# Ligand-free Palladium-catalyzed Intramolecular Heck Reaction of Secondary Benzylic Bromides

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## Supporting information

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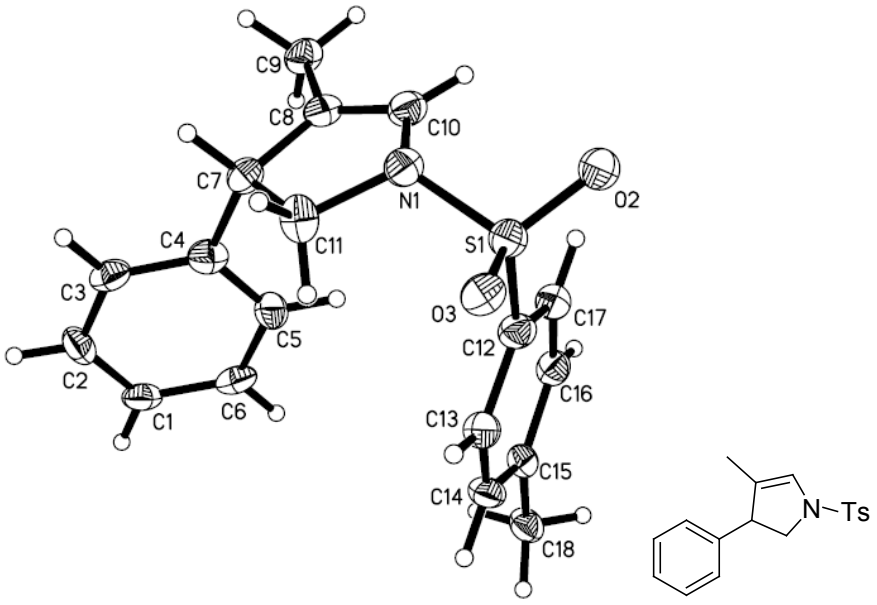
**1. General Information.** Solvents were dried and distilled prior to use. Melting points were uncorrected. IR spectra were collected on Bruker Vector 22 in KBr pellets. $^{1}H$ and $^{13}C$ NMR (TMS used as internal standard) spectra were collected in $CDCl_3$ with a Bruker ARX 300 spectrometer. High resolution mass spectra for all the new compounds were done by a Micromass Q-Tof instrument (ESI). Thin layer chromatography was carried out on Silica Gel 60 F-254 TLC plates. 20 cm × 20 cm Gel 60 F-254 TLC plates were used for Isolation. Flash chromatography was performed on silica gel 60 (200-300 mesh).

**2. Typical procedure for the intramolecular Heck reaction.** Into a dry vial was added substrate **1** (0.5 mmol), freshly dried $K_2CO_3$ (138 mg, 1 mmol), $Pd(OAc)_2$ (1.1 mg, 1 mol%) and freshly distilled DMF (1.0 mL) under a nitrogen atmosphere. The mixture was stirred at 60 $^{o}C$ for 24 h. After cooling, the reaction was quenched with water (10 mL). The aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried with anhydrous $Na_2SO_4$, concentrated and purified by column (EtOAc/petroleum ether, 1:20 v/v) to give the product.

**3. The ORTEP diagram drawing of 2a.**



**4. Spectral data for 2, 3, 4.**

**4-methyl-3-phenyl-1-tosyl-2,3-dihydro-*1*H-pyrrole** (**2a**) White solid, m.p. 64–66 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.67–7.71 (m, 2H), 7.34–7.38 (m, 2H), 7.14–7.17 (m, 3H), 6.74–6.77 (m, 2H), 6.26–6.27 (m, 1H), 3.94 (t, $J$ = 10.7 Hz, 1H), 3.71–3.77 (m, 1H), 3.38 (dd, $J$ = 6.1, 10.8 Hz, 1H ), 2.48 (s, 3H), 1.43 (t, $J$ = 1.3 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 143.52, 141.44, 131.99, 129.42, 128.24, 127.58, 126.98, 126.61, 125.26, 124.72, 55.68, 51.71, 21.17, 11.50 ppm; IR (KBr): $\upsilon$ = 3094, 2947, 1662, 1597, 1493 cm$^{-1}$; MS (HRMS/[M+Na]$^{+}$) Calcd for $C_{18}H_{19}NO_2SNa$: 336.1029, Found: 336.1019.

**3-(4-chlorophenyl)-4-methyl-1-tosyl-2,3-dihydro-*1*H-pyrrole** (**2b**) Colorless oil; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.67–7.69 (m, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.10–7.15 (m, 2H), 6.67–6.72 (m, 2H), 6.25–6.26 (m, 1H), 3.92 (t, $J$ = 11.0 Hz, 1H), 3.74–3.68 (m, 1H), 3.34 (dd, $J$ = 6.0, 10.9 Hz, 1H), 2.49 (s, 3H), 1.42 (t, $J$ = 1.2 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 143.93, 140.36, 132.82, 132.46, 129.77, 128.80, 128.72, 127.98, 126.04, 124.45, 55.88, 51.57, 21.62, 11.85 ppm; IR (KBr): $\upsilon$ = 2921, 1489 cm$^{-1}$; MS (HRMS/[M+Na]$^{+}$) Calcd for $C_{18}H_{18}ClNO_2SNa$: 370.0639, Found: 370.0629.

**3-(3-chlorophenyl)-4-methyl-1-tosyl-2,3-dihydro-*1*H-pyrrole** (**2c**) White solid, m.p. 86–88 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.68 (d, $J$ = 8.3 Hz, 2H), 7.37 (d, $J$ = 8.0 Hz, 2H), 7.07–7.17 (m, 2H), 6.70–6.72 (m, 1H), 6.61–6.62 (m, 1 H), 6.26–6.27 (m, 1H), 3.95 (t, $J$ = 11.0 Hz, 1H), 3.73-3.69 (m, 1H), 3.33 (dd, $J$ = 6.0,

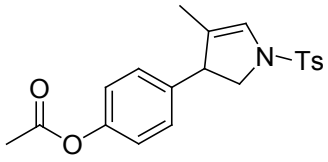
11.0 Hz, 1H), 2.48 (s, 3H), 1.43 (t, $J$ = 1.2 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 144.18, 144.00, 134.62, 132.14, 129.89, 129.85, 127.94, 127.35, 127.28, 126.25, 125.83, 124.17, 55.75, 51.88, 21.75, 11.92 ppm; IR (KBr): $\upsilon$ = 2979, 1650, 1476 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{18}H_{18}ClNO_2SNa$: 370.0639, Found: 370.0646.

**3-(2-chlorophenyl)-4-methyl-1-tosyl-2,3-dihydro-*1*H-pyrrole (2d)**

White solid, m.p. 122–124 $^o$C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.66 (d, $J$ = 8.3 Hz, 2H), 7.26–7.32 (m, 3H), 7.11–713 (m, 1H), 7.01–7.08 (m, 1H), 6.63–6.64 (m, 1H), 6.31–6.32 (m, 1H), 4.26–4.31 (m, 1H), 3.92 (t, $J$ = 10.8 Hz, 1H), 3.38 (dd, $J$ = 5.2, 11.0 Hz, 1H), 2.46 (s, 3H), 1.52 (t, $J$ = 1.2 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 143.83, 139.11, 133.56, 132.57, 129.71, 129.41, 128.20, 128.08, 127.90, 127.24, 126.86, 123.84, 55.25, 47.77, 21.61, 12.09 ppm; IR (KBr): $\upsilon$ = 2975, 1469 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{18}H_{18}ClNO_2SNa$: 370.0639, Found: 370.0650.

**4-methyl-3-p-tolyl-1-tosyl-2,3-dihydro-*1*H-pyrrole (2e)**

White solid, m.p. 46–48 $^o$C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69 (d, $J$ = 8.3 Hz, 2H), 7.36 (d, $J$ = 8.0 Hz, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 6.64 (d, $J$ = 7.9 Hz, 2H), 6.23–6.24 (m, 1H), 3.92 (t, $J$ = 10.7 Hz, 1H), 3.68–3.74 (m, 1H), 3.34 (dd, $J$ = 6.2, 10.8 Hz, 1H), 2.49 (s, 3H), 2.28 (s, 3H), 1.43–1.41 (m, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 143.76, 138.79, 136.64, 132.44, 129.71, 129.31, 128.02, 127.31, 125.48, 125.16, 56.10, 51.83, 21.66, 21.06, 11.92 ppm; IR (KBr): $\upsilon$ = 2925, 2855, 1463 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{19}H_{21}NO_2SNa$: 350.1185, Found: 350.1194.




**4-(4-methyl-1-tosyl-2,3-dihydro-1H-pyrrol-3-yl)phenyl acetate (2f)** Colorless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69-7.65 (m, 2H), 7.34 (d, $J$ = 7.7 Hz, 2H), 6.90-6.85 (m, 2H), 6.77-6.73 (m, 2H), 6.25-6.24 (t, $J$ = 1.6 Hz, 1H), 3.91 (t, $J$ = 10.8 Hz, 1H), 3.77-3.71 (m, 1H), 3.34 (dd, $J$ = 6.0, 10.8 Hz, 1H), 2.46 (s, 3H), 2.27 (s, 3H), 1.42 (t, $J$ = 1.4 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 169.42, 149.60, 143.90, 139.29, 132.38, 129.79, 128.36, 127.98, 125.85, 124.75, 121.71, 55.96, 51.60, 21.61, 21.14, 11.94 ppm; IR (KBr): $\upsilon$ = 2923, 1758, 1597, 1503 cm$^{-1}$; MS (HRMS/[M+Na]$^{+}$) Calcd for $C_{20}H_{21}NO_4SNa$: 394.1084, Found: 394.1080.

