Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Silver Catalyzed Domino Aza-Annulation/Diels-Alder Cyclization of 2-ene-yne Anilines: A Facile One-Pot Access to Carbazole, Dihydrocarbazole and Tetrahydrocarbazole Frameworks

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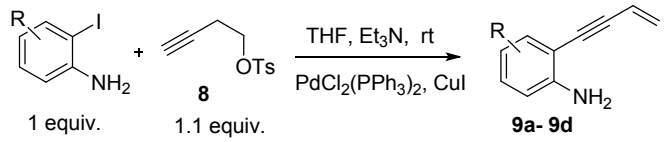
1. General methods

Unless otherwise stated, all the Reagents were purchased from commercial sources and used without purification. Solvents for chromatography were of technical grade. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel (SiO_2 60, 100-200 mesh, Fluka). Solvent mixtures are understood as volume/volume. ^1H and ^{13}C NMR spectra were recorded on either a Bruker DRX 400 spectrometer at 400.13 and 100.62 MHz respectively or Avance 500 spectrometer at 500.13 (^1H) and 125.76 MHz (^{13}C) by using chloroform-*d* ($CDCl_3$), as a solvent and tri methyl silane (TMS) as the internal standard. Data are reported in the following order: chemical shift (d) in ppm; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). HRMS analyses were acquired on single quadruple and carried out using the ESI techniques at 70 eV Chemical yields refer to isolated pure substances. Dichloroethane was dried over CaH_2, and stored in sealed ampoules over 4Å molecular sieves under an atmosphere of dry nitrogen. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula and septa apparatus.

2. Preparation of starting materials:

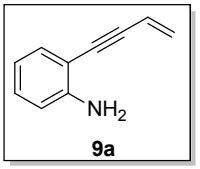
2.1. General procedure for the preparation of 2-(but-3-en-1-yn-1-yl) anilines (9):



A solution of 2-iodoaniline (2.0 g, 9.1 mmol) and Et_3N (10 mL) in THF (10 mL) was degassed with argon. $PdCl_2(PPh_3)_2$ (256 mg, 4 mol%), copper iodide (35 mg, 2 mol %), and alkyne **8**[1] (2.25 g, mmol) were added successively under argon atmosphere at room temperature. The mixture was stirred for 8 h at the same temperature. After completion of the reaction, as monitored by TLC, the mixture was filtered through a Celite pad, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by column chromatography (silica gel, 60−120 mesh) using an ethyl acetate/n-hexane gradient mixture to afford the pure product **9** as a black thick mass in good yield.

2.2. Spectral data of 2-(but-3-en-1-yn-1-yl)anilines (9a)

Spectral data for 2-(but-3-en-1-yn-1-yl)aniline (9a):



Following the general procedure (rt for 8 h), compound **9a**[2] was obtained after column chromatography (hexane:EtOAc 8:2) as a brown colored liquid (1.0 g, 78 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (dd, J = 8.2, 1.5 Hz, 1H), 7.14 – 7.10 (m, 1H), 6.70 (d, J = 7.8 Hz, 2H), 6.07 (dd, J = 17.6, 11.1 Hz, 1H), 5.72 (dd, J = 17.6, 2.0 Hz, 1H), 5.53 (dd, J = 11.1, 2.0 Hz, 1H), 4.20 (bs, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.7, 132.1, 129.7, 126.4, 117.9, 117.1, 114.3, 107.8, 93.4, 86.5 ppm. HRMS calcd for $C_{10}H_{10}N[M + H]^+$: 144.0808; found: 144.0832.

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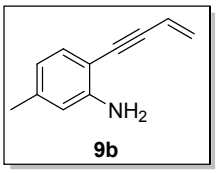
[1] F. Adriana, B. Aurelie, B. Thierry, G. Gerald and B.-R. Sabine, *Tetrahed. Lett.,* 2002, **43,** 787.

[2] K. Hiroyuki, S. Yasuo, T. Jun and I. Nobuharu, *org. Lett.,* 2006, **8**, 895.

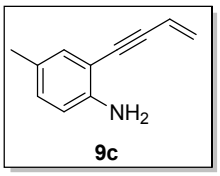
Spectral data for 2-(but-3-en-1-yn-1-yl)-5-methylaniline (9b):



9b

Following the general procedure (rt for 8 h), compound **9b** was obtained after column chromatography (hexane:EtOAc 8:2) as a brown colored liquid (1.1 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (d, J = 7.6 Hz, 1H), 6.53 – 6.49 (m, 2H), 6.05 (dd, J = 17.6, 11.1 Hz, 1H), 5.68 (dd, J = 17.6, 2.0 Hz, 1H), 5.49 (dd, J = 11.1, 2.0 Hz, 1H), 2.25 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.7, 140.1, 131.9, 125.9, 119.1, 117.3, 114.9, 105.0, 92.9, 86.7, 21.6 ppm. HRMS calcd for $C_{11}H_{12}N[M + H]^+$: 158.0964; found: 158.0976.

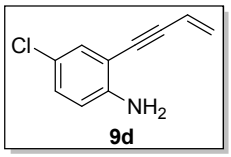
Spectral data for 2-(but-3-en-1-yn-1-yl)-4-methylaniline (9c):



9c

Following the general procedure (rt for 8 h), compound **9c** was obtained after column chromatography (hexane:EtOAc 8:2) as a brown colored liquid (1.1 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, J = 1.4 Hz, 1H), 6.93 (dd, J = 8.2, 2.0 Hz, 1H), 6.61 (d, J = 8.2 Hz, 1H), 6.05 (dd, J = 17.5, 11.2 Hz, 1H), 5.70 (dd, J = 17.5, 2.0 Hz, 1H), 5.51 (dd, J = 11.2, 2.0 Hz, 1H), 4.06 (bs, 2H), 2.20 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.4, 132.2, 130.6, 127.1, 126.2, 117.2, 114.5, 107.8, 93.1, 86.7, 20.2 ppm. HRMS calcd for $C_{11}H_{12}N[M + H]^+$: 158.0964; found: 158.0980.

Spectral data for 2-(but-3-en-1-yn-1-yl)-4-chloroaniline (9d):

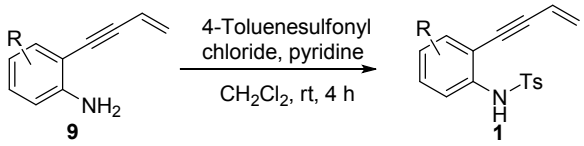


9d

Following the general procedure (rt for 8 h), compound **9d** was obtained after column chromatography (hexane:EtOAc 8:2) as a brown colored liquid (1.03 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, J = 2.4 Hz, 1H), 7.06 (dd, J = 8.7, 2.4 Hz, 1H), 6.61 (d, J = 8.7 Hz, 1H), 6.04 (dd, J = 17.6, 11.1 Hz, 1H), 5.73 (dd, J = 17.6, 2.0 Hz, 1H), 5.56 (dd, J = 11.1, 1.8 Hz, 1H), 4.20 (bs, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 131.3, 129.7, 127.1, 122.2, 116.8, 115.4, 109.1, 94.2, 85.2 ppm. HRMS calcd for $C_{10}H_9ClN[M + H]^+$: 178.0418; found: 178.0427.

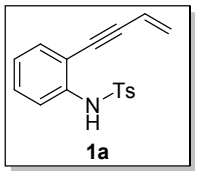
2.3. General procedure for the preparation of N-tosyl 2-ene-yne anilines (1a-1d):

Substrates **1a-d** were prepared by sulfonylation of the corresponding anilines (**9a-d)**. The aniline (1.00 g, 6.98 mmol) was dissolved in dry CH_2Cl_2 (10 mL), and the solution was added with 4-Toluenesulfonyl chloride (1.46 g, 7.67 mmol) and pyridine (1.69 mL, 20.94 mmol). The mixture was stirred at room temperature for 2 h, diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with 1M HCl, brine, dried over Na_2SO_4, and concentrated in vacuo and the resulting crude product was purified by column chromatography (silica gel, 60−120 mesh) using an ethyl acetate/n-hexane gradient mixture to afford the pure product **1** in good yields.



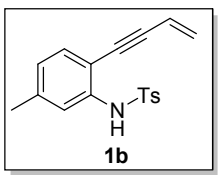
2.4. spectral data for of N-tosyl 2-ene-yne anilines (1a-1d):

Spectral data for N-(2-(but-3-en-1-yn-1-yl)phenyl)-4 methylbenzene sulfonamide (1a):



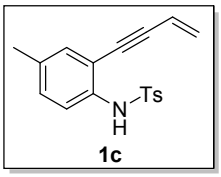
Following the general procedure (rt for 3 h), compound **1a** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (1.87 g, 96%). mp 105 – 110 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.12 (bs, 1H), 7.02 (td, J = 7.6, 0.9 Hz, 1H), 5.98 (dd, J = 17.6, 11.3 Hz, 1H), 5.74 (dd, J = 17.6, 1.8 Hz, 1H), 5.63 (dd, J = 11.1, 1.8 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.0, 137.5, 136.0, 132.0, 129.6, 129.5, 128.2, 127.2, 124.4, 120.0, 116.3, 114.3, 94.7, 84.2, 21.51 ppm. HRMS calcd for $C_{17}H_{16}NO_2S[M + H]^+$: 298.0896; found: 298.0901.

Spectral data for N-(2-(but-3-en-1-yn-1-yl)-5-methylphenyl)-4-methylbenzene sulfonamide (1b):



Following the general procedure (rt for 3 h), compound **1b** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (2.13 g, 98%). mp 151 – 156 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7. 66 (d, J = 8.4 Hz, 2H), 7.41 (s, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 1H), 7.06 (bs, 1H), 6.85 – 6.82 (m, 1H), 5.96 (dd, J = 17.6, 11.1 Hz, 1H), 5.70 (dd, J = 17.6, 1.8 Hz, 1H), 5.59 (dd, J = 11.1, 1.8 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 140.3, 137.3, 136.0, 131.7, 129.5, 127.8, 127.2, 125.5, 120.8, 116.4, 111.5, 94.0, 84.4, 21.7, 21.5 ppm. HRMS calcd for $C_{18}H_{18}NO_2S[M + H]^+$: 312.1053; found: 312.1058.

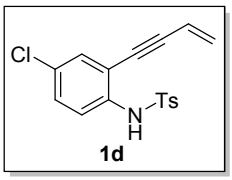
Spectral data for N-(2-(but-3-en-1-yn-1-yl)-4-methylphenyl)-4-methylbenzene sulfonamide (1c):



1c

Following the general procedure (rt for 3 h), compound **1c** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid(2.13 g, 98%). mp 122 – 127 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.62 (m, 2H), 7.48 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 7.09 – 7.06 (m, 2H), 6.99 (bs, 1H), 5.95 (dd, J = 17.6, 11.3 Hz, 1H), 5.70 (dd, J = 17.6, 1.8 Hz, 1H), 5.60 (dd, J = 11.3, 1.8 Hz, 1H), 2.36 (s, 3H), 2.23 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.8, 136.0, 134.9, 134.4, 132.2, 130.4, 129.5, 128.0, 127.2, 120.7, 116.3, 114.6, 94.1, 84.5, 21.5, 20.5 ppm. HRMS calcd for $C_{18}H_{18}NO_2S[M + H]^+$: 312.1053; found: 312.1057.

Spectral data for N-(2-(but-3-en-1-yn-1-yl)-4-chlorophenyl)-4-methylbenzene sulfonamide (1d):

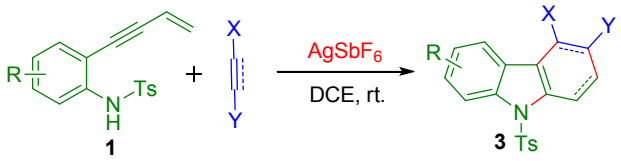


1d

Following the general procedure (rt for 4 h), compound **1d** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid(2.16 g, 93%). mp 120 – 125 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.7 Hz, 1H), 7.26 (d, J = 3.2 Hz, 1H), 7.24 – 7.21 (m, 3H), 7.05 (bs, 1H), 5.96 (dd, J = 17.6, 11.3 Hz, 1H), 5.76 (dd, J = 17.6, 1.8 Hz, 1H), 5.66 (dd, J = 11.3, 1.8 Hz, 1H), 2.38 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.3, 136.0, 135.7, 131.5, 129.8, 129.7, 129.0, 127.2, 121.5, 116.0, 115.9, 95.6, 83.0, 21.5 ppm. HRMS calcd for $C_{17}H_{15}ClNO_2S[M + H]^+$: 332.0507; found: 332.0502.

3. Experimental procedures and characterization of products

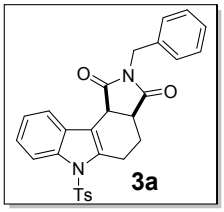
3.1. General procedures for one pot hydroamination/Diels-Alder cycloaddition of 2-(but-3-en-1-yn-1-yl) anilines



To a magnetically stirred solution of 2-(but-3-en-1-yn-1-yl) aniline **1** (0.06g, 0.2 mmol, 1 equiv) and dienophile **2** (0.4 mmol, 2 equi) in DCE (1 mL) was added $AgSbF_6$ (10 mol%) under nitrogen atmosphere and the reaction mixture was stirred at temperature and time specified. After completion of the reaction (monitored by TLC), the reaction mixture was filtered over a short celite bed, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (hexanes:EtOAc) to afford corresponding carbazoles **3**, **6** or **7.**

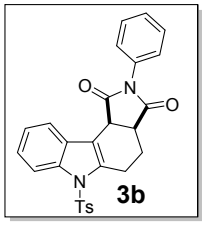
3.2. Spectral data of carbazoles (3a – 3j, 6a – 6c and 7a – 7i)

Spectral data for (3aS,10cS)-2-benzyl-6-tosyl-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2H,3aH)-dione (3a):



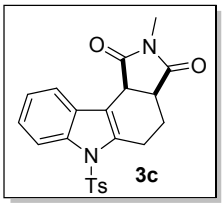
Following the general procedure (rt for 1 h), compound **3a** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (90 mg, 92%). mp 173 – 175 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (dd, J = 6.7, 1.7 Hz, 1H), 7.90 (dd, J = 6.8, 2.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.35 – 7.22 (m, 7H), 7.18 (d, J = 8.2 Hz, 2H), 4.61 (d, J = 14.2 Hz, 1H), 4.53 (d, J = 14.2 Hz, 1H), 4.18 (d, J = 8.1 Hz, 1H), 3.32 – 3.24 (m, 2H), 2.83 (dddd, J = 15.3, 9.6, 5.0, 1.4 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.35 (s, 3H), 1.98 (ddd, J = 14.8, 10.2, 5.2 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.0, 175.7, 145.0, 136.3, 135.9, 135.8, 135.7, 130.0, 128.7, 128.6, 127.9, 126.4, 124.8, 123.8, 120.4, 114.3, 112.0, 42.5, 39.6, 39.4, 22.5, 21.6, 21.0 ppm. HRMS calcd for $C_{28}H_{25}N_2O_4S$ $[M + H]^+$: 485.1530; found: 485.1533.

Spectral data for (3aS,10cS)-2-phenyl-6-tosyl-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2H,3aH)-dione (3b):



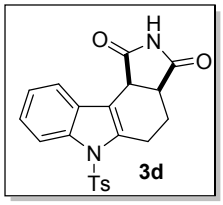
Following the general procedure (rt for 1 h), compound **3b** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid(83.5 mg, 88%). mp 214 – 216 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.27 (m, 3H), 7.17 (d, J = 8.2 Hz, 2H), 7.11 – 7.07 (m, 2H), 4.35 (d, J = 8.1 Hz, 1H), 3.49 (dt, J = 8.1, 5.0 Hz, 1H), 3.36 (dt, J = 17.8, 4.3 Hz, 1H), 3.02 – 2.82 (dddd, J = 15.6, 10.2, 5.2, 1.5 Hz, 1H), 2.57 (dq, J = 13.7, 4.6 Hz, 1H), 2.33 (s, 3H), 2.02 (ddd, J = 18.9, 10.4, 5.2 Hz, 1H)ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.0, 174.8, 145.0, 136.5, 136.0, 135.7, 131.6, 129.9, 129.0, 128.6, 128.5, 126.3, 126.2, 124.9, 123.9, 120.4, 114.4, 112.4, 39.8, 39.6, 22.0, 21.5, 21.0 ppm. HRMS calcd for $C_{27}H_{23}N_2O_4S$ $[M + H]^+$: 471.1373; found: 471.1377.

Spectral data for (3aS,10cS)-2-methyl-1,3-dioxo-6-tosyl-1,2,3,3a,4,5,6,10c-octahydropyrrolo[3,4-c]carbazol-6-ium (3c):



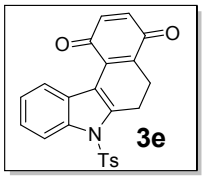
Following the general procedure (rt for 0.5 h), compound **3c** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (73.3 mg, 89%). mp 166 – 168 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 – 8.14 (m, 1H), 7.93 – 7.90 (m, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.20 (d, J = 8.1 Hz, 2H), 4.19 (d, J = 7.9 Hz, 1H), 3.34 – 3.27 (m, 2H), 2.91 (s, 3H), 2.80 (dddd, J = 15.6, 10.4, 5.0, 1.7 Hz, 1H), 2.47 (dq, J = 13.9, 4.7 Hz, 1H), 2.35 (s, 3H), 1.94 (ddt, J = 14.0, 10.5, 5.3 Hz, 1H)ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.3, 176.1, 145.0, 136.3, 135.8, 135.7, 129.9, 128.5, 126.3, 124.7, 123.7, 120.3, 114.2, 112.1, 39.5, 39.4, 24.9, 22.0, 21.5, 20.9 ppm. HRMS calcd for $C_{22}H_{21}N_2O_4S$ $[M + H]^+$: 409.1217; found: 409.1224.

Spectral data for (3aS,10cS)-6-tosyl-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2H,3aH)-dione (3d):



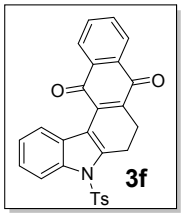
Following the general procedure (rt for 1 h), compound **3d** was obtained after column chromatography (hexane:EtOAc 6:4) as a white solid (66 mg, 83%). mp 196 – 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.77 (s, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.22 (d, J = 8.1 Hz, 1H), 3.40 – 3.30 (m, 2H), 2.91 – 2.81 (m, 1H), 2.45 (dq, J = 9.0, 4.6 Hz, 1H), 2.35 (s, 3H), 1.99 – 1.90 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.3, 176.0, 145.1, 136.2, 135.80, 135.76, 130.0, 128.4, 126.3, 124.8, 123.7, 120.3, 114.2, 111.6, 40.7, 40.6, 21.9, 21.5, 20.8 ppm. HRMS calcd for $C_{21}H_{19}N_2O_4S$ $[M + H]^+$: 395.1060; found: 395.1065.

Spectral data for 7-tosyl-5,6-dihydro-1H-benzo[c]carbazole-1,4(7H)-dione (3e):



Following the general procedure (rt for 0.5 h), compound **3e** was obtained after column chromatography (hexane:EtOAc 8:2) as a brown solid (69.2 mg, 85%). mp 222 – 224 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 7.9 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.79 (s, 2H), 3.33 (dd, J = 10.2, 8.7 Hz, 2H), 2.84 (dd, J = 10.2, 8.7 Hz, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.9, 145.6, 141.5, 137.2, 136.7, 136.4, 136.3, 136.1, 135.5, 130.2, 126.6, 126.2, 124.8, 124.2, 122.8, 114.3, 114.2, 21.6, 21.0, 20.8 ppm. HRMS calcd for $C_{23}H_{18}NO_4S$ $[M + H]^+$: 404.0951; found: 404.0958.

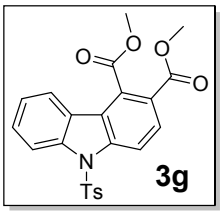
Spectral data for 5-tosyl-6,7-dihydro-5H-naphtho[2,3-c]carbazole-8,13-dione (3f):



Following the general procedure (rt for 0.5 h), compound **3f** was obtained after column chromatography (hexane:EtOAc 8:2) as a brown solid (79.6 mg, 87%). mp 252 – 254 °C. ^{1}H

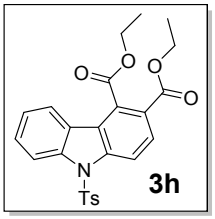
NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, J = 7.0, 1.7 Hz, 1H), 8.18 – 8.15 (m, 1H), 8.12 – 8.09 (m, 1H), 7.96 – 7.93 (m, 1H), 7.75 – 7.71 (m, 4H), 7.37 – 7.30 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 3.38 (dd, J = 10.1, 8.4 Hz, 2H), 3.01 (dd, J = 9.3, 7.5 Hz, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.7, 183.5, 145.6, 141.9, 139.0, 138.8, 137.2, 135.5, 133.6, 133.5, 132.6, 132.0, 130.2, 126.6, 126.5, 126.1, 124.8, 124.1, 123.1, 120.0, 114.9, 114.2, 21.6, 21.6, 20.9 ppm. HRMS calcd for $C_{27}H_{20}NO_4S$ $[M + H]^+$: 454.1108; found: 454.1111.

Spectral data for dimethyl 9-tosyl-9H-carbazole-3,4-dicarboxylate (3g):



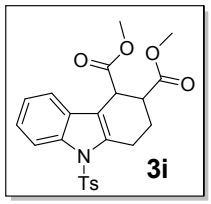
Following the general procedure (45 ^{o}C for 1.5 h), compound **3g** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (67.9 mg, 83%). mp 148 – 150 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (d, J = 8.9 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.2 Hz, 2H), 4.10 (s, 3H), 3.95 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.1, 165.8, 145.6, 141.1, 139.0, 134.5, 129.9, 129.4, 128.8, 128.6, 126.5, 124.5, 123.7, 122.9, 122.7, 121.4, 115.4, 115.0, 53.1, 52.6, 21.5 ppm. HRMS calcd for $C_{23}H_{20}NO_6S$ $[M + H]^+$: 438.1006; found: 438.1013.

Spectral data for diethyl 9-tosyl-9H-carbazole-3,4-dicarboxylate (3h):



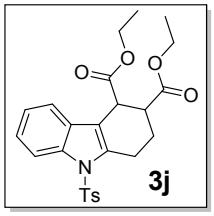
Following the general procedure (45 ^{o}C for 1.5 h), compound **3h** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (70 mg, 80%). mp 122 – 124 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, J = 8.9 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.9 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 4.59 (q, J = 7.2 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.29 (s, 3H), 1.42 (dt, J = 14.6, 7.2 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 165.4, 145.6, 141.0, 139.0, 134.6, 130.0, 129.7, 128.9, 128.5, 126.5, 124.5, 123.9, 123.2, 122.9, 121.6, 115.3, 115.0, 62.3, 61.6, 21.6, 14.3, 14.0 ppm. HRMS calcd for $C_{25}H_{24}NO_6S$ $[M + H]^+$: 466.1319; found: 466.1326.

Spectral data for dimethyl 9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-3,4-dicarboxylate (3i):



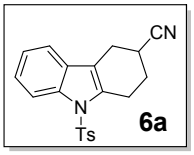
Following the general procedure (45 °C for 2 h), compound **3i** was obtained after column chromatography (hexane:EtOAc 7:3) as a colorless liquid (65.3 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 7.2 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.29 – 4.26 (m, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 3.39 – 3.33 (m, 1H), 2.97– 2.88 (m, 1H), 2.74 (dt, J = 10.7, 5.1 Hz, 1H), 2.53 – 2.46 (m, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 172.1, 144.9, 136.4, 136.3, 136.1, 130.0, 128.8, 126.4, 124.4, 123.4, 119.2, 114.2, 52.1, 52.0, 41.8, 39.4, 24.1, 21.6, 21.3 ppm. HRMS calcd for $C_{23}H_{23}NNaO_6S$ $[M + Na]^+$: 464.1138; found: 464.1142.

Spectral data for diethyl 9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-3,4-dicarboxylate (3j):



Following the general procedure (45 °C for 2 h), compound **3j** was obtained after column chromatography (hexane:EtOAc 8:2) as a colorless liquid (68 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 8.4 Hz, 3H), 7.33 – 7.17 (m, 4H), 4.29 – 4.15 (m, 3H), 4.08 (td, J = 11.4, 7.0 Hz, 2H), 3.36 (dd, J = 18.9, 4.0 Hz, 1H), 2.98 – 2.84 (m, 1H), 2.75 – 2.66 (m, 1H), 2.59 – 2.43 (m, 2H), 2.35 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 171.6, 144.9, 136.5, 136.4, 136.1, 130.0, 128.9, 126.4, 124.4, 123.4, 119.5, 114.5, 114.2, 61.0, 60.9, 41.8, 39.6, 24.2, 21.6, 21.3, 14.2, 14.1 ppm. HRMS calcd for $C_{25}H_{28}NO_6S$ $[M + H]^+$: 470.1632; found: 470.1643.

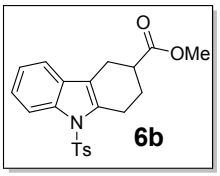
Spectral data for 9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-3-carbonitrile (6a):



Following the general procedure (45 °C for 2 h), compound **6a** was obtained after column chromatography (hexane:EtOAc 8:2) as a colorless liquid (55.1 mg, 78%). ^{1}H NMR (400 MHz,

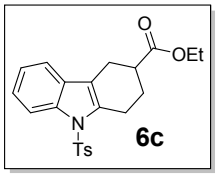
$CDCl_3$): δ 8.19 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 7.3 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.24 (d, J = 8.2 Hz, 2H), 3.94 (t, J = 4.8 Hz, 1H), 3.16 – 2.98 (m, 2H), 2.37 (s, 3H), 2.25 – 1.93 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.2, 136.8, 136.0, 135.9, 130.1, 127.8, 126.4, 124.9, 123.8, 120.2, 118.0, 114.4, 111.5, 26.6, 24.2, 24.0, 21.6, 20.8 ppm. HRMS calcd for $C_{20}H_{19}N_2O_2S$ $[M + H]^+$: 351.1162; found: 351.1177.

Spectral data for methyl 9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-3-carboxylate (6b):



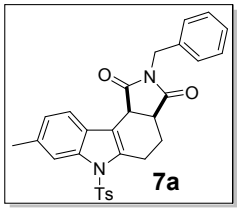
Following the general procedure (45 ^{o}C for 1.5 h), compound **6b** was obtained after column chromatography (hexane:EtOAc 8:2) as a colorless liquid (62 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 3H), 3.80 (t, J = 5.6 Hz, 1H), 3.67 (s, 3H), 3.14 (dt, J = 18.0, 5.5 Hz, 1H), 2.98 – 2.90 (m, 1H), 2.35 (s, 3H), 2.20 – 2.13 (m, 1H), 2.10 – 2.00 (m, 1H), 1.95 – 1.85 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.2, 144.7, 136.9, 136.3, 136.1, 129.9, 129.3, 126.4, 124.0, 123.3, 118.7, 115.2, 114.3, 52.0, 38.4, 25.8, 24.3, 21.5, 20.5 ppm. HRMS calcd for $C_{21}H_{22}NO_4S$ $[M + H]^+$: 384.1264; found: 384.1273.

Spectral data for ethyl 9-tosyl-2,3,4,9-tetrahydro-1H-carbazole-3-carboxylate (6c):



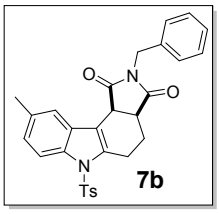
Following the general procedure (45 ^{o}C for 2 h), compound **6c** was obtained after column chromatography (hexane:EtOAc 8:2) as a colorless liquid (61.8 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.22 – 7.18 (m, 3H), 4.17 – 4.08 (m, 2H), 3.77 (t, J = 6.0 Hz, 1H), 3.14 (dt, J = 18.8, 5.7 Hz, 1H), 2.97 – 2.89 (m, 1H), 2.34 (s, 3H), 2.20 – 2.12 (m, 1H), 2.11 – 2.01 (m, 1H), 1.94 – 1.86 (m, 2H), 1.19 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.7, 144.6, 136.8, 136.3, 136.2, 129.8, 129.4, 126.4, 124.0, 123.2, 118.8, 115.4, 114.3, 60.8, 38.7, 25.8, 24.3, 21.5, 20.5, 14.2 ppm. HRMS calcd for $C_{22}H_{24}NO_4S$ $[M + H]^+$: 398.1421; found: 398.1430.

Spectral data for (3aS,10cS)-2-benzyl-8-methyl-6-tosyl-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2H,3aH)-dione (7a):



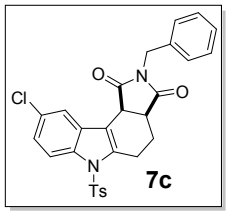
Following the general procedure (rt for 0.5 h), compound **7a** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (91.3 mg, 95%). mp 233 – 235 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.29 – 7.22 (m, 5H), 7.18 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.9 Hz, 1H), 4.60 (d, J = 14.2 Hz, 1H), 4.51 (d, J = 14.2 Hz, 1H), 4.15 (d, J = 8.1 Hz, 1H), 3.30 – 3.19 (m, 2H), 2.84 – 2.75 (m, 1H), 2.49 (s, 3H), 2.39 – 2.32 (m, 4H), 1.96 (qd, J = 10.1, 5.1 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.0, 175.7, 144.8, 136.7, 136.0, 135.6, 135.0 134.9, 129.9, 128.6, 128.5, 127.8, 126.3, 125.2, 119.9, 114.3, 111.9, 42.4, 39.5, 39.3, 22.4, 22.0, 21.6, 20.9 ppm. HRMS calcd for $C_{29}H_{27}N_2O_4S$ $[M + H]^+$: 499.1686; found: 499.1687.

Spectral data for (3aS,10cS)-2-benzyl-9-methyl-6-tosyl-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2H,3aH)-dione (7b):



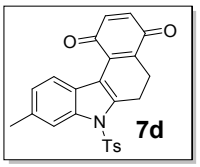
Following the general procedure (rt for 0.5 h), compound **7b** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (89.3 mg, 93%). mp 174 – 175 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.22 (dd, J = 15.3, 7.7 Hz, 5H), 7.17 (s, 1H), 7.16 – 7.12 (m, 3H), 6.09 – 6.04 (m, 1H), 4.24 (d, J = 14.2 Hz, 1H), 3.96 (d, J = 14.2 Hz, 1H), 3.74 – 3.69 (m, 1H), 3.50 (m, 1H), 3.08 (t, J = 7.5 Hz, 1H), 2.99 (dd, J = 15.1, 8.1 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 2.13 (ddd, J = 9.9, 6.9, 3.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.3, 174.7, 144.4, 140.8, 140.1, 135.5, 134.3, 133.9, 129.5, 128.6, 128.3, 128.2, 127.9, 127.4, 127.2, 126.0, 114.8, 102.6, 42.4, 42.3, 41.7, 38.5, 25.1, 21.6, 21.1 ppm. HRMS calcd for $C_{29}H_{27}N_2O_4S$ $[M + H]^+$: 499.1686; found: 499.1691.

