Supporting Information for

Ruthenium-catalysed C−H/C−N bond activation: facile access to isoindolinones

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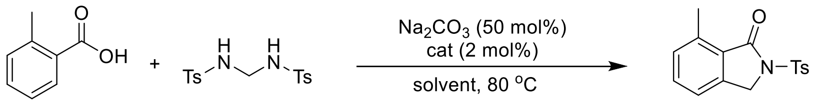
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. The solvents used were purified by distillation over the drying agents. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400/600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 400 (100 MHz) with and 600 (150 MHz) complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm).

2. Optimization of the Reaction Conditions

2.1 Screening of catalyst and solvent[a]

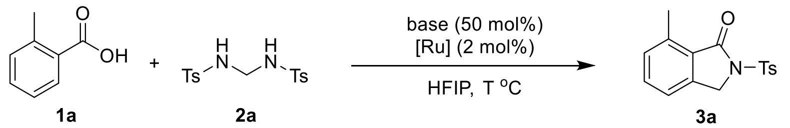


1a **2a** **3a**

entry	catalyst	solvent	base	yield (%)[b]
1	[$RuCl_2$(*p*-cymene)]$_2$	HFIP	Na_2CO_3	32
2	[$RuCl_2$(*p*-cymene)]$_2$	TCE	Na_2CO_3	0
3	[$RuCl_2$(*p*-cymene)]$_2$	CF_3CH_2OH	Na_2CO_3	<5
4	[$RuCl_2$(*p*-cymene)]$_2$	^{t}AmOH	Na_2CO_3	<5
5	[$RuCl_2$(*p*-cymene)]$_2$	CH_3OH	Na_2CO_3	<5
6	[$RuCl_2$(*p*-cymene)]$_2$	toluene	Na_2CO_3	7
7	[$RuCl_2$(*p*-cymene)]$_2$	dioxane	Na_2CO_3	<5
8	[$RuCl_2$(*p*-cymene)]$_2$	CH_3CN	Na_2CO_3	<5
9	[$RuCl_2$(*p*-cymene)]$_2$	DMF	Na_2CO_3	0
10	[IrCp*Cl_2]$_2$	HFIP	Na_2CO_3	8

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2 mol%), base (50 mol%), solvent (1.5 mL) at 80 °C for 16 h. [b]Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. ^{t}AmOH = 2-methylbutan-2-ol. HFIP = hexafluoro-2-propanol. TCE = 2,2,2-trichloroethanol. TFE = 2,2,2-trifluoroethanol.

2.2 Screening of base and temperature[a]

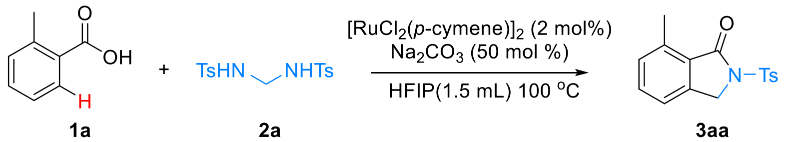


entry	catalyst	solvent	base	temperature (°C)	yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$	HFIP	Na_2CO_3	80	32
2	$[RuCl_2(p\text{-cymene})]_2$	HFIP	K_2CO_3	80	<5
3	$[RuCl_2(p\text{-cymene})]_2$	HFIP	KOAc	80	<5
4	$[RuCl_2(p\text{-cymene})]_2$	HFIP	K_3PO_4	80	<5
5	$[RuCl_2(p\text{-cymene})]_2$	HFIP	Cs_2CO_3	80	<5
6[c]	$[RuCl_2(p\text{-cymene})]_2$	HFIP	Na_2CO_3	90	56
7[d]	$[RuCl_2(p\text{-cymene})]_2$	HFIP	Na_2CO_3	100	75
8[e]	$[RuCl_2(p\text{-cymene})]_2$	HFIP	Na_2CO_3	100	88(91)[f]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2 mol%), base (50 mol%), HFIP (1.5 mL) at the indicated reaction temperature for 16 h. [b]Yields determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c]At 90 °C. [d]At 100 °C. [e]**2a** (0.4 mmol) was used. [f]Isolated yield. [t]AmOH = 2-methylbutan-2-ol. HFIP = hexafluoro-2-propanol. TCE = 2,2,2-trichloroethanol. TFE = 2,2,2-trifluoroethanol.

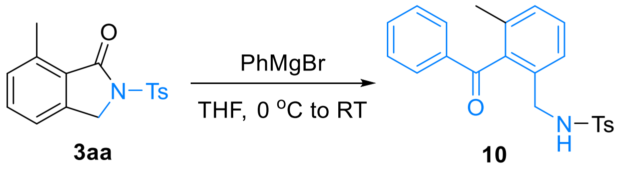
3. General Procedure and Spectral Data of the Products

3.1 General procedure for the synthesis of 3aa-za', 3ab-3ad, 5, 7, 9



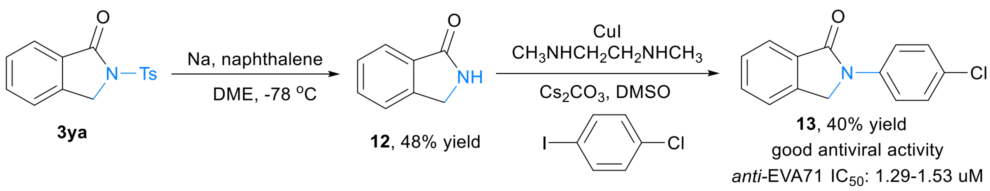
1a (27.2 mg, 0.2 mmol), **2a** (141.6 mg, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.45 mg, 0.004 mmol) and Na_2CO_3 (10.6 mg, 0.1 mmol) were dissolved in HFIP (1.5 mL). Then, the mixture was stirred at 100℃ for 16 h, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) directly to give the desired product **3aa** in 91% isolated yield as a white solid. Other products 3**ba-za', 3ab-ad, 5, 7, 9** were prepared according to the above procedure.

3.2 General procedure for the synthesis of 10



To a 10 mL oven-dried Schlenk tube containing a stirrer bar was mixed with **3aa** (60.2 mg, 0.2 mmol) and anhydrous THF (5 mL). After cooling to 0 °C, the corresponding Grignard reagent PhMgBr (0.4 mmol) was added dropwise to the solution. Until TLC analysis showed the complete consumption of substrate (about 0.5 h), aqueous saturated NH_4Cl was added to neutralize extra Grignard reagent. Next, the resulting mixture was extracted by EtOAc/H_2O. Organic phase was dried over $MgSO_4$ and concentrated. The resulting mixture was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford pure product **10** as a white soild (89% yield).

3.3 General procedure for the synthesis of compounds 12 and 13

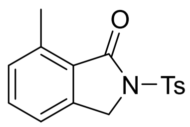


Finely chopped sodium metal (70.0 mg, 3.04 mmol) and naphthalene (450 mg, 3.51mmol) were combined in a flame-dried Schlenk flask followed by the addition of DME (3 mL).The reaction was stirred for 2 h at room temperature under N_2 to provide a dark green solution. In a separate flame-dried Schlenk flask under N_2 was added **3ya** (57.4 mg, 0.20 mmol) and DME (1 mL) followed by cooling to -78 °C. Then, the Na-naphthalenide solution was slowly added to the cooled solution of **3ya** until a dark green color persisted for 5 min with stirring. The reaction was quenched by the addition of MeOH at -78 °C (until the dark green color had been completely discharged) and was then diluted with EtOAc (10 mL). The mixture was washed by brine (20 mL) and the combined organic fractions were dried over $MgSO_4$. Compound **12** was purified by flash column chromatography on silica gel using *n*-hexane:EtOAc (1:1) in 48% isolated yield.

Isoindolin-1-one **12** (66.7 mg, 0.50 mmol) was dissolved in super-dry DMSO (2 mL), and Cs_2CO_3 (405 mg, 1.25 mmol), CuI (19.3 mg, 0.10 mmol) and N^1, N^2-dimethylethane-1, 2-diamine (9 mg, 11 μL, 0.10 mmol) were added to the solution. The resulting mixture was stirred at room temperature for 10 min, after which 4-chloroiodobenzene (178.8 mg, 0.75mmol) was added. Then the mixture was heated to 120 °C. When TLC showed that isoindolin-l-one had been fully converted, the reaction was stopped. The reaction mixture was extracted with ethyl acetate (20 mL) and H_2O (10 mL). The organic layer was combined and washed with brine (10 mL). Then the solution was dried over anhydrous $MgSO_4$, filtered and concentrated, and the crude residue was purified by flash chromatography over silica gel using *n*-hexane:EtOAc (10:1) to afford the title compound **13** in 40% yield.

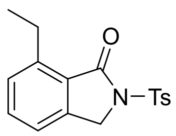
3.4 Spectral data of the products 3aa-za’, 3ab-ad, 5, 7, 9, 10, 12, and 13

Product 3aa



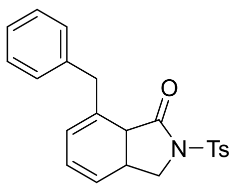
Yield of **3aa**: 91% as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 4.85 (s, 2H), 2.61 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 166.7, 145.0, 141.5, 139.5, 135.4, 133.3, 130.6, 129.7, 128.1, 127.3, 120.6, 49.1, 21.6, 17.4. M.P.: 180.0 – 180.5 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{15}NO_3S$: 302.0845; found: 302.0845.

Product 3ba



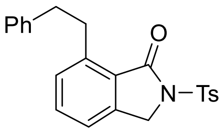
Yield of **3ba**: 98% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 4.85 (s, 2H), 3.06 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 166.4, 146.0, 145.0, 141.7, 135.6, 133.6, 129.7, 128.9, 128.1, 126.7, 120.6, 49.1, 24.0, 21.6, 14.9. M.P.: 158.0 – 158.5 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{17}NO_3S$: 316.1002; found: 316.1001.

Product 3ca



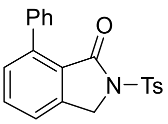
Yield of **3ca**: 84% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.15 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 4.85 (s, 2H), 4.45 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =166.6, 145.1, 142.7, 141.7, 139.7, 135.5, 133.6, 130.0, 129.7, 129.2, 128.4, 128.1, 126.7, 126.2, 121.1, 49.0, 35.8, 21.6. M.P.: 180.0 – 180.5 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{22}H_{19}NO_3S$: 378.1158; found: 378.1157.

Product 3da



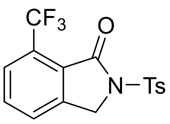
Yield of **3da**: 55% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.19 – 7.11 (m, 2H), 4.85 (s, 2H), 3.32 (dd, *J* = 9.2, 6.9 Hz, 2H), 2.87 (dd, *J* = 9.3, 6.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 166.3, 145.1, 143.5, 141.8, 141.4, 135.5, 133.4, 130.0, 129.8, 128.6, 128.2, 128.1, 127.0, 125.9, 121.0, 49.2, 37.2, 33.2, 21.7. M.P.: 164.0 – 165.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{21}NO_3S$: 392.1315; found: 392.1312.

Product 3ea



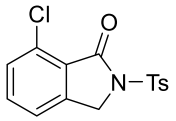
Yield of **3ea**: 46% as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.97 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 3H), 7.43 – 7.37 (m, 4H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.91 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 165.2, 145.0, 142.6, 142.3, 136.5, 135.4, 133.4, 131.0, 129.7, 129.5, 128.2, 128.1, 127.9, 126.0, 122.1, 48.9, 21.6. M.P.: 175.0 – 175.5 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{17}NO_3S$: 364.1002; found: 364.0999.

Product 3fa



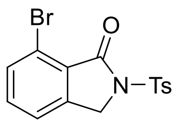
Yield of **3fa**: 43% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.05 (d, *J* = 8.4 Hz, 2H), 7.81 – 7.66 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.95 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 162.5, 145.5, 143.2, 134.8, 133.5, 129.8, 128.34, 128.28 (q, *J* = 34.9 Hz) 127.4, 127.2, 126.6 (q, *J* = 5.6 Hz), 122.1 (q, *J* = 271.9 Hz), 49.1, 21.7. M.P.: 184.0 – 184.5 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{12}F_3NO_3S$: 356.0563; found: 356.0560.

Product 3ga



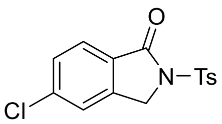
Yield of **3ga**: 71% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.04 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.29 (m, 4H), 4.87 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 163.5, 145.4, 143.3, 135.0, 134.4, 132.9, 130.5, 129.8, 128.3, 126.4, 121.8, 48.6, 21.7. M.P.: 195.0 – 195.5 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{12}ClNO_3S$: 322.0299; found: 322.0298.

Product 3ha



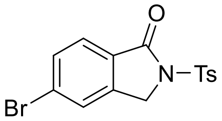
Yield of **3ha**: 58% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.04 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.86 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 163.9, 145.4, 143.6, 135.0, 134.5, 133.8, 129.8, 128.3, 127.8, 122.4, 120.3, 48.3, 21.7. M.P.: 185.0 – 186.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{12}BrNO_3S$: 365.9794; found: 365.9792.

Product 3ia



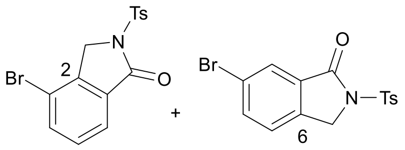
Yield of **3ia**: 34% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.02 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.89 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =165.0, 145.4, 142.4, 140.4, 135.2, 129.8, 129.6, 128.7, 128.2, 126.3, 123.7, 49.3, 21.7. M.P.: 132.0 – 132.5 °C. HRMS (ESI): m/z $[M +Na]^+$ calcd for $C_{15}H_{12}ClNO_3S$: 344.0119; found: 344.0114.

Product 3ja



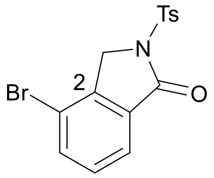
Yield of **3ja**: 46% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.02 (d, *J* = 8.5 Hz, 2H), 7.70 – 7.58 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.89 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) =165.2, 145.5, 142.5, 135.1, 132.5, 129.8, 129.2, 128.9, 128.1, 126.7, 126.4, 49.2, 21.7. M.P.: 142.0 – 142.5 °C. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{15}H_{12}BrNO_3S$: 387.9613; found: 387.9611.

Product 3ka + 3ka'



3ka (C2:C6 = 1:1) **3ka'**

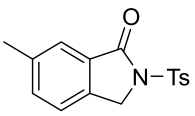
Yield of **3ka + 3ka'**: 57% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm **3ka + 3ka'**)= 8.04 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 7.78 – 7.73 (m, 4H), 7.35 (ddd, *J* = 18.4, 13.8, 8.3 Hz, 7H), 4.86 (s, 2H), 4.82 (s, 2H), 2.43 (s, 6H).



3ka

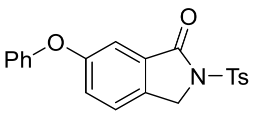
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm **3ka**) =8.04 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.34 (m, 3H), 4.82 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm **3ka**) =165.1, 145.5, 141.4, 136.7, 135.1, 132.3, 130.6, 129.8, 128.2, 123.9, 118.1, 77.0, 50.5, 21.7. M.P.: 150.0 – 150.5 ^{o}C. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{15}H_{12}BrNO_3S$: 387.9613; found: 387.9606.

Product 3la



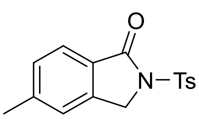
Yield of **3la**: 95% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 10.5, 8.1 Hz, 3H), 4.86 (s, 2H), 2.41 (d, *J* = 5.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.2, 145.1, 139.0, 138.3, 135.4, 135.0, 130.2, 129.7, 128.0, 124.9, 123.0, 49.6, 21.6, 21.2. M.P.: 183.0 – 184.0 ^{o}C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{15}NO_3S$: 302.0845; found: 302.0845.

Product 3ma



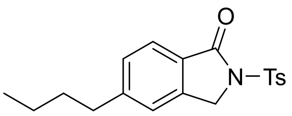
Yield of **3ma**: 58% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 2H), 4.86 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 165.7, 155.4, 152.6, 145.3, 135.3, 132.4, 130.9, 130.5, 130.1, 129.7, 128.1, 124.6, 121.8, 119.4, 119.1, 47.8, 21.7. M.P.: 160.0 – 160.8 ^{o}C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{21}H_{17}NO_4S$:380.0951; found: 380.0949.

Product 3na



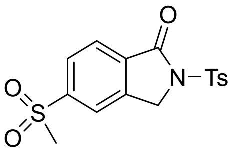
Yield of **3na**: 50% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 3.9 Hz, 2H), 4.85 (s, 2H), 2.45 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.1, 145.1, 141.4, 135.4, 129.9, 129.7 (overlap), 128.0, 127.5, 124.8, 123.6, 49.6, 22.0, 21.6. M.P.: 190.0 – 190.8 ^{o}C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{15}NO_3S$: 302.0845; found: 302.0844.

Product 3oa



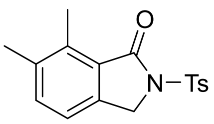
Yield of **3oa**: 52% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.26 (m, 4H), 4.87 (s, 2H), 2.73 – 2.66 (m, 2H), 2.41 (s, 3H), 1.60 (p, *J* = 7.5 Hz, 2H), 1.34(dd, *J* = 15 ,7.4 Hz, 2H), 0.94 – 0.90 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 166.1, 150.1, 145.1, 141.4, 135.5, 129.7, 129.4, 128.1, 127.8, 124.9, 123.0, 49.7, 36.1, 33.4, 22.2, 21.7, 13.8. M.P.: 104.0 – 105 ^{o}C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{21}NO_3S$: 344.1315; found: 344.1313.

Product 3pa



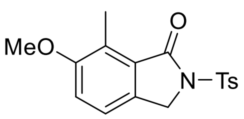
Yield of **3pa**: 32% as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.11 (s, 1H), 8.07 – 7.98 (m, 4H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.01 (s, 2H), 3.09 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 164.2, 145.8, 145.5, 141.7, 134.9, 134.7, 129.9, 128.2, 128.0, 126.3, 123.1, 49.7, 44.4, 21.7. M.P.: 241.0 – 242.0 ^{o}C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{15}NO_5S_2$: 366.0464; found: 366.0466.

Product 3qa



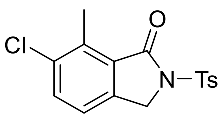
Yield of **3qa**: 75% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (d, *J* = 8.5 Hz, 2H), 7.35 (dd, *J* = 12.8, 7.9 Hz, 3H), 7.16 (d, *J* = 7.7 Hz, 1H), 4.79 (s, 2H), 2.55 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.1, 144.9, 139.2, 138.1, 138.0, 135.5, 134.9, 129.6, 128.1, 127.0, 120.1, 48.5, 21.6, 19.1, 13.1. M.P.: 159.5 – 160.0 ^{o}C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{17}NO_3S$: 316.1002; found: 316.1001.

Product 3ra



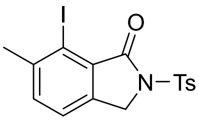
Yield of **3ra**: 91% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 4.78 (s, 2H), 3.85 (s, 3H), 2.49 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 166.9, 157.9, 145.0, 135.5, 132.8, 129.7, 128.1, 128.1, 120.8, 115.6, 56.1, 48.4, 21.6, 9.6. M.P.: 170.5 – 171.0 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{17}NO_4S$: 332.0951; found: 332.0950.

Product 3sa



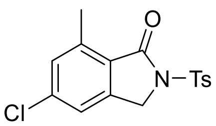
Yield of **3sa**: 82% as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 4.82 (s, 2H), 2.67 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 165.9, 145.3, 139.9, 137.6, 135.6, 135.2, 134.0, 129.8, 128.8, 128.2, 121.5, 48.4, 21.7, 13.6. M.P.: 187.5 – 188.0 °C. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{14}ClNO_3S$: 336.0456; found: 336.0455.

Product 3ta



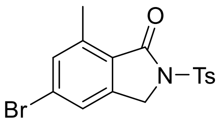
Yield of **3ta**: 48% as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.04 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 13.5, 7.9 Hz, 3H), 4.76 (s, 2H), 2.51 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 164.8, 145.2, 143.9, 141.1, 135.1, 134.5, 130.4, 129.8, 128.3, 122.6, 97.7, 47.1, 27.9, 21.7. M.P.: 178.0 – 179.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{14}INO_3S$: 427.9812; found: 427.9810.

Product 3ua



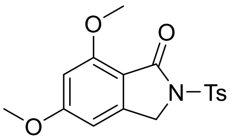
Yield of **3ua**: 94% as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (d, *J* = 7.9 Hz, 2H), 7.64 – 6.83 (m, 4H), 4.83 (s, 2H), 2.58 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =165.7, 145.2, 143.0, 141.2, 139.6, 135.3, 130.9, 129.8, 128.1, 126.0, 121.0, 48.7, 21.6, 17.2. M.P.: 188.5 – 189.0 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{14}ClNO_3S$: 336.0456; found: 336.0453.

Product 3va



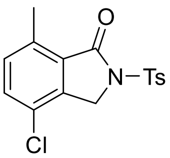
Yield of **3va** : 94% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.01 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.39 – 7.31 (m, 3H), 4.83 (s, 2H), 2.58 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 165.8, 145.2, 143.1, 141.3, 135.2, 133.8, 129.8, 128.2, 128.1, 126.4, 123.9, 48.6, 21.6, 17.2. M.P.: 190.0 – 190.5 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{14}BrNO_3S$: 379.9951; found: 379.9951.

Product 3wa



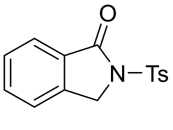
Yield of **3wa**: 57% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.01 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.47 (s, 1H), 6.37 (s, 1H), 4.77 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =166.3, 164.2, 159.8, 145.7, 144.7, 135.7, 129.6, 128.2, 110.8, 99.0, 98.7, 55.9, 55.9, 49.2, 21.6. M.P.: 157.0 – 158.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{17}NO_5S$: 348.0901; found: 348.0900.

Product 3xa



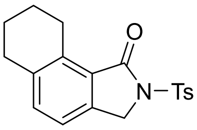
Yield of **3xa**: 72% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 4.82 (s, 2H), 2.59 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 165.8, 145.3, 139.4, 138.1, 135.2, 133.0, 132.2, 129.8, 129.0, 128.1, 126.6, 48.3, 21.7, 16.9. M.P.: 194.0 – 195.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{14}ClNO_3S$:336.0456; found: 336.0455.

Product 3ya



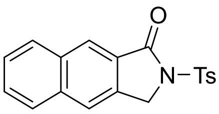
Yield of **3ya**: 56% as a white solid. ^{1}H NMR (600 MHz, CDCl3) δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.91 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ (ppm) = 166.1, 145.2, 141.0, 135.3, 133.8, 130.1, 129.7, 128.8, 128.1, 125.0, 123.3, 49.8, 21.6. M.P.: 210.0 – 211.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{13}NO_3S$: 288.0689; found: 288.0687.

Product 3za



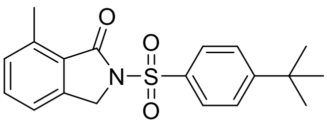
Yield of **3za**: 65% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.00 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 4.80 (s, 2H), 3.14 (s, 2H), 2.77 (s, 2H), 2.41 (s, 3H), 1.76 (t, *J* = 3.4 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 166.9, 144.9, 139.4, 138.6, 138.2, 135.5, 134.8, 129.6, 128.1, 126.8, 119.9, 48.9, 29.4, 24.9, 22.4, 22.0, 21.6. M.P.: 194.0 – 194.6 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}NO_3S$: 342.1158; found: 342.1157.

Product 3za'



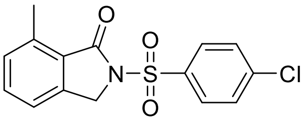
Yield of **3za'**: 59% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.36 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 9.5 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.06 (s, 2H), 2.42 (s, 3H). 13C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.0, 145.3, 136.1, 135.4, 134.8, 132.8, 129.8, 128.8, 128.2, 128.0, 127.8, 126.9, 126.4, 126.1, 122.3, 49.7, 21.7. M.P.: 221.0 – 220.0 °C. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{15}NO_3S$: 338.0845; found: 338.0843.

Product 3ab



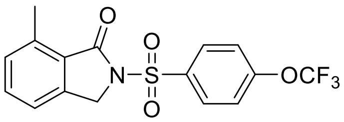
Yield of **3ab**: 92% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.09 – 8.03 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 4.86 (s, 2H), 2.62 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 166.7, 157.8, 141.6, 139.6, 135.4, 133.3, 130.6, 127.9, 127.4, 126.2, 120.6, 49.2, 35.2, 31.0, 17.5. M.P.: 210.0 – 210.2 °C. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{21}NO_3S$: 344.1315; found: 344.1314.

Product 3ac



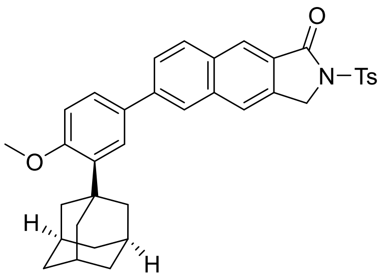
Yield of **3ac**: 85% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.14 – 8.04 (m, 2H), 7.58 – 7.44 (m, 3H), 7.31 – 7.18 (m, 3H), 4.86 (s, 2H), 2.62 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) =166.8, 141.5, 140.7, 139.7, 136.8, 133.6, 130.7, 129.6, 129.4, 127.1, 120.7, 49.2, 17.5. M.P.: 187.0 – 188 ºC. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{15}H_{12}ClNO_3S$: 322.0299; found: 322.0300.

Product 3ad



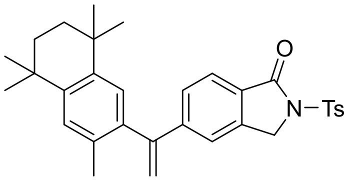
Yield of **3ad**: 61% as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) =8.22 (d, *J* = 8.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.22 (m, 2H), 4.87 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) =166.8, 153.1, 141.5, 139.8, 136.5, 133.6, 130.8, 130.5, 127.1, 120.8, 120.7, 120.1 (q, *J* = 255 Hz), 49.2, 17.5. M.P.: 184.0 – 184.5 ºC. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{16}H_{12}F_3NO_4S$: 372.0512; found: 372.0514.

Product 5



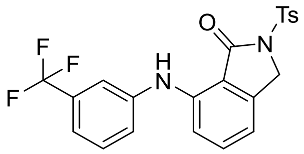
Yield of **5**: 43% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.36 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.04 – 7.99 (m, 2H), 7.92 (s, 1H), 7.81 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 1H), 5.07 (s, 2H), 3.91 (s, 3H), 2.42 (s, 3H), 2.18 (d, *J* = 2.9 Hz, 6H), 2.10 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 166.1, 159.1, 145.2, 141.9, 139.1, 136.6, 135.4, 135.2, 132.0, 131.6, 130.1, 129.8, 128.2, 127.3, 126.8, 126.0, 125.9, 125.8, 124.8, 122.2, 112.1, 55.2, 49.7, 40.5, 37.2, 37.1, 29.0, 21.7. M.P.: 273.0 – 274.0 ºC. HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{36}H_{35}NO_4S$: 578.2360; found: 578.2353.

Product 7



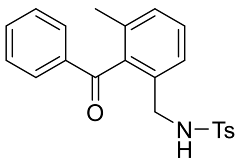
Yield of **7**: 46% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.10 – 7.98 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.41 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.09 (d, *J* = 9.6 Hz, 2H), 5.80 (d, *J* = 1.2 Hz, 1H), 5.36 (d, *J* = 1.2 Hz, 1H), 4.87 (s, 2H), 2.42 (s, 3H), 1.90 (s, 3H), 1.70 (s, 4H), 1.30 (s, 6H), 1.27 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 165.9, 149.0, 147.2, 145.1, 144.7, 142.5, 141.3, 137.6, 135.5, 132.5, 129.7, 129.1, 128.2, 128.1, 128.0, 127.4, 124.9, 121.2, 117.9, 49.8, 35.1, 35.1, 34.0, 33.9, 31.9, 31.8, 21.6, 19.9. M.P.: 209.0 – 209.8 ºC HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{32}H_{35}NO_3S$: 514.2410; found: 514.2410.

Product 9



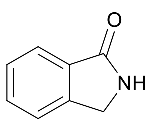
Yield of **9**: 52% as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.54 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.37 (d, *J* = 8.2 Hz, 3H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 4.88 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 168.1, 145.3, 144.0, 142.5, 140.4, 135.6, 135.4, 132.0 (q, *J* = 32.0 Hz), 130.0, 129.8, 128.0, 124.1, 123.8 (q, *J* = 270.9 Hz), 120.1 (q, *J* = 3.8 Hz), 117.5 (q, *J* = 3.8 Hz), 113.6, 112.7, 111.0, 49.8, 21.7. M.P.:189.0 – 190 ºC. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{17}F_3N_2O_3S$: 447.0985; found: 447.0982.

Product 10



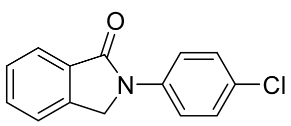
Yield of **10**: 89% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.62 (dd, *J* = 13.5, 7.8 Hz, 5H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (td, *J* = 13.1, 12.2, 7.5 Hz, 5H), 3.84 (d, *J* = 6.3 Hz, 2H), 2.39 (s, 3H), 2.05 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =199.9, 143.2, 139.2, 136.8, 136.5, 134.8, 134.1, 133.5, 130.1, 129.6, 129.5, 129.4, 128.9, 127.5, 127.1, 77.3, 76.7, 45.4, 21.5, 19.7. M.P.: 112.0 – 112.5 ºC HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{21}NO_3S$: 380.1315; found: 380.1314.

Product 12



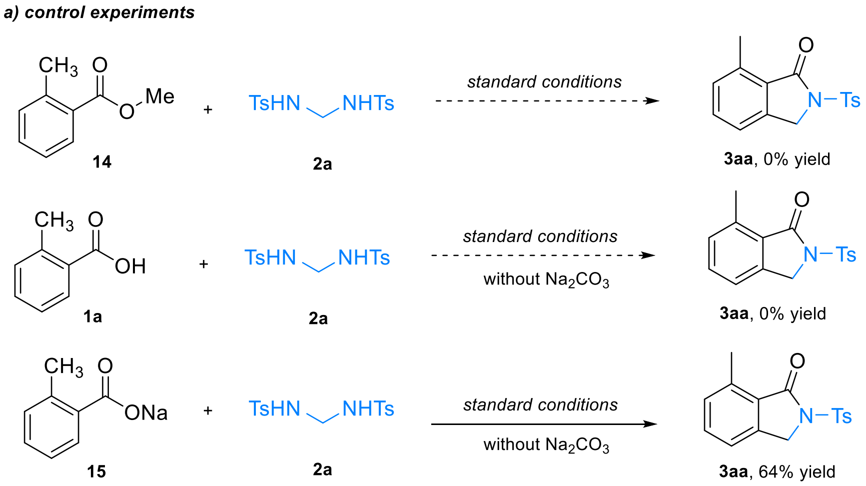
Yield of **12**: 48% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.90 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 6.7 Hz, 2H), 4.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =171.9, 143.6, 132.0, 131.8, 128.0, 123.8, 123.2, 45.7.

Product 13



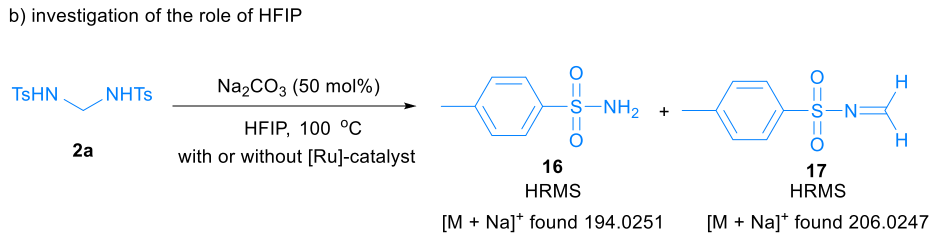
Yield of **13**: 40% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.36 (d, *J* = 8.9 Hz, 2H), 4.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =167.5, 139.8, 138.1, 132.9, 132.3, 129.4, 129.1, 128.5, 124.1, 122.6, 120.3, 50.6.

4. Mechanistic studies



Scheme 1 Control experiments

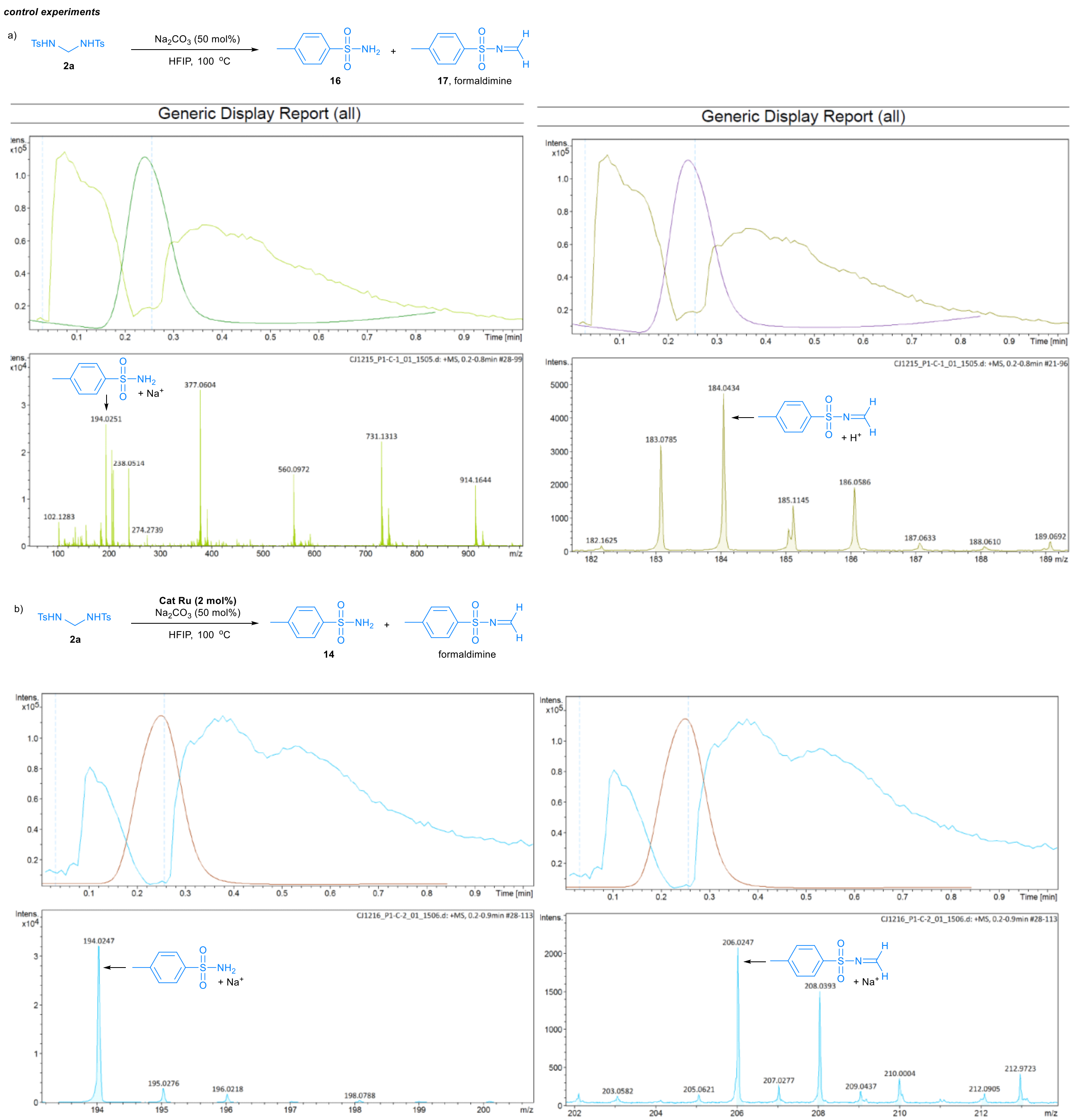
2-methylbenzoate **14** proved to be ineffective for this catalytic system, which demonstrated the importance of the carboxylate group in this reaction. In the absence of base, 2-methylbenzoic acid **1a** failed to react with bis(tosylamido)methane **2a**. Under the standard conditions, sodium 2-methylbenzoate **15** participated in this transformation smoothly to give the expected product 3aa in 64% yield. ***These results indicate the important role of Na_2CO_3 in this reaction.***



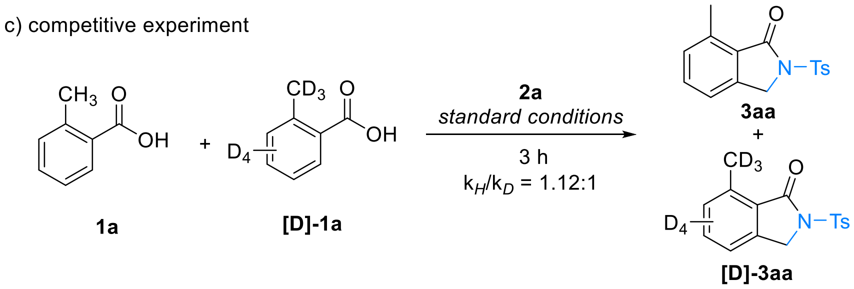
Scheme 2 Investigation of the role of HFIP

2a (70.8 mg, 0.2 mmol) and Na_2CO_3 (10.6 mg, 0.1 mmol) were dissolved in HFIP (1.5 mL) in the presence or absence of $[RuCl_2(p\text{-cymene})]_2$ (2.45 mg, 0.004 mmol). Then, the mixture was stirred at 100℃ for 5 h. The reaction mixture was detected by HRMS.

