Supporting Information for

Organoselenium-Catalyzed Synthesis of Indoles Through Intramolecular C−H Amination

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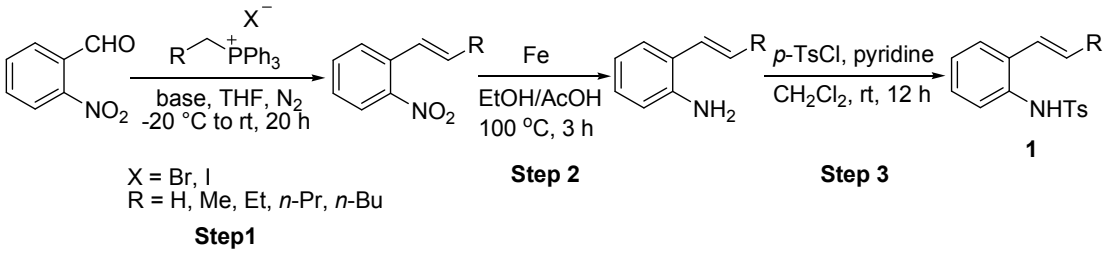
1. General Methods

Unless otherwise stated, commercial reagents were purchased from Alfa, Aladdin, TCI, *J&K,* Accela or Adamas and used without further purification. 1,4-Dioxane, THF, toluene and Et_2O were distilled from sodium prior to use. EtOAc was distilled from P_2O_5. MeCN, DCM and DCE were distilled from calcium hydride. Deuterated chloroform was basified over potassium carbonate. All catalytic reactions were carried out using pre-dried glassware. Reactions were monitored by thin-layer chromatography. Flash column chromatography was carried out using 200-300 mesh silica gel (Qingdao, China), and petroleum ether (60-90 °C) was used.

^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on Brucker ARX 400 MHz spectrometer at ambient temperature. All NMR spectra are referenced to the residual solvent signal. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for $^{13}C\{^1H\}$ NMR are reported as follows: chemical shift (δ ppm), multiplicity (d = doublet, t = triplet, q = quartet), coupling constant (Hz).

MS and HRMS were recorded on Thermo MAT95XP mass spectrometer at analytical center of Sun Yat-Sen University.

2. Procedures for the Preparation of Substrates



Method A: To a solution of triphenylphosphine (1.2 equiv) in dry solvent (acetonitrile or toluene) in a Schlenk tube was added RX (1.3 equiv) dropwise with minimal stirring under a nitrogen atmosphere to give a clear solution. This resulting

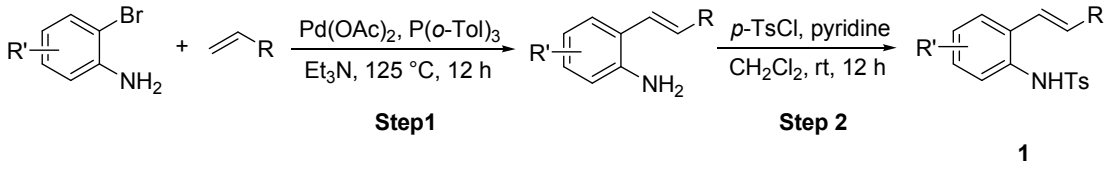
solution was refluxed for hours (36 h in acetonitrile or 48 h in toluene) resulting in the formation of a white precipitate. Then the crude mixture was cooled and the solvent was removed via cannula. The white crystals were washed with Et_2O (10 mL × 3) and the solvent was removed again via cannula to give the phosphonium salt in quantitative yield.

To a solution of phosphonium salt in THF (0.5 M) was added base (1.4 equiv) dropwise at -20 °C under nitrogen. The reaction mixture was stirred at -20 °C for one hour. Then, a solution of 2-nitrobenzaldehyde (1.0 equiv) in THF was added and the mixture was stirred at -20 °C to rt for 20 hours. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with EtOAc (10 mL × 3) and washed with brine. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The obtained residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford the corresponding 2-nitrostyrene product.

To a solution of 2-nitrostyrene (1.0 equiv) in EtOH/AcOH (1:1, v/v, 0.25 M) was added Fe powder (4.0 equiv). The mixture was stirred at 100 °C for 3 hours under nitrogen, and then cooled to room temperature and filtered through a pad of Celite. The solvents were evaporated under reduced pressure. The resulting residue was dissolved in diethyl ether and extracted with 2 M hydrochloric acid. The aqueous fraction was basified using concentrated aqueous sodium hydroxide solution and the product amine was extracted with EtOAc (10 mL × 3). The combined organic fractions were dried over Na_2SO_4, filtered and evaporated under reduced pressure to yield the corresponding product (if necessary, the product was further purified by flash column chromatography on silica gel (eluent: petroleum ether : EtOAc = 100:1, v/v)).

To a solution of 2-styrylaniline (1.0 equiv) in DCM (0.25 M) were added pyridine (1.1 equiv) and *p*-toluenesulfonyl chloride (1.1 equiv) at room temperature under nitrogen. After being stirred at room temperature for 12 hours, the reaction mixture was quenched by the addition of a saturated aqueous solution of NH_4Cl and then the product was extracted with DCM (10 mL × 3). The combined organic phase was

washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether : EtOAc = 100:1→20:1, v/v) to give the corresponding product **1**.[1]



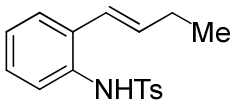
Method B:[2] To a solution of 2-bromoaniline (3.0 mmol, 1.0 equiv) in Et_3N (3.0 mL) were added $Pd(OAc)_2$ (1.0 mol%), P(*o*-Tol)$_3$ (8.0 mol%), and olefin (3.6 mmol, 1.2 equiv). After being stirred at 125 °C for 12 hours, the reaction mixture was poured into water and then the product was extracted with DCM (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether : EtOAc = 30:1, v/v) to afford the corresponding product 2-styrylaniline.

To a solution of 2-styrylaniline (1.0 equiv) in DCM (0.25 M) was added pyridine (1.1 equiv.) and *p*-toluenesulfonyl chloride (1.1 equiv.) at room temperature under nitrogen. After being stirred at room temperature for 12 hours, the reaction mixture was quenched by the addition of a saturated aqueous solution of NH_4Cl and then the product was extracted with DCM (3 × 10 mL), washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether : EtOAc = 100:1→20:1, v/v) to give the corresponding product **1**.

(*E*)-*N*-(2-(But-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1a)

[1] Laha, J. K.; Jethava, K. P.; Dayal, N. *J. Org. Chem*. **2014**, *79*, 8010-8019.

[2] Jang, Y. H.; Youn, S. W. *Org. Lett*. **2014**, *16*, 3720-3723.



Prepared by the Method A: Triphenyl(propyl)phosphonium bromide was synthesized following a previously described procedure.[3] Triphenylphosphine (6.30 g, 24.0 mmol, 1.2 equiv), 1-bromopropane (3.27 mL, 36.0 mmol, 1.8 equiv), and acetonitrile (20.0 mL) were mixed together in a Schlenk flask under a nitrogen atmosphere to give a clear solution, and this solution was heated at 82 °C for 36 h resulting in the formation of a white precipitate. Then the crude mixture was cooled and the solvent was removed via cannula. The white crystals were washed with Et_2O (20 mL × 3) and the solvent was removed again via cannula to give the phosphonium salt in quantitative yield. Use 2-nitrobenzaldehyde (3.02 g, 20.0 mmol, 1.0 equiv) and NaHMDS (2 M) in THF as the base in step 2.[4]

Step 1: 3.37 g, 95% yield and a light yellow oil. Column chromatography: petroleum ether as the eluent.

Step 2: 2.38 g, 90% yield and a yellow oil.

Step 3: 2.56 g, 85% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.1 Hz, 1H), 7.20 (dd, J = 11.9, 5.0 Hz, 3H), 7.08 – 6.97 (m, 2H), 6.75 (s, 1H), 5.90 (d, J = 11.3 Hz, 1H), 5.76 (dt, J = 11.2, 7.3 Hz, 1H), 2.34 (s, 3H), 1.90 (pd, J = 7.5, 1.4 Hz, 2H), 0.90 (t, J = 7.5 Hz, 3H).

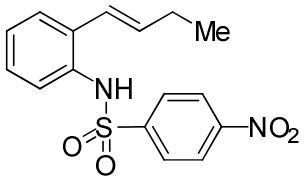
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 139.1, 136.6, 134.2, 129.8, 129.6, 129.5, 129.3, 128.0, 127.1, 124.6, 122.9, 121.2, 77.5, 77.2, 76.8, 21.8, 21.5, 13.9.

HR-ESI-MS m/z calcd. $C_{17}H_{20}O_2NS$ [M + H^+]: 302.12093, found 302.12082.

(*E*)-*N*-(2-(But-1-en-1-yl)phenyl)-4-nitrobenzenesulfonamide (1b)

[3] Hung, K. Y.; Harris, P. W. R.; M. Brimble, A. *Org. Lett*. 2012, 14, 5784-5787.

[4] Arisawa, M.; Fujii, Y.; Kato, H.; Fukuda, H.; Matsumoto, T.; Ito, M.; Abe, H.; Ito, Y.; Shuto, S. *Angew. Chem. Int. Ed*. **2013**, *52*, 1003-1010.



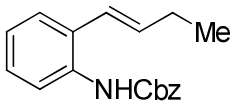
Prepared by the Method A: Use 4-nitrobenzenesulfonyl chloride as a sulfonylation reagent in place of *p*-TsCl. 2-(But-1-en-1-yl)aniline (294.4 mg, 2.0 mmol, 1.0 equiv) was used as the starting material to give the product as a white solid (534.6 mg, 81% yield). Column chromatography: petroleum ether : EtOAc = 100:1→15:1, v/v in step 3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 5.84 – 5.74 (m, 2H), 1.94 – 1.87 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 145.2, 139.8, 133.1, 130.2, 129.9, 128.6, 128.5, 128.5, 128.2, 127.6, 127.4, 125.8, 124.3, 124.3, 122.5, 121.9, 77.5, 77.2, 76.84, 21.9, 14.0.

HR-ESI-MS m/z calcd. $C_{16}H_{15}O_4N_2S$ [M - H^+]: 331.07525, found 331.07532.

(*E*)-Benzyl (2-(but-1-en-1-yl)phenyl)carbamate



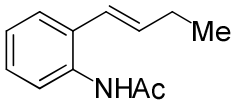
Prepared by the Method A: Use $ClCO_2Bn$ in place of *p*-TsCl. 2-(But-1-en-1-yl)aniline (220.8 mg, 1.5 mmol, 1.0 equiv) was used as the starting material to give the product as a white solid (242.1 mg, 57% yield). Column chromatography: petroleum ether : EtOAc = 100:1→60:1, v/v in step 3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.43 – 7.30 (m, 5H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 6.2 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.73 (s, 1H), 6.25 (d, *J* = 11.2 Hz, 1H), 5.89 – 5.82 (m, 1H), 5.19 (s, 2H), 2.06 – 2.02 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 138.8, 136.2, 135.4, 129.5, 128.7, 128.5, 128.5, 128.0, 123.6, 123.0, 119.1, 67.1, 22.2, 14.0.

HR-ESI-MS m/z calcd. $C_{18}H_{20}O_2N$ [M + H^+]: 282.14886, found 282.14862.

(*E*)-*N*-(2-(But-1-en-1-yl)phenyl)acetamide



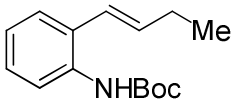
(*E*)-***N***-(2-(But-1-en-1-yl)phenyl)acetamide was synthesized following a previously described procedure.[5] To a solution of 2-(but-1-en-1-yl)aniline (147.2 mg, 1.0 mmol, 1.0 equiv) in DCM (5.0 mL) was added Ac_2O (112.4 μL, 1.2 mmol, 1.2 equiv.) at room temperature under nitrogen. After being stirred at room temperature for 12 hours, the reaction mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ and then the product was extracted with DCM, washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether : EtOAc = 30:1→10:1, v/v) to give the corresponding product (131.5 mg, 70% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.02 (m, 2H), 6.29 (d, *J* = 11.2 Hz, 1H), 5.93 – 5.87 (m, 1H), 2.16 (s, 3H), 2.12 – 2.01 (m, 2H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 138.7, 135.4, 129.4, 127.9, 127.4, 123.8, 123.7, 121.0, 24.8, 22.1, 14.1.

HR-ESI-MS m/z calcd. $C_{12}H_{16}ON$ [M + H^+]: 190.12264, found 190.12267.

(*E*)-*t*-Butyl (2-(but-1-en-1-yl)phenyl)carbamate



(*E*)-*t*-Butyl (2-(but-1-en-1-yl)phenyl)carbamate was synthesized following a previously described procedure.[6] To a solution of 2-(but-1-en-1-yl)aniline (147.2 mg, 1.0 mmol, 1.0 equiv) in EtOH (8.0 mL) was added Boc_2O (436.5 mg, 2.0 mmol, 2.0

[5] Mešková, M.; Putala, M. Tetrahedron Lett. **2011**, *52*, 5379-5383.

[6] Hellal, M.; Cuny, G. D. *J. Org. Chem*. **2010**, *75*, 3465-3468.

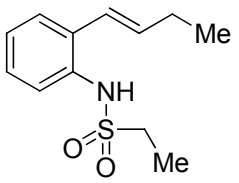
equiv) at room temperature under nitrogen. After being stirred at 90 °C for 24 hours, the solvent was removed and the reaction mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$, then the product was extracted with DCM, washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether : EtOAc = 200:1→100:1, v/v) to give the corresponding product (223.4 mg, 90% yield) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.17 (m, 1H), 7.08 (d, *J* = 6.5 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.52 (s, 1H), 6.27 (d, *J* = 11.2 Hz, 1H), 5.95 – 5.77 (m, 1H), 2.11 – 2.03 (m, 2H), 1.51 (s, 9H), 0.99 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 138.5, 135.9, 129.4, 127.9, 123.8, 122.5, 119.1, 80.5, 28.5, 22.1, 14.1.

HR-ESI-MS m/z calcd. $C_{15}H_{22}O_2N$ [M + H^+]: 248.16451, found 248.16462.

(*E*)-*N*-(2-(But-1-en-1-yl)phenyl)ethanesulfonamide (1b)



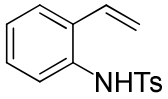
Prepared by the Method A: Use ethanesulfonyl chloride as a sulfonylation reagent in place of *p*-TsCl. 2-(But-1-en-1-yl)aniline (294.4 mg, 2.0 mmol, 1.0 equiv) was used as the starting material to give the product as a light yellow oil (392.3 mg, 82% yield). Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v in step 3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.06 (m, 2H), 6.39 (s, 1H), 6.30 (d, *J* = 11.2 Hz, 1H), 5.98 – 5.91 (m, 1H), 3.13 (q, *J* = 7.4 Hz, 2H), 2.09 – 2.05 (m, 2H), 1.33 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.7, 130.3, 128.5, 127.9, 124.2, 123.0, 118.9, 46.3, 22.1, 14.0, 8.3.

HR-ESI-MS m/z calcd. $C_{12}H_{18}O_2NS$ [M + H^+]: 240.10528, found 240.10543.

4-Methyl-*N*-(2-vinylphenyl)benzenesulfonamide (1d)



Prepared by the Method A: Methyltriphenylphosphonium iodide was synthetized following a literature protocol.[7] To a solution of PPh_3 (3.15 g, 12.0 mmol, 1.2 equiv) in dry THF (20 mL) in a Schlenk tube was added MeI (809.3 μL, 13.0 mmol, 1.3 equiv) dropwise with minimal stirring. A white precipitate was formed immediately. After stirring overnight at room temperature, the solvent was removed via cannula. The white crystals were washed with Et_2O (5 mL × 3) and the solvent was removed again via cannula to give the phosphonium salt in quantitative yield (step 1). Use 2-nitrobenzaldehyde (1.51 g, 10.0 mmol, 1.0 equiv) and NaHMDS (2 M) in THF as the base in step 1.[2] Use HCl in place of AcOH in step 2.[8]

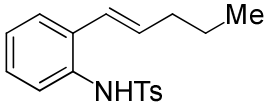
Step 1: 1.18 g, 79% yield and a light yellow oil. Column chromatography: petroleum ether as the eluent.

Step 2: 847.2 mg 90% yield and a yellow oil. Column chromatography: petroleum ether : EtOAc = 200:1→80:1, v/v (step 2)

Step 3: 2-Vinylaniline (238.3 mg, 2.0 mmol, 1.0 equiv) to give the product as a white solid (270 mg, yield 49%). Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v. The NMR data match the reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.25 – 7.11 (m, 4H), 6.61 – 6.46 (m, 2H), 5.50 (dd, J = 17.4, 1.2 Hz, 1H), 5.26 (dd, J = 11.0, 1.1 Hz, 1H), 2.38 (s, 3H).

(*Z*)-4-Methyl-*N*-(2-(pent-1-en-1-yl)phenyl)benzenesulfonamide (1e)



[7] Braddock, D. C.; Clarke, J.; Rzepa, H. S. *Chem. Commun.*, **2013**, *49*, 11176-11178.

[8] Fra, L.; Millan, A.; Souto, J. A.; Muniz, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 7349-7353.

[9] He, H.; Liu, W. B.; Dai, L. X.; You, S. L. *J. Am. Chem. Soc*. **2009**, *131*, 8346-8347.

Prepared by the Method A: Butyltriphenylphosphonium bromide was synthesized following a previously described procedure (step 1).[3] Use 2-nitrobenzaldehyde (755.6 mg, 5.0 mmol, 1.0 equiv) and *n*-BuLi (2.5 M) in hexanes as the base in step 1.[10]

Step 1: 820.0 mg, 86% yield and a light yellow oil. Column chromatography: petroleum ether as the eluent.

Step 2: 622.5 mg, 90% yield and a yellow oil. Column chromatography: petroleum ether : EtOAc = 100:1, v/v.

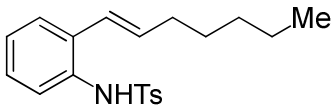
Step 3: 210 g, 17% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 5.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.08 (m, 2H), 6.46 (s, 1H), 6.06 (d, *J* = 15.7 Hz, 1H), 5.95 – 5.88 (m, 1H), 2.38 (s, 3H), 2.12 – 2.01 (m, 2H), 1.49 – 1.32 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.7, 135.9, 132.9, 132.7, 129.7, 127.9, 127.3, 127.2, 126.4, 124.8, 124.1, 35.4, 22.4, 21.7, 13.8.

HR-ESI-MS m/z calcd. $C_{17}H_{20}O_2NS$ [M + H^+]: 302.12093, found 302.12082.

(*E*)-*N*-(2-(Hept-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1f)



Prepared by the Method A: Hexyltriphenylphosphonium bromide was synthesized following the previously described procedure.[11] Use toluene as the solvent, 2-nitrobenzaldehyde (1.51 g, 10.0 mmol, 1.0 equiv) and *n*-BuLi (2.5 M) in hexanes as the base in step 1.[11]

Step 1: 1.97 g, 90% yield and a light yellow oil. Column chromatography: petroleum ether as the eluent.

Step 2: 990.0 mg, 58% yield and a yellow oil. Column chromatography: petroleum ether : EtOAc = 100:1, v/v.

[10] Ceita, L.; Maiti, A. K.; Mestres, R.; Tortajada, A. *J. Chem. Research (S)*, **2001**, 403-404.

[11] Dickschat, J. S.; Helmke, E.; Schulz, S. *Chem. Biodivers.* **2005**, *2*, 318-353.

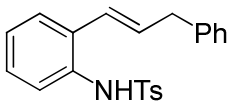
Step 3: 2-(Pent-1-en-1-yl)aniline (378.6 g, 2.0 mmol, 1.0 equiv) to give the product as a white solid (535.8 g, 78% yield). Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.08 (m, 2H), 6.54 (s, 1H), 6.07 (d, *J* = 15.7 Hz, 1H), 5.91 (dt, *J* = 15.6, 6.7 Hz, 1H), 2.38 (s, 3H), 2.10 – 2.04 (m, 2H), 1.37 – 1.25 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.7, 136.2, 132.9, 132.7, 129.7, 127.9, 127.3, 127.2, 126.4, 124.8, 123.83, 33.3, 31.6, 28.9, 22.7, 21.7, 14.2.

HR-ESI-MS m/z calcd. $C_{20}H_{26}O_2NS$ [M + H^+]: 344.16788, found 344.16780.

(*E*)-4-Methyl-*N*-(2-(3-phenylprop-1-en-1-yl)phenyl)benzenesulfonamide (1g)



Prepared by the Method A: Phenethyltriphenylphosphonium bromide was synthesized following a previously described procedure.[12] Use toluene as the solvent, 2-nitrobenzaldehyde (755.6 mg, 5.0 mmol, 1.0 equiv) and *n*-BuLi (2.5 M) in hexanes as the base in step 1.[11]

Step 1: 487.9 mg, 41% yield and a light yellow oil. Column chromatography: petroleum ether as the eluent.

Step 2: 281.3 mg, 77% yield and a light yellow oil. Column chromatography: petroleum ether : EtOAc = 100:1→70 : 1, v/v.

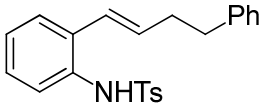
Step 3: 2-(3-Phenylprop-1-en-1-yl)aniline (209.3 mg, 1.0 mmol, 1.0 equiv) to give the product as a white solid (274.1 mg, 75% yield). Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.17 (m, 6H), 7.08 (dd, *J* = 6.2, 3.5 Hz, 4H), 6.59 (s, 1H), 6.08 – 5.95 (m, 2H), 3.24 (d, *J* = 6.7 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 139.7, 136.7, 135.7, 134.5, 129.8, 129.8, 128.8, 128.7, 128.5, 128.3, 127.3, 126.4, 124.9, 124.7, 121.4, 34.5, 21.7.

HR-ESI-MS m/z calcd. $C_{22}H_{22}O_2NS$ [M + H^+]: 364.13658, found 364.13673.

(*E*)-4-Methyl-*N*-(2-(4-phenylbut-1-en-1-yl)phenyl)benzenesulfonamide (1h)



Prepared by the Method A: Triphenyl(3-phenylpropyl)phosphonium bromide was synthesized following a previously described procedure.[12] Use toluene as the solvent, 2-nitrobenzaldehyde (755.6 mg, 5.0 mmol, 1.0 equiv) and *n*-BuLi (2.5 M) in hexanes as the base in step 1.[11]

Step 1: 550.0 mg, 43% yield and a light yellow oil. Column chromatography: petroleum ether as the eluent.

Step 2: 316.1 mg, 85% yield and a light yellow oil. Column chromatography: petroleum ether : EtOAc = 100:1→70 : 1, v/v.

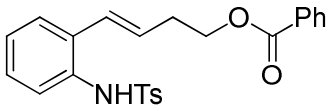
Step 3: 2-(4-Phenylbut-1-en-1-yl)aniline (223.31 mg, 1.0 mmol, 1.0 equiv) to give the product as a white solid (290.9 mg, 77% yield). Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.16 (m, 6H), 7.07 – 6.99 (m, 3H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.39 (s, 1H), 5.89 – 5.77 (m, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 2.21 (q, *J* = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 141.1, 136.7, 136.5, 134.3, 129.8, 129.7, 129.2, 128.5, 128.3, 127.2, 126.2, 124.8, 124.6, 121.3, 35.5, 30.2, 21.6.

HR-ESI-MS m/z calcd. $C_{23}H_{24}O_2NS$ [M + H^+]: 378.15223, found 378.15215.

(*E*)-4-(2-(4-Methylphenylsulfonamido)phenyl)but-3-en-1-yl benzoate (1i)



Prepared by the Method B: But-3-en-1-yl benzoate was synthesized following a previously described procedure.[12]

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[12] Lipshutz, B. H.; Ghorai, S.; Leong, W. W. Y. *J. Org. Chem*, **2009**, *74*, 2854-2857.

Step 1: 2-Bromoaniline (275.2 mg, 1.6 mmol, 1.0 equiv) to give the product as a yellow oil (153.1 mg, 36% yield). Column chromatography: petroleum ether : EtOAc = 50:1→15 : 1, v/v.

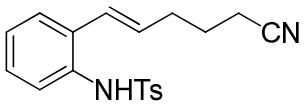
Step 2: 4-(2-Aminophenyl)but-3-en-1-yl benzoate (153.1 mg, 0.57 mmol, 1.0 equiv) to give the product as a white solid (136.6 mg, 57% yield). Column chromatography: petroleum ether : EtOAc = 40:1→8:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.24 – 7.06 (m, 4H), 6.83 (s, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 6.03 – 5.90 (m, 1H), 4.35 (t, *J* = 6.5 Hz, 2H), 2.55 (dd, *J* = 12.9, 6.4 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.9, 136.6, 133.1, 133.1, 132.5, 130.2, 130.1, 129.7, 129.7, 128.5, 128.2, 127.3, 127.2, 127.0, 126.6, 125.2, 64.0, 32.7, 21.6.

HR-ESI-MS m/z calcd. $C_{24}H_{24}O_4NS$ [M + H^+]: 422.14206, found 422.14213.

(*E*)-*N*-(2-(5-Cyanopent-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (1j)



Prepared by the Method B: 2-Bromoaniline (516.1 mg, 3.0 mmol, 1.0 equiv), hex-5-enenitrile (342.5 mg, 3.6 mmol, 1.2 equiv).

Step 1: 330.0 mg, 59% yield and a light yellow oil. Column chromatography: petroleum ether : EtOAc = 100:1→7 : 1, v/v.

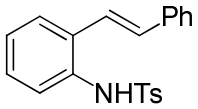
Step 2: 6-(2-Aminophenyl)hex-5-enenitrile (186.3 mg, 1.0 mmol, 1.0 equiv) to give the product as a light yellow oil (295.5 mg, 88% yield). Column chromatography: petroleum ether : EtOAc = 100:1→5:1, v/v.

^{1}H NMR (400 MHz, $CDCl_3$) (*Z* and *E*) δ 7.62 (d, *J* = 8.3 Hz, 3H), 7.35 – 7.20 (m, 6H), 7.19 – 7.07 (m, 3H), 7.02 (d, *J* = 9.3 Hz, 1H), 6.79 (d, *J* = 5.8 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 5.93 – 5.86 (m, 1H), 5.66 – 5.49 (m, 1H), 5.45 – 5.25 (m, 1H), 3.09 (d, *J* = 6.0 Hz, 1H), 2.38 (dd, *J* = 7.9, 4.3 Hz, 5H), 2.33 (t, *J* = 7.1 Hz, 3H), 2.25 (q, *J* = 7.1 Hz, 2H), 1.90 – 1.86 (m, 1H), 1.75 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.8, 136.6, 134.6, 132.9, 132.7, 131.8, 131.0, 130.4, 129.7, 129.7, 128.2, 128.1, 127.6, 127.3, 127.2, 126.9, 126.7, 126.4, 125.5, 125.1, 119.8, 119.4, 34.5, 31.9, 28.3, 24.7, 21.6, 17.4, 16.5.

HR-ESI-MS m/z calcd. $C_{19}H_{21}O_2N_2S$ [M + H^+]: 341.13183, found 341.13166.

(*E*)-4-Methyl-*N*-(2-styrylphenyl)benzenesulfonamide (1k)



Prepared by the Method A: Benzyltriphenylphosphonium bromide was synthesized following a previously described procedure.[12] Use toluene as the solvent, 2-nitrobenzaldehyde (755.6 mg, 5.0 mmol, 1.0 equiv) and *n*-BuLi (2.5 M) in hexanes as the base in step 1.[11]

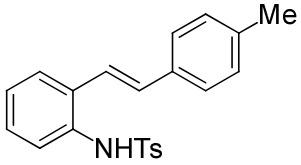
Step 1: 820.0 mg, 73% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1, v/v.

Step 2: 613.2 mg, 86% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→50 : 1, v/v.

Step 3: 910.0 mg, 83% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v. The NMR data match the reported in the literature.[2]

^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.5 Hz, 3H), 7.29 – 6.98 (m, 8H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.69 – 6.56 (m, 2H), 6.13 (s, 1H), 2.33 (s, 3H).

(*E*)-4-Methyl-N-(2-(4-methylstyryl)phenyl)benzenesulfonamide (1l)



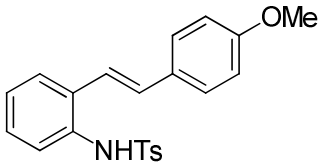
Prepared by the Method B: 2-Bromoaniline (516.1 mg, 3.0 mmol, 1.0 equiv), 1-methyl-4-vinylbenzene (474.8 μL, 3.6 mmol, 1.2 equiv).

Step 1: Product 366.4 mg, 58% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→60 : 1, v/v.

Step 2: 2-(4-Methylstyryl)aniline (272.1 mg, 1.3 mmol, 1.0 equiv) to give the product as a white solid (436.6 mg, 92% yield). Column chromatography: petroleum ether : EtOAc = 100:1→5:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.40 – 7.35 (m, 1H), 7.25 – 7.17 (m, 4H), 7.13 (dd, *J* = 7.9, 6.0 Hz, 4H), 6.80 – 6.69 (m, 3H), 2.35 (s, 3H), 2.28 (s, 3H).

(*E*)-*N*-(2-(4-Methoxystyryl)phenyl)-4-methylbenzenesulfonamide (1m)



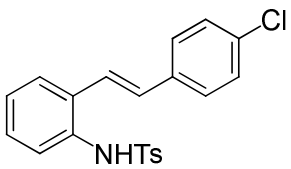
Prepared by the Method B: 2-Bromoaniline (602.1 mg, 3.5 mmol, 1.0 equiv), 1-methoxy-4-vinylbenzene (579.2 μL, 4.2 mmol, 1.2 equiv).

Step 1: 616.0 mg, 81% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→20 : 1, v/v.

Step 2: 2-(4-Methoxystyryl)aniline (337.9 mg, 1.5 mmol, 1.0 equiv) to give the product as a white solid (498.5 mg, 88% yield). Column chromatography: petroleum ether : petroleum ether : EtOAc = 100:1→5:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.35 (dd, *J* = 6.1, 3.1 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 3H), 6.71 (s, 2H), 3.82 (s, 3H), 2.27 (s, 3H).

(*E*)-*N*-(2-(4-Chlorostyryl)phenyl)-4-methylbenzenesulfonamide (1n)



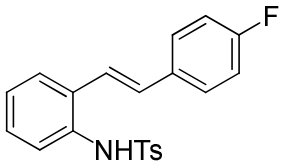
Prepared by the Method B: 2-Bromoaniline (516.1 mg, 3.0 mmol, 1.0 equiv), 1-chloro-4-vinylbenzene (431.6 μL, 3.6 mmol, 1.2 equiv).

Step 1: 481.0 mg, 70% **y**ield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→50:1, v/v.

Step 2: 2-(4-Chlorostyryl)aniline (344.6 mg, 1.5 mg, 1.0 equiv) to give the product as white solide (67% yield). Column chromatography: petroleum ether : EtOAc = 100:1→5:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.49 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.34 – 7.20 (m, 8H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.60 (m, 3H), 2.30 (s, 3H).

(*E*)-*N*-(2-(4-Fluorostyryl)phenyl)-4-methylbenzenesulfonamide (1o)



Prepared by the Method B: 2-Bromoaniline (516.1 mg, 3.0 mmol, 1.0 equiv), 1-fluoro-4-vinylbenzene (429.0 μL, 3.6 mmol, 1.2 equiv).

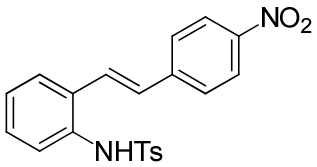
Step 1: 537.6 mg, 84% **y**ield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→50:1, v/v.

Step 2: 2-(4-Fluorostyryl)aniline (344.6 mg, 1.5 mg, 1.0 equiv) to give the product as a white solid (494.3 mg, 90% yield). Column chromatography: petroleum ether : EtOAc = 100:1→5:1, v/v. The NMR data match the reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 2H), 7.51 – 7.43 (m, 1H), 7.34 – 7.27 (m, 3H), 7.24 – 7.18 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.96 (m, 2H), 6.87 – 6.70 (m, 3H), 2.29 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.42.

(*E*)-4-Methyl-*N*-(2-(4-nitrostyryl)phenyl)benzenesulfonamide (1p)



[13] Li, Y. L.; Li, J.; Ma, A. L.; Huang, Y. N.; Deng, J. *J. Org. Chem.* **2015**, *80*, 3841-3851.

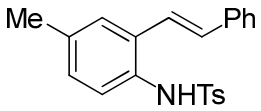
Prepared by the Method B: 2-Bromoaniline (688.1 mg, 4.0 mmol, 1.0 equiv), 1-nitro-4-vinylbenzene (615.6 μL, 4.8 mmol, 1.2 equiv).

Step 1: 541.5 mg, 56% **y**ield and a red solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v.

Step 2: 2-(4-Nitrostyryl)aniline (288.3 mg, 1.2 mmol, 1.0 equiv) to give the product as a yellow solid (415.6 mg, 88% yield). Column chromatography: petroleum ether : petroleum ether : EtOAc = 100:1→5:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.96 – 6.84 (m, 2H), 2.31 (s, 3H).

(*E*)-4-Methyl-*N*-(4-methyl-2-styrylphenyl)benzenesulfonamide (1q)



Prepared by the Method B: 2-Bromo-4-methylaniline (558.2 mg, 3.0 mmol, 1.0 equiv), styrene (413.8 μL, 3.6 mmol, 1.2 equiv).

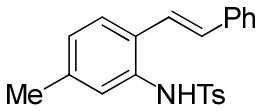
Step 1: 535.3 mg, 85% yield and a light yellow solid. Column chromatography: petroleum ether : EtOAc = 100:1→30:1, v/v.

Step 2: 787.7 mg, 85% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.22 – 7.13 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.88 (m, 2H), 6.70 (d, *J* = 16.1 Hz, 1H), 2.28 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 137.1, 136.9, 136.4, 133.7, 131.0, 130.6, 129.6, 129.08, 128.5, 127.8, 127.1, 126.8, 126.7, 126.6, 123.0, 21.4, 21.1.

(*E*)-4-Methyl-*N*-(5-methyl-2-styrylphenyl)benzenesulfonamide (1r)



Prepared by the Method B: 2-Bromo-5-methylaniline (558.2 mg, 3.0 mmol, 1.0 equiv), styrene (413.8 μL, 3.6 mmol, 1.2 equiv).

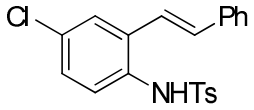
Step 1: 476.0 mg, 76% yield and a light yellow solid. Column chromatography: petroleum ether : EtOAc = = 100:1→30:1, v/v.

Step 2: 641.8 mg, 80% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.18 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.85 – 6.62 (m, 3H), 2.32 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.7, 137.0, 136.6, 133.1, 131.1, 130.5, 129.7, 128.7, 128.2, 127.9, 127.8, 127.2, 126.7, 126.3, 122.6, 77.5, 77.2, 76.8, 21.6, 21.3.

(*E*)-*N*-(4-Chloro-2-styrylphenyl)-4-methylbenzenesulfonamide **(1s)**



Prepared by the Method B: 2-Bromo-4-chloroaniline (619.4 mg, 3.0 mmol, 1.0 equiv), styrene (413.8 μL, 3.6 mmol, 1.2 equiv).

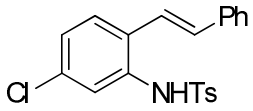
Step 1: 573.0 mg, 83% yield and a light yellow solid. Column chromatography: petroleum ether : EtOAc = 100:1→30:1, v/v.

Step 2: 697.5 mg, 73% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.34 – 7.23 (m, 6H), 7.16 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.13 – 7.07 (m, 3H), 6.82 (d, *J* = 16.1 Hz, 1H), 6.71 (d, *J* = 16.1 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 136.4, 136.2, 135.3, 133.0, 133.0, 131.8, 129.8, 129.8, 128.7, 128.6, 128.5, 128.2, 127.2, 127.0, 126.2, 121.5, 21.6.

(*E*)-*N*-(5-Chloro-2-styrylphenyl)-4-methylbenzenesulfonamide (1t)



Prepared by the Method B: 2-Bromo-5-chloroaniline (619.4 mg, 3.0 mmol, 1.0 equiv), styrene (413.8 μL, 3.6 mmol, 1.2 equiv).

