

Supporting Information

Stainless steel-initiated chloro sulfoximidations of allenes under solvent-free conditions in a ball mill

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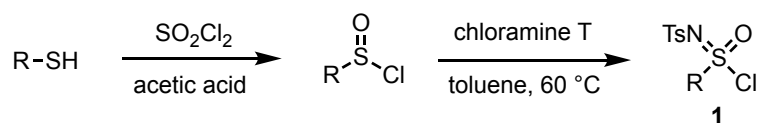
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1. General information

Unless otherwise indicated, all materials were purchased from commercial suppliers and used without further purification. Mechanochemical reactions were performed in a RETSCH Mixer Mill MM400. Both jars and balls were made of stainless steel. The reactions were monitored by thin layer chromatography (TLC) with aluminium sheets silica gel 60 F₂₅₄ from Merck, and flash column chromatography purifications were performed using silica gel 60 (40-63 μ m) from Merck. ¹H and ¹³C{¹H} NMR spectra were recorded with an Agilent VNMRs 600 in deuterated solvents. Chemical shifts (δ) are reported in parts per million (ppm) and spin-spin coupling constants (J) are given in Hz. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. The IR spectra were recorded with a PerkinElmer Spectrum 100 spectrometer with an attached UATR device Diamond KRS-5. All IR data were collected by attenuated total reflectance (ATR) and wavenumbers are given in cm⁻¹. Mass spectra were recorded with a Finnigan SSQ Finnigan 7000 spectrometer (EI, 70 eV). High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL spectrometer.

2. Preparation of starting materials

2.1 Preparation of *N*-tosylsulfoximidoyl chlorides^{S1}



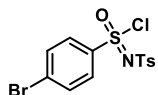
Syntheses of sulfinyl chlorides

The thiophenol derivative (19.8 mmol) and acetic acid (1.14 mL, 19.8 mmol) was charged into a 50 mL flask, and the reaction was stirred at -78 °C for 10 min. Then, sulfuryl chloride (3.57 mL, 43.9 mmol) was added dropwise to the frozen mixture over a period of 30 min. When the addition was completed, the reaction mixture was stirred at the same temperature for 45 min, slowly warmed to room temperature and then stirred for a further 3 h. The solution was concentrated under reduced pressure (CAUTION: without warming because of explosion risks) to give the desired crude sulfinyl chloride, which was used without further purification.

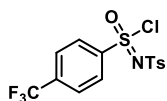
Syntheses of *N*-tosylsulfoximidoyl chlorides **1**

Dried chloramine T (5.58 g, 19.8 mmol) was added to sulfinic chloride (19.8 mmol) in dry toluene (50 mL). When the addition was completed, the reaction mixture was heated at 60 °C for 3 h with stirring. After cooling to room temperature, the solids were filtered off and then washed with toluene. The filtrate was concentrated and purified using filtration through a silica gel column chromatography with pentane/ethyl acetate as the eluent to give *N*-tosylsulfoximidoyl chloride **1**.

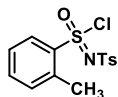
Note: Chloramine-T trihydrate was dried for 8 h under high vacuum at 80 °C (oil bath).

4-Bromo-*N*-tosylbenzenesulfonimidoyl chloride (1d)

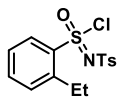
Following the general procedure afforded the product as a yellow solid (6.8 g, 83% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.97 – 7.94 (m, 2H), 7.93 – 7.88 (m, 2H), 7.77 – 7.73 (m, 2H), 7.37 – 7.33 (m, 2H), 2.44 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 144.8, 141.6, 138.3, 133.3, 131.6, 129.9, 128.4, 127.6, 21.8. **MS** (EI, 70 eV): m/z (%) = 376 (10), 374 (100), 372 (91), 236 (22), 205 (11), 203 (11). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_3\text{BrClS}_2\text{Na}^+$ 429.8945, found 429.8943. **IR** (ATR): ν = 3094, 1564, 1331, 1280, 1157, 1109, 1002, 817 cm^{-1} .

***N*-Tosyl-4-(trifluoromethyl)benzenesulfonimidoyl chloride (1e)**

Following the general procedure afforded the product as a yellow solid (5.2 g, 65% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.20 (d, J = 8.5 Hz, 2H), 8.00 – 7.93 (m, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 145.7, 145.0, 138.1, 137.1 (q, J = 33.8 Hz), 129.9, 127.7, 127.6, 127.2 (q, J = 3.6 Hz), 122.7 (q, J = 273.5 Hz), 21.8. **MS** (EI, 70 eV): m/z (%) = 399 (13), 397 (30), 362 (100), 155 (95), 91 (82). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_3\text{ClF}_3\text{S}_2\text{Na}^+$ 419.9713, found 419.9709. **IR** (ATR): ν = 3105, 2927, 1596, 1402, 1314, 1161, 1007, 843, 705 cm^{-1} .

2-Methyl-*N*-tosylbenzenesulfonimidoyl chloride (1f)

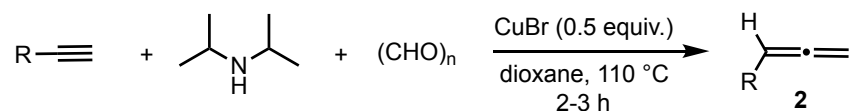
Following the general procedure afforded the product as a yellow solid (6.1 g, 89% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.08 (dd, J = 8.5, 1.3 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.61 (td, J = 7.5, 1.3 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 2.70 (s, 3H), 2.44 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 144.6, 140.9, 138.6, 138.5, 135.7, 134.1, 129.8, 128.6, 127.6, 127.0, 21.8, 20.5. **MS** (EI, 70 eV): m/z (%) = 343 (11), 290 (12), 188 (10), 152 (81), 136 (29), 91 (100). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_3\text{ClS}_2\text{Na}^+$ 365.9996, found 365.9996. **IR** (ATR): ν = 3095, 2929, 2164, 1595, 1466, 1335, 1283, 1106, 774 cm^{-1} .

2-Ethyl-*N*-tosylbenzenesulfonimidoyl chloride (1g)

Following the general procedure afforded the product as a yellow solid (4.6 g, 64% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.07 (dd, J = 8.3, 1.3 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.65 (td, J = 7.5, 1.3 Hz, 1H), 7.47 (dd, J = 7.8, 1.3 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 3.08 (ddq, J = 37.3, 14.9, 7.5 Hz, 2H), 2.45 (s, 3H), 1.27 (t, J = 7.5 Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 144.5, 144.3, 140.6, 138.5, 135.6, 132.2, 129.7, 128.4, 127.5, 126.6, 25.5, 21.7, 14.7. **MS** (EI, 70 eV): m/z (%) = 358 (2), 323 (15), 322 (79), 304 (17), 166 (19), 151 (100). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{ClS}_2\text{Na}^+$ 380.0152, found 380.0150. **IR** (ATR): ν = 3357, 2982, 1594, 1467, 1331, 1282, 1157, 814, 661 cm^{-1} .

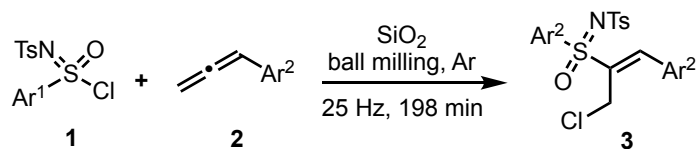
2.2. Preparation of allenes 2

Allenes **2i** and **2j** were commercially available and used as received. Other known allenes were prepared following to a literature report,^{S2} but under modified conditions.



To a well-stirred solution of a terminal alkyne (10.0 mmol) in dioxane (20 mL) was added paraformaldehyde (1.8 g, 20.0 mmol), CuBr (718 mg, 5.0 mmol), and diisopropylamine (2.8 mL, 20.0 mmol) in air. The resulting mixture was stirred at 110 °C (reflux) for 2-3 h. After cooling to room temperature, the reaction mixture was filtered and washed with pentane. The combined organic phases were diluted with pentane (200 mL), washed with water (5 x 150 mL), dried over Na₂SO₄, and concentrated in vacuo. The product was purified by flash column chromatography using pentane as eluent to afford pure terminal allene **2**.

3. Stainless steel-initiated chloro sulfoximidations of allenes

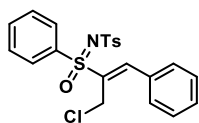


3.1. General procedure

A combination of **1** (0.3 mmol), **2** (0.2 mmol), and silica gel (corresponding to 1.4 mmol by weight calculated for SiO₂) was placed in a stainless-steel milling jar (10 mL) with 10 stainless-steel balls (diameter, 5 mm) under argon. After grinding for 198 min at a frequency of 25 Hz, the mixture in the jar was washed out with DCM (3 x 3 mL). The solvent was concentrated in vacuo, and the product was purified by flash column chromatography on silica gel (*n*-pentane/DCM or *n*-pentane/EtOAc) to afford desired products.

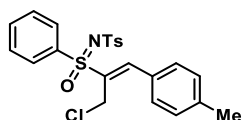
3.2. Characterizing data

(*E*)-*N*-[(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene]-4-methylbenzenesulfonamide (**3aa**)



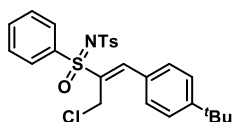
Following the general procedure afforded the product as an off-white foam (68.5 mg, 77% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 3H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.65 (m, 1H), 7.64 – 7.61 (m, 2H), 7.59 – 7.55 (m, 2H), 7.52 – 7.46 (m, 3H), 7.29 – 7.23 (m, 2H), 4.66 (d, *J* = 13.3 Hz, 1H), 4.59 (d, *J* = 13.3 Hz, 1H), 2.39 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 144.9, 143.2, 140.8, 137.9, 136.2, 134.5, 132.2, 131.4, 130.5, 129.6, 129.4, 129.4, 128.8, 126.9, 37.5, 21.7. MS (EI, 70 eV): *m/z* (%) = 445 (4), 367 (18), 277 (33), 166 (18), 138 (100), 125 (37), 115 (81), 91 (46). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₁NO₃ClS₂⁺ 446.0646, found 446.0643. IR (ATR): ν = 3062, 2924, 1614, 1447, 1315, 1236, 1151, 1060, 914, 736 cm⁻¹.

(E)-N-{{3-Chloro-1-(p-tolyl)prop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzenesulfonamide (3ab)



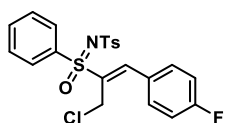
Following the general procedure afforded the product as an off-white foam (67.0 mg, 73% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.04 – 8.01 (m, 2H), 7.99 (s, 1H), 7.86 – 7.81 (m, 2H), 7.64 – 7.60 (m, 1H), 7.56 – 7.47 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.19 (m, 2H), 4.63 (d, *J* = 13.3 Hz, 1H), 4.56 (d, *J* = 13.3 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 145.0, 143.1, 142.3, 140.9, 138.0, 134.6, 134.4, 130.7, 130.1, 129.5, 129.4, 128.7, 126.9, 37.7, 21.7, 21.7. MS (EI, 70 eV): *m/z* (%) = 460 (6), 382 (28), 278 (12), 181 (37), 155 (22), 139 (100), 129 (63). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₃H₂₃NO₃ClS₂⁺ 460.0802, found 460.0795. IR (ATR): ν = 3030, 2923, 1603, 1446, 1315, 1235, 1152, 1061, 915, 811, 736 cm⁻¹.

(E)-N-{{1-[4-(tert-Butyl)phenyl]prop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzenesulfonamide (3ac)



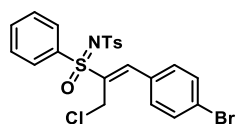
Following the general procedure afforded the product as an off-white foam (72.2 mg, 72% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.94 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.44 – 7.41 (m, 2H), 7.20 – 7.12 (m, 2H), 4.59 (d, *J* = 13.3 Hz, 1H), 4.53 (d, *J* = 13.3 Hz, 1H), 2.29 (s, 3H), 1.25 (s, 9H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 155.3, 144.8, 143.1, 140.8, 138.0, 134.7, 134.3, 130.6, 129.5, 129.4, 129.3, 128.6, 126.9, 126.4, 37.8, 35.2, 31.2, 21.6. MS (EI, 70 eV): *m/z* (%) = 502 (2), 424 (15), 278 (8), 262 (9), 191 (20), 139 (56). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₉NO₃ClS₂⁺ 502.1271, found 502.1266. IR (ATR): ν = 3064, 2961, 1604, 1446, 1317, 1152, 1061, 914, 732 cm⁻¹.

(E)-N-{{3-Chloro-1-(4-fluorophenyl)prop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzenesulfonamide (3ad)



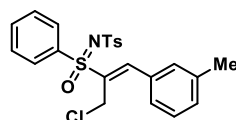
Following the general procedure afforded the product as an off-white foam (73.2 mg, 79% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.08 – 7.99 (m, 3H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.63 (m, 3H), 7.60 – 7.52 (m, 2H), 7.29 – 7.24 (m, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 4.65 (d, *J* = 13.3 Hz, 1H), 4.56 (d, *J* = 13.3 Hz, 1H), 2.39 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 164.4 (d, *J* = 254.5 Hz), 143.6, 143.2, 140.8, 137.7, 135.9, 134.5, 132.9 (d, *J* = 9.0 Hz), 129.6, 129.4, 128.7, 128.4 (d, *J* = 3.3 Hz), 126.8, 116.7 (d, *J* = 21.9 Hz), 37.4, 21.7. MS (EI, 70 eV): *m/z* (%) = 427 (3), 386 (49), 278 (98), 155 (26), 139 (100), 91 (9). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO₃ClFS₂⁺ 464.0552, found 464.0544. IR (ATR): ν = 3067, 2925, 1598, 1508, 1446, 1315, 1235, 1153, 1062, 732 cm⁻¹.

(E)-N-{{1-(4-Bromophenyl)-3-chloroprop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzene-sulfonamide (3ae)



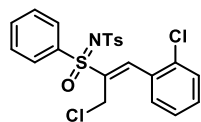
Following the general procedure afforded the product as an off-white foam (65.9 mg, 63% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.94 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.17 (m, 2H), 4.56 (d, *J* = 13.3 Hz, 1H), 4.48 (d, *J* = 13.3 Hz, 1H), 2.33 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 143.5, 143.2, 140.7, 137.5, 137.0, 134.6, 132.7, 131.8, 131.0, 129.7, 129.5, 128.8, 126.8, 126.2, 37.2, 21.7. MS (EI, 70 eV): *m/z* (%) = 448 (6), 277 (43), 244 (5), 155 (19), 139 (100), 91 (27). HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₂H₁₉NO₃ClBrS₂Na⁺ 545.9570, found 545.9566. IR (ATR): ν = 3064, 2924, 1617, 1586, 1315, 1152, 1062, 911, 729 cm⁻¹.

(E)-N-{{3-Chloro-1-(*m*-tolyl)prop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzenesulfonamide (3af)

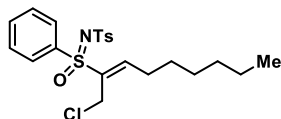


Following the general procedure afforded the product as an off-white foam (63.3 mg, 69% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.02 – 7.97 (m, 3H), 7.84 – 7.80 (m, 2H), 7.64 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 7.42 – 7.36 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.22 – 7.18 (m, 2H), 4.60 (d, *J* = 13.2 Hz, 1H), 4.54 (d, *J* = 13.2 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 145.3, 143.1, 140.9, 139.2, 138.0, 135.9, 134.4, 132.2, 132.2, 131.2, 129.6, 129.4, 129.2, 128.7, 127.4, 126.9, 37.6, 21.7, 21.5. MS (EI, 70 eV): *m/z* (%) = 460 (3), 382 (4), 277 (8), 181 (20), 155 (24), 139 (100), 125 (40). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₃H₂₃NO₃ClS₂⁺ 460.0802, found 460.0796. IR (ATR): ν = 3062, 2923, 2163, 1615, 1446, 1315, 1235, 1152, 1062, 734 cm⁻¹.

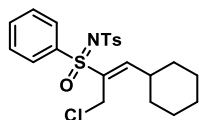
(E)-N-{{3-Chloro-1-(2-chlorophenyl)prop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzene-sulfonamide (3ag)



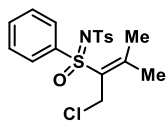
Following the general procedure afforded the product as an off-white foam (57.5 mg, 60% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.02 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.55 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.33 (td, *J* = 7.7, 1.7 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 – 7.17 (m, 2H), 4.50 (d, *J* = 13.2 Hz, 1H), 4.43 (d, *J* = 13.2 Hz, 1H), 2.33 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 143.1, 142.1, 140.7, 139.1, 137.4, 135.1, 134.5, 131.8, 130.8, 130.2, 129.7, 129.5, 129.3, 128.7, 127.3, 126.8, 36.9, 21.6. MS (EI, 70 eV): *m/z* (%) = 479 (2), 277 (15), 155 (20), 149 (37), 139 (100), 125 (42), 115 (40), 91 (48). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₀NO₃Cl₂S₂⁺ 480.0256, found 480.0250. IR (ATR): ν = 3064, 2924, 1621, 1442, 1317, 1237, 1152, 1061, 915, 747 cm⁻¹.

(E)-N-[(1-Chloronon-2-en-2-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene]-4-methylbenzenesulfonamide (3ah)

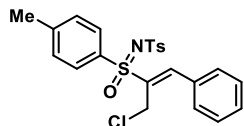
Following the general procedure afforded the product as an off-white foam (72.5 mg, 80% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.87 (m, 2H), 7.79 – 7.73 (m, 2H), 7.62 – 7.55 (m, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.22 – 7.12 (m, 3H), 4.35 (d, *J* = 13.4 Hz, 1H), 4.31 (d, *J* = 13.4 Hz, 1H), 2.37 – 2.27 (m, 5H), 1.52 – 1.41 (m, 2H), 1.34 – 1.16 (m, 6H), 0.85 – 0.72 (m, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 151.0, 143.0, 140.9, 137.6, 137.1, 134.4, 129.6, 129.4, 128.5, 126.8, 35.7, 31.5, 29.7, 29.1, 27.9, 22.6, 21.6, 14.1. MS (EI, 70 eV): *m/z* (%) = 455 (2), 418 (11), 300 (14), 277 (48), 155 (24), 139 (100), 125 (46). HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₂H₂₈NO₃ClS₂Na⁺ 476.1091, found 476.1083. IR (ATR): ν = 2927, 2858, 1633, 1447, 1317, 1152, 1062, 996, 738 cm⁻¹.

(E)-N-[(3-Chloro-1-cyclohexylprop-1-en-2-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene]-4-methylbenzenesulfonamide (3ai)

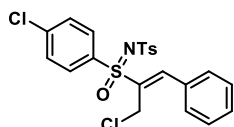
Following the general procedure afforded the product as an off-white foam (73.9 mg, 82% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.95 – 7.88 (m, 2H), 7.80 – 7.73 (m, 2H), 7.62 – 7.57 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.00 (d, *J* = 10.6 Hz, 1H), 4.39 (d, *J* = 13.3 Hz, 1H), 4.31 (d, *J* = 13.3 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.34 (s, 3H), 1.82 – 1.62 (m, 5H), 1.32 – 1.14 (m, 5H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 154.5, 143.0, 140.9, 137.5, 135.5, 134.3, 129.5, 129.4, 128.5, 126.8, 39.2, 35.7, 31.2, 31.1, 25.6, 25.1, 25.1, 21.6. MS (EI, 70 eV): *m/z* (%) = 452 (18), 300 (8), 298 (24), 277 (69), 155 (29), 139 (100). HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₇NO₃ClS₂⁺ 452.1115, found 452.1110. IR (ATR): ν = 3064, 2928, 2854, 2163, 1631, 1446, 1316, 1152, 1060, 913, 735 cm⁻¹.

N-[(1-Chloro-3-methylbut-2-en-2-yl)(oxo)(phenyl)-λ⁶-sulfaneylidene]-4-methylbenzenesulfonamide (3aj)

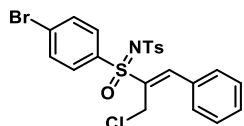
Following the general procedure afforded the product as an off-white foam (64.3 mg, 81% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.83 (d, *J* = 13.0 Hz, 1H), 4.61 (d, *J* = 13.0 Hz, 1H), 2.39 (s, 3H), 2.10 (s, 3H), 1.93 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 157.9, 142.9, 140.9, 139.3, 134.0, 133.7, 129.4, 129.3, 127.9, 126.7, 39.7, 24.9, 23.2, 21.6. MS (EI, 70 eV): *m/z* (%) = 400 (8), 397 (19), 362 (27), 295 (34), 277 (96), 155 (36), 139 (100), 125 (93). HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₈H₂₀NO₃ClS₂Na⁺ 420.0465, found 420.0463. IR (ATR): ν = 3061, 2924, 1616, 1446, 1313, 1224, 1150, 1058, 812, 758 cm⁻¹.

(E)-N-[(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)(p-tolyl)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (3ba)

Following the general procedure afforded the product as an off-white foam (67.9 mg, 74% yield). **¹H NMR** (600 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.95 – 7.92 (m, 2H), 7.89 – 7.85 (m, 2H), 7.64 – 7.59 (m, 2H), 7.50 – 7.45 (m, 3H), 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 4.64 (d, J = 13.2 Hz, 1H), 4.57 (d, J = 13.2 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H). **¹³C {¹H} NMR** (151 MHz, Chloroform-*d*) δ 145.8, 144.5, 143.0, 140.9, 136.3, 134.6, 132.2, 131.3, 130.4, 130.2, 129.4, 129.3, 128.7, 126.8, 37.5, 21.8, 21.6. **MS** (EI, 70 eV): m/z (%) = 459 (3), 381(12), 291 (37), 167 (14), 155 (10), 139 (100), 115 (32), 91 (22). **HRMS** (ESI) m/z : $[M+H]^+$ calcd for C₂₃H₂₃O₃NCIS₂⁺ 460.0802, found 460.0797. **IR** (ATR): ν = 3059, 2924, 2164, 1597, 1448, 1315, 1152, 1061, 812, 723 cm⁻¹.

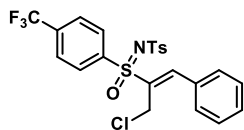
(E)-N-[(3-Chloro-1-phenylprop-1-en-2-yl)(4-chlorophenyl)(oxo)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (3ca)

Following the general procedure afforded the product as an off-white foam (59.4 mg, 62% yield). **¹H NMR** (600 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 8.02 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 7.69 – 7.60 (m, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.53 – 7.48 (m, 3H), 7.32 – 7.22 (m, 2H), 4.69 (d, J = 13.3 Hz, 1H), 4.62 (d, J = 13.3 Hz, 1H), 2.42 (s, 3H). **¹³C {¹H} NMR** (151 MHz, Chloroform-*d*) δ 145.3, 143.3, 141.5, 140.6, 136.6, 135.8, 132.1, 131.6, 130.5, 130.2, 129.9, 129.5, 129.4, 126.9, 37.5, 21.7. **MS** (EI, 70 eV): m/z (%) = 403 (3), 401 (8), 311 (14), 175 (11), 167 (19), 159 (28), 139 (100). **HRMS** (ESI) m/z : $[M+H]^+$ calcd for C₂₂H₂₀NO₃Cl₂S₂⁺ 480.0256, found 480.0250. **IR** (ATR): ν = 3091, 2925, 1612, 1575, 1316, 1153, 1061, 817, 759 cm⁻¹.

(E)-N-[(4-Bromophenyl)(3-chloro-1-phenylprop-1-en-2-yl)(oxo)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (3da)

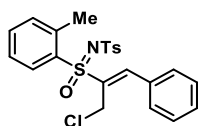
Following the general procedure afforded the product as an off-white foam (61.7mg, 59% yield). **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.85 – 7.82 (m, 2H), 7.80 – 7.75 (m, 2H), 7.63 – 7.60 (m, 2H), 7.56 – 7.51 (m, 2H), 7.44 – 7.37 (m, 3H), 7.21 – 7.16 (m, 2H), 4.59 (d, J = 13.3 Hz, 1H), 4.51 (d, J = 13.3 Hz, 1H), 2.31 (s, 3H). **¹³C {¹H} NMR** (151 MHz, Chloroform-*d*) δ 145.4, 143.3, 140.6, 137.2, 135.7, 132.9, 132.0, 131.6, 130.5, 130.2, 130.1, 129.5, 129.4, 126.9, 37.5, 21.7. **MS** (EI, 70 eV): m/z (%) = 523 (1), 448 (11), 358 (15), 355 (14), 205 (21), 167 (23). **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for C₂₂H₁₉NO₃BrClS₂⁺ 545.9570, found 545.9565. **IR** (ATR): ν = 3063, 2923, 2855, 2163, 1613, 1570, 1316, 1237, 1152, 1059, 817, 751 cm⁻¹.

(E)-N-[(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)(4-(trifluoromethyl)phenyl)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (3ea)



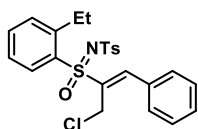
Following the general procedure afforded the product as an off-white foam (65.7 mg, 64% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.12 (d, $J = 8.3$ Hz, 2H), 8.04 (s, 1H), 7.82 – 7.76 (m, 2H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.58 – 7.52 (m, 2H), 7.47 – 7.37 (m, 3H), 7.23 – 7.13 (m, 2H), 4.62 (d, $J = 13.3$ Hz, 1H), 4.54 (d, $J = 13.3$ Hz, 1H), 2.31 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 146.13, 143.46, 142.17, 140.44, 135.95 (q, $J = 33.2$ Hz), 135.37, 131.91, 131.75, 130.51, 129.51, 129.46, 129.39, 126.87, 126.63 (q, $J = 3.6$ Hz), 123.11 (q, $J = 273.2$ Hz), 37.44, 21.64. **MS** (EI, 70 eV): m/z (%) = 514 (6), 478 (2), 436 (47), 346 (20), 193 (11), 167 (18), 139 (100). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{ClF}_3\text{S}_2\text{Na}^+$ 536.0339, found 536.0325. **IR** (ATR): $\nu = 3061, 2925, 2161, 1610, 1319, 1149, 1058, 1008, 727$ cm^{-1} .

(E)-N-[(3-Chloro-1-phenylprop-1-en-2-yl)(oxo)(*o*-tolyl)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (3fa)



Following the general procedure afforded the product as an off-white foam (45.9 mg, 50% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.36 (dd, $J = 8.1, 1.4$ Hz, 1H), 8.07 (s, 1H), 7.89 – 7.82 (m, 2H), 7.69 – 7.63 (m, 2H), 7.57 (td, $J = 7.5, 1.4$ Hz, 1H), 7.52 – 7.48 (m, 3H), 7.44 (td, $J = 8.0, 1.2$ Hz, 1H), 7.29 (dt, $J = 7.5, 1.0$ Hz, 1H), 7.25 – 7.22 (m, 2H), 4.49 (d, $J = 13.4$ Hz, 1H), 4.45 (d, $J = 13.4$ Hz, 1H), 2.54 (s, 3H), 2.38 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 145.4, 143.1, 141.0, 139.8, 134.8, 134.0, 133.8, 133.4, 132.0, 131.4, 131.4, 130.4, 129.4, 129.4, 127.1, 126.8, 37.4, 21.6, 20.3. **MS** (EI, 70 eV): m/z (%) = 460 (2), 382 (19), 306 (12), 292 (13), 235 (6), 220 (5), 167 (20). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_3\text{S}_2\text{ClNa}^+$ 482.0622, found 482.0620. **IR** (ATR): $\nu = 3058, 2925, 2856, 2160, 1615, 1455, 1317, 1148, 1076, 750$ cm^{-1} .

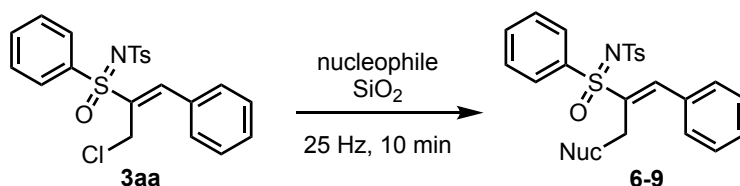
(E)-N-[(3-Chloro-1-phenylprop-1-en-2-yl)(2-ethylphenyl)(oxo)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (3ga)



Following the general procedure afforded the product as an off-white foam (43.5 mg, 46% yield). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.36 (dd, $J = 8.2, 1.4$ Hz, 1H), 8.06 (s, 1H), 7.89 – 7.82 (m, 2H), 7.68 – 7.60 (m, 3H), 7.54 – 7.48 (m, 3H), 7.46 – 7.37 (m, 2H), 7.26 – 7.23 (m, 2H), 4.49 (d, $J = 13.4$ Hz, 1H), 4.45 (d, $J = 13.4$ Hz, 1H), 3.02 (dq, $J = 14.9, 7.5$ Hz, 1H), 2.88 (dq, $J = 14.9, 7.5$ Hz, 1H), 2.38 (s, 3H), 1.22 (t, $J = 7.5$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 145.9, 144.8, 143.0, 141.0, 134.9, 133.8, 132.1, 131.4, 131.4, 130.4, 129.4, 129.4, 126.9, 126.8, 37.5, 25.3, 21.7, 14.9. **MS** (EI, 70 eV): m/z (%) = 475 (11), 396 (35), 321 (22), 254 (35), 220 (20), 139 (100). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_3\text{ClS}_2\text{Na}^+$ 496.0778, found 496.0774. **IR** (ATR): $\nu = 3062, 2970,$

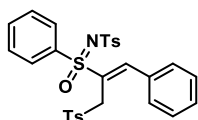
2928, 1617, 1449, 1316, 1151, 1076, 753 cm^{-1} .

4. Transformations



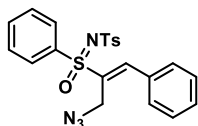
Compound **3aa** (44.5 mg, 0.1 mmol), the nucleophile (0.2 mmol), and silica gel (corresponding to 0.5 mmol by weight calculated for SiO_2) were placed in a stainless-steel milling jar (5 mL) with one stainless-steel balls (diameter, 7 mm) under air atmosphere. After grinding for 10 min at a frequency of 25 Hz, the mixture in the jar was washed out with DCM (3×2 mL). The solvent was concentrated in vacuo, and the product was purified by flash column chromatography on silica gel (*n*-pentane/EtOAc) to afford desired products.

