Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Dearomative [4 + 2] annulations between 3-nitroindoles and enals through oxidative N-heterocyclic carbene catalysis †

Hua Huang,[a,#] Qing-Zhu Li,[b,#] Yan-Qing Liu,[a,b] Hai-Jun Leng,[a,b] Peng Xiang,[b] Qing-Song Dai,[b] Xiang-Hong He,[a] Wei Huang,[a*] Jun-Long Li [b*]

[a] *State Key Laboratory of Southwestern Chinese Medicine Resources, School of Pharmacy, Chengdu University of Traditional Chinese Medicine, Chengdu 611137, China*

[b] *Antibiotics Research and Re-evaluation Key Laboratory of Sichuan Province, Sichuan Industrial Institute of Antibiotics, Chengdu University, Chengdu 610052, China*

Supplementary 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. 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 containing a 254 nm fluorescent indicator.
- Organic solutions were concentrated at 30-50 ℃ 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.

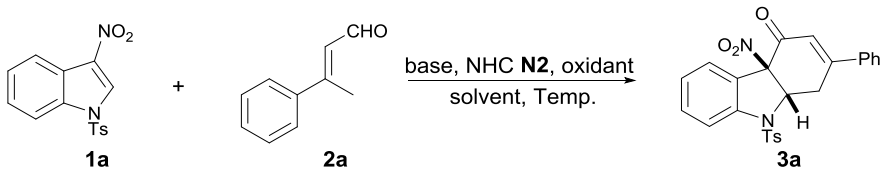
- Commercial reagents and solvents were obtained from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical. The 3-nitroindoles substrates were prepared according to literature procedure[1]. The 3-phenyl crotonaldehyde substrates were prepared according to literature procedure[2]. The nitrothiophene were prepared according to literature procedure[3].

Instrumentation.

- Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with *JEOL* 600MHz spectrometers. 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 ($CHCl_3$) or DMSO-d^6: δ 2.54 (DMSO)). 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* 600MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.00 ($CHCl_3$) or δ 39.52 (DMSO)). 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) ionization source.

2. Further Optimization Studies

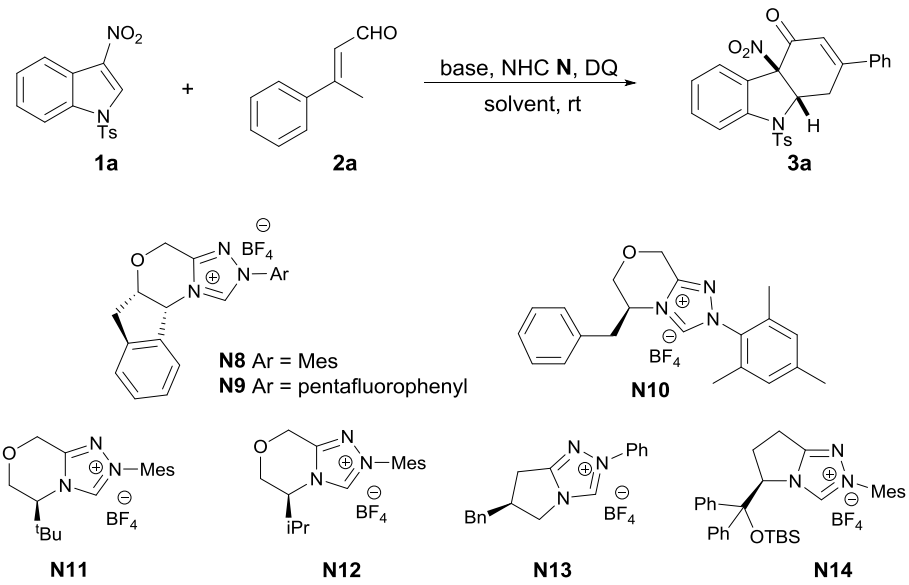
Table 1. Optimization of reaction conditions for racemic product **3a**[a].



entry	solvent	base	Temp. (℃)	oxidant	yield[%][b]
1[c]	Tol	K_2CO_3	rt	DQ	26
2	DCM	K_2CO_3	rt	DQ	23
3	THF	K_2CO_3	rt	DQ	39
4	MeCN	K_2CO_3	rt	DQ	35
5	C_6H_5Cl	K_2CO_3	rt	DQ	36
6[d]	Mesitylene	DABCO	rt	DQ	32
7	Mesitylene	NaOAc	rt	DQ	25
8	Mesitylene	$PhCO_2Na$	rt	DQ	22
9[d]	Mesitylene	DBU	rt	DQ	trace
10	Mesitylene	K_3PO_4	rt	CCl_4	trace
11	Mesitylene	K_3PO_4	-10	DQ	60

[a] Reactions condition: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv),base (0.15 mmol, 1.5 equiv), oxidant (0.2 mmol, 2.0 equiv) and NHC **N** (0.02 mmol, 0.2 equiv) in 1.0 mL of solvent for 6 hours. [b] Isolated yield. [c] DQ: 4,4'-diphenoquinone. [d] DABCO: triethylenediamine; DBU: 1,8-diazabicyclo [5.4.0]-7-Undecene.

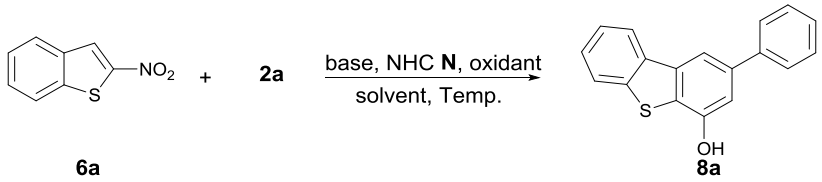
Table 2. Optimization of reaction conditions for asymmetric product **3a**[a].



entry	solvent	NHC **N**	base	yield[%][b]	e.r. (%)[c]
1[d]	THF	**N8**	K_2CO_3	23	58:42
2	Tol	**N8**	K_2CO_3	28	37:63
3	DCM	**N8**	K_2CO_3	37	59:41
4	MeCN	**N8**	K_2CO_3	17	84:16
5	MeCN	**N8**	K_3PO_4	9	80:20
6	MeCN	**N8**	DBU	<5	-
7	MeCN	**N8**	TEA	18	87:13
8	MeCN	**N8**	DABCO	<5	-
9	MeCN	**N8**	NaOAc	12	80:20
10	DCM	**N8**	K_3PO_4	41	59:41
11	DCM	**N8**	TEA	23	63:37
12	DCM	**N8**	DABCO	18	65:35
13[d]	DCM	**N9**	K_3PO_4	N.R.	-
14	DCM	**N10**	K_3PO_4	50	38:62
15	DCM	**N11**	K_3PO_4	trace	-
16	DCM	**N12**	K_3PO_4	trace	-
17	DCM	**N13**	K_3PO_4	13	51:49
18	DCM	**N14**	K_3PO_4	26	62:38

[a] Reactions condition: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv),base (0.15 mmol, 1.5 equiv), oxidant (0.2 mmol, 2.0 equiv) and NHC **N** (0.02 mmol, 0.2 equiv) in 1.0 mL of solvent for 20 hours. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.[d] DQ: 4,4'-diphenoquinone; N.R.: no reaction; DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone.

Table 3. Optimization of reaction conditions for racemic product **8a**[a].



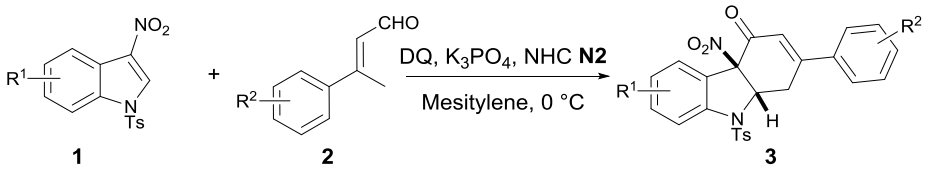
6a **8a**

entry	solvent	base	Temp. (^{o}C)	oxidant	yield[%][b]
1	Tol	K_3PO_4	rt	DQ	52
2	DCM	K_3PO_4	rt	DQ	56
3	THF	K_3PO_4	rt	DQ	19
4	MeCN	K_3PO_4	rt	DQ	33
5	Mesitylene	K_3PO_4	rt	DQ	57
6	Mesitylene	K_2CO_3	rt	DQ	27
7[c]	Mesitylene	TMG	rt	DQ	N.R. [c]
8	Mesitylene	DABCO	rt	DQ	14
9	Mesitylene	NaOAc	rt	DQ	<5
10	Mesitylene	DBU	rt	DQ	17
11	Mesitylene	TEA	rt	DQ	10
12	Mesitylene	K_3PO_4	0	DQ	59
13	Mesitylene	K_3PO_4	40	DQ	43

[a] Reactions condition: **6a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv),base (0.15 mmol, 1.5 equiv), oxidant (0.2 mmol, 2.0 equiv) and NHC **N2** (0.02 mmol, 0.2 equiv) in 1.0 mL of solvent for 20 hours. [b] Isolated yield. [c] N.R.: no reaction

3. General Procedure for the Preparation of Product 3

*3.1 General Procedure for the Synthesis of Product **3***



To a flame-dried Schlenk tube were added 3-nitroindole **1** (0.1 mmol), enals **2** (0.2 mmol), K_3PO_4 (0.15 mmol), DQ (0.2 mmol) and NHC **N2** catalyst (0.02 mmol), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the mesitylene (1.0 mL) were added. The resulting suspension was stirred at 0 °C for 6 hours. Then the resulting reaction mixture was purified through column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1 to 20/1) to afford the corresponding products **3a**–**3x**, which was dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-NMR, HRMS.

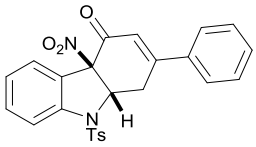
*Procedure for the asymmetric synthesis of product **3a***

To a flame-dried Schlenk tube were added 3-nitroindole **1a** (0.1 mmol, 31.6 mg), enal **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and NHC **N8** catalyst (0.02 mmol, 8.4 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the MeCN (1.0 mL) were added. The resulting suspension was stirred at room temperature for 20 hours. Then the resulting reaction mixture was purified through column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1 to 20/1) to afford corresponding chiral product **3a**, which was dried under vacuum and further analyzed by ^{1}H NMR, ^{13}C NMR, HRMS, chiral HPLC analysis, *etc.*

*3.2 Procedure for the gram-scale synthesis of product **3a***

To a flame-dried Schlenk tube were added 3-nitroindole **1a** (3.2 mmol, 1.01g), enal **2a** (6.4 mmol, 932.7 mg), K_3PO_4 (4.8 mmol, 1.02 g), DQ (6.4 mmol, 2.61 g) and NHC **N2** catalyst (0.64 mmol, 201.1 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the mesitylene (30.0 mL) were added. The resulting suspension was stirred at 0 ^{o}C for 48 hours. Then the resulting reaction mixture was purified through column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1 to 20/1) to afford the corresponding product **3a** (870 mg, 59%).

4a-nitro-2-phenyl-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3a



To a flame-dried Schlenk tube were added 3-nitroindole **1a** (0.1 mmol, 31.6 mg), enals **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the mesitylene (1.0 mL) were added. The resulting suspension was stirred at 0 ^oC for 6 hours to afford **3a** (38.2 mg, m.p. = 137 – 142 ℃) in 83% yield as white solid.

Prepared according to the procedure for the asymmetric synthesis to afford **3a** (8.3 mg) in 18% yield. The enantiomeric ratio was determined to be 87:13 by chiral HPLC analysis on Chiralpak IC column (*n*-hexane/DCM/2-propanol, 0.8 mL/min), UV 254 nm, t_{major} = 14.0 min, t_{minor} = 17.5 min; $[\alpha]_D^{25}$ = + 62.0 (*c* = 0.05 in CH_2Cl_2).

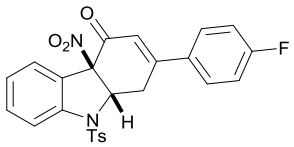
NMR and HRMS data for the product **3a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.49 (m, 1H), 7.48 – 7.46 (m, 2H), 7.28 – 7.25 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 1.8 Hz, 1H), 5.54 (t, *J* = 8.4 Hz, 1H), 3.80 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.89 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.4, 145.2, 142.0, 136.5, 134.2, 133.3, 131.6, 130.0, 129.1, 128.5, 126.6, 125.7, 123.4, 122.8, 116.8, 96.6, 66.6, 33.5, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{20}N_2O_5S$ $[M+H]^+$: 461.1166, found: 461.1162.

2-(4-fluorophenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3b



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2b** (0.2 mmol, 32.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3b** (35.4 mg, m.p. 155 – 160 ℃) in 74% yield as white solid.

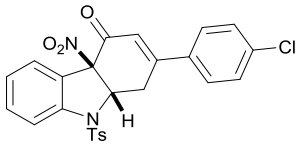
NMR and HRMS data for the product **3b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.56 (m, 4H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.18 – 7.15 (m, 4H), 6.62 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.76 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.87 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.5, 164.7 (d, $^1J_{C\text{-}F}$ = 252.8 Hz), 158.0, 145.3, 142.0, 134.2, 133.3, 132.7, 130.0, 128.8 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 128.6, 126.6, 125.8, 123.2, 122.7, 116.9, 116.4 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 96.5, 66.5, 33.6, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}FN_2O_5S$ $[M+H]^+$: 479.1071, found: 479.1065.

2-(4-chlorophenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3c



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2c** (0.2 mmol, 36.1 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 6 h to afford **3c** (31.2 mg, m.p. = 141 – 145 ℃) in 63% yield as white solid.

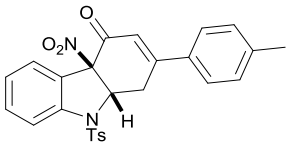
NMR and HRMS data for the product **3c**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.53 – 7.52 (m, 4H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 2.4 Hz, 1H), 5.52 (t, *J* = 7.8 Hz, 1H), 3.75 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.87 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.5, 157.8, 145.3, 142.0, 137.9, 134.9, 134.1, 133.3, 130.0, 129.5, 128.6, 127.9, 126.6, 125.8, 123.6, 122.7, 116.9, 96.6, 66.5, 33.4, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}ClN_2O_5S$ $[M+H]^+$: 495.0776(^{35}Cl), 497.0746(^{37}Cl), found: 495.0772(^{35}Cl), 497.0743(^{37}Cl).

4a-nitro-2-(p-tolyl)-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3d



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2d** (0.2 mmol, 32.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in

1mL mesitylene at 0 °C for 6 h to afford **3d** (35.1 mg, m.p. = 137 – 140 ℃) in 74% yield as white solid.

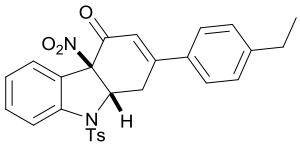
NMR and HRMS data for the product **3d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 3.0 Hz, 1H), 5.53 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.85 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.2, 145.2, 142.5, 142.0, 134.3, 133.5, 133.2, 130.0, 129.9, 128.5, 126.6, 125.7, 122.9, 122.4, 116.8, 96.7, 66.6, 33.4, 21.6, 21.5.

HRMS (ESI) *m/z* calcd for $C_{26}H_{22}N_2O_5S$ $[M+H]^+$: 475.1322, found: 475.1315.

2-(4-ethylphenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3e



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2e** (0.2 mmol, 34.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 6 h to afford **3e** (41.0 mg, m.p. 138 – 144 ℃) in 84% yield as white solid.

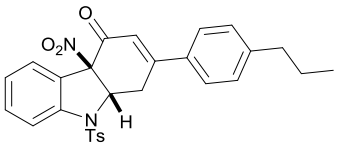
NMR and HRMS data for the product **3e**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.54 – 7.52 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 3.0 Hz, 1H), 5.53 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.81 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.85 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.71 (q, *J* = 7.8 Hz, 2H),2.37 (s, 3H), 1.26 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.3, 148.7, 145.2, 142.0, 134.3, 133.8, 133.2, 130.0, 128.7, 128.6, 126.8, 126.6, 125.7, 122.9, 122.5, 116.8, 96.7, 66.6, 33.4, 28.8, 21.6, 15.2.

HRMS (ESI) *m/z* calcd for $C_{27}H_{24}N_2O_5S$ $[M+Na]^+$: 511.1298, found: 511.1295.

4a-nitro-2-(4-propylphenyl)-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3f



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2f** (0.2 mmol, 37.7 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3f** (45.7 mg, m.p. = 57 – 60 ℃) in 91% yield as white solid.

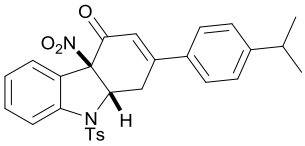
NMR and HRMS data for the product **3f**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 4H), 7.28 – 7.25 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 3.0 Hz, 1H), 5.53 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.81 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.86 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.70 – 1.63 (m, 2H), 0.95 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.3, 147.2, 145.2, 142.0, 134.3, 133.8, 133.2, 130.0, 129.3, 128.6, 126.7, 126.6, 125.7, 122.9, 122.5, 116.8, 96.7, 66.6, 37.8, 33.4, 24.2, 21.6, 13.7.

HRMS (ESI) *m/z* calcd for $C_{28}H_{26}N_2O_5S$ $[M+H]^+$: 503.1035, found: 503.1626.

2-(4-isopropylphenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3g



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2g** (0.2 mmol, 37.7 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3g** (39.7 mg, m.p. = 101 – 106 ℃) in 79% yield as white solid.

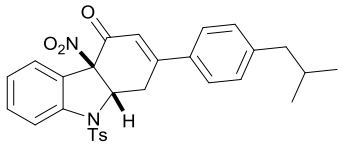
NMR and HRMS data for the product **3g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.54 – 7.52 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.80 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.99 – 2.94 (m, 1H), 2.86 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.37 (s, 3H), 1.27 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.3, 153.3, 145.2, 142.0, 134.3, 134.0, 133.2, 133.0, 128.6, 127.3, 126.8, 126.6, 125.7, 122.9, 122.5, 116.8, 96.7, 66.7, 34.1, 33.4, 23.7, 21.6.

HRMS (ESI) *m/z* calcd for $C_{28}H_{26}N_2O_5S$ $[M+Na]^+$: 525.1455, found: 525.1462.

2-(4-isobutylphenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3h



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2h** (0.2 mmol, 40.5 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3h** (47.0 mg, m.p. = 65 – 70 ℃) in 91% yield as white solid.

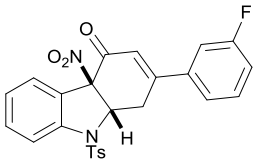
NMR and HRMS data for the product **3h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 4H), 7.27 – 7.24 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 1.8 Hz, 1H), 5.53 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.81 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.86 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.53 (d, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 1.93 – 1.86 (m, 1H), 0.91 (d, *J* = 7.2, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.3, 146.3, 145.2, 142.0, 134.3, 133.8, 133.2, 130.0, 129.9, 128.6, 126.6, 126.5, 125.7, 122.9, 122.5, 116.8, 96.7, 66.7, 45.2, 33.4, 30.1, 22.3, 21.6.

HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_2O_5S$ $[M+Na]^+$: 539.1611, found: 539.1613.

2-(3-fluorophenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3i



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2i** (0.2 mmol, 32.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3i** (30.1 mg, m.p. = 149 – 154 ℃) in 63% yield as white solid.

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

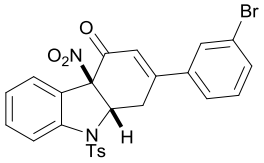
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.25 (m,

2H), 7.22 – 7.20 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 3.0 Hz, 1H), 5.52 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.75 (dd, *J* = 18.0, 7.8 Hz, 1H), 2.89 (dd, *J* = 17.4, 8.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 163.0 (d, $^1J_{C\text{-}F}$ = 247.1 Hz), 157.7, 145.3, 142.1, 138.8, 134.2, 133.3, 130.8 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 130.0, 128.6, 126.7, 125.8, 124.2, 122.6, 122.4, 118.4 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 116.9, 113.6 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 96.6, 66.5, 33.5, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}FN_2O_5S$ $[M+H]^+$: 479.1071, found: 479.1074.

2-(3-bromophenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3j



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2j** (0.2 mmol, 45.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 6 h to afford **3j** (29.1 mg, m.p. = 155 – 160 ℃) in 54% yield as white solid.

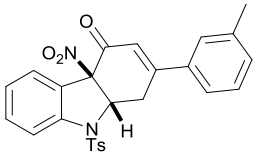
NMR and HRMS data for the product **3j**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.53 – 7.50 (m, 3H), 7.36 – 7.34 (m, 1H), 7.28 – 7.26 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.64 (s, 1H), 5.52 (t, *J* = 7.8 Hz, 1H), 3.73 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.87 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.5, 157.6, 145.3, 142.1, 138.7, 134.3, 134.2, 133.4, 130.6, 130.0, 129.6, 128.5, 126.6, 125.8, 125.2, 124.3, 123.4, 122.6, 116.9, 96.6, 66.5, 33.5, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}BrN_2O_5S$ $[M+H]^+$: 539.0271(^{79}Br), 541.0250(^{81}Br), found: 539.0274(^{79}Br), 541.0255(^{81}Br).

4a-nitro-2-(m-tolyl)-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3k



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2k** (0.2 mmol, 32.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in

1mL mesitylene at 0 ^{o}C for 6 h to afford **3k** (34.2 mg, m.p. = 140 – 142 ℃) in 72% yield as white solid.

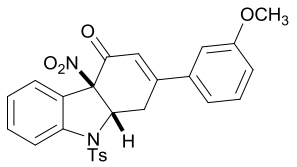
NMR and HRMS data for the product **3k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 6.0 Hz, 2H), 7.35 (t, *J* = 6.6 Hz, 1H), 7.31 (d, *J* =7.2 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.66 (d, *J* =2.4 Hz, 1H), 5.53 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.80 (dd, *J* = 18.0, 7.2 Hz, 1H), 2.87 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.6, 145.2, 142.0, 138.9, 136.5, 134.2, 133.2, 132.4, 130.0, 129.0, 128.5, 127.3, 126.6, 125.7, 123.8, 123.2, 122.8, 116.8, 96.7, 66.6, 33.6, 21.6, 21.4.

HRMS (ESI) *m/z* calcd for $C_{26}H_{22}N_2O_5S$ $[M+H]^+$: 475.1322, found: 475.1313.

2-(3-methoxyphenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3l



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2l** (0.2 mmol, 35.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 6 h to afford **3l** (31.9 mg, m.p. = 144 – 148 ℃) in 65% yield as white solid.

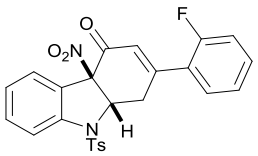
NMR and HRMS data for the product **3l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 78 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.19 – 7.16 (m, 3H), 7.06 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.65 (s, 1H), 5.53 (t, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.78 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.87 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.7, 160.0, 159.4, 145.2, 142.0, 138.0, 134.2, 133.3, 130.2, 130.0, 128.5, 126.6, 125.7, 123.6, 122.8, 119.1, 117.3, 116.9, 111.9, 96.7, 66.6, 55.4, 33.6, 21.6.

HRMS (ESI) *m/z* calcd for $C_{26}H_{22}N_2O_6S^+$ $[M+H]^+$: 491.1271, found: 491.1276.

2-(2-fluorophenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3m



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2m** (0.2 mmol, 32.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3m** (12.9 mg, m.p. = 127 – 130 ℃) in 27% yield as white solid.

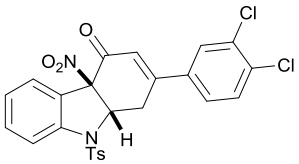
NMR and HRMS data for the product **3m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.29 – 7.24 (m, 2H), 7.18 – 7.15 (m, 3H), 6.62 (d, *J* = 3.0 Hz, 1H), 5.51 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.68 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.94 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 160.1 (d, $^1J_{C\text{-}F}$ = 252.8 Hz), 155.8, 145.2, 142.1, 134.3, 133.3, 132.7 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 130.0, 129.0, 128.6, 127.0 (d, $^3J_{C\text{-}F}$ = 4.4 Hz), 126.6, 125.8, 125.5 (d, $^2J_{C\text{-}F}$ = 11.4 Hz), 124.8, 122.5, 116.9, 116.7, 96.7, 66.7, 34.7, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}FN_2O_5S$ $[M+Na]^+$: 501.0891, found: 501.0895.