Spectral data for (3aS,10cS)-2-benzyl-9-chloro-6-tosyl-4,5,6,10c-tetrahydropyrrolo[3,4-c]carbazole-1,3(2H,3aH)-dione (7c):



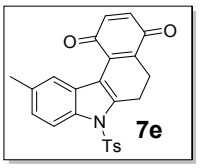
Following the general procedure (rt for 1 h), compound **7c** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (78 mg, 83%). mp 226 – 228 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 8.9 Hz, 1H), 7.89 (s, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.30 – 7.23 (m, 6H), 7.20 (d, J = 7.9 Hz, 2H), 4.62 (d, J = 14.2 Hz, 1H), 4.53 (d, J = 14.2 Hz, 1H), 4.11 (d, J = 7.9 Hz, 1H), 3.30 – 3.20 (m, 2H), 2.83 (ddd, J = 14.5, 9.5, 5.2 Hz, 1H), 2.41 – 2.29 (m, 4H), 2.04 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.7, 175.4, 145.3, 137.2, 135.54, 135.49, 134.6, 130.1, 129.8, 129.6, 128.7, 128.5, 127.9, 126.3, 124.9, 120.1, 115.2, 111.4, 42.5, 39.4, 39.1, 22.4, 21.6, 21.0 ppm. HRMS calcd for $C_{28}H_{24}ClN_2O_4S$ $[M + H]^+$: 519.1140; found: 519.1138.

Spectral data for 9-methyl-7-tosyl-5,6-dihydro-1H-benzo[c]carbazole-1,4(7H)-dione (7d):



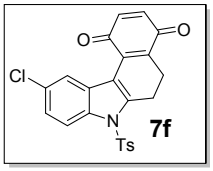
Following the general procedure (rt for 0.5 h), compound **7d** was obtained after column chromatography (hexane:EtOAc 9:1) as a brown solid (74 mg, 92%). mp 192 – 194 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 1H), 6.77 (s, 2H), 3.29 (t, J = 9.0 Hz, 2H), 2.82 (t, J = 9.0 Hz, 2H), 2.50 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.9, 145.4, 140.9, 137.6, 136.6, 136.3, 136.0, 135.5, 134.9, 130.1, 126.5, 125.6, 123.9, 122.3, 114.2, 21.9, 21.6, 20.9, 20.8 ppm. HRMS calcd for $C_{24}H_{20}NO_4S$ $[M + H]^+$: 418.1108; found: 418.1116.

Spectral data for 10-methyl-1,4-dioxo-7-tosyl-4,5,6,7-tetrahydro-1H-benzo[c]carbazol-7-ium (7e):



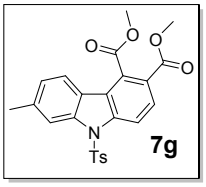
Following the general procedure (rt for 0.5 h), compound **7e** was obtained after column chromatography (hexane:EtOAc 9:1) as a brown solid (70 mg, 90%). mp 233 – 234 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.66 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.6 Hz, 1H), 6.79 (s, 2H), 3.31 (t, J = 9.0 Hz, 2H), 2.83 (t, J = 9.0 Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.9, 145.4, 141.5, 136.7, 136.3, 136.2, 136.0, 135.4, 133.7, 130.1, 129.9, 126.5, 126.4, 126.1, 122.5, 114.1, 113.8, 21.6, 21.5, 20.9, 20.7 ppm. HRMS calcd for $C_{24}H_{20}NO_4S$ $[M + H]^+$: 418.1108; found: 418.1112.

Spectral data for 10-chloro-7-tosyl-5,6-dihydro-1H-benzo[c]carbazole-1,4(7H)-dione (7f):



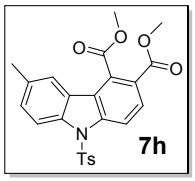
Following the general procedure (rt for 0.5 h), compound **7f** was obtained after column chromatography (hexane:EtOAc 9:1) as a brown solid (65 mg, 82%). mp 250 – 252 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, J = 8.9 Hz, 1H), 7.93 (d, J = 1.5 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.30 (dd, J = 9.0, 1.8 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.80 (s, 2H), 3.32 (t, J = 8.7 Hz, 2H), 2.84 (t, J = 8.7 Hz, 2H), 2.37 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.7, 145.9, 142.6, 136.5, 136.4, 136.1, 135.5, 135.1, 130.2, 130.1, 127.5, 126.5, 124.9, 122.7, 115.1, 113.6, 21.6, 20.83, 20.76 ppm. HRMS calcd for $C_{23}H_{17}ClNO_4S$ $[M + H]^+$: 438.0561; found: 438.0562.

Spectral data for dimethyl 7-methyl-9-tosyl-9H-carbazole-3,4-dicarboxylate (7g):



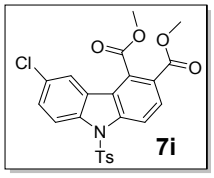
Following the general procedure (45 °C for 1 h), compound **7g** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (75.7 mg, 87%). mp 175 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 8.8 Hz, 1H), 8.18 (s, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 7.9 Hz, 2H), 4.09 (s, 3H), 3.94 (s, 3H), 2.56 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.2, 165.9, 145.6, 141.1, 139.5, 139.3, 134.6, 130.0, 129.0, 128.4, 126.5, 125.9, 123.1, 122.7, 121.4, 121.0, 115.4, 115.2, 53.1, 52.6, 22.4, 21.6 ppm. HRMS calcd for $C_{24}H_{22}NO_6S$ $[M + H]^+$: 452.1162; found: 452.1167.

Spectral data for dimethyl 6-methyl-9-tosyl-9H-carbazole-3,4-dicarboxylate (7h):



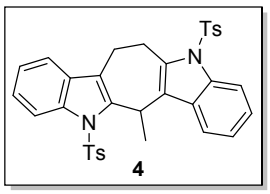
Following the general procedure (45 °C for 1.5 h), compound **7h** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid (73.1 mg, 84%). mp 149 – 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 8.9 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 7.5 Hz, 2H), 7.50 (s, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 7.5 Hz, 2H), 4.10 (s, 3H), 3.94 (s, 3H), 2.46 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.1, 165.9, 145.5, 141.3, 137.1, 134.4, 134.2, 129.9, 129.3, 128.7, 126.5, 123.9, 122.9, 122.6, 121.4, 115.4, 114.7, 53.1, 52.6, 21.5 ppm. HRMS calcd for $C_{24}H_{22}NO_6S$ $[M + H]^+$: 452.1162; found: 452.1167.

Spectral data for dimethyl 6-chloro-9-tosyl-9H-carbazole-3,4-dicarboxylate (7i):



Following the general procedure (45 °C for 2 h), compound **7i** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (58 mg, 68%). mp 158 – 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 8.9 Hz, 1H), 8.31 (d, J = 9.1 Hz, 1H), 8.19 (d, J = 8.9 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.68 (s, 1H), 7.66 (s, 1H), 7.52 (dd, J = 9.0, 2.0 Hz, 1H), 7.15 (d, J = 8.2 Hz, 2H), 4.11 (s, 3H), 3.95 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.7, 165.7, 146.0, 141.4, 137.3, 134.2, 130.3, 130.0, 129.6, 129.5, 128.7, 126.5, 125.1, 123.1, 121.9, 121.4, 116.1, 115.6, 53.3, 52.7, 21.6. HRMS calcd for $C_{23}H_{19}ClNO_6S$ $[M + H]^+$: 472.0616; found: 472.0624.

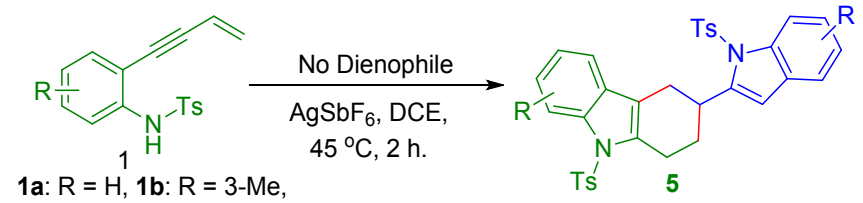
3.3 Spectral data for 6-methyl-5,11-ditosyl-6,11,12,13-tetrahydro-5H-cyclohepta[1,2-b:4,5-b']diindole (4):



Compound **4** was obtained after column chromatography (hexane:EtOAc 8:2) as a white solid. mp 188 – 190 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 – 8.18 (m, 2H), 7.62 – 7.54 (m, 3H), 7.44

(d, J = 8.2 Hz, 3H), 7.32 (dd, J = 6.0, 3.2 Hz, 2H), 7.62 – 7.27 (m, 2H), 7.17 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.2 Hz, 2H), 5.41 (q, J = 7.0 Hz, 1H), 3.56 – 3.49 (m, 1H), 3.14 – 2.98 (m, 3H), 2.34 (s, 3H), 2.20 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 144.5, 140.0, 136.4, 136.1, 135.8, 130.2, 129.9, 129.6, 126.3, 126.0, 124.4, 123.5, 121.3, 120.5, 117.9, 117.8, 115.4, 114.8, 28.2, 25.8, 22.2, 21.6, 21.4, 20.9 ppm. HRMS calcd for $C_{34}H_{31}N_2O_4S_2$ [M + H]$^+$: 595.1720; found: 595.1725.

3.4 General procedures for synthesis of 3-indolyl-tetrahydrocarbazoles (5).

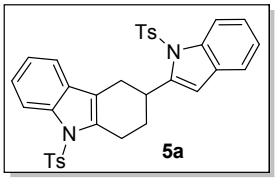


1a: R = H, **1b**: R = 3-Me,
1c: R = 4-Me, **1d**: R = 4-Cl

To a magnetically stirred solution of 2-(but-3-en-1-yn-1-yl) aniline **1** (0.06g, 0.2 mmol, 1 equiv) in DCE (1 mL) was added $AgSbF_6$ (10 mol%) under nitrogen atmosphere and the reaction mixture was stirred at temperature and time specified. After completion of the reaction (monitored by TLC), the reaction mixture was filtered over a short celite bed, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (hexanes:EtOAc) to afford corresponding 3-indolyl-tetrahydrocarbazoles **5a – d**.

3.5 Spectral data of 3-indolyl-tetrahydrocarbazoles (5a – 5d)

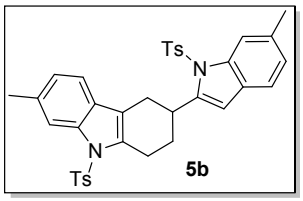
Spectral data for 9-tosyl-3-(1-tosyl-1H-indol-2-yl)-2,3,4,9-tetrahydro-1H-carbazole (5a):



Following the general procedure (45 °C for 2 h), compound **5a** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (52 mg, 87%). mp 207 – 209 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H), 7.68 (dd, J = 8.2, 5.5 Hz, 4H), 7.30 (ddd, J = 8.6, 6.1, 2.6 Hz, 2H), 7.25 (s, 2H), 7.23 (s, 1H), 7.22 – 7.14 (m, 3H), 6.78 (t, J = 7.5 Hz, 1H), 5.96 (d, J = 7.8 Hz, 1H), 5.70 (s, 1H), 4.72 (d, J = 5.5 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.90 – 2.80 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.25 – 2.18 (m, 1H), 2.06 (tdd, J = 12.7, 6.0, 2.8 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.78 – 1.67 (m, 1H) ppm. ^{13}C NMR (101 MHz,

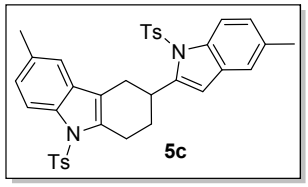
$CDCl_3$): δ 145.1, 144.7, 142.9, 138.1, 137.5, 136.6, 136.5, 136.1, 130.0, 129.8, 129.3, 129.1, 126.4, 124.3, 123.9, 123.7, 122.8, 120.3, 118.6, 118.5, 115.2, 114.6, 112.1, 31.9, 29.5, 24.6, 21.6, 18.6 ppm. HRMS calcd for $C_{34}H_{31}N_2O_4S_2$ $[M + H]^+$: 595.1720; found: 595.1726.

Spectral data for 7-methyl-3-(6-methyl-1-tosyl-1H-indol-2-yl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (5b):



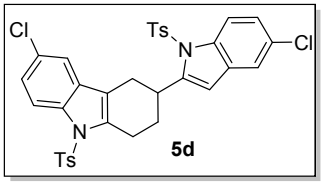
Following the general procedure (45 ^oC for 2 h), compound **5b** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (55.2 mg, 92%). Mp 227 – 229 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.96 (s, 1H), 7.65 (dd, J = 8.2, 2.3 Hz, 4H), 7.23 (d, J = 8.2 Hz, 4H), 7.07 (d, J = 7.9 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.60 (d, J = 7.9 Hz, 1H), 5.81 (d, J = 7.9 Hz, 1H), 5.64 (s, 1H), 4.64 (d, J = 4.4 Hz, 1H), 3.17 (dq, J = 18.0, 3.1 Hz, 1H), 2.79 (ddd, J = 16.6, 9.8, 5.5 Hz, 1H), 2.49 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H), 2.21 – 2.14 (m, 1H), 2.06 – 1.97 (m, 1H), 1.83 – 1.76 (m, 1H), 1.73 – 1.63 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.9, 144.6, 142.2, 138.6, 136.9, 136.8, 136.2, 134.3, 133.8, 130.0, 129.8, 127.0, 126.9, 126.3, 125.1, 124.1, 119.9, 118.6, 118.1, 115.4, 114.8, 112.0, 31.9, 29.4, 24.6, 22.0, 21.9, 21.6, 18.6 ppm. HRMS calcd for $C_{36}H_{34}N_2NaO_4S_2$ $[M + Na]^+$: 645.1852; found: 645.1868.

Spectral data for 6-methyl-3-(5-methyl-1-tosyl-1H-indol-2-yl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (5c):



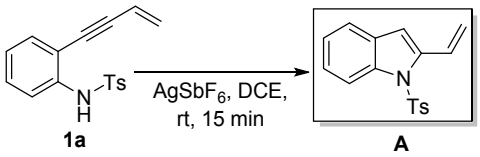
Following the general procedure (45 ^oC for 2 h), compound **5c** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (54 mg, 90%). mp 263 – 264 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.26 (s, 1H), 7.24 (d, J = 2.9 Hz, 2H), 7.22 (s, 1H), 7.12 (d, J = 8.6 Hz, 1H), 6.99 – 6.95 (m, 2H), 5.87 (s, 1H), 5.59 (s, 1H), 4.66 (d, J = 5.2 Hz, 1H), 3.26 – 3.18 (m, 1H), 2.80 (ddd, J = 17.4, 11.0, 6.3 Hz, 1H), 2.39 (s, 6H), 2.37 (s, 3H), 2.29 – 2.21 (m, 2H), 2.04 (s, 3H), 1.86 – 1.77 (m, 1H), 1.73 – 1.63 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.9, 144.6, 142.8, 137.6, 136.7, 136.3, 136.1, 134.7, 133.3, 132.4, 130.0, 129.8, 129.6, 129.5, 126.4, 125.6, 125.2, 120.3, 118.6, 118.4, 114.9, 114.3, 112.1, 32.0, 29.4, 24.7, 21.7, 21.6, 21.2, 20.9, 18.5 ppm. HRMS calcd for $C_{36}H_{35}N_2O_4S_2$ $[M + H]^+$: 623.2033; found: 623.2037.

Spectral data for 6-chloro-3-(5-chloro-1-tosyl-1H-indol-2-yl)-9-tosyl-2,3,4,9-tetrahydro-1H-carbazole (5d):



Following the general procedure (45 ^{o}C for 2 h), compound **5d** was obtained after column chromatography (hexane:EtOAc 7:3) as a white solid (45.6 mg, 76%). mp 251 – 253 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 9.0 Hz, 1H), 7.67 – 7.63 (m, 4H), 7.31 – 7.28 (m, 3H), 7.27 – 7.24 (m, 2H), 7.18 (d, J = 2.0 Hz, 1H), 7.12 (dd, J = 8.9, 2.0 Hz, 1H), 5.86 (d, J = 1.8 Hz, 1H), 5.58 (s, 1H), 4.61 (d, J = 5.3 Hz, 1H), 3.23 (ddd, J = 18.0, 4.9, 2.6 Hz, 1H), 2.87 – 2.77 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 2.30 – 2.23 (m, 1H), 2.11 – 2.02 (m, 1H), 1.89 – 1.81 (m, 1H), 1.72 – 1.63 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.0, 145.1, 143.8, 139.2, 136.6, 136.0, 135.8, 134.8, 130.5, 130.3, 130.0, 129.5, 128.9, 126.4, 126.1, 124.6, 124.1, 120.0, 117.9, 117.6, 116.4, 115.6, 111.4, 32.0, 29.3, 24.6, 21.9, 21.7, 18.4 ppm. HRMS calcd for $C_{34}H_{29}Cl_2N_2O_4S_2$ $[M + H]^+$: 663.0940; found: 663.0927.

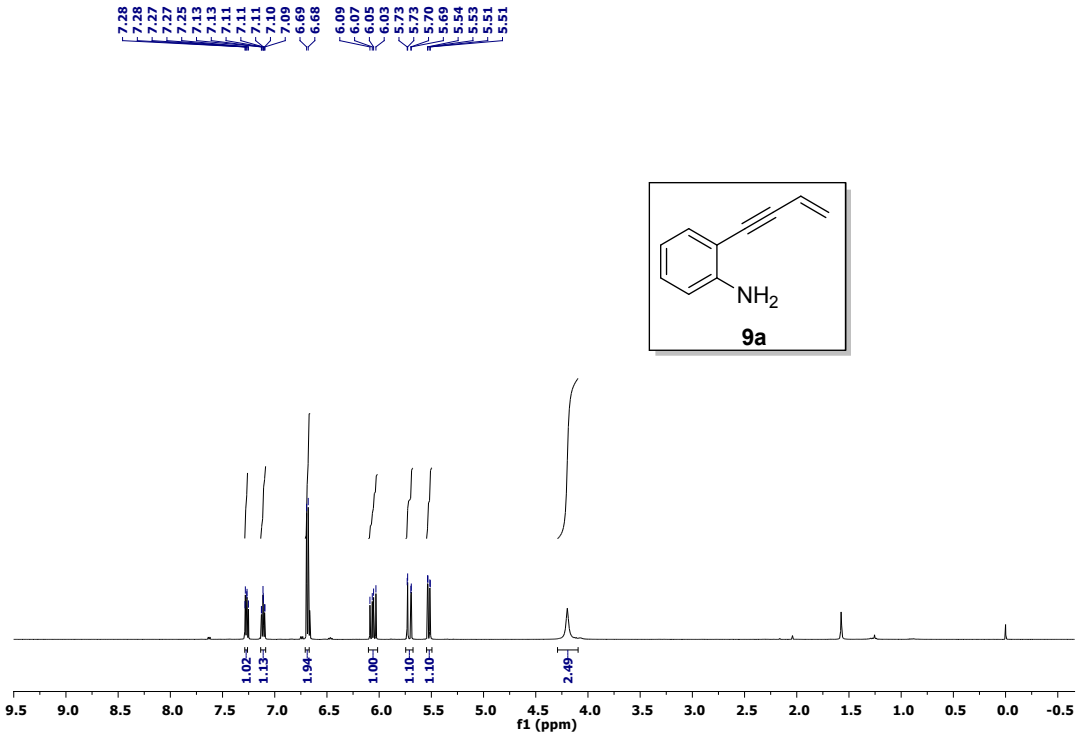
3.6. General procedure and characterization of intermediate A

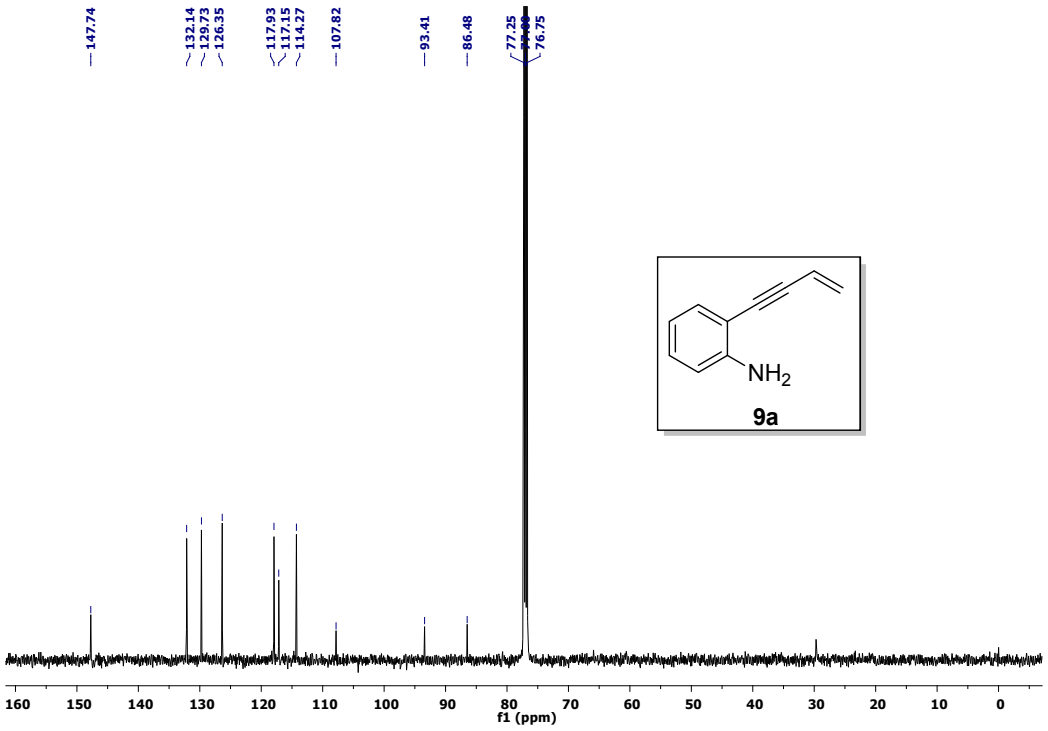


To a magnetically stirred solution of 2-(but-3-en-1-yn-1-yl) aniline **1a** (0.06g, 0.2 mmol, 1 equiv) in DCE (1 mL) was added $AgSbF_6$ (10 mol%) under nitrogen atmosphere and the reaction mixture was stirred at ambient temperature for 15 mins. After complete consumption of the starting material (reaction monitored by TLC), the reaction mixture was filtered over a short celite bed, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (hexanes:EtOAc 9:1) to afford 1-tosyl-2-vinyl-1H-indole **A** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (dd, J = 8.4, 0.8 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.37 (ddd, J = 17.2, 11.0, 0.8 Hz, 1H), 7.29 (ddd, J = 8.6, 7.2, 1.2 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.15 (d, J = 7.9 Hz, 2H), 6.72 (s, 1H), 5.70 (dd, J = 17.4, 1.5 Hz, 1H), 5.39 (dd, J = 11.2, 1.5 Hz, 1H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.7, 139.8, 137.2, 135.5, 129.9, 129.6, 127.7, 126.6, 124.7, 123.9, 120.7, 117.8, 115.1, 108.8, 21.5 ppm. HRMS calcd for $C_{17}H_{16}NO_2S$ $[M + H]^+$: 298.0896; found: 298.0901.

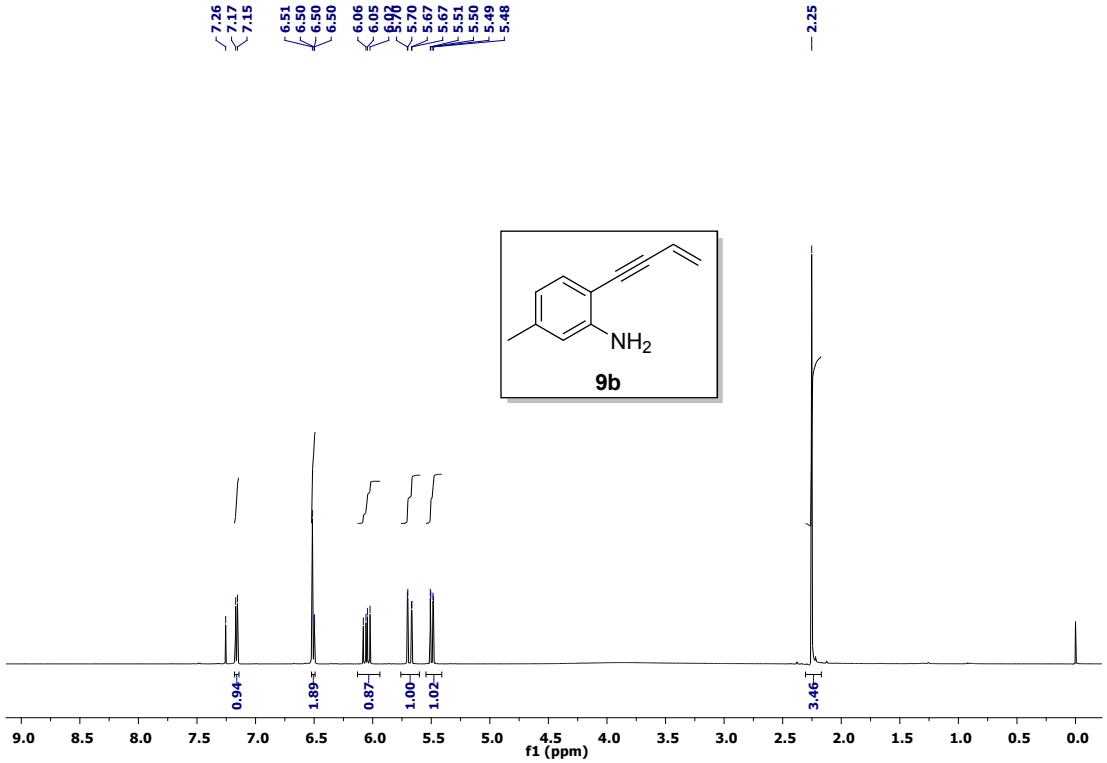
4. ^{1}H and ^{13}C Spectra of the compounds

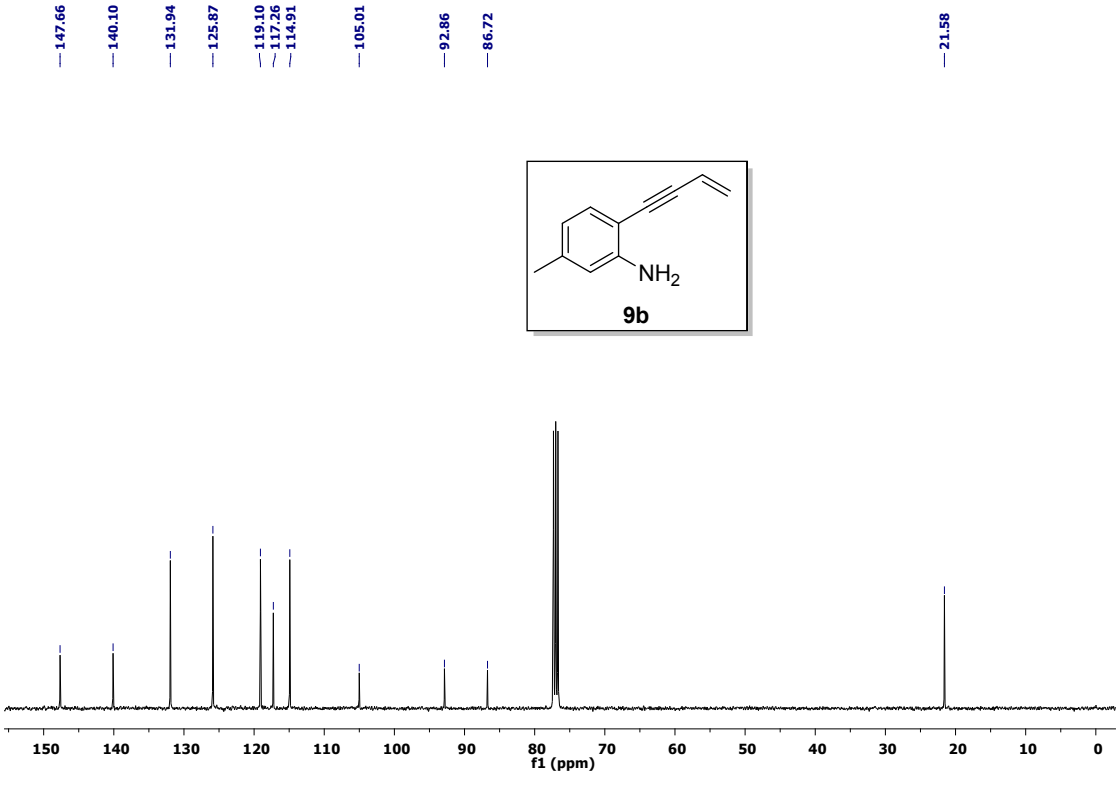
Copy of ^{1}H NMR and ^{13}C NMR spectra of **9a**