**3-(4-tert-butylphenyl)-4-methyl-1-tosyl-2,3-dihydro-1H-pyrrole (2g)** White solid, m.p. 104-106 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.73-7.68 (m, 2H), 7.36 (d, $J$ = 7.9 Hz, 2H), 7.20-7.16 (m, 2H), 6.71-6.66 (m, 2H), 6.26-6.25 (m, 1H), 3.93 (t, $J$ = 10.6 Hz, 1H), 3.76-3.70 (m, 1H), 3.38 (dd, $J$ = 6.2, 10.7 Hz, 1H), 2.50 (s, 3H), 1.44 (t, $J$ = 1.4 Hz, 3H), 1.29 (s, 9H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 149.85, 143.75, 138.66, 132.56, 129.77, 128.04, 127.05, 125.49, 125.46, 125.26, 56.05, 51.74, 34.41, 31.36, 21.66, 12.03 ppm; IR (KBr): $\upsilon$ = 2960, 2868, 1596, 1509 cm$^{-1}$; MS (HRMS/[M+Na]$^{+}$) Calcd for $C_{22}H_{27}NO_2SNa$: 392.1655, Found: 392.1666.

**4-(4-methyl-1-tosyl-2,3-dihydro-*1*H-pyrrol-3-yl)benzonitrile** (**2h**) White solid, m.p. 144–146 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.65–7.69 (m, 2H), 7.43–7.47 (m, 2H), 7.35 (d, $J$ = 7.8 Hz, 2H), 6.90–6.87 (m, 2H), 6.29–6.30 (m, 1H), 3.91 (t, $J$ = 10.8 Hz, 1H), 3.75–3.80 (m, 1H), 3.35–3.40 (dd, $J$ = 5.2, 10.9 Hz, 1H), 2.49 (s, 3H), 1.42 (t, $J$ = 1.1 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ =

147.32, 144.16, 132.54, 132.23, 129.87, 128.19, 127.98, 126.71, 123.75, 118.66, 111.04, 55.55, 52.09, 21.68, 11.93 ppm; IR (KBr): $\upsilon$ = 2924, 2882, 2223, 1601 $cm^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{19}H_{18}N_2O_2SNa$: 361.0981, Found: 361.0973.

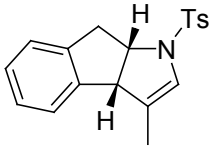
**4-(4-methyl-1-tosyl-2,5-dihydro-*1*H-pyrrol-3-yl)benzonitrile** (**3h**) White solid, m.p. 168–170 °C; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.78-7.73 (m, 2H), 7.64-7.60 (m, 2H), 7.33 (d, $J$ = 7.8 Hz, 2H), 7.30-7.27 (m, 2H), 4.39-4.44 (m, 2H), 4.20-4.22 (m, 2H), 2.43 (s, 3H), 1.81 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 143.82, 138.41, 133.82, 132.81, 132.33, 129.95, 128.67, 128.07, 127.57, 118.62, 111.13, 60.07, 57.18, 21.61, 13.05 ppm; IR (KBr): $\upsilon$ = 2921, 2853, 2226, 1602 $cm^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{19}H_{18}N_2O_2SNa$: 361.0981, Found: 361.0987.

**4-methyl-3-phenyl-1-(phenylsulfonyl)-2,3-dihydro-1H-pyrrole (2i)** White solid, m.p. 143-145 °C. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.85-7.80 (m, 2H), 7.67-7.64 (m, 1H), 7.60-7.55 (m, 2H), 7.18-7.15 (m, 3H), 6.76-6.72 (m, 2H), 6.28-6.27 (m, 1H), 3.97 (t, $J$ = 10.8 Hz, 1H), 3.78-3.72 (m, 1H), 3.38 (dd, $J$ = 6.3, 10.8 Hz, 1H), 1.43 (s, 3H) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 141.70, 135.43, 132.99, 129.16, 128.71, 128.24, 127.96, 127.37, 127.08, 125.51, 56.07, 52.20, 11.93 ppm; IR (KBr): $\upsilon$ = 3064, 2878, 1581 $cm^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{17}H_{17}NO_2SNa$: 322.0872, Found: 322.0870.

**3-(4-tert-butylphenyl)-4-methyl-1-(phenylsulfonyl)-2,3-dihydro-1H-pyrrole (2j)** White solid, m.p. 92-94 °C. $^1H$ NMR (300 MHz, $CDCl_3$):

$\delta$ = 7.85-7.81 (m, 2H), 7.68-7.64 (m, 1H), 7.60-7.57 (m, 2H), 7.20-7.16 (m, 2H), 6.70-6.67 (m, 2H), 6.28-6.27 (m, 1H), 3.95 (t, $J$ = 10.8 Hz, 1H), 3.77-3.71 (m, 1H), 3.38 (dd, $J$ = 6.4, 10.8 Hz, 1H), 1.44 (t, $J$ = 1.1 Hz, 3H), 1.28 (s, 9H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 149.90, 138.52, 132.98, 129.16, 127.97, 127.80, 127.03, 125.58, 125.38, 125.31, 56.10, 51.69, 34.45, 31.36, 12.04 ppm; IR (KBr): $\upsilon$ = 3061, 2961, 2870, 1510, 1468 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{21}H_{25}NO_2SNa$: 378.1498, Found: 378.1486.

**3-(4-tert-butylphenyl)-4-methylene-1-(phenylsulfonyl)pyrrolidine (4j)** White solid, m.p. 115-117 $^o$C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.87-7.84 (m, 2H), 7.65-7.62 (m, 1H), 7.60-7.56 (m, 2H), 7.32-7.28 (m, 2H), 7.06-7.02 (m, 2H), 5.03 (d, $J$ = 2.0 Hz, 1H), 4.69 (d, $J$ = 2.2 Hz, 1H), 4.16-4.09 (m, 1H), 3.96-3.90 (m, 1H), 3.83-3.75 (m, 2H), 3.24-3.15 (m, 1H), 1.30 (s, 9H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 148.04, 136.39, 132.99, 129.18, 127.97, 127.87, 127.79, 127.02, 125.61, 109.23, 55.52, 52.49, 48.92, 34.44, 31.35 ppm; IR (KBr): $\upsilon$ = 3061, 2960, 2868, 1510, 1470 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{21}H_{25}NO_2SNa$: 378.1498, Found: 378.1503.

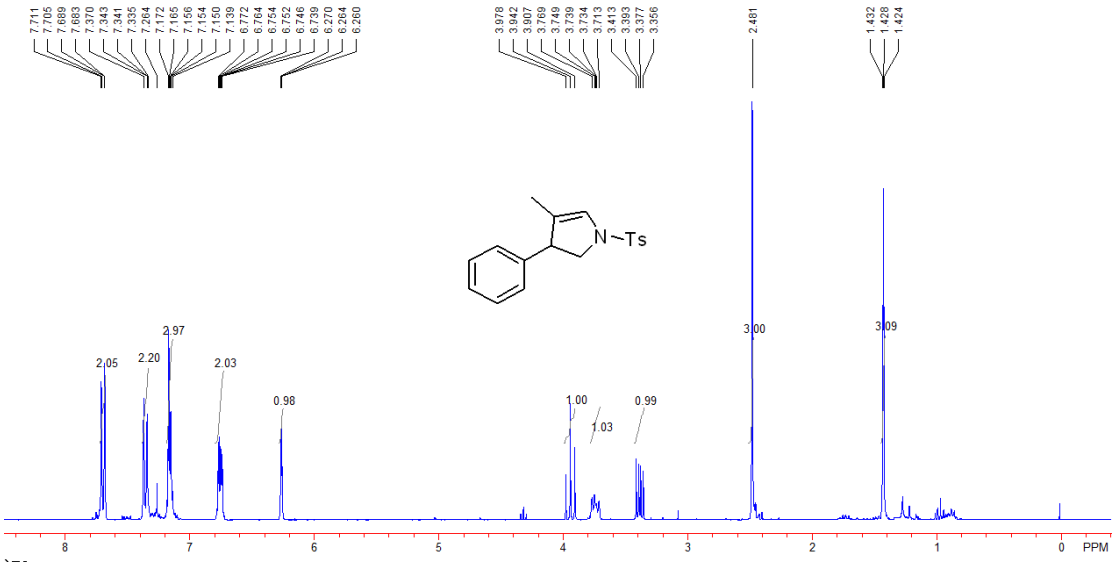



**3-methyl-1-tosyl-1,3a,8,8a-tetrahydroindeno[*2,1-b*]pyrrole (2k)** White solid, m.p. 148–150 $^o$C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.71–7.75 (m, 2H), 7.35 (d, $J$ = 7.9 Hz, 2H), 7.16–7.1624 (m, 4H), 6.03 (s, 1H), 4.54–4.61 (m, 1H), 4.00–4.04 (m, 1H), 3.41–3.55 (m, 2H), 2.46 (s, 3H), 1.76–1.75 (m, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 143.76, 141.20, 140.89, 133.75, 129.84, 129.73, 127.70, 127.50, 126.73, 125.12, 124.14, 124.05, 64.28, 57.71, 41.22, 21.68, 12.28 ppm; IR (KBr): $\upsilon$ = 2975, 2922, 1452 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{19}H_{19}NO_2SNa$: 348.1029, Found: 348.1016.

