

Supporting Information

β -and Z-Selective Metal-Free Cyanation of Ynamides: A Direct Approach to Piperidines Fused to Arenes

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General remarks

All reactions were carried out under an inert atmosphere of argon in dried glassware, unless otherwise noted. Conventional solvents (THF, CH₂Cl₂) are stored on molecular sieves and sampled under argon. Toluene, CH₃CN, CHCl₃ were used as received.

NMR Spectra (¹H, ¹³C, ¹⁹F) were performed at 298 K. ¹H (500 MHz or 300 MHz) and ¹³C (126 MHz) NMR chemical shifts are reported relative to residual protiated solvent. ¹⁹F (282 MHz or 471 MHz) NMR chemical shifts are reported without any calibration. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz) and integration.

HRMS data were recorded on a microTOF spectrometer equipped with an orthogonal electrospray (ESI) interface.

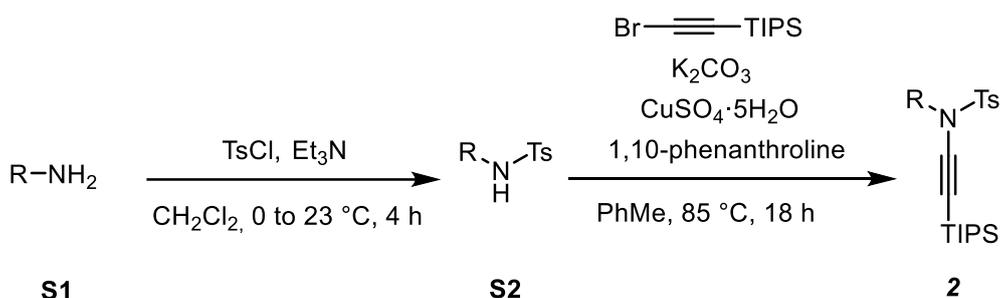
Thin layer chromatography was performed using Merck TLC silica gel 60 F254 aluminum sheets using petroleum ether/EtOAc as eluant and visualized using permanganate stain, ninhydrin stain, vanillin stain and/or UV light. Merck Geduran® 40-63 μm silica gel was used for column chromatography.

Melting points were recorded with a SMP3 Stuart Scientific microscope in open capillary tubes and are uncorrected.

Infrared spectra were reported in frequency of absorption using Alpha Bruker Optics spectrometer.

Experimental procedure & characterization data

General procedure for the preparation of ynamides¹



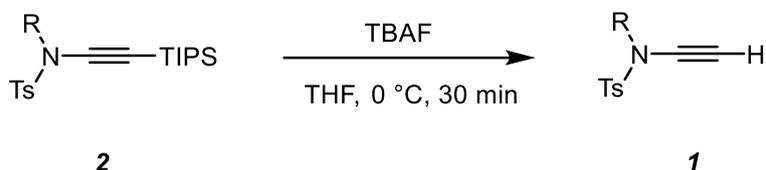
Primary amine **S1** (4.5 mmol, 1 equiv) was dissolved in CH₂Cl₂ (0.3 M), TsCl (4.95 mmol, 1.1 equiv) and Et₃N (11.25 mmol, 2.5 equiv) were added successively at 0 °C. After stirring at room temperature for 4 hours, the mixture was diluted with aqueous solution of HCl (1 N). The aqueous layer was extracted with CH₂Cl₂ (3x) and Et₂O (1x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over MgSO₄, concentrated under reduced pressure.

Sulfonamide **S2** (2 mmol, 1 equiv), CuSO₄·5H₂O (0.3 mmol, 15 mol%), 1,10-phenanthroline (0.6 mmol, 30 mol%), K₂CO₃ (5 mmol, 2.5 equiv), the bromoacetylenic derivative (2.3 mmol, 1.15 equiv)

¹ Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett.* 2004, **6**, 1151–1154.

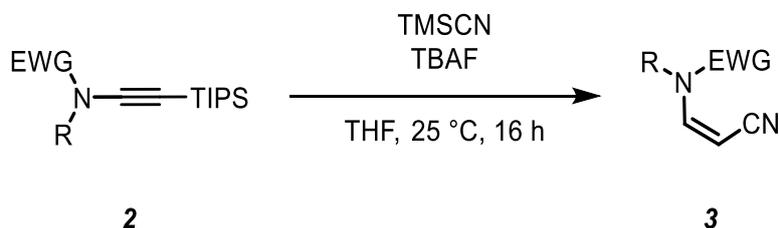
were dissolved in PhMe (0.1 M) and the reaction mixture was heated to 85 °C with a heating block for 18 h. After cooling down to room temperature, the mixture was filtered on a pad of silica gel and washed with EtOAc. The filtrate was then concentrated under reduced pressure and the crude material was purified by column chromatography on silica gel using a mixture Petroleum Ether/EtOAc as eluent to afford the desired TIPS protected ynamide **2**.

The (2-bromoethynyl)tris(propan-2-yl)silane was synthesized according to the literature².



TIPS protected ynamide **2** (2.0 mmol, 1.0 equiv) was dissolved in THF (0.1 M) and cooled at 0 °C. A TBAF solution (2.2 mmol, 1.1 equiv, 1 M in THF) was added dropwise and the resulting mixture was stirred at 0 °C for 30 min. The mixture was allowed to warm up to room temperature and was hydrolyzed with H₂O. The aqueous layer was extracted with EtOAc (3x), washed with a saturated aqueous solution of NaCl, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc as eluent or just by washing with cold *n*-pentane to afford the desired ynamide **1**.

General procedure for the preparation of (*Z*)β-cyano-enamides **3**



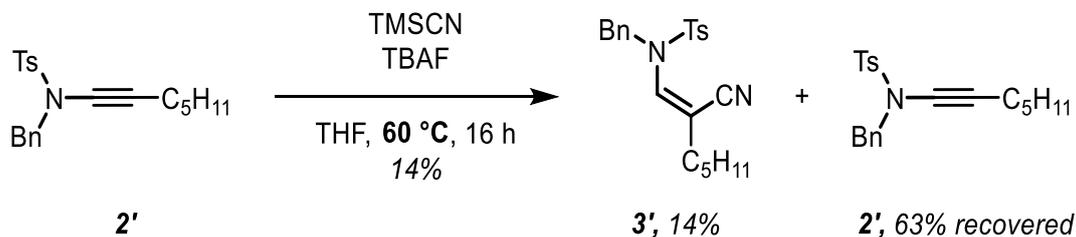
TIPS protected ynamide **2** (0.1 mmol, 1.0 equiv) was dissolved in THF (0.1 M), TMSCN (0.12 mmol, 1.2 equiv) and a TBAF solution (0.2 mmol, 2.0 equiv, 1 M in THF) were subsequently added and the solution was stirred at 25 °C for 4-16h until TLC detected SM all consumed. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a mixture Petroleum Ether/EtOAc, as eluent to afford the desired β-cyano-enamides **3a-z**.

Gram-scale procedure for the preparation of (*Z*)β-cyano-enamides **3a**

TIPS protected ynamide **2a** (1.0 g, 2.26 mmol, 1.0 equiv) was dissolved in THF (23 mL, 0.1 M), TMSCN (0.36 mL, 2.72 mmol, 1.2 equiv) and a TBAF solution (4.53 mL, 4.53 mmol, 2.0 equiv, 1 M in THF) were subsequently added and the solution was stirred at 25 °C for 16 h. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a mixture Petroleum Ether/EtOAc, as eluent to afford the desired β-cyano-enamides **3a** as a white solid (570 mg, 1.82 mmol, 81%)

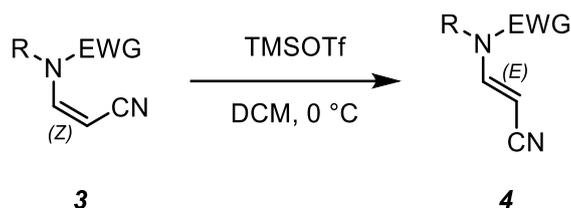
²H. Hofmeister, K. Annen, H. Laurent, R. Wiechert, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 727–729.

Procedure for the preparation of substituted (*Z*) β -cyano-enamides **3'**



Alkyl substituted ynamide **2'** (0.5 mmol, 1.0 equiv) was dissolved in THF (0.1 M), TMSCN (0.60 mmol, 1.2 equiv) and a TBAF solution (1.0 mmol, 2.0 equiv, 1 M in THF) were subsequently added and the solution was stirred at 60 °C for 16 h. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a mixture Petroleum Ether/EtOAc, as eluent to afford the desired β -cyano-enamides **3'** as a colorless oil.

General procedure for the preparation of (*E*) β -cyano-enamides **4**



Z- β -cyano-enamides **3** (0.1 mmol, 1.0 equiv) was dissolved in DCM (0.1 M) and cooled to 0 °C, TMSOTf (0.02 mmol, 0.2 equiv) were subsequently added and the solution was stirred at 0 °C for 1 h. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a mixture Petroleum Ether/EtOAc, as eluent to afford the desired *E*- β -cyano-enamides **4a**, **4h**, **4p**, **4t**, **4u**.

Optimization of isomerization

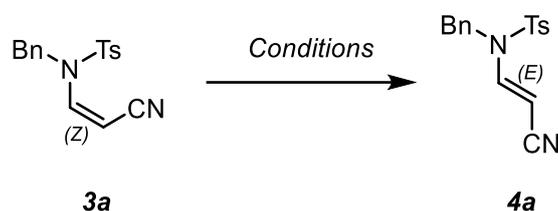
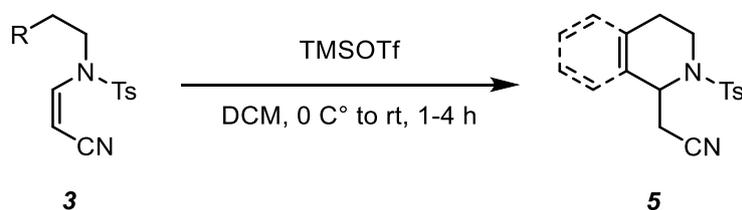


Table S1. Optimization of isomerization

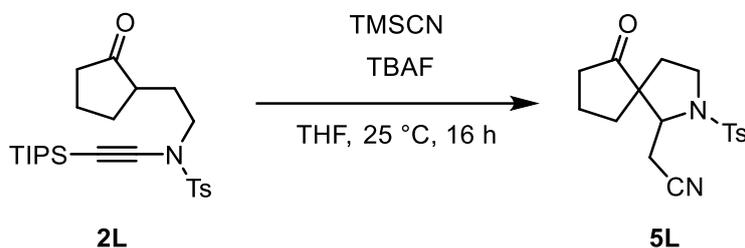
Entry	Catalyst	Conditions	Yield
1	TMSOTf (0.2 equiv)	DCM, 0 °C, 1 h	90%
2	Sc(OTf) ₃ (0.2 equiv)	DCM, 25 °C, 4 h	No reaction
3	ZrCl ₄ (0.2 equiv)	DCM, 25 °C, 4 h	No reaction
4	TFA (1.0 equiv)	DCM, 25 °C, 4 h	No reaction
5	TfOH (1.0 equiv)	DCM, 0 °C, 4 h	No reaction
6	TBSOTf (0.2 equiv)	DCM, 25 °C, 4 h	74%
7	None	THF, reflux, 6 h	No reaction
8	None	MeCN, 420 nm, 6 h	No reaction

General procedure for the preparation of piperidines **5A-5K**



β-cyano enamides **3** (0.1 mmol, 1.0 equiv) was dissolved in DCM (0.1 M) and cooled to 0 °C, TMSOTf (0.1 mmol, 1.0 equiv) were subsequently added and the solution was stirred at 0 °C for 1 to 4 h until complete conversion of the starting material, monitored by TLC. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc, as eluent to afford the desired product **5A-5K**.

General procedure for the preparation of spiro-tosyl pyrrolidine **5L**



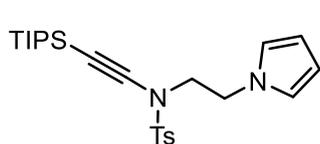
Ynamide **2L** (0.1 mmol, 1.0 equiv) was dissolved in THF (0.1 M), TMSCN (0.2 mmol, 2.0 equiv) and a TBAF solution (0.3 mmol, 3.0 equiv, 1 M in THF) were subsequently added and the solution was stirred at 25 °C for 16 h. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a mixture Petroleum Ether/EtOAc, as eluent to afford the desired spiro-tosyl pyrrolidine **5L**.

Characterization data

Data for ynamides **1a**³, **2a**³, **2b**⁴, **2c**⁵, **2d**³, **2e**⁴, **2f**⁶, **2g**⁴, **2h-2i**⁷, **2j-2l**³, **2n**⁷, **2q**³, **2r**⁸, **2s-2v**⁴, **2x**⁹, **2z**⁷, **2E**³, **2L**¹⁰ can be found in literature.

Compound **2m**

N-(2-(1H-pyrrol-1-yl)ethyl)-4-methyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₂₄H₃₆N₂O₂SSi
MW: 444.71 g.mol⁻¹
white solid
72%

¹H NMR (500 MHz, CDCl₃): δ = 7.66 – 7.64 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.26 (d, *J* = 8.5 Hz, 2H), 6.61 – 6.60 (t, *J* = 2.1 Hz, 2H), 6.12 – 6.11 (t, *J* = 2.1 Hz, 2H), 4.16 – 4.14 (t, *J* = 6.8 Hz, 2H), 3.68 – 3.66 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.04 (s, 21H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.0, 134.3, 129.8, 128.0, 120.8, 109.0, 95.5, 70.7, 52.1, 47.1, 21.8, 18.8, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₄H₃₇N₂O₂SSi 445.2339; Found 445.2340.

³ Hourtoule, M.; Miesch, L. *Org. Lett.* **2022**, *24*, 3896–3900.

⁴ Gommenginger, C.; Hourtoule, M.; Menghini, M.; Miesch, L. *Org. Biomol. Chem.* **2024**, *22*, 940

⁵ Takai, R.; Shimbo, D.; Tada, N.; Itoh, A. *J. Org. Chem.* **2021**, *86*, 4699–4713.

⁶ Lu, F.; Li, Z.; Wang, Y.; Liu, G.; Niu, G.; Wang, G.; Zhao, X. *Org. Biomol. Chem.* **2024**, *22*, 8097

⁷ Zheng, Y.; Moegle, B.; Ghosh, S.; Perfetto, A.; Luise, D.; Ciofini, I.; Miesch, L. *Chem. Eur. J.* **2022**, *28*, e202103598.

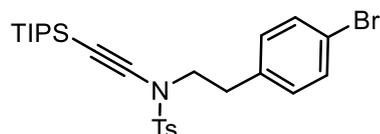
⁸ Zeng, L.; Jin, J.; He, J.; Cui, S. *Chem. Commun.* **2021**, *57*, 6792–6795.

⁹ Zheng, Y.; Perfetto, A.; Luise, D.; Ciofini, I.; Miesch, L. *Org. Lett.* **2021**, *23*, 5528–5532.

¹⁰ Beltran, F.; Andna, L.; Miesch, L. *Org. Chem. Front.*, **2019**, *6*, 373–376.

IR (neat): $\nu = 2942, 2864, 2155, 1366, 1171 \text{ cm}^{-1}$

Compound 2o *N*-(4-bromophenethyl)-4-methyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



$\text{C}_{26}\text{H}_{36}\text{BrNO}_2\text{SSi}$
MW: $534.63 \text{ g}\cdot\text{mol}^{-1}$
white solid
81%

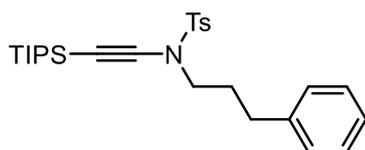
^1H NMR (500 MHz, CDCl_3): $\delta = 7.64 - 7.63$ (d, $J = 8.3 \text{ Hz}$, 2H), $7.34 - 7.32$ (d, $J = 8.3 \text{ Hz}$, 2H), $7.26 - 7.24$ (d, $J = 8.3 \text{ Hz}$, 2H), $7.02 - 7.00$ (d, $J = 8.3 \text{ Hz}$, 2H), $3.60 - 3.57$ (t, $J = 7.2 \text{ Hz}$, 2H), $2.91 - 2.88$ (d, $J = 7.2 \text{ Hz}$, 2H), 2.44 (s, 3H), 1.07 (s, 3H), 1.06 (s, 18H) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 144.7, 136.7, 134.7, 131.7, 130.8, 129.7, 127.7, 120.8, 96.0, 70.6, 52.5, 33.7, 21.8, 18.8, 18.6, 11.5, 11.4$ ppm.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{36}\text{BrNaNO}_2\text{SSi}$ 556.1312; Found 556.1314.

IR (neat): $\nu = 2941, 2863, 2162, 1368, 1168 \text{ cm}^{-1}$

Compound 2p 4-methyl-*N*-(3-phenylpropyl)-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



$\text{C}_{27}\text{H}_{39}\text{NO}_2\text{SSi}$
MW: $469.76 \text{ g}\cdot\text{mol}^{-1}$
white solid
85%

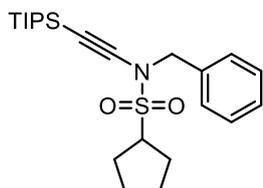
^1H NMR (500 MHz, CDCl_3): $\delta = 7.79 - 7.77$ (d, $J = 8.3 \text{ Hz}$, 2H), $7.32 - 7.30$ (d, $J = 8.3 \text{ Hz}$, 2H), $7.28 - 7.25$ (m, 2H), $7.20 - 7.17$ (m, 1H), $7.15 - 7.14$ (m, 2H), $3.36 - 3.34$ (t, $J = 6.9 \text{ Hz}$, 2H), $2.68 - 2.64$ (d, $J = 7.4 \text{ Hz}$, 2H), 2.44 (s, 3H), $2.01 - 1.95$ (m, 2H), 1.06 (s, 3H), 1.05 (s, 18H) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 144.5, 141.0, 134.6, 129.6, 128.4, 128.4, 127.7, 126.0, 96.2, 69.6, 50.8, 32.4, 29.4, 21.6, 18.6, 11.4$ ppm.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{27}\text{H}_{39}\text{KNO}_2\text{SSi}$ 508.2108, Found 508.2110.

IR (neat): $\nu = 2941, 2864, 2161, 1366, 1169 \text{ cm}^{-1}$

Compound 2t *N*-benzyl-*N*-((triisopropylsilyl)ethynyl)cyclopentanesulfonamide



$\text{C}_{23}\text{H}_{37}\text{NO}_2\text{SSi}$
MW: $419.70 \text{ g}\cdot\text{mol}^{-1}$
yellow oil
17%

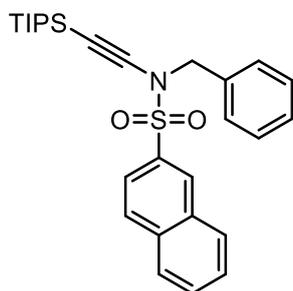
^1H NMR (500 MHz, CDCl_3): $\delta = 7.42 - 7.40$ (m, 2H), $7.35 - 7.33$ (m, 3H), 4.61 (s, 2H), 3.70 (m, 1H), $2.16 - 2.11$ (m, 2H), $2.01 - 1.97$ (m, 2H), $1.83 - 1.79$ (m, 2H), $1.62 - 1.59$ (m, 2H), 0.99 (s, 21H) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 135.2, 129.0, 128.7, 129.5, 97.0, 69.8, 62.9, 55.8, 29.1, 25.7, 18.7, 11.5$ ppm.

HRMS (ESI-TOF) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{37}\text{NaNO}_2\text{SSi}$ 442.2212; Found 442.2216.

IR (neat): $\nu = 2942, 2864, 2163, 1356, 1153 \text{ cm}^{-1}$

Compound 2u *N*-benzyl-*N*-((triisopropylsilyl)ethynyl)naphthalene-2-sulfonamide



$\text{C}_{28}\text{H}_{35}\text{NO}_2\text{SSi}$
MW: $477.74 \text{ g}\cdot\text{mol}^{-1}$
white solid
92%

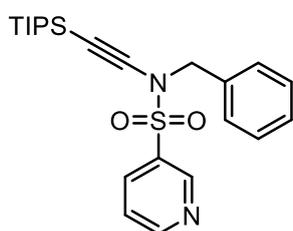
^1H NMR (500 MHz, CDCl_3): $\delta = 8.41$ (d, $J = 1.6$ Hz, 1H), 7.93 – 7.91 (m, 3H), 7.84 – 7.82 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.68 – 7.65 (td, $J = 6.9, 1.3$ Hz, 1H), 7.63 – 7.62 (td, $J = 6.9, 1.3$ Hz, 1H), 7.31 – 7.29 (m, 2H), 7.25 – 7.23 (m, 3H), 4.57 (s, 2H), 0.92 (s, 21H) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 135.2, 134.5, 134.3, 132.0, 129.6, 129.4, 129.3, 129.1, 129.0, 128.4, 128.3, 127.9, 127.6, 122.6, 96.3, 70.4, 55.7, 18.5, 11.3$ ppm.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{28}\text{H}_{35}\text{KNO}_2\text{SSi}$ 516.1795; Found 516.1802.

IR (neat): $\nu = 2940, 2863, 2164, 1347, 1159 \text{ cm}^{-1}$

Compound 2w *N*-benzyl-*N*-((triisopropylsilyl)ethynyl)pyridine-3-sulfonamide



$\text{C}_{23}\text{H}_{32}\text{N}_2\text{O}_2\text{SSi}$
MW: $428.67 \text{ g}\cdot\text{mol}^{-1}$
white solid
78%

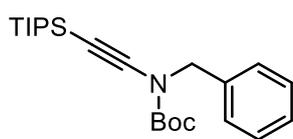
^1H NMR (500 MHz, CDCl_3): $\delta = 9.00$ (dd, $J = 2.3, 0.9$ Hz, 1H), 8.80 – 8.79 (dd, $J = 4.8, 1.6$ Hz, 1H), 8.04 – 8.02 (ddd, $J = 8.1, 2.3, 1.6$ Hz, 1H), 7.39 – 7.36 (ddd, $J = 8.1, 4.8, 0.9$ Hz, 1H), 7.29 – 7.27 (m, 5H), 4.59 (s, 2H), 0.96 (s, 21H) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 154.0, 148.5, 135.4, 134.5, 133.9, 129.1, 128.8, 128.7, 123.6, 95.7, 71.4, 56.1, 18.6, 11.4$ ppm.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{23}\text{H}_{32}\text{KN}_2\text{O}_2\text{SSi}$ 467.1591; Found 467.1595.

IR (neat): $\nu = 2942, 2864, 2164, 1373, 1173 \text{ cm}^{-1}$

Compound 2y tert-butyl benzyl((triisopropylsilyl)ethynyl)carbamate



$\text{C}_{23}\text{H}_{37}\text{NO}_2\text{Si}$
MW: $387.64 \text{ g}\cdot\text{mol}^{-1}$
white solid
78%

^1H NMR (500 MHz, CDCl_3): $\delta = 7.37 - 7.28$ (m, 5H), 4.57 (s, 2H), 1.49 (s, 9H), 1.01 (s, 3H), 1.08 (s, 18H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 154.2, 136.4, 128.6, 128.4, 127.8, 97.9, 82.5, 68.5, 53.1, 28.1, 18.6, 11.4 ppm.

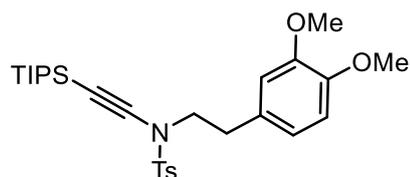
HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₈H₁₇F₃KN₄O₂S 426.2231; Found 426.2237.

IR (neat): ν = 2941, 2864, 1274, 1719, 1155 cm⁻¹

IR (neat): ν = 2940, 2863, 2163, 1367, 1168 cm⁻¹

Compound 2A

N-(3,4-dimethoxyphenethyl)-4-methyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₂₈H₄₁NO₄SSi
MW: 515.78 g.mol⁻¹
white solid
90%

¹H NMR (500 MHz, CDCl₃): δ = 7.67 – 7.65 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.24 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.75 (d, *J* = 8.1 Hz, 1H), 6.71 – 6.69 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.64 (d, *J* = 1.9 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.59 – 3.56 (t, *J* = 7.5 Hz, 2H), 2.91 – 2.88 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.06 (s, 21H) ppm.

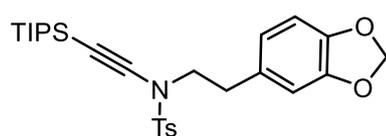
¹³C NMR (126 MHz, CDCl₃): δ = 149.0, 148.0, 144.6, 134.8, 130.3, 129.7, 127.8, 121.0, 112.2, 111.4, 96.3, 70.2, 56.0, 55.8, 53.0, 33.9, 21.8, 18.8, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₈H₄₂NO₄SSi 516.2596; Found 516.2598.

IR (neat): ν = 2941, 2863, 2162, 1367, 1167 cm⁻¹

Compound 2B

N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-4-methyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₂₇H₃₇NO₄SSi
MW: 499.74 g.mol⁻¹
white solid
29%

¹H NMR (500 MHz, CDCl₃): δ = 7.71 – 7.69 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.26 (d, *J* = 7.9 Hz, 2H), 6.68 – 6.67 (d, *J* = 7.9 Hz, 1H), 6.62 – 6.59 (m, 2H), 5.92 (s, 2H), 3.54 – 3.51 (t, *J* = 7.5 Hz, 2H), 2.87 – 2.84 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.06 (s, 21H) ppm.

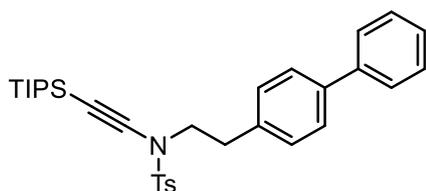
¹³C NMR (126 MHz, CDCl₃): δ = 147.8, 146.5, 144.6, 134.8, 131.4, 129.7, 127.8, 122.1, 109.4, 108.5, 101.0, 96.2, 70.3, 53.0, 34.1, 21.8, 18.8, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₂₇H₃₇KNO₄SSi 538.1850; Found 538.1856.

IR (neat): ν = 2940, 2863, 2163, 1365, 1167 cm⁻¹

Compound 2C

N-(2-([1,1'-biphenyl]-4-yl)ethyl)-4-methyl-N-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₃₂H₄₁NO₂SSi
MW: 531.83g.mol⁻¹
white solid
33%

¹H NMR (500 MHz, CDCl₃): δ = 7.71 – 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.56 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.47 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.33 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.22 (t, *J* = 8.2 Hz, 4H), 3.64 – 3.61 (t, *J* = 7.5 Hz, 2H), 3.01 – 2.98 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.07 (s, 21H) ppm.

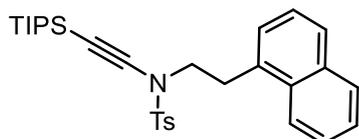
¹³C NMR (126 MHz, CDCl₃): δ = 144.6, 140.9, 139.8, 136.8, 134.8, 129.8, 129.7, 129.5, 128.9, 127.8, 127.4, 127.4, 127.1, 96.2, 70.4, 52.7, 34.0, 21.7, 18.8, 11.5, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₃₂H₄₂NO₂SSi 532.2706; Found 532.2708.

IR (neat): ν = 2941, 2863, 2164, 1370, 1168 cm⁻¹

Compound 2D

4-methyl-N-(2-(naphthalen-1-yl)ethyl)-N-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₃₀H₃₉NO₂SSi
MW: 505.79g.mol⁻¹
white solid
65%

¹H NMR (500 MHz, CDCl₃): δ = 8.00 – 7.98 (m, 1H), 7.85 – 7.84 (m, 1H), 7.73 – 7.71 (m, 3H), 7.51 – 7.47 (m, 2H), 7.38 – 7.33 (m, 2H), 7.25 – 7.23 (d, *J* = 8.5 Hz, 2H), 3.70 – 3.67 (m, 2H), 3.47 – 3.44 (m, 2H), 2.41 (s, 3H), 1.11 (s, 21H) ppm.

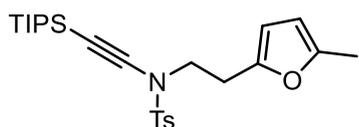
¹³C NMR (126 MHz, CDCl₃): δ = 144.6, 134.8, 134.0, 133.6, 131.9, 129.8, 129.0, 127.8, 127.7, 127.4, 126.4, 125.8, 125.7, 123.3, 96.5, 70.1, 52.2, 32.0, 22.0, 21.8, 18.8, 11.6 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₃₀H₃₉KNO₂SSi 544.2102; Found 544.2087.

IR (neat): ν = 2941, 2863, 2161, 1369, 1168 cm⁻¹

Compound 2F

4-methyl-N-(2-(5-methylfuran-2-yl)ethyl)-N-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₂₅H₃₇NO₃SSi
MW: 459.72g.mol⁻¹
white solid
72%

¹H NMR (500 MHz, CDCl₃): δ = 7.77 – 7.76 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.29 (d, *J* = 8.5 Hz, 2H), 5.90 – 5.89 (d, *J* = 2.9 Hz, 1H), 5.82 – 5.81 (dd, *J* = 2.9, 1 Hz, 1H), 3.60 – 3.57 (t, *J* = 7.6 Hz, 2H), 2.93 – 2.90 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.22 (s, 3H), 1.05 (s, 21H) ppm.

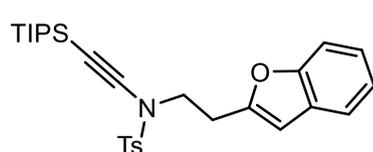
¹³C NMR (126 MHz, CDCl₃): δ = 151.3, 149.5, 144.7, 134.8, 129.7, 127.9, 107.6, 106.2, 96.0, 70.1, 50.1, 27.0, 21.8, 18.8, 18.6, 13.6, 11.5, 11.4 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₅H₃₇NaNO₃SSi 482.2156; Found 482.2153.

IR (neat): ν = 2942, 2864, 2161, 1369, 1169 cm⁻¹

Compound 2G

N-(2-(benzofuran-2-yl)ethyl)-4-methyl-N-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₂₈H₃₇NO₃SSi
MW: 495.75g.mol⁻¹
white solid
31%

¹H NMR (500 MHz, CDCl₃): δ = 7.70 – 7.68 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.42 (m, 1H), 7.38 – 7.36 (m, 1H), 7.24 – 7.20 (td, *J* = 7.3, 1.4 Hz, 1H), 7.19 – 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.16 – 7.15 (d, *J* = 8.5, 2H), 6.39 (d, *J* = 1.0 Hz, 1H), 3.78 – 3.75 (t, *J* = 7.1 Hz, 2H), 3.14 – 3.11 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.05 (s, 21H) ppm.

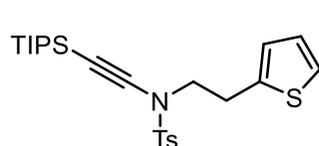
¹³C NMR (126 MHz, CDCl₃): δ = 154.9, 154.4, 144.7, 134.8, 129.8, 128.8, 127.7, 123.8, 122.7, 120.7, 111.0, 104.2, 95.7, 70.5, 49.5, 27.5, 21.8, 18.8, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₈H₃₇NaNO₃SSi 518.2161; Found 518.2163.

IR (neat): ν = 2942, 2864, 2161, 1370, 1169 cm⁻¹

Compound 2H

4-methyl-N-(2-(thiophen-2-yl)ethyl)-N-((triisopropylsilyl)ethynyl)benzenesulfonamide



C₂₄H₃₅NO₂S₂Si
MW: 461.19g.mol⁻¹
white solid
65%

¹H NMR (500 MHz, CDCl₃): δ = 7.75 – 7.73 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.28 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.13 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.91 – 6.89 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.82 – 6.81 (dd, *J* = 3.4, 1.1 Hz, 1H), 3.61 – 3.58 (t, *J* = 7.6 Hz, 2H), 3.18 – 3.15 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.06 (s, 21H) ppm.

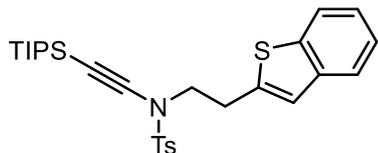
¹³C NMR (126 MHz, CDCl₃): δ = 144.6, 139.5, 134.5, 129.7, 127.7, 127.0, 125.8, 124.2, 95.8, 70.3, 52.6, 28.3, 21.7, 18.6, 11.4 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₄H₃₆NO₂S₂Si 462.1934; Found 462.1951.

IR (neat): ν = 2941, 2863, 2158, 1369, 1168 cm⁻¹

Compound 2I

N-(2-(benzo[*b*]thiophen-2-yl)ethyl)-4-methyl-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



$C_{28}H_{37}NO_2S_2Si$
MW: 511.84g.mol⁻¹
white solid
26%

¹H NMR (500 MHz, CDCl₃): δ = 7.74 – 7.73 (m, 1H), 7.66 – 7.64 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.32 – 7.29 (td, *J* = 7.2, 1.3 Hz, 1H), 7.28 – 7.25 (td, *J* = 7.2, 1.3 Hz, 1H), 7.12 – 7.10 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 0.9 Hz, 1H), 3.74 – 3.71 (t, *J* = 7.2 Hz, 2H), 3.25 – 3.22 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.05 (s, 21H) ppm.

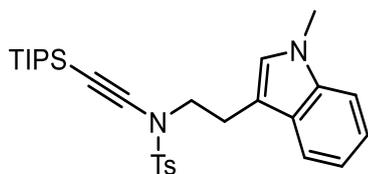
¹³C NMR (126 MHz, CDCl₃): δ = 144.6, 140.7, 140.1, 139.8, 134.6, 129.6, 127.7, 124.3, 124.0, 123.2, 122.8, 122.3, 95.7, 70.8, 52.2, 29.3, 21.7, 18.8, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₈H₃₇NaNO₂S₂Si 534.1927; Found 534.1929.

IR (neat): ν = 2941, 2863, 2159, 1369, 1169 cm⁻¹

Compound 2J

4-methyl-*N*-(2-(1-methyl-1H-indol-2-yl)ethyl)-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



$C_{29}H_{40}N_2O_2SSi$
MW: 508.79 g.mol⁻¹
white solid
93%

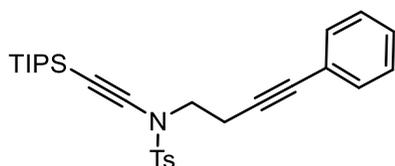
¹H NMR (500 MHz, CDCl₃): δ = 7.69 – 7.67 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.52 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.26 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.20 (m, 3H), 7.10 – 7.07 (m, 1H), 6.85 (s, 1H), 3.69 (s, 3H), 3.64 – 3.51 (t, *J* = 7.8 Hz, 2H), 3.12 – 3.09 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.08 (s, 21H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.4, 137.1, 134.9, 129.6, 127.7, 127.7, 127.3, 121.7, 119.1, 118.7, 110.2, 109.4, 96.4, 70.0, 52.0, 32.7, 24.0, 21.8, 18.8, 18.6 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₉H₄₁N₂O₂SSi 509.0650; Found 509.0563.

Compound 2K

4-methyl-*N*-(4-phenylbut-3-yn-1-yl)-*N*-((triisopropylsilyl)ethynyl)benzenesulfonamide



$C_{28}H_{37}NO_2SSi$
MW: 479.75 g.mol⁻¹
white solid
49%

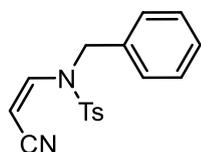
¹H NMR (500 MHz, CDCl₃): δ = 7.83 – 7.81 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.29 – 7.27 (m, 5H), 3.63 – 3.59 (t, *J* = 7.3 Hz, 2H), 2.78 – 2.75 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.04 (s, 21H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.8, 134.8, 131.8, 129.8, 128.3, 128.1, 127.9, 123.3, 95.7, 85.4, 82.6, 70.3, 60.2, 21.8, 19.3, 18.8, 11.5 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₈H₃₈NO₂Si 480.2386; Found 480.2387.

IR (neat): ν = 2941, 2863, 2155, 1370, 1168 cm⁻¹

Compound 3a (Z)-N-benzyl-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₁₇H₁₆N₂O₂S
MW: 312.39 mol⁻¹
White solid
m.p.: 123 °C
92%

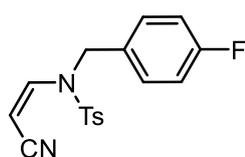
¹H NMR (400 MHz, CDCl₃): δ = 7.64 – 7.62 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.35 (d, *J* = 10.5 Hz, 1H), 7.32 – 7.30 (m, 3H), 7.29 – 7.26 (m, 4H), 5.11 (s, 2H), 4.45 (d, *J* = 10.5 Hz, 1H), 2.45 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.4, 141.3, 135.2, 134.5, 130.4, 128.7, 127.9, 127.4, 127.1, 116.3, 74.0, 48.9, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₇H₁₆NaN₂O₂S 335.0822; Found 335.0825.

IR (neat): ν = 2217, 1620, 1366, 1167, 663 cm⁻¹

Compound 3b (Z)-N-(2-cyanovinyl)-N-(4-fluorobenzyl)-4-methylbenzenesulfonamide



C₁₇H₁₅N₂FO₂S
MW: 330.37 g.mol⁻¹
white solid
86%

¹H NMR (500 MHz, CDCl₃): δ = 7.64 – 7.62 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.34 (d, *J* = 10.5 Hz, 1H), 7.34 – 7.32 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.25 (m, 2H), 5.06 (s, 2H), 4.21 (s, 2H), 4.46 – 4.44 (d, *J* = 10., 1H), 2.45 (s, 3H) ppm.

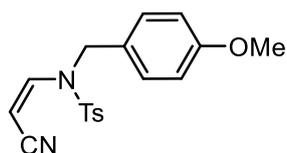
¹³C NMR (126 MHz, CDCl₃): δ = 163.5 (*J* = 247.01 Hz), 145.6, 141.2, 135.1, 130.4, 130.3 (*J* = 3.2 Hz), 129.1 (*J* = 8.2 Hz), 127.3, 116.3, 115.8 (*J* = 21.7 Hz), 74.0, 48.3, 21.8 ppm.

¹⁹F NMR (282 MHz, CDCl₃): δ = -114.41 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₇H₁₆FN₂O₂S 331.0909; Found 331.0910.

IR (neat): ν = 2208, 1620, 1360, 1167, 681 cm⁻¹

Compound 3c (Z)-N-(2-cyanovinyl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide



C₁₈H₁₈N₂O₃S
MW: 342.41 g.mol⁻¹
white solid
88%

¹H NMR (500 MHz, CDCl₃): δ = 7.63 - 7.61 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.31 (d, *J* = 10.5 Hz, 1H), 7.31 – 7.30 (d, *J* = 7.8 Hz, 2H), 7.23 – 7.21 (d, *J* = 8.8 Hz, 2H), 6.83 – 6.82 (d, *J* = 8.8 Hz, 2H), 5.03 (s, 2H), 4.44 – 4.42 (d, *J* = 10.5 Hz, 1H), 3.78 (s, 3H), 2.44 (s, 3H) ppm.

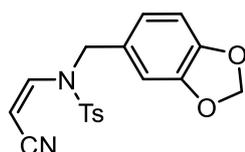
¹³C NMR (126 MHz, CDCl₃): δ = 159.4, 145.3, 141.3, 135.3, 130.3, 128.7, 127.3, 126.4, 116.5, 114.1, 73.9, 55.4, 48.5, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₈H₁₈KN₂O₃S 381.0669; Found 381.0673.

IR (neat): ν = 2207, 1617, 1356, 1167, 681 cm⁻¹

Compound 3d

(Z)-N-(benzo[d][1,3]dioxol-5-ylmethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₁₈H₁₆N₂O₄S
MW: 356.39 g.mol⁻¹
white solid
91%

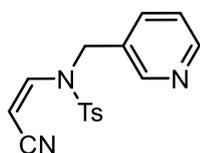
¹H NMR (400 MHz, CDCl₃): δ = 7.62 - 7.60 (d, J = 8.4 Hz, 2H), 7.34 - 7.32 (d, J = 10.5 Hz, 1H), 7.32 - 7.0 (d, J = 7.9 Hz, 2H), 6.78 - 6.71 (m, 3H), 5.92 (s, 2H), 5.00 (s, 2H), 4.46 - 4.44 (d, J = 10.5 Hz, 1H), 2.44 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 148.0, 147.3, 145.3, 141.3, 135.2, 130.2, 128.1, 127.2, 120.9, 116.3, 180.3, 107.7, 101.2, 73.9, 48.6, 21.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₈H₁₆NaN₂O₄ 379.0722; Found 379.0726.

IR (neat): ν = 2208, 1619, 1357, 1165, 683 cm⁻¹

Compound 3e (Z)-N-(2-cyanovinyl)-4-methyl-N-(pyridin-3-ylmethyl)benzenesulfonamide



C₁₆H₁₅N₃O₂S
MW: 313.37 g.mol⁻¹
colorless oil
80%

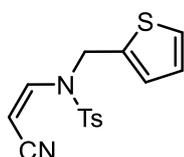
¹H NMR (300 MHz, CDCl₃): δ = 8.54-8.52 (m, 2H), 7.65 - 7.62 (d, J = 8.4 Hz, 2H), 7.62 - 7.59 (m, 1H), 7.40 - 7.36 (d, J = 10.4 Hz, 1H), 7.34 - 7.31 (d, J = 8.1 Hz, 2H), 7.24 - 7.21 (m, 1H), 5.12 (s, 2H), 4.49 - 4.46 (d, J = 10.4 Hz, 1H), 2.45 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 149.4, 148.8, 145.8, 141.1, 134.9, 134.8, 130.5, 130.4, 127.3, 123.5, 116.2, 74.1, 46.7, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₆N₃O₂S 314.0957; Found 314.0957.

IR (neat): ν = 2208, 1620, 1357, 1166, 683 cm⁻¹

Compound 3f (Z)-N-(2-cyanovinyl)-4-methyl-N-(thiophen-2-ylmethyl)benzenesulfonamide



C₁₅H₁₄N₂O₂S₂
MW: 318.40 g.mol⁻¹
colorless oil
86%

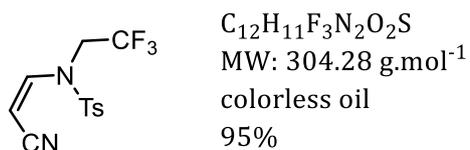
¹H NMR (500 MHz, CDCl₃): δ = 7.61 – 7.60 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.28 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.23 (d, *J* = 10.5 Hz, 1H), 7.23 – 7.22 (m, 1H), 7.11 – 7.10 (m, 1H), 6.91 – 6.89 (m, 1H), 5.30 (s, 2H), 4.52 – 4.50 (d, *J* = 10.5 Hz, 1H), 2.43 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.4, 140.9, 136.9, 135.2, 130.3, 128.3, 127.3, 126.6, 126.5, 116.5, 74.0, 44.3, 21.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₅H₁₄NaN₂O₂S₂ 341.0389; Found 341.0390.

IR (neat): ν = 2207, 1618, 1357, 1165, 678 cm⁻¹

Compound 3g (Z)-N-(2-cyanovinyl)-4-methyl-N-(2,2,2-trifluoroethyl)benzenesulfonamide



¹H NMR (400 MHz, CDCl₃): δ = 7.71 - 7.70 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.38 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.17 (d, *J* = 10.5 Hz, 1H), 4.67 – 4.61 (q, *J* = 8.0 Hz, 2H), 4.65 – 4.63 (d, *J* = 10.5 Hz, 1H), 2.47 (s, 3H) ppm.

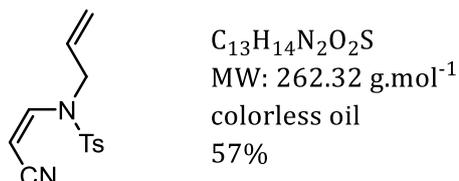
¹³C NMR (126 MHz, CDCl₃): δ = 146.3, 140.8, 134.5, 130.6, 127.6, 126.5 – 119.8 (q, *J* = 282.2 Hz), 115.4, 76.3, 45.8 (q, *J* = 36.5 Hz), 21.9 ppm.

¹⁹F NMR (282 MHz, CDCl₃): δ = -69.01 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₂H₁₁F₃NaN₂O₂S 327.0385; Found 327.0378.

IR (neat): ν = 2211, 1621, 1362, 1164, 673 cm⁻¹

Compound 3h (Z)-N-allyl-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



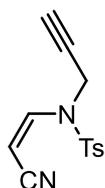
¹H NMR (300 MHz, CDCl₃): δ = 7.64 - 7.61 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.37 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (d, *J* = 10.5 Hz, 1H), 5.74 – 5.63 (m, 1H), 5.21 – 5.18 (m, 1H), 5.16 – 5.14 (m, 1H), 4.43 – 4.40 (m, 2H), 4.40 – 4.36 (d, *J* = 10.5 Hz, 1H), 2.39 (s, 3H) ppm

¹³C NMR (126 MHz, CDCl₃): δ = 145.4, 140.7, 135.0, 130.5, 130.3, 127.4, 118.5, 116.6, 72.7, 47.4, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₃H₁₄NaN₂O₂S 285.0668; Found 285.0661.

IR (neat): ν = 2207, 1618, 1356, 1165, 679 cm⁻¹

Compound 3i (Z)-N-(2-cyanovinyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide



$C_{13}H_{12}N_2O_2S$
MW: 260.31 $g \cdot mol^{-1}$
colorless oil
57%

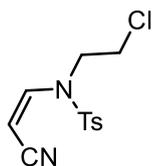
1H NMR (500 MHz, $CDCl_3$): δ = 7.74 - 7.73 (d, J = 8.4 Hz, 2H), 7.37 - 7.35 (d, J = 8.6 Hz, 2H), 7.20 - 7.17 (d, J = 10.5 Hz, 1H), 4.74 - 4.73 (d, J = 2.5 Hz, 2H), 4.59 - 4.56 (d, J = 10.6 Hz, 1H), 2.45 (s, 3H), 2.19 (t, J = 2.5 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.8, 140.0, 134.7, 130.3, 127.7, 116.0, 76.1, 75.3, 74.4, 35.6, 21.8 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{12}NaN_2O_2S$ 283.0511; Found 283.0498.

IR (neat): ν = 2209, 1619, 1362, 1165, 673 cm^{-1}

Compound 3j (Z)-N-(2-chloroethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



$C_{12}H_{13}ClN_2O_2S$
MW: 284.75 $g \cdot mol^{-1}$
colorless oil
53%

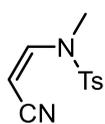
1H NMR (500 MHz, $CDCl_3$): δ = 7.71 - 7.69 (d, J = 8.5 Hz, 2H), 7.39 - 7.37 (d, J = 8.5 Hz, 2H), 7.28 - 7.26 (d, J = 10.6 Hz, 1H), 4.52 - 4.50 (d, J = 10.5 Hz, 1H), 4.08 - 4.05 (t, J = 7.2 Hz, 2H), 3.74 - 3.72 (t, J = 7.2 Hz, 2H), 2.46 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.0, 141.2, 134.3, 130.6, 127.4, 116.0, 72.9, 45.6, 40.0, 21.8 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}NaClN_2O_2S$ 307.0278; Found 307.0280.

IR (neat): ν = 2208, 1619, 1357, 1166, 680 cm^{-1}

Compound 3k (Z)-N-(2-cyanovinyl)-N,4-dimethylbenzenesulfonamide



$C_{11}H_{12}N_2O_2S$
MW: 236.28 $g \cdot mol^{-1}$
colorless oil
68%

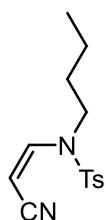
1H NMR (500 MHz, $CDCl_3$): δ = 7.68 - 7.66 (d, J = 8.4 Hz, 2H), 7.38 - 7.36 (d, J = 4.9 Hz, 2H), 7.31 - 7.29 (d, J = 10.3 Hz, 1H), 4.45 - 4.43 (d, J = 10.3 Hz, 1H), 3.39 (s, 3H), 2.46 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.5, 142.4, 134.0, 130.5, 127.4, 116.9, 72.8, 33.1, 21.8 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}NaN_2O_2S$ 259.0511; Found 259.0520

IR (neat): ν = 2207, 1622, 1358, 1162, 678 cm^{-1}

Compound 3l (Z)-N-butyl-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



$C_{14}H_{18}N_2O_2S$
MW: 278.37 g.mol⁻¹
colorless oil
54%

¹H NMR (500 MHz, CDCl₃): δ = 7.68 - 7.66 (d, J = 8.4 Hz, 2H), 7.37 - 7.35 (d, J = 8.6 Hz, 2H), 7.27 - 7.25 (d, J = 10.5 Hz, 1H), 4.42 - 4.40 (d, J = 10.5 Hz, 1H), 3.73 - 3.70 (m, 2H), 2.45 (s, 3H), 1.71 - 1.63 (m, 2H), 1.40 - 1.35 (m, 2H), 0.93 - 0.90 (t, J = 7.4 Hz, 3H) ppm.

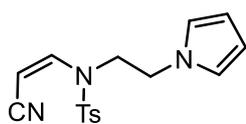
¹³C NMR (126 MHz, CDCl₃): δ = 145.2, 141.1, 135.0, 130.3, 127.2, 116.6, 71.6, 45.8, 30.5, 21.7, 19.0, 13.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₁₈NaN₂O₂S 301.0981; Found 301.0978.

IR (neat): ν = 2207, 1617, 1356, 1167, 681 cm⁻¹

Compound 3m

(Z)-N-(2-(1H-pyrrol-1-yl)ethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



$C_{16}H_{17}N_3O_2S$
MW: 315.39 g.mol⁻¹
colorless oil
51%

¹H NMR (500 MHz, CDCl₃): δ = 7.68 - 7.67 (d, J = 8.5 Hz, 2H), 7.38 - 7.36 (d, J = 8.5 Hz, 2H), 7.31 - 7.28 (d, J = 10.5 Hz, 1H), 6.79 (t, J = 2.0 Hz, 2H), 6.15 (t, J = 2.0 Hz, 2H), 4.41 - 4.40 (d, J = 10.5 Hz, 1H), 4.21-4.19 (m, 2H), 3.98 - 3.95 (m, 2H), 2.38 (s, 3H) ppm.

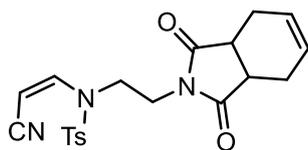
¹³C NMR (126 MHz, CDCl₃): δ = 145.7, 141.1, 134., 130.4, 127.2, 121.0, 116.4, 108.8, 72.1, 47.6, 46.4, 21.6 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₆H₁₇NaN₃O₂S 338.0932; Found 338.0934.

IR (neat): ν = 2208, 1618, 1357, 1163, 676 cm⁻¹

Compound 3n

(Z)-N-(2-cyanovinyl)-N-(2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-isoindol-2-yl)ethyl)-4-methylbenzenesulfonamide



$C_{20}H_{21}N_3O_4S$
MW: 399.46 g.mol⁻¹
colorless oil
56%

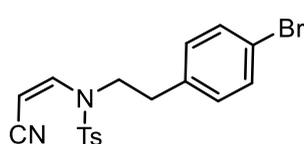
¹H NMR (500 MHz, CDCl₃): δ = 7.59 - 7.58 (d, J = 8.4 Hz, 2H), 7.35 - 7.33 (d, J = 7.9 Hz, 2H), 7.24 - 7.22 (d, J = 10.6 Hz, 1H), 5.91 - 5.90 (m, 2H), 4.56 - 4.54 (d, J = 10.6 Hz, 1H), 3.96 - 3.95 (m, 2H), 3.89 - 3.87 (m, 2H), 3.19 - 3.17 (m, 2H), 2.60 - 2.55 (m, 2H), 2.44 (s, 3H), 2.31 - 2.26 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 180.3, 145.5, 140.8, 134.2, 130.3, 127.7, 127.0, 116.4, 72.9, 42.5, 39.0, 36.1, 23.1, 21.5 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₀H₂₁N₃O₄S 422.1145; Found 422.1131.

IR (neat): ν = 2209, 1703, 1338, 11165, 679 cm⁻¹

Compound 3o (Z)-N-(4-bromophenethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₁₈H₁₇BrN₂O₂S
MW: 405.31 g.mol⁻¹
colorless oil
34%

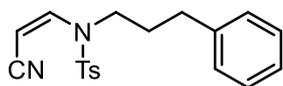
¹H NMR (500 MHz, CDCl₃): δ = 7.68 - 7.67 (d, J = 8.4 Hz, 2H), 7.42 - 7.40 (d, J = 8.6 Hz, 2H), 7.37 - 7.35 (d, J = 8.6 Hz, 2H), 7.32 - 7.30 (d, J = 10.6 Hz, 1H), 7.21 - 7.20 (d, J = 8.4 Hz, 2H), 4.49 - 4.47 (d, J = 10.6 Hz, 1H), 3.92 - 3.89 (m, 2H), 3.03 - 2.99 (m, 2H), 2.45 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.7, 141.2, 136.1, 134.8, 131.9, 131.1, 130.5, 127.48, 121.0, 117.1, 71.9, 47.2, 34.6, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₈H₁₇NaBrN₂O₂S 427.0074; Found 427.0086.

IR (neat): ν = 2206, 1619, 1332, 1164, 681 cm⁻¹

Compound 3p (Z)-N-(2-cyanovinyl)-4-methyl-N-(3-phenylpropyl)benzenesulfonamide



C₁₉H₂₀N₂O₂S
MW: 340.44 g.mol⁻¹
colorless oil
58%

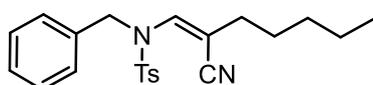
¹H NMR (500 MHz, CDCl₃): δ = 7.62 - 7.60 (d, J = 8.4 Hz, 2H), 7.34 - 7.32 (d, J = 8.5 Hz, 2H), 7.30 - 7.27 (m, 3H), 7.21 - 7.18 (m, 3H), 4.44 - 4.42 (d, J = 10.5 Hz, 1H), 3.78-3.75 (m, 2H), 2.69 - 2.66 (m, 2H), 2.45 (s, 3H), 2.04 - 1.98 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.5, 141.2, 140.8, 134.9, 130.4, 128.6, 128.6, 127.4, 126.2, 116.8, 71.7, 45.8, 32.0, 30.3, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₉H₂₀KN₂O₂S 379.0877; Found 379.0872.

IR (neat): ν = 2205, 1617, 1358, 1164, 681 cm⁻¹

Compound 3' (Z)-N-benzyl-N-(2-cyanohept-1-en-1-yl)-4-methylbenzenesulfonamide



C₂₂H₂₆N₂O₂S
MW: 382.52 g.mol⁻¹
colorless oil
14%

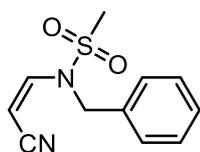
¹H NMR (300 MHz, CDCl₃): δ = 7.68 – 7.65 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.26 (m, 7H), 7.09 (s, 1H), 5.05 (s, 2H), 2.45 (s, 3H), 2.12 (t, *J* = 7.3 Hz, 2H), 1.44 – 1.34 (m, 2H), 1.12 – 1.02 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.0, 137.0, 135.7, 134.9, 130.3, 128.6, 127.9, 127.6, 127.2, 117.7, 94.5, 49.3, 34.0, 30.4, 28.2, 22.3, 21.8, 14.1 ppm.

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₂₂H₂₆N₂NaO₂S 405.1622; Found 405.1607.

IR (neat): ν = 2206, 1630, 1362, 1167, 667 cm⁻¹

Compound 3q (Z)-N-benzyl-N-(2-cyanovinyl)methanesulfonamide



C₁₁H₁₂N₂O₂S
MW: 236.28 g.mol⁻¹
colorless oil
63%

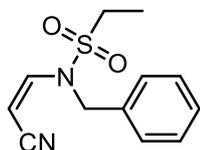
¹H NMR (300 MHz, CDCl₃): δ = 7.41 – 7.39 (m, 4H), 7.38 – 7.34 (m, 1H), 7.22 – 7.19 (d, *J* = 10.5 Hz, 1H), 5.28 (s, 2H), 4.55 – 4.51 (d, *J* = 10.5, 1H), 2.85 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 141.5, 134.9, 129.4, 128.7, 127.9, 116.4, 74.2, 49.3, 42.1 ppm.

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₁₁H₁₂NaN₂O₂S 259.0512; Found 259.0522.

IR (neat): ν = 2208, 1620, 1348, 1156, 767 cm⁻¹

Compound 3r (Z)-N-benzyl-N-(2-cyanovinyl)ethanesulfonamide



C₁₂H₁₄N₂O₂S
MW: 250.31 g.mol⁻¹
colorless oil
64%

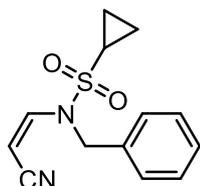
¹H NMR (500 MHz, CDCl₃): δ = 7.42 – 7.37 (m, 4H), 7.35 – 7.33 (m, 1H), 7.20 – 7.17 (d, *J* = 10.5 Hz, 1H), 5.2 (s, 2H), 4.49 – 4.48 (d, *J* = 10.5 Hz, 1H), 3.01 – 2.96 (q, *J* = 7.5 Hz, 2H), 1.34 – 1.31 (t, *J* = 7.5 Hz, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 142.0, 134.8, 129.0, 128.4, 127.6, 116.3, 73.6, 49.3, 49.3, 8.0 ppm.

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₁₂H₁₄NaN₂O₂S 273.0668; Found 273.0676.

IR (neat): ν = 2208, 1619, 1346, 1150, 726 cm⁻¹

Compound 3s (Z)-N-benzyl-N-(2-cyanovinyl)cyclopropanesulfonamide



C₁₃H₁₄N₂O₂S
MW: 262.32 g.mol⁻¹
colorless oil
86%

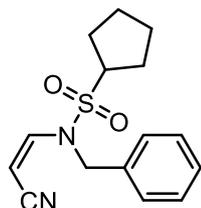
¹H NMR (400 MHz, CDCl₃): δ = 7.41 – 7.36 (m, 4H), 7.33 – 7.30 (m, 1H), 7.20 – 7.17 (d, *J* = 10.5 Hz, 1H), 5.30 (s, 2H), 4.47 – 4.44 (d, *J* = 10.5 Hz, 1H), 2.27 – 2.22 (m, 1H), 1.12 – 1.19 (m, 2H), 1.02 – 0.97 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 141.8, 135.1, 128., 128.2, 127.3, 116.4, 73.2, 49.3, 31.9, 6.5 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₃H₁₄NaN₂O₂S 285.0655; Found 285.0668.

IR (neat): ν = 2207, 1619, 1349, 1152, 712 cm⁻¹

Compound 3t (Z)-N-benzyl-N-(2-cyanovinyl)cyclopentanesulfonamide



C₁₅H₁₈N₂O₂S
MW:290.38 g.mol⁻¹
white soild
60%

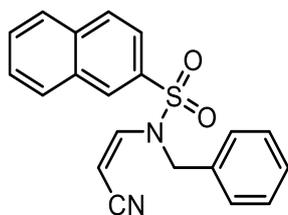
¹H NMR (500 MHz, CDCl₃): δ = 7.41 – 7.36 (m, 4H), 7.33 – 7.20 (m, 1H), 7.20 – 7.18 (d, *J* = 10.3 Hz, 1H), 5.26 (s, 2H), 4.45 – 4.43 (d, *J* = 10.3 Hz, 1H), 3.34 – 3.30 (m, 1H), 2.01 – 1.96 (m, 4H), 1.83 – 1.80 (m, 2H), 1.64 – 1.61 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 142.3, 134.9, 128.9, 128.3, 127.5, 116.5, 73.6, 64.1, 49.5, 28.1, 25.5 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₅H₁₈NaN₂O₂S 313.0981; Found 313.0986.

IR (neat): ν = 2207, 1618, 1325, 1149, 695 cm⁻¹

Compound 3u (Z)-N-benzyl-N-(2-cyanovinyl)naphthalene-2-sulfonamide



C₂₀H₁₆N₂O₂S
MW:348.42 g.mol⁻¹
colorless oil
86%

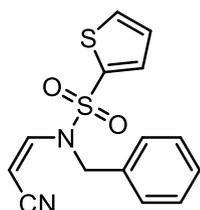
¹H NMR (500 MHz, CDCl₃): δ = 8.33 – 8.32 (d, *J* = 2.1 Hz, 1H), 7.98 – 7.96 (d, *J* = 8.8 Hz, 1H), 7.94 – 7.92 (d, *J* = 10.0 Hz, 2H), 7.72 – 7.69 (td, *J* = 8.0 Hz, 1.3 Hz, 1H), 7.67 – 7.65 (dd, *J* = 8 Hz, 1.3 Hz, 1H), 7.66 – 7.64 (dd, *J* = 8.7 Hz, 2.1 Hz, 1H), 7.46 – 7.44 (d, *J* = 10.5 Hz, 1H), 7.30 – 7.21 (m, 5H), 5.18 (s, 2H), 4.49 – 4.47 (d, *J* = 10.5 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 141.4, 135.4, 134.8, 134.4, 132.1, 130.3, 129.9, 129.6, 129.6, 128.7, 128.2, 128.2, 128.0, 127.2, 121.6, 116.2, 74.2, 49.2 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₀H₁₆NaN₂O₂S 371.0824; Found 371.0801.

IR (neat): ν = 2208, 1621, 1353, 1167, 680 cm⁻¹

Compound 3v (Z)-N-benzyl-N-(2-cyanovinyl)thiophene-2-sulfonamide



$C_{14}H_{12}N_2O_2S_2$
MW:304.38 g.mol⁻¹
colorless oil
82%

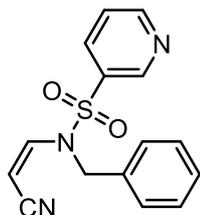
¹H NMR (500 MHz, CDCl₃): δ = 7.69 – 7.68 (dd, J = 5.0, 1.4 Hz, 1H), 7.55 – 7.54 (dd, J = 3.8, 1.4 Hz, 1H), 7.35 – 7.33 (d, J = 10.6 Hz, 1H), 7.32 – 7.29 (m, 5H), 7.10 – 7.08 (dd, J = 3.8, 5.0 Hz, 1H), 5.20 (s, 2H), 4.53 – 4.51 (d, J = 10.6 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 140.9, 138.5, 134.4, 134.2, 134.0, 128.8, 128.1, 127.1, 116.1, 75.1, 49.2 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₁₂NaN₂O₂S₂ 327.0232; Found 327.0219.

IR (neat): ν = 2208, 1620, 1364, 1164, 682 cm⁻¹

Compound 3w (Z)-N-benzyl-N-(2-cyanovinyl)pyridine-3-sulfonamide



$C_{15}H_{13}N_3O_2S$
MW:299.34 g.mol⁻¹
colorless oil
89%

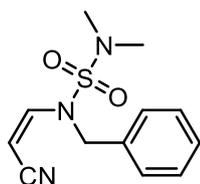
¹H NMR (500 MHz, CDCl₃): δ = 8.93 – 8.92 (dd, J = 2.5, 0.9 Hz, 1H), 8.82 – 8.81 (dd, J = 4.9, 1.6 Hz, 1H), 7.25 – 7.23 (ddd, J = 8.1, 2.5, 1.6 Hz, 1H), 7.41 – 7.38 (ddd, J = 8.1, 4.9, 0.9 Hz, 1H), 7.38 – 7.36 (d, J = 10.6 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.24 – 7.22 (m, 2H), 5.21 (s, 2H), 4.59 – 4.57 (d, J = 10.6 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 154.4, 148.0, 140.8, 135.3, 134.8, 133.8, 128.9, 128.3, 127.4, 124.1, 115.8, 75.6, 49.4 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₅H₁₄N₃O₂S 300.0801; Found 300.0795.

IR (neat): ν = 2210, 1621, 1326, 1171, 732 cm⁻¹

Compound 3x (Z)-N-benzyl-N-(2-cyanovinyl)-N',N'-dimethylsulfonamide



$C_{12}H_{15}N_3O_2S$
MW:265.33 g.mol⁻¹
colorless oil
57%

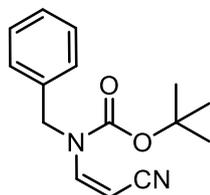
¹H NMR (500 MHz, C₆D₆): δ = 7.39 – 7.38 (d, J = 7.8 Hz, 2H), 7.13 – 7.10 (t, J = 7.4 Hz, 2H), 7.04 – 7.01 (t, J = 7.4 Hz, 1H), 6.78 – 6.76 (d, J = 10.4 Hz, 1H), 4.96 (s, 2H), 3.61 – 3.60 (d, J = 10.4 Hz, 1H), 2.01 (s, 6H) ppm.

¹³C NMR (126 MHz, C₆D₆): δ = 143.3, 136.7, 129.7, 128.5, 117.5, 73.2, 50.7, 38.1 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₂H₁₅NaN₃O₂S 288.0777; Found 288.0764.

IR (neat): ν = 2206, 1616, 1328, 1155, 719 cm⁻¹

Compound 3y tert-butyl (Z)-benzyl(2-cyanovinyl)carbamate



C₁₅H₁₈N₂O₂
MW: 258.32 g.mol⁻¹
colorless oil
29%

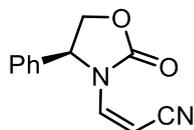
¹H NMR (500 MHz, CDCl₃): δ = 7.51 - 7.49 (d, *J* = 10.7 Hz, 1H), 7.37 - 7.33 (m, 2H), 7.29 - 7.27 (m, 1H), 7.25 - 7.23 (m, 2H), 5.20 (s, 2H), 4.43 - 4.41 (d, *J* = 10.7 Hz, 1H), 1.46 (s, 9H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 152.3, 142.4, 136.5, 128.6, 127.4, 126.5, 116.9, 84.1, 72.4, 47.6, 27.9 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₅H₁₈NaN₂O₂ 281.1260; Found 281.1245.

IR (neat): ν = 2205, 1726, 1624, 1331, 1150, 726 cm⁻¹

Compound 3z (S,Z)-3-(2-oxo-4-phenyloxazolidin-3-yl)acrylonitrile



C₁₂H₁₀N₂O₂
MW: 214.22 g.mol⁻¹
colorless oil
33%

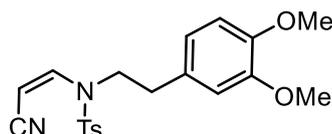
¹H NMR (400 MHz, CDCl₃): δ = 7.44 - 7.41 (m, 3H), 7.30 - 7.28 (m, 2H), 7.26 - 7.24 (d, *J* = 10.1 Hz, 1H), 5.89 - 5.86 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.78 (t, *J* = 8.5 Hz, 1H), 4.59 - 4.56 (d, *J* = 10.1 Hz, 1H), 4.31-4.28 (dd, *J* = 8.5, 2.6 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 155.3, 138.5, 137.7, 129.7, 129.6, 129.4, 127.0, 125.9, 116.2, 71.7, 57.3 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₂H₁₀NaN₂O₂ 237.0633; Found 237.0634.

IR (neat): ν = 2200, 1759, 1632, 1412, 1211, 752 cm⁻¹

Compound 3A (Z)-N-(2-cyanovinyl)-N-(3,4-dimethoxyphenethyl)-4-methylbenzenesulfonamide



C₂₀H₂₂N₂O₄S
MW: 386.47 g.mol⁻¹
colorless oil
52%

¹H NMR (500 MHz, CDCl₃): δ = 7.69 - 7.68 (d, *J* = 8.4 Hz, 2H), 7.36 - 7.34 (d, *J* = 7.8 Hz, 2H), 7.32 - 7.30 (d, *J* = 10.6 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.85 - 6.63 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.80 - 6.78 (d, *J* = 8.1 Hz, 1H), 4.48 - 4.46 (d, *J* = 10.6 Hz, 1H), 3.94-3.90 (m, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.0 - 2.97 (m, 2H), 2.44 (s, 3H) ppm.

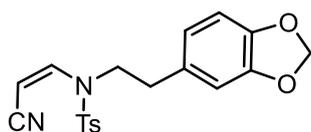
¹³C NMR (126 MHz, CDCl₃): δ = 149.1, 148.0, 145.5, 141.2, 134.9, 130.5, 129.8, 127.4, 121.3, 117.3, 112.6, 111.4, 71.7, 56.0, 56.0, 47.7, 34.7, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₀H₂₂NaN₂O₄S 409.1192; Found 409.1178.

IR (neat): ν = 2206, 1617, 1330, 1160, 678 cm⁻¹

Compound 3B

(Z)-N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₁₉H₁₈N₂O₄S
MW: 370.42 g.mol⁻¹
white solid
35%

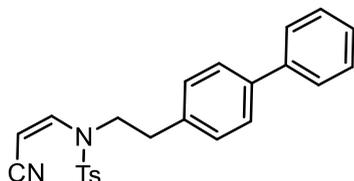
¹H NMR (500 MHz, CDCl₃): δ = 7.70 - 7.68 (d, J = 8.4 Hz, 2H), 7.37 - 7.35 (d, J = 8.4 Hz, 2H), 7.32 - 7.30 (d, J = 10.6, 1H), 6.82 (d, J = 1.7, 1H), 6.79 - 6.77 (dd, J = 8.1, 1.7 Hz, 1H), 7.74 - 7.772 (d, J = 7.9 Hz, 1H), 5.91 (s, 2H), 4.48 - 4.46 (d, J = 10.6 Hz, 1H), 3.91-3.88 (m, 2H), 2.97 - 2.93 (m, 2H), 2.45 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 147.9, 146.6, 145.6, 141.2, 134.9, 130.9, 130.5, 127.4, 122.4, 117.1, 109.7, 108.6, 101.0, 71.8, 47.6, 34.8, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₉N₂O₄S 371.1058; Found 371.1060.

IR (neat): ν = 2941, 2864, 2207, 2164, 1618, 1358, 1164, 679 cm⁻¹

Compound 3C (Z)-N-(2-([1,1'-biphenyl]-4-yl)ethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₂₄H₂₂N₂O₂S
MW: 402.51 g.mol⁻¹
white solid
50%

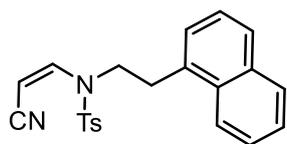
¹H NMR (500 MHz, CDCl₃): δ = 7.72 - 7.70 (d, J = 8.4 Hz, 2H), 7.57 - 7.55 (m, 2H), 7.54 - 7.52 (d, J = 8.2 Hz, 2H), 7.44 - 7.40 (m, 4H), 7.37 - 7.33 (m, 4H), 4.51 - 4.49 (d, J = 10.5 Hz, 1H), 4.00-3.97 (m, 2H), 3.11 - 3.07 (m, 2H), 2.45 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.6, 141.2, 141.0, 140.0, 136.3, 134.9, 130.5, 129.8, 128.9, 127.6, 127.4, 127.4, 127.2, 117.1, 71.8, 47.5, 34.8, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₄H₂₂NaN₂O₂S 425.1278; Found 425.1294.

IR (neat): ν = 2206, 1618, 1332, 1163, 678 cm⁻¹

Compound 3D (Z)-N-(2-cyanovinyl)-4-methyl-N-(2-(naphthalen-1-yl)ethyl)benzenesulfonamide



$C_{22}H_{20}N_2O_2S$
MW: 376.47 g.mol⁻¹
white solid
60%

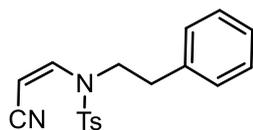
¹H NMR (500 MHz, CDCl₃): δ = 8.29 – 8.27 (d, J = 8.5 Hz, 1H), 7.88 – 7.86 (d, J = 8.2 Hz, 1H), 7.76 – 7.74 (d, J = 8.3 Hz, 1H), 6.68 – 7.66 (d, J = 8.4 Hz, 2H), 7.66 – 7.65 (m, 1H), 7.64 – 7.61 (m, 1H), 7.53 – 7.50 (m, 1H), 7.42 – 7.39 (m, 2H), 7.30 – 7.28 (d, J = 8.7 Hz, 2H), 4.55 – 4.53 (d, J = 10.5 Hz, 1H), 4.03–3.99 (m, 2H), 3.64 – 3.61 (m, 2H), 2.40 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.6, 141.4, 134.6, 134.0, 133.3, 132.0, 130.5, 129.0, 128.1, 127.8, 127.4, 126.5, 126.0, 125.8, 123.6, 117.1, 71.8, 46.6, 32.6, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₂₂H₂₀KN₂O₂S 415.0877; Found 415.0869.

IR (neat): ν = 2207, 1619, 1356, 1164, 680 cm⁻¹

Compound 3E (Z)-N-(2-cyanovinyl)-4-methyl-N-phenethylbenzenesulfonamide



$C_{18}H_{18}N_2O_2S$
MW: 326.41 g.mol⁻¹
colorless oil
51%

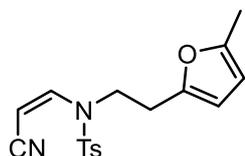
¹H NMR (400 MHz, CDCl₃): δ = 7.69 - 7.67 (d, J = 8.3 Hz, 2H), 7.53 – 7.28 (m, 6H), 7.27 – 7.20 (m, 2H), 4.48 – 4.46 (d, J = 10.5 Hz, 1H), 3.96–3.92 (m, 2H), 3.05 – 3.00 (m, 2H), 2.43 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.5, 141.1, 137.2, 134.9, 130.48, 129.36, 128.81, 127.4, 127.0, 117.0, 71.8, 47.5, 35.1, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₈H₁₈KN₂O₂S 365.0720; Found 365.0725.

IR (neat): ν = 2206, 1618, 1356, 1164, 679 cm⁻¹

Compound 3F (Z)-N-(2-cyanovinyl)-4-methyl-N-(2-(5-methylfuran-2-yl)ethyl)benzenesulfonamide



$C_{17}H_{18}N_2O_3S$
MW: 330.40 g.mol⁻¹
colorless oil
66%

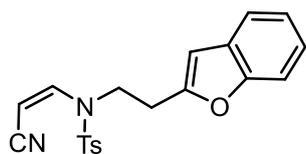
¹H NMR (500 MHz, CDCl₃): δ = 7.71 - 7.69 (d, J = 8.4 Hz, 2H), 7.37 – 7.35 (d, J = 8.6 Hz, 2H), 7.29 – 7.27 (d, J = 10.6 Hz, 1H), 6.03 – 6.02 (d, J = 3.0 Hz, 1H), 5.84 – 5.83 (dd, J = 3.1, 1.1 Hz, 1H), 4.47 – 4.45 (d, J = 10.6 Hz, 1H), 4.03–4.00 (m, 2H), 2.99 – 2.97 (m, 2H), 2.46 (s, 3H), 2.25 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 151.4, 148.8, 145.5, 141.1, 135.0, 130.5, 127.4, 116.4, 108.2, 106.3, 72.2, 44.9, 27.7, 21.8, 13.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₇H₁₈NaN₂O₃S 353.0930; Found 353.0926.

IR (neat): ν = 2209, 1620, 1358, 1165, 680 cm⁻¹

Compound 3G (Z)-N-(2-(benzofuran-2-yl)ethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₂₀H₁₈N₂O₃S
MW: 366.44 g.mol⁻¹
white solid
34%

¹H NMR (500 MHz, CDCl₃): δ = 7.71 - 7.69 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.46 (dq, *J* = 7.6, 0.7 Hz, 1H), 7.43 – 7.41 (dq, *J* = 8.1, 1.0 Hz, 1H), 7.34 – 7.32 (m, 3H), 7.24 – 7.21 (td, *J* = 7.2, 1.4 Hz, 1H), 7.19 – 7.16 (td, *J* = 7.4, 1.1 Hz, 1H), 6.55 (d, *J* = 0.9 Hz, 1H), 4.51 – 4.49 (d, *J* = 10.6 Hz, 1H), 4.17-4.14 (m, 2H), 3.22 – 3.19 (m, 2H), 2.44 (s, 3H) ppm.

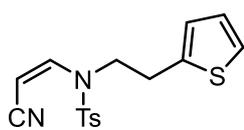
¹³C NMR (126 MHz, CDCl₃): δ = 155.0, 153.6, 145.7, 141.1, 134.7, 130.5, 128.8, 127.4, 123.9, 122.7, 120.8, 116.5, 111.1, 104.6, 72.3, 44.4, 28.2, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₀H₁₉N₂O₃S 367.1106; Found 367.1111.

IR (neat): ν = 2208, 1619, 1359, 1165, 679 cm⁻¹

Compound 3H

(Z)-N-(2-cyanovinyl)-4-methyl-N-(2-(thiophen-2-yl)ethyl)benzenesulfonamide



C₁₆H₁₆N₂O₂S₂
MW: 332.44 g.mol⁻¹
colorless oil
60%

¹H NMR (500 MHz, CDCl₃): δ = 7.71 - 7.69 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.36 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.31 (d, *J* = 10.6 Hz, 1H), 7.16 – 7.15 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.99 – 6.98 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.94 – 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 4.50 – 4.48 (d, *J* = 10.6 Hz, 1H), 4.00 – 3.97 (m, 2H), 3.25 – 3.22 (m, 2H), 2.46 (s, 3H) ppm.

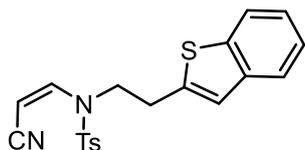
¹³C NMR (126 MHz, CDCl₃): δ = 145.7, 141.0, 138.4, 134.7, 130.5, 127.4, 127.4, 127.3, 126.5, 124.4, 116.7, 72.0, 47.3, 29.2, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₆H₁₆NaN₂O₂S₂ 355.0545; Found 355.0536.

IR (neat): ν = 2207, 1616, 1329, 1164, 675 cm⁻¹

Compound 3I

(Z)-N-(2-(benzo[*b*]thiophen-2-yl)ethyl)-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₂₀H₁₈N₂O₂S₂
MW: 382.50 g.mol⁻¹
white solid
26%

¹H NMR (500 MHz, CDCl₃): δ = 7.77 - 7.75 (m, 1H), 7.71 – 7.69 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.67 (m, 1H), 7.35 – 7.33 (m, 3H), 7.32 – 7.28 (m, 2H), 7.19 (s, 1H), 4.52 – 4.50 (d, *J* = 10.5 Hz, 1H), 4.09-4.05 (m, 2H), 3.33 – 3.30 (m, 2H), 2.44 (s, 3H) ppm.

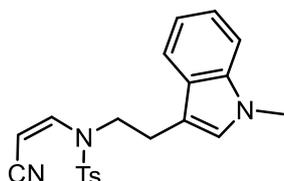
¹³C NMR (126 MHz, CDCl₃): δ = 145.7, 141.1, 140.1, 139.8, 139.5, 134.6, 130.6, 127.5, 124.4, 124.1, 123.3, 123.1, 122.3, 116.8, 72.1, 47.0, 30.2, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₂₀H₁₈KN₂O₂S₂ 421.0441; Found 421.0440.

IR (neat): ν = 2206, 1619, 1359, 1165, 678 cm⁻¹

Compound 3J

(Z)-N-(2-cyanovinyl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)ethyl)benzenesulfonamide



C₂₁H₂₁N₃O₂S
MW: 379.48 g.mol⁻¹
colorless oil
42%

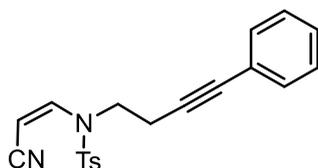
¹H NMR (500 MHz, CDCl₃): δ = 7.71 - 7.70 (d, J = 8.5 Hz, 2H), 7.71 - 7.68 (m, 1H), 7.38 - 7.36 (d, J = 10.5 Hz, 1H), 7.34 - 7.32 (d, J = 8.6 Hz, 2H), 7.30 - 7.28 (dt, J = 8.2, 1.0 Hz, 1H), 7.25 - 7.22 (td, J = 8.2, 1.2 Hz, 1H), 7.18 - 7.15 (td, J = 8.0, 1.2 Hz, 1H), 7.10 (s, 1H), 4.49 - 4.47 (d, J = 10.5 Hz, 1H), 3.95 - 3.92 (m, 2H), 3.72 (s, 3H), 3.23 - 3.19 (m, 2H), 2.42 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.5, 141.3, 137.0, 135.0, 130.5, 128.0, 127.9, 127.5, 121.7, 119.2, 118.8, 117.0, 109.4, 109.4, 71.5, 46.9, 32.8, 24.9, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₂N₃O₂S 380.1426; Found 380.1427.

