

Supporting Information for

**Visible Light-Promoted NH-Halogenation of Sulfoximines
With Dichloromethane or Dibromomethane**

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1. General information

If not otherwise stated all chemicals were purchased from commercial suppliers and used without further purification. Solvents for flash column chromatography purifications were of technical grade and were distilled before use. Flash column chromatography was conducted with silica 60 M (0.04–0.063 mm) as the stationary phase, which was purchased from MACHERY-NAGEL. Thin-layer chromatography (TLC) was performed with silica coated alumina plates TLC silica gel 60 F254 from Merck and the products were visualized using UV-light ($\lambda = 254$ nm). Melting points (m.p.) were measured on a BÜCHI Melting Point M-560 apparatus using open-end capillaries, a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded either on a Varian Mercury 300, Varian VNMRS 400, Varian VNMRS 600, Bruker Avance Neo 400 or Bruker Avance Neo 600 at $25\text{ }^{\circ}\text{C}$, if not otherwise stated, and were processed and analyzed with the program MestReNova. Chemical shifts (δ) are given in parts per million (ppm). Proton and carbon NMR spectra were referenced to the solvent residue signal of the non-deuterated solvent (CHCl_3 : ^1H NMR: $\delta = 7.26$ ppm, CDCl_3 : $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 77.0$ ppm; $(\text{CH}_3)_2\text{SO}$: ^1H NMR: $\delta = 2.50$ ppm, $(\text{CD}_3)_2\text{SO}$: $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 39.52$ ppm; $(\text{CH}_3)_2\text{CO}$: ^1H NMR: $\delta = 2.05$ ppm, $(\text{CD}_3)_2\text{CO}$: $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 29.84, 206.26$ ppm). Carbon spectra were measured by proton broadband decoupling. The multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), m (multiplet), and combinations thereof. The spin-spin coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were recorded neat on a PerkinElmer Spectrum 100 FT-IR spectrometer with an attached UATR device with a KRS-5 crystal for a single reflection. Mass spectra were recorded on a Finnigan SSQ 7000 mass spectrometer [electron ionization (EI), 70 eV; chemical ionization (CI), methane, 100 eV]. The signals are given according to their m/z values and corresponding relative intensities are reported in parenthesis. High resolution mass (HRMS) spectra were recorded either as ESI (electrospray ionization, positive mode) on a Thermo Fisher Scientific LTQ Orbitrap XL mass spectrometer or as EI on a Finnigan MAT 95 XP mass spectrometer. The *NH*-sulfoximines were prepared in accordance with previously published synthetic strategies.^[S1] The sulfoximidoyl-containing hypervalent iodine(III) reagents were synthesized following previous reports.^[S2] For details of the synthesis of *p*-TolIF₂, see ref. [S3].

2. General procedure for *N*-halogenations of *NH*-sulfoximines

Under an atmosphere of air, sulfoximine **4** (0.2 mmol), 4-(difluoroiodo)toluene (**5**, 0.3 mmol, 1.5 equiv.), and DCM (1.5 mL) were added into a sealable reaction tube (15 mL). Then, the reaction mixture was stirred under irradiation with blue light provided by LEDs (5 W) at room temperature for 24 h. Finally, the product was purified by flash column chromatography (ethyl acetate/ *n*-pentane = 1/2 to 1/4). *Note: In all reactions, freshly prepared p-TolIF₂ was used.*

3. ^1H and ^{19}F NMR spectra of the crude reaction mixture stemming from an experiment with deuterated chloroform (CDCl_3)

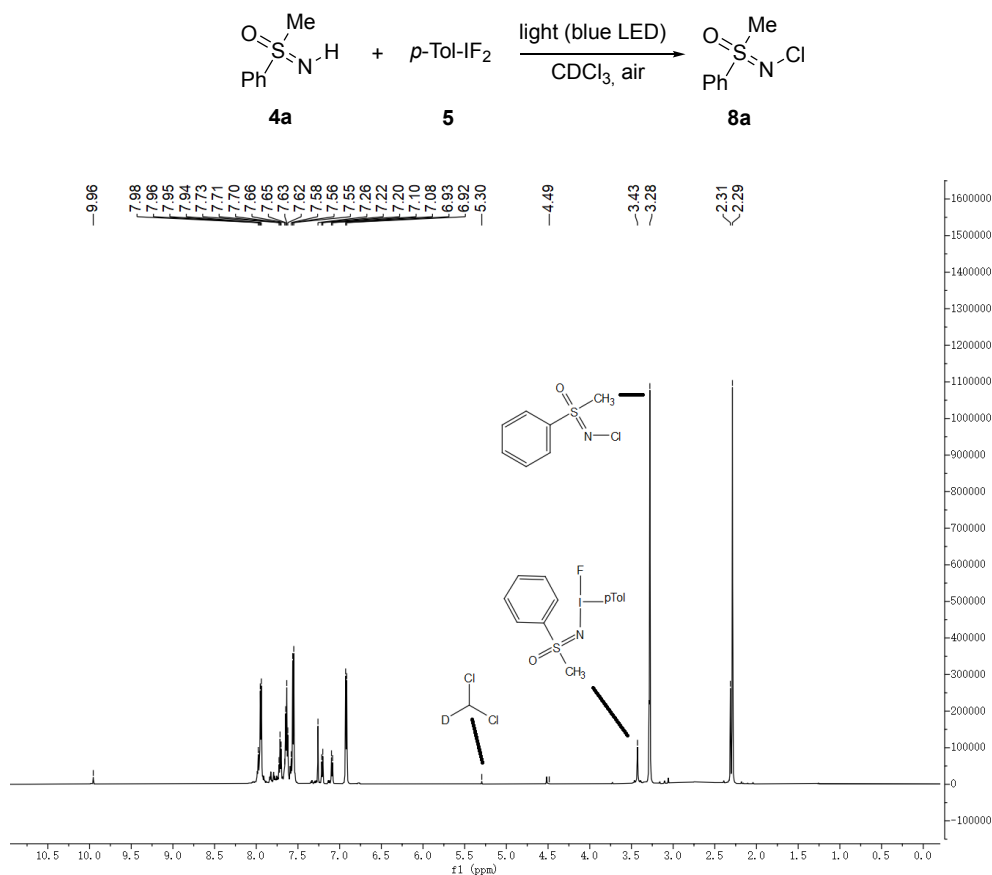


Figure S1. ^1H NMR (600 MHz, CDCl_3) spectrum of reaction mixtures

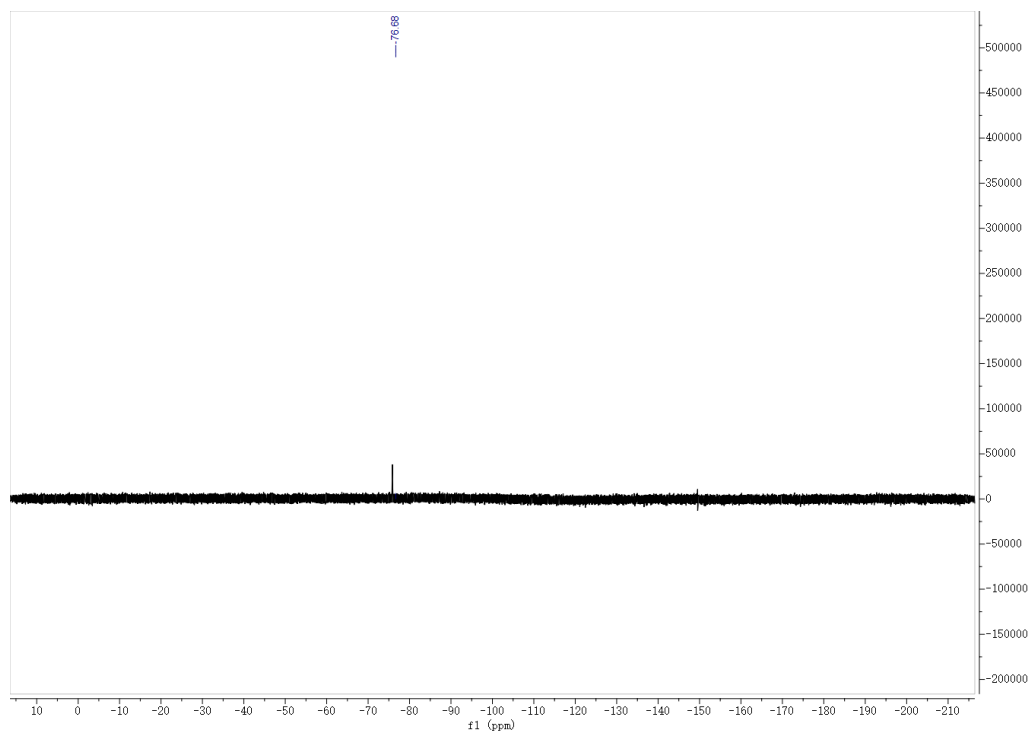
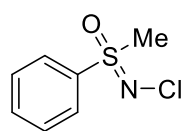


Figure S2. ^{19}F NMR (600 MHz, CDCl_3) spectrum of reaction mixtures.

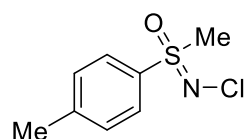
4. Characterizing data

(Chloroimino)(methyl)(phenyl)- λ^6 -sulfanone (8a)



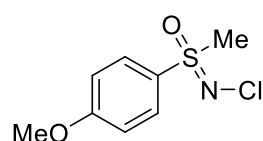
Following the general procedure afforded the product as a white solid (36 mg, 95% yield). **m.p.:** 73.9-74.5 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.95 – 7.90 (m, 2H), 7.72 – 7.67 (m, 1H), 7.64 – 7.58 (m, 2H), 3.25 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 136.4, 134.2, 129.7, 129.0, 42.0. The spectroscopic data are in accordance with the previously reported data.^[S4,S5]

(Chloroimino)(methyl)(p-tolyl)- λ^6 -sulfanone (8b)



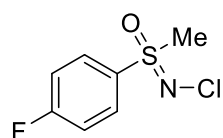
Following the general procedure afforded the product as a white solid (39 mg, 97% yield). **m.p.:** 65.7-67.8 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.81 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.24 (s, 3H), 2.47 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 145.4, 133.2, 130.4, 129.1, 42.2, 21.6. **MS (EI):** m/z (%) = 205 (14), 203 (40), 155 (8), 154 (34), 140 (13), 139 (100), 111 (7), 107 (12), 106 (14), 91 (40), 78 (17), 77 (31), 65 (67), 63 (70), 51 (58). **IR (ATR):** ν = 3015, 2963, 2928, 1592, 1489, 1449, 1402, 1260, 1207, 1089, 998, 942, 800, 764, 700, 657 cm⁻¹. **HRMS (ESI):** m/z [M+Na⁺] calcd for [C₈H₁₀ClNOS+Na]⁺: 226.0064, found: 226.0066.

(Chloroimino)(4-methoxyphenyl)(methyl)- λ^6 -sulfanone (8c)



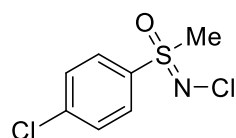
Following the general procedure afforded the product as a white solid (42 mg, 96% yield). **m.p.:** 110.4-112.1 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.87 – 7.84 (m, 2H), 7.09 – 7.06 (m, 2H), 3.90 (s, 3H), 3.24 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 164.3, 131.3, 127.2, 115.1, 55.8, 42.4. **HRMS (ESI):** m/z [M+Na⁺] calcd for [C₈H₁₀ClNO₂S+Na]⁺: 242.0013, found: 242.0016. The spectroscopic data are in accordance with the previously reported data.^[S4]

(Chloroimino)(4-fluorophenyl)(methyl)- λ^6 -sulfanone (8d)

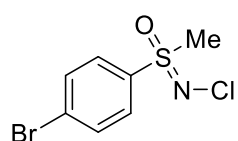


Following the general procedure afforded the product as a yellow solid (36 mg, 88% yield). **m.p.:** 86.6-88.5 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.97 – 7.92 (m, 2H), 7.32 – 7.27 (m, 2H), 3.26 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 166.1 (d, J_{C-H} = 258.3 Hz) 132.2 (d, J_{C-H} = 2.8 Hz), 132.1 (d, J_{C-H} = 9.8 Hz), 117.2 (d, J_{C-H} = 22.8 Hz), 42.3. **MS (EI):** m/z (%) = 209 (41), 208 (17), 207 (100), 158 (37), 143 (62), 115 (11), 95 (9), 49 (11). **IR (ATR):** ν = 3104, 3025, 2930, 2167, 1585, 1489, 1402, 1315, 1215, 1160, 1089, 992, 962, 834, 765, 659 cm⁻¹. **HRMS (ESI):** m/z [M+H⁺] calcd for [C₇H₇ClFNOS+H]⁺: 207.9994, found: 207.9998.

(Chloroimino)(4-chlorophenyl)(methyl)- λ^6 -sulfanone (8e)

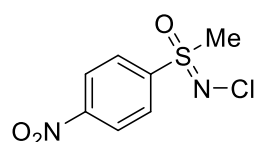


Following the general procedure afforded the product as a yellow solid (39 mg, 89% yield). **m.p.:** 89.5-90.5 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.86 (dq, J = 9.2, 2.6, 1.8 Hz, 2H), 7.59 (dq, J = 9.2, 2.6, 1.8 Hz, 2H), 3.26 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 141.1, 134.8, 130.6, 130.1, 42.1. The spectroscopic data are in accordance with the previously reported data.^[S4]

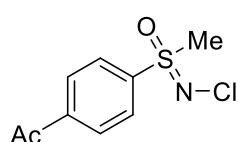
(4-Bromophenyl)(chloroimino)(methyl)- λ^6 -sulfanone (8f)

reported data.^[S4]

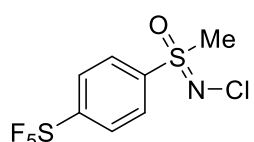
Following the general procedure afforded the product as a yellow solid (48 mg, 91% yield). **m.p.:** 100.1-103.2 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.78 (qd, J = 8.8, 1.7 Hz, 4H), 3.26 (d, J = 1.3 Hz, 3H). **¹³C {¹H}** (151 MHz, CDCl₃) δ 135.5, 133.1, 130.7, 129.7, 42.1. The spectroscopic data are in accordance with the previously

(Chloroimino)(methyl)(4-nitrophenyl)- λ^6 -sulfanone (8g)

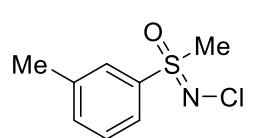
Following the general procedure afforded the product as a yellow solid (38 mg, 81% yield). **m.p.:** 98.4-101.3 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.49 – 8.43 (m, 2H), 8.16 – 8.12 (m, 2H), 3.33 (s, 3H). **¹³C {¹H}** (151 MHz, CDCl₃) δ 151.2, 142.8, 131.0, 130.7, 124.9, 42.0. **MS (EI):** m/z (%) = 236 (38), 235 (16), 234 (100), 185 (60), 170 (15), 63 (8), 50 (17). **IR (ATR):** ν = 3103, 3055, 3021, 2922, 2861, 1606, 1523, 1402, 1345, 1316, 1221, 1088, 998, 955, 857, 771, 736, 718, 681, 656 cm⁻¹. **HRMS (ESI):** m/z [M+H⁺] calcd for [C₇H₇ClN₂O₃S+H]⁺: 234.9934, found: 234.9936.

(4-Acetylphenyl)(chloroimino)(methyl)- λ^6 -sulfanone (8h)

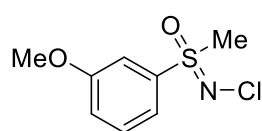
Following the general procedure afforded the product as a white solid (41 mg, 88% yield). **m.p.:** 72.0-74.8 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.18 – 8.14 (m, 2H), 8.06 – 8.02 (m, 2H), 3.29 (s, 3H), 2.67 (s, 3H). **¹³C {¹H}** (151 MHz, CDCl₃) δ 196.5, 141.3, 140.6, 129.6, 129.4, 42.0, 26.9. **MS (EI):** m/z (%) = 233 (37.9), 232 (23), 231 (100), 182 (22), 167 (54), 152 (11), 50 (3). **IR (ATR):** ν = 3092, 3054, 3007, 2921, 2855, 1770, 1688, 1574, 1395, 1358, 1316, 1257, 1217, 1093, 1072, 996, 962, 943, 837, 780, 746, 657 cm⁻¹. **HRMS (ESI):** m/z [M+Na⁺] calcd for [C₉H₁₀ClNO₂S+Na]⁺: 254.0013, found: 254.0013.

(Chloroimino)(methyl)[4-(pentafluoro- λ^6 -sulfaneyl)phenyl]- λ^6 -sulfanone (8i)

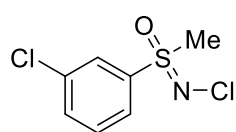
Following the general procedure afforded the product as a yellow solid (51 mg, 81% yield). **m.p.:** 89.0-91.8 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.06 (d, J = 8.8 Hz, 2H), 8.04 – 8.00 (m, 2H), 3.30 (s, 3H). **¹³C {¹H}** (151 MHz, CDCl₃) δ 157.9, 157.8, 157.7, 140.2, 130.0, 127.8, 127.7, 127.7, 127.7, 127.6, 42.0. **MS (EI):** m/z (%) = 317 (42), 316 (17), 315 (100), 267 (9), 266 (73), 251 (48), 250 (11), 143 (21), 95 (7), 63 (6). **IR (ATR):** ν = 3013, 2927, 1577, 1451, 1424, 1311, 1218, 1123, 1084, 997, 955, 760, 711 cm⁻¹. **HRMS (ESI):** m/z [M+Na⁺] calcd for [C₇H₇ClF₅NOS₂+Na]⁺: 337.9470, found: 337.9475.

(Chloroimino)(methyl)(m-tolyl)- λ^6 -sulfanone (8j)

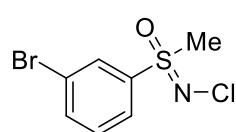
Following the general procedure afforded the product as a white solid (37 mg, 92% yield). **m.p.:** 88.6-89.6 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.74 (d, J = 5.9 Hz, 2H), 7.50 (d, J = 4.7 Hz, 2H), 3.25 (s, 3H), 2.47 (s, 3H). **¹³C {¹H}** (151 MHz, CDCl₃) δ 140.2, 136.3, 135.0, 129.6, 129.3, 126.1, 42.1, 21.3. **MS (EI):** m/z (%) = 205 (38), 204 (18), 203 (100), 154 (41), 91 (9), 65 (7). **IR (ATR):** ν = 3017, 2926, 2332, 1597, 1475, 1407, 1311, 1216, 1145, 1089, 990, 857, 790, 760, 682 cm⁻¹. **HRMS (ESI):** m/z [M+Na⁺] calcd for [C₈H₁₀ClNOS+Na]⁺: 226.0064, found: 226.0062.

(Chloroimino)(3-methoxyphenyl)(methyl)- λ^6 -sulfanone (8k)

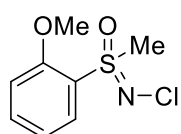
Following the general procedure afforded the product as a white oil (39 mg, 90% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 (d, $J = 6.7$ Hz, 2H), 7.44 – 7.42 (m, 1H), 7.21 (dd, $J = 5.7, 2.8$ Hz, 1H), 3.88 (s, 3H), 3.25 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 160.5, 137.7, 130.8, 121.1, 120.8, 113.4, 55.8, 42.1. **MS (EI):** m/z (%) = 221 (40), 220 (25), 219 (100), 186 (25), 185 (13), 170 (41), 155 (67), 124 (21), 122 (15), 107 (9), 92 (9), 77 (9). **IR (ATR):** $\nu = 3010, 2926, 2838, 2650, 1595, 1479, 1428, 1318, 1286, 1218, 1148, 1092, 1031, 1002, 853, 788, 761, 678$ cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_8\text{H}_{10}\text{ClNO}_2\text{S}+\text{H}]^+$: 220.0194, found: 220.0204.

(Chloroimino)(3-chlorophenyl)(methyl)- λ^6 -sulfanone (8l)

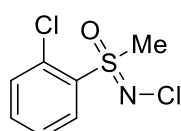
Following the general procedure afforded the product as a yellow viscous oil (38 mg, 87% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.92 (q, $J = 1.6$ Hz, 1H), 7.81 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.68 – 7.65 (m, 1H), 7.57 (t, $J = 7.9$ Hz, 1H), 3.27 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 138.3, 136.0, 134.4, 131.0, 129.1, 127.8, 127.2, 42.1. **MS (EI):** m/z (%) = 227 (15), 226 (17), 225 (72), 224 (25), 223 (100), 190 (14), 176 (17), 174 (45), 159 (43), 111 (15), 50 (12). **IR (ATR):** $\nu = 3070, 3017, 2927, 1727, 1628, 1576, 1462, 1409, 1317, 1222, 1161, 1117, 1078, 1007, 889, 786, 746, 670$ cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_7\text{H}_7\text{Cl}_2\text{NOS}+\text{H}]^+$: 223.9698, found: 223.9699.

(3-Bromophenyl)(chloroimino)(methyl)- λ^6 -sulfanone (8m)

Following the general procedure afforded the product as a yellow oil (48 mg, 89% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 1.8$ Hz, 1H), 7.86 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.84 – 7.81 (m, 1H), 7.50 (td, $J = 7.9, 1.3$ Hz, 1H), 3.27 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 138.5, 137.3, 132.0, 131.2, 127.6, 123.7, 42.1. **MS (EI):** m/z (%) = 271 (29), 270 (17), 269 (100), 267 (74), 220 (40), 218 (40), 205 (31), 203 (31), 139 (11). **IR (ATR):** $\nu = 3067, 3020, 2998, 2918, 2856, 2342, 1720, 1568, 1459, 1404, 1317, 1215, 1158, 1088, 1009, 944, 887, 779, 733, 672$ cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_7\text{H}_7\text{ClBrNOS}+\text{H}]^+$: 267.9030, found: 267.9120.

(Chloroimino)(2-methoxyphenyl)(methyl)- λ^6 -sulfanone (8n)

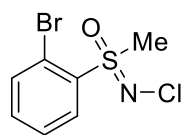
Following the general procedure afforded the product as a white solid (35 mg, 81% yield). **m.p.:** 83.3-85.5 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.01 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.64 (t, $J = 7.9$ Hz, 1H), 7.18 – 7.13 (m, 1H), 7.08 (d, $J = 8.3$ Hz, 1H), 3.98 (s, 2H), 3.42 (s, 2H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 156.9, 136.2, 132.4, 123.5, 120.9, 112.7, 56.5, 40.0. **MS (EI):** m/z (%) = 222 (22), 221 (43), 220 (59), 219 (100), 174 (29), 155 (51), 154 (14), 153 (86), 125 (23), 120 (14), 97 (14), 63 (24), 51 (15). **IR (ATR):** $\nu = 3042, 3010, 2930, 2844, 2024, 1584, 1475, 1434, 1407, 1277, 1249, 1206, 1134, 1066, 996, 963, 940, 857, 801, 762, 674$ cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_8\text{H}_{10}\text{ClNO}_2\text{S}+\text{H}]^+$: 220.0194, found: 220.0205.

(Chloroimino)(2-chlorophenyl)(methyl)- λ^6 -sulfanone (8o)

Following the general procedure afforded the product as a yellow solid (34 mg, 77% yield). **m.p.:** 106.4-108.3 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.21 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.65 – 7.58 (m, 2H), 7.53 (ddd, $J = 8.2, 6.9, 1.5$ Hz, 1H), 3.47 (s, 3H). ^{13}C $\{^1\text{H}\}$

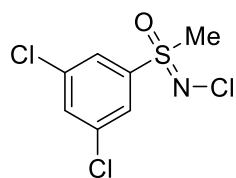
(151 MHz, CDCl₃) δ 135.2, 133.8, 133.7, 132.6, 132.4, 127.7, 40.1. **MS (EI):** m/z (%) = 227 (15), 225 (72), 224 (18), 223 (100), 176 (20), 174 (55), 161 (18), 159 (48), 131 (11). **IR (ATR):** ν = 3087, 3019, 2932, 2855, 1738, 1570, 1445, 1318, 1251, 1213, 1134, 1105, 1043, 996, 959, 779, 748, 659 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₇H₇Cl₂NOS+Na]⁺: 245.9518, found: 245.9518.

(2-Bromophenyl)(chloroimino)(methyl)- λ^6 -sulfanone (8p)



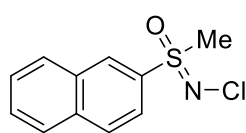
Following the general procedure afforded the product as a yellow solid (43 mg, 89% yield). **m.p.:** 139.2-141.4 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.24 (dt, J = 7.9, 1.5 Hz, 1H), 7.81 (dd, J = 7.9, 1.3 Hz, 1H), 7.58 (td, J = 7.6, 1.4 Hz, 1H), 7.52 (tt, J = 7.6, 1.6 Hz, 1H), 3.47 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 136.0, 135.4, 135.1, 133.9, 128.3, 120.8, 39.8. **MS (EI):** m/z (%) = 271 (29), 269 (100), 269 (77), 220 (50), 218 (48), 205 (33), 203 (32), 139 (6). **IR (ATR):** ν = 3083, 3019, 2932, 2322, 1566, 1428, 1250, 1214, 1130, 1096, 1030, 992, 959, 776, 747, 712 cm⁻¹. **HRMS (ESI):** m/z [M+H]⁺ calcd for [C₇H₇ClBrNOS+H]⁺: 267.9193, found: 267.9195.

(Chloroimino)(3,5-dichlorophenyl)(methyl)- λ^6 -sulfanone (8q)



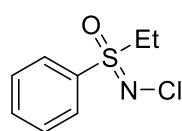
Following the general procedure afforded the product as a yellow solid (42 mg, 82% yield). **m.p.:** 121.2-122.8 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.80 (d, J = 1.9 Hz, 2H), 7.67 (t, J = 1.9 Hz, 1H), 3.28 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 139.7, 136.8, 134.2, 127.5, 42.0. **MS (EI):** m/z (%) = 261 (35), 259 (100), 257 (90), 210 (27), 208 (38), 195 (27), 192 (40), 162 (13), 145 (11), 49 (13). **IR (ATR):** ν = 3080, 3008, 2924, 2333, 1566, 1397, 1315, 1220, 1135, 1093, 1011, 955, 867, 798, 749, 662 cm⁻¹. **HRMS (ESI):** m/z [M+H]⁺ calcd for [C₇H₆Cl₃NOS+H]⁺: 257.9309, found: 257.9316.

(Chloroimino)(methyl)(naphthalen-2-yl)- λ^6 -sulfanone (8r)

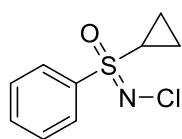


Following the general procedure afforded the product as a white solid (45 mg, 95% yield). **m.p.:** 92.4-94.5 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.57 (d, J = 1.9 Hz, 1H), 8.06 (d, J = 8.7 Hz, 1H), 8.03 – 8.01 (m, 1H), 7.96 (dd, J = 8.3, 1.2 Hz, 1H), 7.84 (dd, J = 8.7, 1.9 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.66 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 3.34 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 135.5, 133.3, 132.5, 131.7, 130.2, 129.7, 129.4, 128.0, 127.9, 123.0, 42.2. **MS (EI):** m/z (%) = 241 (39), 239 (100), 190 (33), 175 (58), 127 (14). **IR (ATR):** ν = 3012, 2926, 2290, 1621, 1558, 1500, 1401, 1348, 1206, 1131, 1069, 1004, 960, 937, 906, 853, 818, 764, 657 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₁₁H₁₀CINOS+Na]⁺: 262.0064, found: 262.0064.

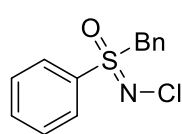
(Chloroimino)(ethyl)(phenyl)- λ^6 -sulfanone (8s)



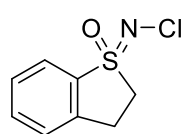
Following the general procedure afforded the product as a solid (33 mg, 82% yield). **m.p.:** 68.2-70.0 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.92 – 7.88 (m, 2H), 7.72 – 7.68 (m, 1H), 7.62 (dd, J = 8.4, 7.1 Hz, 2H), 3.44 (dq, J = 15.0, 7.5 Hz, 1H), 3.35 (dq, J = 14.7, 7.5 Hz, 1H), 1.31 (t, J = 7.5 Hz, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 134.6, 134.1, 129.8, 129.7, 48.8, 7.7. **MS (EI):** m/z (%) = 328 (16), 206 (23), 205 (42), 204 (61), 203 (100), 154 (17), 126 (54), 125 (37), 78 (14), 51 (16). **IR (ATR):** ν = 2986, 2940, 1471, 1444, 1405, 1232, 1200, 1088, 967, 777, 759, 728, 684, 658 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₈H₁₀CINOS+H]⁺: 204.0244, found: 204.0248.

(Chloroimino)(cyclopropyl)(phenyl)- λ^6 -sulfanone (8t)

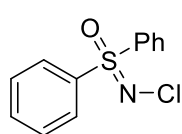
Following the general procedure afforded the product as a solid (35 mg, 82% yield). **m.p.:** 80.9-81.8 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.92 – 7.88 (m, 2H), 7.70 – 7.66 (m, 1H), 7.61 (dd, J = 8.4, 7.1 Hz, 2H), 2.71 (tt, J = 8.0, 4.7 Hz, 1H), 1.64 (dddd, J = 10.4, 7.4, 5.7, 4.5 Hz, 1H), 1.26 (dtd, J = 9.2, 7.7, 5.7 Hz, 1H), 1.09 (ddt, J = 10.5, 7.5, 5.2 Hz, 1H), 0.96 (dtd, J = 9.2, 7.7, 5.5 Hz, 1H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 136.7, 133.8, 129.6, 129.1, 77.2, 77.0, 76.8, 31.0, 6.3, 5.4. **MS (EI):** m/z (%) = 217 (40), 215 (100), 166 (18), 125 (22), 77 (8), 51 (13). **IR (ATR):** ν = 3054, 2996, 2930, 1481, 1454, 1405, 1212, 1200, 1008, 967, 777, 759, 728, 684, 657 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₉H₁₀ClNOS+Na]⁺: 238.0064, found: 238.0063.

Benzyl(chloroimino)(phenyl)- λ^6 -sulfanone (8u)

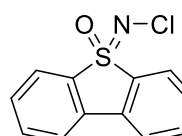
Following the general procedure afforded the product as a white solid (41 mg, 77% yield). **m.p.:** 74.4-75.6 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.64 – 7.58 (m, 3H), 7.48 – 7.44 (m, 2H), 7.33 – 7.29 (m, 1H), 7.23 (dd, J = 8.4, 7.0 Hz, 2H), 7.05 – 7.02 (m, 2H), 4.68 – 4.55 (m, 2H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 134.1, 133.7, 131.2, 130.1, 129.2, 129.2, 128.6, 127.1, 60.5, 60.3, 21.0, 14.1. **MS (EI):** m/z (%) = 267 (23), 265 (22), 265 (58), 249 (11), 232 (26), 230 (50), 214 (18), 183 (16), 125 (62), 91 (100), 51 (22). **IR (ATR):** ν = 3054, 2987, 2962, 2929, 1772, 1492, 1446, 1404, 1259, 1210, 1142, 1086, 1024, 972, 928, 880, 785, 752, 686 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₁₃H₁₂ClNOS+Na]⁺: 288.0220, found: 288.0223.

1-(Chloroimino)-1 λ^4 -thiochromane 1-oxide (8v)

Following the general procedure afforded the product as a yellow oil (35 mg, 87% yield). **m.p.:** 76.1-78.7 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.85 (d, J = 7.8 Hz, 1H), 7.62 (td, J = 7.6, 1.2 Hz, 1H), 7.49 (td, J = 7.6, 1.0 Hz, 1H), 7.43 – 7.38 (m, 1H), 4.00 (ddd, J = 13.4, 6.1, 4.8 Hz, 1H), 3.56 (ddd, J = 13.4, 9.1, 7.6 Hz, 1H), 3.42 (dd, J = 8.8, 5.0 Hz, 2H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 138.5, 136.1, 134.1, 128.6, 127.3, 123.8, 50.1, 26.7. **MS (EI):** m/z (%) = 204 (12), 203 (40), 202 (33), 201 (100), 152 (31), 135 (37), 91 (6). **IR (ATR):** ν = 2994, 2940, 2853, 2728, 2328, 1720, 1467, 1432, 1258, 1207, 1133, 1064, 981, 955, 791, 755, 698 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₈H₈ClNOS+Na]⁺: 223.9907, found: 223.9904.

(Chloroimino)diphenyl- λ^6 -sulfanone (8w)

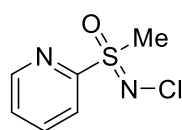
Following the general procedure afforded the product as a white solid (49 mg, 98% yield). **m.p.:** 147.0-148.1 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.03 – 7.99 (m, 4H), 7.64 – 7.58 (m, 2H), 7.57 – 7.52 (m, 4H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 137.4, 133.8, 129.6, 128.9. **MS (EI):** m/z (%) = 253 (39), 252 (22), 251 (100), 202 (42), 154 (14), 51 (9). **IR (ATR):** ν = 3067, 2923, 2662, 2325, 1742, 1577, 1445, 1225, 1161, 1086, 1021, 962, 802, 759, 724, 684 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₁₂H₁₀ClNOS+Na]⁺: 274.0064, found: 274.0070.

5-(Chloroimino)-5H-5 λ^4 -dibenzo[b,d]thiophene 5-oxide (8x)

Following the general procedure afforded the product as a white solid (47 mg, 96% yield). **m.p.:** 157.7-158.9 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.00 – 7.96 (m, 2H), 7.86 – 7.82 (m, 2H), 7.68 (td, J = 7.6, 1.1 Hz, 2H), 7.55 (td, J = 7.6, 1.1 Hz, 2H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 135.7, 134.3, 132.7, 130.4, 124.0, 122.0. **MS (EI):** m/z (%) = 251 (36), 250 (18), 249 (93), 201 (24), 200 (100), 184 (16), 172 (41), 171 (45), 167 (12), 166 (22), 139 (10). **IR**

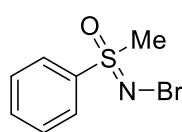
(ATR): $\nu = 2922, 2324, 2116, 1582, 1475, 1444, 1264, 1444, 1264, 1220, 1123, 1065, 954, 869, 749, 705$ cm^{-1} . HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{12}\text{H}_8\text{ClNO}_2\text{S}+\text{H}]^+$: 250.0088, found: 250.0089.

(Chloroimino)(methyl)(pyridin-2-yl)- λ^6 -sulfanone (8y)



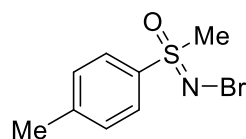
Following the general procedure afforded the product as a yellow oil (33 mg, 88% yield). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.78 (ddd, $J = 4.7, 1.8, 0.8$ Hz, 1H), 8.19 (dt, $J = 7.9, 1.0$ Hz, 1H), 8.01 (td, $J = 7.8, 1.7$ Hz, 1H), 7.59 (ddd, $J = 7.7, 4.7, 1.1$ Hz, 1H), 3.44 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 155.0, 150.6, 138.1, 127.6, 124.6, 37.9. MS (EI): m/z (%) = 192 (39), 191 (42), 190 (100), 141 (16), 140 (16), 78 (58), 67 (11), 51 (67). IR (ATR): $\nu = 3013, 2962, 2926, 1577, 1423, 1311, 1257, 1219, 1122, 1084, 999, 789, 760, 709$ cm^{-1} . HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_6\text{H}_7\text{ClN}_2\text{OS}+\text{H}]^+$: 191.0040, found: 191.0040.

(Bromoimino)(methyl)(phenyl)- λ^6 -sulfanone (9a)



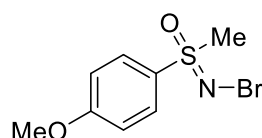
Following the general procedure afforded the product as a yellow solid (43 mg, 93% yield). m.p.: 77.4-79.0 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.92 – 7.87 (m, 2H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 2H), 3.30 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 177.6, 137.8, 134.0, 129.7, 128.7, 42.6. The spectroscopic data are in accordance with the previously reported data.^[S5]

(Bromoimino)(methyl)(p-tolyl)- λ^6 -sulfanone (9b)



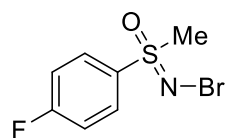
Following the general procedure afforded the product as a yellow solid (44 mg, 90% yield). m.p.: 85.7-87.2. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.79 – 7.74 (m, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 3.27 (s, 3H), 2.46 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 145.1, 134.7, 130.3, 128.7, 42.7, 21.6. The spectroscopic data are in accordance with the previously reported data.^[S5]

(Bromoimino)(4-methoxyphenyl)(methyl)- λ^6 -sulfanone (9c)

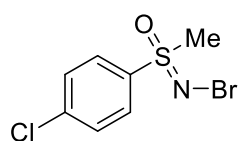


Following the general procedure afforded the product as a yellow solid (48 mg, 91% yield). m.p.: 69.0-71.0 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.77 – 7.74 (m, 2H), 7.02 – 6.98 (m, 2H), 3.84 (s, 3H), 3.22 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 172.3, 163.1, 130.0, 114.0, 54.8, 41.9. The spectroscopic data are in accordance with the previously reported data.^[S5]

(Bromoimino)(4-fluorophenyl)(methyl)- λ^6 -sulfanone (9d)

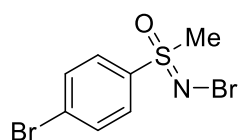


Following the general procedure afforded the product as a yellow solid (41 mg, 83% yield). m.p.: 78.5-80.0 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.94 – 7.89 (m, 2H), 7.30 – 7.26 (m, 2H), 3.30 (s, 3H). ^{13}C $\{^1\text{H}\}$ (151 MHz, CDCl_3) δ 166.1 (d, $J_{\text{C-F}} = 253.6$ Hz), 133.7 (d, $J_{\text{C-F}} = 3.1$ Hz), 131.7 (d, $J_{\text{C-F}} = 9.7$ Hz), 117.1 (d, $J_{\text{C-F}} = 22.8$ Hz), 42.8. MS (EI): m/z (%) = 254 (16), 253 (96), 252 (18), 251 (100), 190 (18), 188 (18), 158 (22), 143 (60), 110 (14), 109 (24), 75 (23), 63 (17). IR (ATR): $\nu = 3099, 3065, 3037, 1583, 1489, 1402, 1315, 1208, 1159, 1088, 986, 954, 841, 816, 754, 701$ cm^{-1} . HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_7\text{H}_7\text{FBrNO}_2\text{S}+\text{Na}]^+$: 273.9308, found: 273.9312.

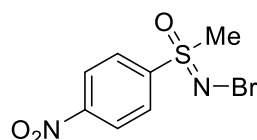
(Bromoimino)(4-chlorophenyl)(methyl)- λ^6 -sulfanone (9e)

reported data.^[S5]

Following the general procedure afforded the product as a yellow solid (45 mg, 84% yield). **m.p.:** 96.5-97.9 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.85 – 7.82 (m, 2H), 7.60 – 7.57 (m, 2H), 3.30 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 140.9, 136.4, 130.3, 130.0, 42.7. The spectroscopic data are in accordance with the previously

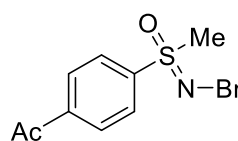
(Bromoimino)(4-bromophenyl)(methyl)- λ^6 -sulfanone (9f)

Following the general procedure afforded the product as a yellow solid (52 mg, 85% yield). **m.p.:** 107.2-109.1 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.75 (s, 4H), 3.29 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 137.0, 133.0, 130.3, 129.5, 42.6. The spectroscopic data are in accordance with the previously reported data.^[S5]

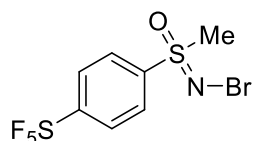
(Bromoimino)(methyl)(4-nitrophenyl)- λ^6 -sulfanone (9g)

previously reported data.^[S5]

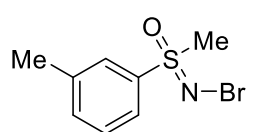
Following the general procedure afforded the product as a yellow solid (42 mg, 76% yield). **m.p.:** 95.6-98.0 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.41 – 8.37 (m, 2H), 8.07 – 8.03 (m, 2H), 3.31 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 151.0, 144.1, 130.3, 124.8, 42.4. The spectroscopic data are in accordance with the

(4-Acetylphenyl)(bromoimino)(methyl)- λ^6 -sulfanone (9h)

Following the general procedure afforded the product as a yellow oil (42 mg, 78% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.16 – 8.14 (m, 2H), 8.01 – 7.99 (m, 2H), 3.32 (s, 3H), 2.67 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 196.6, 142.0, 141.1, 129.4, 129.2, 42.5, 26.9. **MS (EI):** m/z (%) = 278 (15), 277 (65), 276 (15), 275 (100), 198 (25), 197 (23), 183 (11), 120 (15), 75 (13), 63 (8). **IR (ATR):** ν = 3092, 3054, 3007, 2921, 2855, 1770, 1688, 1574, 1395, 1358, 1316, 1257, 1217, 1093, 1072, 996, 962, 943, 837, 780, 746, 657 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₉H₁₀BrNO₂S+Na]⁺: 297.9508, found: 297.9507.

(Bromoimino)(methyl)[4-(pentafluoro- λ^6 -sulfaneyl)phenyl]- λ^6 -sulfanone (9i)

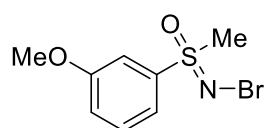
Following the general procedure afforded the product as a yellow solid (58 mg, 81% yield). **m.p.:** 90.6-93.0 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.04 – 7.99 (m, 4H), 3.33 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 157.8, 157.6, 157.5, 141.6, 129.6, 127.6, 127.6, 127.6, 42.5. **MS (EI):** m/z (%) = 361 (11), 360 (27), 359 (100), 358 (89), 282 (15), 281 (19), 205 (23), 204 (15), 172 (28), 171 (37), 78 (11), 77(32), 51 (17). **IR (ATR):** ν = 3013, 2932, 2842, 2164, 1756, 1639, 1591, 1497, 1462, 1369, 1310, 1255, 1194, 1139, 1089, 1017, 979, 911, 836, 804, 766, 711 cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₇H₇BrF₅NOS+Na]⁺: 381.8965, found: 381.8968.

(Bromoimino)(methyl)(m-tolyl)- λ^6 -sulfanone (9j)

Following the general procedure afforded the product as a yellow oil (44 mg, 90% yield). **¹H NMR (600 MHz, CDCl₃)** δ 7.71 (s, 1H), 7.71 – 7.68 (m, 1H), 7.48 (dd, J = 4.6, 1.9 Hz, 2H), 3.28 (s, 3H), 2.46 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ ¹³C NMR (151 MHz, CDCl₃) δ 140.1, 137.7, 134.8, 129.5, 129.0, 125.8, 42.6, 21.3.

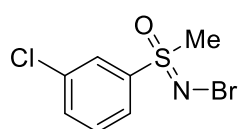
MS (EI): m/z (%) = 249 (17), 249 (15), 215 (21), 170 (33), 169 (37), 155 (23), 154 (65), 139 (41), 106 (84), 91 (100), 89 (25), 65 (69). **IR (ATR):** ν = 3037, 3010, 2926, 2322, 1601, 1477, 1407, 1321, 1216, 1145, 1089, 990, 857, 790, 760, 696 cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_8\text{H}_{10}\text{BrNOS}+\text{Na}]^+$: 269.9959, found: 269.9960.

(Bromoiimino)(3-methoxyphenyl)(methyl)- λ^6 -sulfanone (9k)



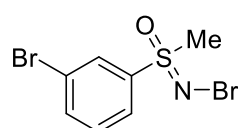
Following the general procedure afforded the product as a yellow solid (48 mg, 87% yield). **m.p.:** 62.2-63.3 °C. **^1H NMR (600 MHz, CDCl_3)** δ 7.51 – 7.44 (m, 2H), 7.38 (t, J = 2.1 Hz, 1H), 7.18 (ddd, J = 8.1, 2.6, 1.2 Hz, 1H), 3.87 (s, 3H), 3.28 (s, 3H). **^{13}C { ^1H }** (151 MHz, CDCl_3) δ 160.3, 139.0, 130.6, 120.7, 120.4, 113.1, 55.7, 42.6. **MS (EI):** m/z (%) = 265 (43), 264 (21), 263 (100), 186 (22), 185 (23), 171 (25), 170 (11), 108 (11), 77 (9). **IR (ATR):** ν = 3081, 3014, 2917, 2019, 1575, 1459, 1404, 1213, 1112, 1079, 1005, 980, 948, 878, 781, 745, 669 cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_8\text{H}_{10}\text{BrNO}_2\text{S}+\text{H}]^+$: 263.9668, found: 263.9670

(Bromoiimino)(3-chlorophenyl)(methyl)- λ^6 -sulfanone (9l)



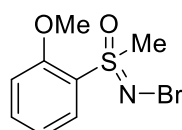
Following the general procedure afforded the product as a yellow viscous oil (44 mg, 82% yield). **m.p.:** 98.1-100.0 °C. **^1H NMR (600 MHz, CDCl_3)** δ 7.83 (t, J = 1.9 Hz, 1H), 7.72 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.59 (ddd, J = 8.0, 2.1, 1.0 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 3.25 (s, 3H). **^{13}C { ^1H }** (151 MHz, CDCl_3) δ 139.8, 135.9, 134.1, 130.9, 128.8, 126.8, 42.6. **MS (EI):** m/z (%) = 271 (30), 270 (16), 269 (100), 267 (77), 206 (17), 204 (13), 174 (29), 159 (24), 111 (18), 75 (15). **IR (ATR):** ν = 3017, 2915, 1568, 1458, 1403, 1216, 1104, 1007, 840, 774, 728, 668 cm^{-1} . **HRMS (ESI):** m/z $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_7\text{H}_7\text{BrClNOS}+\text{Na}]^+$: 289.9012, found: 289.9015.