Both byproduct $TsNH_2$ ($[M + Na]^+$ found 194.0251) and formaldimine species ($[M + Na]^+$ found 206.0247) were detected by HRMS. ***These results suggested that the acidic solvent HFIP may promote the decomposition process of bis(tosylamido)methane 2a to reactive formaldimine intermediate.***

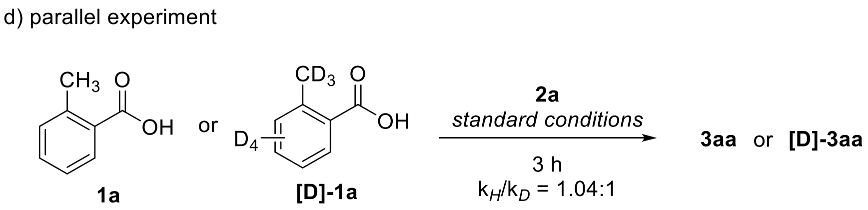


Scheme 3 Investigation of the role of HFIP



1a (13.6 mg, 0.1 mmol), **[D]-1a** (14.3 mg, 0.1 mmol), and **2a** (141.6 mg, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.45 mg, 0.004 mmol) and Na_2CO_3 (10.6 mg, 0.1 mmol) were dissolved in HFIP

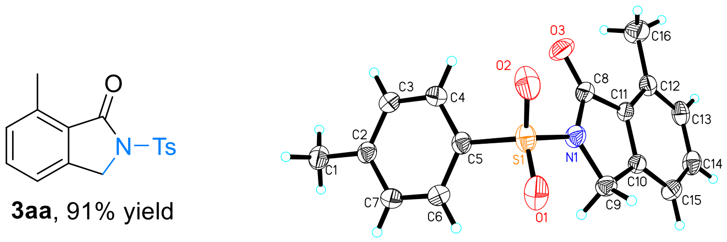
(1.5 mL). Then, the mixture was stirred at 100 °C for 3 h. Yields determined by 1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard: k_H/k_D = 1.12:1.

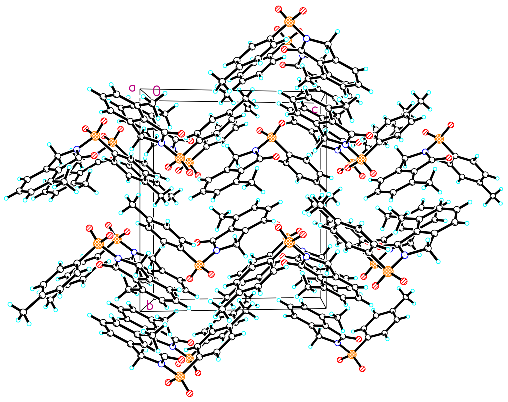


1a (27.2 mg, 0.2 mmol) or **[D]-1a** (28.6 mg, 0.2 mmol), and **2a** (141.6 mg, 0.4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.45 mg, 0.004 mmol) and Na_2CO_3 (10.6 mg, 0.1 mmol) were dissolved in HFIP (1.5 mL), respectively. Then, the mixture was stirred at 100 ℃ for 3 h. Yields determined by 1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard: k_H/k_D = 1.04:1.

There are no significant kinetic isotope effects (KIE) in both competitive (k_H/k_D = 1.12:1) and parallel (k_H/k_D = 1.04:1) reactions, indicating the ruthenium-catalyzed C−H bond activation may not be the rate-determining step in this transformation.

5. X-Ray structure of 3aa

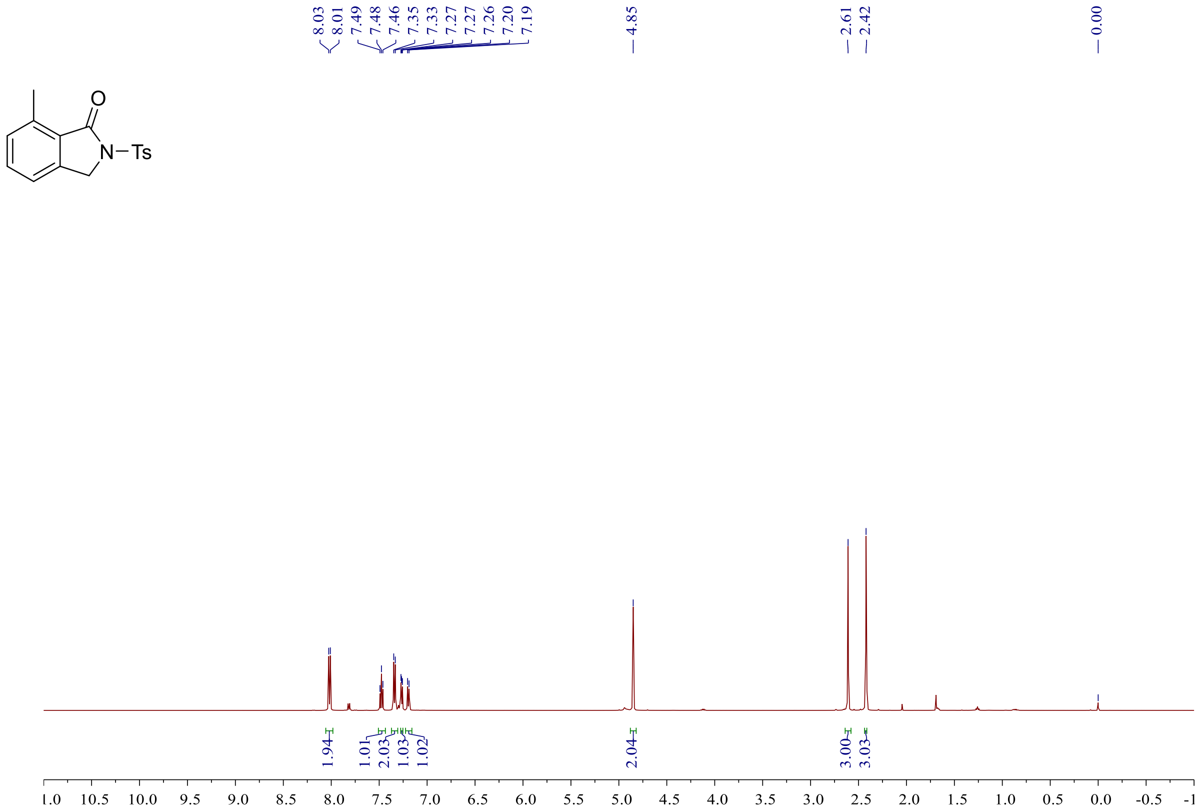


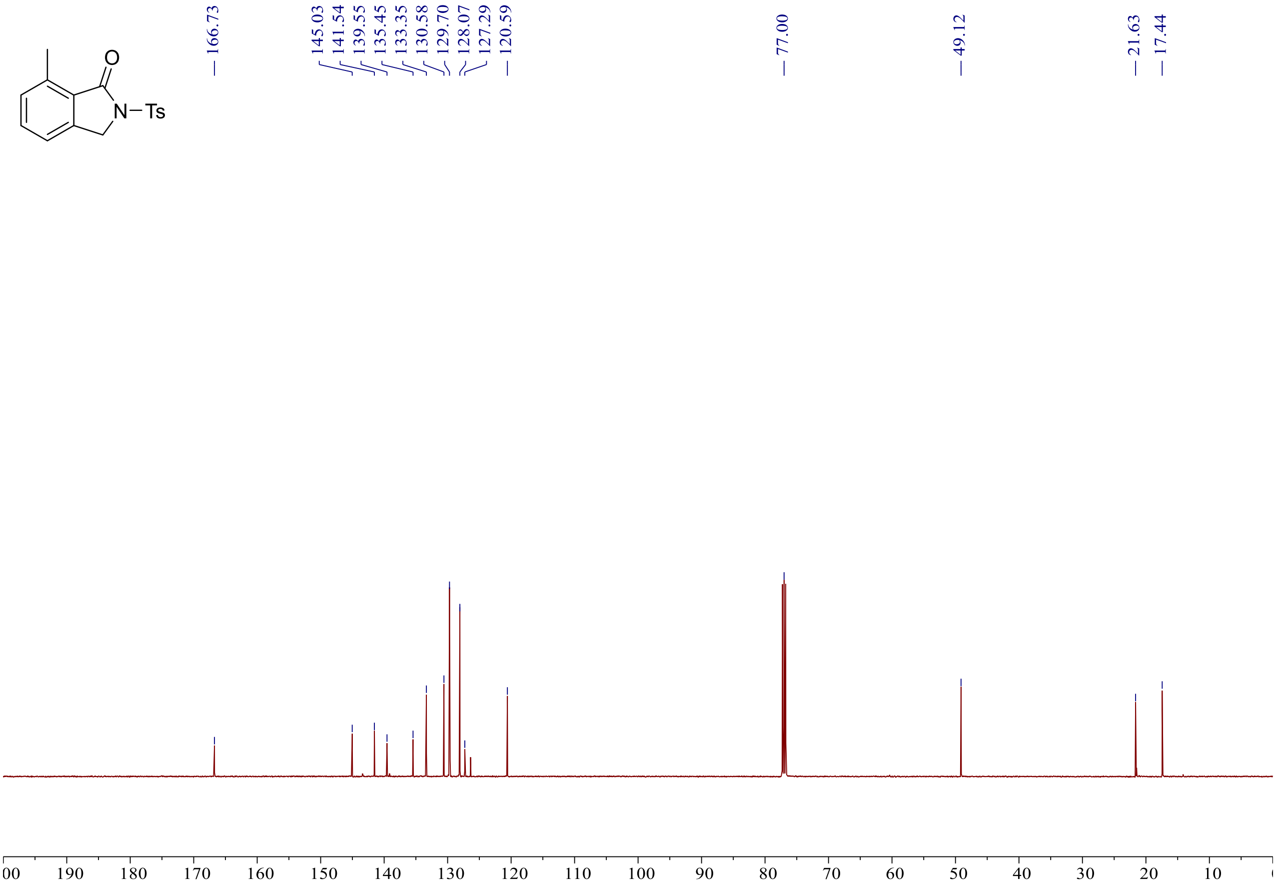


CCDC number: 2039860

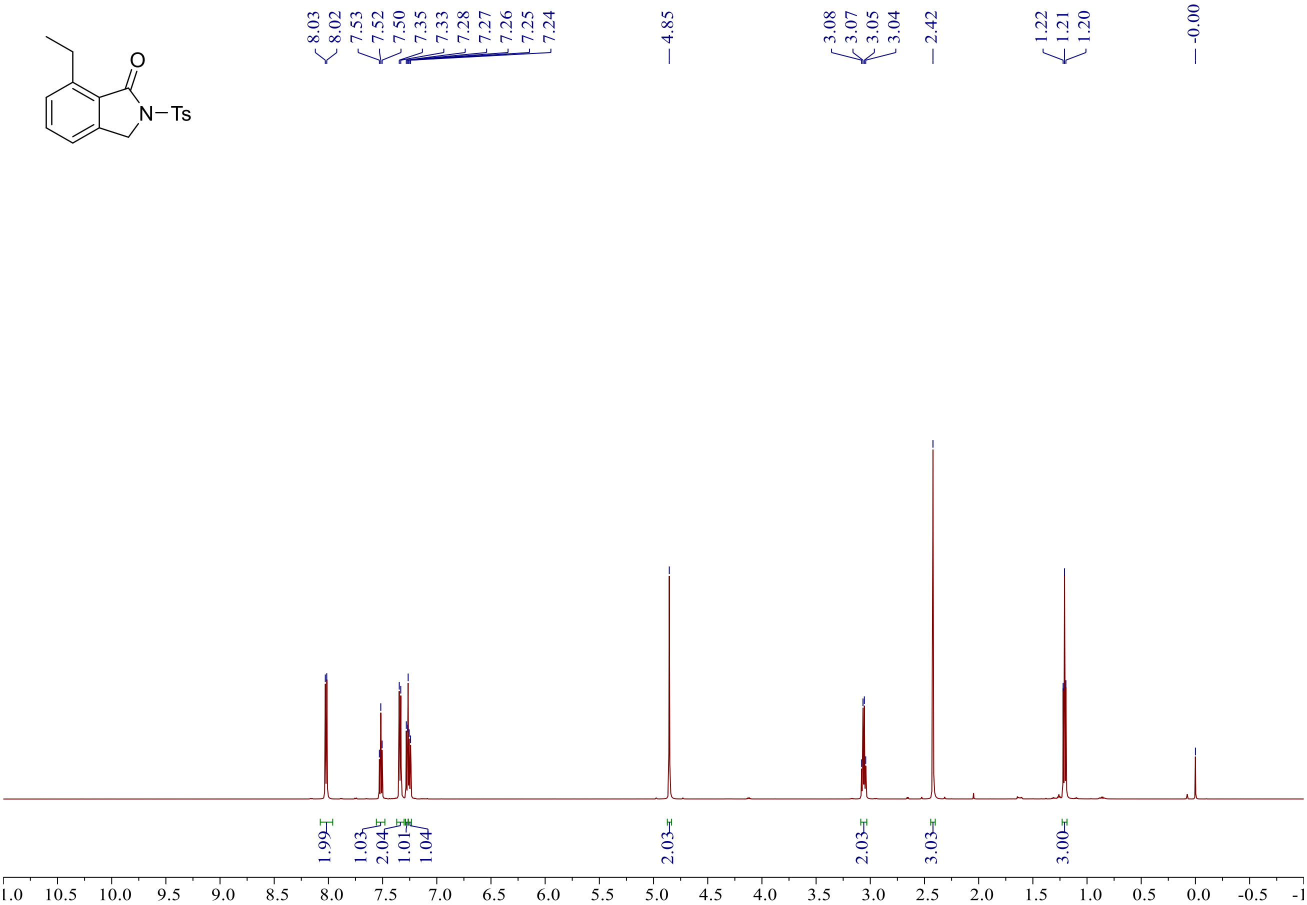
6. NMR Spectra of products 3aa-3za’, 3ab-3ad, 5, 7, 9, 10, 12, 13

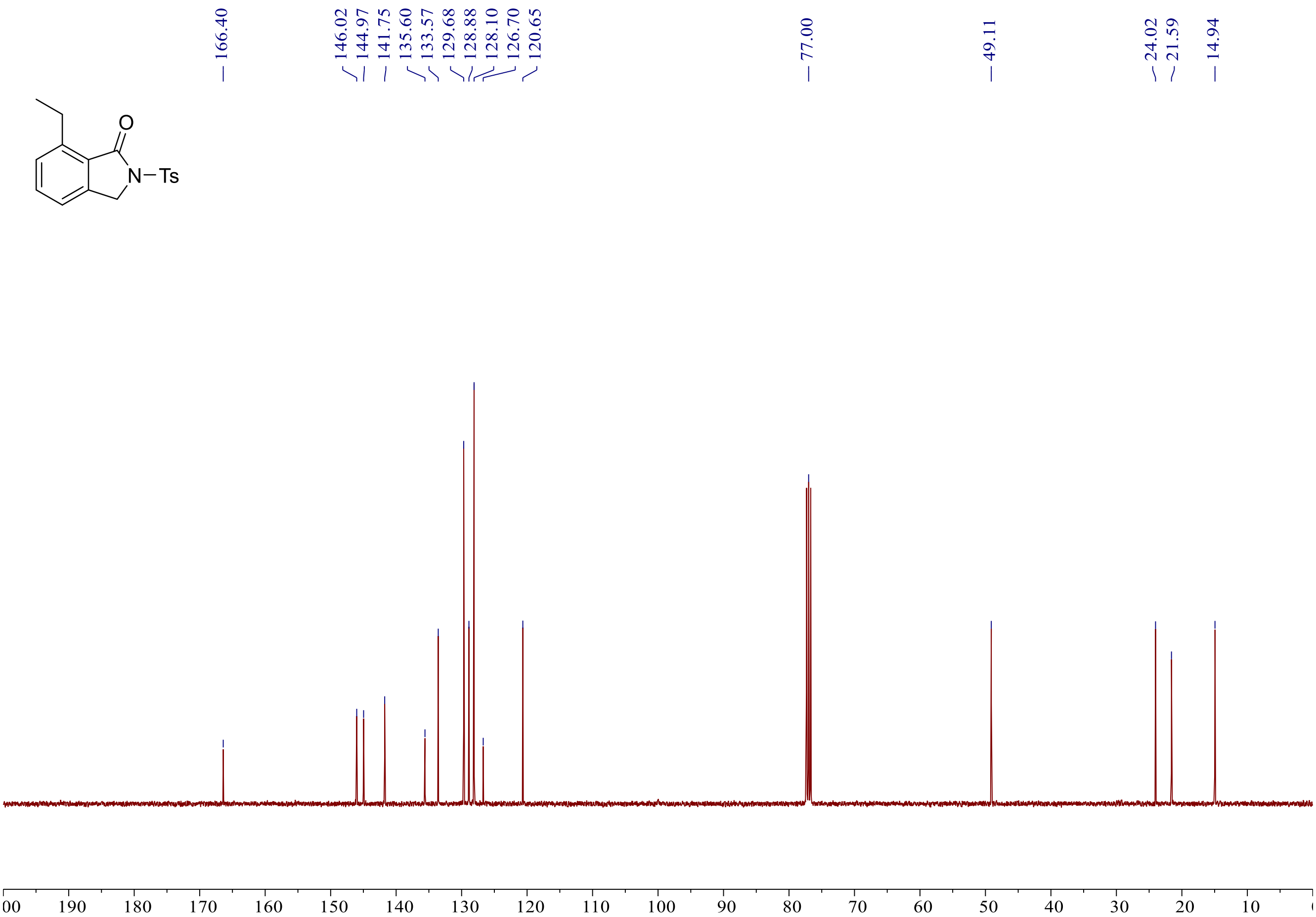
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 3aa



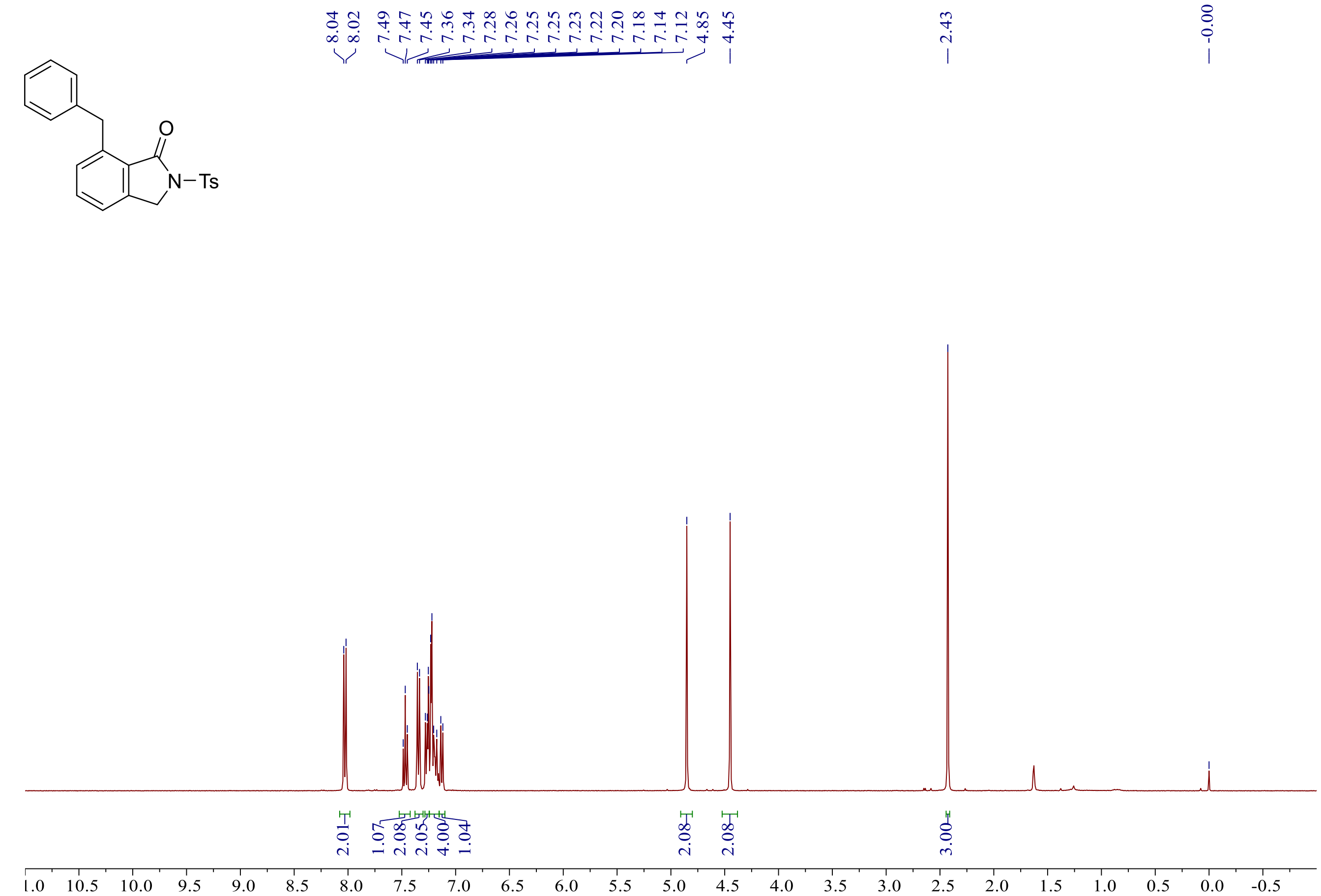


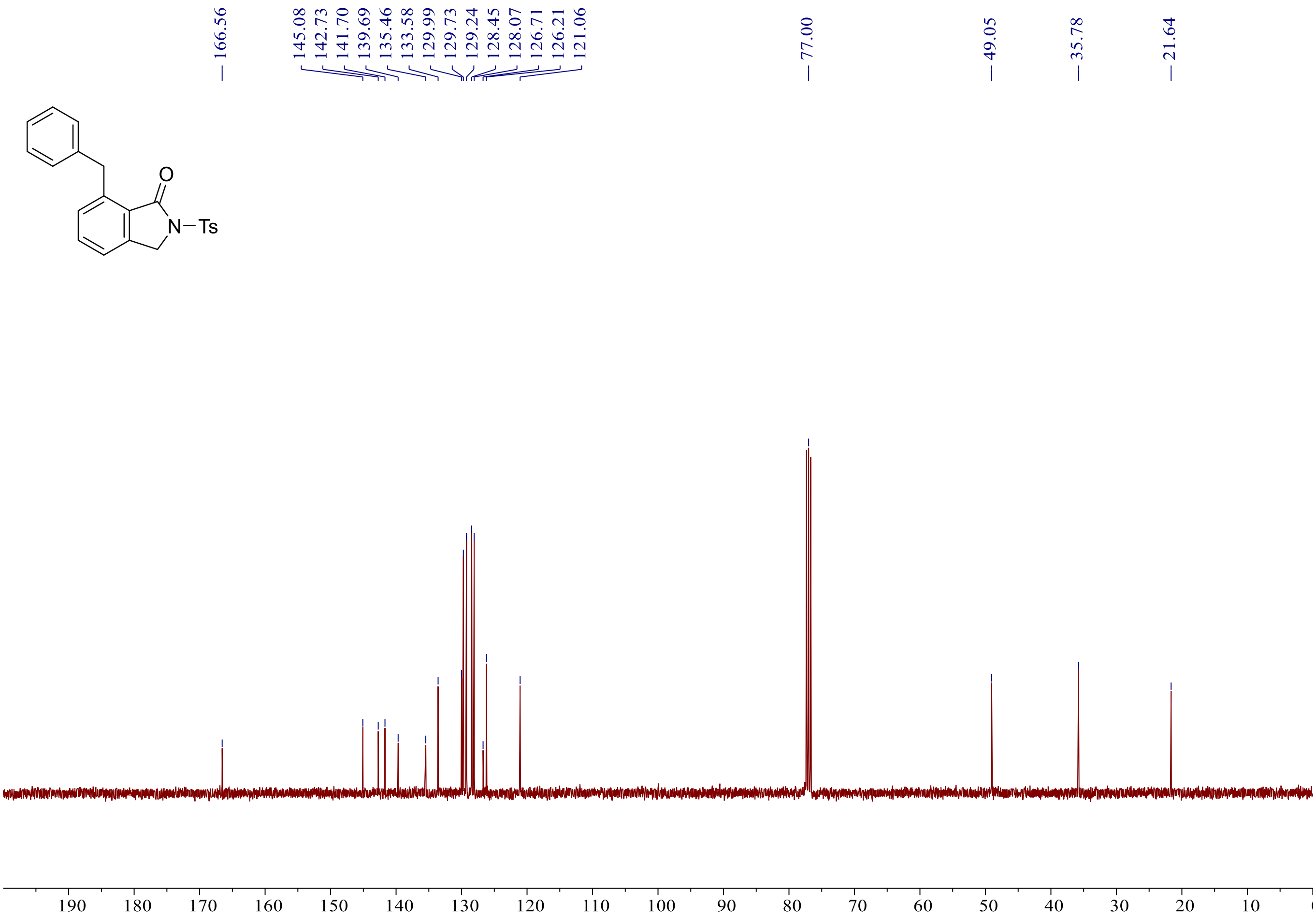
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectra of product 3ba



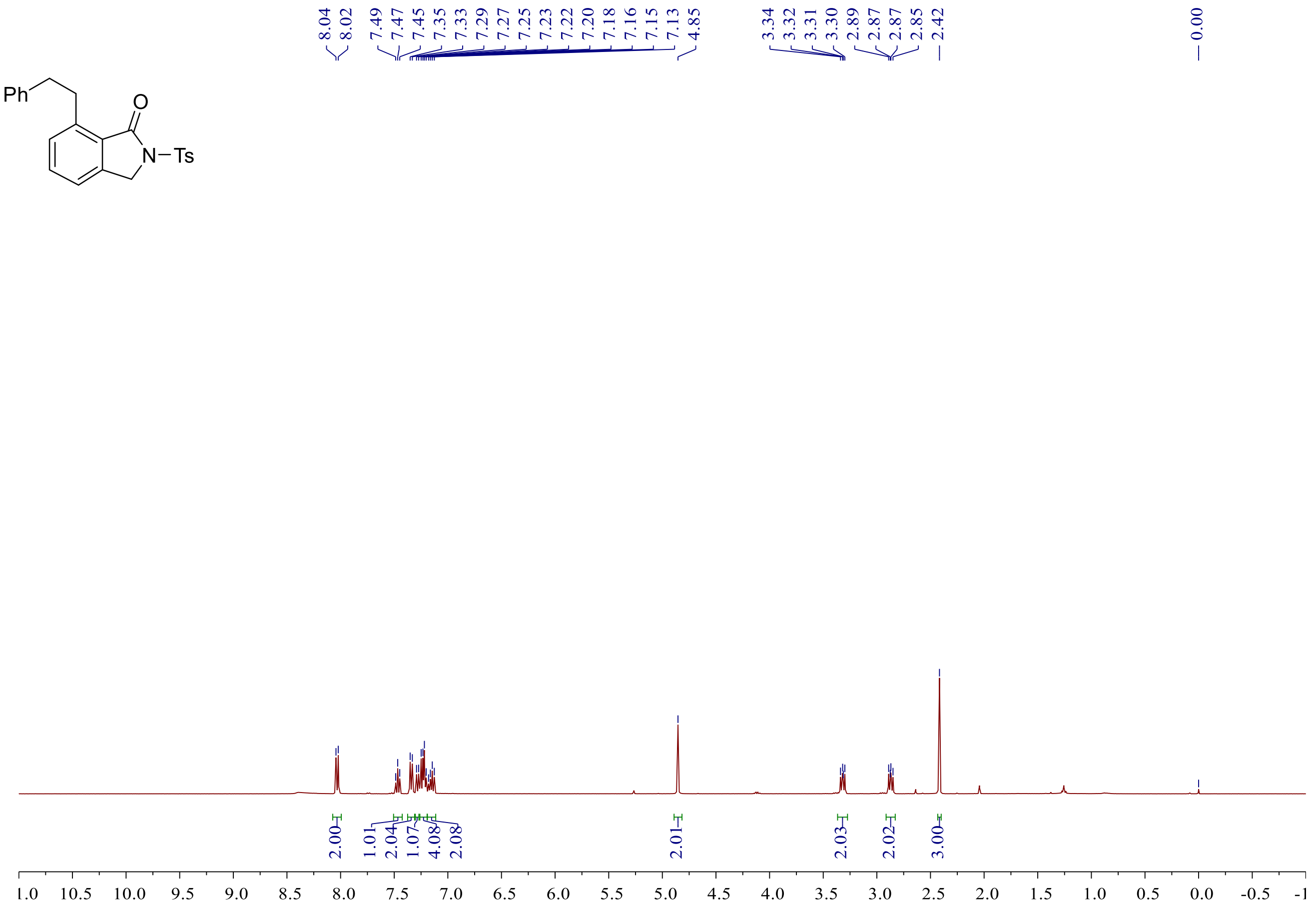


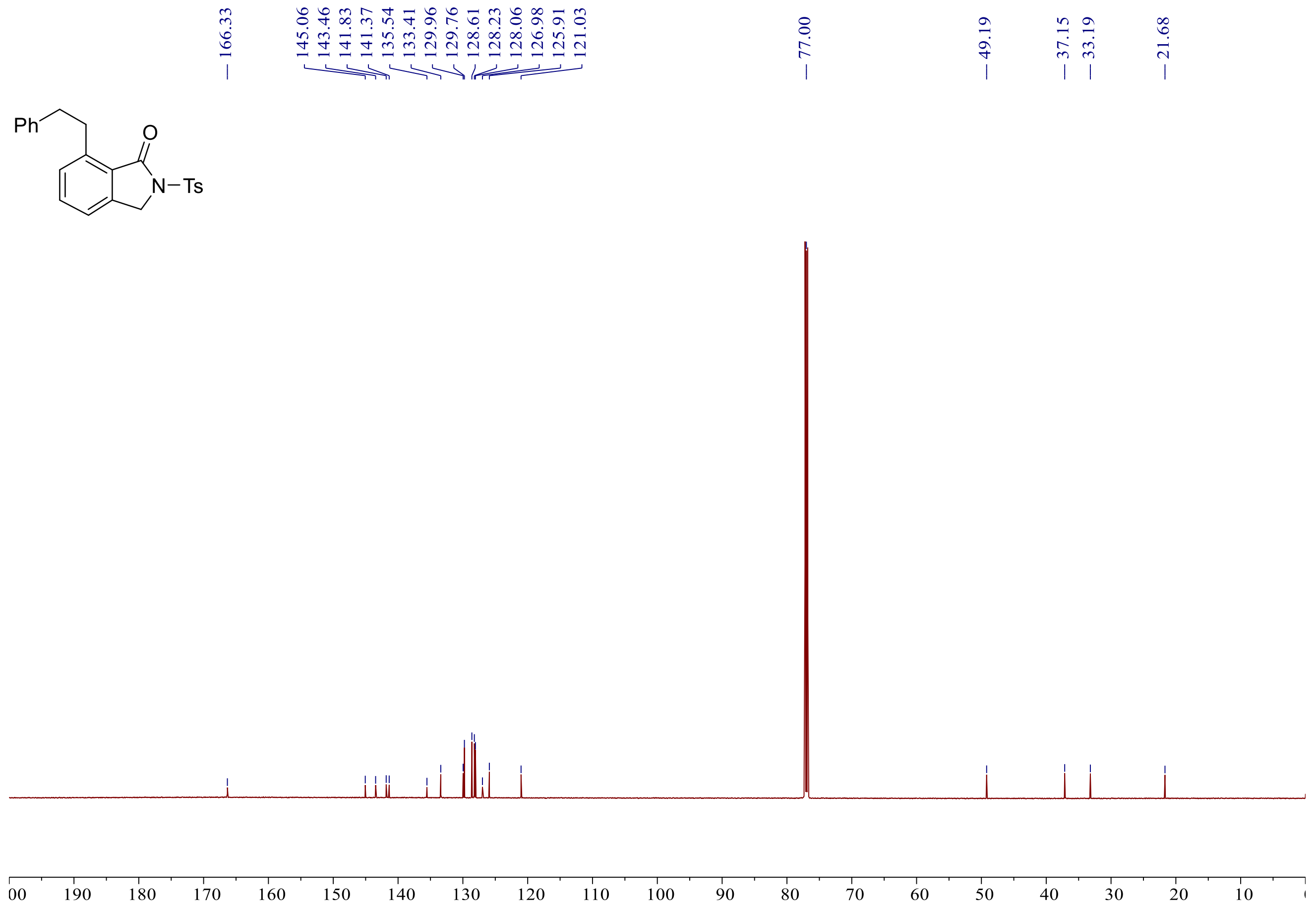
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ca