(*E*)-4-Methyl-*N*-[oxo(phenyl)(1-phenyl-3-tosylprop-1-en-2-yl)- λ^6 -sulfaneylidene]benzenesulfonamide (**6**)



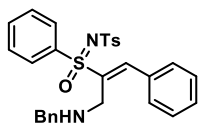
With sodium *p*-toluenesulfonate (38.8 mg, 0.2 mmol). Off-white foam (51.9 mg, 92% yield). ^1H NMR (600 MHz, Chloroform-*d*) δ 8.15 (dd, $J = 8.5, 1.4$ Hz, 2H), 8.12 (s, 1H), 7.83 (d, $J = 8.1$ Hz, 2H), 7.70 – 7.66 (m, 1H), 7.62 – 7.54 (m, 6H), 7.44 – 7.38 (m, 3H), 7.23 (dd, $J = 8.2, 3.8$ Hz, 4H), 4.86 (d, $J = 15.3$ Hz, 1H), 4.58 (d, $J = 15.3$ Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 148.7, 145.2, 143.1, 140.8, 137.3, 137.0, 134.5, 132.4, 131.7, 131.0, 130.0, 129.5, 129.4, 129.2, 129.1, 128.0, 126.8, 55.1, 21.8, 21.6. MS (EI, 70 eV): m/z (%) = 411(2), 410 (11), 287 (20), 155 (16), 115 (100), 91 (23). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_5\text{S}_2^+$ 566.1124, found 566.1122. IR (ATR): $\nu = 3061, 3029, 2949, 1599, 1446, 1299, 1232, 1058, 810, 755$ cm^{-1} .

(*E*)-*N*-[(3-Azido-1-phenylprop-1-en-2-yl)(oxo)(phenyl)- λ^6 -sulfaneylidene]-4-methylbenzenesulfonamide (**7**)



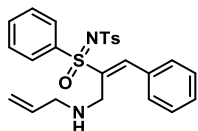
With sodium azide (13.0 mg, 0.2 mmol). Off-white foam (40.7 mg, 90% yield). ^1H NMR (600 MHz, Chloroform-*d*) δ 8.0 – 8.0 (m, 3H), 7.8 – 7.8 (m, 2H), 7.6 – 7.6 (m, 1H), 7.6 – 7.5 (m, 2H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 3H), 7.2 – 7.1 (m, 2H), 4.4 (d, $J = 14.9$ Hz, 1H), 4.3 (d, $J = 14.9$ Hz, 1H), 2.3 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 145.1, 143.1, 140.8, 137.6, 134.9, 134.5, 132.1, 131.3, 130.2, 129.8, 129.4, 129.3, 128.5, 126.9, 46.4, 21.7. MS (EI, 70 eV): m/z (%) = 453 (1), 368 (39), 278 (47), 174 (12), 140 (14), 139 (100), 91 (64). HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_3\text{S}_2\text{Na}^+$ 475.0869, found 475.0866. IR (ATR): $\nu = 3063, 2925, 2096, 1619, 1447, 1314, 1151, 1068, 750, 685$ cm^{-1} .

(E)-N-{{3-(Benzylamino)-1-phenylprop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzene-sulfonamide (8)



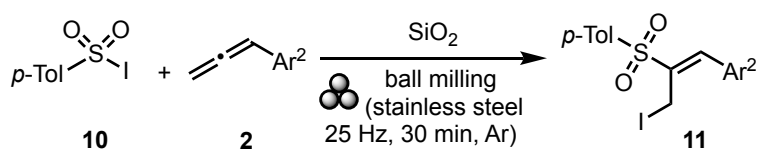
With benzyl amine (21.8 μL, 0.2 mmol). Off-white foam (45.4 mg, 88% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 3H), 7.91 – 7.85 (m, 2H), 7.68 – 7.60 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.34 – 7.30 (m, 1H), 7.29 – 7.22 (m, 6H), 3.71 (s, 2H), 3.48 (s, 2H), 2.39 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 143.0, 142.9, 141.1, 139.4, 137.9, 137.3, 134.0, 132.7, 130.6, 129.6, 129.4, 128.9, 128.6, 128.5, 128.5, 127.3, 126.9, 53.8, 44.7, 21.6. **MS** (EI, 70 eV): *m/z* (%) = 517 (6), 412 (14), 368 (20), 346 (12), 297 (15), 295 (100), 286 (13). **HRMS** (ESI) *m/z*: [M+H]⁺ calcd for C₂₉H₂₉N₂O₃S₂⁺ 517.1614, found 517.1607. **IR** (ATR): ν = 3334, 3060, 2923, 1600, 1448, 1313, 1151, 1057, 743 cm⁻¹.

(E)-N-{{3-(Allylamino)-1-phenylprop-1-en-2-yl}(oxo)(phenyl)-λ⁶-sulfaneylidene}-4-methylbenzene-sulfonamide (9)



With allyl amine (15.0 μL, 0.2 mmol). Off-white foam (37.3 mg, 80% yield). ¹H NMR (600 MHz, Chloroform-*d*) δ 8.06 – 8.01 (m, 2H), 7.97 (s, 1H), 7.90 – 7.84 (m, 2H), 7.71 – 7.67 (m, 2H), 7.67 – 7.62 (m, 1H), 7.56 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.80 – 5.71 (m, 1H), 5.09 – 4.99 (m, 2H), 3.53 (d, *J* = 2.0 Hz, 2H), 3.15 – 3.09 (m, 2H), 2.38 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 143.1, 142.9, 141.1, 138.1, 137.6, 136.0, 134.1, 132.8, 130.6, 130.6, 129.6, 129.4, 129.0, 128.5, 126.9, 116.7, 52.1, 44.7, 21.6. **MS** (EI, 70 eV): *m/z* (%) = 467 (3), 296 (40), 278 (17), 171 (37), 149 (100). **HRMS** (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₇N₂O₃S₂⁺ 467.1458, found 467.1452. **IR** (ATR): ν = 3334, 3063, 2923, 1725, 1725, 1621, 1447, 1313, 1150, 1059, 921, 750 cm⁻¹.

5. Reactions between 4-tolylsulfonyl iodide (10) and allenes



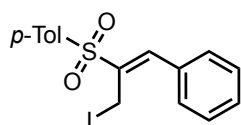
5.1. General procedure and characterizing data

GP1: A mixture of **10** (112.8 mg, 0.4 mmol), **2** (0.44 mmol), and silica gel (120 mg, corresponding to 2.0 mmol

by weight calculated for SiO₂) was placed in a stainless-steel milling jar (10 mL) with 10 stainless-steel balls (diameter, 5 mm) under argon. After grinding for 30 min at a frequency of 25 Hz, the mixture in the jar was washed out with DCM (3 × 3 mL). The solvent was concentrated in vacuo, and the product was purified by flash column chromatography on silica gel (*n*-pentane/EtOAc) to afford desired products.

GP2: A mixture of **10** (112.8 mg, 0.4 mmol), **2** (0.44 mmol) was placed in a stainless-steel milling jar (10 mL) with 10 stainless-steel balls (diameter, 5 mm) under argon. After grinding for 30 min at a frequency of 25 Hz, the mixture in the jar was washed out with DCM (3 × 3 mL). The solvent was concentrated in vacuo. The residue was evaporated under high vacuum to remove the volatile allene **2**, and pure product was obtained without further purification.

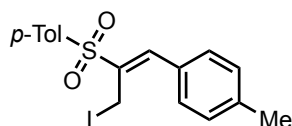
(E)-1-[(3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl]-4-methylbenzene (11a)



Following GP1 and GP2 afforded the product as a yellow solid in 96% (153 mg, 0.38 mmol) and quantitative yield (159.2 mg, 0.4 mmol), respectively.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.54 – 7.43 (m, 3H), 7.37 (d, *J* = 7.9 Hz, 2H), 4.30 (s, 2H), 2.46 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 145.0, 140.2, 138.8, 136.9, 133.1, 130.4, 130.3, 130.0, 129.3, 128.7, 21.8, –5.8. MS (ESI) [M+Na]⁺: 420.97. The compound has already been described.^{S3}

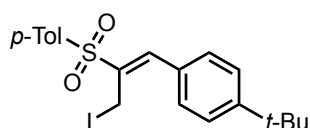
(E)-1-[[3-Iodo-1-(*p*-tolyl)prop-1-en-2-yl]sulfonyl]-4-methylbenzene (11b)



Following GP1 afforded the product as a yellow solid (150.0 mg, 91%).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.31 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H). ¹³C {¹H} NMR (151 MHz, Chloroform-*d*) δ 144.9, 141.2, 140.3, 137.5, 137.1, 130.7, 130.3, 130.1, 130.0, 21.8, 21.7, –5.2. The compound has already been described.^{S3}

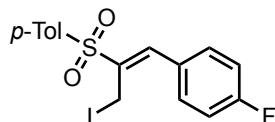
(E)-1-(*Tert*-butyl)-4-(3-iodo-2-tosylprop-1-en-1-yl)benzene (11c)



Following GP1 afforded the product as a brown oil (155.0 mg, 85%).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.84 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.32 (s, 2H), 2.44 (s, 3H), 1.34 (s, 9H). $^{13}\text{C } \{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 154.2, 144.8, 140.2, 137.5, 137.2, 130.7, 130.3, 130.0, 128.7, 126.4, 35.1, 31.2, 21.8, -5.1. The compound has already been described.^{S3}

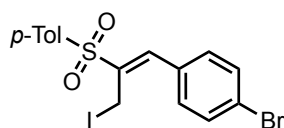
(*E*)-1-Fluoro-4-(3-iodo-2-tosylprop-1-en-1-yl)benzene (11d)



Following GP1 afforded the product as a yellow solid (154.0 mg, 93%).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.84 (d, $J = 8.0$ Hz, 2H), 7.63 (dd, $J = 8.5, 5.3$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 8.4$ Hz, 2H), 4.26 (s, 2H), 2.45 (s, 3H). $^{13}\text{C } \{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 164.4, 162.8, 145.1, 138.9, 138.5, 136.9, 132.7 (d, $J = 8.6$ Hz), 130.1, 129.3 (d, $J = 3.4$ Hz), 128.8, 116.6 (d, $J = 21.8$ Hz), 21.8, -6.0. **MS** (EI, 70 eV): m/z (%) = 417 (5), 289 (100), 225 (20), 155 (23), 133 (41), 91 (20). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{FISNa}^+$ 438.9635, found 438.9626. **IR** (ATR): $\nu = 3513, 2922, 2332, 1596, 1504, 1298, 1130, 811$ cm^{-1} .

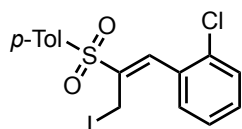
(*E*)-1-Bromo-4-(3-iodo-2-tosylprop-1-en-1-yl)benzene (11e)



Following GP1 afforded the product as a yellow solid (170.0 mg, 89%).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.23 (s, 2H), 2.44 (s, 3H). $^{13}\text{C } \{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 145.1, 139.6, 138.7, 136.7, 132.6, 132.0, 131.7, 130.1, 128.8, 125.0, 21.8, -6.4. **MS** (EI, 70 eV): m/z (%) = 477 (1), 349 (100), 270 (21), 206 (22), 195 (20), 155 (30), 115 (74), 91 (43). **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{BrIS Na}^+$ 498.8834, found 498.8828. **IR** (ATR): $\nu = 3487, 2922, 2326, 1586, 1397, 1155, 1005, 805$ cm^{-1} .

(*E*)-1-Chloro-2-(3-iodo-2-tosylprop-1-en-1-yl)benzene (11g)



Following GP1 afforded the product as a yellow solid (155.0 mg, 90%).

$^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.88 (d, $J = 8.3$ Hz, 2H), 7.71 – 7.65 (m, 1H), 7.49 – 7.45 (m, 1H), 7.41 – 7.35 (m, 4H), 4.11 (s, 2H), 2.46 (s, 3H). $^{13}\text{C } \{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 145.2, 141.4, 138.0, 136.6, 134.9, 132.0, 131.1, 130.3, 130.1, 128.8, 128.7, 127.3, 21.8, -7.8. The compound has already been described.^{S3}

5.2. Calculation of the green metrics for compound 11

The calculations were based on the following equations:

$$\text{E factor} = \frac{\text{mass of waste}}{\text{mass of product}}$$

$$\text{Mass Intensity (MI)} = \frac{\text{total mass in process}}{\text{mass of product}}$$

$$\text{Reaction mass efficiency (RME)(\%)} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100$$

$$\text{Molar efficiency (Mol. E) (\%)} = \frac{\text{moles product}}{(\text{moles reactants} + \text{moles cat.} + \text{moles solvent} + \text{moles additives})} \times 100$$

Table S1 Green metrics of compound 11 in a ball mill and in solution

entry	method	E factor	MI	RME (%)	Mol. E (%)
1	GP1	0.85	1.85	93.4	13.4
2	GP2	0.03	1.03	97.2	47.6
3	ref S3	17.08	18.08	61.1	1.3

Ball milling process:

$$\text{E factor (GP1)} = \frac{m(10) + m(2a) + m(\text{silica gel}) - m(11)}{m(11)} = \frac{112.8 + 51.0 + 120.0 - 153.0}{153.0} = 0.85$$

$$\text{E factor (GP2)} = \frac{m(10) + m(2a) - m(11)}{m(11)} = \frac{112.8 + 51.0 - 159.2}{159.2} = 0.03$$

$$\text{Mass Intensity (GP1)} = \frac{m(10) + m(2a) + m(\text{silica gel})}{m(11)} = \frac{112.8 + 51.0 + 120.0}{153.0} = 1.85$$

$$\text{Mass Intensity (GP2)} = \frac{m(10) + m(2a)}{m(11)} = \frac{112.8 + 51.0}{159.2} = 1.03$$

$$\text{Reaction mass efficiency (\%)(GP1)} = \frac{m(11)}{m(10) + m(2a)} \times 100 = \frac{153.0}{112.8 + 51.0} \times 100 = 93.4\%$$

$$\text{Reaction mass efficiency (\%)(GP2)} = \frac{m(11)}{m(10) + m(2a)} \times 100 = \frac{159.2}{112.8 + 51.0} \times 100 = 97.2\%$$

$$\text{Molar efficiency (\%)(GP1)} = \frac{n(11)}{n(10) + n(2a) + n(\text{silica gel})} \times 100 = \frac{0.38}{0.4 + 0.44 + 2.0} \times 100 = 13.4\%$$

$$\text{Molar efficiency (\%)(GP2)} = \frac{n(11)}{n(10) + n(2a)} \times 100 = \frac{0.4}{0.4 + 0.44} \times 100 = 47.6\%$$

Solution-based process: the reaction was carried out with **10** (0.3 mmol, 84.6 mg), **2a** (0.45 mmol, 52.2 mg), CuI (0.12 mmol, 22.9 mg), and 1,10-phen (0.15 mmol, 27.0 mg) in 1 mL DCM (15.6 mmol, 1325.0 mg), affording product **11a** in 70% yield (0.21 mmol, 83.6 mg).^{S3}

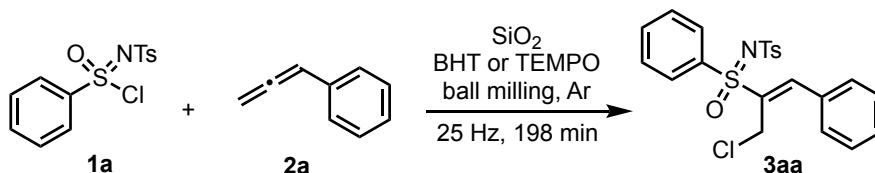
$$\begin{aligned} \text{E factor (solution)} &= \frac{m(10) + m(2a) + m(\text{CuI}) + m(1,10 - \text{phen}) + m(\text{DCM}) - m(11)}{m(11)} \\ &= \frac{84.6 + 52.2 + 22.9 + 27.0 + 1325.0 - 83.6}{83.6} = 17.08 \end{aligned}$$

$$\begin{aligned} \text{Mass Intensity (solution)} &= \frac{m(10) + m(2a) + m(\text{CuI}) + m(1,10 - \text{phen}) + m(\text{DCM})}{m(11)} \\ &= \frac{84.6 + 52.2 + 22.9 + 27.0 + 1325.0}{83.6} = 18.08 \end{aligned}$$

$$\text{Reaction mass efficiency (\%)(solution)} = \frac{m(11)}{m(10) + m(2a)} \times 100 = \frac{83.6}{84.6 + 52.2} \times 100 = 61.1\%$$

$$\begin{aligned} \text{Molar efficiency (\%)(solution)} &= \frac{n(11)}{n(10) + n(2a) + n(\text{CuI}) + n(1,10 - \text{phen}) + n(\text{DCM})} \times 100 \\ &= \frac{0.21}{0.3 + 0.45 + 0.12 + 0.15 + 15.6} \times 100 = 1.3\% \end{aligned}$$

6. Radical trapping experiments



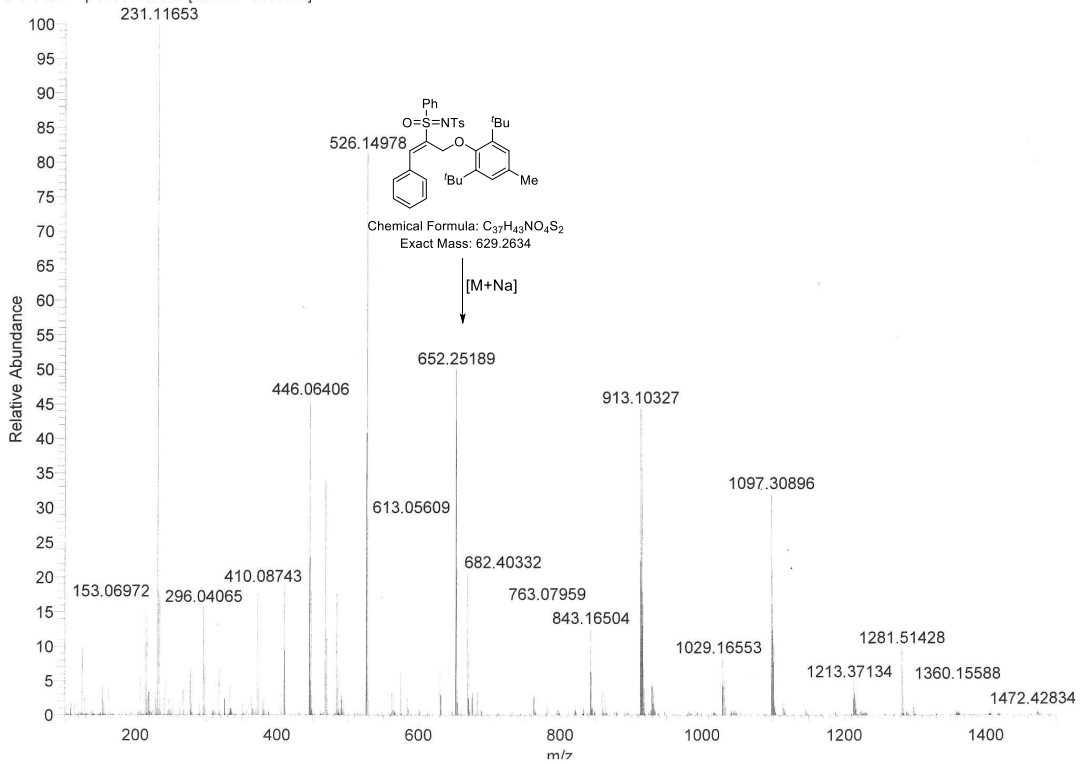
A combination of **1a** (98.7 mg, 0.3 mmol), **2a** (23.2 mg, 0.2 mmol), BHT (44.1 mg, 0.2 mmol) or TEMPO (31.3 mg, 0.2 mmol), and silica gel (corresponding to 1.4 mmol by weight calculated for SiO₂) was placed in a stainless-steel milling jar (10 mL) with 10 stainless-steel balls (diameter, 5 mm) under argon. After grinding for 198 min at a frequency of 25 Hz, the yield of the crude product was determined by ¹H NMR analysis using CH₂Br₂ (14 μL) as the internal standard.

D:\Data2\Bolm\bo-kds-10-7-3_211006130009
gel. in MeOH angles.

10/11/2021 9:03:32 AM

Kong\KDS-10-7-3

bo-kds-10-7-3_211006130009 #16 RT: 0.24 AV: 1 NL: 1.85E7
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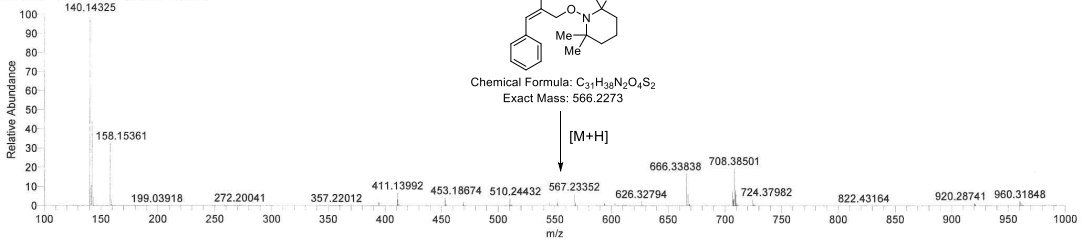


D:\Data2\Bolm\bo-kds-10-7-4_211006130009
gel. in MeOH angles.

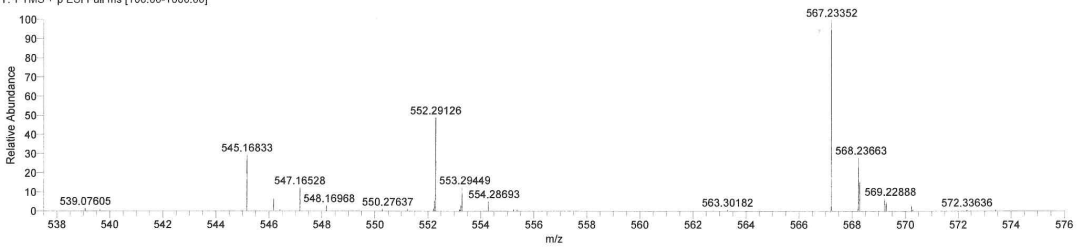
10/11/2021 9:07:53 AM

Kong\KDS-10-7-4

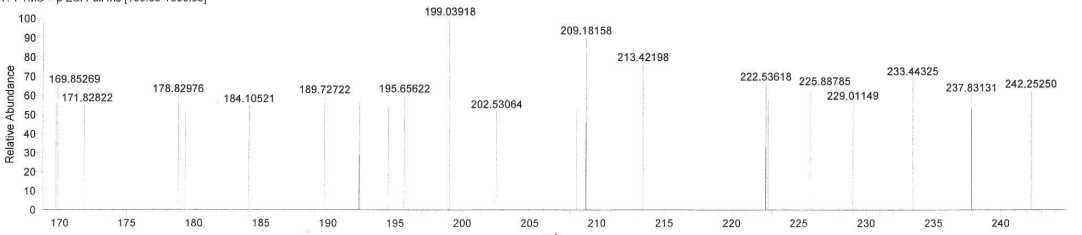
bo-kds-10-7-4_211006130009 #20 RT: 0.28 AV: 1 NL: 1.01E8
T: FTMS + p ESI Full ms [100.00-1000.00]



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T: FTMS + p ESI Full ms [100.00-1000.00]



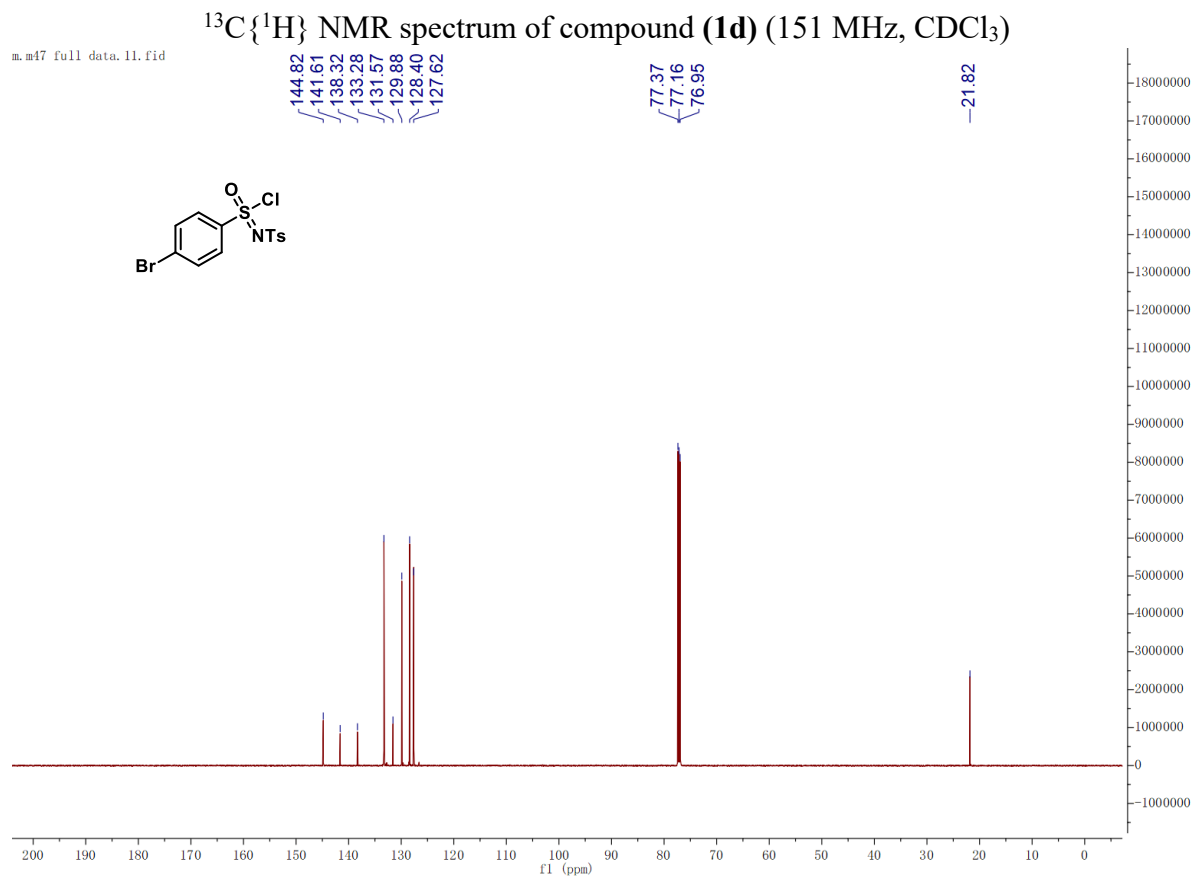
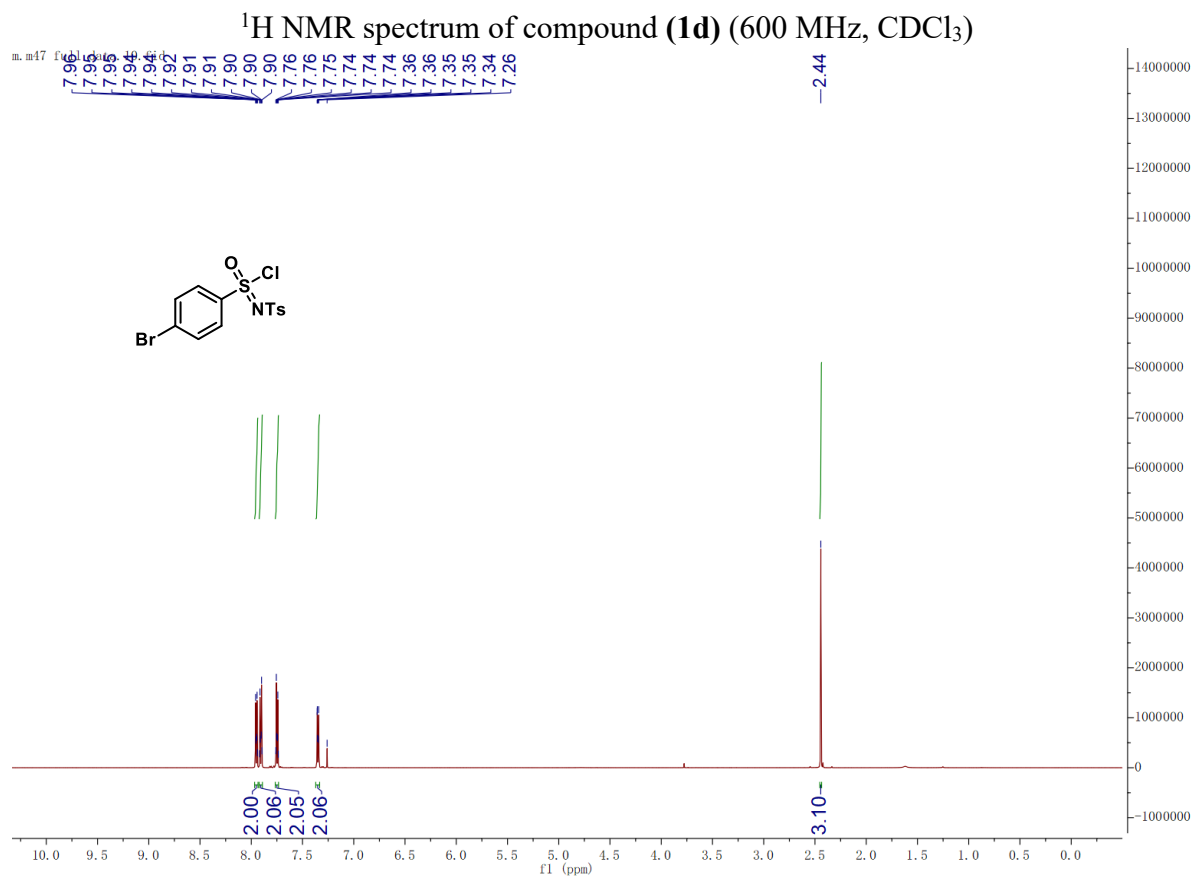
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T: FTMS + p ESI Full ms [100.00-1000.00]

