

Me₃SiBr-promoted cascade electrophilic thiocyanation/cyclization of *ortho*-alkynylanilines to synthesize indole derivatives

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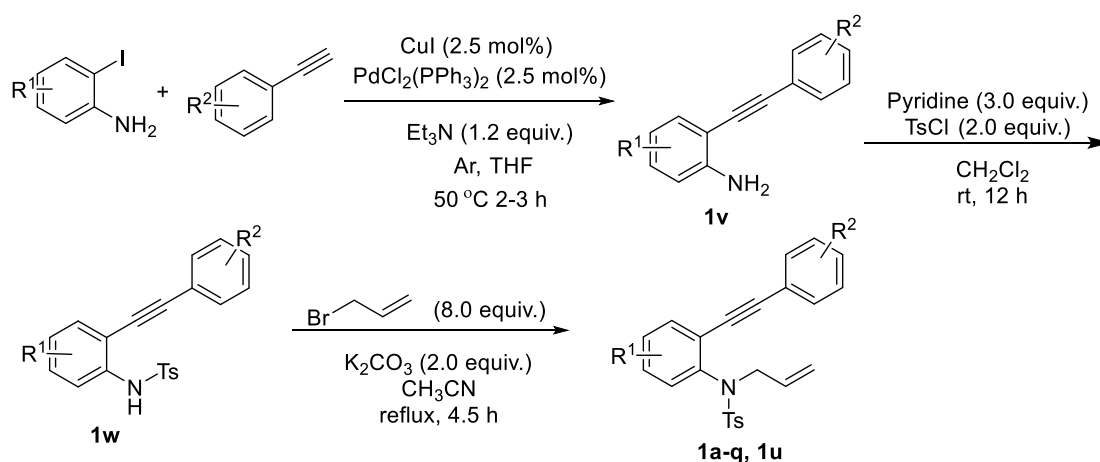
1. General Information

All chemicals were bought from commercial companies and used directly unless noted. The solvents were dried by standard methods when necessary. All reactions monitored by TLC. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 400 or 700 instrument in CDCl_3 . All the NMR spectra were referenced to residual CHCl_3 (7.26 ppm, ^1H ; 77.16 ppm, $^{13}\text{C}\{^1\text{H}\}$). Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet; coupling constant(s) are in Hz, integration). Data for $^{13}\text{C}\{^1\text{H}\}$ NMR are reported in terms of chemical shift (δ , ppm). The high resolution mass spectrum (HRMS) were recorded on an Agilent (Q-TOF6520) unit with an ESI source. IR spectra were measured on a Shimadzu IRAffinity-1s spectrometer. Melting points were measured on a binocular microscope XT4A melting point apparatus (uncorrected).

2. Preparation of Reagents and ortho-Alkynylanilines.

Reagents **2a–d** were prepared according to the literatures.^[1]

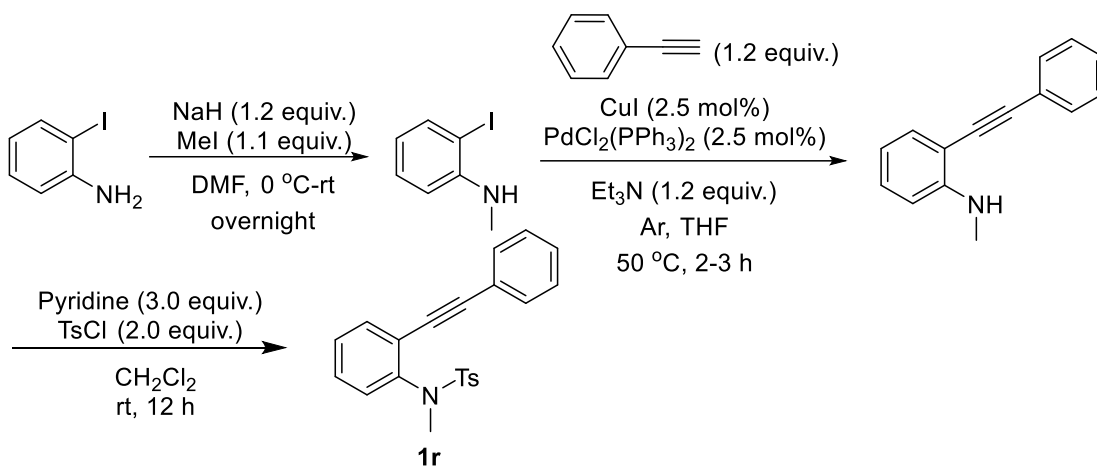
ortho-Alkynylanilines **1a–u** were prepared according to the literature.^[2]



Procedure for the Synthesis of 1a–q, 1u.^[2a–2c,2f] Under argon atmosphere, to a 50 mL flask equipped with a stir bar was charged with CuI (0.125 mmol, 2.5 mol%), 2-iodoaniline (5.0 mmol, 1.0 equiv.), bis(triphenylphosphine) dichloropalladium (0.125 mmol, 2.5 mol%) and dry THF (10 mL, 0.5 M) and Et_3N (1.2 equiv.) at room temperature, phenylethyne (6.0 mmol, 1.2 equiv.) were added to the flask by syringe. The flask was capped and stirred in an oil bath at 50°C for 2–3 h. After heating 2–3 h, the reaction mixture was cooled to room temperature, quenched with 25 mL of aqueous saturated NH_4Cl and extracted with EtOAc . The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give the product as a yellow solid.

Add pyridine (3.0 equiv.) and tosyl chloride (2.0 equiv.) in sequence at 0 °C to the solution of the yellow solid obtained above in dichloromethane over a period of 15 minutes. Stir the reaction mixture at room temperature for 12 h. Monitor the completion of the reaction by thin layer chromatography. Quench the reaction mass with ice water. Extract the mixture with dichloromethane. Wash the combined organic layer with 2M HCl and brine solution. Dry the combined organic layers and evaporate the solvent to obtain crude residue, followed by flash column chromatography to obtain the pure intermediate.

To the acetonitrile solution of intermediate (0.5 M) was added allyl bromide (8.0 equiv.) and K₂CO₃ (2.0 equiv.) at room temperature. Reflux the mixture for 4.5 h. Dissolve the residue in EtOAc after removal of the solvent. Wash the organic layer successively with water and brine. Dry the mixture over Na₂SO₄ and concentrate it. Purify the residue by column chromatography using hexane / EtOAc (v/v, 20 /1) as eluent affording **1a–q**, **1u**.



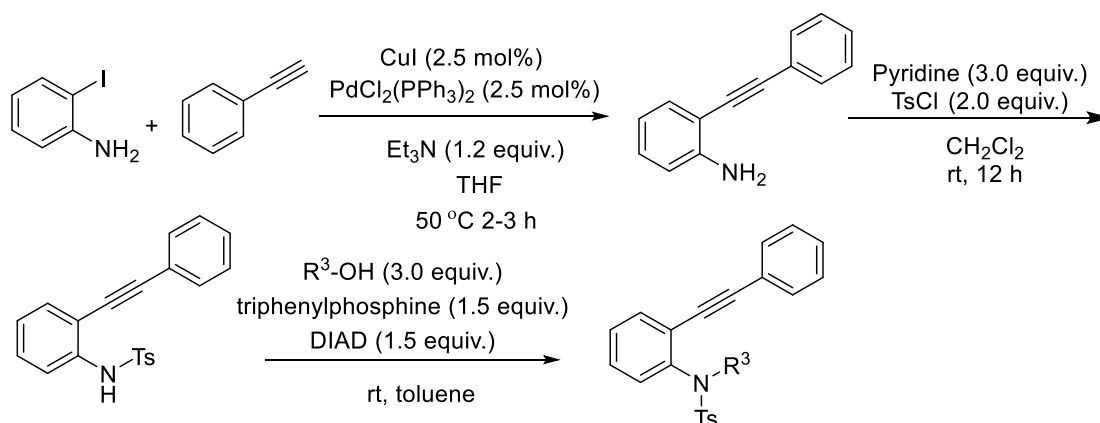
Procedure for the Synthesis of **1r**.^[2d]

Under argon atmosphere, NaH (2.4 mmol, 1.2 equiv.) was added to an oven-dried flask containing dry DMF (7.2 mL, 3.0 M). Then 2-iodo aniline (2.0 mmol, 1.0 equiv.) in dry DMF (2.0 mL, 1.0 M) was added dropwise to it at 0 °C and the mixture was stirred for 30 minutes. Then MeI (2.2 mmol, 1.1 equiv.) in dry DMF (2.2 mL, 1.0 M) was added slowly and the reaction mixture was warmed to rt and stirred overnight. After that, water was added and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with brine solution, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to get the crude product which was purified by column chromatography (silica gel, PE/EtOAc) to afford 2-iodo-*N*-methylaniline.

Under argon atmosphere, to a 50 mL flask equipped with a stir bar was charged with CuI (0.125 mmol, 2.5 mol%), 2-iodo-*N*-methylaniline (5.0 mmol, 1.0 equiv.), bis(triphenylphosphine) dichloropalladium (0.125 mmol, 2.5 mol%) and dry THF (10 mL, 0.5 M) and Et₃N (1.2 equiv.) at room temperature, phenylethyne (6.0 mmol, 1.2 equiv.) were added to the flask by syringe. The reaction mixture was stirred in an oil bath at 50 °C for 2-3 h. On completion, the reaction mixture was cooled to room temperature, quenched with 25 mL of aqueous saturated NH₄Cl and extracted with

EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give the product as a yellow solid.

Add pyridine (3.0 equiv.) and tosyl chloride (2.0 equiv.) in sequence at 0 °C to the solution of the yellow solid obtained above in dichloromethane over a period of 15 minutes. Stir the reaction mixture at room temperature for 12 h. Monitor the completion of the reaction by thin layer chromatography. Quench the reaction mass with ice water. Extract the mixture with dichloromethane. Wash the combined organic layer with 2M HCl and brine solution. Dry the combined organic layers and evaporate the solvent to obtain crude residue, followed by flash column chromatography to obtain the pure intermediate.

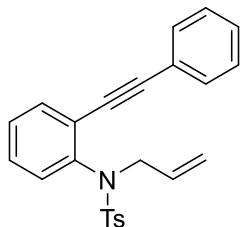


Procedure for the Synthesis of 1s, 1t.^[2a, 2c, 2e] Under argon atmosphere, to a 50 mL flask equipped with a stir bar was charged with CuI (0.125 mmol, 2.5 mol%), 2-Iodoaniline (5.0 mmol, 1.0 equiv.), bis(triphenylphosphine) dichloropalladium (0.125 mmol, 2.5 mol%) and dry THF (10 mL, 0.5 M) and Et₃N (1.2 equiv.) at room temperature, phenylethyne (6.0 mmol, 1.2 equiv.) were added to the flask by syringe. The flask was capped and stirred in an oil bath at 50 °C for 2-3 h. After heating 2-3 h, the reaction mixture was cooled to room temperature, quenched with 25 mL of aqueous saturated NH₄Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give the product as a yellow solid.

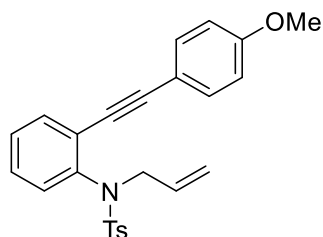
Add pyridine (3.0 equiv.) and tosyl chloride (2.0 equiv.) in sequence at 0 °C to the solution of the yellow solid obtained above in dichloromethane over a period of 15 minutes. Stir the reaction mixture at room temperature for 12 h. Monitor the completion of the reaction by thin layer chromatography. Quench the reaction mass with ice water. Extract the mixture with dichloromethane. Wash the combined organic layer with 2M HCl and brine solution. Dry the combined organic layers and evaporate the solvent to obtain crude residue, followed by flash column chromatography to obtain the pure intermediate.

The obtained *N*-p-toluenesulfonyl-2-alkynylaniline (1.0 equiv.) was dissolved in dry toluene (10 mL), and then R³OH (3.0 equiv.) and triphenylphosphine (1.5 equiv.) were added to the solution under a nitrogen atmosphere. The reaction mixture was

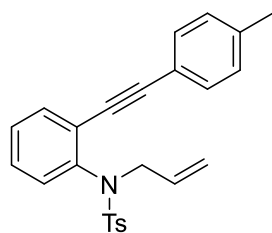
stirred at rt for 5 min, and then diisopropyl azodicarboxylate (DIAD) (1.5 equiv) was added to the solution slowly. The reaction mixture was stirred at room temperature until TLC indicated the total consumption of *N*-*p*-toluenesulfonyl-2-alkynylaniline. Then the solvent was removed directly in vacuo, and the residue was purified by flash column chromatography with PE and EtOAc as eluent to afford the desired product.



***N*-Allyl-*N*-(2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1a).**^[2a] Pale yellow solid; 686 mg, 89% yield; mp: 82–84 °C (lit. 83–85 °C)^[2a]; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.43–7.40 (m, 1H), 7.25–7.18 (m, 8H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.85–5.75 (m, 1H), 5.05–4.95 (m, 2H), 4.30 (d, *J* = 6.4 Hz, 2H), 3.13 (s, 3H) ppm.

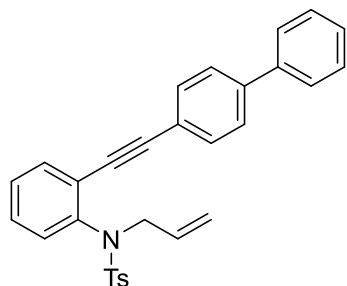


***N*-Allyl-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1b).** Pale yellow solid; 699 mg, 84% yield; mp: 81–83 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.50–7.47 (m, 1H), 7.35–7.28 (m, 3H), 7.24 (d, *J* = 9.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.95–5.85 (m, 1H), 5.15–5.05 (m, 2H), 4.39 (d, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 2.27 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 143.2, 139.6, 137.3, 133.3, 133.2, 133.0, 132.4, 129.4, 128.4, 128.1, 127.7, 124.1, 118.6, 115.0, 113.8, 94.4, 85.2, 55.4, 53.1, 21.4 ppm; IR (KBr) 2839, 2367, 2217, 1607, 1513, 1349, 1289, 1163, 1092, 1030, 725, 662, 583 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₂₅H₂₃NNaO₃S [M + Na]⁺ 440.1291, found 440.1296.

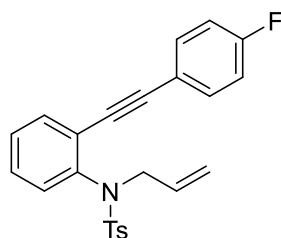


***N*-Allyl-*N*-(2-(*p*-tolyethynyl)phenyl)-4-methylbenzenesulfonamide (1c).** Pale yellow solid; 592 mg, 74% yield; mp: 65–67 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.41–7.38 (m, 1H), 7.26–7.18 (m, 3H), 7.09–7.07 (m, 2H), 7.05–7.01 (m, 4H), 5.85–5.75 (m, 1H), 5.04–4.95 (m, 2H), 4.30 (d, *J* = 6.4 Hz, 2H), 2.29 (s, 3H), 2.15 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 139.7, 138.7, 137.3, 133.3, 132.5, 131.4, 129.5, 128.9, 128.6, 128.1, 127.7, 123.9, 119.8, 118.6, 94.5, 85.8, 53.1, 21.6, 21.4 ppm; IR (KBr) 2922, 2360, 2219, 1943–1542, 1349, 1164, 1092,

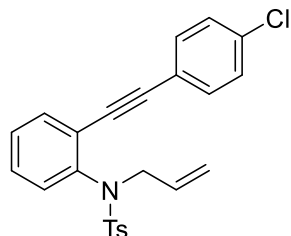
816, 724, 583 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 402.1522, found 402.1505.



***N*-(2-((1,1'-Biphenyl)-4-ylethynyl)phenyl)-*N*-allyl-4-methylbenzenesulfonamide (1d).** White solid; 700 mg, 76% yield; mp: 85–87 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.4$ Hz, 2H), 7.62–7.60 (m, 2H), 7.55 (dt, $J = 8.4$ Hz, 1.6 Hz, 2H), 7.52–7.45 (m, 3H), 7.40–7.28 (m, 6H), 7.12 (d, $J = 8.0$ Hz, 2H), 5.94–5.84 (m, 1H), 5.14–5.04 (m, 2H), 4.39 (d, $J = 6.4$ Hz, 2H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 141.2, 140.3, 139.9, 137.3, 133.4, 133.3, 132.4, 131.9, 129.5, 129.0, 128.8, 128.2, 127.8, 127.7, 127.0, 126.9, 123.9, 121.8, 118.7, 94.2, 87.2, 53.2, 21.4 ppm. IR (KBr) 2925, 2356, 1992–1141, 1163, 1091, 871, 840, 664, 584 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{30}\text{H}_{26}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 464.1679, found 464.1683.

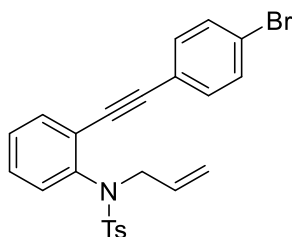


***N*-Allyl-*N*-(2-((4-fluorophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1e).** Pale yellow solid; 501 mg, 62% yield; mp: 98–100 °C ; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.4$ Hz, 2H), 7.53–7.51 (m, 1H), 7.37–7.28 (m, 5H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.04 (t, $J = 8.8$ Hz, 2H), 5.93–5.83 (m, 1H), 5.13–5.05 (m, 2H), 4.36 (d, $J = 6.4$ Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 162.6 (d, $J = 248.6$ Hz), 143.2, 139.9, 137.3, 133.4 (d, $J = 8.3$ Hz), 133.3, 133.2, 132.1, 129.5, 128.9, 128.2, 127.7, 124.0, 119.0 (d, $J = 3.6$ Hz), 118.8, 115.5 (d, $J = 22.2$ Hz), 93.1, 86.2, 53.3, 21.4 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -110.4 ppm; IR (KBr) 2924, 2363, 1967–1517, 1507, 1349, 1164, 1092, 723, 668, 584 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{FNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 406.1272, found 406.1254.



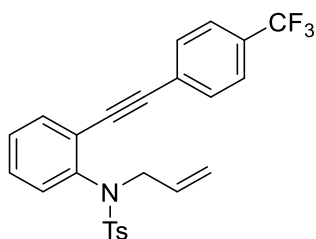
***N*-Allyl-*N*-(2-((4-chlorophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1f).** White solid; 404 mg, 48% yield; mp: 100–102 °C ; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.4$ Hz, 2H), 7.53–7.51 (m, 1H), 7.38–7.25 (m, 7H), 7.16 (d, $J = 8.4$ Hz, 2H), 5.93–5.83 (m, 1H), 5.13–5.05 (m, 2H), 4.36 (d, $J = 6.4$ Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C

NMR (100 MHz, CDCl₃) δ 143.3, 140.0, 137.3, 134.5, 133.3, 133.1, 132.7, 132.1, 129.5, 129.1, 128.6, 128.2, 127.7, 123.8, 121.4, 118.8, 93.0, 87.5, 53.3, 21.4 ppm; IR (KBr) 2366, 1946–1388, 1163, 1090, 1014, 828, 669, 581, 546 cm⁻¹; HRMS (ESI) m/z : calcd. for C₂₄H₂₁ClNO₂S [M + H]⁺ 422.0976, found 422.0957.



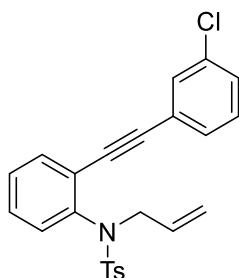
***N*-Allyl-*N*-(2-((4-bromophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1g).**

White solid; 808 mg, 87% yield; mp: 95–97 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.4 Hz, 2H), 7.44–7.41 (m, 1H), 7.39–7.36 (m, 2H), 7.26–7.22 (m, 2H), 7.21–7.18 (m, 1H), 7.10–7.04 (m, 4H), 5.83–5.73 (m, 1H), 5.03–4.95 (m, 2H), 4.25 (d, J = 6.4 Hz, 2H), 2.19 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 140.0, 137.3, 133.4, 133.1, 132.9, 132.1, 131.5, 129.5, 129.1, 128.2, 127.7, 123.8, 122.8, 121.9, 118.8, 93.1, 87.7, 53.4, 21.4 ppm; IR (KBr) 2922, 2356, 1999–1395, 1349, 1164, 1092, 1069, 1010, 870, 735, 669, 581, 546 cm⁻¹; HRMS (ESI) m/z : calcd. for C₂₄H₂₁BrNO₂S [M + H]⁺ 466.0471, found 466.0476.



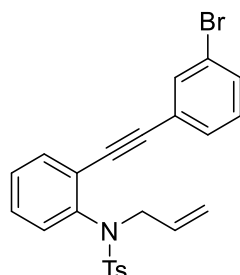
***N*-Allyl-*N*-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-4-**

methylbenzenesulfonamide (1h). Pale yellow solid; 774 mg, 85% yield; mp: 88-90 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.47–7.45 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.30–7.23 (m, 2H), 7.18–7.16 (m, 1H), 7.06 (d, J = 8.4 Hz, 2H), 5.83–5.73 (m, 1H), 5.03–4.96 (m, 2H), 4.25 (d, J = 6.4 Hz, 2H), 2.17 (s, 3H) ppm; ¹³C NMR (100 MHz) δ 143.3, 140.3, 137.2, 133.5, 133.0, 131.9, 131.7, 130.1 (q, J = 32.4 Hz), 129.5, 129.4, 128.3, 127.7, 126.7, 125.1 (q, J = 3.8 Hz), 123.9 (q, J = 270.5 Hz), 123.6, 118.9, 92.6, 88.9, 53.5, 21.4 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.8 ppm; IR (KBr) 3069, 2927, 2223, 1923, 1615, 1484, 1448, 1066, 927, 843, 728, 664, 581 cm⁻¹; HRMS (ESI) m/z : calcd. for C₂₅H₂₁F₃NO₂S [M + H]⁺ 456.1240, found 456.1238.



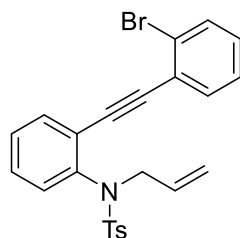
***N*-Allyl-*N*-(2-((3-chlorophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1i).**

Yellow oil; 587 mg, 70% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.4$ Hz, 2H), 7.53–7.51 (m, 1H), 7.39–7.32 (m, 4H), 7.27 (m, 1H), 7.23–7.16 (m, 4H), 5.94–5.84 (m, 1H), 5.14–5.06 (m, 2H), 4.37 (d, $J = 6.8$ Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 140.1, 137.3, 134.0, 133.5, 133.1, 132.5, 131.2, 129.6, 129.6, 129.5, 129.2, 128.7, 128.2, 127.7, 124.5, 123.3, 118.8, 92.6, 87.6, 53.2, 21.4 ppm; IR (KBr) 3067, 2924, 1992–1609, 1597, 1559, 1490, 1351, 1218, 1163, 1092, 926, 859, 715, 664, 585, 545 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{BrNO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 422.0976, found 422.0977.



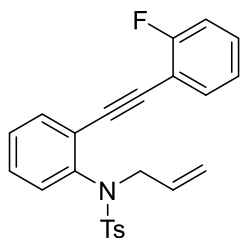
***N*-Allyl-*N*-(2-((3-bromophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1j).**

Yellow oil; 855 mg, 92% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.41–7.39 (m, 1H), 7.36 (dt, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.26–7.19 (m, 4H), 7.16–7.14 (m, 1H), 7.11–7.04 (m, 3H), 5.82–5.72 (m, 1H), 5.02–4.94 (m, 2H), 4.25 (d, $J = 6.4$ Hz, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 140.1, 137.3, 134.1, 133.5, 133.1, 132.5, 131.6, 130.1, 129.7, 129.6, 129.3, 129.3, 128.2, 127.7, 124.8, 123.3, 122.0, 118.9, 92.5, 87.8, 53.3, 21.5 ppm; IR (KBr) 3065, 2923, 1992–1624, 1555, 1490, 1448, 1350, 1163, 1092, 995, 854, 739, 584, 545 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{BrNO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 466.0471, found 466.0470.



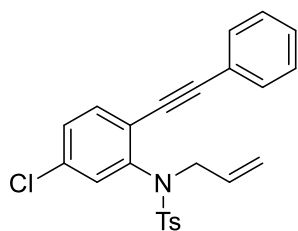
***N*-Allyl-*N*-(2-((2-bromophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1k).**

Pale yellow solid; 749 mg, 81% yield; mp: 80–82 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.58–7.56 (m, 1H), 7.40–7.31 (m, 3H), 7.29–7.28 (m, 2H), 7.24–7.19 (m, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 5.97–5.87 (m, 1H), 5.16–5.07 (m, 2H), 4.46 (d, $J = 6.8$ Hz, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 139.7, 137.1, 133.9, 133.5, 133.5, 133.3, 132.6, 132.4, 129.6, 129.4, 129.2, 128.2, 127.7, 126.8, 125.2, 125.1, 123.5, 118.8, 92.6, 90.5, 53.6, 21.4 ppm; IR (KBr) 3069, 1599, 1491, 1350, 1266, 1217, 1164, 1092, 926, 840, 754, 663, 545 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{BrNO}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 466.0471, found 466.0475.



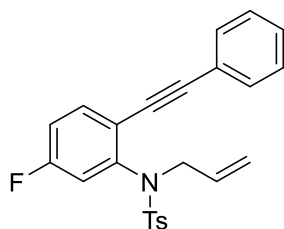
***N*-Allyl-*N*-(2-((2-fluorophenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1l).**

Pale yellow solid; 558 mg, 69% yield; mp: 83–85 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.29–7.28 (m, 2H), 7.26–7.16 (m, 3H), 7.04–6.96 (m, 4H), 5.86–5.76 (m, 1H), 5.04 (d, *J* = 17.2 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.35 (d, *J* = 6.4 Hz, 2H), 2.08 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 162.4, (d, *J* = 50 Hz), 143.1, 139.9, 137.1, 133.5, 133.4, 133.3 (d, *J* = 2.0 Hz) 132.8, 130.2 (d, *J* = 8.0 Hz), 129.3, 129.2, 128.1, 127.6, 123.8 (d, *J* = 3.0 Hz), 123.3, 118.6, 115.6, 115.3, 111.60 (d, *J* = 15.0 Hz), 91.16, (d, *J* = 3.0 Hz), 87.5, 53.2, 21.3 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -108.9 ppm; IR (KBr) 3065, 2925, 2027–1517, 1499, 1349, 1224, 1165, 1093, 927, 852, 757, 727, 664 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₂₄H₂₁FNO₂S [M + H]⁺ 406.1272, found 406.1274.



***N*-Allyl-*N*-(5-chloro-2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1m).**

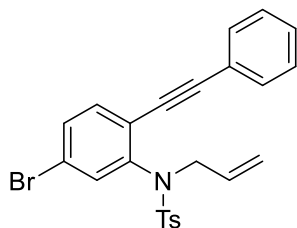
Pale yellow solid; 497 mg, 59% yield; mp: 116–118 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.35–7.33 (m, 1H), 7.27–7.18 (m, 7H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.82–5.72 (m, 1H), 5.06–4.99 (m, 2H), 4.28 (d, *J* = 6.4 Hz, 2H), 2.15 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 140.9, 136.9, 134.1, 134.0, 132.8, 132.6, 131.5, 129.6, 128.7, 128.6, 128.2, 127.7, 122.5, 122.4, 119.2, 95.2, 85.5, 53.1, 21.4 ppm; IR (KBr) 2923, 2851, 2347–1395, 1352, 1165, 1091, 1069, 928, 895, 757, 738, 664, 593, 546 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₂₄H₂₁ClNO₂S [M + H]⁺ 422.0976, found 422.0974.



***N*-Allyl-*N*-(5-fluoro-2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1n).**

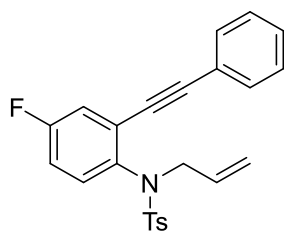
White solid; 273 mg, 34% yield; mp: 104–106 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 8.4 Hz, 6.0 Hz, 1H), 7.28–7.17 (m, 5H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.01–6.93 (m, 2H), 5.83–5.73 (m, 1H), 5.06–4.98 (m, 2H), 4.29 (d, *J* = 6.8 Hz, 2H), 2.15 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 161.9 (d, *J* = 250.5 Hz), 143.5, 141.5 (d, *J* = 10.2 Hz), 136.9, 134.5 (d, *J* = 9.2 Hz), 132.9, 131.4, 129.6, 128.6,

128.2, 127.6, 122.7, 120.0 (d, $J = 4.0$ Hz), 119.9 (d, $J = 22.6$ Hz), 119.1, 115.6 (d, $J = 21.9$ Hz), 94.0, 85.4, 53.1, 21.4 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -190.3 ppm; IR (KBr) 2924, 1842–1417, 1349, 1165, 1091, 668 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{FNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 406.1272, found 406.1258.



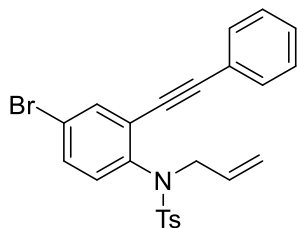
***N*-Allyl-*N*-(5-bromo-2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1o).**

Pale yellow solid; 544 mg, 58% yield; mp: 126–128 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 2H), 7.40–7.40 (m, 1H), 7.37–7.35 (m, 1H), 7.29–7.18 (m, 6H), 7.04 (d, $J = 8.4$ Hz, 2H), 5.82–5.72 (m, 1H), 5.06–4.99 (m, 2H), 4.27 (d, $J = 6.8$ Hz, 2H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 140.9, 136.9, 135.4, 134.2, 132.8, 131.4, 129.6, 128.8, 128.2, 127.7, 122.9, 122.5, 122.0, 119.2, 95.4, 85.6, 53.1, 21.4 ppm; IR (KBr) 2954, 2925, 2363, 1943–1395, 1350, 1165, 1091, 757, 668, 590 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{BrNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 466.0471 found 466.0471.



***N*-Allyl-*N*-(4-fluoro-2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1p).**

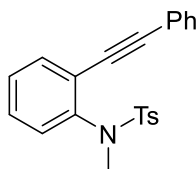
Pale yellow solid; 672 mg, 83% yield; mp: 101–103 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.0$ Hz, 2H), 7.28–7.18 (m, 6H), 7.10 (dd, $J = 8.8$ Hz, 2.8 Hz, 1H), 7.03 (d, $J = 8.4$ Hz, 2H), 6.97–6.91 (m, 1H), 5.84–5.74 (m, 1H), 5.04–4.98 (m, 2H), 4.27 (d, $J = 6.4$ Hz, 2H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 161.5 (d, $J = 247.0$ Hz), 143.4, 137.1, 135.9, (d, $J = 3.0$ Hz), 134.1 (d, $J = 9.0$ Hz), 133.1, 131.6, 129.6, 128.9, 128.3, 127.6, 125.7 (d, $J = 10.0$ Hz), 122.4, 119.8, 119.6, 119.0, 116.1 (d, $J = 23.0$ Hz), 95.1, 85.3 (d, $J = 3.0$ Hz), 53.3, 21.4 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -112.9 ppm; IR (KBr) 3067, 2217, 1604, 1577, 1497, 1417, 1351, 1194, 1164, 1091, 813, 712, 664, 615, 547 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{FNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 406.1272, found 406.1273.



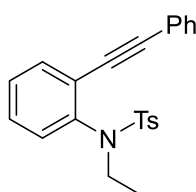
***N*-Allyl-*N*-(4-bromo-2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1q).**

Pale yellow solid; 533 mg, 57% yield; mp: 93–95 °C; ^1H NMR (400 MHz, CDCl_3) δ

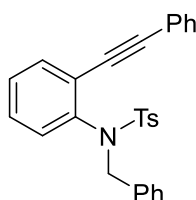
7.56–7.54 (m, 3H), 7.36 (dd, $J = 2.4$ Hz, 8.4 Hz, 1H), 7.30–7.22 (m, 3H), 7.19–7.17 (m, 2H), 7.10 (d, $J = 8.4$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 2H), 5.82–5.72 (m, 1H), 5.05–4.98 (m, 2H), 4.27 (d, $J = 6.8$ Hz, 2H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 138.9, 137.0, 135.9, 133.8, 132.9, 131.9, 131.5, 129.6, 128.9, 128.3, 127.6, 125.7, 122.3, 121.8, 119.1, 95.5, 85.0, 53.1, 21.4 ppm; IR (KBr) 2918, 1989–1369, 1350, 1219, 1165, 930, 852, 736, 596, 546 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{21}\text{BrNO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 466.0471, found 466.0474.



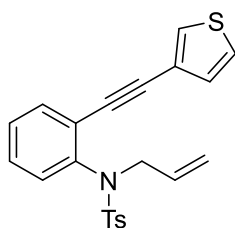
***N*-Methyl-*N*-(2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1r).** Pale yellow solid; 274 mg, 38% yield; mp: 66–68 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.0$ Hz, 2H), 7.54–7.52 (m, 1H), 7.42–7.27 (m, 8H), 7.14 (d, $J = 8.4$ Hz, 2H), 3.39 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 143.3, 142.3, 136.3, 133.6, 131.4, 130.8, 129.5, 129.0, 128.5, 128.2, 128.0, 127.8, 122.9, 122.8, 94.2, 86.2, 38.1, 21.4 ppm; IR (KBr) 2923, 1707–1496, 1349, 1155, 901, 837, 760, 722, 651 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$ 362.1209, found 362.1192.



***N*-Ethyl-*N*-(2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1s).** White solid; 279 mg, 88% yield; mp: 62–64 °C^[2e]; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2H), 7.52–7.50 (m, 1H), 7.34–7.25 (m, 8H), 7.09 (d, $J = 7.6$ Hz, 2H), 3.81 (q, $J = 7.2$ Hz, 2H), 2.21 (s, 3H) 1.16 (t, $J = 6.8$ Hz, 3H) ppm.

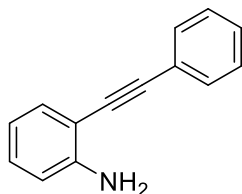


***N*-Benzyl-*N*-(2-(phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1t).** Colorless oil; 244 mg, 78% yield^[2e]; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2H), 7.44–7.42 (m, 1H), 7.34–7.31 (m, 3H), 7.30–7.26 (m, 4H), 7.22–7.17 (m, 5H), 7.15–7.13 (m, 1H), 7.10 (d, $J = 8.4$ Hz, 2H), 4.98 (s, 2H), 2.21 (s, 3H) ppm.

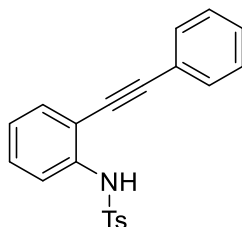


***N*-Allyl-*N*-(2-(thiophen-3-ylethynyl)phenyl)-4-methylbenzenesulfonamide (1u).**

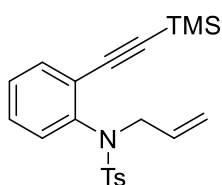
Pale yellow solid; 618 mg, 79% yield; mp: 80–82 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.25–7.19 (m, 5H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.91–6.89 (m, 1H), 5.84–5.74 (m, 1H), 5.04–4.95 (m, 2H), 4.27 (d, *J* = 6.4 Hz, 2H), 2.20 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 143.3, 139.8, 137.3, 133.3, 133.2, 132.4, 129.7, 129.4, 128.8, 128.7, 128.1, 127.7, 125.2, 123.8, 122.0, 118.7, 89.5, 86.0, 53.2, 21.4 ppm; IR (KBr) 2923, 1992–1369, 1164, 1092, 864, 780, 720, 668, 585 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₂₂H₂₀NO₂S₂ [M + H]⁺ 394.0930, found 394.0936.



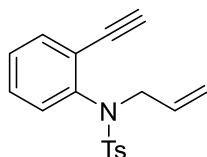
2-(Phenylethynyl)aniline (1v). Pale yellow solid; 824 mg, 75% yield; mp: 89–91 °C^[2a]; ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.51 (m, 2H), 7.38–7.31 (m, 4H), 7.16–7.11 (m, 1H), 6.73 (t, *J* = 7.2 Hz, 2H), 4.34 (s, 2H) ppm.



***N*-(2-(Phenylethynyl)phenyl)-4-methylbenzenesulfonamide (1w).** White solid; 1.29 g, 90% yield; mp: 112–114 °C^[2a]; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.48–7.46 (m, 2H), 7.40–7.36 (m, 4H), 7.31–7.27 (m, 1H), 7.21 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.08–7.04 (m, 1H), 3.33 (s, 3H) ppm.



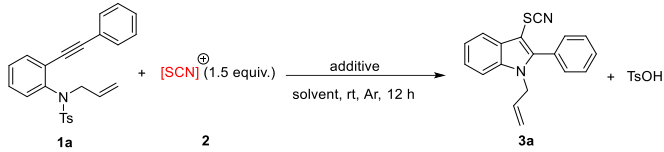
***N*-Allyl-*N*-(2-((trimethylsilyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (1x).** Yellow oil; 1.52g, 58% yield^[2f]; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.29–7.26 (m, 1H), 7.15–7.06 (m, 5H), 5.74–5.64 (m, 1H), 4.96–4.87 (m, 2H), 4.16 (d, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 0.01 (s, 9H) ppm.



***N*-Allyl-*N*-(2-ethynylphenyl)-4-methylbenzenesulfonamide (1y).** Colorless oil; 278 mg, 90% yield^[2g]; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.47 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.33–7.24 (m, 4H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.87–5.77 (m, 1H), 5.08–5.00 (m, 2H), 4.28 (d, *J* = 9.2 Hz, 2H), 2.97 (s, 1H), 2.42 (s, 3H) ppm.

