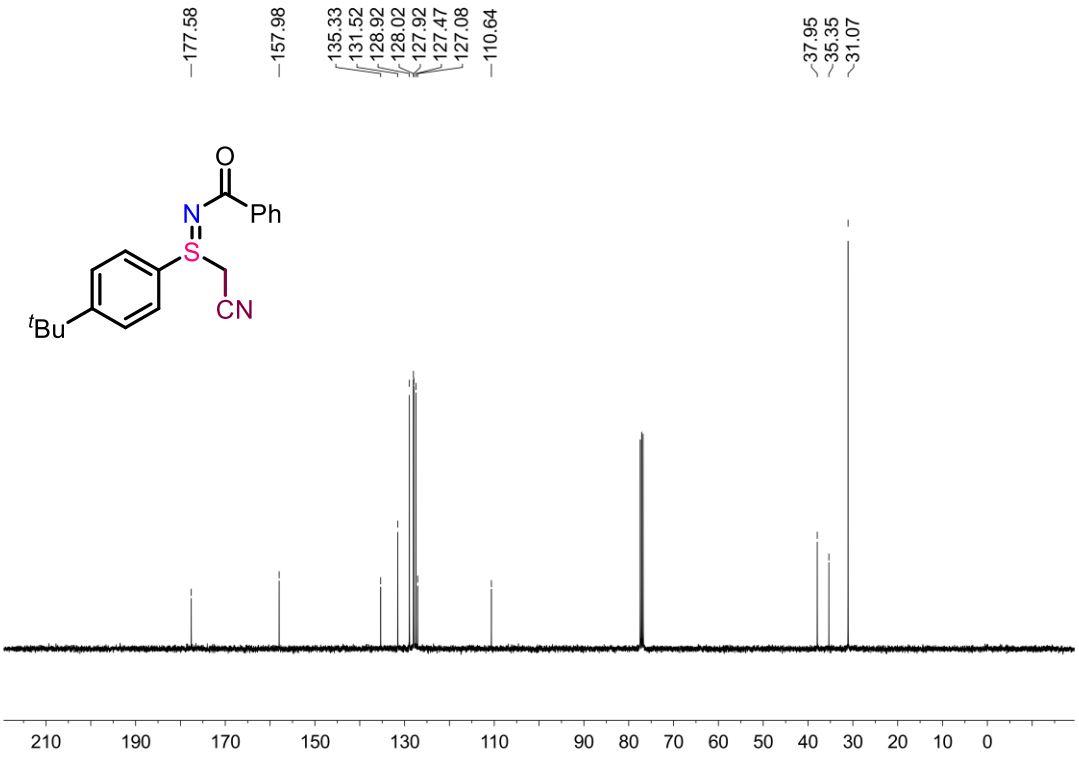
^{13}C NMR spectrum of compound **4a** (100 MHz, $CDCl_3$)



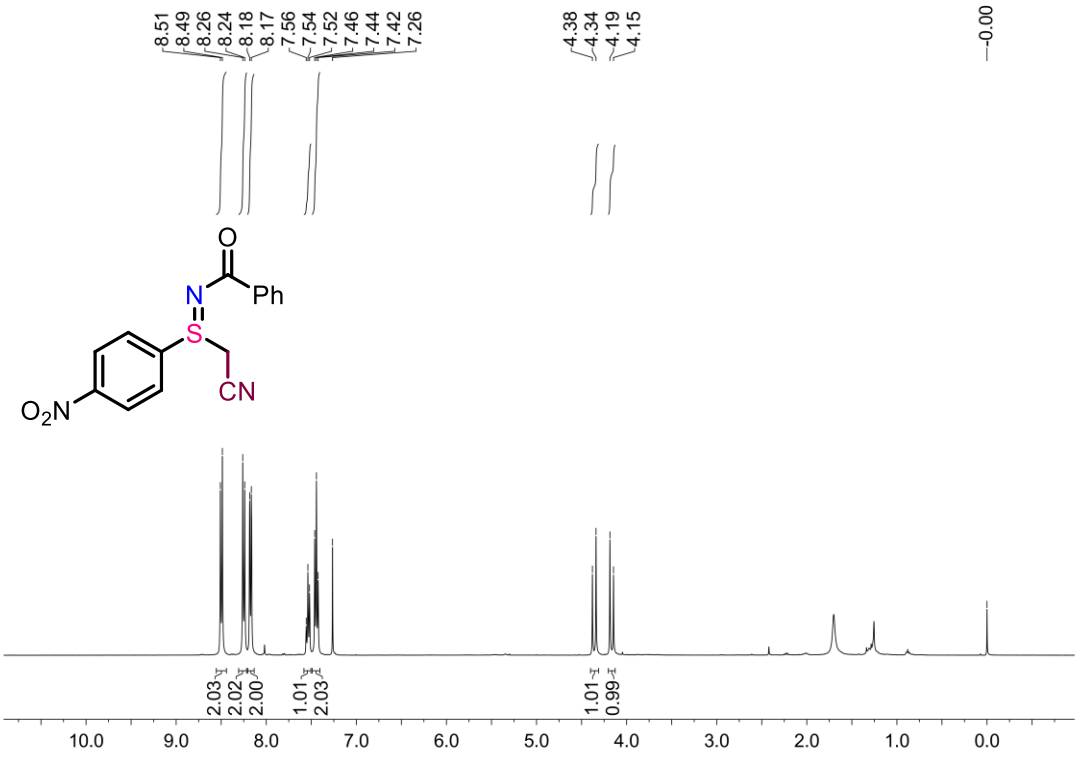
^{1}H NMR spectrum of compound **4b** (400 MHz, $CDCl_3$)



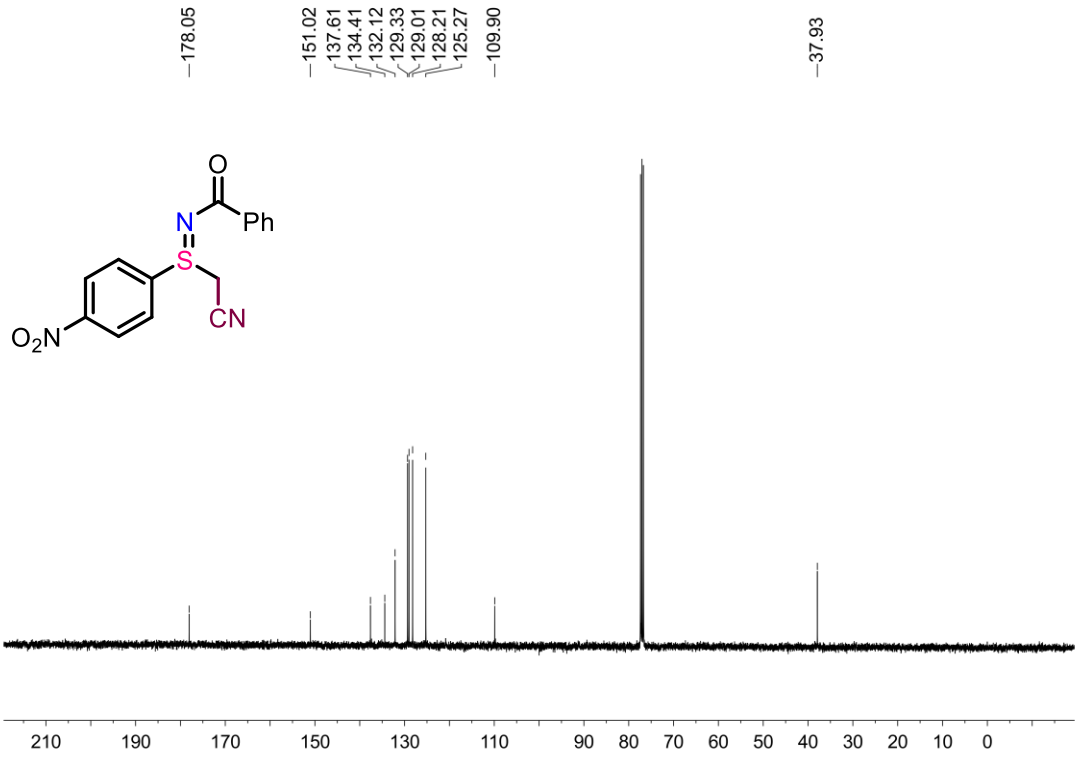
^{13}C NMR spectrum of compound **4b** (100 MHz, $CDCl_3$)