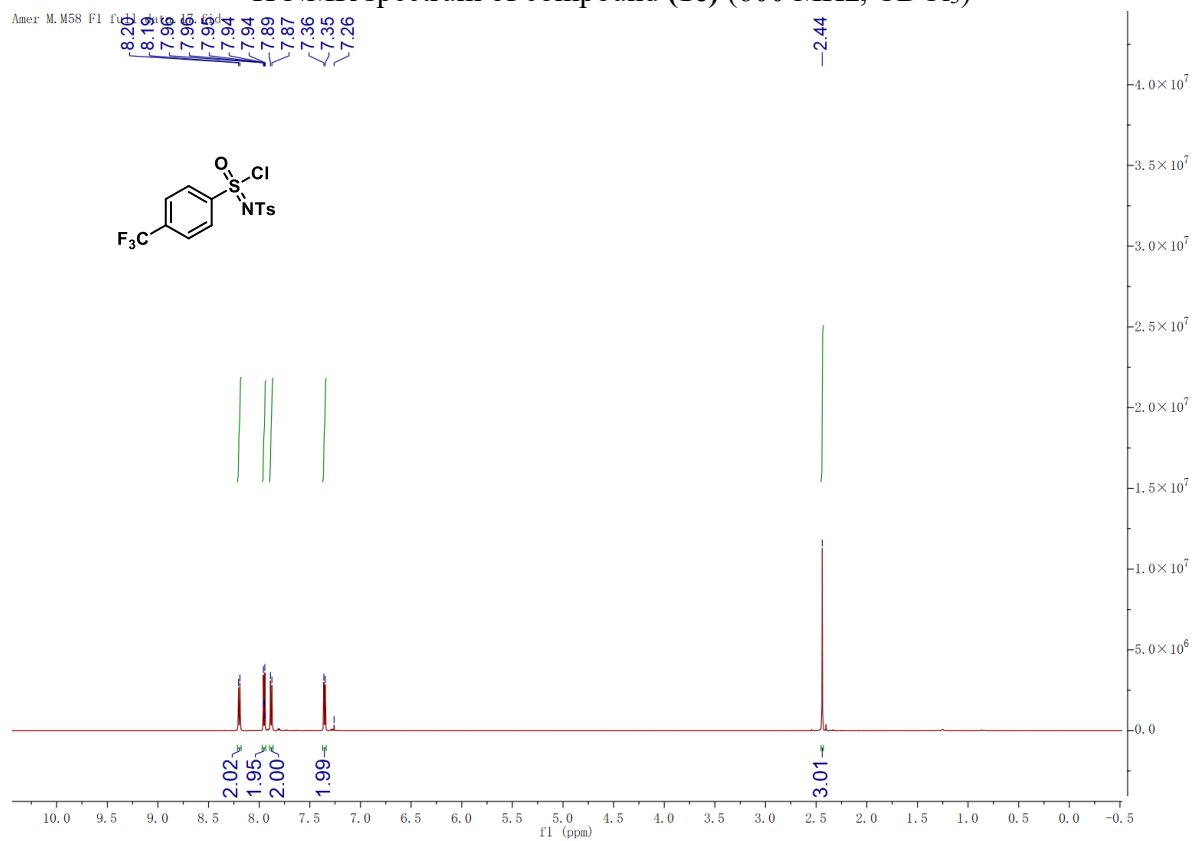
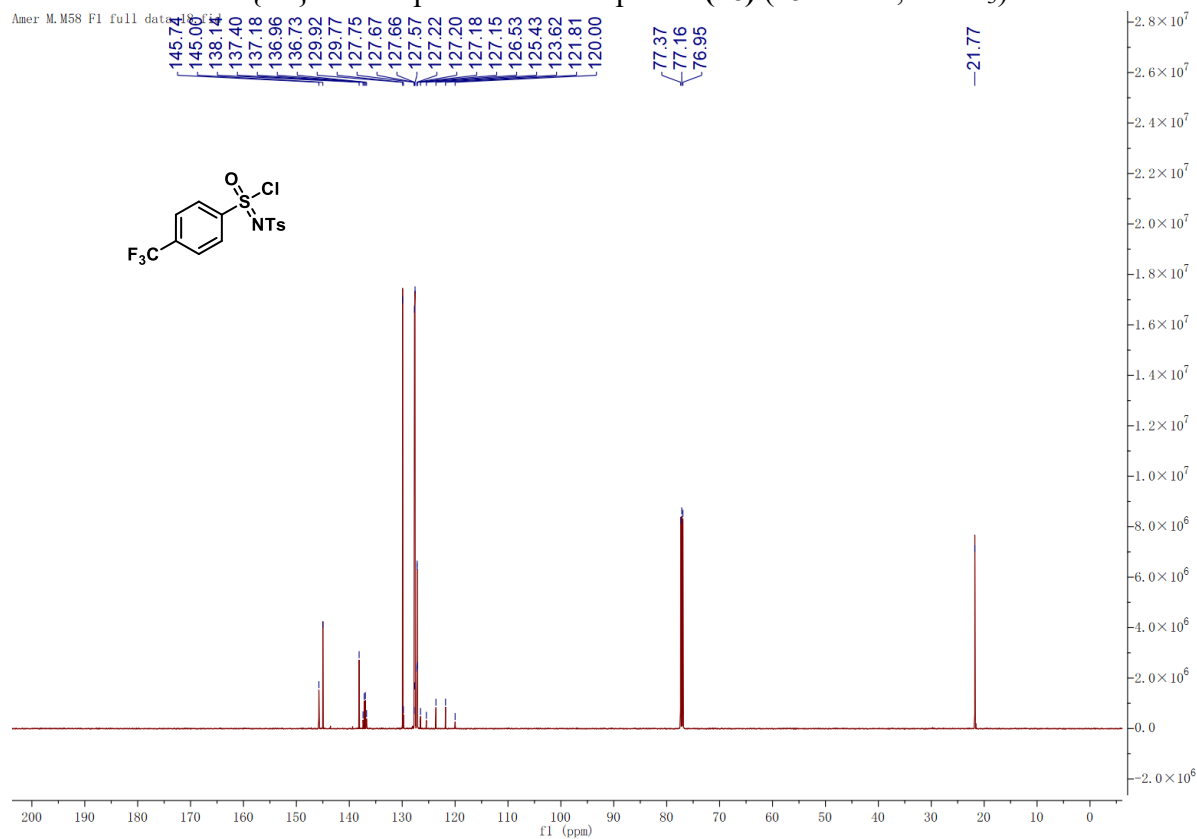


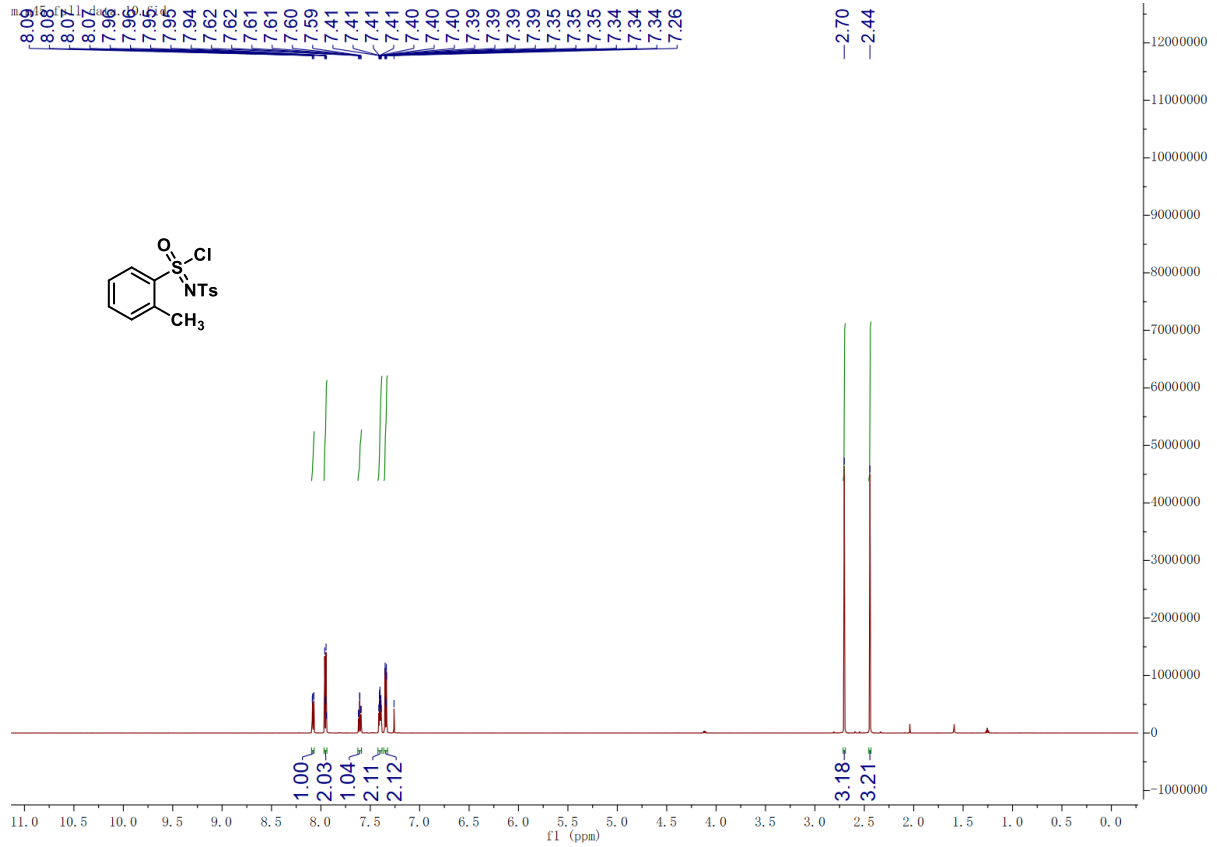
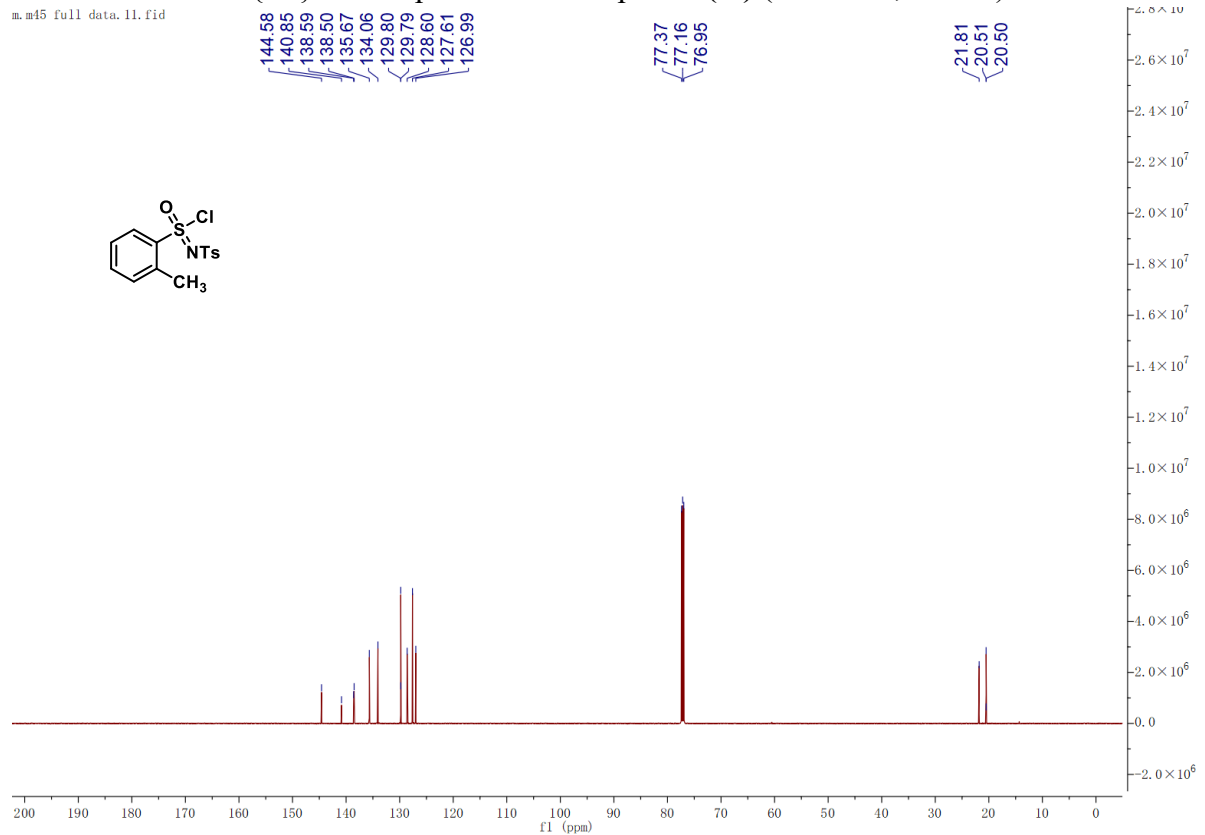
7. References

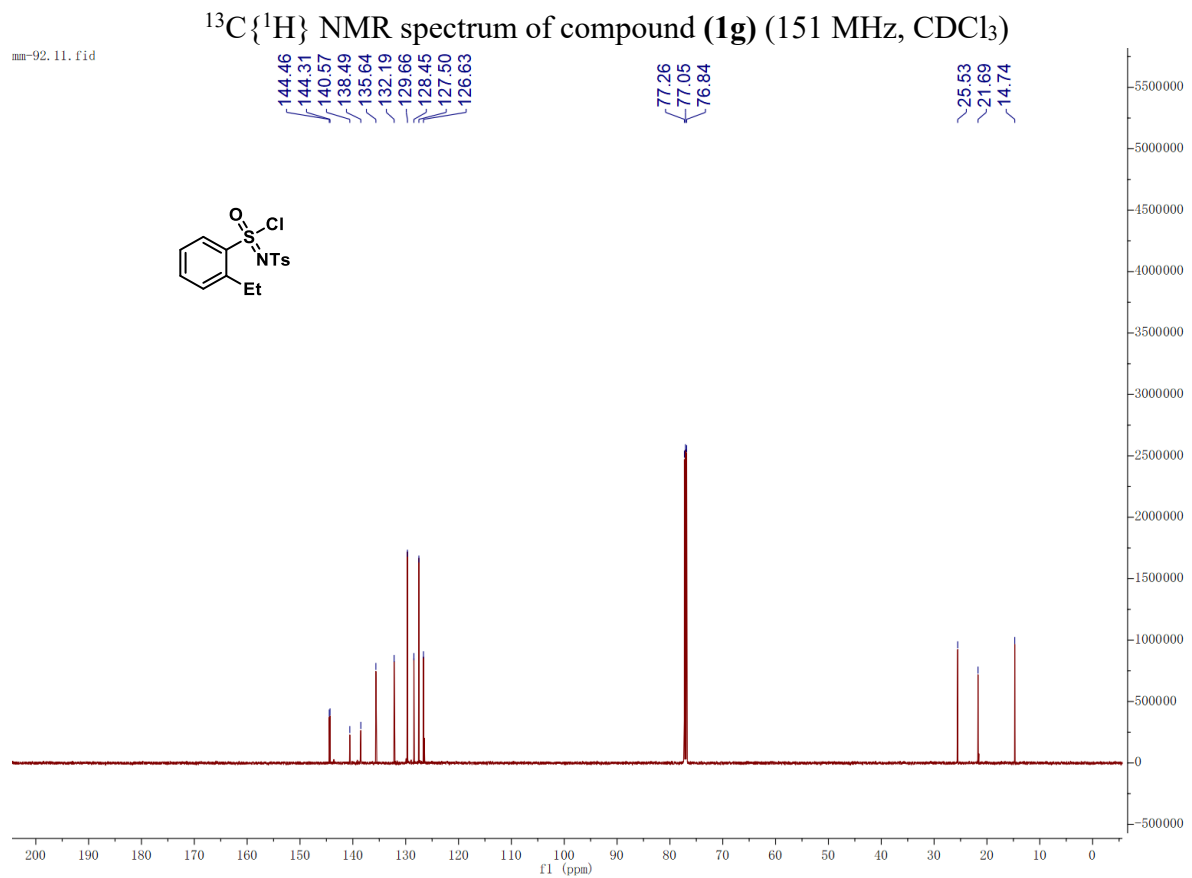
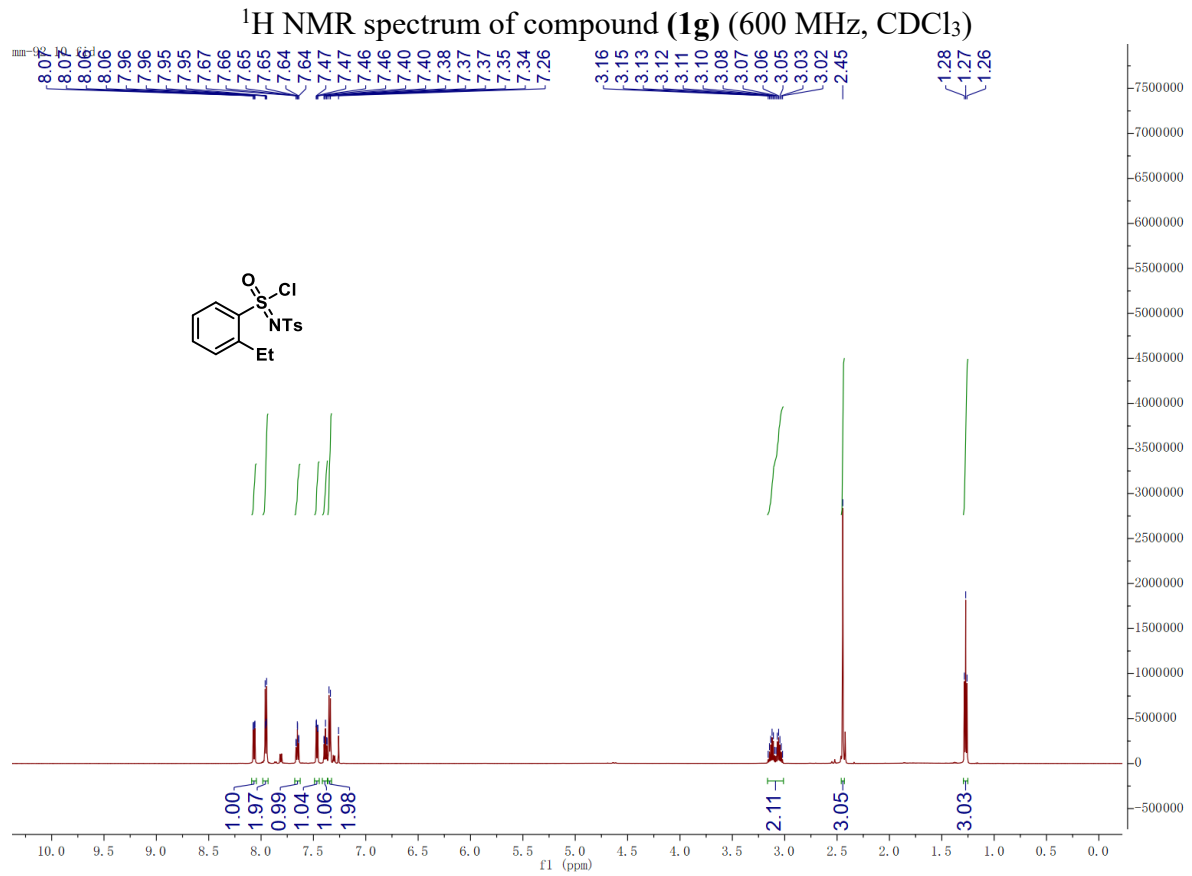
- S1 R. Kowalczyk, A. J. F. Edmunds, R. G. Hall and C. Bolm, *Org. Lett.*, 2011, **13**, 768-771.
- S2 J. Kuang and S. Ma, *J. Org. Chem.*, 2009, **74**, 1763-1765.
- S3 N. Lu, Z. Zhang, N. Ma, C. Wu, G. Zhang, Q. Liu and T. Liu, *Org. Lett.*, 2018, **20**, 4318-4322.

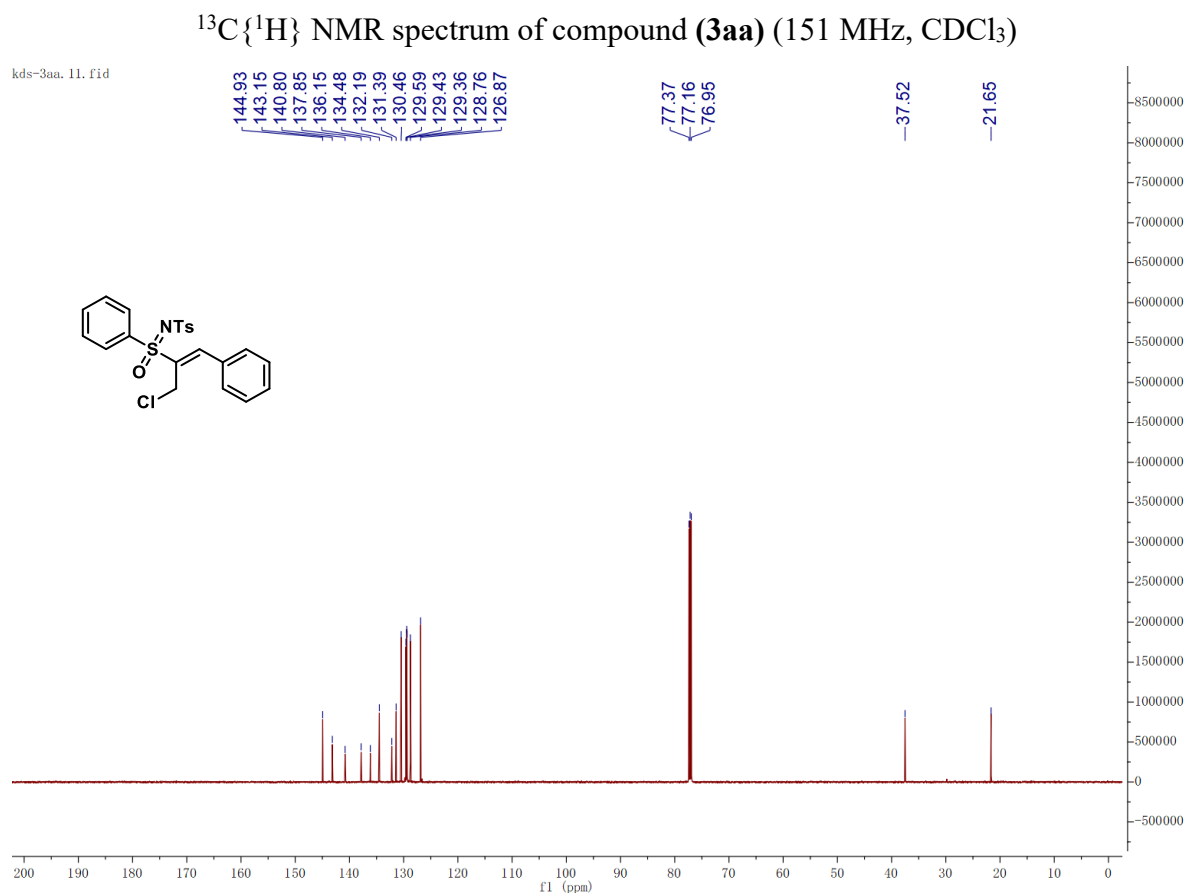
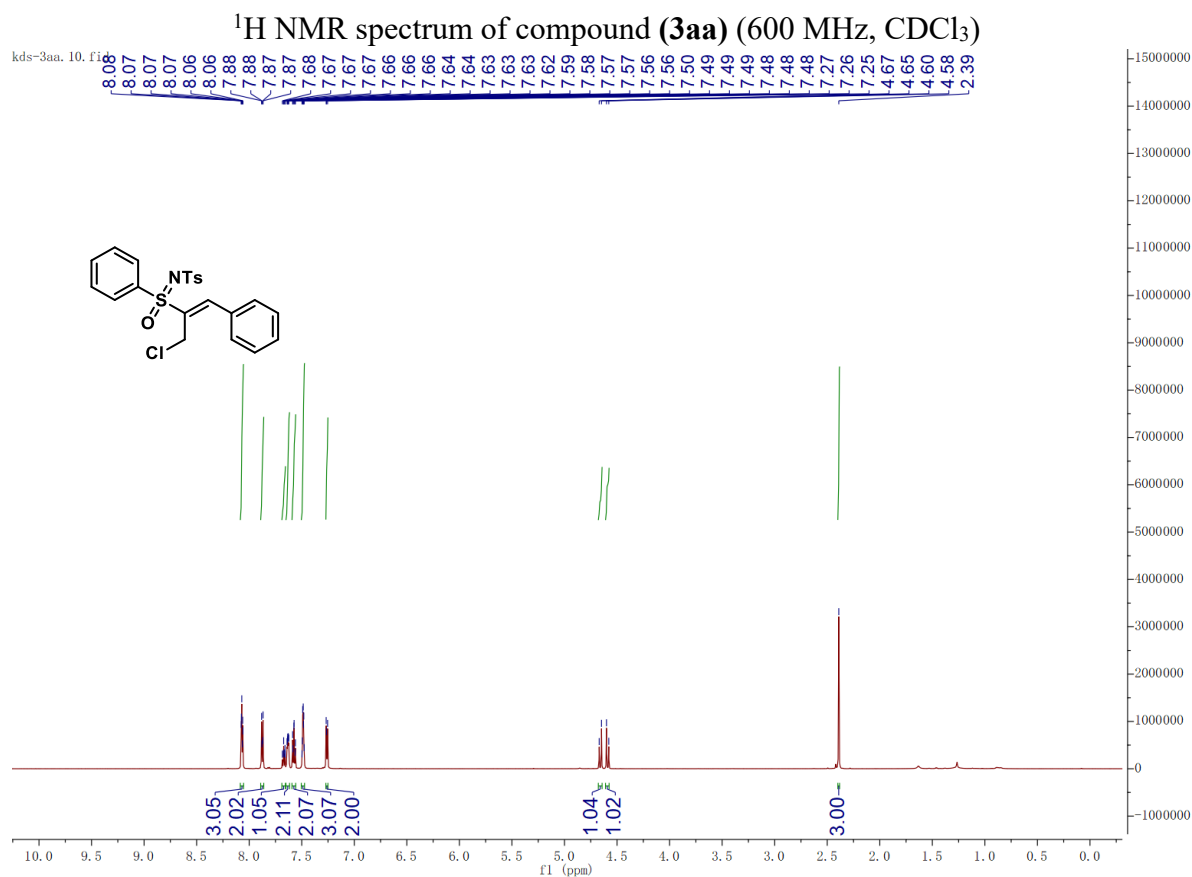
8. NMR spectra