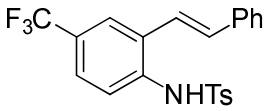
Step 1: 566.3 mg, 82% yield and a light yellow solid. Column chromatography: petroleum ether : EtOAc = 100:1→30:1, v/v.

Step 2: 641.8 mg, 68% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 4.5 Hz, 4H), 7.27 (dd, *J* = 7.0, 3.5 Hz, 1H), 7.18 – 7.09 (m, 4H), 6.81 (d, *J* = 16.1 Hz, 1H), 6.72 (d, *J* = 16.1 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 136.5, 136.2, 134.3, 133.6, 132.7, 131.4, 129.9, 128.7, 128.4, 127.5, 127.2, 127.1, 126.8, 126.2, 121.5, 21.6.

(*E*)-4-Methyl-*N*-(2-styryl-4-(trifluoromethyl)phenyl)benzenesulfonamide (1u)



Prepared by the Method B: 2-Bromo-4-(trifluoromethyl)aniline (720.1 mg, 3.0 mmol, 1.0 equiv), styrene (413.8 μL, 3.6 mmol, 1.2 equiv).

Step 1: 591.0 mg, 75% yield and a light yellow solid. Column chromatography: petroleum ether : EtOAc = 100:1→30:1, v/v.

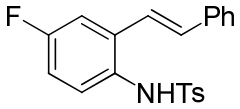
Step 2: 704.4 mg, 75% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 3H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.45 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 16.1 Hz, 1H), 6.82 (d, *J* = 16.1 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 136.6, 136.2, 136.2, 134.3, 132.4, 130.0, 128.8, 128.7, 128.5, 128.2, 127.2, 127.0, 125.3, 125.1, 125.1, 124.8, 124.0, 123.9, 122.6, 121.2, 77.5, 77.2, 76.8, 21.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.39.

(*E*)-*N*-(4-Fluoro-2-styrylphenyl)-4-methylbenzenesulfonamide (1v)



Prepared by the Method B: 2-Bromo-4-fluoroaniline (570.0 mg, 3.0 mmol, 1.0 equiv), styrene (413.8 μL, 3.6 mmol, 1.2 equiv).

Step 1: 266.2 mg, 42% **y**ield and a light yellow solid. Column chromatography: petroleum ether : EtOAc = 100:1→30:1, v/v.

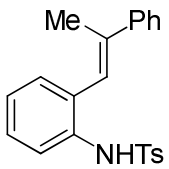
Step 2: 366.0 mg, 75% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→10:1, v/v. The NMR data match the reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.28 (ddd, *J* = 8.7, 7.7, 4.0 Hz, 6H), 7.19 (dd, *J* = 9.7, 2.9 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.97 – 6.88 (m, 2H), 6.84 (d, *J* = 16.1 Hz, 1H), 6.72 (d, *J* = 16.1 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 160.5, 144.1, 136.6, 136.5, 136.4, 136.2, 132.6, 130.3, 130.2, 129.8, 129.1, 129.0, 128.8, 128.7, 128.4, 127.3, 127.0, 122.0, 122.0, 115.4, 115.2, 112.6, 112.4, 21.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.83.

(*E*)-4-Methyl-*N*-(2-(2-phenylprop-1-en-1-yl)phenyl)benzenesulfonamide (3)



Prepared by the Method A: Triphenyl(1-phenylethyl)phosphonium bromide was synthesized following a previously described procedure.[12] Use toluene as the solvent

and 2-nitrobenzaldehyde (755.6 mg, 5.0 mmol, 1.0 equiv) and *n*-BuLi (2.5 M) in hexanes as the base in step 1.[11]

Step 1: 784.3 mg, 66% yield and a light yellow solid. Column chromatography: petroleum ether.

Step 2: 496.4 mg, 74% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→70:1, v/v.

Step 3: 514.9 mg, 94% yield and a white solid. Column chromatography: petroleum ether : EtOAc = 100:1→20:1, v/v. The NMR data match the reported in the literature.[2]

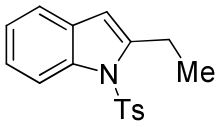
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 5.8 Hz, 3H), 7.36 (dd, *J* = 5.8, 4.4 Hz, 4H), 7.35 – 7.29 (m, 1H), 7.28 – 7.23 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.59 (s, 1H), 6.21 (s, 1H), 2.36 (s, 3H), 1.88 (d, *J* = 1.2 Hz, 3H).

3. General Procedure for the Synthesis of Indoles via C–H Amination

Method C: To a solution of substrate **1** or **3** (0.1 mmol, 1.05 equiv) in dioxane (1.0 mL) were added NFSI (0.1 mmol, 1.0 equiv) and PhSeSePh (10 mol%). The resulting mixture was stirred at 30 °C for 18 h under nitrogen atmosphere. After the reaction was completed, K_2CO_3 was added to the reaction mixture to eliminate HF. The resulting mixture was stirred at room temperature for 10 minutes, and then concentrated under reduced pressure. The residue was directly purified by flash column chromatography on silica gel to give the corresponding product **2** or **4**.

4. Charaterization Data for Products

2-Ethyl-1-tosyl-1*H*-indole (2a)



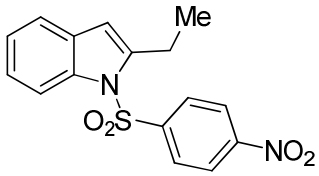
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2a** (23.5 mg, 79 % yield) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.13 (m, 4H), 6.38 (s, 1H), 3.02 (q, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.33 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 144.0, 137.4, 136.4, 129.9, 126.4, 123.9, 123.5, 120.2, 114.8, 107.8, 22.5, 21.7, 13.1.

HR-ESI-MS m/z calcd. $C_{17}H_{18}O_2NS$ [M + H^+]: 300.10528, found 300.10532.

2-Ethyl-1-((4-nitrophenyl)sulfonyl)-1*H*-indole (2b)



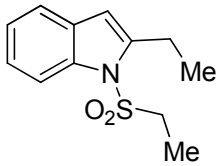
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2b** (20.1 mg, 61 % yield) as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.19 (m, 2H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.47 – 7.40 (m, 1H), 7.26 (dqd, *J* = 14.9, 7.3, 1.3 Hz, 2H), 6.45 (d, *J* = 0.7 Hz, 1H), 3.00 (qd, *J* = 7.3, 1.2 Hz, 2H), 1.36 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 144.3, 143.8, 137.2, 130.1, 127.7, 124.6, 124.4, 120.7, 114.8, 109.4, 22.7, 13.1.

HR-ESI-MS m/z calcd. $C_{16}H_{13}O_4N_2S$ [M - H^+]: 329.06015, found 329.06009.

2-Ethyl-1-(ethylsulfonyl)-1*H*-indole (2c)



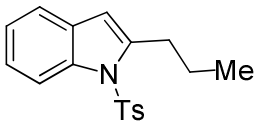
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2c** (12.9 mg, 54 % yield) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 6.2, 2.6 Hz, 1H), 7.49 (dd, *J* = 5.8, 3.1 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.45 (s, 1H), 3.23 (q, *J* = 7.4 Hz, 2H), 3.00 (q, *J* = 7.3 Hz, 2H), 1.37 (t, *J* = 7.4 Hz, 3H), 1.19 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 137.2, 129.7, 124.0, 123.5, 120.4, 114.2, 107.0, 22.37, 13.2, 7.9.

HR-ESI-MS m/z calcd. $C_{12}H_{16}O_2NS$ [M - H^+]: 238.08963, found 238.08975.

2-Propyl-1-tosyl-1*H*-indole (2e)



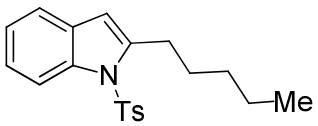
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2e** (22.0 mg, 70 % yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.08 (m, 4H), 6.37 (s, 1H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.82 – 1.73 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 142.4, 137.3, 136.3, 130.0, 129.9, 126.4, 123.9, 123.56, 120.2, 114.9, 108.8, 31.2, 22.3, 21.7, 14.1.

HR-ESI-MS m/z calcd. $C_{18}H_{20}O_2NS$ [M - H^+]: 314.12093, found 314.12099.

2-Pentyl-1-tosyl-1*H*-indole (2f)



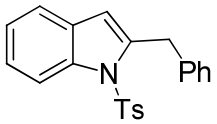
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2f** (25.8 mg, 76 % yield) as a light yellow oil. The NMR data match the reported in the literature data.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.28 – 7.13 (m, 4H), 6.37 (s, 1H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.81 – 1.66 (m, 2H), 1.47 – 1.30 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H).

[14] Swamy, N. K.; Yazici, A.; Pyne, G. S. *J. Org. Chem.* **2010**, *75*, 3412-3419.

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 142.7, 137.3, 136.4, 130.0, 129.9, 126.4, 123.9, 123.55, 120.1, 114.9, 108.7, 31.7, 29.1, 28.7, 22.6, 21.7, 14.2.

2-Benzyl-1-tosyl-1*H*-indole (2g)



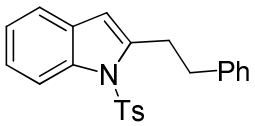
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2g** (21.6 mg, 60 % yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.31 – 7.16 (m, 7H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.10 (s, 1H), 4.35 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 141.1, 138.1, 137.3, 136.2, 129.9, 129.5, 128.6, 126.8, 126.5, 124.2, 123.6, 120.4, 114.8, 111.0, 35.4, 21.7.

HR-ESI-MS m/z calcd. $C_{22}H_{20}O_2NS$ [M + H^+]: 362.12093, found 362.12101.

2-Phenethyl-1-tosyl-1*H*-indole (2h)



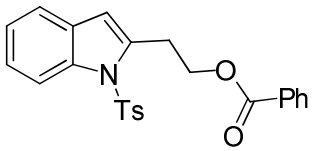
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2h** (31.5 mg, 84 % yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.18 (m, 7H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.38 (s, 1H), 3.39 – 3.21 (m, 2H), 3.14 – 2.98 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 141.5, 141.3, 137.3, 136.2, 129.9, 129.9, 128.6, 128.56, 126.4, 126.3, 124.1, 123.7, 120.3, 115.0, 109.5, 35.7, 31.2, 21.7.

HR-ESI-MS m/z calcd. $C_{23}H_{22}O_2NS$ [M + H^+]: 376.13658, found 376.13648.

2-(1-Tosyl-1H-indol-2-yl)ethyl benzoate (2i)



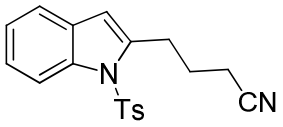
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 20:1, v/v) to afford **2i** (26.9 mg, 64 % yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 3H), 7.30 – 7.15 (m, 4H), 6.52 (s, 1H), 4.71 (t, *J* = 6.5 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 145.0, 137.6, 137.3, 136.0, 133.1, 130.2, 130.0, 129.7, 128.5, 126.4, 124.4, 123.8, 120.5, 115.0, 110.4, 63.4, 28.9, 21.7.

HR-ESI-MS m/z calcd. $C_{24}H_{22}O_4NS$ [M + H^+]: 420.12641, found 420.12652.

4-(1-Tosyl-1*H*-indol-2-yl)butanenitrile (2j)



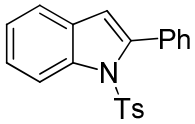
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 20:1, v/v) to afford **2j** (10.5 mg, 31 % yield) as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.19 (t, *J* = 6.2 Hz, 2H), 6.46 (s, 1H), 3.17 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 2.23 – 2.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 139.2, 137.5, 130.0, 126.3, 124.6, 123.9, 120.5, 115.1, 110.7, 28.2, 25.2, 21.7, 16.7.

HR-ESI-MS m/z calcd. $C_{19}H_{19}O_2N_2S$ [M + H^+]: 339.11618, found 339.11609.

2-Phenyl-1-tosyl-1*H*-indole (2k)

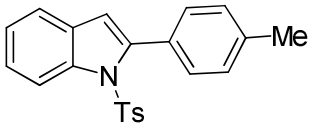


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2k** (31.0 mg, 89 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 4H), 7.35 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 0.6 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 142.2, 138.4, 134.7, 132.5, 130.7, 130.4, 129.3, 128.8, 127.6, 126.9, 124.9, 124.4, 120.8, 116.8, 113.8, 21.6.

2-(*p*-Tolyl)-1-tosyl-1*H*-indole (2l)



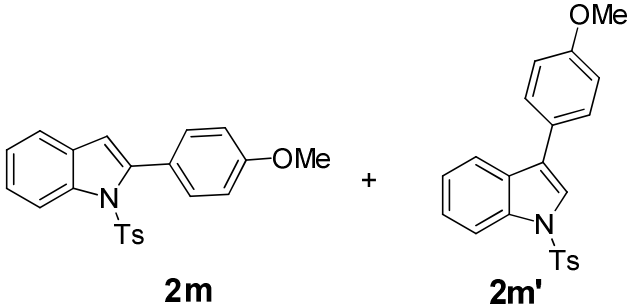
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2l** (35.5 mg, 98 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 7.3, 4.7 Hz, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.25 – 7.19 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.49 (s, 1H), 2.43 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 142.4, 138.7, 138.3, 134.7, 130.8, 130.3, 129.6, 129.26, 128.4, 126.9, 124.7, 124.4, 120.7, 116.8, 113.4, 21.6, 21.6.

2-(4-Methoxyphenyl)-1-tosyl-1*H*-indole (2m)

and 3-(4-Methoxyphenyl)-1-tosyl-1*H*-indole (2m')



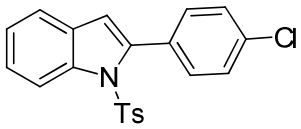
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2m** (36.6 mg, 97 % yield (**2m**, 87%; **2m'**, 10%)) as a white solid. The NMR data match the reported in the literature.[2]

Signals relate to **2m:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.3 Hz, 3H), 7.32 (dd, *J* = 11.4, 4.1 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.47 (s, 1H), 3.87 (s, 3H), 2.31 (s, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 144.6, 142.1, 138.2, 134.7, 131.7, 130.8, 130.0, 129.3, 129.1, 127.0, 126.9, 124.9, 124.8, 124.6, 124.4, 123.6, 122.4, 120.640, 120.540, 116.8, 114. 5, 113.9, 113.1, 113.0, 55.4, 21.6.

HR-ESI-MS m/z calcd. $C_{22}H_{20}O_3NS$ [M + H^+]: 378.11584, found 378.11572.

2-(4-Chlorophenyl)-1-tosyl-1*H*-indole (2n)

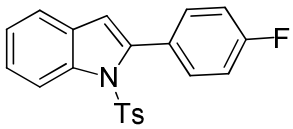


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2n** (37.8 mg, 99 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.34 (m, 6H), 7.28 – 7.23 (m, 3H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.53 (s, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.9, 138.4, 134.8, 134.5, 131.6, 131.0, 130.5, 130.4, 129.4, 127.9, 127.6, 126.9, 126.8, 125.2, 124.6, 120.9, 116. 8, 114.2, 21.6.

2-(4-Fluorophenyl)-1-tosyl-1*H*-indole (2o)



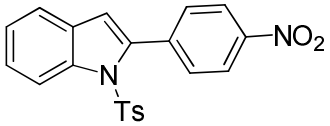
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2o** (36.3 mg, 99 % yield) as a white solid. The NMR data match the reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 11.4, 3.9 Hz, 3H), 7.10 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.51 (s, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 161.9, 144.8, 141.0, 138.3, 134.7, 132.23, 132.2 130.5, 129.4, 128.5, 128.5, 126.8, 125.0, 124.5, 120.8, 116.7, 114.8, 114.6, 113.8, 21.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.56.

2-(4-Nitrophenyl)-1-tosyl-1*H*-indole (2p)

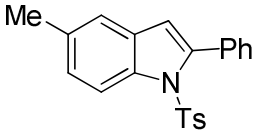


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 60:1, v/v) to afford **2p** (38.4 mg, 98 % yield) as a yellow solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (t, *J* = 8.8 Hz, 3H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.32 – 7.22 (m, 3H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.70 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 145.2, 139.7, 139.0, 138.9, 133.9, 130.8, 130.4, 129.5, 126.7, 126.0, 125.0, 123.0, 121.4, 116.9, 116.3, 21.7.

5-Methyl-2-phenyl-1-tosyl-1*H*-indole (2q)

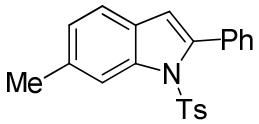


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2q** (32.8 mg, 91 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.50 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.28 – 7.23 (m, 2H), 7.20 (s, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.46 (s, 1H), 2.39 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.3, 136.6, 134.6, 134.1, 132.6, 130.9, 130.4, 129.26, 128.7, 127.6, 126.9, 126.3, 120.8, 116.5, 113.8, 21.6, 21.4.

6-Methyl-2-phenyl-1-tosyl-1*H*-indole (2r)

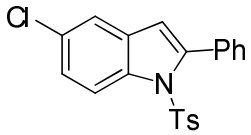


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2r** (31.6 mg, 88 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.48 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.40 (dd, *J* = 7.0, 3.5 Hz, 3H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.48 (s, 1H), 2.52 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 141.6, 138.8, 135.0, 134.7, 132.7, 130.4, 129.3, 128.6, 128.4, 127.6, 126.9, 125.9, 120.3, 116.9, 113.8, 22.2, 21.7.

5-Chloro-2-phenyl-1-tosyl-1*H*-indole (2s)

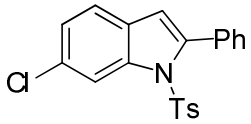


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2s** (33.1 mg, 87 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.38 (m, 6H), 7.30 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.46 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0 143.7, 136.7, 134.4, 132.0, 131.8, 130.5, 130.1, 129.4, 129.1, 127.7, 126.9, 125.0, 120.4, 117.8, 112.8, 21.7.

6-Chloro-2-phenyl-1-tosyl-1*H*-indole (2t)

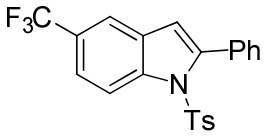


Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2t** (36.4 mg, 95 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 0.9 Hz, 1H), 7.48 – 7.38 (m, 5H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.24 (dd, *J* = 12.7, 5.0 Hz, 3H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.48 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 142.8, 138.7, 134.6, 132.0, 130.7, 130.5, 129.5, 129.0, 127.0, 127.7, 126.9, 125.0, 121.5, 116.8, 113.0, 21.7.

2-Phenyl-1-tosyl-5-(trifluoromethyl)-1*H*-indole (2u)



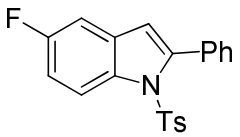
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **2u** (38.7 mg, 93 % yield) as a white solid. The NMR data match the reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.8 Hz, 1H), 7.74 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.51 – 7.36 (m, 5H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.58 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 143.8, 139.7, 134.7, 131.7, 130.7, 130.6, 130.1, 129.6, 129.6, 129.2, 127.7, 127.0, 126.9, 126.8, 126.4, 126.0, 123.3, 121.5, 121.5, 118.3, 118.2, 116.8, 112.9, 21.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -61.27.

5-Fluoro-2-phenyl-1-tosyl-1*H*-indole (2v)



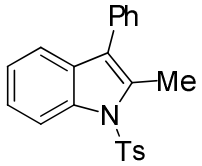
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford 2v (35.0 mg, 96 % yield) as a white solid. The NMR data match the reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 9.7, 4.4 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.42 (d, *J* = 6.4 Hz, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.05 (dd, *J* = 14.8, 8.3 Hz, 4H), 6.49 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 159.1, 144.9, 144.1, 134.6, 134.3, 132.1, 131.8, 131.7, 130.4, 129.4, 129.0, 127.7, 126.9, 118.0, 117.9, 113.5, 113.4, 112.8, 112.5, 106.5, 106.3, 21.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -118.54.

2-Methyl-3-phenyl-1-tosyl-1*H*-indole (4)



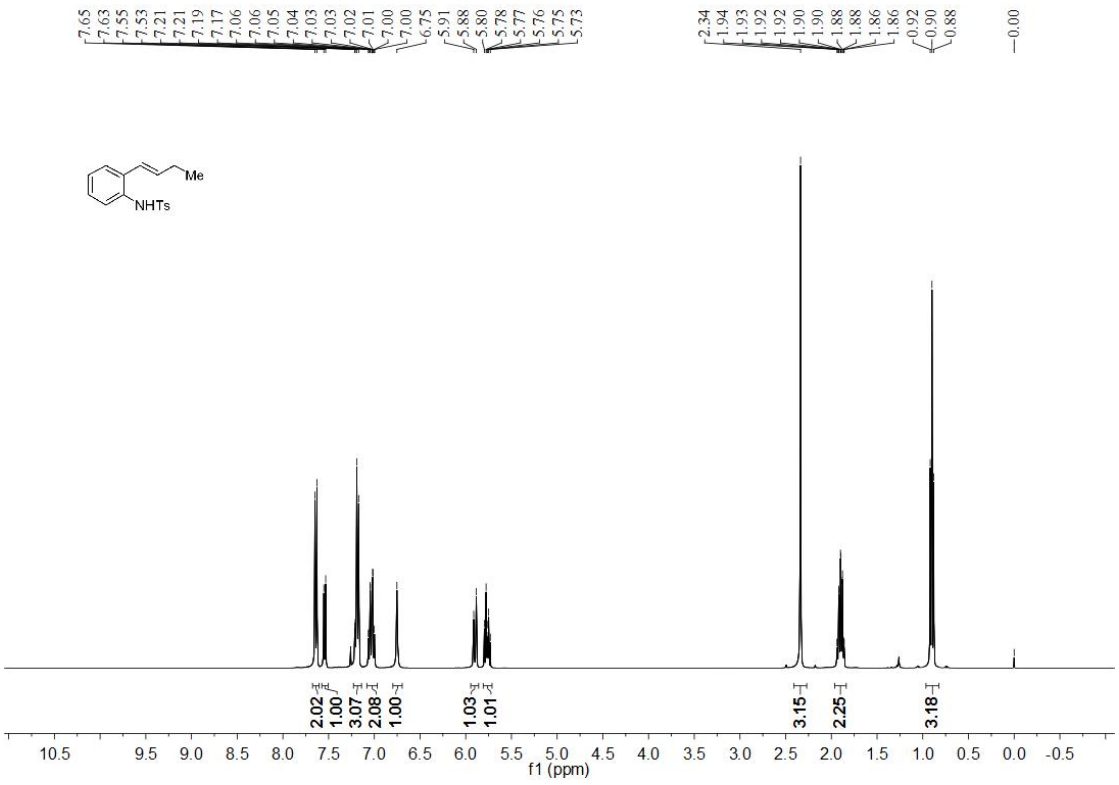
Prepared by the method C. Column chromatography (eluent: petroleum ether : EtOAc = 100:1, v/v) to afford **4** (35.7 mg, 99 % yield) as a white solid. The NMR data match the reported in the literature.[2]

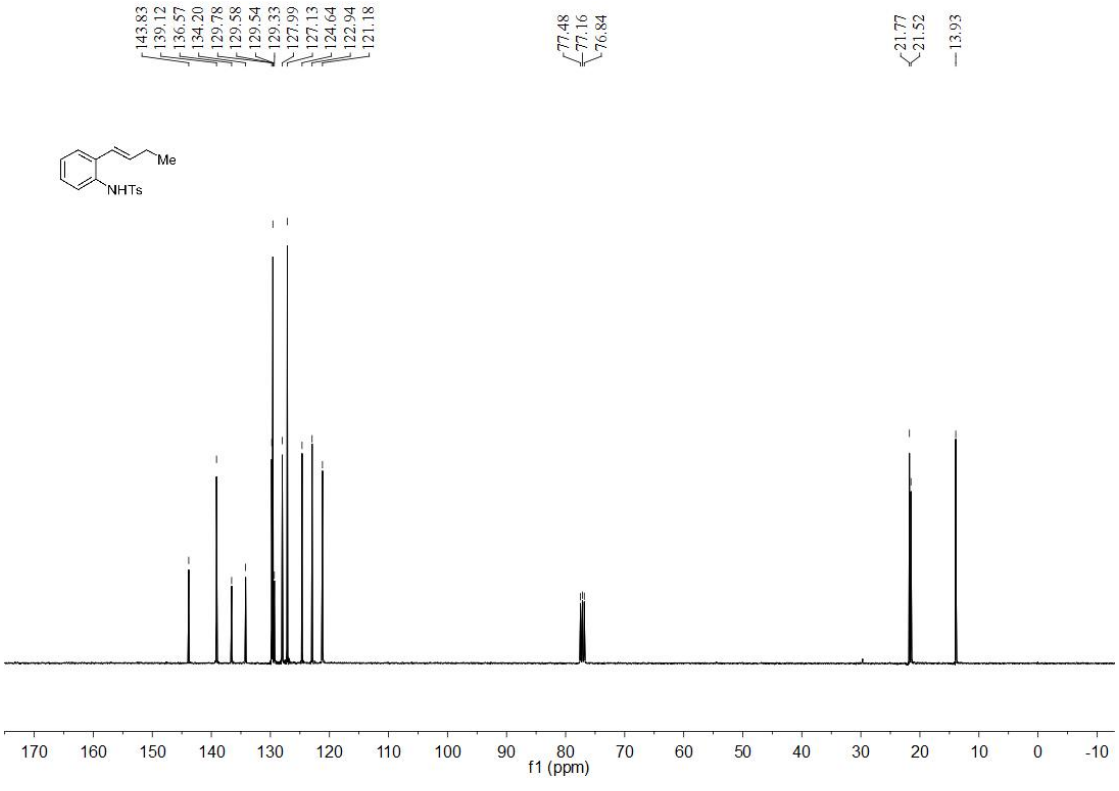
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.35 (t, *J* = 6.7 Hz, 3H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.17 (m, 3H), 2.59 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.5, 136.4, 133.2, 133.2, 130.2, 130.1, 130.0, 128.7, 127.4, 126.5, 124.4, 123.6, 122.7, 119.3, 114.6, 21.7, 13.7.

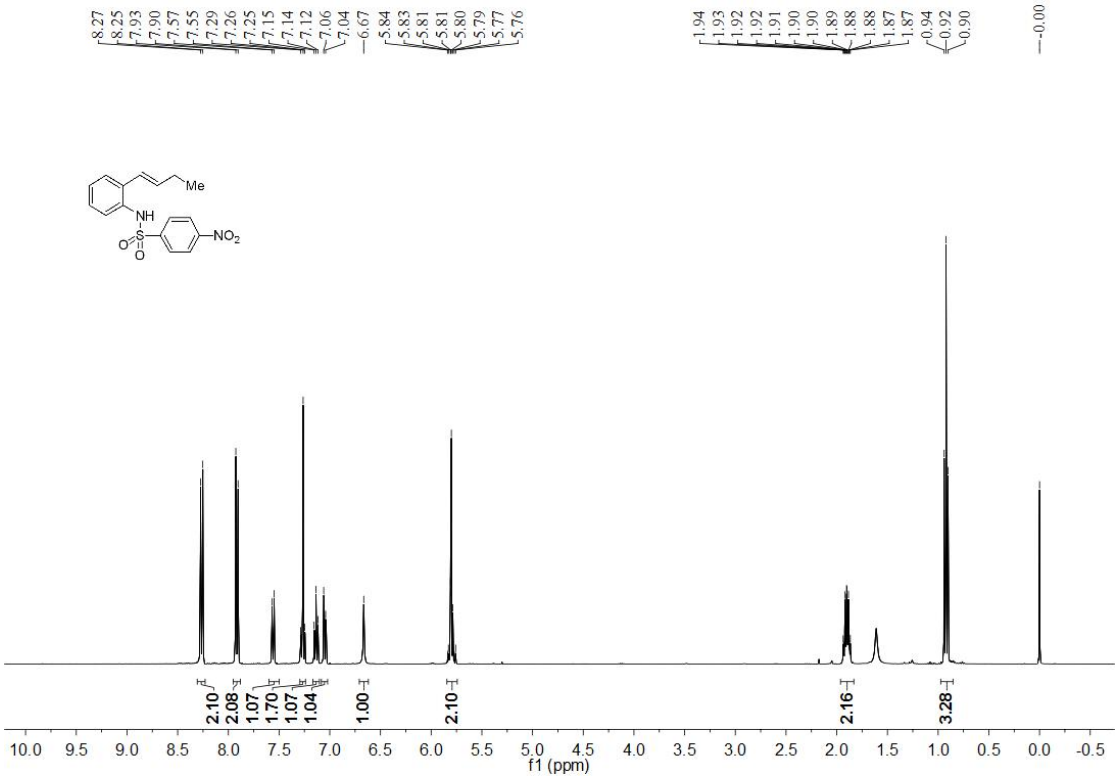
5. NMR Spectra for Substrates and Products

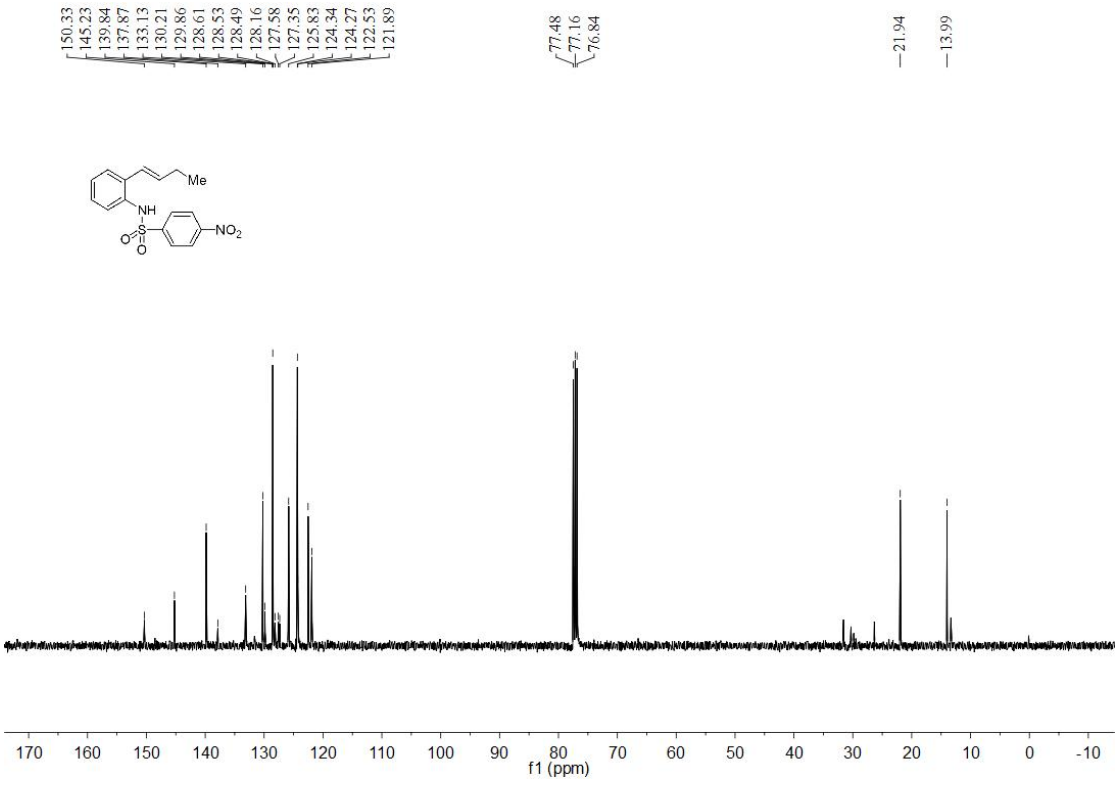
NMR Spectra of Substrate 1a



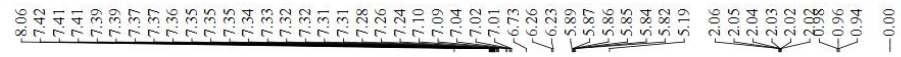


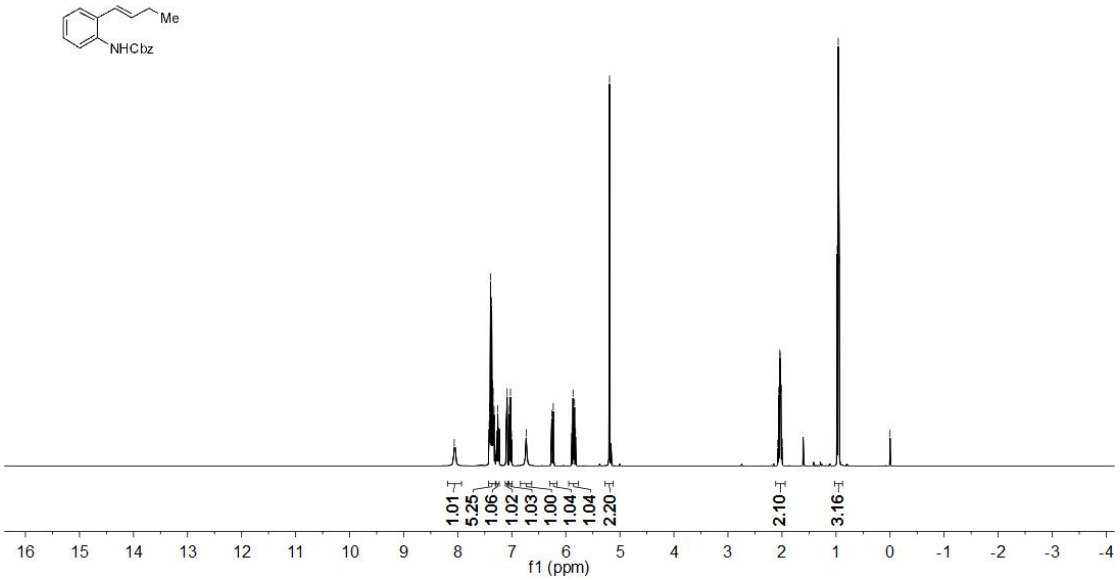
NMR Spectra of Substrate 1b

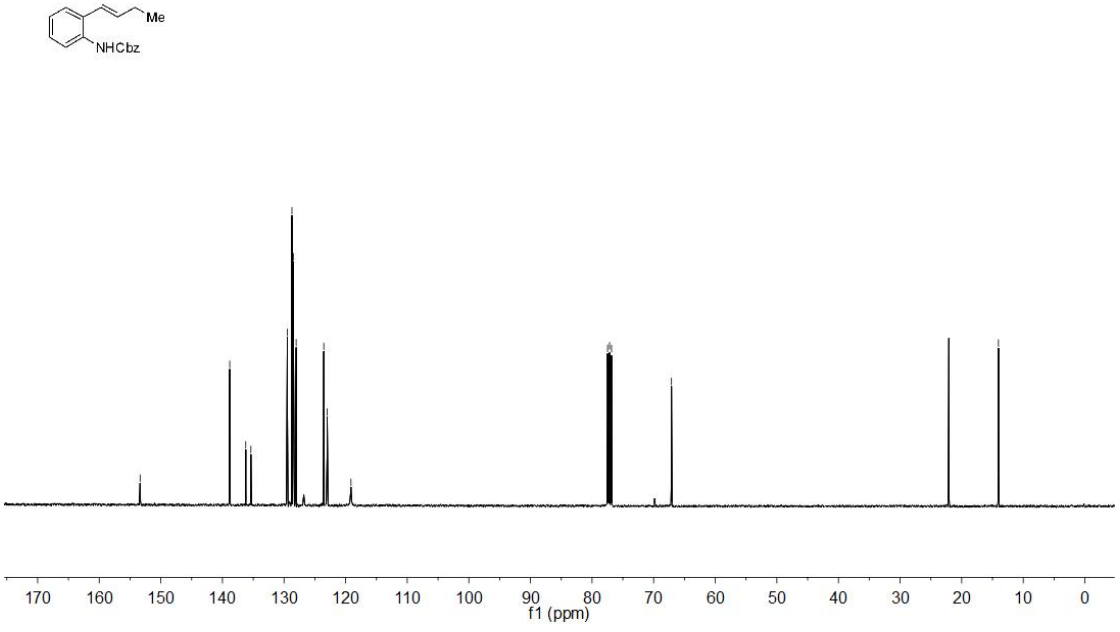




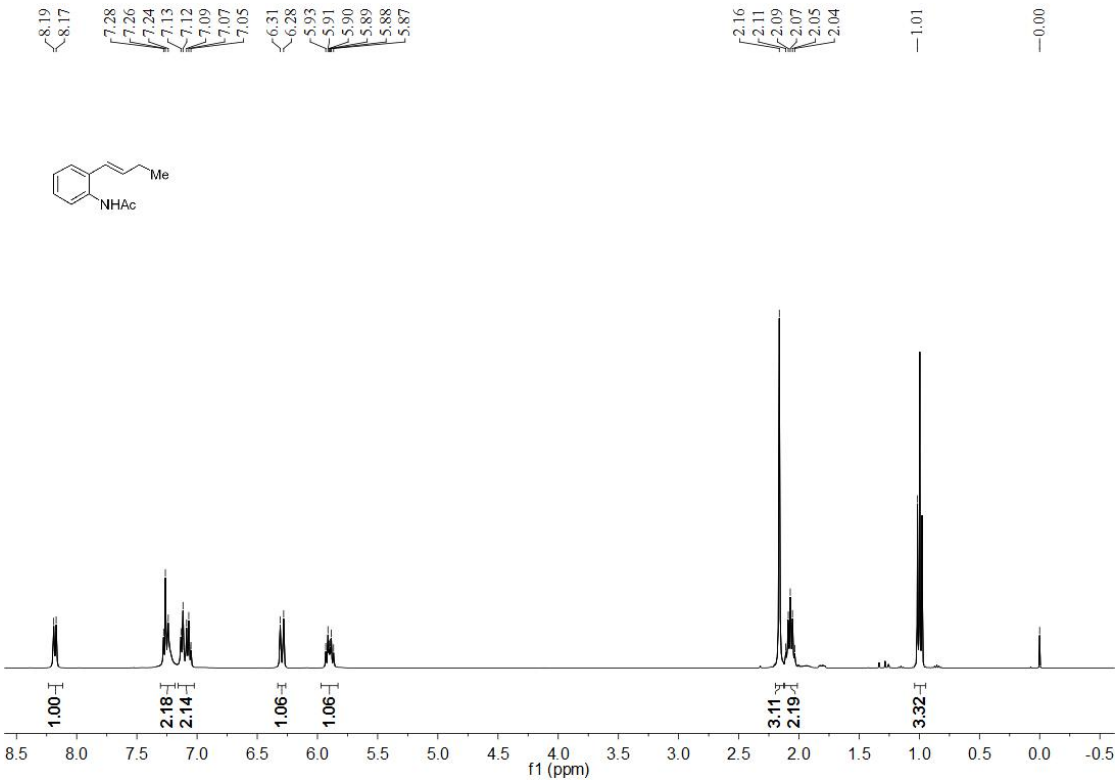
NMR Spectra of Substrate *N*-Cbz-Protected 1