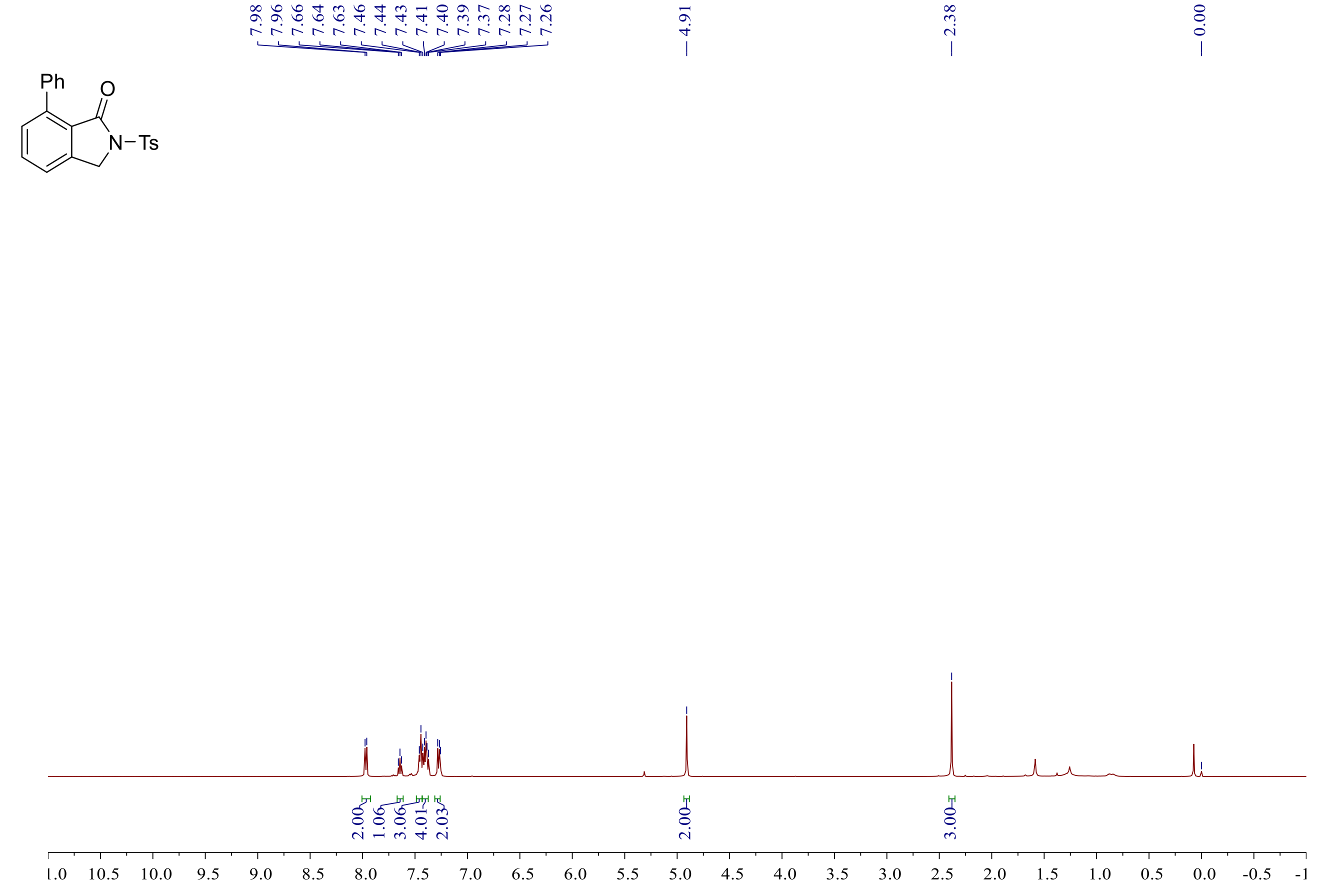


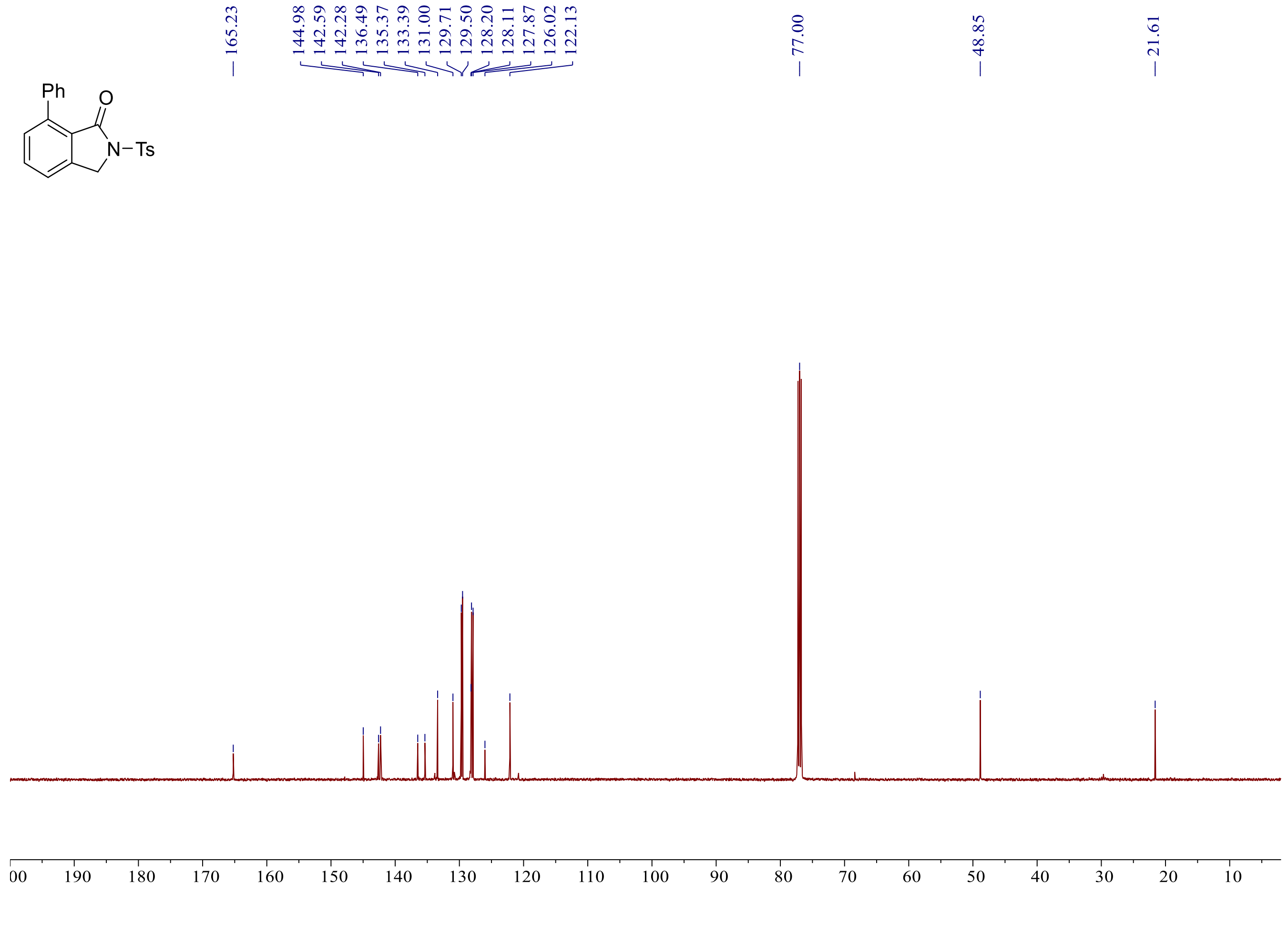
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (150 MHz, $CDCl_3$) spectra of product 3da



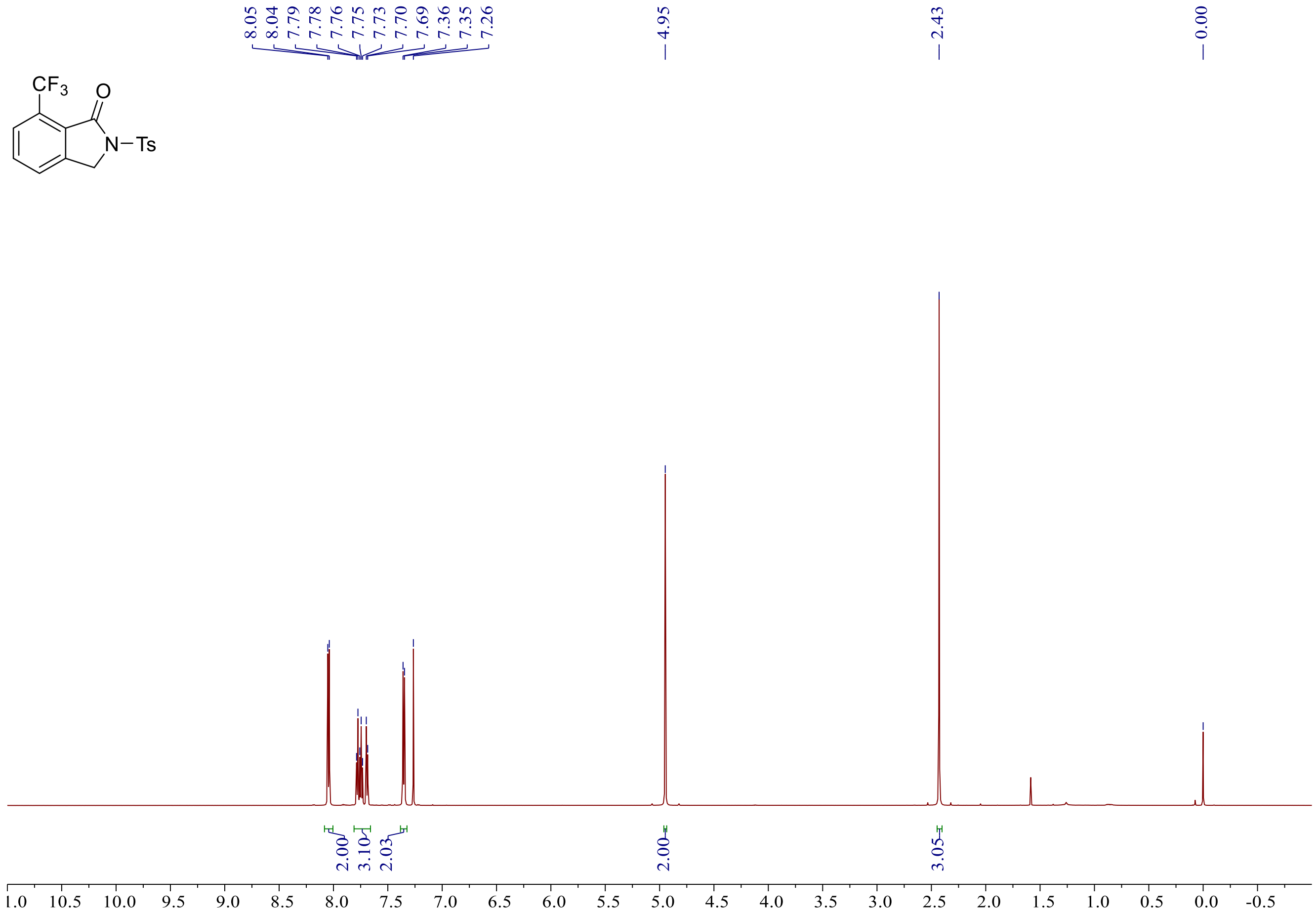


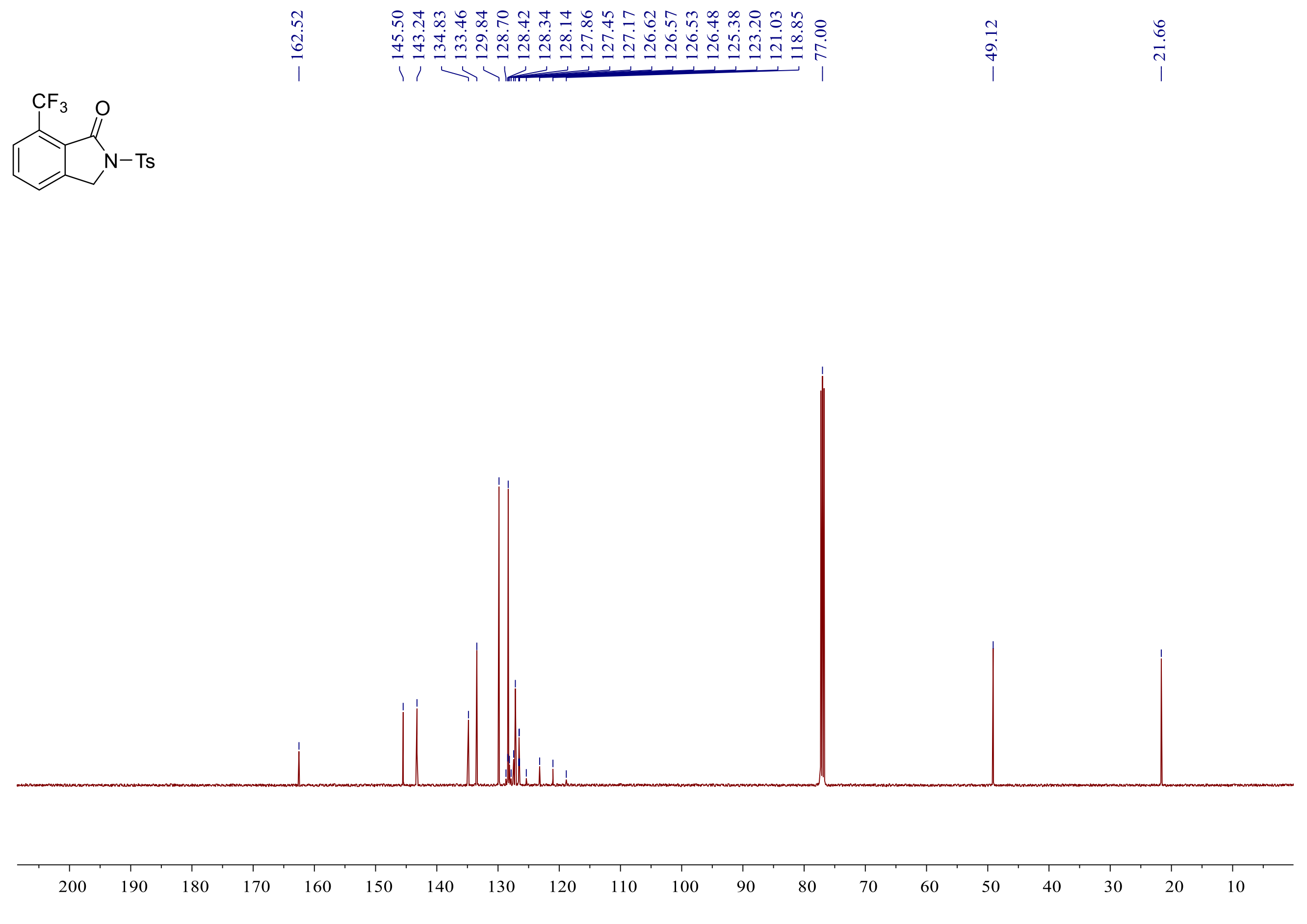
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 3ea



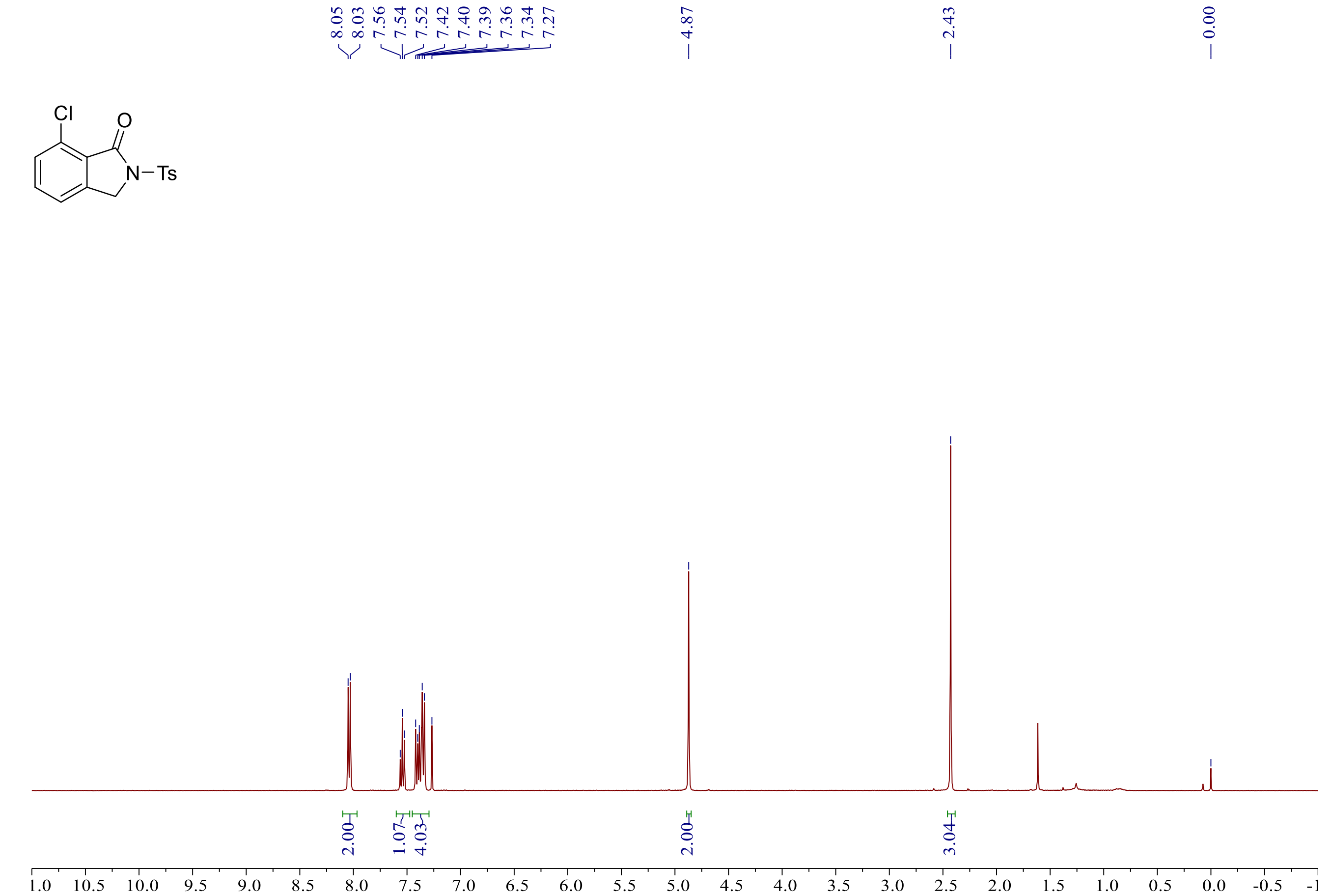


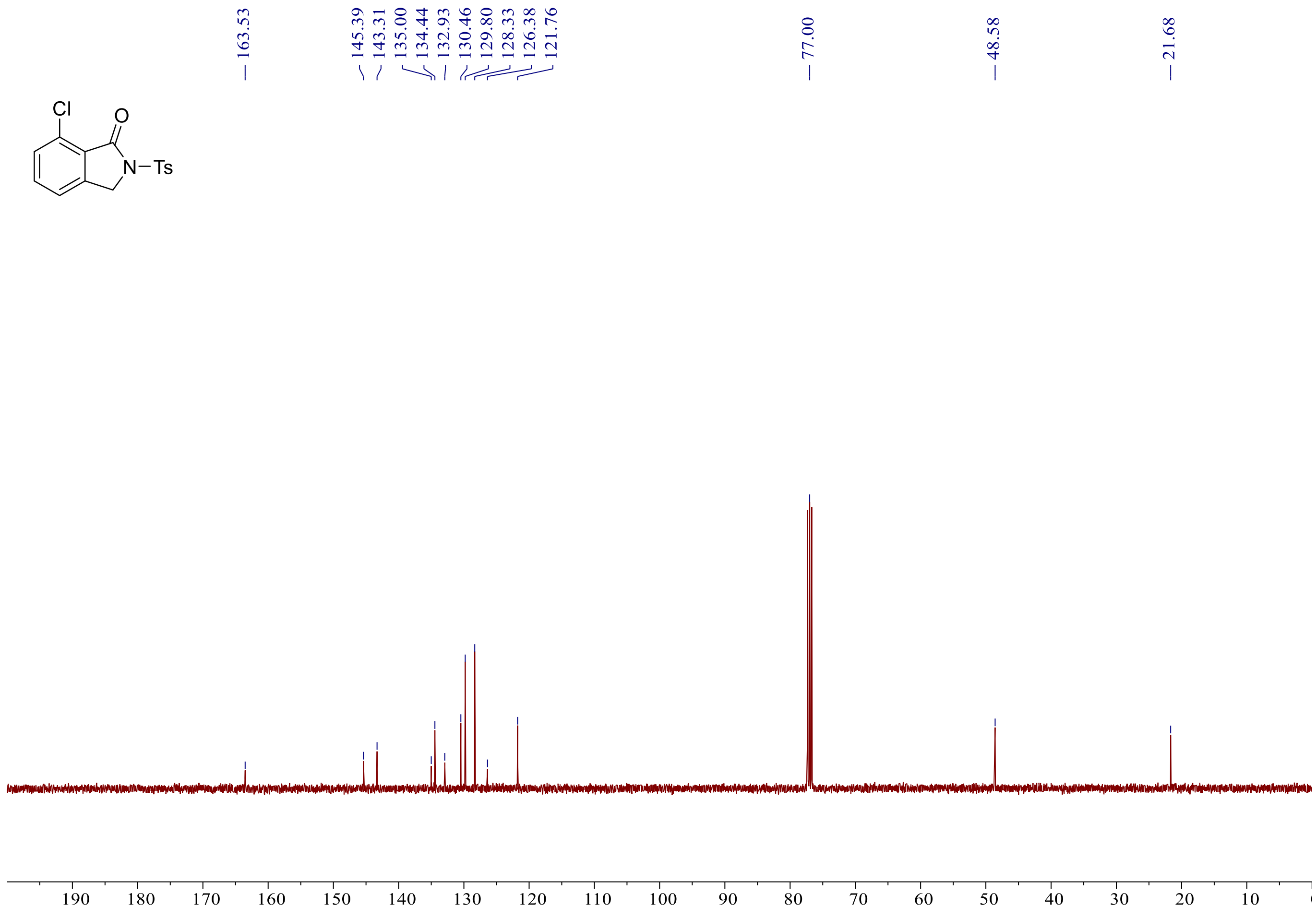
[1]H NMR (600 MHz, $CDCl_3$) and [13]C NMR (125 MHz, $CDCl_3$) spectra of product 3fa



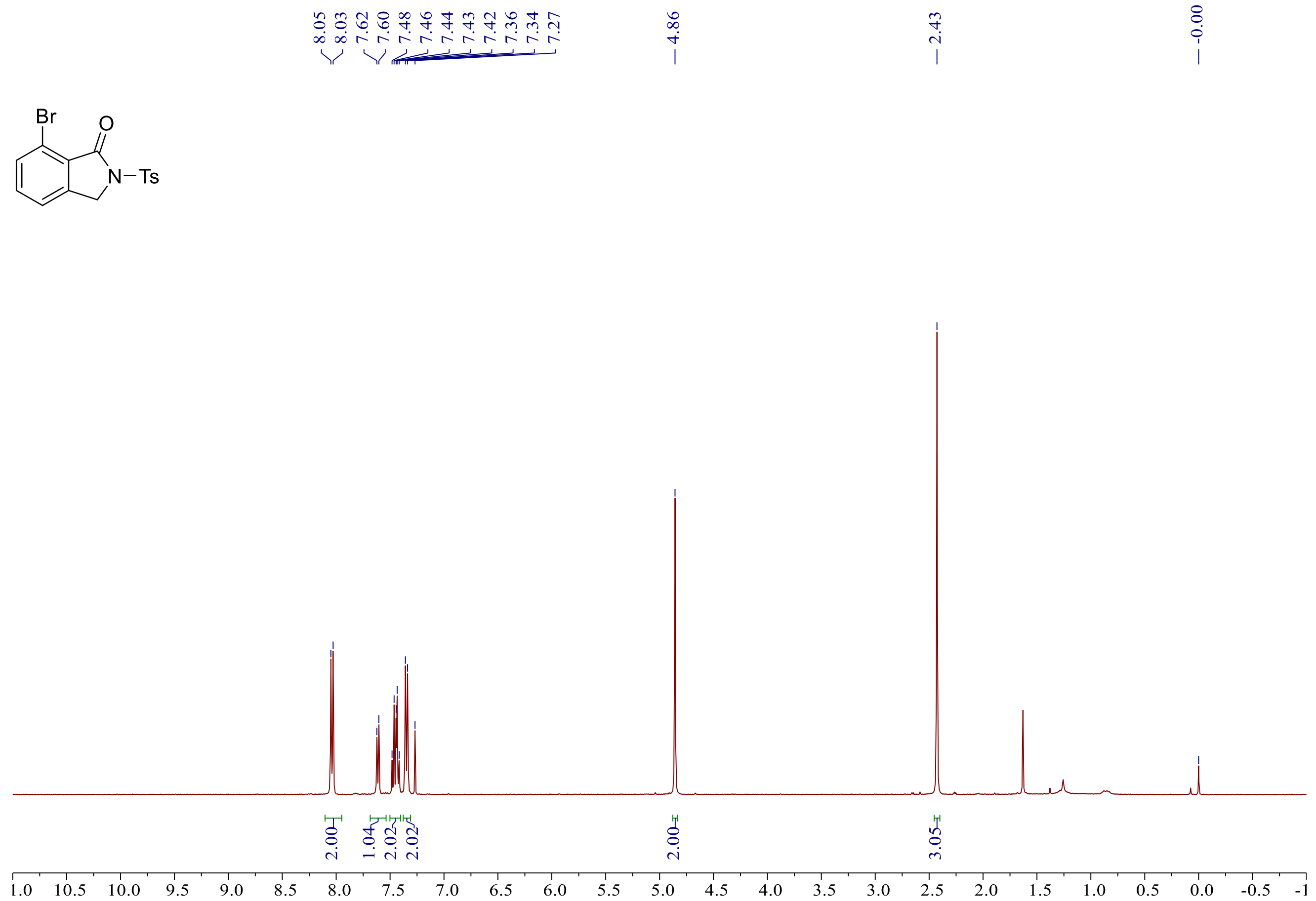


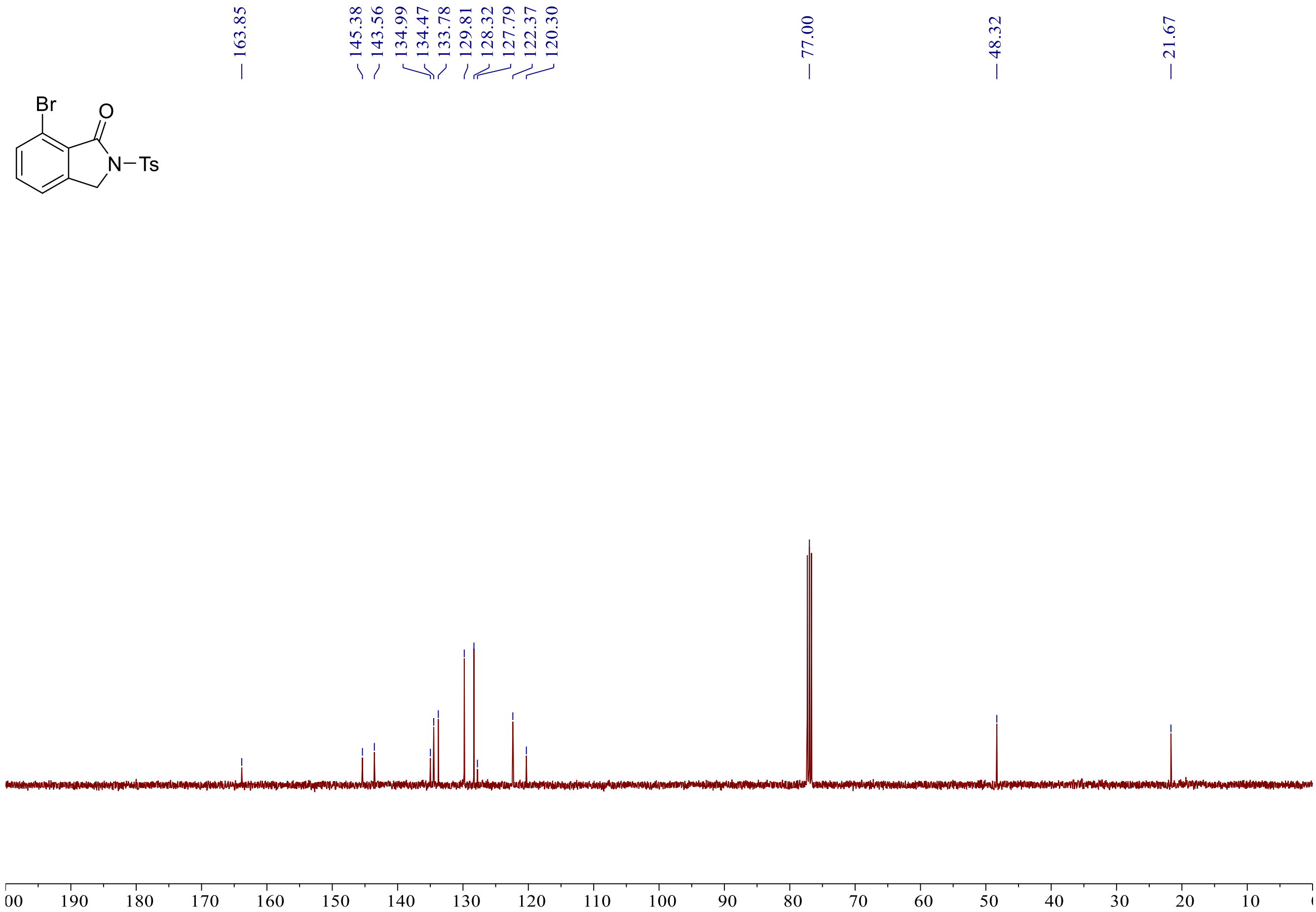
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ga



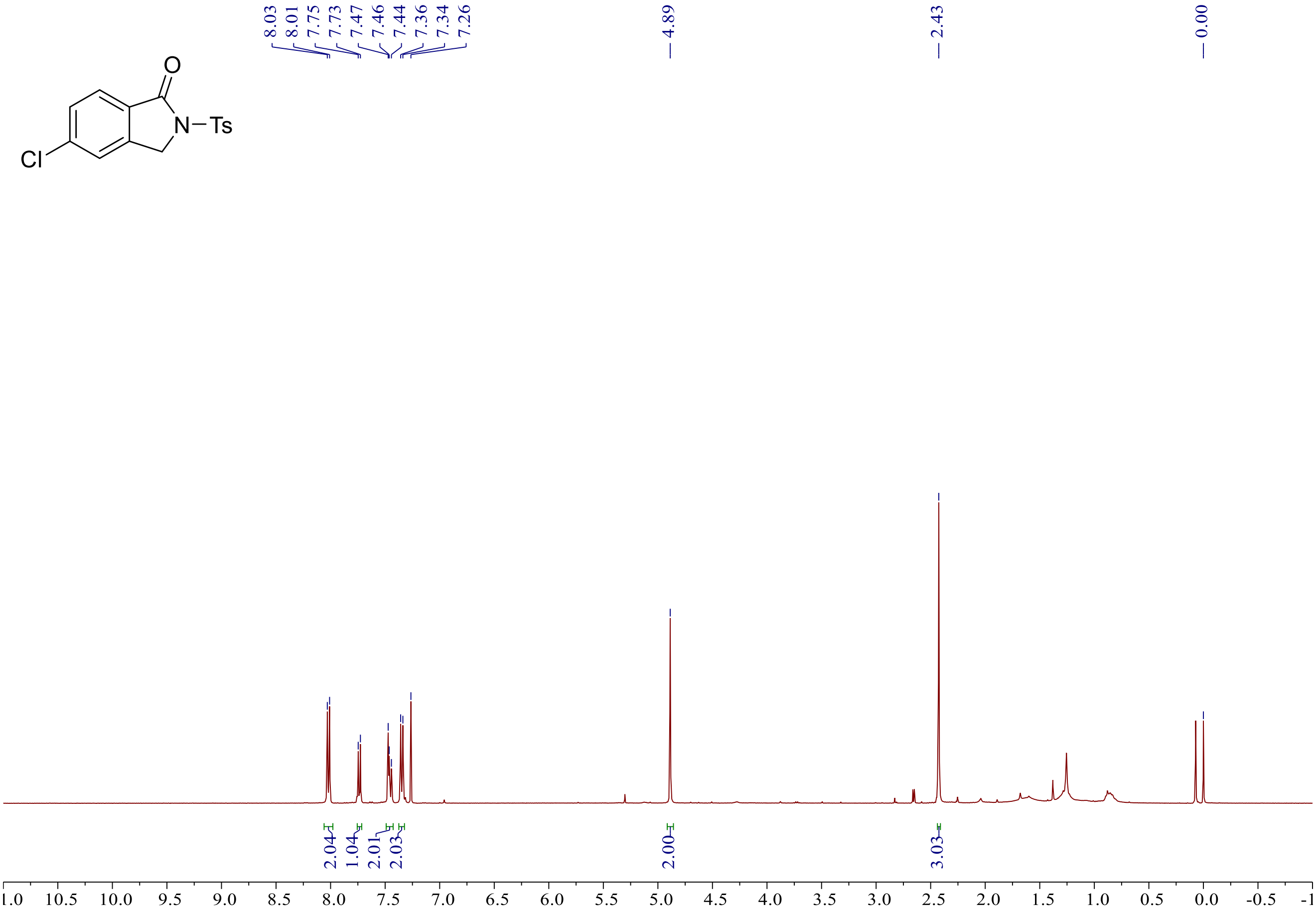


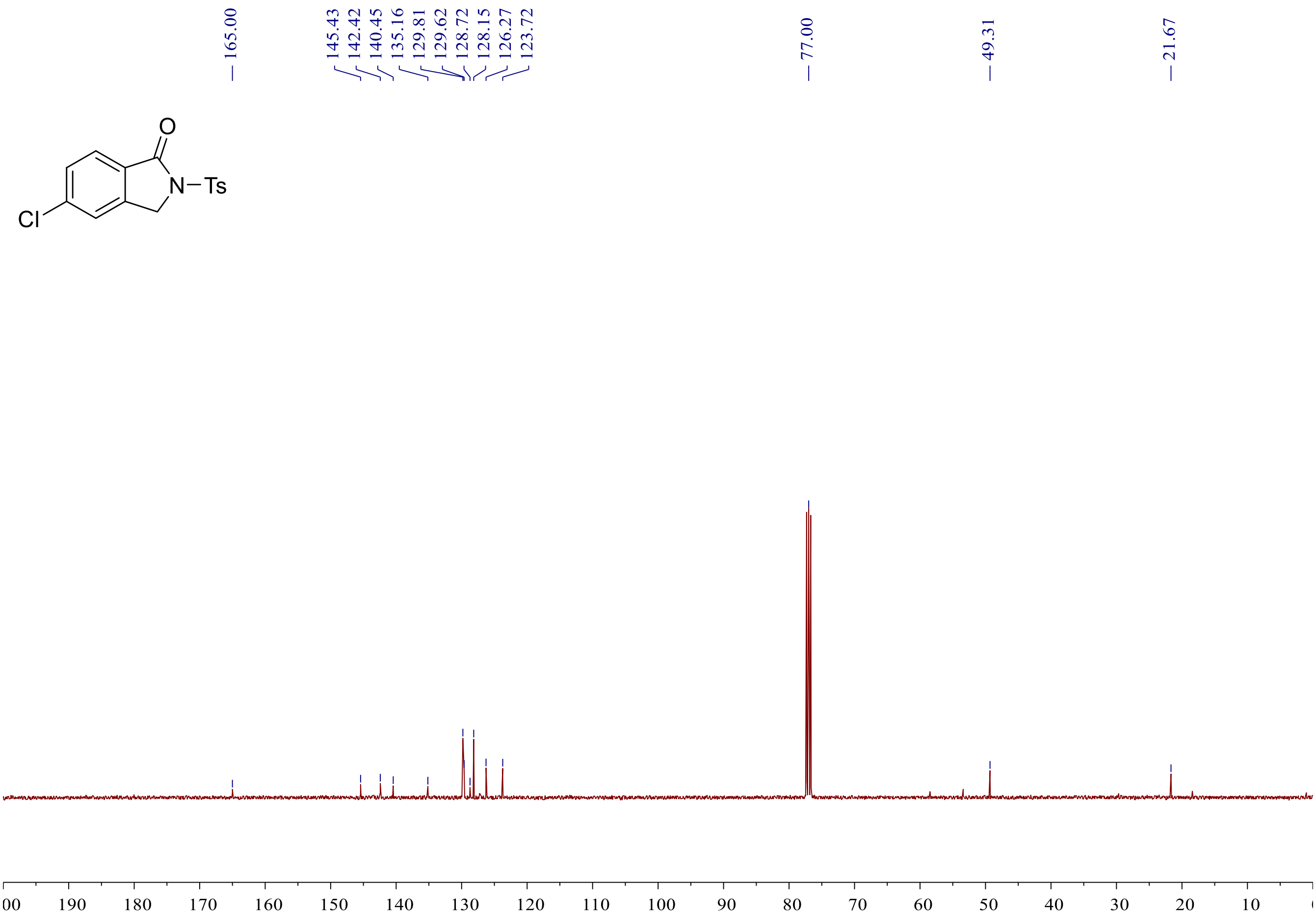
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ha