2-(3,4-dichlorophenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3n



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2n** (0.2 mmol, 43.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3n** (32.3 mg, m.p. = 131 – 136 ℃) in 61% yield as white solid.

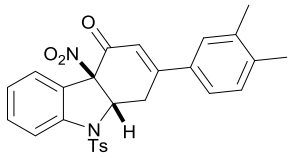
NMR and HRMS data for the product **3n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.71 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.86 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.4, 156.4, 145.4, 142.0, 136.4, 135.9, 134.1, 133.7, 133.4, 131.1, 130.0, 128.5, 128.5, 126.6, 125.8, 125.6, 124.3, 122.5, 116.9, 96.5, 66.4, 33.3, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{18}Cl_2N_2O_5S$ $[M+H]^+$: 529.0386(^{35}Cl), 531.0357(^{37}Cl), found: 529.0395(^{35}Cl), 531.0360(^{37}Cl).

2-(3,4-dimethylphenyl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3o



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2o** (0.2 mmol, 34.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 6 h to afford **3o** (39.5 mg, m.p. = 140 – 143 ℃) in 81% yield as white solid.

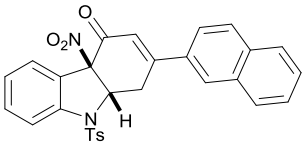
NMR and HRMS data for the product **3o**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.35 (s, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.83 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 159.5, 145.2, 142.0, 141.2, 137.5, 134.3, 134.0, 133.2, 130.4, 130.0, 128.6, 127.8, 126.6, 125.7, 124.2, 123.0, 122.3, 116.8, 96.7, 66.7, 33.4, 21.6, 19.8.

HRMS (ESI) *m/z* calcd for $C_{27}H_{24}N_2O_5S^+$ $[M+Na]^+$: 511.1298, found: 511.1301.

2-(naphthalen-2-yl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3p



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2p** (0.2 mmol, 39.3 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in

1mL mesitylene at 0 ^{o}C for 6 h to afford **3p** (30.6 mg, m.p. = 160 – 165 ℃) in 60% yield as white solid.

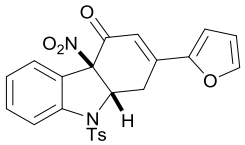
NMR and HRMS data for the product **3p**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.10 (s, 1H), 7.91 (t, *J* = 8.4 Hz, 2H), 7.86 (t, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.60 – 7.55 (m, 5H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 3.0 Hz, 1H), 5.60 (t, *J* = 7.8 Hz, 1H), 3.97 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.99 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.6, 158.9, 145.3, 142.0, 134.6, 134.3, 133.6, 133.3, 132.9, 130.0, 129.1, 129.0, 128.6, 128.2, 127.7, 127.6, 127.2, 126.7, 125.7, 123.6, 122.9, 116.9, 96.7, 66.7, 33.5, 21.6.

HRMS (ESI) *m/z* calcd for $C_{29}H_{22}N_2O_5S$ $[M+H]^+$: 511.1322, found: 511.1316.

2-(furan-3-yl)-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3q



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2q** (0.2 mmol, 27.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 6 h to afford **3q** (40.5 mg, m.p. = 146 – 149 ℃) in 90% yield as white solid.

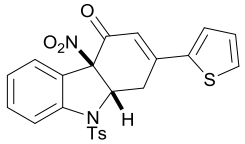
NMR and HRMS data for the product **3q**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H) 7.56 – 7.52 (m, 3H), 7.26 – 7.23 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 3.6 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.50 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.69 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.71 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.2, 150.3, 147.1, 145.7, 145.2, 141.9, 134.2, 133.2, 130.0, 128.6, 126.6, 125.7, 123.0, 118.5, 116.8, 116.2, 113.3, 96.8, 66.2, 30.7, 21.6.

HRMS (ESI) *m/z* calcd for $C_{23}H_{18}N_2O_6S$ $[M+Na]^+$: 473.0778, found: 473.0770.

4a-nitro-2-(thiophen-3-yl)-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3r



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1a** (0.1 mmol, 31.6 mg), **2r** (0.2 mmol, 30.4 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3r** (39.2 mg, m.p. = 159 – 162 ℃) in 84% yield as white solid.

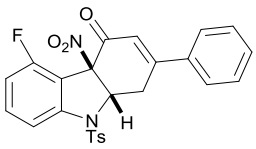
NMR and HRMS data for the product **3r**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 6.0 Hz, 2H), 7.56 – 7.54 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.24 (m, 1H), 7.18 – 7.17 (m, 3H), 6.63 (d, *J* = 1.8 Hz, 1Hz), 5.53 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.84 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.84 (dd, *J* = 17.4, 9.0Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.1, 151.8, 145.3, 141.9, 140.5, 134.2, 133.2, 131.7, 130.0, 130.0, 129.0, 128.5, 126.6, 125.7, 123.0, 120.2, 116.9, 96.7, 66.2, 33.2, 21.6.

HRMS (ESI) *m/z* calcd for $C_{23}H_{18}N_2O_5S_2$ $[M+Na]^+$: 489.0549, found: 489.0553.

5-fluoro-4a-nitro-2-phenyl-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3s



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1b** (0.1 mmol, 33.4 mg), **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3s** (31.6 mg, m.p. = 164 – 165 ℃) in 66% yield as white solid.

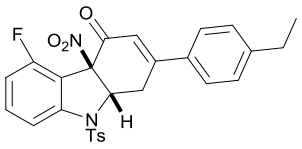
NMR and HRMS data for the product **3s**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.62 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.52 (m, 5H), 7.51 – 7.45 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.93 (t, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 6.60 (t, *J* = 6.6 Hz, 1H), 3.81 (dd, *J* = 18.0, 7.8 Hz, 1H), 2.95 (dd, *J* = 18.0, 9.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 183.2, 161.3 (d, $^1J_{C\text{-}F}$ = 260.0 Hz), 158.4, 145.5, 143.7, 136.3, 135.3 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 134.3, 131.6, 130.1, 129.1, 126.7, 126.6, 123.2, 113.0 (d, $^2J_{C\text{-}F}$ = 20.1 Hz), 112.3, 110.5 (d, $^2J_{C\text{-}F}$ = 17.3 Hz), 97.9, 67.4, 33.8, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}FN_2O_5S$ $[M+H]^+$: 479.1071, found: 479.1069.

2-(4-ethylphenyl)-5-fluoro-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3t



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1b** (0.1 mmol, 33.4 mg), **2e** (0.2 mmol, 34.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3t** (38.0 mg, m.p. = 152 – 155℃) in 75% yield as white solid.

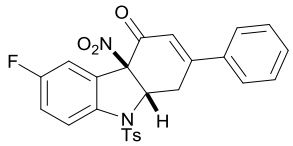
NMR and HRMS data for the product **3t**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.61 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.51 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 5.59 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.81 (dd, *J* = 18.0, 7.2 Hz, 1H), 2.92 (dd, *J* = 18.0, 7.8 Hz, 1H), 2.70 (q, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 1.26 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 183.1, 161.3 (d, $^1J_{C\text{-}F}$ = 258.5 Hz), 158.3, 148.7, 145.5, 143.7, 135.2 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 134.3, 133.5, 130.1, 128.7, 126.7, 122.4, 113.0 (d, $^2J_{C\text{-}F}$ = 20.1 Hz), 112.3, 110.7, 110.5, 98.0, 67.4, 33.7, 28.7, 21.6, 15.1.

HRMS (ESI) *m/z* calcd for $C_{27}H_{23}FN_2O_5S$ $[M+Na]^+$: 529.1204, found: 529.1202.

6-fluoro-4a-nitro-2-phenyl-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3u



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1c** (0.1 mmol, 33.4 mg), **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3u** (28.7 mg, m.p. = 159 – 164 ℃) in 60% yield as white solid.

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

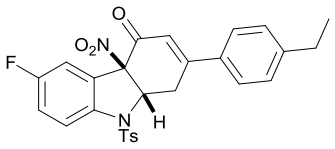
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.60 – 7.59 (m, 2H), 7.53 – 7.46 (m, 5H), 7.34 (dd, *J* = 7.8, 3.0 Hz, 1H), 7.28 (dd, *J* = 8.4, 3.0 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 3.0 Hz, 1H), 5.52 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.89 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.1, 160.0 (d, $^1J_{C\text{-}F}$ = 245.6 Hz), 159.6, 145.5, 138.2, 136.5, 133.9, 131.8, 130.1, 129.2, 126.7, 126.7, 124.6 (d, $^3J_{C\text{-}F}$ = 8.6 Hz),

123.3, 120.5 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 118.3 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 24.5 Hz), 95.9, 66.9, 33.4, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}FN_2O_5S$ $[M+H]^+$: 479.1071, found: 479.1067.

2-(4-ethylphenyl)-6-fluoro-4a-nitro-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3v



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1c** (0.1 mmol, 33.4 mg), **2e** (0.2 mmol, 34.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 6 h to afford **3v** (42.0 mg, m.p. = 149 – 153℃) in 83% yield as white solid.

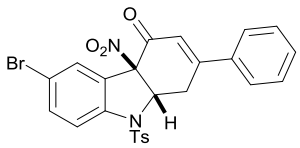
NMR and HRMS data for the product **3v**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.80 (dd, *J* = 9.0, 4.2 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 7.8, 3.0 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 1.8 Hz, 1H), 5.51 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.4, 7.8 Hz, 1H), 2.85 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.71 (q, *J* = 7.8 Hz, 2H),2.38 (s, 3H), 1.27 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.0, 160.4 (d, $^{1}J_{C\text{-}F}$ = 244.1 Hz), 159.5, 148.9, 145.4, 138.2, 133.9, 133.7, 130.1, 128.7, 126.8, 126.7, 124.7 (d, $^{3}J_{C\text{-}F}$ = 10.1 Hz), 122.4, 120.4 (d, $^{2}J_{C\text{-}F}$ = 24.5 Hz) 118.3 (d, $^{3}J_{C\text{-}F}$ = 7.2 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 95.9, 66.9, 33.2, 28.8, 21.6, 15.2.

HRMS (ESI) *m/z* calcd for $C_{27}H_{23}FN_2O_5S$ $[M+Na]^+$: 529.1204, found: 529.1204.

6-bromo-4a-nitro-2-phenyl-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3w



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1d** (0.1 mmol, 39.5 mg), **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 6 h to afford **3w** (34.0 mg, m.p. = 112 – 117 ℃) in 63% yield as white solid.

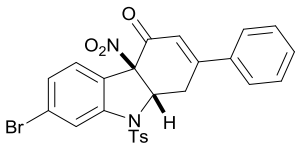
NMR and HRMS data for the product **3w**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.59 – 7.58 (m, 2H), 7.53 – 7.51 (m, 3H), 7.49 – 7.47 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 3.0 Hz, 1H), 5.50 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.88 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.0, 159.5, 145.6, 141.1, 136.4, 136.2, 133.9, 131.8, 131.5, 130.2, 129.2, 126.7, 126.6, 124.6, 123.3, 118.5, 118.2, 95.8, 66.7, 33.4, 21.6.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}BrN_2O_5S$ $[M+H]^+$: 539.0271(^{79}Br), 541.0250(^{81}Br), found: 539.0265(^{79}Br), 541.0251(^{81}Br).

7-bromo-4a-nitro-2-phenyl-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 3x



The general procedure was the same as the synthesis of product **3a**. Reactions were performed with **1e** (0.1 mmol, 39.5 mg), **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 6 h to afford **3x** (30.2 mg, m.p. = 134 – 137 ℃) in 56% yield as white solid.

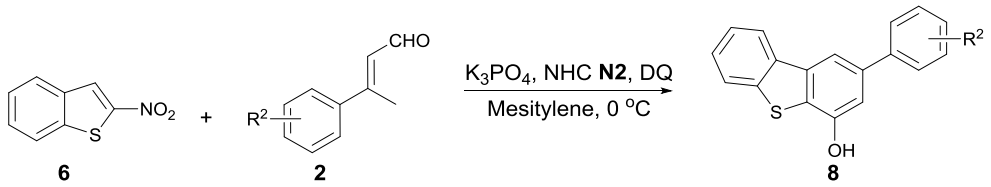
NMR and HRMS data for the product **3x**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.01 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.53 – 7.46 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 3.0 Hz, 1H), 5.49 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.80 (dd, *J* = 17.4, 7.2 Hz, 1H), 2.88 (dd, *J* = 16.8, 9.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 184.1, 159.4, 145.6, 143.1, 136.4, 134.0, 131.8, 130.2, 129.7, 129.2, 129.0, 127.7, 126.7, 126.6, 123.3, 121.8, 119.9, 95.9, 66.8, 33.4, 21.7.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}BrN_2O_5S$ $[M+H]^+$: 539.0271(^{79}Br), 541.0250(^{81}Br), found: 539.0265(^{79}Br), 541.0251(^{81}Br).

4. General Procedure for the Synthesis of Product 8.

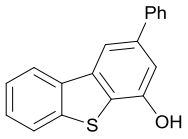


To a flame-dried Schlenk tube were added nitrothiophene **6** (0.1 mmol), enals **2** (0.2 mmol), K_3PO_4 (0.15 mmol), DQ (0.2 mmol) and NHC **N2** catalyst (0.02 mmol), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the mesitylene (1.0 mL) were added. The resulting suspension was stirred at 0 ^oC for 20 hours. Then the resulting reaction mixture was purified through column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1 to 20/1) to afford corresponding products **8a** – **8r**, which was dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-NMR, HRMS.

*Procedure for the synthesis of product **8a***

To a flame-dried Schlenk tube were added nitrothiophene **6a** (0.1 mmol, 18.0 mg), enal **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and NHC **N2** catalyst (0.02 mmol, 6.3 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the mesitylene (1.0 mL) were added. The resulting suspension was stirred at 0 ^oC for 20 hours. Then the resulting reaction mixture was purified through column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1 to 20/1) to afford corresponding product **8a**, which was dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-NMR, HRMS.

2-phenyldibenzo[b,d]thiophen-4-ol 8a



To a flame-dried Schlenk tube were added nitrothiophene **6a** (0.1 mmol, 18.0 mg), enal **2a** (0.2 mmol, 29.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and NHC **N2** catalyst (0.02 mmol, 6.3 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of Ar, the mesitylene (1.0 mL) were added. The resulting suspension was stirred at 0 ^oC for 20 hours to afford **8a** (16.3 mg, m.p. = 161 – 163 ℃) in 59% yield as white solid.

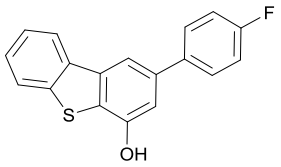
NMR and HRMS data for the product **8a**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 – 8.18 (m, 1H), 7.98 (s, 1H), 7.91 – 7.89 (m, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.47 (m, 4H), 7.40 – 7.38 (m, 1H), 7.13 (s, 1H), 5.64 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.6, 141.0, 140.0, 139.8, 138.2, 135.9, 128.9, 127.4, 127.4, 127.0, 125.7, 124.5, 123.2, 122.0, 113.1, 111.2.

HRMS (ESI) *m/z* calcd for $C_{18}H_{12}OS$ $[M+H]^+$: 277.0682, found: 277.0677.

2-(4-fluorophenyl)dibenzo[b,d]thiophen-4-ol 8b



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2b** (0.2 mmol, 32.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8b** (19.1 mg, m.p. = 187 – 188 ℃) in 65% yield as white solid.

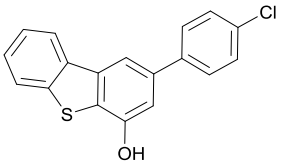
NMR and HRMS data for the product **8b**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.18 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 6.6 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.17 (t, *J* = 8.4 Hz, 2H), 7.07 (s, 1H), 5.36 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 162.6 (d, $^1J_{C\text{-}F}$ = 245.6 Hz), 150.6, 140.0, 138.9, 138.4, 137.2, 135.9, 128.9 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 127.1, 125.8, 124.6, 123.2, 122.0, 115.7 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 113.1, 111.2.

HRMS (ESI) *m/z* calcd for $C_{18}H_{11}FOS$ $[M+H]^+$: 295.0587, found: 295.0583.

2-(4-chlorophenyl)dibenzo[b,d]thiophen-4-ol 8c



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2c** (0.2 mmol, 36.1 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8c** (17.1 mg, m.p. = 179 – 182 ℃) in 55% yield as white solid.

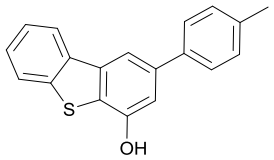
NMR and HRMS data for the product **8c**:

^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 10.73 (s, 1H) 8.48 – 8.46 (m, 1H), 8.19 (s, 1H), 8.07 – 8.06 (m, 1H), 7.82 – 7.81 (m, 2H), 7.61 – 7.59 (m, 2H), 7.57 – 7.54 (m, 2H), 7.23 (s, 1H).

^{13}C-NMR (150 MHz, DMSO-d_6) δ (ppm): 152.6, 139.2, 139.1, 137.5, 137.5, 135.7, 132.2, 128.9, 128.6, 127.2, 125.4, 124.7, 123.3, 122.6, 111.3, 110.0.

HRMS (ESI) *m/z* calcd for $C_{18}H_{11}ClOS$ $[M+H]^+$: 311.0292(^{35}Cl), 313.0262(^{37}Cl), found: 311.0286(^{35}Cl), 313.0270(^{37}Cl).

2-(p-tolyl)dibenzo[b,d]thiophen-4-ol 8d



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2d** (0.2 mmol, 32.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 20 h to afford **8d** (21.5 mg, m.p. = 158 – 162 ℃) in 74% yield as white solid.

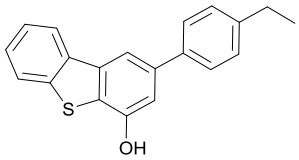
NMR and HRMS data for the product **8d**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 – 8.18 (m, 1H), 7.96 (s, 1H), 7.91 – 7.89 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.11 (s, 1H), 5.36 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.5, 139.9, 139.7, 138.2, 138.1, 137.2, 135.9, 129.6, 128.9, 124.5, 123.1, 122.0, 112.9, 111.1, 21.1.

HRMS (ESI) *m/z* calcd for $C_{19}H_{14}OS$ $[M+H]^+$: 291.0838, found: 291.0836.

2-(p-tolyl)dibenzo[b,d]thiophen-4-ol 8e

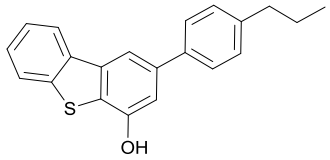


The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2e** (0.2 mmol, 34.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 20 h to afford **8e** (20.1 mg, m.p. = 170 – 173 ℃) in 66% yield as white solid.

NMR and HRMS data for the product **8e**:

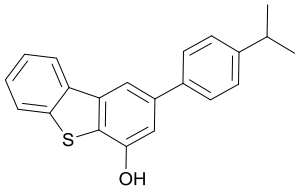
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 – 8.18 (m, 1H), 7.97 (s, 1H), 7.90 – 7.89 (m, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.11 (s, 1H), 5.53 (s, 1H), 2.73 (q, *J* = 7.8 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm):150.5, 143.6, 139.9, 139.7, 138.3, 138.2, 135.9, 128.4, 127.2, 127.0, 125.4, 124.5, 123.1, 122.0, 112.9, 111.1, 28.5, 15.6.
HRMS (ESI) *m/z* calcd for $C_{20}H_{16}OS$ $[M+H]^+$: 305.0995, found: 305.0988.

2-(4-propylphenyl)dibenzo[b,d]thiophen-4-ol 8f



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2f** (0.2 mmol, 37.7 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 20 h to afford **8f** (23.3 mg, m.p. = 156 – 161 ℃) in 73% yield as white solid.
NMR and HRMS data for the product **8f**:
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 – 8.17 (m, 1H), 7.97 (s, 1H), 7.90 – 7.88 (m, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.46 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 5.40 (s, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.5, 142.1, 139.9, 139.7, 138.3, 138.2, 136.0, 129.0, 127.1, 126.9, 125.4, 124.5, 123.1, 122.0, 112.9, 111.2, 37.7, 24.6, 13.9.
HRMS (ESI) *m/z* calcd for $C_{21}H_{18}OS$ $[M+H]^+$: 319.1151, found: 319.1145.

2-(4-isopropylphenyl)dibenzo[b,d]thiophen-4-ol 8g



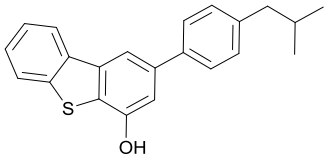
The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2g** (0.2 mmol, 37.7 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 20 h to afford **8g** (23.9 mg, m.p. = 169 – 171 ℃) in 75% yield as white solid.
NMR and HRMS data for the product **8g**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 – 8.17 (m, 1H), 7.97 (s, 1H), 7.90 – 7.89 (m, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 5.51 (s, 1H), 3.01 – 2.97 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.5, 148.2, 139.9, 139.7, 138.4, 138.2, 135.9, 127.2, 127.0, 125.4, 124.5, 123.2, 122.0, 113.0, 111.2, 33.8, 24.0.

HRMS (ESI) *m/z* calcd for $C_{21}H_{18}OS$ $[M+H]^+$: 319.1151, found: 319.1150.

2-(4-isobutylphenyl)dibenzo[b,d]thiophen-4-ol 8h



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2h** (0.2 mmol, 40.5 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8h** (24.3 mg, m.p. = 138 – 141 ℃) in 73% yield as white solid.

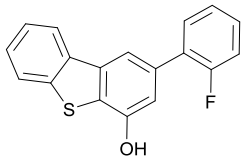
NMR and HRMS data for the product **8h**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.17 – 8.16 (m, 1H), 7.96 (s, 1H), 7.88 – 7.87 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.24 (d, *J* = 6.6 Hz, 2H), 7.10 (s, 1H), 5.51 (s, 1H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.94 – 1.90 (m, 1H), 0.95 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.5, 141.1, 139.9, 139.7, 138.3, 138.2, 135.9, 129.6, 127.0, 126.9, 125.4, 124.5, 123.1, 122.0, 112.9, 111.1, 45.1, 30.2, 22.4.

HRMS (ESI) *m/z* calcd for $C_{22}H_{20}OS$ $[M+H]^+$: 333.1308, found: 333.1303.

2-(2-fluorophenyl)dibenzo[b,d]thiophen-4-ol 8i



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2m** (0.2 mmol, 32.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8i** (18.2 mg, m.p. = 154 – 155 ℃) in 62% yield as white solid.

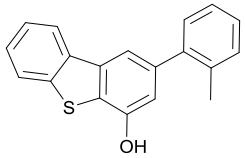
NMR and HRMS data for the product **8i**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.16 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.38 – 7.34 (m, 1H), 7.27 – 7.24 (m, 1H), 7.20 (t, *J* = 9.0 Hz, 1H), 7.11 (s, 1H), 5.39 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 159.7 (d, $^1J_{C\text{-}F}$ = 247.1 Hz), 150.2, 139.9, 137.9, 135.8, 133.8, 130.9, 129.1 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 128.7 (d, $^3J_{C\text{-}F}$ = 12.9 Hz), 127.0, 126.1, 124.5, 124.4, 123.1, 122.0, 116.2 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 115.0, 112.8.

HRMS (ESI) *m/z* calcd for $C_{18}H_{11}FOS$ $[M+H]^+$: 295.0587, found: 295.0585

2-(o-tolyl)dibenzo[b,d]thiophen-4-ol 8j



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2q** (0.2 mmol, 32.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 20 h Prepared according to the general procedure to afford **8j** (12.2 mg, m.p. = 157 – 160 ℃) in 42% yield as white solid.

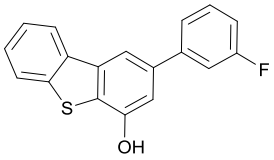
NMR and HRMS data for the product **8j** :

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.11 (d, *J* = 6.6 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.72 (s, 1H), 7.49 – 7.45 (m, 2H), 7.33 – 7.28 (m, 4H), 6.86 (s, 1H), 5.52 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 149.9, 141.5, 140.1, 139.9, 137.7, 135.9, 135.5, 130.4, 129.9, 127.5, 127.0, 125.8, 125.1, 124.5, 123.1, 122.0, 115.2, 113.2, 20.5.

HRMS (ESI) *m/z* calcd for $C_{19}H_{14}OS$ $[M+H]^+$: 291.0838, found: 291.0833.

