Electronic Supplementary Information

Vaska's Complex – PMHS Combination Enabled Mild and Chemoselective Reduction of Sulfoxides to Sulfides with Low Catalyst Loading

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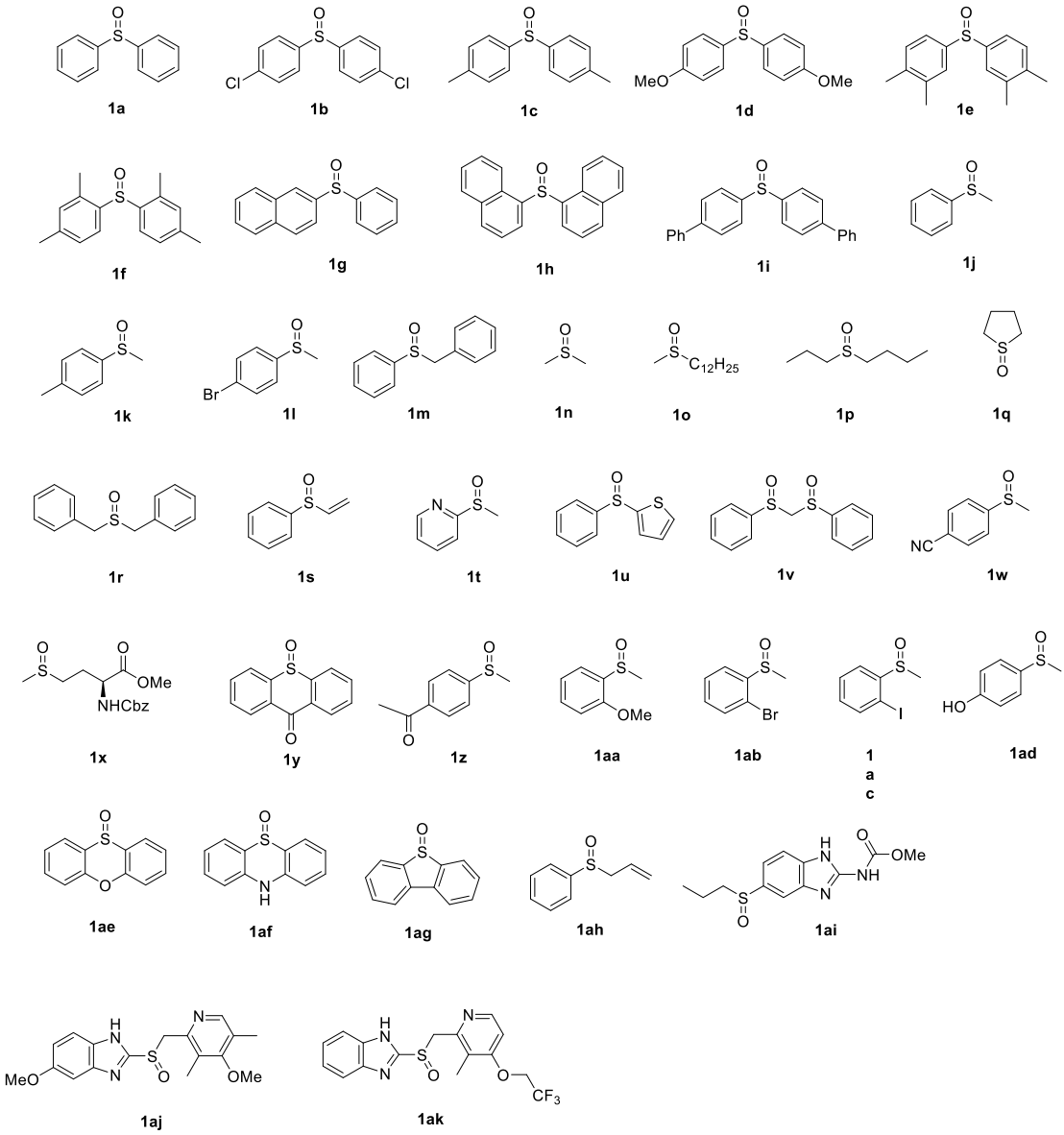
1. General information

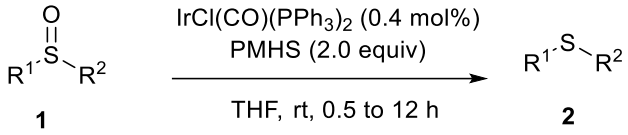
All reactions were performed anhydrously under nitrogen atmosphere. All reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields were calculated based on the weights of chromatographically isolated products or determined by GC methods or ^{1}H NMR. Reactions were monitored by thin-layer chromatography (TLC) on plates (GF254) supplied by Yantai Chemicals (China). The TLC spots were visualized under ultraviolet light or by staining with an ethanolic solution of phosphomolybdic acid and cerium sulfate or iodine vapor. Flash column chromatography was performed using silica gel (200-300 mesh) from Qingdao Haiyang Chemicals. Melting points were determined on a Büchi M560 Automatic Melting Point apparatus and are uncorrected. NMR spectra were recorded on Bruker AV III 400 and Bruker AV III 500 instruments, and calibrated with tetramethylsilane (TMS) (δ H = 0.00 ppm.) and $CDCl_3$ (δ C = 77.00 ppm.) as internal references. Multiplicities were designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet. Infrared (IR) spectra were measured on a Nicolet FT-380 spectrometer using film KBr pellet techniques. High-resolution mass spectra analyses were performed on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics) with a 7-T magnet (Magnex) and an electrospray ionization (ESI) source (Apollo II, Bruker Daltonics) under positive-ion mode. Optical rotations were measured on an Anton Paar MCP-500 polarimeter. THF were distilled over sodium benzophenone ketyl under N_2. Dichloromethane was distilled over calcium hydride under N_2. sulfoxides **1e**[1], **1f**[1], **1g**[2], **1h**[1], **1i**[1], **1u**[2], **1v**[3], **1y**[2], **1ag**[2] were prepared according to the procedures described in the literature. All other commercially available compounds were used as received.

2. The structures of all sulfoxides used



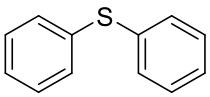
3. General procedure and the reductions of sulfoxides

General procedure:



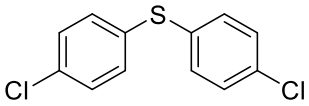
To a flame-dried Schlenk tube were added a sulfoxide **1** (1.0 mmol), $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%) and THF (4 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, poly(methylhydrosiloxane) (PMHS) (444 μL, 2 mmol, 2 equiv) was added, and the resulting mixture was stirred at room temperature (25 ℃) for 30 min to 12 h. The resulting mixture was filtered through a short pad of Celite and washed with ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel eluting with EtOAc/*n*-hexane to afford the desired sulfide **2**.

Diphenylsulfane[4]



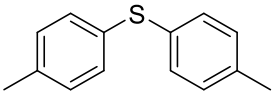
Following the general procedure, the reaction of sulfoxide **1a** (202.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL), 3 h gave, after FC (eluent: *n*-hexane), sulfide **2a** as a pale-yellow oil (182.5 mg, yield: 98%); IR (film) $\tilde{\nu}$: 3058, 2964, 1783, 1579, 1474, 1438, 1024, 736, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.29 - 7.26 (m, 2H), 7.24 – 7.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 130.9, 129.1, 126.99; HRMS (ESI) *m/z* for $C_{12}H_{11}S^+$ ($[M+H]^+$): 187.0576; found: 187.0575.

Bis(4-chlorophenyl)sulfane[3]



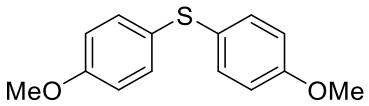
Following the general procedure, the reaction of sulfoxide **1b** (271.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2b** as a white solid (231.1 mg, yield: 91%); M. p. 86 - 88 °C (lit.: M. p. 88 - 89 °C)[5]; IR (film) $\tilde{\nu}$: 2938, 2834, 1591, 1491, 1285, 1244, 1171, 1031, 824 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.3 Hz, 1H), 7.26 (d, *J* = 2.5 Hz, 3H), 7.25 (d, *J* = 4.4 Hz, 3H), 7.23 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 133.4, 132.3, 129.5; HRMS (ESI) *m/z* for $C_{12}H_9Cl_2S^+$ ($[M+H]^+$): 254.9797; found: 254.9791.

Di-*p*-tolylsulfane[6]



Following the general procedure, the reaction of sulfoxide **1c** (230.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2c** as a white solid (199.1 mg, yield: 93%); M. p. 56 - 58 °C (lit.: M. p. 53 – 55 °C)[6]; IR (film) $\tilde{\nu}$: 3019, 2920, 1584, 1491, 1282, 1088, 1015, 803 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 4H), 7.10 - 7.08 (m, 4H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 132.6, 131.0, 129.8, 21.0 (2C); HRMS (ESI) *m/z* for $C_{14}H_{15}S^+$ ($[M+H]^+$): 215.0889; found: 215.0891.

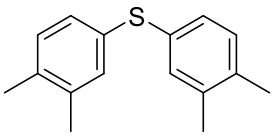
Bis(4-methoxyphenyl)sulfane[6]



Following the general procedure, the reaction of sulfoxide **1d** (262.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2d** as a white solid (233.8 mg, yield: 95%); M. p. 47 - 49 °C (lit.: M. p. 43 - 44 °C)[6]; IR (film) $\tilde{\nu}$: 2965, 2841, 1591, 1496,

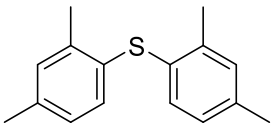
1285, 1248, 1184, 1184, 1032, 837, 813 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 6.85 – 6.79 (m, 4H), 3.76 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 132.8, 127.5, 114.8, 55.4; HRMS (ESI) *m/z* for $C_{14}H_{15}O_2S^+$ ($[M+H]^+$): 247.0787; found: 247.0789.

Bis(3,4-dimethylphenyl)sulfane[6]



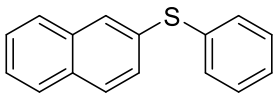
Following the general procedure, the reaction of sulfoxide **1e** (258.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2e** as a white solid (227.6 mg, yield: 94%); M. p. 144 - 146 °C (lit.: M. p. 145 - 147 °C)[6]; **IR** (film) $\tilde{\nu}$: 2975, 2933, 1592, 1449, 1023, 877, 807, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 - 7.13 (m, 2H), 7.08 – 6.99 (m, 4H), 2.20 (s, 6H), 2.18 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 135.4, 132.8, 132.1, 130.3, 128.5, 19.6, 19.3; HRMS (ESI) *m/z* for $C_{16}H_{19}S^+$ ($[M+H]^+$): 243.1202; found: 243.1213.

Bis(2,4-dimethylphenyl)sulfane[7]



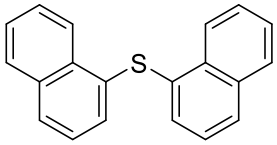
Following the general procedure, the reaction of sulfoxide **1f** (258.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2f** as a white solid (237.3 mg, yield: 98%); M. p. 134 - 136 °C ; IR (film) $\tilde{\nu}$: 2920, 2856, 1602, 1474, 1232, 1050, 874, 810, 724 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 - 7.55 (m, 2H), 7.13 - 7.11 (m, 2H), 6.99 (s, 2H), 2.35 (s, 6H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 138.7, 136.2, 131.4, 127.6, 125.9, 21.0, 18.23; HRMS (ESI) *m/z* for $C_{16}H_{19}S^+$ ($[M+H]^+$): 243.1202; found: 243.1209.

Naphthalen-2-yl(phenyl)sulfane[8]



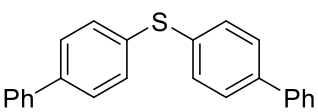
Following the general procedure, the reaction of sulfoxide **1g** (252.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2g** as a yellow oil (214.8 mg, yield: 91%); IR (film) $\tilde{\nu}$: 3054, 2956, 1582, 1477, 1438, 1132, 1024, 813, 741, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.65 (m, 4H), 7.45 – 7.32 (m, 5H), 7.28 - 7.25 (m, 2H), 7.23 – 7.19 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.9, 133.9, 133.1, 132.4, 131.1, 130.0, 129.4, 128.9, 128.9, 127.9, 127.5, 127.2, 126.7, 126.3; HRMS (ESI) *m/z* for $C_{16}H_{13}S^+$ ($[M+H]^+$): 237.0732; found: 237.0731.

Di(naphthalen-1-yl)sulfane[6]



Following the general procedure, the reaction of sulfoxide **1h** (302.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2h** as a brown solid (277.5 mg, yield: 97%); M. p. 184 - 186 °C (lit.: M. p. 176 - 178 °C)[6]; IR (film) $\tilde{\nu}$: 3053, 2919, 1562, 1502, 1379, 1254, 969, 789, 768 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 - 8.39 (m, 2H), 7.89 - 7.85 (m, 2H), 7.78 - 7.74 (m, 2H), 7.54 - 7.50(m, 4H), 7.35 – 7.28 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 132.6, 132.4, 129.9, 128.6, 127.9, 126.7, 126.4, 125.9, 125.1; HRMS (ESI) *m/z* for $C_{19}H_{14}S^+$ ($[M+H]^+$): 274.0811; found: 274.0802.

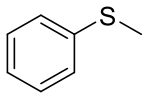
Di([1,1'-biphenyl]-4-yl)sulfane[7]



Following the general procedure, the reaction of sulfoxide **1s** (354.5 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4

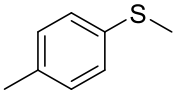
mL) gave, after FC (eluent: *n*-hexane), sulfide **2s** as a white solid (308.0 mg, yield: 91%); M. p. 197 - 199 °C, IR (film) $\tilde{\nu}$: 2963, 1592, 1479, 1395, 837, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 8H), 7.47 – 7.40 (m, 8H), 7.36 – 7.32 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 140.1, 134.8, 131.4, 128.8, 127.9, 127.5, 126.9; HRMS (ESI) *m/z* for $C_{24}H_{19}S^+$ ($[M+H]^+$): 339.1202; found: 339.1198.

Methyl(phenyl)sulfane[5]



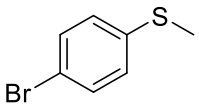
Following the general procedure, the reaction of sulfoxide **1j** (140.0 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2j** as a colorless oil (115.5 mg, yield: 93%); IR (film) $\tilde{\nu}$: 2958, 2873, 1465, 1378, 704 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 7.10 - 7.05 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.6, 126.3, 124.7, 15.5; HRMS (ESI) *m/z* for $C_7H_9S^+$ ($[M+H]^+$): 125.0419; found: 125.0413.

Methyl(*p*-tolyl)sulfane[5]



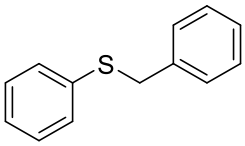
Following the general procedure, the reaction of sulfoxide **1k** (154.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2k** as a pale-yellow oil (129.9 mg, yield: 94%); IR (film) $\tilde{\nu}$: 2917, 1580, 1492, 799 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 2H), 7.10 – 7.06 (m, 2H), 2.44 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 134.7, 129.6, 127.3, 20.9, 16.5; HRMS (ESI) *m/z* for $C_8H_{11}S^+$ ($[M+H]^+$): 139.0576; found: 139.0579.

(4-Bromophenyl)(methyl)sulfane[5]



Following the general procedure, the reaction of sulfoxide **1l** (154.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2l** as a white solid (174.7 mg, yield: 86%); M. p. 38 – 39 °C (lit.: M. p. 34 – 36 °C)[5]; IR (film) $\tilde{\nu}$: 2922, 1473, 1093, 1007, 806 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.15 – 7.08 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 131.8, 128.1, 118.6, 15.9; HRMS (ESI) *m/z* for $C_7H_8BrS^+$ ($[M+H]^+$): 202.9525; found: 202.9527.

Benzyl(phenyl)sulfane[9]

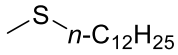


Following the general procedure, the reaction of sulfoxide **1m** (216.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 2), sulfide **2m** as a colorless oil (168.1 mg, yield: 84%); IR (film) $\tilde{\nu}$: 2960, 1453, 1441, 1035, 743, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 5H), 7.24 – 7.20 (m, 3H), 7.19 – 7.13 (m, 1H), 4.09 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 136.3, 129.7, 128.8, 128.4, 127.1, 126.3, 38.9; HRMS (ESI) *m/z* for $C_{13}H_{13}S^+$ ($[M+H]^+$): 201.0732; found: 201.0735.

Dimethylsulfane[5]

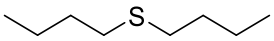
Following the general procedure, the reaction of sulfoxide **1n** (78.1 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave. The crude reaction mixture was analyzed by GC analysis using a tetradecane as internal standard and a 91% yield of title compound **2n** was calculated. Due to the extremely volatile nature of this compound, purification was not performed.

Dodecyl(methyl)sulfane[4]



Following the general procedure, the reaction of sulfoxide **1o** (232. mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave. The crude reaction mixture was analyzed by ^1H NMR spectroscopy using a trimethoxybenzene internal standard and a 85% yield of title compound **2o** was calculated.

Dibutylsulfane[4]

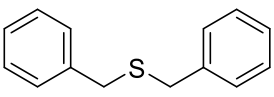


Following the general procedure, the reaction of sulfoxide **1p** (162.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave. The crude reaction mixture was analyzed by GC analysis using a tetradecane as internal standard and a 87% yield of title compound **2p** was calculated. Due to the extremely volatile nature of this compound, purification was not performed.

Tetrahydrothiophene[5]

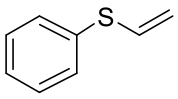
Following the general procedure, the reaction of sulfoxide **1q** (104.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave. The crude reaction mixture was analyzed by GC analysis using a tetradecane as internal standard and Due to the extremely volatile nature of this compound, purification was not performed.

Dibenzylsulfane[8]



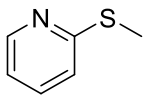
Following the general procedure, the reaction of sulfoxide **1r** (230.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2r** as a colorless oil (168.1 mg, yield: 82%); IR (film) $\tilde{\nu}$: 3027, 2914, 1600, 1493, 1452, 1071, 769, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 8H), 7.25 – 7.19 (m, 2H), 3.58 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 128.9, 128.4, 126.9, 35.5; HRMS (ESI) *m/z* for $C_{13}H_{14}S^+$ ($[M+H]^+$): 202.0811; found: 202.0801.

Phenyl(vinyl)sulfane[10]



Following the general procedure, the reaction of sulfoxide **1s** (152.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2s** as a colorless oil (118.5 mg, yield: 87%); IR (film) $\tilde{\nu}$: 3059, 1584, 1479, 1439, 1093, 1023, 956, 744, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.26 - 7.22 (m, 2H), 7.19 -7.15 (m, 1H), 6.48 (dd, *J* = 16.6, 9.6 Hz, 1H), 5.32 – 5.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.1, 131.7, 130.2, 128.9, 126.9, 115.2; HRMS (ESI) *m/z* for $C_8H_9S^+$ ($[M+H]^+$): 137.0419; found: 137.0420.

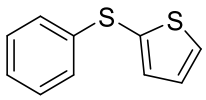
2-(Methylthio)pyridine[11]



Following the general procedure, the reaction of sulfoxide **1t** (141.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2t** as a pale-yellow oil (116.3 mg, yield: 93%); IR (film) $\tilde{\nu}$: 3044, 2925, 1581, 1455, 1126, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 - 8.41 (m, 1H), 7.46 - 7.42 (m, 1H), 7.15 - 7.13 (m, 1H), 6.95 - 6.92 (m, 1H),

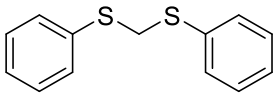
2.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 149.2, 135.5, 121.2, 118.9, 12.9; HRMS (ESI) *m/z* for $C_6H_8NS^+$ ($[M+H]^+$): 126.0372; found:126.0378 .

2-(Phenylthio)thiophene[12]



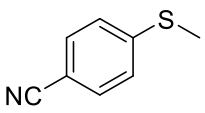
Following the general procedure, the reaction of sulfoxide **1u** (208.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2u** as a yellow oil (176.6 mg, yield: 92%); IR (film) $\tilde{\nu}$: 3072, 2924, 1582, 1476, 1439, 1402, 1217, 1080, 1023, 847, 738, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 5.4 Hz, 1H), 7.25 (d, *J* = 3.6, 1H), 7.21 – 7.15 (m, 4H), 7.12 – 7.07 (m, 1H), 7.00 (dd, *J* = 5.4, 3.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 135.9, 131.2, 131.0, 128.9, 127.8, 127.0, 125.9; HRMS (ESI) *m/z* for $C_{10}H_9S^+$ ($[M+H]^+$): 193.0140; found: 193.0141.

Bis(phenylthio)methane[8]



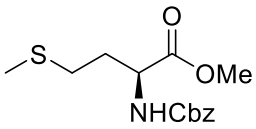
Following the general procedure, the reaction of sulfoxide **1v** (264.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), the **2v** product as a white solid (192.6 mg, yield: 83%); M. p. 37 – 40 °C (lit.: M. p. 39 – 41 °C)[8]; IR (film) $\tilde{\nu}$: 3057, 2961, 1582, 1479, 1438, 1199, 1087, 1024, 737, 688 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 4H), 7.33 – 7.28 (m, 4H), 7.27 – 7.21 (m, 2H), 4.34 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 130.8, 129.1, 127.2, 40.6; HRMS (ESI) *m/z* for $C_{13}H_{13}S_2^+$ ($[M+H]^+$): 233.0453; found: 233.0452.

4-(Methylthio)benzonitrile[13]



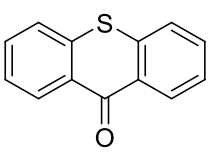
Following the general procedure, the reaction of sulfoxide **1w** (165.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2w** as a white solid (135.6 mg, yield: 91%); M. p. 59 – 61 °C (lit.: M. p. 61 – 63 °C)[13]; IR (film) $\tilde{\nu}$: 2928, 2222, 1596, 1484, 1402, 1087, 817 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.31 – 7.21 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 132.1, 125.4, 118.9, 107.6, 14.6; HRMS (ESI) *m/z* for $C_8H_8NS^+$ ($[M+H]^+$): 150.0372; found: 150.0373.

Methyl ((benzyloxy)carbonyl)-*L*-methioninate[14]



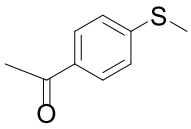
Following the general procedure, the reaction of sulfoxide **1x** (313.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL), 60 ℃, 8 h gave, after FC (eluent: EtOAc/*n*-hexane = 1: 2), sulfide **2x** as a white solid (220.1 mg, yield: 74%); M. p. 41 - 43 °C (lit.: M. p. 44 – 46 °C)[6]; IR (film) $\tilde{\nu}$: 3342, 3028, 2956, 1721, 1531, 1297, 1217, 1130, 1052, 754, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 5.49 (s, 1H), 5.11 (s, 2H), 4.52 - 4.48 (m, 1H), 3.75 (s, 3H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.19 - 2.12(m, 1H), 2.08 (s, 3H), 2.00 - 1.93 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 155.9, 136.2, 128.6, 128.3, 128.2, 77.3, 67.1, 53.1, 52.6, 31.9, 29.9, 15.5; HRMS (ESI) *m/z* for $C_{14}H_{20}NO_4S^+$ ($[M+H]^+$): 298.1108; found: 298.1108.

9*H*-Thioxanthen-9-one[8]



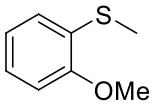
Following the general procedure, the reaction of sulfoxide **1y** (228.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL), 6 h gave, after FC (eluent: EtOAc/*n*-hexane = 1: 2), sulfide **2y** as a white solid (169.8 mg, yield: 80%); M. p. 210 - 212 °C (lit.: M. p. 207 – 209 °C)[8]; IR (film) $\tilde{\nu}$: 3052, 1654, 1590, 1433, 1320, 1161, 1031, 729, 664 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 - 8.61 (m, 2H), 7.66 – 7.56 (m, 4H), 7.50 - 7.47 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 137.3, 132.3, 129.9, 129.2, 126.3, 125.9; HRMS (ESI) *m/z* for $C_{13}H_9OS^+$ ($[M+H]^+$): 213.0369; found: 213.0368.