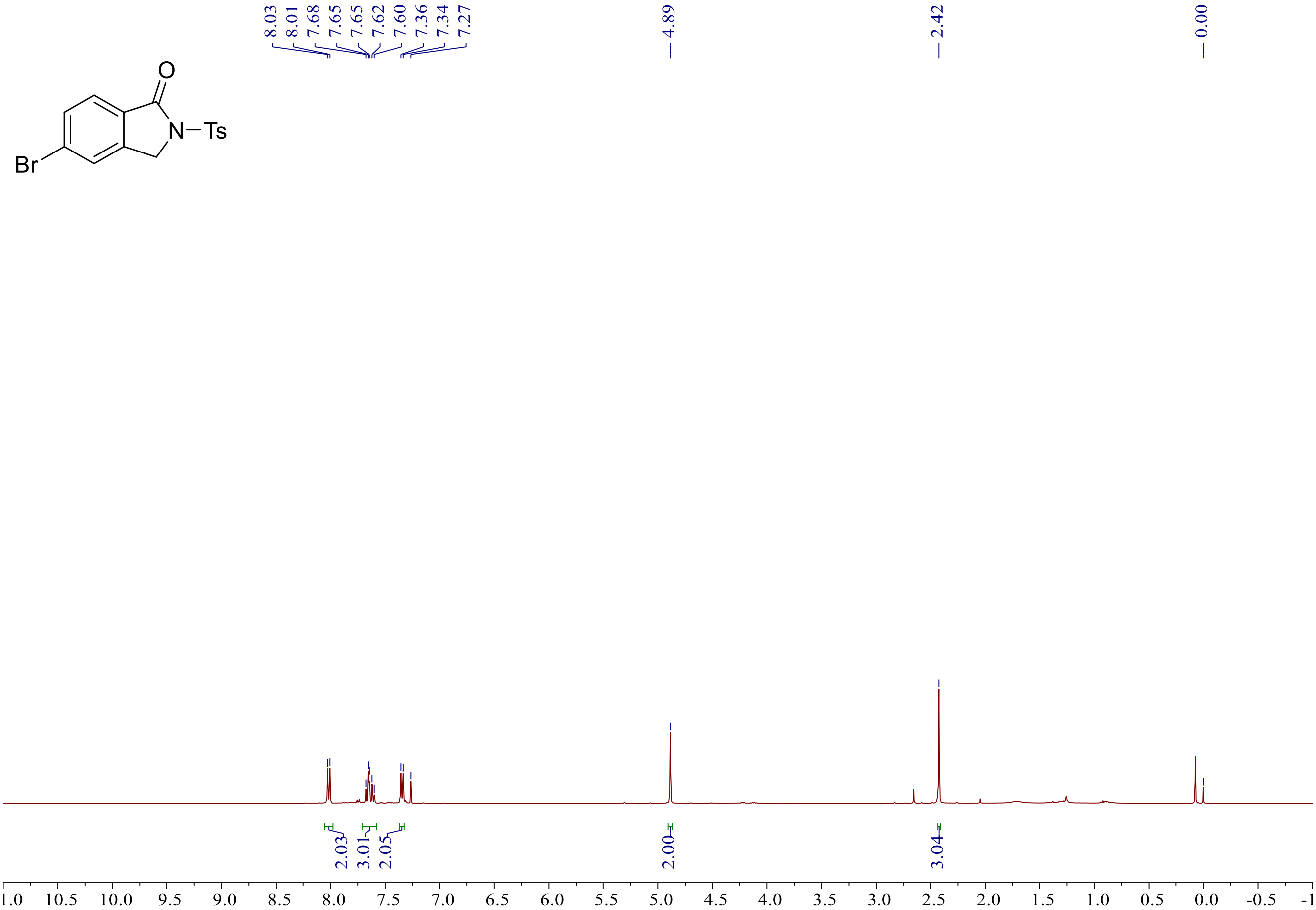


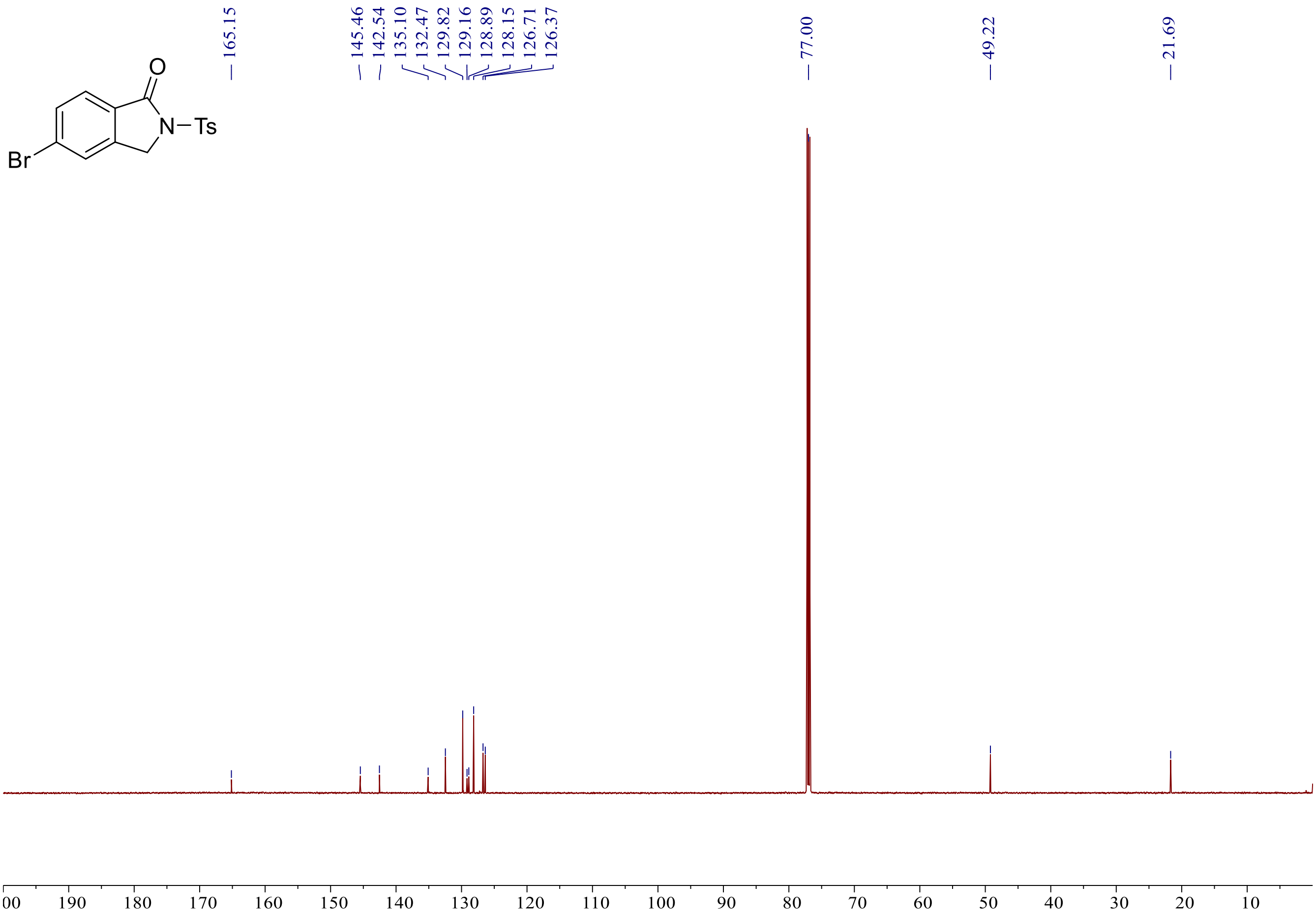
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of product 3ia



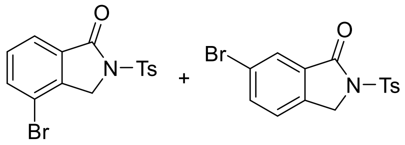


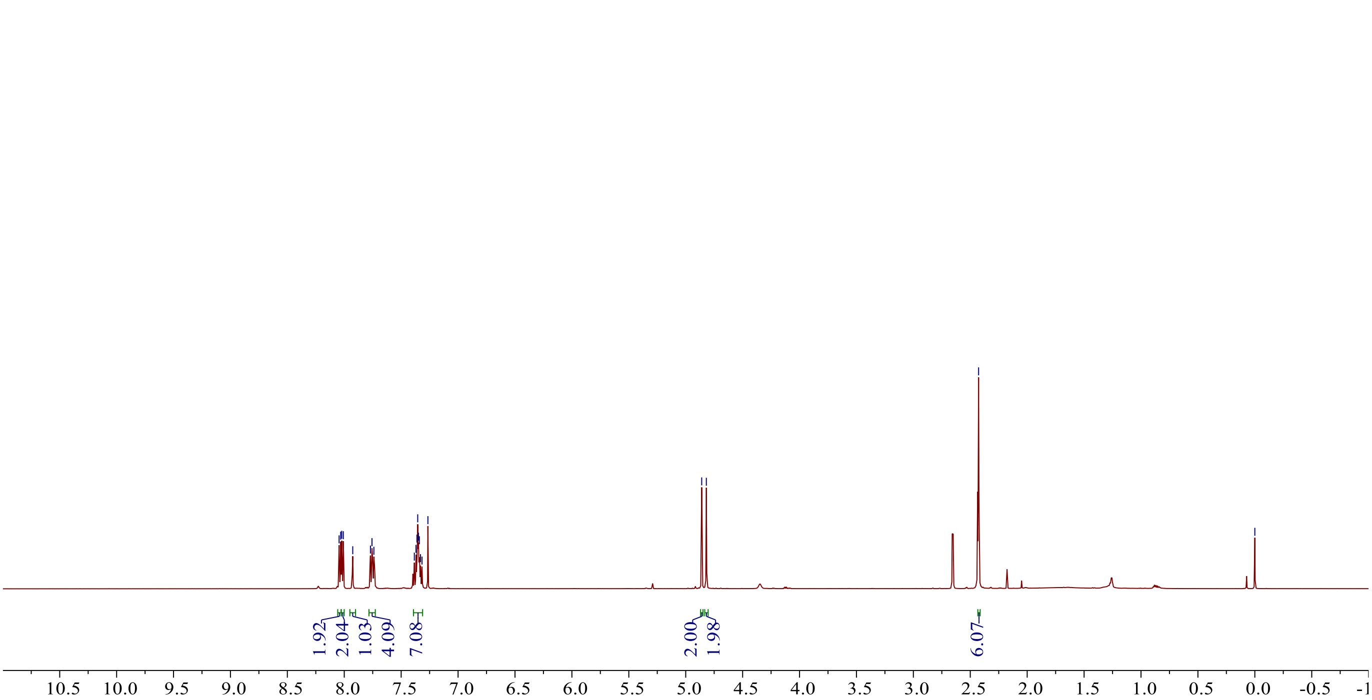
[1]H NMR (400 MHz, CDCl$_3$) and [13]C NMR (150 MHz, CDCl$_3$) spectrum of product 3ja



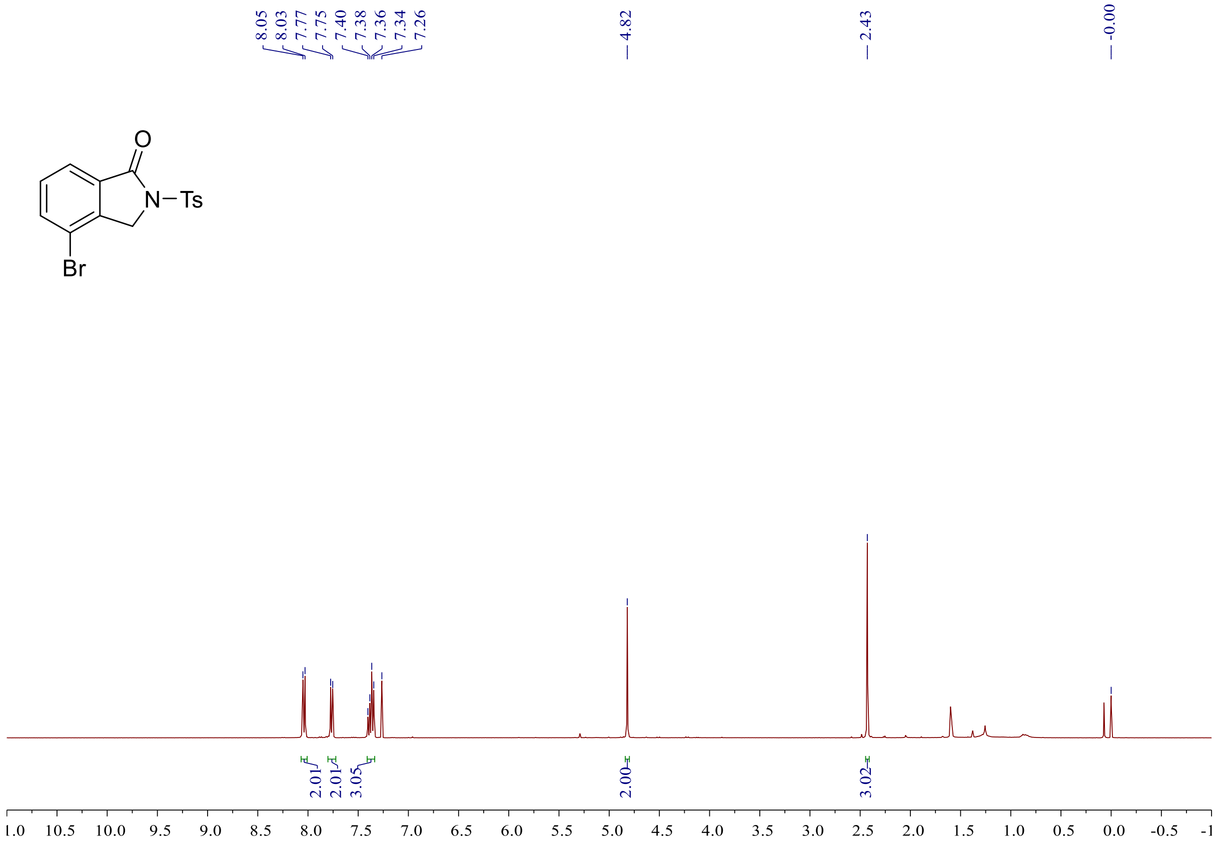


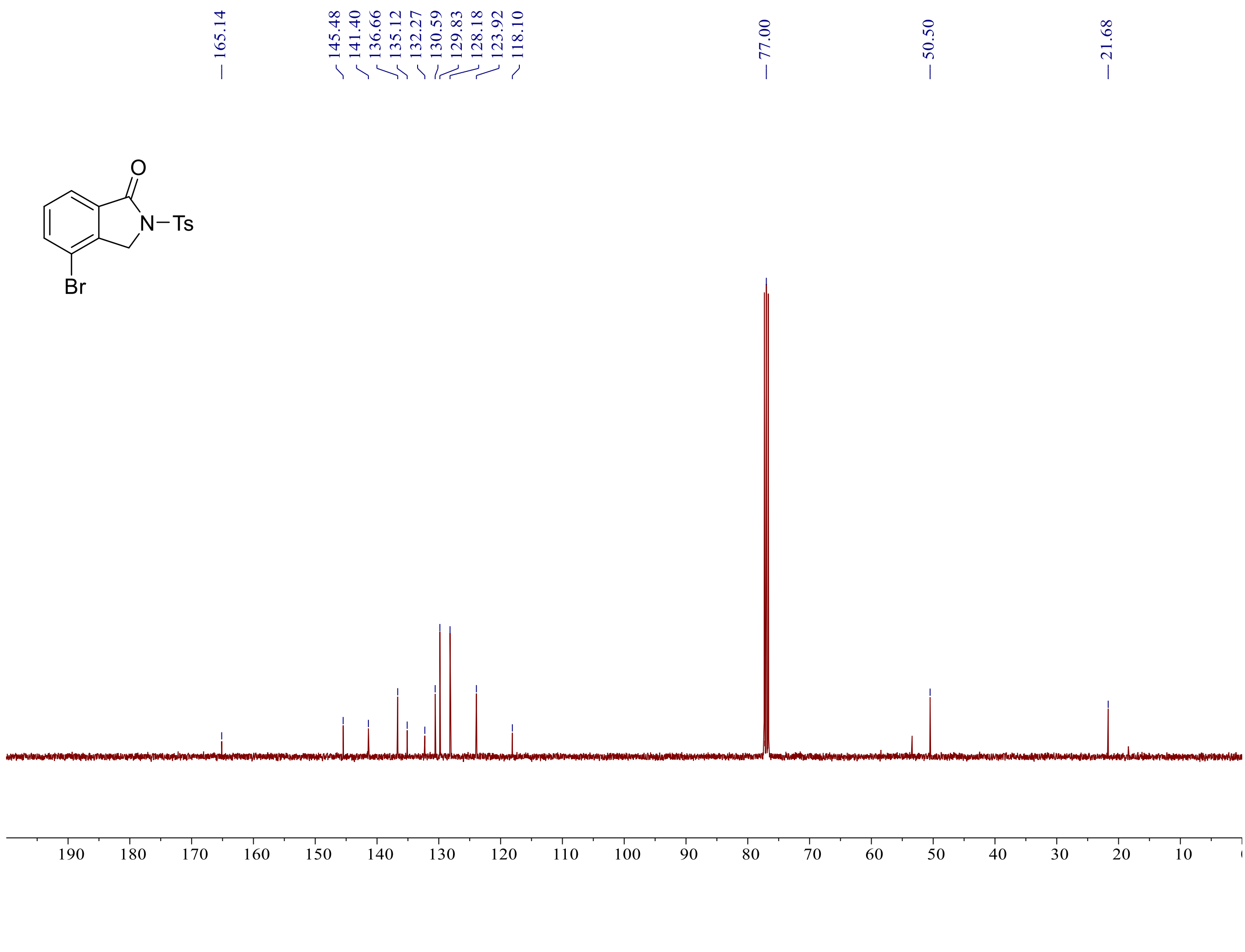
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of product 3ka + 3ka'



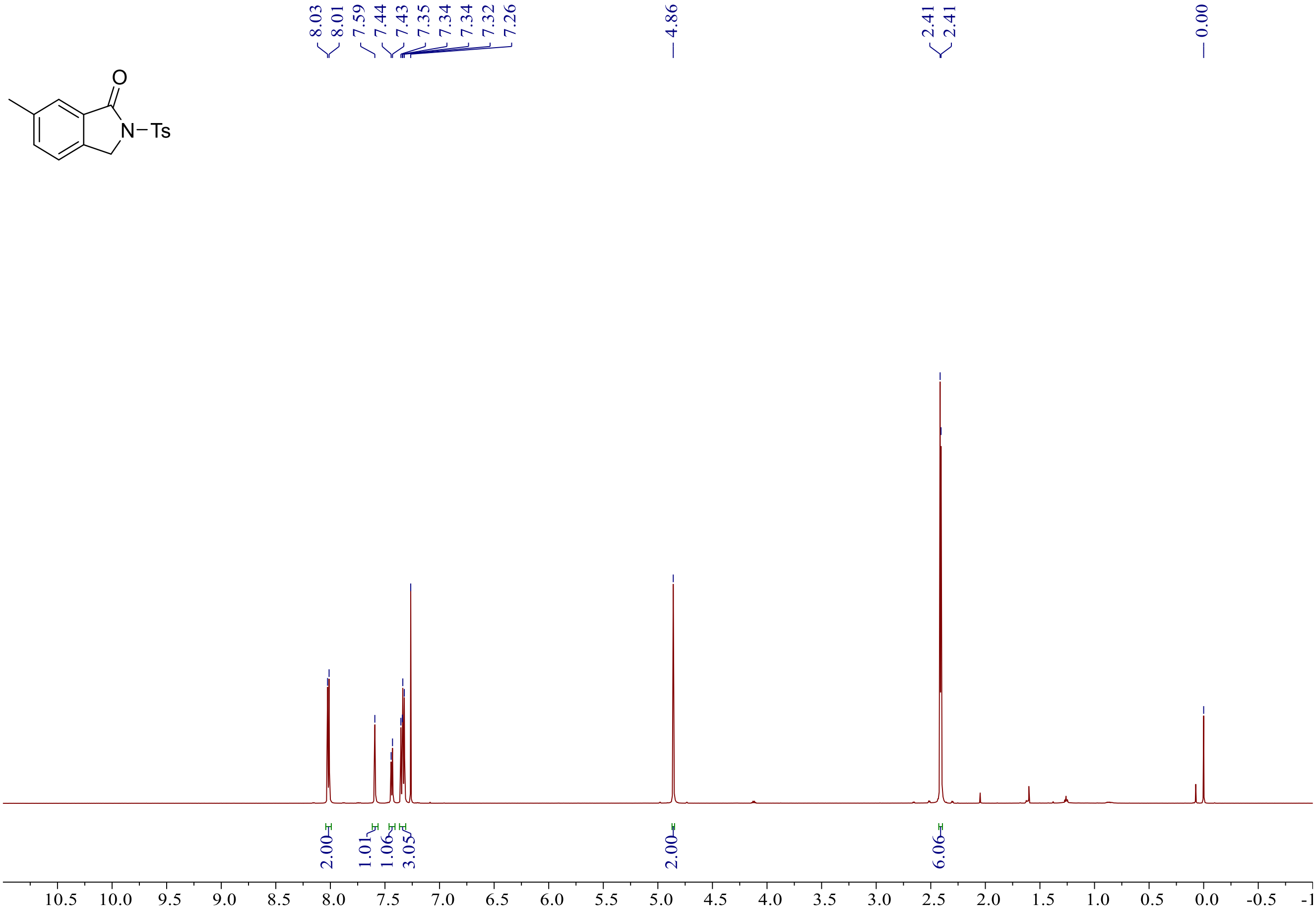


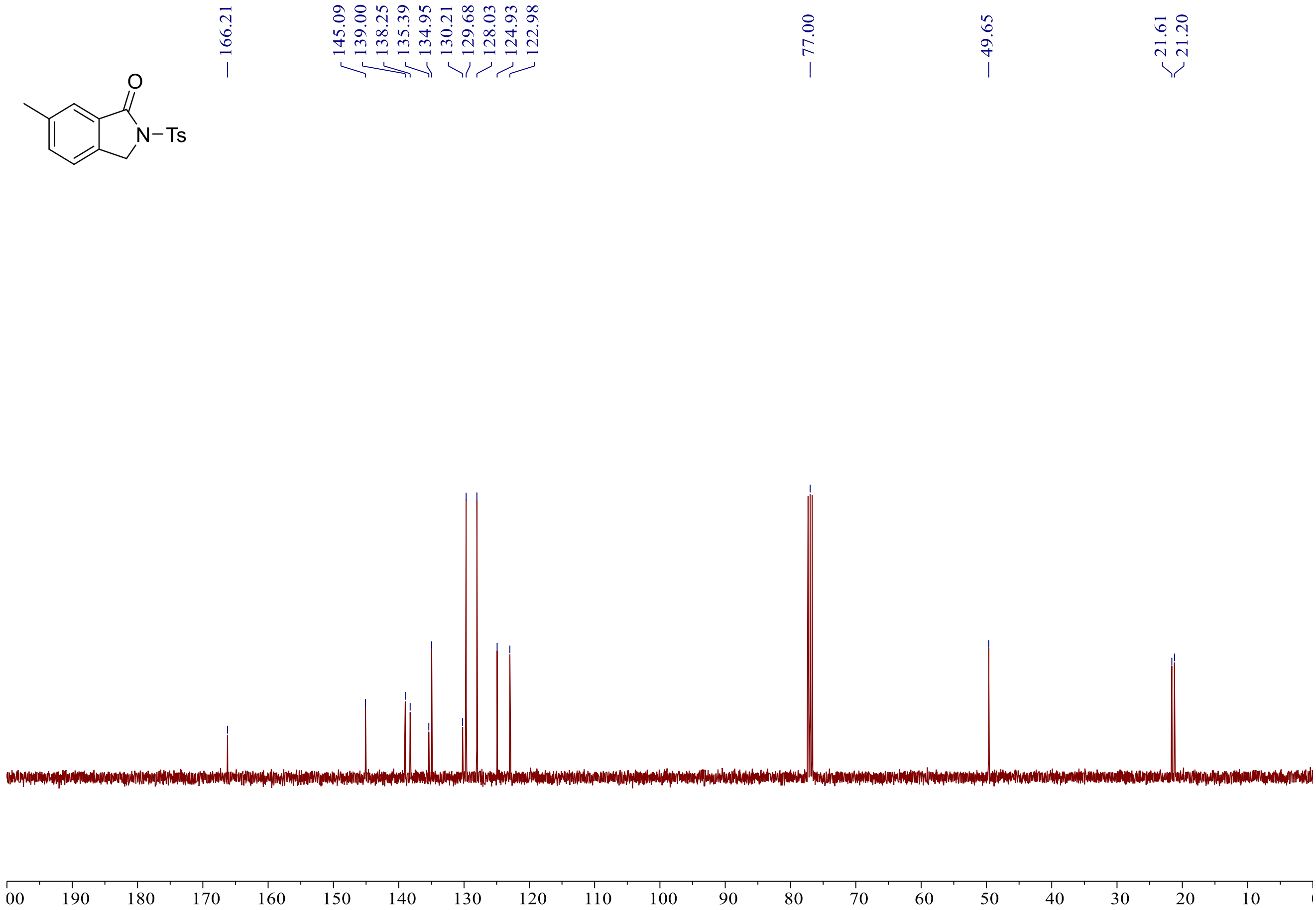
[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of product 3ka



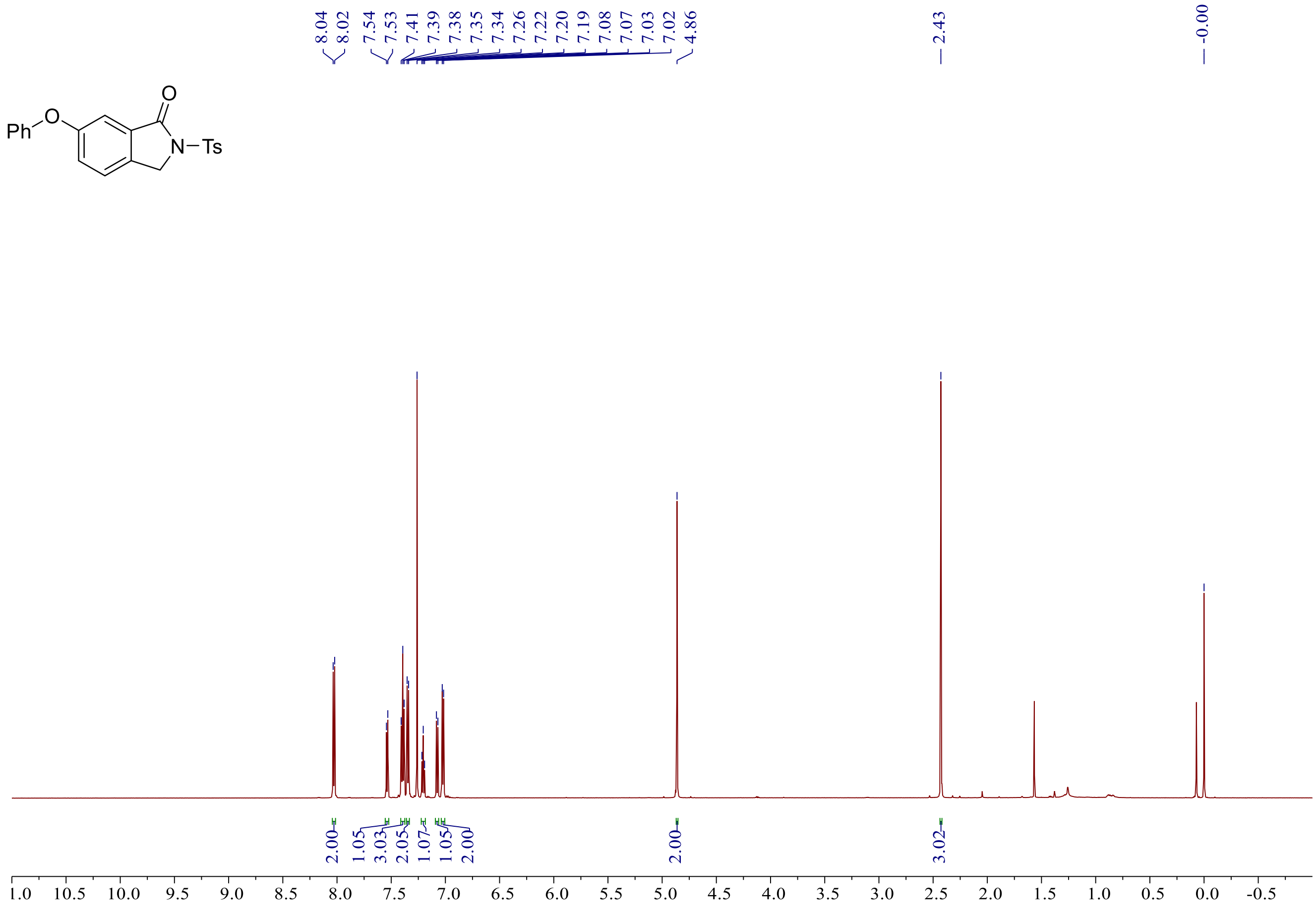


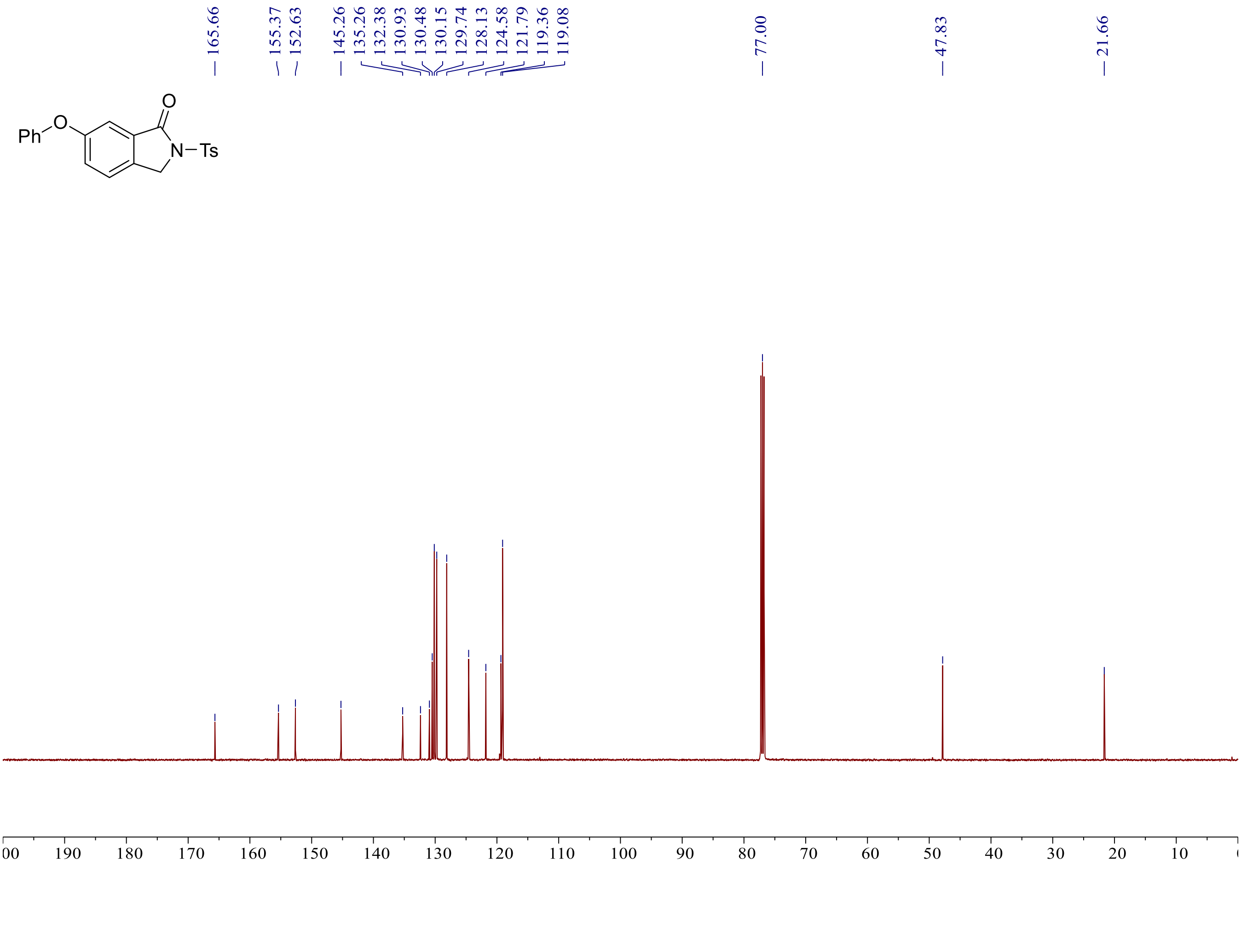
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3la



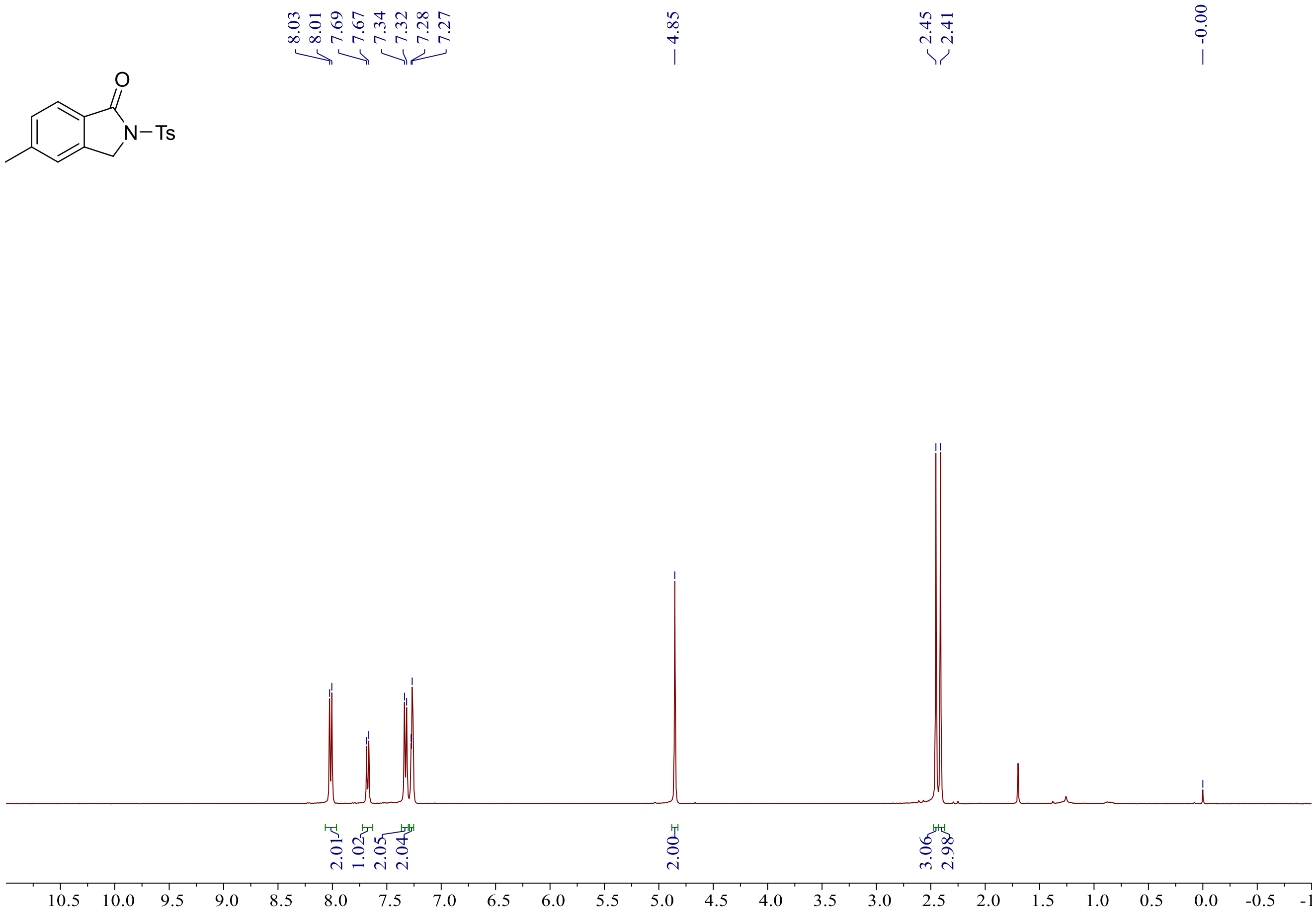


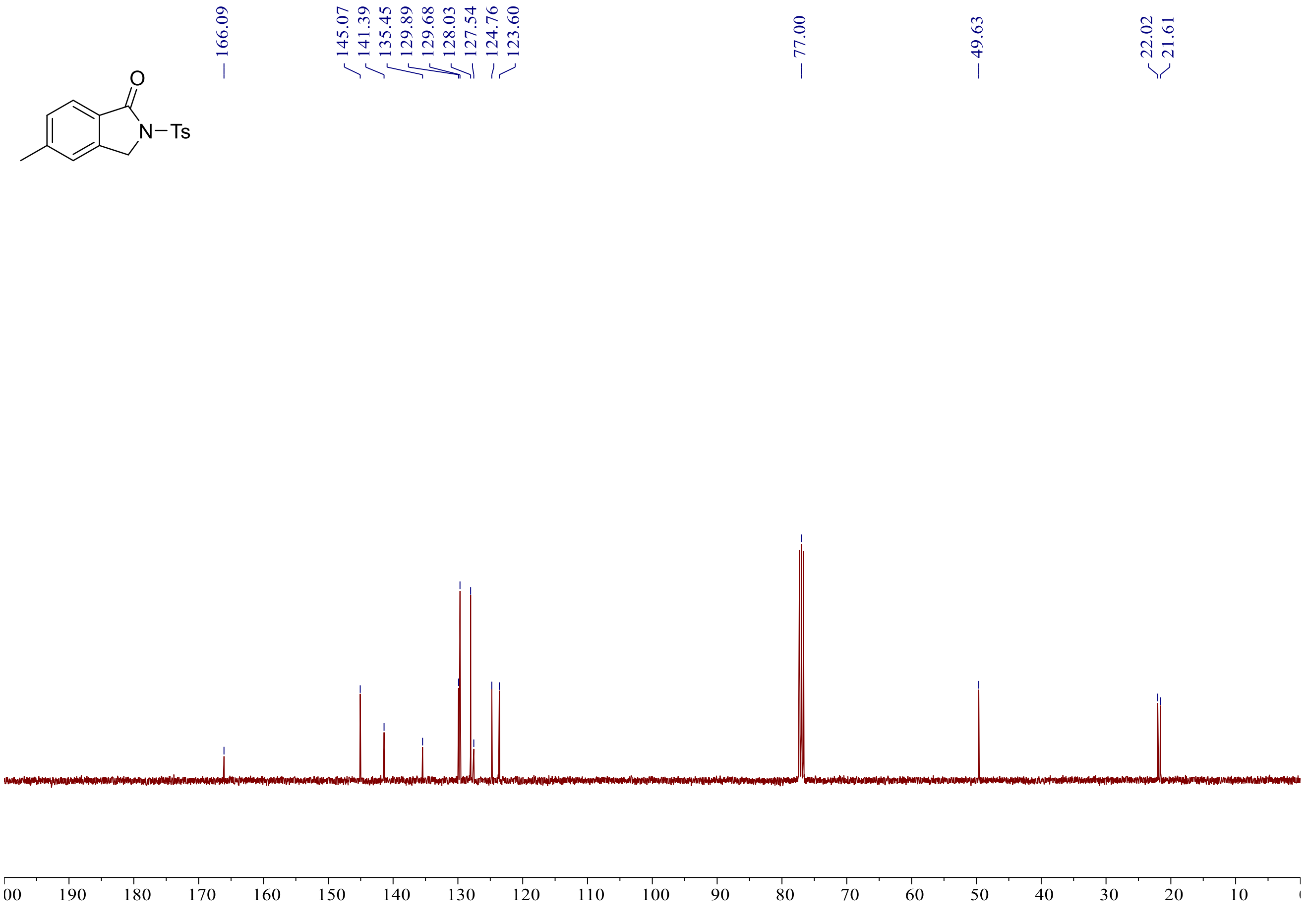
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 3ma