(Bromoiimino)(3-bromophenyl)(methyl)- λ^6 -sulfanone (9m)



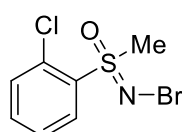
Following the general procedure afforded the product as a yellow solid (50 mg, 81% yield). **m.p.:** 86.6-87.5 °C. **^1H NMR (600 MHz, CDCl_3)** δ 8.03 (t, J = 1.9 Hz, 1H), 7.81 (dddd, J = 11.2, 8.0, 1.9, 1.0 Hz, 2H), 7.49 (t, J = 7.9 Hz, 1H), 3.30 (s, 3H). **^{13}C { ^1H }** (151 MHz, CDCl_3) δ 139.9, 137.0, 131.6, 131.1, 127.3, 123.6, 42.6. The spectroscopic data are in accordance with the previously reported data.^[S5]

(Bromoiimino)(2-methoxyphenyl)(methyl)- λ^6 -sulfanone (9n)



Following the general procedure afforded the product as a yellow solid (40 mg, 76% yield). **m.p.:** 71.5-72.6 °C. **^1H NMR (600 MHz, CDCl_3)** δ 7.98 (dd, J = 7.9, 1.7 Hz, 1H), 7.62 (ddd, J = 8.6, 7.4, 1.7 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.07 (d, J = 8.3 Hz, 1H), 3.97 (s, 3H), 3.45 (s, 3H). **^{13}C { ^1H }** (151 MHz, CDCl_3) δ 156.8, 135.9, 131.9, 124.9, 120.8, 112.7, 56.5, 40.6. The spectroscopic data are in accordance with the previously reported data.^[S5]

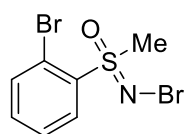
(Bromoiimino)(2-chlorophenyl)(methyl)- λ^6 -sulfanone (9o)



Following the general procedure afforded the product as a yellow solid (42 mg, 78% yield). **m.p.:** 121.6-123.4 °C. **^1H NMR (600 MHz, CDCl_3)** δ 8.17 (dd, J = 7.9, 1.6 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.52 (ddd, J = 7.9, 7.1, 1.6 Hz, 1H), 3.49 (s, 3H). **^{13}C { ^1H }** (151 MHz, CDCl_3) δ 135.1, 135.0, 133.2, 132.4, 132.3, 127.6, 40.5. The spectroscopic

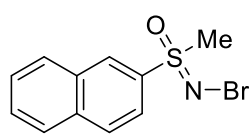
data are in accordance with the previously reported data.^[S5]

(Bromoiimino)(2-bromophenyl)(methyl)- λ^6 -sulfanone (9p)



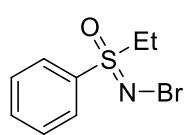
Following the general procedure afforded the product as a yellow solid (49 mg, 79% yield). **m.p.:** 107.5-109.1 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.21 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.79 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.56 (td, $J = 7.7, 1.3$ Hz, 1H), 7.49 (td, $J = 7.6, 1.7$ Hz, 1H), 3.50 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 136.8, 135.9, 134.9, 133.5, 128.2, 120.7, 40.3. The spectroscopic data are in accordance with the previously reported data.^[S5]

(Bromoiimino)(methyl)(naphthalen-2-yl)- λ^6 -sulfanone (9r)



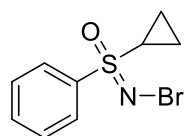
Following the general procedure afforded the product as a yellow solid (53 mg, 94% yield). **m.p.:** 149.3-152.9 °C. **¹H NMR (600 MHz, CDCl₃)** δ 8.46 (d, $J = 1.9$ Hz, 1H), 7.96 (dd, $J = 16.4, 8.4$ Hz, 2H), 7.89 – 7.86 (m, 1H), 7.74 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.62 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.58 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 3.30 (s, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 135.4, 134.7, 132.4, 131.2, 130.1, 129.5, 129.4, 128.0, 127.8, 122.8, 42.6. **MS (EI):** m/z (%) = 285 (7), 284 (20), 283 (100), 282 (95), 205 (17), 129 (45). **IR (ATR):** $\nu = 3065, 2109, 1567, 1472, 1444, 1223, 1086, 963, 759, 722, 684$ cm⁻¹. **HRMS (ESI) m/z :** [M+Na]⁺ calcd for [C₁₂H₁₀BrNOS+Na]⁺: 317.9559, found: 317.9561.

(Bromoiimino)(ethyl)(phenyl)- λ^6 -sulfanone (9s)



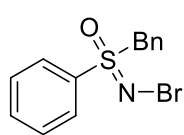
Following the general procedure afforded the product as a yellow solid (42 mg, 85% yield). **m.p.:** 61.3-63.1 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.82 – 7.79 (m, 2H), 7.64 – 7.60 (m, 1H), 7.55 (dd, $J = 8.3, 7.2$ Hz, 2H), 3.40 (dq, $J = 14.9, 7.5$ Hz, 1H), 3.31 (dq, $J = 14.7, 7.4$ Hz, 1H), 1.23 (t, $J = 7.5$ Hz, 3H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 136.1, 133.9, 129.6, 129.5, 49.4, 8.1. **MS (EI):** m/z (%) = 250 (45), 249 (100), 248 (26), 247 (99), 215 (15), 170 (15), 140 (32), 126 (31), 125 (41), 97 (17), 78 (25), 77 (54), 51 (62). **IR (ATR):** $\nu = 2983, 2937, 1474, 1446, 1410, 1382, 1233, 1198, 1090, 1050, 967, 784, 761, 725, 683$ cm⁻¹. **HRMS (ESI):** m/z [M+Na]⁺ calcd for [C₈H₁₀BrNOS+Na]⁺: 269.9559, found: 269.9561.

(Bromoiimino)(cyclopropyl)(phenyl)- λ^6 -sulfanone (9t)



Following the general procedure afforded the product as a yellow solid (41 mg, 80% yield). **m.p.:** 93.9-95.0 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.86 (dd, $J = 7.8, 1.6$ Hz, 2H), 7.68 – 7.64 (m, 1H), 7.59 (t, $J = 7.7$ Hz, 2H), 2.76 (tt, $J = 7.9, 4.7$ Hz, 1H), 1.65 – 1.58 (m, 1H), 1.24 (dtd, $J = 9.1, 7.7, 5.7$ Hz, 1H), 1.08 (ddt, $J = 10.4, 7.3, 5.2$ Hz, 1H), 0.95 (dtd, $J = 9.1, 7.7, 5.5$ Hz, 1H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 138.2, 133.6, 129.5, 128.7, 77.2, 77.0, 76.8, 31.3, 6.4, 6.0. The spectroscopic data are in accordance with the previously reported data.^[S5]

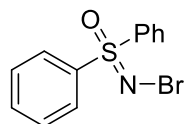
Benzyl(bromoiimino)(phenyl)- λ^6 -sulfanone (9u)



Following the general procedure afforded the product as a yellow solid (46 mg, 75% yield). **m.p.:** 92.9-93.4 °C. **¹H NMR (600 MHz, CDCl₃)** δ 7.61 (tt, $J = 7.3, 1.3$ Hz, 1H), 7.58 – 7.56 (m, 2H), 7.47 – 7.43 (m, 2H), 7.32 – 7.29 (m, 1H), 7.22 (t, $J = 7.7$ Hz, 2H), 7.04 – 7.01 (m, 2H), 4.67 – 4.59 (m, 2H). **¹³C {¹H} (151 MHz, CDCl₃)** δ 135.1, 133.9, 131.1, 129.8, 129.1, 129.1, 128.6, 127.6, 61.2. **MS (EI):** m/z (%) = 311 (10), 310 (87), 309 (100), 308 (54),

232 (15), 231 (25), 141 (16), 78 (15), 77 (23), 51 (32). **IR (ATR):** $\nu = 3063, 2931, 1680, 1527, 1443, 1415, 1299, 1223, 1146, 1089, 1056, 1016, 996, 925, 792, 726, 686 \text{ cm}^{-1}$. **HRMS (ESI) m/z :** $[M+Na]^+$ calcd for $[C_{13}H_{12}BrNOS+Na]^+$: 331.9715, found: 331.9720.

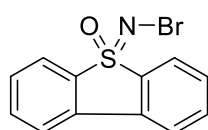
(Bromoimino)diphenyl- λ^6 -sulfanone (9w)



data.^[S5]

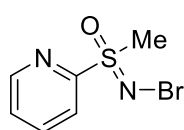
Following the general procedure afforded the product as a yellow solid (56 mg, 95% yield). **m.p.:** 114.8-115.9 °C. **1H NMR (600 MHz, $CDCl_3$)** δ 7.93 – 7.89 (m, 4H), 7.54 – 7.50 (m, 2H), 7.46 (dd, $J = 8.5, 7.1 \text{ Hz}$, 4H). **^{13}C { 1H }** (151 MHz, $CDCl_3$) δ 138.3, 133.5, 129.5, 128.6. The spectroscopic data are in accordance with the previously reported

5-(Bromoimino)-5H-5 λ^4 -dibenzo[*b,d*]thiophene 5-oxide (9x)



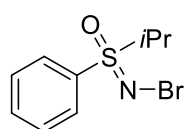
Following the general procedure afforded the product as a yellow solid (55 mg, 94% yield). **m.p.:** 156.7-158.3 °C. **1H NMR (600 MHz, $CDCl_3$)** δ 7.96 (dt, $J = 7.7, 0.8 \text{ Hz}$, 1H), 7.80 (dd, $J = 7.8, 1.0 \text{ Hz}$, 1H), 7.65 (td, $J = 7.6, 1.1 \text{ Hz}$, 1H), 7.53 (td, $J = 7.6, 1.1 \text{ Hz}$, 1H). **^{13}C { 1H }** (151 MHz, $CDCl_3$) δ 136.6, 134.1, 132.4, 130.1, 123.6, 121.9. **MS (EI):** m/z (%) = 295 (31), 294 (81), 293 (100), 215 (13), 184 (16), 172 (41), 171 (45), 167 (12), 166 (22), 139 (10), 51 (24). **IR (ATR):** $\nu = 2088, 1580, 1476, 1443, 1217, 1163, 1121, 1064, 950, 872, 751, 705 \text{ cm}^{-1}$. **HRMS (ESI):** m/z $[M+Na]^+$ calcd for $[C_{12}H_8BrNOS+Na]^+$: 315.9402, found: 315.9407.

(Bromoimino)(methyl)(pyridin-2-yl)- λ^6 -sulfanone (9y)



Following the general procedure afforded the product as a yellow solid (40 mg, 86% yield). **m.p.:** 75.7-76.2 °C. **1H NMR (600 MHz, $CDCl_3$)** δ 8.75 (ddd, $J = 4.7, 1.8, 0.9 \text{ Hz}$, 1H), 8.15 (dt, $J = 7.9, 1.0 \text{ Hz}$, 1H), 8.00 (td, $J = 7.8, 1.7 \text{ Hz}$, 1H), 7.57 (ddd, $J = 7.6, 4.7, 1.1 \text{ Hz}$, 1H), 3.46 (s, 3H). **^{13}C { 1H }** (151 MHz, $CDCl_3$) δ 155.9, 150.5, 138.0, 127.4, 124.0, 38.7. **MS (EI):** m/z (%) = 237 (43), 236 (100), 235 (44), 234 (95), 218 (9), 140 (15), 78 (40), 51 (34). **IR (ATR):** $\nu = 3025, 2918, 1772, 1577, 1449, 1423, 1398, 1214, 1124, 1082, 988, 820, 785, 753 \text{ cm}^{-1}$. **HRMS (ESI):** m/z $[M+H]^+$ calcd for $[C_6H_7BrN_2OS+H]^+$: 234.9535, found: 234.9536.

(Bromoimino)(isopropyl)(phenyl)- λ^6 -sulfanone (9z)

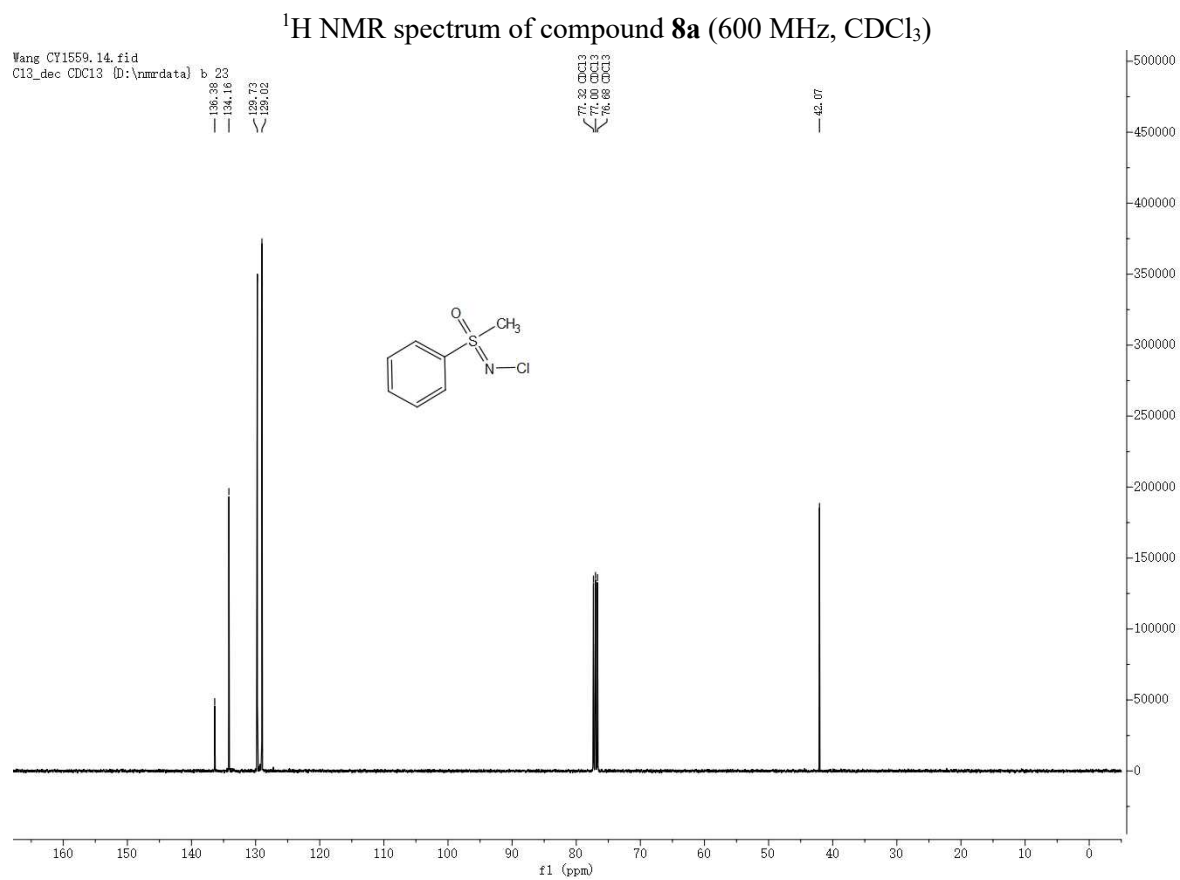
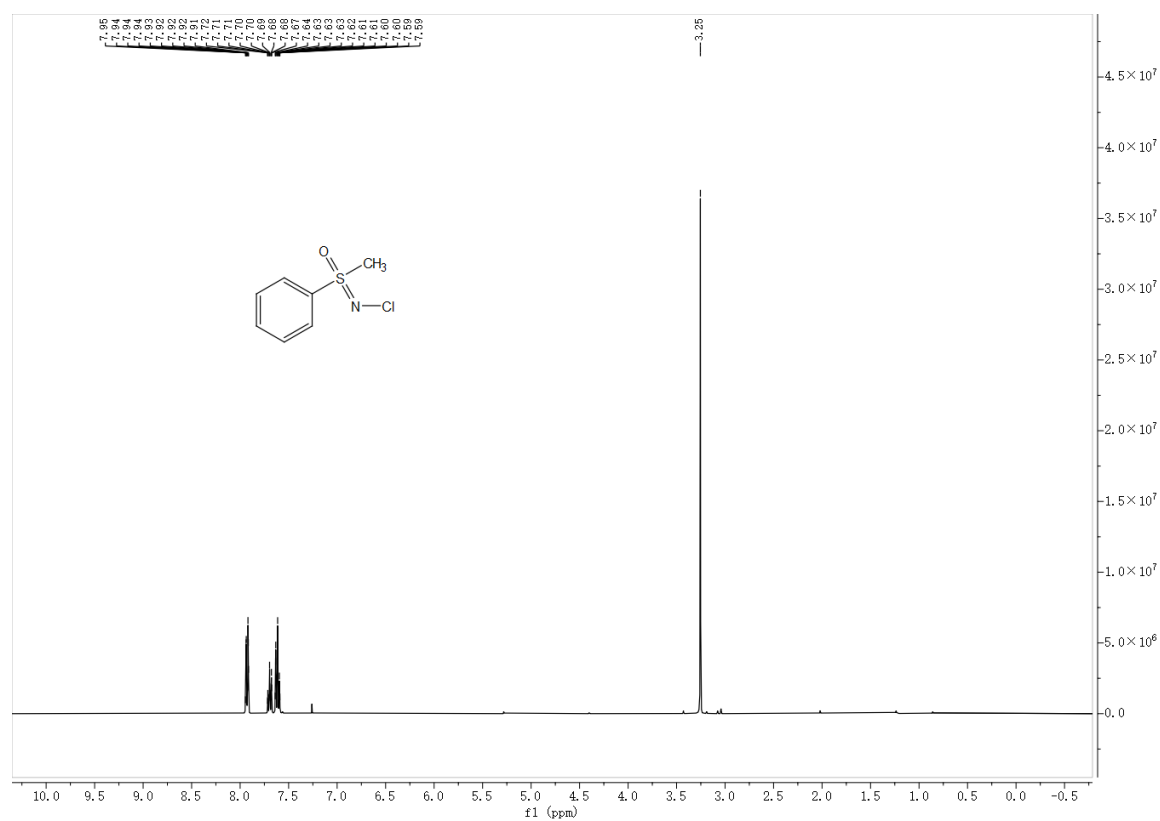


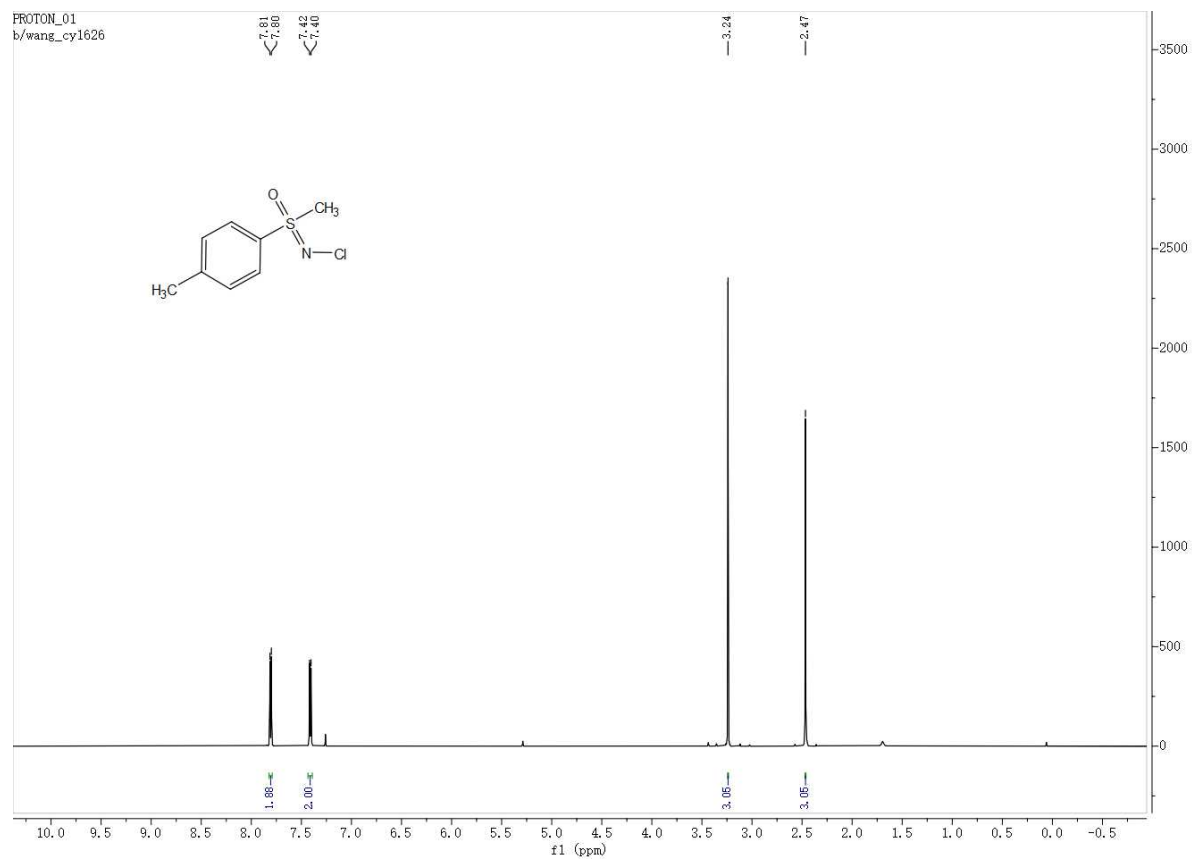
Following the general procedure afforded the product as a yellow oil (39 mg, 76% yield). **1H NMR (600 MHz, $CDCl_3$)** δ 7.85 – 7.82 (m, 2H), 7.70 – 7.66 (m, 1H), 7.60 (dd, $J = 8.4, 7.1 \text{ Hz}$, 2H), 3.60 (hept, $J = 6.9 \text{ Hz}$, 1H), 1.42 (d, $J = 6.9 \text{ Hz}$, 3H), 1.26 (d, $J = 6.9 \text{ Hz}$, 3H). **^{13}C { 1H }** (151 MHz, $CDCl_3$) δ 134.8, 133.8, 130.3, 129.4, 56.1, 17.3, 16.2. **MS (EI):** m/z (%) = 264 (77), 263 (100), 262 (78), 261 (92), 221 (34), 219 (34), 184 (39), 140 (19), 126 (22), 77 (79), 51 (26). **IR (ATR):** $\nu = 2982, 2934, 2089, 1446, 1384, 1259, 1206, 1089, 966, 875, 758, 718, 689, 659 \text{ cm}^{-1}$. **HRMS (ESI):** m/z $[M+Na]^+$ calcd for $[C_9H_{12}BrNOS+Na]^+$: 283.9715, found: 283.9720.

5. Reference

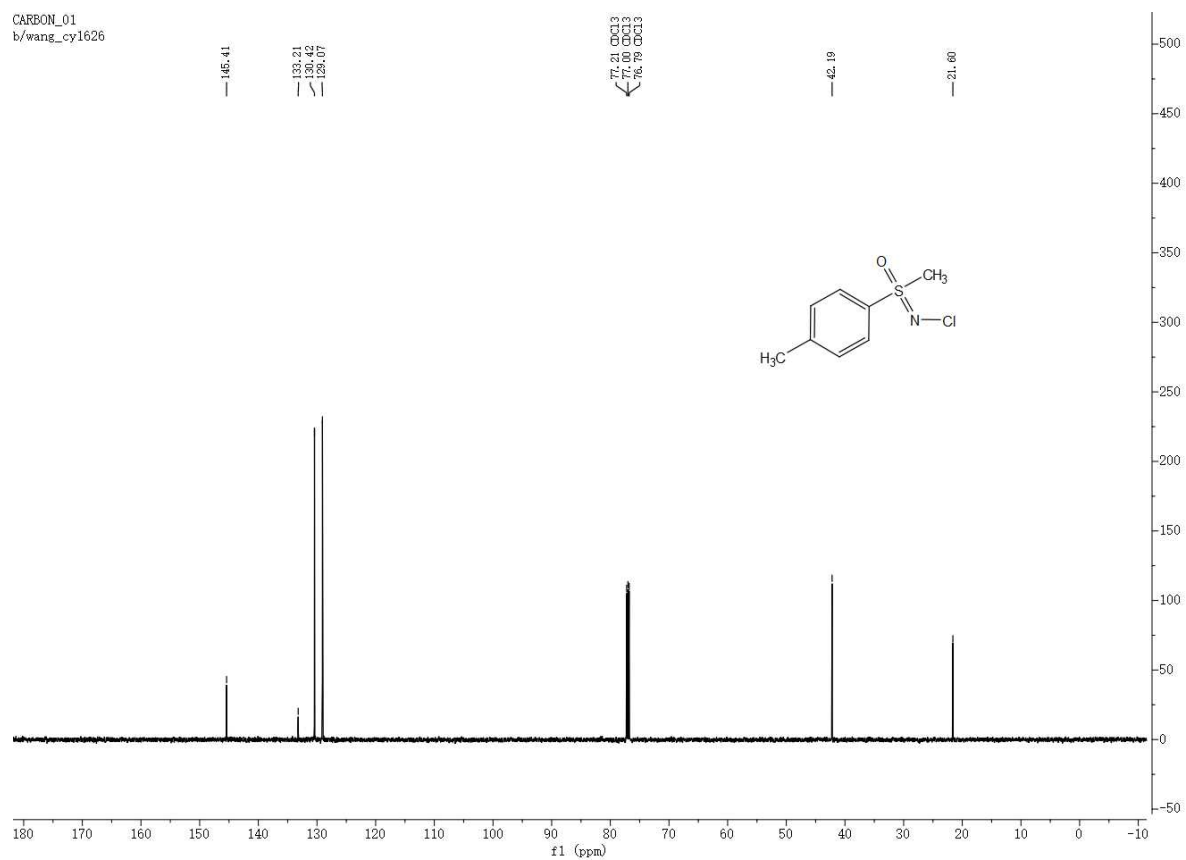
- [S1] a) A. Pandey and C. Bolm, Metal-Free Synthesis of *N*-Cyano-Substituted Sulfilimines and Sulfoximines, *Synthesis*, 2010, 29225–2925; b) A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi, Synthesis of NH-sulfoximines from sulfides by chemoselective one-pot N- and O-transfers, *Chem. Commun.*, 2017, **53**, 348–351.
- [S2] For preparation of sulfoximidoyl-containing hypervalent iodine(III) reagents, see: a) H. Wang, Y. Cheng, P. Becker, G. Raabe and C. Bolm, Synthesis of Sulfoximidoyl-Containing Hypervalent Iodine(III) Reagents and Their Use in Transition-Metal-Free Sulfoximinations of Alkynes, *Angew. Chem. Int. Ed.*, 2016, **55**, 12655–12658; b) H. Wang, D. Zhang, H. Sheng and C. Bolm, *J. Org. Chem.*, 2017, **82**, 11854–11858; c) H. Wang, D. Zhang and C. Bolm, Sulfoximinations of Benzylic C–H bonds by Photocatalysis, *Angew. Chem. Int. Ed.*, 2018, **57**, 5863–5866; for preparation of *p*-TolIF₂, see: d) B. Xing, C. Ni and J. Hu, Hypervalent Iodine(III)-Catalyzed Balz–Schiemann Fluorination under Mild Conditions, *Angew. Chem. Int. Ed.*, 2018, **57**, 9896–9900; e) Z. Zhao, A. J. and G. K. Murphy, Difluorinative ring expansions of benzo-fused carbocycles and heterocycles are achieved with *p*-(difluoroiodo)toluene, *Chem. Commun.*, 2019, **55**, 14821–14824; f) M. A. Arrica and T. Wirth, Fluorinations of α -Seleno Carboxylic Acid Derivatives with Hypervalent (Difluoroiodo)toluene, *Eur. J. Org. Chem.* **2005**, 395–403.
- [S3] C. Wang, Y. Tu, D. Ma and C. Bolm, Photocatalytic Fluoro Sulfoximinations of Styrenes, *Angew. Chem. Int. Ed.*, 2020, **59**, 14134–14137.
- [S4] D. L. Priebbenow and C. Bolm, C–H Activation of Methyl Arenes in the MnO₂-Mediated Aroylation of *N*-Chlorosulfoximines, *Org. Lett.*, 2014, **16**, 1650–1652.
- [S5] C. Bohnen and C. Bolm, *N*-Trifluoromethylthiolated Sulfoximines, *Org. Lett.*, 2015, **17**, 3011–3013.

6. NMR spectra

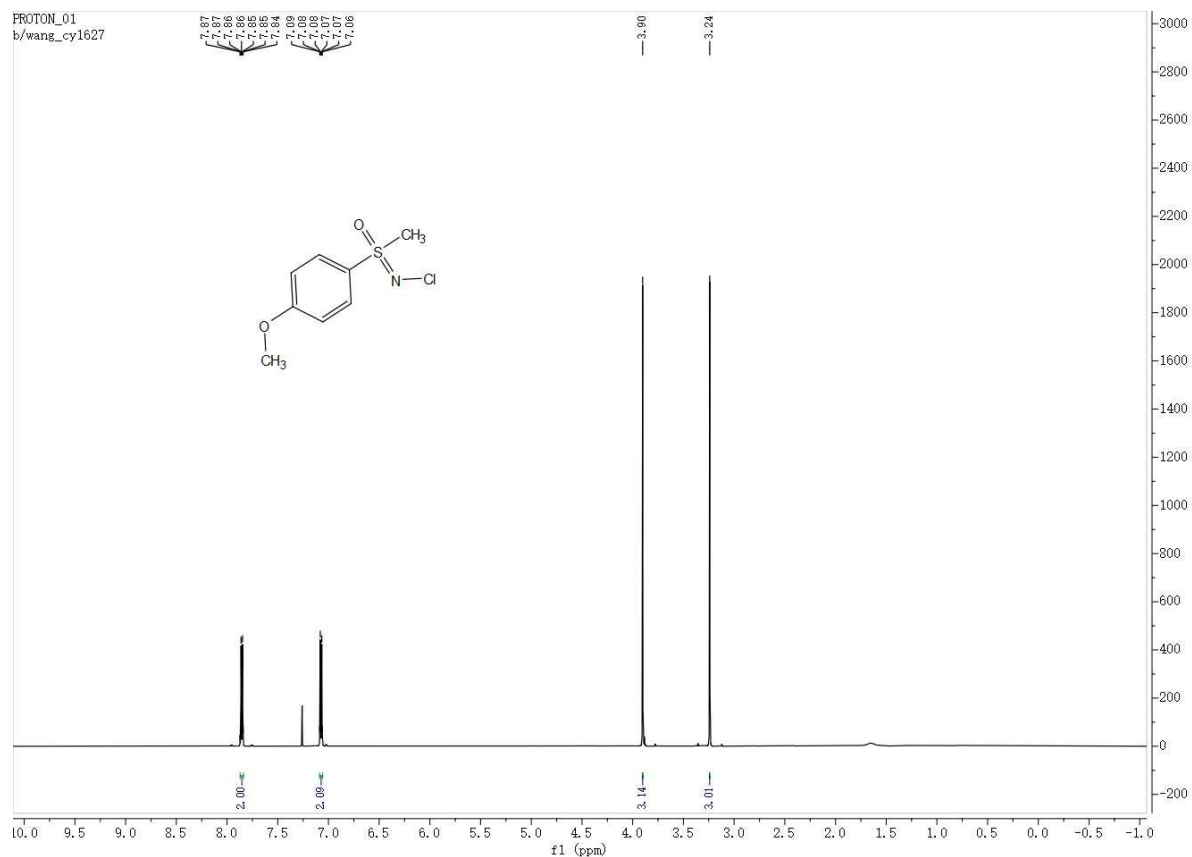




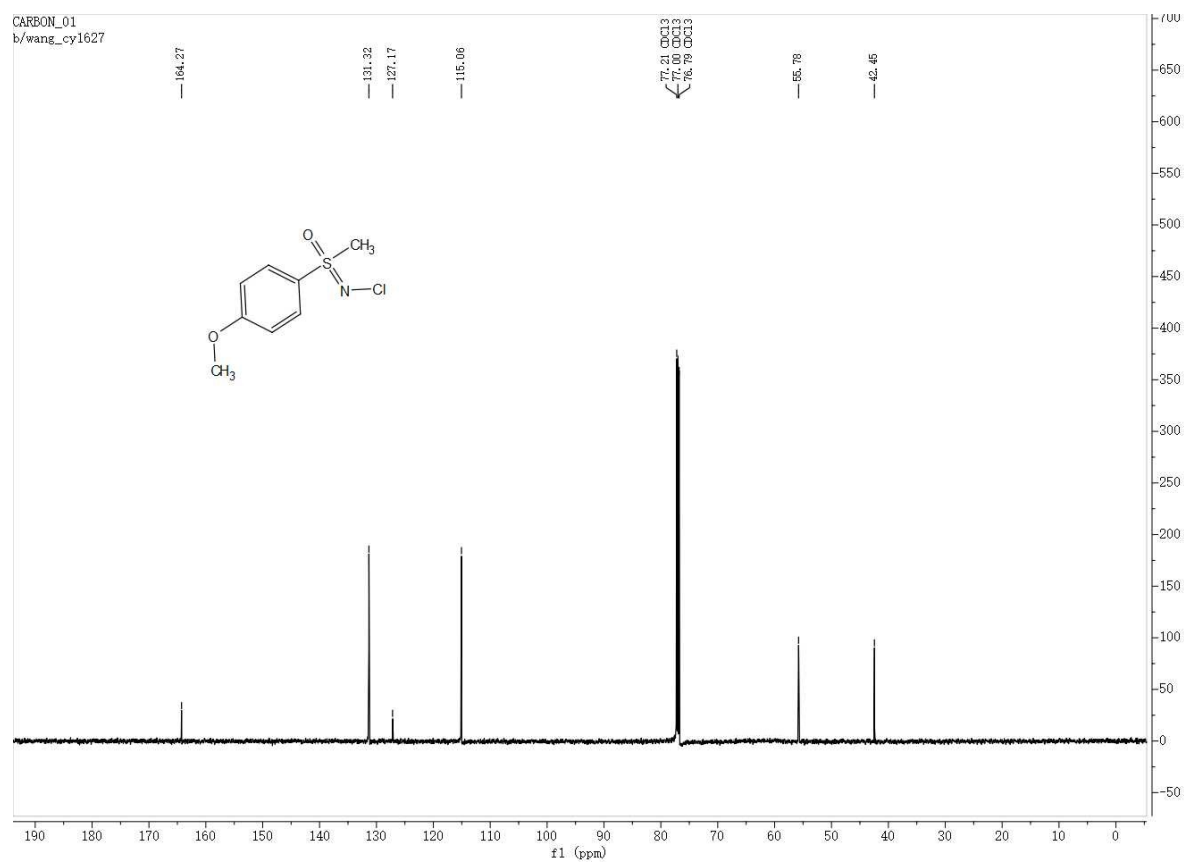
^1H NMR spectrum of compound **8b** (600 MHz, CDCl_3)



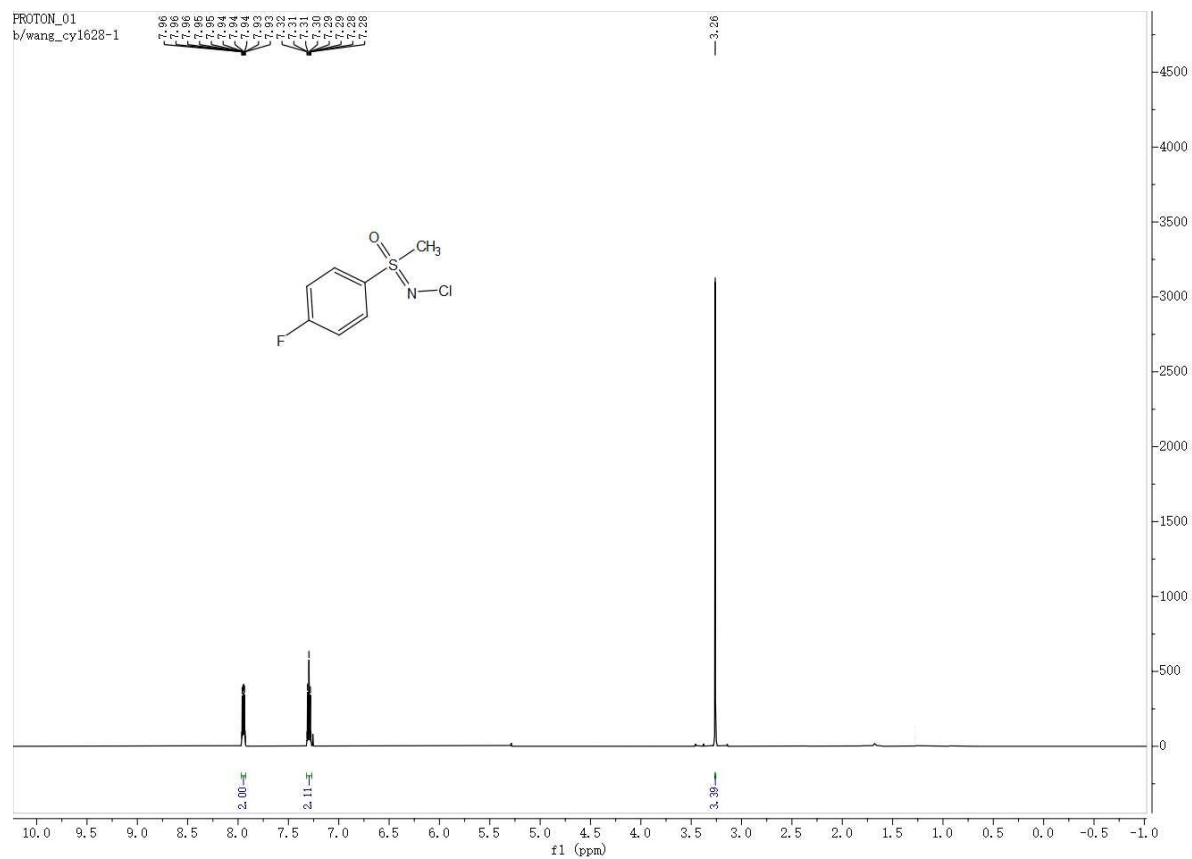
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8b** (151 MHz, CDCl_3)



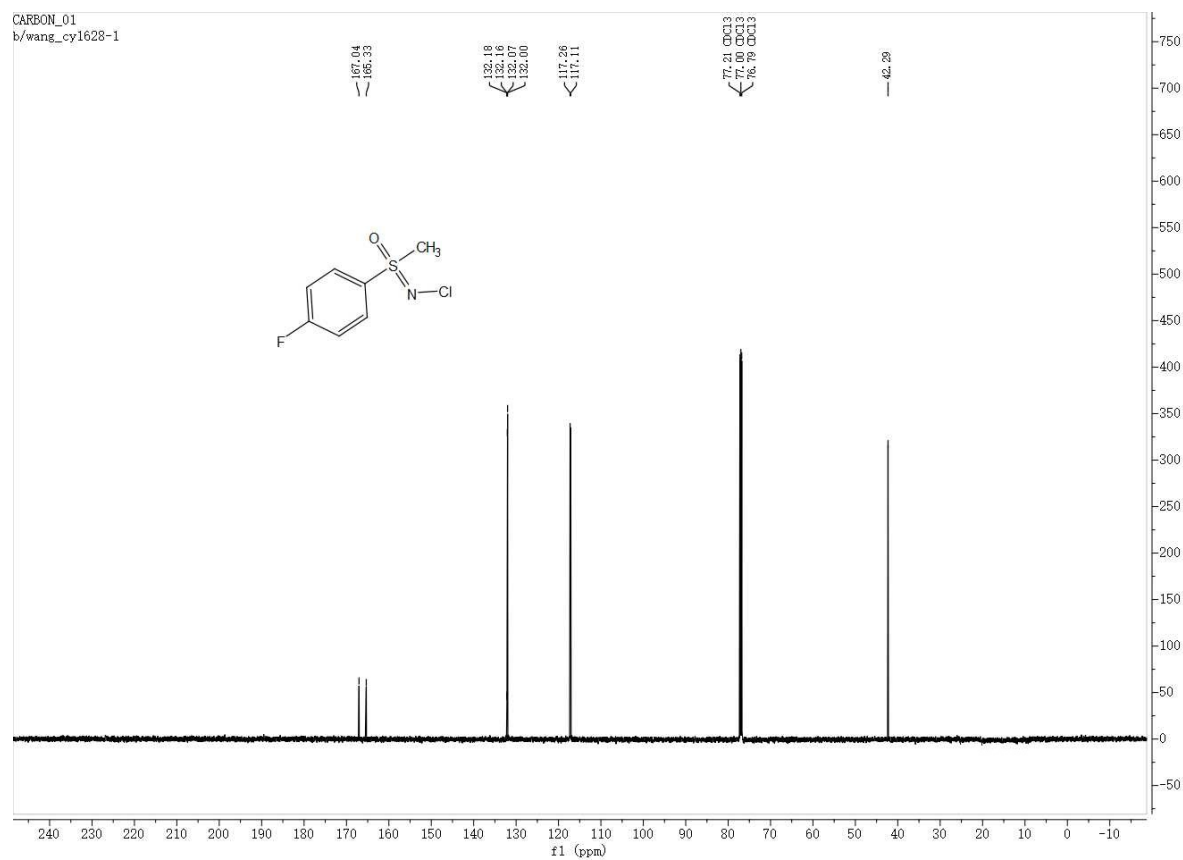
^1H NMR spectrum of compound **8c** (600 MHz, CDCl_3)



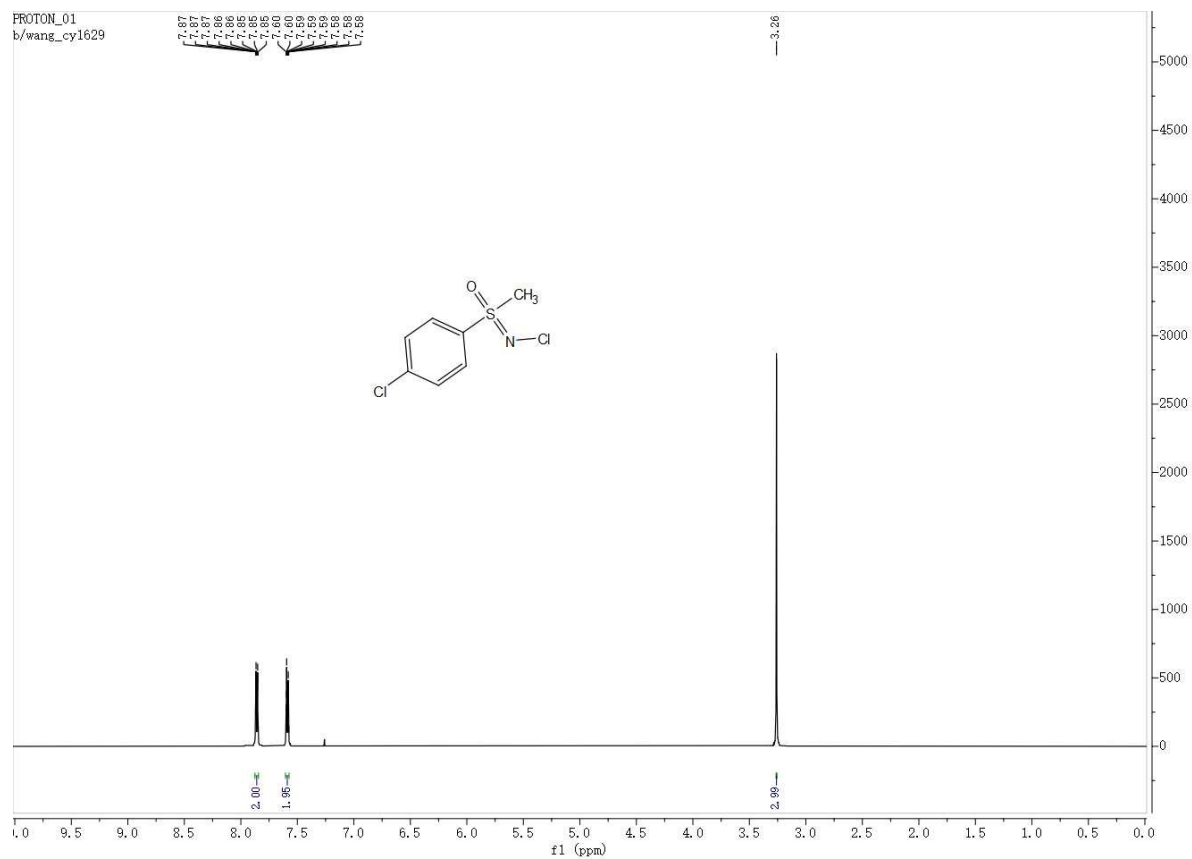
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8c** (151 MHz, CDCl_3)



^1H NMR spectrum of compound **8d** (600 MHz, CDCl_3)



