Sulphur Ylide-Mediated Cyclopropanation and Subsequent Spirocyclopropane Rearrangement Reactions

Qing-Song Dai,[a,d,e] Jun-Long Li,[c,d] Qi-Wei Wang,[a,c,d,*] Si-Lin Yang,[d] Ying-Mao Tao,[d] Mei-Hao He,[d] Qing-Zhu Li,[c,d] Bo Han [b,c,*] and Xiang Zhang [c,d,*]

[a] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China. E-mail: wqw@cioc.ac.cn*
[b] *State Key Laboratory of Southwestern Chinese Medicine Resources, Hospital of Chengdu University of Traditional Chinese Medicine, School of Pharmacy, Chengdu University of Traditional Chinese Medicine, Chengdu 611137, China. E-mail: hanbo@cdutcm.edu.cn*
[c] *Institute for Advanced Study, Chengdu University, Chengdu 610106, China. E-mail: XZhang_CDU@hotmail.com*
[d] *Antibiotics Research and Re-evaluation Key Laboratory of Sichuan Province, Sichuan Industrial Institute of Antibiotics, School of Pharmacy, Chengdu University, Chengdu 610106, PR China.*
[e] *University of Chinese Academy of Sciences, Beijing 100049, China.*

Supporting Information

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1. General Information

General Procedures

- All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed using silica gel (40–63 μm, 230–400 mesh).
- Analytical thin layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and I_2.
- Organic solutions were concentrated at 30–50 °C on rotary evaporators at ~10 torr followed by drying on vacuum pump at ~1 torr. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials

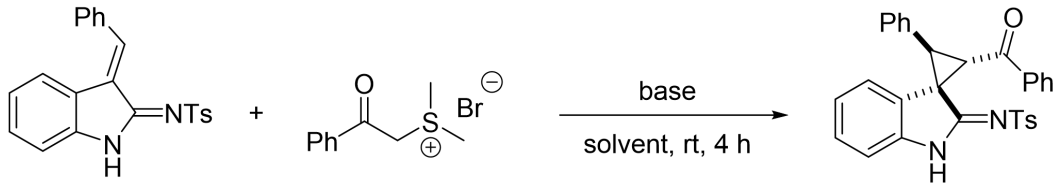
- Commercial reagents and solvents were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin, Leyan, and Energy Chemical used as received with the following exceptions: THF, Et_2O and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.[1] The aza-dienes **1**[2] and sulphonium bromides **2**[3] were prepared according to literature procedure.

Instrumentation

- Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with JEOL-600M. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with JEOL 150 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.0 ($CHCl_3$)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (C_q = fully substituted carbon)].
- High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2 using an electrospray (ESI) ionisation source.
- Melting points were recorded on WRX-X-4A melting point apparatus.

2. Further Optimization Studies

Table S1. Optimisation of (2+1) Cascade [a]

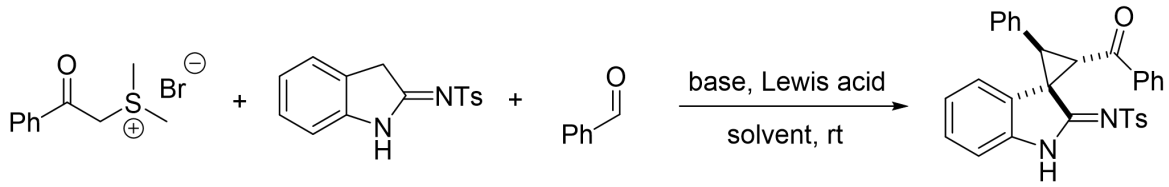


1a **2a** **3a**

Entry	Base	Solvent	Yield (%) [b]	dr [c]
1	Cs_2CO_3	DCM	81	5:1
2	Cs_2CO_3	toluene	50	6:1
3	Cs_2CO_3	MeCN	83	6:1
4	Cs_2CO_3	$CHCl_3$	33	7:1
5	Cs_2CO_3	THF	<5	-
6	Cs_2CO_3	EtOH	75	6:1
7	Cs_2CO_3	EA	74	6:1
8	K_3PO_4	MeCN	62	5:1
9	K_2CO_3	MeCN	87	6:1
10	NaOAc	MeCN	34	5:1
11	$NaHCO_3$	MeCN	46	2:1
12	Et_3N	MeCN	11	6:1
13	DBU	MeCN	48	10:1
14	TMG	MeCN	<5	-
15	DBACO	MeCN	82	5:1
16 [d]	K_2CO_3	MeCN	85	6:1

[a] Unless otherwise noted, reactions were performed with 0.10 mmol of **1a**, 0.12 mmol of **2a** and 0.12 mmol of base in 1.0 mL of solvent at room temperature for 4 hours. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis of the crude reaction. [d] The reaction was performed at 0 °C.

Table S2. Optimisation of (1+1+1) Cascade [a]



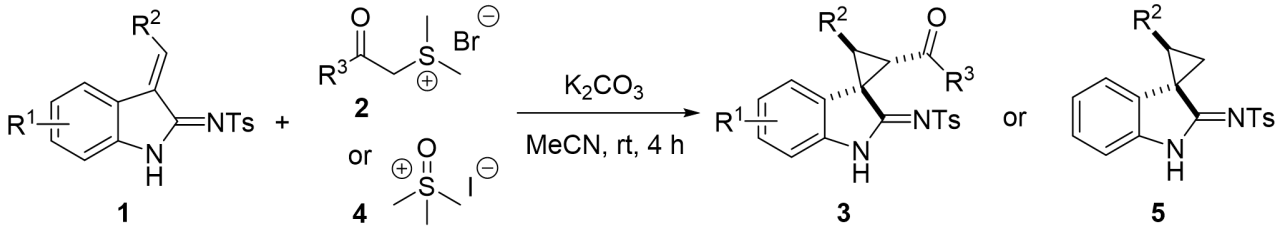
2a **6a** **7a** **3a**

Entry	Lewis acid	Base	Solvent	Yield (%) [b]	dr [c]
1	$BF_3{\cdot}OEt_2$	K_2CO_3	MeCN	61	5:1
2	$Mg(OTf)_2$	K_2CO_3	MeCN	<5	-
3	$Sc(OTf)_3$	K_2CO_3	MeCN	<5	-
4	$Al(O\textit{i}Pr)_3$	K_2CO_3	MeCN	59	4:1
5	$BF_3{\cdot}OEt_2$	K_2CO_3	DCM	58	3:1
6	$BF_3{\cdot}OEt_2$	K_2CO_3	THF	<5	-
7	$BF_3{\cdot}OEt_2$	K_2CO_3	toluene	61	7:1
8	$BF_3{\cdot}OEt_2$	K_3PO_4	toluene	71	4:1
9	$BF_3{\cdot}OEt_2$	Cs_2CO_3	toluene	73	7:1
10	$BF_3{\cdot}OEt_2$	Et_3N	toluene	<5	-
11	$BF_3{\cdot}OEt_2$	DBU	toluene	<5	-
12	$BF_3{\cdot}OEt_2$	TMG	toluene	<5	-
13	$BF_3{\cdot}OEt_2$	DBACO	toluene	<5	-
14[d]	$BF_3{\cdot}OEt_2$	Cs_2CO_3	toluene	23	5:1
15[e]	$BF_3{\cdot}OEt_2$	Cs_2CO_3	toluene	36	4:1

[a] Unless otherwise noted, reactions were performed with 0.12 mmol of **2a**, 0.1 mmol of **6a**, 0.15 mmol of **7a**, 0.12 mmol of base and 0.1 mmol Lewis acid in 1.0 mL of solvent at room temperature for 12 hours. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis of the crude reaction. [d] 0.5 mL solvent was used. [e] 2 mL solvent was used.

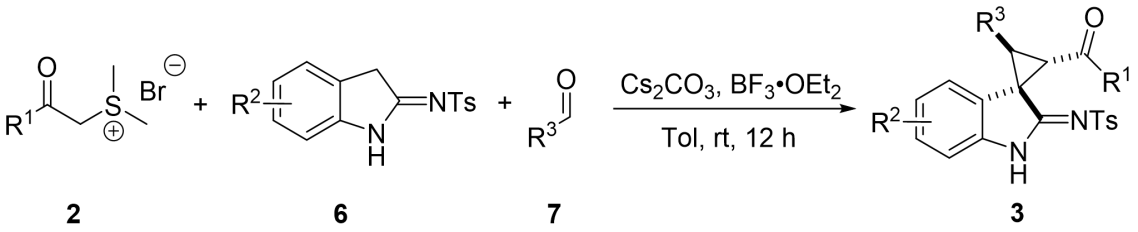
3. General Procedure for the Preparation of Products 3 or 5

Procedure A**: the direct annulation of **1** and **2** or **4



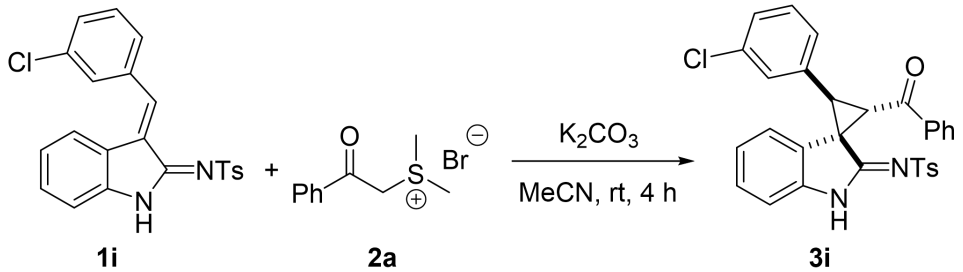
A glass tube was charged with aza-dienes **1** (0.10 mmol), sulphonium bromides **2** (0.12 mmol) or Corey-Chaykovsky reagent **4** (0.12 mmol), K_2CO_3 (0.12 mmol) in 1 mL MeCN. The mixture was stirred at room temperature for 4 hours. Then the mixture was concentrated and purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 15:1 to 5:1 to afford the corresponding product **3** or **5**.

Procedure B**: the three-component reaction of **2, 6** and **7



A glass tube was charged with sulphonium bromides **2** (0.12 mmol), iminoindoline **6** (0.10 mmol), aldehyde **7** (0.12 mmol), Cs_2CO_3 (0.12 mmol) and BF_3•OEt_2 (0.1 mmol) in 1 mL toluene. The mixture was stirred at room temperature for 12 hours. Then the mixture was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 15:1 to 5:1 to afford the corresponding product **3**.

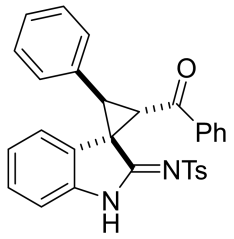
Procedure for large-scale synthesis of 3d



A glass tube was charged with aza-diene **1i** (20 mmol, 1.052 g), sulphonium bromide **2a** (24

mmol, 626.4 mg), K_2CO_3 (24 mmol, 331.2 mg) in 20 mL MeCN. The mixture was stirred at room temperature for 4 hours. Then the mixture was concentrated and purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 15:1 to 5:1 to afford the corresponding product **3i** (948.6 mg) in 90% yield as light yellow solid. The diastereomeric ratio was determined to be 9:1 by crude ^{1}H-NMR analysis.

N-((Z)-2-benzoyl-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3a



Prepared according to the ***General Procedure A*** to afford **3a** (42.8 mg) in 87% yield as light yellow solid, m.p. = 181 – 184 ^{o}C. The diastereomeric ratio was determined to be 6:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3a** (35.9 mg) in 73% yield as light yellow solid. The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis.

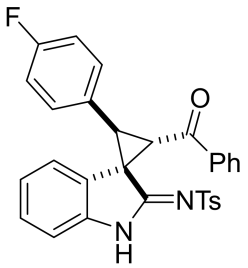
NMR and HRMS data for the product **3a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.32 – 7.27 (m, 3H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.11 – 7.06 (m, 5H), 7.05 – 7.01 (m, 2H), 4.47 (d, *J* = 9.0 Hz, 1H), 4.25 (d, *J* = 9.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.2, 165.6, 142.5, 140.9, 138.7, 136.5, 133.9, 131.9, 129.5, 129.1, 128.9, 128.5, 127.9, 127.5, 126.5, 126.0, 123.6, 122.0, 110.0, 43.8, 43.0, 42.3, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{24}N_2O_3S+Na^+$: 515.1400, found: 515.1407.

N-((Z)-2-benzoyl-3-(4-fluorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3b



Prepared according to the ***General Procedure A*** to afford **3b** (46.4 mg) in 91% yield as white solid, m.p. = 218 – 220 °C. The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis.

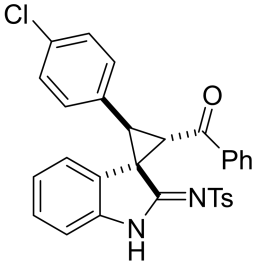
NMR and HRMS data for the product **3b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.24 (s, 1H), 7.96 (d, *J* = 6.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 3.0 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 – 7.00 (m, 4H), 6.65 – 6.60 (m, 2H), 4.42 (d, *J* = 9.0 Hz, 1H), 4.18 (d, *J* = 9.0 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.1, 165.0, 162.0 (d, *J* = 244.2 Hz, 1C), 143.0, 140.9, 138.5, 136.4, 134.0, 131.0 (d, *J* = 8.6 Hz, 1C), 129.1, 128.9, 128.5, 128.0, 127.6, 126.3, 123.7, 122.0, 114.7(d, *J* = 21.6 Hz, 1C), 110.0, 43.5, 42.9, 41.4, 21.4.

HRMS (ESI) m/z calculated for $C_{30}H_{23}FN_2O_3S+Na^+$: 533.1306, found: 533.1312.

N-((Z)-2-benzoyl-3-(4-chlorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide 3c



Prepared according to the ***General Procedure A*** to afford **3c** (44.3 mg) in 84% yield as white solid, m.p. = 223 – 225 °C. The diastereomeric ratio was determined to be 11:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3c** (24.2 mg) in 46% yield as white solid. The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis.

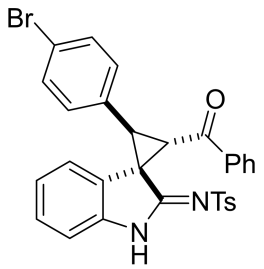
NMR and HRMS data for the product **3c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.21 (s, 1H), 7.96 – 7.92 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.06 – 7.00 (m, 4H), 6.90 (d, *J* = 7.8 Hz, 2H), 4.41 (d, *J* = 7.8 Hz, 1H), 4.16 (d, *J* = 9.0 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.0, 165.0, 143.1, 140.9, 138.4, 136.4, 134.0, 133.4, 130.7, 130.5, 129.2, 128.9, 128.5, 128.1, 127.9, 126.1, 125.9, 123.7, 122.0, 111.0, 43.5, 42.8, 41.2, 21.6.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1002, 550.1050.

N-((Z)-2-benzoyl-3-(4-bromophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide 3d



Prepared according to the ***General Procedure A*** to afford **3d** (40.0 mg) in 70% yield as white solid, m.p. = 234 – 239 °C. The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3d** (33.7 mg) in 59% yield as white solid. The diastereomeric ratio was determined to be 6:1 by crude ^{1}H-NMR analysis.

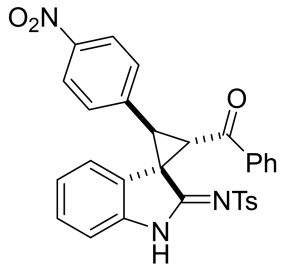
NMR and HRMS data for the product **3d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.25 (s, 1H), 7.95 – 7.92 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.41 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.09 – 7.01 (m, 4H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.40 (d, *J* = 9.0 Hz, 1H), 4.14 (d, *J* = 9.0 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.9, 165.0, 143.1, 141.0, 138.4, 136.4, 134.0, 131.1, 131.0, 130.8, 129.3, 128.9, 128.5, 128.1, 126.1, 125.9, 123.7, 122.0, 121.6, 111.0, 43.5, 42.8, 41.2, 21.7.

HRMS (ESI) m/z calculated for $C_{30}H_{23}BrN_2O_3S+Na^+$: 593.0505(^{79}Br), 595.0485 (^{81}Br), found: 593.0501, 595.0474.

N-((Z)-2-benzoyl-3-(4-nitrophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3e



Prepared according to the ***General Procedure A*** to afford **3e** (41.3 mg) in 77% yield as white solid, m.p. = 232 – 234 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

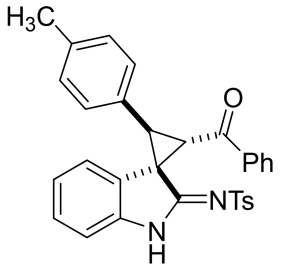
NMR and HRMS data for the product **3e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.26 (s, 1H), 7.95 (d, *J* = 6.6 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.08 – 7.02 (m, 4H), 4.44 (d, *J* = 8.4 Hz, 1H), 4.23 (d, *J* = 8.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.5, 164.4, 146.7, 143.7, 141.1, 139.8, 138.4, 136.2, 134.2, 130.3, 129.0, 129 .0, 128.6, 128.5, 125.9, 125.5, 123.9, 122.7, 122.1, 111.2, 43.2, 42.5, 40.5, 21.3.

HRMS (ESI) m/z calculated for $C_{30}H_{23}N_3O_5S+Na^+$: 560.1251, found: 560.1248.

N-((Z)-2-benzoyl-3-(p-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3f



Prepared according to the ***General Procedure A*** to afford **3f** (44.5 mg) in 88% yield as light yellow solid, m.p. = 225 – 226 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3f** (27.8 mg) in 55% yield as light yellow solid. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H-NMR analysis.

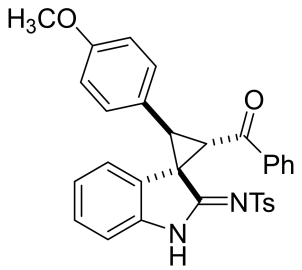
NMR and HRMS data for the product **3f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.04 – 7.01 (m, 4H), 6.84 (d, *J* = 7.2 Hz, 2H), 4.45 (d, *J* = 8.4 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.3, 165.6, 142.4, 140.8, 138.7, 136.9, 136.5, 133.9, 129.4, 128.9, 128.9, 128.8, 128.5, 128.5, 127.8, 126.6, 126.1, 123.6, 122.0, 110.9, 43.9, 43.1, 42.3, 21.5, 21.2.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_3S+H^+$: 507.1737, found: 507.1744.

N-((Z)-2-benzoyl-3-(4-methoxyphenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3g



Prepared according to the ***General Procedure A*** to afford **3g** (48.0 mg) in 92% yield as yellow solid, m.p. = 200 – 202 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

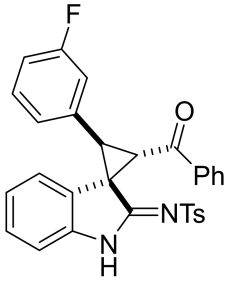
NMR and HRMS data for the product **3g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.19 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 6.6 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.18 (m, 1H),7.09 (d, *J* = 7.8 Hz, 2H), 7.07 – 7.00 (m, 4H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.45 (d, *J* = 9.0 Hz, 1H), 4.19 (d, *J* = 9.0 Hz, 1H), 3.73 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.3, 165.5, 158.9, 142.5, 140.8, 138.6, 136.5, 133.9, 130.6, 129.0, 128.9, 128.5, 128.1, 127.8, 126.6, 125.9, 123.7, 123.6, 122.0, 113.2, 110.8, 54.9, 43.9, 43.1, 42.2, 21.5.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_4S+H^+$: 523.1686, found: 523.1692.

N-((Z)-2-benzoyl-3-(3-fluorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide 3h



Prepared according to the ***General Procedure A*** to afford **3h** (38.8 mg) in 76% yield as white solid, m.p. = 204 – 208 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

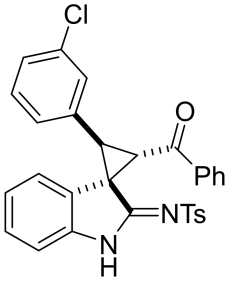
NMR and HRMS data for the product **3h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.12 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.06 – 6.96 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.82 – 6.78 (m, 1H), 6.71 – 6.66 (m, 1H), 4.42 (d, *J* = 9.0 Hz, 1H), 4.19 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.9, 165.2, 162.2 (d, *J* = 244.2 Hz, 1C), 142.8, 140.9, 138.7, 136.4, 134.5, 134.0, 129.6, 129.3 (d, *J* = 7.2 Hz, 1C),, 128.9, 128.5, 128.1, 126.1, 126.0, 125.2, 123.7, 122.1, 116.5 (d, *J* = 23.1 Hz, 1C), 114.5(d, *J* = 21.6 Hz, 1C), 110.9, 43.5, 42.8, 41.4, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}FN_2O_3S+Na^+$: 533.1306, found: 533.1306.

N-((Z)-2-benzoyl-3-(3-chlorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide 3i



Prepared according to the ***General Procedure A*** to afford **3i** (49.5 mg) in 94% yield as light

yellow solid, m.p. = 207 – 211 °C. The diastereomeric ratio was determined to be 9:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3i** (30.0 mg) in 57% yield as light yellow solid. The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis.

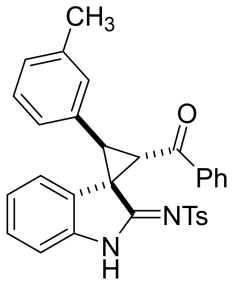
NMR and HRMS data for the product **3i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.10 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.09 (s, 1H), 7.06 – 7.01 (m, 3H), 6.97 – 6.93 (m, 2H), 4.42 (d, *J* = 9.0 Hz, 1H), 4.18 (d, *J* = 9.0 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.8, 165.1, 142.8, 140.9, 138.6, 136.4, 134.1, 134.1, 133.8, 129.5, 129.2, 129.0, 129.0, 128.5, 128.1, 127.7, 127.7, 126.0, 125.9, 123.8, 122.1, 110.9, 43.4, 42.6, 41.2, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1013, 550.1040.

N-((Z)-2-benzoyl-3-(m-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzene sulfonamide 3j



Prepared according to the ***General Procedure A*** to afford **3j** (47.0 mg) in 93% yield as white solid, m.p. = 191 – 193 °C. The diastereomeric ratio was determined to be 6:1 by crude ^{1}H-NMR analysis.

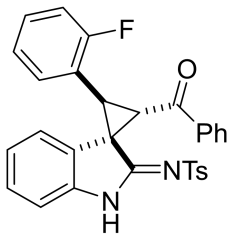
NMR and HRMS data for the product **3j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.29 – 7.25 (m, 3H), 7.23 – 7.19 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.05 – 7.01 (m, 2H), 6.97 (d, *J* = 4.8 Hz, 2H), 6.95 (s, 1H), 6.91 – 6.87 (m, 1H), 4.47 (d, *J* = 9.0 Hz, 1H), 4.22 (d, *J* = 9.0 Hz, 1H), 2.40 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.2, 165.7, 142.4, 140.8, 138.8, 137.4, 136.6, 133.9, 131.8, 130.2, 129.0, 128.9, 128.5, 128.3, 127.9, 126.6, 126.6, 126.0, 123.7, 122.1, 110.8, 43.8, 43.0, 42.4, 21.5, 21.2.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_3S+Na^+$: 529.1556, found: 529.1563.

N-((Z)-2-benzoyl-3-(2-fluorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3k



Prepared according to the ***General Procedure A*** to afford **3k** (41.3 mg) in 81% yield as white solid, m.p. = 214 – 218 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

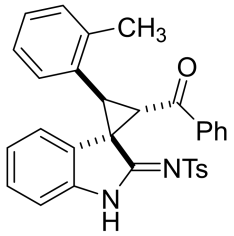
NMR and HRMS data for the product **3k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.17 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.28 – 7.25 (m, 1H), 7.24 – 7.19 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.06 – 6.98 (m, 3H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.57 (t, *J* = 9.0 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H), 4.10 (d, *J* = 8.4 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.0, 165.5, 161.5 (d, *J* = 245.7 Hz, 1C), 142.6, 141.0, 138.7, 136.5, 134.0, 131.1, 129.2, 129.1, 128.9, 128.5, 128.0, 126.2, 125.9, 123.7, 123.4 (d, *J* = 2.9 Hz, 1C), 122.1, 119.9 (d, *J* = 14.4 Hz, 1C), 114.7 (d, *J* = 20.1 Hz, 1C), 110.9, 42.8, 42.8, 35.7, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}FN_2O_3S+Na^+$: 533.1306, found: 533.1306.

N-((Z)-2-benzoyl-3-(o-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3l



Prepared according to the ***General Procedure A*** to afford **3l** (43.5 mg) in 86% yield as yellow solid, m.p. = 178 – 182 °C. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3l** (29.9 mg) in 59% yield as yellow solid. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

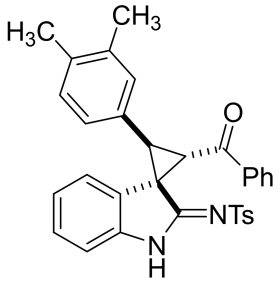
NMR and HRMS data for the product **3l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.07 (s, 1H), 7.94 (d, *J* = 6.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.07 – 7.01 (m, 4H), 6.82 – 6.79 (m, 1H), 4.45 (d, *J* = 8.4 Hz, 1H), 4.05 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.3, 165.6, 142.5, 140.7, 138.6, 137.6, 136.5, 133.9, 131.1, 129.6, 129.5, 129.1, 128.9, 128.5, 127.9, 127.7, 126.3, 126.0, 125.5, 123.8, 122.0, 110.9, 43.6, 43.3, 41.4, 21.5, 19.2.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_3S+Na^+$: 529.1556, found: 529.1550.

<u>N-((Z)-2-benzoyl-3-(3,4-dimethylphenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3m</u>



Prepared according to the ***General Procedure A*** to afford **3m** (37.4 mg) in 72% yield as light yellow solid, m.p. = 219 – 223 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **3m**:

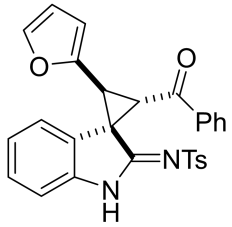
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.11 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.2

Hz, 1H), 7.45 – 7.41 (m, 2H), 7.30 – 7.27 (m, 3H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.08 – 7.00 (m, 4H), 6.92 – 6.87 (m, 2H), 6.80 (d, *J* = 7.2 Hz, 1H), 4.46 (d, *J* = 9.0 Hz, 1H), 4.20 (d, *J* = 9.0 Hz, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.3, 165.7, 142.3, 140.8, 138.7, 136.6, 135.9, 135.5, 133.9, 130.7, 129.1, 128.9, 128.8, 128.5, 127.8, 126.9, 126.7, 126.0, 123.6, 122.1, 110.8, 43.9, 43.0, 42.5, 21.6, 19.5, 19.4.

HRMS (ESI) m/z calculated for $C_{32}H_{28}N_2O_3S+Na^+$: 543.1713, found: 543.1706.

N-((Z)-2-benzoyl-3-(furan-2-yl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3n



Prepared according to the ***General Procedure A*** to afford **3n** (36.6 mg) in 76% yield as yellow solid, m.p. = 182 – 185 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3n** (35.2 mg) in 73% yield as yellow solid. The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis.

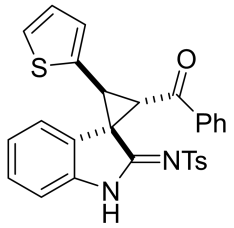
NMR and HRMS data for the product **3n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.43 – 7.38 (m, 2H), 7.24 – 7.18 (m, 4H), 7.05 – 7.00 (m, 3H), 6.20 (d, *J* = 3.6 Hz, 1H), 6.06 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.38 (d, *J* = 9.0 Hz, 1H), 4.03 (d, *J* = 9.0 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.4, 164.9, 146.1, 142.9, 141.9, 140.9, 138.7, 136.3, 134.0, 129.2, 128.9, 128.5, 128.1, 126.4, 125.6, 123.7, 122.0, 111.0, 110.3, 110.3, 42.9, 42.1, 34.4, 21.5.

HRMS (ESI) m/z calculated for $C_{28}H_{22}N_2O_4S+Na^+$: 505.1192, found: 505.1187.

N-((Z)-2-benzoyl-3-(thiophen-2-yl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3o



Prepared according to the ***General Procedure A*** to afford **3o** (40.8 mg) in 82% yield as gray solid, m.p. = 179 – 184 °C. The diastereomeric ratio was determined to be 12:1 by crude ^{1}H-NMR analysis.

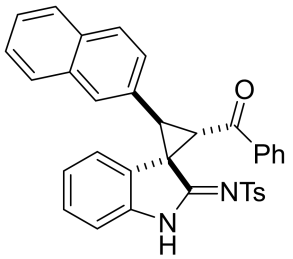
NMR and HRMS data for the product **3o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.12 (br s, 1H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 6.6 Hz, 1H), 6.90 (d, *J* = 4.2 Hz, 1H), 6.71 (dd, *J* = 6.4, 4.8 Hz, 1H), 4.43 (d, *J* = 8.4 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.6, 164.8, 142.7, 140.9, 138.8, 136.3, 134.5, 134.0, 129.1, 128.9, 128.5, 128.2, 128.1, 126.5, 126.3, 125.9, 125.4, 123.7, 122.0, 111.0, 44.1, 43.9, 37.0, 21.5.

HRMS (ESI) m/z calculated for $C_{28}H_{22}N_2O_3S_2$+Na^+: 521.0964, found: 521.0966.

N-((Z)-2-benzoyl-3-(naphthalen-2-yl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3p



Prepared according to the ***General Procedure A*** to afford **3p** (30.9 mg) in 57% yield as light yellow solid, m.p. = 239 – 243 °C. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3p** (26.0 mg) in 48% yield as light yellow solid. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

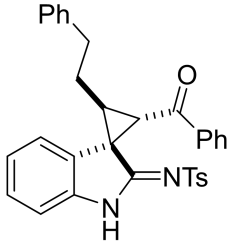
NMR and HRMS data for the product **3p**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.11 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.50 – 7.40 (m, 5H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.09 – 7.02 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 7.8 Hz, 2H), 4.63 (d, *J* = 9.0 Hz, 1H), 4.39 (d, *J* = 9.0 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.3, 165.4, 142.2, 140.9, 138.0, 136.5, 134.0, 132.9, 132.8, 129.5, 129.0, 128.6, 128.5, 128.5, 128.0, 127.8, 127.6, 127.4, 127.3, 126.5, 126.0, 125.8, 125.3, 123.7, 122.1, 110.9, 43.9, 42.9, 42.4, 21.4.

HRMS (ESI) m/z calculated for $C_{34}H_{26}N_2O_3S+Na^+$: 565.1556, found: 565.1554.

N-((Z)-2-benzoyl-3-phenethylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3q



Prepared according to the ***General Procedure A*** to afford **3q** (28.6 mg) in 55% yield as white solid, m.p. = 177 – 180 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

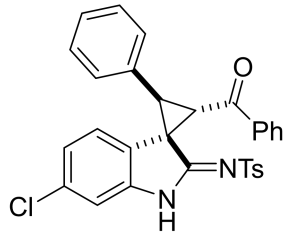
NMR and HRMS data for the product **3q**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.07 – 7.02 (m, 3H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.85 – 6.82 (m, 2H), 3.72 (d, *J* = 9.0 Hz, 1H), 2.90 – 2.84 (m, 1H), 2.61 – 2.54 (m, 1H), 2.53 – 2.47 (m, 1H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.30 – 2.22 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.4, 166.8, 143.2, 140.4, 140.3, 139.4, 136.6, 133.6, 129.5, 128.6, 128.5, 128.2, 128.2, 127.5, 126.9, 126.3, 125.7, 123.5, 122.0, 110.7, 45.4, 42.5, 38.9, 35.2, 25.6, 21.6.

HRMS (ESI) m/z calculated for $C_{32}H_{28}N_2O_3S+Na^+$: 543.1713, found: 543.1703.

N-((Z)-2-benzoyl-6'-chloro-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3r



Prepared according to the ***General Procedure A*** to afford **3r** (33.7 mg) in 64% yield as white solid, m.p. = 234 – 236 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

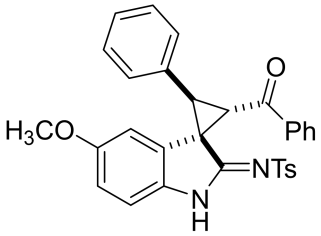
NMR and HRMS data for the product **3r**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.09 (s, 1H), 7.93 (d, *J* = 6.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.15 – 7.12 (m, 2H), 7.12 – 7.04 (m, 5H), 7.03 – 6.99 (m, 2H), 4.45 (d, *J* = 9.0 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.1, 165.5, 142.7, 141.9, 138.4, 136.4, 134.1, 131.6, 129.5, 129.2, 129.0, 128.5, 128.1, 127.6, 126.1, 124.9, 123.7, 123.1, 111.5, 43.4, 43.1, 42.6, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1018, 550.1052.

<u>N-((Z)-2-benzoyl-5'-methoxy-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3s</u>



Prepared according to the ***General Procedure A*** to afford **3s** (39.2 mg) in 75% yield as white solid, m.p. = 178 – 180 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **3s**:

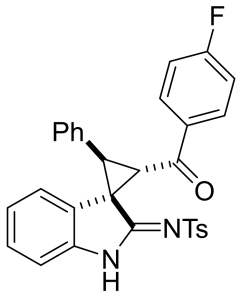
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.02 (s, 1H), 7.94 (d, *J* = 6.6 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.12 – 7.05 (m, 5H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* =

9.0 Hz, 1H), 4.20 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.1, 165.6, 156.5, 142.4, 138.9, 136.6, 134.4, 133.9, 131.9, 129.5, 129.1, 128.9, 128.5, 127.9, 127.5, 126.0, 113.4, 111.4, 108.4, 55.8, 44.0, 42.9, 42.5, 21.5.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_4S+Na^+$: 545.1505, found: 545.1510.

N-((Z)-2-(4-fluorobenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide 3t



Prepared according to the ***General Procedure A*** to afford **3t** (39.8 mg) in 78% yield as light yellow solid, m.p. = 223 – 226 °C. The diastereomeric ratio was determined to be 8:1 by crude ^{1}H-NMR analysis.

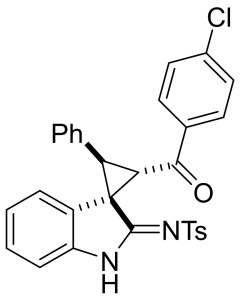
NMR and HRMS data for the product **3t**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.13 (s, 1H), 7.98 – 7.93 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.12 – 7.02 (m, 9H), 4.41 (d, *J* = 9.0 Hz, 1H), 4.23 (d, *J* = 9.0 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.6, 166.2 (d, *J* = 255.8 Hz, 1C), 165.5, 142.5, 140.9, 138.6, 133.0, 131.8, 131.2 (d, *J* = 10.0 Hz, 1C), 129.5, 129.1, 128.0, 127.9, 127.5, 126.3, 126.1, 123.7, 122.0, 116.1 (d, *J* = 21.6 Hz, 1C), 111.0, 43.7, 42.9, 42.3, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}FN_2O_3S+Na^+$: 533.1306, found: 533.1306.

N-((Z)-2-(4-chlorobenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methyl benzenesulfonamide 3u



Prepared according to the ***General Procedure A*** to afford **3u** (37.9 mg) in 72% yield as white solid, m.p. = 247 – 249 °C. The diastereomeric ratio was determined to be 10:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3u** (23.7 mg) in 45% yield as white solid. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

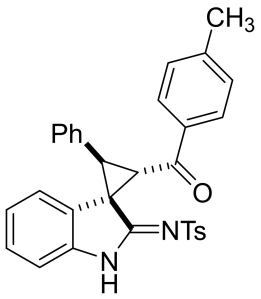
NMR and HRMS data for the product **3u**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.13 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.12 – 7.06 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.40 (d, *J* = 9.0 Hz, 1H), 4.23 (d, *J* = 9.0 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.0, 165.4, 142.6, 140.9, 140.5, 138.6, 134.8, 131.7, 129.8, 129.5, 129.2, 129.1, 128.1, 127.9, 127.5, 126.2, 126.1, 123.7, 121.9, 111.0, 43.7, 42.9, 42.3, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1012, 550.1042.

<u>4-methyl-N-((Z)-2-(4-methylbenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene) benzenesulfonamide 3v</u>



Prepared according to the ***General Procedure A*** to afford **3v** (38.0 mg) in 75% yield as light yellow solid, m.p. = 226 – 228 °C. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3v** (24.3 mg) in 48% yield as light yellow solid. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

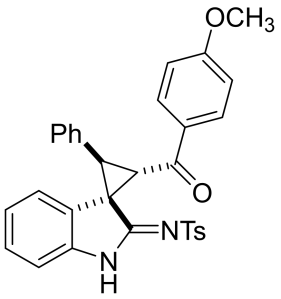
NMR and HRMS data for the product **3v**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.10 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.22 – 7.14 (m, 5H), 7.10 – 7.06 (m, 5H), 7.05 – 7.01 (m, 2H), 4.44 (d, *J* = 9.0 Hz, 1H), 4.24 (d, *J* = 9.0 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.6, 165.7, 145.0, 142.5, 140.8, 138.7, 134.1, 132.0, 129.6, 129.1, 128.6, 127.9, 127.8, 127.4, 126.6, 126.1, 123.6, 122.1, 110.9, 43.6, 43.1, 42.3, 21.7, 21.5.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_3S+Na^+$: 529.1556, found: 529.1560.

N-((Z)-2-(4-methoxybenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3w



Prepared according to the ***General Procedure A*** to afford **3w** (44.4 mg) in 85% yield as light yellow solid, m.p. = 233 – 236 °C. The diastereomeric ratio was determined to be 3:1 by crude ^{1}H-NMR analysis.

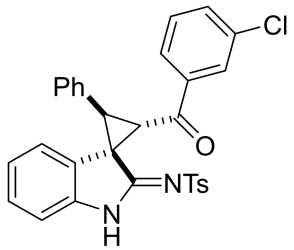
NMR and HRMS data for the product **3w**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.07 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.28 – 7.27 (m, 3H), 7.23 – 7.19 (m, 1H), 7.17 – 7.14 (m, 2H), 7.10 – 7.06 (m, 5H), 7.05 – 7.00 (m, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.42 (d, *J* = 9.0 Hz, 1H), 4.23 (d, *J* = 9.0 Hz, 1H), 3.83 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 190.3, 165.8, 164.2, 142.5, 140.8, 138.7, 132.1, 130.9, 129.7, 129.5, 129.1, 127.9, 127.8, 127.4, 126.7, 126.0, 123.6, 122.1, 114.1, 110.8, 55.5, 43.5, 43.0, 42.3, 21.5.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_4S+Na^+$: 545.1505, found: 545.1511.

N-((Z)-2-(3-chlorobenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3x



Prepared according to the ***General Procedure A*** to afford **3x** (28.5 mg) in 54% yield as light yellow solid, m.p. = 237 – 240 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3x** (27.4 mg) in 52% yield as light yellow solid. The diastereomeric ratio was determined to be 7:1 by crude ^{1}H-NMR analysis.

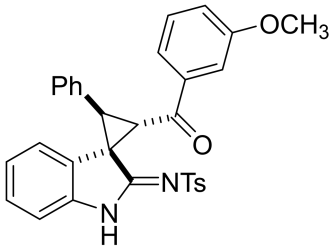
NMR and HRMS data for the product **3x**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.09 (s, 1H), 7.95 – 7.93 (m, 1H), 7.79 – 7.75 (m, 1H), 7.54 – 7.50 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.11 – 7.02 (m, 7H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.24 (d, *J* = 8.4 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.1, 165.3, 142.6, 140.9, 138.6, 138.0, 135.3, 133.9, 131.7, 130.3, 129.5, 129.1, 128.3, 128.1, 128.0, 127.6, 126.8, 126.2, 126.1, 123.7, 122.0, 111.0, 43.9, 42.9, 42.4, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1016, 550.1048.

N-((Z)-2-(3-methoxybenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3y



Prepared according to the ***General Procedure A*** to afford **3y** (45.4 mg) in 87% yield as white solid, m.p. = 189 – 194 °C. The diastereomeric ratio was determined to be 6:1 by crude ^{1}H-NMR analysis.

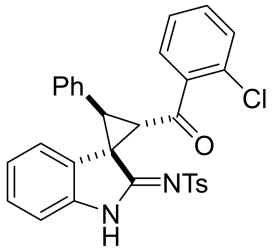
NMR and HRMS data for the product **3y**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.07 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.46 (m, 1H), 7.33 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 7.16 (d, *J* = 6.6 Hz, 2H), 7.11 – 7.07 (m, 6H), 7.05 – 7.01 (m, 2H), 4.46 (d, *J* = 9.0 Hz, 1H), 4.24 (d, *J* = 9.0 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 192.0, 165.6, 159.9, 142.5, 140.9, 138.7, 137.8, 131.9, 129.9, 129.5, 129.1, 127.9, 127.5, 126.4, 126.0, 123.7, 122.0, 121.3, 121.0, 111.9, 110.9, 55.4, 43.8, 43.4, 42.4, 21.5.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_4S+Na^+$: 545.1505, found: 545.1504.

N-((Z)-2-(2-chlorobenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3z



Prepared according to the ***General Procedure A*** to afford **3z** (34.8 mg) in 66% yield as white solid, m.p. = 200 – 204 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **3z**:

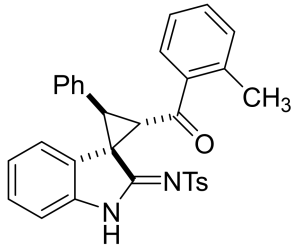
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.08 (s, 1H), 7.49 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.14 (m, 2H), 7.11 – 7.04 (m, 7H), 4.32 (d, *J* = 9.0 Hz, 1H), 4.30 (d, *J* = 8.4 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 194.2, 165.5, 142.4, 141.1, 138.7, 138.1, 132.9, 132.3,

131.8, 130.9, 130.1, 129.5, 129.0, 128.1, 127.9, 127.4, 127.1, 126.4, 126.1, 123.6, 122.8, 110.9, 47.0, 45.4, 42.9, 21.5.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010($^{35}Cl$), 550.1044 ($^{37}Cl$), found: 549.1018, 550.1037.

4-methyl-N-((Z)-2-(2-methylbenzoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene) benzenesulfonamide 3aa



Prepared according to the ***General Procedure A*** to afford **3aa** (45.0 mg) in 89% yield as light yellow solid, m.p. = 214 – 215 °C. The diastereomeric ratio was determined to be 18:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3aa** (21.8 mg) in 43% yield as light yellow solid. The diastereomeric ratio was determined to be 2:1 by crude ^{1}H-NMR analysis.

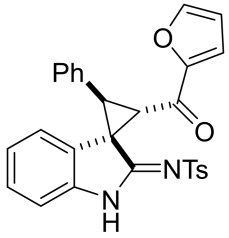
NMR and HRMS data for the product **3aa**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.12 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.28 – 7.19 (m, 5H), 7.17 – 7.14 (m, 2H), 7.11 – 7.04 (m, 7H), 4.30 (d, *J* = 9.0 Hz, 1H), 4.26 (d, *J* = 9.0 Hz, 1H), 2.49 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 195.1, 165.5, 142.5, 140.9, 138.9, 138.7, 137.1, 132.3, 132.0, 131.9, 129.6, 129.4, 129.1, 128.0, 127.9, 127.4, 126.5, 126.2, 126.0, 123.6, 122.5, 110.9, 45.7, 44.4, 42.6, 21.5, 21.3.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_3S+Na^+$: 529.1556, found: 529.1552.

N-((Z)-2-(furan-2-carbonyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-meth ylbenzenesulfonamide 3ab



Prepared according to the ***General Procedure A*** to afford **3ab** (36.2 mg) in 75% yield as white solid, m.p. = 198 – 199 °C. The diastereomeric ratio was determined to be 5:1 by crude ^{1}H-NMR analysis.

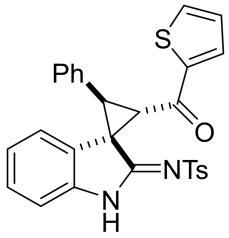
NMR and HRMS data for the product **3ab**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.11 (s, 1H), 7.60 (d, *J* = 1.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.11 – 7.05 (m, 6H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.37 (d, *J* = 9.0 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 180.4, 165.6, 152.5, 147.6, 142.4, 141.0, 138.7, 131.8, 129.5, 129.0, 127.9, 127.9, 127.4, 126.4, 126.0, 123.6, 122.7, 119.1, 112.7, 110.9, 44.1, 42.8, 41.9, 21.4.

HRMS (ESI) m/z calculated for $C_{28}H_{22}N_2O_4S+Na^+$: 505.1192, found: 505.1195.

4-methyl-N-((Z)-2-phenyl-3-(thiophene-2-carbonyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 3ac



Prepared according to the ***General Procedure A*** to afford **3ac** (44.3 mg) in 89% yield as light yellow solid, m.p. = 197 – 200 °C. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3ac** (34.4 mg) in 69% yield as light yellow solid. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **3ac**:

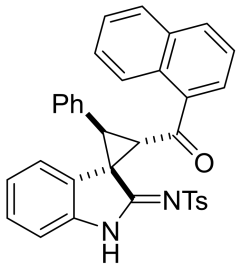
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.12 (s, 1H), 7.76 (d, *J* = 3.0 Hz, 1H), 7.64 (d, *J* = 4.8

Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.11 – 7.05 (m, 8H), 4.37 (d, *J* = 9.0 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 165.6, 143.9, 142.5, 141.0, 138.7, 135.1, 133.5, 131.8, 129.5, 129.1, 128.6, 127.9, 127.5, 126.4, 126.0, 123.7, 122.4, 110.9, 43.9, 43.7, 42.3, 21.5.

HRMS (ESI) m/z calculated for $C_{28}H_{22}N_2O_3S_2$+Na^+: 521.0964, found: 521.0967.

N-((Z)-2-(1-naphthoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3ad



Prepared according to the ***General Procedure A*** to afford **3ad** (33.1 mg) in 61% yield as white solid, m.p. = 219 – 221 °C. The diastereomeric ratio was determined to be 20:1 by crude ^{1}H-NMR analysis.

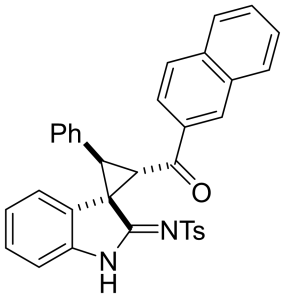
NMR and HRMS data for the product **3ad**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.16 (s, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 6.0 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.12 – 7.02 (m, 7H), 4.47 (d, *J* = 9.0 Hz, 1H), 4.37 (d, *J* = 8.4 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 194.7, 165.5, 142.5, 141.0, 138.7, 134.4, 134.0, 133.9, 131.9, 130.3, 129.7, 129.6, 129.1, 128.6, 128.5, 128.0, 127.9, 127.5, 126.7, 126.6, 126.1, 125.5, 124.6, 123.7, 122.6, 110.9, 46.0, 44.7, 42.7, 21.5.

HRMS (ESI) m/z calculated for $C_{34}H_{26}N_2O_3S$+Na^+: 565.1556, found: 565.1553.

N-((Z)-2-(2-naphthoyl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 3ae



Prepared according to the ***General Procedure A*** to afford **3ae** (45.0 mg) in 83% yield as light yellow solid, m.p. = 242 – 244 °C. The diastereomeric ratio was determined to be 6:1 by crude ^{1}H-NMR analysis.

Prepared according to the ***General Procedure B*** to afford chiral **3ae** (22.8 mg) in 42% yield as light yellow solid. The diastereomeric ratio was determined to be 4:1 by crude ^{1}H-NMR analysis.

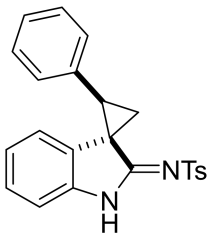
NMR and HRMS data for the product **3ae**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.20 (s, 1H), 8.44 (s, 1H), 7.99 – 7.96 (m, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.23 – 7.17 (m, 3H), 7.15 – 7.08 (m, 5H), 7.07 – 7.02 (m, 2H), 4.64 (d, *J* = 9.0 Hz, 1H), 4.32 (d, *J* = 9.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.9, 165.7, 142.5, 141.0, 138.8, 135.8, 133.8, 132.3, 132.0, 130.8, 129.9, 129.6, 129.1, 128.9, 128.8, 127.9, 127.6, 127.5, 126.9, 126.5, 126.1, 123.6, 123.6, 122.0, 111.0, 43.9, 43.4, 42.5, 21.5.

HRMS (ESI) m/z calculated for $C_{34}H_{26}N_2O_3S+Na^+$: 565.1556, found: 565.1557.

4-methyl-N-((Z)-2-phenylspiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 5a



Prepared according to the ***General Procedure A*** to afford **5a** (34.1 mg) in 88% yield as light yellow solid, m.p. = 99 – 103 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

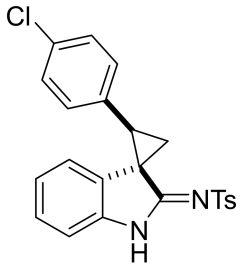
NMR and HRMS data for the product **5a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.17 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.26 (m, 5H), 7.16 – 7.11 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.72 (t, *J* = 7.8 Hz, 1H), 5.97 (d, *J* = 7.2 Hz, 1H), 3.46 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 2.29 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.16 (dd, *J* = 8.4, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.4, 143.0, 140.9, 139.4, 134.3, 129.9, 129.4, 128.4, 127.8, 127.7, 127.0, 126.3, 122.8, 120.8, 110.8, 39.6, 36.7, 25.6, 21.5.

HRMS (ESI) m/z calculated for $C_{23}H_{20}N_2O_2S+Na^+$:411.1138, found: 411.1139.

N-((Z)-2-(4-chlorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 5b



Prepared according to the ***General Procedure A*** to afford **5b** (35.9 mg) in 85% yield as light yellow solid, m.p. = 192 – 196 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

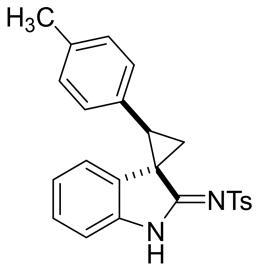
NMR and HRMS data for the product **5b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.09 – 7.04 (m, 3H), 6.78 (t, *J* = 7.2 Hz, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 3.38 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 2.28 (dd, *J* = 8.4, 4.8 Hz, 1H), 2.09 (dd, *J* = 8.4, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.1, 143.1, 141.0, 139.2, 133.7, 132.9, 131.3, 129.4, 128.7, 127.4, 127.2, 126.3, 122.9, 120.8, 111.0, 38.6, 36.6, 25.5, 21.5.

HRMS (ESI) m/z calculated for $C_{23}H_{19}ClN_2O_2S+Na^+$: 445.0748(^{35}Cl), 447.0718 (^{37}Cl), found: 445.0743, 447.0715.

4-methyl-N-((Z)-2-(p-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 5c



Prepared according to the ***General Procedure A*** to afford **5c** (31.0 mg) in 77% yield as light yellow solid, m.p. = 116 – 120 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

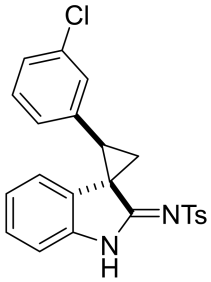
NMR and HRMS data for the product **5c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.09 – 7.04 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.74 (t, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 7.2 Hz, 1H), 3.42 (t, *J* = 7.8 Hz, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 2.27 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.14 (dd, *J* = 7.8, 3.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.5, 142.9, 140.9, 139.4, 137.5, 131.2, 129.7, 129.4, 129.1, 127.9, 126.9, 126.3, 122.8, 120.9, 110.8, 39.6, 36.8, 25.8, 21.5, 21.2.

HRMS (ESI) m/z calculated for $C_{24}H_{22}N_2O_2S+Na^+$:425.1294, found: 425.1293.

N-((Z)-2-(3-chlorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 5d



Prepared according to the ***General Procedure A*** to afford **5d** (37.6 mg) in 89% yield as light yellow solid, m.p. = 182 – 185 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **5d**:

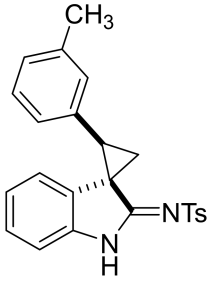
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.17 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.22 – 7.14 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.00 (d, *J* = 7.8 Hz, 1H), 3.39 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H),

2.27 (dd, *J* = 9.6, 4.8 Hz, 1H), 2.11 (dd, *J* = 9.0, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.0, 143.1, 141.0, 139.2, 136.4, 134.3, 129.8, 129.7, 129.5, 128.3, 128.0, 127.3, 126.3, 122.9, 120.8, 111.0, 38.6, 36.6, 25.3, 21.5.

HRMS (ESI) m/z calculated for $C_{23}H_{19}ClN_2O_2S+Na^+$: 445.0748(^{35}Cl), 447.0718 (^{37}Cl), found: 445.0740, 447.0721.

4-methyl-N-((Z)-2-(m-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 5e



Prepared according to the ***General Procedure A*** to afford **5e** (32.6 mg) in 81% yield as light yellow solid, m.p. = 140 – 142 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

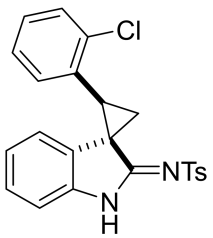
NMR and HRMS data for the product **5e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.17 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.11 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.97 – 6.89 (m, 2H), 6.74 (t, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 7.2 Hz, 1H), 3.43 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 2.28 (s, 3H), 2.26 (dd, *J* = 9.6, 4.8 Hz, 1H), 2.15 (dd, *J* = 8.4, 4.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.5, 142.9, 140.9, 139.4, 138.1, 134.1, 130.6, 129.4, 128.5, 128.3, 127.9, 126.9, 126.9, 126.3, 122.8, 120.9, 110.8, 39.7, 36.8, 25.7, 21.5, 21.3.

HRMS (ESI) m/z calculated for $C_{24}H_{22}N_2O_2S+Na^+$: 425.1294, found: 425.1295.

N-((Z)-2-(2-chlorophenyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 5f



Prepared according to the ***General Procedure A*** to afford **5f** (32.1 mg) in 76% yield as gray solid, m.p. = 174 – 177 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

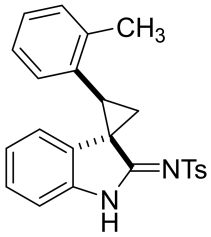
NMR and HRMS data for the product **5f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.20 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 6.6 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 7.07 – 7.04 (m, 1H), 6.69 (t, *J* = 7.8 Hz, 1H), 5.88 (d, *J* = 7.8 Hz, 1H), 3.26 (t, *J* = 9.0 Hz, 1H), 2.42 (dd, *J* = 9.6, 4.8 Hz, 1H), 2.40 (s, 3H), 2.18 (dd, *J* = 9.0, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.4, 143.0, 141.1, 139.4, 137.0, 133.0, 130.0, 129.4, 129.2, 127.2, 126.7, 126.2, 122.7, 119.5, 110.9, 38.7, 36.8, 24.4, 21.5.

HRMS (ESI) m/z calculated for $C_{23}H_{19}ClN_2O_2S+Na^+$: 445.0748(^{35}Cl), 447.0718 (^{37}Cl), found: 445.0740, 447.0717.

4-methyl-N-((Z)-2-(o-tolyl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 5g



Prepared according to the ***General Procedure A*** to afford **5g** (30.2 mg) in 75% yield as light yellow solid, m.p. = 173 – 176 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

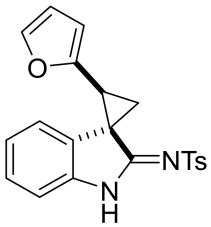
NMR and HRMS data for the product **5g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.21 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.14 – 7.10 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.67 (t, *J* = 7.2 Hz, 1H), 5.87 (d, *J* = 7.8 Hz, 1H), 3.20 (t, *J* = 9.0 Hz, 1H), 2.40 (s, 3H), 2.36 (dd, *J* = 9.6, 4.8 Hz, 1H), 2.21 (dd, *J* = 8.4, 4.2 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.5, 143.0, 140.6, 139.5, 139.1, 133.1, 129.9, 129.4, 128.4, 128.0, 127.7, 127.0, 126.2, 125.8, 122.8, 120.0, 110.8, 39.3, 36.6, 25.2, 21.5, 18.8.

HRMS (ESI) m/z calculated for $C_{24}H_{22}N_2O_2S+Na^+$: 425.1294, found: 425.1301.

N-((Z)-2-(furan-2-yl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)-4-methylbenzenesulfonamide 5h



Prepared according to the ***General Procedure A*** to afford **5h** (29.9 mg) in 79% yield as red solid, m.p. = 140 – 144 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

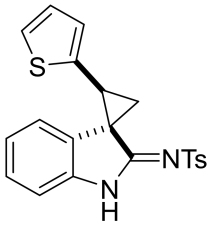
NMR and HRMS data for the product **5h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.07 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.34 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.28 (d, *J* = 3.6 Hz, 1H), 3.22 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 2.32 – 2.25 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.3, 149.3, 143.1, 142.3, 141.0, 139.2, 129.4, 127.5, 127.4, 126.3, 123.2, 120.2, 110.9, 110.7, 110.0, 37.3, 32.4, 24.0, 21.5.

HRMS (ESI) m/z calculated for $C_{21}H_{18}N_2O_3S+Na^+$: 401.0930, found: 401.0928.

4-methyl-N-((Z)-2-(thiophen-2-yl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 5i



Prepared according to the ***General Procedure A*** to afford **5i** (29.2 mg) in 74% yield as white solid, m.p. = 134 – 137 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **5i**:

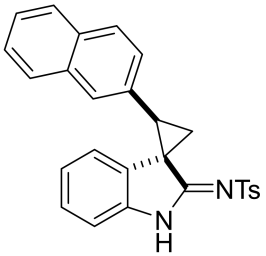
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.12 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.95 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.90 –

6.87 (m, 1H), 6.81 (t, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 7.8 Hz, 1H), 3.39 (t, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 2.34 (dd, *J* = 9.0, 4.8 Hz, 1H), 2.18 (dd, *J* = 7.8, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 169.6, 143.1, 141.0, 139.2, 138.0, 129.4, 127.9, 127.3, 127.2, 126.8, 126.3, 125.7, 123.0, 120.4, 110.9, 37.5, 33.8, 26.6, 21.5.

HRMS (ESI) m/z calculated for $C_{21}H_{18}N_2O_2S_2+Na^+$: 417.0702, found: 419.0699.

4-methyl-N-((Z)-2-(naphthalen-2-yl)spiro[cyclopropane-1,3'-indolin]-2'-ylidene)benzenesulfonamide 5j



Prepared according to the ***General Procedure A*** to afford **5j** (31.5 mg) in 72% yield as light yellow solid, m.p. = 189 – 191 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

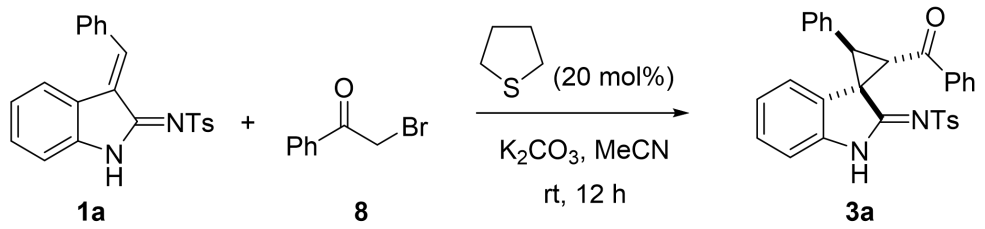
NMR and HRMS data for the product **5j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.21(s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.82 – 7.78 (m, 2H), 7.73 – 7.67 (m, 2H), 7.51 – 7.44 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.13 – 7.05 (m, 3H), 6.62 (t, *J* = 7.8 Hz, 1H), 5.96 (d, *J* = 7.2 Hz, 1H), 3.60 (t, *J* = 9.0 Hz, 1H), 2.43 (s, 3H), 2.37 (dd, *J* = 9.0, 4.8 Hz, 1H), 2.30 (dd, *J* = 7.8, 4.8 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 170.4, 143.0, 140.9, 139.4, 133.1, 132.8, 132.0, 129.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.7, 127.0, 126.3, 126.2, 122.9, 120.7, 110.9, 39.8, 36.8, 25.7, 21.5.