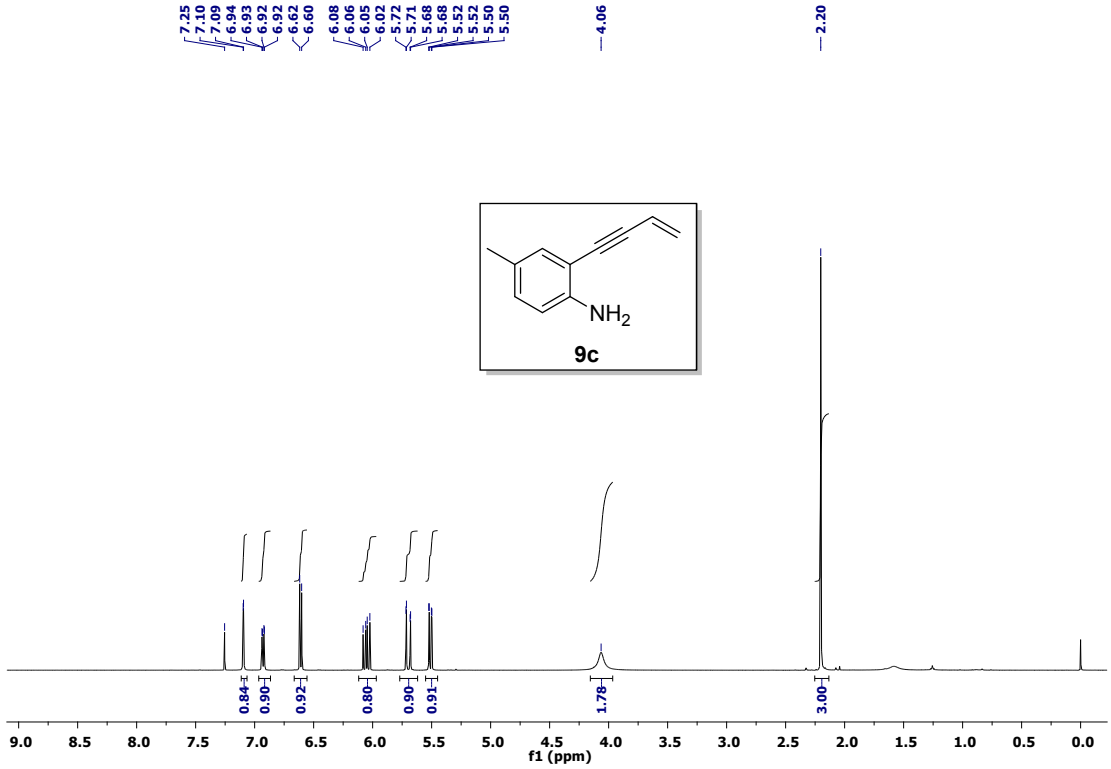


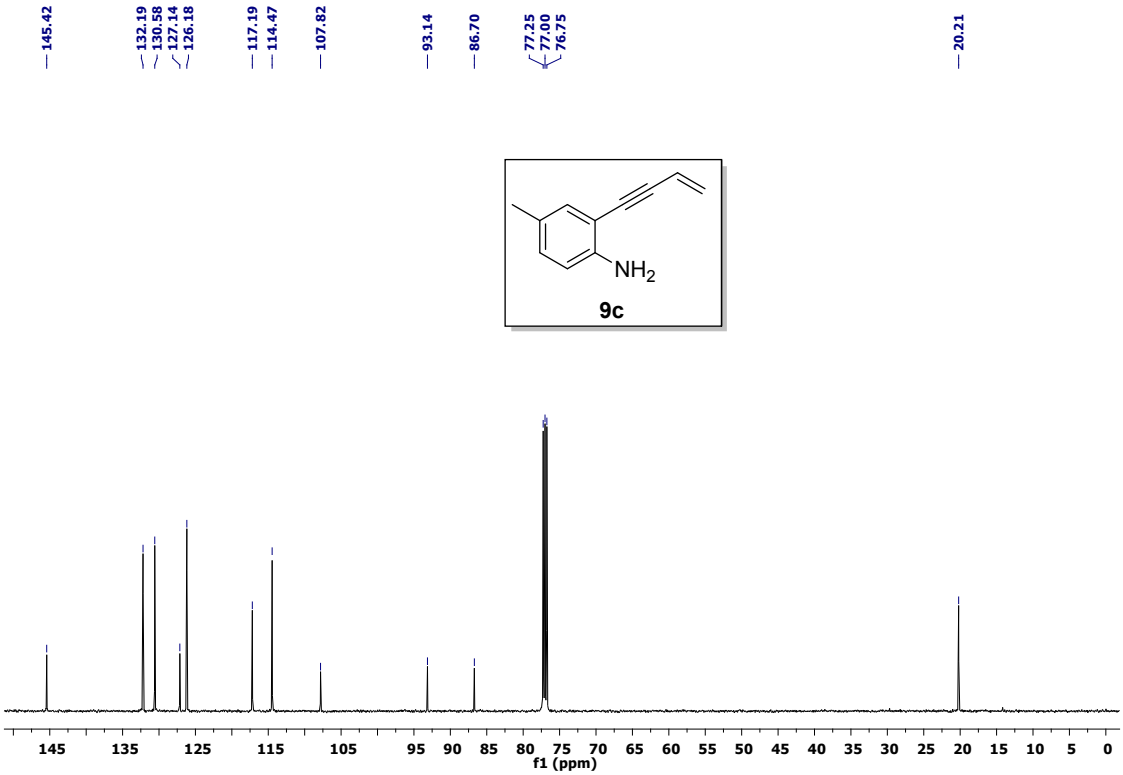
Copy of ^{1}H NMR and ^{13}C NMR spectra of **9b**



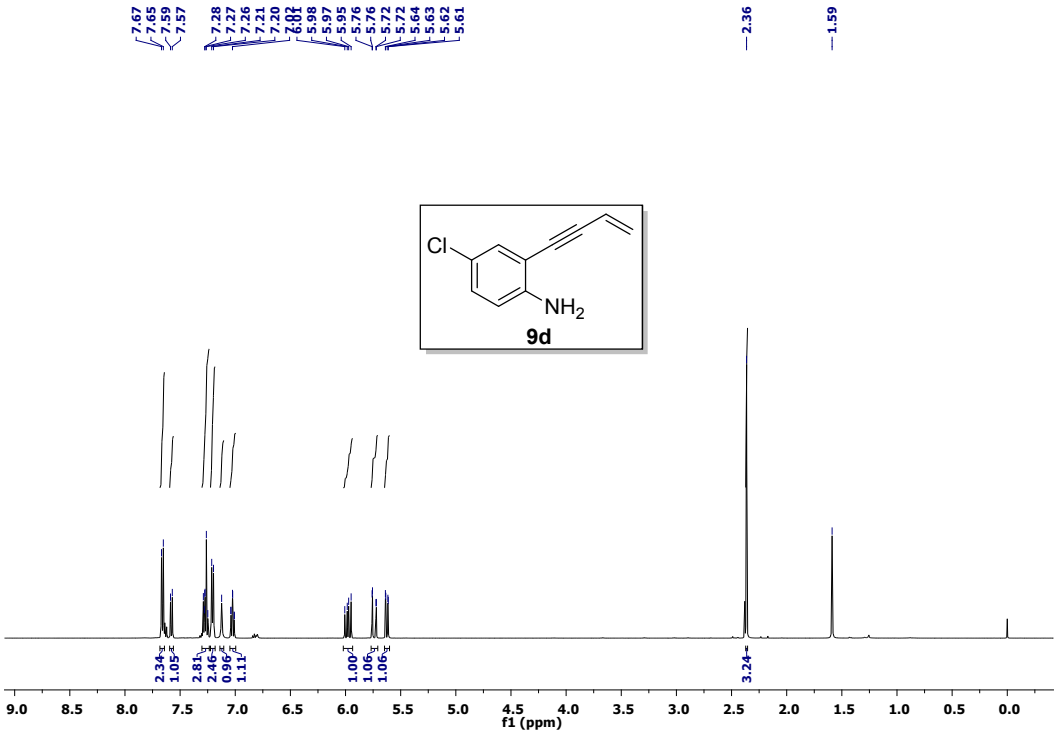


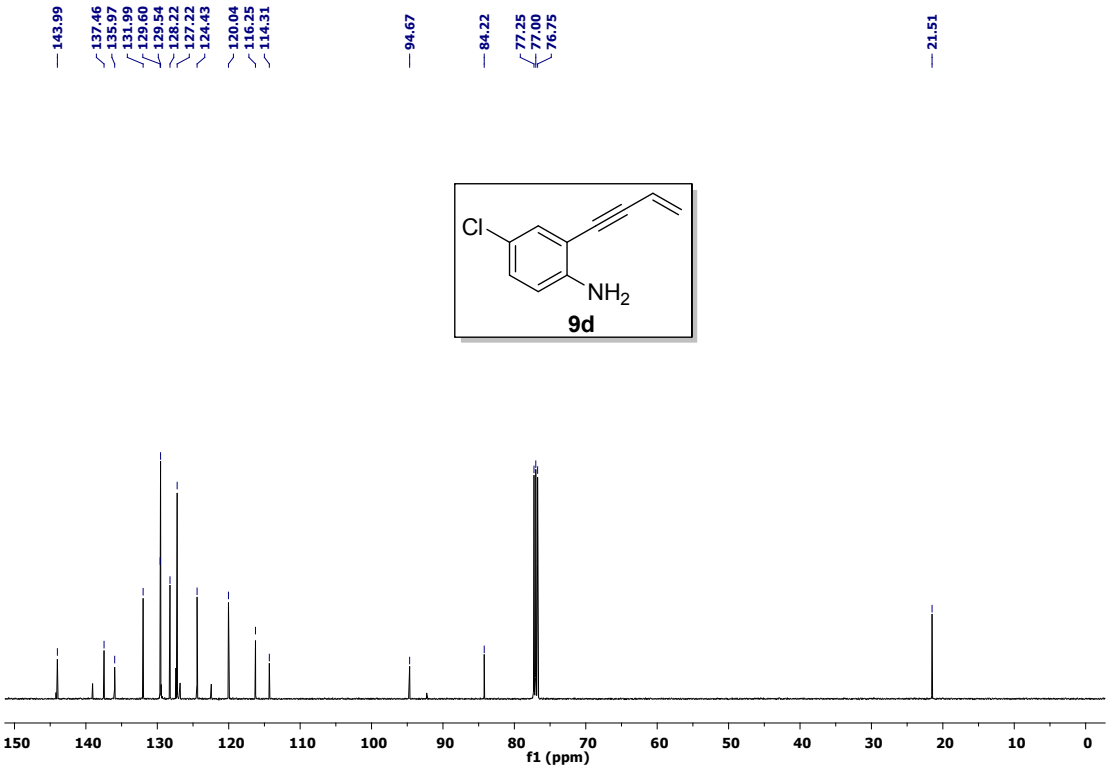
Copy of ^{1}H NMR and ^{13}C NMR spectra of **9c**



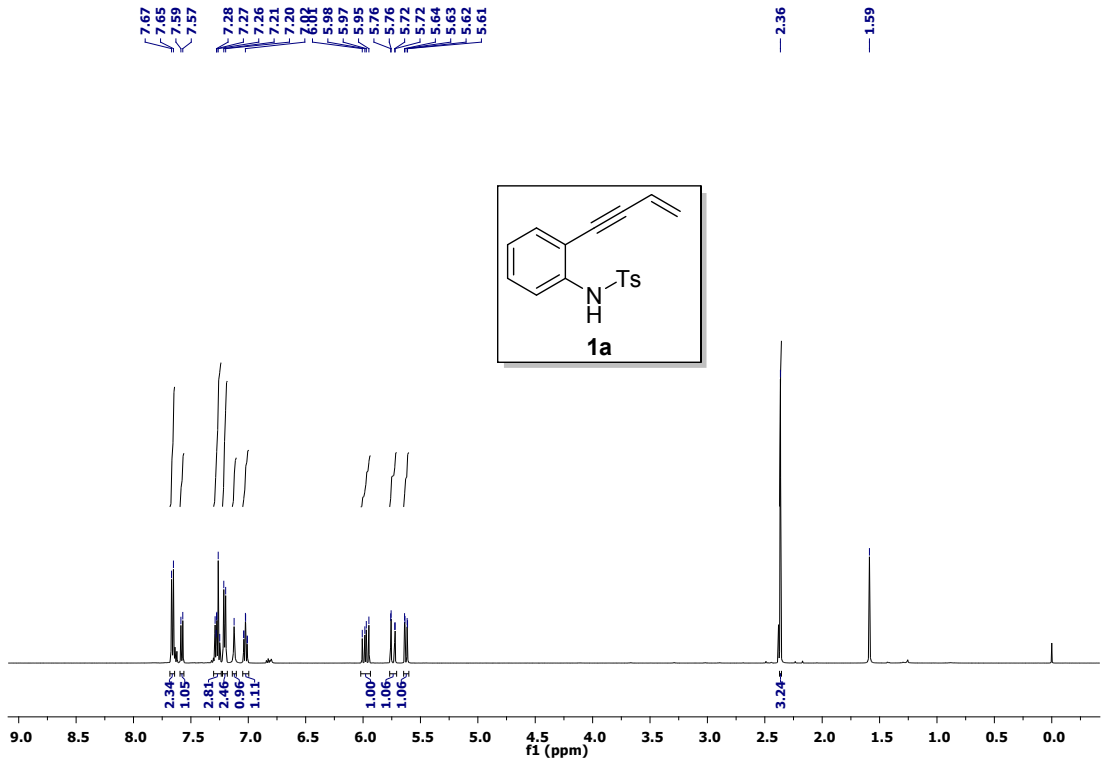


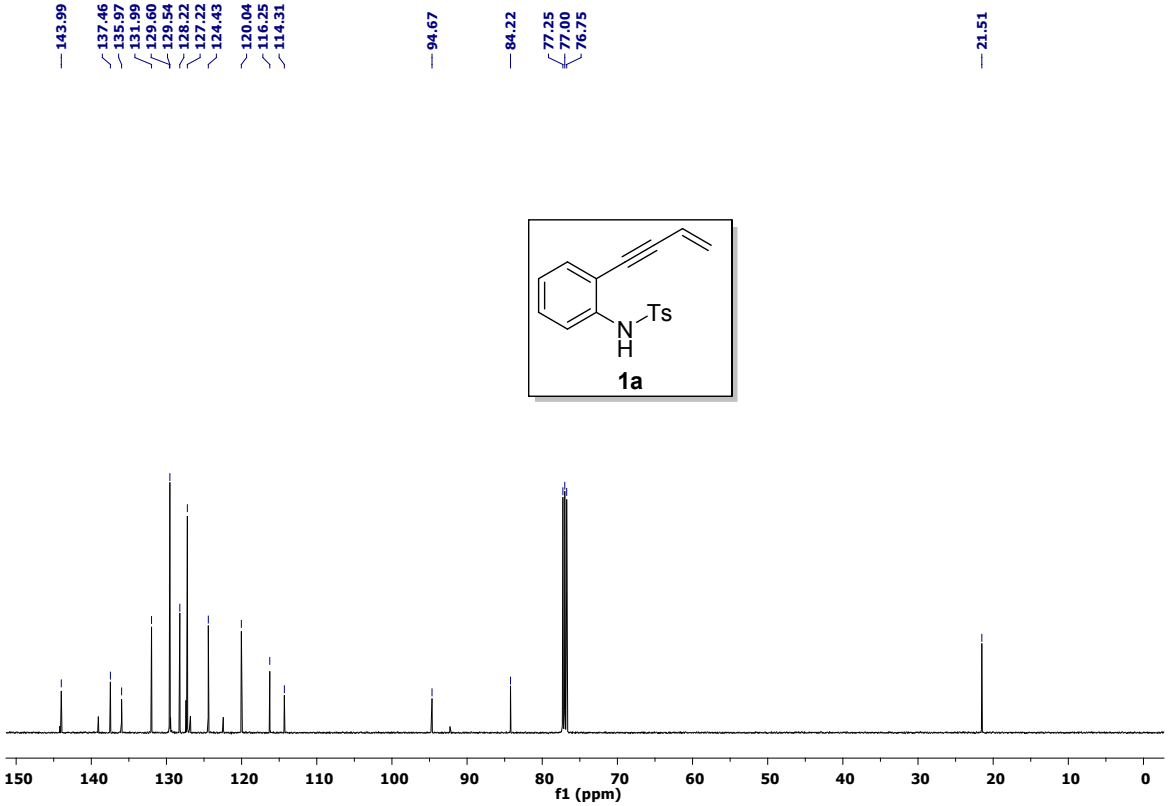
Copy of ^{1}H NMR and ^{13}C NMR spectra of **9d**



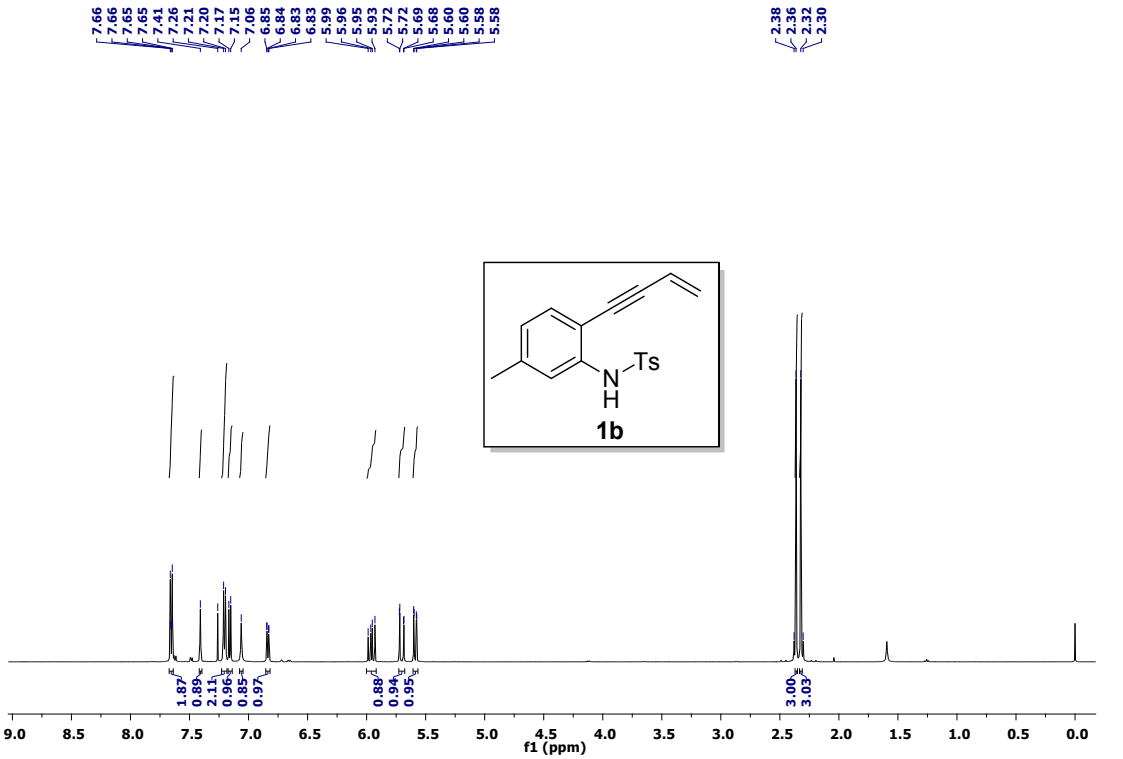


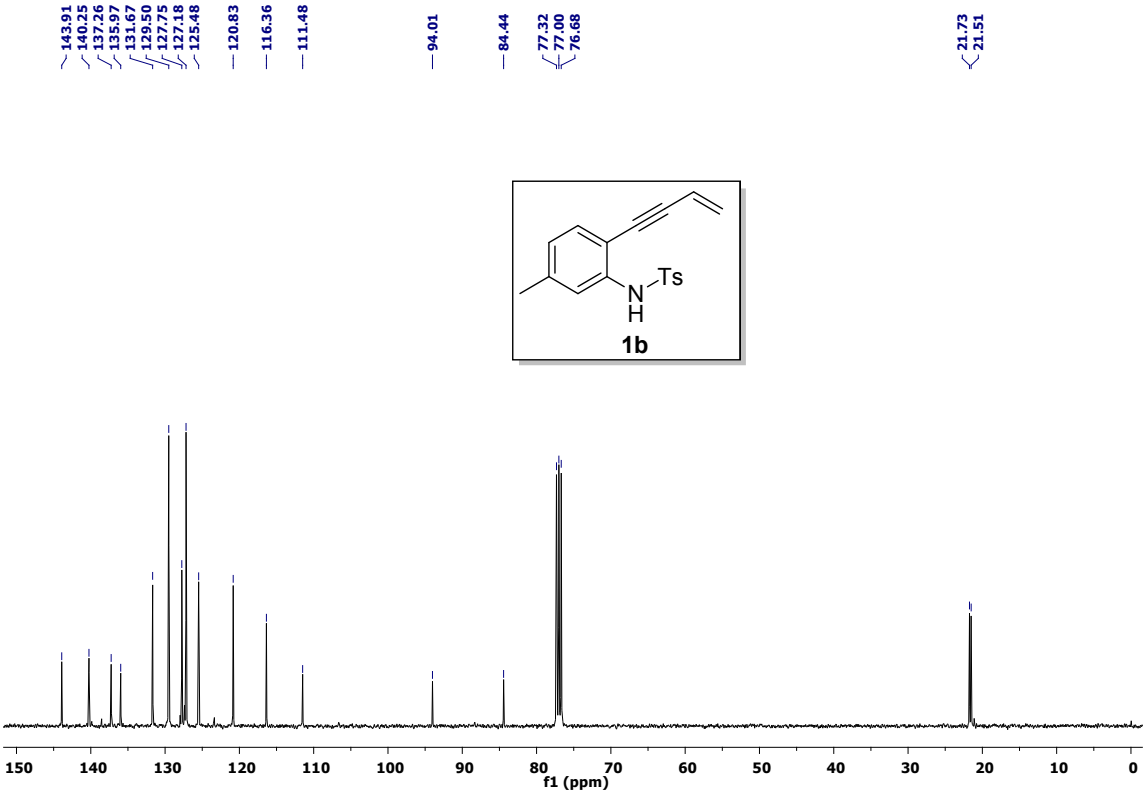
Copy of ^{1}H NMR and ^{13}C NMR spectra of **1a**



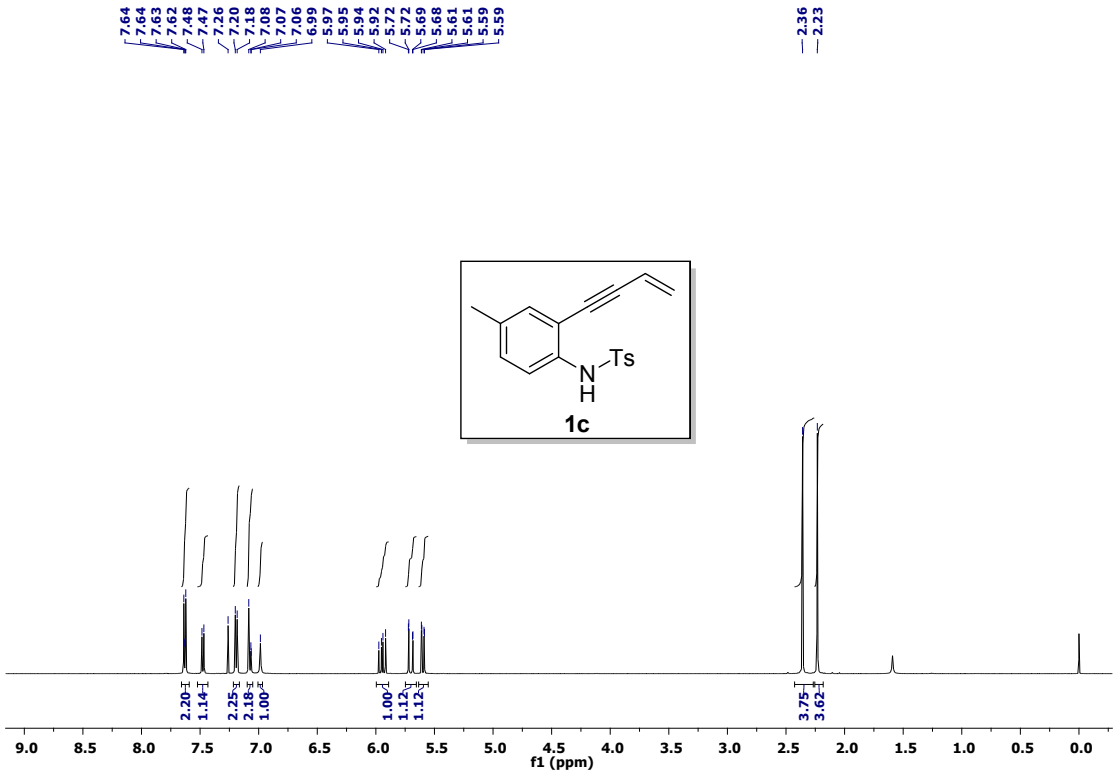


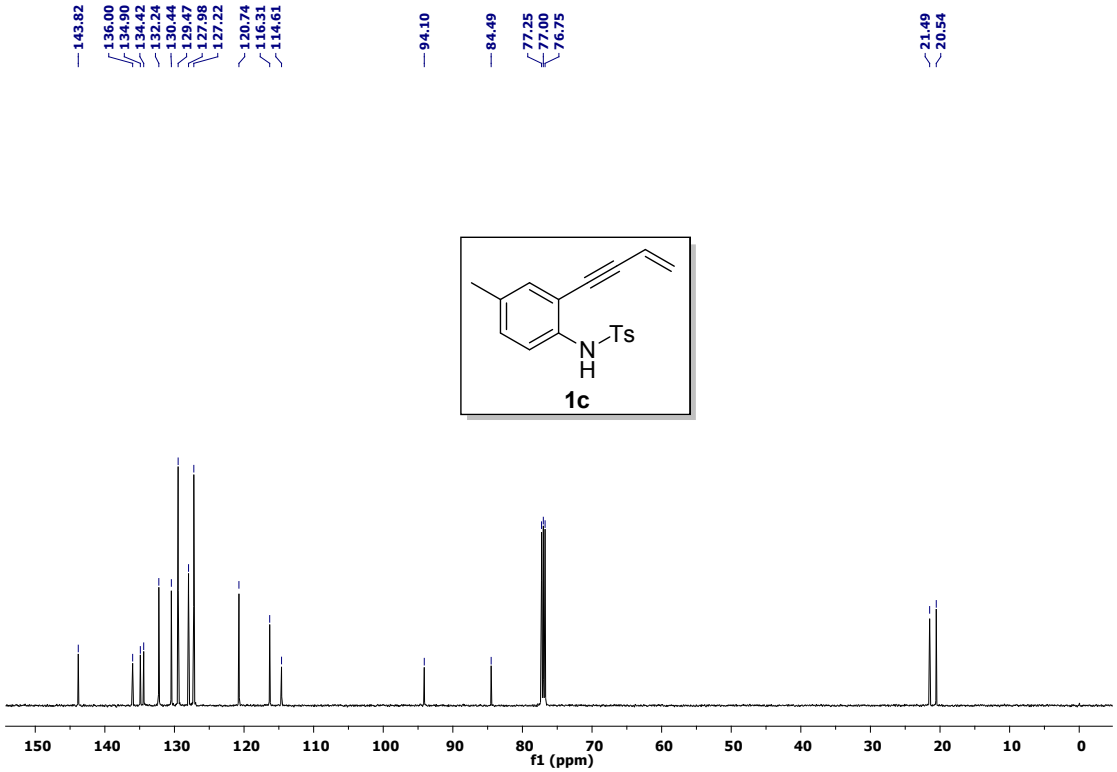
Copy of ^{1}H NMR and ^{13}C NMR spectra of **1b**



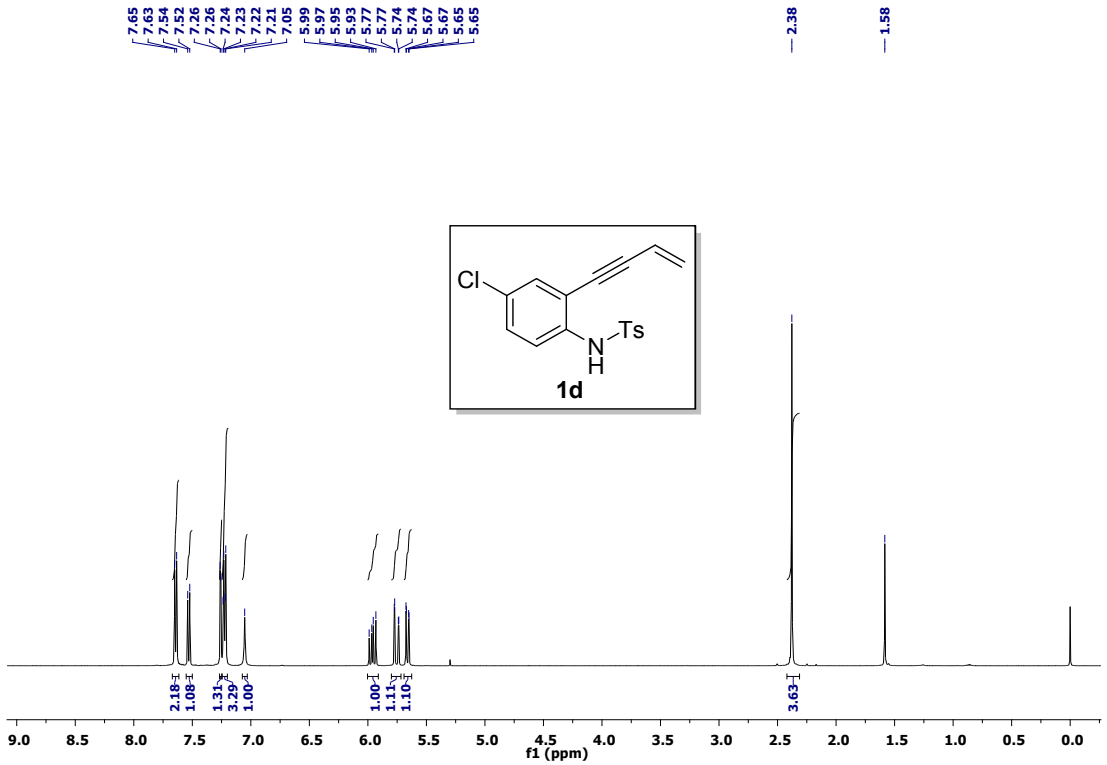


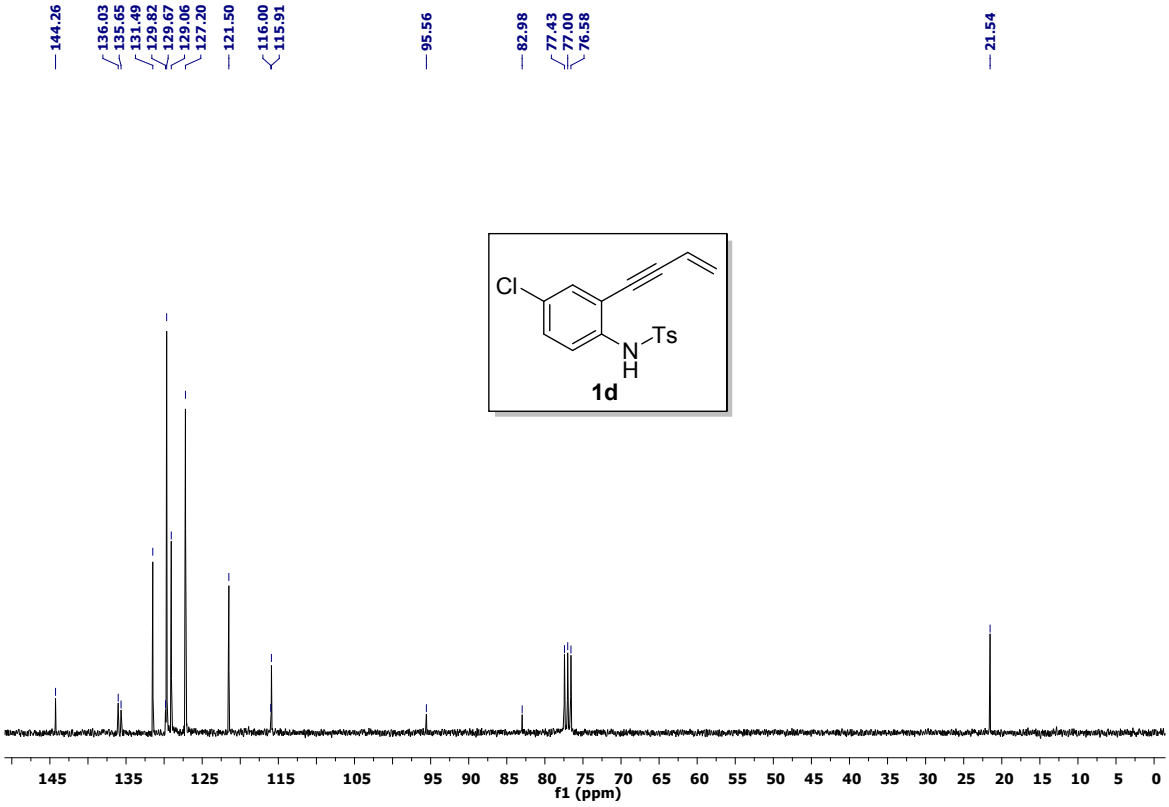
Copy of ^{1}H NMR and ^{13}C NMR spectra of **1c**