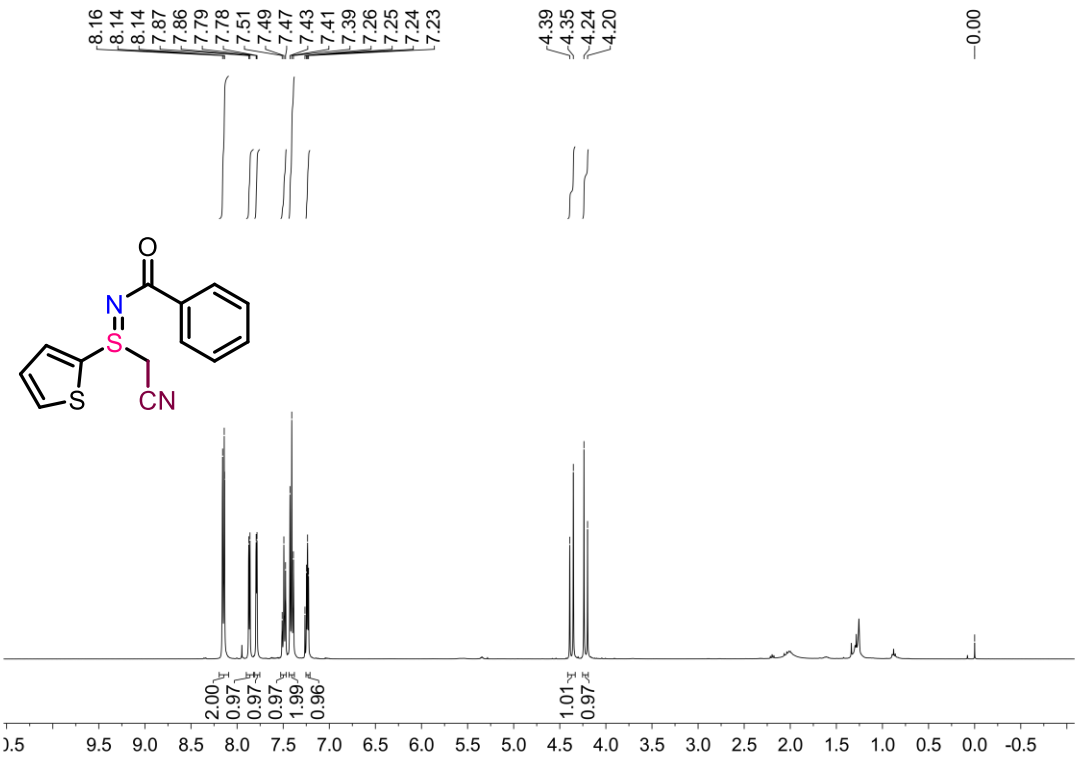
^{1}H NMR spectrum of compound **4c** (400 MHz, $CDCl_3$)



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

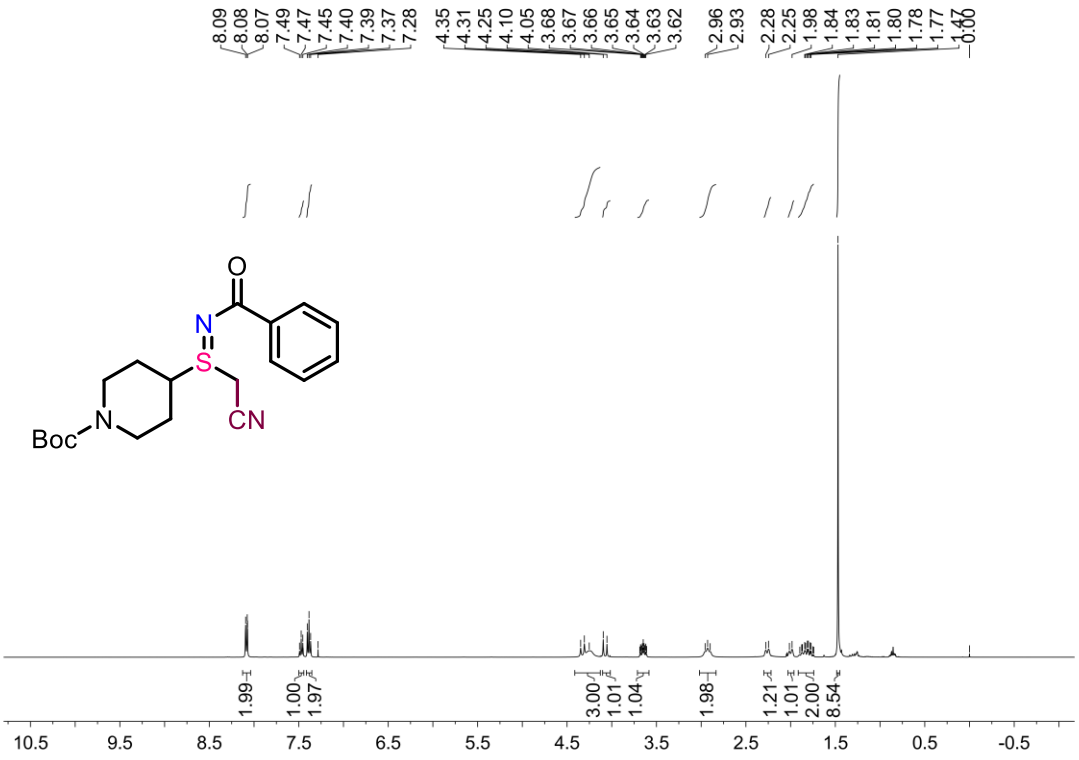


^{1}H NMR spectrum of compound **4d** (400 MHz, $CDCl_3$)

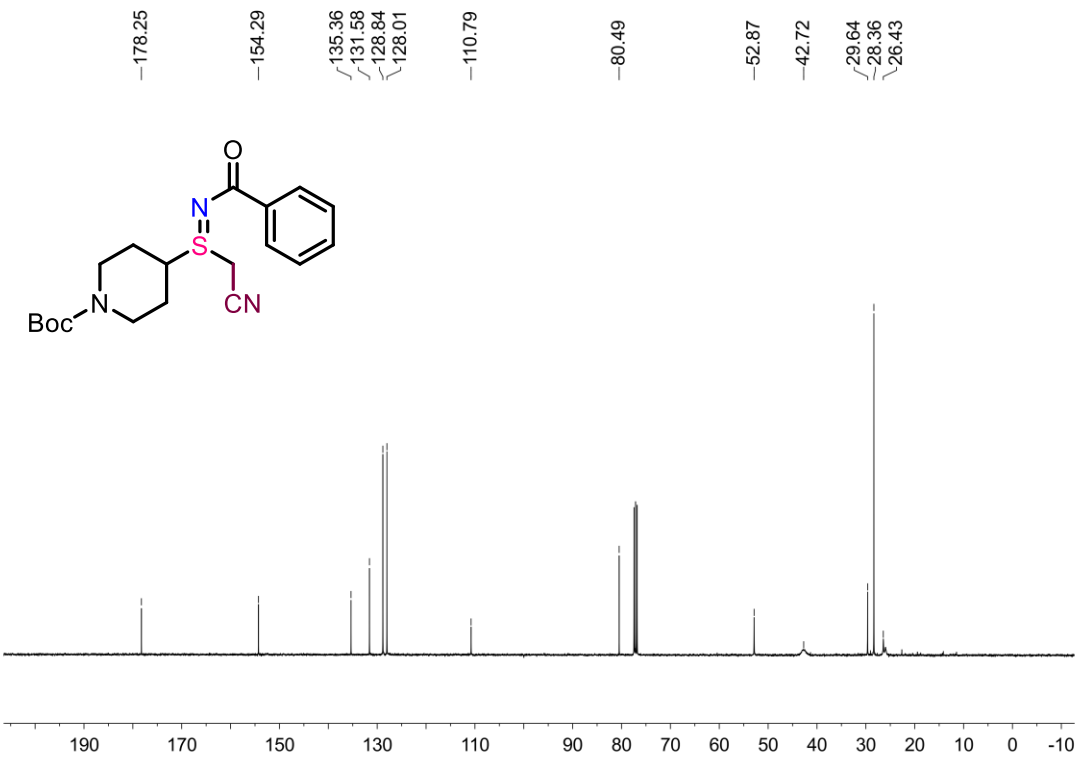


^{13}C NMR spectrum of compound **4d** (100 MHz, $CDCl_3$)