HRMS (ESI) m/z calculated for $C_{27}H_{22}N_2O_2S+Na^+$:461.1294, found: 461.1294.

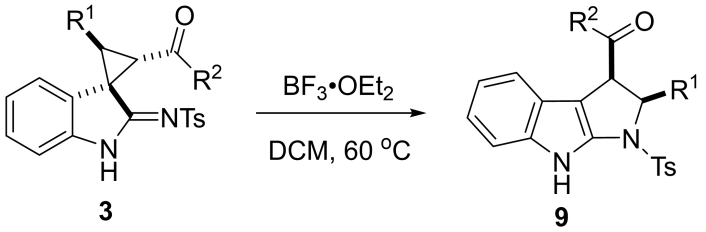
4. Procedure for sulphide-catalyzed (2+1) annulation



A glass reaction tube was charged with iminoindole **1a** (0.1 mmol), bromide **8** (0.15 mmol), thiophane (0.02 mmol) and K_2CO_3 (0.12 mmol) in 1.0 mL MeCN. The mixture was stirred at room temperature for 12 hours. Then the mixture was concentrated, and purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 20:1 to 15:1 to afford the corresponding product **3a** (30.5 mg) in 62% yield as light yellow solid. The diastereomeric ratio was determined to be 1:1 by crude ^{1}H-NMR analysis.

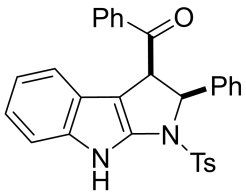
5. Investigation for the Rearrangement of 3

*5.1 General procedure for the ring-opening rearrangement of **3***



A Schlenck tube was charged with **3** (0.1 mmol), $BF_3 \cdot OEt_2$ **2** (1 mmol), H_2O (0.1 mmol) in 1 mL DCM. The mixture was stirred at 60 °C for 12 hours. Then the mixture was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate from 15:1 to 10:1 to afford the corresponding product **9**.

phenyl(2-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-3-yl)methanone 9a



Prepared according to the general procedure to afford **9a** (19.7 mg) in 40% yield as light yellow solid, m.p. = 210 – 214 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

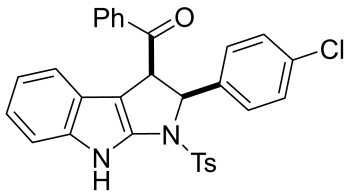
NMR and HRMS data for the product **9a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.86 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.60 (m, 3H), 7.50 – 7.45 (m, 2H), 7.41 – 7.36 (m, 4H), 7.35 – 7.29 (m, 4H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 7.2 Hz, 1H), 5.90 (d, *J* = 3.6 Hz, 1H), 4.98 (d, *J* = 4.8 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 195.6, 144.9, 141.4, 141.2, 137.8, 136.2, 133.7, 132.0, 130.0, 128.9, 128.7, 128.7, 128.3, 128.0, 126.4, 123.4, 120.8, 120.7, 117.7, 111.9, 99.5, 72.2, 56.4, 21.7.

HRMS (ESI) m/z calculated for $C_{30}H_{24}N_2O_3S+Na^+$: 515.1400, found: 515.1396.

(2-(4-chlorophenyl)-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-3-yl)(phenyl)methanone 9b



Prepared according to the general procedure to afford **9b** (18.4 mg) in 35% yield as yellow solid, m.p. = 194 – 196 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

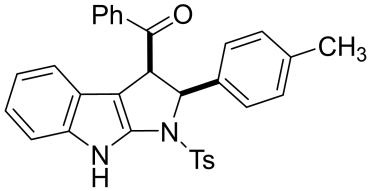
NMR and HRMS data for the product **9b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.83 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.60 (m, 3H), 7.52 – 7.46 (m, 2H), 7.35 – 7.29 (m, 7H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.86 (d, *J* = 4.8 Hz, 1H), 4.93 (d, *J* = 4.8 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 195.4, 145.1, 141.2, 139.6, 137.8, 136.1, 134.1, 133.8, 131.8, 130.1, 129.1, 128.8, 128.7, 128.0, 127.9, 123.2, 120.9, 117.7, 111.9, 99.3, 71.5, 56.3, 21.7.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1018, 550.1054.

<u>phenyl(2-(p-tolyl)-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-3-yl)methanone 9c</u>



Prepared according to the general procedure to afford **9c** (16.2 mg) in 32% yield as yellow solid, m.p. = 205 – 208 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

NMR and HRMS data for the product **9c**:

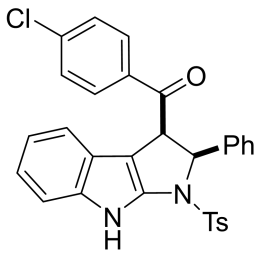
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.85 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.59 (m, 3H), 7.49 – 7.45 (m, 2H), 7.34 – 7.30 (m, 2H), 7.29 – 7.27 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.83 (d, *J* = 4.8 Hz, 1H), 4.97 (d, *J* = 4.8 Hz, 1H), 2.46 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 195.7, 144.8, 141.4, 138.2, 138.1, 137.7, 136.2, 133.6, 132.0, 130.0, 129.6, 128.7, 128.7, 128.0, 126.4, 123.4, 120.7, 120.7, 117.6, 111.9, 99.5, 72.2,

56.3, 21.7, 21.2.

HRMS (ESI) m/z calculated for $C_{31}H_{26}N_2O_3S+Na^+$: 529.1556, found: 529.1556.

(4-chlorophenyl)(2-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-3-yl)methanone 9d



Prepared according to the general procedure to afford **9d** (19.5 mg) in 37% yield as yellow solid, m.p. = 197 – 200 °C. The diastereomeric ratio was determined to be >20:1 by crude ^{1}H-NMR analysis.

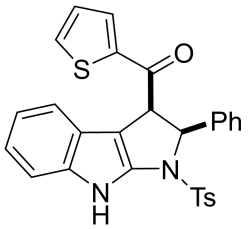
NMR and HRMS data for the product **9d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.85 (s, 1H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.38 – 7.28 (m, 8H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.83 (d, *J* = 4.8 Hz, 1H), 4.91 (d, *J* = 4.8 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 194.5, 144.9, 141.6, 141.0, 140.3, 137.8, 134.4, 132.0, 130.1, 130.0, 129.1, 129.0, 128.4, 128.0, 126.4, 123.3, 120.9, 120.8, 117.5, 112.0, 99.2, 72.3, 56.2, 21.7.

HRMS (ESI) m/z calculated for $C_{30}H_{23}ClN_2O_3S+Na^+$: 549.1010(^{35}Cl), 550.1044 (^{37}Cl), found: 549.1014, 550.1039.

(2-phenyl-1-tosyl-1,2,3,8-tetrahydropyrrolo[2,3-b]indol-3-yl)(thiophen-2-yl)methanone 9e



Prepared according to the general procedure to afford **9e** (17.9 mg) in 36% yield as yellow solid, m.p. = 197 – 201 °C. The diastereomeric ratio was determined to be >20:1 by crude

^{1}H-NMR analysis.

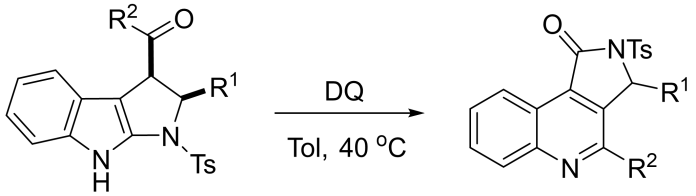
NMR and HRMS data for the product **9e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.87 (s, 1H), 7.80 (s, 1H), 7.70 (d, *J* = 4.2 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.35 (m, 5H), 7.34 – 7.27 (m, 3H), 7.18 – 7.14 (m, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.76 (d, *J* = 4.2 Hz, 1H), 4.82 (d, *J* = 4.8 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 188.6, 145.0, 142.9, 141.7, 140.9, 137.8, 135.0, 132.9, 131.8, 130.1, 129.9, 128.9, 128.3, 128.2, 128.0, 126.5, 123.4, 120.9, 117.5, 112.0, 99.7, 72.9, 57.2, 21.7.

HRMS (ESI) m/z calculated for $C_{28}H_{22}N_2O_3S_2+H^+$: 499.1145, found: 499.1153.

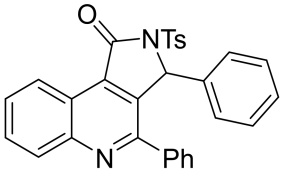
5.2 General procedure for the oxidation/rearrangement of ***9***



9 **10**

The product **9** (0.1 mmol) was dissolved in toluene (1.0 mL). To this solution was added DQ (0.2 mmol). Then the reaction was stirred for 12 hours at 40 °C. Then the mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether/ dichloromethane/ methanol = 150:150:0.5) to afford **10**, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, *etc*.

3,4-diphenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one 10a



The reaction provided 26.0 mg of **10a** in 53% yield as yellow solid, m.p. = 248 – 251 °C.

NMR and HRMS data for the product **10a**:

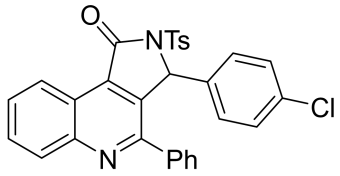
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.05 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.38 – 7.32 (m, 7H), 7.10 – 7.05 (m, 3H), 6.94 –

6.90 (m, 2H), 6.60 – 6.57 (m, 3H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.9, 155.7, 148.3, 144.9, 138.8, 137.8, 135.3, 133.5, 131.9, 130.8, 129.9, 129.2, 129.1, 128.5, 128.5, 128.3, 128.2, 128.0, 128.0, 123.5, 121.8, 64.5, 21.6.

HRMS (ESI) m/z calculated for $C_{30}H_{22}N_2O_3S+Na^+$: 513.1243, found: 513.1244.

3-(4-chlorophenyl)-4-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one 10b



The reaction provided 24.7 mg of **10b** in 47% yield as yellow solid, m.p. = 192 – 195 °C.

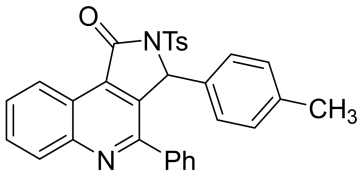
NMR and HRMS data for the product **10b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.03 (d, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.76 (t, *J* = 6.6 Hz, 1H), 7.43 – 7.35 (m, 7H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.57 (s, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.8, 155.5, 148.4, 145.2, 138.3, 137.7, 135.3, 134.3, 132.3, 131.8, 131.0, 129.9, 129.7, 129.4, 129.3, 129.2, 128.6, 128.2, 128.1, 127.9, 123.5, 121.8, 63.7, 21.6.

HRMS (ESI) m/z calculated for $C_{30}H_{21}ClN_2O_3S+Na^+$: 547.0854(^{35}Cl), 548.0887 (^{37}Cl), found: 547.0853, 548.0885.

4-phenyl-3-(p-tolyl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one 10c



The reaction provided 21.2 mg of **10c** in 42% yield as yellow solid, m.p. = 161 – 165 °C.

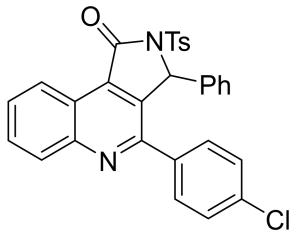
NMR and HRMS data for the product **10c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.05 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.39 – 7.32 (m, 7H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.57 (s, 1H), 6.47 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.0, 155.7, 148.3, 144.8, 138.9, 138.2, 137.8, 135.4, 131.8, 130.7, 130.5, 129.9, 129.2, 129.1, 129.0, 128.7, 128.4, 128.4, 128.2, 128.1, 123.5, 121.9, 64.4, 21.6, 21.1.

HRMS (ESI) m/z calculated for $C_{31}H_{24}N_2O_3S+Na^+$: 527.1400, found: 527.1400.

4-(4-chlorophenyl)-3-phenyl-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one 10d



The reaction provided 23.6 mg of **10d** in 45% yield as yellow solid, m.p. = 224 – 226 °C.

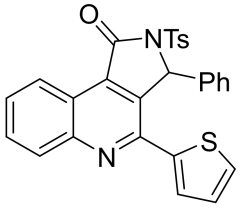
NMR and HRMS data for the product **10d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.77 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.30 (m, 6H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.99 – 6.95 (m, 2H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.56 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.7, 154.3, 148.3, 145.0, 138.5, 136.2, 135.5, 135.3, 133.4, 132.2, 131.0, 129.8, 129.6, 129.4, 129.2, 128.7, 128.6, 128.2, 128.0, 123.6, 121.9, 64.4, 21.6.

HRMS (ESI) m/z calculated for $C_{30}H_{21}ClN_2O_3S+Na^+$: 547.0854(^{35}Cl), 548.0887 (^{37}Cl), found: 547.0851, 548.0877.

3-phenyl-4-(thiophen-2-yl)-2-tosyl-2,3-dihydro-1H-pyrrolo[3,4-c]quinolin-1-one 10e



The reaction provided 23.8 mg of **10e** in 48% yield as yellow solid, m.p. = 243 – 245 °C.

NMR and HRMS data for the product **10e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.02 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.72 – 7.69 (m, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.13 – 7.10 (m, 2H), 7.06 – 7.02 (m, 3H), 6.98 (d,

J = 7.8 Hz, 2H), 6.75 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 165.6, 148.2, 144.9, 141.3, 136.6, 135.3, 133.6, 132.8, 131.0, 129.5, 129.4, 129.3, 129.2, 129.0, 128.9, 128.4, 127.9, 127.7, 123.5, 121.6, 64.6, 21.6.

HRMS (ESI) m/z calculated for $C_{28}H_{20}N_2O_3S_2$+Na^+: 519.0808, found: 519.0802.

5.3 Proposed reaction mechanism

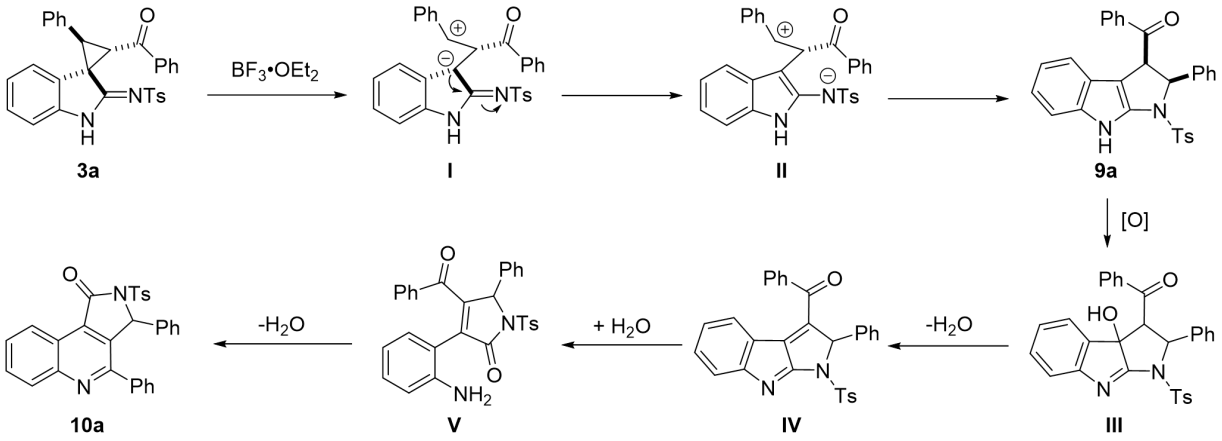
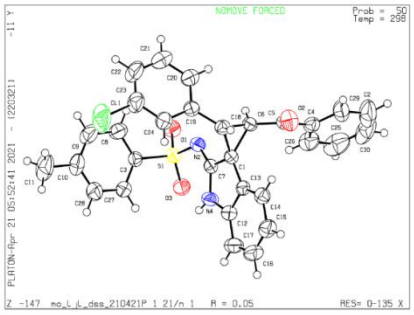
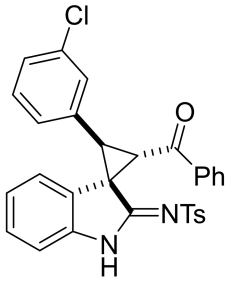


Figure S1. Proposed mechanism.

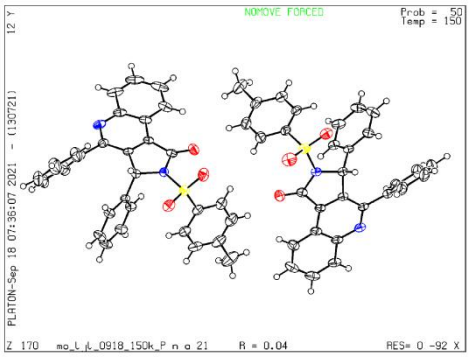
6. Crystal Data and Structure Refinement





3i (CCDC 2118406)

Identification code	**3i**
Empirical formula	$C_{30}H_{23}ClN_2O_3S$
Formula weight	527.01
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.9731(6)
b/Å	15.1155(6)
c/Å	13.3582(6)
α/°	90
β/°	94.384(2)
γ/°	90
Volume/Å^3	2611.8(2)
Z	4
ρ_{calc}g/cm^3	1.340
μ/mm^{-1}	0.261
F(000)	1096.0
Crystal size/mm^3	0.35 × 0.18 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.076 to 55.09
Index ranges	$-16 \le h \le 16$, $-18 \le k \le 19$, $-17 \le l \le 17$
Reflections collected	57430
Independent reflections	6009 [R_{int} = 0.1401, R_{sigma} = 0.0652]
Data/restraints/parameters	6009/0/335
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1069
Final R indexes [all data]	R_1 = 0.1145, wR_2 = 0.1301
Largest diff. peak/hole / e Å^{-3}	0.20/-0.36



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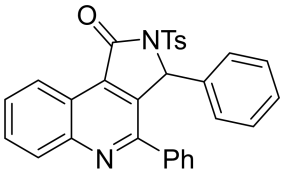
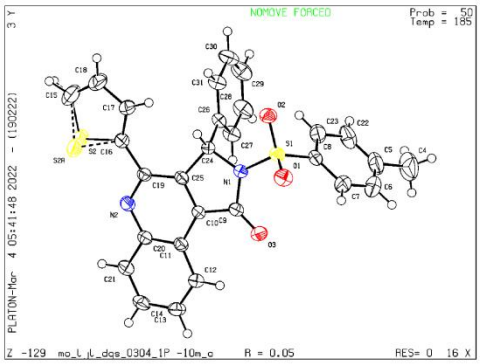


10a (CCDC 2118408)

Identification code	**10a**
Empirical formula	$C_{30}H_{22}N_2O_3S$
Formula weight	490.55
Temperature/K	150.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	21.023(3)
b/Å	12.4076(16)
c/Å	18.781(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4899.0(13)
Z	8
ρ_{calc}g/cm^3	1.330
μ/mm^{-1}	0.168
F(000)	2048.0
Crystal size/mm^3	0.32 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.812 to 55.114
Index ranges	$-23 \le h \le 27$, $-16 \le k \le 14$, $-24 \le l \le 21$
Reflections collected	43968
Independent reflections	10630 [R_{int} = 0.0676, R_{sigma} = 0.0586]
Data/restraints/parameters	10630/1/651
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.0929
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1018
Largest diff. peak/hole / e Å^{-3}	0.19/-0.33
Flack parameter	0.46(4)



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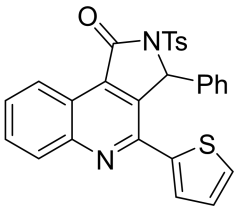


10e (CCDC 2156349)

Identification code	**10e**
Empirical formula	$C_{28}H_{20}N_2O_3S_2$
Formula weight	496.58
Temperature/K	185.0
Crystal system	triclinic
Space group	P-1
a/Å	11.4722(9)
b/Å	11.6024(9)
c/Å	11.8100(11)
α/°	112.336(3)
β/°	91.537(3)
γ/°	112.501(3)
Volume/Å^3	1315.76(19)
Z	2
ρ_{calc}g/cm^3	1.253
μ/mm^{-1}	0.233
F(000)	516.0
Crystal size/mm^3	0.43 × 0.35 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.924 to 55.142
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	29591
Independent reflections	6044 [R_{int} = 0.0948, R_{sigma} = 0.0721]
Data/restraints/parameters	6044/0/321
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1188
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.1357
Largest diff. peak/hole / e Å^{-3}	0.40/-0.47

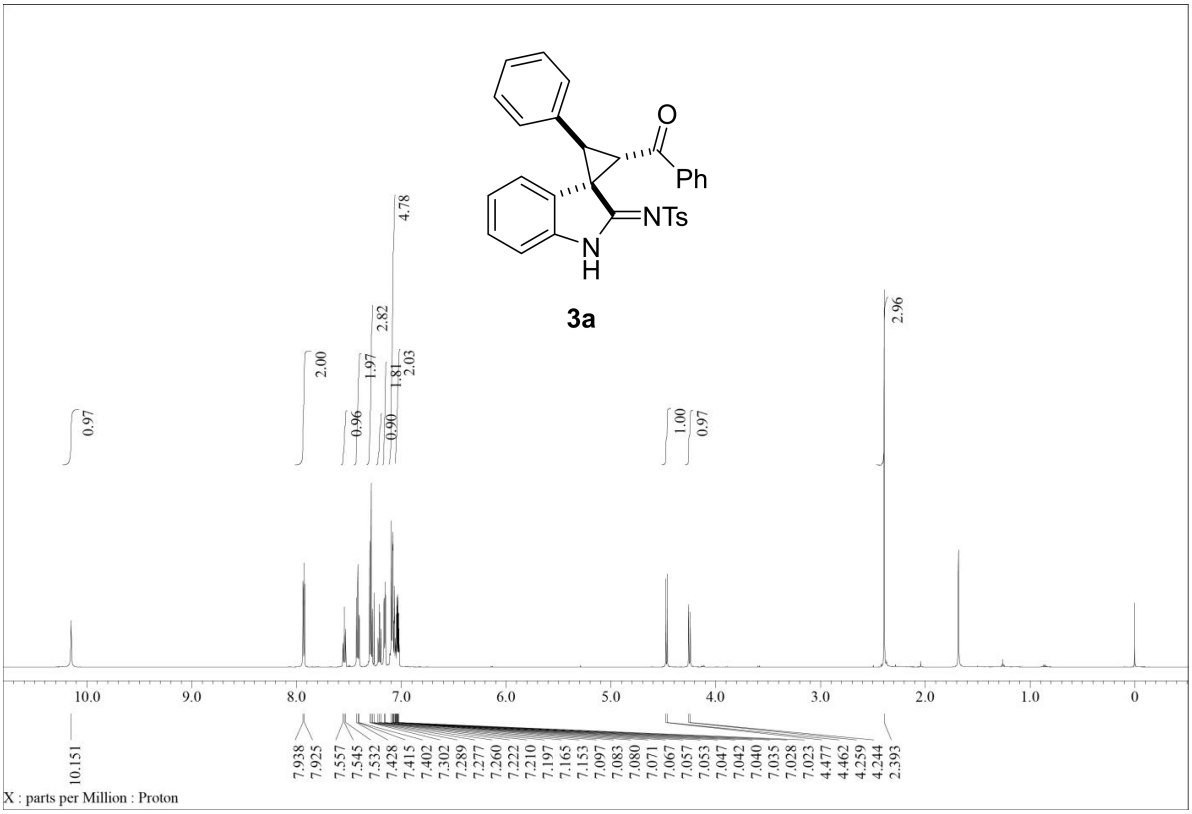
7. References and Notes

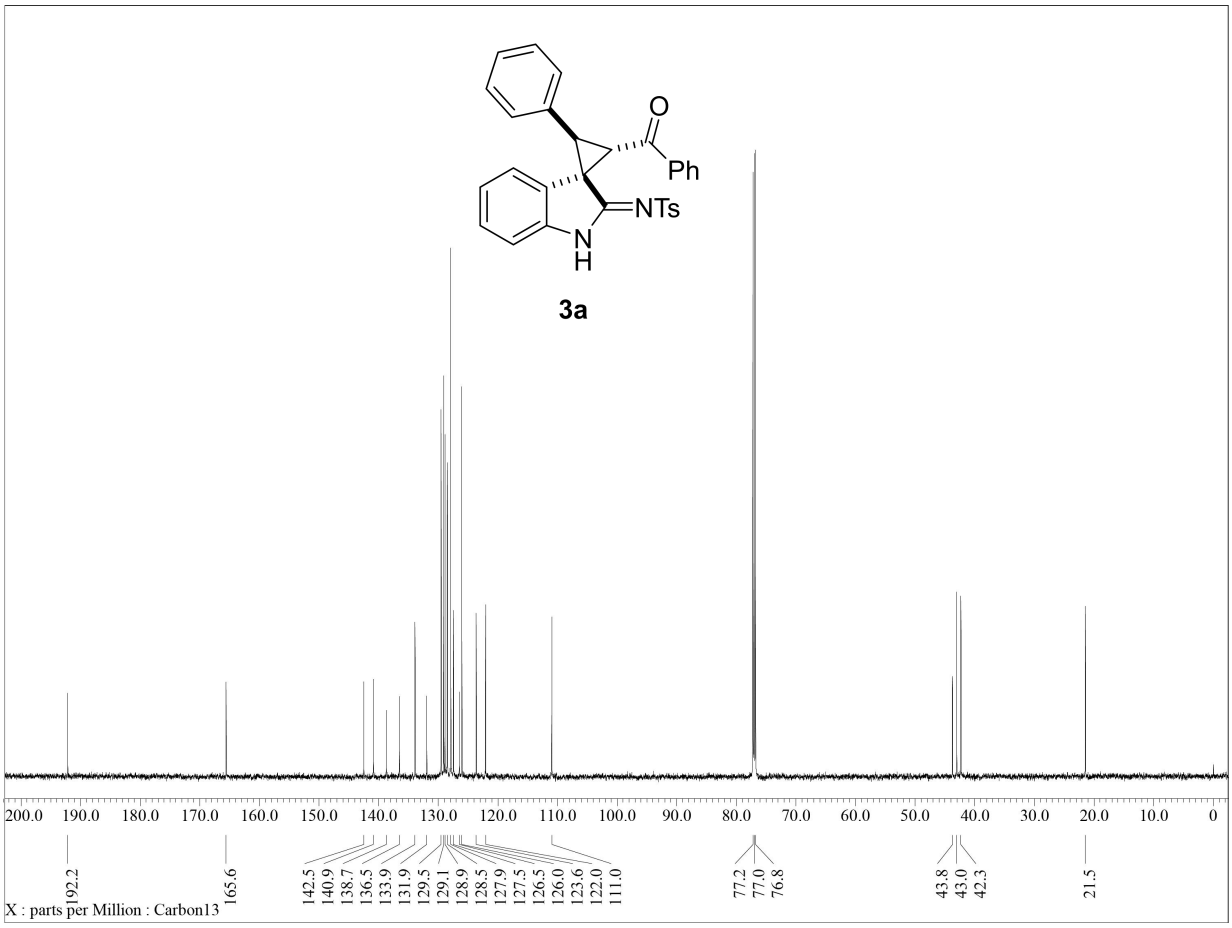
1 (a) E. Krell, *Handbook of Laboratory Distillation*, Elseriver Publishing Company: Amsterdam-London-New York. 1963; (b) M. J. Rosengart, *The Technique of Distillation and Rectification in the Laboratory*, VEB Verlag Technik: Berlin, 1954; (c) F. Stage, *Angew. Chem.*, 1947, **19**, 175.

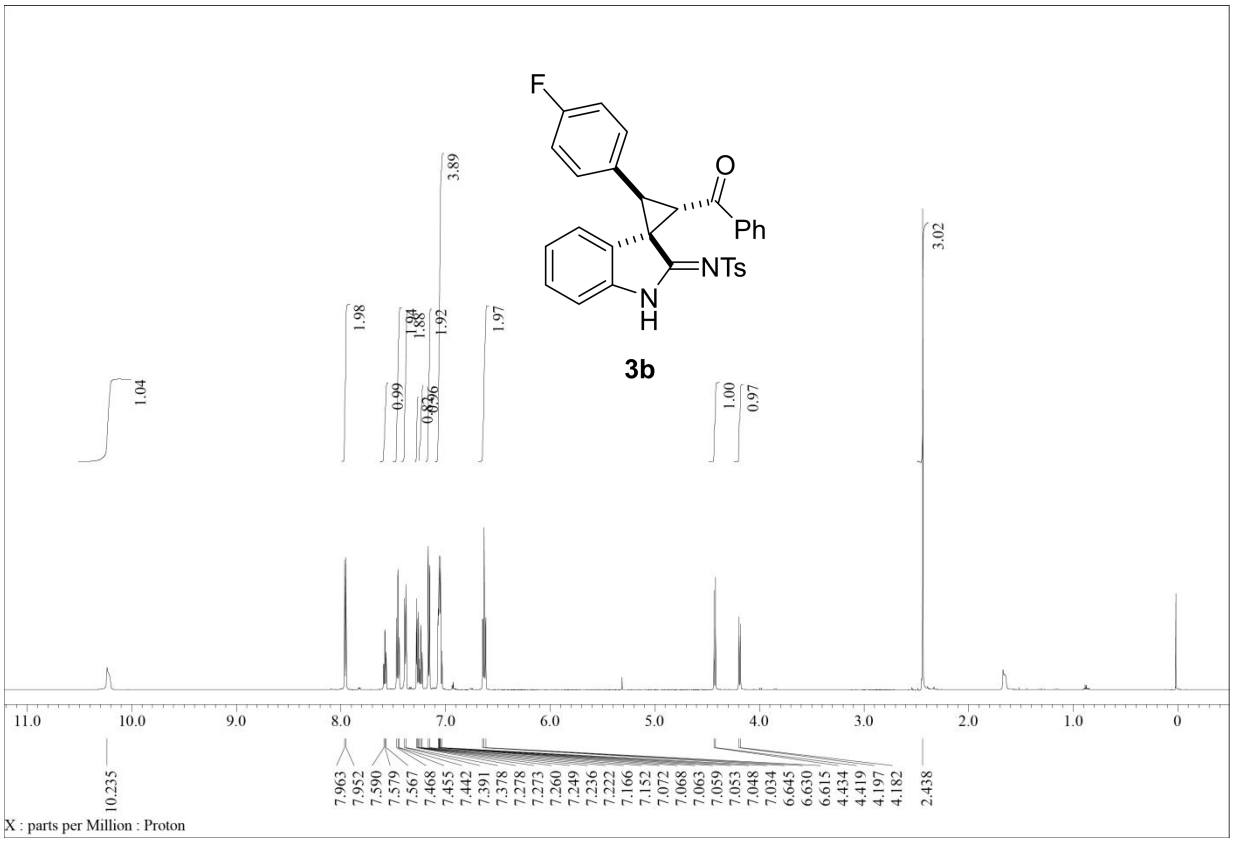
2 K. Moriyama, K. Ishida, H. Togo, *Chem. Common.*, 2015, **51**, 2273.

3 S. K. Chittimalla and C. Bandi, *RSC Adv.*, 2013, **3**, 13663.

8. NMR Spectra



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O
Ph
NTs
N
H
3b
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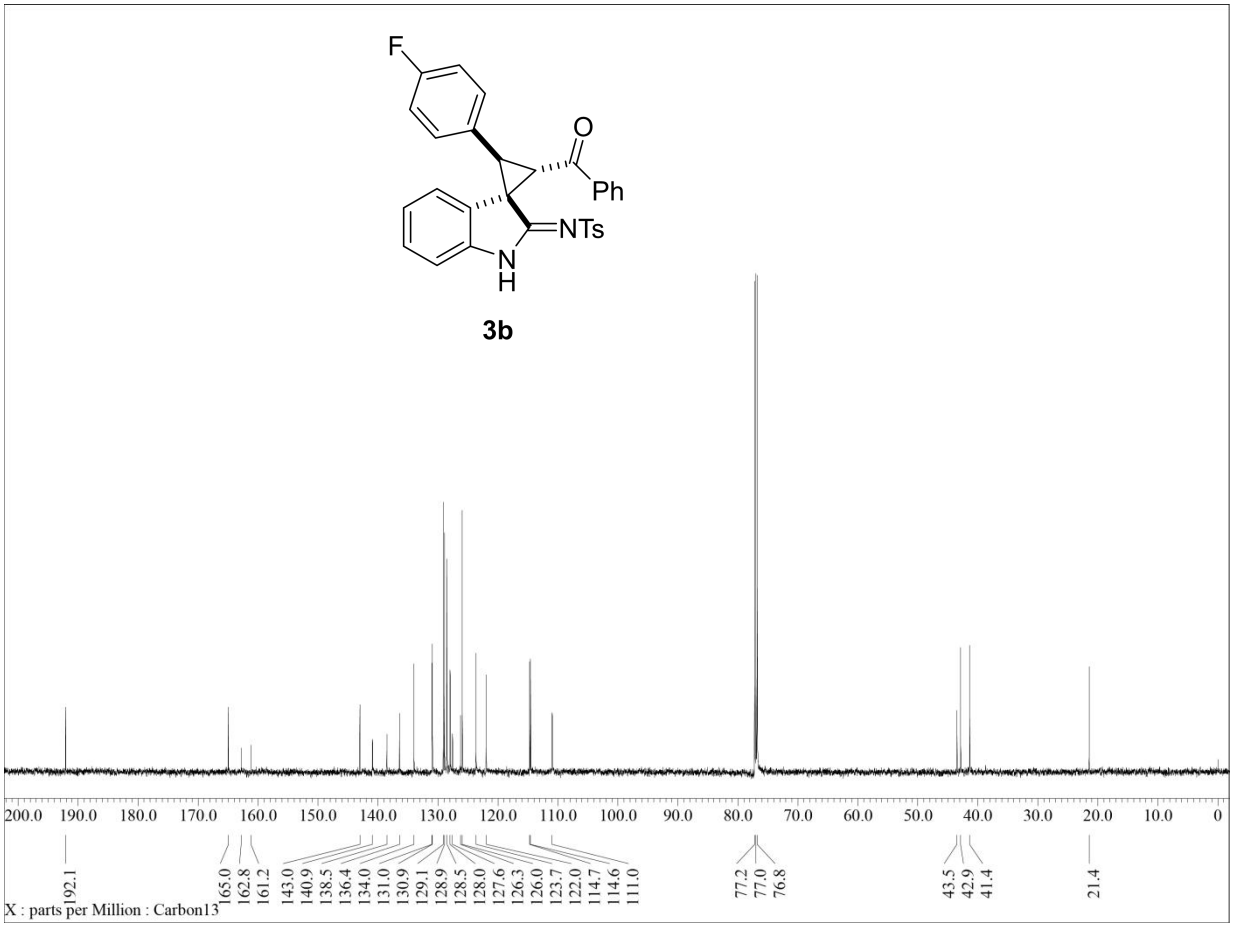
1.98
1.97
1.92
1.04
0.99
1.00
0.97
3.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.235
7.963
7.952
7.590
7.579
7.567
7.468
7.455
7.442
7.391
7.378
7.278
7.273
7.260
7.249
7.236
7.222
7.166
7.152
7.072
7.068
7.063
7.059
7.053
7.048
7.034
6.645
6.630
6.615
4.434
4.419
4.197
4.182
2.438
X : parts per Million : Proton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O
Ph
NTs
N
H
3b
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.1
165.0
162.8
161.2
143.0
140.9
138.5
136.4
134.0
131.0
130.9
129.1
128.9
128.5
128.0
127.6
126.3
126.0
123.7
122.0
114.7
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111.0
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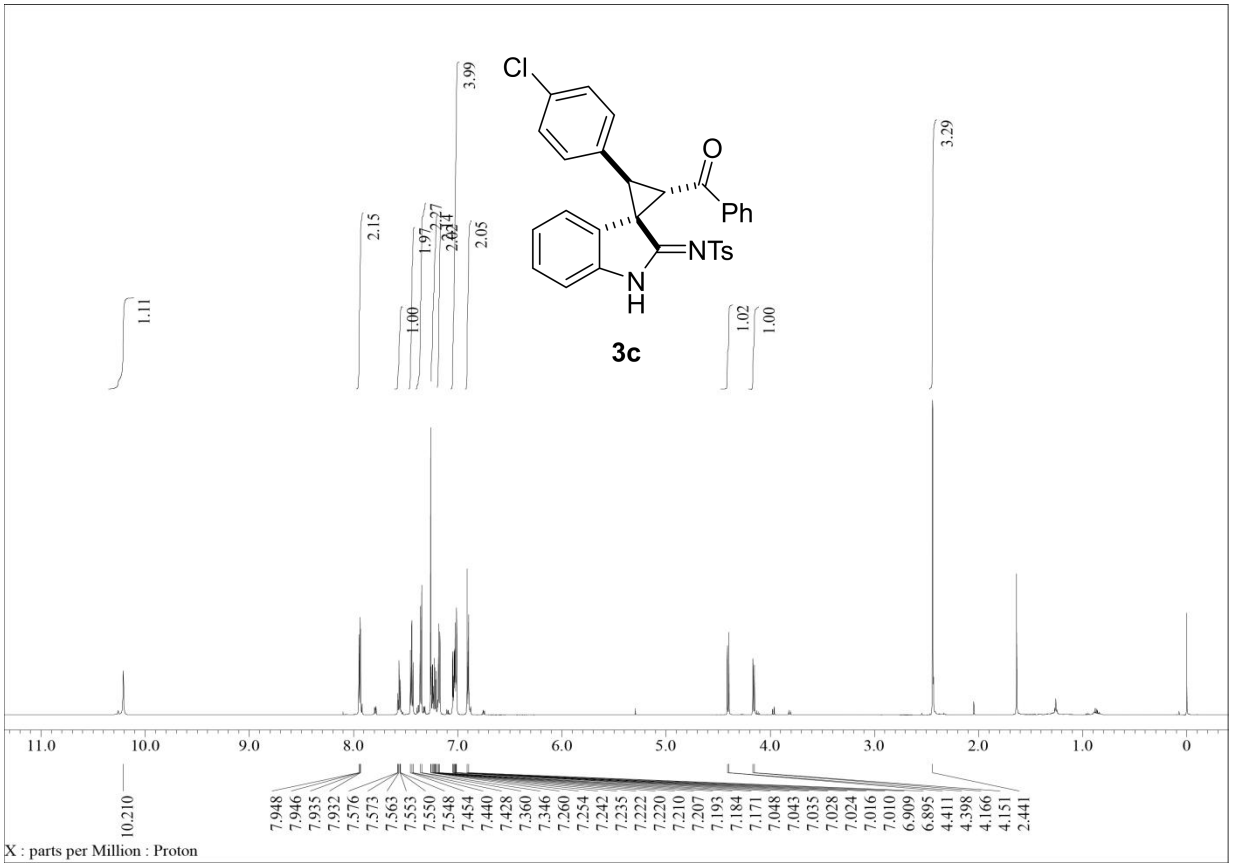
77.0
76.8
43.5
42.9
41.4
21.4
X : parts per Million : Carbon13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O
Ph
NTs
N
H
3c
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3.29
2.15
1.97
2.27
2.02
2.34
2.05
1.11
1.00
1.02
1.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.210
7.948
7.946
7.935
7.932
7.576
7.573
7.563
7.553
7.550
7.548
7.454
7.440
7.428
7.360
7.346
7.260
7.254
7.242
7.235
7.222
7.220
7.210
7.207
7.193
7.184
7.171
7.048
7.043
7.035
7.028
7.024
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6.895
4.411
4.398
4.166
4.151
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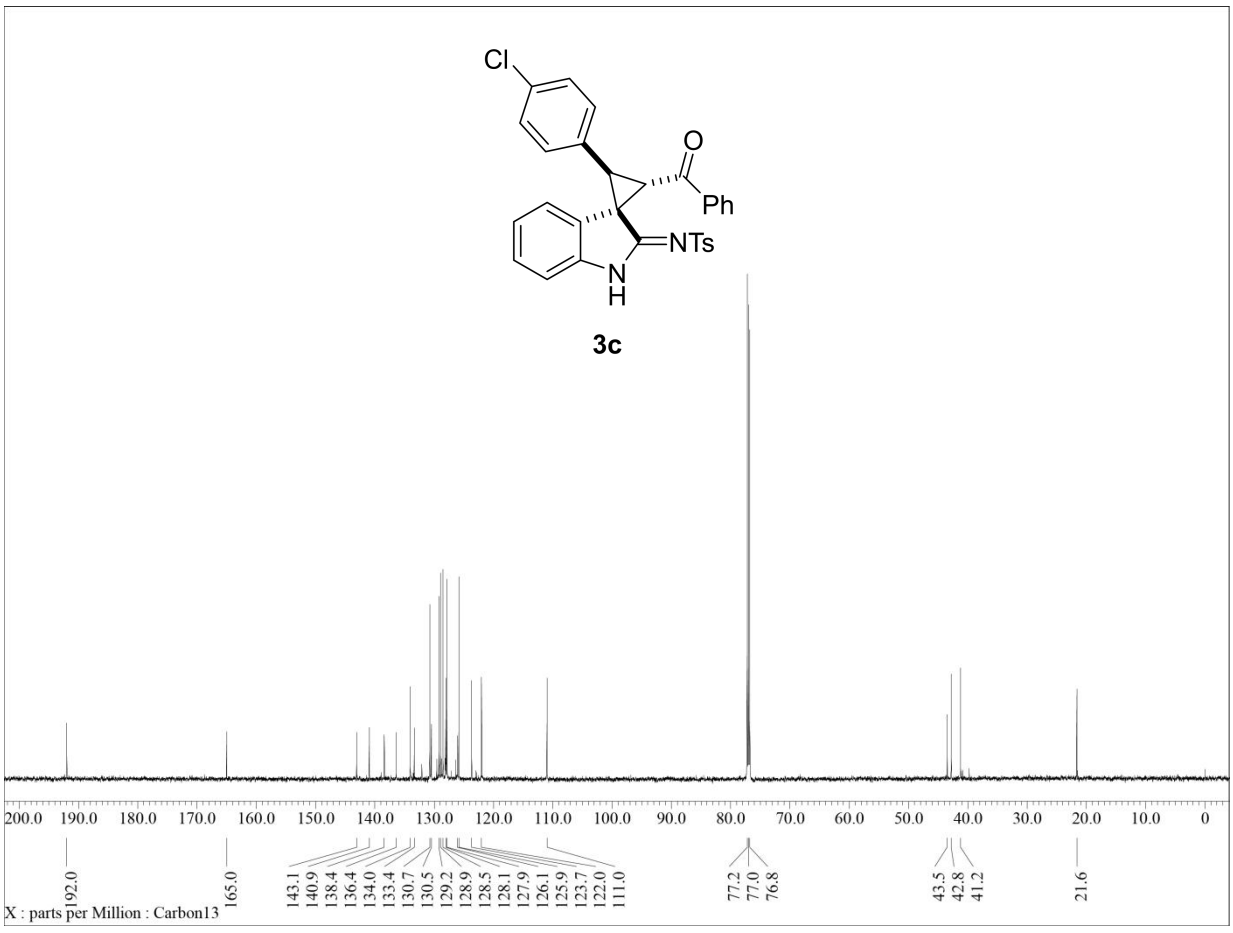
X : parts per Million : Proton


Cl
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Ph
NTs
N
H
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160.0
150.0
140.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.0
165.0
143.1
140.9
138.4
136.4
134.0
133.4
130.7
130.5
129.2
128.9
128.5
128.1
127.9
126.1
125.9
123.7
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77.0
76.8
43.5
42.8
41.2
21.6
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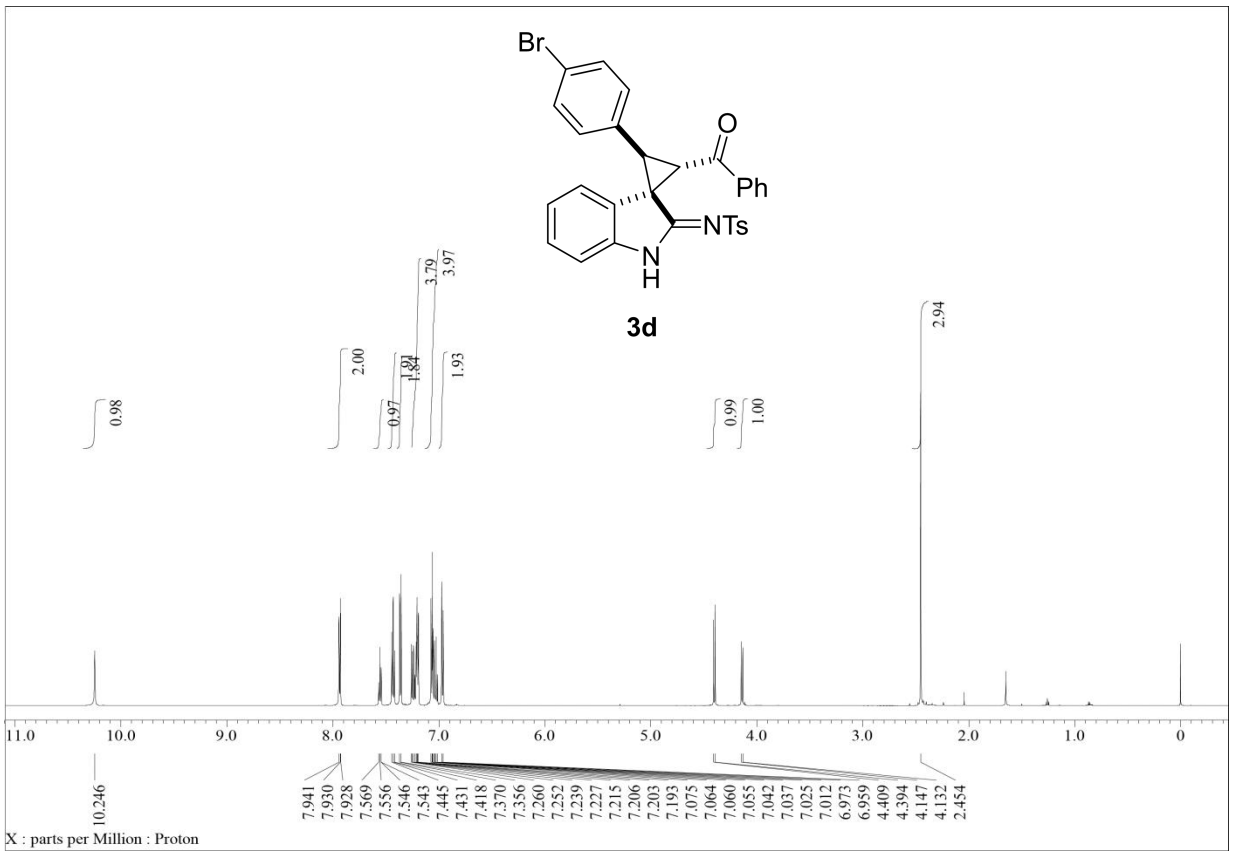
Br
O
Ph
NTs
N
H
3d
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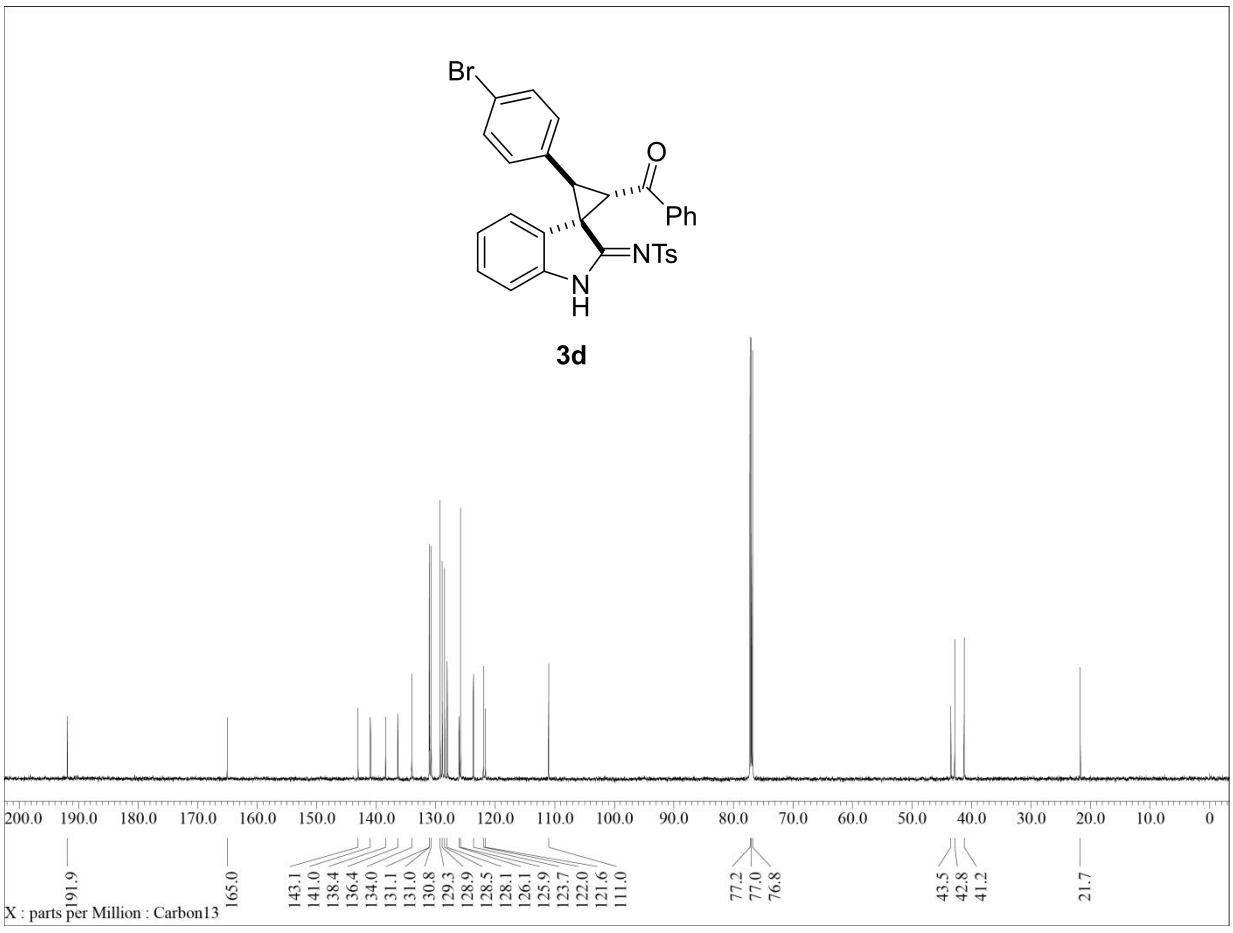
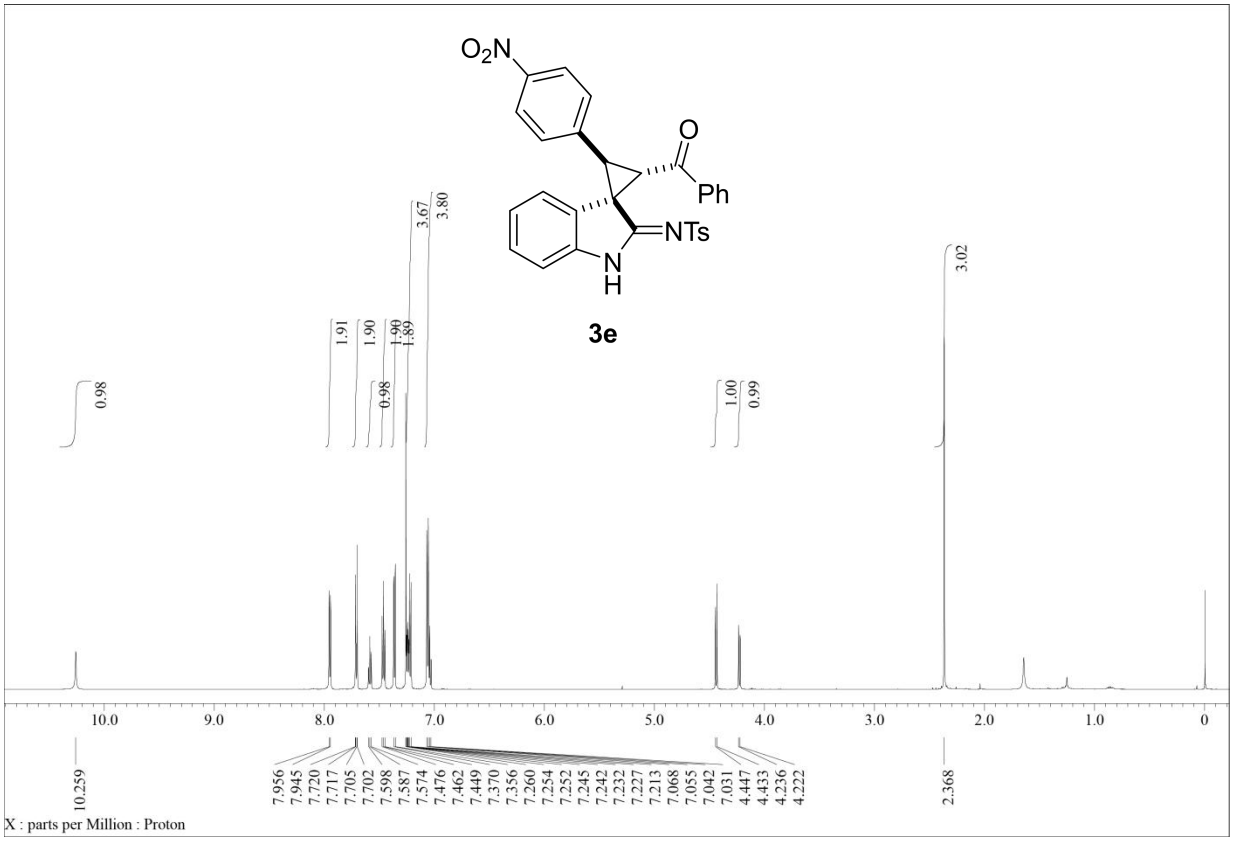
2.00
0.97
1.91
1.84
3.79
3.97
1.93
0.99
1.00
2.94
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.246
7.941
7.930
7.928
7.569
7.556
7.546
7.543
7.445
7.431
7.418
7.370
7.356
7.260
7.252
7.239
7.227
7.215
7.206
7.203
7.193
7.075
7.064
7.060
7.055
7.042
7.037
7.025
7.012
6.973
6.959
4.409
4.394
4.147
4.132
2.454
X : parts per Million : Proton


Br
O
Ph
NTs
N
H
3d
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.9
165.0
143.1
141.0
138.4
136.4
134.0
131.1
131.0
130.8
129.3
128.9
128.5
128.1
126.1
125.9
123.7
122.0
121.6
111.0
77.2
77.0
76.8
43.5
42.8
41.2
21.7
X : parts per Million : Carbon13


O2N
O
Ph
NTs
N
H
3e
3.67
3.80
3.02
1.91
1.90
1.99
1.89
0.98
0.98
1.00
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.259
7.956
7.945
7.720
7.717
7.705
7.702
7.598
7.587
7.574
7.476
7.462
7.449
7.370
7.356
7.260
7.254
7.252
7.245
7.242
7.232
7.227
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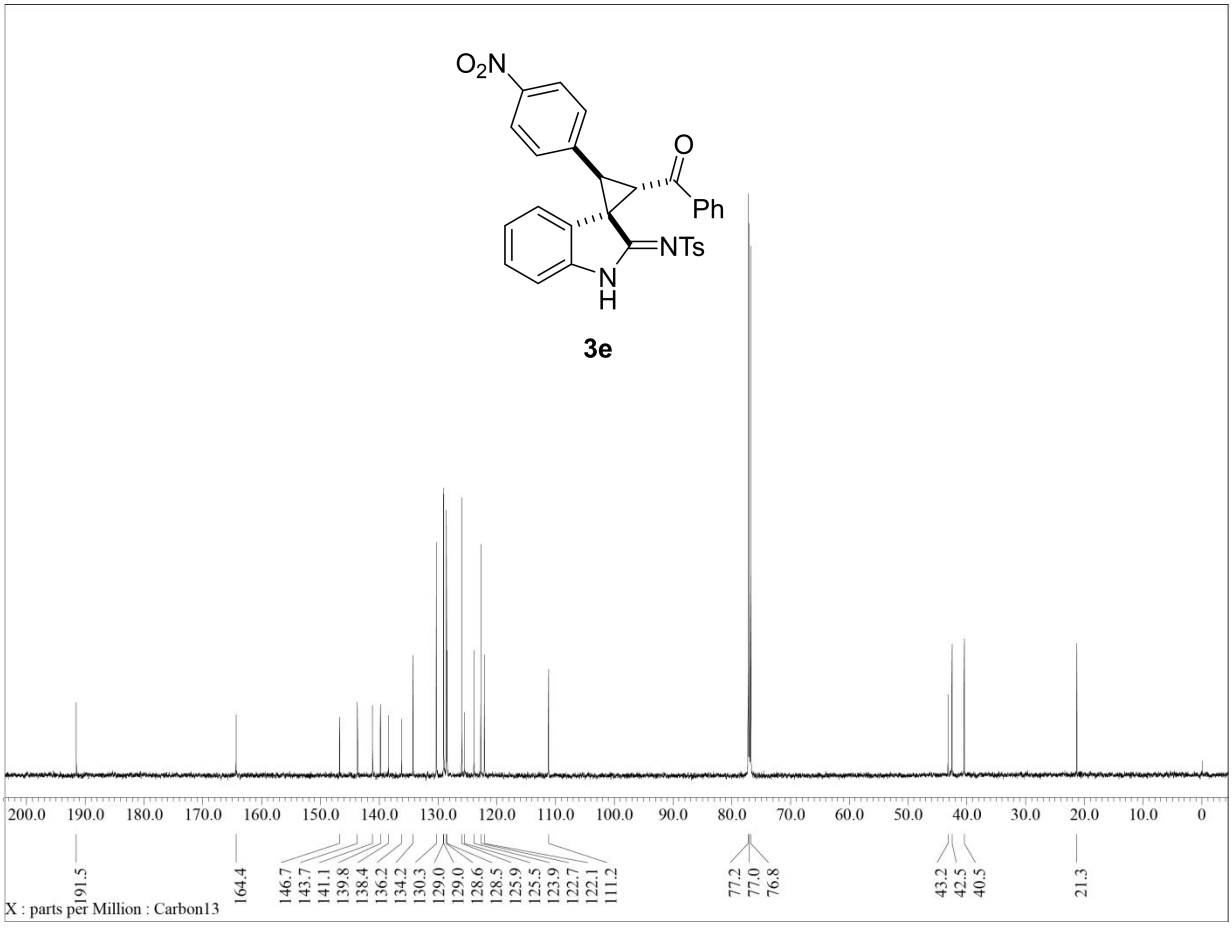
7.068
7.055
7.042
7.031
4.447
4.433
4.236
4.222
2.368
X : parts per Million : Proton