1-(4-(Methylthio)phenyl)ethan-1-one[18]



Following the general procedure, the reaction of sulfoxide **1z** (168.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (555 μL, 2.0 mmol, 2.0 equiv), THF (4 mL) gave, after FC (eluent: PE), sulfide **2z** as a white solid (123.3 mg, yield: 81%), M. p. 80 - 81 °C (lit.: M. p. 80.5 – 81.5 °C)[19]; IR (film) $\tilde{\nu}$: 3010, 1605, 1580, 1273, 1103, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.55 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 145.8, 133.4, 128.6, 124.9, 26.3, 14.6.

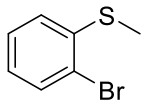
(2-Methoxyphenyl)(methyl)sulfane[15]



Following the general procedure, the reaction of sulfoxide **1aa** (170.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2aa** as a colorless oil (138.8 mg, yield: 90%); IR (film) $\tilde{\nu}$: 2919, 2835, 1576, 1450, 1240, 1062, 1023, 742 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 2H), 6.95 (m, 1H), 6.82 (m, 1H), 3.87 (s, 3H), 2.41 (s, 3H).

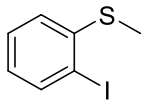
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 132.7, 131.7, 124.2, 121.3, 110.4, 55.4, 40.9. HRMS (ESI) *m/z* for $C_8H_{11}OS^+$ ($[M+H]^+$): 155.0525 ; found: 155.0523.

(2-Bromophenyl)(methyl)sulfane[8]



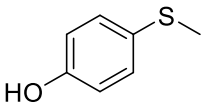
Following the general procedure, the reaction of sulfoxide **1ab** (219.1 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL), gave, after FC (eluent: *n*-hexane), sulfide **2ab** as a colorless oil (199.1 mg, yield: 99%); IR (film) $\tilde{\nu}$: 2919, 1576, 1449, 1250, 1111, 1030, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 - 7.45 (m, 1H), 7.25 - 7.21 (m, 1H), 7.07 - 7.05 (m, 1H), 6.95 - 6.92 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 132.3, 127.6, 125.4, 125.1, 121.4, 15.4; HRMS (ESI) *m/z* for $C_7H_8BrS^+$ ($[M+H]^+$): 202.9525; found: 202.9524.

(2-Bromophenyl)(methyl)sulfane[17]



Following the general procedure, the reaction of sulfoxide **1ac** (113 mg, 0.5 mmol) with $IrCl(CO)(PPh_3)_2$ (1.9 mg, 0.4 mol%), PMHS (222 μL, 1 mmol, 1 equiv), THF (2 mL) gave, after FC (eluent: PE), sulfide **2ac** as a light yellow oil (102.5 mg, yield: 82%); IR (film) $\tilde{\nu}$: 2935, 1571, 1250, 1104, 652 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75(m, 1H), 7.34-7.29 (m, 1H), 7.09-7.06 (m, 1H), 8.84-6.80 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.1, 128.6, 125.8, 124.7, 97.2, 16.9.

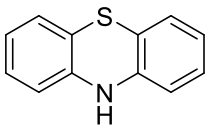
4-(Methylthio)phenol[5]



Following the general procedure, the reaction of sulfoxide **1ad** (156.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4

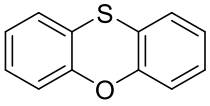
mL) gave, after FC (eluent: EtOAc/*n*-hexane = 1: 2), sulfide **2ad** a white solid (116.2 mg, yield: 83%); M. p. 81 – 82 °C (lit.: M. p. 77 – 79 °C)[5]; IR (film) $\tilde{\nu}$: 3233, 2804, 1584, 1499, 1281, 1015, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.21 (m, 2H), 6.85 – 6.70 (m, 2H), 4.88 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 130.4, 128.9, 116.0, 18.0; HRMS (ESI) *m/z* for $C_7H_9OS^+$ ($[M+H]^+$): 141.0369; found: 141.0368.

10*H*-Phenothiazine[16]



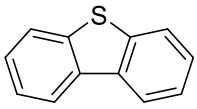
Following the general procedure, the reaction of sulfoxide **1ae** (215.0 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2ae** as a white solid (197.1 mg, yield: 99%); M. p. 181 - 183 °C (lit.: M. p. 180 – 184 °C)[16]; IR (film) $\tilde{\nu}$: 3331, 1573, 1481, 1311, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, J = 7.4 Hz, 4H), 6.81 (t, J = 7.5 Hz, 2H), 6.52 (d, J = 7.9 Hz, 2H), 5.78 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 127.3, 126.8, 122.6, 118.3, 114.4, 114.4. HRMS (ESI) *m/z* for $C_{12}H_{10}NS^+$ ($[M+H]^+$): 200.0528; found: 200.0531`.

Phenoxathiine[8]



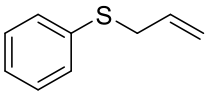
Following the general procedure, the reaction of sulfoxide **1af** (216.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL) gave, after FC (eluent: *n*-hexane), sulfide **2af** as a white solid (188.0 mg, yield: 94%); M. p. 53 - 55 °C (lit.: M. p. 54 – 56 °C)[8]; IR (film) $\tilde{\nu}$: 3072, 1586, 1449, 1259, 1224, 1081, 760, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 4H), 7.01-6.97 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 127.7, 126.8, 124.5, 120.1, 117.8; HRMS (ESI) *m/z* for $C_{12}H_9OS^+$ ($[M+H]^+$): 201.0369; found: 201.0372.

Dibenzo[*b*,*d*]thiophene[8]



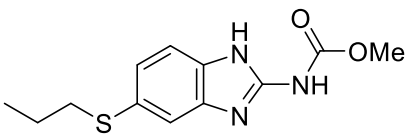
Following the general procedure, the reaction of sulfoxide **1ag** (200.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (444 μL, 2 mmol, 2 equiv), THF (4 mL), gave, after FC (eluent: EtOAc/*n*-hexane = 1: 2), sulfide **2ag** as a white solid (160.1 mg, yield: 87%); M. p. 83 - 85 °C (lit.: M. p. 87 – 89 °C)[8]; IR (film) $\tilde{\nu}$: 2922, 1426, 1307, 1230, 1126, 1066, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13-8.10 (m, 2H), 7.84-7.81 (m, 2H), 7.48 – 7.38 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 135.5, 126.6, 124.3, 122.8, 121.5; HRMS (ESI) *m/z* for $C_{12}H_9S^+$ ($[M+H]^+$): 185.0419; found: 185.0421.

Allyl(phenyl)sulfane[20]



Following the general procedure, the reaction of sulfoxide **1ah** (166.2 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (555 μL, 2.0 mmol, 2.0 equiv), THF (4 mL) gave, after FC (eluent: PE), sulfide **2ah** as a colorless oil (109.5 mg, yield: 73%); IR (film) $\tilde{\nu}$: 3063, 1514, 1479, 1437, 961, 723 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34-7.32 (m, 2H), 7.27-7.24 (m, 2H), 7.19 – 7.13 (m, 1H), 5.86 (m, 1H), 5.16 – 5.02 (m, 2H), 3.53 (dt, *J* = 6.9, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.7, 133.5, 129.7, 128.7, 126.1, 117.6, 37.1.

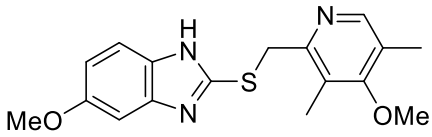
Methyl (5-(propylthio)-1*H*-benzo[*d*]imidazol-2-yl)carbamate[6]



Following the general procedure, the reaction of sulfoxide **1ai** (218.3 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (555 μL, 2.5 mmol, 2.5 equiv), THF

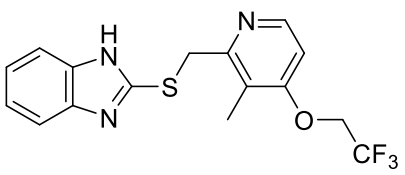
(4 mL), 80℃, 12 h gave, after FC (eluent: EtOAc), sulfide **2ai** as a white solid (196.3 mg, yield: 74%); M. p. 201 - 203 °C (lit.: M. p. 206 - 208 °C)[6]; IR (film) $\tilde{v}$: 3323, 1713, 2956, 1633, 1443, 1326, 1195, 1269, 1096, 958, 760 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, *J* = 1.7 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.12-7.10 (m, 1H), 3.77 (s, 3H), 3.34 (s, 1H), 2.86 (t, *J* = 7.1 Hz, 2H), 2.52-2.50 (m, 1H), 1.59-1.50 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.8, 147.8, 126.8, 124.0, 115.7, 114.1, 52.5, 36.7, 22.1, 13.1; HRMS (ESI) *m/z* for $C_{12}H_{16}N_3O_2S^+$ ($[M+H]^+$): 266.0958; found: 266.0957.

5-Methoxy-2-(((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)thio)-1*H*-benzo[*d*]imidazole[6]



Following the general procedure, the reaction of sulfoxide **1aj** (345.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (555 μL, 2.5 mmol, 2.5 equiv), THF (4 mL), 80 ℃, 12 h gave, after FC (eluent: EtOAc/*n*-hexane = 2: 1), sulfide **2aj** as a colorless oil (273.2 mg, yield: 83%)[6]; IR (film) $\tilde{v}$: 2932, 1567, 1265, 1198, 1156, 1073, 804 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.83-6.81 (m, 1H), 4.37 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 155.9, 155.8, 150.6, 148.3, 126.4, 125.5, 111.0, 60.0, 55.8, 35.0, 13.4, 11.2; HRMS (ESI) *m/z* for $C_{17}H_{20}N_3O_2S^+$ ($[M+H]^+$): 330.1271; found: 330.1266.

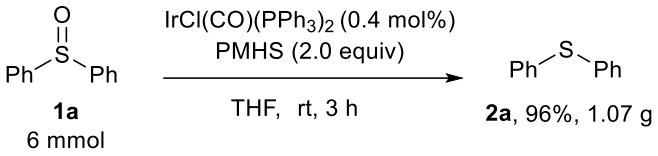
2-(((3-Methyl-4-(2,2,2-trifluoroethoxy)pyridin-2-yl)methyl)thio)-1*H*-benzo[*d*]imidazole[6]



Following the general procedure, the reaction of sulfoxide **1ak** (369.4 mg, 1.0 mmol) with $IrCl(CO)(PPh_3)_2$ (3.2 mg, 0.4 mol%), PMHS (555 μL, 2.5 mmol, 2.5 equiv), THF: CH_2Cl_2= 3: 1 (4 mL), 80 ℃, 12 h gave, after FC (eluent: EtOAc/*n*-hexane = 1: 2), sulfide **2ak** as a white solid (250.9 mg, yield: 71%); M. p. 154 - 156 °C (lit.: M. p. 150 - 152 °C)[6]; IR (film) $\tilde{\nu}$: 3326, 3053, 1576, 1408, 1254, 1199, 1160, 974, 760, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 5.7 Hz, 1H), 7.60 – 7.46 (m, 2H), 7.20-7.17 (m, 2H), 6.71 (d, *J* = 5.7 Hz, 1H), 4.45 – 4.39 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 157.6, 151.2, 147.4, 122.8 (q, J_{C-F} = 277.9 Hz), 122.0, 121.7, 105.9, 65.5 (q, J_{C-F} = 36.5 Hz), 34.8, 10.6; ^{19}F NMR ((376 MHz, Chloroform-*d*) δ -73.73; HRMS (ESI) *m/z* for $C_{16}H_{15}F_3N_3OS^+$([M+H]$^+$): 354.0882; found: 354.0877.

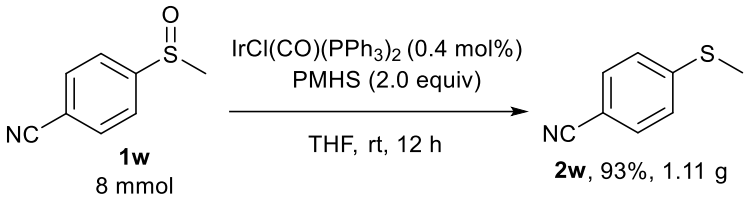
4. Gram-scale reactions

4.1 Gram-scale reduction of sulfoxide **1a**



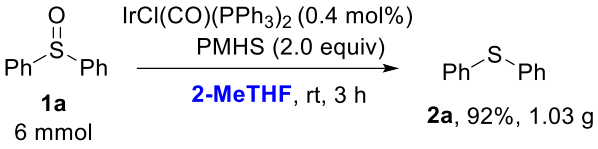
To a flame-dried Schlenk tube were added sulfoxide **1a** (1.21 g, 6 mmol), $IrCl(CO)(PPh_3)_2$ (19.2 mg, 0.4 mol%) and THF (16 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (2.7 mL, 12.0 mmol) was added, and the resulting mixture was stirred at room temperature for 3 h. The resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (120 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2a** in 96% yield (1.07 g) as a pale-yellow oil.

4.2 Gram-scale reduction of sulfoxide **1w**



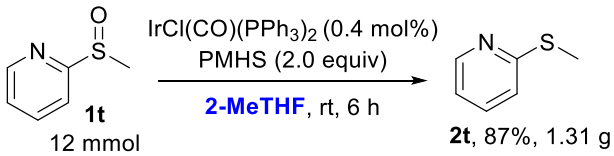
To a flame-dried round bottle flask were added sulfoxide **1w** (1.32 g, 8 mmol), $IrCl(CO)(PPh_3)_2$ (25.6 mg, 0.4 mol%) and THF (16 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (3.6 mL, 16.0 mmol) was added, and the resulting mixture was stirred at room temperature for 12 h. The resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (160 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2w** in 93% yield (1.11 g) as a white solid.

4.3 Gram-scale reduction of sulfoxide **1a** in 2-MeTHF



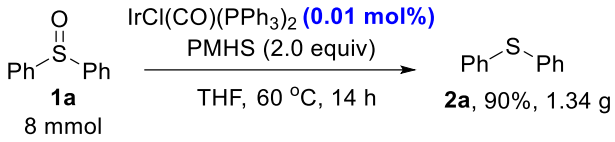
To a flame-dried round bottle flask were added sulfoxide **1a** (1.21 g, 6 mmol), $IrCl(CO)(PPh_3)_2$ (19.2 mg, 0.4 mol%) and 2-MeTHF (12 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (2.7 mL, 12.0 mmol) was added, and the resulting mixture was stirred at room temperature for 3 h. The resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (120 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2a** in 92% yield (1.03 g) as a pale-yellow oil.

4.3 Gram-scale reduction of sulfoxide **1t** in 2-MeTHF



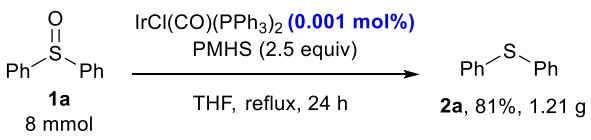
To a flame-dried round bottle flask were added sulfoxide **1t** (1.69 g, 12 mmol), $IrCl(CO)(PPh_3)_2$ (38.4 mg, 0.4 mol%) and 2-MeTHF (24 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (5.3 mL, 24.0 mmol) was added, and the resulting mixture was stirred at room temperature for 6 h. The resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (200 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2t** in 87% yield (1.31 g) as a pale-yellow oil.

4.4 Gram-scale reaction at 0.01 mol % catalyst loading



To a flame-dried round bottle flask equipped with a stir bar were added sulfoxide **1a** (1.62 g, 8 mmol), $IrCl(CO)(PPh_3)_2$ (0.64 mg, 0.01 mol%) and THF (16 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (3.6 mL, 16.0 mmol) was added, and the resulting mixture was stirred at 60 ℃ for 14 h. After cooling down to room temperature, the resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (160 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2a** in 90% yield (1.34 g) as a pale-yellow oil.

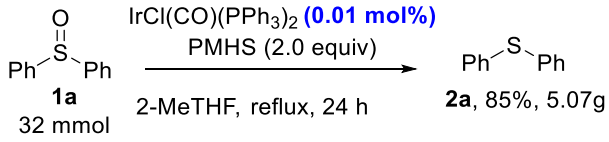
5. Gram-scale reaction at 0.001 mol % catalyst loading



Preparation of highly diluted $IrCl(CO)(PPh_3)_2$/THF solution: 7.8 mg (0.01 mmol) of $IrCl(CO)(PPh_3)_2$ was added to 100 mL of THF, and 1.0 mL of the resultant solution was further diluted to 0.00001 mmol/ mL, from which 1.0 mL was used for the reaction.

To a flame-dried round bottle flask equipped with a stir bar were added sulfoxide **1a** (1.62 g, 8 mmol), $IrCl(CO)(PPh_3)_2$/ THF solution (1.0 mL of the abovementioned solution, 0.001 mol %), and THF (16 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (3.6 mL, 16.0 mmol) was added, and the resulting mixture was stirred at reflux for 24 hours. After cooling down to room temperature, the resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (160 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2a** in 84% yield (1.25 g) as a pale-yellow oil.

6. Gram-scale reaction(32 mmol) at 0.01 mol % catalyst loading



To a flame-dried round bottle flask equipped with a stir bar were added sulfoxide **1a** (6.47 g, 32 mmol), $IrCl(CO)(PPh_3)_2$ (2.5 mg, 0.01 mol%) and 2-MeTHF (60 mL) under N_2 atmosphere at room temperature. After being stirred at room temperature for 5 min, PMHS (28.2 mL, 64.0 mmol) was added, and the resulting mixture was stirred at reflux for 24 hours. After cooling down to room temperature, the resulting mixture was filtered through a short pad of Celite eluting with ethyl acetate (160 mL), the residue was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether to give sulfide **2a** in 85% yield (5.07 g) as a pale-yellow oil.

6. Reference

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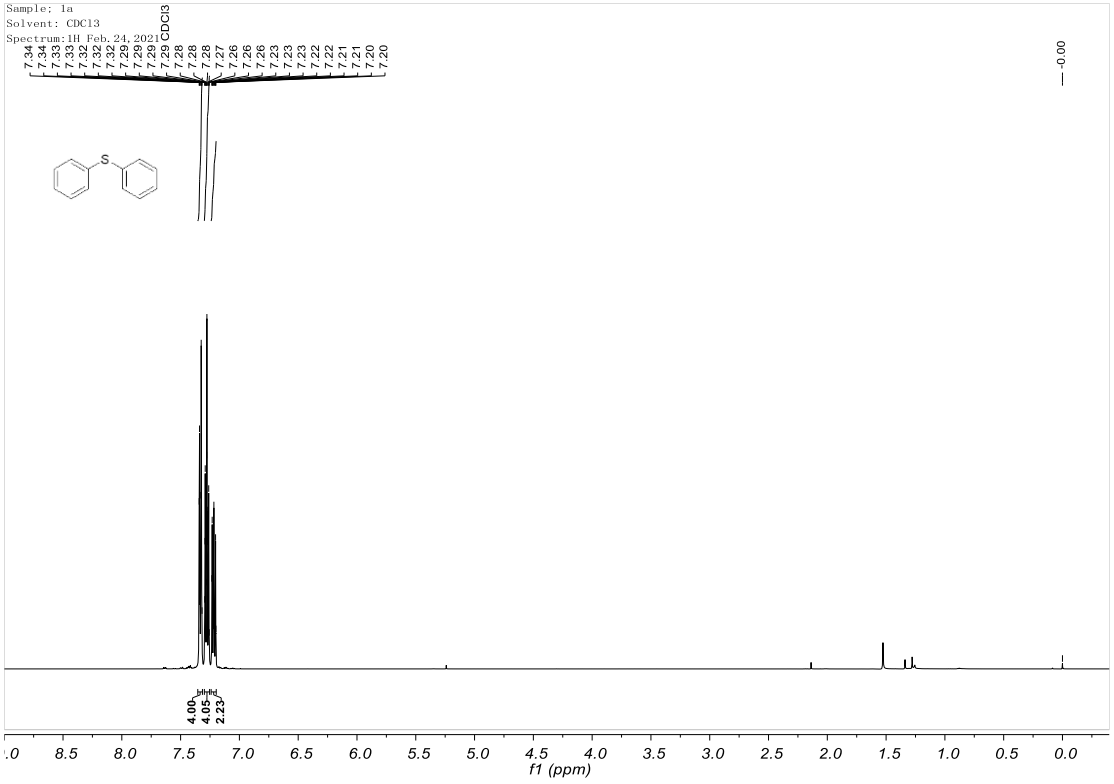
7. NMR spectra of products