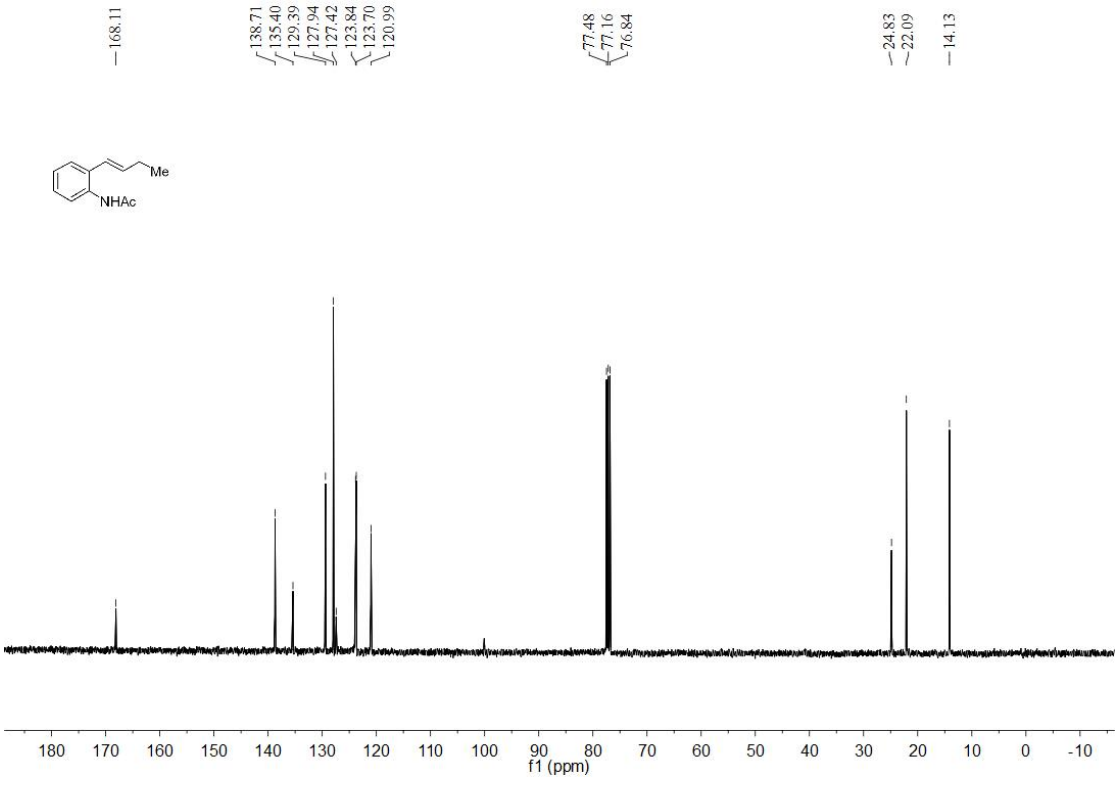




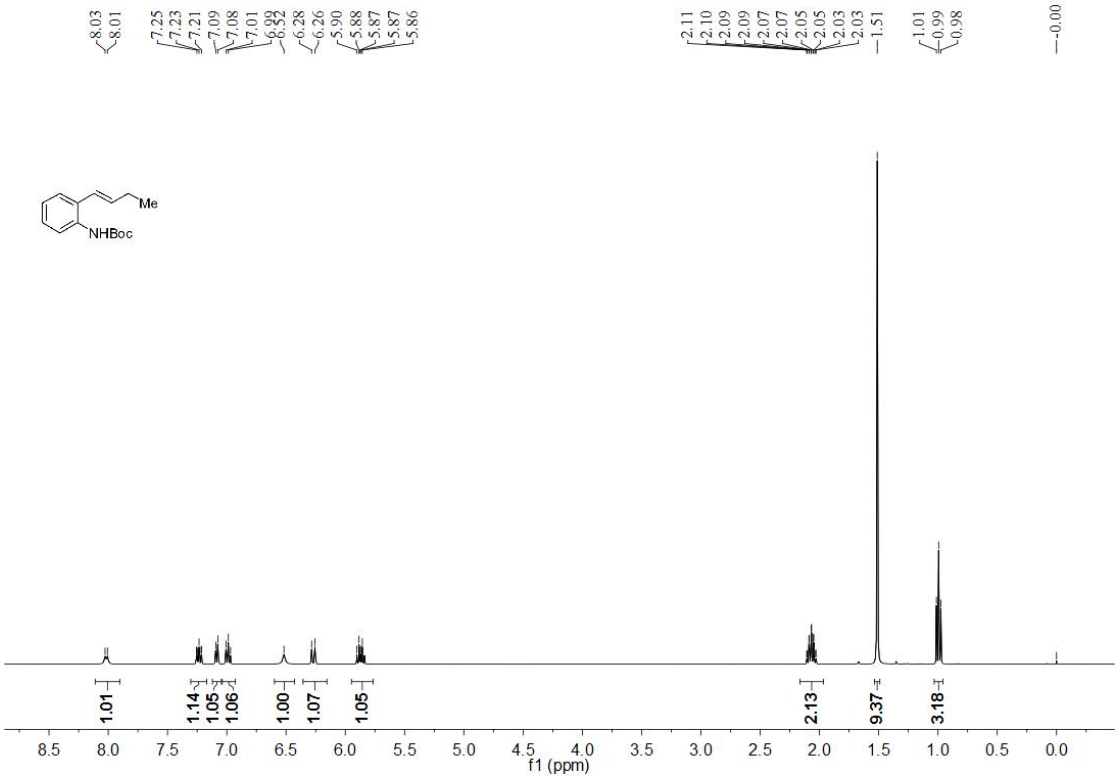


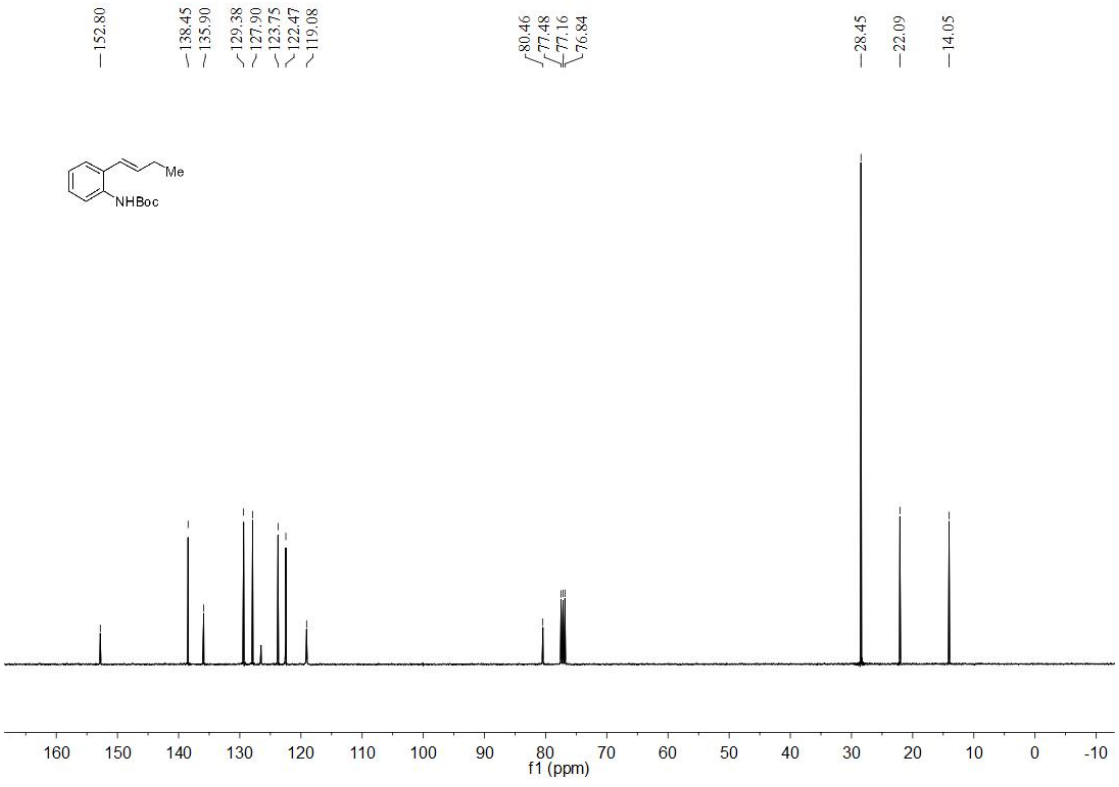
NMR Spectra of Substrate *N*-Ac-Protected 1



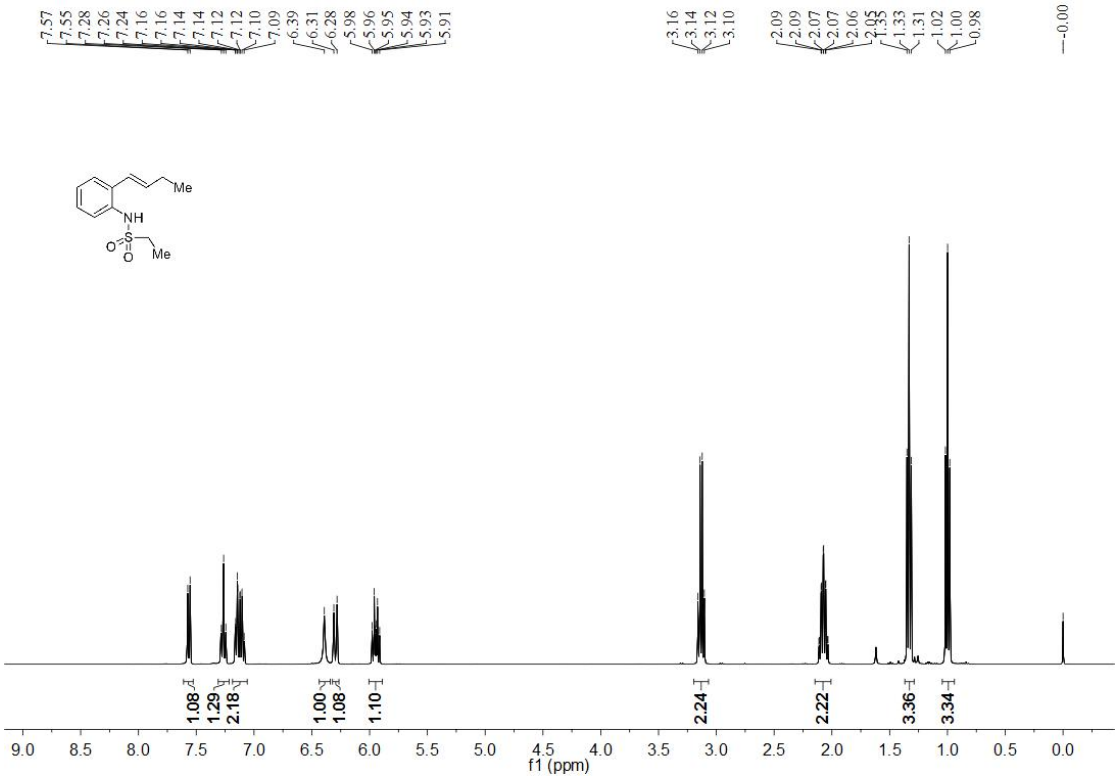


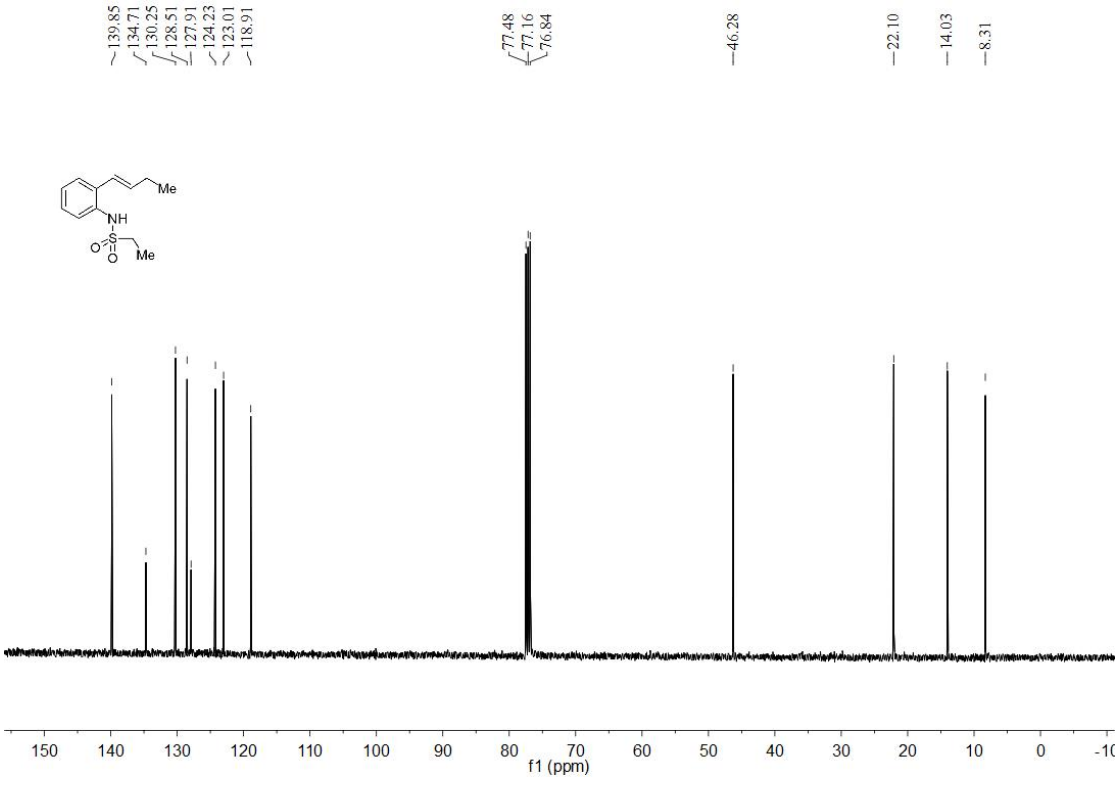
NMR Spectra of Substrate *N*-Boc-Protected 1