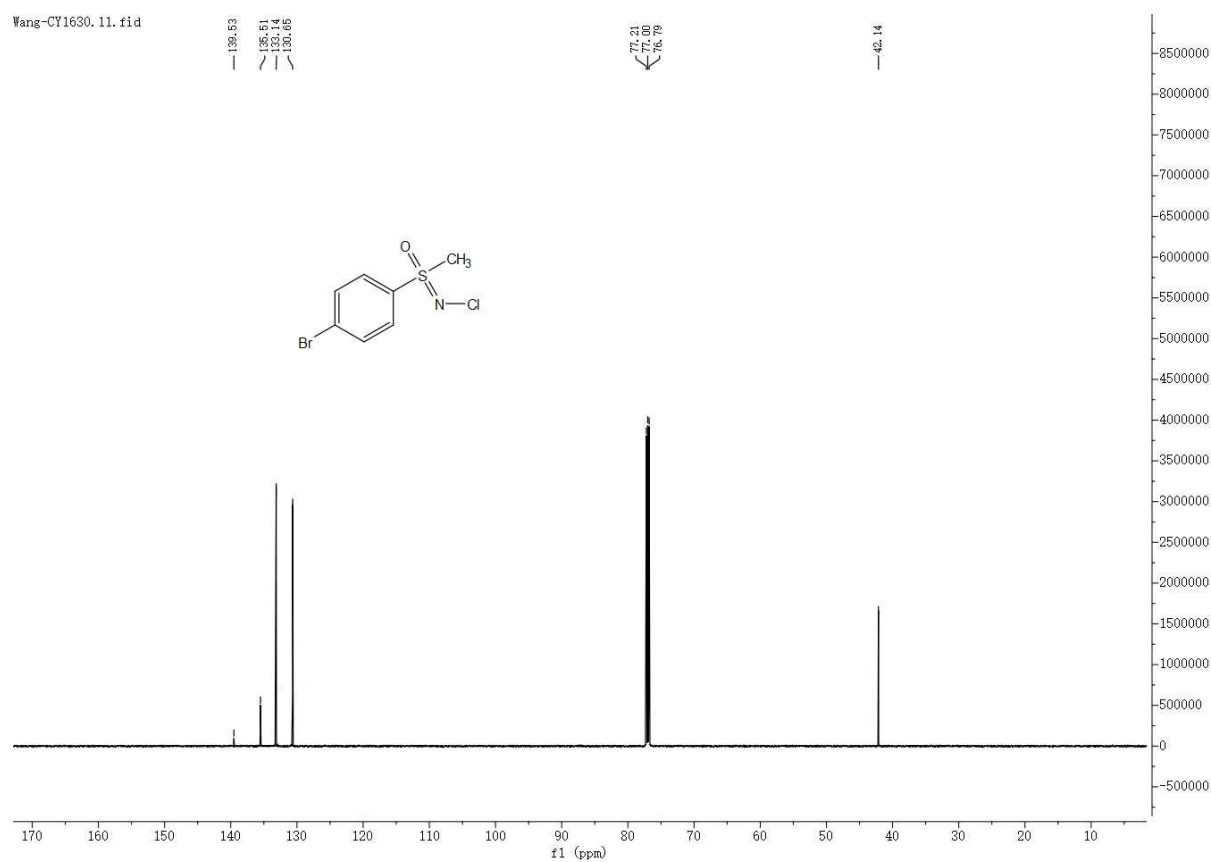
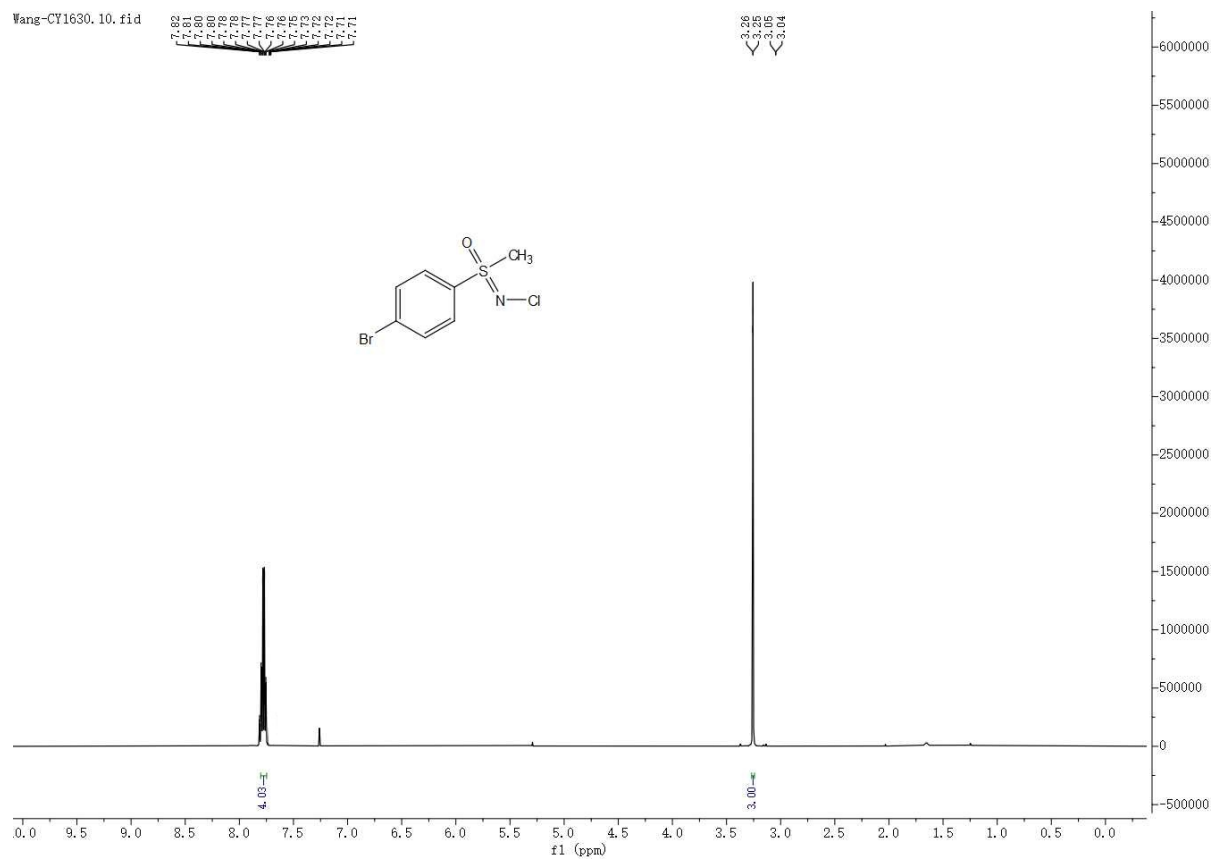
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8d** (151 MHz, CDCl_3)



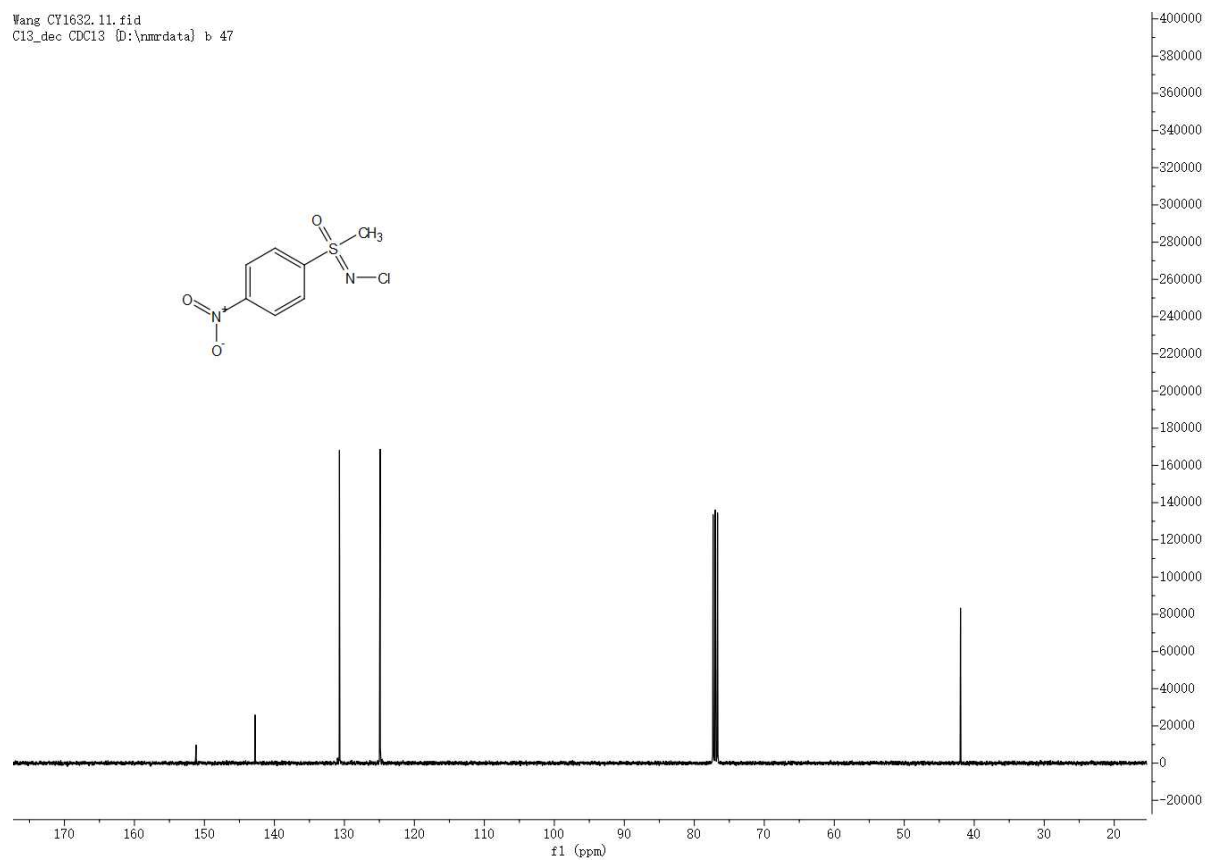
^1H NMR spectrum of compound **8e** (600 MHz, CDCl_3)

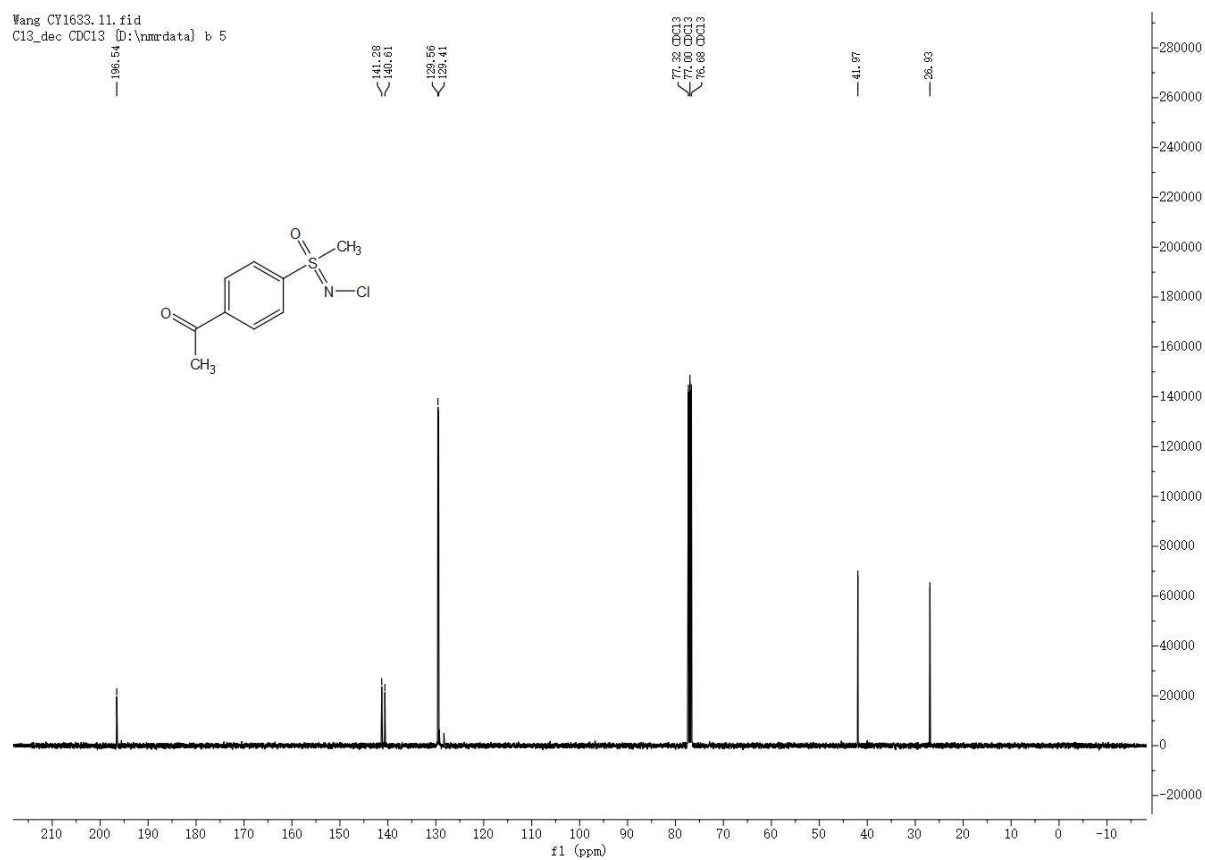


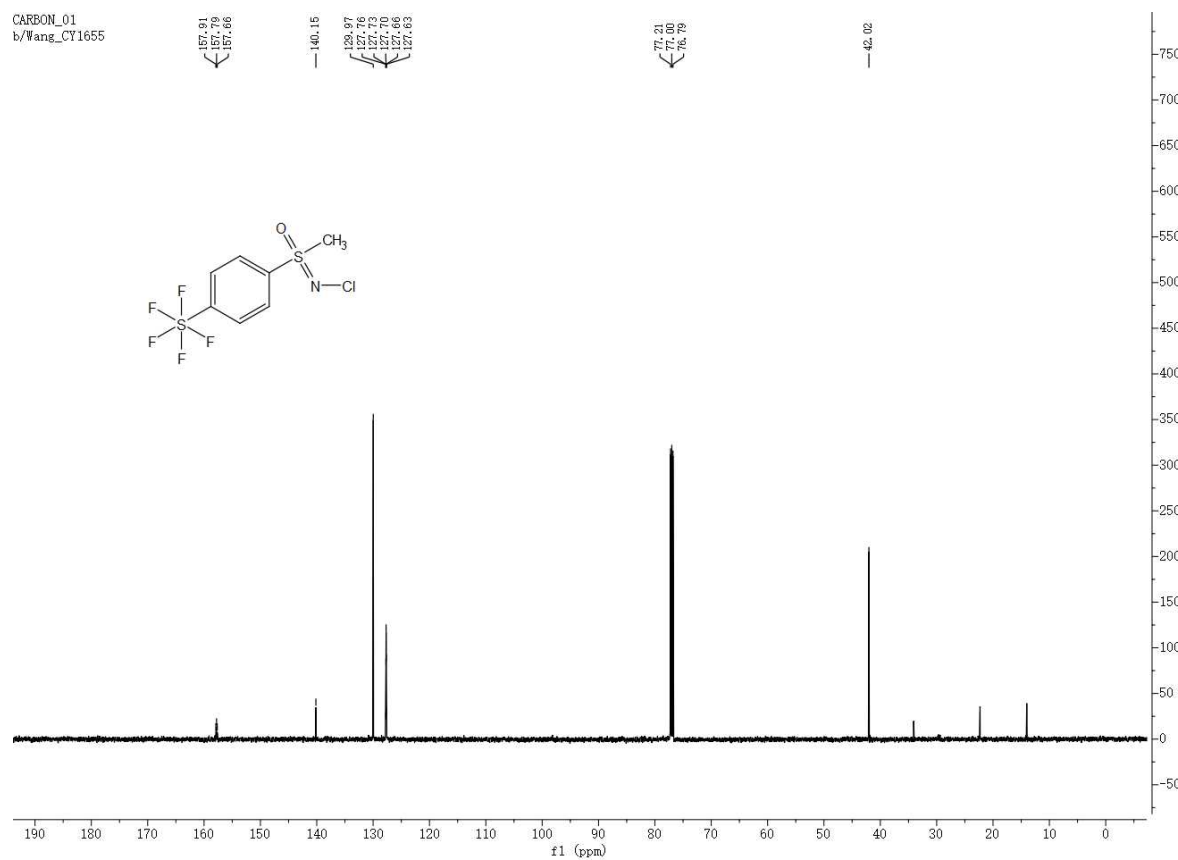
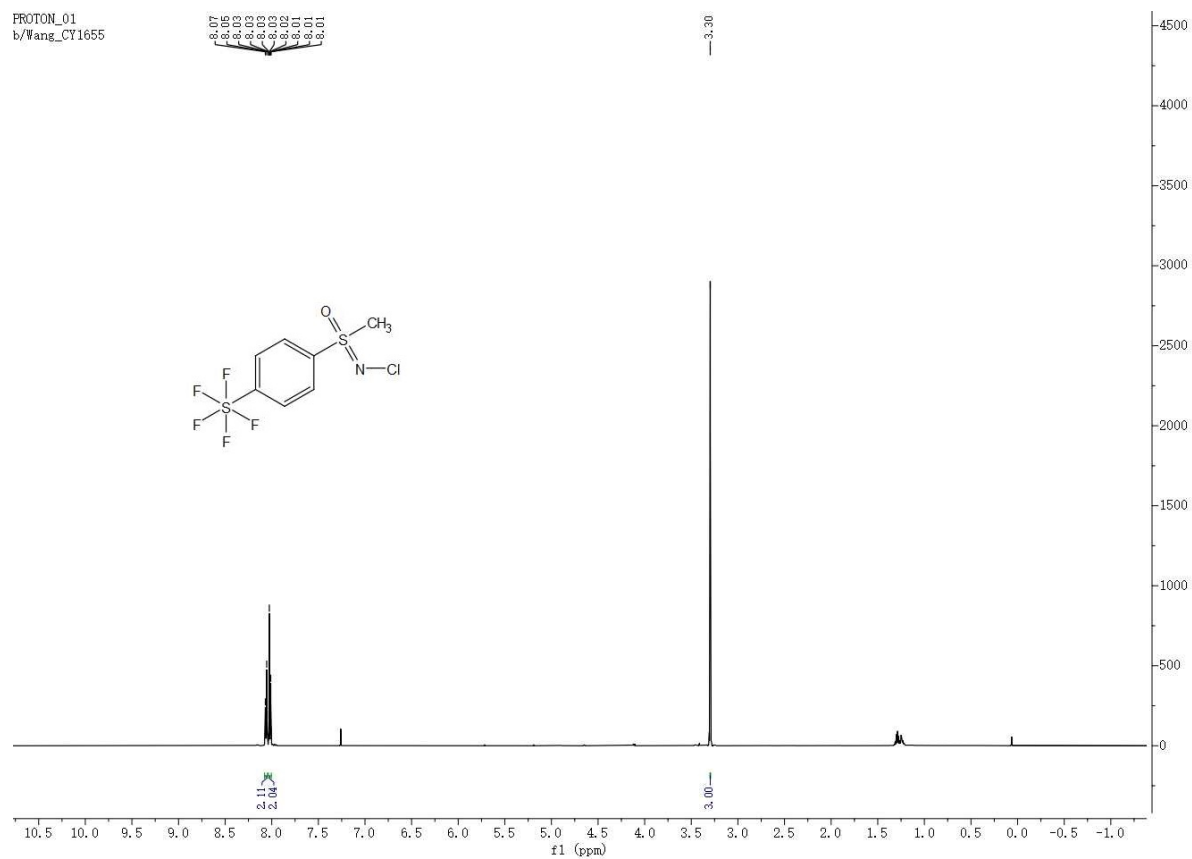
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8e** (151 MHz, CDCl_3)

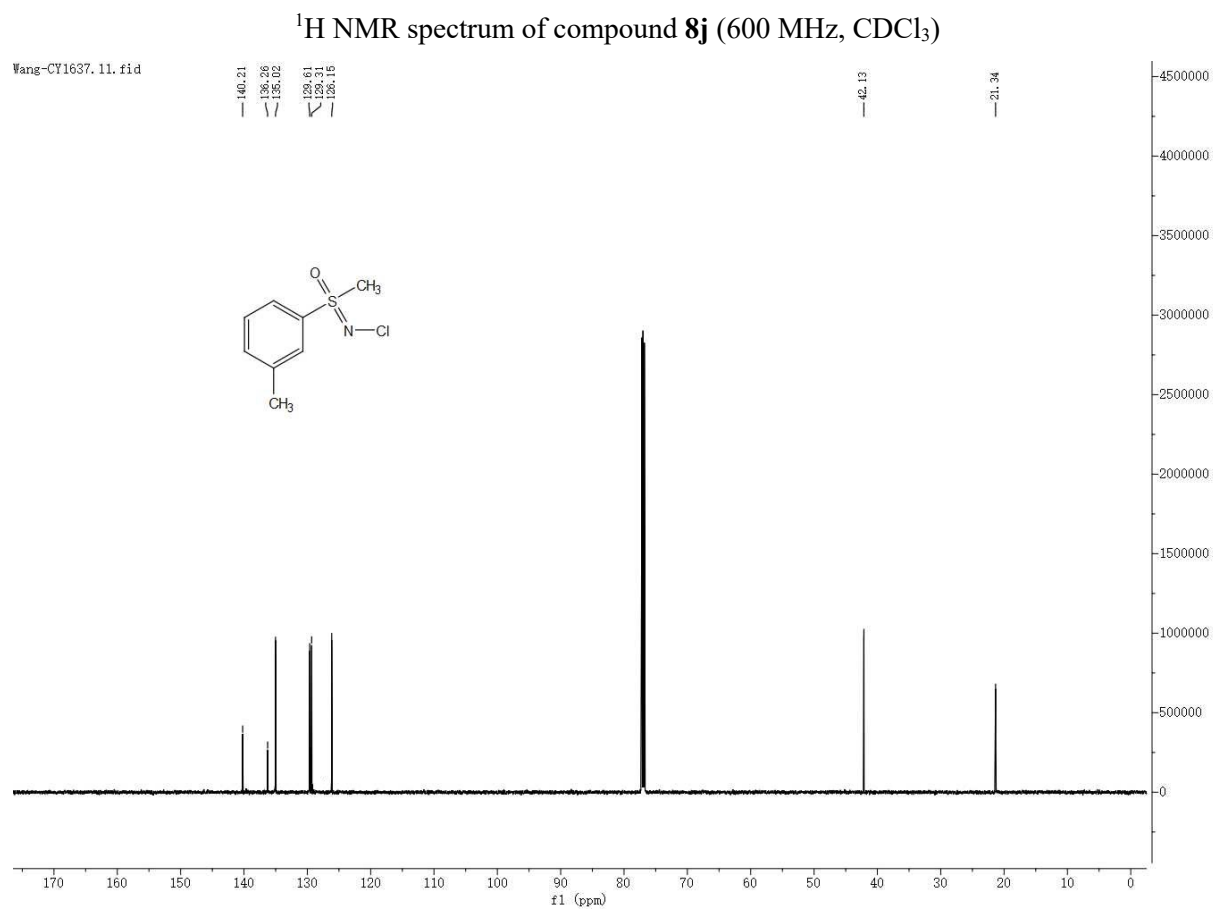
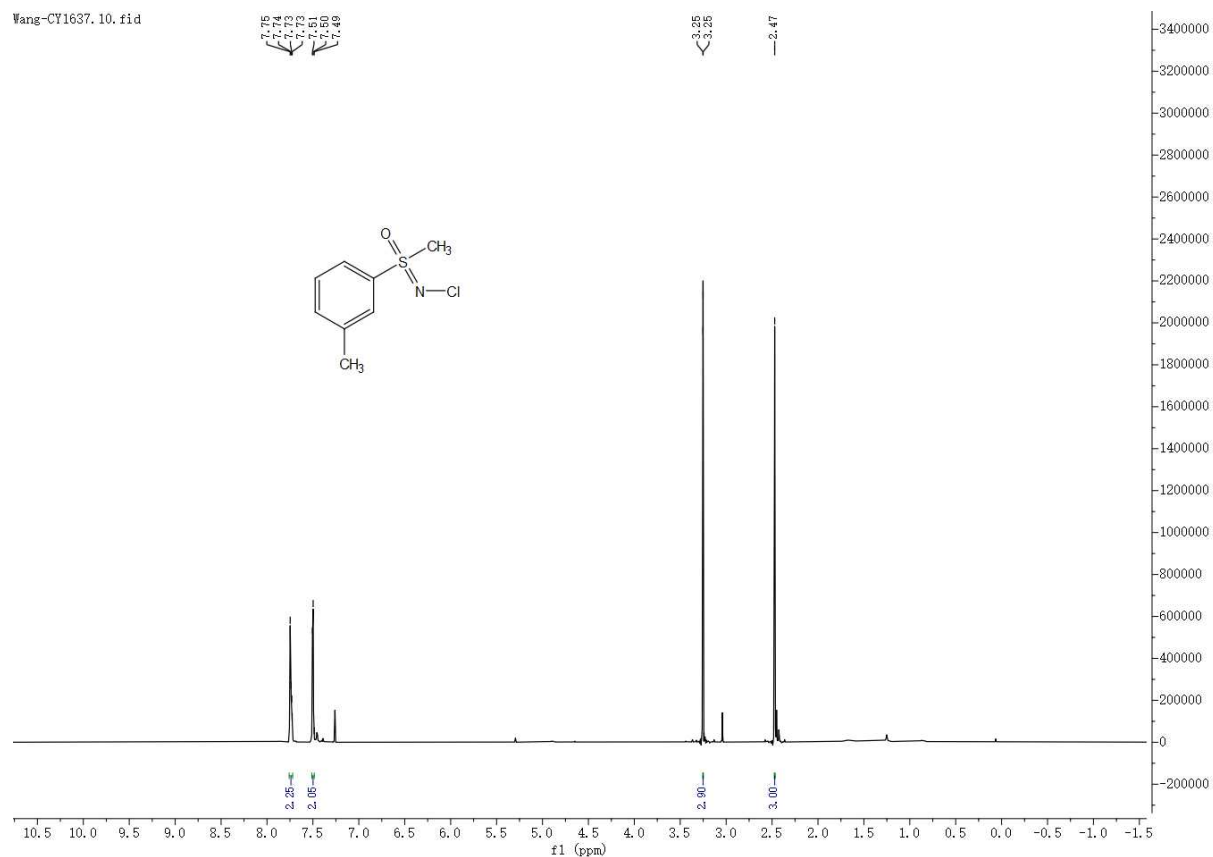


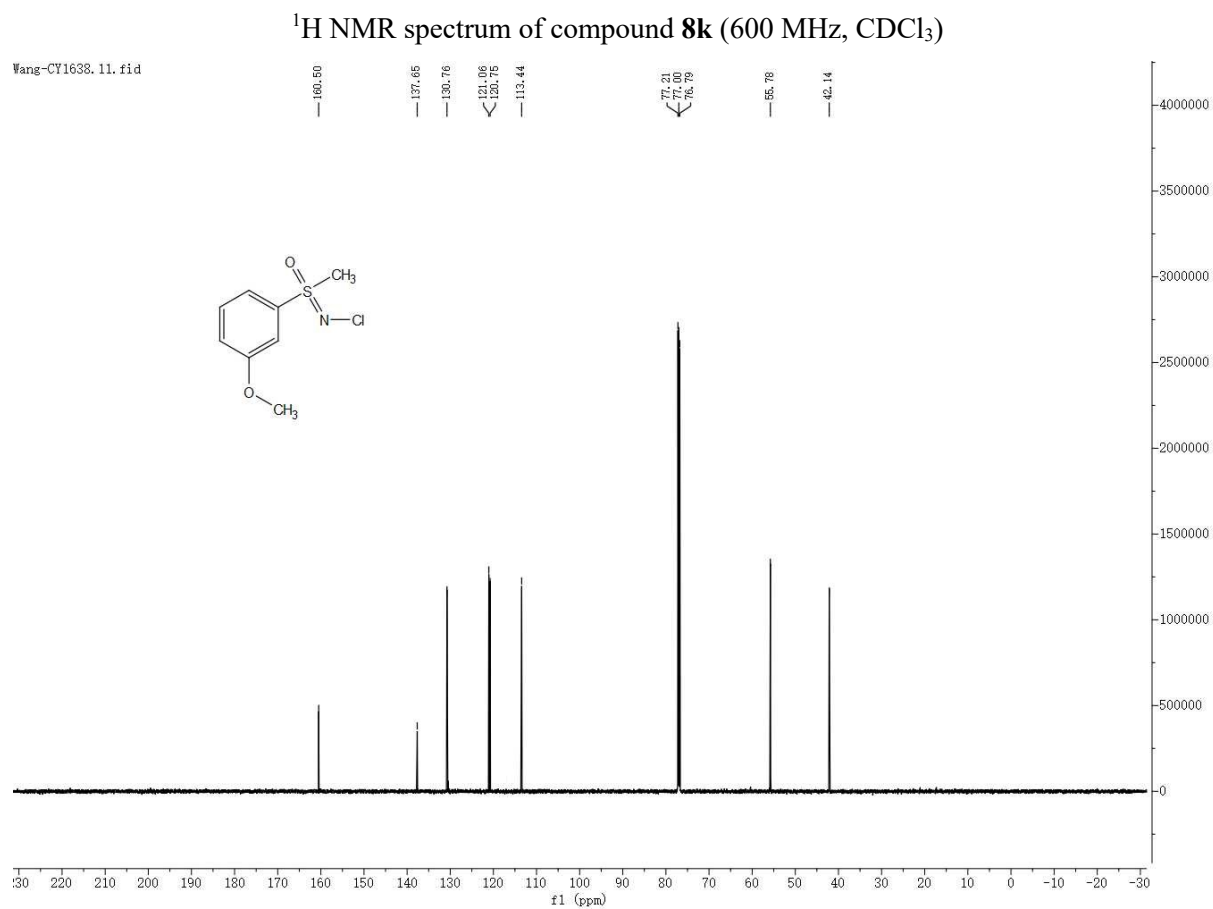
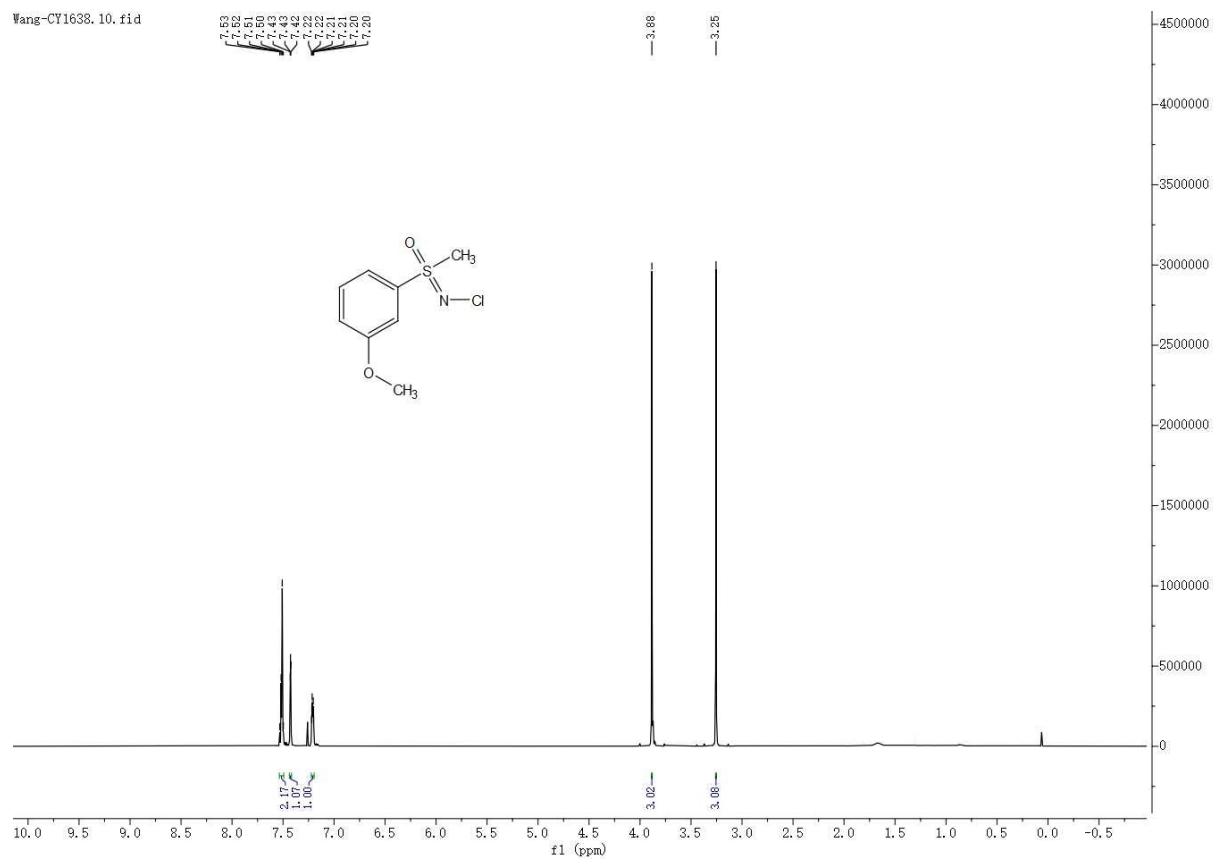
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8f** (151 MHz, CDCl_3)

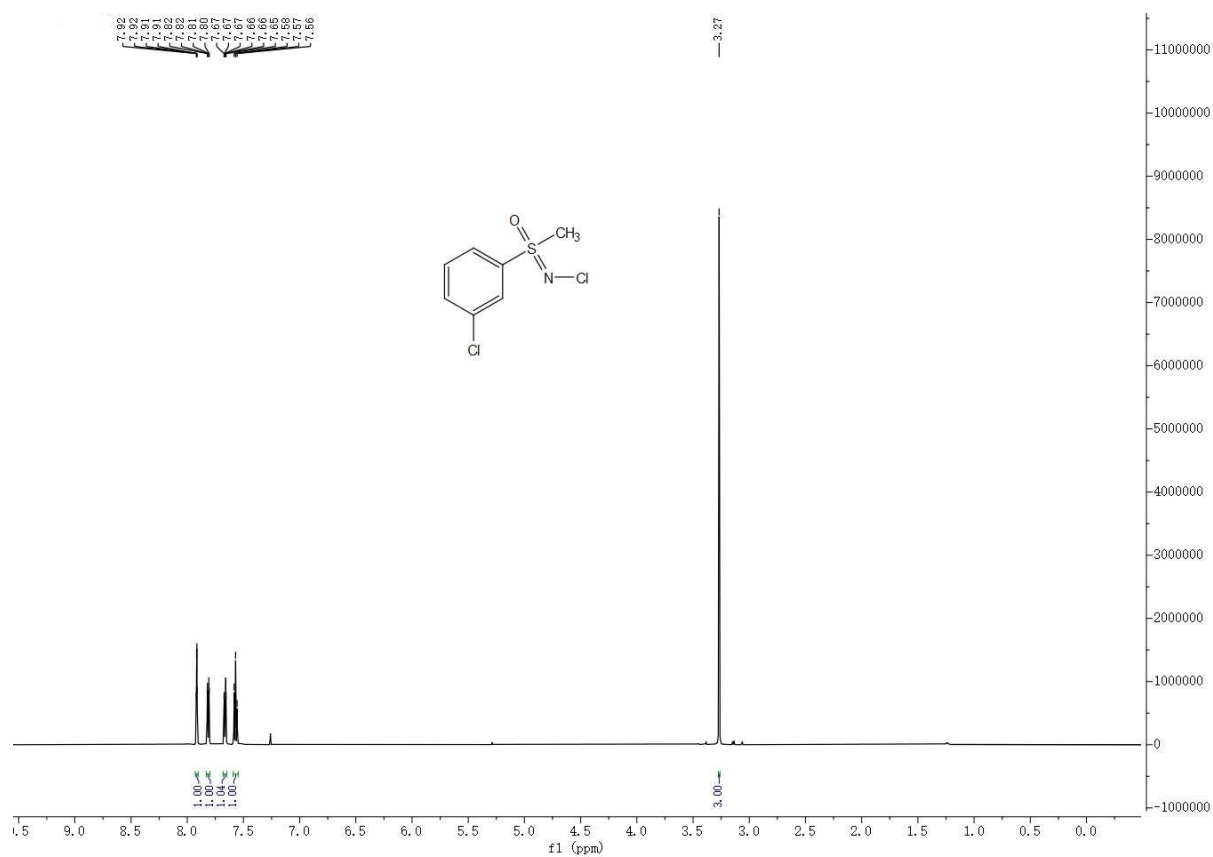
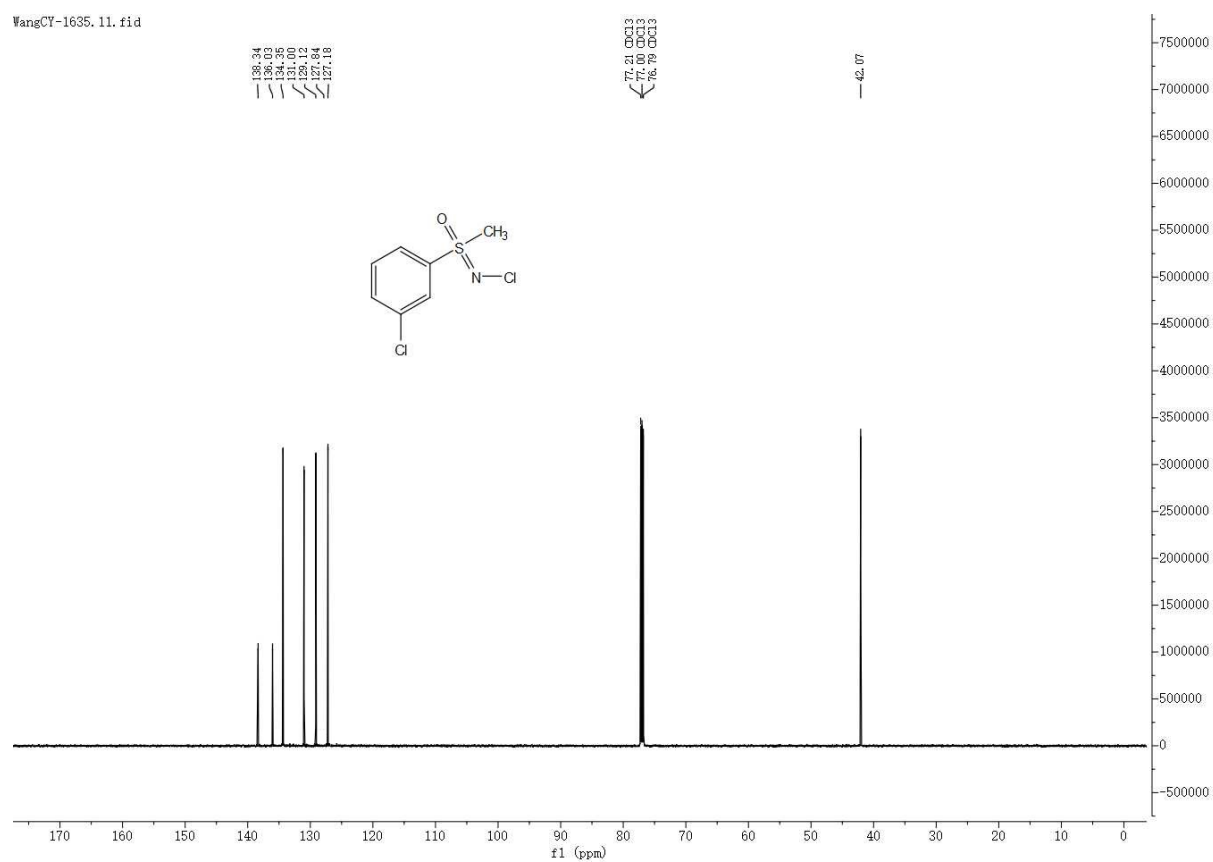


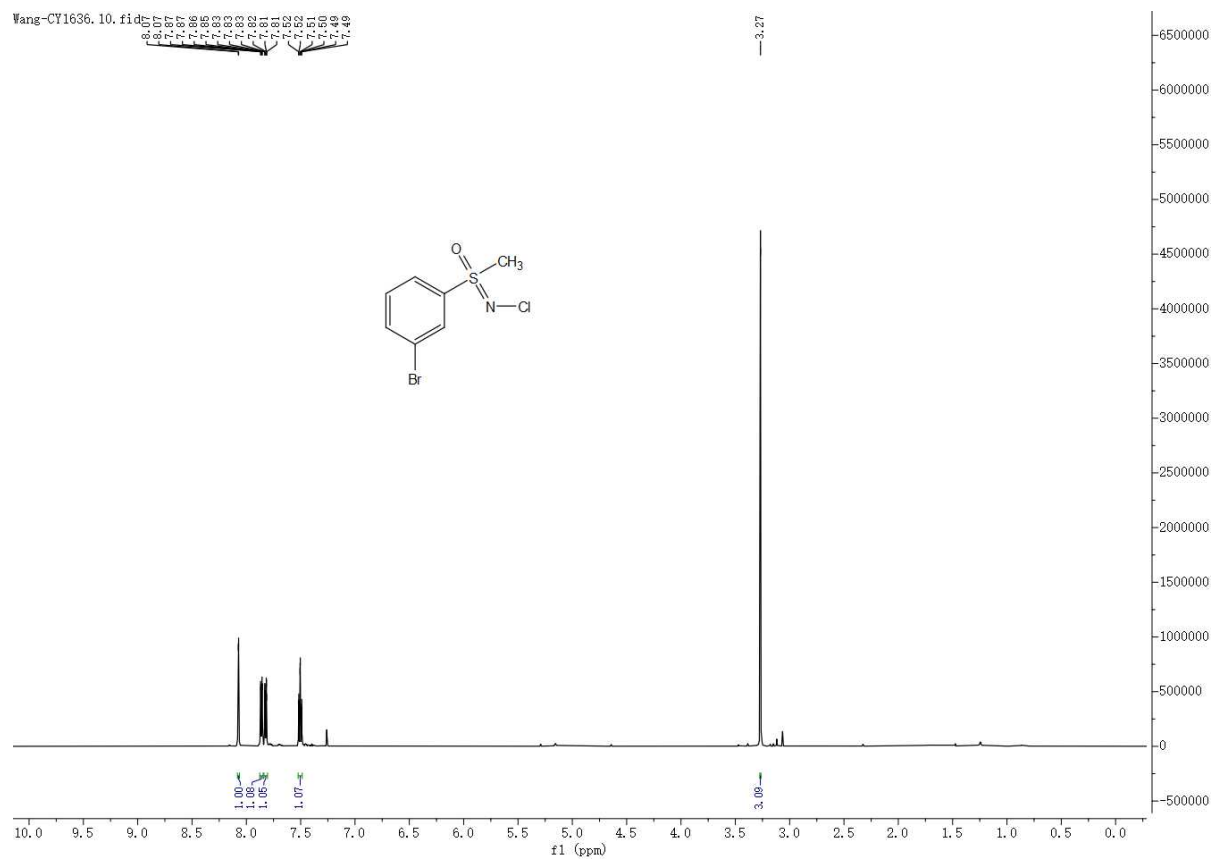




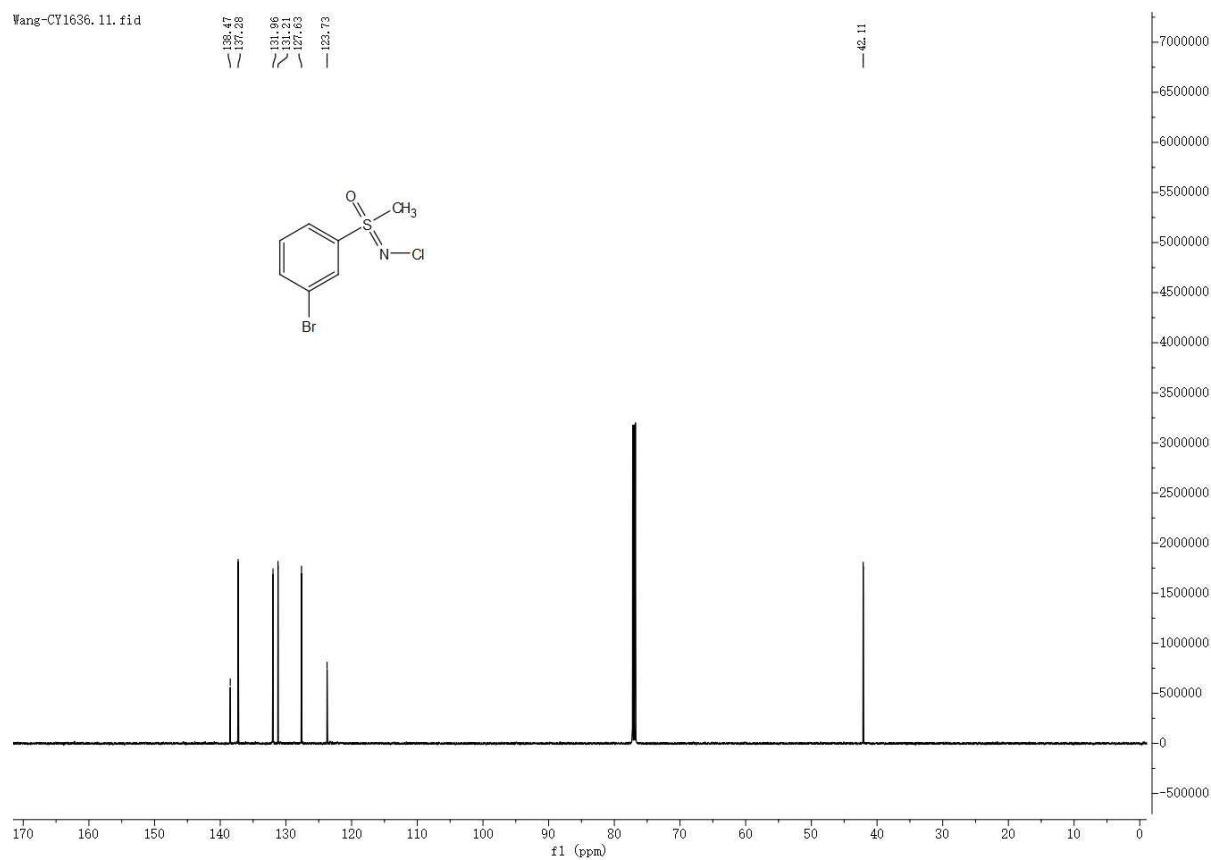




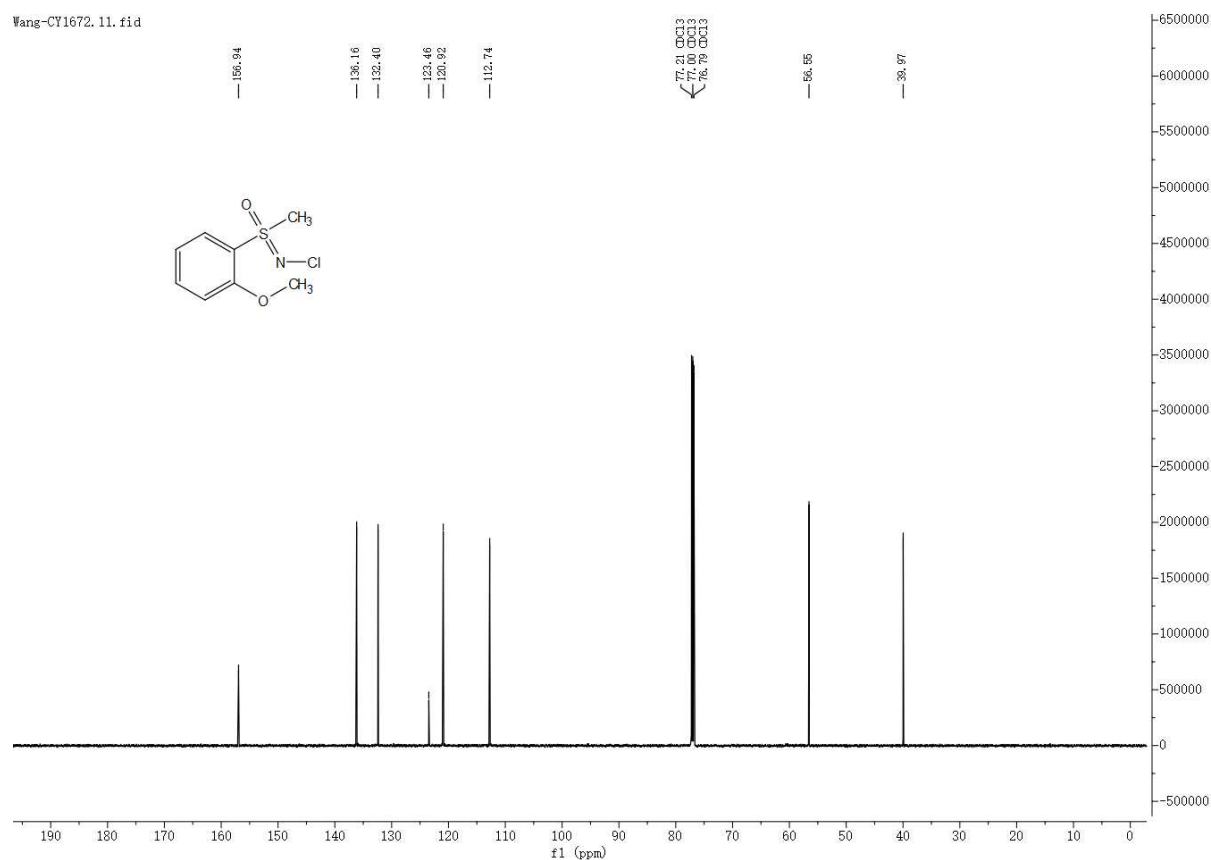
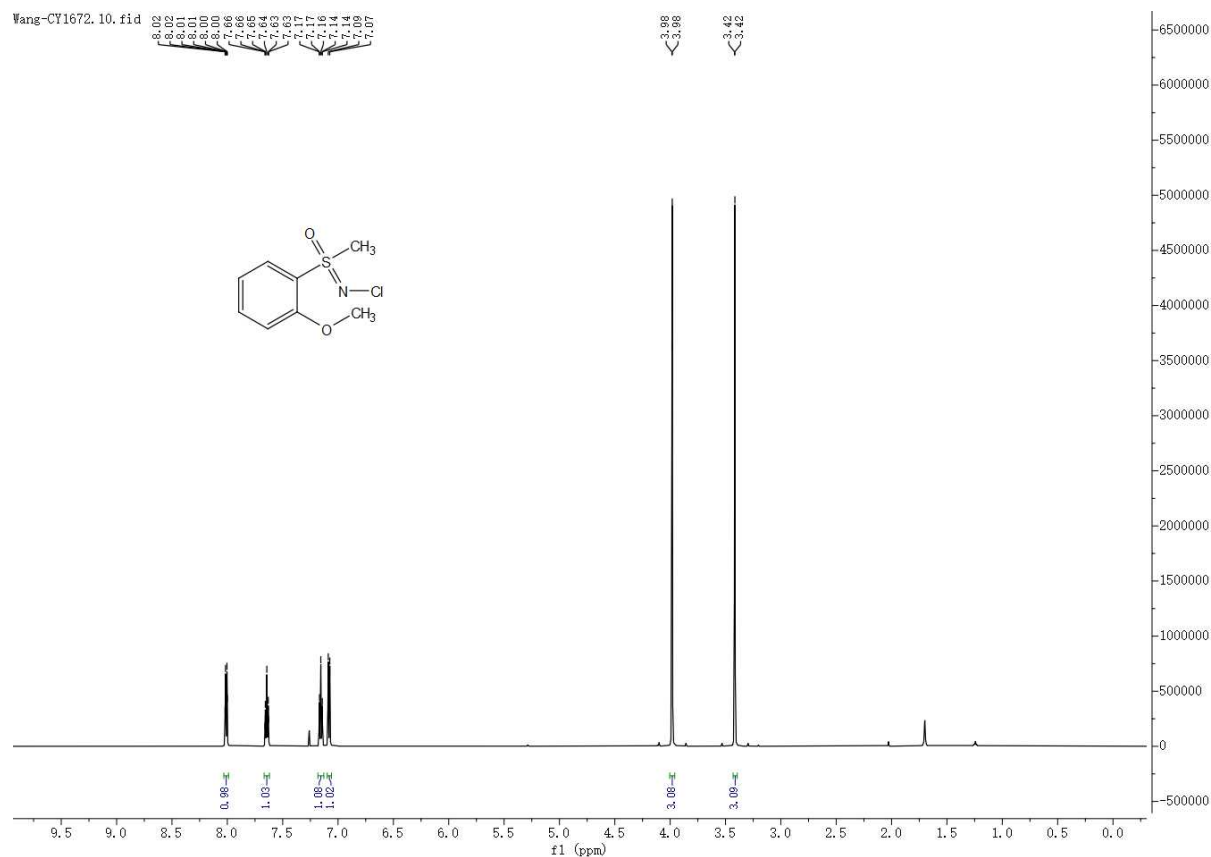
 ^1H NMR spectrum of compound **8I** (600 MHz, CDCl_3) ^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8I** (151 MHz, CDCl_3)