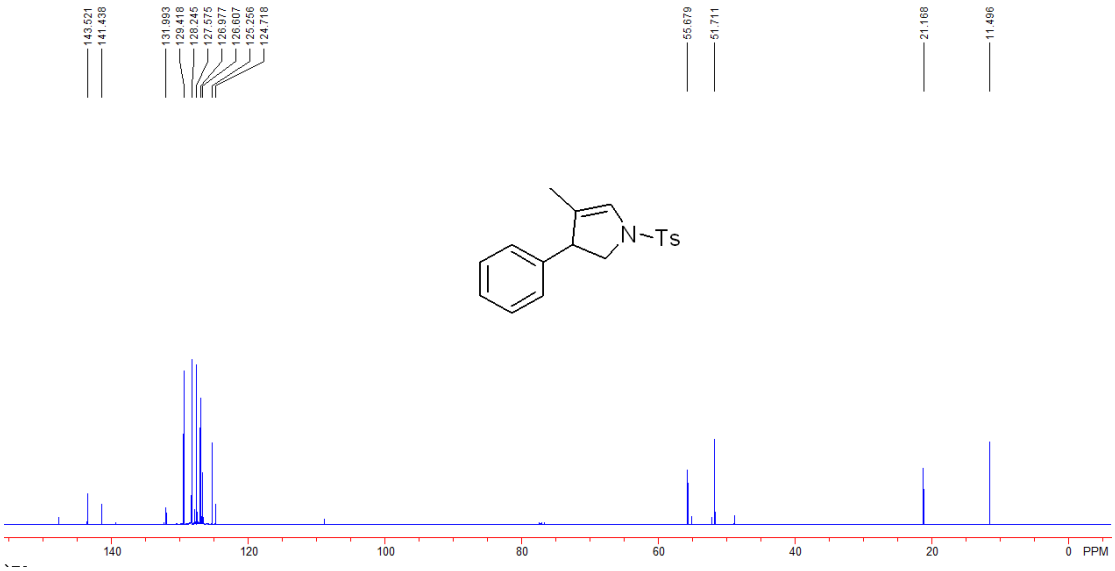
**3-methylene-1-tosyl-1,2,3,3a,8,8a-hexahydroindeno[*2,1-b*]pyrrole** (**4k**) White solid, m.p. 157–159 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.75 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.3 Hz, 2H), 7.20–7.24 (m, 4H), 5.12–5.14 (m, 1H), 4.95 – 4.97 (m, 1H), 4.41–4.44 (m, 1H), 4.04–4.07 (m, 1H), 3.92 (s, 2H), 3.52 (dd, $J$ = 2.1, 17.4 Hz, 1H), 3.29 (dd, $J$ = 6.3, 17.4 Hz, 1H), 2.45 (s, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 145.92, 143.66, 141.31, 134.37, 129.83, 129.78, 127.80, 127.70, 126.93, 125.15, 123.97, 107.79, 65.09, 55.25, 53.29, 40.15, 21.62 ppm; IR (KBr): $\upsilon$ = 2914, 2857, 1666, 1595 cm$^{-1}$; MS (HRMS/$[M+Na]^+$) Calcd for $C_{19}H_{19}NO_2SNa$: 348.1029, Found: 348.1022.

## 5. $^{1}$H and $^{13}$C NMR spectra for products 2, 3, 4

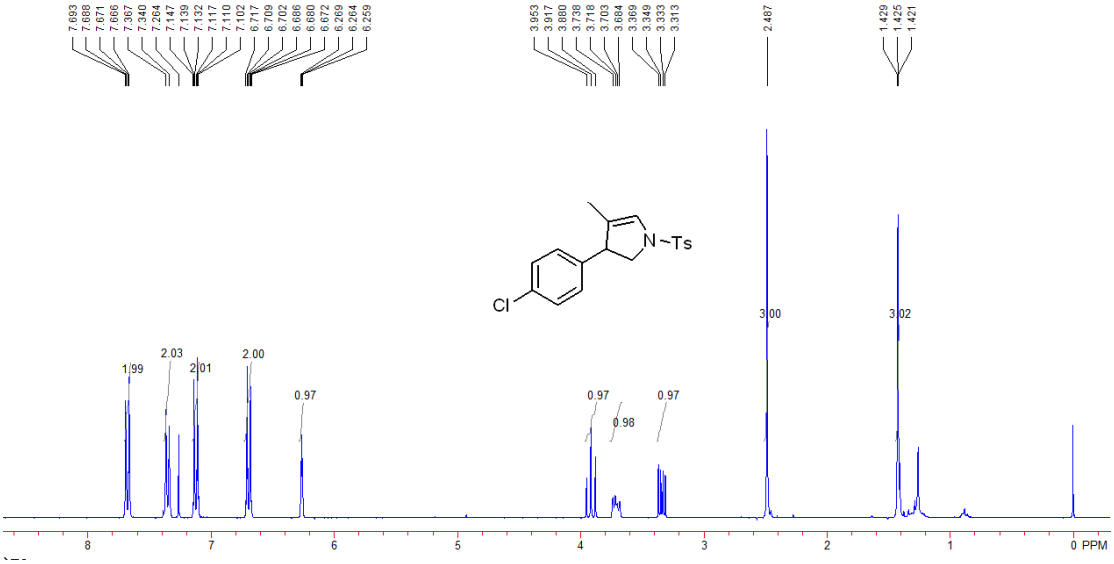
**2a** $^{1}$H NMR (300 MHz, $CDCl_3$):



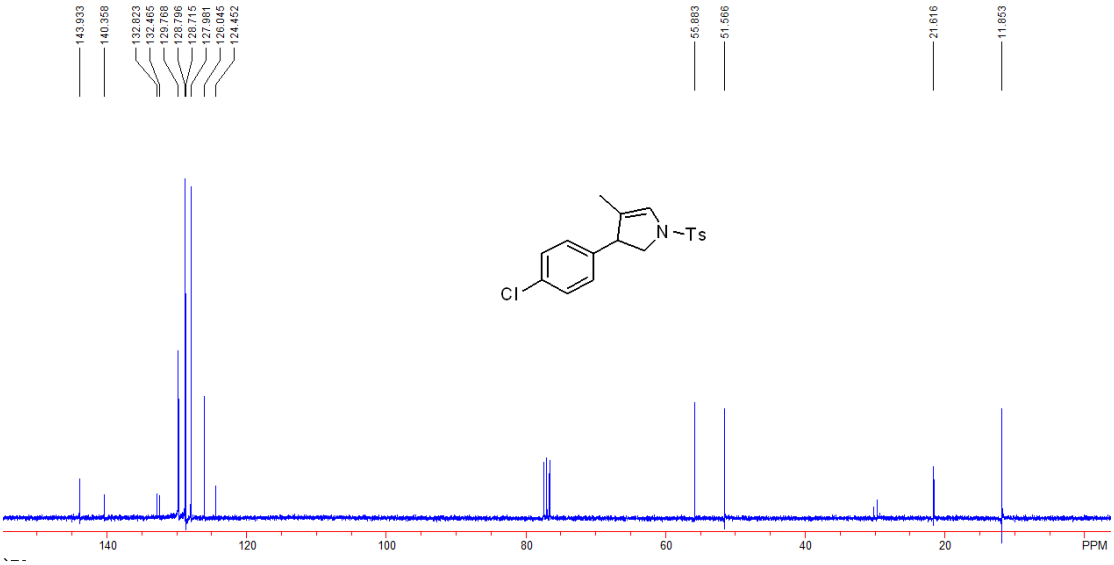

**2a** $^{13}$C NMR (75 MHz, $CDCl_3$):



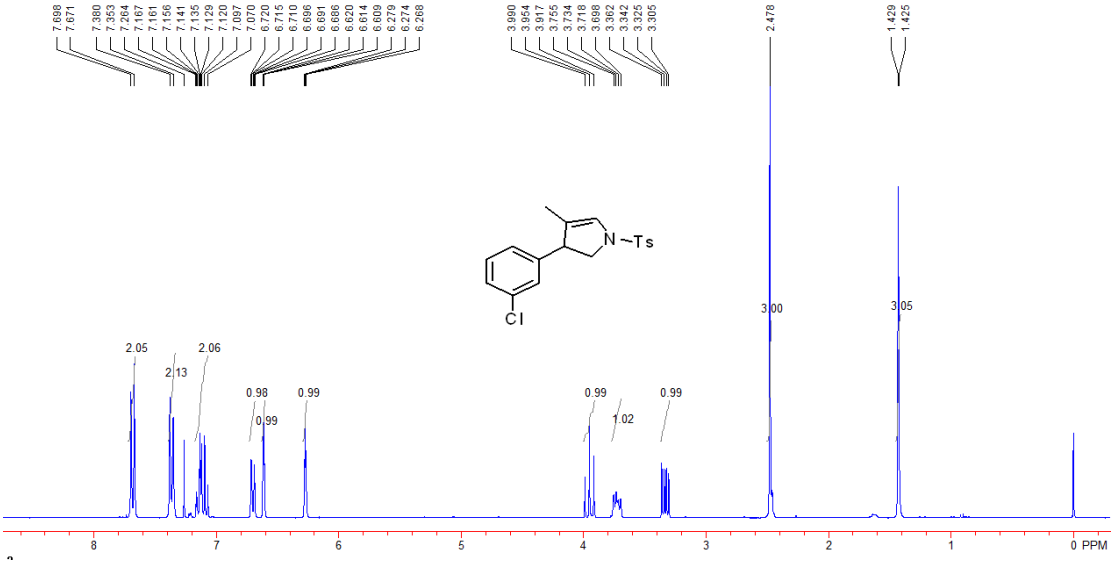
**2b** $^{1}$H NMR (300 MHz, $CDCl_3$):