O2N
O
Ph
NTs
N
H
3e
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
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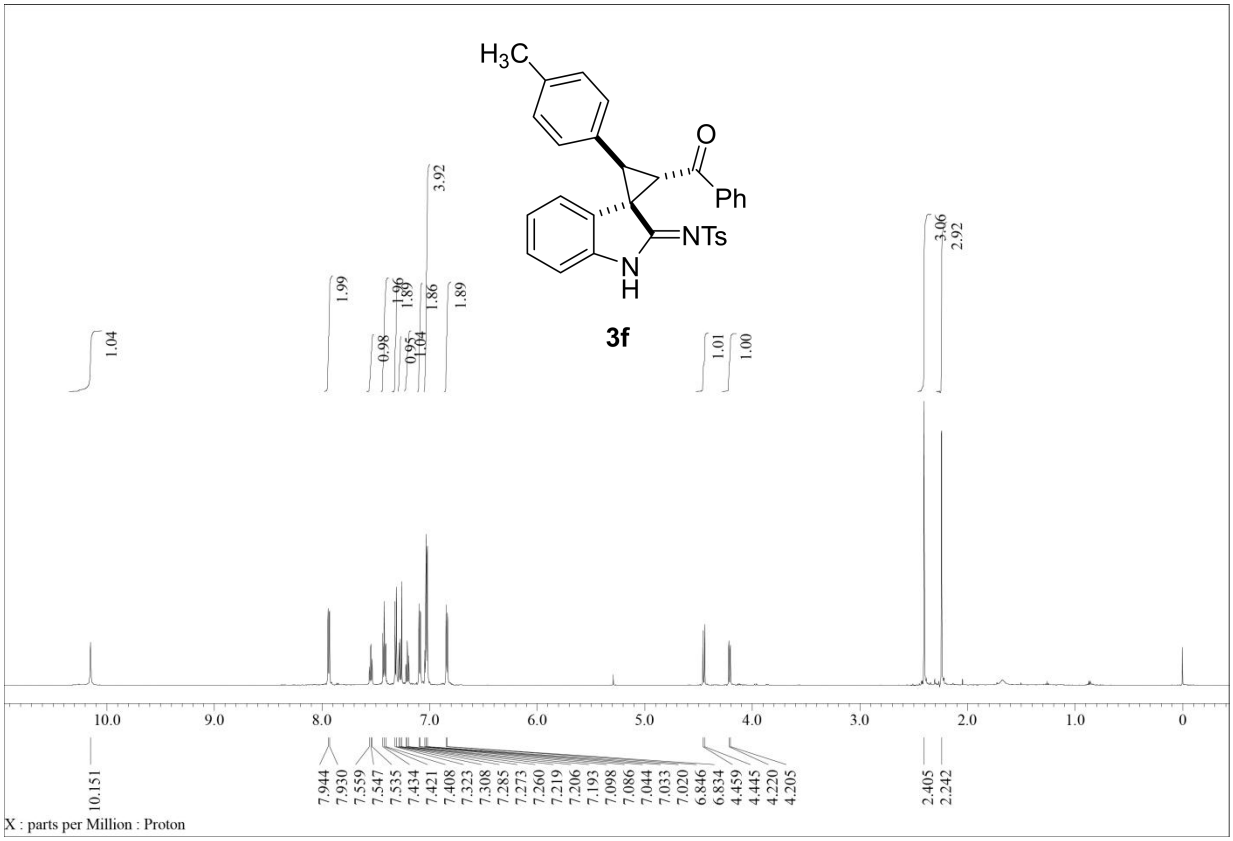
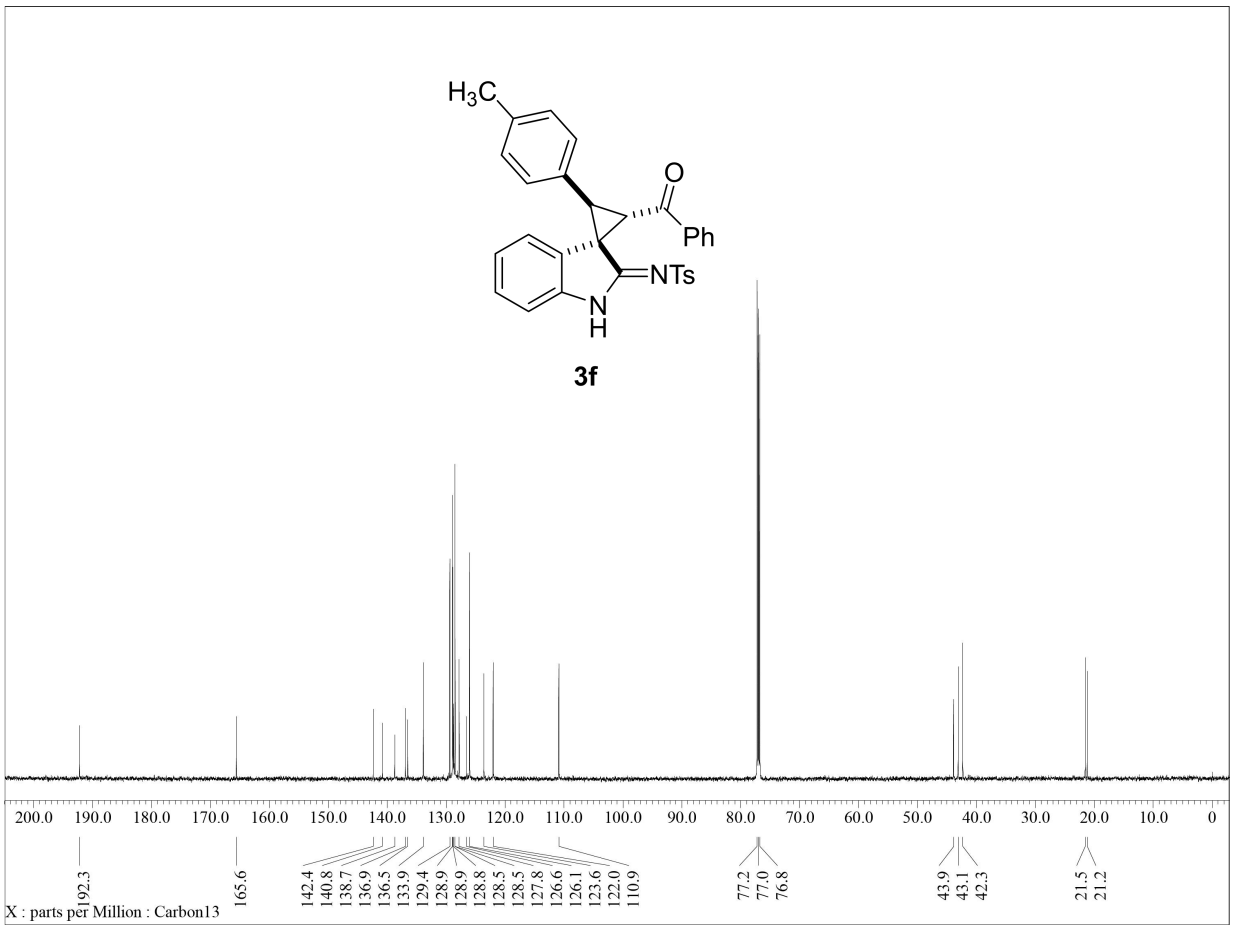
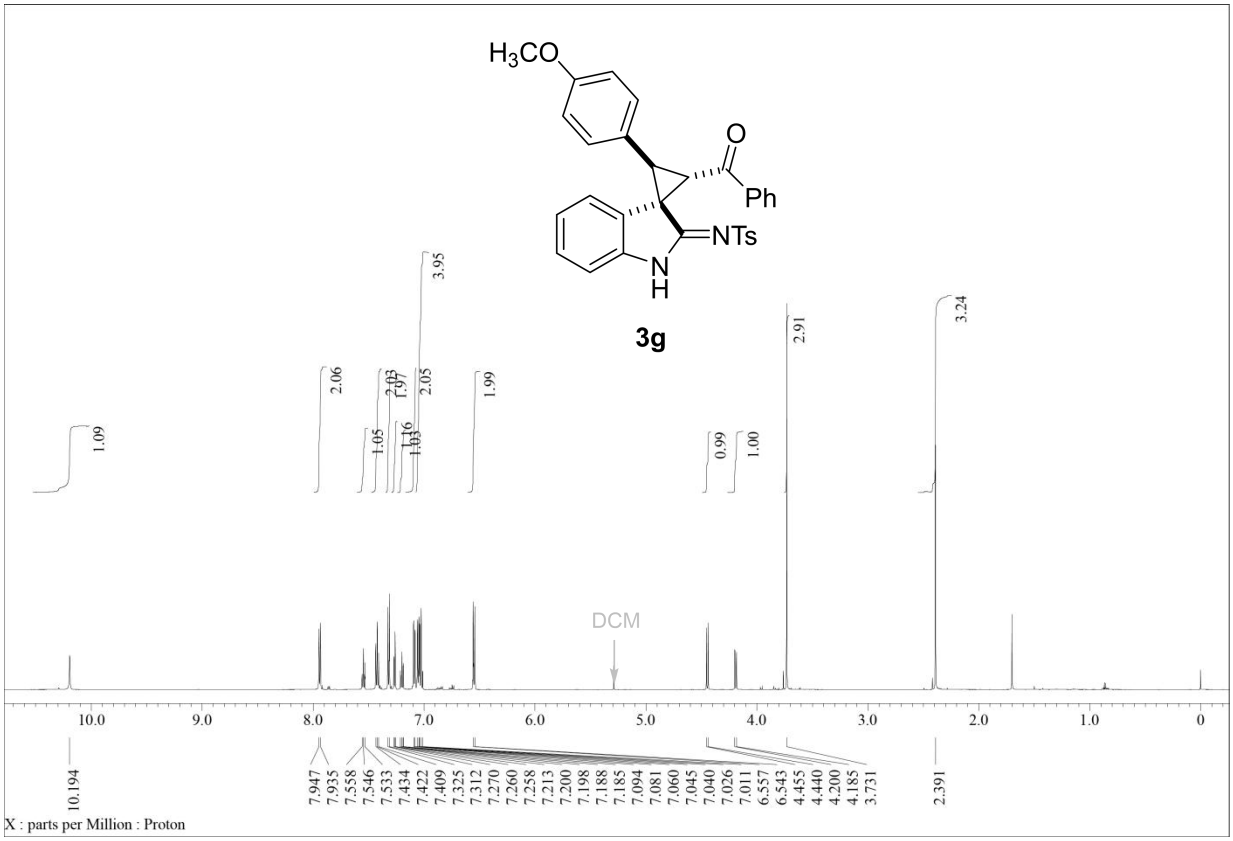
40.0
30.0
20.0
10.0
0
191.5
164.4
146.7
143.7
141.1
139.8
138.4
136.2
134.2
130.3
129.0
129.0
128.6
128.5
125.9
125.5
123.9
122.7
122.1
111.2
77.2
77.0
76.8
43.2
42.5
40.5
21.3
X : parts per Million : Carbon13


H3C
O
Ph
NTs
N
H
3f
X : parts per Million : Proton


H3C
O
Ph
NTs
N
H
3f
X : parts per Million : Carbon13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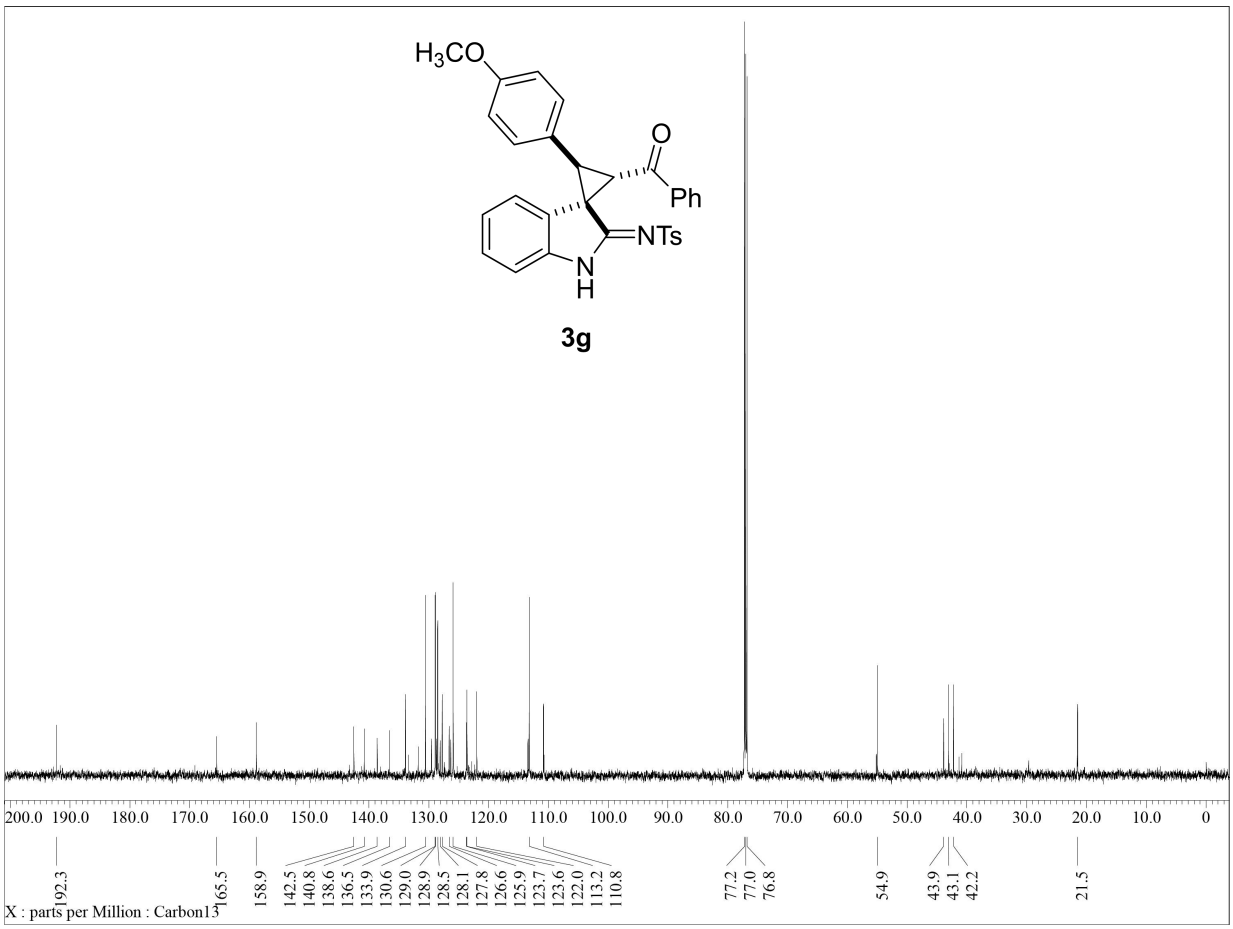
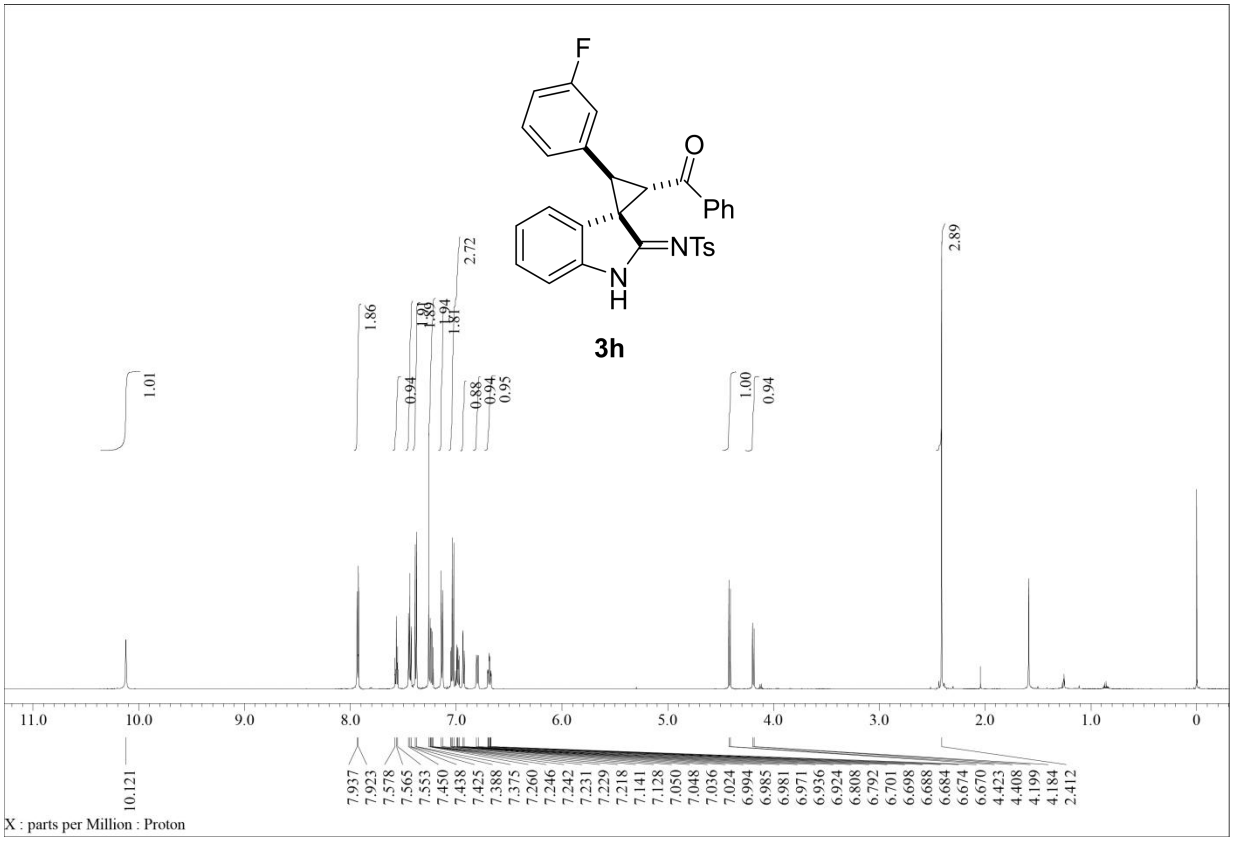
O
Ph
NTs
N
H
3g
DCM
X : parts per Million : Proton


H3CO
O
Ph
NTs
N
H
3g
X : parts per Million : Carbon13


F
O
Ph
NTs
N
H
3h
2.72
1.86
1.81
1.89
1.94
1.84
2.89
1.01
0.94
0.88
0.94
0.95
1.00
0.94
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.121
7.937
7.923
7.578
7.565
7.553
7.450
7.438
7.425
7.388
7.375
7.260
7.246
7.242
7.231
7.229
7.218
7.141
7.128
7.050
7.048
7.036
7.024
6.994
6.985
6.981
6.971
6.936
6.924
6.808
6.792
6.701
6.698
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6.674
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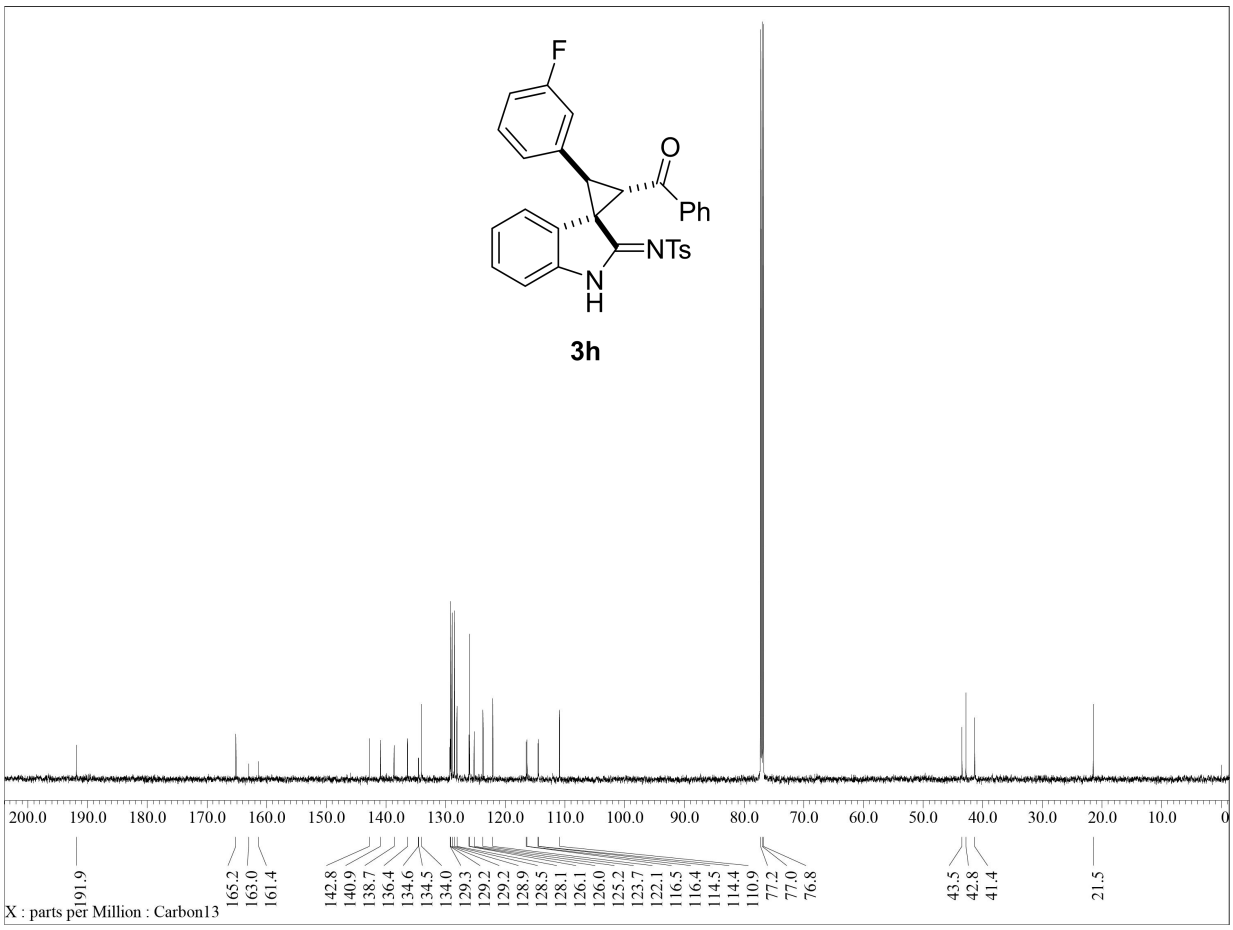
4.408
4.199
4.184
2.412
X : parts per Million : Proton


F
O
Ph
NTs
N
H
3h
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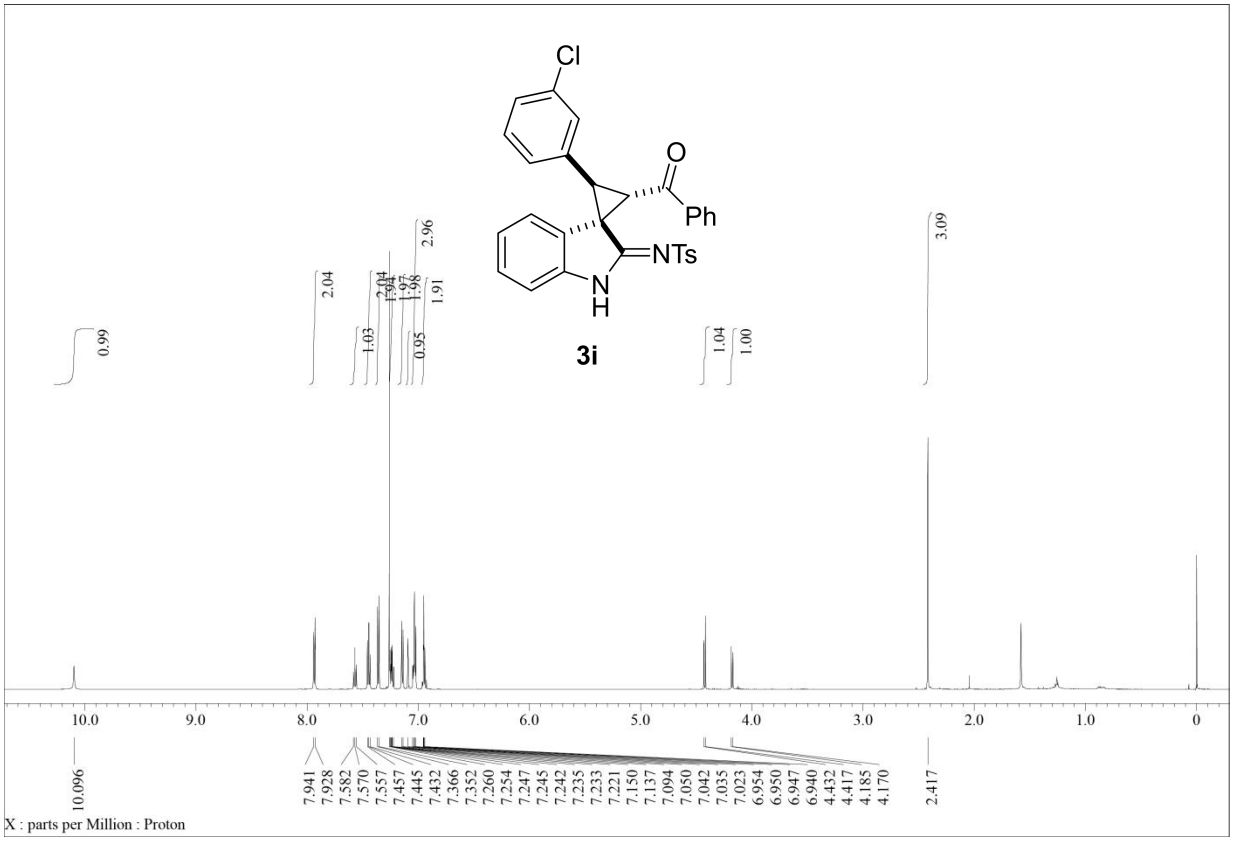
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.9
165.2
163.0
161.4
142.8
140.9
138.7
136.4
134.6
134.5
134.0
129.3
129.2
129.2
128.9
128.5
128.1
126.1
126.0
125.2
123.7
122.1
116.5
116.4
114.5
114.4
110.9
77.2
77.0
76.8
43.5
42.8
41.4
21.5
X : parts per Million : Carbon13


Cl
O
Ph
NTs
N
H
3i
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2.04
1.03
2.04
1.94
1.97
1.98
2.96
1.91
0.95
1.04
1.00
3.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.096
7.941
7.928
7.582
7.570
7.557
7.457
7.445
7.432
7.366
7.352
7.260
7.254
7.247
7.245
7.242
7.235
7.233
7.221
7.150
7.137
7.094
7.050
7.042
7.035
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6.947
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4.185
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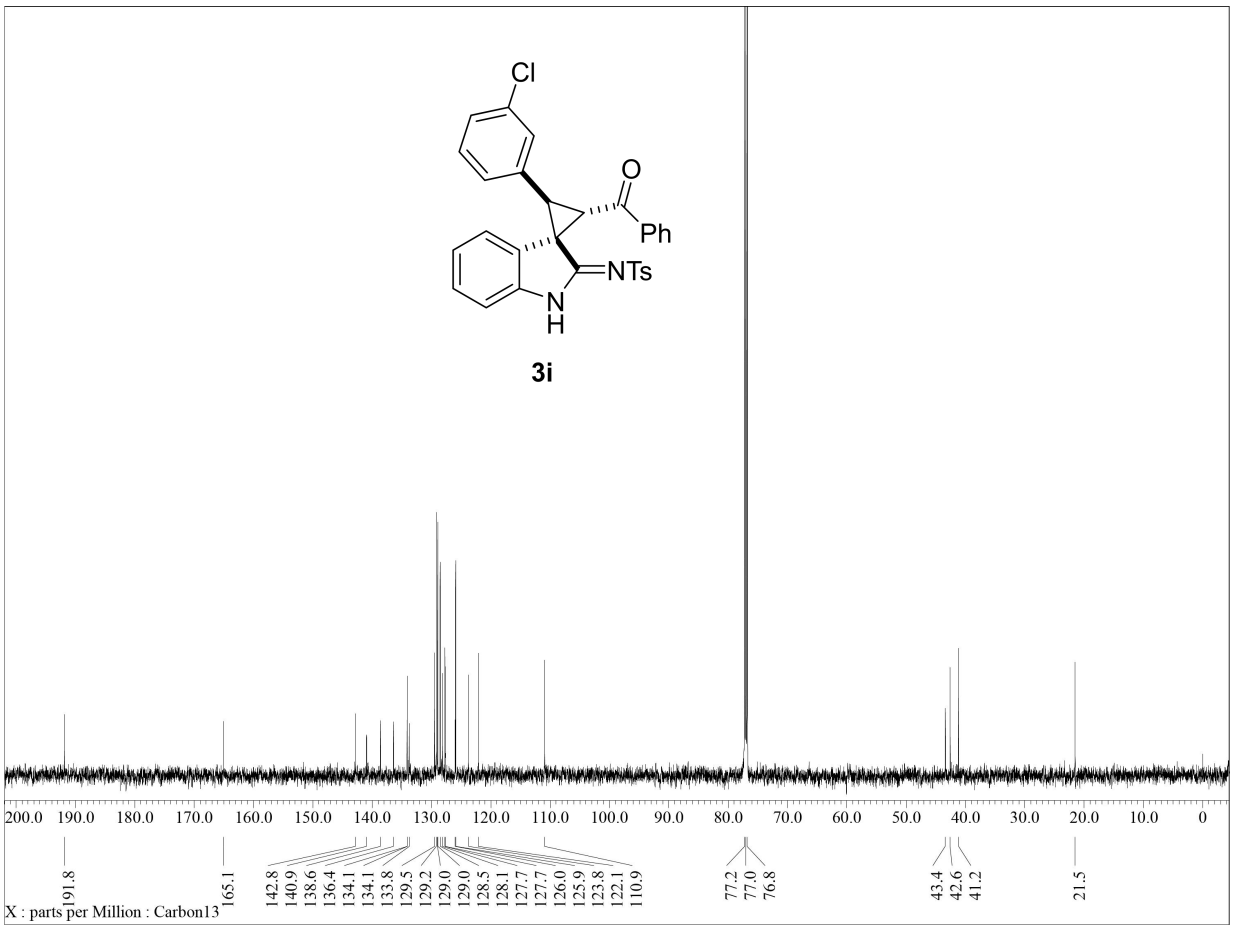
X : parts per Million : Proton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Ph
NTs
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H
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150.0
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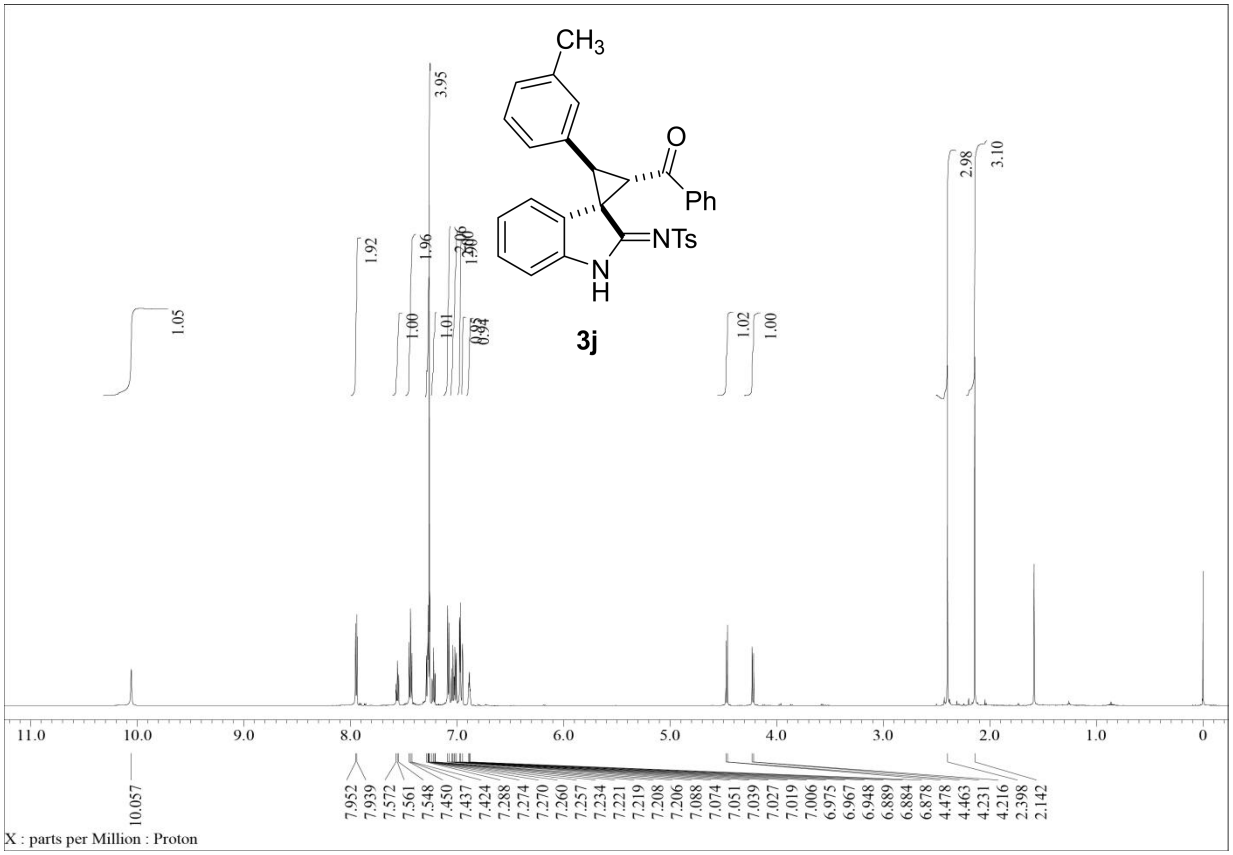
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.8
165.1
142.8
140.9
138.6
136.4
134.1
134.1
133.8
129.5
129.2
129.0
129.0
128.5
128.1
127.7
127.7
126.0
125.9
123.8
122.1
110.9
77.2
77.0
76.8
43.4
42.6
41.2
21.5
X : parts per Million : Carbon13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Ph
NTs
N
H
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1.92
1.96
1.05
1.00
1.01
1.02
1.00
2.98
3.10
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.057
7.952
7.939
7.572
7.561
7.548
7.450
7.437
7.424
7.288
7.274
7.270
7.260
7.257
7.234
7.221
7.219
7.208
7.206
7.088
7.074
7.051
7.039
7.027
7.019
7.006
6.975
6.967
6.948
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6.884
6.878
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4.463
4.231
4.216
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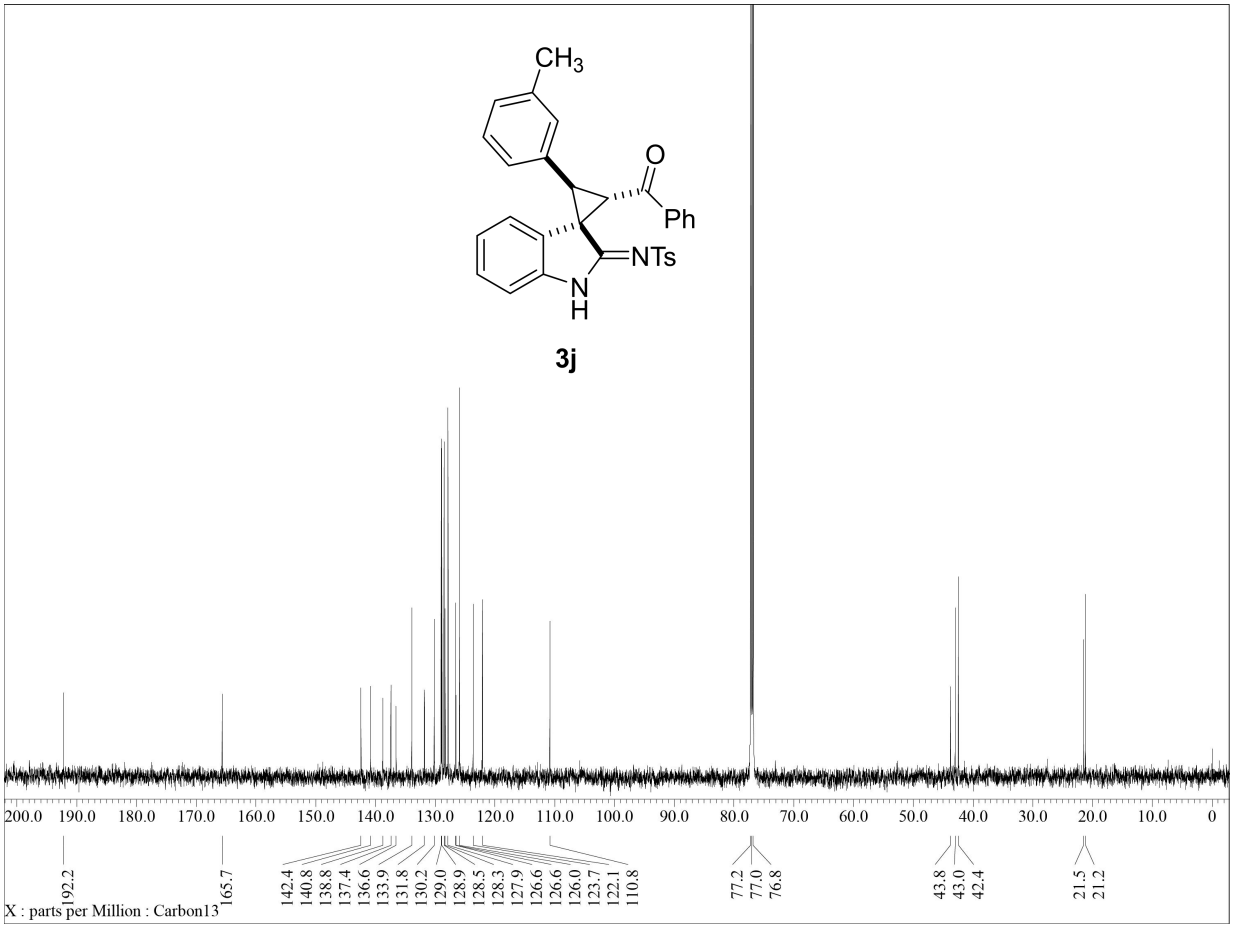
2.142
X : parts per Million : Proton


CH3
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Ph
NTs
N
H
3j
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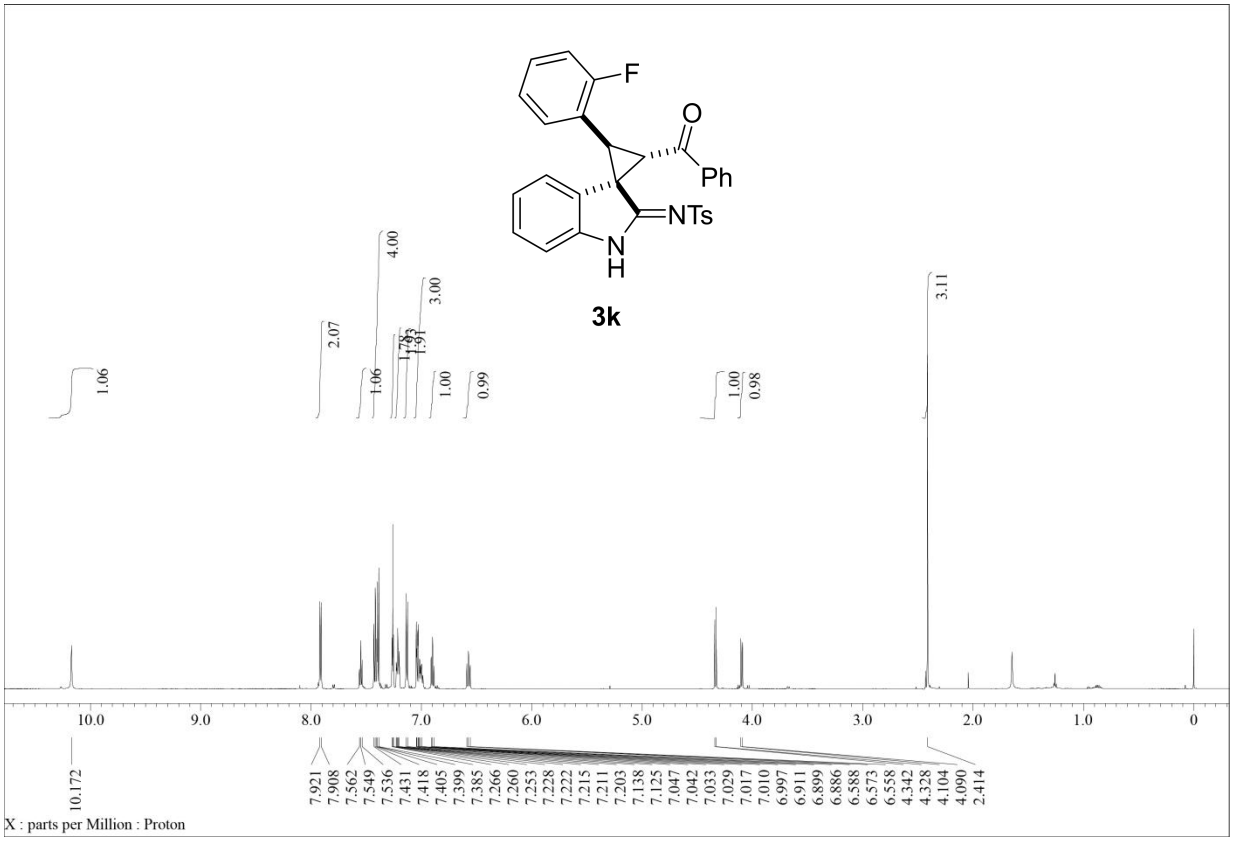
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.2
165.7
142.4
140.8
138.8
137.4
136.6
133.9
131.8
130.2
129.0
128.9
128.5
128.3
127.9
126.6
126.6
126.0
123.7
122.1
110.8
77.2
77.0
76.8
43.8
43.0
42.4
21.5
21.2
X : parts per Million : Carbon13


F
O
Ph
NTs
N
H
3k
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3.00
3.11
2.07
1.06
1.06
1.00
0.99
1.00
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.172
7.921
7.908
7.562
7.549
7.536
7.431
7.418
7.405
7.399
7.385
7.266
7.260
7.253
7.228
7.222
7.215
7.211
7.203
7.138
7.125
7.047
7.042
7.033
7.029
7.017
7.010
6.997
6.911
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6.573
6.558
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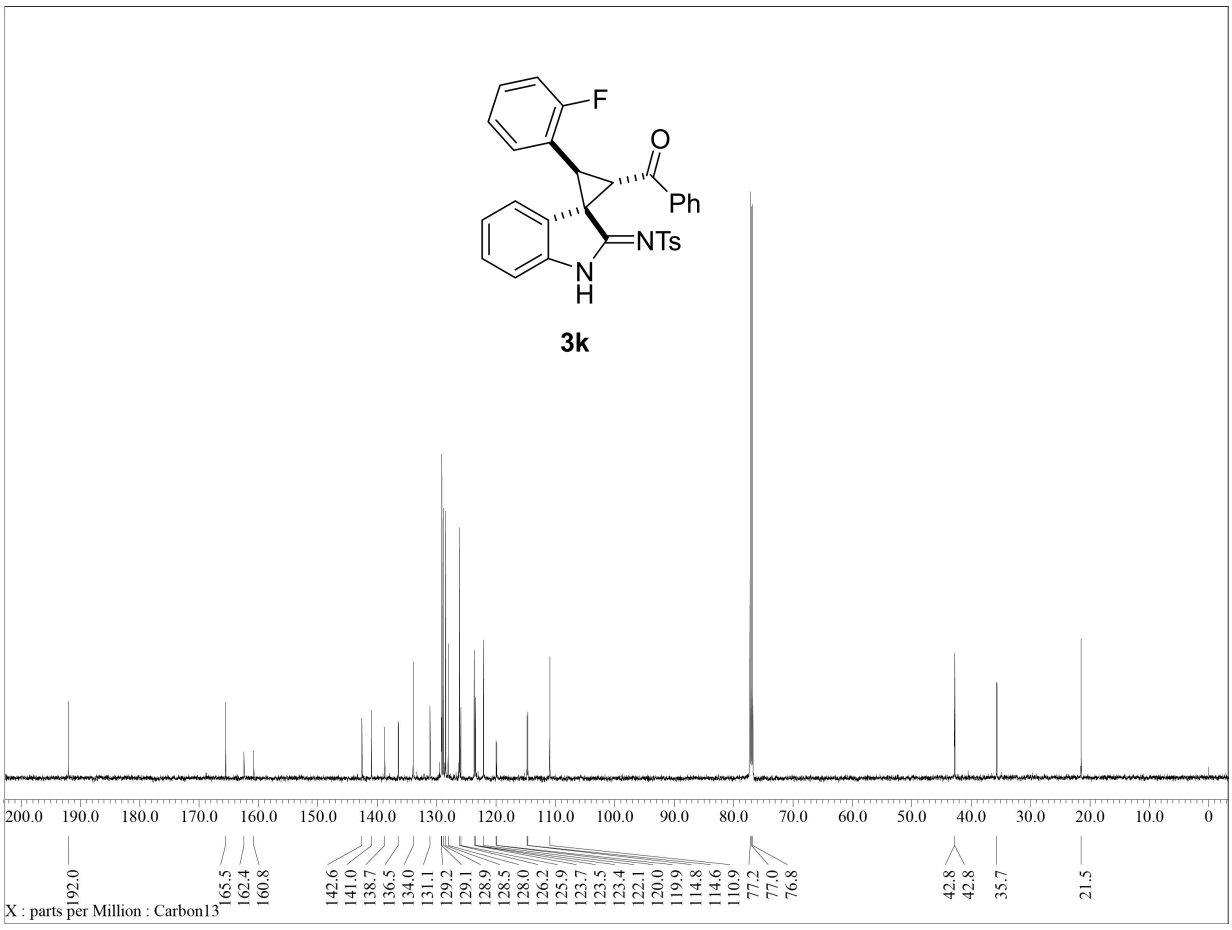
4.328
4.104
4.090
2.414
X : parts per Million : Proton


F
O
Ph
NTs
N
H
3k
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.0
165.5
162.4
160.8
142.6
141.0
138.7
136.5
134.0
131.1
129.2
129.1
128.9
128.5
128.0
126.2
125.9
123.7
123.5
123.4
122.1
120.0
119.9
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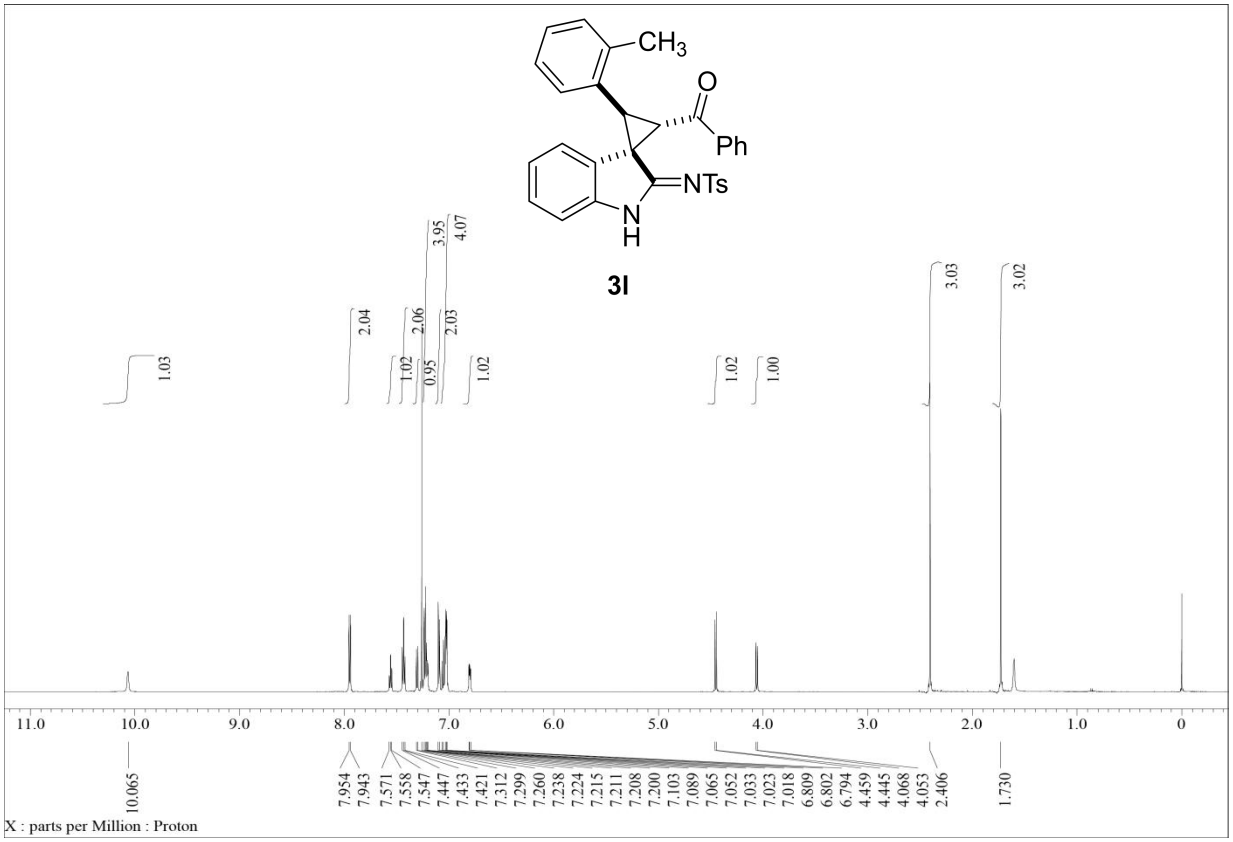
114.6
110.9
77.2
77.0
76.8
42.8
42.8
35.7
21.5
X : parts per Million : Carbon13


CH3
O
Ph
NTs
N
H
3l
3.95
4.07
3.03
3.02
2.04
2.06
2.03
1.03
1.02
0.95
1.02
1.02
1.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.065
7.954
7.943
7.571
7.558
7.547
7.447
7.433
7.421
7.312
7.299
7.260
7.238
7.224
7.215
7.211
7.208
7.200
7.103
7.089
7.065
7.052
7.033
7.023
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4.445
4.068
4.053
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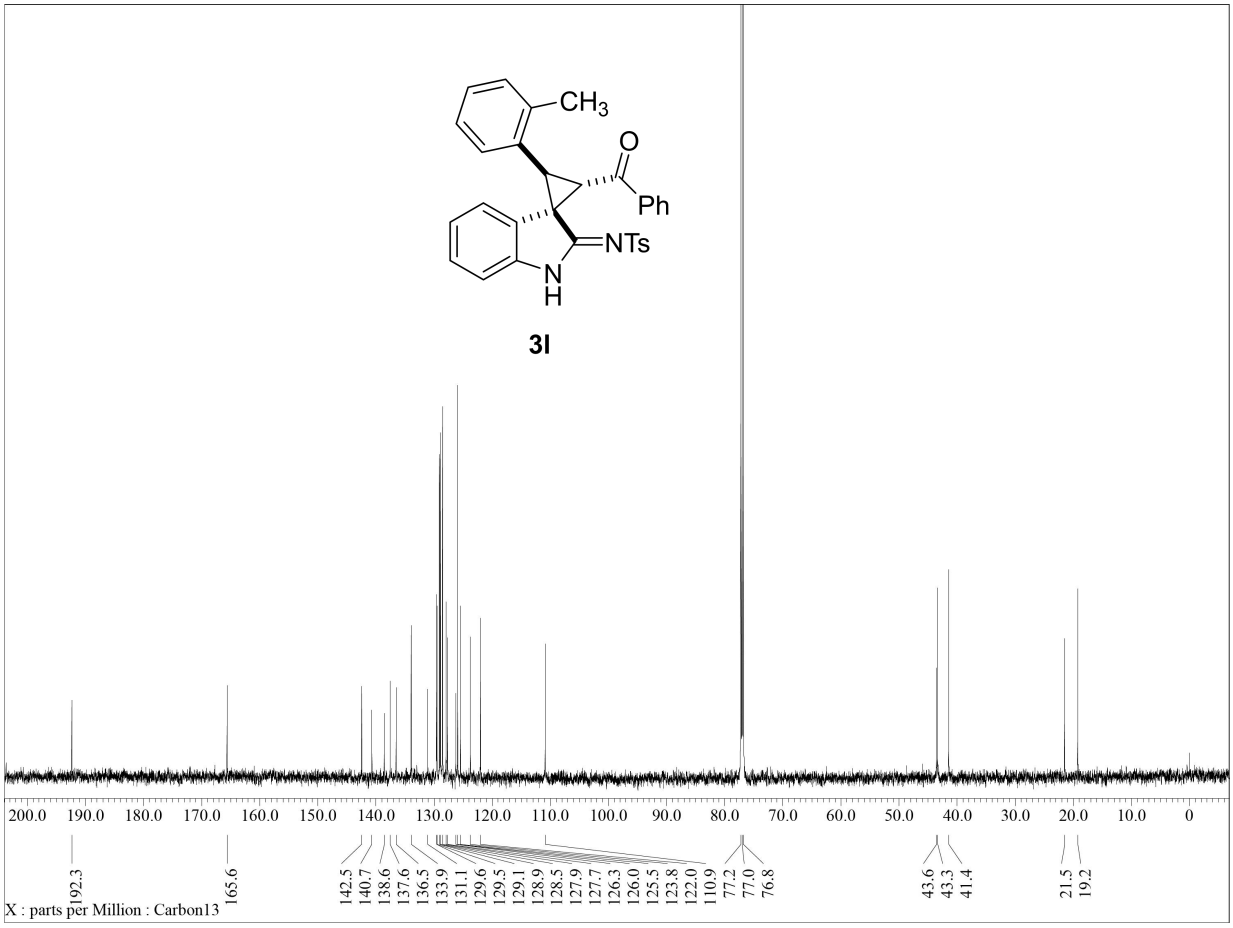
1.730
X : parts per Million : Proton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O
Ph
NTs
N
H
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150.0
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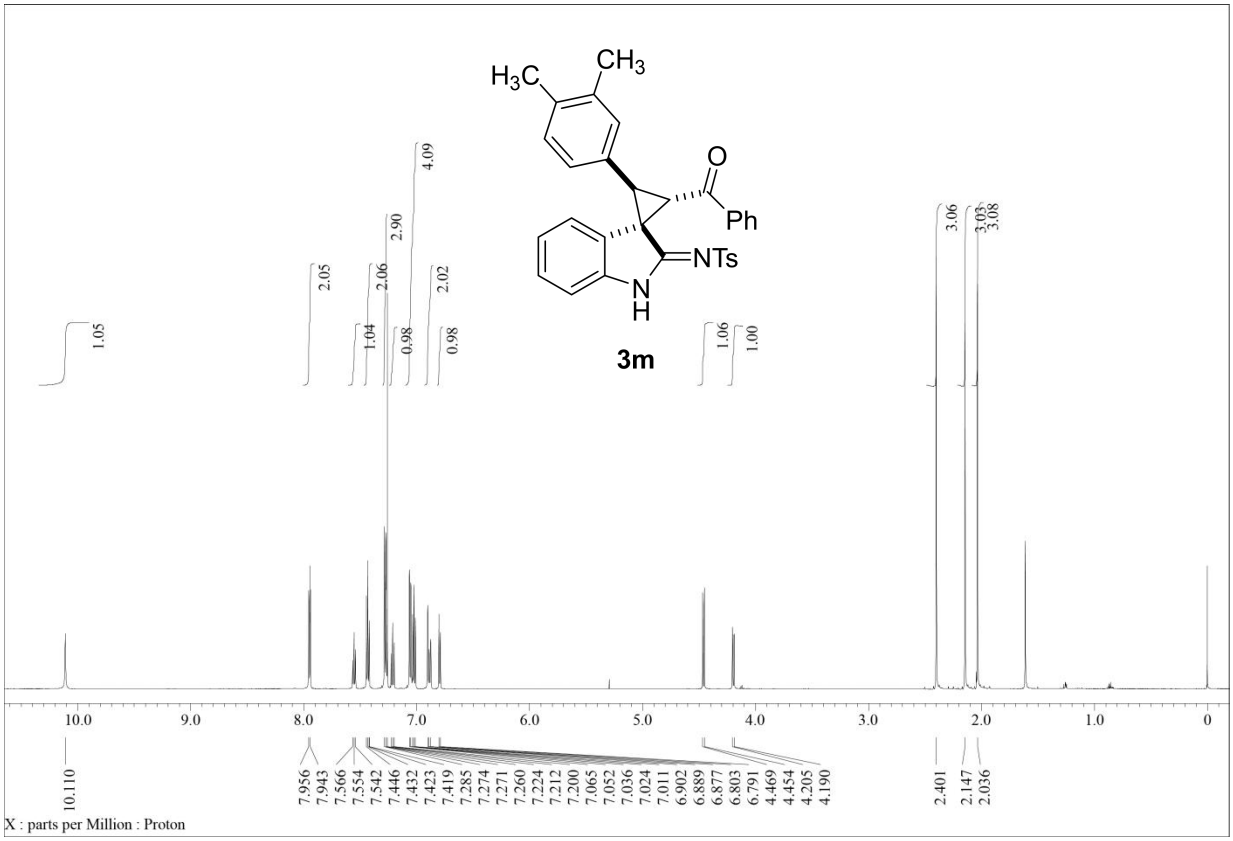
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.3
165.6
142.5
140.7
138.6
137.6
136.5
133.9
131.1
129.6
129.5
129.1
128.9
128.5
127.9
127.7
126.3
126.0
125.5
123.8
122.0
110.9
77.2
77.0
76.8
43.6
43.3
41.4
21.5
19.2
X : parts per Million : Carbon13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CH3
O
Ph
NTs
N
H
3m
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2.05
1.04
2.06
0.98
2.90
4.09
0.98
2.02
1.06
1.00
3.06
3.03
3.08
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.110
7.956
7.943
7.566
7.554
7.542
7.446
7.432
7.423
7.419
7.285
7.274
7.271
7.260
7.224
7.212
7.200
7.065
7.052
7.036
7.024
7.011
6.902
6.889
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6.791
4.469
4.454
4.205
4.190
2.401
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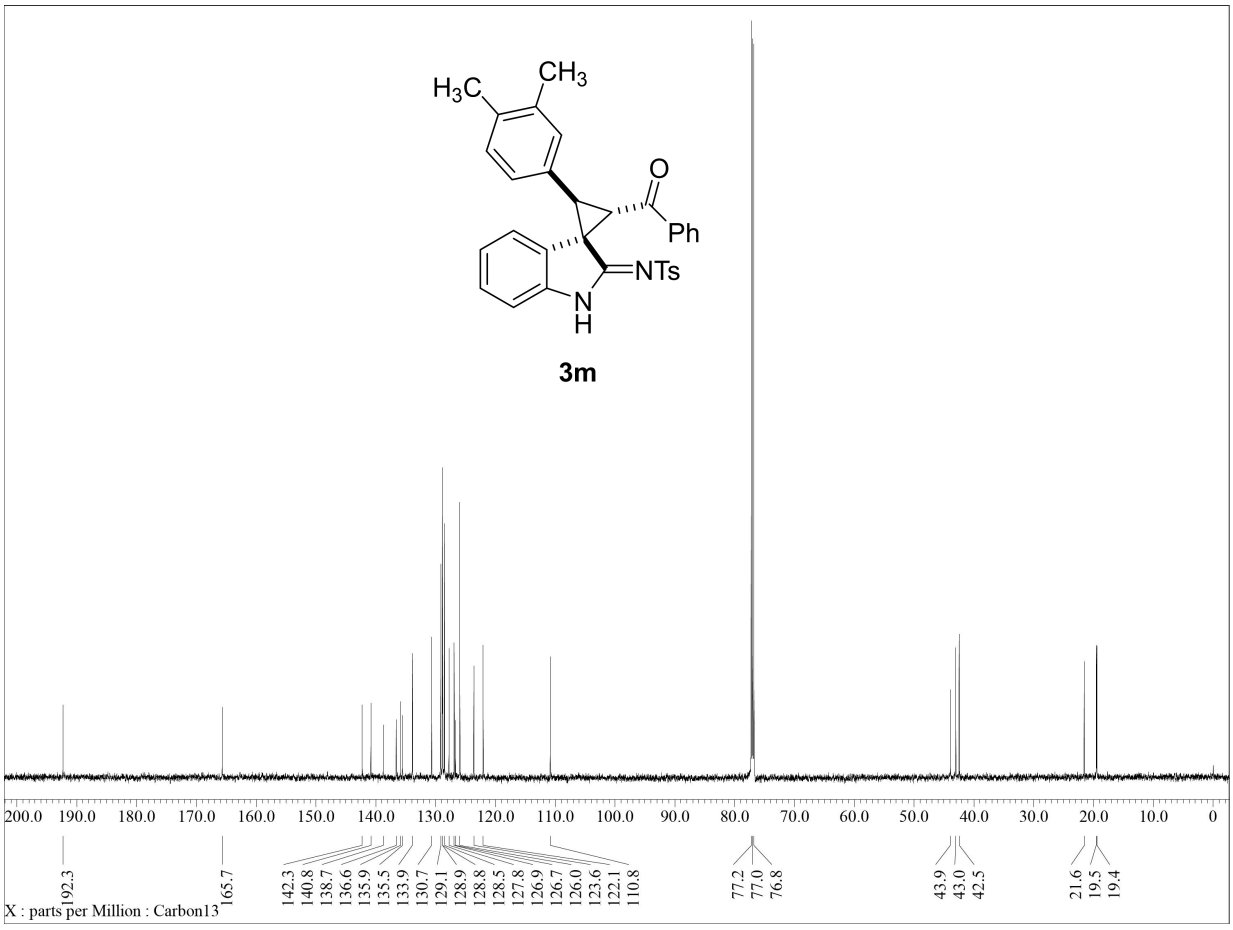
2.036
X : parts per Million : Proton