IR (neat): ν = 2207, 1617, 1329, 1164, 686 cm⁻¹

Compound 3K (Z)-N-(2-cyanovinyl)-4-methyl-N-(4-phenylbut-3-yn-1-yl)benzenesulfonamide



C₂₀H₁₈N₂O₂S
MW: 350.44 g.mol⁻¹
white solid
54%

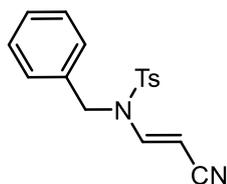
¹H NMR (500 MHz, CDCl₃): δ = 7.73 - 7.71 (d, J = 8.4 Hz, 2H), 7.40 - 7.38 (m, 2H), 7.38 - 7.36 (d, J = 8.6 Hz, 2H), 7.30 - 7.28 (d, J = 10.6 Hz, 1H), 7.28 - 7.26 (m, 3H), 4.50 - 4.48 (d, J = 10.6 Hz, 1H), 4.07-4.04 (m, 2H), 2.87 - 2.84 (m, 2H), 2.45 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.5, 140.9, 134.7, 131.7, 130.4, 128.2, 128.0, 127.3, 123.3, 116.1, 84.5, 83.0, 72.5, 44.4, 21.7, 20.0 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₀H₁₉N₂O₂S 351.1161; Found 351.1162.

IR (neat): ν = 2208, 1618, 1357, 1165, 678 cm⁻¹

Compound 4a (E)-N-benzyl-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₁₇H₁₆N₂O₂S
MW: 312.09 g.mol⁻¹
white solid
90%

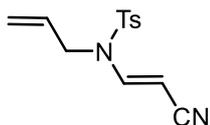
¹H NMR (300 MHz, CDCl₃): δ = 7.80 – 7.77 (d, *J* = 14.6 Hz, 1H), 7.72 – 7.70 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.36 (d, *J* = 8.6, 2H), 7.32 – 7.29 (m, 3H), 7.17 – 7.15 (m, 2H), 4.56 (s, 2H), 4.32 – 4.29 (d, *J* = 14.6, 1H), 2.47 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.7, 145.1, 134.9, 133.1, 130.6, 129.2, 128.4, 127.5, 126.7, 117.8, 77.6, 49.7, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₇H₁₆NaN₂O₂S 335.0822; Found 335.0828.

IR (neat): ν = 2216, 1620, 1364, 1159, 660 cm⁻¹

Compound 4h (E)-N-allyl-N-(2-cyanovinyl)-4-methylbenzenesulfonamide



C₁₃H₁₄N₂O₂S
MW: 262.32 g.mol⁻¹
colorless oil
85%

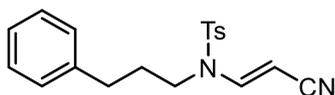
¹H NMR (300 MHz, CDCl₃): δ = 7.75 - 7.73 (d, *J* = 14.5 Hz, 1H), 7.70 – 7.68 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.36 (d, *J* = 8.4 Hz, 2H), 5.54 – 5.47 (m, 1H), 5.22 – 5.19 (m, 1H), 5.15 – 5.11 (m, 1H), 4.47 – 4.44 (d, *J* = 14.5 Hz, 1H), 4.06 – 4.04 (m, 2H), 2.46 (s, 3H) ppm

¹³C NMR (126 MHz, CDCl₃): δ = 145.6, 144.9, 134.9, 130.5, 129.5, 127.5, 119.5, 118.0, 76.6, 48.2, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₃H₁₄NaN₂O₂S 258.0668; Found 285.0670.

IR (neat): ν = 2213, 1620, 1356, 1161, 948 cm⁻¹

Compound 4p (E)-N-(2-cyanovinyl)-4-methyl-N-(3-phenylpropyl)benzenesulfonamide



C₁₉H₂₀N₂O₂S
MW: 340.44 g.mol⁻¹
colorless oil
91%

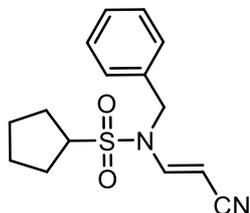
¹H NMR (500 MHz, CDCl₃): δ = 7.69 - 7.66 (d, *J* = 14.6 Hz, 1H), 7.64 – 7.63 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.34 (d, *J* = 8.6 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.24 – 7.21 (m, 1H), 7.13 – 7.11 (m, 2H), 4.13 – 4.10 (d, *J* = 14.6 Hz, 1H), 3.31-3.27 (m, 2H), 2.62 – 2.59 (m, 2H), 2.45 (s, 3H), 1.89 – 1.84 (m, 2H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.5, 145.0, 140.1, 134.9, 130.5, 128.8, 128.5, 127.4, 126.7, 118.1, 75.2, 44.9, 32.8, 27.8, 21.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₉H₂₀KN₂O₂S 379.0877; Found 379.0885.

IR (neat): ν = 2196, 1601, 1361, 1139, 947 cm⁻¹

Compound 4t (*E*)-*N*-benzyl-*N*-(2-cyanovinyl)cyclopentanesulfonamide



C₁₅H₁₈N₂O₂S
MW: 290.38 g.mol⁻¹
white solid
73%

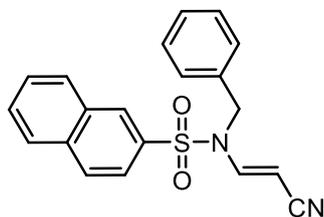
¹H NMR (500 MHz, C₆D₆): δ = 7.45 – 7.42 (d, *J* = 14.5 Hz, 1H), 7.03 – 6.98 (m, 3H), 6.95 – 6.93 (m, 2H), 4.05 (s, 2H), 3.89 – 3.86 (d, *J* = 14.5 Hz, 1H), 2.64 – 2.58 (m, 1H), 1.65 – 1.57 (m, 2H), 1.32 – 1.28 (m, 4H), 1.03 – 0.97 (m, 2H) ppm.

¹³C NMR (126 MHz, C₆D₆): δ = 145.0, 134.1, 129.2, 128.4, 126.9, 117.5, 77.1, 63.1, 49.6, 27.9, 25.5 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₅H₁₈NaN₂O₂S 313.0981; Found 313.0993.

IR (neat): ν = 2208, 1619, 1349, 1153, 956 cm⁻¹

Compound 4u (*E*)-*N*-benzyl-*N*-(2-cyanovinyl)naphthalene-2-sulfonamide



C₂₀H₁₆N₂O₂S
MW: 348.42 g.mol⁻¹
white solid
m.p.: 115 °C
88%

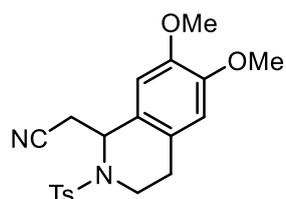
¹H NMR (500 MHz, CDCl₃): δ = 8.43 – 8.2 (d, *J* = 2.5 Hz, 1H), 8.04 – 8.02 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.98 (dd, *J* = 8 Hz, 0.8 Hz, 1H), 7.96 – 7.95 (dd, *J* = 8.2 Hz, 0.8 Hz, 1H), 7.89 – 7.87 (d, *J* = 14.5 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.69 – 7.66 (m, 1H), 7.30 – 7.21 (m, 3H), 7.19 – 7.17 (m, 2H), 4.63 (s, 2H), 4.36 – 4.33 (d, *J* = 14.5 Hz, 1H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 145.1, 135.5, 134.4, 133.0, 132.2, 130.5, 130.0, 129.6, 129.6, 129.2, 128.5, 128.4, 128.2, 126.6, 121.6, 117.8, 77.8, 49.8 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₀H₁₆NaN₂O₂S 371.0824; Found 371.0826.

IR (neat): ν = 2210, 1617, 1353, 1167, 953 cm⁻¹

Compound 5A 2-(6,7-dimethoxy-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile



C₂₀H₂₂N₂O₄S
MW: 386.47 g.mol⁻¹
white solid
67%

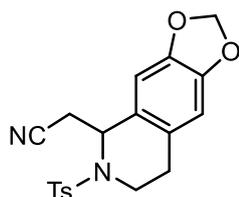
¹H NMR (500 MHz, CDCl₃): δ = 7.70 - 7.69 (d, *J* = 8.4 Hz, 2H), 7.26 - 7.24 (d, *J* = 8.6 Hz, 2H), 6.65 (s, 1H), 6.51 (s, 1H), 5.15 - 5.13 (t, *J* = 5.9 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.62 - 3.60 (dd, *J* = 7.4, 4.8 Hz, 2H), 2.95 - 2.94 (d, *J* = 5.9 Hz, 2H), 2.73 (dt, *J* = 16.3, 4.7 Hz, 1H), 2.60 (dt, *J* = 16.1, 7.4 Hz, 1H), 2.38 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 148.9, 148.0, 144.0, 136.2, 129.9, 127.3, 126.1, 124.4, 117.5, 111.6, 109.7, 56.2, 56.0, 52.4, 40.7, 27.6, 127.1, 21.6 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₀H₂₂NaN₂O₄S 409.1190; Found 409.1192.

IR (neat): ν = 2254, 1331, 1158 cm⁻¹

Compound 5B 2-(6-tosyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinolin-5-yl)acetonitrile



C₁₉H₁₈N₂O₄S
MW: 370.42 g.mol⁻¹
white solid
69%

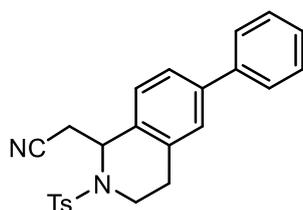
¹H NMR (500 MHz, CDCl₃): δ = 7.70 - 7.68 (d, *J* = 8.3 Hz, 2H), 7.27 - 7.25 (d, *J* = 8.6 Hz, 2H), 6.59 (s, 1H), 6.51 (s, 1H), 5.93 (d, *J* = 1.4 Hz, 1H), 5.92 (d, *J* = 1.4 Hz, 1H), 5.09 - 5.07 (t, *J* = 5.6 Hz, 1H), 3.86 - 3.63 (ddd, *J* = 13.0, 8.9, 4.5 Hz, 1H), 3.54 - 3.51 (dt, *J* = 13.0, 5.5 Hz, 1H), 2.99 - 2.95 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.93 - 2.89 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.75 - 2.70 (dt, *J* = 16.2, 5.1 Hz, 1H), 2.63 - 2.57 (ddd, *J* = 16.2, 8.9, 5.2 Hz, 1H), 2.39 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 147.7, 146.8, 144.1, 136.0, 130.0, 127.8, 127.4, 125.5, 117.4, 108.9, 106.8, 101.4, 52.9, 41.0, 28.0, 27.7, 21.7 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₉H₁₉N₂O₄S 371.1057; Found 371.1060.

IR (neat): ν = 2249, 1485, 1157 cm⁻¹

Compound 5C 2-(6-phenyl-2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile



C₂₄H₂₂N₂O₂S
MW: 402.51 g.mol⁻¹
white solid
72%

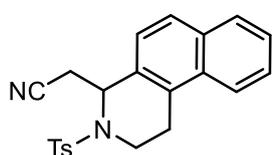
¹H NMR (500 MHz, CDCl₃): δ = 7.74 - 7.72 (d, *J* = 8.4 Hz, 2H), 7.56 - 7.54 (m, 2H), 7.46 - 7.43 (m, 3H), 7.38 - 7.34 (m, 2H), 7.28 - 7.25 (d, *J* = 8.6 Hz, 2H), 7.17 - 7.15 (d, *J* = 8.0 Hz, 1H), 5.26 - 5.23 (t, *J* = 5.8 Hz, 1H), 3.76 - 3.70 (ddd, *J* = 13.0, 8.8, 4.5 Hz, 1H), 3.61 - 3.60 (dt, *J* = 13.0, 5.4 Hz, 1H), 3.05 - 3.03 (d, *J* = 5.8 Hz, 2H), 2.92 - 2.87 (dt, *J* = 16.4, 5.0 Hz, 1H), 2.81 - 2.75 (ddd, *J* = 16.4, 8.8, 5.2 Hz, 1H), 2.38 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.1, 140.1, 140.1, 135.8, 133.0, 132.9, 129.9, 129.6, 128.9, 127.7, 127.3, 127.0, 127.0, 125.6, 117.4, 52.9, 41.0, 27.9, 27.4, 21.6 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₄H₂₂NaN₂O₂S 425.1294; Found 425.1301.

IR (neat): ν = 2249, 1334, 1161 cm⁻¹

Compound 5D 2-(3-tosyl-1,2,3,4-tetrahydrobenzo[f]isoquinolin-4-yl)acetonitrile



C₂₂H₂₀N₂O₂S
MW: 376.47 g.mol⁻¹
white solid
m.p.: 173 °C
83%

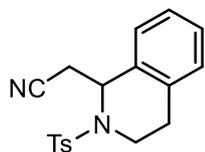
¹H NMR (500 MHz, CDCl₃): δ = 7.85 - 7.81 (m, 2H), 7.75 - 7.71 (m, 3H), 7.55 - 7.49 (m, 2H), 7.24 - 7.22 (d, *J* = 8.6 Hz, 1H), 7.20 - 7.19 (d, *J* = 8.6 Hz, 2H), 5.39 - 5.37 (t, *J* = 5.8 Hz, 1H), 3.96 - 3.92 (dddd, *J* = 14.0, 6.2, 3.6, 0.9 Hz, 1H), 3.79 - 3.73 (ddd, *J* = 14.0, 10.4, 4.6 Hz, 1H), 3.19 - 3.15 (dt, *J* = 16.7, 4.1 Hz, 1H), 3.13 - 3.08 (dd, *J* = 16.9, 5.5 Hz, 1H), 3.05 - 3.00 (dd, *J* = 16.9, 5.8 Hz, 1H), 2.99 (m, 1H), 2.32 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.1, 136.3, 132.8, 131.7, 130.0, 130.0, 130.0, 128.8, 127.7, 127.4, 127.0, 126.5, 124.2, 123.0, 117.4, 52.8, 39.8, 26.8, 23.7, 21.6 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₂H₂₀NaN₂O₂S 399.1125; Found 399.1138.

IR (neat): ν = 2249, 1332, 1156 cm⁻¹

Compound 5E 2-(2-tosyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile



C₁₈H₁₈N₂O₂S
MW: 326.41 g.mol⁻¹
colorless oil
41%

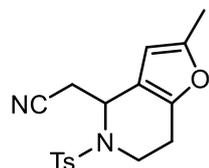
¹H NMR (500 MHz, CDCl₃): δ = 7.70 - 7.69 (d, *J* = 8.3 Hz, 2H), 7.26 - 7.24 (d, *J* = 8.1 Hz, 2H), 7.22 - 7.20 (m, 2H), 7.17 - 7.15 (m, 1H), 7.08 - 7.06 (m, 1H), 5.21 - 5.18 (t, *J* = 5.7 Hz, 1H), 3.73 - 3.67 (m, 1H), 3.58 - 3.53 (dt, *J* = 13.1, 5.5 Hz, 1H), 3.04 (dd, *J* = 16.8, 6.2 Hz, 1H), 2.94 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.87 - 2.81 (dt, *J* = 16.3, 5.1 Hz, 1H), 2.74 - 2.68 (ddd, *J* = 16.3, 8.9, 5.3 Hz, 1H), 2.38 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.1, 135.9, 134.1, 132.7, 130.0, 129.2, 128.2, 127.4, 127.1, 127.0, 117.3, 52.8, 41.0, 27.9, 27.7, 21.6 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₈H₁₈NaN₂O₂S 349.0977; Found 349.0981.

IR (neat): ν = 2252, 1333, 1159 cm⁻¹

Compound 5F 2-(2-methyl-5-tosyl-4,5,6,7-tetrahydrofuro[3,2-c]pyridin-4-yl)acetonitrile



C₁₇H₁₈N₂O₃S
MW: 330.40 g.mol⁻¹
colorless oil
35%

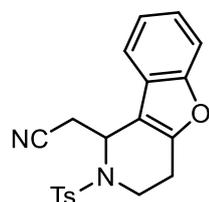
¹H NMR (500 MHz, CDCl₃): δ = 7.68 - 7.66 (d, *J* = 8.4 Hz, 2H), 7.26 - 7.24 (d, *J* = 8.6 Hz, 2H), 5.96 (s, 1H), 5.12 - 5.10 (t, *J* = 5.9 Hz, 1H), 4.13 - 4.08 (m, 1H), 3.50 - 3.43 (m, 1H), 2.82 - 2.81 (m, 2H), 2.45 - 2.41 (m, 1H), 2.40 (s, 3H), 2.39 - 2.36 (m, 1H), 2.23 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 152.0, 146.8, 144.7, 137.5, 130.1, 127.0, 117.3, 115.8, 104.1, 49.3, 39.8, 25.3, 22.4, 21.7, 13.6 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₇H₁₈NaN₂O₃S 353.0930; Found 353.0925.

IR (neat): ν = 2249, 1335, 1159 cm⁻¹

Compound 5G 2-(2-tosyl-1,2,3,4-tetrahydrobenzofuro[3,2-c]pyridin-1-yl)acetonitrile



C₂₀H₁₈N₂O₃S
MW: 366.44 g.mol⁻¹
white solid
95%

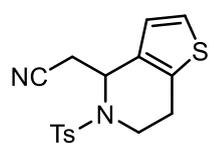
¹H NMR (500 MHz, CDCl₃): δ = 7.72 - 7.70 (d, *J* = 8.4 Hz, 2H), 7.44 - 7.43 (m, 2H), 7.32 - 7.27 (m, 2H), 7.24 - 7.22 (d, *J* = 8.4 Hz, 2H), 5.52 - 5.50 (t, *J* = 5.2 Hz, 1H), 4.23 - 4.21 (dd, *J* = 6.0, 1.6 Hz, 1H), 3.79 - 3.73 (ddd, *J* = 15.1, 11.1, 4.8 Hz, 1H), 3.14 - 3.09 (dd, *J* = 16.9, 12.0, 1H), 3.01 - 2.97 (dd, *J* = 16.9, 5.6 Hz, 1H), 2.68 - 2.62 (m, 2H), 2.38 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 152.0, 146.8, 144.7, 137.5, 130.1, 127.0, 117.3, 115.8, 104.1, 49.3, 39.8, 25.3, 22.4, 21.7, 13.6 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₀H₁₉N₂O₃S 367.1107; Found 367.1111.

IR (neat): ν = 2248, 1333, 1158 cm⁻¹

Compound 5H 2-(5-tosyl-4,5,6,7-tetrahydrothieno[3,2-c]pyridin-4-yl)acetonitrile



C₁₆H₁₆N₂O₂S₂
MW: 332.44 g.mol⁻¹
colorless oil
43%

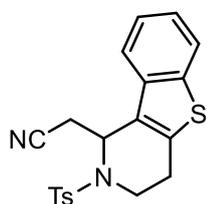
¹H NMR (500 MHz, CDCl₃): δ = 7.69 - 7.68 (d, *J* = 8.4 Hz, 2H), 7.26 - 7.24 (d, *J* = 8.6 Hz, 2H), 7.17 - 7.16 (dd, *J* = 5.2, 0.8 Hz, 1H), 6.91 - 6.90 (d, *J* = 5.2 Hz, 1H), 5.32 - 5.29 (t, *J* = 5.8 Hz, 1H), 4.09 - 4.05 (ddd, *J* = 14.5, 5.8, 1.9 Hz, 1H), 3.55 - 3.49 (ddd, *J* = 14.5, 11.5, 4.3 Hz, 1H), 2.97 - 2.85 (dd, *J* = 16.7, 6.2 Hz, 1H), 2.89 - 2.85 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.72 - 2.67 (ddd, *J* = 16.4, 4.3, 1.9 Hz, 1H), 2.60 - 2.53 (dq, *J* = 16.4, 5.8, 1.3 Hz, 1H), 2.39 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.2, 137.2, 135.1, 131.4, 130.0, 127.1, 124.7, 124.7, 117.3, 50.9, 40.2, 25.9, 23.8, 21.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₆H₁₆NaN₂O₂S₂ 355.0545; Found 355.0543.

IR (neat): ν = 2249, 1330, 1155 cm⁻¹

Compound 5I 2-(2-tosyl-1,2,3,4-tetrahydrobenzo[4,5]thieno[3,2-c]pyridin-1-yl)acetonitrile



C₂₀H₁₈N₂O₂S₂
MW: 382.08 g.mol⁻¹
colorless oil
88%

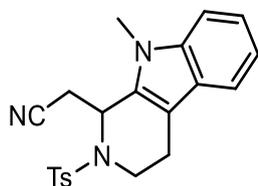
¹H NMR (500 MHz, CDCl₃): δ = 7.80 - 7.78 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.72 - 7.70 (d, *J* = 8.5 Hz, 2H), 7.56 - 7.54 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.43 - 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37 - 7.33 (td, *J* = 7.5, 1.2 Hz, 1H), 7.21 - 7.20 (d, *J* = 8.5 Hz, 2H), 5.62 - 5.60 (m, 1H), 4.08 - 4.03 (ddd, *J* = 14.6, 6.0, 2.2 Hz, 1H), 3.79 - 3.73 (ddd, *J* = 14.6, 11.0, 4.8 Hz, 1H), 3.17 - 3.13 (dd, *J* = 17.2, 4.0, 1H), 3.03 - 2.98 (dd, *J* = 17.2, 7.0 Hz, 1H), 2.83 - 2.79 (ddd, *J* = 16.9, 4.8, 2.2 Hz, 1H), 2.77 - 2.70 (ddd, *J* = 16.9, 11.0, 1.5 Hz, 1H), 2.38 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.2, 138.7, 137.4, 136.7, 136.1, 130.0, 127.3, 125.6, 124.9, 124.8, 123.1, 120.2, 117.1, 50.0, 39.7, 24.6, 24.0, 21.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₀H₁₈NaN₂O₂S₂ 405.0702; Found 405.0686.

IR (neat): ν = 2249, 1333, 1160 cm⁻¹

Compound 5J 2-(9-methyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)acetonitrile



C₂₁H₂₁N₃O₂S
MW: 379.48 g.mol⁻¹
colorless oil
70%

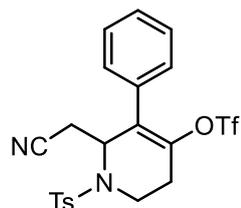
¹H NMR (500 MHz, CDCl₃): δ = 7.71 - 7.70 (d, *J* = 8.3 Hz, 2H), 7.40 - 7.38 (d, *J* = 7.9 Hz, 1H), 7.30 - 7.23 (m, 2H), 7.19 - 7.17 (d, *J* = 7.9 Hz, 2H), 7.11 - 7.08 (m, 1H), 5.55 - 5.53 (t, *J* = 6.0 Hz, 1H), 4.08 - 4.04 (ddd, *J* = 14.6, 6.0, 1.8 Hz, 1H), 3.71 (s, 3H), 3.62 - 3.56 (ddd, *J* = 14.6, 11.3, 5.2 Hz, 1H), 3.03 (dd, *J* = 17.2, 4.9 Hz, 1H), 2.92 (dd, *J* = 17.2, 6.9 Hz, 1H), 2.69 - 2.64 (m, 2H), 2.32 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.1, 137.9, 136.9, 130.5, 129.9, 127.3, 126.2, 122.8, 119.9, 118.8, 116.7, 109.4, 109.1, 48.2, 39.7, 30.6, 25.1, 21.6, 20.1 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₂N₃O₂S 380.1410; Found 380.1427.

IR (neat): ν = 2252, 1338, 1159 cm⁻¹

Compound 5K 6-(cyanomethyl)-5-phenyl-1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate



C₂₁H₁₉F₃N₂O₅S₂
MW: 500.51 g.mol⁻¹
white solid
41%

¹H NMR (500 MHz, CDCl₃): δ = 7.73 - 7.71 (d, *J* = 8.3 Hz, 2H), 7.52 - 7.46 (m, 3H), 7.40 - 7.38 (d, *J* = 8.5 Hz, 2H), 7.30 - 7.28 (m, 2H), 4.67 - 4.65 (td, *J* = 3.9, 1.8 Hz, 1H), 3.75 - 3.70 (ddd, *J* = 10.5, 8.5, 5.2 Hz, 1H), 3.50 - 3.46 (ddd, *J* = 10.5, 8.3, 7.3 Hz, 1H), 3.06 - 3.02 (m, 1H), 2.89 - 2.85 (dd, *J* = 16.9, 4.1 Hz, 1H), 2.78 - 2.71 (ddd, *J* = 16.9, 8.3, 5.2 Hz, 1H), 2.48 (s, 3H), 2.16 - 2.12 (dd, *J* = 16.9, 3.8 Hz, 1H) ppm.

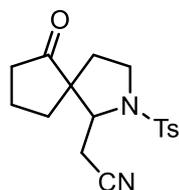
¹³C NMR (126 MHz, CDCl₃): δ = 145.1, 142.4, 133.9, 133.9, 131.4, 130.9, 130.4, 129.7, 128.7, 127.6, 122.0 (q, *J* = 321.0 Hz), 116.5, 57.7, 47.5, 29.2, 24.3, 21.8 ppm.

¹⁹F NMR (282 MHz, CDCl₃): δ = -74.40 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₁H₂₀N₂O₅F₃S₂ 501.0757; Found 501.0760.

IR (neat): ν = 2249, 1416, 1213, 1164 cm⁻¹

Compound 5L 2-(6-oxo-2-tosyl-2-azaspiro[4.4]nonan-1-yl)acetonitrile



C₁₇H₂₀N₂O₃S
MW: 332.42 g.mol⁻¹
colorless oil
42%

5L was obtained as two separable diastereoisomers (dr 4:1), only one isomer was described in ¹H and ¹³C.

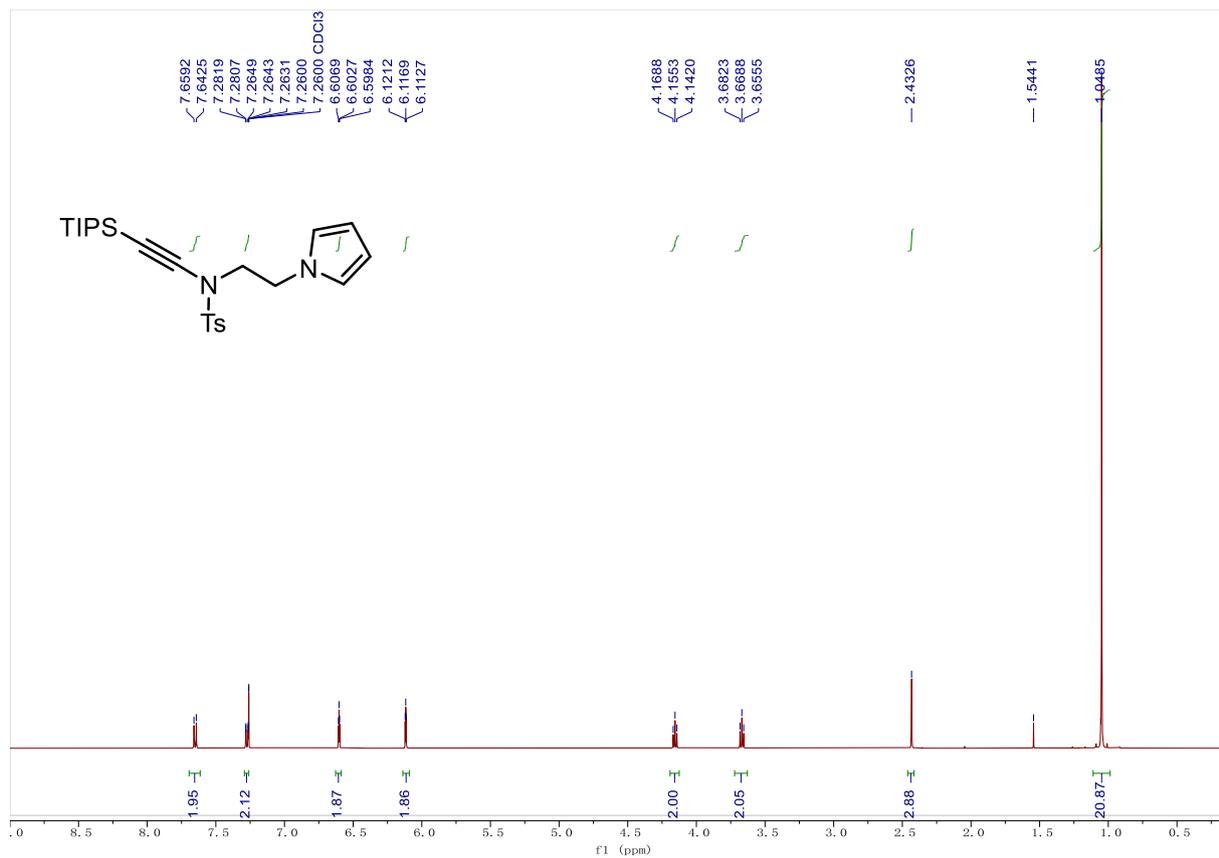
¹H NMR (500 MHz, CDCl₃): δ = 7.77 - 7.75 (d, *J* = 8.3 Hz, 2H), 7.39 - 7.37 (d, *J* = 8.6 Hz, 2H), 3.77 - 3.75 (dd, *J* = 7.1, 2.7 Hz, 1H), 3.63 - 3.59 (ddd, *J* = 9.7, 7.1, 3.3 Hz, 1H), 3.11 (td, *J* = 9.5, 6.6 Hz, 1H), 3.10 (dd, *J* = 17.1, 7.1 Hz, 1H), 2.79 - 2.75 (dd, *J* = 17.1, 2.7 Hz, 1H), 2.47 (s, 3H), 2.33 - 2.28 (m, 1H), 2.15 - 2.01 (m, 5H), 1.88 - 1.81 (m, 1H), 1.74 - 1.69 (ddd, *J* = 13.0, 6.6, 3.3 Hz, 1H), ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 216.8, 144.2, 133.2, 129.7, 128.2, 117.7, 58.8, 58.4, 46.5, 35.6, 32.6, 31.1, 22.8, 21.7, 19.2 ppm.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₇H₂₁N₂O₃S 333.1265; Found 333.1267.

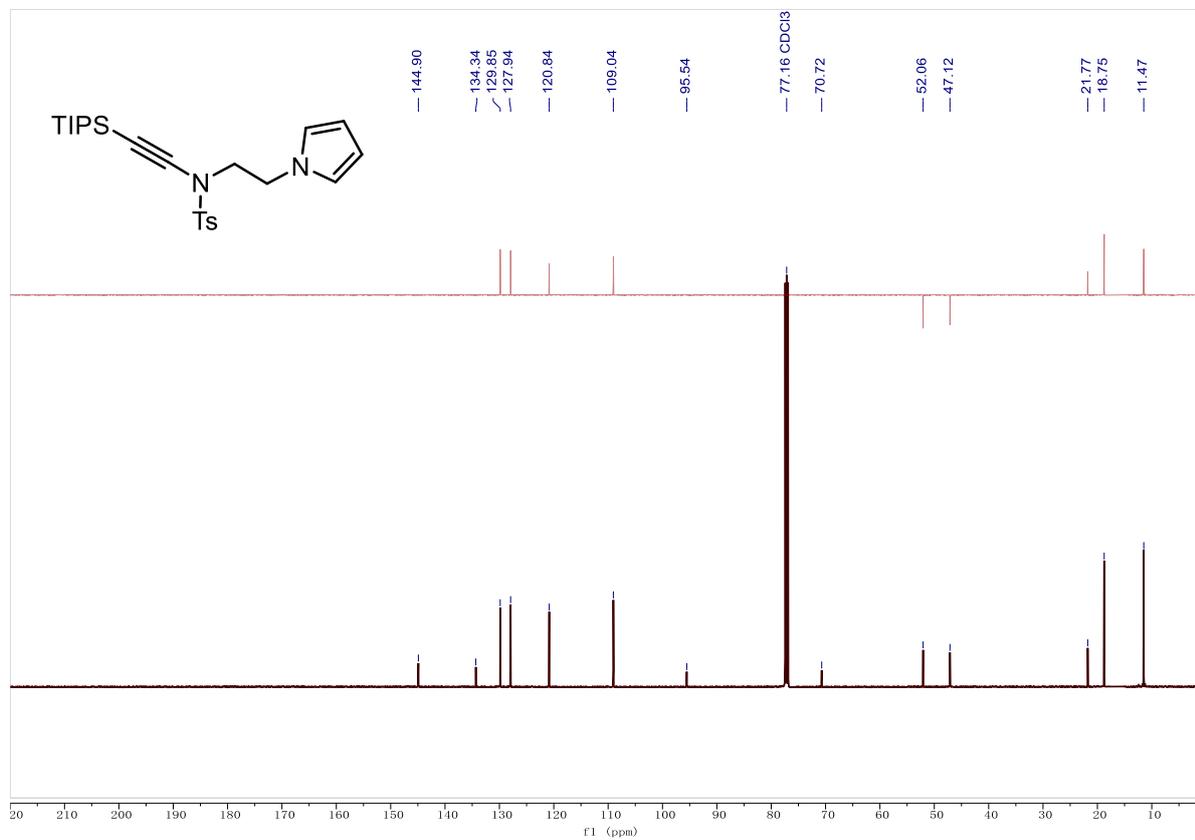
IR (neat): ν = 2248, 1736, 1339, 1160 cm⁻¹

NMR Spectra

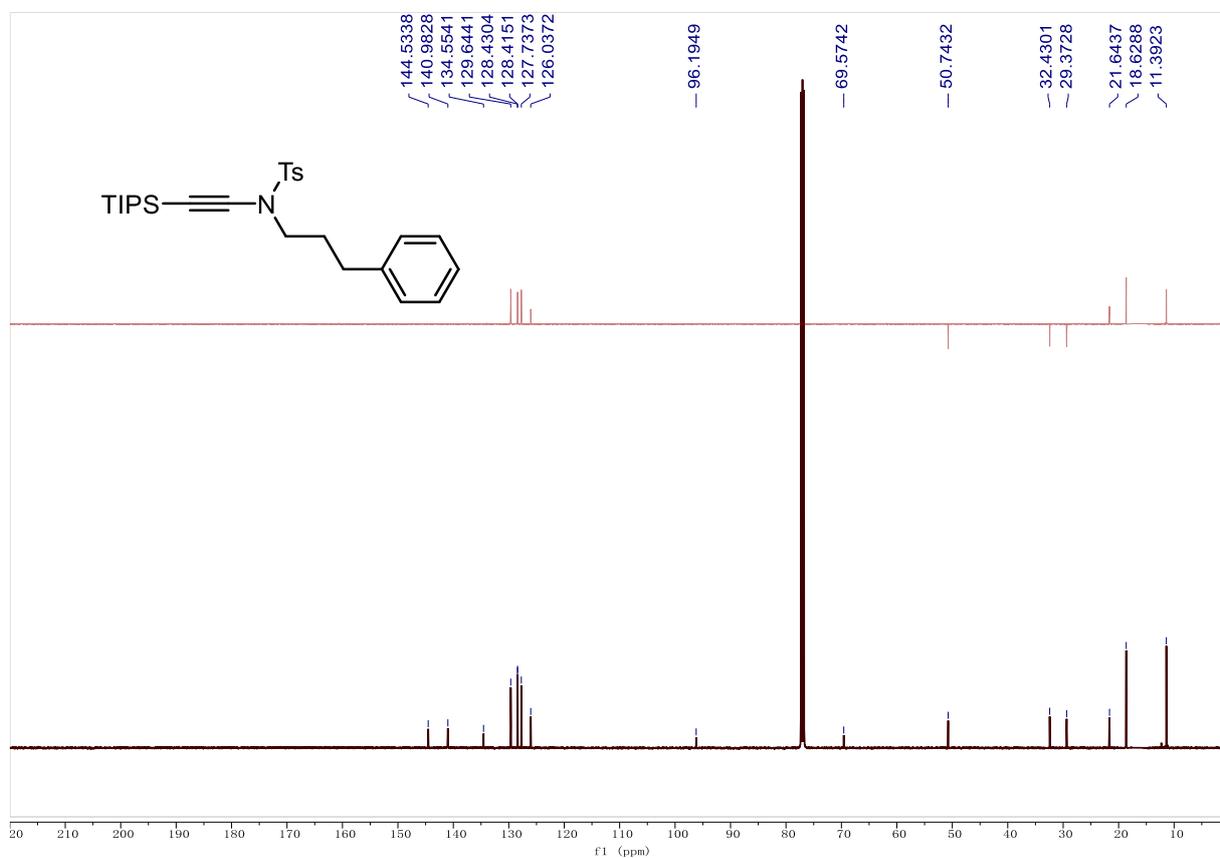
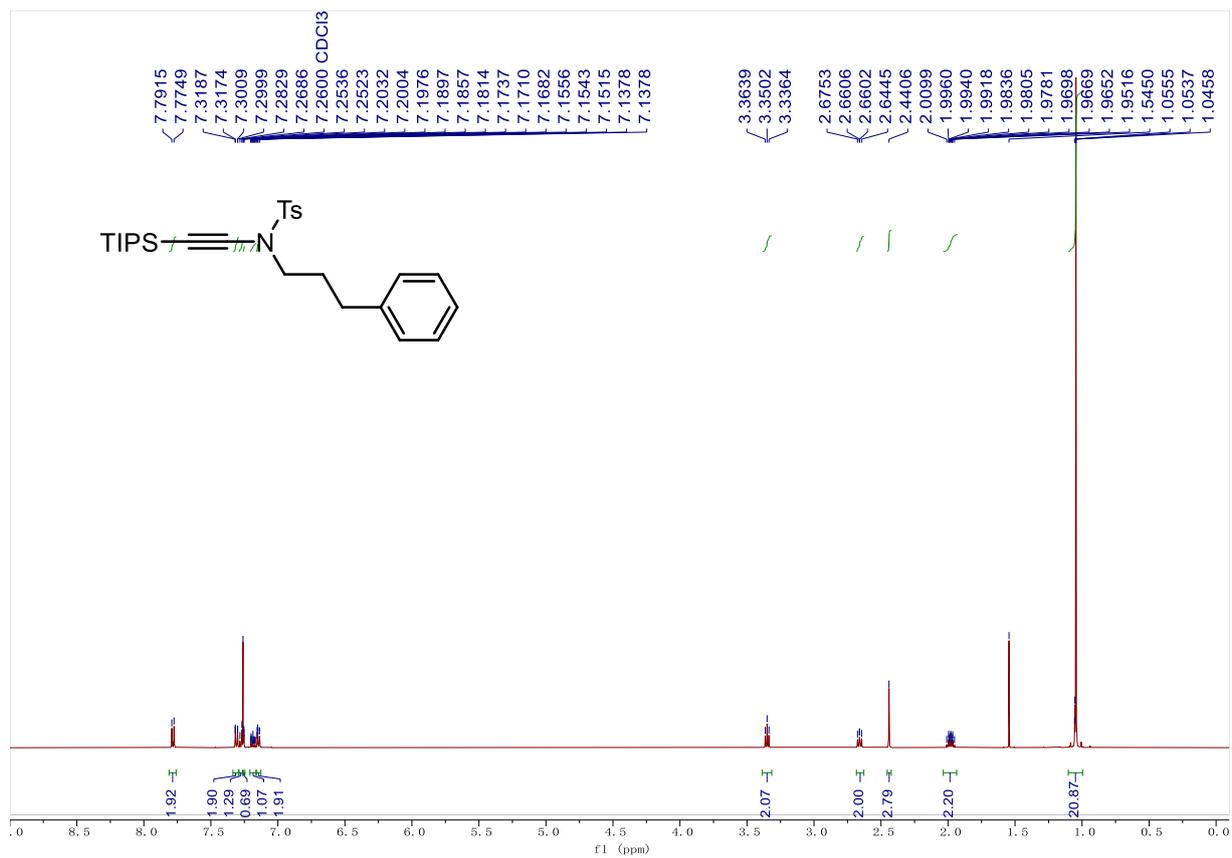


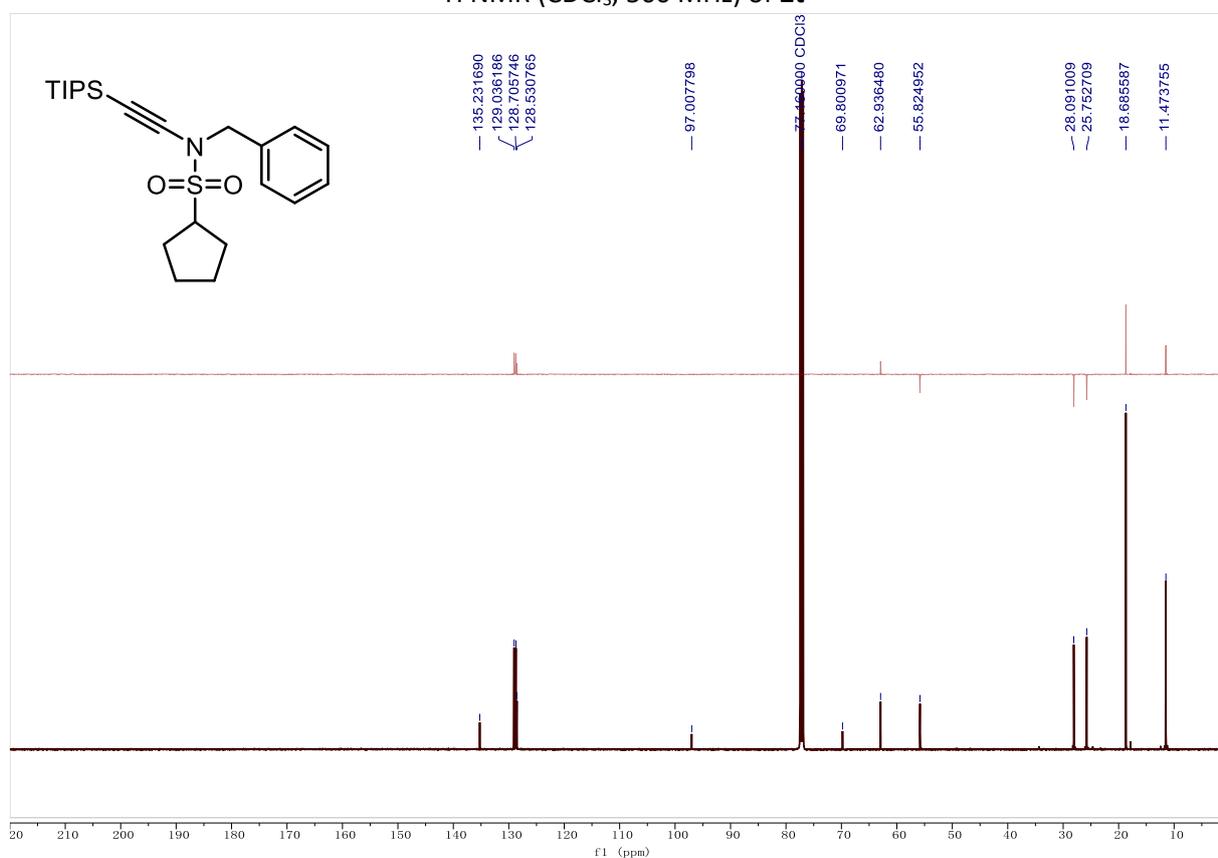
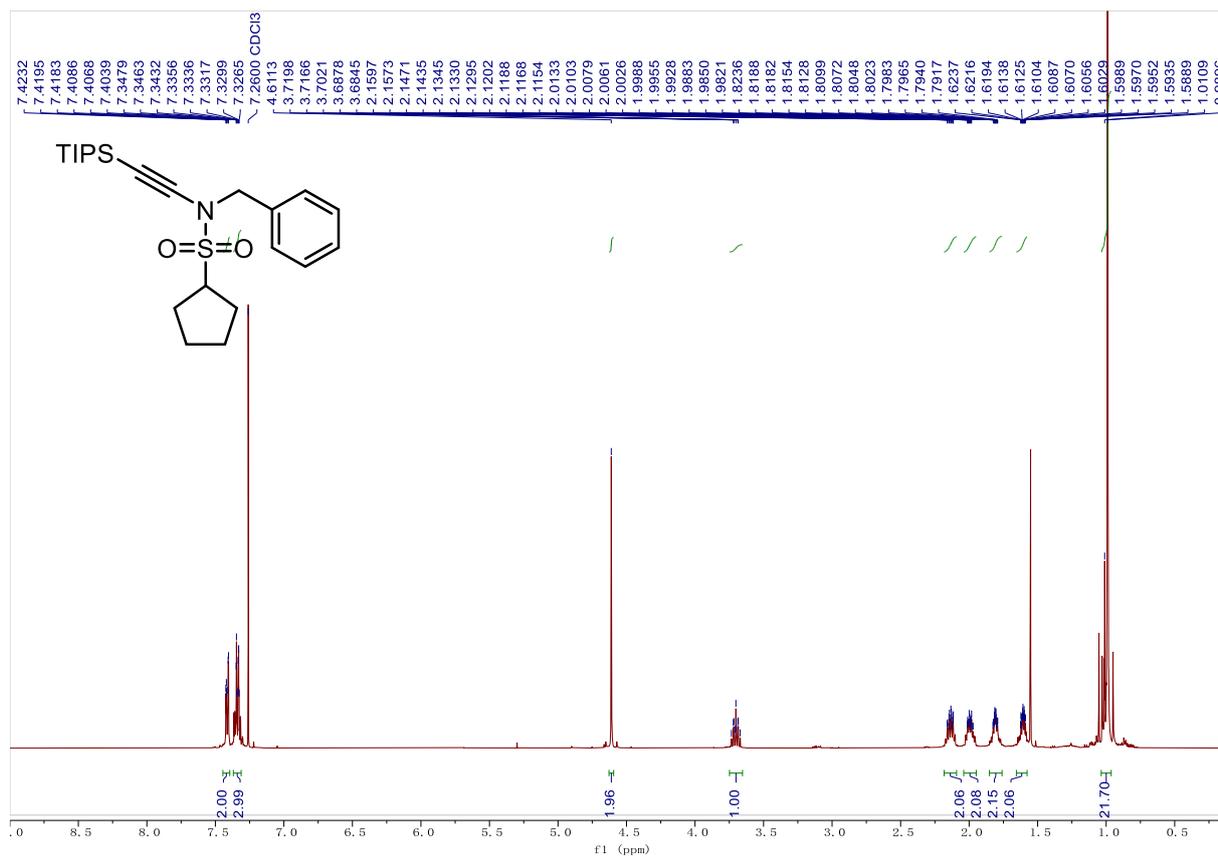
¹H NMR (CDCl₃, 500 MHz) of 2m

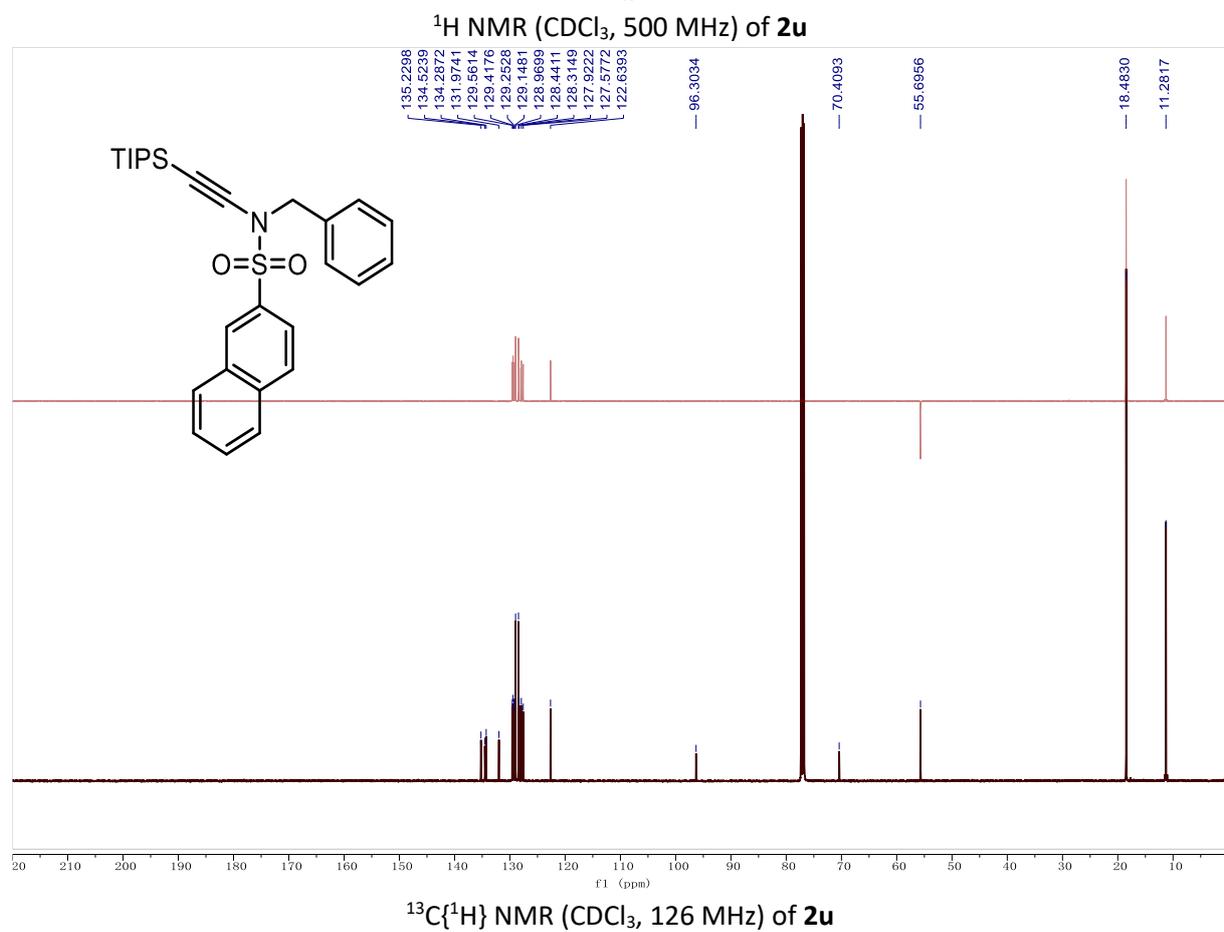
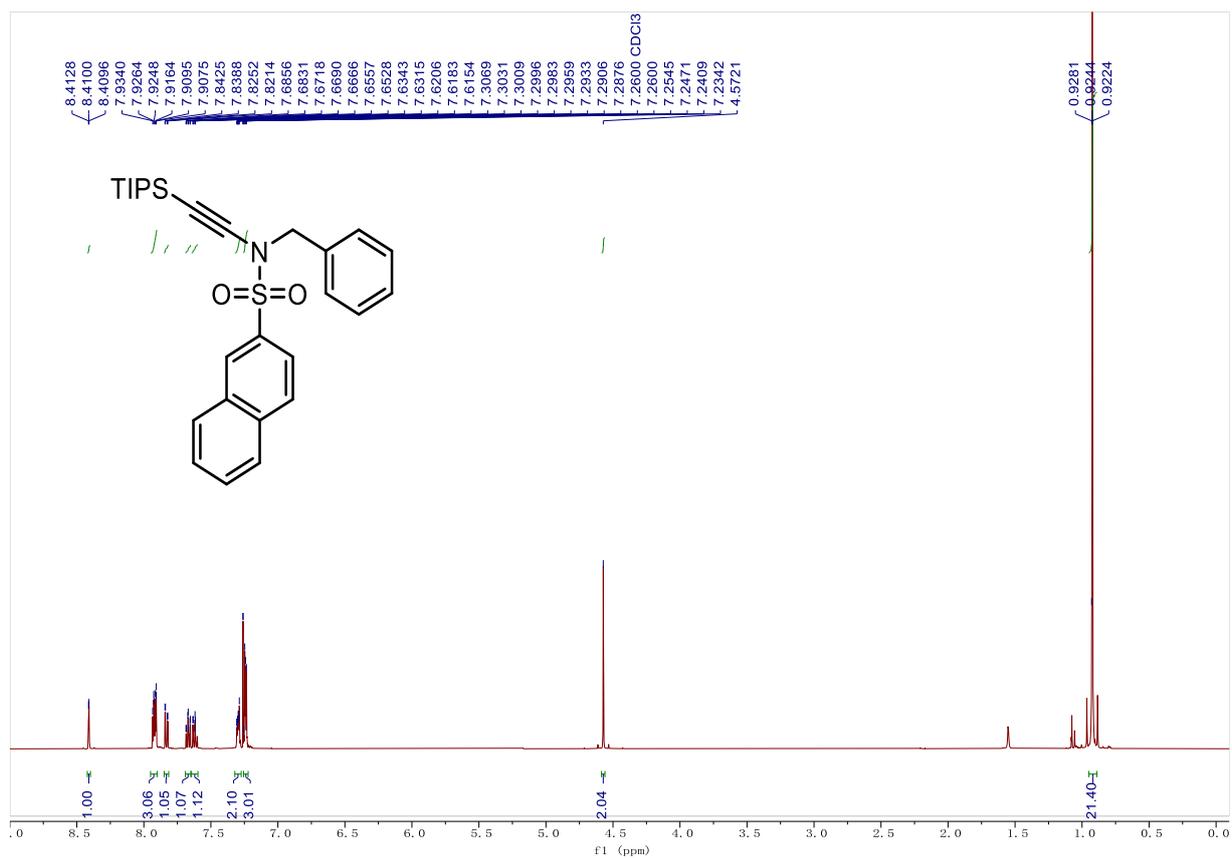
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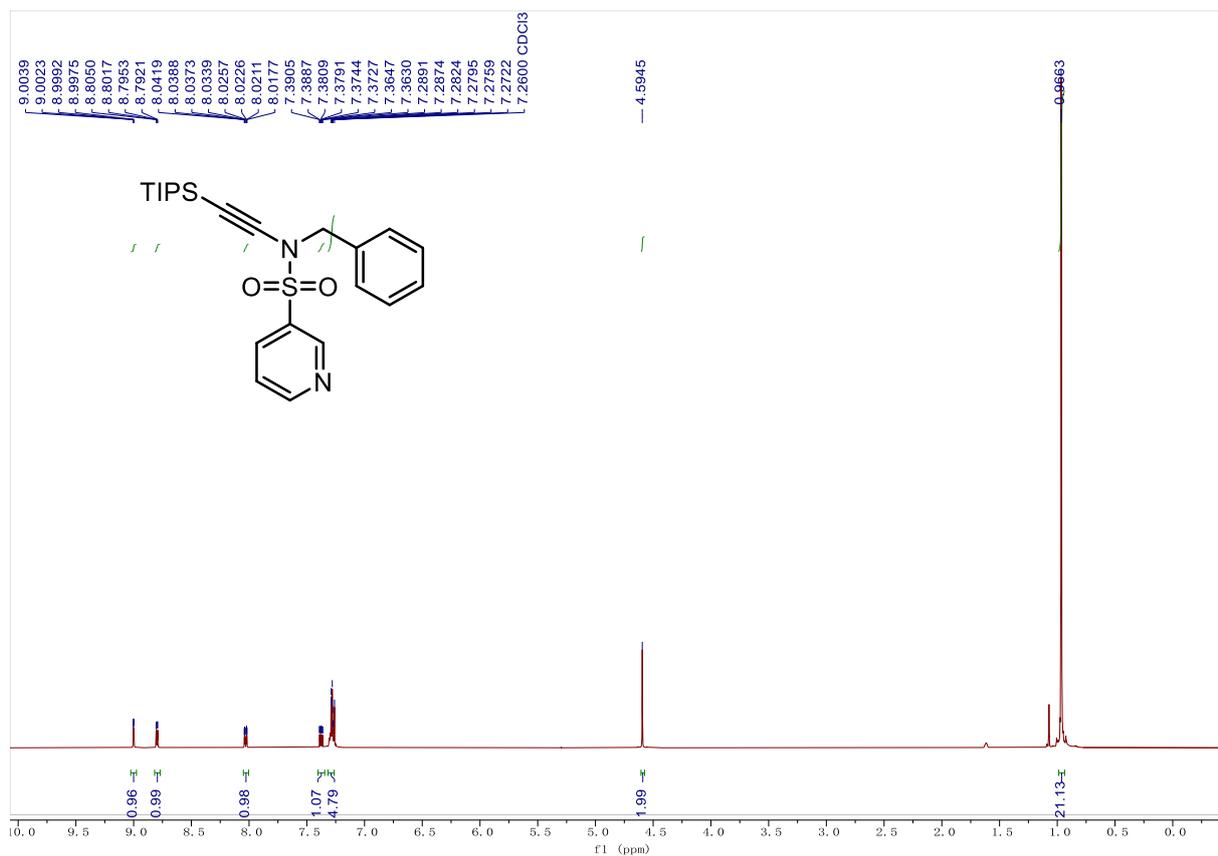


¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2m

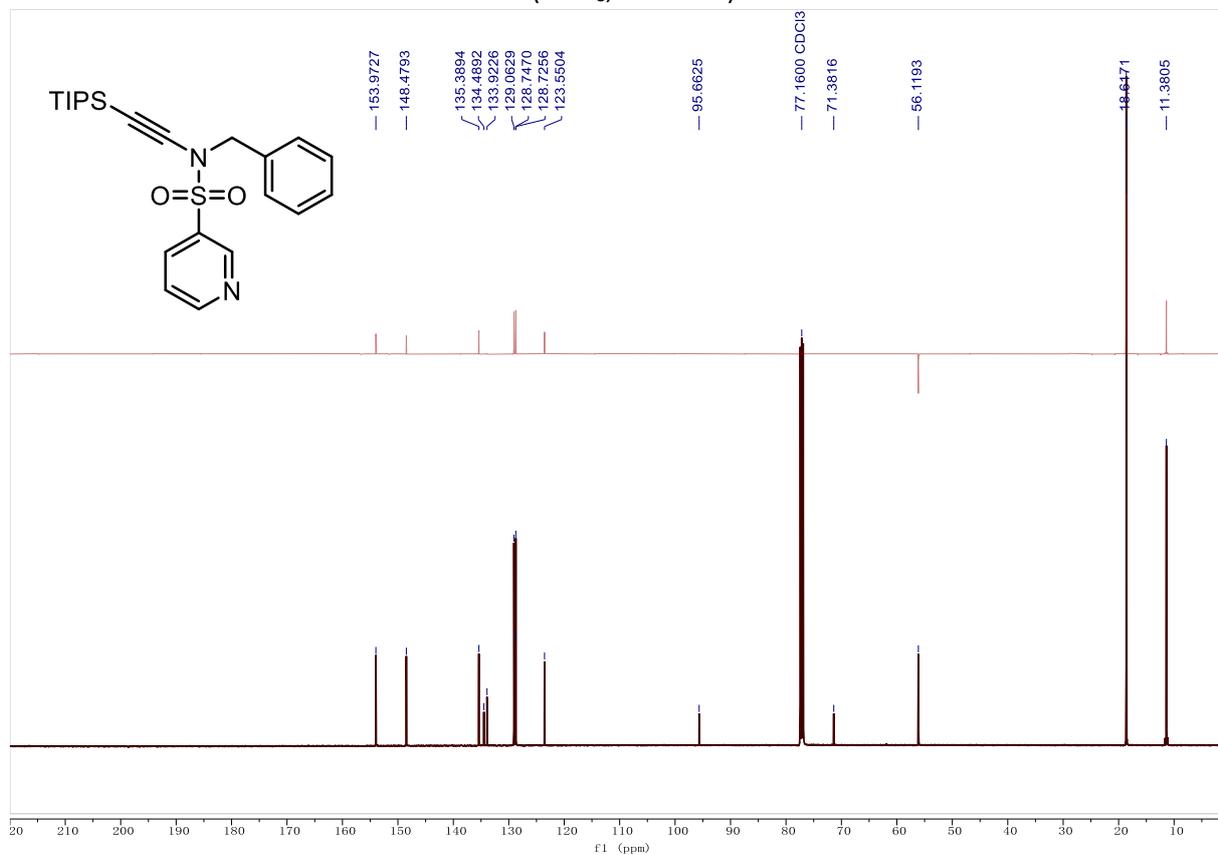




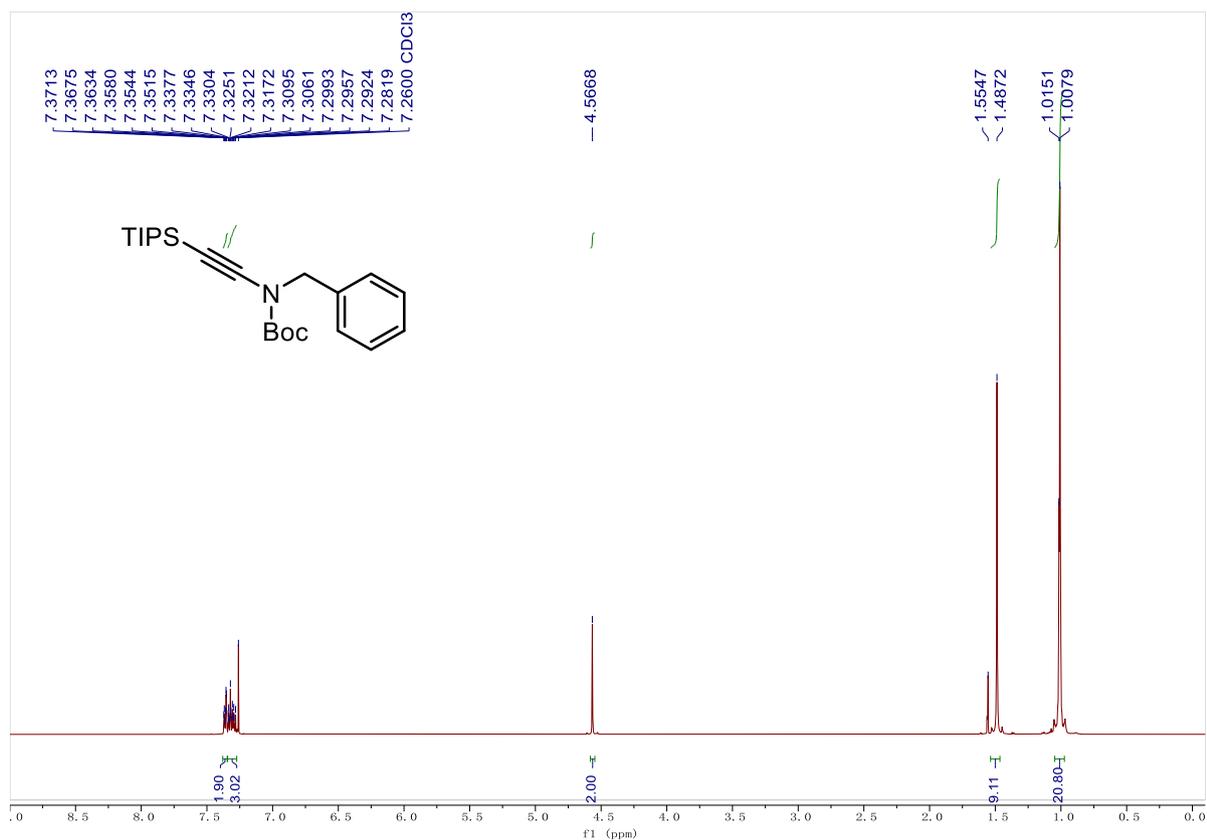




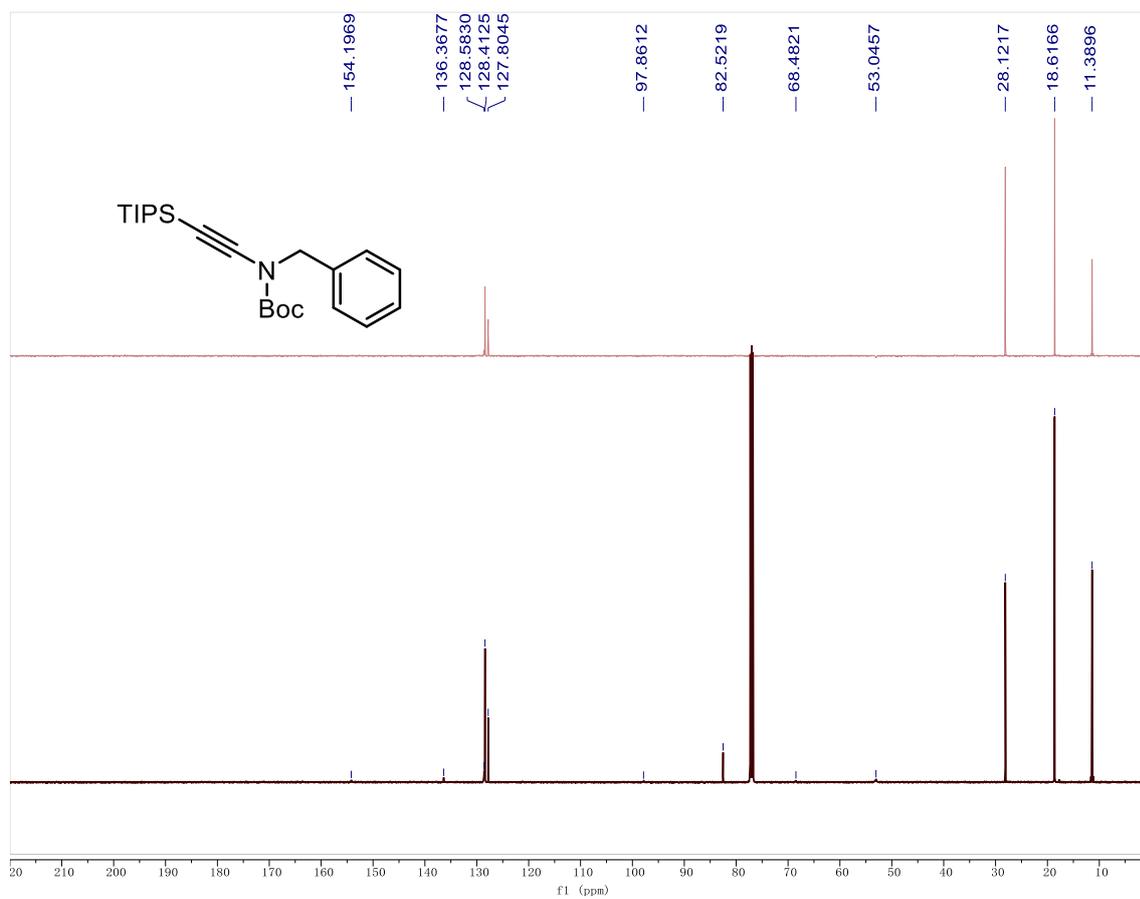
1H NMR (CDCl₃, 500 MHz) of **2w**



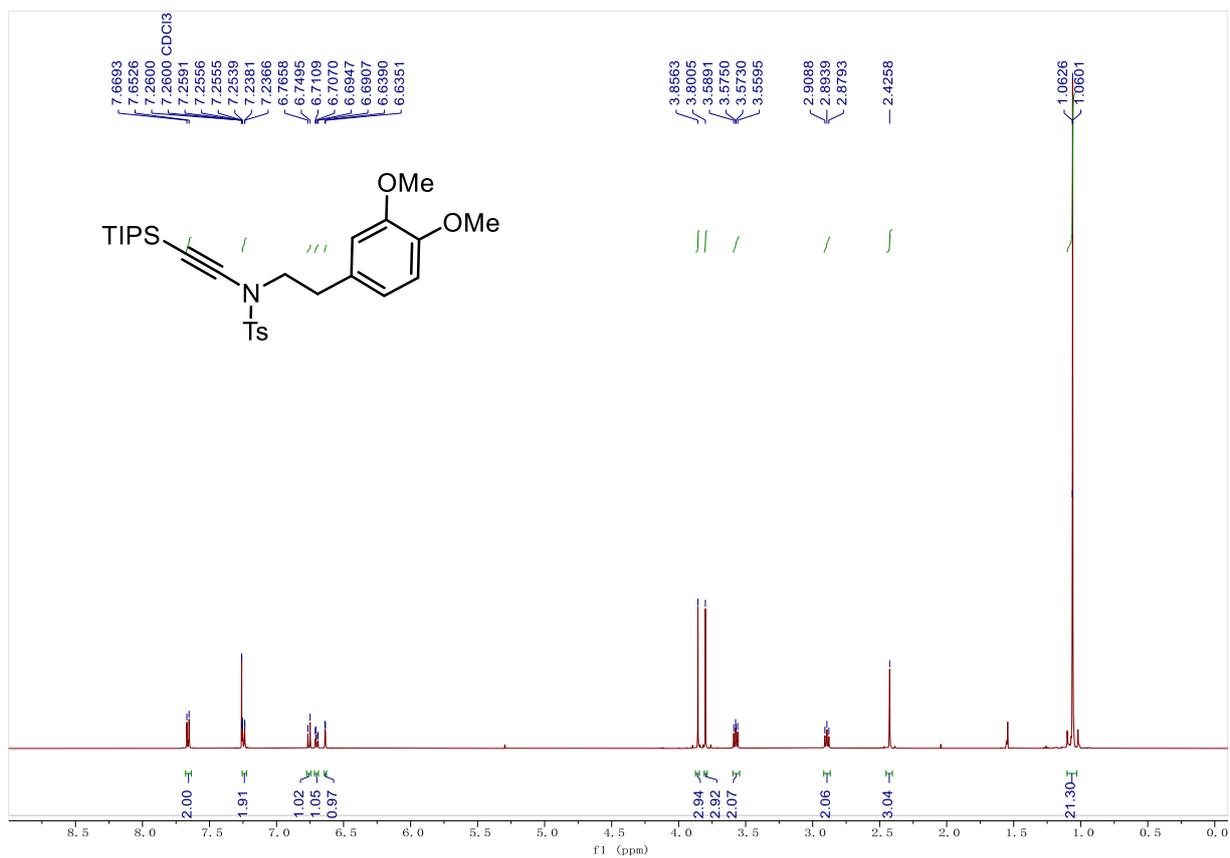
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **2w**



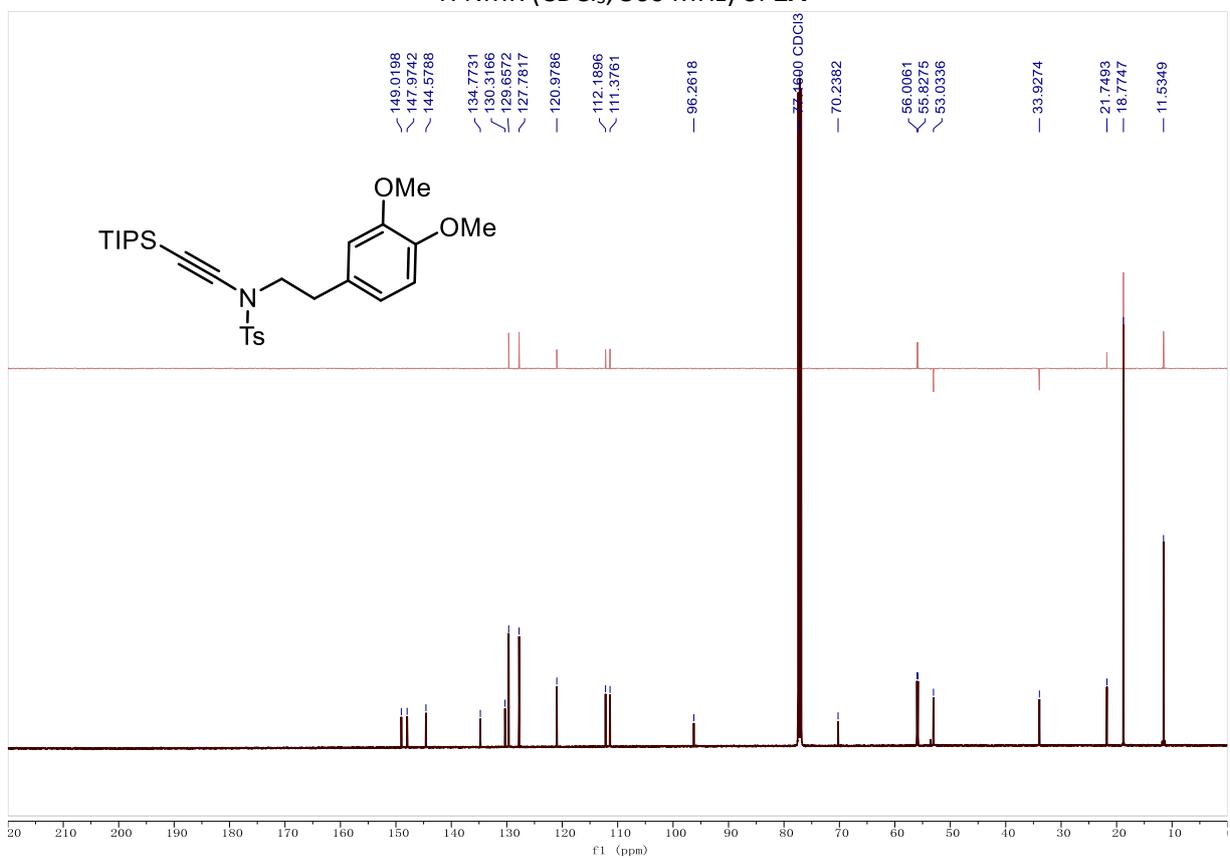
¹H NMR (CDCl₃, 500 MHz) of **2y**



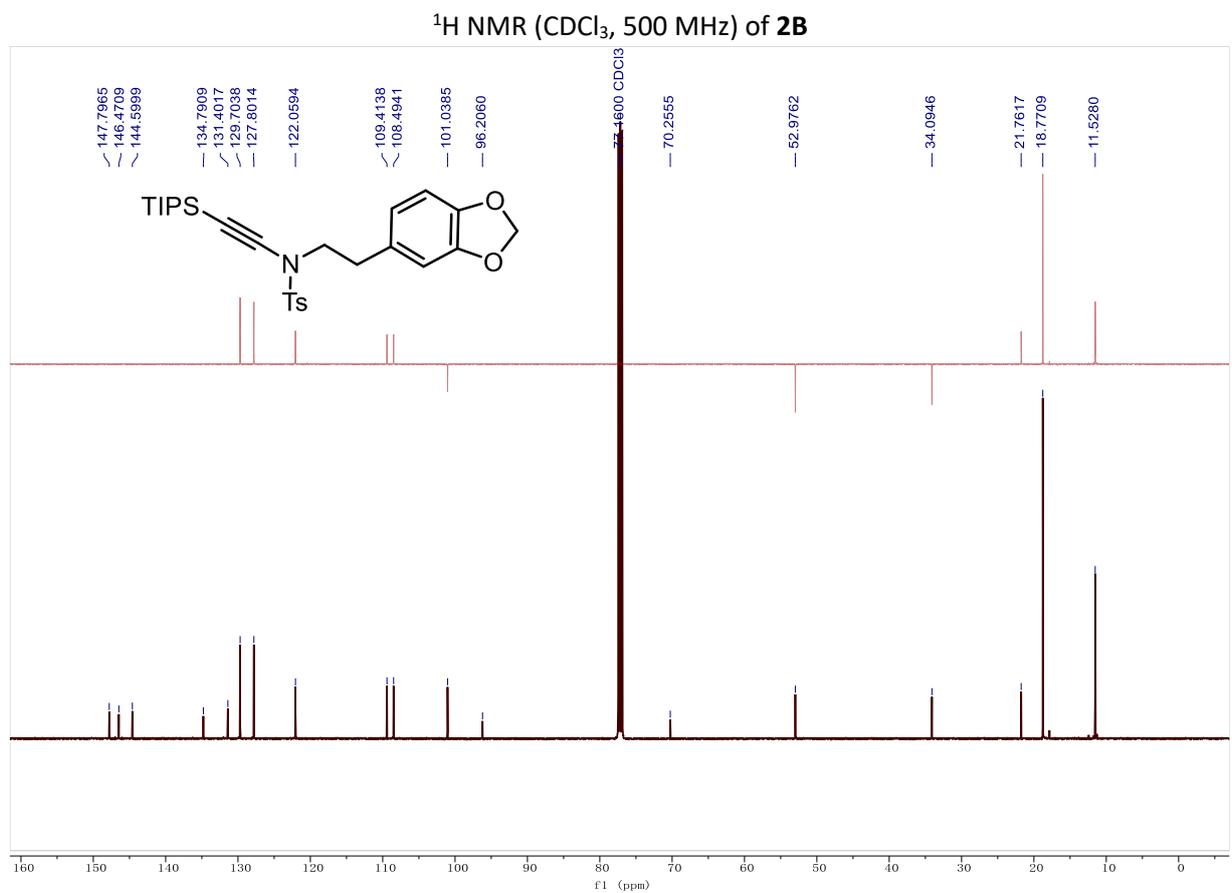
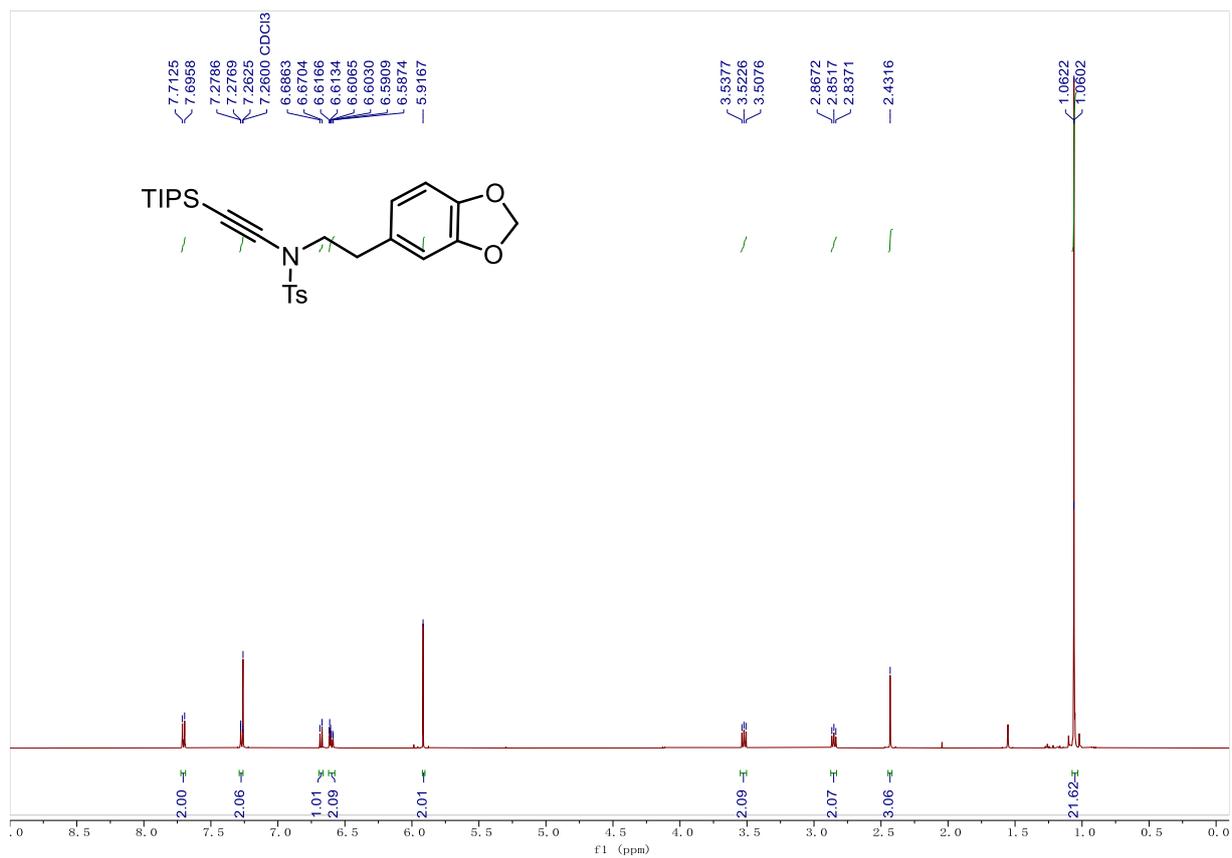
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **2y**