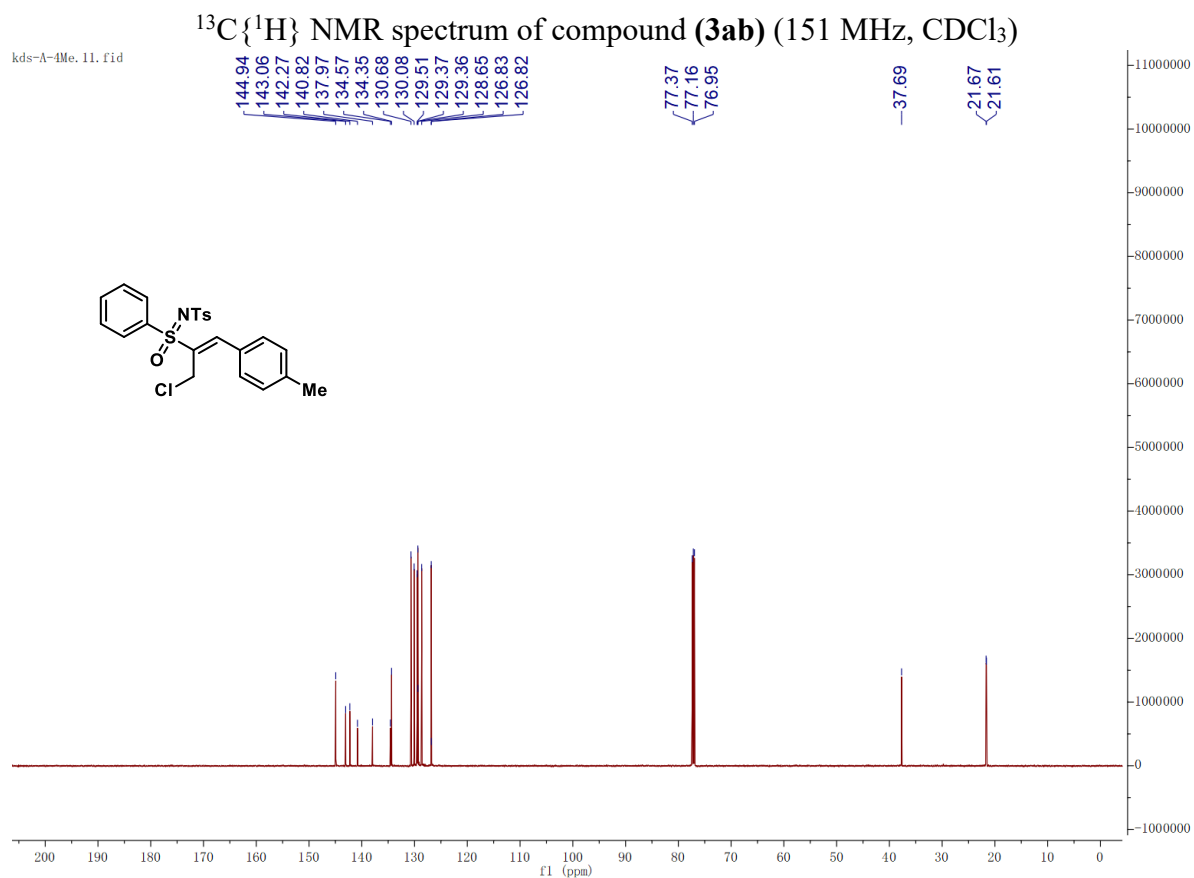
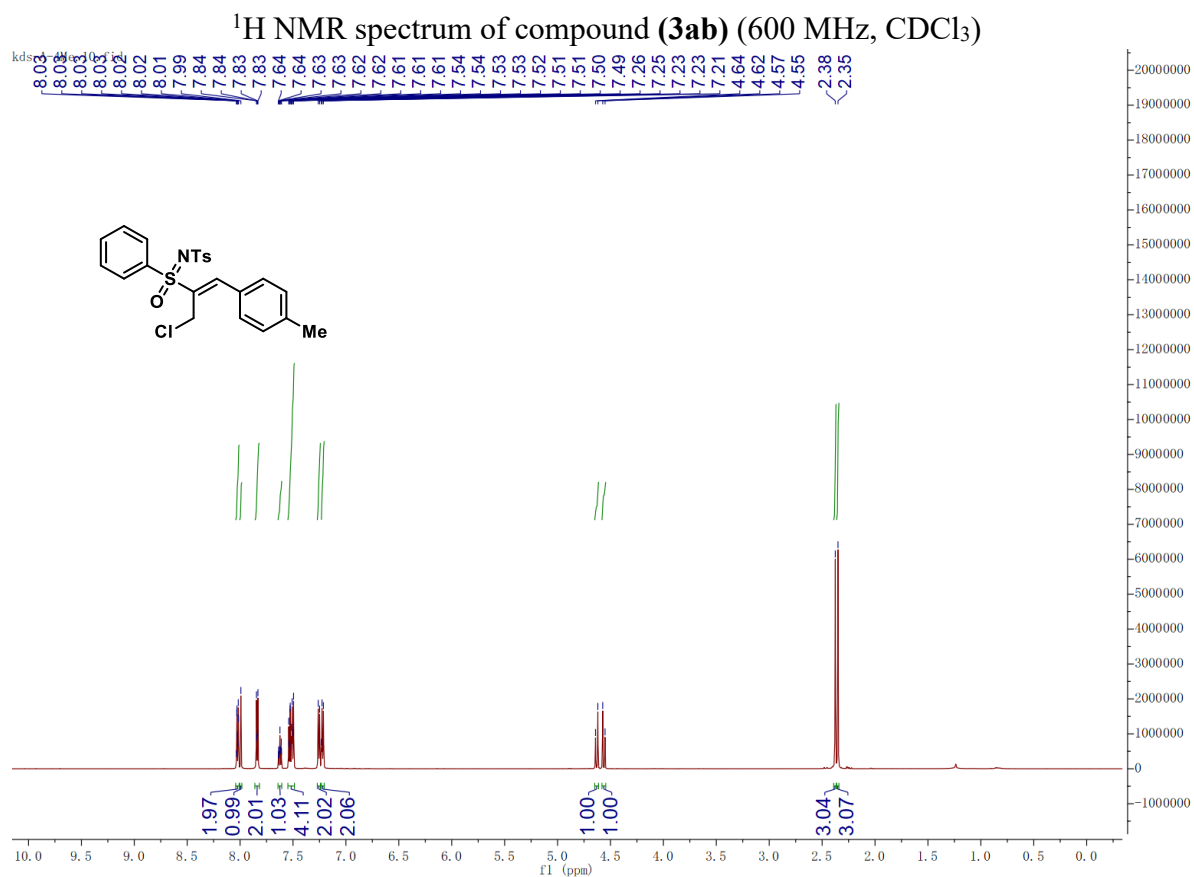


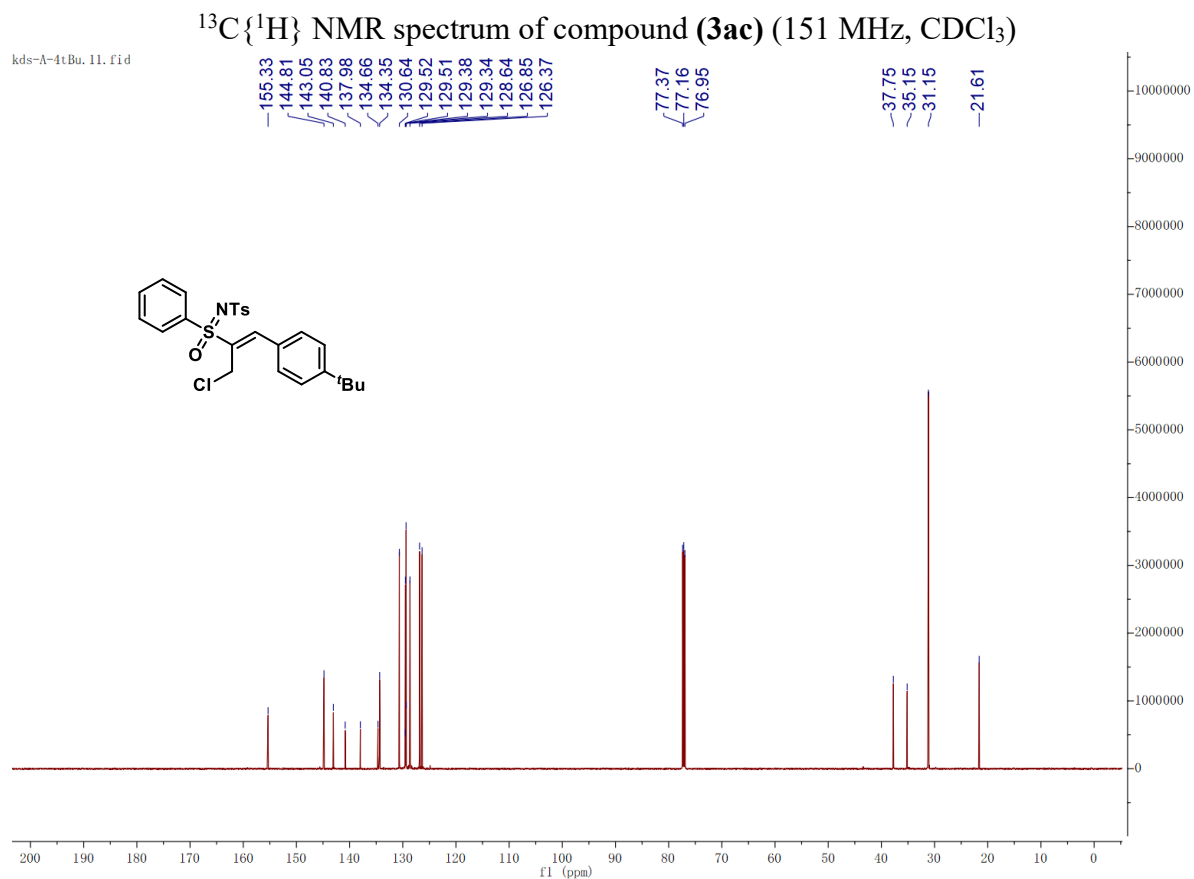
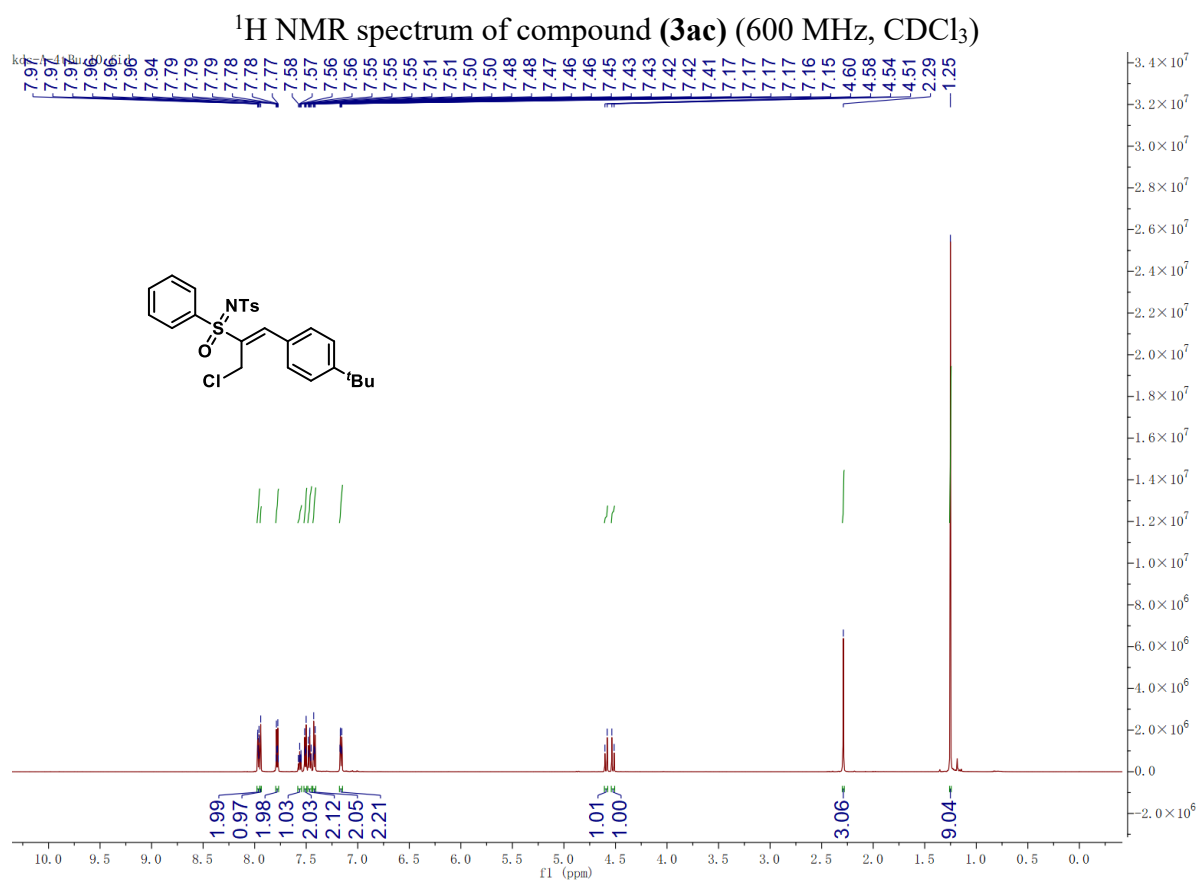
¹H NMR spectrum of compound (1e) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (1e) (151 MHz, CDCl₃)

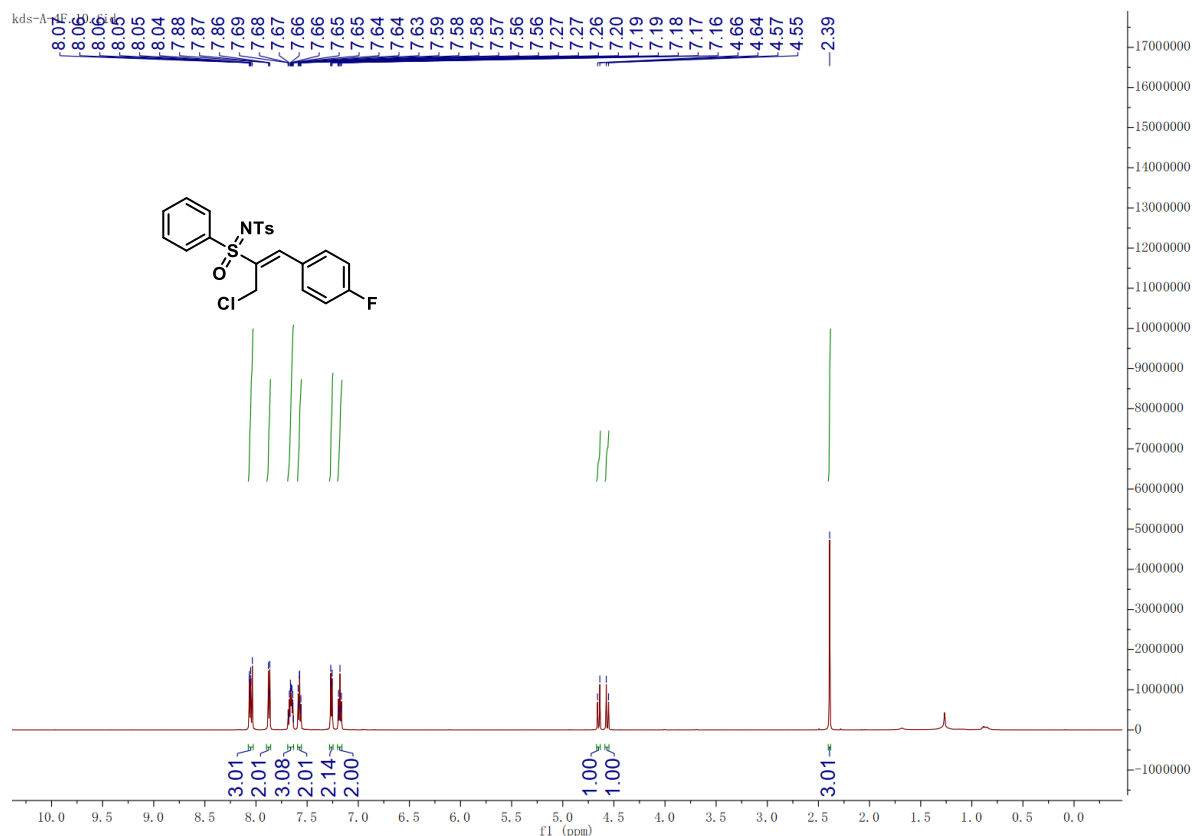
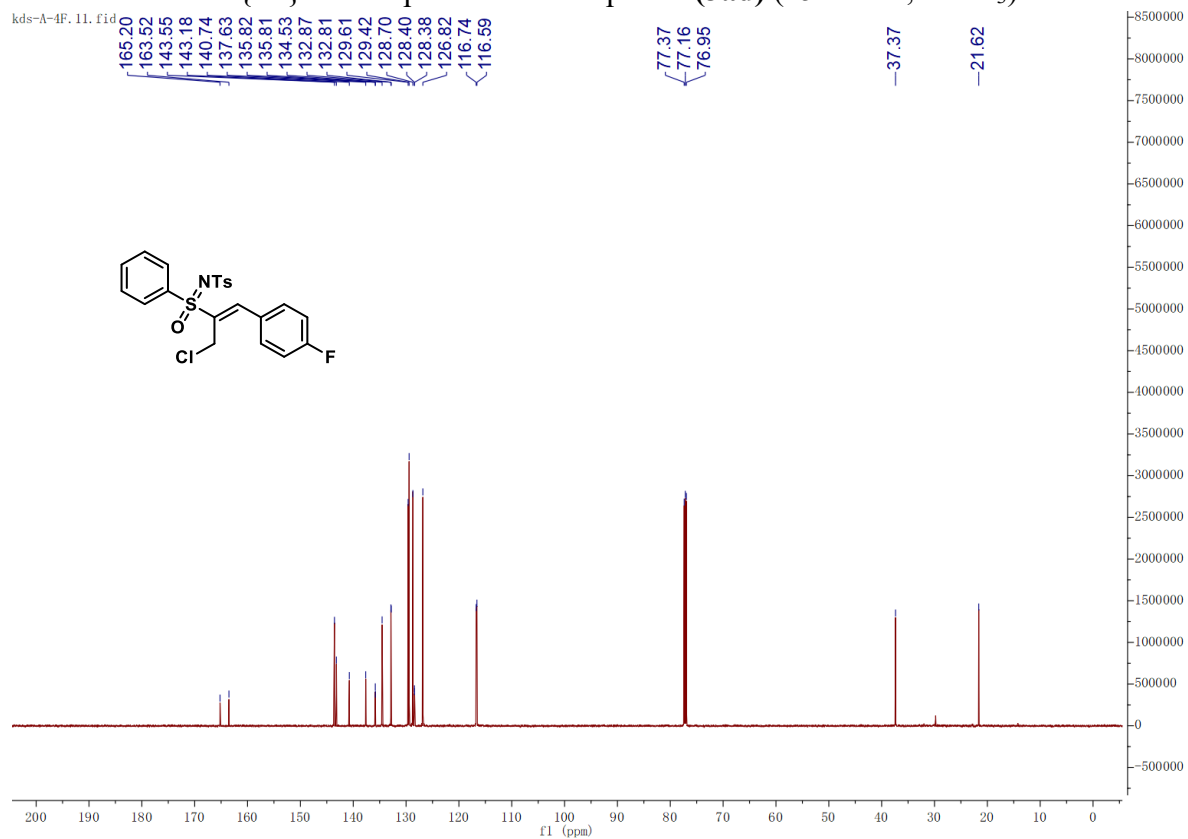
^1H NMR spectrum of compound (**1f**) (600 MHz, CDCl_3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (**1f**) (151 MHz, CDCl_3)

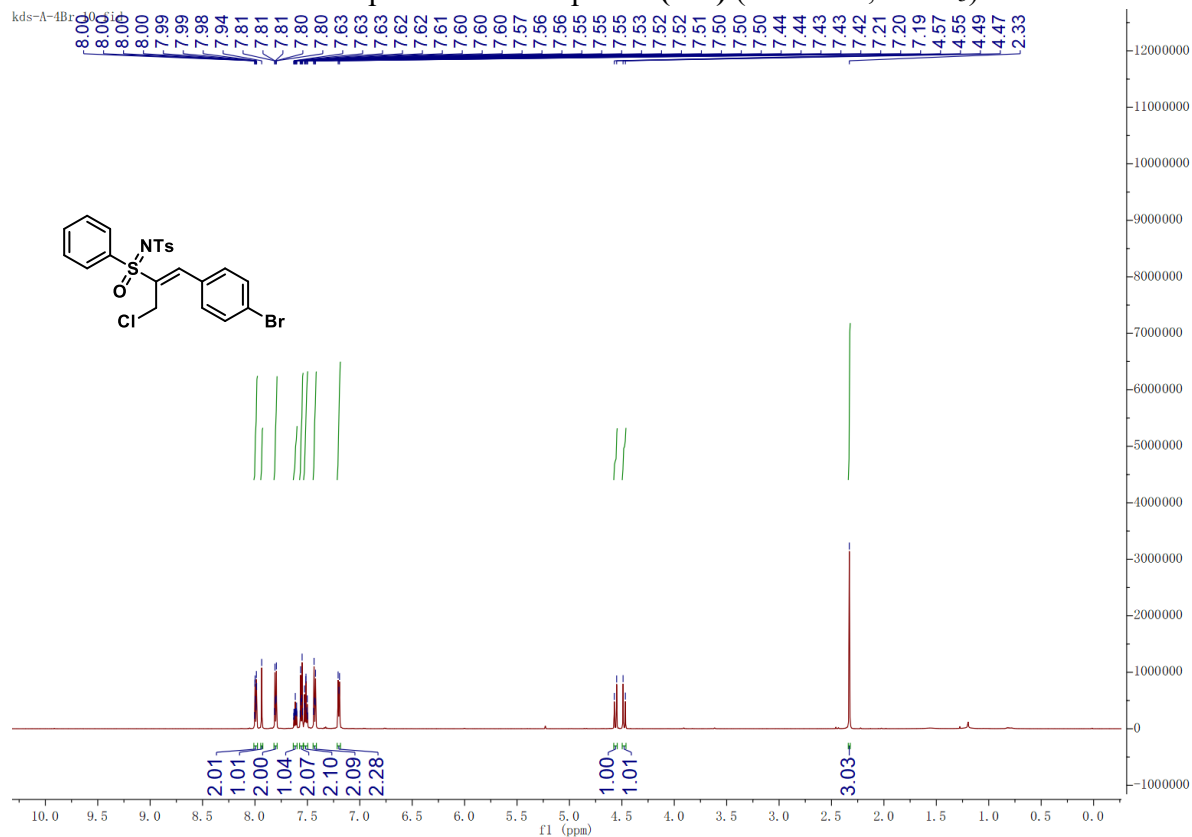


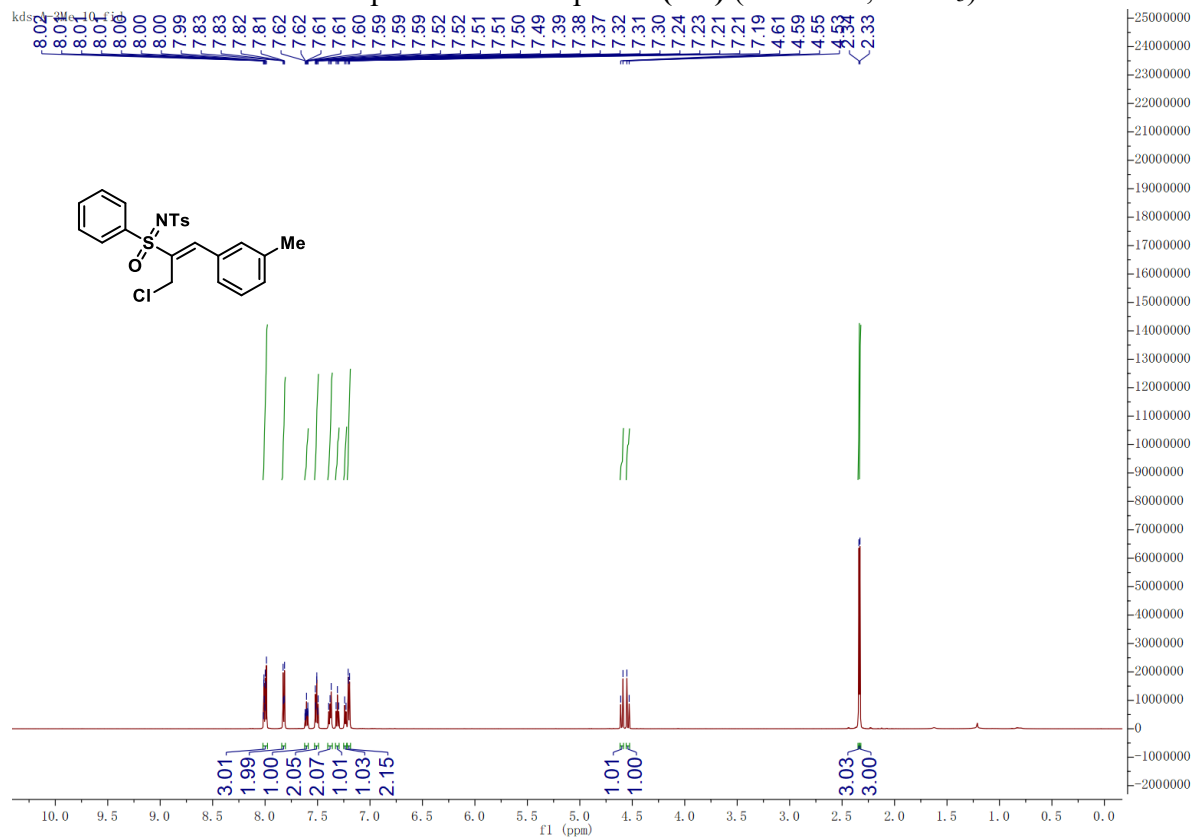
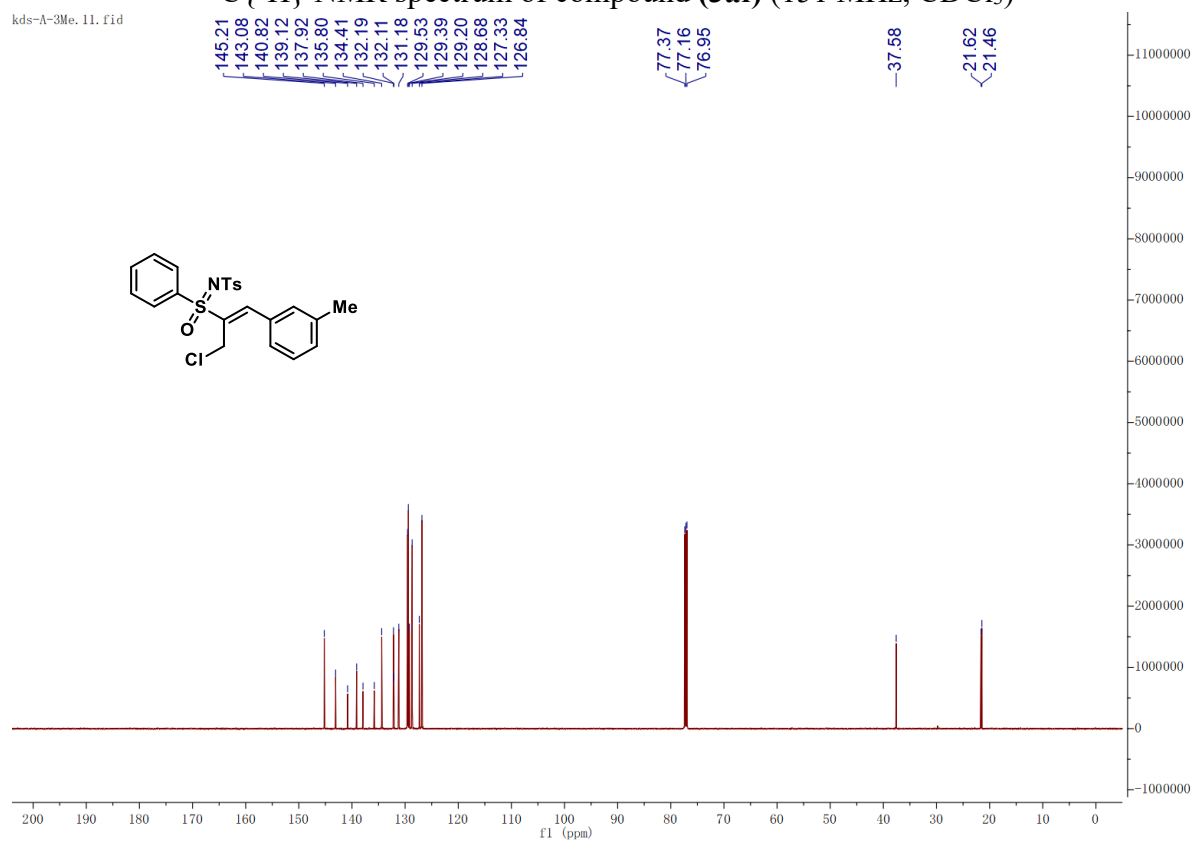


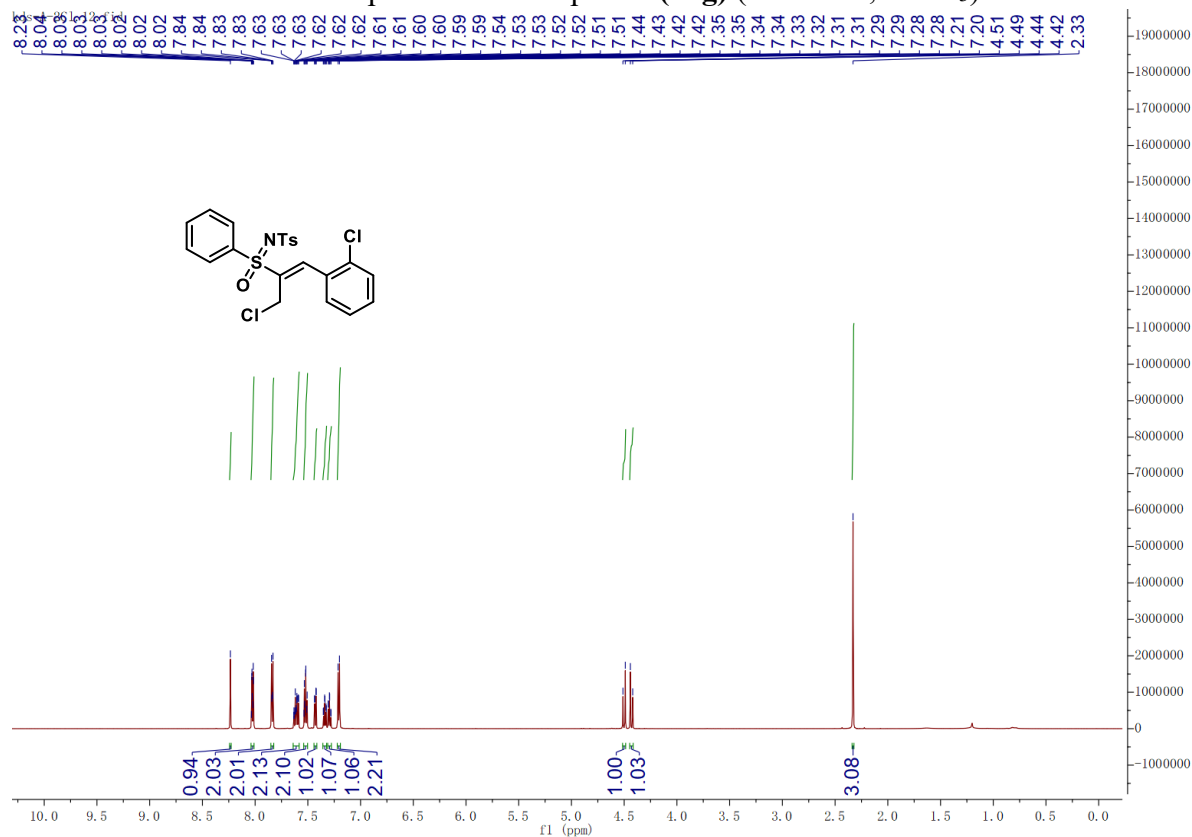
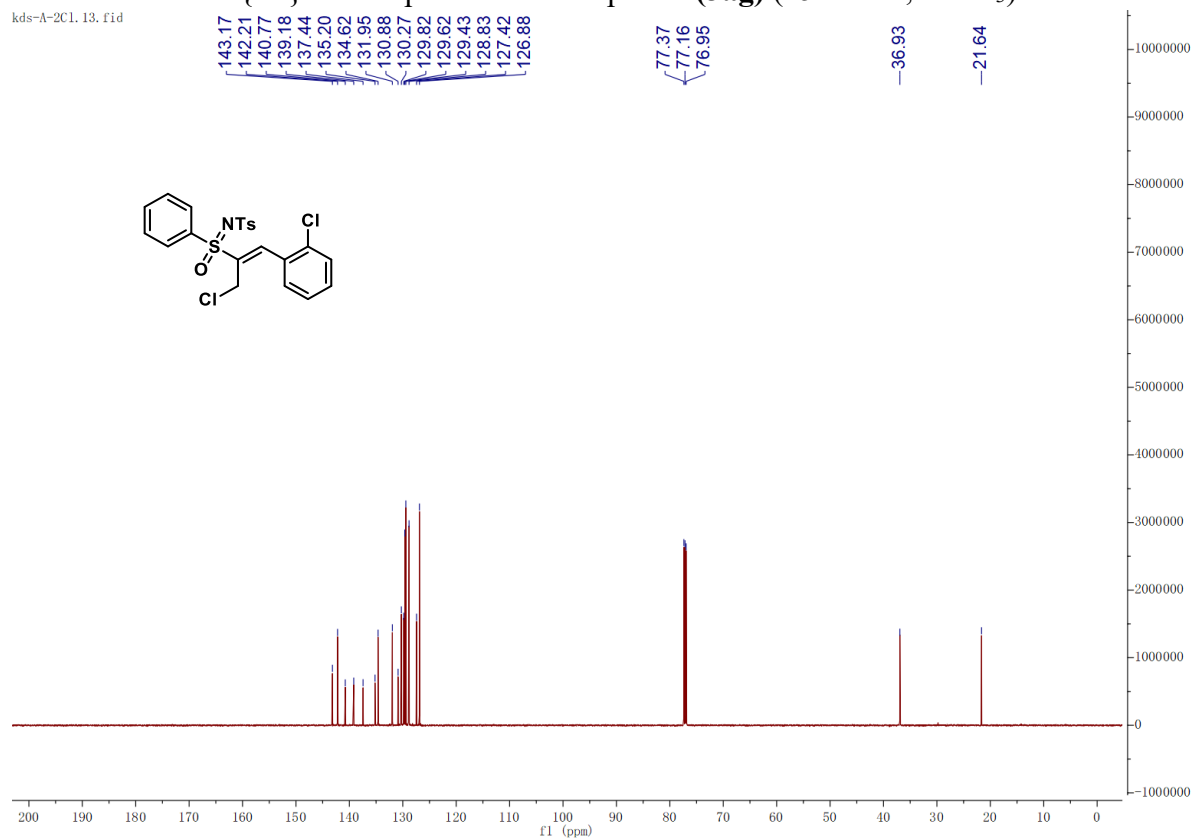