H3C
CH3
O
Ph
NTs
N
H
3m
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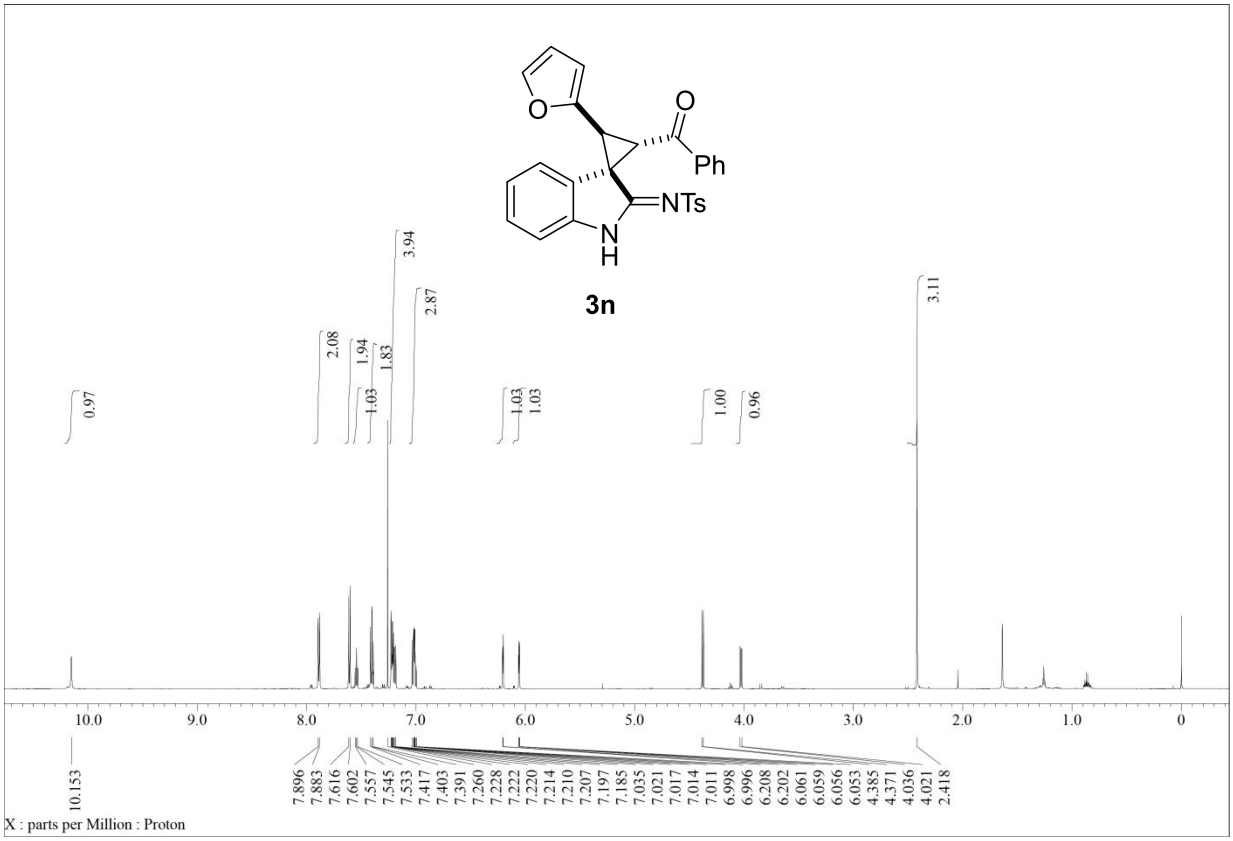
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.3
165.7
142.3
140.8
138.7
136.6
135.9
135.5
133.9
130.7
129.1
128.9
128.8
128.5
127.8
126.9
126.7
126.0
123.6
122.1
110.8
77.2
77.0
76.8
43.9
43.0
42.5
21.6
19.5
19.4
X : parts per Million : Carbon13


O
O
Ph
NTs
N
H
3n
3.94
2.87
2.08
1.94
1.83
1.03
1.03
1.03
0.97
1.00
0.96
3.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.153
7.896
7.883
7.616
7.602
7.557
7.545
7.533
7.417
7.403
7.391
7.260
7.228
7.222
7.220
7.214
7.210
7.207
7.197
7.185
7.035
7.021
7.017
7.014
7.011
6.998
6.996
6.208
6.202
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6.059
6.056
6.053
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4.036
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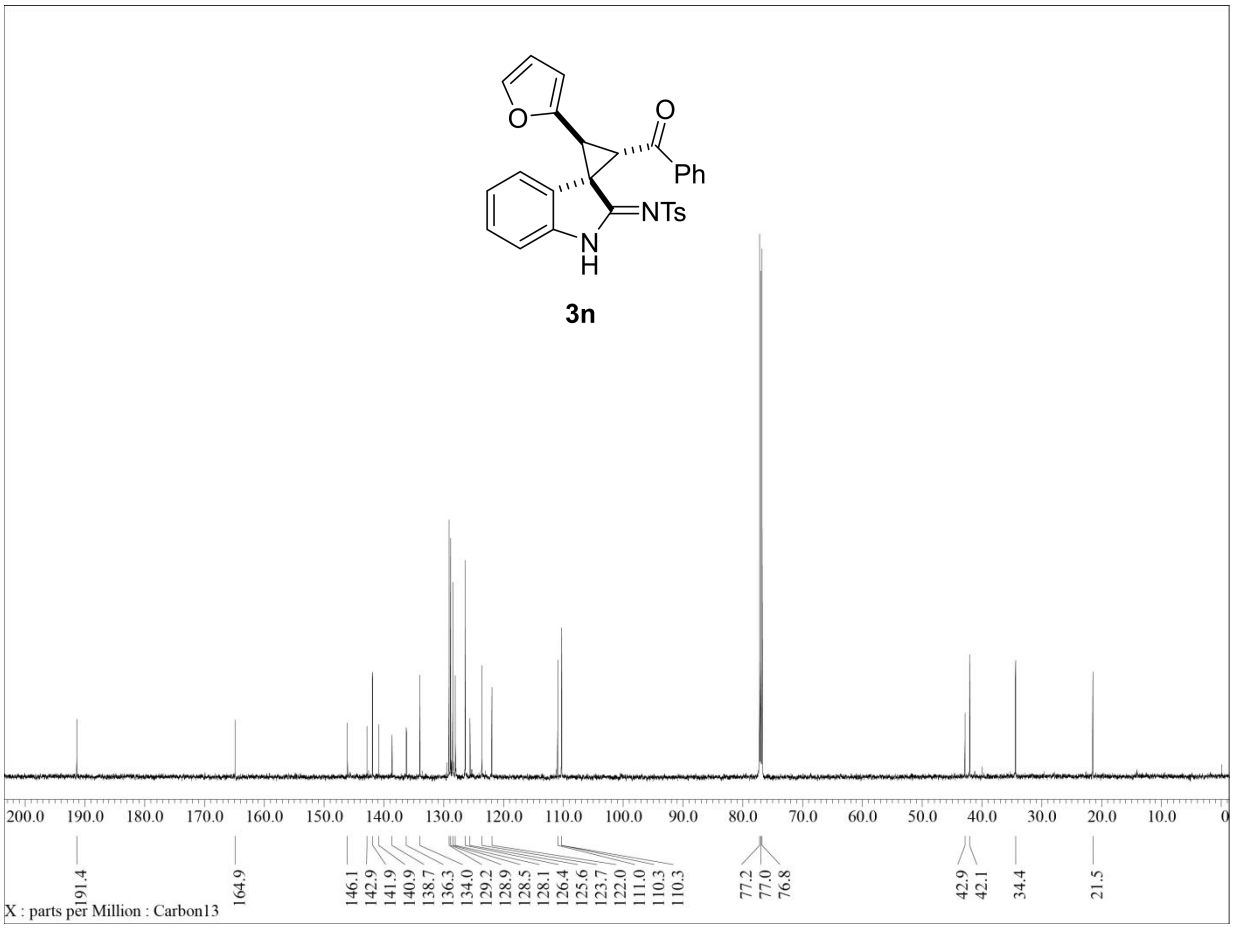
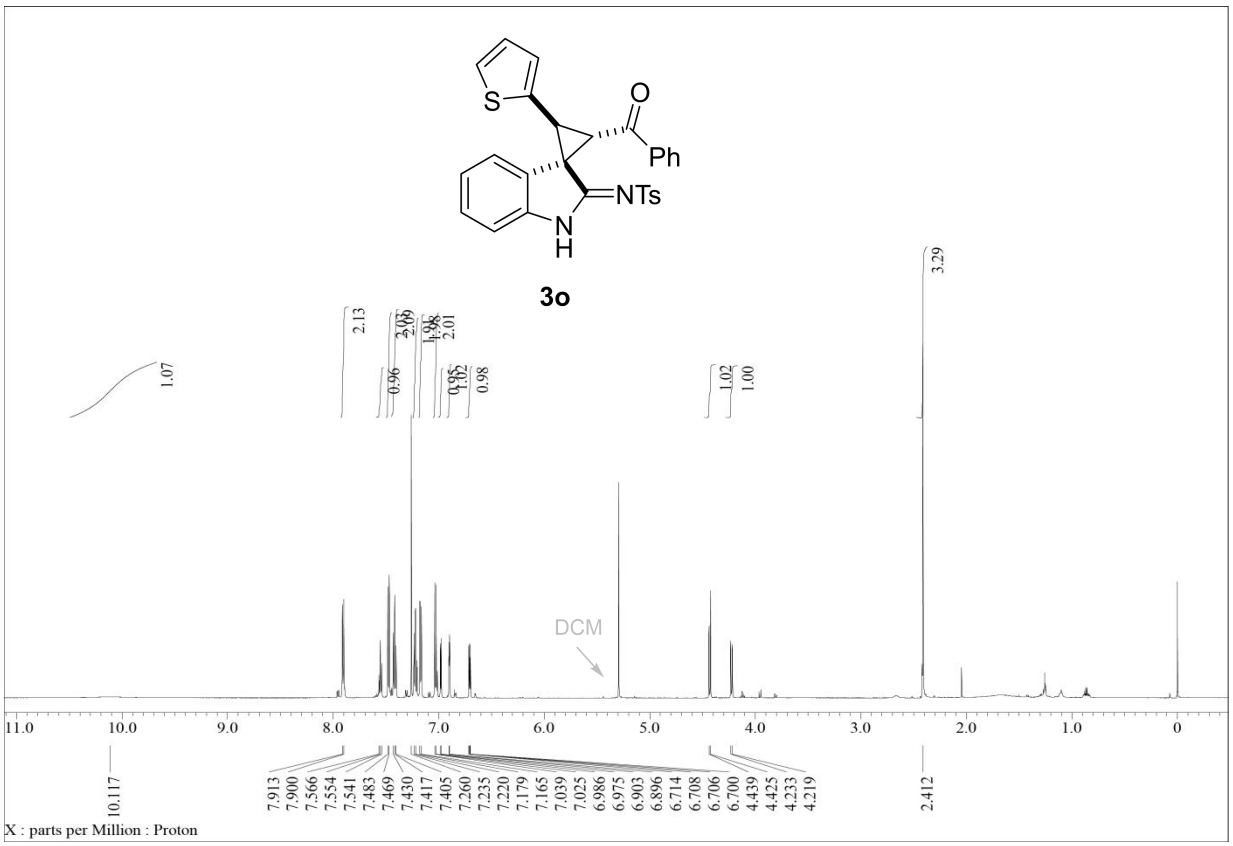
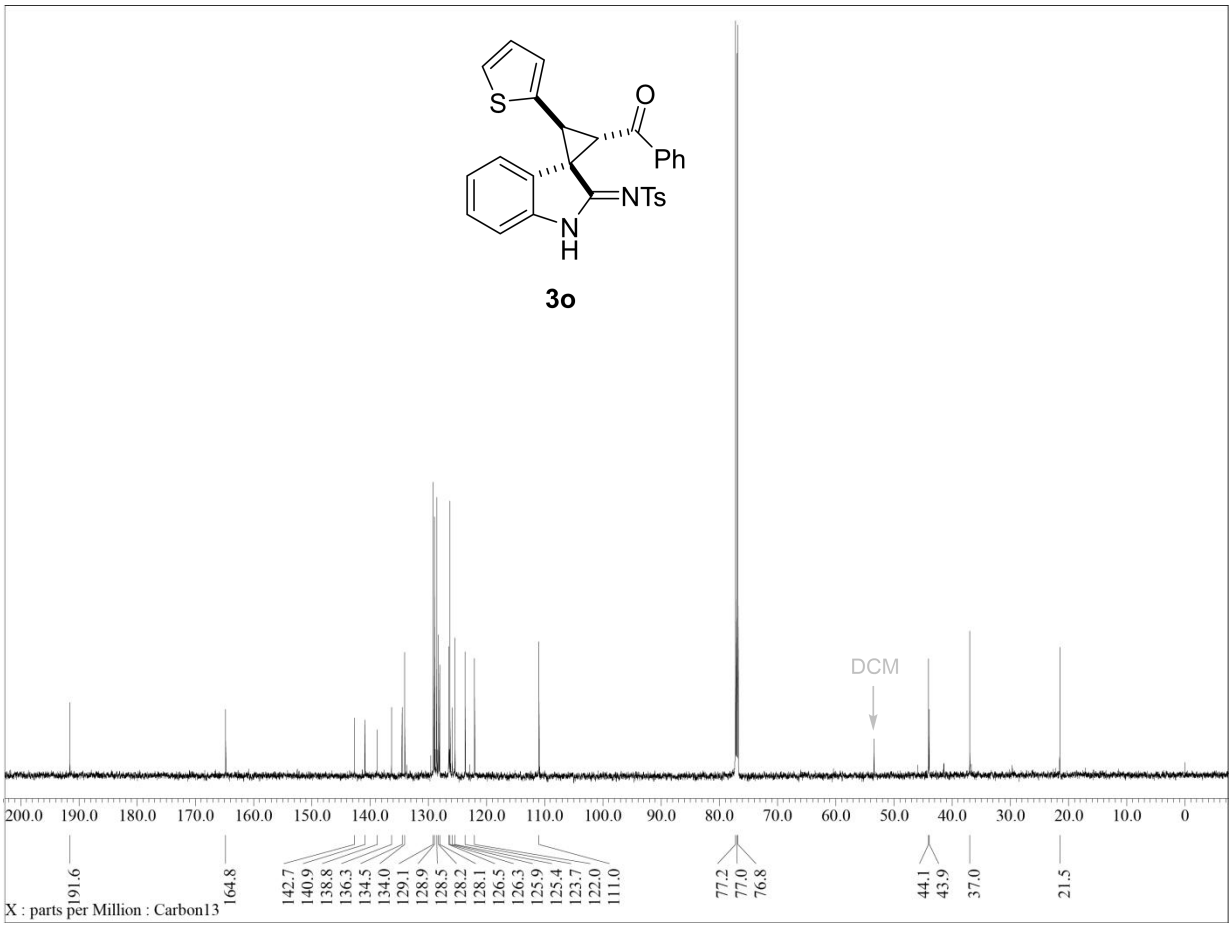
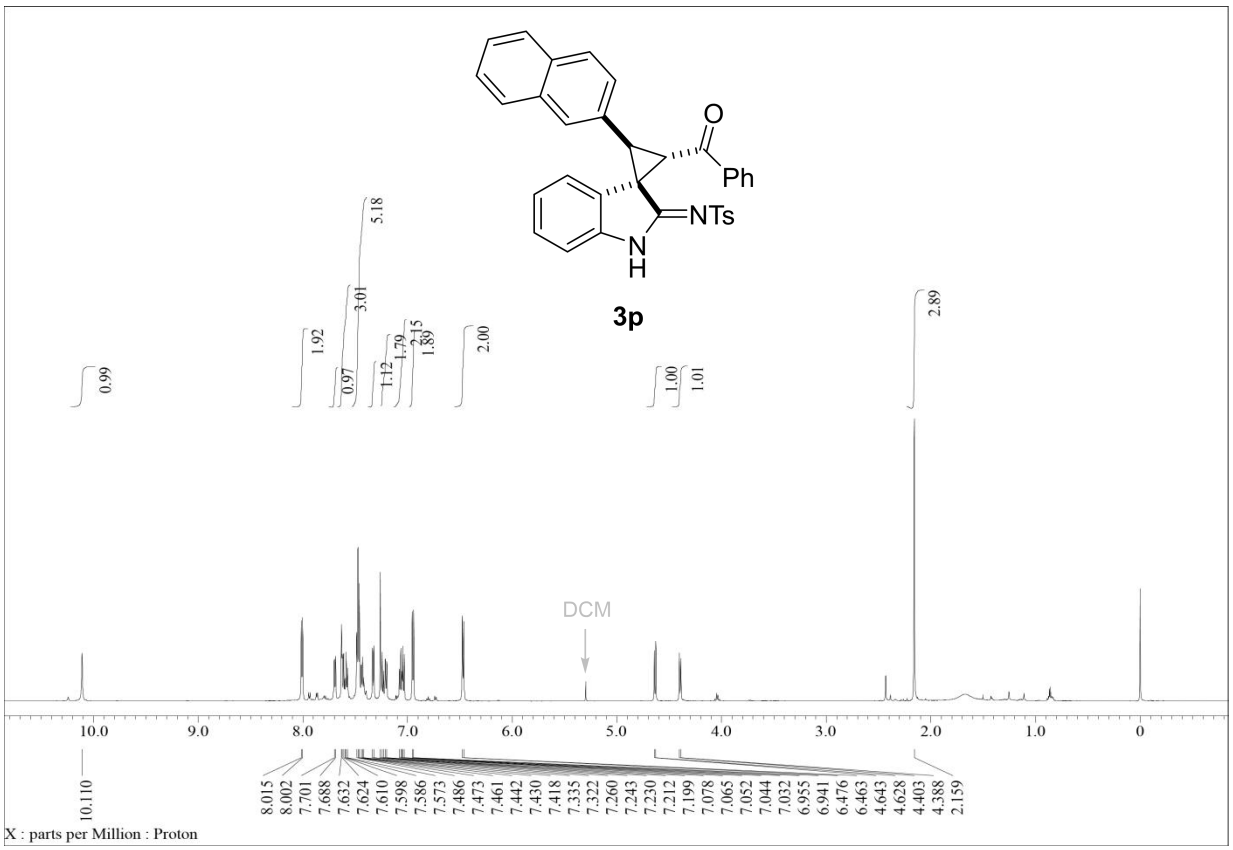
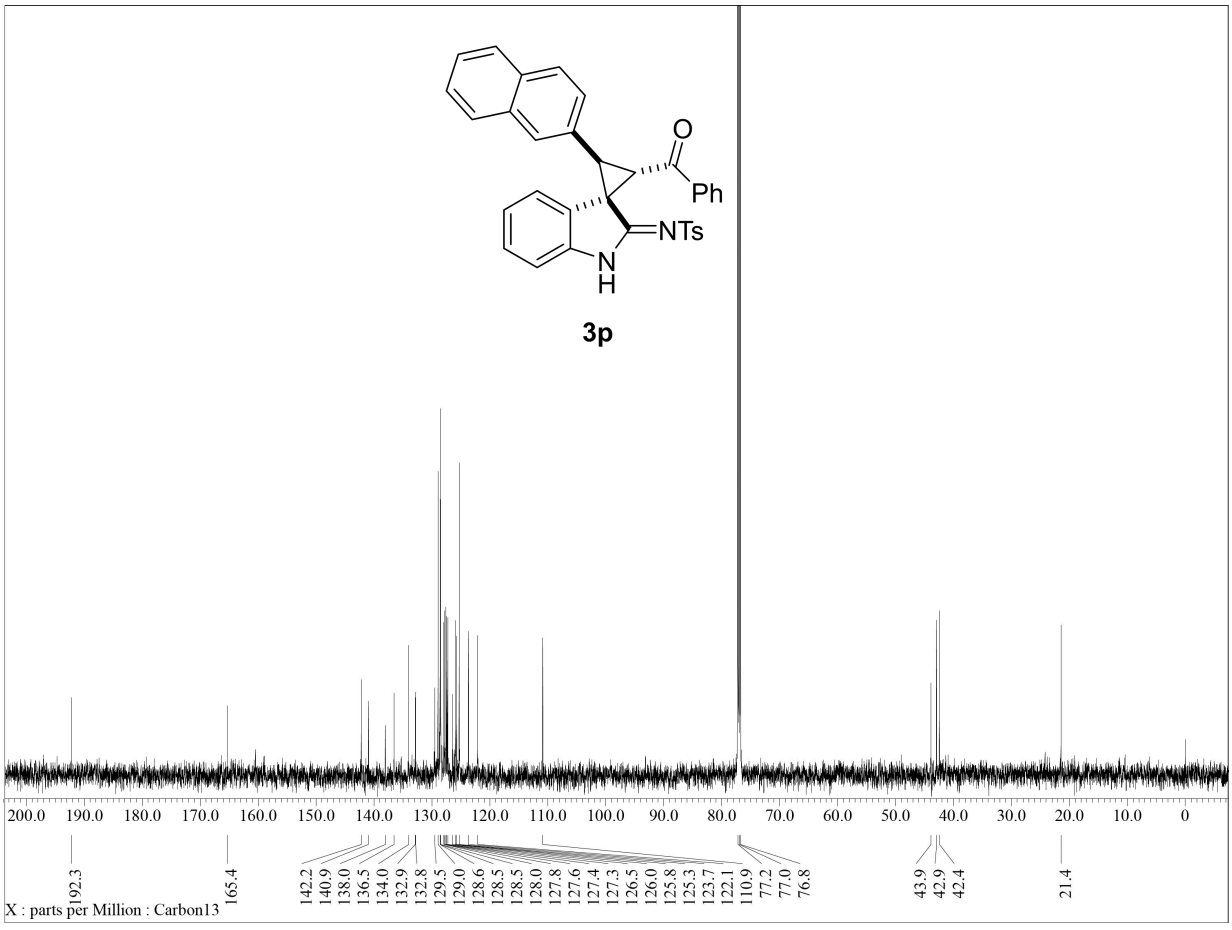
X : parts per Million : Proton

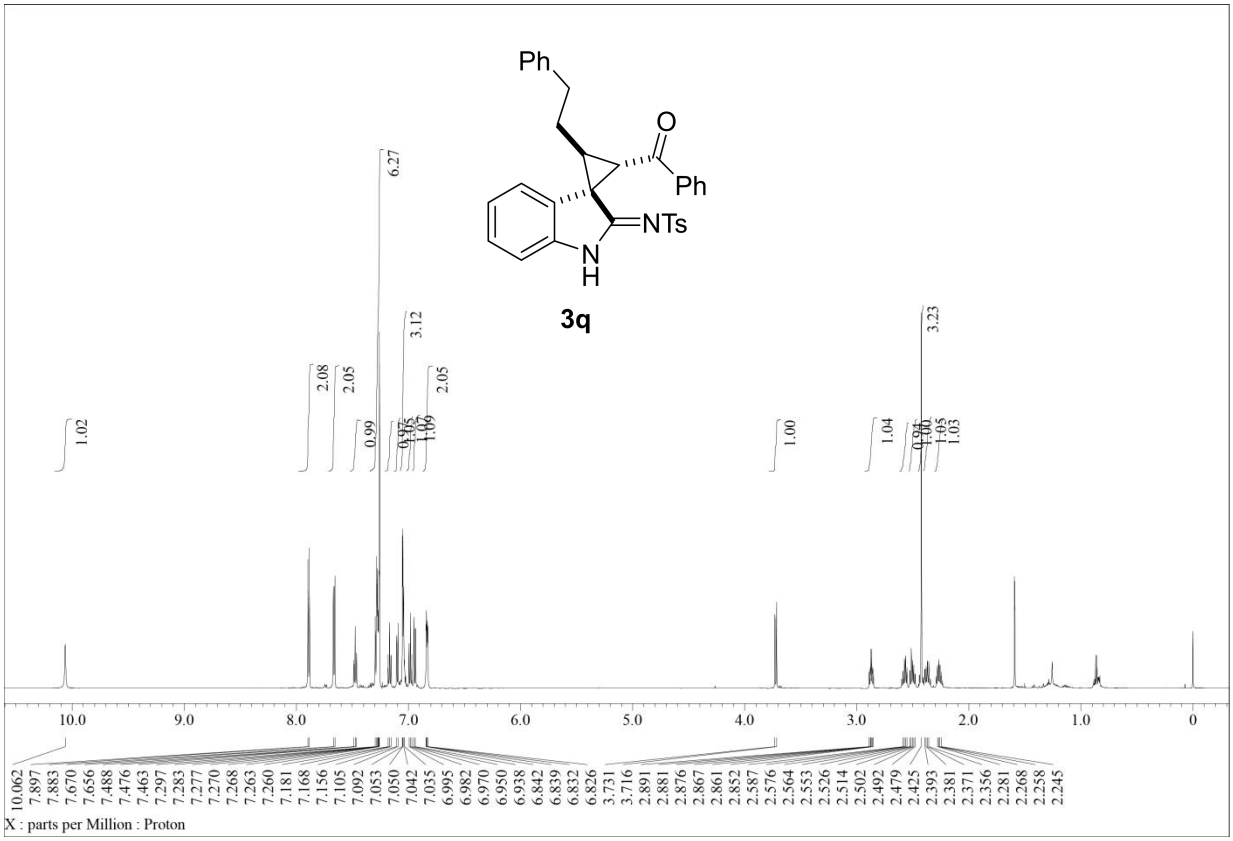

O
O
Ph
NTs
N
H
3n
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.4
164.9
146.1
142.9
141.9
140.9
138.7
136.3
134.0
129.2
128.9
128.5
128.1
126.4
125.6
123.7
122.0
111.0
110.3
110.3
77.2
77.0
76.8
42.9
42.1
34.4
21.5
X : parts per Million : Carbon13


S
O
Ph
NTs
N
H
3o
DCM
X : parts per Million : Proton


S
O
Ph
NTs
N
H
3o
DCM
X : parts per Million : Carbon13


O
Ph
NTs
N
H
3p
5.18
3.01
1.92
0.97
1.12
1.79
2.15
1.89
2.00
0.99
1.00
1.01
2.89
DCM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.110
8.015
8.002
7.701
7.688
7.632
7.624
7.610
7.598
7.586
7.573
7.486
7.473
7.461
7.442
7.430
7.418
7.335
7.322
7.260
7.243
7.230
7.212
7.199
7.078
7.065
7.052
7.044
7.032
6.955
6.941
6.476
6.463
4.643
4.628
4.403
4.388
2.159
X : parts per Million : Proton


O
Ph
NTs
N
H
3p
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.3
165.4
142.2
140.9
138.0
136.5
134.0
132.9
132.8
129.5
129.0
128.6
128.5
128.5
128.0
127.8
127.6
127.4
127.3
126.5
126.0
125.8
125.3
123.7
122.1
110.9
77.2
77.0
76.8
43.9
42.9
42.4
21.4
X : parts per Million : Carbon13


Ph
O
Ph
NTs
N
H
3q
6.27
3.12
2.08
2.05
2.05
3.23
1.02
0.99
1.00
1.04
1.05
1.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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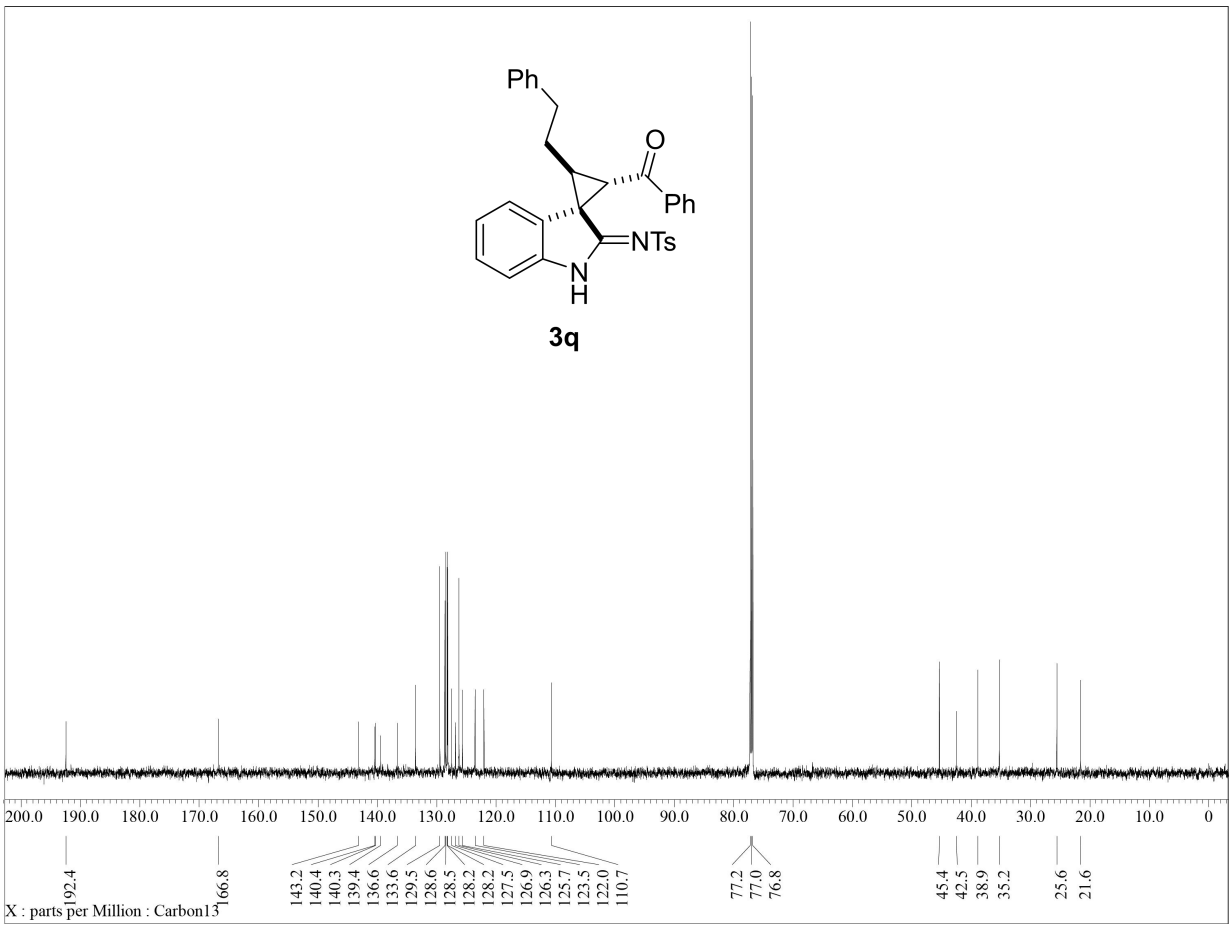
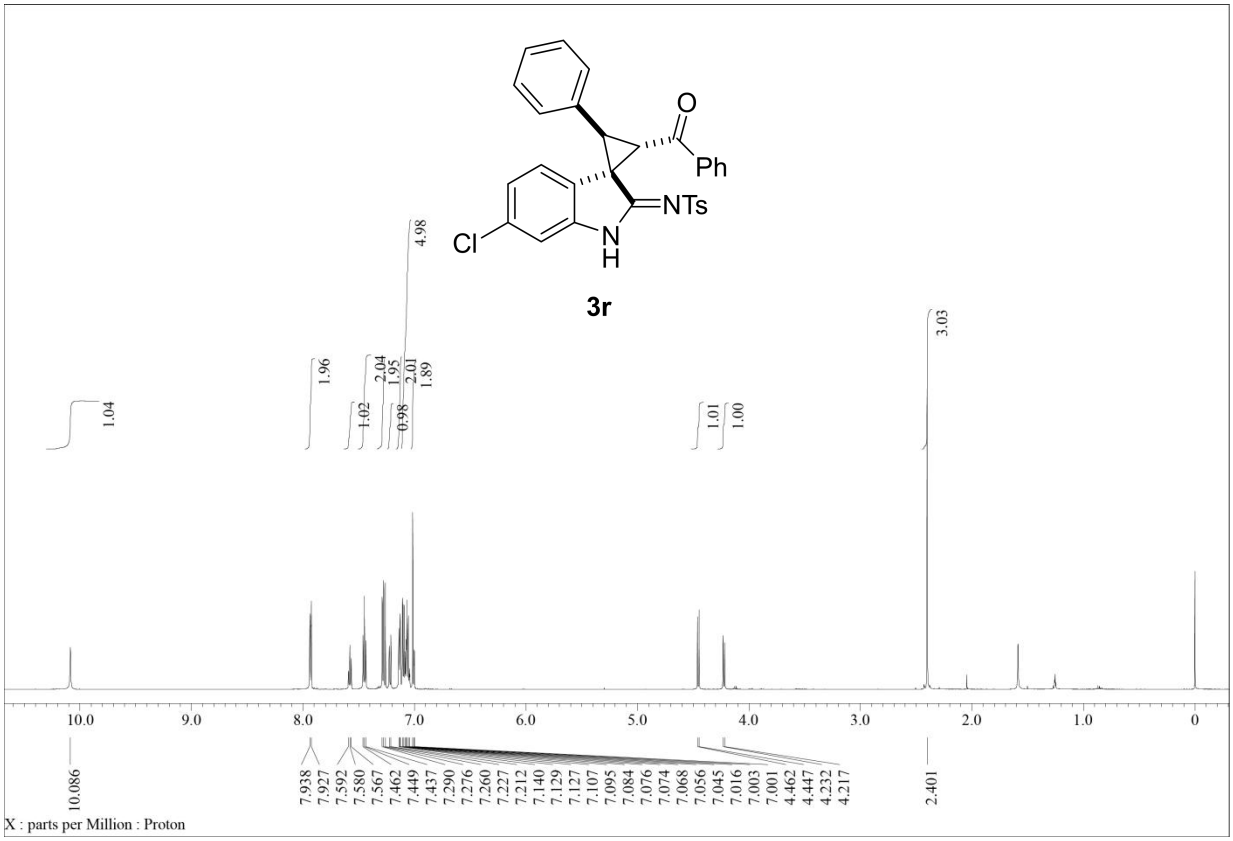
7.883
7.670
7.656
7.488
7.476
7.463
7.297
7.283
7.277
7.270
7.268
7.263
7.260
7.181
7.168
7.156
7.105
7.092
7.053
7.050
7.042
7.035
6.995
6.982
6.970
6.950
6.938
6.842
6.839
6.832
6.826
3.731
3.716
2.891
2.881
2.876
2.867
2.861
2.852
2.587
2.576
2.564
2.553
2.526
2.514
2.502
2.492
2.479
2.425
2.393
2.381
2.371
2.356
2.281
2.268
2.258
2.245
X : parts per Million : Proton


Ph
O
Ph
NTs
N
H
3q
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.4
166.8
143.2
140.4
140.3
139.4
136.6
133.6
129.5
128.6
128.5
128.2
128.2
127.5
126.9
126.3
125.7
123.5
122.0
110.7
77.2
77.0
76.8
45.4
42.5
38.9
35.2
25.6
21.6
X : parts per Million : Carbon13


O
Ph
NTs
Cl
N
H
3r
4.98
1.96
2.04
1.95
2.01
1.89
1.04
1.02
0.98
1.01
1.00
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.086
7.938
7.927
7.592
7.580
7.567
7.462
7.449
7.437
7.290
7.276
7.260
7.227
7.212
7.140
7.129
7.127
7.107
7.095
7.084
7.076
7.074
7.068
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7.016
7.003
7.001
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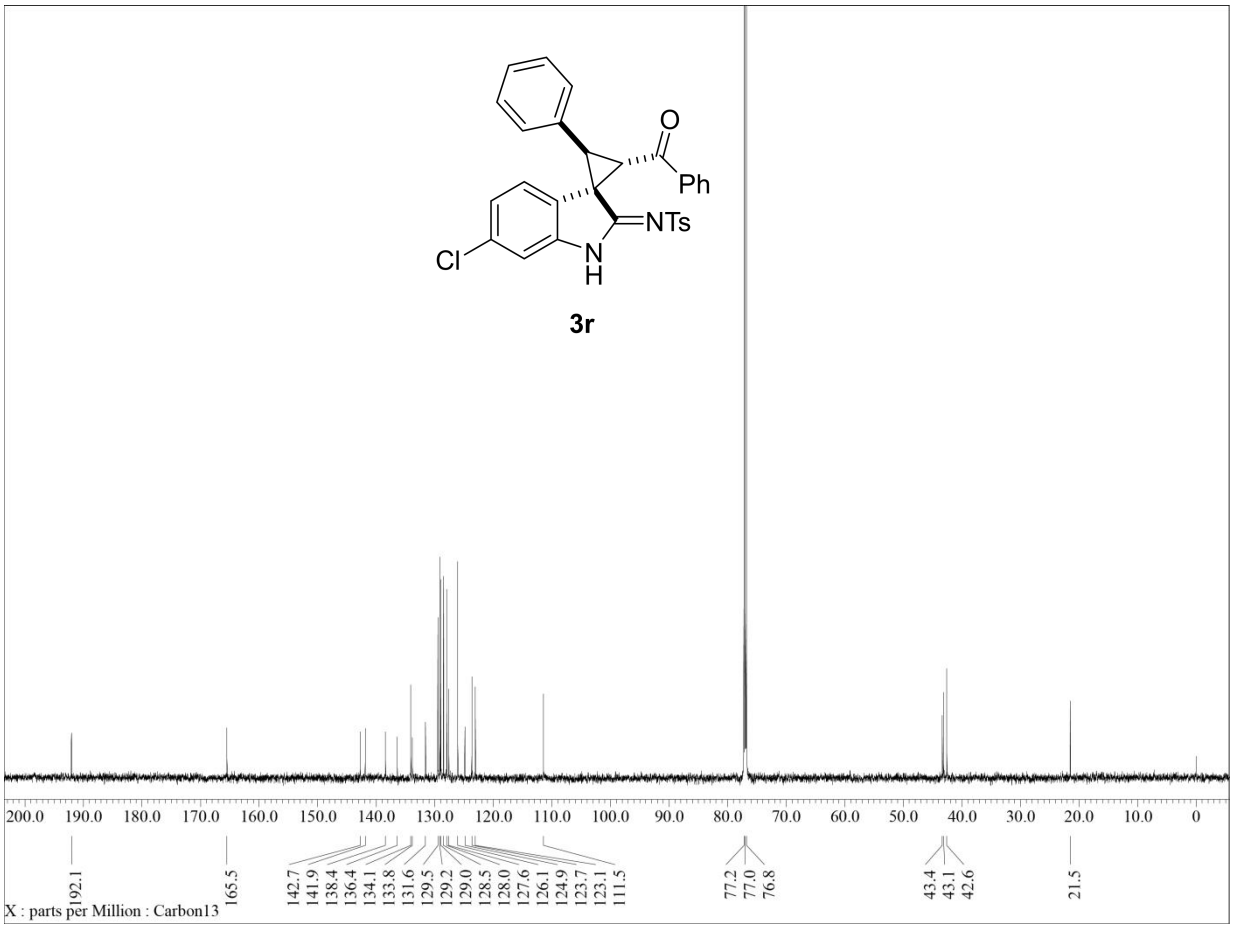
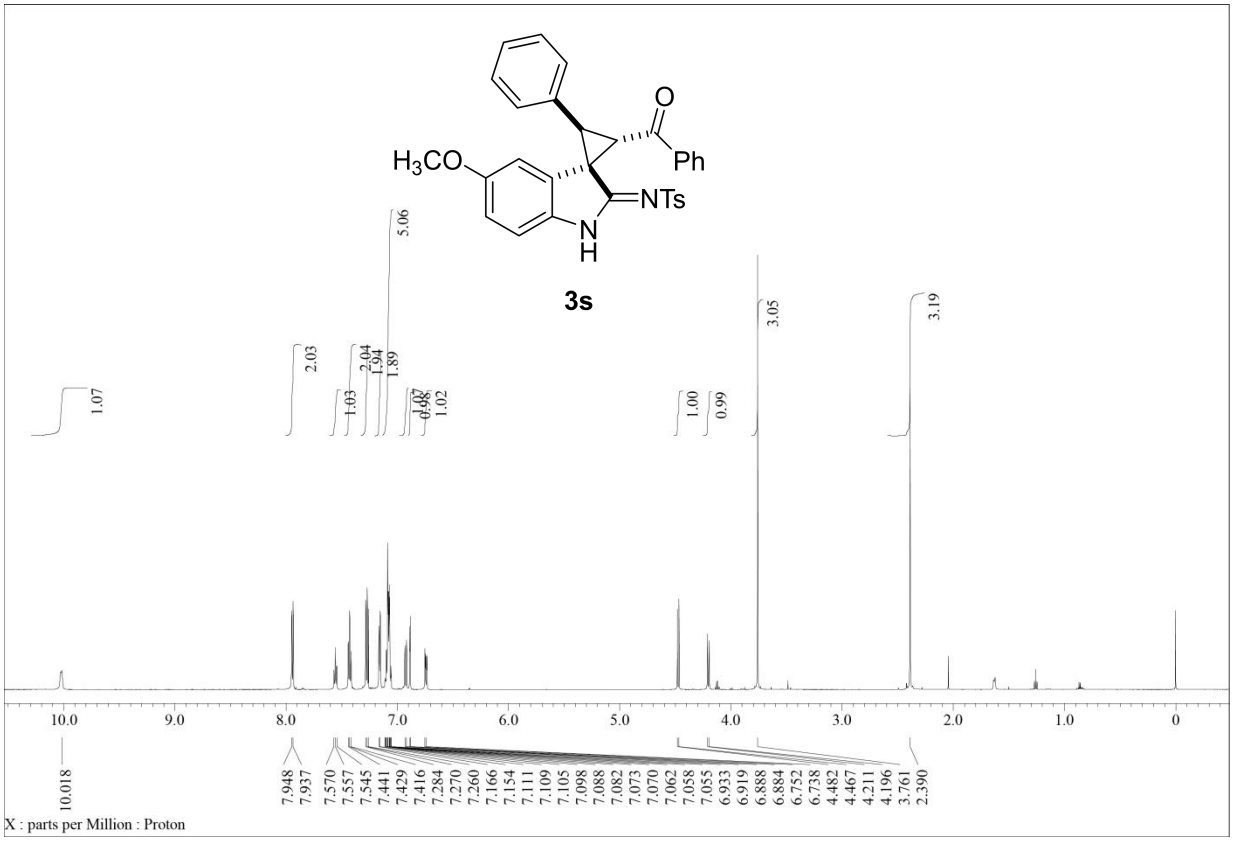
4.447
4.232
4.217
2.401
X : parts per Million : Proton


O
Ph
NTs
Cl
N
H
3r
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.1
165.5
142.7
141.9
138.4
136.4
134.1
133.8
131.6
129.5
129.2
129.0
128.5
128.0
127.6
126.1
124.9
123.7
123.1
111.5
77.2
77.0
76.8
43.4
43.1
42.6
21.5
X : parts per Million : Carbon13


O
Ph
H3CO
NTs
N
H
3s
5.06
3.05
3.19
2.03
2.04
1.94
1.89
1.07
1.03
1.02
1.00
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.018
7.948
7.937
7.570
7.557
7.545
7.441
7.429
7.416
7.284
7.270
7.260
7.166
7.154
7.111
7.109
7.105
7.098
7.088
7.082
7.073
7.070
7.062
7.058
7.055
6.933
6.919
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6.884
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4.211
4.196
3.761
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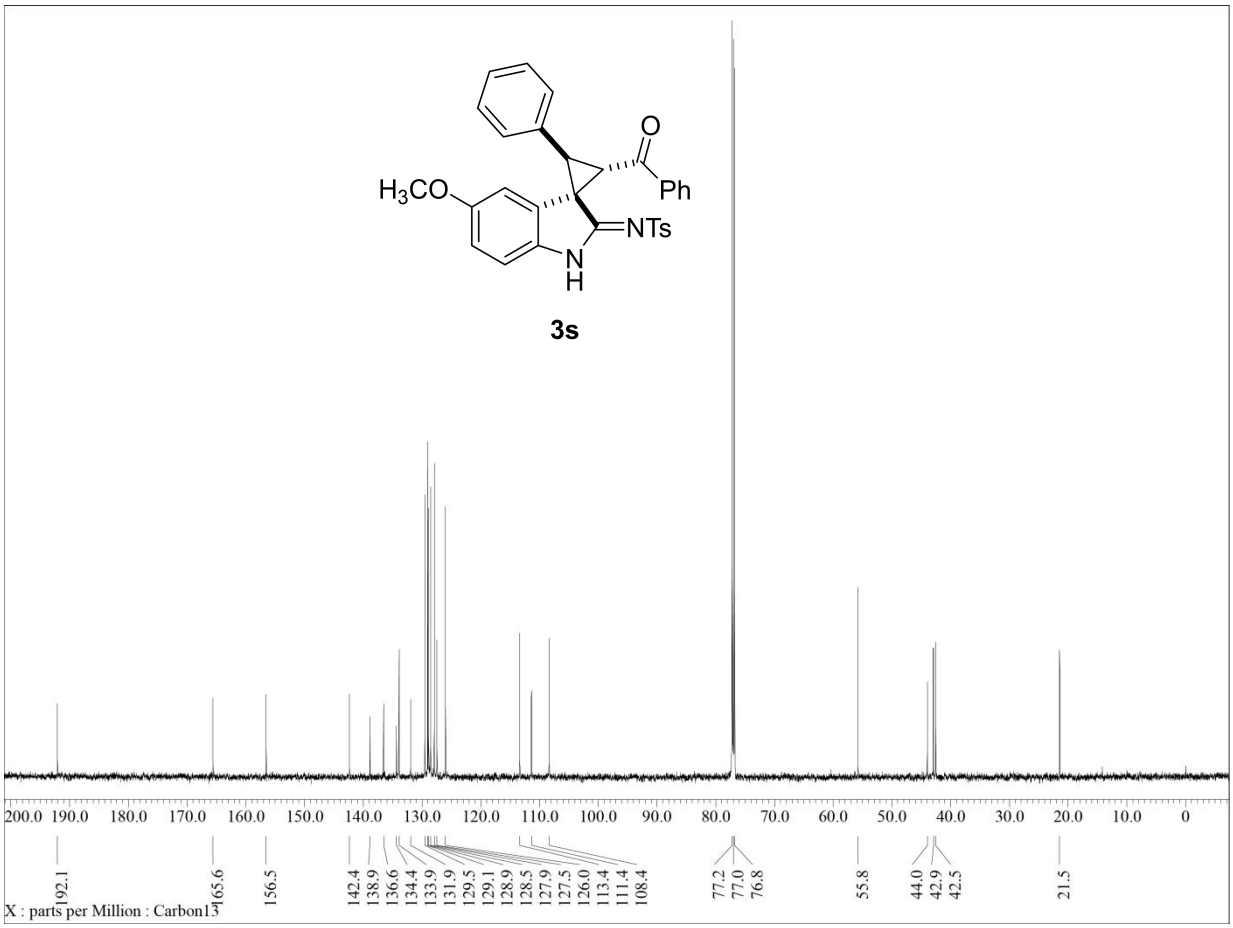
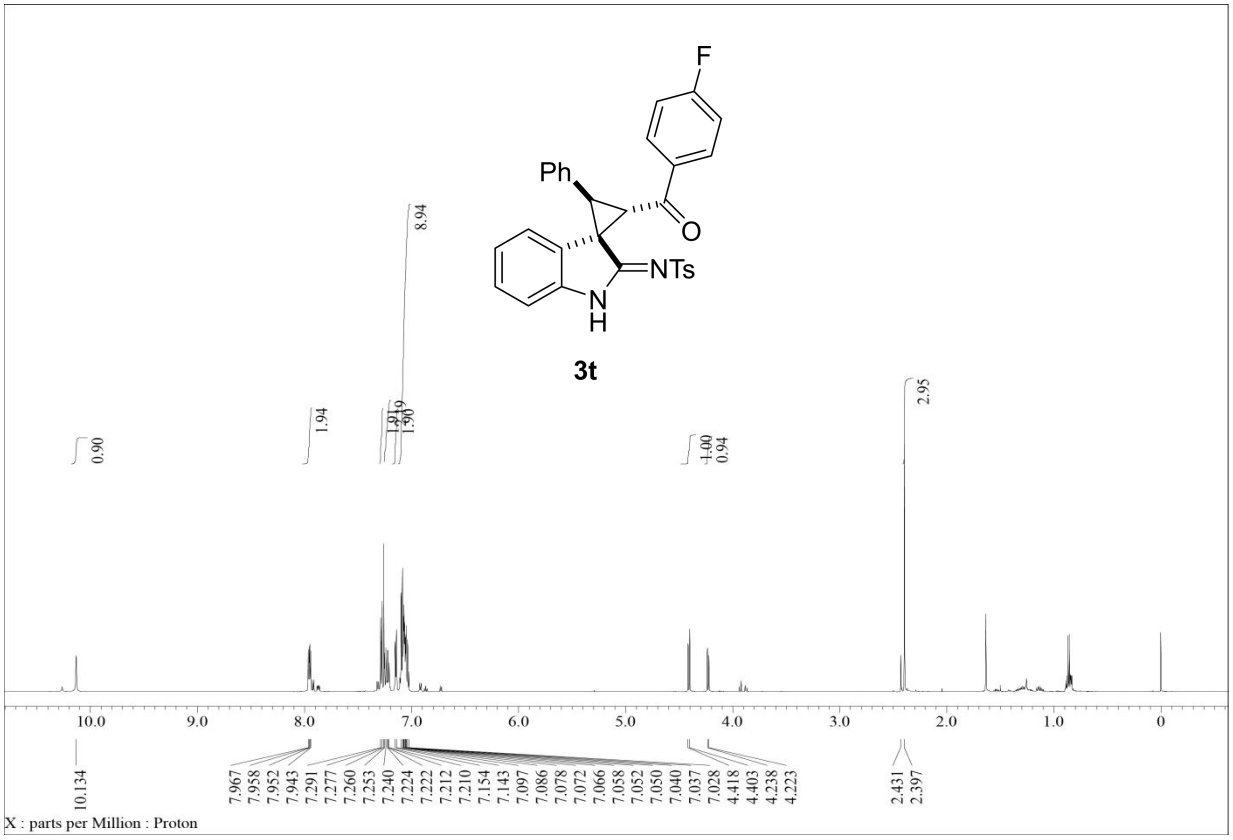
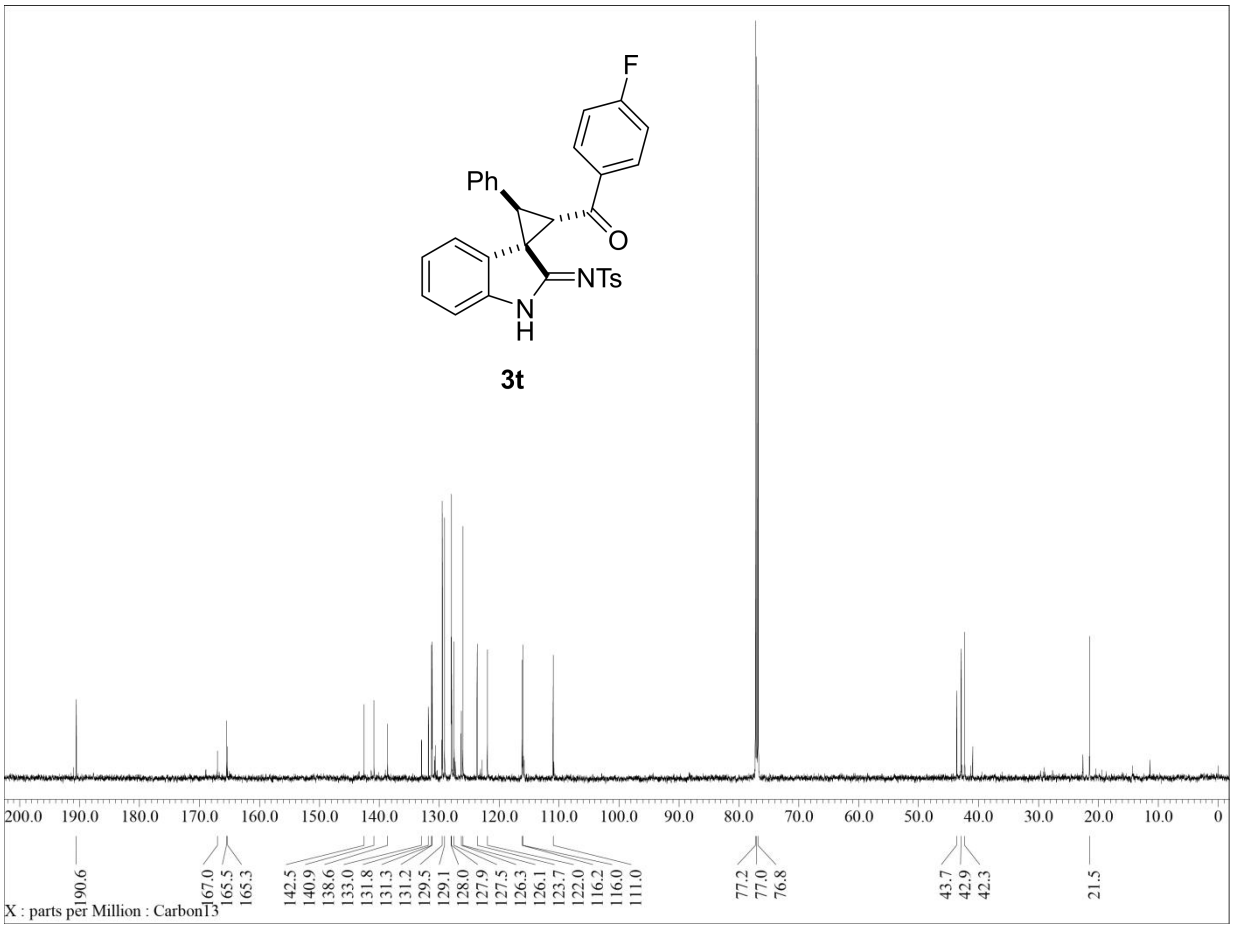

O
Ph
H3CO
NTs
N
H
3s
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
192.1
165.6
156.5
142.4
138.9
136.6
134.4
133.9
131.9
129.5
129.1
128.9
128.5
127.9
127.5
126.0
113.4
111.4
108.4
77.2
77.0
76.8
55.8
44.0
42.9
42.5
21.5
X : parts per Million : Carbon13


F
Ph
O
NTs
N
H
3t
8.94
1.94
1.91
1.90
0.90
1.00
0.94
2.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.134
7.967
7.958
7.952
7.943
7.291
7.277
7.260
7.253
7.240
7.224
7.222
7.212
7.210
7.154
7.143
7.097
7.086
7.078
7.072
7.066
7.058
7.052
7.050
7.040
7.037
7.028
4.418
4.403
4.238
4.223
2.431
2.397
X : parts per Million : Proton


F
Ph
O
NTs
N
H
3t
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
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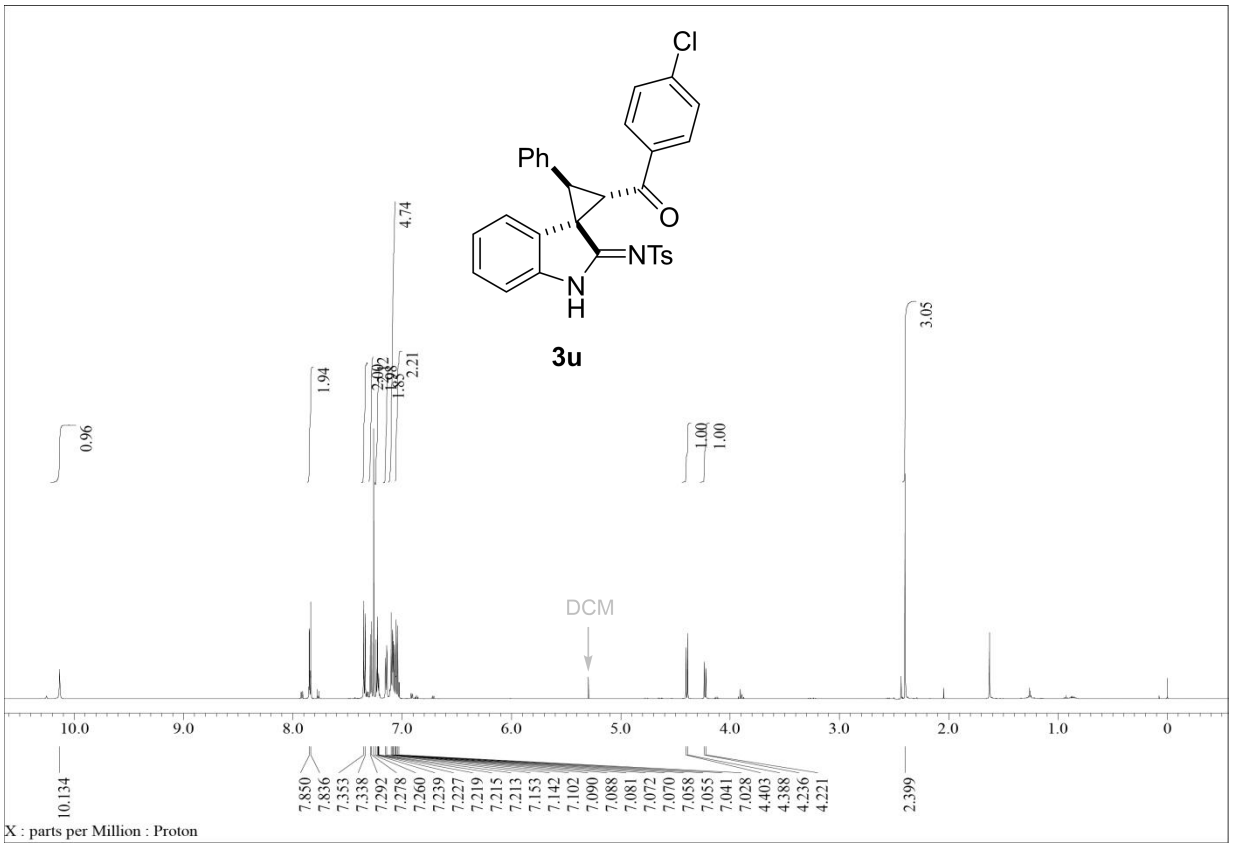
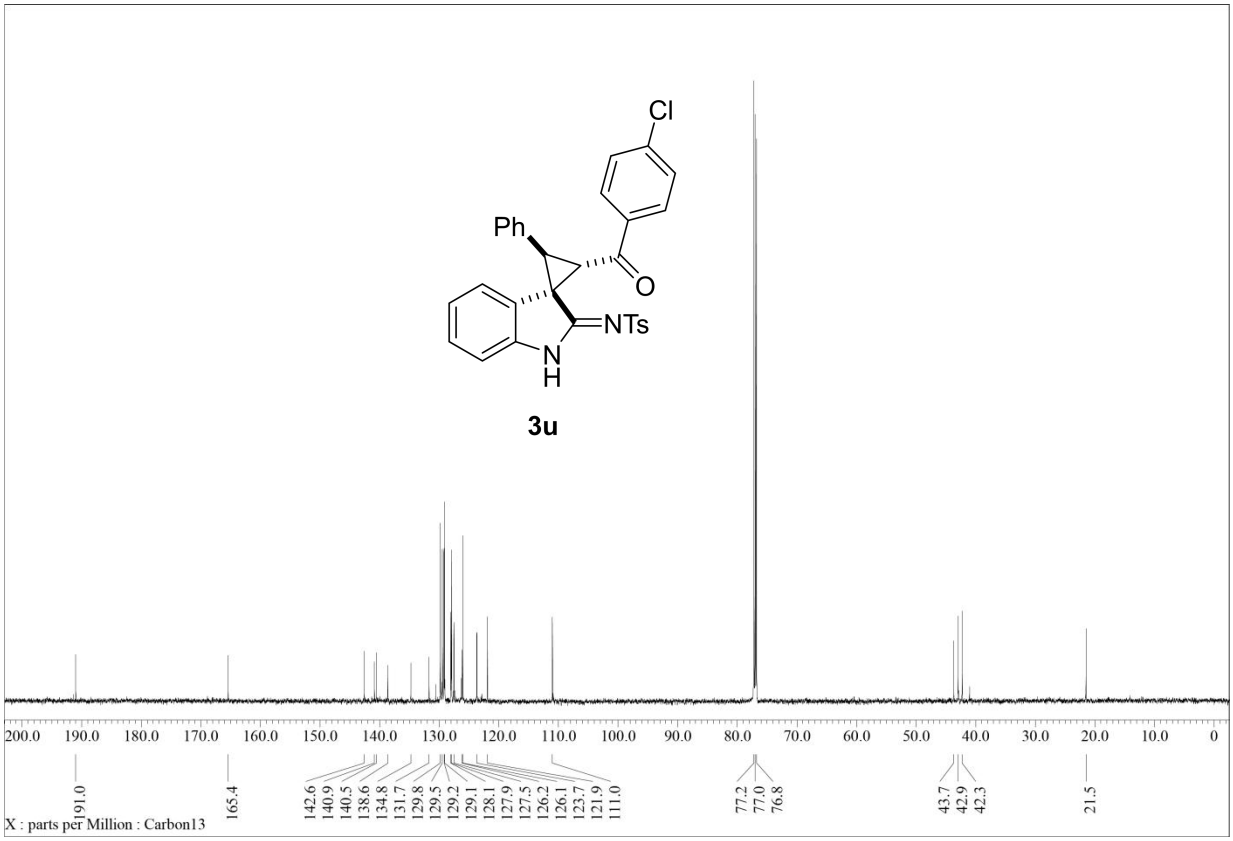
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.6
167.0
165.5
165.3
142.5
140.9
138.6
133.0
131.8
131.3
131.2
129.5
129.1
128.0
127.9
127.5
126.3
126.1
123.7
122.0
116.2
116.0
111.0
77.2
77.0
76.8
43.7
42.9
42.3
21.5
X : parts per Million : Carbon13