2-(3-fluorophenyl)dibenzo[b,d]thiophen-4-ol 8k



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2i** (0.2 mmol, 32.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 °C for 20 h to afford **8k** (17.4 mg, m.p. = 170 – 174 ℃) in 59% yield as white solid.

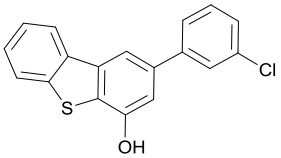
NMR and HRMS data for the product **8k**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 – 8.17 (m, 1H), 7.95 (s, 1H), 7.92 – 7.89 (m, 1H), 7.51 – 7.48 (m, 2H), 7.46 – 7.42 (m, 2H), 7.38 – 7.36 (m, 1H), 7.09 – 7.06 (m, 2H), 5.55 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 163.2 (d, $^1J_{C\text{-}F}$ = 244.2 Hz), 150.6, 143.2 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 140.0, 138.3 (d, $^2J_{C\text{-}F}$ = 17.3 Hz), 135.8, 130.4, 130.3, 127.2, 126.3, 124.6, 123.2, 123.0, 122.0, 114.3 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 114.1 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 113.1, 111.0.

HRMS (ESI) *m/z* calcd for $C_{18}H_{11}FOS$ $[M+H]^+$: 295.0587, found: 295.0579.

2-(3-chlorophenyl)dibenzo[b,d]thiophen-4-ol 8l



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2r** (0.2 mmol, 36.1 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8l** (15.9 mg, m.p. = 177 – 178 ℃) in 51% yield as white solid.

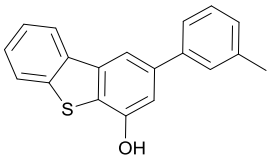
NMR and HRMS data for the product **8l**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 – 8.19 (m, 1H), 7.94 (s, 1H), 7.91 – 7.89 (m, 1H), 7.66 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.08 (s, 1H), 5.52 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.7, 142.8, 140.0, 138.3, 138.3, 135.8, 134.7, 130.1, 127.5, 127.4, 127.2, 126.3, 125.5, 124.6, 123.2, 122.1, 113.1, 111.0.

HRMS (ESI) *m/z* calcd for $C_{18}H_{11}ClOS$ $[M+H]^+$: 311.0292(^{35}Cl), 313.0262(^{37}Cl), found: 311.0283(^{35}Cl), 313.0266(^{37}Cl).

2-(m-tolyl)dibenzo[b,d]thiophen-4-ol 8m



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2k** (0.2 mmol, 32.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8m** (21.8 mg, m.p. = 160 – 163 ℃) in 75% yield as white solid.

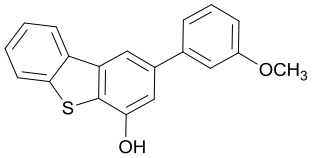
NMR and HRMS data for the product **8m**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 – 8.18 (m, 1H), 7.97 (s, 1H), 7.90 – 7.88 (m, 1H), 7.49 – 7.46 (m, 4H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 5.74 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm):150.5, 140.9, 139.9, 139.9, 138.5, 138.2, 135.9, 128.7, 128.1, 127.0, 125.6, 124.4, 123.1, 122.0, 113.0, 111.2, 21.5.

HRMS (ESI) *m/z* calcd for $C_{19}H_{14}OS$ $[M+H]^+$: 291.0838, found: 291.0831.

2-(3-methoxyphenyl)dibenzo[b,d]thiophen-4-ol 8n



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2l** (0.2 mmol, 35.2 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8n** (12.3 mg, m.p. = 152 – 157 ℃) in 40% yield as white solid.

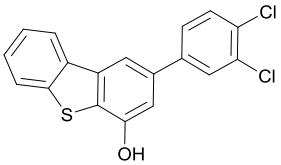
NMR and HRMS data for the product **8n**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 – 8.17 (m, 1H), 7.96 (s, 1H), 7.90 – 7.89 (m, 1H), 7.50 – 7.46 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.21 (s, 1H),7.11 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.60 (s, 1H), 3.90 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.0, 150.5, 142.5, 139.9, 139.6, 138.2, 135.9, 129.9, 127.0, 125.8, 124.5, 123.2, 122.0, 119.9, 113.2, 113.1, 112.7, 111.2, 55.4.

HRMS (ESI) *m/z* calcd for $C_{19}H_{14}O_2S$ $[M+H]^+$: 307.0786, found: 307.0786.

2-(3,4-dichlorophenyl)dibenzo[b,d]thiophen-4-ol 8o



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2n** (0.2 mmol, 43.0 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^oC for 20 h to afford **8o** (18.0 mg, m.p. = 168 – 172 ℃) in 52% yield as white solid.

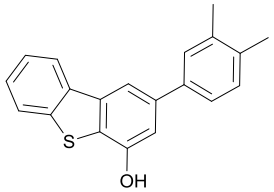
NMR and HRMS data for the product **8o** :

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.19 – 8.18 (m, 1H), 7.91 – 7.89 (m, 1H), 7.75 (s, 1H), 7.54 – 7.47 (m, 5H), 7.05 (s, 1H), 5.68 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.8, 141.0, 140.0, 138.4, 137.1, 135.7, 132.9, 131.5, 130.7, 129.1, 127.3, 126.6, 126.5, 124.6, 123.2, 122.1, 112.9, 110.7.

HRMS (ESI) *m/z* calcd for $C_{18}H_{10}Cl_2OS$ $[M+H]^+$: 344.9902(^{35}Cl), 346.9873(^{37}Cl), found: 344.9905(^{35}Cl), 346.9867(^{37}Cl).

2-(3,4-dimethylphenyl)dibenzo[b,d]thiophen-4-ol 8p



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2o** (0.2 mmol, 34.8 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 20 h to afford **8p** (25.3 mg, m.p. 173 – 174 ℃) in 83% yield as white solid.

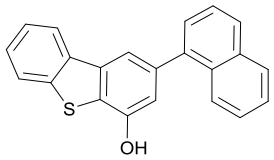
NMR and HRMS data for the product **8p**:

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 – 8.19 (m, 1H), 7.96 (s, 1H), 7.90 – 7.89 (m, 1H), 7.48 – 7.47 (m, 3H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 5.33 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 150.5, 140.0, 139.9, 138.6, 138.2, 137.0, 136.0, 135.9, 130.2, 128.6, 126.9, 125.4, 124.7, 124.5, 123.1, 122.0, 113.0, 111.2, 19.9, 19.4.

HRMS (ESI) *m/z* calcd for $C_{20}H_{16}OS$ $[M+H]^+$: 305.0995, found: 305.0991.

2-(naphthalen-1-yl)dibenzo[b,d]thiophen-4-ol 8q



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2s** (0.2 mmol, 39.3 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 20 h to afford **8q** (20.2 mg, m.p. = 180 – 183 ℃) in 62% yield as white solid.

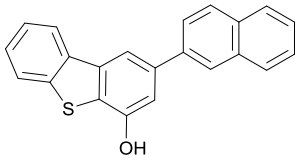
NMR and HRMS data for the product **8q**:

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ (ppm): 10.71 (s, 1H), 8.38 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.61 – 7.50 (m, 5H), 7.08 (s, 1H),.

^{13}C-NMR (150 MHz, DMSO-*d*$_6$) δ (ppm): 151.9, 139.7, 139.1, 138.4, 137.0, 135.7, 133.4, 131.1, 128.3, 127.6, 127.1, 127.0, 126.4, 125.9, 125.5, 124.9, 124.7, 123.2, 122.5, 114.2, 113.3.

HRMS (ESI) *m/z* calcd for $C_{22}H_{14}OS$ $[M+Na]^+$: 349.0658, found: 349.0661.

2-(naphthalen-2-yl)dibenzo[b,d]thiophen-4-ol 8r



The general procedure was the same as the synthesis of product **6a**. Reactions were performed with **6a** (0.1 mmol, 18.0 mg), **2p** (0.2 mmol, 39.3 mg), K_3PO_4 (0.15 mmol, 31.8 mg), DQ (0.2 mmol, 81.7 mg) and **NHC N2** catalyst (0.02 mmol, 6.3 mg) in 1mL mesitylene at 0 ^{o}C for 20 h to afford **8r** (13.1 mg, m.p. = 178 – 183 ℃) in 40% yield as white solid.

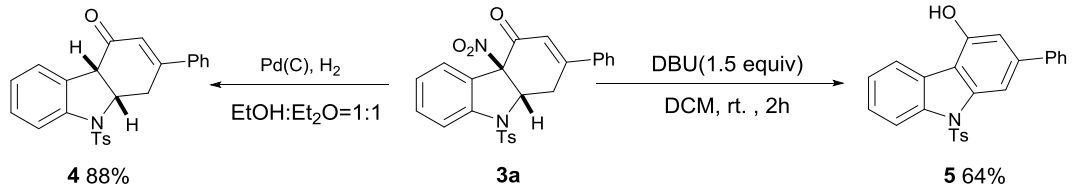
NMR and HRMS data for the product **8r**:

^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.25 – 8.22 (m, 1H), 8.12 (s, 1H), 8.10 (s, 1H), 7.96 – 7.89 (m, 4H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.48 (m, 4H), 7.25 (s, 1H), 5.60 (s, 1H).

^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm): 150.7, 140.0, 139.7, 138.3, 138.3, 135.9, 133.7, 132.7, 128.6, 128.2, 127.7, 127.1, 126.4, 126.0, 126.0, 125.8, 125.7, 124.5, 123.2, 122.1, 113.4, 111.4.

HRMS (ESI) *m/z* calcd for $C_{22}H_{14}OS$ $[M+Na]^+$: 349.0658, found: 349.0651.

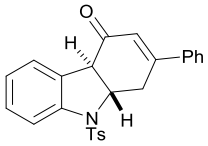
5. Synthetic Transformations of the Product 3a



*Procedure for the synthesis of compound **4**.*

A glass tube was charged with compound **3a** (46.0 mg, 0.1 mmol) and Pd(C) (4.6 mg, 10 %) in a mixed solution of EtOH (0.5 mL) and Et_2O (0.5 mL) under hydrogen (1 atm). The mixture was stirred at room temperature for 12 h. When the reaction was complete, the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) to give compound **4**, which was dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-HMR, HRMS.

2-phenyl-9-tosyl-1,4a,9,9a-tetrahydro-4H-carbazol-4-one 4



Purification of the crude product via column chromatography delivered **4** (36.6 mg, m.p. = 107 – 112 ℃) in 88% yield as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.34 – 7.30 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.12 (m, 1H), 6.49 (d, *J* = 3.0 Hz, 1H), 4.97 – 4.92 (m, 1H), 3.54 (d, *J* = 7.8 Hz, 1H), 3.33 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.95 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 193.9, 157.7, 144.5, 140.8, 137.6, 135.3, 130.7, 129.9, 129.1, 129.0, 128.9, 126.7, 126.4, 126.0, 125.0, 124.9, 118.3, 61.8, 49.5, 31.5, 21.6.

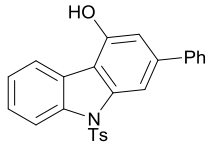
HRMS (ESI) *m/z* calcd for $C_{25}H_{21}NO_3S$ $[M+Na]^+$: 438.1134, found: 438.1135.

*Procedure for the synthesis of compound **5**.*

A glass tube was charged with compound **3a** (46.0 mg, 0.1 mmol) in 2.0 mL DCM. Subsequently, DBU (22.8 mg, 0.15 mmol) was added. The mixture was stirred at room temperature for 12 hours. When the reaction was complete, the mixture was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate

= 15:1) to give the desired product **5**, which was dried under vacuum and further analyzed by 1H-NMR, 13C-HMR, HRMS.

2-phenyl-9-tosyl-9H-carbazol-4-ol 5



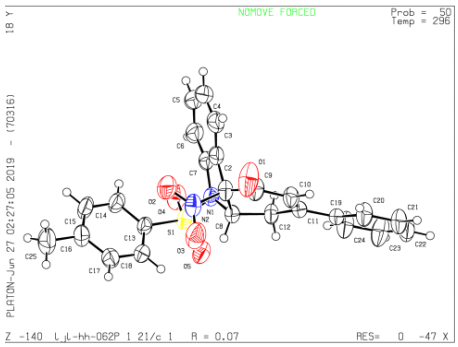
Purification of the crude product via column chromatography delivered **5** (26.5 mg, m.p. = 116 – 120 ℃) in 64% yield as white solid

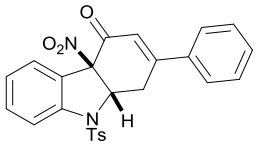
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.32 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 7.2 Hz, 1H), 8.18 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.45 (m, 3H), 7.40 – 7.36 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.96 (s, 1H), 5.80 (s, 1H), 2.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 151.5, 144.9, 141.6, 140.9, 140.5, 138.1, 134.9, 129.7, 128.8, 127.7, 127.5, 126.5, 125.3, 124.1, 123.0, 114.6, 113.8, 109.3, 106.4, 21.5.

HRMS (ESI) *m/z* calcd for $C_{25}H_{19}NO_3S$ $[M+H]^+$: 414.1158, found: 414.1158.

6. Crystal Data and Structure Refinement for Product 3a





3a

Identification code	**3a**
Empirical formula	$C_{25}H_{20}N_2O_5S$
Formula weight	460.49
Temperature/K	296.26(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.0391(5)
b/Å	15.7147(5)
c/Å	11.2733(4)
α/°	90
β/°	110.729(4)
γ/°	90
Volume/Å^3	2160.43(15)
Z	4
ρ_{calc}g/cm^3	1.416
μ/mm^{-1}	1.684
F(000)	960.0
Crystal size/mm^3	0.5 ×0.3 ×0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.18 to 143.328
Index ranges	$-15 \leq h \leq 15$, $-13 \leq k \leq 19$, $-12 \leq l \leq 13$
Reflections collected	11854
Independent reflections	4162 [R_{int} = 0.0369, R_{sigma} = 0.0325]
Data/restraints/parameters	4162/0/299
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0689, wR_2 = 0.1744
Final R indexes [all data]	R_1 = 0.0747, wR_2 = 0.1842
Largest diff. peak/hole / e Å^{-3}	0.42/-0.63

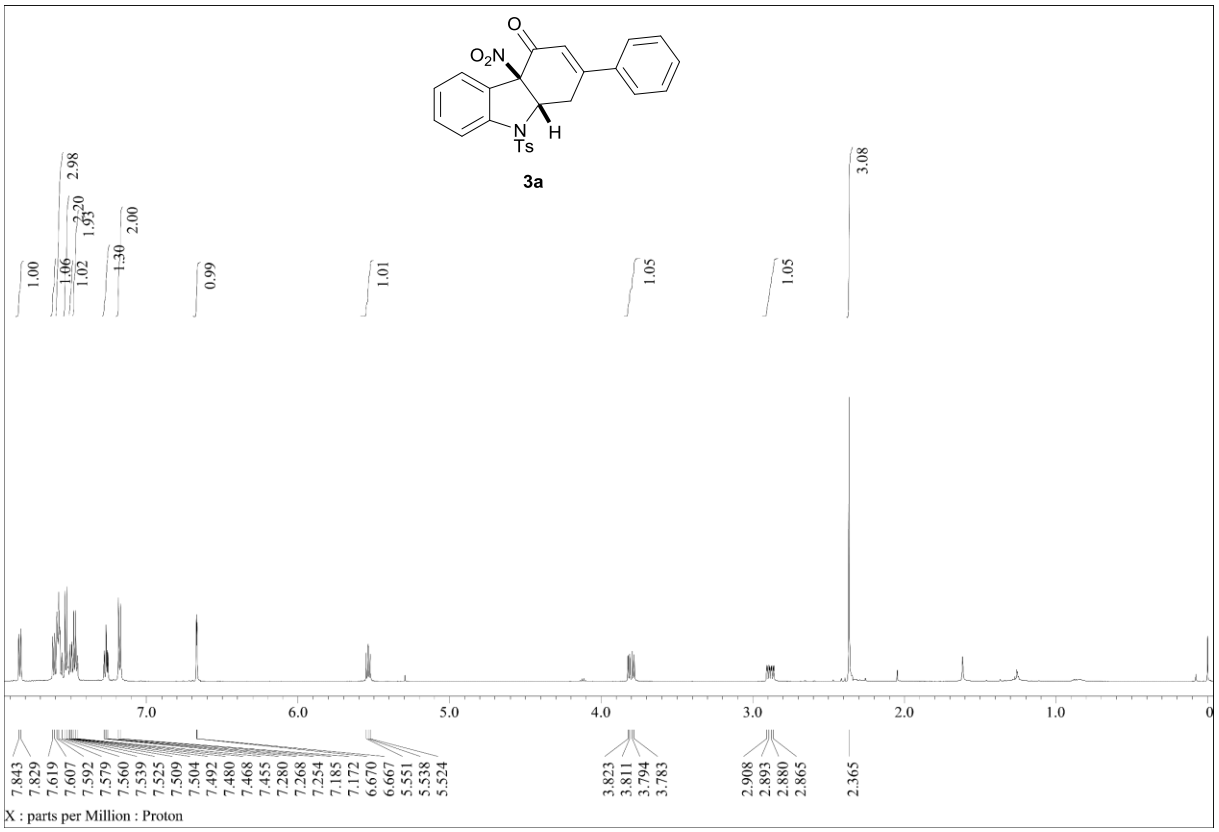
7. References and Notes

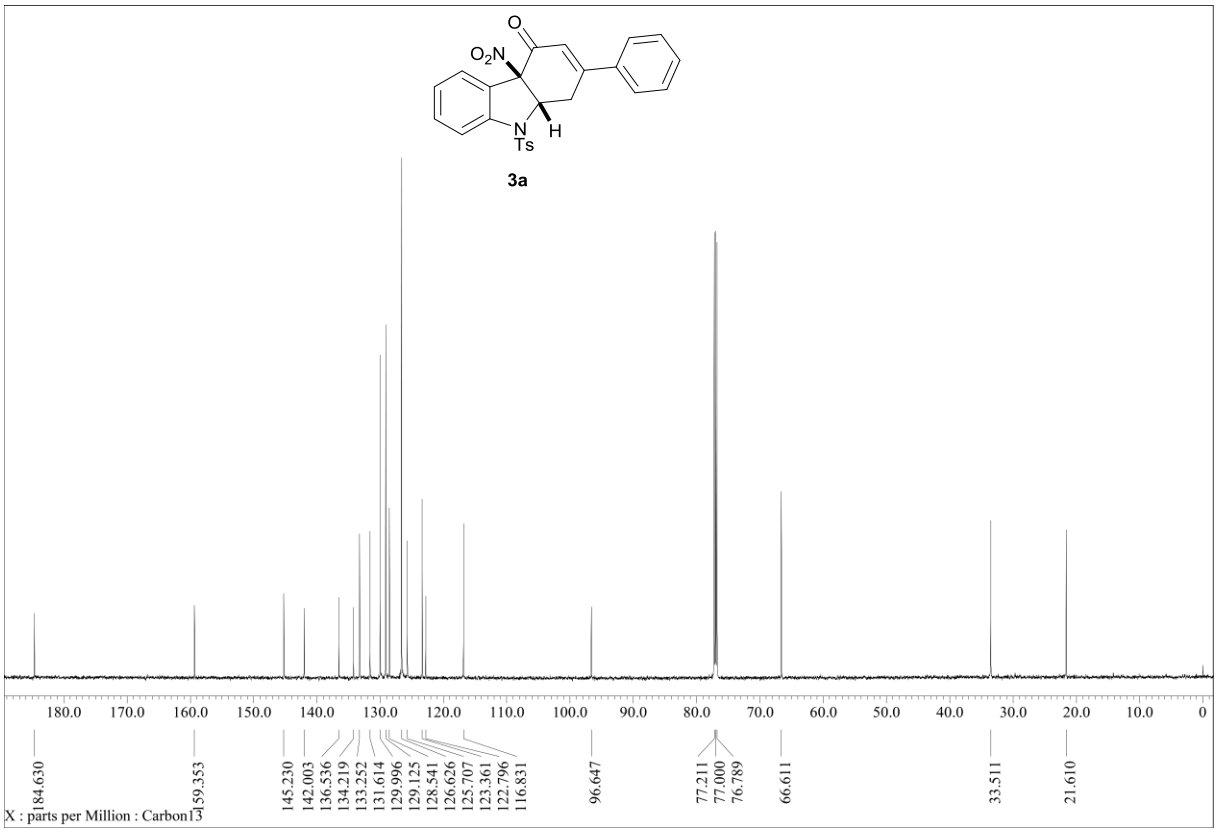
[1] E. T. Pelkey, G. W. Gribble, Synthesis and Reactions of N-Protected 3-Nitroindoles, *Synthesis*, 1999, **7**, 1117.

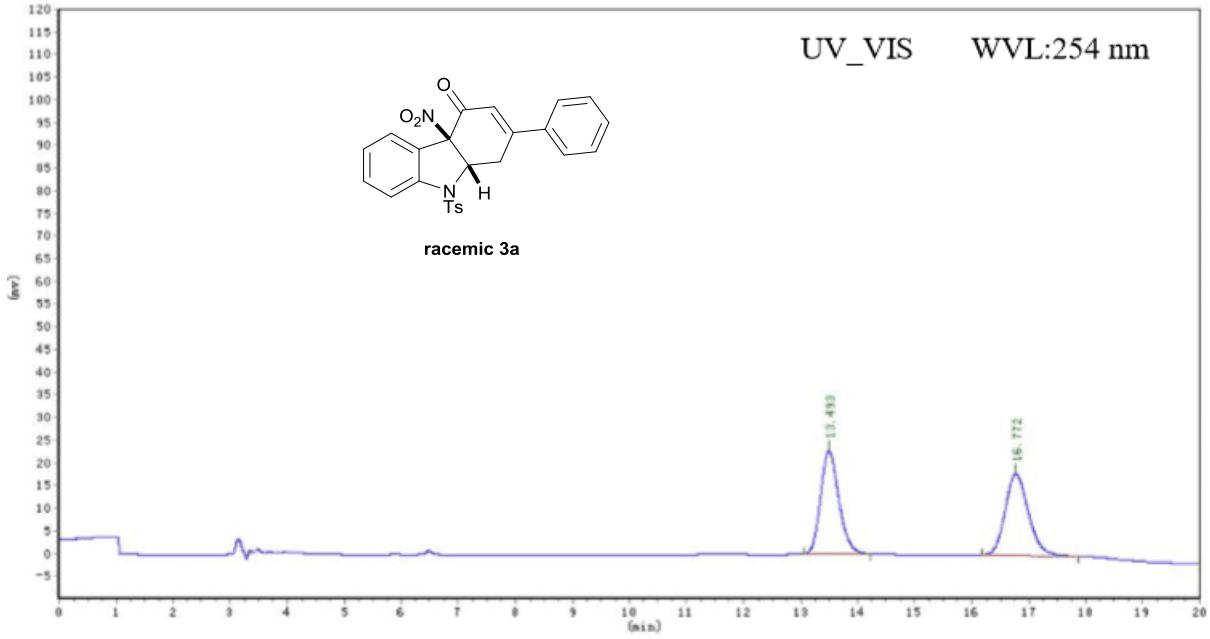
[2] R. J. Rahaim, Jr. and R. E. Maleczka, C−O Hydrogenolysis Catalyzed by Pd-PMHS Nanoparticles in the Company of Chloroarenes, *Org. Lett.*, 2011, **13**, 584.

[3] Q. Cheng, H. Zhang, W. Yue and S. You, Palladium-Catalyzed Highly Stereoselective Dearomative [3 + 2] Cycloaddition of Nitrobenzofurans, *Chem.*, 2017, **3**, 428.