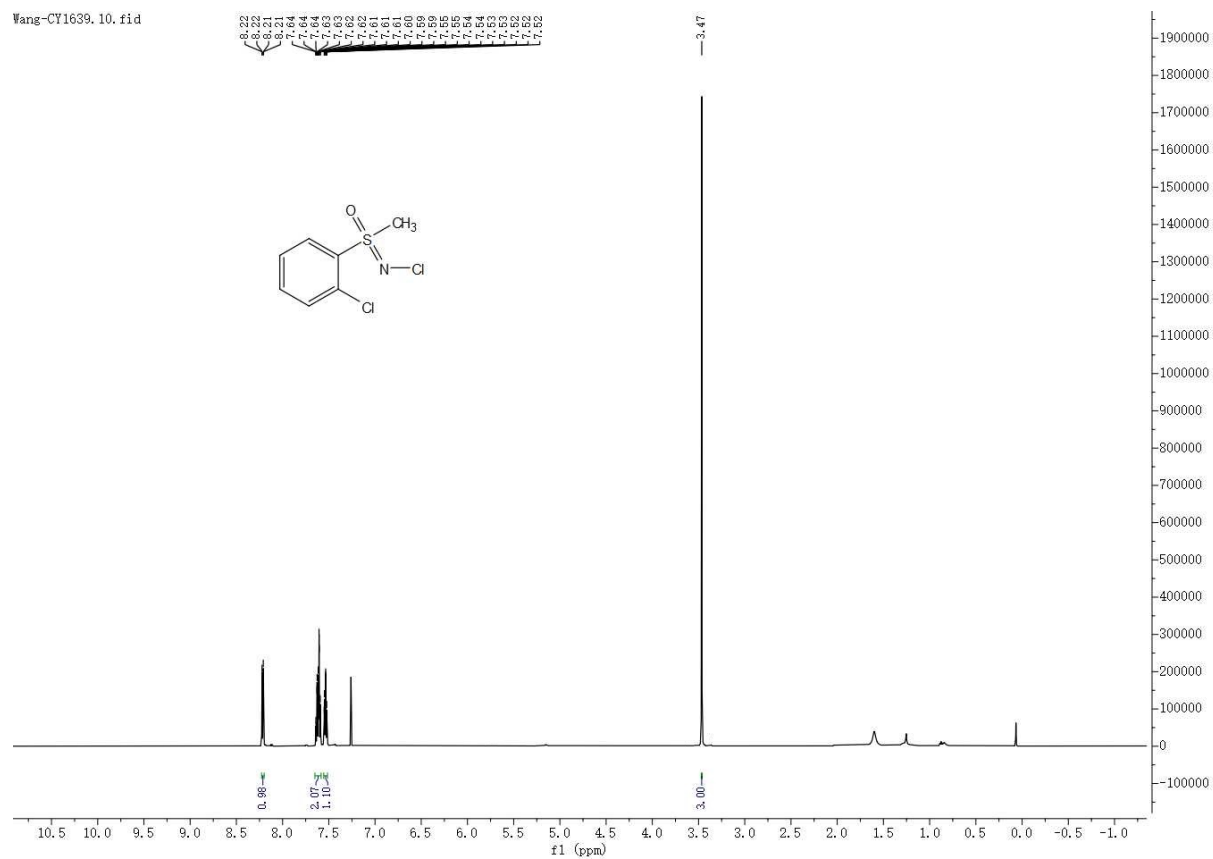


^1H NMR spectrum of compound **8m** (600 MHz, CDCl_3)

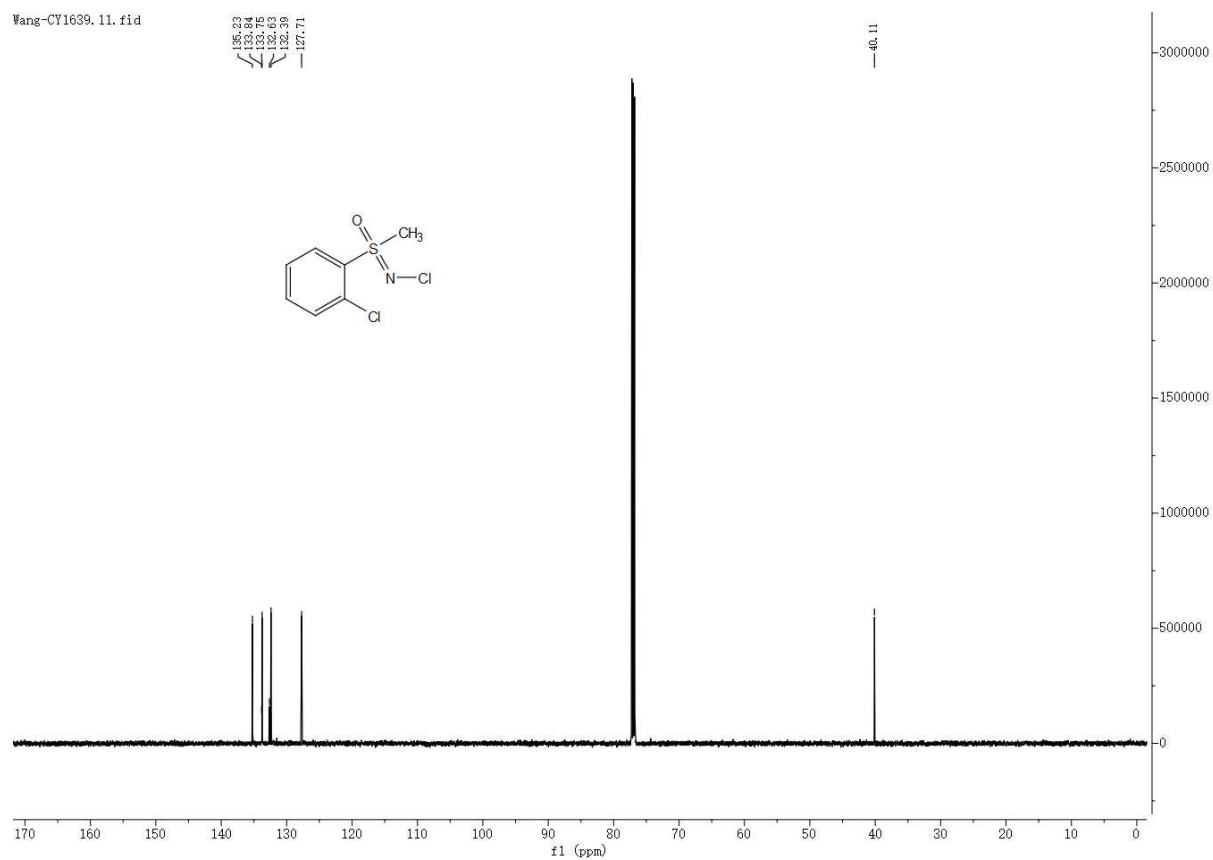


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8m** (151 MHz, CDCl_3)

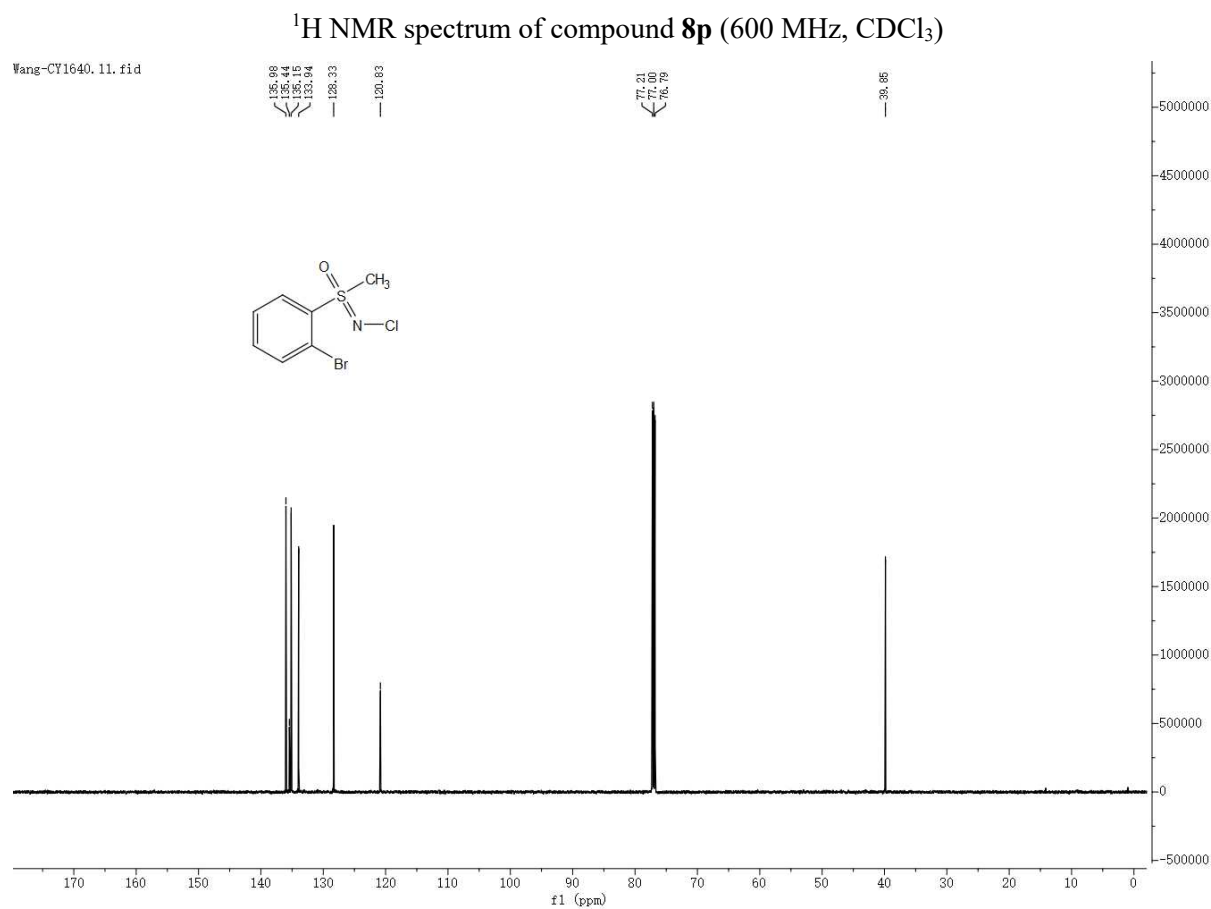
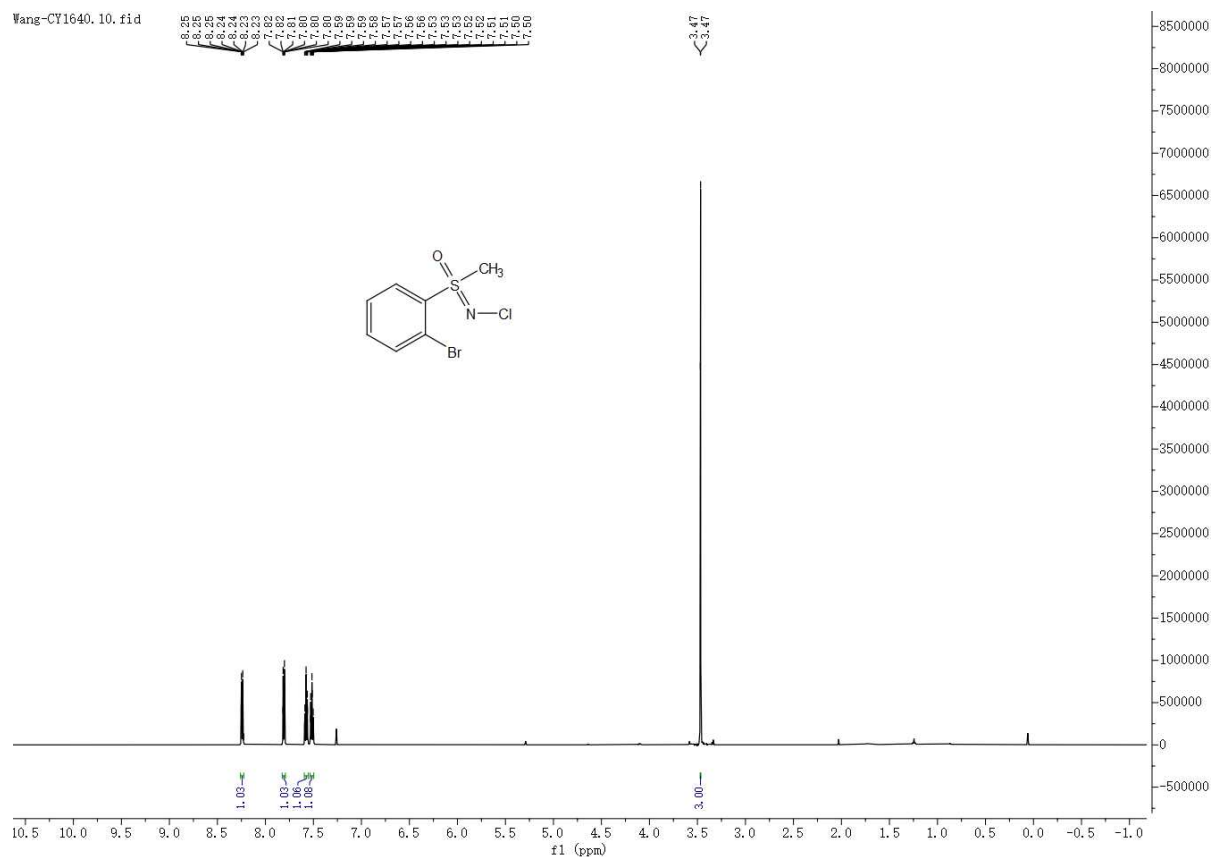




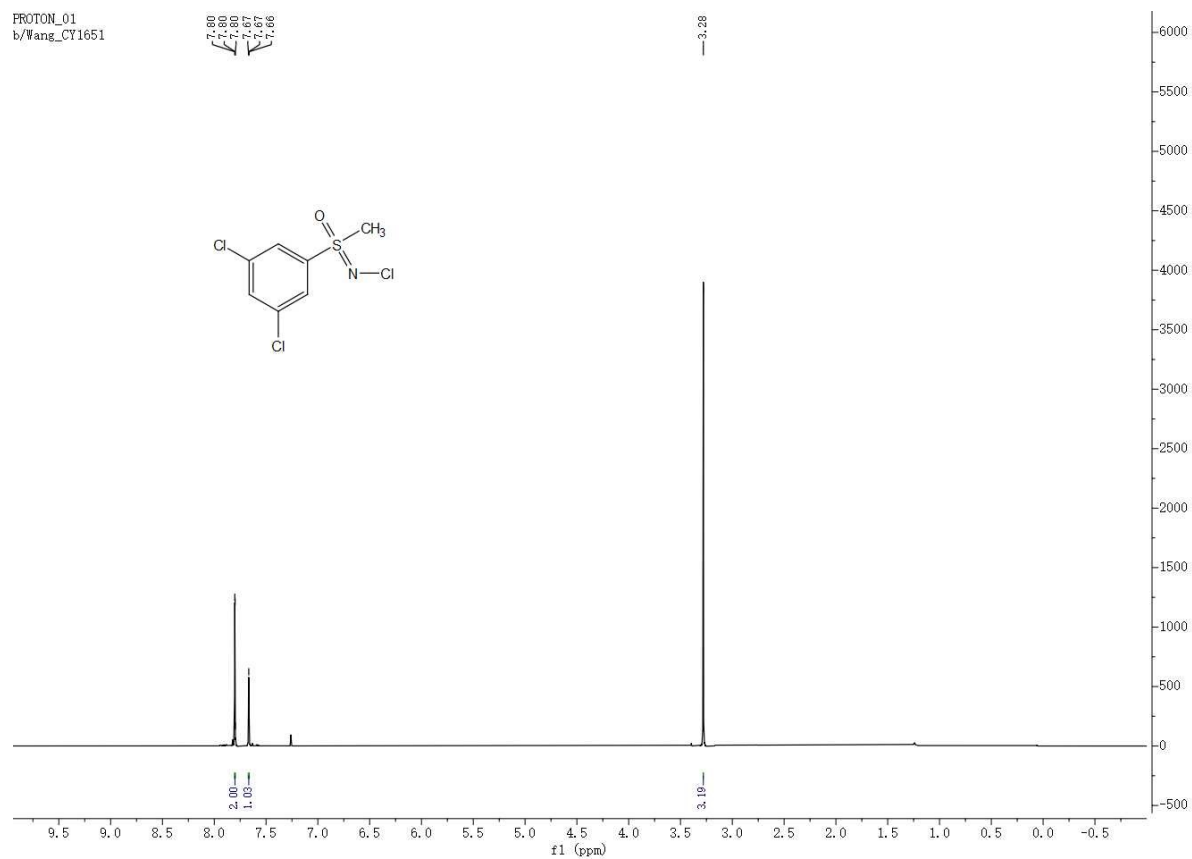
^1H NMR spectrum of compound **8o** (600 MHz, CDCl_3)



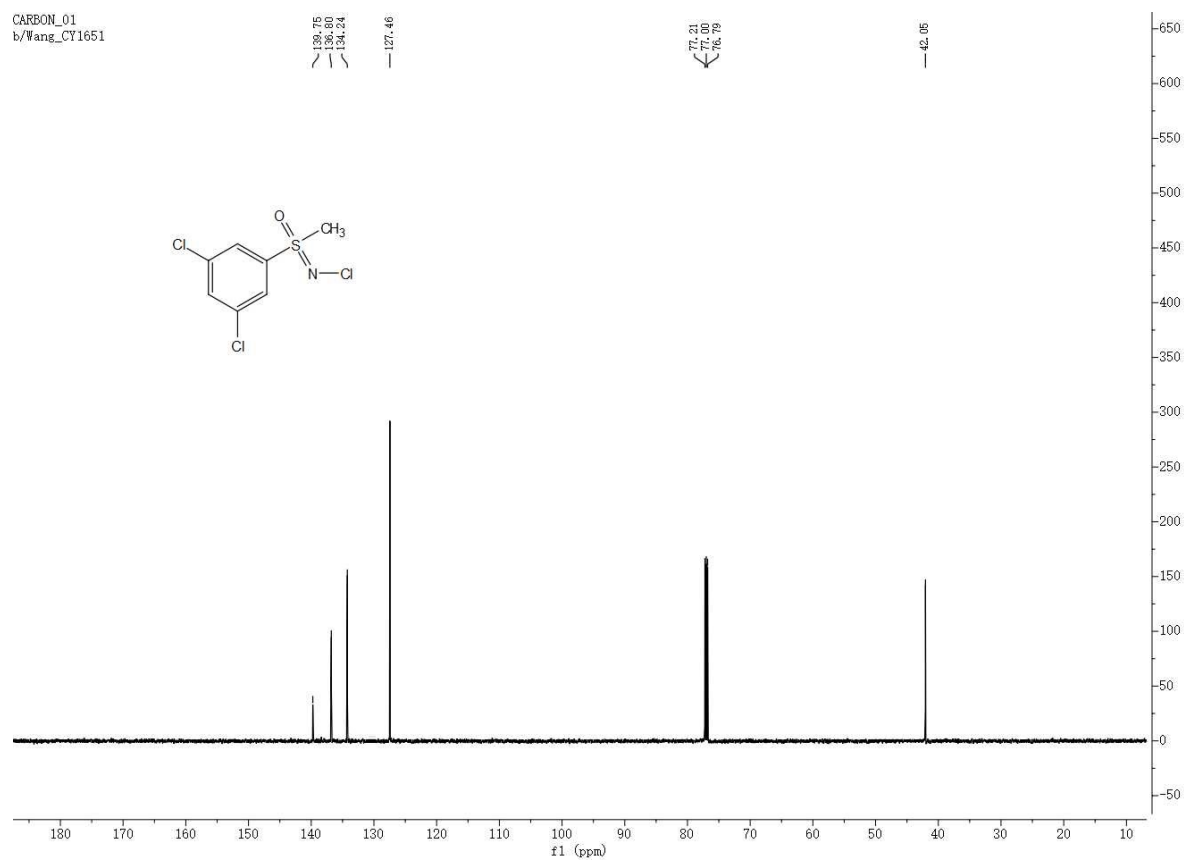
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8o** (151 MHz, CDCl_3)



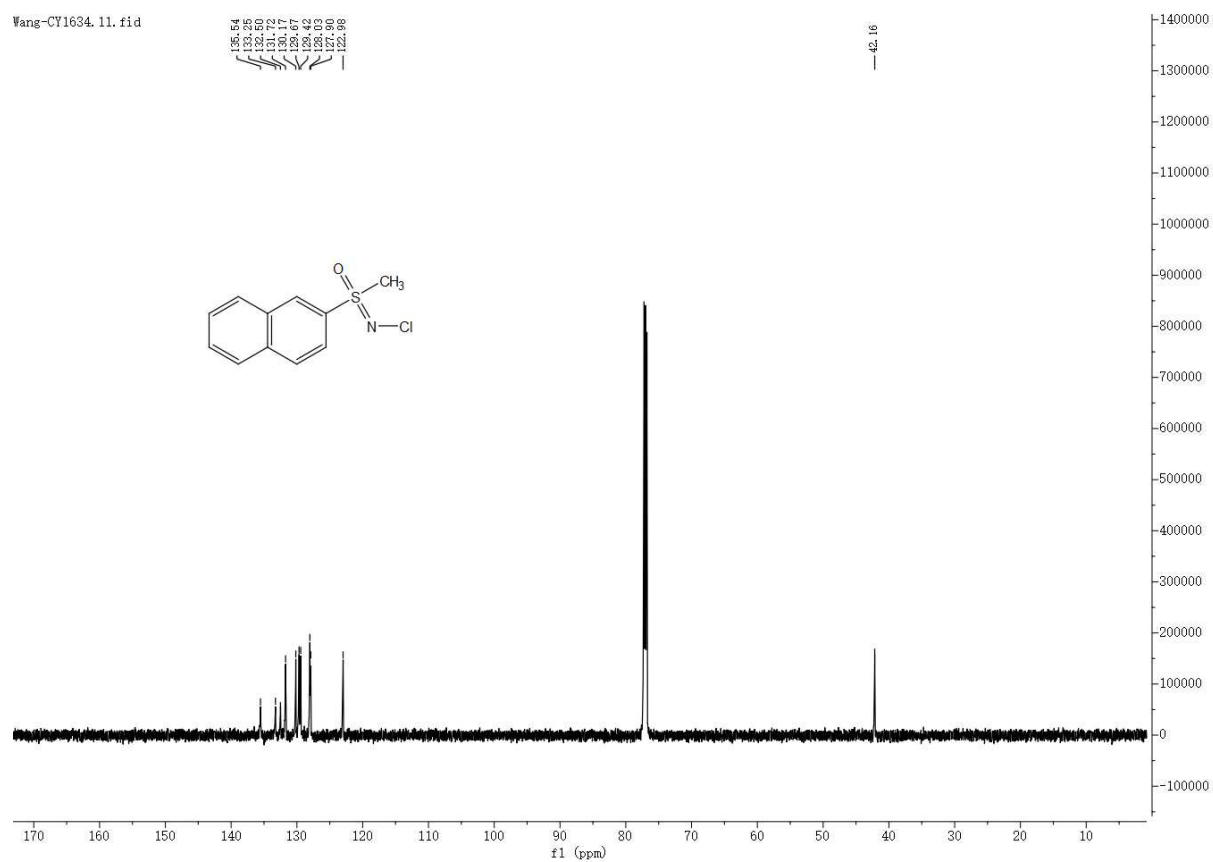
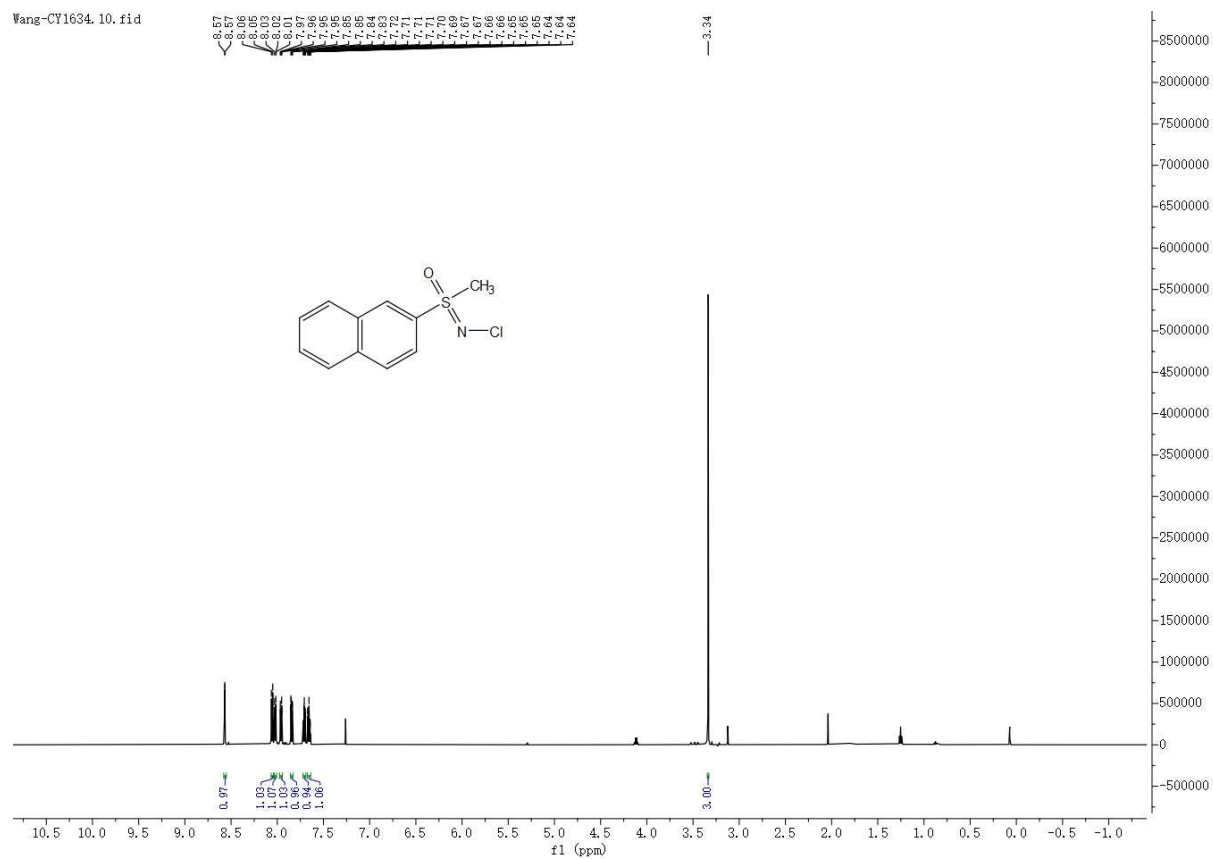
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8p** (151 MHz, CDCl_3)

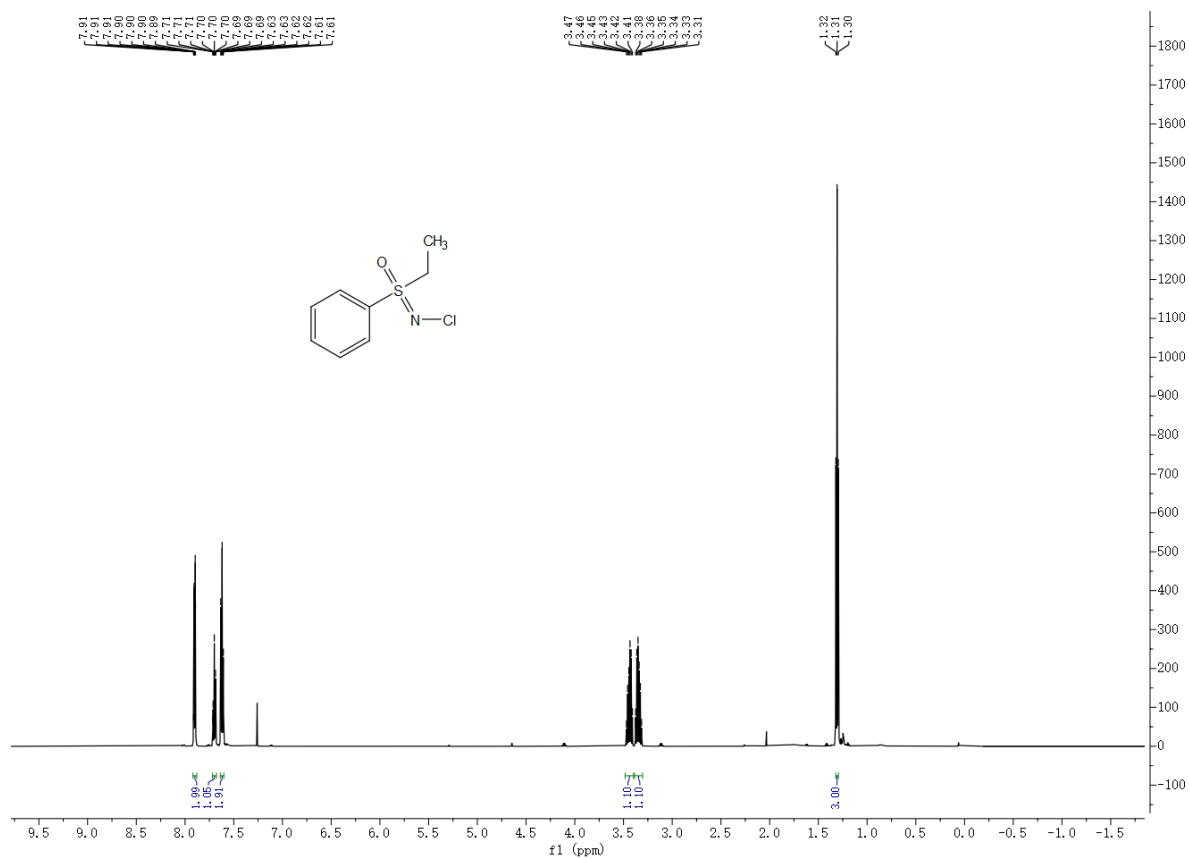


^1H NMR spectrum of compound **8q** (600 MHz, CDCl_3)

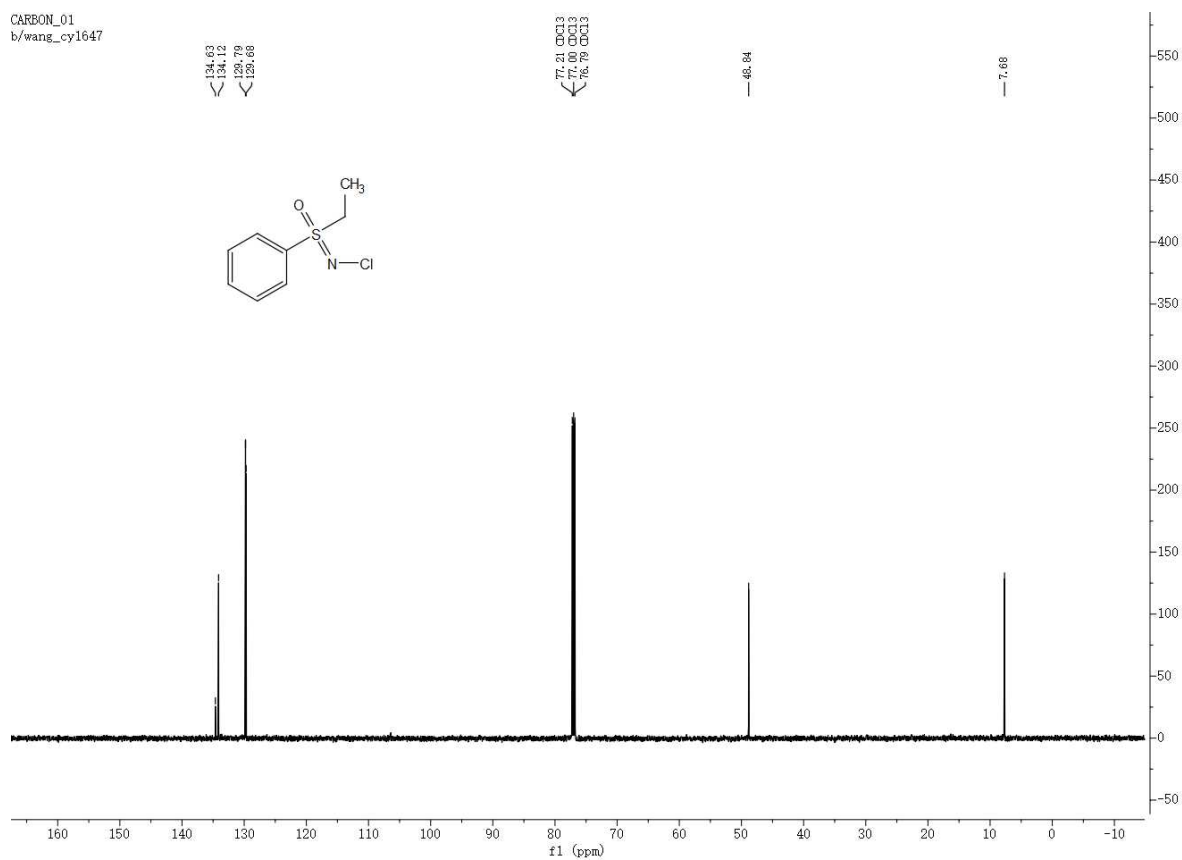


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8q** (151 MHz, CDCl_3)

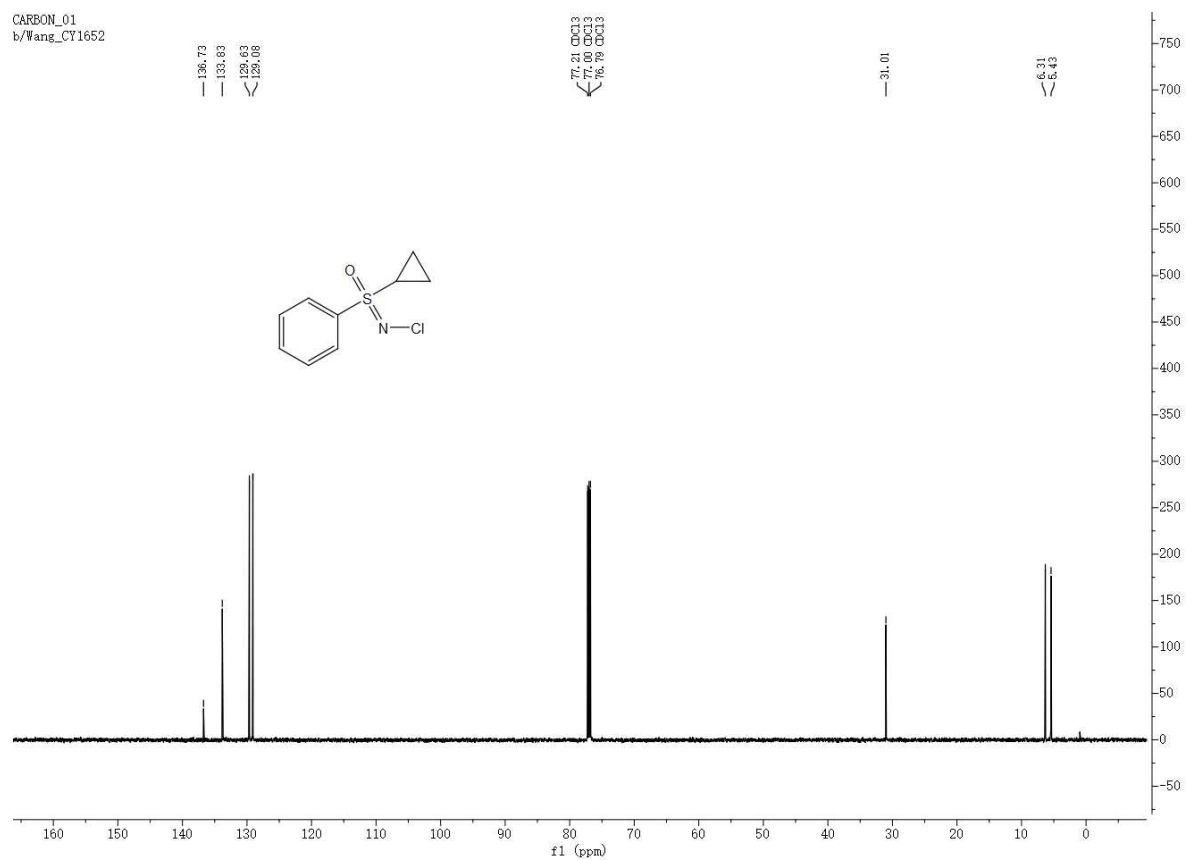
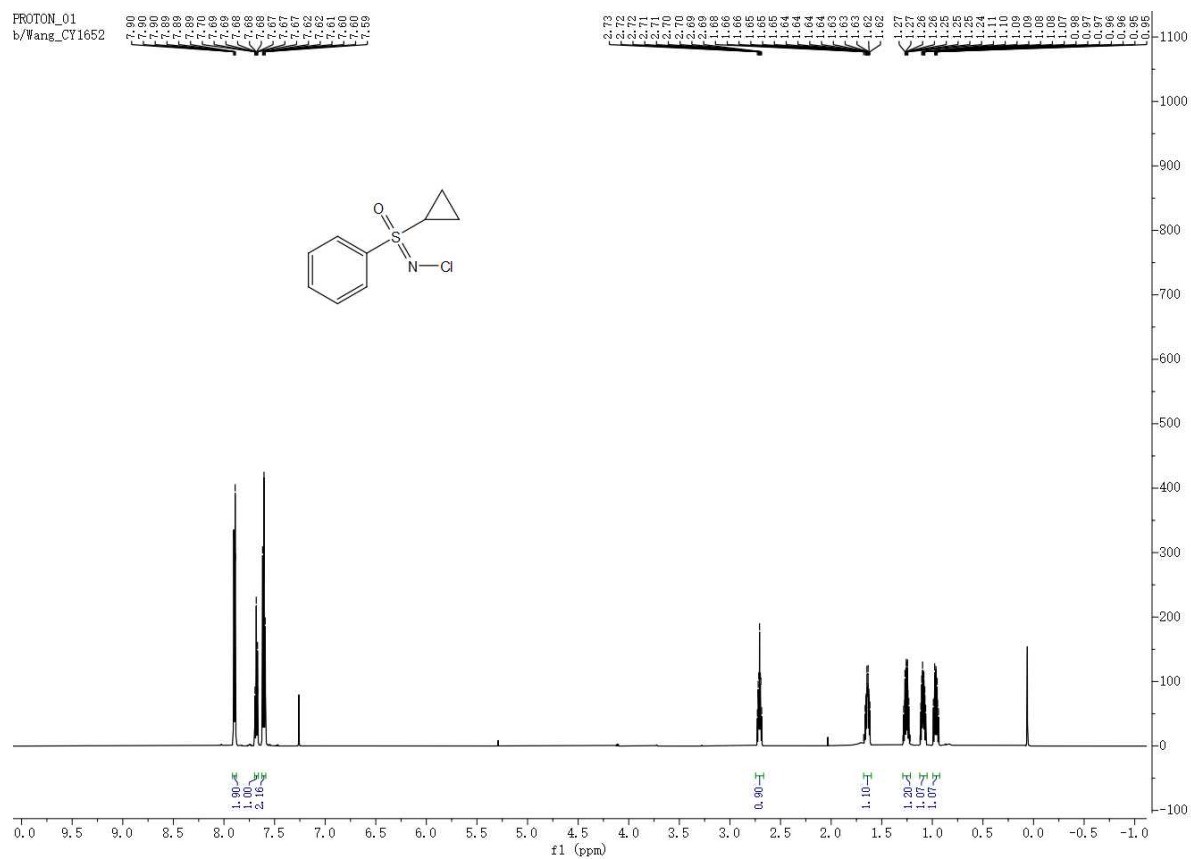


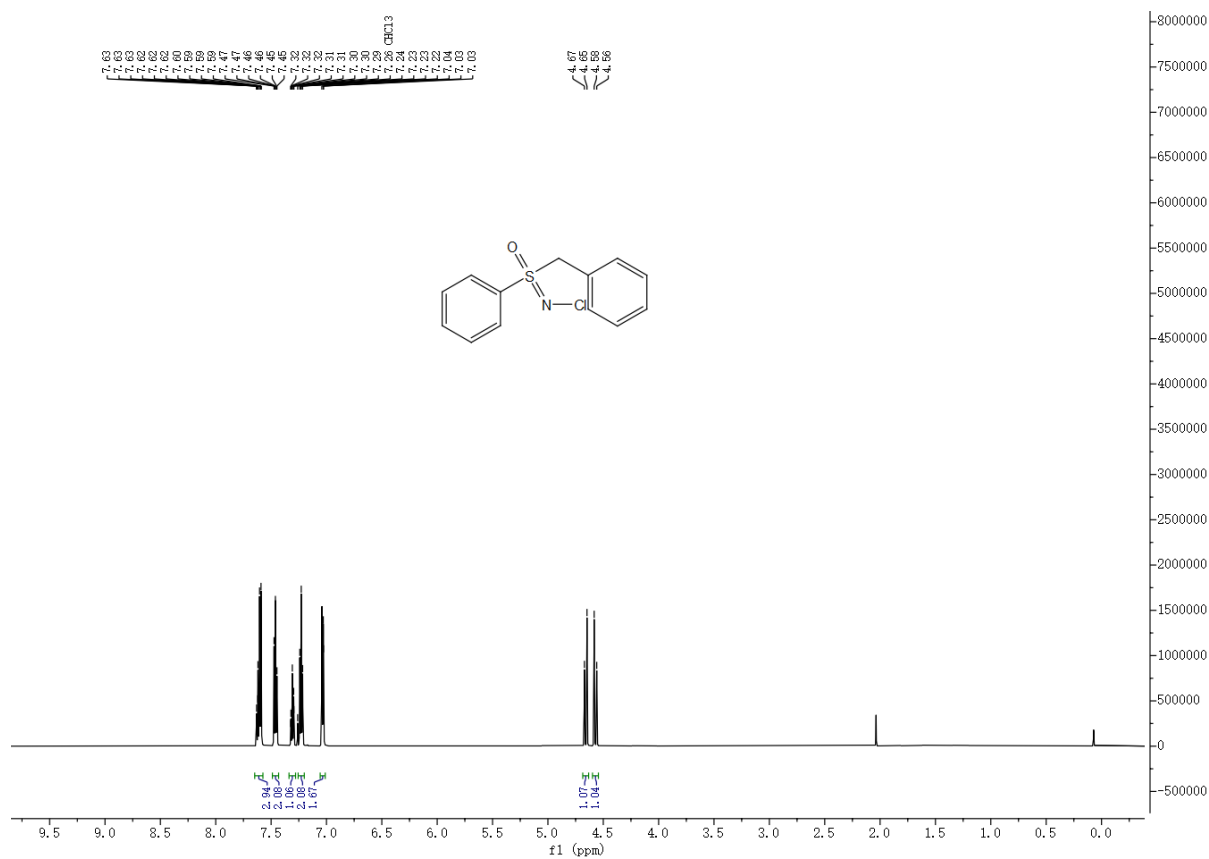


^1H NMR spectrum of compound **8s** (600 MHz, CDCl_3)