Fig. 1. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2a



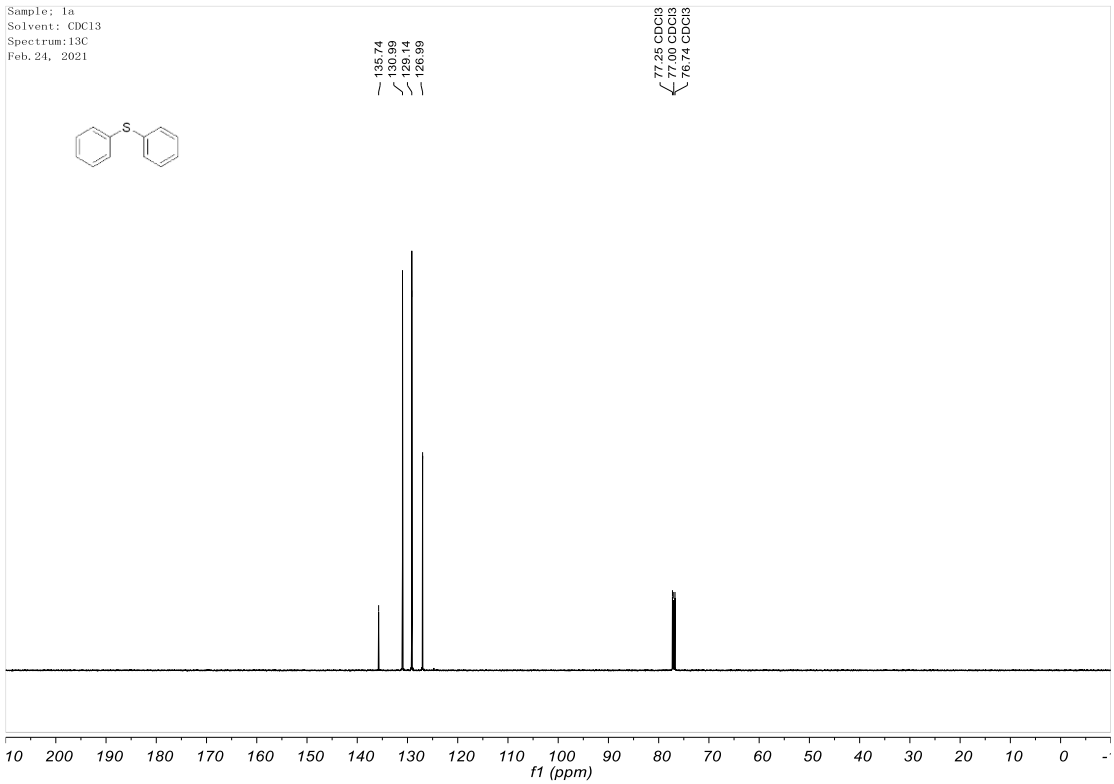


Fig. 2. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2b

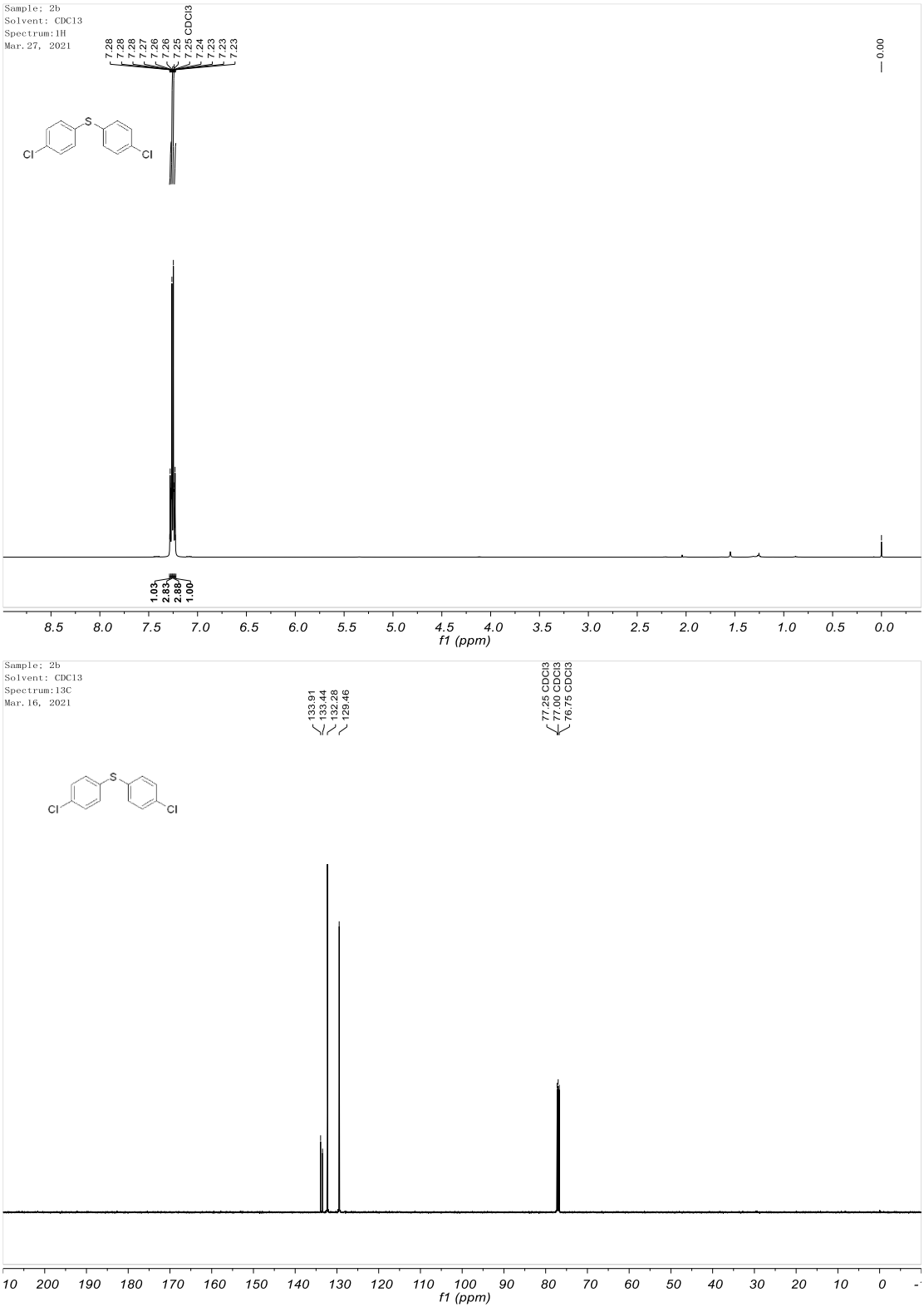


Fig. 3. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2c

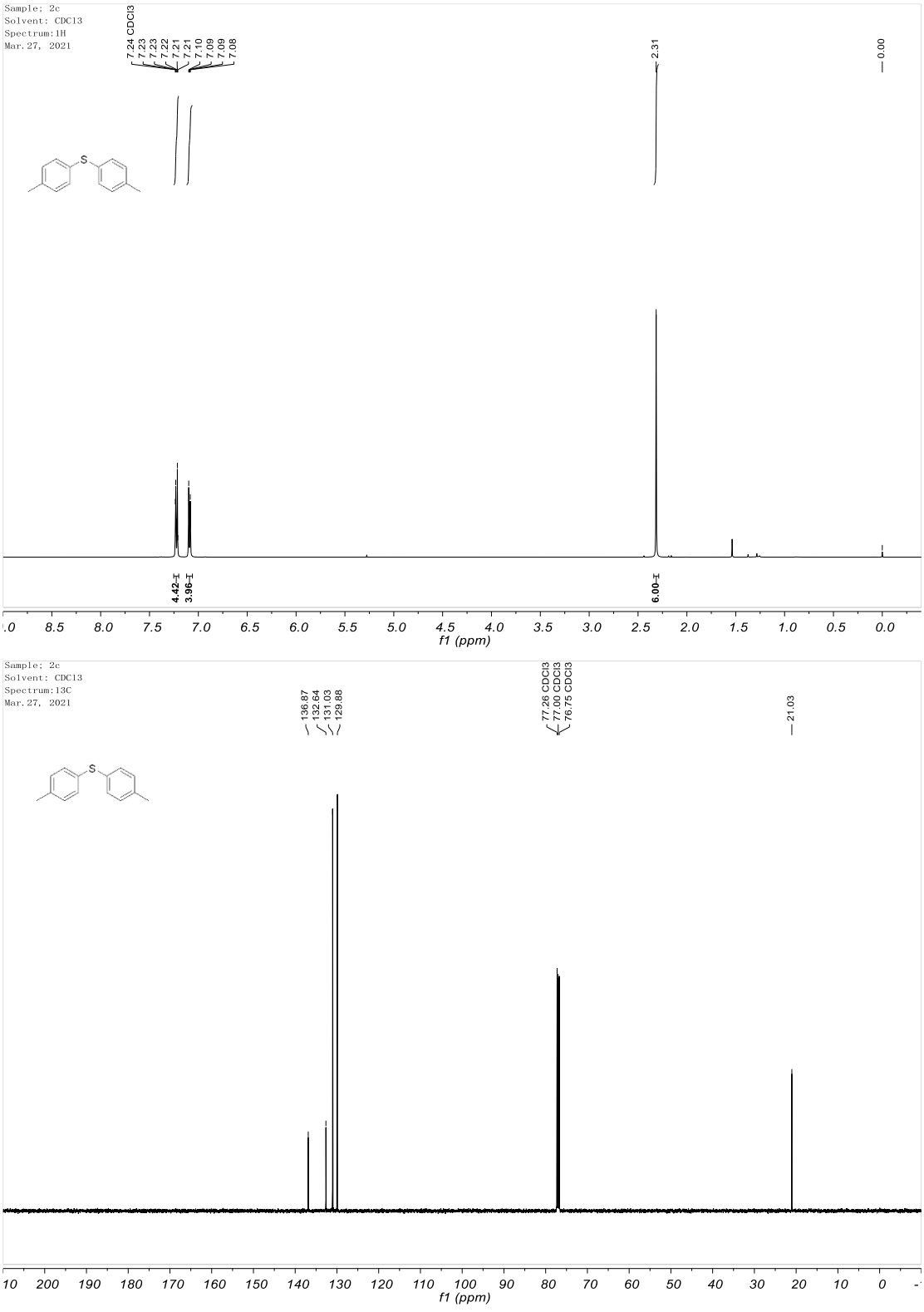
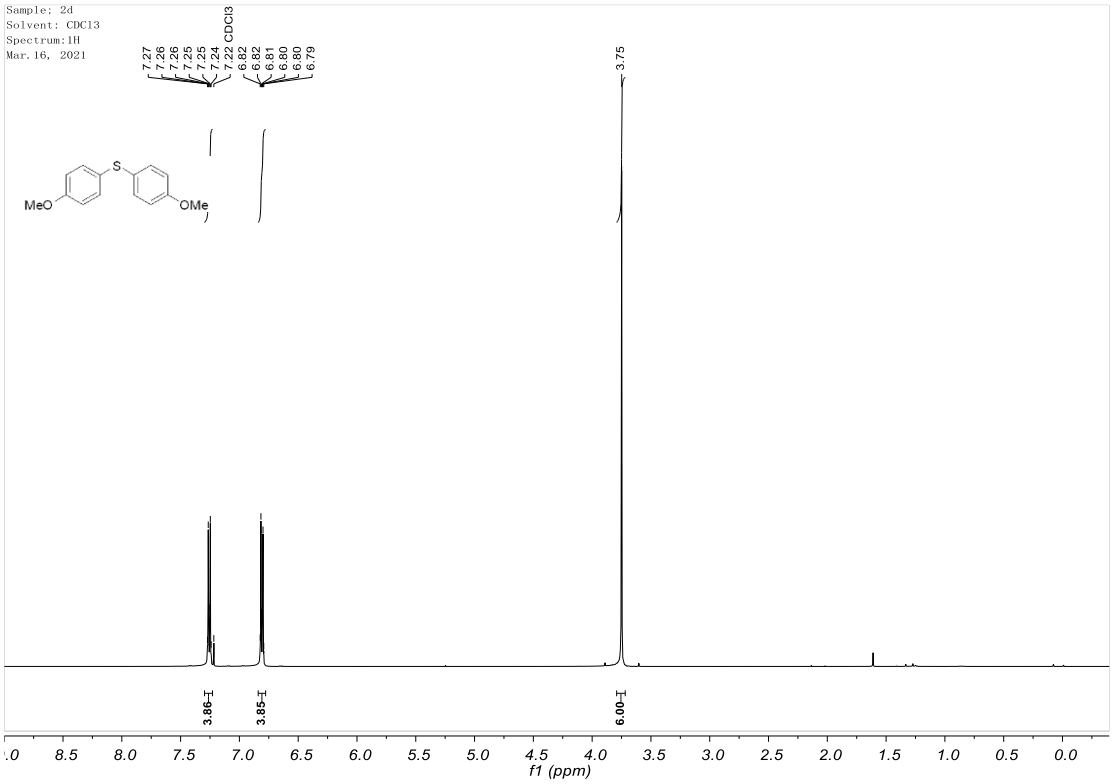


Fig. 4. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2d



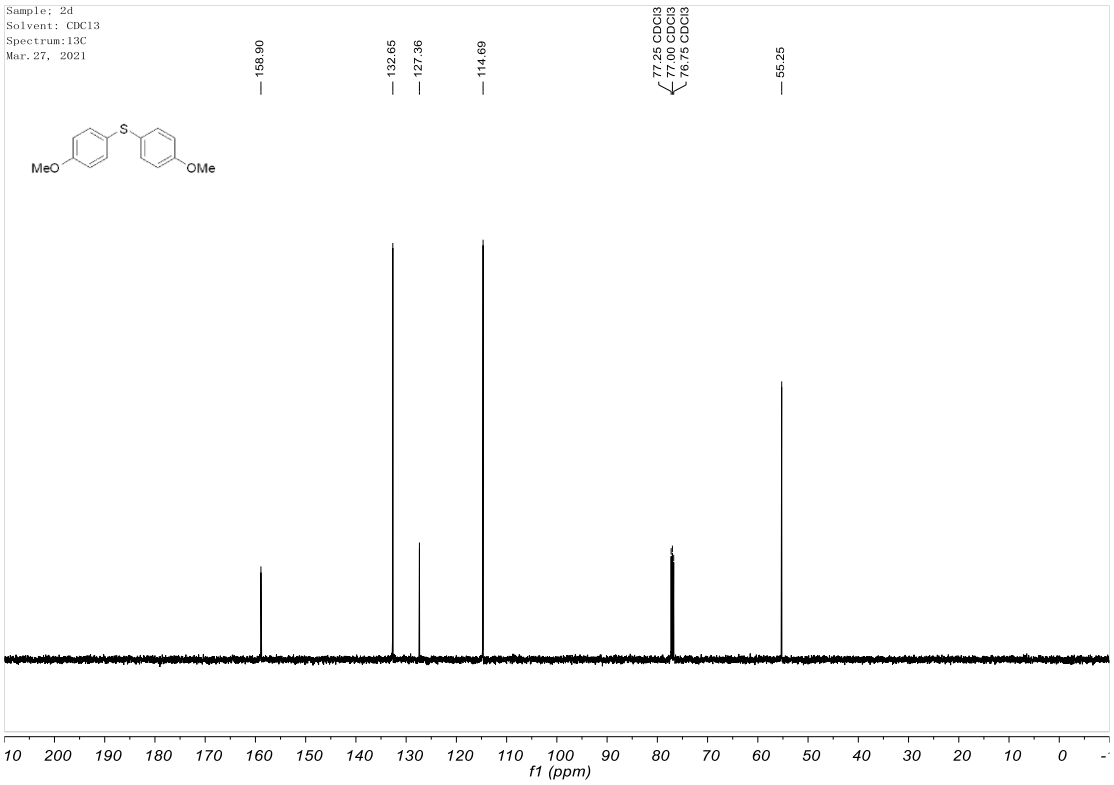
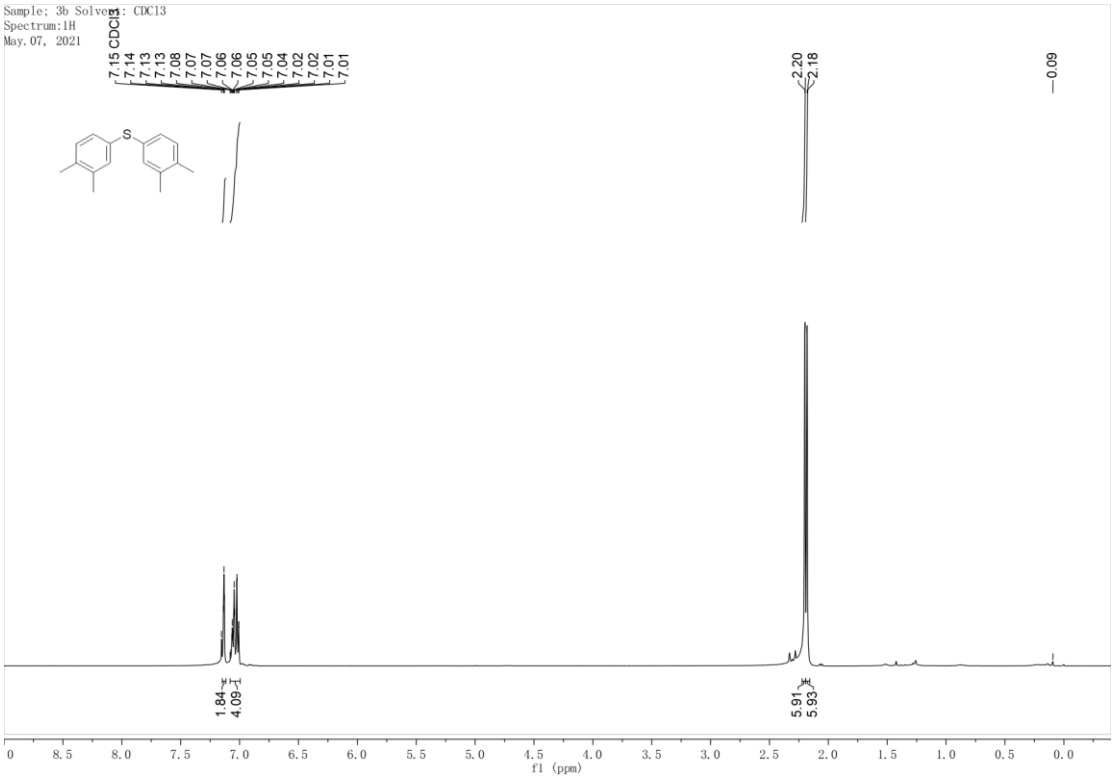


Fig. 5. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2e



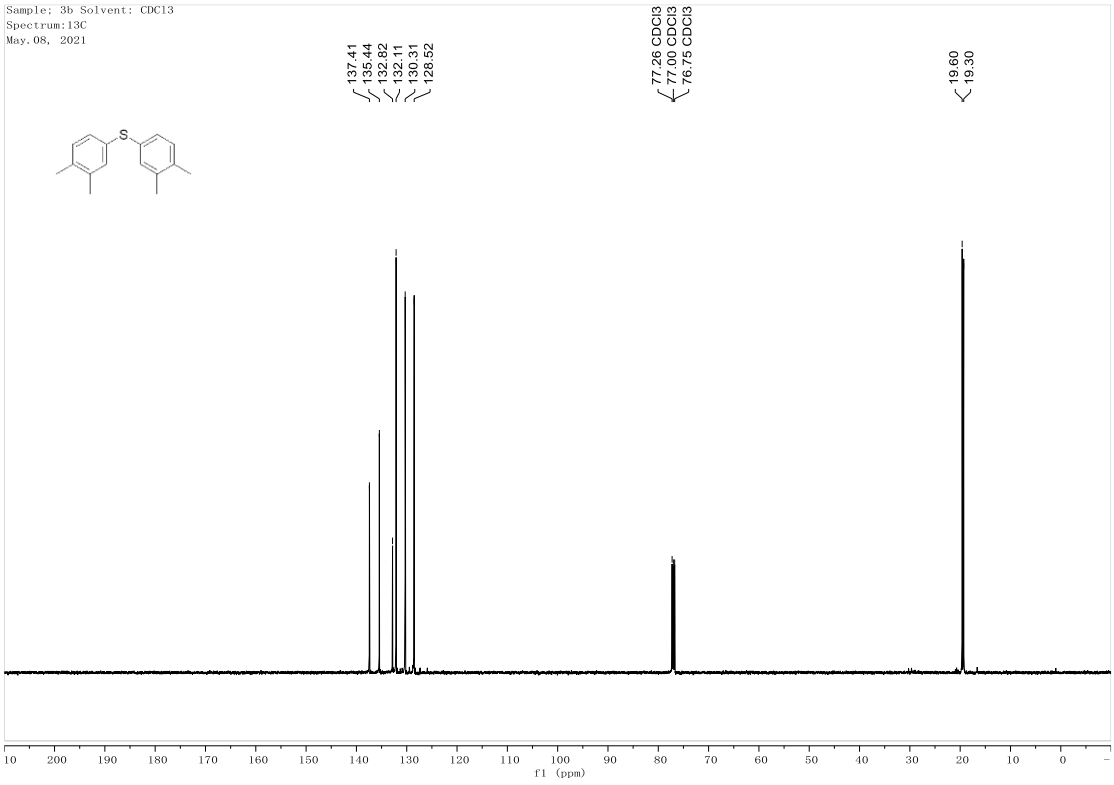
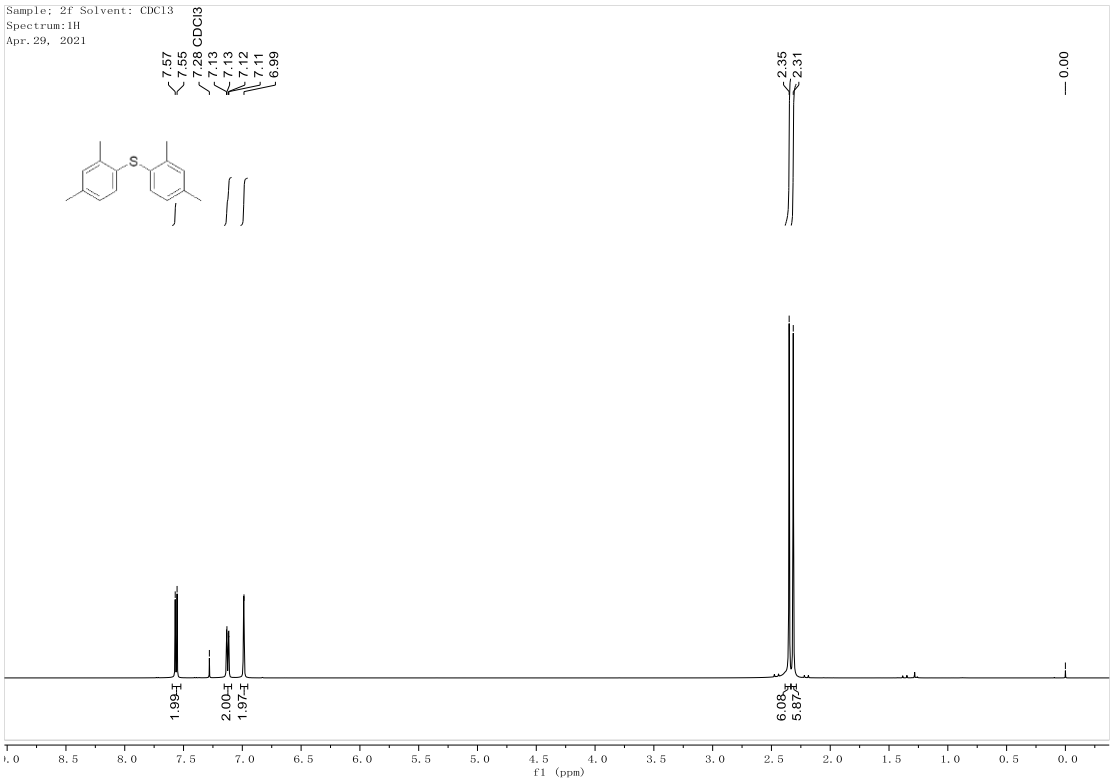