3. Optimization of Reaction Conditions

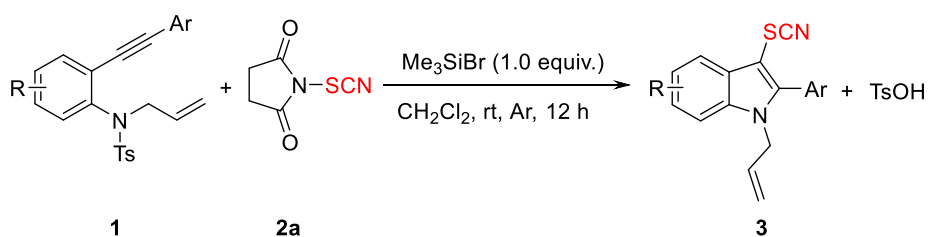
Table S1: screening of various acid^a



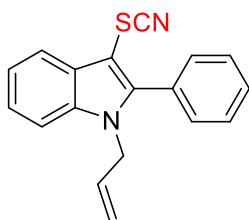
| Entry | [SCN] ⁺ | Additive | Solvent | Yield ^b (%) |
|----------------|--------------------|-----------------------|---------------------------------|------------------------|
| 1 | NTS | <i>p</i> -TsOH | CH ₂ Cl ₂ | NR |
| 2 | NTS | Tf ₂ NH | CH ₂ Cl ₂ | 17 |
| 3 | NTS | Me ₃ SiI | CH ₂ Cl ₂ | 33 |
| 4 | NTS | Me ₃ SiOTf | CH ₂ Cl ₂ | 59 |
| 5 ^c | NTS | Me ₃ SiOTf | CH ₂ Cl ₂ | 65 |

^a Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol, 1.5 equiv.), additive (0.02 mmol, 20 mol%), solvent (2.0 mL), rt, Ar, 12 h. ^b Isolated yields. ^c **1a** (0.1 mmol), **2** (0.2 mmol, 2.0 equiv.), additive (0.1 mmol, 1.0 equiv.), solvent (2.0 mL), rt, Ar, 12 h.

4. General Procedure for the Synthesis of 3



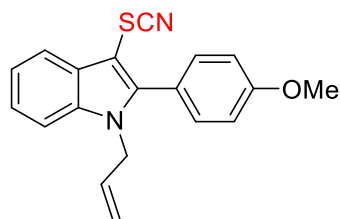
Me₃SiBr (12.5 μL, 0.1 mmol, 1.0 equiv.) and dichloromethane (2.0 mL) were added to a 25 mL Schlenk tube containing **1** (0.1 mmol, 1.0 equiv.) under argon atmosphere. Then **2a** (31.2 mg, 0.2 mmol, 2.0 equiv.) was added. The reaction was carried out at room temperature for 12 h. After completion of the reaction, the product **3** was purified by column chromatography on silica gel with petroleum ether (PE)/ethyl acetate.



1-Allyl-2-phenyl-3-thiocyanato-1H-indole (**3a**).

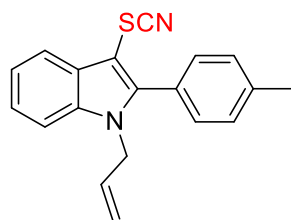
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 26.0 mg (90%); mp: 124–125 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89–7.85 (m, 1H), 7.58–7.55 (m, 3H), 7.51–7.49 (m, 2H), 7.42–7.34 (m, 3H), 5.97–5.88 (m, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.69–4.67 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 136.6, 132.6, 130.5, 129.8, 129.1,

128.7, 128.6, 123.7, 122.1, 119.1, 117.4, 112.1 (SCN), 111.1, 90.1, 47.4 ppm; IR (KBr) 3080, 3030, 2922, 2853, 2147 (SCN), 1645, 1576, 1458, 1391, 1182, 916, 746 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$ 291.0950, found 291.0932.



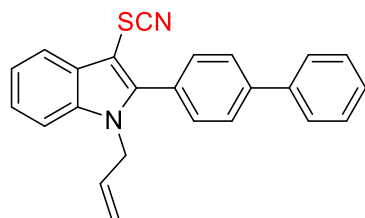
1-Allyl-2-(4-methoxyphenyl)-3-thiocyanato-1H-indole (3b).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 28.0 mg (88%); mp: 94–96 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.83 (m, 1H), 7.44–7.40 (m, 2H), 7.38–7.32 (m, 3H), 7.08–7.05 (m, 2H), 5.96–5.87 (m, 1H), 5.20 (d, $J = 10.4$ Hz, 1H), 4.94 (d, $J = 17.2$ Hz, 1H), 4.67–4.65 (m, 2H), 3.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 146.5, 136.6, 132.8, 131.8, 128.7, 123.5, 122.0, 121.2, 118.9, 117.3, 114.2, 112.3 (SCN), 111.0, 89.8, 55.4, 47.3 ppm; IR (KBr) 2936, 2153 (SCN), 1612, 1541, 1458, 1292, 1252, 1179, 1028, 746 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{OS}$ $[\text{M} + \text{H}]^+$ 321.1056, found 321.1045.



1-Allyl-3-thiocyanato-2-(p-tolyl)-1H-indole (3c).

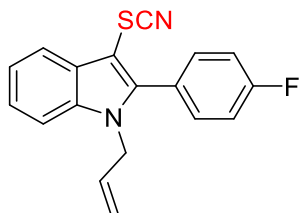
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 25.7 mg (85%); mp: 88–90 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.82 (m, 1H), 7.39–7.32 (m, 7H), 5.96–5.87 (m, 1H), 5.20 (d, $J = 10.4$ Hz, 1H), 4.94 (d, $J = 17.2$ Hz, 1H), 4.67–4.65 (m, 2H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 139.9, 136.6, 132.7, 130.3, 129.5, 128.6, 126.1, 123.5, 122.0, 119.0, 117.3, 112.2 (SCN), 111.1, 89.9, 47.3, 24.5 ppm; IR (KBr) 2924, 2153 (SCN), 1647, 1458, 1184, 824, 746 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$ 305.1107, found 305.1091.



2-([1,1'-Biphenyl]-4-yl)-1-allyl-3-thiocyanato-1H-indole (3d).

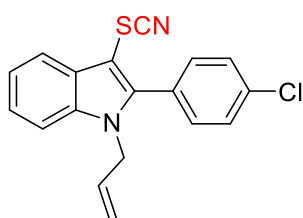
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); Pale yellow solid; 30.8 mg (84%); mp: 146–148 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.85 (m, 1H), 7.79–7.76 (m, 2H), 7.70–7.67 (m, 2H), 7.58–7.55 (m, 2H), 7.52–7.48 (m, 2H), 7.43–7.34 (m, 4H), 6.00–5.91 (m, 1H), 5.24 (d, $J = 10.4$ Hz,

1H), 4.98 (d, $J = 17.2$ Hz, 1H), 4.73–4.71 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 142.5, 140.1, 136.7, 132.7, 130.9, 129.0, 128.7, 128.0, 127.9, 127.4, 127.2, 123.7, 122.1, 119.1, 117.4, 112.2 (SCN), 111.1, 90.2, 47.5 ppm; IR (KBr) 3061, 2920, 2351, 2147 (SCN), 1643, 1456, 1182, 849, 735, 696 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$ 367.1264, found 367.1257.



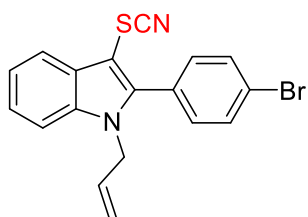
1-Allyl-2-(4-fluorophenyl)-3-thiocyanato-1H-indole (3e).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid ; 21.1 mg (69%); mp: 98–100 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.83 (m, 1H), 7.50–7.45 (m, 2H), 7.40–7.33 (m, 3H), 7.28–7.22 (m, 2H), 5.96–5.87 (m, 1H), 5.21 (d, $J = 10.4$ Hz, 1H), 4.92 (d, $J = 17.2$ Hz, 1H), 4.66–4.64 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 163.6 (d, $J = 250.0$ Hz), 145.3, 136.6, 132.5, 132.5 (d, $J = 13.0$ Hz), 128.5, 125.1 (d, $J = 4.0$ Hz), 123.9, 122.2, 119.1, 117.4, 116.0 (d, $J = 21.0$ Hz), 112.0 (SCN), 111.0, 90.5, 47.3 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -110.4 ppm; IR (KBr) 3063, 2920, 2153 (SCN), 1647, 1489, 1231, 1159, 745 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{FN}_2\text{S}$ $[\text{M} + \text{H}]^+$ 309.0856, found 309.0875.



1-Allyl-2-(4-chlorophenyl)-3-thiocyanato-1H-indole (3f).

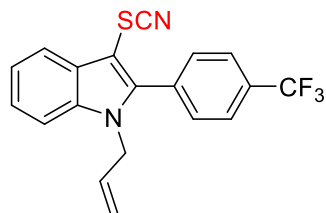
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid ; 22.2 mg (69%); mp: 87–89 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.83 (m, 1H), 7.55–7.52 (m, 2H), 7.45–7.42 (m, 2H), 7.40–7.34 (m, 3H), 5.96–5.87 (m, 1H), 5.22 (d, $J = 9.6$ Hz, 1H), 4.92 (d, $J = 16.4$ Hz, 1H), 4.67–4.65 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 136.7, 136.2, 132.5, 131.8, 129.1, 128.5, 127.5, 124.0, 122.3, 119.1, 117.5, 111.9 (SCN), 111.1, 90.6, 47.4 ppm; IR (KBr) 2851, 2155 (SCN), 1460, 1377, 1263, 1190, 745 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{ClN}_2\text{S}$ $[\text{M} + \text{H}]^+$ 325.0561, found 325.0556.



1-Allyl-2-(4-bromophenyl)-3-thiocyanato-1H-indole (3g).

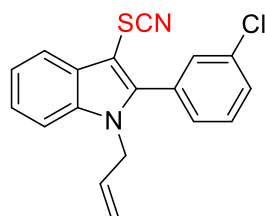
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v)

to 30:1); White solid ; 23.9 mg (65%); mp: 96–98 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88–7.83 (m, 1H), 7.71–7.68 (m, 2H), 7.41–7.34 (m, 5H), 5.96–5.87 (m, 1H), 5.22 (d, $J = 10.4$ Hz, 1H), 4.92 (d, $J = 17.2$ Hz, 1H), 4.67–4.65 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 136.7, 132.5, 132.1, 132.0, 128.5, 128.0, 124.5, 124.0, 122.3, 119.1, 117.5, 111.9 (SCN), 111.1, 90.6, 47.4 ppm; IR (KBr) 2955, 2924, 2850, 2154 (SCN), 1732, 1460, 1377, 1263, 1186, 1013, 843, 745 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{BrN}_2\text{S}$ $[\text{M} + \text{H}]^+$ 369.0056, found 369.0046.



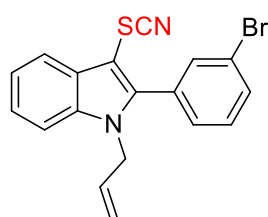
1-Allyl-3-thiocyanato-2-(4-(trifluoromethyl)phenyl)-1H-indole (3h).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid ; 9.9 mg (28%); mp: 94–96 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.86 (m, 1H), 7.83 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.43–7.35 (m, 3H), 5.97–5.88 (m, 1H), 5.23 (d, $J = 10.8$ Hz, 1H), 4.93 (d, $J = 17.2$ Hz, 1H), 4.68–4.66 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 136.8, 132.8, 132.4, 131.5 (q, $J = 32.4$ Hz), 131.0, 128.5, 125.8 (q, $J = 4.0$ Hz), 124.2, 123.8 (q, $J = 270.8$ Hz), 122.4, 119.3, 117.6, 111.7 (SCN), 111.2, 91.1, 47.4 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -62.8 ppm; IR (KBr) 3061, 2922, 2851, 2154 (SCN), 1620, 1458, 1323, 1169, 1128, 1018, 854, 743 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{19}\text{H}_{13}\text{F}_3\text{N}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$ 381.0644, found 381.0652.



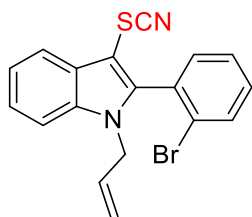
1-Allyl-2-(3-chlorophenyl)-3-thiocyanato-1H-indole (3i).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 22.4 mg (70%); mp: 90–92 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87–7.84 (m, 1H), 7.54–7.48 (m, 3H), 7.40–7.35 (m, 4H), 5.96–5.87 (m, 1H), 5.23 (d, $J = 10.4$ Hz, 1H), 4.93 (d, $J = 16.8$ Hz, 1H), 4.68–4.66 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 136.7, 134.7, 132.4, 130.9, 130.3, 130.1, 130.0, 128.8, 128.4, 124.1, 122.3, 119.2, 117.6, 111.8 (SCN), 111.1, 90.8, 47.4 ppm; IR (KBr) 3063, 2924, 2153 (SCN), 1645, 1566, 1458, 1381, 1186, 926, 800, 741 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{ClN}_2\text{S}$ $[\text{M} + \text{H}]^+$ 325.0561, found 325.0558.



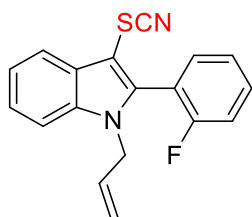
1-Allyl-2-(3-bromophenyl)-3-thiocyanato-1*H*-indole (3j).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 26.5 mg (72%); mp: 75–77 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87–7.84 (m, 1H), 7.70–7.67 (m, 1H), 7.63 (s, 1H), 7.46–7.43 (m, 2H), 7.41–7.33 (m, 3H), 5.97–5.87 (m, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 4.93 (d, *J* = 16.8 Hz, 1H), 4.68–4.66 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 136.6, 133.2, 132.9, 132.4, 131.1, 130.3, 129.3, 128.4, 124.1, 122.7, 122.3, 119.2, 117.6, 111.8 (SCN), 111.1, 90.9, 47.4 ppm; IR (KBr) 3059, 2294, 2853, 2153 (SCN), 1456, 1186, 800, 745 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₁₈H₁₄BrN₂S [M + H]⁺ 369.0056, found 369.0052.



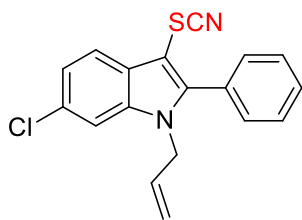
1-Allyl-2-(2-bromophenyl)-3-thiocyanato-1*H*-indole (3k).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); colourless oil; 20.5 mg (56%); ¹H NMR (400 MHz, CDCl₃) δ 7.89–7.85 (m, 1H), 7.79–7.76 (m, 1H), 7.51–7.47 (m, 1H), 7.45–7.40 (m, 3H), 7.38–7.34 (m, 2H), 5.85–5.87 (m, 1H), 5.13 (d, *J* = 9.6 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 4.71–4.64 (m, 1H), 4.52–4.45 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 136.3, 133.1, 132.8, 132.2, 131.7, 130.7, 128.2, 127.6, 125.1, 123.8, 122.1, 119.2, 117.7, 111.5 (SCN), 111.1, 91.2, 47.5 ppm; IR (KBr) 2922, 2361, 2154 (SCN), 1458, 1389, 1186, 1028, 795 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₁₈H₁₄BrN₂S [M + H]⁺ 369.0056, found 369.0051.



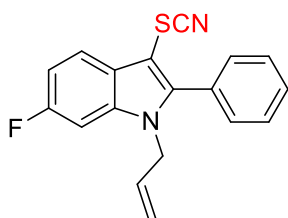
1-Allyl-2-(2-fluorophenyl)-3-thiocyanato-1*H*-indole (3l).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 19.9 mg (65%); mp: 98–100 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.88–7.85 (m, 1H), 7.58–7.53 (m, 1H), 7.46–7.42 (m, 2H), 7.38–7.32 (m, 3H), 7.27 (t, *J* = 9.5 Hz, 1H), 5.88–5.78 (m, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 4.93 (d, *J* = 16.8 Hz, 1H), 4.72–4.56 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 160.3 (d, *J* = 248 Hz), 140.0, 136.8, 132.7 (d, *J* = 2.0 Hz), 132.3, 132.2, 128.5, 124.6 (d, *J* = 4.0 Hz), 123.8, 122.1, 119.1, 117.6, 117.1 (d, *J* = 15.0 Hz), 116.3 (d, *J* = 22.0 Hz), 111.6 (SCN), 111.2, 91.9, 47.6 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -111.6 ppm; IR (KBr) 2920, 2363, 2153 (SCN), 1458, 1389, 1215, 1182, 845 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₁₈H₁₄FN₂S [M + H]⁺ 309.0856, found 309.0874.



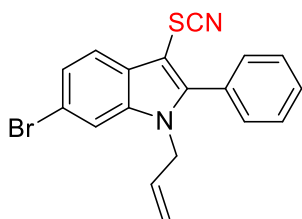
1-Allyl-6-chloro-2-phenyl-3-thiocyanato-1H-indole (3m).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 25.2 mg (78%) ; mp: 71–73 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.57–7.54 (m, 3H), 7.49–7.45 (m, 2H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.32–7.30 (m, 1H), 5.94–5.85 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.94 (d, *J* = 17.2 Hz, 1H), 4.64–4.62 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 147.1, 137.0, 132.2, 130.4, 130.0, 129.7, 128.8, 128.7, 127.1, 122.9, 120.0, 117.7, 111.8 (SCN), 111.2, 90.7, 47.5 ppm; IR (KBr) 3065, 2922, 2853, 2151 (SCN), 1607, 1470, 926, 845, 700 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₁₈H₁₄ClN₂S [M + H]⁺ 325.0561, found 325.0576.



1-Allyl-6-fluoro-2-phenyl-3-thiocyanato-1H-indole (3n).

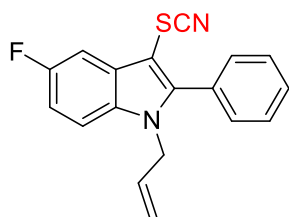
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 30.8 mg (85%) ; mp: 109–111 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 8.8 Hz, 5.2 Hz, 1H), 7.56–7.54 (m, 3H), 7.48–7.46 (m, 2H), 7.13–7.06 (m, 2H), 5.94–5.84 (m, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.62–4.61 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 160.6 (d, *J* = 239.0 Hz), 146.9 (d, *J* = 3.0 Hz), 136.8 (d, *J* = 12.0 Hz), 132.2, 130.4, 130.0, 128.9, 128.8, 124.9, 120.1 (d, *J* = 10.0 Hz), 117.7, 111.9 (SCN), 111.0, 110.8, 98.0, 97.7, 90.5, 47.5 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -117.5 ppm; IR (KBr) 2924, 2154 (SCN), 1829, 741, 700 cm⁻¹; HRMS (ESI) *m/z*: calcd. for C₁₈H₁₄FN₂S [M + H]⁺ 309.0856, found 309.0847.



1-Allyl-6-bromo-2-phenyl-3-thiocyanato-1H-indole (3o).

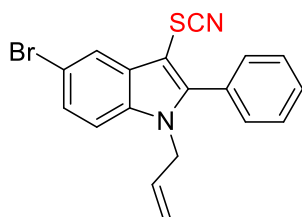
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 32.9 mg (89%) ; mp: 79–81 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.57–7.54 (m, 4H), 7.49–7.43 (m, 3H), 5.94–5.85 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.93 (d, *J* = 17.2 Hz, 1H), 4.64–4.62 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 147.0, 137.4, 132.2, 130.4, 130.0, 128.8, 128.6, 127.5, 125.4, 120.4, 117.7, 117.2, 114.1, 111.7 (SCN), 90.8, 47.4 ppm; IR (KBr) 2922, 2153 (SCN),

1383, 1333, 1179, 1053, 1028, 924 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{BrN}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 369.0056, found 369.0046.



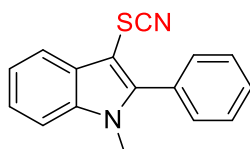
1-Allyl-5-fluoro-2-phenyl-3-thiocyanato-1H-indole (3p).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 26.3 mg (85%); mp: 102–104 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.55 (m, 3H), 7.50–7.48 (m, 3H), 7.33–7.30 (m, 1H), 7.08 (t, $J = 8.8$ Hz, 1H), 5.95–5.86 (m, 1H), 5.22 (d, $J = 10.8$ Hz, 1H), 4.94 (d, $J = 17.2$ Hz, 1H), 4.66–4.64 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 159.2 (d, $J = 238.0$ Hz), 147.9, 133.0, 132.4, 130.4, 130.0, 129.4 (d, $J = 10.0$ Hz), 128.9, 128.8, 117.6, 112.2 (d, $J = 25.9$ Hz), 112.2 (d, $J = 9.4$ Hz), 111.9 (SCN), 104.3 (d, $J = 24.0$ Hz), 90.2 (d, $J = 5.1$ Hz), 47.6 ppm; ^{19}F NMR (376 MHz, CDCl_3) δ -120.6 ppm; IR (KBr) 2955, 2924, 2154 (SCN), 1732, 1464, 1377, 1082, 853, 748 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{FN}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 309.0856, found 309.0845.



1-Allyl-5-bromo-2-phenyl-3-thiocyanato-1H-indole (3q).

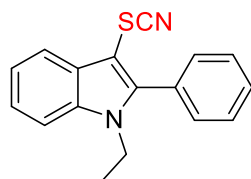
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 22.8 mg (62%); mp: 145–147 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 2.0$ Hz, 1H), 7.57–7.54 (m, 3H), 7.50–7.46 (m, 2H), 7.43 (dd, $J = 8.8$ Hz, 2.0 Hz, 1H), 7.27–7.25 (m, 1H), 5.94–5.85 (m, 1H), 5.22 (d, $J = 10.4$ Hz, 1H), 4.91 (d, $J = 17.2$ Hz, 1H), 4.66–4.64 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 147.5, 135.3, 132.3, 130.4, 130.3, 130.0, 128.9, 128.6, 126.7, 121.7, 117.6, 115.6, 112.6 (SCN), 111.8, 89.9, 47.5 ppm; IR (KBr) 2920, 2149 (SCN), 1460, 1391, 1180, 916, 853, 799, 698 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{18}\text{H}_{14}\text{BrN}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 369.0056, found 369.0050.



1-Methyl-2-phenyl-3-thiocyanato-1H-indole (3r).

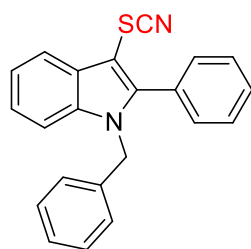
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 12.0 mg (45%); mp: 76–78 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.86–7.84 (m, 1H), 7.60–7.54 (m, 3H), 7.49–7.47 (m, 2H), 7.44–7.42 (m, 1H),

7.40–7.33 (m, 2H), 3.70 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 137.2, 130.7, 129.6, 129.2, 128.8, 128.5, 123.6, 122.0, 119.0, 112.2 (SCN), 110.3, 89.6, 31.8 ppm; IR (KBr) 2922, 2851, 2359, 2150 (SCN), 1470, 1381, 1240, 912, 700 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$ 265.0794, found 265.0780.



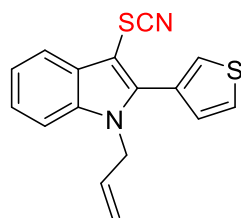
1-Ethyl-2-phenyl-3-thiocyanato-1H-indole (3s).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 11.0 mg (40%) ; mp: 105–107 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.86–7.84 (m, 1H), 7.59–7.55 (m, 3H), 7.48–7.44 (m, 3H), 7.39–7.32 (m, 2H), 4.14 (q, $J = 7.2\text{Hz}$, 2H), 1.30 (t, $J = 7.2\text{Hz}$, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 136.0, 130.5, 129.7, 129.5, 128.8, 128.7, 123.5, 121.9, 119.1, 112.2 (SCN), 110.5, 89.8, 39.8, 15.4 ppm; IR (KBr) 3059, 2976, 2928, 2153 (SCN), 1603, 1387, 1342, 743, 700 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$ 279.0951, found 279.0960.



1-Benzyl-2-phenyl-3-thiocyanato-1H-indole (3t).

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 15.0 mg (44%) ; mp: 156–158 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.6\text{ Hz}$, 1H), 7.51–7.31 (m, 7H), 7.29–7.24 (m, 4H), 6.95–6.93 (m, 2H), 5.31 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 136.8, 136.7, 130.5, 130.4, 129.8, 128.9, 128.8, 127.7, 126.0, 125.9, 123.9, 122.2, 120.4, 119.1, 112.1 (SCN), 111.3, 90.6, 48.5 ppm; IR (KBr) 2922, 2153 (KBr), 1867, 1634, 1454, 1385, 1177, 1074, 1028, 835, 804, 698 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{S}$ $[\text{M} + \text{H}]^+$ 341.1107, found 341.1131.

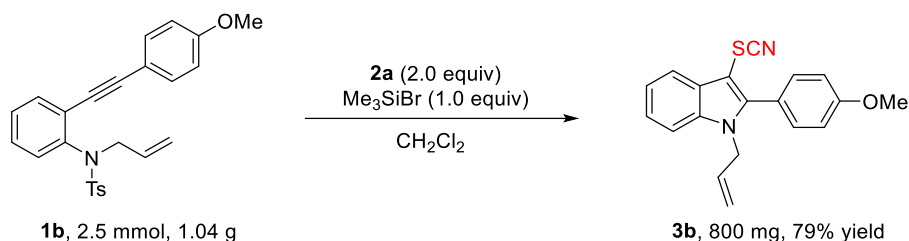


1-Allyl-2-(thiophen-3-yl)-3-thiocyanato-1H-indole (3u).

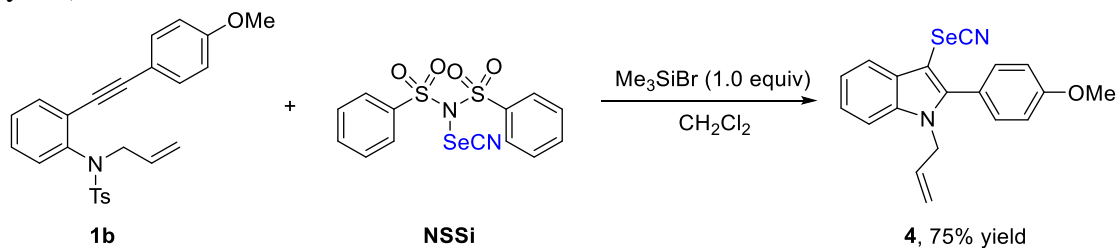
Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v) to 30:1); White solid; 29.2 mg (99%) ; mp: 126–127 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.86–7.82 (m, 1H), 7.62–7.61 (m, 1H), 7.53 (dd, $J = 4.8\text{ Hz}$, 3.2 Hz, 1H), 7.38–7.30 (m, 4H), 6.02–5.93 (m, 1H), 5.24 (d, $J = 10.4\text{ Hz}$, 1H), 4.95 (d, $J = 17.2\text{ Hz}$, 1H),

4.73–4.72, (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 136.7, 132.8, 129.0, 128.6, 128.6, 127.7, 126.6, 123.8, 122.1, 119.0, 117.3, 112.2 (SCN), 110.9, 90.2, 47.4 ppm; IR (KBr) 2922, 2147 (SCN), 1458, 924, 748 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{S}_2$ $[\text{M} + \text{H}]^+$ 297.0515, found 297.0501.

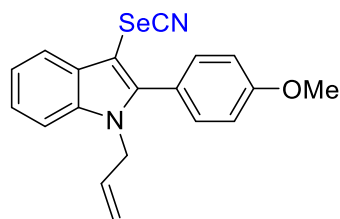
5. Gram Scale Reaction, Selenocyanation Reaction and Derivatization of Products



Gram Scale Reaction. In a 100-mL drying flask under argon atmosphere, **1b** (1.04 g, 2.5 mmol) was added dichloromethane (50 mL) and Me_3SiBr (312.5 μL , 2.5 mmol, 1.0 equiv.) were added, followed by reagent **2a** (0.78 g, 5.0 mmol, 2.0 equiv.). The reaction was carried out for 12 h at room temperature. After completion of the reaction, the solution was concentrated in vacuum purification of the residue by flash chromatography (petroleum ether/ethyl acetate) afforded the product **3b** (800 mg, 79% yield).



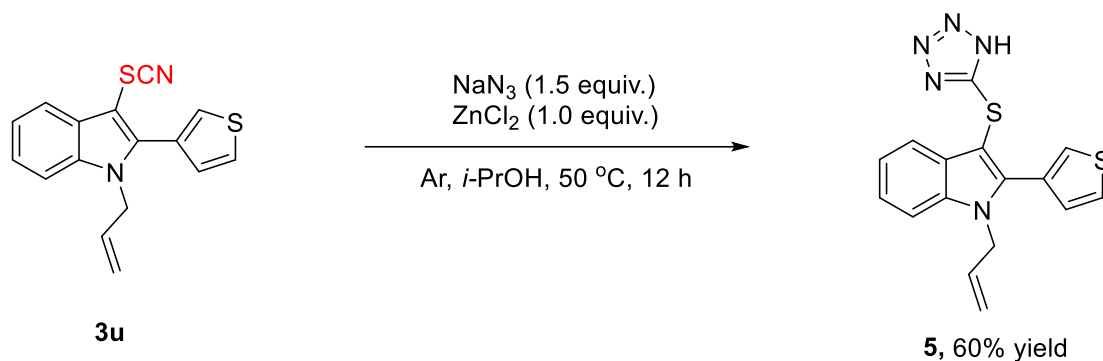
Selenocyanation Reaction. Me_3SiBr (12.5 μL , 0.1 mmol, 1.0 equiv.) and dichloromethane (2.0 mL) were added to a 25 mL Schlenk tube containing **1b** (41.7 mg, 0.1 mmol, 1.0 equiv.) under argon atmosphere. Then **NSSi** (80.3 mg, 0.2 mmol, 2.0 equiv.) was added. The reaction was carried out at room temperature for 12 h. After completion of the reaction, the product **4** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate.



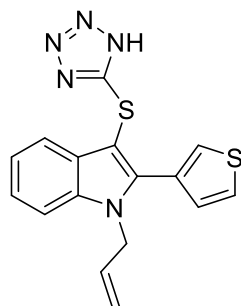
1-Allyl-2-(4-methoxyphenyl)-3-selenocyanato-1H-indole.

Column chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 80:1 (v/v))

to 30:1); White solid; 27.4 mg (75%) ; mp: 97–99 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.77 (m, 1H), 7.42–7.38 (m, 2H), 7.37–7.31 (m, 3H), 7.08–7.04 (m, 2H), 5.96–5.87 (m, 1H), 5.20 (d, $J = 10.0$ Hz, 1H), 4.93 (d, $J = 17.2$ Hz, 1H), 4.68–4.66 (m, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 146.6, 136.8, 132.9, 132.0, 129.7, 123.4, 121.9, 119.9, 117.2, 114.1, 110.9 (SeCN), 102.3, 88.7, 55.4, 47.4 ppm; IR (KBr) 2924, 2149 (SeCN), 1611, 1456, 1250, 1177, 1028, 839 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{OSe}$ $[\text{M} + \text{H}]^+$ 369.0501, found 369.0491.



Derivatization of Products. To an oven-dried flask was added **3u** (60.6 mg, 0.205 mmol), then **3s** was dissolved in 6.0 mL *i*-PrOH at room temperature. NaN_3 (20 mg, 0.205 mmol) was added to the system. Then the system was heated to 50 °C and stirred for 12 h. Then, the reaction was quenched by 6.0 mL H_2O , extracted by EtOAc (3 \times 10.0 ml). The organic the organic layer was collected and dried over Na_2SO_4 , then concentrated and charged on silica gel and separated by column chromatography (CH_2Cl_2 : MeOH = 7:1) to afford the desired product **5** (40 mg, 60% yield).

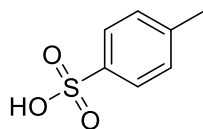


3-((1H-tetrazol-5-yl)thio)-1-Allyl-2-(thiophen-3-yl)-1H-indole.

Column chromatography (silica gel, CH_2Cl_2 : MeOH = 7:1 (v/v)); White solid; 40.0 mg (60%) ; mp: 73–75 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.80 (m, 1H), 7.73 (dd, $J = 5.2$ Hz, 2.8 Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.33–7.29 (m, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 6.04–5.95 (m, 1H), 5.17 (dd, $J = 10.4$ Hz, 1.6 Hz, 1H), 4.96 (dd, $J = 17.2$ Hz, 1.6 Hz, 1H), 4.85–4.83 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 155.8, 142.2, 137.1, 134.2, 129.7, 129.2, 129.2, 128.2, 127.3, 123.4, 121.7, 118.7, 117.1, 111.8, 94.1, 47.2 ppm; IR (KBr) 2924, 1724, 1646, 1460, 1411, 1341, 1302, 1205, 1178, 1016, 924, 867, 808, 744, 701 cm^{-1} ; HRMS (ESI) m/z : calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_5\text{S}_2$ $[\text{M} - \text{H}]^-$ 338.0539, found 338.0522.

6. Mechanism Study

The byproduct of the starting materials of **1a-u** was isolated and identified as *p*-toluene sulfonic acid.



¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H) ppm; HRMS (ESI) *m/z*: calcd. for C₇H₉O₃S [M + H]⁺ 173.0267, found 173.0260.

7. Single Crystal X-Ray Data for Compound **3c** (CCDC 2321248)

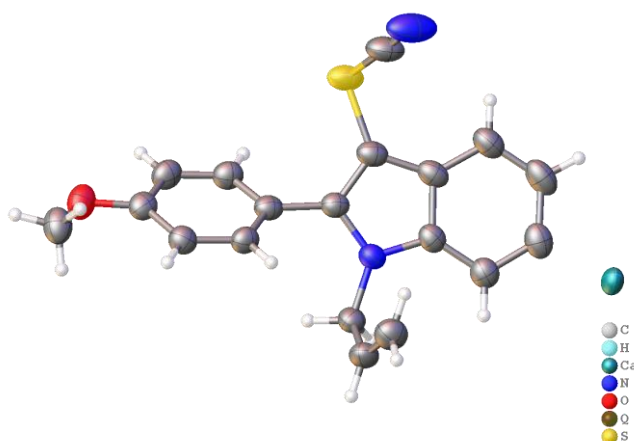


Table 1 Crystal data and structure refinement for test.