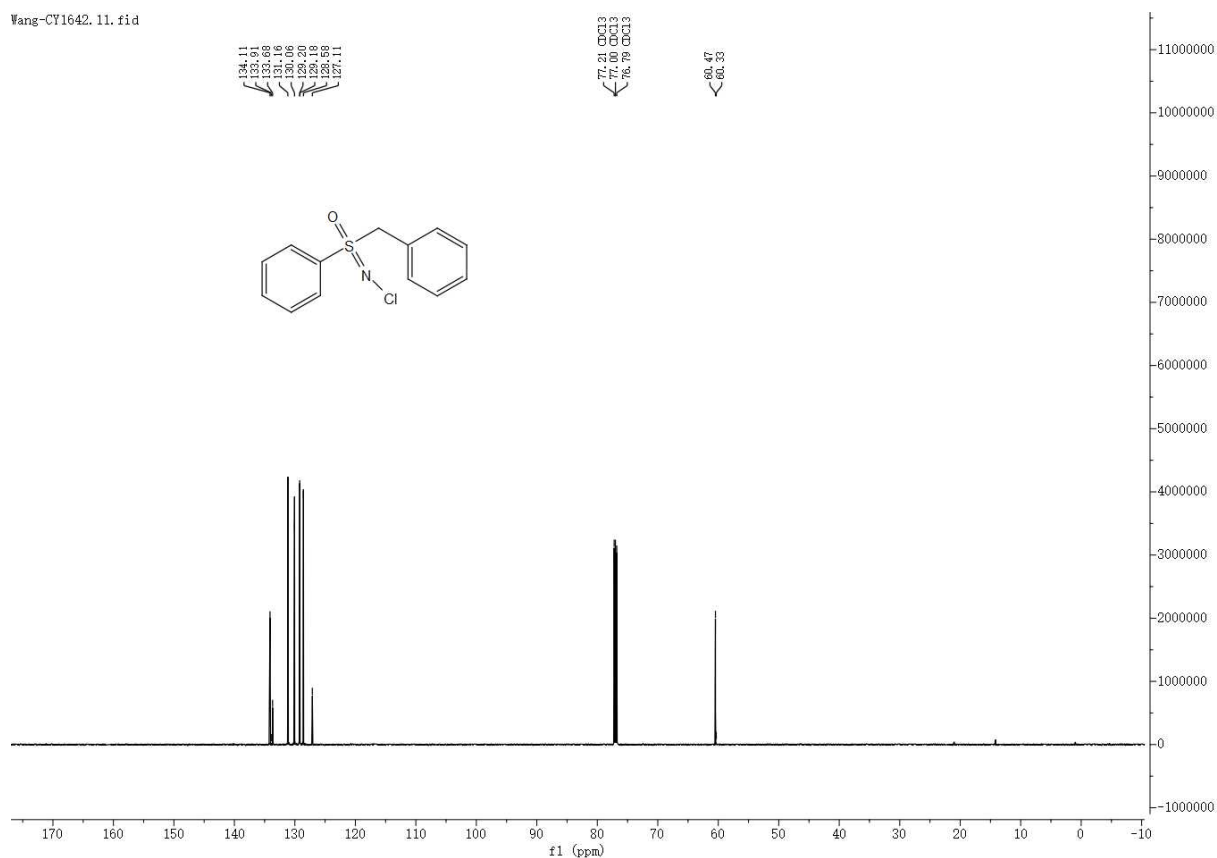


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **8s** (151 MHz, CDCl_3)

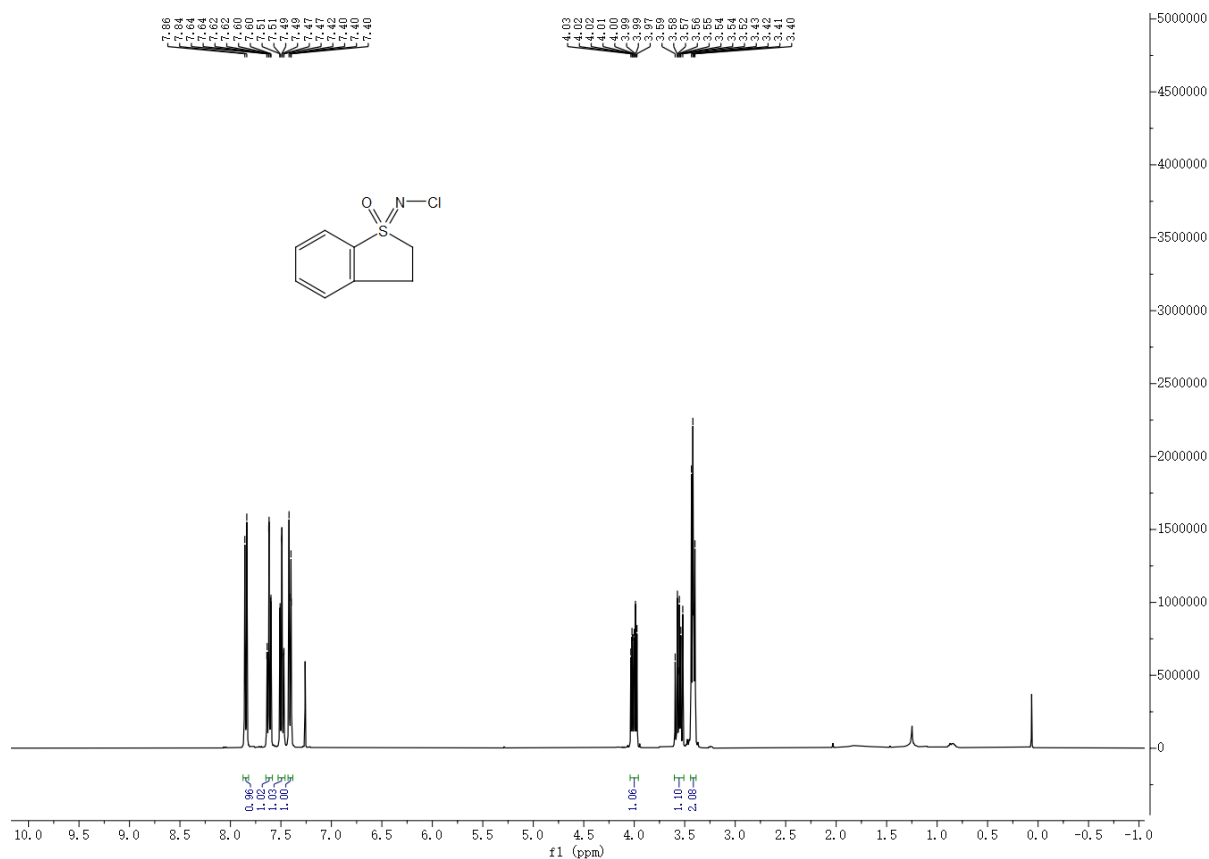




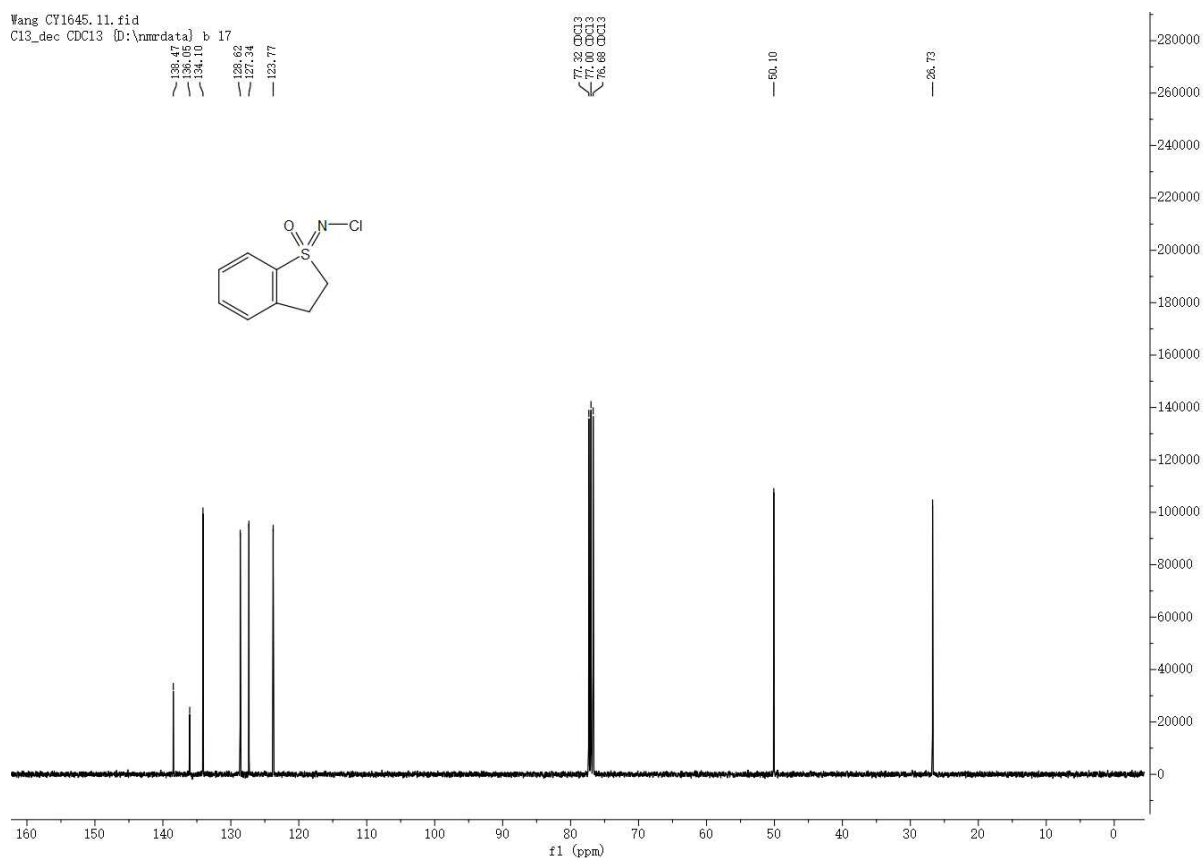
¹H NMR spectrum of compound **8u** (600 MHz, CDCl₃)



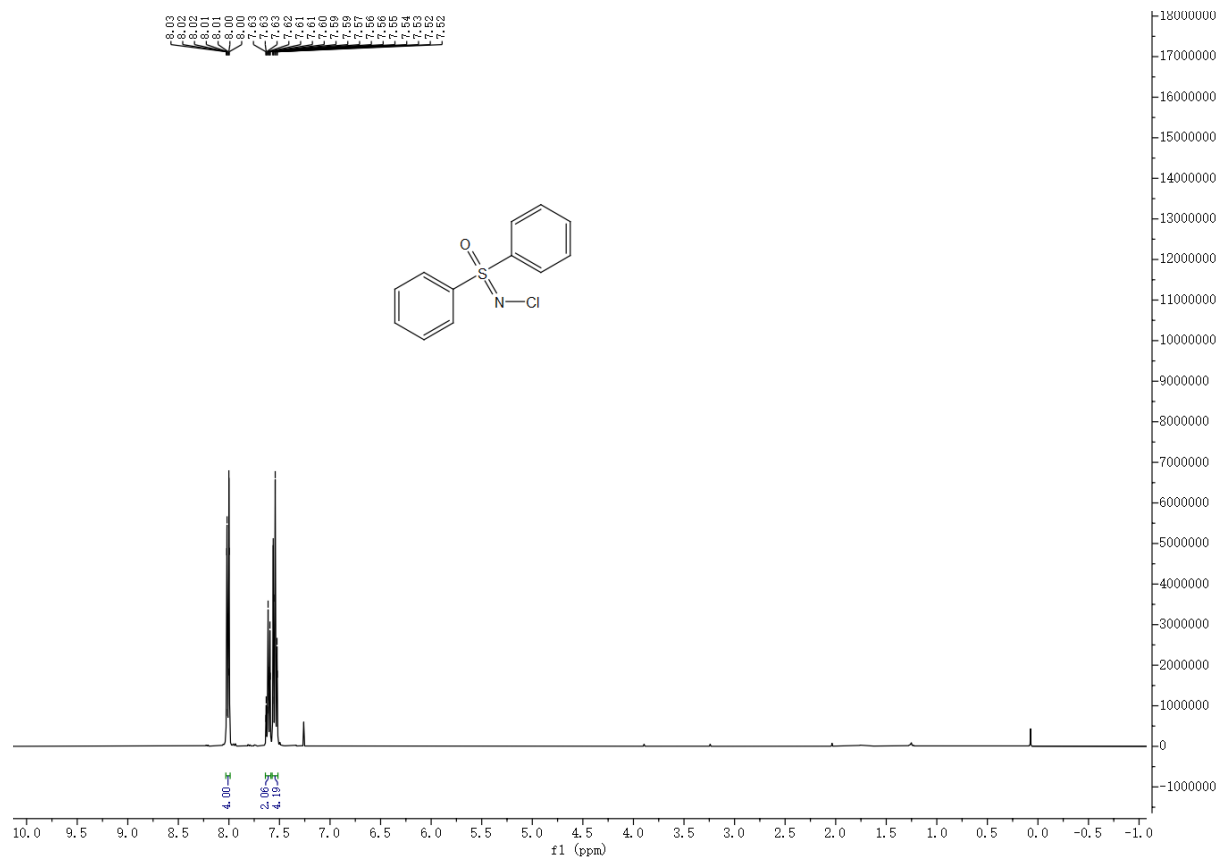
¹³C {¹H} NMR spectrum of compound **8u** (151 MHz, CDCl₃)



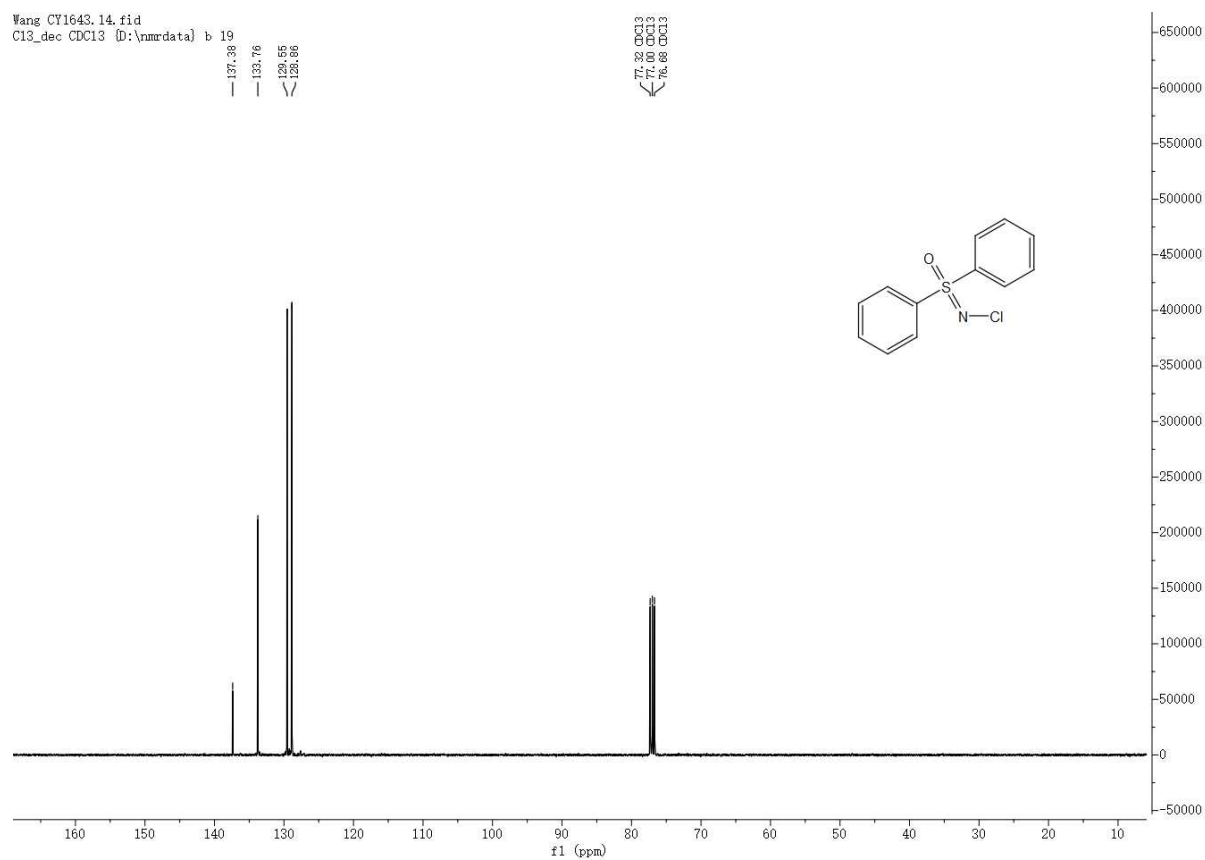
¹H NMR spectrum of compound **8v (600 MHz, CDCl₃)**



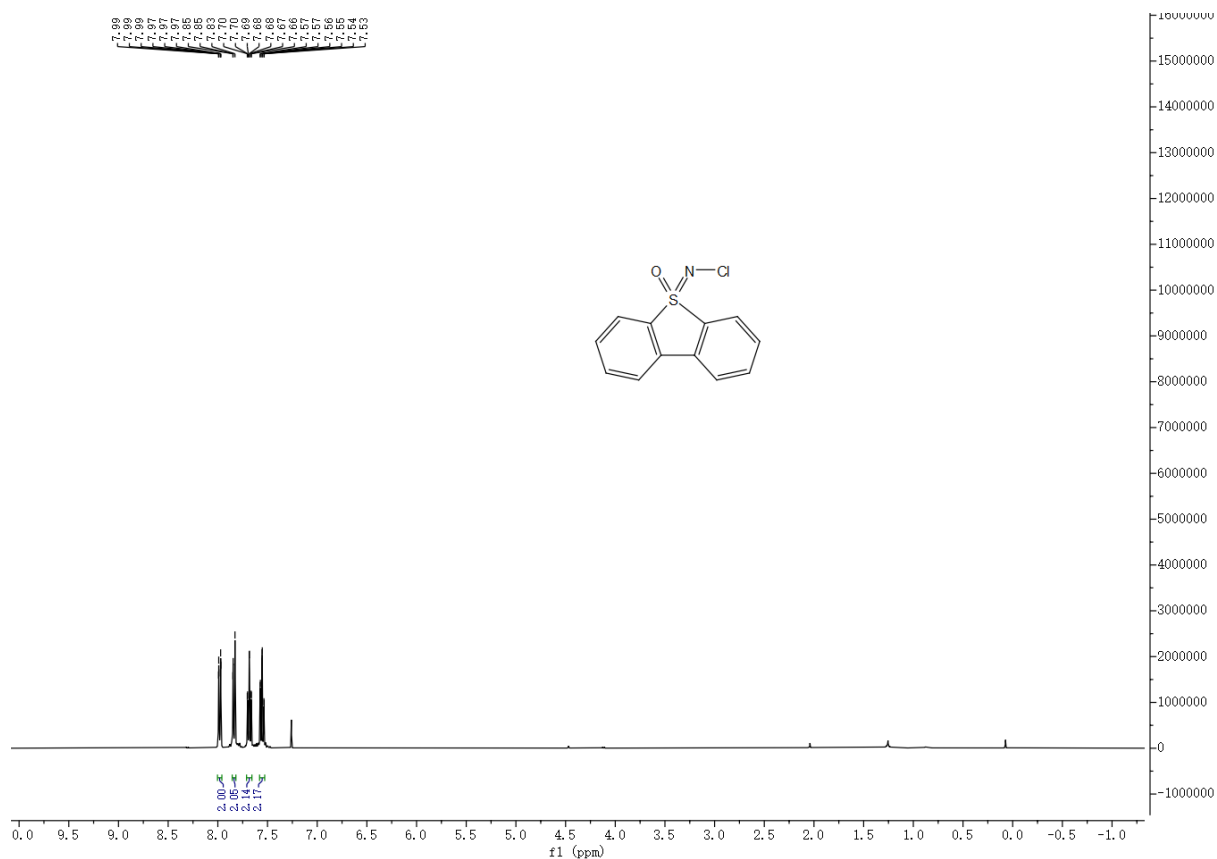
¹³C {¹H} NMR spectrum of compound **8v (151 MHz, CDCl₃)**



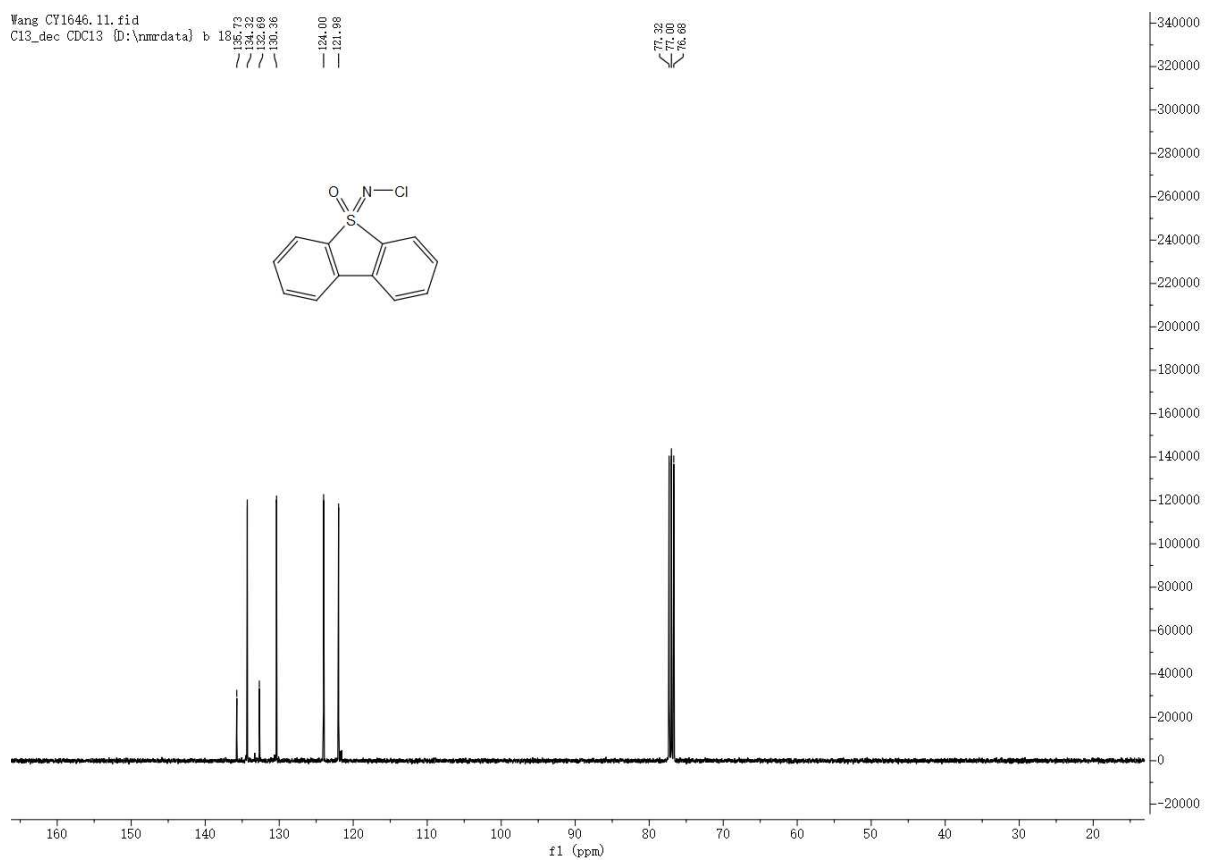
¹H NMR spectrum of compound **8w** (600 MHz, CDCl₃)



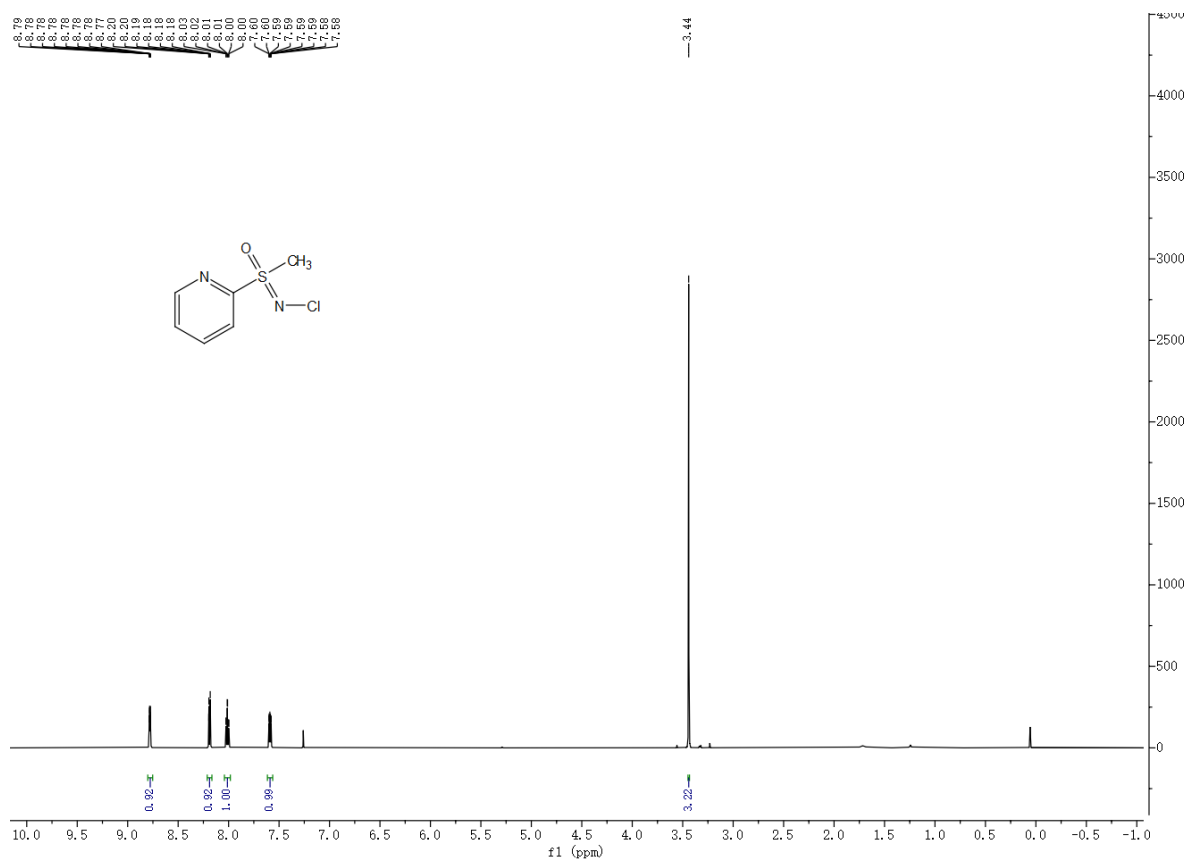
¹³C {¹H} NMR spectrum of compound **8w** (151 MHz, CDCl₃)



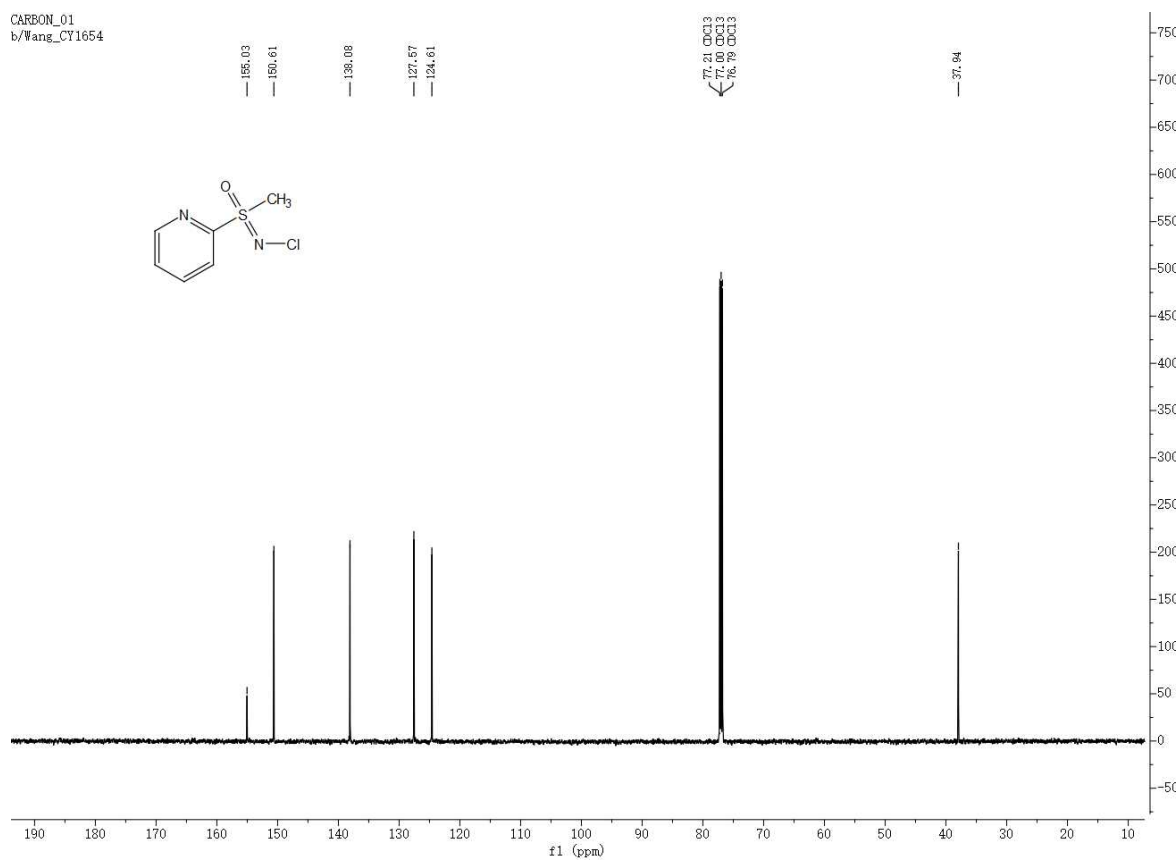
¹H NMR spectrum of compound **8x** (600 MHz, CDCl₃)



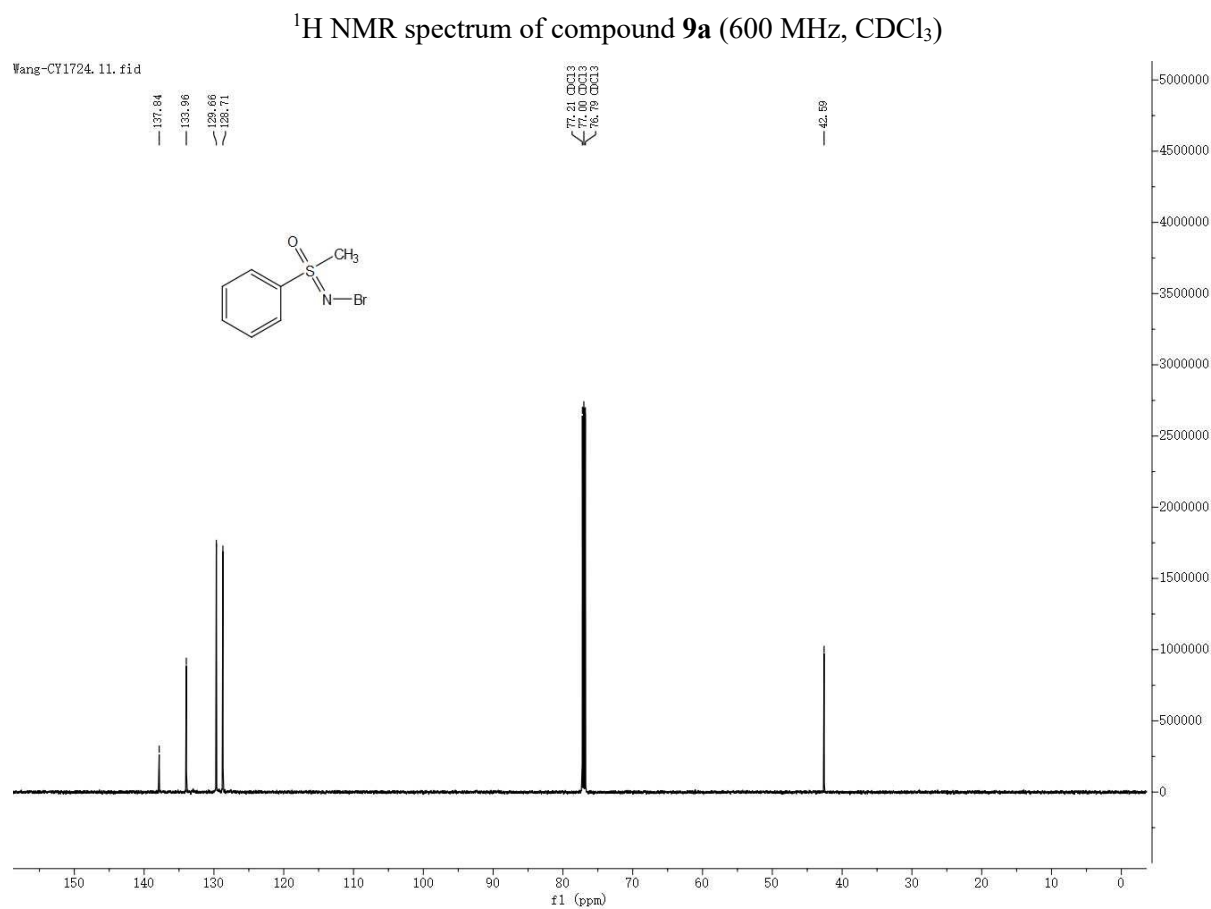
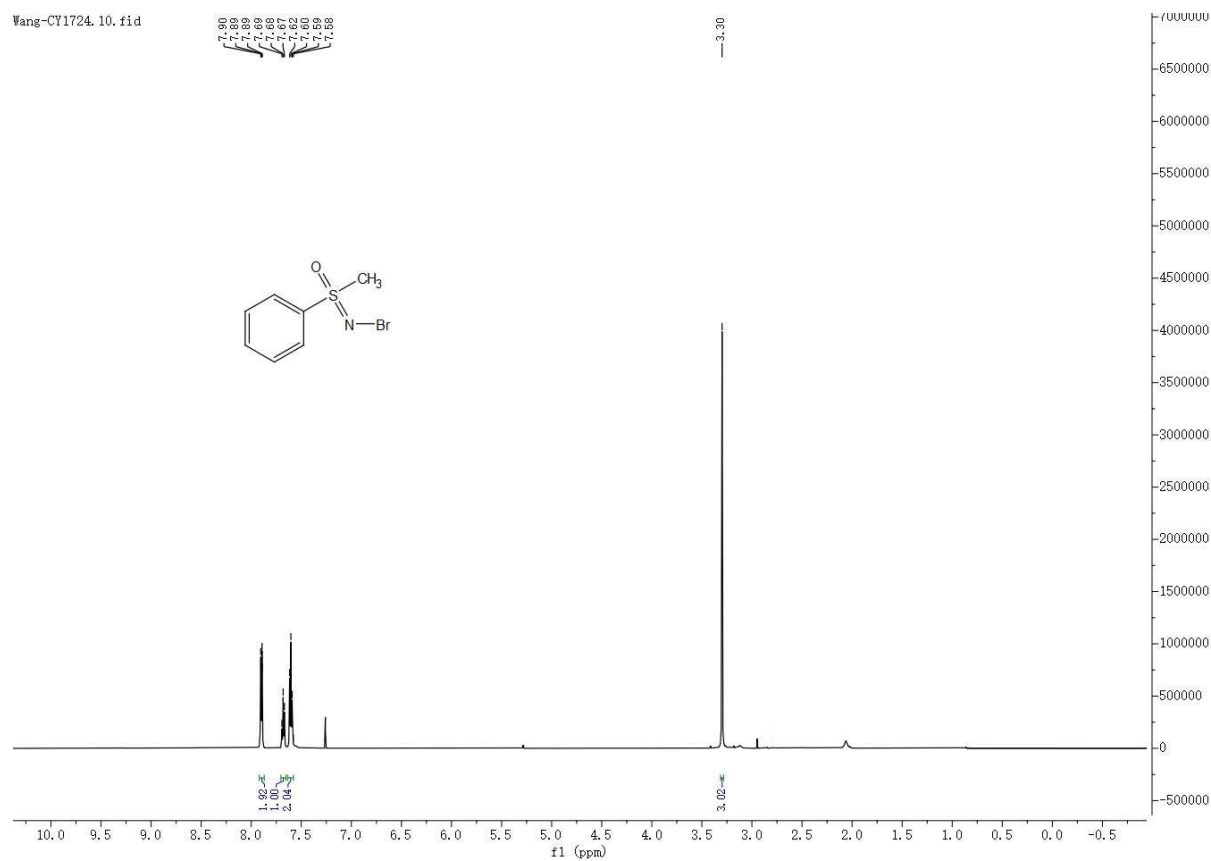
¹³C {¹H} NMR spectrum of compound **8x** (151 MHz, CDCl₃)



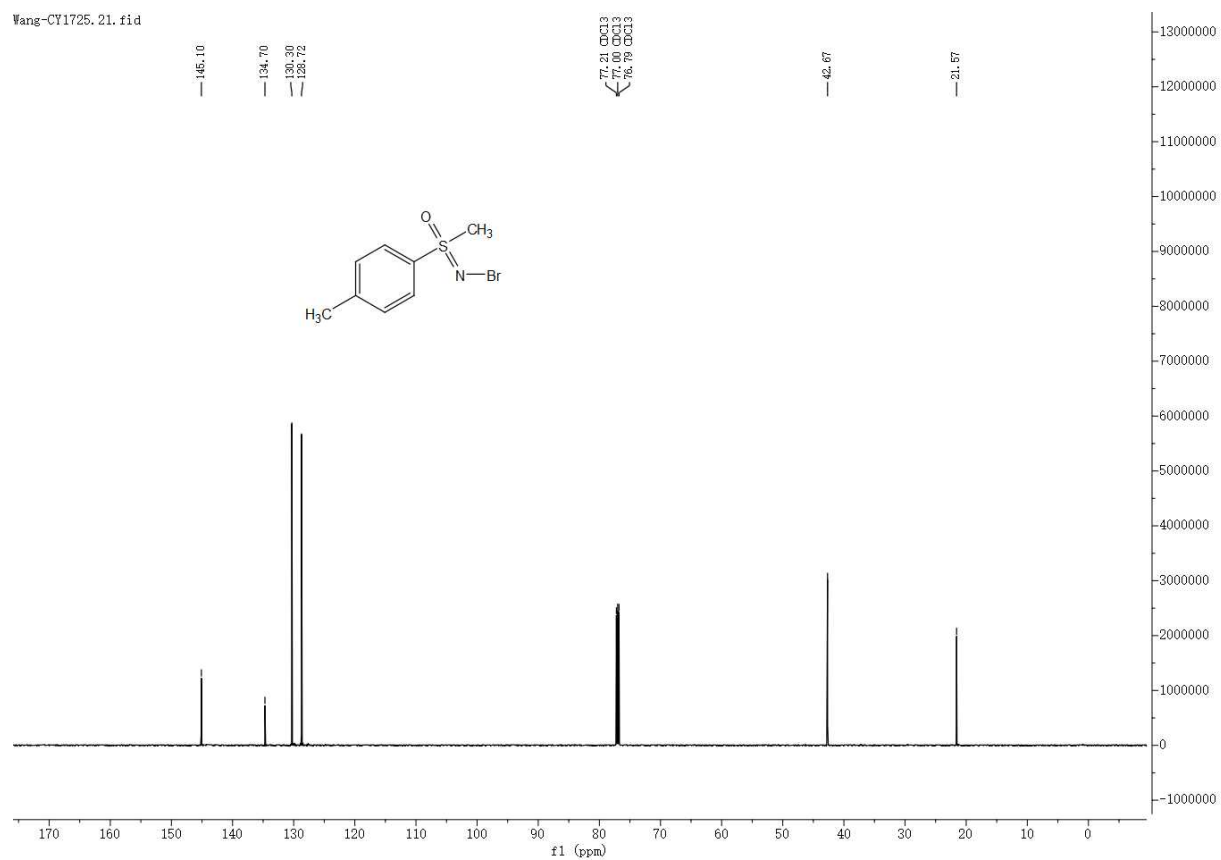
¹H NMR spectrum of compound **8y** (600 MHz, CDCl₃)

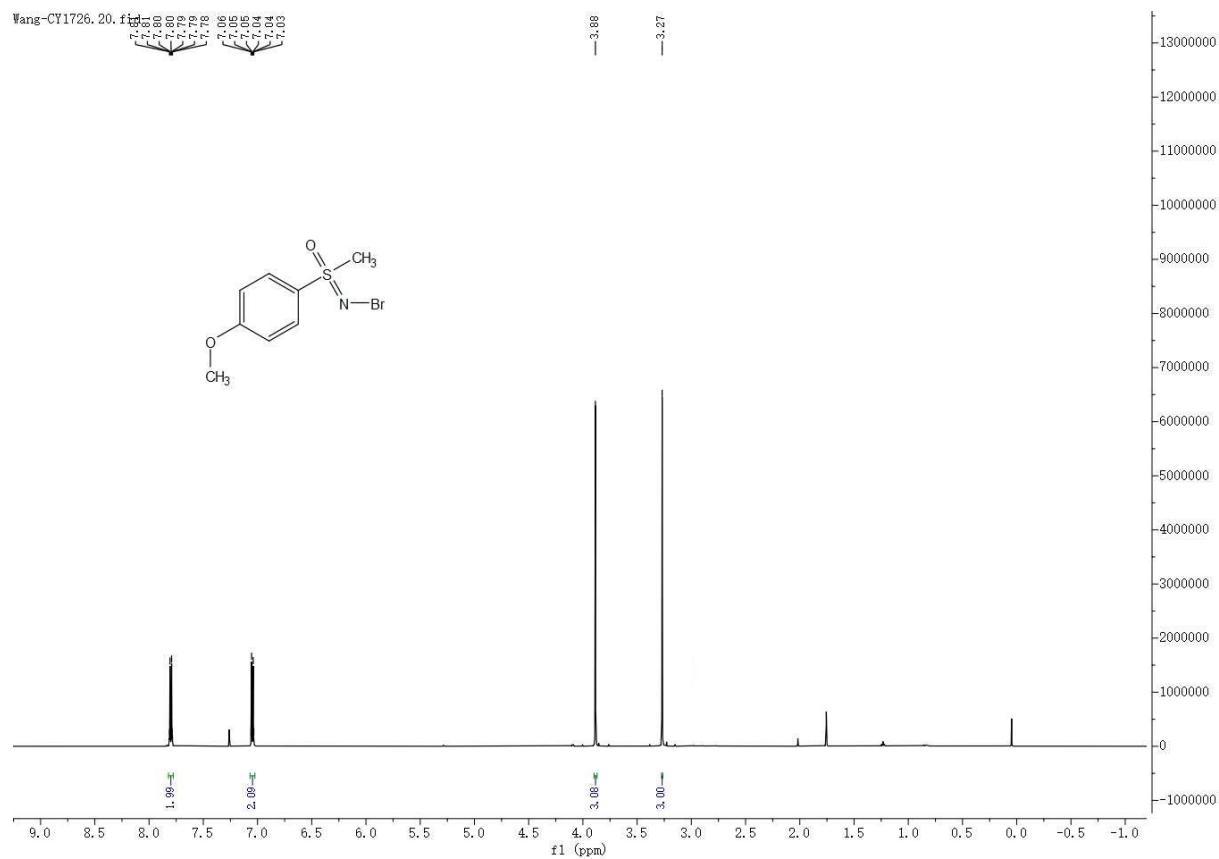


¹³C {¹H} NMR spectrum of compound **8y** (151 MHz, CDCl₃)

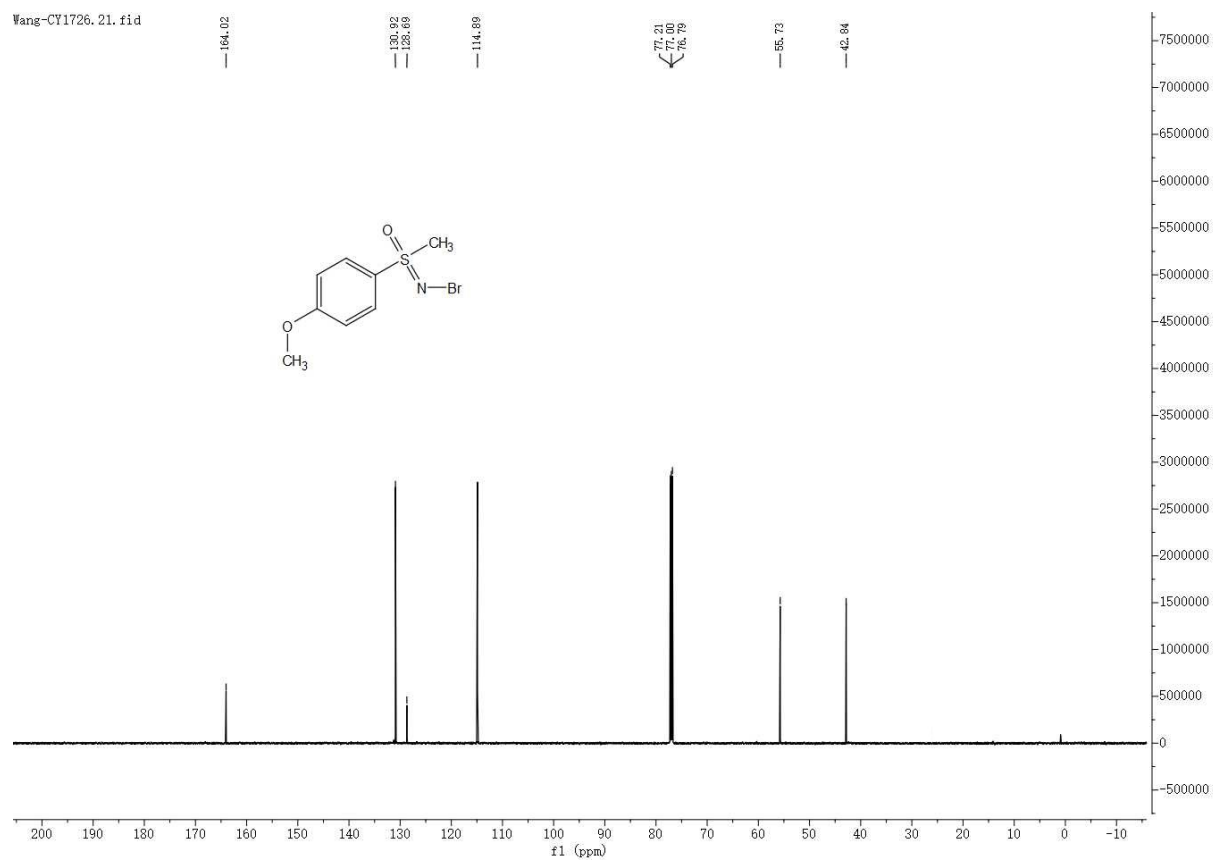


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9a** (151 MHz, CDCl_3)