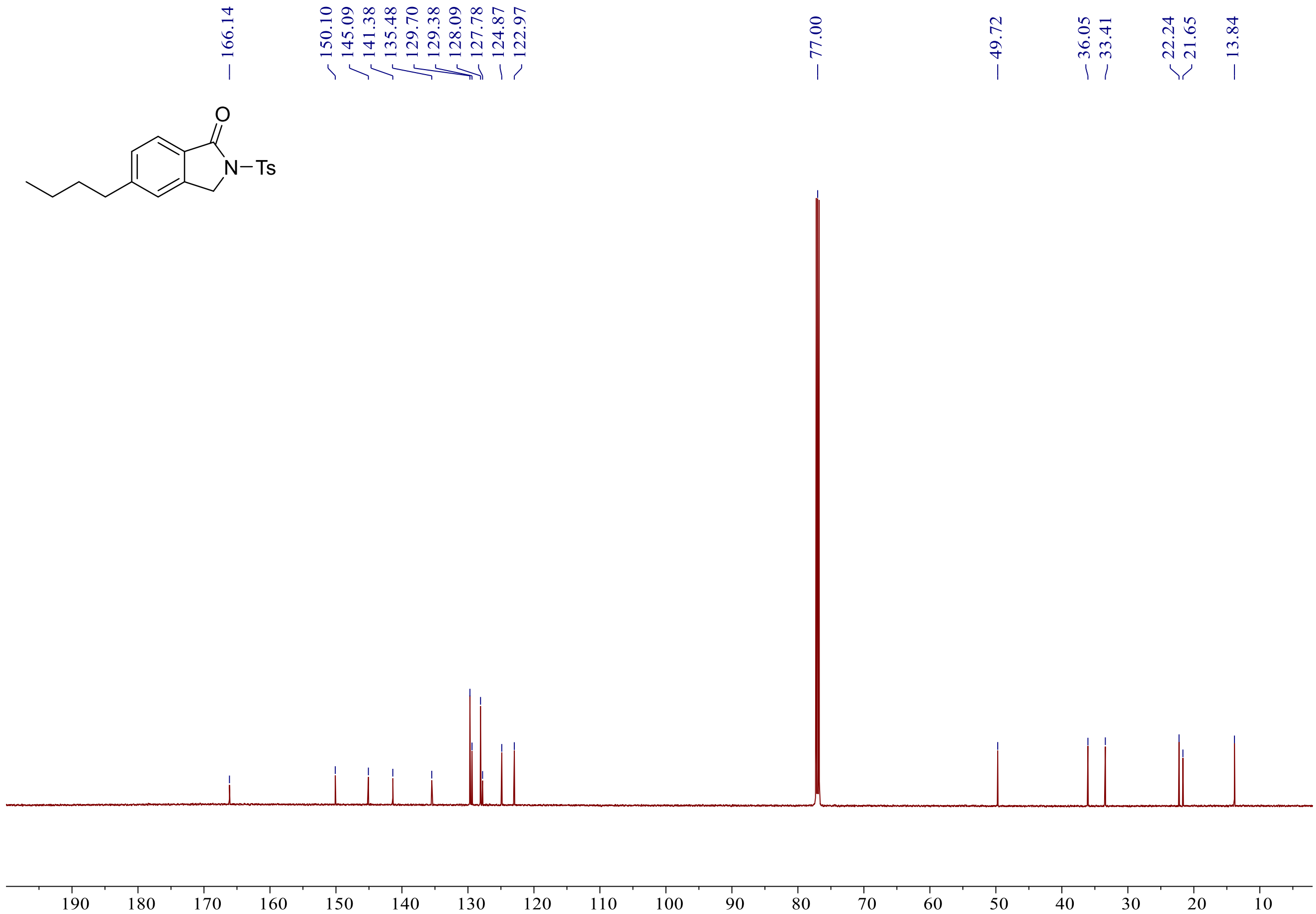


[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectra of product 3na

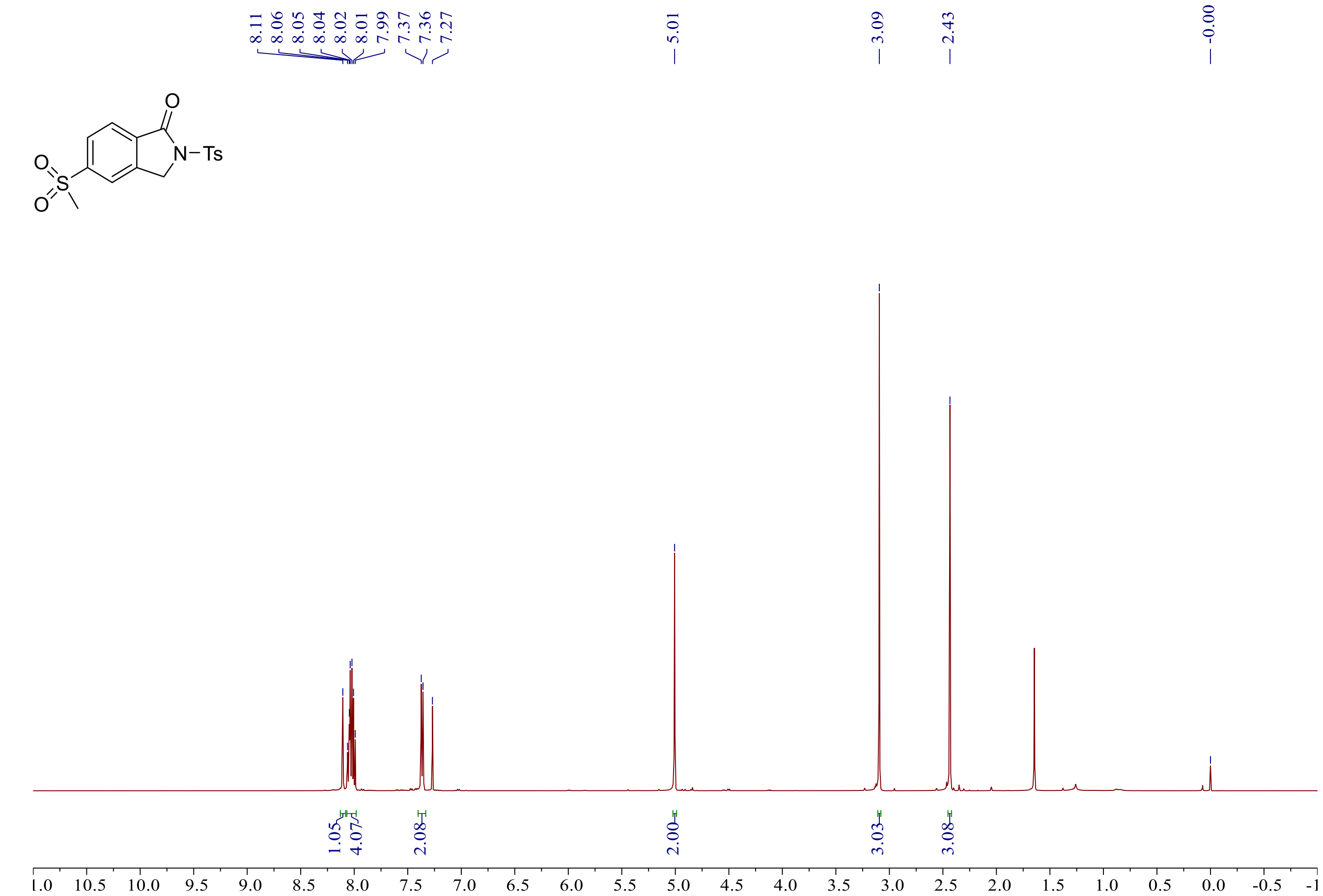


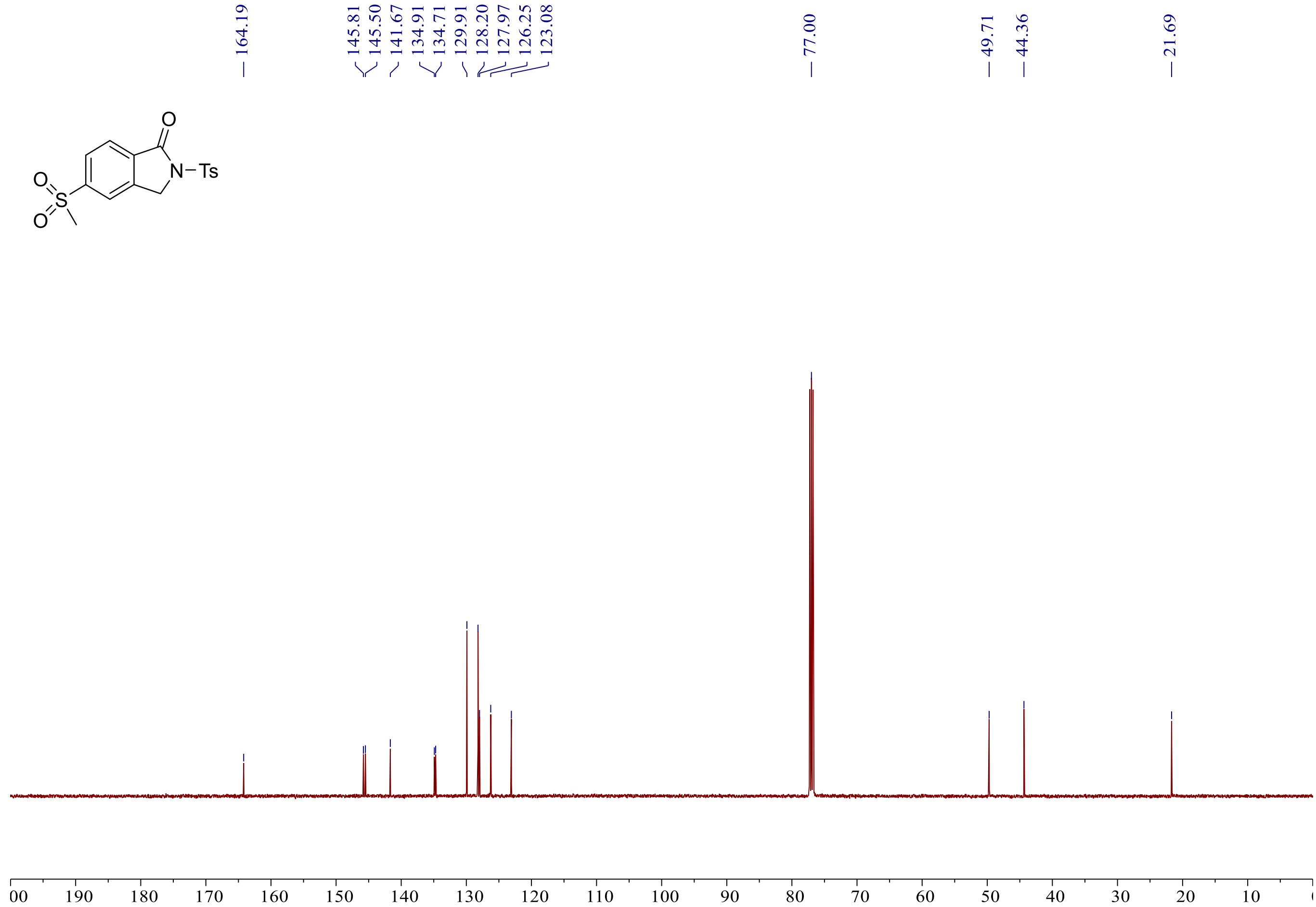


[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (150 MHz, $CDCl_3$) spectra of product 3oa

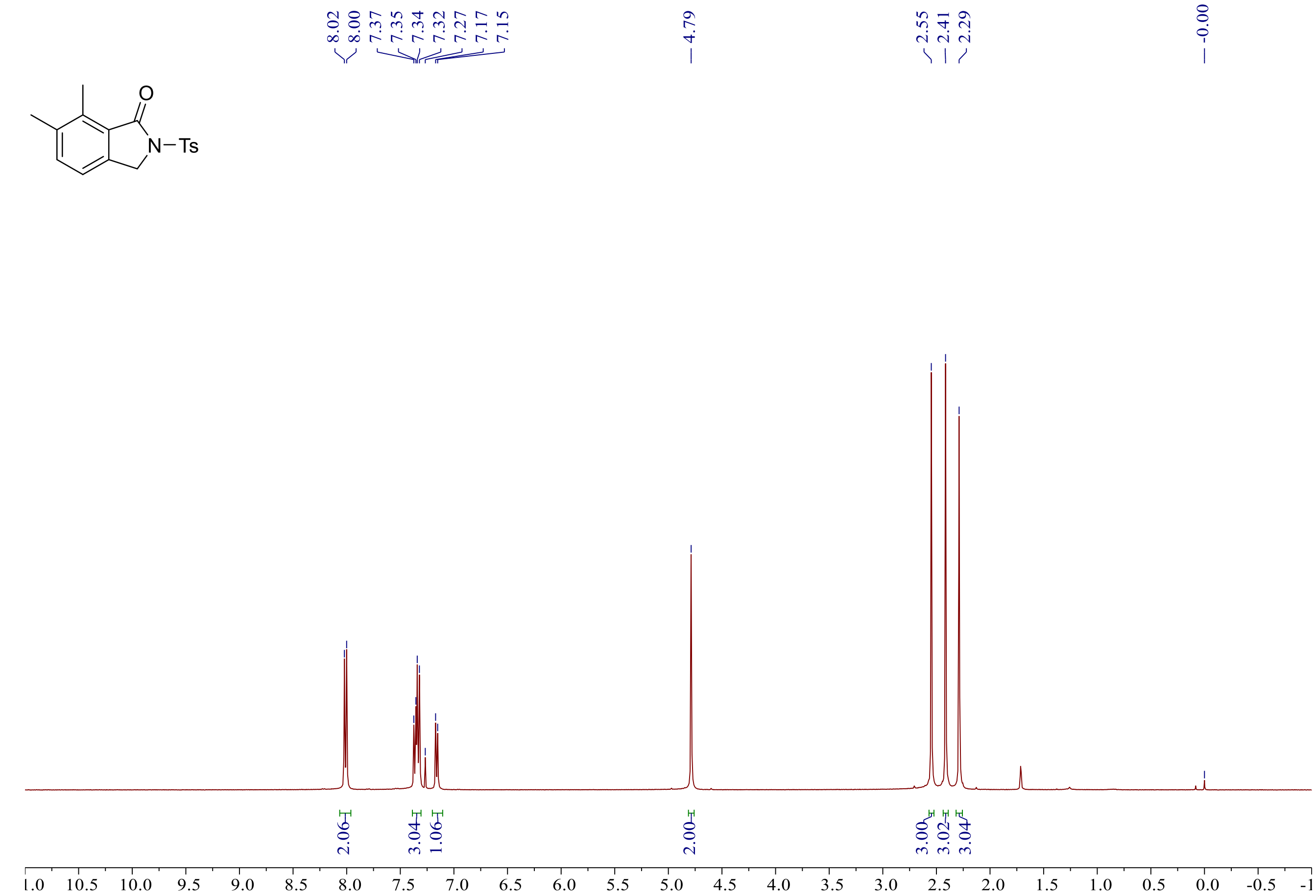


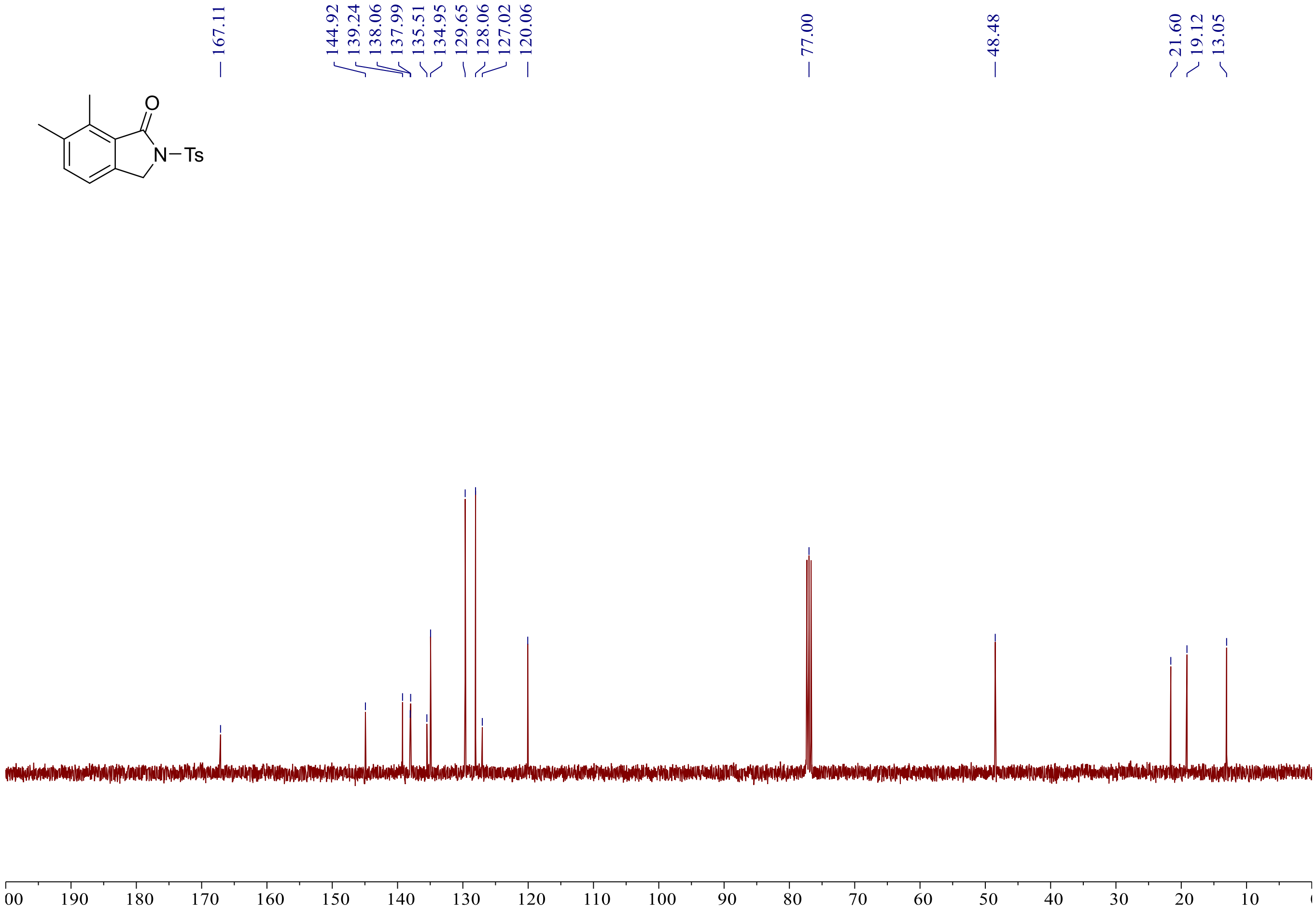
[1]H NMR (500 MHz, $CDCl_3$) and [13]C NMR (125 MHz, $CDCl_3$) spectra of product 3pa



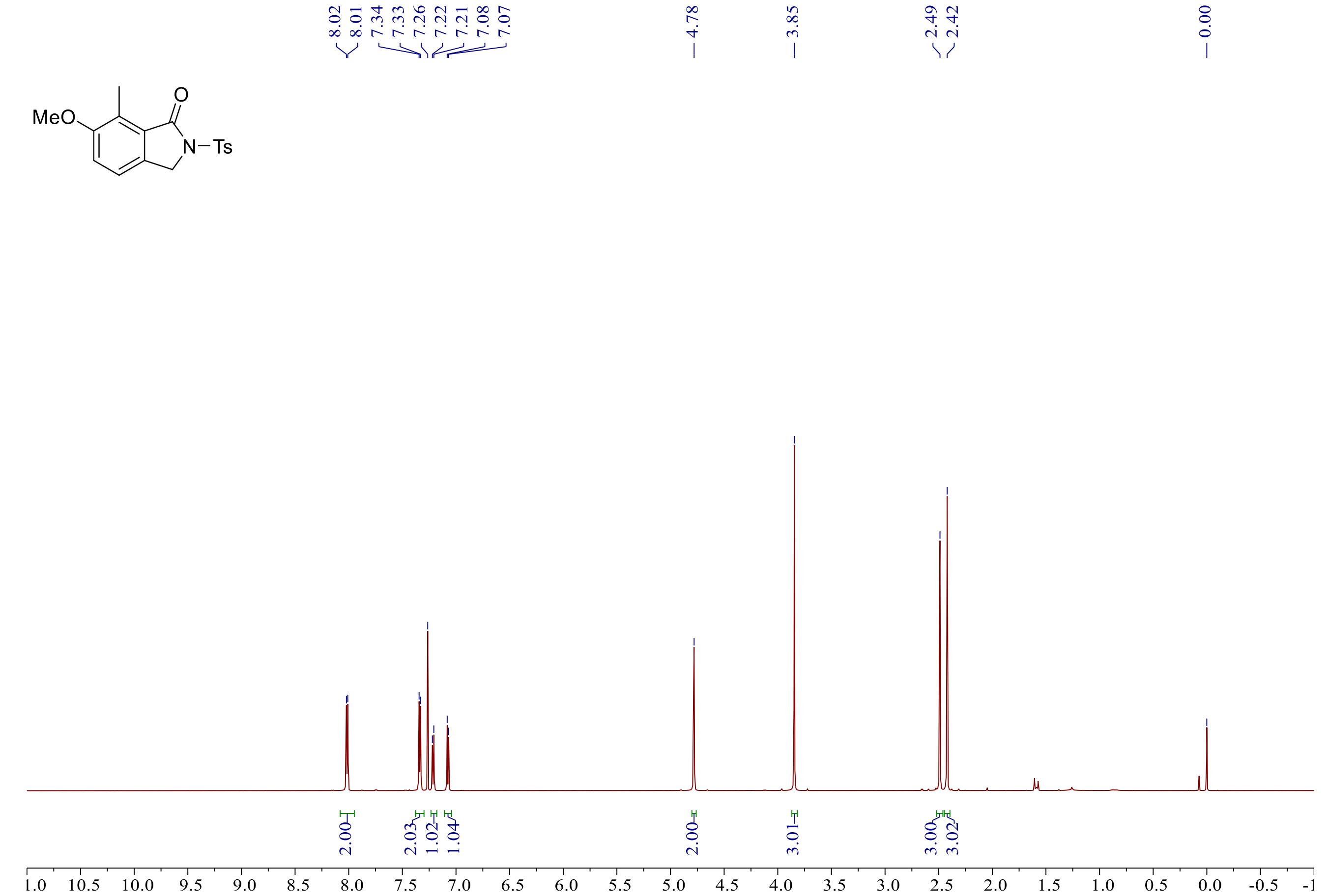


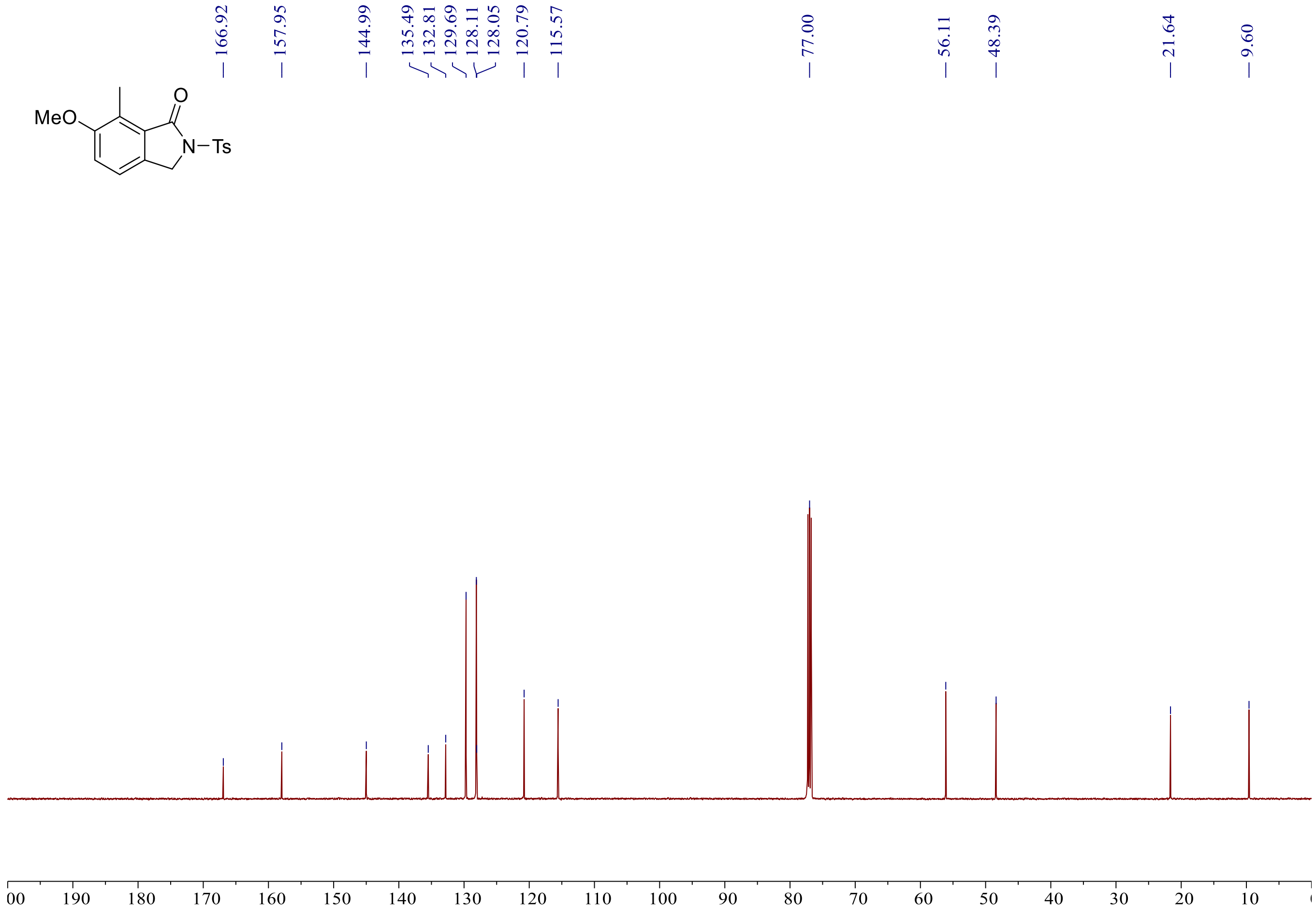
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3qa



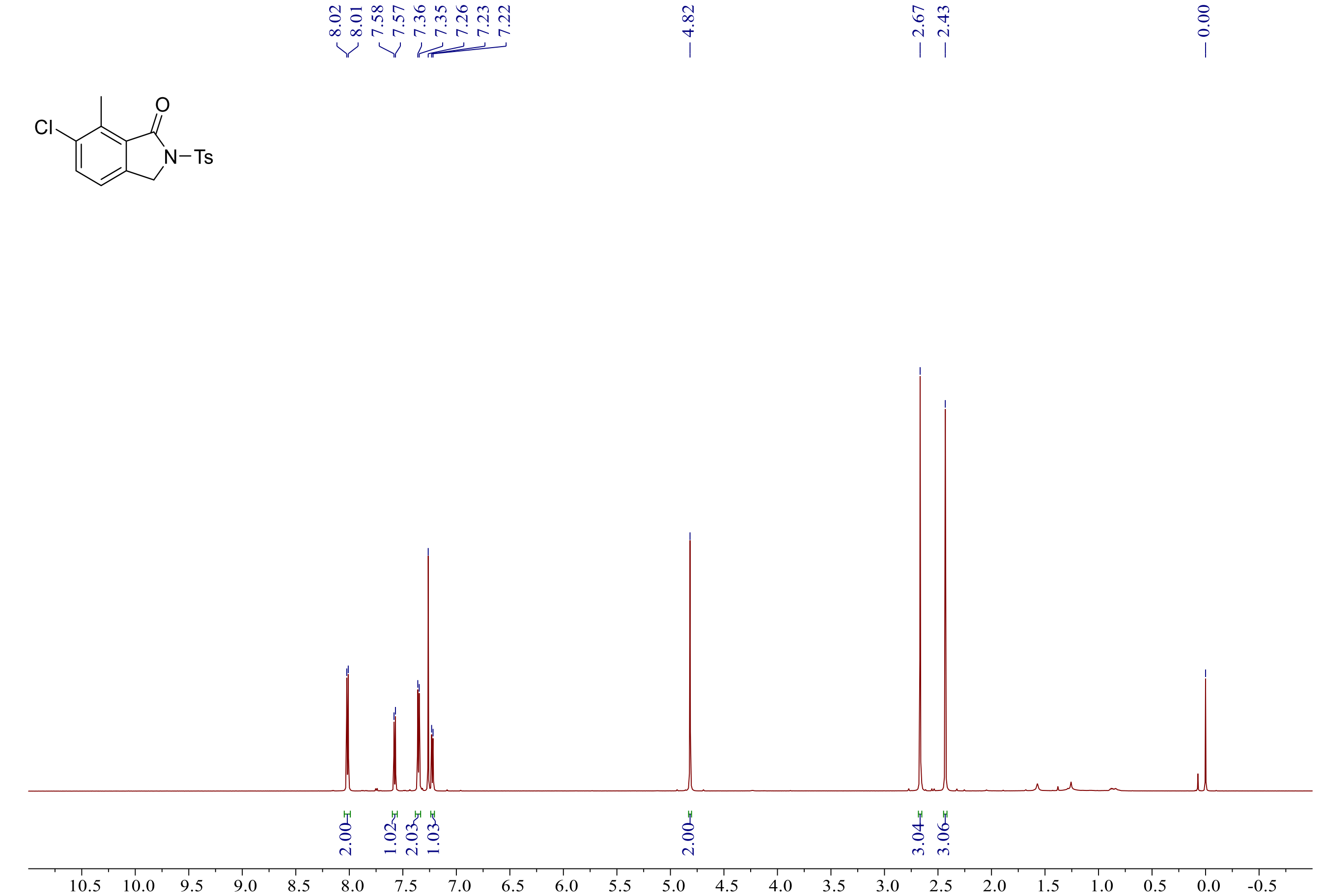


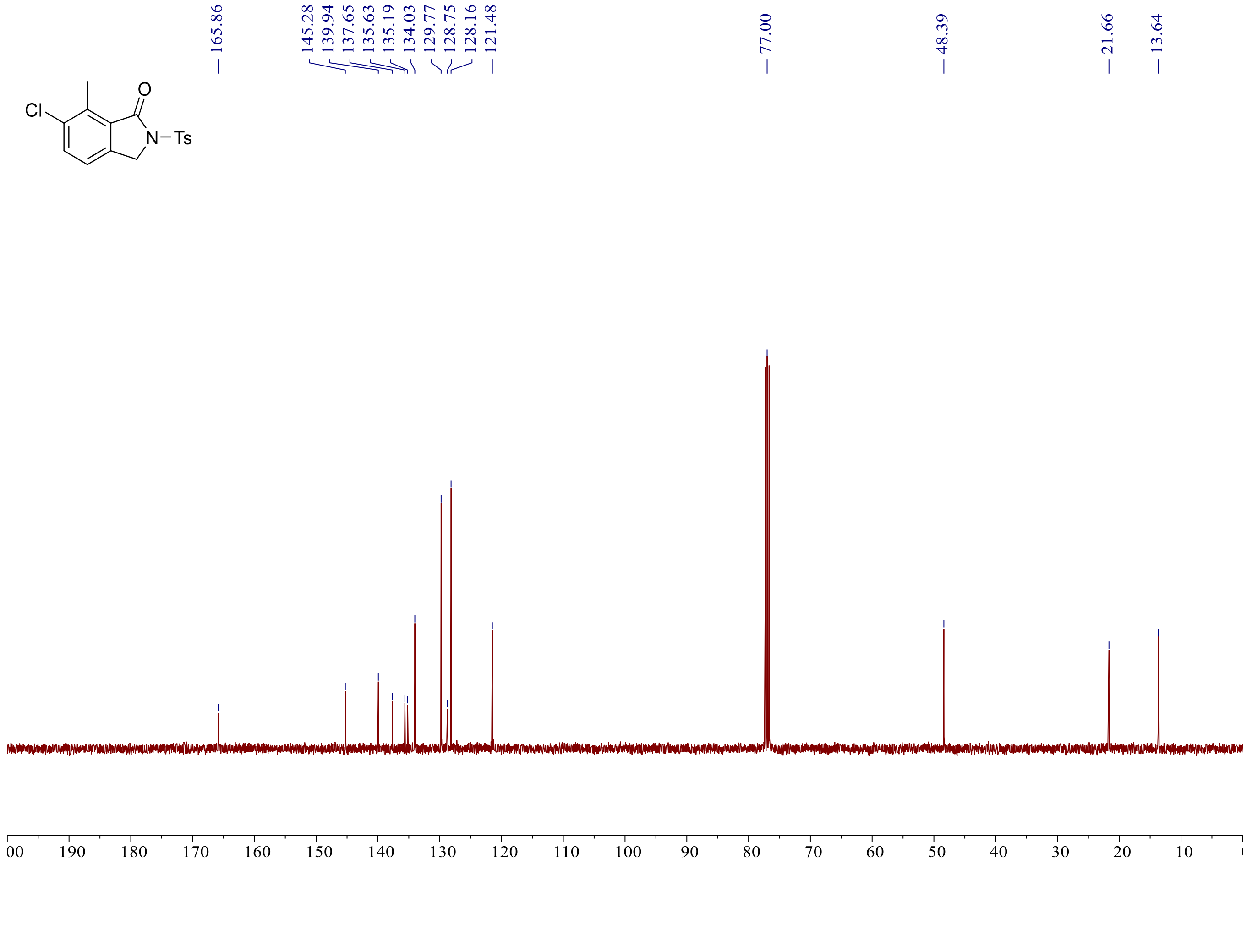
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 3ra