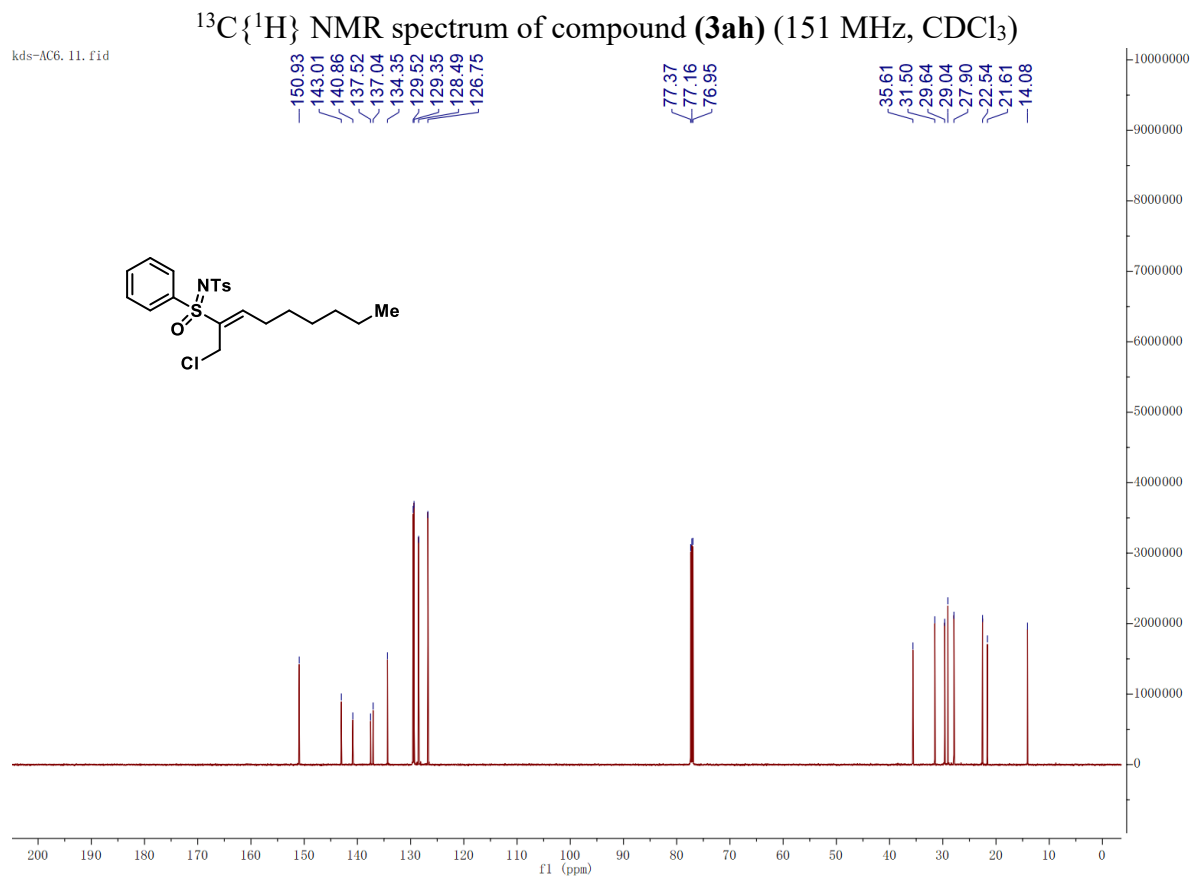
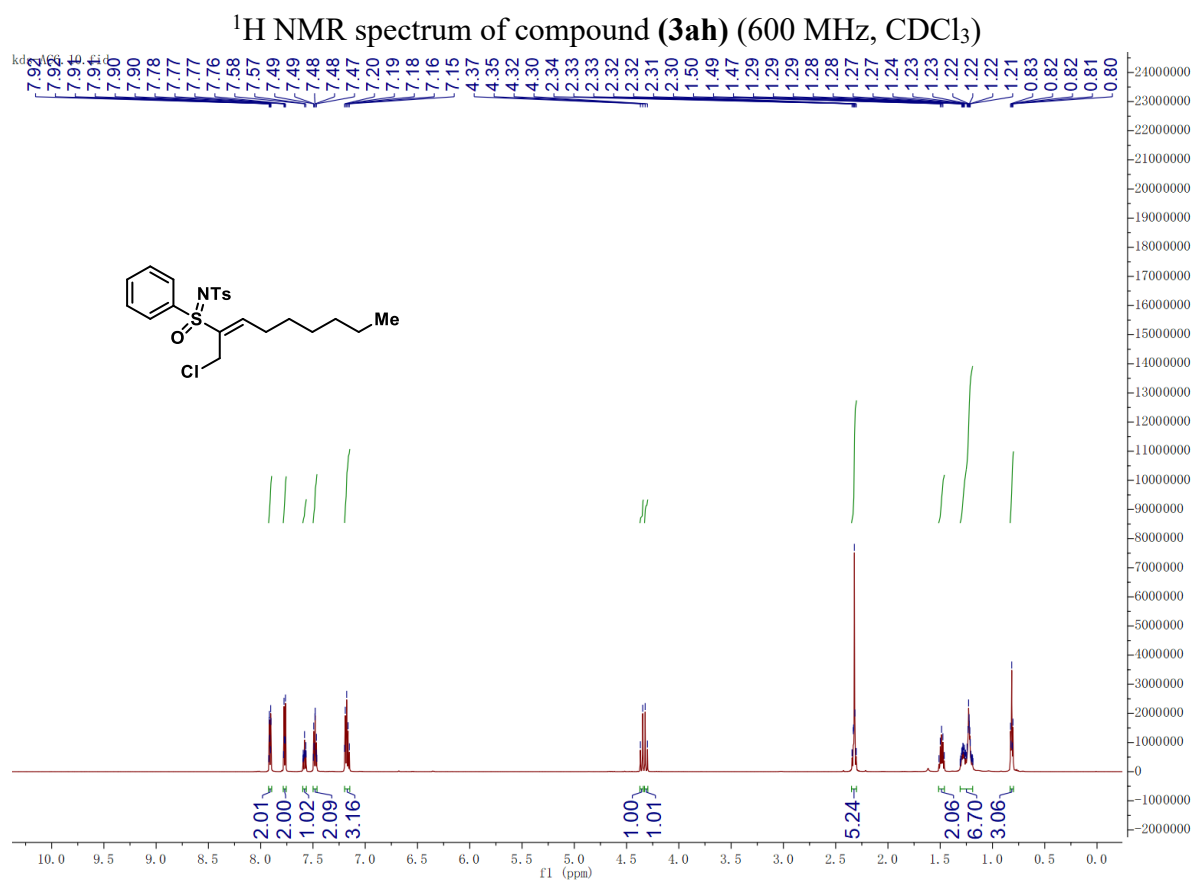


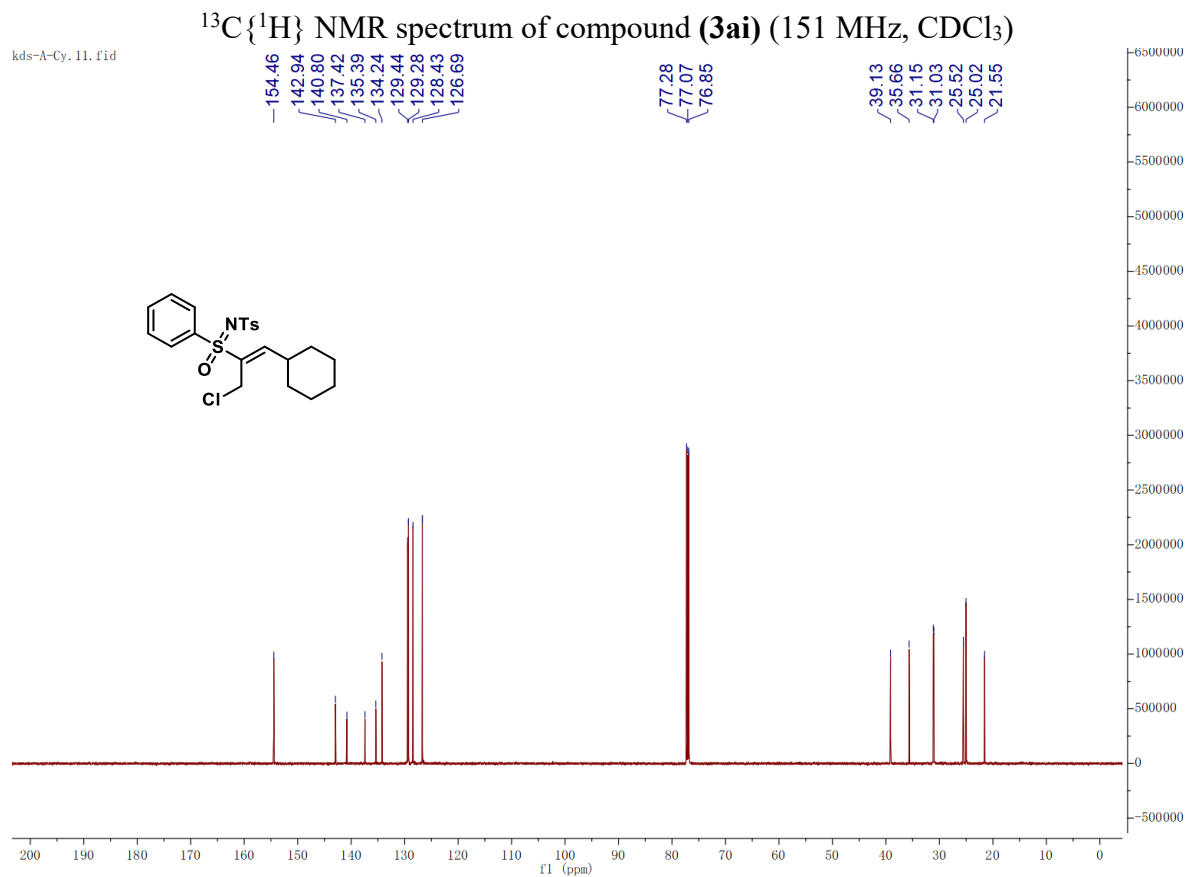
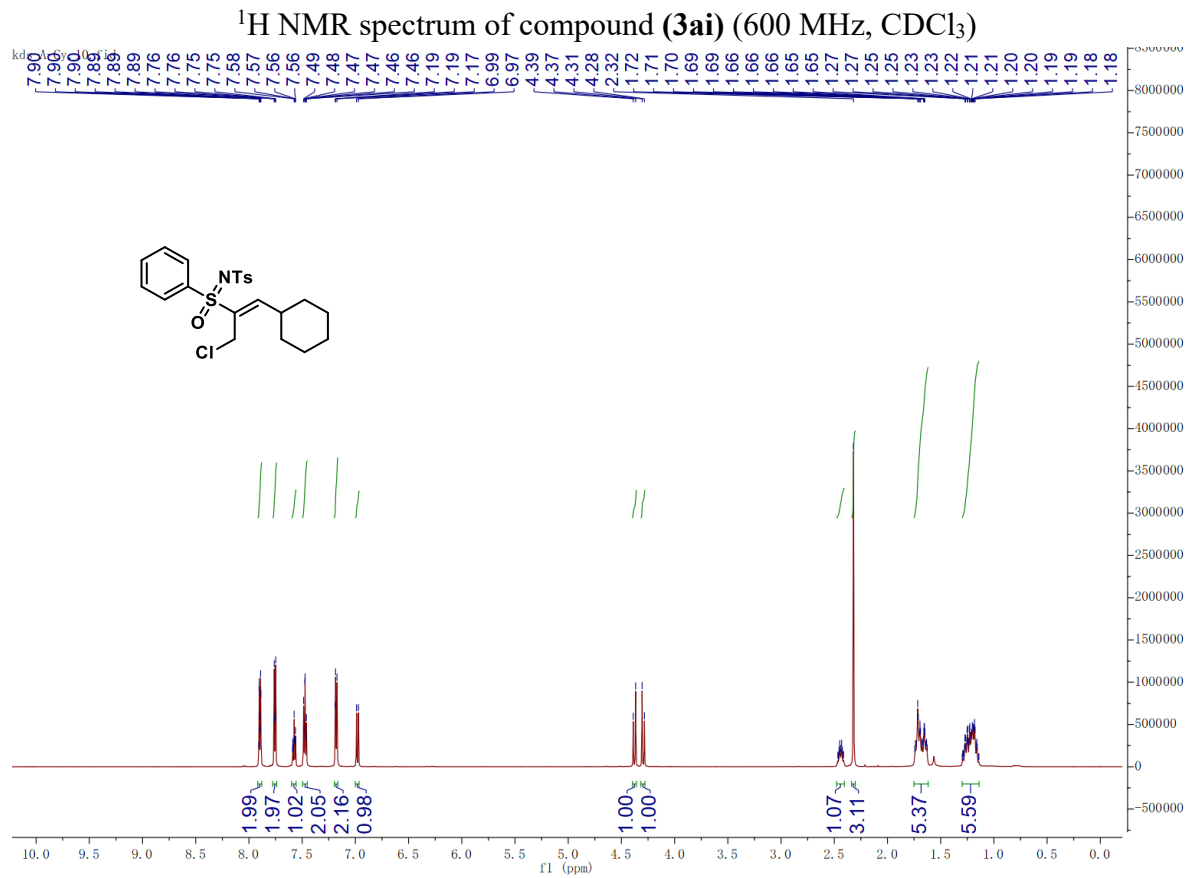
^1H NMR spectrum of compound (**3ad**) (600 MHz, CDCl_3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (**3ad**) (151 MHz, CDCl_3)

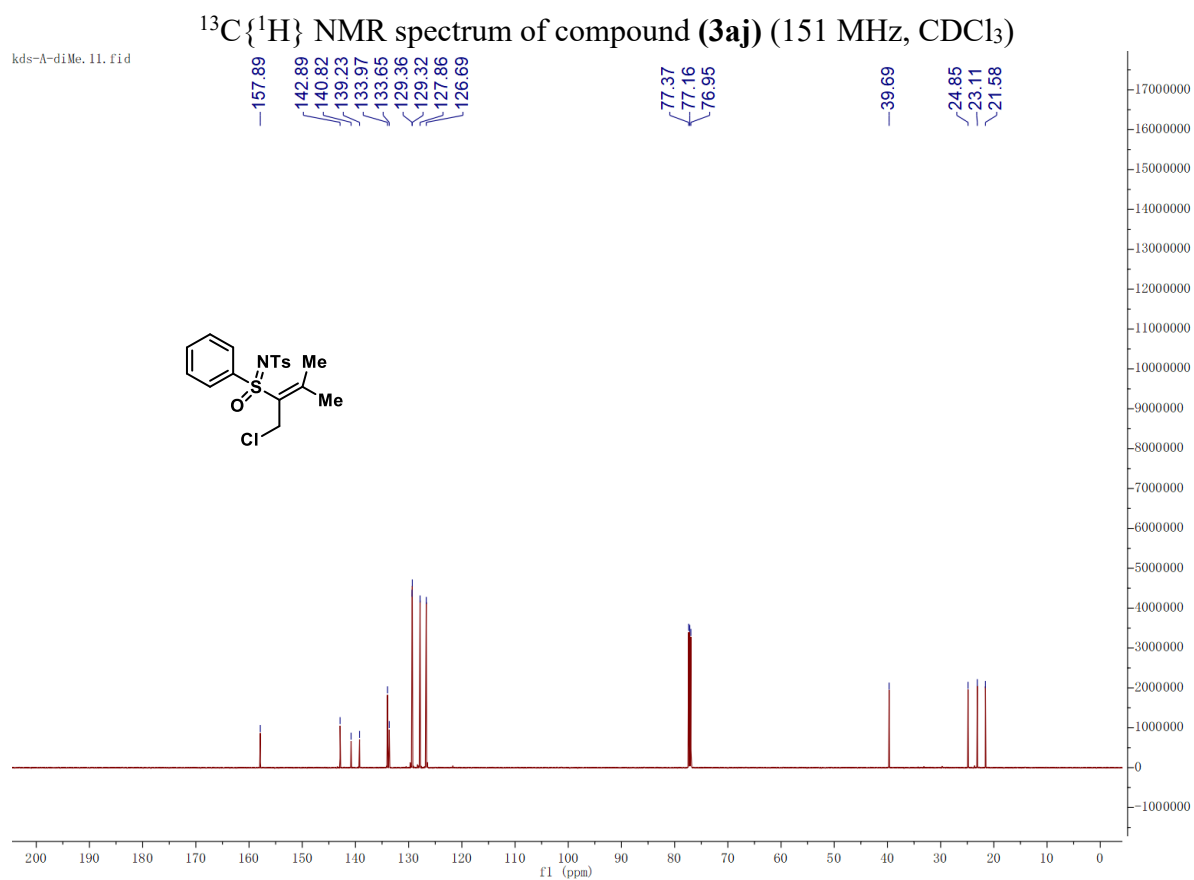
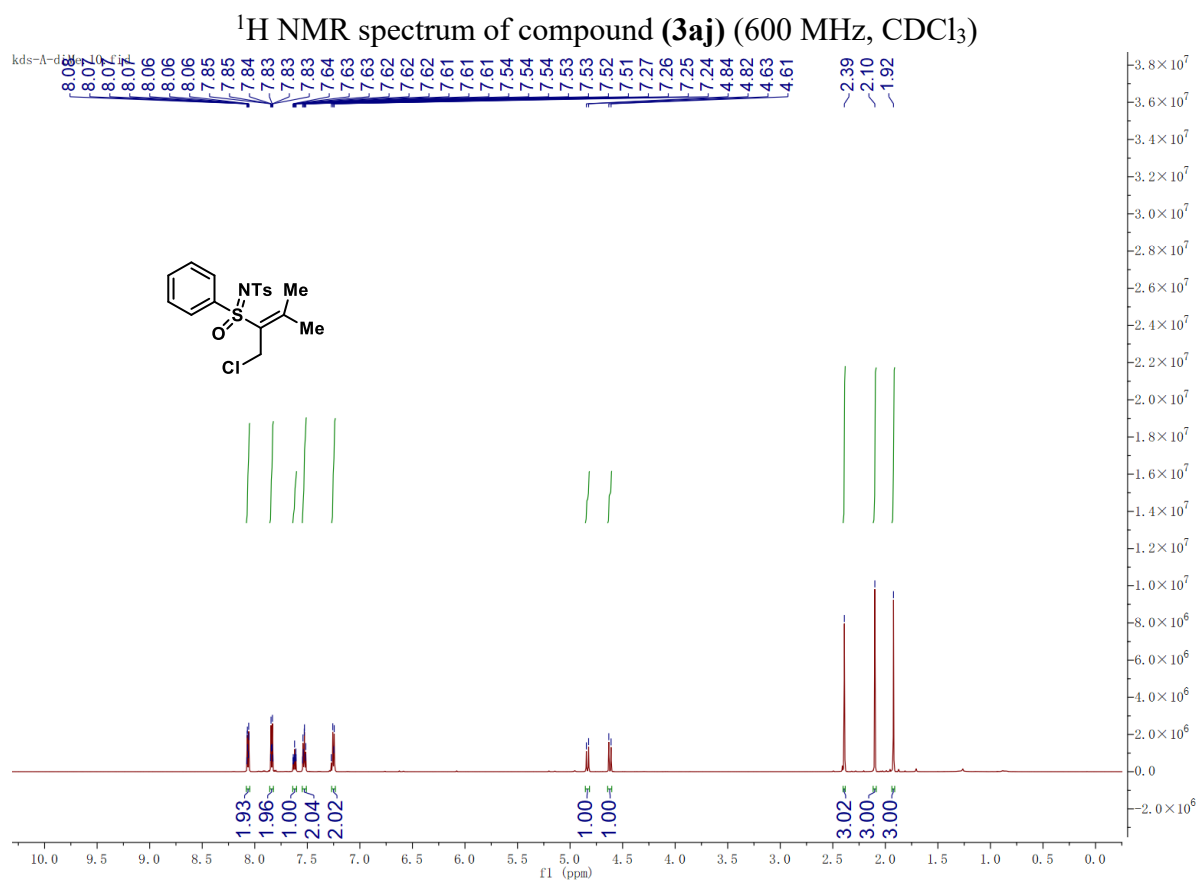
^1H NMR spectrum of compound (**3ae**) (600 MHz, CDCl_3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (**3ae**) (151 MHz, CDCl_3)

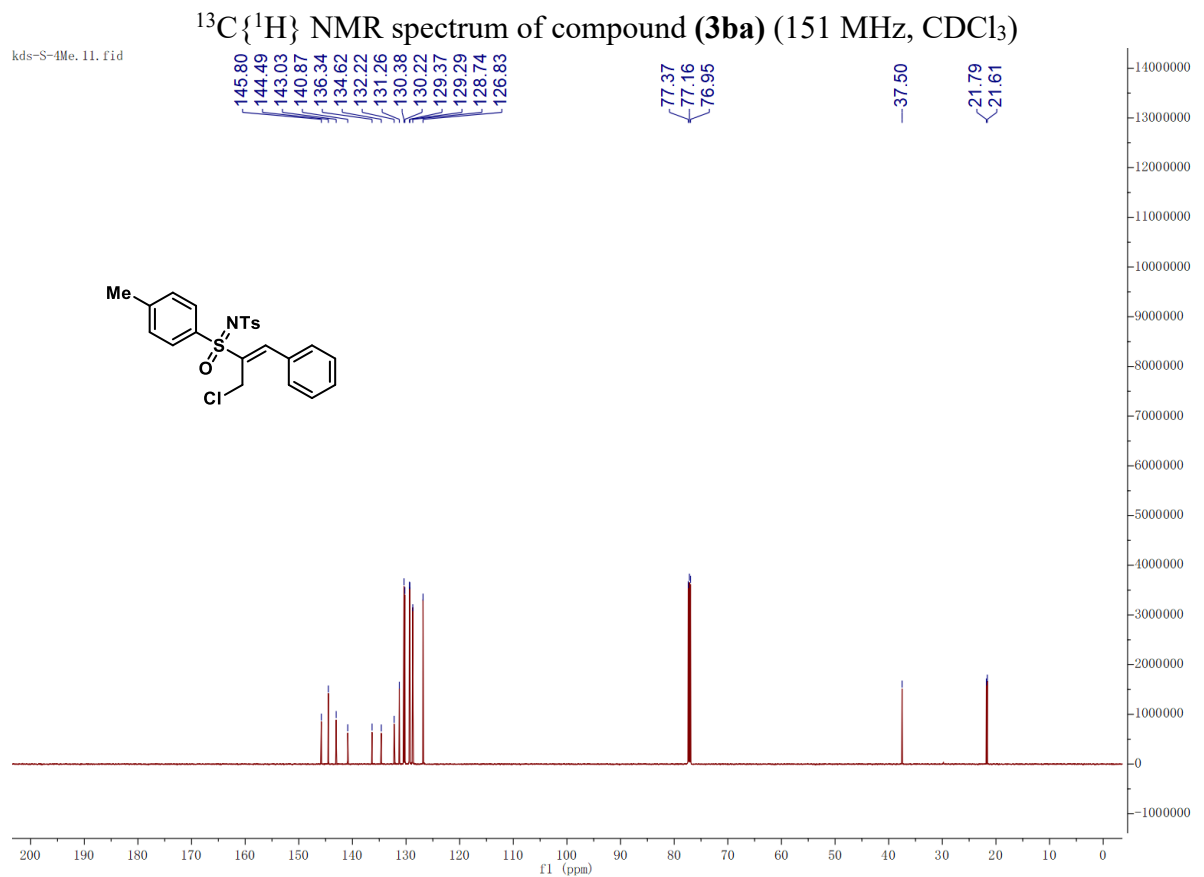
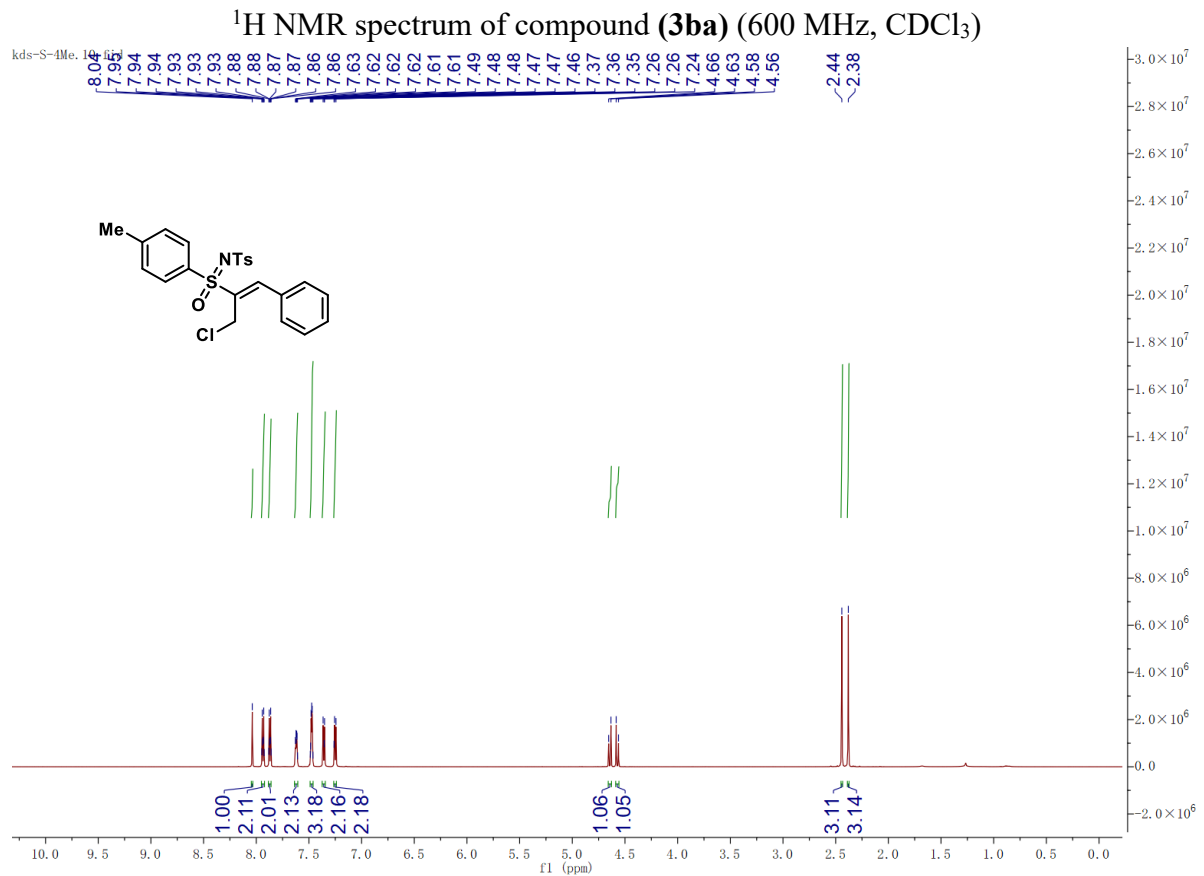
¹H NMR spectrum of compound (3af) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (3af) (151 MHz, CDCl₃)