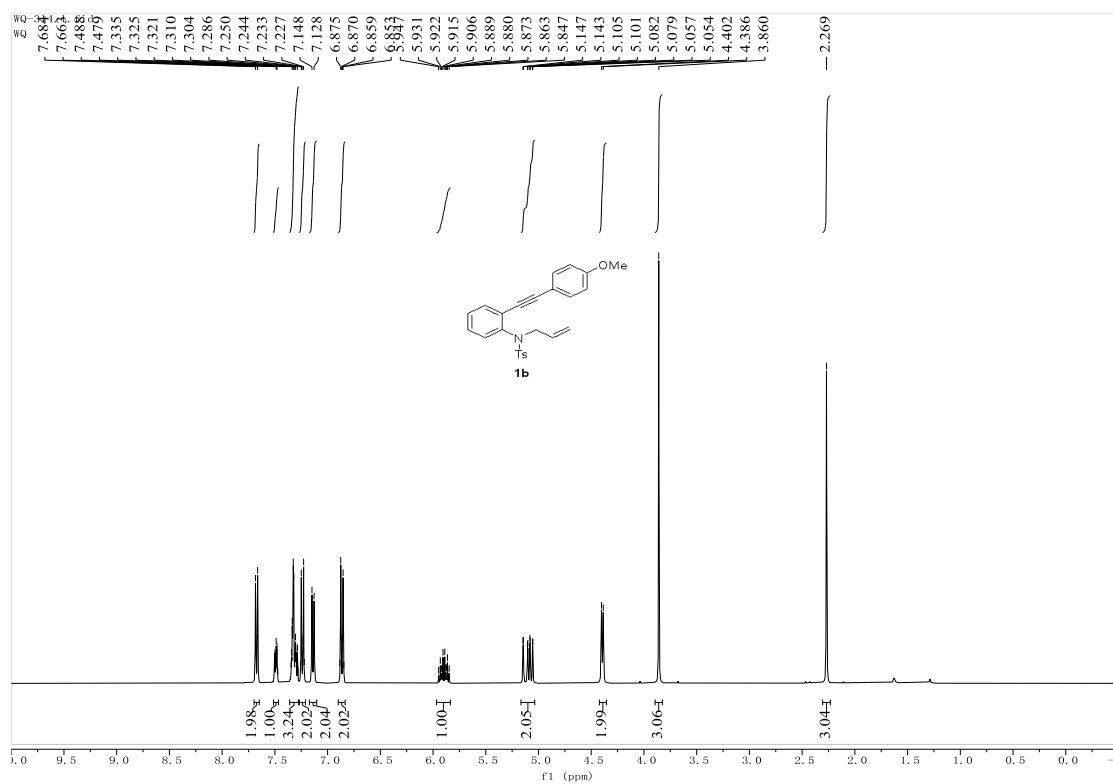
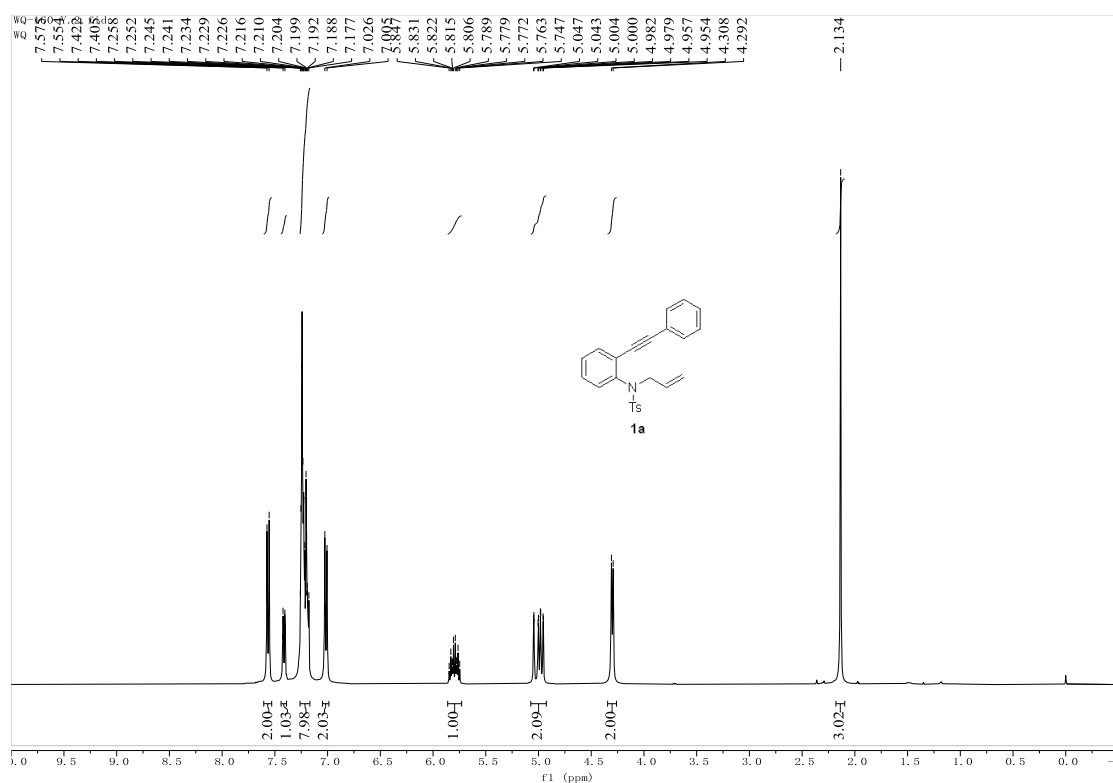
| | |
|-------------------------------|---|
| Identification code | test |
| Empirical formula | C ₁₉ H ₁₅ CaN ₂ OS |
| Formula weight | 359.47 |
| Temperature/K | 296 |
| Crystal system | monoclinic |
| Space group | P21/n |
| <i>a</i> /Å | 9.39200(10) |
| <i>b</i> /Å | 12.6535(2) |
| <i>c</i> /Å | 14.9156(2) |
| α /° | 90 |
| β /° | 102.255(2) |
| γ /° | 90 |
| Volume/Å ³ | 1732.20(4) |
| <i>Z</i> | 4 |
| ρ calc/g cm ³ | 1.378 |

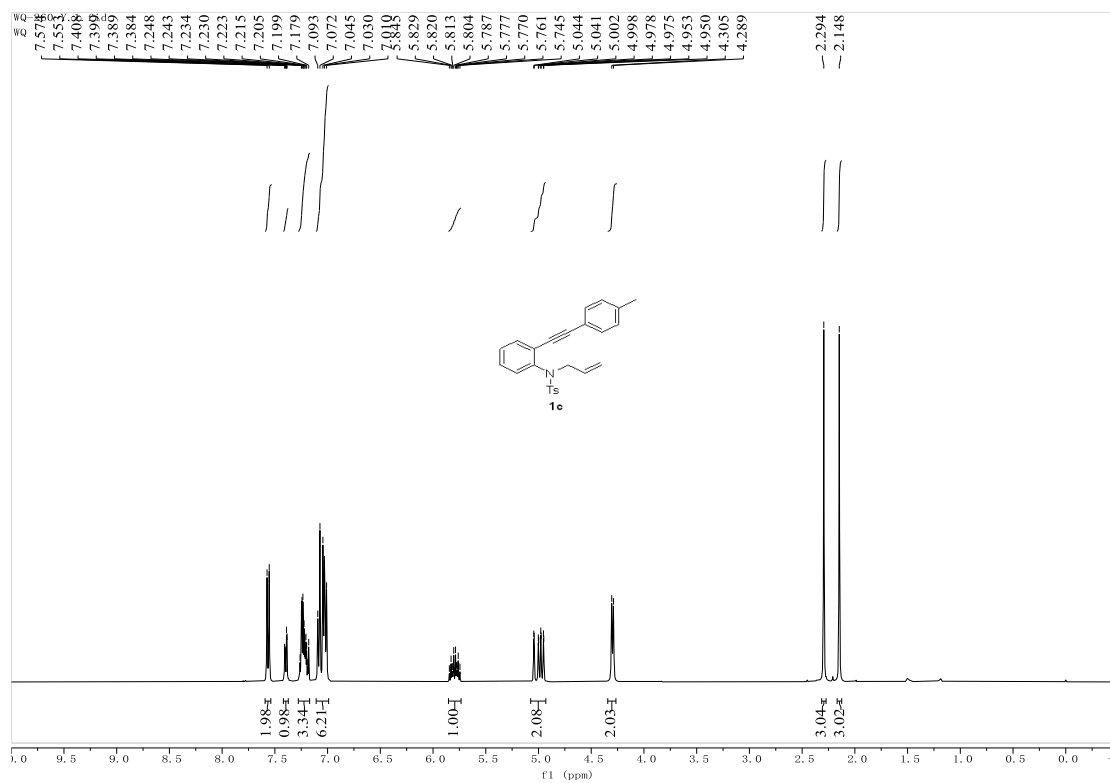
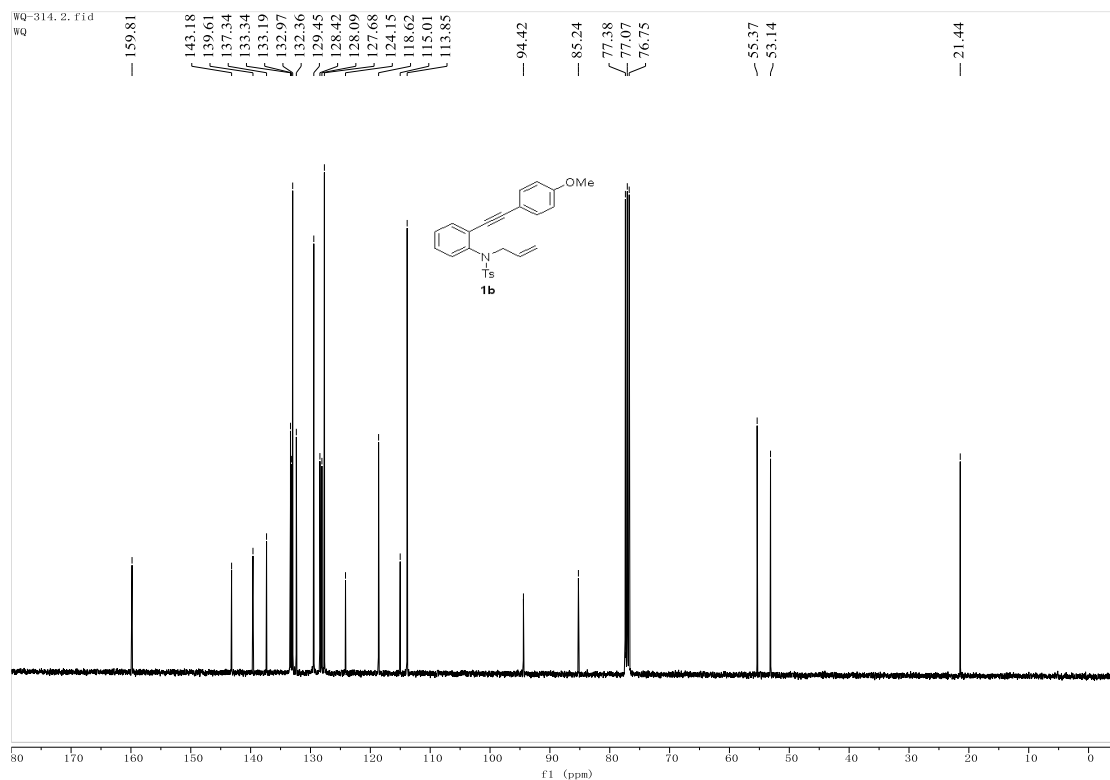
| | |
|--|--|
| μ /mm ⁻¹ | 4.304 |
| F(000) | 748.0 |
| Crystal size/mm ³ | 0.22 × 0.19 × 0.15 |
| Radiation | CuK α (λ = 1.54184) |
| 2 Θ range for data collection/ $^{\circ}$ | 9.256 to 152.402 |
| Index ranges | -10 \leq h \leq 11, -12 \leq k \leq 15, -18 \leq l \leq 18 |
| Reflections collected | 16805 |
| Independent reflections | 3506 [R _{int} = 0.0304, R _{sigma} = 0.0217] |
| Data/restraints/parameters | 3506/0/218 |
| Goodness-of-fit on F ² | 1.081 |
| Final R indexes [$I \geq 2\sigma(I)$] | R1 = 0.0788, wR2 = 0.2472 |
| Final R indexes [all data] | R1 = 0.0834, wR2 = 0.2539 |
| Largest diff. peak/hole / e \AA^{-3} | 0.86/-0.93 |
| CCDC | 2321248 |

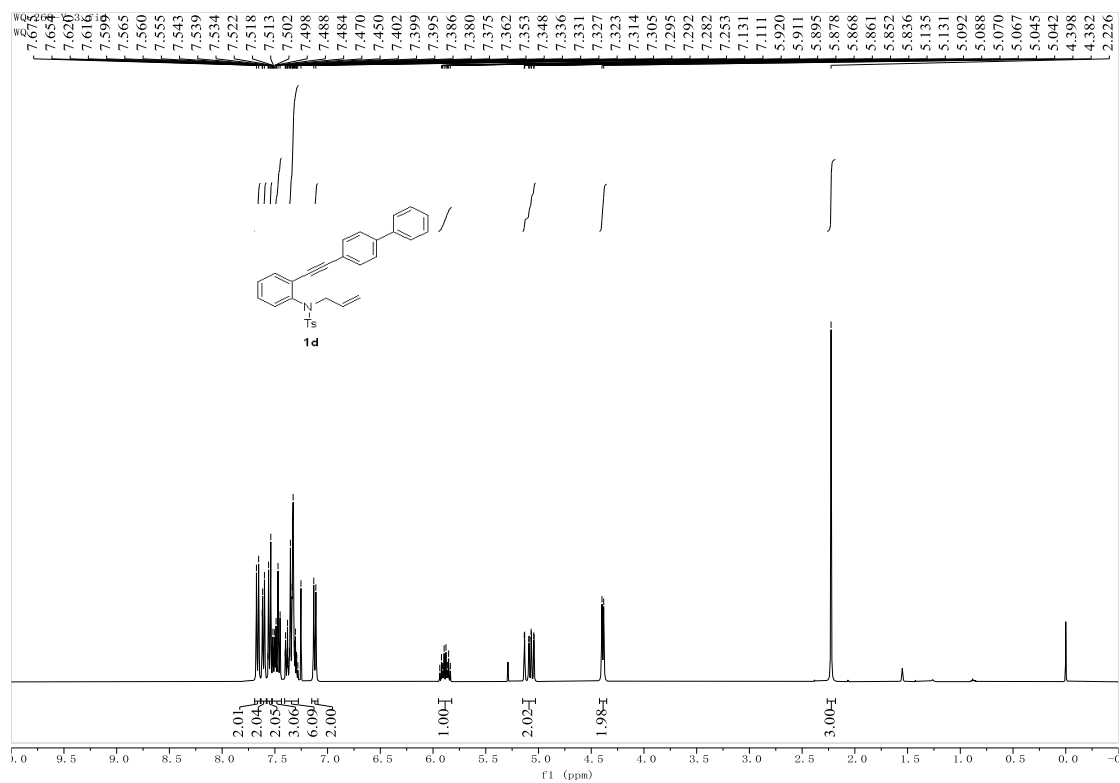
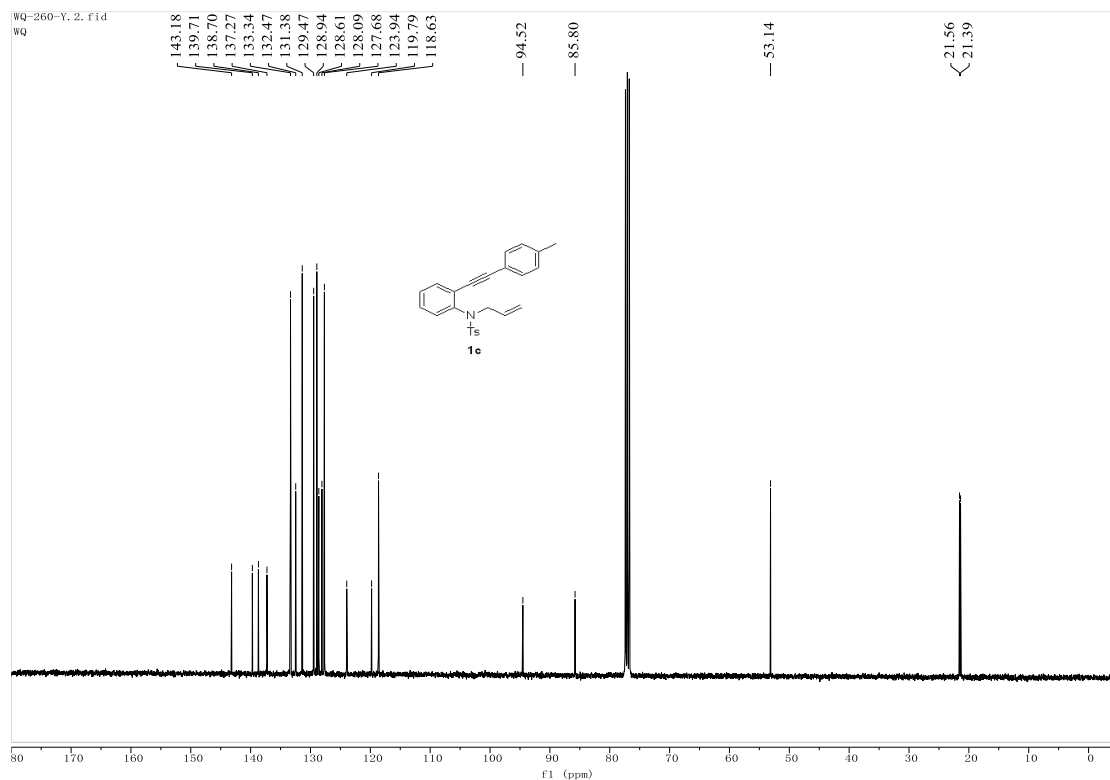
8. References

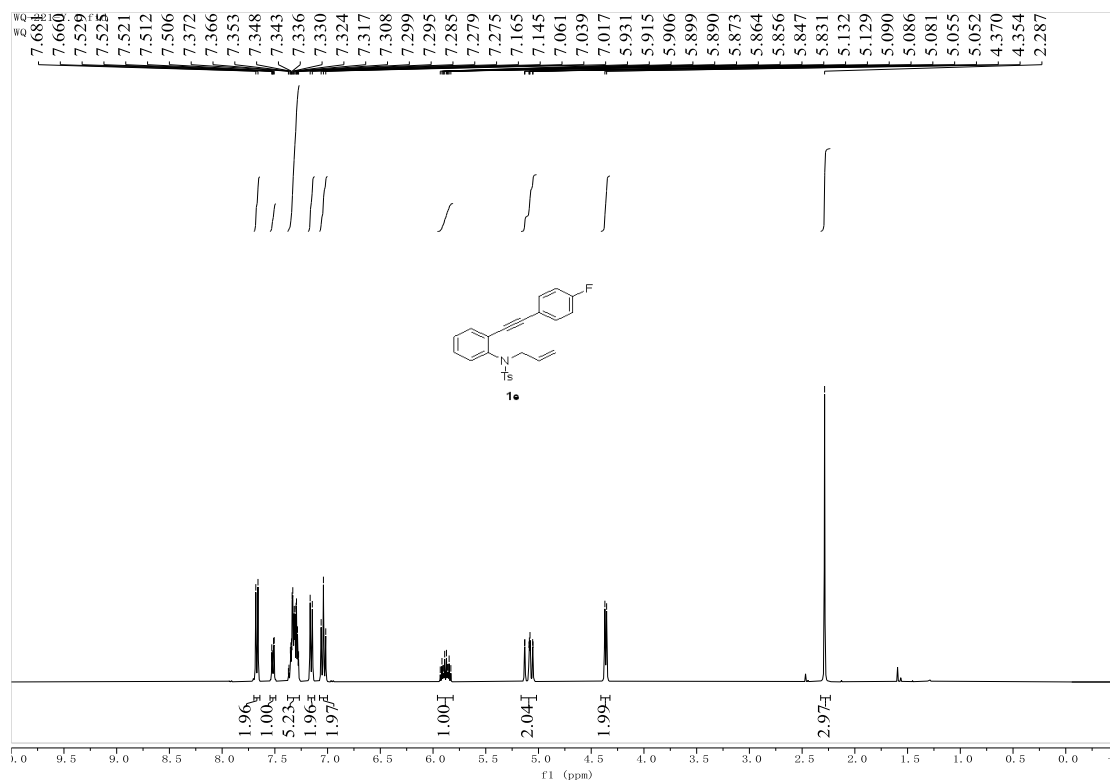
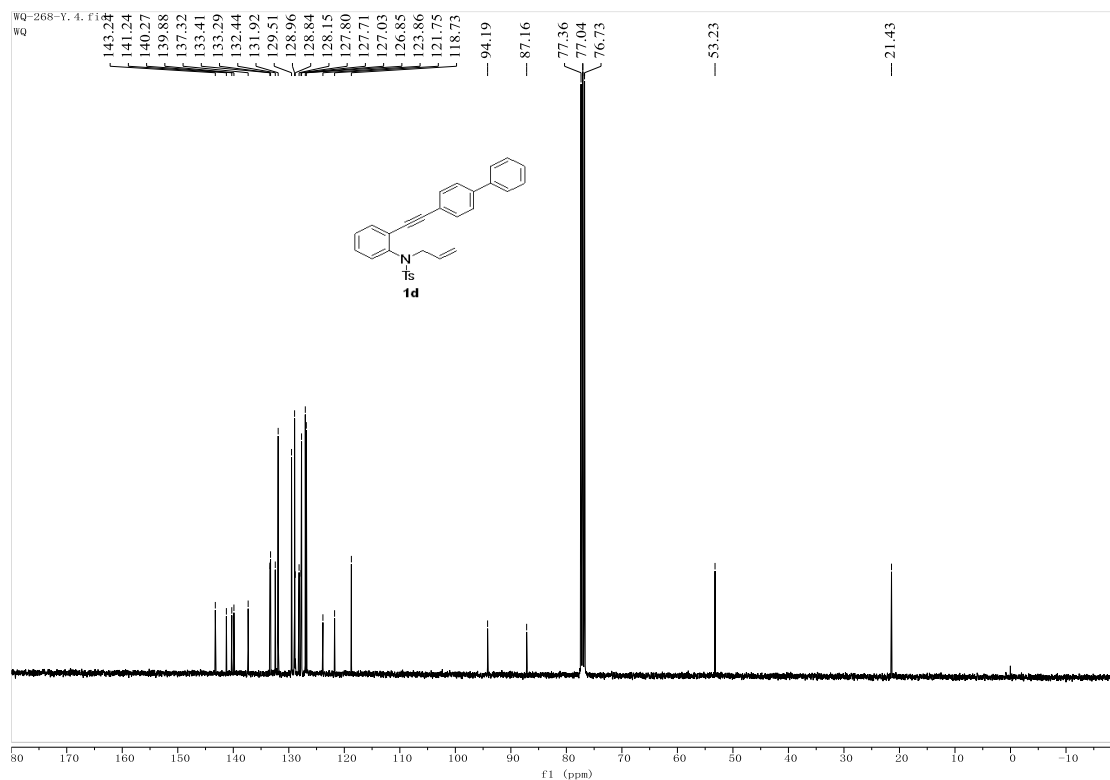
- [1] (a) Wu, D.; Qiu, J.; Karmaker, P. G.; Yin, H.; Chen, F.-X. *J. Org. Chem.* **2018**, *83*, 1576–1583;
 (b) Qiu, J.; Wu, D.; Karmaker, P. G.; Yin, H.; Chen, F.-X. *Org. Lett.* **2018**, *20*, 1600–1603;
 (c) Li, C.; Long, P.; Wu, H.; Yin, H.; Chen, F.-X. *Org. Biomol. Chem.* **2019**, *17*, 7131–7134.
- [2] (a) Dhage, Y. D.; Shirai, T.; Arima, M.; Nakazima, A.; Hikawa, H.; Kusakabe, I. A. T.; Takahashi, K.; Kato, K. *RSC Adv.* **2015**, *5*, 42623–42627.
 (b) Jillella, R.; Oh, D. H.; Oh, C. H. *New J. Chem.* **2018**, *42*, 16886–16890.
 (c) Dapkekara, A. B.; Satyanarayana G. *Chem. Commun.* **2023**, *59*, 8719–8722.
 (d) Mandala, M.; Balamurugan, R. *Chem. Commun.* **2022**, *58*, 9778–9781.
 (e) Li, X.; Cheng, Y.; Li, Y.; Sun, F.; Zhan, X.; Yang, Z.; Yang, J.; Du Y. *J. Org. Chem.* **2024**, *89*, 2039–2049.
 (f) Qiu, J.; Sako, M.; Tanaka, T.; Matsuzaki, T.; Takehara, T.; Suzuki, T.; Ohno, S.; Murai, K.; Arisawa, M. *Org. Lett.* **2021**, *23*, 4284–4288.
 (g) Yoshika, S.; Fujii, Y.; Tsujino, H.; Uno, T.; Fujioka, H.; Arisawa, M. *Chem. Commun.*, **2017**, *53*, 5970.

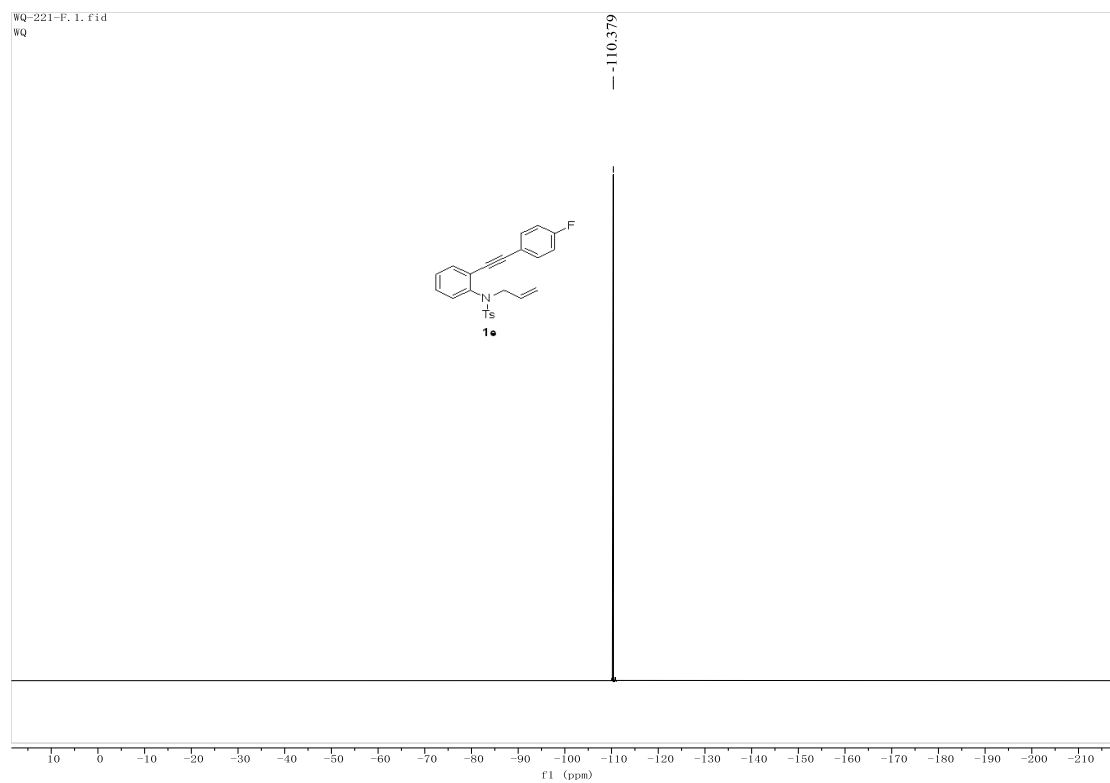
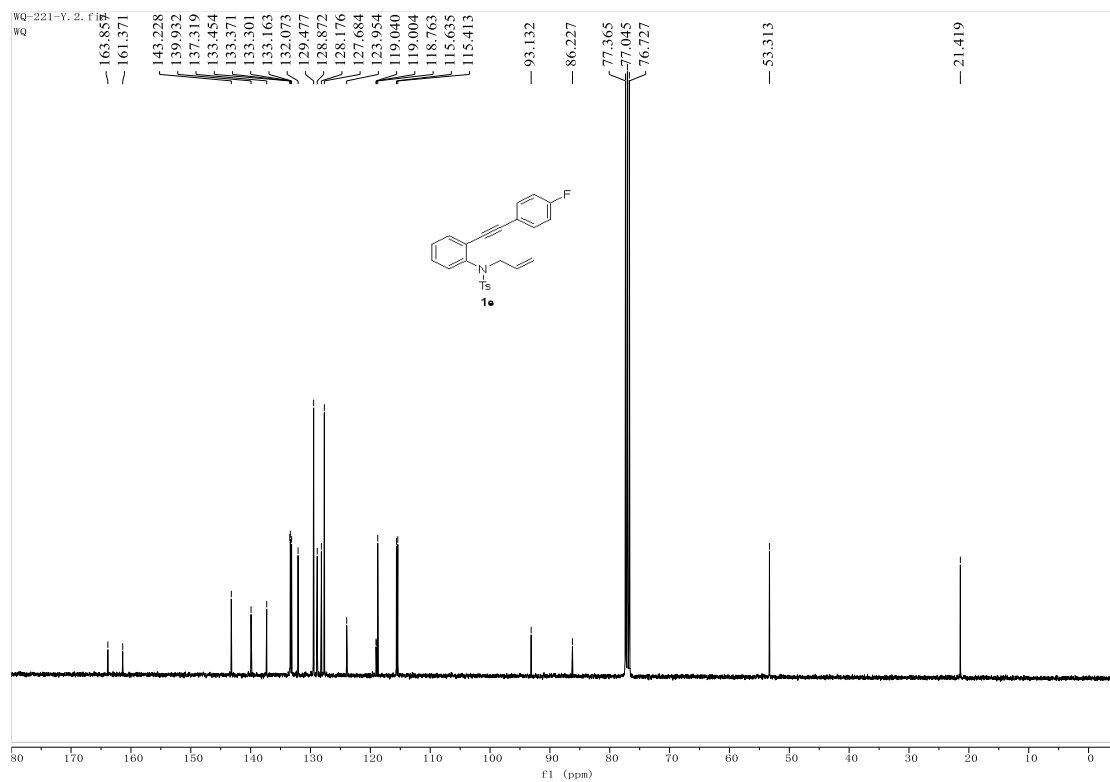
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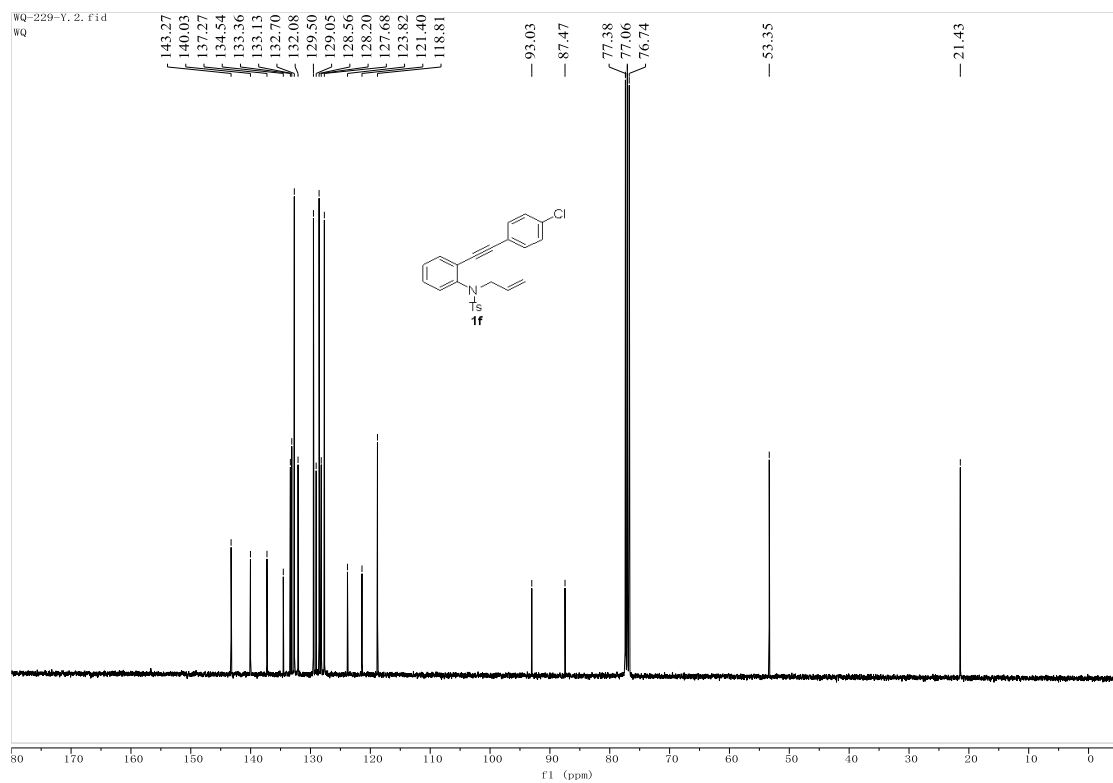
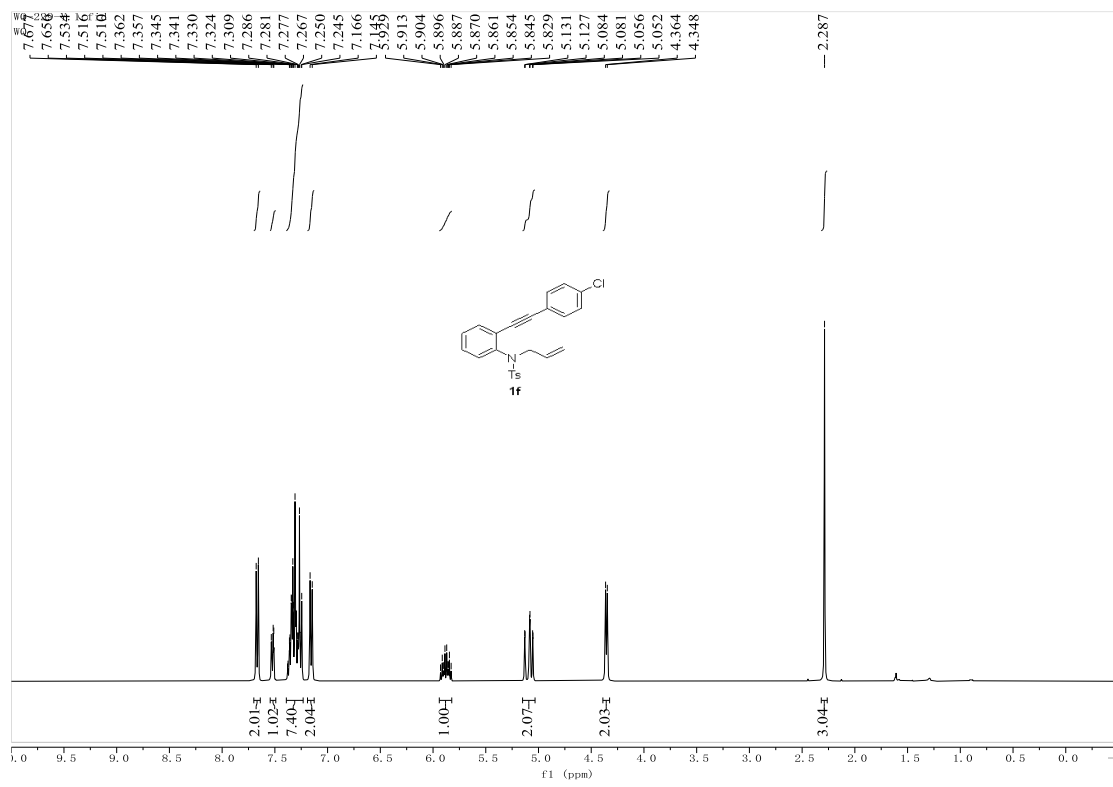


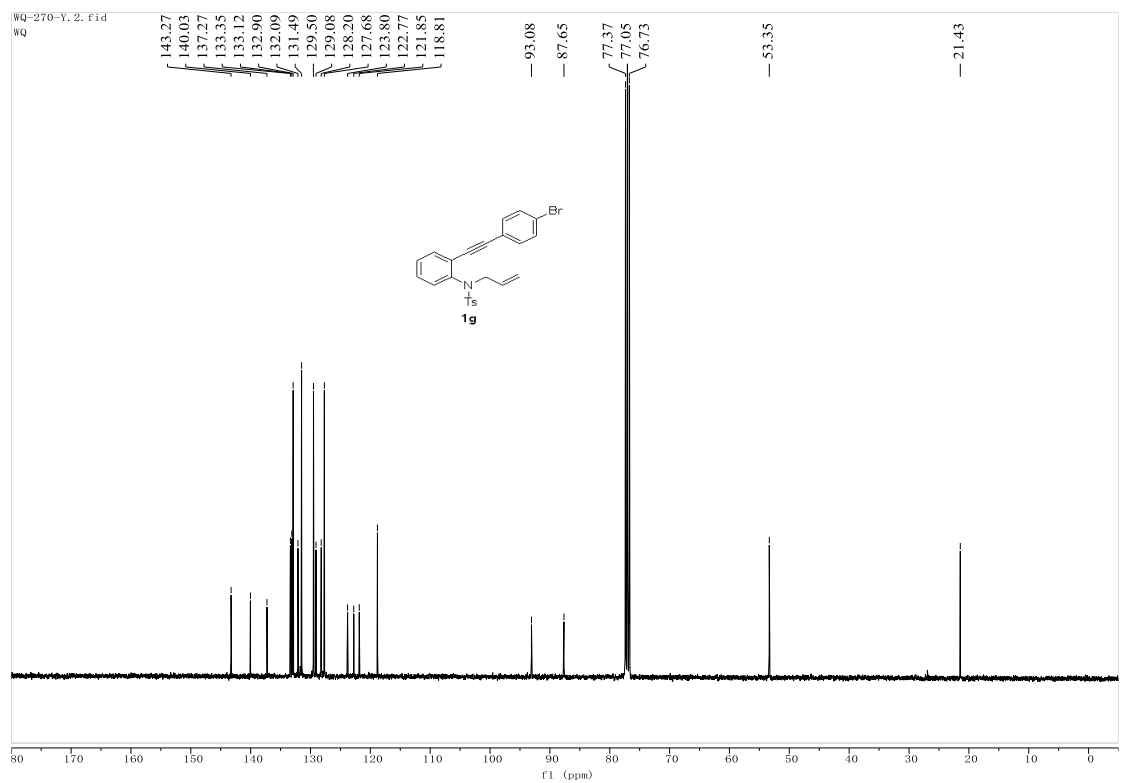
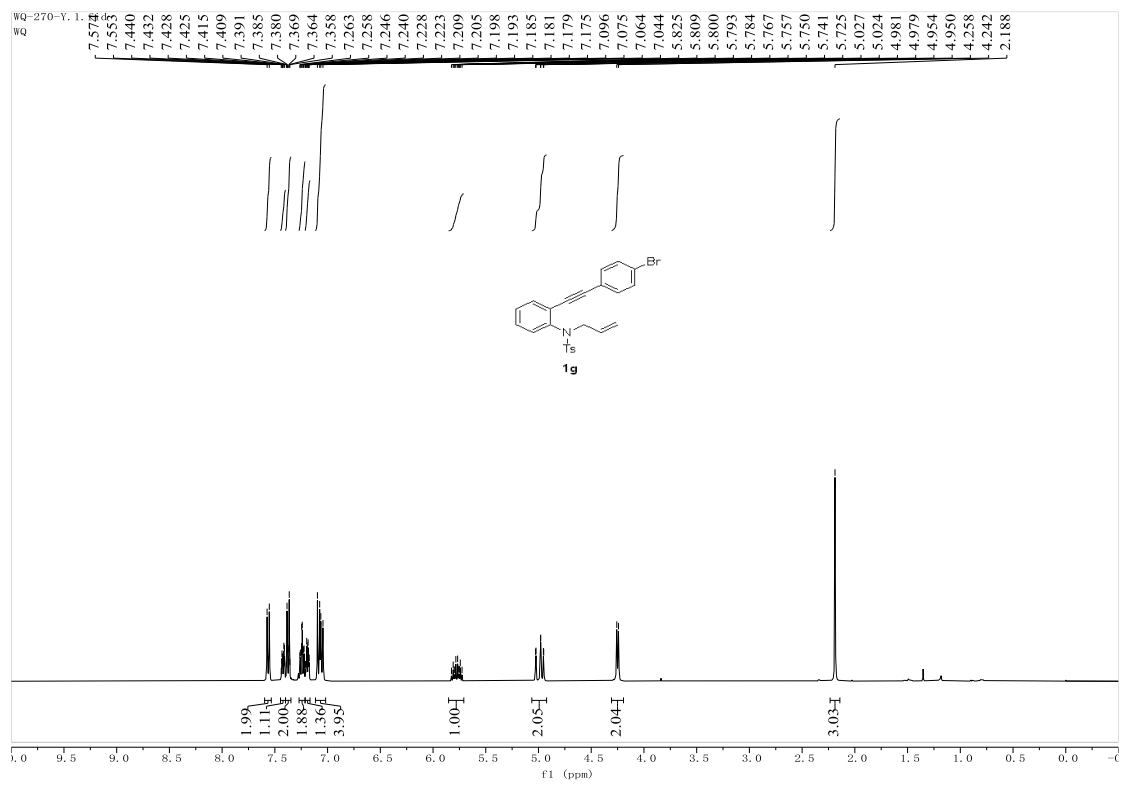