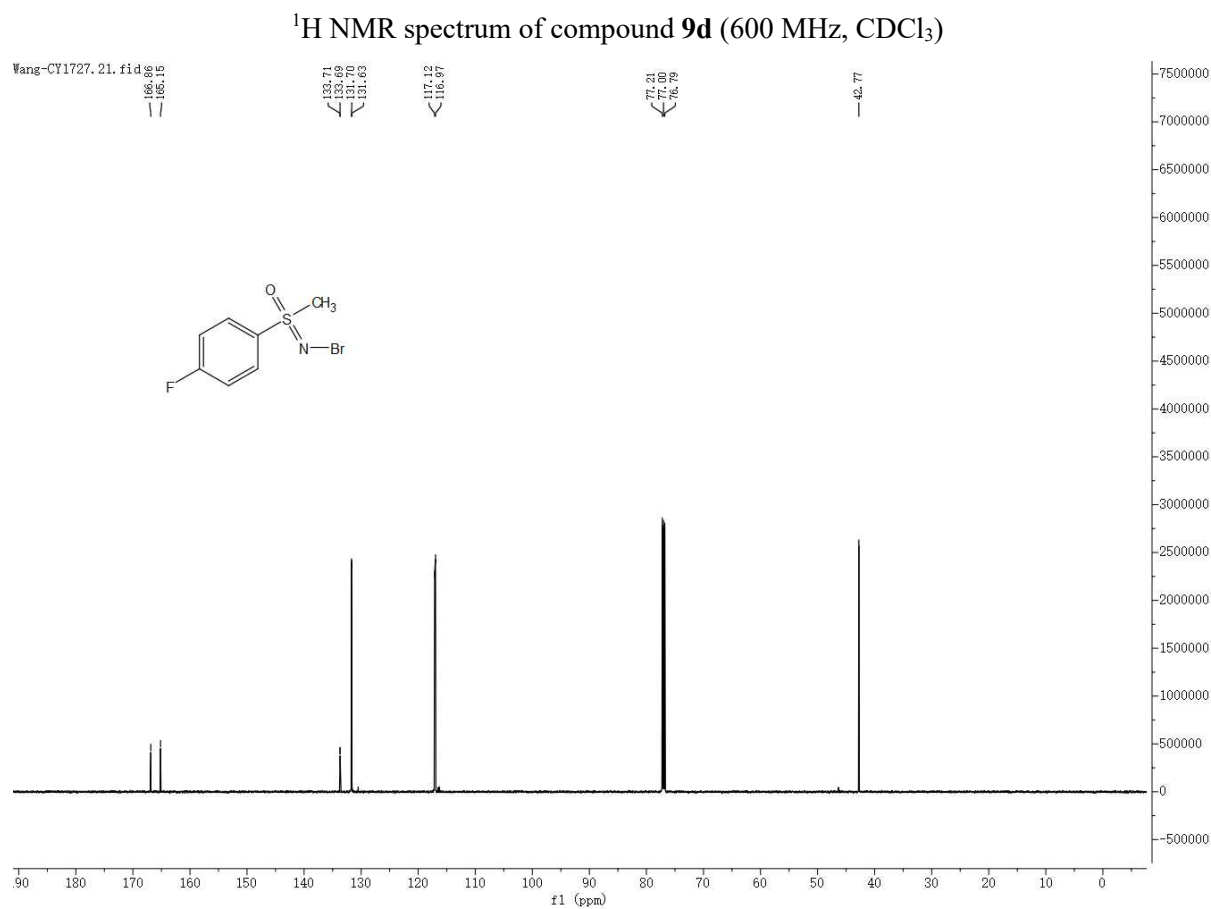
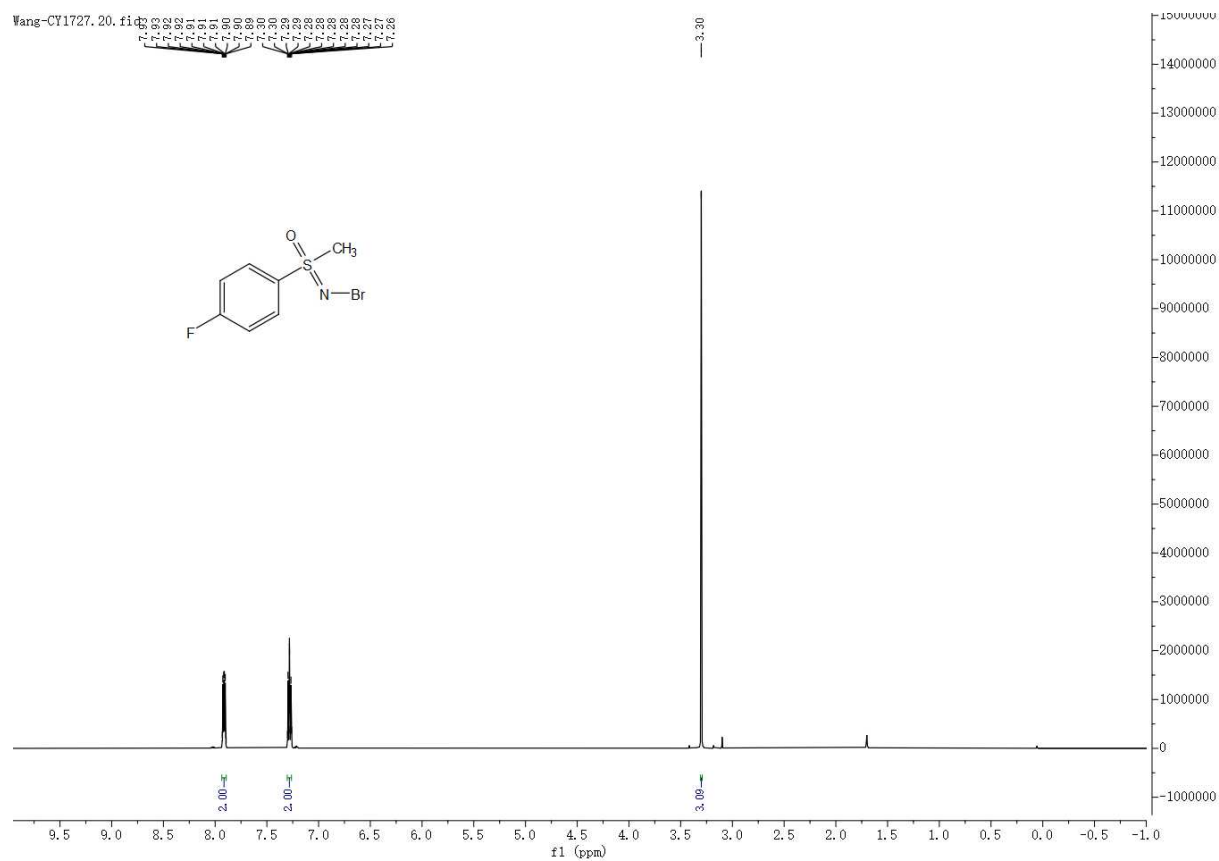


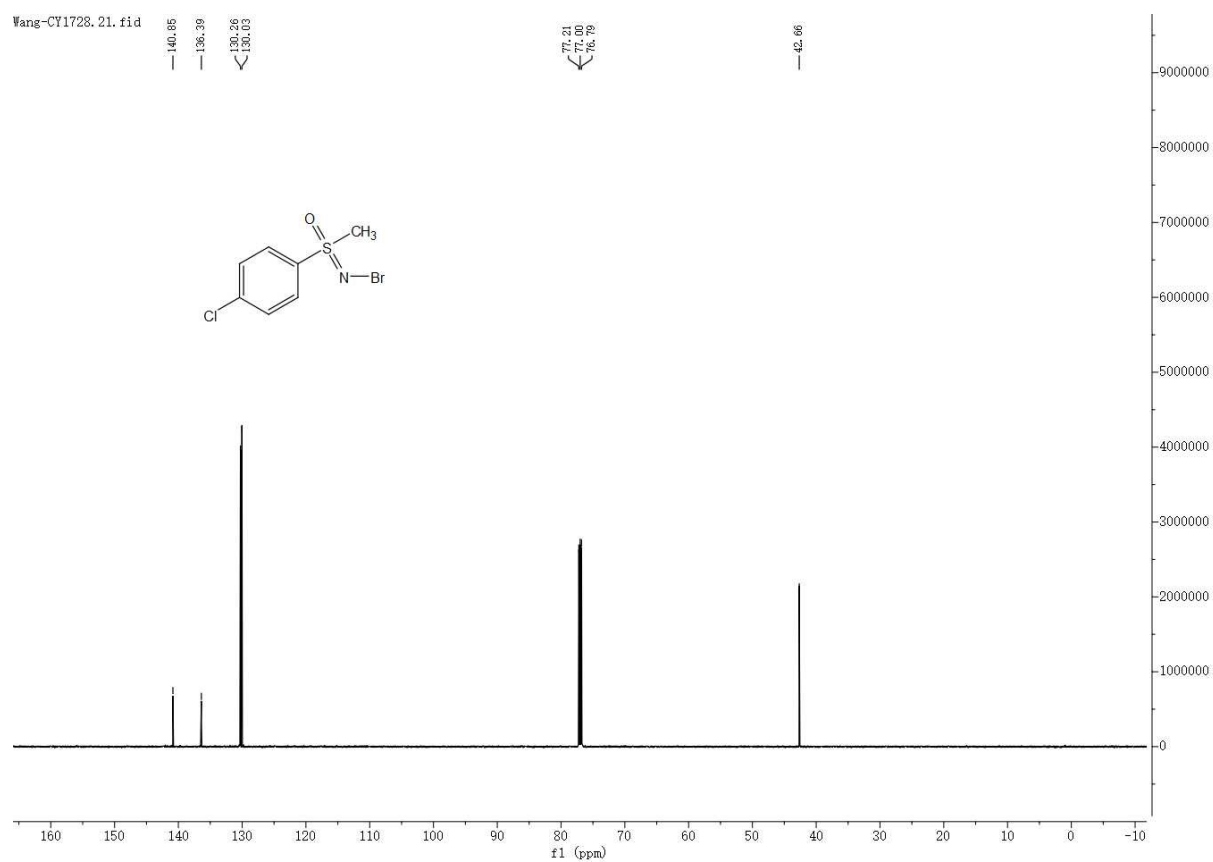
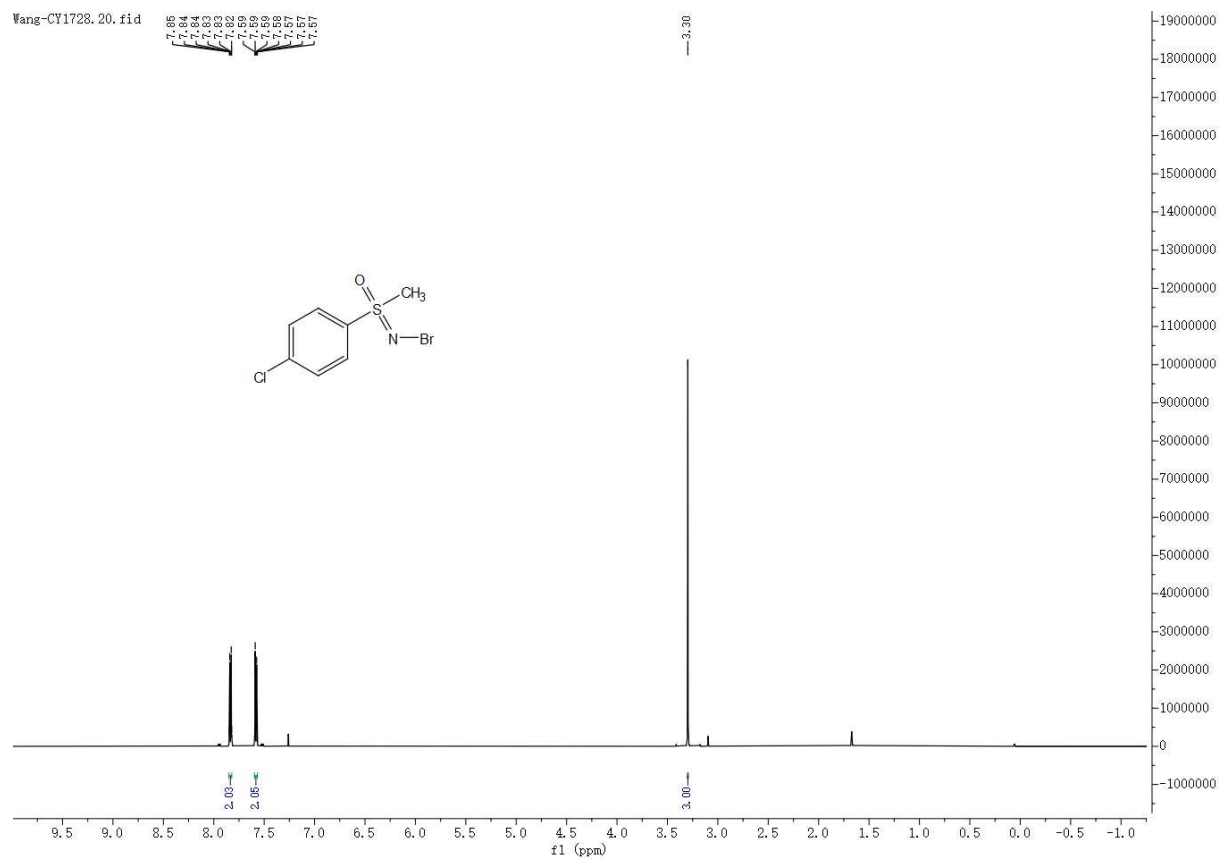


^1H NMR spectrum of compound **9c** (600 MHz, CDCl_3)

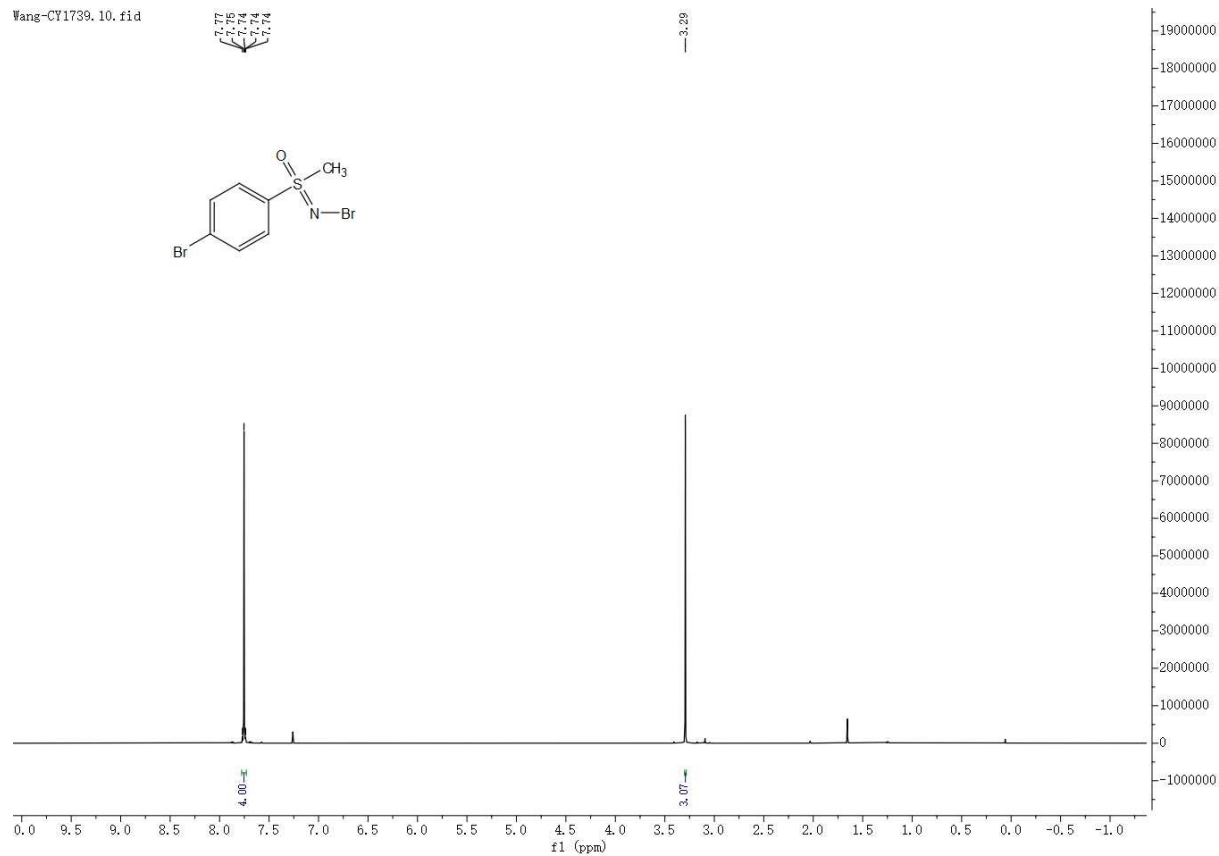


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9c** (151 MHz, CDCl_3)

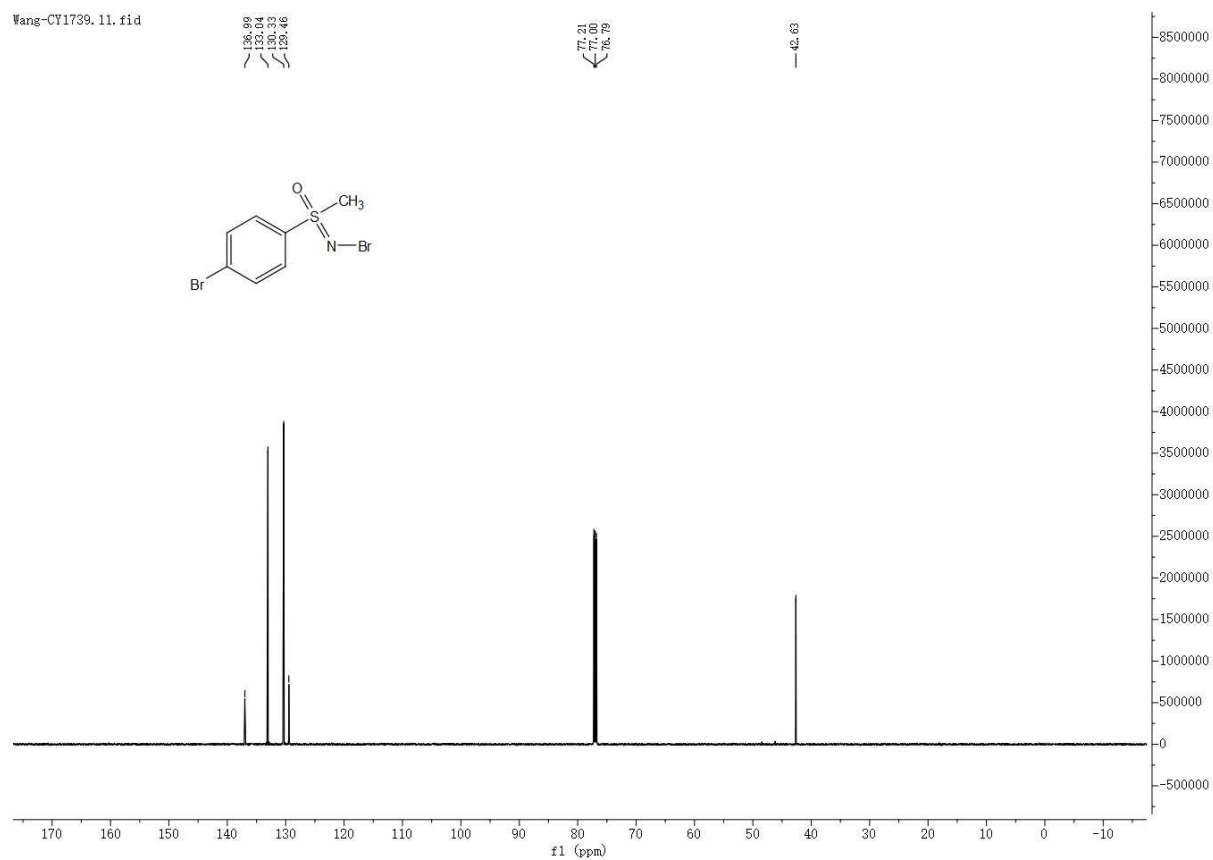


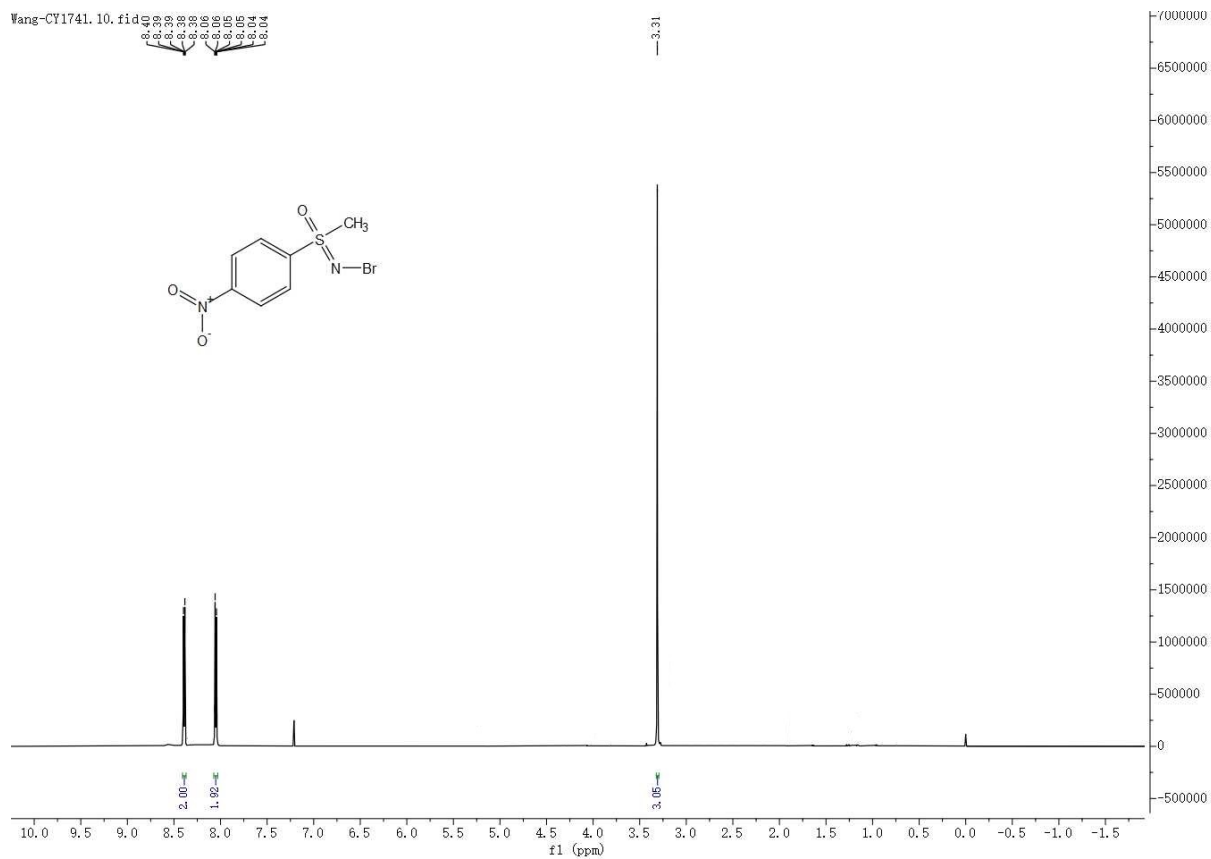


Wang-CY1739_10.fid

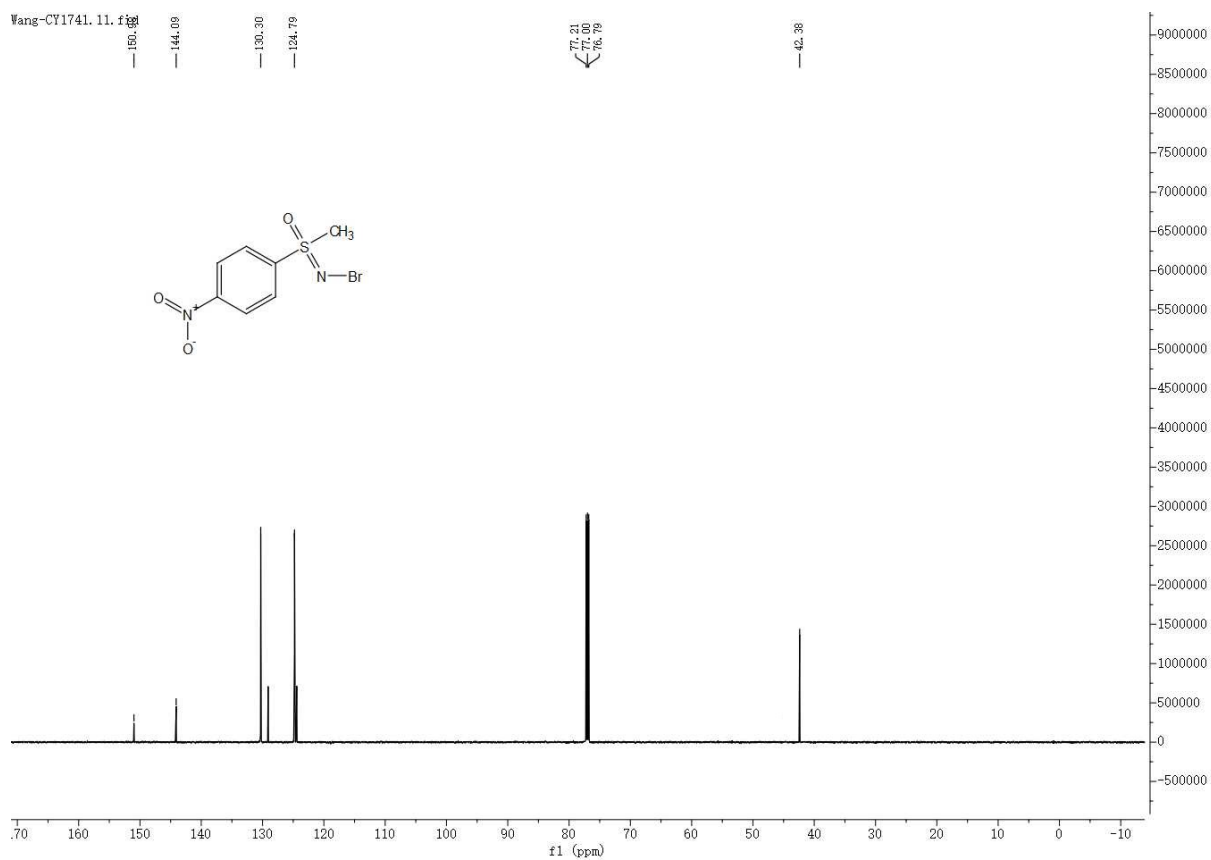
 ^1H NMR spectrum of compound **9f** (600 MHz, CDCl_3)

Wang-CY1739_11.fid

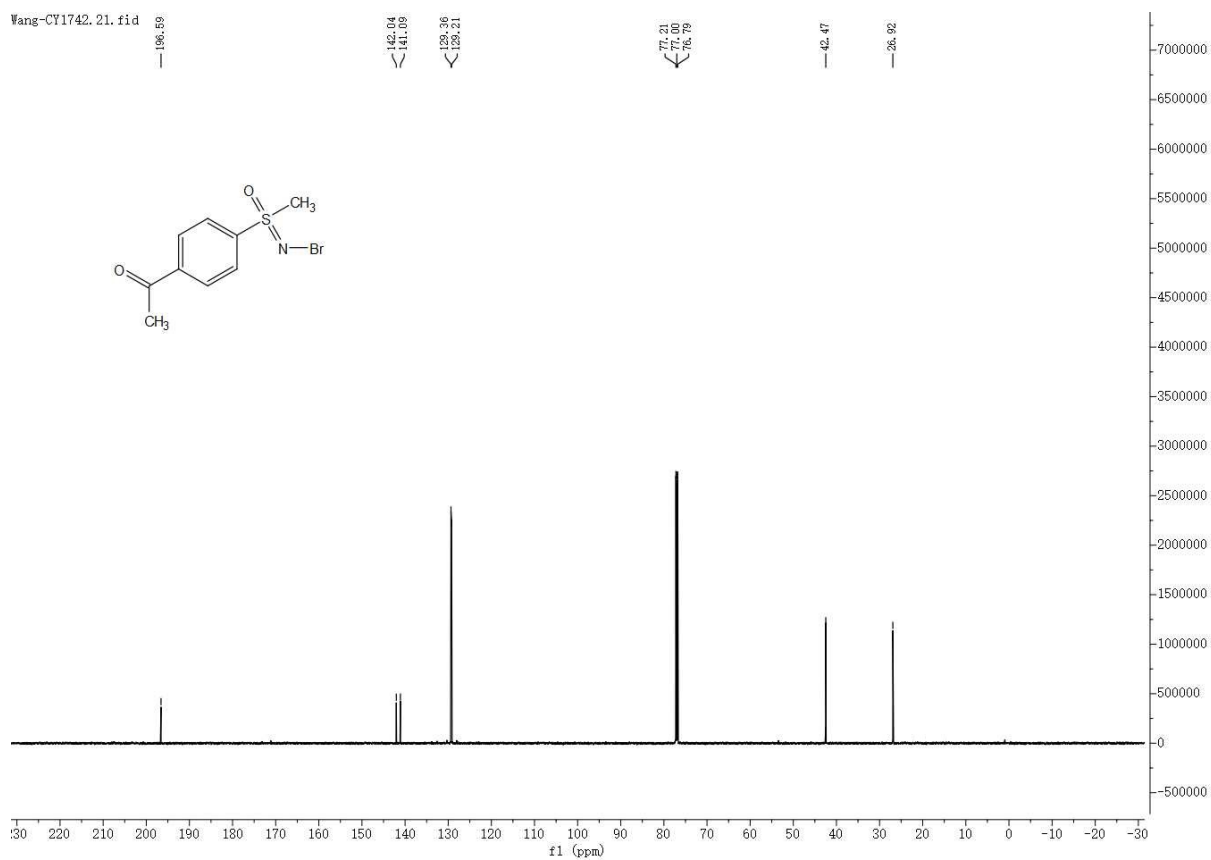
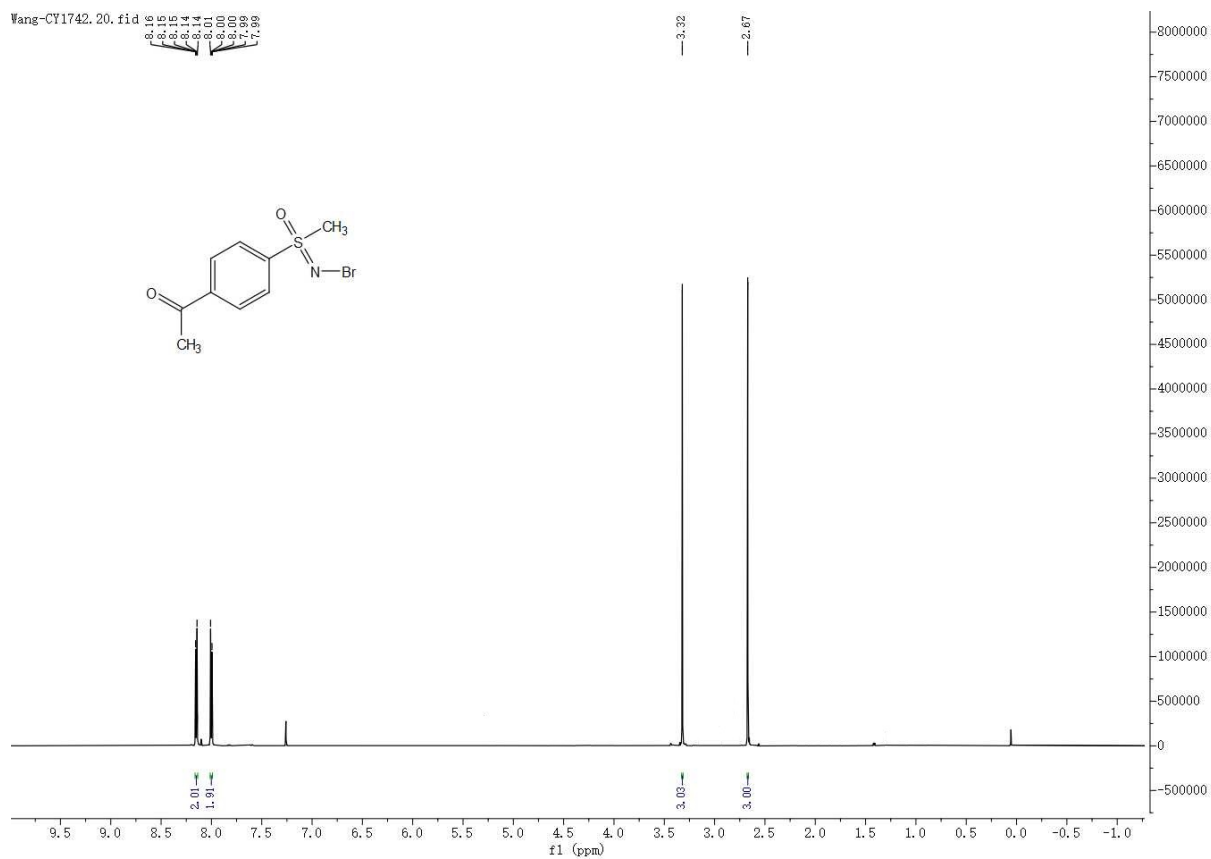
 ^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9f** (151 MHz, CDCl_3)

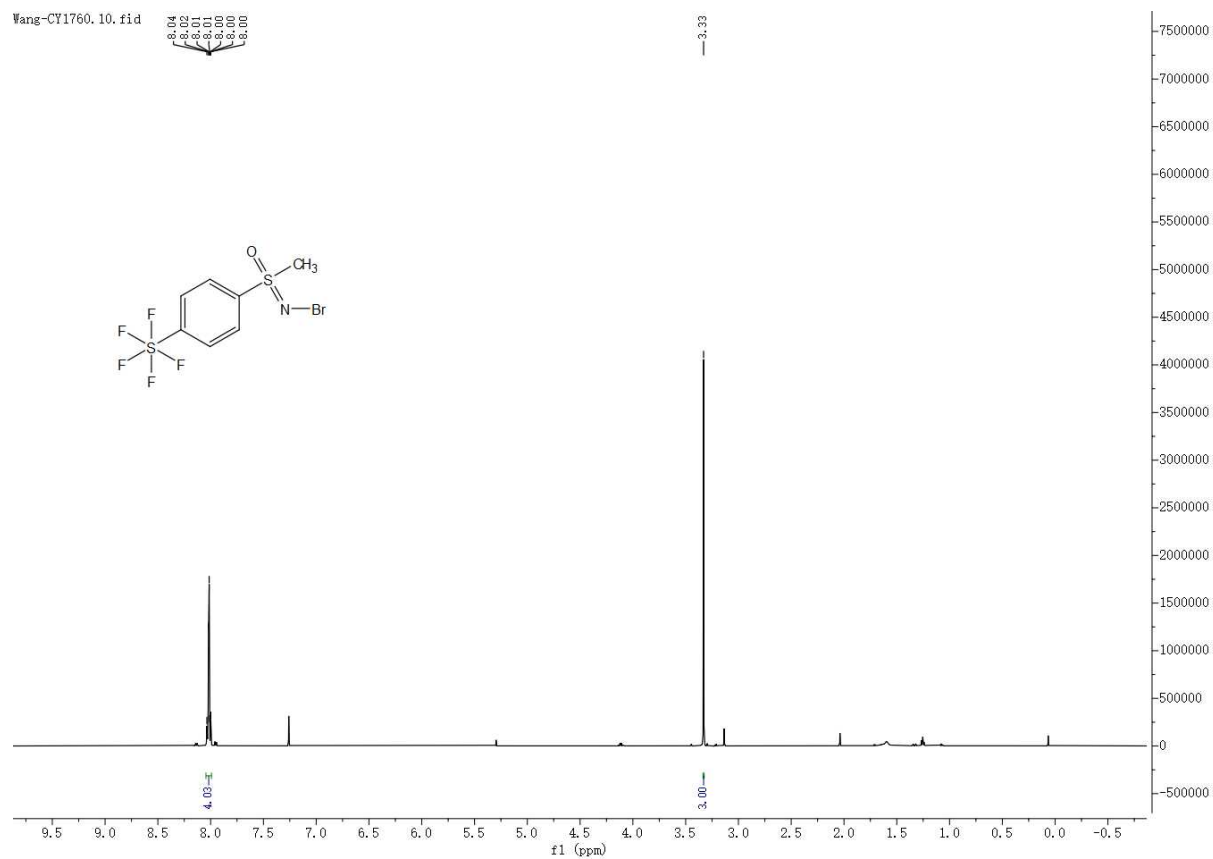


^1H NMR spectrum of compound **9g** (600 MHz, CDCl_3)

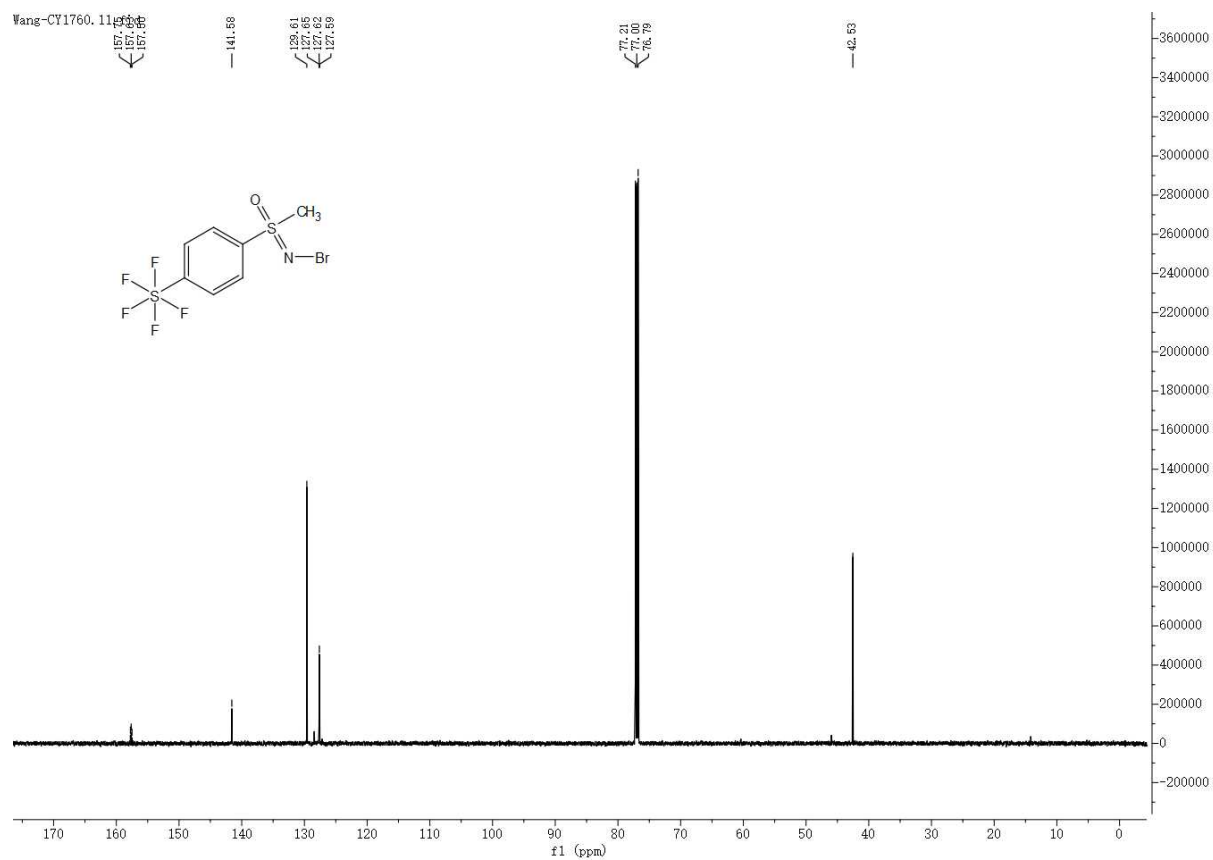


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9g** (151 MHz, CDCl_3)

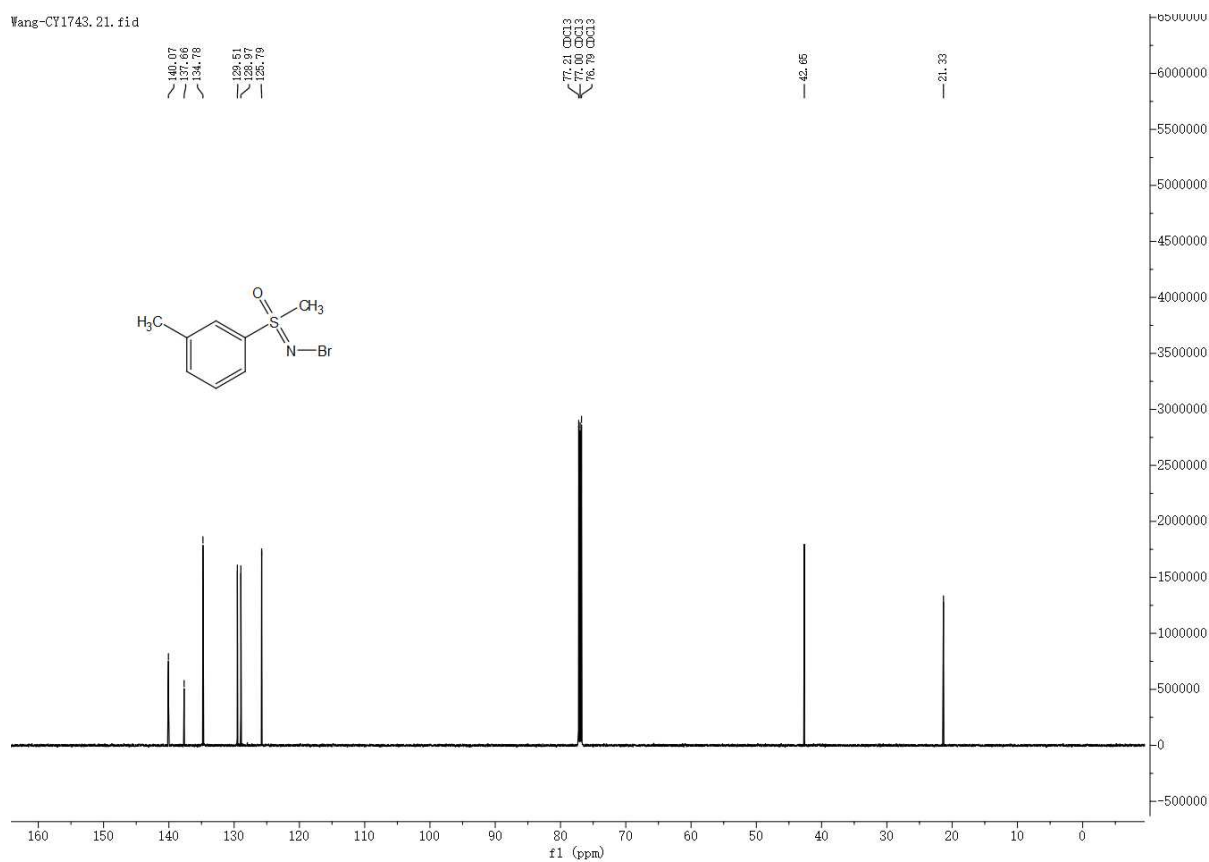
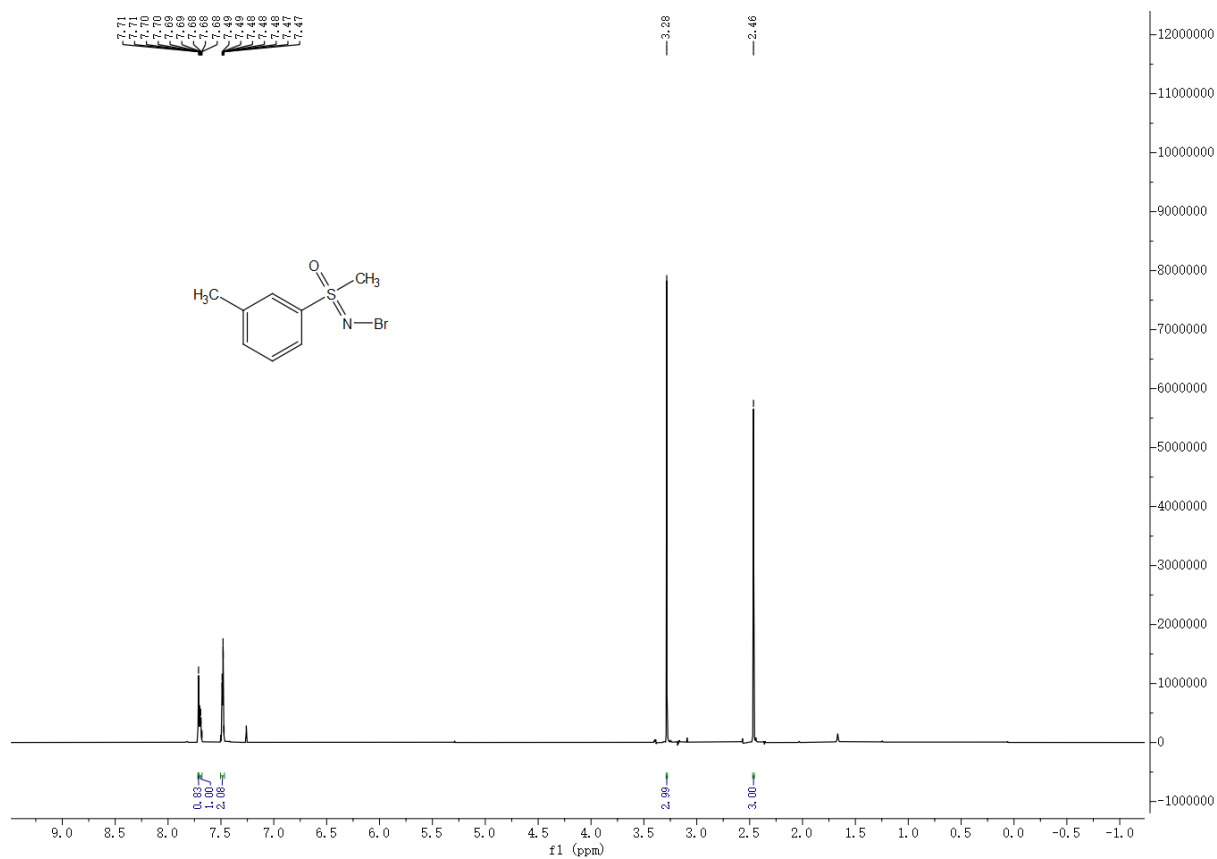