8. NMR of the Products







No.	Ret. Time	Height	Area	Rel. Area
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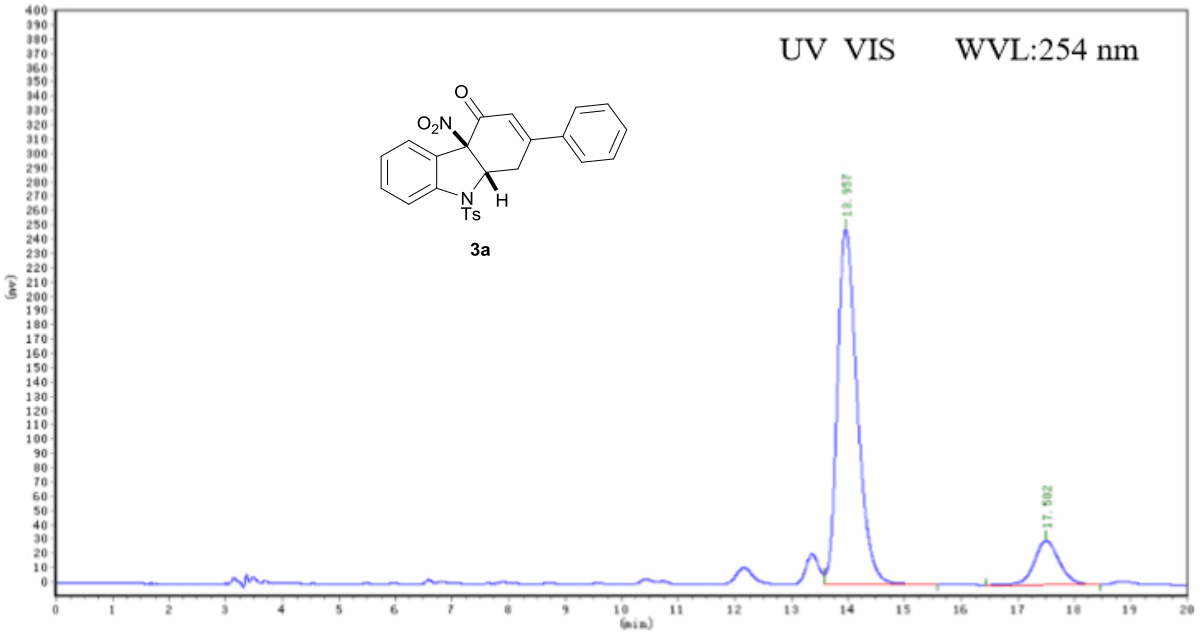
2	16.772	17938.270	508549.781	50.1767
Total		40600.936	1013517.000	100.0000



No.	Ret. Time	Height	Area	Rel. Area
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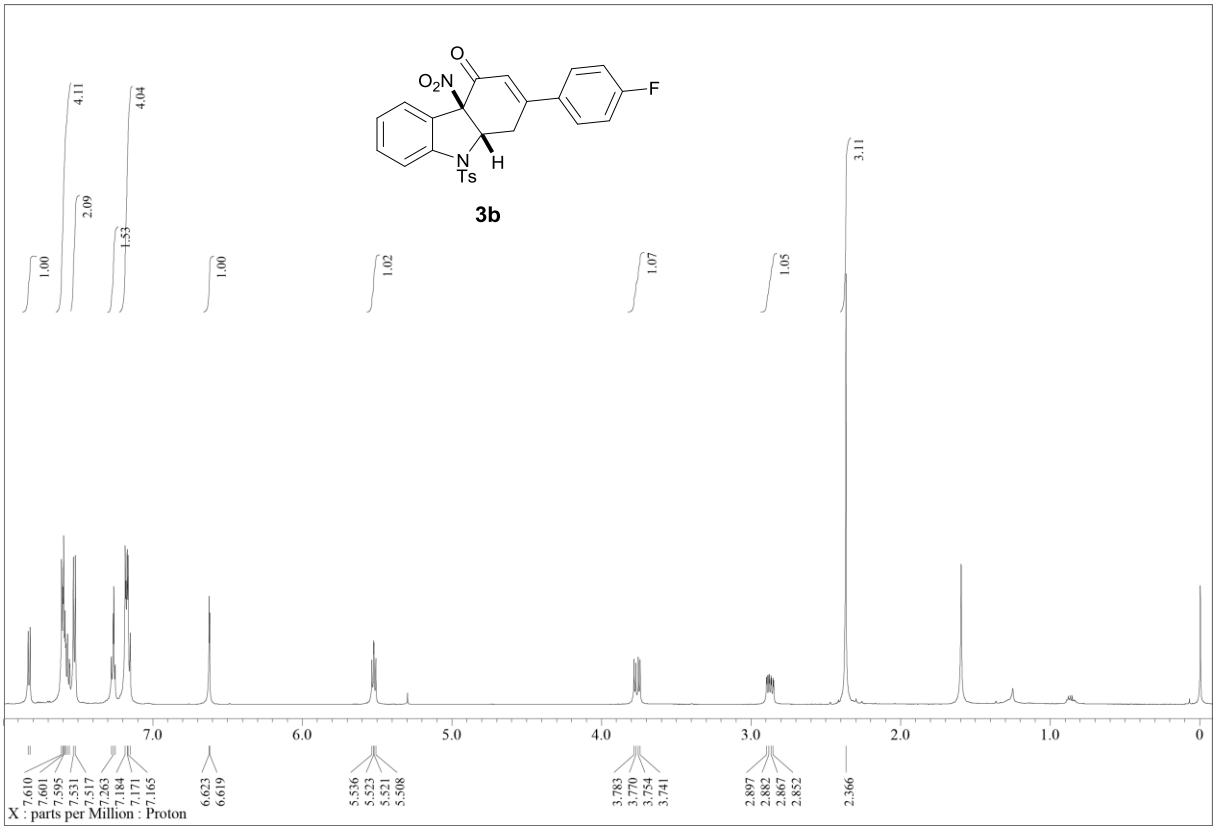
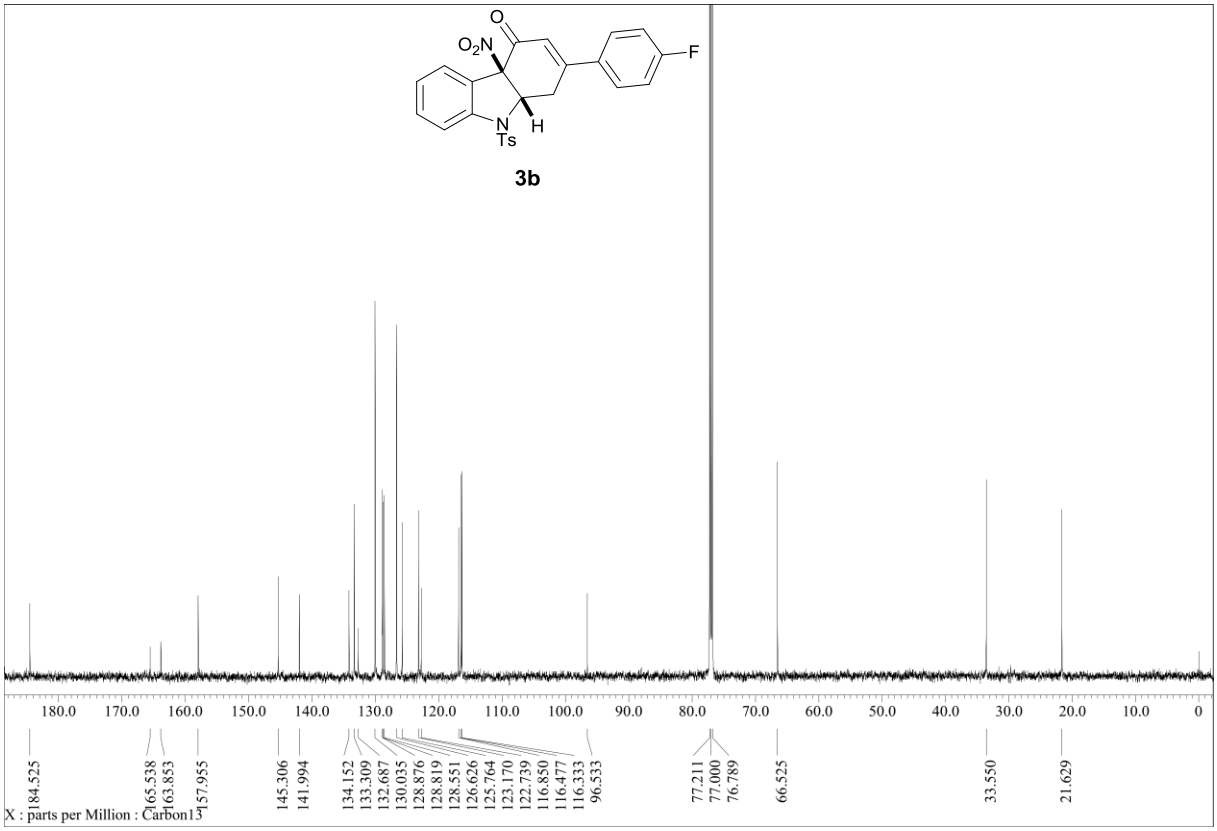
2	17.502	30758.172	944329.188	13.4457
Total		279605.406	7023284.688	100.0000

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N
Ts
H
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120.0
110.0
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30.0
20.0
10.0
0
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165.538
163.853
157.955
145.306
141.994
134.152
133.309
132.687
130.035
128.876
128.819
128.551
126.626
125.764
123.170
122.739
116.850
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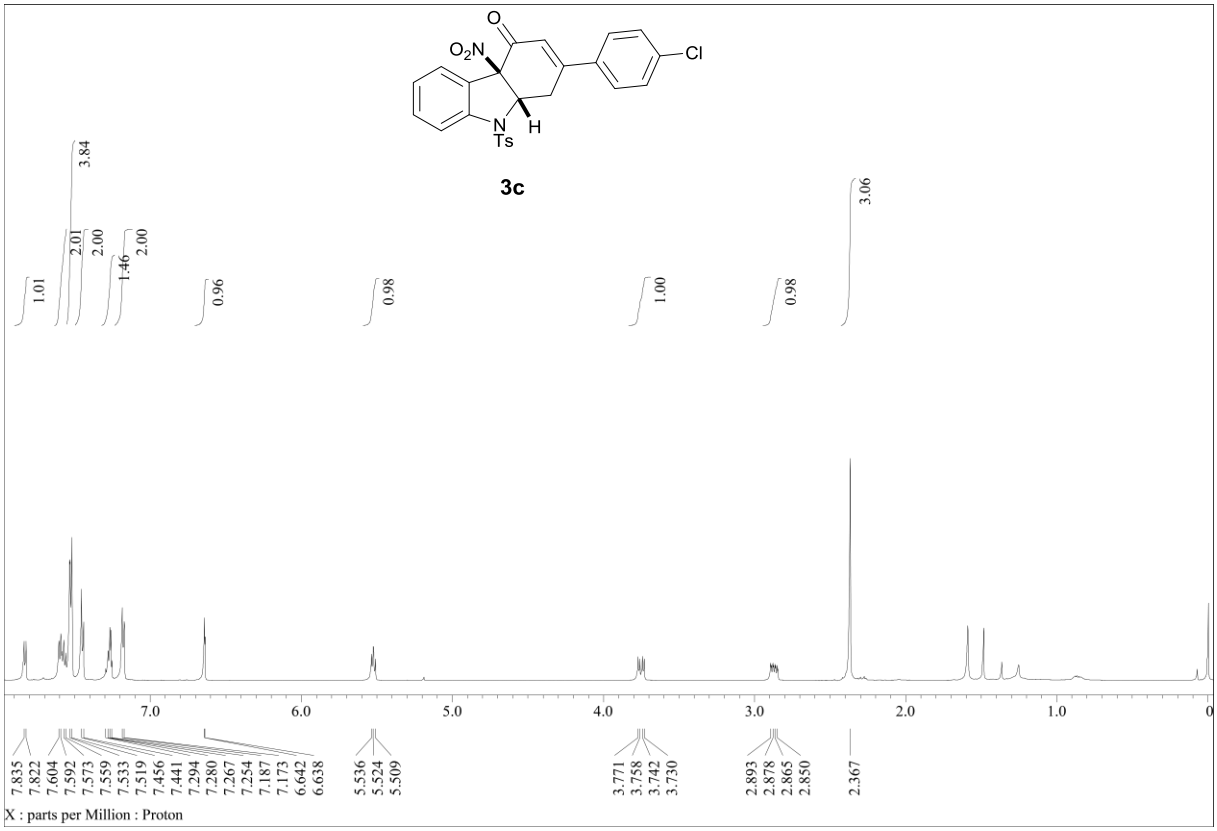
X : parts per Million : Carbon13

3b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Cl
N
Ts
H
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1.46
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1.00
0.98
3.06
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.835
7.822
7.604
7.592
7.573
7.559
7.533
7.519
7.456
7.441
7.294
7.280
7.267
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5.536
5.524
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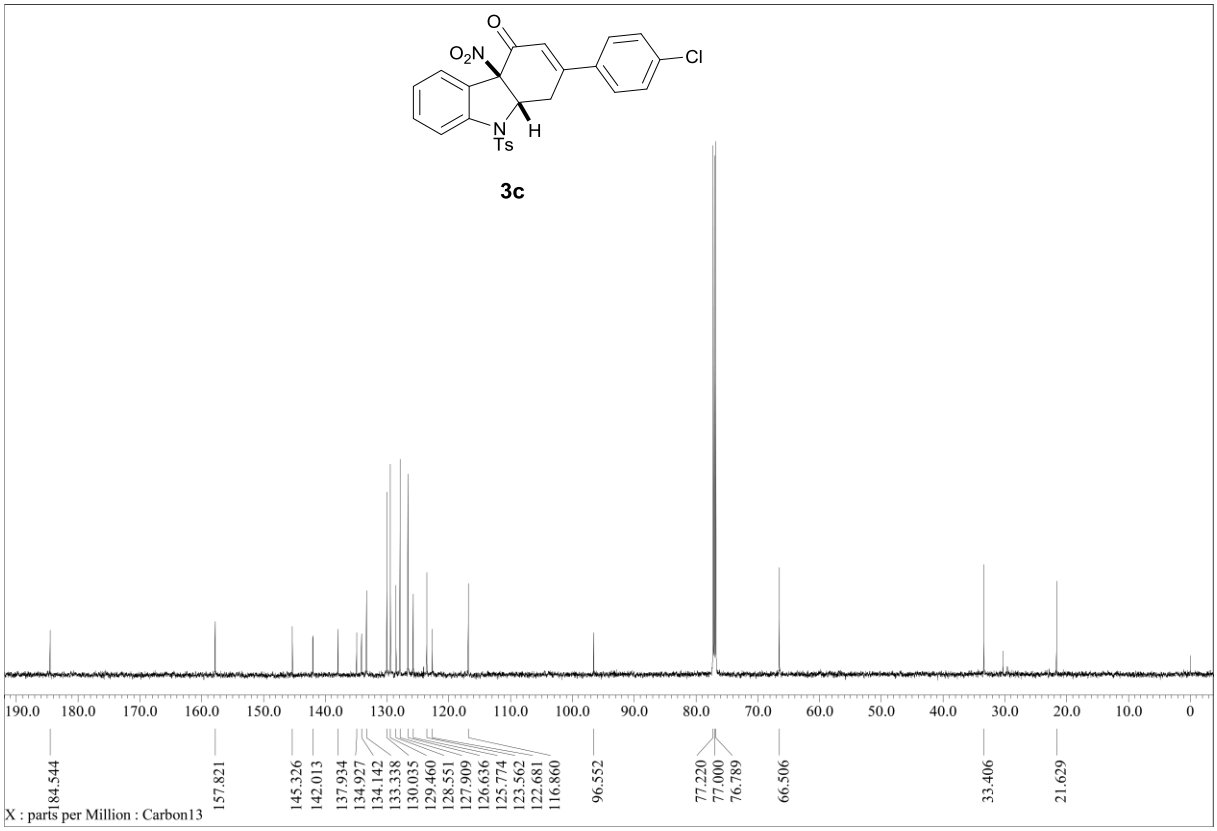
X : parts per Million : Proton

3c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O2N
Cl
N
H
Ts
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184.544
157.821
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142.013
137.934
134.927
134.142
133.338
130.035
129.460
128.551
127.909
126.636
125.774
123.562
122.681
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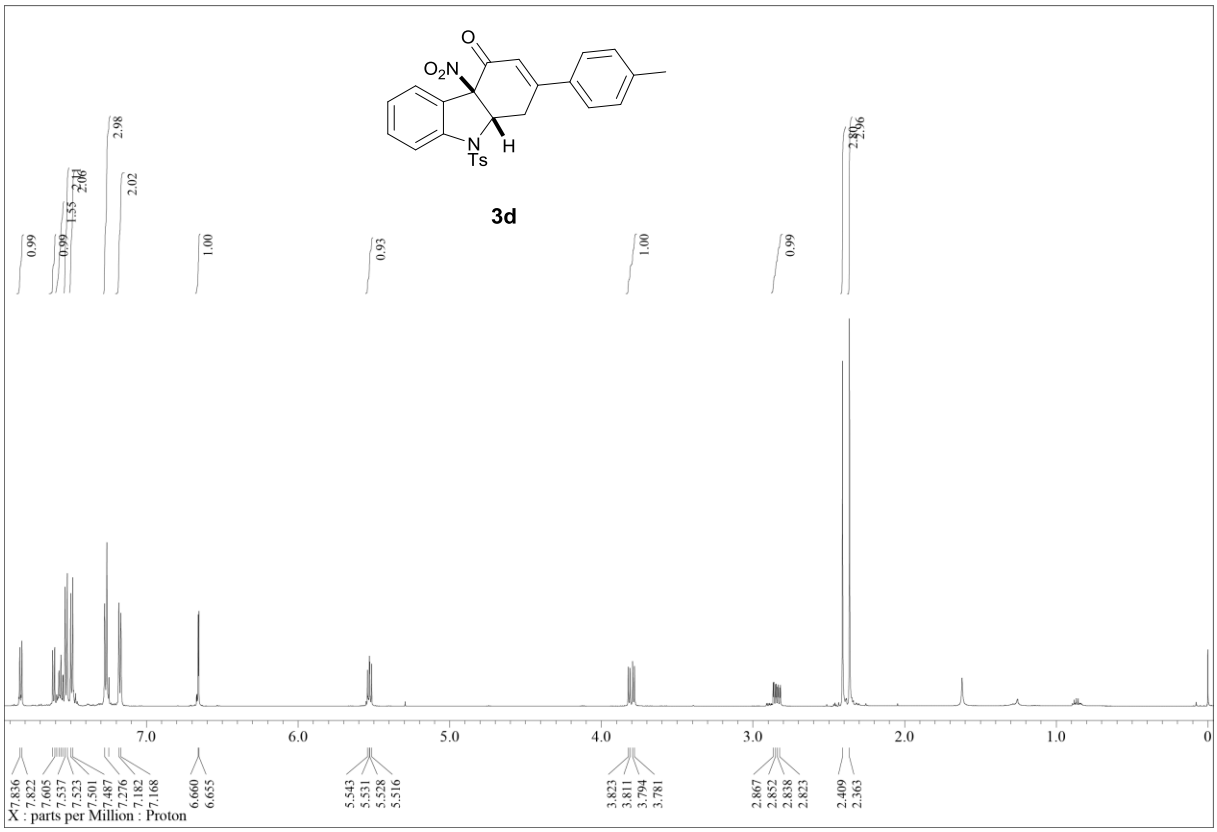
77.000
76.789
66.506
33.406
21.629
X : parts per Million : Carbon13

3c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H
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2.11
2.98
2.02
1.00
0.93
1.00
0.99
2.80
2.96
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.836
7.822
7.605
7.537
7.523
7.501
7.487
7.276
7.182
7.168
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6.655
5.543
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5.528
5.516
3.823
3.811
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2.867
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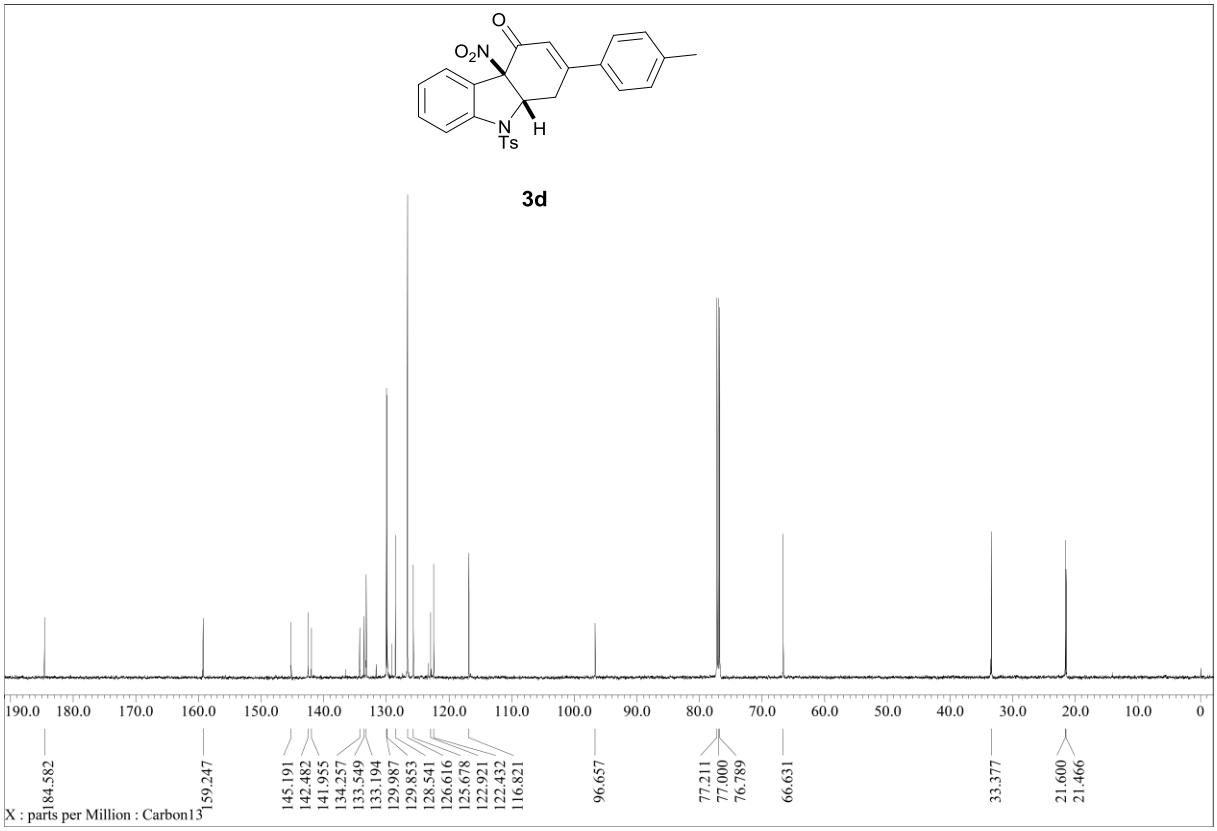
2.823
2.409
2.363
X : parts per Million : Proton