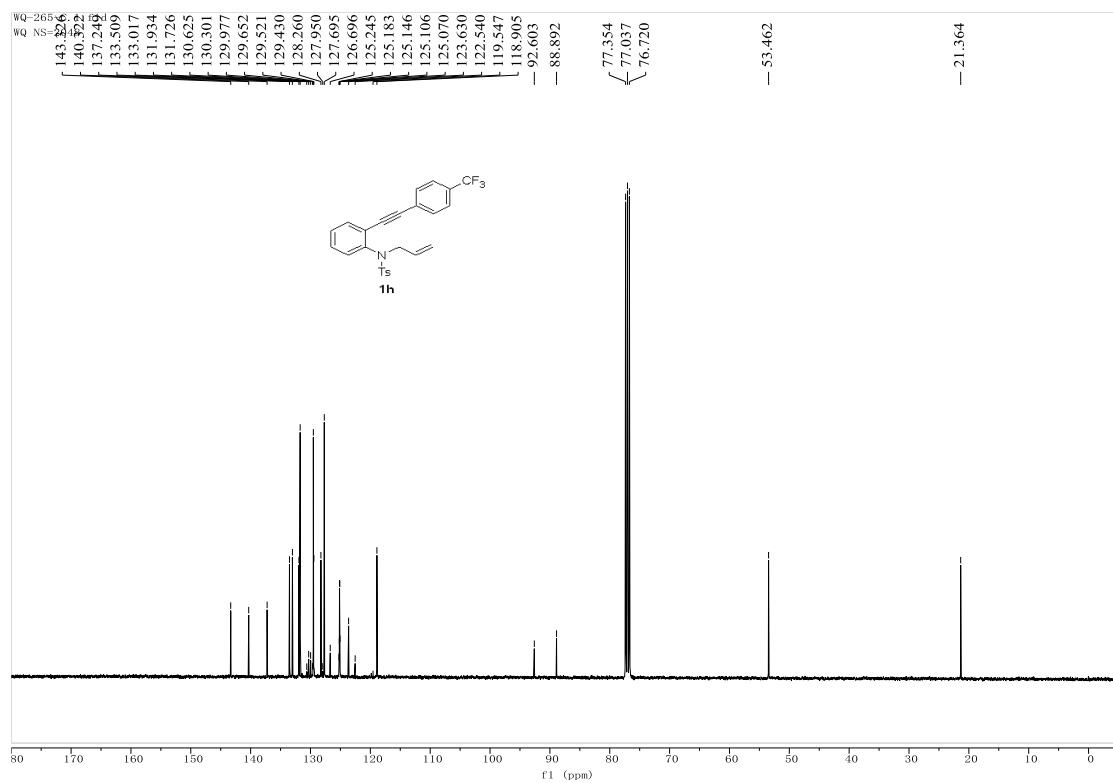
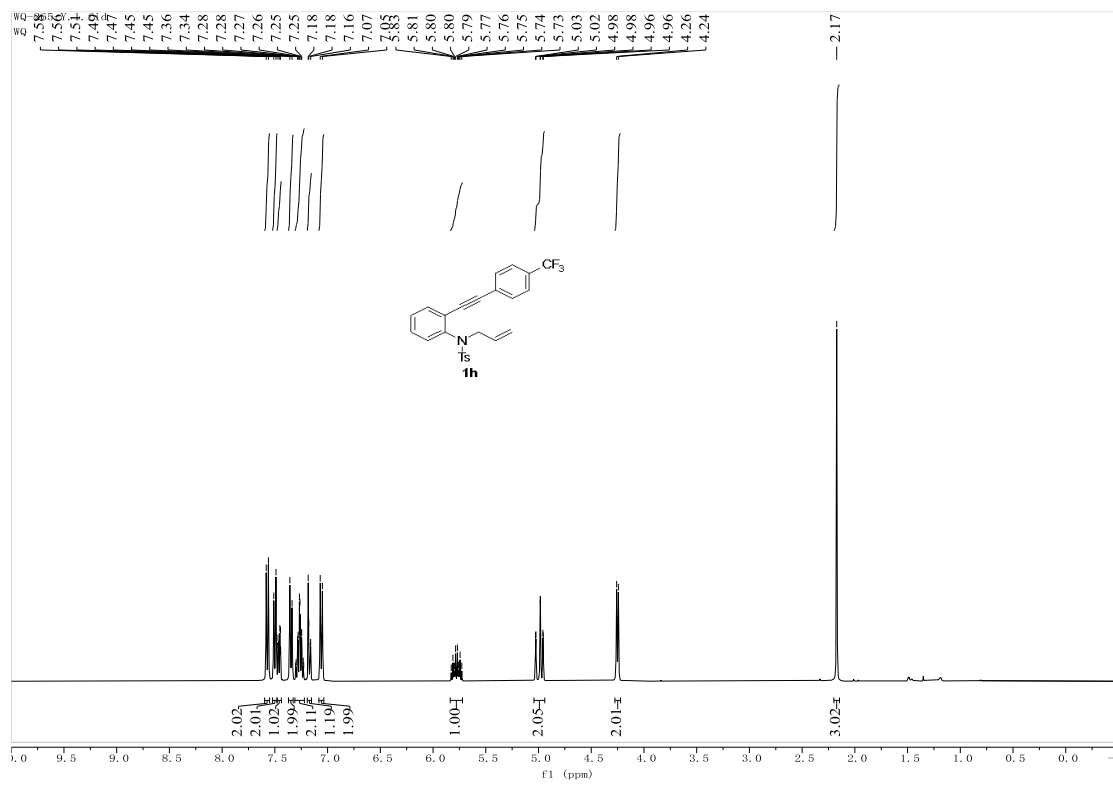




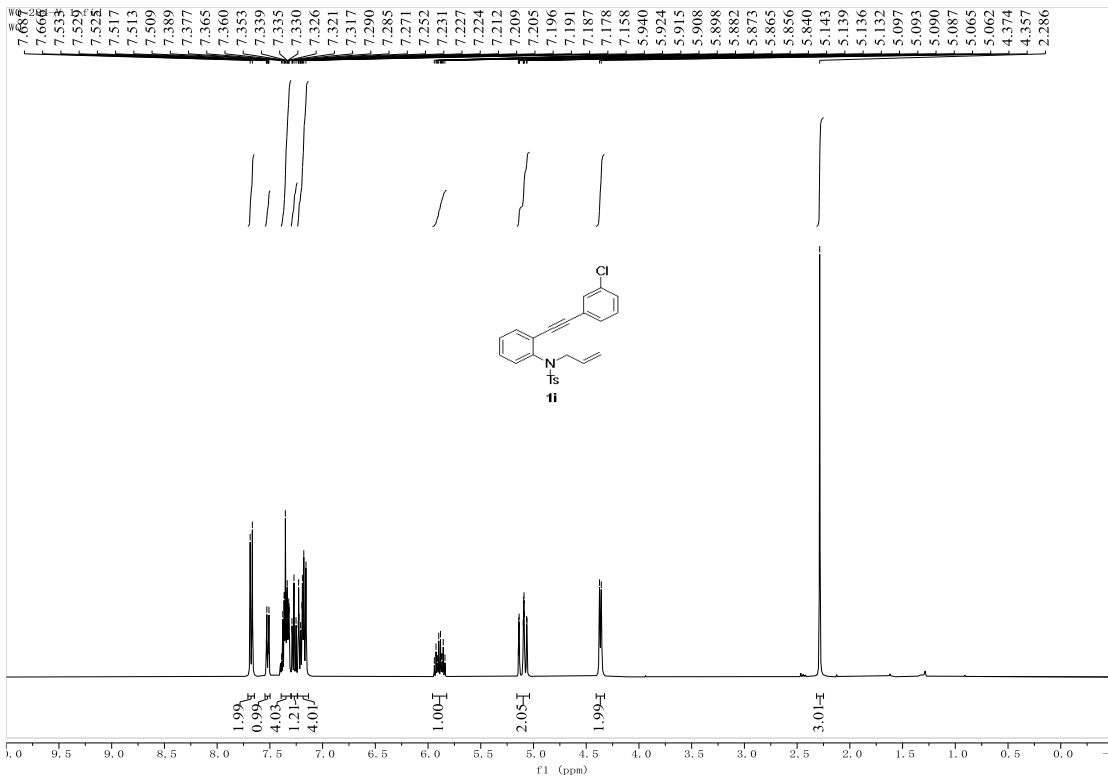
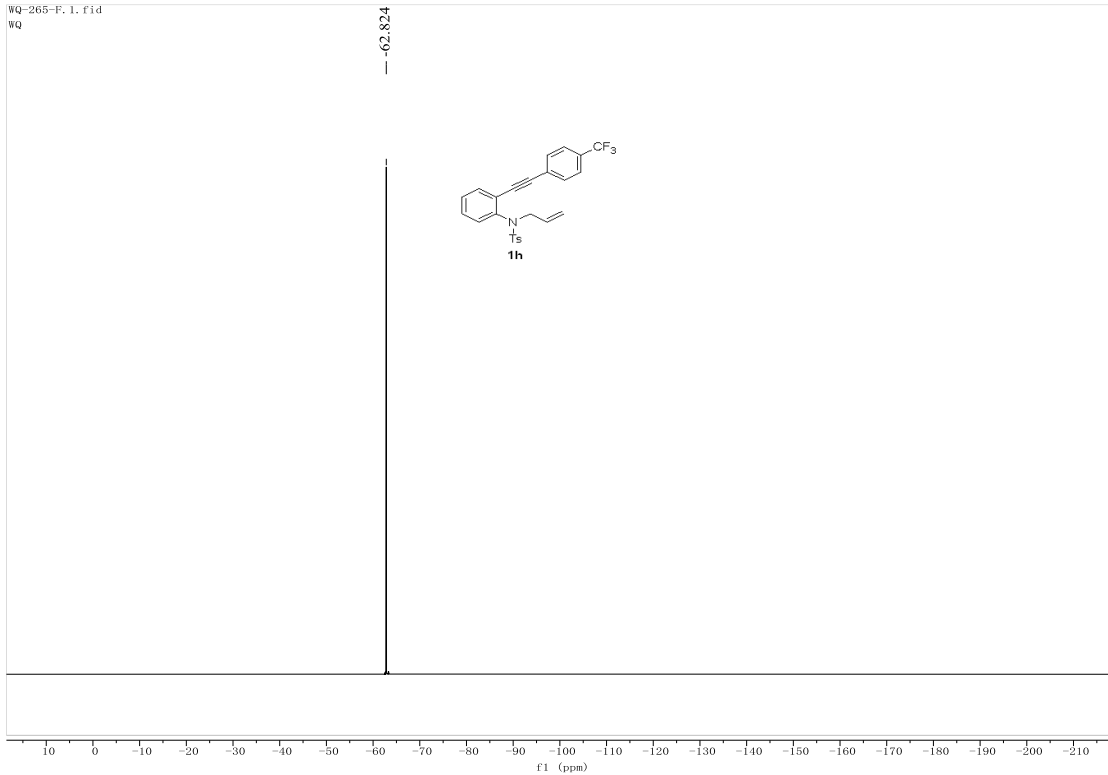


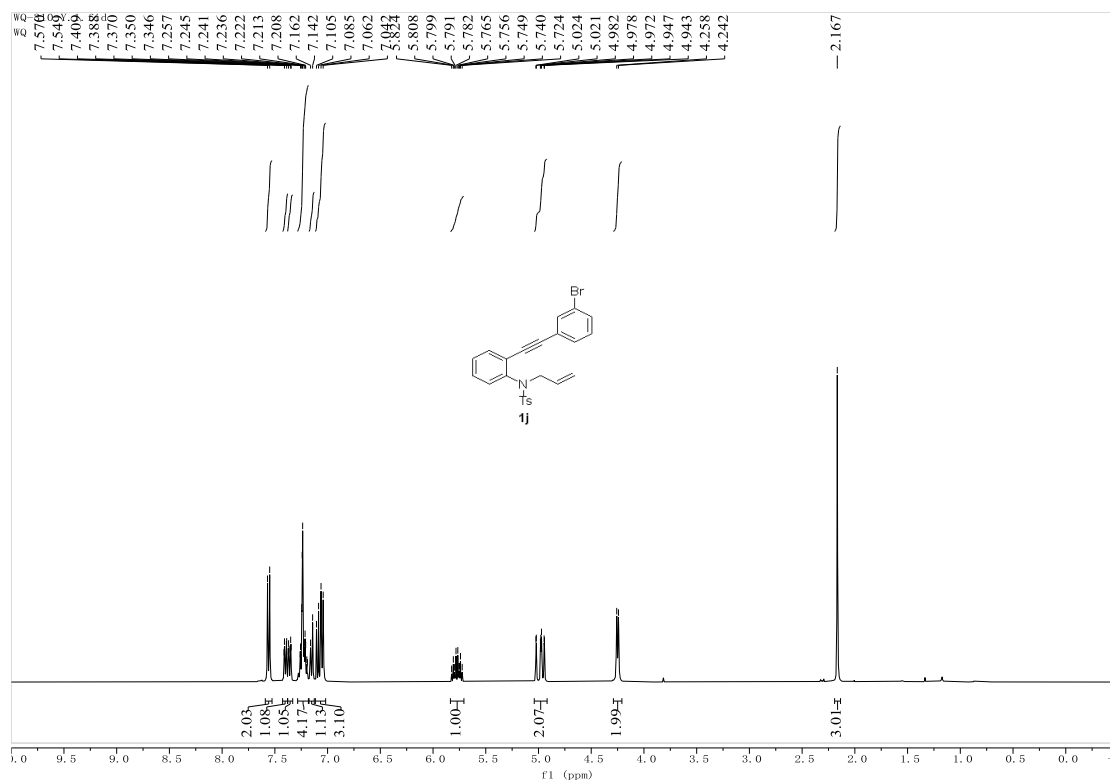
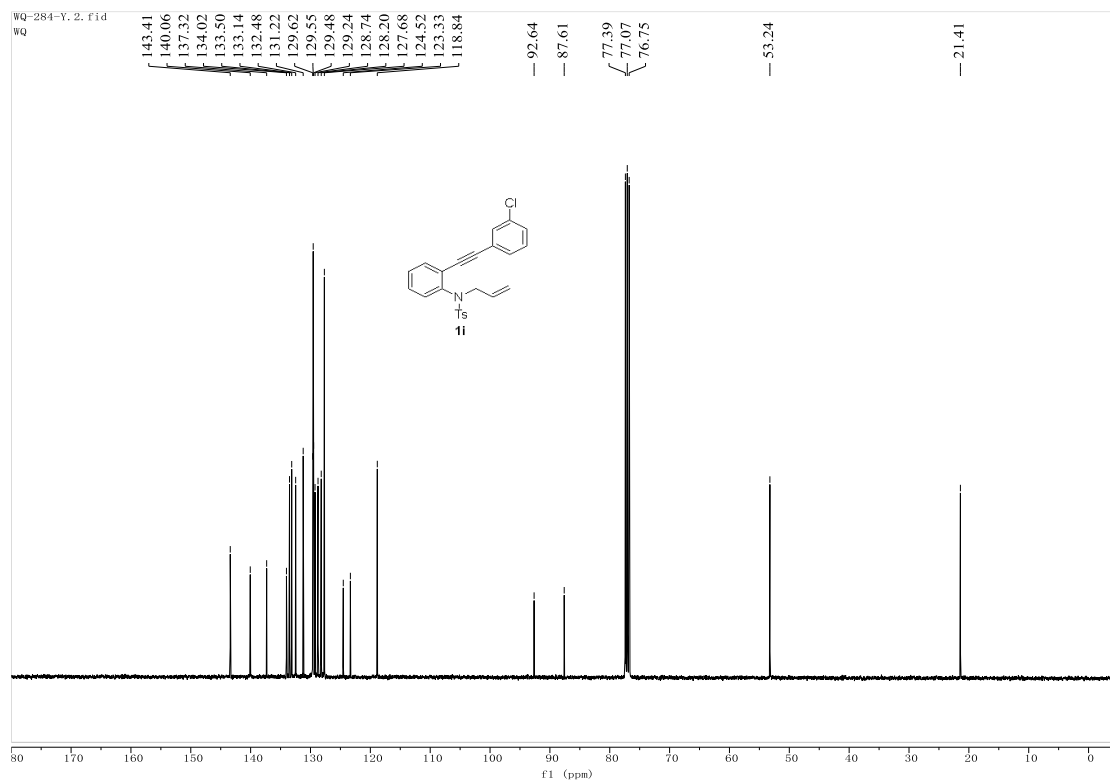


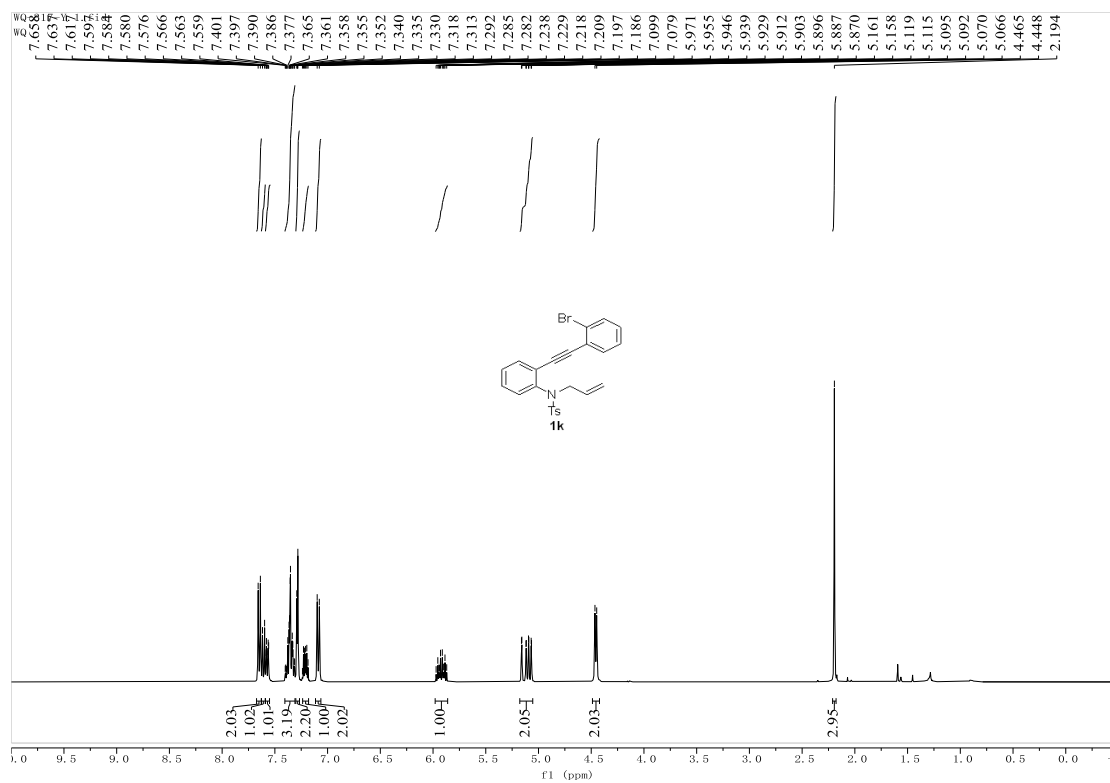
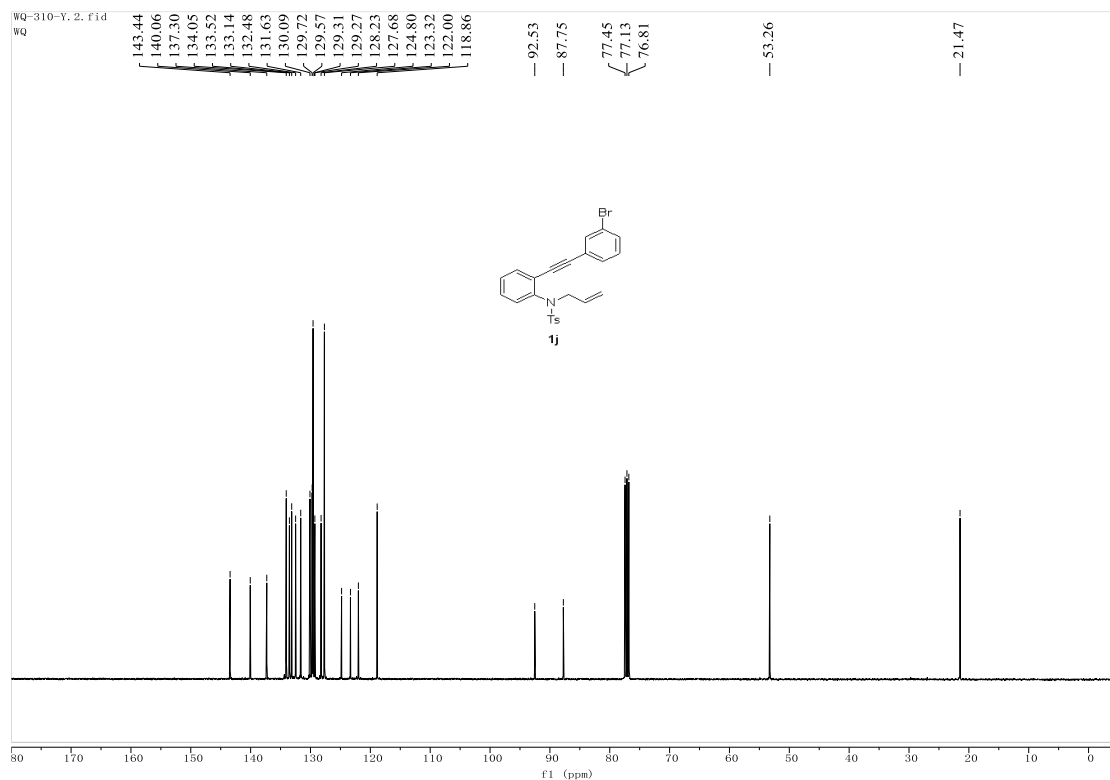


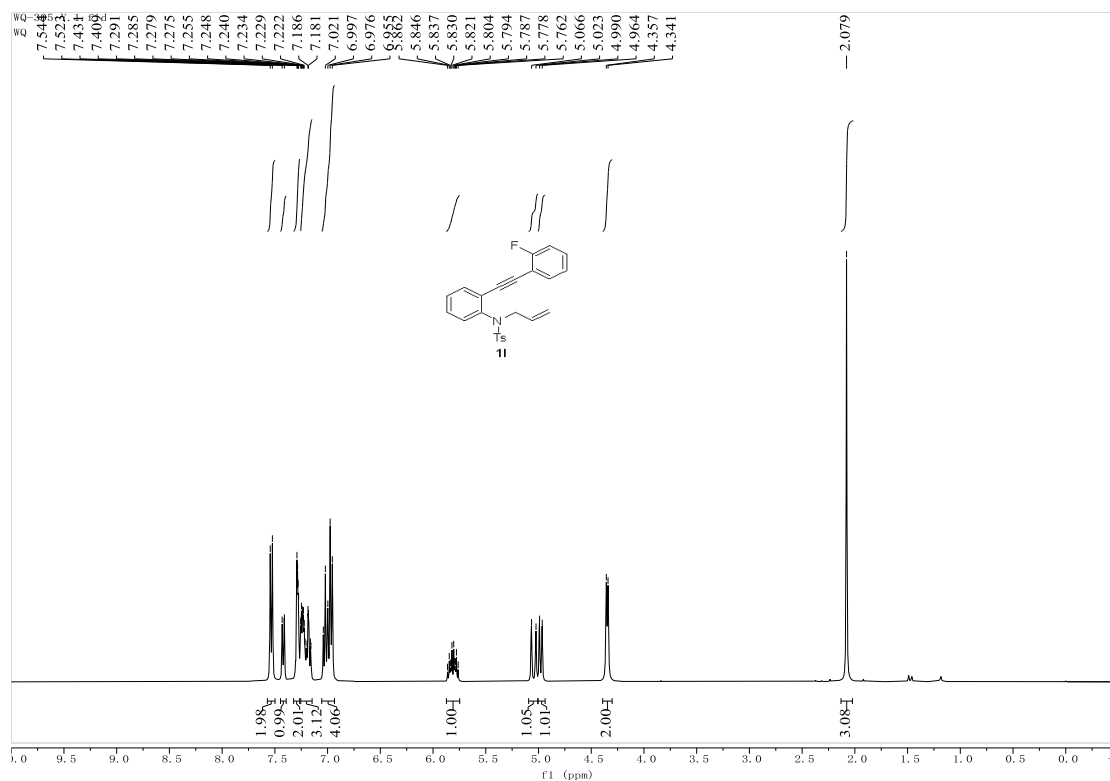
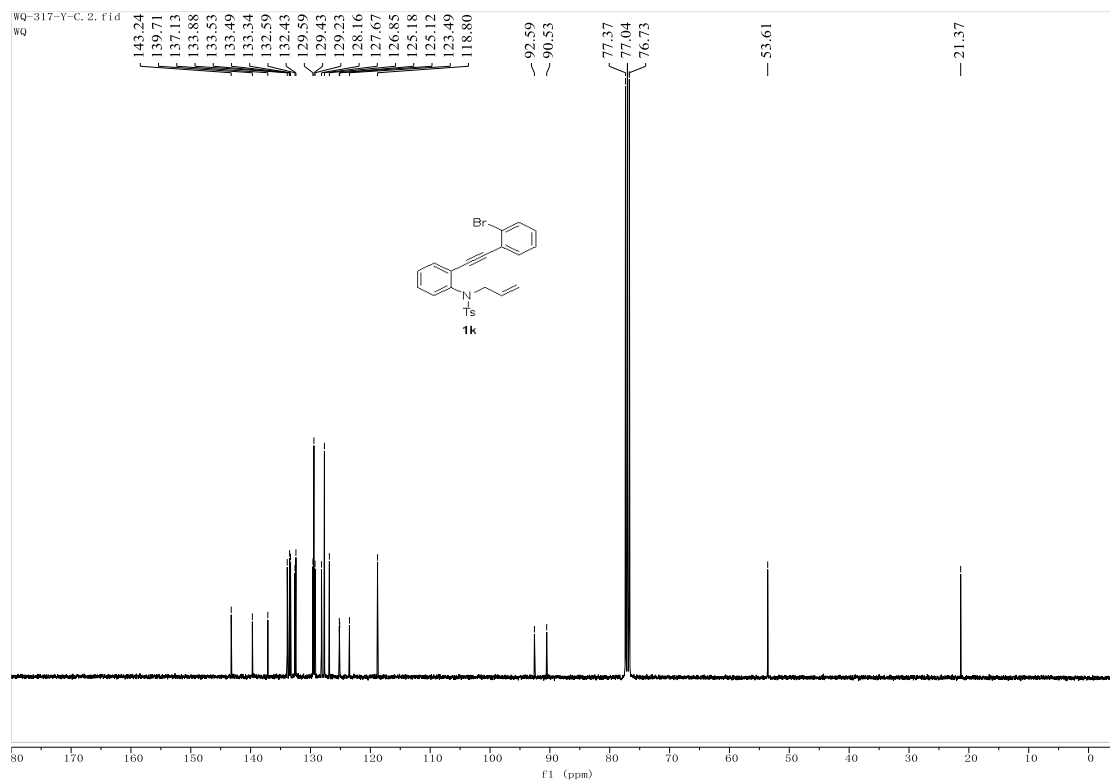


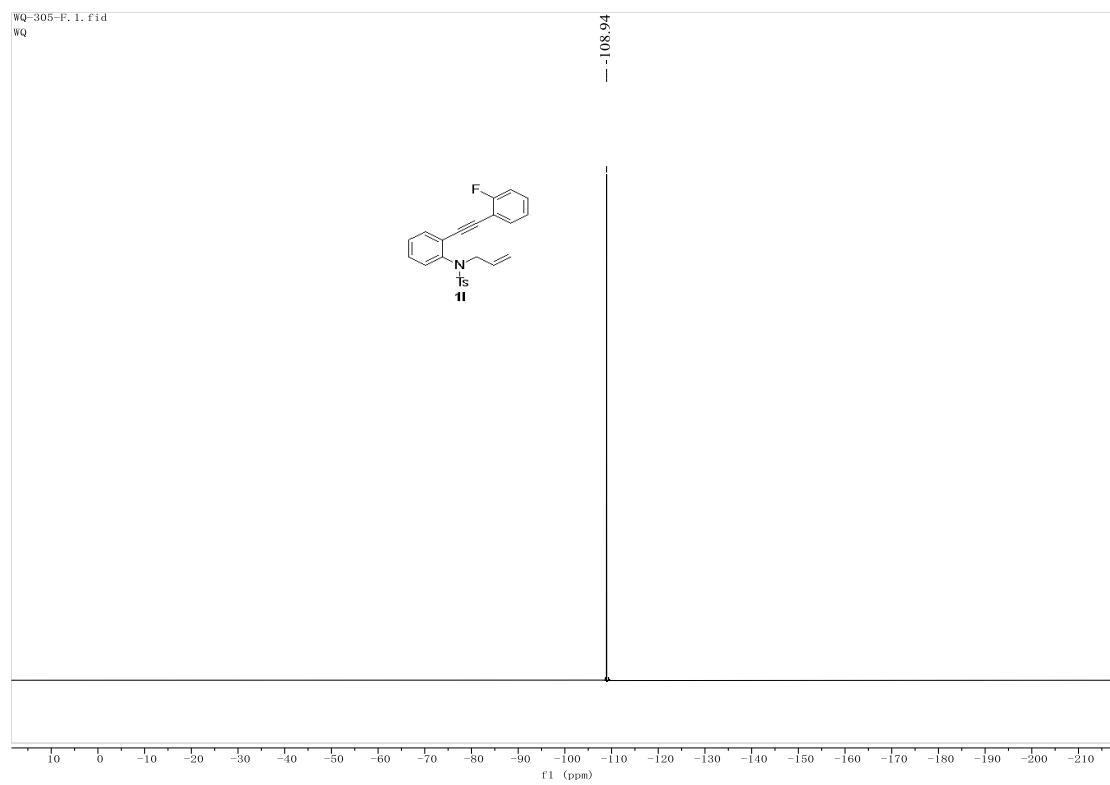
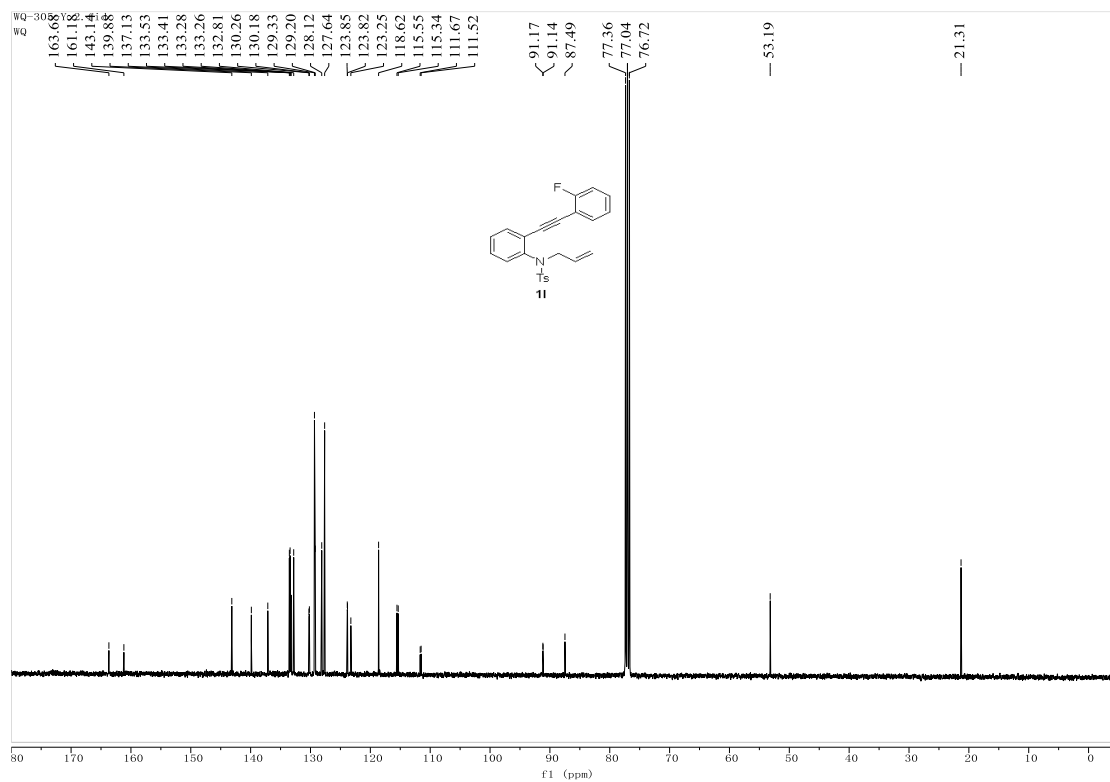
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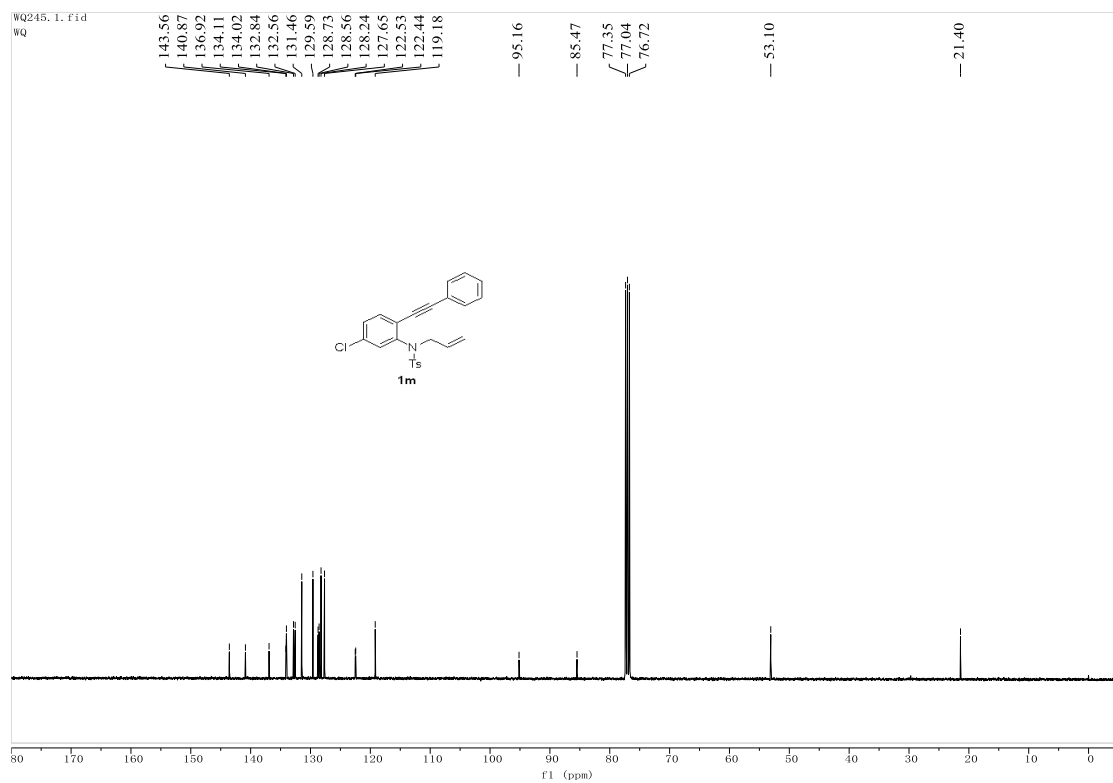
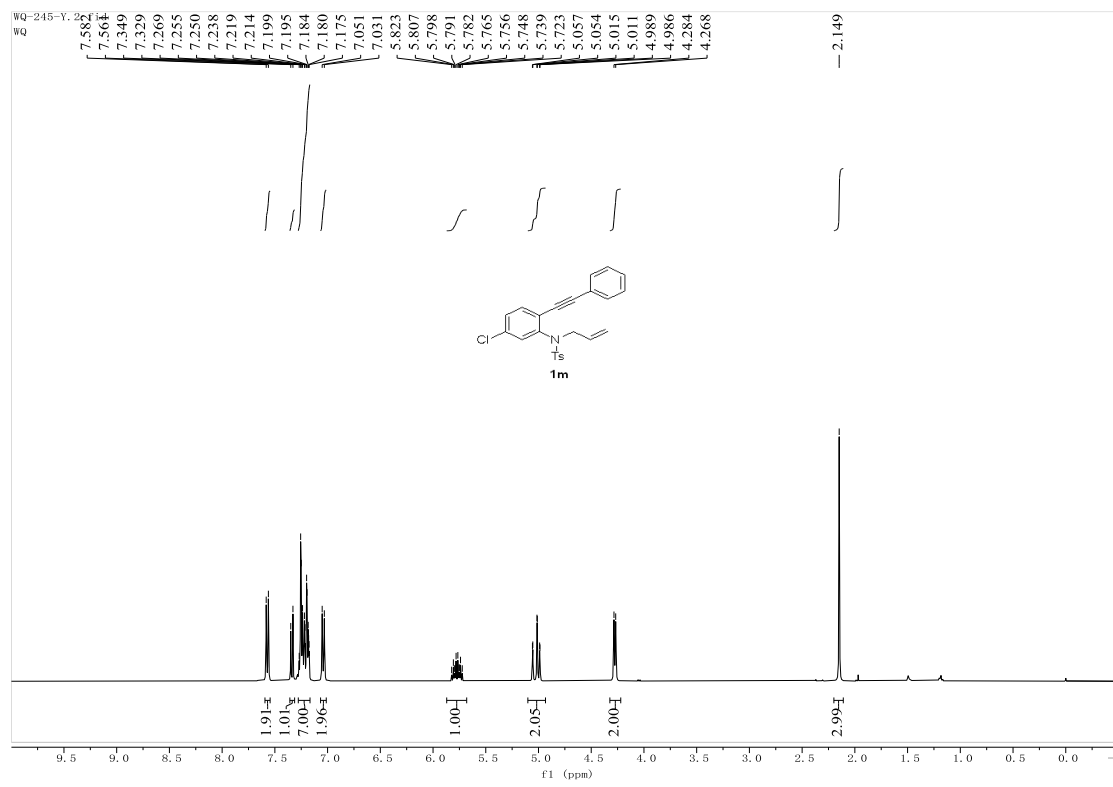