Fig. 6. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2f



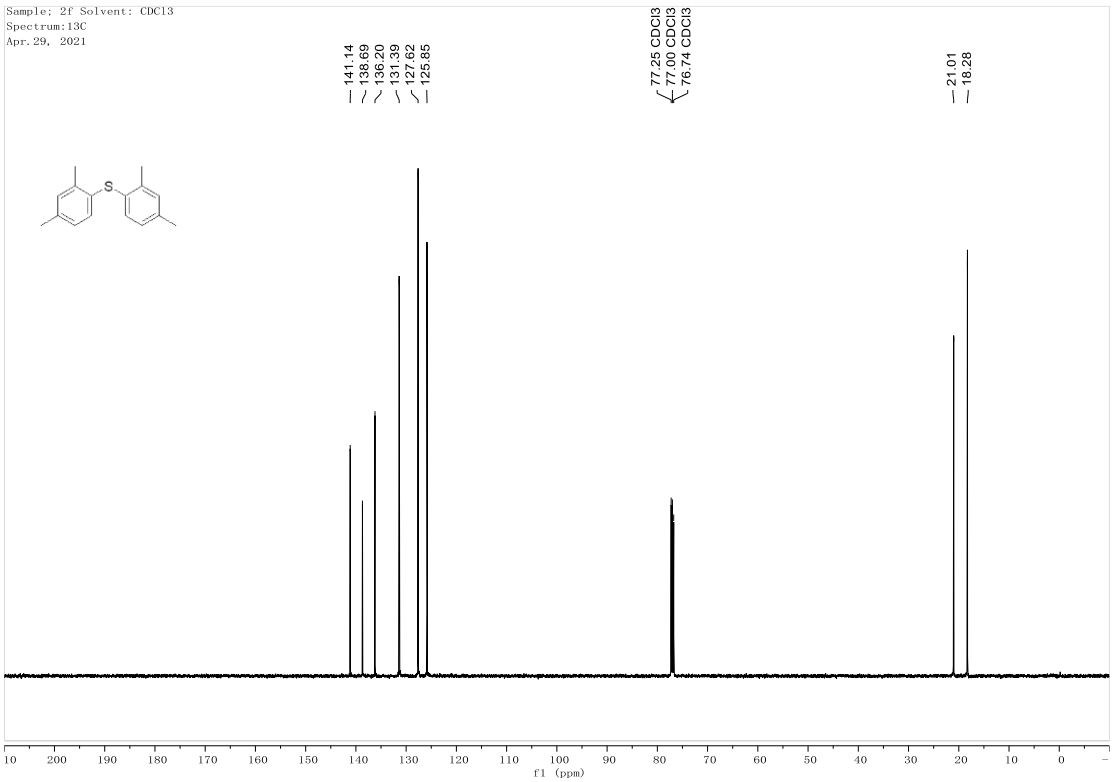


Fig. 7. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2g

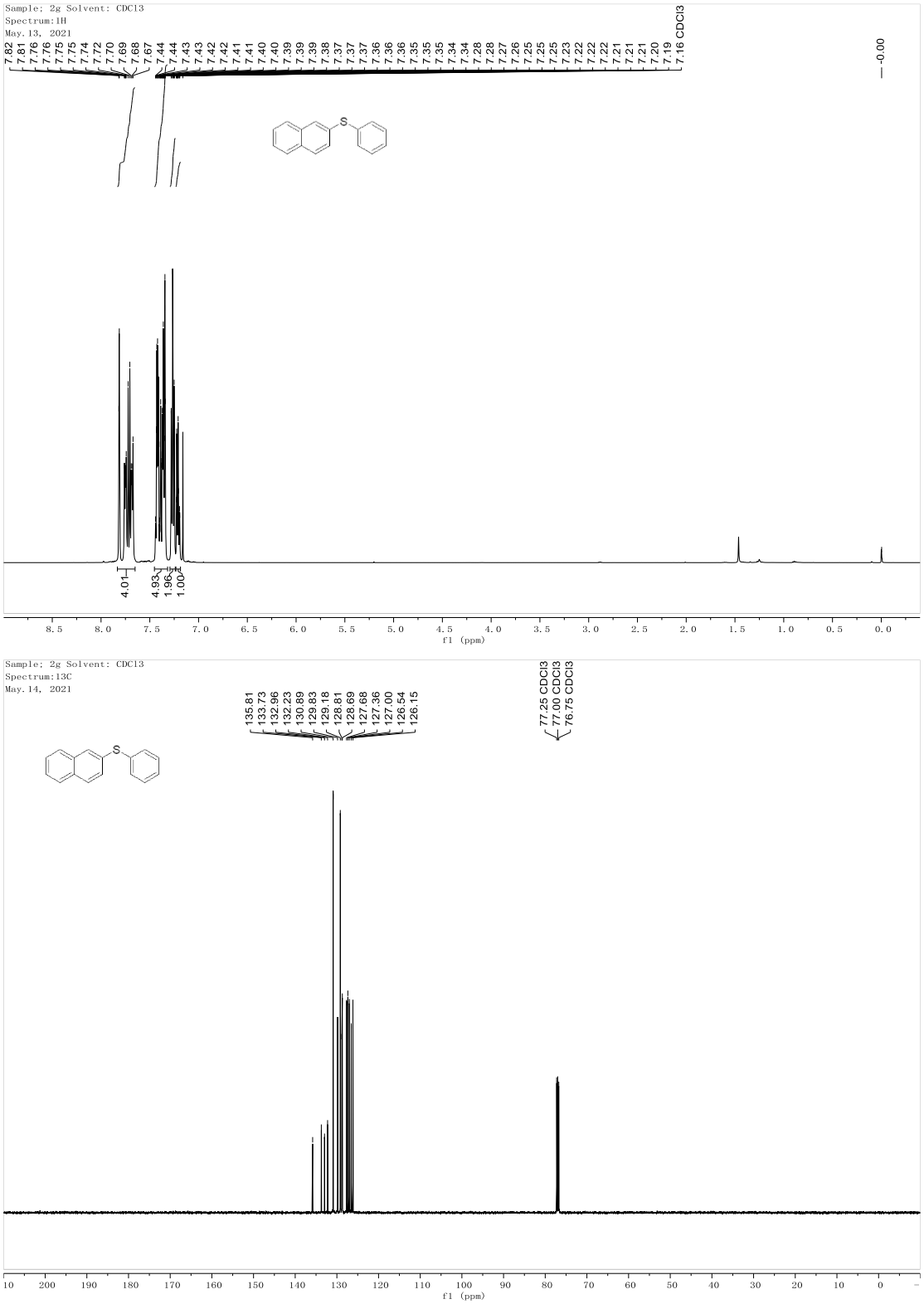


Fig. 8. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 2h

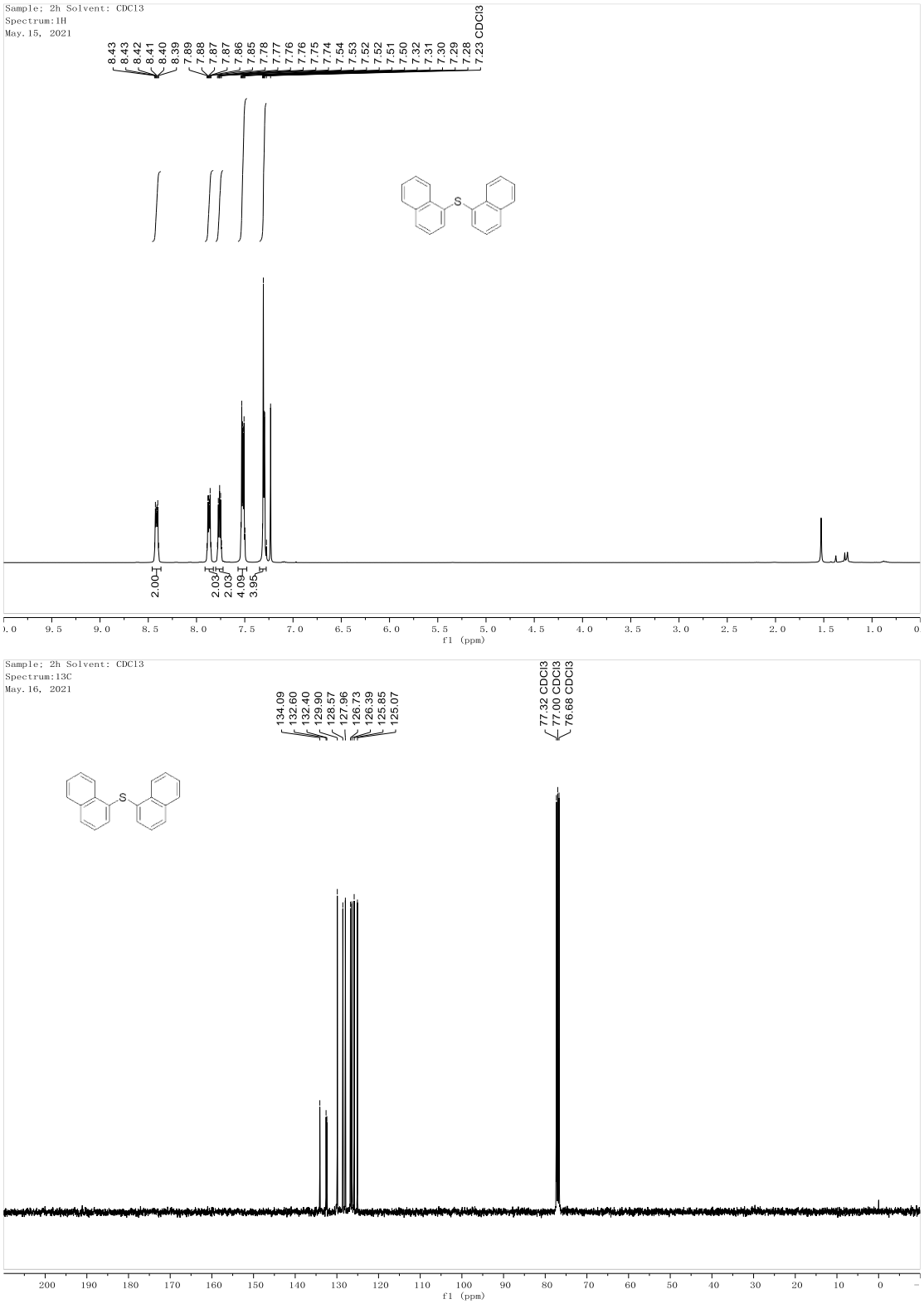
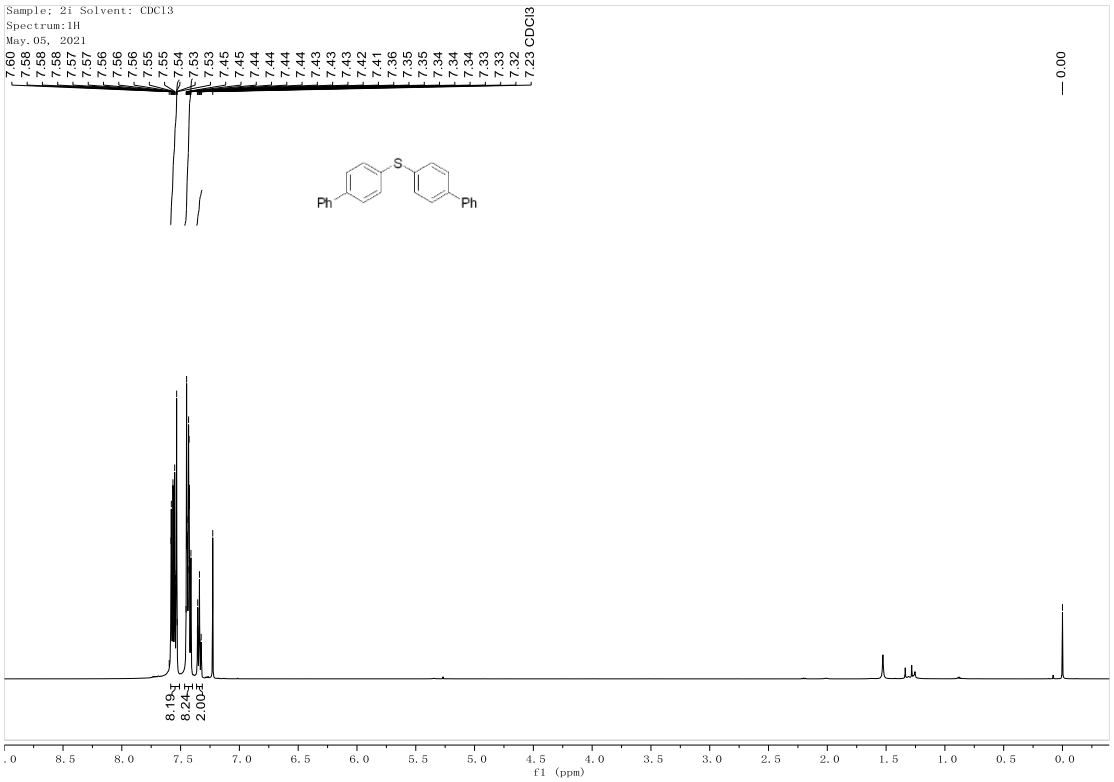


Fig. 9. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2i



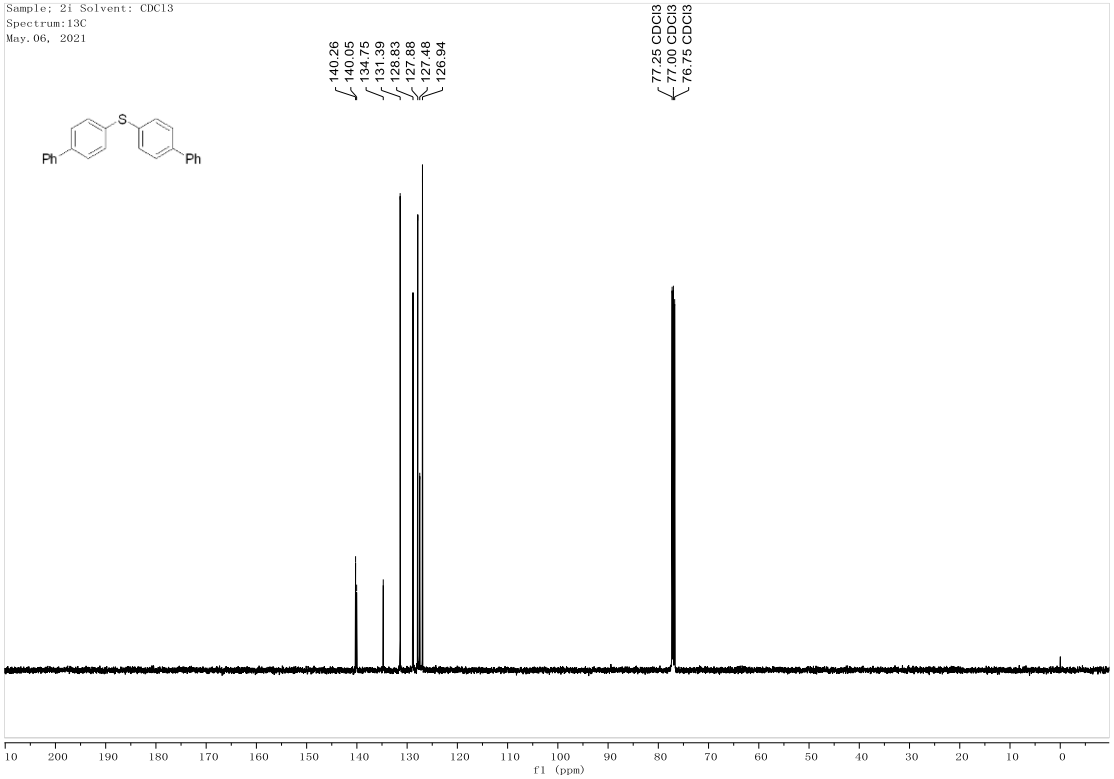


Fig. 10. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2j

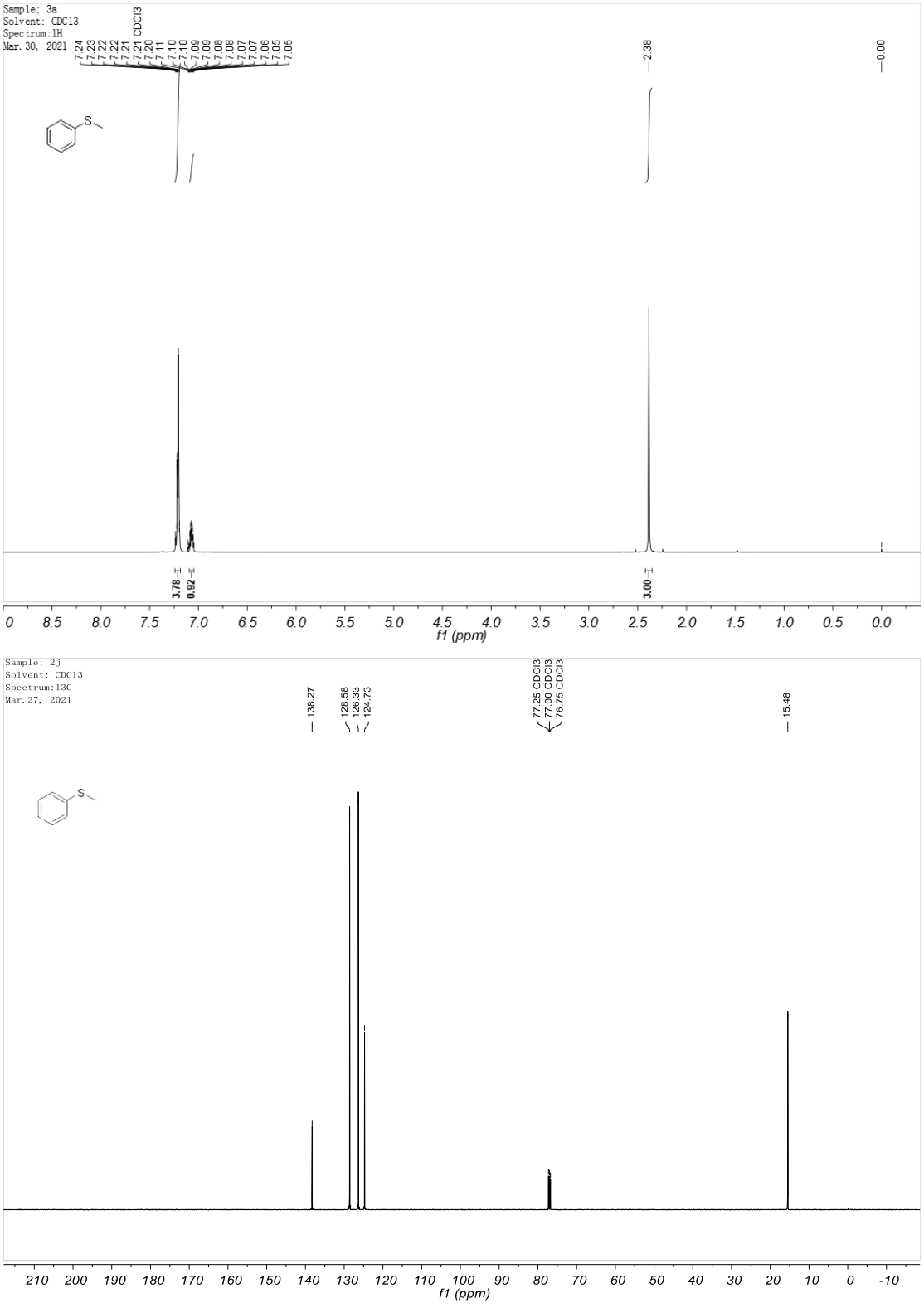


Fig. 11. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2k

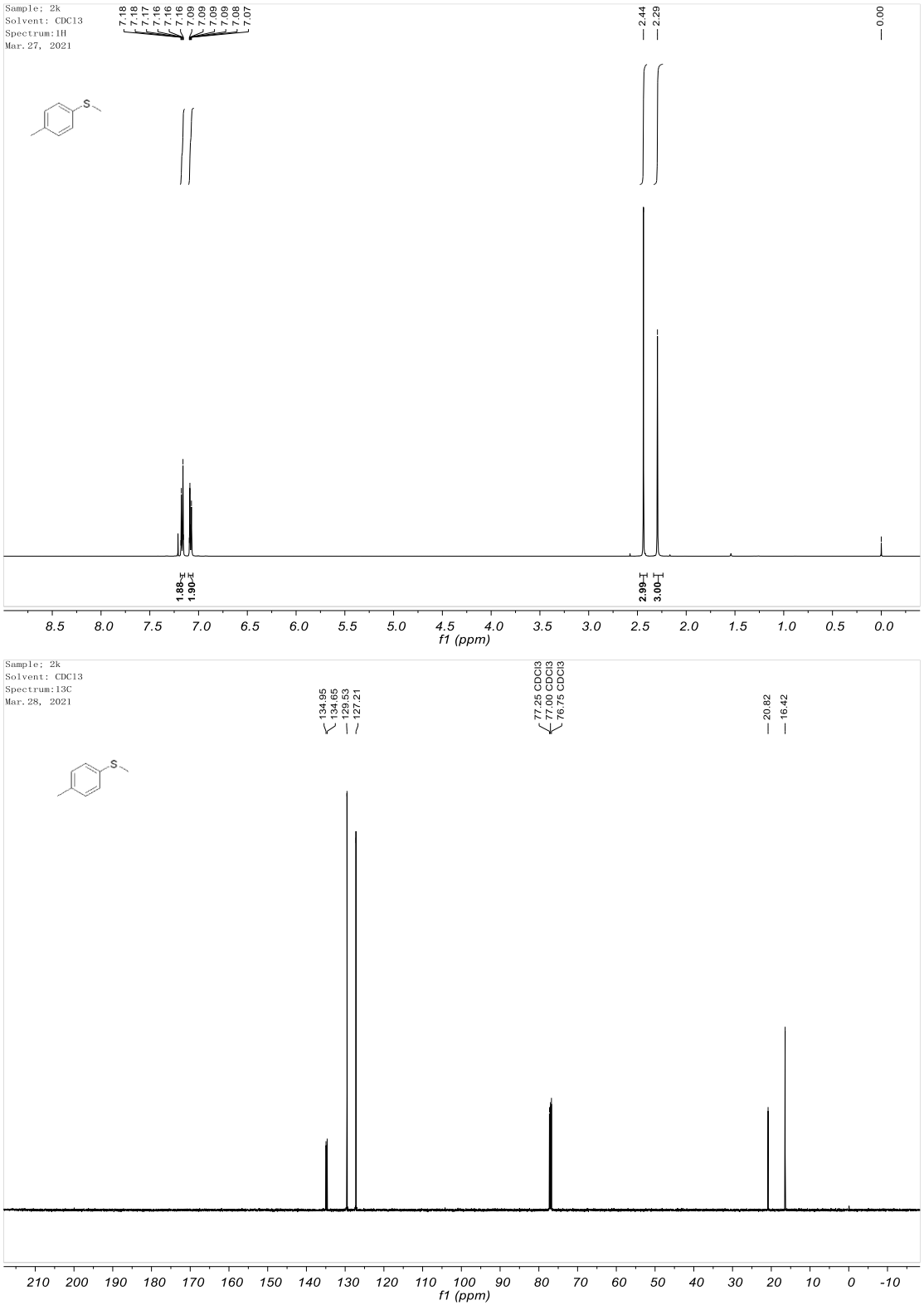


Fig. 11. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2l

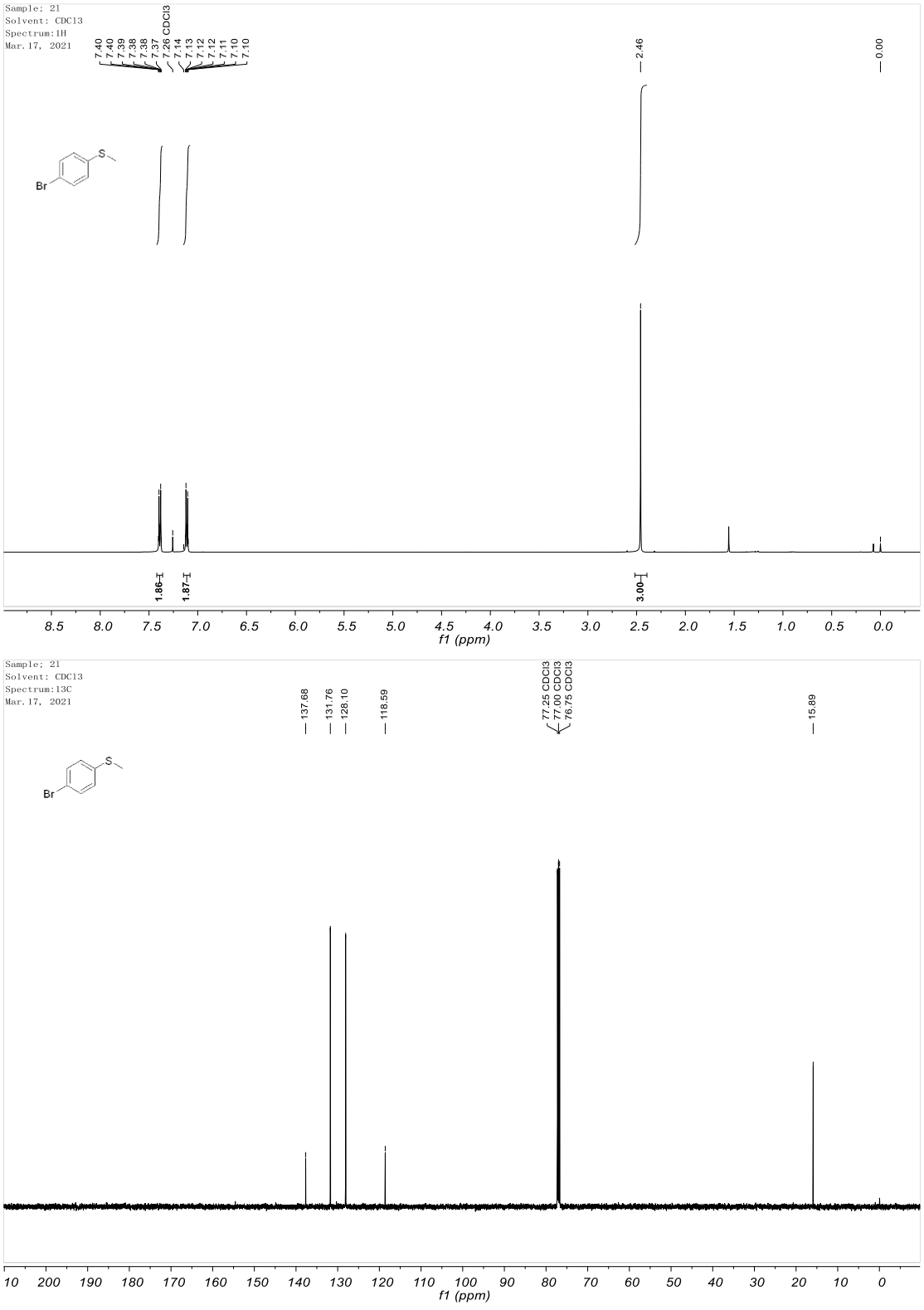
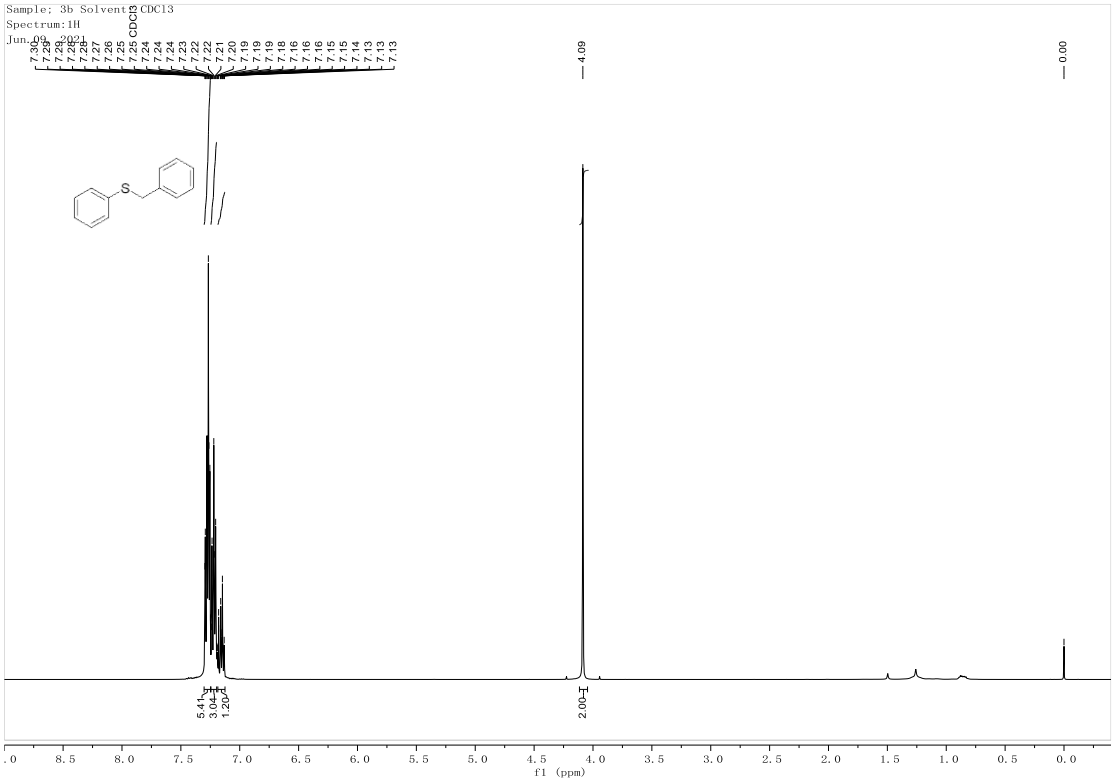