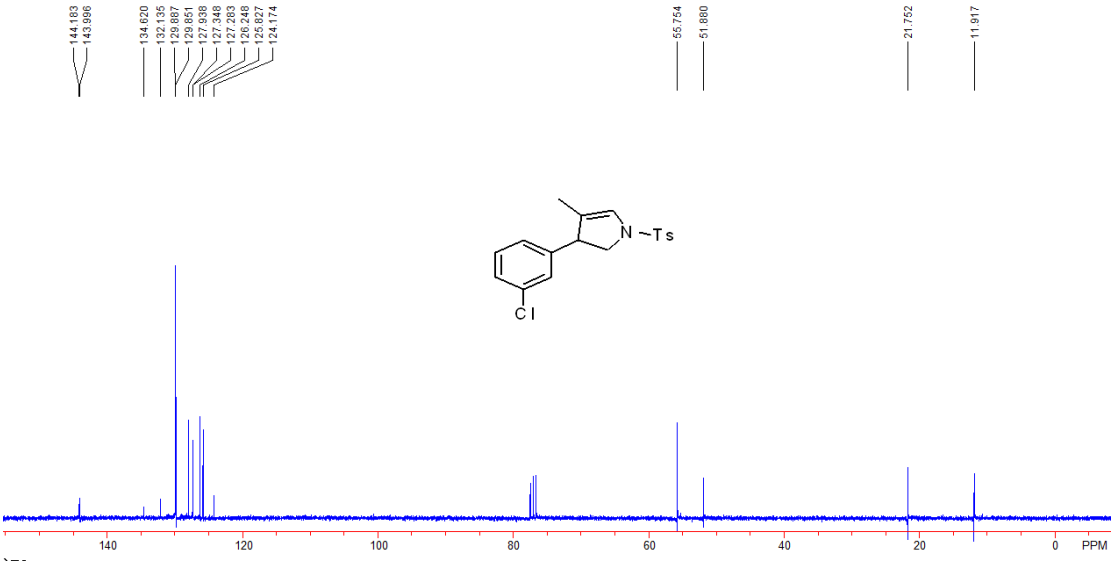

**2b** $^{13}$C NMR (75 MHz, $CDCl_3$):



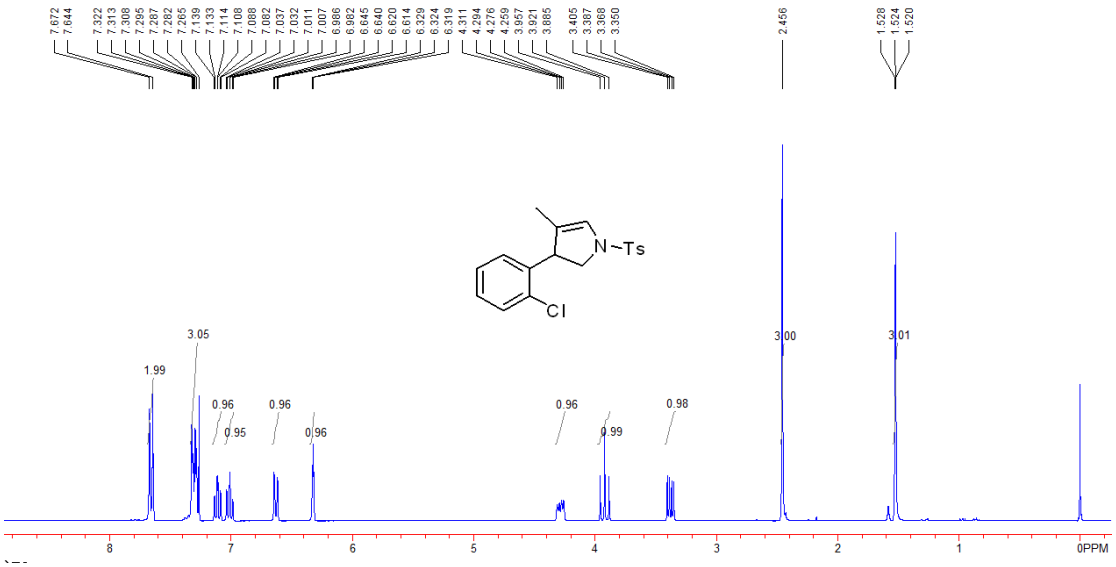
**2c** $^{1}$H NMR (300 MHz, $CDCl_3$):



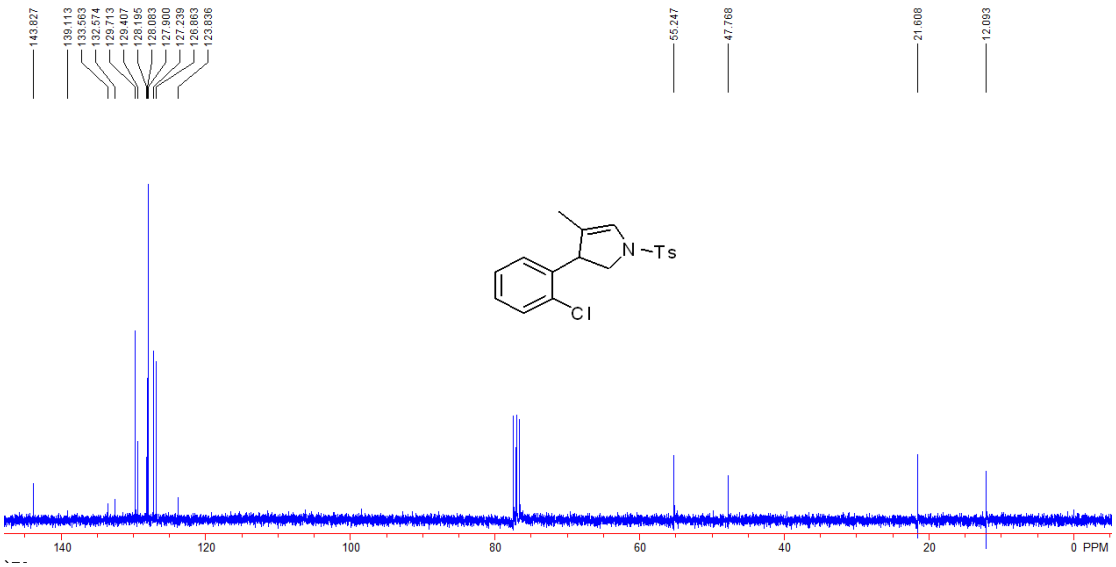

**2c** $^{13}$C NMR (75 MHz, $CDCl_3$):



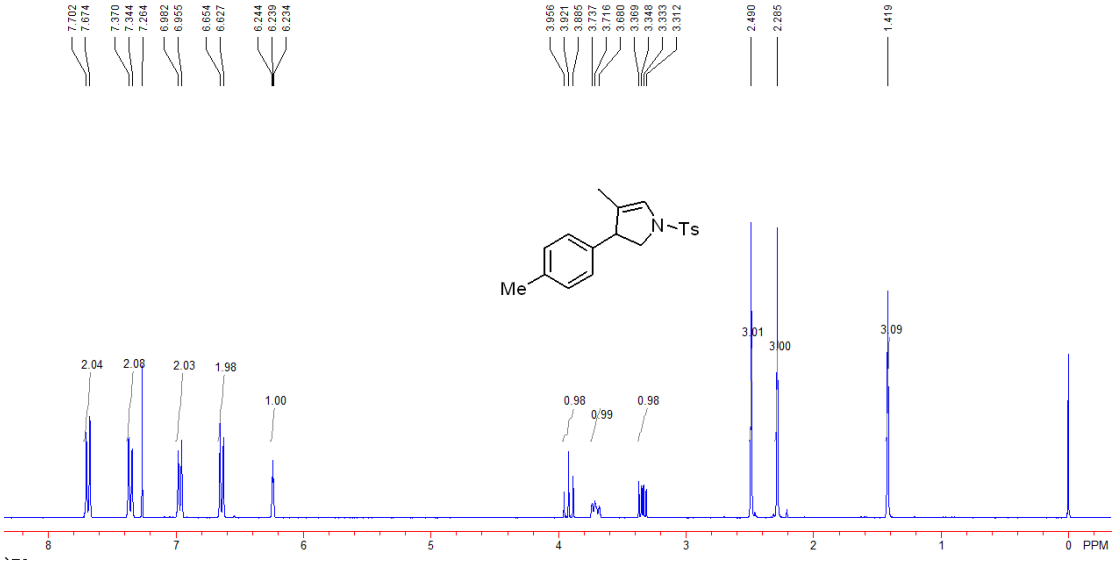
**2d** $^{1}$H NMR (300 MHz, $CDCl_3$):