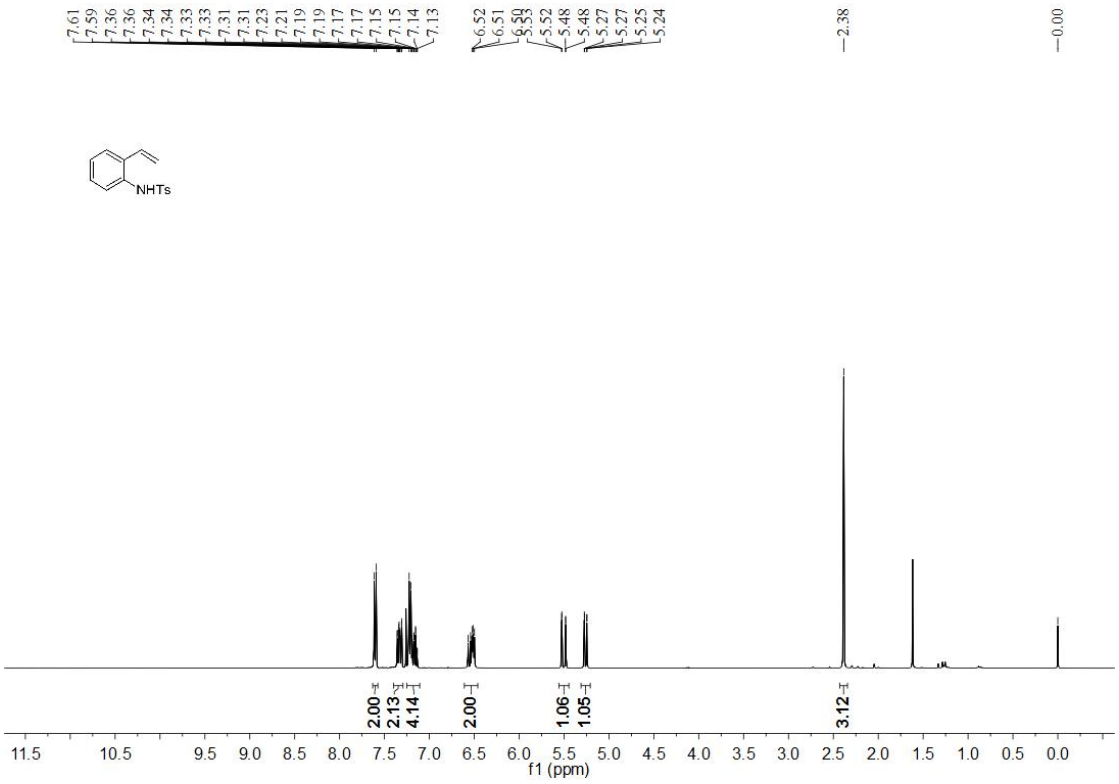


NMR Spectra of Substrate 1c

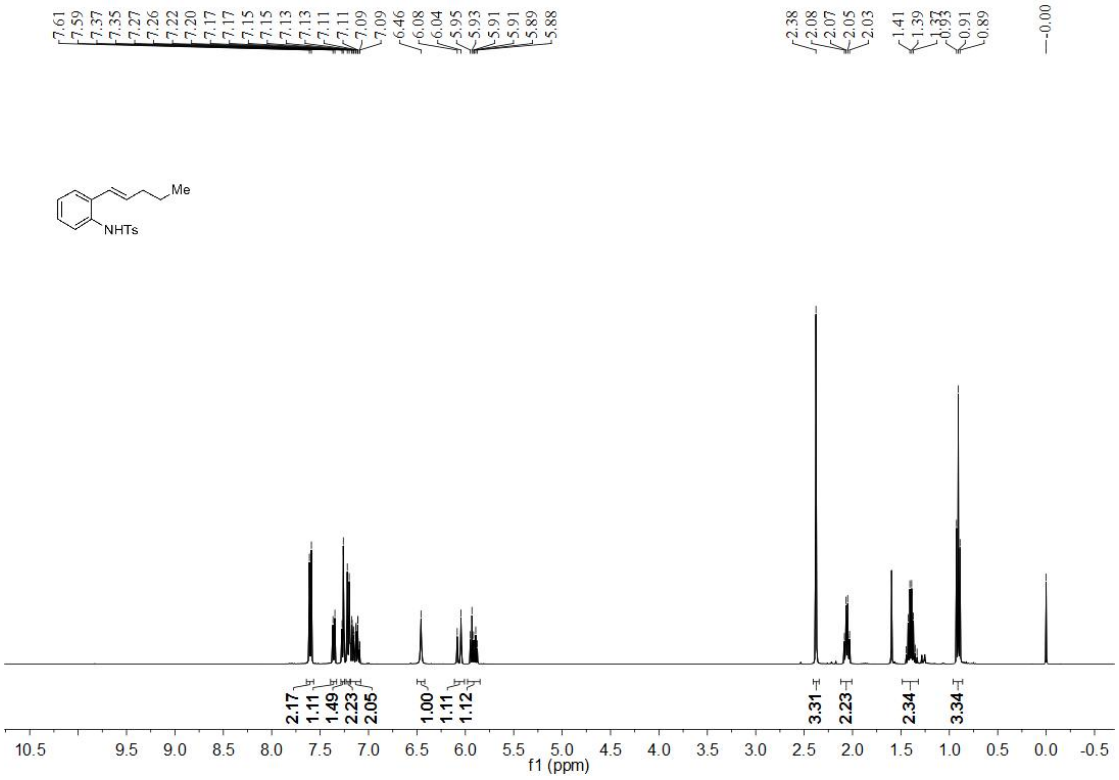


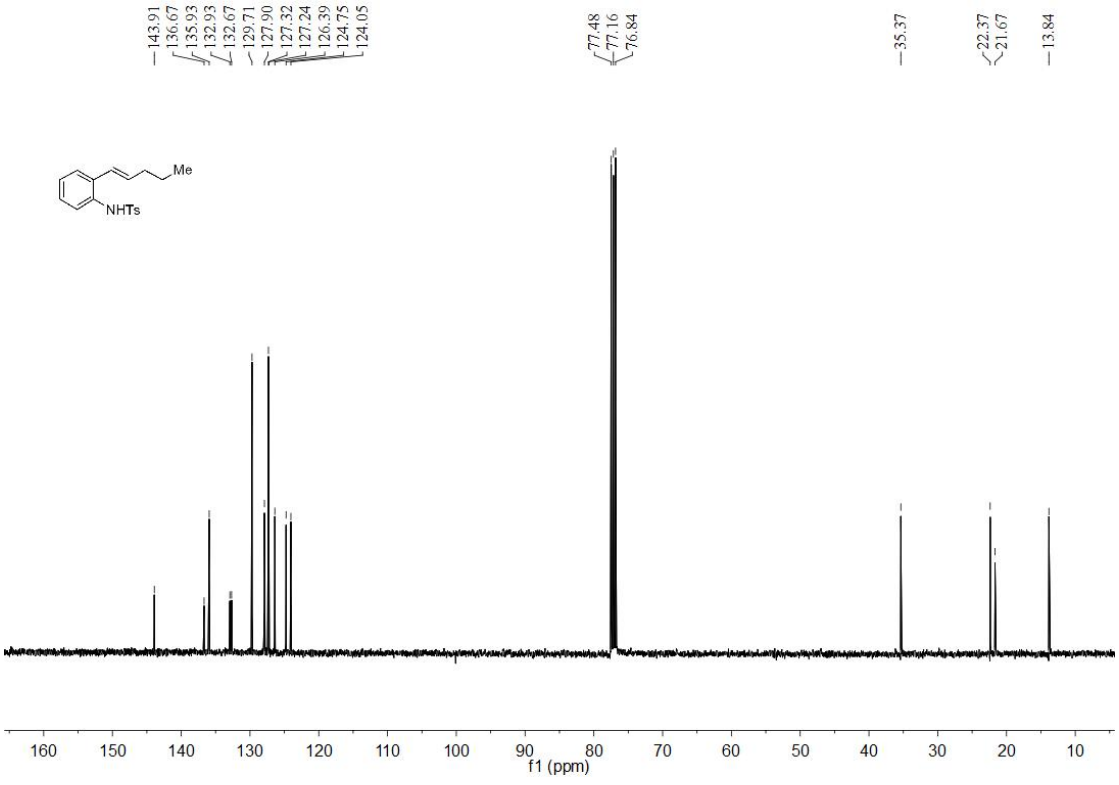


NMR Spectrum of Substrate 1d

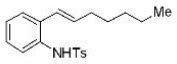


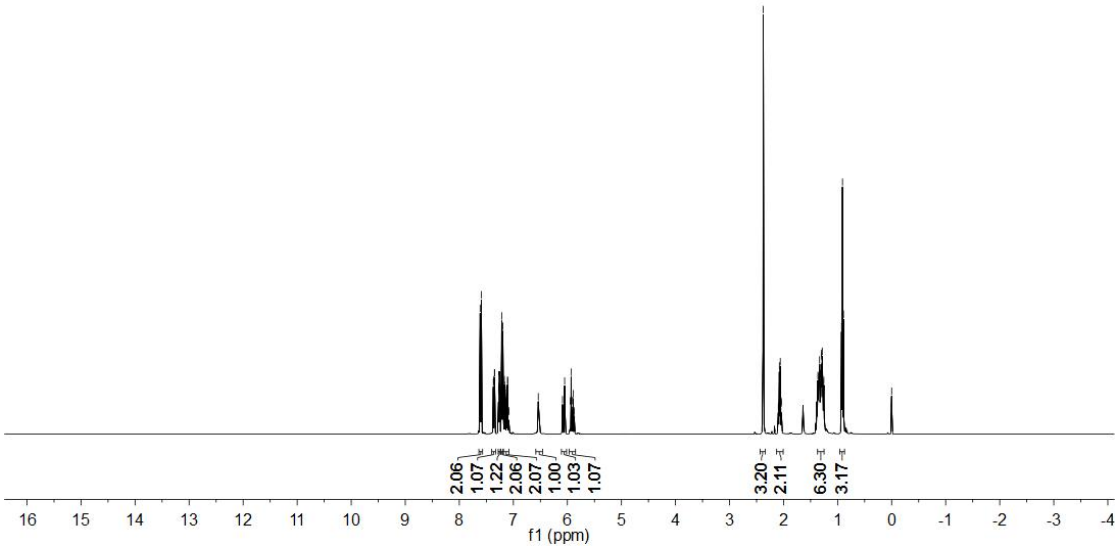
NMR Spectra of Substrate 1e

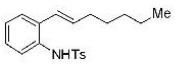


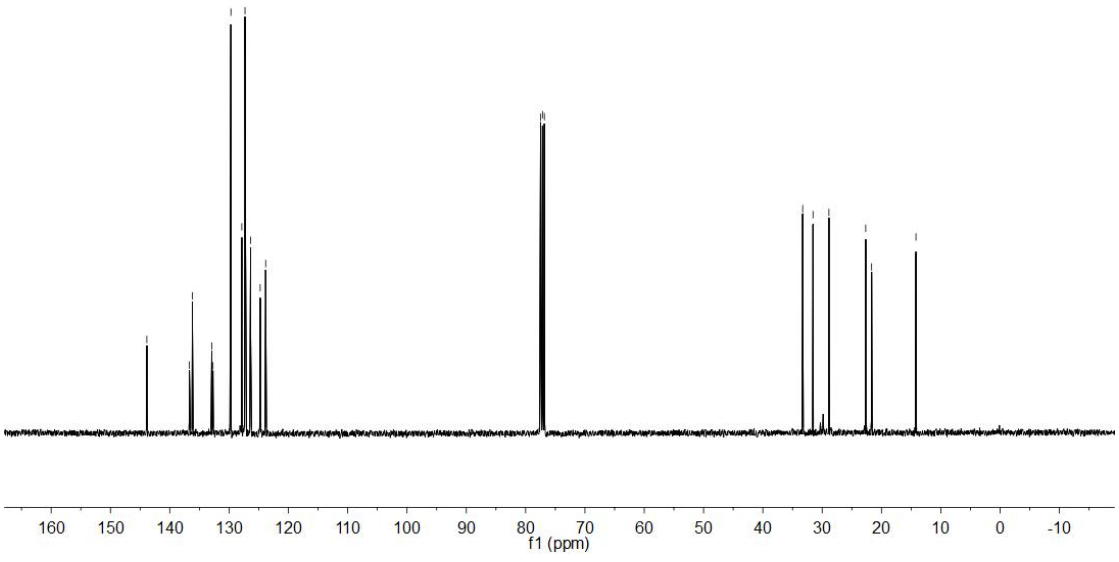


NMR Spectra of Substrate 1f

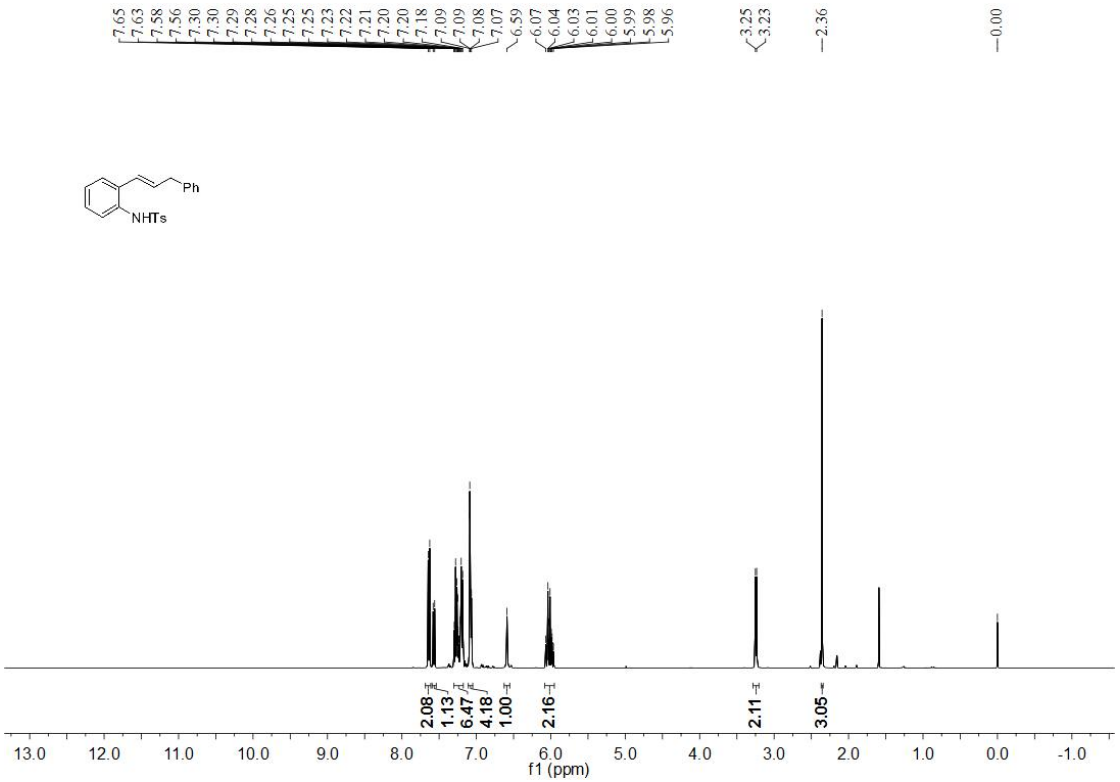


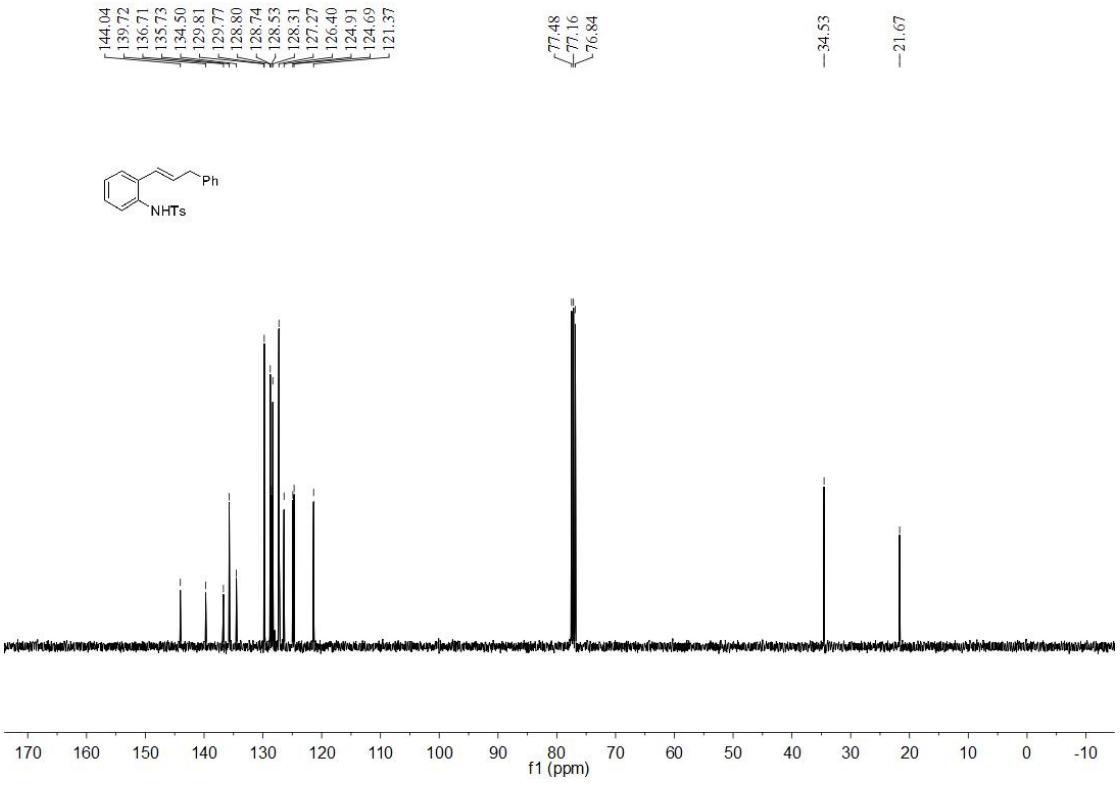




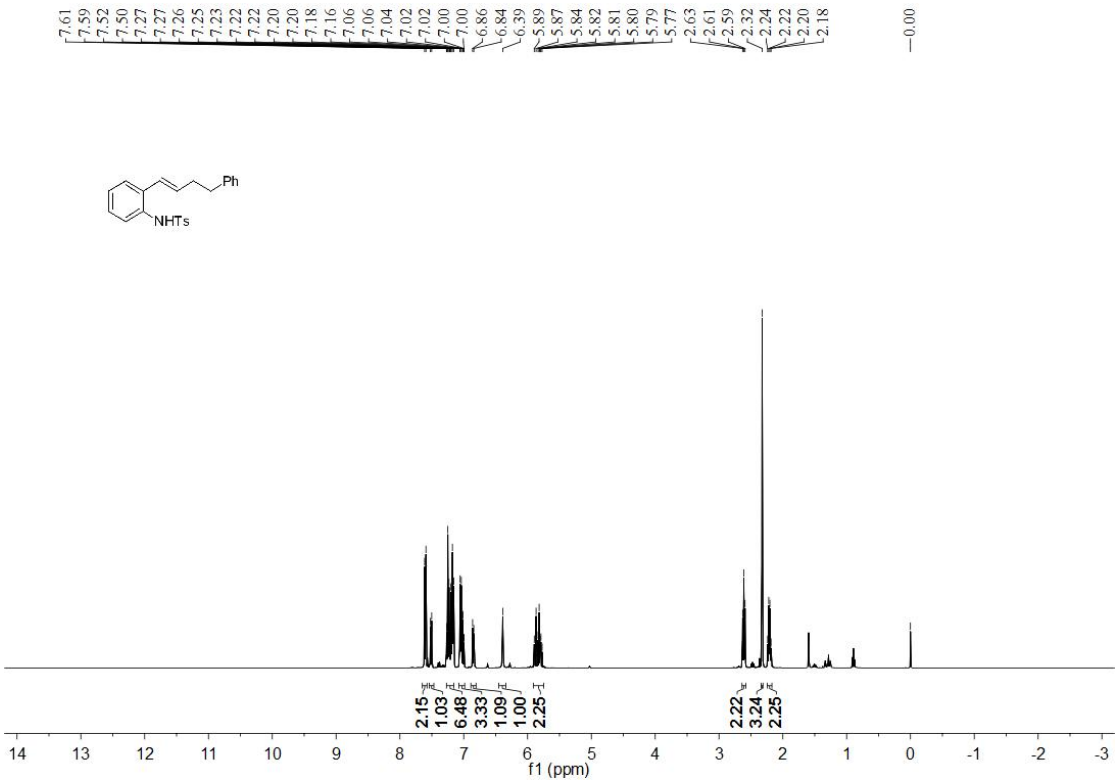


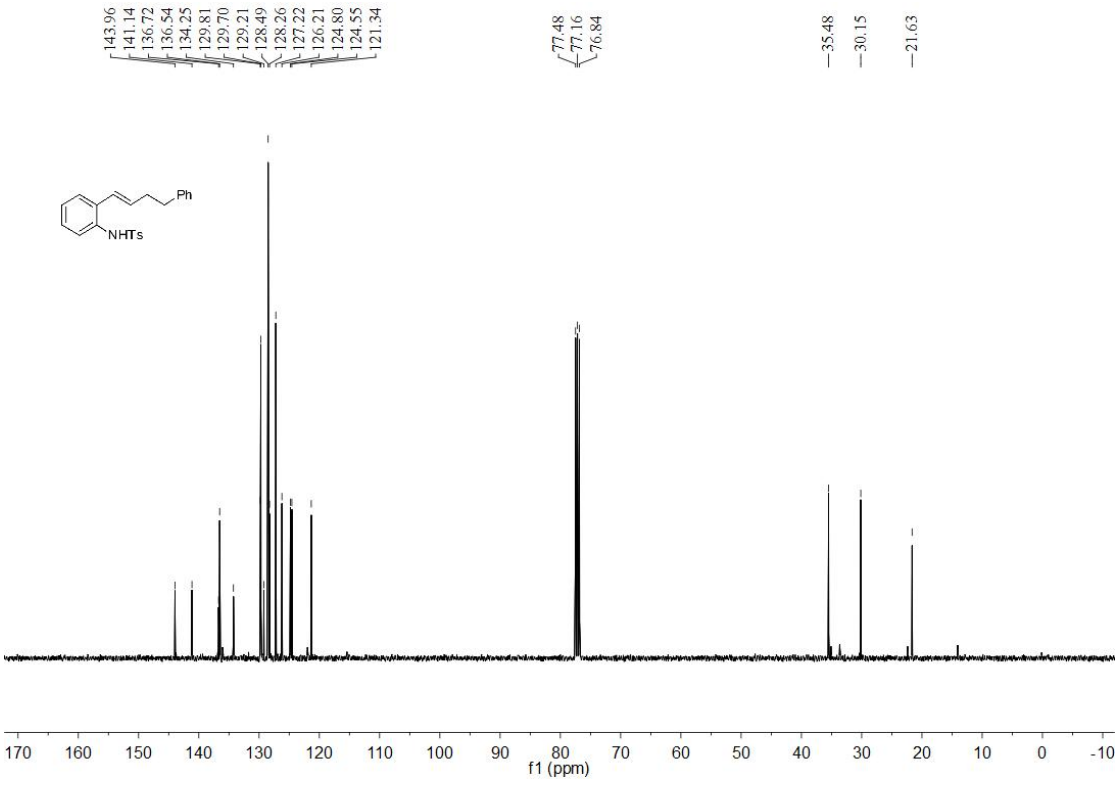
NMR Spectra of Substrate 1g



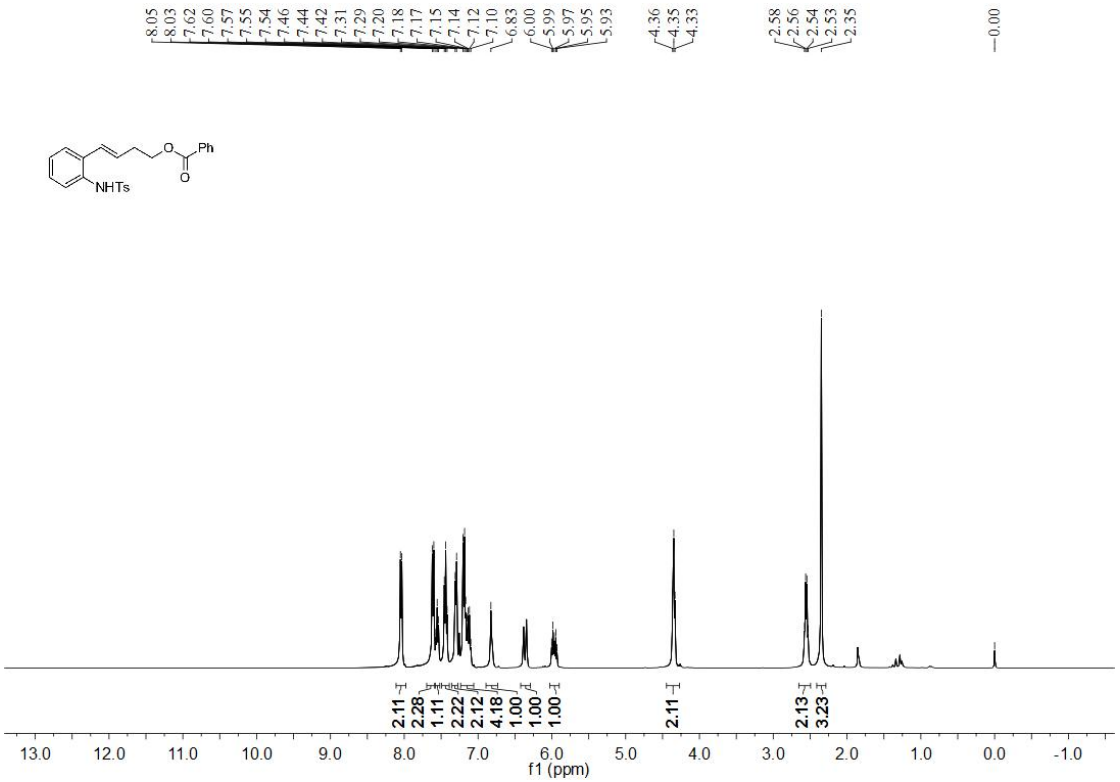


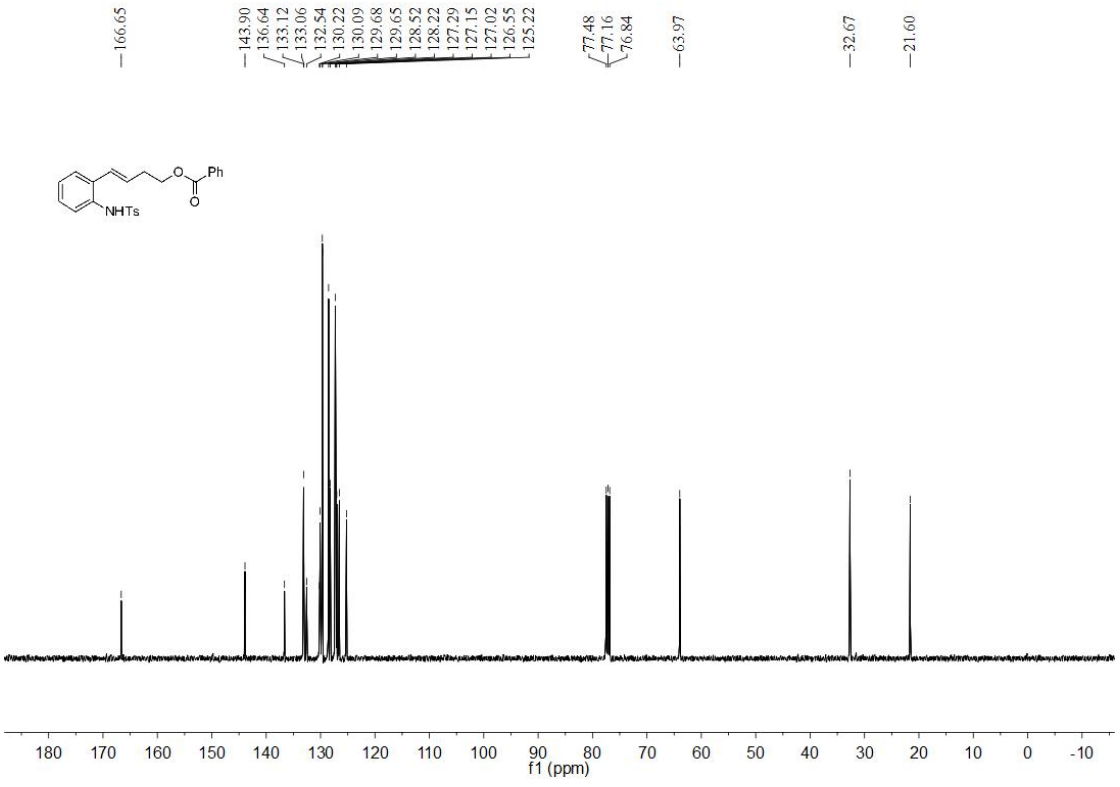
NMR Spectra of Substrate 1h



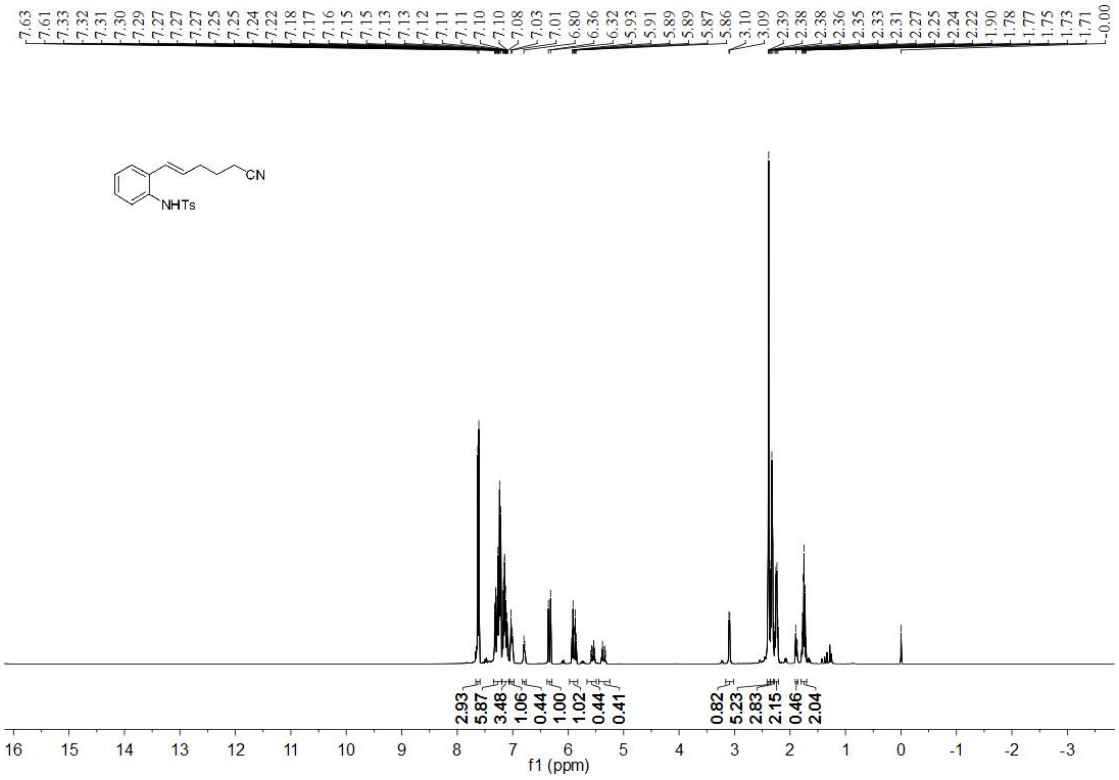


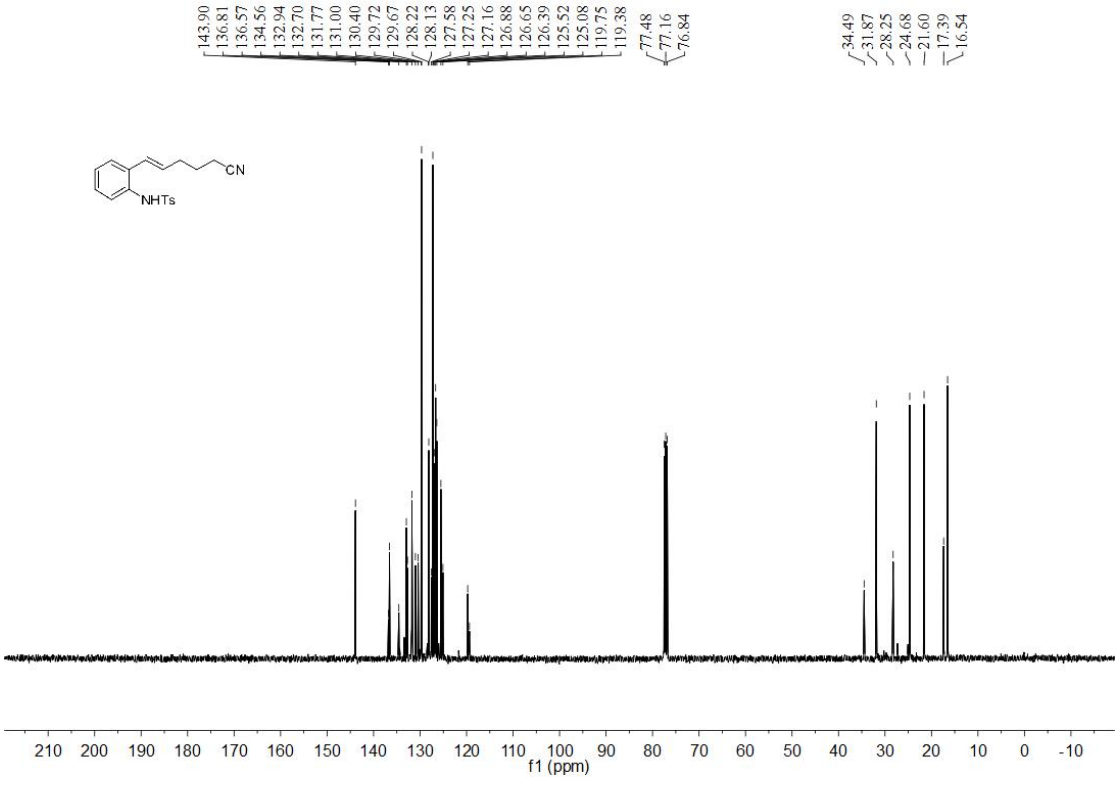
NMR Spectra of Substrate 1i



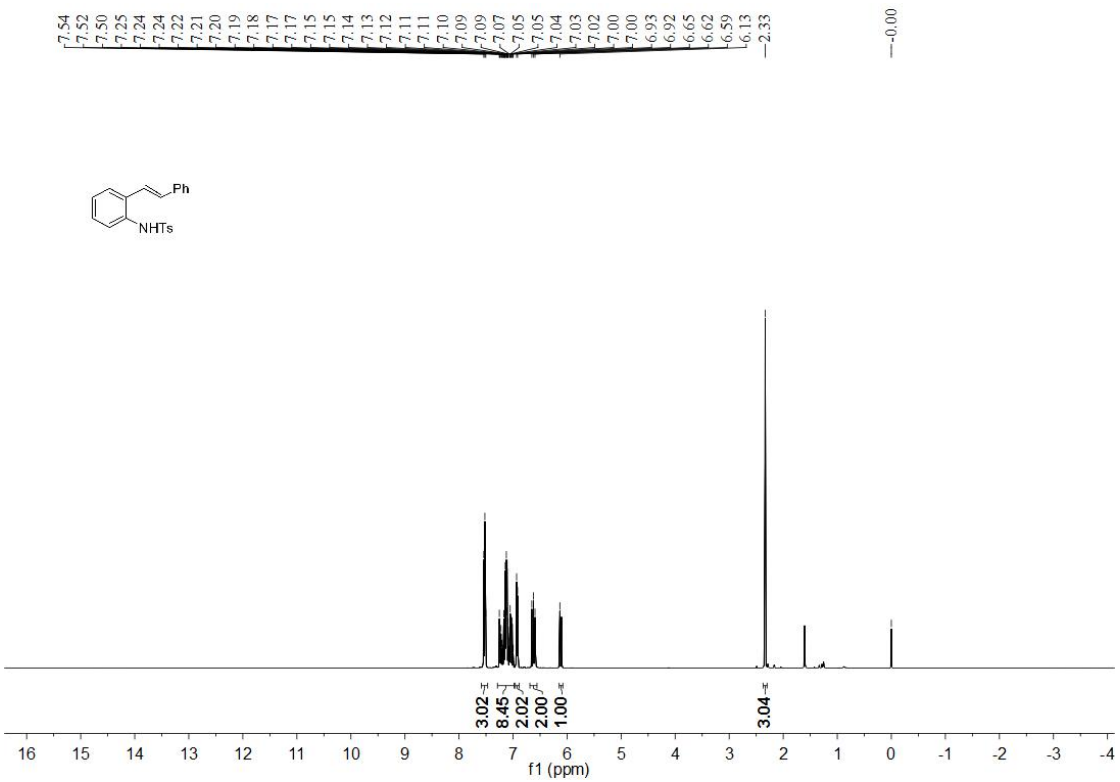