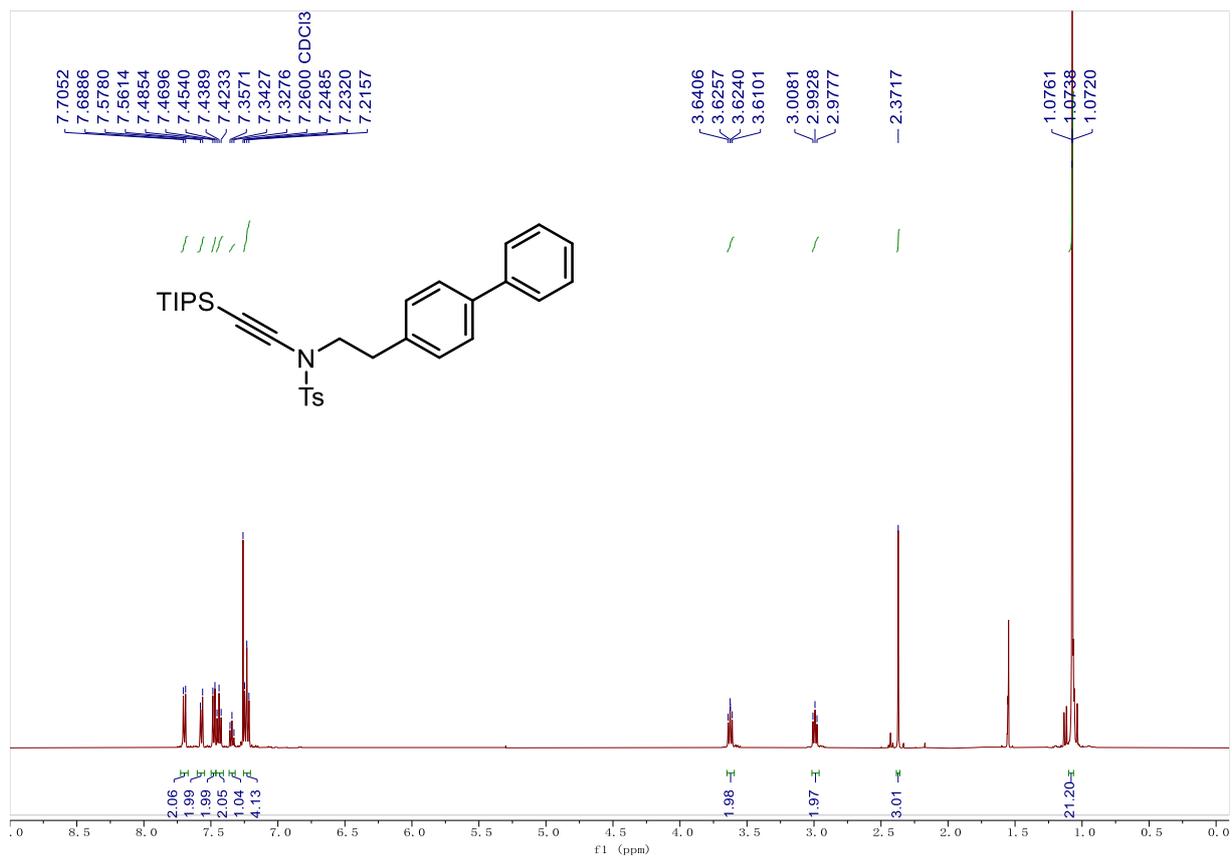
¹H NMR (CDCl₃, 500 MHz) of 2A



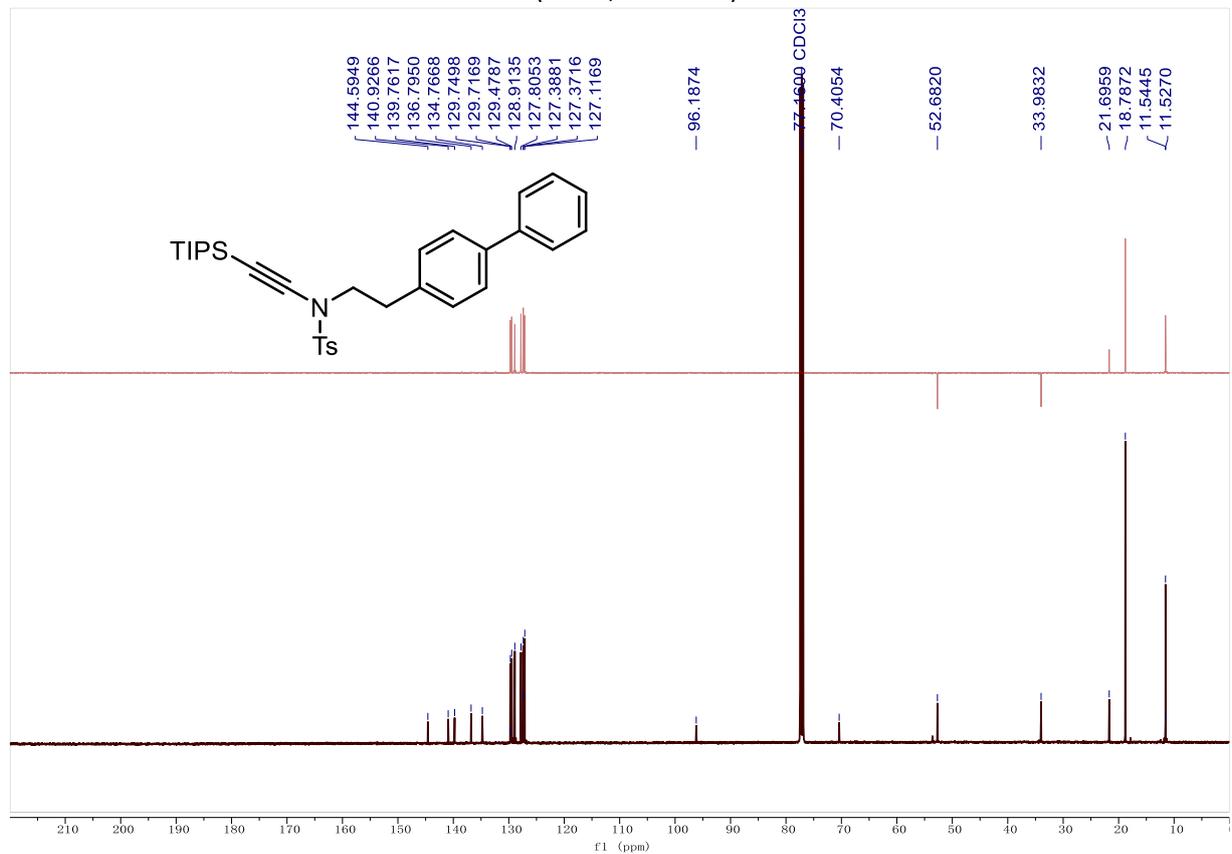
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2A



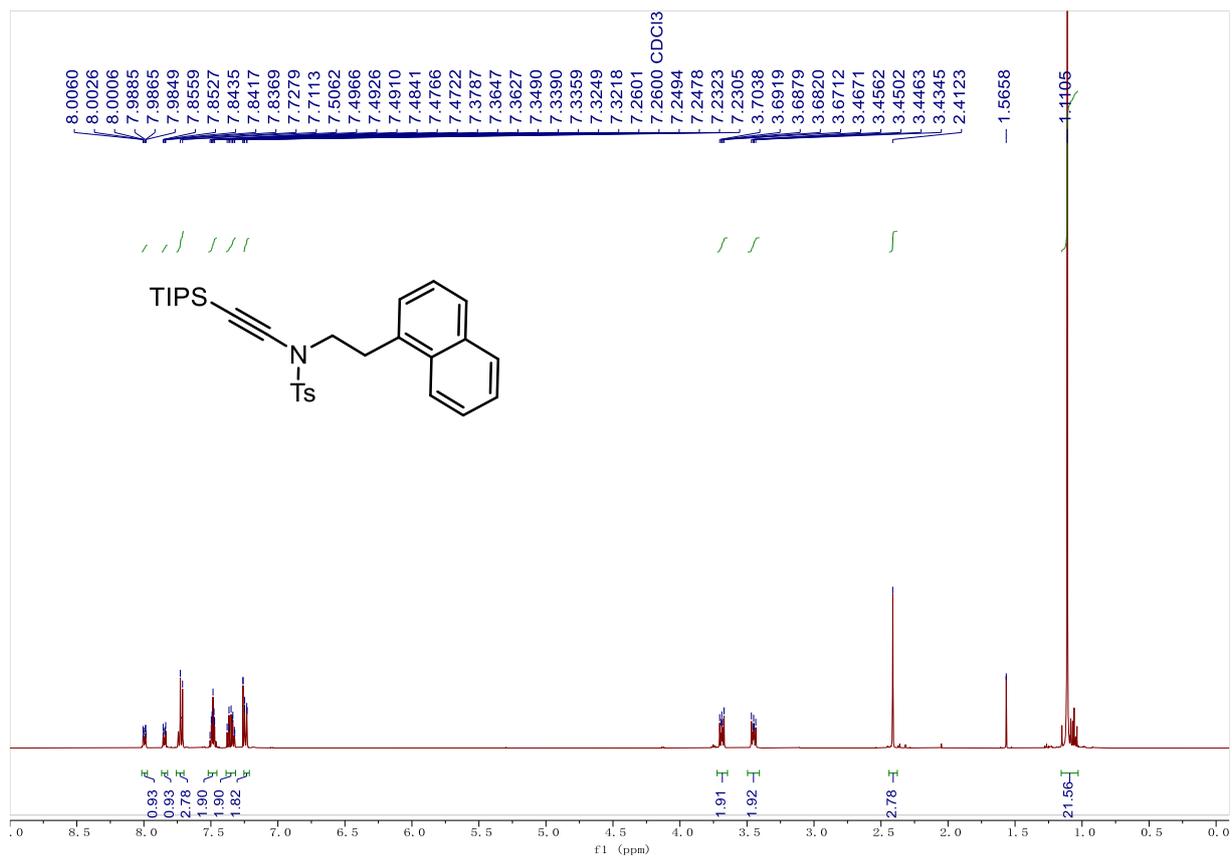
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2B



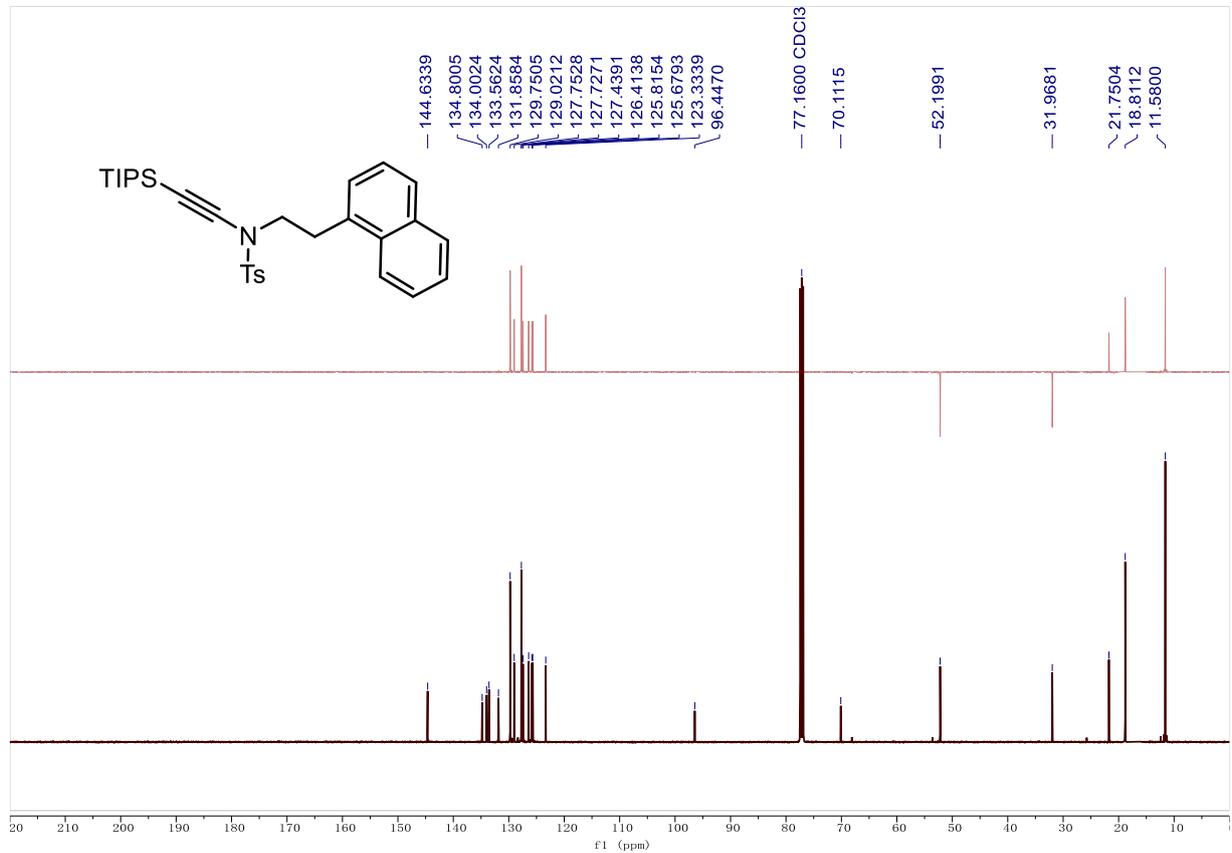
¹H NMR (CDCl₃, 500 MHz) of 2C



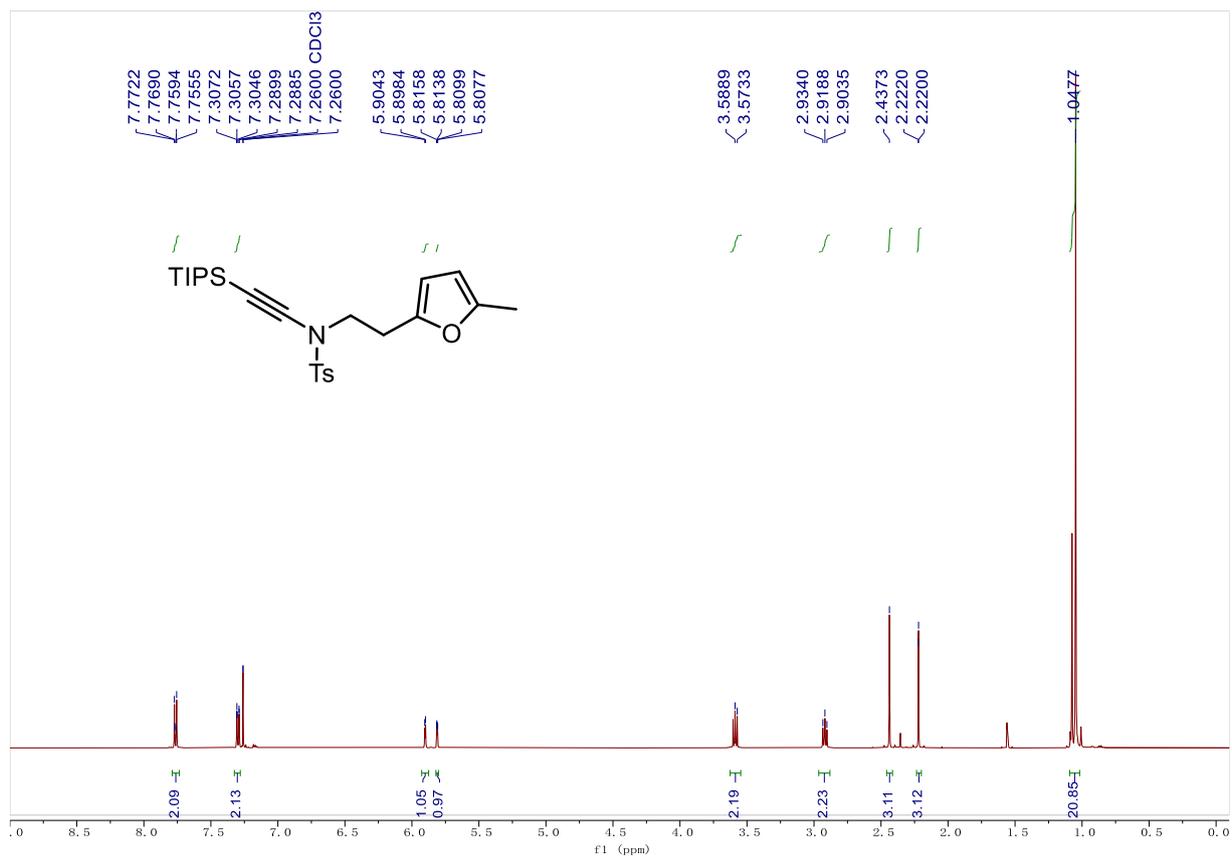
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2C



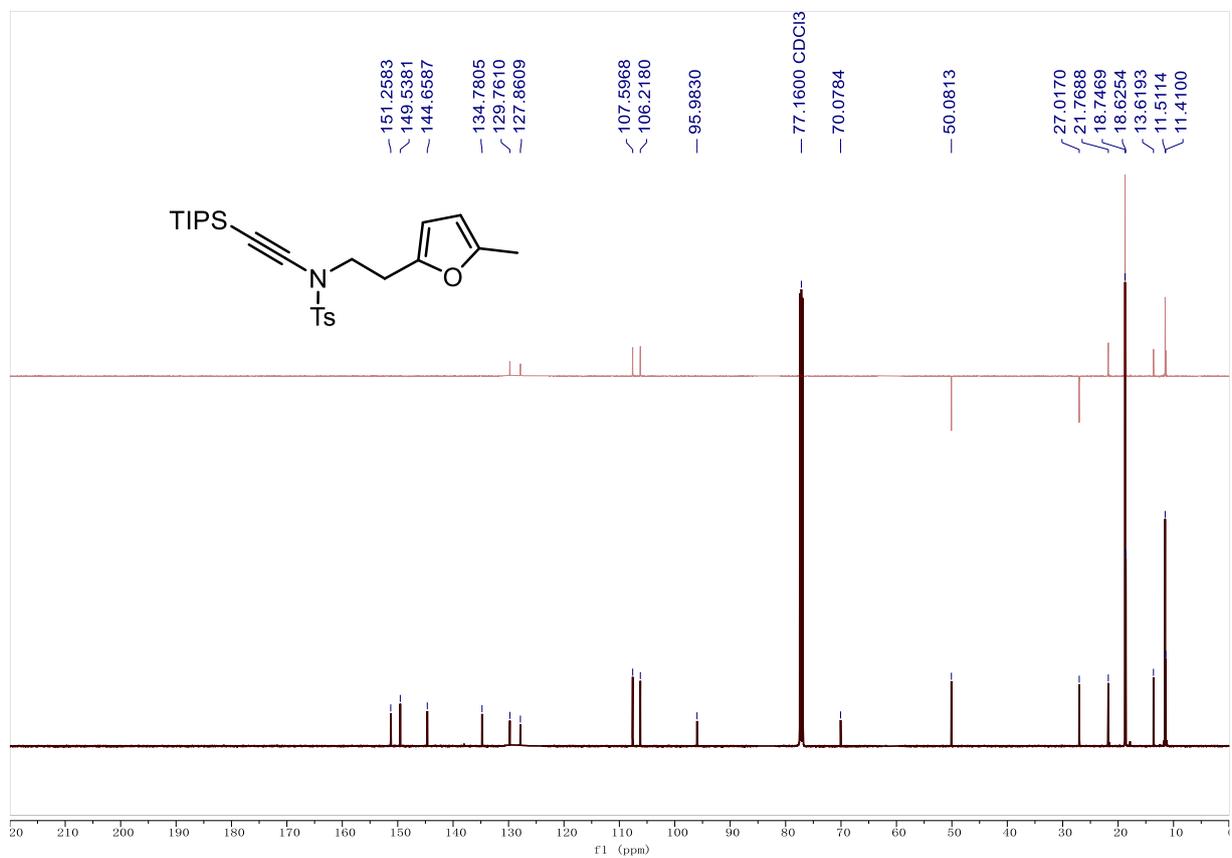
¹H NMR (CDCl₃, 500 MHz) of 2D



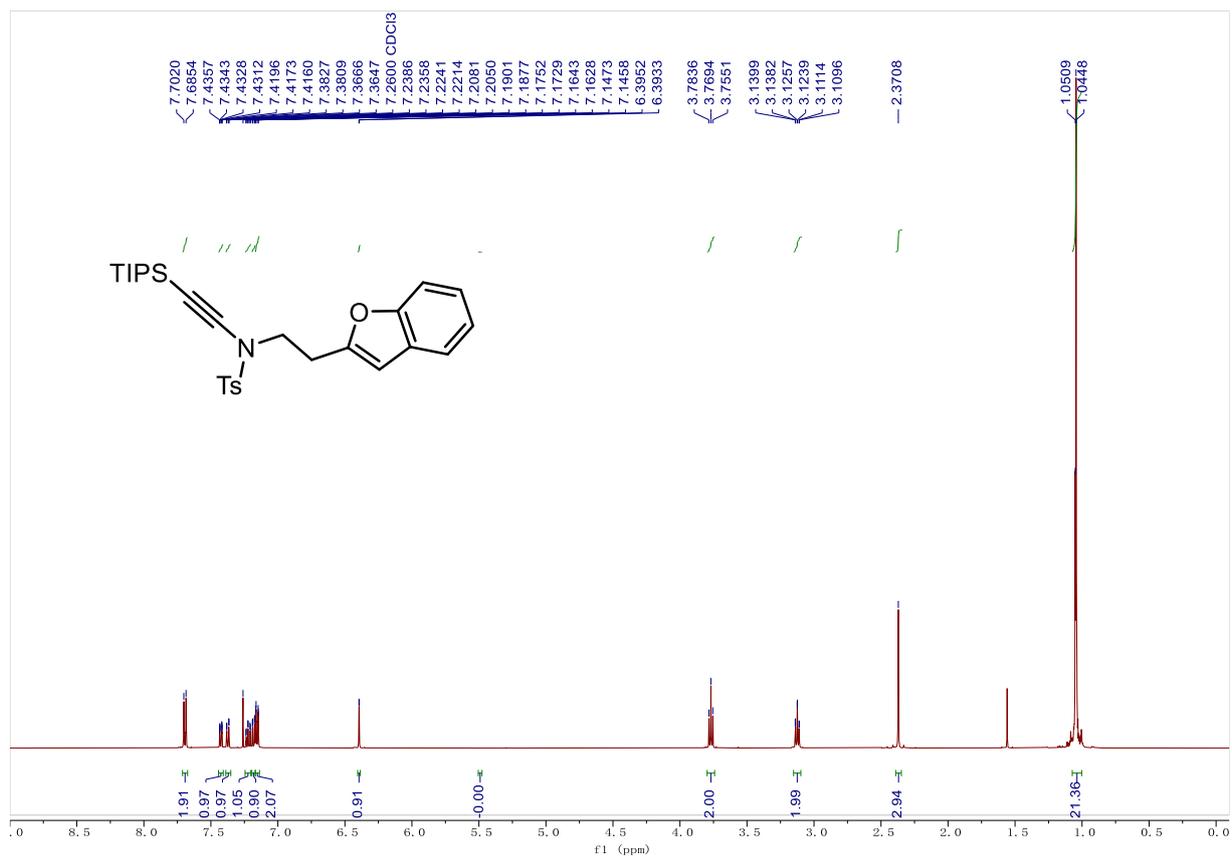
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2D



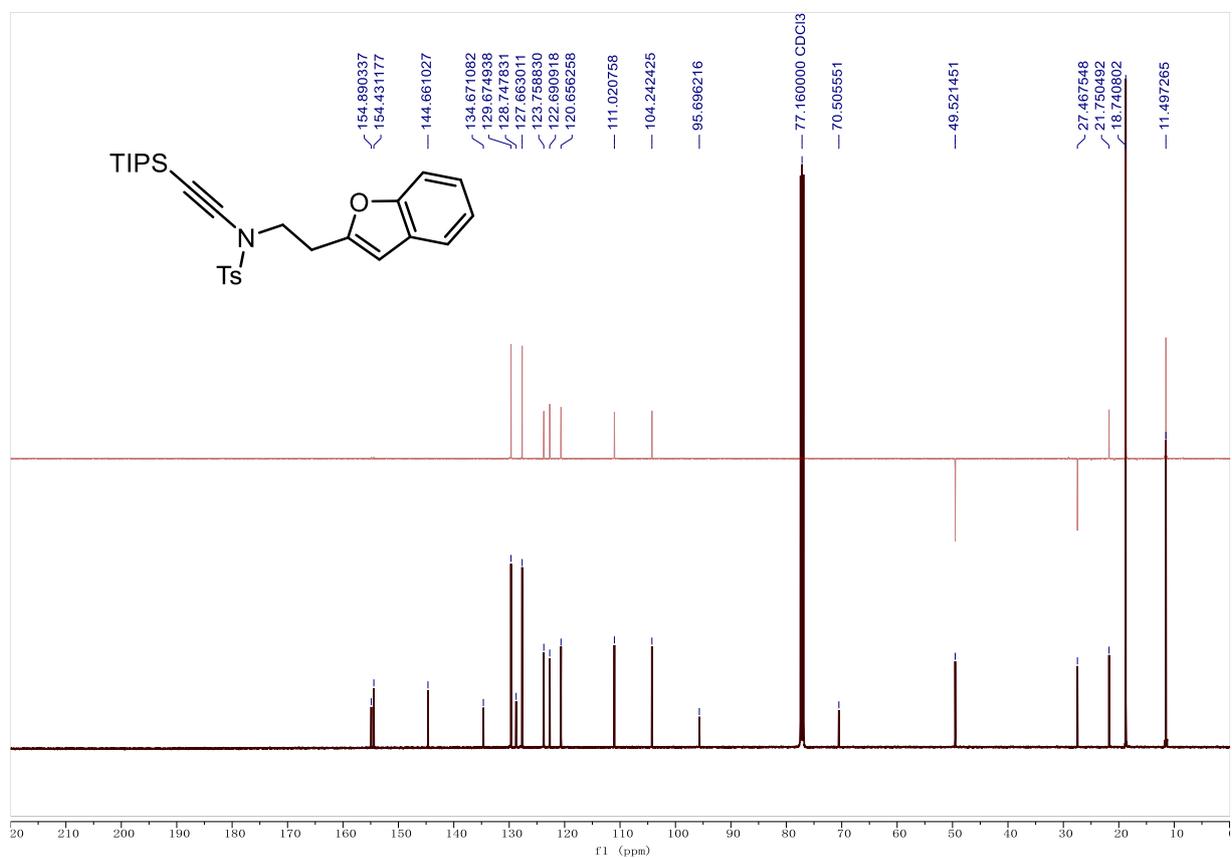
¹H NMR (CDCl₃, 500 MHz) of 2F



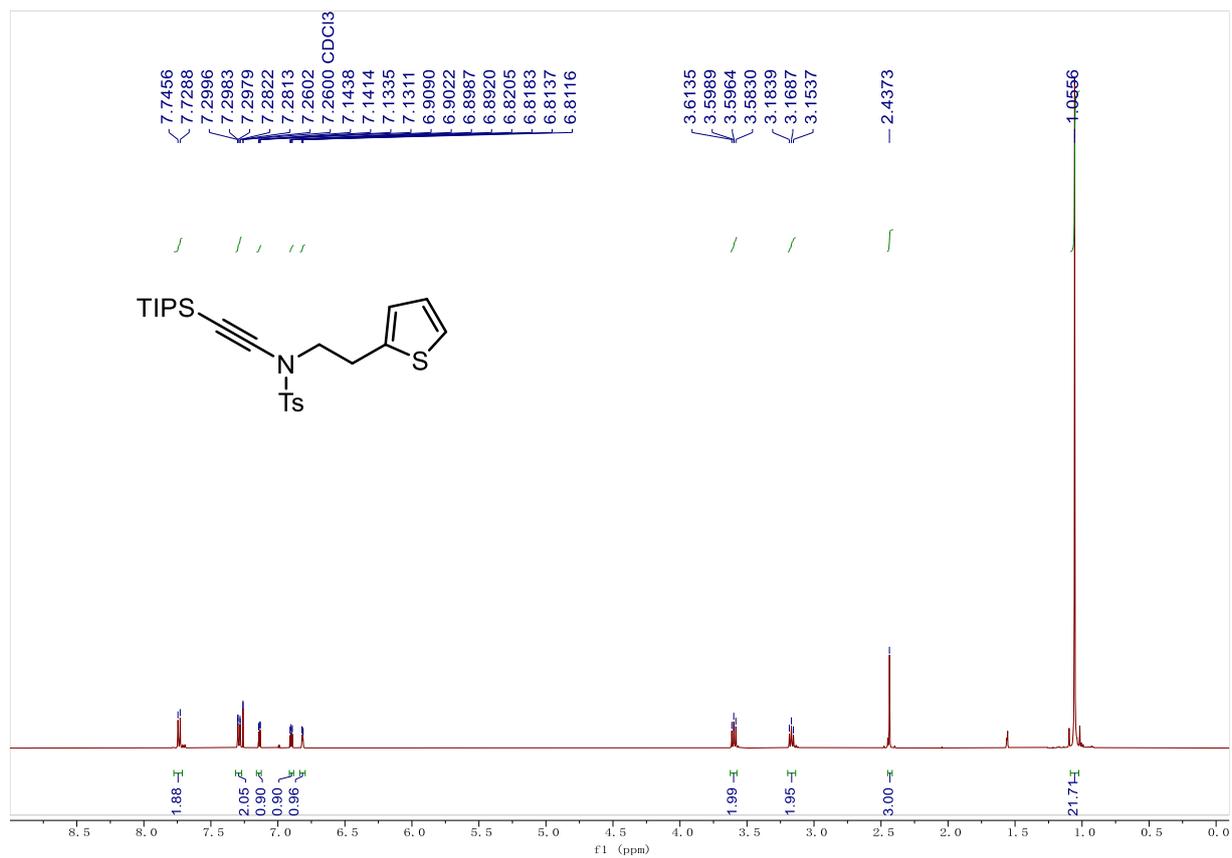
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2F



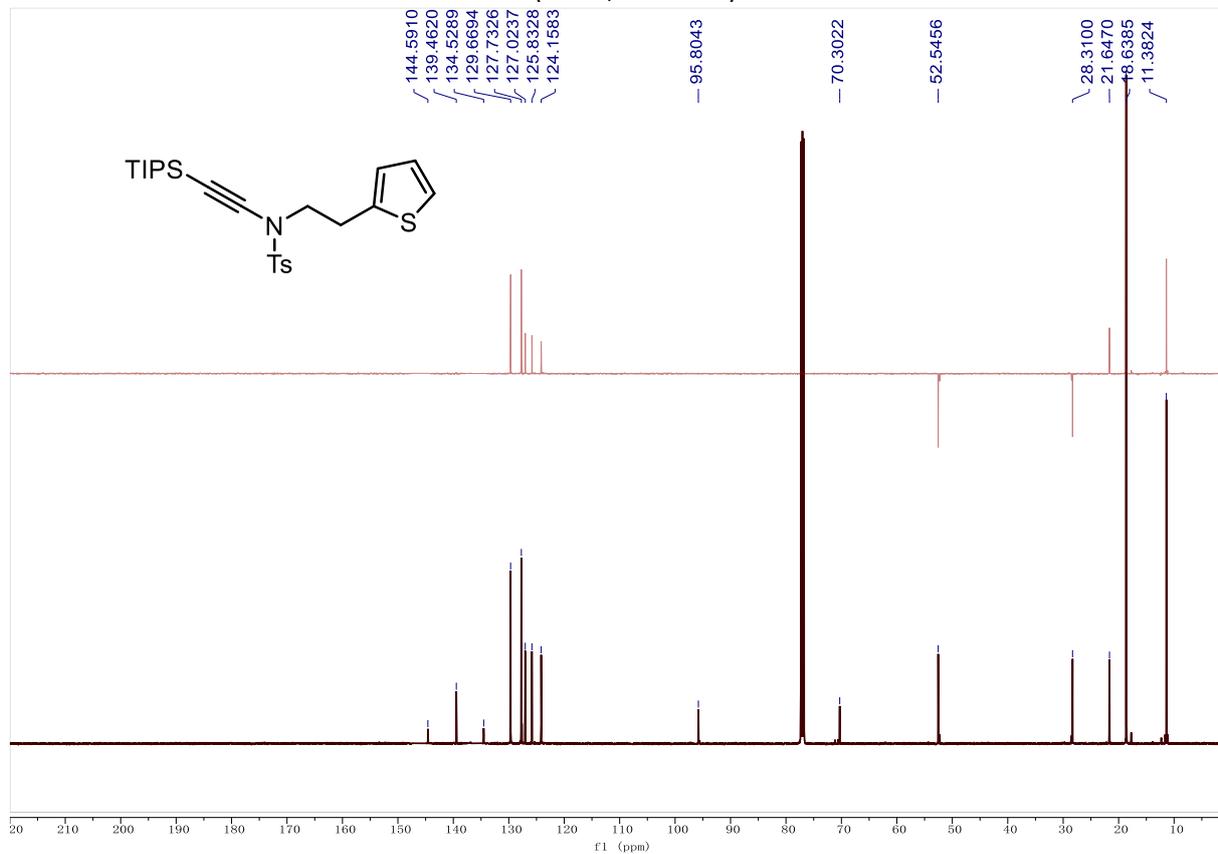
¹H NMR (CDCl₃, 500 MHz) of 2G



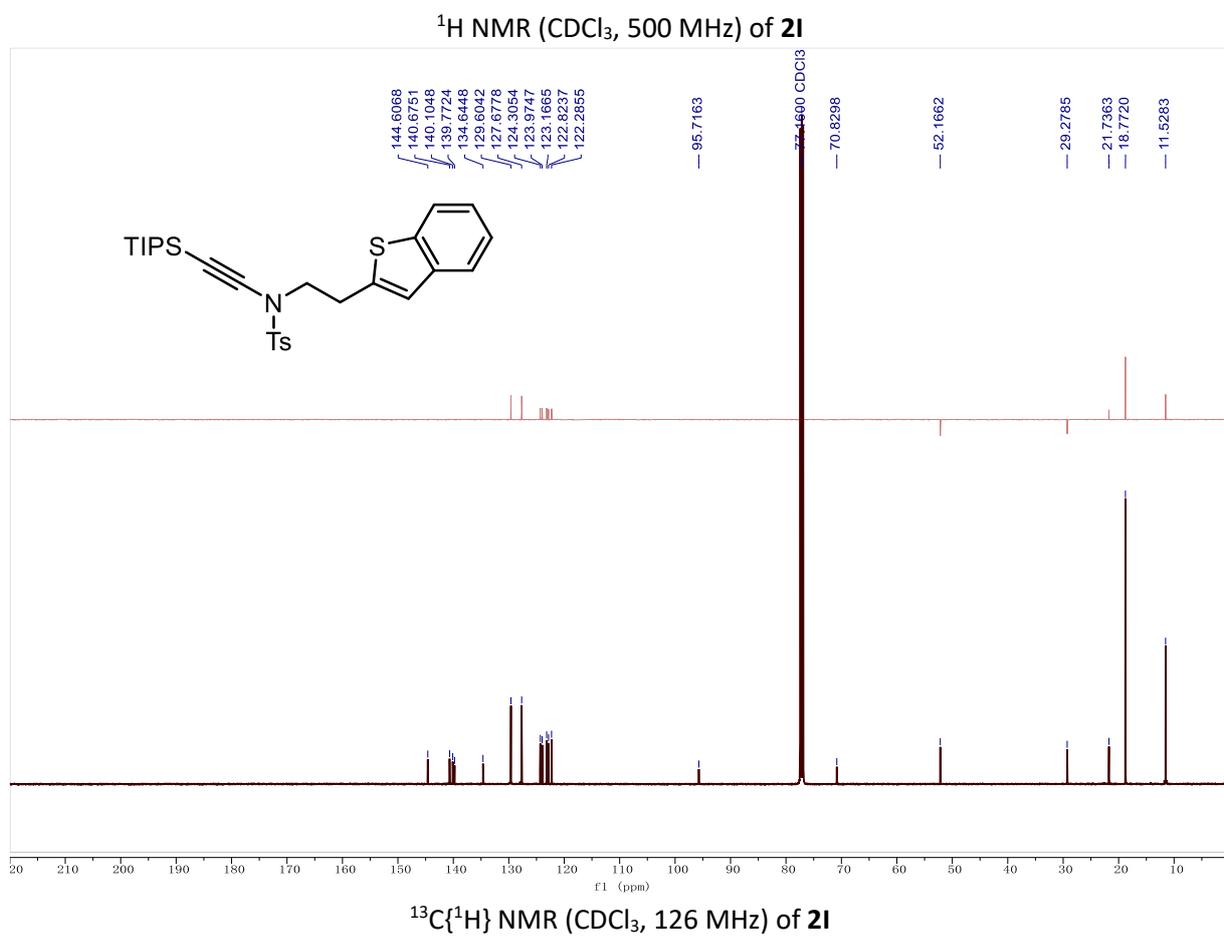
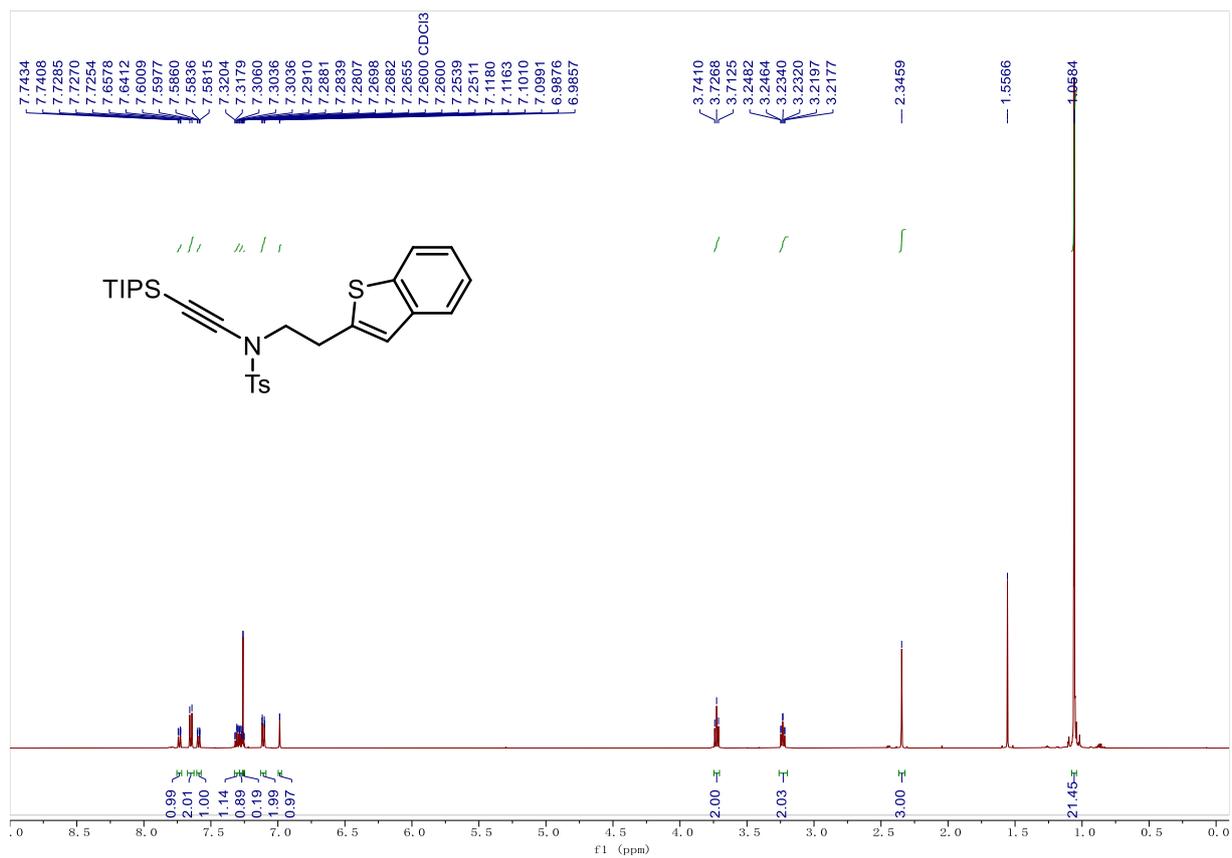
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2G

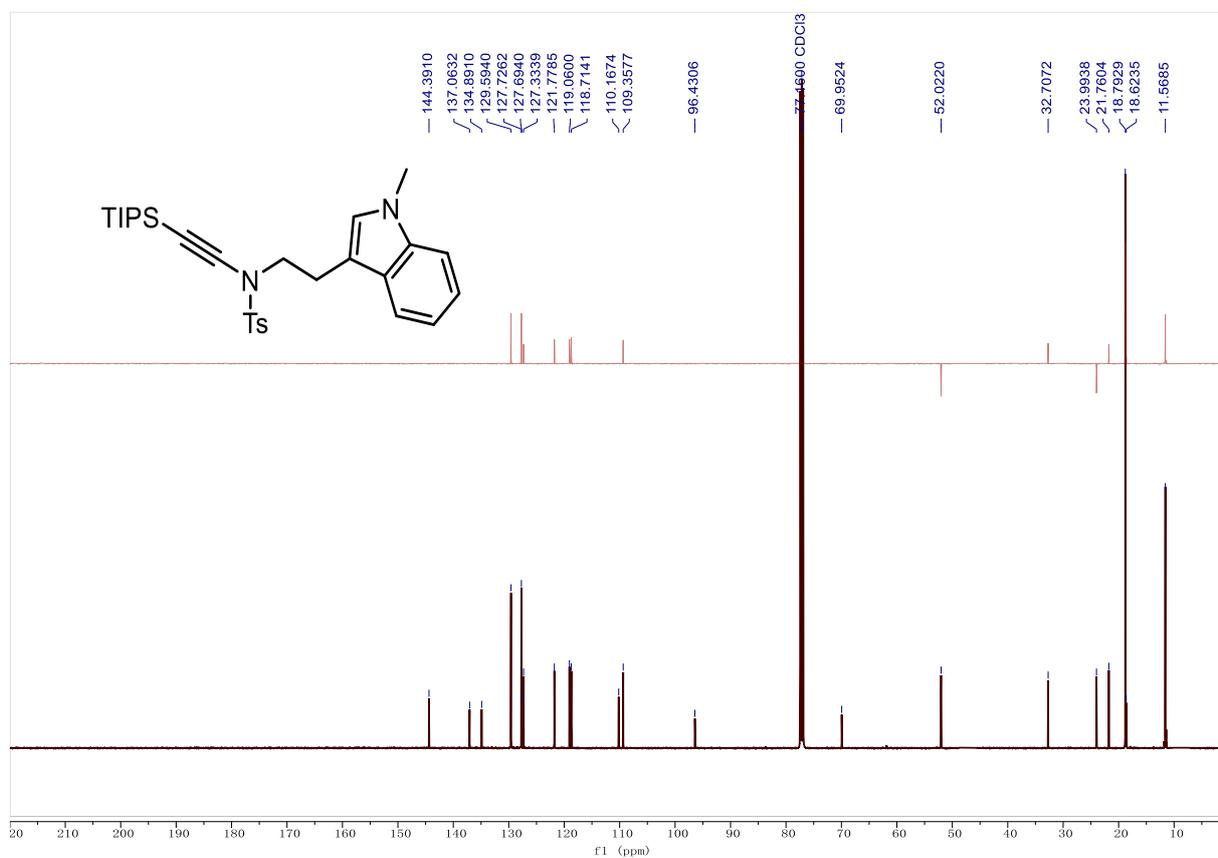
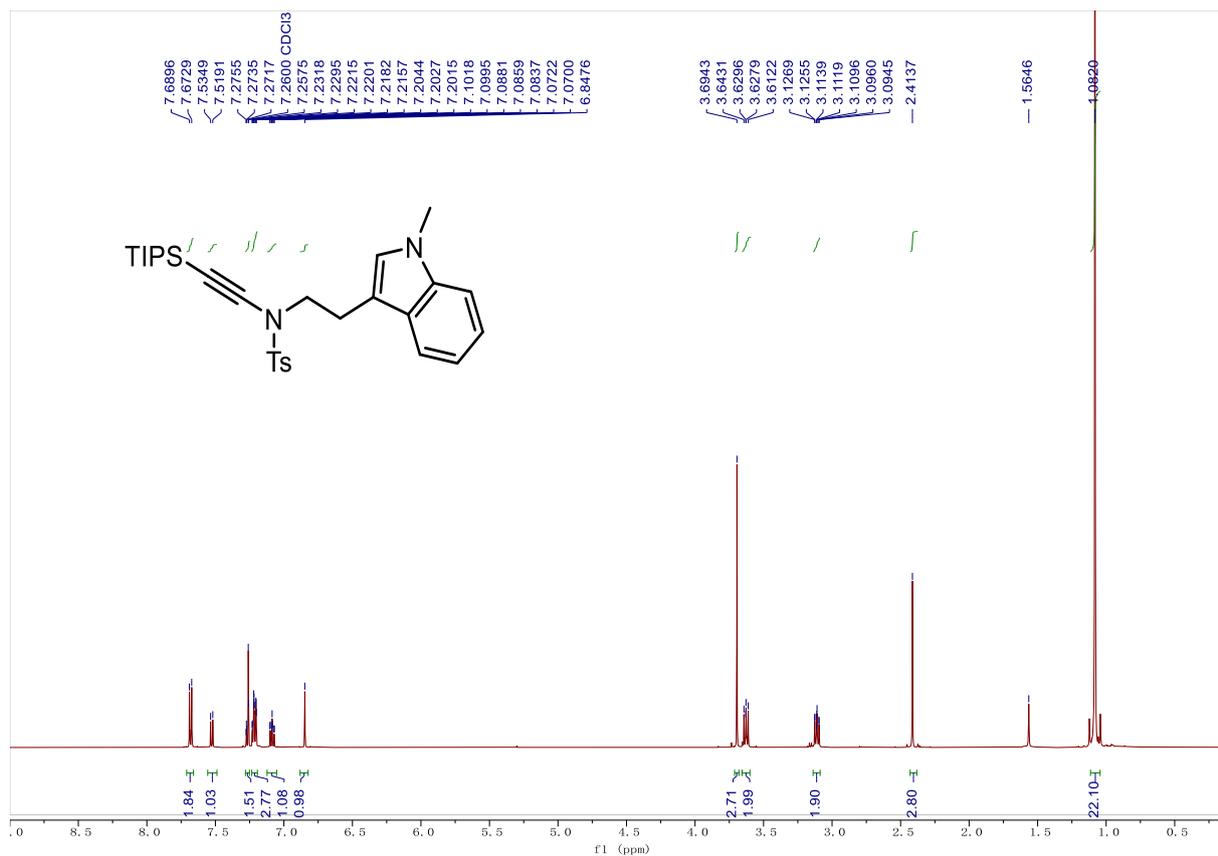


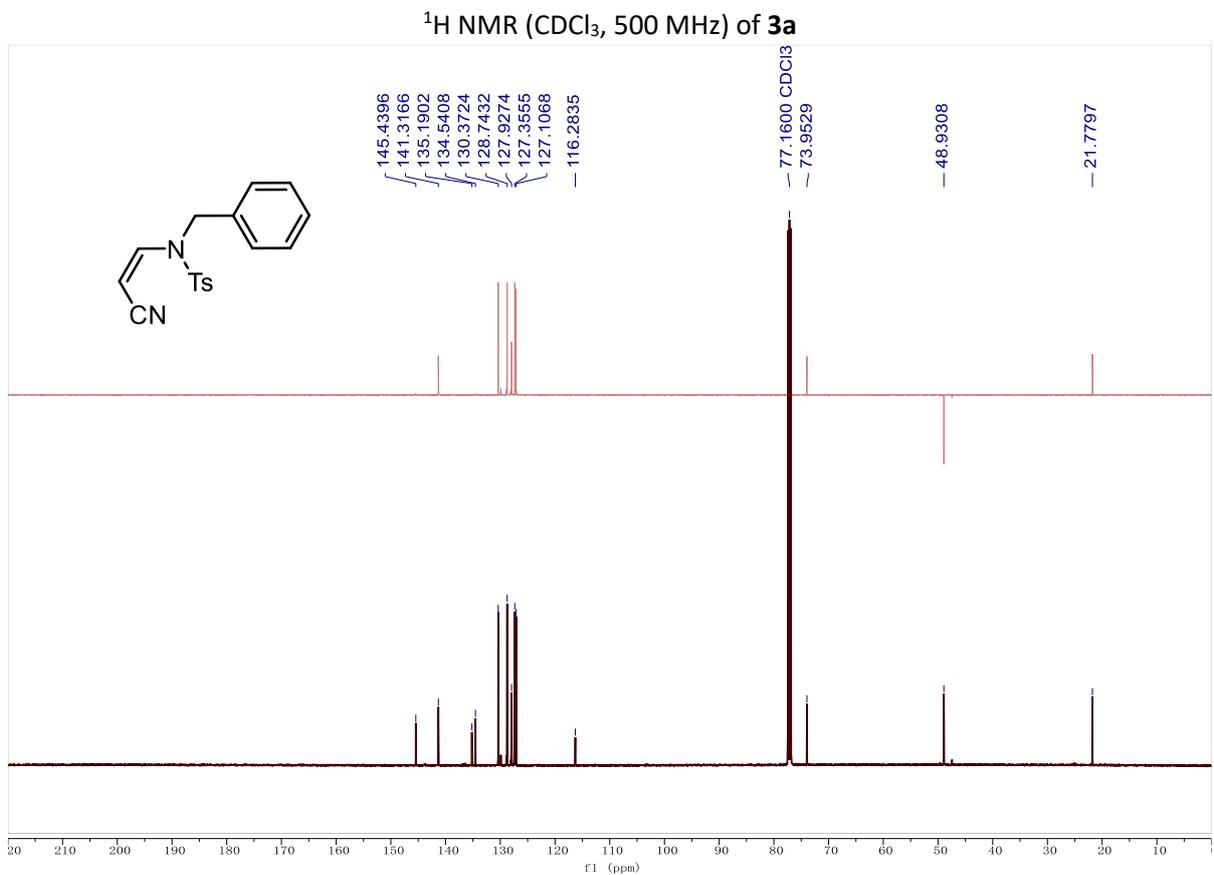
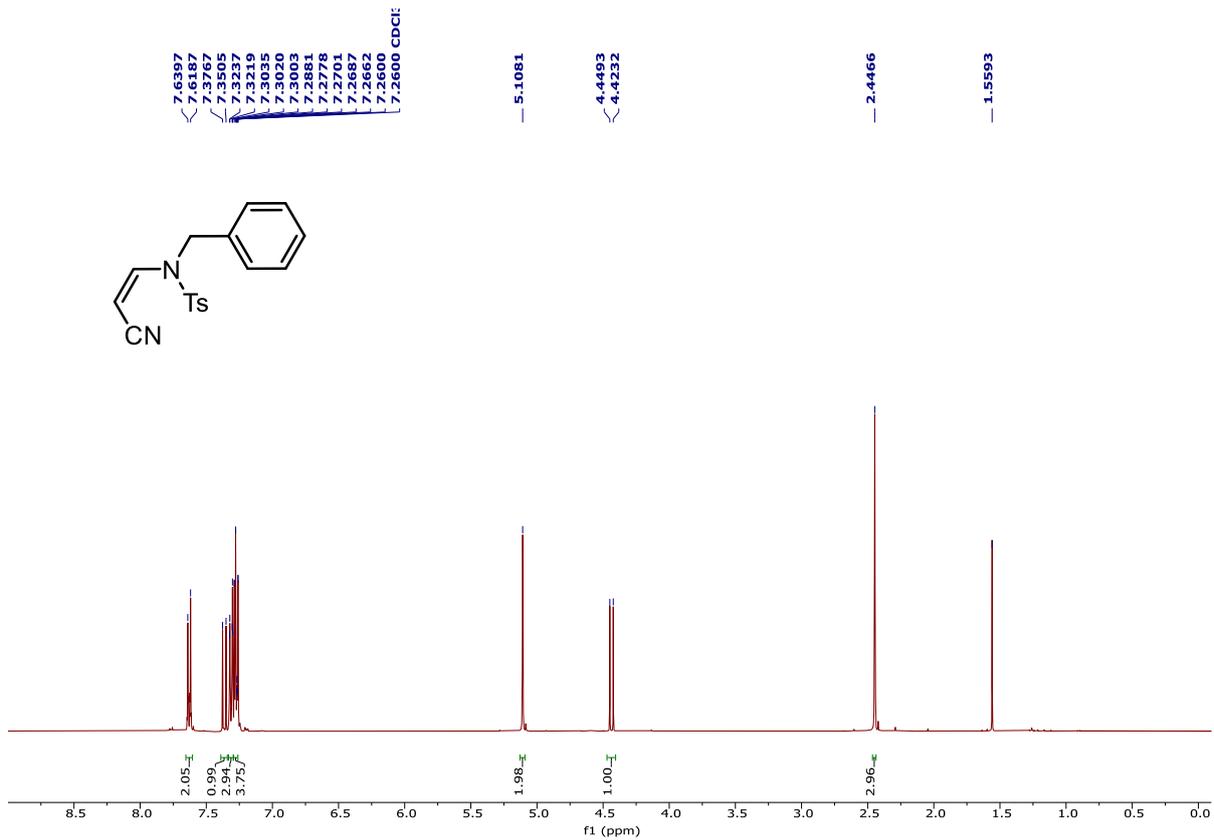
¹H NMR (CDCl₃, 500 MHz) of 2H



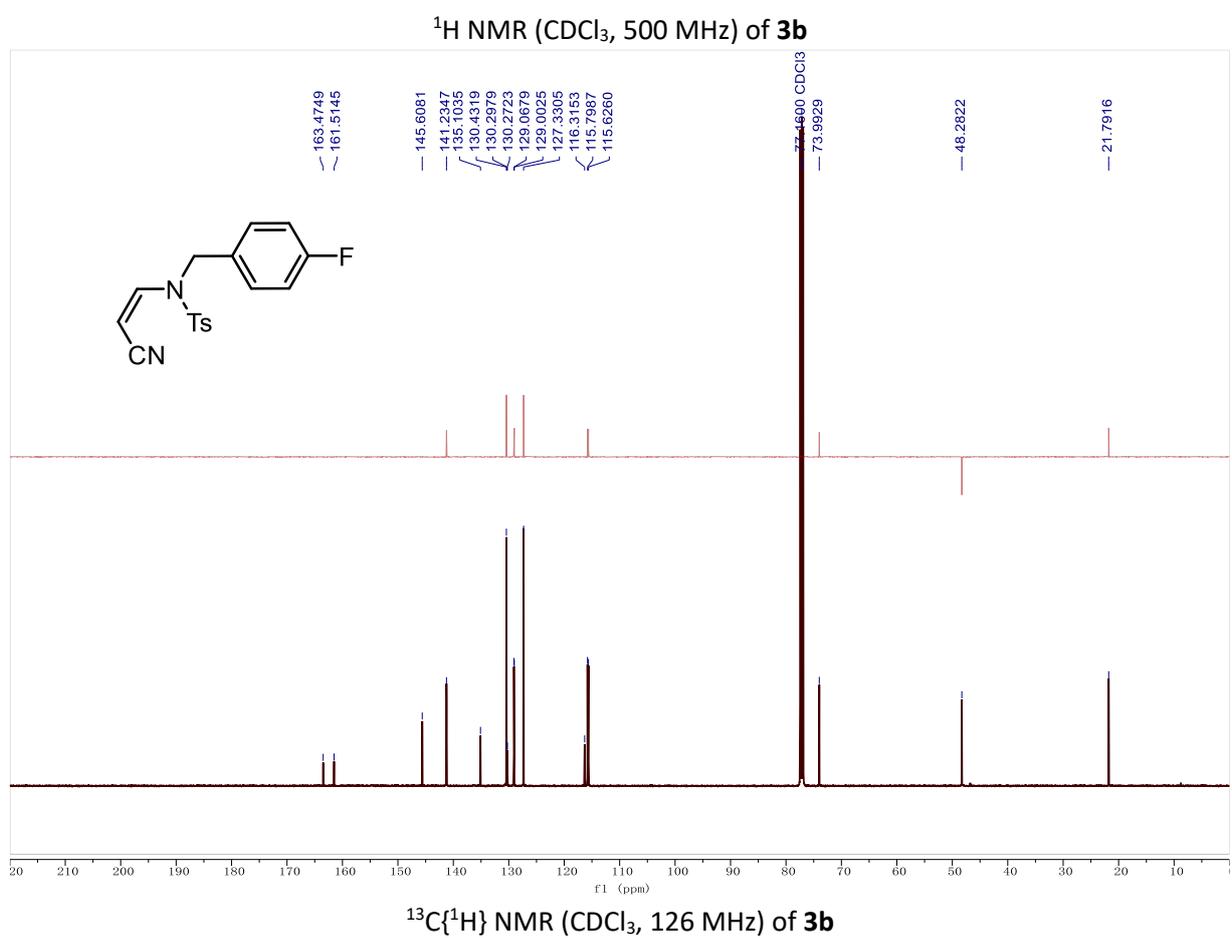
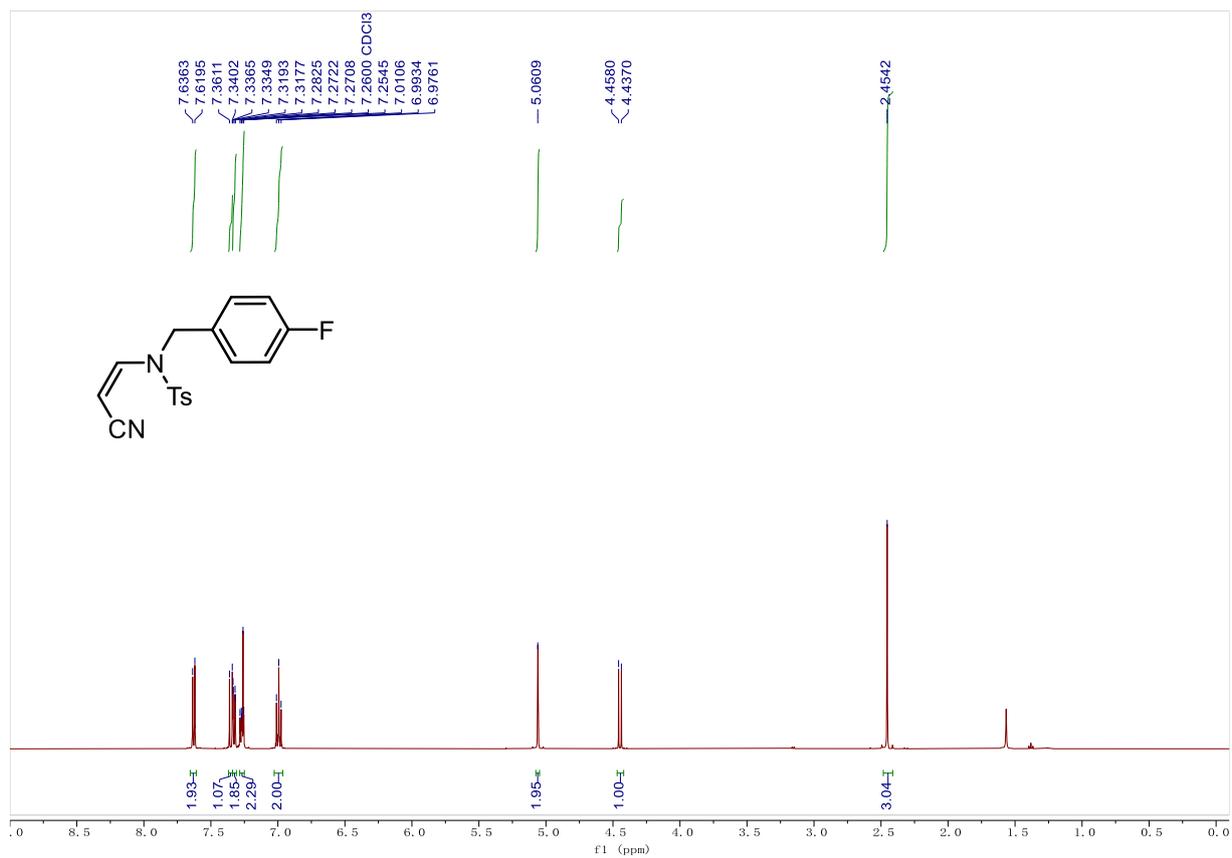
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2H

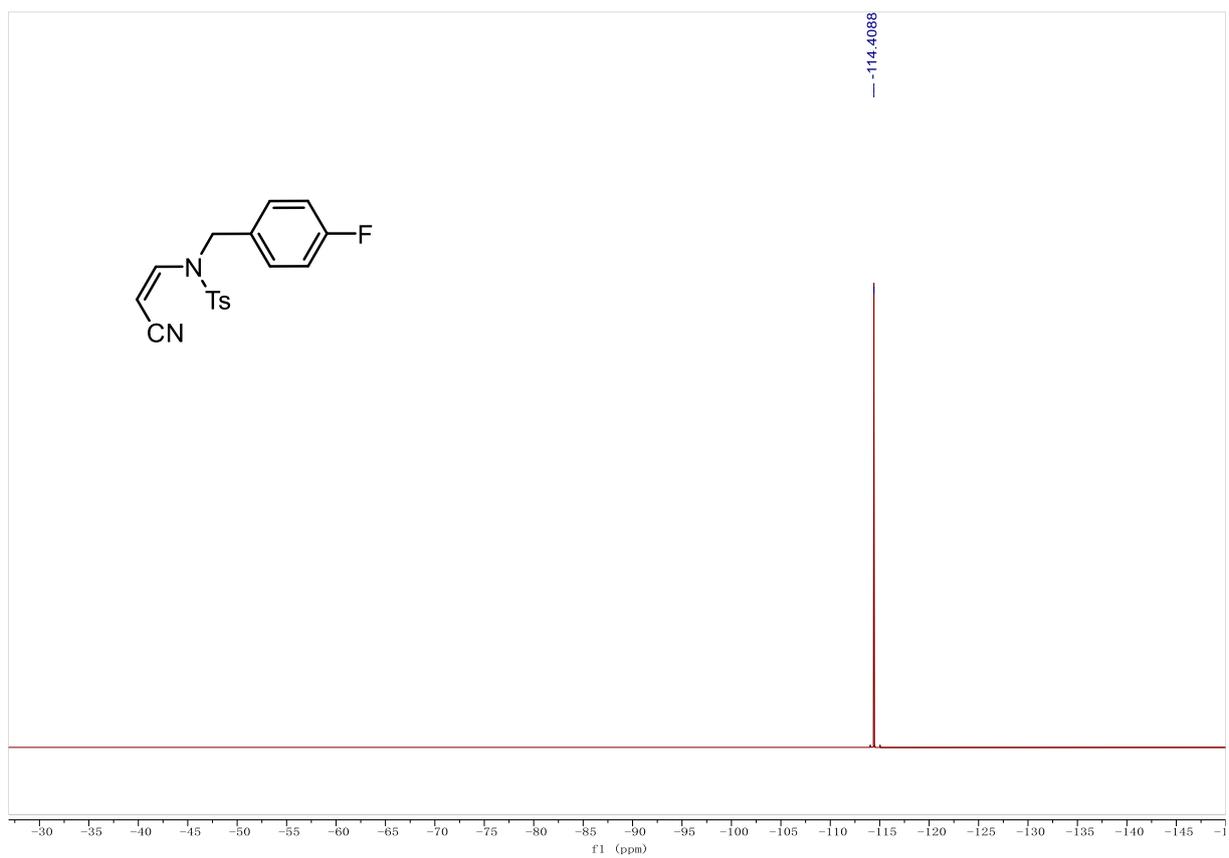




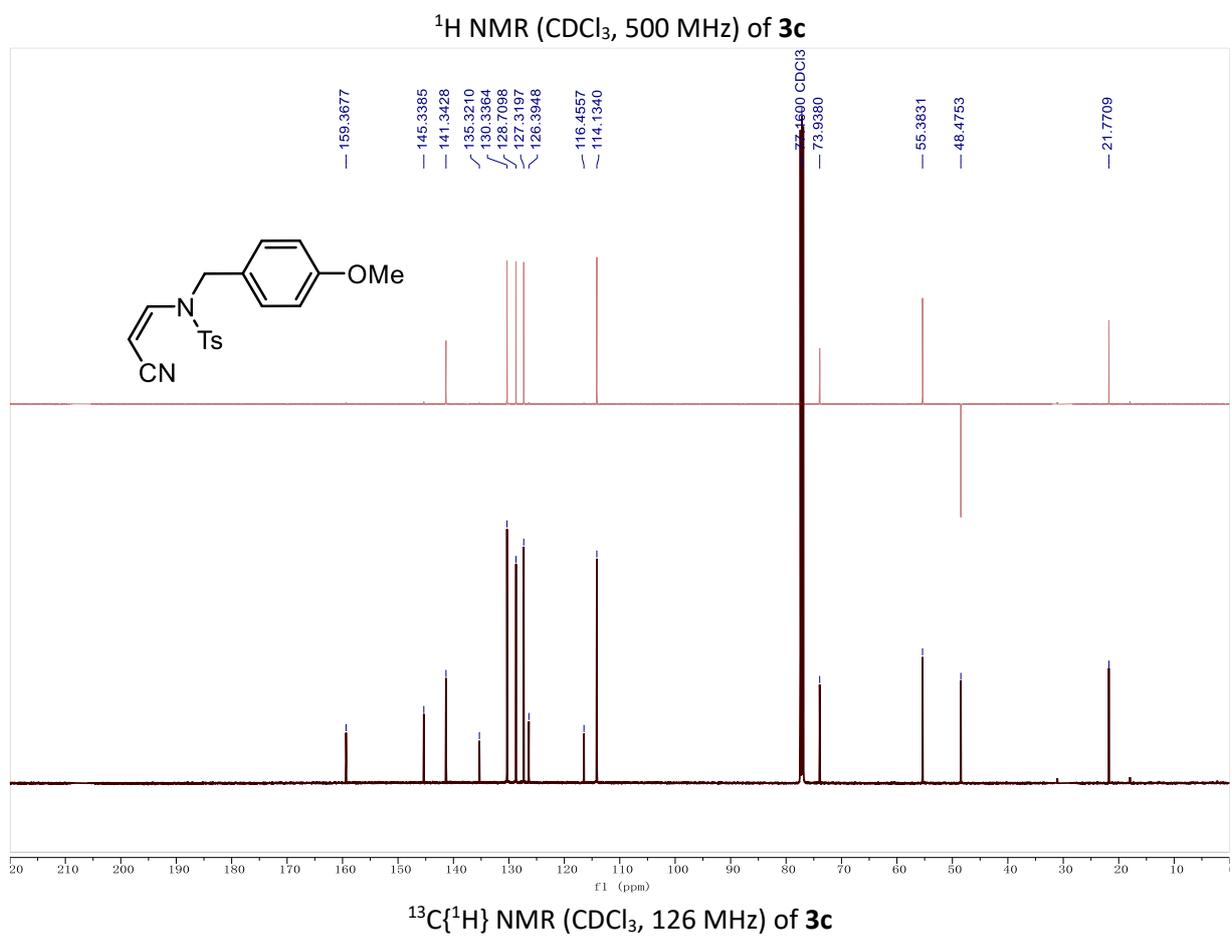
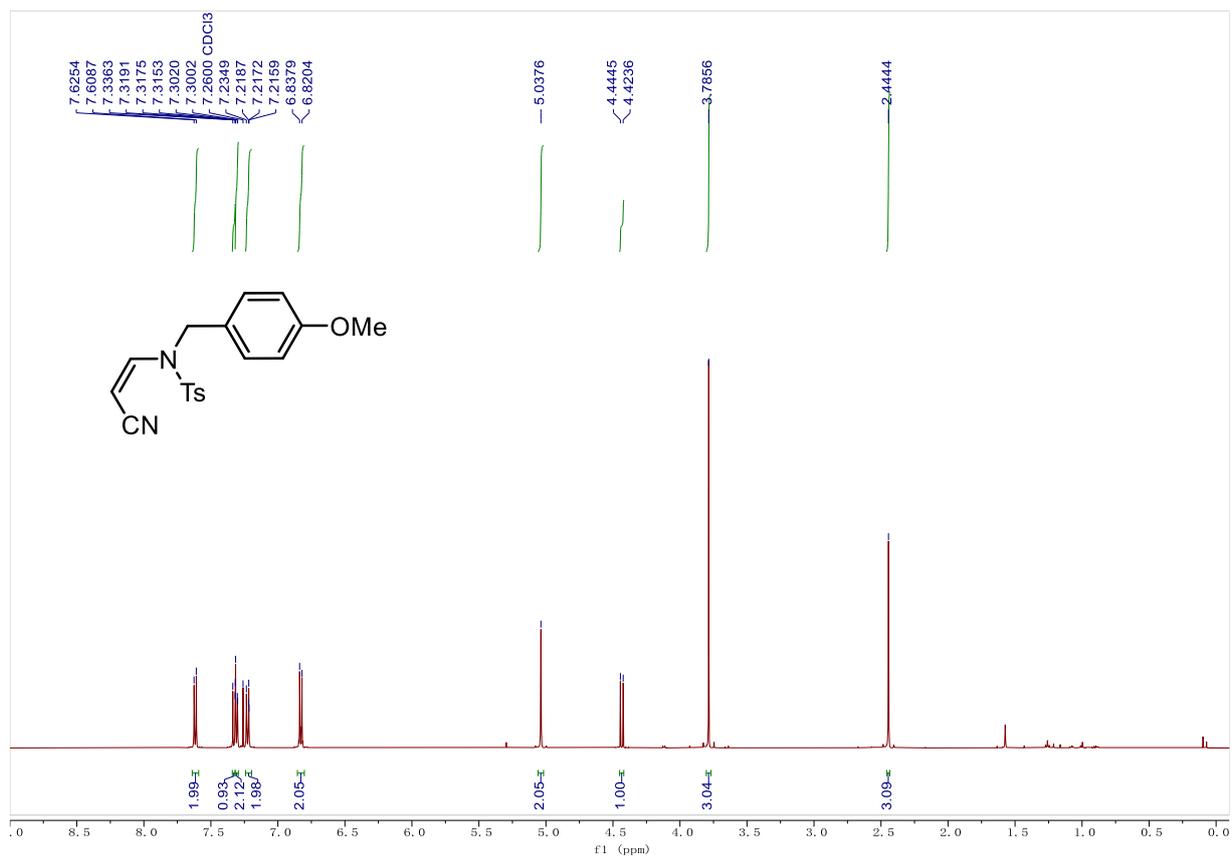


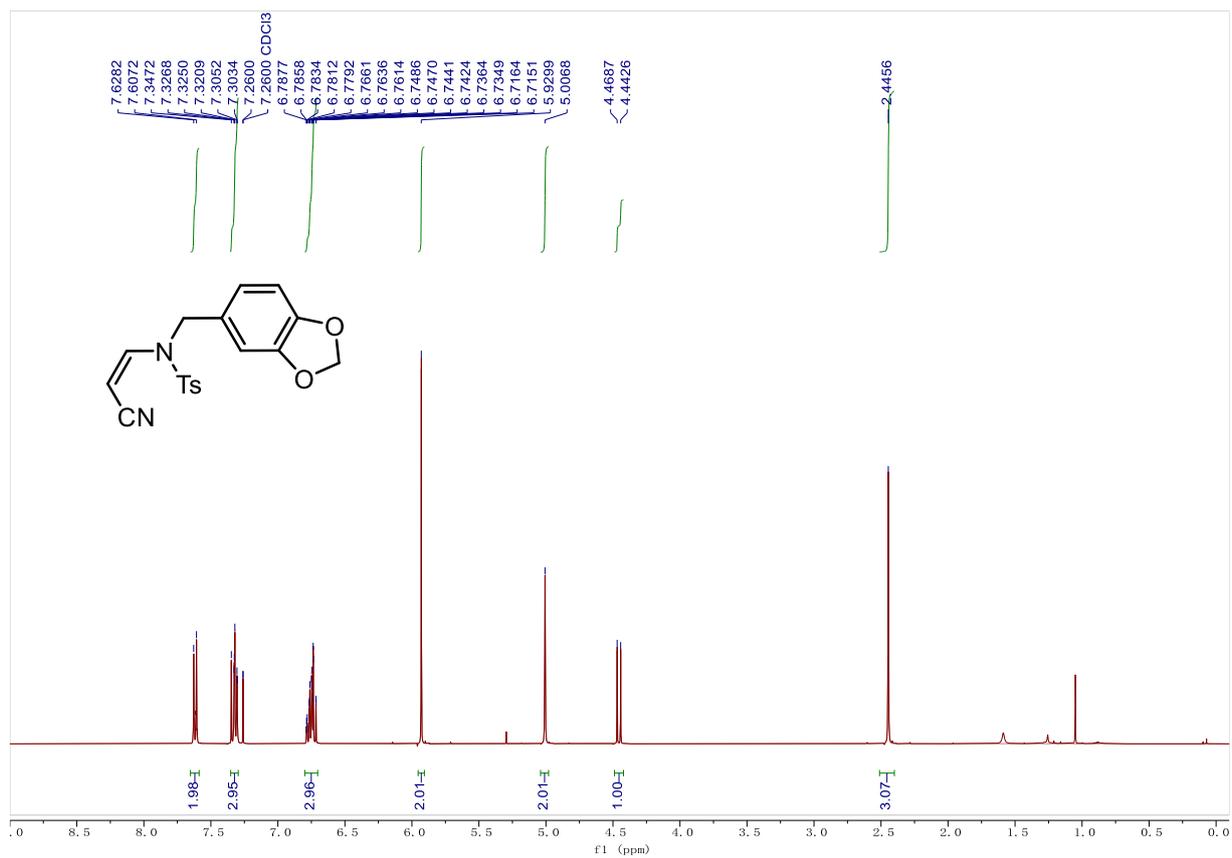
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3a