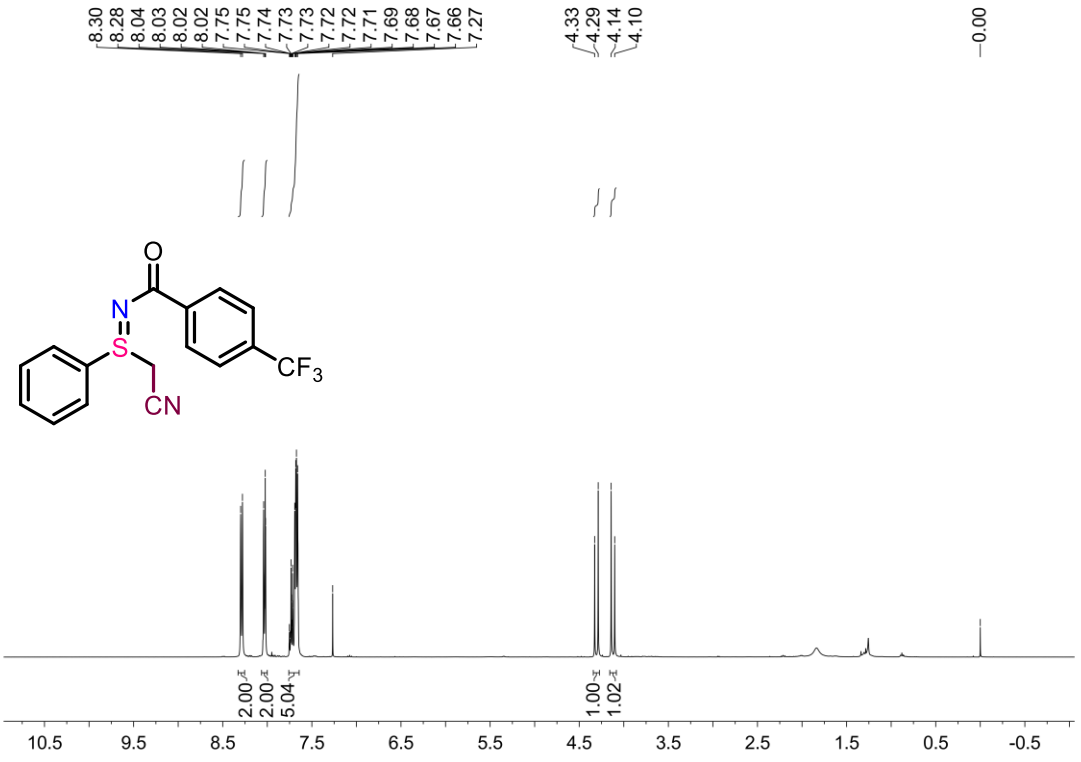
^{1}H NMR spectrum of compound **4e** (400 MHz, $CDCl_3$)



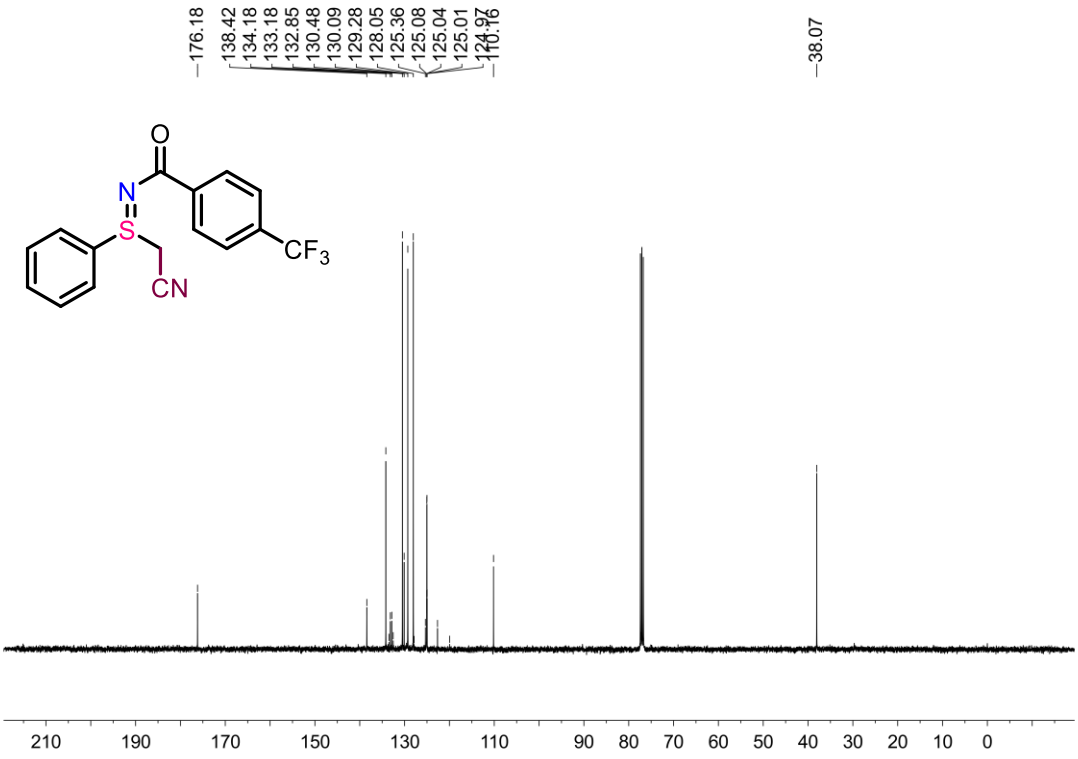
^{13}C NMR spectrum of compound **4e** (100 MHz, $CDCl_3$)



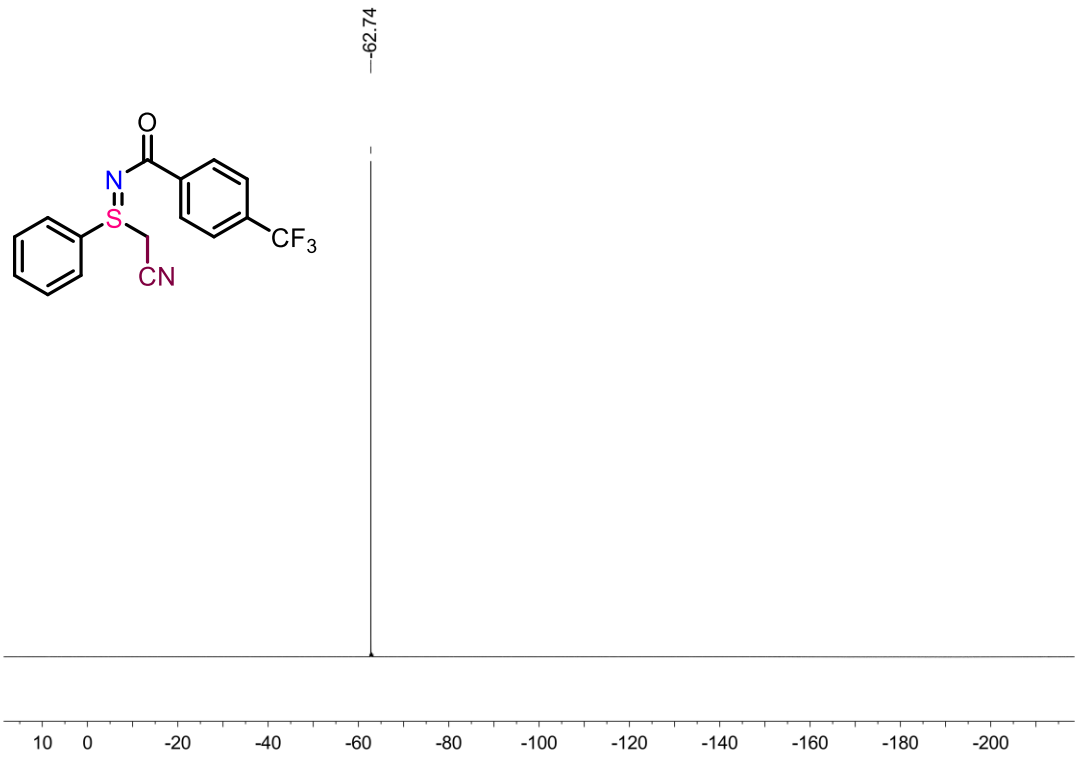
^{1}H NMR spectrum of compound **4f** (400 MHz, $CDCl_3$)