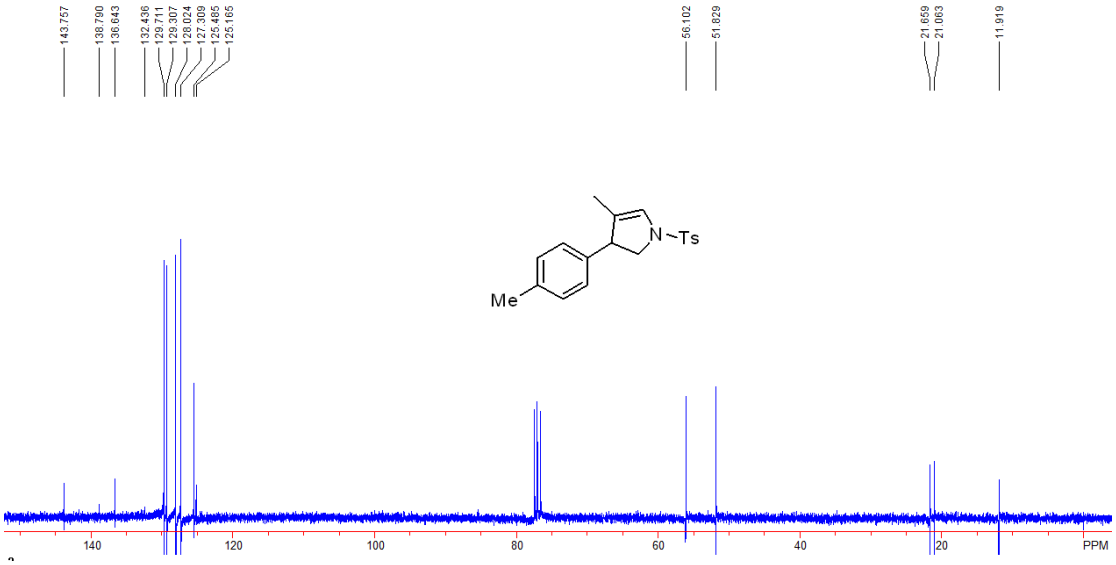

**2d** $^{13}$C NMR (75 MHz, $CDCl_3$):



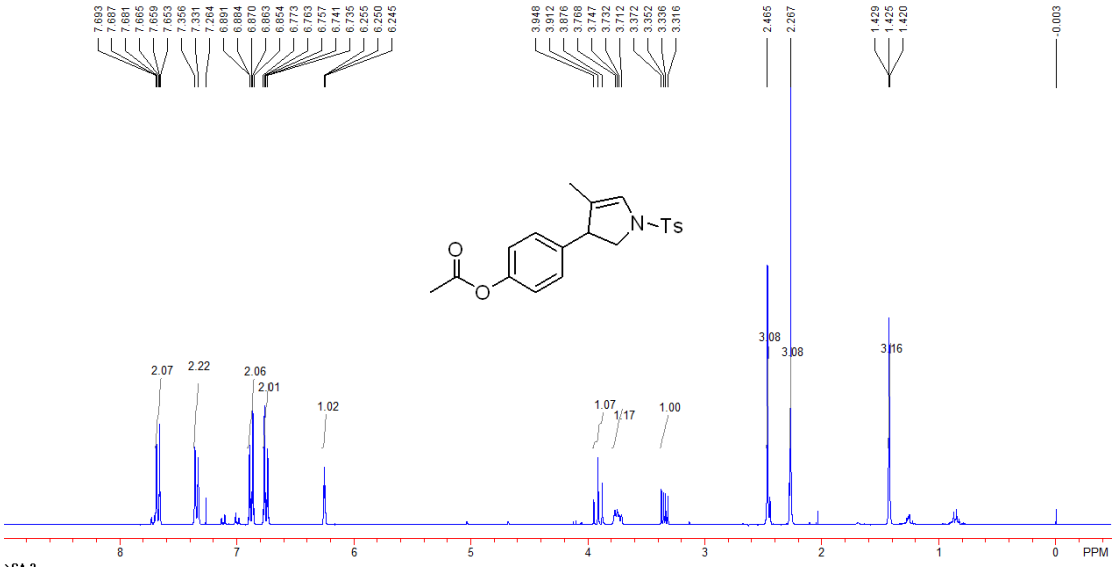
**2e** $^{1}$H NMR (300 MHz, $CDCl_3$):



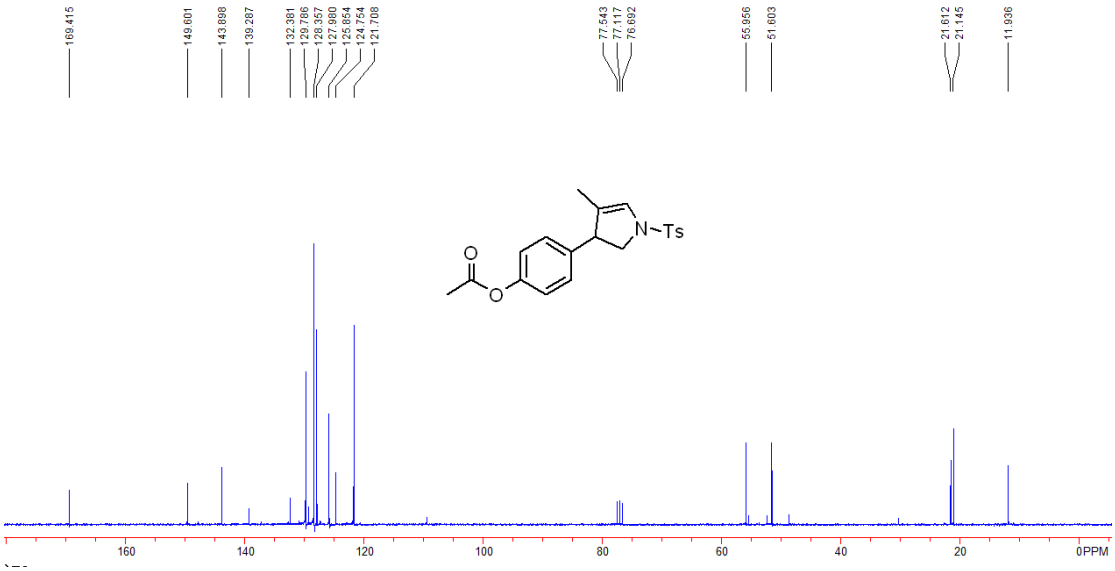

**2e** $^{13}$C NMR (75 MHz, $CDCl_3$):



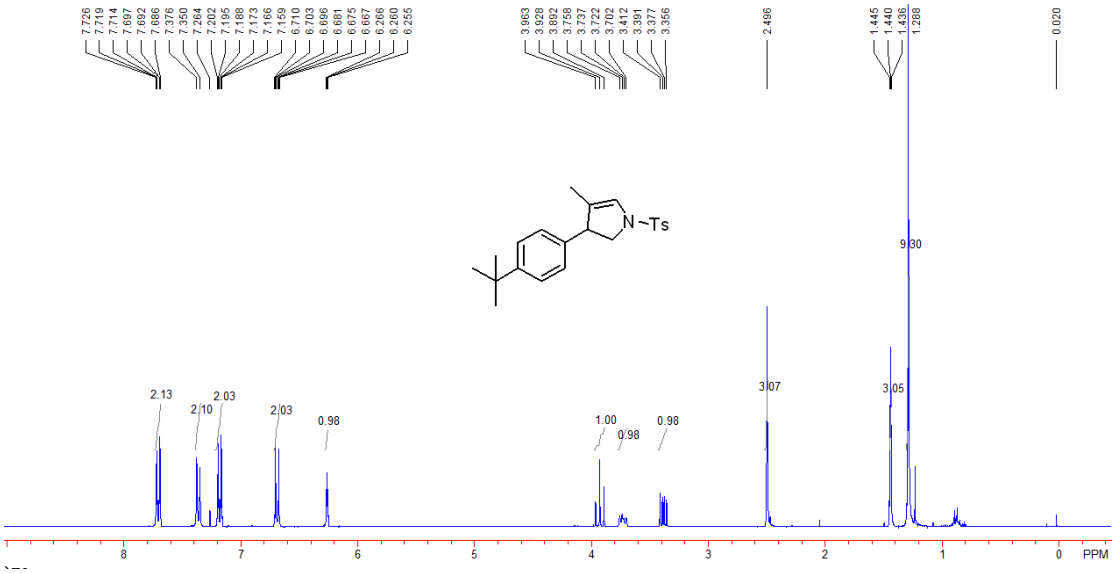
**2f** $^{1}$H NMR (300 MHz, $CDCl_3$):