NMR Spectra of Substrate 1j

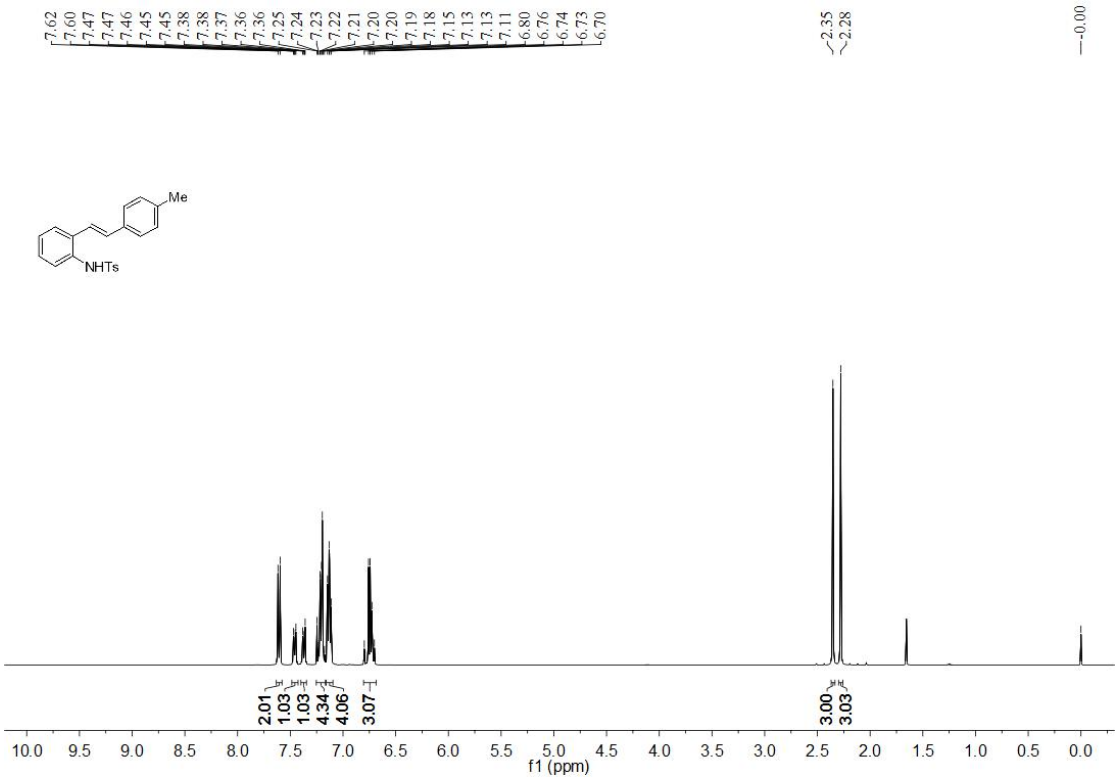




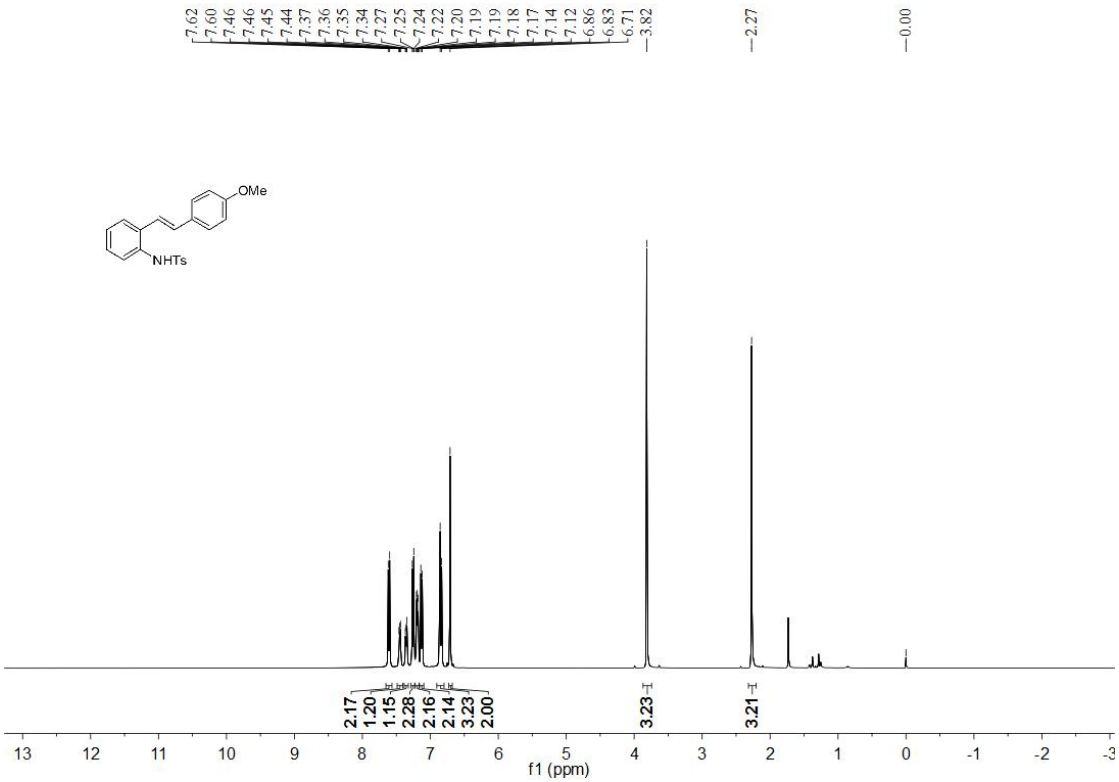
NMR Spectra of Substrate 1k



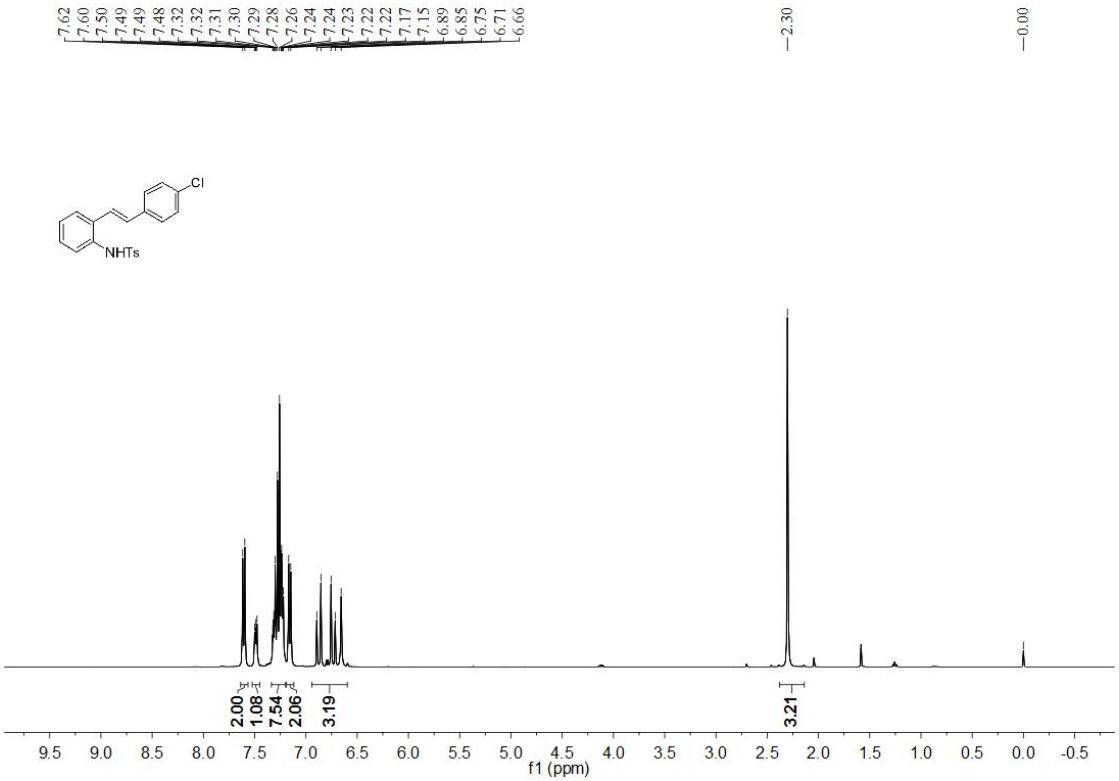
NMR Spectra of Substrate 1l



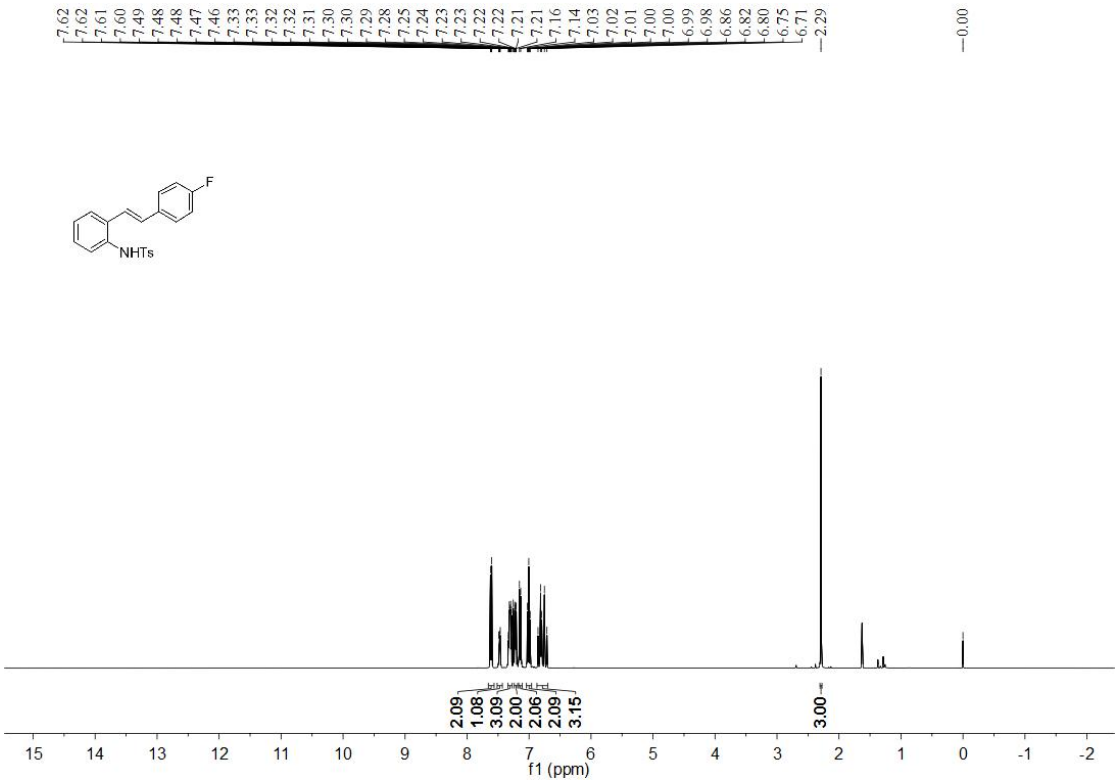
NMR Spectrum of Substrate 1m



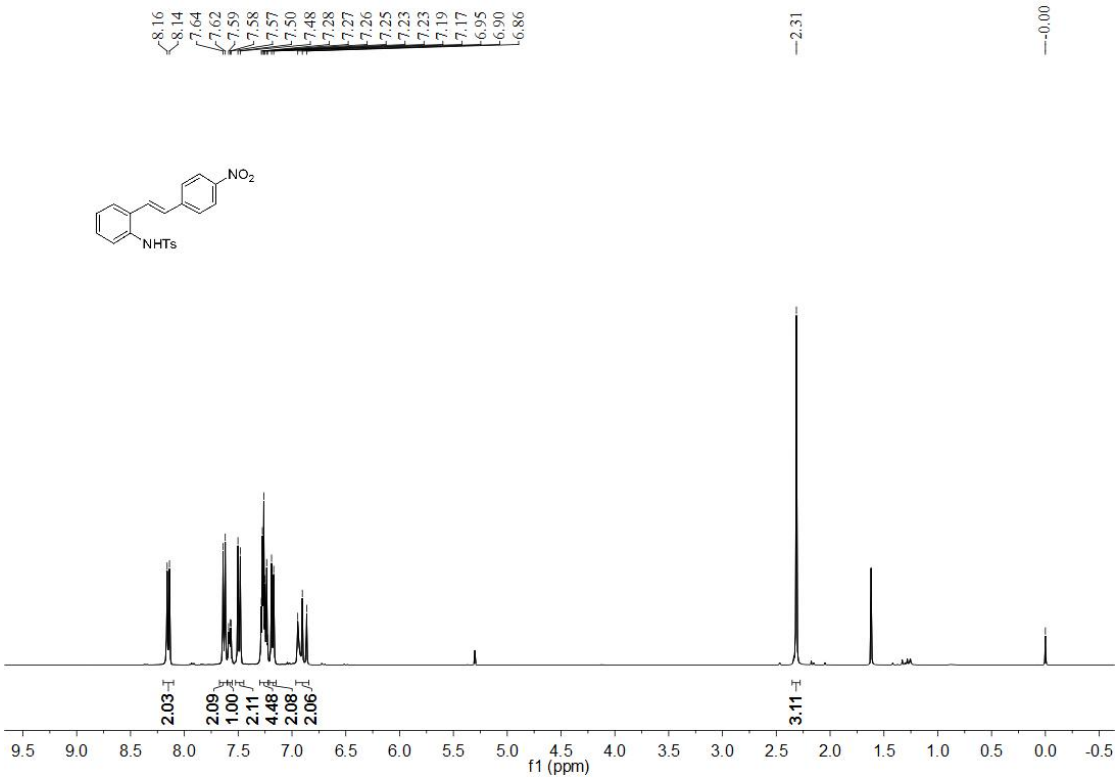
NMR Spectrum of Substrate 1n



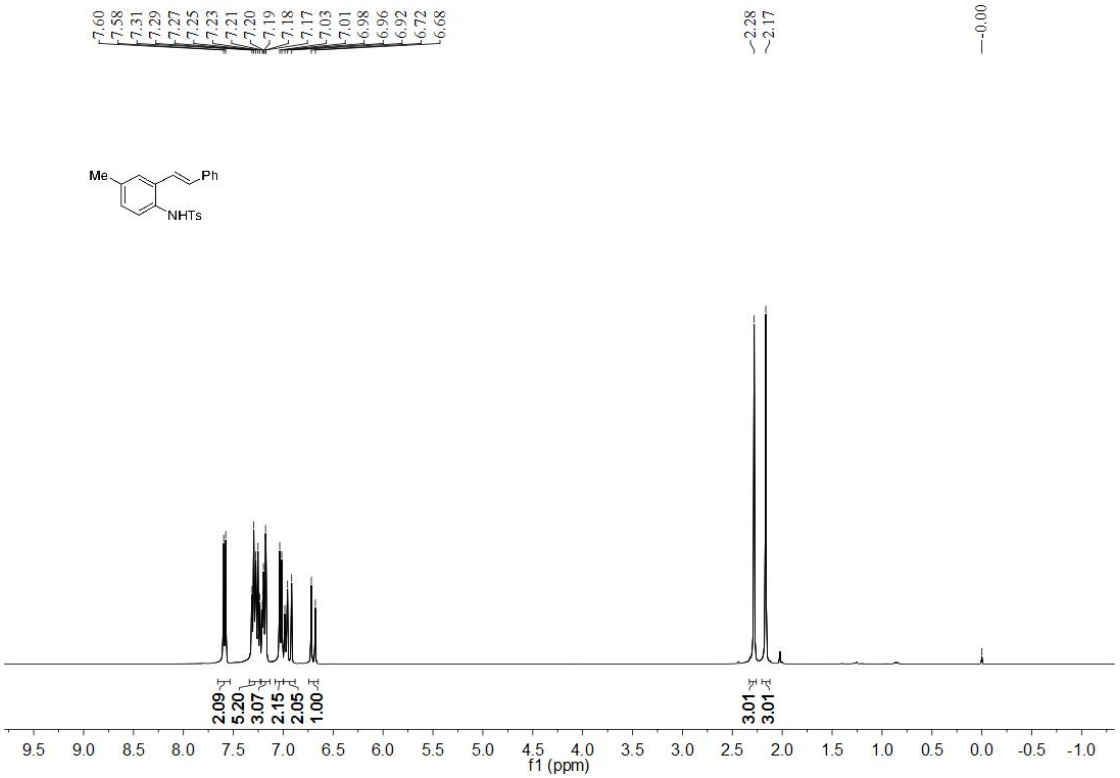
NMR Spectrum of Substrate 1o

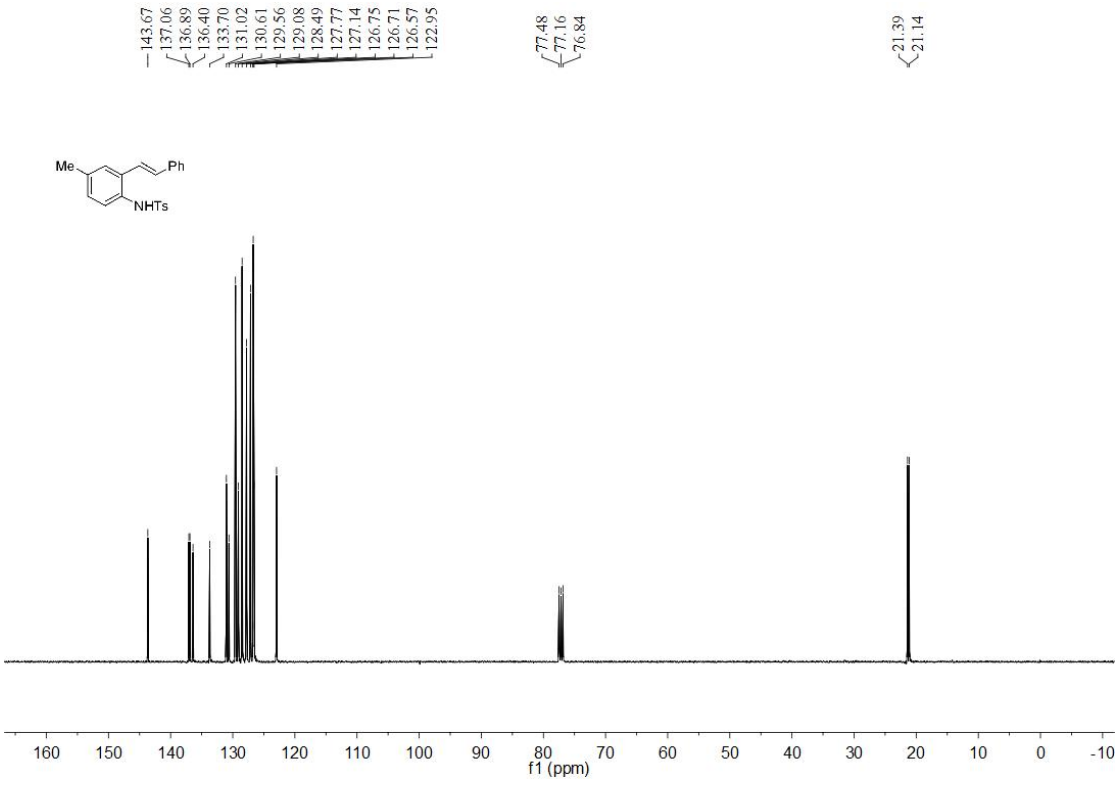


NMR Spectrum of Substrate 1p

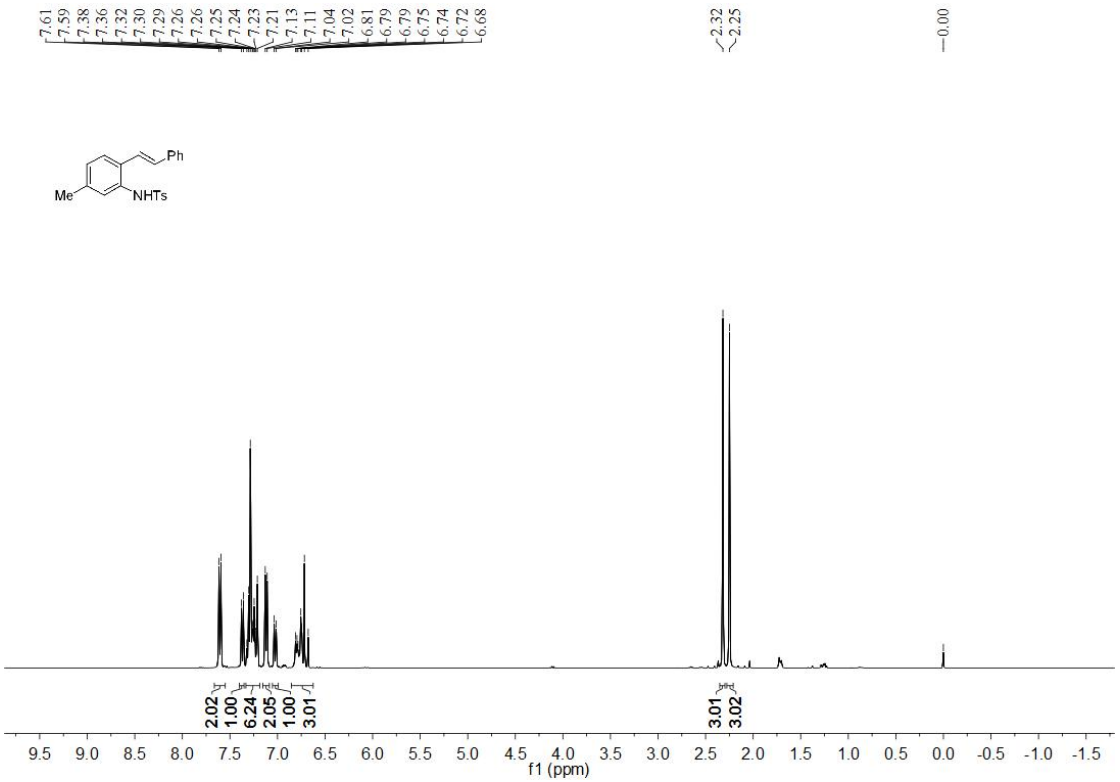


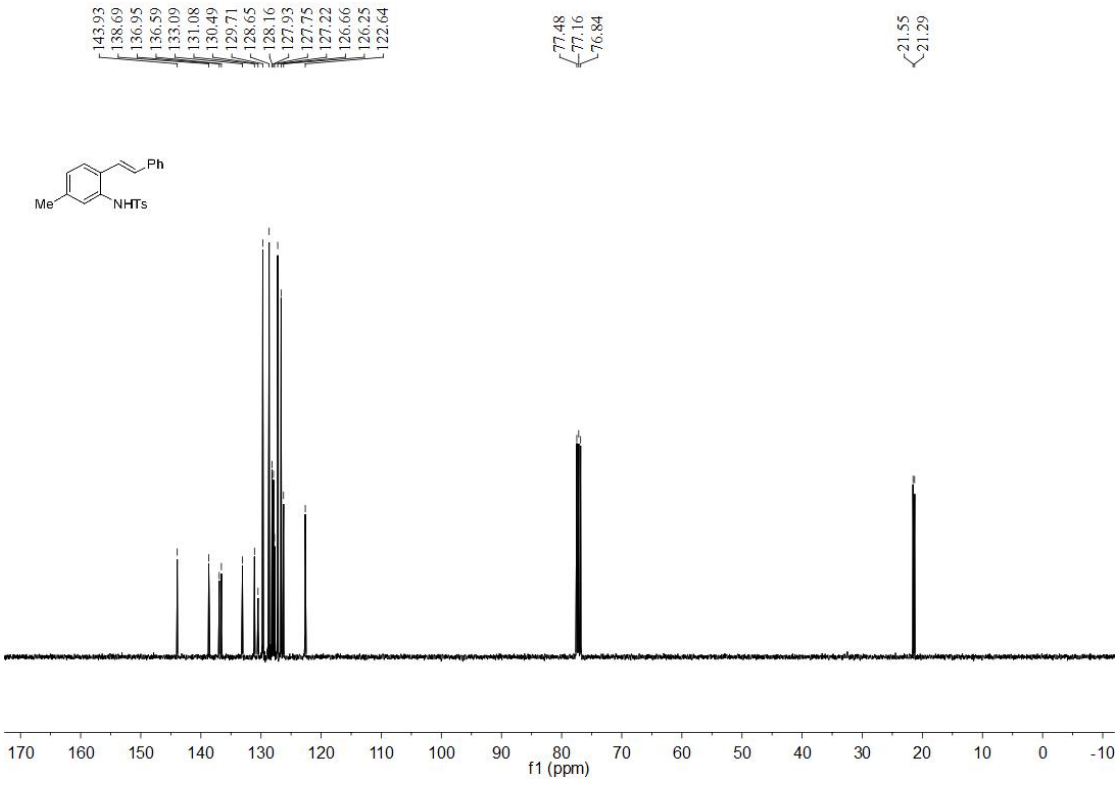
NMR Spectra of Substrate 1q



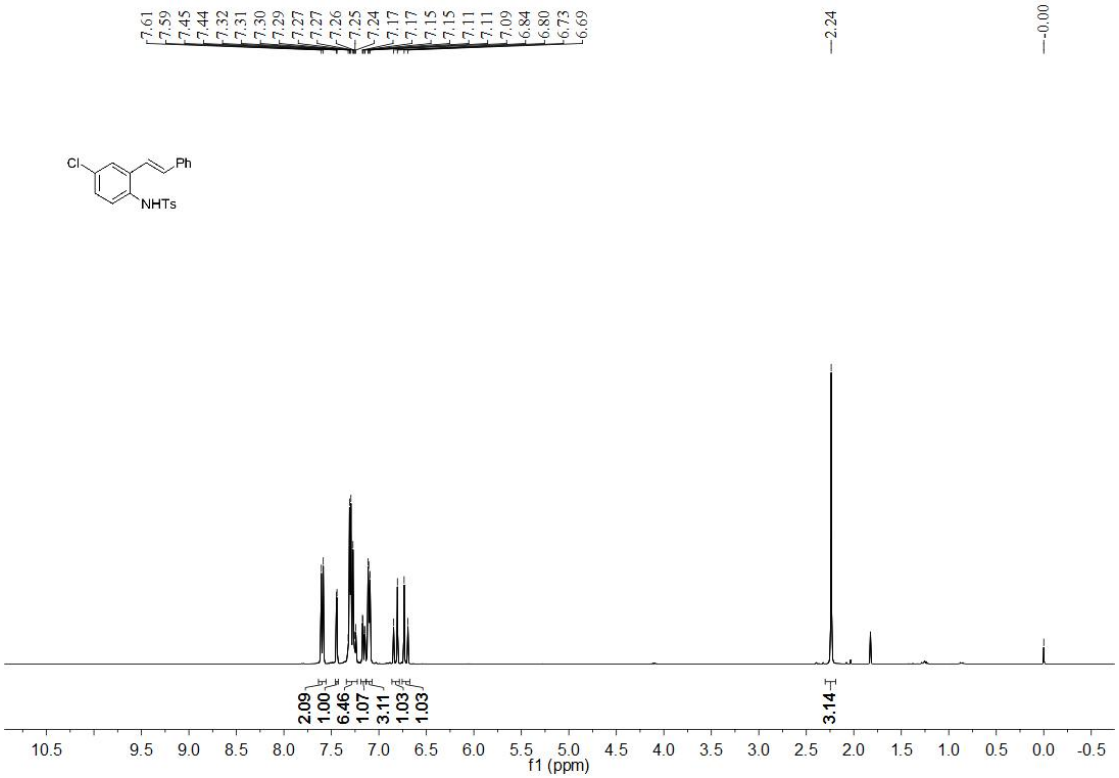


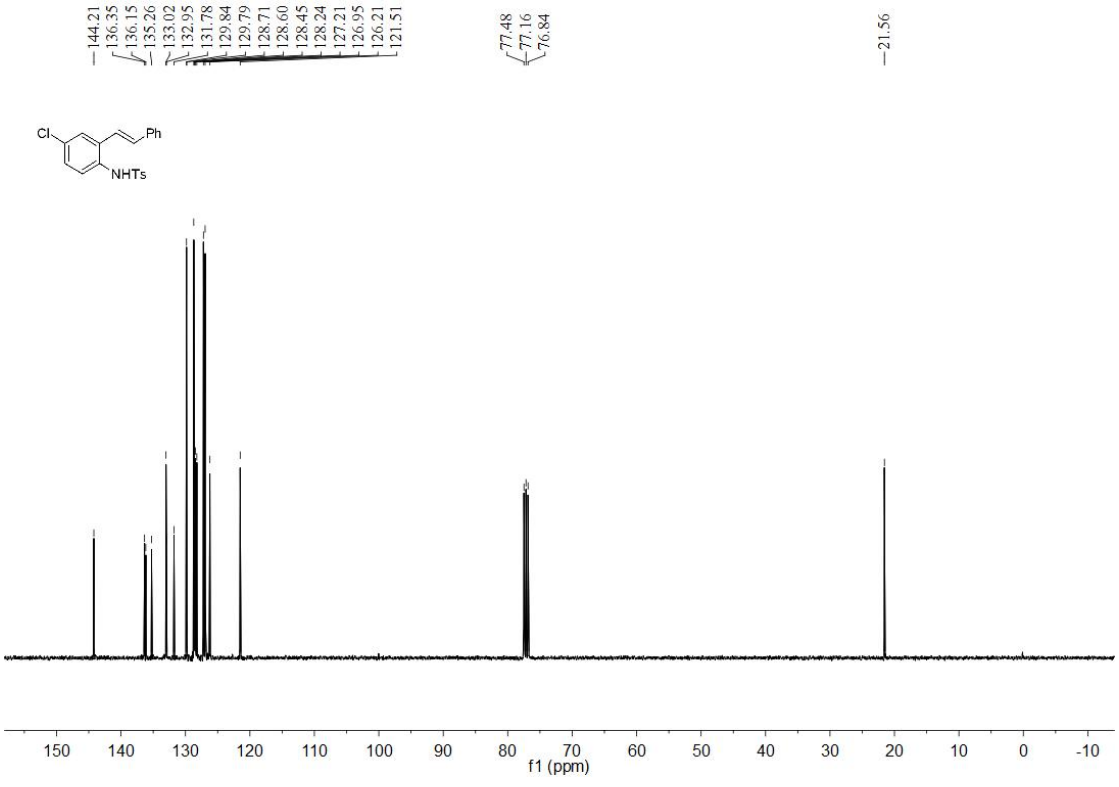
NMR Spectra of Substrate 1r



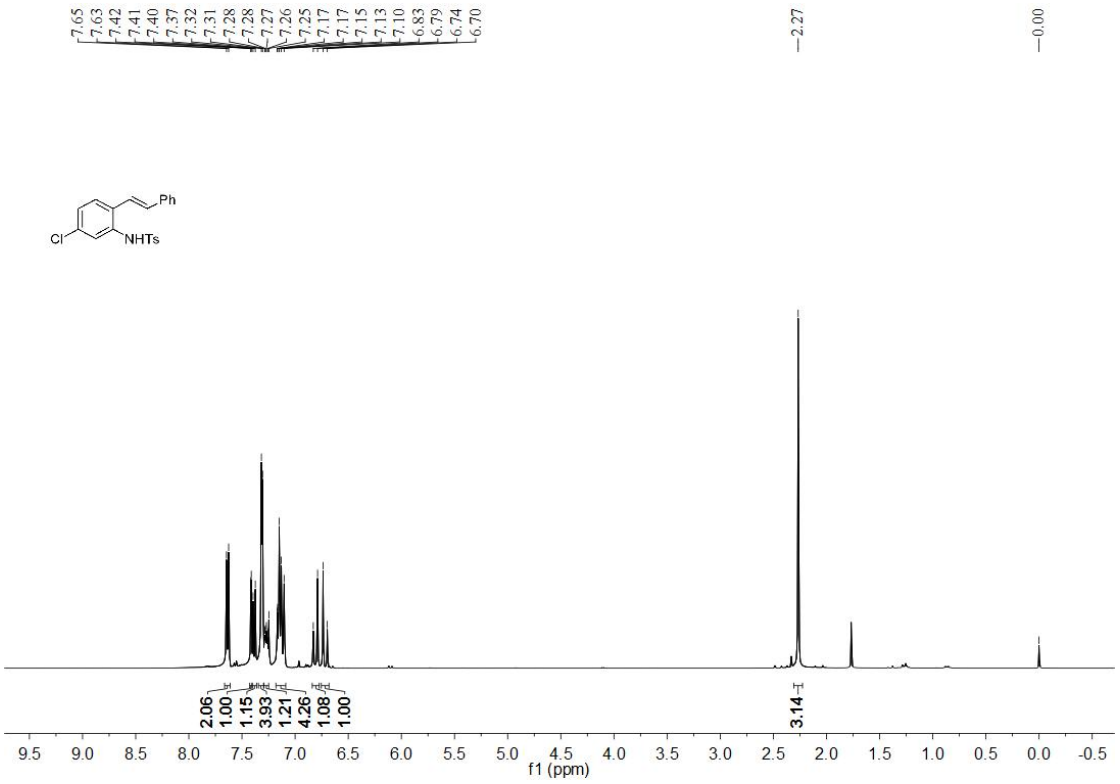


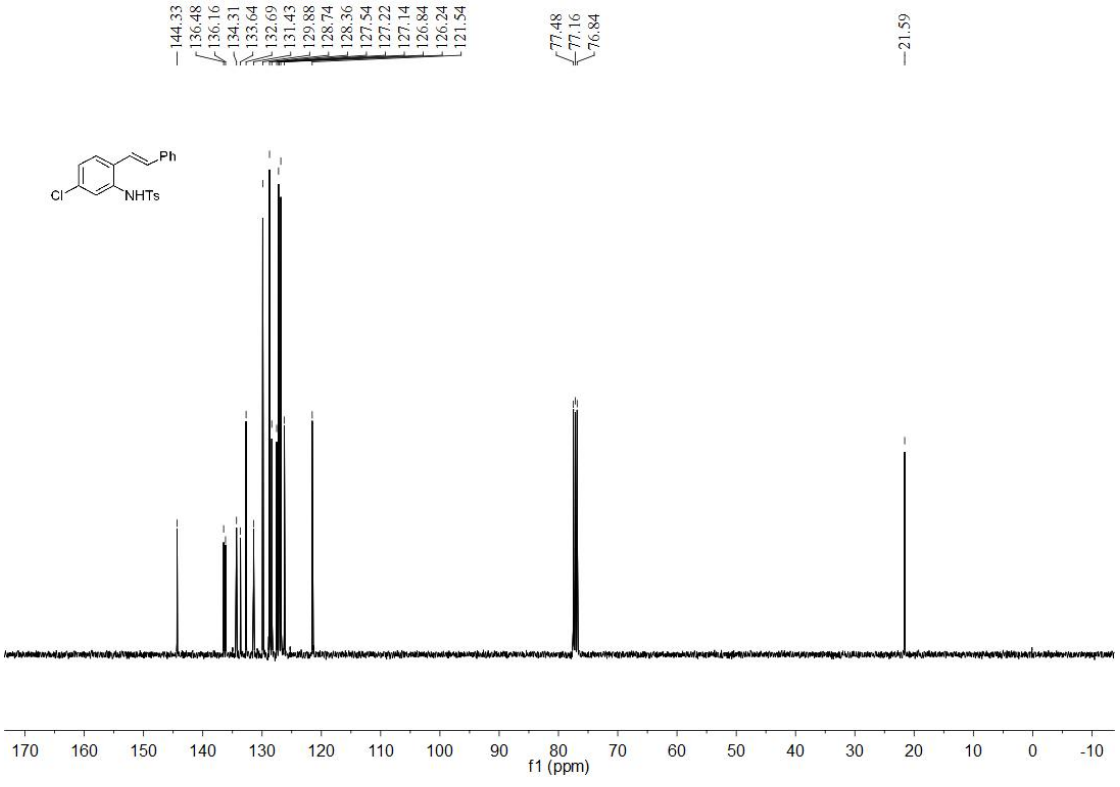
NMR Spectra of Substrate 1s