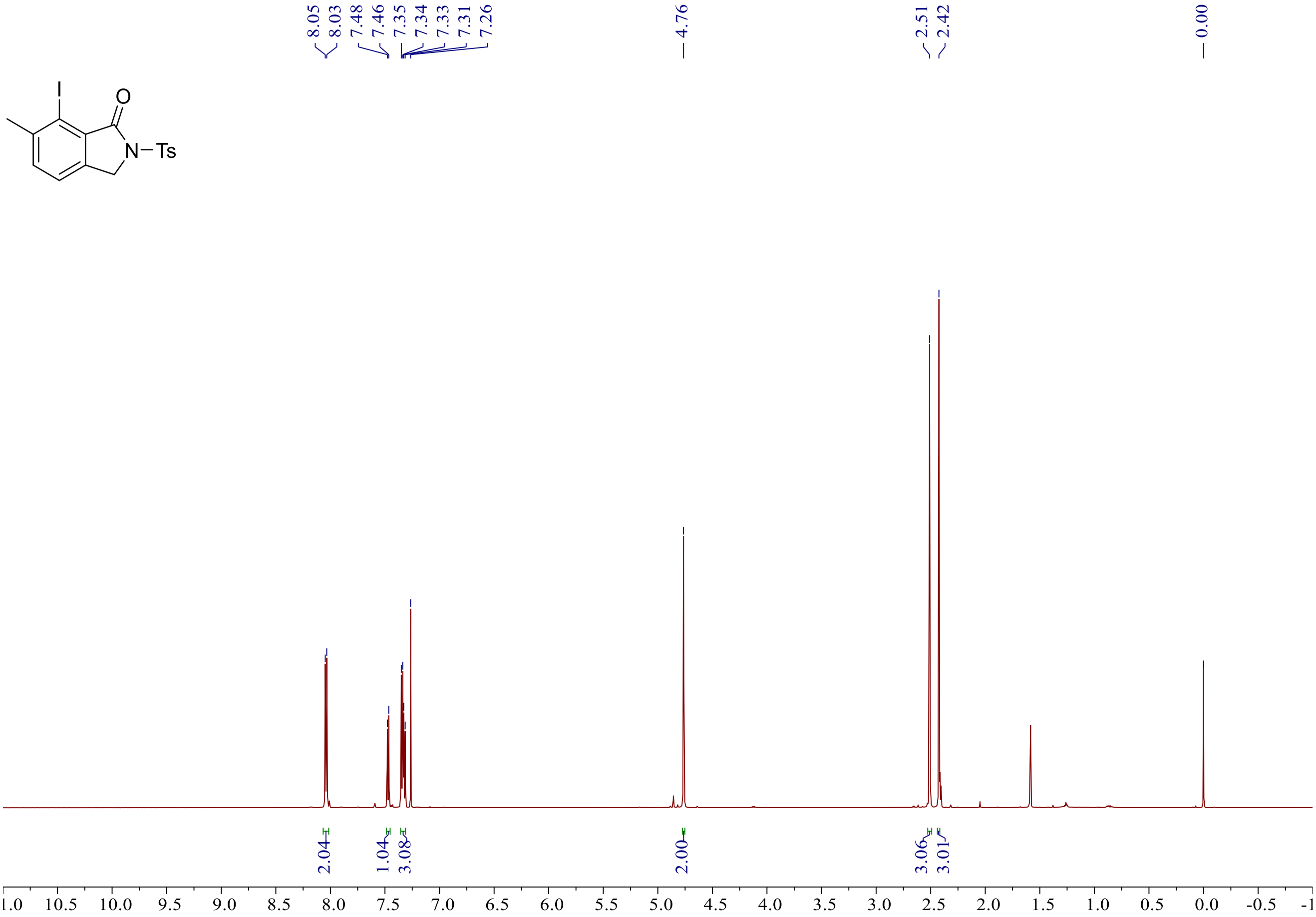


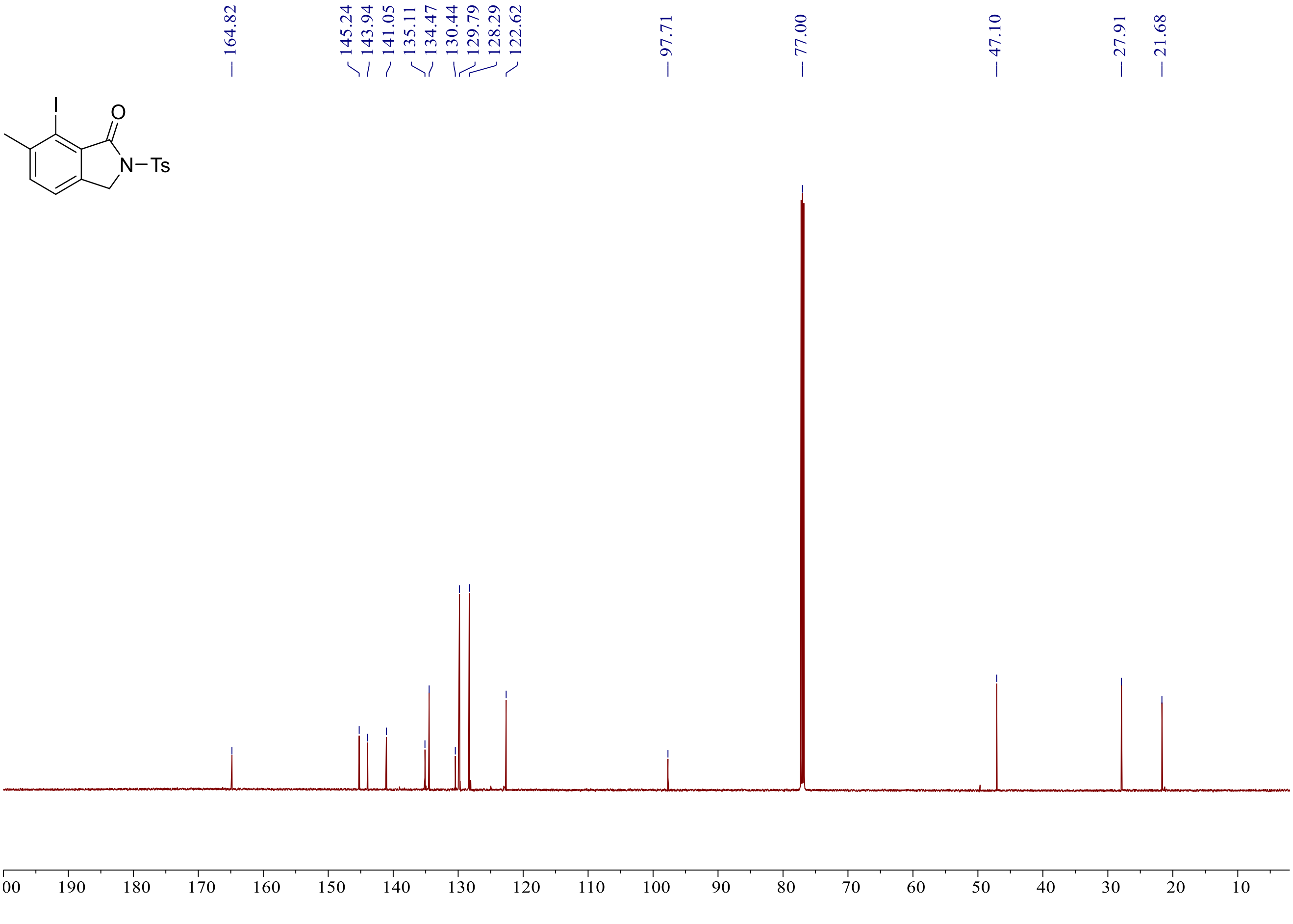
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 3sa



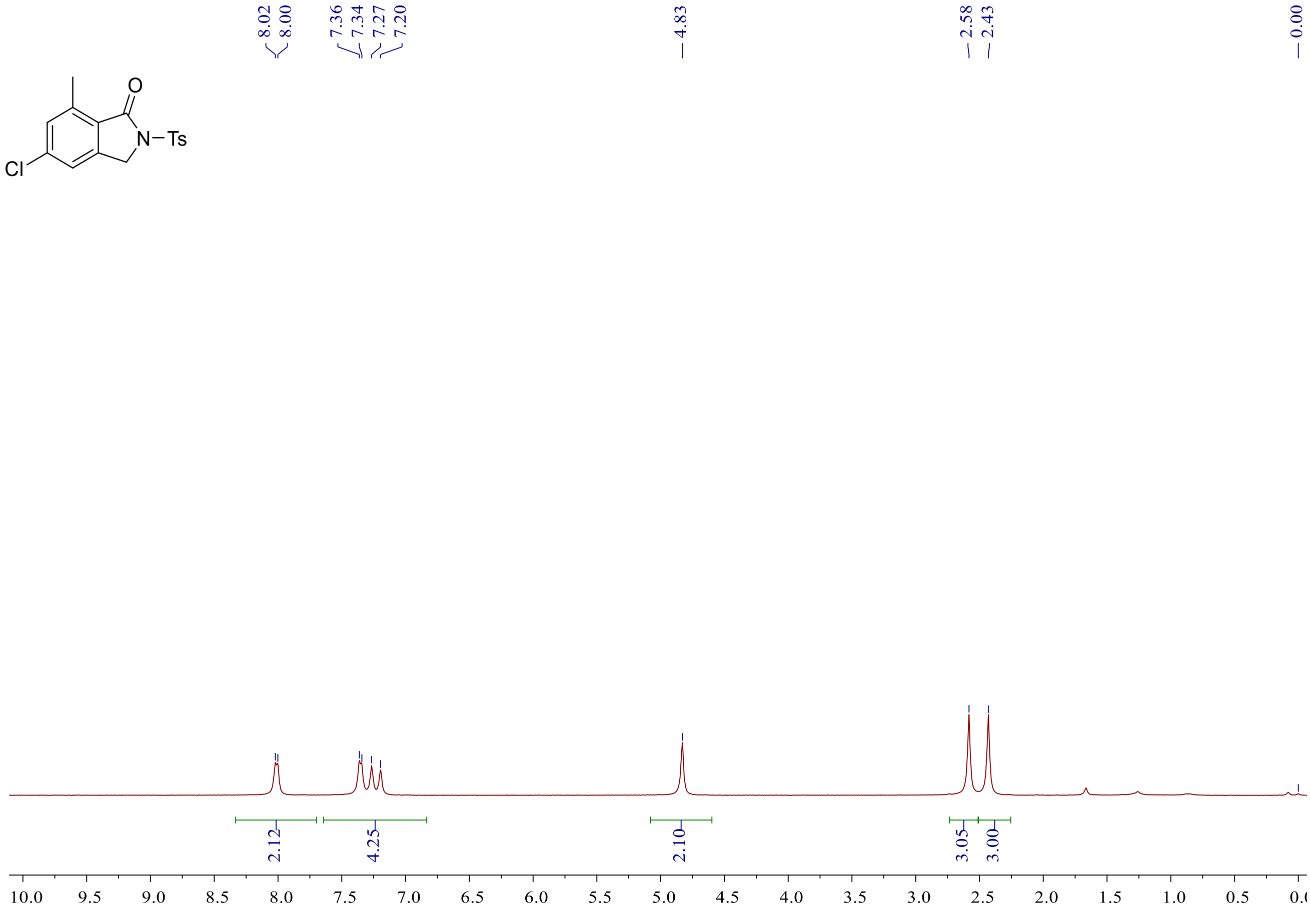


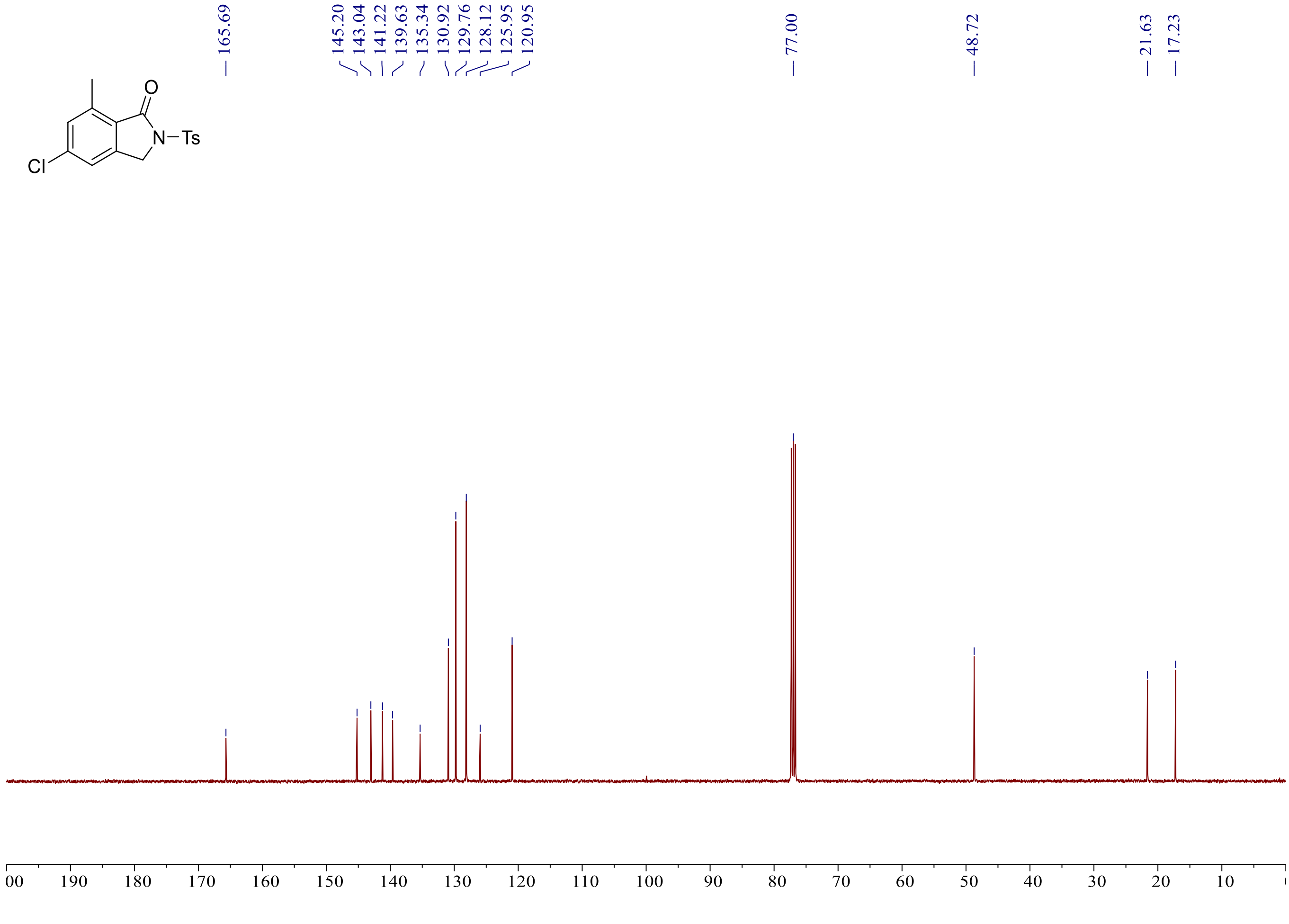
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectra of product 3ta



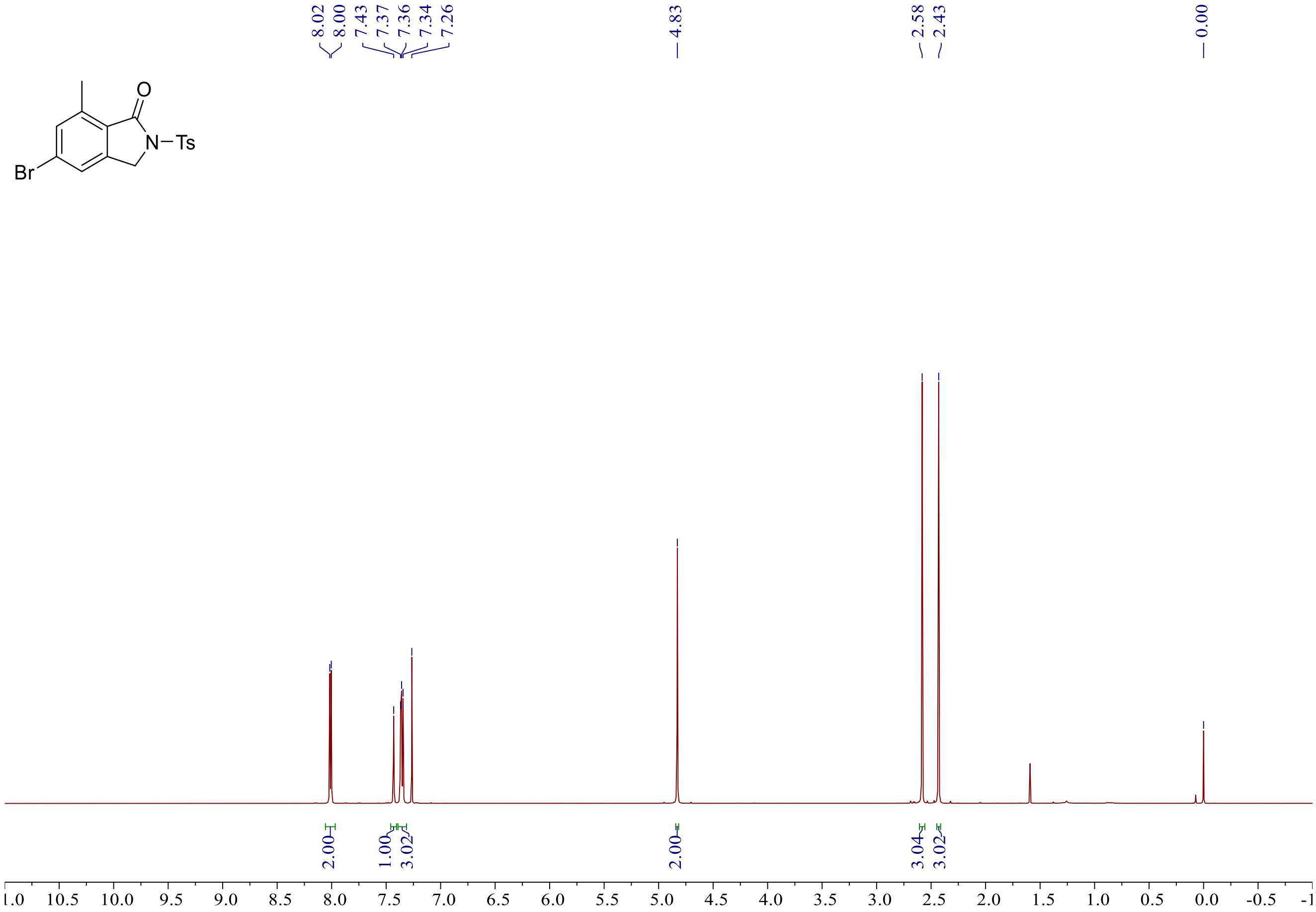


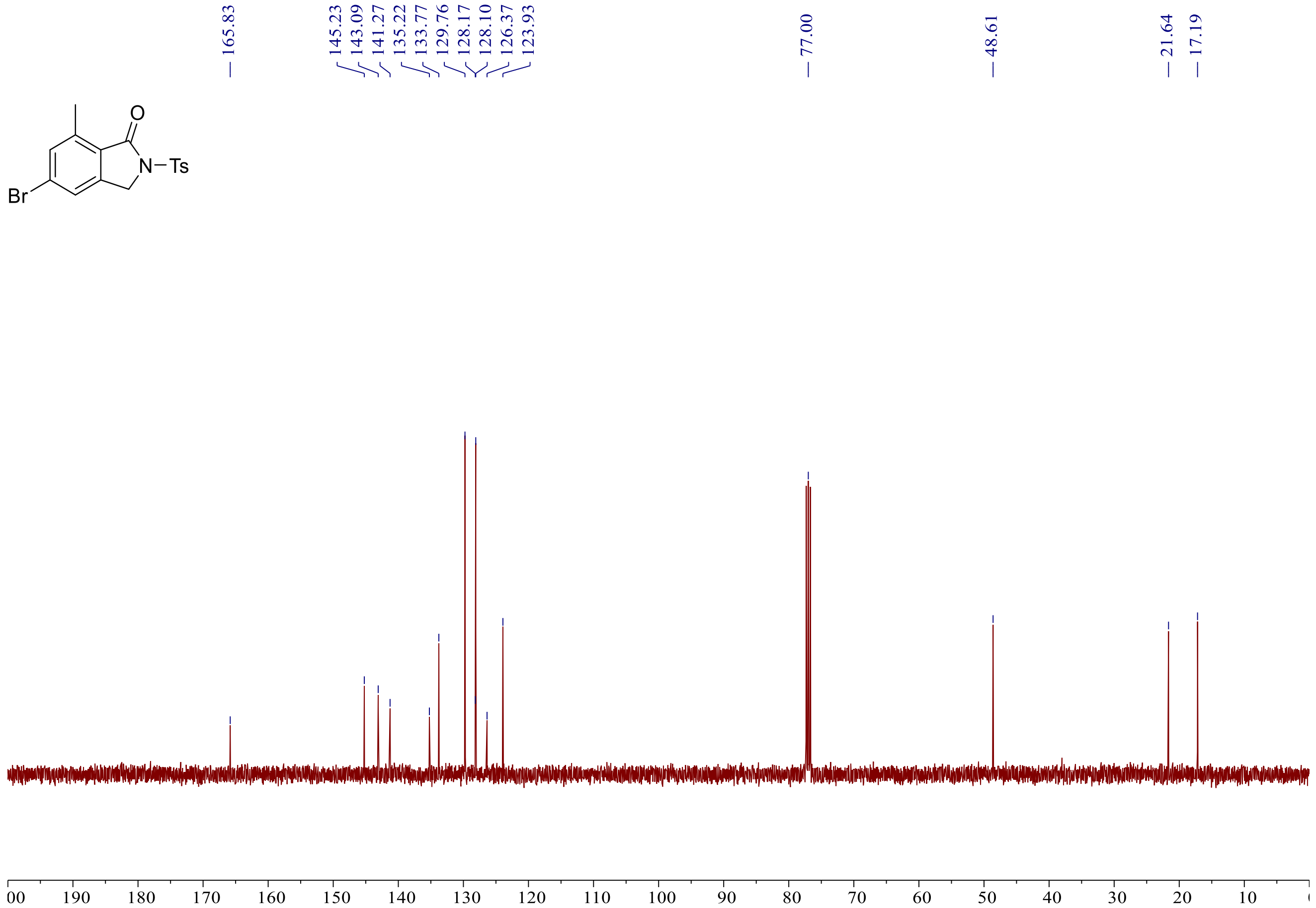
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ua



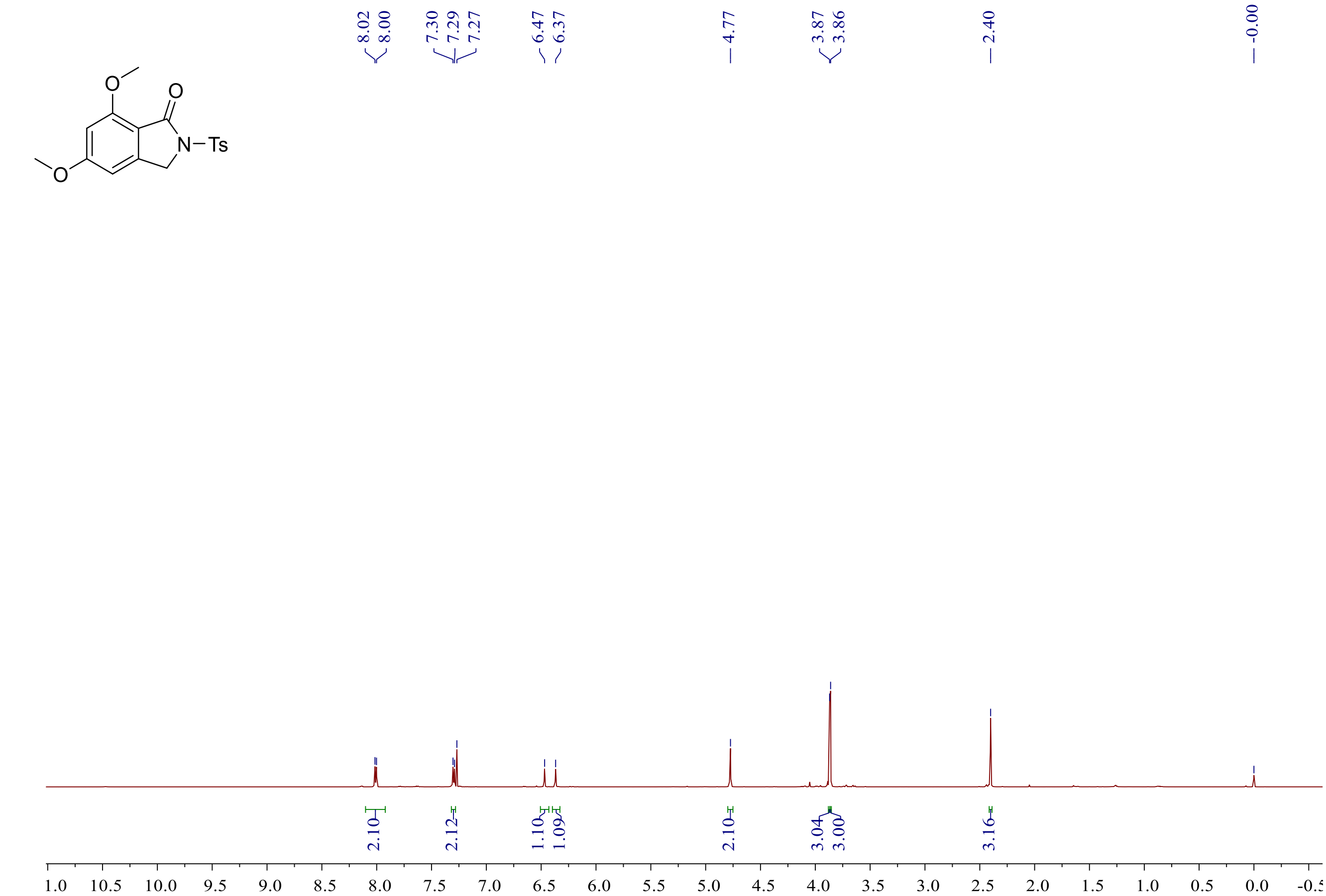


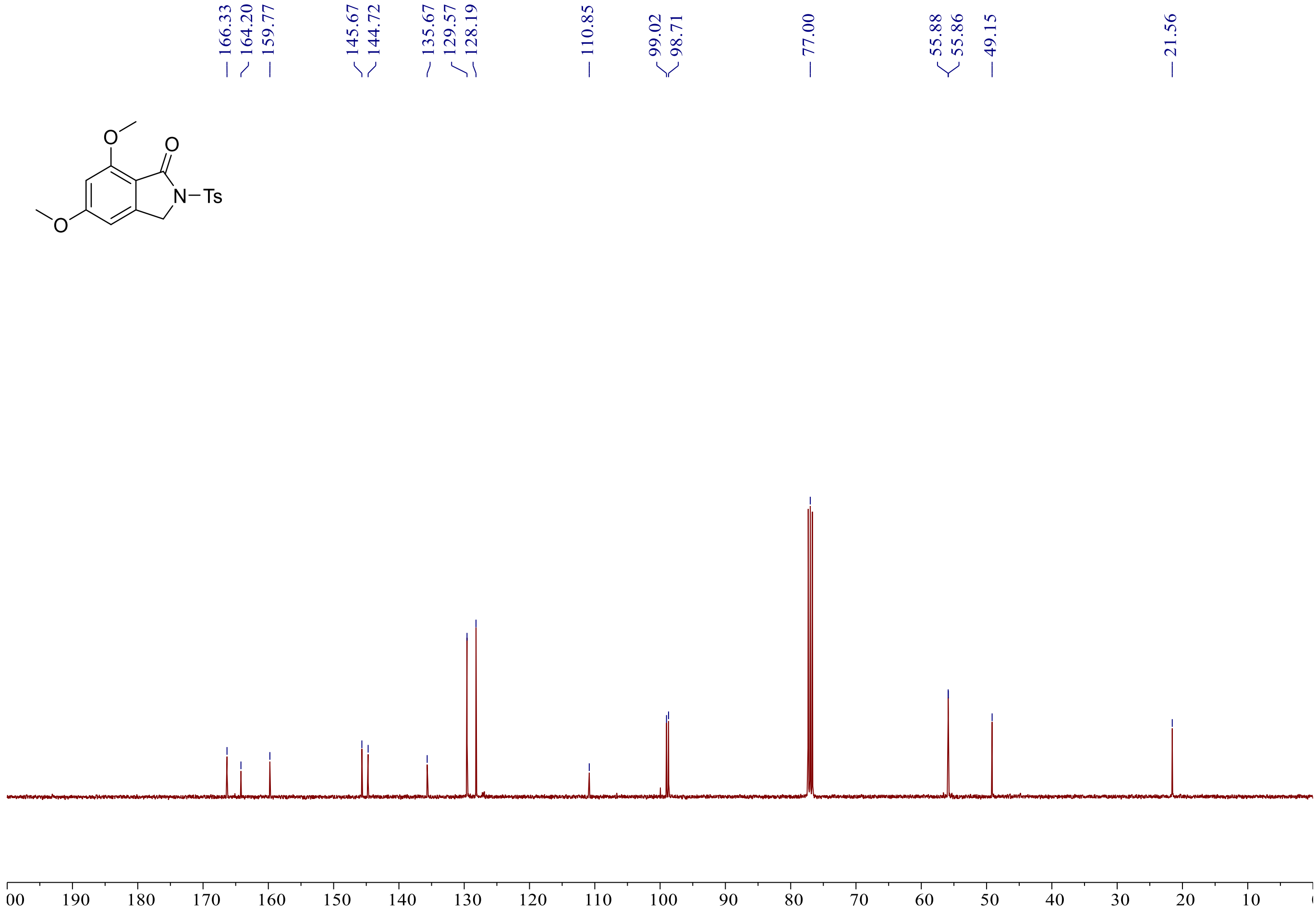
[1]H NMR (600 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectra of product 3va



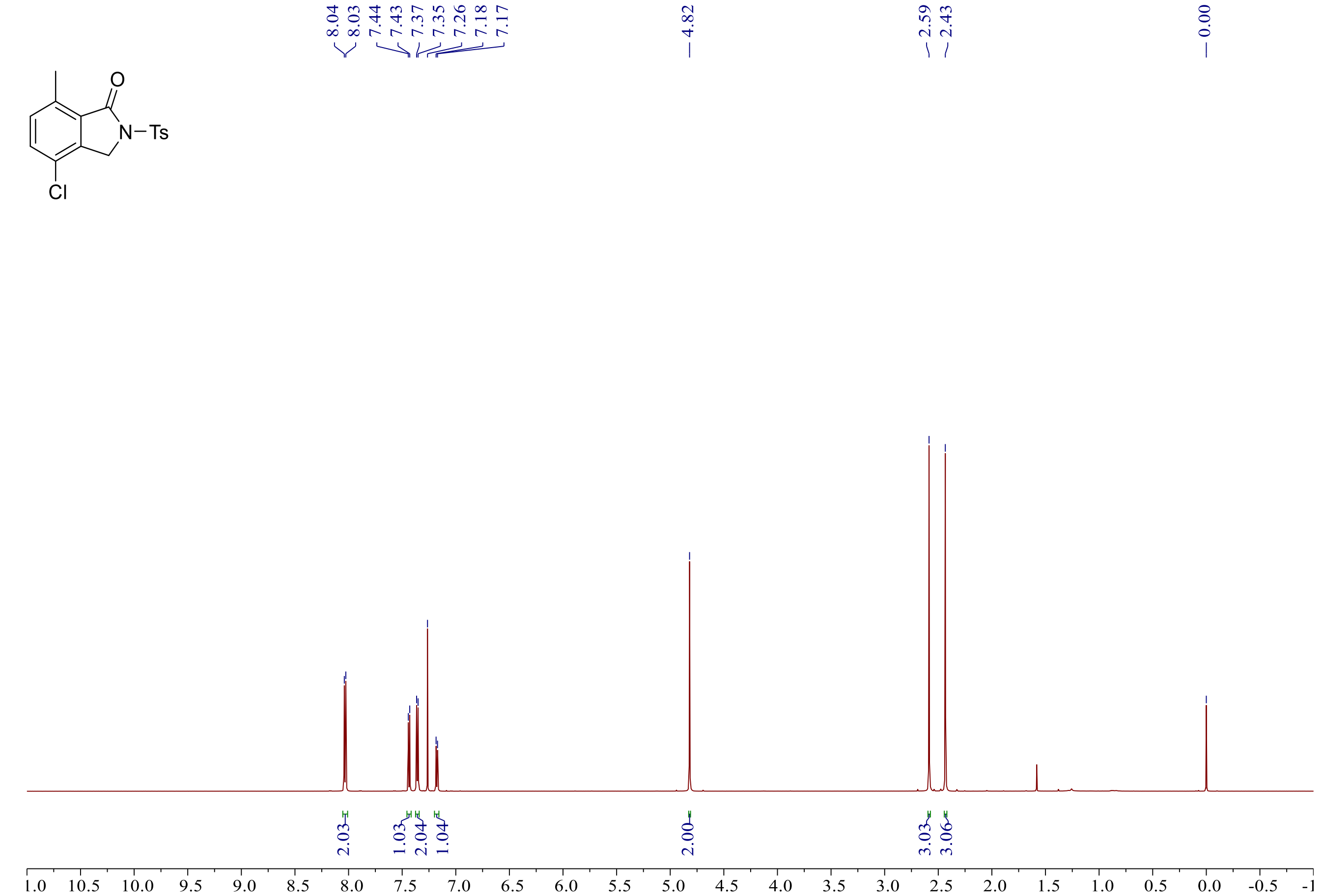


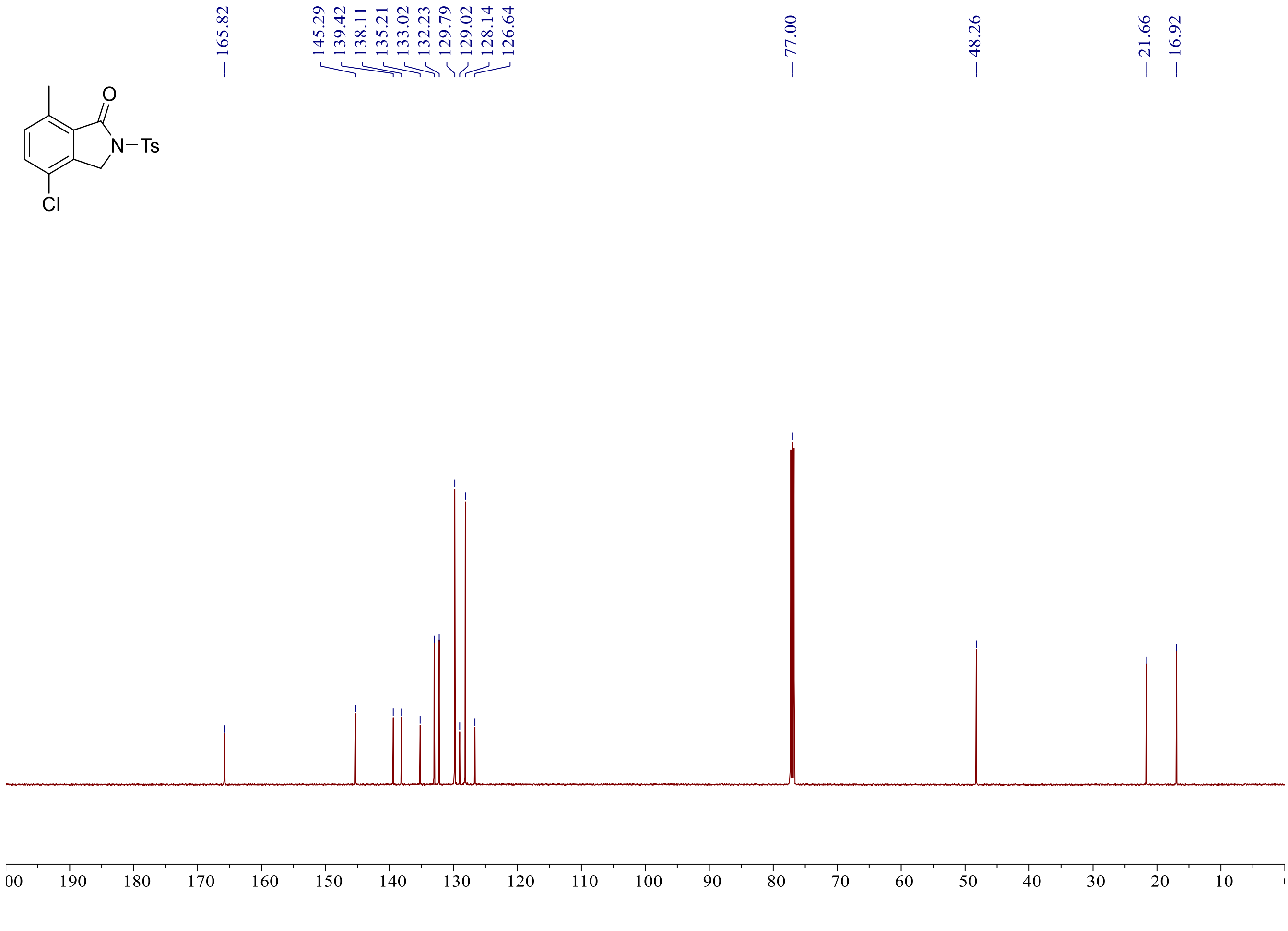
[1]H NMR (600 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectra of product 3wa