3d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O2N
N
Ts
H
3d
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133.549
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126.616
125.678
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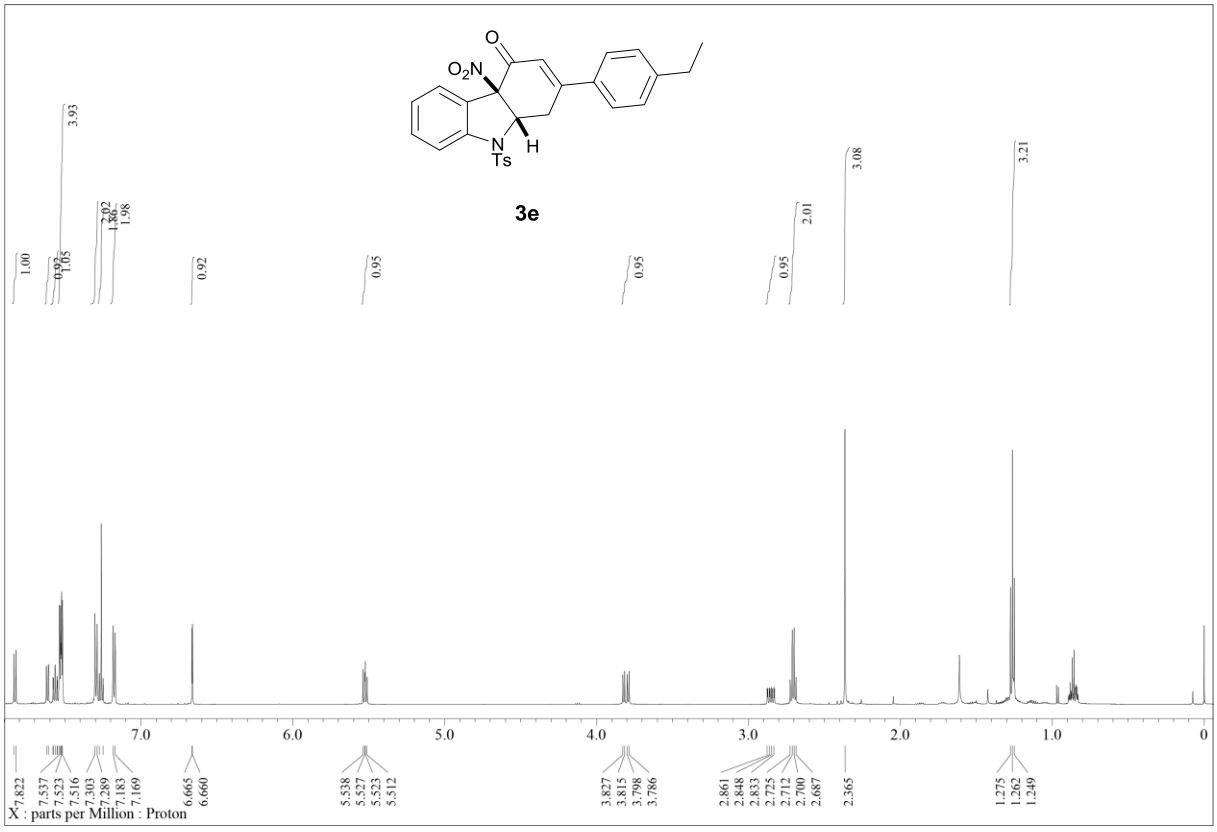
X : parts per Million : Carbon13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O2N
N
Ts
H
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0.95
0.95
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3.08
3.21
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.822
7.537
7.523
7.516
7.303
7.289
7.183
7.169
6.665
6.660
5.538
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5.523
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3.815
3.798
3.786
2.861
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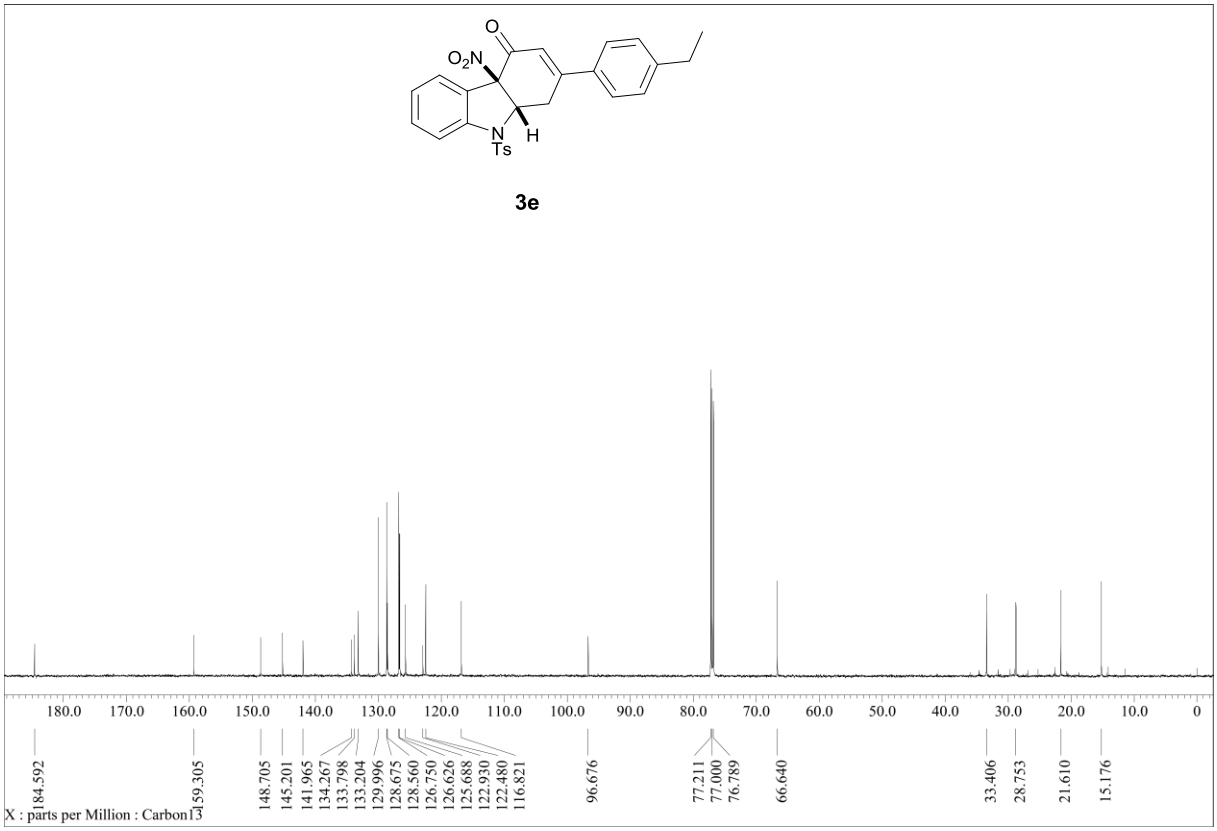
1.262
1.249
X : parts per Million : Proton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O2N
N
H
Ts
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160.0
150.0
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130.0
120.0
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70.0
60.0
50.0
40.0
30.0
20.0
10.0
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148.705
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133.204
129.996
128.675
128.560
126.750
126.626
125.688
122.930
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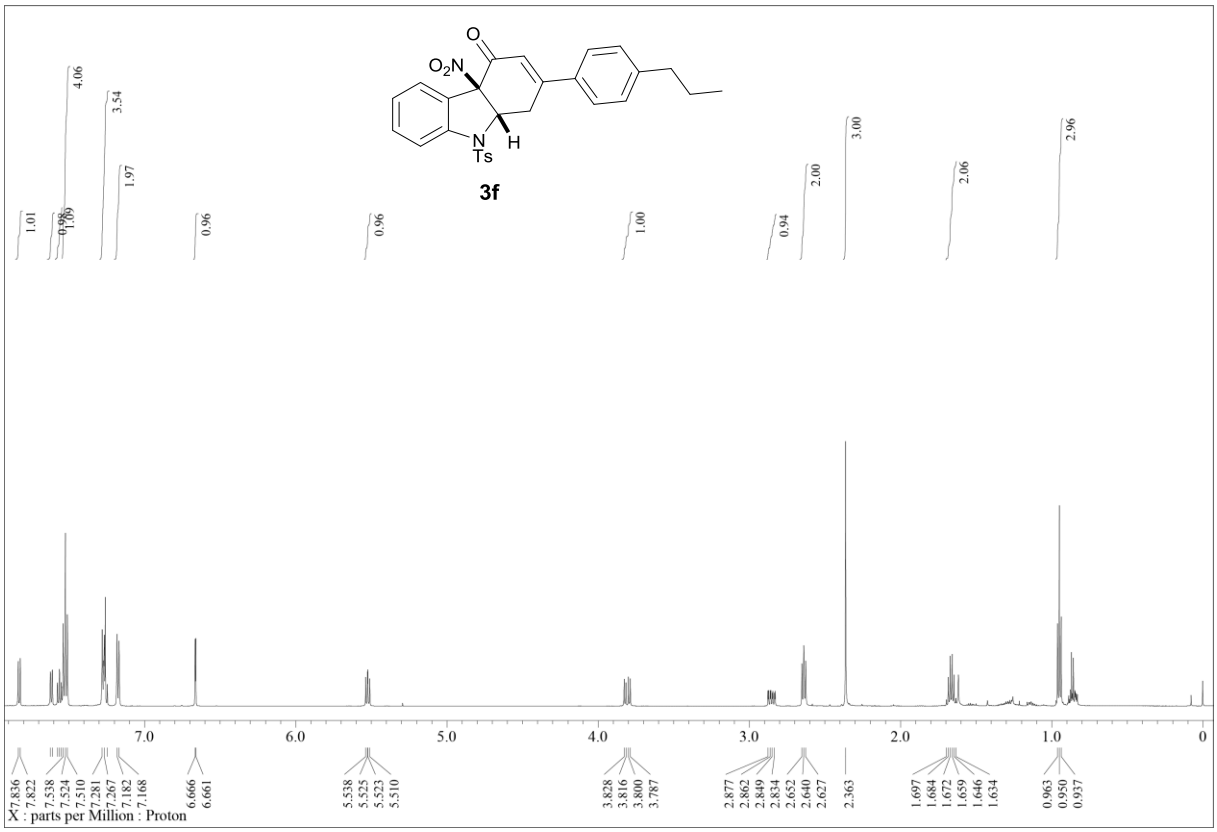
28.753
21.610
15.176
X : parts per Million : Carbon13

3e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O2N
N
H
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0.96
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0.94
2.00
3.00
2.06
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7.0
6.0
5.0
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2.0
1.0
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7.538
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7.182
7.168
6.666
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5.525
5.523
5.510
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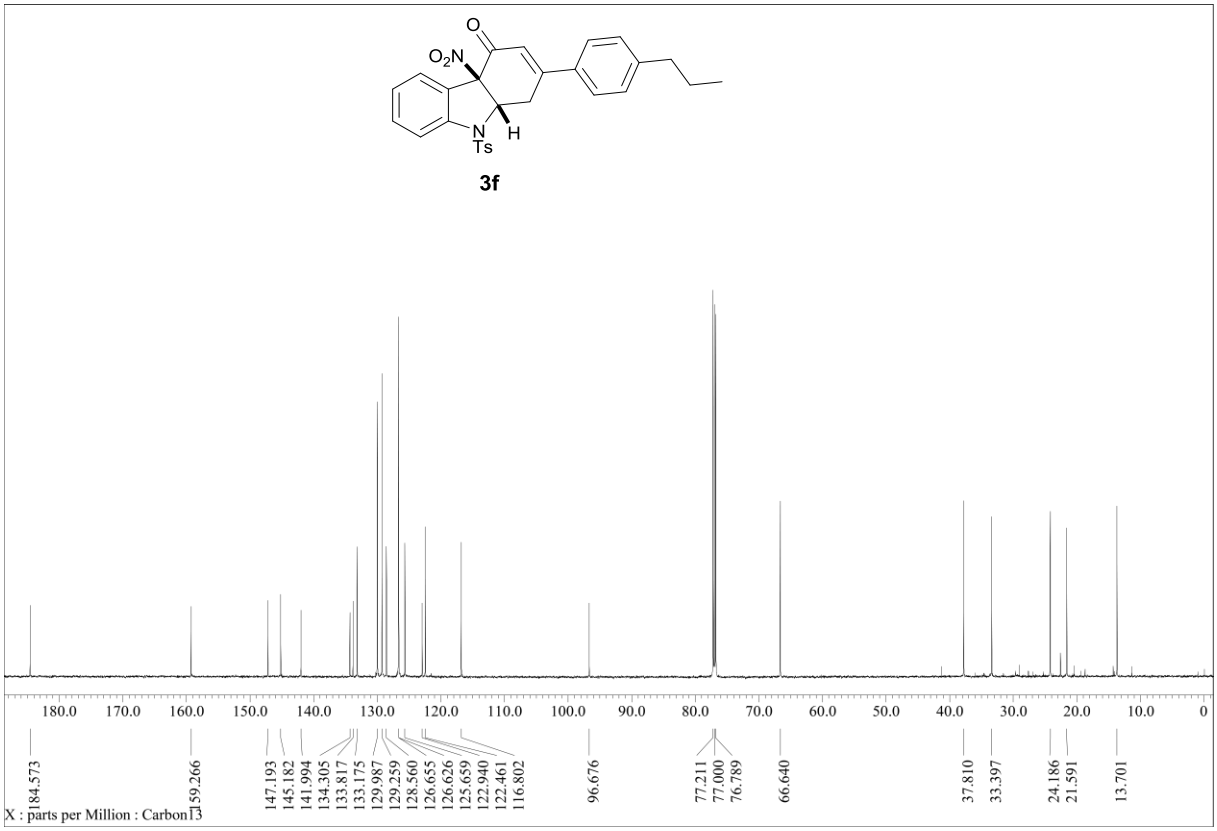
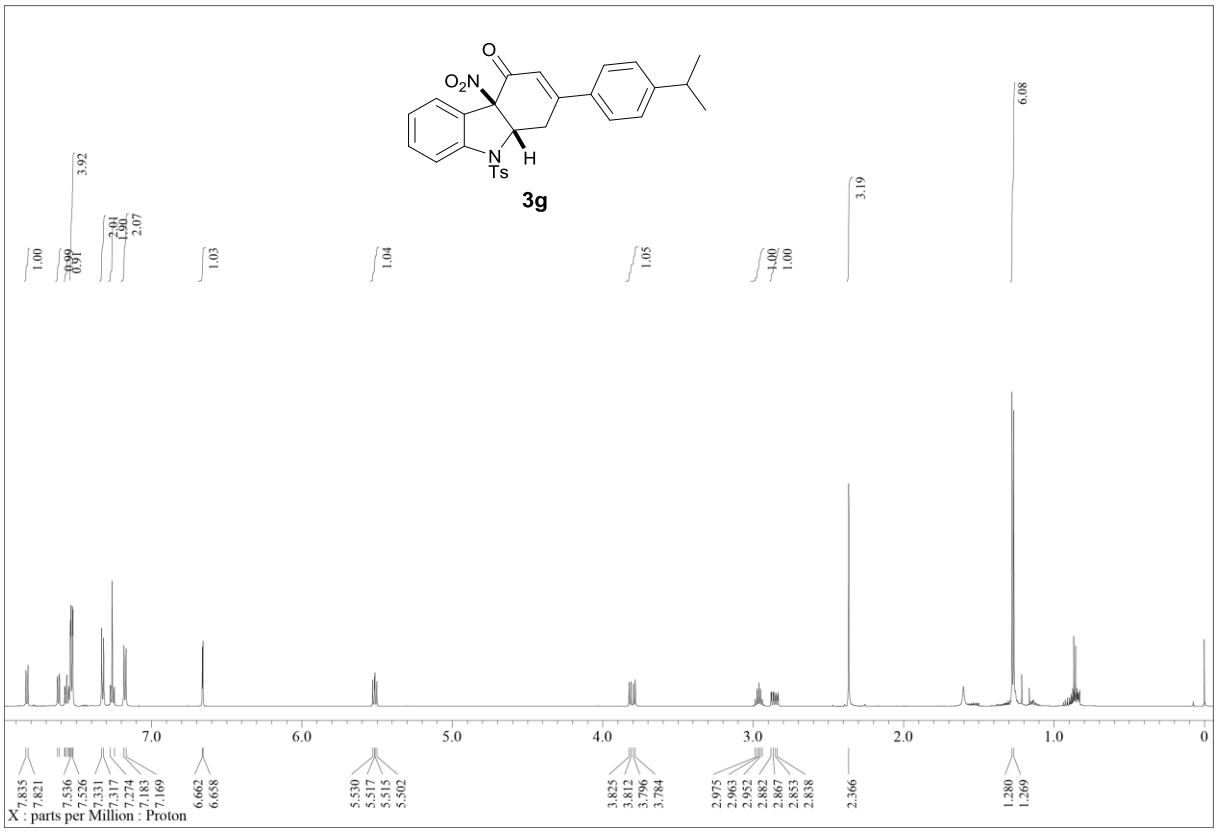
2.862
2.849
2.834
2.652
2.640
2.627
2.363
1.697
1.684
1.672
1.659
1.646
1.634
0.963
0.950
0.937
X : parts per Million : Proton

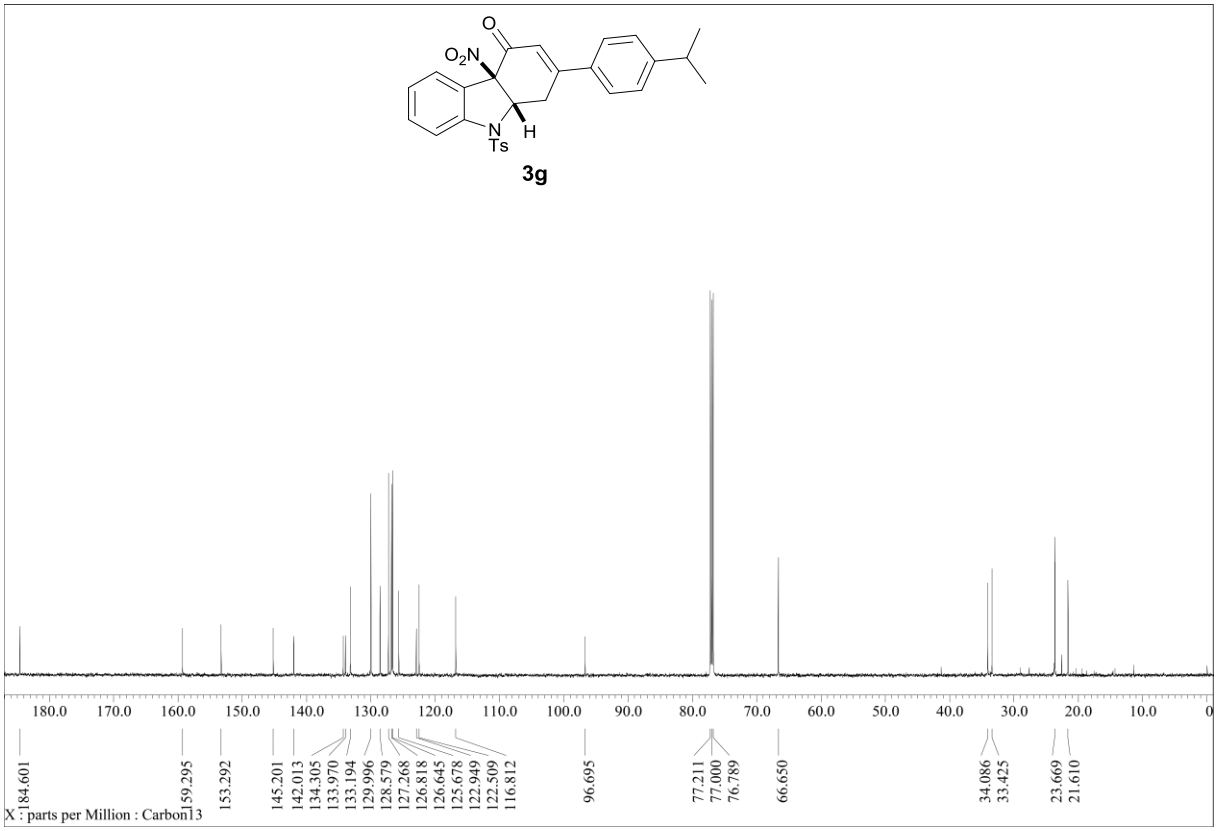
3f

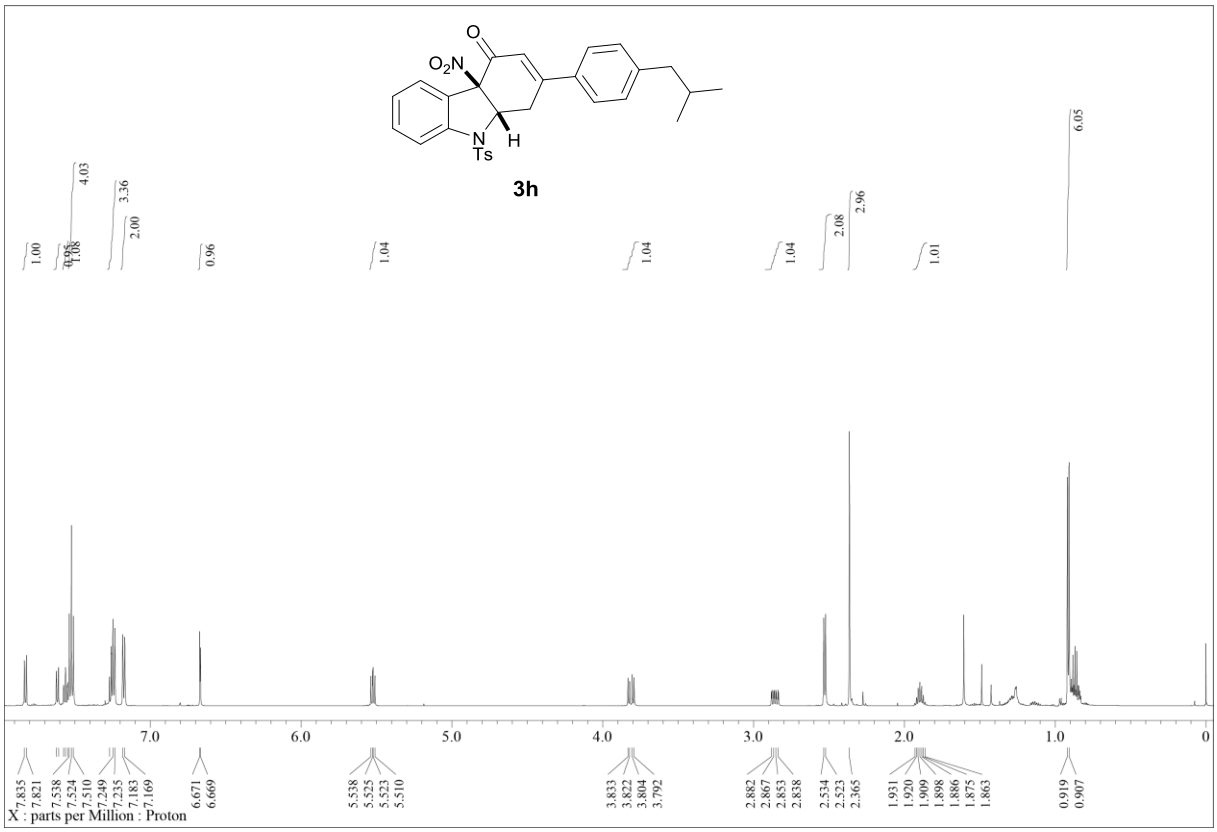

O
O2N
N
Ts
H
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.573
159.266
147.193
145.182
141.994
134.305
133.817
133.175
129.987
129.259
128.560
126.655
126.626
125.659
122.940
122.461
116.802
96.676
77.211
77.000
76.789
66.640
37.810
33.397
24.186
21.591
13.701
X : parts per Million : Carbon13