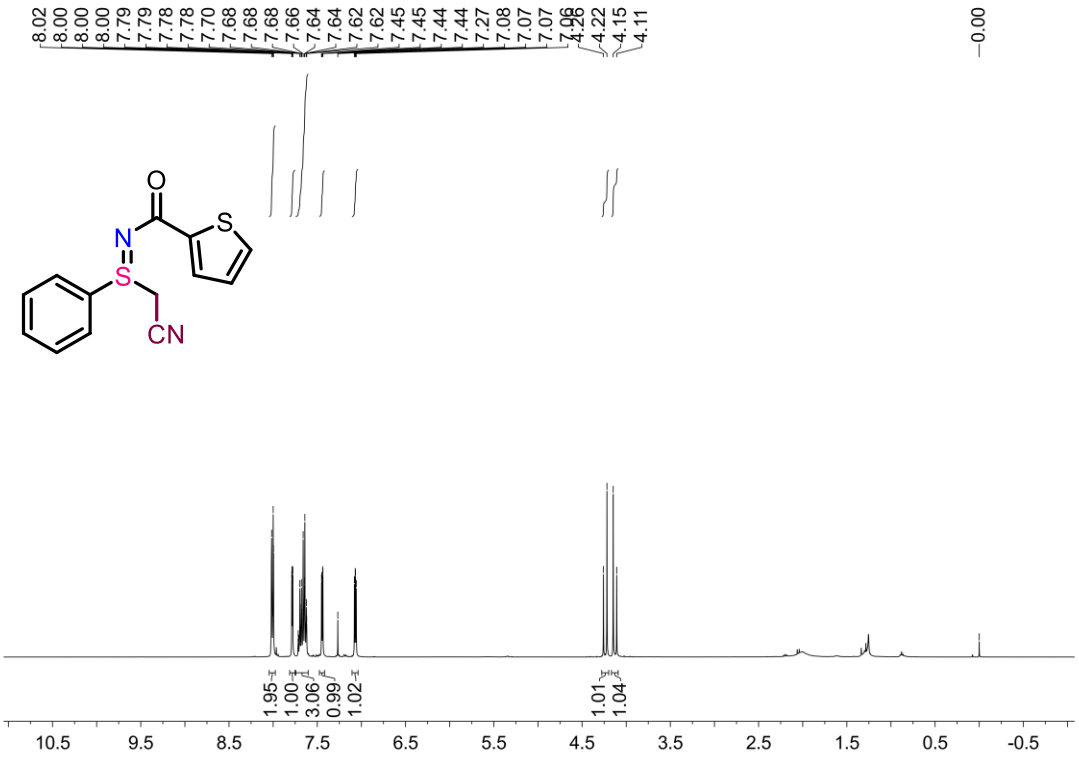
^{13}C NMR spectrum of compound **4f** (100 MHz, $CDCl_3$)



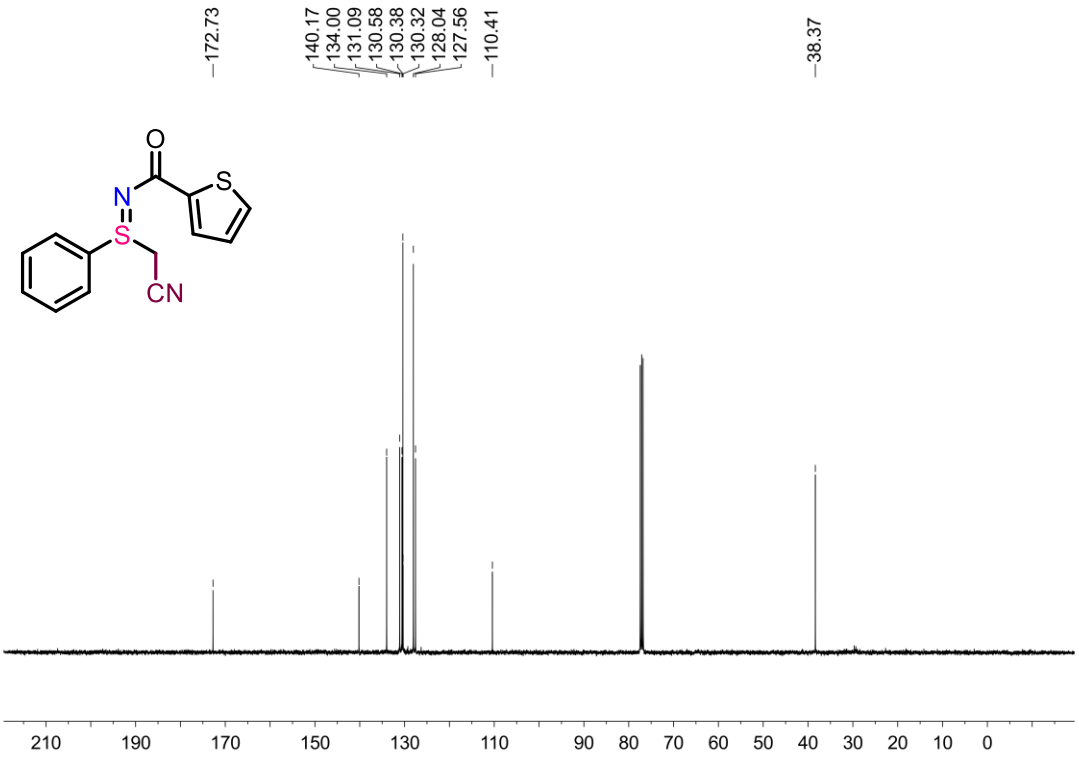
^{19}F NMR spectrum of compound **4f** (376 MHz, $CDCl_3$)