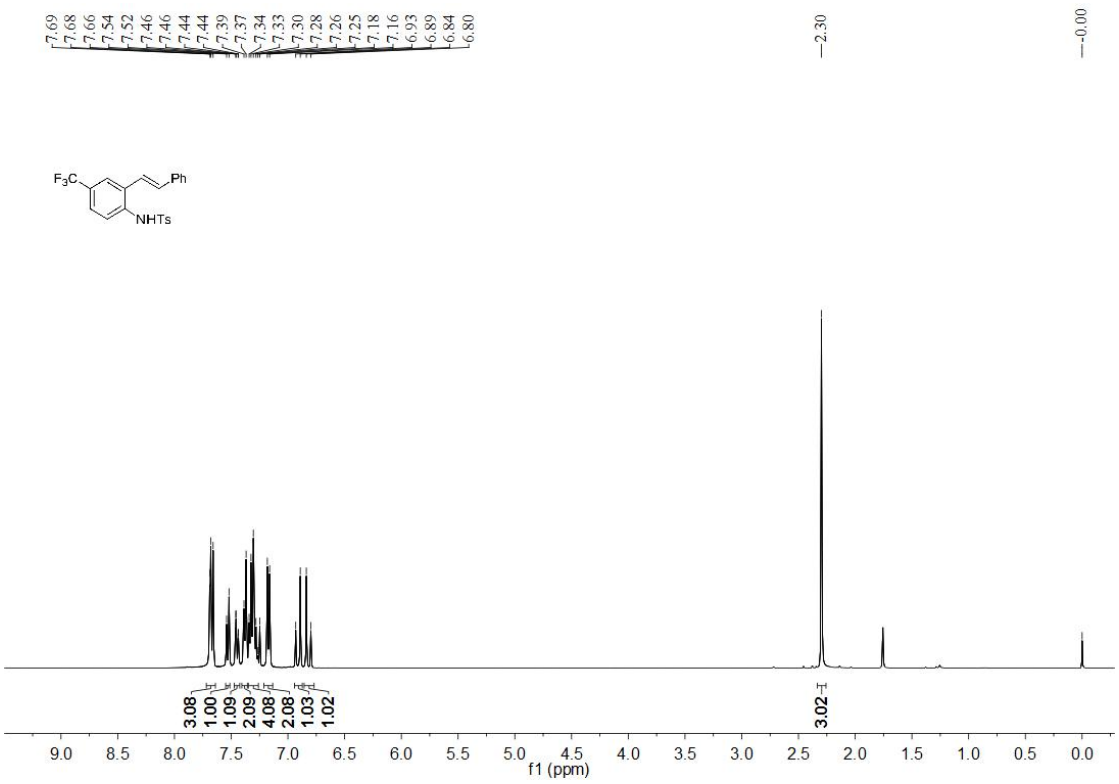


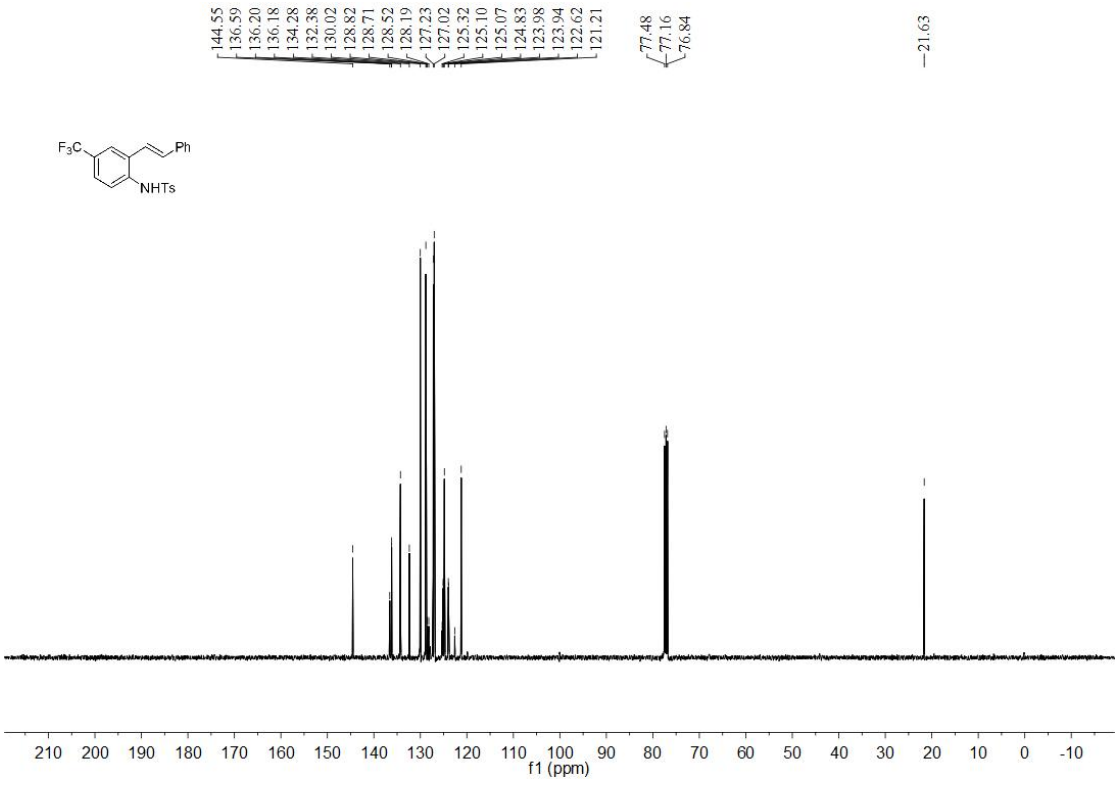
NMR Spectra of Substrate 1t



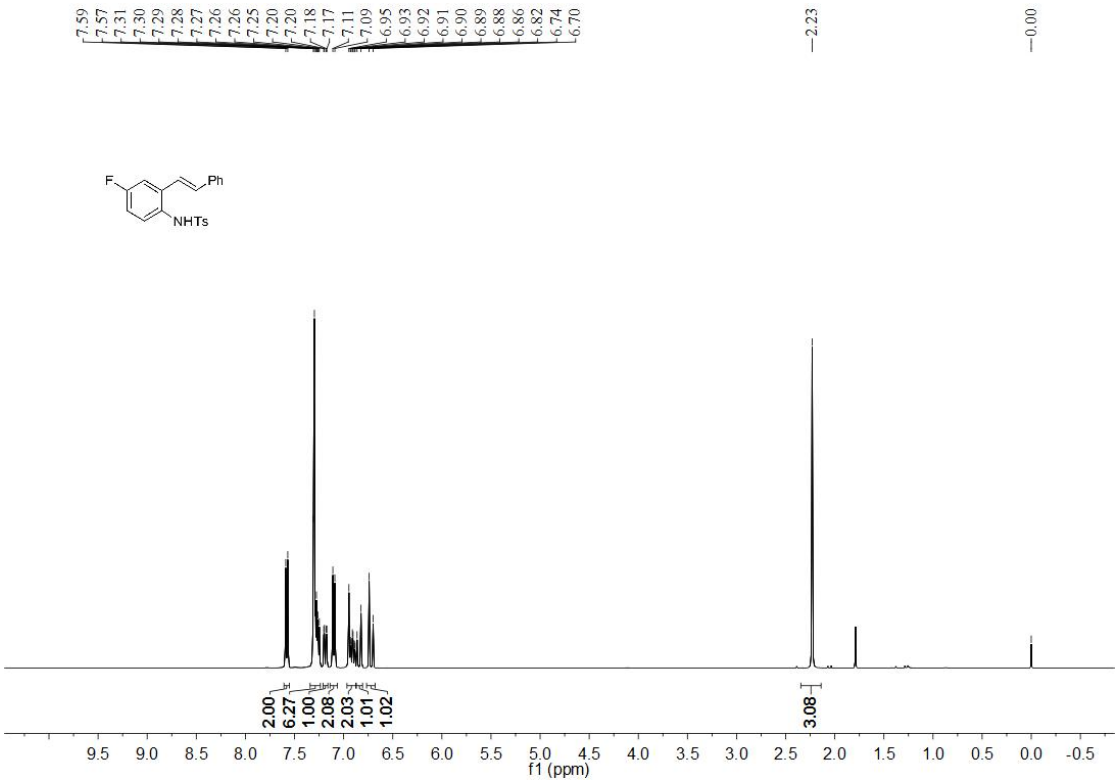


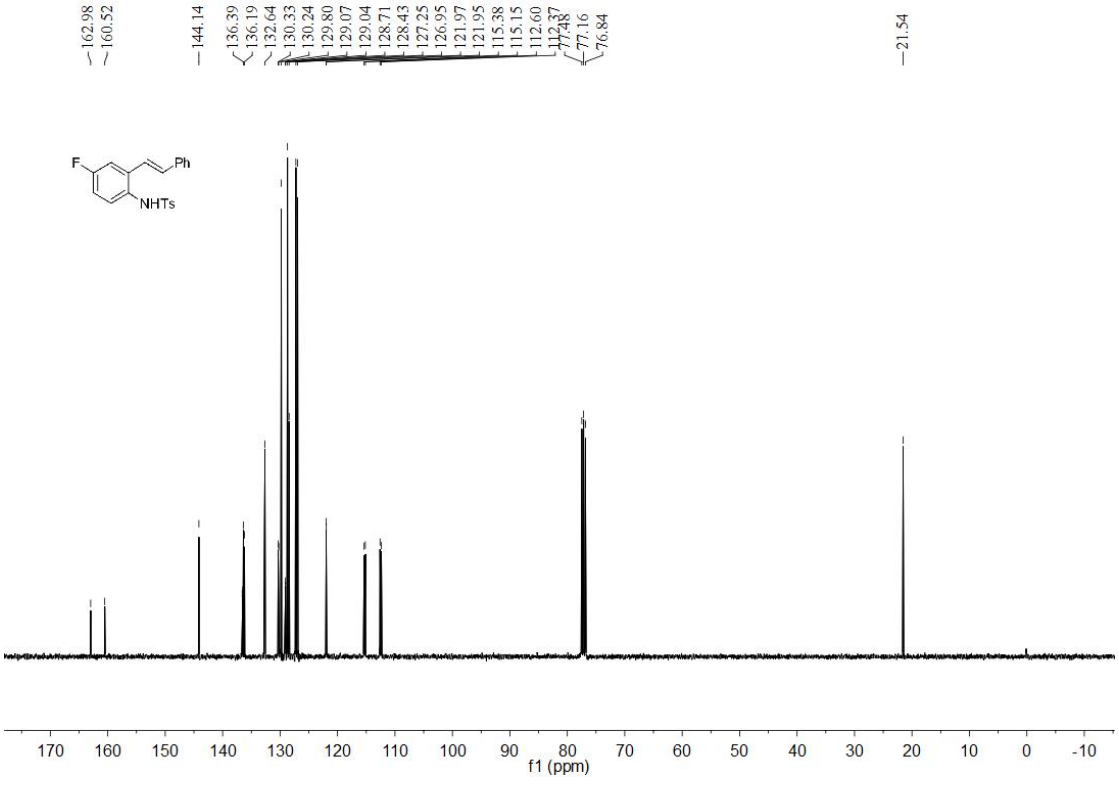
NMR Spectra of Substrate 1u



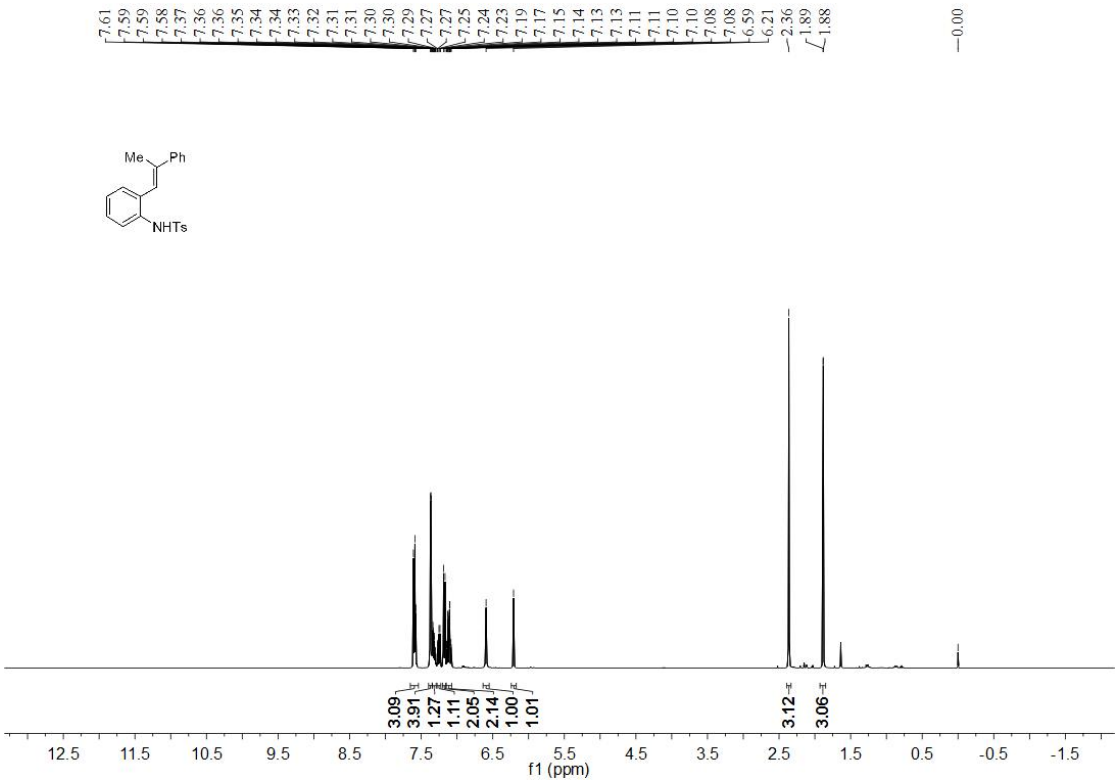


NMR Spectra of Substrate 1v

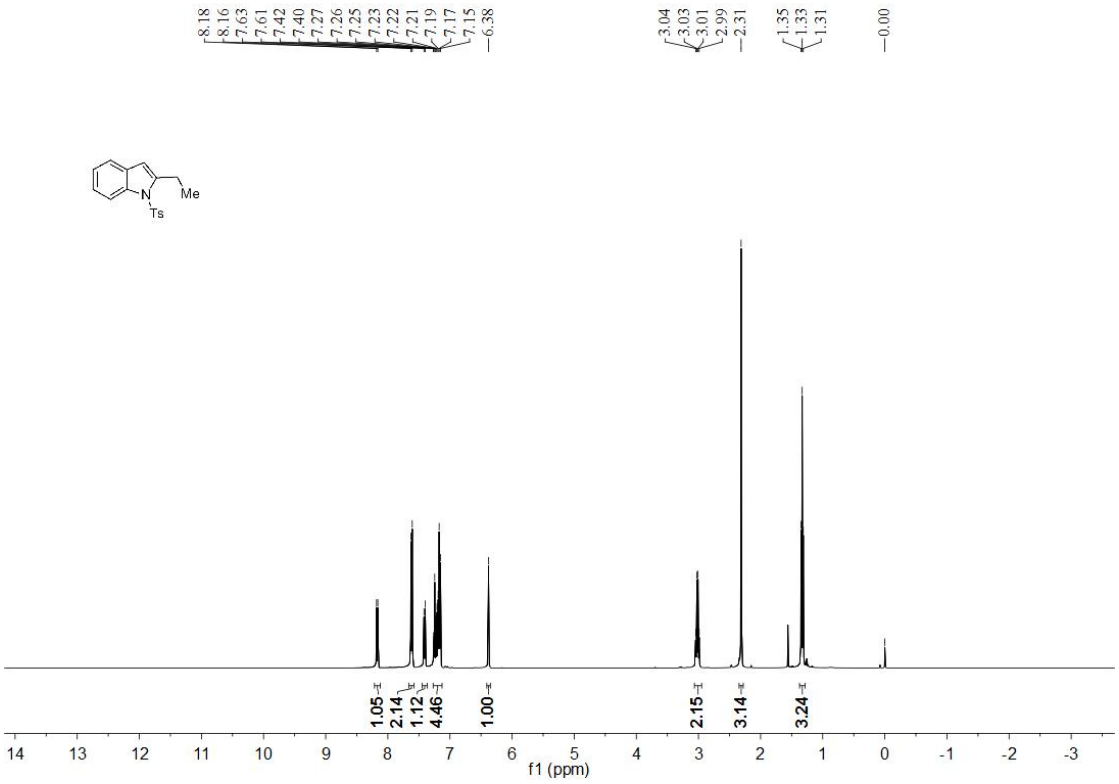


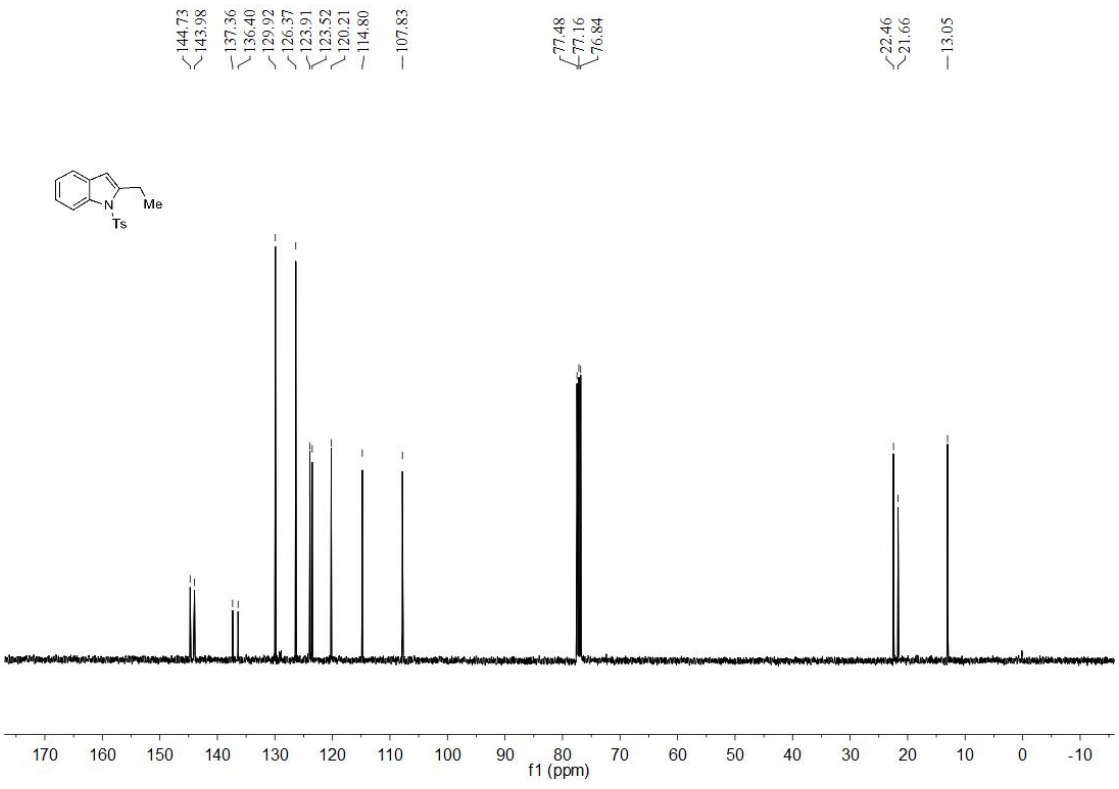


NMR Spectrum of Substrate 3

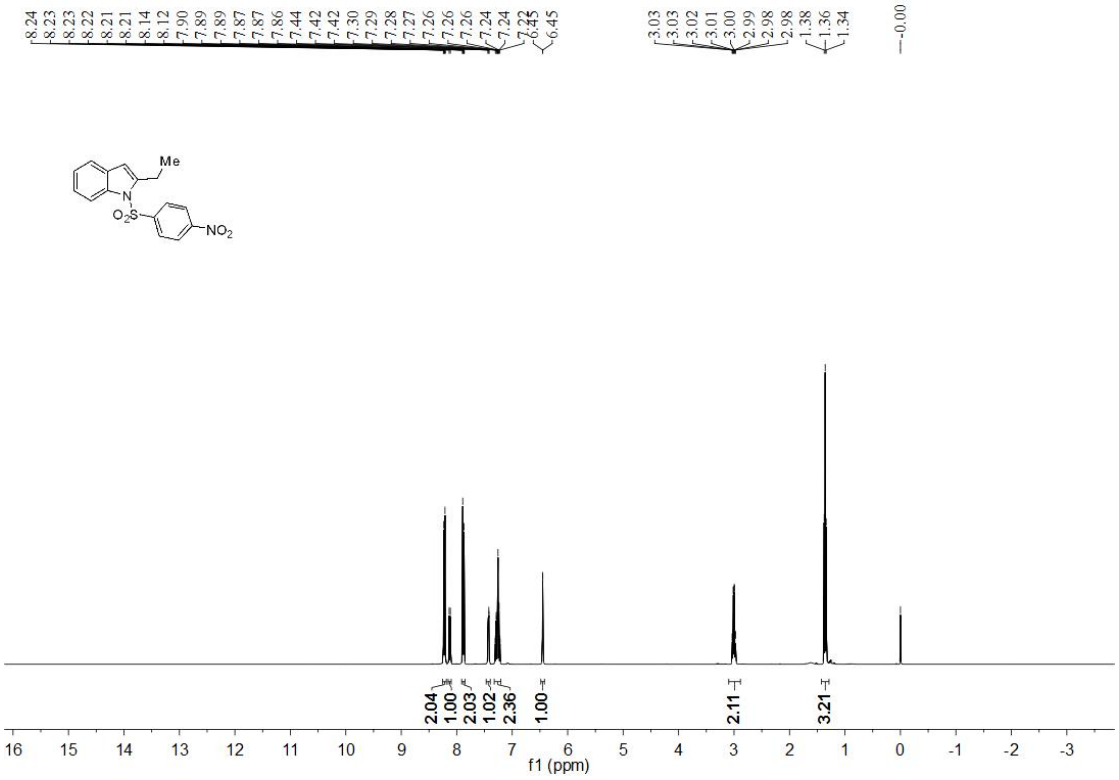


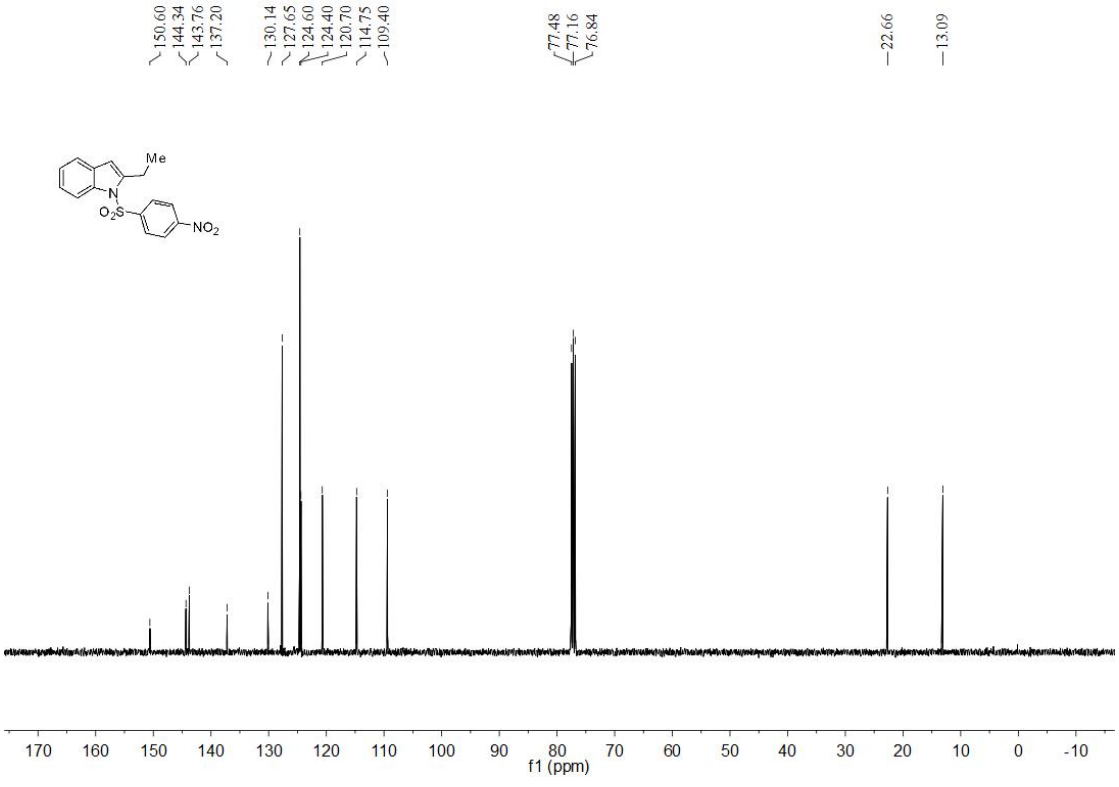
NMR Spectra of Product 2a



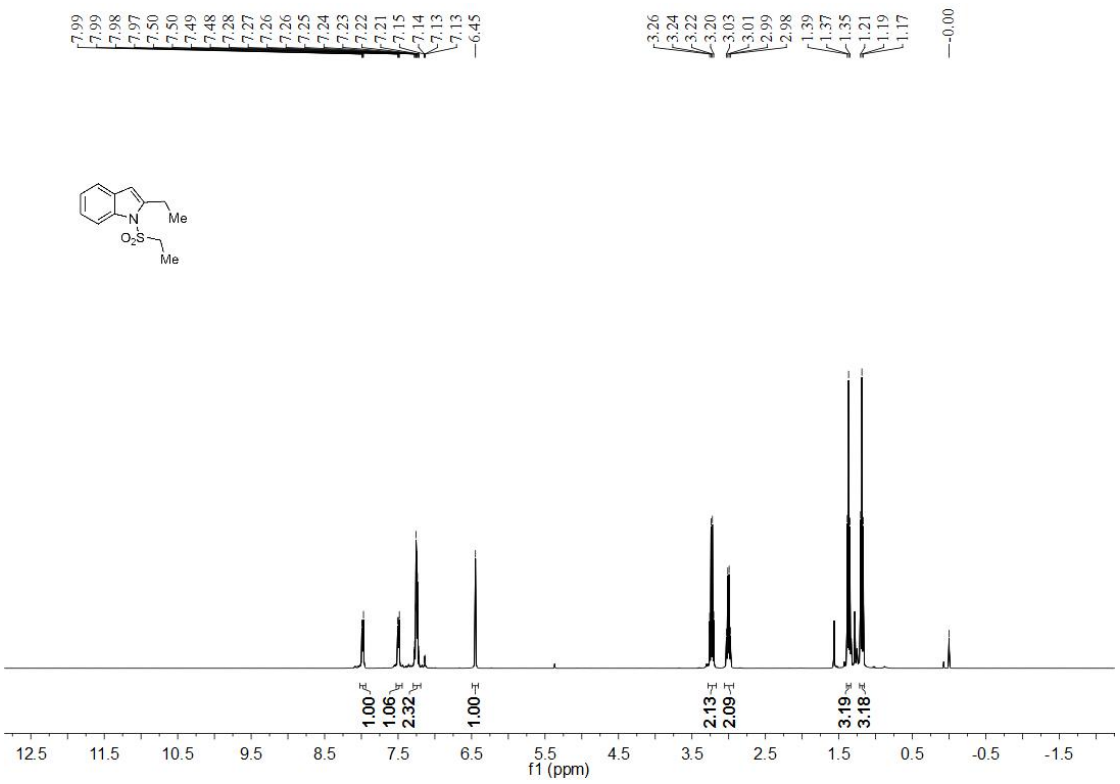


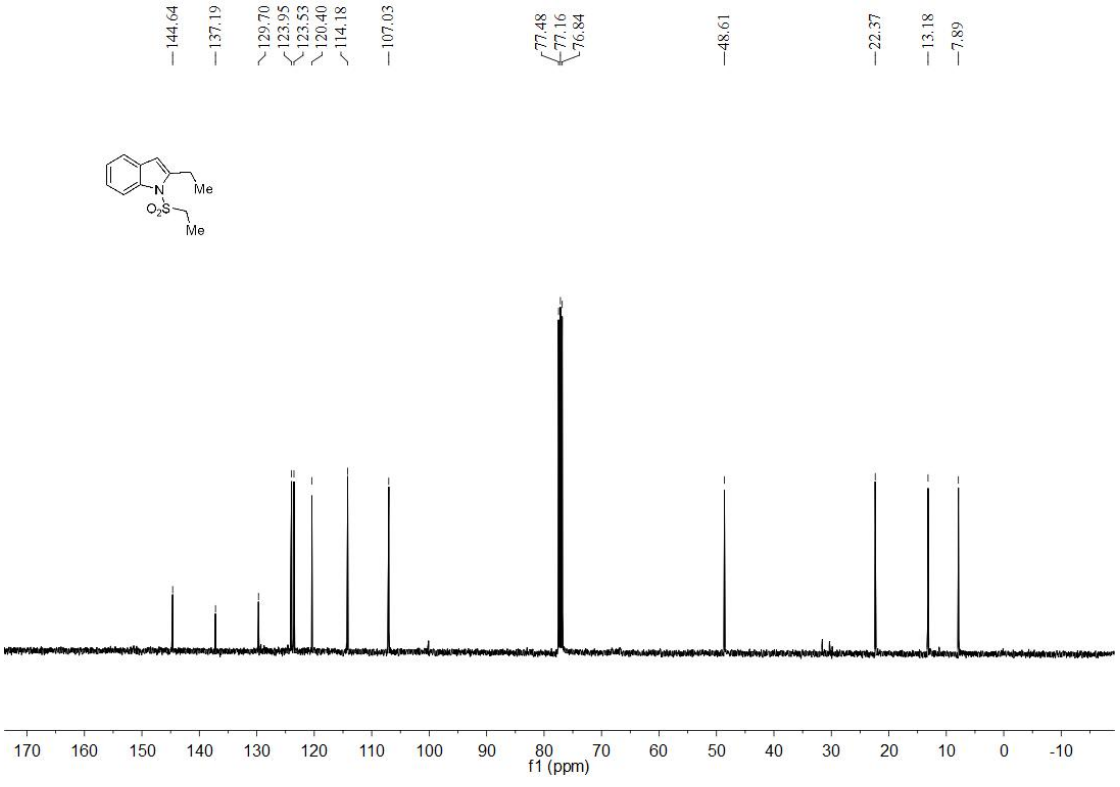
NMR Spectra of Product 2b



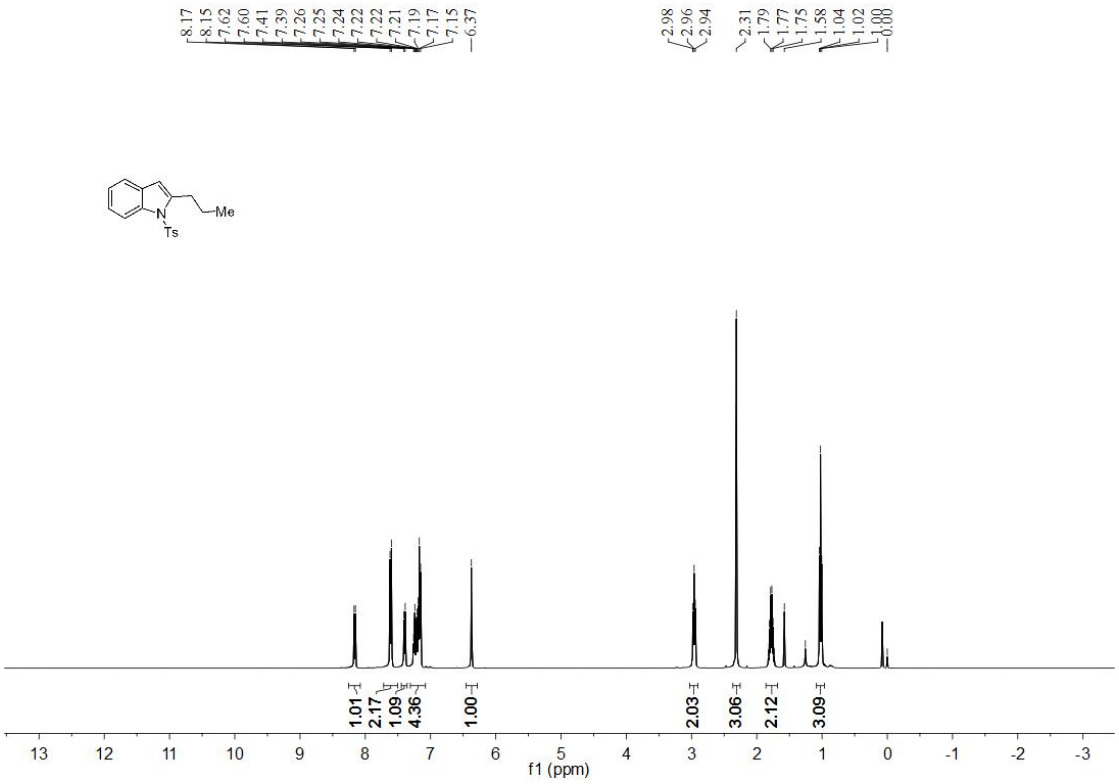


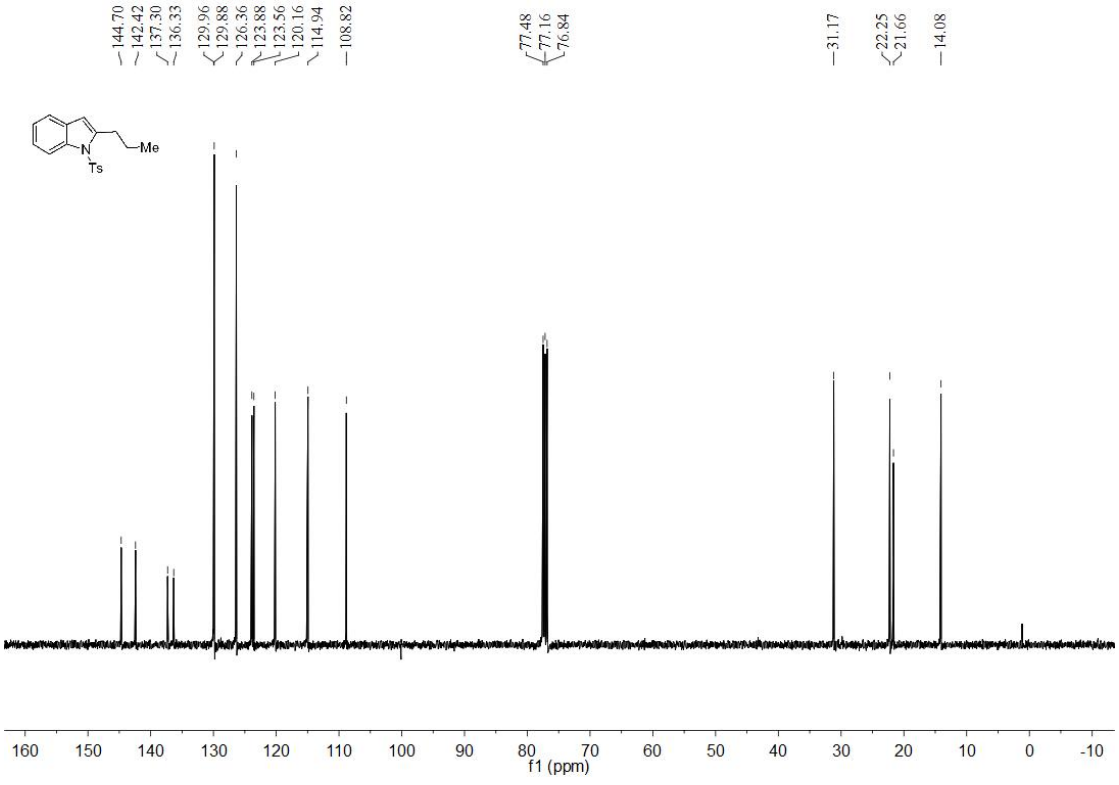
NMR Spectra of Product 2c



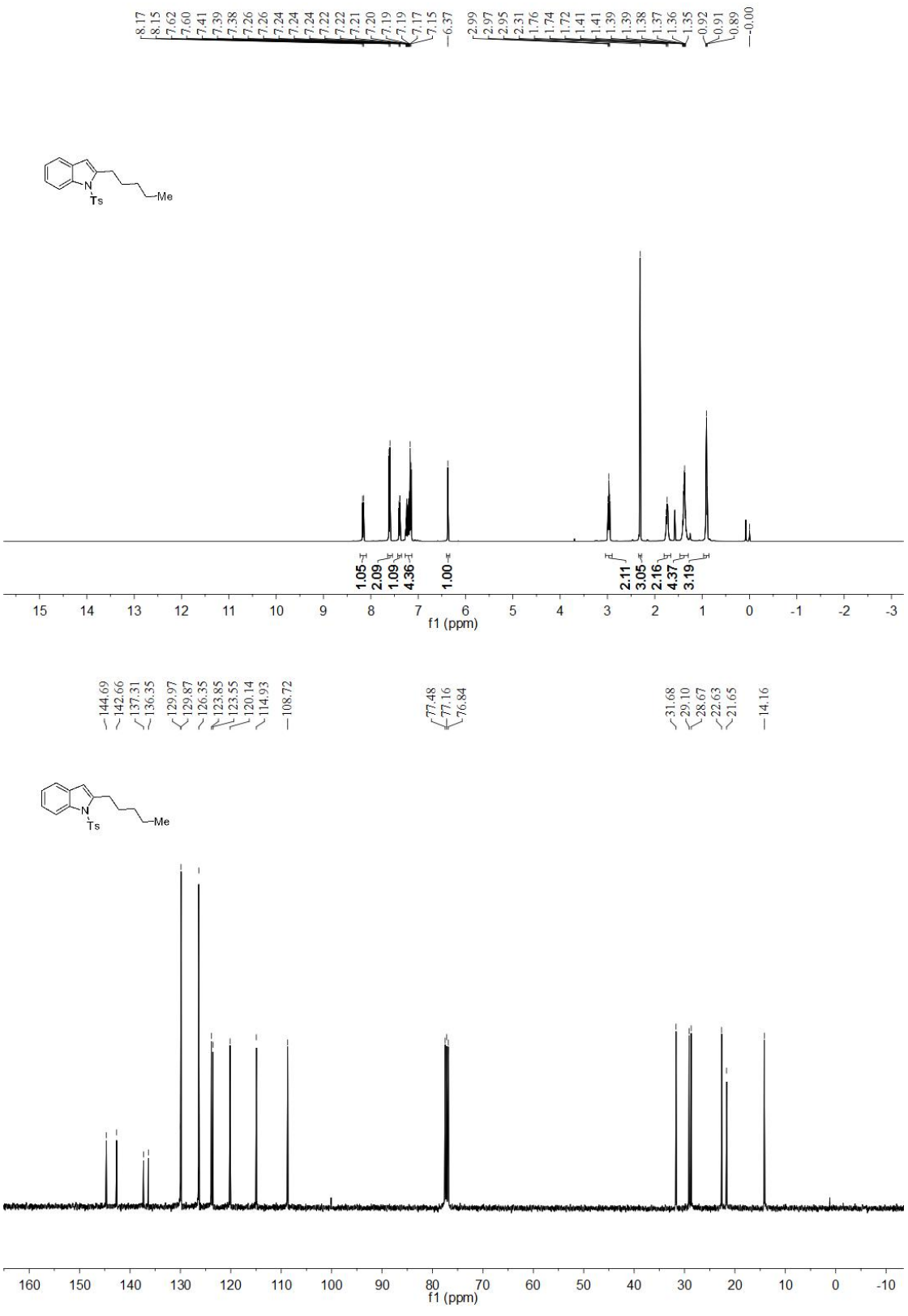


NMR Spectra of Product 2e

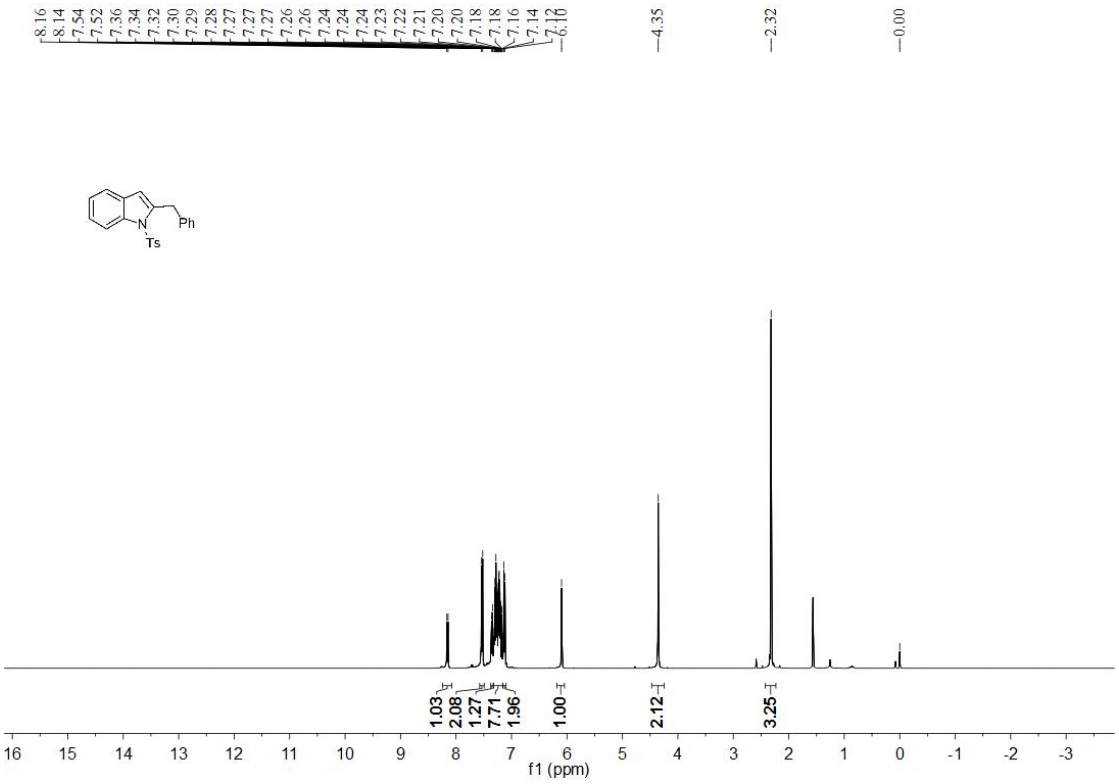


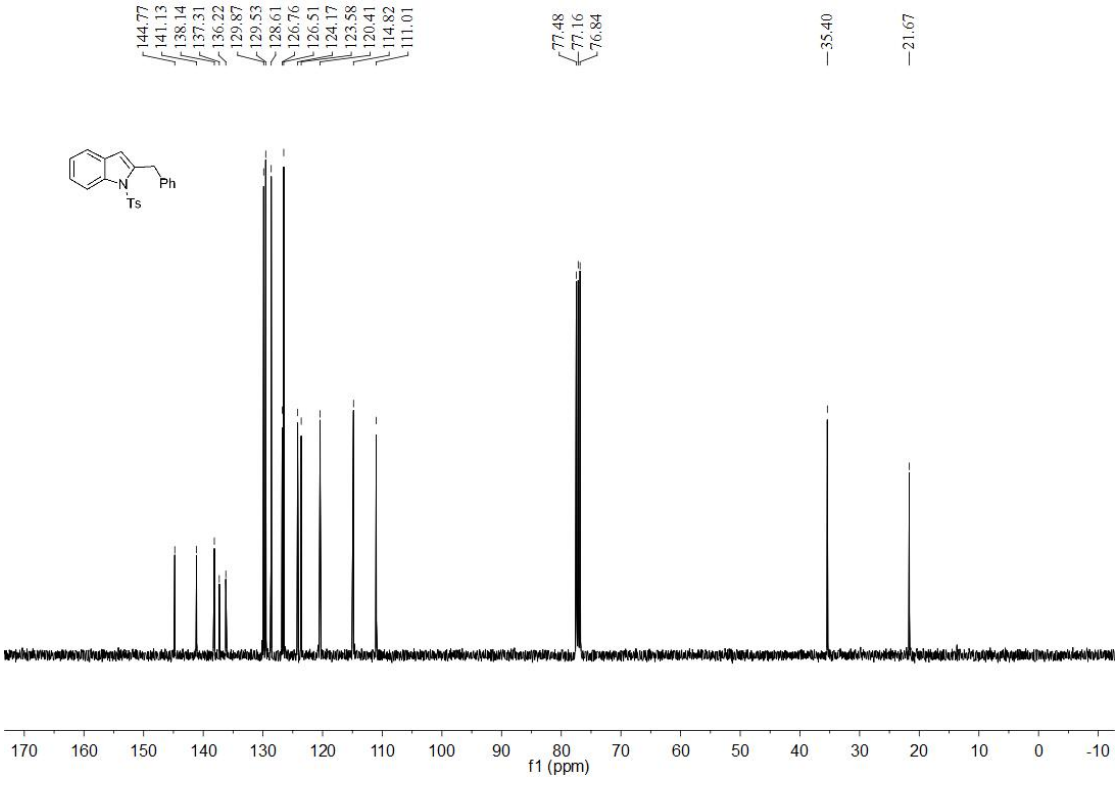