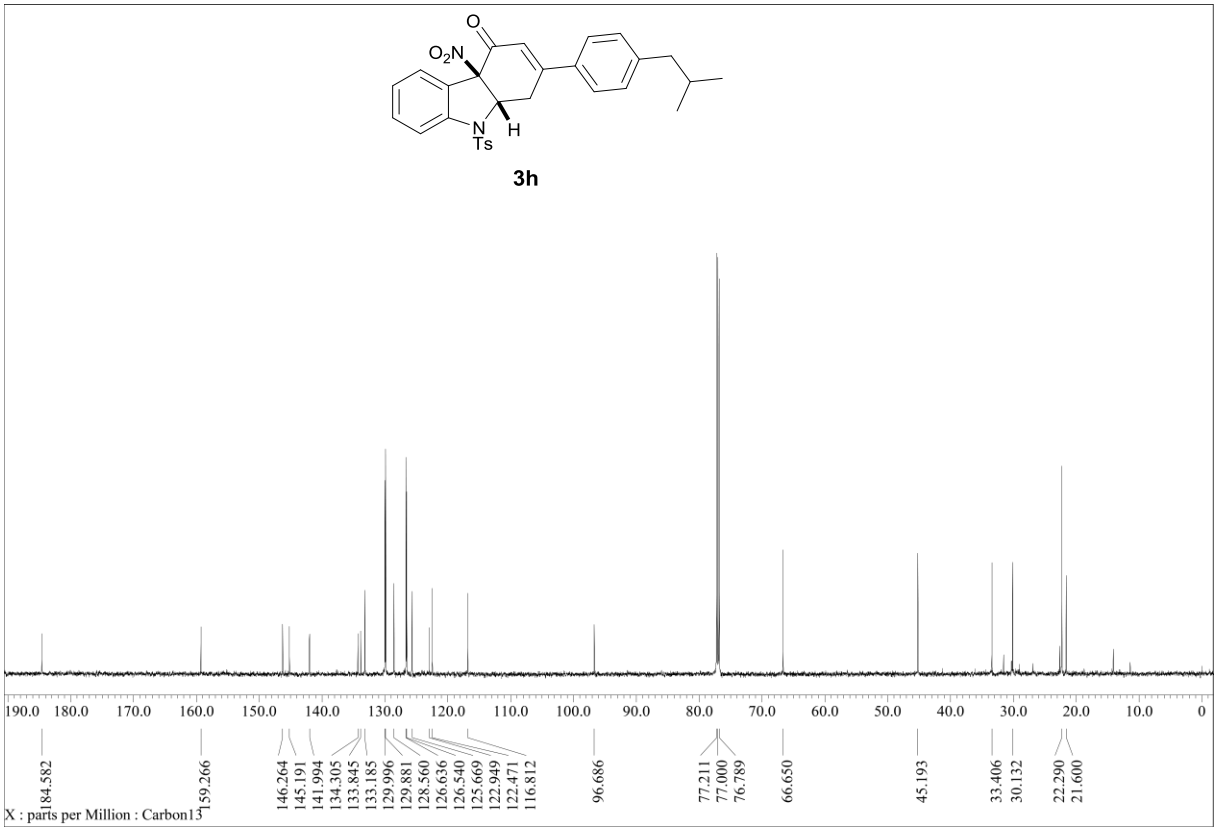
3f

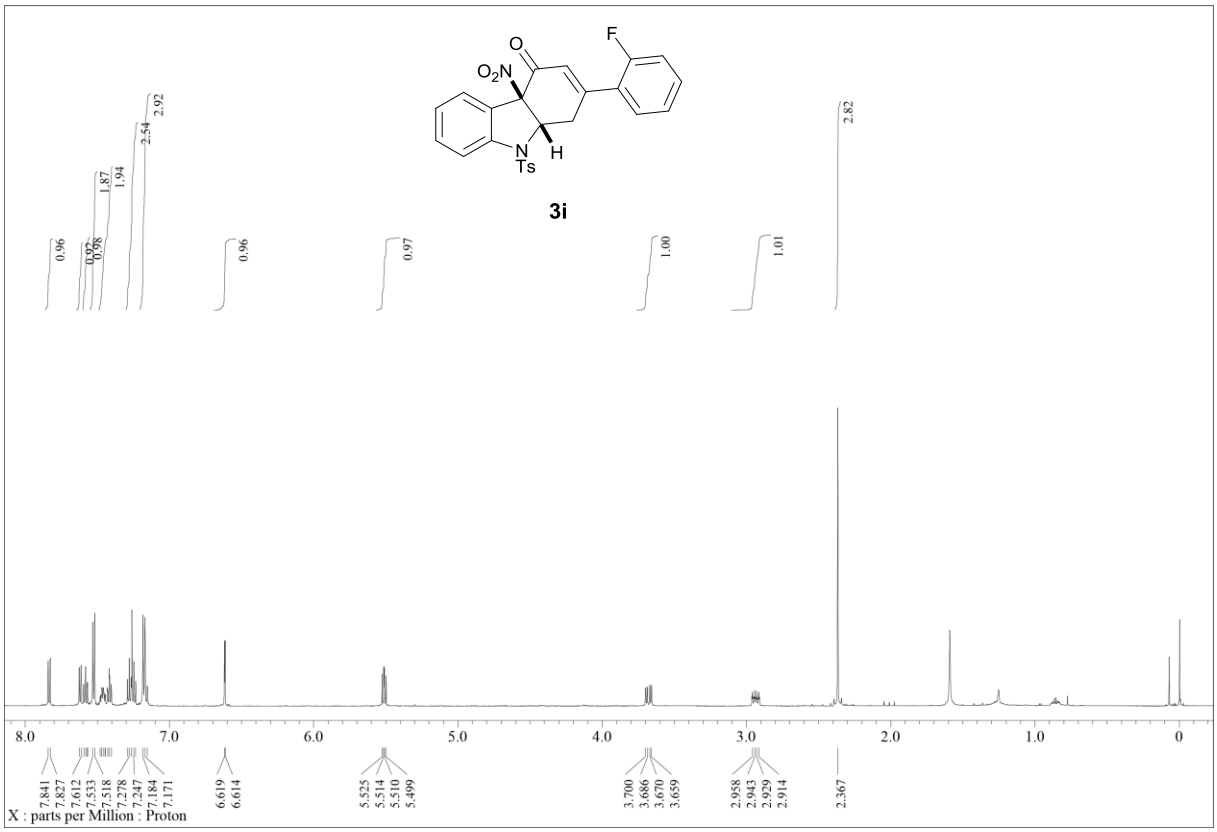

O
O2N
N
Ts
H
1.00
0.99
0.91
3.92
2.01
1.90
2.07
1.03
1.04
1.05
1.00
1.00
3.19
6.08
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.835
7.821
7.536
7.526
7.331
7.317
7.274
7.183
7.169
6.662
6.658
5.530
5.517
5.515
5.502
3.825
3.812
3.796
3.784
2.975
2.963
2.952
2.882
2.867
2.853
2.838
2.366
1.280
1.269
X : parts per Million : Proton

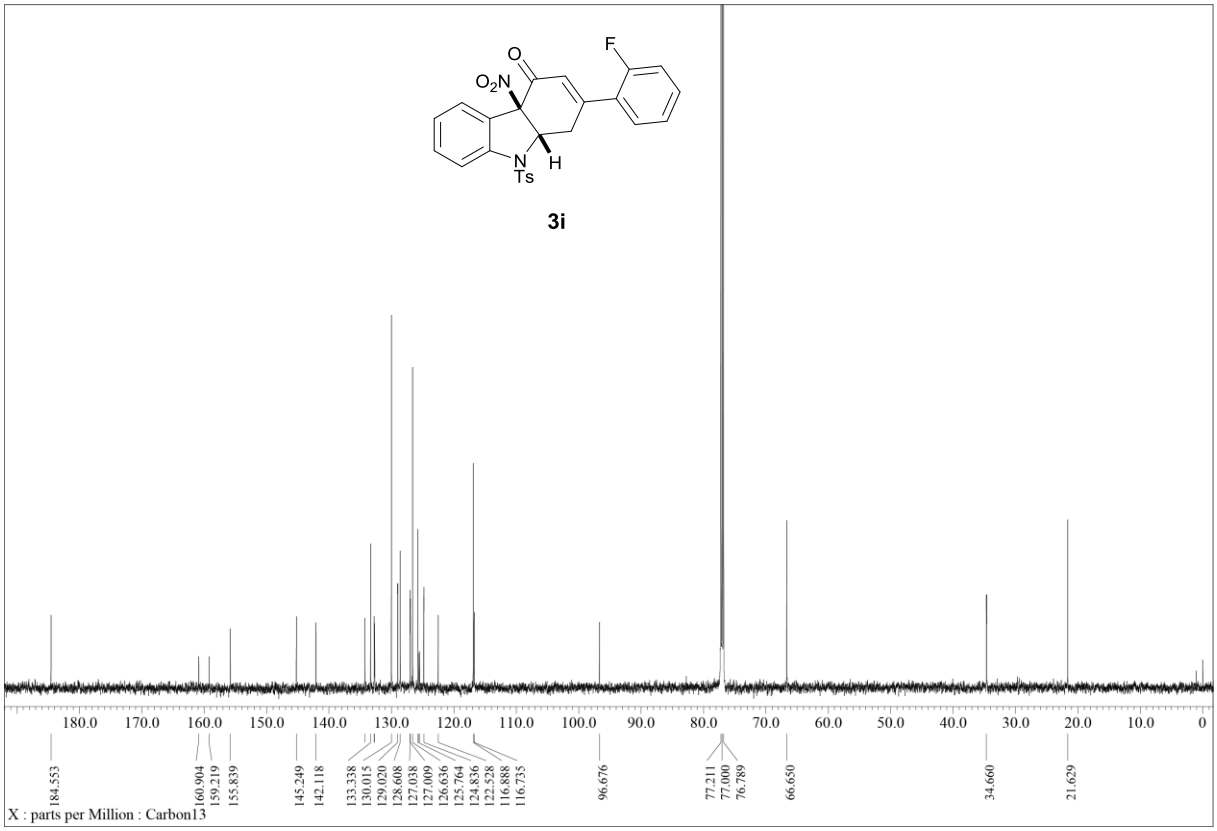
3g

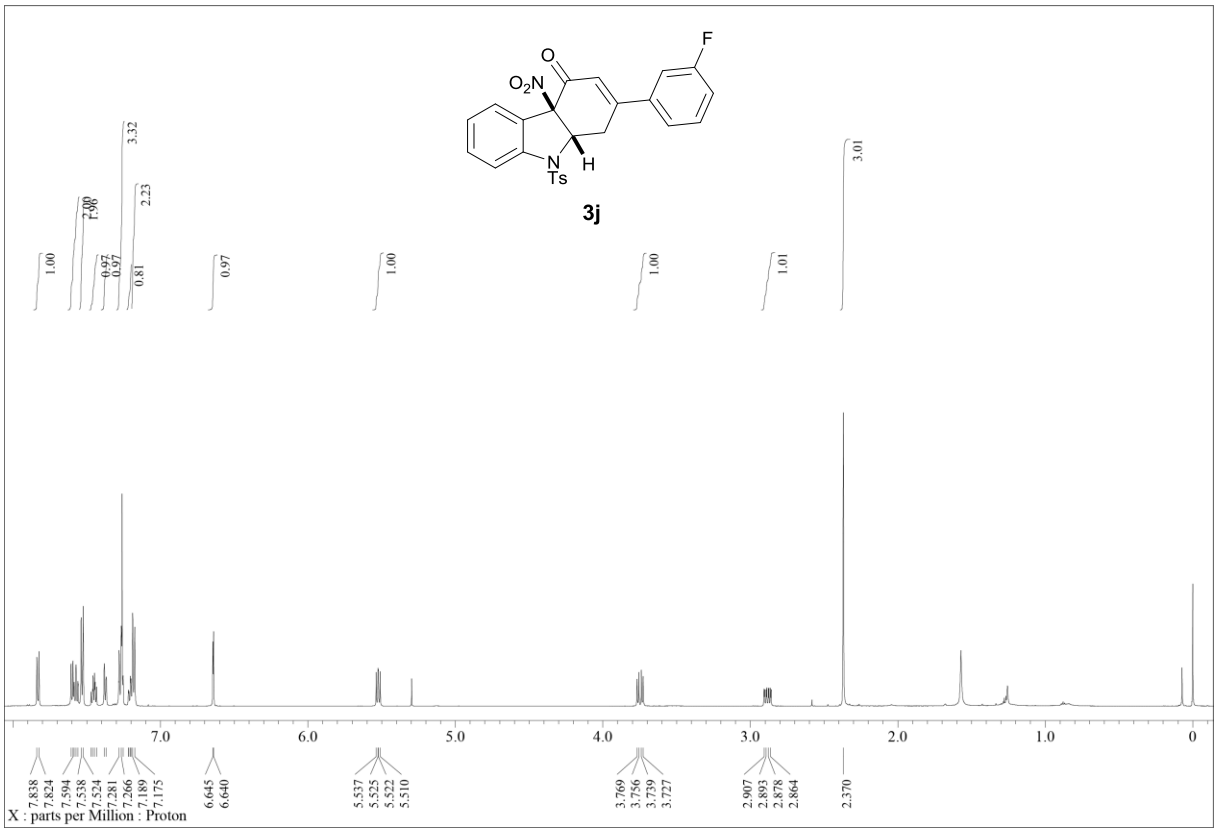

O
O2N
N
Ts
H
3g
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.601
159.295
153.292
145.201
142.013
134.305
133.970
133.194
129.996
128.579
127.268
126.818
126.645
125.678
122.949
122.509
116.812
96.695
77.211
77.000
76.789
66.650
34.086
33.425
23.669
21.610
X : parts per Million : Carbon13

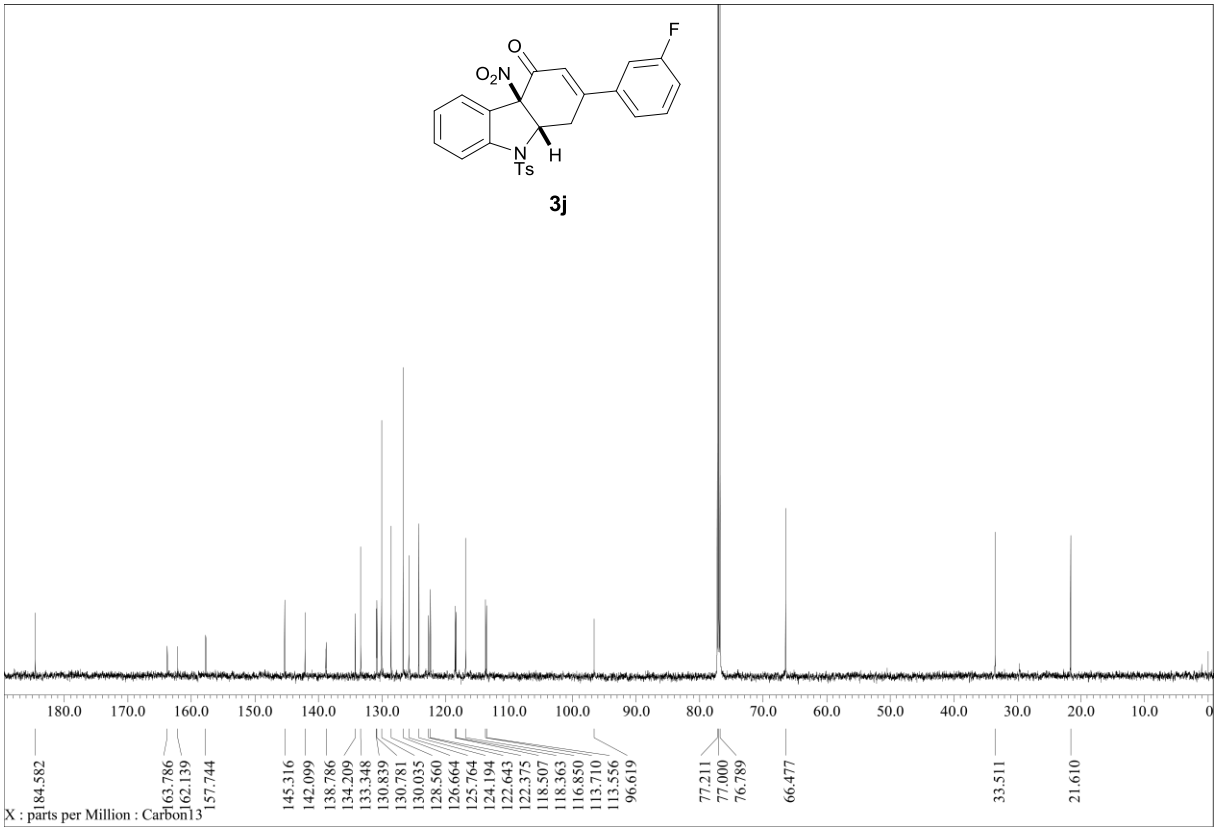

O
O2N
N
Ts
H
3h
1.00
4.03
3.36
2.00
0.96
1.04
1.04
1.04
2.08
2.96
1.01
6.05
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.835
7.821
7.538
7.524
7.510
7.249
7.235
7.183
7.169
6.671
6.669
5.538
5.525
5.523
5.510
3.833
3.822
3.804
3.792
2.882
2.867
2.853
2.838
2.534
2.523
2.365
1.931
1.920
1.909
1.898
1.886
1.875
1.863
0.919
0.907
X : parts per Million : Proton

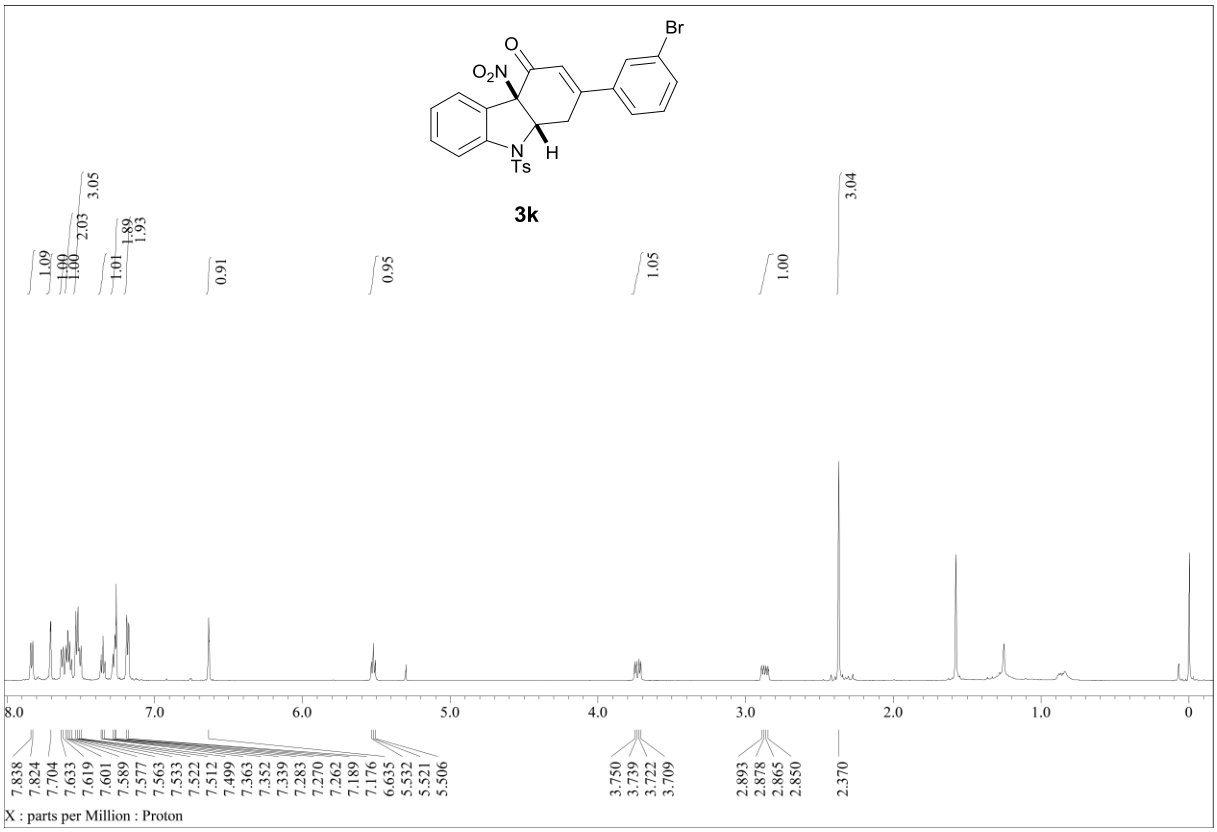

O
O2N
N
Ts
H
3h
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.582
159.266
146.264
145.191
141.994
134.305
133.845
133.185
129.996
129.881
128.560
126.636
126.540
125.669
122.949
122.471
116.812
96.686
77.211
77.000
76.789
66.650
45.193
33.406
30.132
22.290
21.600
X : parts per Million : Carbon13

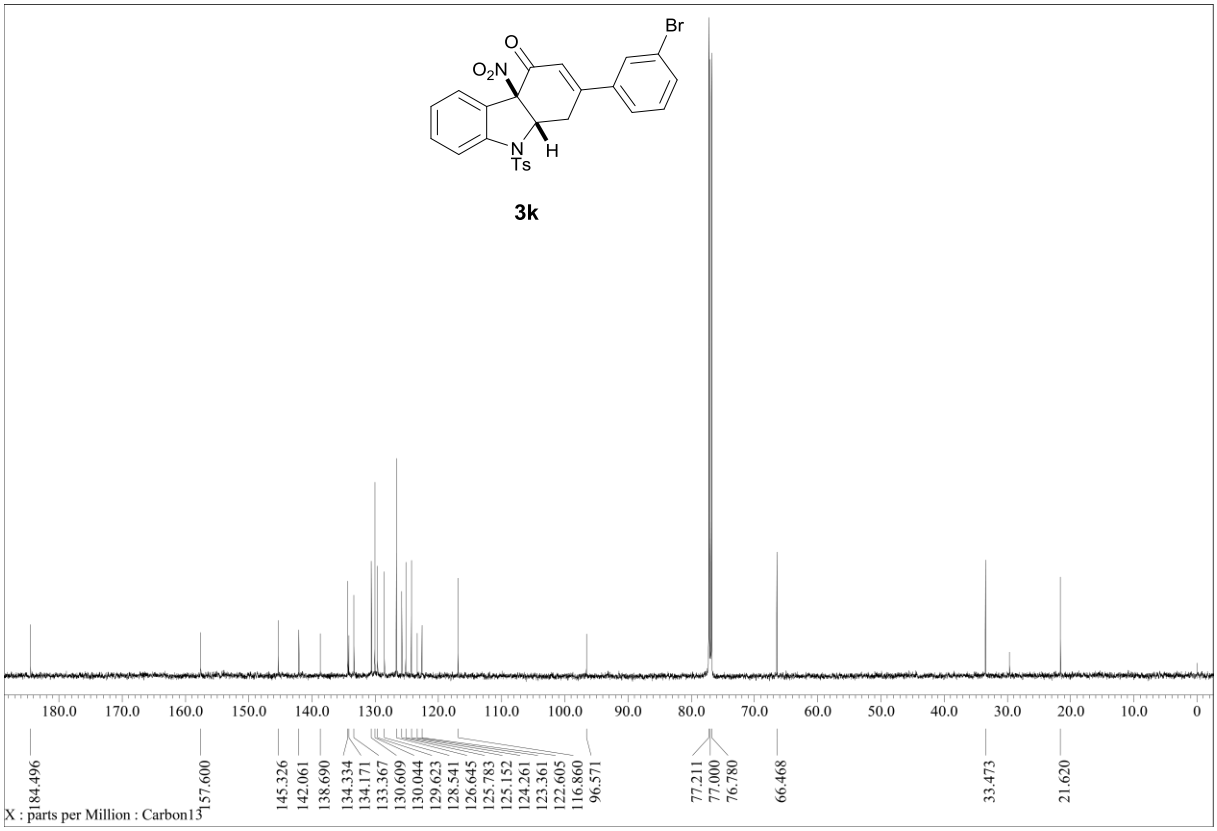

O
O2N
F
N
Ts
H
3i
0.96
0.96
0.97
1.00
1.01
2.82
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.841
7.827
7.612
7.533
7.518
7.278
7.247
7.184
7.171
6.619
6.614
5.525
5.514
5.510
5.499
3.700
3.686
3.670
3.659
2.958
2.943
2.929
2.914
2.367
X : parts per Million : Proton


O
F
O2N
N
H
Ts
3i
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
184.553
160.904
159.219
155.839
145.249
142.118
133.338
130.015
129.020
128.608
127.038
127.009
126.636
125.764
124.836
122.528
116.888
116.735
96.676
77.211
77.000
76.789
66.650
34.660
21.629
X : parts per Million : Carbon13

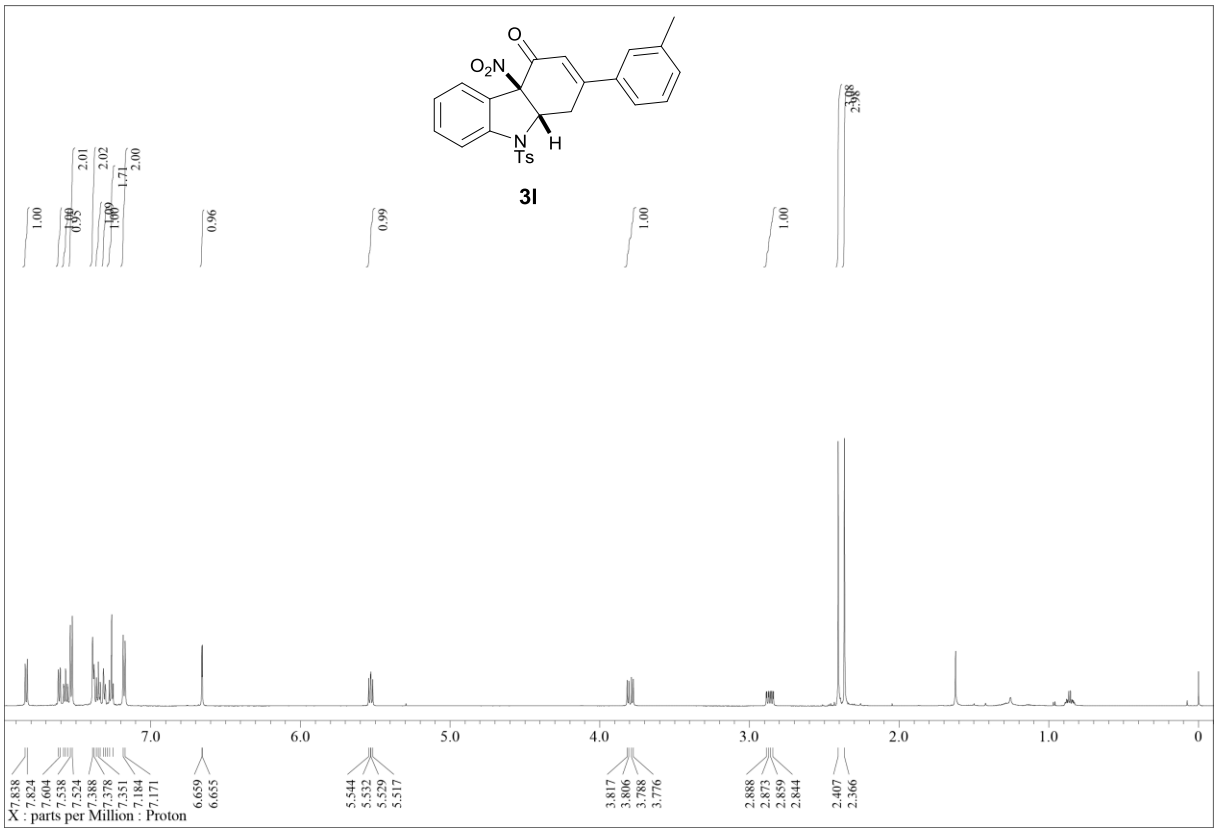

O
F
O2N
N
H
Ts
3j
3.32
2.23
3.01
1.00
0.97
0.97
0.97
0.81
0.97
1.00
1.00
1.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.838
7.824
7.594
7.538
7.524
7.281
7.266
7.189
7.175
6.645
6.640
5.537
5.525
5.522
5.510
3.769
3.756
3.739
3.727
2.907
2.893
2.878
2.864
2.370
X : parts per Million : Proton