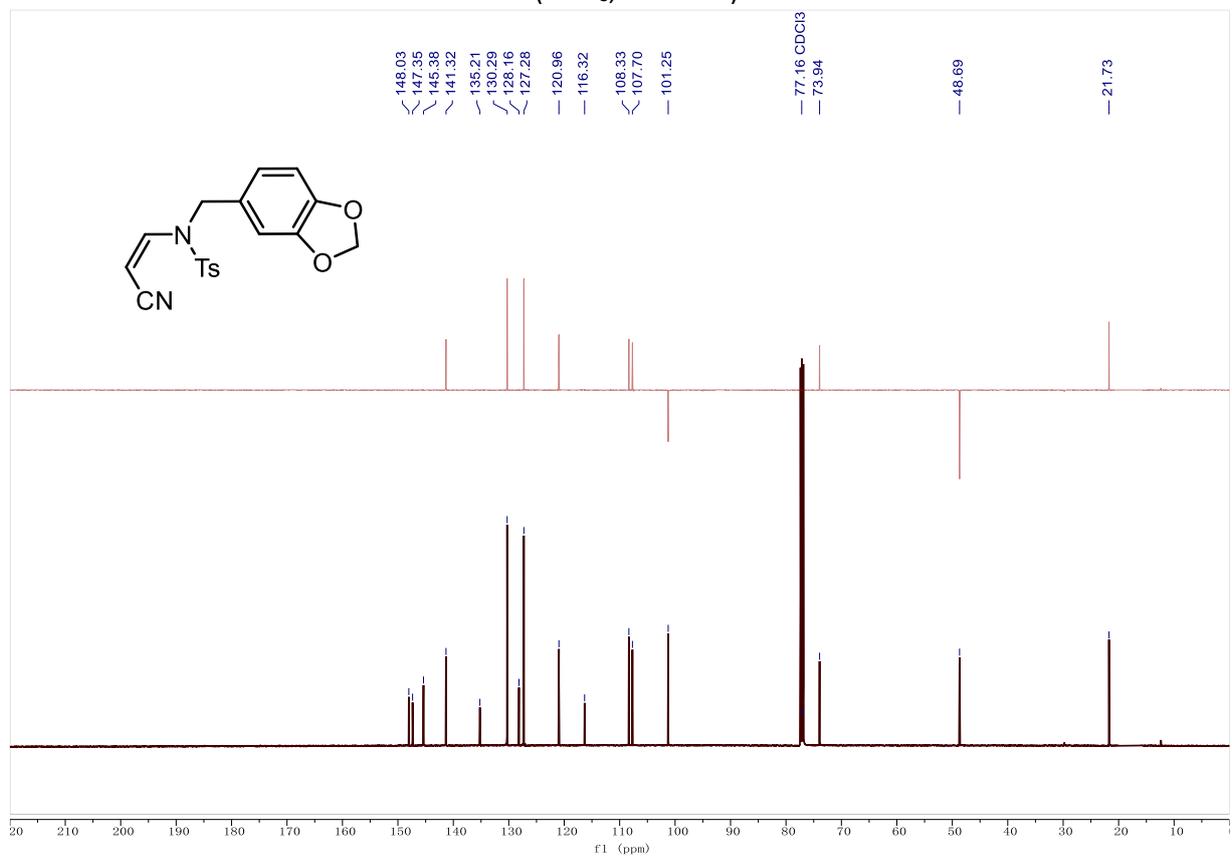


$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3b**

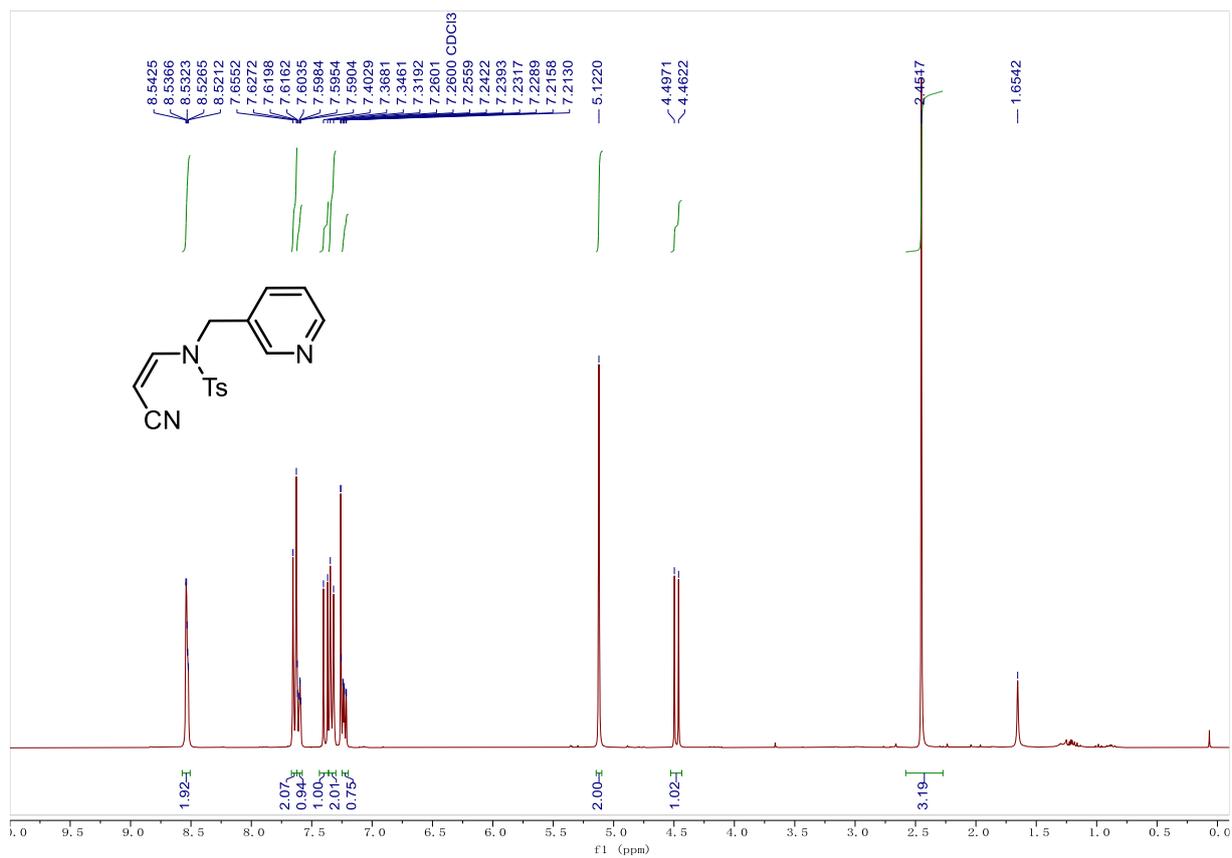




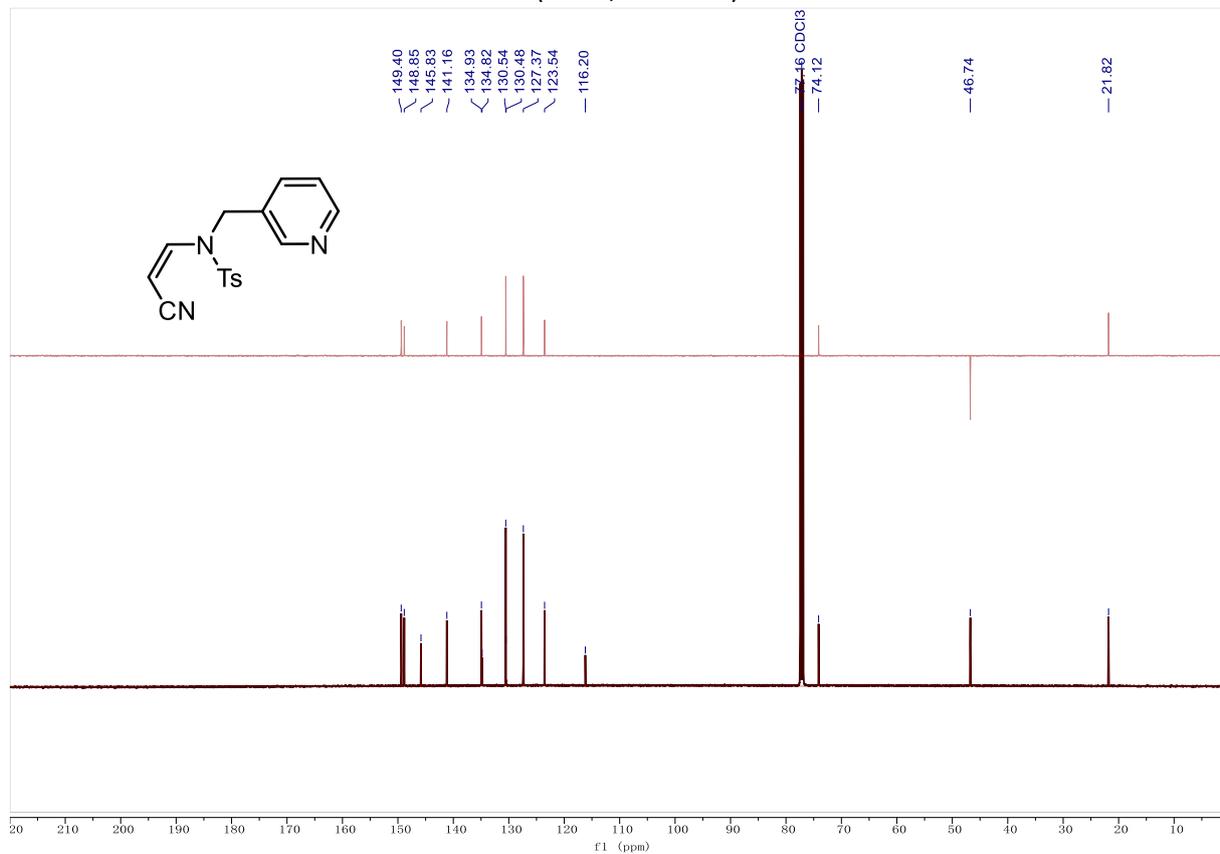
¹H NMR (CDCl₃, 500 MHz) of 3d



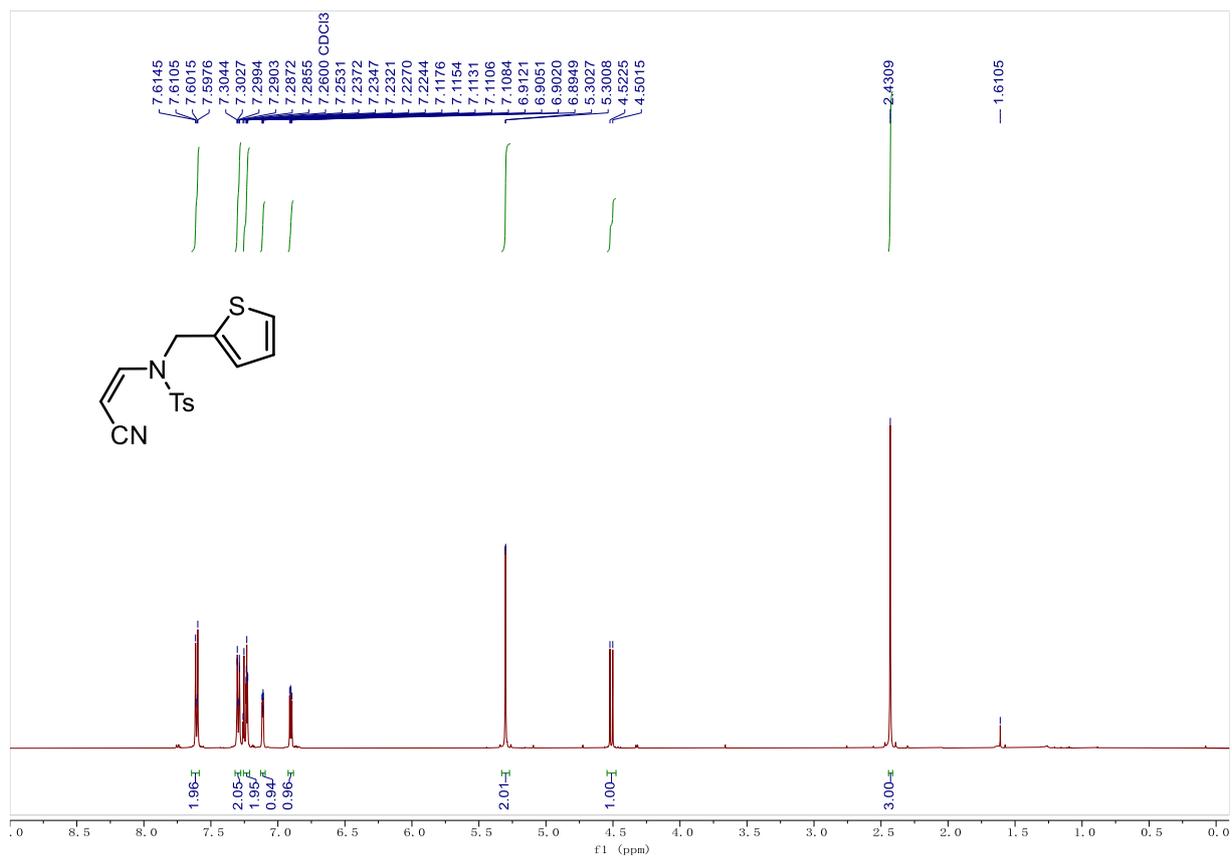
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3d



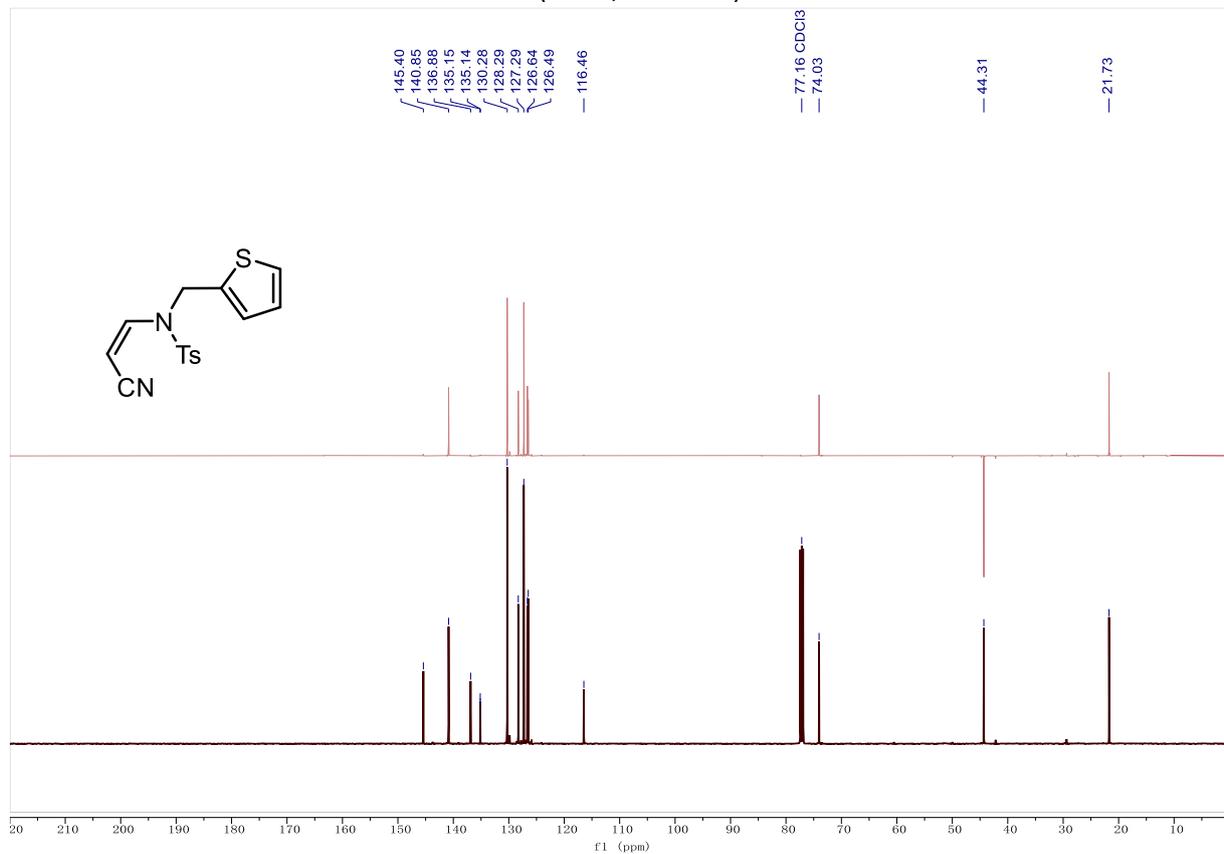
¹H NMR (CDCl₃, 500 MHz) of 3e



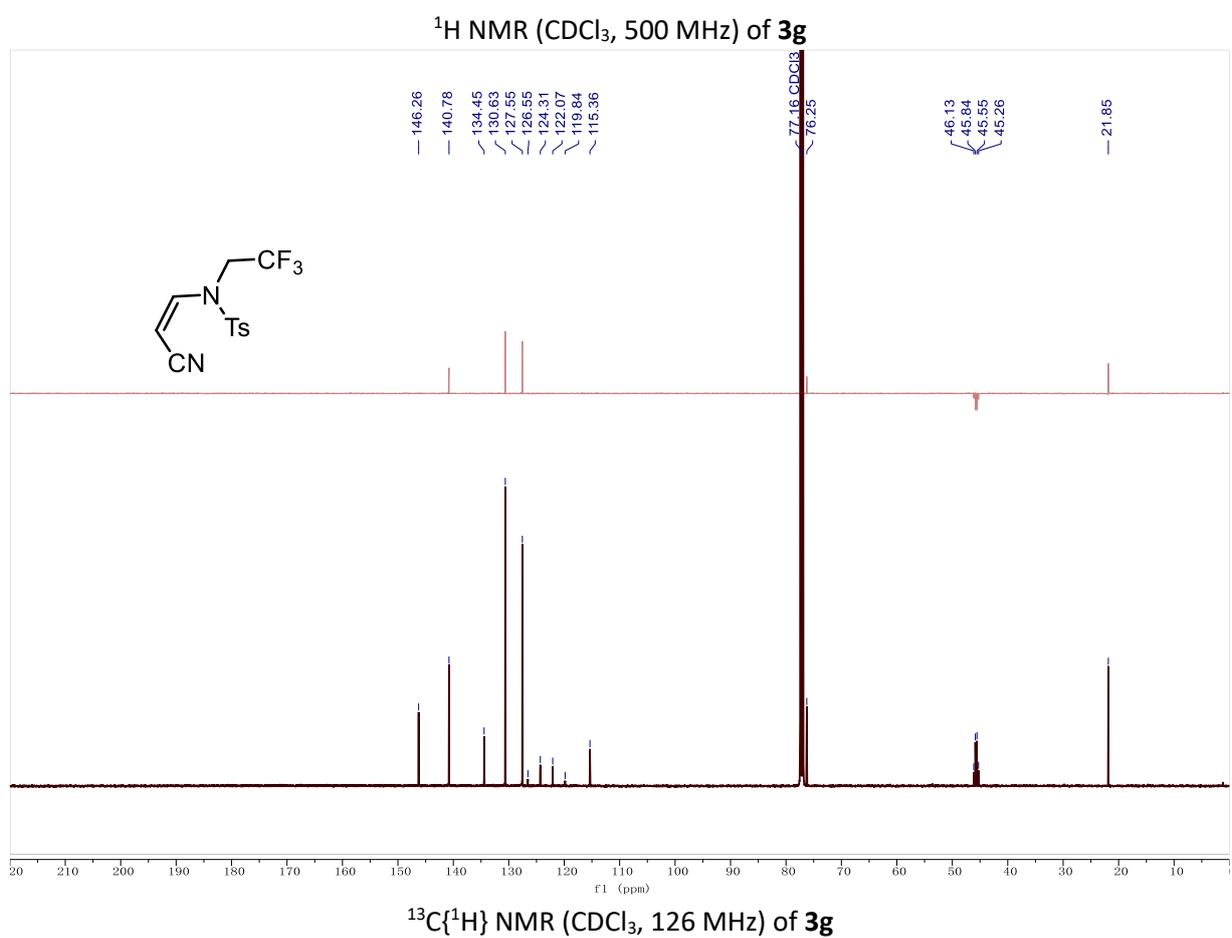
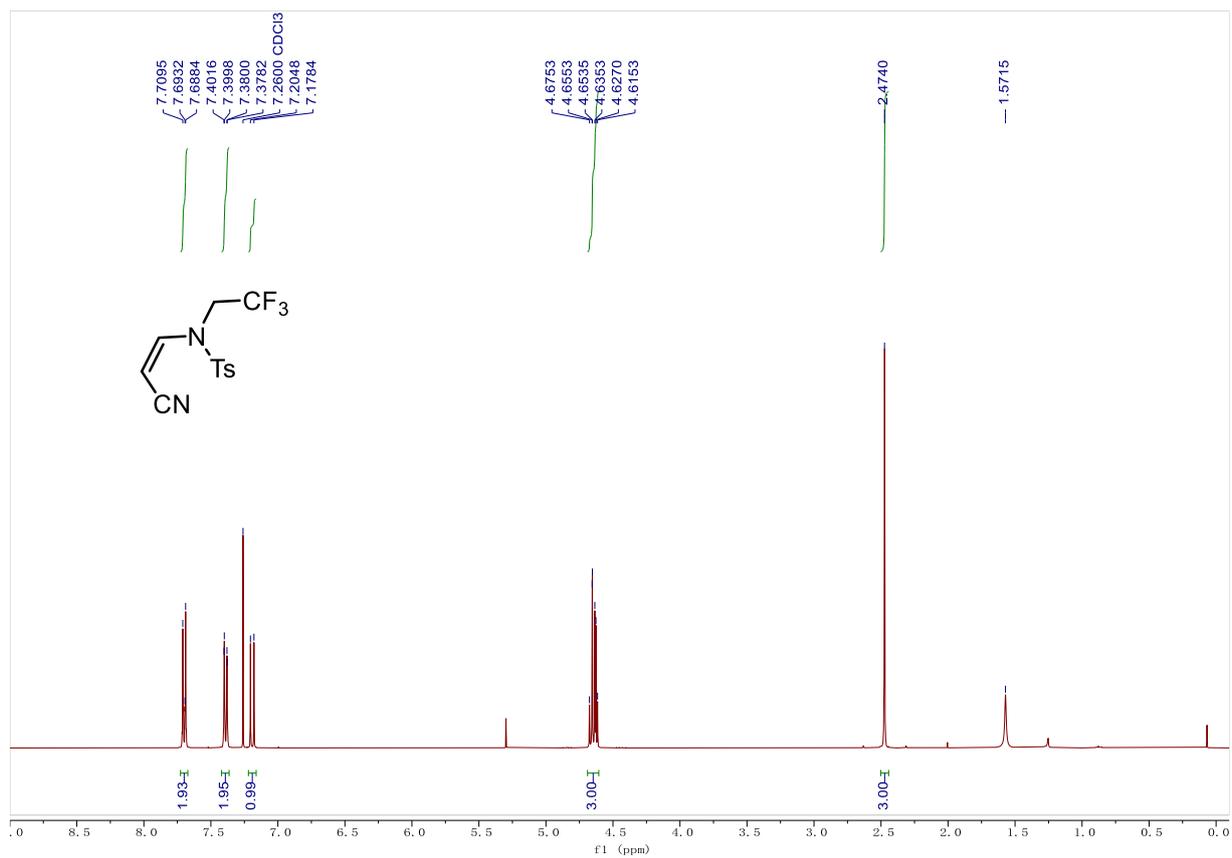
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3e

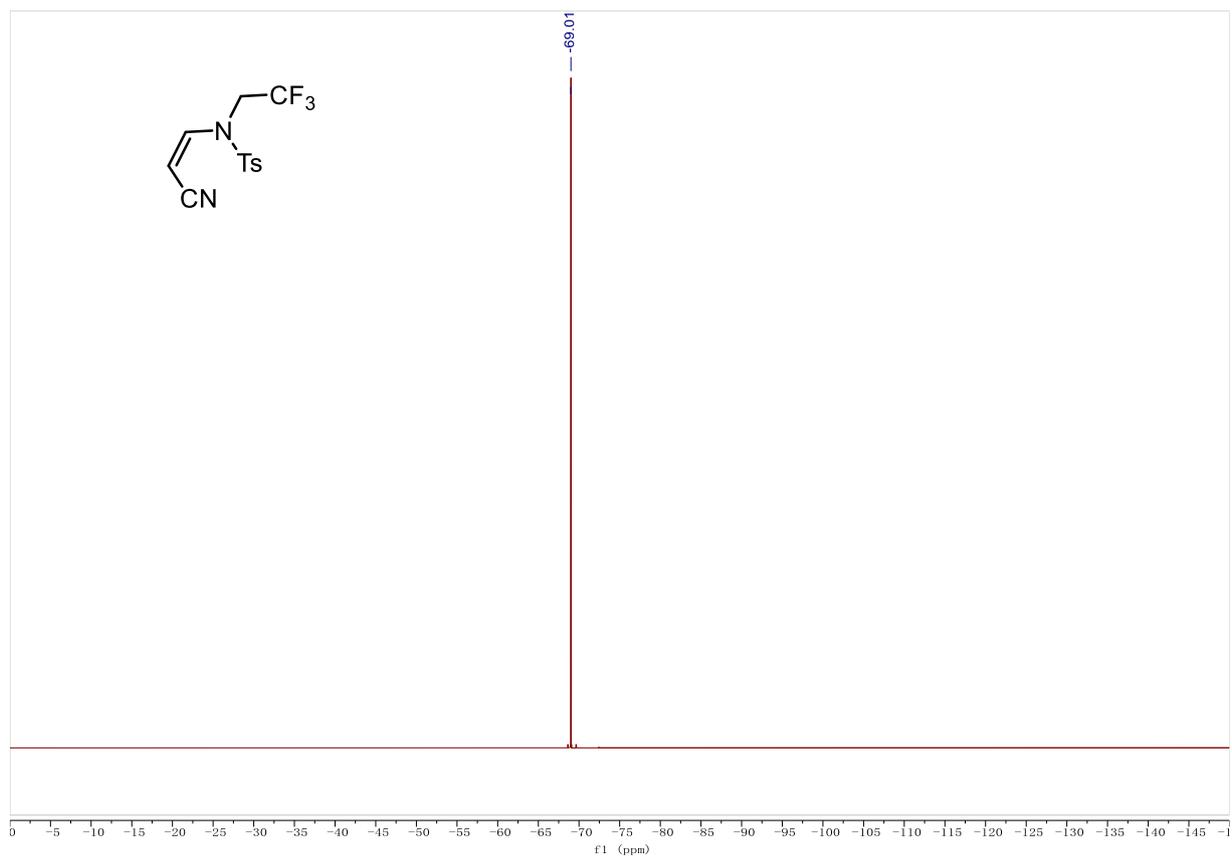


¹H NMR (CDCl₃, 500 MHz) of 3f

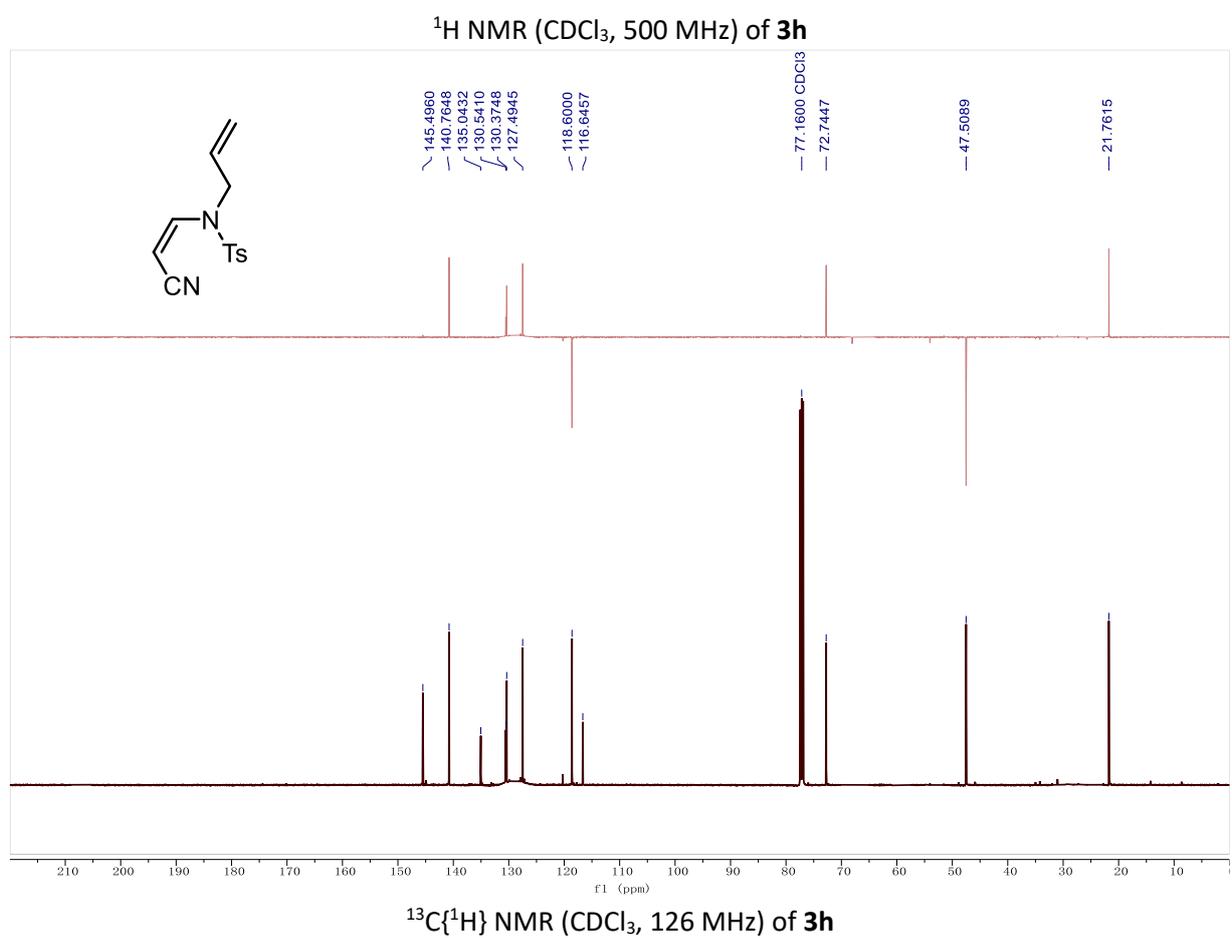
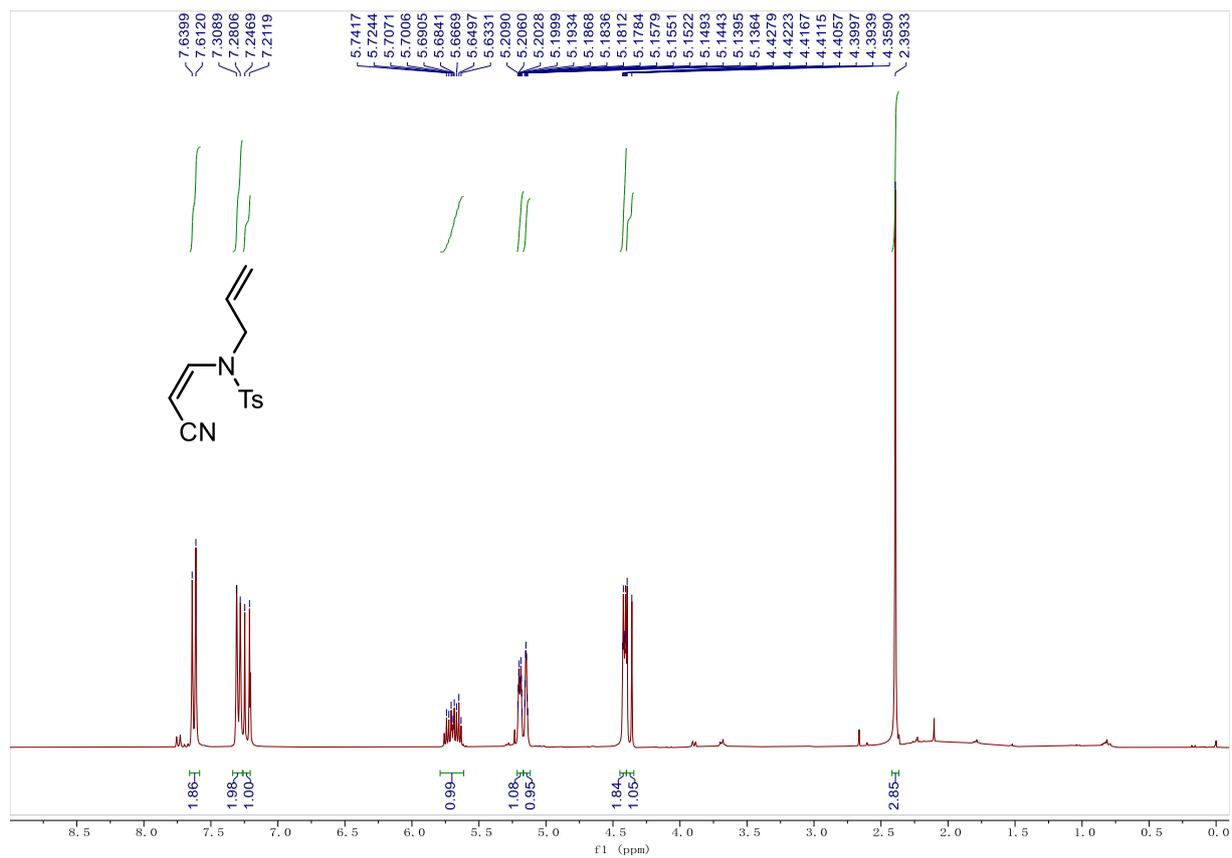


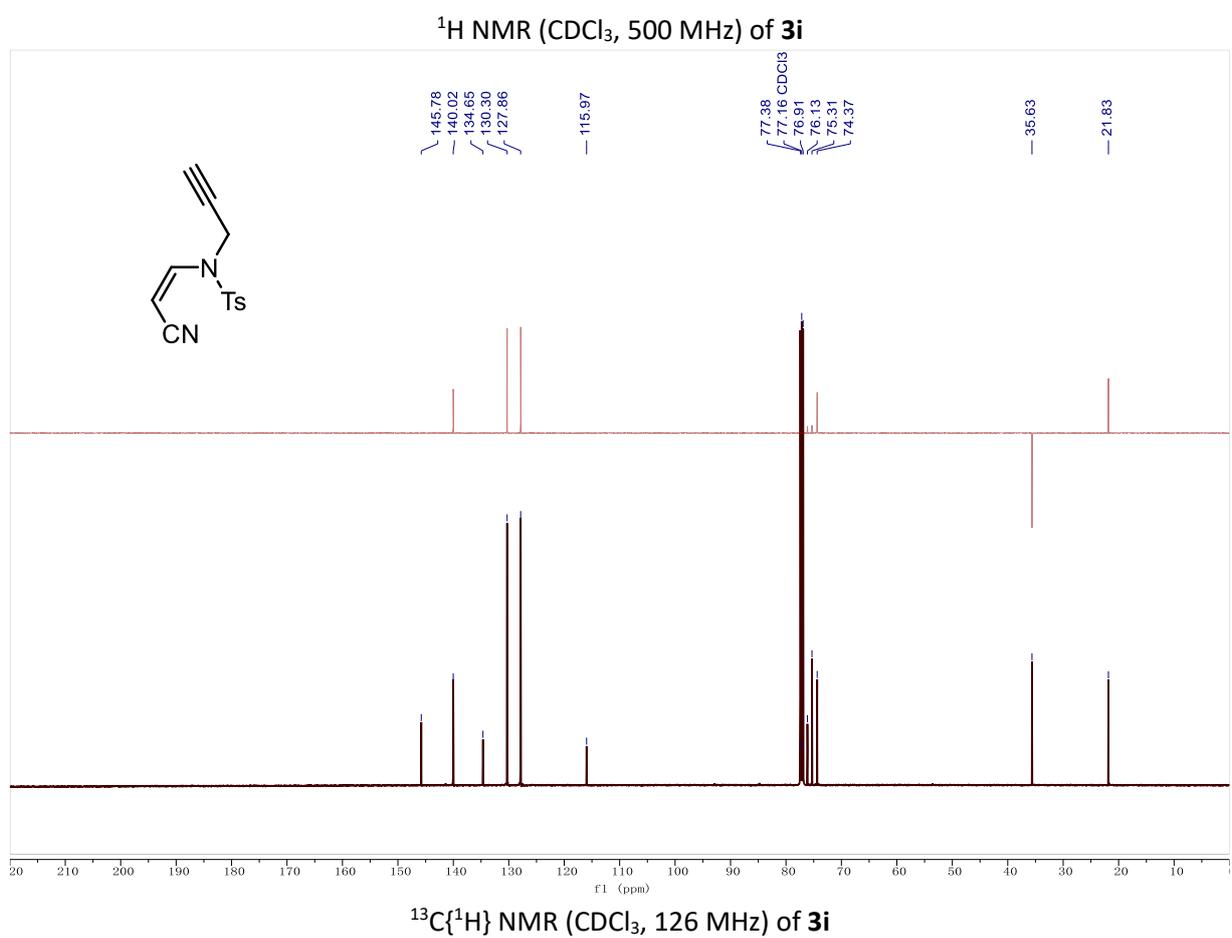
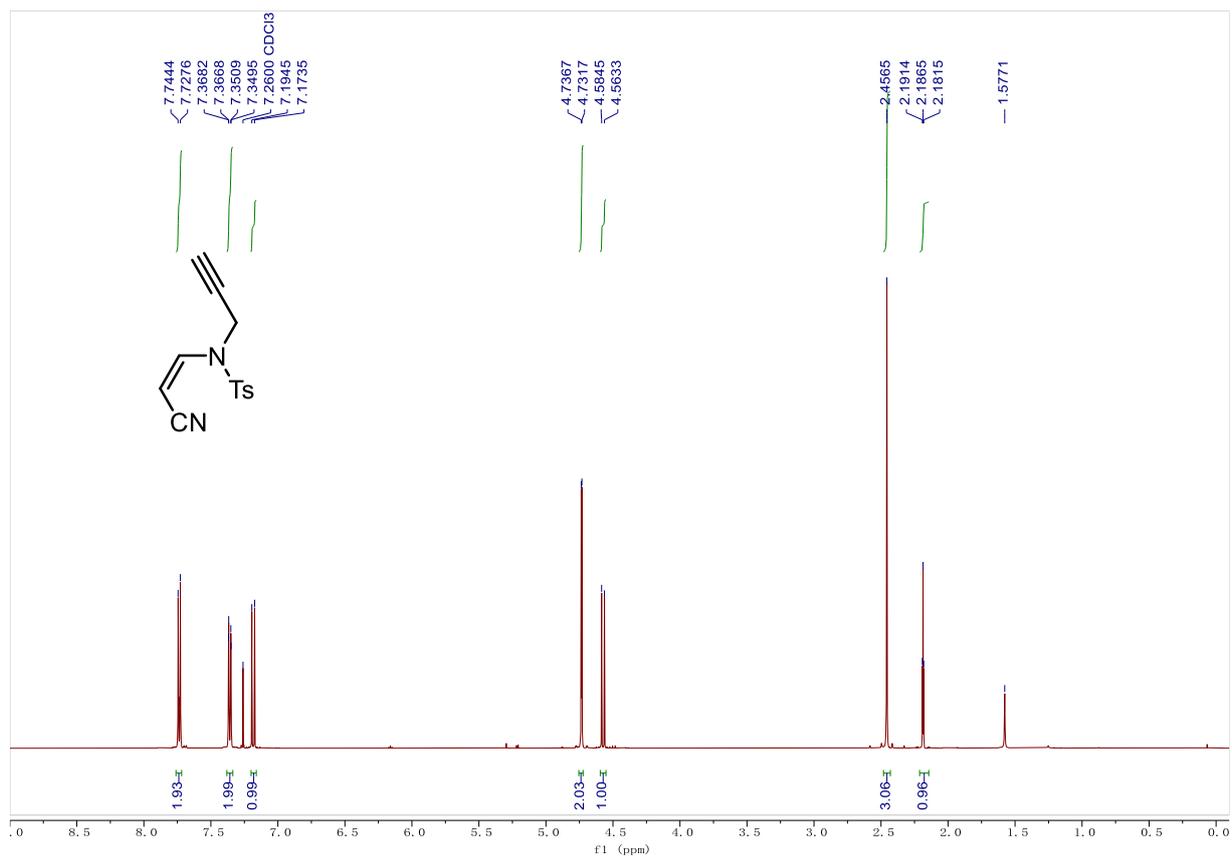
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3f

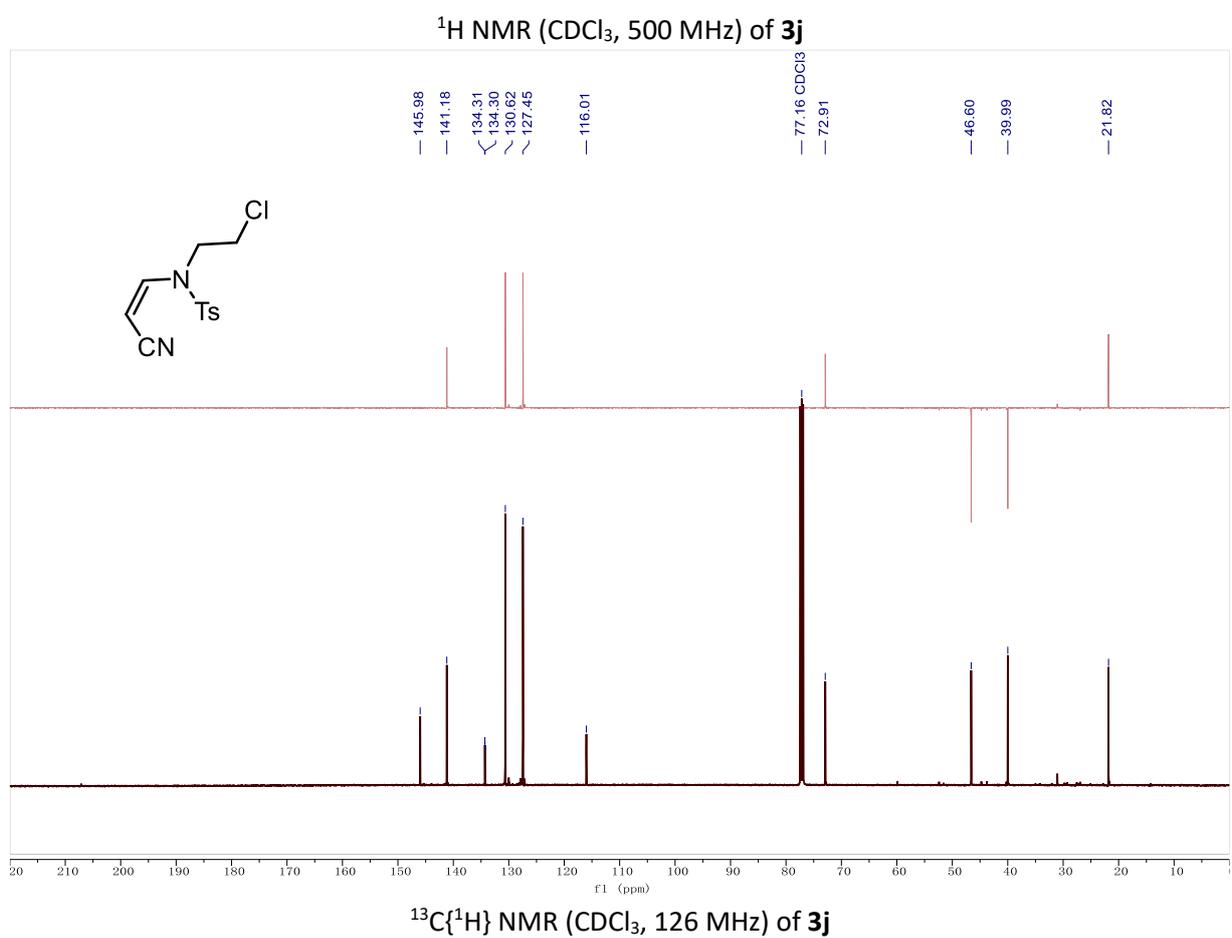
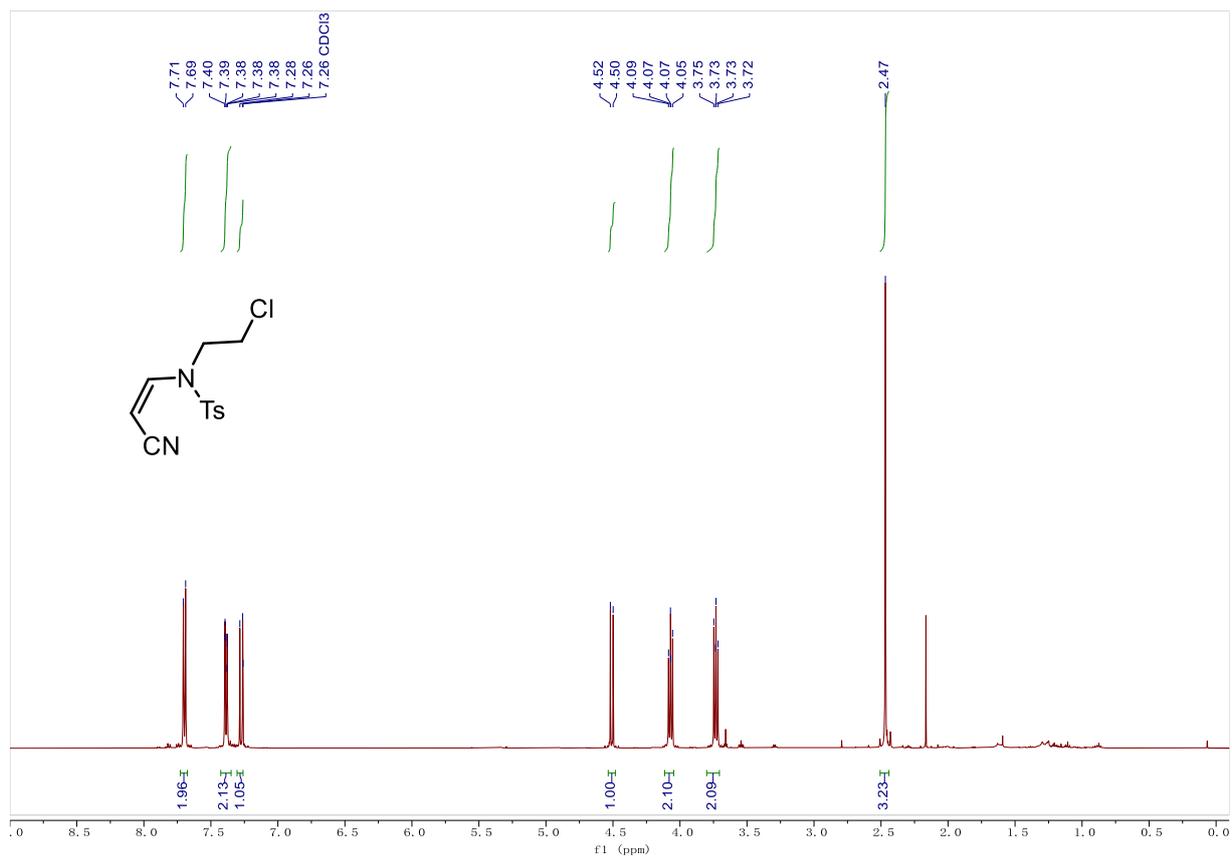


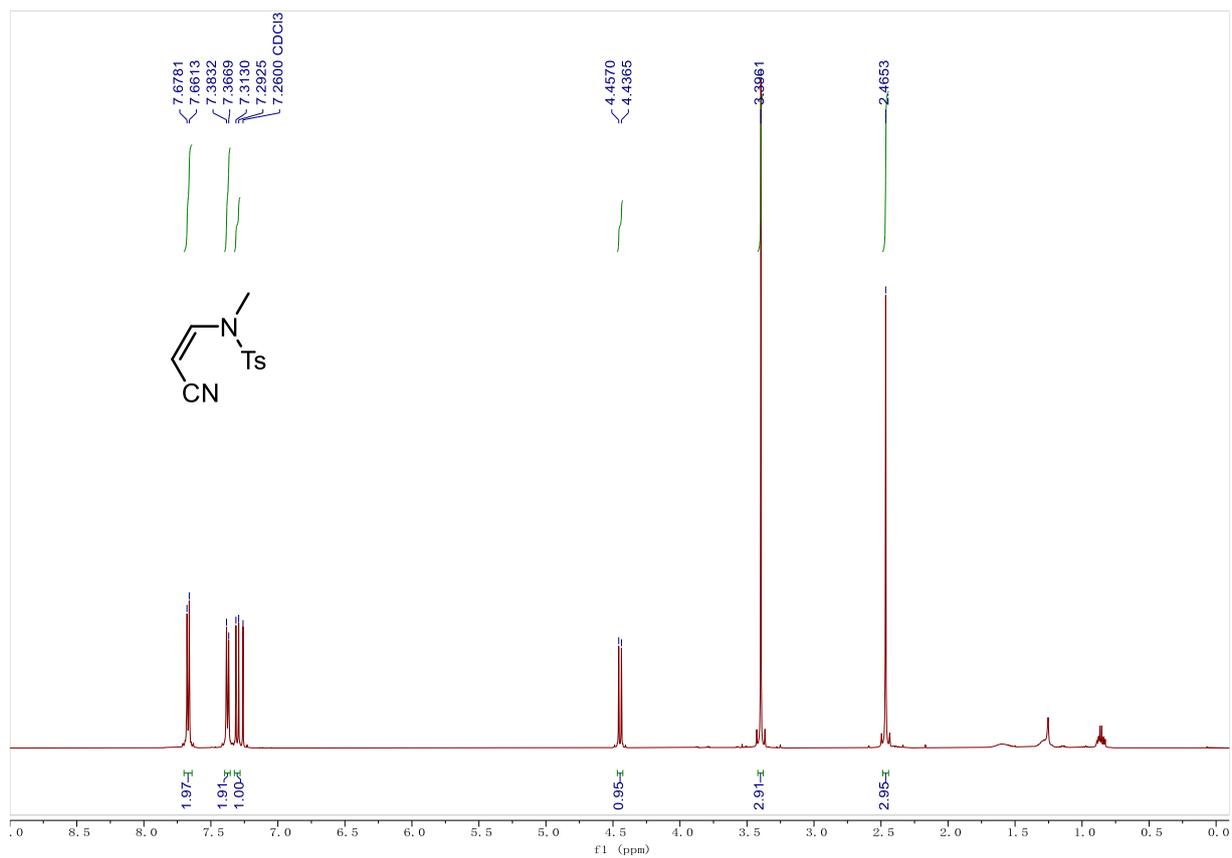


$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 471 MHz) of **3g**

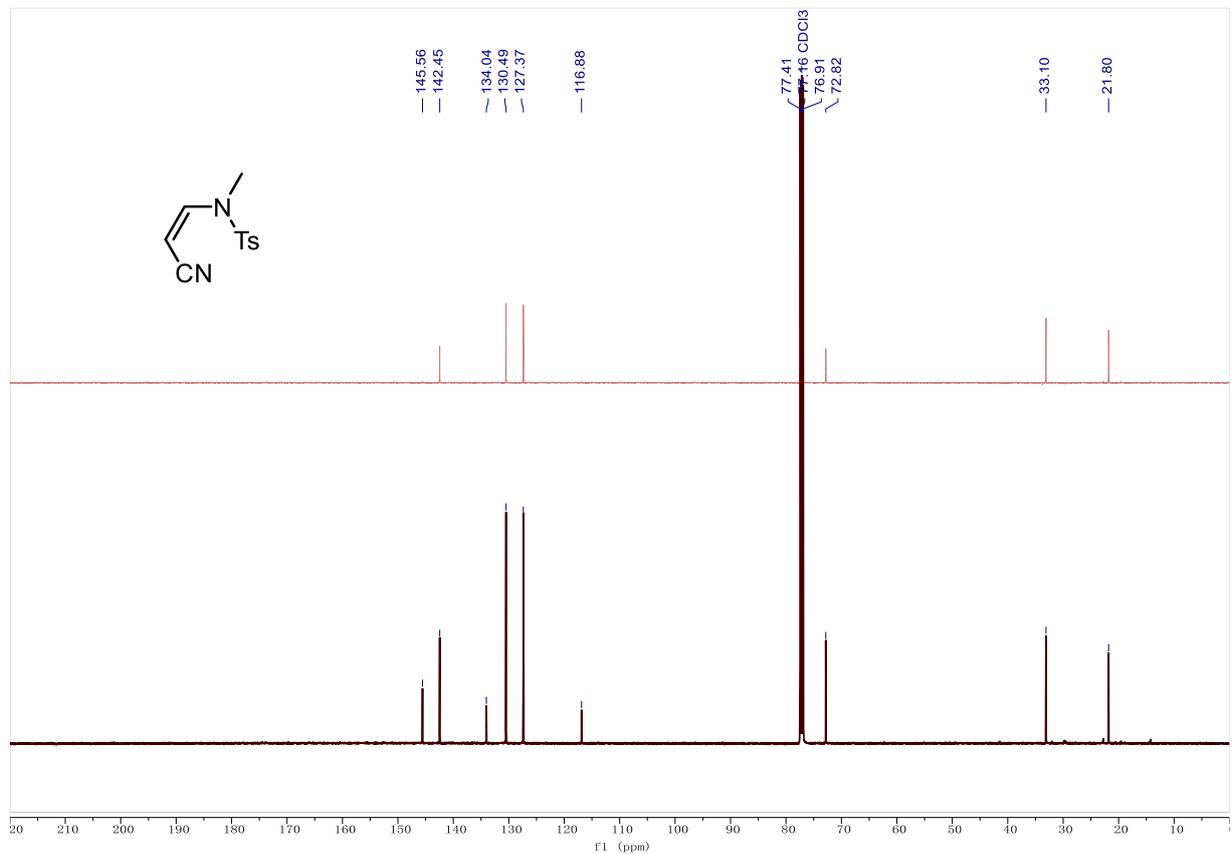




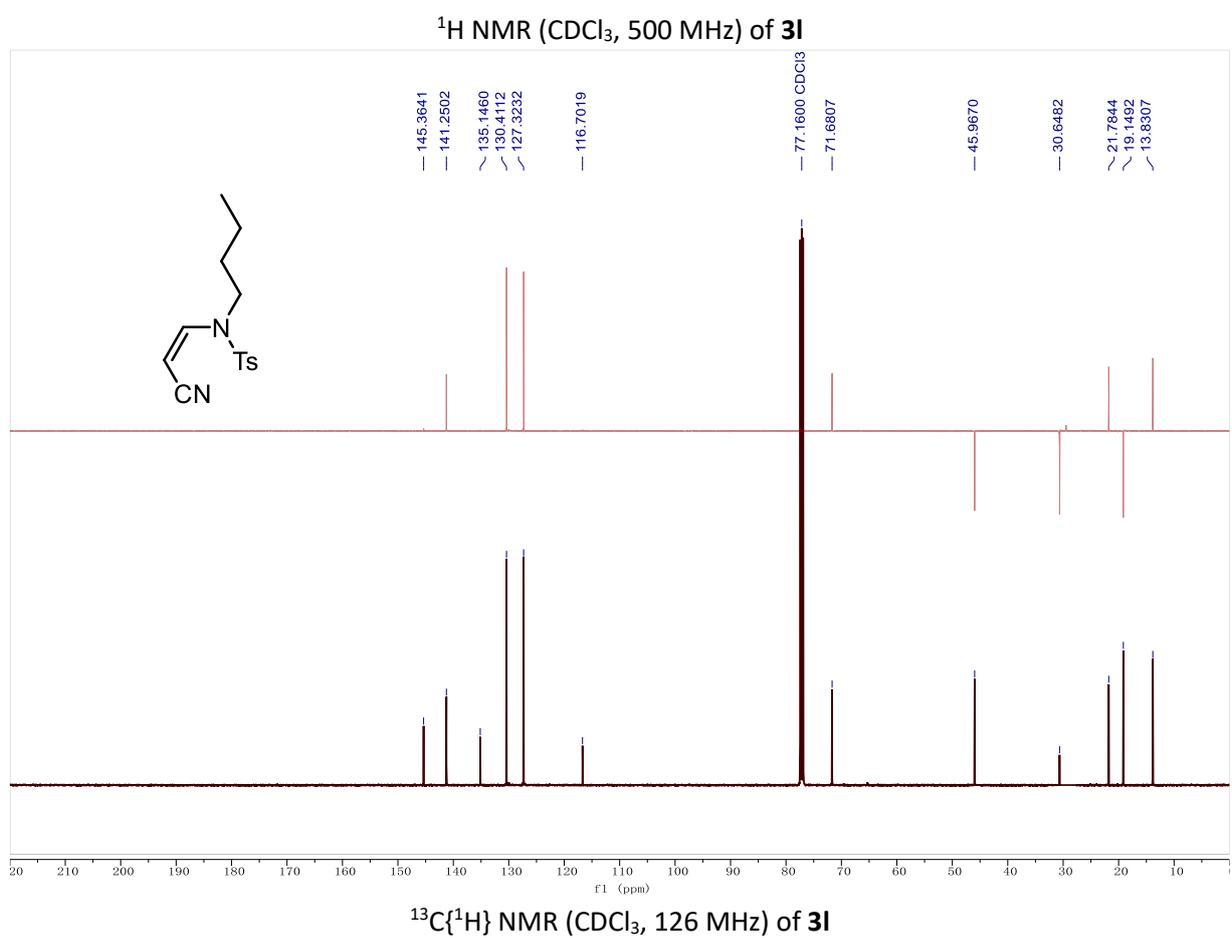
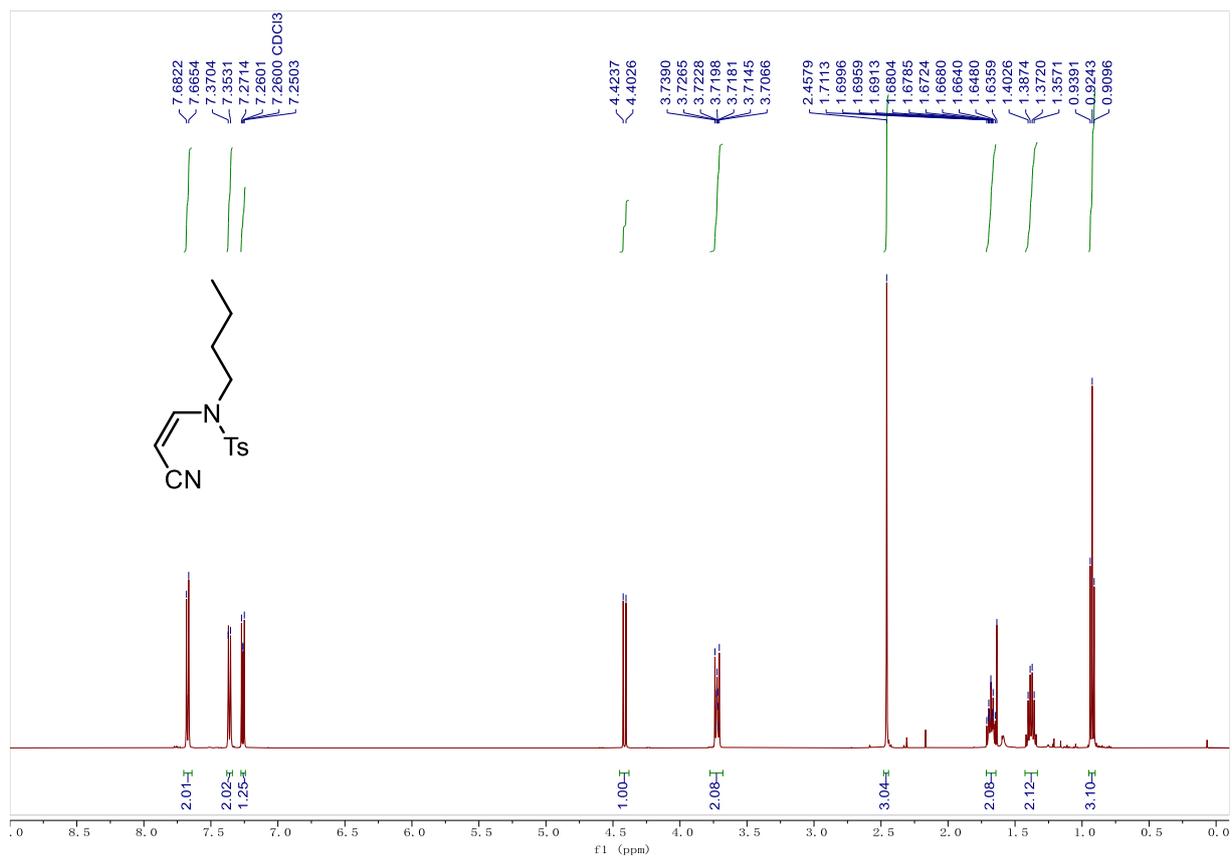


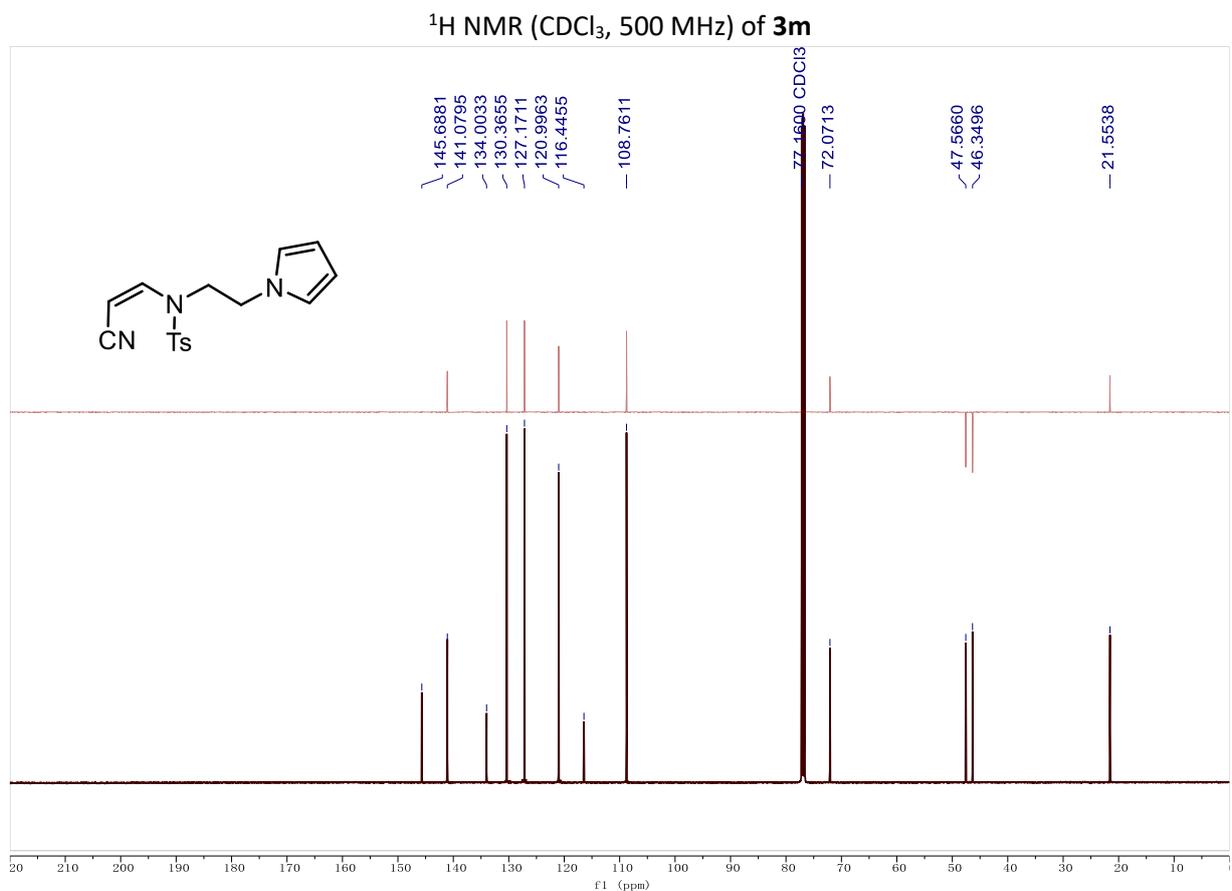
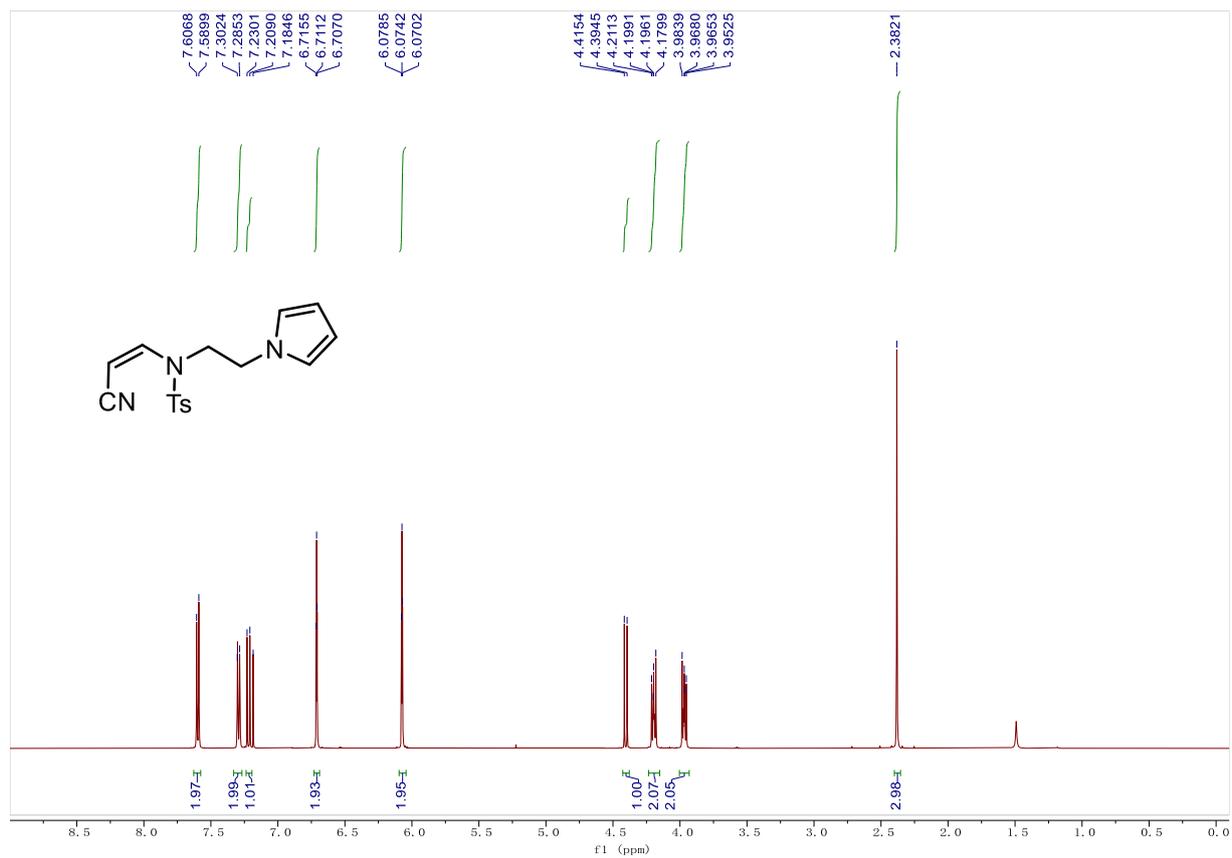


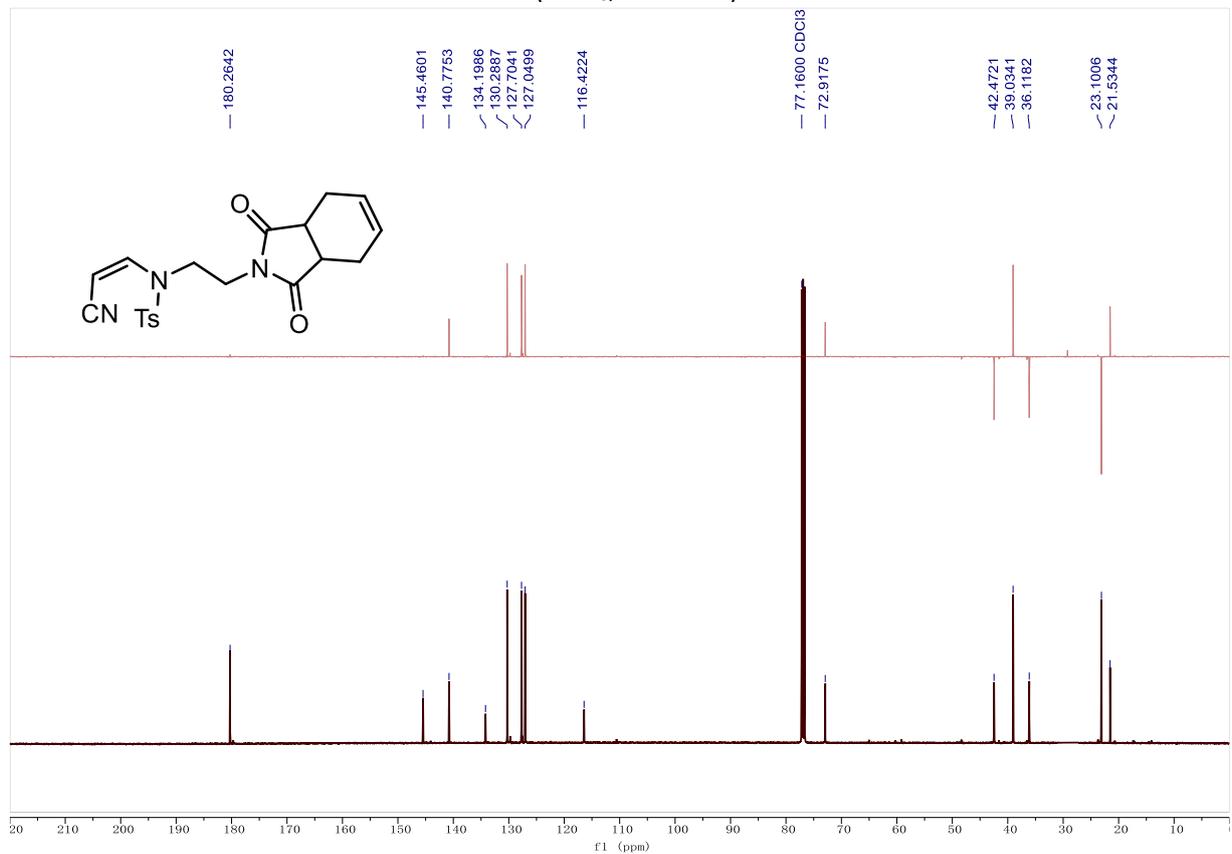
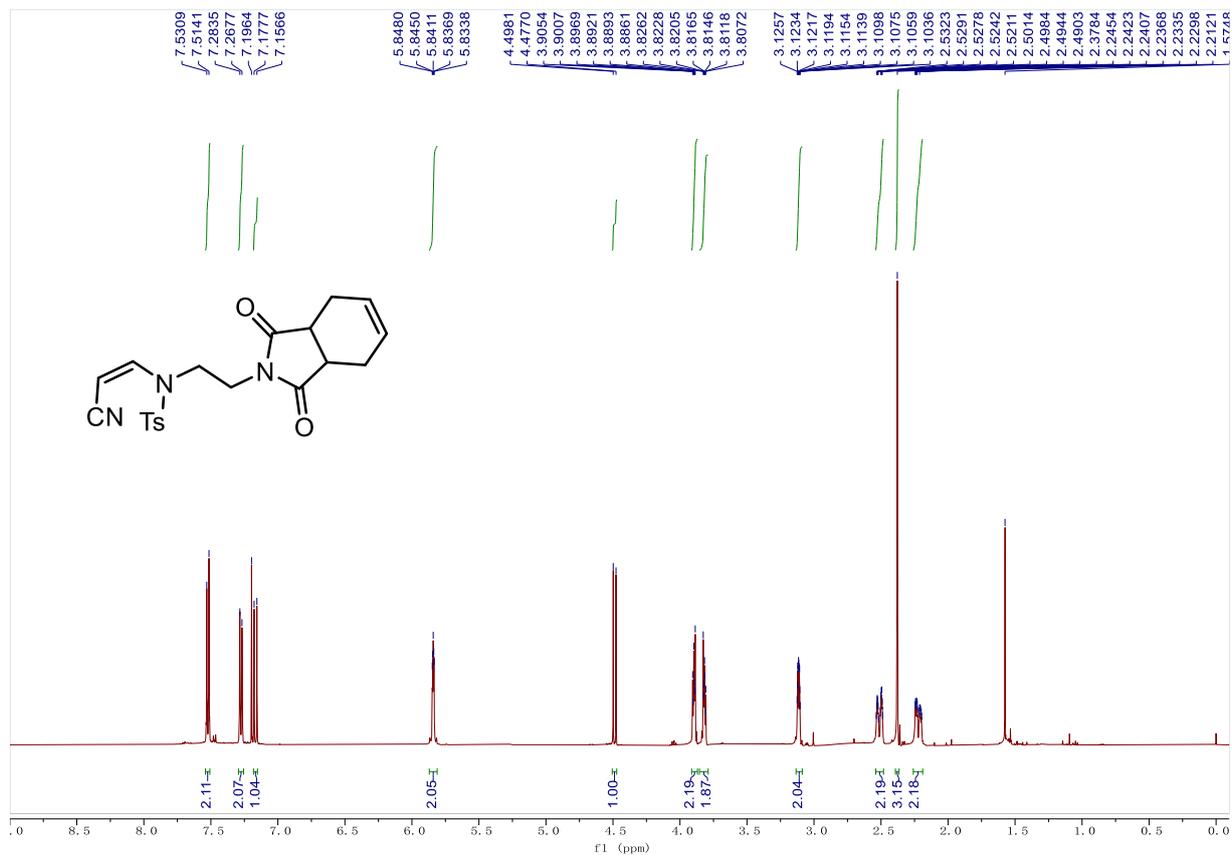
^1H NMR (CDCl_3 , 500 MHz) of **3k**

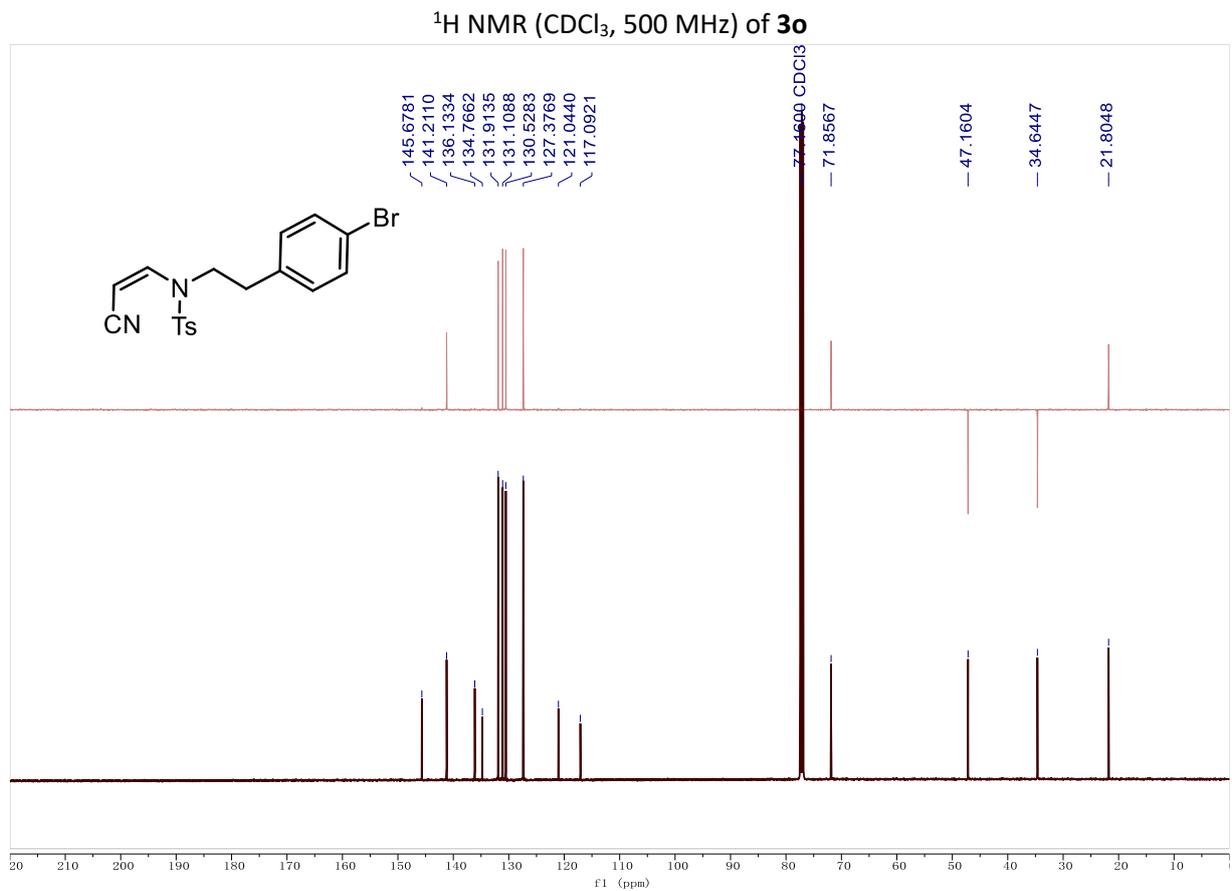
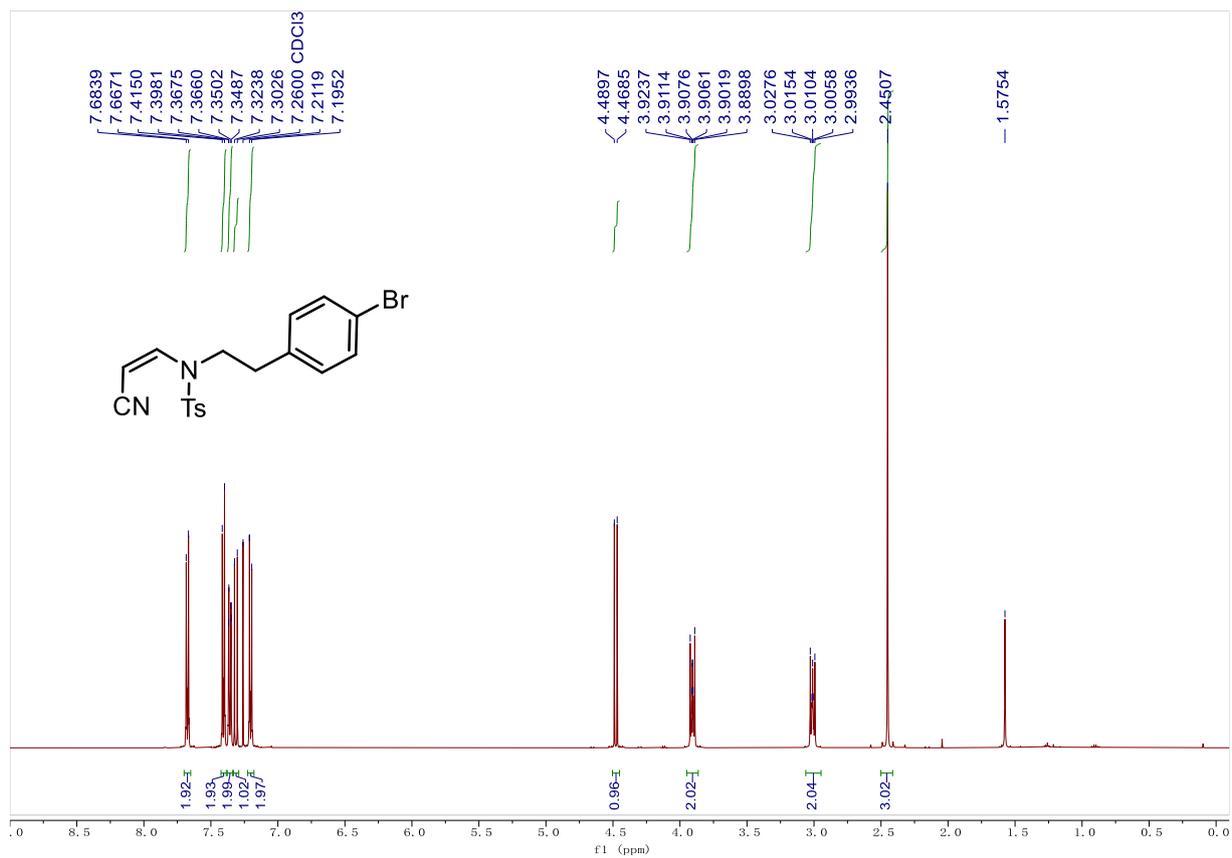


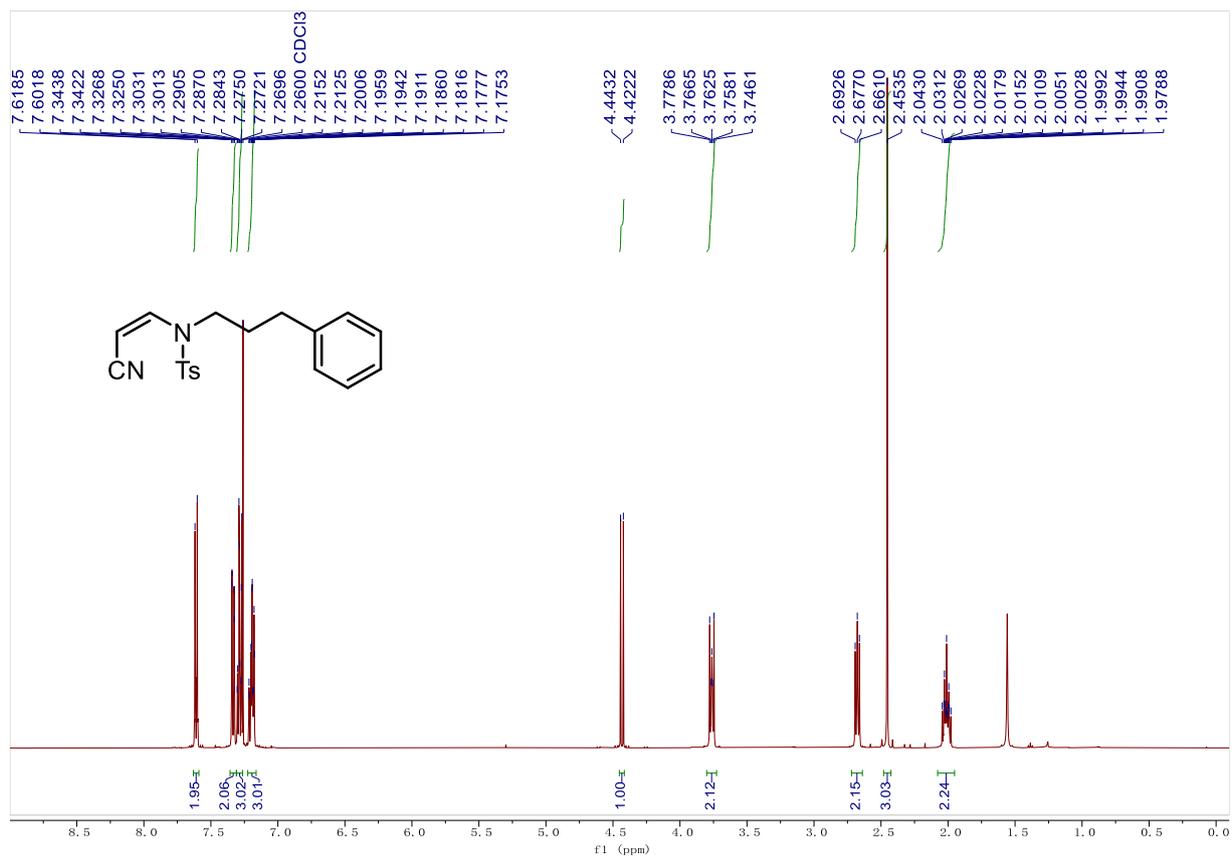
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz) of **3k**