Fig. 12. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2m



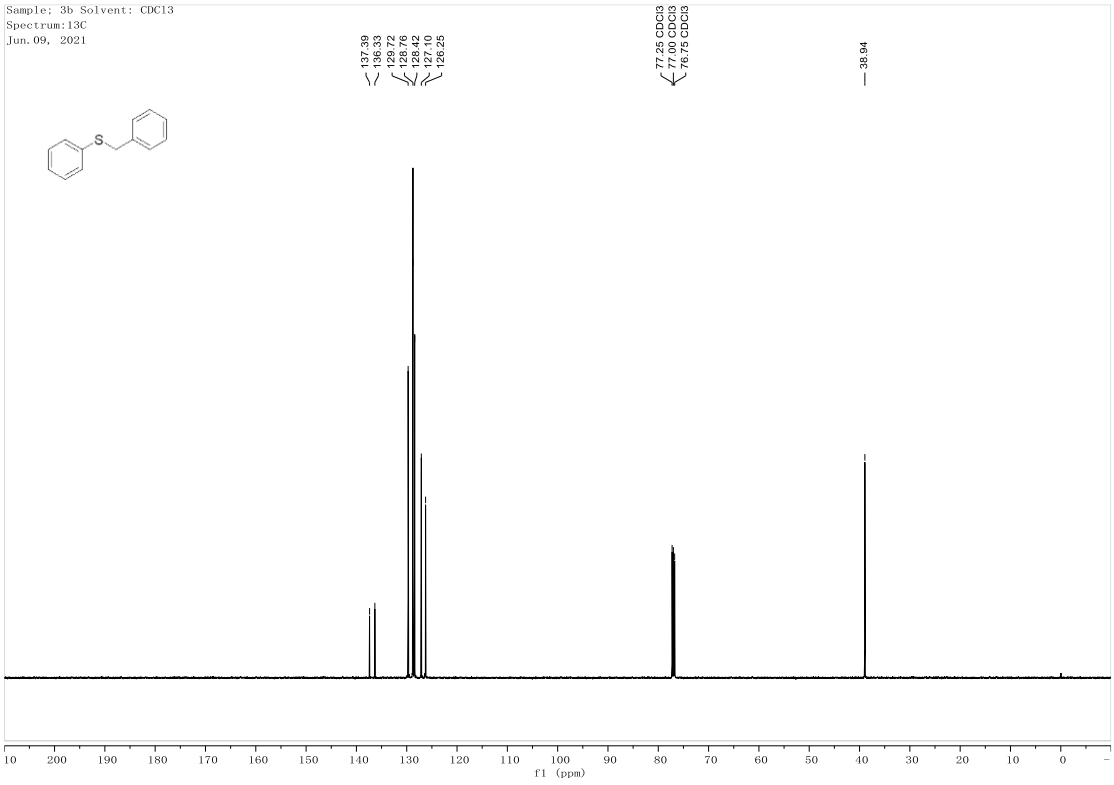


Fig. 13. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2r

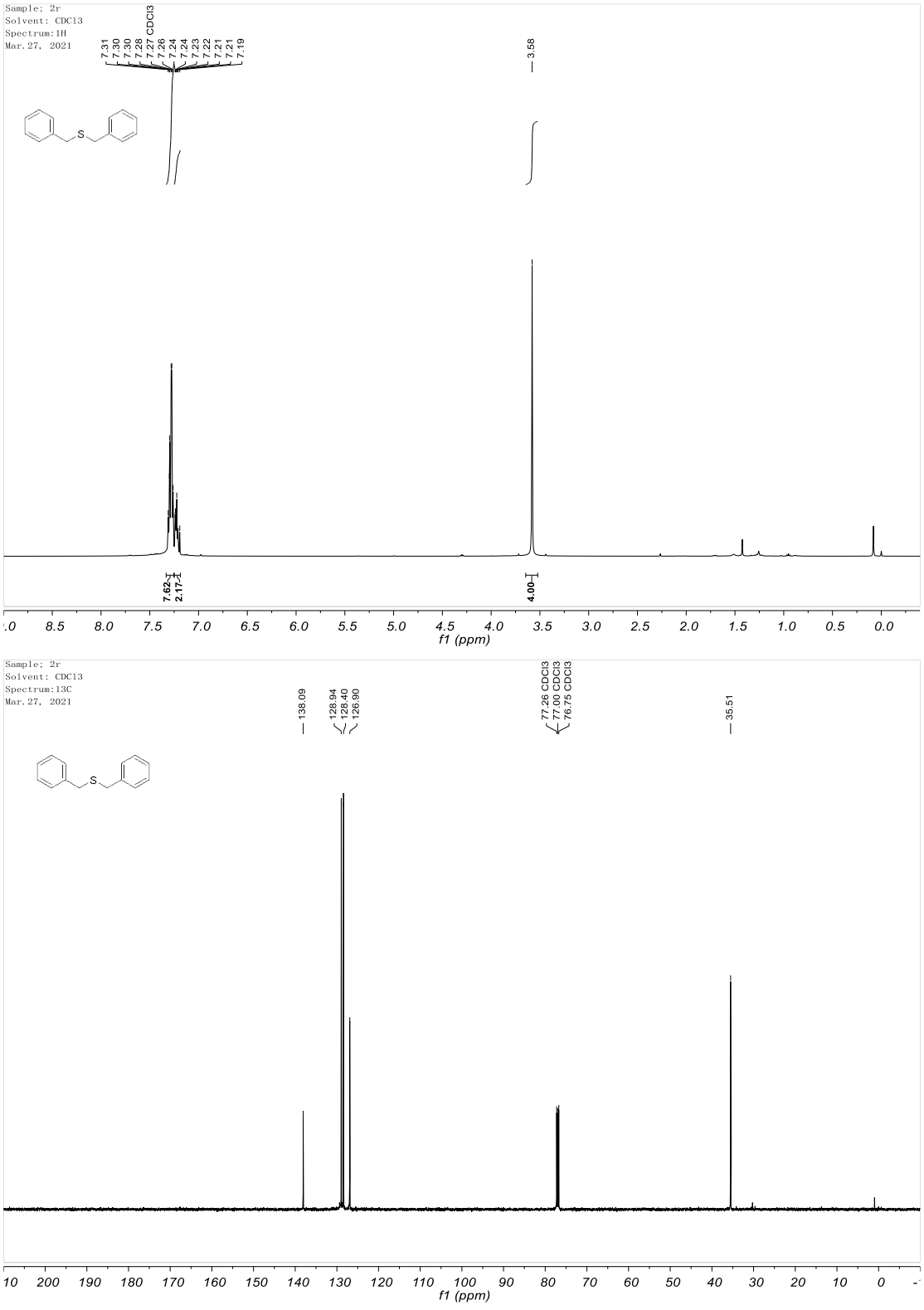


Fig. 14. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2s

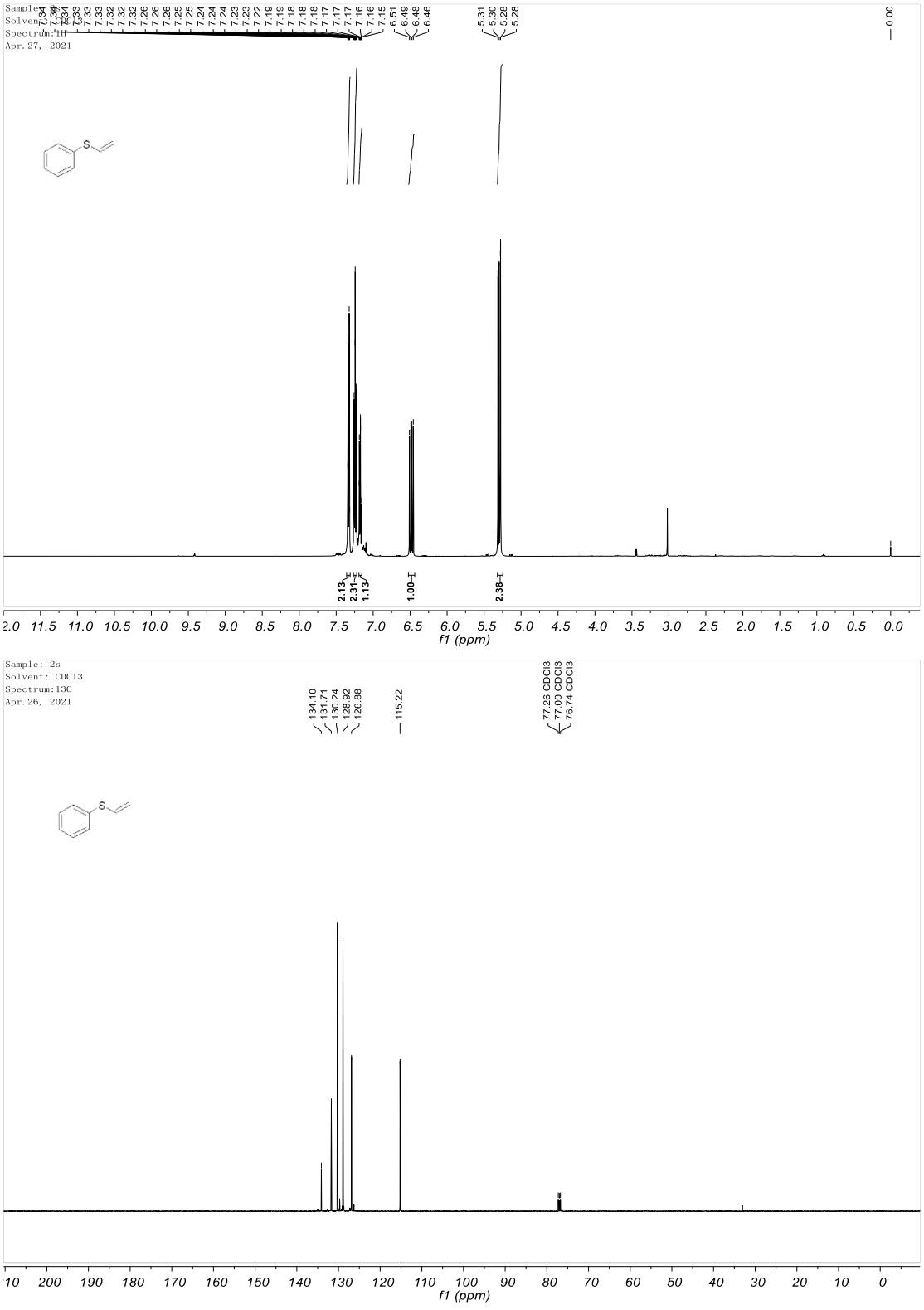


Fig. 15. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2t

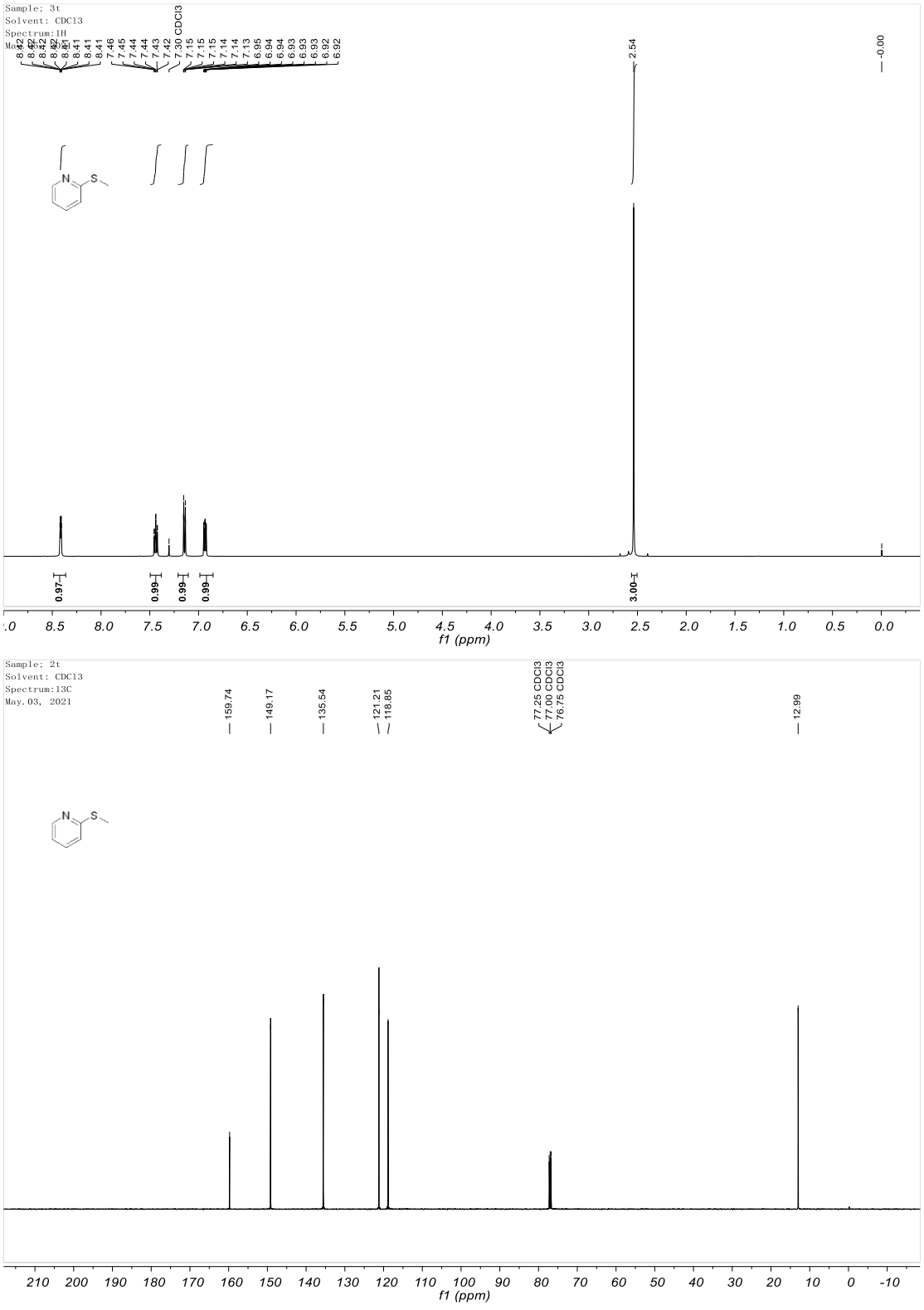


Fig. 16. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2u

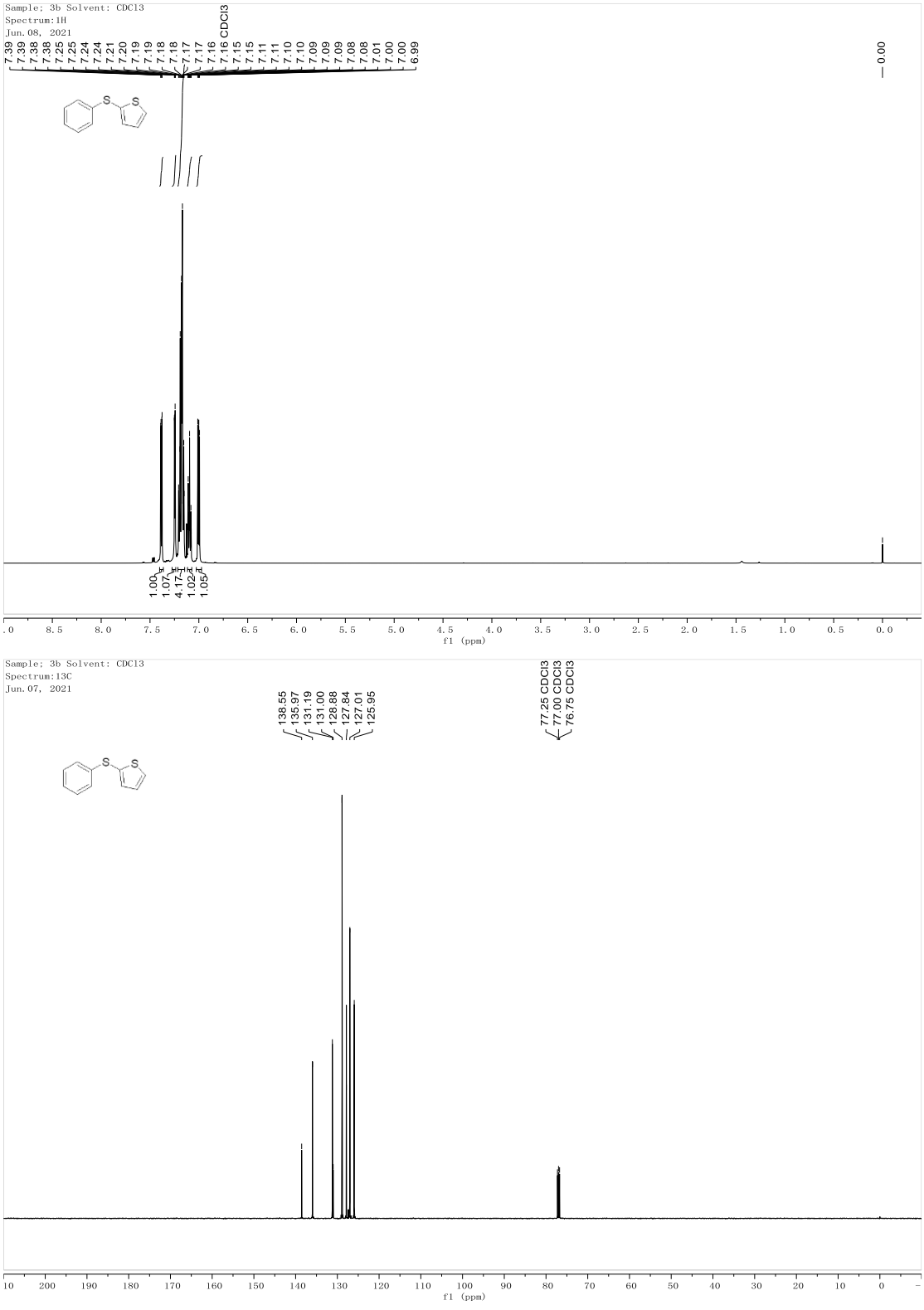


Fig. 17. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2v