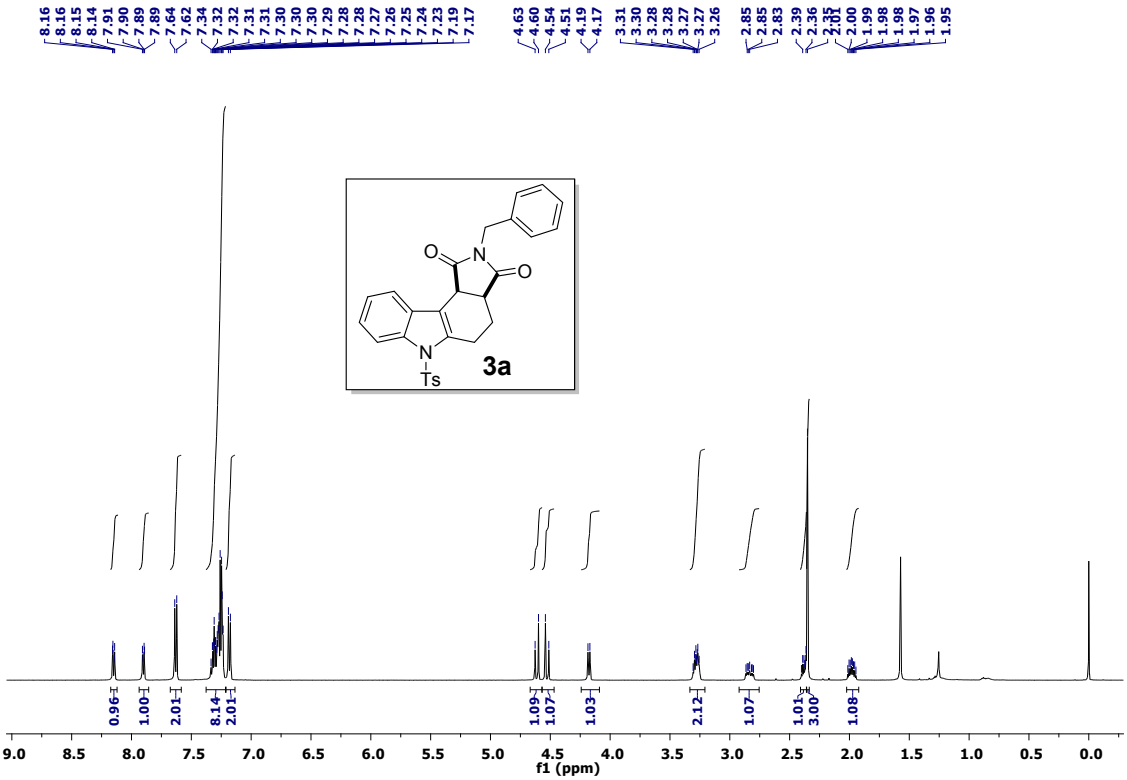


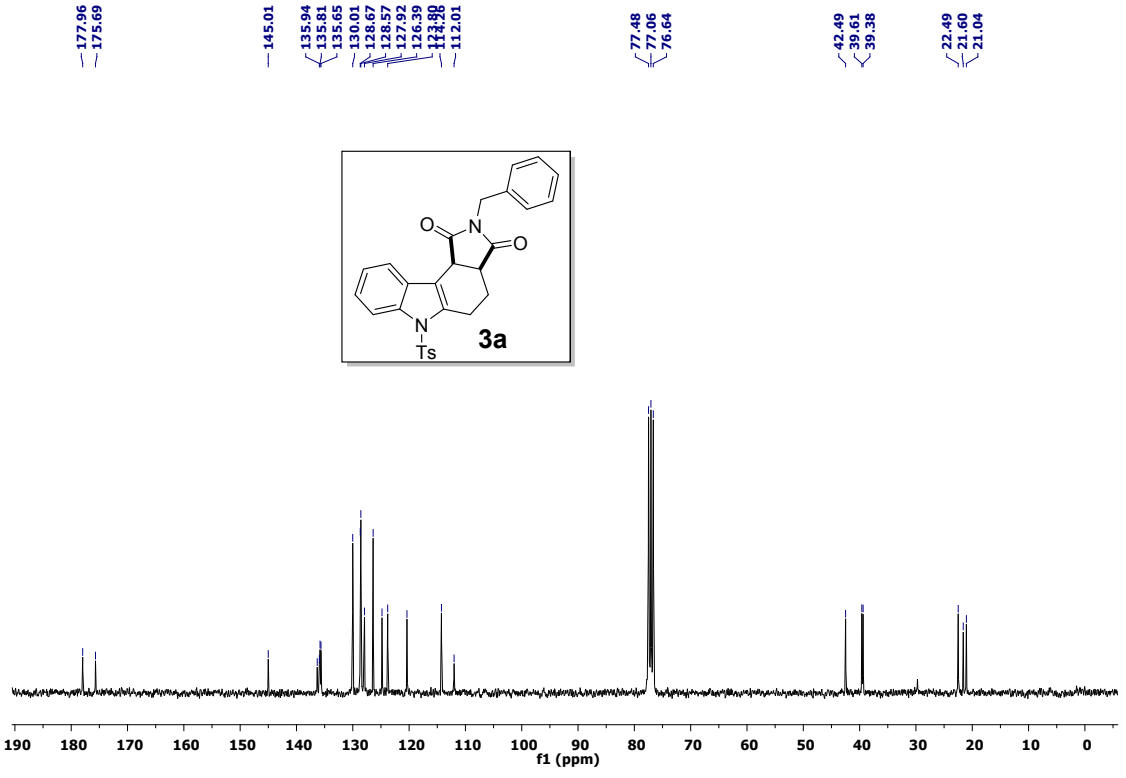
Copy of ^{1}H NMR and ^{13}C NMR spectra of **1d**



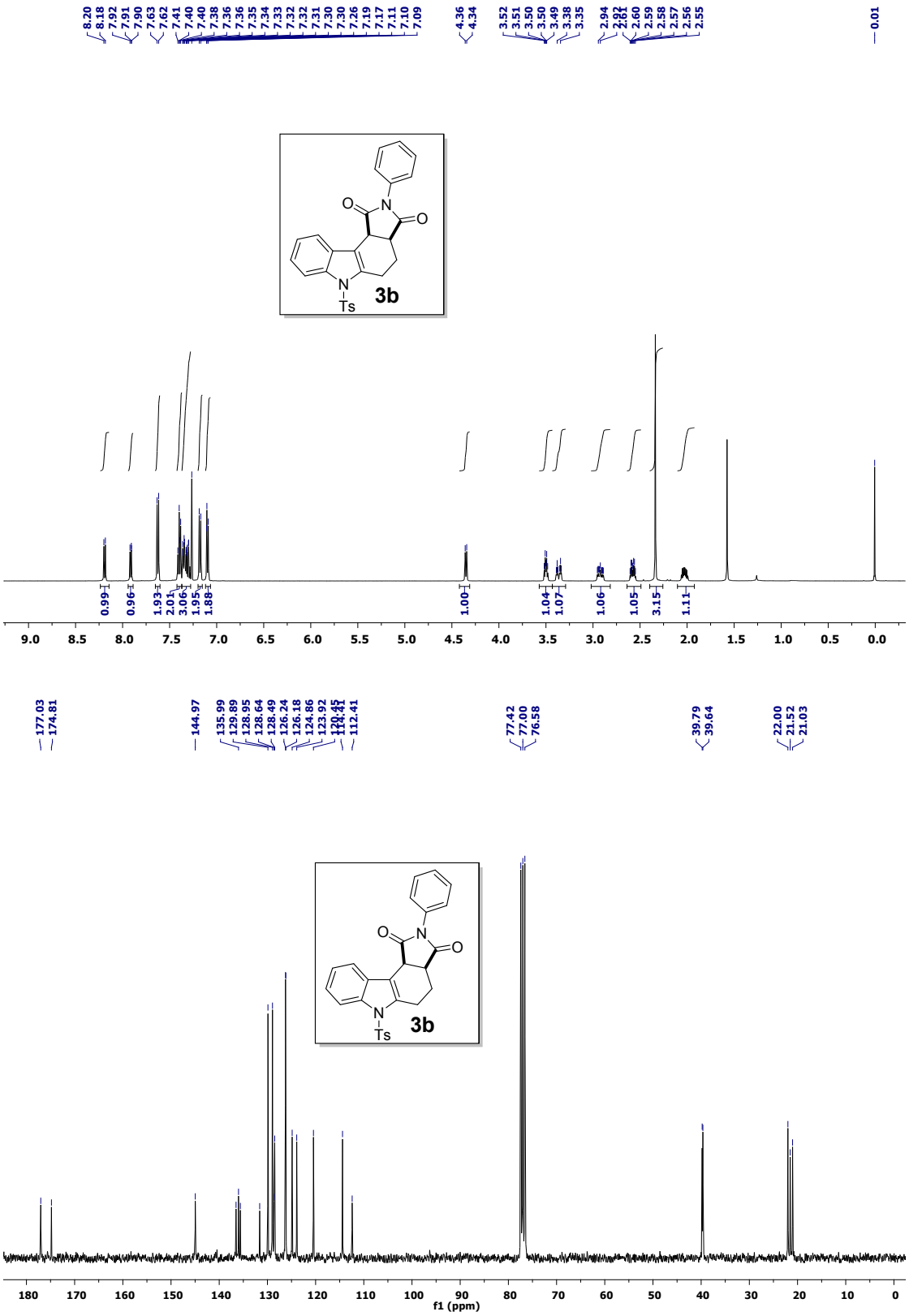


Copy of ^{1}H NMR and ^{13}C NMR spectra of **3a**

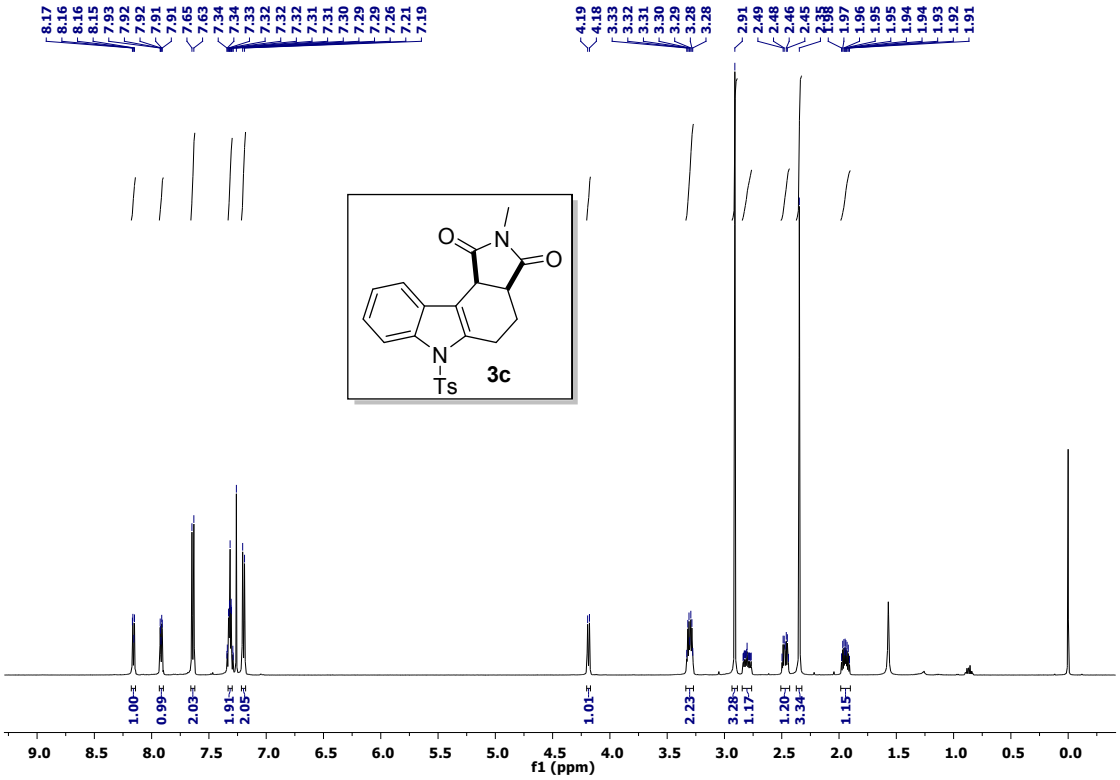


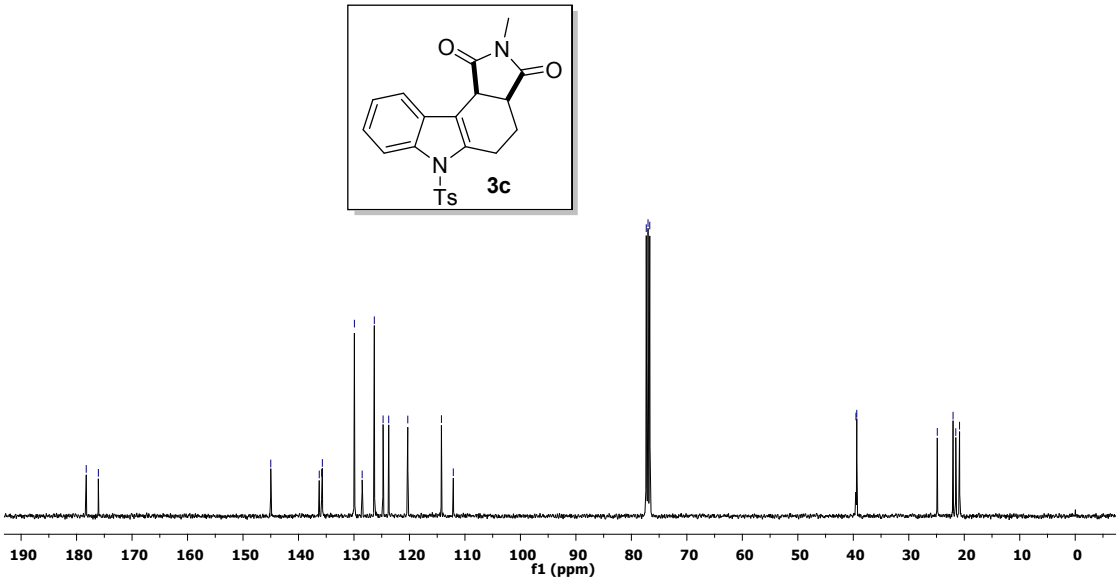


Copy of ^{1}H NMR and ^{13}C NMR spectra of **3b**



Copy of ^{1}H NMR and ^{13}C NMR spectra of **3c**





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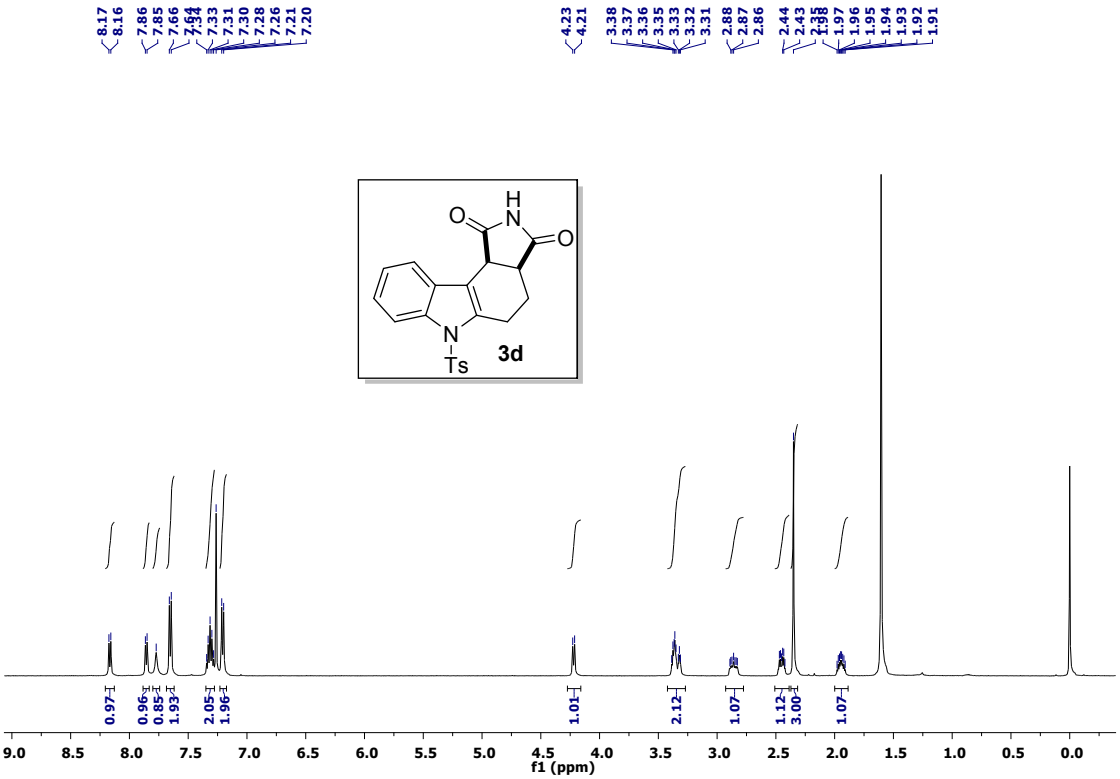
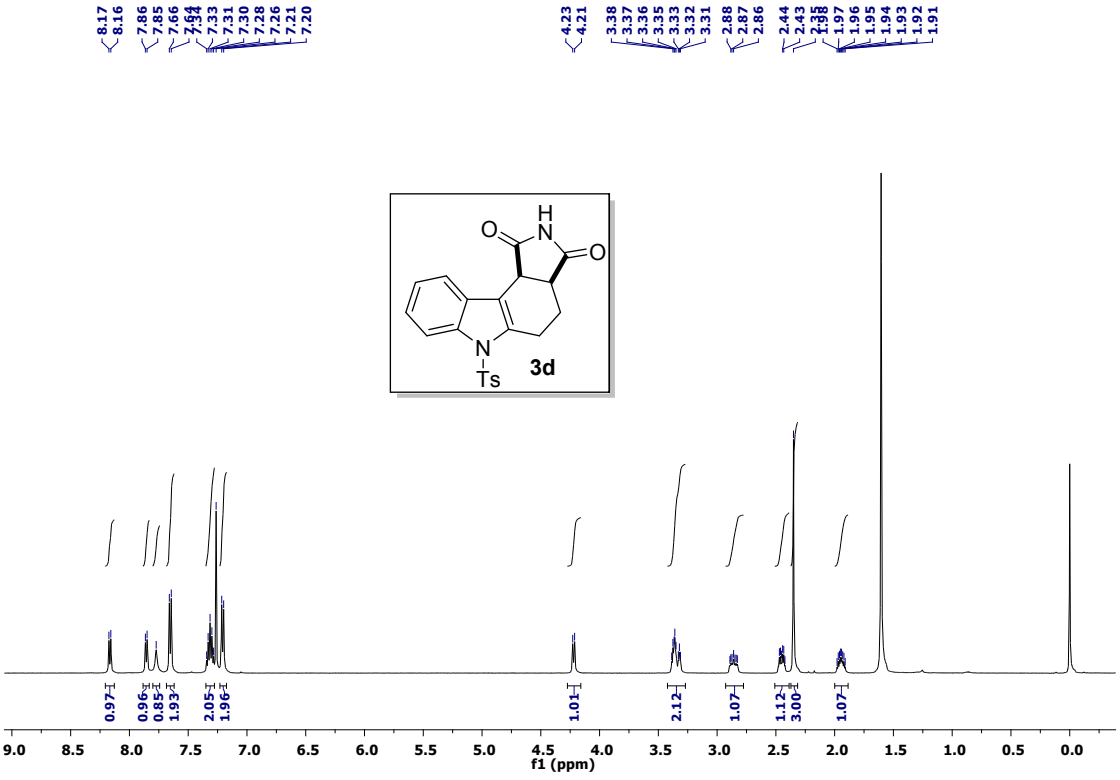
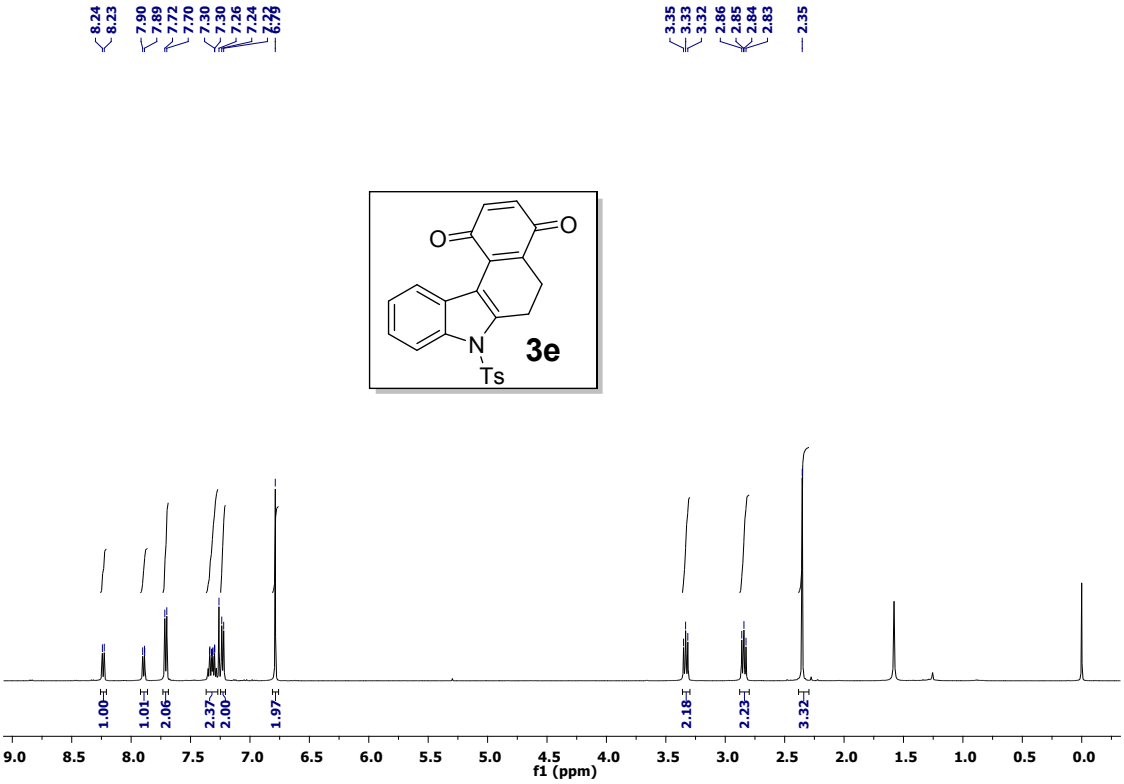
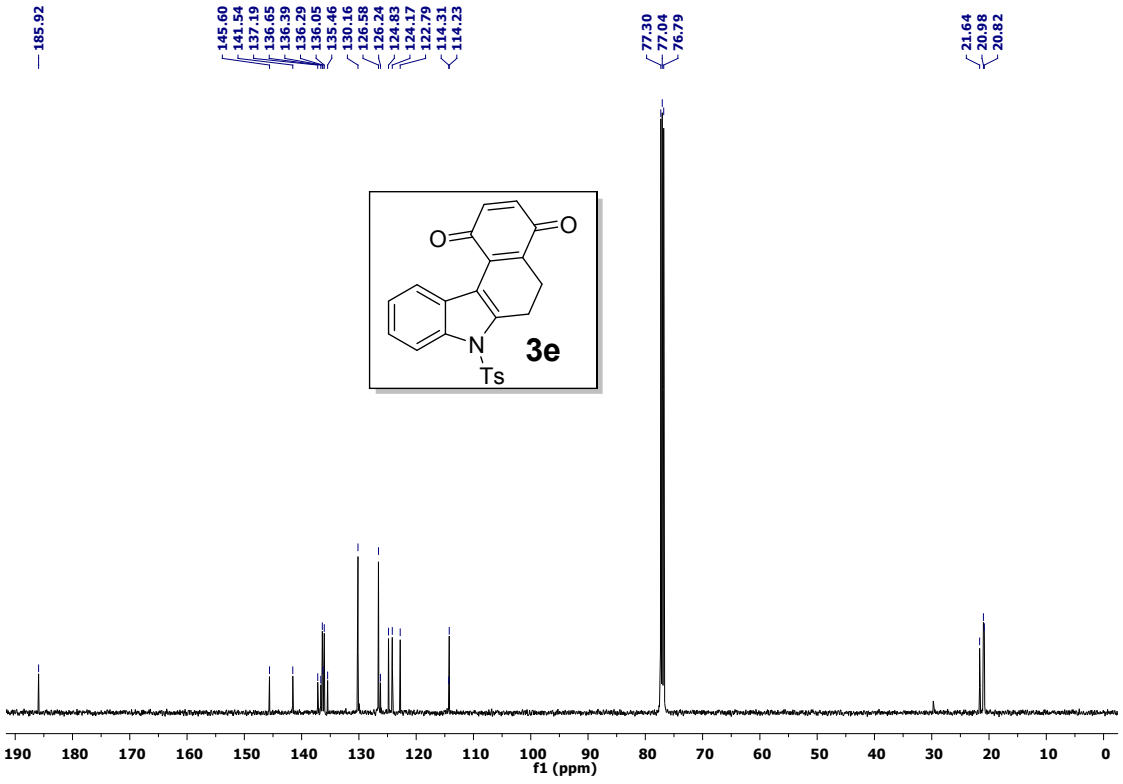


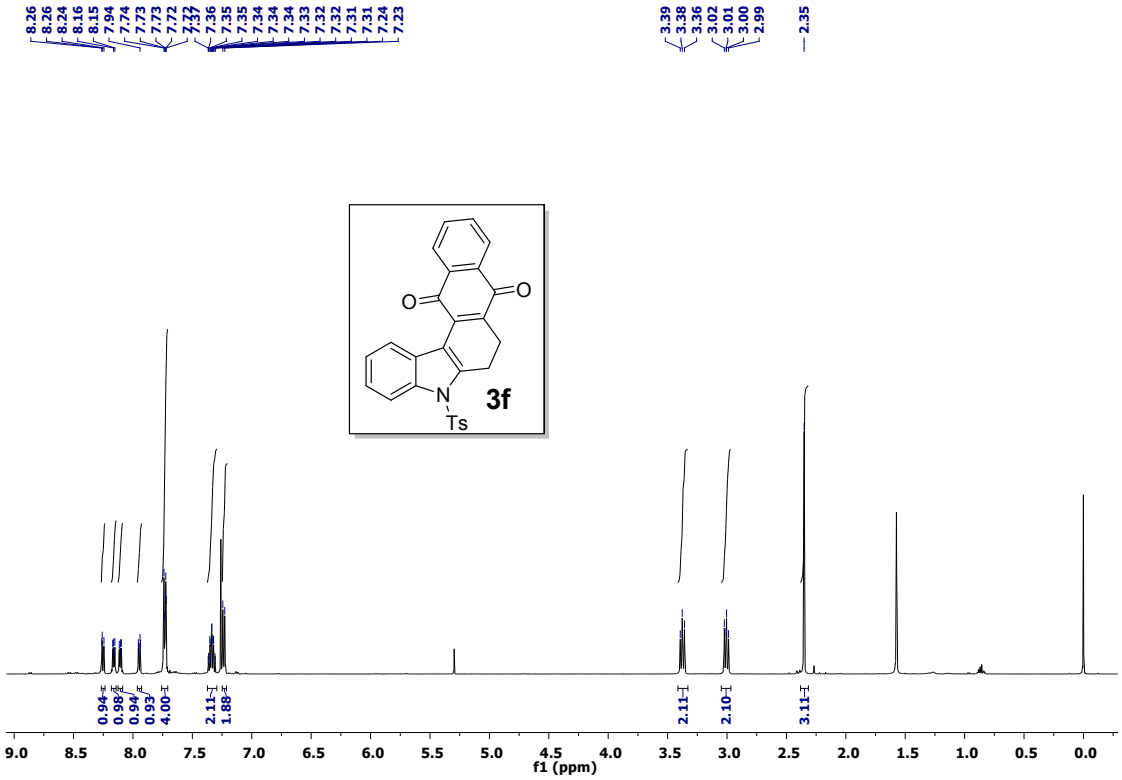


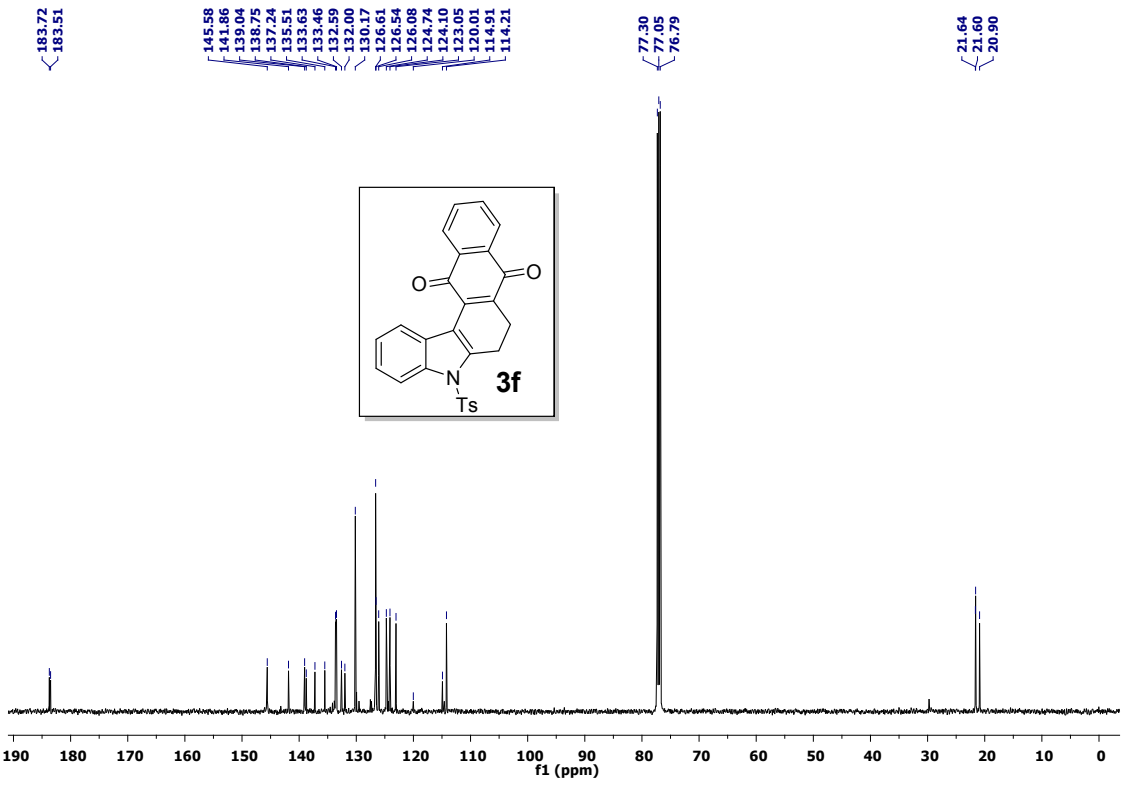
Copy of ^{1}H NMR and ^{13}C NMR spectra of **3e**