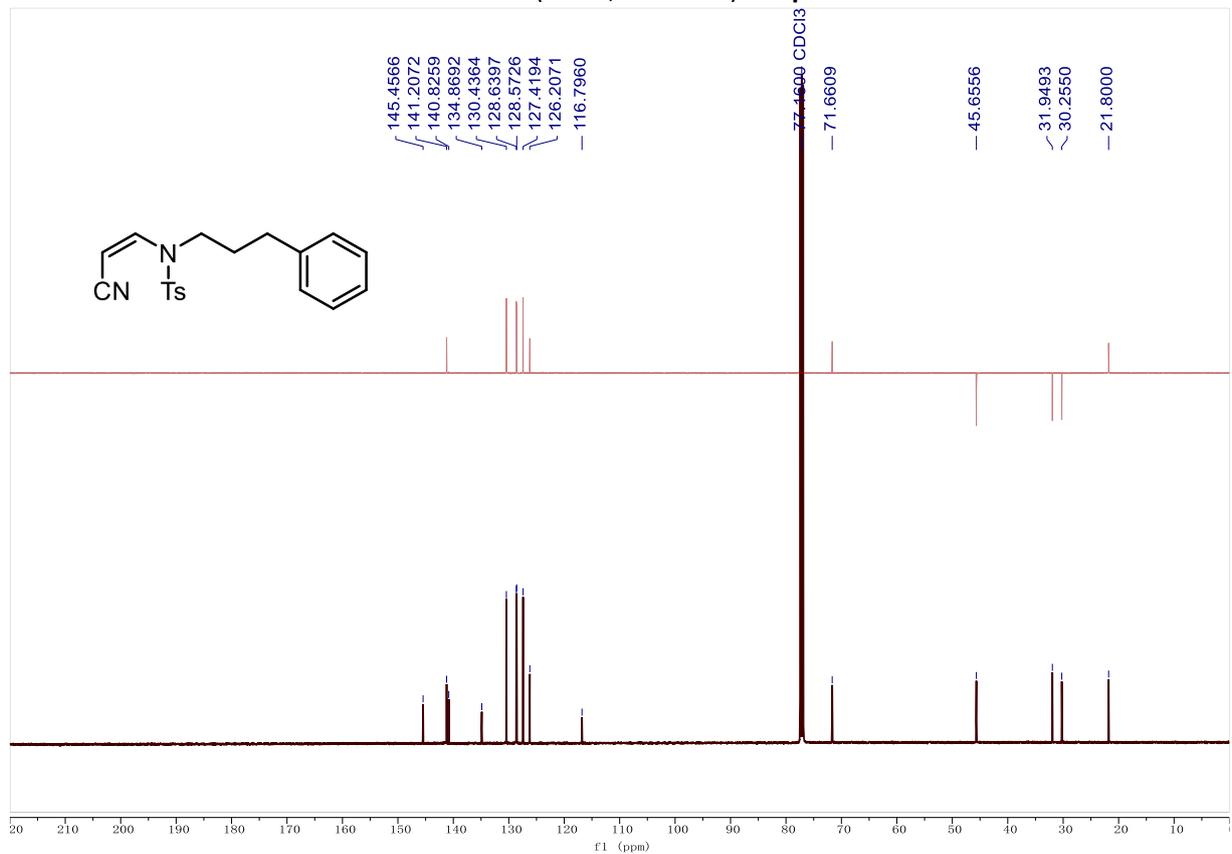




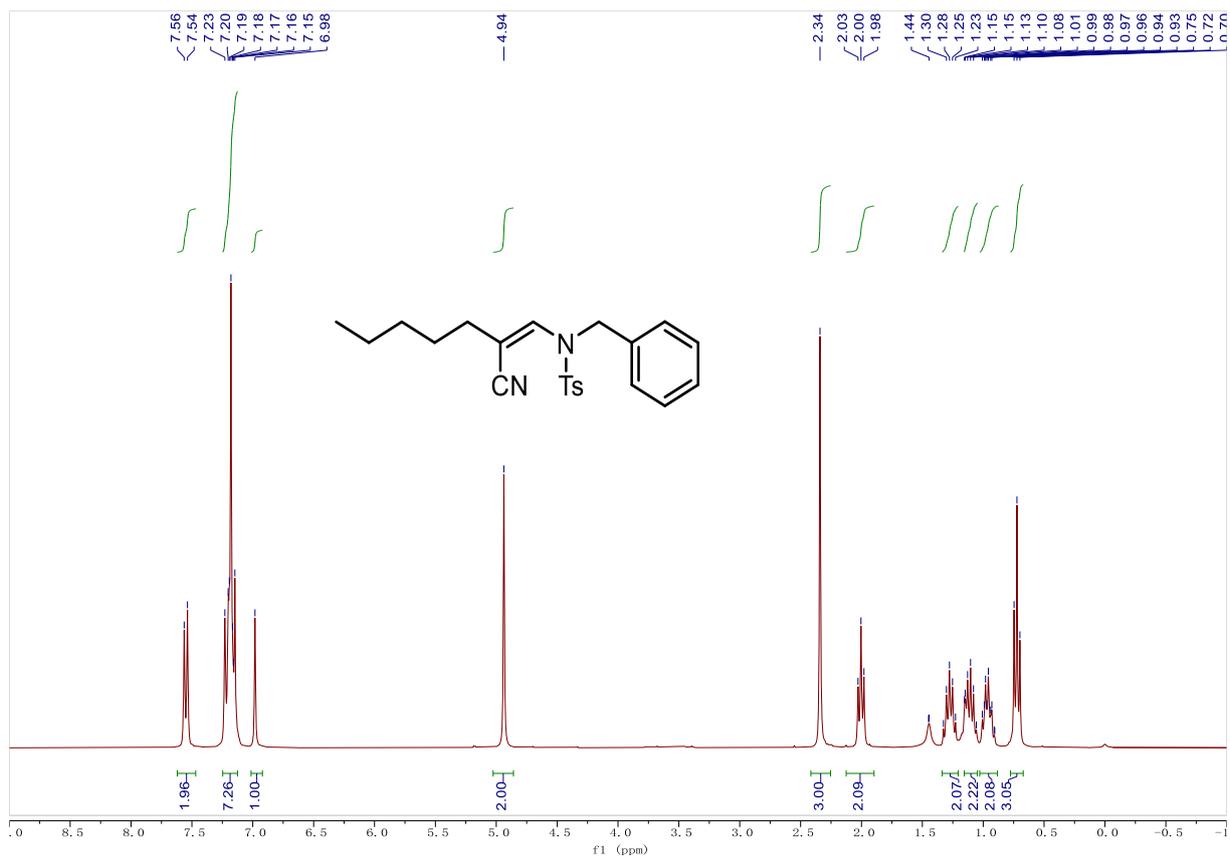




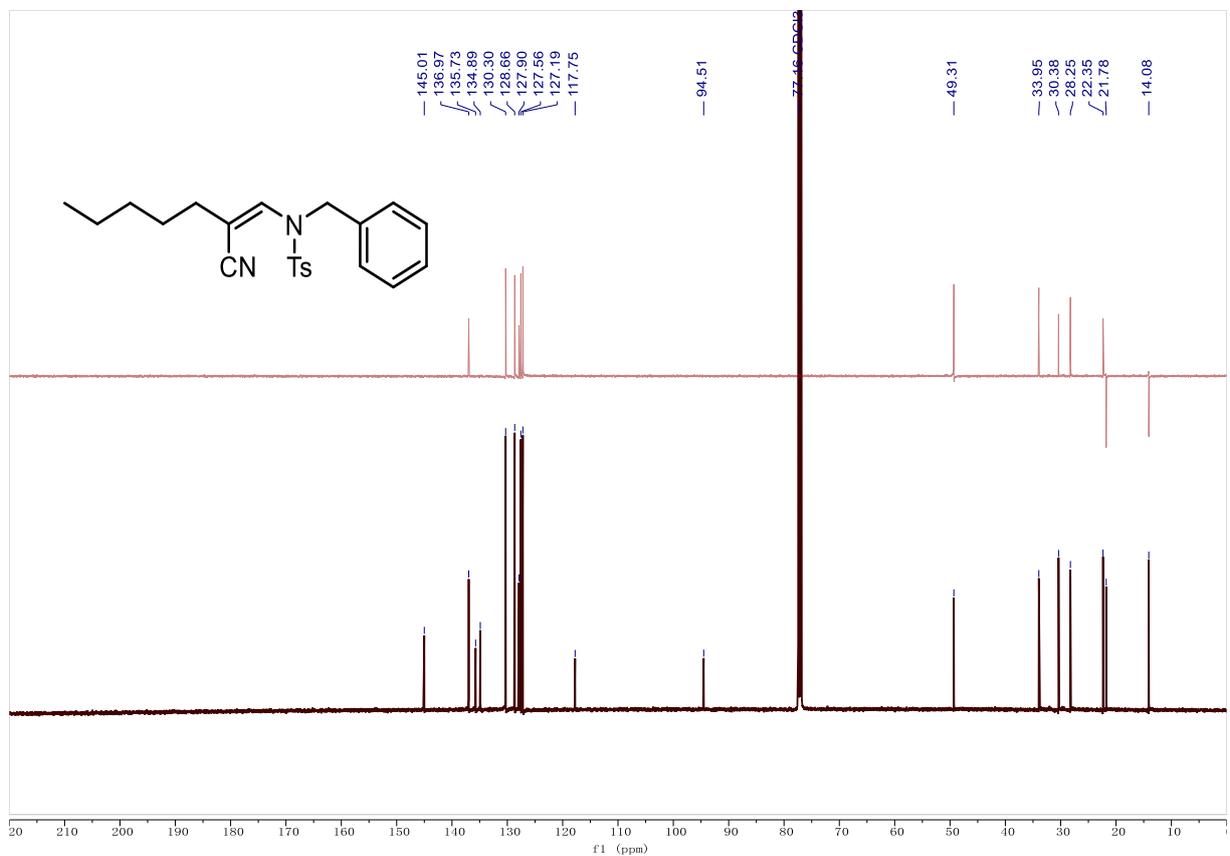
¹H NMR (CDCl₃, 500 MHz) of 3p



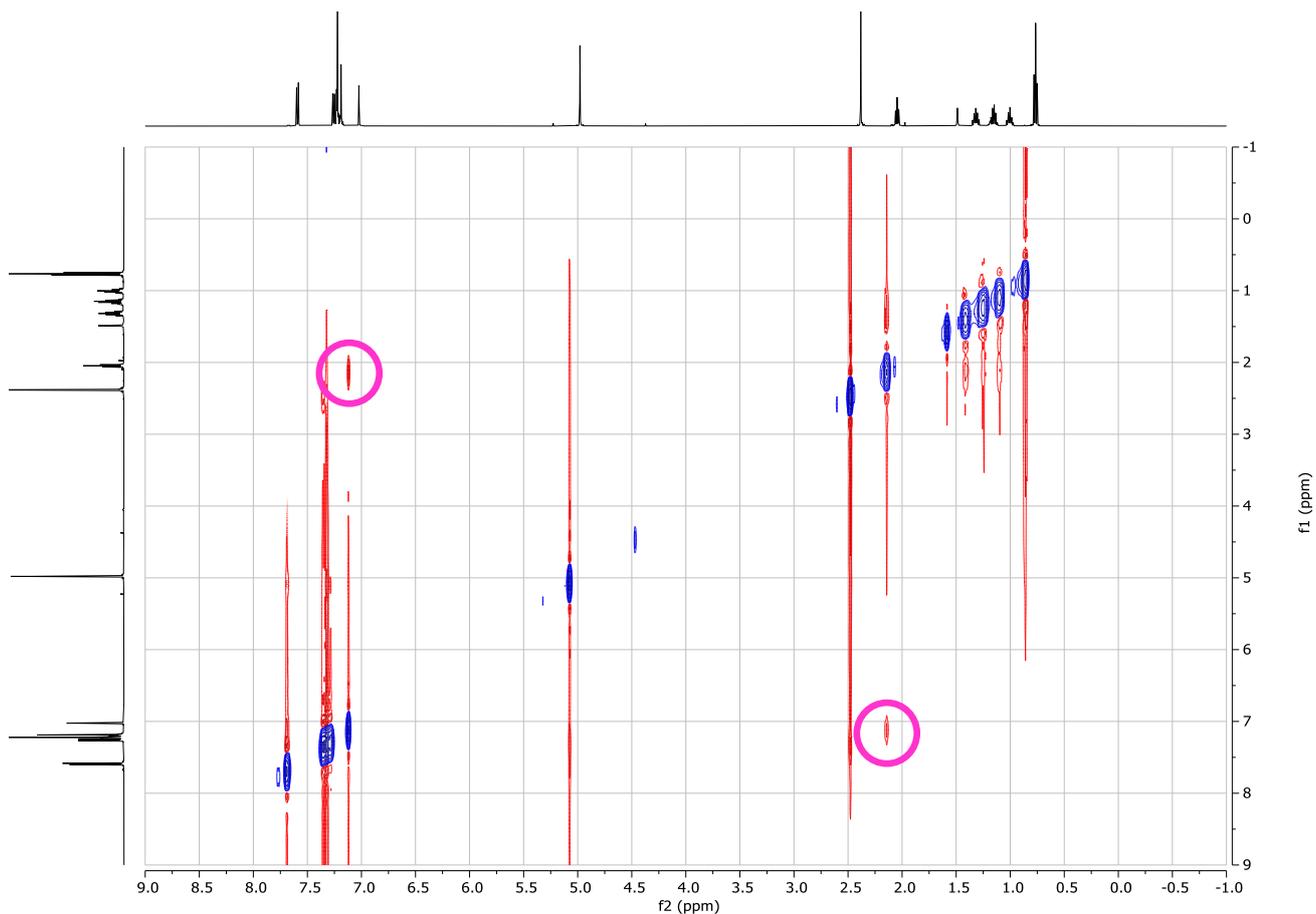
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3p



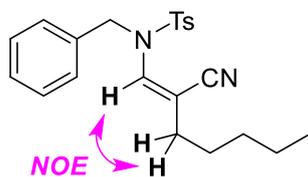
¹H NMR (CDCl₃, 300 MHz) of **3'**

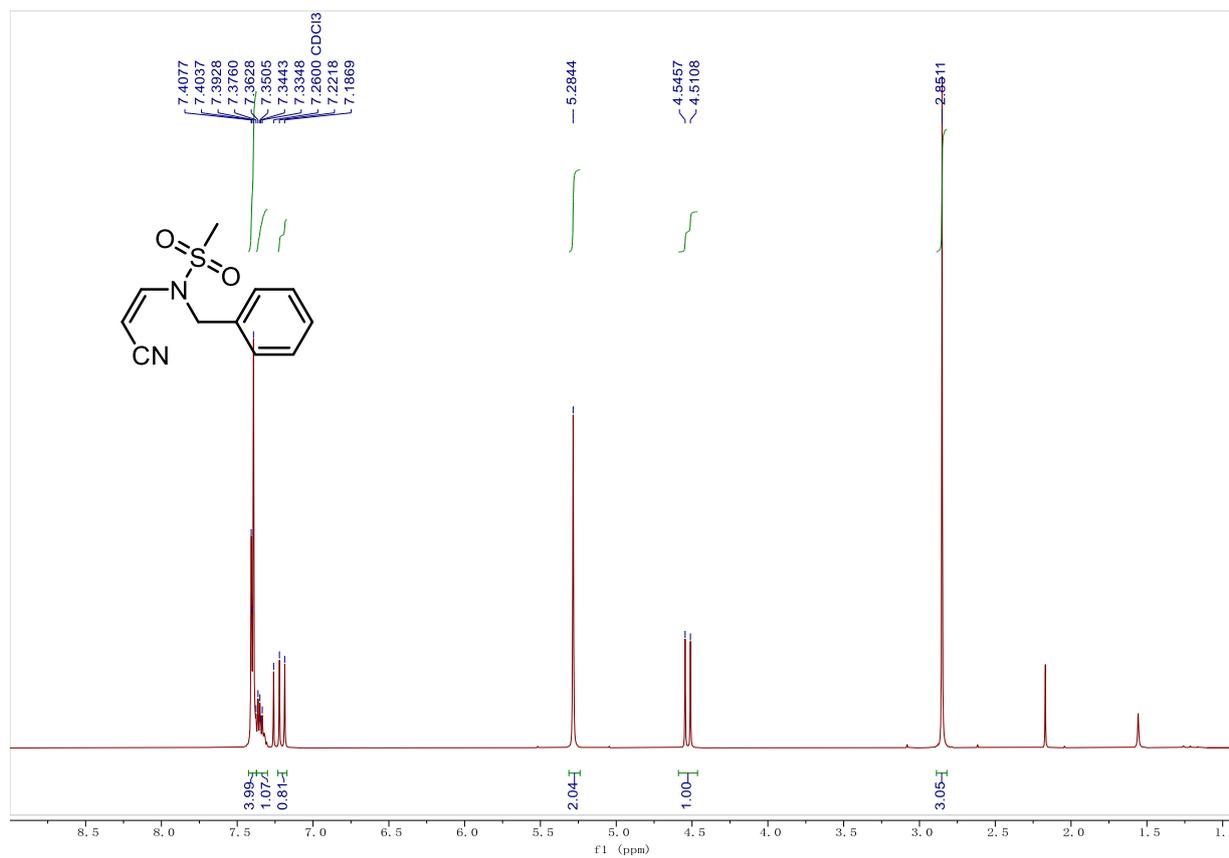


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3'**

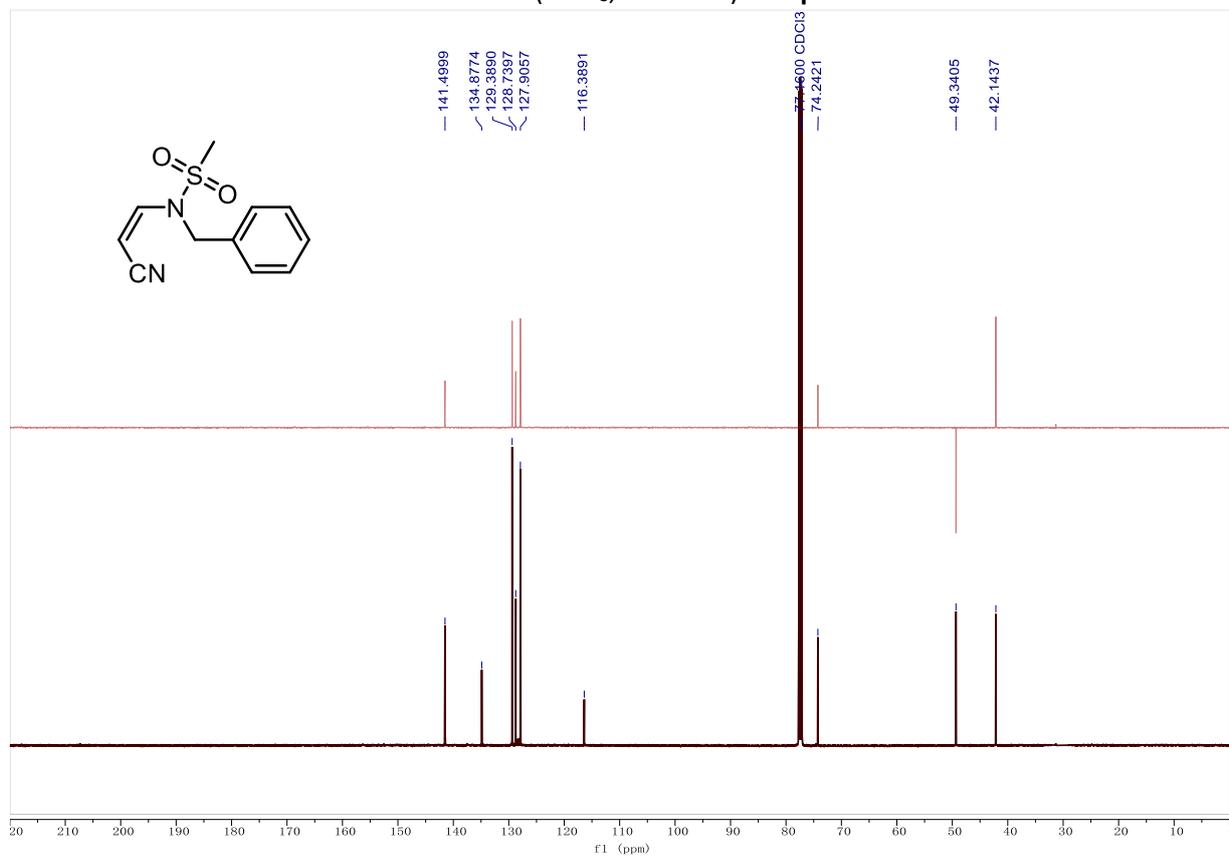


2D NOESY NMR (CDCl₃, 500 MHz) of **3'**

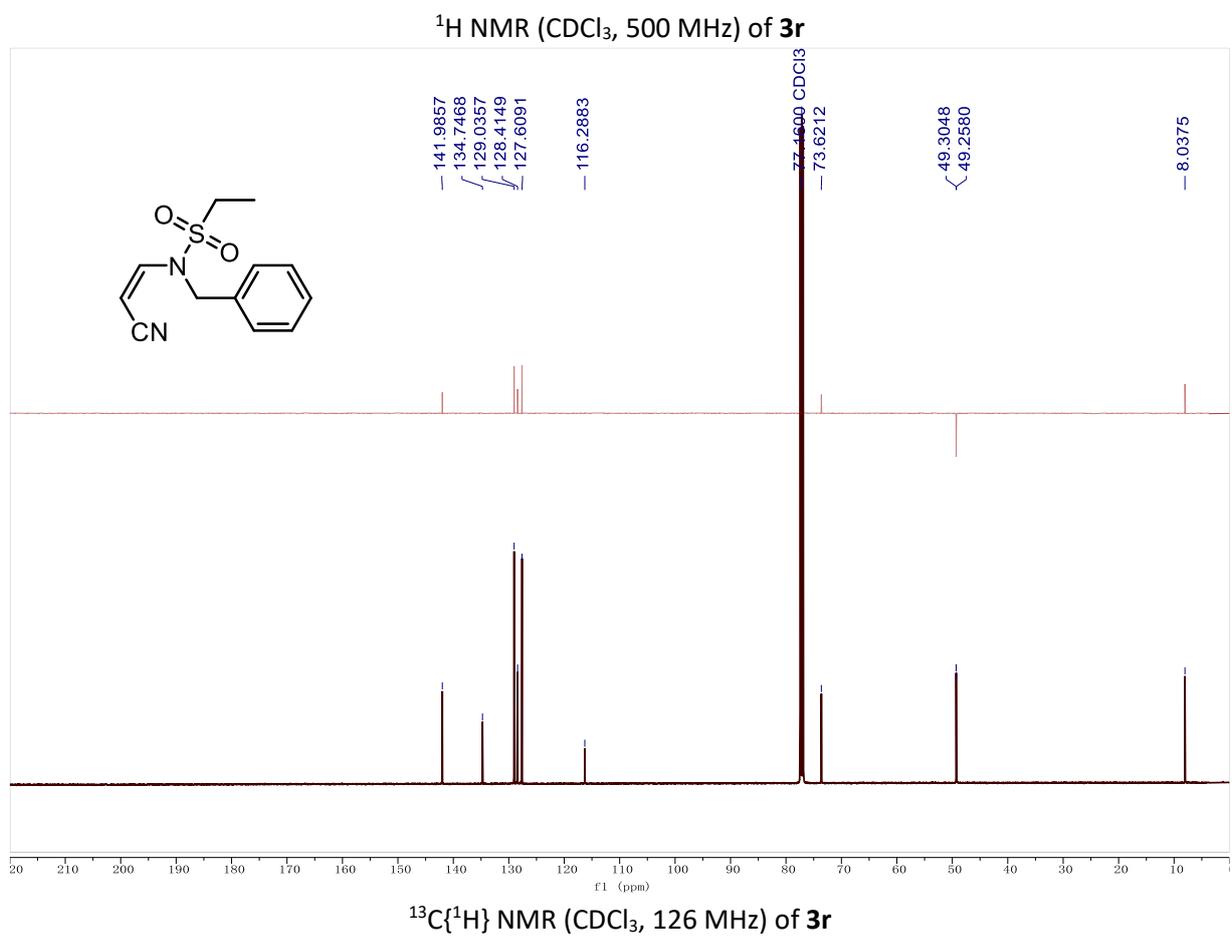
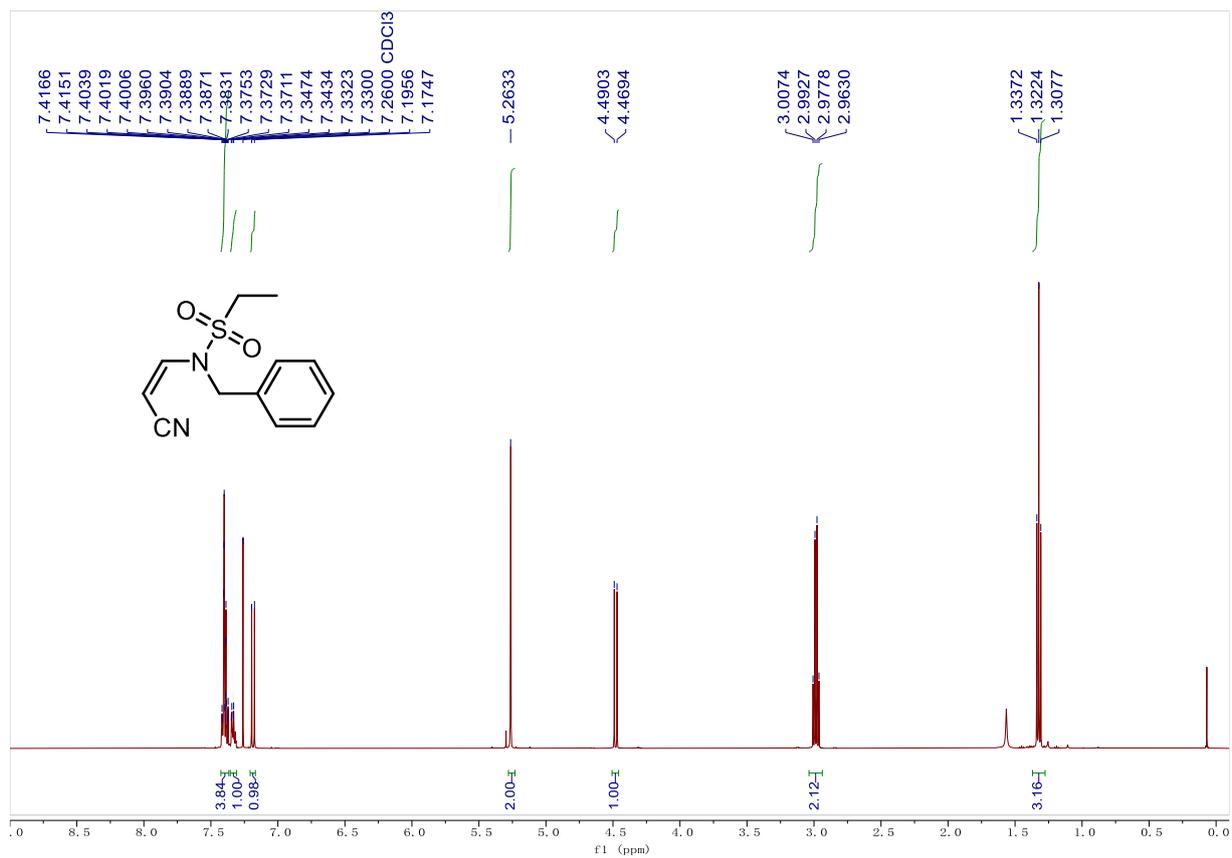


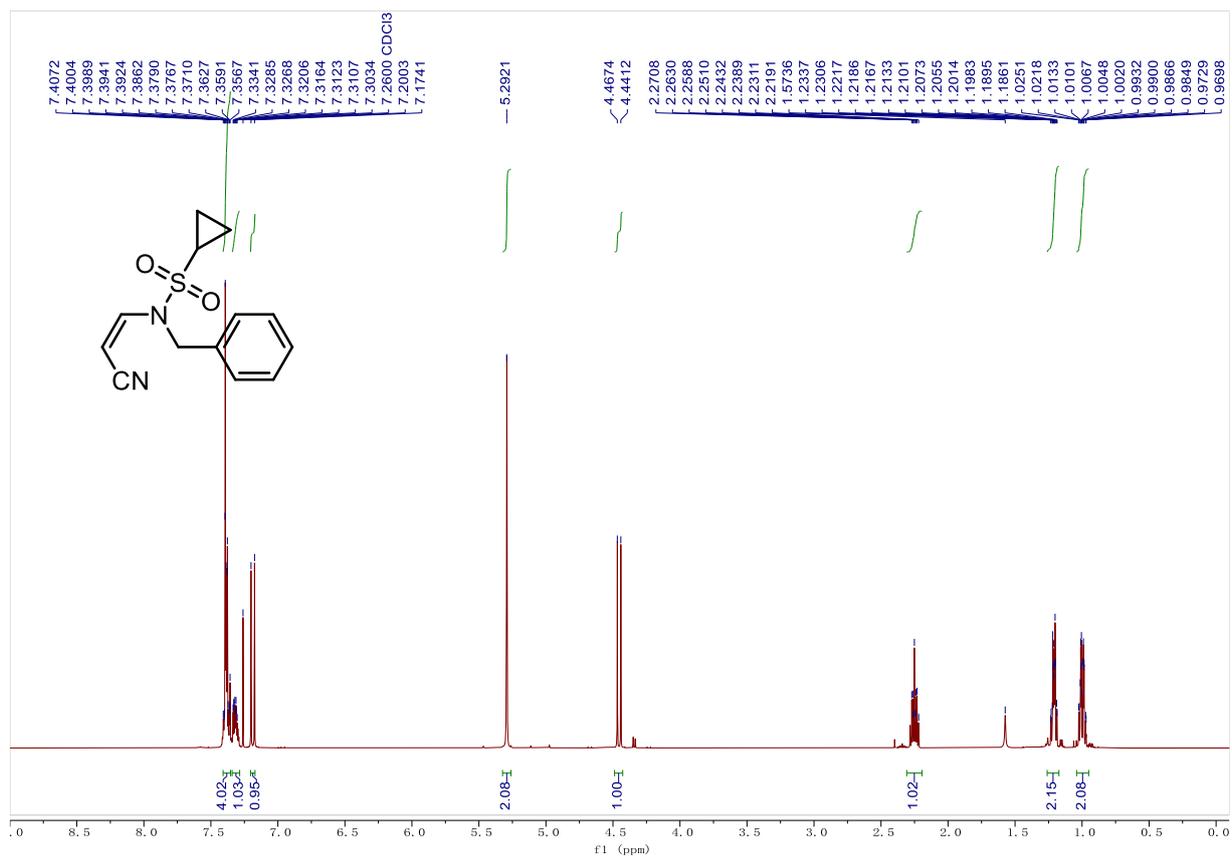


¹H NMR (CDCl₃, 500 MHz) of **3q**

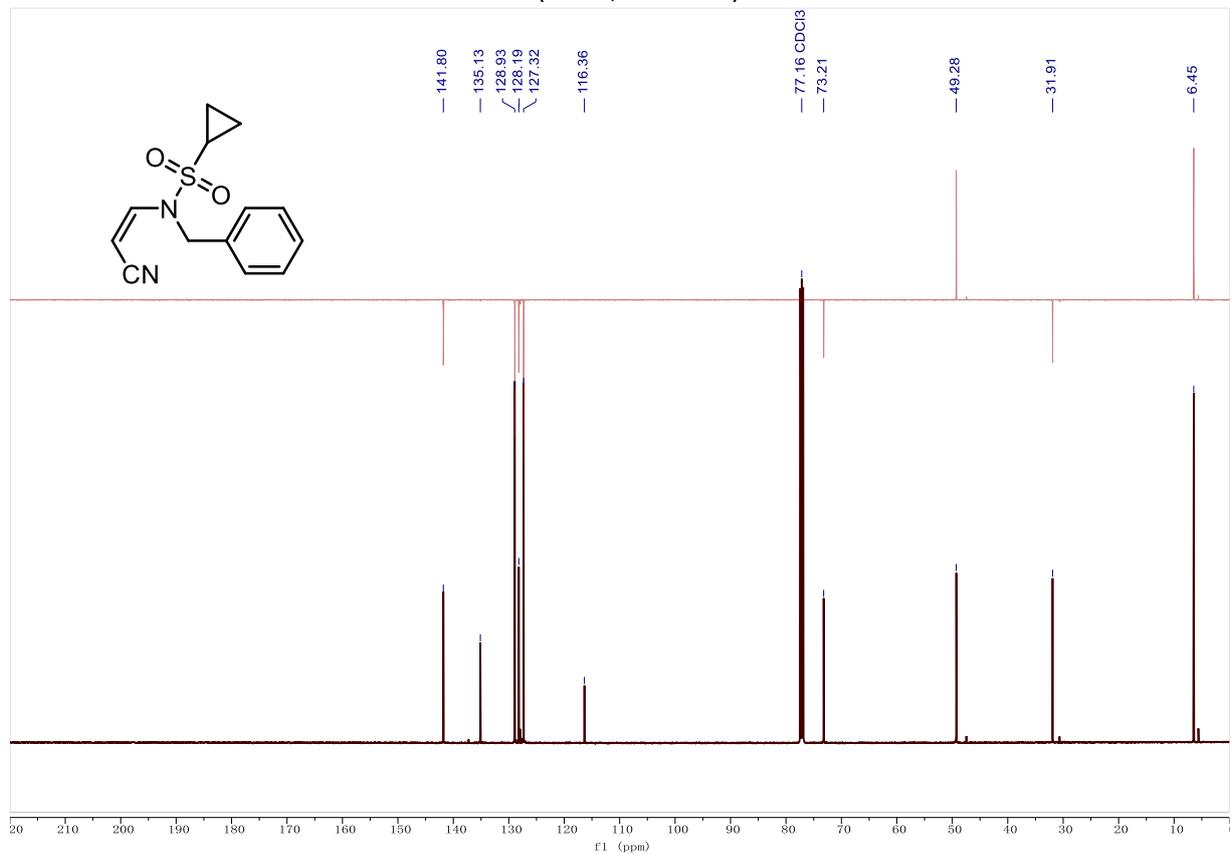


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3q**

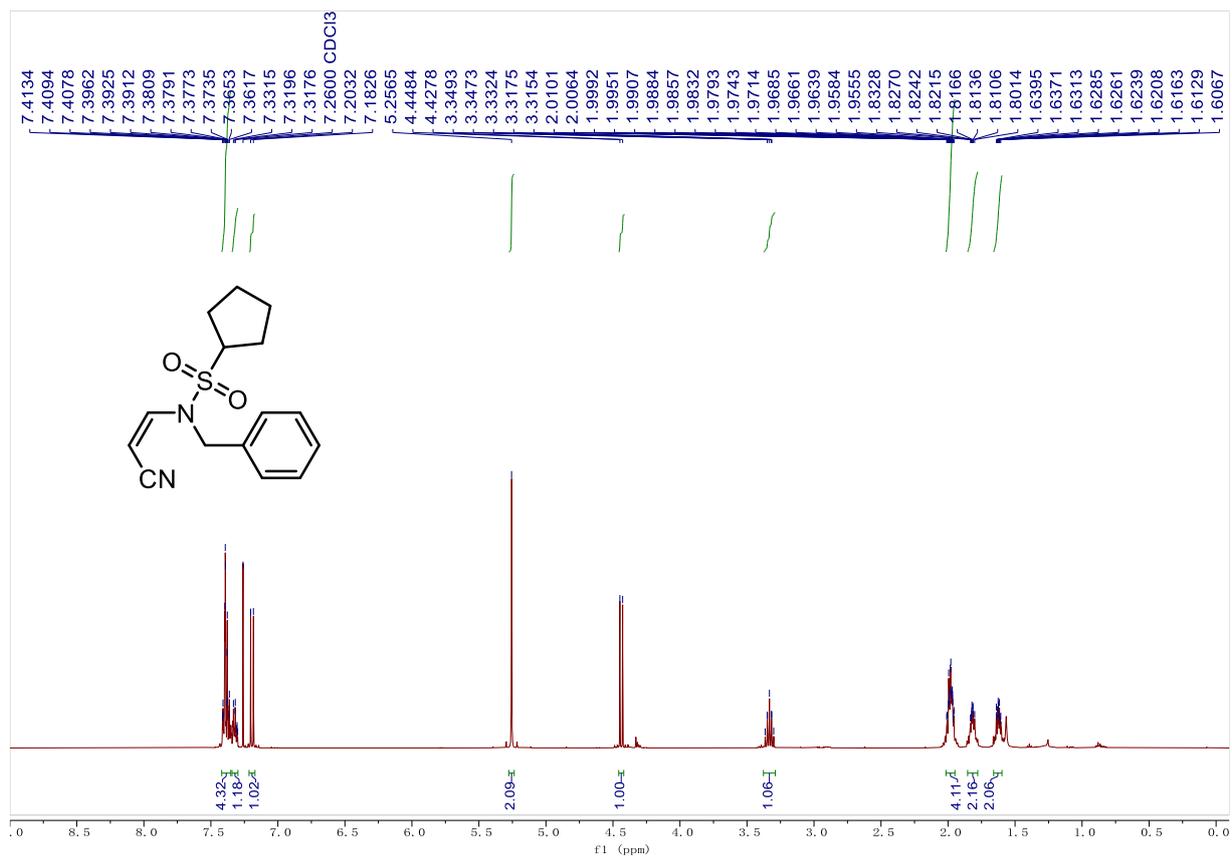




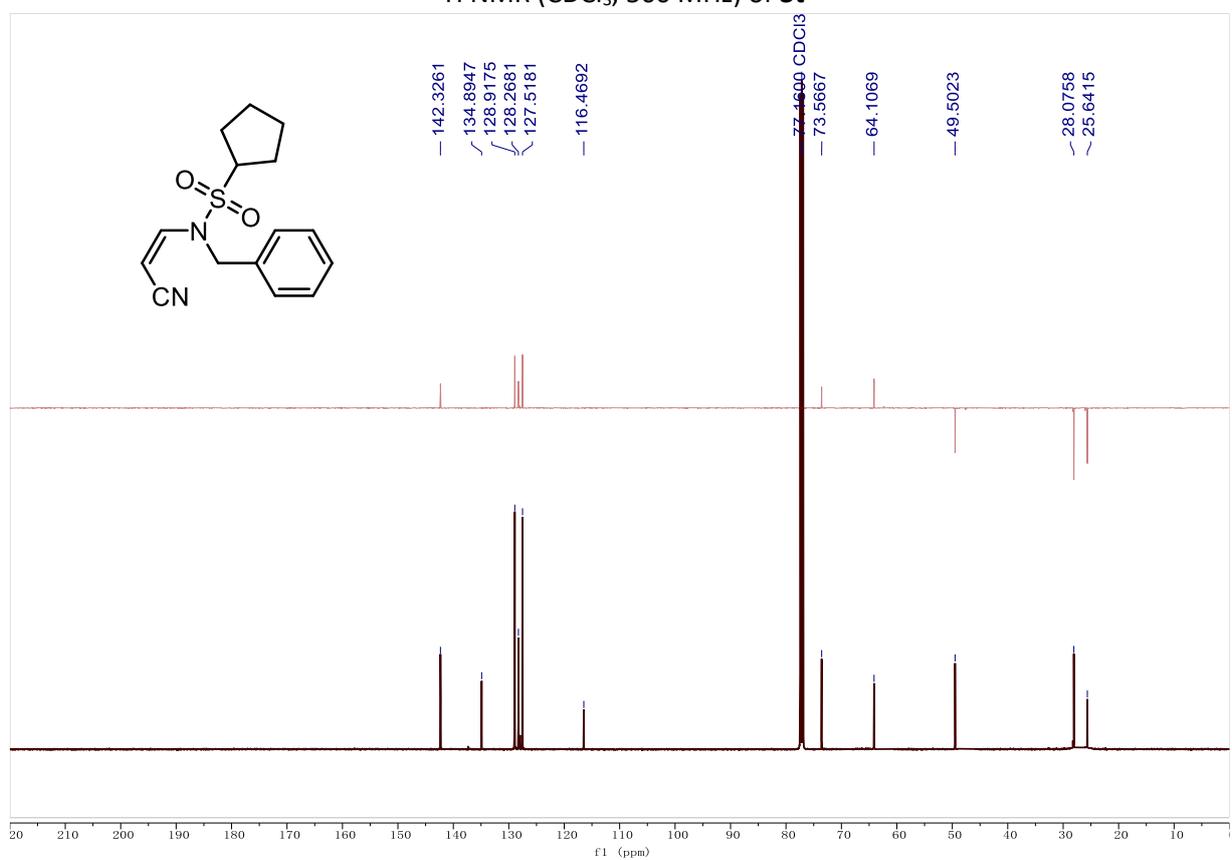
¹H NMR (CDCl₃, 500 MHz) of 3s



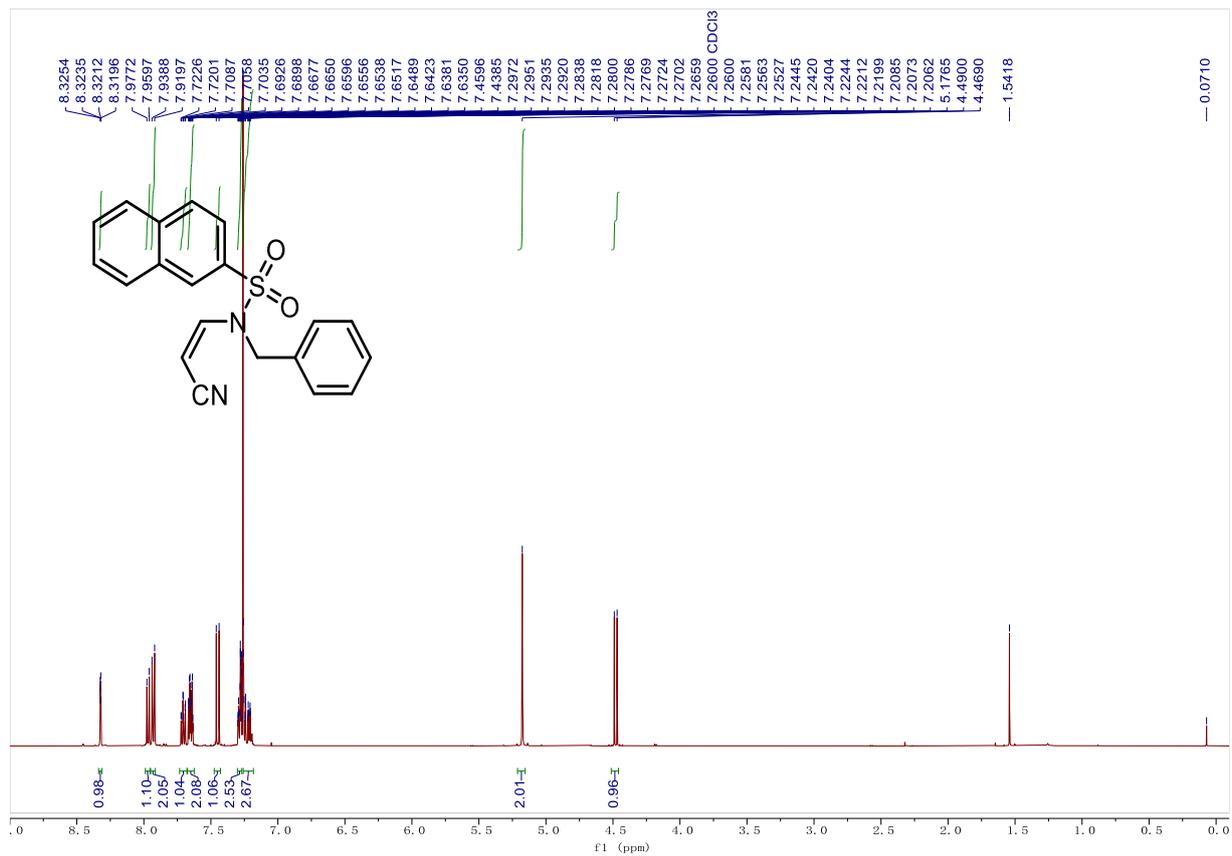
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3s



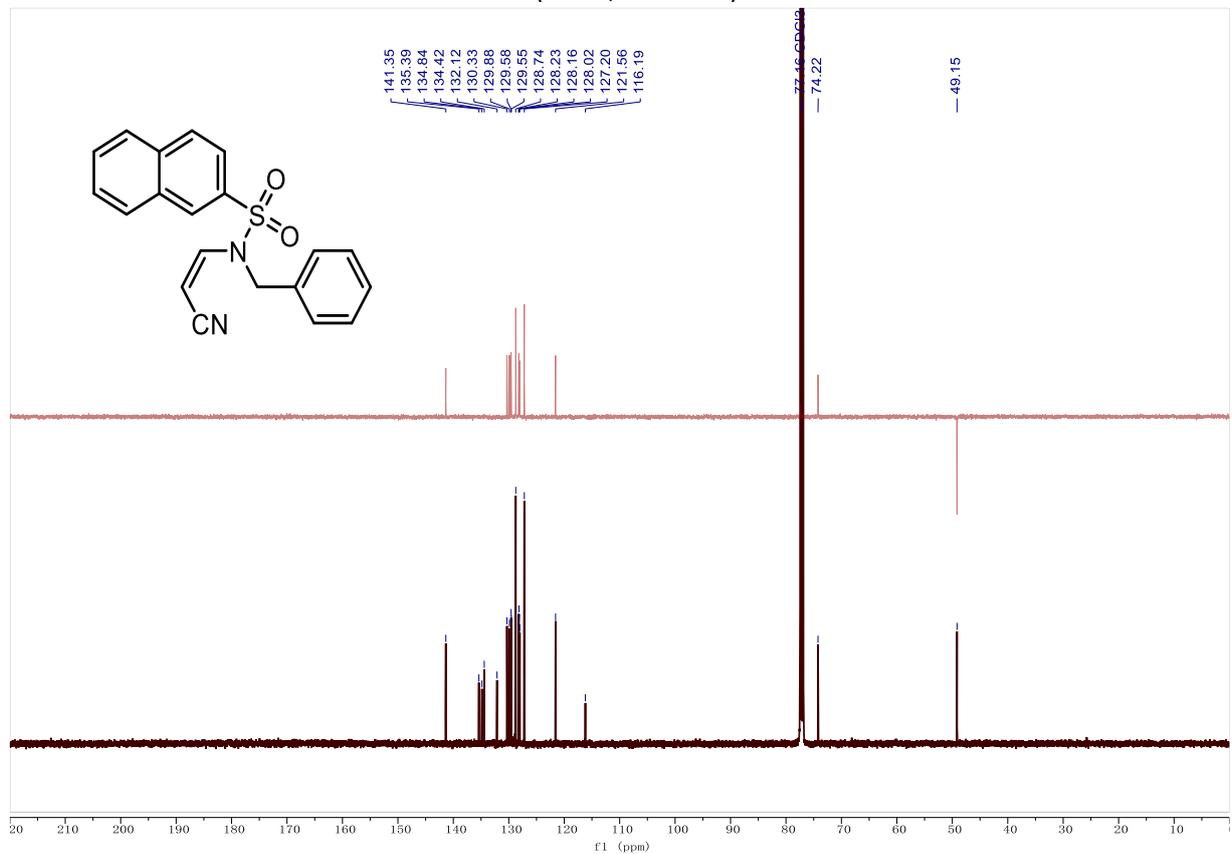
¹H NMR (CDCl₃, 500 MHz) of 3t



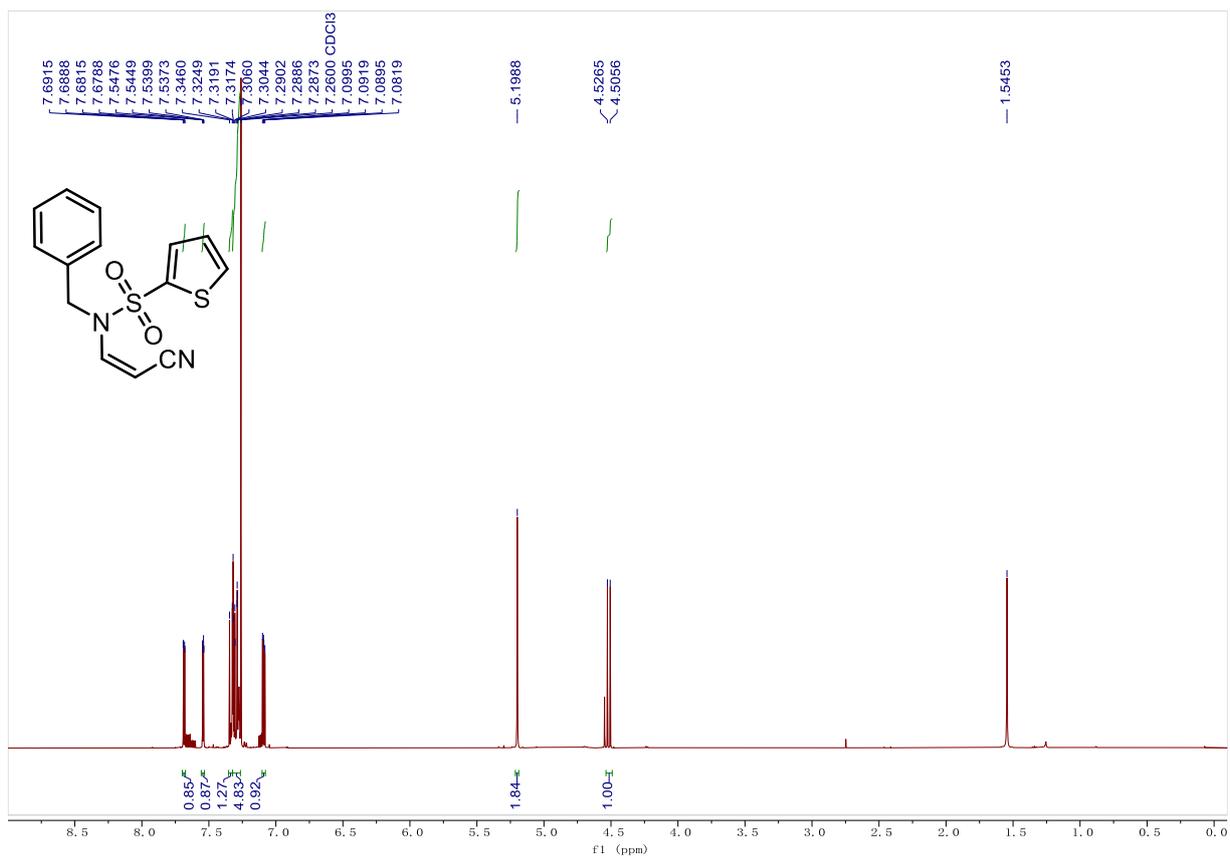
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3t



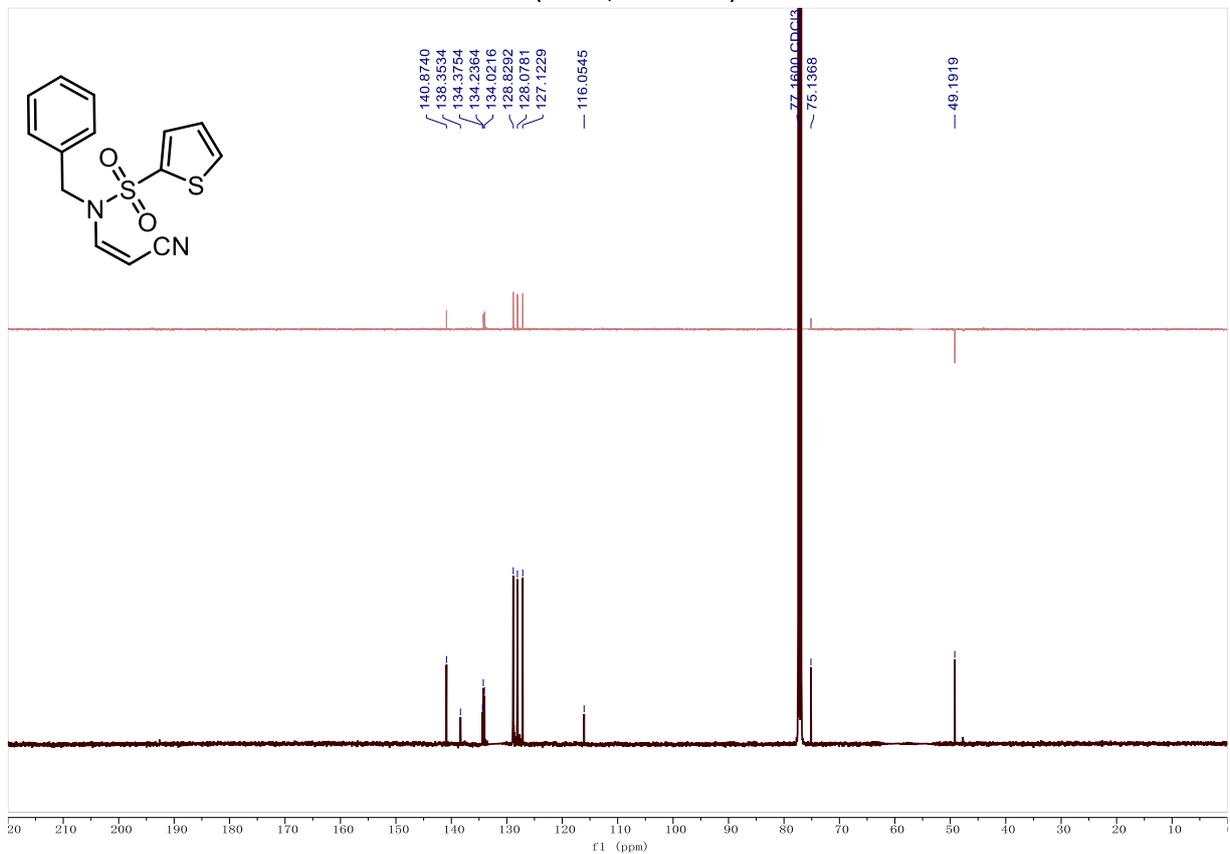
$^1\text{H NMR}$ (CDCl₃, 500 MHz) of 3u



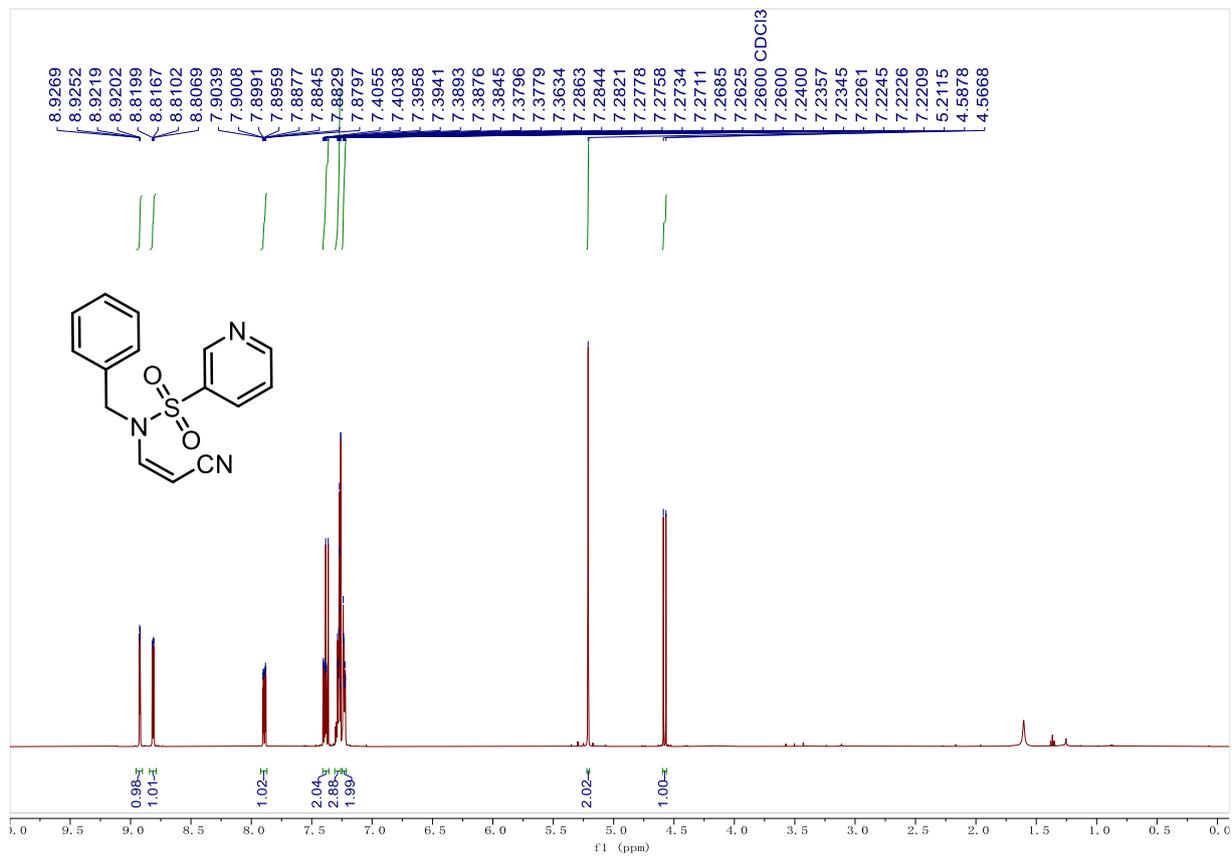
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz) of 3u



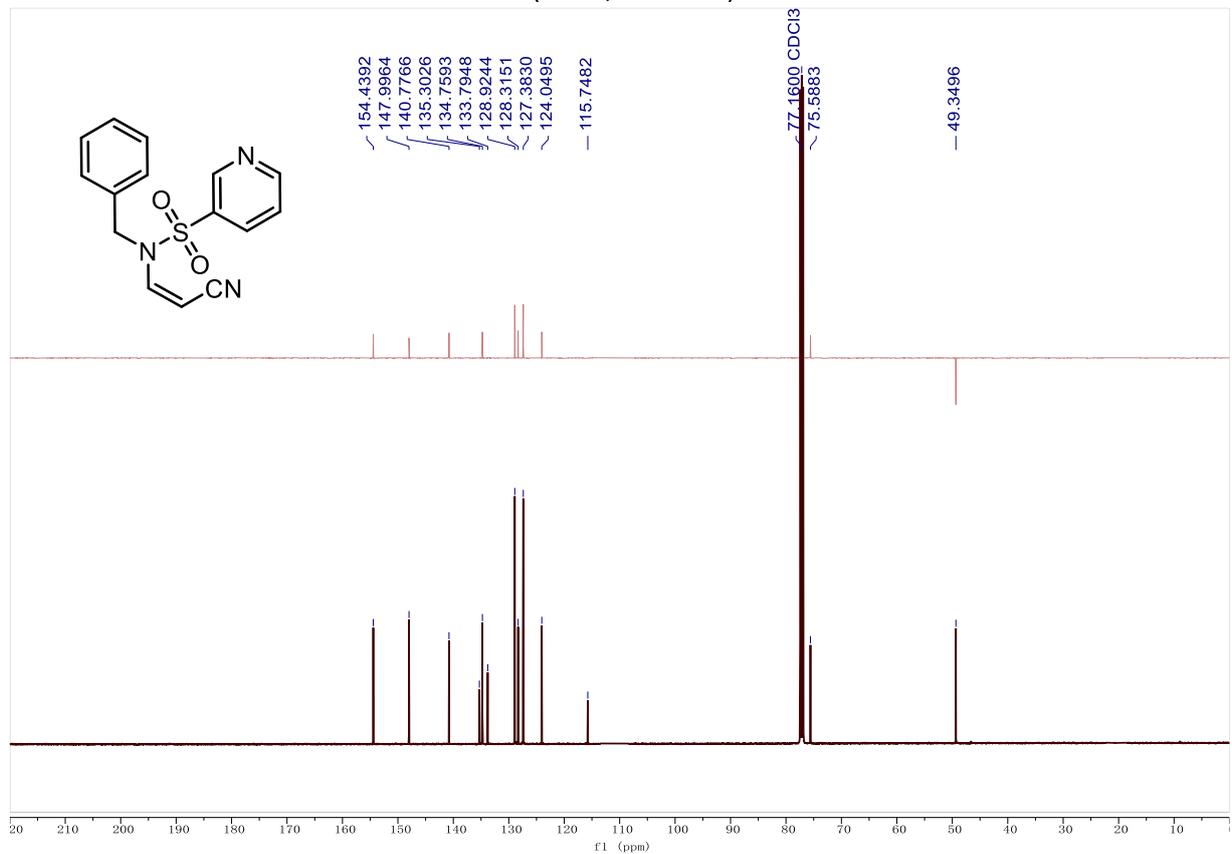
¹H NMR (CDCl₃, 500 MHz) of 3v



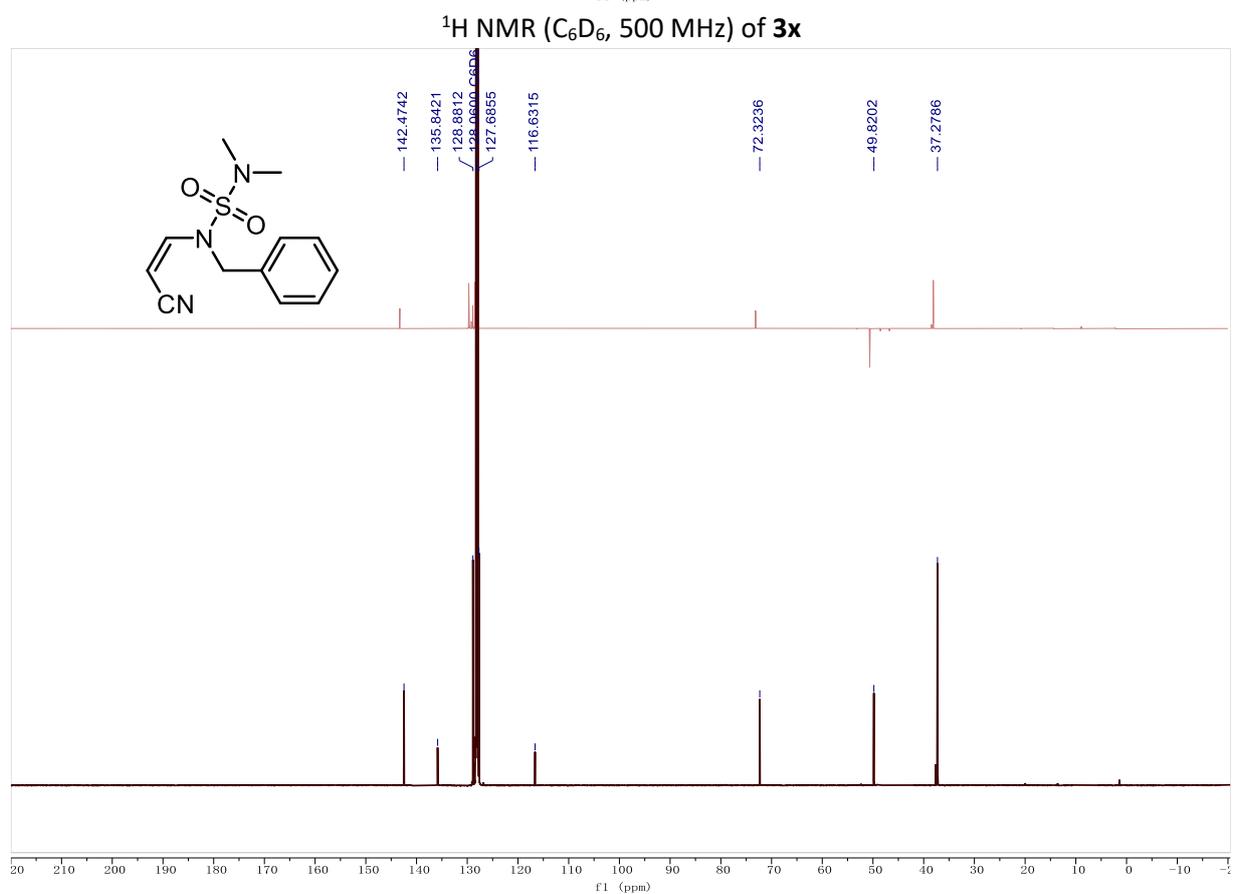
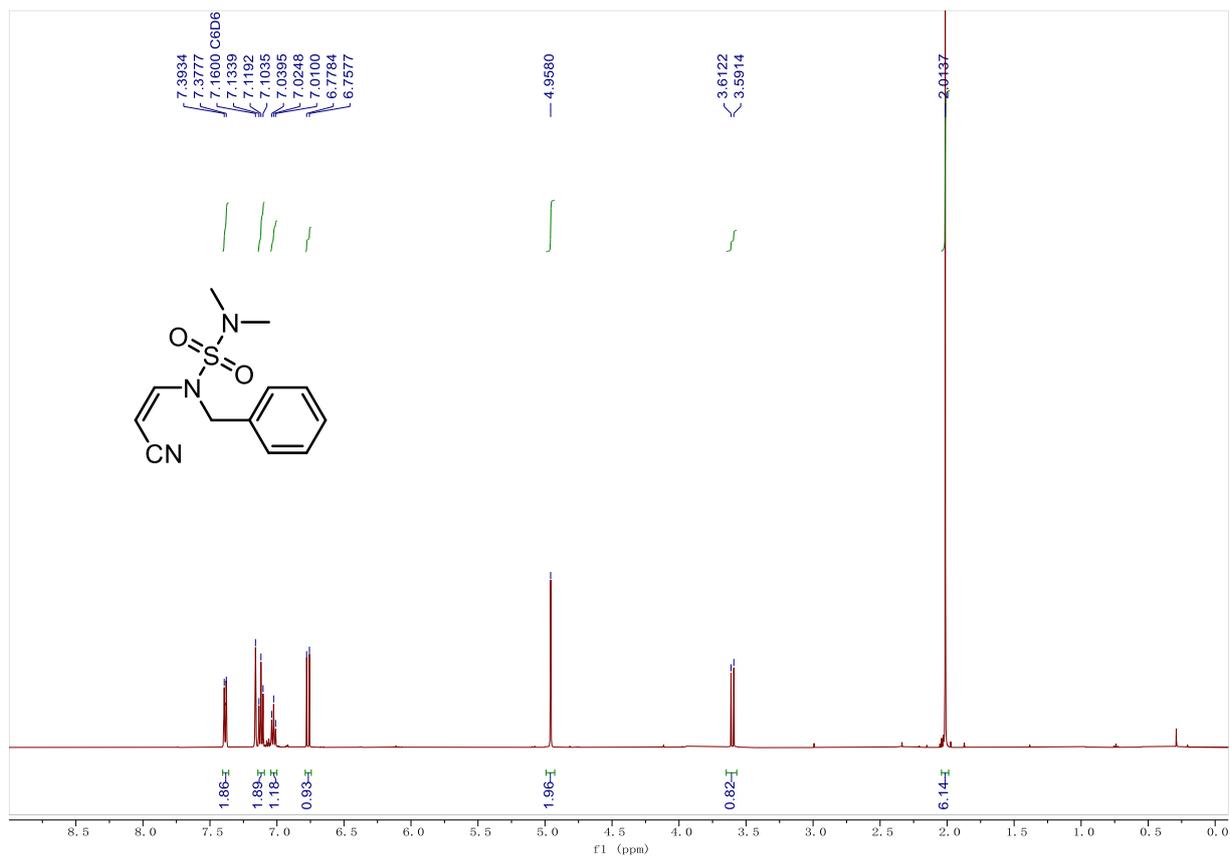
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3v



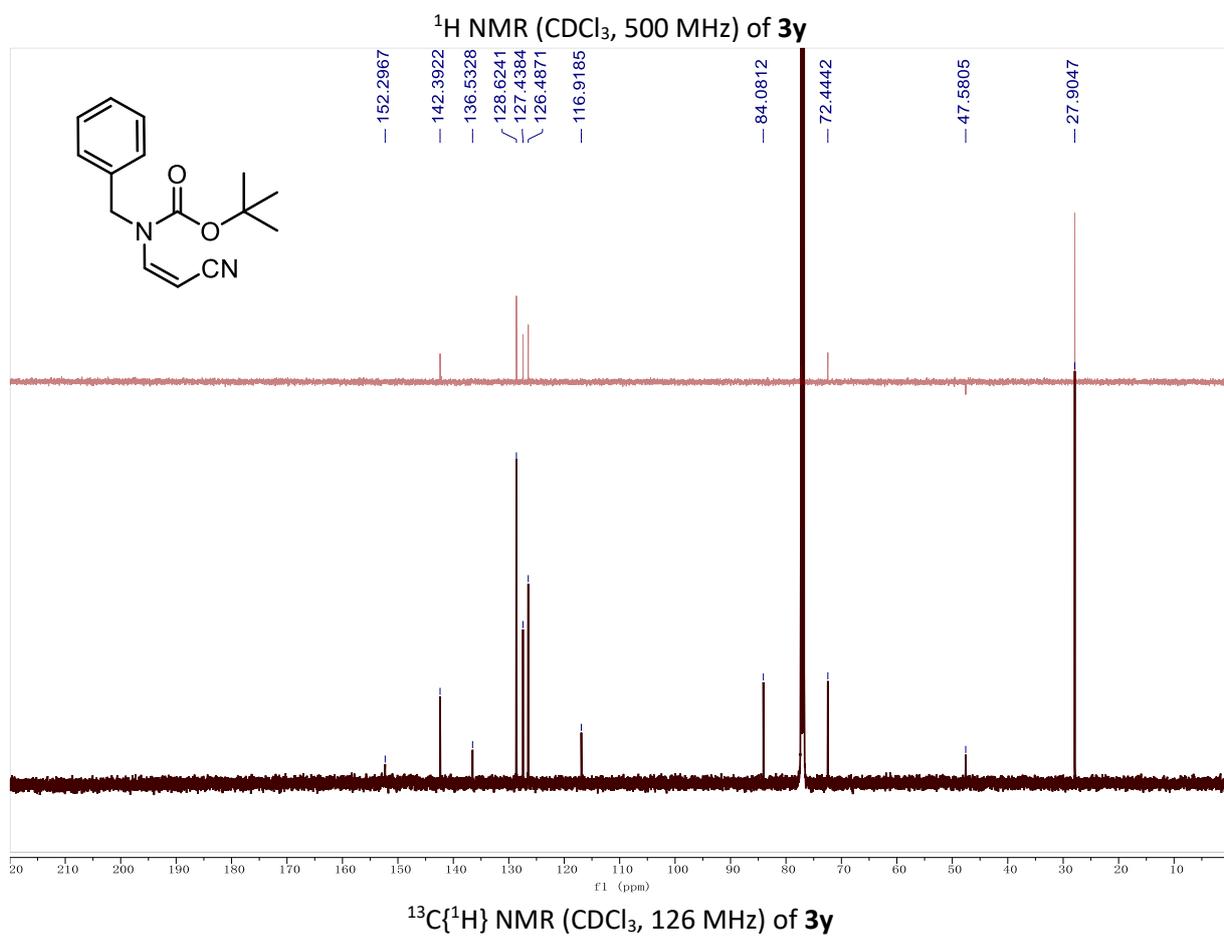
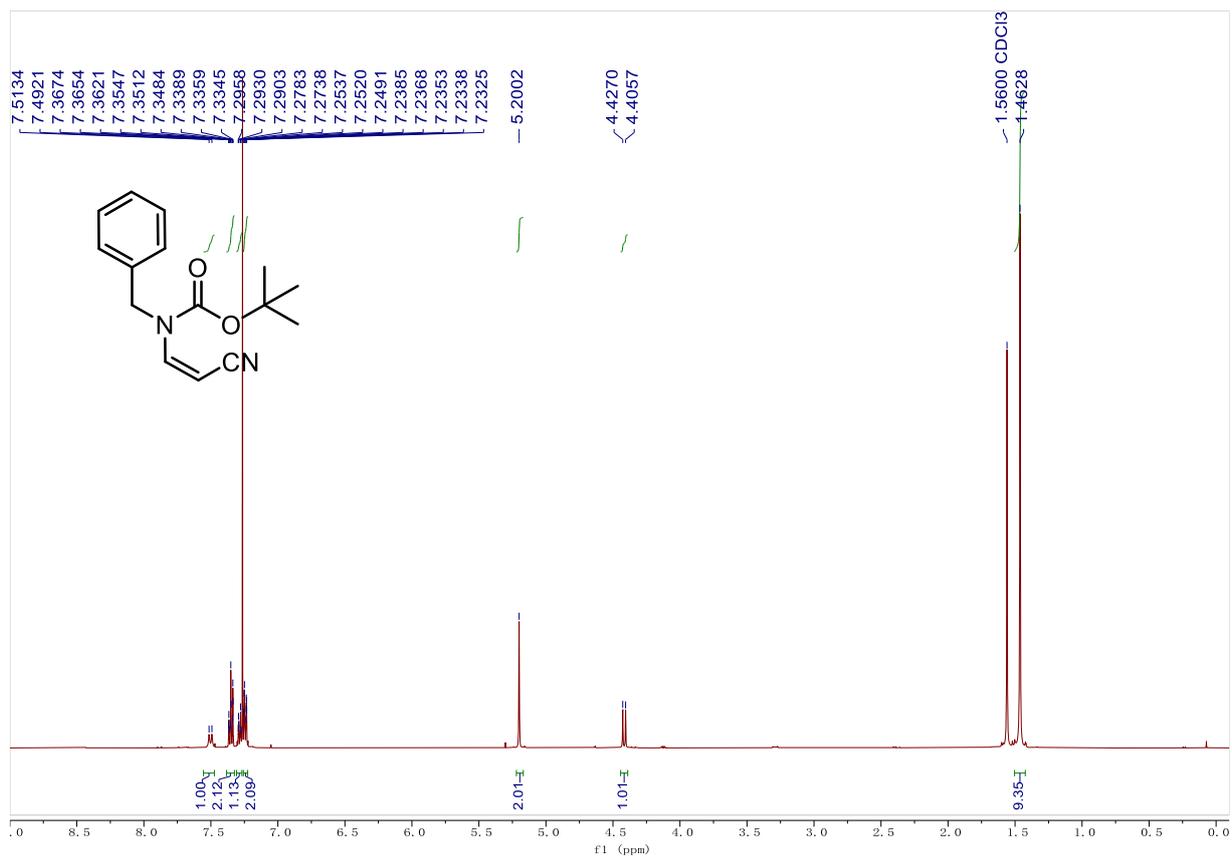
¹H NMR (CDCl₃, 500 MHz) of **3w**

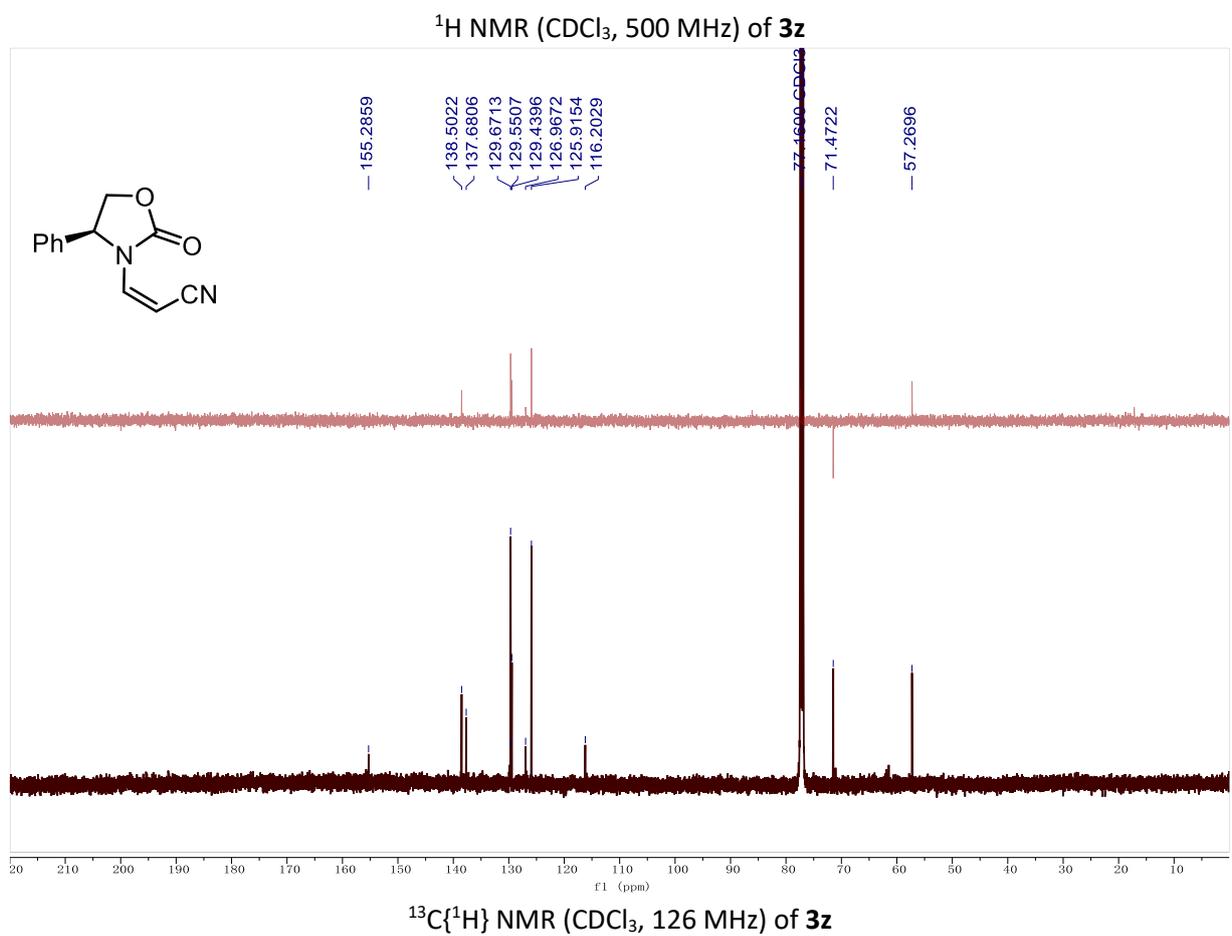
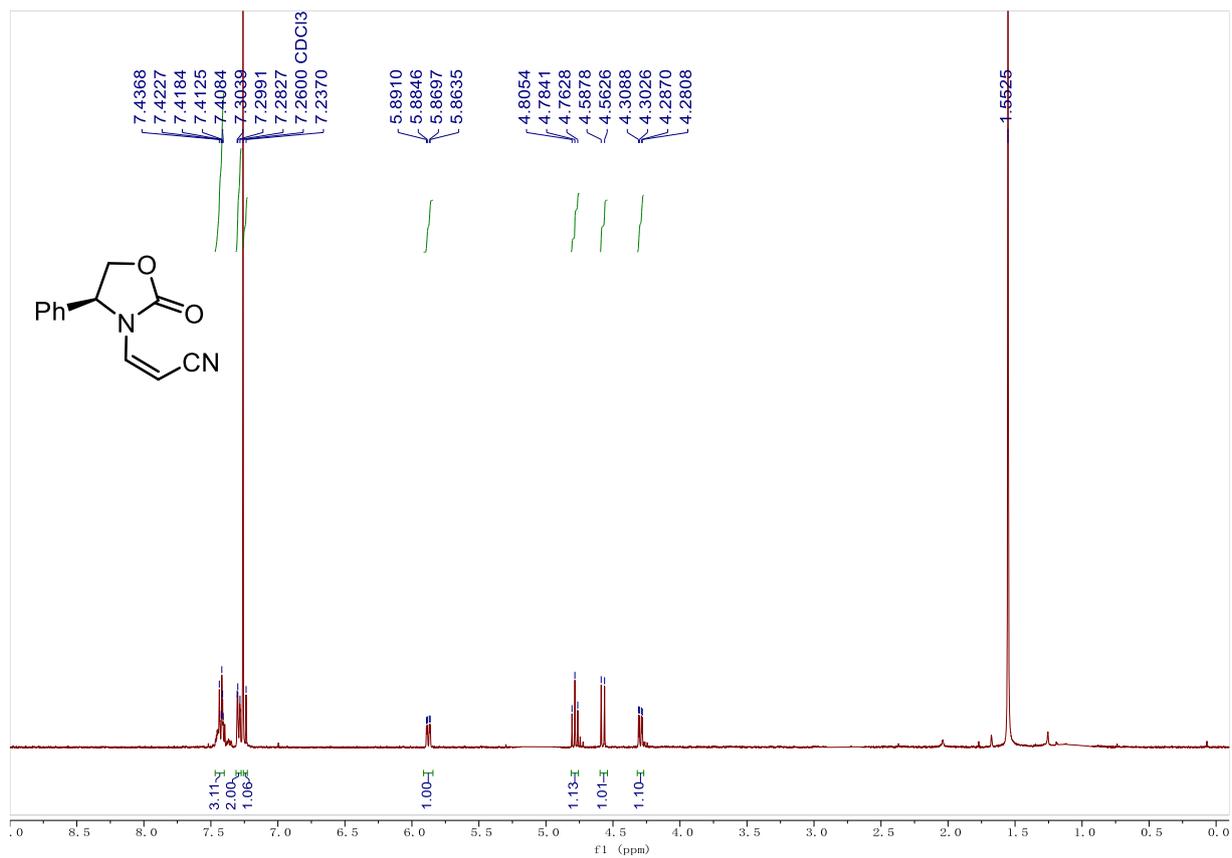