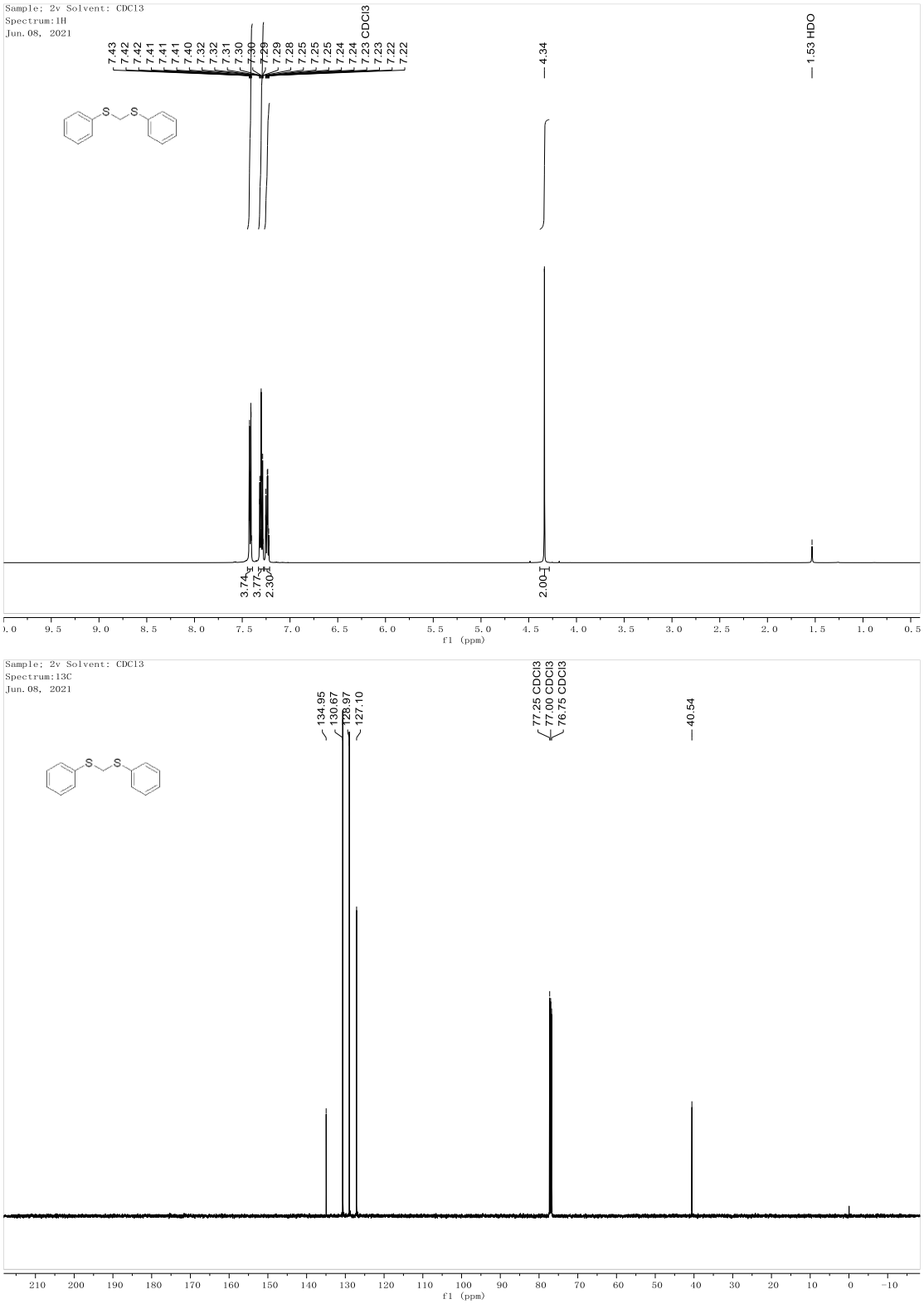


Fig. 18. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2w

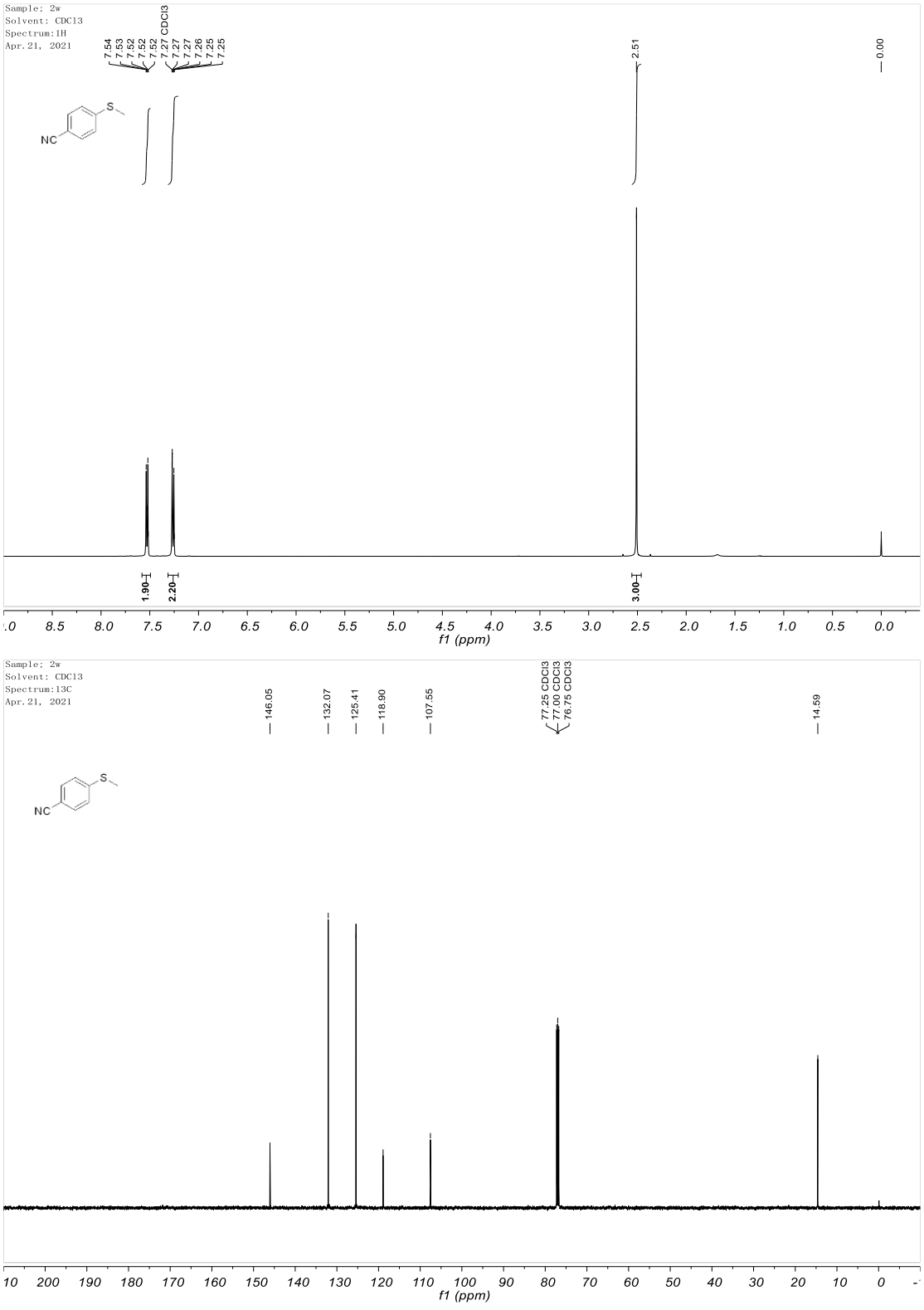
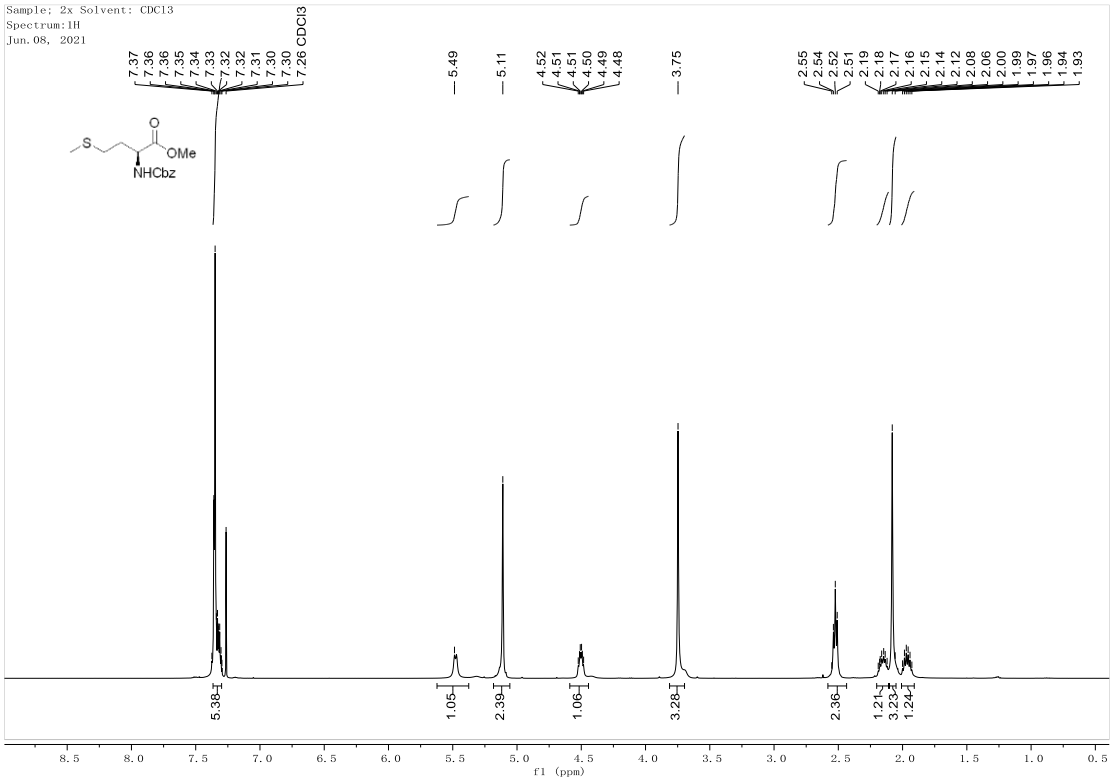


Fig. 19. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2x



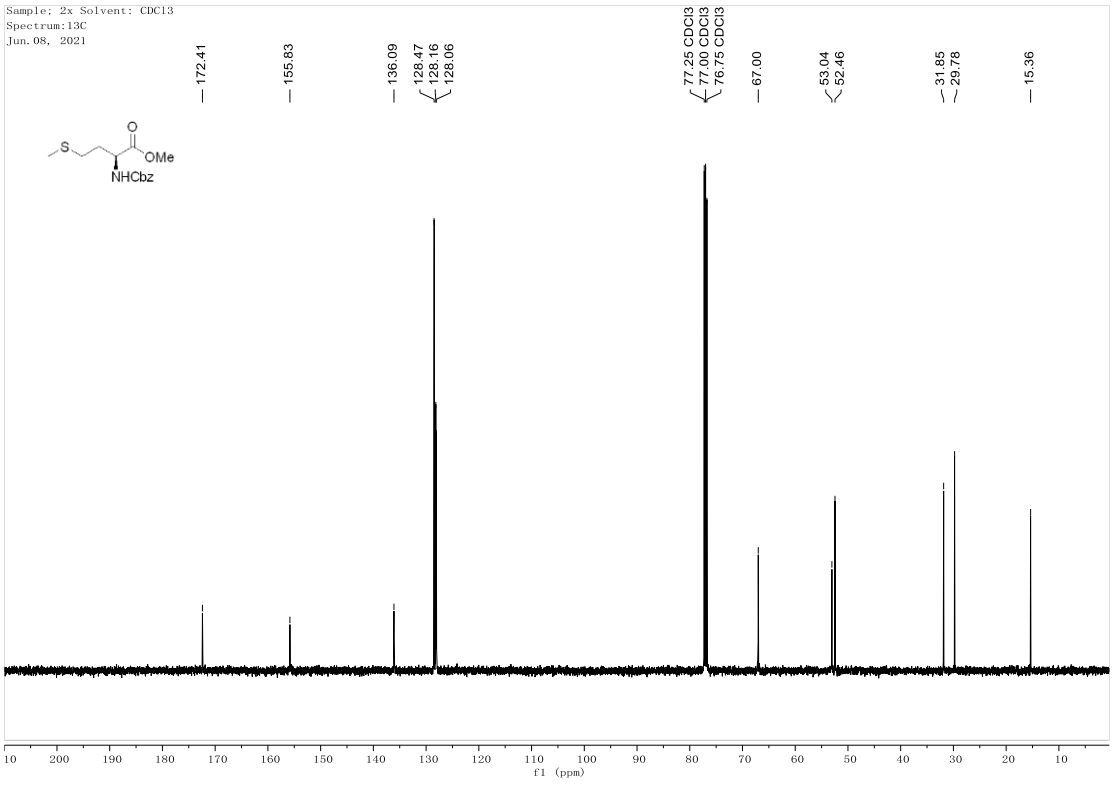


Fig. 20. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2y

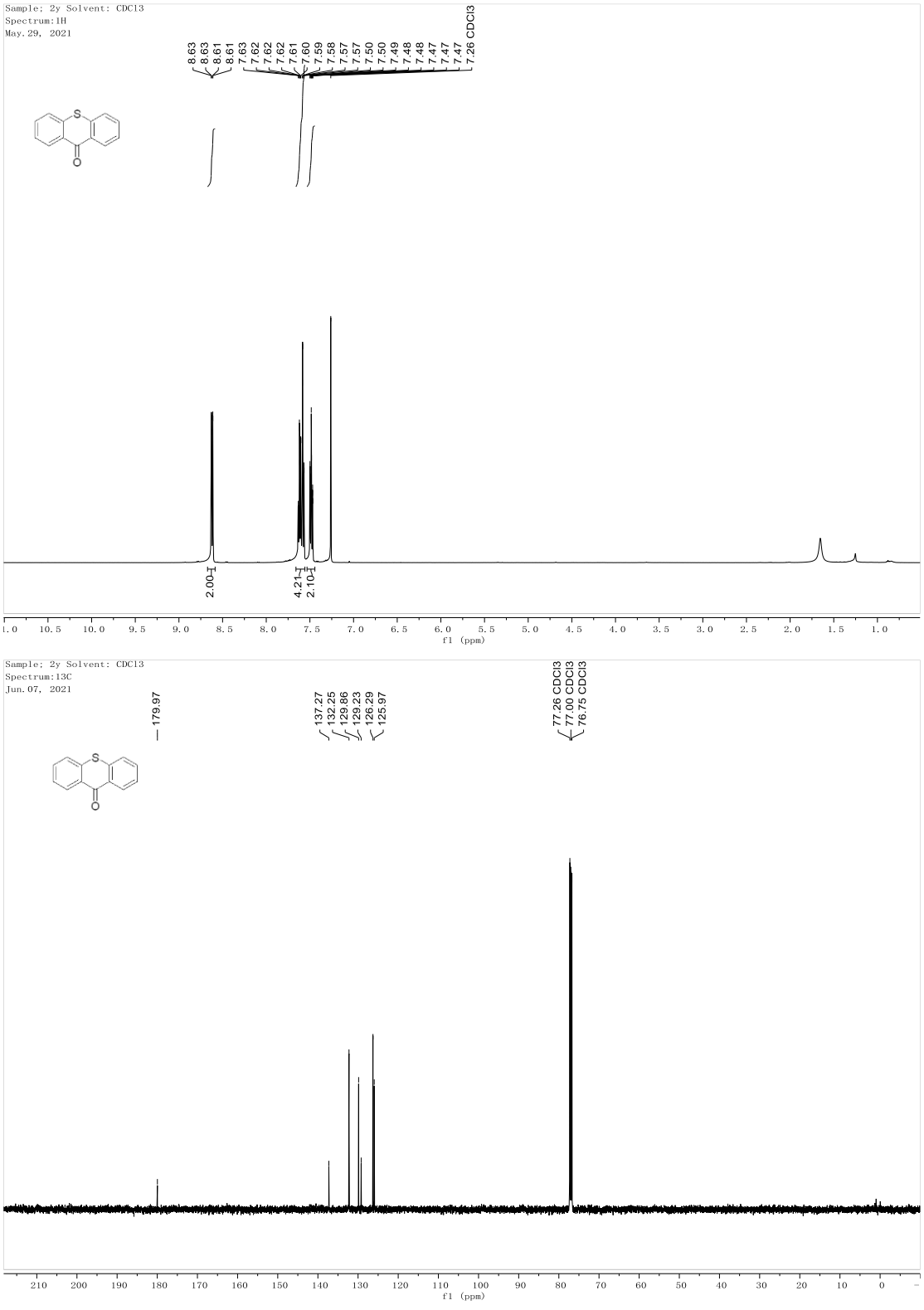
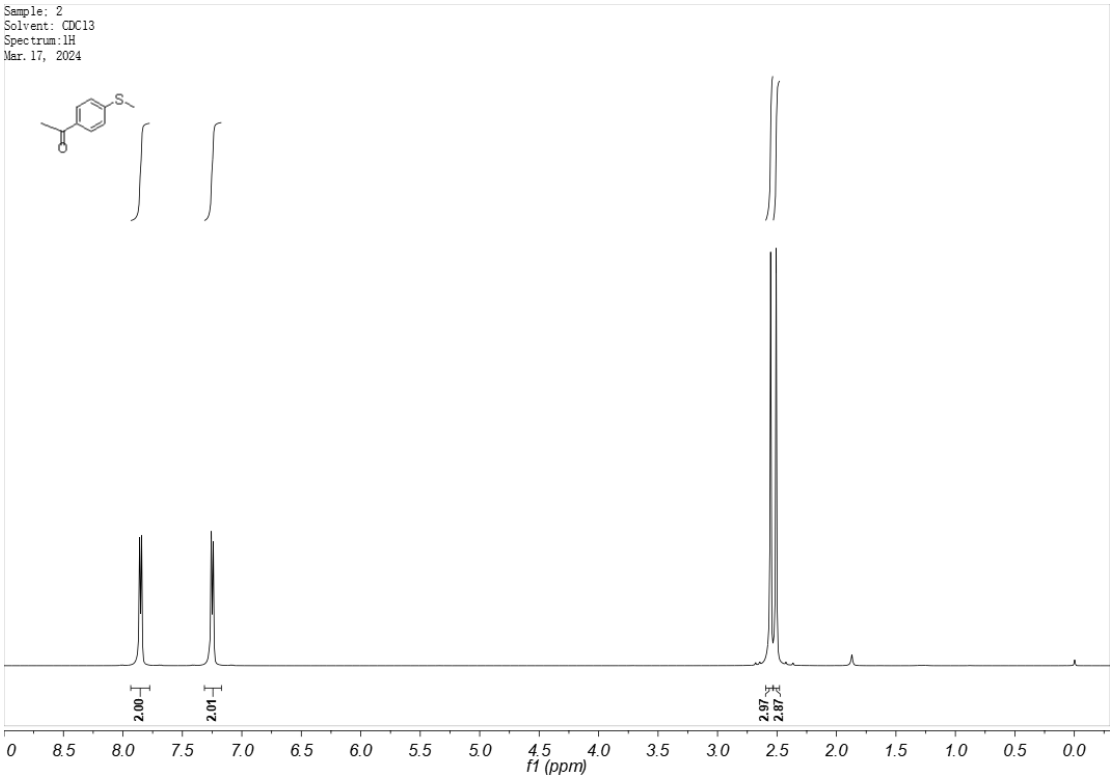


Fig. 21. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2z



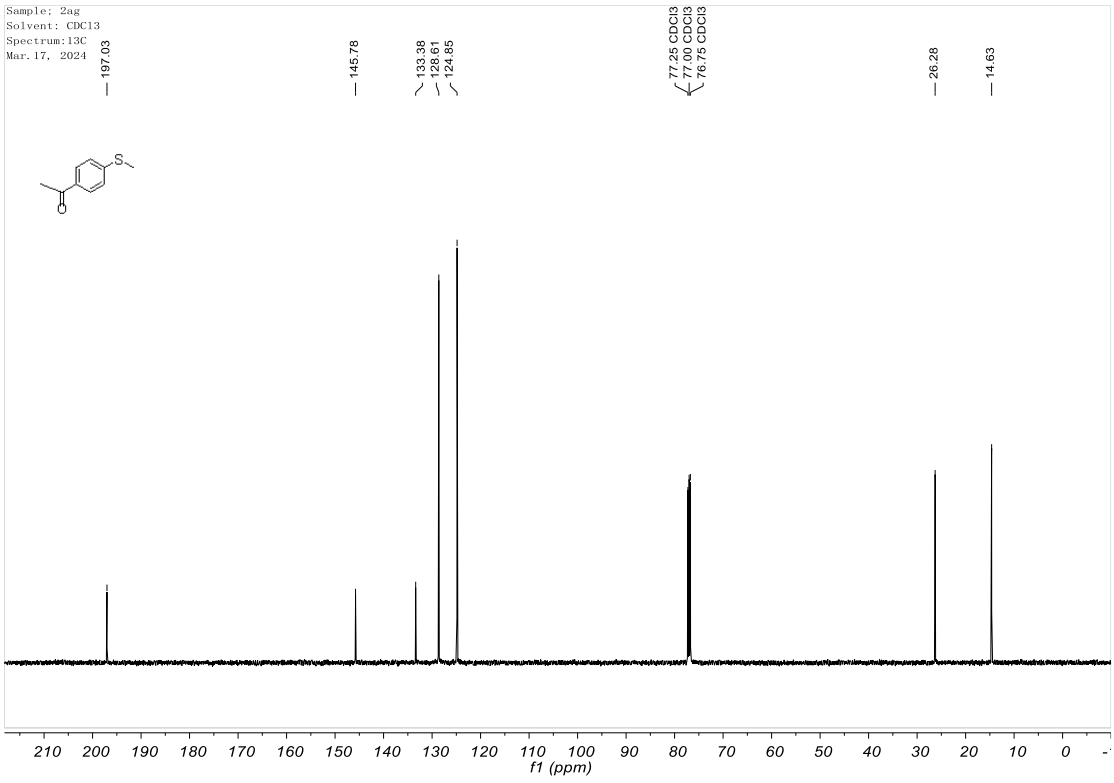
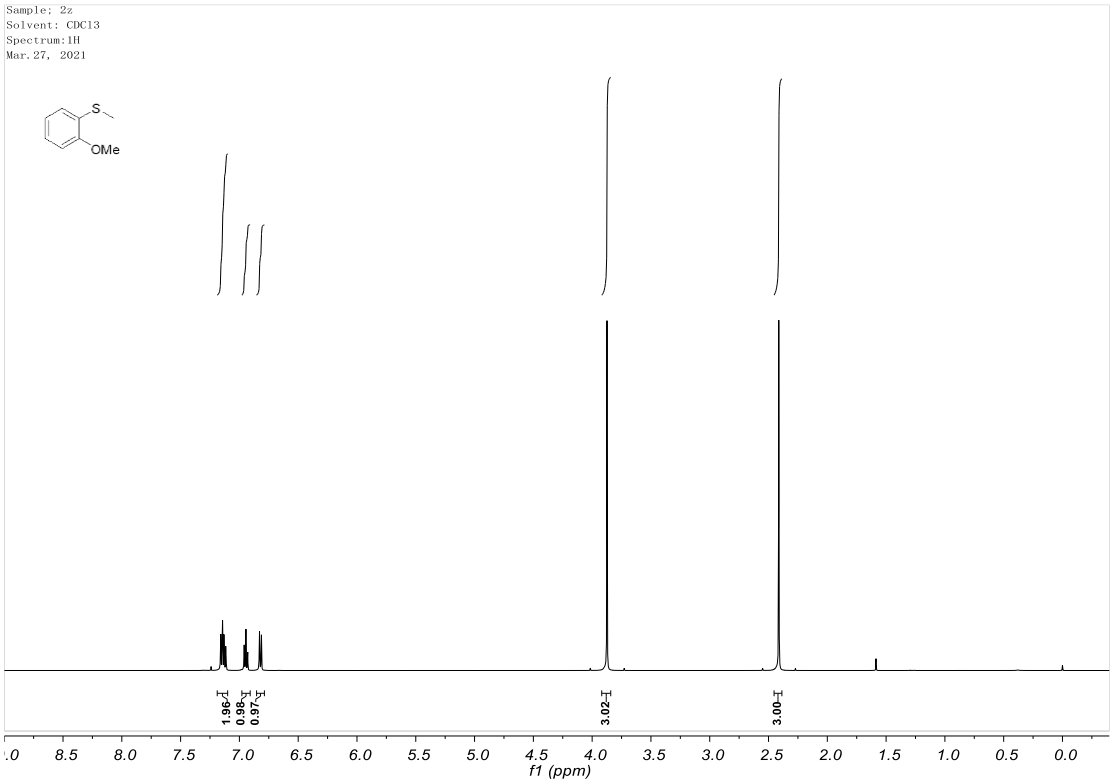