F
O
O2N
N
Ts
H
3j
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
184.582
163.786
162.139
157.744
145.316
142.099
138.786
134.209
133.348
130.839
130.781
130.035
128.560
126.664
125.764
124.194
122.643
122.375
118.507
118.363
116.850
113.710
113.556
96.619
77.211
77.000
76.789
66.477
33.511
21.610
X : parts per Million : Carbon13

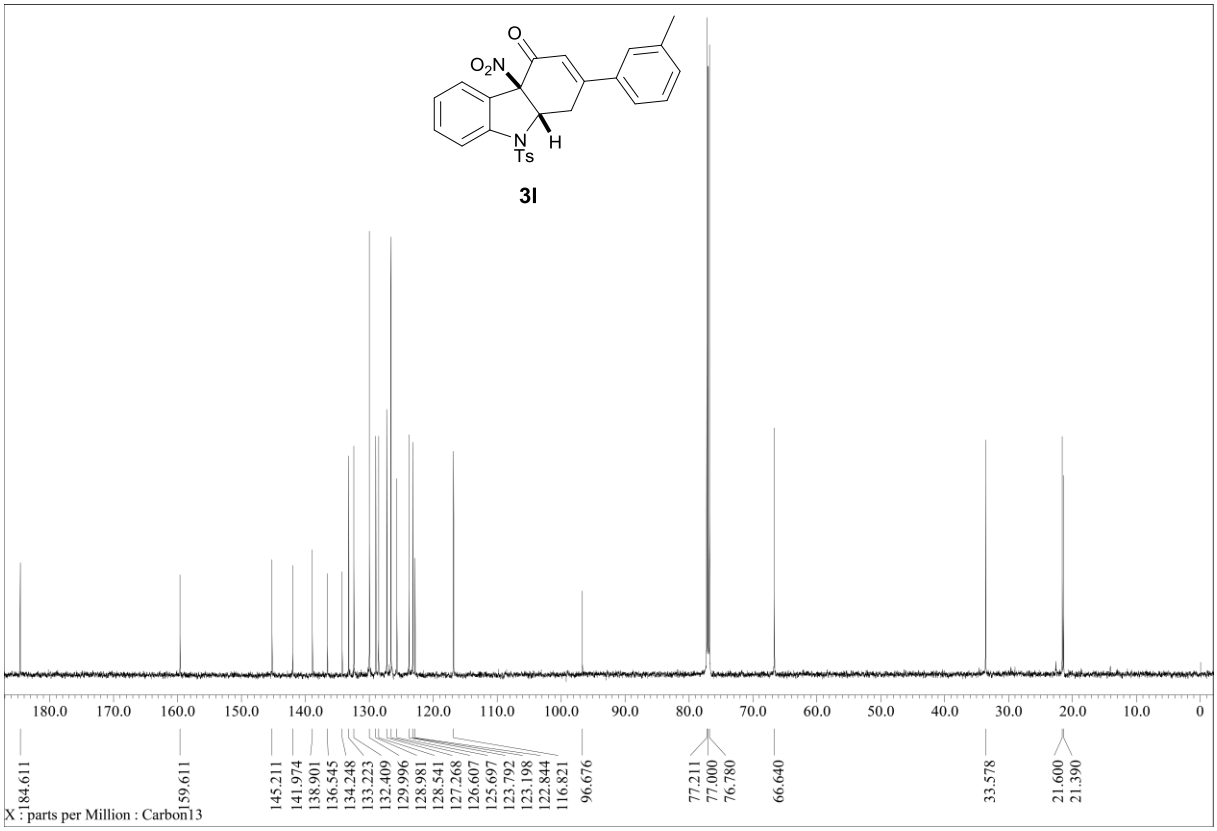

Br
O
O2N
N
Ts
H
3k
3.05
2.03
1.89
1.93
1.09
1.00
1.00
1.01
0.91
0.95
1.05
1.00
3.04
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.838
7.824
7.704
7.633
7.619
7.601
7.589
7.577
7.563
7.533
7.522
7.512
7.499
7.363
7.352
7.339
7.283
7.270
7.262
7.189
7.176
6.635
5.532
5.521
5.506
3.750
3.739
3.722
3.709
2.893
2.878
2.865
2.850
2.370
X : parts per Million : Proton

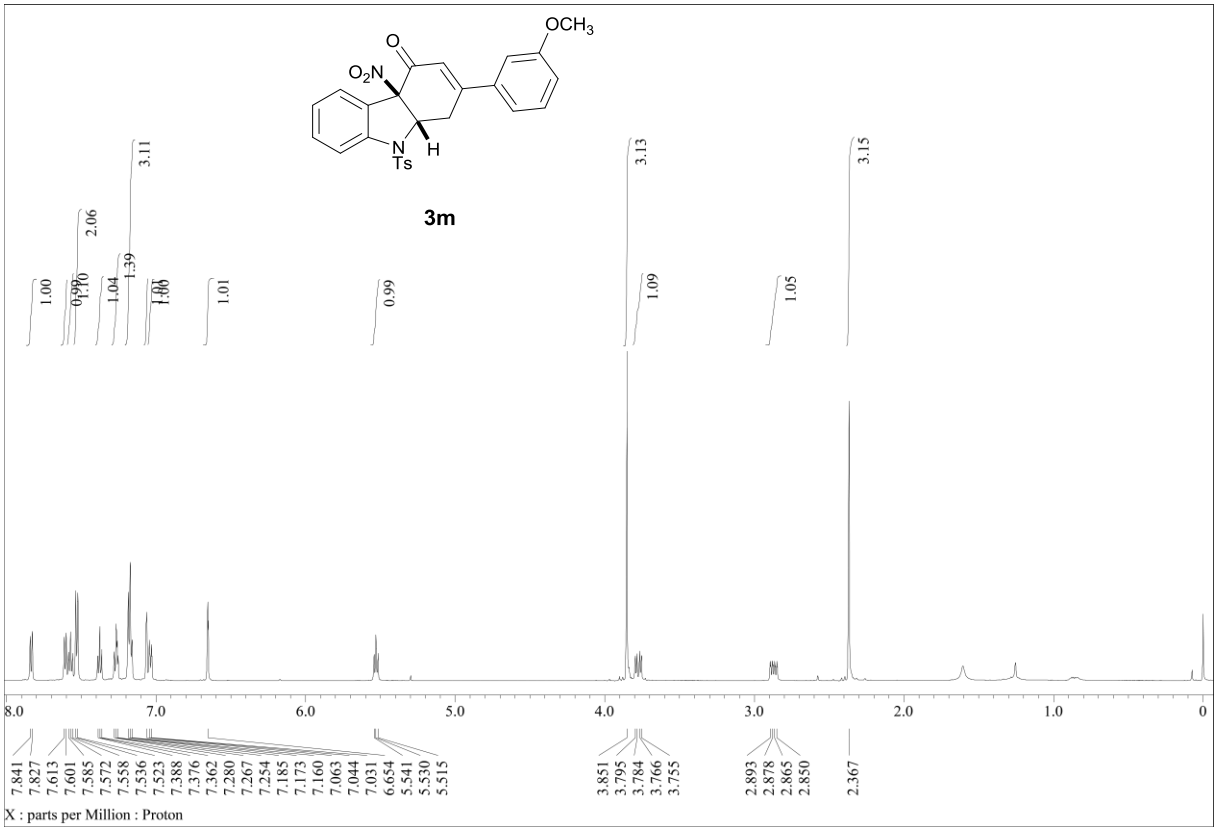

Br
O
O2N
N
H
Ts
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.496
157.600
145.326
142.061
138.690
134.334
134.171
133.367
130.609
130.044
129.623
128.541
126.645
125.783
125.152
124.261
123.361
122.605
116.860
96.571
77.211
77.000
76.780
66.468
33.473
21.620
X : parts per Million : Carbon13

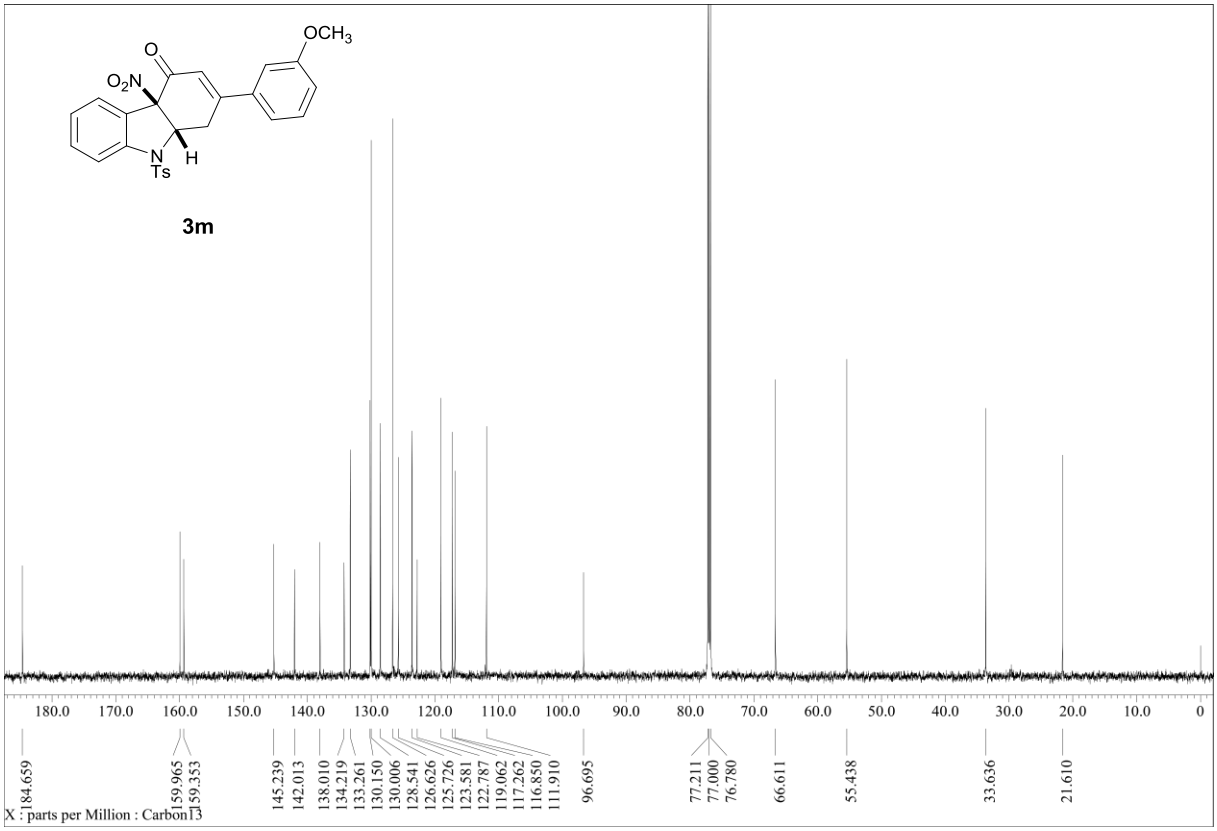
3k

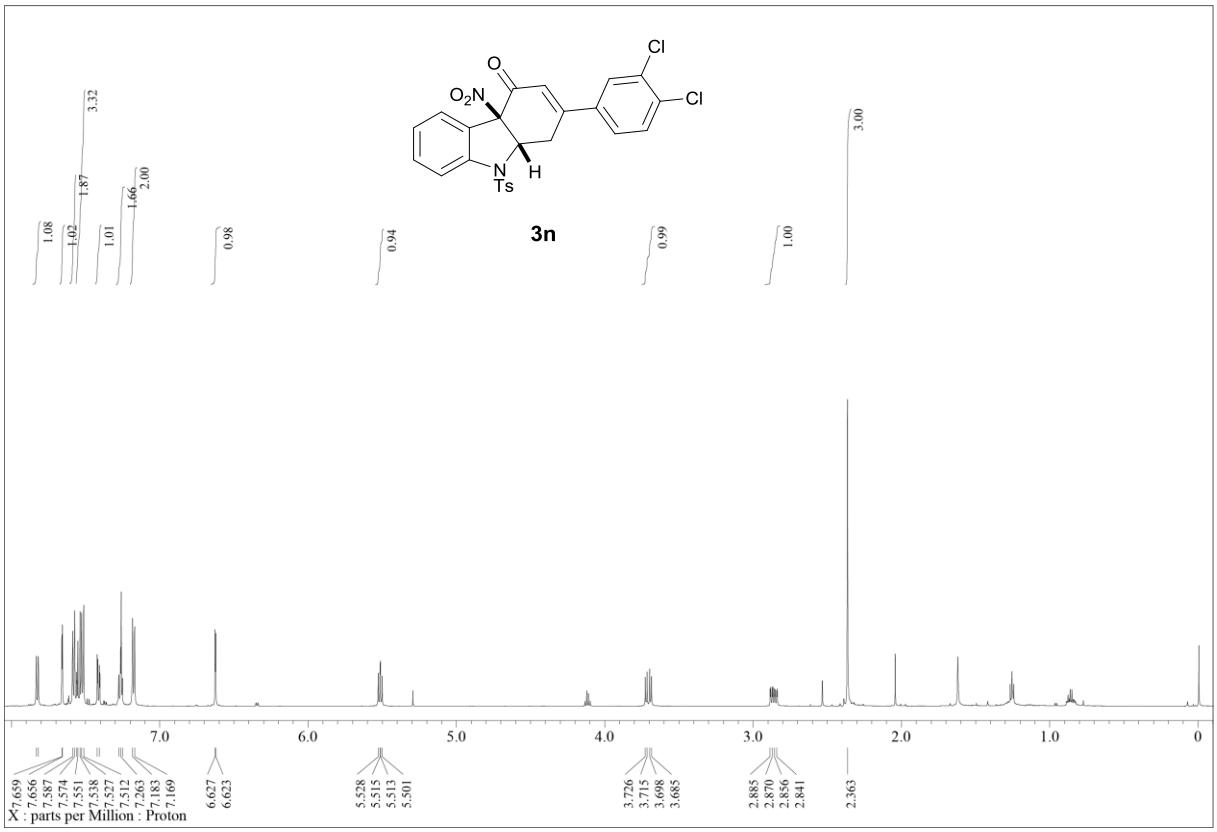

O
O2N
N
H
Ts
1.00
2.01
2.02
1.71
2.00
0.96
0.99
1.00
1.00
2.98
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.838
7.824
7.604
7.538
7.524
7.388
7.378
7.351
7.184
7.171
6.659
6.655
5.544
5.532
5.529
5.517
3.817
3.806
3.788
3.776
2.888
2.873
2.859
2.844
2.407
2.366
X : parts per Million : Proton

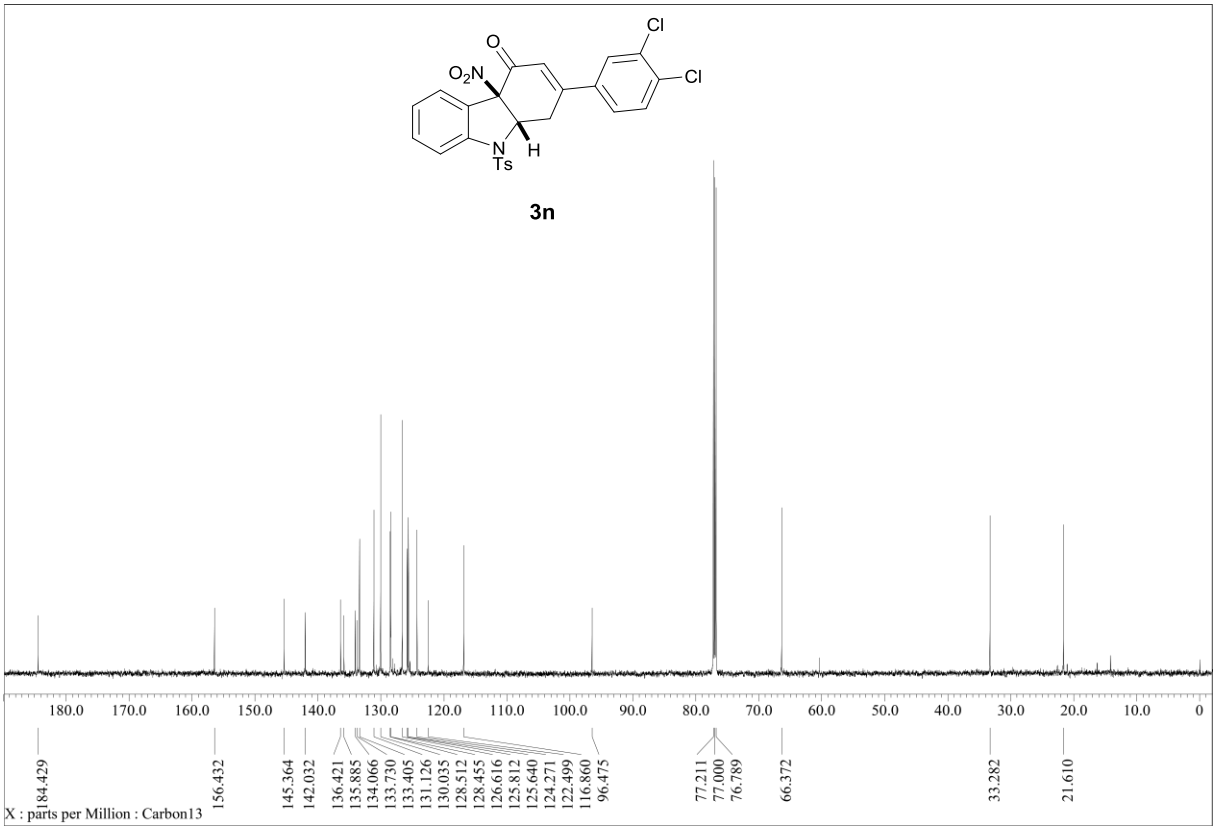
3l


O
O2N
N
Ts
H
3l
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
184.611
159.611
145.211
141.974
138.901
136.545
134.248
133.223
132.409
129.996
128.981
128.541
127.268
126.607
125.697
123.792
123.198
122.844
116.821
96.676
77.211
77.000
76.780
66.640
33.578
21.600
21.390
X : parts per Million : Carbon13

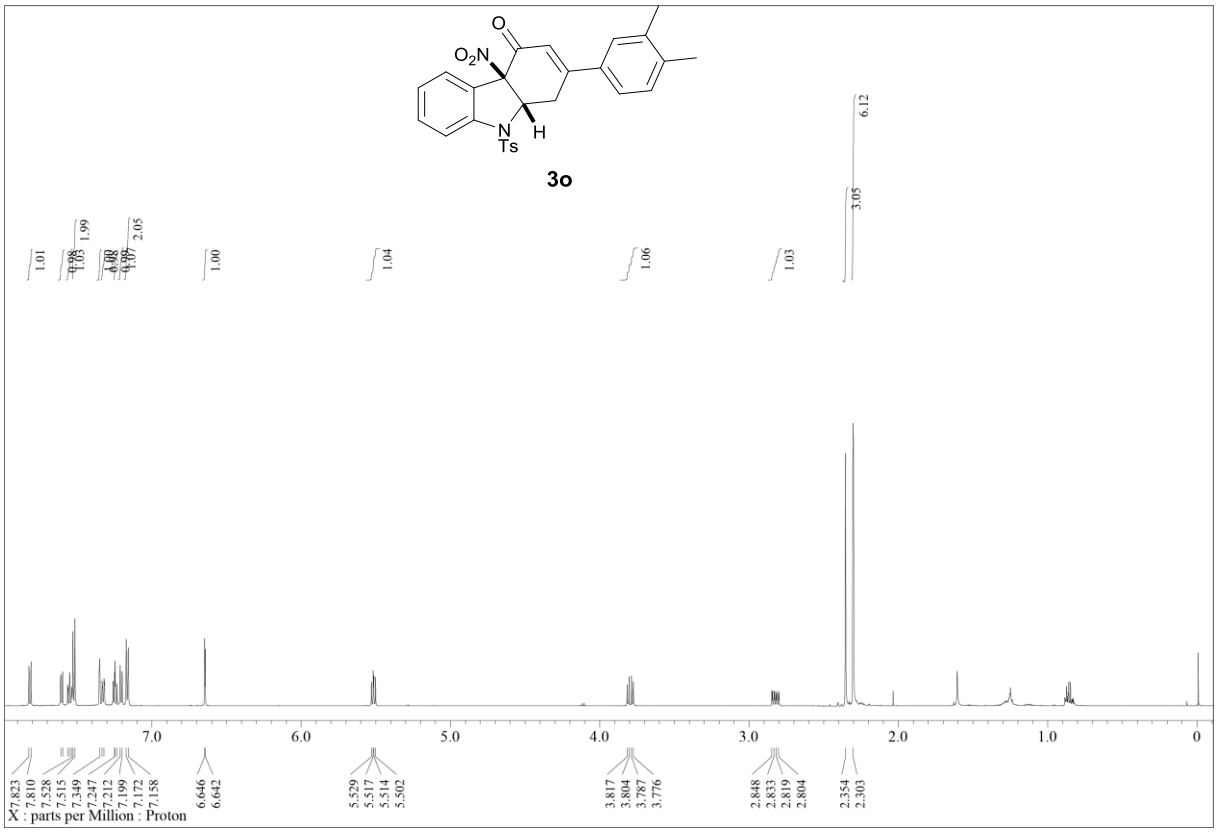

OCH3
O
O2N
N
Ts
H
3m
3.11
2.06
1.39
1.00
1.04
1.01
0.99
3.13
1.09
1.05
3.15
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.841
7.827
7.613
7.601
7.585
7.572
7.558
7.536
7.523
7.388
7.376
7.362
7.280
7.267
7.254
7.185
7.173
7.160
7.063
7.044
7.031
6.654
5.541
5.530
5.515
3.851
3.795
3.784
3.766
3.755
2.893
2.878
2.865
2.850
2.367
X : parts per Million : Proton


OCH3
O
O2N
N
Ts
H
3m
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
184.659
159.965
159.353
145.239
142.013
138.010
134.219
133.261
130.150
130.006
128.541
126.626
125.726
123.581
122.787
119.062
117.262
116.850
111.910
96.695
77.211
77.000
76.780
66.611
55.438
33.636
21.610
X : parts per Million : Carbon13