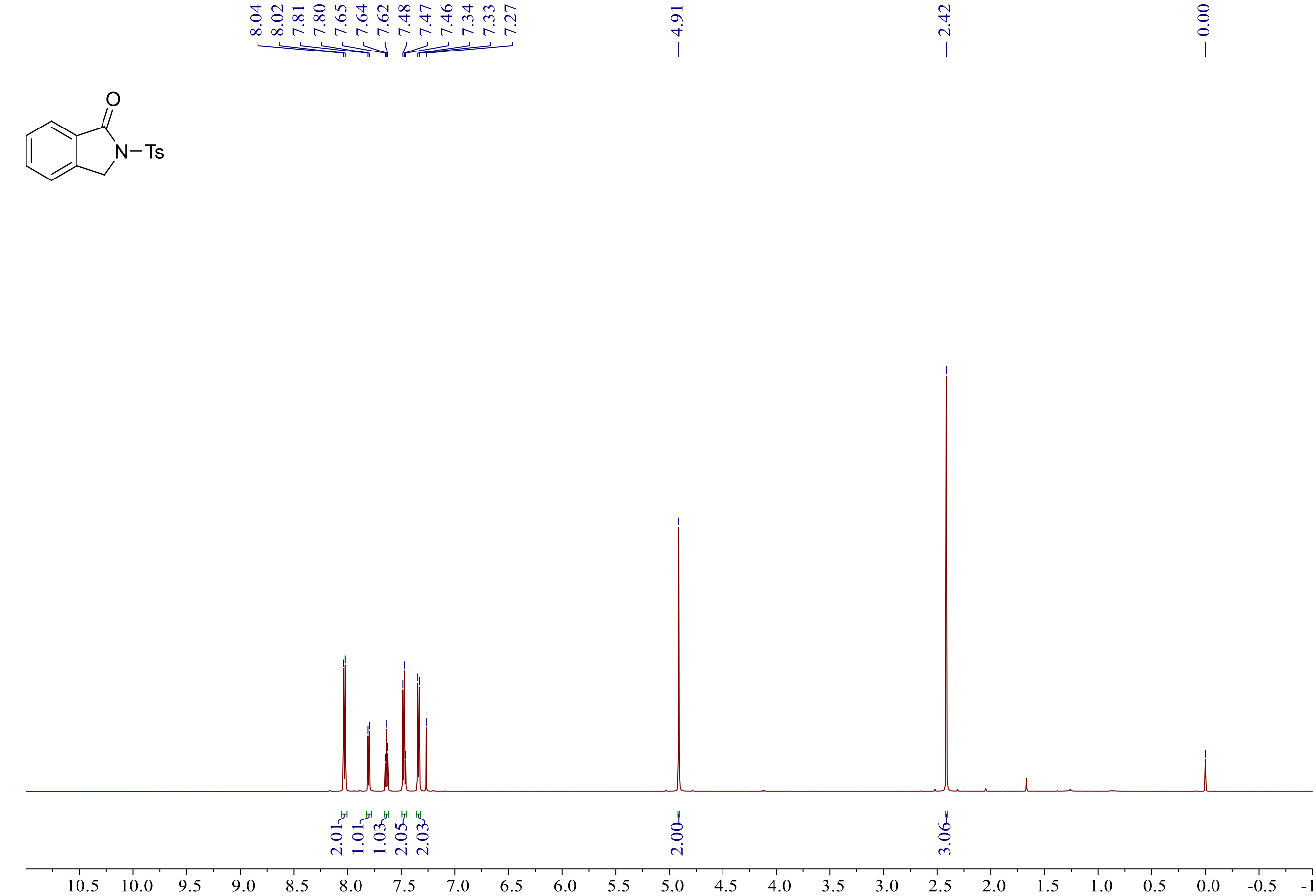


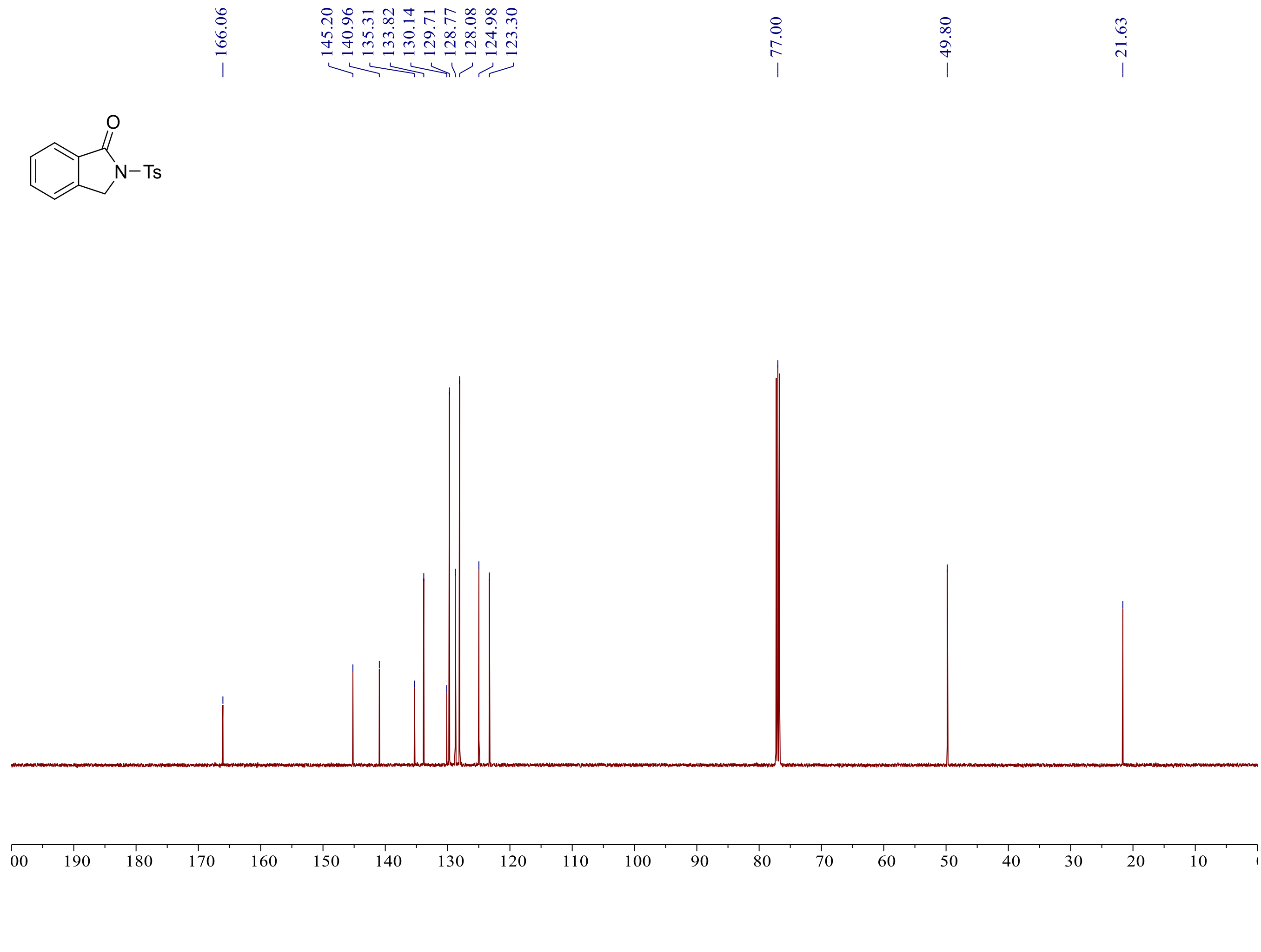
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of product 3xa



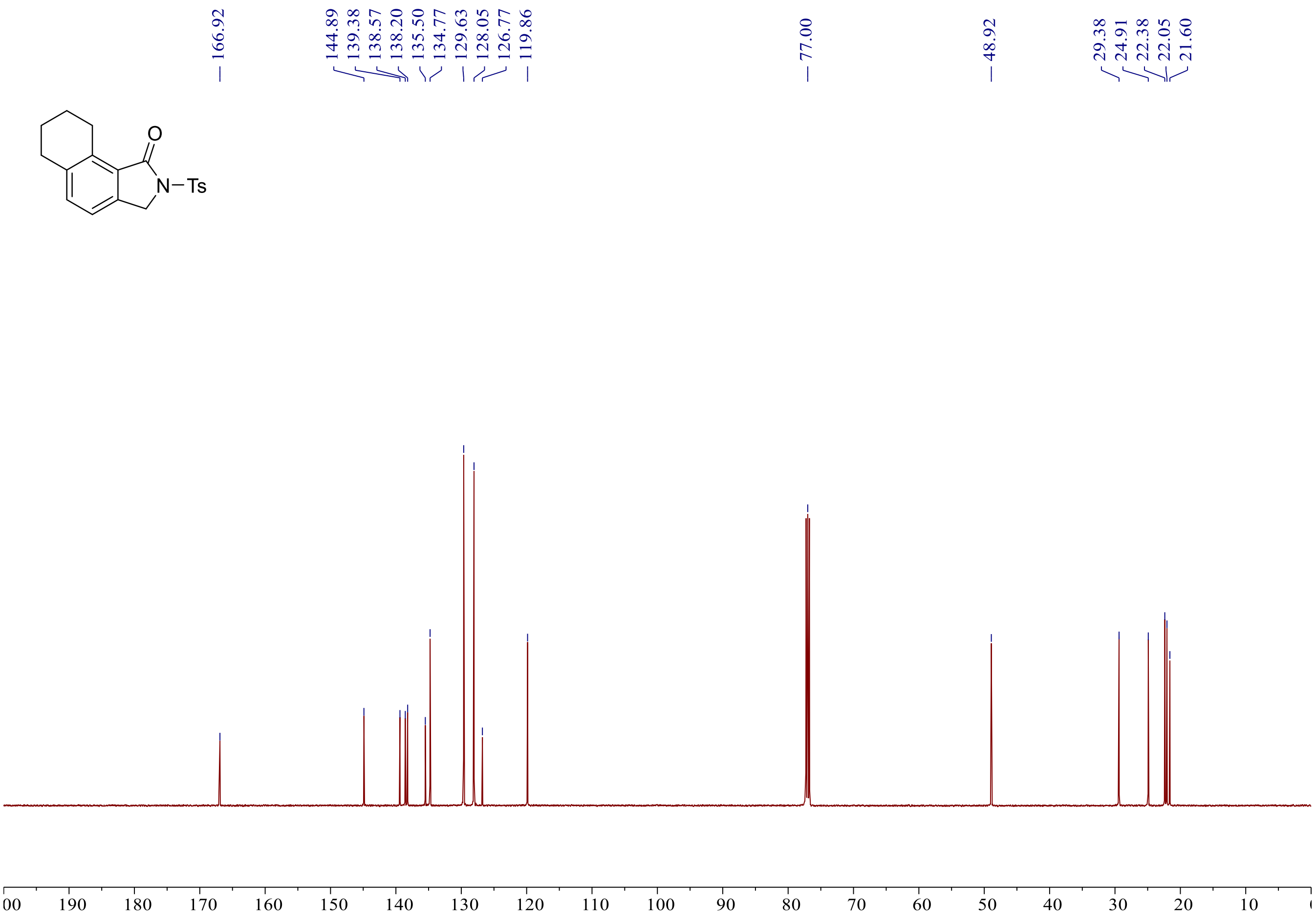


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of product 3ya

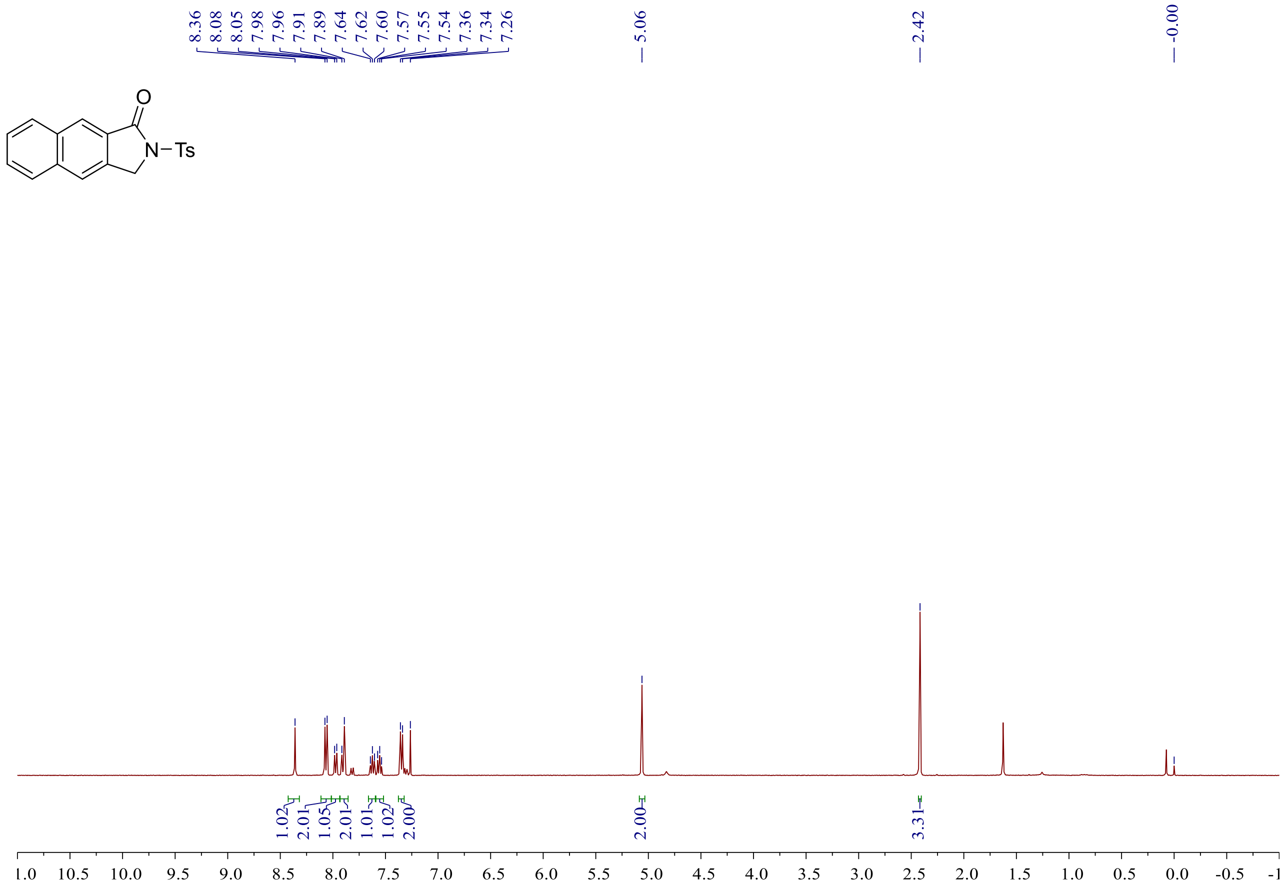


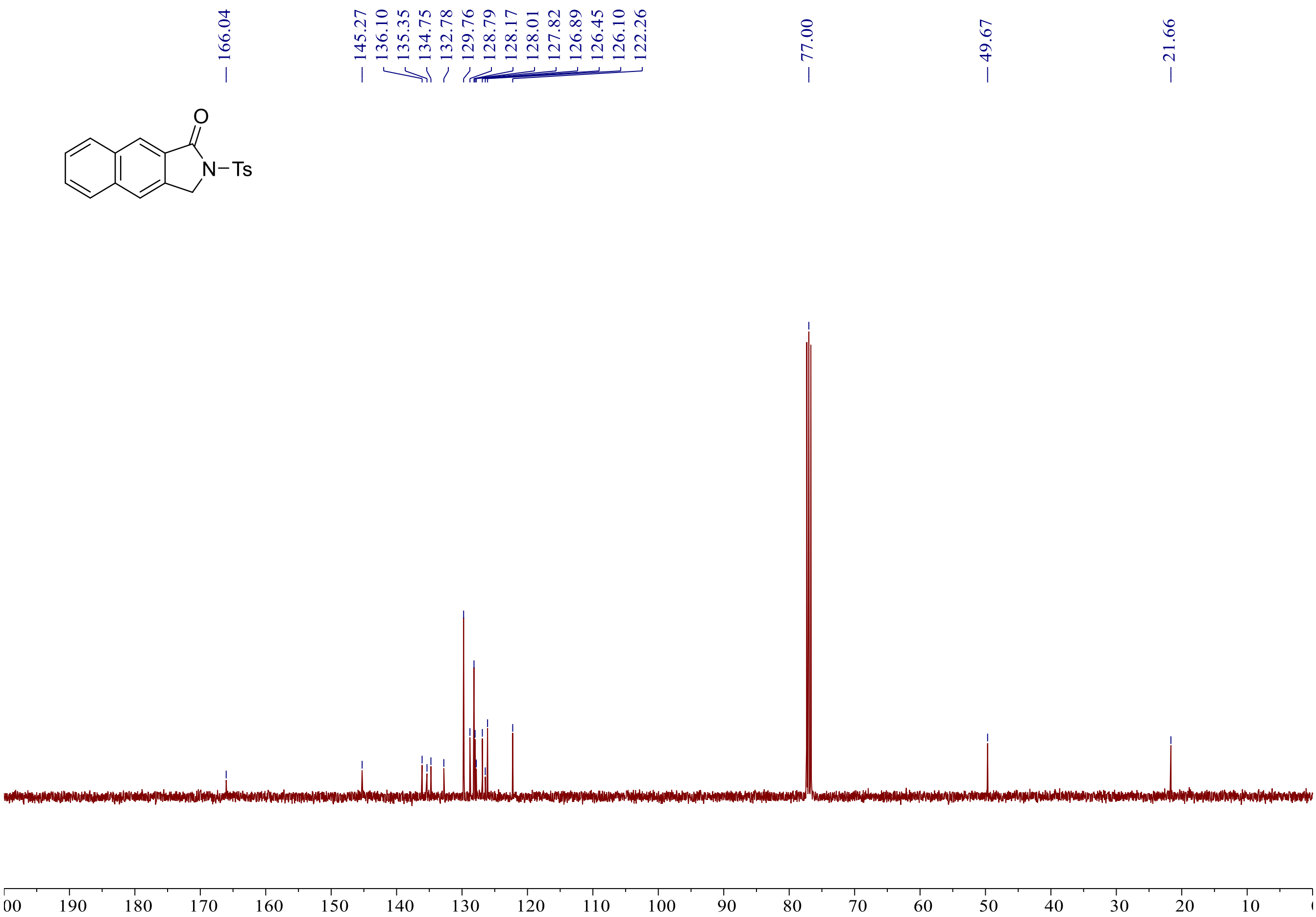


[1]H NMR (600 MHz, $CDCl_3$) and [13]C NMR (125 MHz, $CDCl_3$) spectrum of product 3za

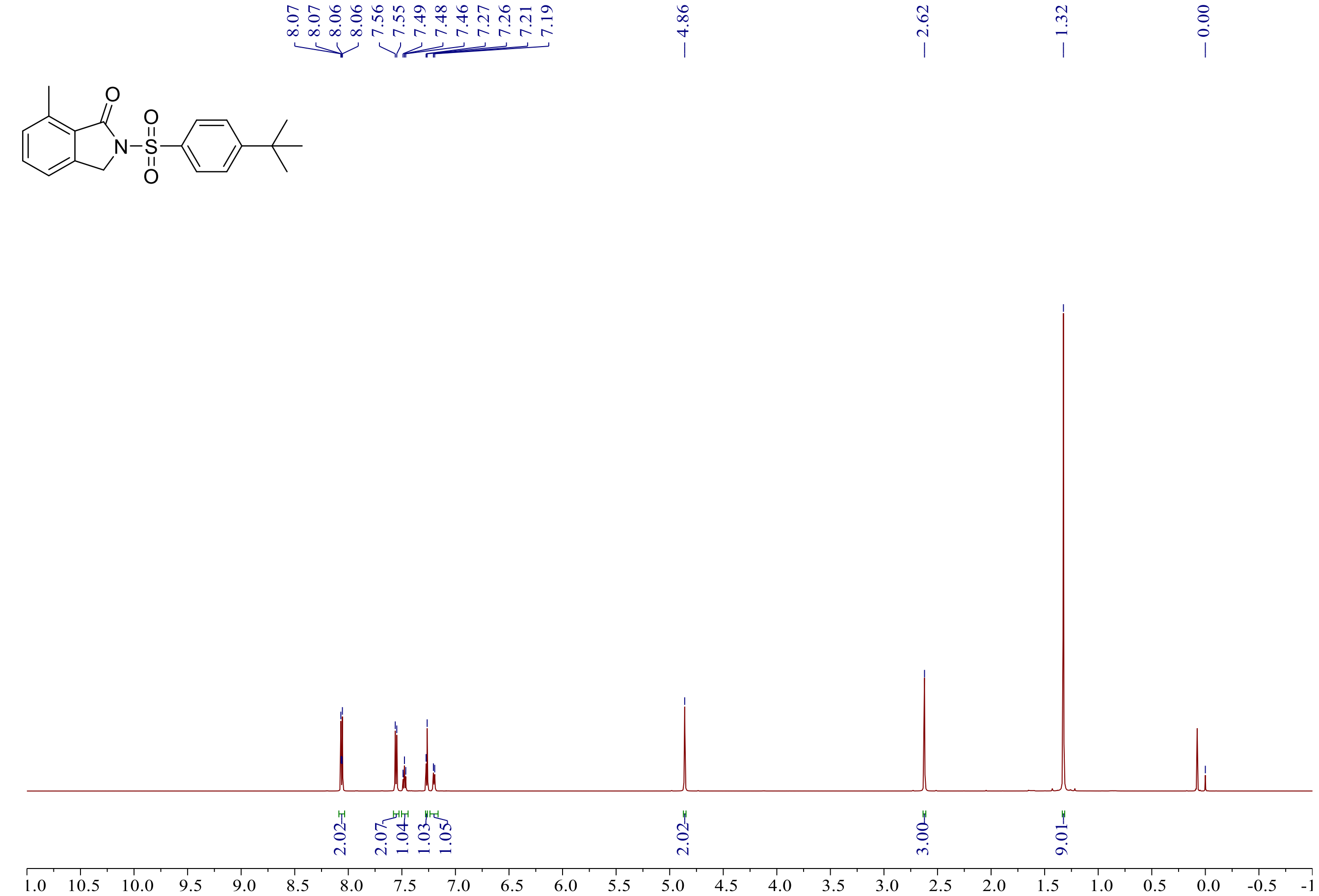


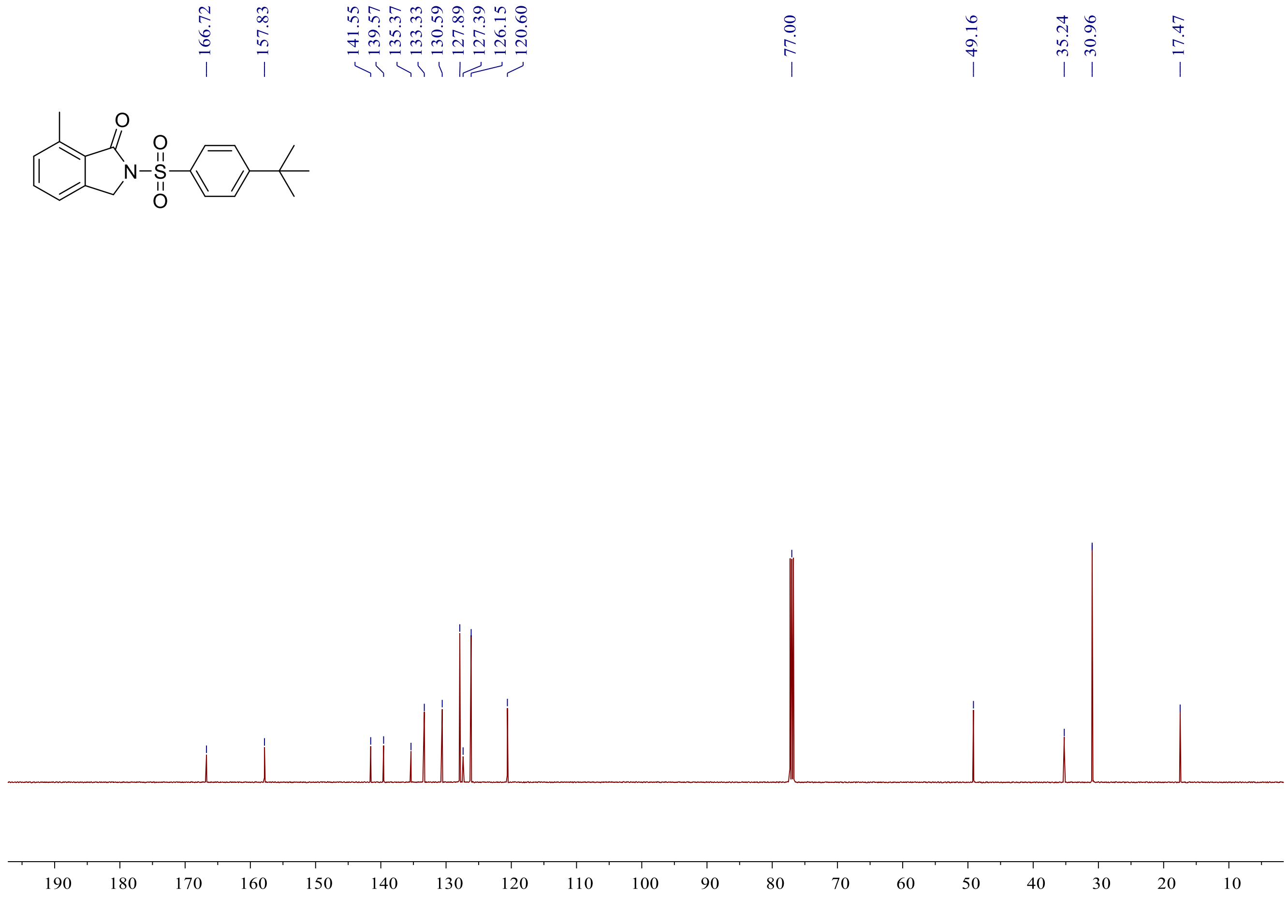
[1]H NMR (400 MHz, CDCl$_3$) and [13]C NMR (100 MHz, CDCl$_3$) spectrum of product 3za'



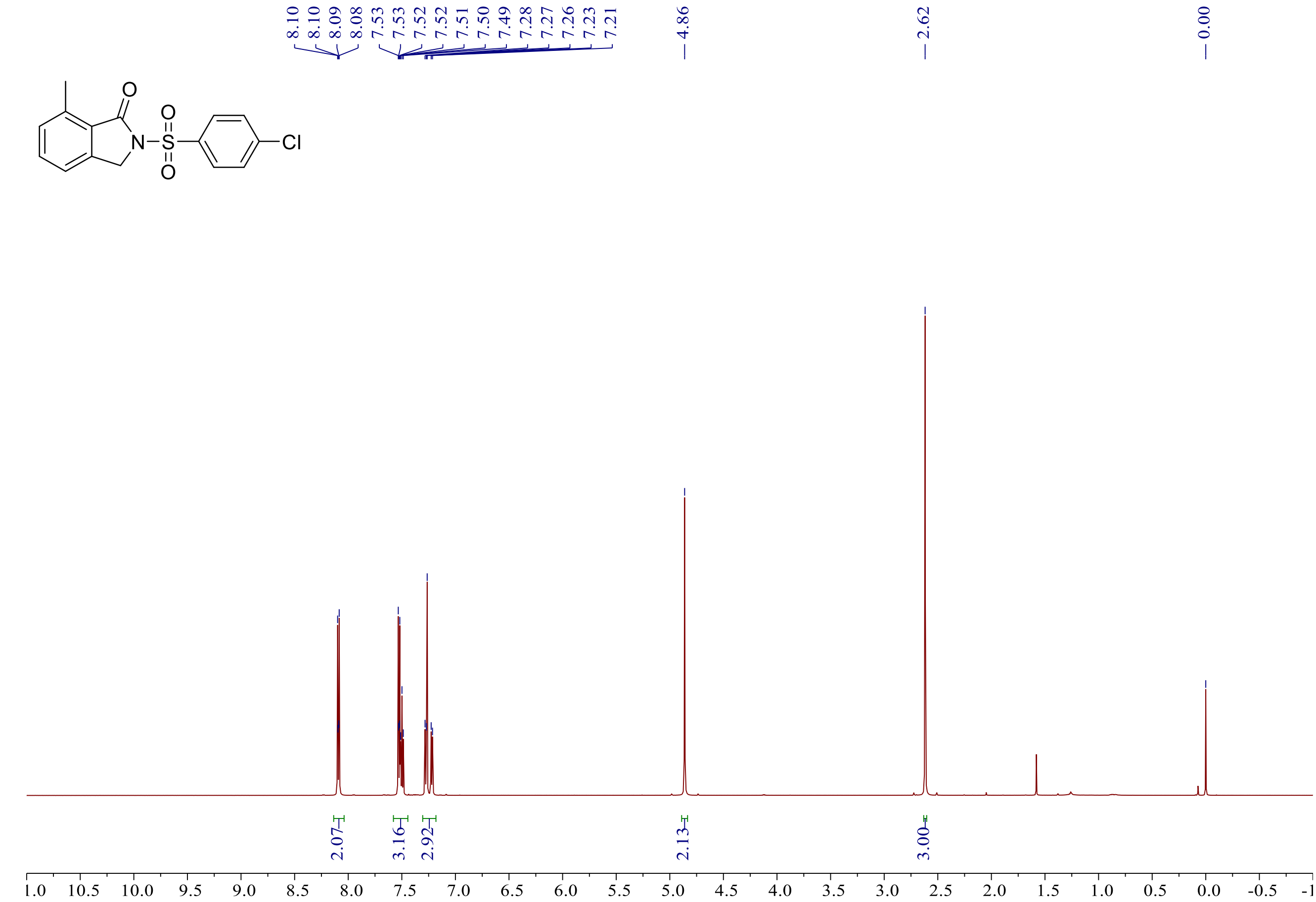


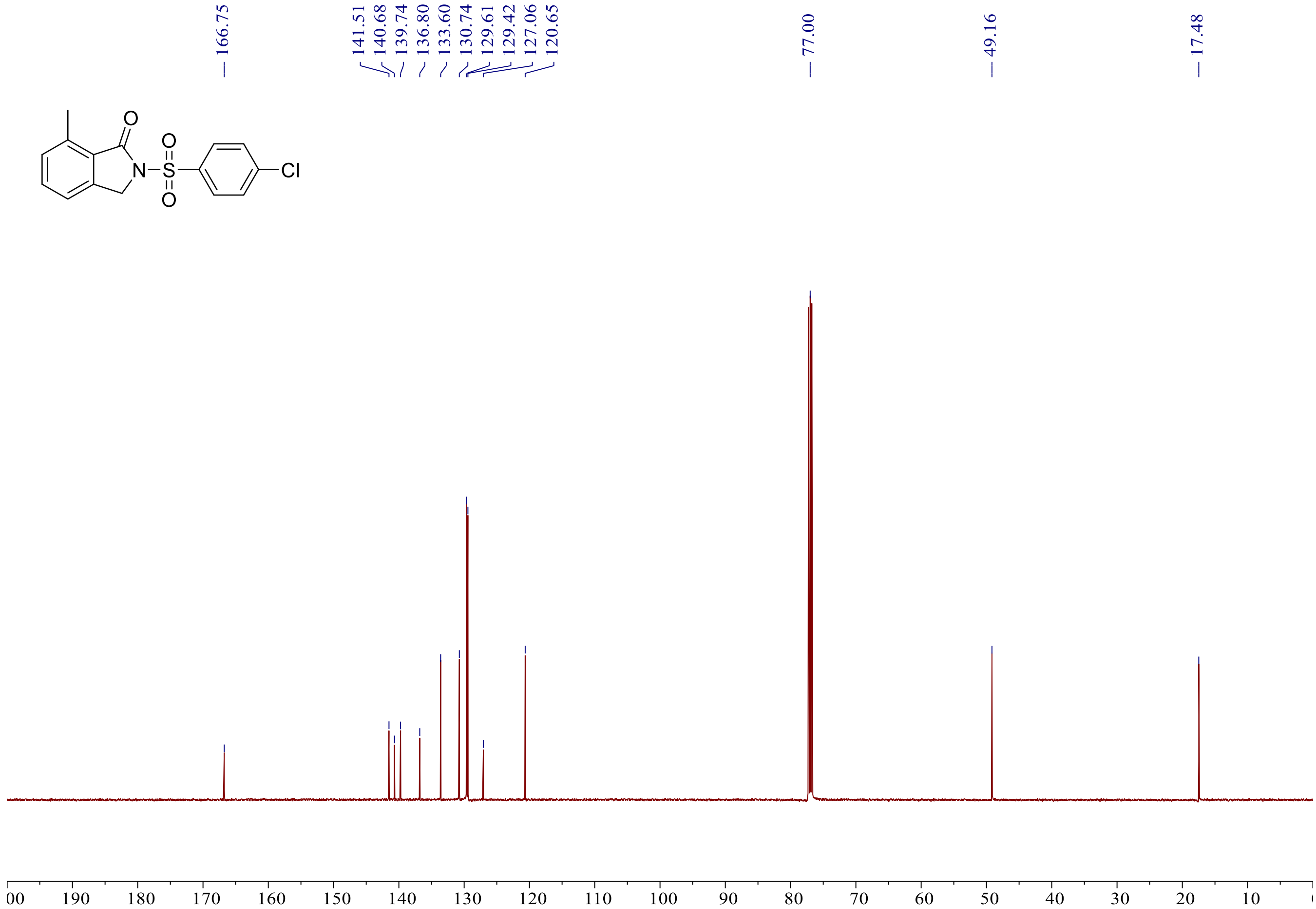
[1]H NMR (600 MHz, $CDCl_3$) and [13]C NMR (125 MHz, $CDCl_3$) spectrum of product 3ab