Fig. 22. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2aa



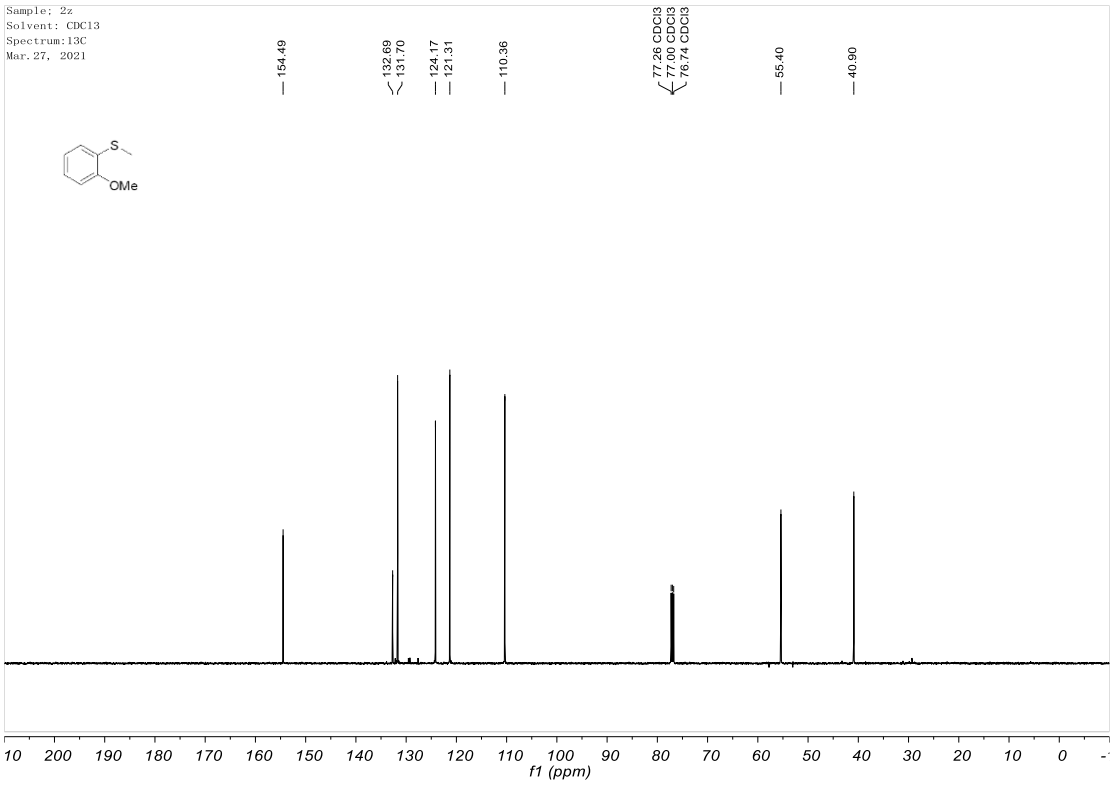
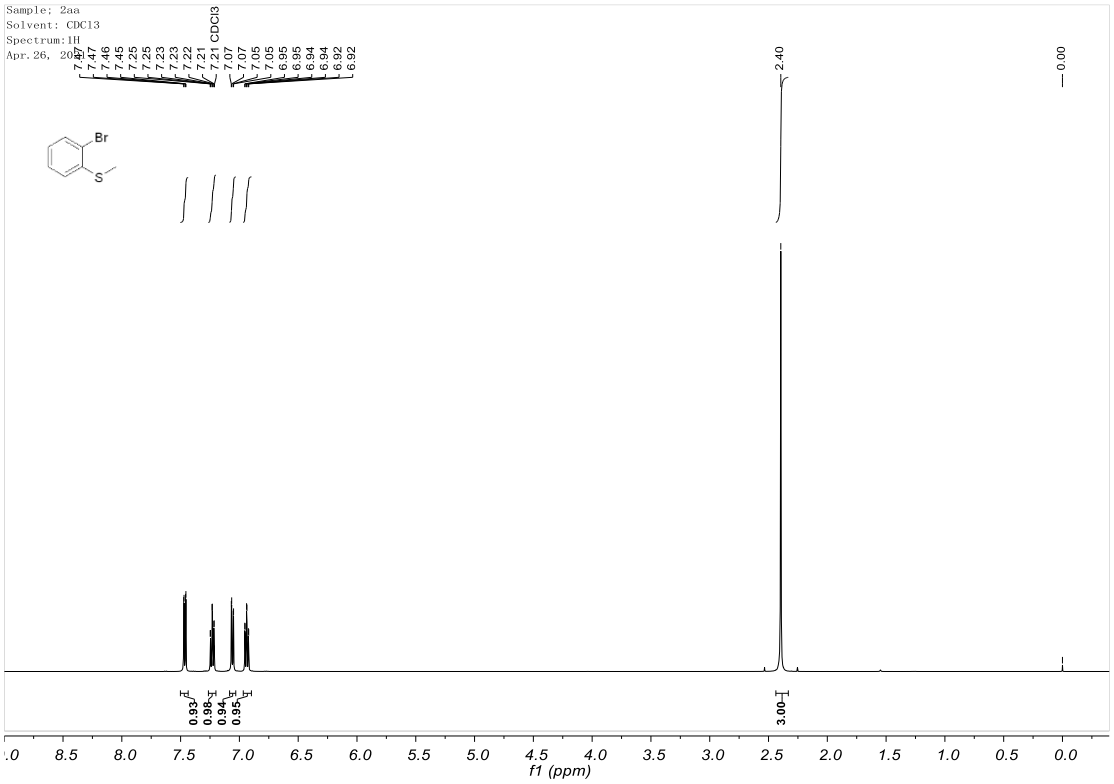


Fig. 23. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2ab



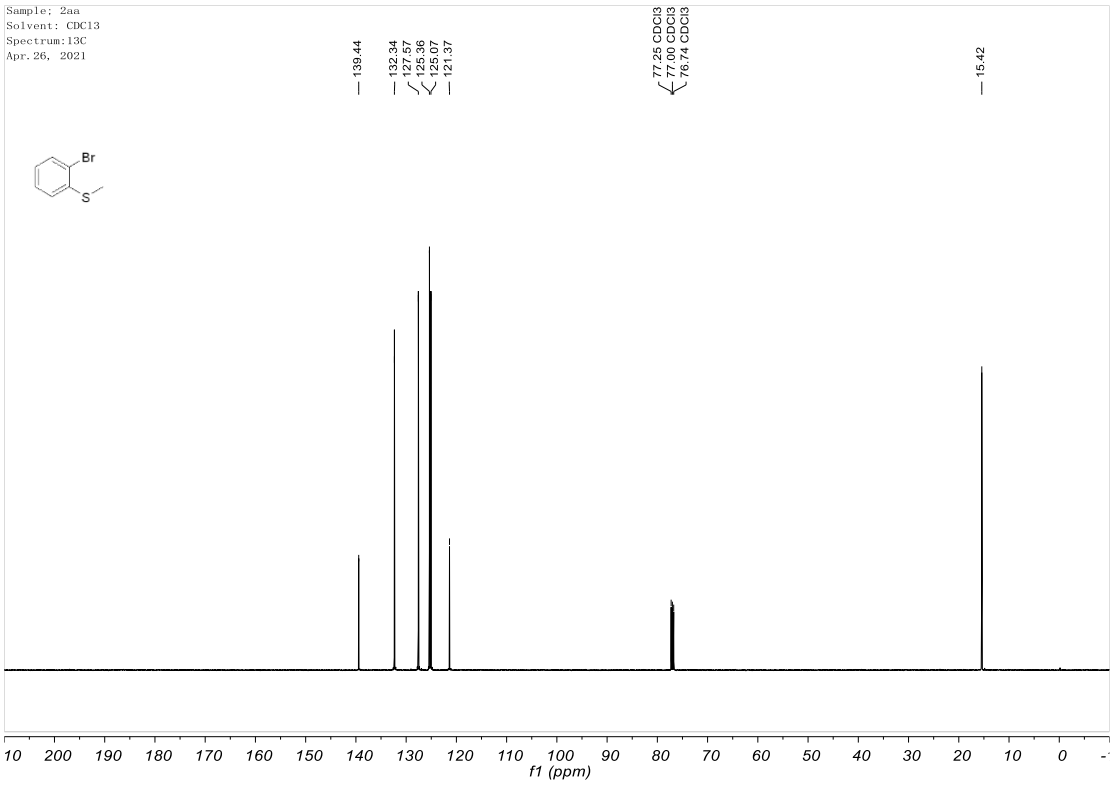
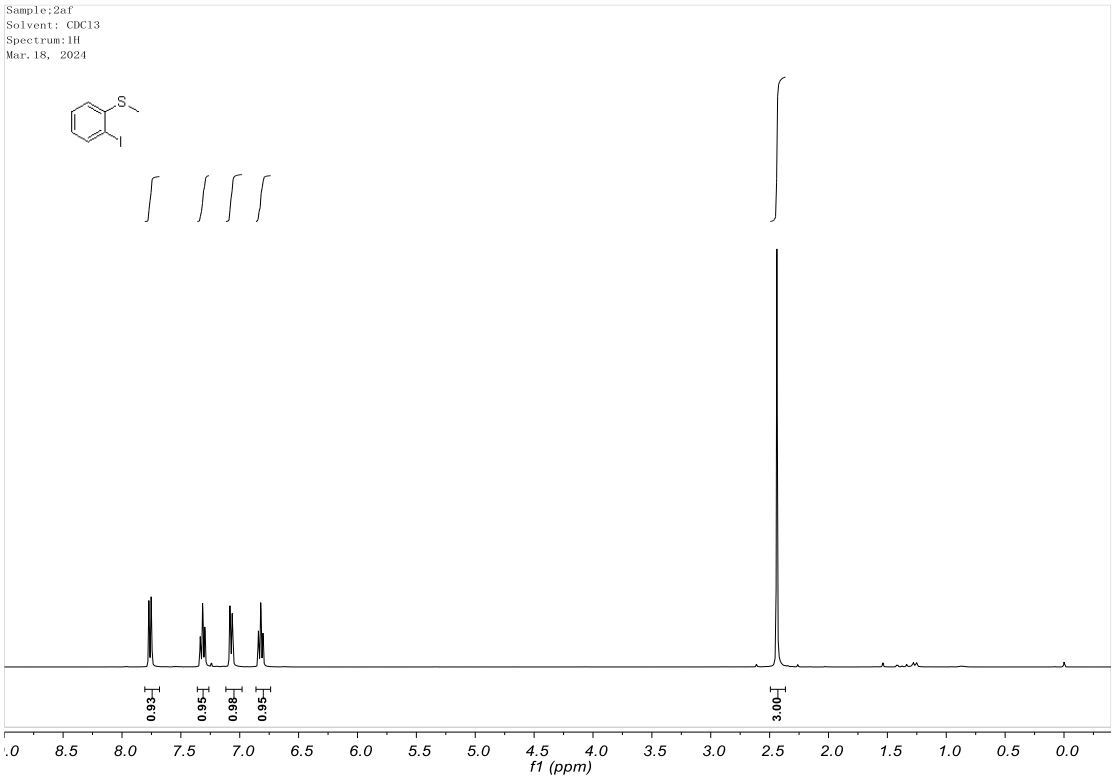


Fig. 24. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 2ac



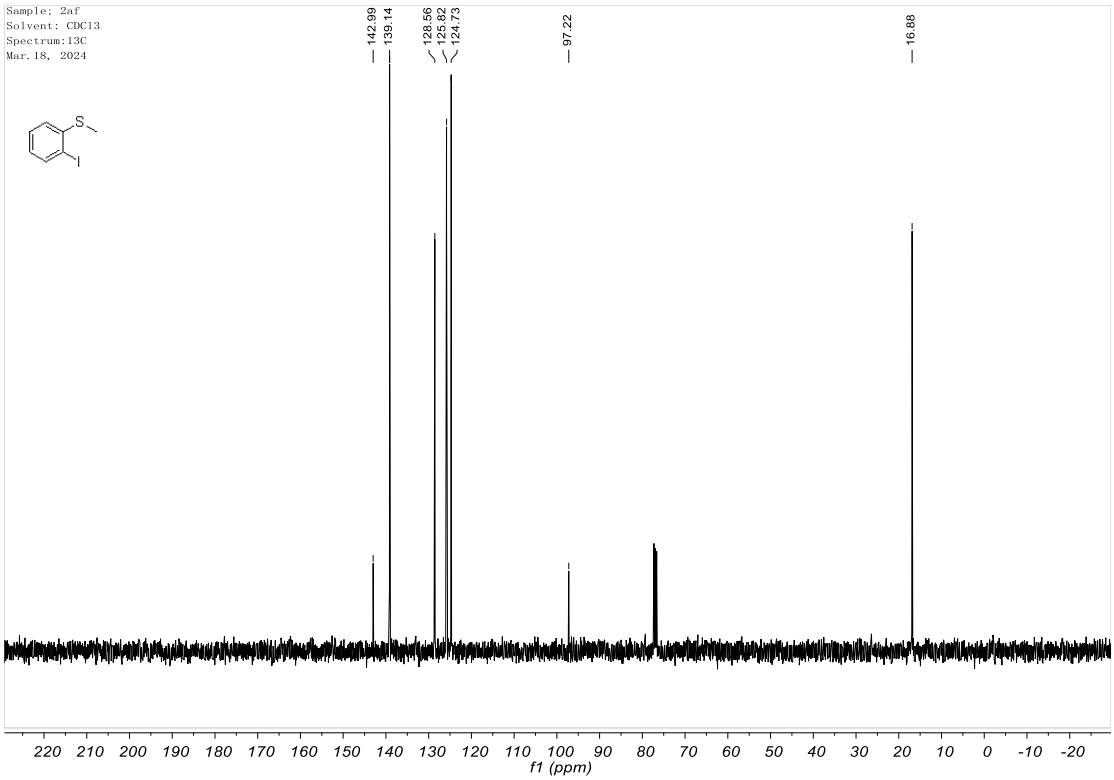


Fig. 25. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2ad

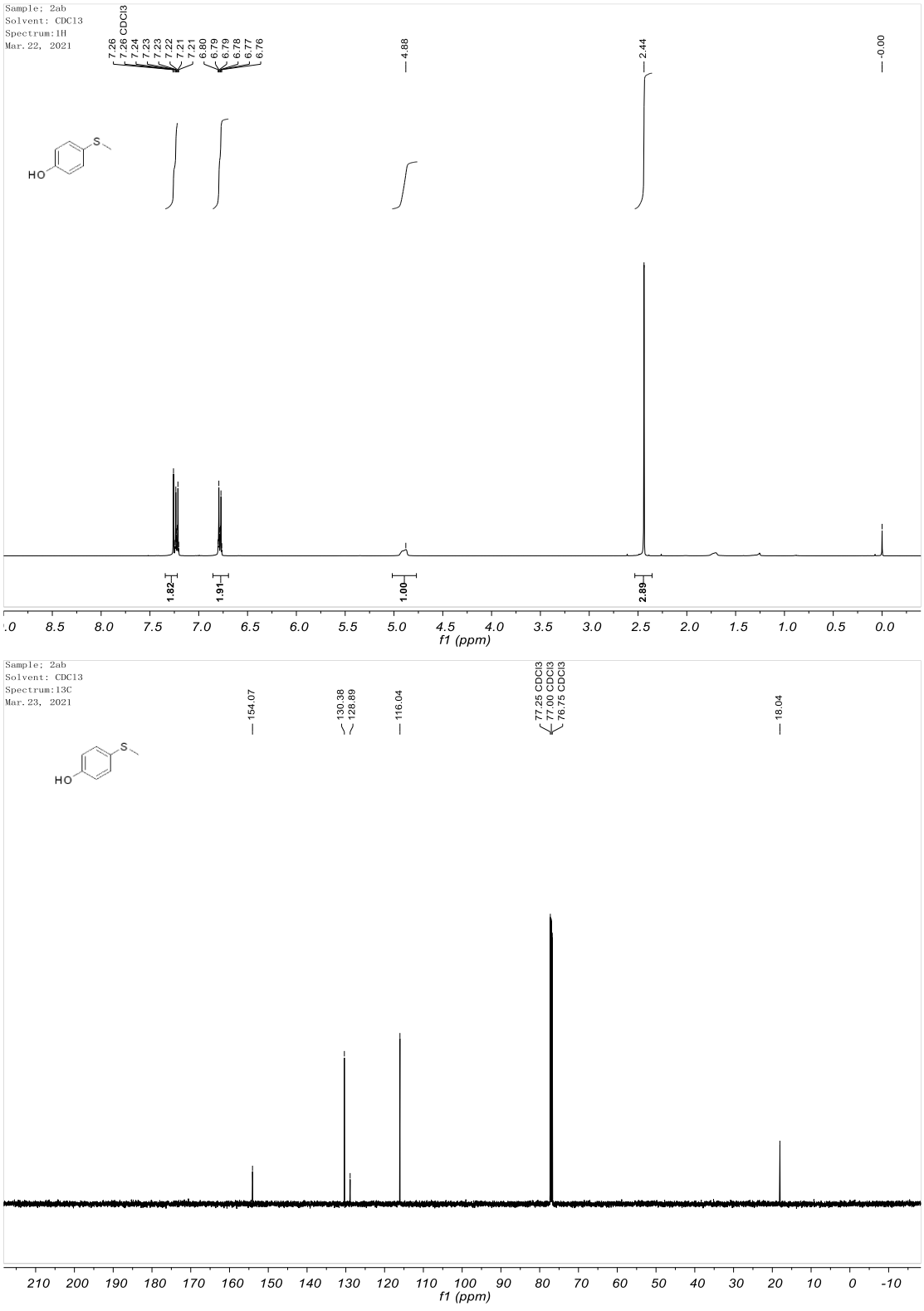
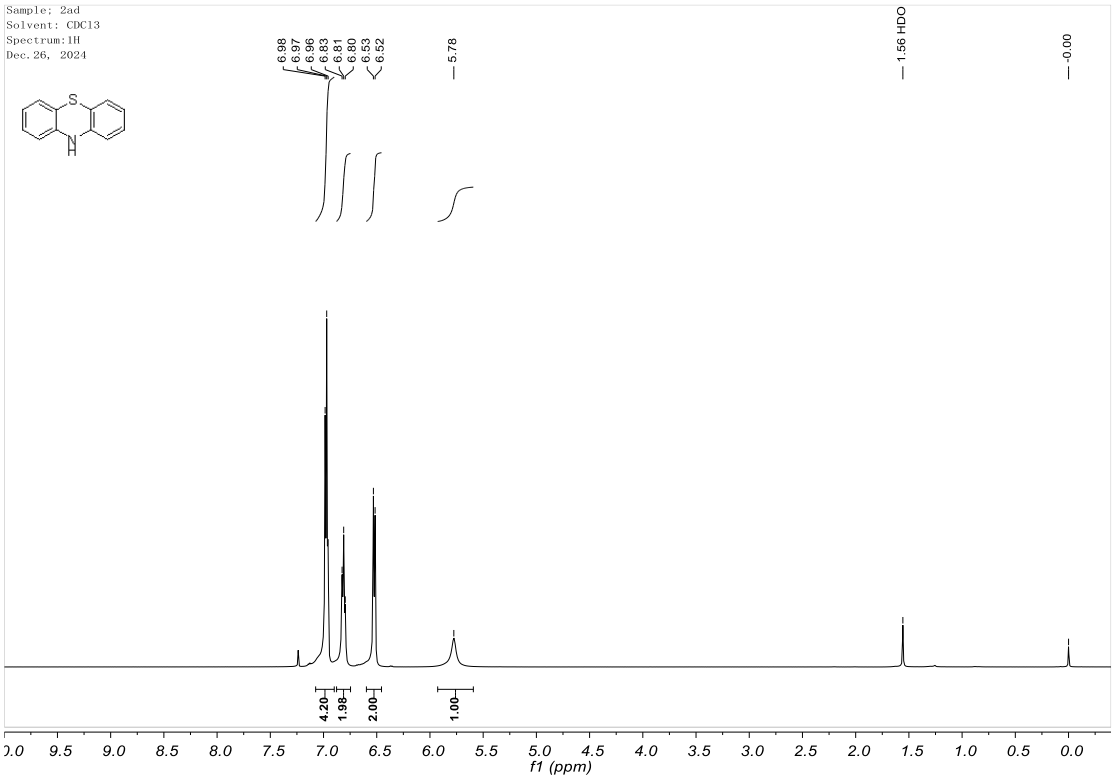


Fig. 26. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2ae



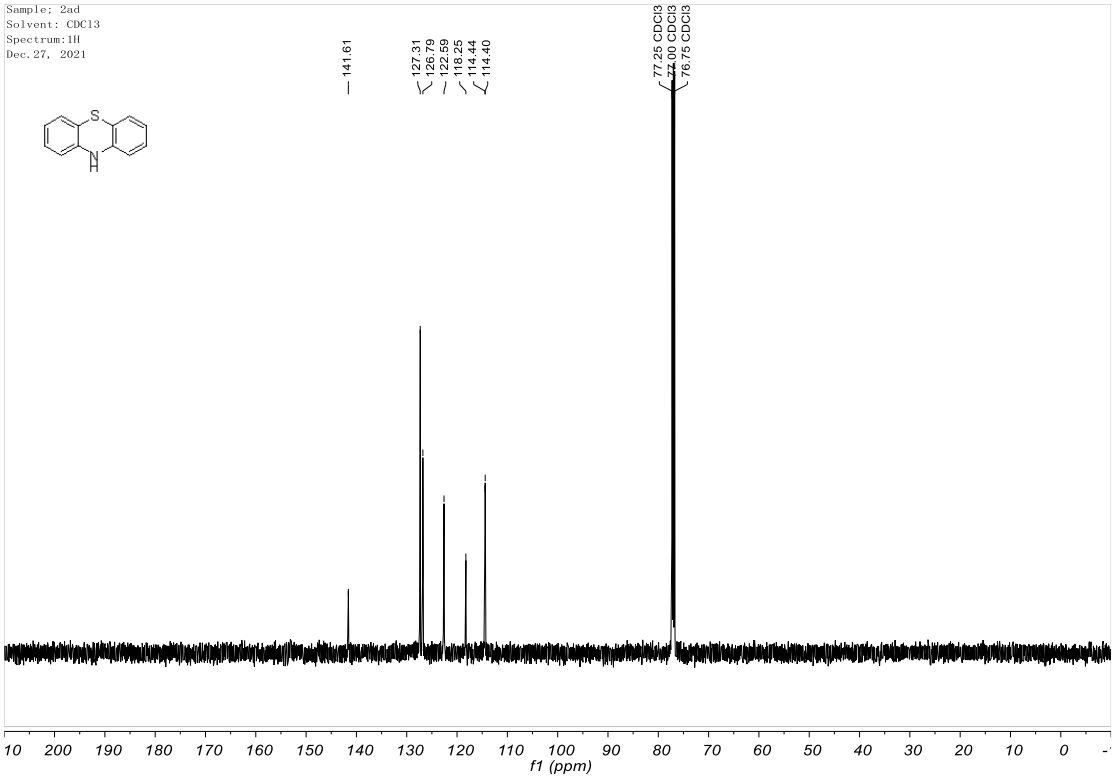


Fig. 27. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2af

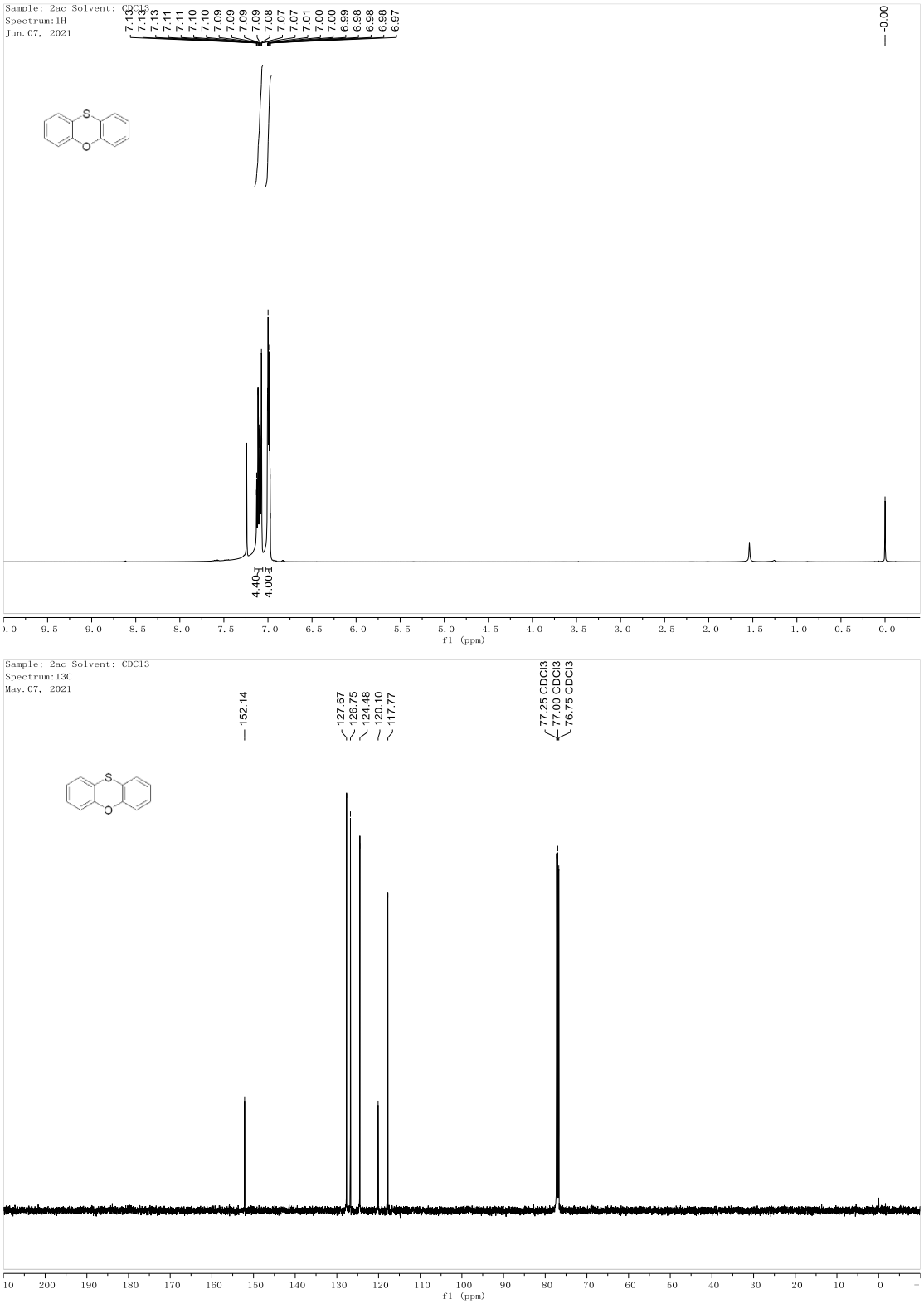


Fig. 28. ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (126 MHz, $CDCl_3$) spectra of 2ag