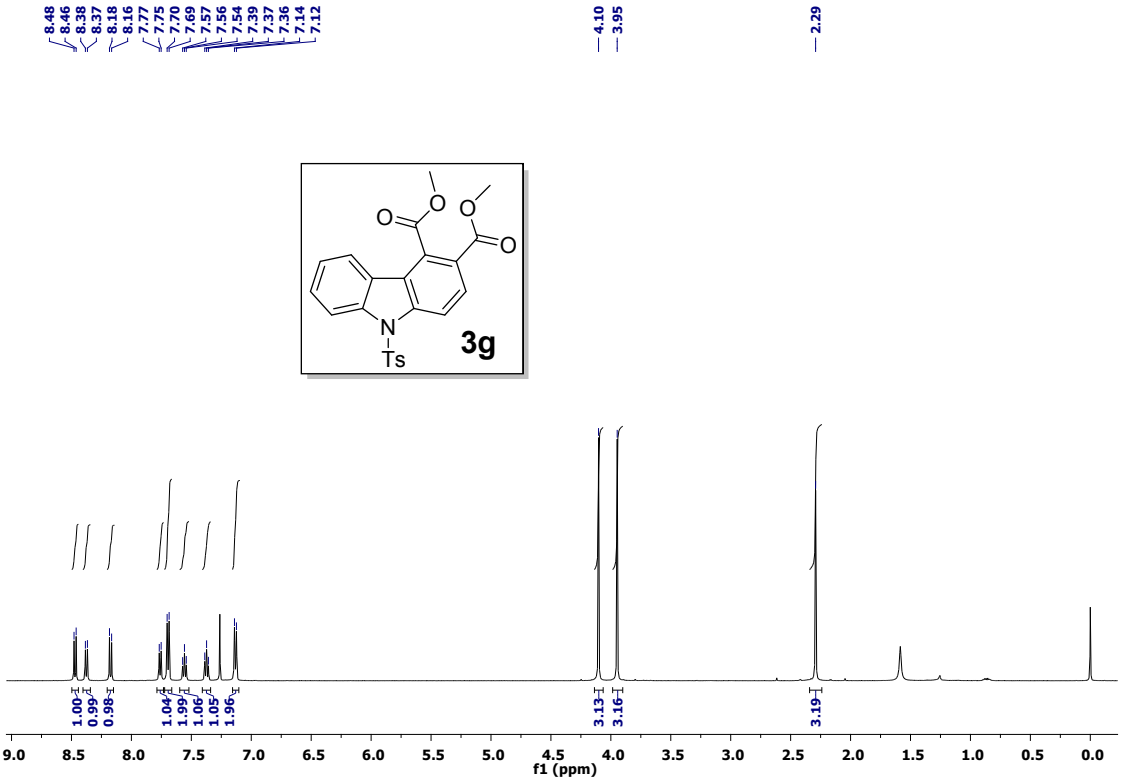


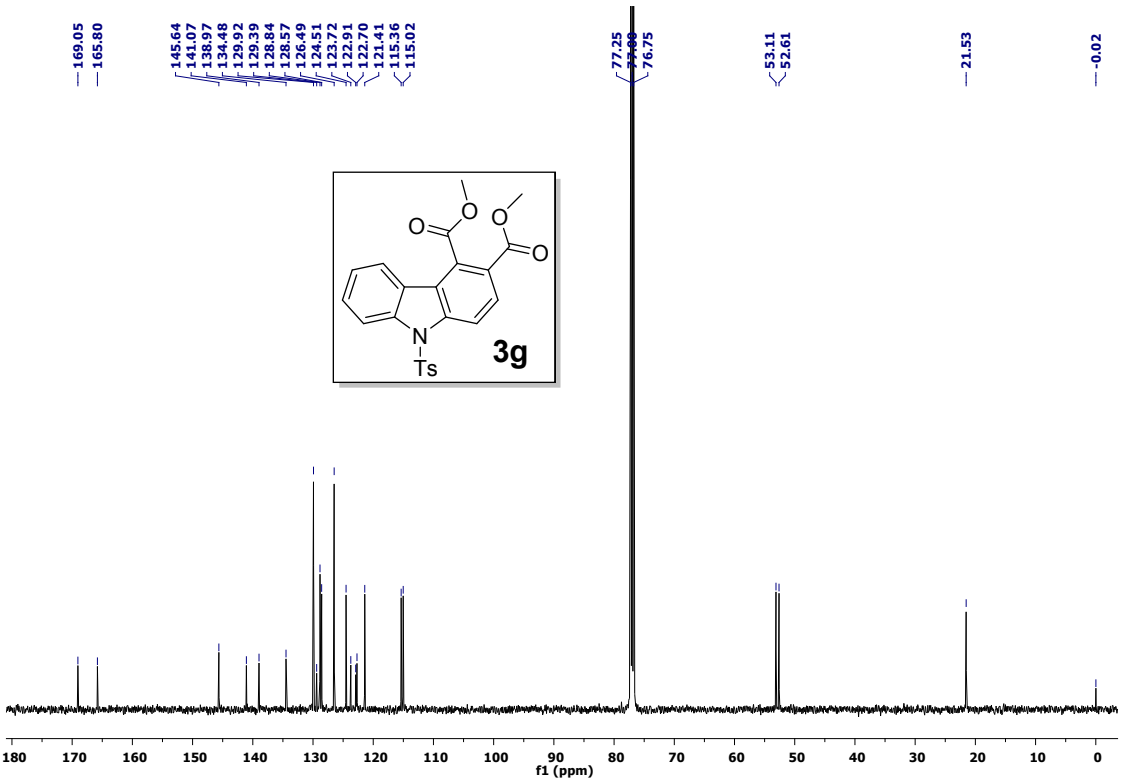
Copy of ^{1}H NMR and ^{13}C NMR spectra of **3f**



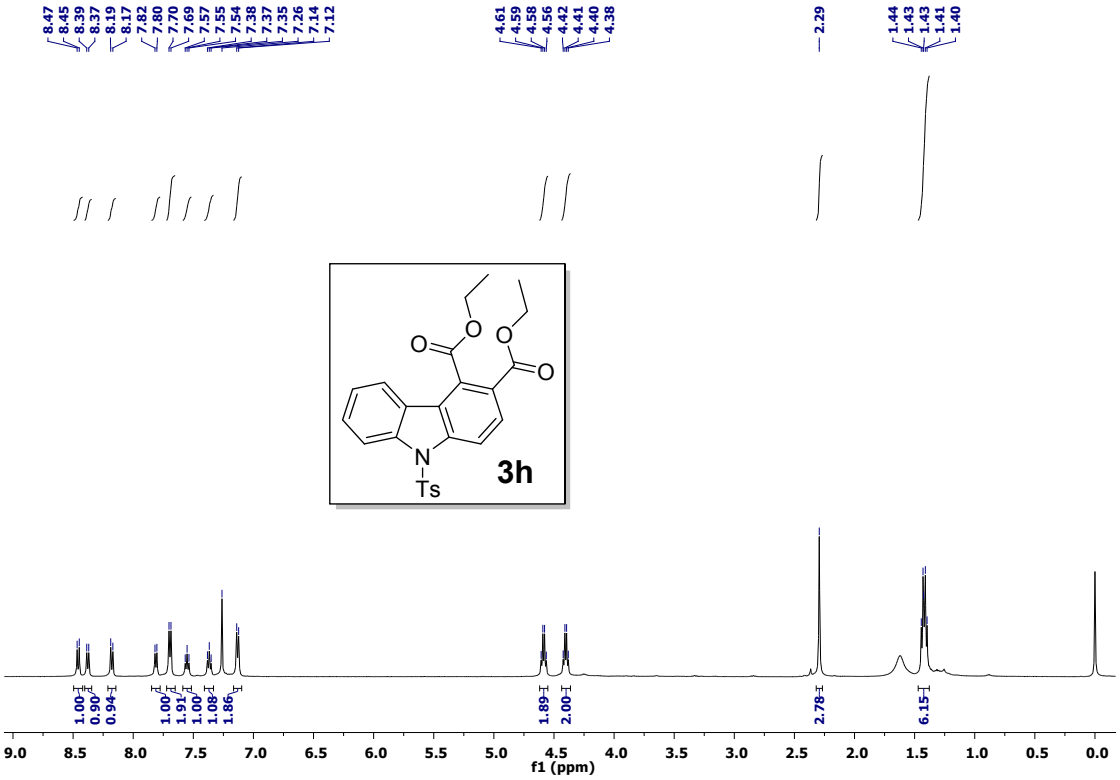


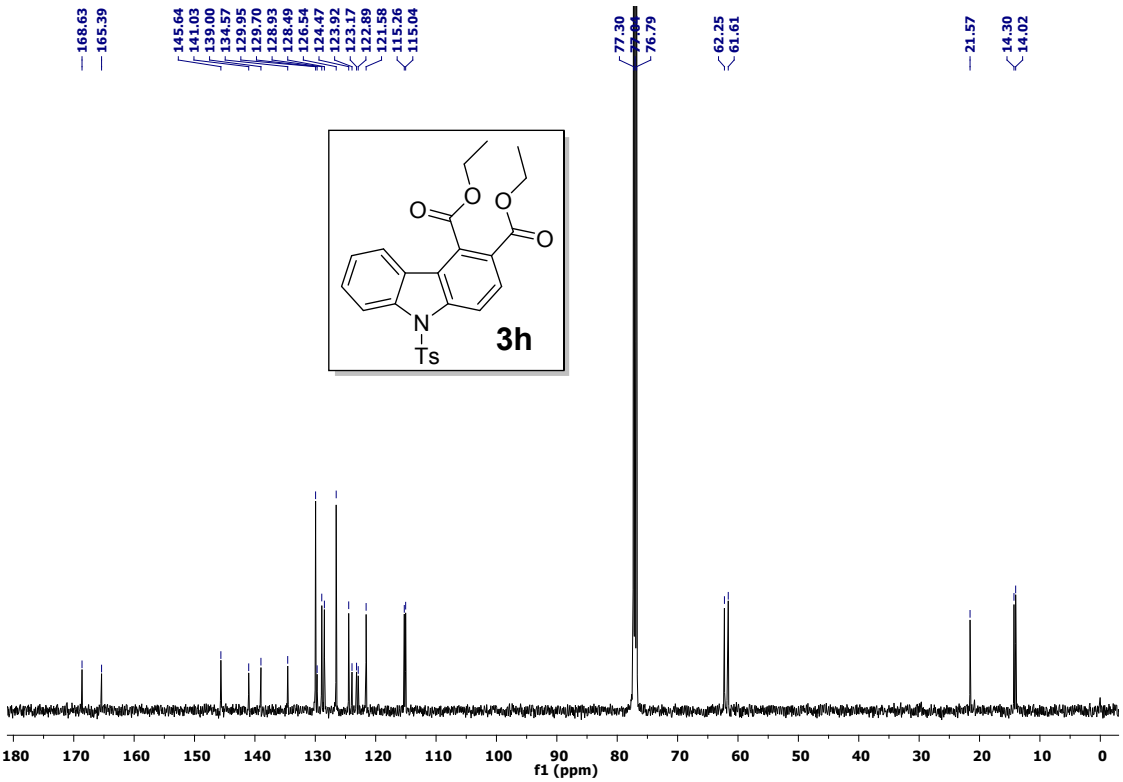
Copy of ^{1}H NMR and ^{13}C NMR spectra of **3g**



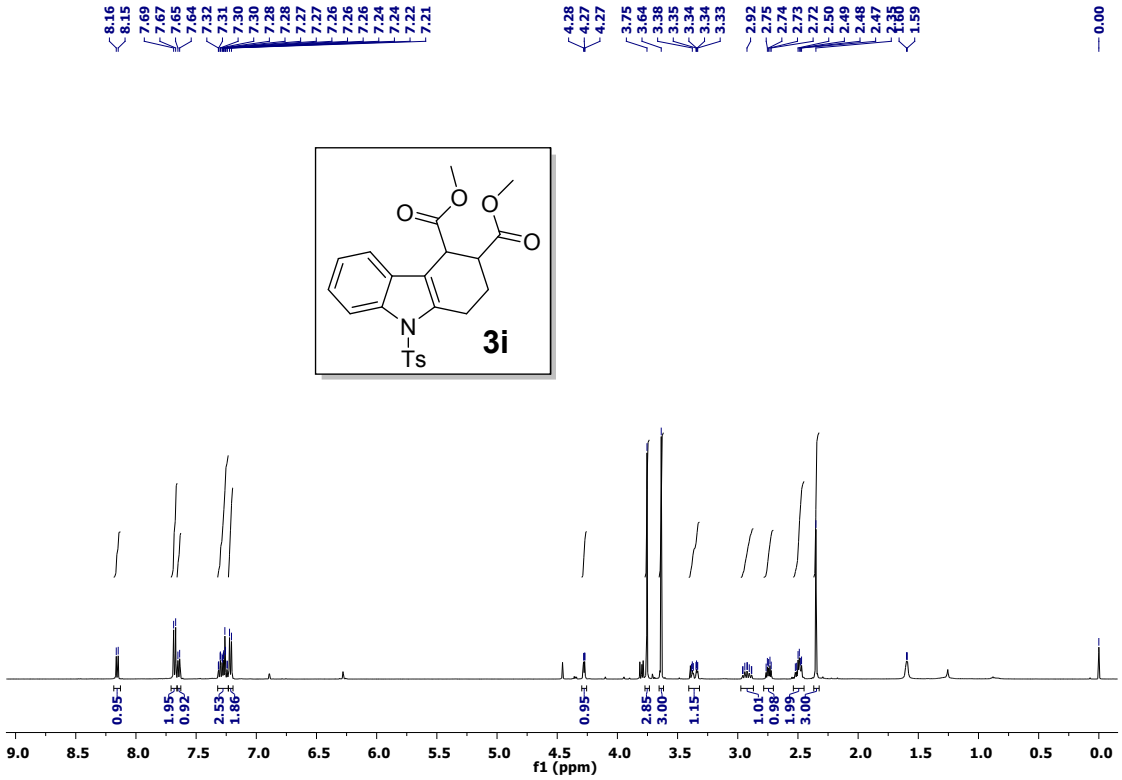


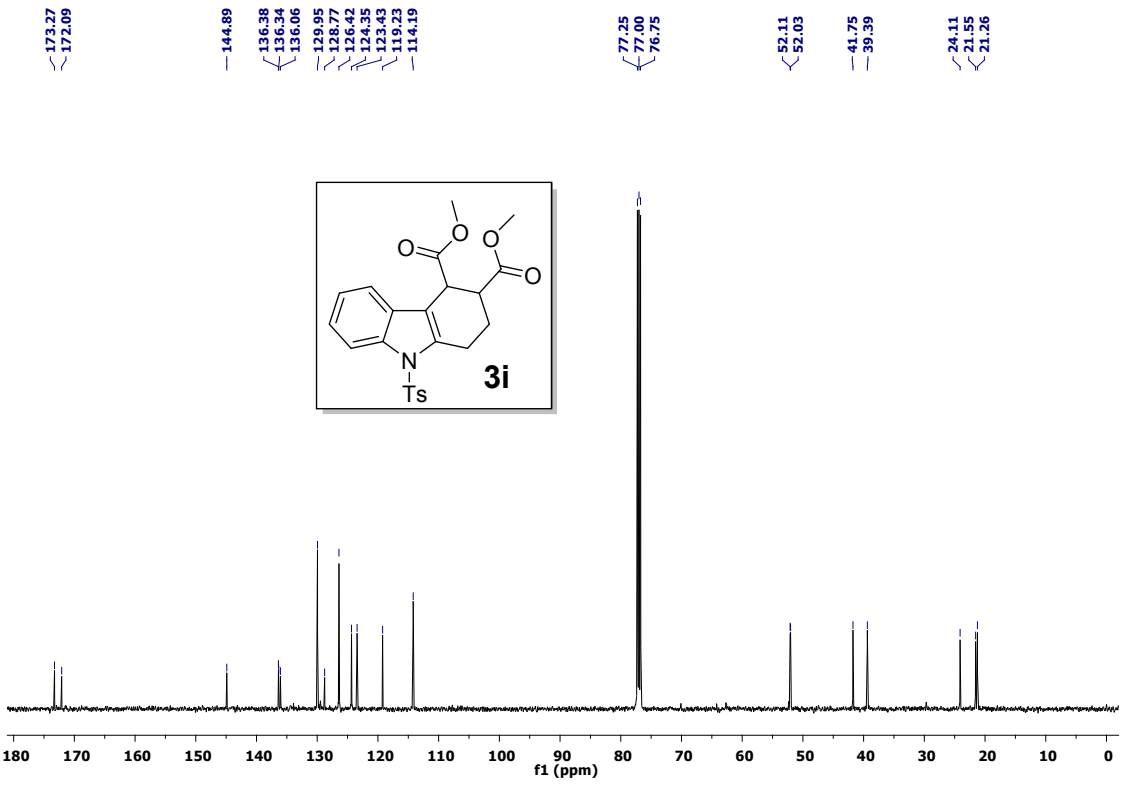
Copy of ^{1}H NMR and ^{13}C NMR spectra of **3h**



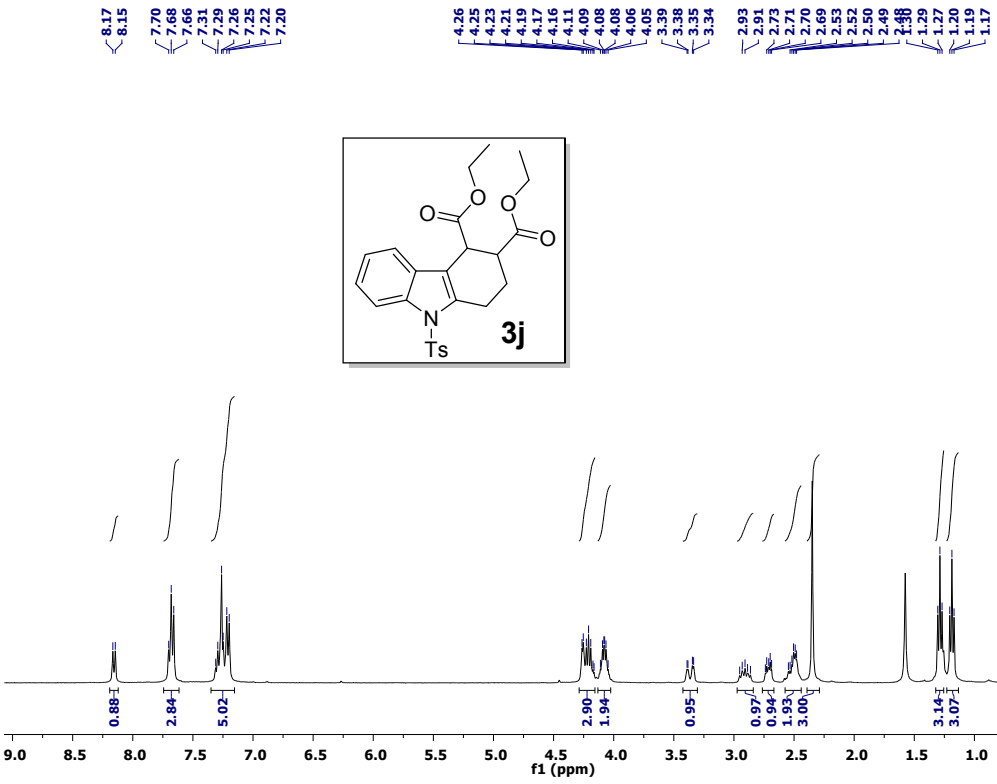


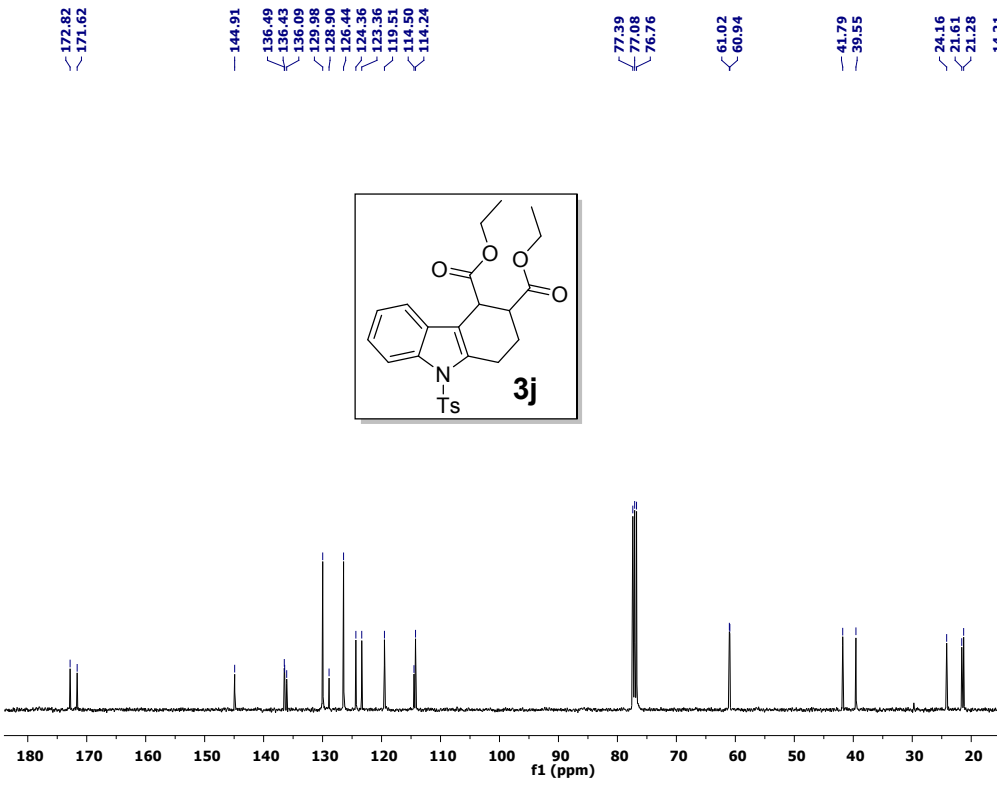
Copy of ^{1}H NMR and ^{13}C NMR spectra of **3i**



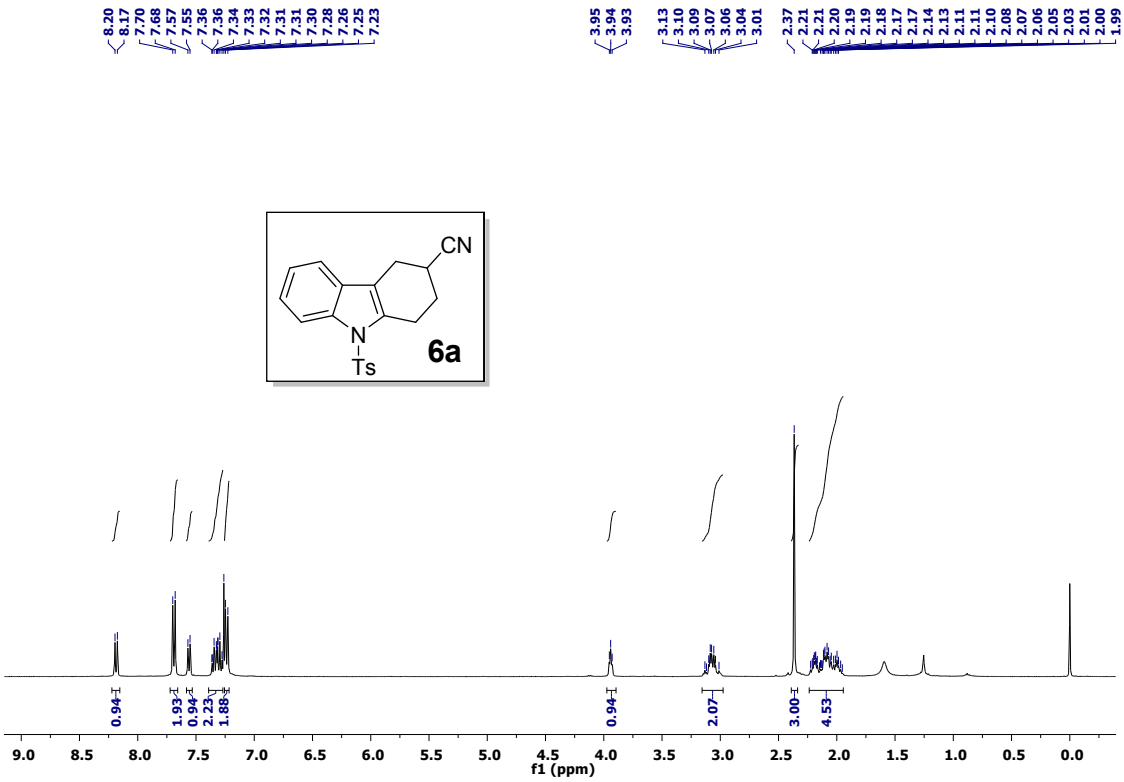


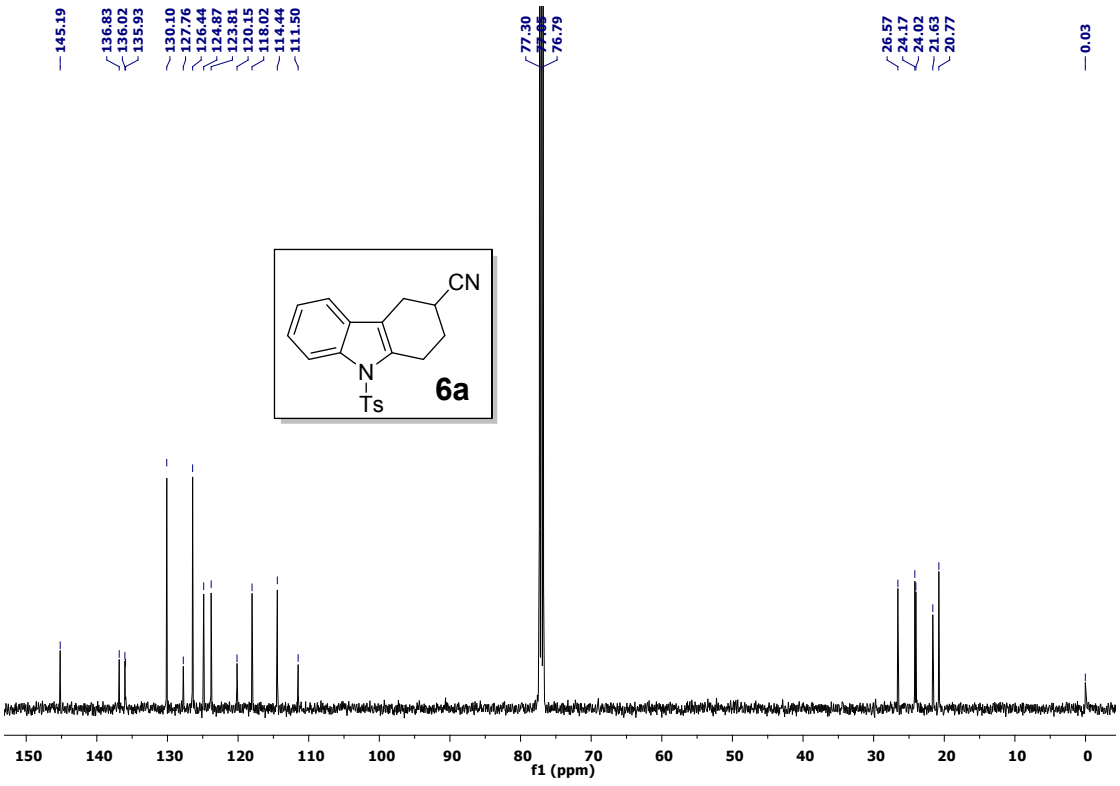
Copy of ^{1}H NMR and ^{13}C NMR spectra of **3j**



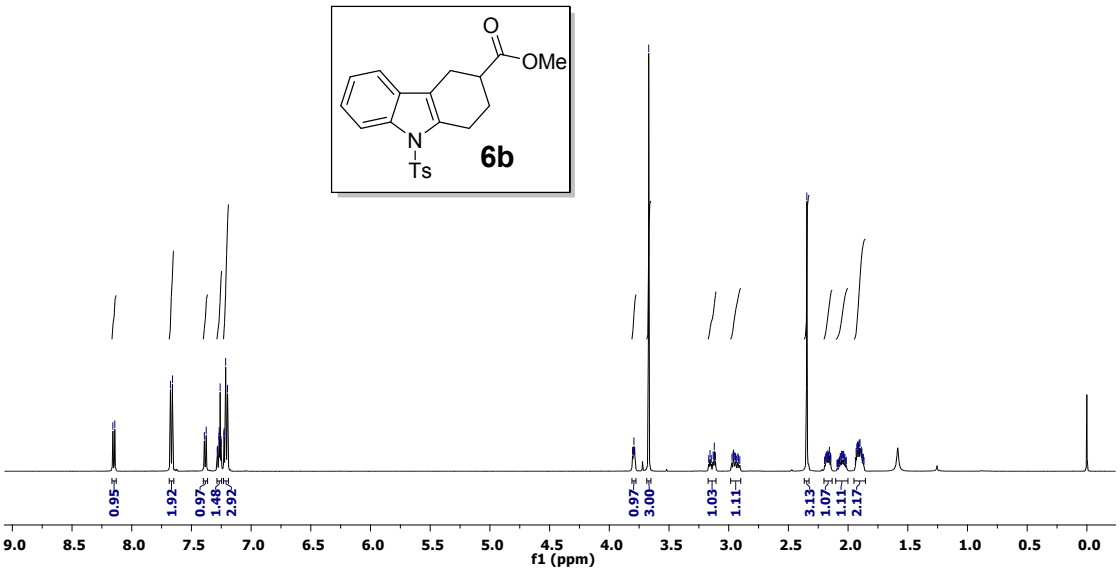


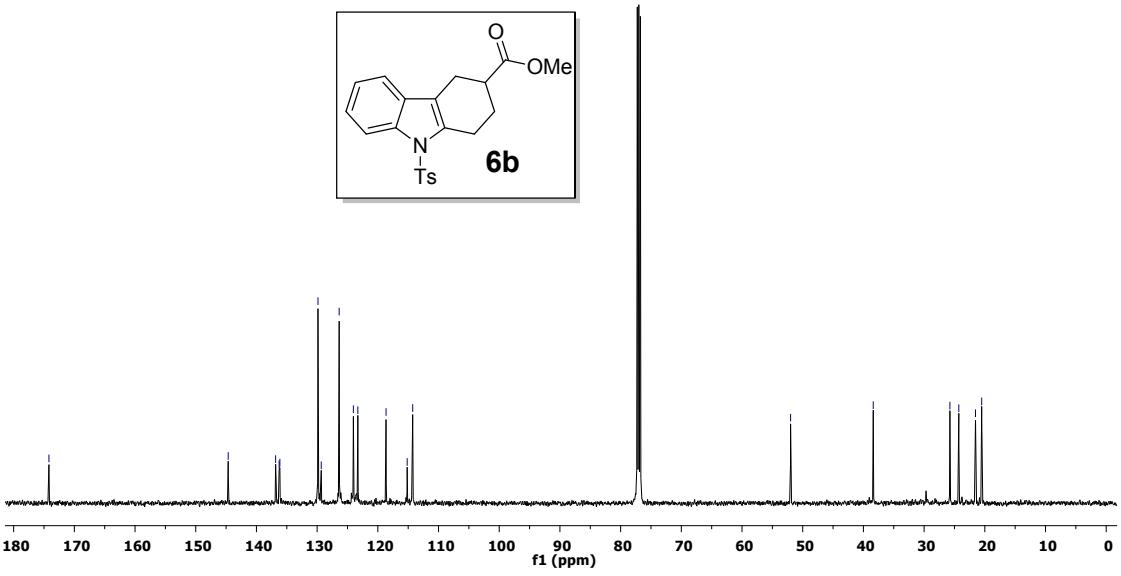
Copy of ^{1}H NMR and ^{13}C NMR spectra of **6a**