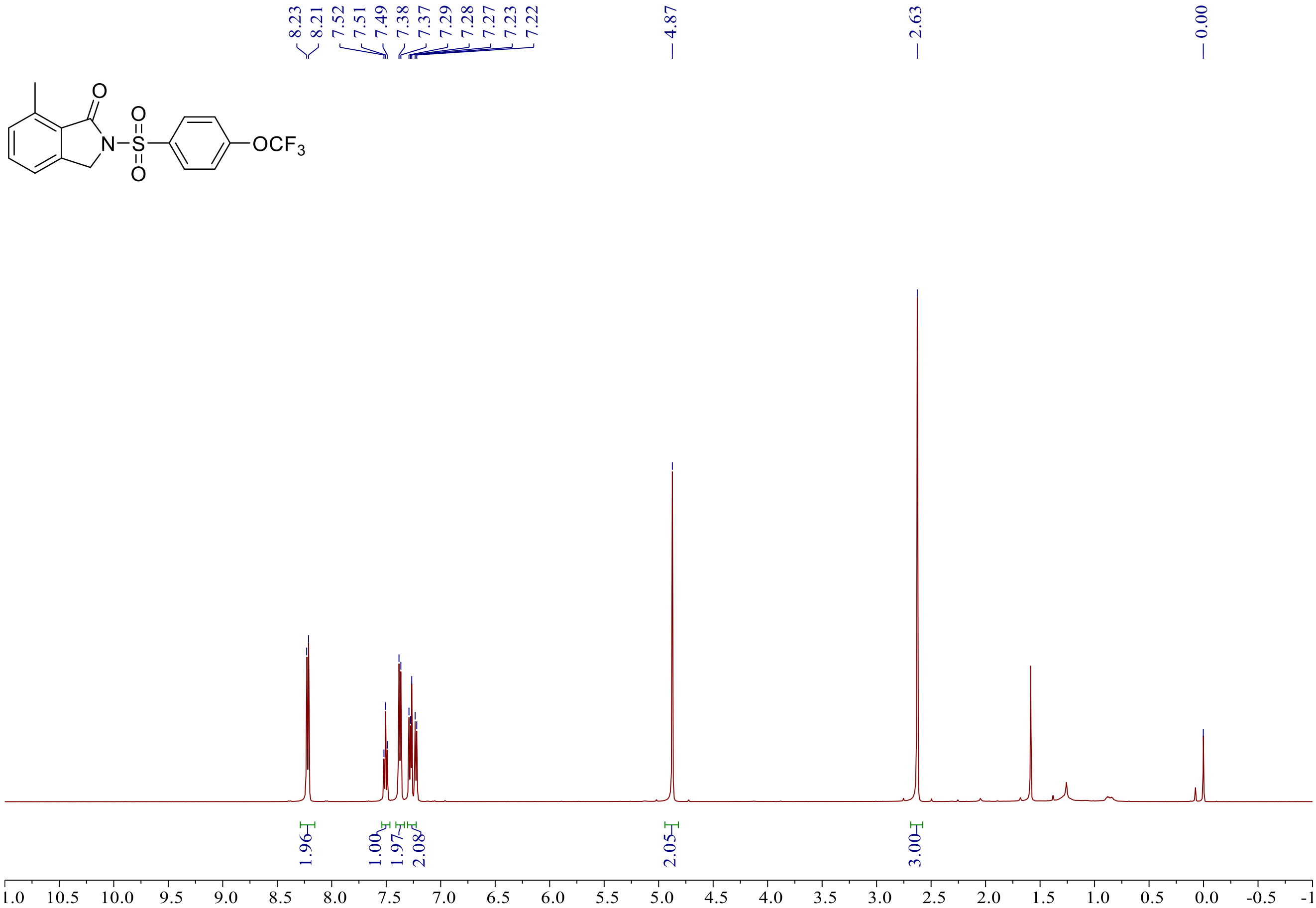


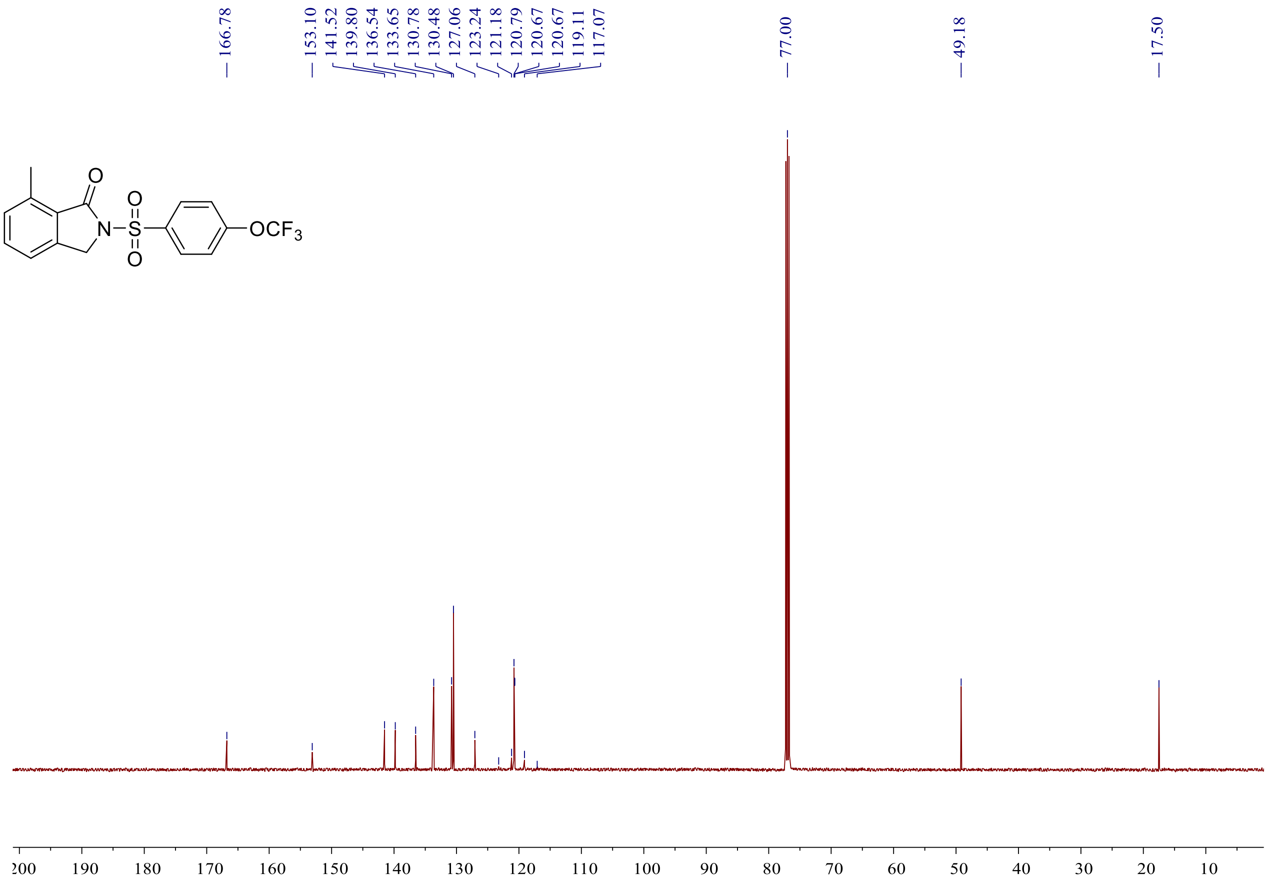
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of product 3ac



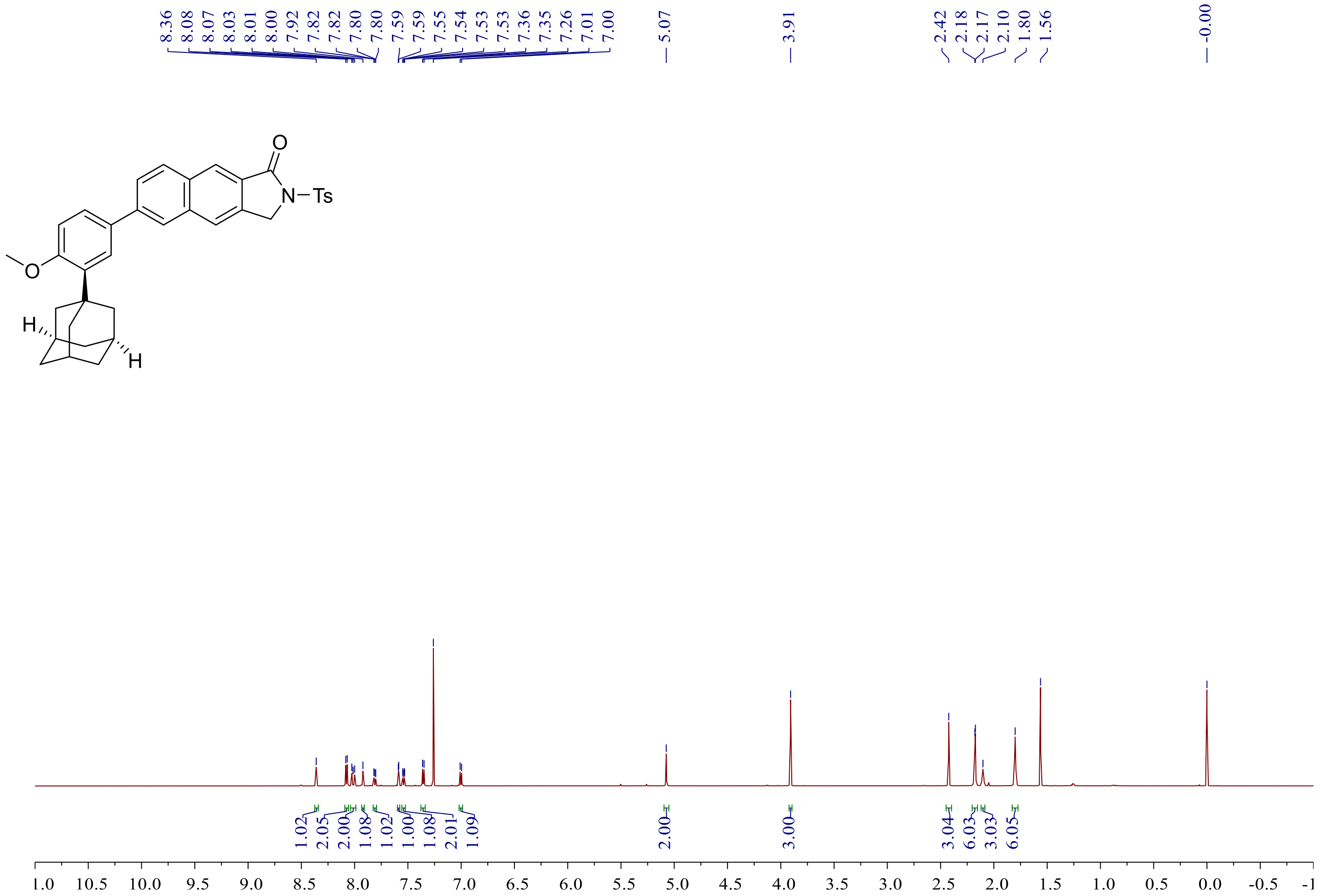


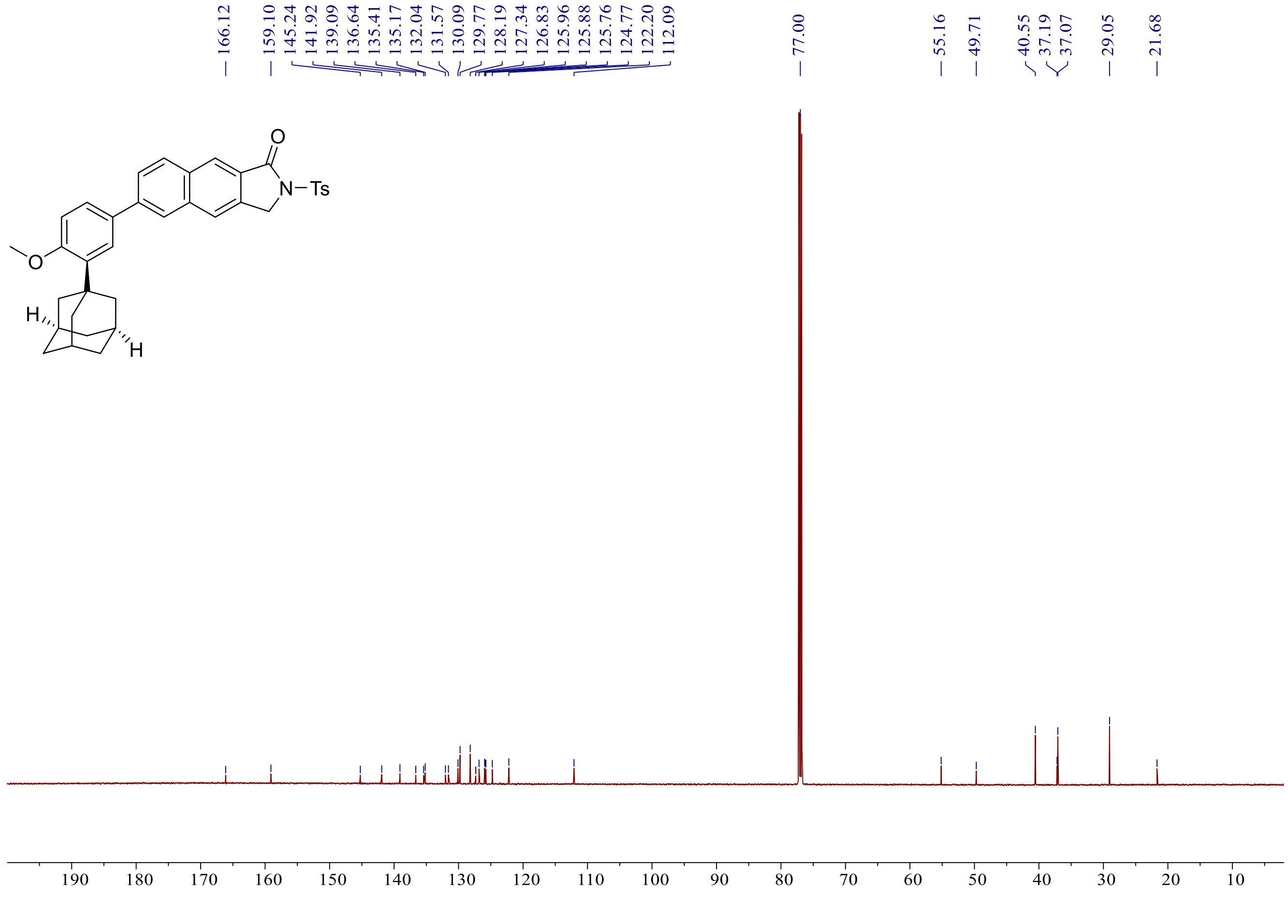
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of product 3ad



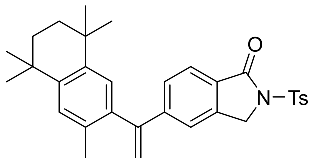


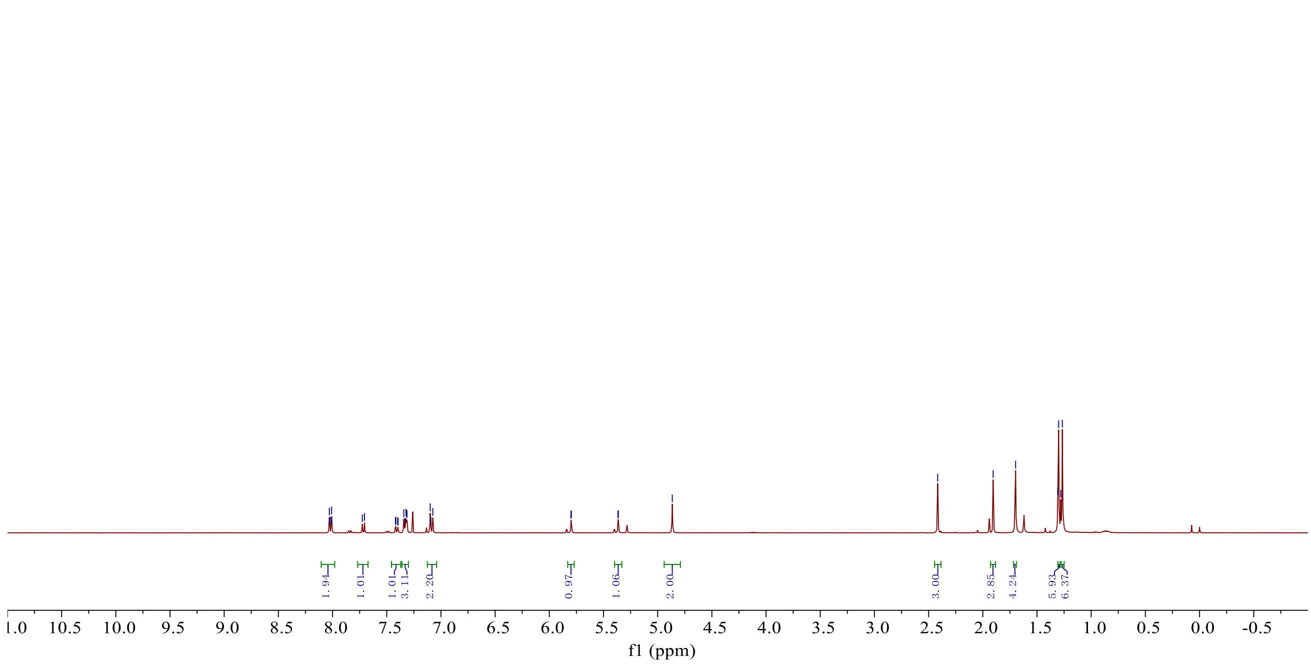
[1]H NMR (600 MHz, $CDCl_3$) and [13]C NMR (150 MHz, $CDCl_3$) spectrum of product 5

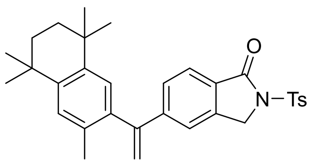


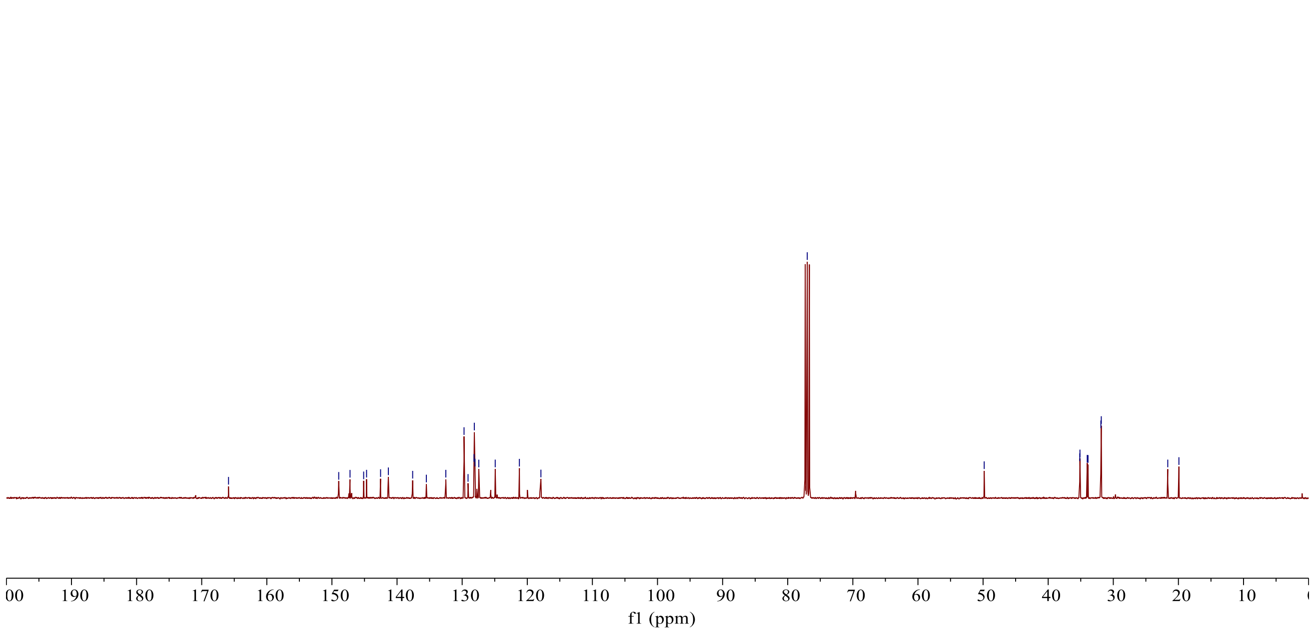


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 7

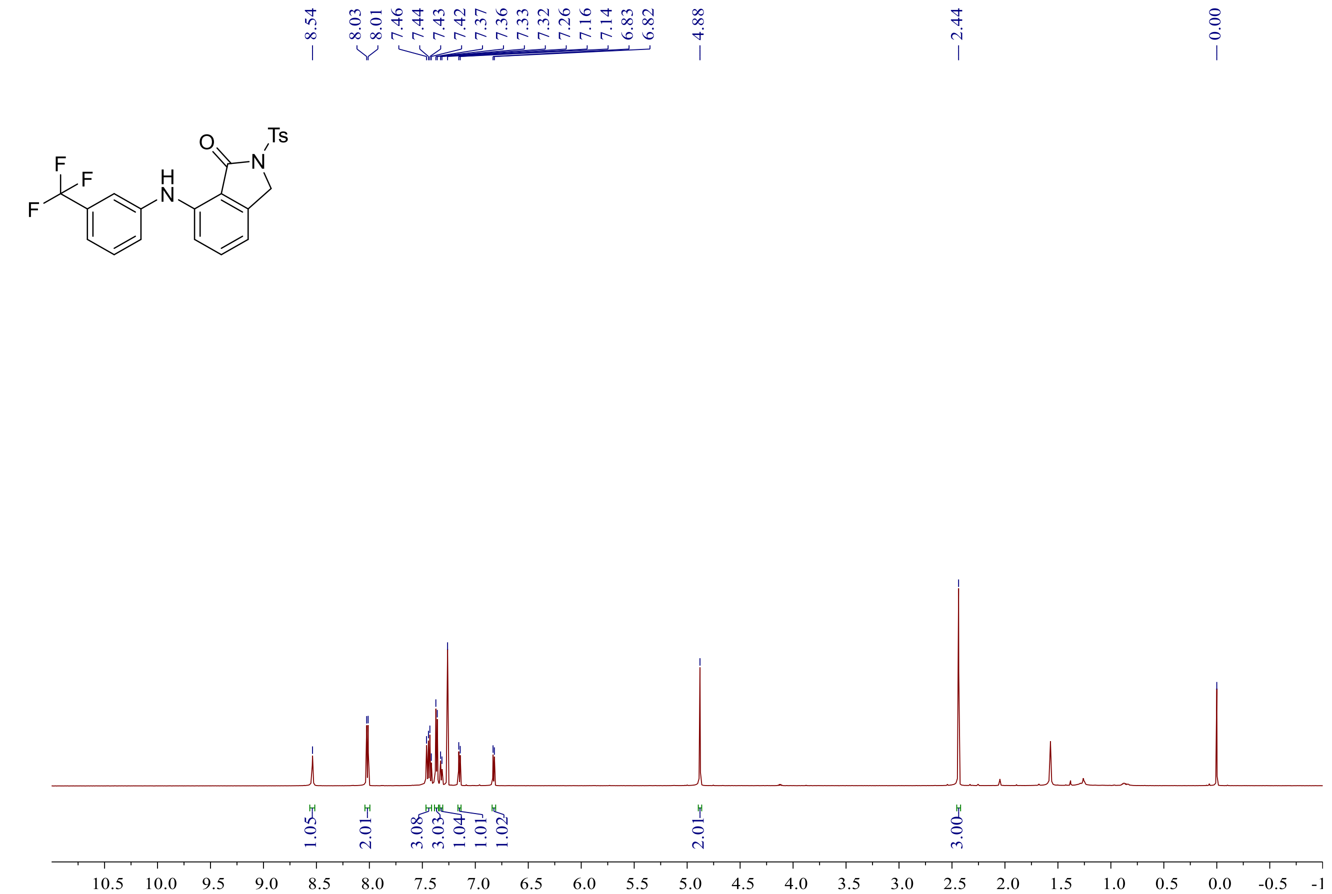


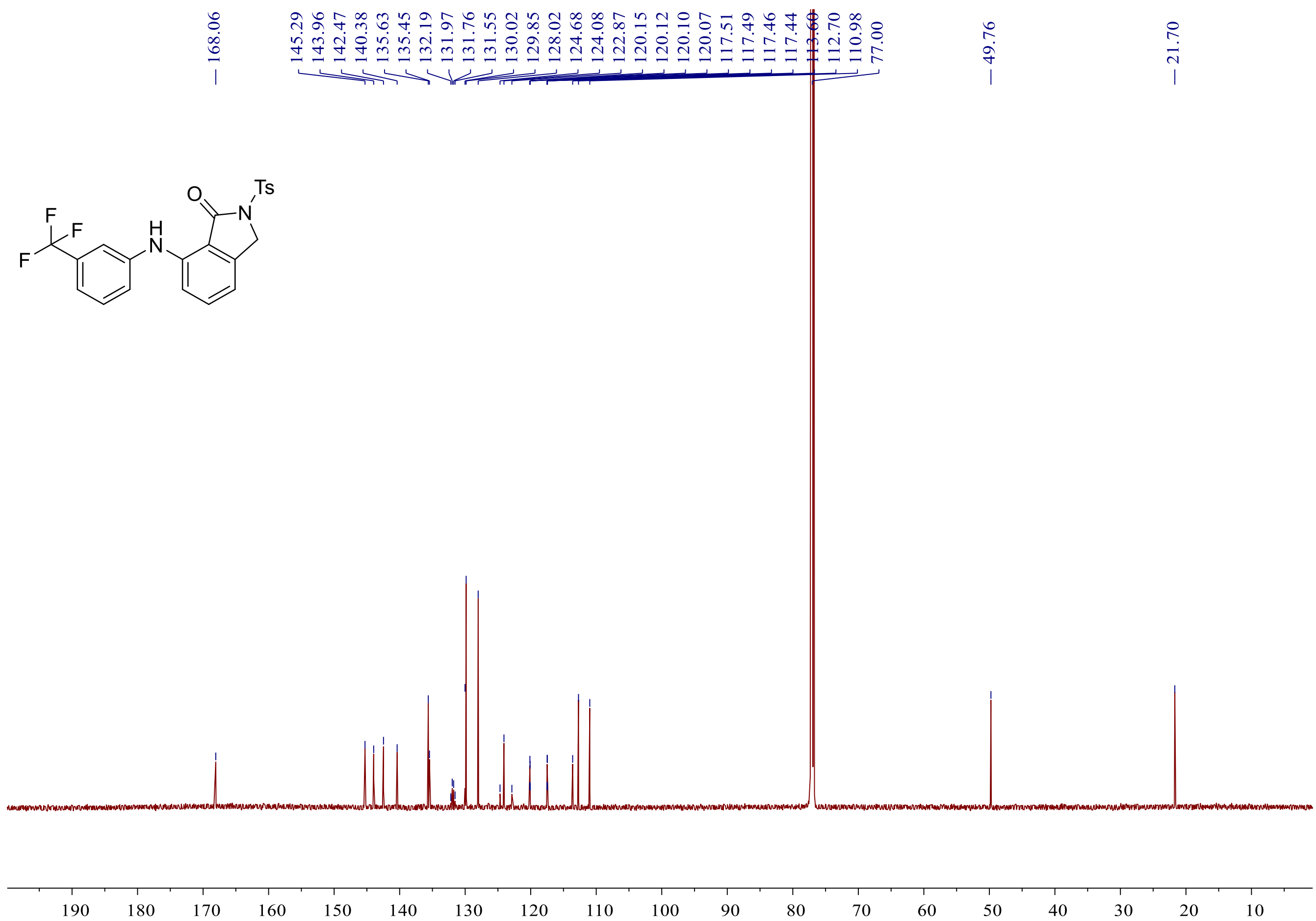




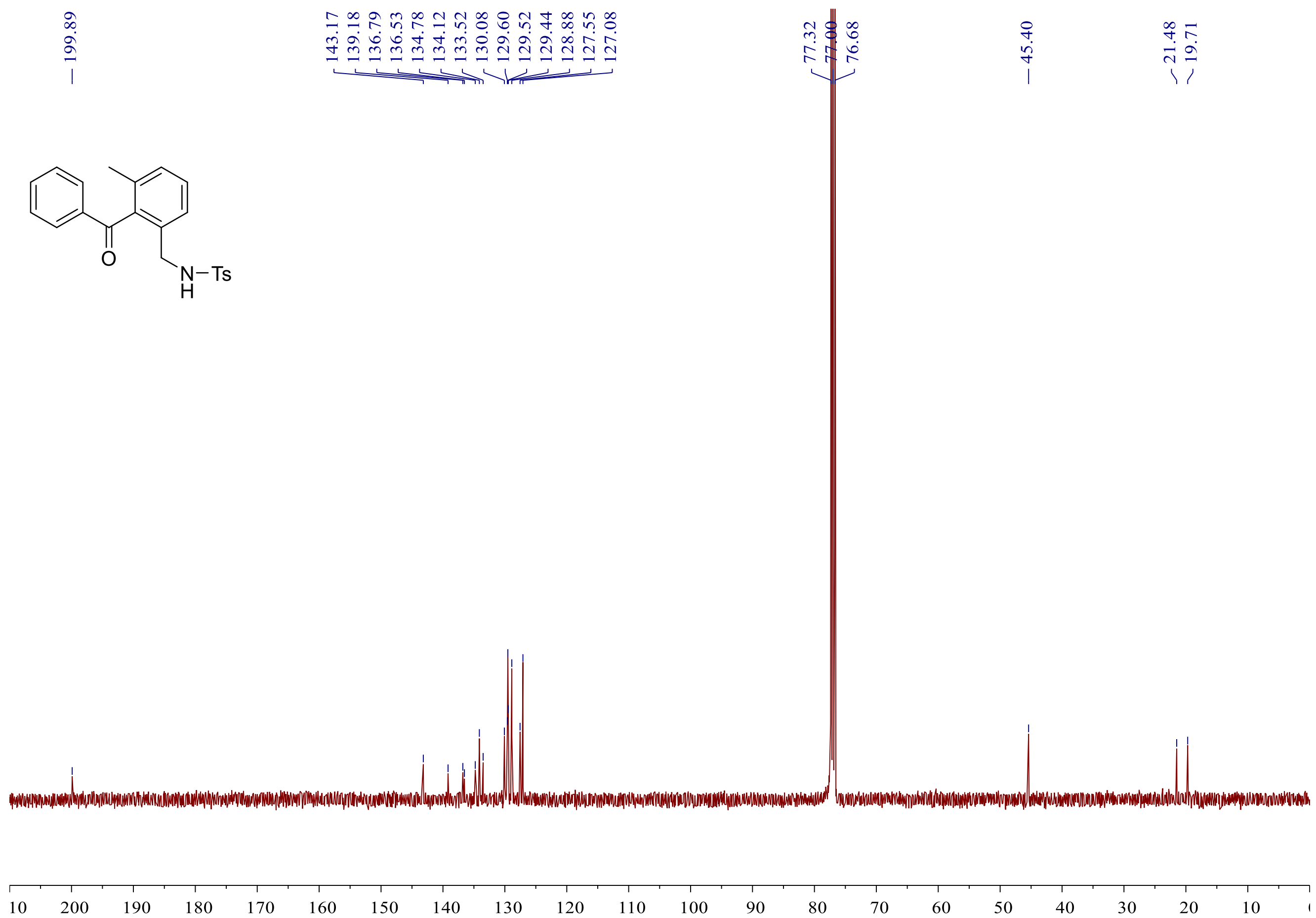


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 9

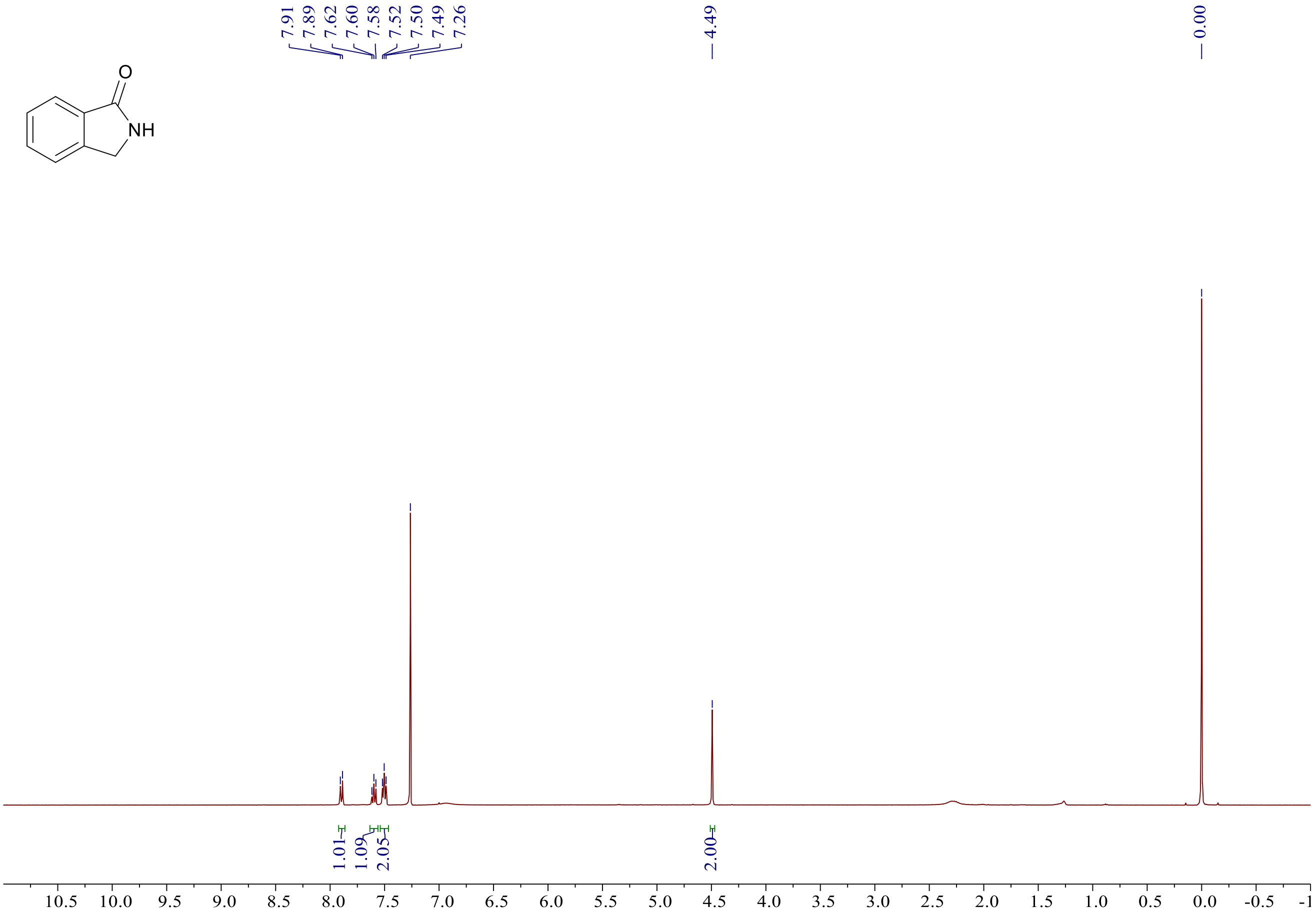


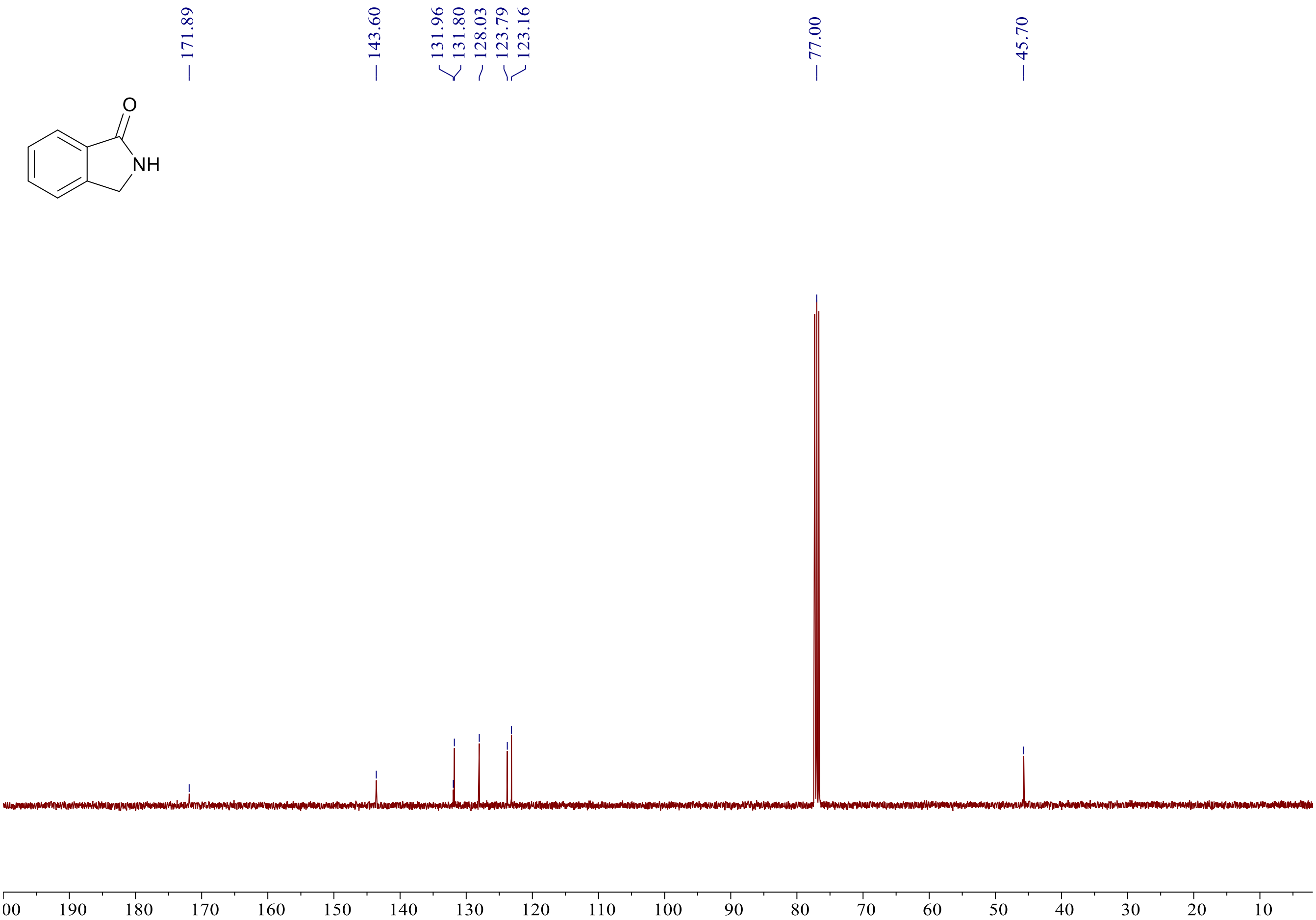


[1]H NMR (400 MHz, CDCl$_3$) and [13]C NMR (100 MHz, CDCl$_3$) spectrum of product 10



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 12





[1]H NMR (400 MHz, $CDCl_3$) and [13]C NMR (100 MHz, $CDCl_3$) spectrum of product 13