NMR Spectra of Product 2f

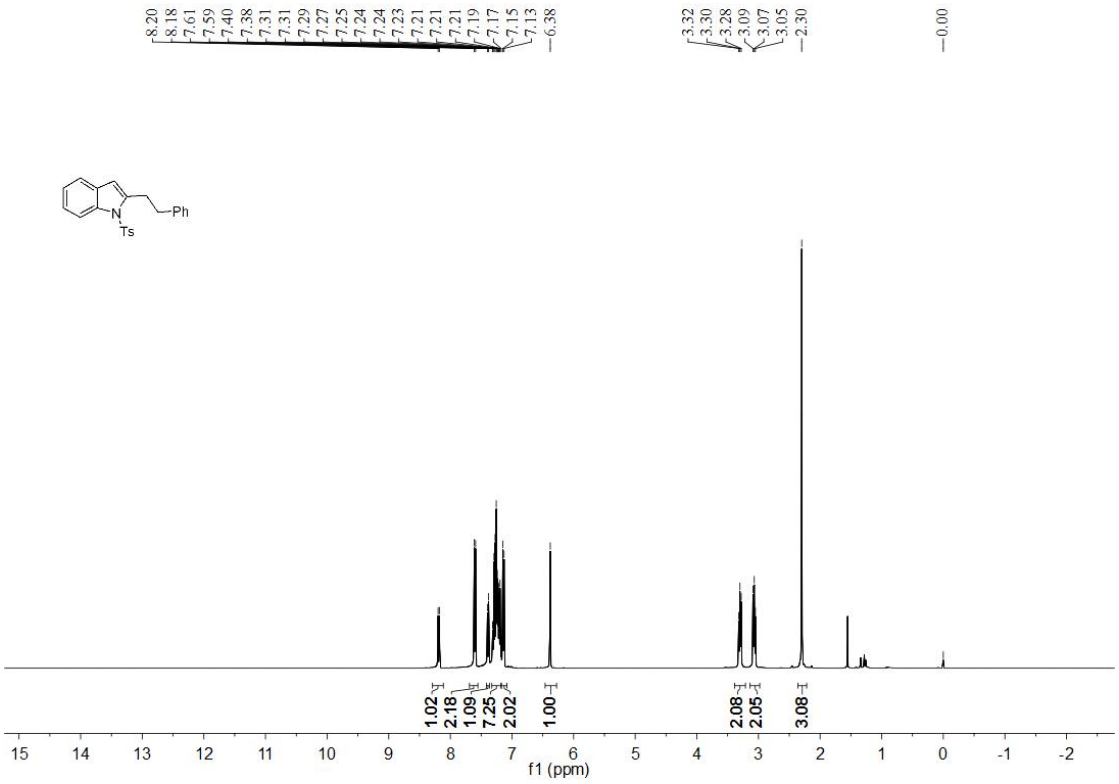


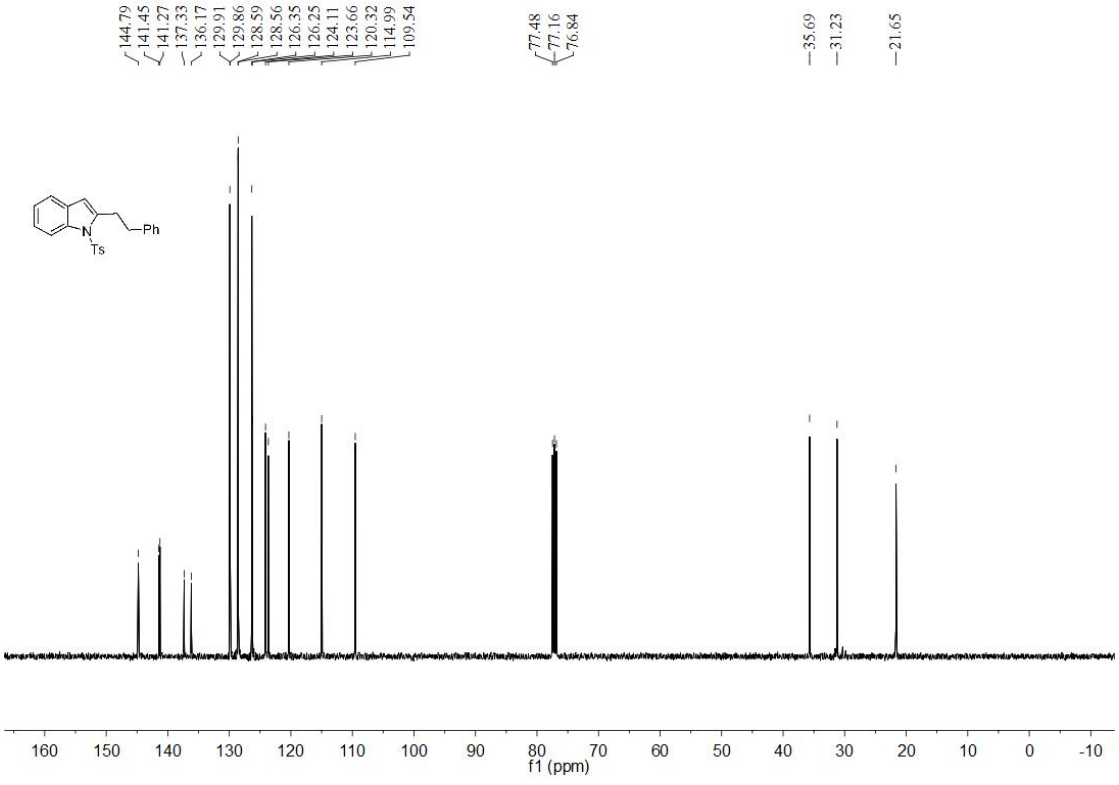
NMR Spectra of Product 2g



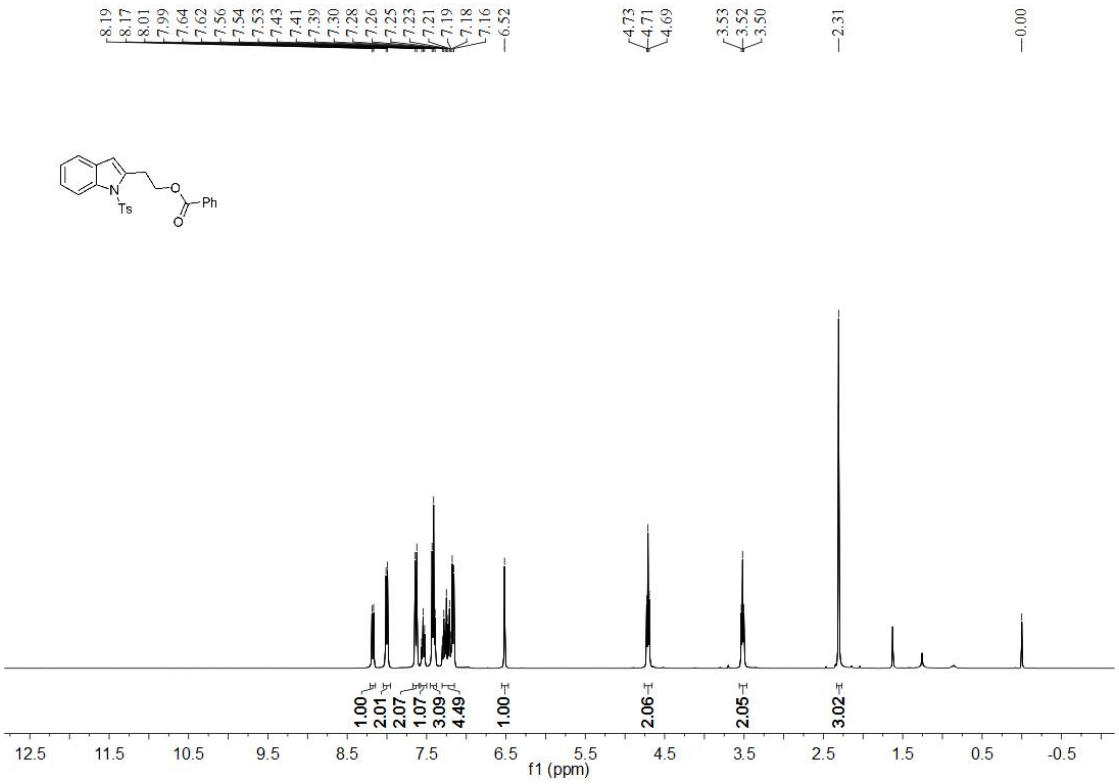


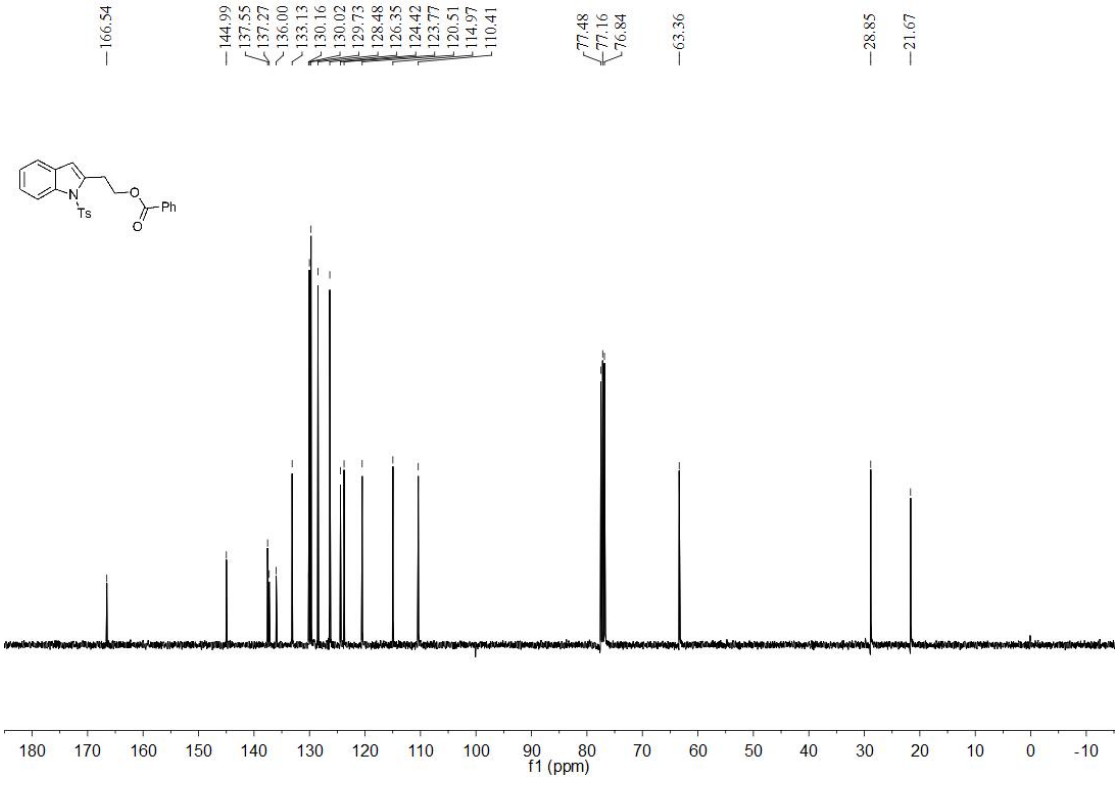
NMR Spectra of Product 2h



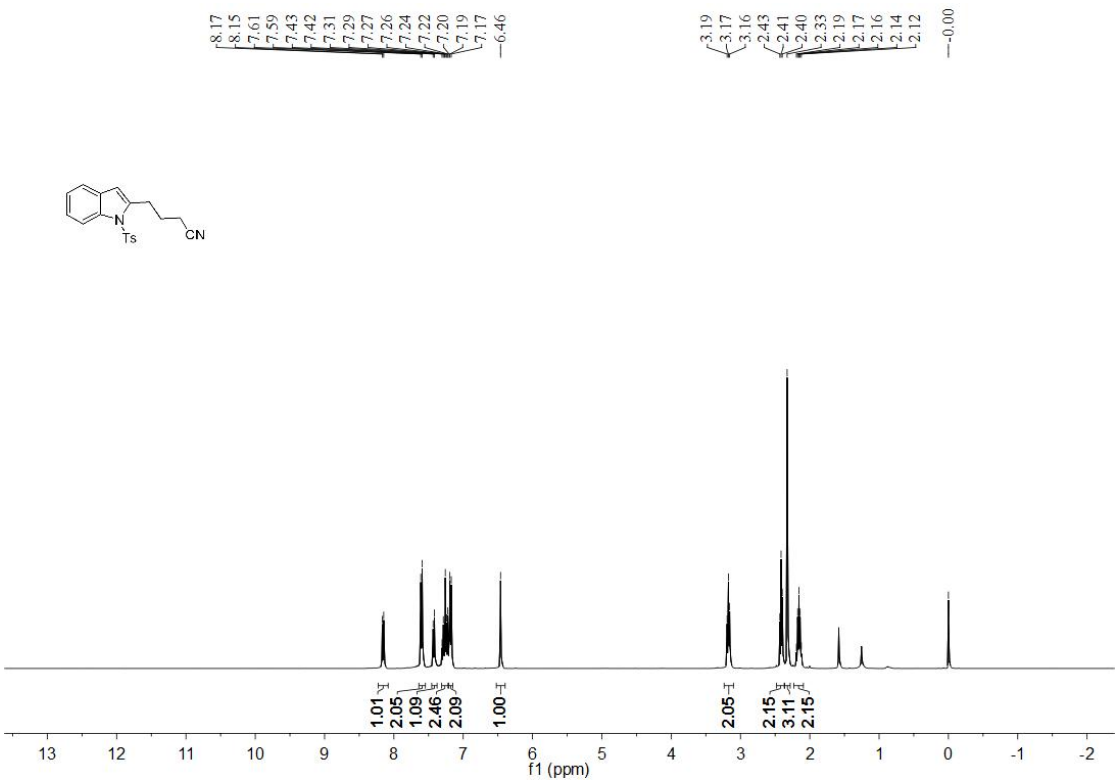


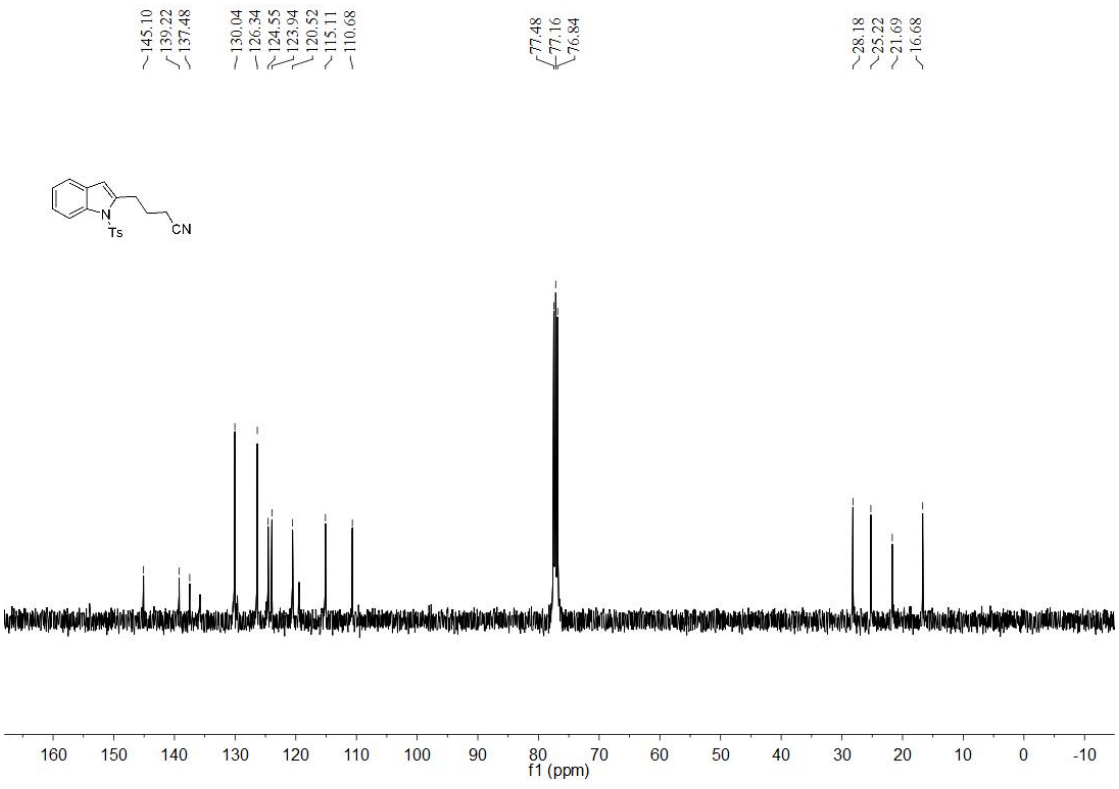
NMR Spectra of Product 2i



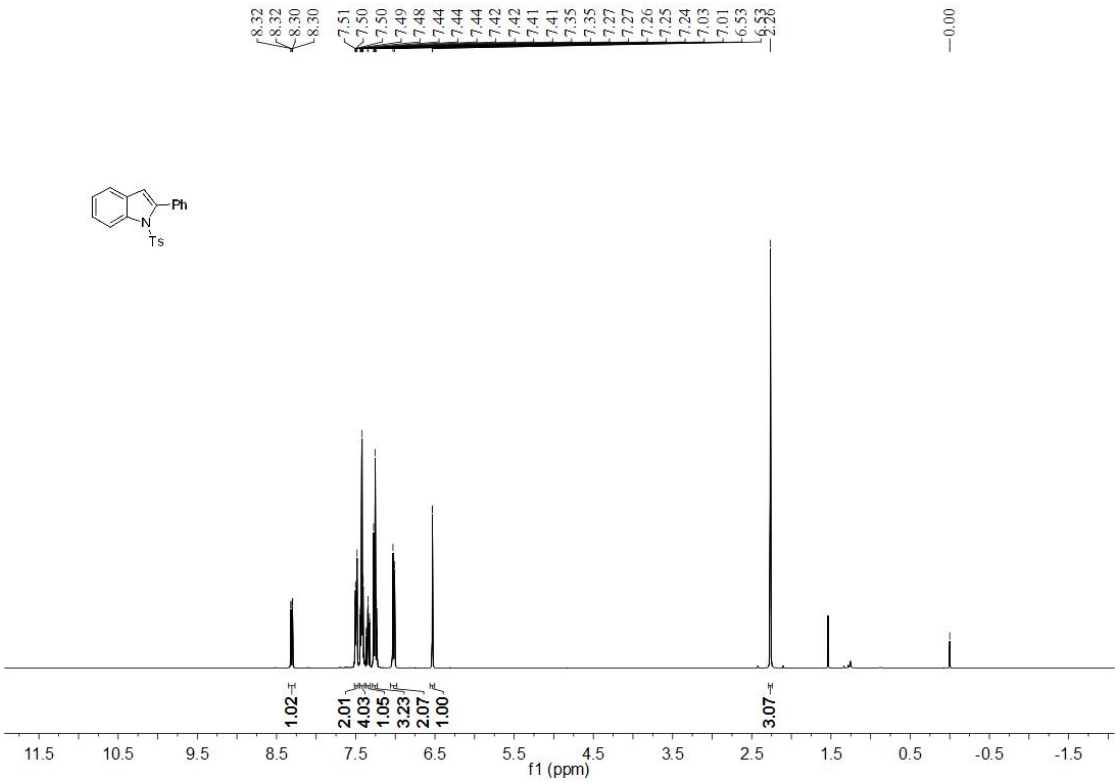


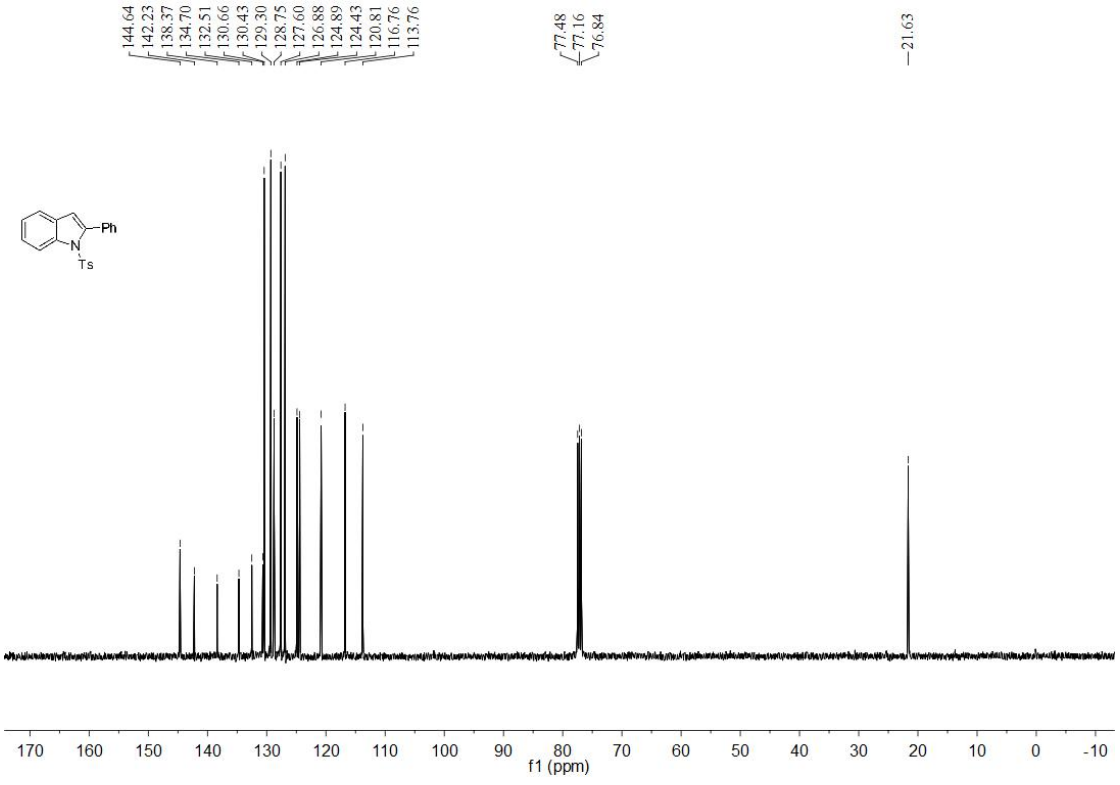
NMR Spectra of Product 2j



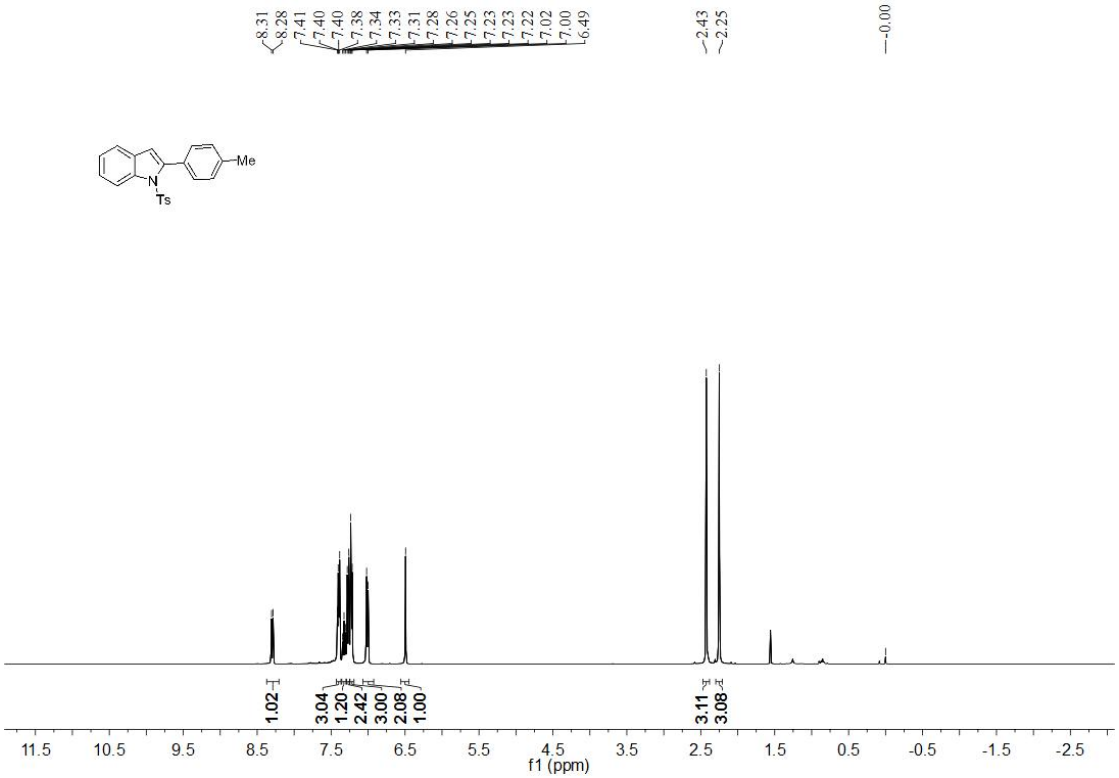


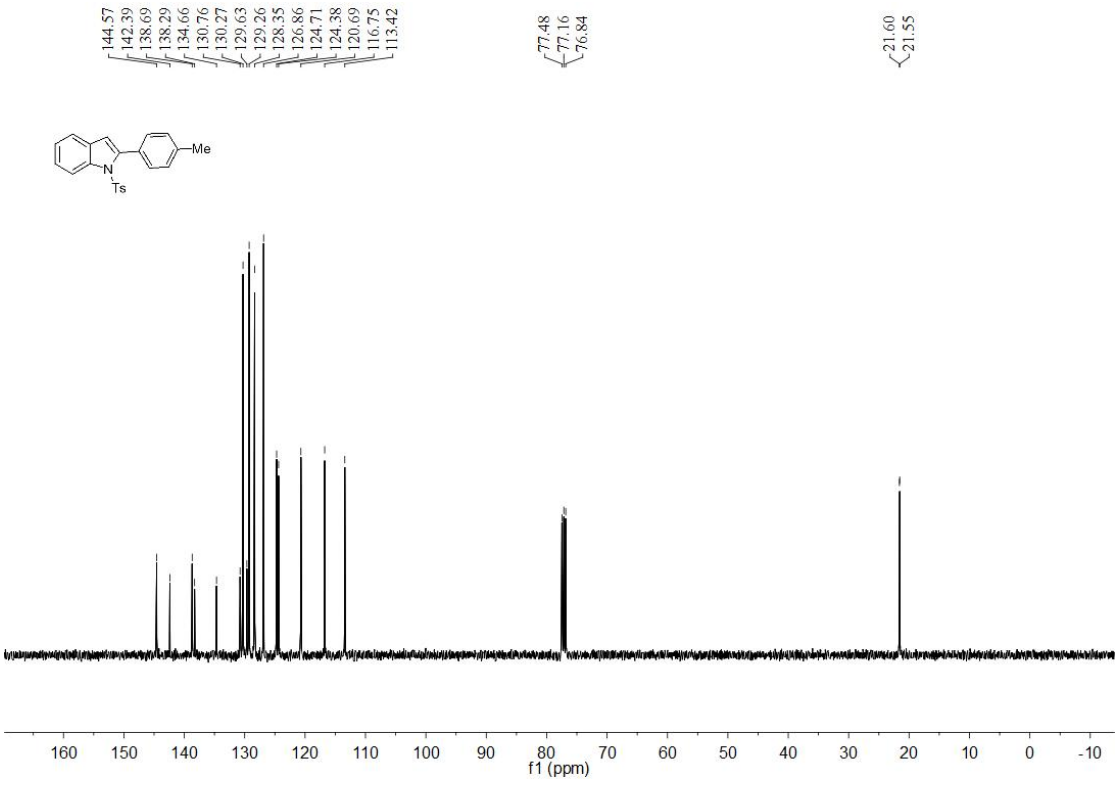
NMR Spectra of Product 2k



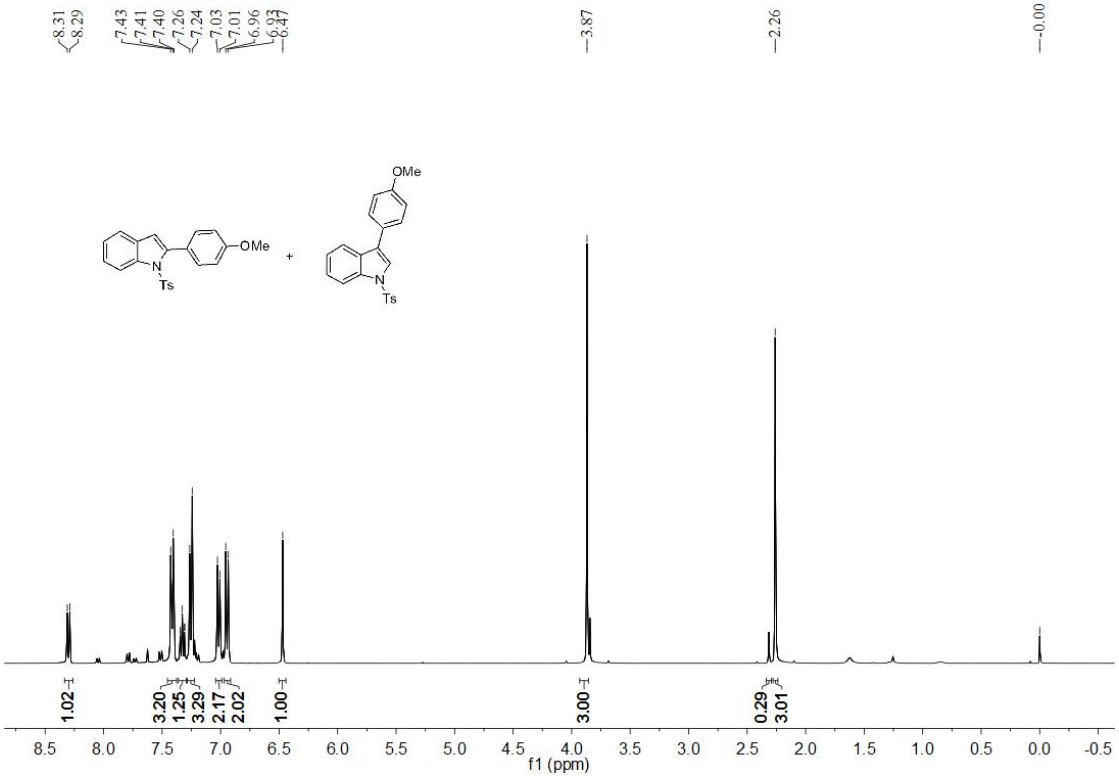


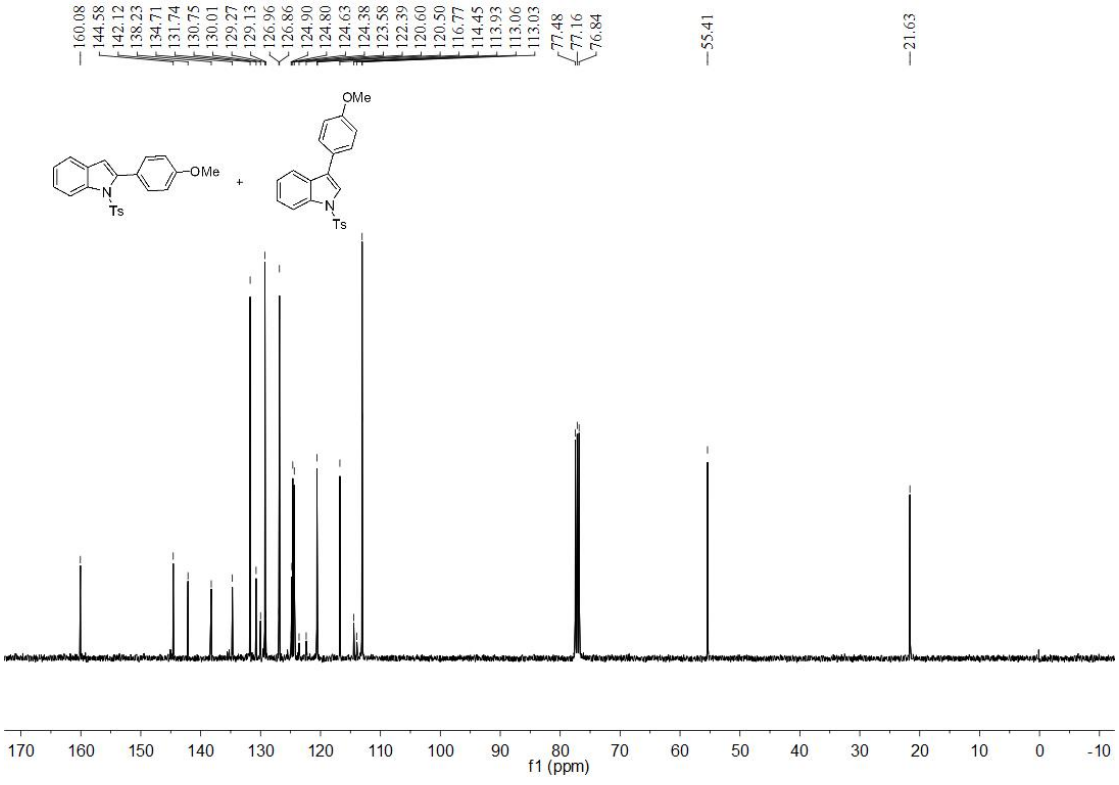
NMR Spectra of Product 2l



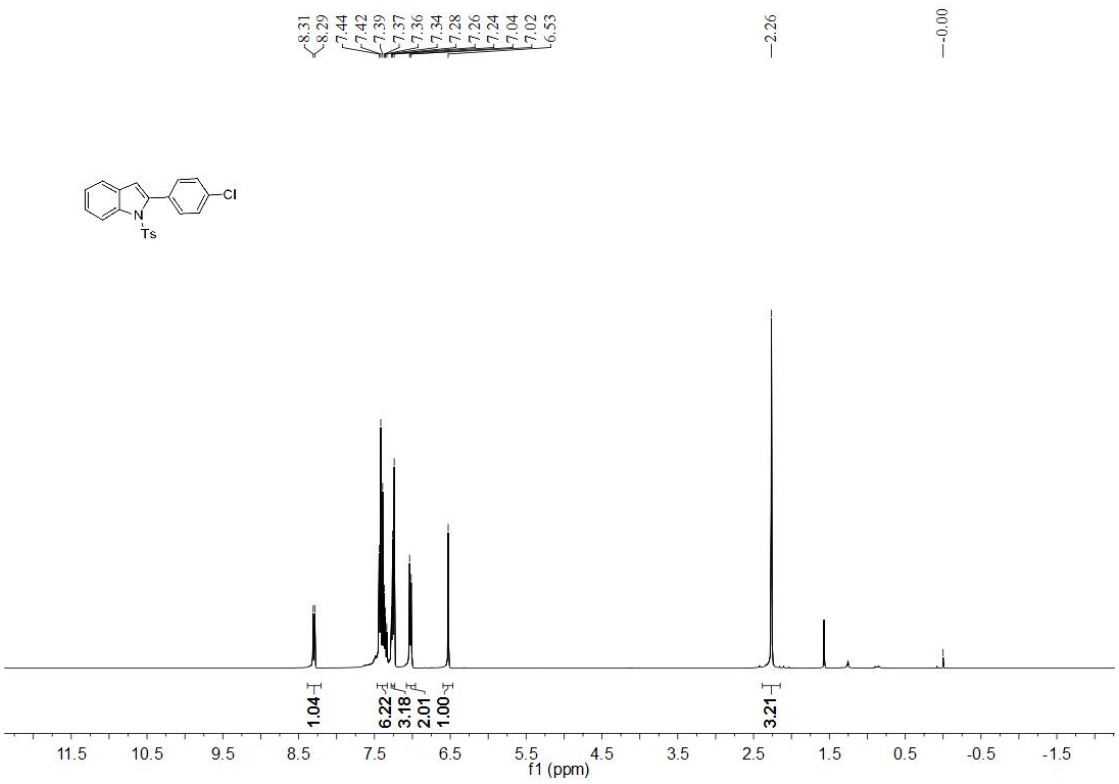


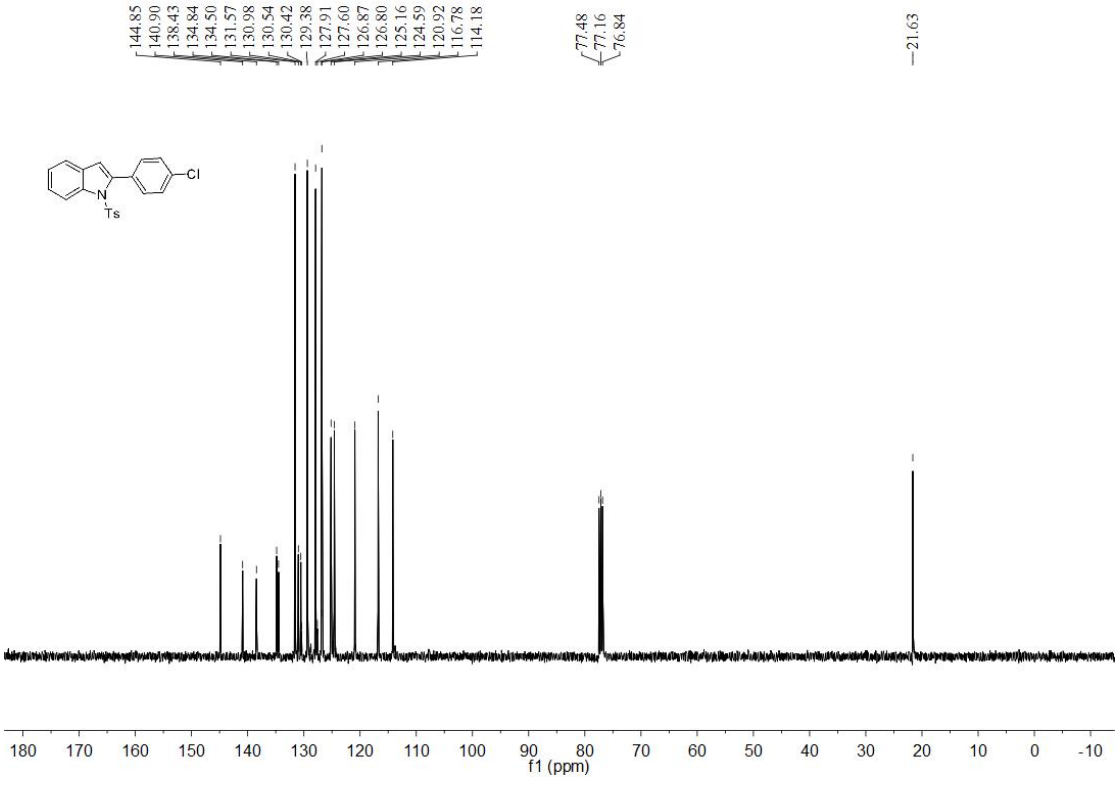
NMR Spectra of Product 2m



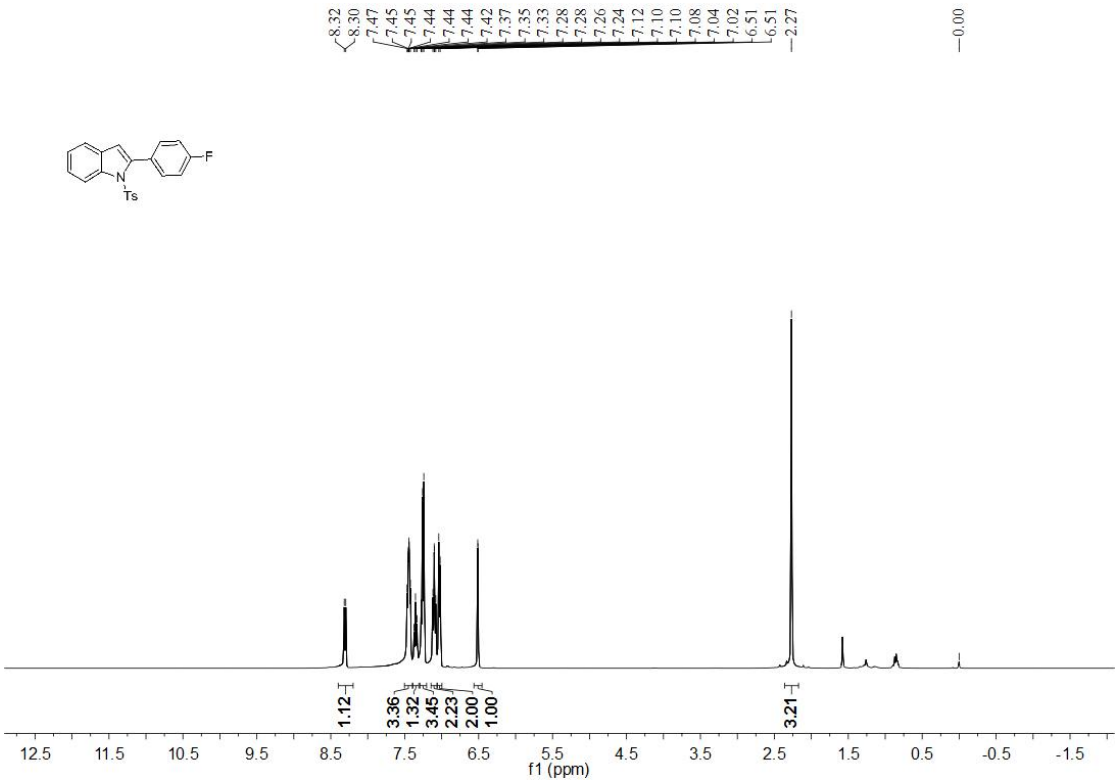