Cl
Ph
O
NTs
N
H
3u
4.74
3.05
1.94
2.21
0.96
1.00
1.00
DCM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.134
7.850
7.836
7.353
7.338
7.292
7.278
7.260
7.239
7.227
7.219
7.215
7.213
7.153
7.142
7.102
7.090
7.088
7.081
7.072
7.070
7.058
7.055
7.041
7.028
4.403
4.388
4.236
4.221
2.399
X : parts per Million : Proton


Cl
Ph
O
NTs
N
H
3u
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
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60.0
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40.0
30.0
20.0
10.0
0
191.0
165.4
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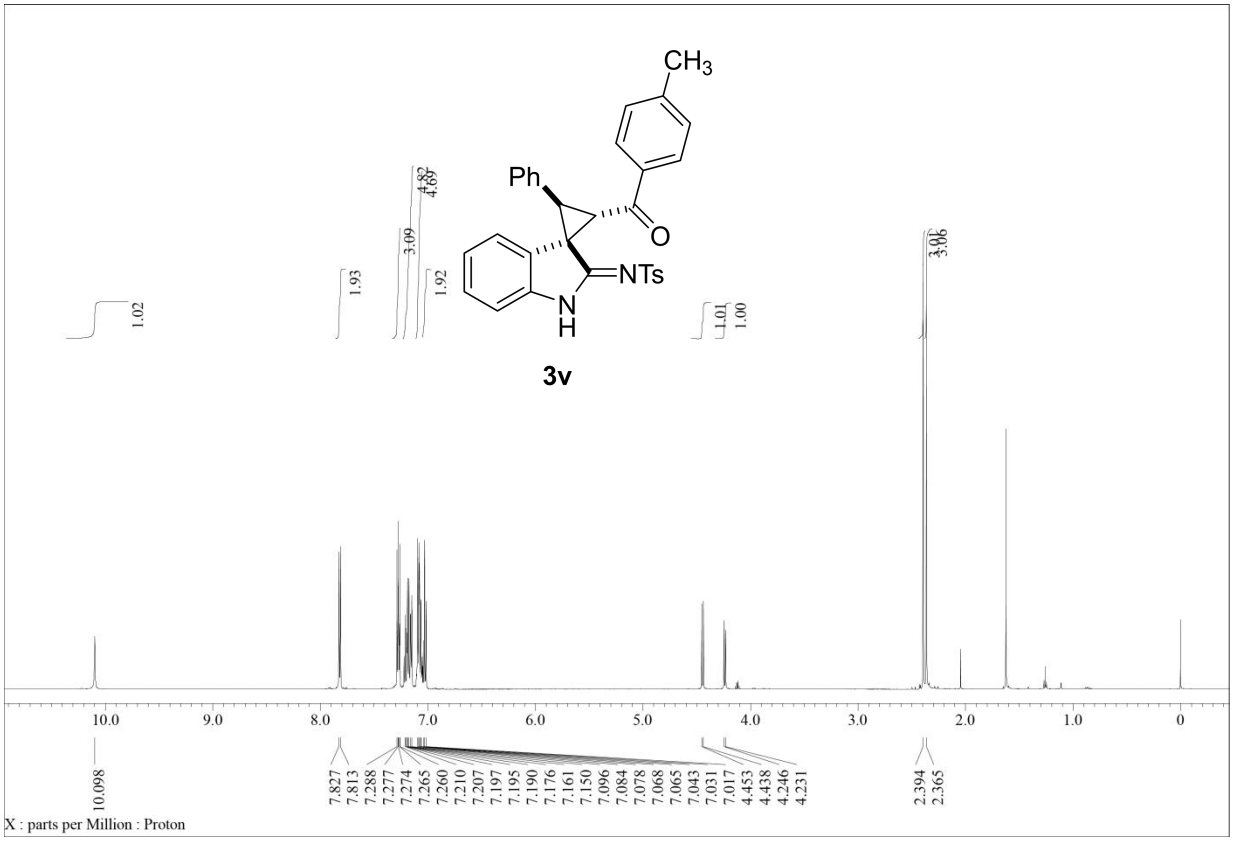
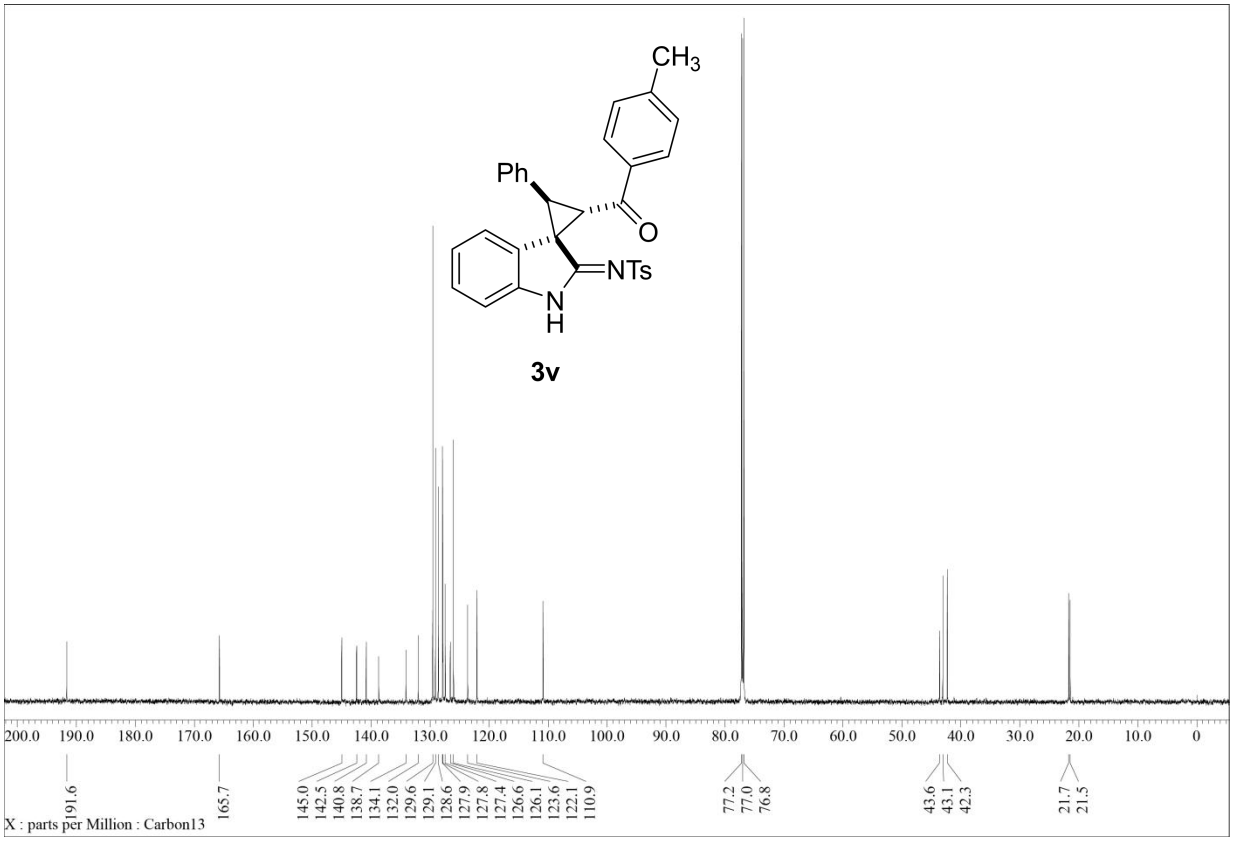
140.9
140.5
138.6
134.8
131.7
129.8
129.5
129.2
129.1
128.1
127.9
127.5
126.2
126.1
123.7
121.9
111.0
77.2
77.0
76.8
43.7
42.9
42.3
21.5
X : parts per Million : Carbon13


CH3
Ph
O
NTs
N
H
3v
1.02
1.93
3.09
4.82
4.69
1.92
1.01
1.00
3.01
3.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.098
7.827
7.813
7.288
7.277
7.274
7.265
7.260
7.210
7.207
7.197
7.195
7.190
7.176
7.161
7.150
7.096
7.084
7.078
7.068
7.065
7.043
7.031
7.017
4.453
4.438
4.246
4.231
2.394
2.365
X : parts per Million : Proton


CH3
Ph
O
NTs
N
H
3v
200.0
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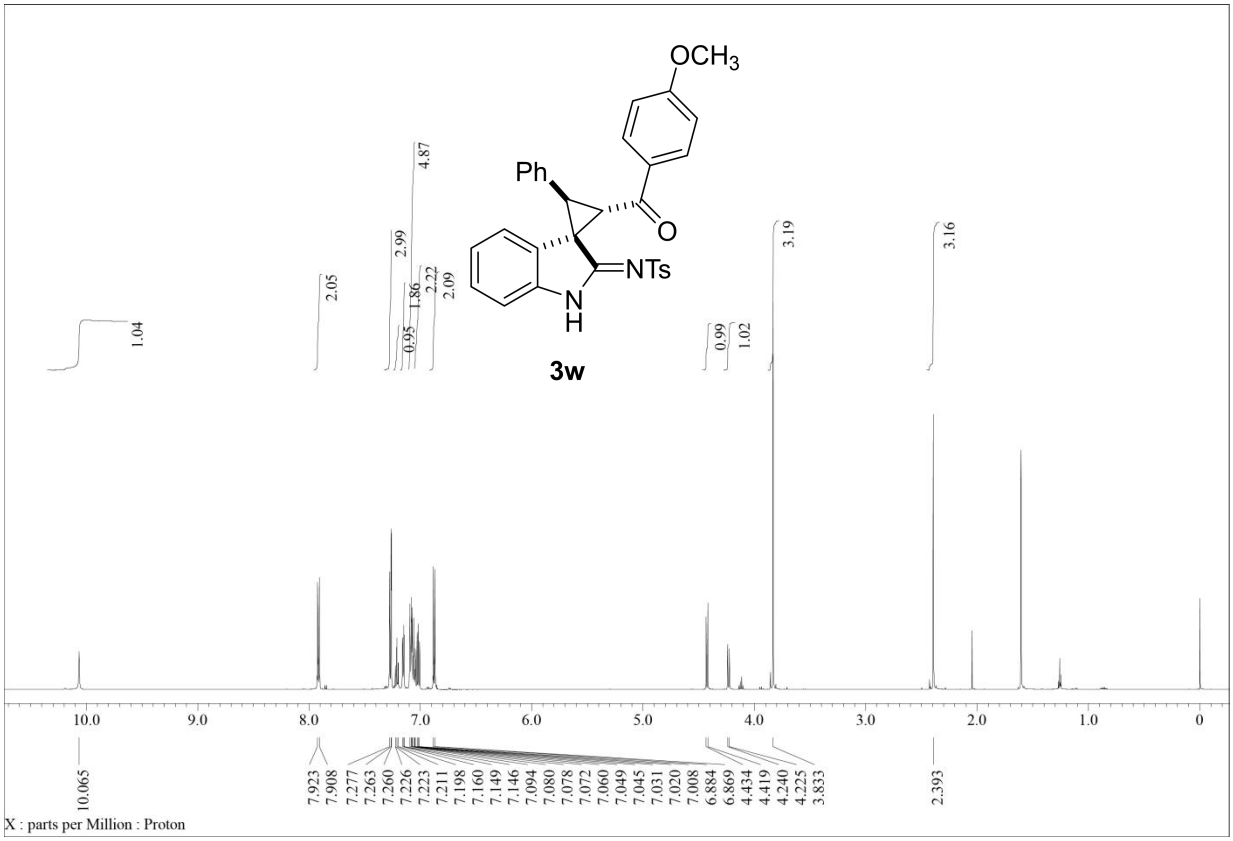
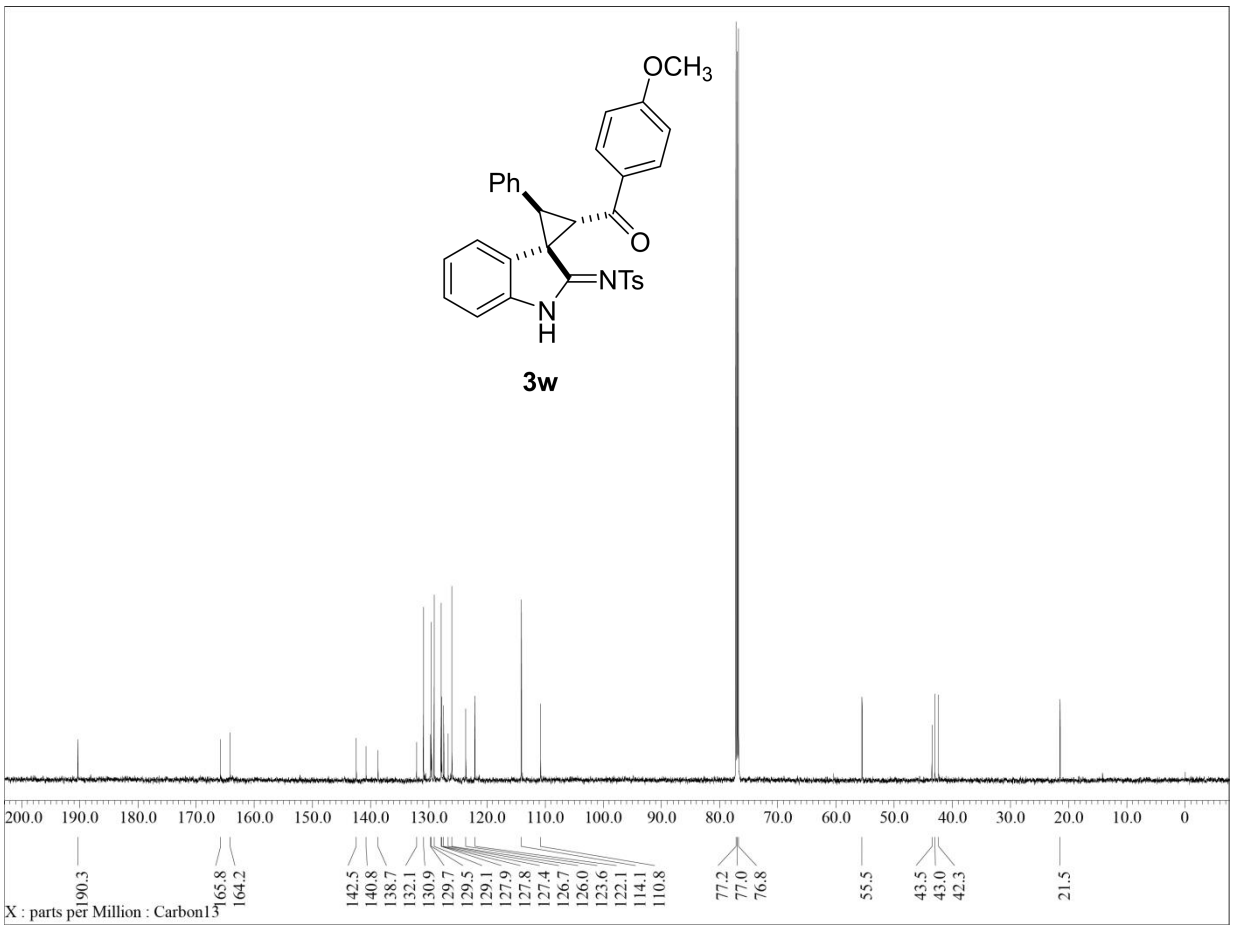
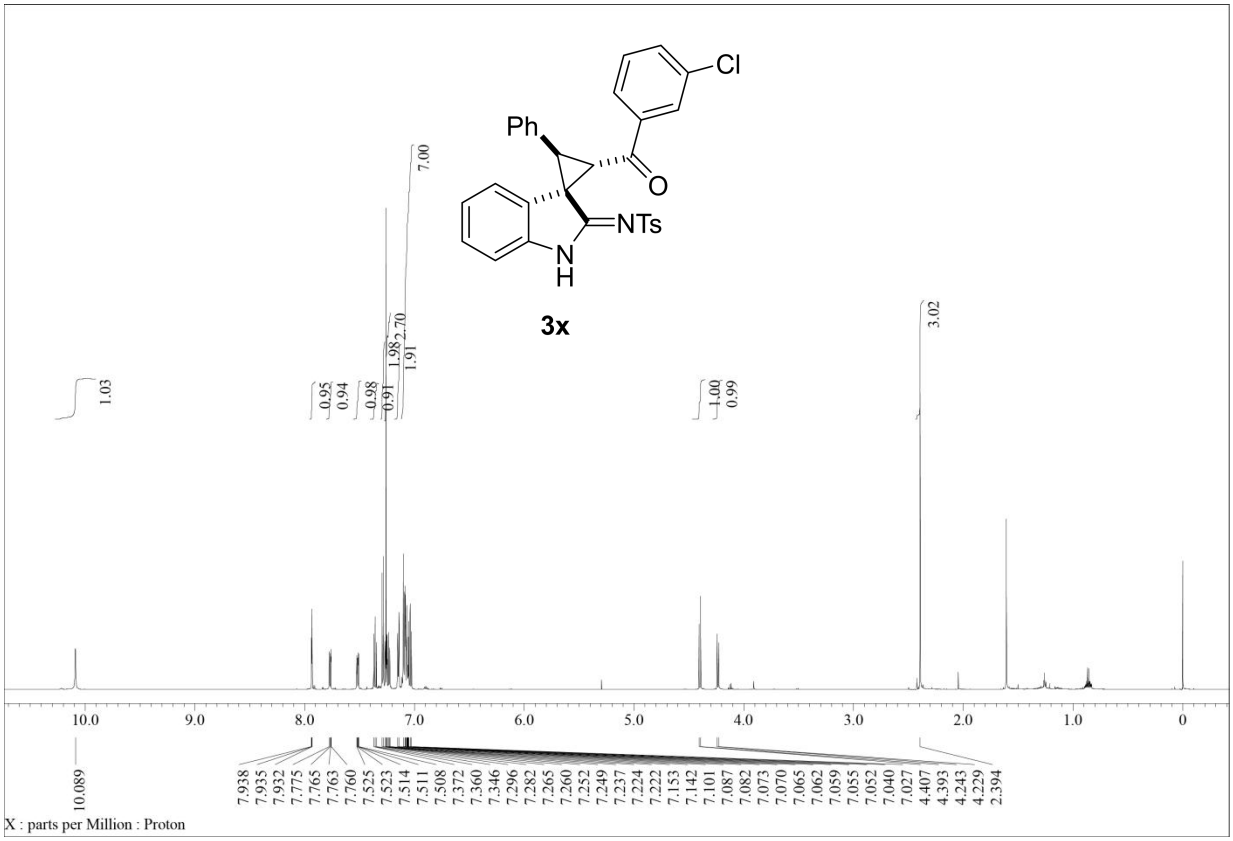
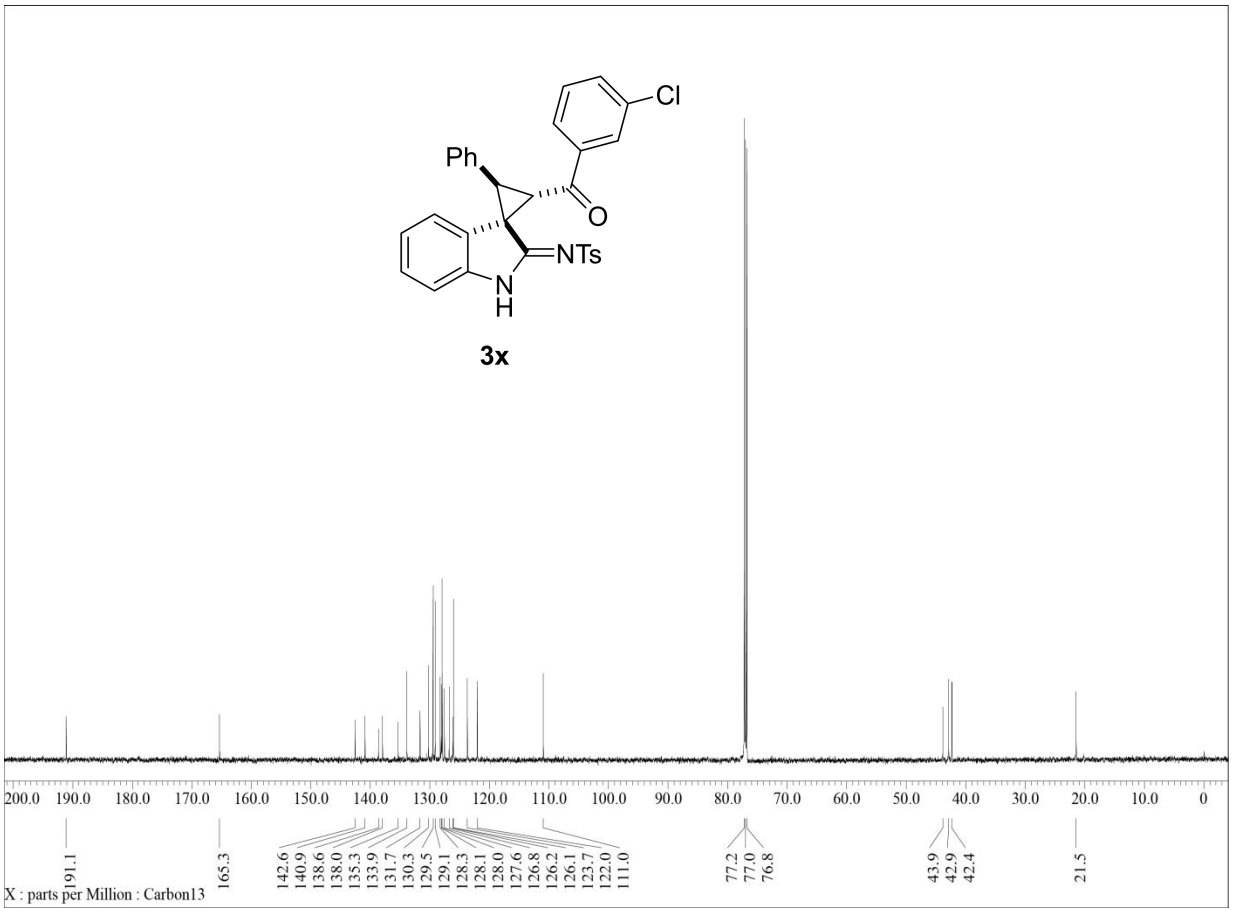
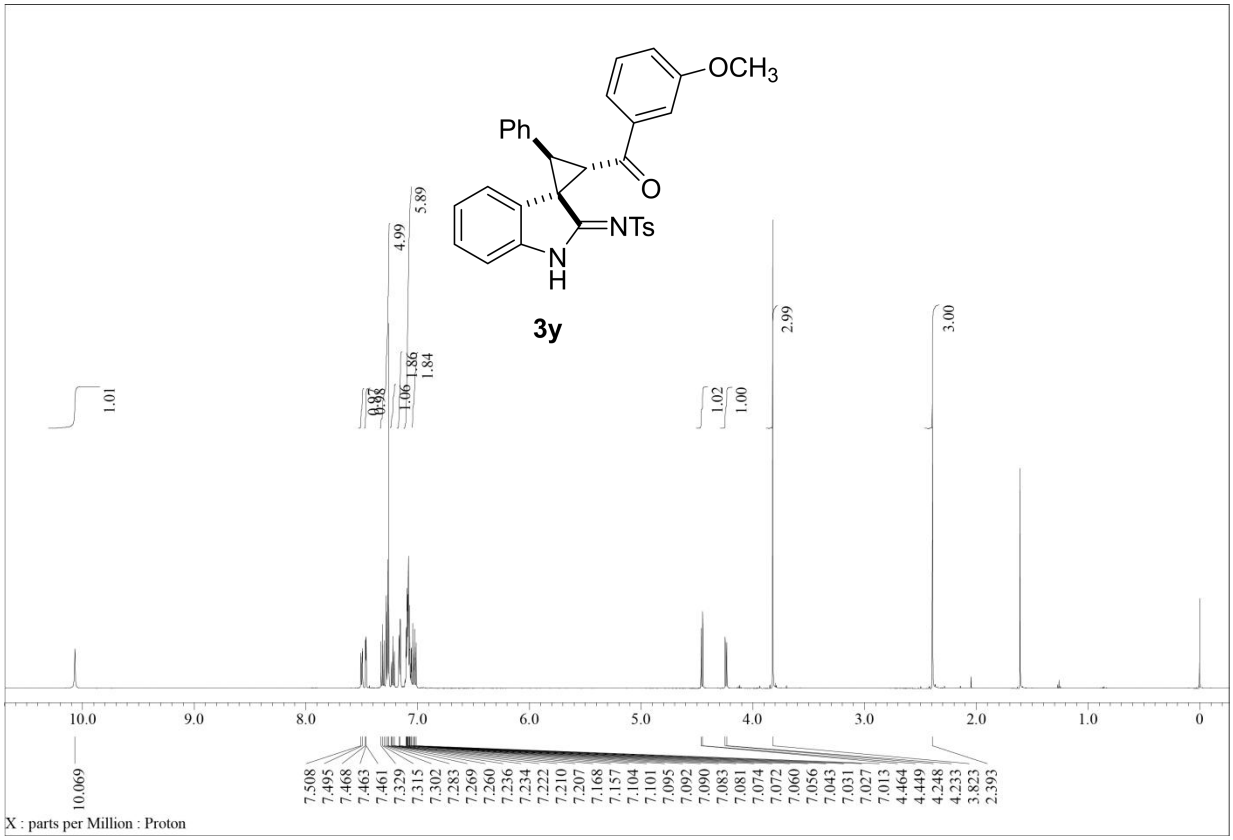
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.6
165.7
145.0
142.5
140.8
138.7
134.1
132.0
129.6
129.1
128.6
127.9
127.8
127.4
126.6
126.1
123.6
122.1
110.9
77.2
77.0
76.8
43.6
43.1
42.3
21.7
21.5
X : parts per Million : Carbon13

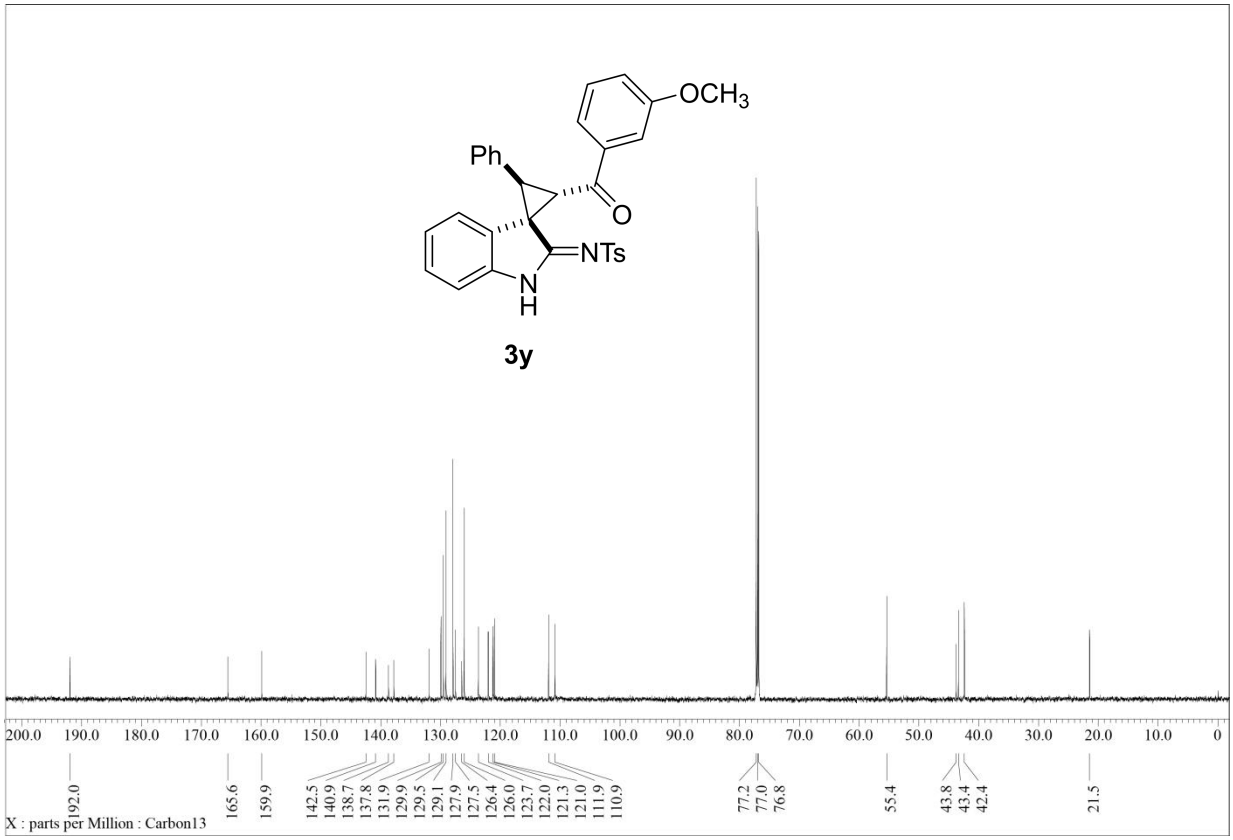

OCH3
Ph
O
NTs
N
H
3w
4.87
2.99
2.05
1.86
2.22
2.09
1.04
0.95
0.99
1.02
3.19
3.16
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.065
7.923
7.908
7.277
7.263
7.260
7.226
7.223
7.211
7.198
7.160
7.149
7.146
7.094
7.080
7.078
7.072
7.060
7.049
7.045
7.031
7.020
7.008
6.884
6.869
4.434
4.419
4.240
4.225
3.833
2.393
X : parts per Million : Proton

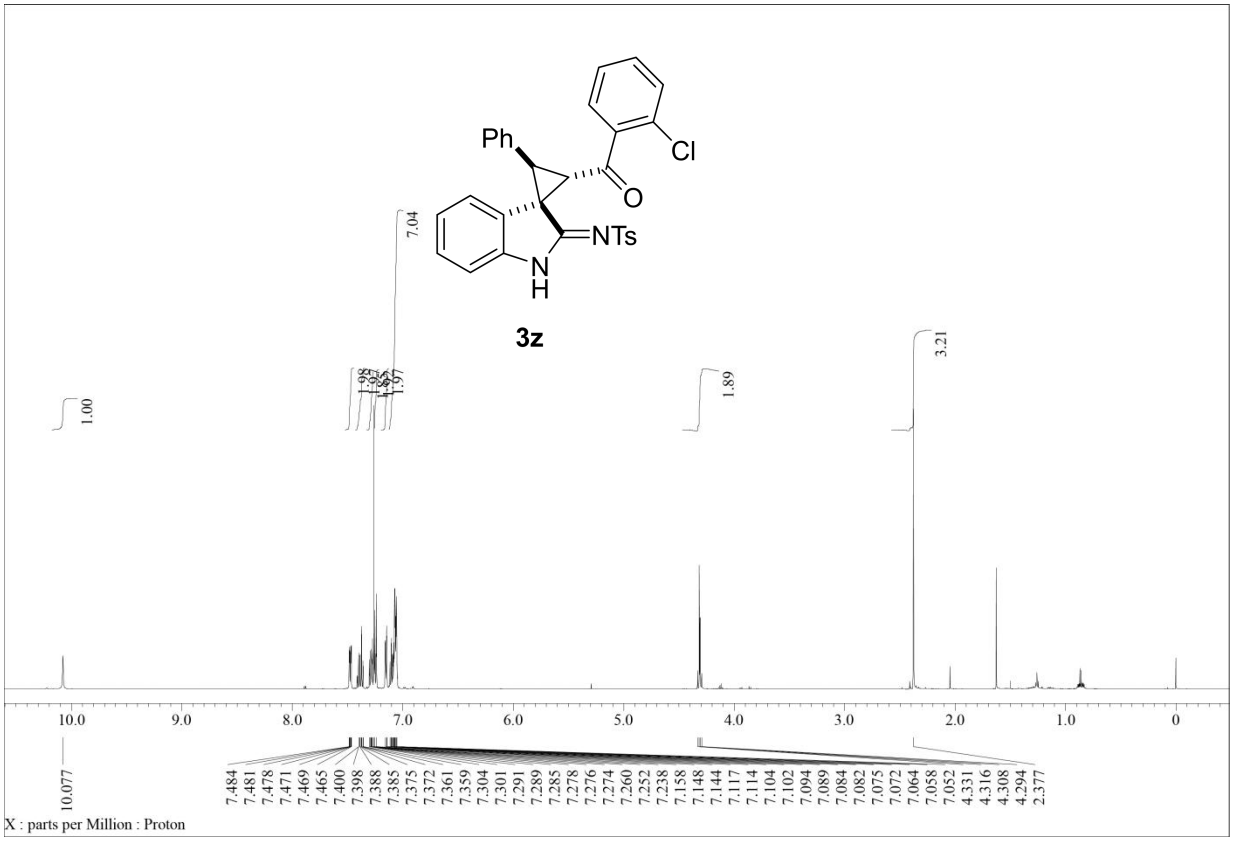

OCH3
Ph
O
NTs
N
H
3w
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
190.3
165.8
164.2
142.5
140.8
138.7
132.1
130.9
129.7
129.5
129.1
127.9
127.8
127.4
126.7
126.0
123.6
122.1
114.1
110.8
77.2
77.0
76.8
55.5
43.5
43.0
42.3
21.5
X : parts per Million : Carbon13

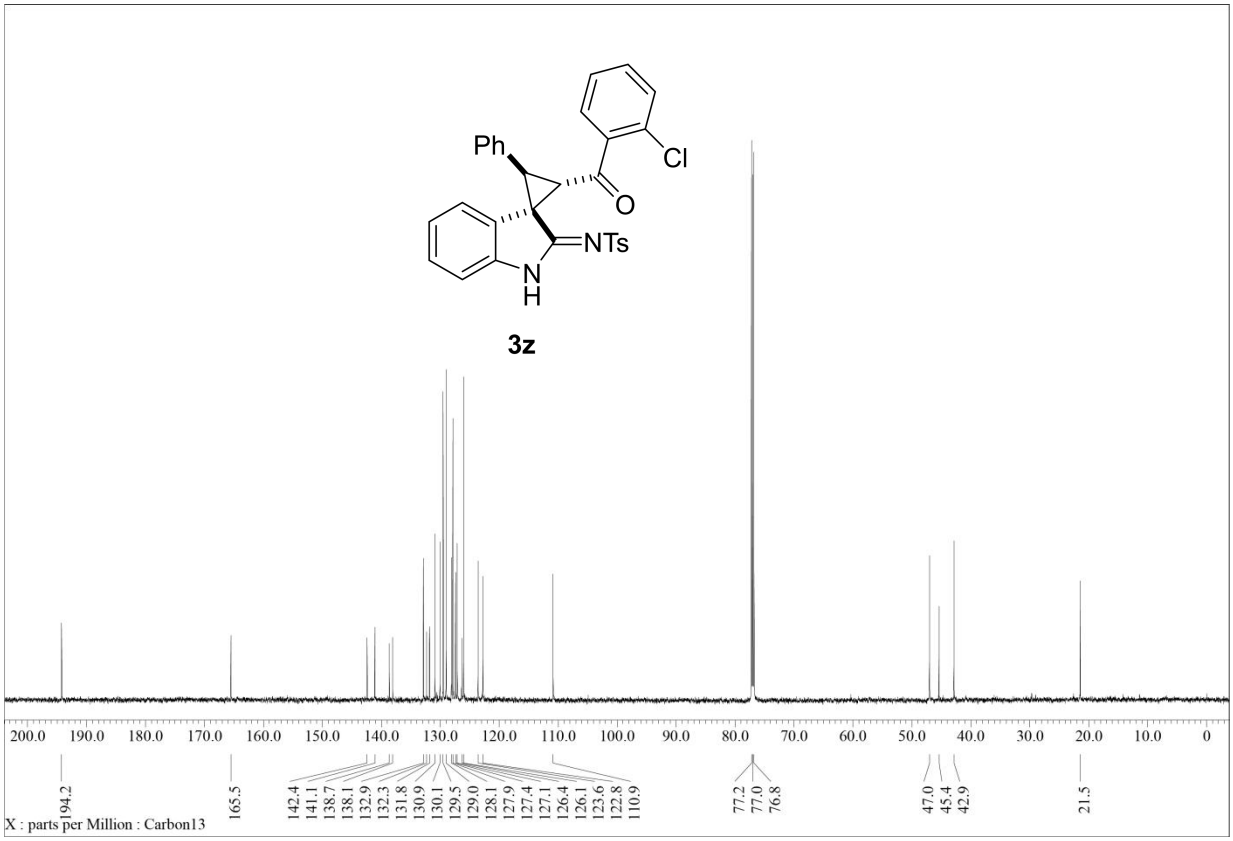

Cl
Ph
O
NTs
N
H
3x
7.00
2.70
1.98
1.91
1.03
0.95
0.94
0.98
0.91
1.00
0.99
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.089
7.938
7.935
7.932
7.775
7.765
7.763
7.760
7.525
7.523
7.514
7.511
7.508
7.372
7.360
7.346
7.296
7.282
7.265
7.260
7.252
7.249
7.237
7.224
7.222
7.153
7.142
7.101
7.087
7.082
7.073
7.070
7.065
7.062
7.059
7.055
7.052
7.040
7.027
4.407
4.393
4.243
4.229
2.394
X : parts per Million : Proton

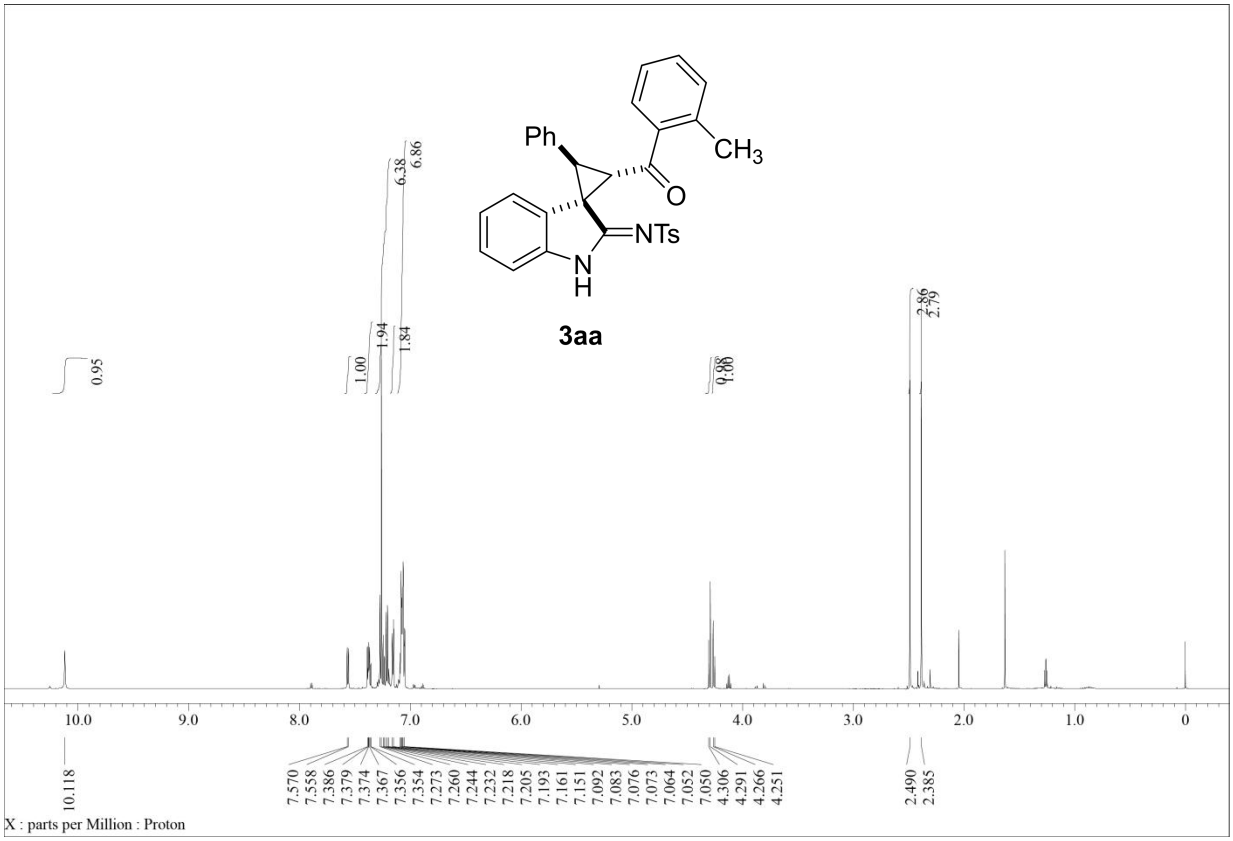

Cl
Ph
O
NTs
N
H
3x
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.1
165.3
142.6
140.9
138.6
138.0
135.3
133.9
131.7
130.3
129.5
129.1
128.3
128.1
128.0
127.6
126.8
126.2
126.1
123.7
122.0
111.0
77.2
77.0
76.8
43.9
42.9
42.4
21.5
X : parts per Million : Carbon13

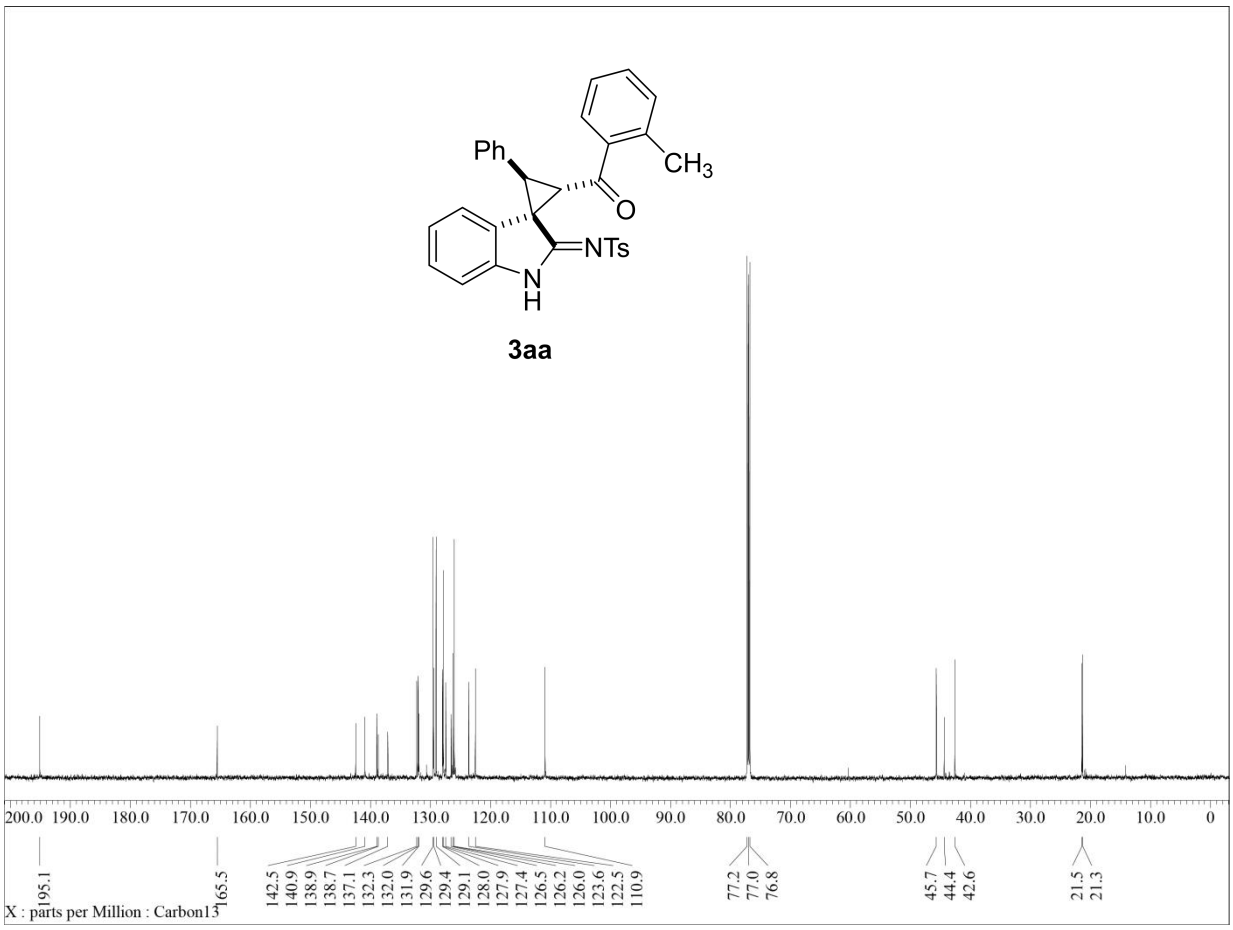

OCH3
Ph
O
NTs
N
H
3y
X : parts per Million : Proton

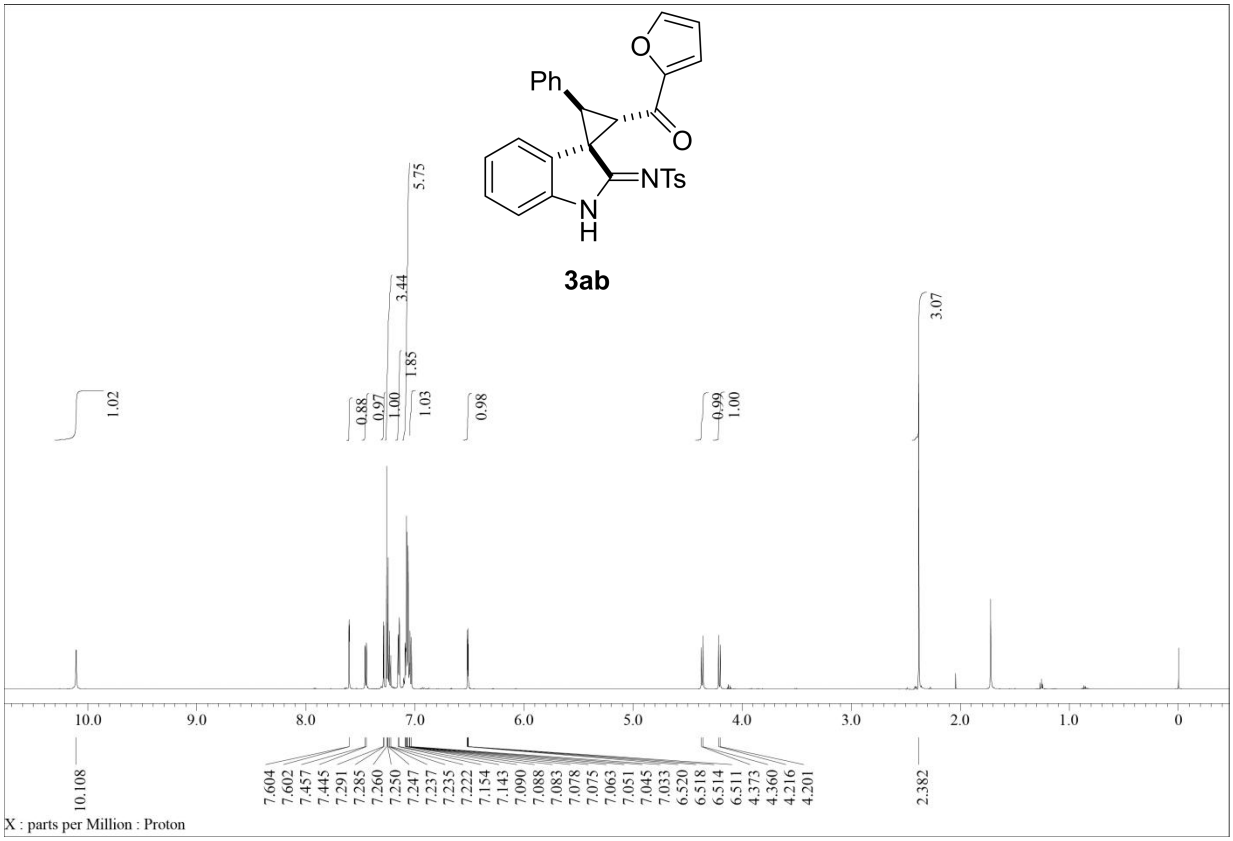

OCH3
Ph
O
NTs
N
H
3y
X : parts per Million : Carbon13


Ph
Cl
O
NTs
N
H
3z
7.04
1.00
1.98
1.92
1.95
1.97
1.89
3.21
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.077
7.484
7.481
7.478
7.471
7.469
7.465
7.400
7.398
7.388
7.385
7.375
7.372
7.361
7.359
7.304
7.301
7.291
7.289
7.285
7.278
7.276
7.274
7.260
7.252
7.238
7.158
7.148
7.144
7.117
7.114
7.104
7.102
7.094
7.089
7.084
7.082
7.075
7.072
7.064
7.058
7.052
4.331
4.316
4.308
4.294
2.377
X : parts per Million : Proton


Ph
Cl
O
NTs
N
H
3z
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
194.2
165.5
142.4
141.1
138.7
138.1
132.9
132.3
131.8
130.9
130.1
129.5
129.0
128.1
127.9
127.4
127.1
126.4
126.1
123.6
122.8
110.9
77.2
77.0
76.8
47.0
45.4
42.9
21.5
X : parts per Million : Carbon13


Ph
CH3
O
NTs
N
H
3aa
X : parts per Million : Proton


Ph
CH3
O
NTs
N
H
3aa
X : parts per Million : Carbon13


Ph
O
O
NTs
N
H
3ab
1.02
0.88
0.97
1.00
3.44
5.75
1.85
1.03
0.98
0.99
1.00
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.108
7.604
7.602
7.457
7.445
7.291
7.285
7.260
7.250
7.247
7.237
7.235
7.222
7.154
7.143
7.090
7.088
7.083
7.078
7.075
7.063
7.051
7.045
7.033
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6.518
6.514
6.511
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4.216
4.201
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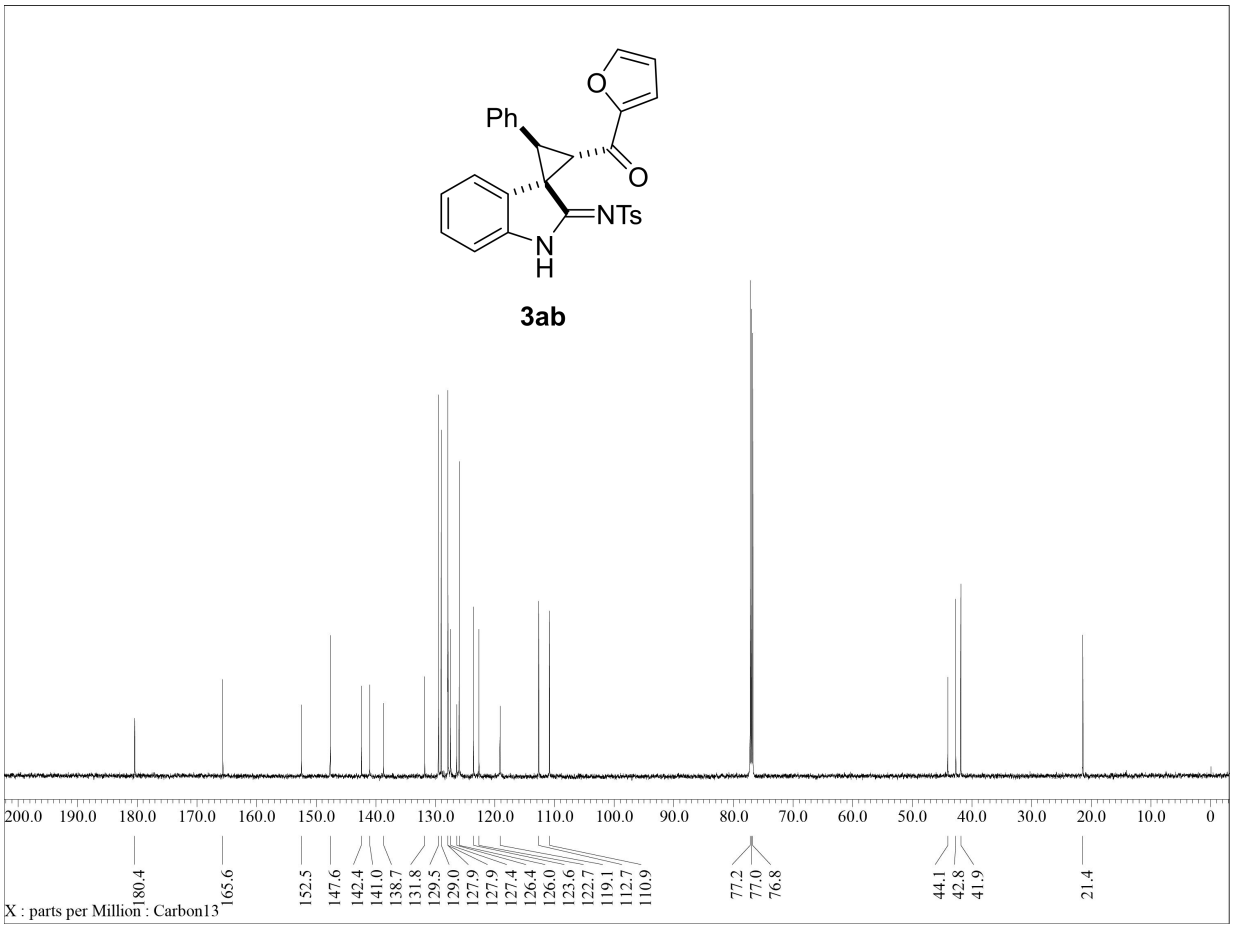
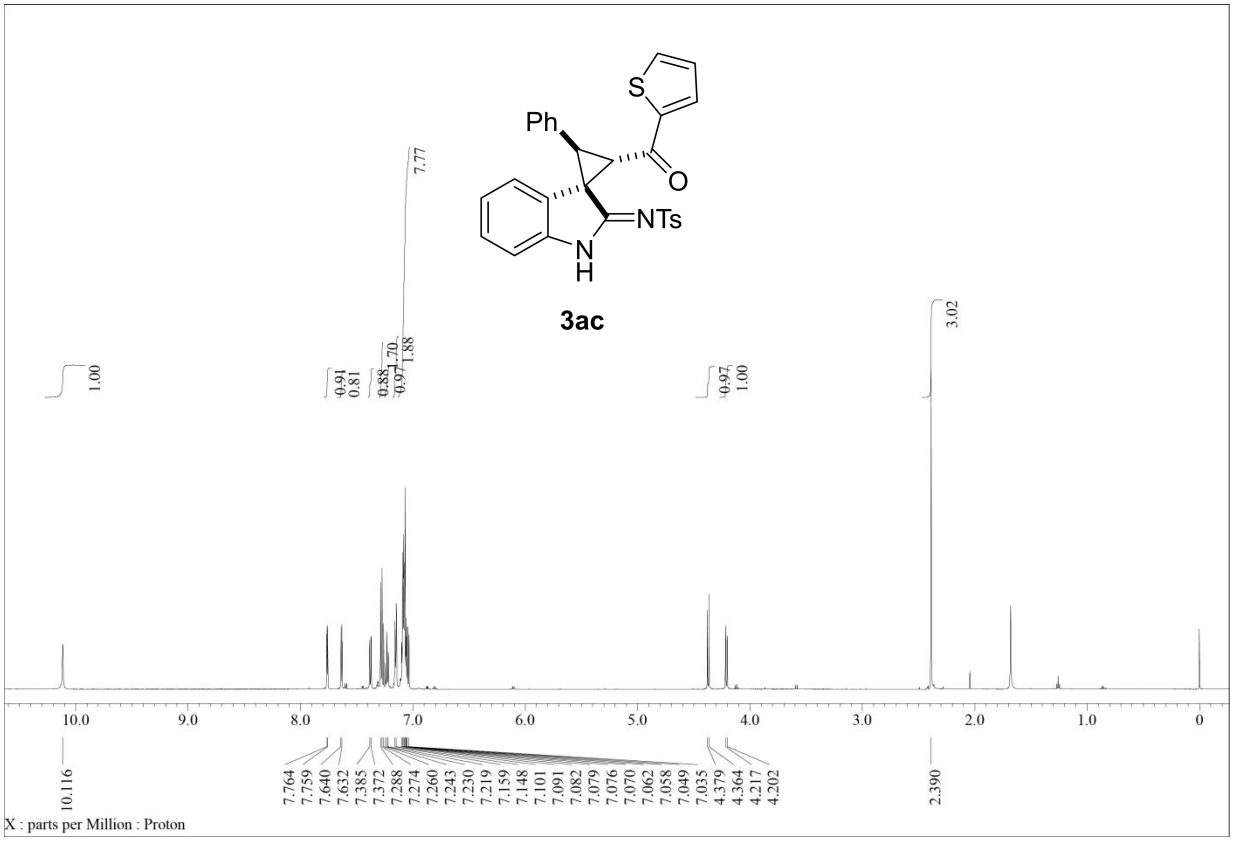
X : parts per Million : Proton


Ph
O
O
NTs
N
H
3ab
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.4
165.6
152.5
147.6
142.4
141.0
138.7
131.8
129.5
129.0
127.9
127.9
127.4
126.4
126.0
123.6
122.7
119.1
112.7
110.9
77.2
77.0
76.8
44.1
42.8
41.9
21.4
X : parts per Million : Carbon13