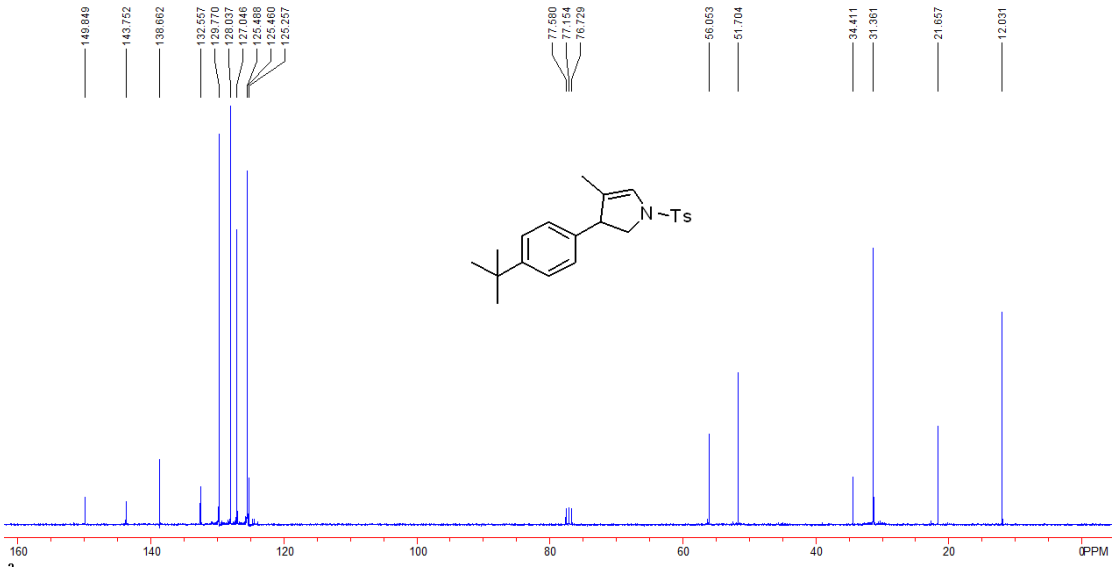

**2f** $^{13}$C NMR (75 MHz, $CDCl_3$):



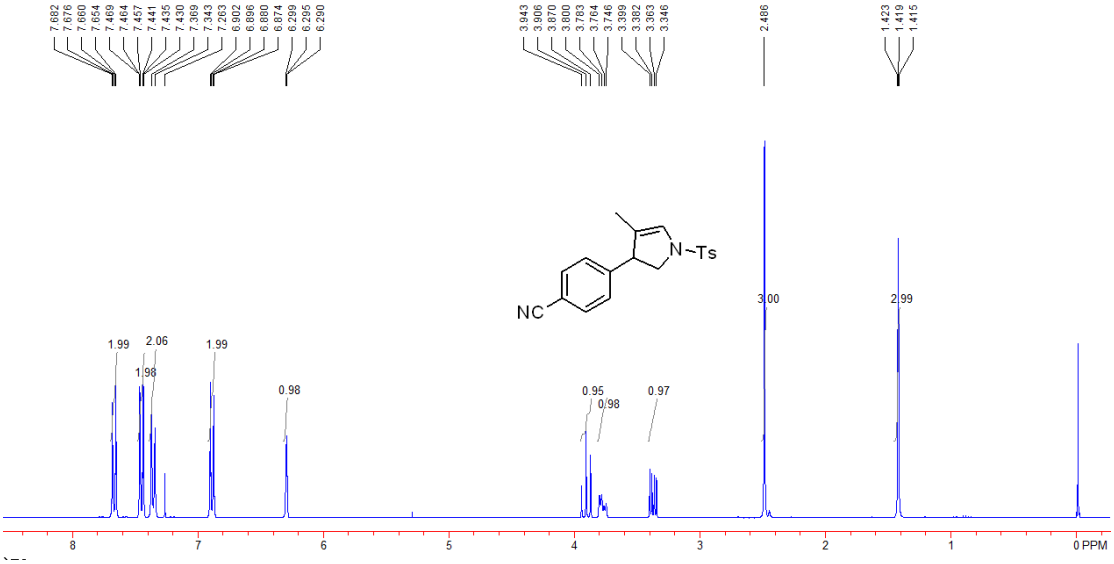
**2g** $^{1}$H NMR (300 MHz, $CDCl_3$):



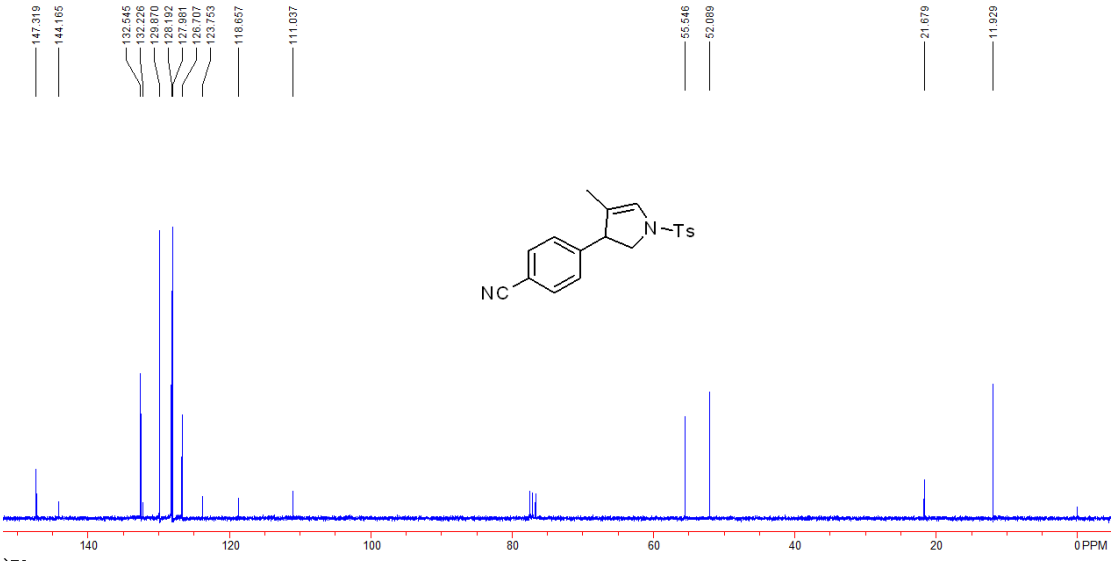

**2g** $^{13}$C NMR (75 MHz, $CDCl_3$):



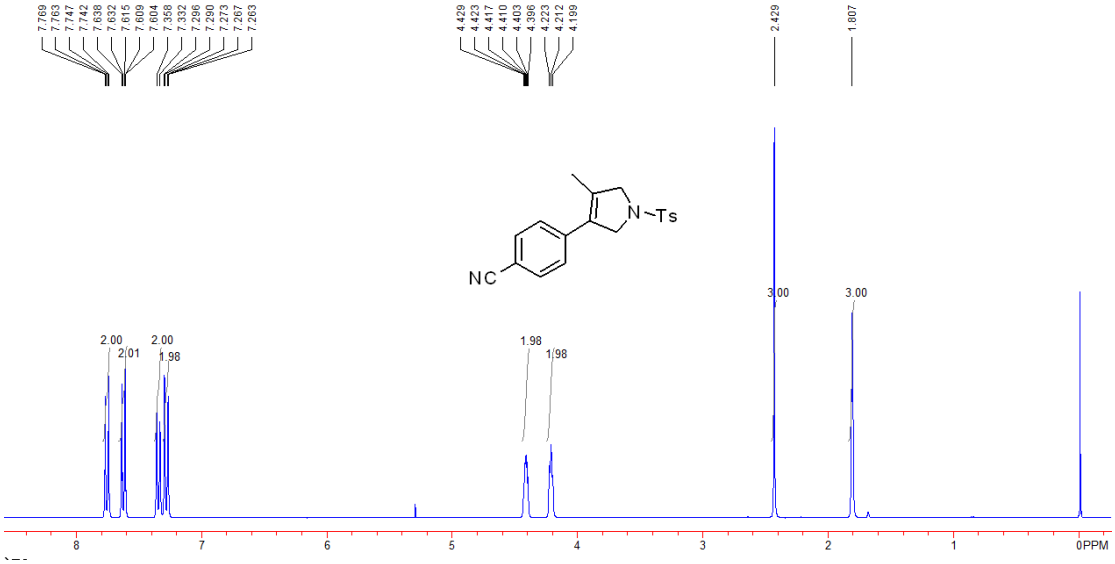
**2h** $^{1}$H NMR (300 MHz, $CDCl_3$):