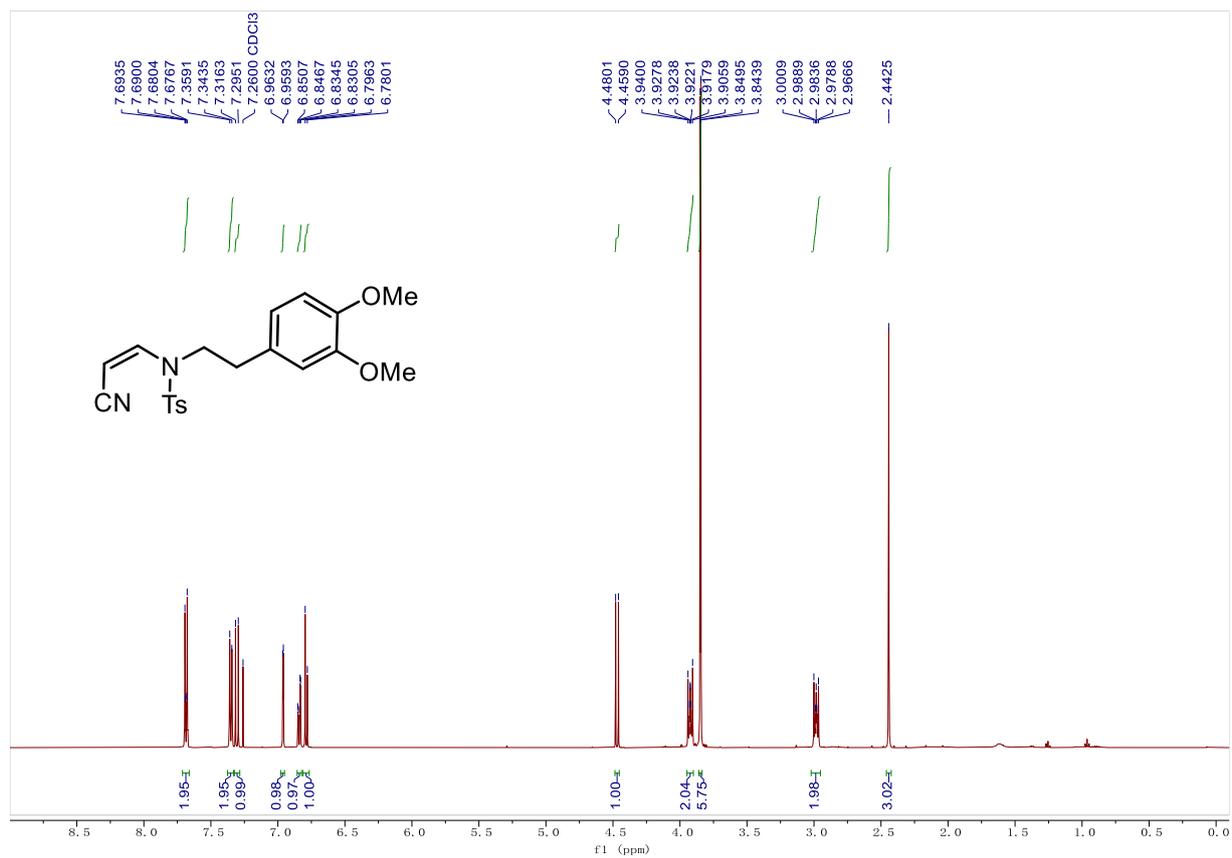
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3w**



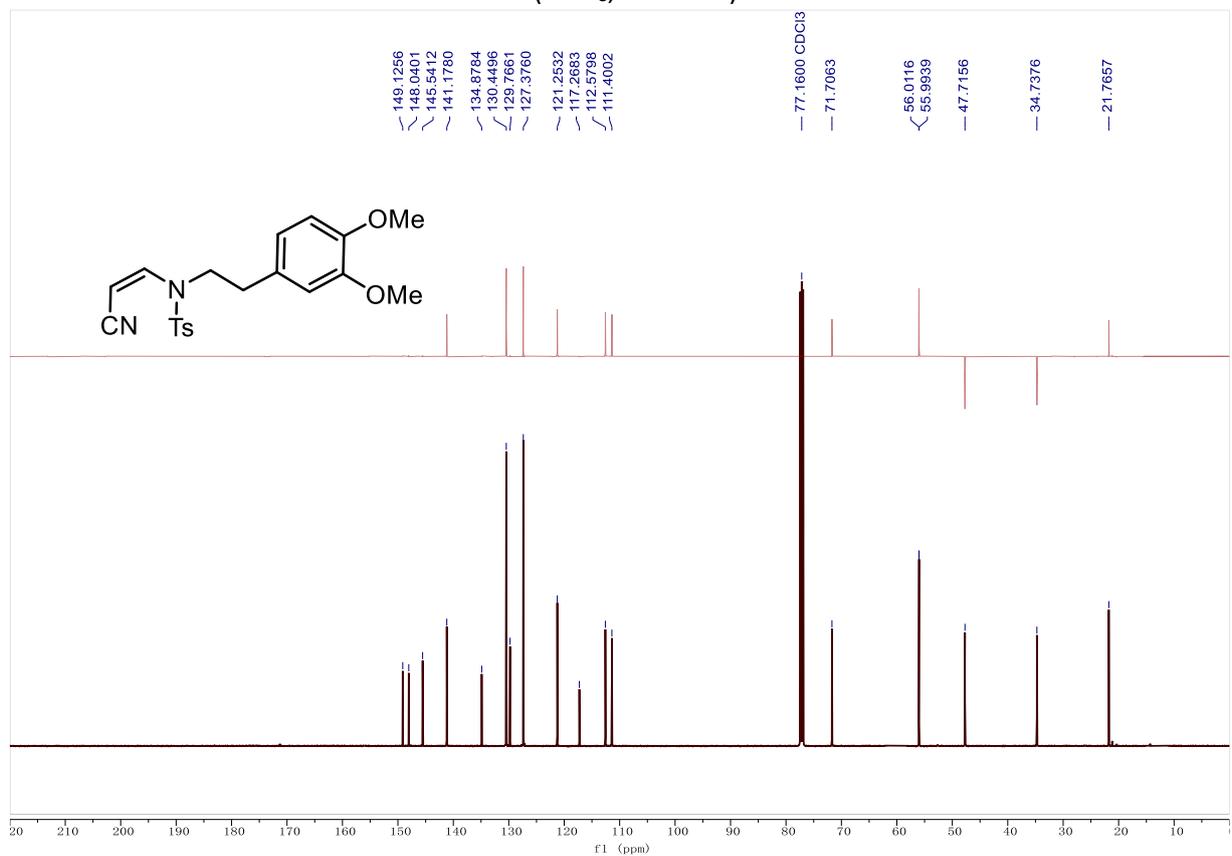
$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz) of **3x**



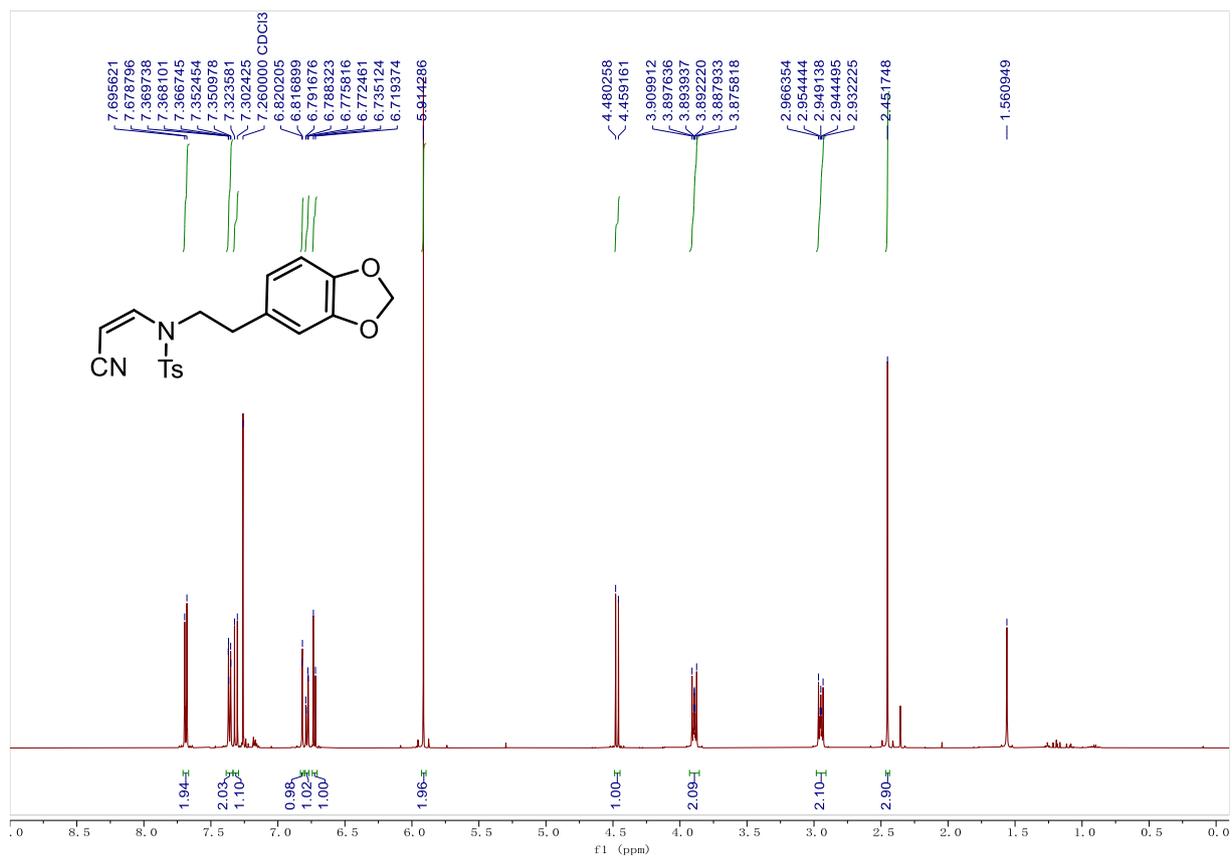




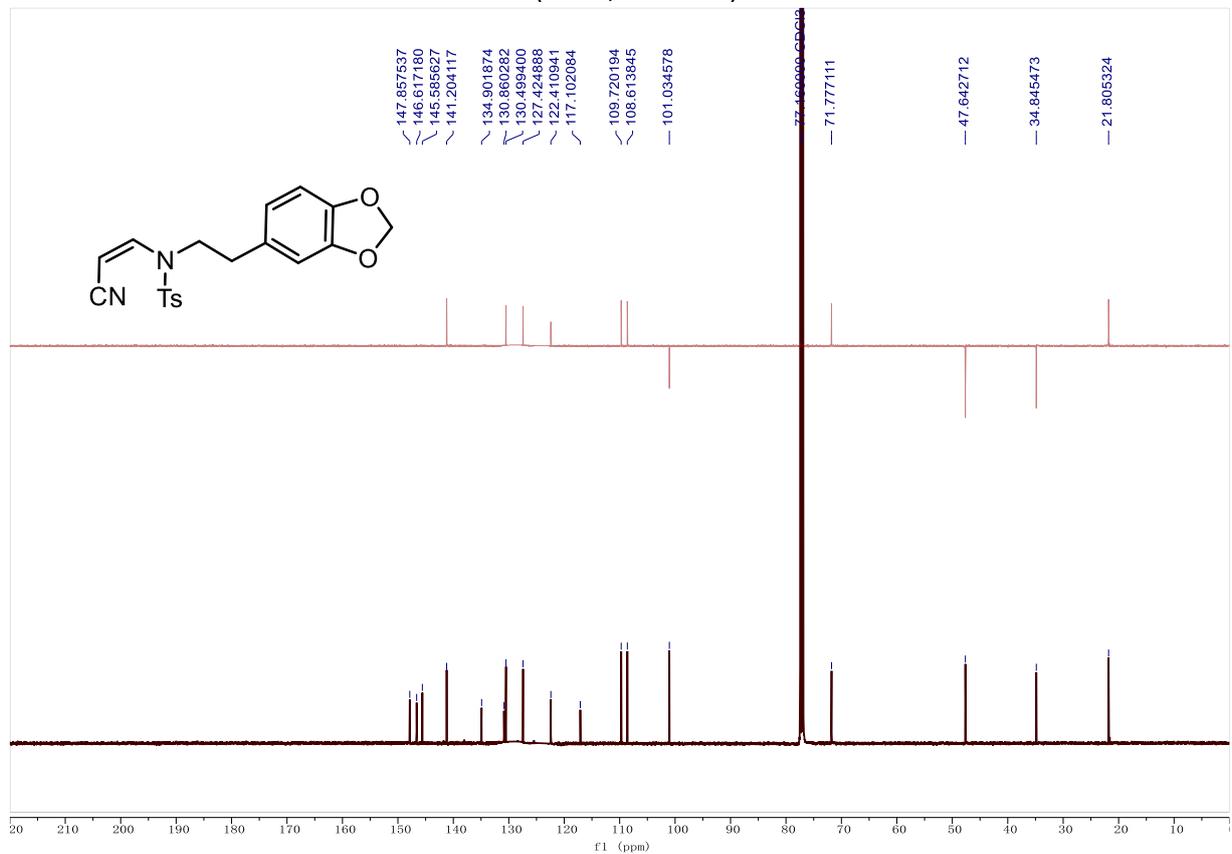
¹H NMR (CDCl₃, 500 MHz) of 3A



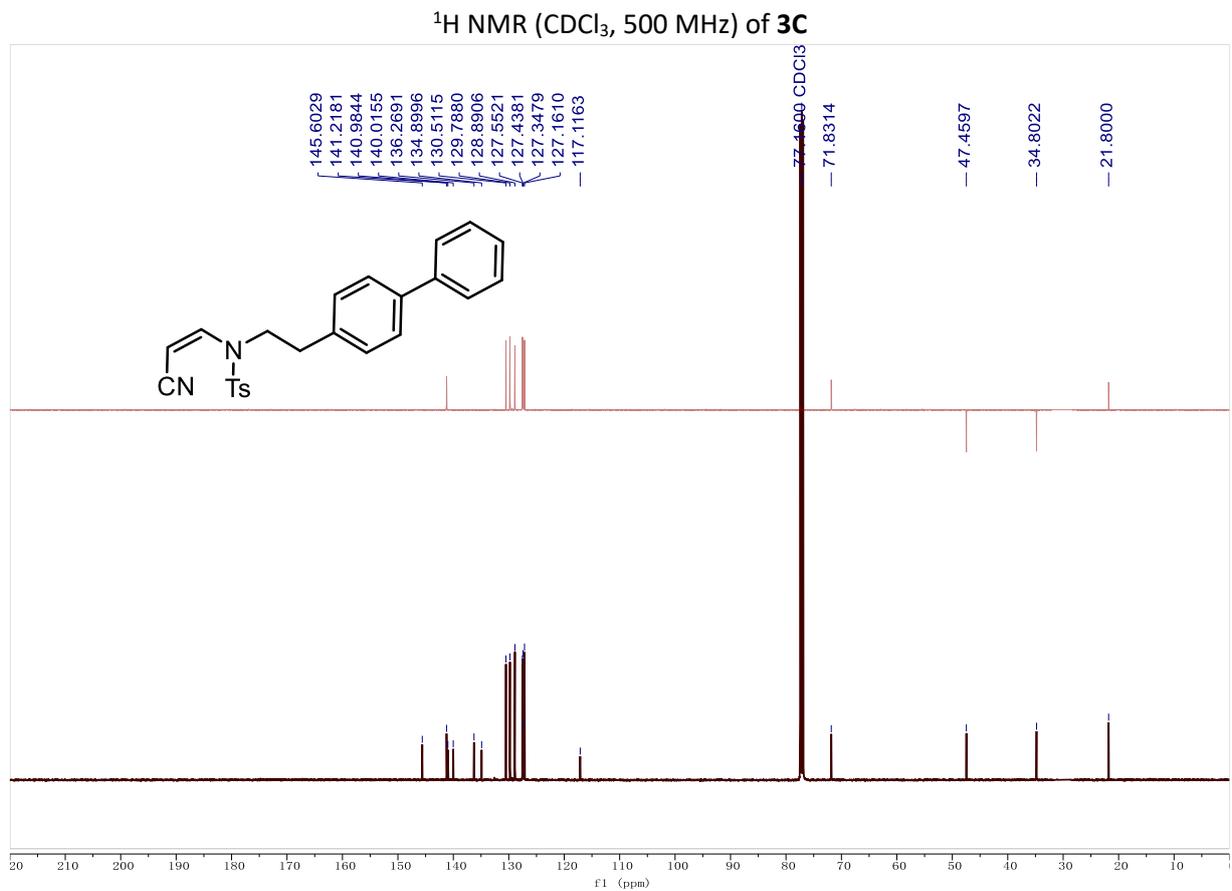
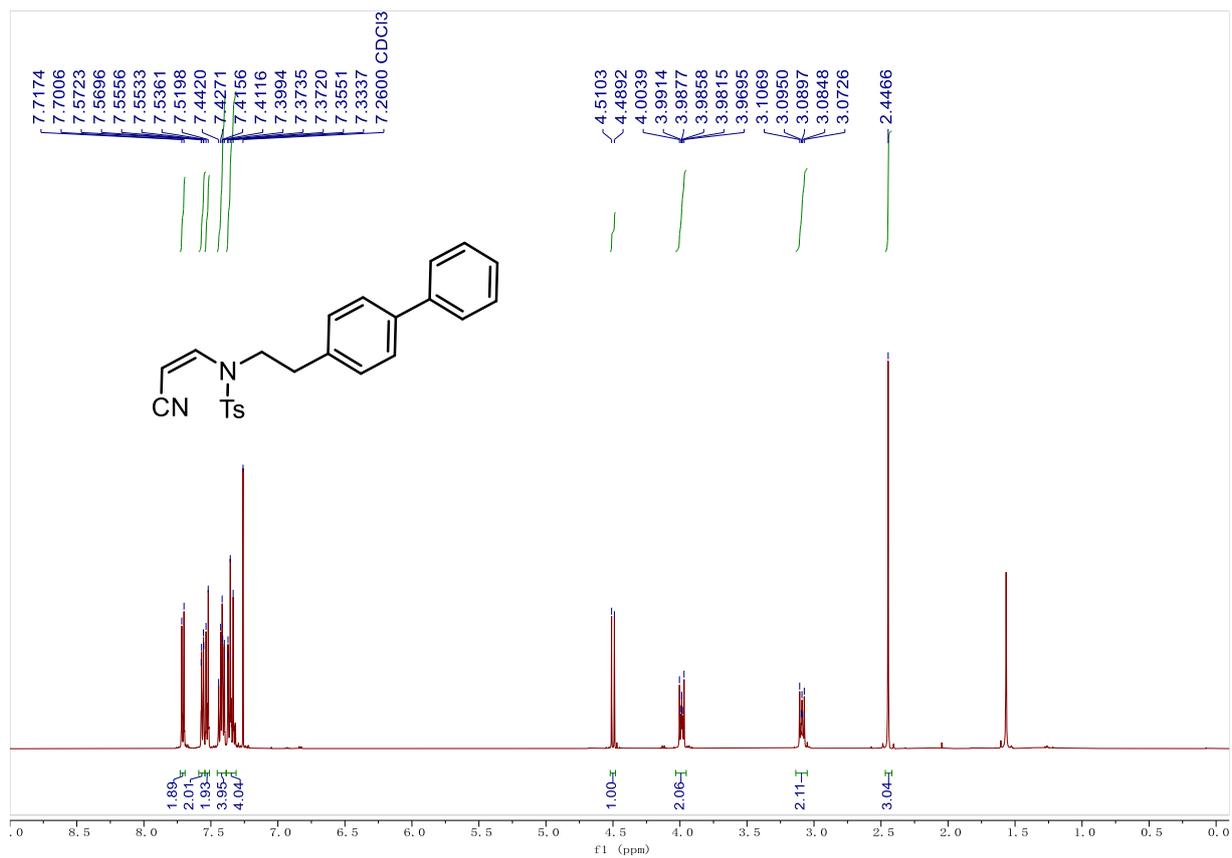
¹³C NMR (CDCl₃, 126 MHz) of 3A



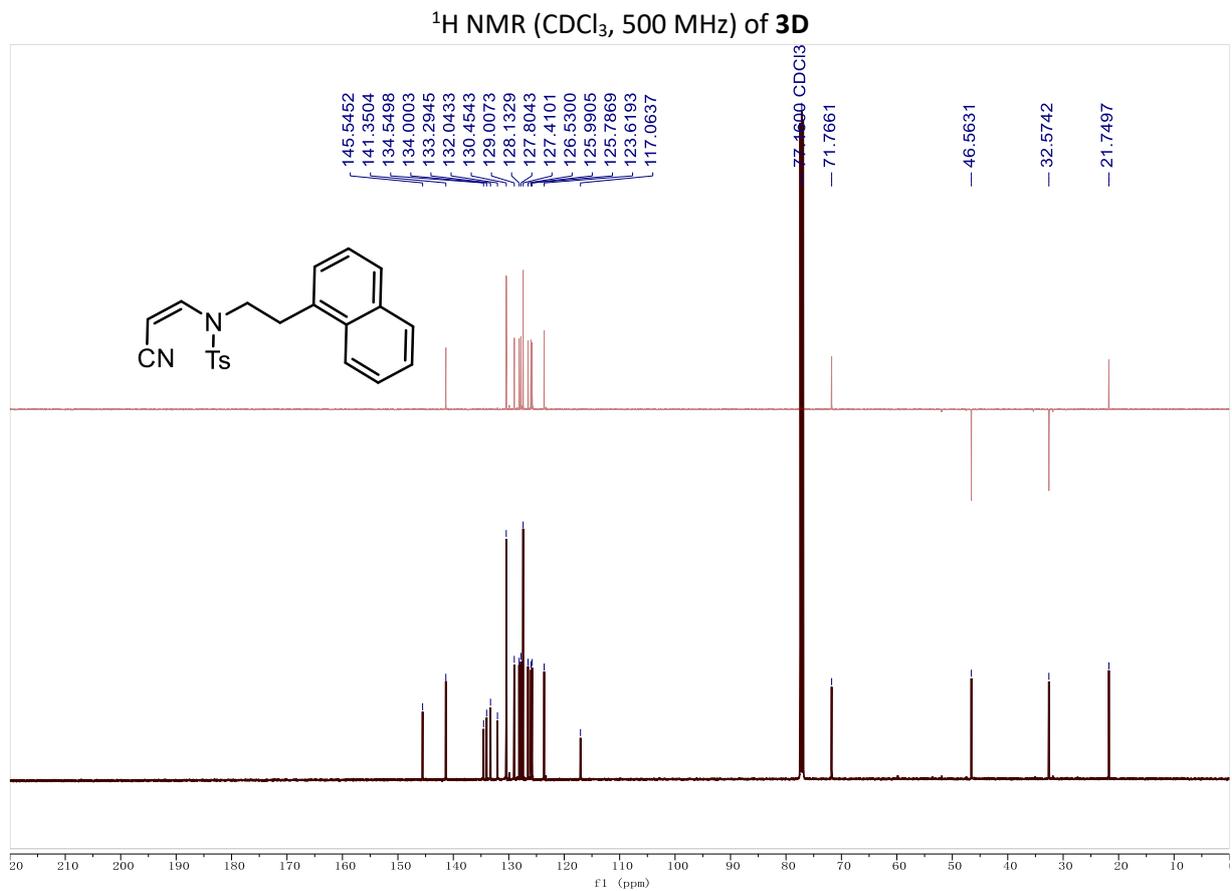
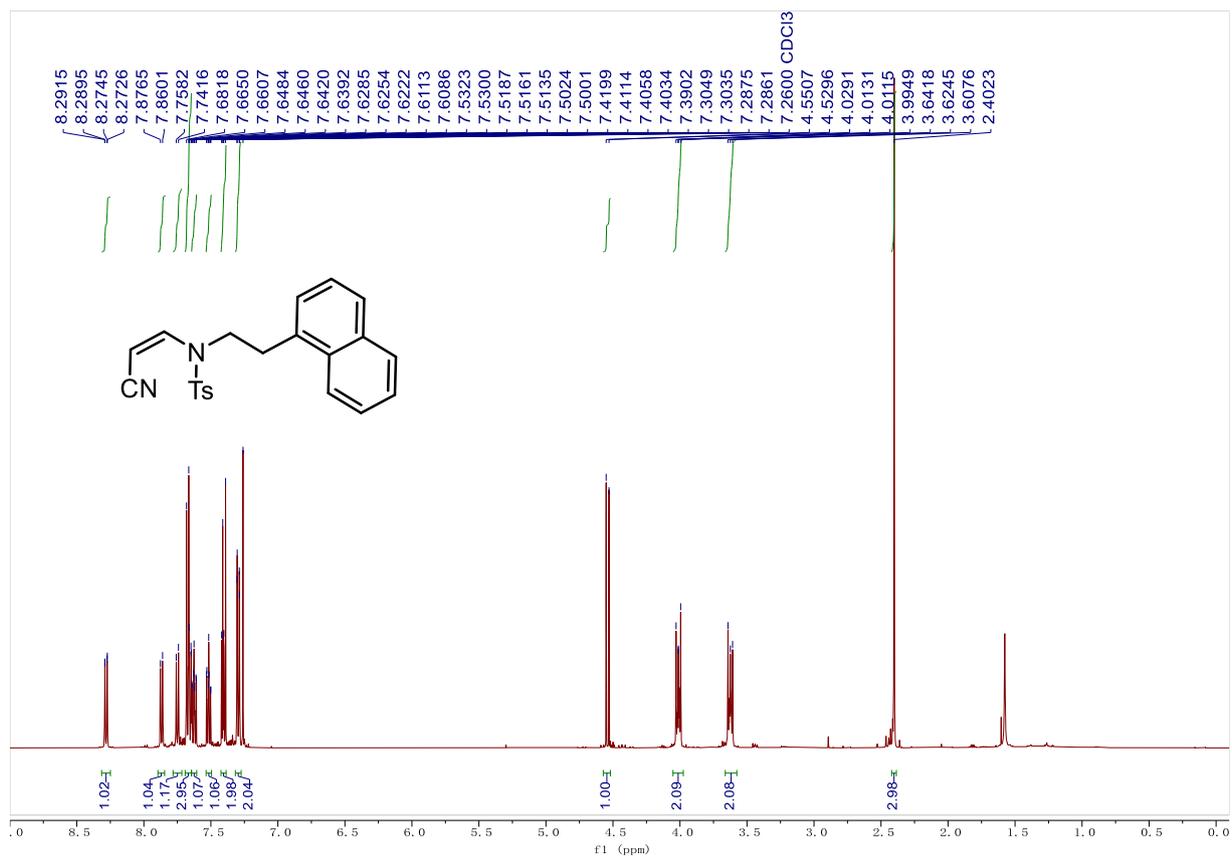
¹H NMR (CDCl₃, 500 MHz) of **3B**

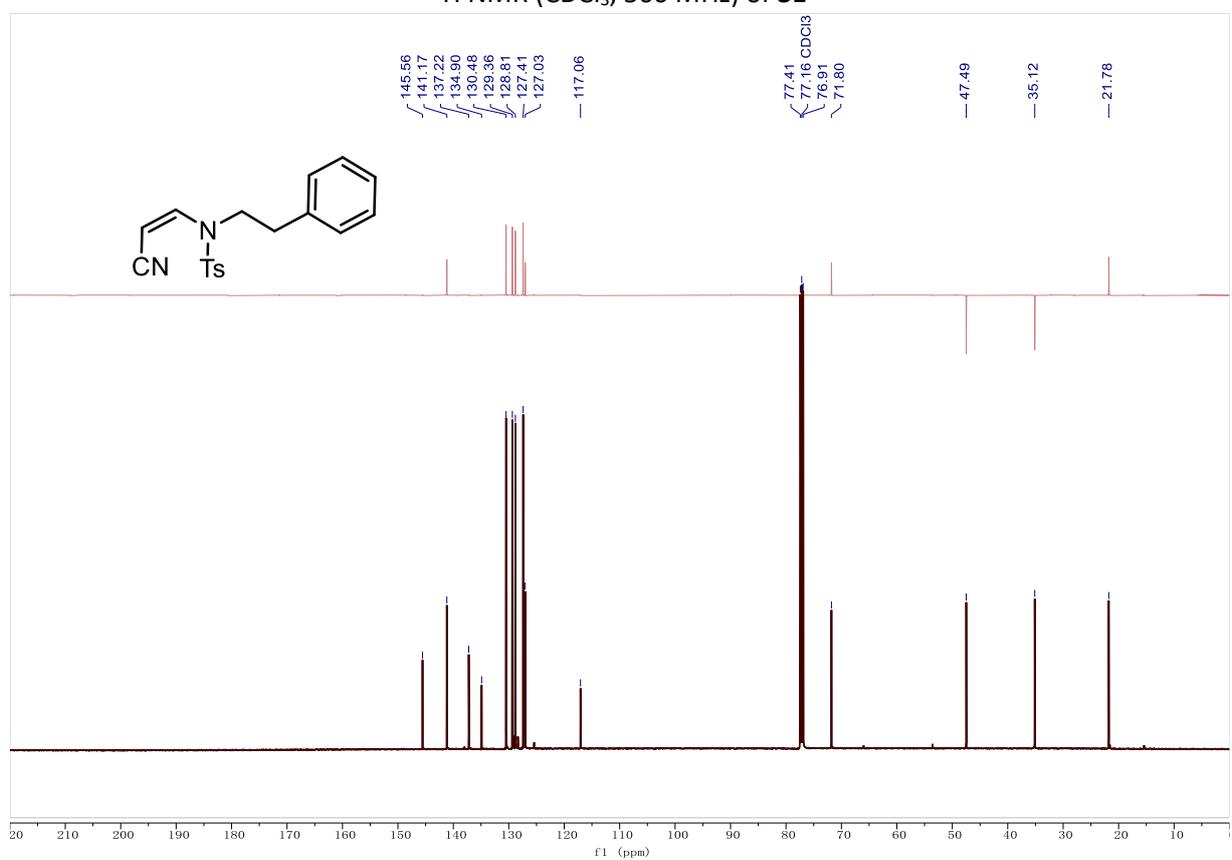
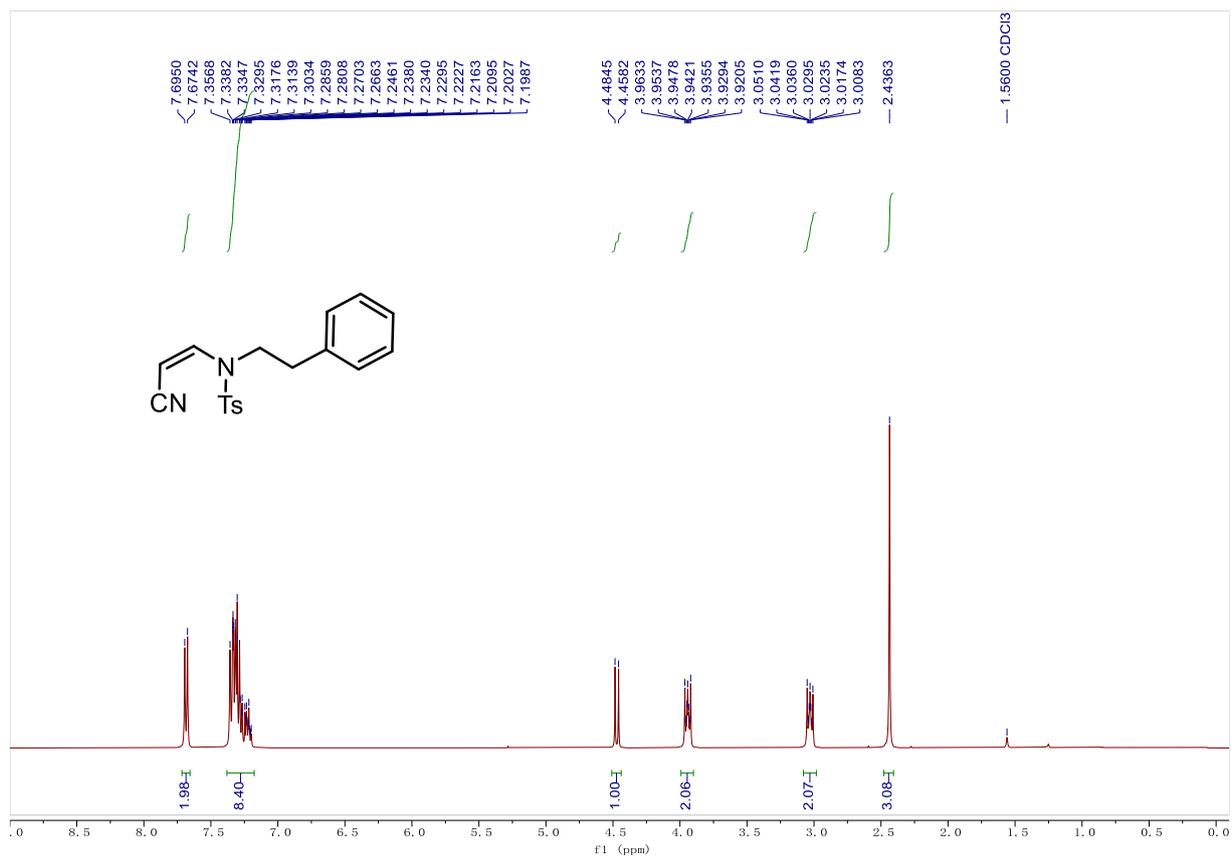


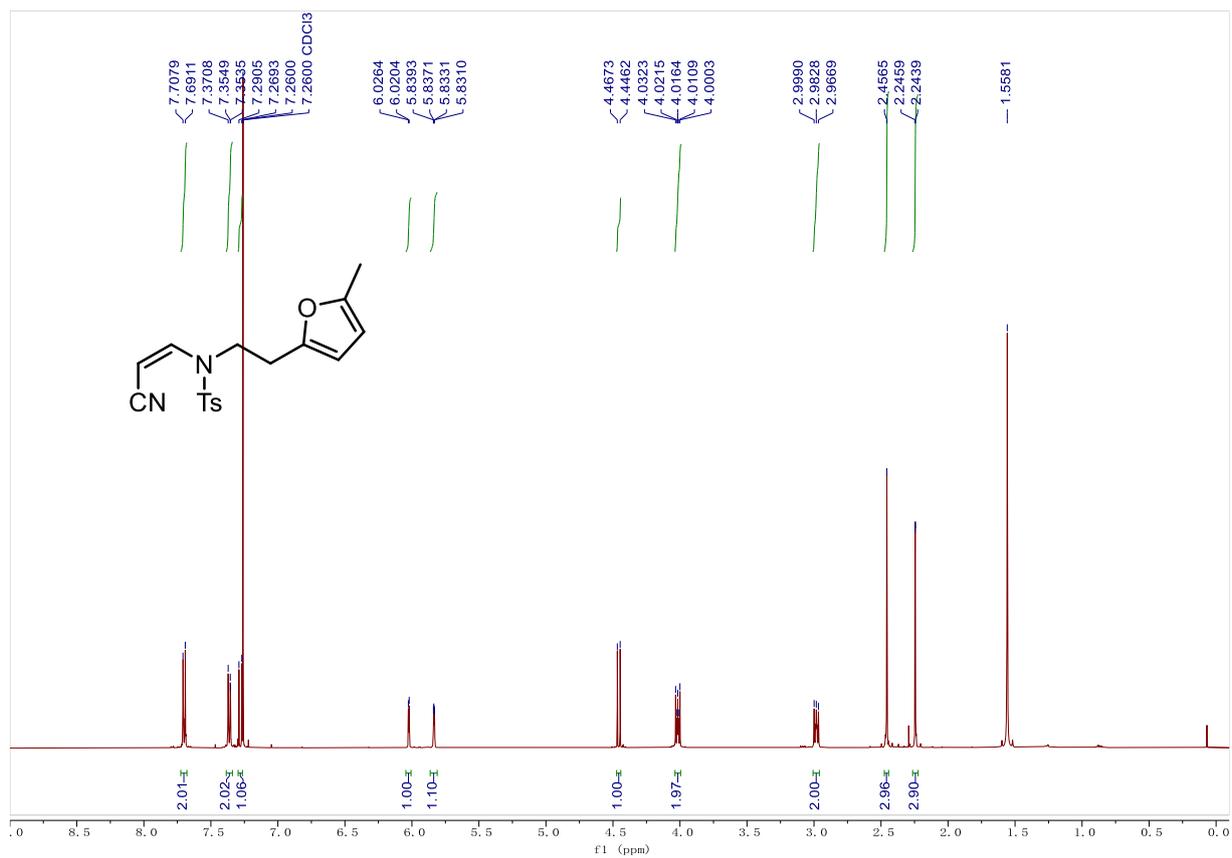
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3B**



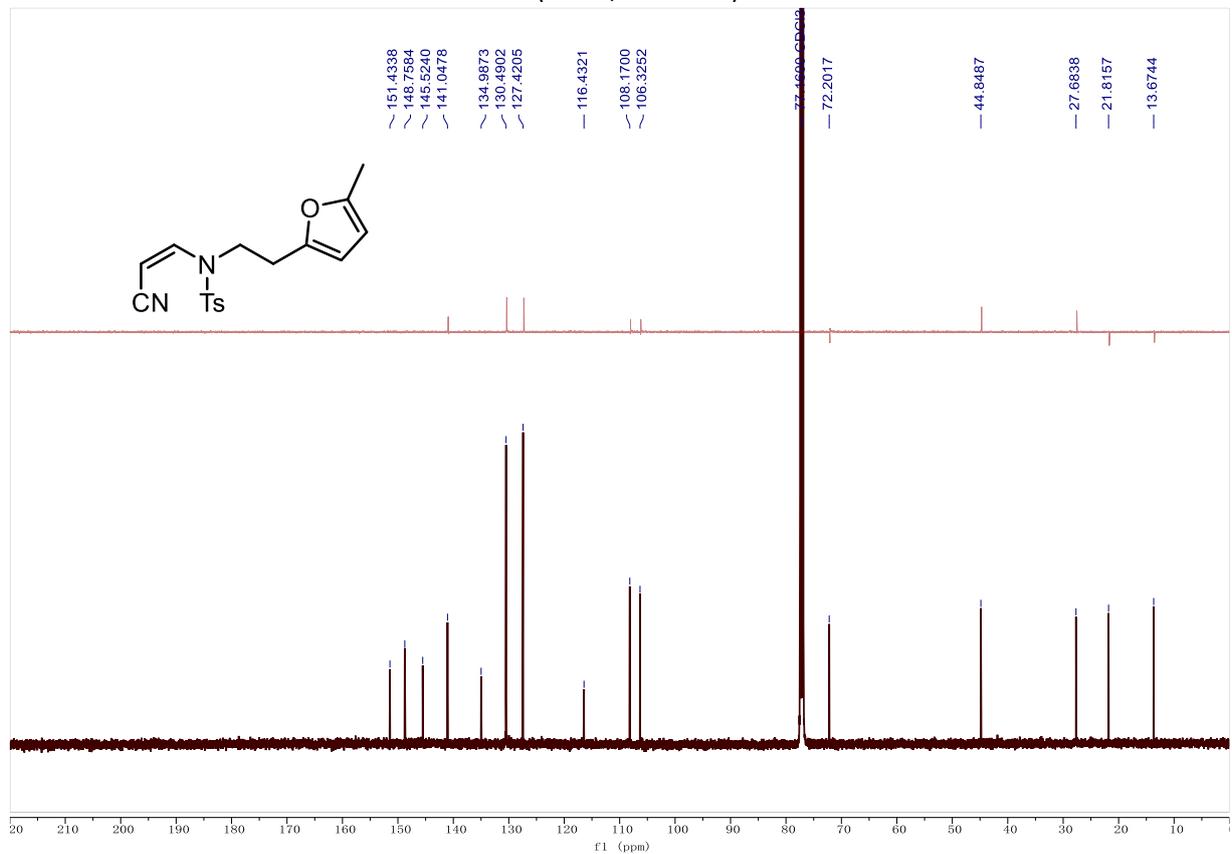
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3C**



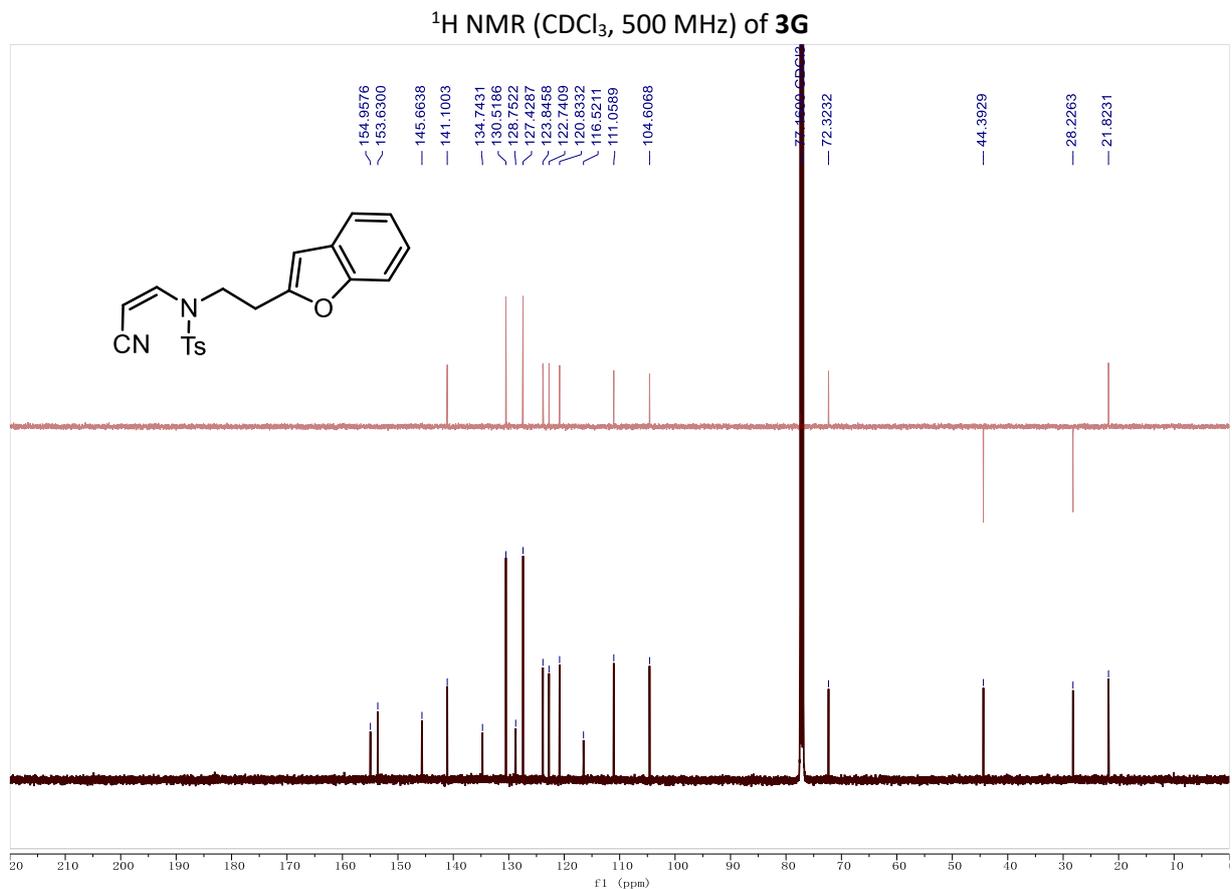
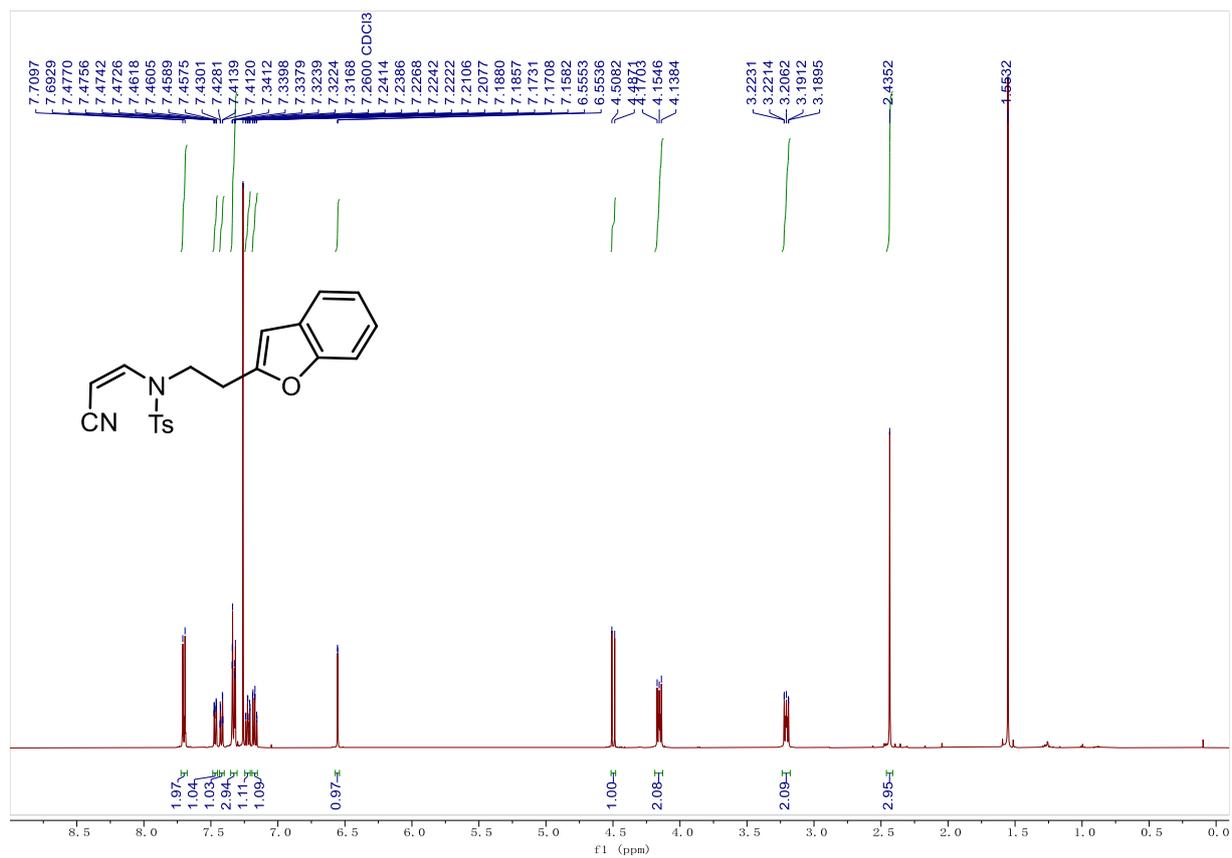


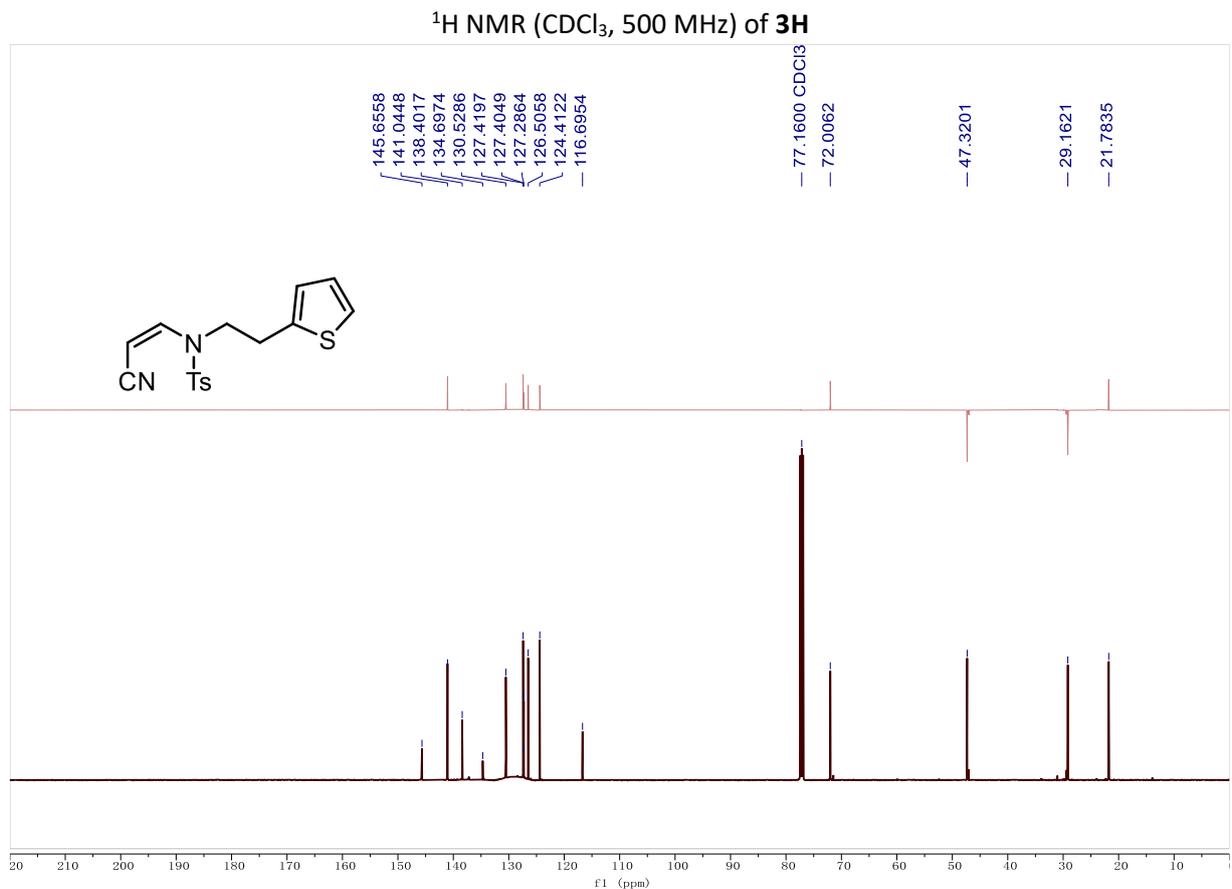
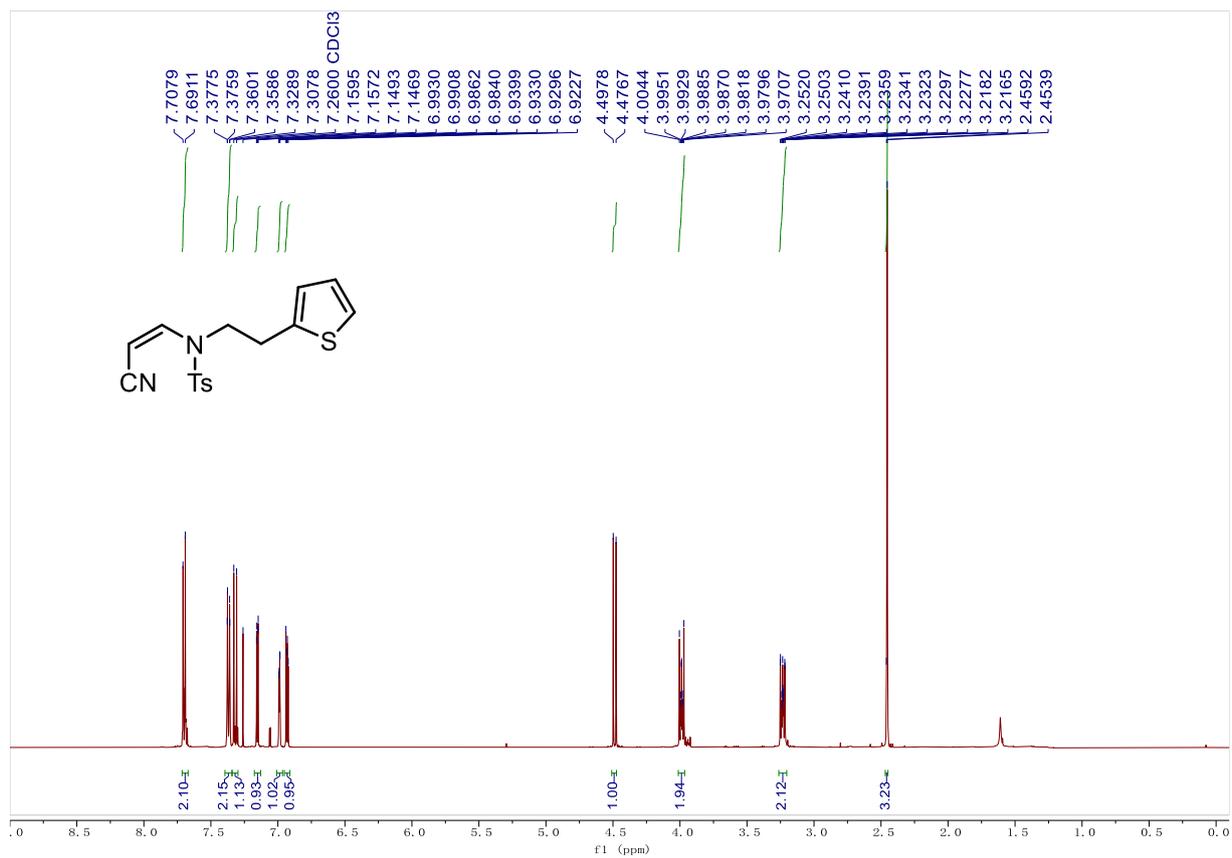


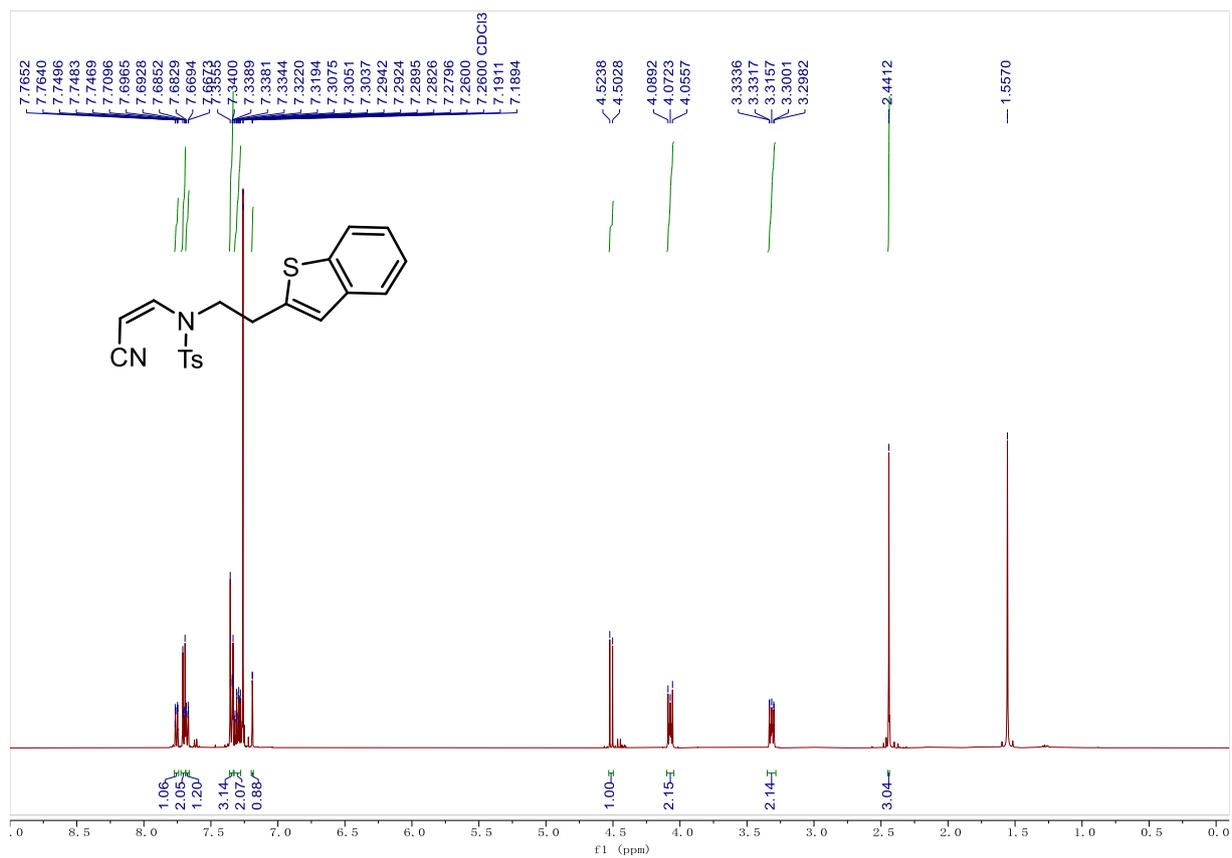
¹H NMR (CDCl₃, 500 MHz) of 3F



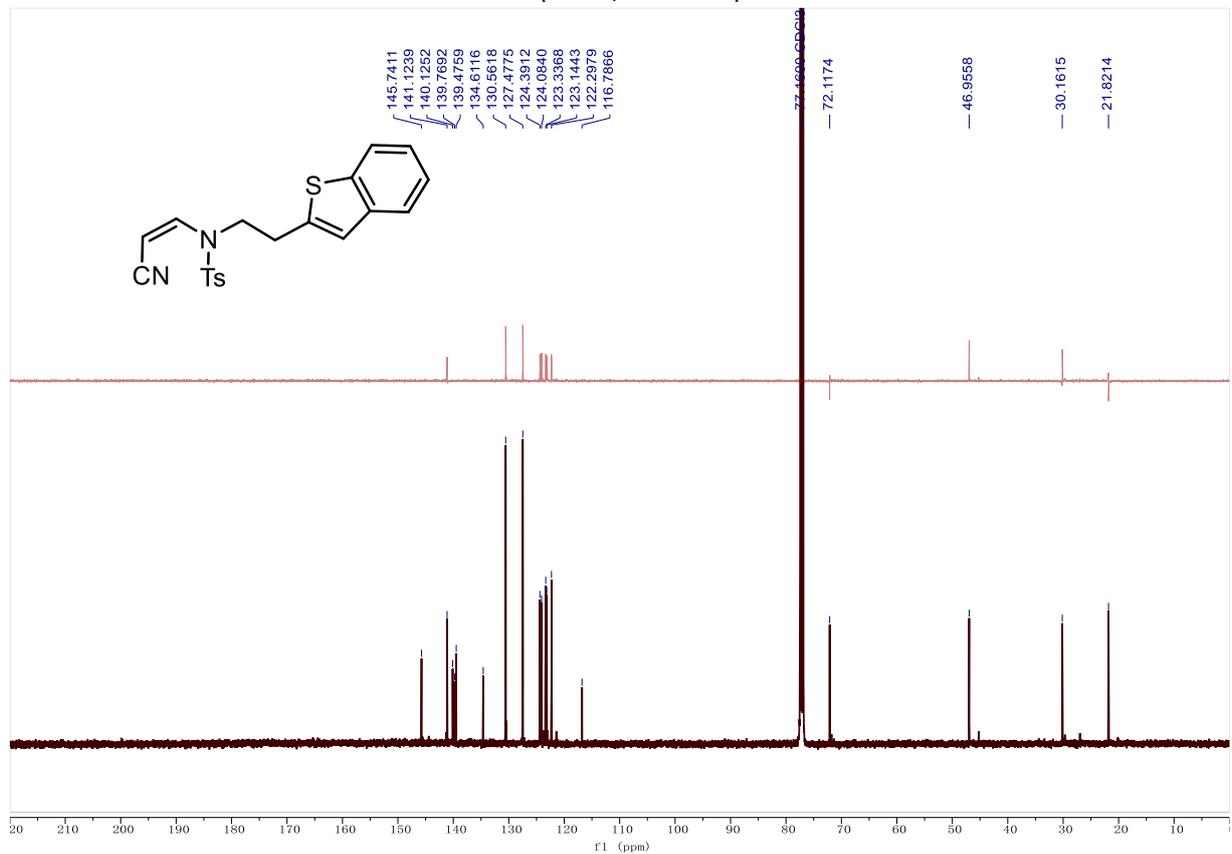
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3F



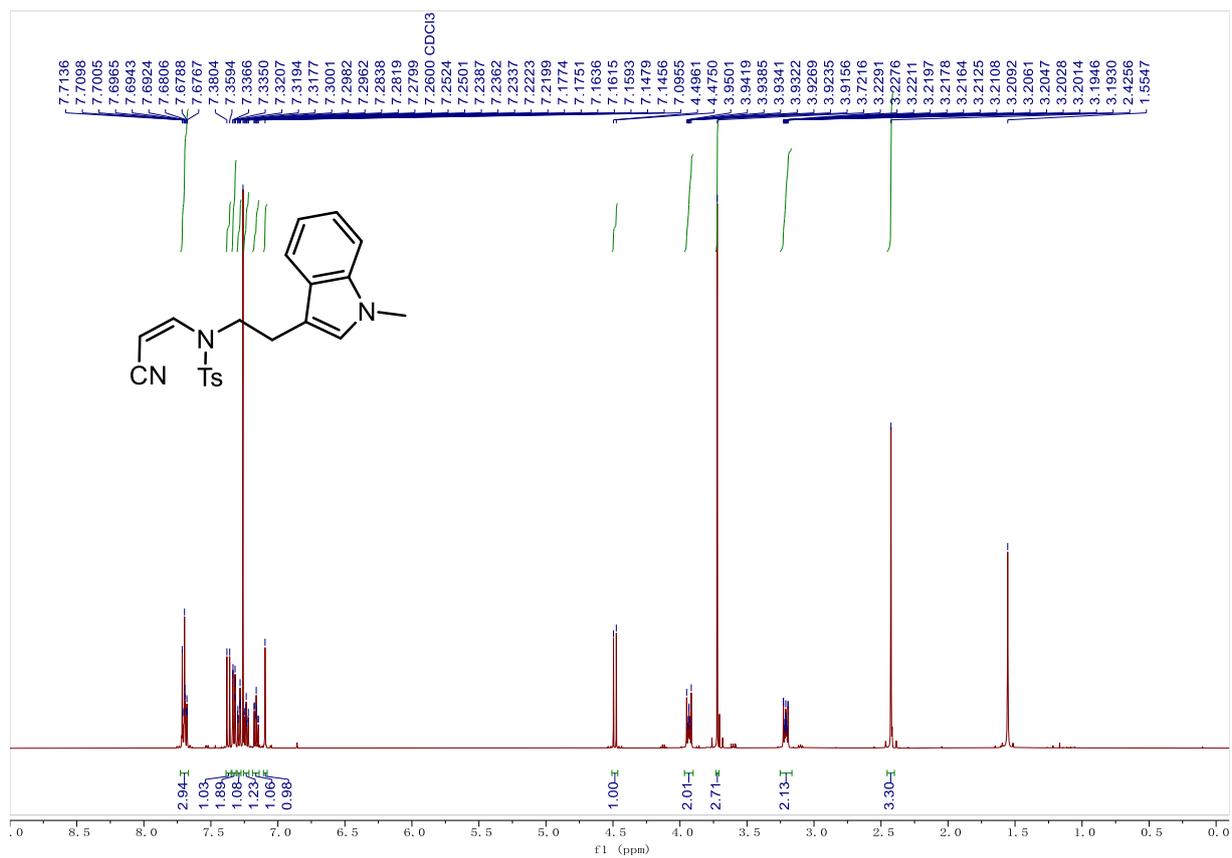




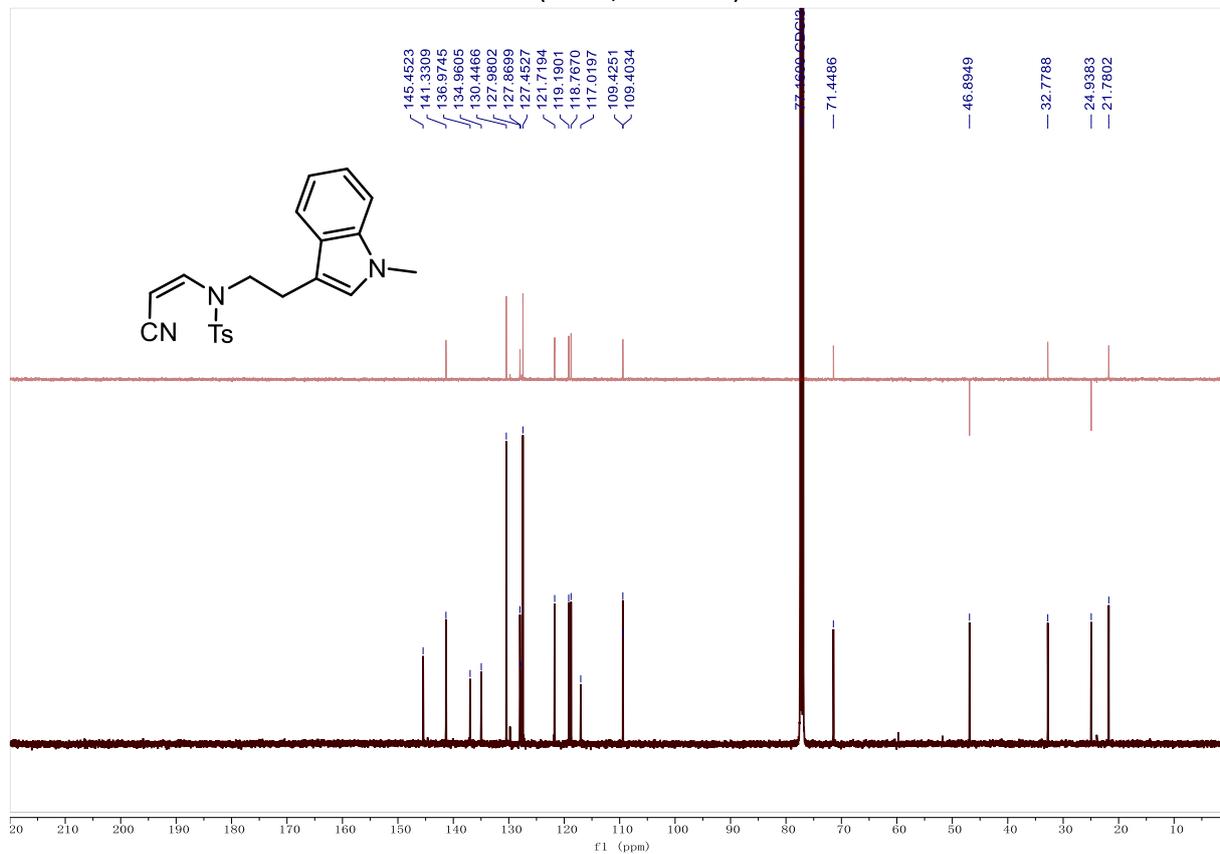
¹H NMR (CDCl₃, 500 MHz) of 3I



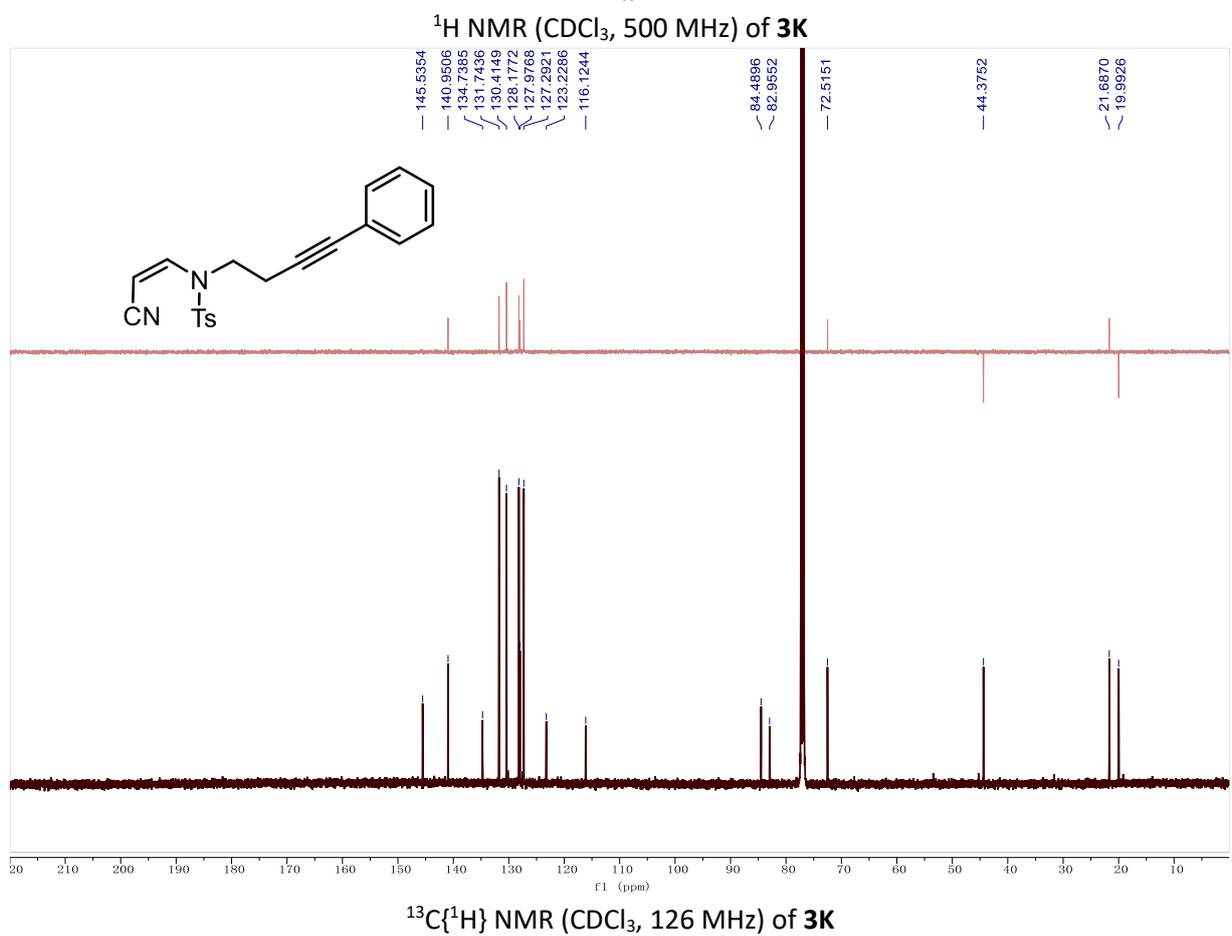
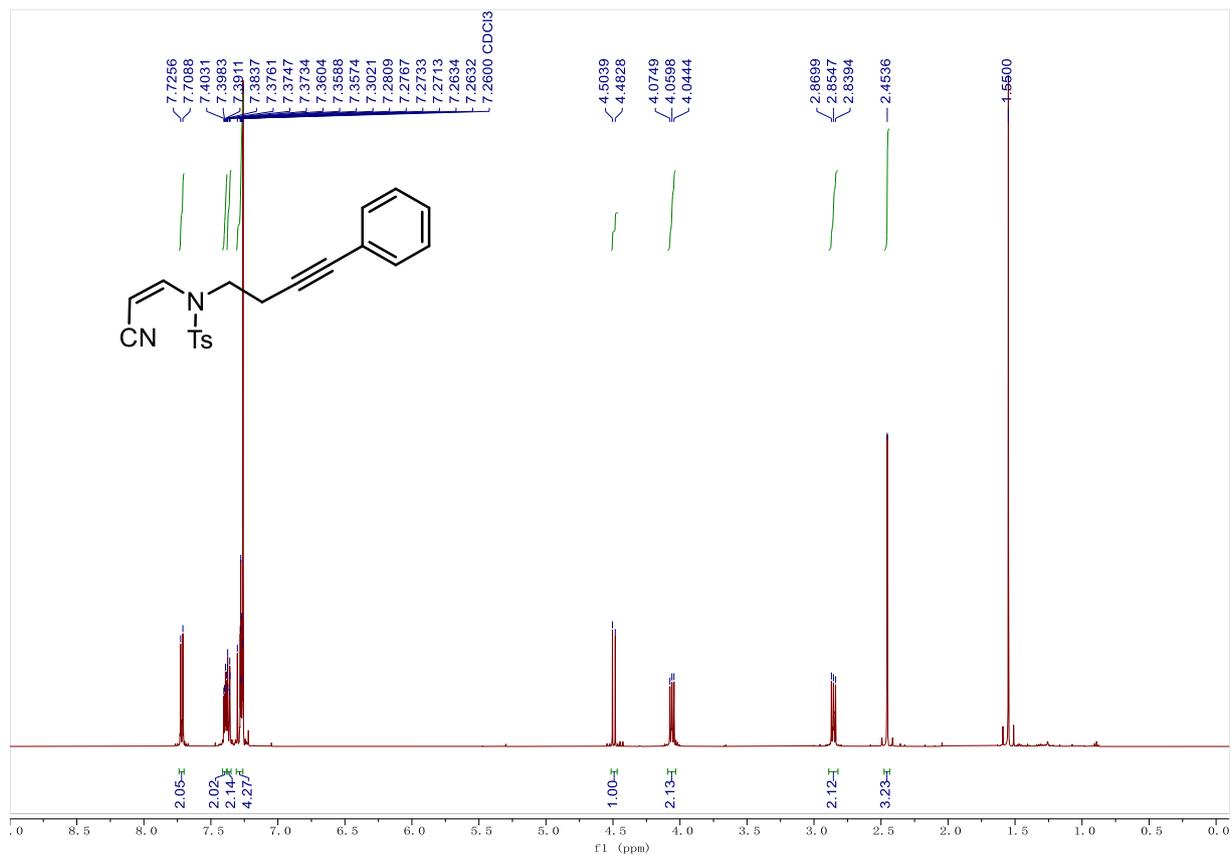
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3I