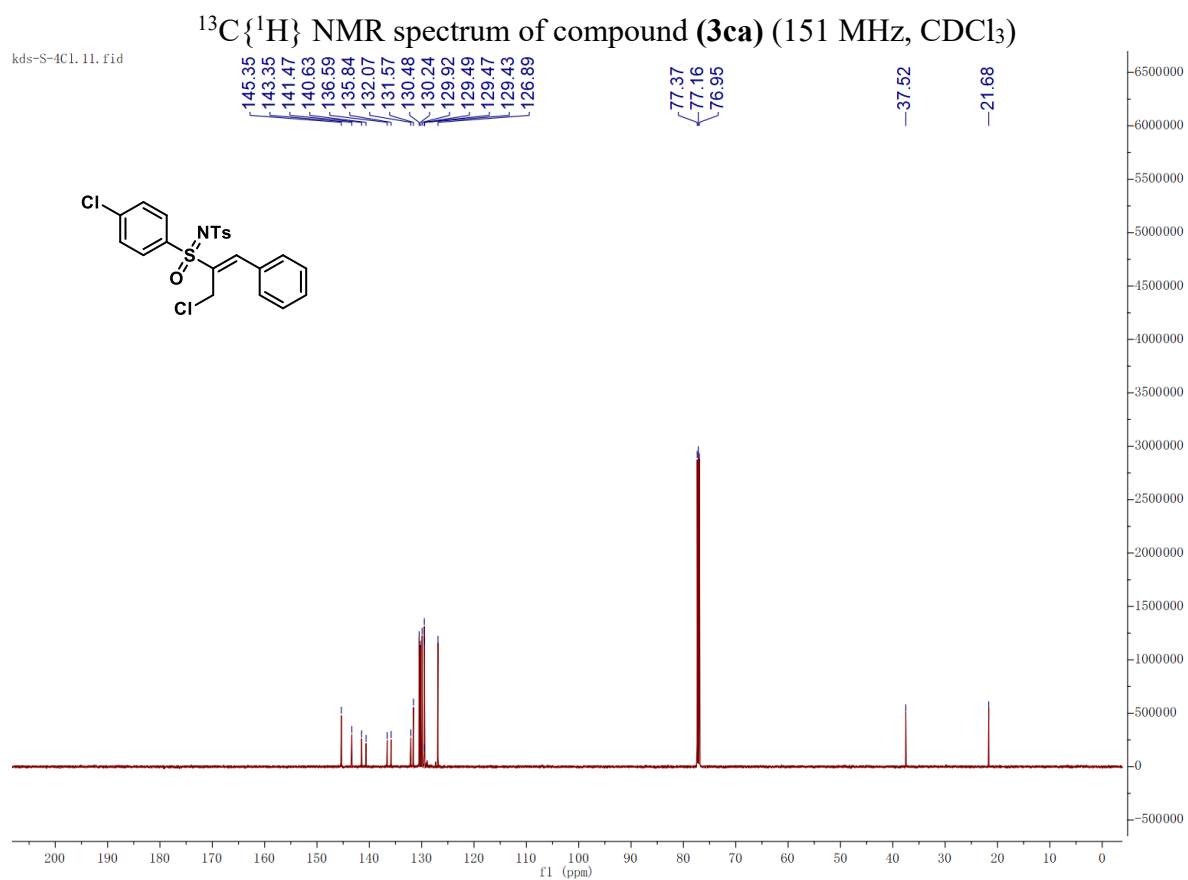
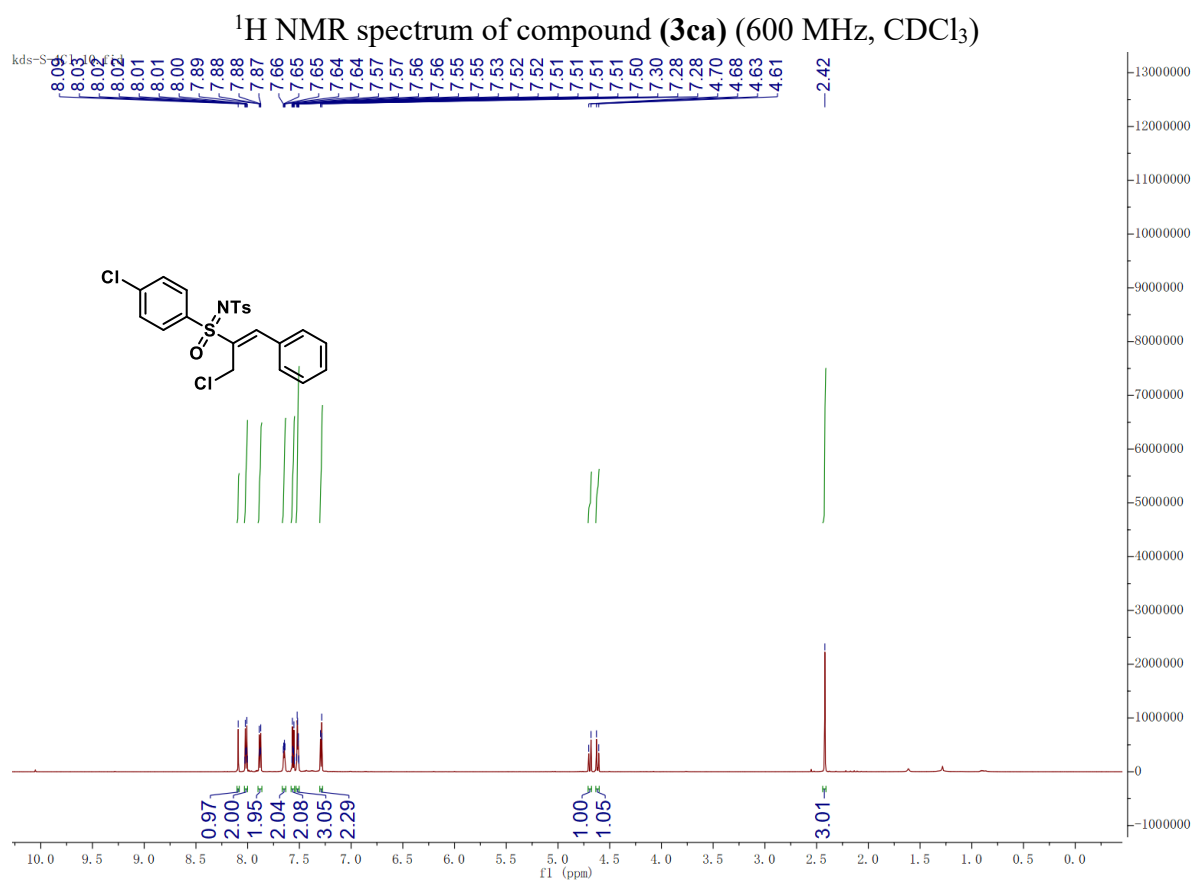
¹H NMR spectrum of compound (**3ag**) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (**3ag**) (151 MHz, CDCl₃)

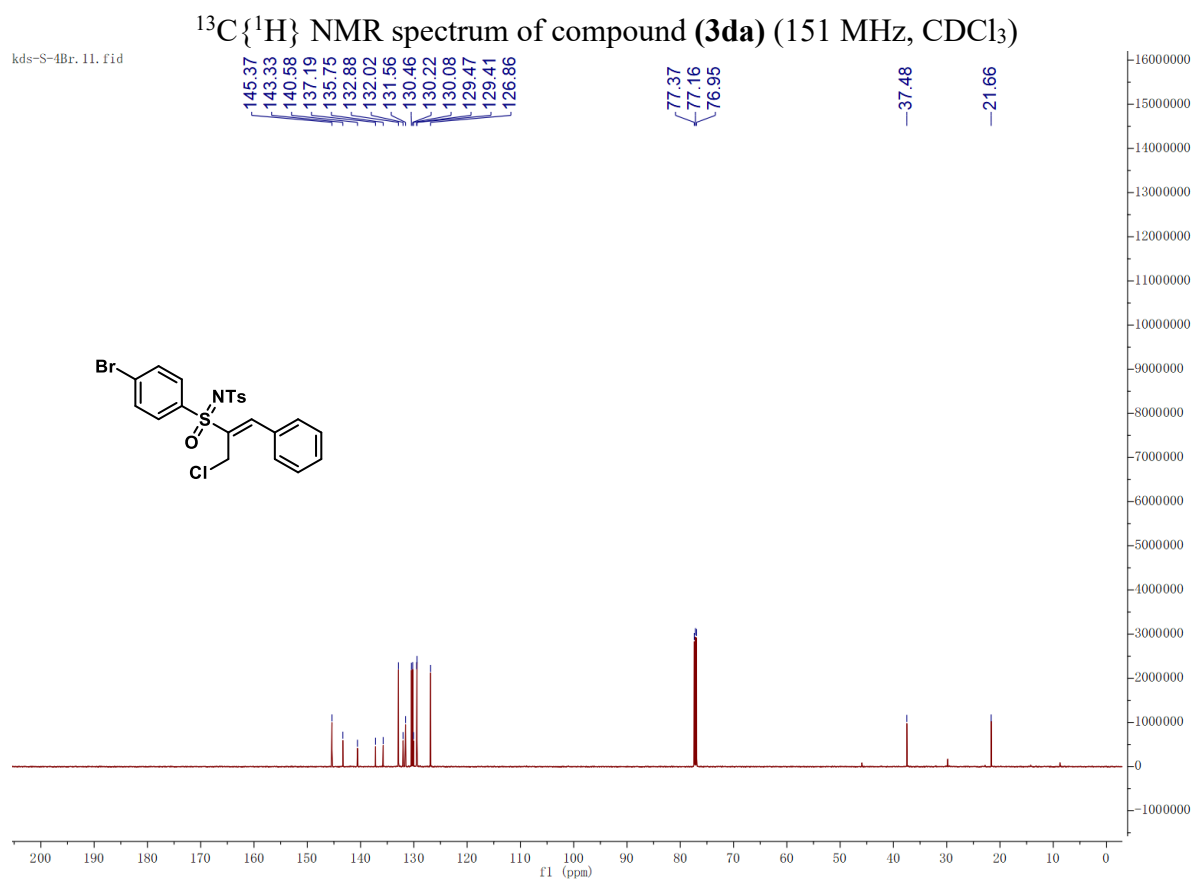
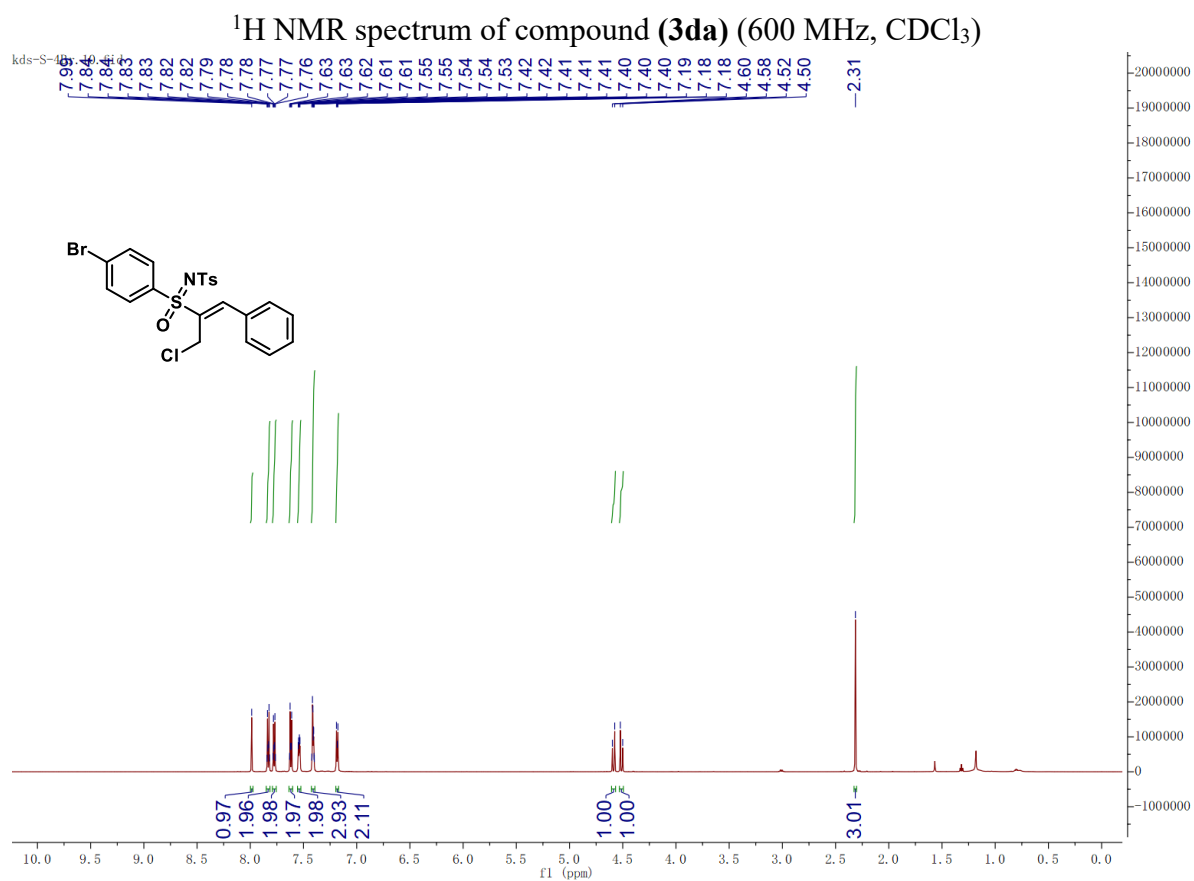


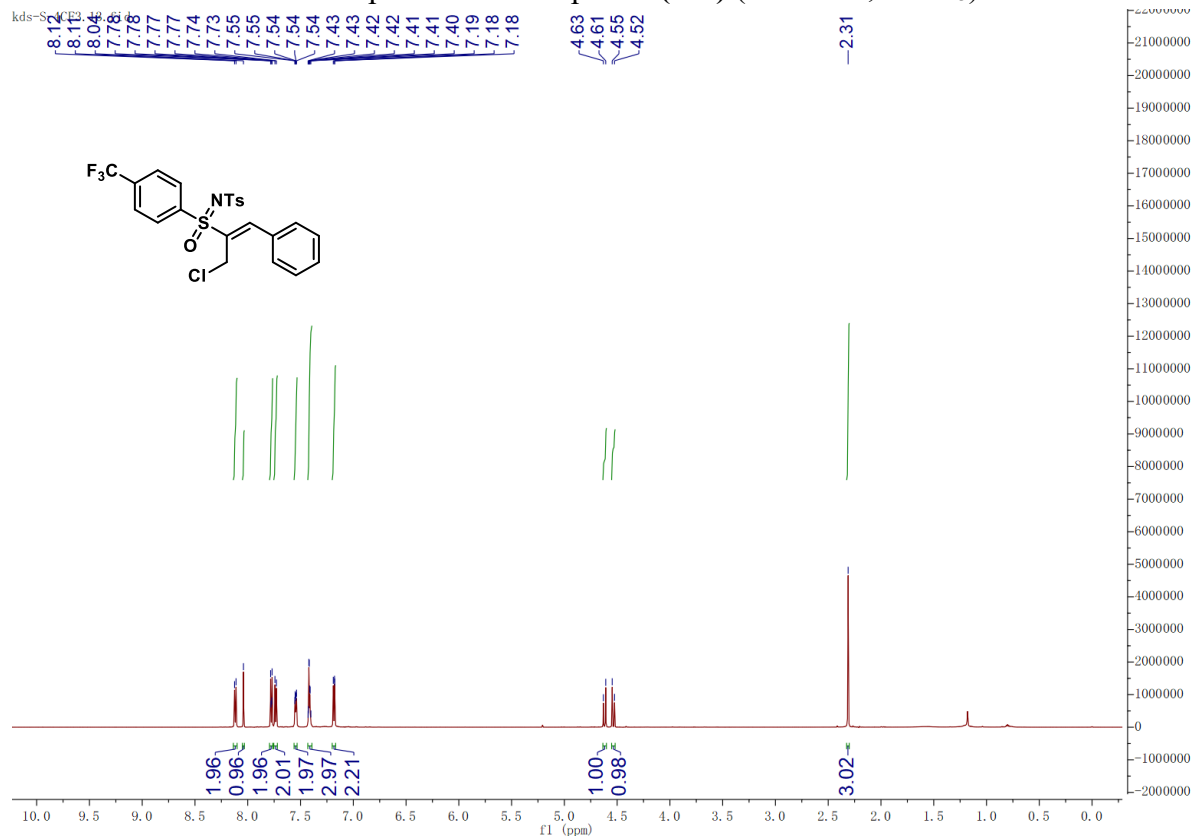
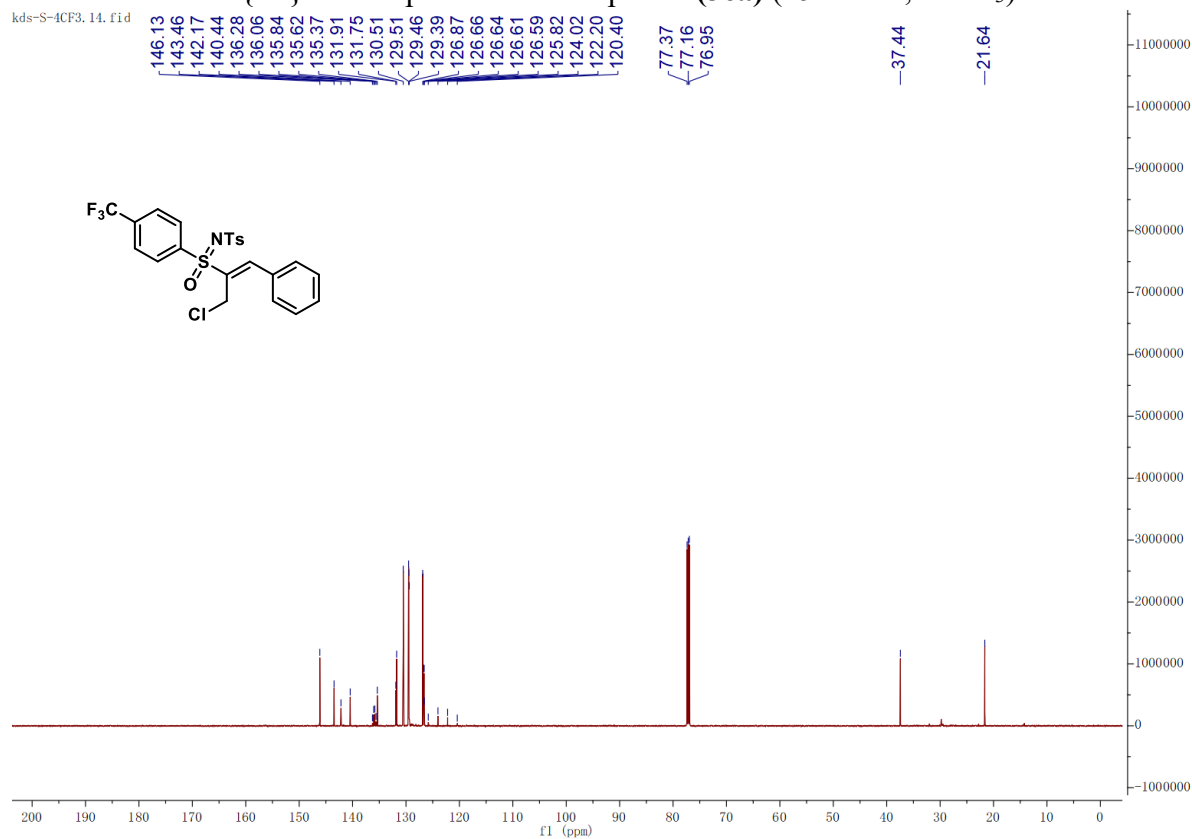


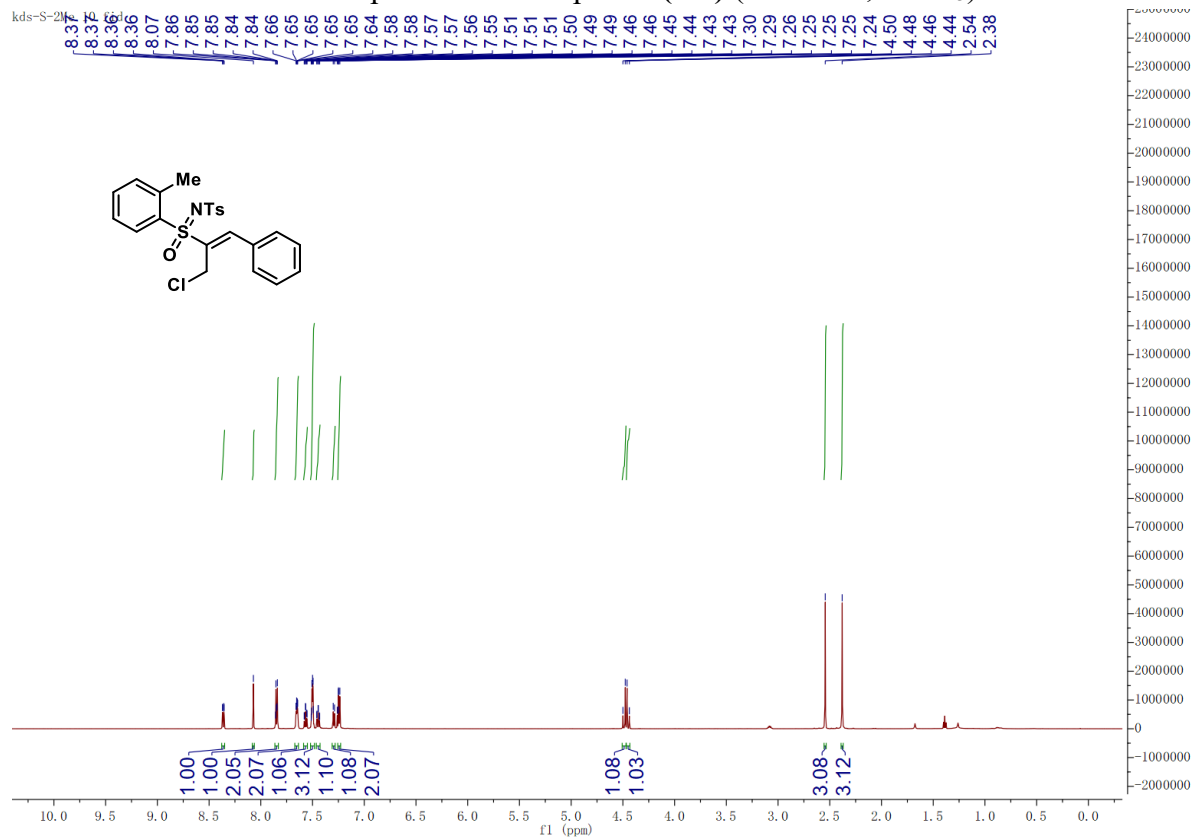
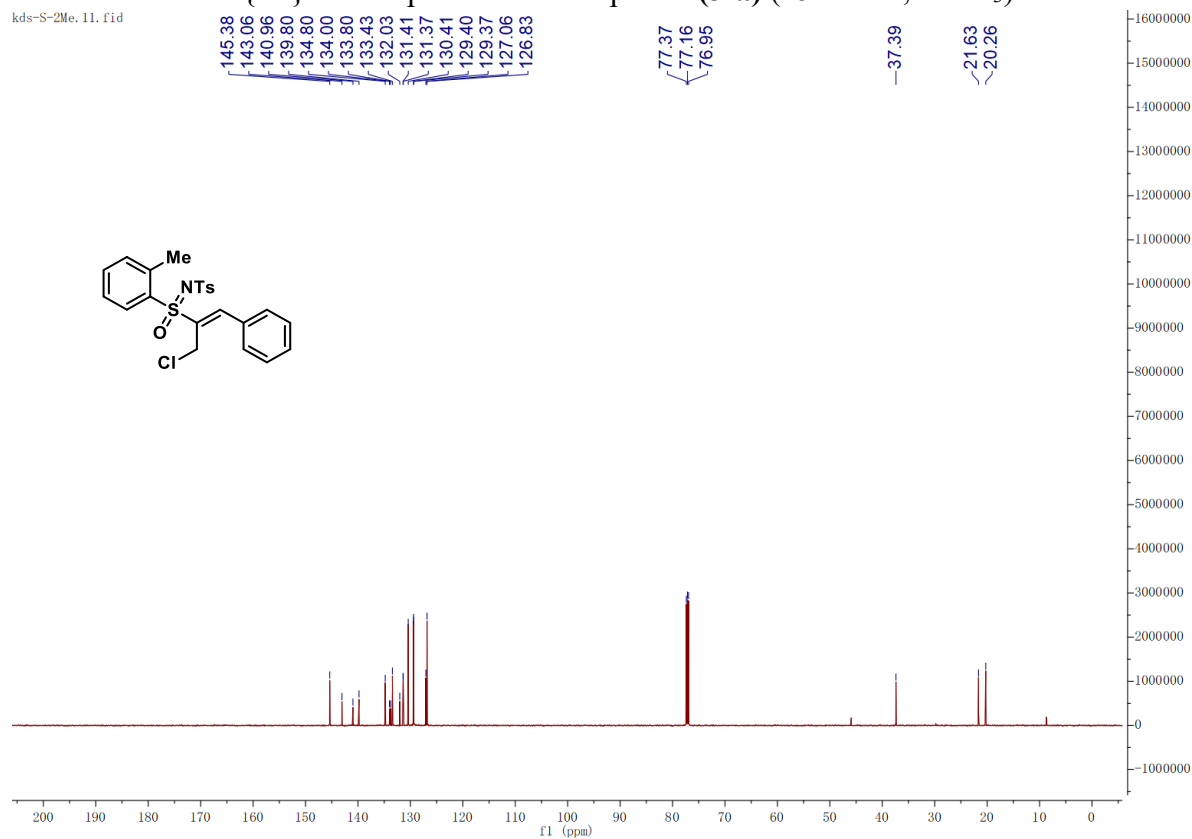


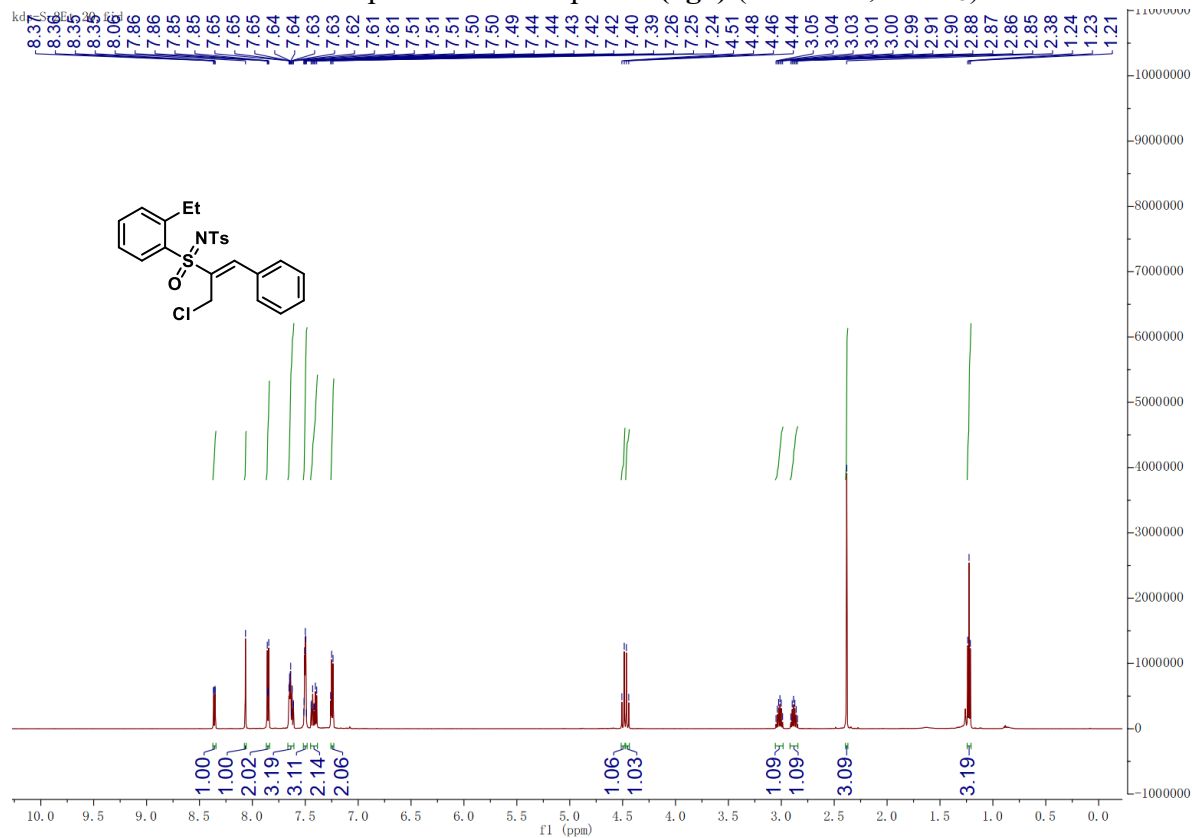
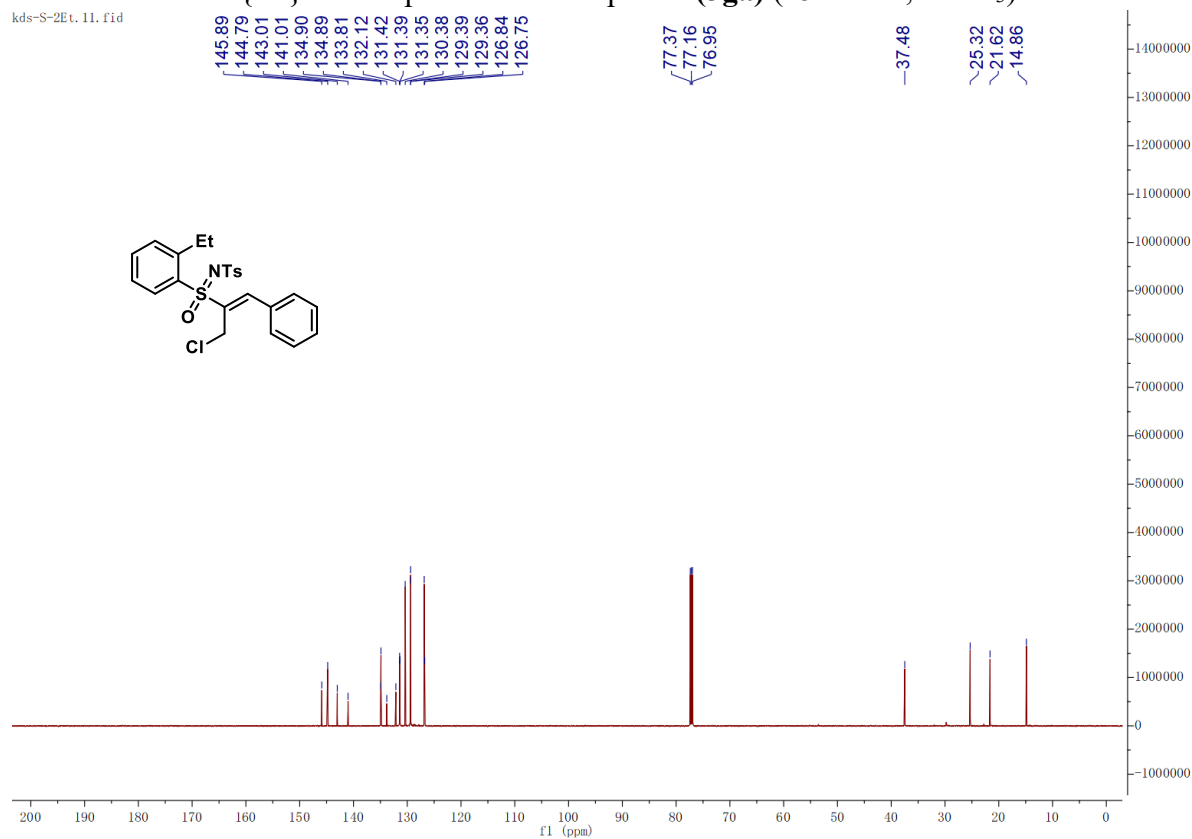