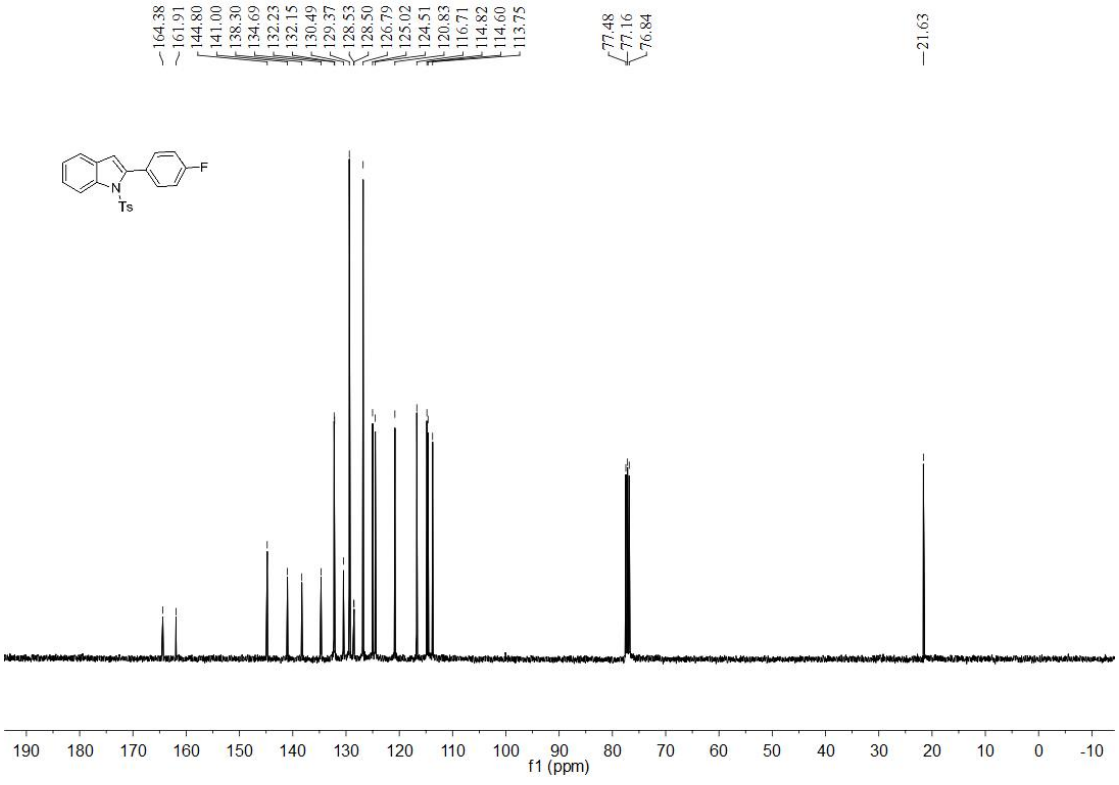
NMR Spectra of Product 2n



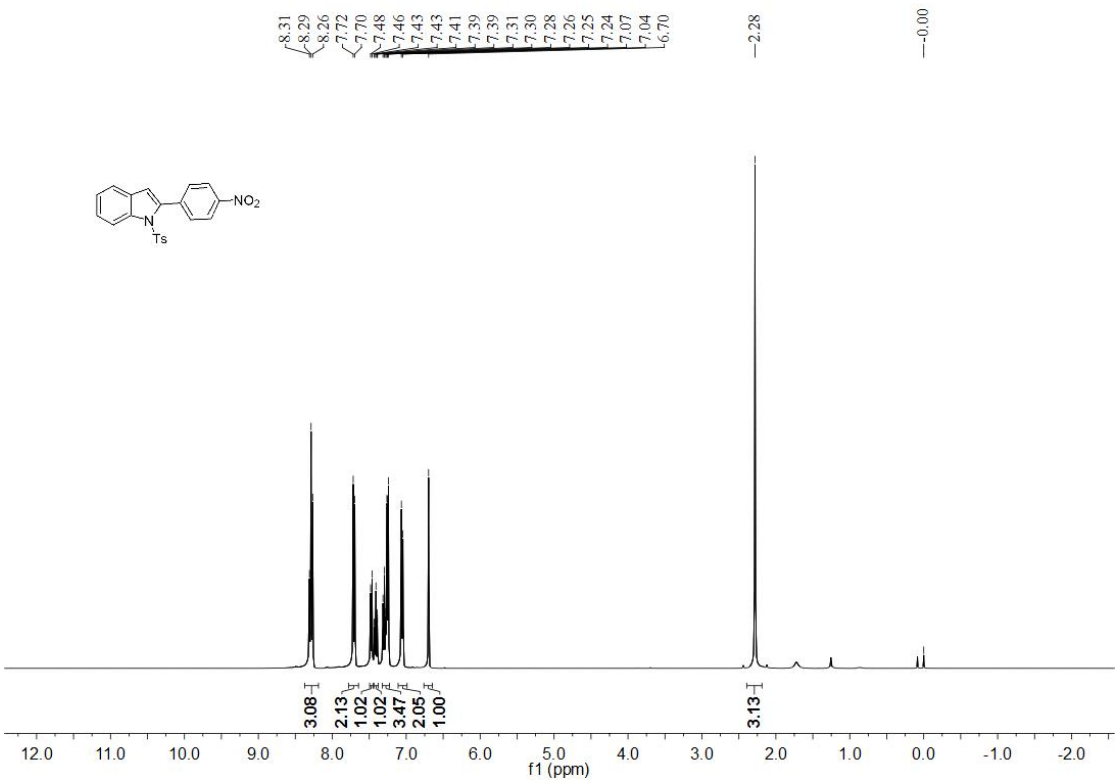


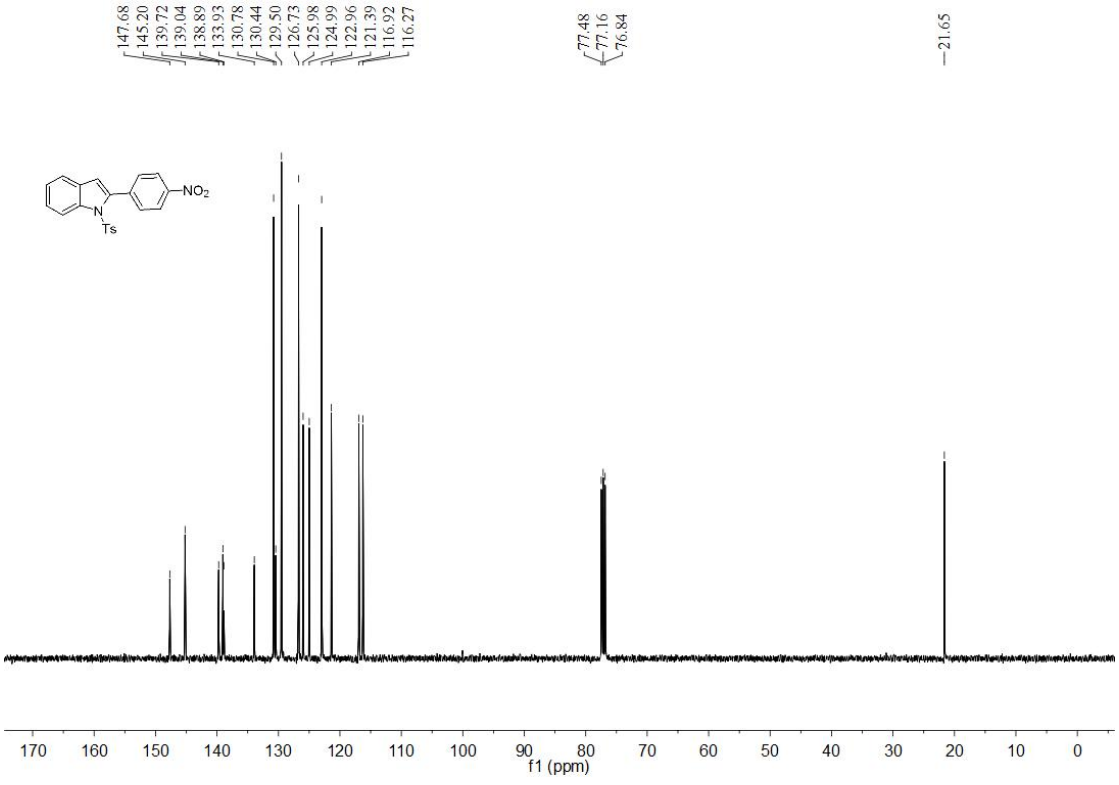
NMR Spectra of Product 2o



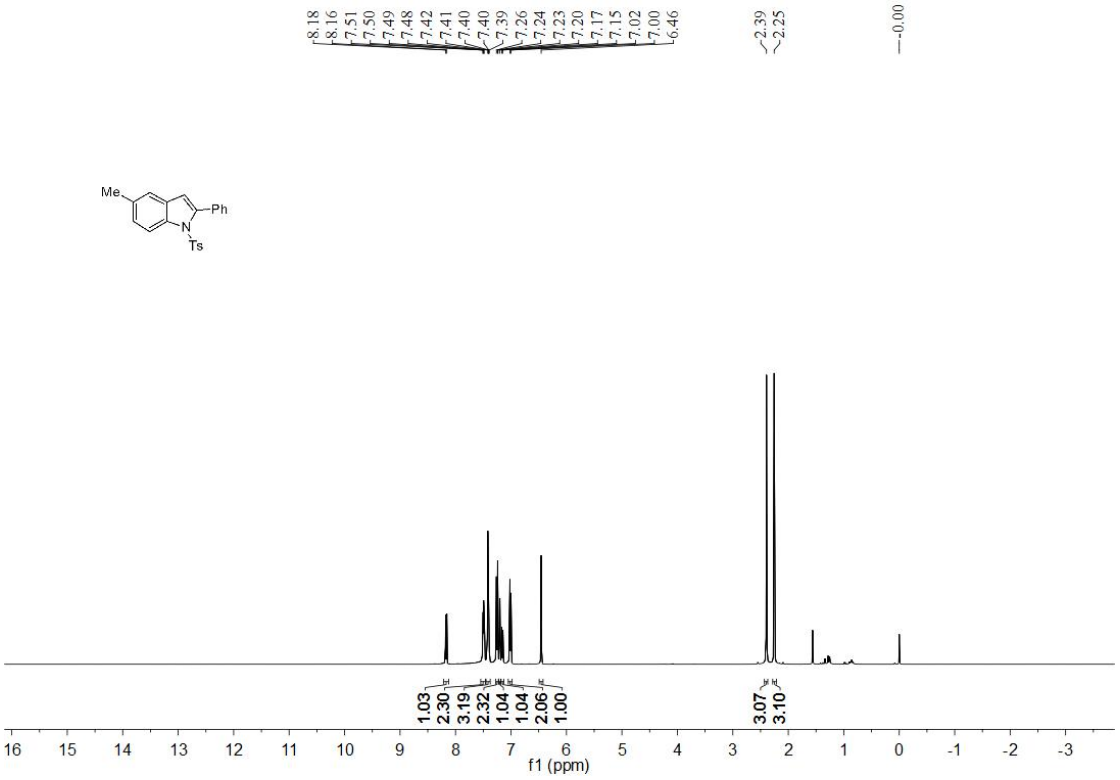


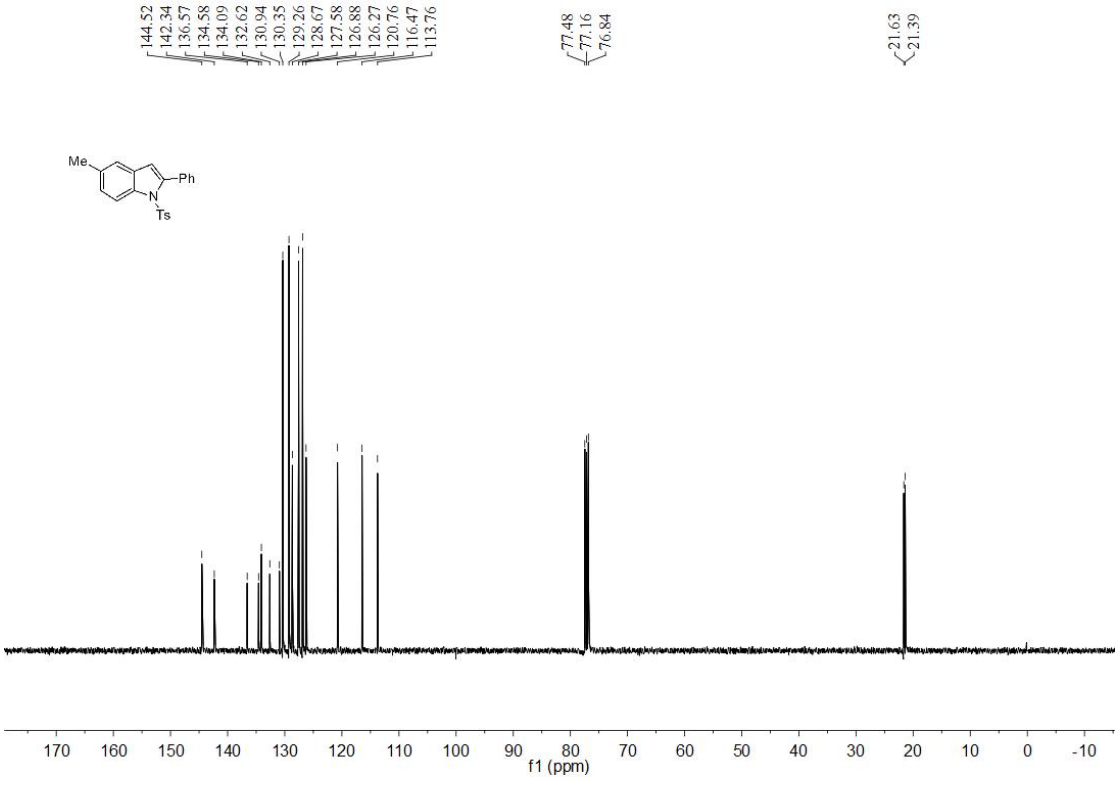
NMR Spectra of Product 2p



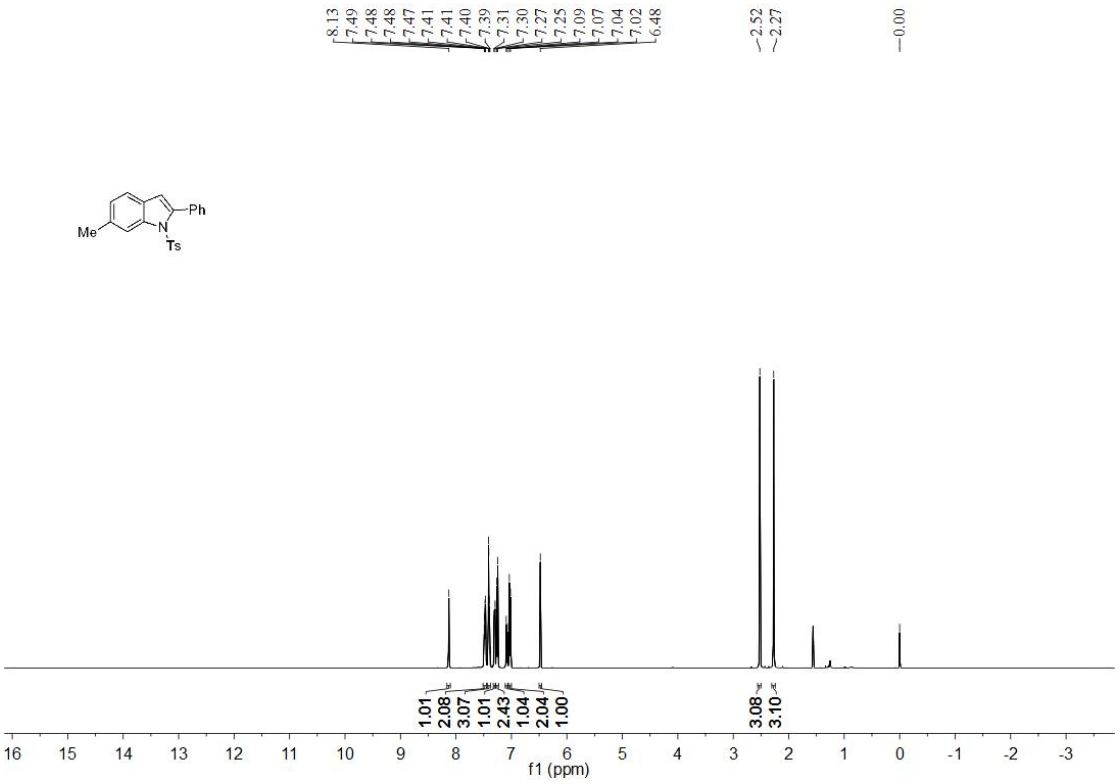


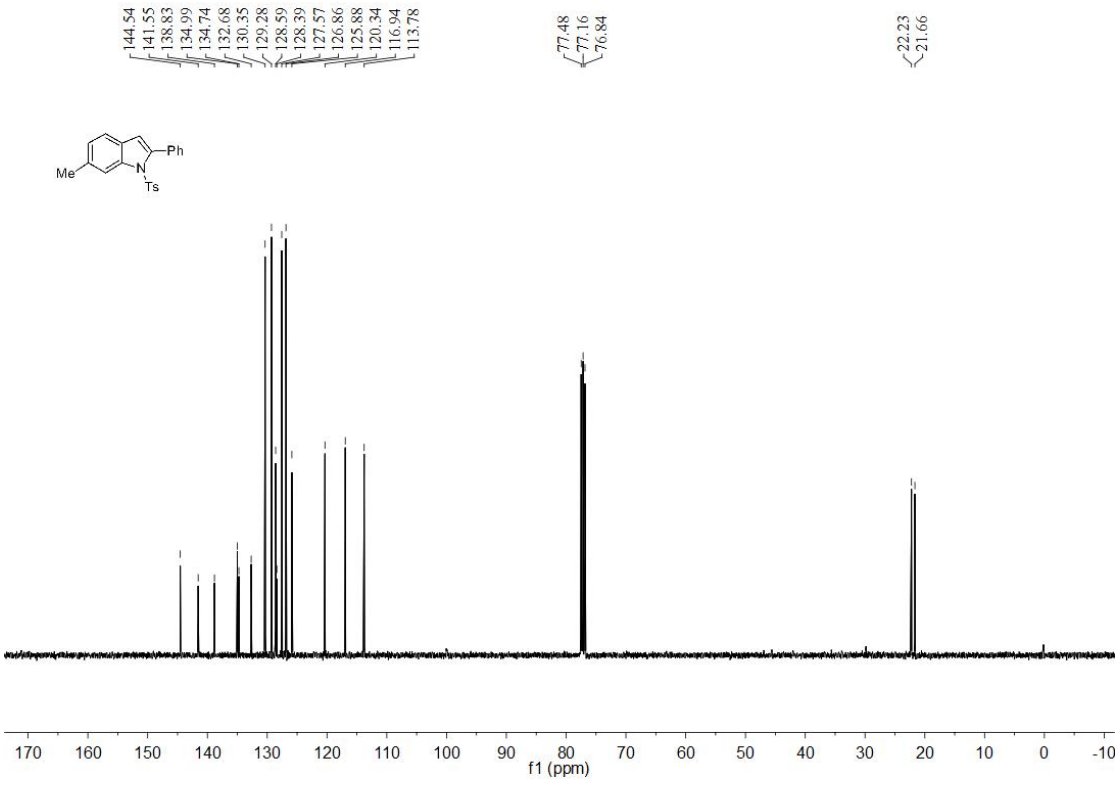
NMR Spectra of Product 2q



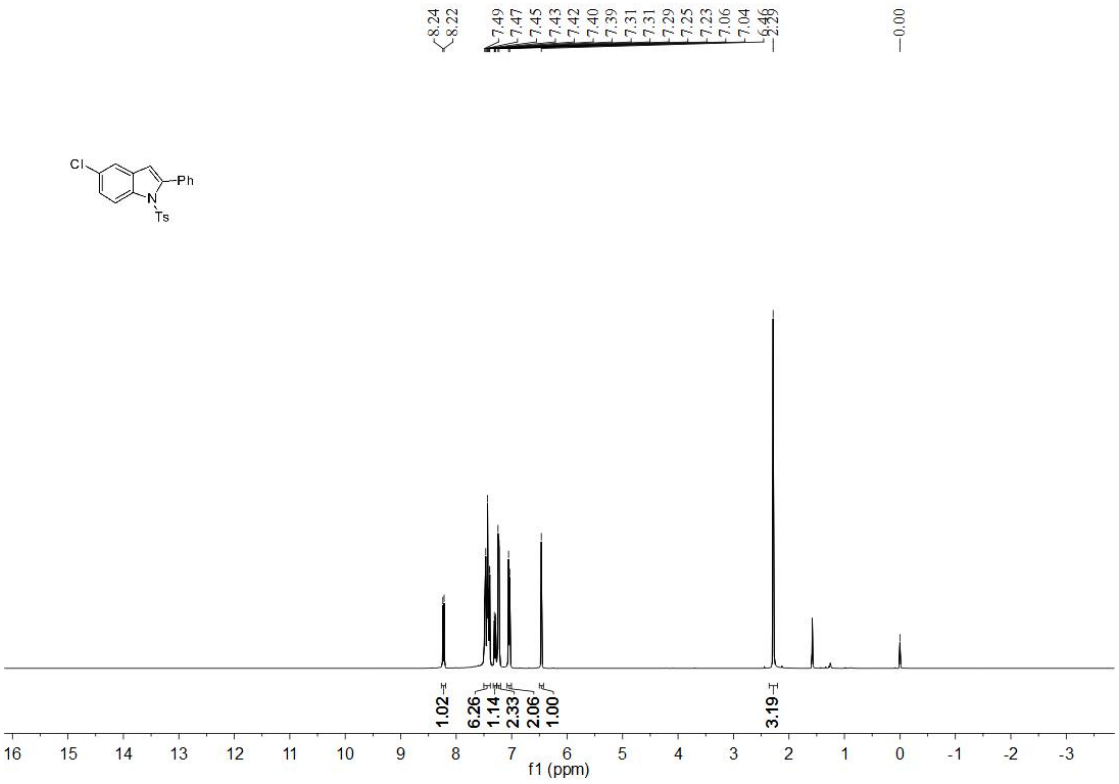


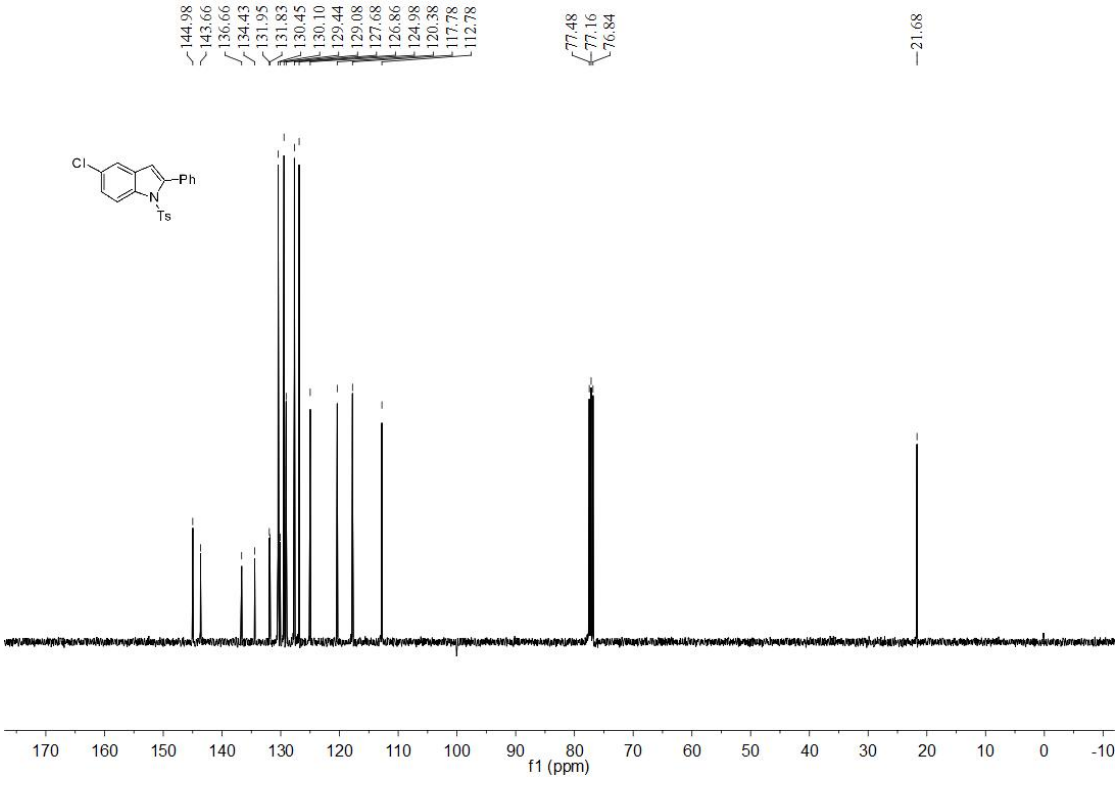
NMR Spectra of Product 2r



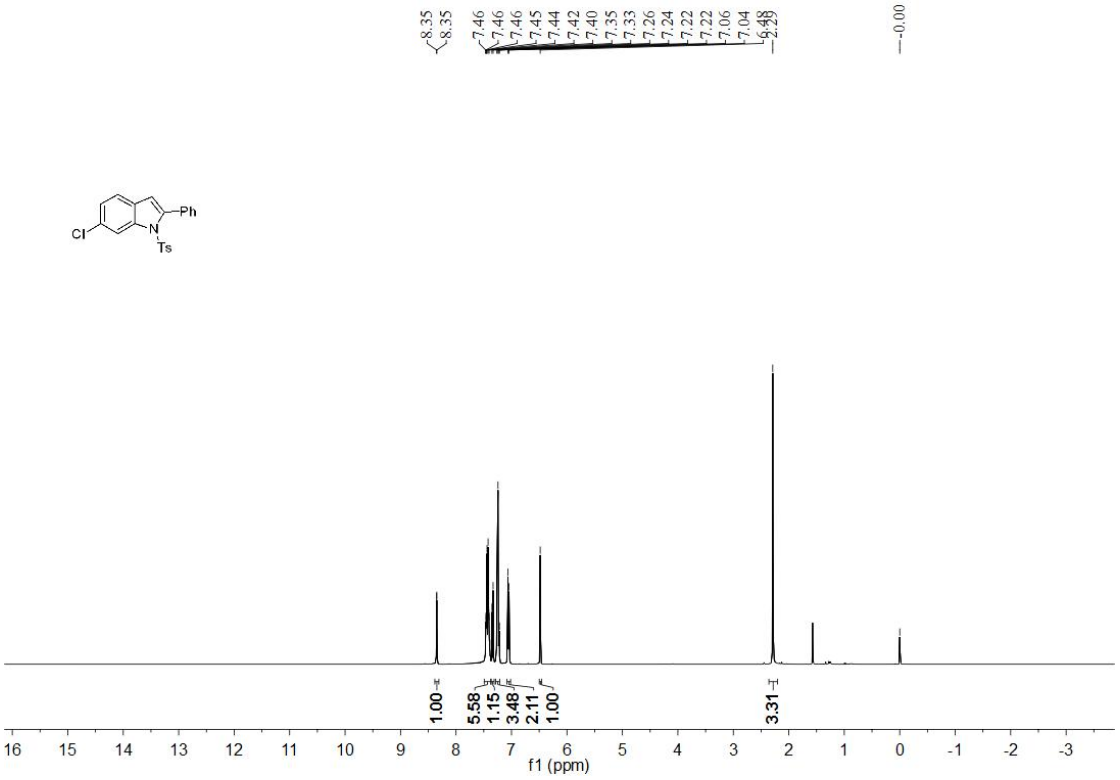


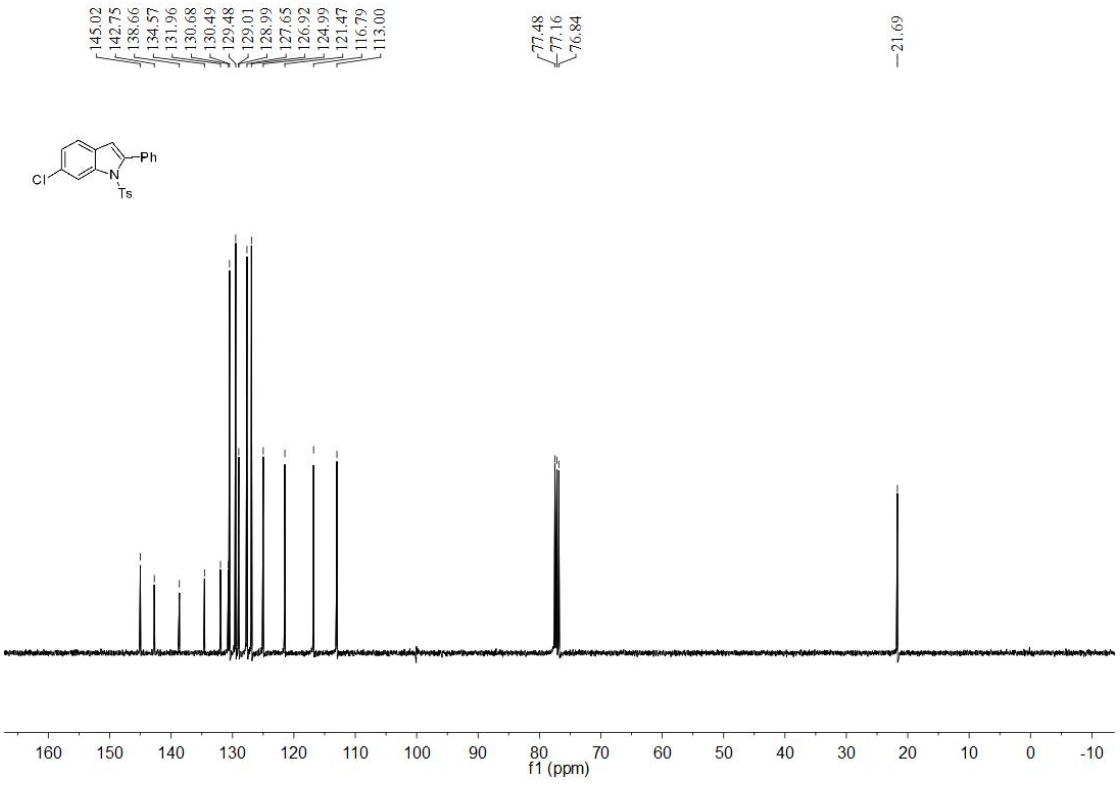
NMR Spectra of Product 2s



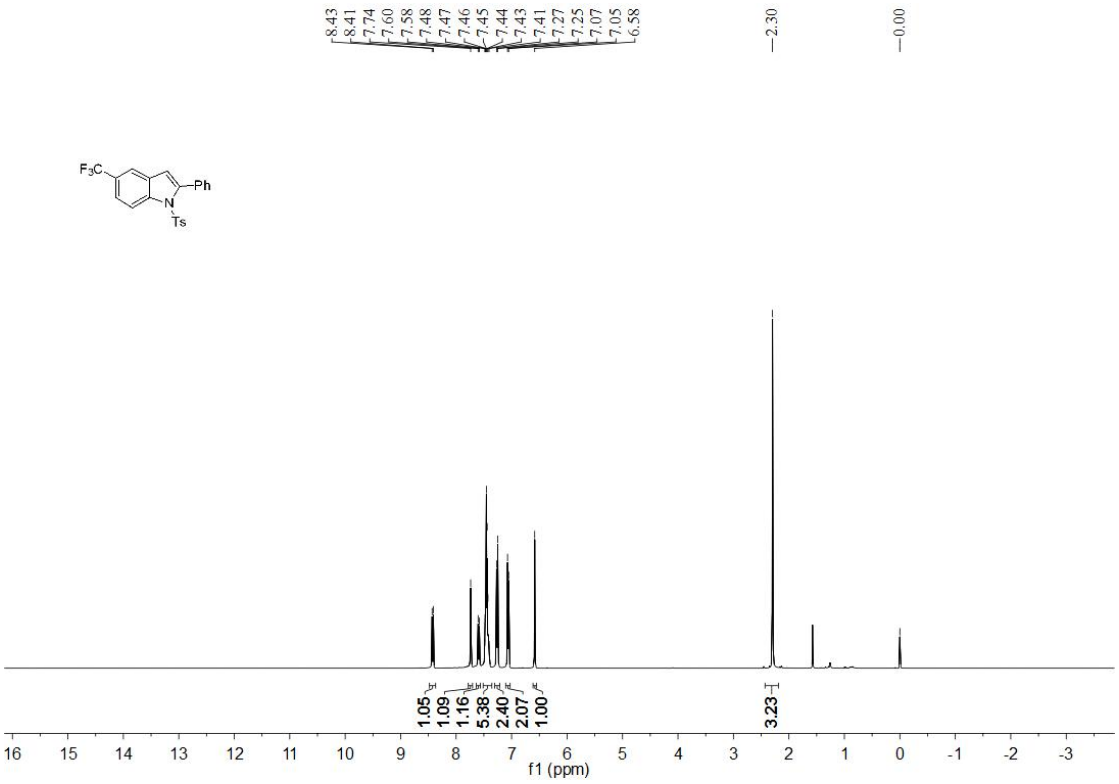


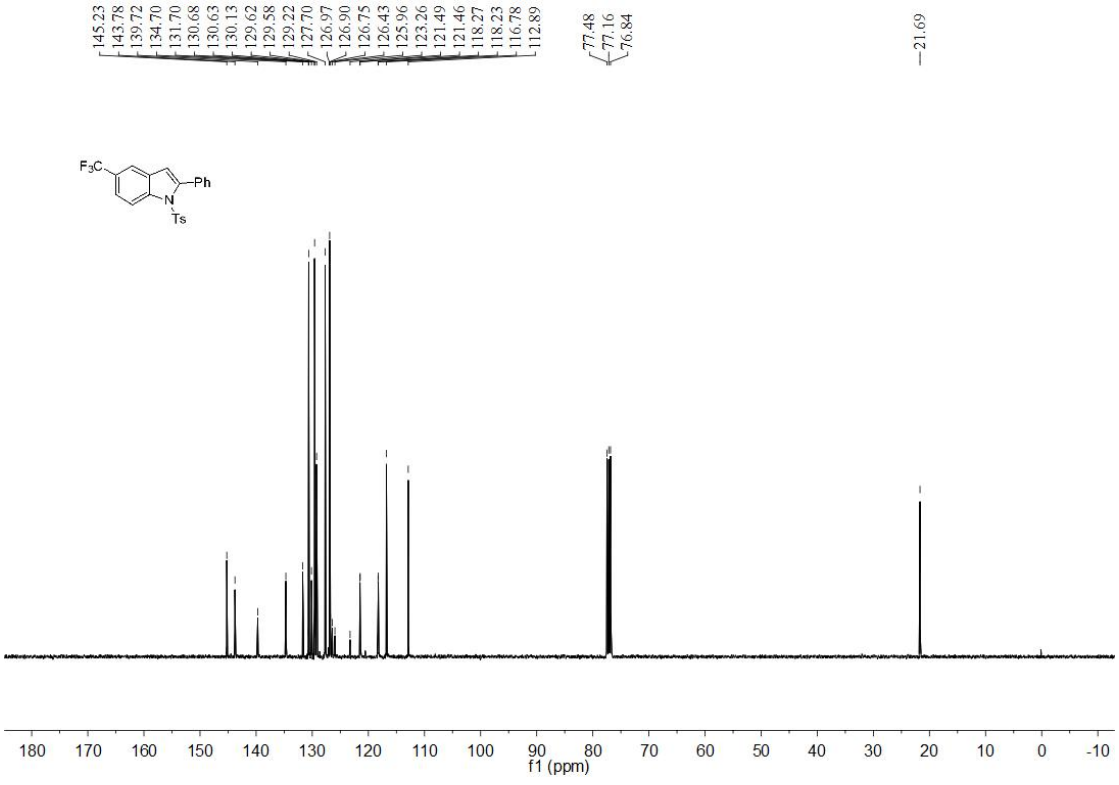
NMR Spectra of Product 2t



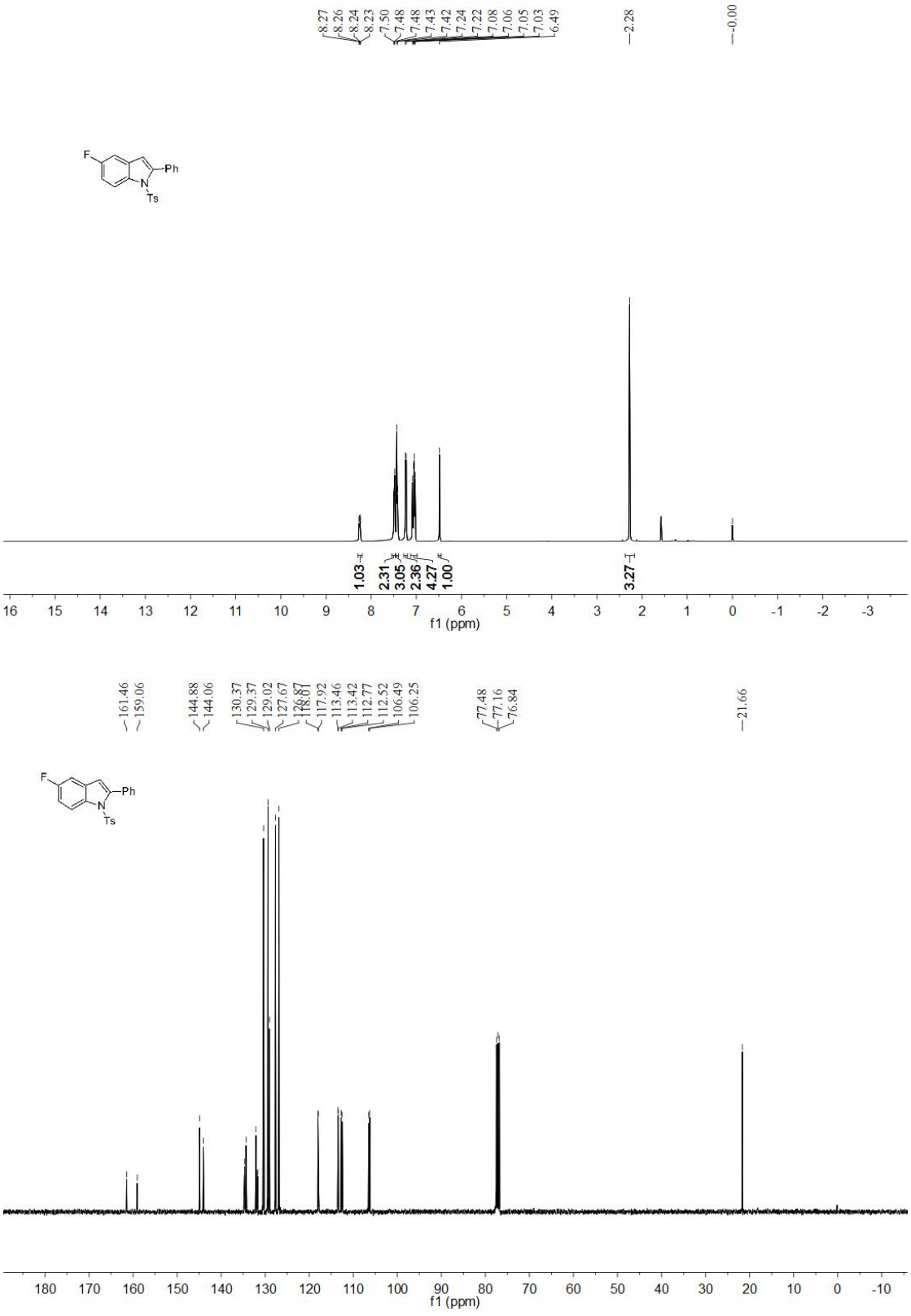


NMR Spectra of Product 2u





NMR Spectra of Product 2v



NMR Spectra of Product 4