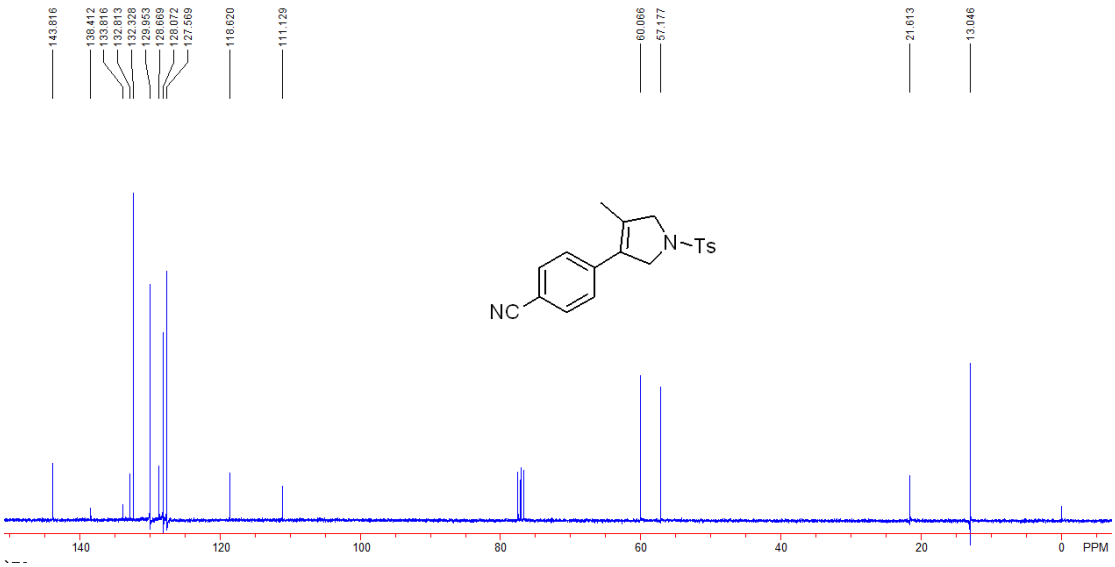

**2h** $^{13}$C NMR (75 MHz, $CDCl_3$):



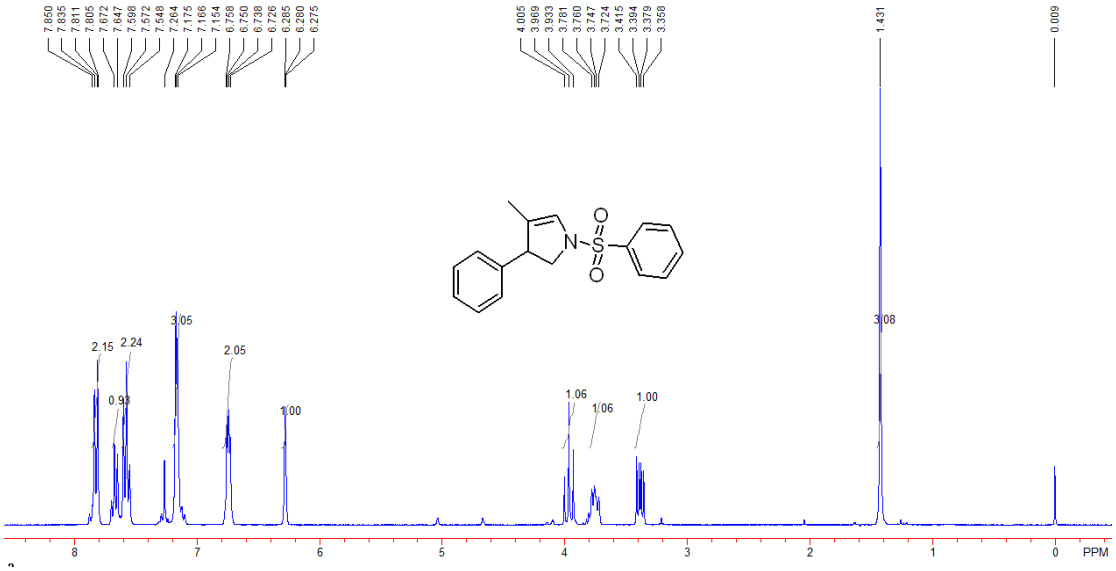
**3h** $^{1}$H NMR (300 MHz, $CDCl_3$):



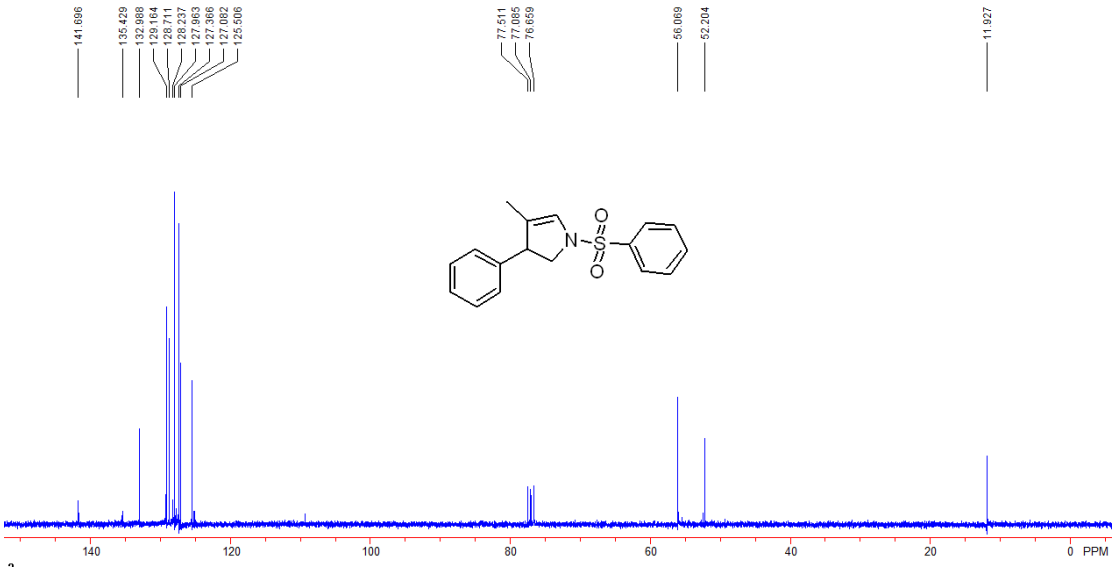

**3h** $^{13}$C NMR (75 MHz, $CDCl_3$):



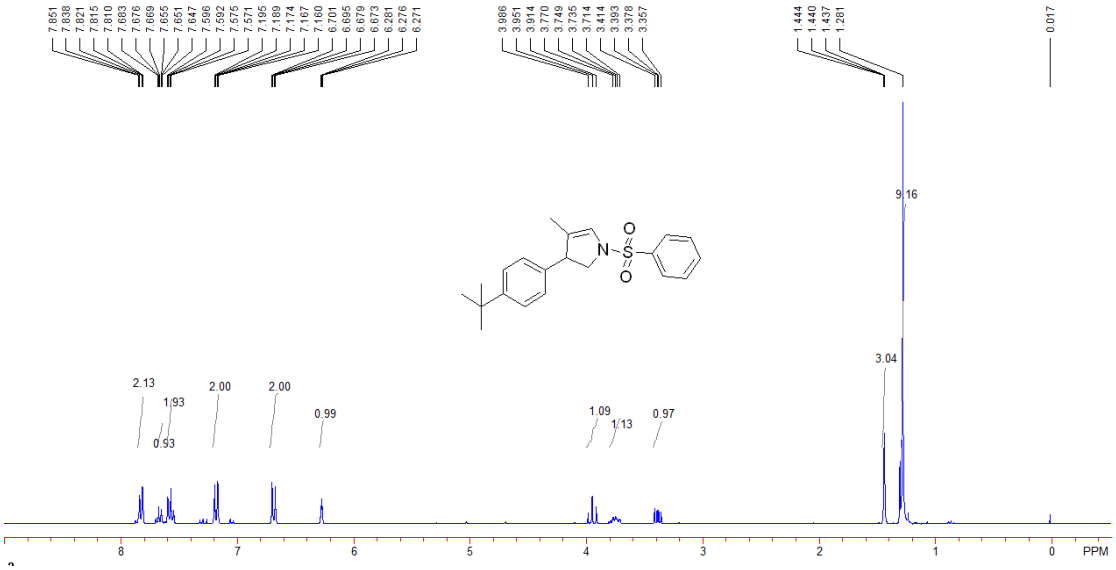
**2i** $^{1}$H NMR (300 MHz, $CDCl_3$):



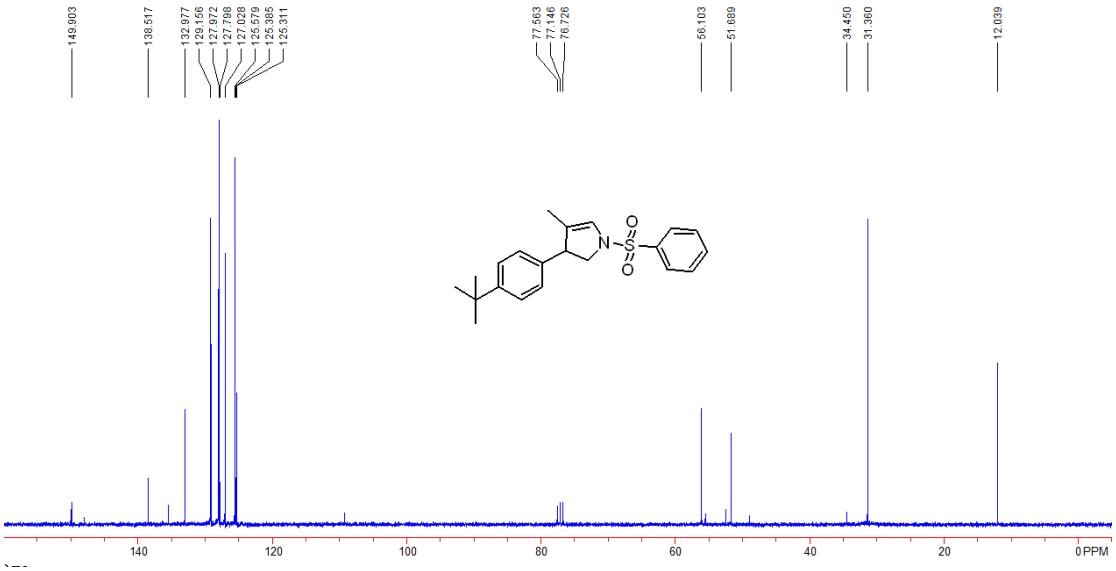

**2i** $^{13}$C NMR (75 MHz, $CDCl_3$):



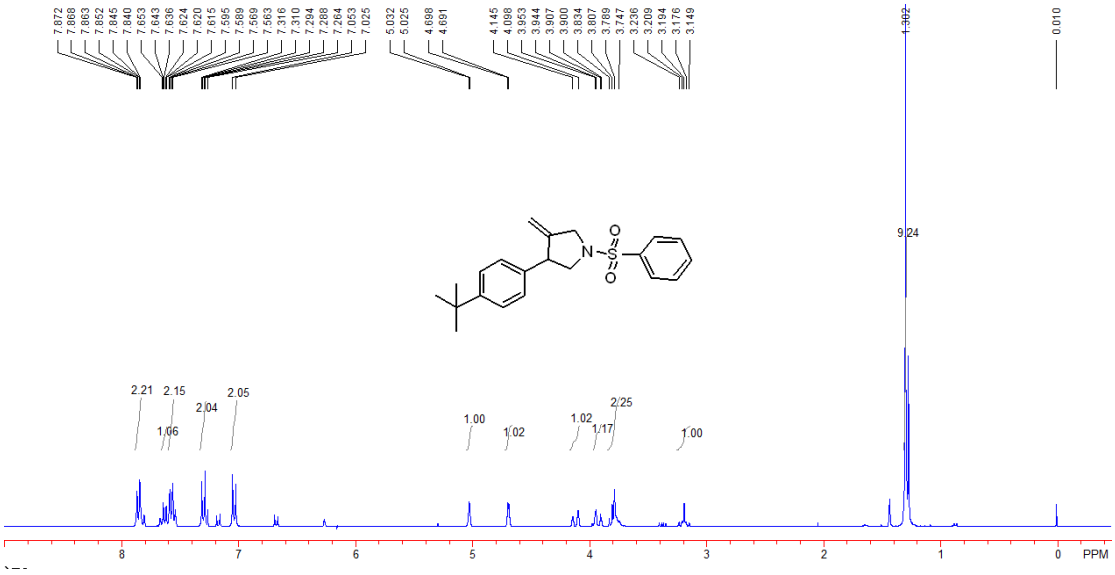
**2j** $^{1}$H NMR (300 MHz, $CDCl_3$):