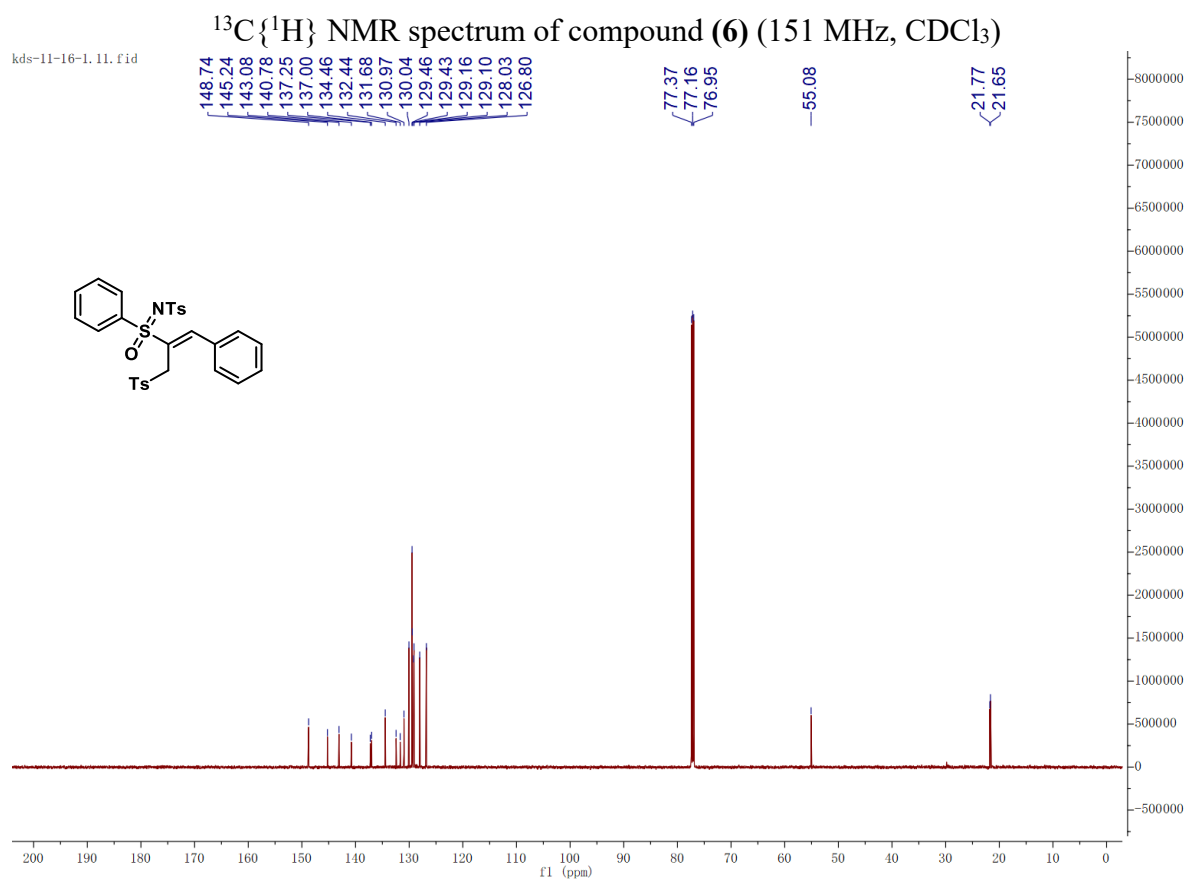
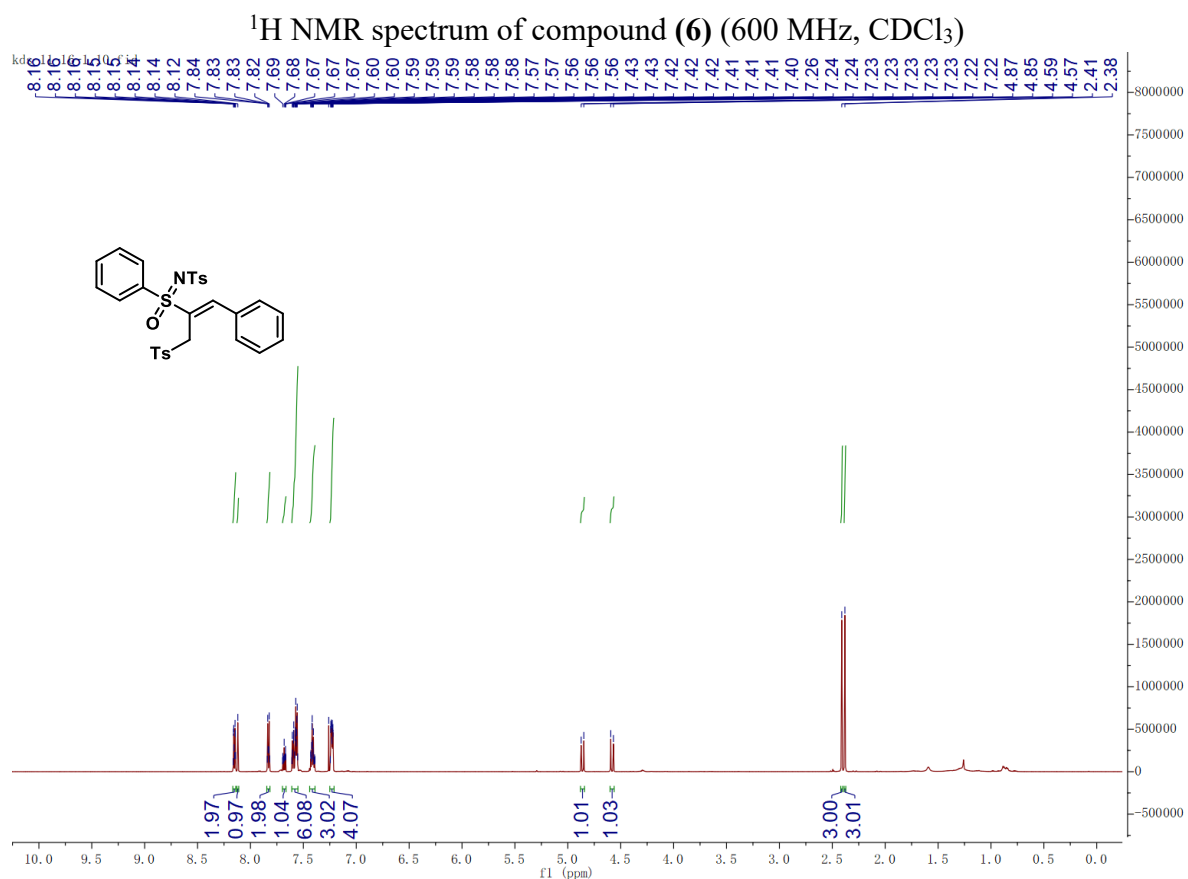


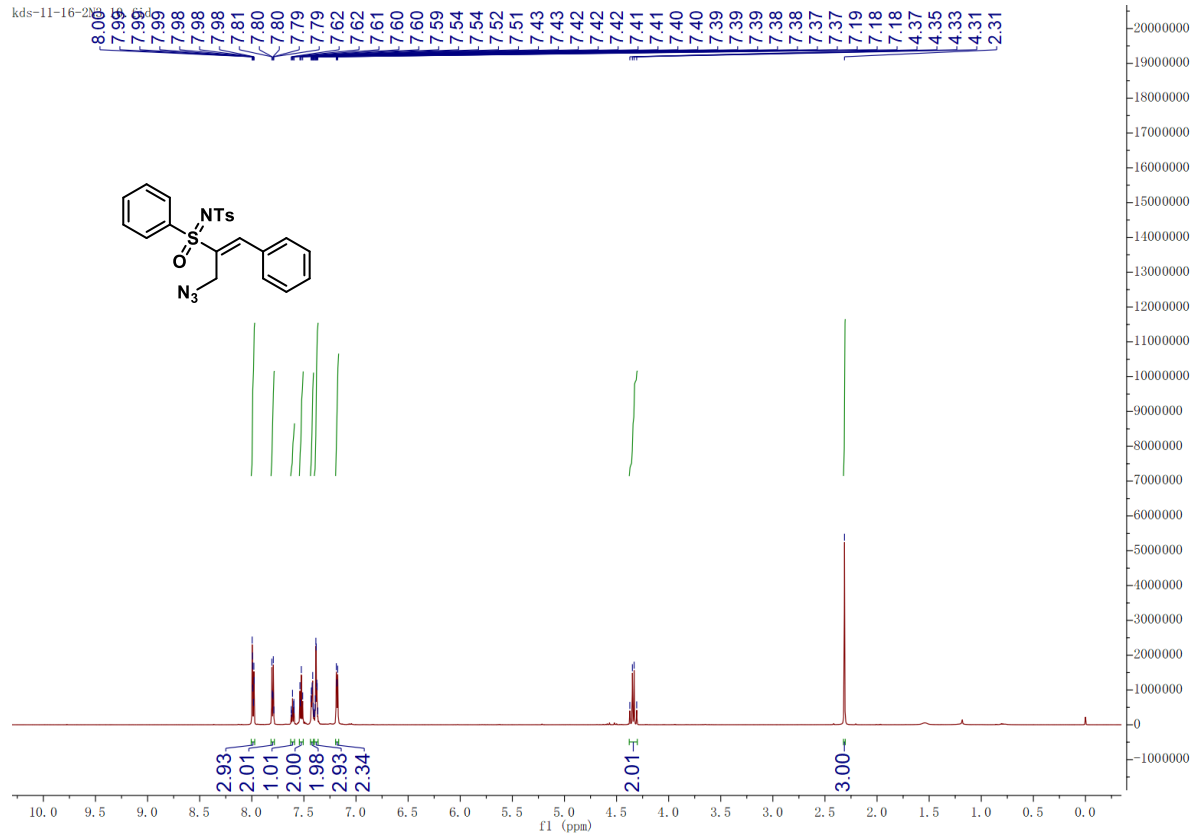
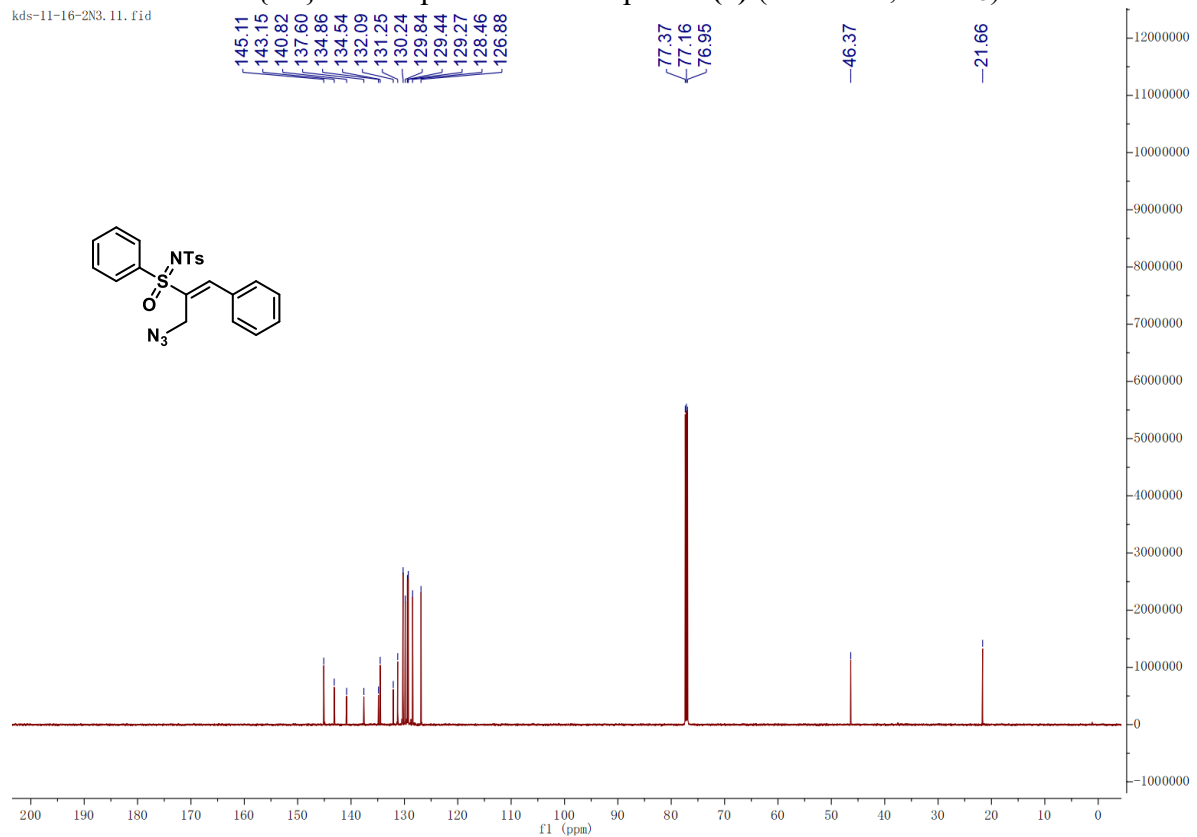


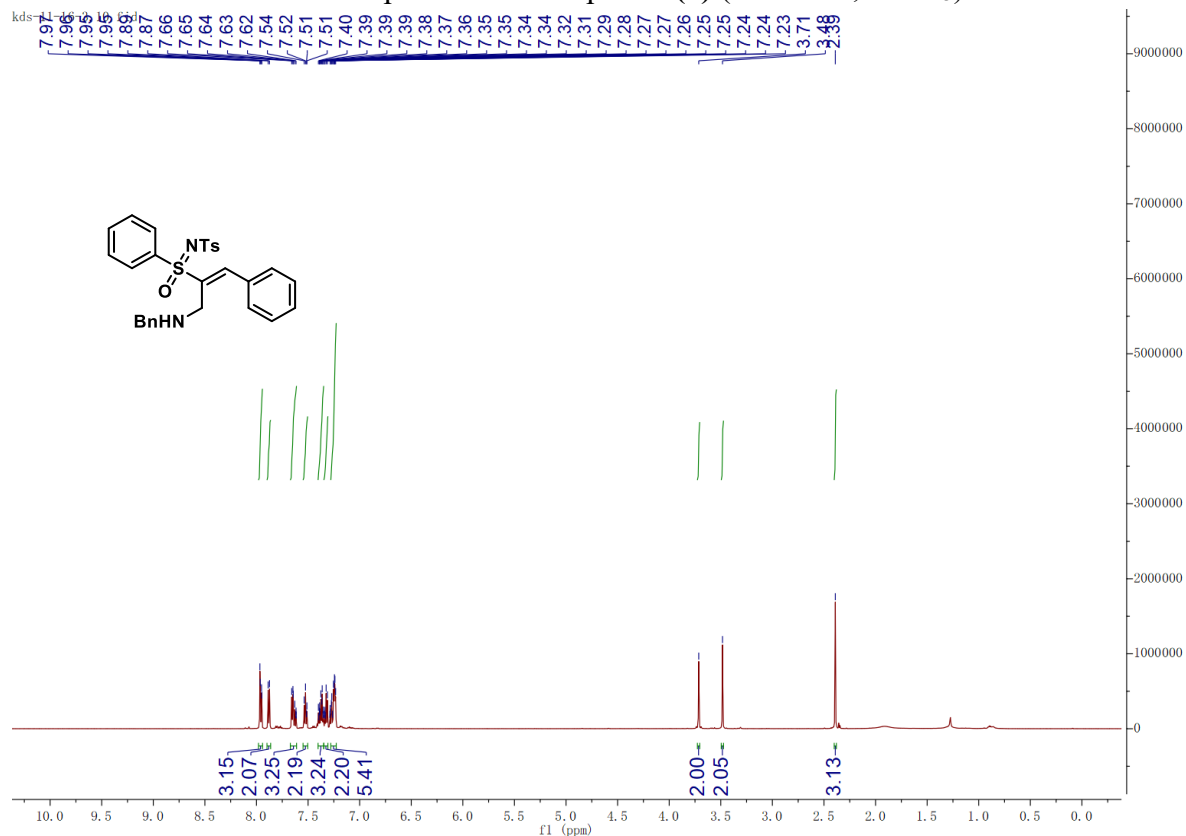
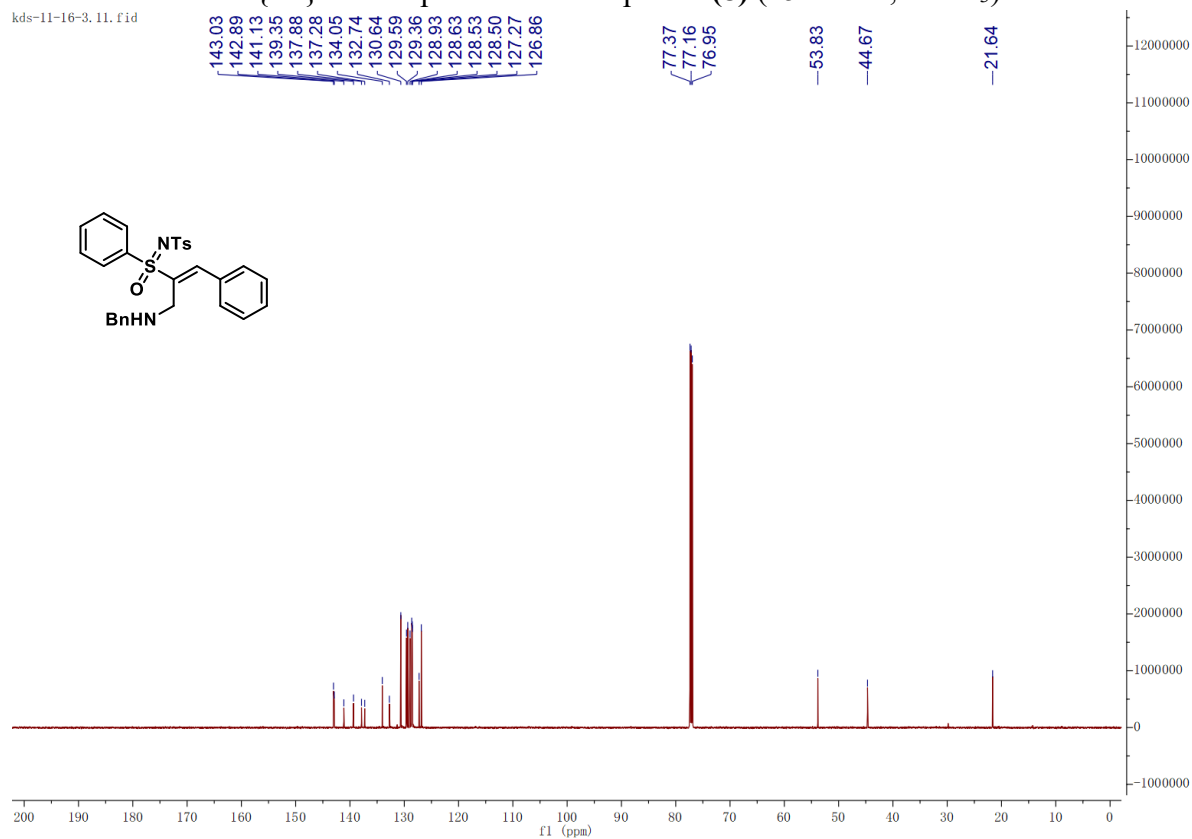
^1H NMR spectrum of compound (**3ea**) (600 MHz, CDCl_3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (**3ea**) (151 MHz, CDCl_3)

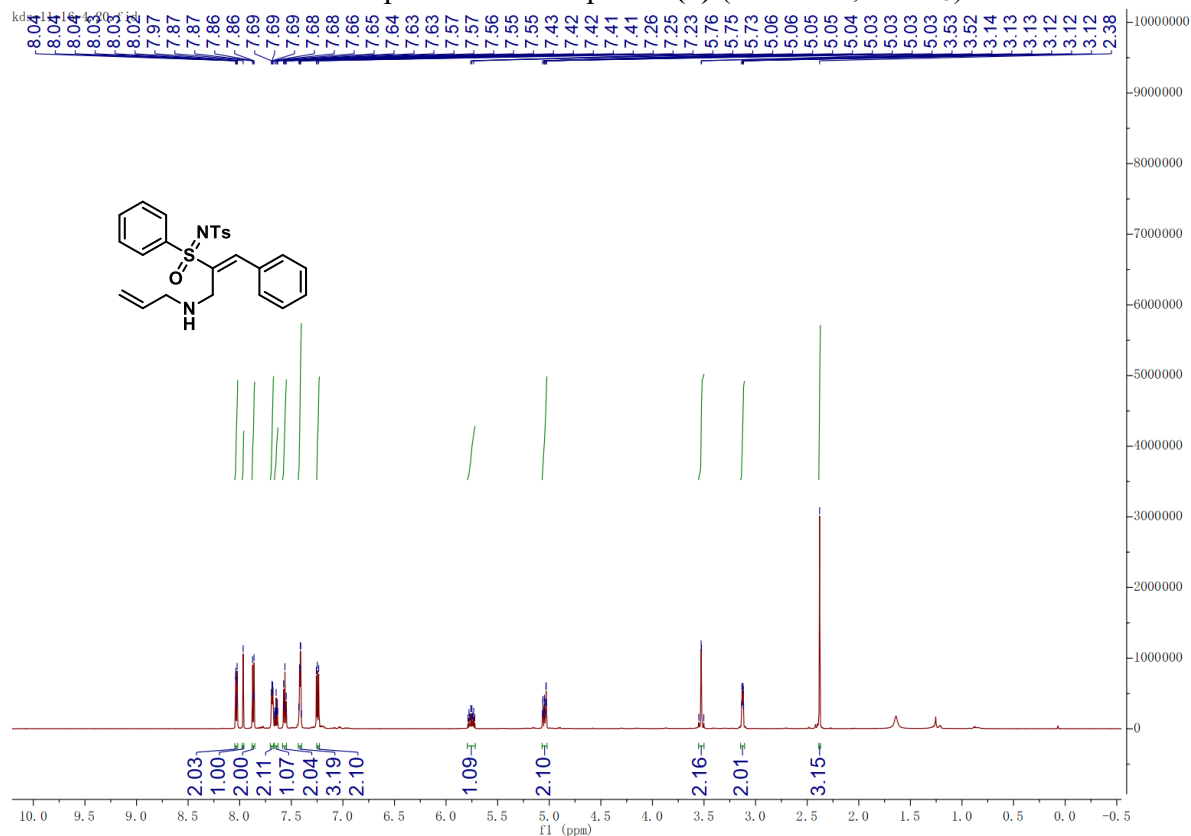
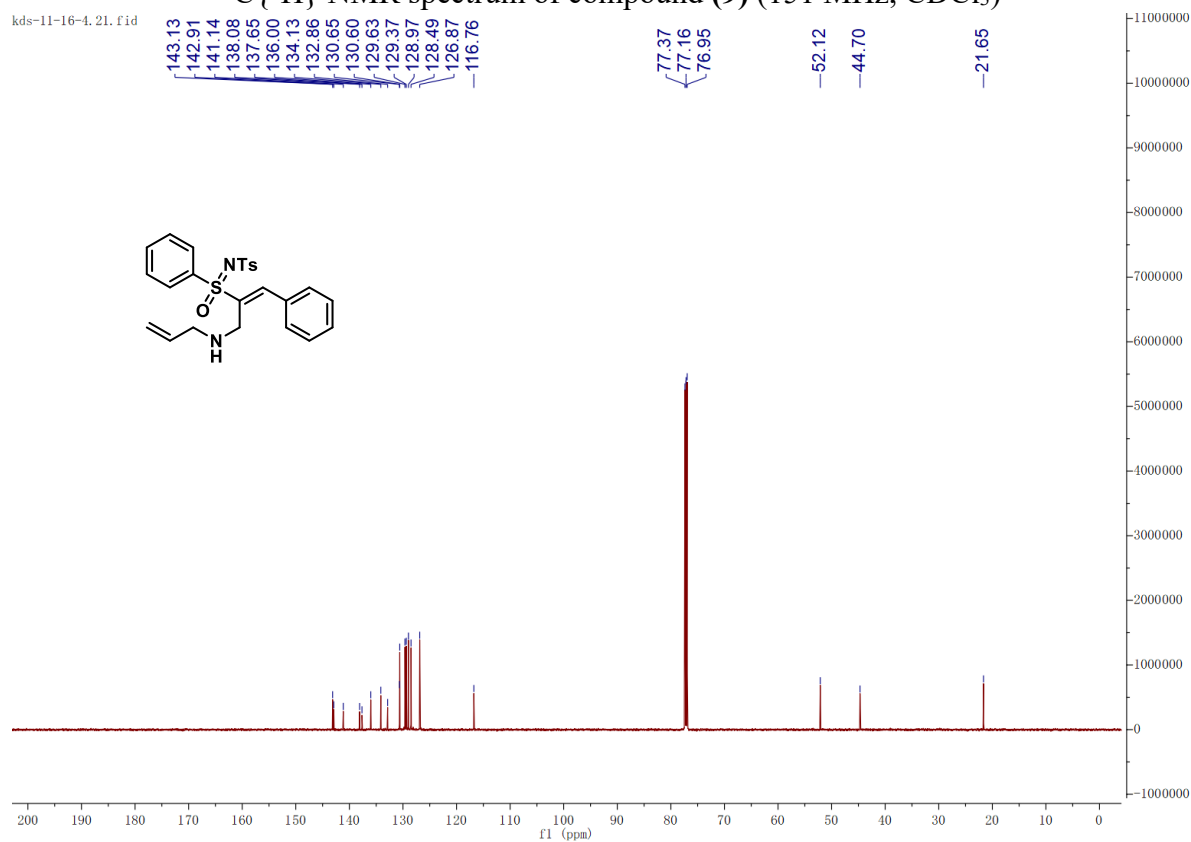
^1H NMR spectrum of compound (3fa) (600 MHz, CDCl_3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (3fa) (151 MHz, CDCl_3)