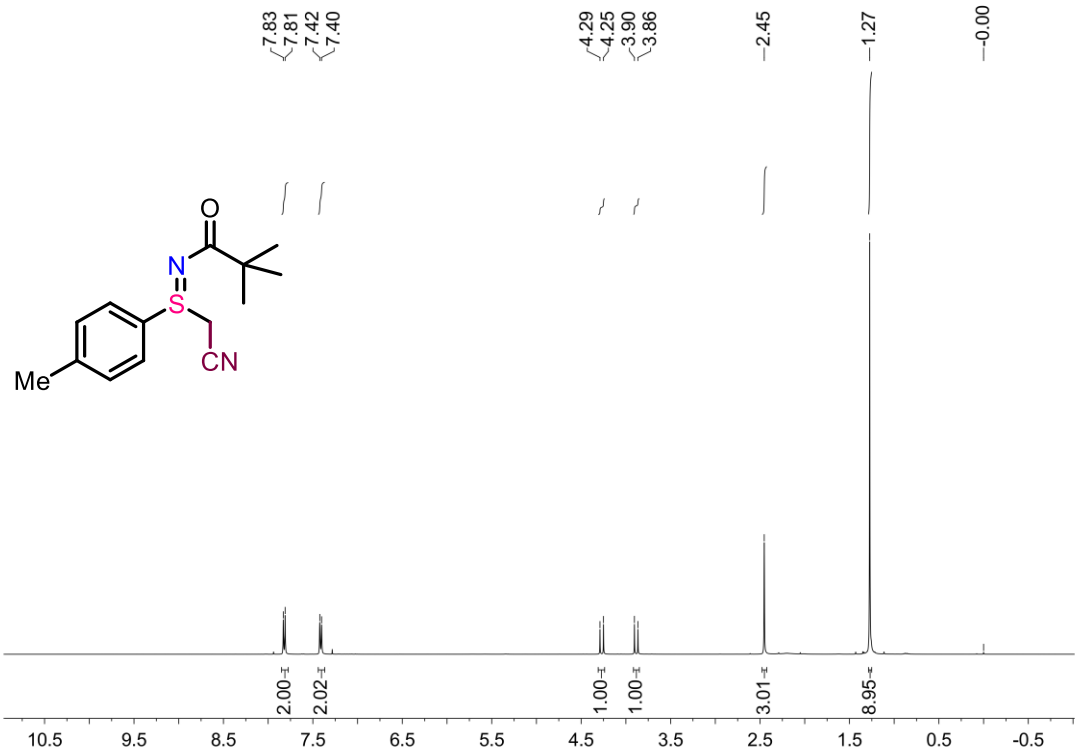
^{1}H NMR spectrum of compound **4g** (400 MHz, $CDCl_3$)



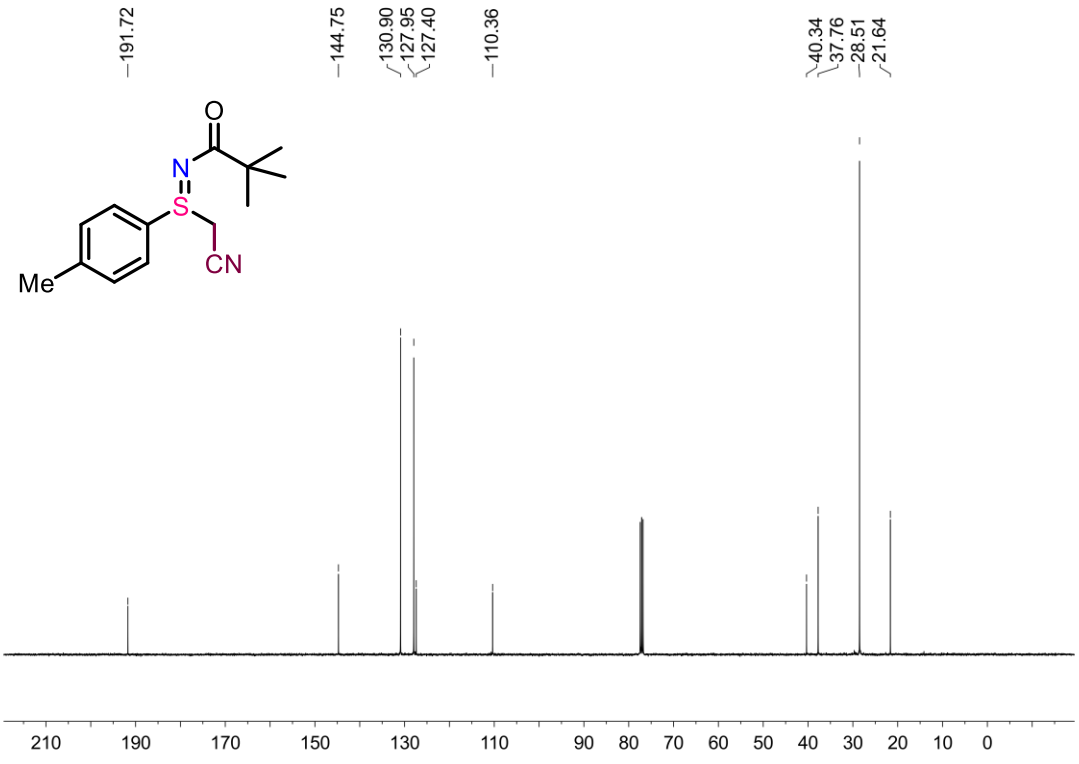
^{13}C NMR spectrum of compound **4g** (100 MHz, $CDCl_3$)



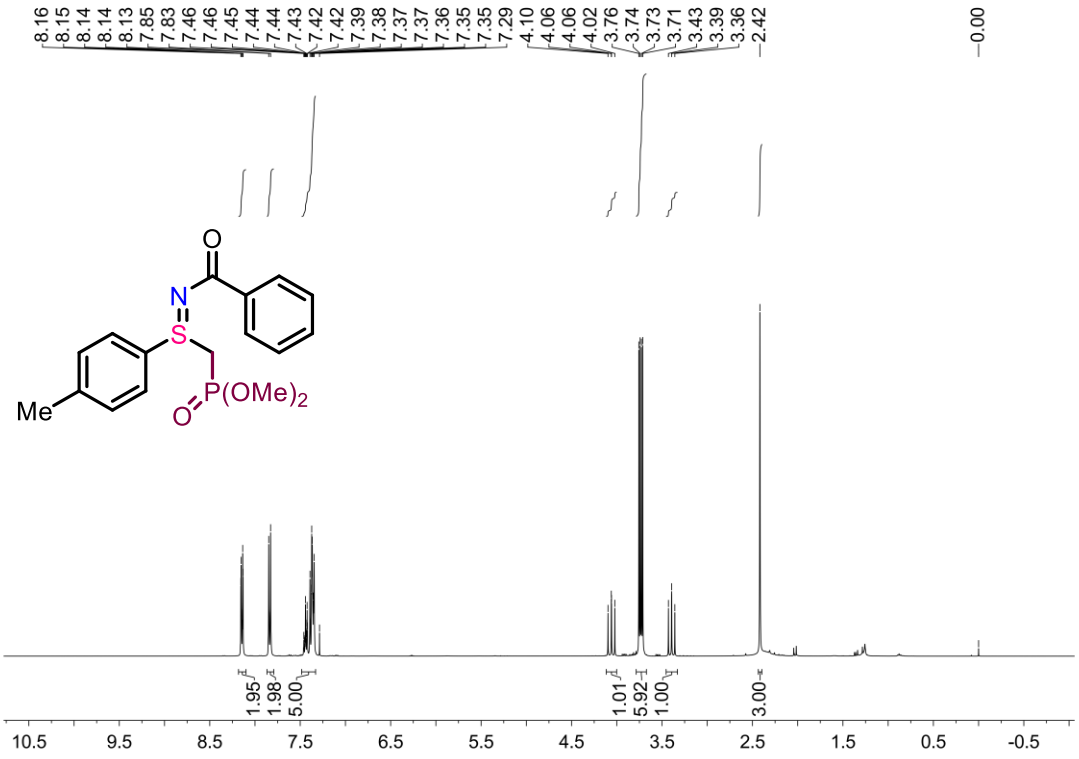
^{1}H NMR spectrum of compound **4h** (400 MHz, $CDCl_3$)