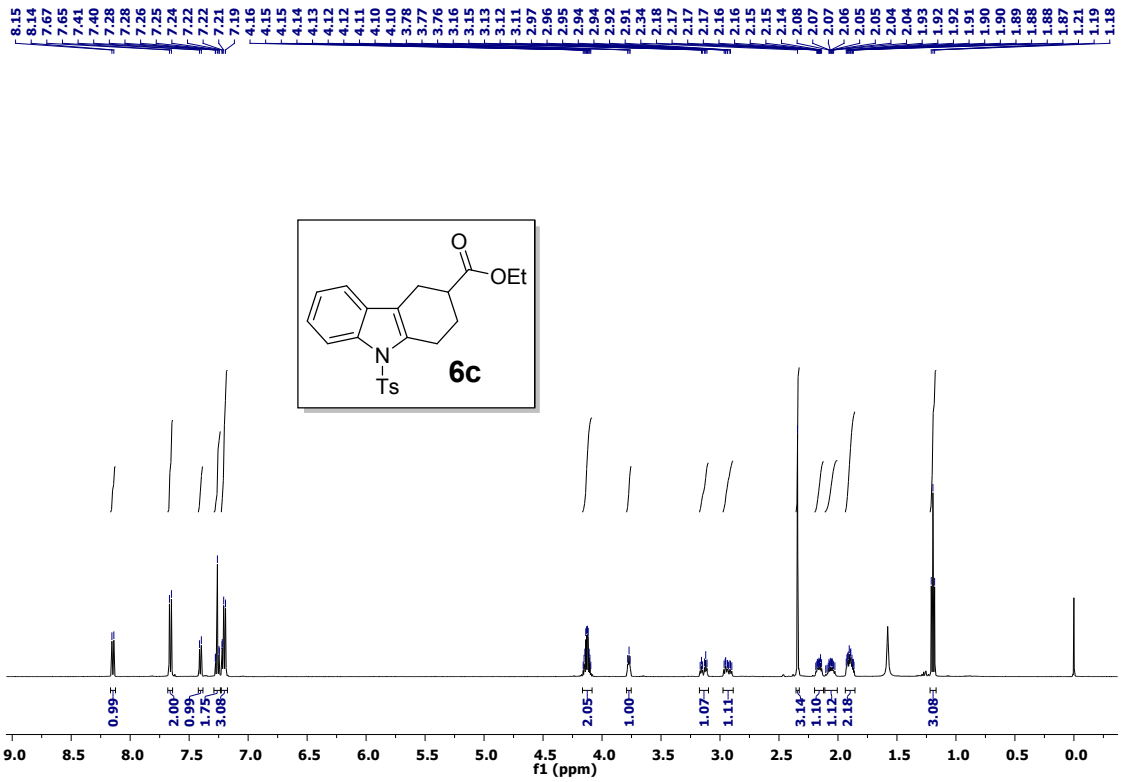


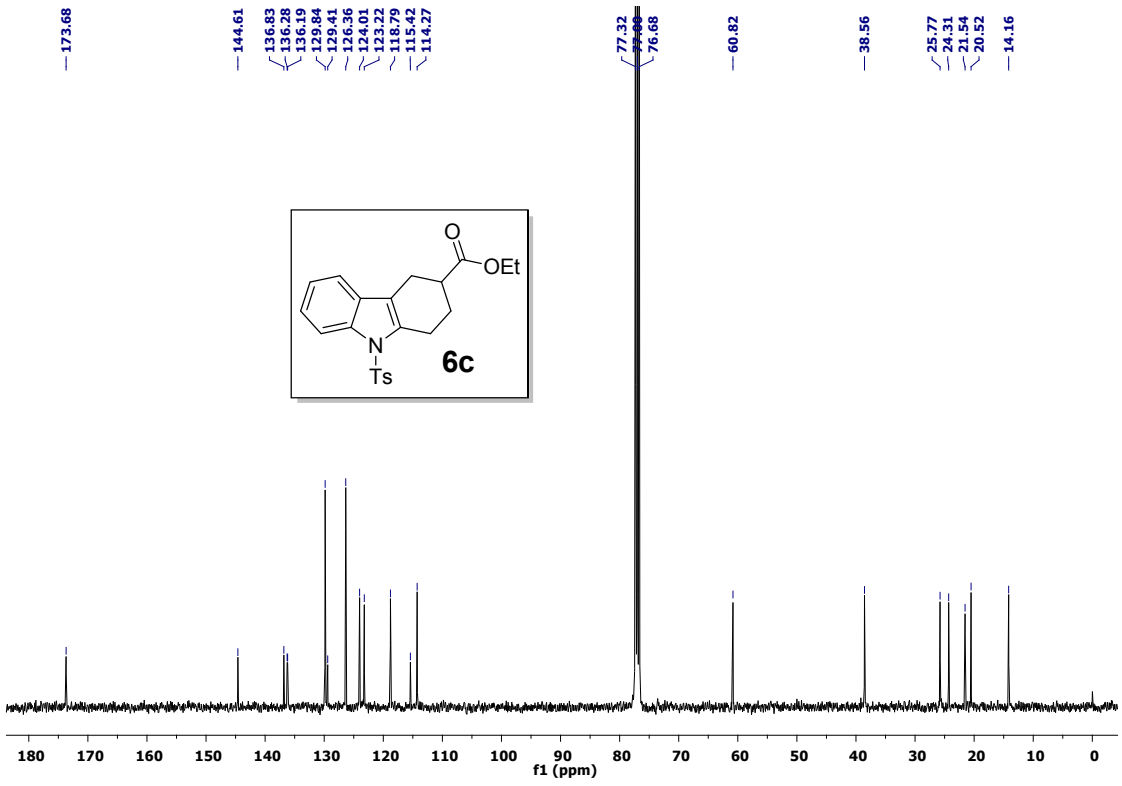
Copy of ^{1}H NMR and ^{13}C NMR spectra of **6b**



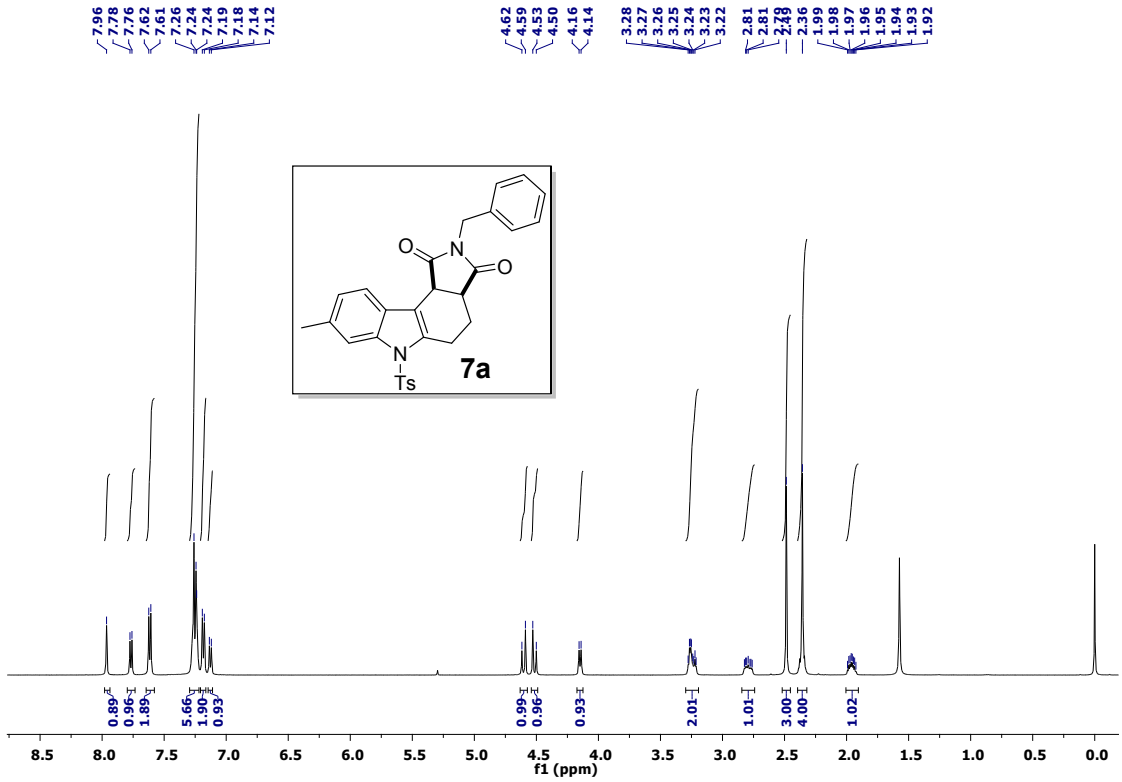


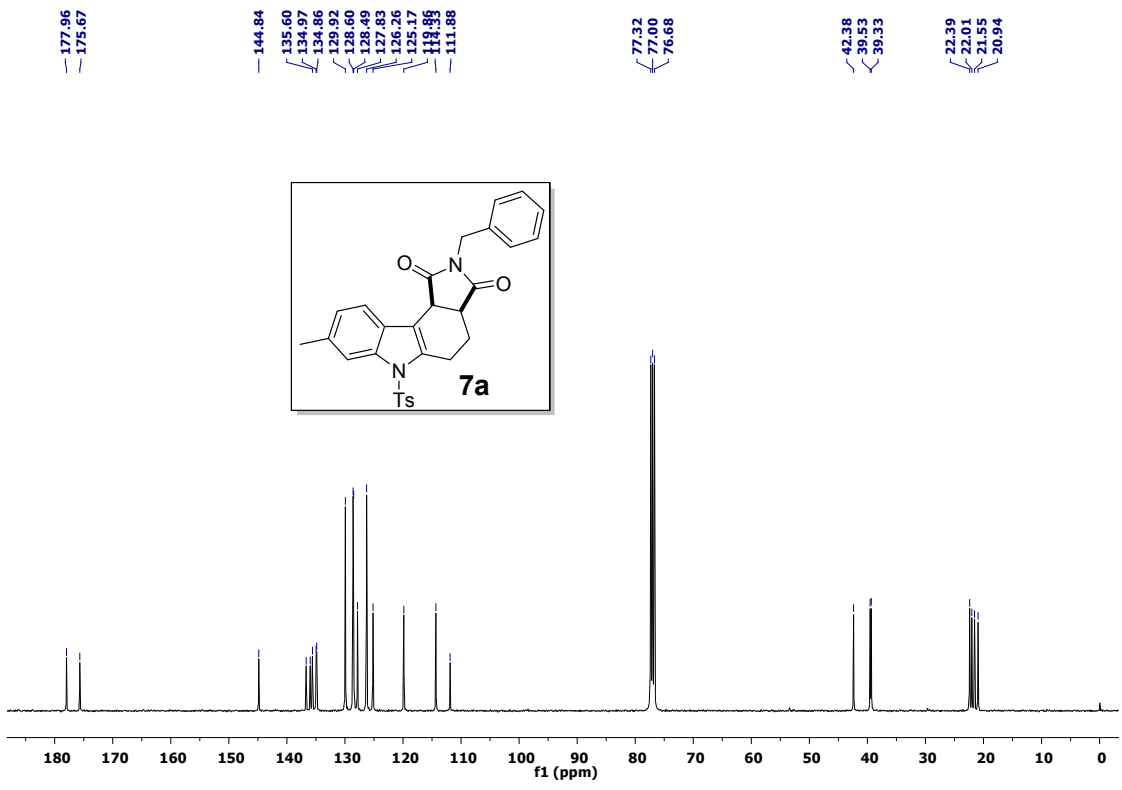
Copy of ^{1}H NMR and ^{13}C NMR spectra of **6c**



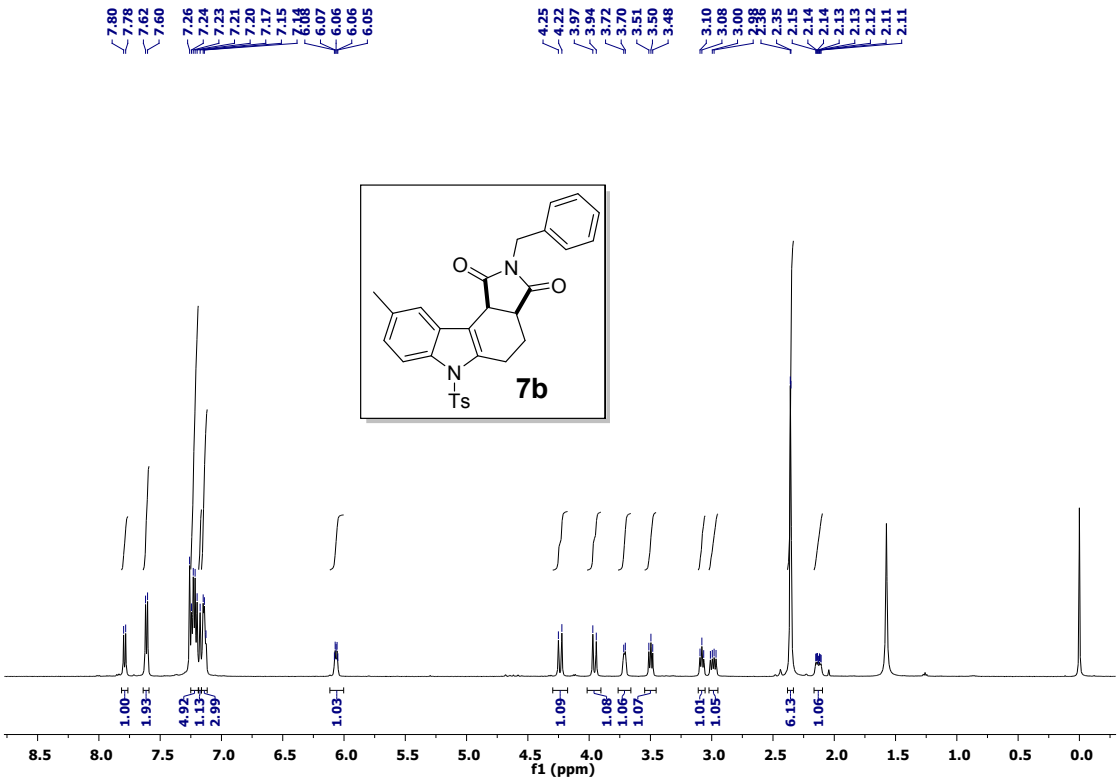


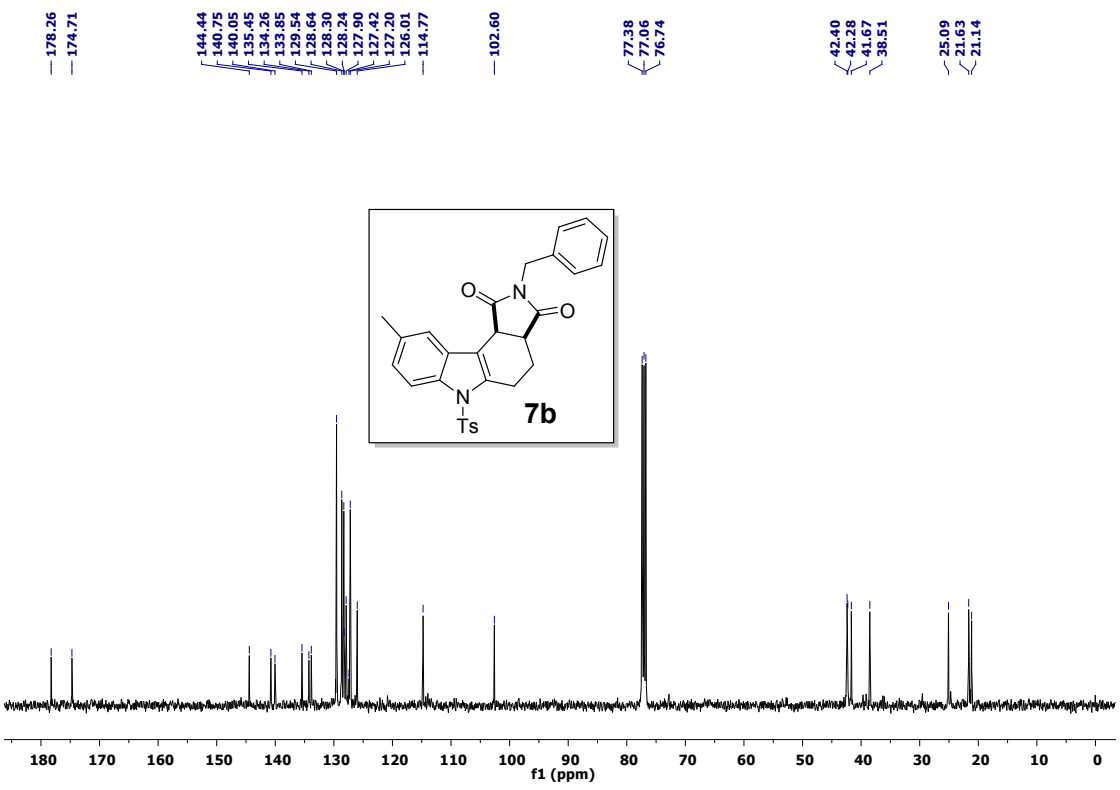
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7a**



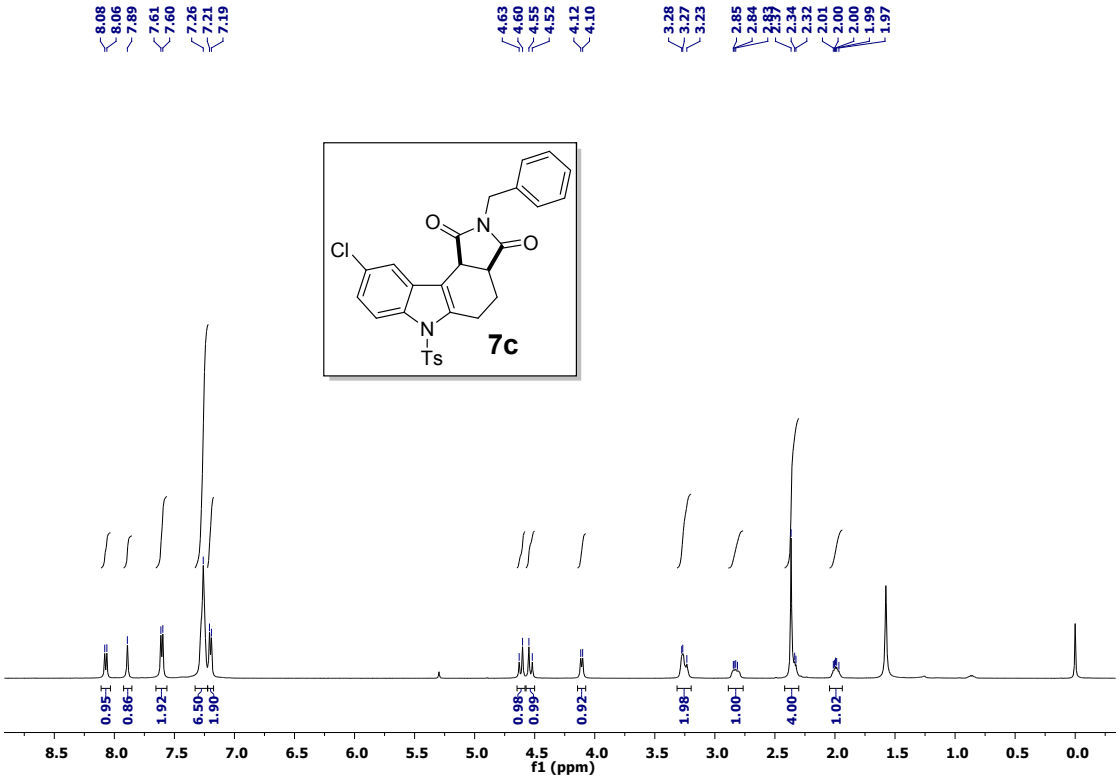


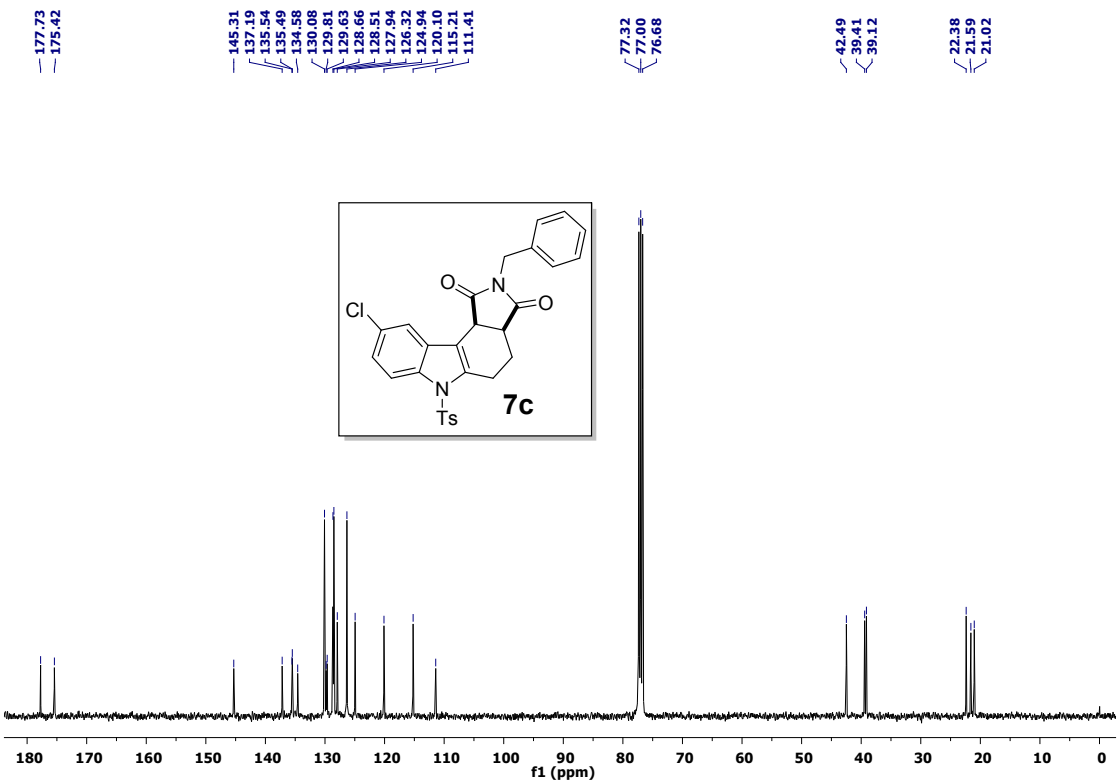
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7b**



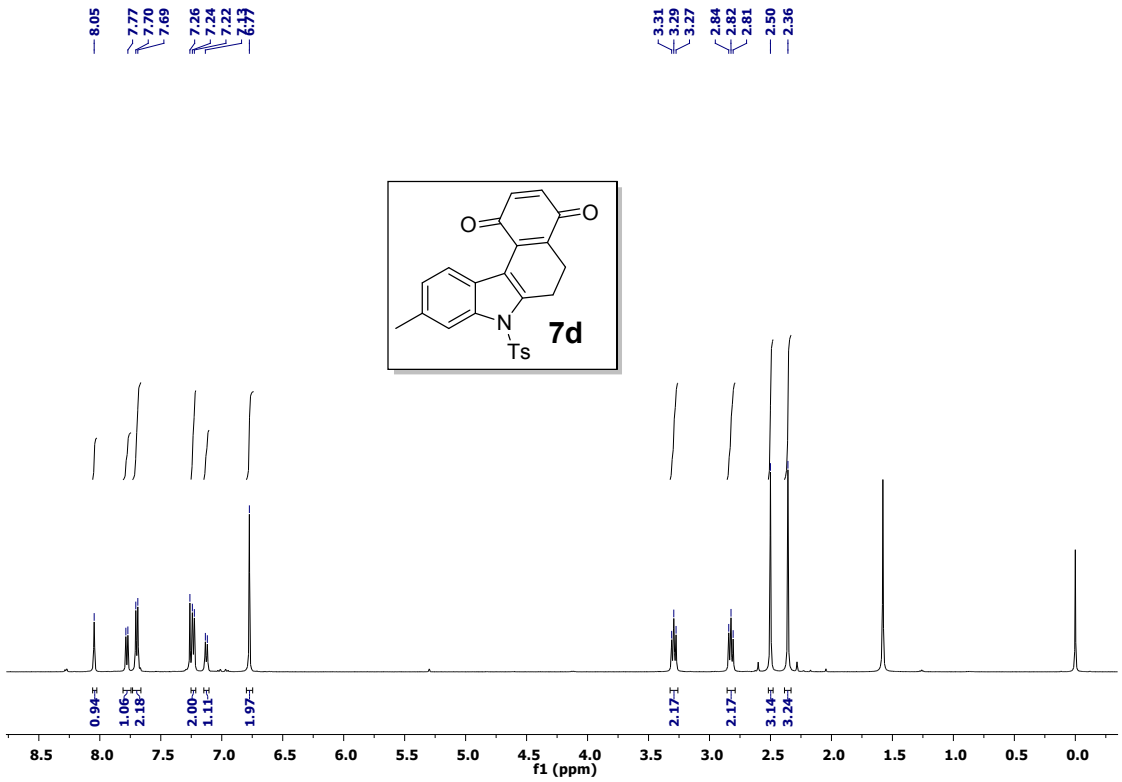


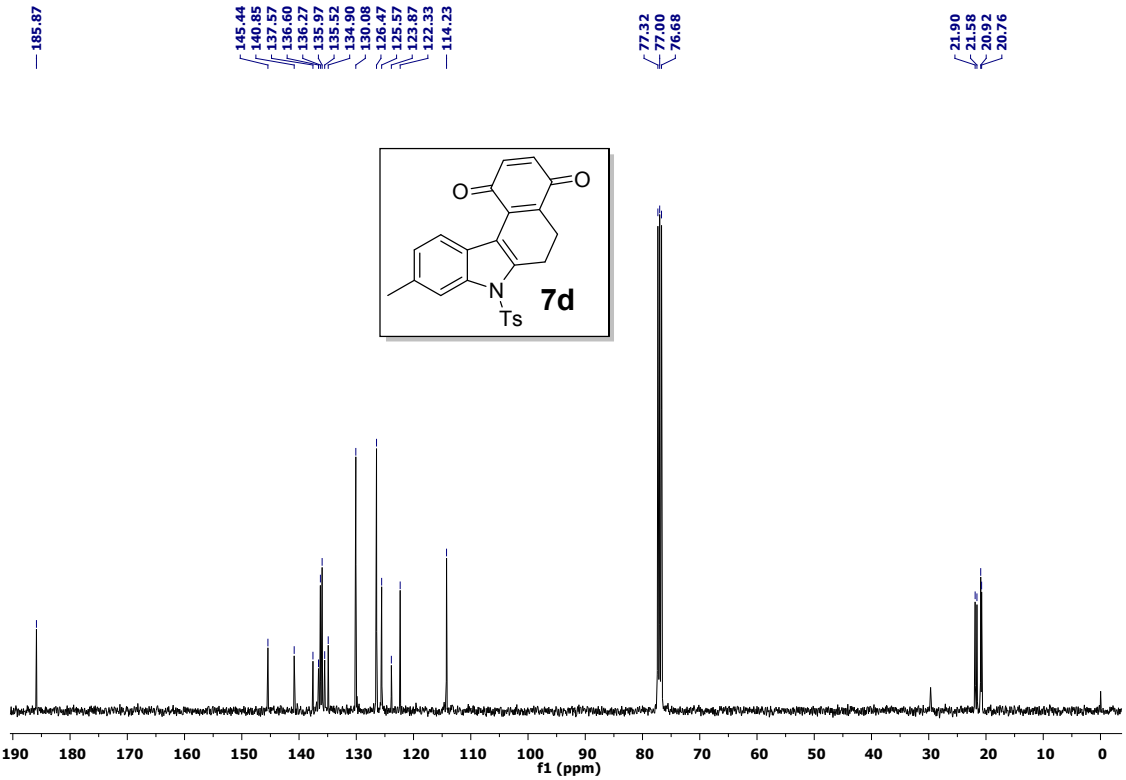
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7c**