S
Ph
O
NTs
N
H
3ac
7.77
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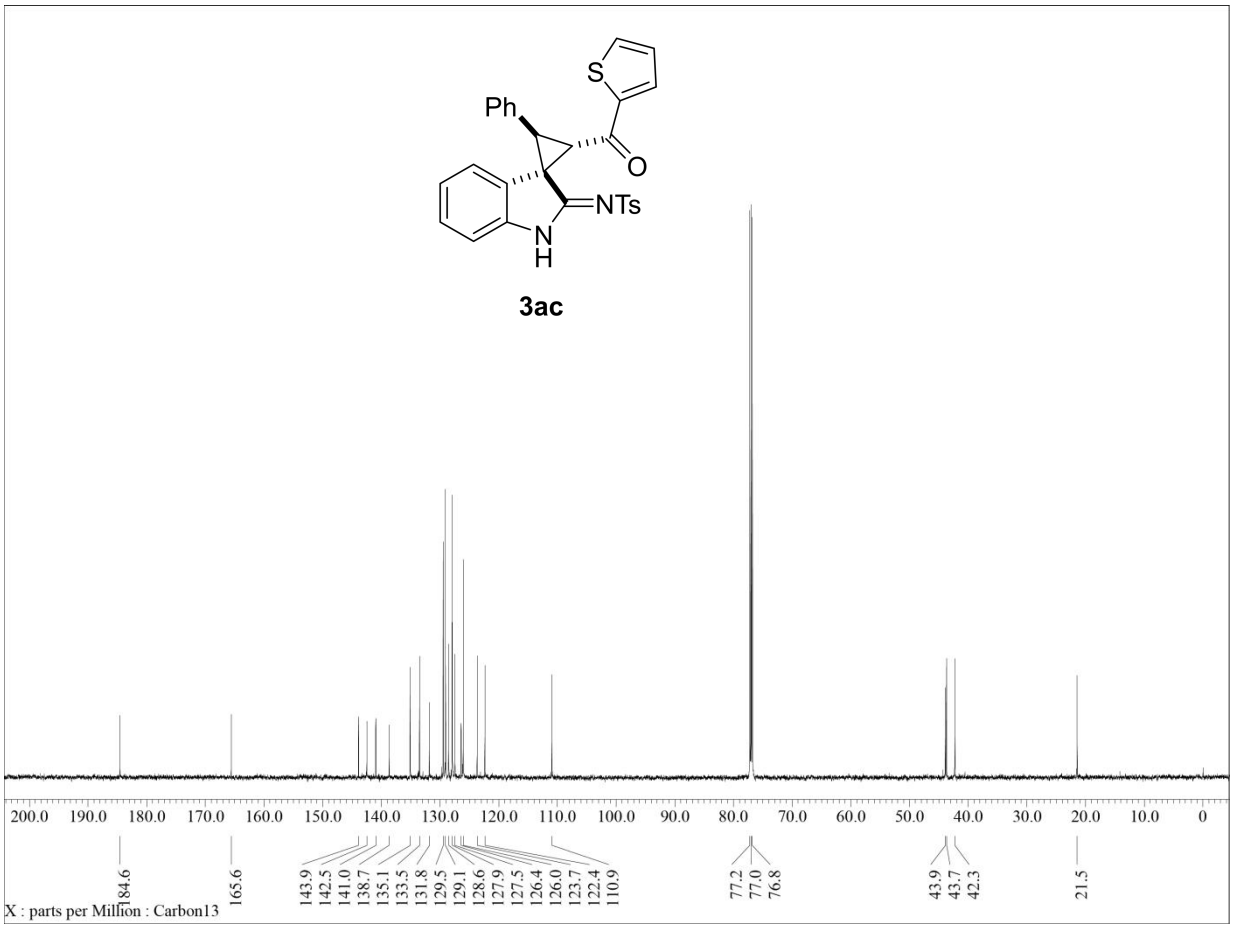
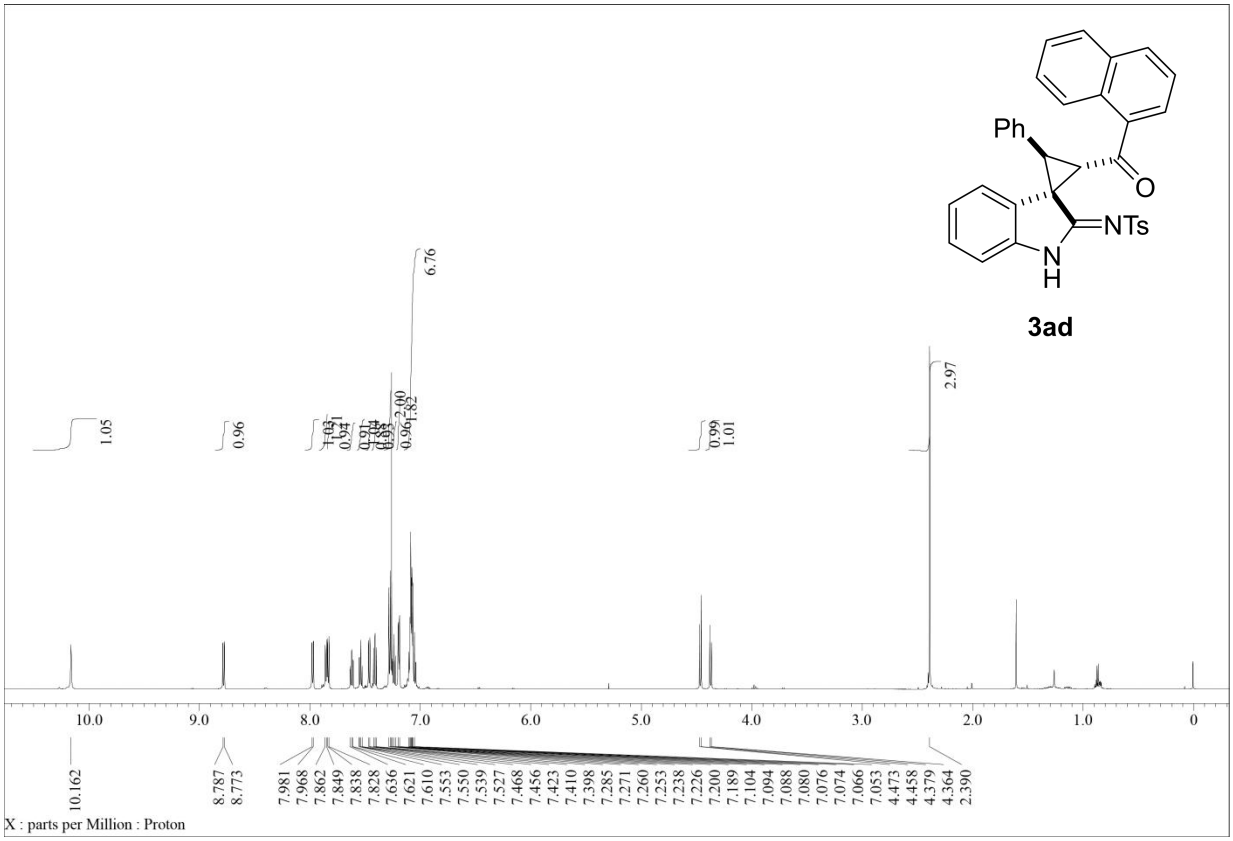
0.81
0.88
1.70
0.97
1.88
0.97
1.00
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.116
7.764
7.759
7.640
7.632
7.385
7.372
7.288
7.274
7.260
7.243
7.230
7.219
7.159
7.148
7.101
7.091
7.082
7.079
7.076
7.070
7.062
7.058
7.049
7.035
4.379
4.364
4.217
4.202
2.390
X : parts per Million : Proton


S
Ph
O
NTs
N
H
3ac
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.6
165.6
143.9
142.5
141.0
138.7
135.1
133.5
131.8
129.5
129.1
128.6
127.9
127.5
126.4
126.0
123.7
122.4
110.9
77.2
77.0
76.8
43.9
43.7
42.3
21.5
X : parts per Million : Carbon13


Ph
O
NTs
N
H
3ad
6.76
2.97
1.05
0.96
2.00
1.82
0.99
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.162
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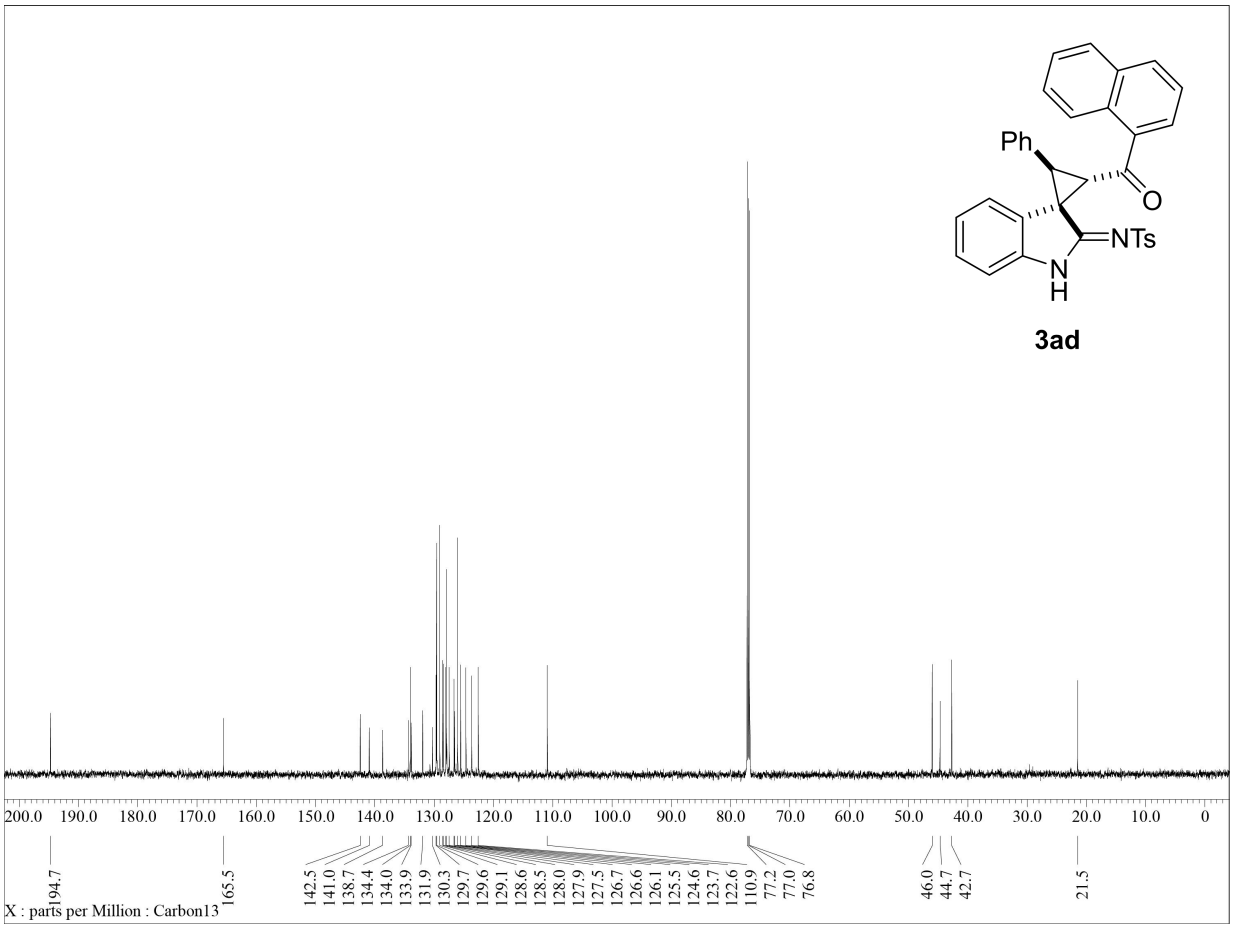
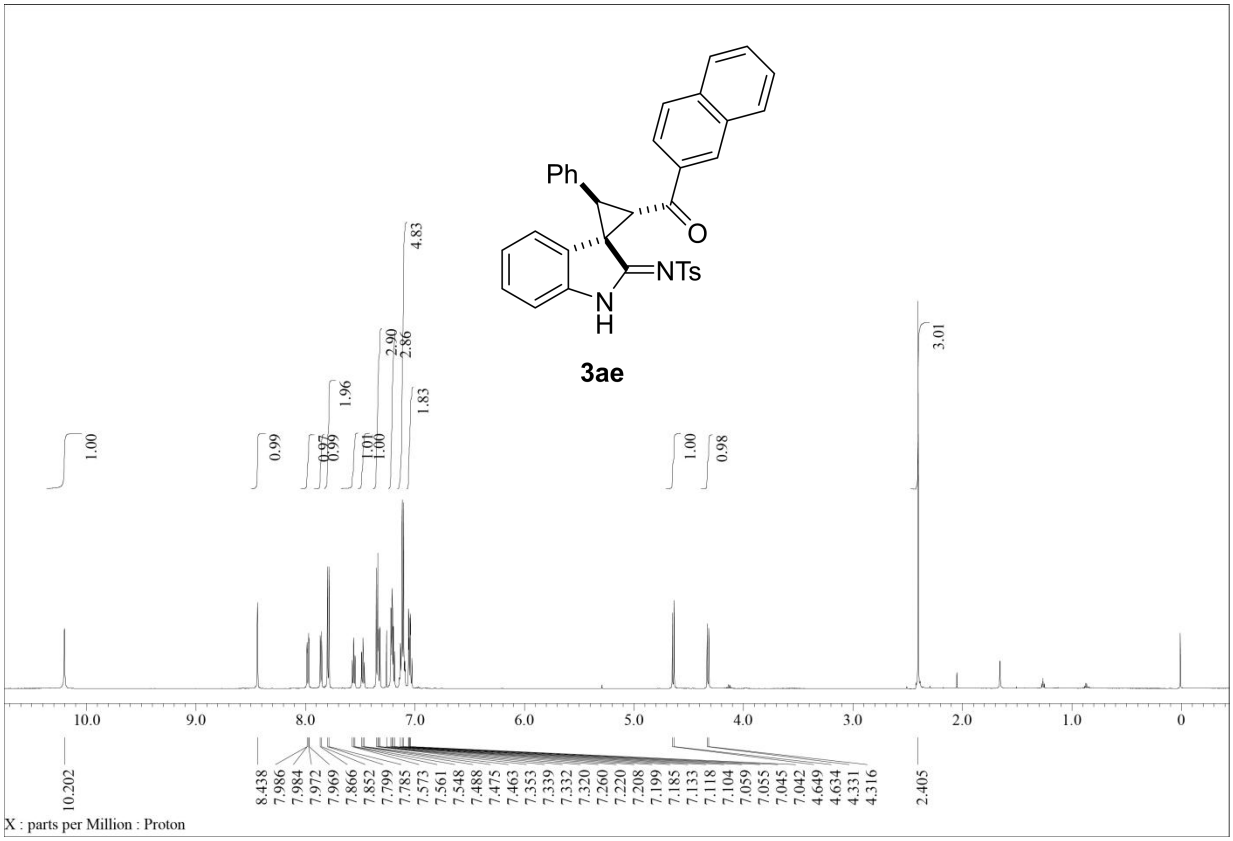
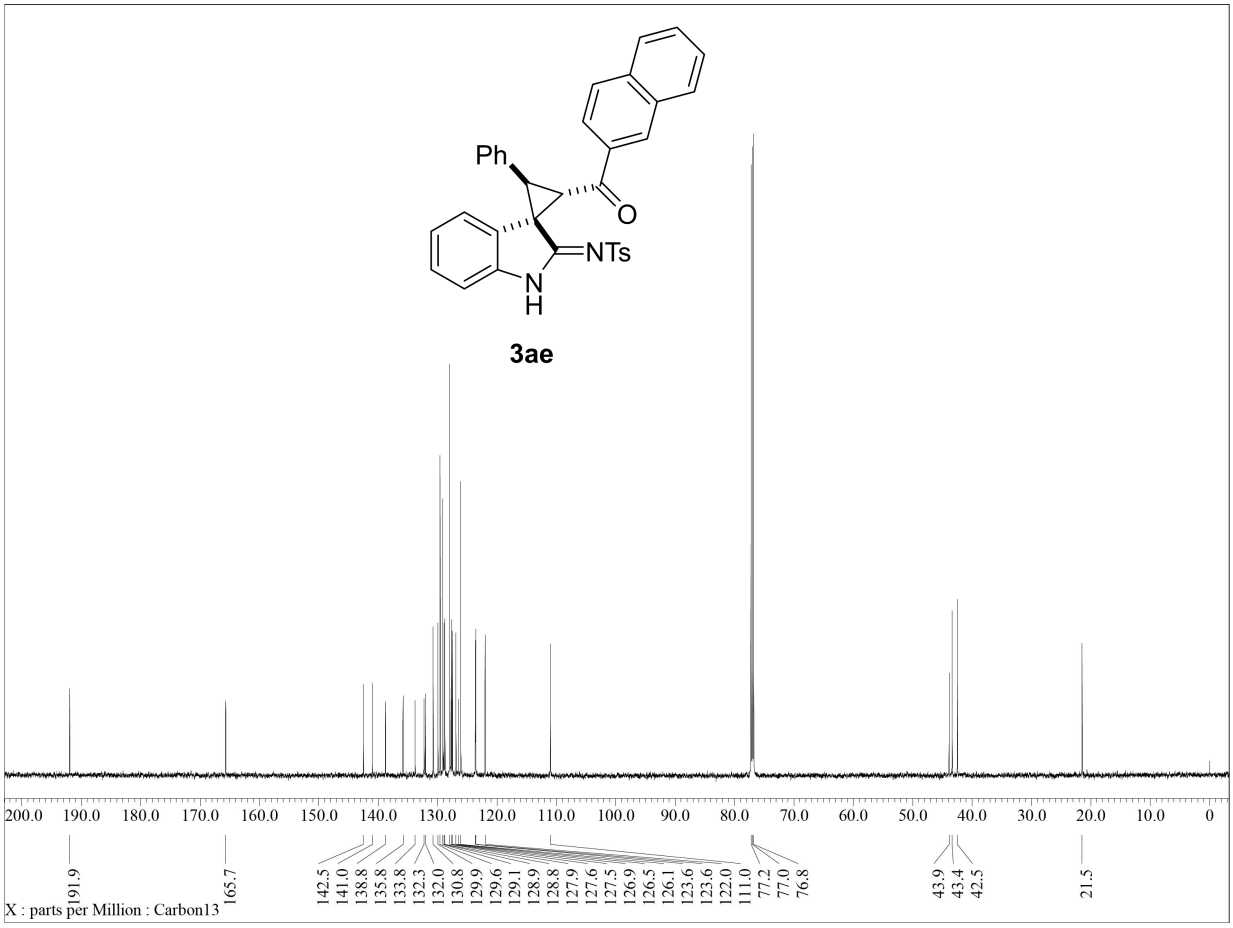
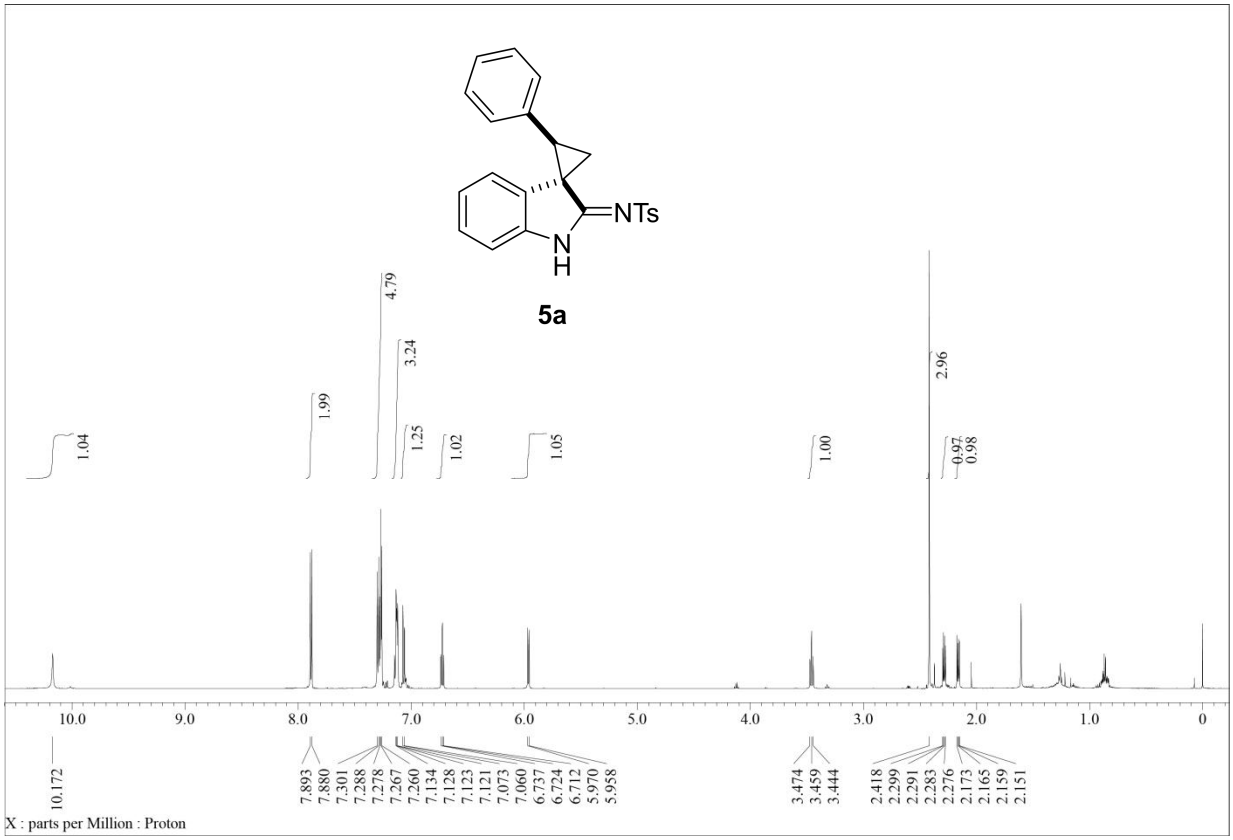
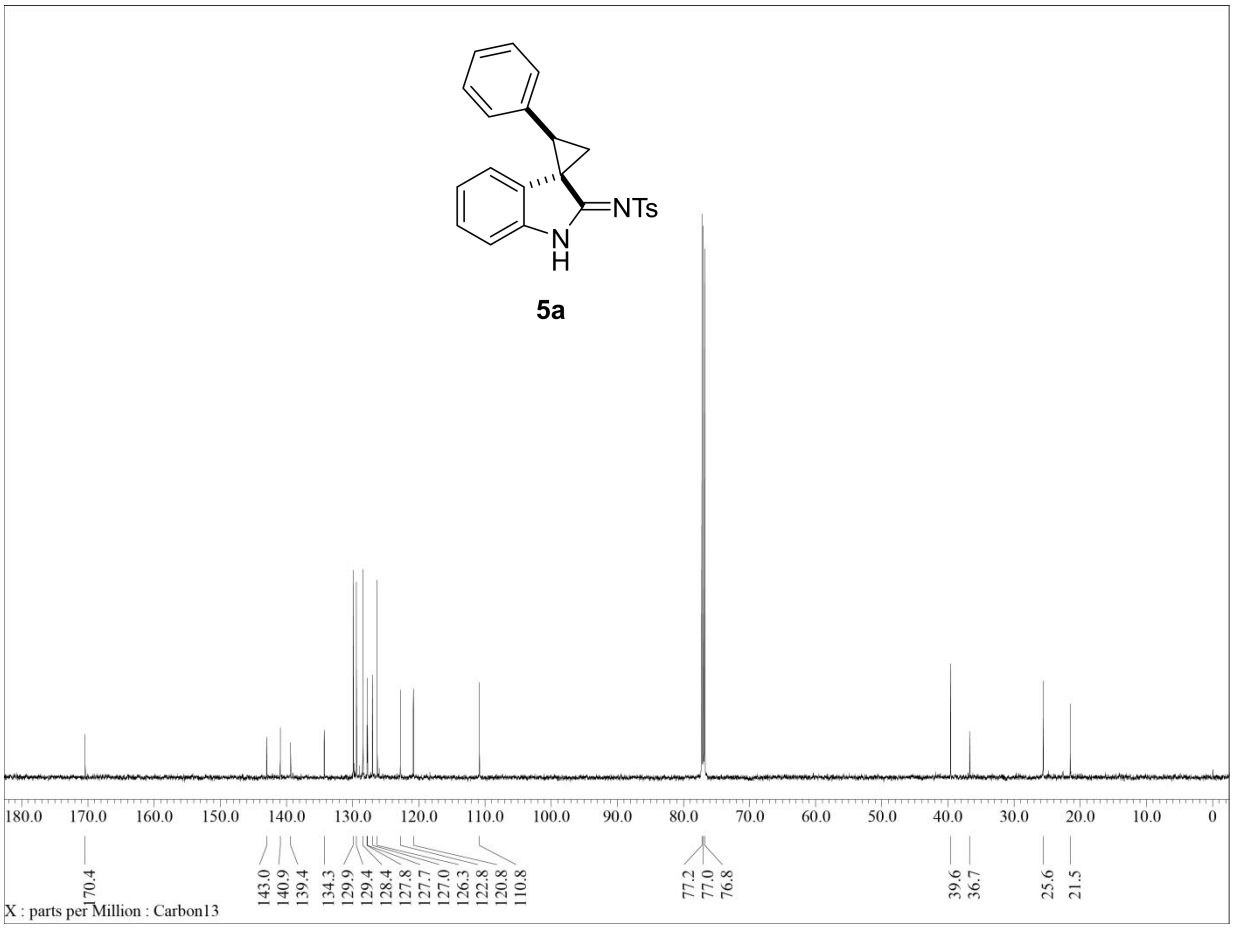
7.862
7.849
7.838
7.828
7.636
7.621
7.610
7.553
7.550
7.539
7.527
7.468
7.456
7.423
7.410
7.398
7.285
7.271
7.260
7.253
7.238
7.226
7.200
7.189
7.104
7.094
7.088
7.080
7.076
7.074
7.066
7.053
4.473
4.458
4.379
4.364
2.390
X : parts per Million : Proton

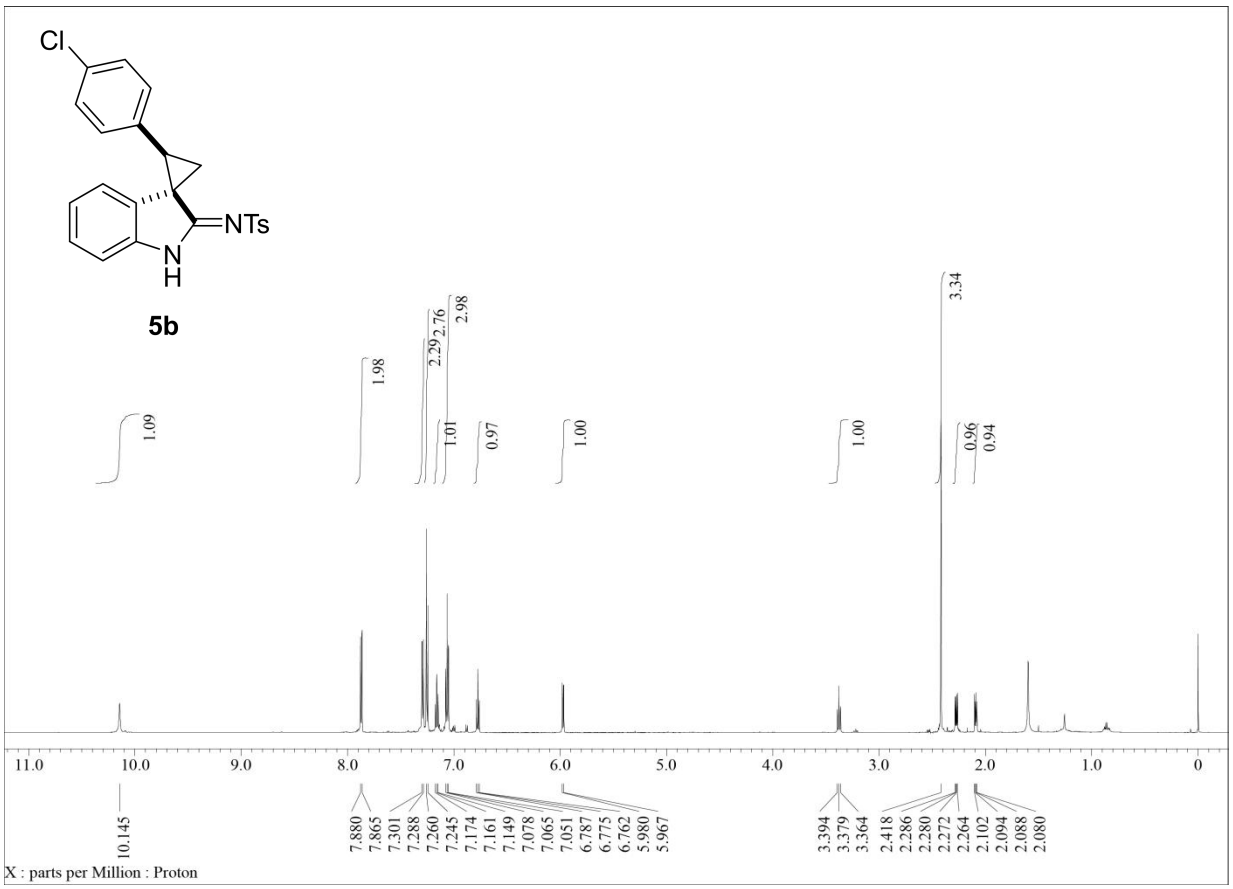

Ph
O
NTs
N
H
3ad
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
194.7
165.5
142.5
141.0
138.7
134.4
134.0
133.9
131.9
130.3
129.7
129.6
129.1
128.6
128.5
128.0
127.9
127.5
126.7
126.6
126.1
125.5
124.6
123.7
122.6
110.9
77.2
77.0
76.8
46.0
44.7
42.7
21.5
X : parts per Million : Carbon13

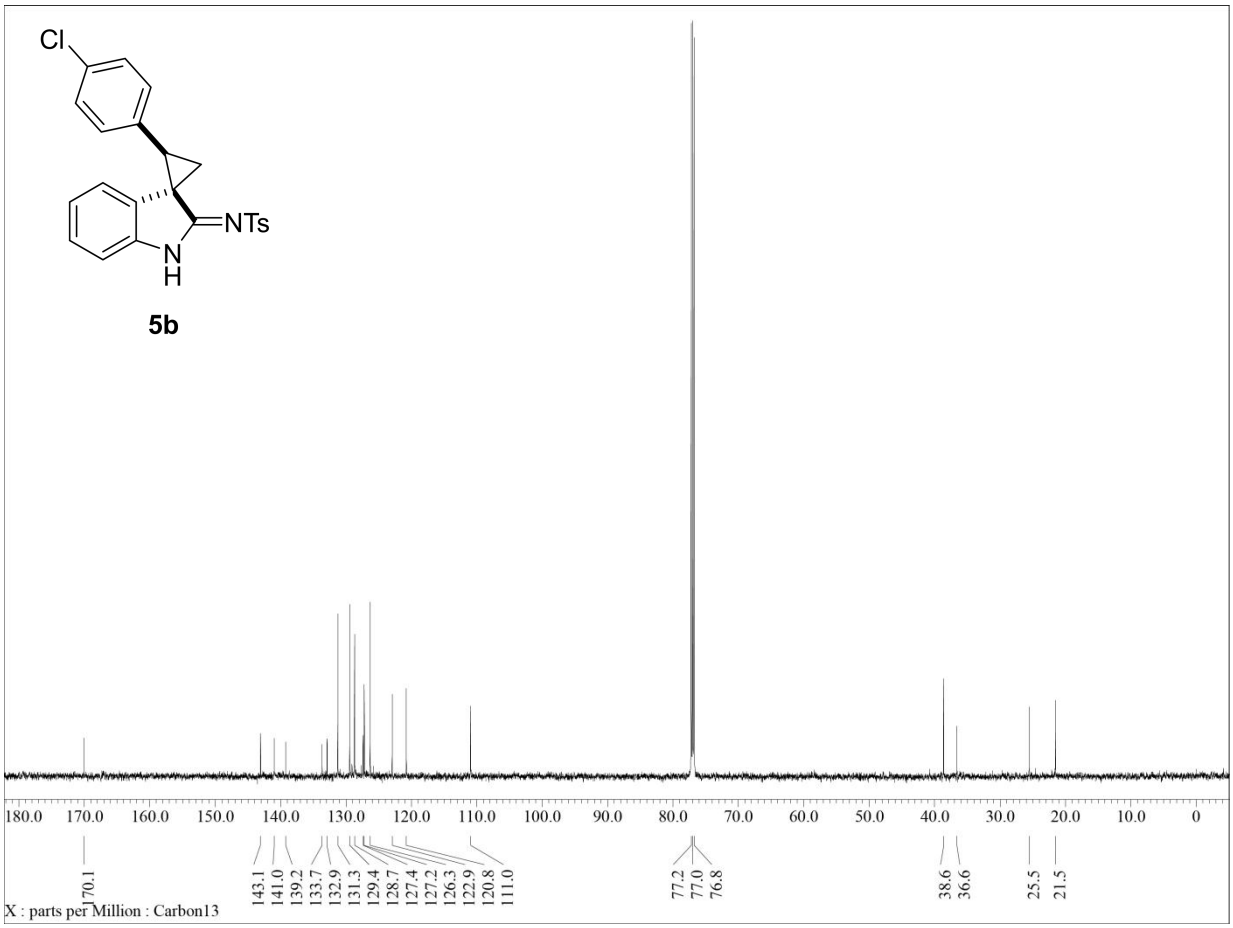

Ph
O
NTs
N
H
3ae
4.83
2.90
2.86
1.96
1.83
3.01
1.00
0.99
0.97
0.99
1.01
1.00
1.00
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.202
8.438
7.986
7.984
7.972
7.969
7.866
7.852
7.799
7.785
7.573
7.561
7.548
7.488
7.475
7.463
7.353
7.339
7.332
7.320
7.260
7.220
7.208
7.199
7.185
7.133
7.118
7.104
7.059
7.055
7.045
7.042
4.649
4.634
4.331
4.316
2.405
X : parts per Million : Proton

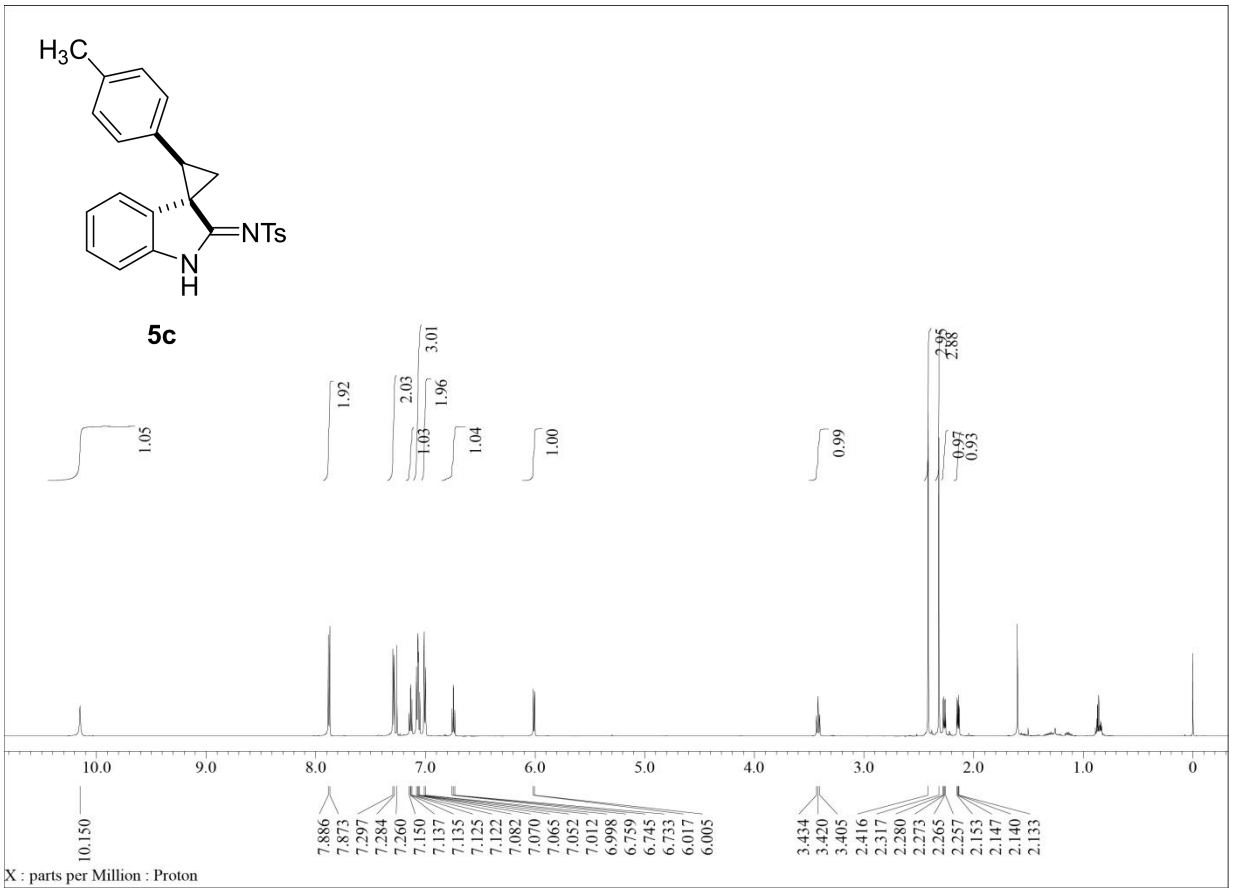

Ph
O
NTs
N
H
3ae
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
191.9
165.7
142.5
141.0
138.8
135.8
133.8
132.3
132.0
130.8
129.9
129.6
129.1
128.9
128.8
127.9
127.6
127.5
126.9
126.5
126.1
123.6
123.6
122.0
111.0
77.2
77.0
76.8
43.9
43.4
42.5
21.5
X : parts per Million : Carbon13

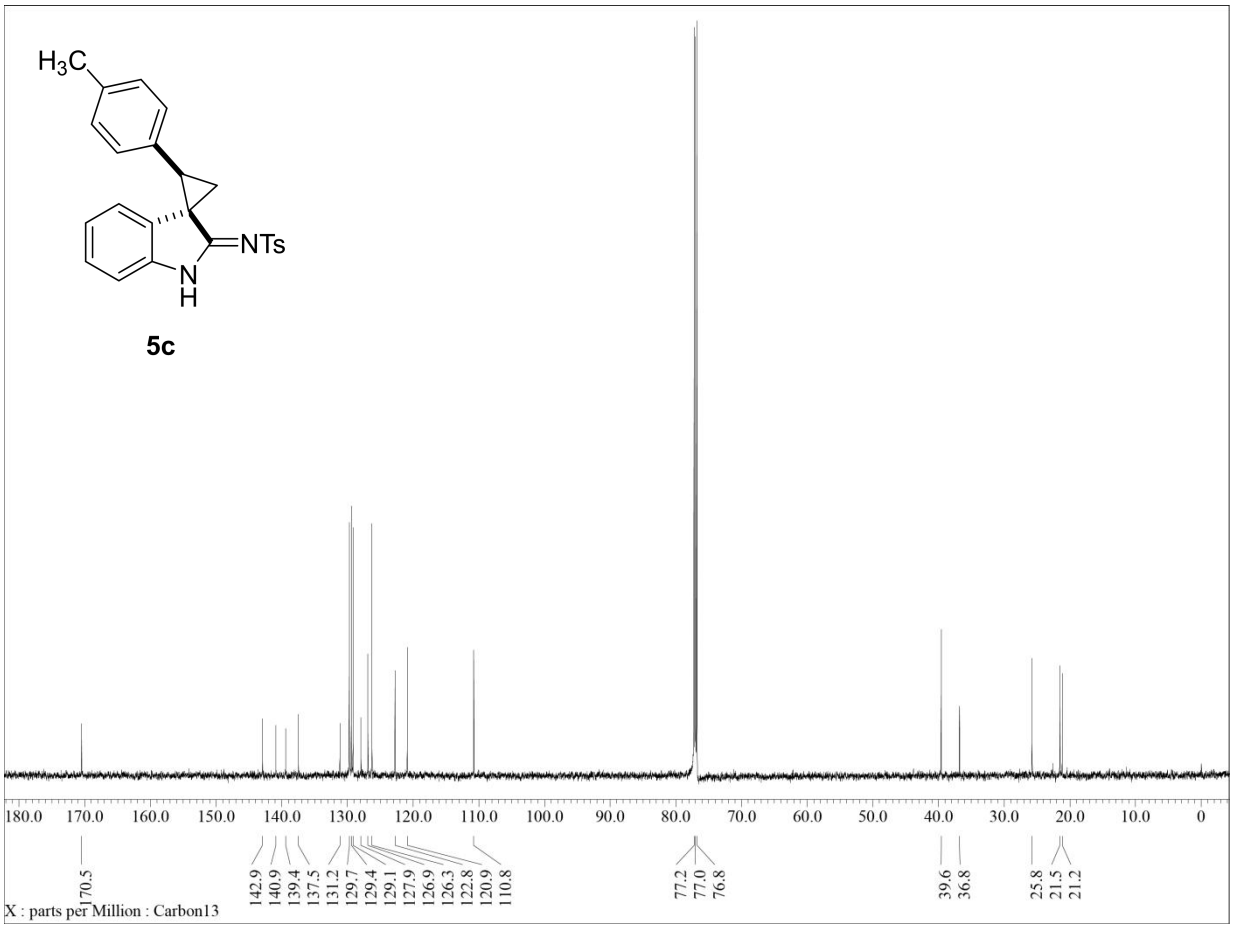

NTs
N
H
5a
4.79
3.24
2.96
1.99
1.25
1.04
1.02
1.05
1.00
0.97
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.172
7.893
7.880
7.301
7.288
7.278
7.267
7.260
7.134
7.128
7.123
7.121
7.073
7.060
6.737
6.724
6.712
5.970
5.958
3.474
3.459
3.444
2.418
2.299
2.291
2.283
2.276
2.173
2.165
2.159
2.151
X : parts per Million : Proton

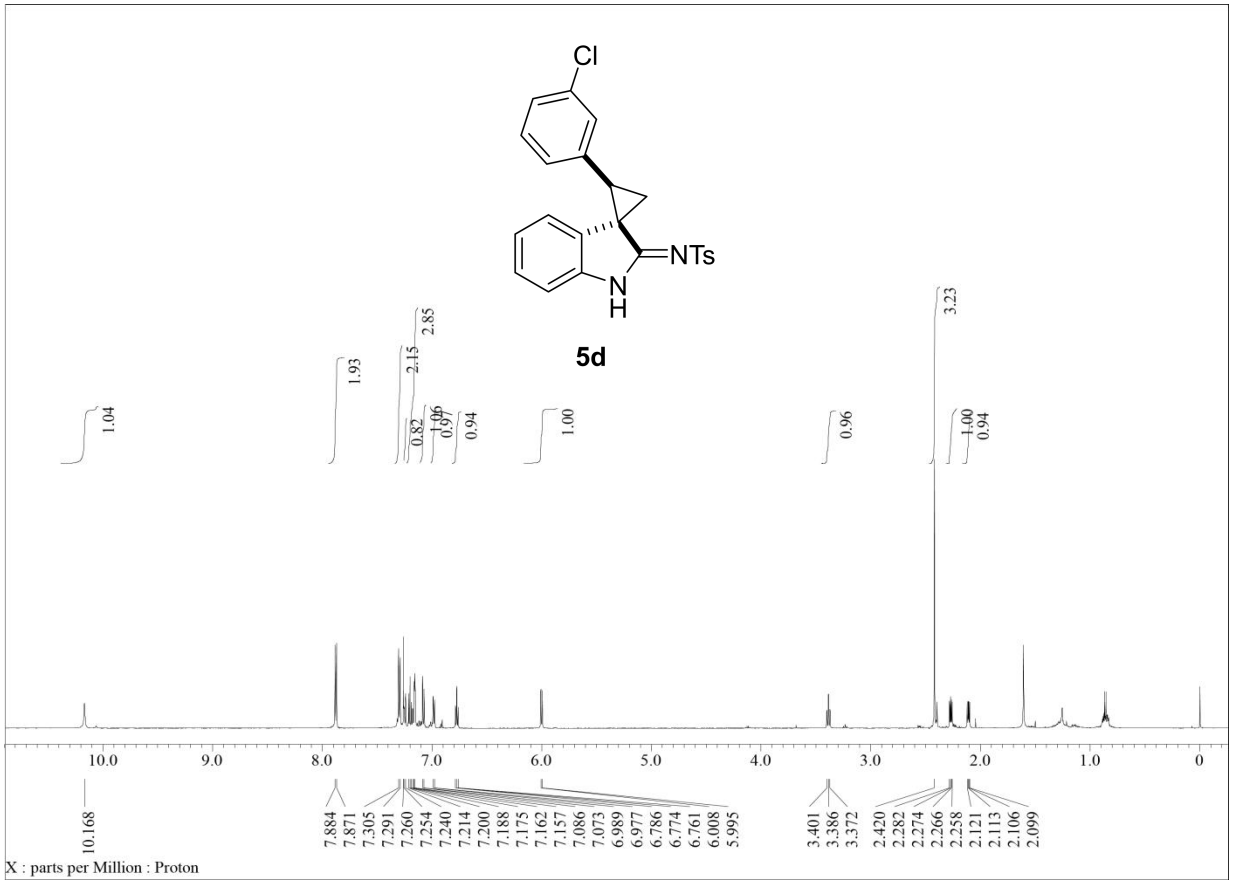

NTs
N
H
5a
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.4
143.0
140.9
139.4
134.3
129.9
129.4
128.4
127.8
127.7
127.0
126.3
122.8
120.8
110.8
77.2
77.0
76.8
39.6
36.7
25.6
21.5
X : parts per Million : Carbon13

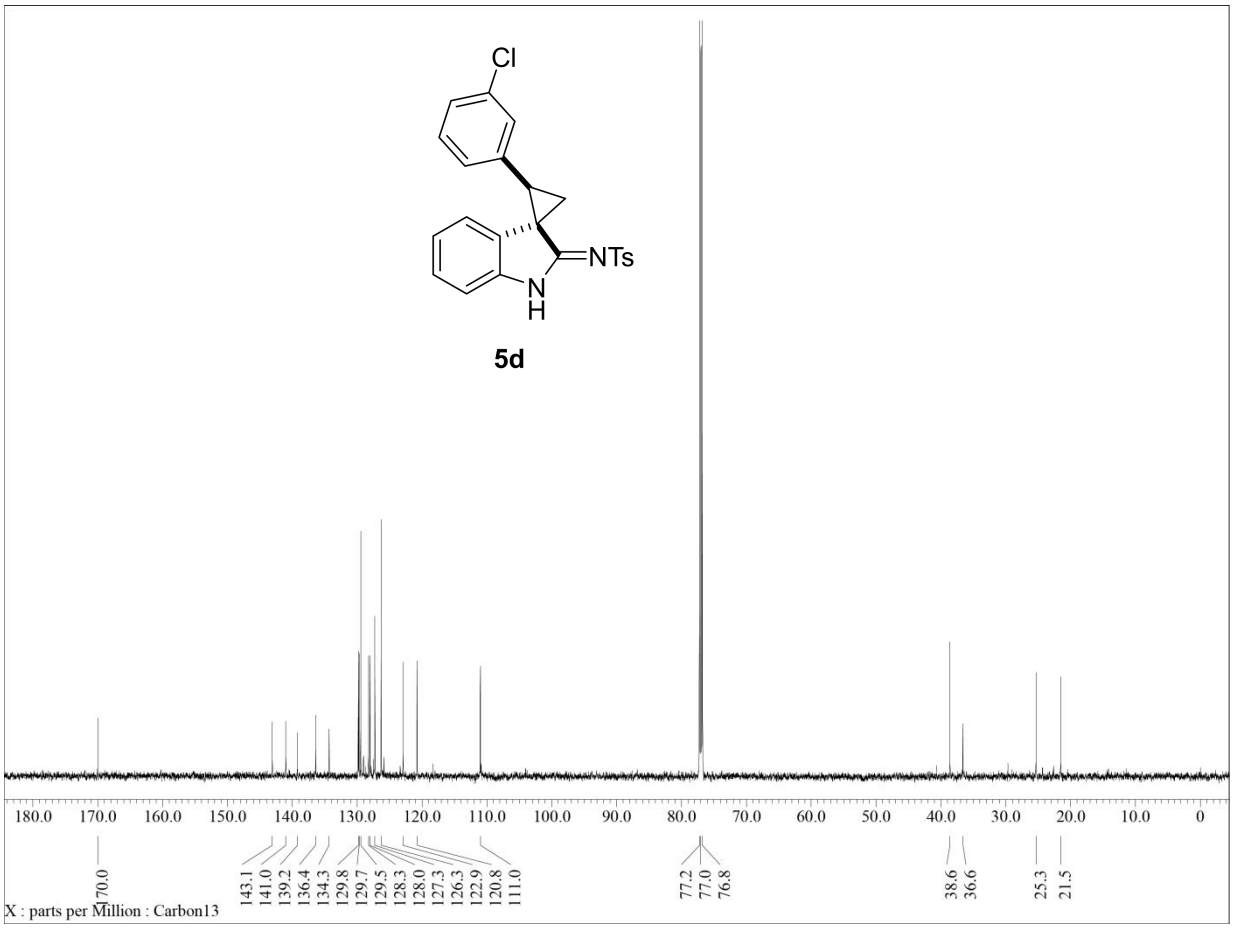

Cl
NTs
N
H
5b
1.09
1.98
2.29
2.76
2.98
1.01
0.97
1.00
1.00
3.34
0.96
0.94
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.145
7.880
7.865
7.301
7.288
7.260
7.245
7.174
7.161
7.149
7.078
7.065
7.051
6.787
6.775
6.762
5.980
5.967
3.394
3.379
3.364
2.418
2.286
2.280
2.272
2.264
2.102
2.094
2.088
2.080
X : parts per Million : Proton

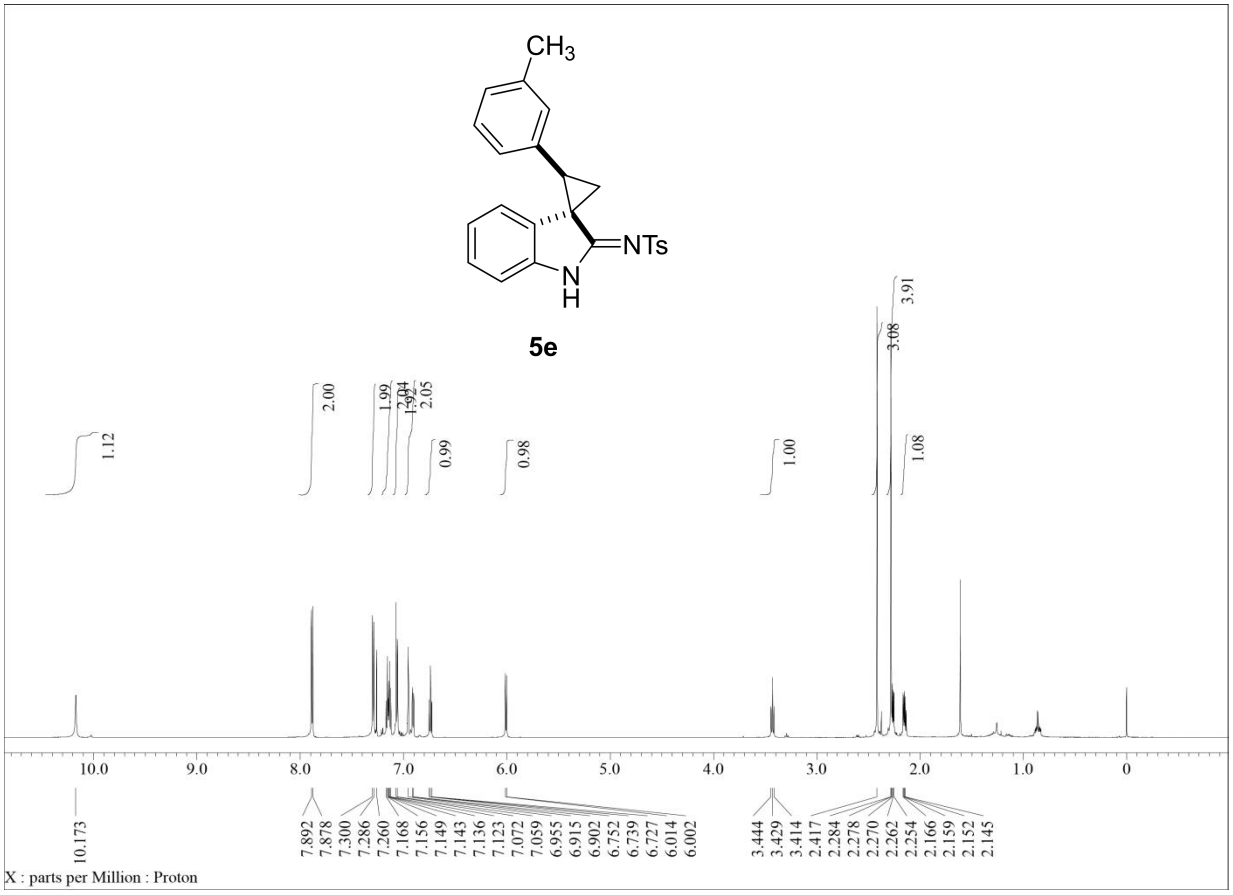

Cl
NTs
N
H
5b
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.1
143.1
141.0
139.2
133.7
132.9
131.3
129.4
128.7
127.4
127.2
126.3
122.9
120.8
111.0
77.2
77.0
76.8
38.6
36.6
25.5
21.5
X : parts per Million : Carbon13

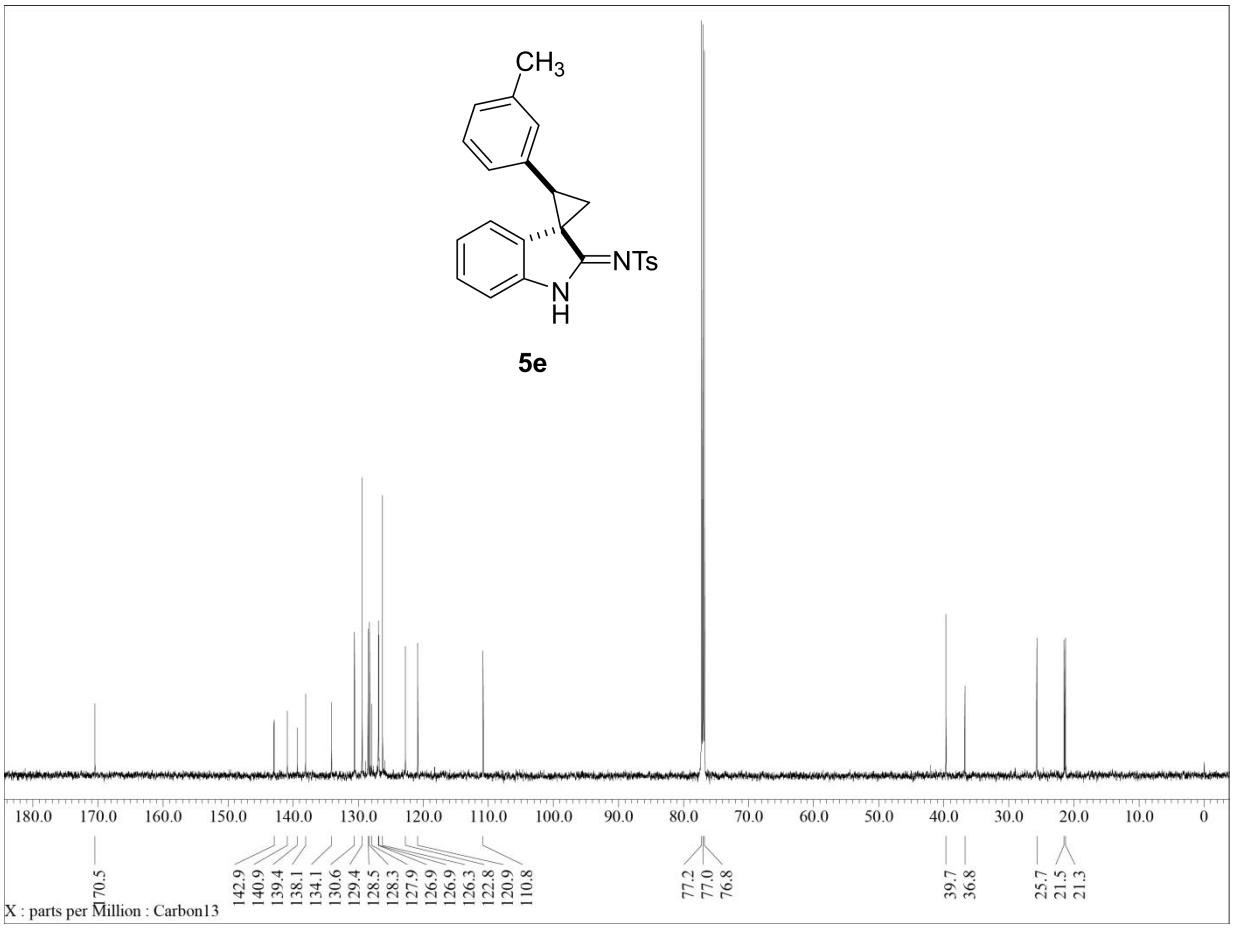

H3C
NTs
N
H
5c
1.05
1.92
2.03
3.01
1.96
1.03
1.04
1.00
0.99
2.95
2.88
0.97
0.93
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.150
7.886
7.873
7.297
7.284
7.260
7.150
7.137
7.135
7.125
7.122
7.082
7.070
7.065
7.052
7.012
6.998
6.759
6.745
6.733
6.017
6.005
3.434
3.420
3.405
2.416
2.317
2.280
2.273
2.265
2.257
2.153
2.147
2.140
2.133
X : parts per Million : Proton

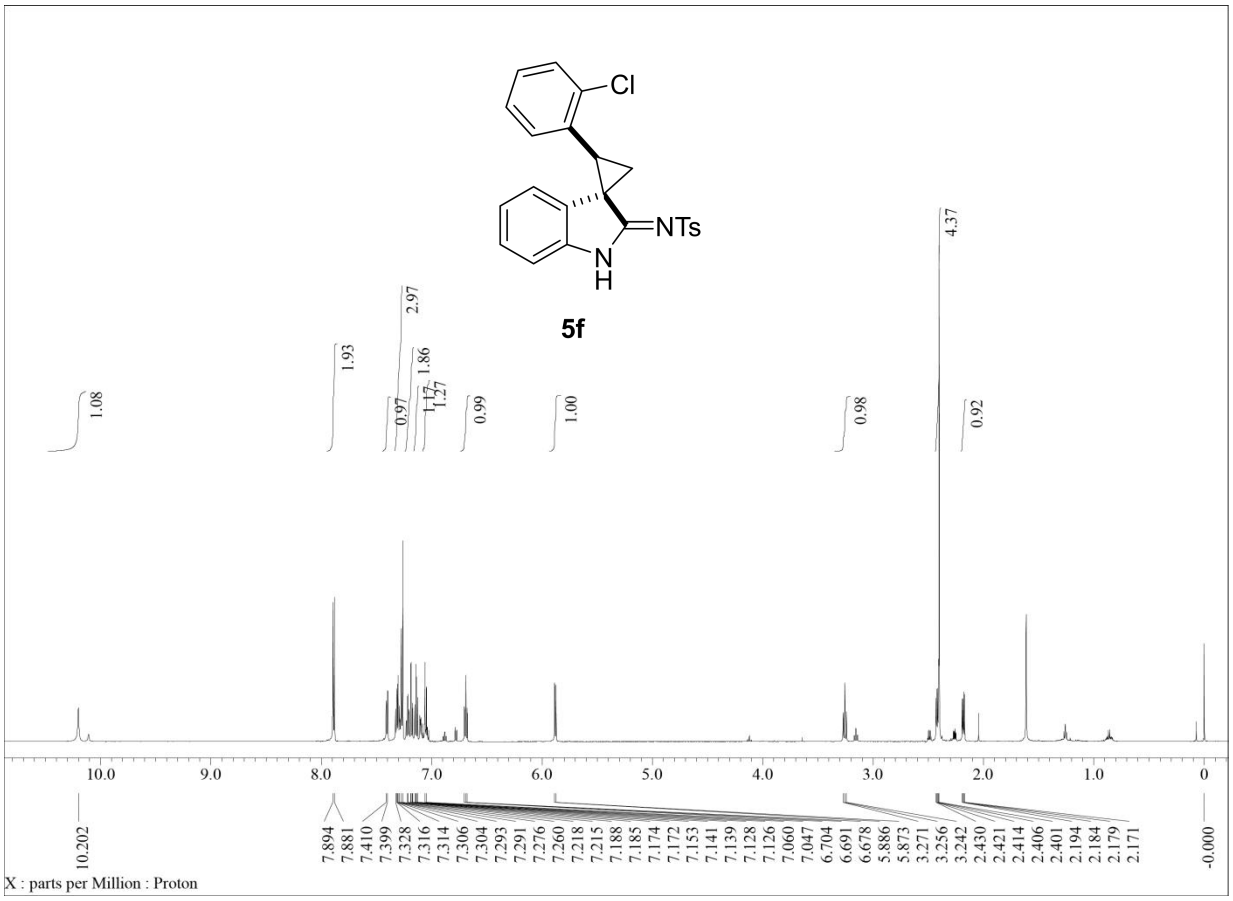

H3C
NTs
N
H
5c
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.5
142.9
140.9
139.4
137.5
131.2
129.7
129.4
129.1
127.9
126.9
126.3
122.8
120.9
110.8
77.2
77.0
76.8
39.6
36.8
25.8
21.5
21.2
X : parts per Million : Carbon13