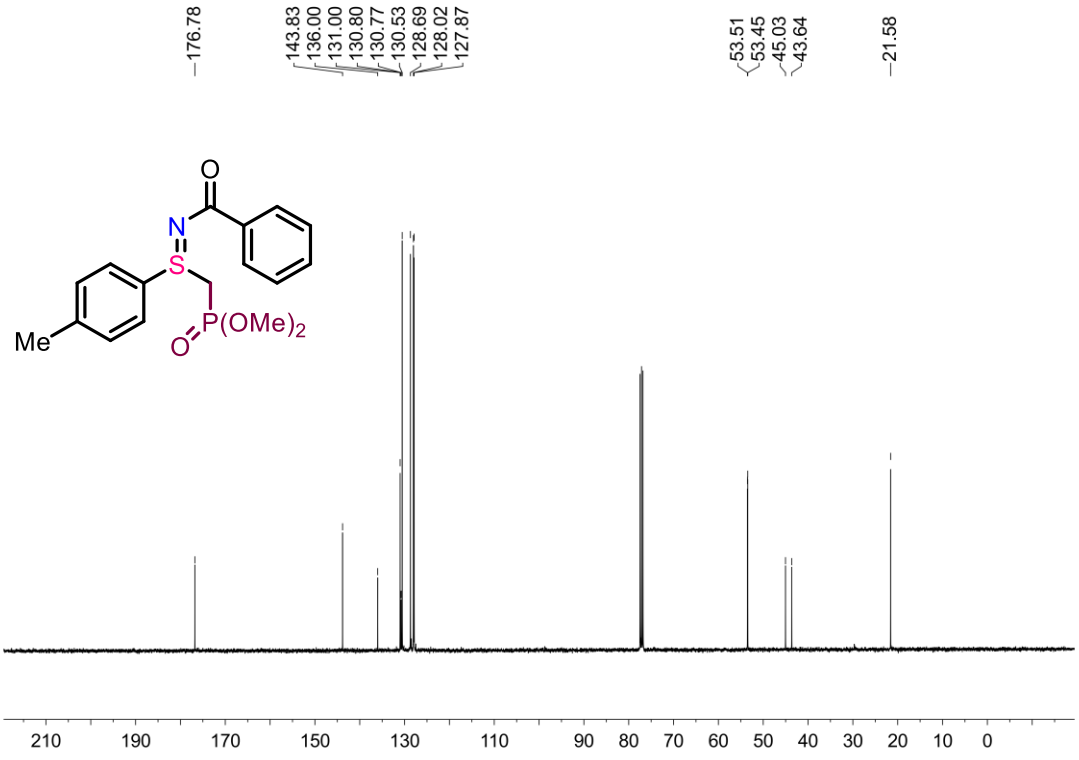
^{13}C NMR spectrum of compound **4h** (100 MHz, $CDCl_3$)



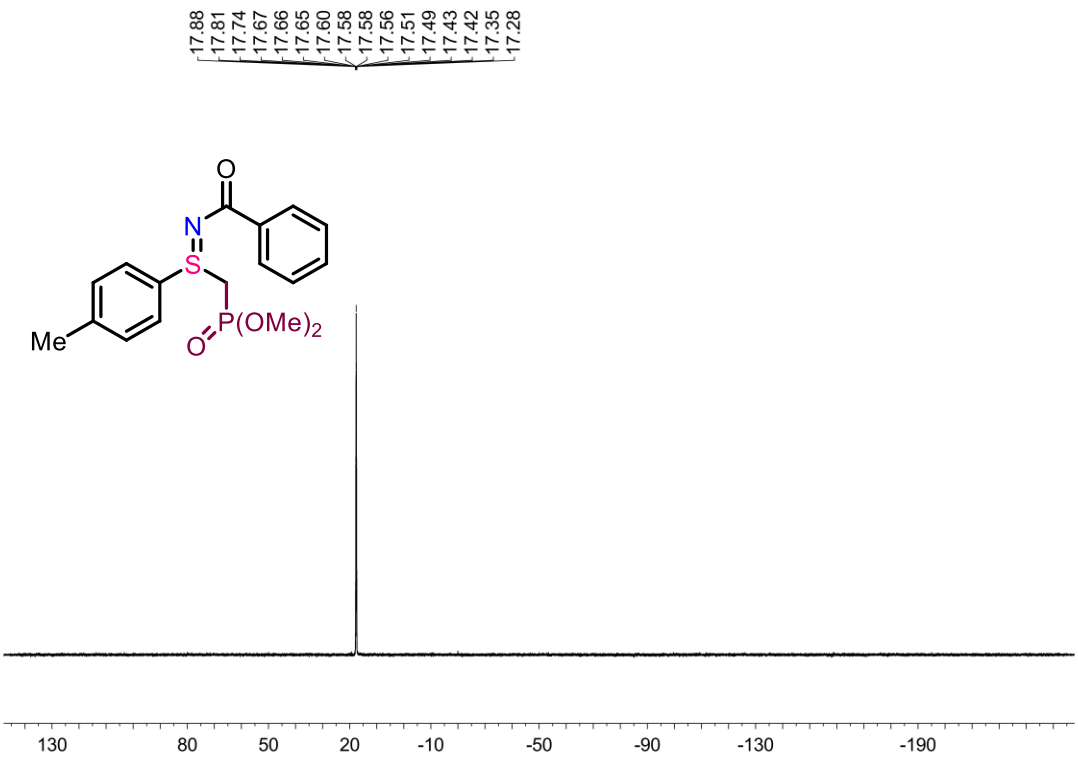
^{1}H NMR spectrum of compound **5a** (400 MHz, $CDCl_3$)



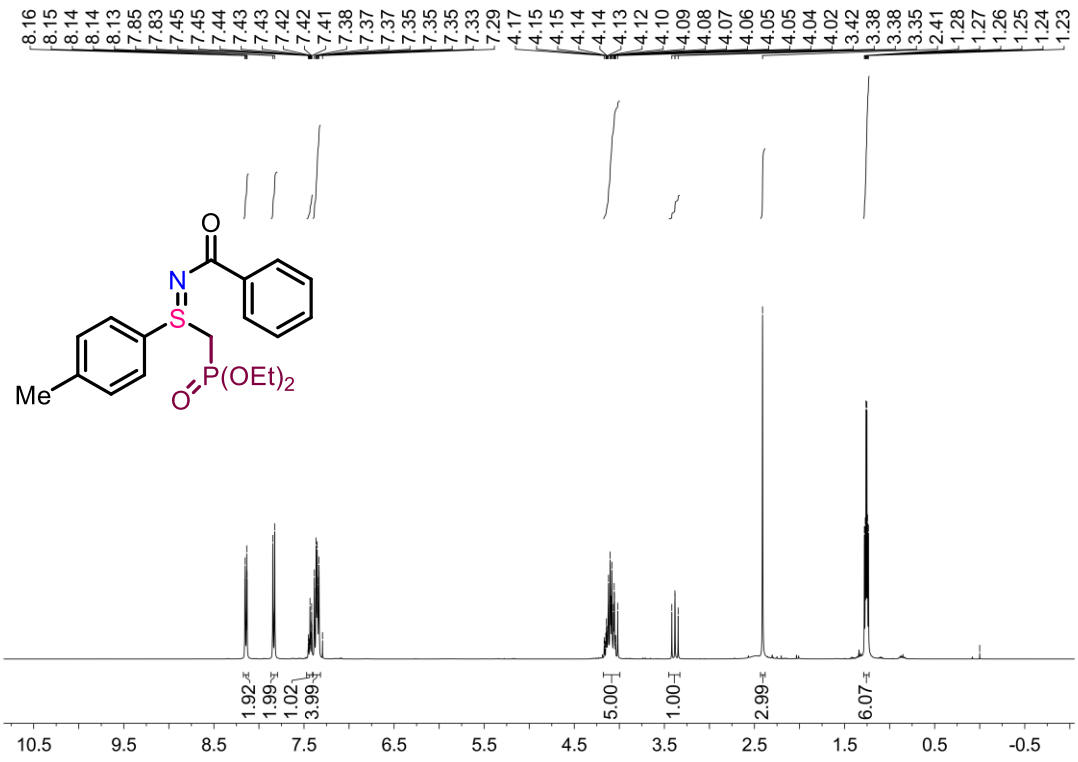
^{13}C NMR spectrum of compound **5a** (100 MHz, $CDCl_3$)