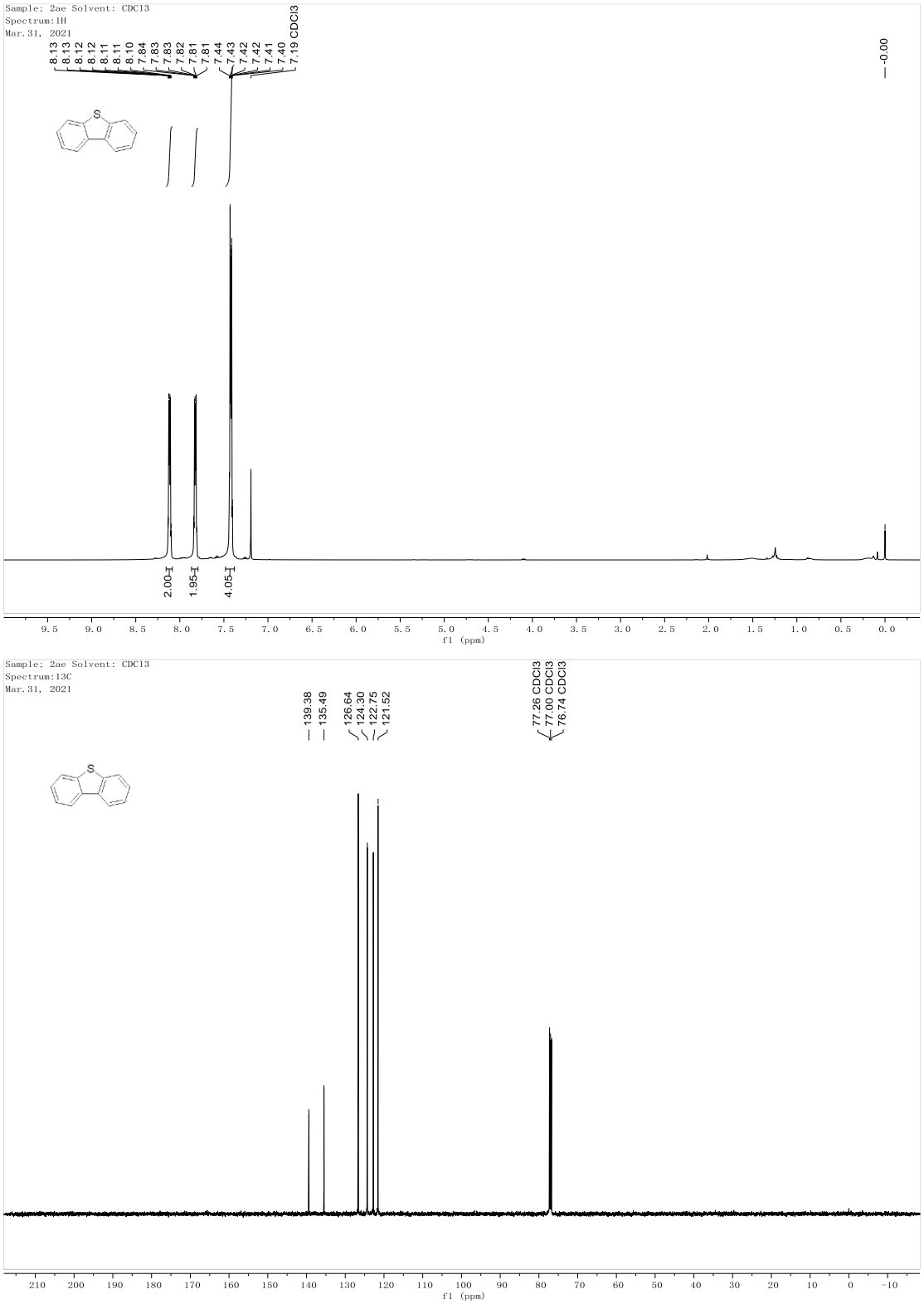


Fig. 29. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 2ah

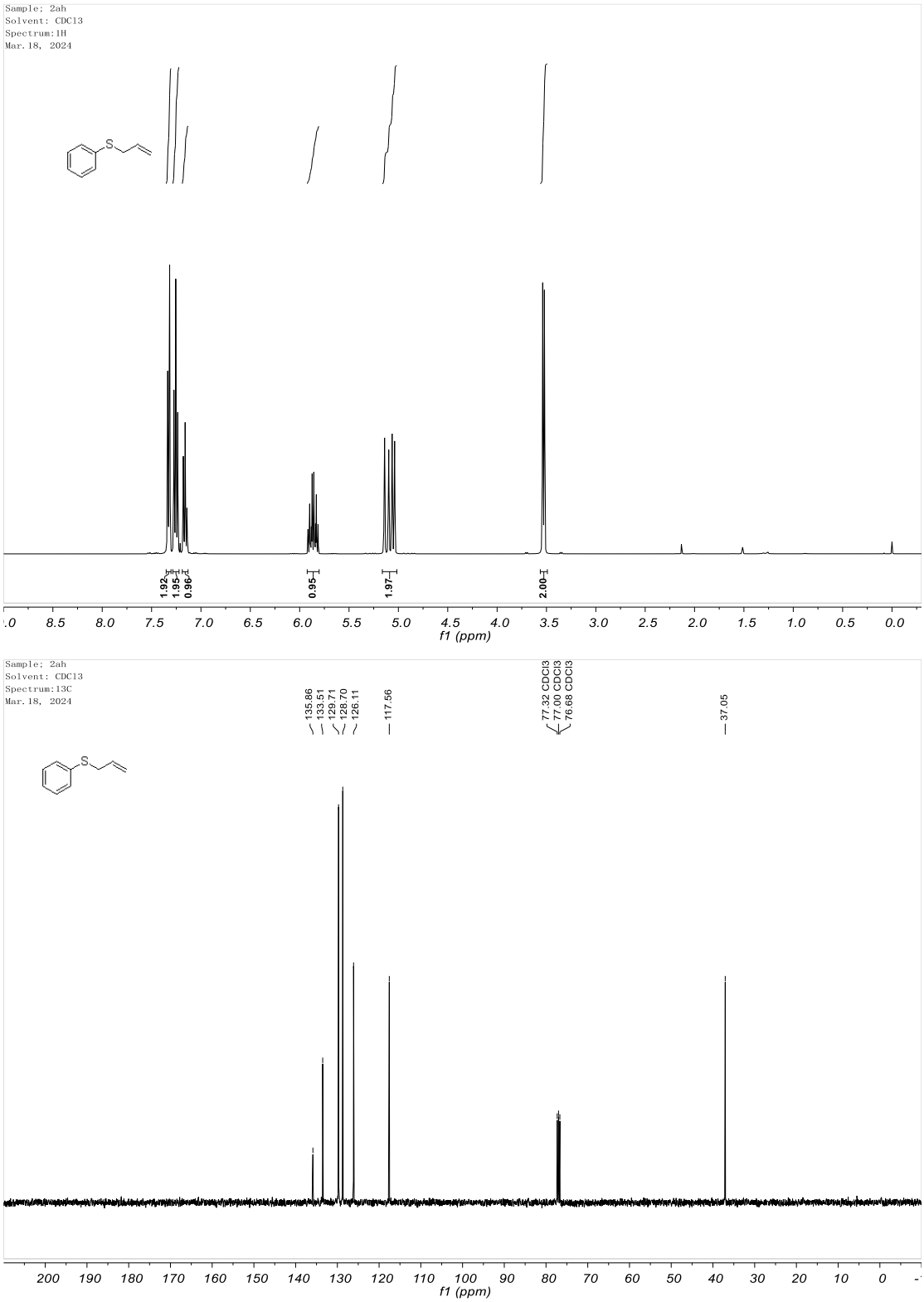


Fig. 30. ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (101 MHz, DMSO-d_6) spectra of 2ai

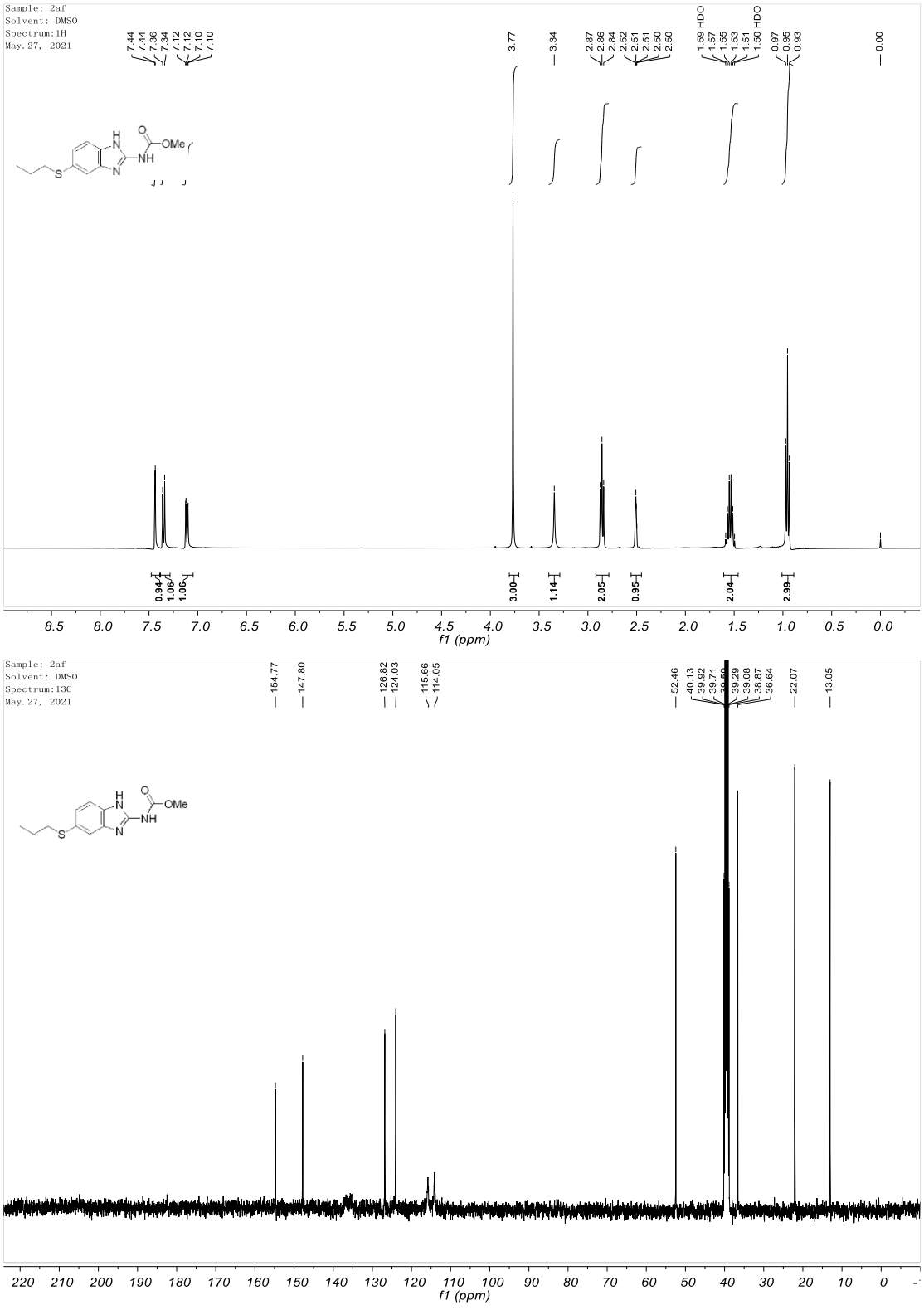


Fig. 31. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR spectra of 2aj

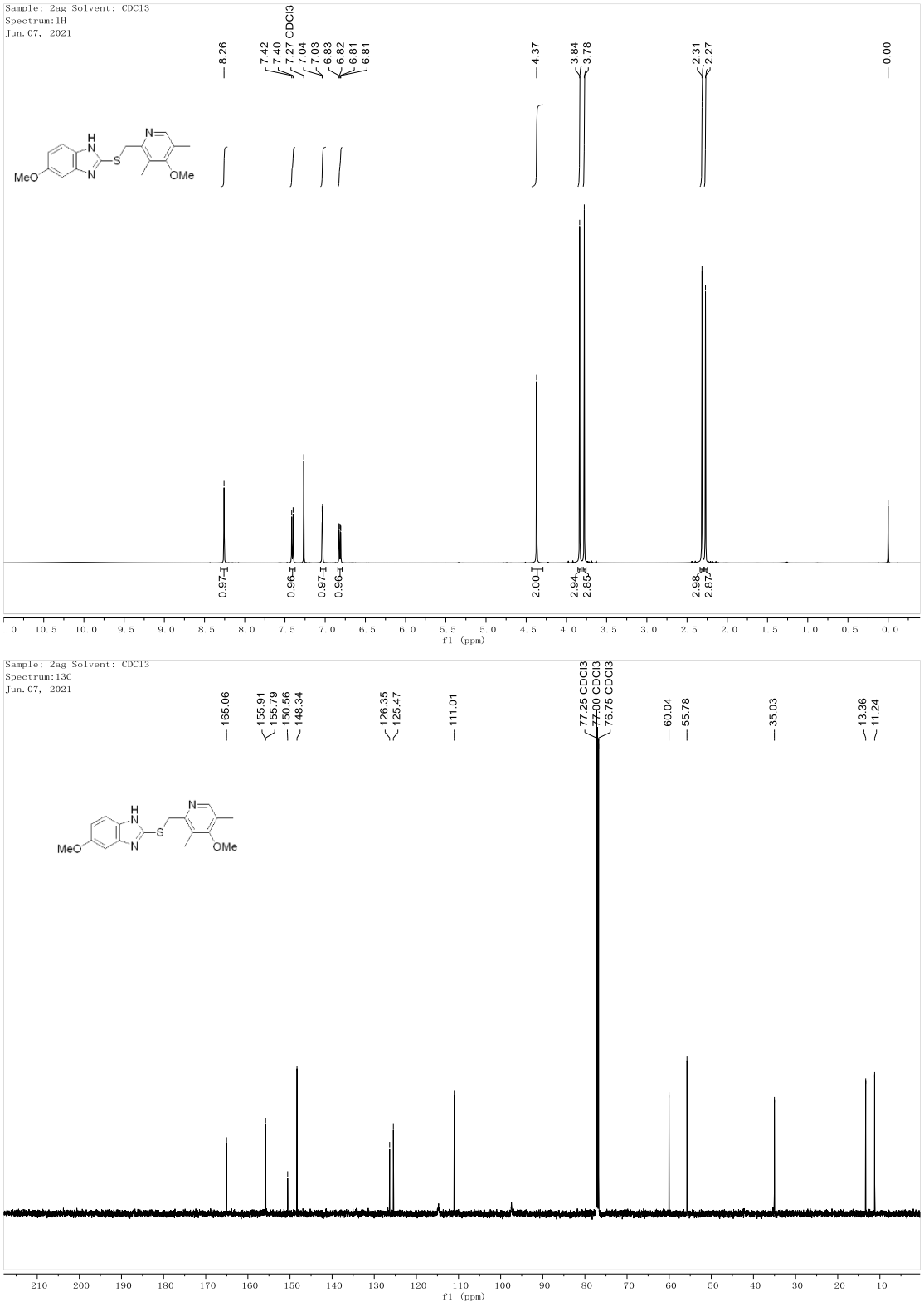
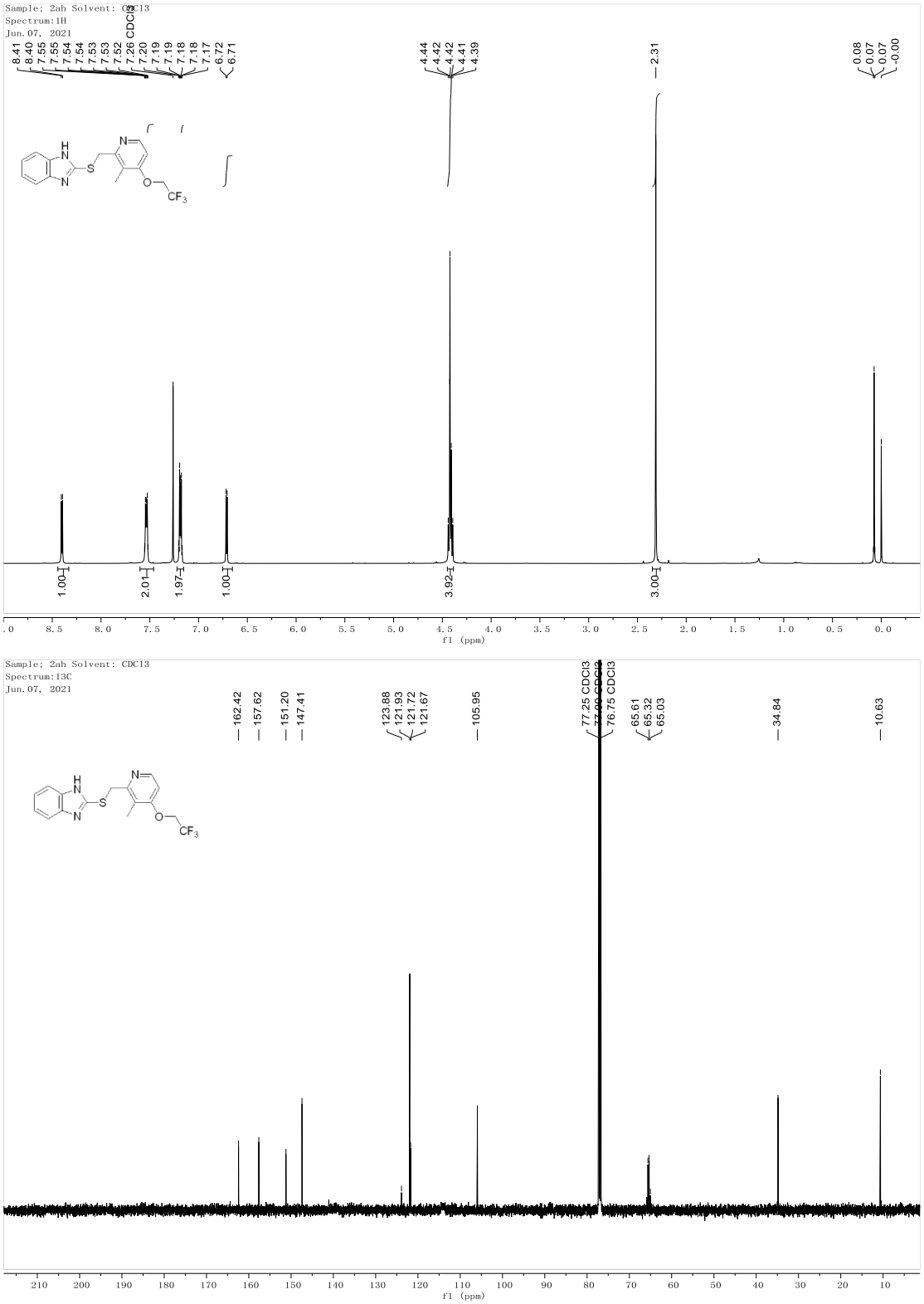
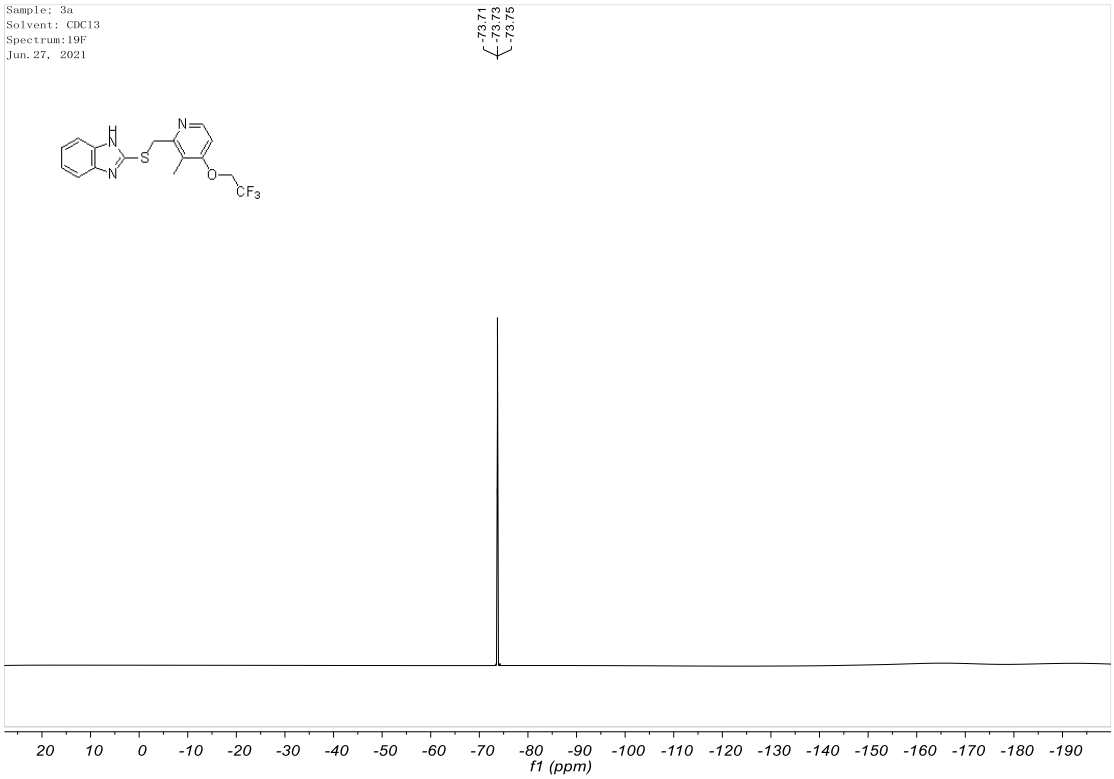


Fig. 32. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectra of 2ak




Sample; 3a
Solvent: CDCl3
Spectrum:19F
Jun.27, 2021
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-73.73
-73.75
N
H
N
S
O
CF3
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f1 (ppm)