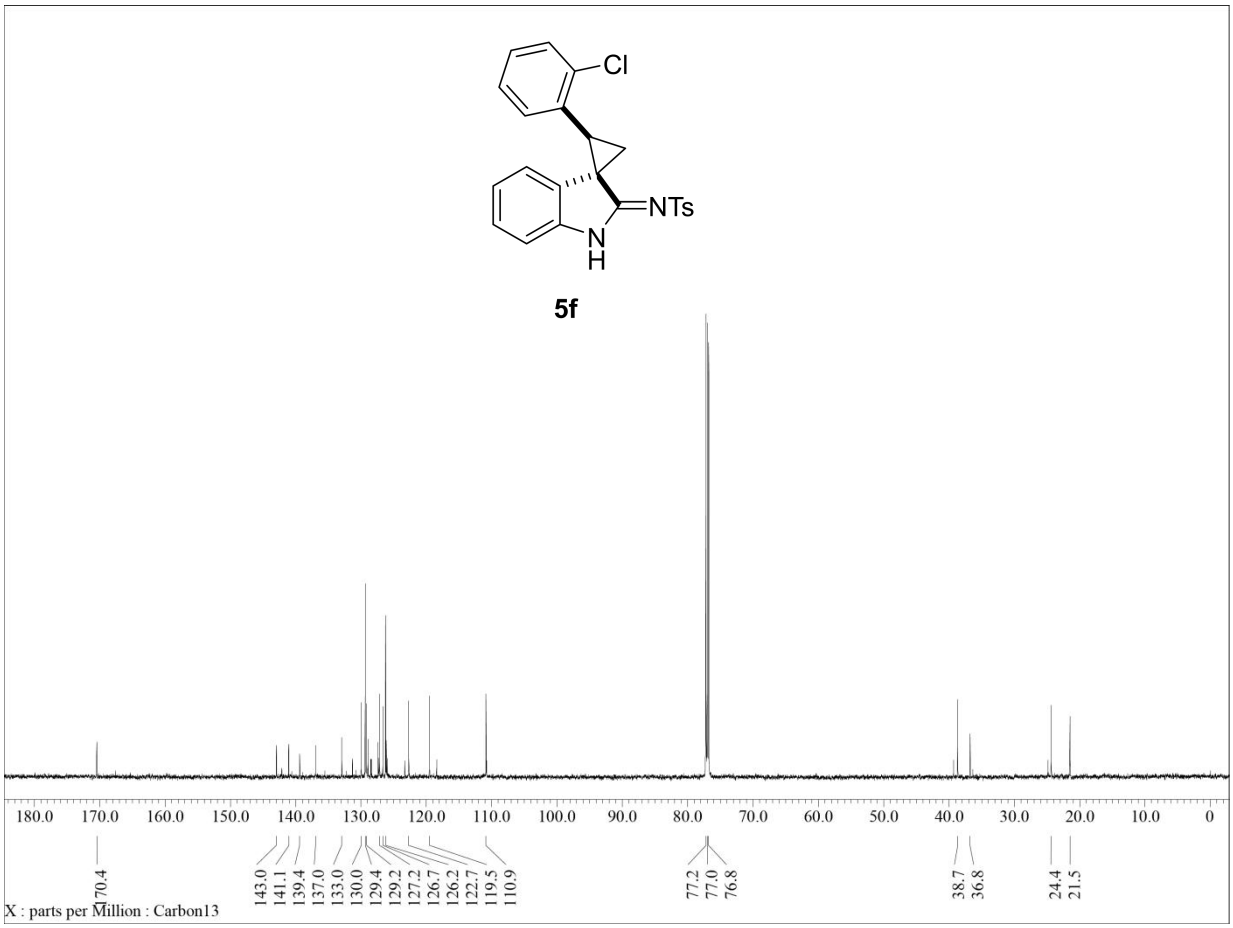

Cl
NTs
N
H
5d
1.04
1.93
2.15
2.85
0.82
1.06
0.97
0.94
1.00
0.96
3.23
1.00
0.94
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.168
7.884
7.871
7.305
7.291
7.260
7.254
7.240
7.214
7.200
7.188
7.175
7.162
7.157
7.086
7.073
6.989
6.977
6.786
6.774
6.761
6.008
5.995
3.401
3.386
3.372
2.420
2.282
2.274
2.266
2.258
2.121
2.113
2.106
2.099
X : parts per Million : Proton

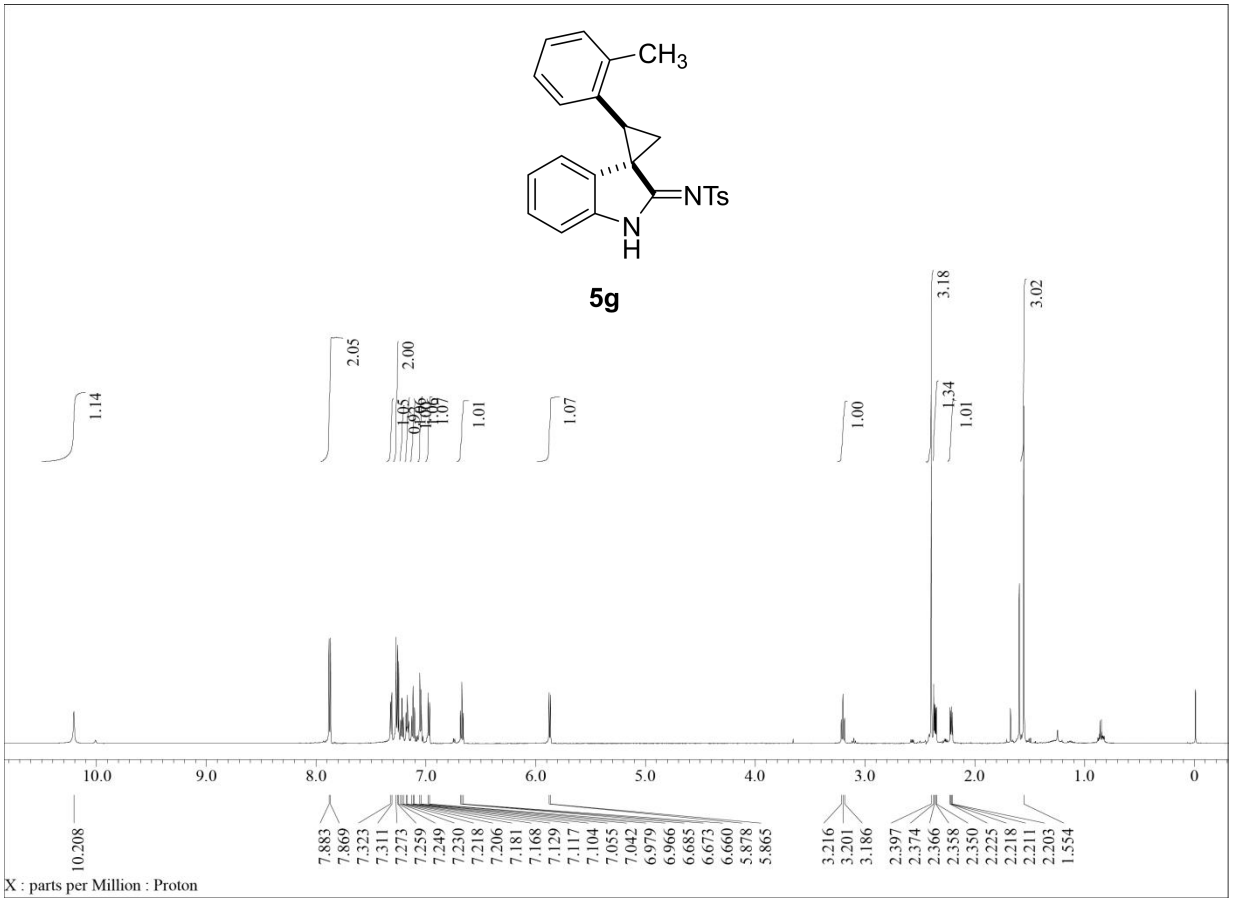

Cl
NTs
N
H
5d
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.0
143.1
141.0
139.2
136.4
134.3
129.8
129.7
129.5
128.3
128.0
127.3
126.3
122.9
120.8
111.0
77.2
77.0
76.8
38.6
36.6
25.3
21.5
X : parts per Million : Carbon13

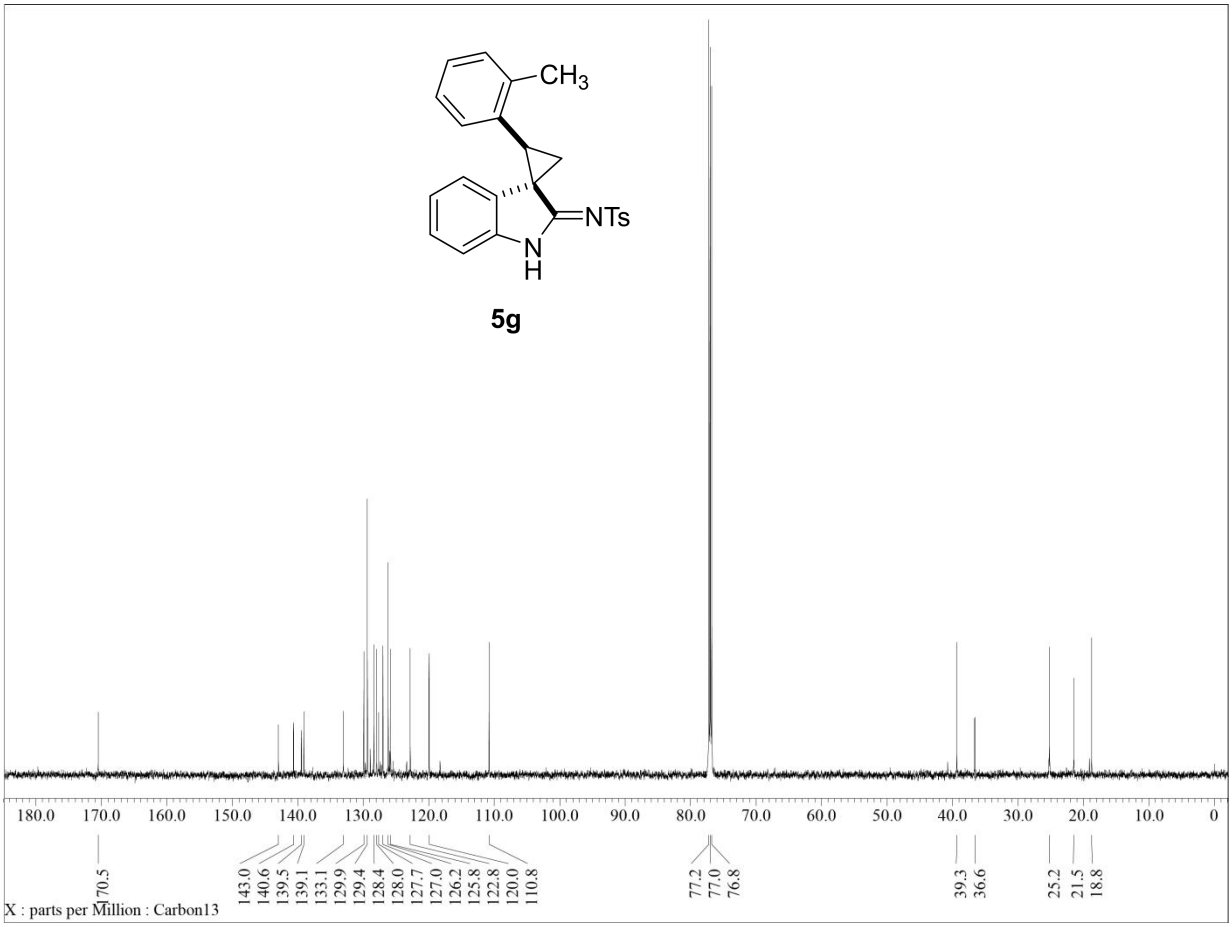

CH3
NTs
N
H
5e
2.00
1.99
2.04
2.05
1.12
0.99
0.98
1.00
3.08
3.91
1.08
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.173
7.892
7.878
7.300
7.286
7.260
7.168
7.156
7.149
7.143
7.136
7.123
7.072
7.059
6.955
6.915
6.902
6.752
6.739
6.727
6.014
6.002
3.444
3.429
3.414
2.417
2.284
2.278
2.270
2.262
2.254
2.166
2.159
2.152
2.145
X : parts per Million : Proton

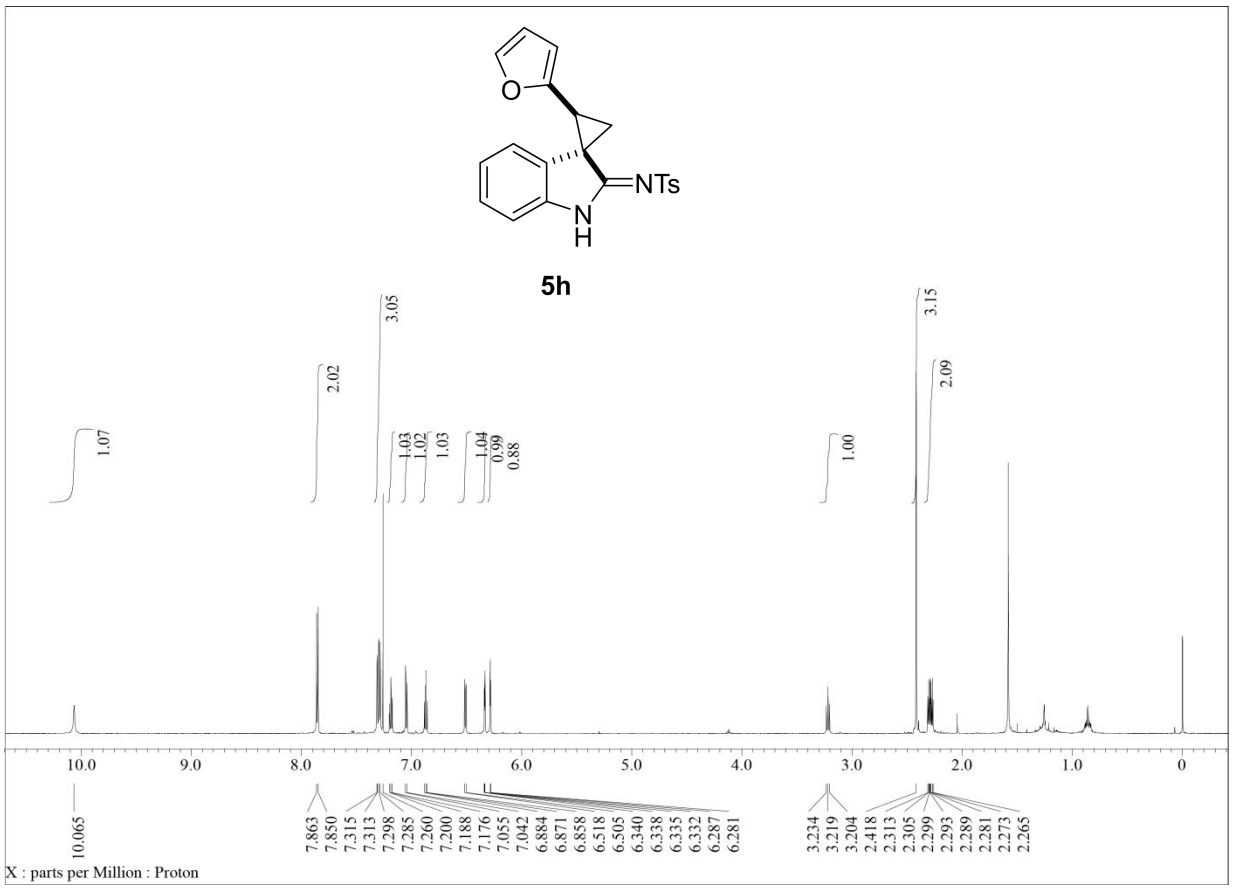

CH3
NTs
N
H
5e
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.5
142.9
140.9
139.4
138.1
134.1
130.6
129.4
128.5
128.3
127.9
126.9
126.9
126.3
122.8
120.9
110.8
77.2
77.0
76.8
39.7
36.8
25.7
21.5
21.3
X : parts per Million : Carbon13

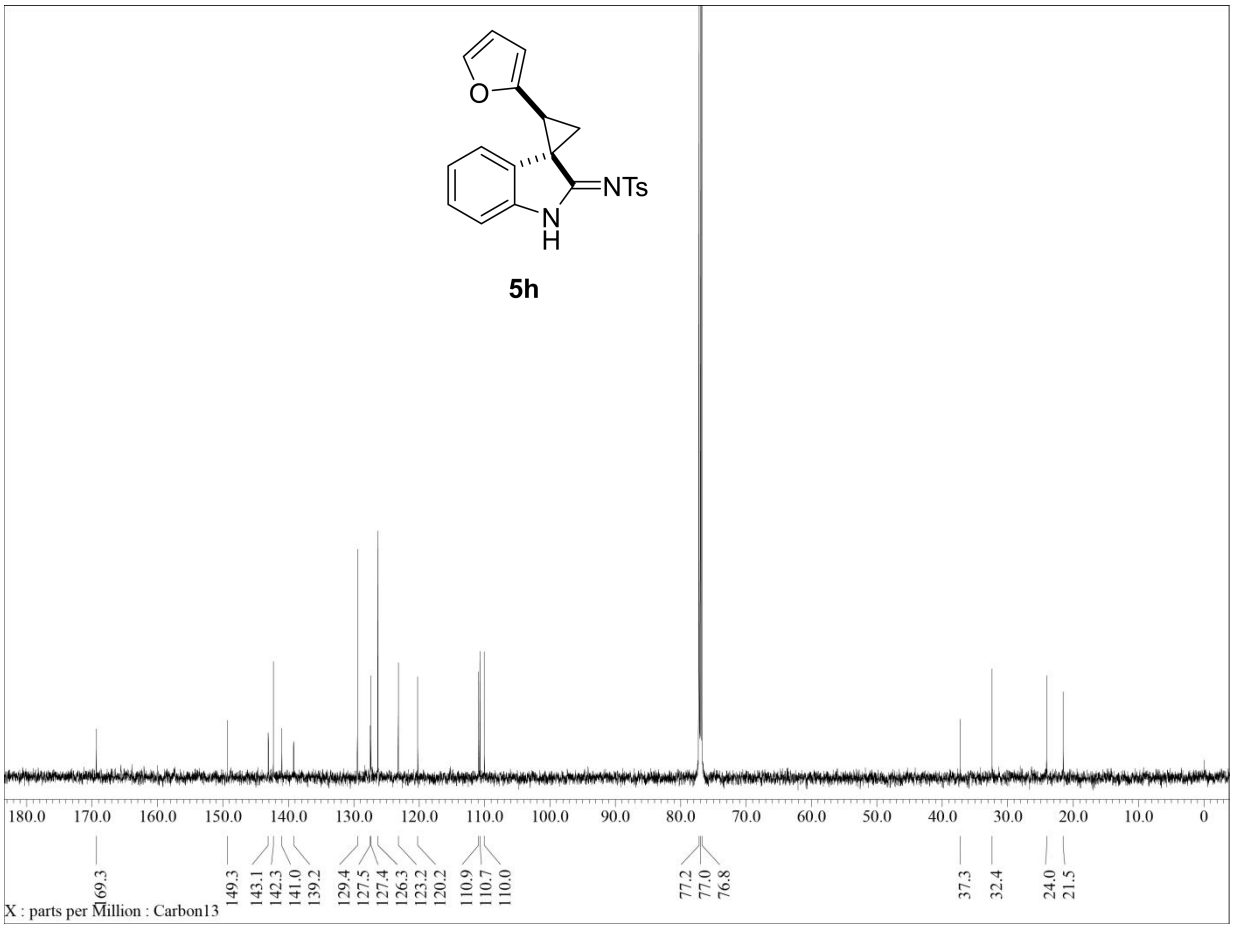

Cl
NTs
N
H
5f
4.37
2.97
1.93
1.86
1.27
1.08
0.97
0.99
1.00
0.98
0.92
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.202
7.894
7.881
7.410
7.399
7.328
7.316
7.314
7.306
7.304
7.293
7.291
7.276
7.260
7.218
7.215
7.188
7.185
7.174
7.172
7.153
7.141
7.139
7.128
7.126
7.060
7.047
6.704
6.691
6.678
5.886
5.873
3.271
3.256
3.242
2.430
2.421
2.414
2.406
2.401
2.194
2.184
2.179
2.171
-0.000
X : parts per Million : Proton

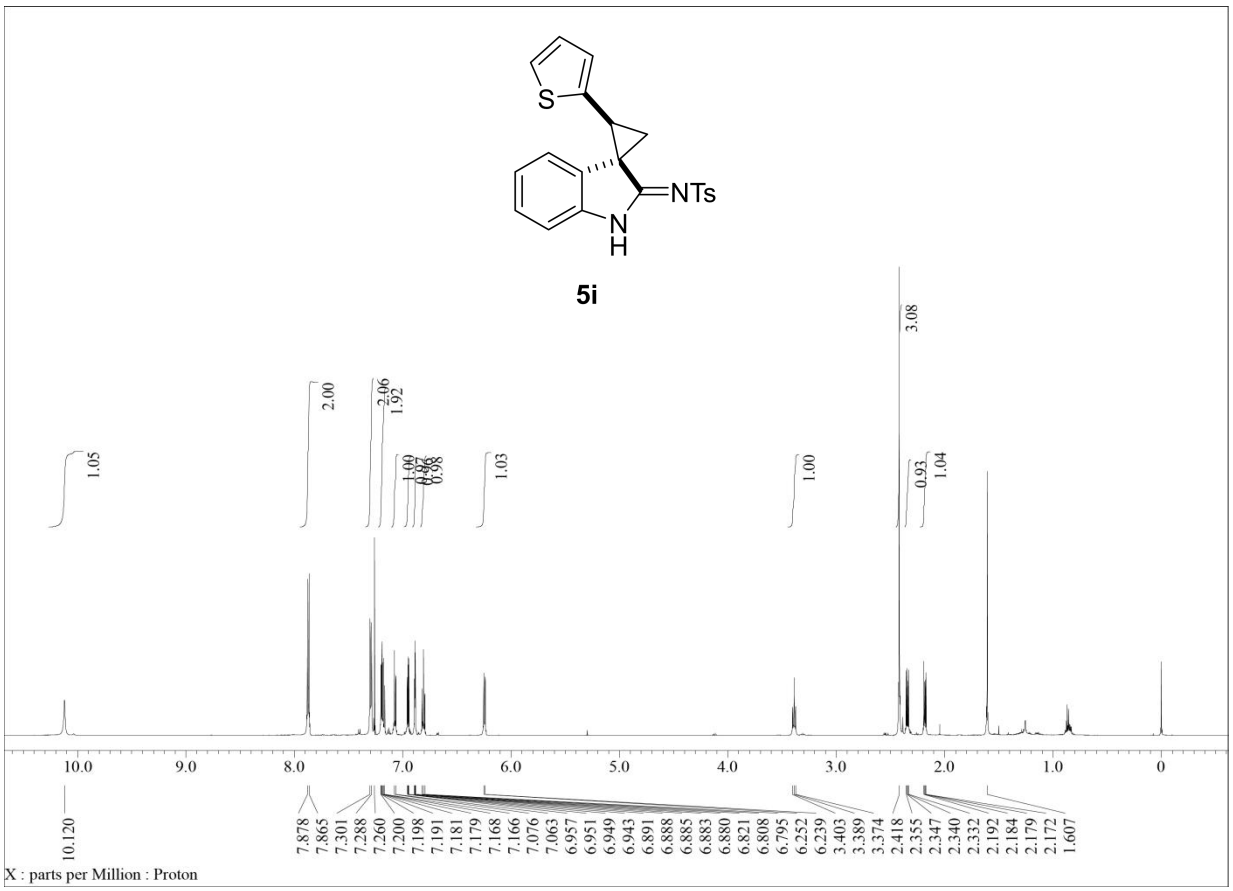

Cl
NTs
N
H
5f
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.4
143.0
141.1
139.4
137.0
133.0
130.0
129.4
129.2
127.2
126.7
126.2
122.7
119.5
110.9
77.2
77.0
76.8
38.7
36.8
24.4
21.5
X : parts per Million : Carbon13

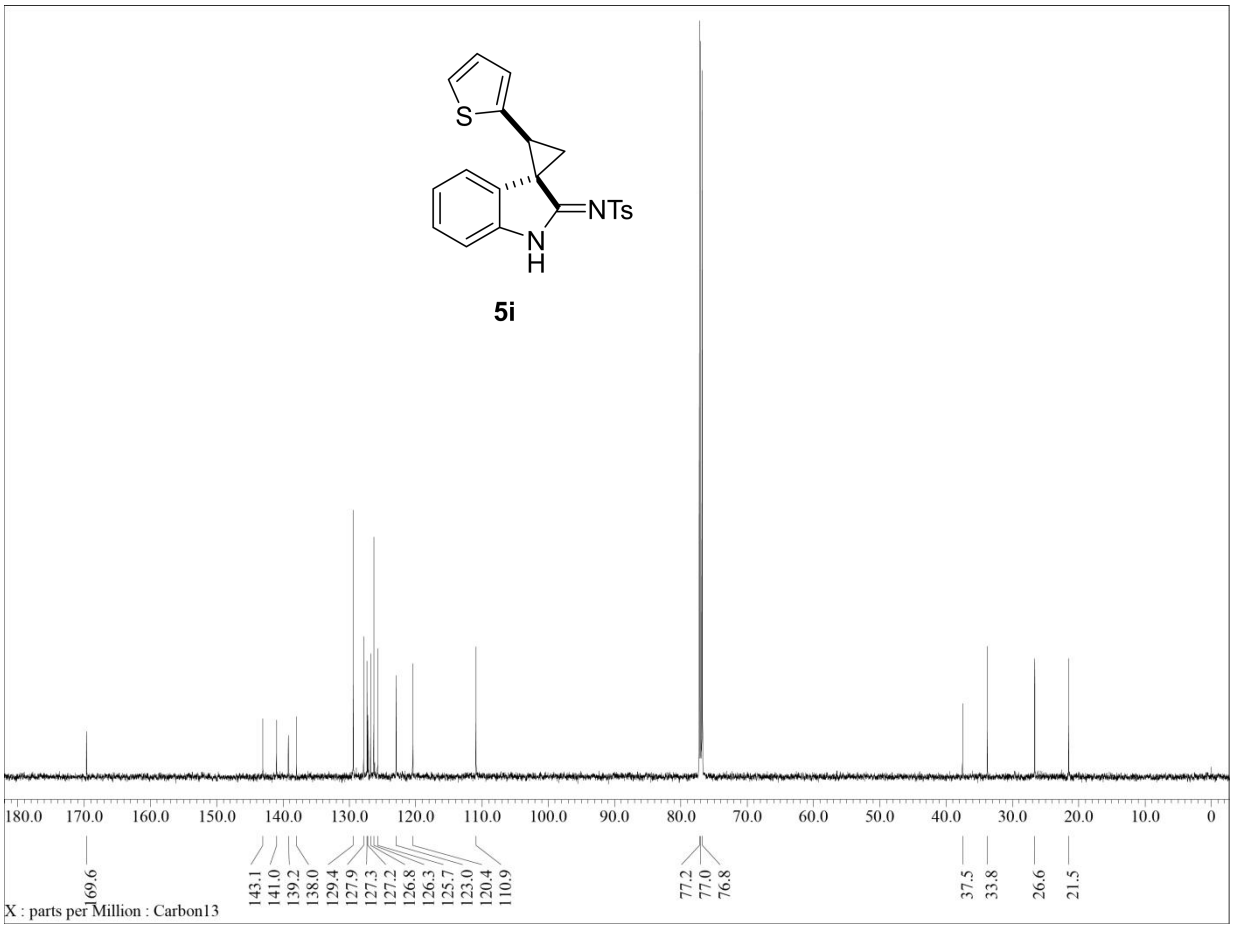

CH3
NTs
N
H
5g
3.18
3.02
2.05
2.00
1.14
1.34
1.01
1.07
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.208
7.883
7.869
7.323
7.311
7.273
7.259
7.249
7.230
7.218
7.206
7.181
7.168
7.129
7.117
7.104
7.055
7.042
6.979
6.966
6.685
6.673
6.660
5.878
5.865
3.216
3.201
3.186
2.397
2.374
2.366
2.358
2.350
2.225
2.218
2.211
2.203
1.554
X : parts per Million : Proton

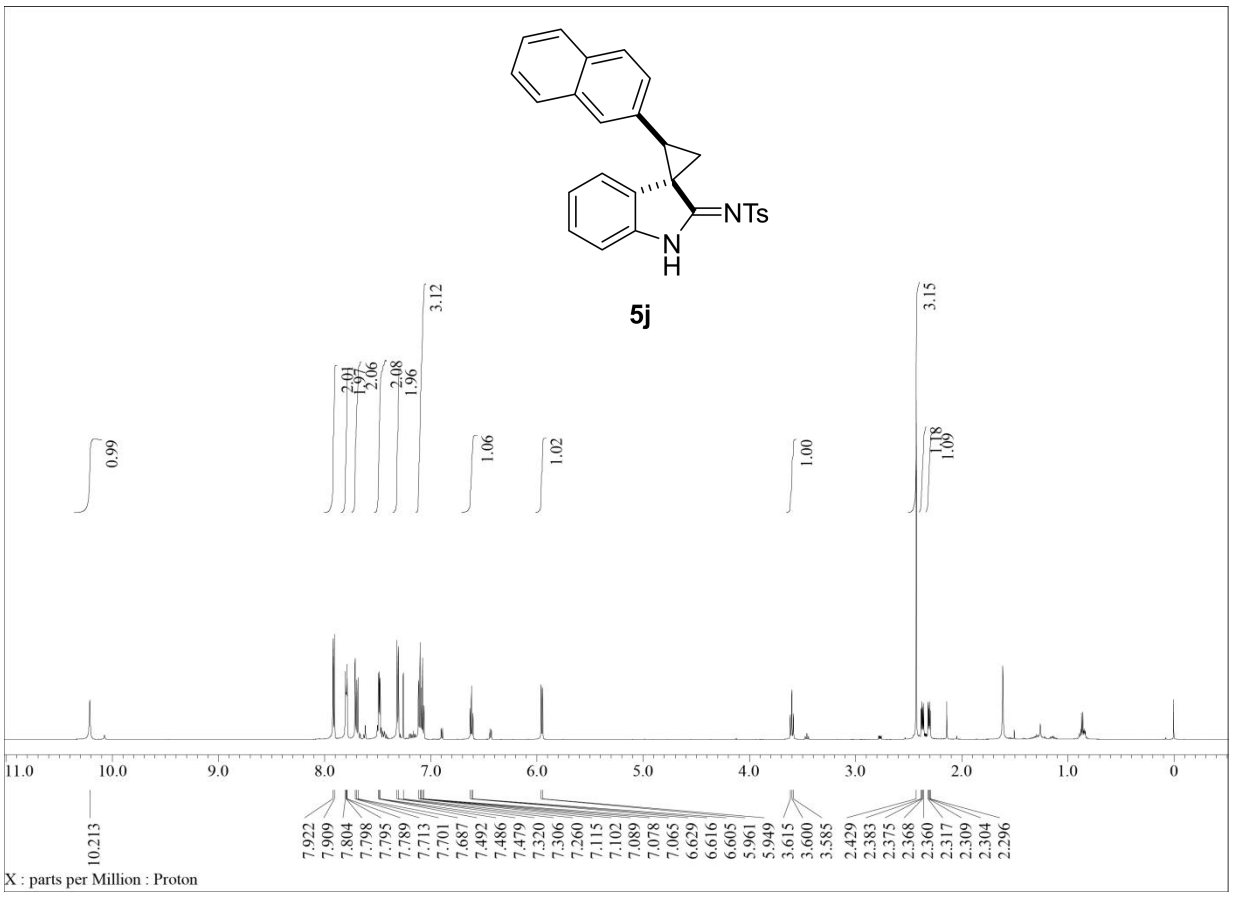

CH3
NTs
N
H
5g
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.5
143.0
140.6
139.5
139.1
133.1
129.9
129.4
128.4
128.0
127.7
127.0
126.2
125.8
122.8
120.0
110.8
77.2
77.0
76.8
39.3
36.6
25.2
21.5
18.8
X : parts per Million : Carbon13

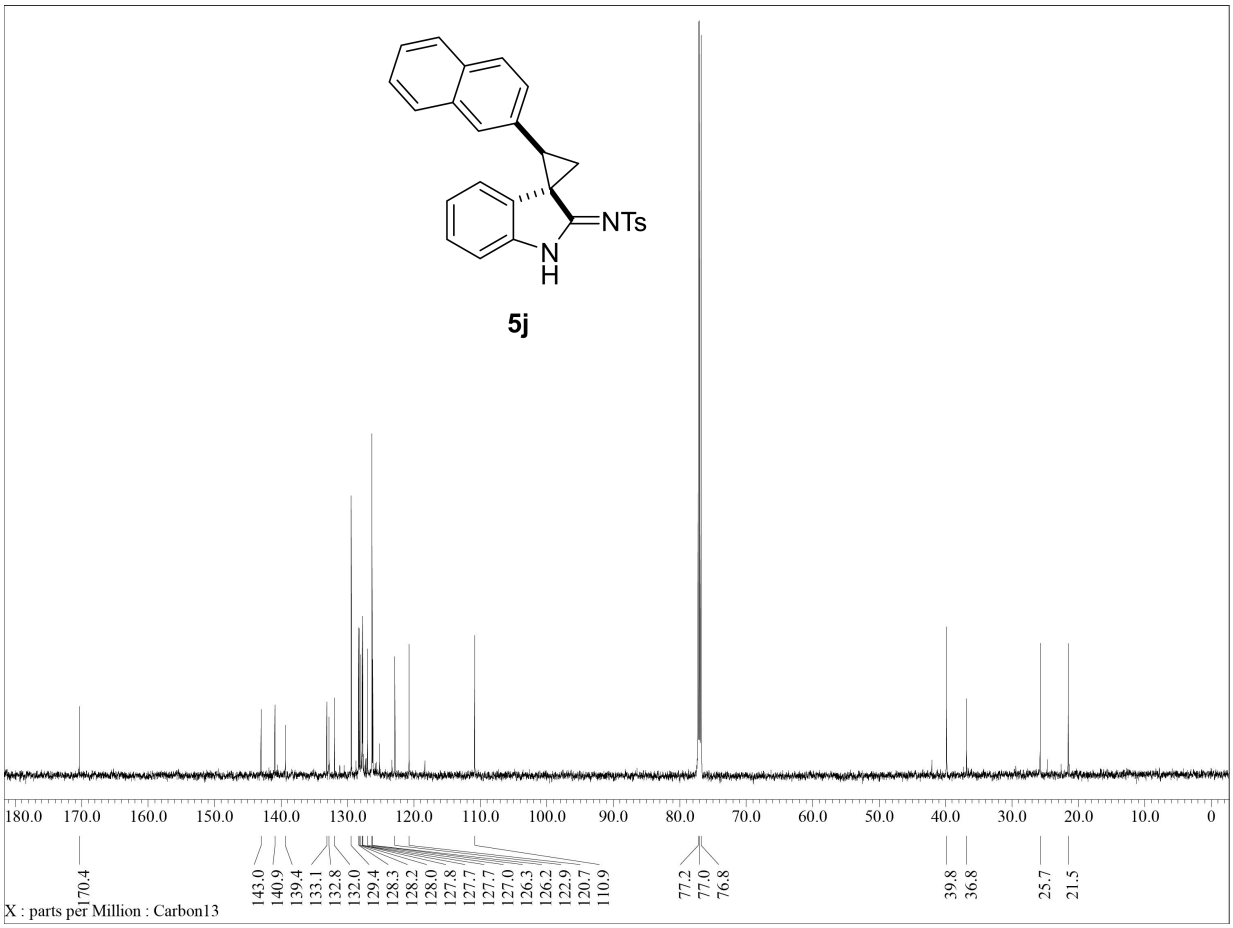

O
NTs
N
H
5h
3.05
3.15
2.02
2.09
1.07
1.03
1.02
1.03
1.04
0.99
0.88
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.065
7.863
7.850
7.315
7.313
7.298
7.285
7.260
7.200
7.188
7.176
7.055
7.042
6.884
6.871
6.858
6.518
6.505
6.340
6.338
6.335
6.332
6.287
6.281
3.234
3.219
3.204
2.418
2.313
2.305
2.299
2.293
2.289
2.281
2.273
2.265
X : parts per Million : Proton

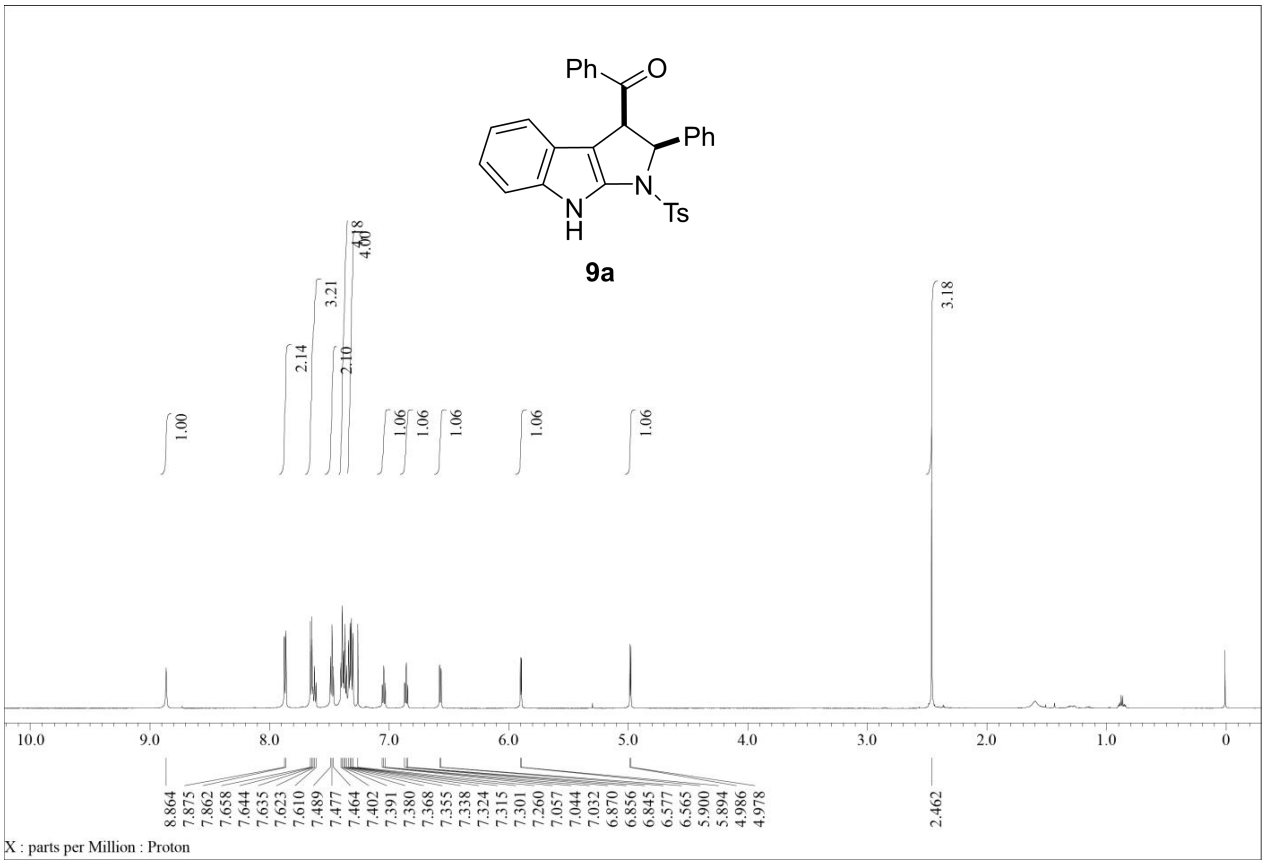

O
NTs
N
H
5h
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.3
149.3
143.1
142.3
141.0
139.2
129.4
127.5
127.4
126.3
123.2
120.2
110.9
110.7
110.0
77.2
77.0
76.8
37.3
32.4
24.0
21.5
X : parts per Million : Carbon13


S
NTs
N
H
5i
3.08
2.00
2.06
1.92
1.05
1.03
1.00
0.93
1.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.120
7.878
7.865
7.301
7.288
7.260
7.200
7.198
7.191
7.181
7.179
7.168
7.166
7.076
7.063
6.957
6.951
6.949
6.943
6.891
6.888
6.885
6.883
6.880
6.821
6.808
6.795
6.252
6.239
3.403
3.389
3.374
2.418
2.355
2.347
2.340
2.332
2.192
2.184
2.179
2.172
1.607
X : parts per Million : Proton


S
NTs
N
H
5i
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.6
143.1
141.0
139.2
138.0
129.4
127.9
127.3
127.2
126.8
126.3
125.7
123.0
120.4
110.9
77.2
77.0
76.8
37.5
33.8
26.6
21.5
X : parts per Million : Carbon13


NTs
N
H
5j
0.99
2.01
1.97
2.06
2.08
1.96
3.12
1.06
1.02
1.00
3.15
1.18
1.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.213
7.922
7.909
7.804
7.798
7.795
7.789
7.713
7.701
7.687
7.492
7.486
7.479
7.320
7.306
7.260
7.115
7.102
7.089
7.078
7.065
6.629
6.616
6.605
5.961
5.949
3.615
3.600
3.585
2.429
2.383
2.375
2.368
2.360
2.317
2.309
2.304
2.296
X : parts per Million : Proton


NTs
N
H
5j
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.4
143.0
140.9
139.4
133.1
132.8
132.0
129.4
128.3
128.2
128.0
127.8
127.7
127.7
127.0
126.3
126.2
122.9
120.7
110.9
77.2
77.0
76.8
39.8
36.8
25.7
21.5
X : parts per Million : Carbon13


Ph
O
Ph
N
Ts
N
H
9a
1.00
2.14
3.21
2.10
4.18
4.00
1.06
1.06
1.06
1.06
1.06
3.18
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.864
7.875
7.862
7.658
7.644
7.635
7.623
7.610
7.489
7.477
7.464
7.402
7.391
7.380
7.368
7.355
7.338
7.324
7.315
7.301
7.260
7.057
7.044
7.032
6.870
6.856
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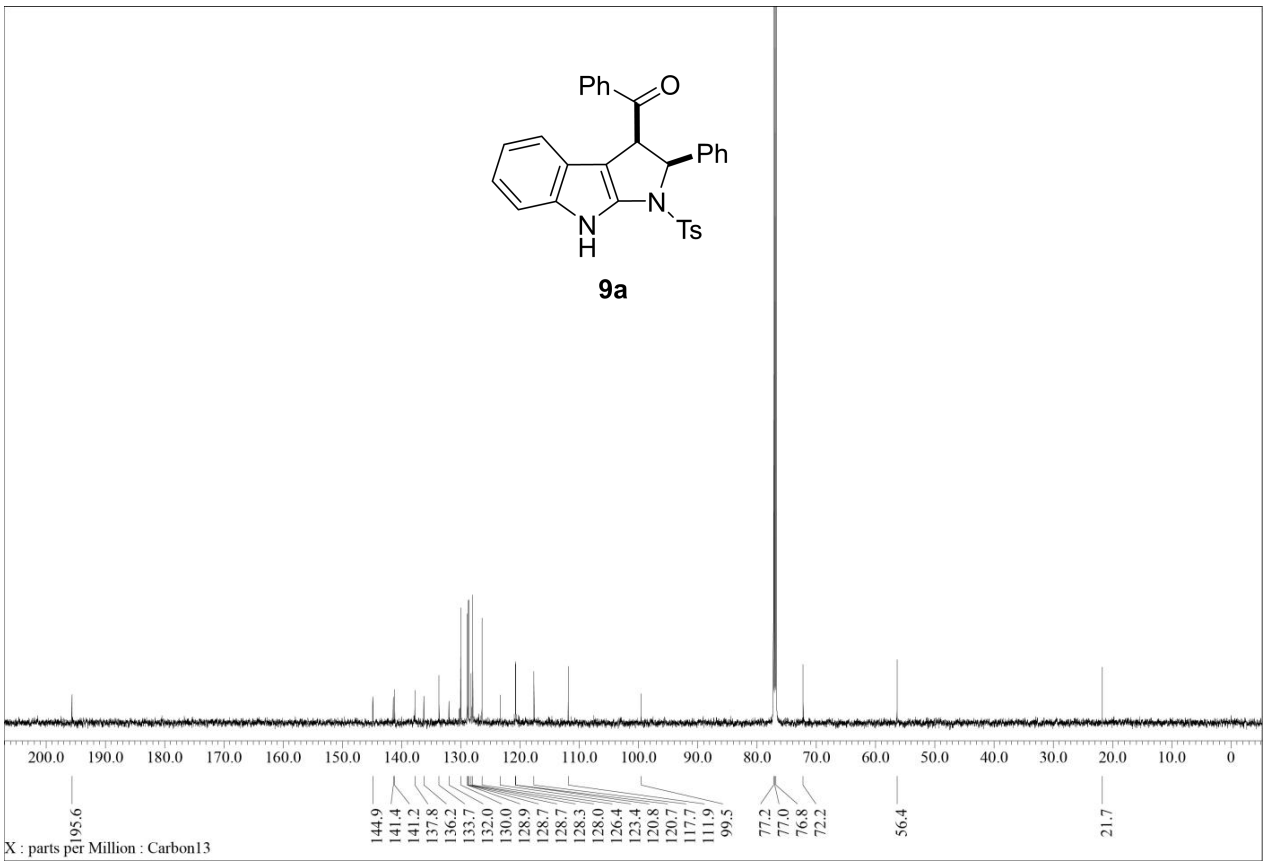
6.577
6.565
5.900
5.894
4.986
4.978
2.462
X : parts per Million : Proton


Ph
O
Ph
N
Ts
N
H
9a
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180.0
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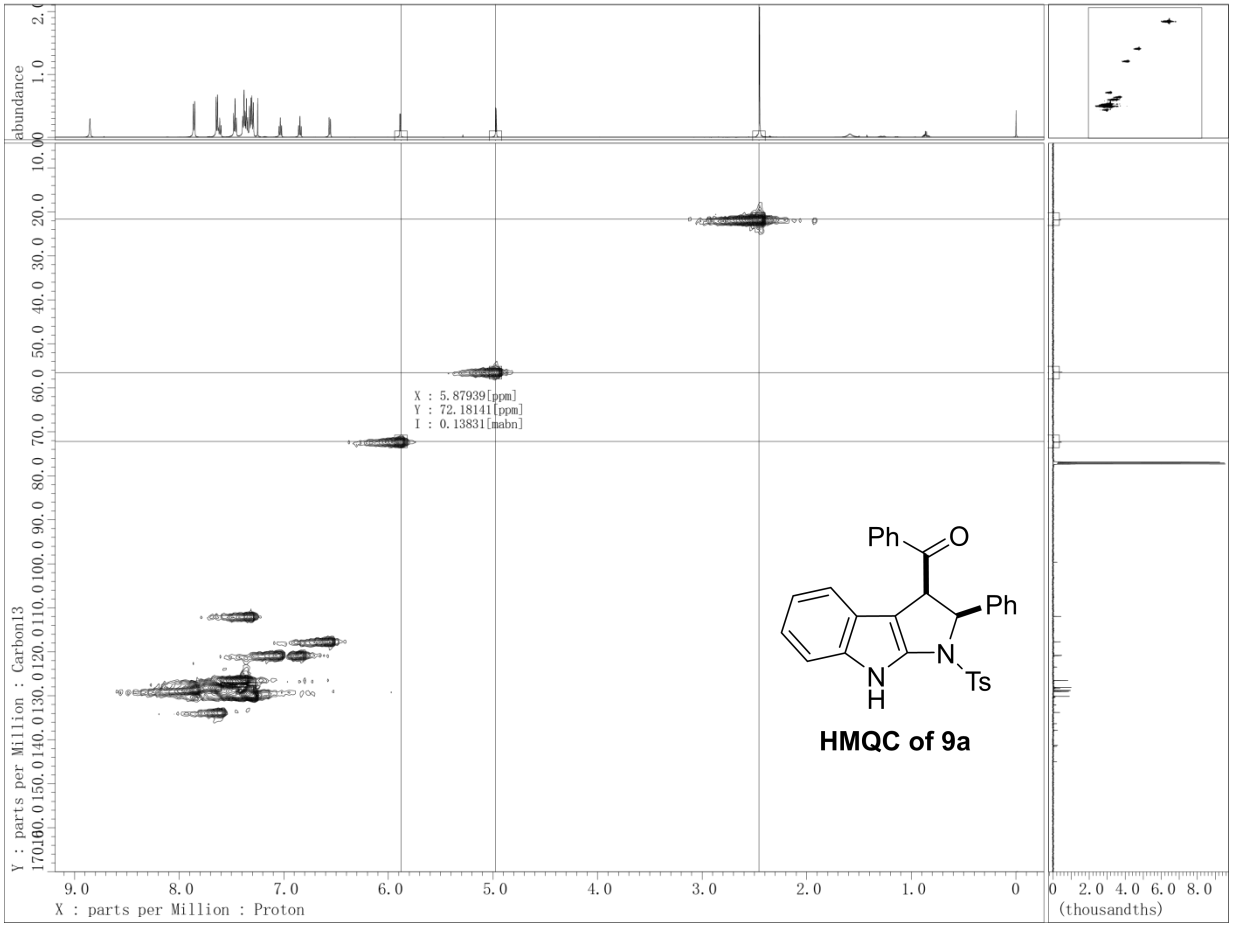
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
195.6
144.9
141.4
141.2
137.8
136.2
133.7
132.0
130.0
128.9
128.7
128.7
128.3
128.0
126.4
123.4
120.8
120.7
117.7
111.9
99.5
77.2
77.0
76.8
72.2
56.4
21.7
X : parts per Million : Carbon13



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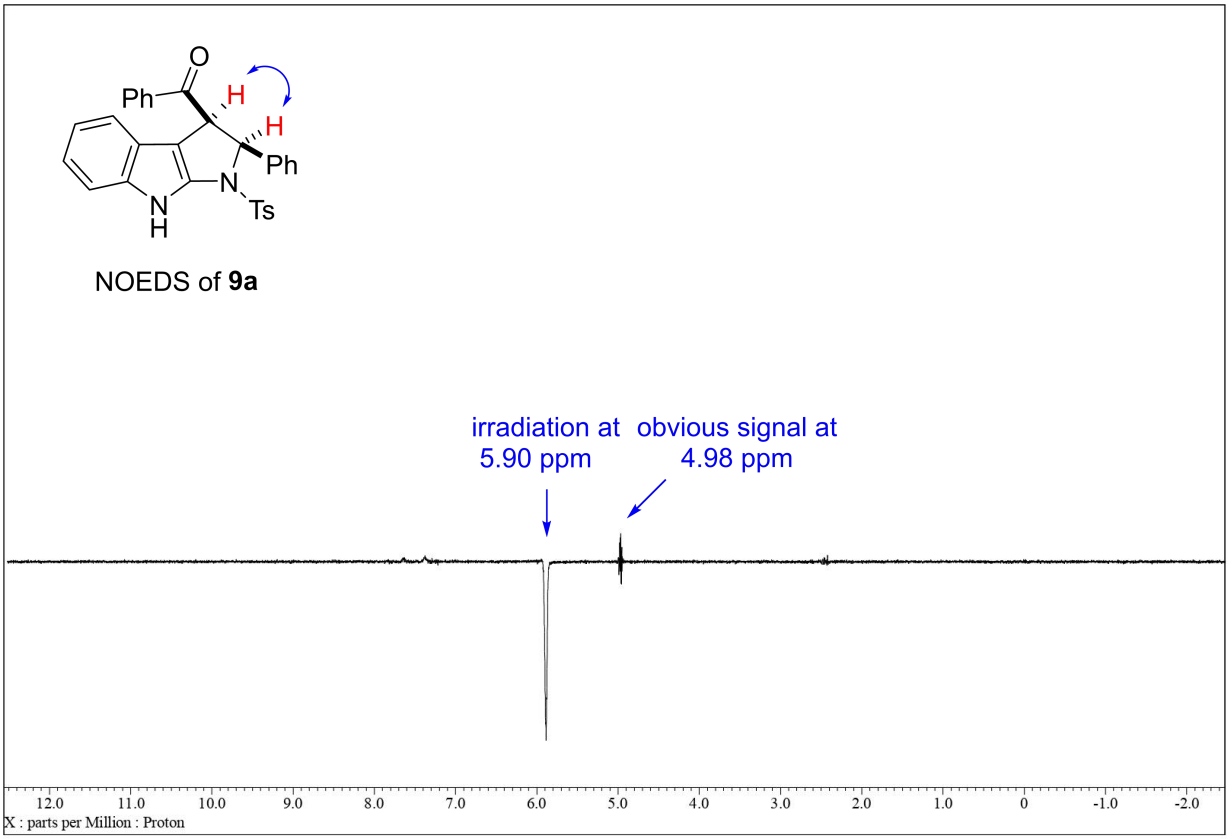
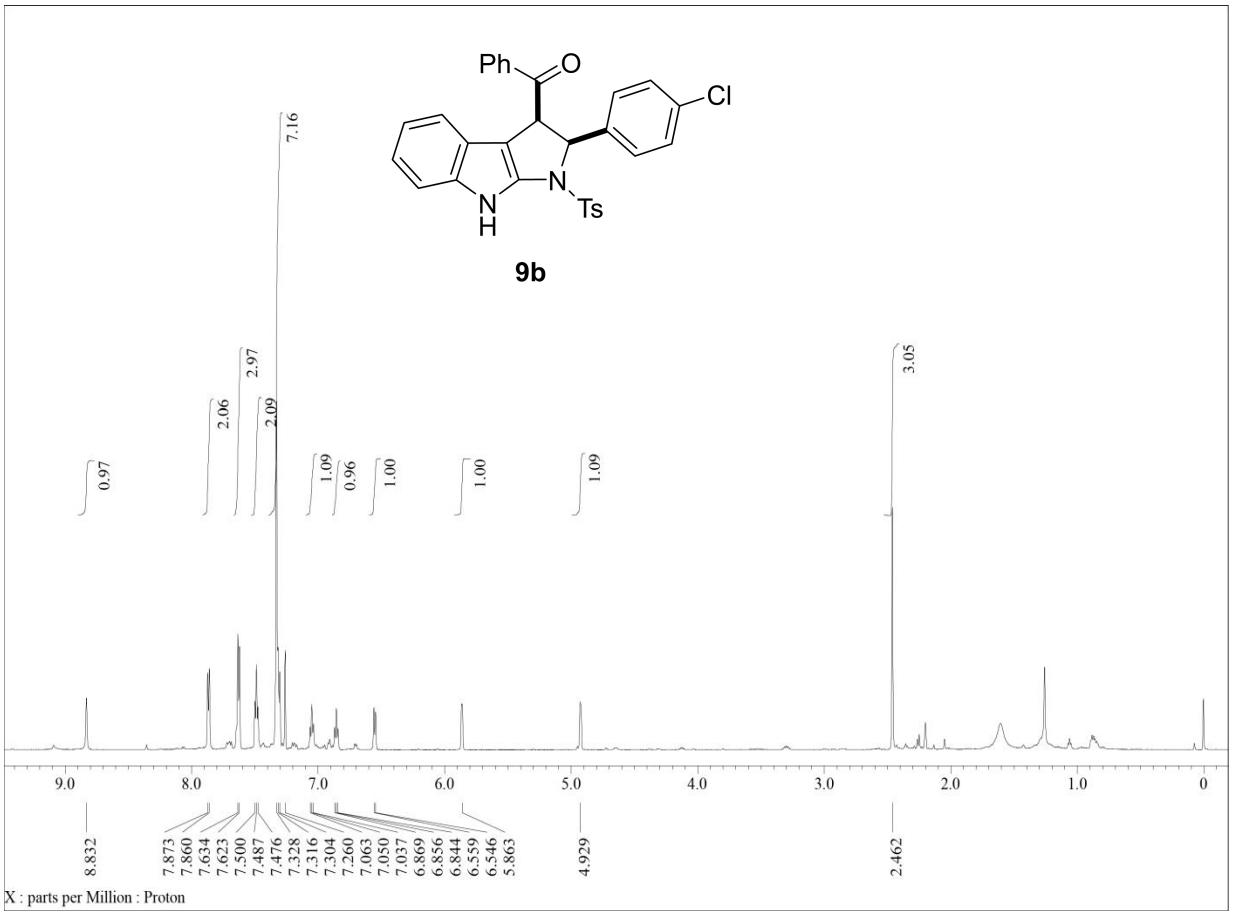