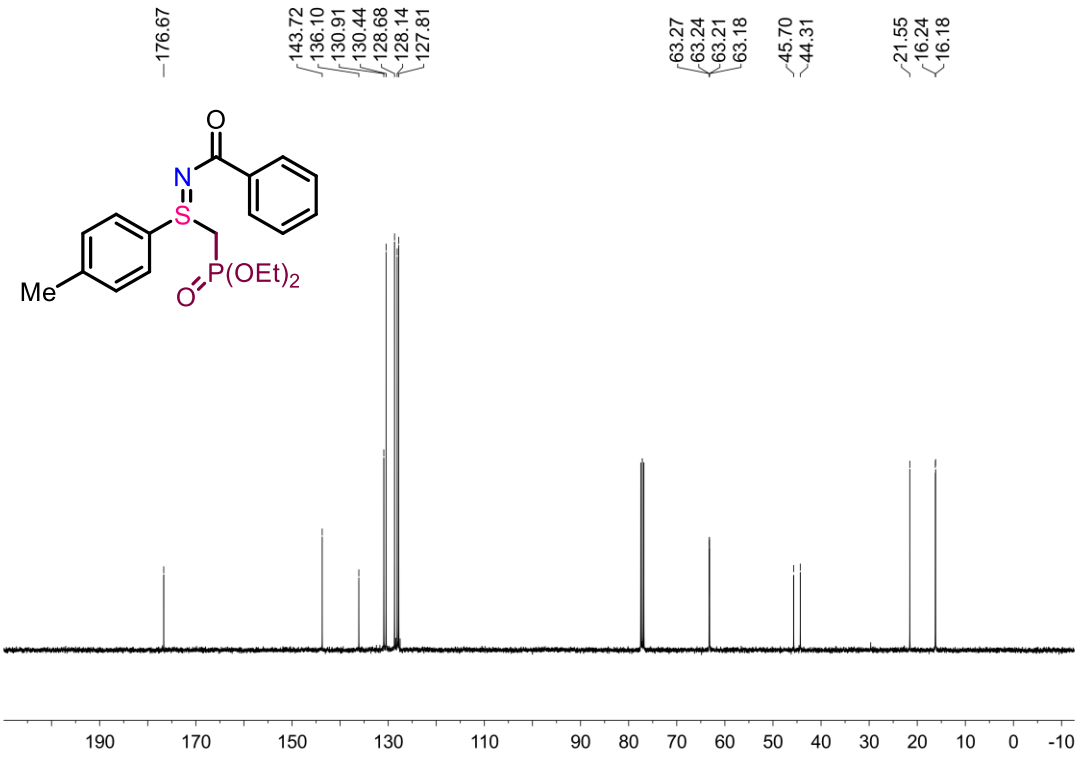
^{31}P NMR spectrum of compound **5a** (162 MHz, $CDCl_3$)



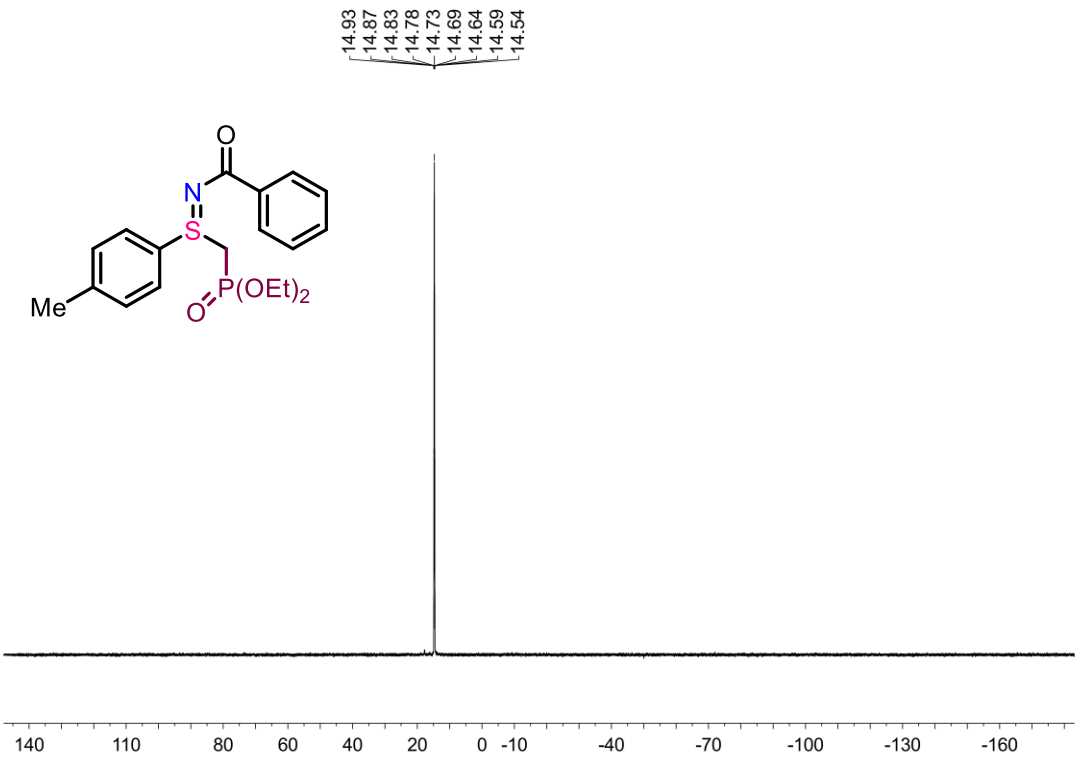
^{1}H NMR spectrum of compound **5b** (400 MHz, $CDCl_3$)



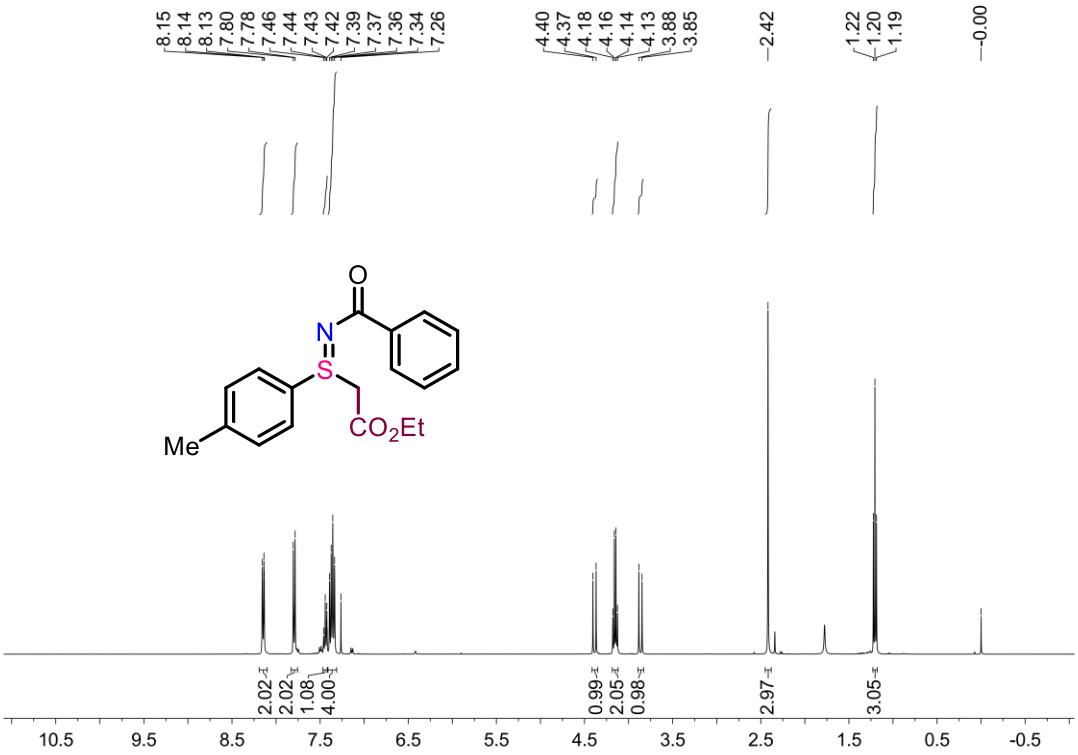
^{13}C NMR spectrum of compound **5b** (100 MHz, $CDCl_3$)