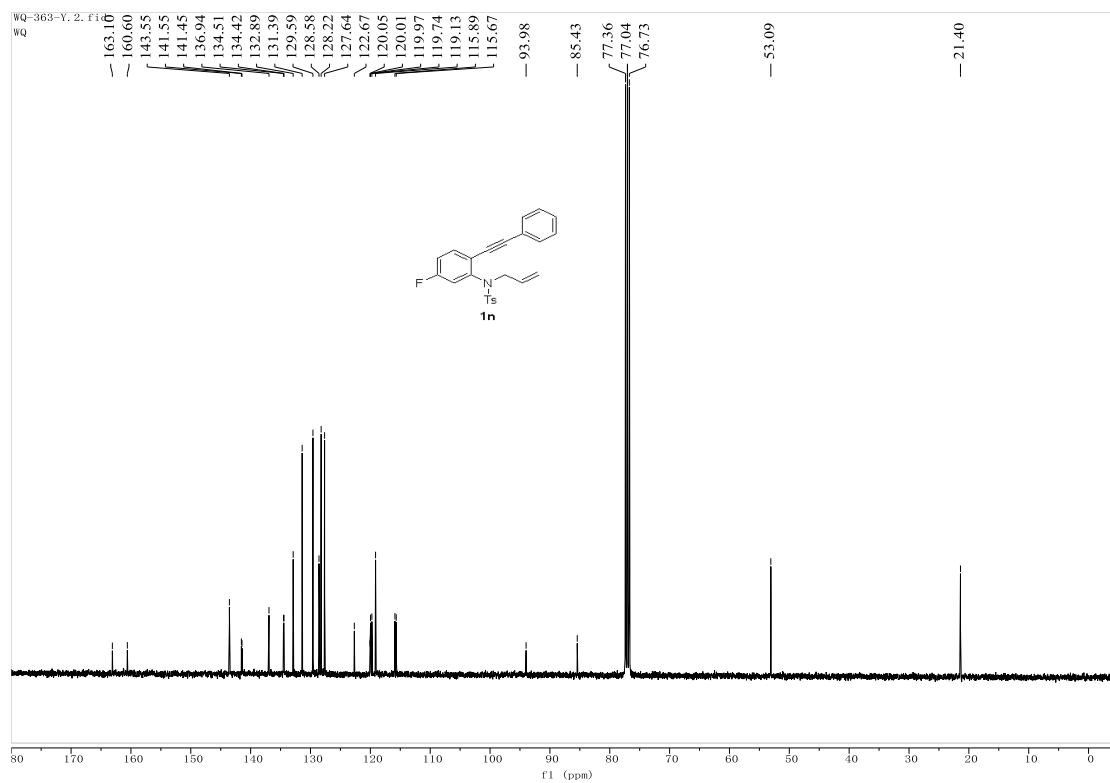
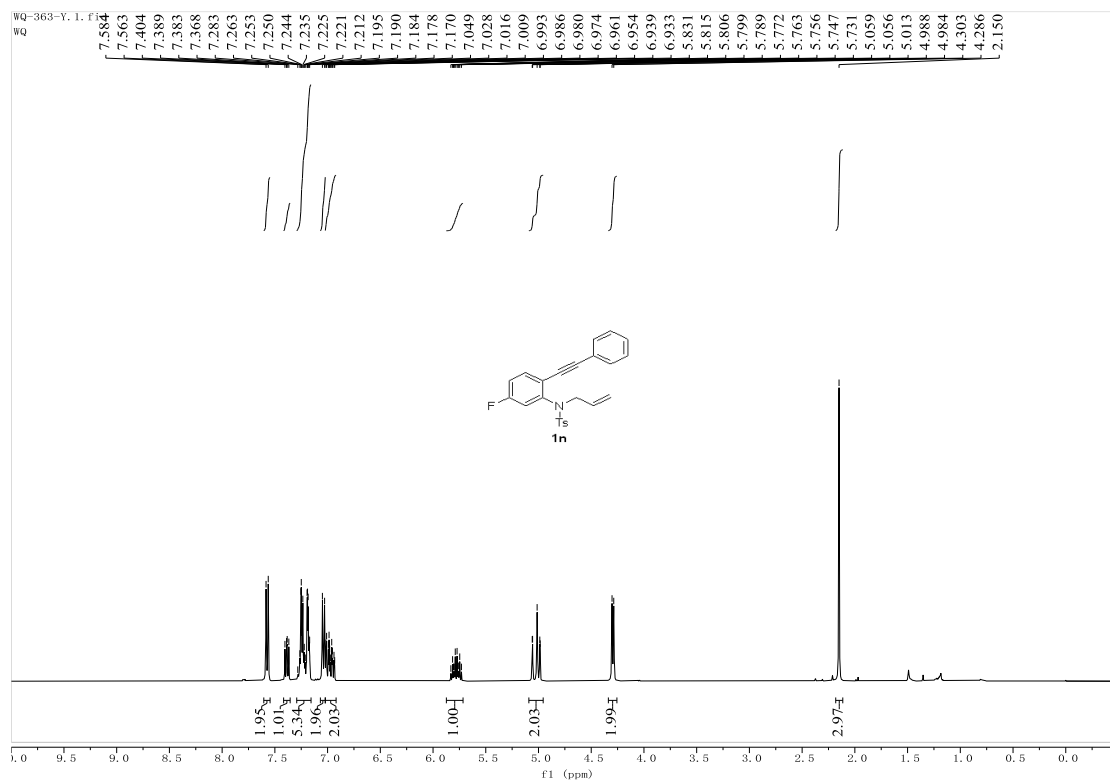




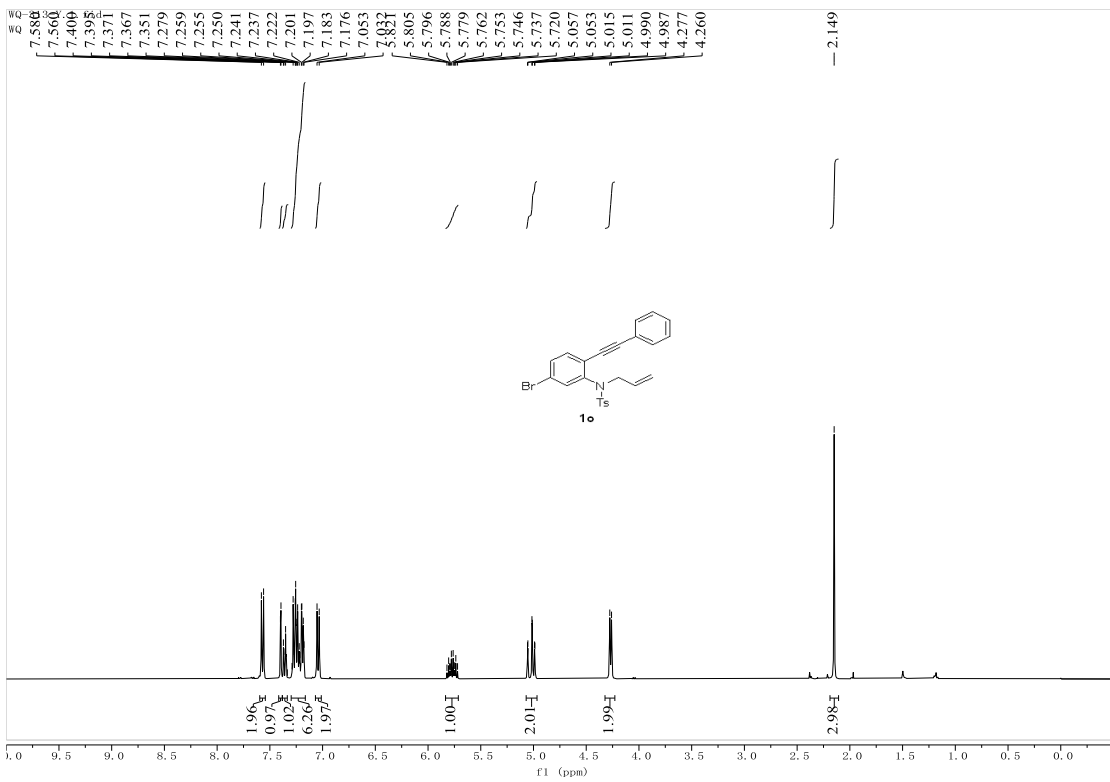
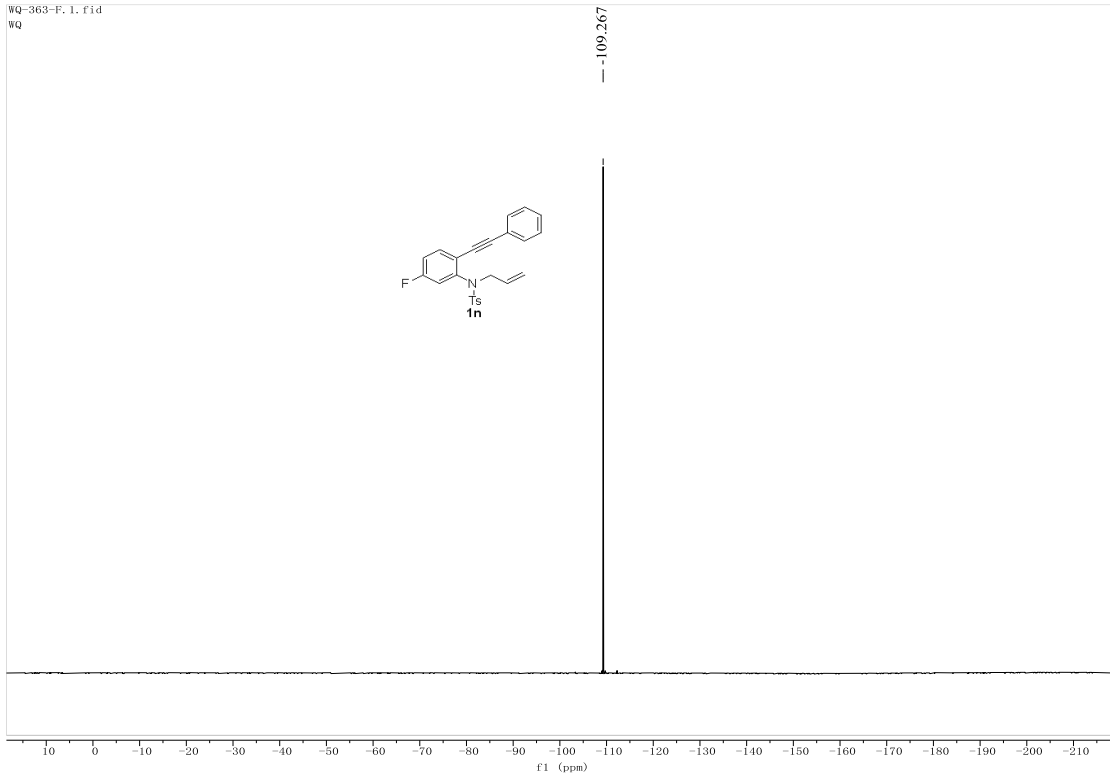


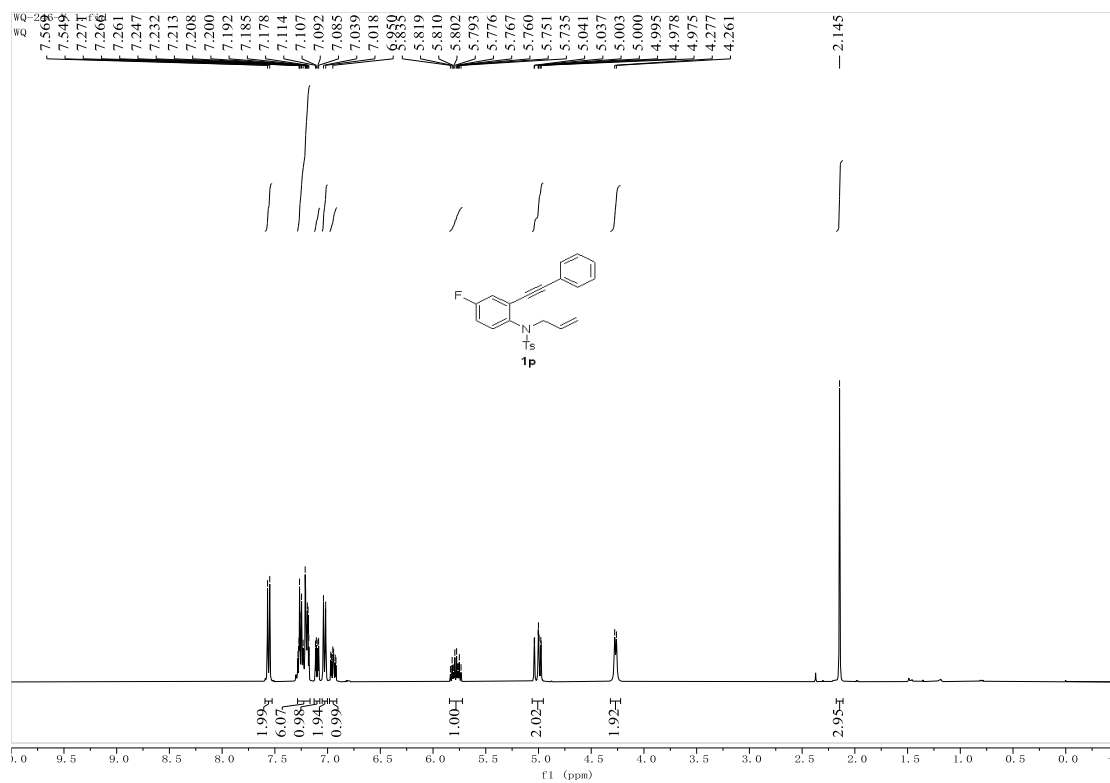
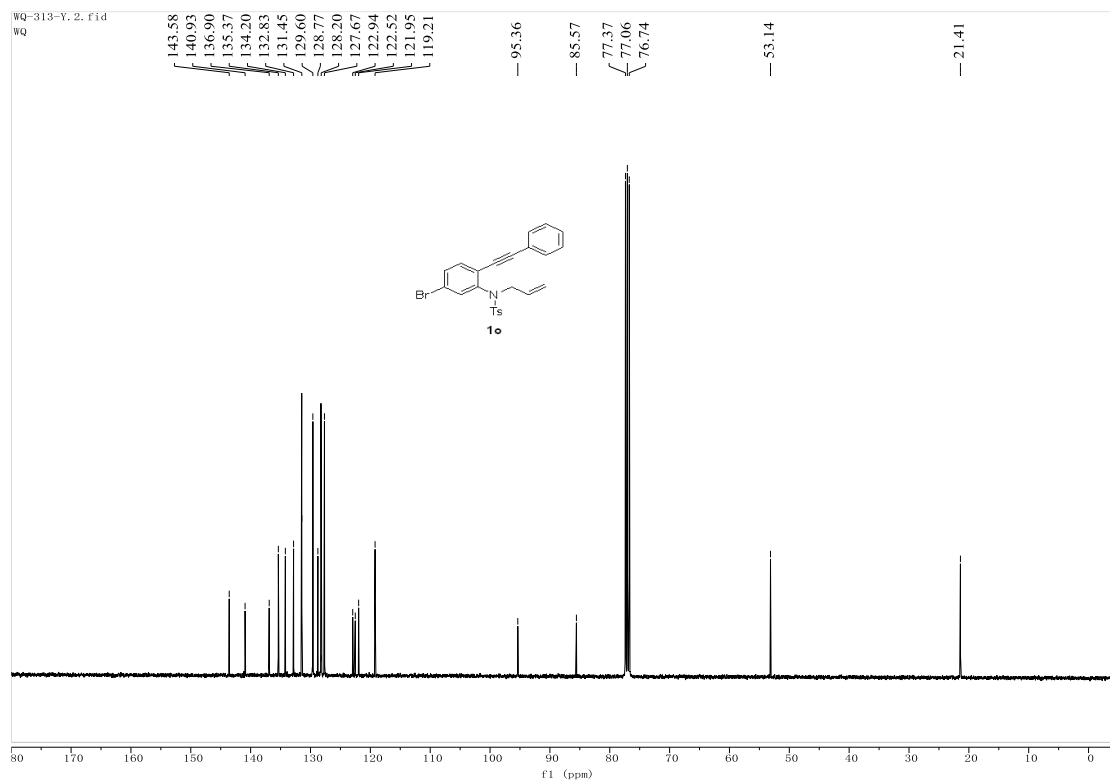


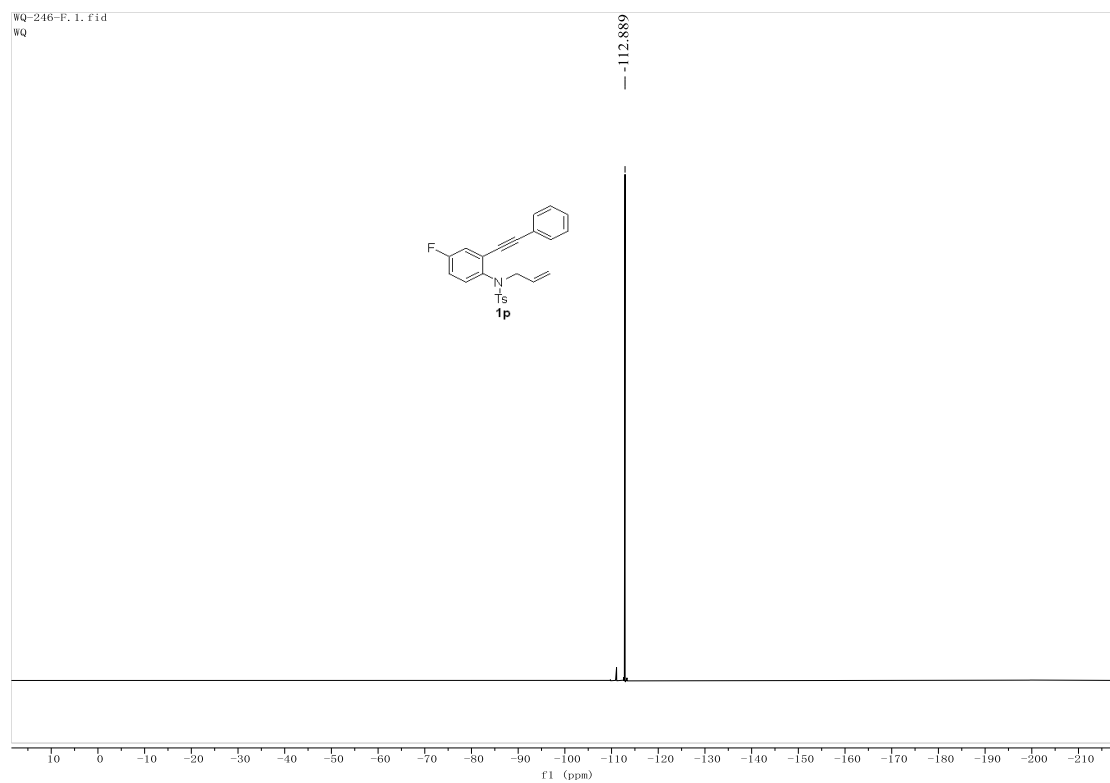
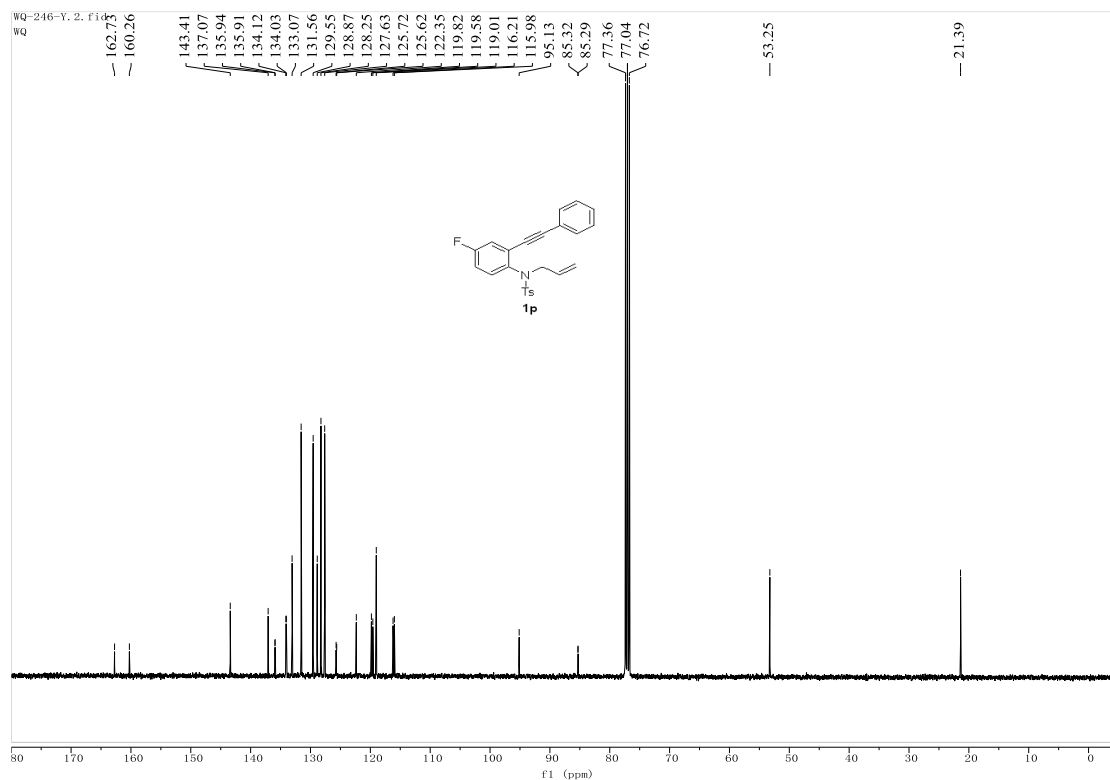


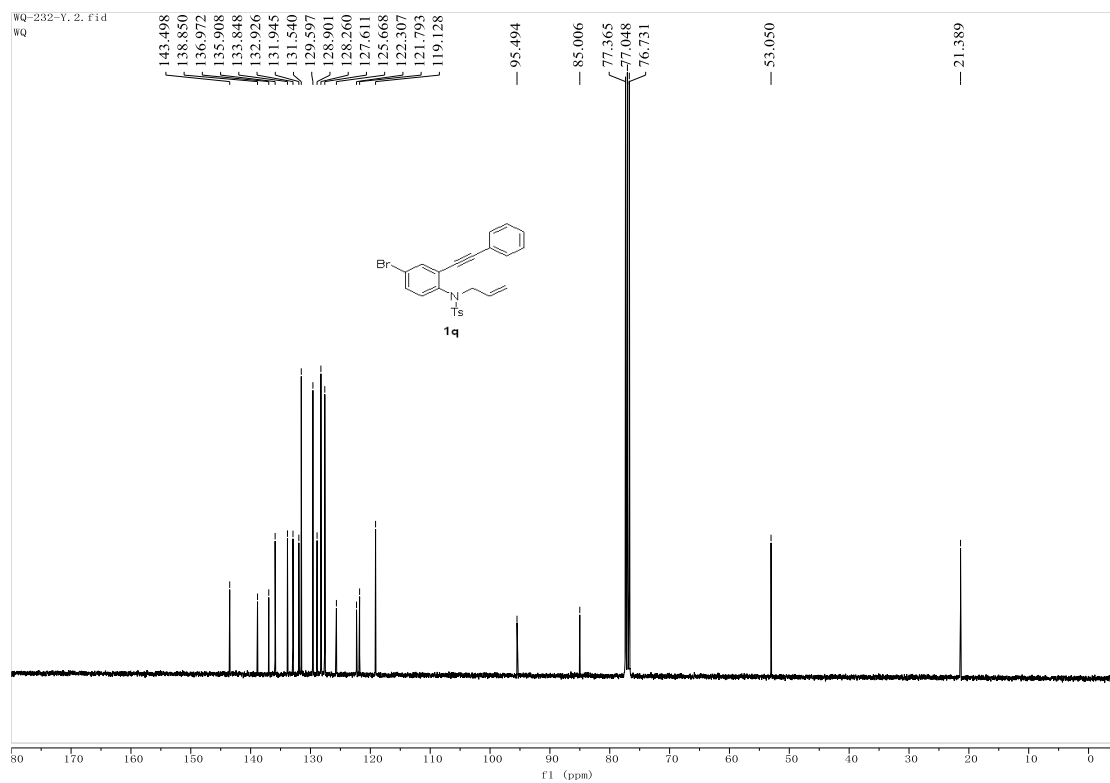
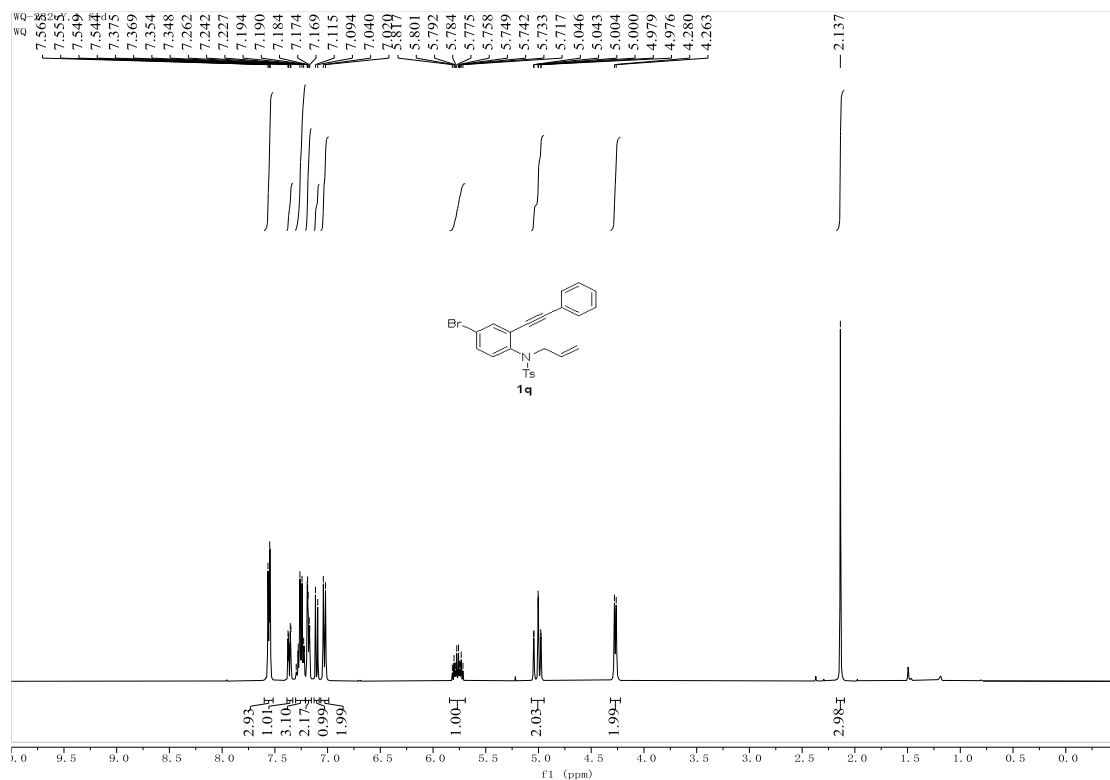


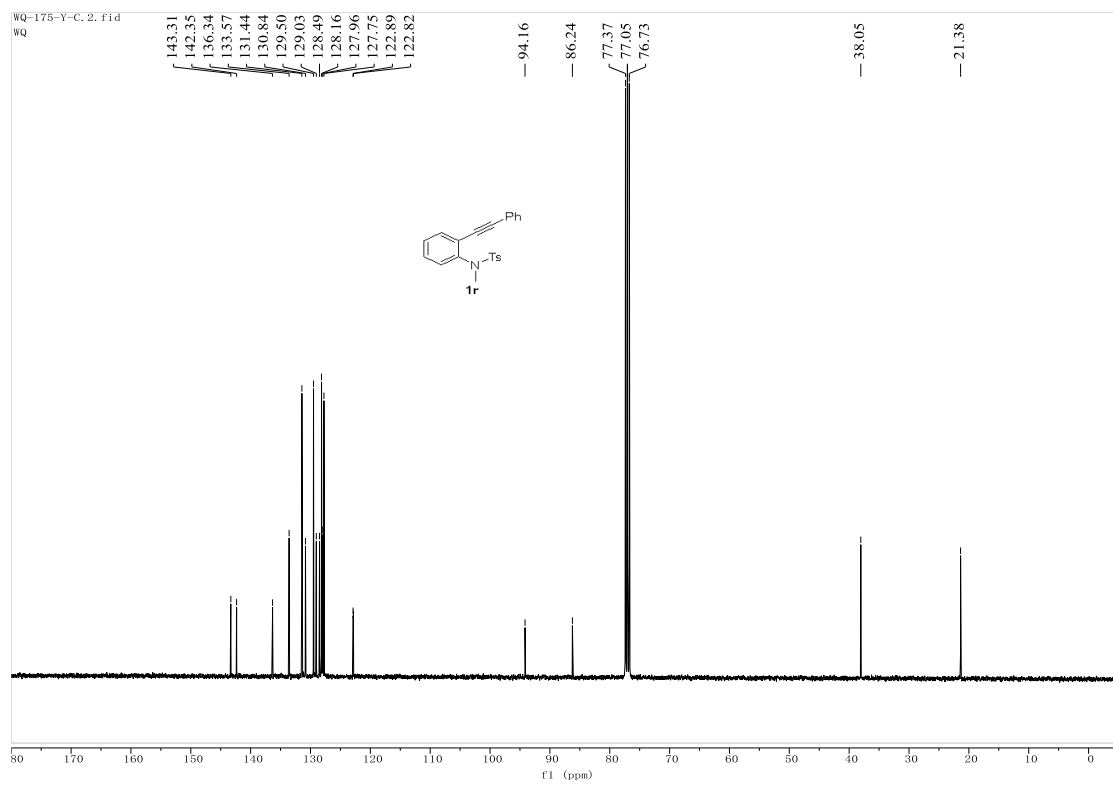
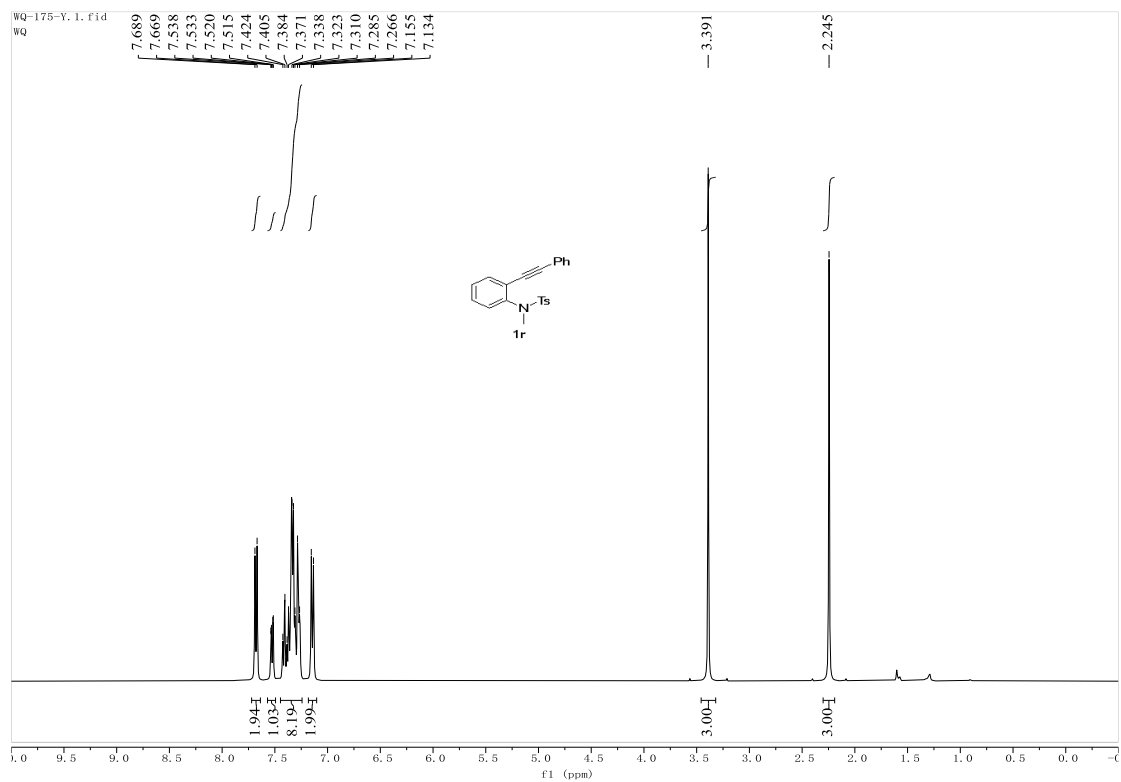
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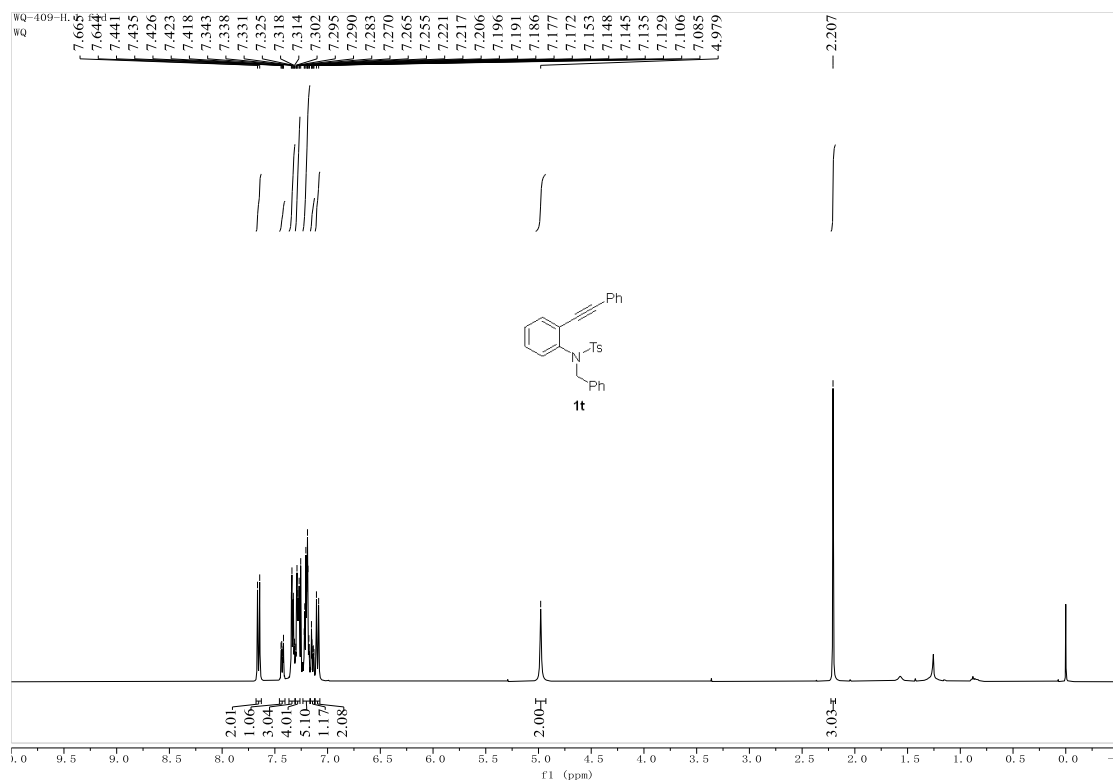
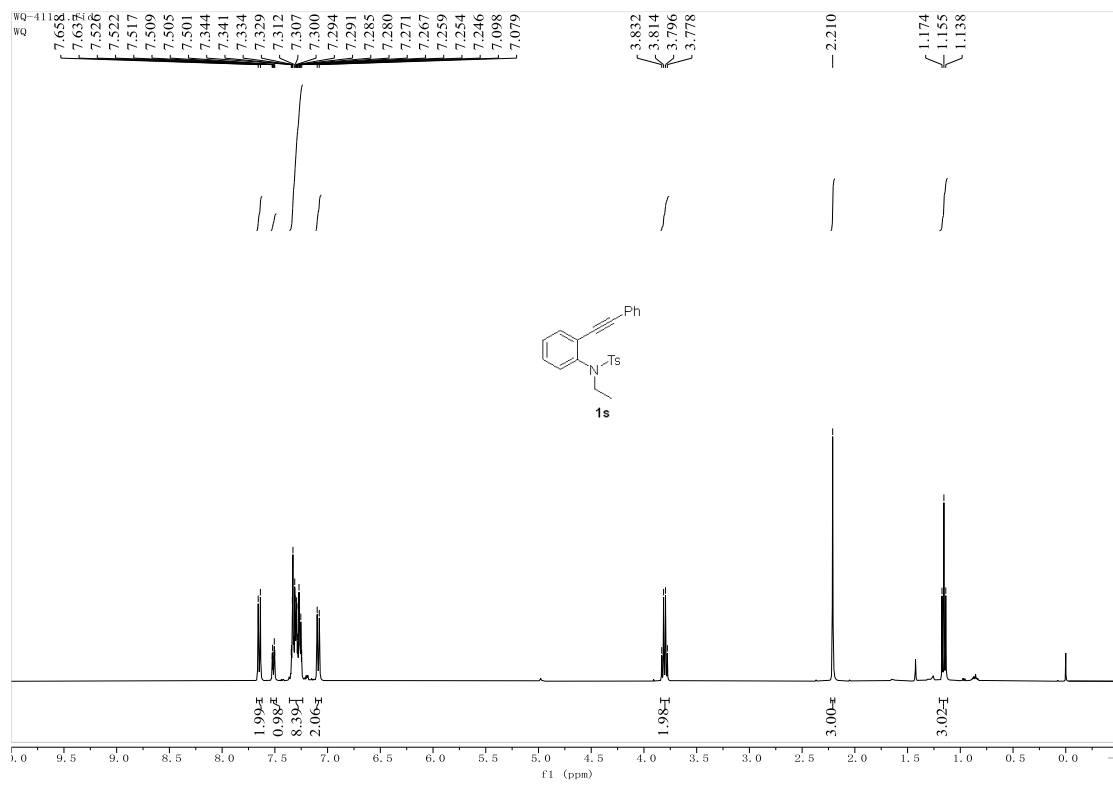