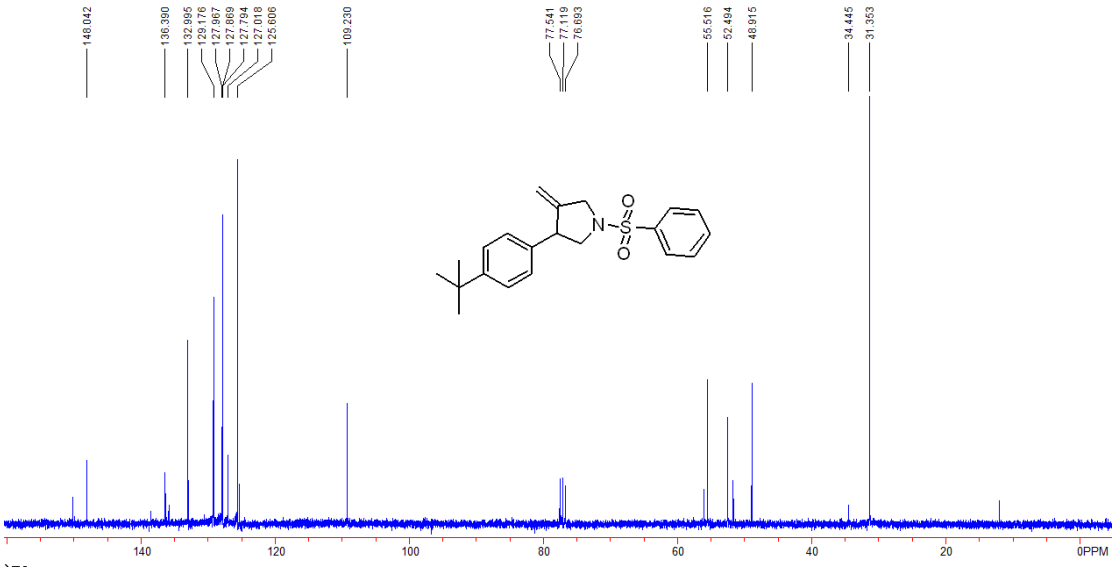

**2j** $^{13}$C NMR (75 MHz, $CDCl_3$):



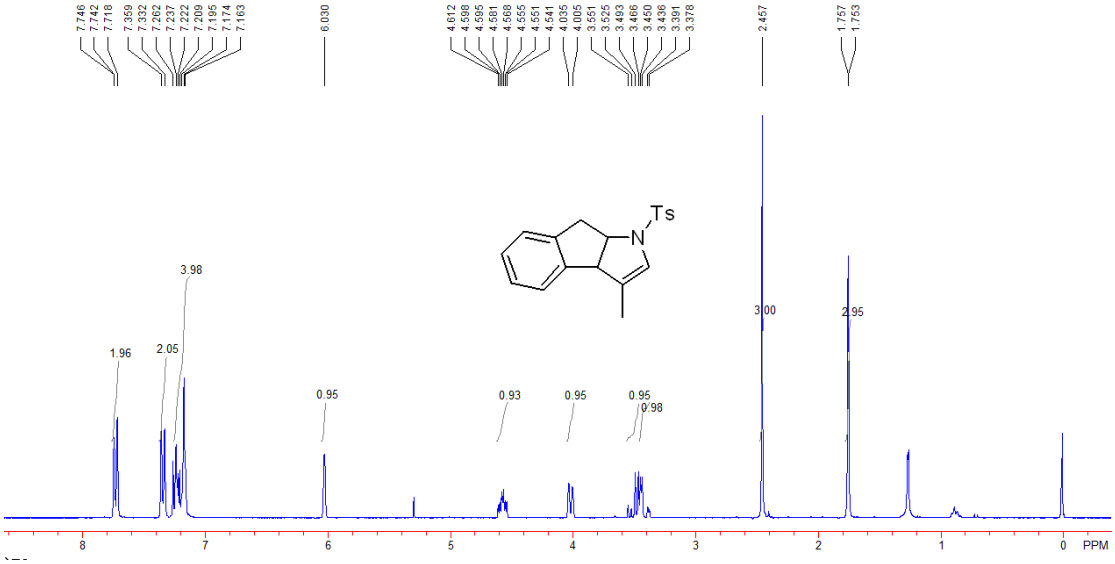
**4j** $^{1}$H NMR (300 MHz, $CDCl_3$):



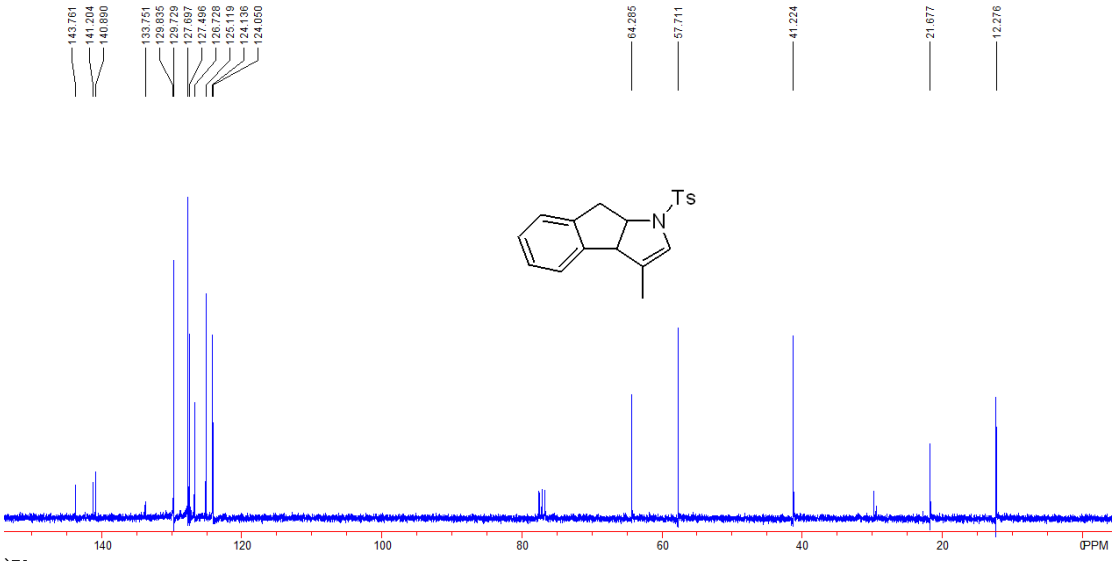

**4j** $^{13}$C NMR (75 MHz, $CDCl_3$):



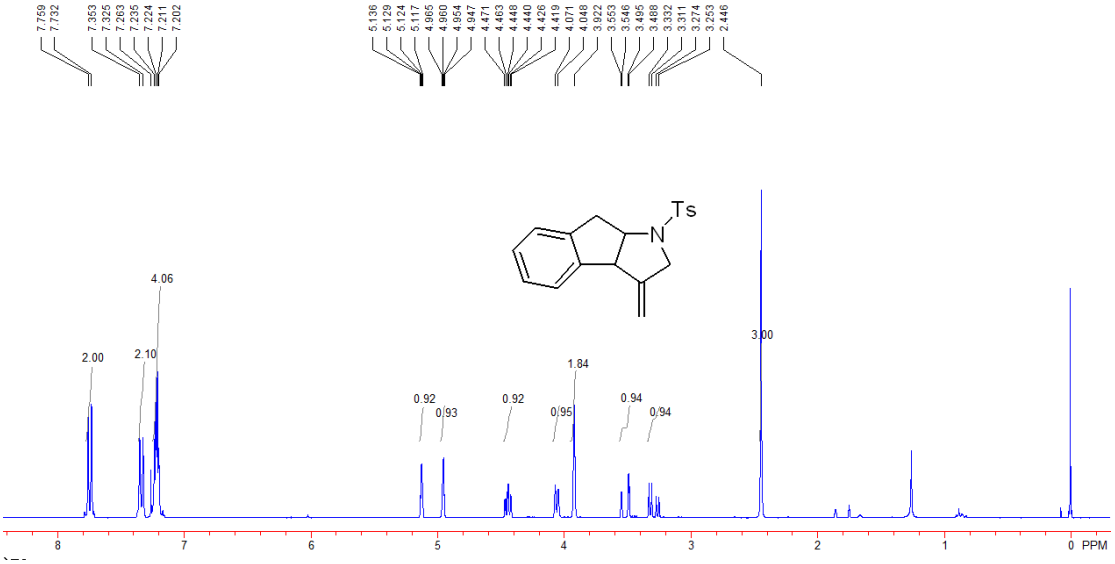
**2k** $^{1}$H NMR (300 MHz, $CDCl_3$):




**2k** $^{13}$C NMR (75 MHz, $CDCl_3$):



**4k** $^{1}$H NMR (300 MHz, $CDCl_3$):




**4k** $^{13}$C NMR (75 MHz, $CDCl_3$):