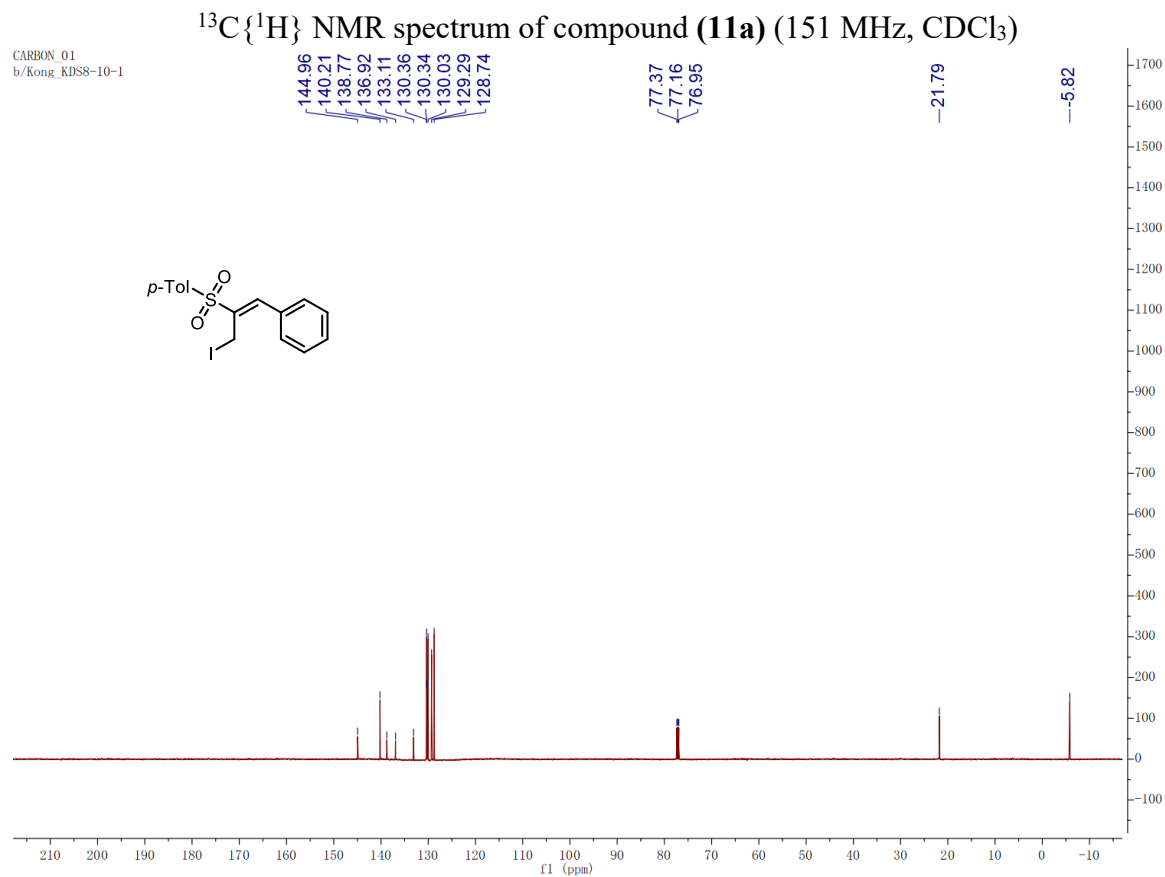
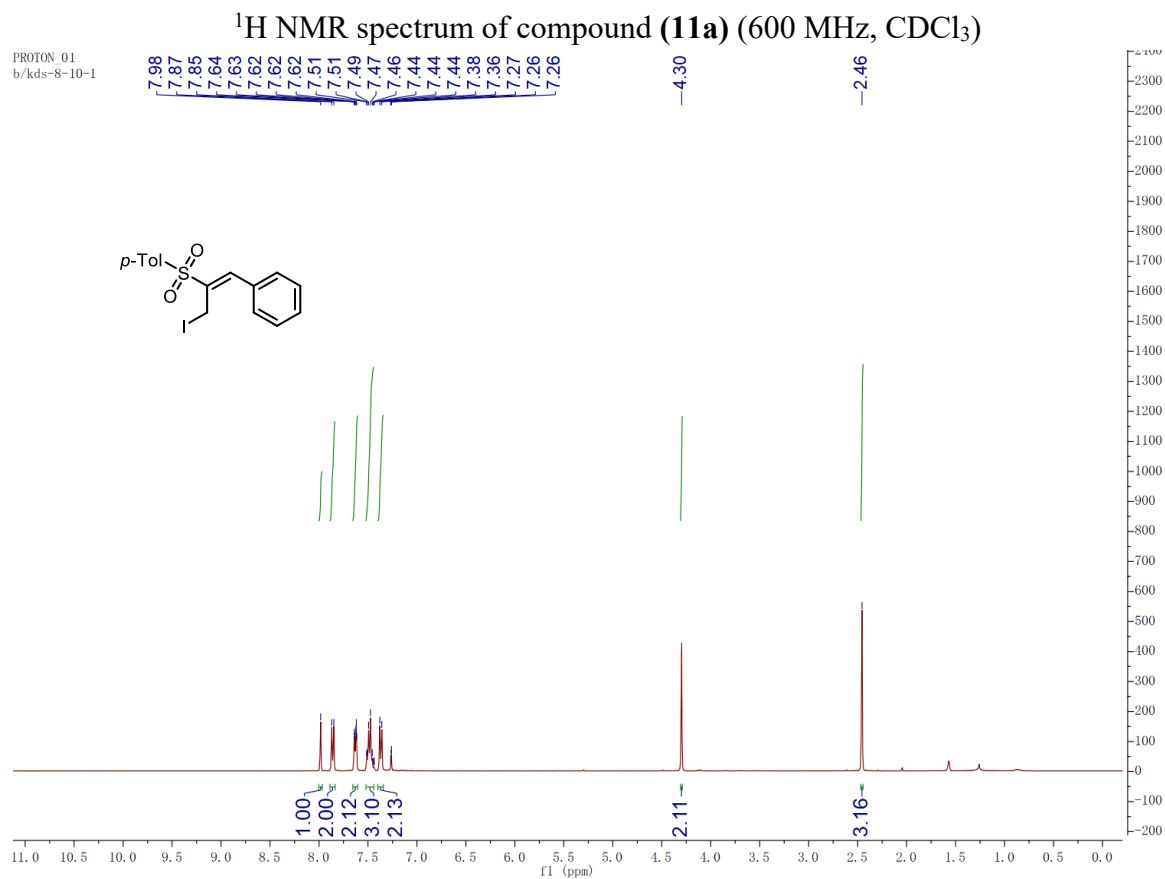
¹H NMR spectrum of compound (**3ga**) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (**3ga**) (151 MHz, CDCl₃)



¹H NMR spectrum of compound (7) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (7) (151 MHz, CDCl₃)

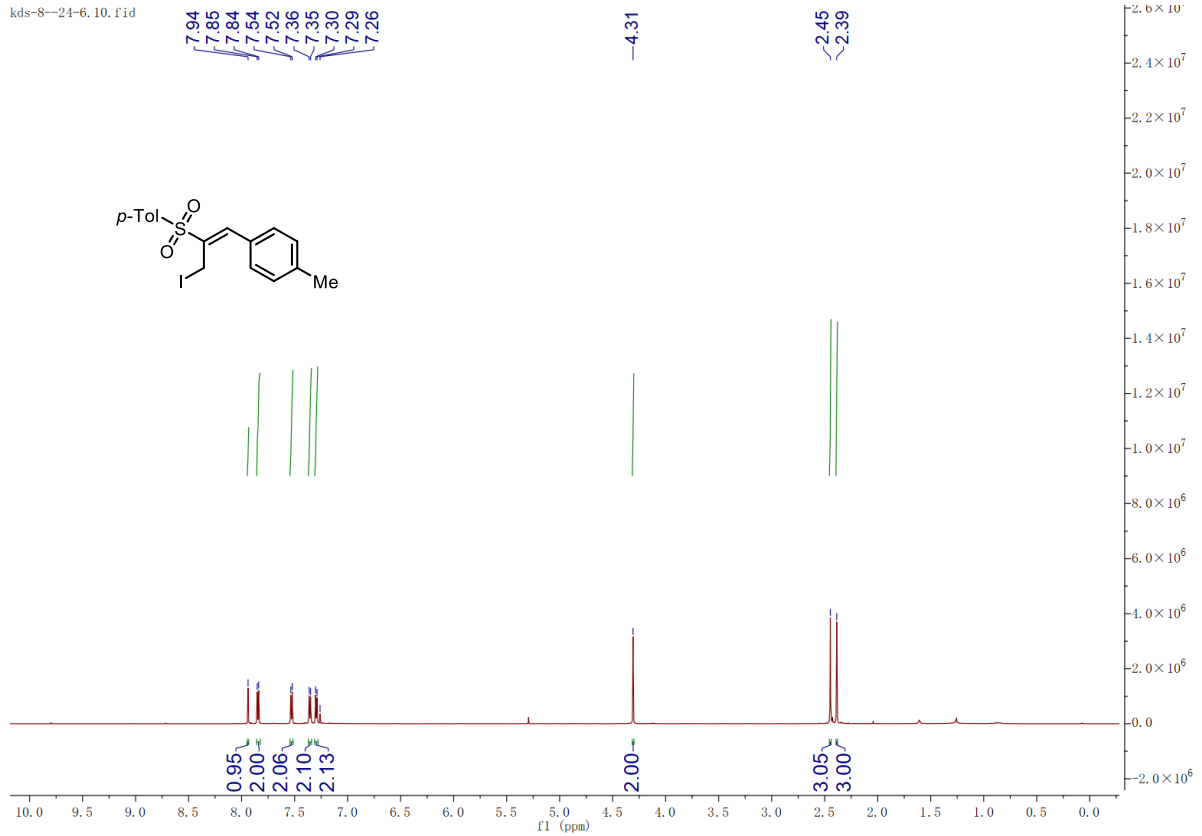
¹H NMR spectrum of compound (8) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (8) (151 MHz, CDCl₃)

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

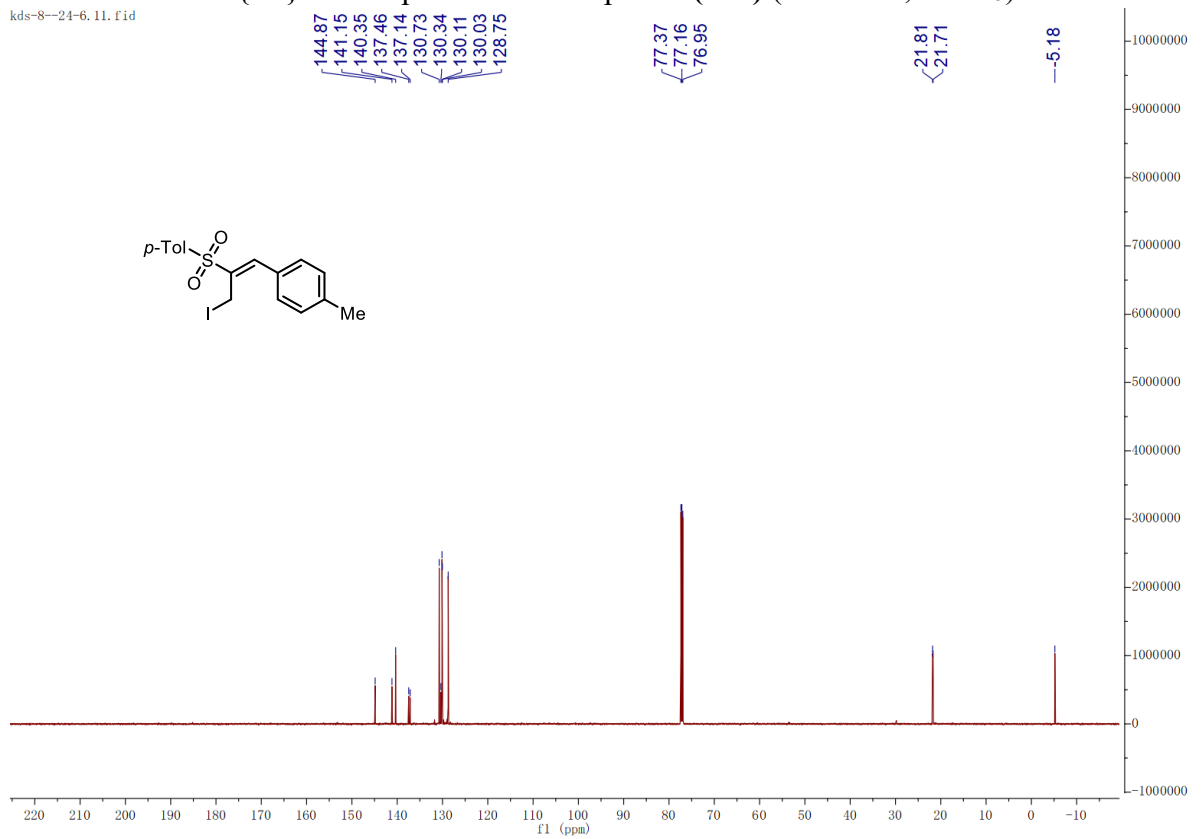


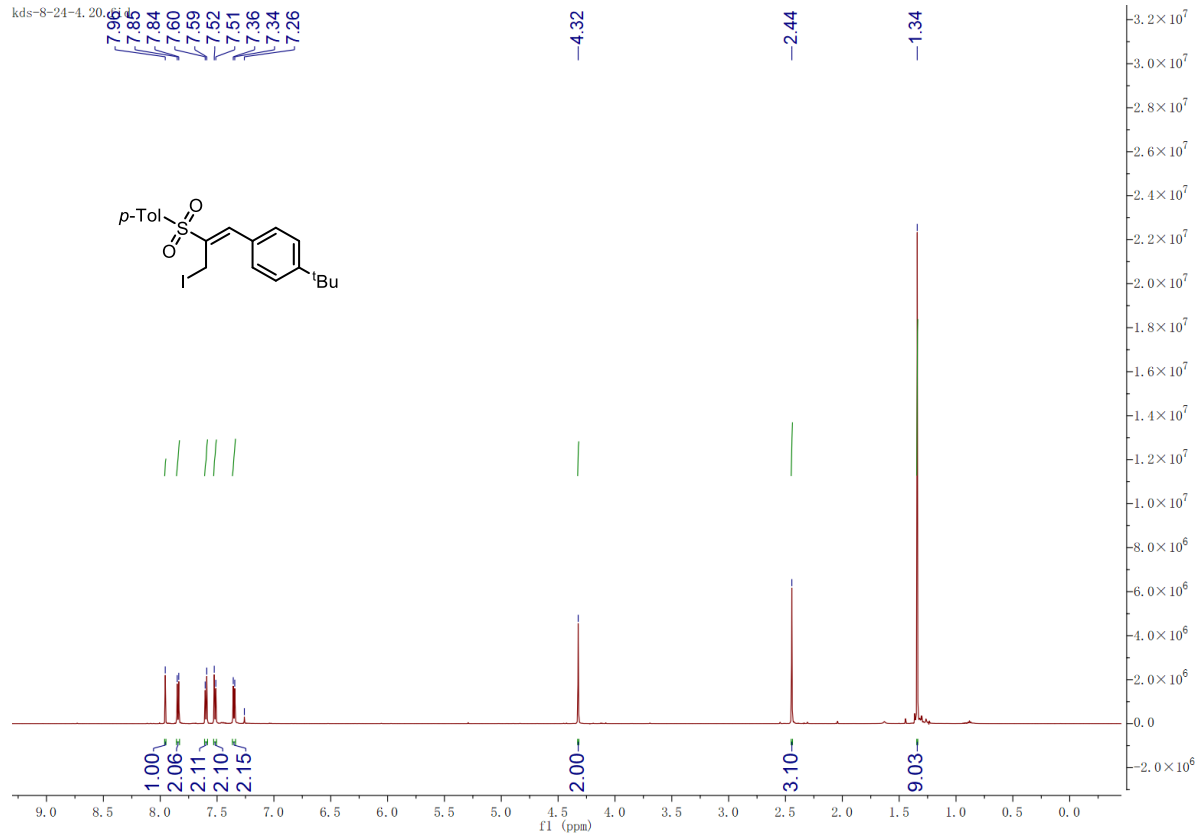
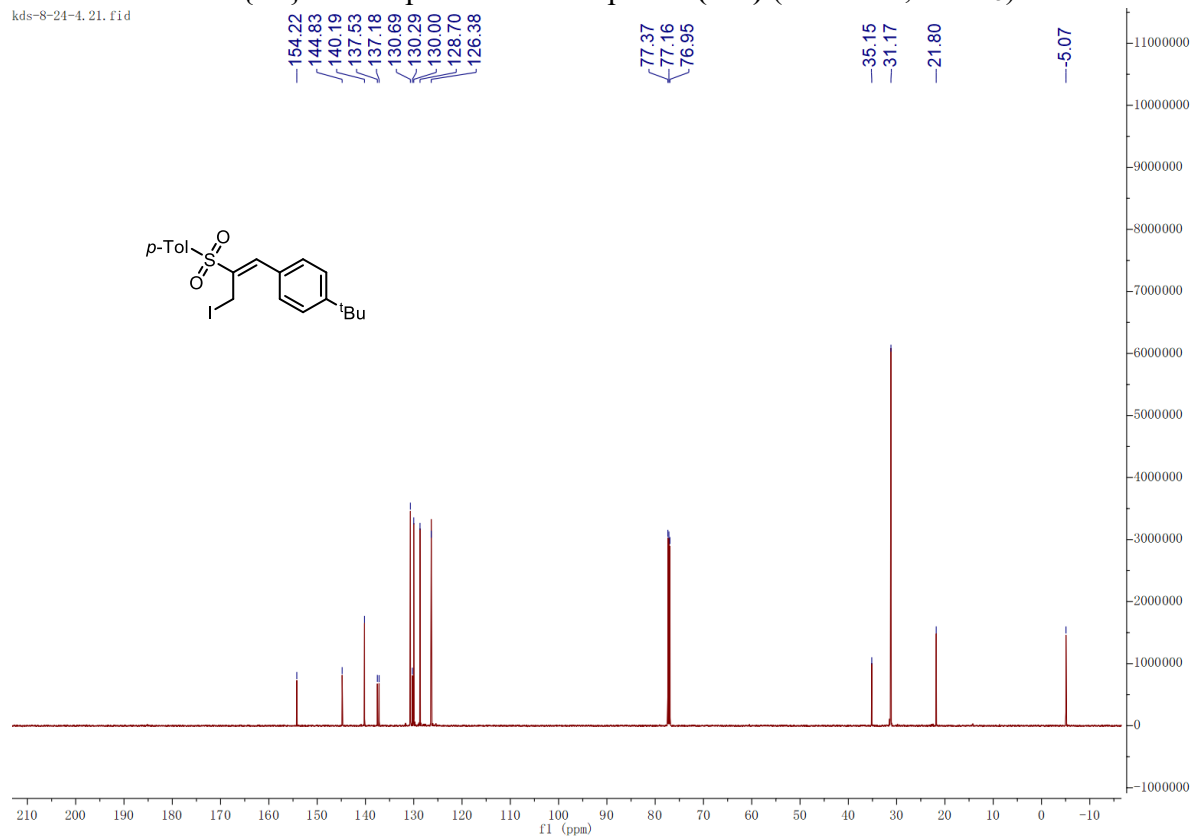
¹H NMR spectrum of compound (11b) (600 MHz, CDCl₃)

kds-8--24-6.10.fid

¹³C {¹H} NMR spectrum of compound (11b) (151 MHz, CDCl₃)

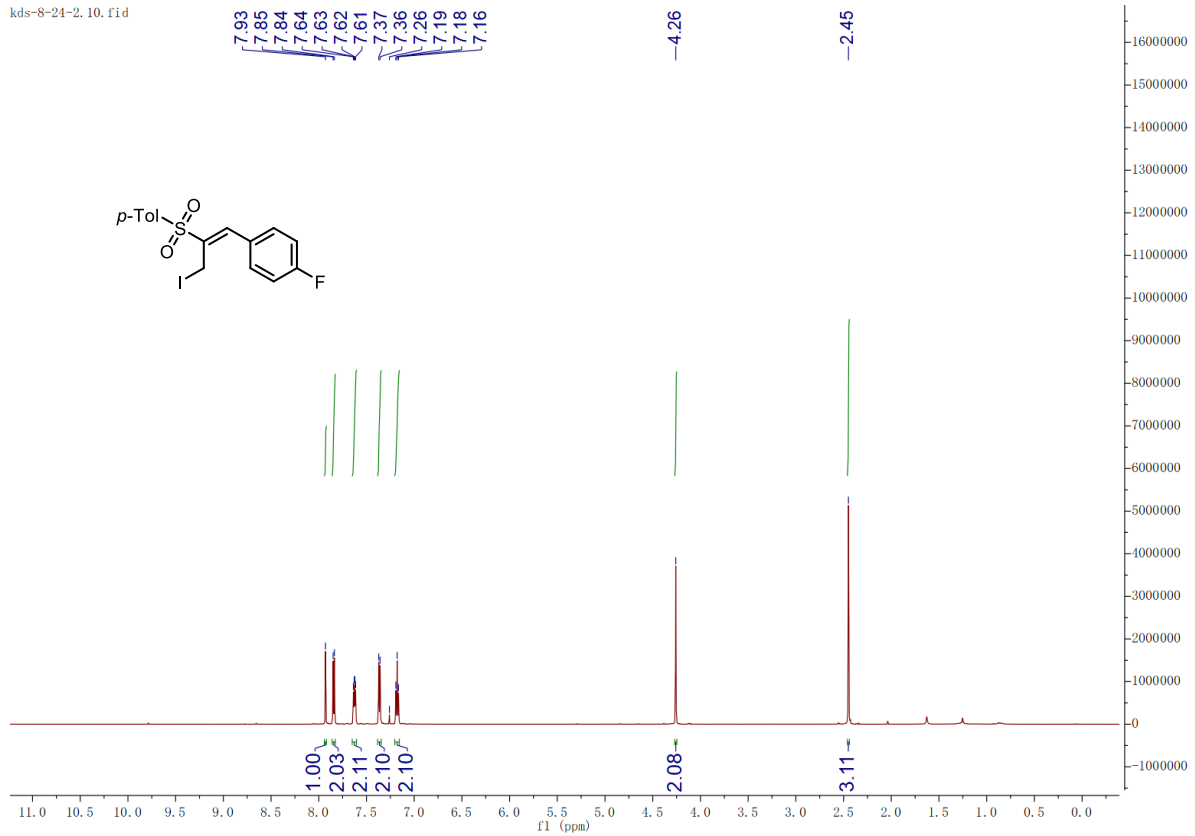
kds-8--24-6.11.fid



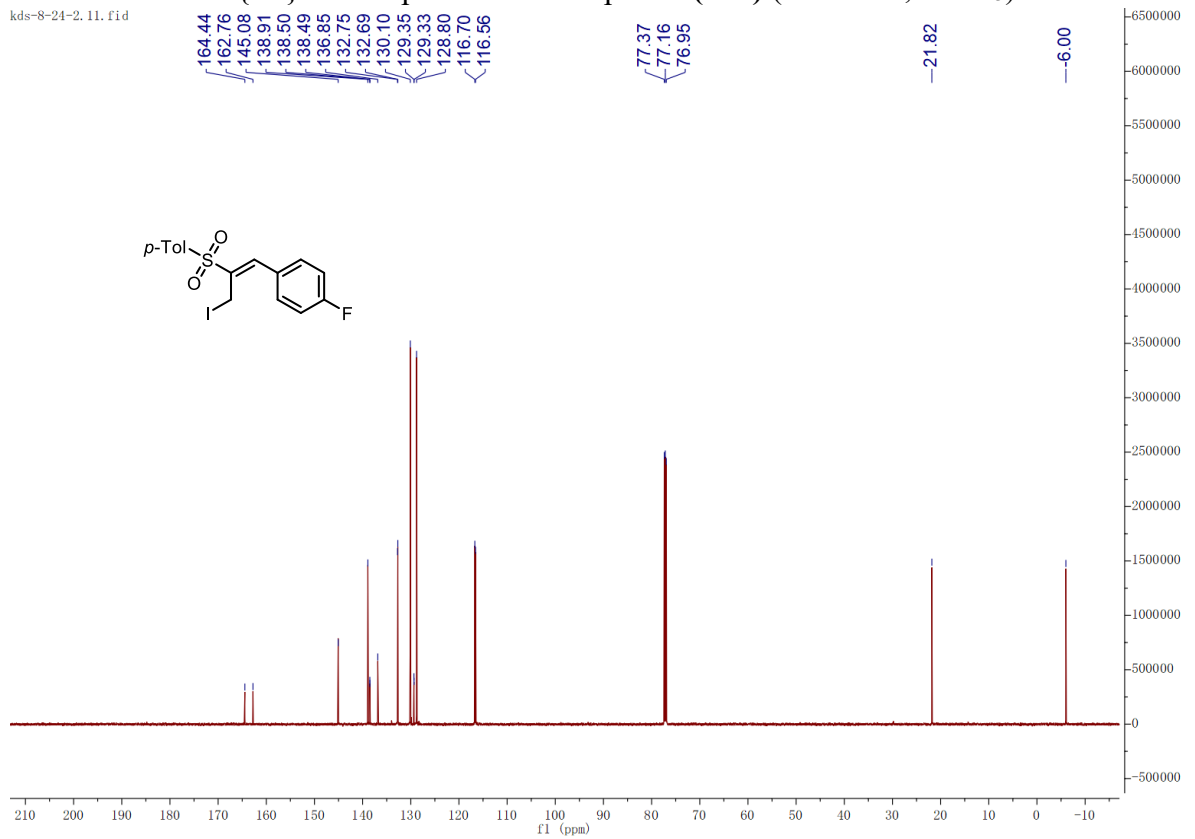
¹H NMR spectrum of compound (11c) (600 MHz, CDCl₃)¹³C{¹H} NMR spectrum of compound (11c) (151 MHz, CDCl₃)

^1H NMR spectrum of compound (11d) (600 MHz, CDCl_3)

kds-8-24-2.10.fid

 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (11d) (151 MHz, CDCl_3)

kds-8-24-2.11.fid

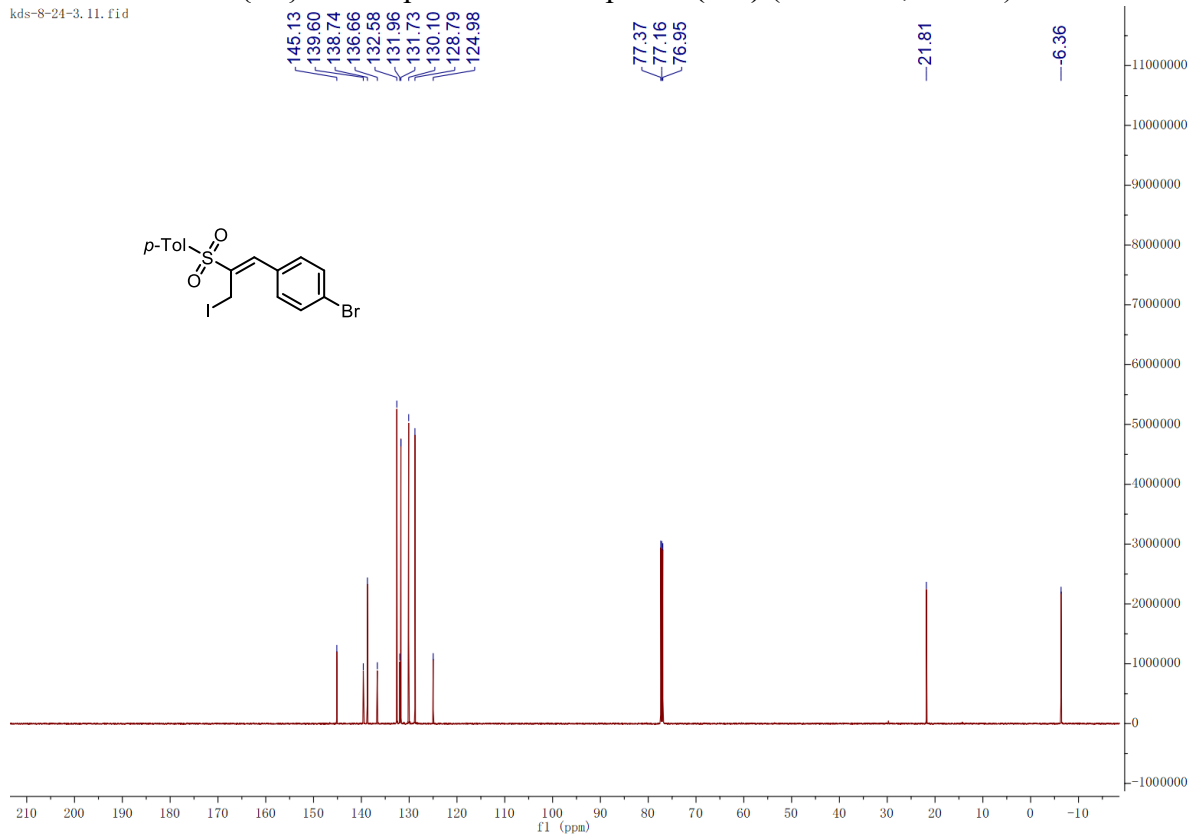


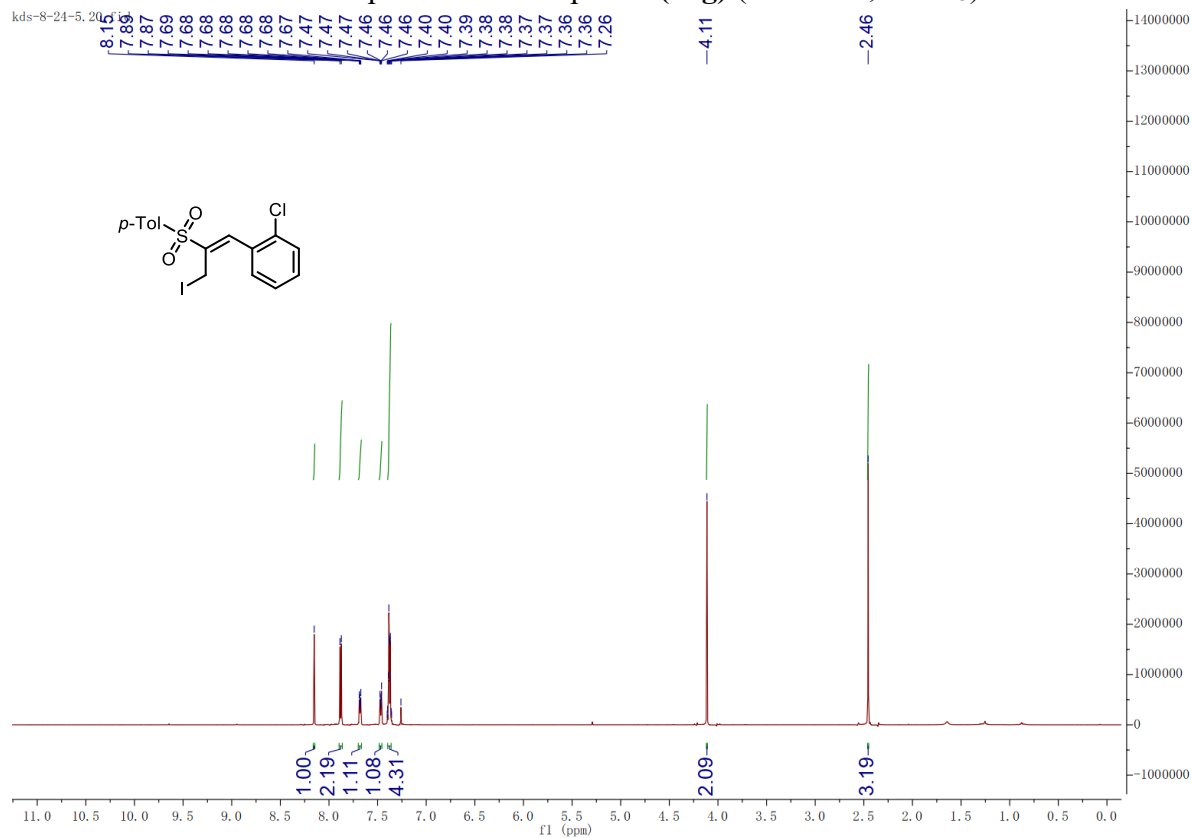
¹H NMR spectrum of compound (11e) (600 MHz, CDCl₃)

kds-8-24-3.10.fid

¹³C{¹H} NMR spectrum of compound (11e) (151 MHz, CDCl₃)

kds-8-24-3.11.fid



^1H NMR spectrum of compound (**11g**) (600 MHz, CDCl_3) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound (**11g**) (151 MHz, CDCl_3)