NOEDS of **9a**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Cl
N
H
N
Ts
9b
7.16
2.97
2.06
2.09
3.05
0.97
1.09
0.96
1.00
1.00
1.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.832
7.873
7.860
7.634
7.623
7.500
7.487
7.476
7.328
7.316
7.304
7.260
7.063
7.050
7.037
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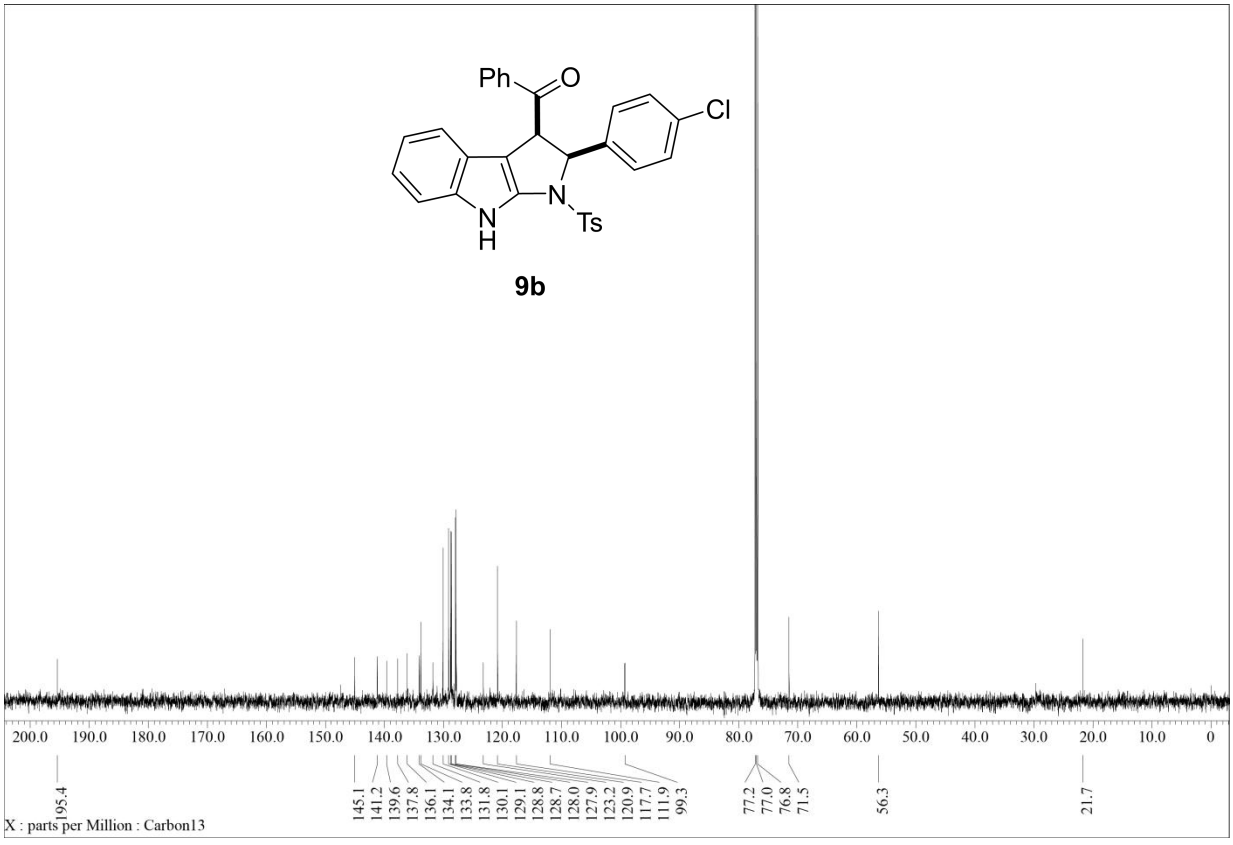
6.856
6.844
6.559
6.546
5.863
4.929
2.462
X : parts per Million : Proton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H
N
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145.1
141.2
139.6
137.8
136.1
134.1
133.8
131.8
130.1
129.1
128.8
128.7
128.0
127.9
123.2
120.9
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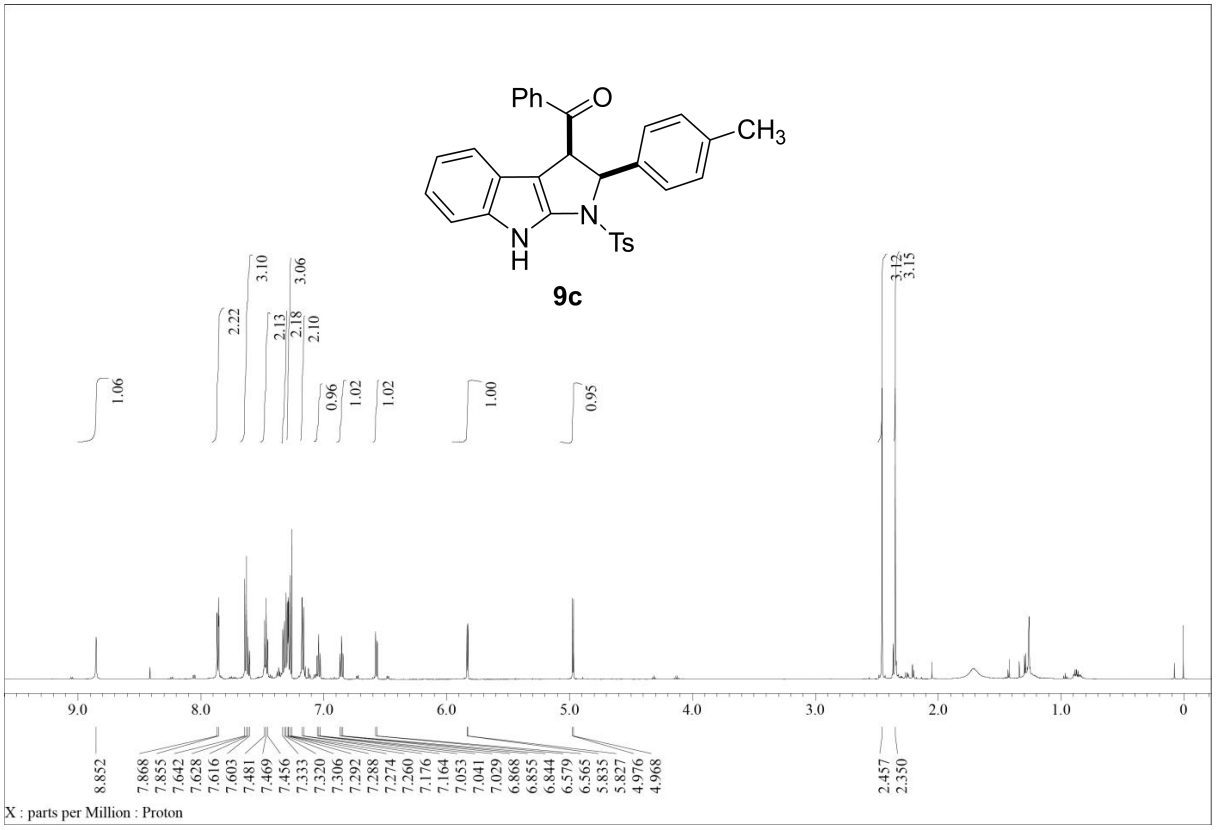
111.9
99.3
77.2
77.0
76.8
71.5
56.3
21.7
X : parts per Million : Carbon13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O
CH3
N
Ts
H
9c
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2.13
2.18
3.06
2.10
0.96
1.02
1.02
1.00
0.95
3.12
3.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.852
7.868
7.855
7.642
7.628
7.616
7.603
7.481
7.469
7.456
7.333
7.320
7.306
7.292
7.288
7.274
7.260
7.176
7.164
7.053
7.041
7.029
6.868
6.855
6.844
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6.565
5.835
5.827
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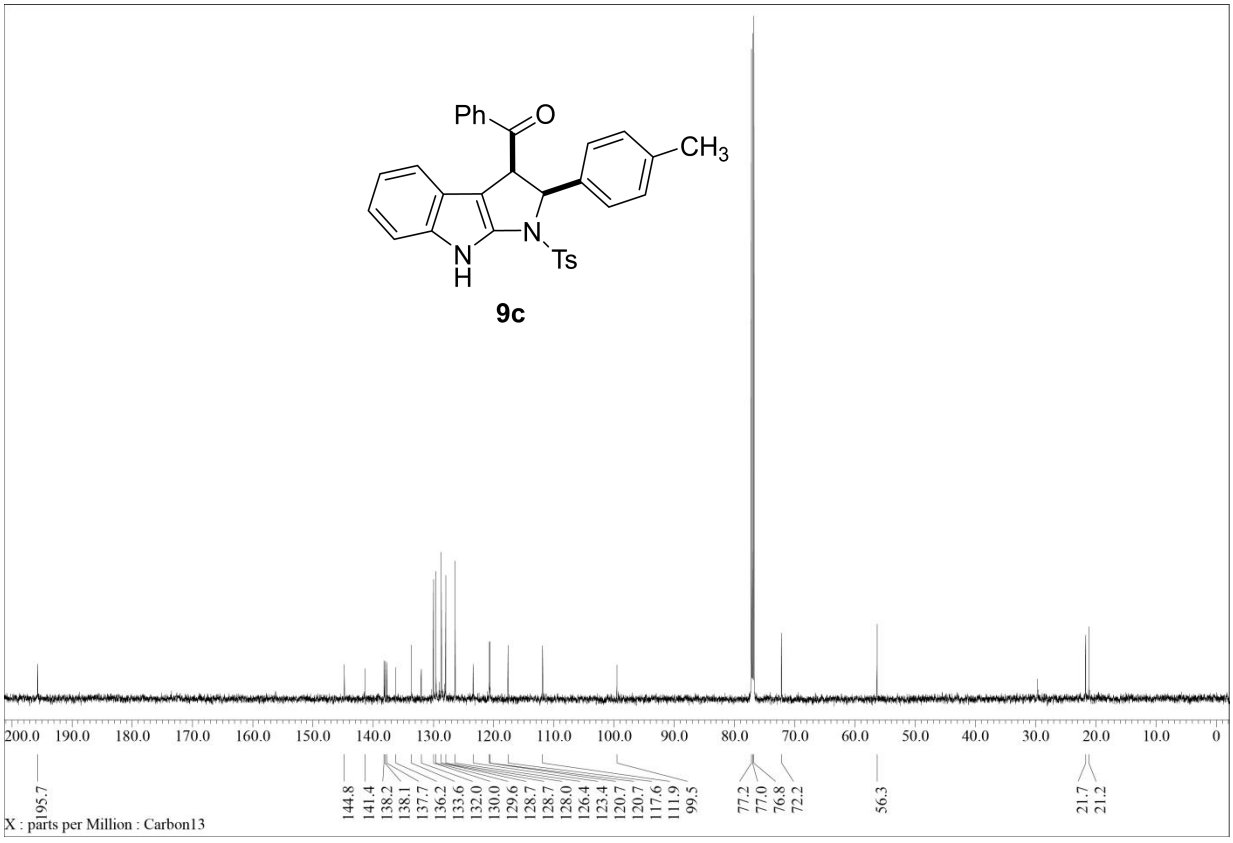
4.968
2.457
2.350
X : parts per Million : Proton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CH3
N
Ts
H
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150.0
140.0
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60.0
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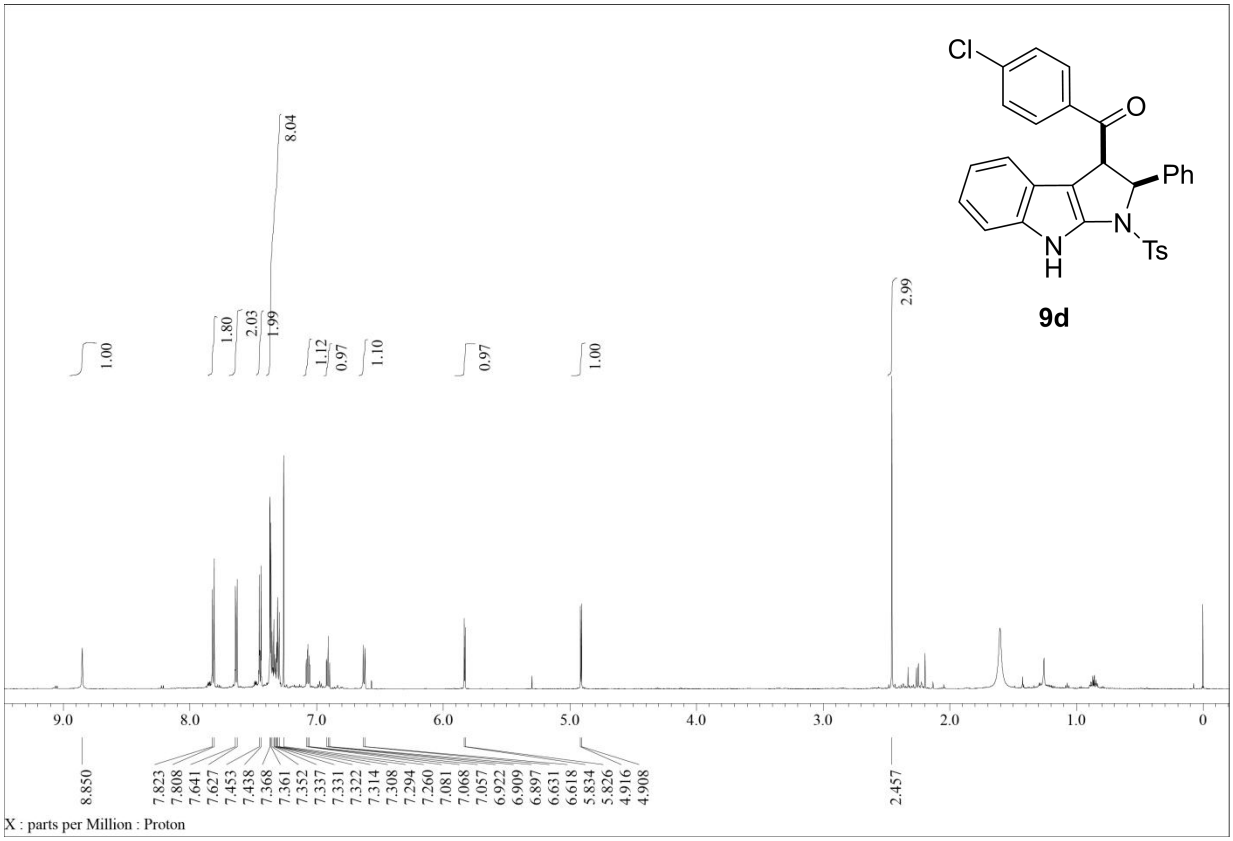
40.0
30.0
20.0
10.0
0
195.7
144.8
141.4
138.2
138.1
137.7
136.2
133.6
132.0
130.0
129.6
128.7
128.7
128.0
126.4
123.4
120.7
120.7
117.6
111.9
99.5
77.2
77.0
76.8
72.2
56.3
21.7
21.2
X : parts per Million : Carbon13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Ph
N
Ts
N
H
9d
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2.99
1.80
2.03
1.99
1.12
0.97
1.10
0.97
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.850
7.823
7.808
7.641
7.627
7.453
7.438
7.368
7.361
7.352
7.337
7.331
7.322
7.314
7.308
7.294
7.260
7.081
7.068
7.057
6.922
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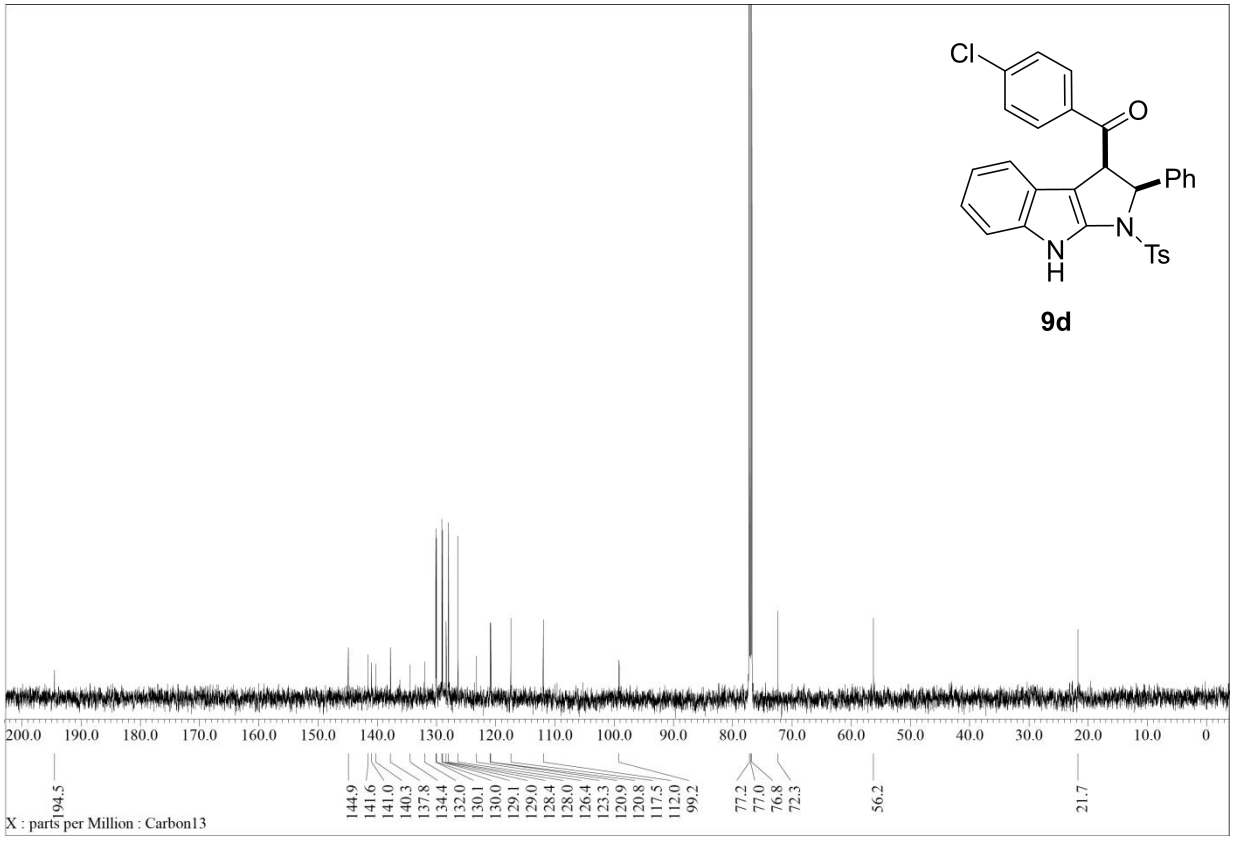
6.631
6.618
5.834
5.826
4.916
4.908
2.457
X : parts per Million : Proton


Cl
O
Ph
N
Ts
N
H
9d
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180.0
170.0
160.0
150.0
140.0
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120.0
110.0
100.0
90.0
80.0
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30.0
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0
194.5
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140.3
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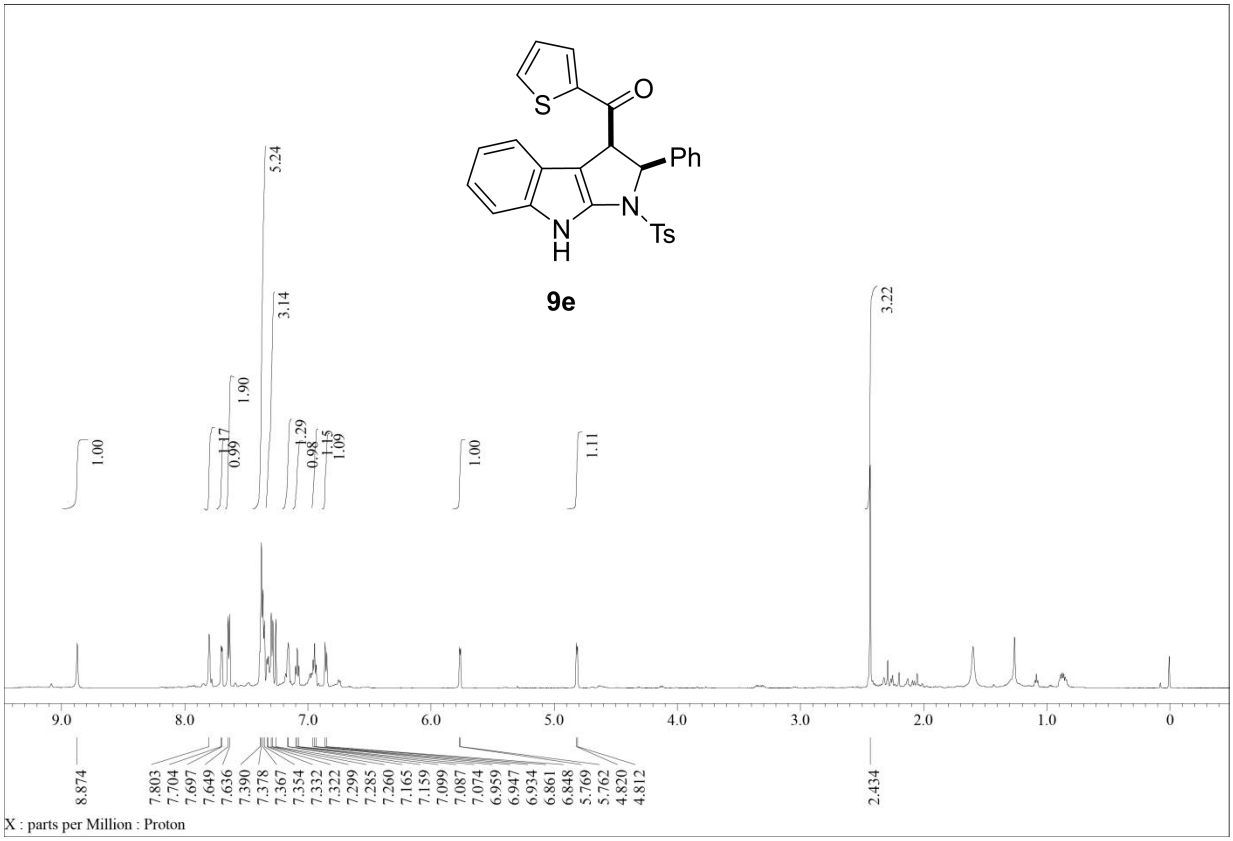
129.0
128.4
128.0
126.4
123.3
120.9
120.8
117.5
112.0
99.2
77.2
77.0
76.8
72.3
56.2
21.7
X : parts per Million : Carbon13


S
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Ph
N
Ts
H
9e
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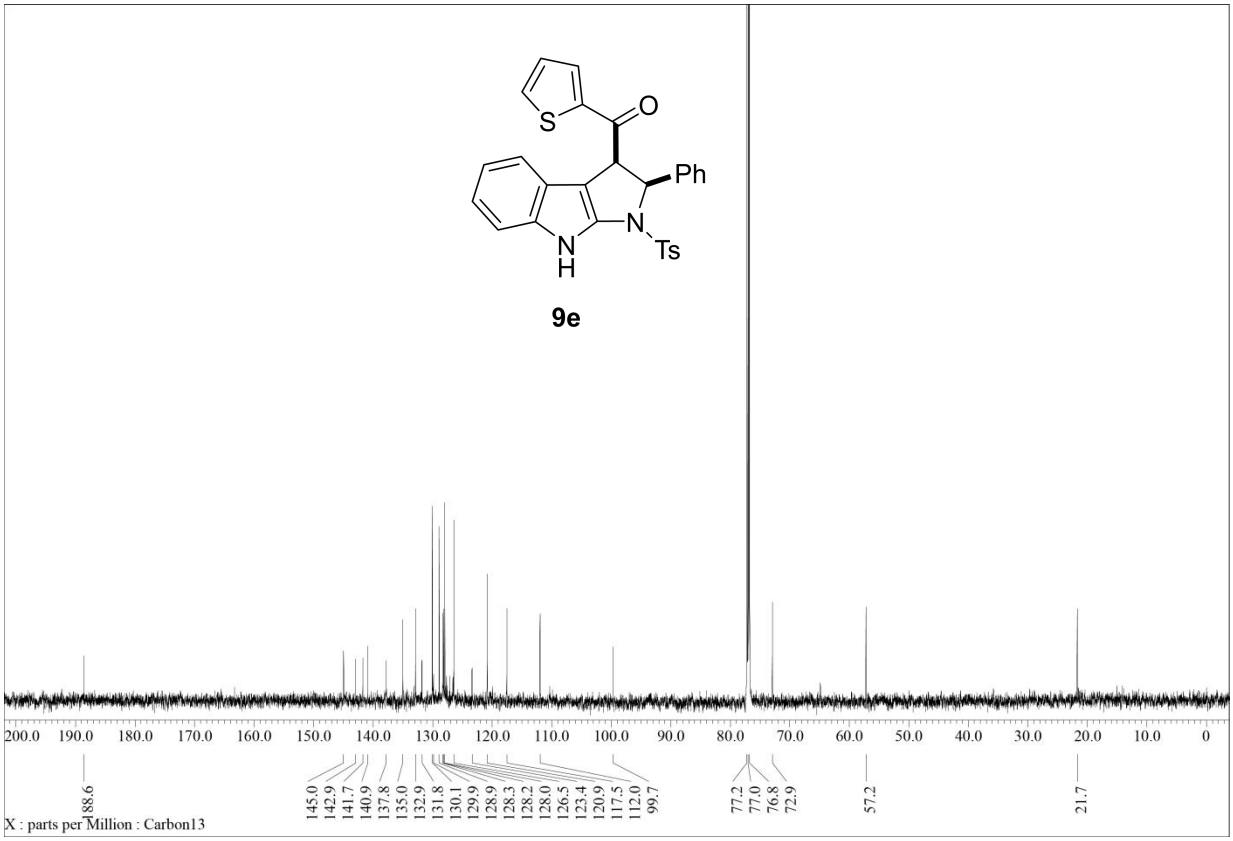
3.14
3.22
1.90
1.17
0.99
1.29
0.98
1.15
1.09
1.00
1.00
1.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.874
7.803
7.704
7.697
7.649
7.636
7.390
7.378
7.367
7.354
7.332
7.322
7.299
7.285
7.260
7.165
7.159
7.099
7.087
7.074
6.959
6.947
6.934
6.861
6.848
5.769
5.762
4.820
4.812
2.434
X : parts per Million : Proton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O
Ph
N
Ts
H
9e
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180.0
170.0
160.0
150.0
140.0
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120.0
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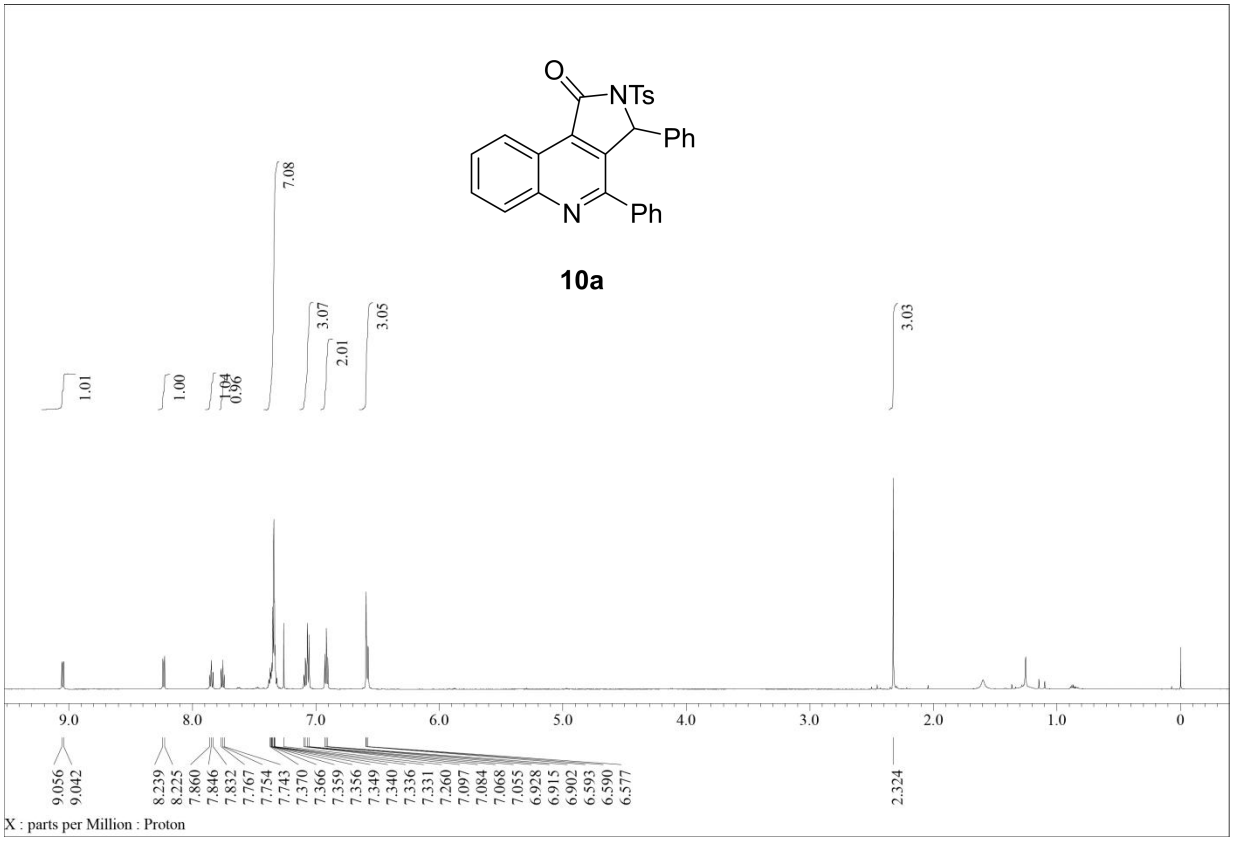
50.0
40.0
30.0
20.0
10.0
0
188.6
145.0
142.9
141.7
140.9
137.8
135.0
132.9
131.8
130.1
129.9
128.9
128.3
128.2
128.0
126.5
123.4
120.9
117.5
112.0
99.7
77.2
77.0
76.8
72.9
57.2
21.7
X : parts per Million : Carbon13


O
NTs
Ph
N
Ph
10a
7.08
3.07
3.05
2.01
3.03
1.01
1.00
1.04
0.96
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.056
9.042
8.239
8.225
7.860
7.846
7.832
7.767
7.754
7.743
7.370
7.366
7.359
7.356
7.349
7.340
7.336
7.331
7.260
7.097
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6.593
6.590
6.577
2.324
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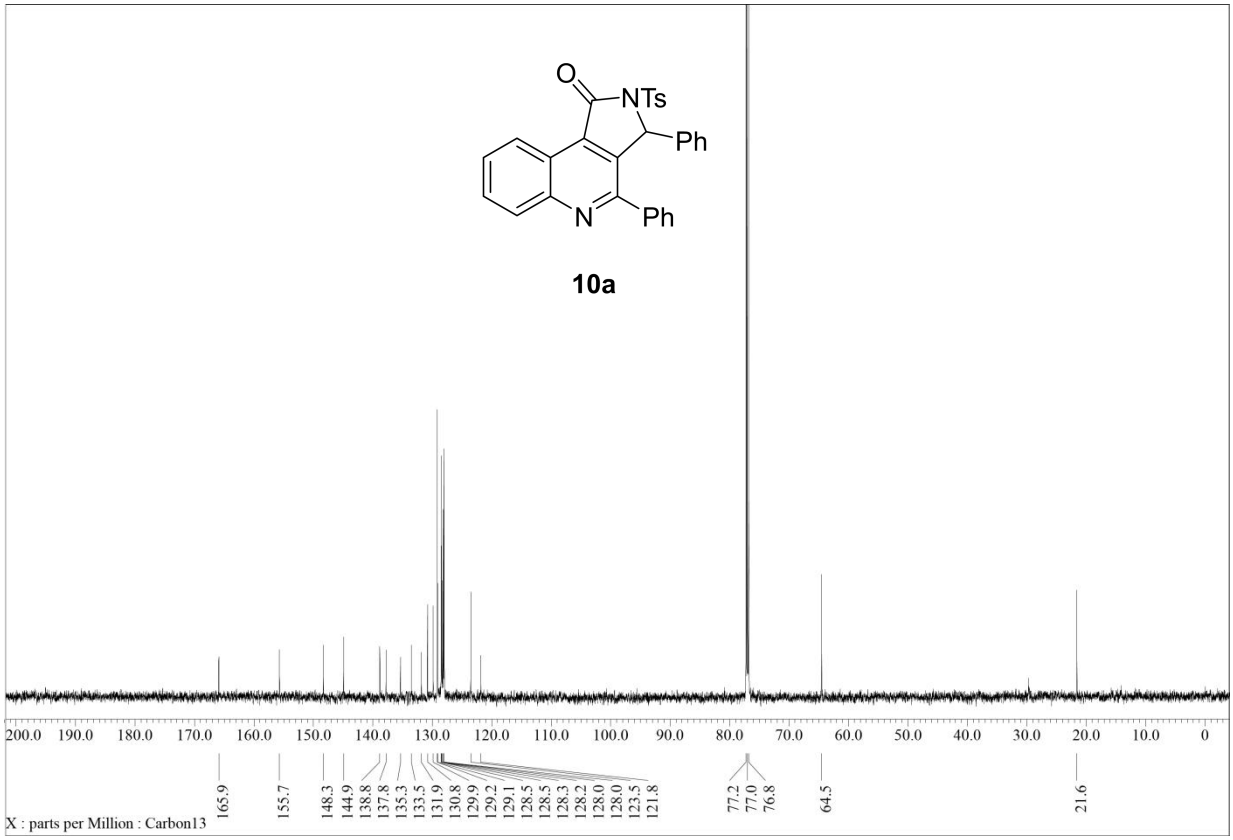
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NTs
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N
Ph
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160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.9
155.7
148.3
144.9
138.8
137.8
135.3
133.5
131.9
130.8
129.9
129.2
129.1
128.5
128.5
128.3
128.2
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128.0
123.5
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77.2
77.0
76.8
64.5
21.6
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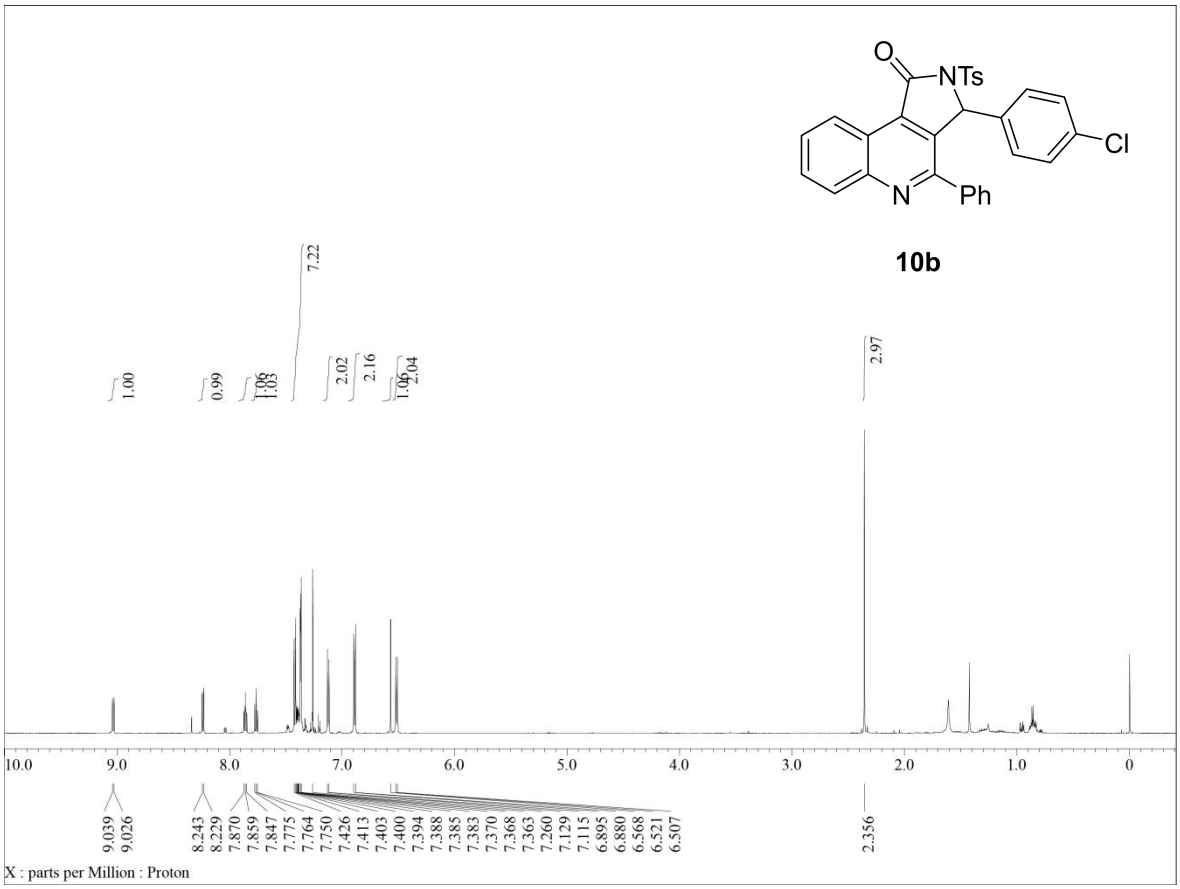
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NTs
Cl
N
Ph
10b
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2.97
1.00
0.99
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2.16
2.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.039
9.026
8.243
8.229
7.870
7.859
7.847
7.775
7.764
7.750
7.426
7.413
7.403
7.400
7.394
7.388
7.385
7.383
7.370
7.368
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6.521
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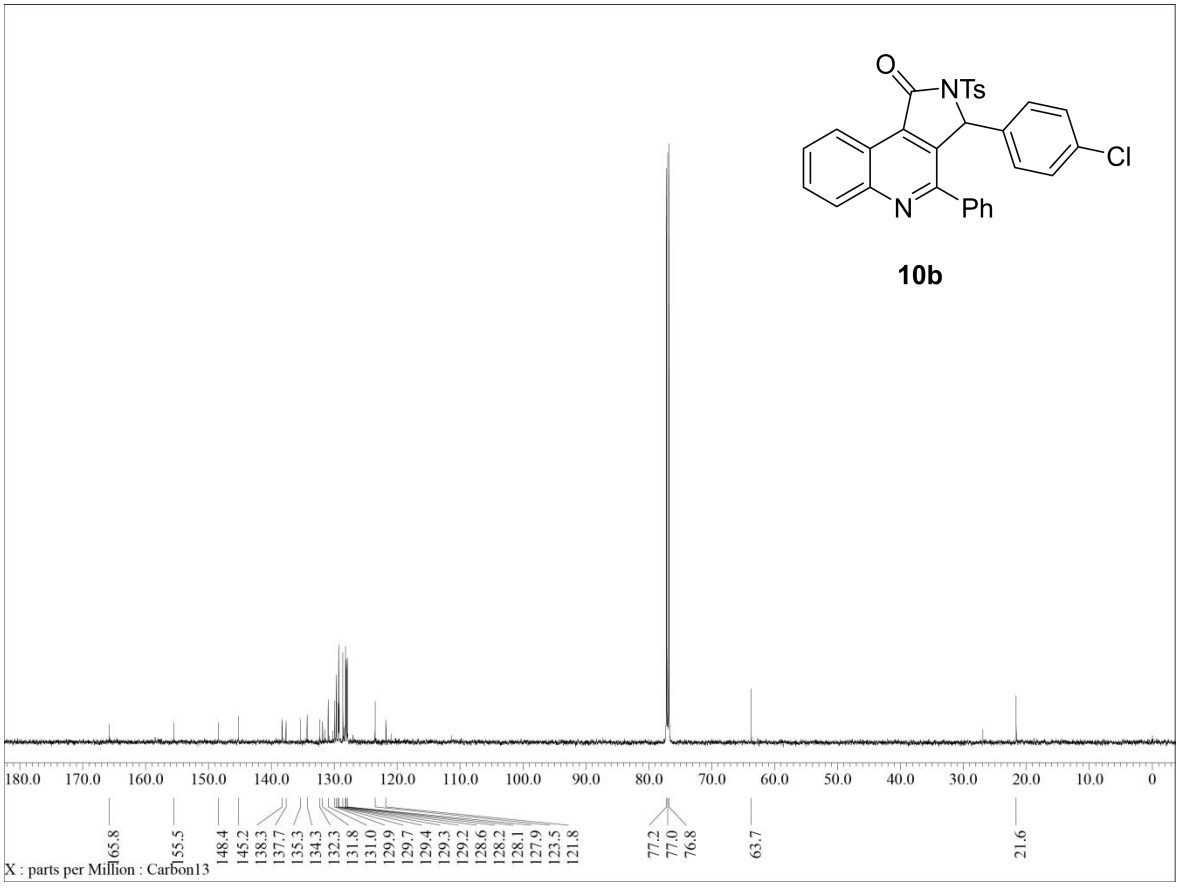
O
NTs
Cl
N
Ph
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160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.8
155.5
148.4
145.2
138.3
137.7
135.3
134.3
132.3
131.8
131.0
129.9
129.7
129.4
129.3
129.2
128.6
128.2
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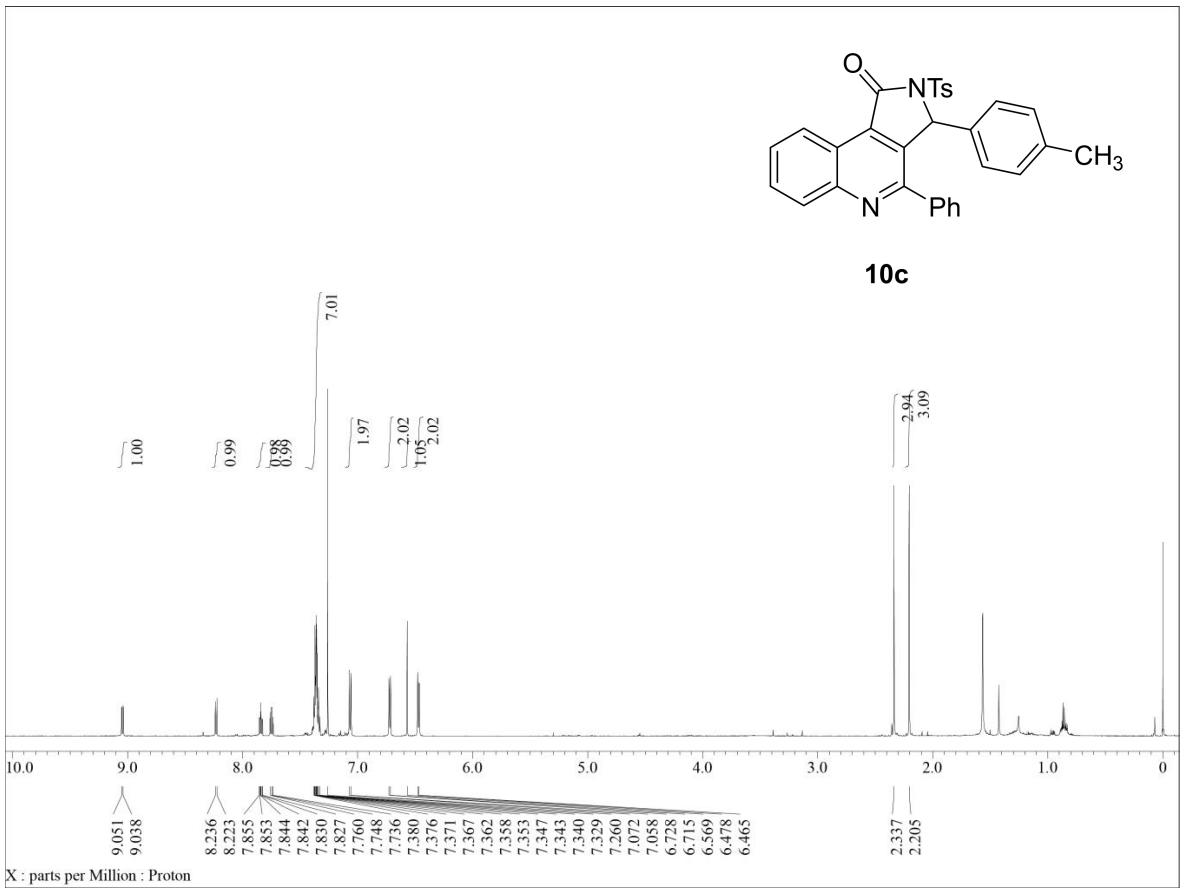
127.9
123.5
121.8
77.2
77.0
76.8
63.7
21.6
X : parts per Million : Carbon13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CH3
N
Ph
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1.97
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1.05
2.02
2.94
3.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.051
9.038
8.236
8.223
7.855
7.853
7.844
7.842
7.830
7.827
7.760
7.748
7.736
7.380
7.376
7.371
7.367
7.362
7.358
7.353
7.347
7.343
7.340
7.329
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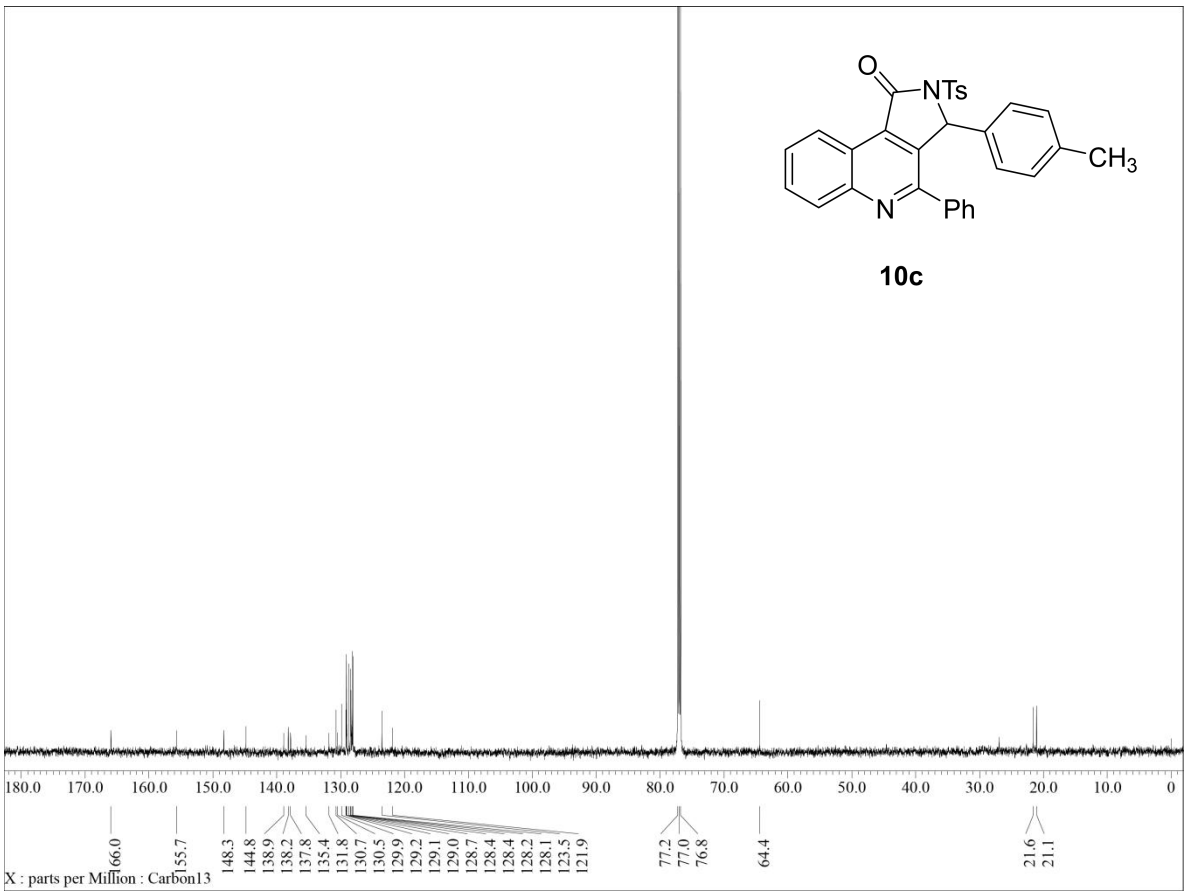
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Ph
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
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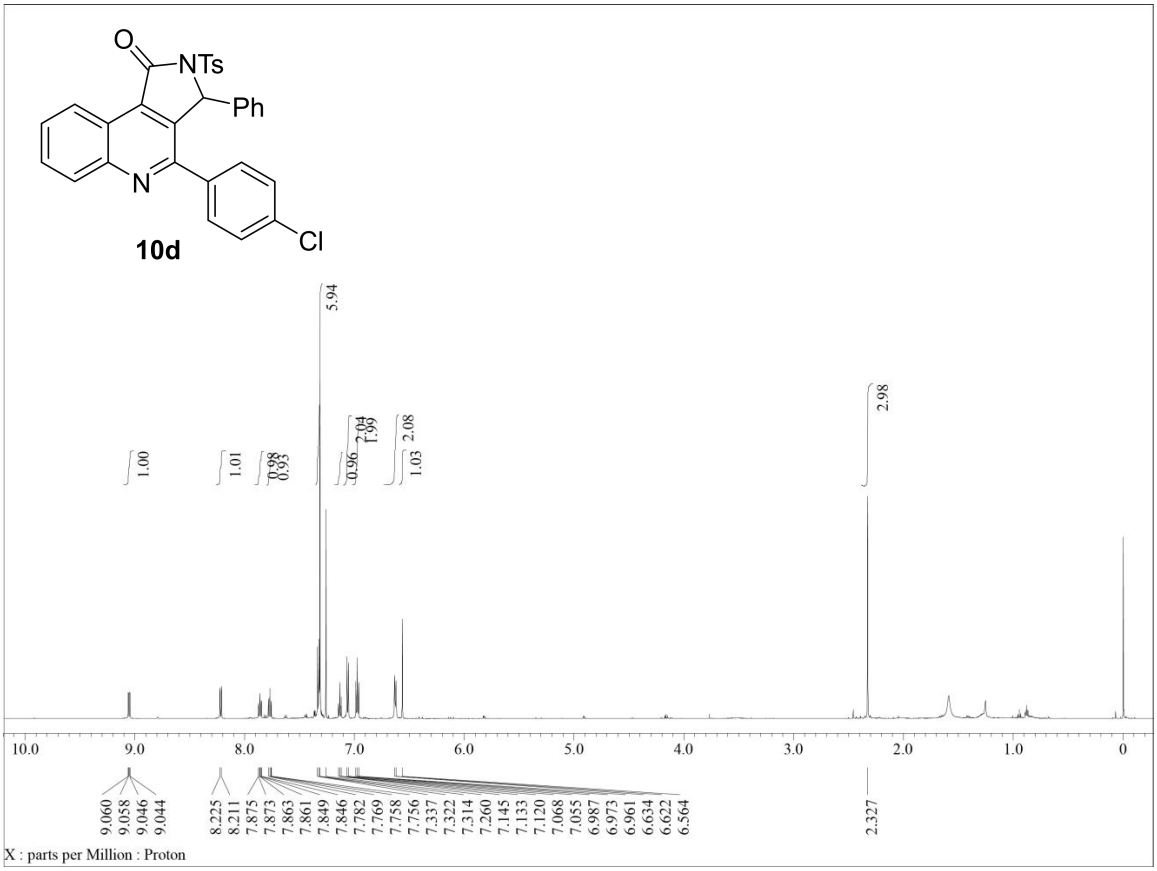
50.0
40.0
30.0
20.0
10.0
0
66.0
55.7
148.3
144.8
138.9
138.2
137.8
135.4
131.8
130.7
130.5
129.9
129.2
129.1
129.0
128.7
128.4
128.4
128.2
128.1
123.5
121.9
77.2
77.0
76.8
64.4
21.6
21.1
X : parts per Million : Carbon13


O
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Cl
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1.01
0.98
0.93
0.96
2.04
1.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.060
9.058
9.046
9.044
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8.211
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7.849
7.846
7.782
7.769
7.758
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7.337
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7.314
7.260
7.145
7.133
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6.622
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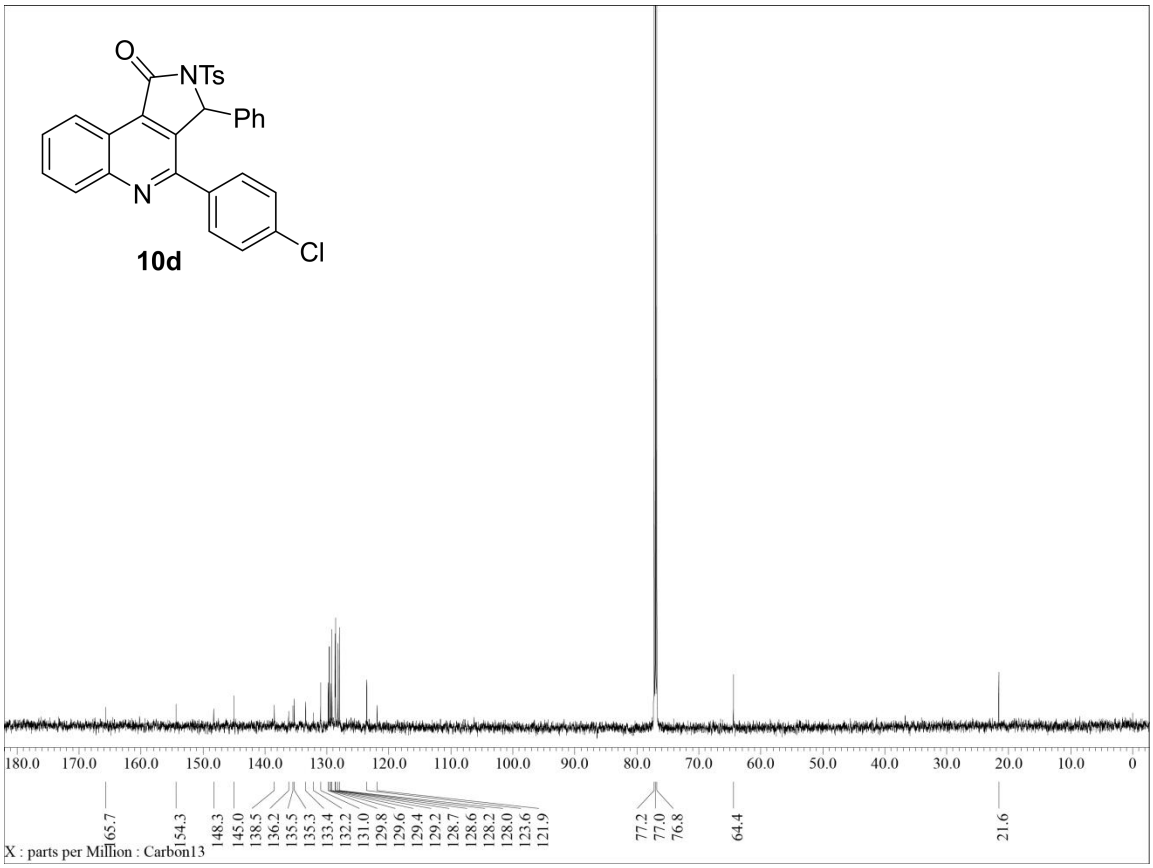
2.327
X : parts per Million : Proton


O
NTs
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N
Cl
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150.0
140.0
130.0
120.0
110.0
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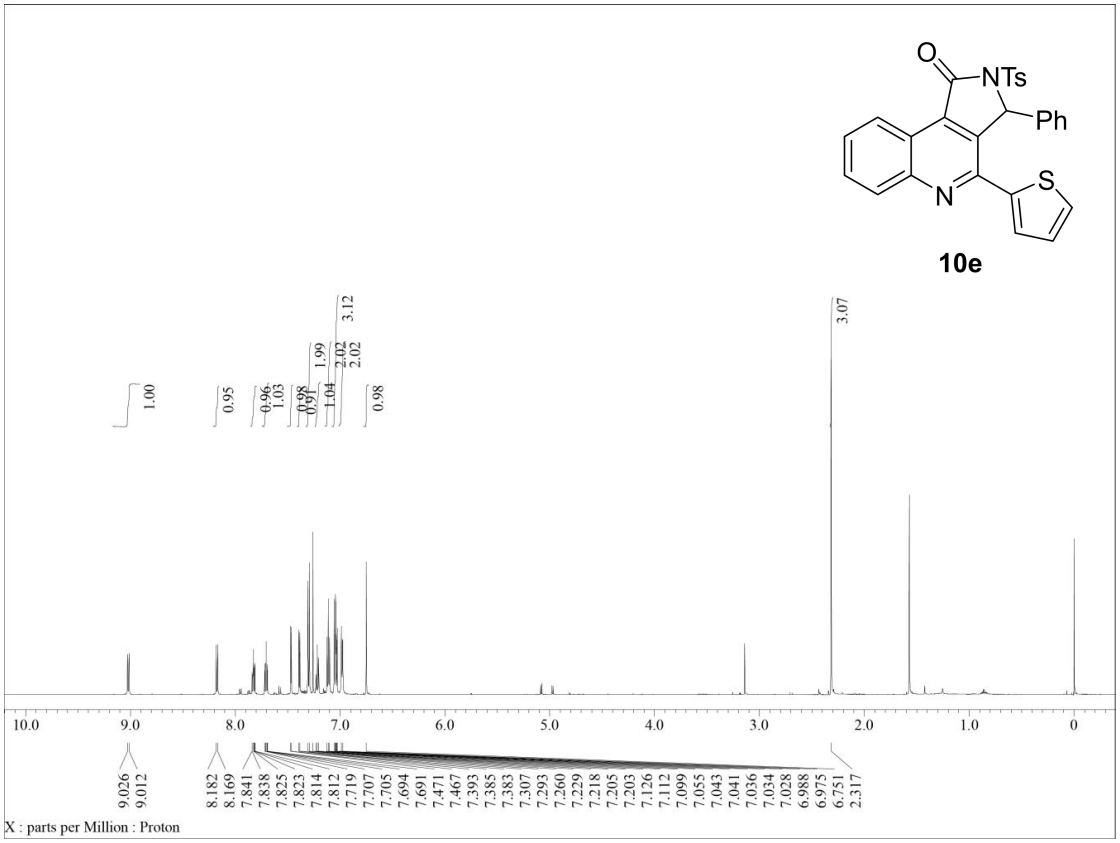
20.0
10.0
0
165.7
154.3
148.3
145.0
138.5
136.2
135.5
135.3
133.4
132.2
131.0
129.8
129.6
129.4
129.2
128.7
128.6
128.2
128.0
123.6
121.9
77.2
77.0
76.8
64.4
21.6
X : parts per Million : Carbon13


O
NTs
Ph
S
N
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0.96
1.03
0.98
0.97
1.99
1.04
2.02
2.02
3.12
0.98
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.026
9.012
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7.825
7.823
7.814
7.812
7.719
7.707
7.705
7.694
7.691
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7.467
7.393
7.385
7.383
7.307
7.293
7.260
7.229
7.218
7.205
7.203
7.126
7.112
7.099
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7.036
7.034
7.028
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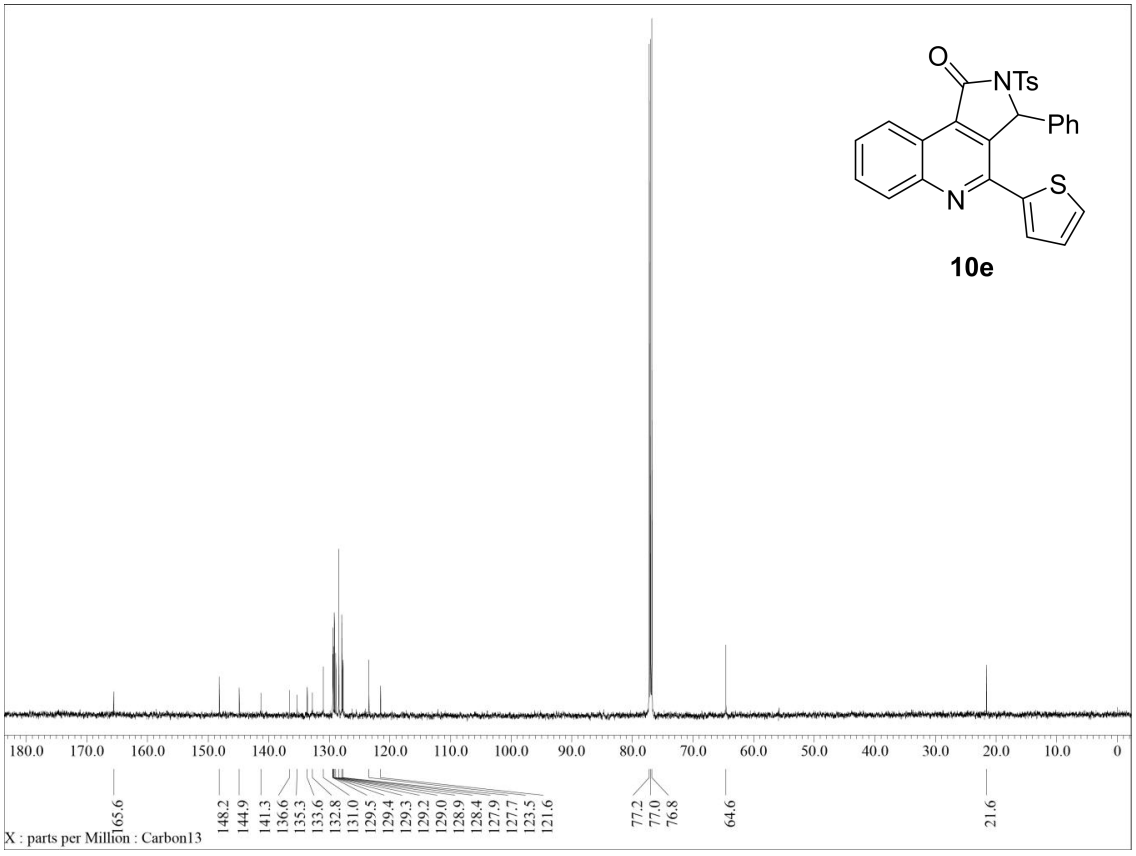
O
NTs
Ph
S
N
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140.0
130.0
120.0
110.0
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30.0
20.0
10.0
0
165.6
148.2
144.9
141.3
136.6
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131.0
129.5
129.4
129.3
129.2
129.0
128.9
128.4
127.9
127.7
123.5
121.6
77.2
77.0
76.8
64.6
21.6
X : parts per Million : Carbon13