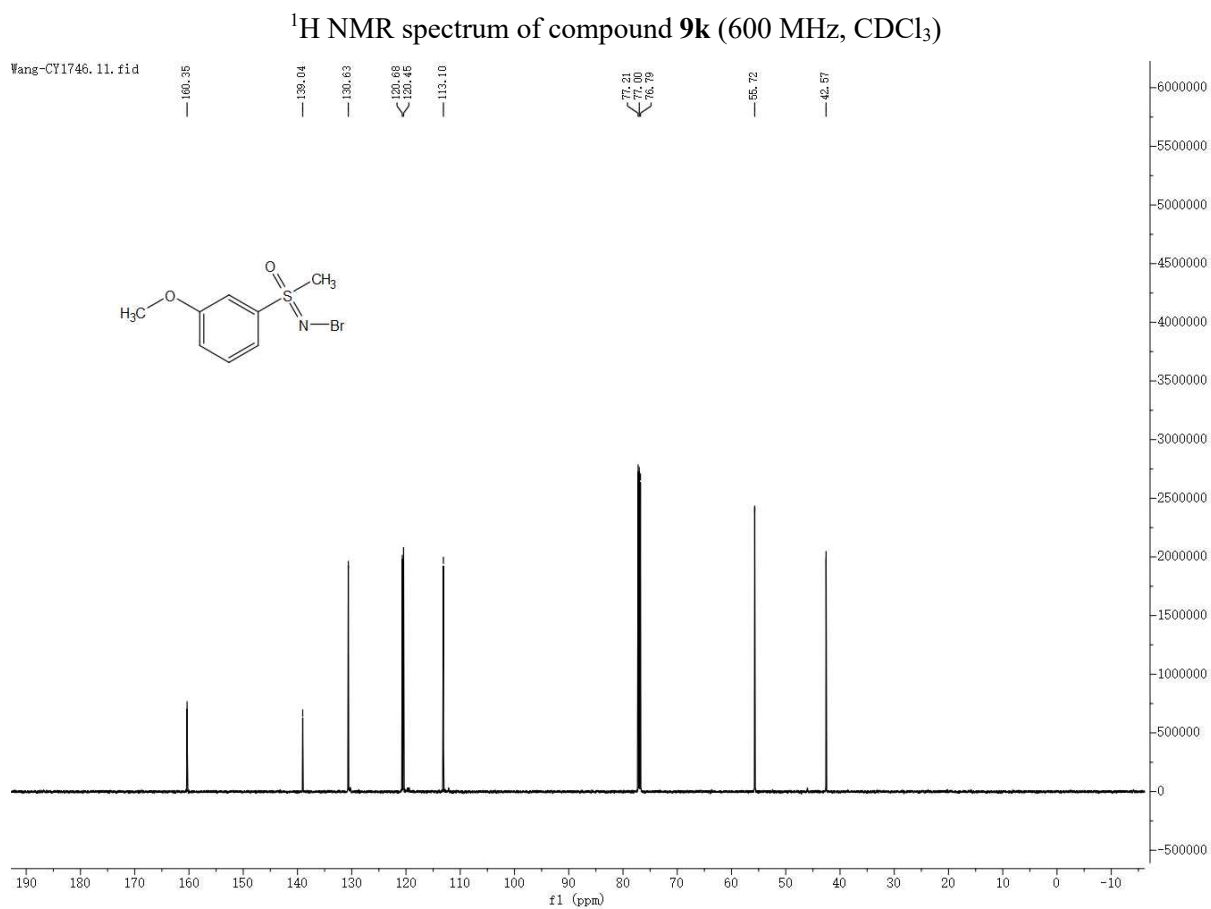
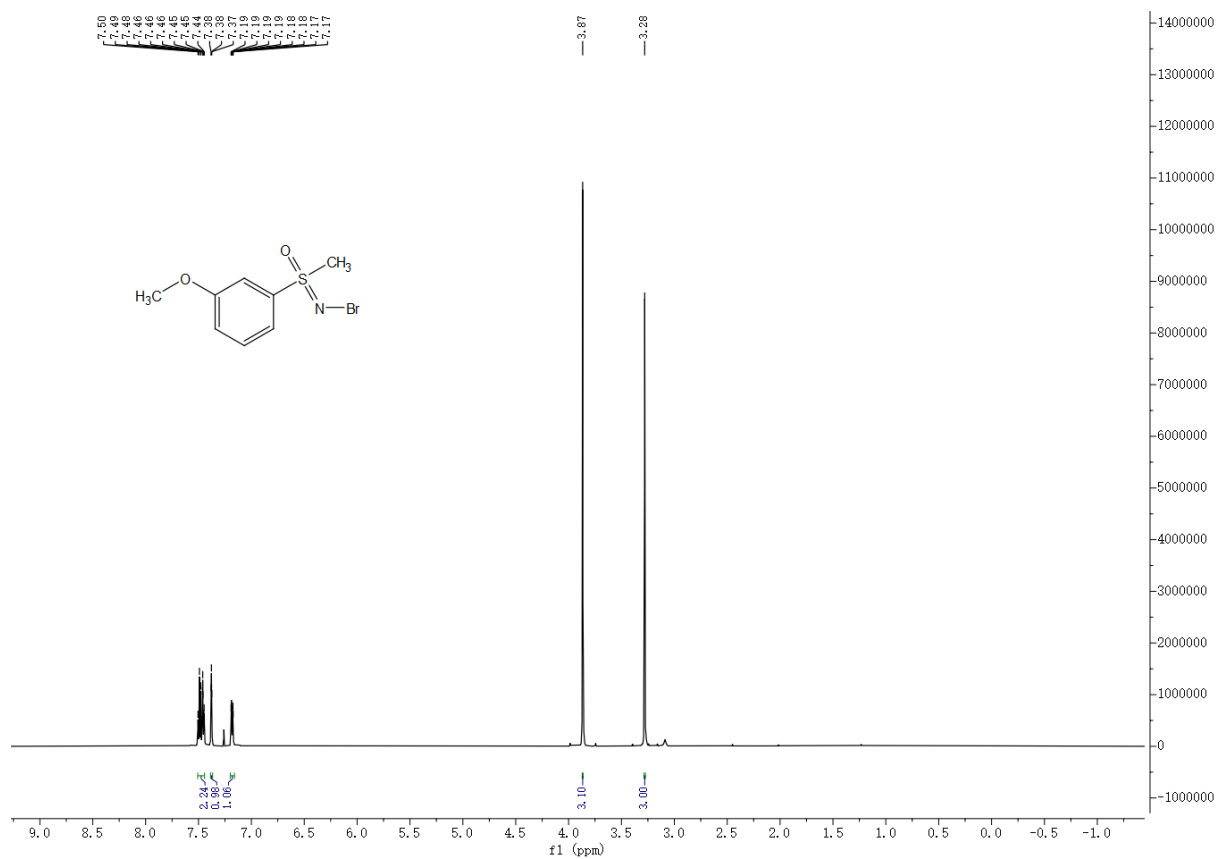


^1H NMR spectrum of compound **9i** (600 MHz, CDCl_3)

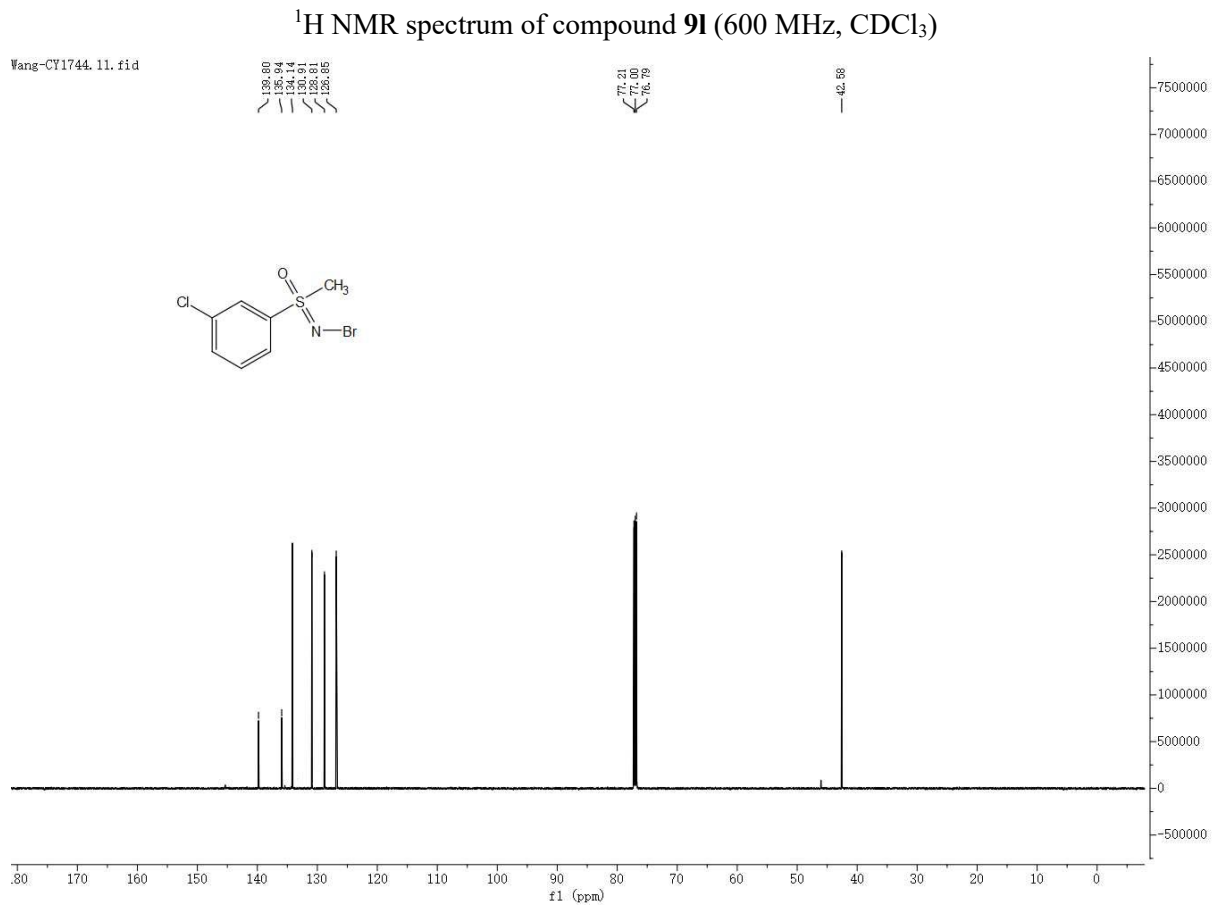
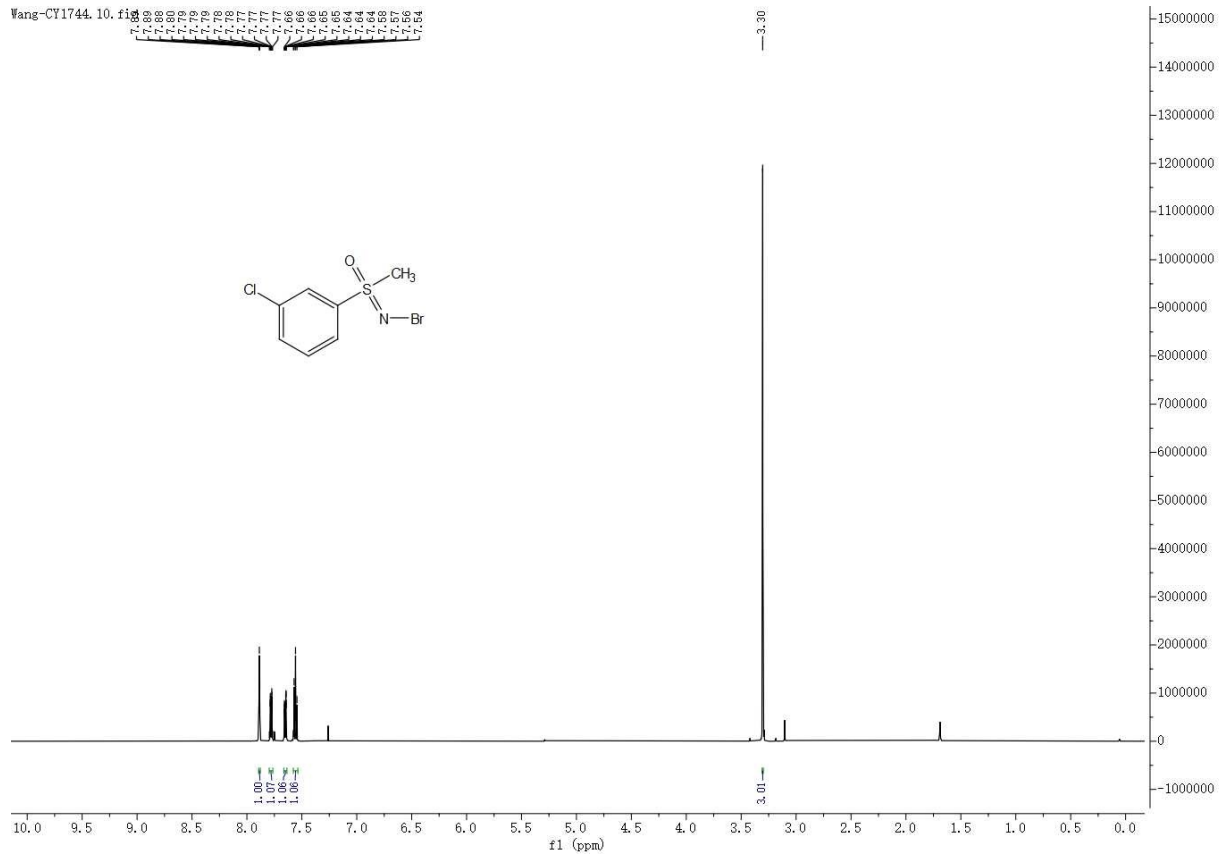


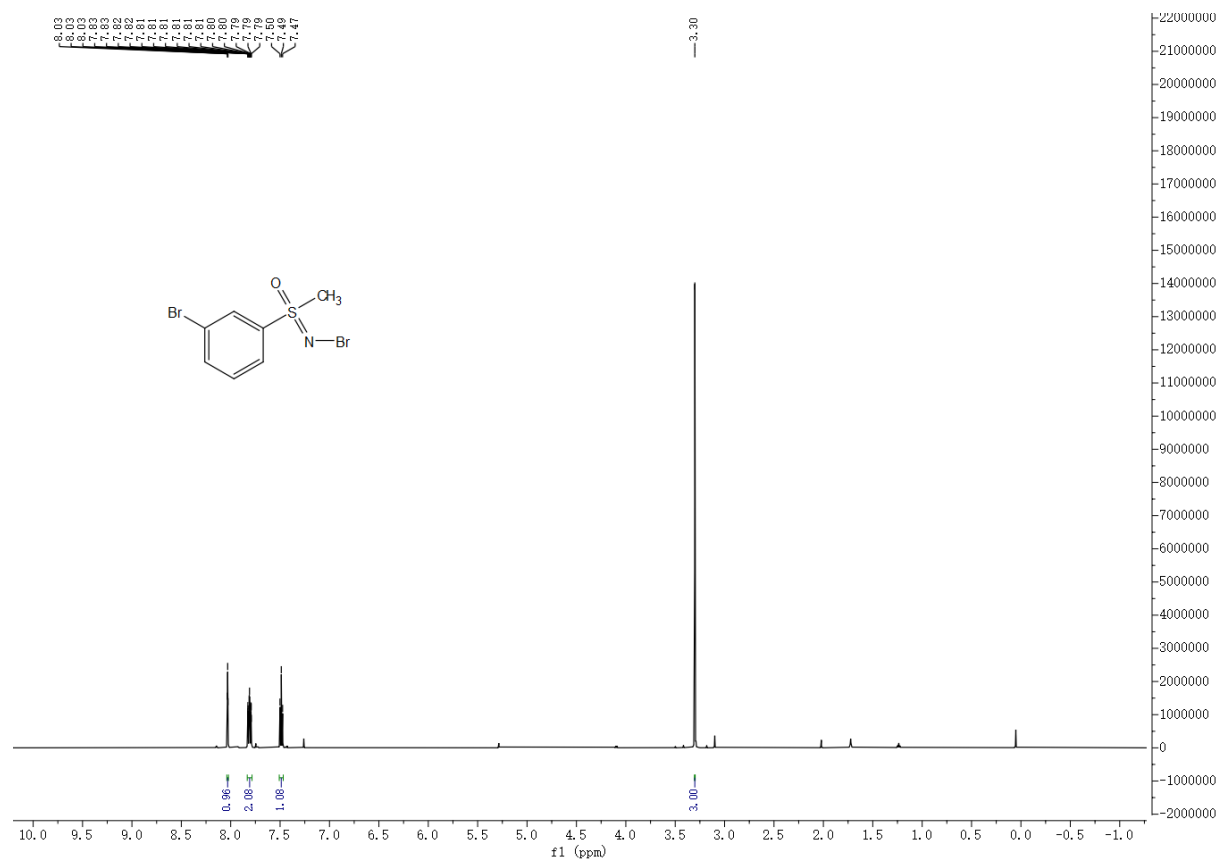
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9i** (151 MHz, CDCl_3)



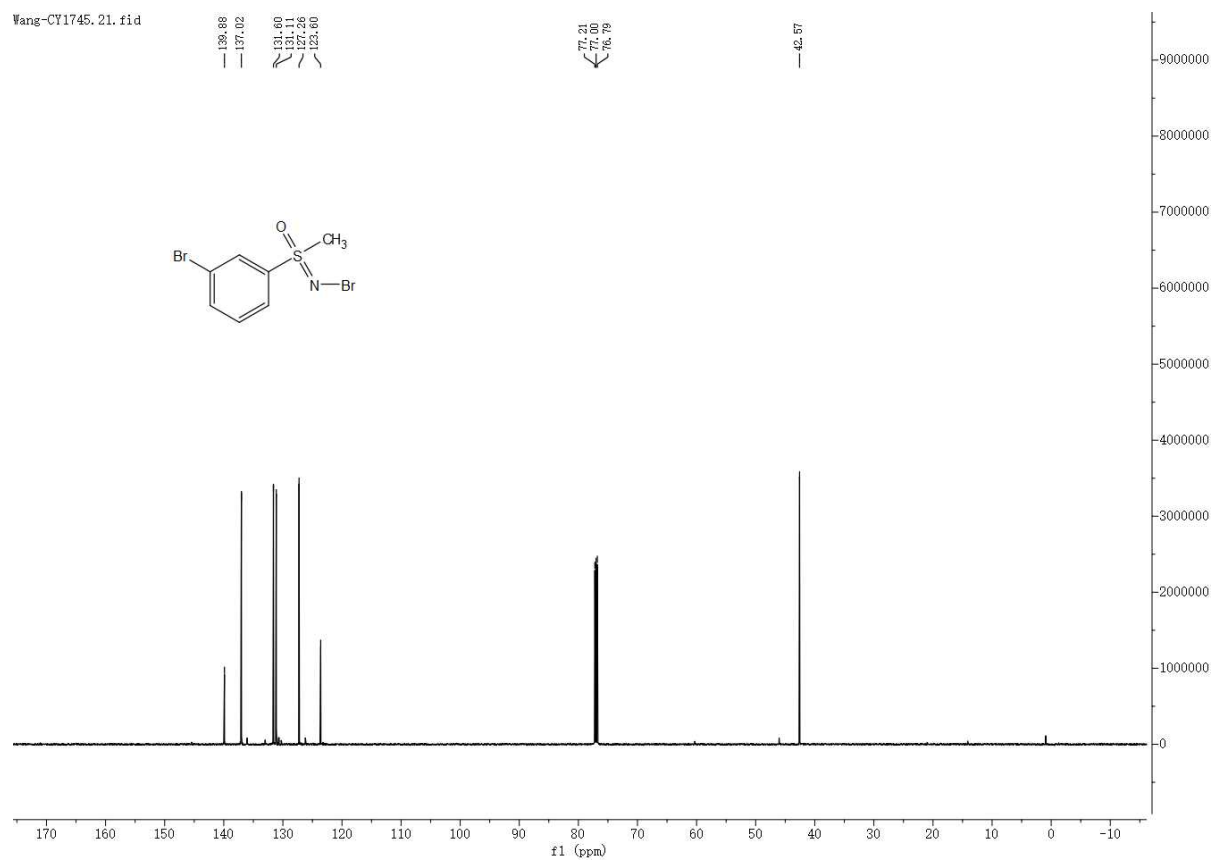


¹³C {¹H} NMR spectrum of compound 9k (151 MHz, CDCl₃)

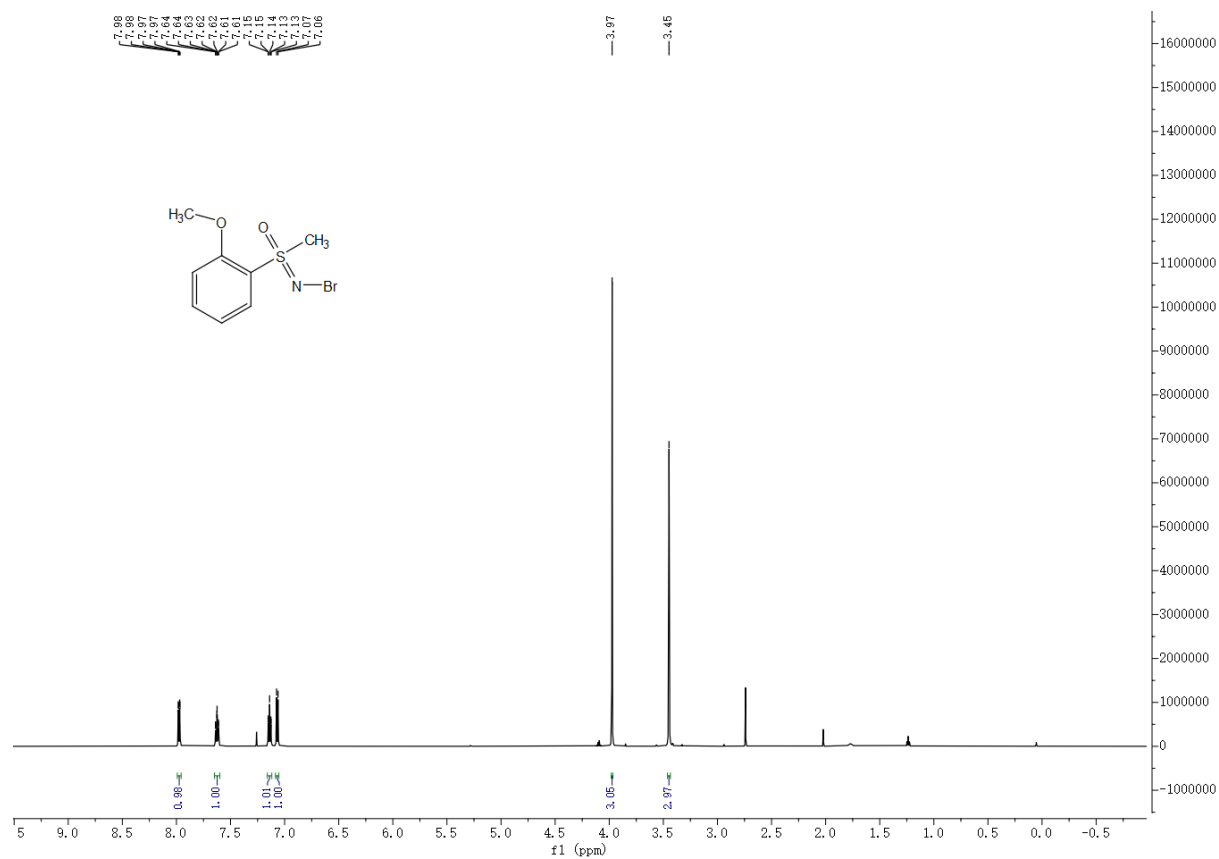




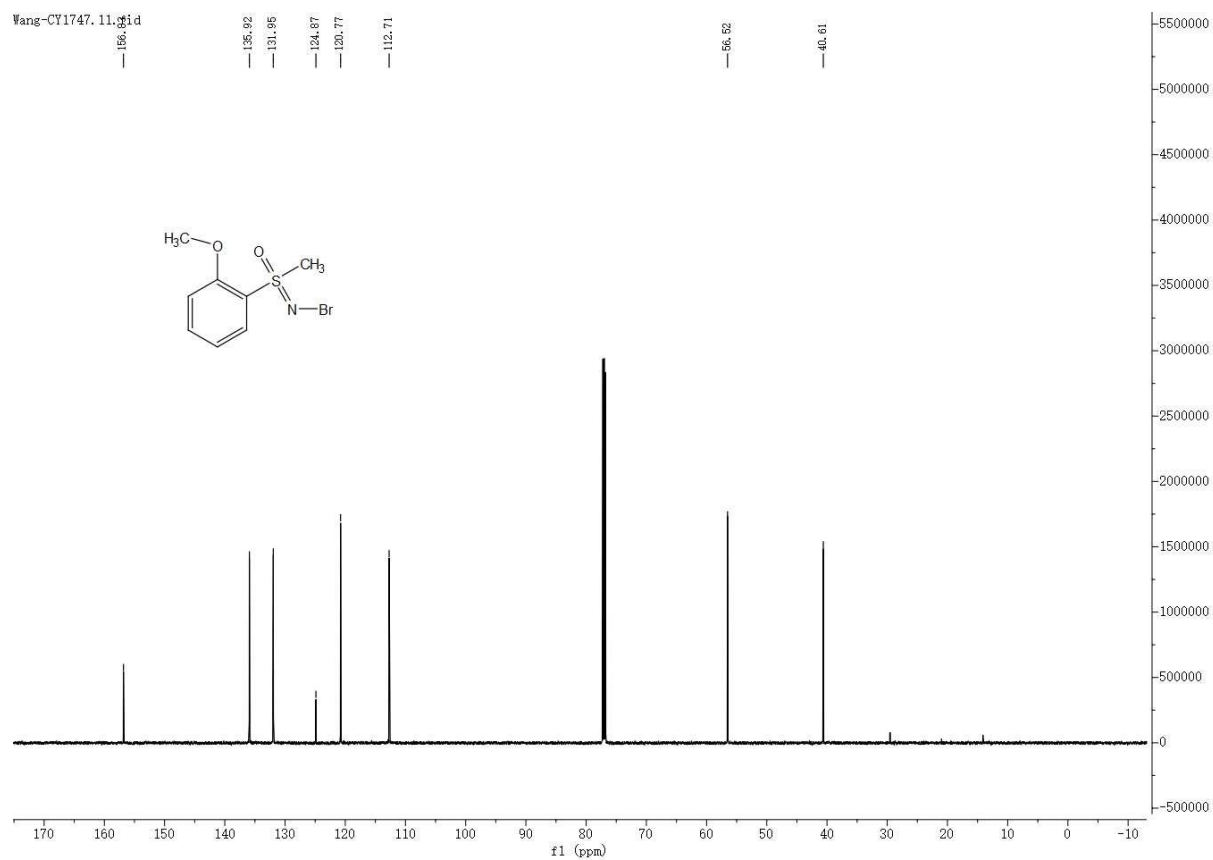
¹H NMR spectrum of compound **9m** (600 MHz, CDCl₃)



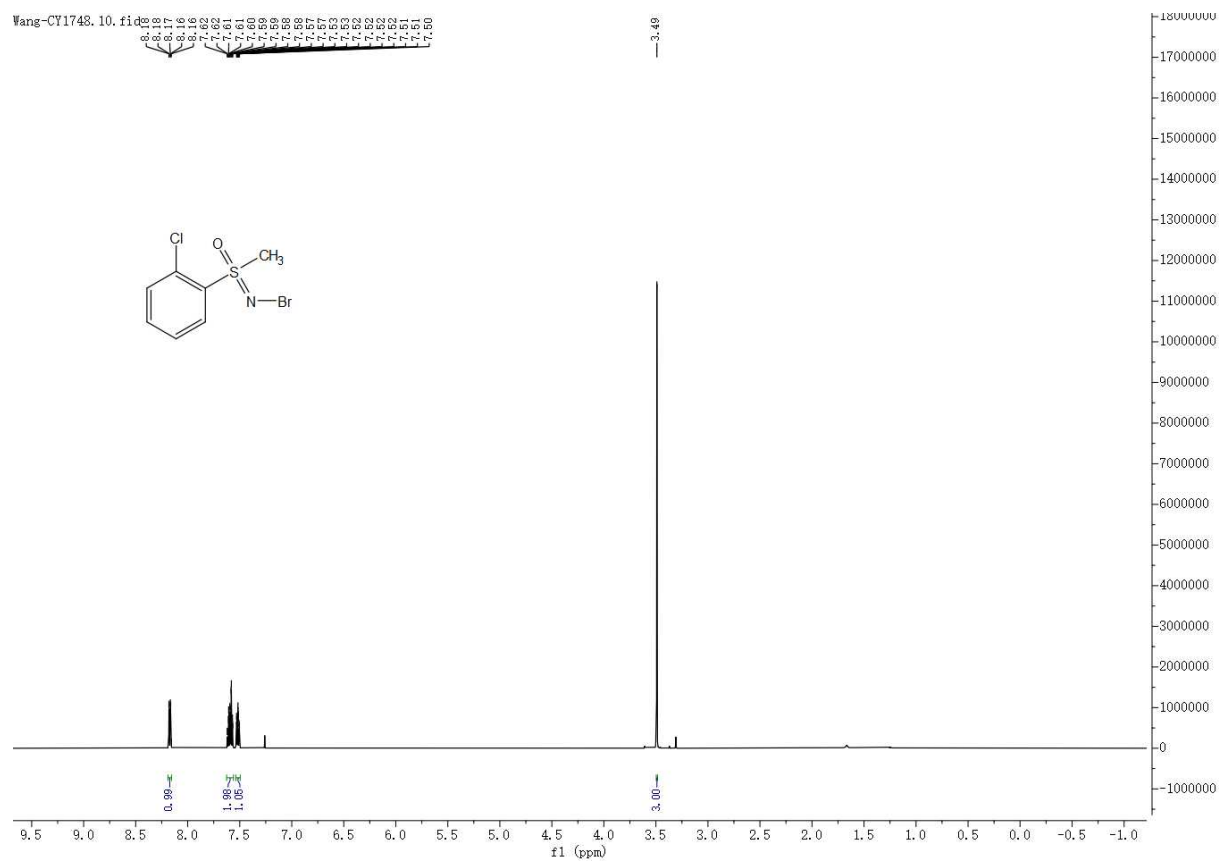
¹³C {¹H} NMR spectrum of compound **9m** (151 MHz, CDCl₃)



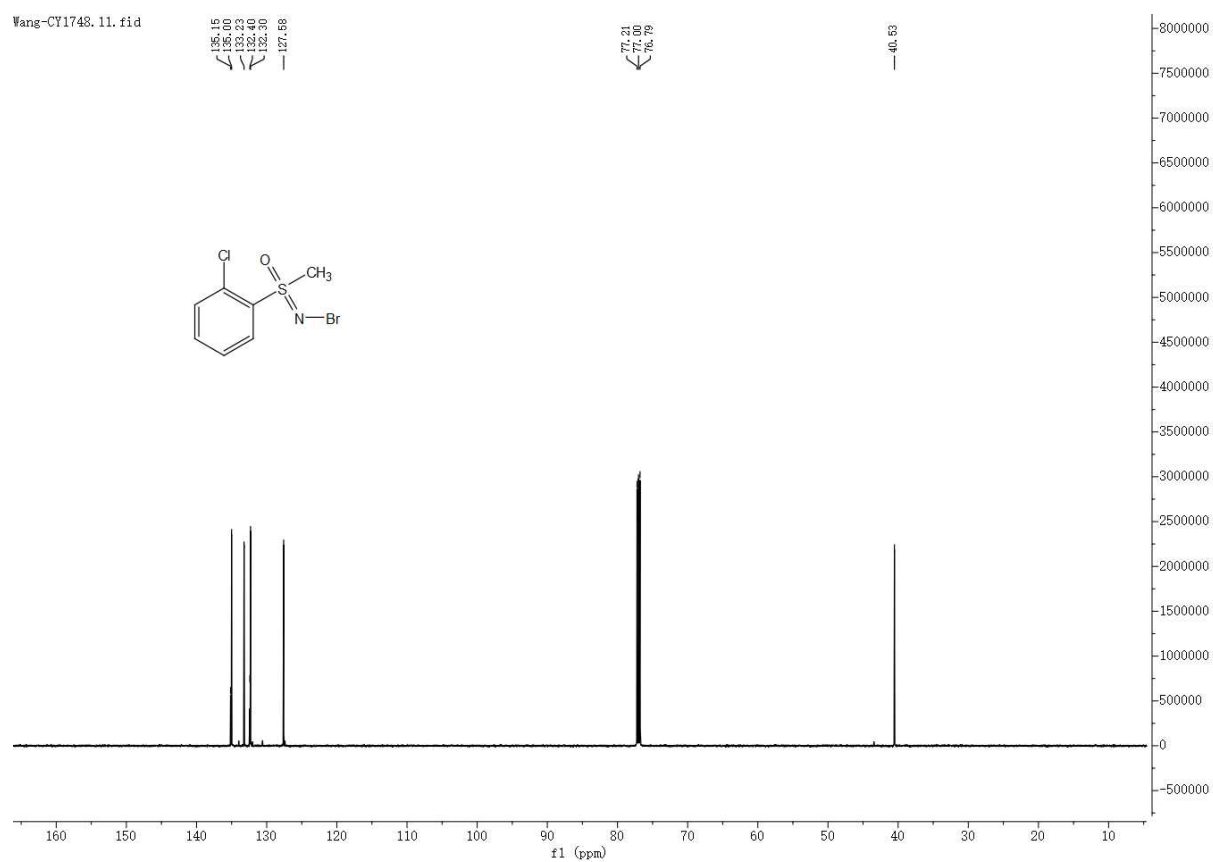
¹H NMR spectrum of compound **9n** (600 MHz, CDCl₃)



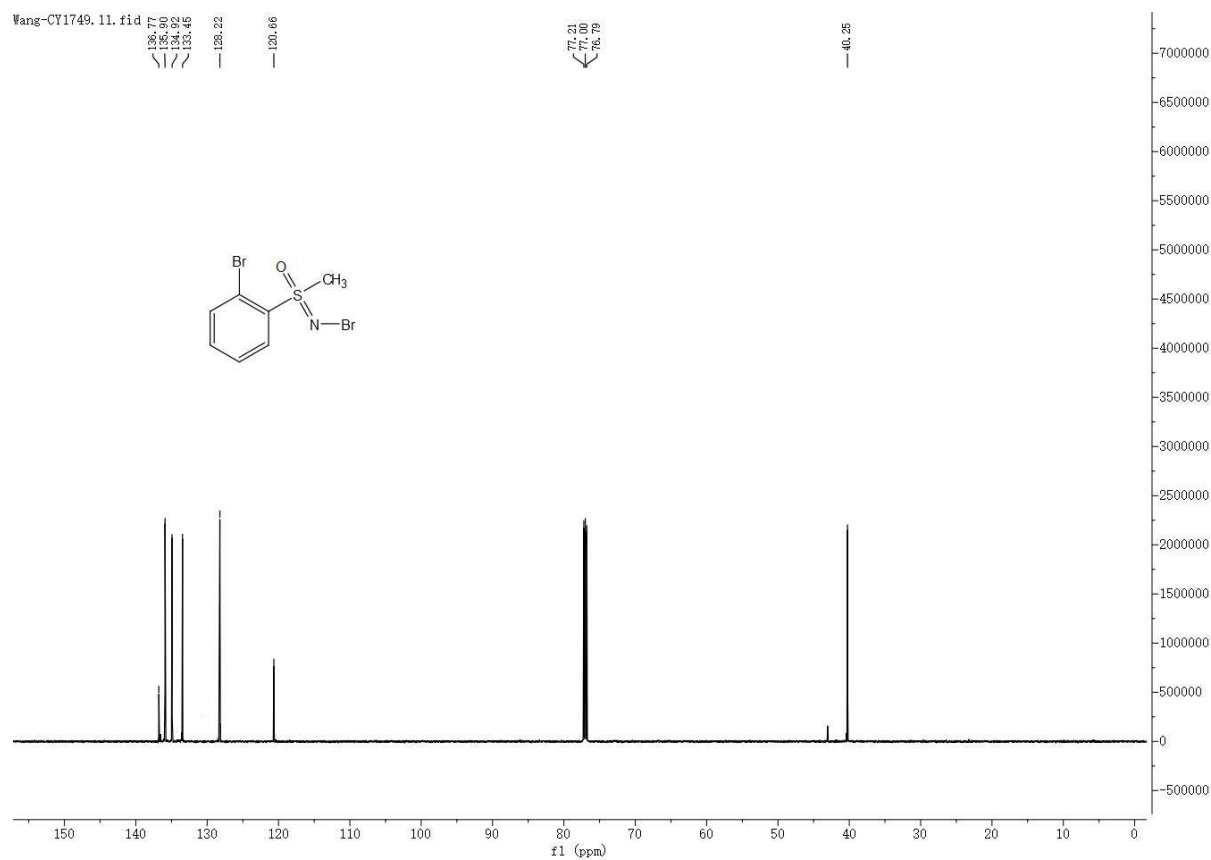
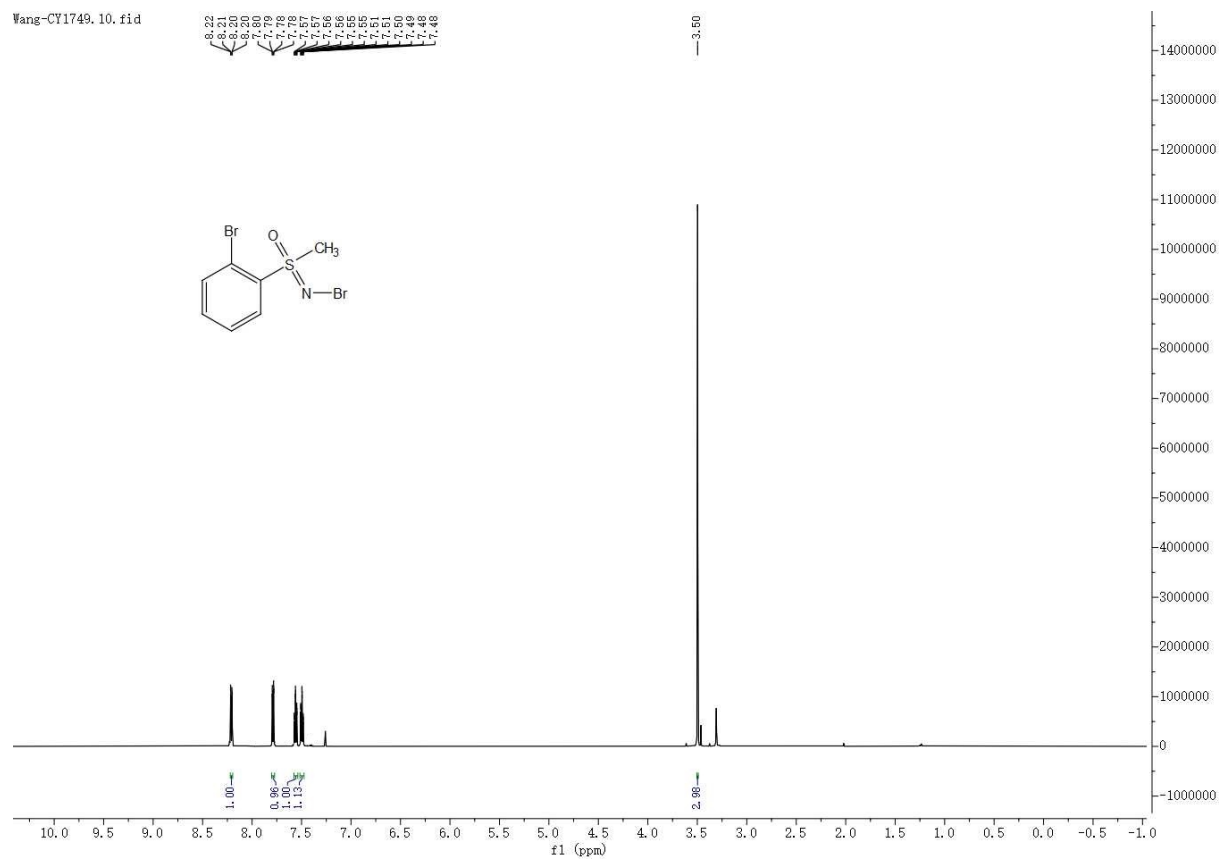
¹³C {¹H} NMR spectrum of compound **9n** (151 MHz, CDCl₃)



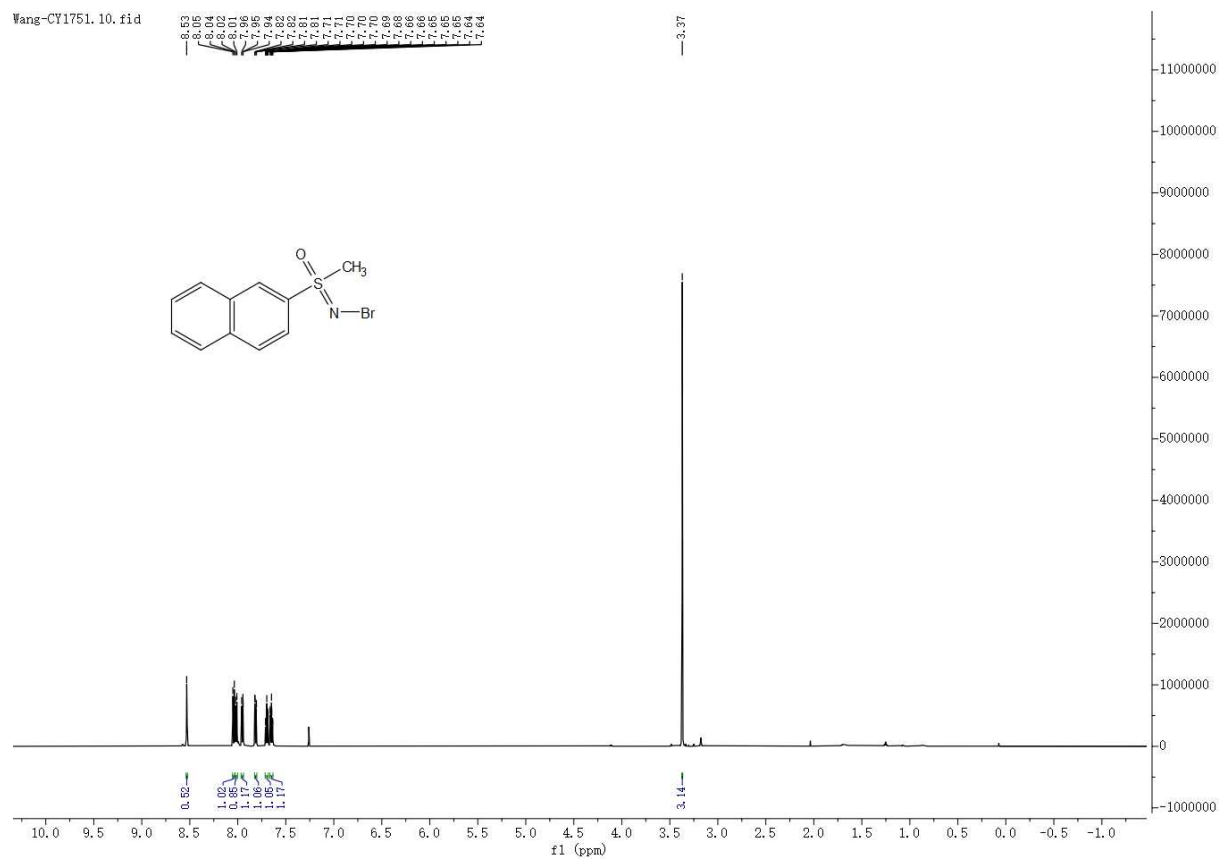
^1H NMR spectrum of compound **9o** (600 MHz, CDCl_3)