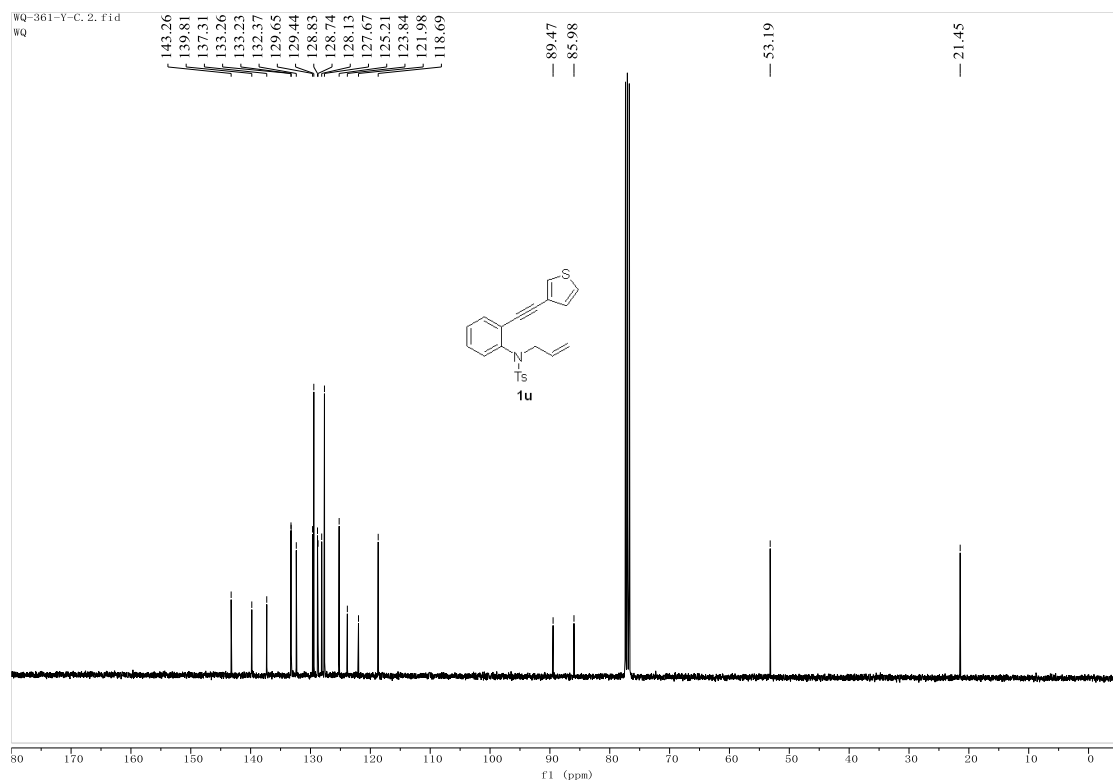
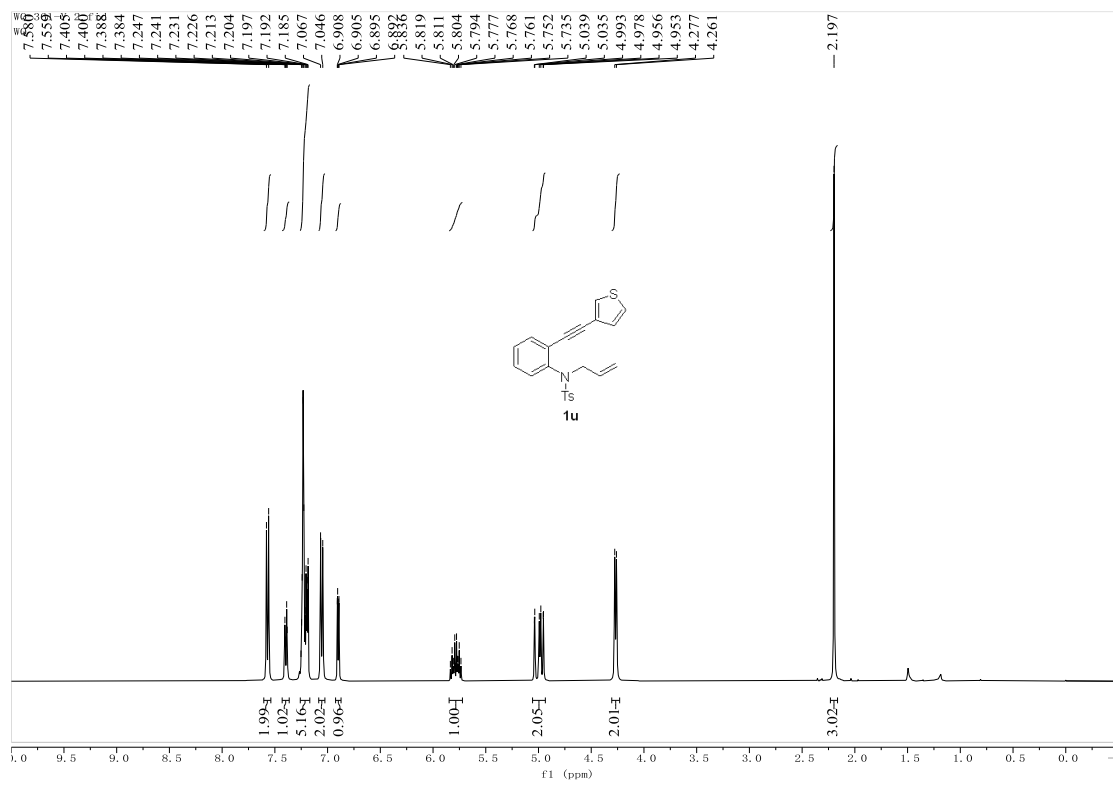


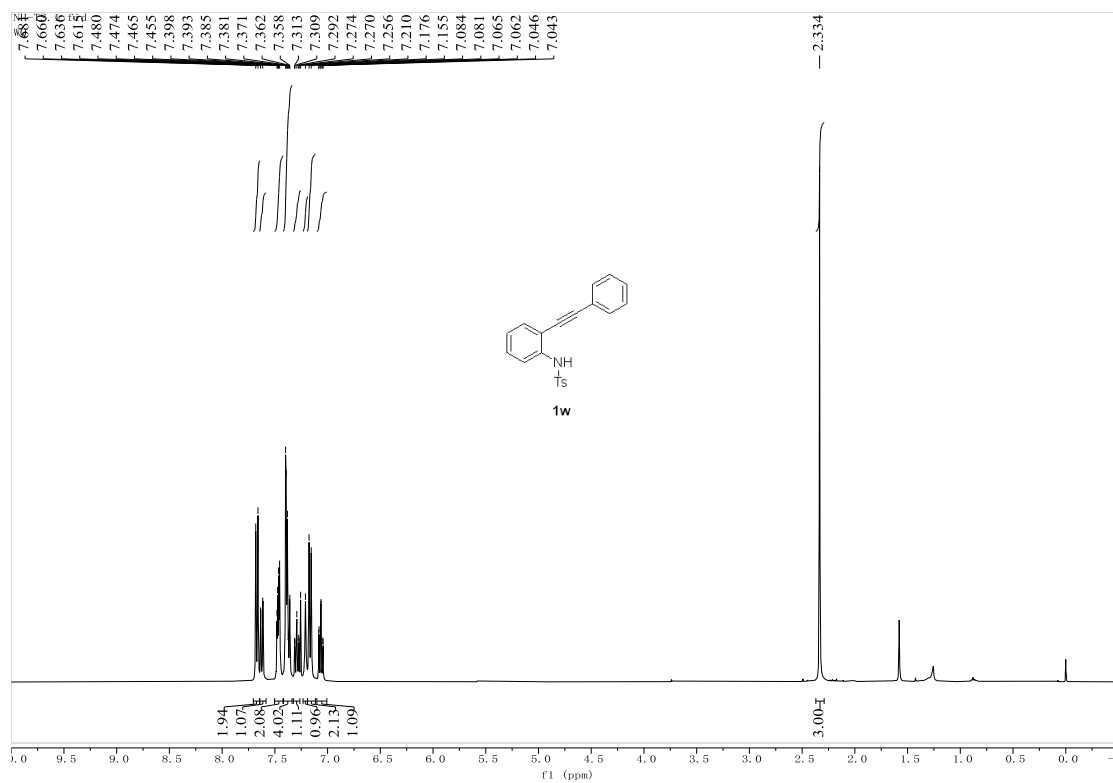
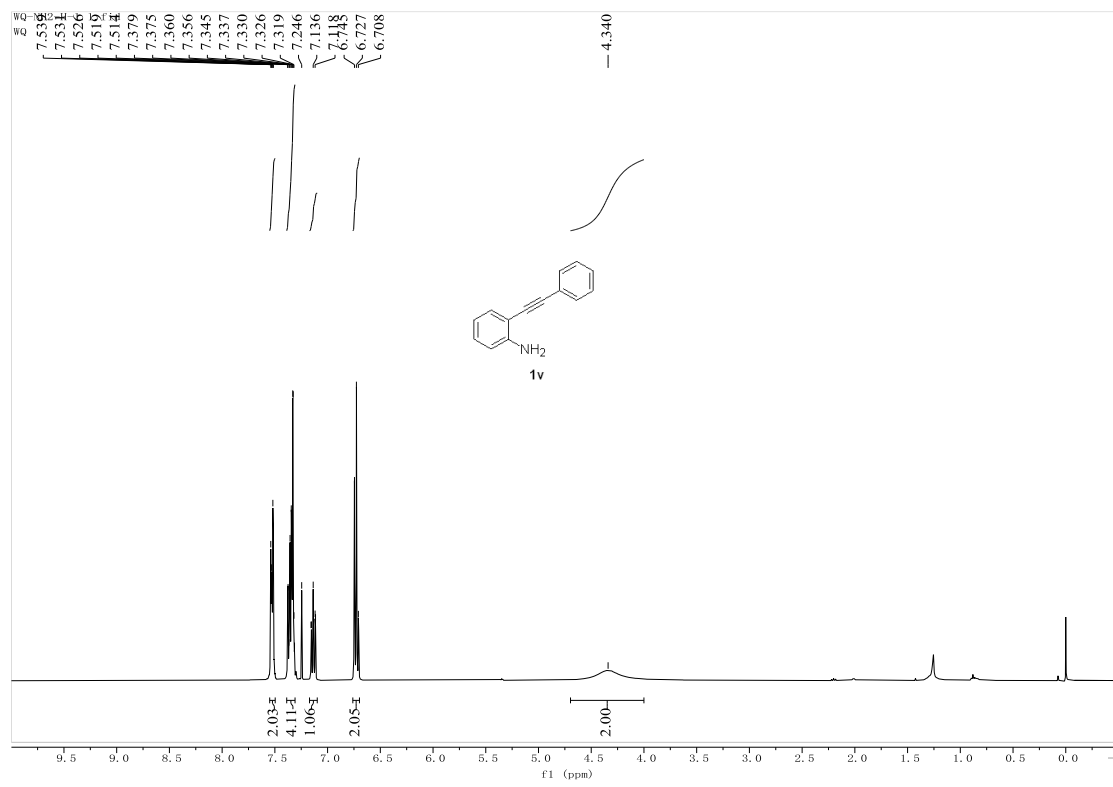


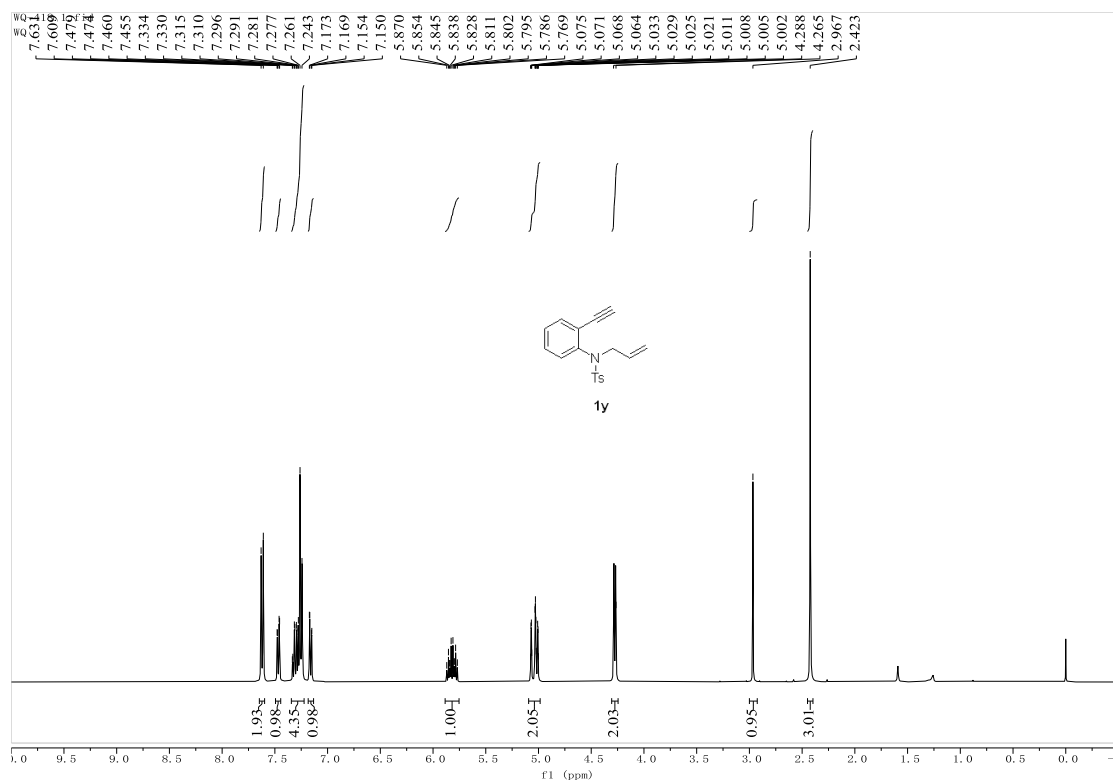
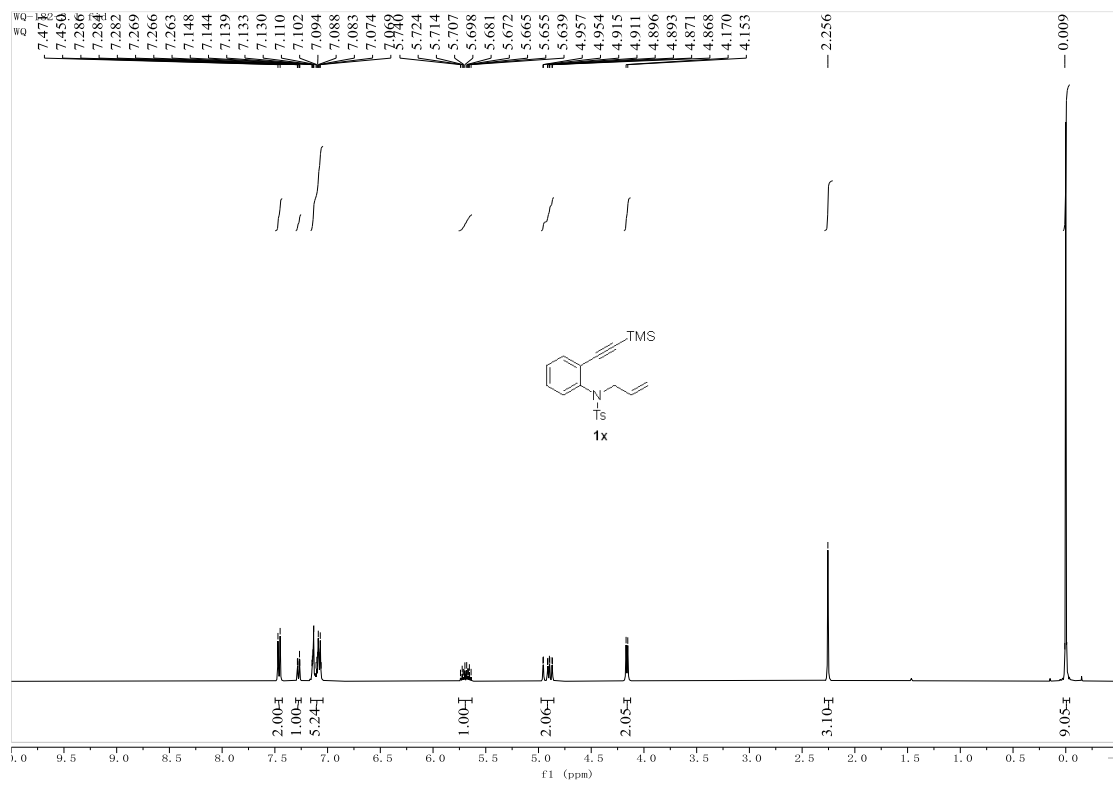


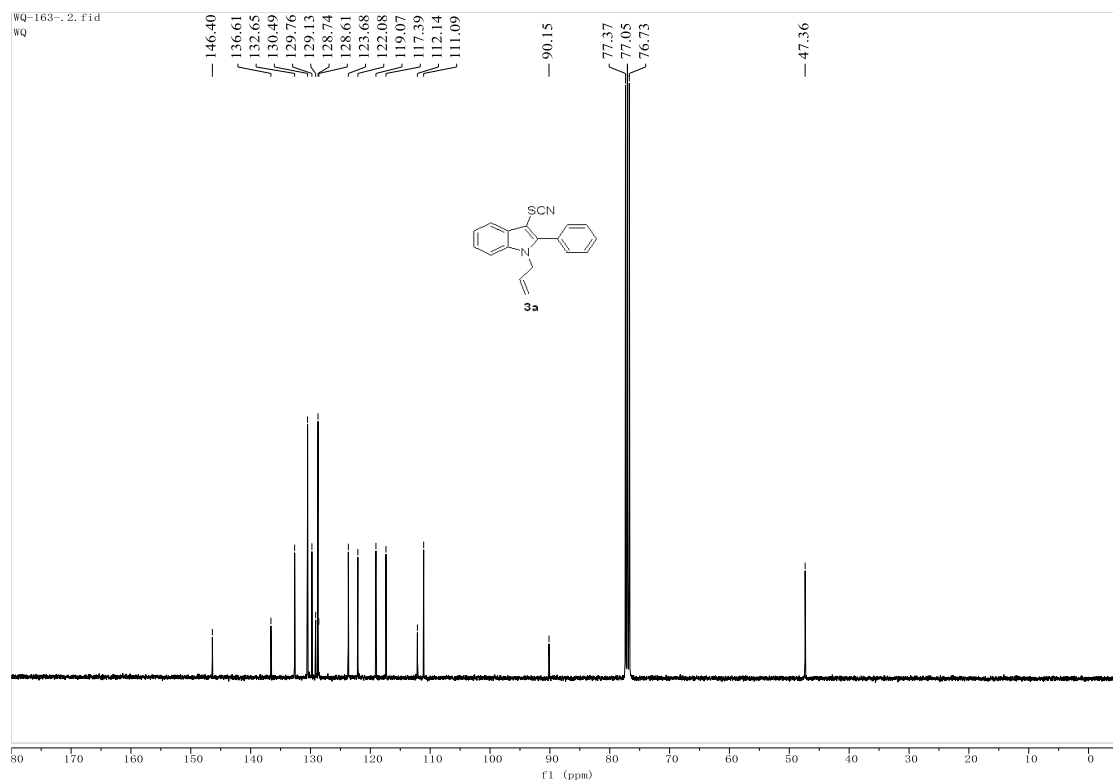
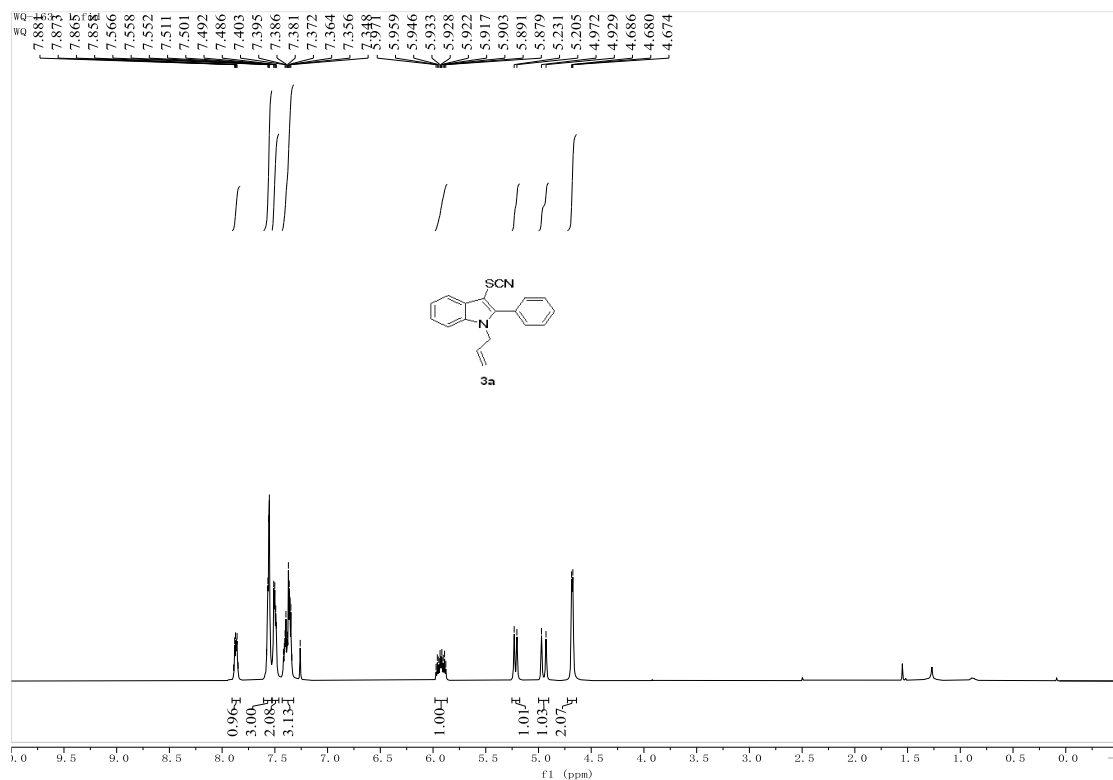


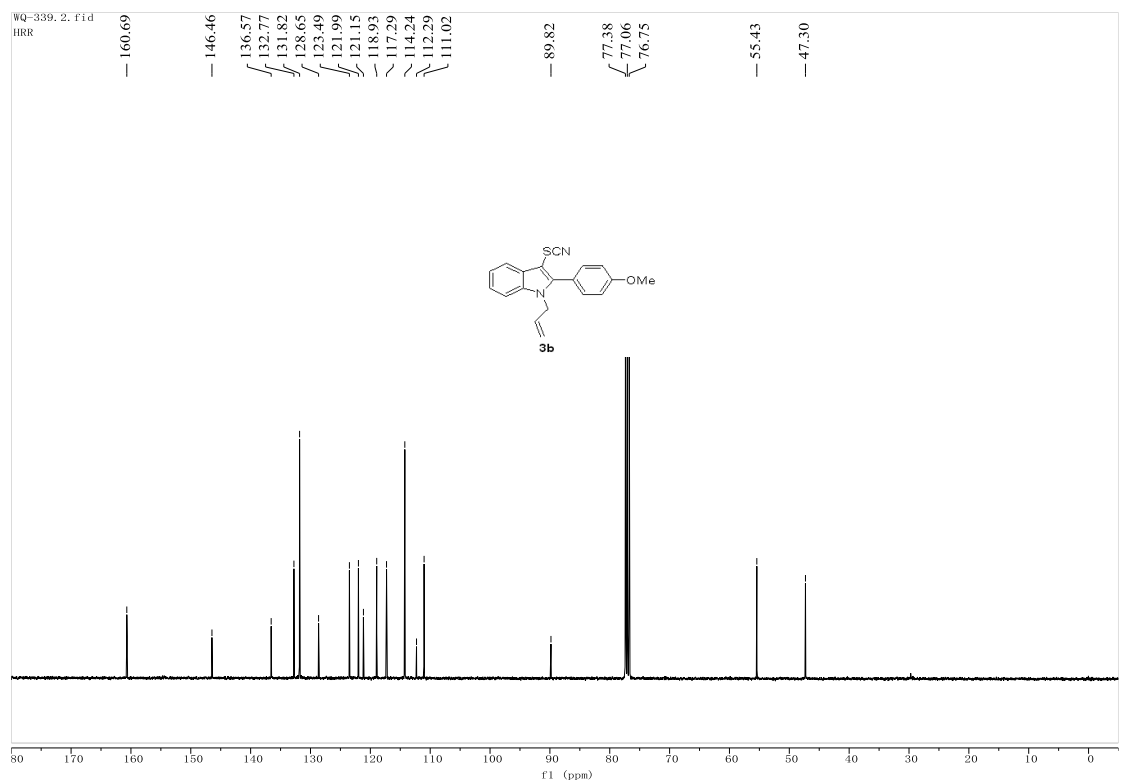
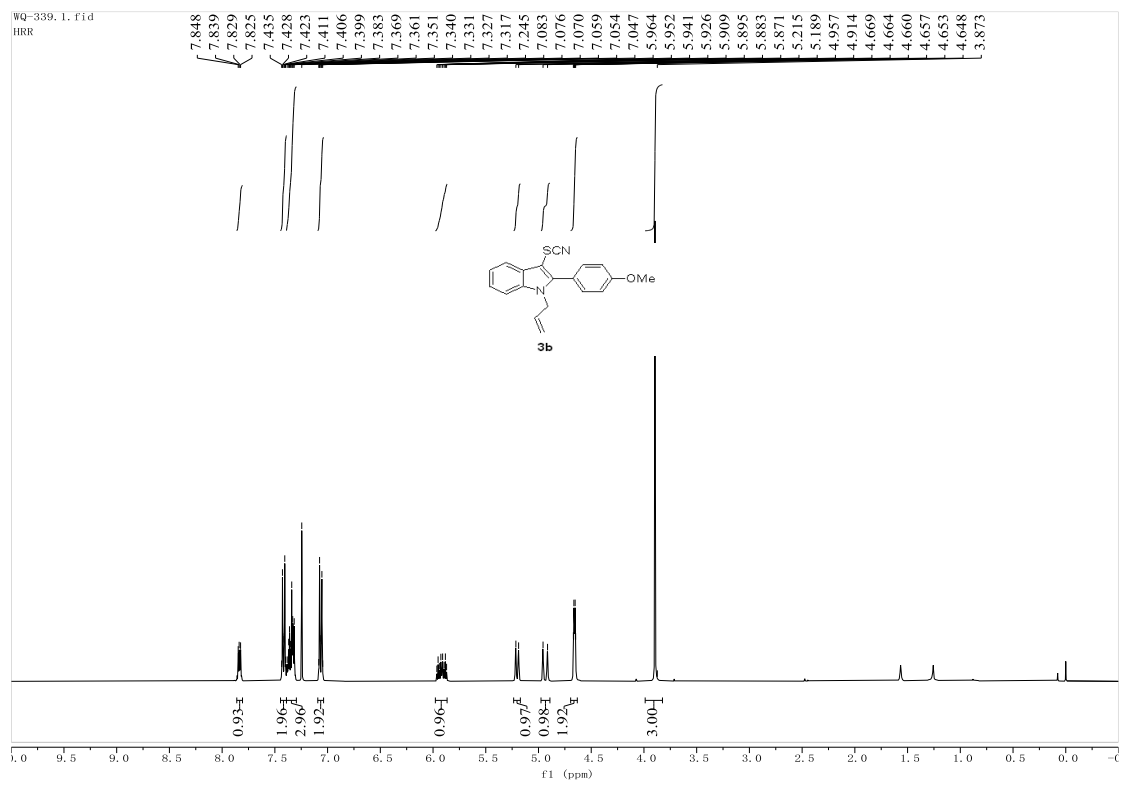


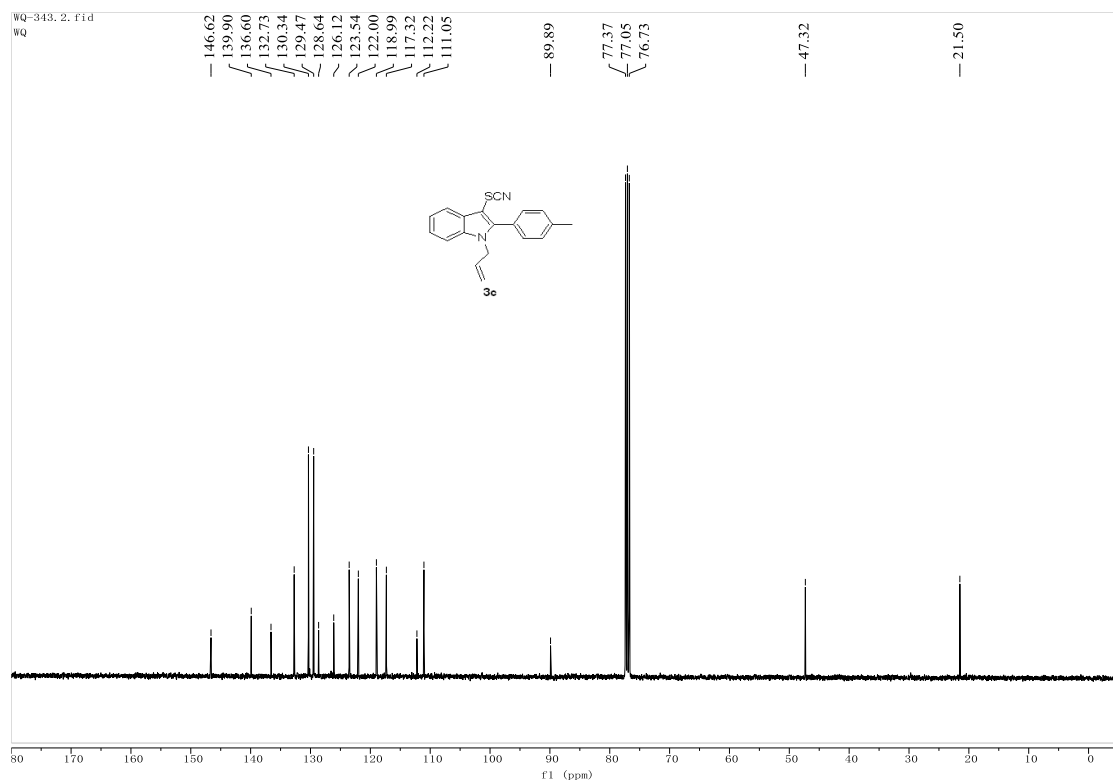
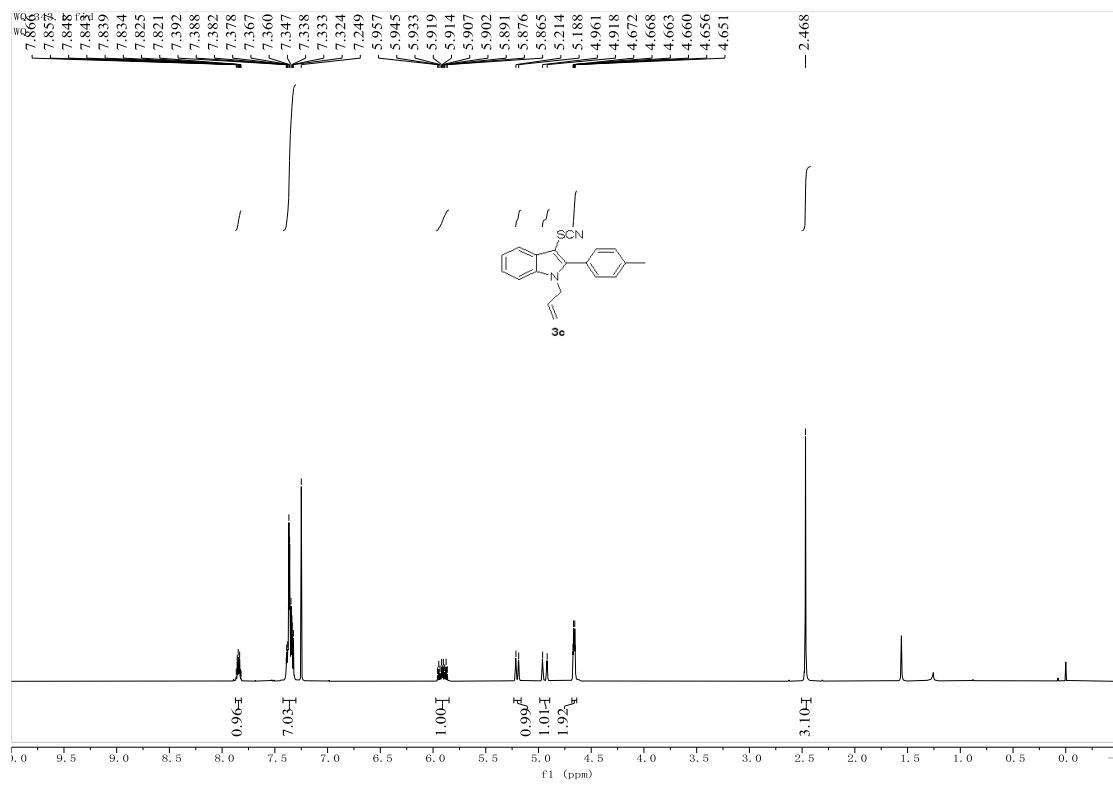


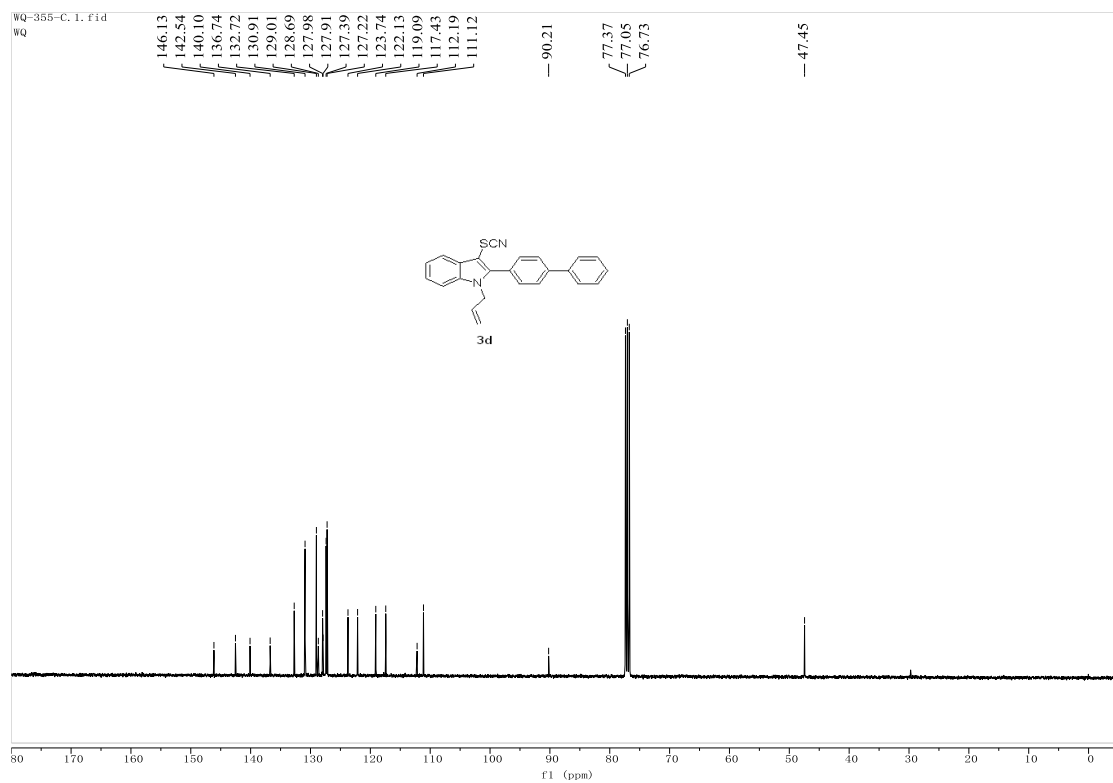
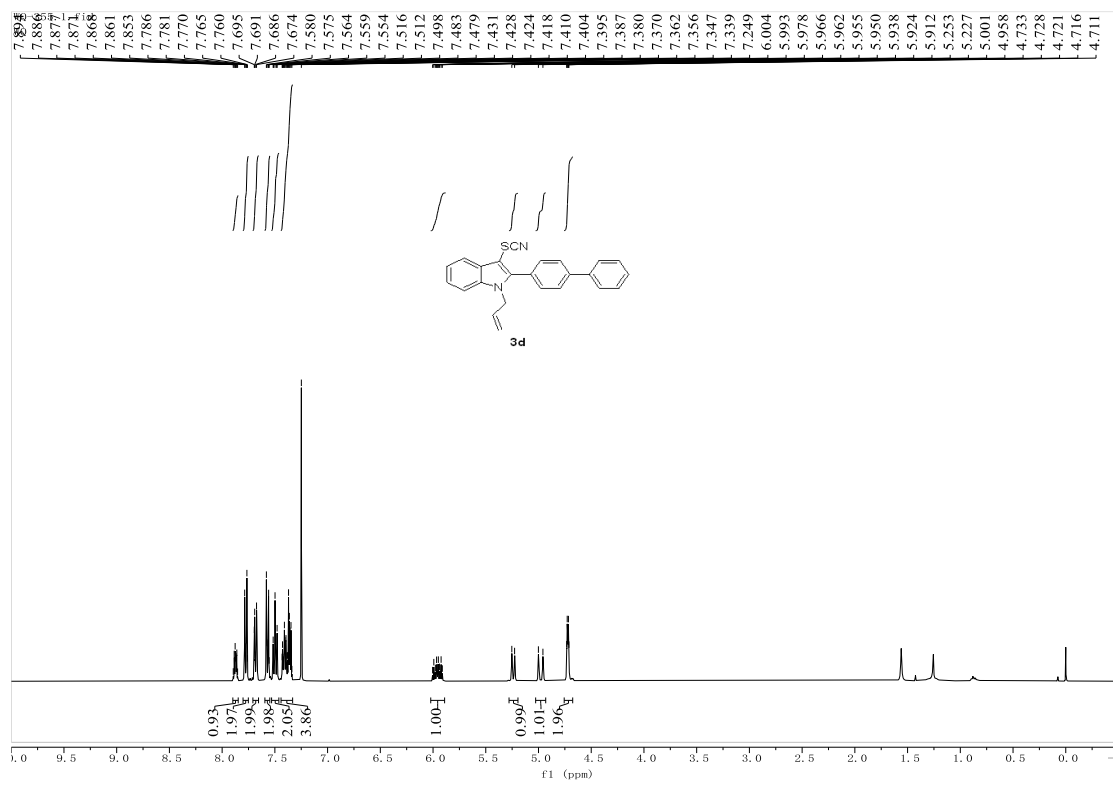