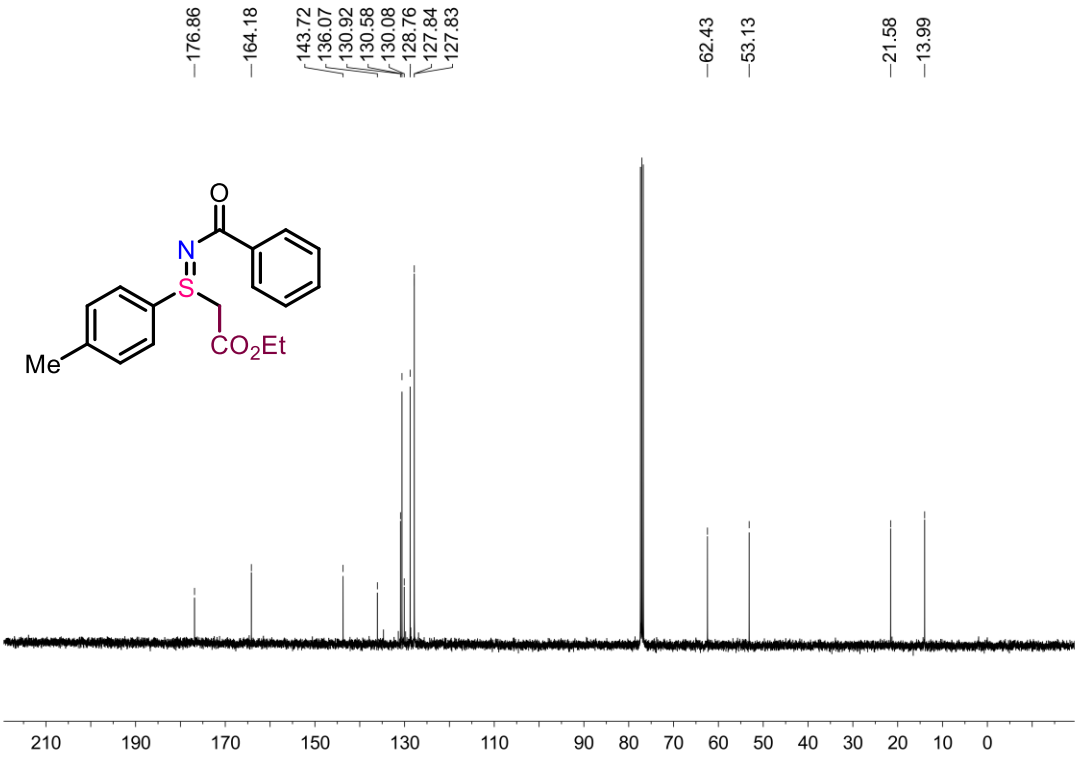
^{31}P NMR spectrum of compound **5b** (162 MHz, $CDCl_3$)



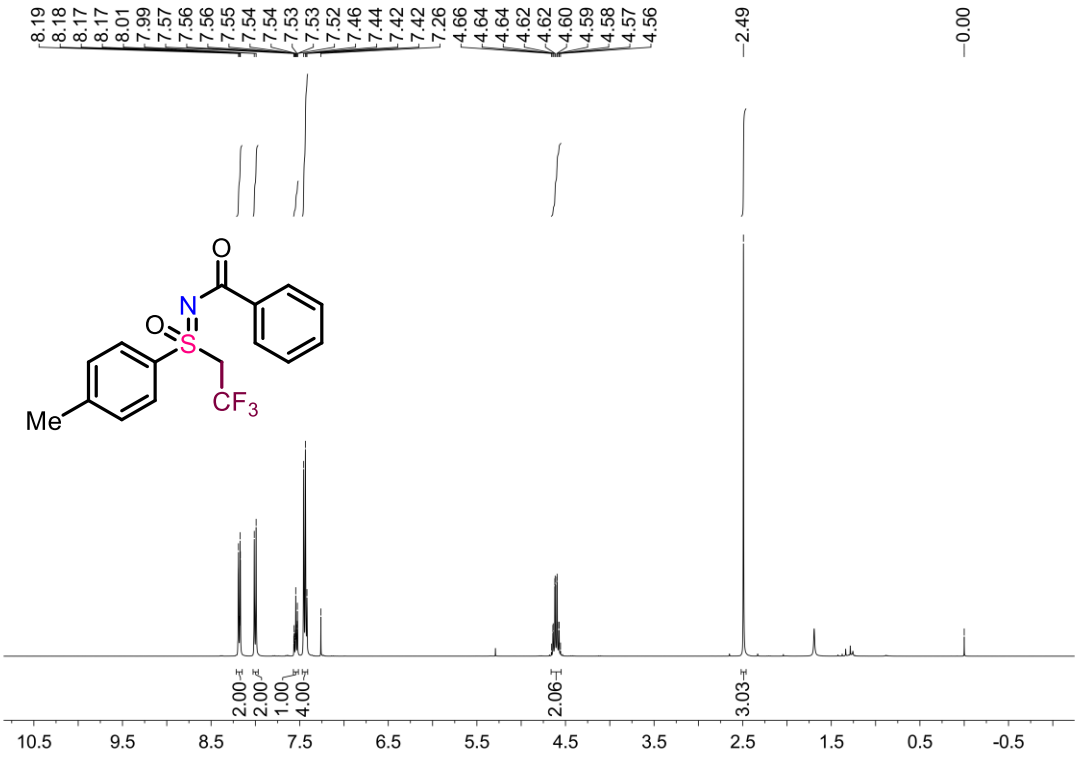
^{1}H NMR spectrum of compound **5c** (400 MHz, $CDCl_3$)



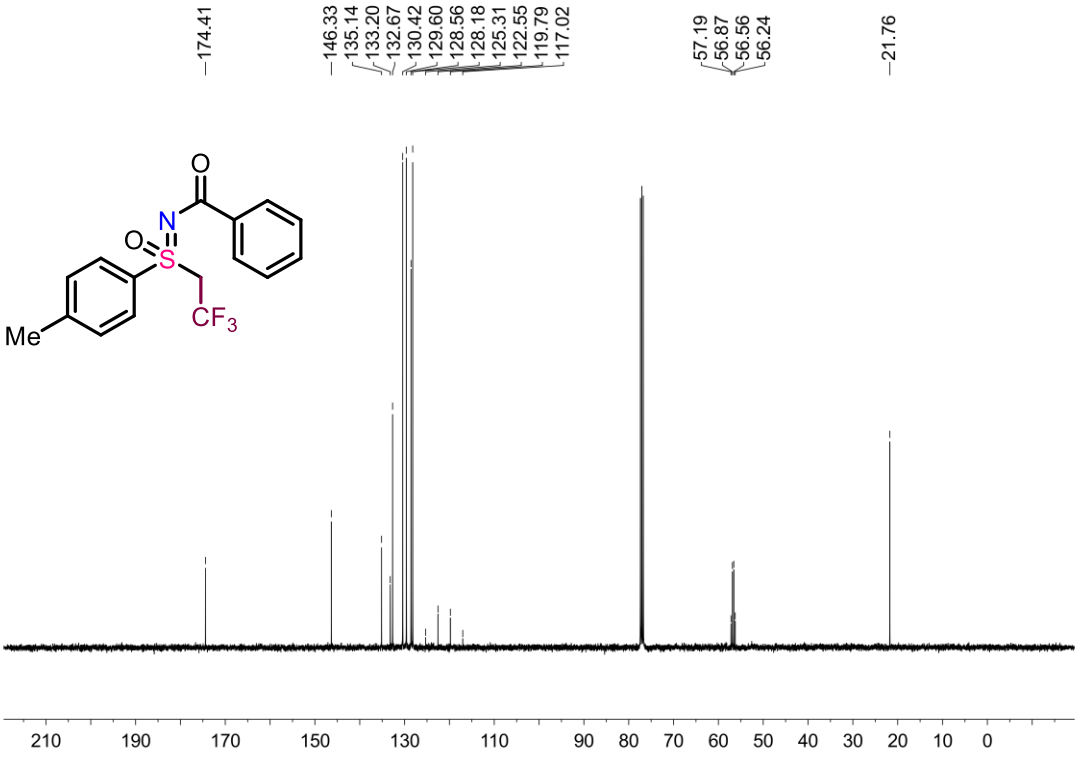
^{13}C NMR spectrum of compound **5c** (100 MHz, $CDCl_3$)



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



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



^{19}F NMR spectrum of compound **6** (376 MHz, $CDCl_3$)