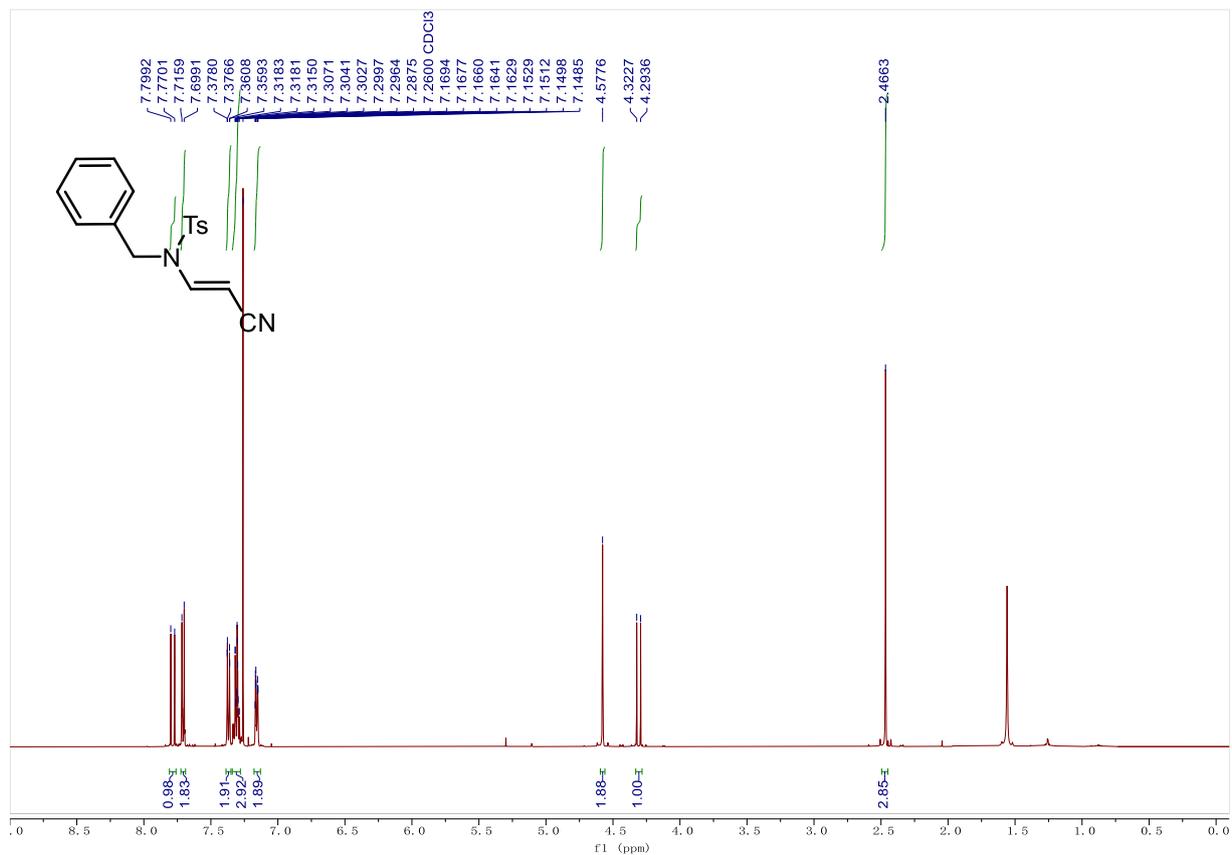


¹H NMR (CDCl₃, 500 MHz) of 3J

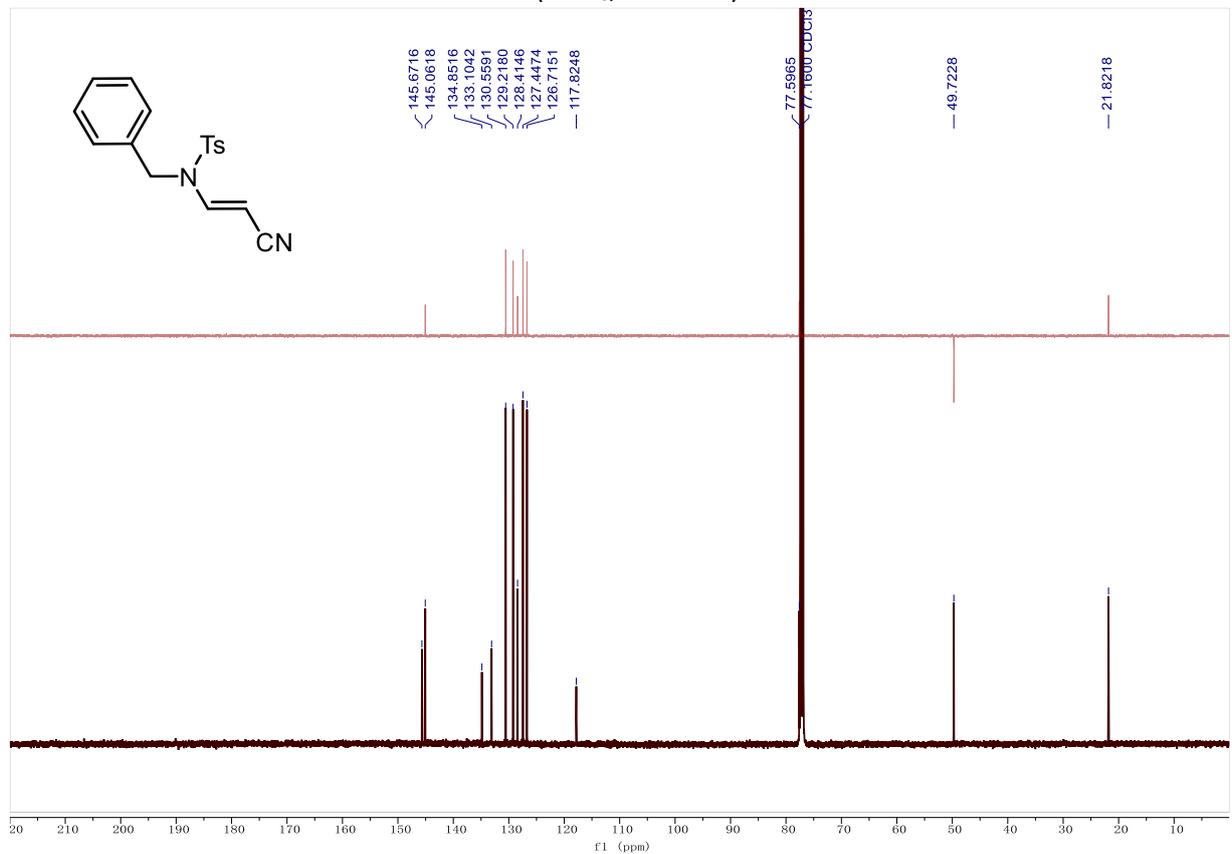


¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3J

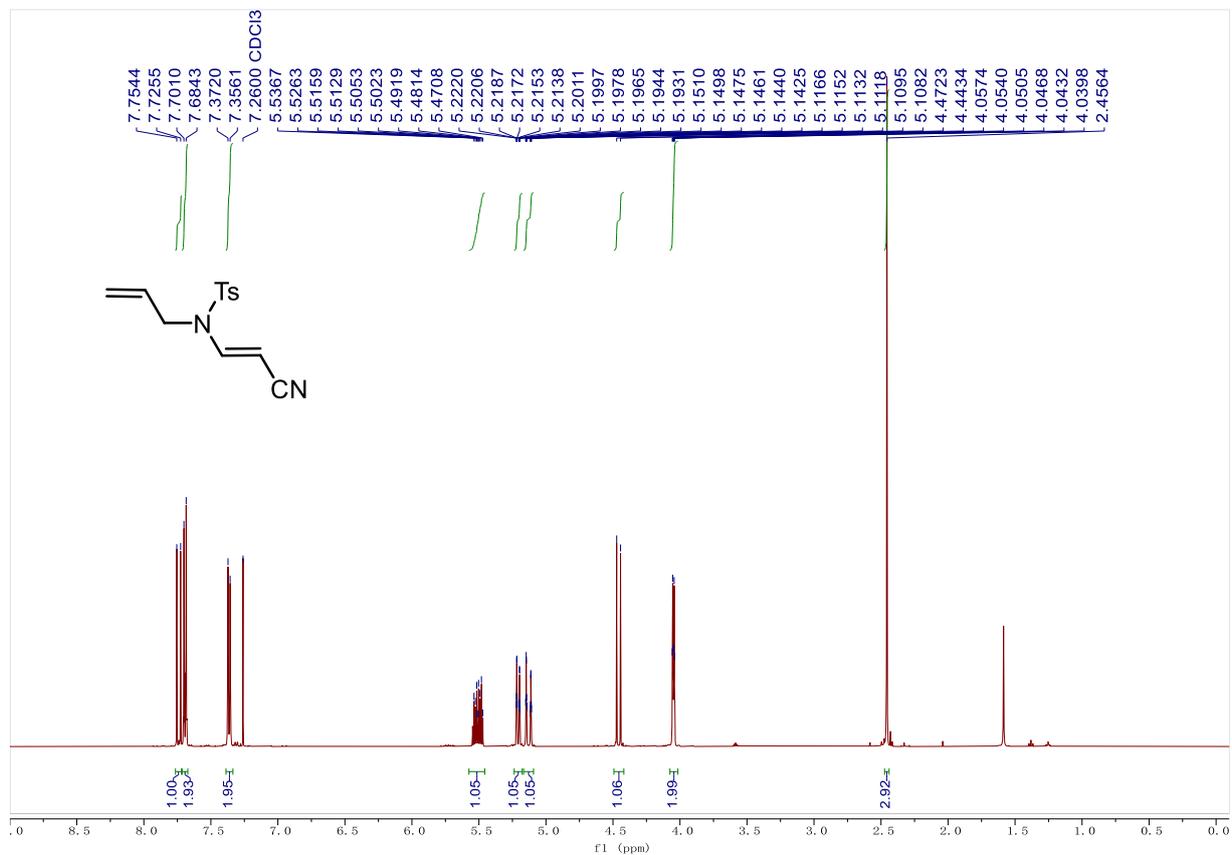




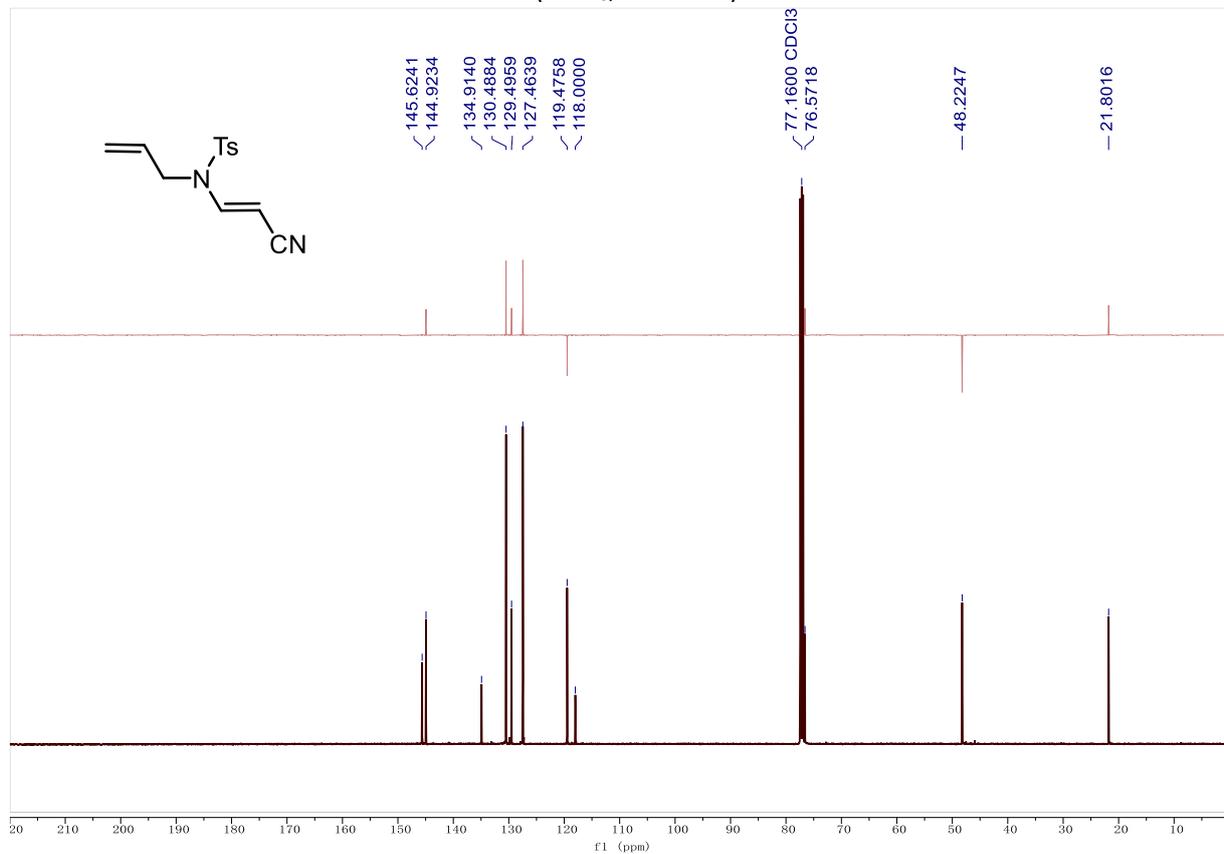
$^1\text{H NMR}$ (CDCl₃, 500 MHz) of 4a



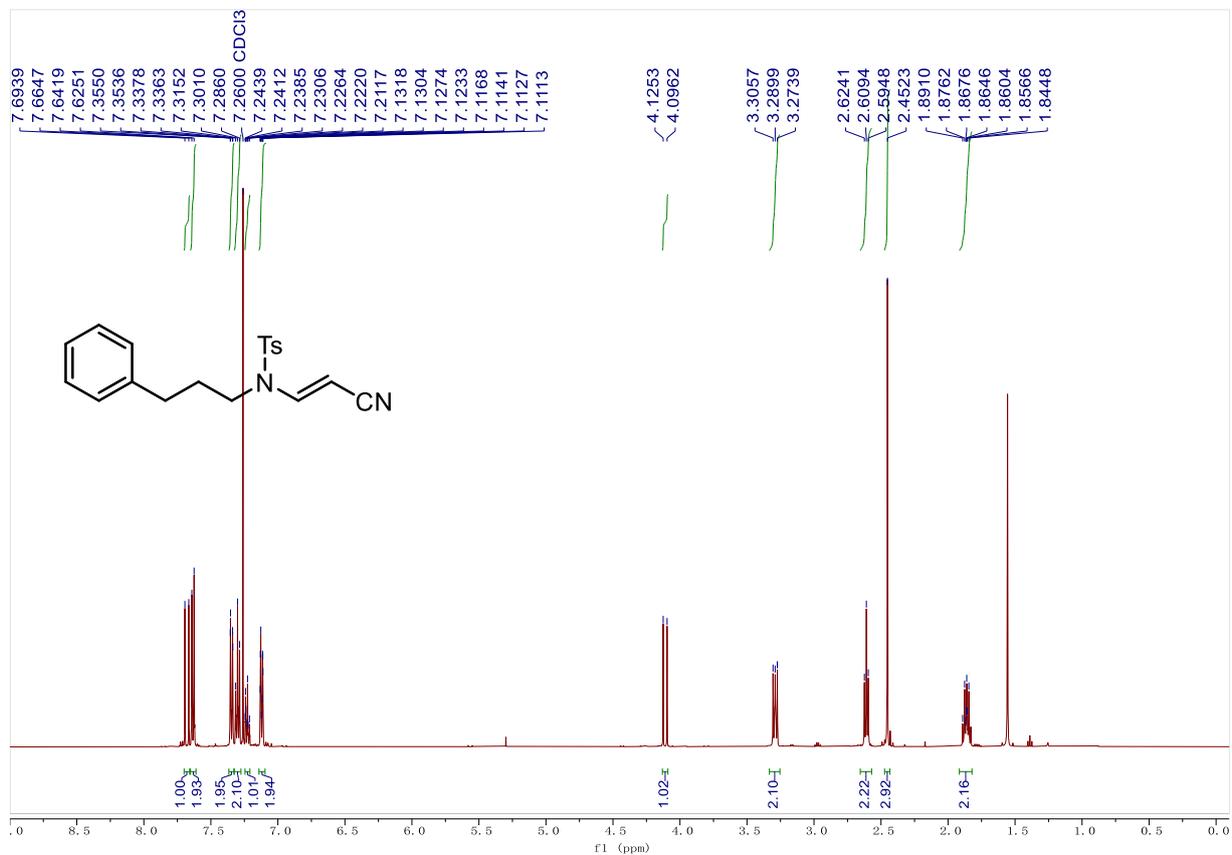
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz) of 4a



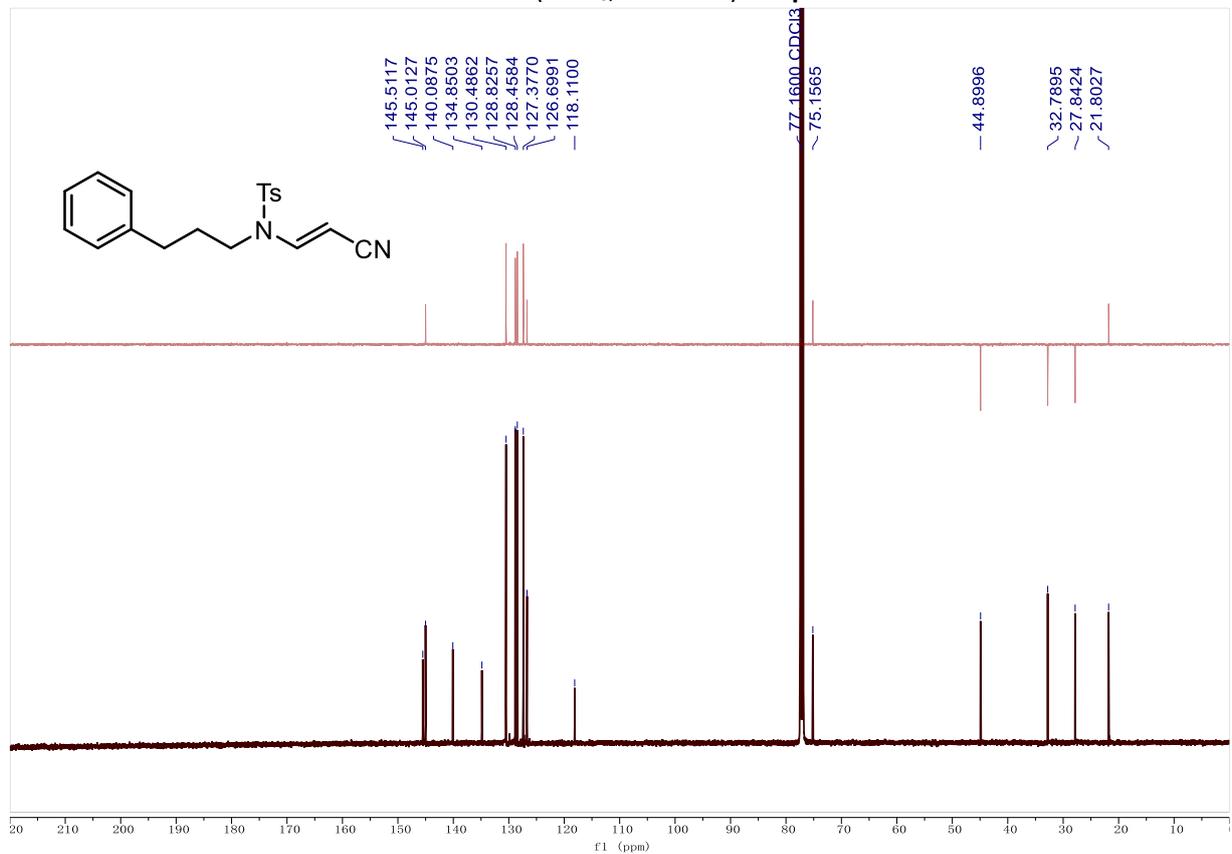
^1H NMR (CDCl₃, 500 MHz) of 4h



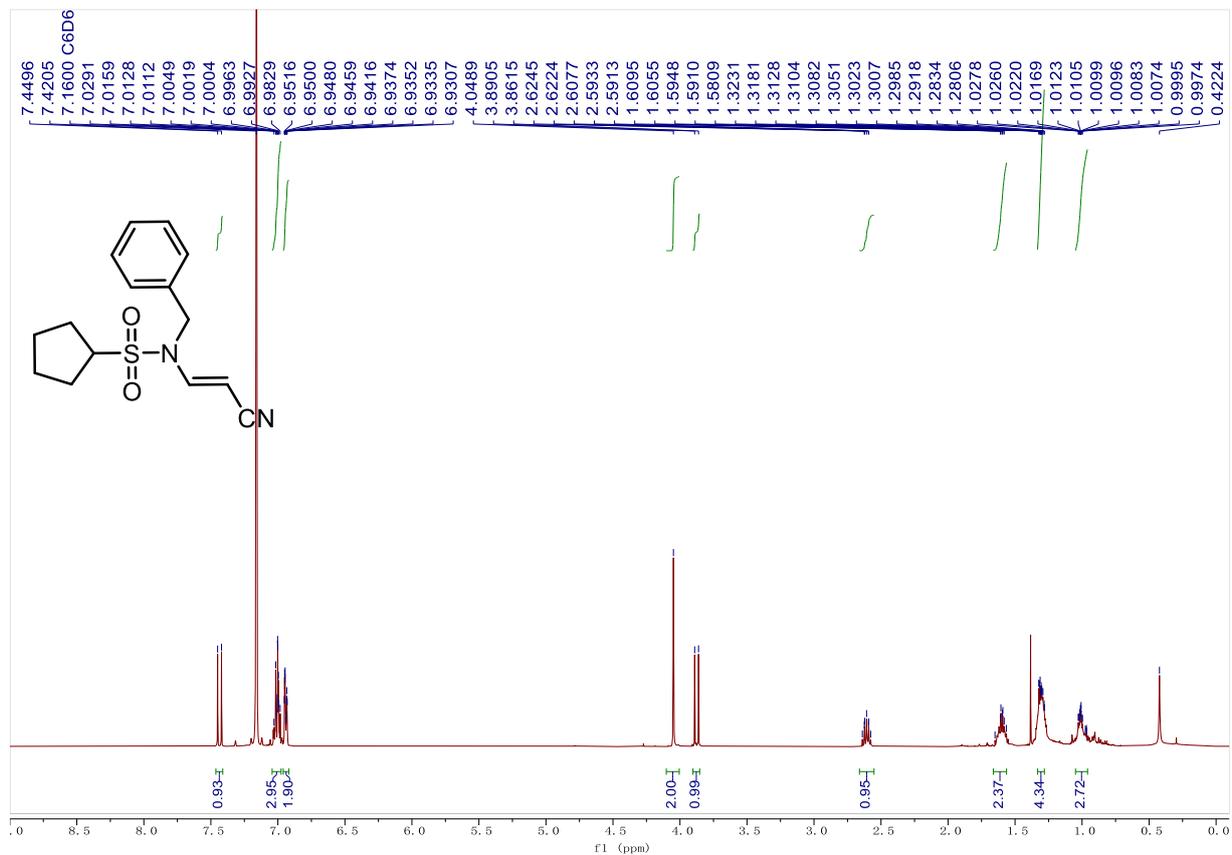
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz) of 4h



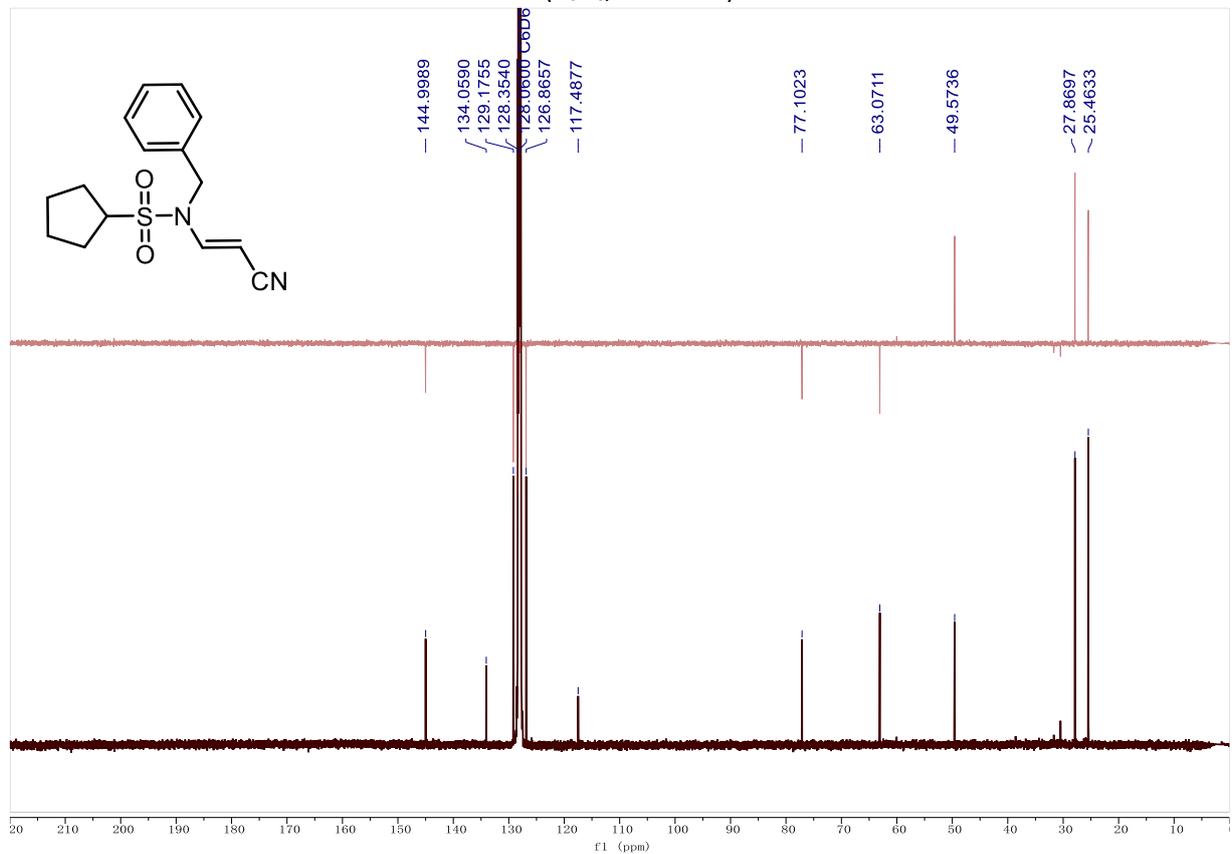
¹H NMR (CDCl₃, 500 MHz) of 4p



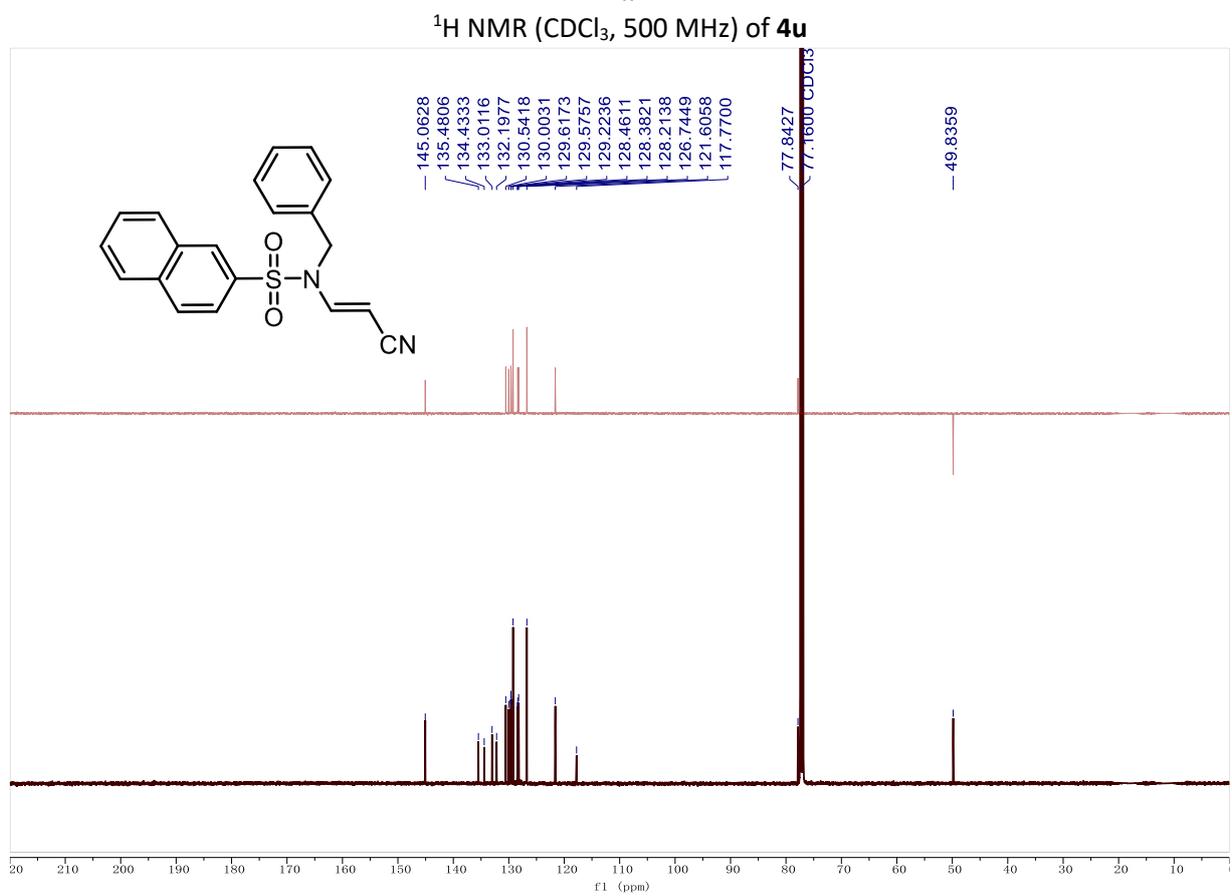
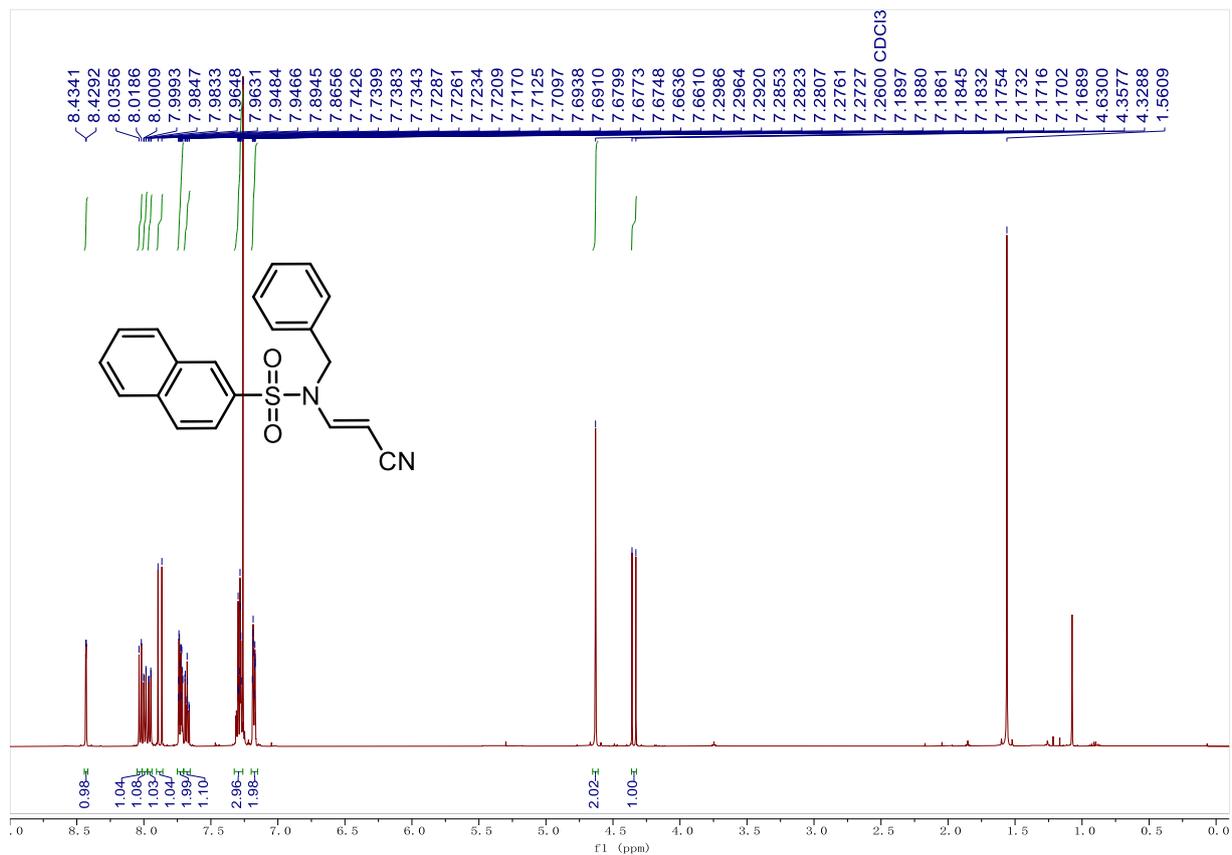
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 4p

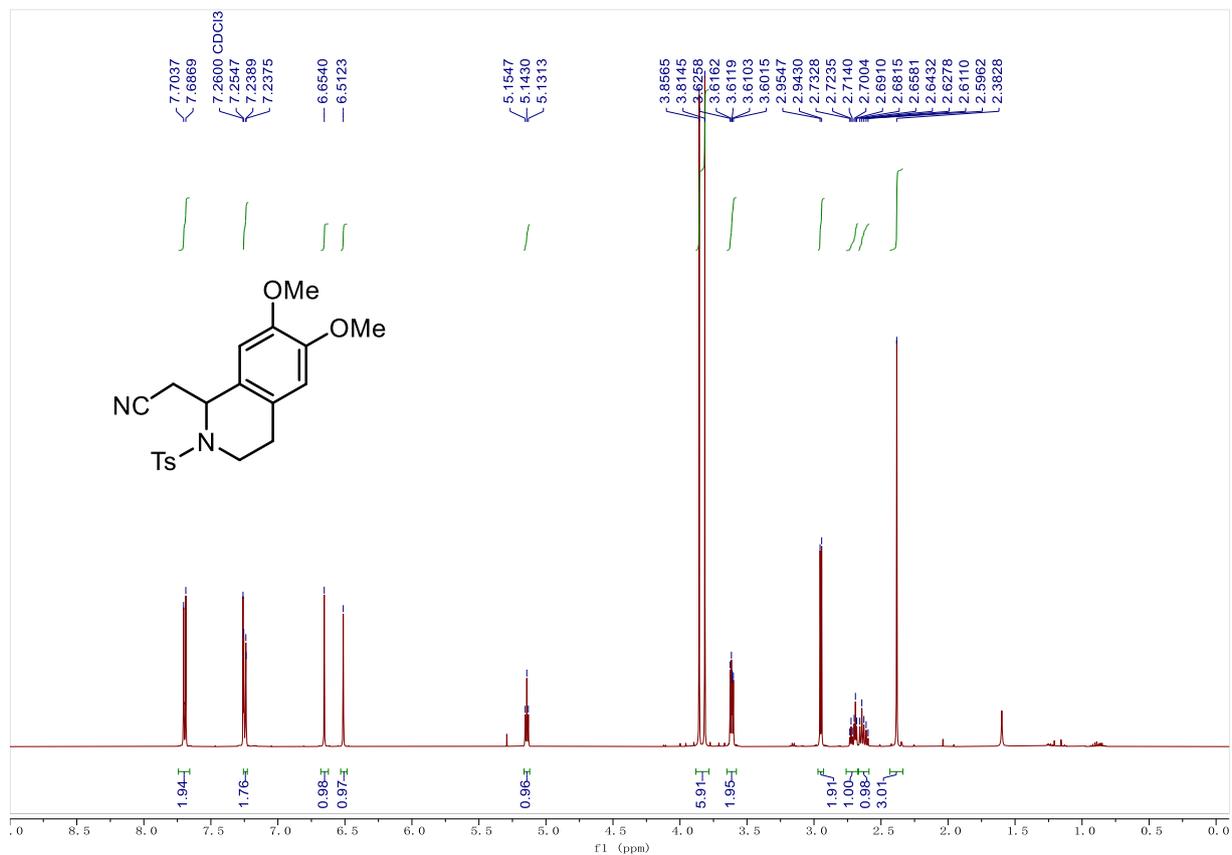


¹H NMR (C₆D₆, 500 MHz) of 4t

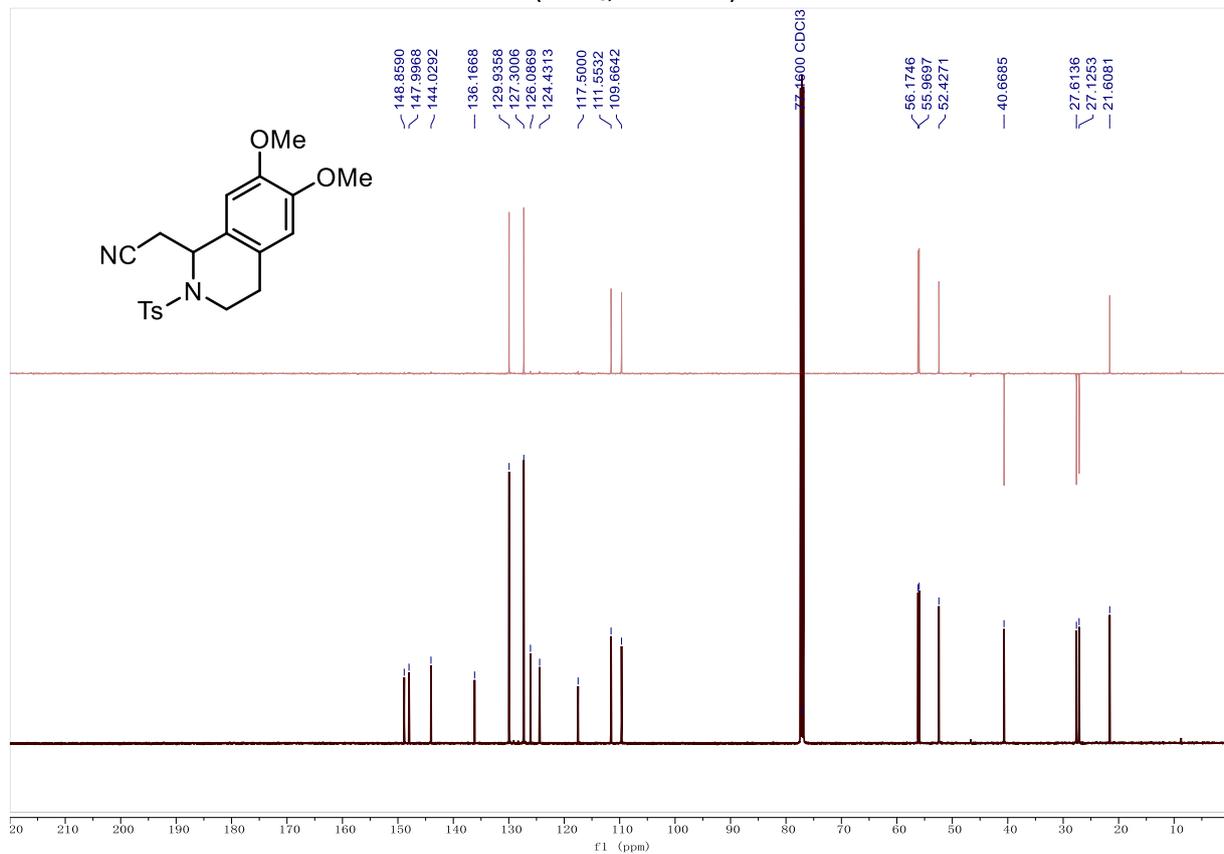


¹³C{¹H} NMR (C₆D₆, 126 MHz) of 4t

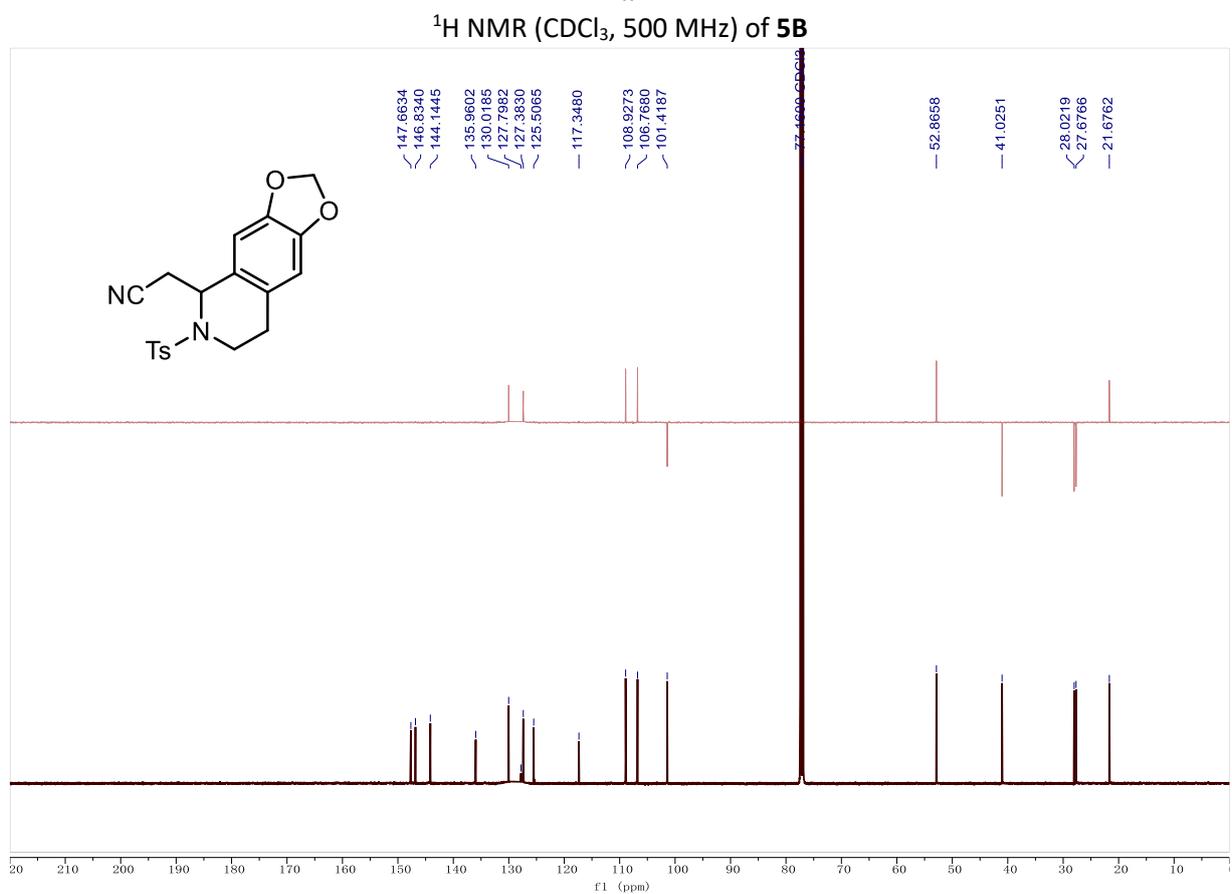
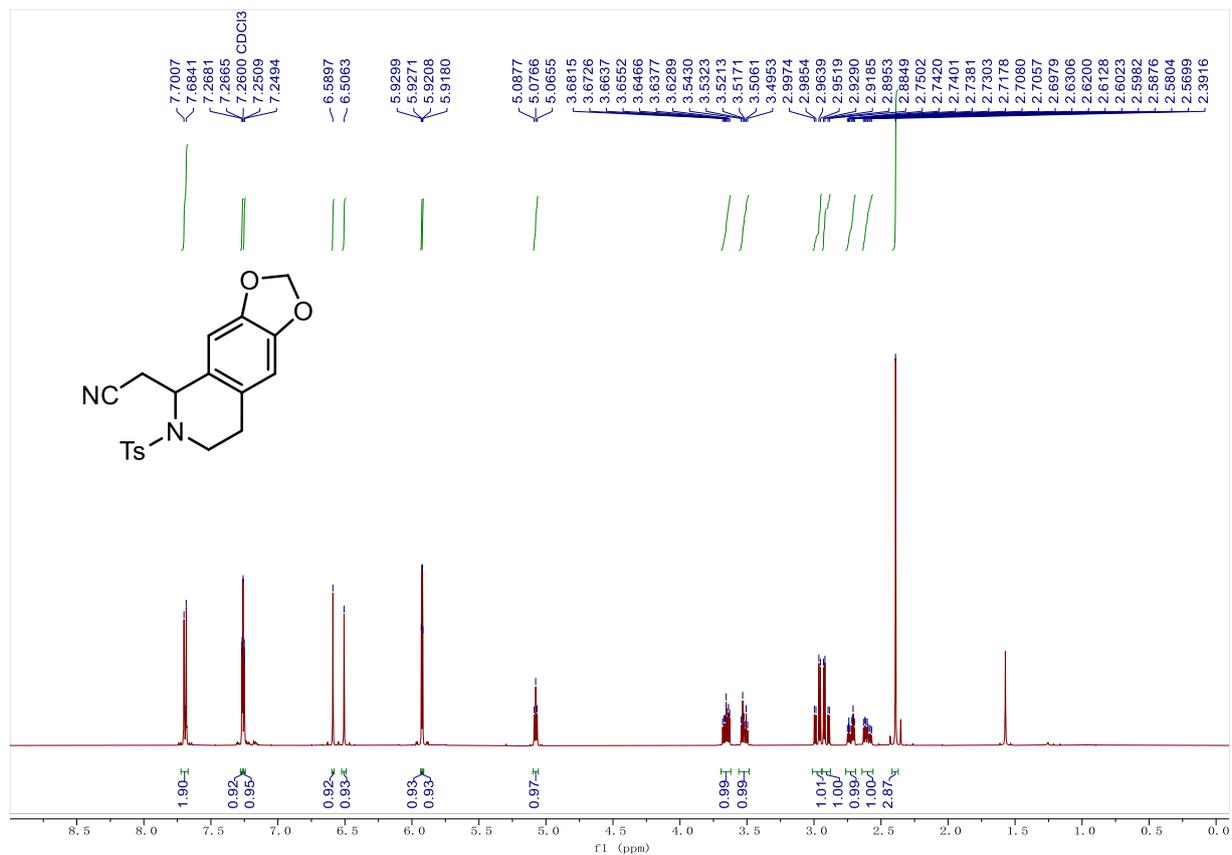


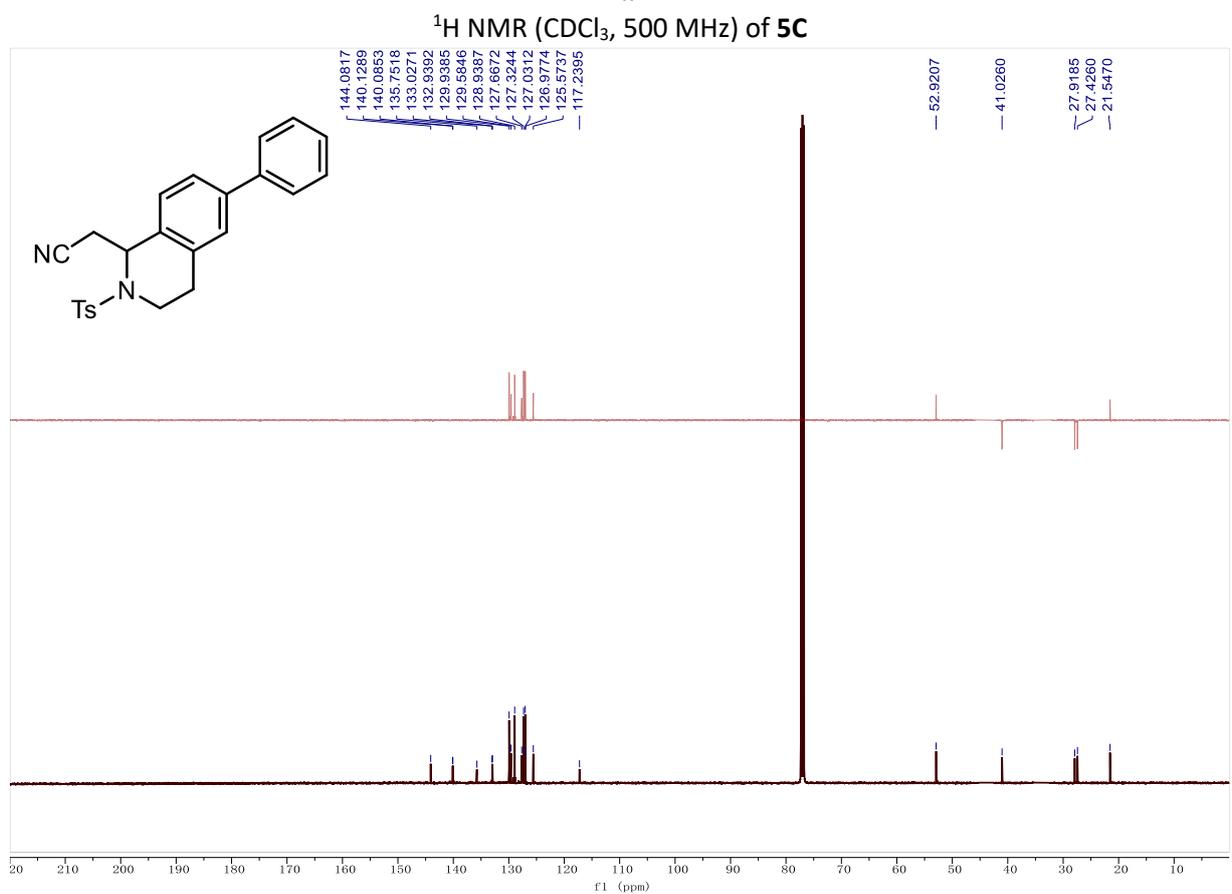
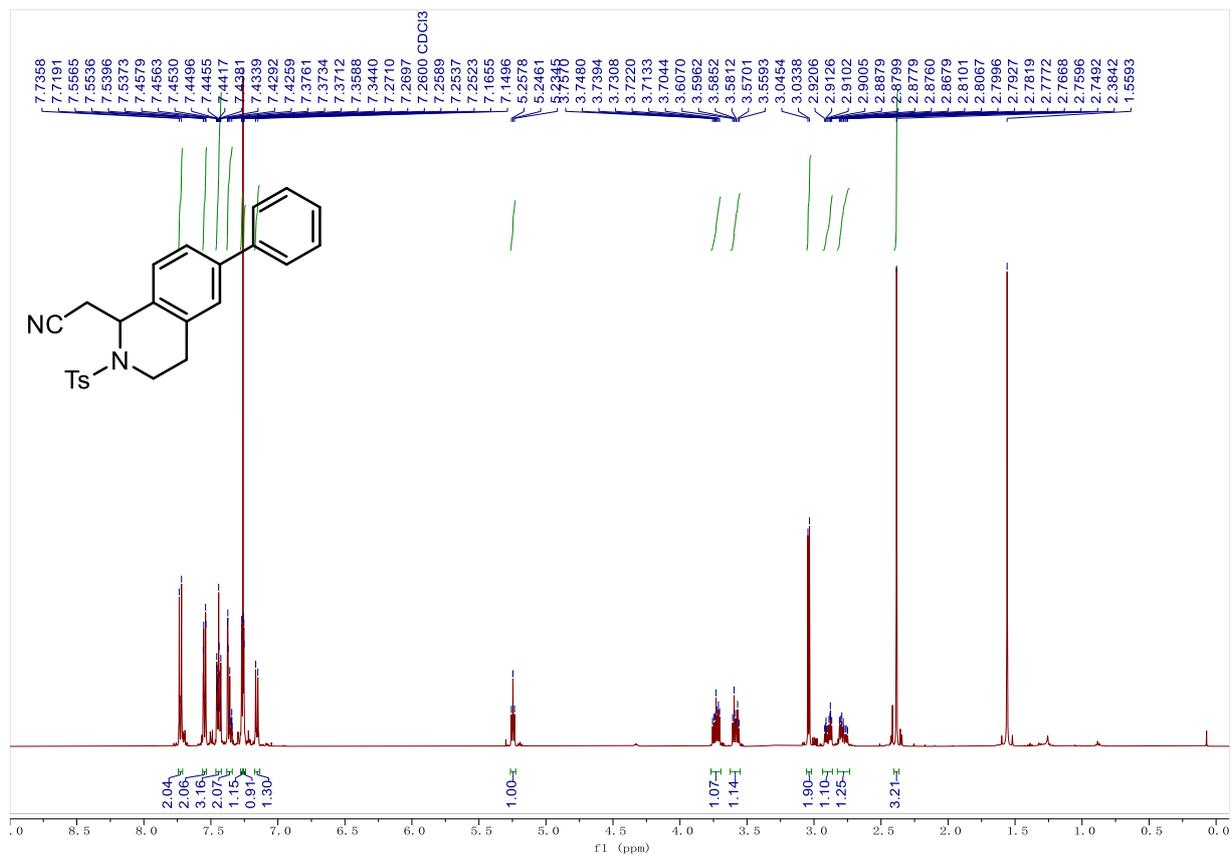


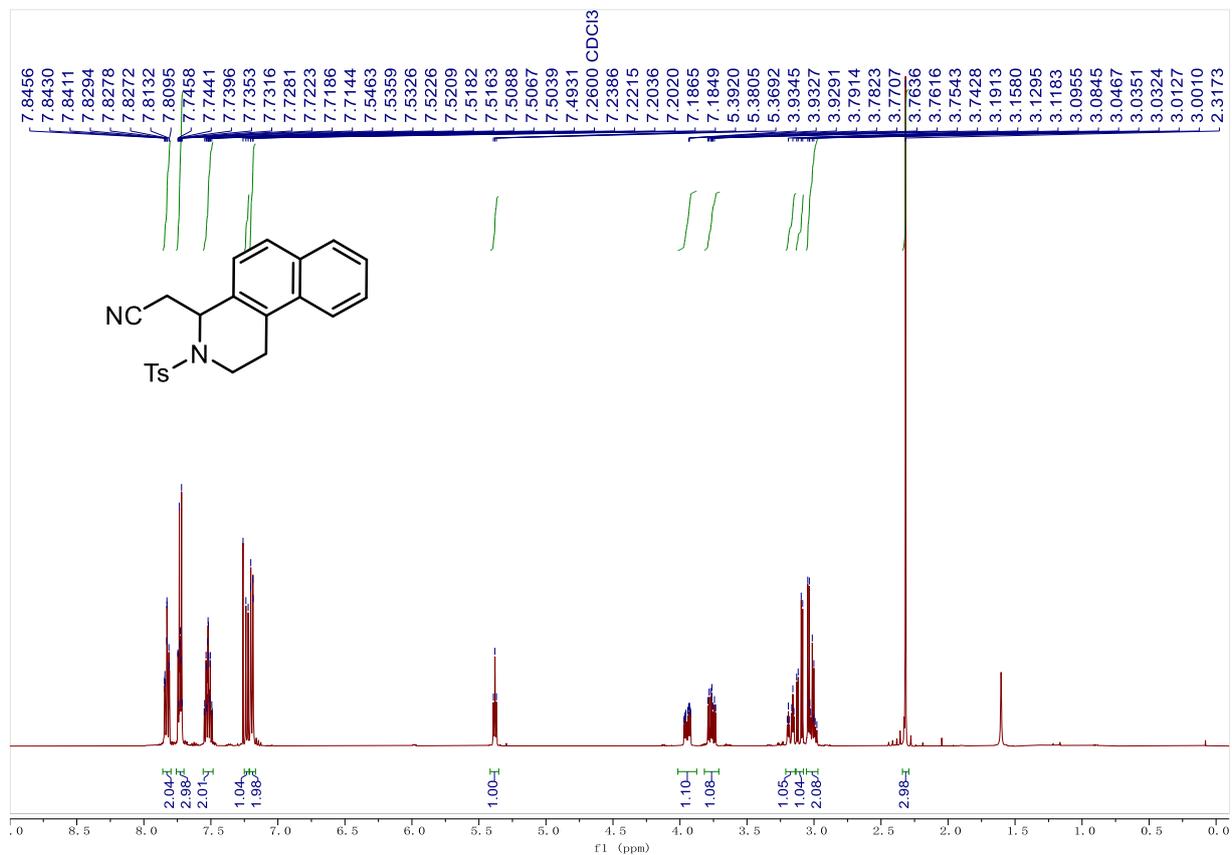
¹H NMR (CDCl₃, 500 MHz) of 5A



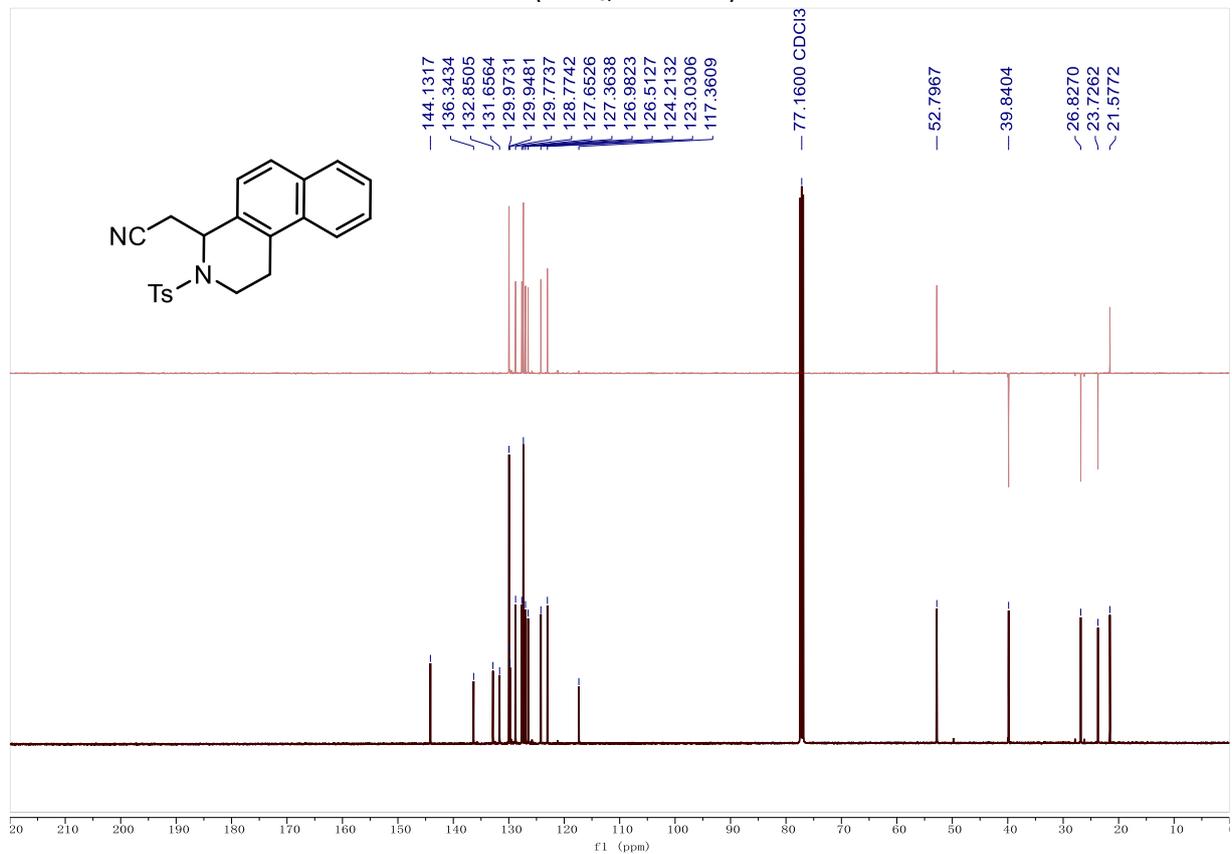
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 5A



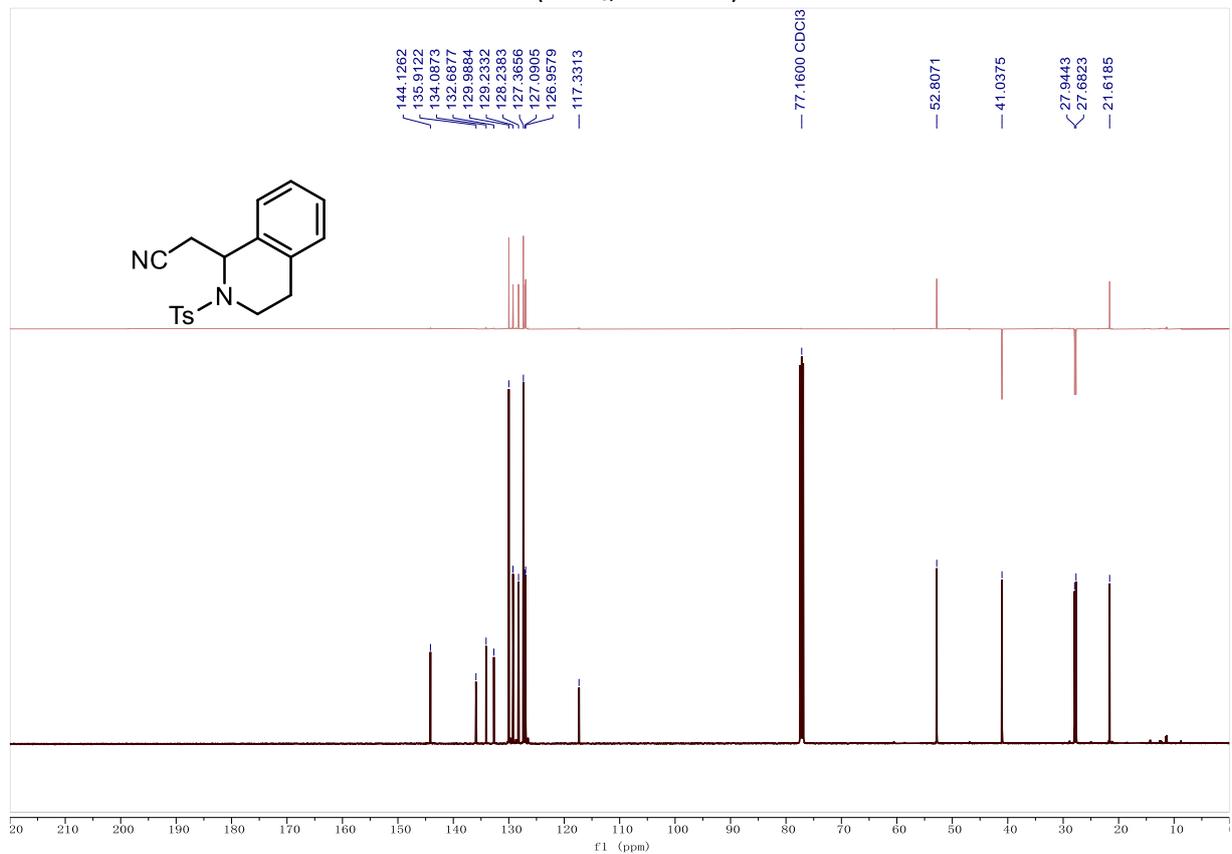
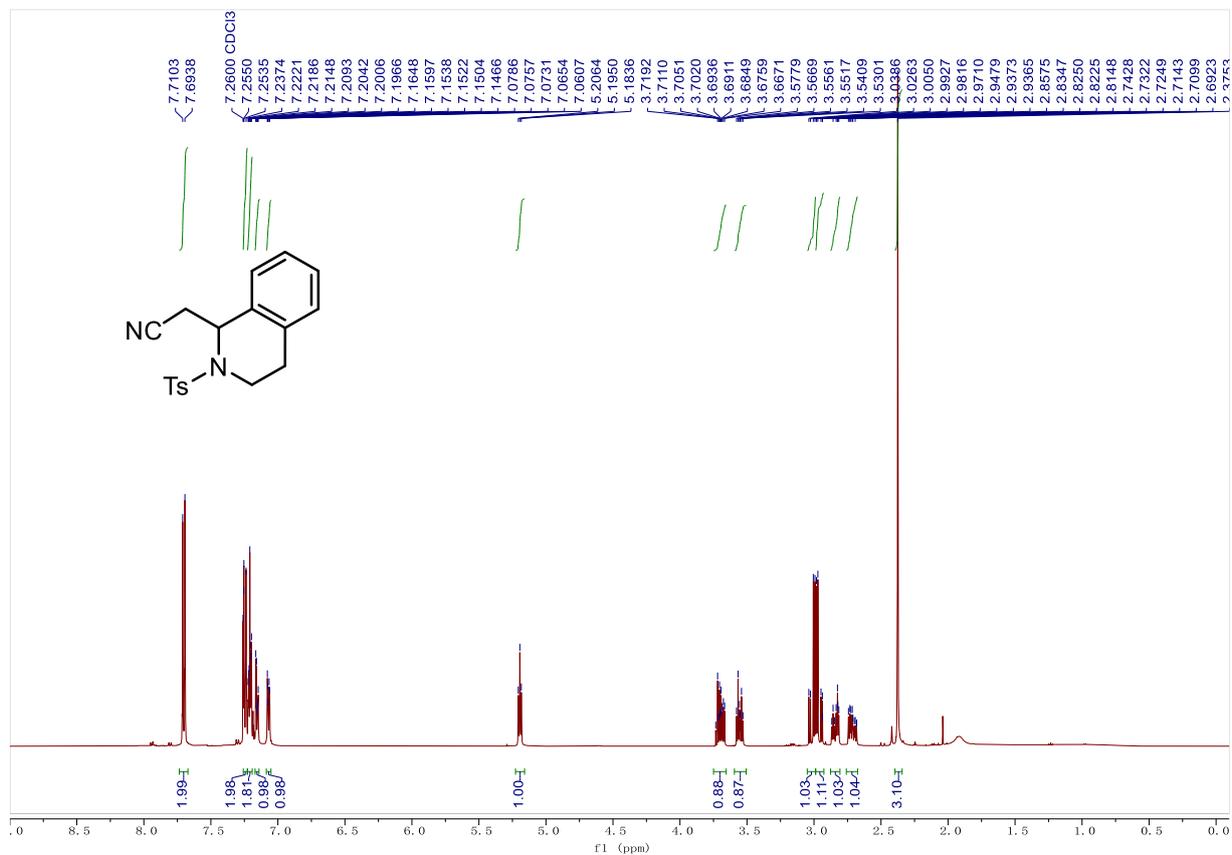


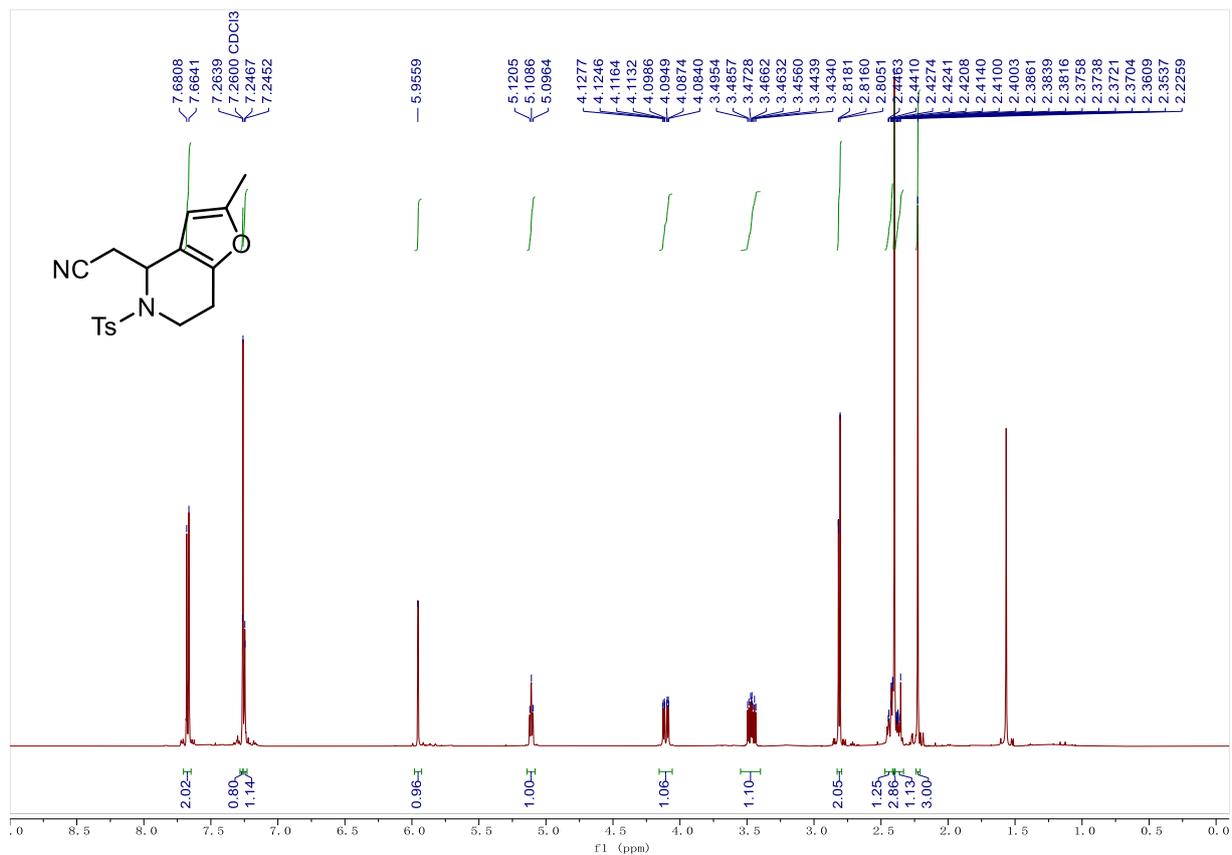


¹H NMR (CDCl₃, 500 MHz) of 5D

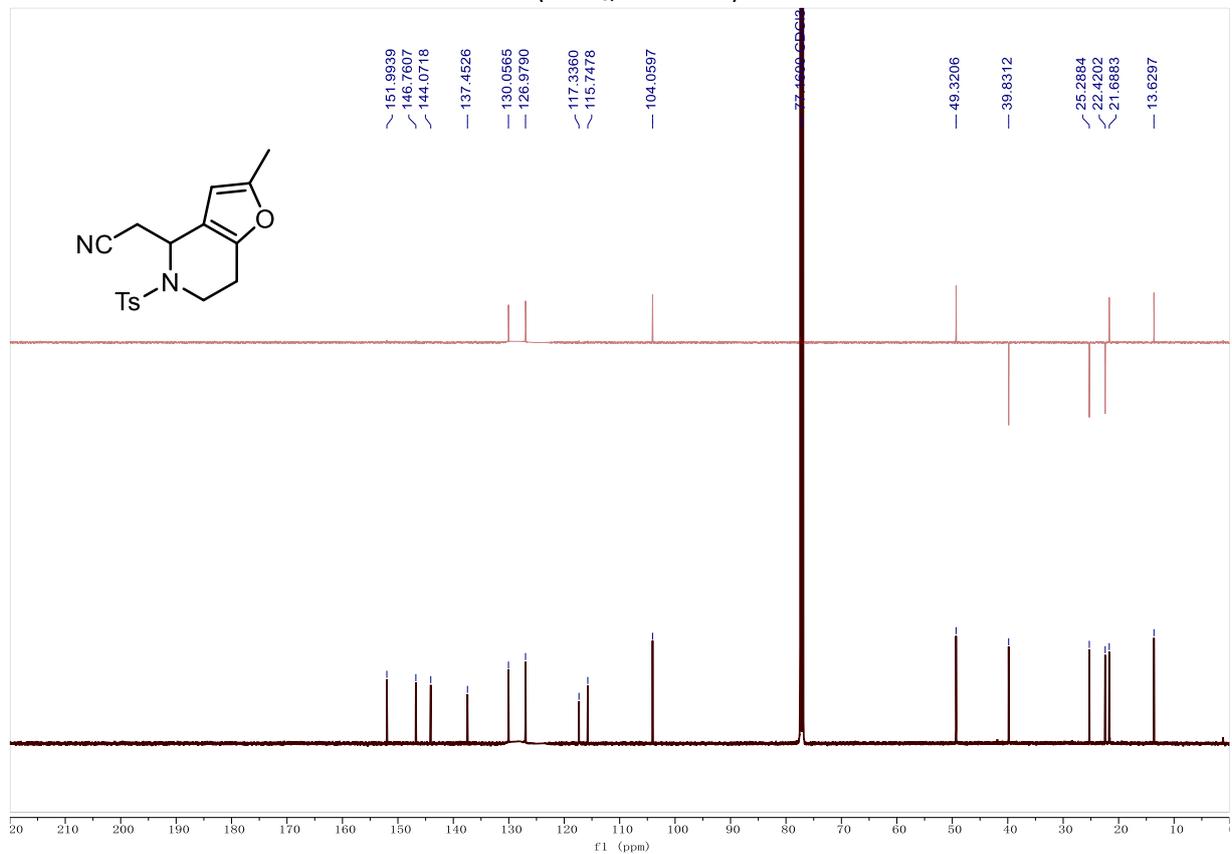


¹³C NMR (CDCl₃, 126 MHz) of 5D

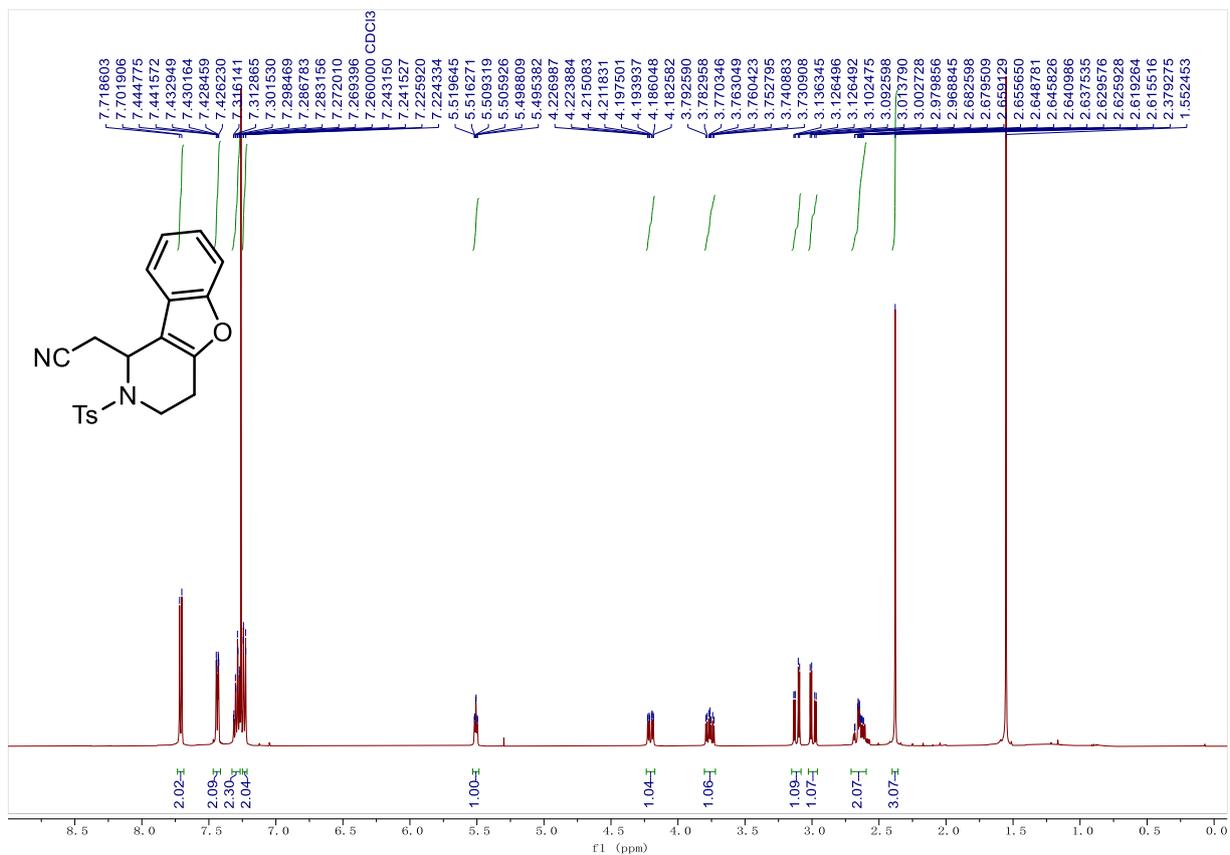




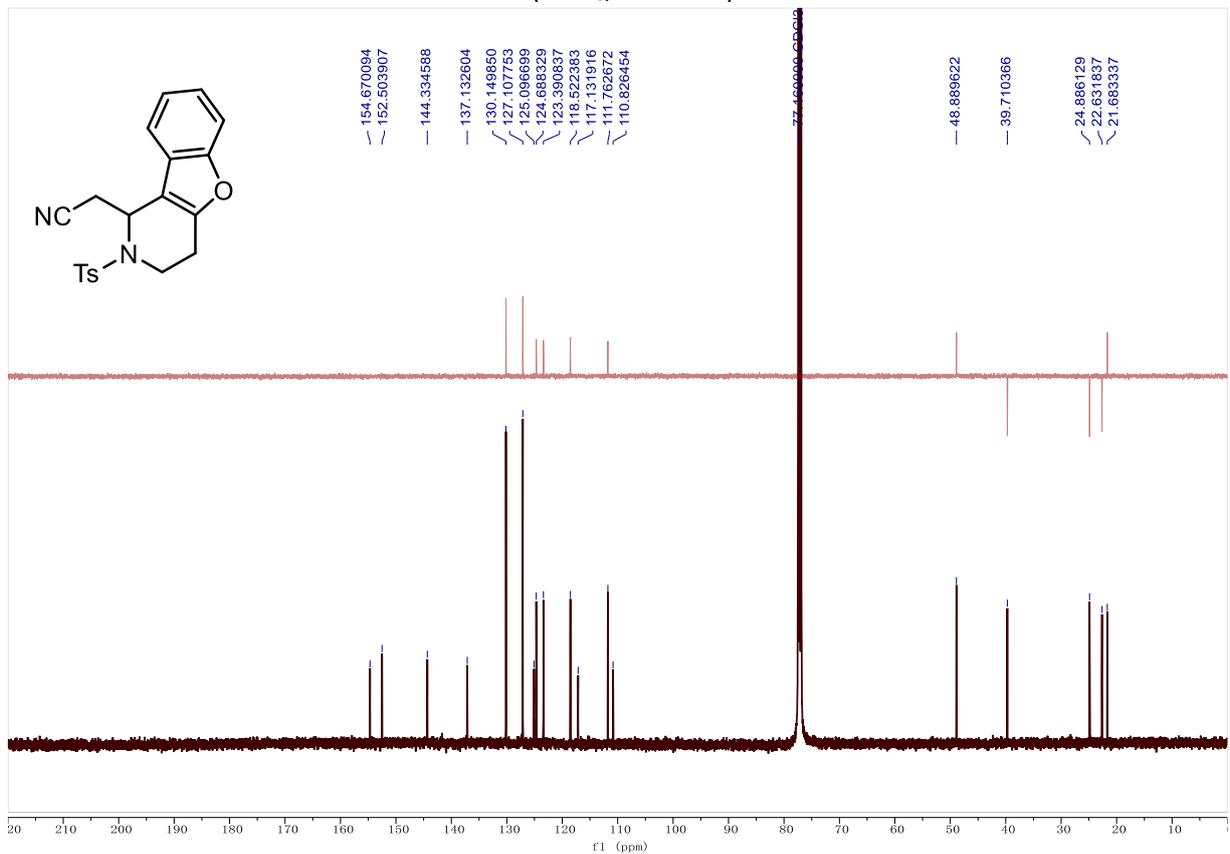
¹H NMR (CDCl₃, 500 MHz) of 5F



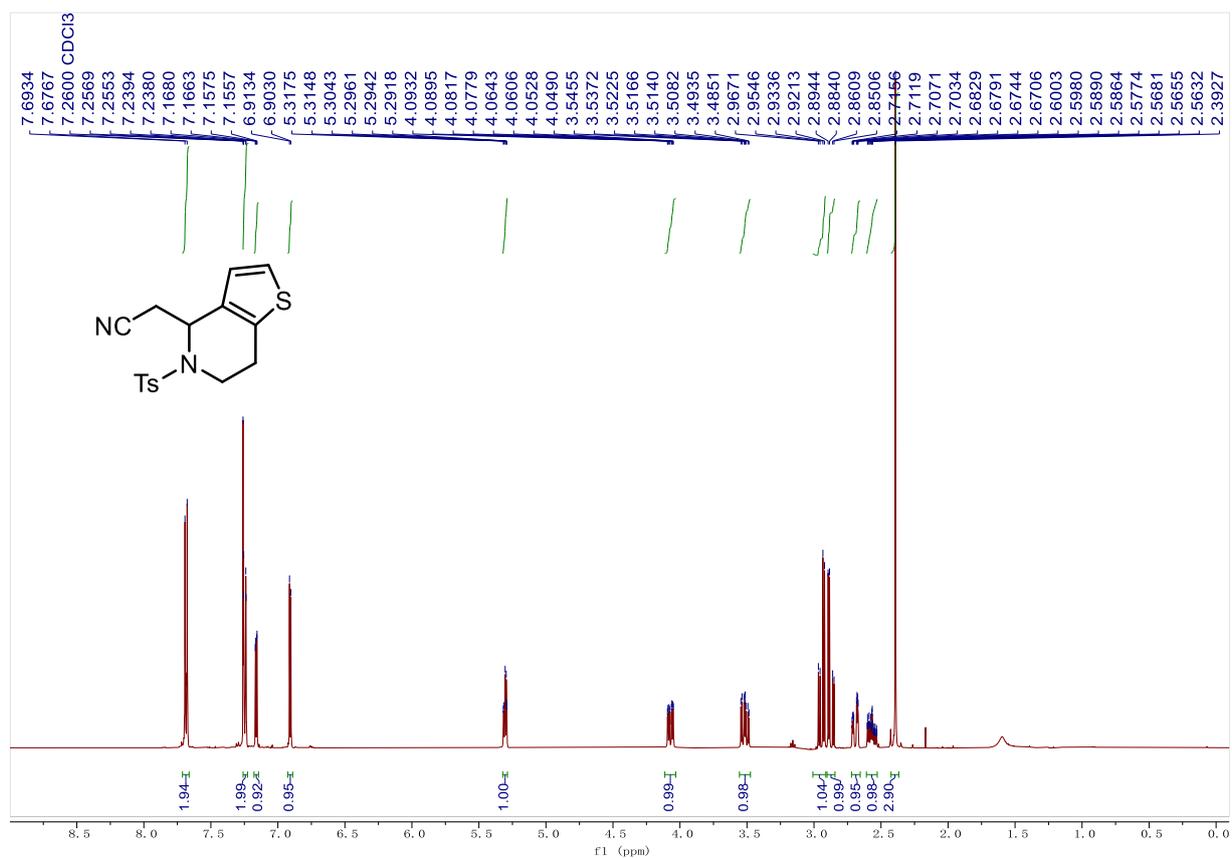
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 5F