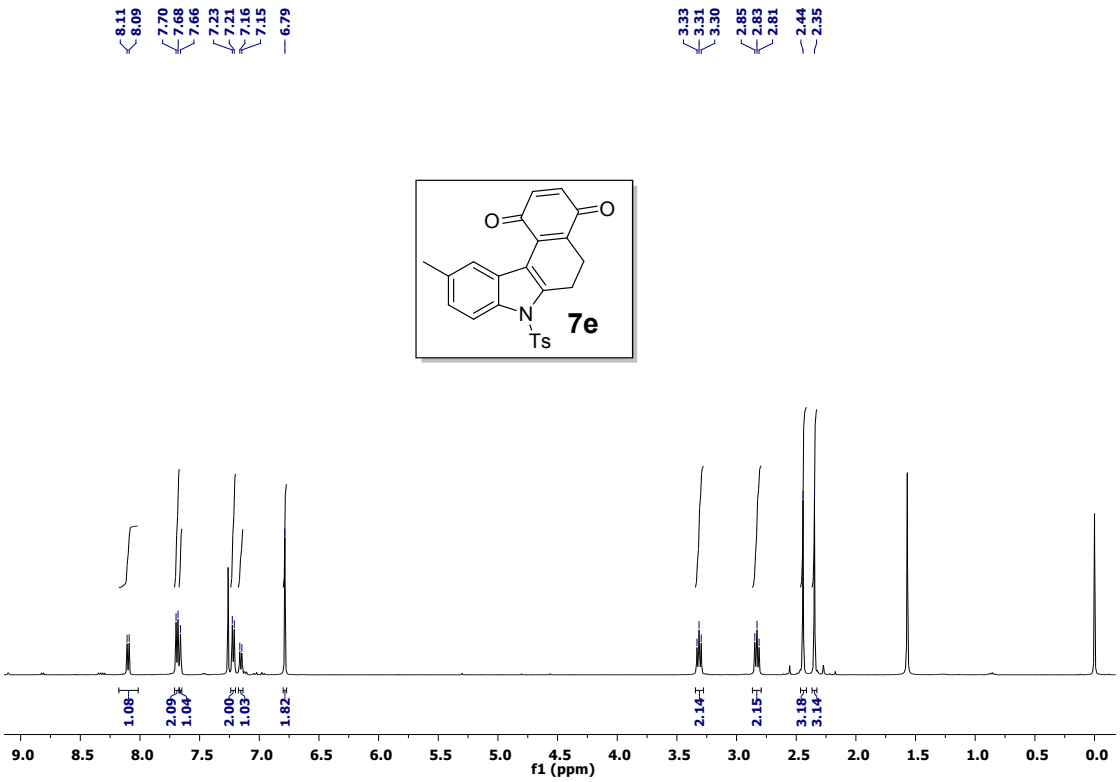


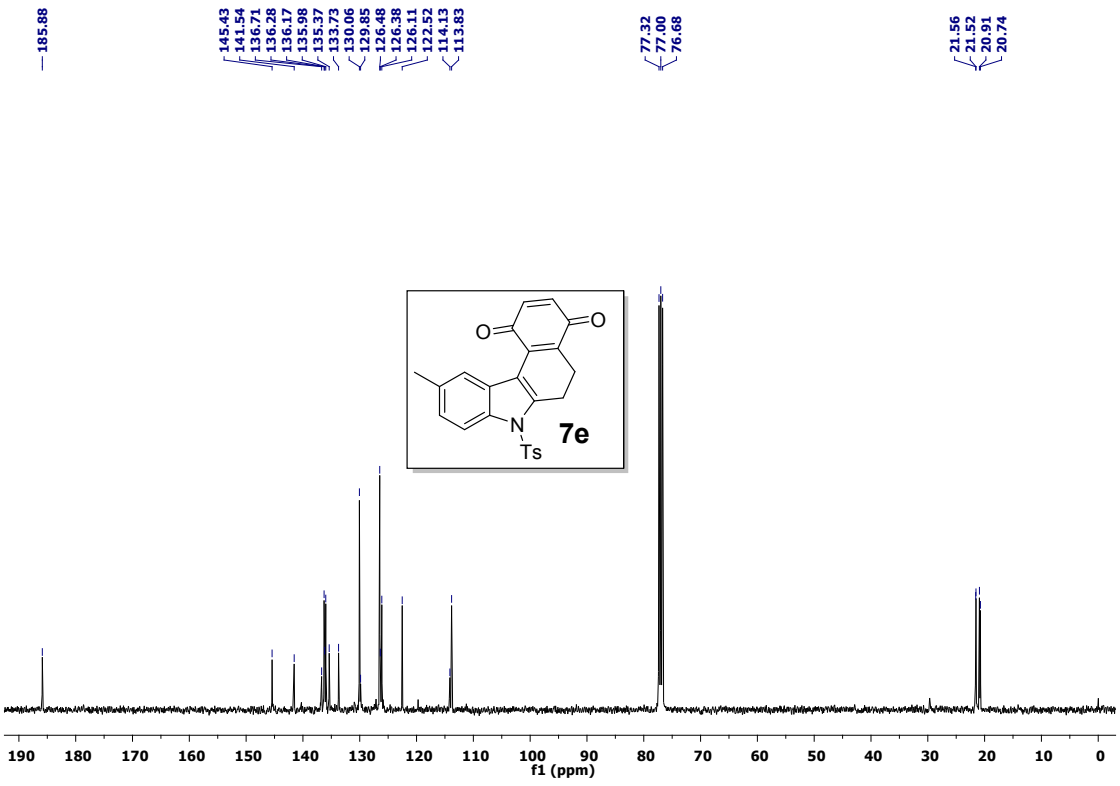
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7d**



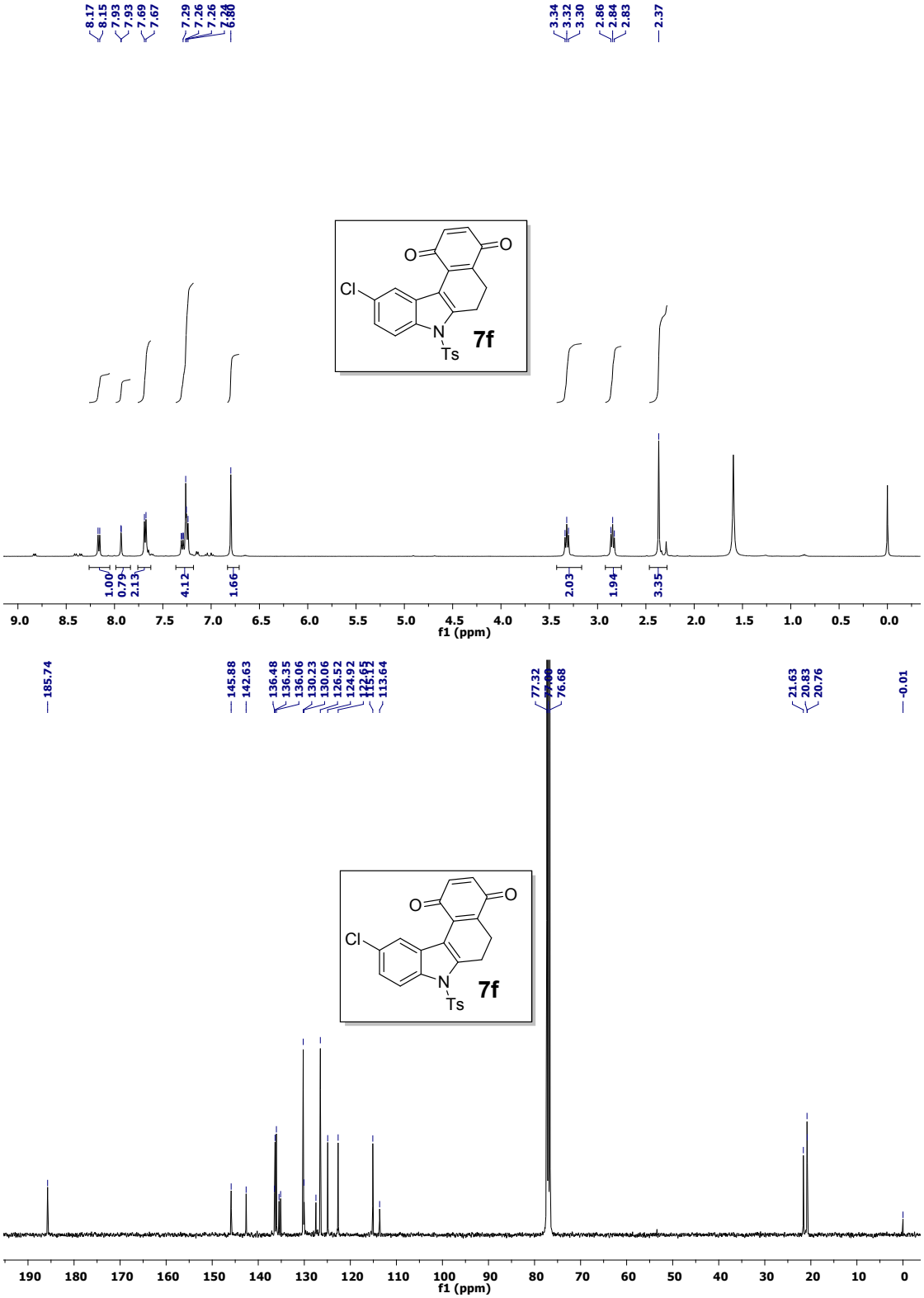


Copy of ^{1}H NMR and ^{13}C NMR spectra of **7e**

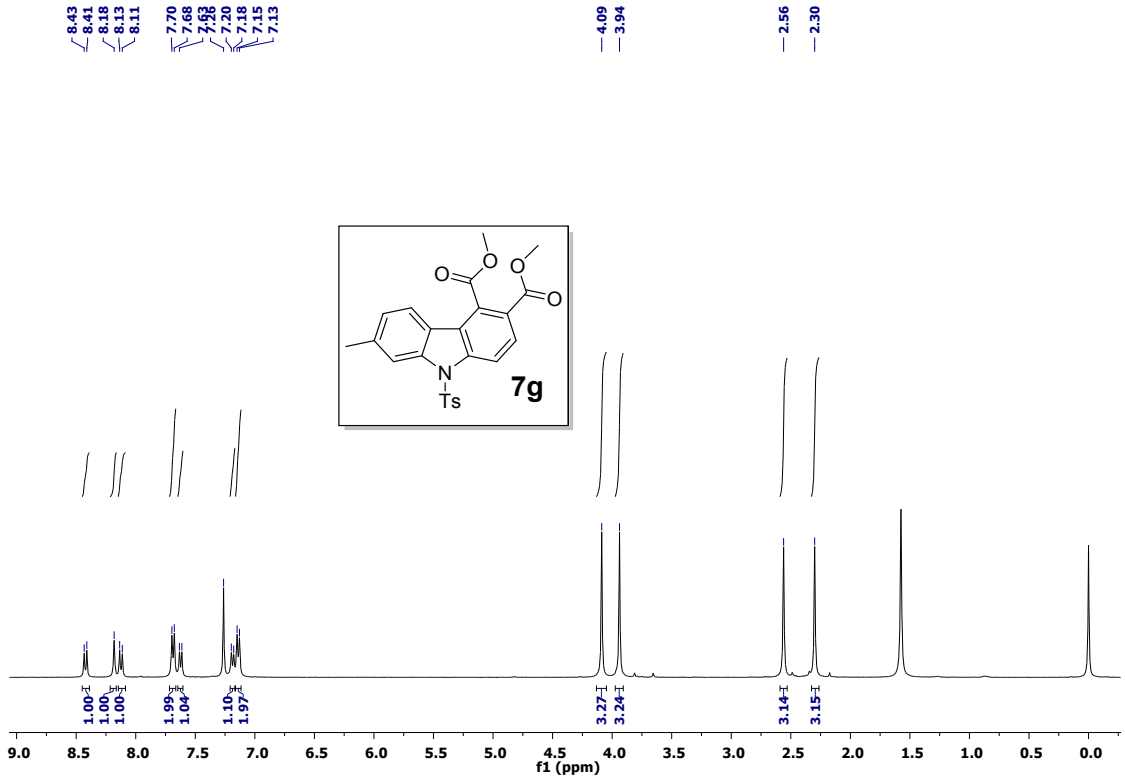


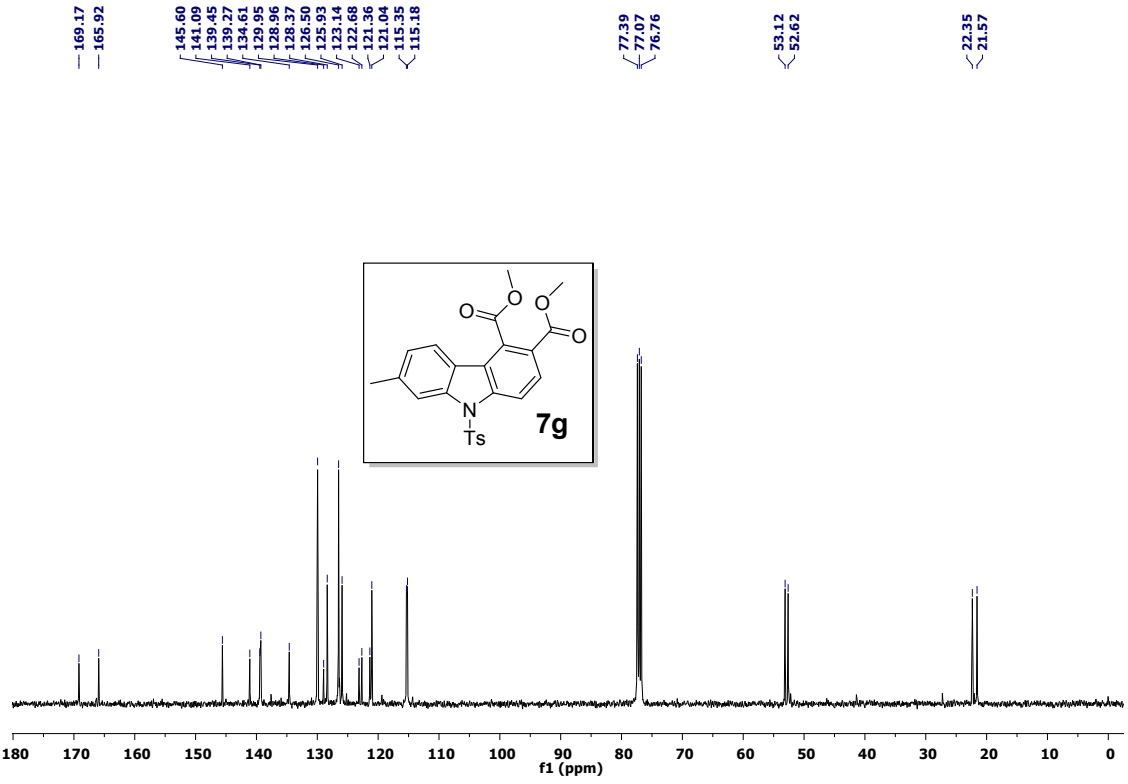


Copy of ^{1}H NMR and ^{13}C NMR spectra of **7f**

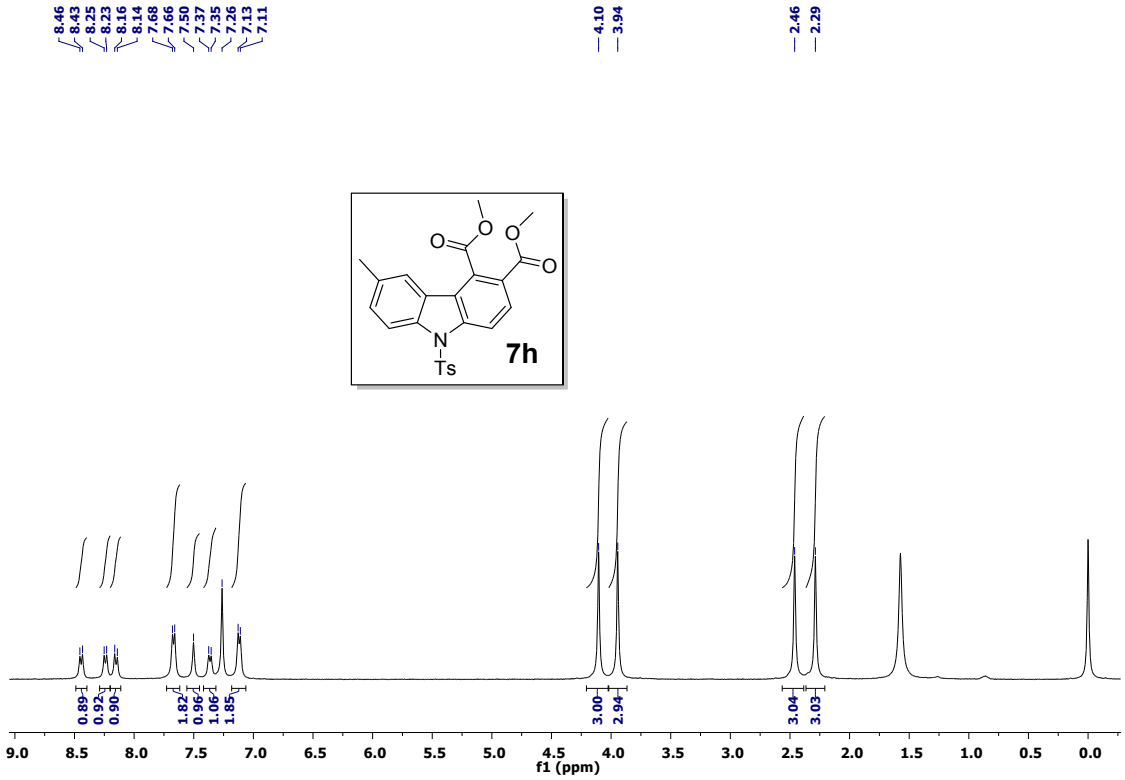


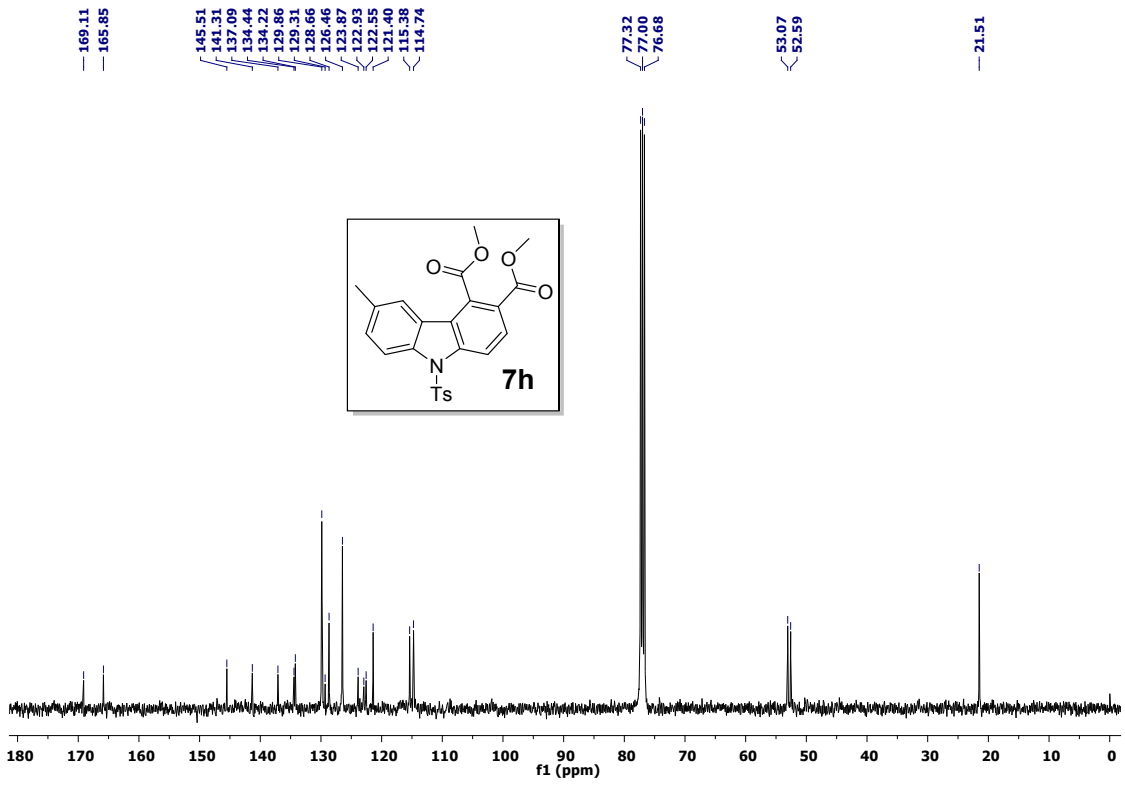
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7g**



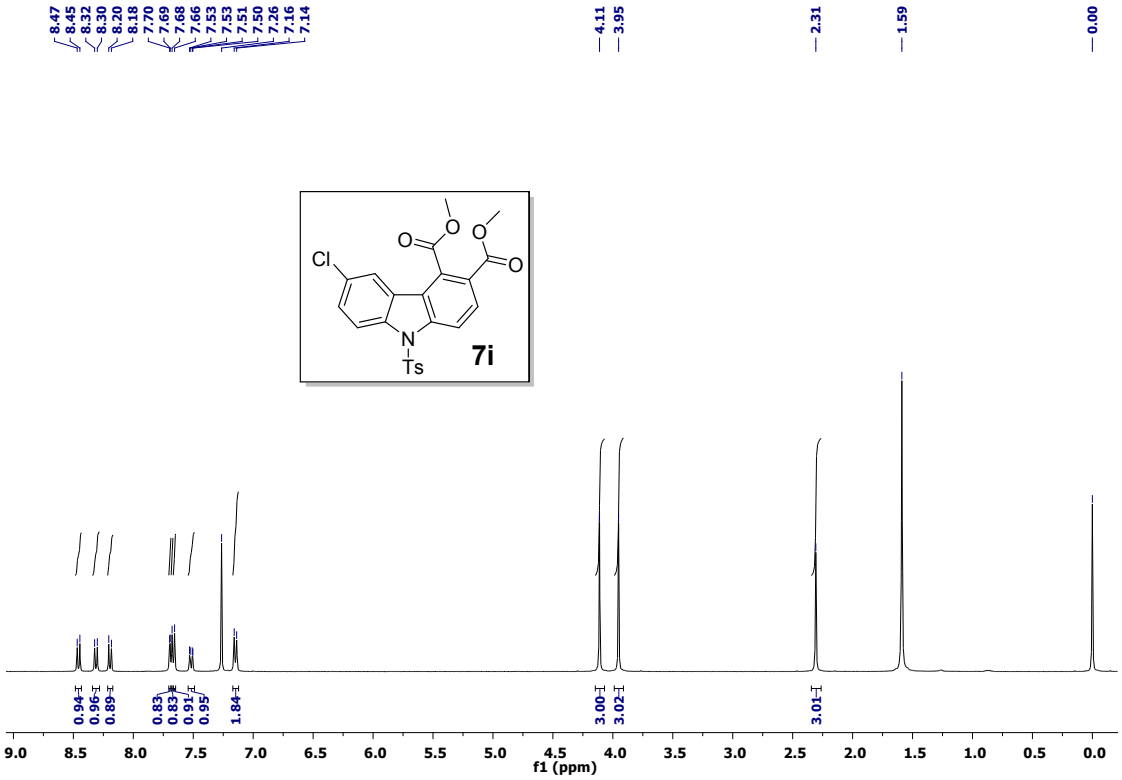


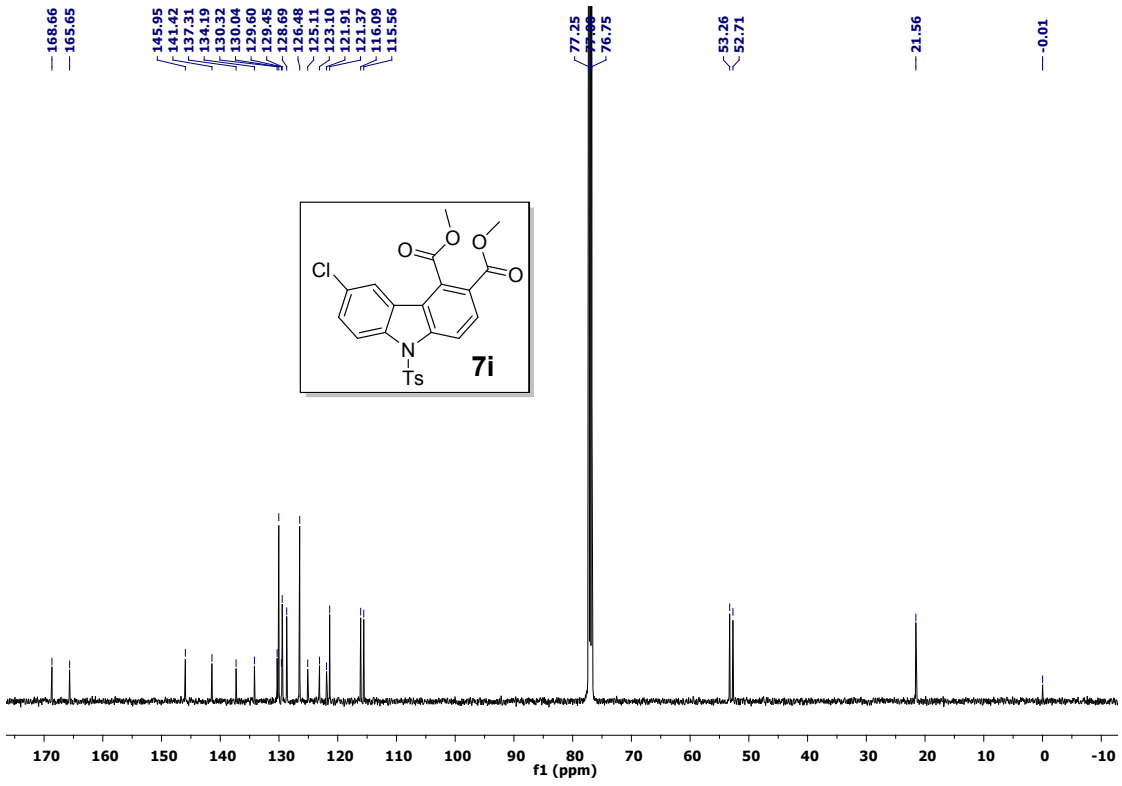
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7h**



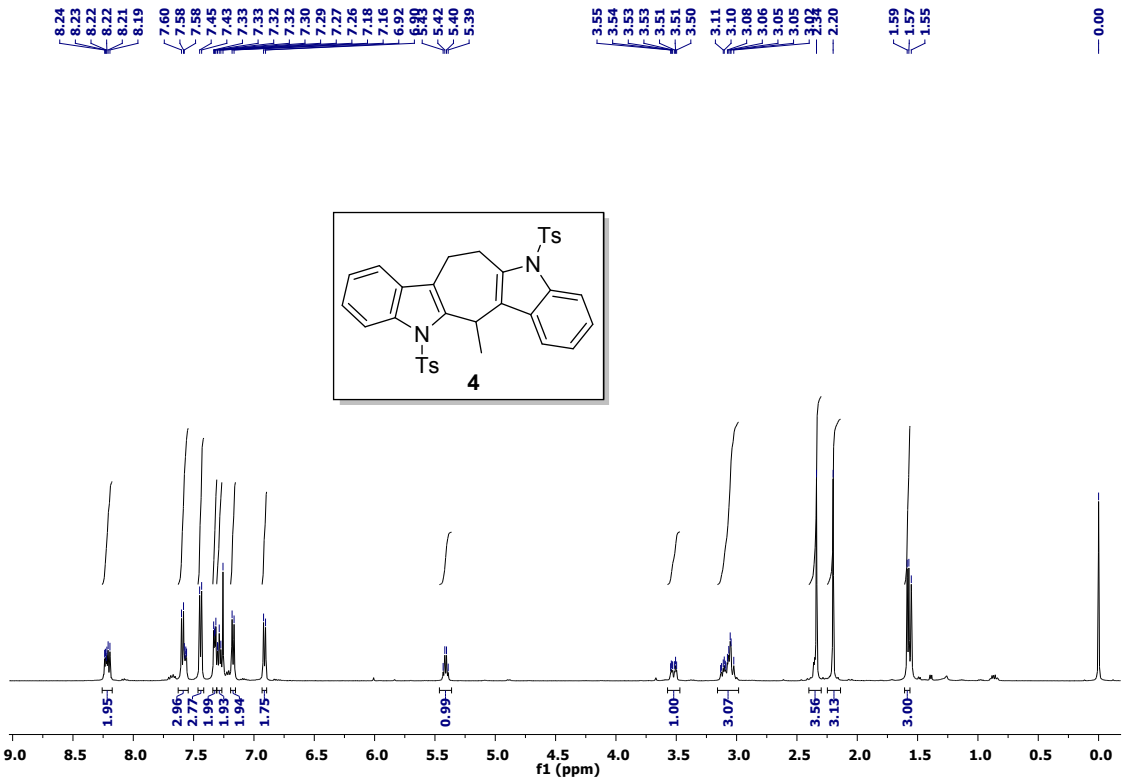


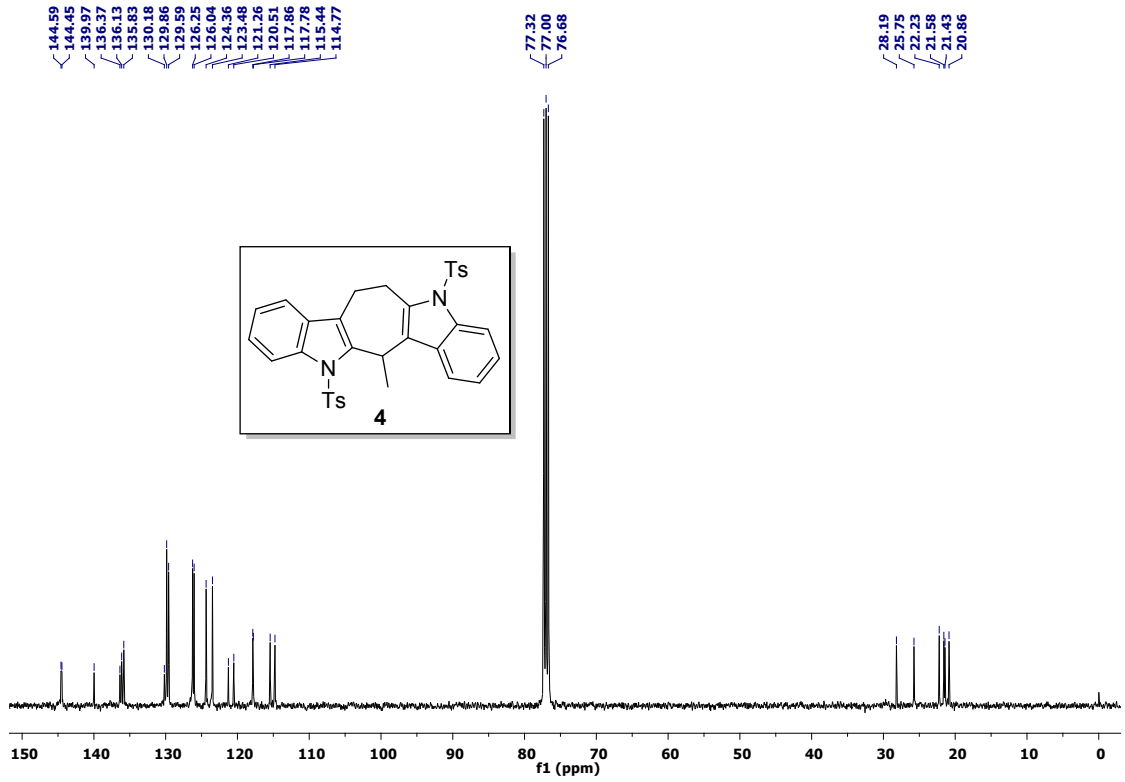
Copy of ^{1}H NMR and ^{13}C NMR spectra of **7i**