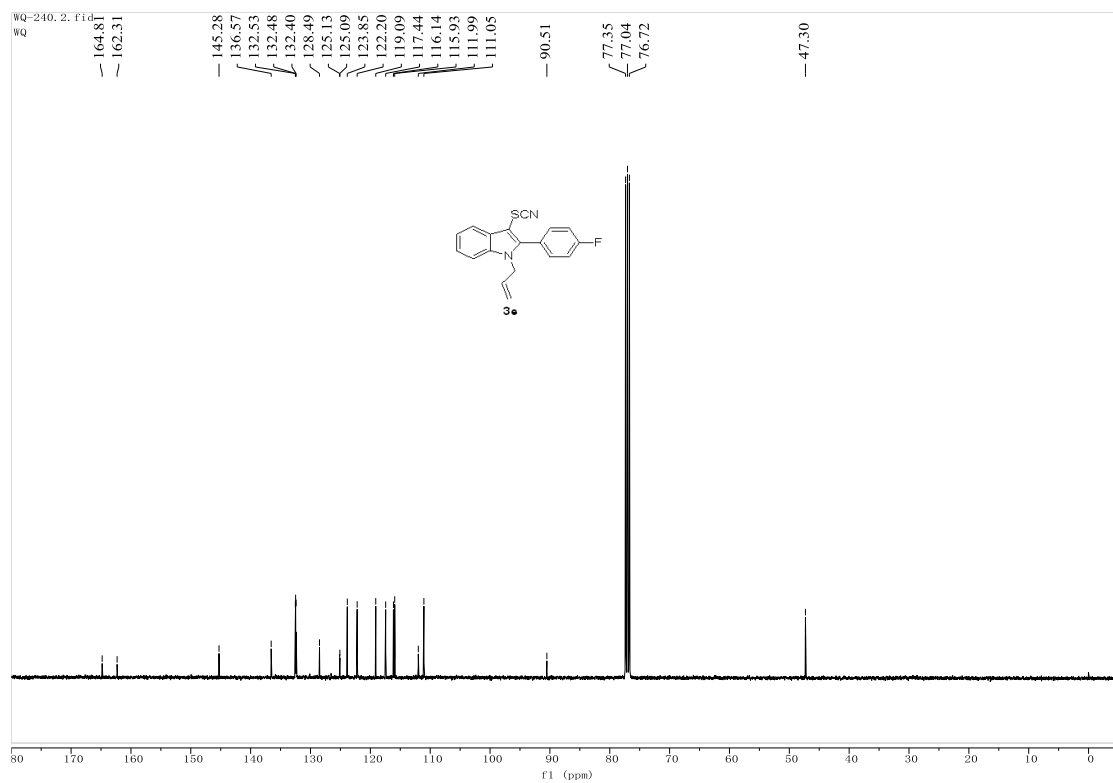
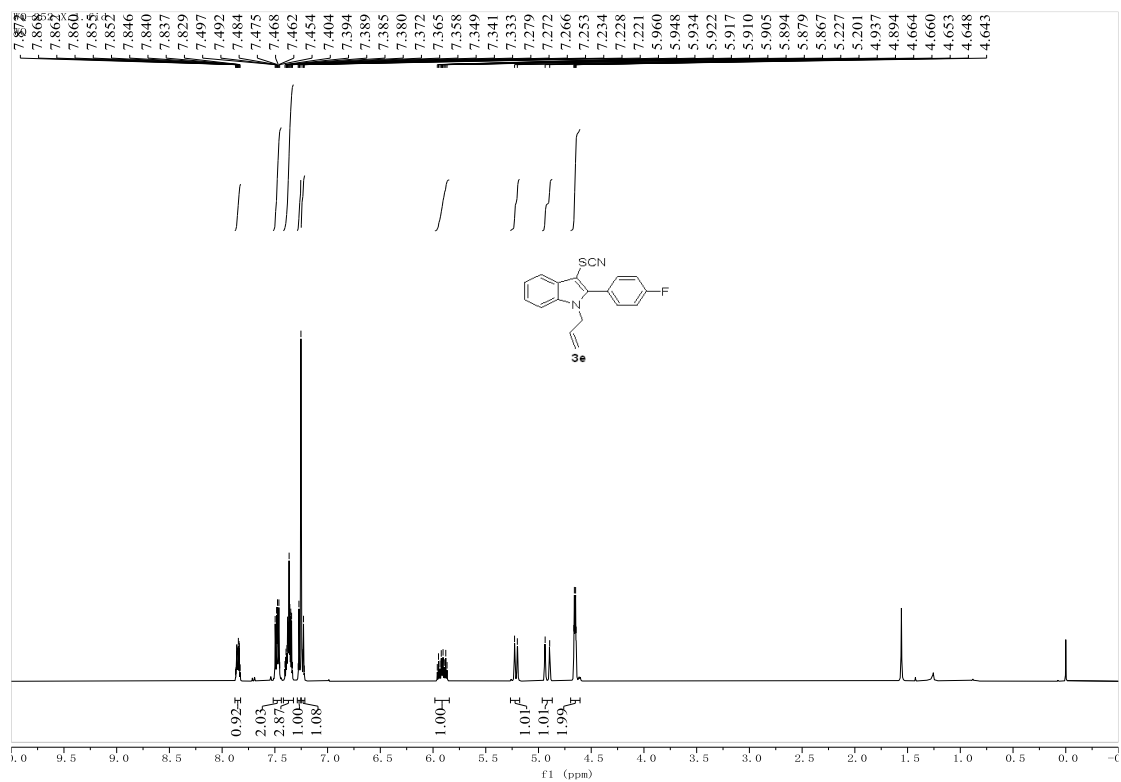




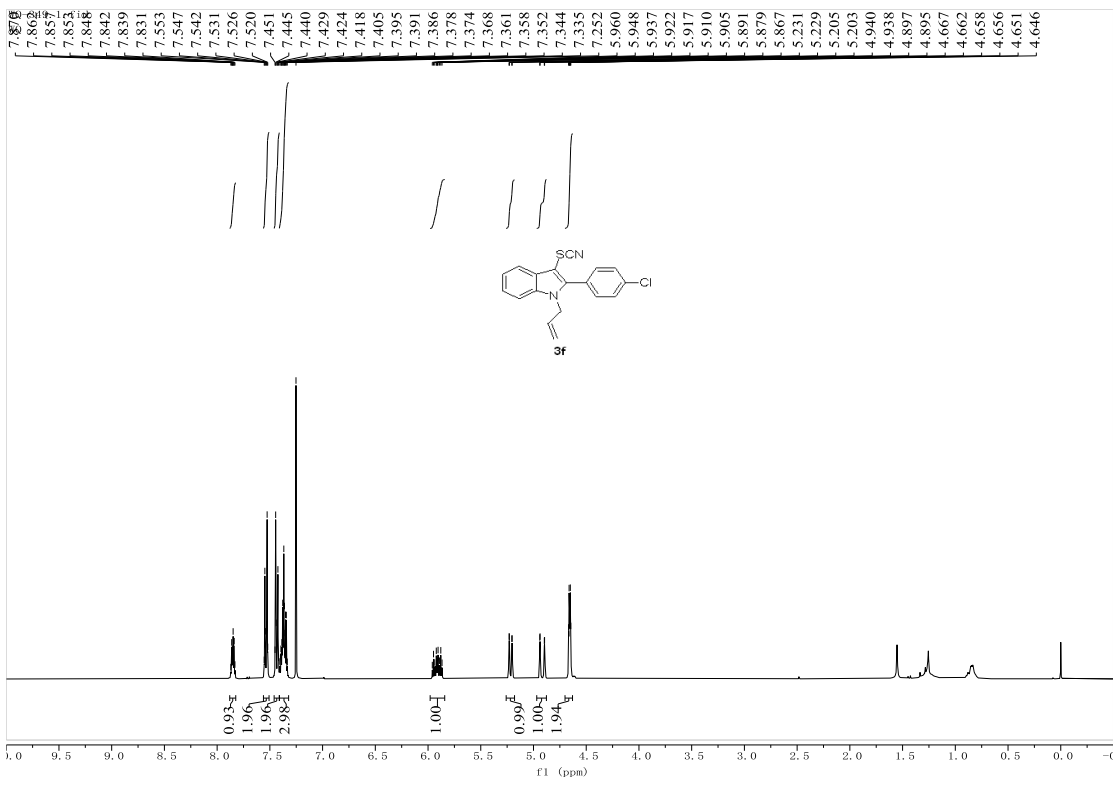
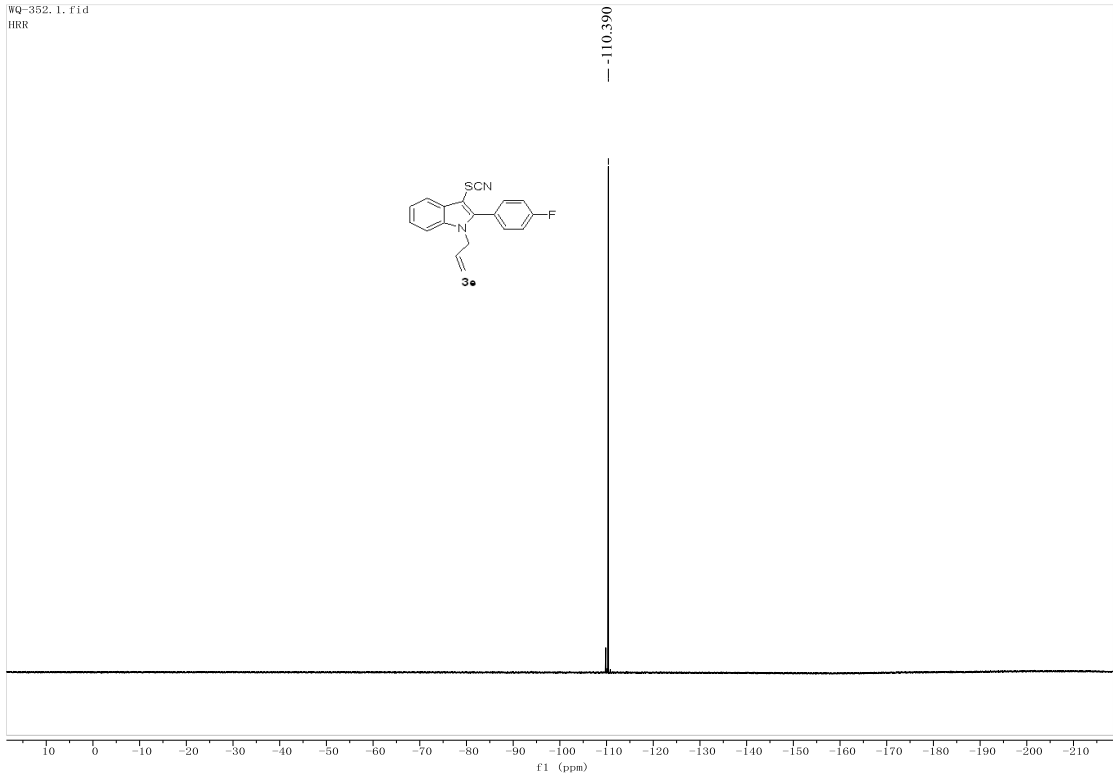


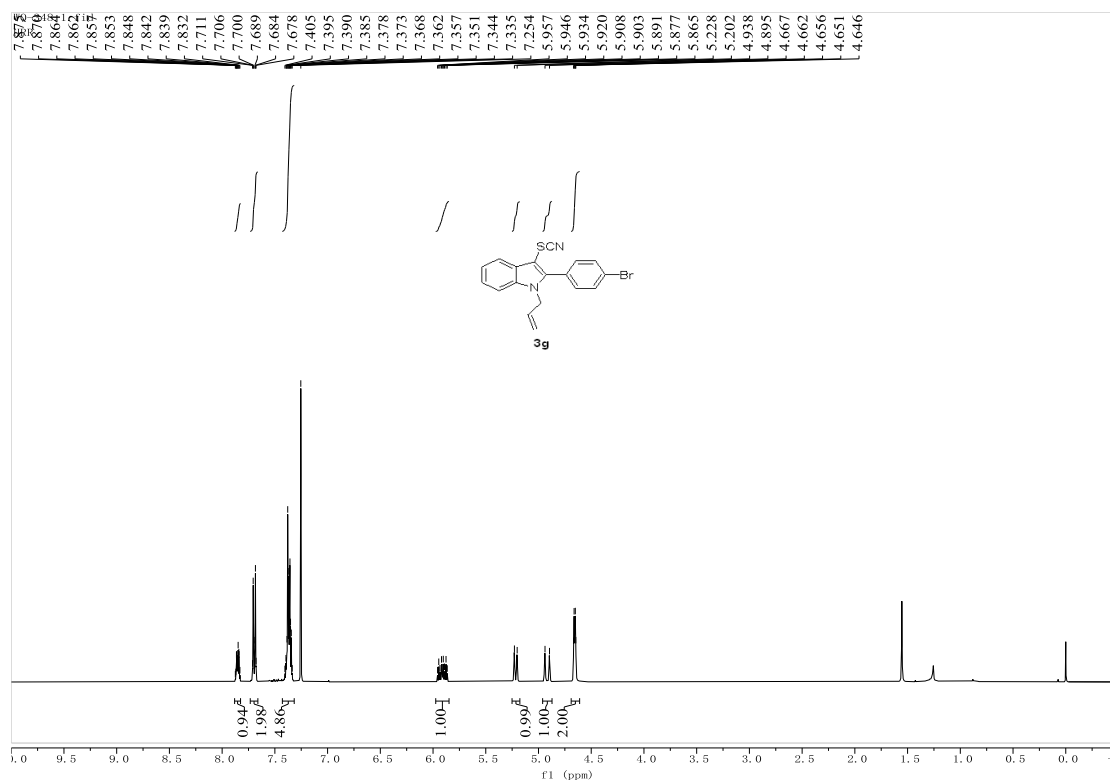
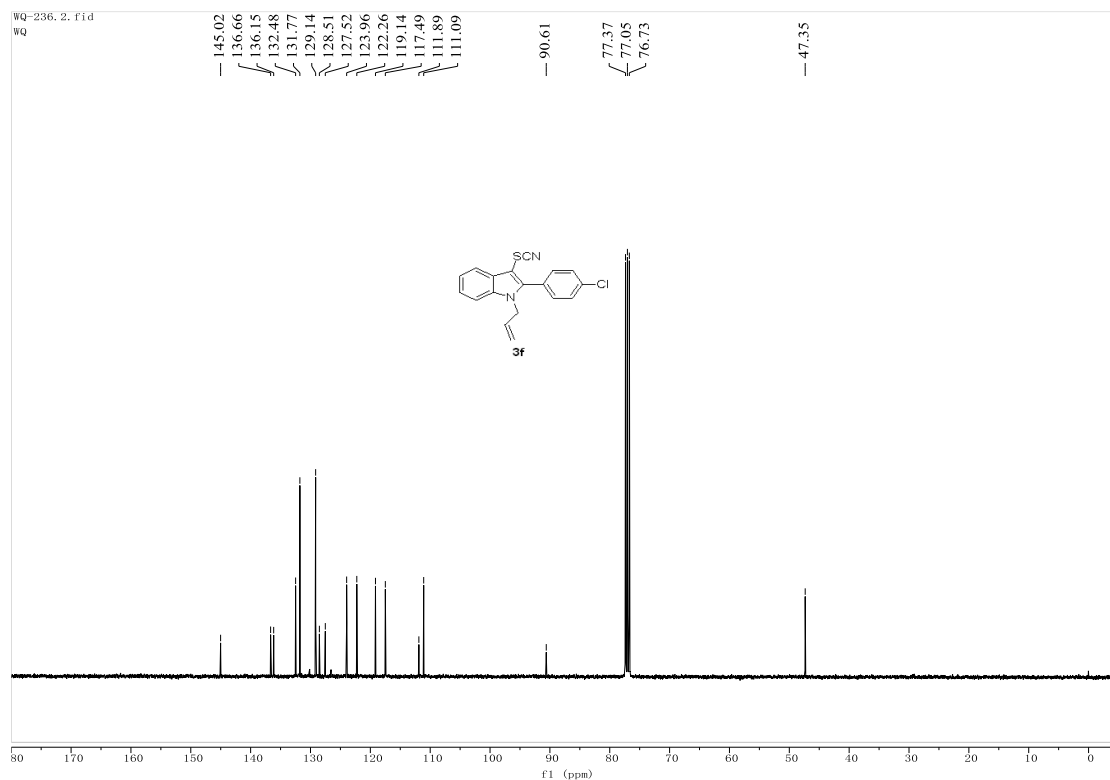


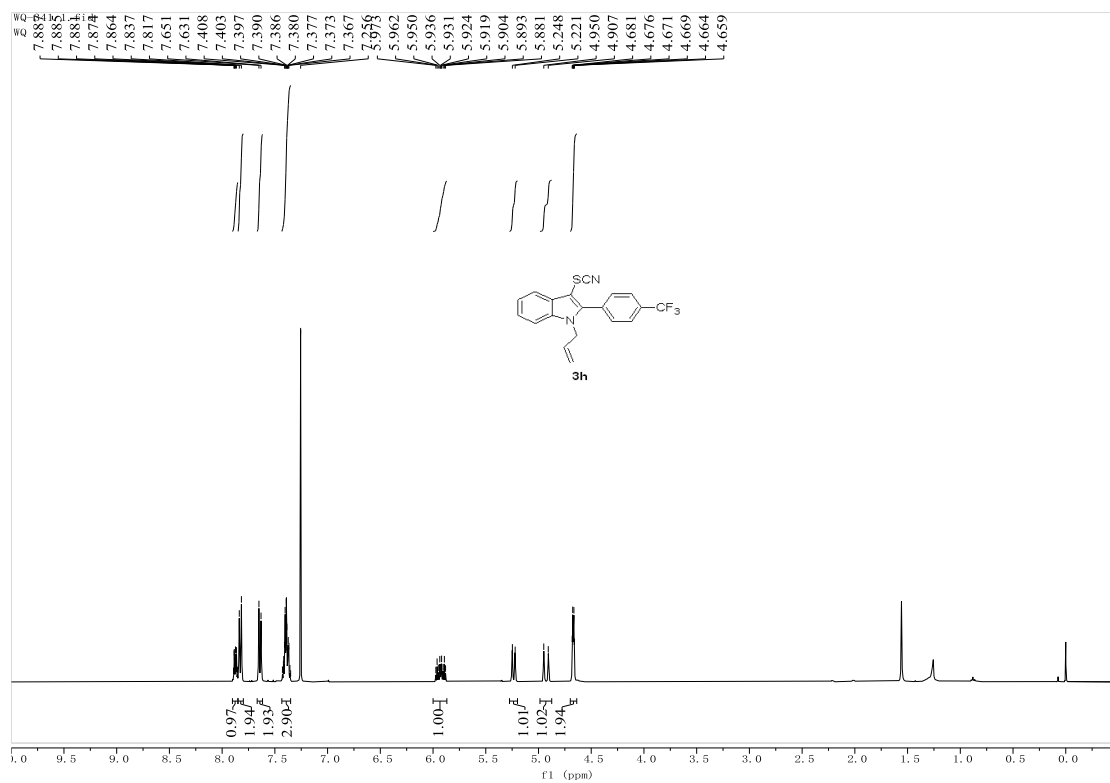
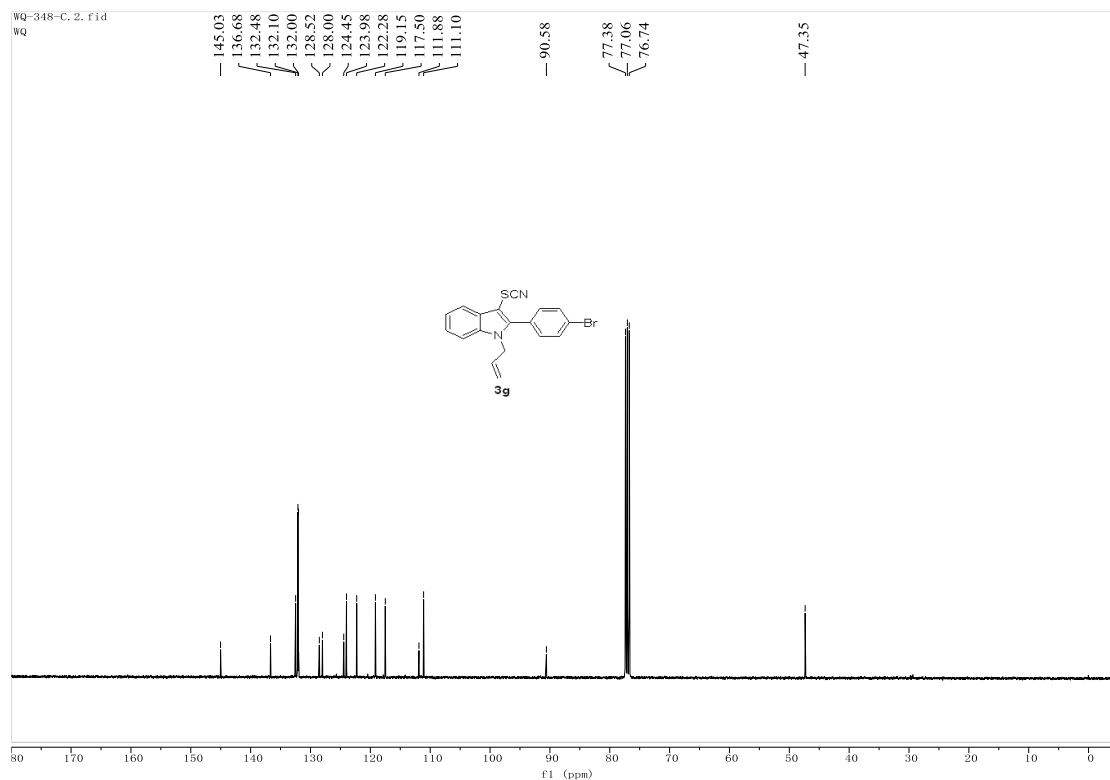


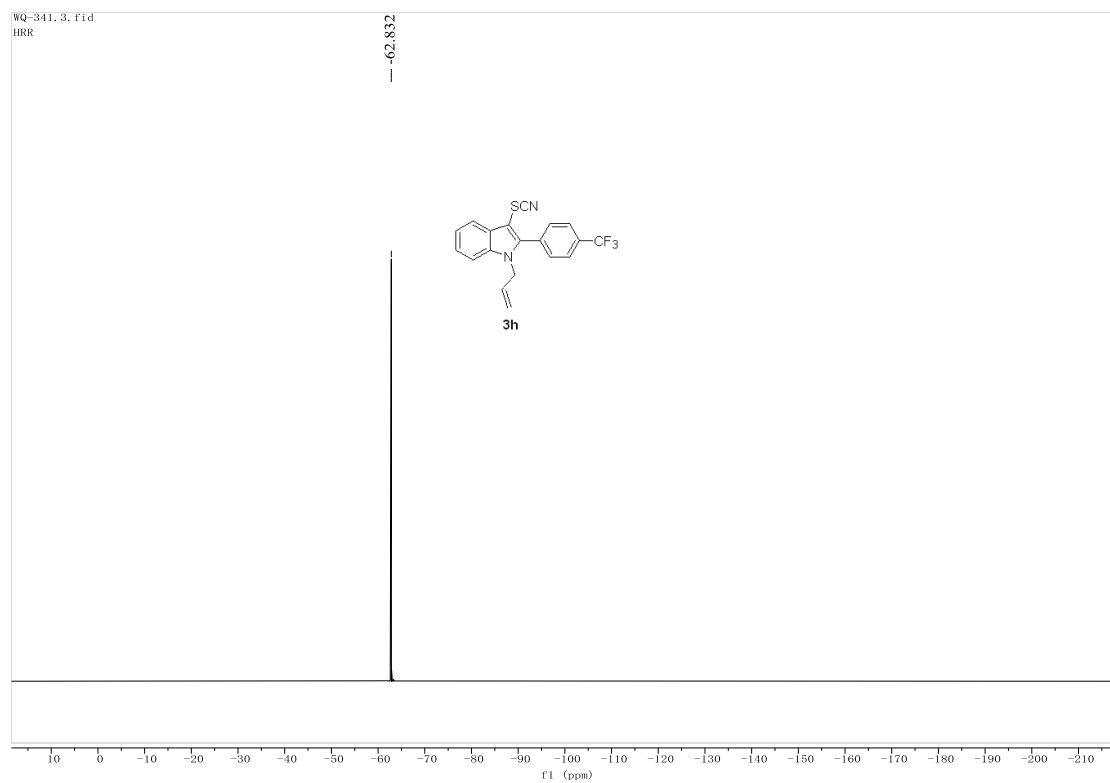
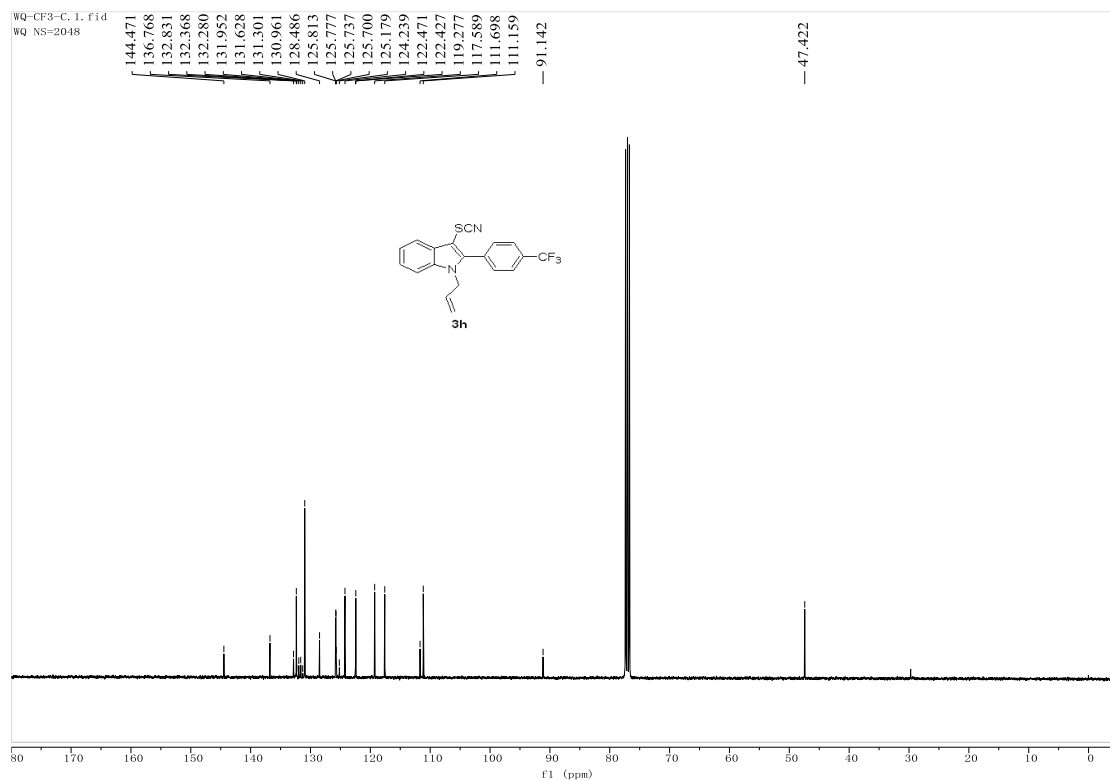


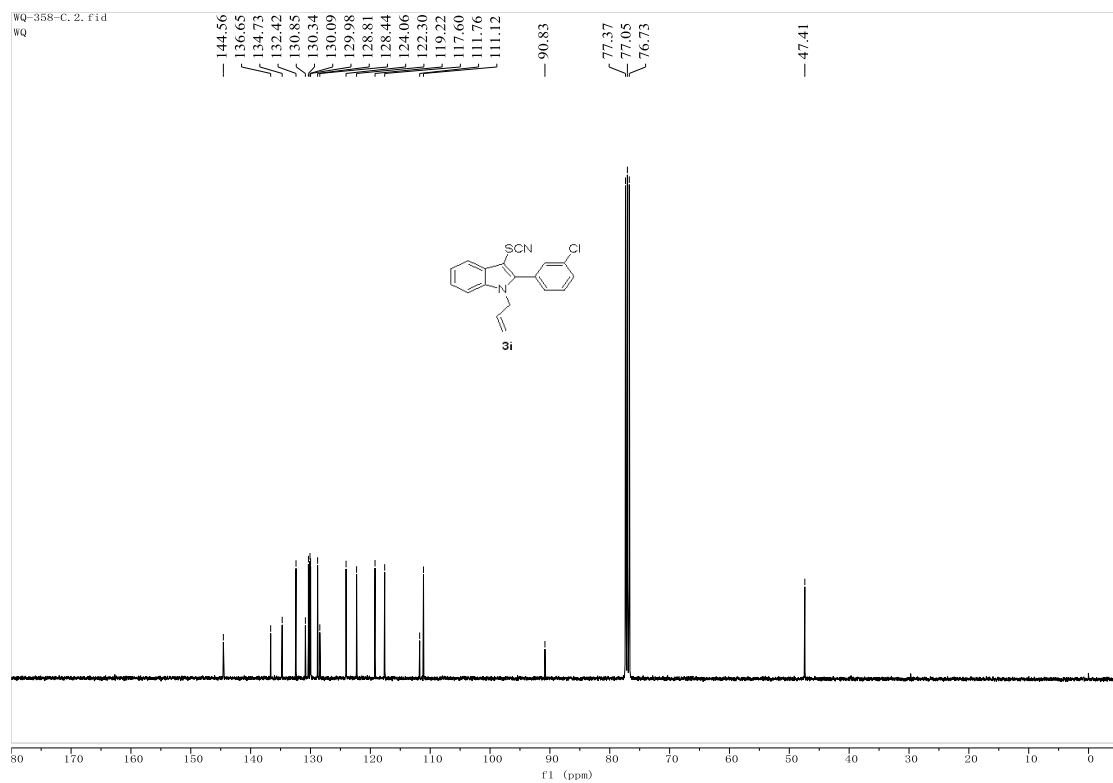
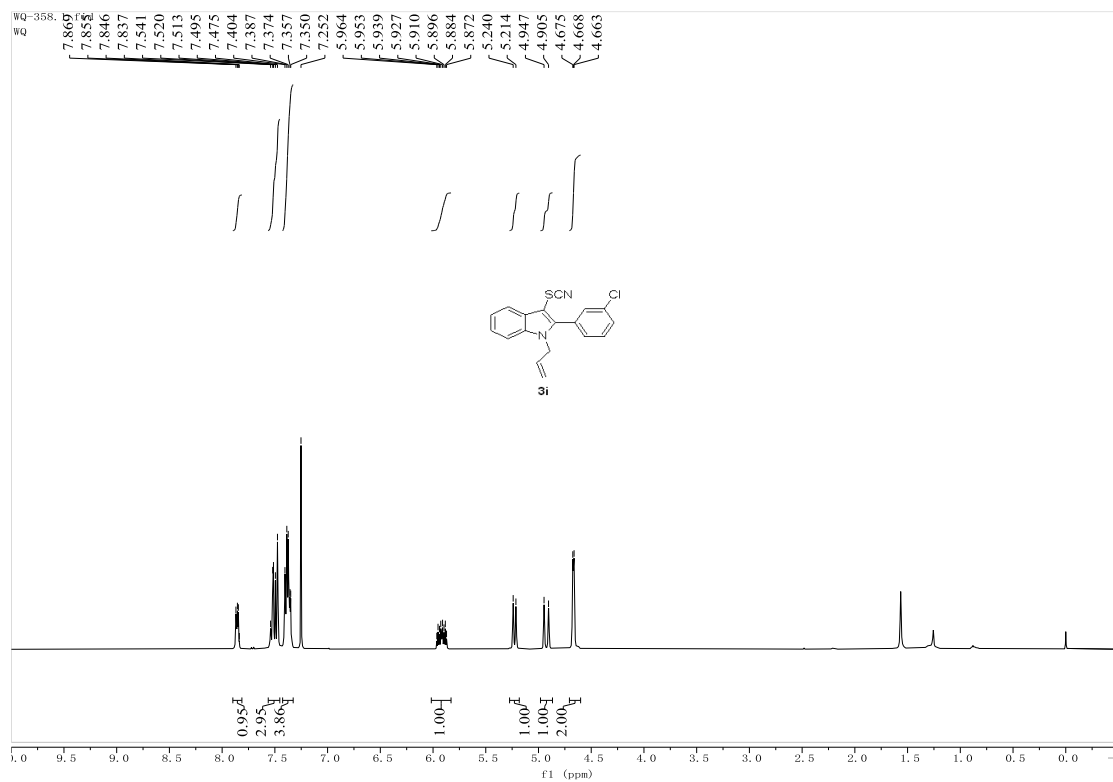
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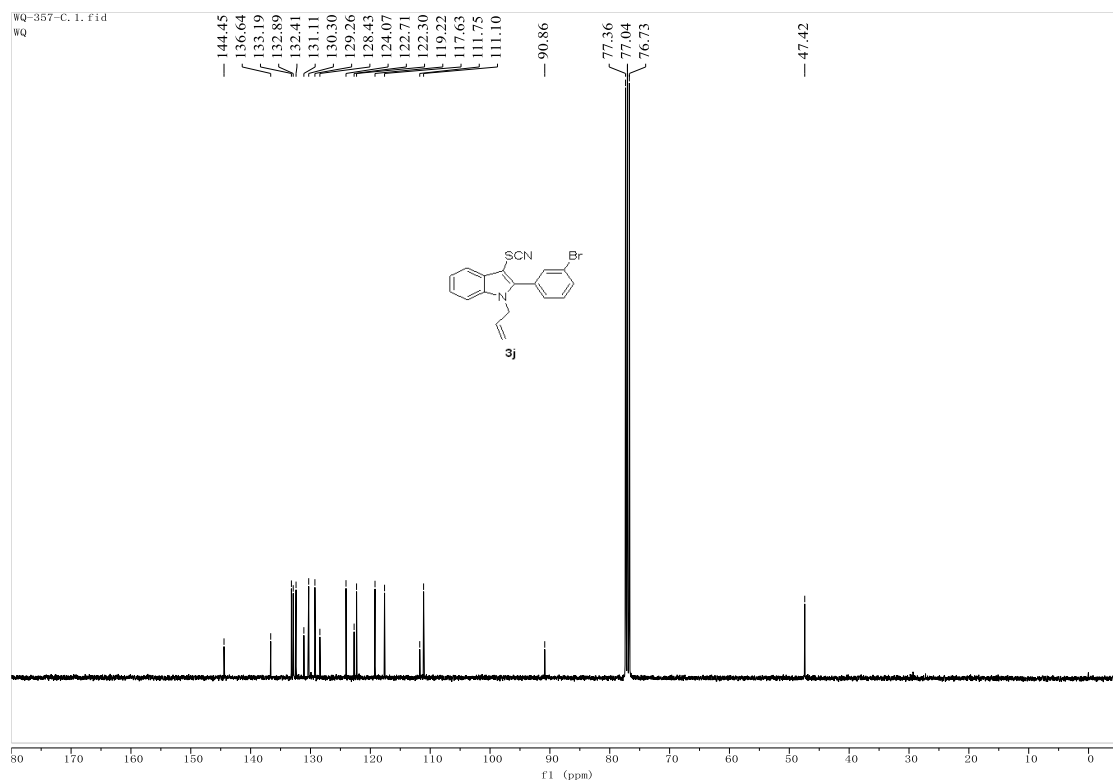
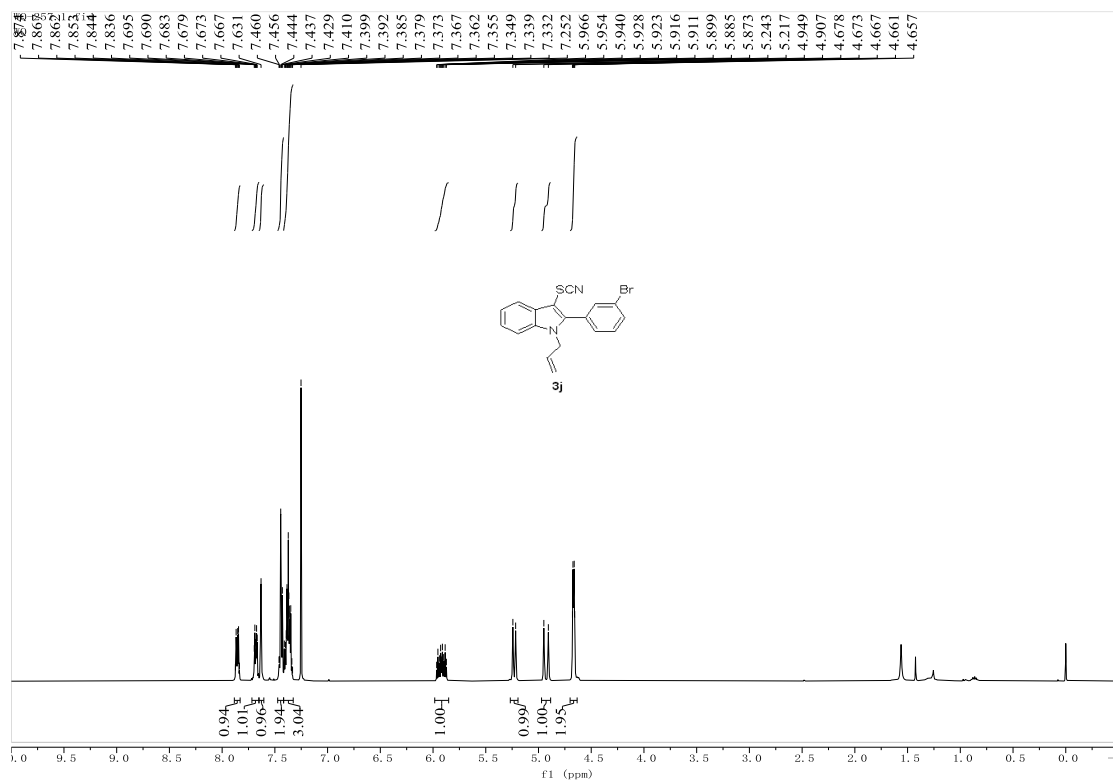