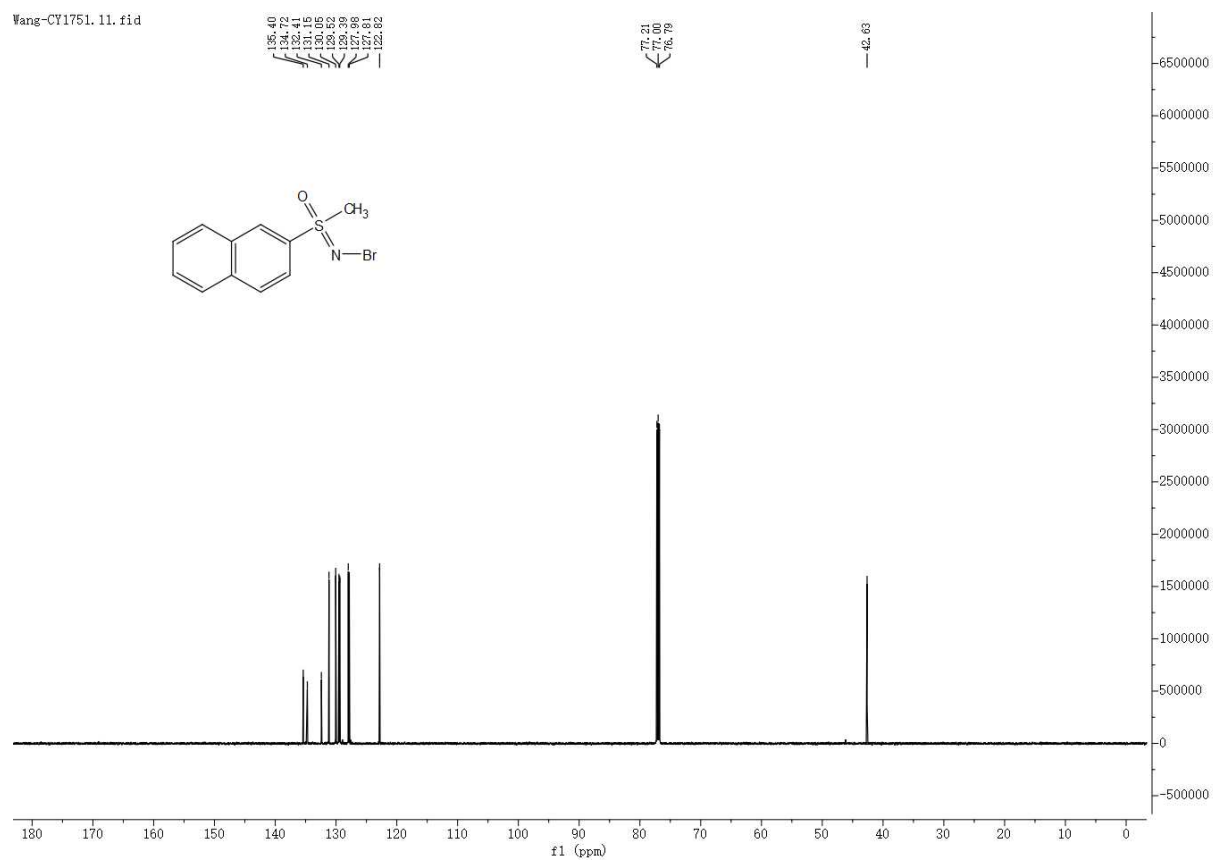
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9o** (151 MHz, CDCl_3)



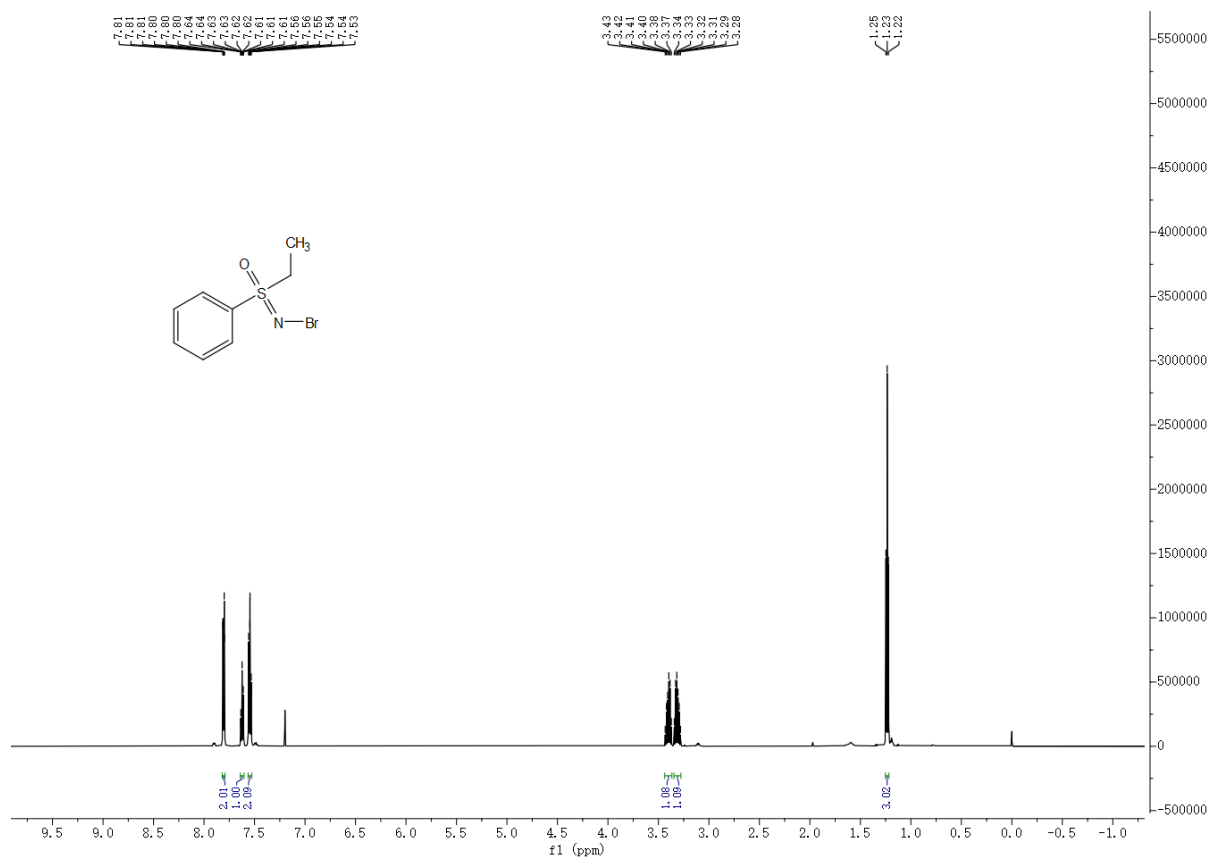
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9p** (151 MHz, CDCl_3)



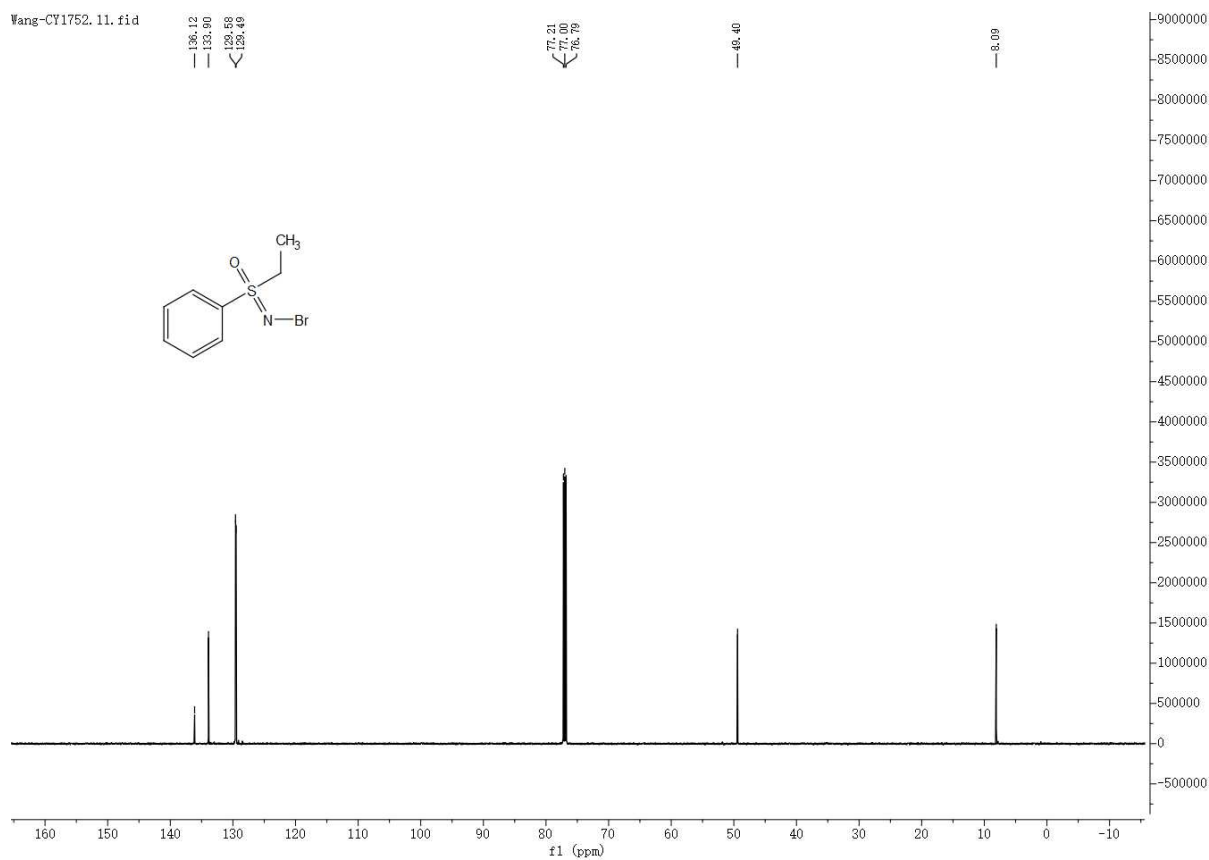
^1H NMR spectrum of compound **9r** (600 MHz, CDCl_3)



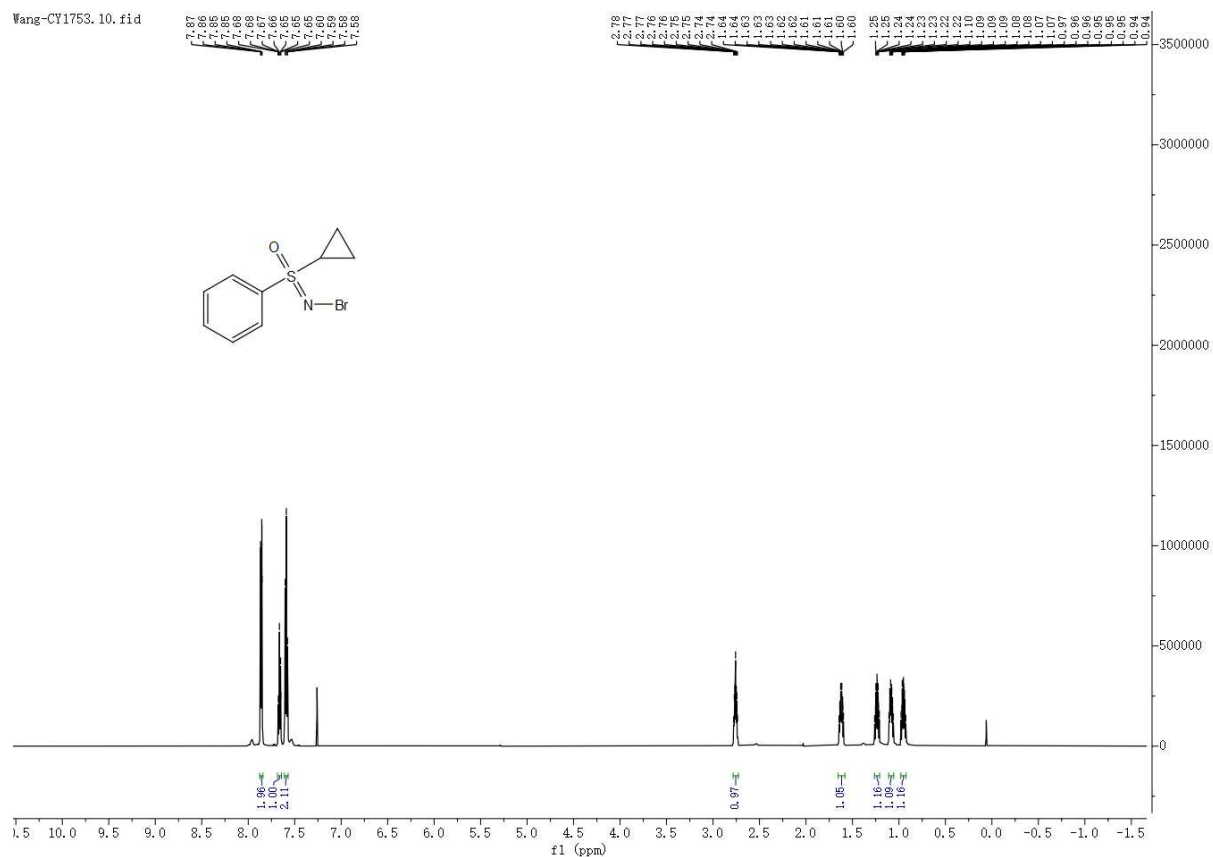
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9r** (151 MHz, CDCl_3)



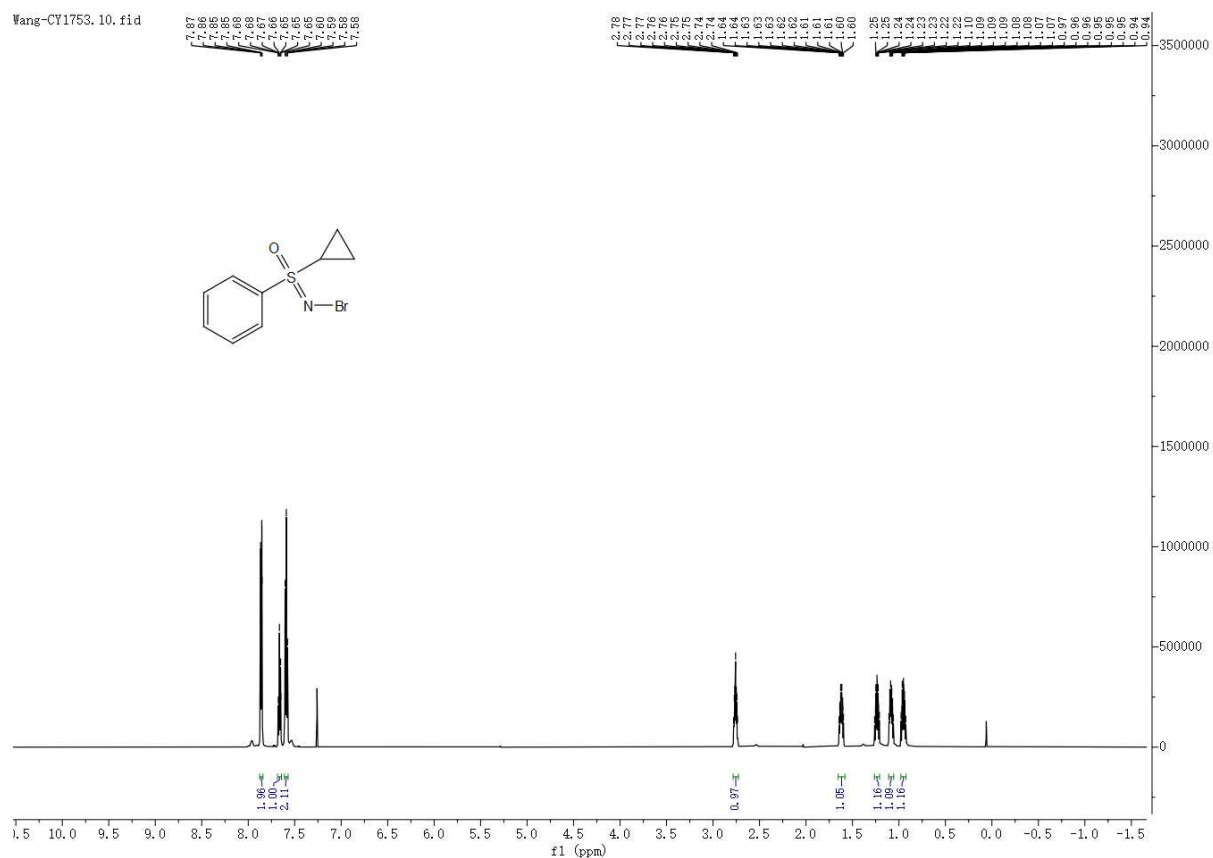
¹H NMR spectrum of compound **9s** (600 MHz, CDCl₃)



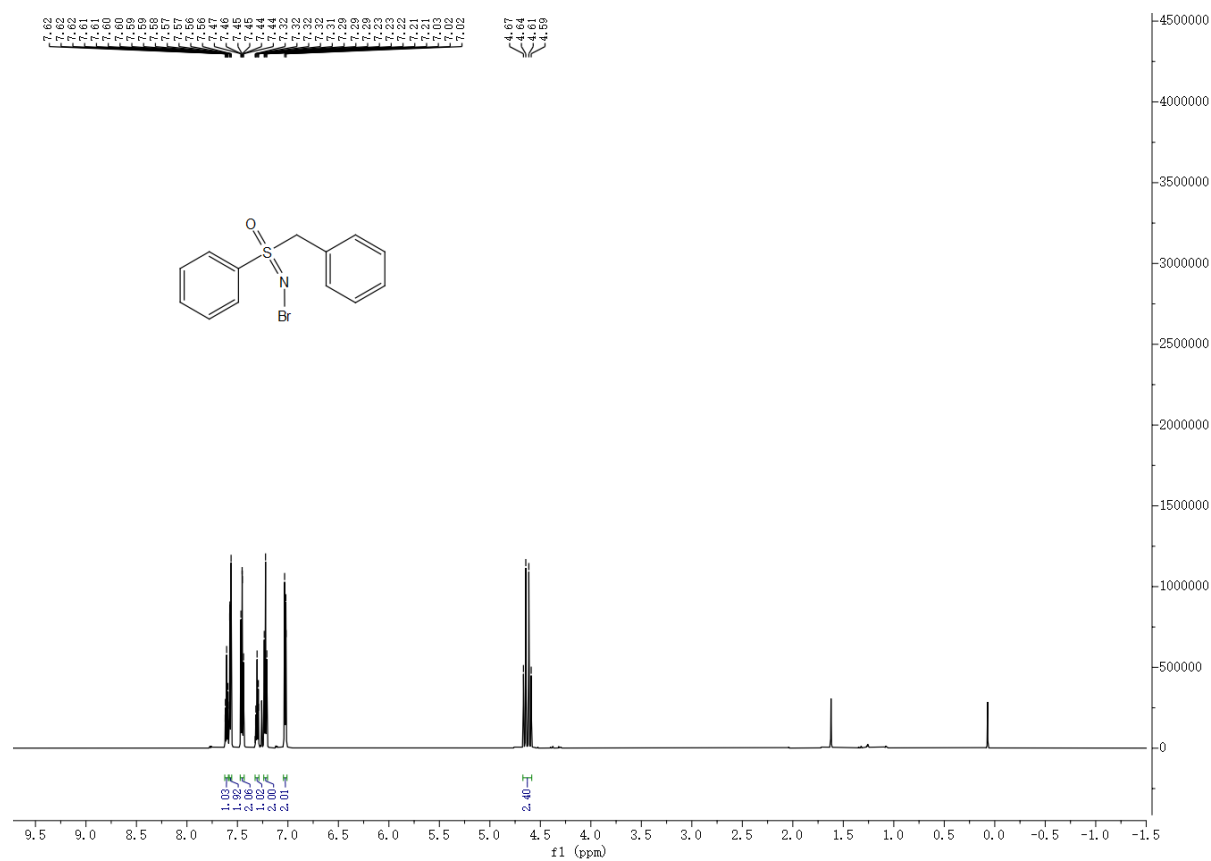
¹³C {¹H} NMR spectrum of compound **9s** (151 MHz, CDCl₃)



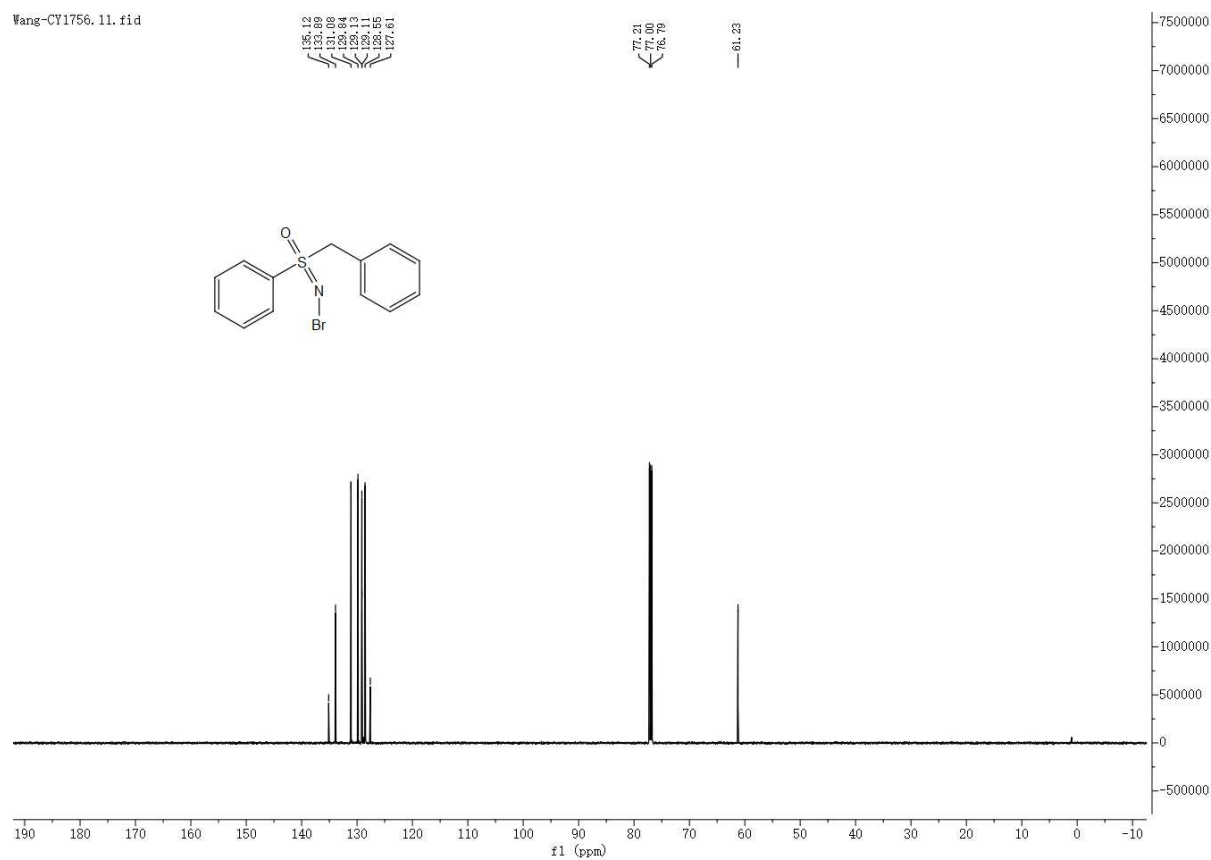
^1H NMR spectrum of compound **9t** (600 MHz, CDCl_3)



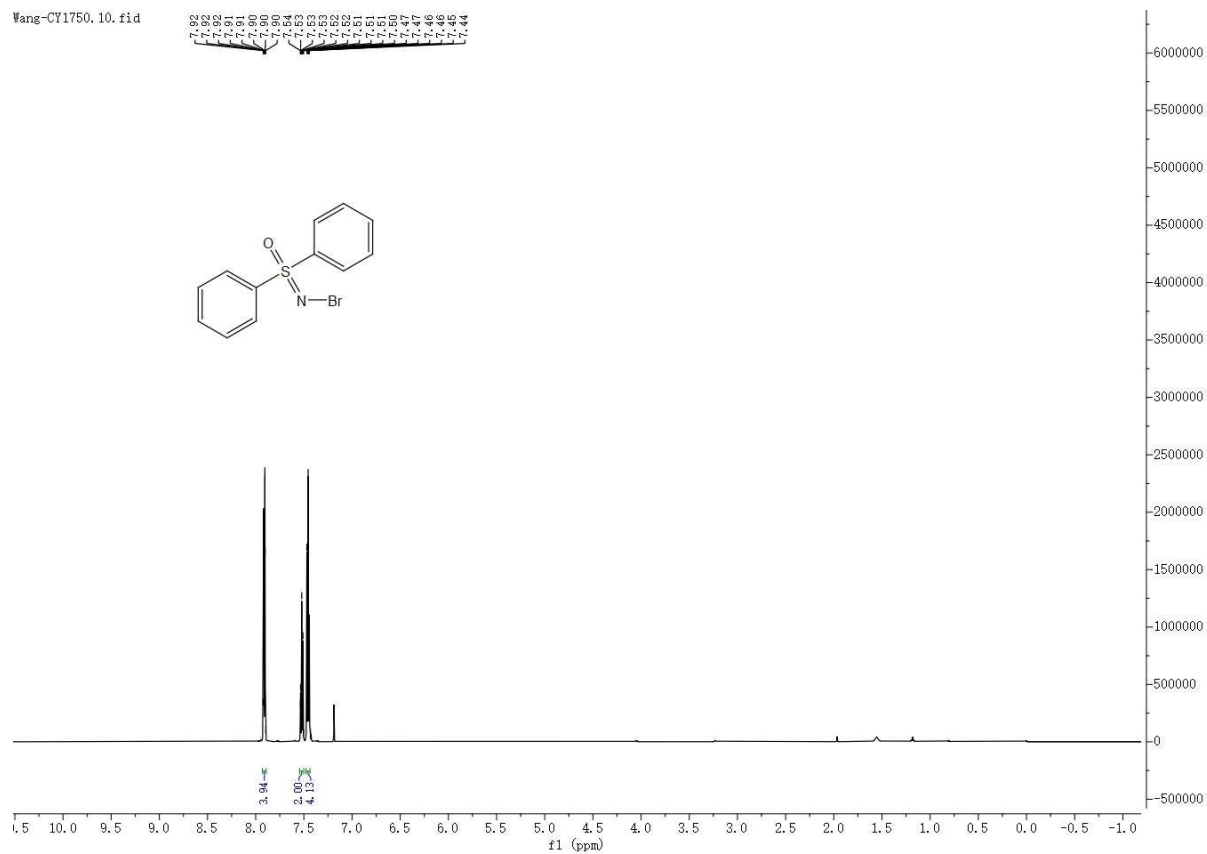
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9t** (151 MHz, CDCl_3)



^1H NMR spectrum of compound **9u** (600 MHz, CDCl_3)



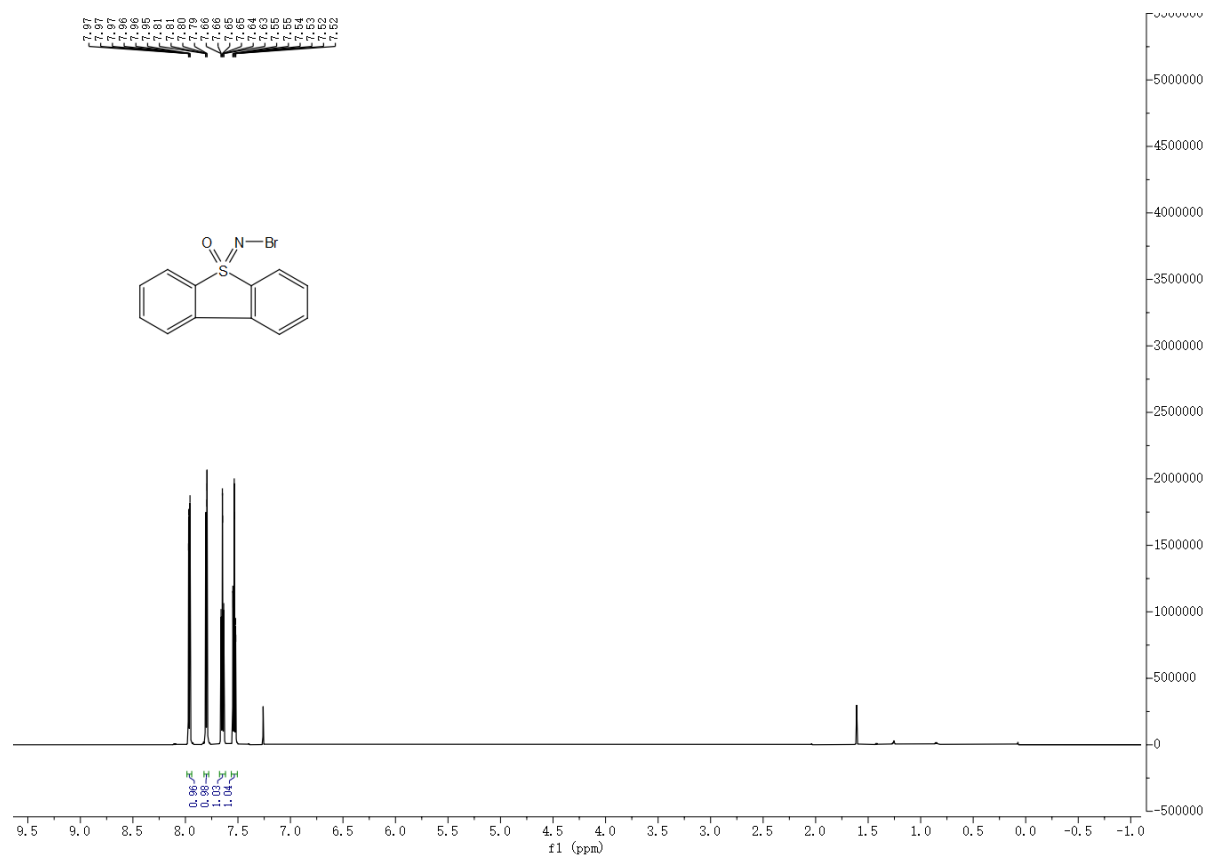
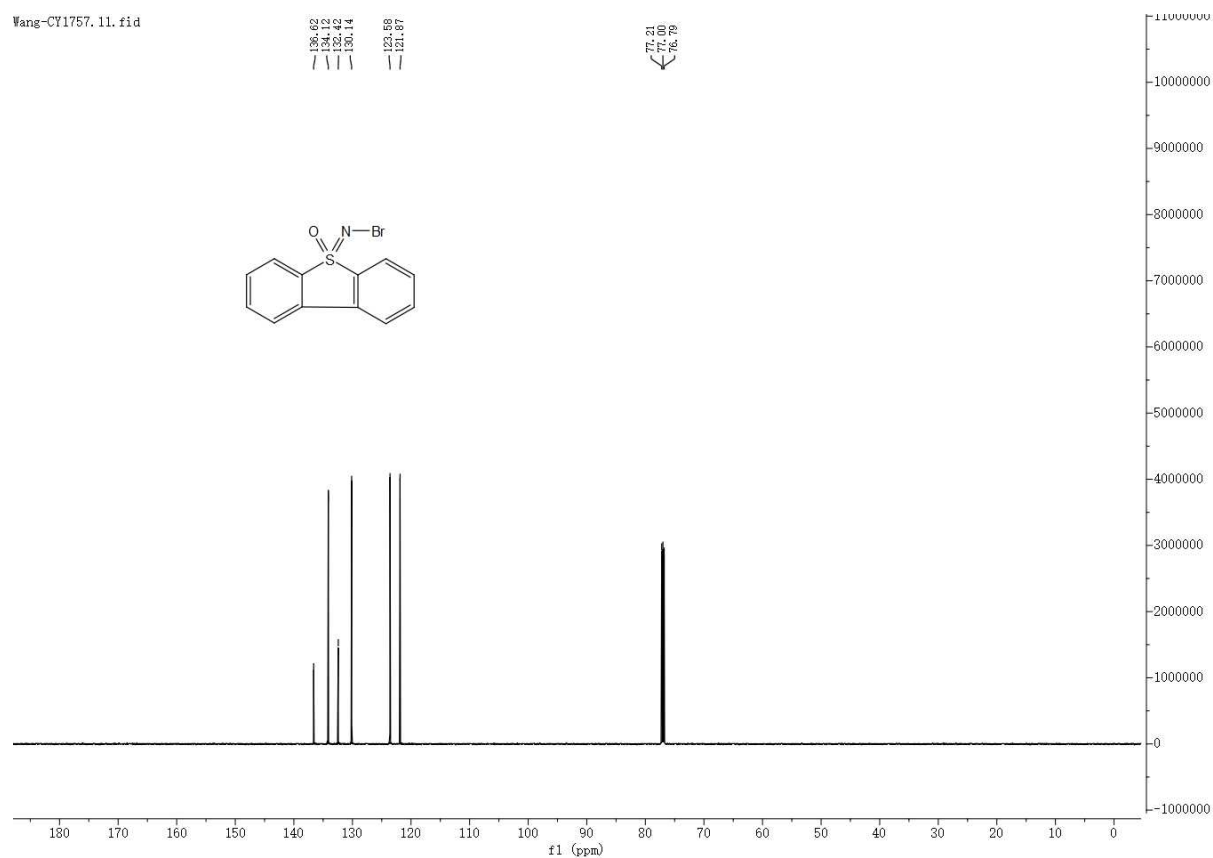
^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9u** (151 MHz, CDCl_3)

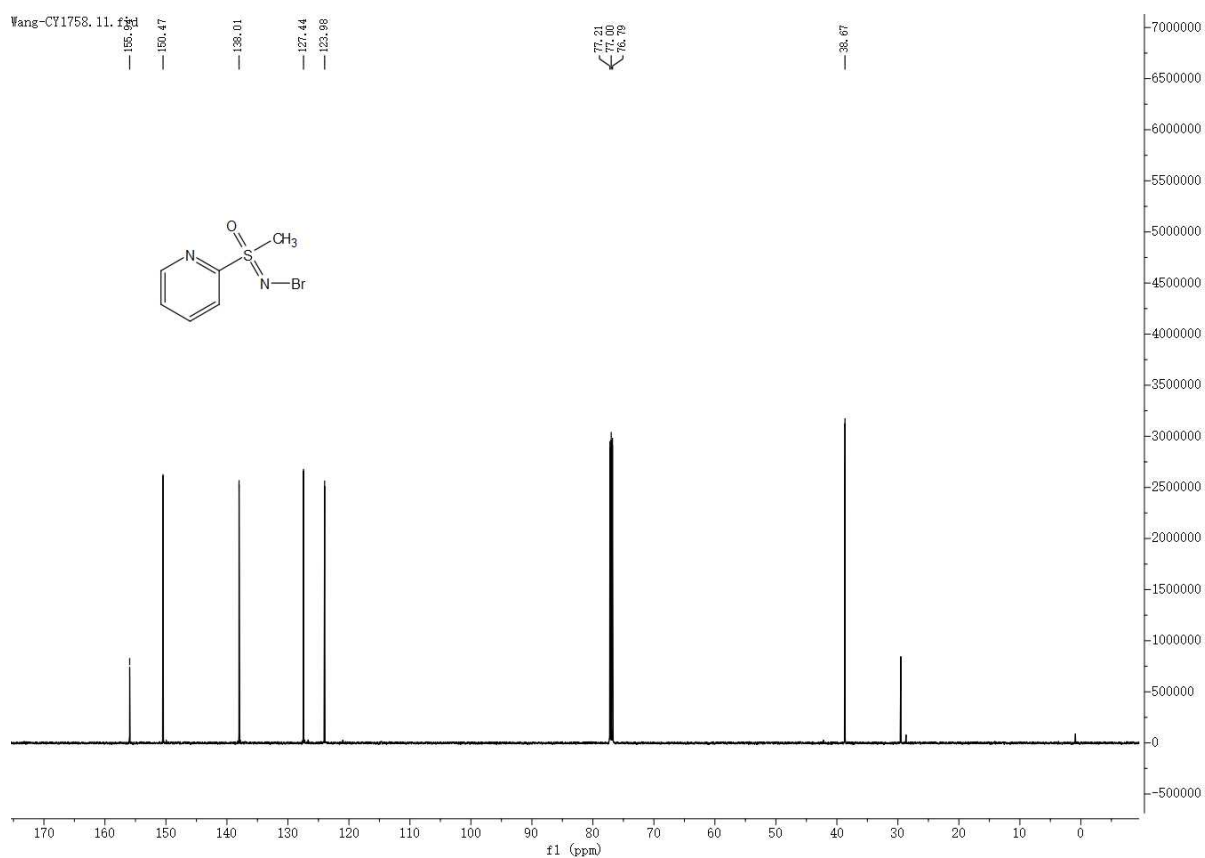
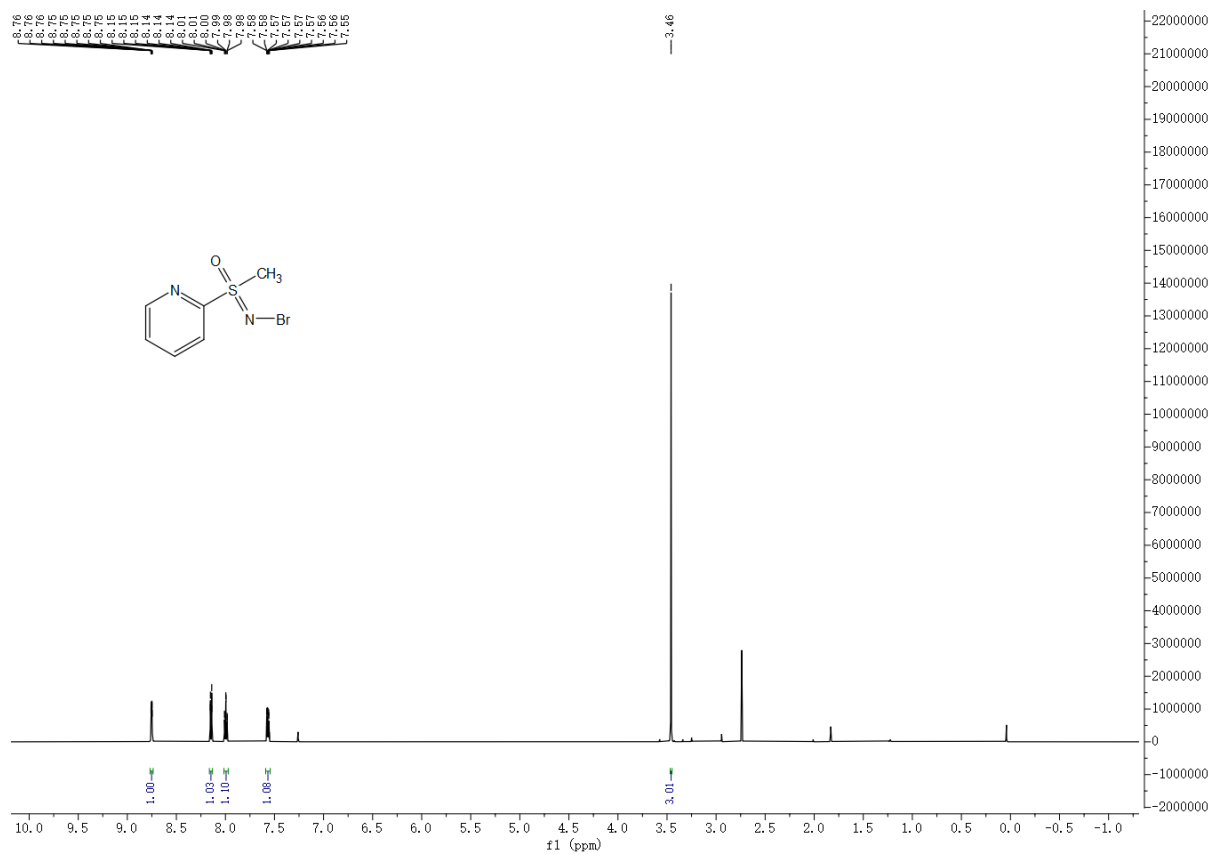


^1H NMR spectrum of compound **9w** (600 MHz, CDCl_3)

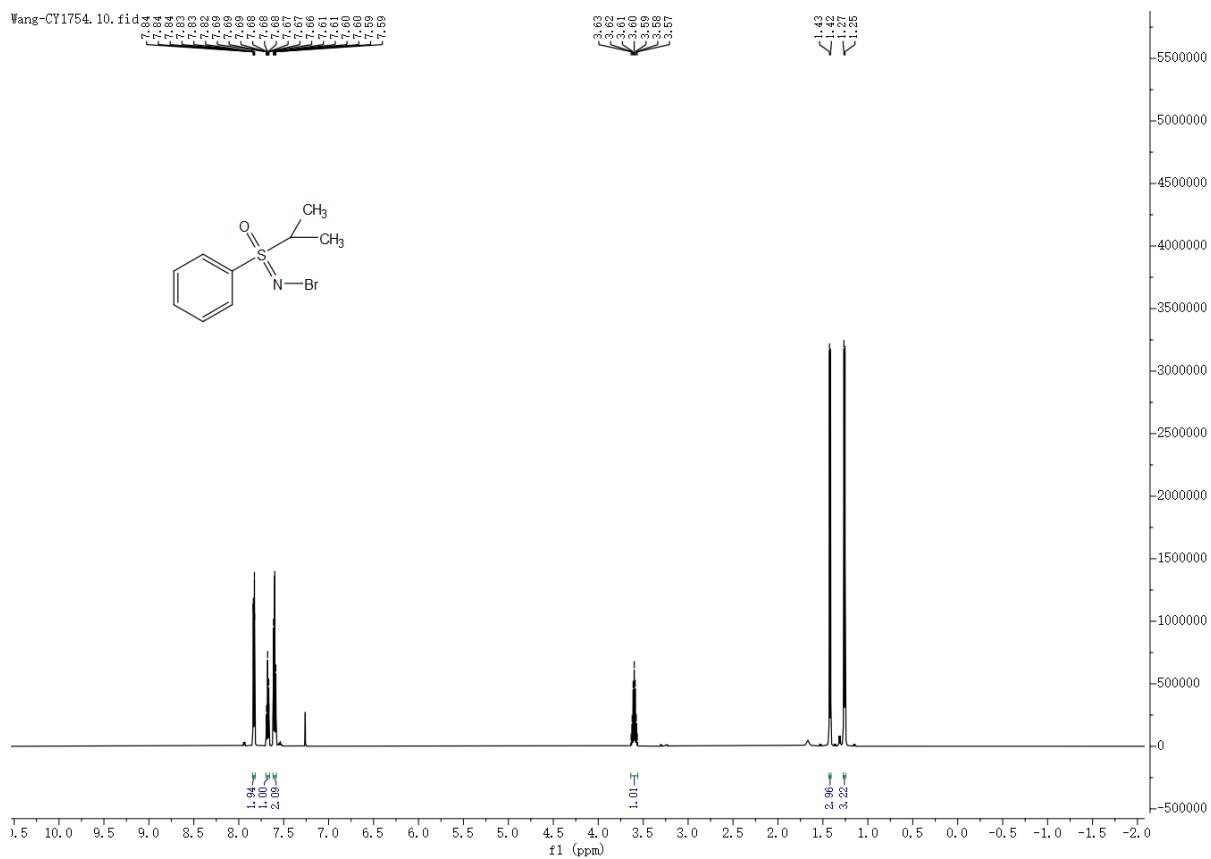


^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9w** (151 MHz, CDCl_3)

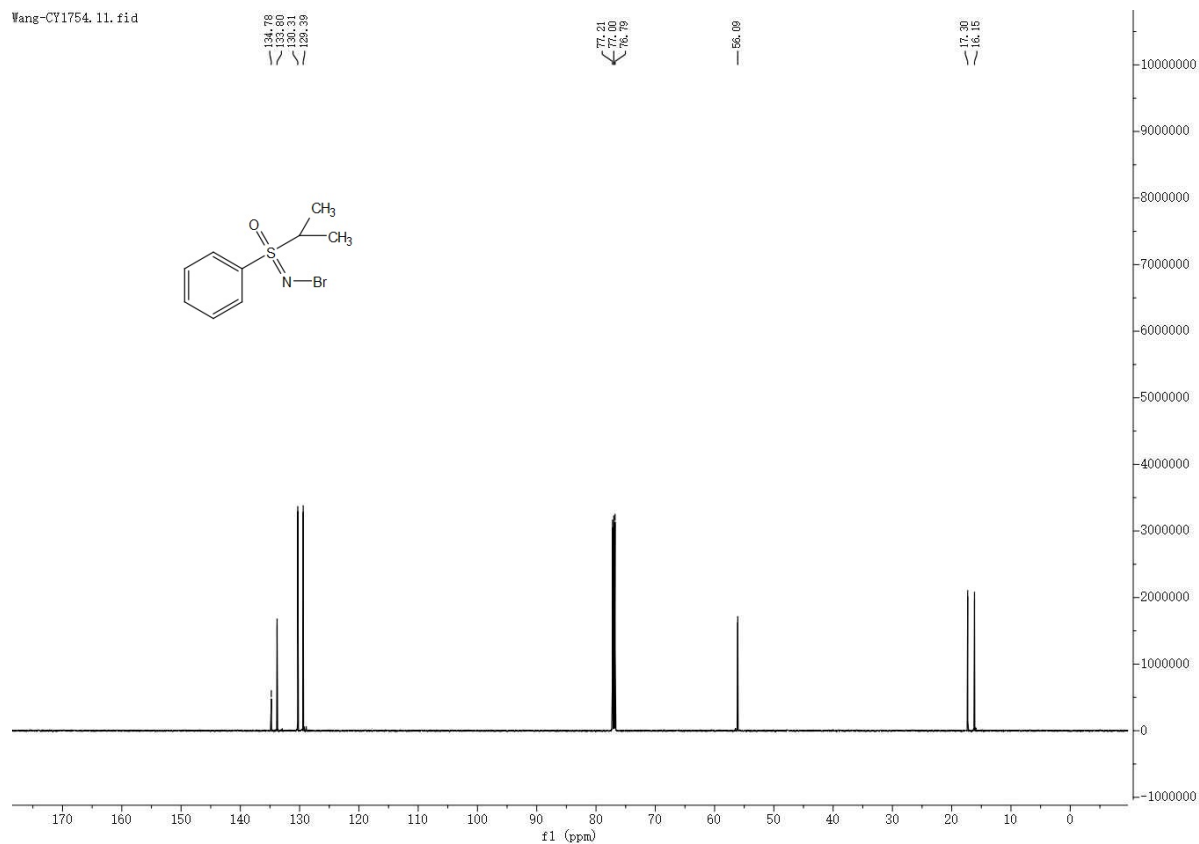
 ^1H NMR spectrum of compound **9x** (600 MHz, CDCl_3) ^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9x** (151 MHz, CDCl_3)



^{13}C $\{^1\text{H}\}$ NMR spectrum of compound **9y** (151 MHz, CDCl_3)



^1H NMR spectrum of compound **9z** (600 MHz, CDCl_3)



^{13}C { ^1H } NMR spectrum of compound **9z** (151 MHz, CDCl_3)