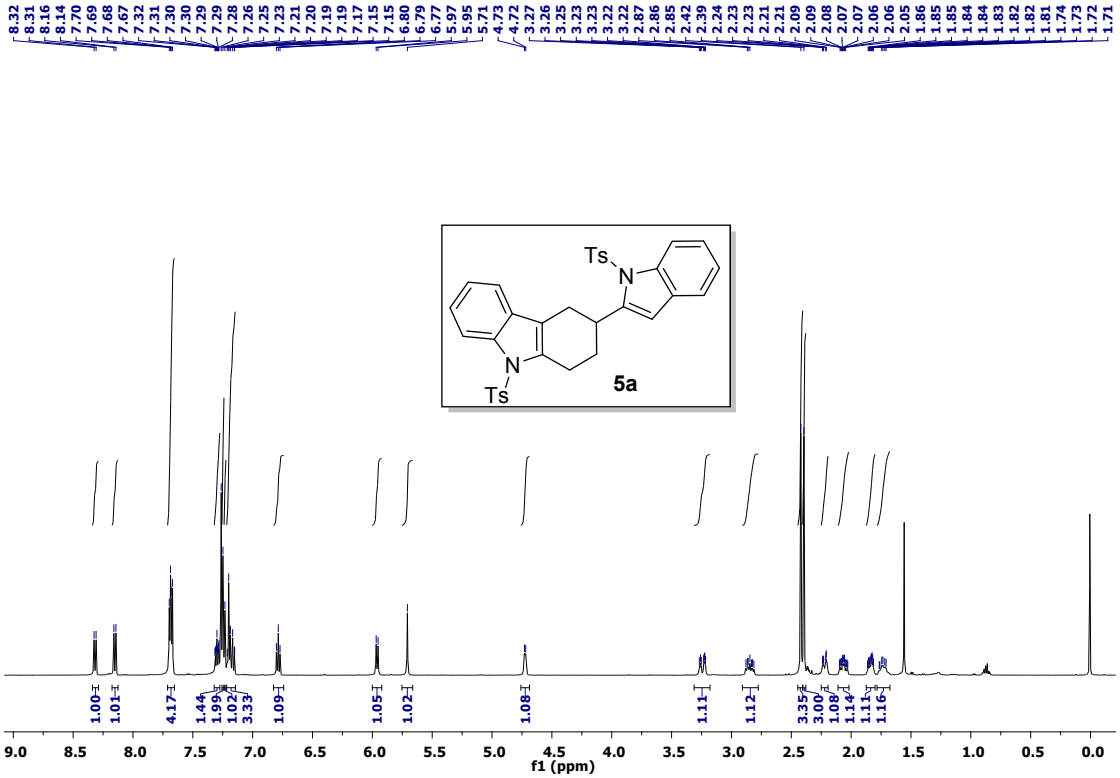


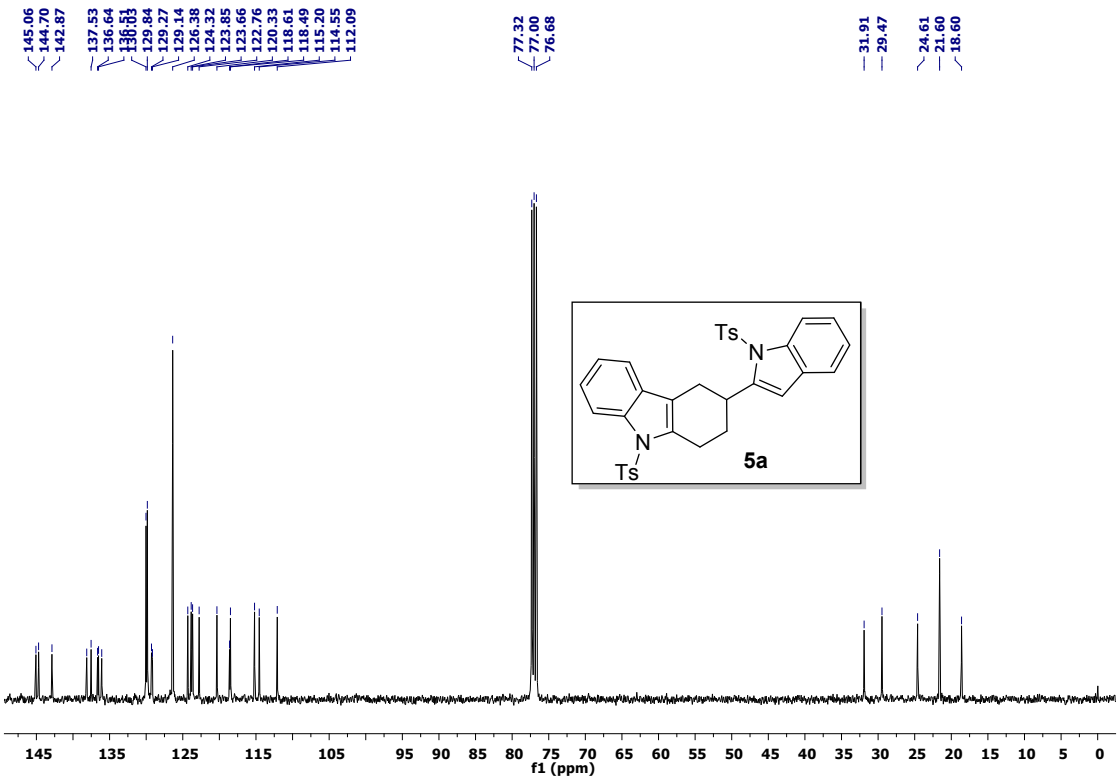
Copy of ^{1}H NMR and ^{13}C NMR spectra of **4**



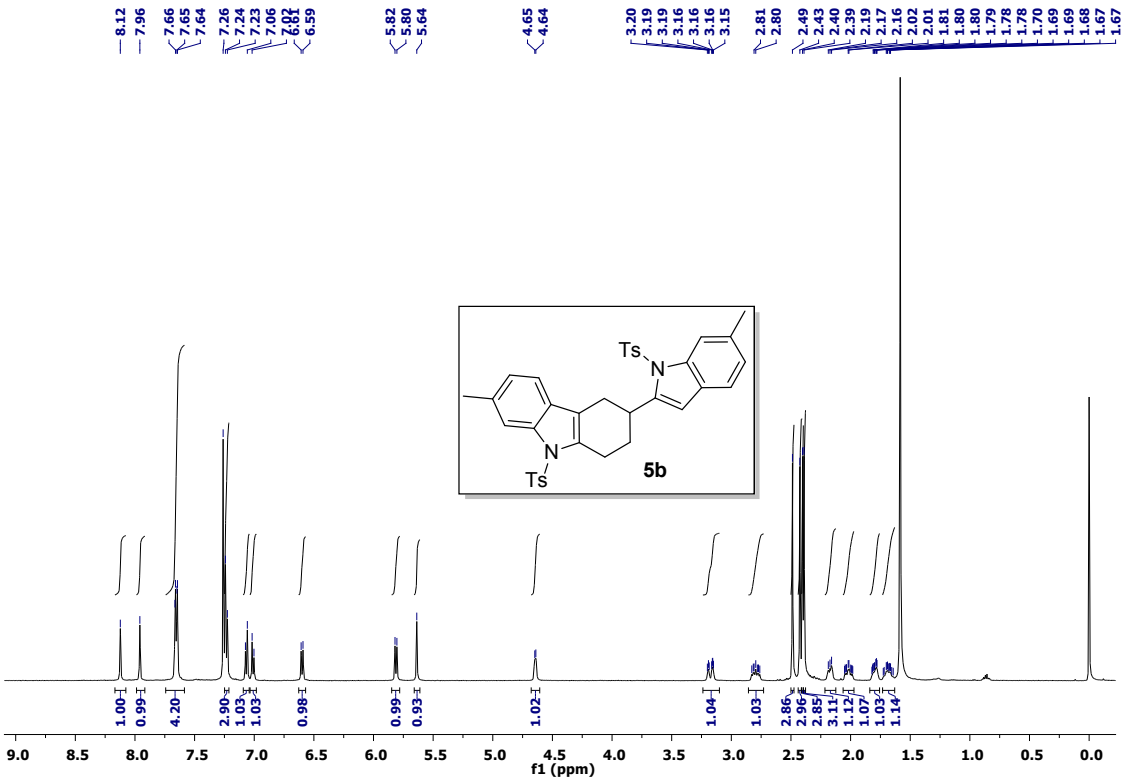


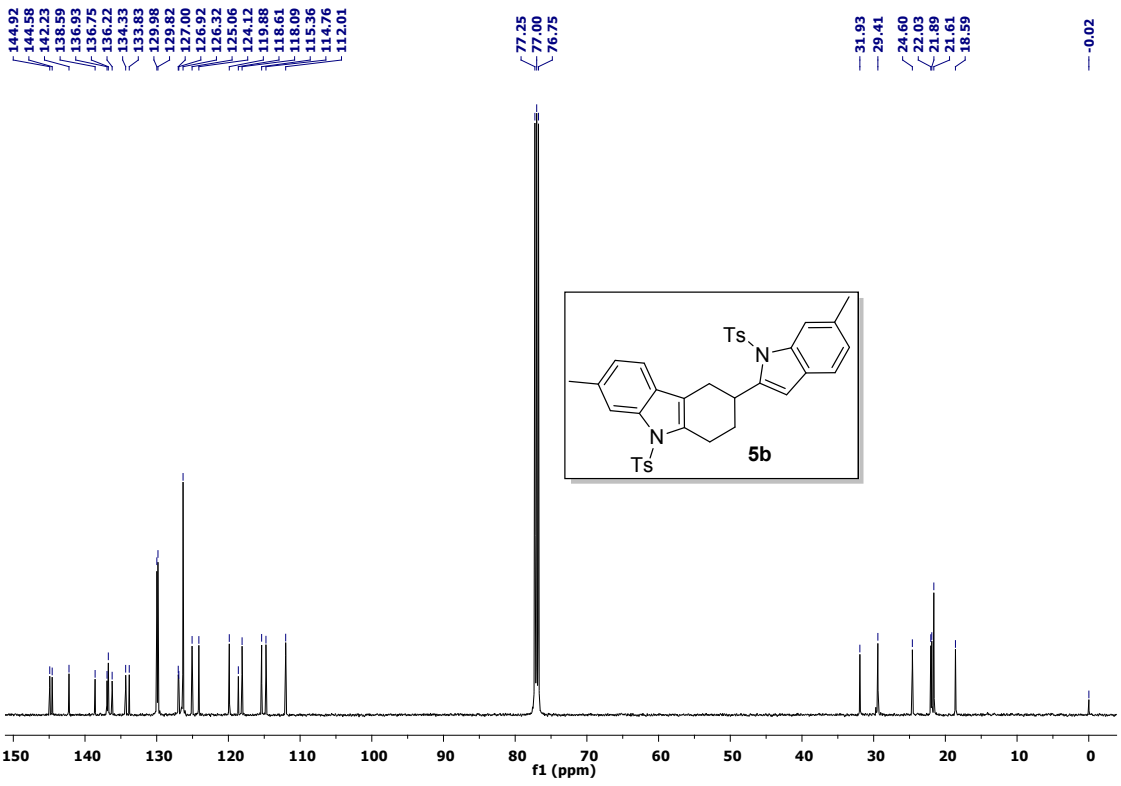
Copy of ^{1}H NMR and ^{13}C NMR spectra of **5a**



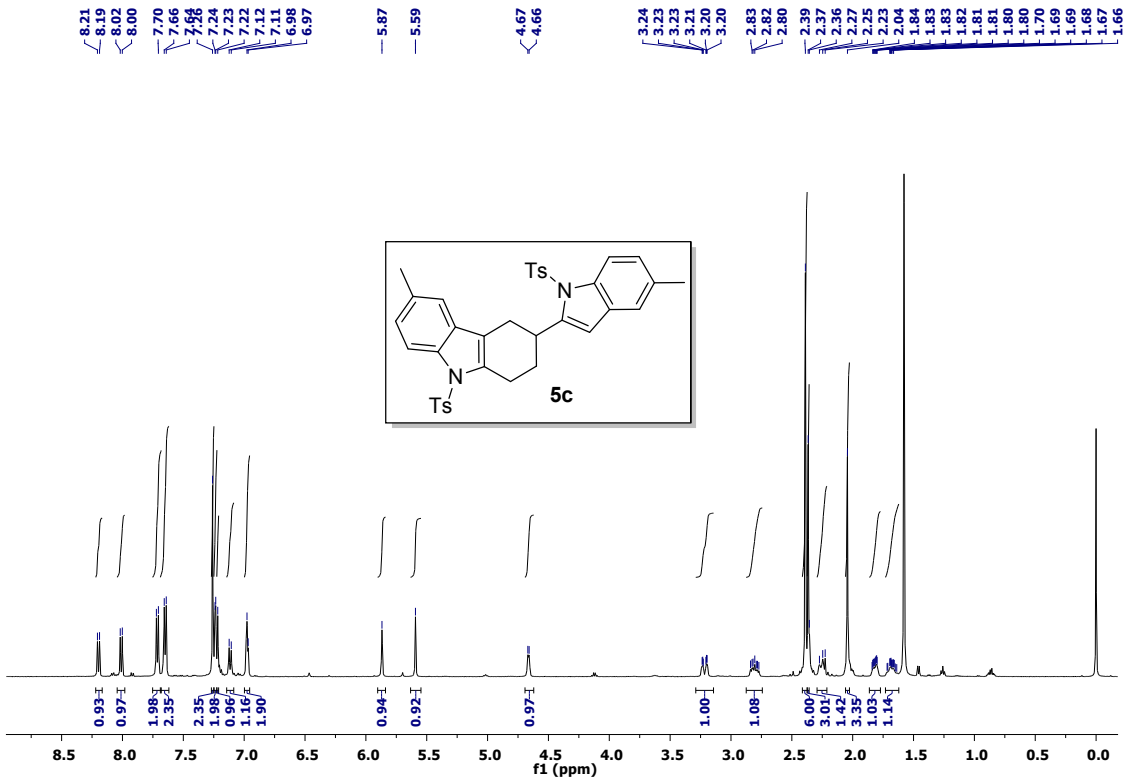


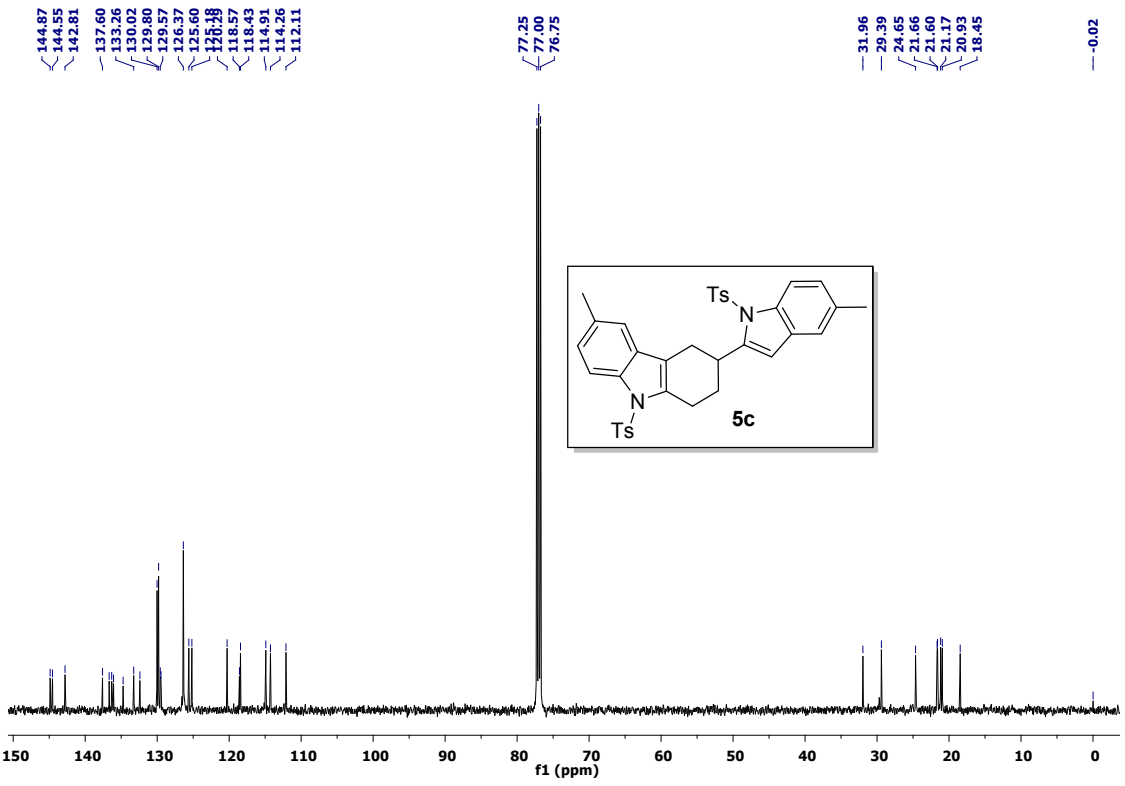
Copy of ^{1}H NMR and ^{13}C NMR spectra of **5b**



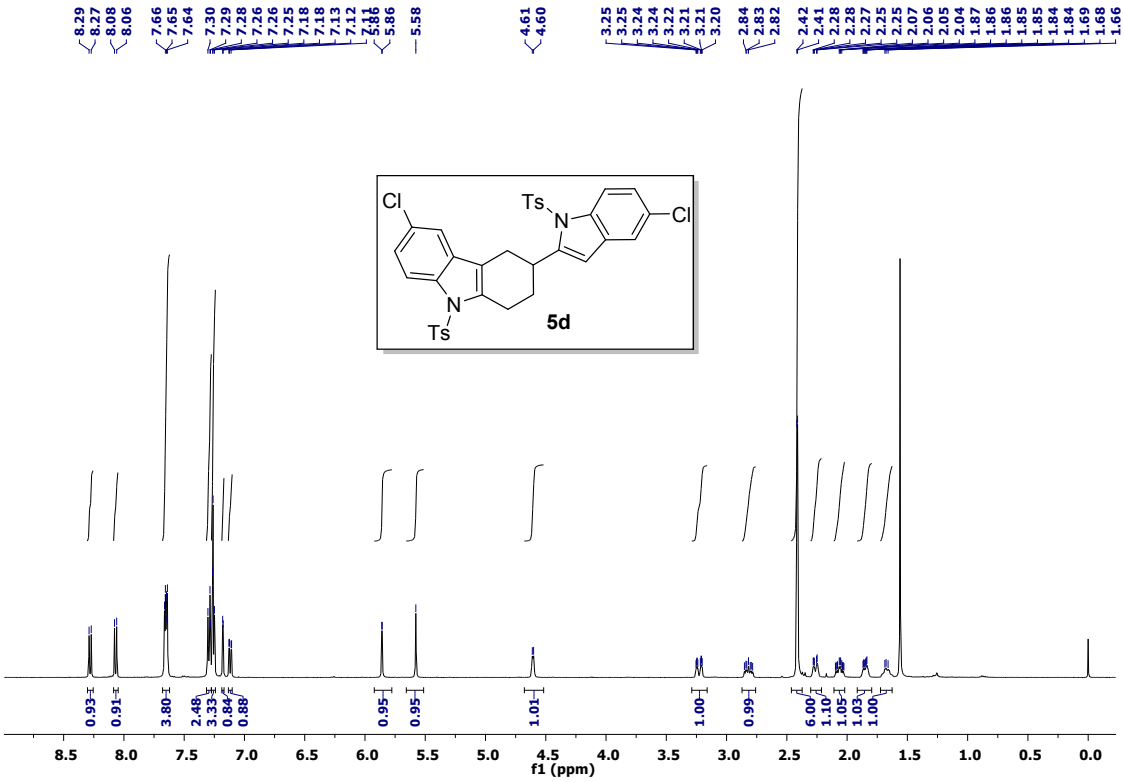


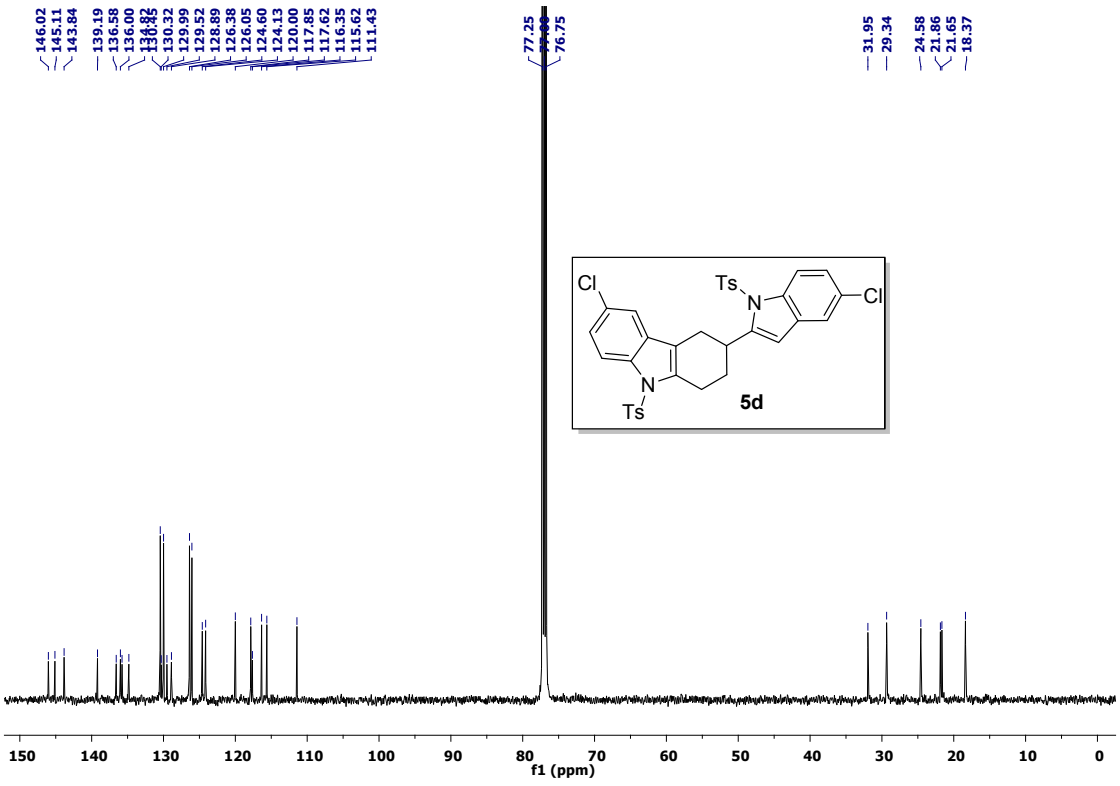
Copy of ^{1}H NMR and ^{13}C NMR spectra of **5c**



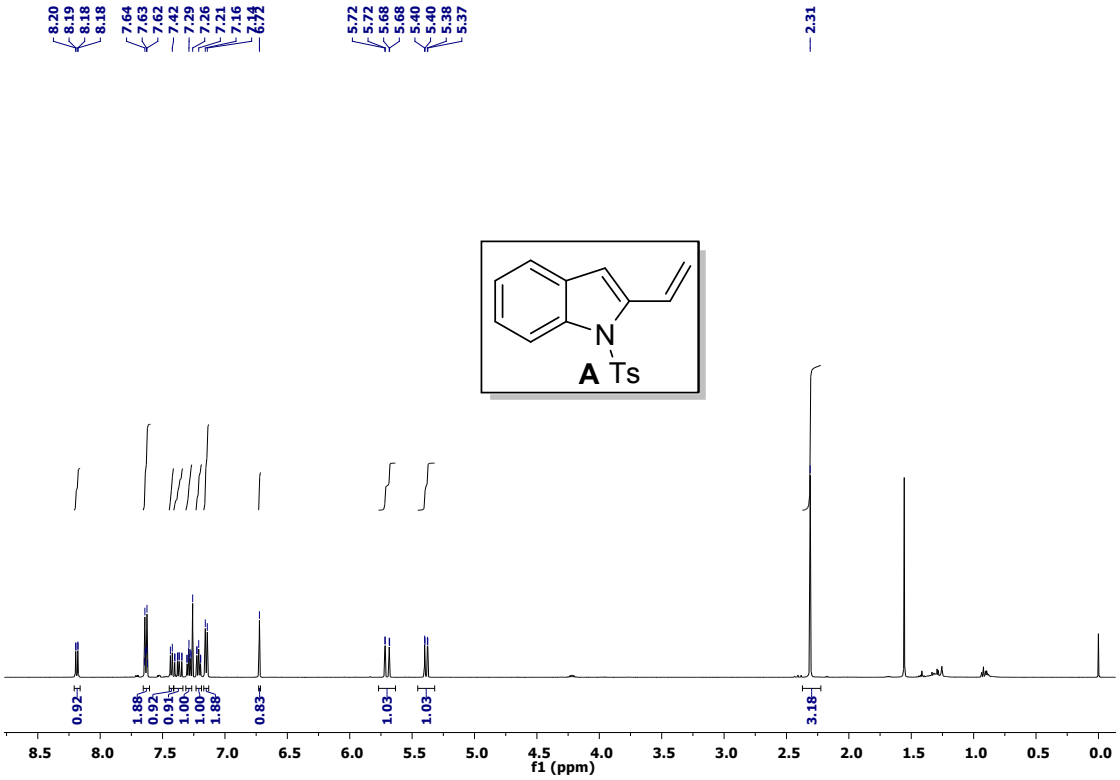


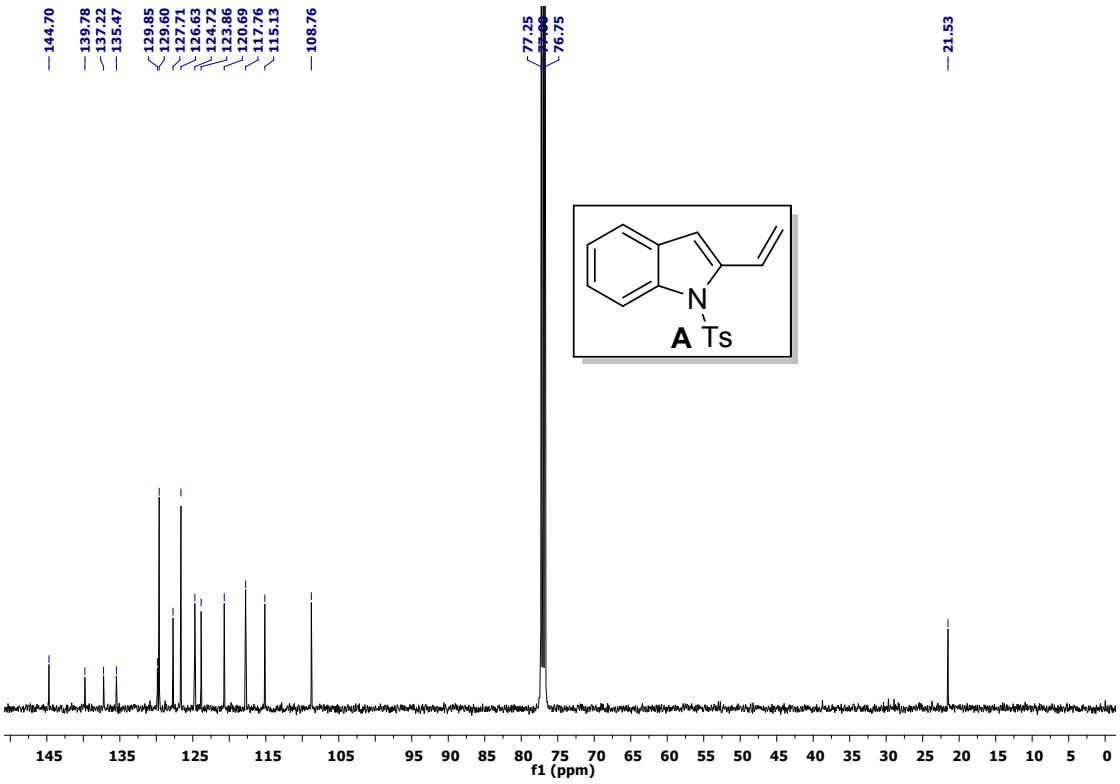
Copy of ^{1}H NMR and ^{13}C NMR spectra of **5d**



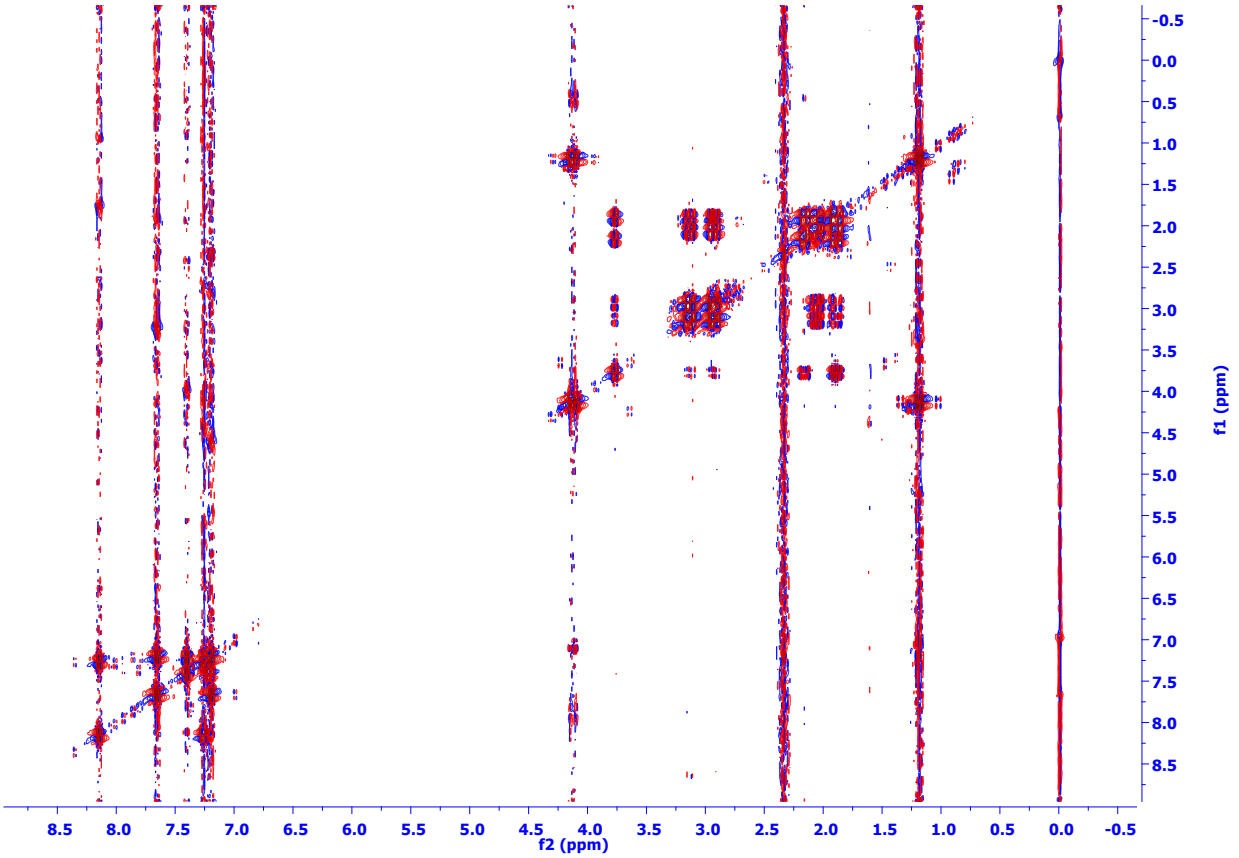


Copy of ^{1}H NMR and ^{13}C NMR spectra of **A**





5. 2D ^{1}H-^{1}H DQFCOSY spectrum of compound of 5c recorded at 500 MHz NMR spectrometer.



Expansion of 2D ^{1}H-^{1}H DQFCOSY spectrum of compound of 5c recorded at 500 MHz NMR spectrometer.