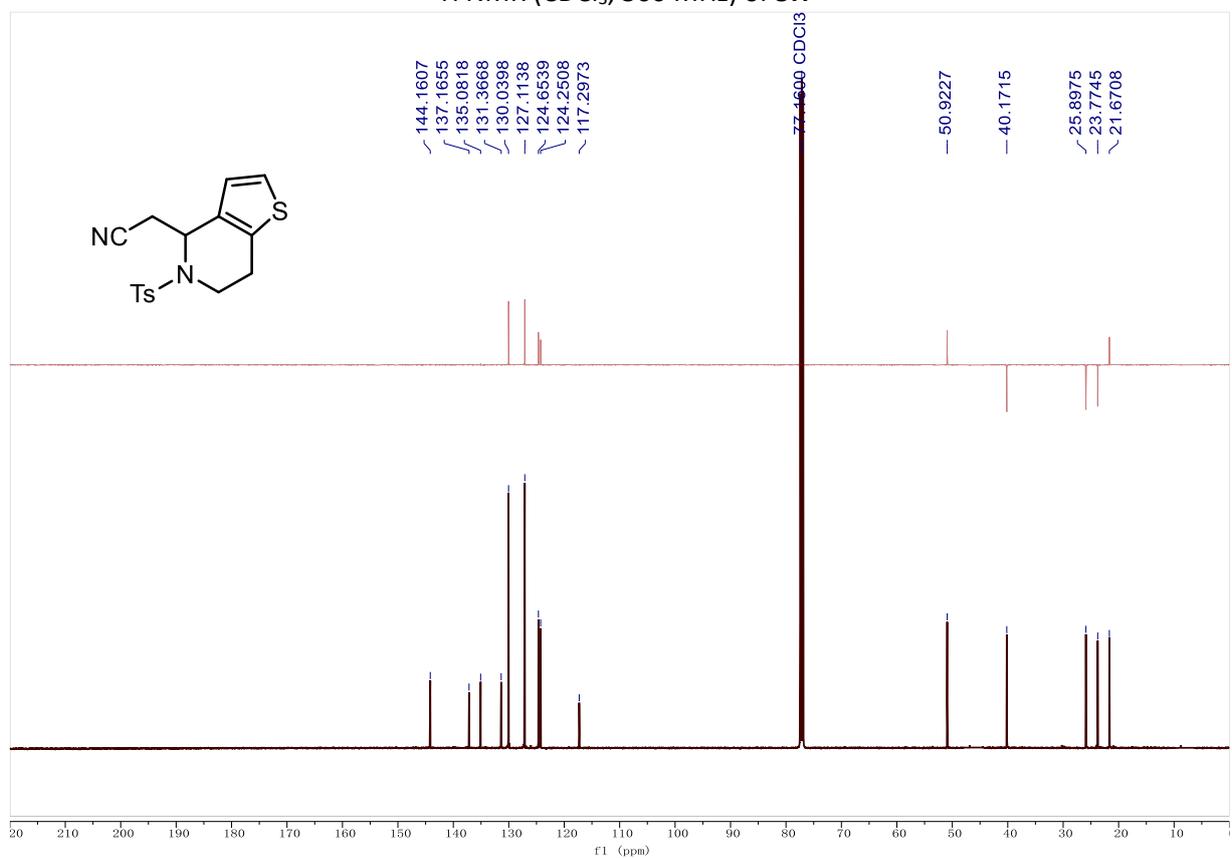
¹H NMR (CDCl₃, 500 MHz) of 5G



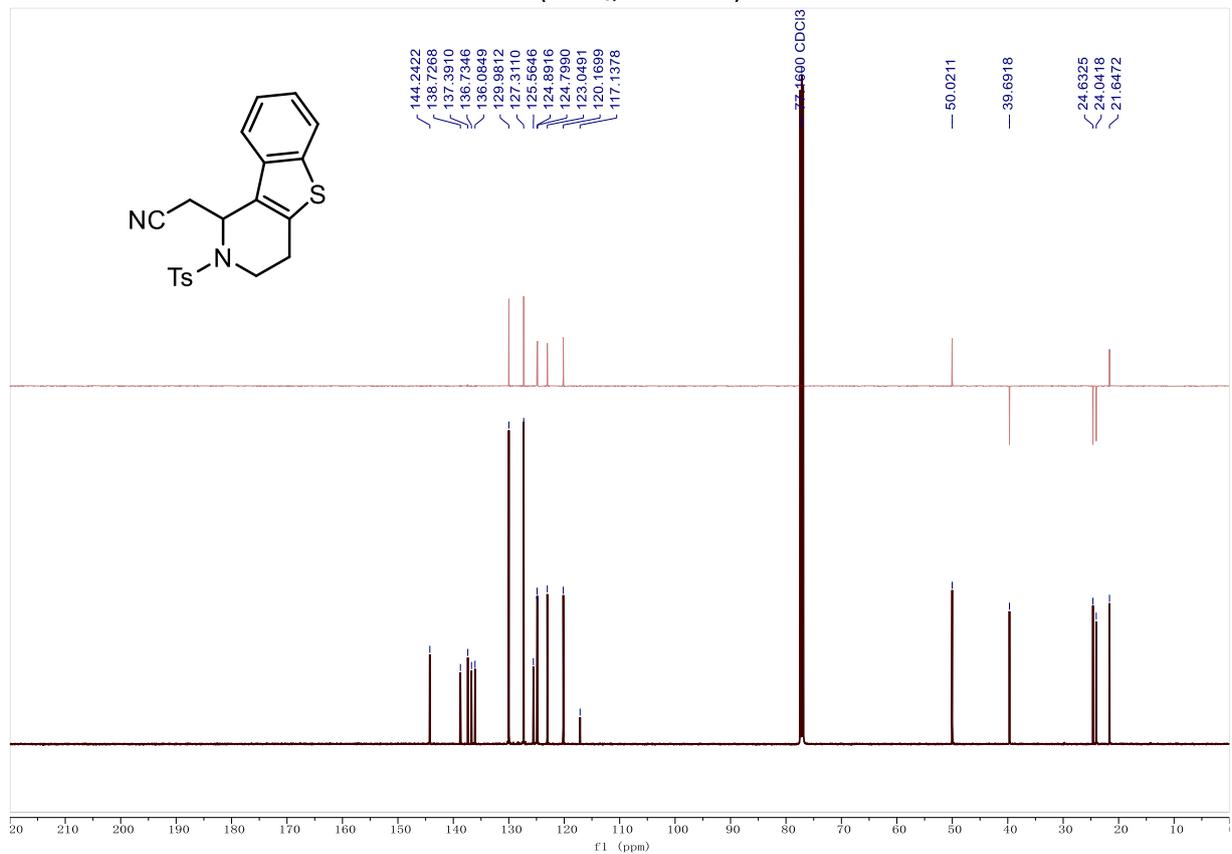
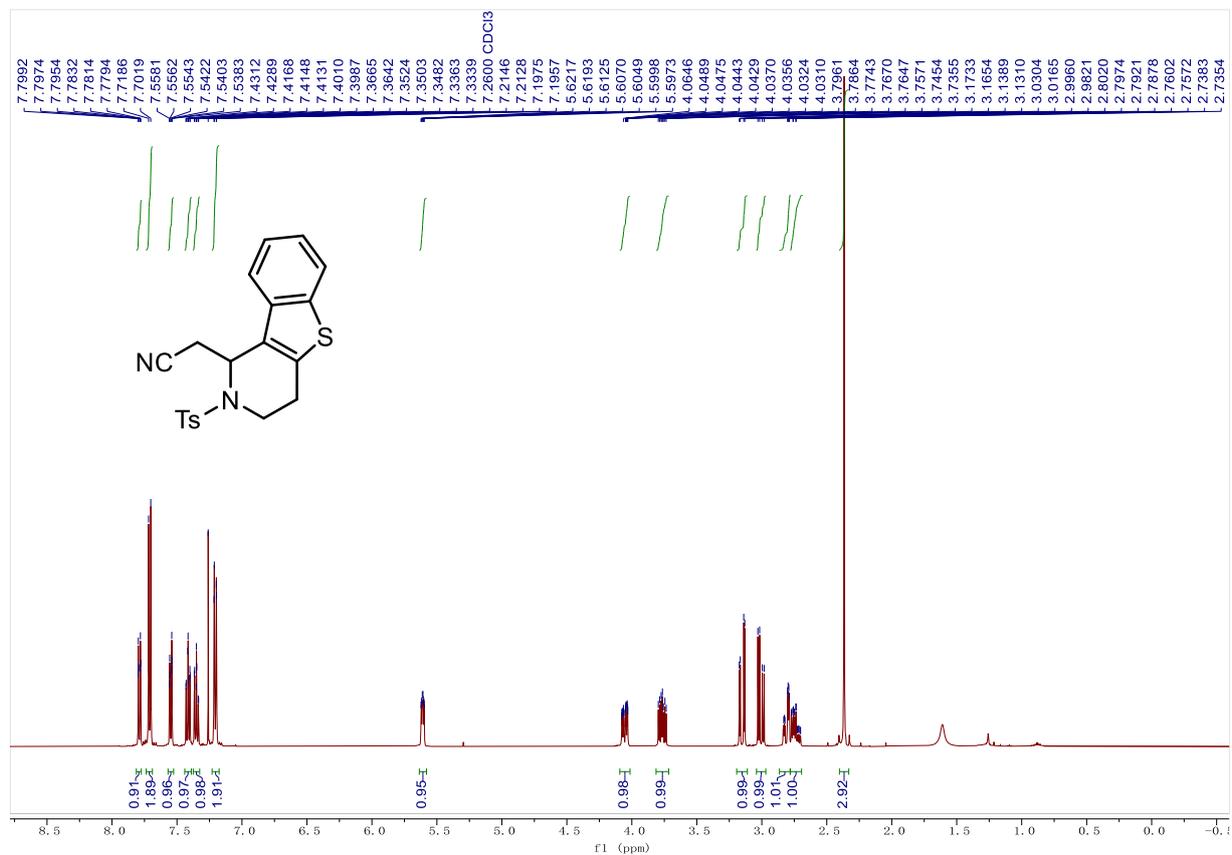
¹³C NMR (CDCl₃, 126 MHz) of 5G

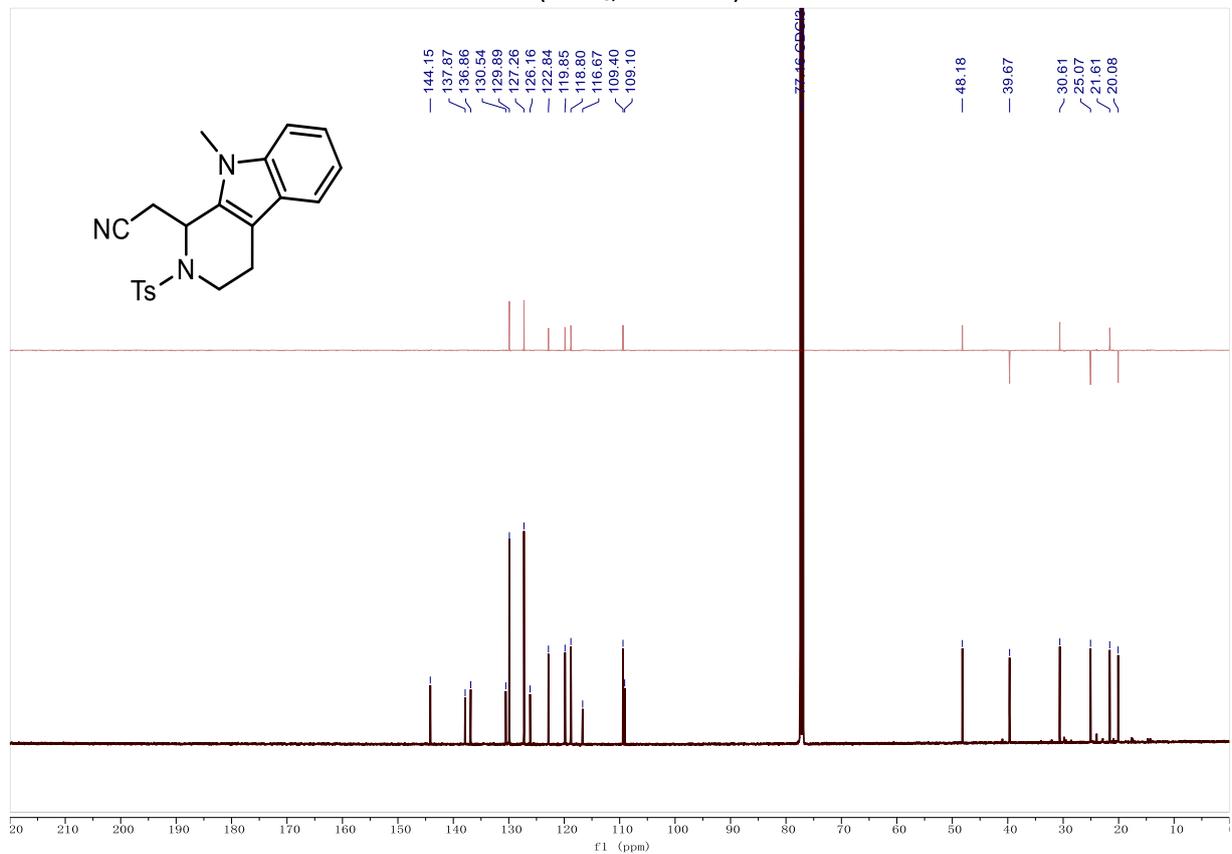
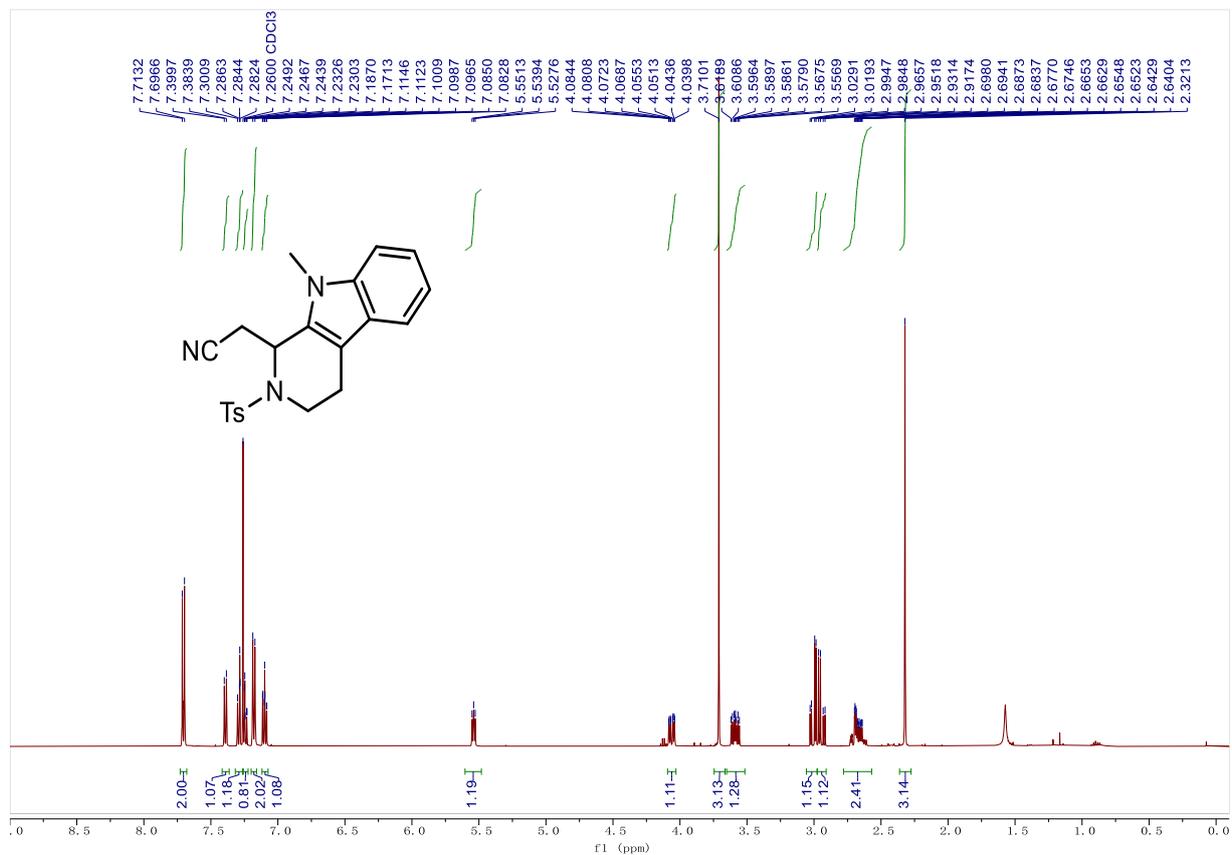


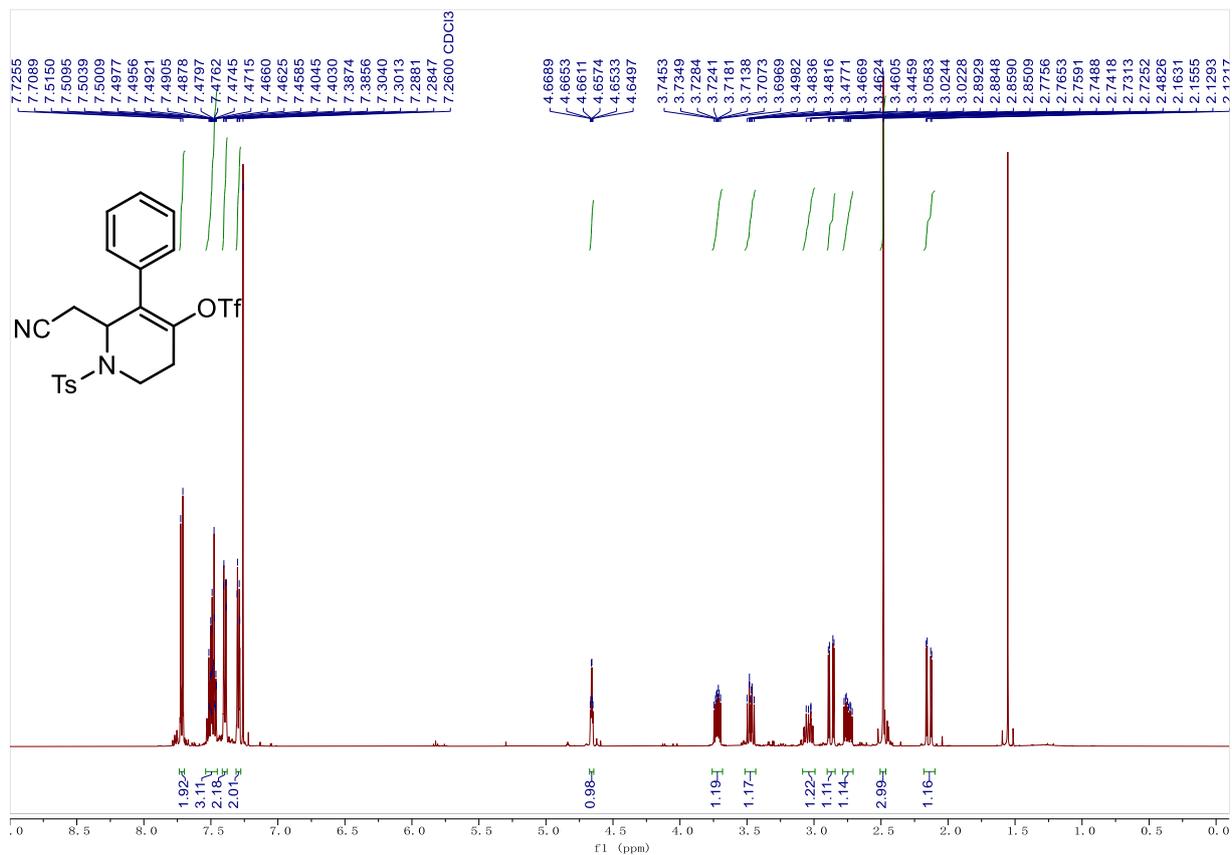
¹H NMR (CDCl₃, 500 MHz) of 5H



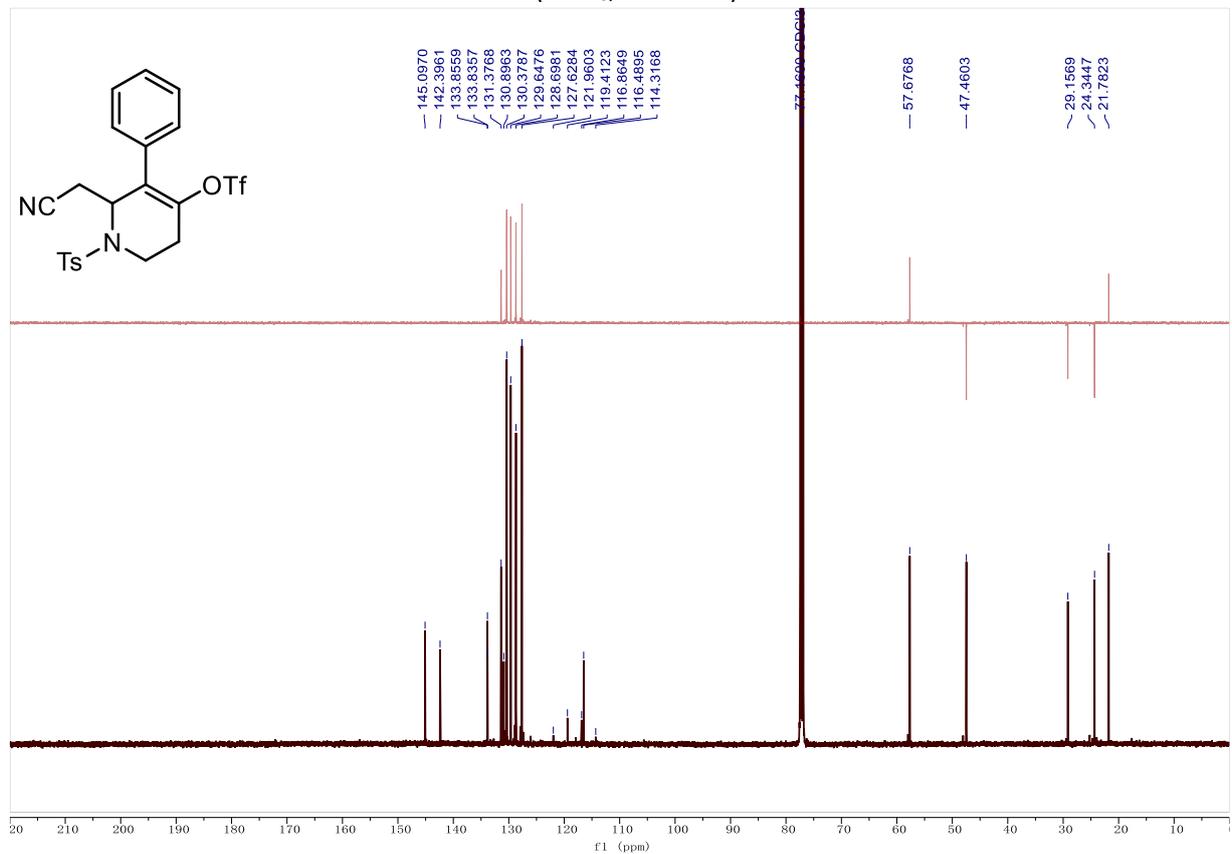
¹³C NMR (CDCl₃, 126 MHz) of 5H



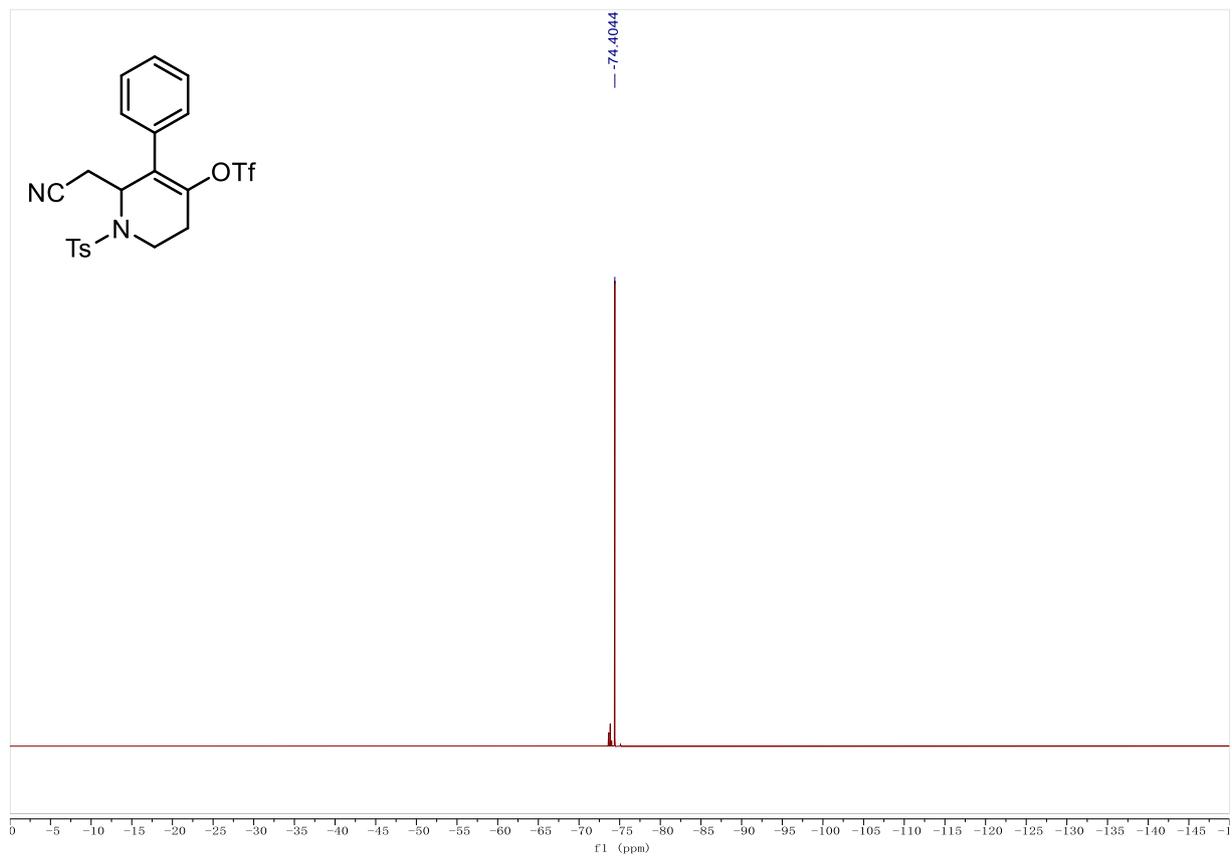




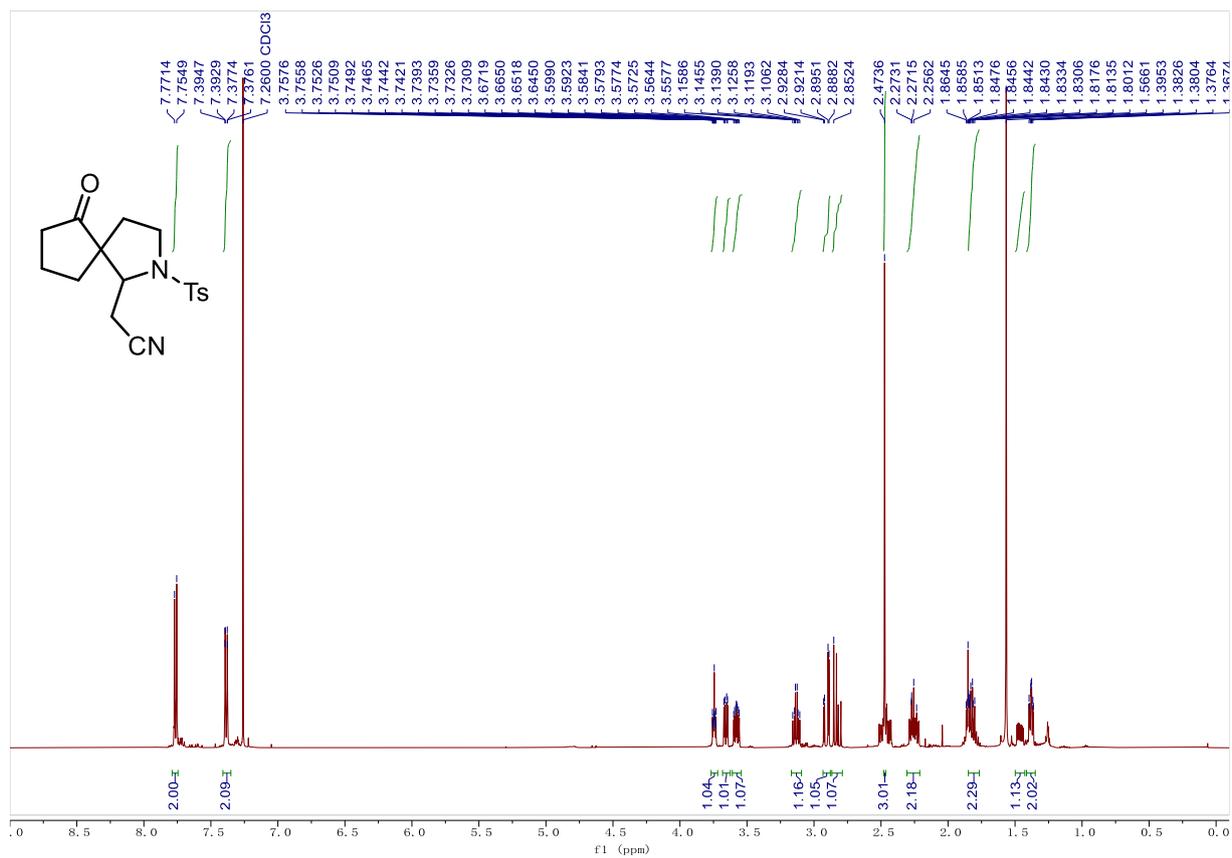
¹H NMR (CDCl₃, 500 MHz) of 5K



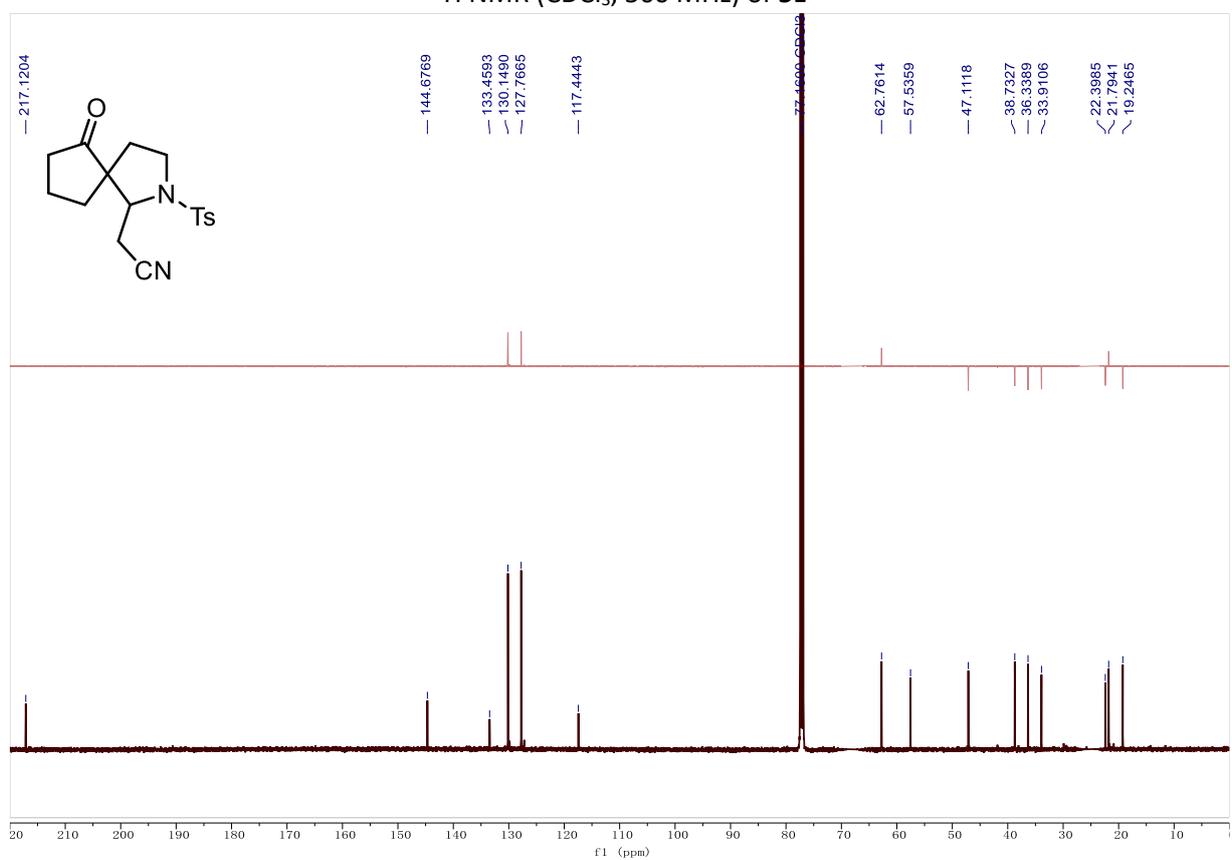
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 5K



$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 471 MHz) of **5K**



¹H NMR (CDCl₃, 500 MHz) of 5L



¹³C{¹H} NMR (CDCl₃, 126 MHz) of 5L

X-Ray Crystallography data

The absolute stereochemistry of products **3a** and **4a** were determined by X-ray diffraction. The X-ray crystallography data have been deposited in Cambridge Crystallography Data Center (CCDC 2499446, 2499448 and 2499449). The X-ray diffraction data were collected at and 173 K on a Bruker SMART CCD diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction data were corrected for absorption using the SADABS program¹⁰. The structures were solved using SHELXS97¹¹ and refined by full matrix least squares on F2 using SHELXL-2014 in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model)¹².

Method of crystallization: The single crystals of **2a**, **4u** and **5D** were cultivated via slow solvent evaporation of a solution in mixed *n*-hexane /CH₂Cl₂ at 4 °C

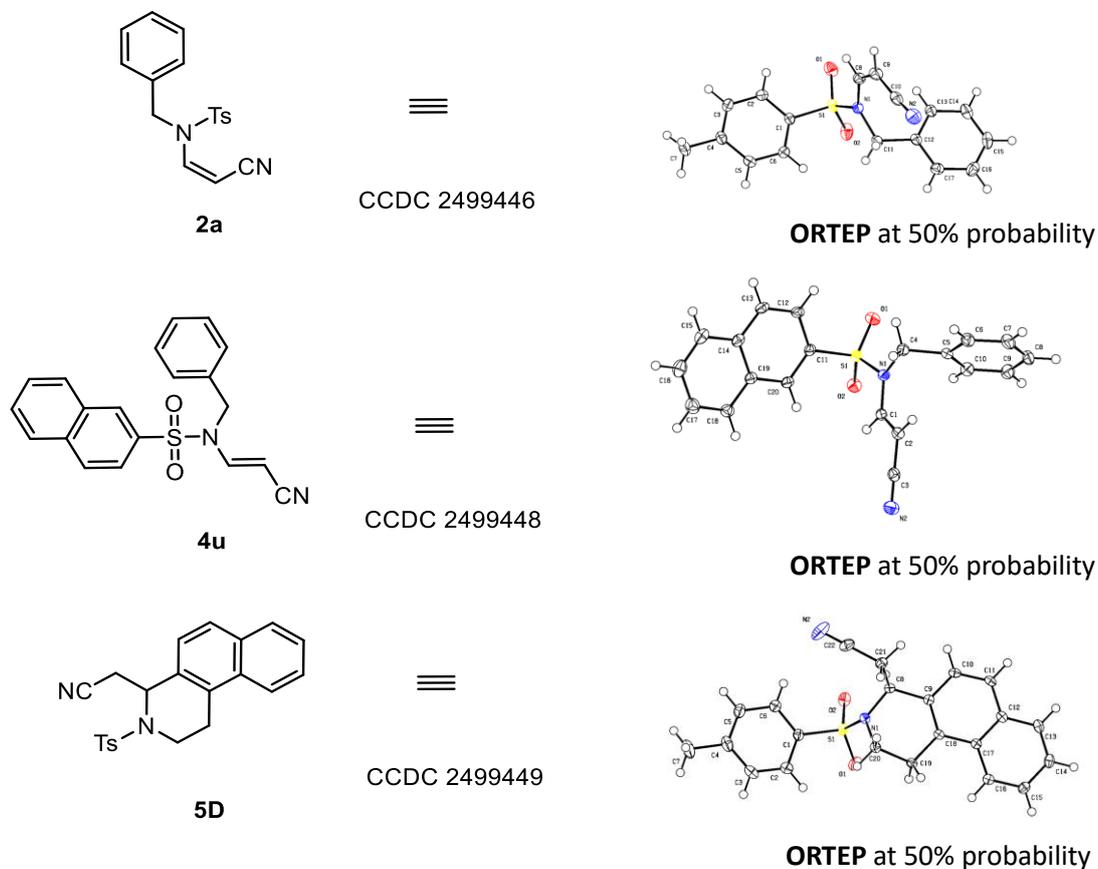


Table 1. Crystal data and structure refinement for 2a.

Identification code	2a
Empirical formula	C ₁₇ H ₁₆ N ₂ O ₂ S
Formula weight	312.38

¹⁰ Bruker. SADABS. Bruker AXS Inc.: Madison, Wisconsin, USA 2001.

¹¹ M. Sheldrick, Acta Crystallogr. Sect. A Found. Crystallogr. 2008, 64, 112–122

¹² G. M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem. 2015, 71, 3-8

Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 5.8452(11) Å alpha = 90 deg. b = 14.181(3) Å beta = 90 deg. c = 18.552(4) Å gamma = 90 deg.
Volume	1537.7(5) Å ³
Z, Calculated density	4, 1.349 Mg/m ³
Absorption coefficient	0.219 mm ⁻¹
F(000)	656
Crystal size	0.180 x 0.100 x 0.100 mm
Theta range for data collection	2.196 to 27.862 deg.
Limiting indices	-7<=h<=7, -18<=k<=18, -23<=l<=24
Reflections collected / unique	22022 / 3674 [R(int) = 0.0296]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7188
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3674 / 0 / 200
Goodness-of-fit on F ²	1.049
Final R indices [I>2sigma(I)]	R ₁ = 0.0250, wR ₂ = 0.0642
R indices (all data)	R ₁ = 0.0262, wR ₂ = 0.0650
Absolute structure parameter	-0.005(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.229 and -0.232 e.Å ⁻³

Table 2. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) for 2a. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
N(1)	6248(3)	4577(1)	5309(1)	19(1)
S(1)	4378(1)	3806(1)	5655(1)	19(1)
O(1)	2374(2)	4332(1)	5855(1)	28(1)
O(2)	4235(3)	3061(1)	5136(1)	29(1)
C(1)	5641(3)	3367(1)	6449(1)	17(1)
C(2)	4468(3)	3486(1)	7096(1)	21(1)
C(3)	5423(4)	3139(1)	7730(1)	24(1)
C(4)	7534(3)	2685(1)	7723(1)	22(1)
C(5)	8661(3)	2562(1)	7065(1)	22(1)
C(6)	7741(3)	2901(1)	6426(1)	20(1)
C(7)	8602(4)	2346(2)	8416(1)	33(1)
C(8)	6124(3)	5501(1)	5542(1)	22(1)
C(9)	7467(3)	6242(1)	5375(1)	25(1)

C(10)	9444(3)	6271(1)	4923(1)	24(1)
N(2)	11052(3)	6369(1)	4572(1)	33(1)
C(11)	7932(3)	4243(1)	4779(1)	18(1)
C(12)	7275(3)	4449(1)	4002(1)	17(1)
C(13)	5199(3)	4853(1)	3813(1)	22(1)
C(14)	4676(3)	5016(1)	3089(1)	28(1)
C(15)	6214(4)	4777(1)	2553(1)	28(1)
C(16)	8285(4)	4367(1)	2740(1)	28(1)
C(17)	8820(3)	4202(1)	3460(1)	23(1)

Table 3. Bond lengths [Å] and angles [deg] for 2a.

Atom	Length/Å	Atom	Length/Å
N(1)-C(8)	1.383(2)	C(8)-C(9)	1.347(3)
N(1)-C(11)	1.470(2)	C(8)-H(8)	0.9500
N(1)-S(1)	1.6737(15)	C(9)-C(10)	1.429(3)
S(1)-O(2)	1.4322(13)	C(9)-H(9)	0.9500
S(1)-O(1)	1.4379(14)	C(10)-N(2)	1.151(3)
S(1)-C(1)	1.7615(16)	C(11)-C(12)	1.519(2)
C(1)-C(2)	1.391(2)	C(11)-H(11A)	0.9900
C(1)-C(6)	1.395(2)	C(11)-H(11B)	0.9900
C(2)-C(3)	1.392(2)	C(12)-C(13)	1.388(2)
C(2)-H(2)	0.9500	C(12)-C(17)	1.396(2)
C(3)-C(4)	1.392(3)	C(13)-C(14)	1.396(2)
C(3)-H(3)	0.9500	C(13)-H(13)	0.9500
C(4)-C(5)	1.399(2)	C(14)-C(15)	1.383(3)
C(4)-C(7)	1.507(2)	C(14)-H(14)	0.9500
C(5)-C(6)	1.388(2)	C(15)-C(16)	1.387(3)
C(5)-H(5)	0.9500	C(15)-H(15)	0.9500
C(6)-H(6)	0.9500	C(16)-C(17)	1.393(3)
C(7)-H(7A)	0.9800	C(16)-H(16)	0.9500
C(7)-H(7B)	0.9800	C(17)-H(17)	0.9500
C(7)-H(7C)	0.9800		
Atom	Angles/°	Atom	Angles/°
C(8)-N(1)-C(11)	123.34(14)	H(7B)-C(7)-H(7C)	109.5
C(8)-N(1)-S(1)	117.73(12)	C(9)-C(8)-N(1)	129.57(17)
C(11)-N(1)-S(1)	118.92(11)	C(9)-C(8)-H(8)	115.2
O(2)-S(1)-O(1)	120.56(9)	N(1)-C(8)-H(8)	115.2
O(2)-S(1)-N(1)	105.15(8)	C(8)-C(9)-C(10)	128.96(16)
O(1)-S(1)-N(1)	106.96(8)	C(8)-C(9)-H(9)	115.5
O(2)-S(1)-C(1)	109.11(8)	C(10)-C(9)-H(9)	115.5
O(1)-S(1)-C(1)	108.04(8)	N(2)-C(10)-C(9)	174.56(18)
N(1)-S(1)-C(1)	106.12(8)	N(1)-C(11)-C(12)	113.82(13)

C(2)-C(1)-C(6)	121.20(15)	N(1)-C(11)-H(11A)	108.8
C(2)-C(1)-S(1)	118.15(13)	C(12)-C(11)-H(11A)	108.8
C(6)-C(1)-S(1)	120.64(12)	N(1)-C(11)-H(11B)	108.8
C(1)-C(2)-C(3)	119.22(16)	C(12)-C(11)-H(11B)	108.8
C(1)-C(2)-H(2)	120.4	H(11A)-C(11)-H(11B)	107.7
C(3)-C(2)-H(2)	120.4	C(13)-C(12)-C(17)	119.15(15)
C(2)-C(3)-C(4)	120.75(16)	C(13)-C(12)-C(11)	122.73(15)
C(2)-C(3)-H(3)	119.6	C(17)-C(12)-C(11)	118.11(15)
C(4)-C(3)-H(3)	119.6	C(12)-C(13)-C(14)	120.22(17)
C(3)-C(4)-C(5)	118.89(15)	C(12)-C(13)-H(13)	119.9
C(3)-C(4)-C(7)	120.47(17)	C(14)-C(13)-H(13)	119.9
C(5)-C(4)-C(7)	120.63(17)	C(15)-C(14)-C(13)	120.58(18)
C(6)-C(5)-C(4)	121.33(16)	C(15)-C(14)-H(14)	119.7
C(6)-C(5)-H(5)	119.3	C(13)-C(14)-H(14)	119.7
C(4)-C(5)-H(5)	119.3	C(14)-C(15)-C(16)	119.38(17)
C(5)-C(6)-C(1)	118.59(15)	C(14)-C(15)-H(15)	120.3
C(5)-C(6)-H(6)	120.7	C(16)-C(15)-H(15)	120.3
C(1)-C(6)-H(6)	120.7	C(15)-C(16)-C(17)	120.39(17)
C(4)-C(7)-H(7A)	109.5	C(15)-C(16)-H(16)	119.8
C(4)-C(7)-H(7B)	109.5	C(17)-C(16)-H(16)	119.8
H(7A)-C(7)-H(7B)	109.5	C(16)-C(17)-C(12)	120.28(17)
C(4)-C(7)-H(7C)	109.5	C(16)-C(17)-H(17)	119.9
H(7A)-C(7)-H(7C)	109.5	C(12)-C(17)-H(17)	119.9

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2a. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^*b^* U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
N(1)	24(1)	15(1)	17(1)	-1(1)	-2(1)	0(1)
S(1)	20(1)	19(1)	18(1)	1(1)	-6(1)	-3(1)
O(1)	18(1)	33(1)	32(1)	6(1)	-6(1)	1(1)
O(2)	43(1)	24(1)	21(1)	-2(1)	-8(1)	-12(1)
C(1)	19(1)	15(1)	16(1)	0(1)	-4(1)	-2(1)
C(2)	21(1)	22(1)	21(1)	-2(1)	1(1)	4(1)
C(3)	30(1)	26(1)	17(1)	0(1)	3(1)	2(1)
C(4)	28(1)	18(1)	20(1)	2(1)	-4(1)	-1(1)
C(5)	21(1)	20(1)	26(1)	2(1)	-2(1)	3(1)
C(6)	21(1)	21(1)	19(1)	0(1)	2(1)	1(1)
C(7)	43(1)	34(1)	23(1)	7(1)	-8(1)	7(1)
C(8)	26(1)	19(1)	20(1)	-4(1)	-3(1)	3(1)
C(9)	32(1)	17(1)	26(1)	-4(1)	-5(1)	0(1)
C(10)	31(1)	15(1)	26(1)	1(1)	-9(1)	-3(1)

N(2)	36(1)	26(1)	38(1)	2(1)	-1(1)	-4(1)
C(11)	20(1)	15(1)	19(1)	0(1)	-4(1)	4(1)
C(12)	20(1)	12(1)	19(1)	0(1)	-2(1)	-2(1)
C(13)	22(1)	25(1)	20(1)	3(1)	-1(1)	3(1)
C(14)	27(1)	30(1)	27(1)	8(1)	-7(1)	0(1)
C(15)	40(1)	25(1)	19(1)	6(1)	-5(1)	-10(1)
C(16)	35(1)	24(1)	23(1)	-1(1)	9(1)	-5(1)
C(17)	22(1)	19(1)	27(1)	0(1)	2(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2a.

Atom	x	y	z	U(eq)
H(2)	3032	3799	7104	25
H(3)	4625	3214	8172	29
H(5)	10086	2240	7055	26
H(6)	8523	2817	5982	24
H(7A)	9604	2838	8610	50
H(7B)	9500	1775	8321	50
H(7C)	7395	2203	8766	50
H(8)	4913	5634	5868	26
H(9)	7041	6825	5587	30
H(11A)	8126	3553	4836	22
H(11B)	9425	4544	4881	22
H(13)	4129	5020	4177	27
H(14)	3251	5294	2964	33
H(15)	5855	4892	2061	33
H(16)	9345	4197	2374	33
H(17)	10243	3921	3584	28

Table 6. Torsion angles [deg] for 2a.

Atom	Angles/ $^\circ$	Atom	Angles/ $^\circ$
C(8)-N(1)-S(1)-O(2)	156.72(13)	C(4)-C(5)-C(6)-C(1)	-0.4(3)
C(11)-N(1)-S(1)-O(2)	-23.39(14)	C(2)-C(1)-C(6)-C(5)	-0.7(2)
C(8)-N(1)-S(1)-O(1)	27.43(14)	S(1)-C(1)-C(6)-C(5)	-179.56(13)
C(11)-N(1)-S(1)-O(1)	-152.68(12)	C(11)-N(1)-C(8)-C(9)	-3.0(3)
C(8)-N(1)-S(1)-C(1)	-87.73(14)	S(1)-N(1)-C(8)-C(9)	176.87(16)
C(11)-N(1)-S(1)-C(1)	92.16(13)	N(1)-C(8)-C(9)-C(10)	-1.9(3)
O(2)-S(1)-C(1)-C(2)	-125.66(13)	C(8)-N(1)-C(11)-C(12)	-80.82(19)
O(1)-S(1)-C(1)-C(2)	7.08(15)	S(1)-N(1)-C(11)-C(12)	99.29(14)
N(1)-S(1)-C(1)-C(2)	121.51(13)	N(1)-C(11)-C(12)-C(13)	-4.5(2)
O(2)-S(1)-C(1)-C(6)	53.24(15)	N(1)-C(11)-C(12)-C(17)	176.79(14)
O(1)-S(1)-C(1)-C(6)	-174.02(13)	C(17)-C(12)-C(13)-C(14)	-0.5(3)
N(1)-S(1)-C(1)-C(6)	-59.59(14)	C(11)-C(12)-C(13)-C(14)	-179.20(16)

C(6)-C(1)-C(2)-C(3)	0.6(2)	C(12)-C(13)-C(14)-C(15)	0.1(3)
S(1)-C(1)-C(2)-C(3)	179.53(13)	C(13)-C(14)-C(15)-C(16)	0.4(3)
C(1)-C(2)-C(3)-C(4)	0.5(3)	C(14)-C(15)-C(16)-C(17)	-0.4(3)
C(2)-C(3)-C(4)-C(5)	-1.5(3)	C(15)-C(16)-C(17)-C(12)	0.0(3)
C(2)-C(3)-C(4)-C(7)	177.58(17)	C(13)-C(12)-C(17)-C(16)	0.4(2)
C(3)-C(4)-C(5)-C(6)	1.4(3)	C(11)-C(12)-C(17)-C(16)	179.21(15)
C(7)-C(4)-C(5)-C(6)	-177.63(17)		

Table 7. Crystal data and structure refinement for 4u.

Identification code	3u
Empirical formula	C ₂₀ H ₁₆ N ₂ O ₂ S
Formula weight	348.41
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 17.190(3) Å alpha = 90 deg. b = 5.8404(9) Å beta = 91.004(6) deg. c = 18.305(4) Å gamma = 90 deg.
Volume	1837.5(6) Å ³
Z, Calculated density	4, 1.259 Mg/m ³
Absorption coefficient	0.191 mm ⁻¹
F(000)	728
Crystal size	0.200 x 0.100 x 0.100 mm
Theta range for data collection	3.223 to 27.882 deg.
Limiting indices	-22<=h<=22, -6<=k<=7, -23<=l<=24
Reflections collected / unique	42313 / 4367 [R(int) = 0.0535]
Completeness to theta = 25.242	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5510
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4367 / 0 / 226
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0974
R indices (all data)	R1 = 0.0391, wR2 = 0.1009
Extinction coefficient	n/a
Largest diff. peak and hole	0.383 and -0.390 e.Å ⁻³

Table 8. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) for 4u. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	2567(1)	4803(1)	4872(1)	17(1)
O(1)	1984(1)	6252(2)	4552(1)	25(1)

O(2)	2461(1)	2370(2)	4917(1)	22(1)
N(1)	3367(1)	5176(2)	4374(1)	18(1)
C(1)	3949(1)	3554(2)	4434(1)	17(1)
C(2)	4655(1)	3727(2)	4131(1)	19(1)
C(3)	5184(1)	1854(2)	4216(1)	20(1)
N(2)	5598(1)	312(2)	4279(1)	27(1)
C(4)	3511(1)	7381(2)	4011(1)	19(1)
C(5)	3555(1)	7164(2)	3184(1)	17(1)
C(6)	3901(1)	8945(2)	2797(1)	23(1)
C(7)	3934(1)	8868(3)	2038(1)	29(1)
C(8)	3635(1)	6994(3)	1660(1)	28(1)
C(9)	3299(1)	5207(3)	2041(1)	26(1)
C(10)	3248(1)	5297(2)	2803(1)	21(1)
C(11)	2819(1)	5845(2)	5750(1)	17(1)
C(12)	2525(1)	8001(2)	5971(1)	19(1)
C(13)	2747(1)	8844(2)	6641(1)	20(1)
C(14)	3275(1)	7629(2)	7104(1)	19(1)
C(15)	3532(1)	8515(2)	7791(1)	24(1)
C(16)	4053(1)	7317(3)	8217(1)	29(1)
C(17)	4342(1)	5169(3)	7985(1)	28(1)
C(18)	4101(1)	4251(2)	7331(1)	22(1)
C(19)	3562(1)	5456(2)	6873(1)	17(1)
C(20)	3317(1)	4576(2)	6184(1)	17(1)

Table 9. Bond lengths [Å] and angles [deg] for 4u.

Atom	Length/Å	Atom	Length/Å
S(1)-O(1)	1.4291(10)	C(9)-C(10)	1.3993(19)
S(1)-O(2)	1.4353(10)	C(9)-H(9)	0.9500
S(1)-N(1)	1.6778(11)	C(10)-H(10)	0.9500
S(1)-C(11)	1.7637(13)	C(11)-C(20)	1.3756(17)
N(1)-C(1)	1.3814(15)	C(11)-C(12)	1.4183(16)
N(1)-C(4)	1.4715(15)	C(12)-C(13)	1.3696(18)
C(1)-C(2)	1.3464(17)	C(12)-H(12)	0.9500
C(1)-H(1)	0.9500	C(13)-C(14)	1.4207(18)
C(2)-C(3)	1.4294(17)	C(13)-H(13)	0.9500
C(2)-H(2)	0.9500	C(14)-C(15)	1.4223(18)
C(3)-N(2)	1.1520(18)	C(14)-C(19)	1.4286(17)
C(4)-C(5)	1.5234(16)	C(15)-C(16)	1.370(2)
C(4)-H(4A)	0.9900	C(15)-H(15)	0.9500
C(4)-H(4B)	0.9900	C(16)-C(17)	1.416(2)
C(5)-C(10)	1.3931(17)	C(16)-H(16)	0.9500
C(5)-C(6)	1.3964(17)	C(17)-C(18)	1.3703(19)
C(6)-C(7)	1.3926(19)	C(17)-H(17)	0.9500

C(6)-H(6)	0.9500	C(18)-C(19)	1.4243(17)
C(7)-C(8)	1.388(2)	C(18)-H(18)	0.9500
C(7)-H(7)	0.9500	C(19)-C(20)	1.4182(17)
C(8)-C(9)	1.387(2)	C(20)-H(20)	0.9500
C(8)-H(8)	0.9500		

Atom	Angles/°	Atom	Angles/°
O(1)-S(1)-O(2)	121.34(6)	C(8)-C(9)-H(9)	119.8
O(1)-S(1)-N(1)	105.99(6)	C(10)-C(9)-H(9)	119.8
O(2)-S(1)-N(1)	105.44(5)	C(5)-C(10)-C(9)	119.90(12)
O(1)-S(1)-C(11)	109.12(6)	C(5)-C(10)-H(10)	120.0
O(2)-S(1)-C(11)	108.61(6)	C(9)-C(10)-H(10)	120.0
N(1)-S(1)-C(11)	105.11(6)	C(20)-C(11)-C(12)	122.25(11)
C(1)-N(1)-C(4)	120.58(10)	C(20)-C(11)-S(1)	118.75(9)
C(1)-N(1)-S(1)	117.84(8)	C(12)-C(11)-S(1)	118.95(9)
C(4)-N(1)-S(1)	120.33(8)	C(13)-C(12)-C(11)	118.72(11)
C(2)-C(1)-N(1)	124.91(11)	C(13)-C(12)-H(12)	120.6
C(2)-C(1)-H(1)	117.5	C(11)-C(12)-H(12)	120.6
N(1)-C(1)-H(1)	117.5	C(12)-C(13)-C(14)	121.29(11)
C(1)-C(2)-C(3)	118.29(11)	C(12)-C(13)-H(13)	119.4
C(1)-C(2)-H(2)	120.9	C(14)-C(13)-H(13)	119.4
C(3)-C(2)-H(2)	120.9	C(13)-C(14)-C(15)	122.01(12)
N(2)-C(3)-C(2)	178.51(15)	C(13)-C(14)-C(19)	119.17(11)
N(1)-C(4)-C(5)	112.78(10)	C(15)-C(14)-C(19)	118.82(12)
N(1)-C(4)-H(4A)	109.0	C(16)-C(15)-C(14)	120.43(12)
C(5)-C(4)-H(4A)	109.0	C(16)-C(15)-H(15)	119.8
N(1)-C(4)-H(4B)	109.0	C(14)-C(15)-H(15)	119.8
C(5)-C(4)-H(4B)	109.0	C(15)-C(16)-C(17)	120.78(13)
H(4A)-C(4)-H(4B)	107.8	C(15)-C(16)-H(16)	119.6
C(10)-C(5)-C(6)	119.32(12)	C(17)-C(16)-H(16)	119.6
C(10)-C(5)-C(4)	122.56(11)	C(18)-C(17)-C(16)	120.39(13)
C(6)-C(5)-C(4)	118.10(11)	C(18)-C(17)-H(17)	119.8
C(7)-C(6)-C(5)	120.49(13)	C(16)-C(17)-H(17)	119.8
C(7)-C(6)-H(6)	119.8	C(17)-C(18)-C(19)	120.32(13)
C(5)-C(6)-H(6)	119.8	C(17)-C(18)-H(18)	119.8
C(8)-C(7)-C(6)	120.03(13)	C(19)-C(18)-H(18)	119.8
C(8)-C(7)-H(7)	120.0	C(20)-C(19)-C(18)	121.62(11)
C(6)-C(7)-H(7)	120.0	C(20)-C(19)-C(14)	119.10(11)
C(9)-C(8)-C(7)	119.82(12)	C(18)-C(19)-C(14)	119.26(11)
C(9)-C(8)-H(8)	120.1	C(11)-C(20)-C(19)	119.43(11)
C(7)-C(8)-H(8)	120.1	C(11)-C(20)-H(20)	120.3
C(8)-C(9)-C(10)	120.41(13)	C(19)-C(20)-H(20)	120.3

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4u. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^*b^* U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
S(1)	18(1)	16(1)	18(1)	2(1)	0(1)	1(1)
O(1)	23(1)	27(1)	26(1)	3(1)	-3(1)	6(1)
O(2)	24(1)	17(1)	25(1)	1(1)	0(1)	-4(1)
N(1)	22(1)	14(1)	17(1)	2(1)	4(1)	3(1)
C(1)	23(1)	14(1)	14(1)	0(1)	-1(1)	1(1)
C(2)	21(1)	18(1)	19(1)	2(1)	0(1)	1(1)
C(3)	20(1)	22(1)	18(1)	4(1)	3(1)	-2(1)
N(2)	24(1)	27(1)	30(1)	9(1)	7(1)	4(1)
C(4)	26(1)	13(1)	18(1)	2(1)	1(1)	0(1)
C(5)	18(1)	16(1)	16(1)	2(1)	-1(1)	3(1)
C(6)	29(1)	18(1)	23(1)	3(1)	0(1)	-1(1)
C(7)	35(1)	29(1)	24(1)	10(1)	4(1)	3(1)
C(8)	27(1)	40(1)	16(1)	3(1)	-2(1)	10(1)
C(9)	22(1)	33(1)	22(1)	-6(1)	-6(1)	2(1)
C(10)	20(1)	22(1)	22(1)	0(1)	-1(1)	-1(1)
C(11)	18(1)	16(1)	16(1)	1(1)	5(1)	1(1)
C(12)	20(1)	16(1)	22(1)	5(1)	7(1)	4(1)
C(13)	24(1)	14(1)	23(1)	1(1)	11(1)	2(1)
C(14)	19(1)	16(1)	20(1)	0(1)	8(1)	-3(1)
C(15)	26(1)	21(1)	25(1)	-5(1)	8(1)	-6(1)
C(16)	26(1)	35(1)	24(1)	-7(1)	0(1)	-6(1)
C(17)	24(1)	35(1)	25(1)	1(1)	-3(1)	0(1)
C(18)	20(1)	22(1)	23(1)	2(1)	3(1)	2(1)
C(19)	17(1)	16(1)	18(1)	2(1)	6(1)	-1(1)
C(20)	18(1)	14(1)	19(1)	1(1)	5(1)	1(1)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 4u.

Atom	x	y	z	U(eq)
H(1)	3844	2215	4710	20
H(2)	4797	5060	3867	23
H(4A)	4006	8030	4202	23
H(4B)	3089	8461	4133	23
H(6)	4114	10218	3054	28
H(7)	4162	10099	1778	35
H(8)	3661	6935	1143	33
H(9)	3102	3914	1783	31
H(10)	3005	4086	3059	25

H(12)	2182	8844	5661	23
H(13)	2544	10269	6800	24
H(15)	3340	9948	7955	29
H(16)	4223	7933	8672	34
H(17)	4705	4361	8286	34
H(18)	4294	2803	7182	26
H(20)	3495	3123	6025	21

Table 12. Torsion angles [deg] for 4u.

Atom	Angles/°	Atom	Angles/°
O(1)-S(1)-N(1)-C(1)	-162.83(9)	O(1)-S(1)-C(11)-C(12)	-8.71(11)
O(2)-S(1)-N(1)-C(1)	-33.00(10)	O(2)-S(1)-C(11)-C(12)	-142.95(9)
C(11)-S(1)-N(1)-C(1)	81.68(10)	N(1)-S(1)-C(11)-C(12)	104.60(10)
O(1)-S(1)-N(1)-C(4)	29.88(11)	C(20)-C(11)-C(12)-C(13)	0.02(18)
O(2)-S(1)-N(1)-C(4)	159.70(9)	S(1)-C(11)-C(12)-C(13)	-177.43(9)
C(11)-S(1)-N(1)-C(4)	-85.62(10)	C(11)-C(12)-C(13)-C(14)	1.55(18)
C(4)-N(1)-C(1)-C(2)	-5.52(18)	C(12)-C(13)-C(14)-C(15)	177.88(12)
S(1)-N(1)-C(1)-C(2)	-172.78(10)	C(12)-C(13)-C(14)-C(19)	-1.82(18)
N(1)-C(1)-C(2)-C(3)	-177.26(11)	C(13)-C(14)-C(15)-C(16)	-178.75(12)
C(1)-N(1)-C(4)-C(5)	73.69(14)	C(19)-C(14)-C(15)-C(16)	0.95(18)
S(1)-N(1)-C(4)-C(5)	-119.37(10)	C(14)-C(15)-C(16)-C(17)	-0.5(2)
N(1)-C(4)-C(5)-C(10)	19.44(16)	C(15)-C(16)-C(17)-C(18)	-0.2(2)
N(1)-C(4)-C(5)-C(6)	-162.19(11)	C(16)-C(17)-C(18)-C(19)	0.5(2)
C(10)-C(5)-C(6)-C(7)	0.45(19)	C(17)-C(18)-C(19)-C(20)	178.41(12)
C(4)-C(5)-C(6)-C(7)	-177.97(12)	C(17)-C(18)-C(19)-C(14)	-0.08(18)
C(5)-C(6)-C(7)-C(8)	-1.1(2)	C(13)-C(14)-C(19)-C(20)	0.53(17)
C(6)-C(7)-C(8)-C(9)	0.4(2)	C(15)-C(14)-C(19)-C(20)	-179.18(11)
C(7)-C(8)-C(9)-C(10)	1.0(2)	C(13)-C(14)-C(19)-C(18)	179.06(11)
C(6)-C(5)-C(10)-C(9)	0.95(19)	C(15)-C(14)-C(19)-C(18)	-0.65(17)
C(4)-C(5)-C(10)-C(9)	179.29(12)	C(12)-C(11)-C(20)-C(19)	-1.28(18)
C(8)-C(9)-C(10)-C(5)	-1.7(2)	S(1)-C(11)-C(20)-C(19)	176.17(9)
O(1)-S(1)-C(11)-C(20)	173.75(9)	C(18)-C(19)-C(20)-C(11)	-177.52(11)
O(2)-S(1)-C(11)-C(20)	39.51(11)	C(14)-C(19)-C(20)-C(11)	0.97(17)
N(1)-S(1)-C(11)-C(20)	-72.94(11)		

Table 13. Crystal data and structure refinement for 5D.

Identification code	4E
Empirical formula	C ₂₂ H ₂₀ N ₂ O ₂ S
Formula weight	376.46
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 18.6005(7) Å alpha = 90 deg.

	b = 7.9576(3) Å beta = 105.5750(10) deg. c = 12.8515(5) Å gamma = 90 deg.
Volume	1832.37(12) Å ³
Z, Calculated density	4, 1.365 Mg/m ³
Absorption coefficient	0.197 mm ⁻¹
F(000)	792
Crystal size	0.200 x 0.140 x 0.100 mm
Theta range for data collection	2.273 to 27.924 deg.
Limiting indices	-24 ≤ h ≤ 24, -10 ≤ k ≤ 10, -14 ≤ l ≤ 16
Reflections collected / unique	42942 / 4380 [R(int) = 0.0627]
Completeness to theta = 25.242	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5943
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4380 / 0 / 245
Goodness-of-fit on F ²	1.027
Final R indices [I > 2σ(I)]	R1 = 0.0371, wR2 = 0.0964
R indices (all data)	R1 = 0.0434, wR2 = 0.1021
Extinction coefficient	n/a
Largest diff. peak and hole	0.452 and -0.451 e.Å ⁻³

Table 14. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) for 5D. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
N(1)	7442(1)	2886(1)	7484(1)	15(1)
S(1)	7745(1)	1082(1)	8058(1)	16(1)
O(1)	7394(1)	-284(1)	7371(1)	24(1)
O(2)	7672(1)	1159(1)	9144(1)	21(1)
C(1)	8697(1)	1051(2)	8107(1)	17(1)
C(2)	8927(1)	383(2)	7247(1)	26(1)
C(3)	9683(1)	327(2)	7310(1)	31(1)
C(4)	10214(1)	884(2)	8231(1)	27(1)
C(5)	9970(1)	1566(2)	9075(1)	25(1)
C(6)	9215(1)	1667(2)	9019(1)	21(1)
C(7)	11036(1)	744(3)	8309(2)	40(1)
C(8)	6981(1)	3990(2)	7953(1)	15(1)
C(9)	6165(1)	3990(2)	7308(1)	14(1)
C(10)	5651(1)	4783(2)	7792(1)	16(1)
C(11)	4904(1)	4774(2)	7300(1)	16(1)
C(12)	4625(1)	3931(2)	6301(1)	15(1)
C(13)	3846(1)	3813(2)	5809(1)	18(1)
C(14)	3579(1)	2954(2)	4858(1)	19(1)
C(15)	4081(1)	2222(2)	4341(1)	19(1)

C(16)	4839(1)	2326(2)	4797(1)	16(1)
C(17)	5134(1)	3164(2)	5794(1)	13(1)
C(18)	5922(1)	3234(2)	6309(1)	13(1)
C(19)	6466(1)	2455(2)	5758(1)	15(1)
C(20)	7269(1)	2971(2)	6295(1)	15(1)
C(21)	7309(1)	5792(2)	8068(1)	20(1)
C(22)	8021(1)	5845(2)	8904(1)	26(1)
N(2)	8566(1)	5842(2)	9574(1)	44(1)

Table 15. Bond lengths [Å] and angles [deg] for 5D.

Atom	Length/Å	Atom	Length/Å
N(1)-C(8)	1.4650(16)	C(10)-C(11)	1.3639(19)
N(1)-C(20)	1.4762(16)	C(10)-H(10)	0.9500
N(1)-S(1)	1.6429(11)	C(11)-C(12)	1.4172(18)
S(1)-O(2)	1.4394(10)	C(11)-H(11)	0.9500
S(1)-O(1)	1.4410(10)	C(12)-C(13)	1.4197(18)
S(1)-C(1)	1.7559(14)	C(12)-C(17)	1.4235(17)
C(1)-C(6)	1.3903(19)	C(13)-C(14)	1.372(2)
C(1)-C(2)	1.393(2)	C(13)-H(13)	0.9500
C(2)-C(3)	1.387(2)	C(14)-C(15)	1.4095(19)
C(2)-H(2)	0.9500	C(14)-H(14)	0.9500
C(3)-C(4)	1.394(2)	C(15)-C(16)	1.3760(18)
C(3)-H(3)	0.9500	C(15)-H(15)	0.9500
C(4)-C(5)	1.393(2)	C(16)-C(17)	1.4181(17)
C(4)-C(7)	1.510(2)	C(16)-H(16)	0.9500
C(5)-C(6)	1.3907(19)	C(17)-C(18)	1.4394(17)
C(5)-H(5)	0.9500	C(18)-C(19)	1.5152(16)
C(6)-H(6)	0.9500	C(19)-C(20)	1.5239(17)
C(7)-H(7A)	0.9800	C(19)-H(19A)	0.9900
C(7)-H(7B)	0.9800	C(19)-H(19B)	0.9900
C(7)-H(7C)	0.9800	C(20)-H(20A)	0.9900
C(8)-C(9)	1.5213(17)	C(20)-H(20B)	0.9900
C(8)-C(21)	1.5499(18)	C(21)-C(22)	1.465(2)
C(8)-H(8)	1.0000	C(21)-H(21A)	0.9900
C(9)-C(18)	1.3785(17)	C(21)-H(21B)	0.9900
C(9)-C(10)	1.4215(17)	C(22)-N(2)	1.140(2)

Atom	Angles/°	Atom	Angles/°
C(8)-N(1)-C(20)	114.17(10)	C(9)-C(10)-H(10)	119.4
C(8)-N(1)-S(1)	120.51(8)	C(10)-C(11)-C(12)	120.14(12)
C(20)-N(1)-S(1)	117.21(9)	C(10)-C(11)-H(11)	119.9
O(2)-S(1)-O(1)	118.72(6)	C(12)-C(11)-H(11)	119.9

O(2)-S(1)-N(1)	106.71(6)	C(11)-C(12)-C(13)	121.10(12)
O(1)-S(1)-N(1)	109.88(6)	C(11)-C(12)-C(17)	119.40(12)
O(2)-S(1)-C(1)	108.80(6)	C(13)-C(12)-C(17)	119.50(12)
O(1)-S(1)-C(1)	107.38(6)	C(14)-C(13)-C(12)	120.74(12)
N(1)-S(1)-C(1)	104.46(6)	C(14)-C(13)-H(13)	119.6
C(6)-C(1)-C(2)	120.86(13)	C(12)-C(13)-H(13)	119.6
C(6)-C(1)-S(1)	119.24(11)	C(13)-C(14)-C(15)	119.98(12)
C(2)-C(1)-S(1)	119.89(11)	C(13)-C(14)-H(14)	120.0
C(3)-C(2)-C(1)	119.20(14)	C(15)-C(14)-H(14)	120.0
C(3)-C(2)-H(2)	120.4	C(16)-C(15)-C(14)	120.49(12)
C(1)-C(2)-H(2)	120.4	C(16)-C(15)-H(15)	119.8
C(2)-C(3)-C(4)	121.05(15)	C(14)-C(15)-H(15)	119.8
C(2)-C(3)-H(3)	119.5	C(15)-C(16)-C(17)	121.04(12)
C(4)-C(3)-H(3)	119.5	C(15)-C(16)-H(16)	119.5
C(5)-C(4)-C(3)	118.66(14)	C(17)-C(16)-H(16)	119.5
C(5)-C(4)-C(7)	120.84(16)	C(16)-C(17)-C(12)	118.22(11)
C(3)-C(4)-C(7)	120.50(16)	C(16)-C(17)-C(18)	122.18(11)
C(6)-C(5)-C(4)	121.21(14)	C(12)-C(17)-C(18)	119.59(11)
C(6)-C(5)-H(5)	119.4	C(9)-C(18)-C(17)	118.93(11)
C(4)-C(5)-H(5)	119.4	C(9)-C(18)-C(19)	121.39(11)
C(5)-C(6)-C(1)	118.97(14)	C(17)-C(18)-C(19)	119.66(11)
C(5)-C(6)-H(6)	120.5	C(18)-C(19)-C(20)	111.96(10)
C(1)-C(6)-H(6)	120.5	C(18)-C(19)-H(19A)	109.2
C(4)-C(7)-H(7A)	109.5	C(20)-C(19)-H(19A)	109.2
C(4)-C(7)-H(7B)	109.5	C(18)-C(19)-H(19B)	109.2
H(7A)-C(7)-H(7B)	109.5	C(20)-C(19)-H(19B)	109.2
C(4)-C(7)-H(7C)	109.5	H(19A)-C(19)-H(19B)	107.9
H(7A)-C(7)-H(7C)	109.5	N(1)-C(20)-C(19)	111.79(10)
H(7B)-C(7)-H(7C)	109.5	N(1)-C(20)-H(20A)	109.3
N(1)-C(8)-C(9)	112.59(10)	C(19)-C(20)-H(20A)	109.3
N(1)-C(8)-C(21)	109.60(10)	N(1)-C(20)-H(20B)	109.3
C(9)-C(8)-C(21)	111.18(10)	C(19)-C(20)-H(20B)	109.3
N(1)-C(8)-H(8)	107.8	H(20A)-C(20)-H(20B)	107.9
C(9)-C(8)-H(8)	107.8	C(22)-C(21)-C(8)	110.56(12)
C(21)-C(8)-H(8)	107.8	C(22)-C(21)-H(21A)	109.5
C(18)-C(9)-C(10)	120.70(12)	C(8)-C(21)-H(21A)	109.5
C(18)-C(9)-C(8)	122.46(11)	C(22)-C(21)-H(21B)	109.5
C(10)-C(9)-C(8)	116.82(11)	C(8)-C(21)-H(21B)	109.5
C(11)-C(10)-C(9)	121.10(12)	H(21A)-C(21)-H(21B)	108.1
C(11)-C(10)-H(10)	119.5	N(2)-C(22)-C(21)	177.57(17)

Table 16. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 5E. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^*b^* U_{12}]$

Atom	U11	U22	U33	U23	U13	U12
N(1)	16(1)	16(1)	14(1)	2(1)	5(1)	2(1)
S(1)	15(1)	14(1)	17(1)	3(1)	2(1)	-2(1)
O(1)	24(1)	16(1)	29(1)	1(1)	-1(1)	-5(1)
O(2)	20(1)	26(1)	18(1)	8(1)	6(1)	-1(1)
C(1)	16(1)	14(1)	21(1)	2(1)	4(1)	1(1)
C(2)	25(1)	25(1)	27(1)	-7(1)	5(1)	4(1)
C(3)	29(1)	30(1)	36(1)	-6(1)	14(1)	8(1)
C(4)	20(1)	22(1)	40(1)	3(1)	11(1)	4(1)
C(5)	18(1)	25(1)	30(1)	0(1)	2(1)	-2(1)
C(6)	19(1)	22(1)	21(1)	-1(1)	5(1)	-1(1)
C(7)	23(1)	40(1)	62(1)	0(1)	17(1)	6(1)
C(8)	16(1)	14(1)	14(1)	-1(1)	5(1)	-1(1)
C(9)	16(1)	11(1)	14(1)	2(1)	6(1)	-1(1)
C(10)	22(1)	14(1)	15(1)	-1(1)	8(1)	-1(1)
C(11)	20(1)	15(1)	18(1)	0(1)	10(1)	2(1)
C(12)	18(1)	11(1)	16(1)	4(1)	7(1)	1(1)
C(13)	16(1)	16(1)	22(1)	7(1)	8(1)	3(1)
C(14)	15(1)	18(1)	22(1)	7(1)	2(1)	1(1)
C(15)	21(1)	17(1)	16(1)	2(1)	1(1)	-1(1)
C(16)	19(1)	14(1)	15(1)	2(1)	6(1)	1(1)
C(17)	16(1)	10(1)	15(1)	2(1)	5(1)	0(1)
C(18)	15(1)	11(1)	13(1)	2(1)	6(1)	0(1)
C(19)	17(1)	15(1)	13(1)	0(1)	5(1)	1(1)
C(20)	16(1)	17(1)	14(1)	2(1)	6(1)	1(1)
C(21)	20(1)	17(1)	21(1)	-3(1)	5(1)	-4(1)
C(22)	29(1)	25(1)	24(1)	-5(1)	5(1)	-10(1)
N(2)	39(1)	48(1)	34(1)	-1(1)	-7(1)	-17(1)

Table 17. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5D.

Atom	x	y	z	U(eq)
H(2)	8570	-30	6625	31
H(3)	9841	-98	6717	37
H(5)	10327	1970	9700	30
H(6)	9054	2150	9594	25
H(7A)	11133	-317	7983	60
H(7B)	11322	773	9070	60
H(7C)	11188	1686	7924	60
H(8)	7007	3565	8694	18
H(10)	5831	5328	8470	19
H(11)	4569	5335	7627	20
H(13)	3505	4335	6143	21
H(14)	3057	2853	4548	23

H(15)	3895	1651	3674	22
H(16)	5170	1828	4437	19
H(19A)	6332	2806	4991	18
H(19B)	6425	1215	5779	18
H(20A)	7613	2221	6044	18
H(20B)	7351	4132	6076	18
H(21A)	7386	6158	7369	23
H(21B)	6951	6577	8259	23

Table 12. Torsion angles [deg] for 5D.

Atom	Angles/°	Atom	Angles/°
C(8)-N(1)-S(1)-O(2)	-17.29(11)	C(8)-C(9)-C(10)-C(11)	-176.75(12)
C(20)-N(1)-S(1)-O(2)	-164.15(9)	C(9)-C(10)-C(11)-C(12)	1.56(19)
C(8)-N(1)-S(1)-O(1)	112.65(10)	C(10)-C(11)-C(12)-C(13)	175.87(12)
C(20)-N(1)-S(1)-O(1)	-34.21(11)	C(10)-C(11)-C(12)-C(17)	-2.92(18)
C(8)-N(1)-S(1)-C(1)	-132.44(10)	C(11)-C(12)-C(13)-C(14)	-178.13(12)
C(20)-N(1)-S(1)-C(1)	80.70(10)	C(17)-C(12)-C(13)-C(14)	0.66(19)
O(2)-S(1)-C(1)-C(6)	-22.04(13)	C(12)-C(13)-C(14)-C(15)	-1.97(19)
O(1)-S(1)-C(1)-C(6)	-151.71(11)	C(13)-C(14)-C(15)-C(16)	1.5(2)
N(1)-S(1)-C(1)-C(6)	91.63(12)	C(14)-C(15)-C(16)-C(17)	0.20(19)
O(2)-S(1)-C(1)-C(2)	156.70(12)	C(15)-C(16)-C(17)-C(12)	-1.48(18)
O(1)-S(1)-C(1)-C(2)	27.03(13)	C(15)-C(16)-C(17)-C(18)	177.47(12)
N(1)-S(1)-C(1)-C(2)	-89.64(12)	C(11)-C(12)-C(17)-C(16)	179.86(11)
C(6)-C(1)-C(2)-C(3)	0.4(2)	C(13)-C(12)-C(17)-C(16)	1.05(18)
S(1)-C(1)-C(2)-C(3)	-178.32(12)	C(11)-C(12)-C(17)-C(18)	0.88(18)
C(1)-C(2)-C(3)-C(4)	1.8(2)	C(13)-C(12)-C(17)-C(18)	-177.93(11)
C(2)-C(3)-C(4)-C(5)	-2.6(2)	C(10)-C(9)-C(18)-C(17)	-3.96(18)
C(2)-C(3)-C(4)-C(7)	177.24(16)	C(8)-C(9)-C(18)-C(17)	174.69(11)
C(3)-C(4)-C(5)-C(6)	1.2(2)	C(10)-C(9)-C(18)-C(19)	177.09(11)
C(7)-C(4)-C(5)-C(6)	-178.63(15)	C(8)-C(9)-C(18)-C(19)	-4.26(18)
C(4)-C(5)-C(6)-C(1)	0.9(2)	C(16)-C(17)-C(18)-C(9)	-176.41(12)
C(2)-C(1)-C(6)-C(5)	-1.7(2)	C(12)-C(17)-C(18)-C(9)	2.53(17)
S(1)-C(1)-C(6)-C(5)	176.98(11)	C(16)-C(17)-C(18)-C(19)	2.56(18)
C(20)-N(1)-C(8)-C(9)	41.66(14)	C(12)-C(17)-C(18)-C(19)	-178.51(11)
S(1)-N(1)-C(8)-C(9)	-106.14(11)	C(9)-C(18)-C(19)-C(20)	-13.31(16)
C(20)-N(1)-C(8)-C(21)	-82.64(13)	C(17)-C(18)-C(19)-C(20)	167.75(11)
S(1)-N(1)-C(8)-C(21)	129.57(10)	C(8)-N(1)-C(20)-C(19)	-60.70(14)
N(1)-C(8)-C(9)-C(18)	-9.36(17)	S(1)-N(1)-C(20)-C(19)	88.21(11)
C(21)-C(8)-C(9)-C(18)	114.06(13)	C(18)-C(19)-C(20)-N(1)	44.20(14)
N(1)-C(8)-C(9)-C(10)	169.34(11)	N(1)-C(8)-C(21)-C(22)	-69.25(14)
C(21)-C(8)-C(9)-C(10)	-67.24(14)	C(9)-C(8)-C(21)-C(22)	165.64(12)
C(18)-C(9)-C(10)-C(11)	1.97(19)		