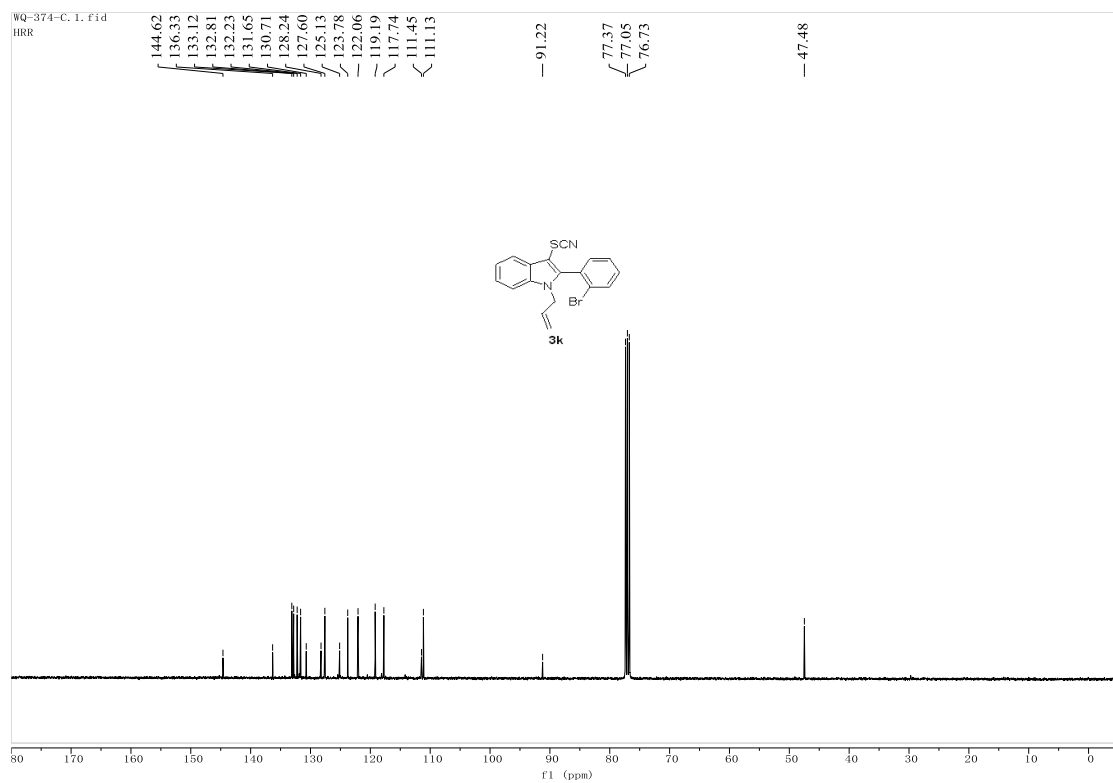
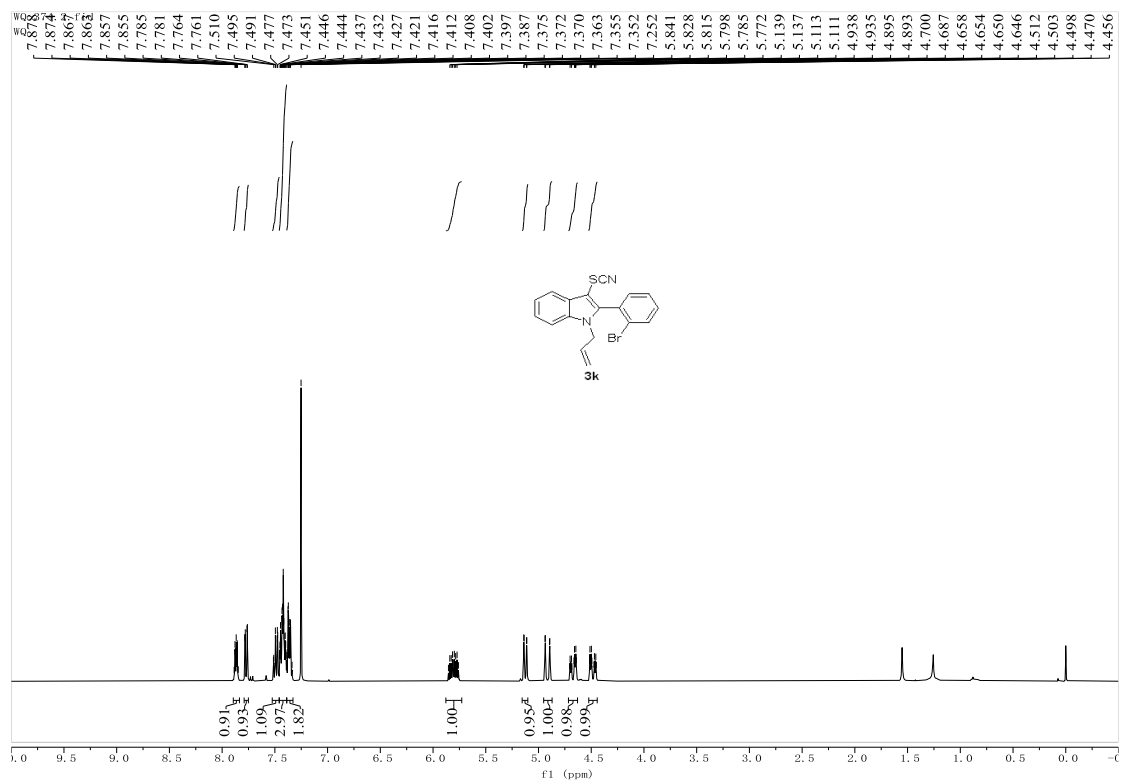


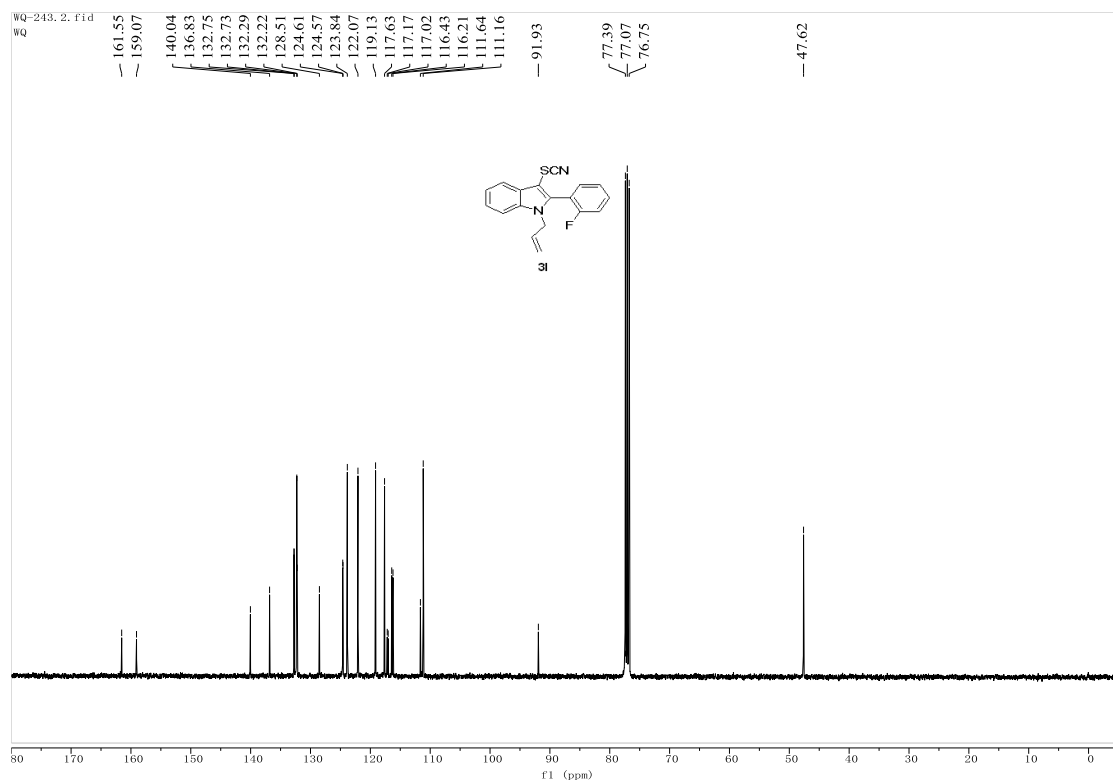
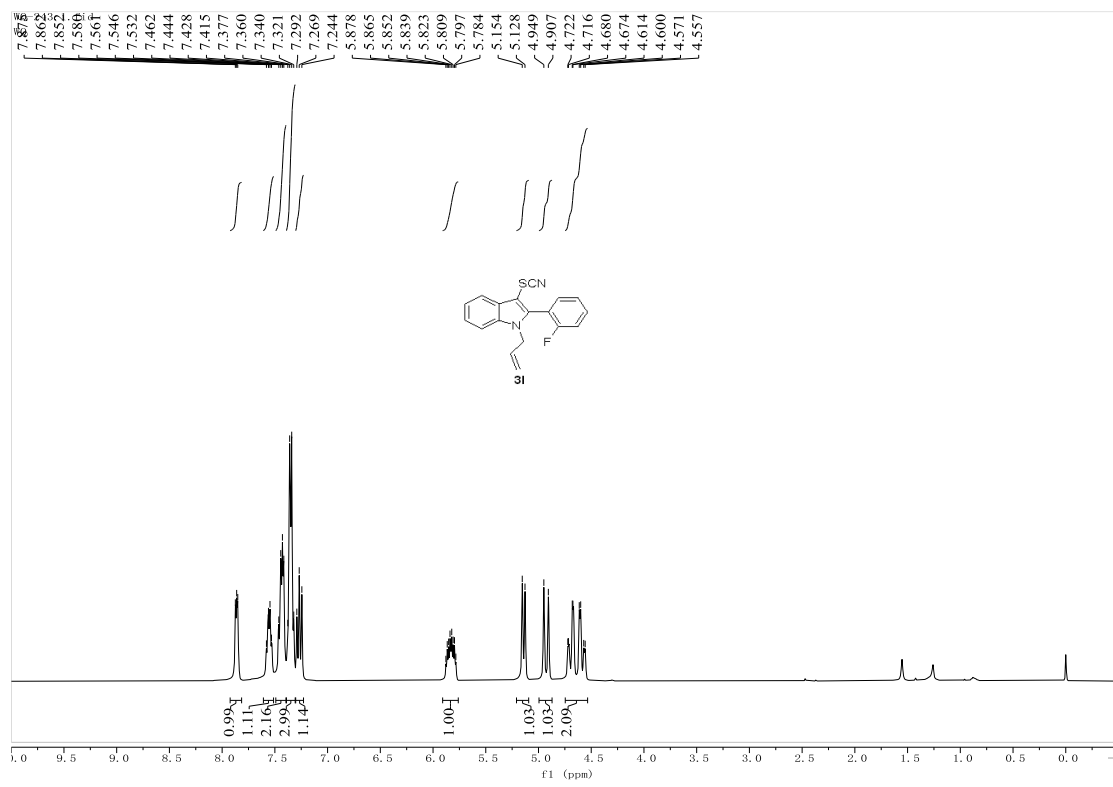




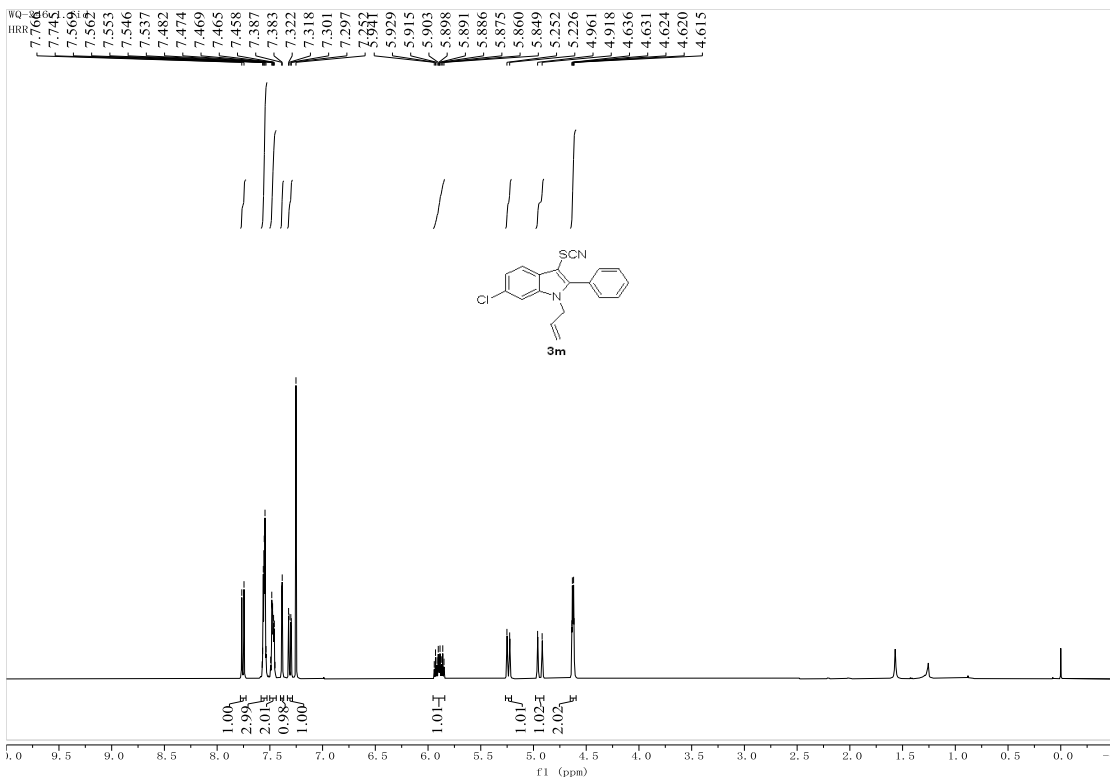
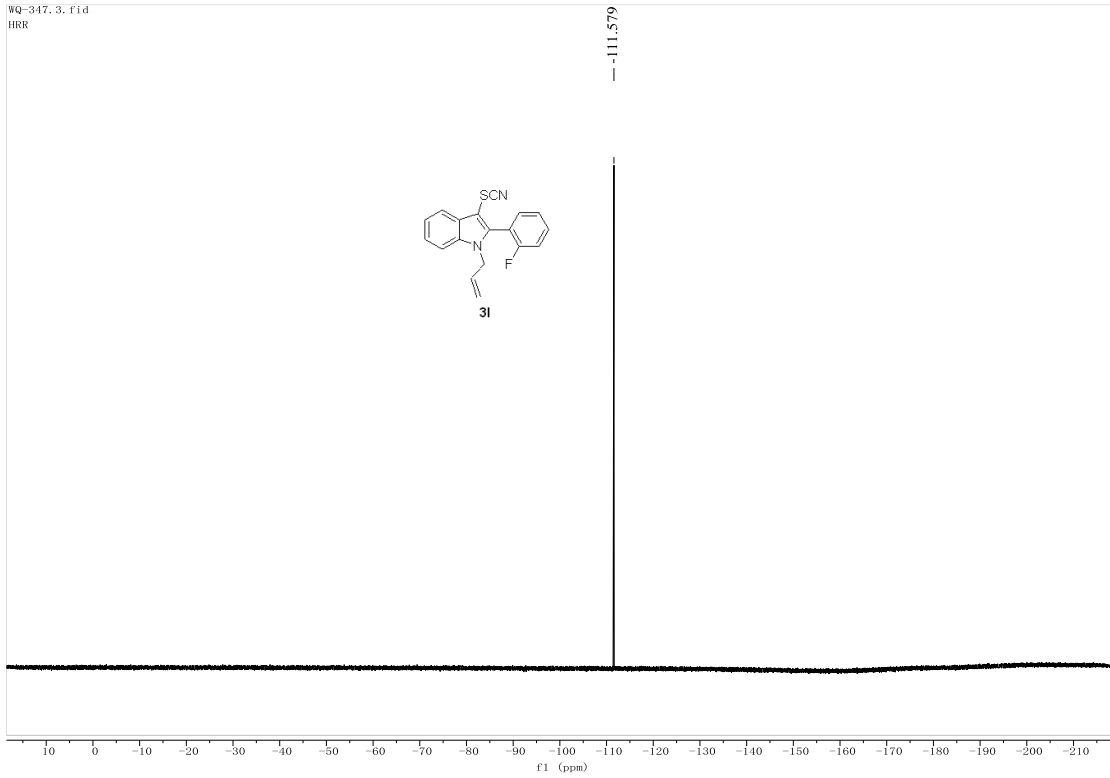


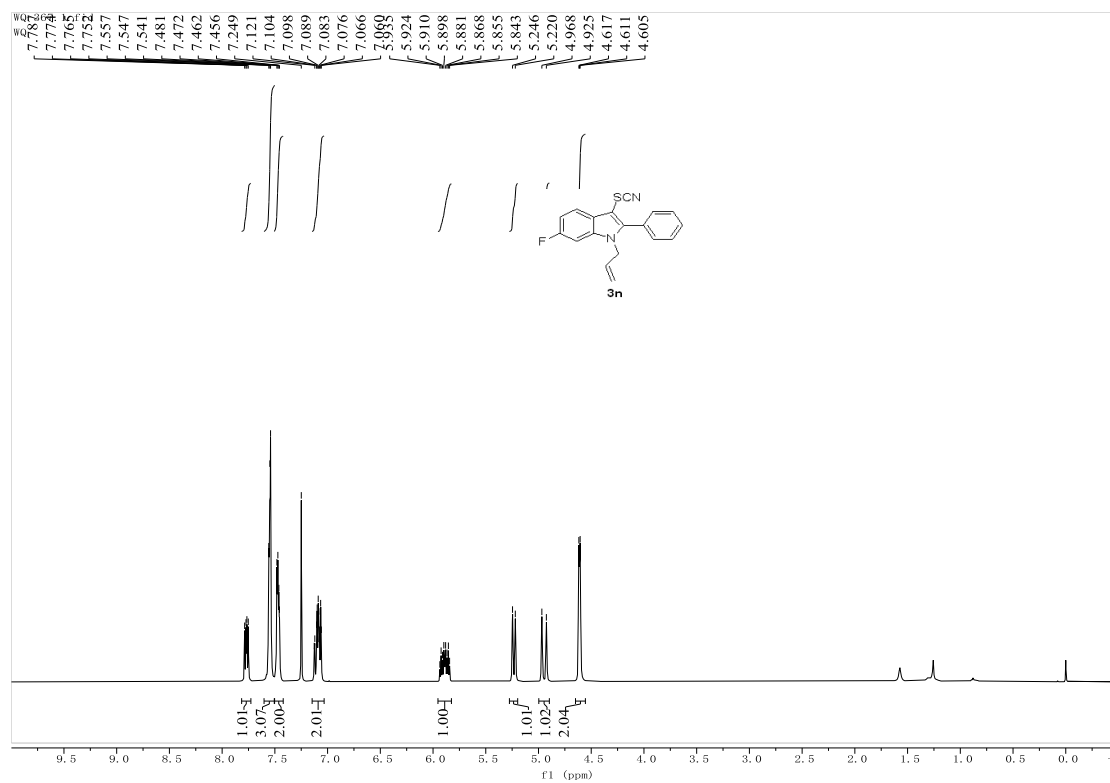
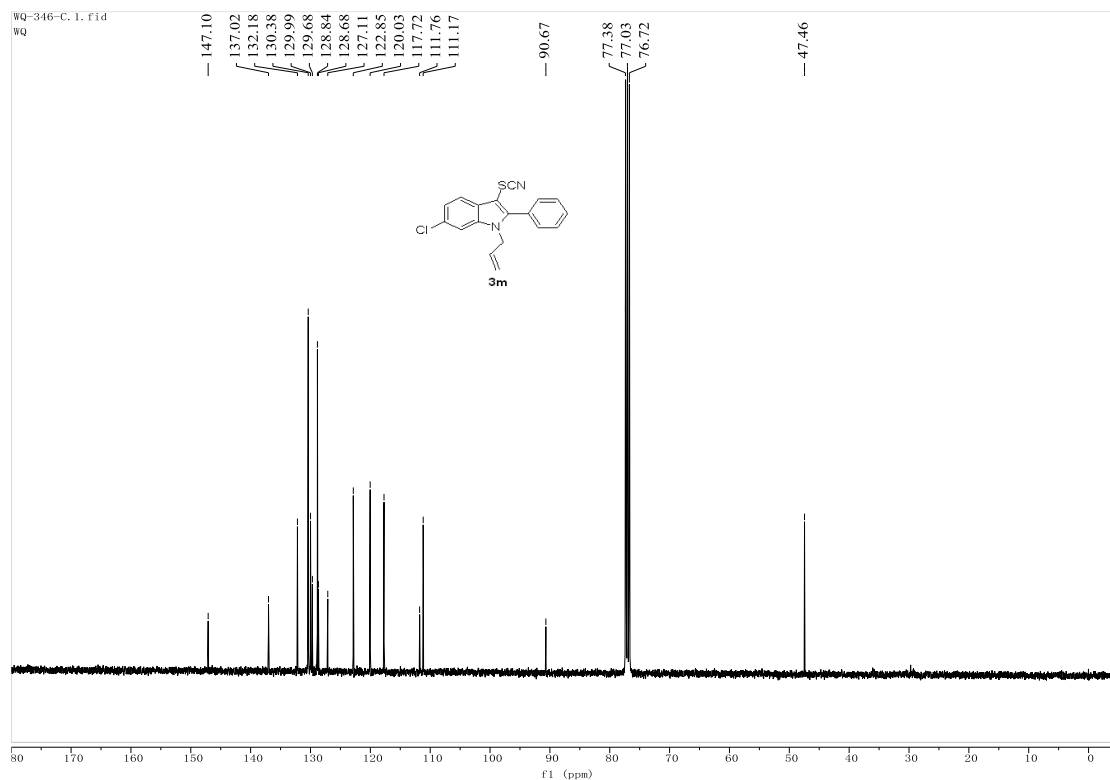


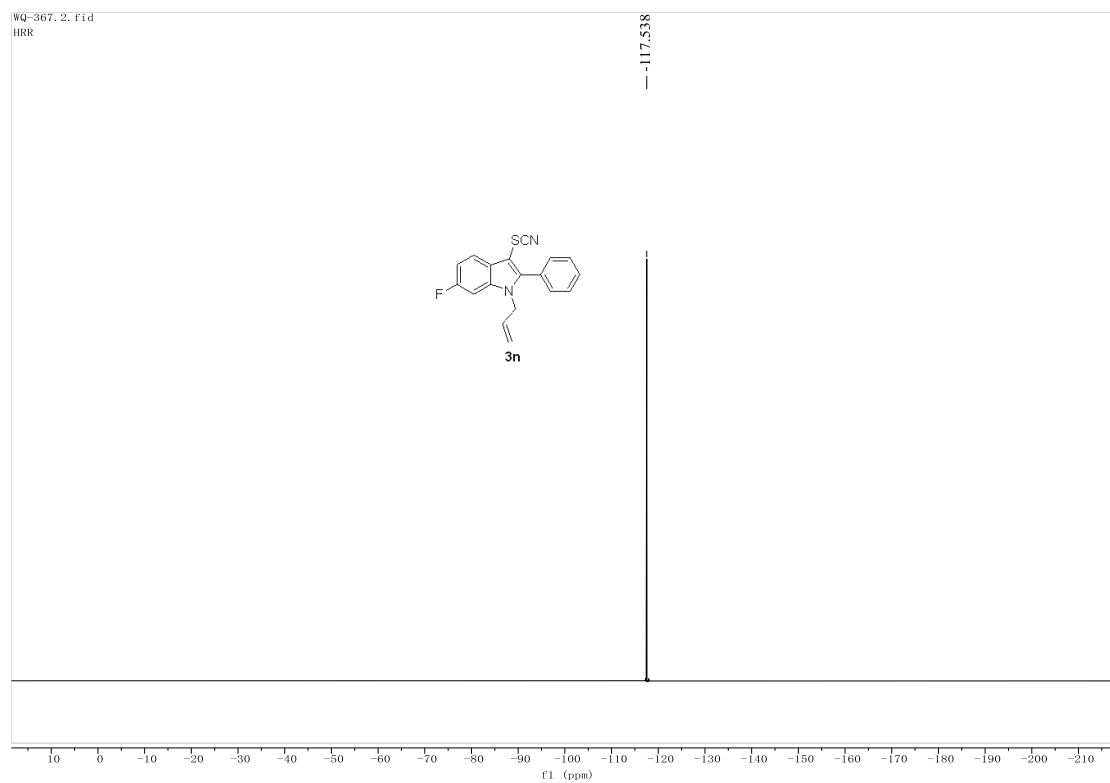
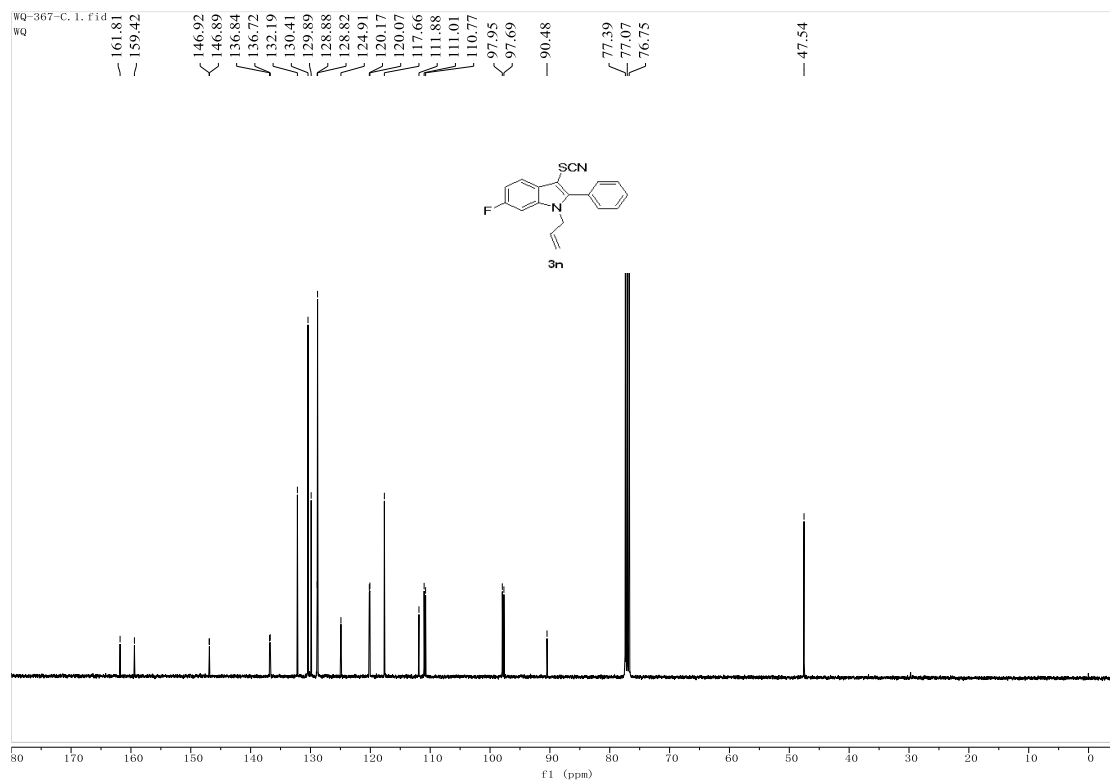


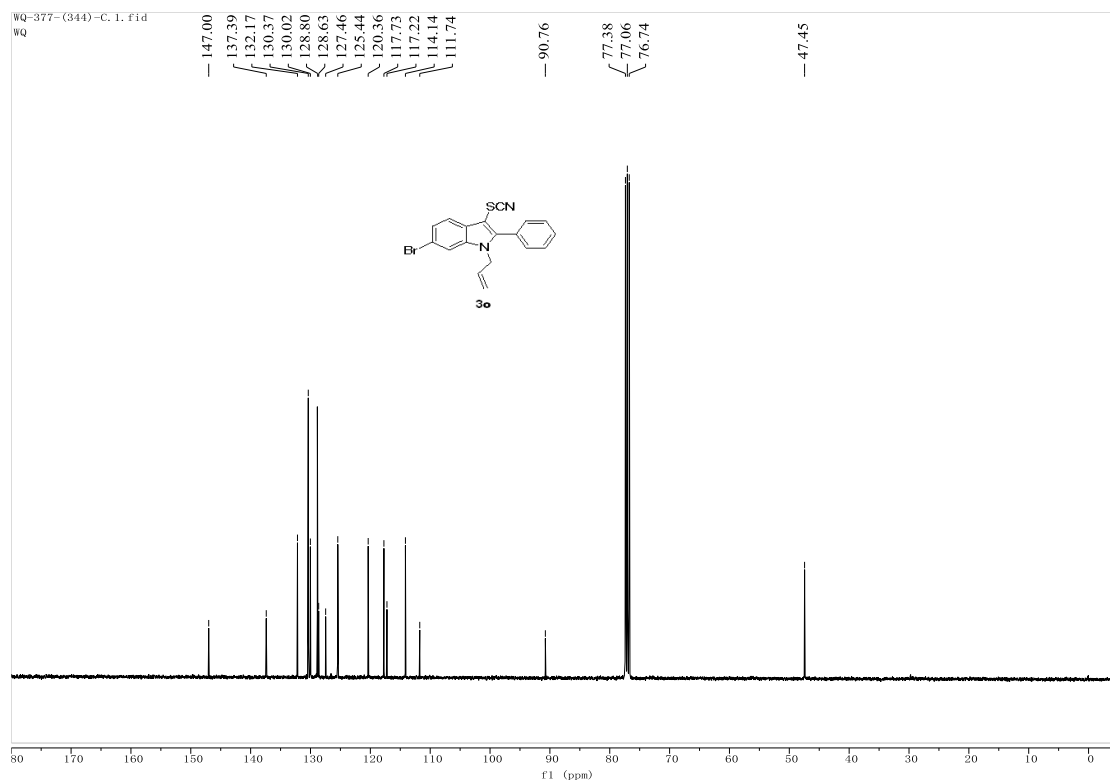
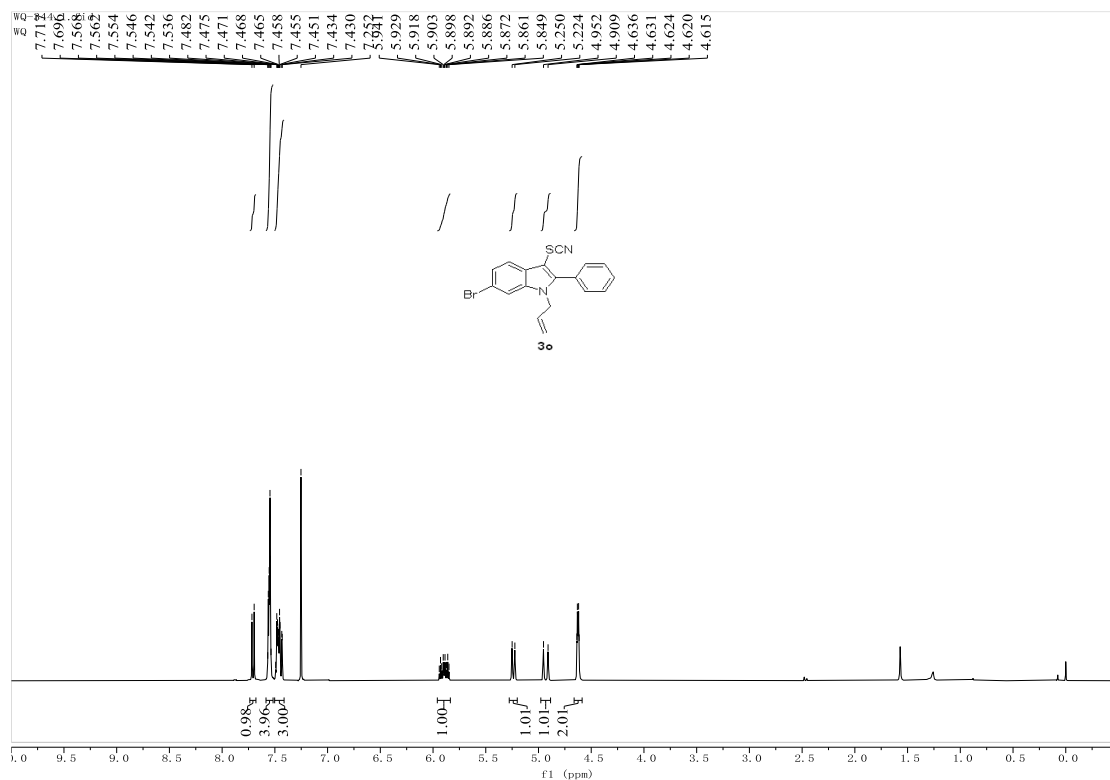


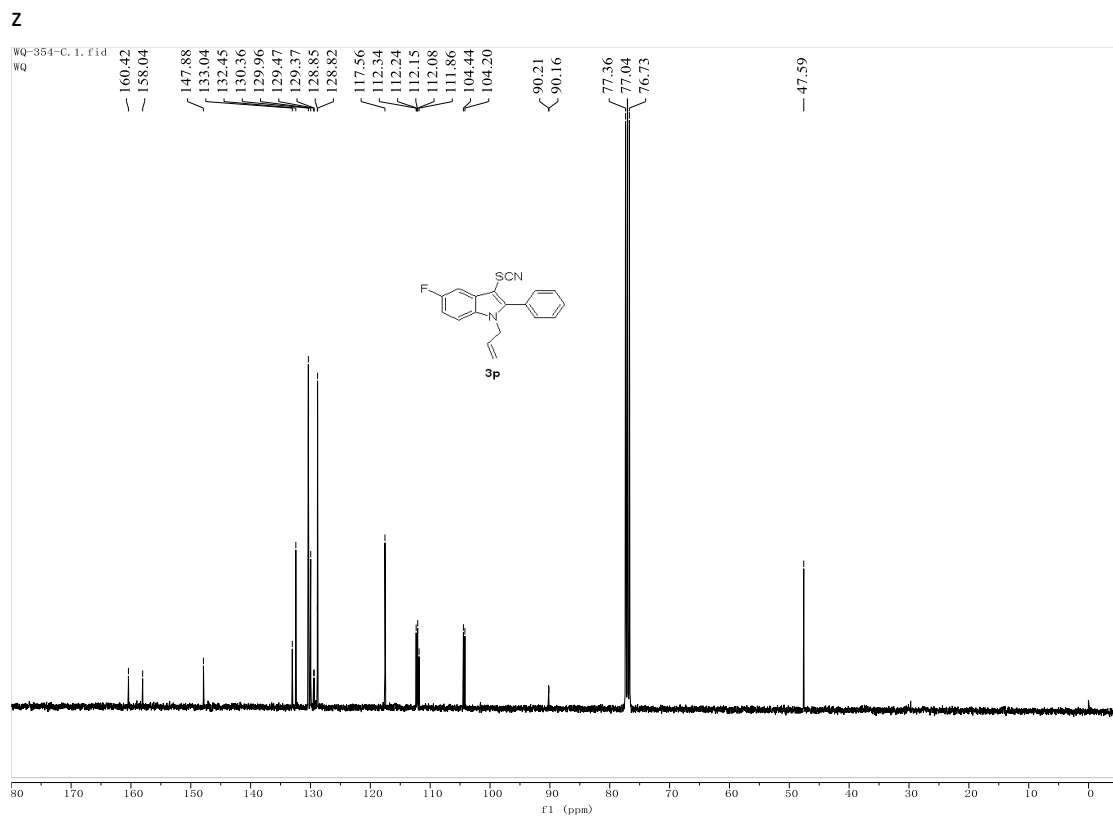
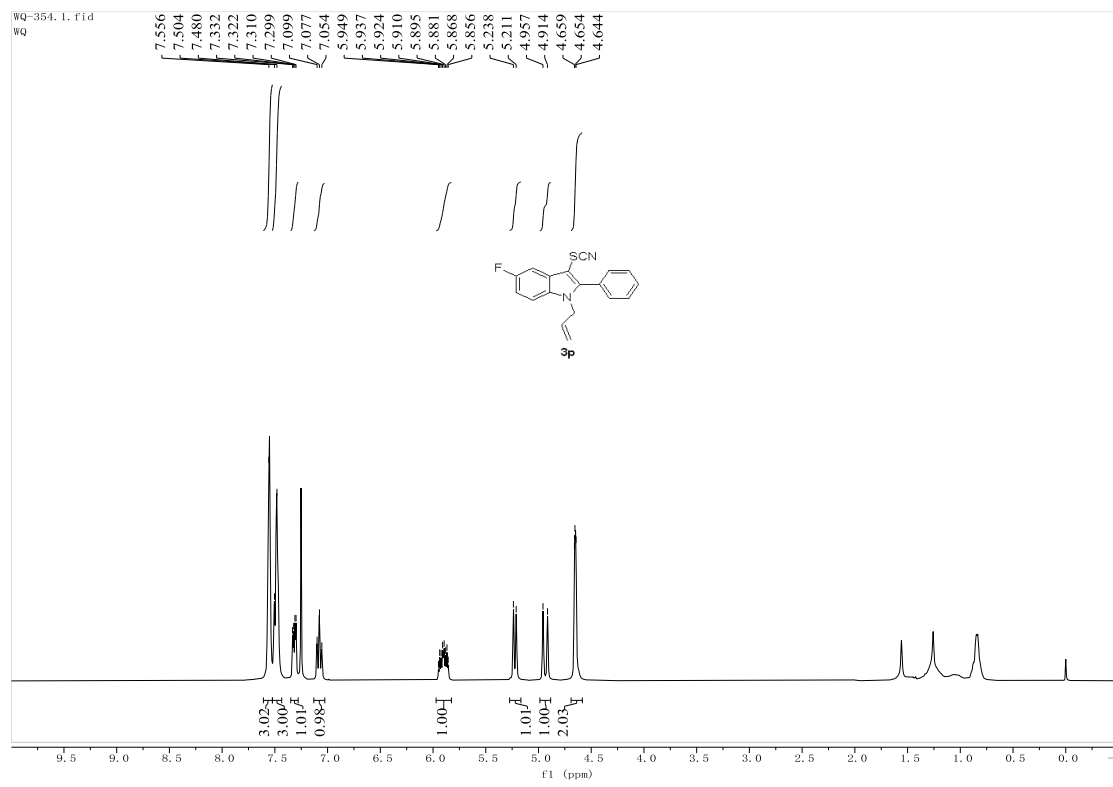
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HRR











WQ-354.2.Fid
HRR