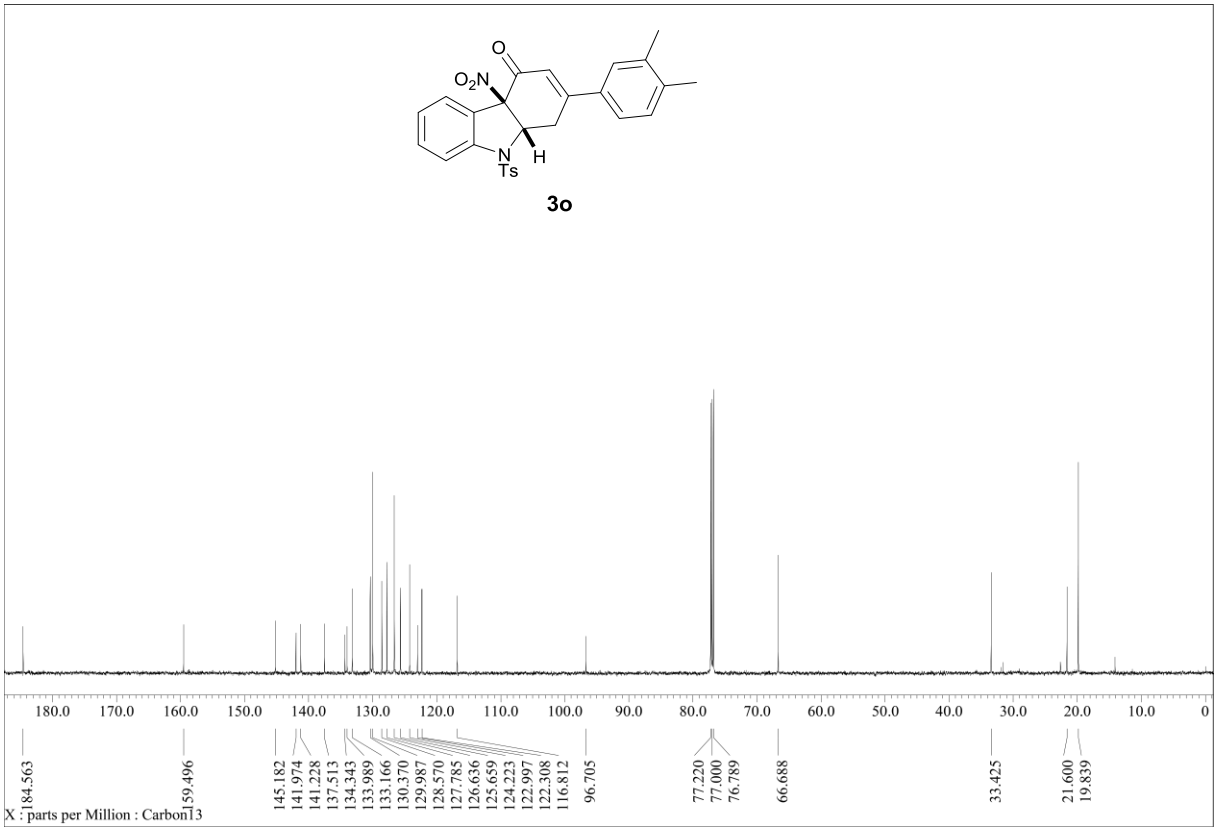

Cl
Cl
O
O2N
N
Ts
H
3n
3.32
1.87
2.00
1.66
1.08
1.02
1.01
0.98
0.94
0.99
1.00
3.00
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.659
7.656
7.587
7.574
7.551
7.538
7.527
7.512
7.263
7.183
7.169
6.627
6.623
5.528
5.515
5.513
5.501
3.726
3.715
3.698
3.685
2.885
2.870
2.856
2.841
2.363
X : parts per Million : Proton

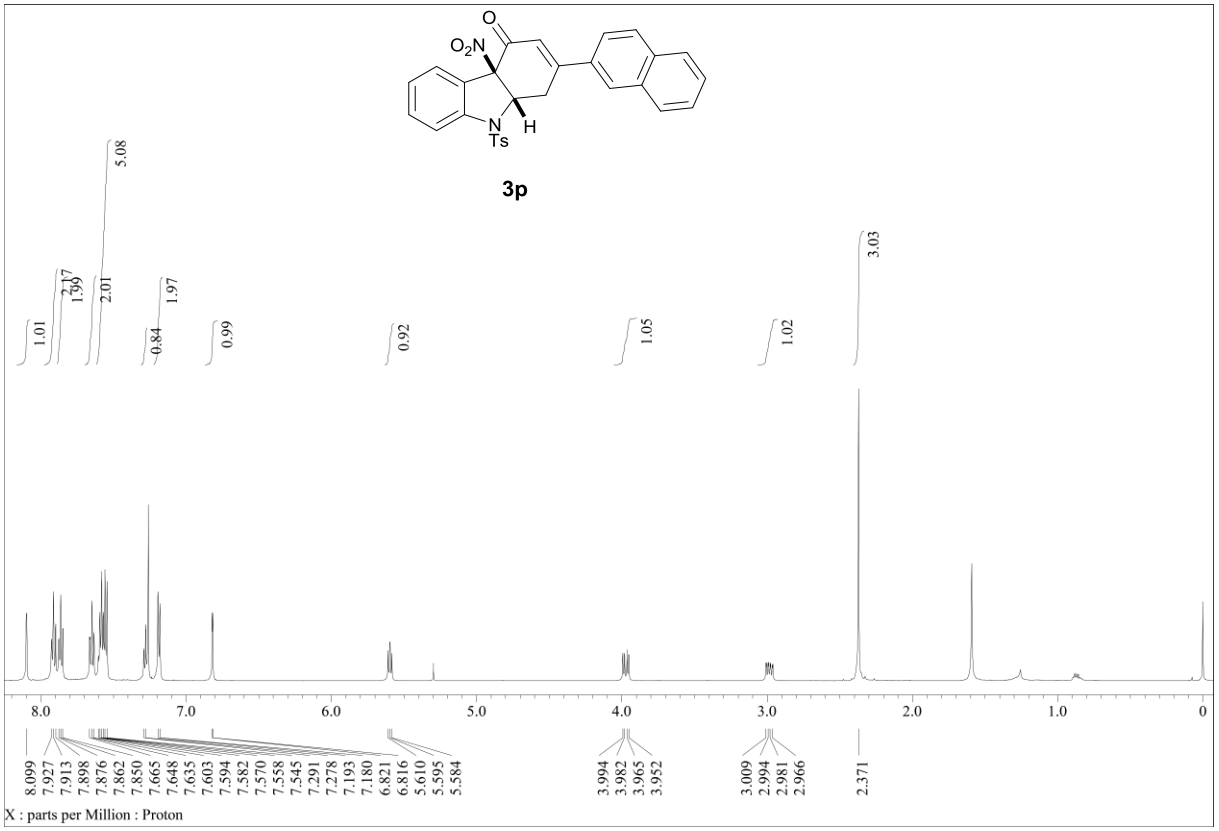

Cl
Cl
O
O2N
N
H
Ts
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.429
156.432
145.364
142.032
136.421
135.885
134.066
133.730
133.405
131.126
130.035
128.512
128.455
126.616
125.812
125.640
124.271
122.499
116.860
96.475
77.211
77.000
76.789
66.372
33.282
21.610
X : parts per Million : Carbon13

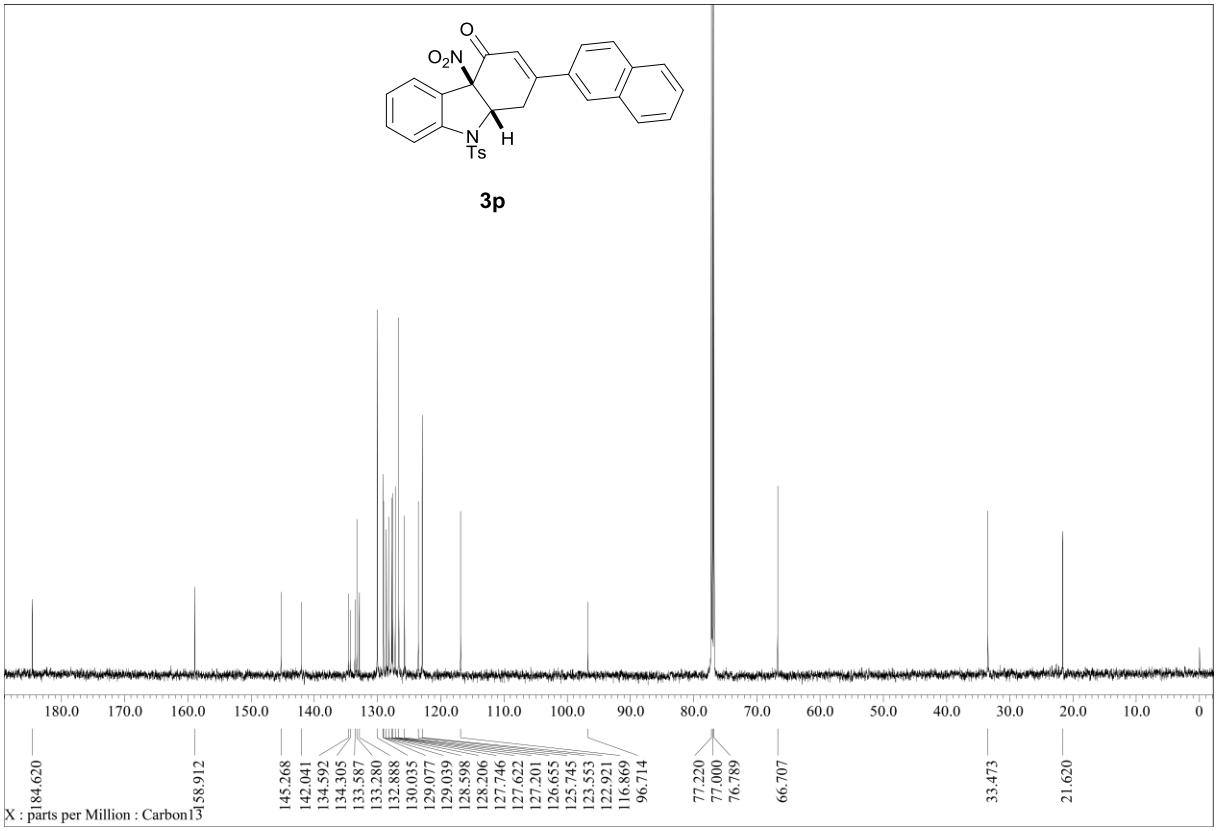
3n

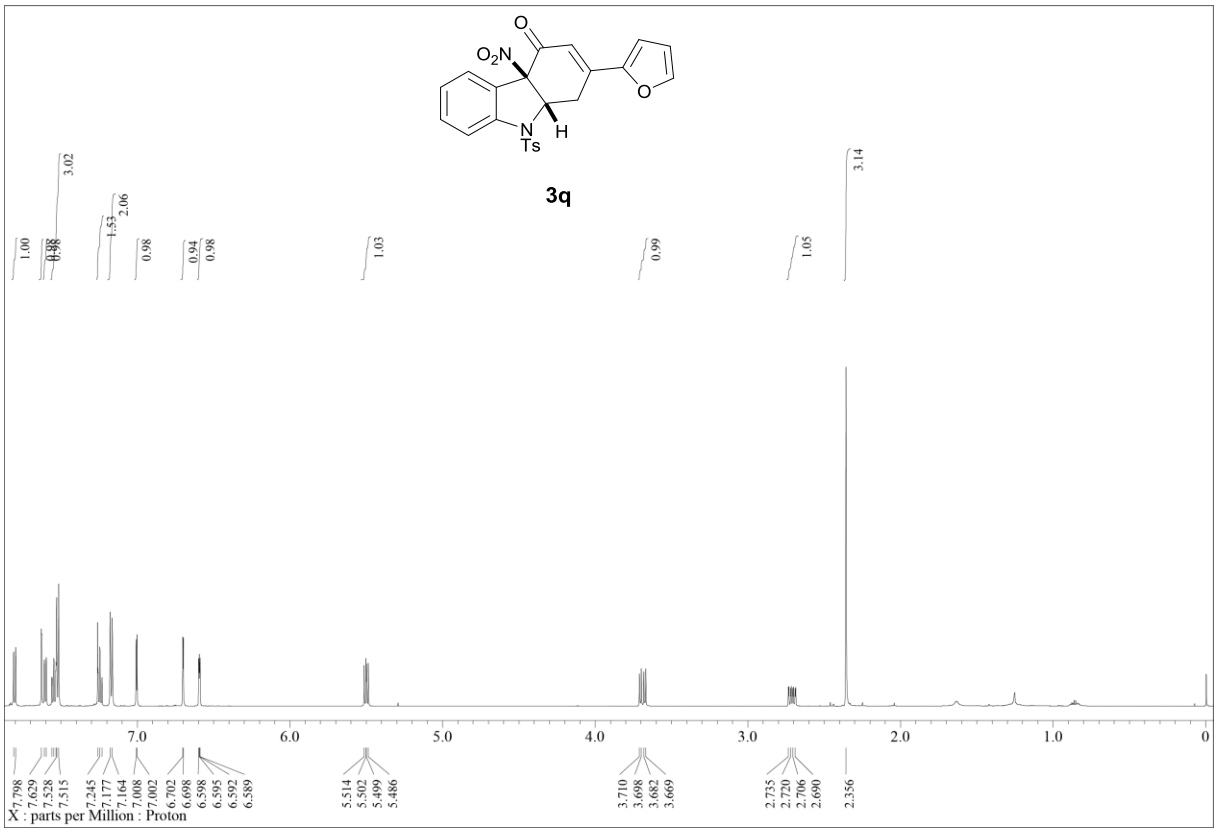

O
O2N
N
H
Ts
6.12
3.05
1.01
1.99
2.05
1.00
1.04
1.06
1.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.823
7.810
7.528
7.515
7.349
7.247
7.212
7.199
7.172
7.158
6.646
6.642
5.529
5.517
5.514
5.502
3.817
3.804
3.787
3.776
2.848
2.833
2.819
2.804
2.354
2.303
X : parts per Million : Proton

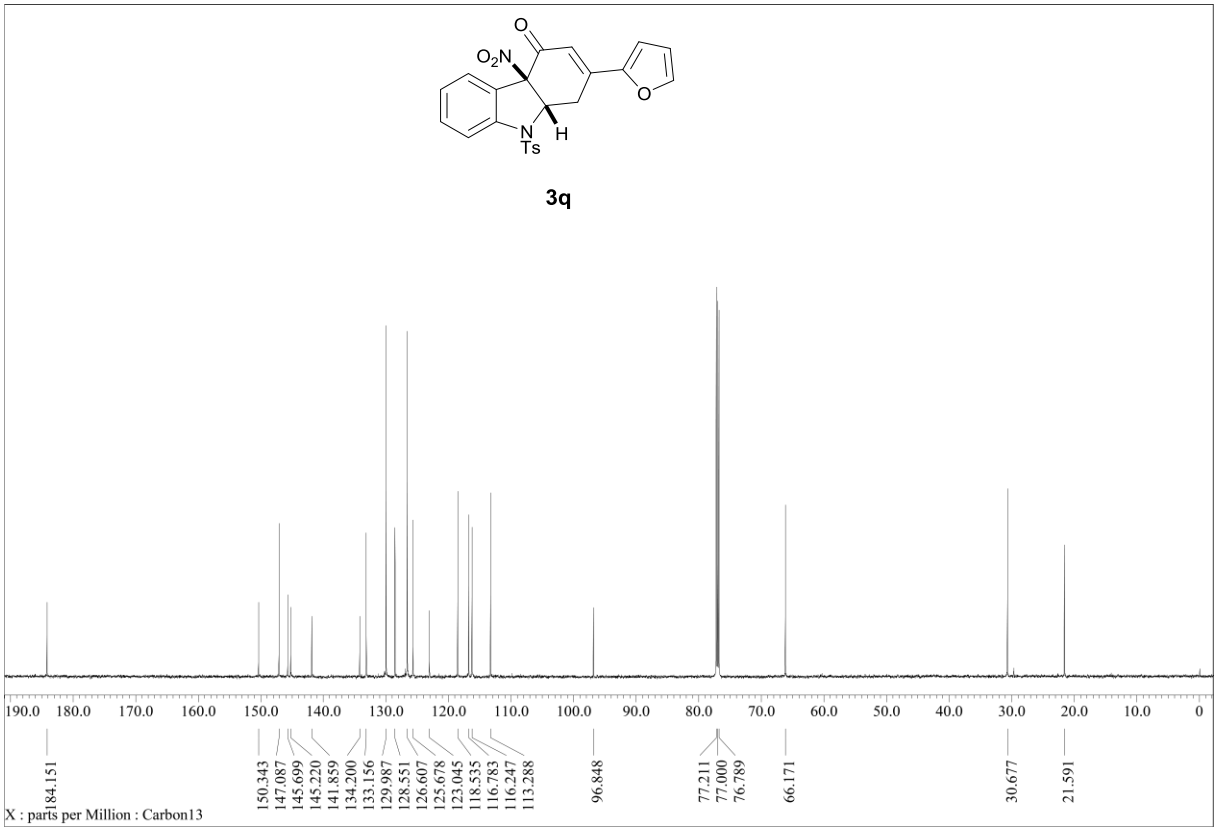
3o


O
O2N
N
Ts
H
3o
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
184.563
159.496
145.182
141.974
141.228
137.513
134.343
133.989
133.166
130.370
129.987
128.570
127.785
126.636
125.659
124.223
122.997
122.308
116.812
96.705
77.220
77.000
76.789
66.688
33.425
21.600
19.839
X : parts per Million : Carbon13

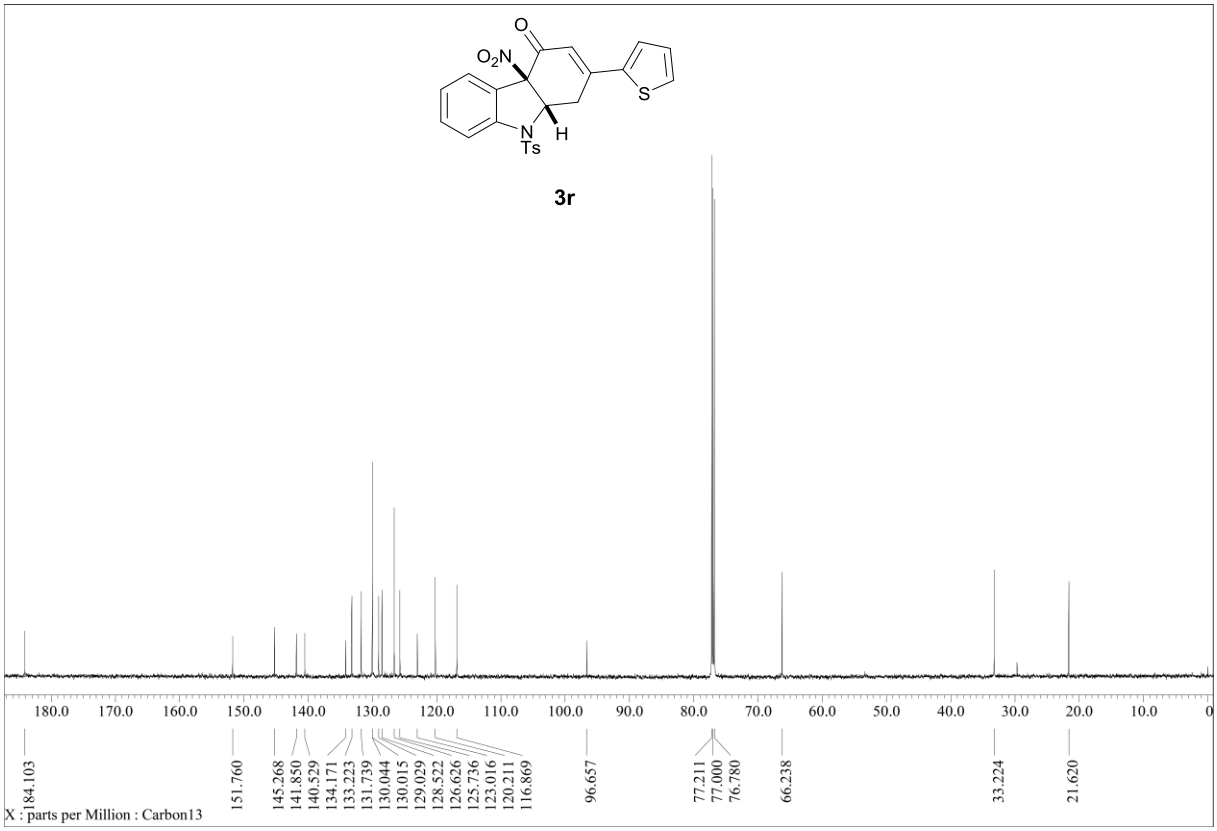

O
O2N
N
Ts
H
3p
5.08
3.03
2.17
1.99
2.01
1.97
1.01
0.84
0.99
0.92
1.05
1.02
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.099
7.927
7.913
7.898
7.876
7.862
7.850
7.665
7.648
7.635
7.603
7.594
7.582
7.570
7.558
7.545
7.291
7.278
7.193
7.180
6.821
6.816
5.610
5.595
5.584
3.994
3.982
3.965
3.952
3.009
2.994
2.981
2.966
2.371
X : parts per Million : Proton

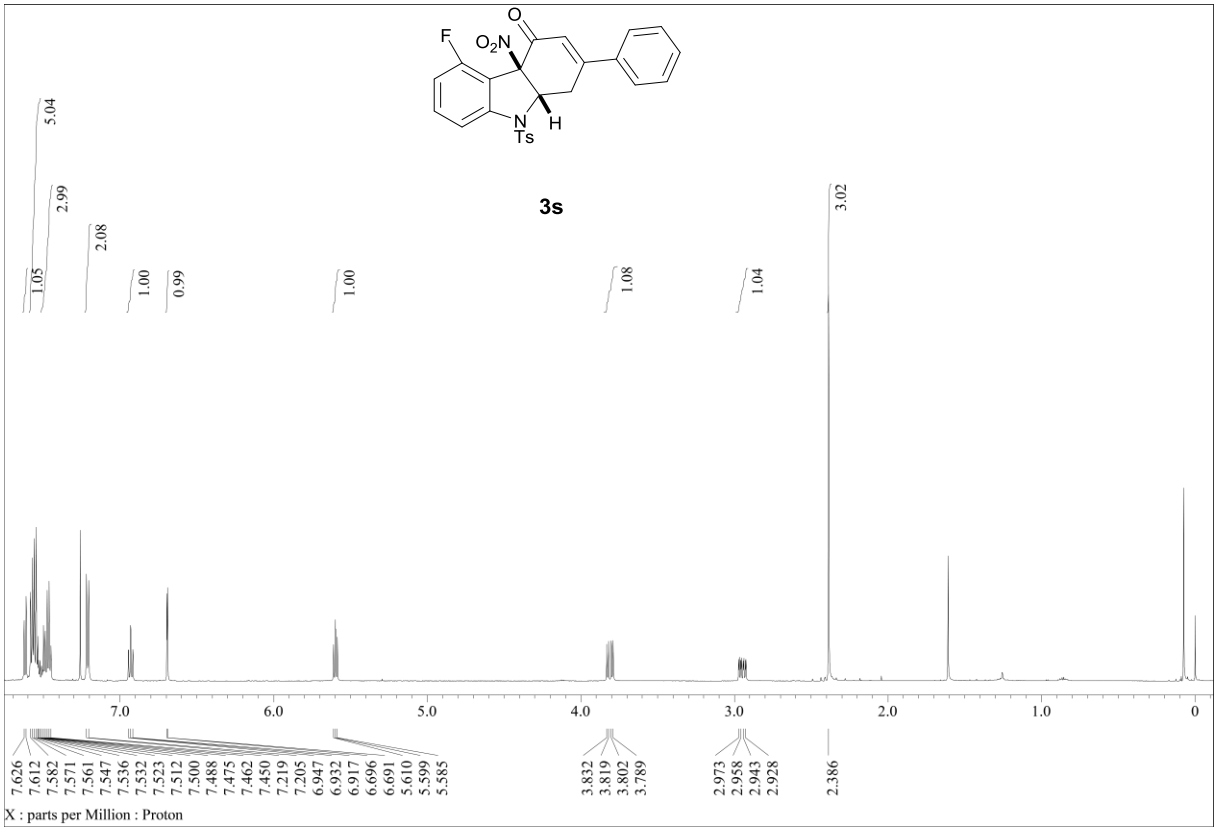

O
O2N
N
Ts
H
3p
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.620
158.912
145.268
142.041
134.592
134.305
133.587
133.280
132.888
130.035
129.077
129.039
128.598
128.206
127.746
127.622
127.201
126.655
125.745
123.553
122.921
116.869
96.714
77.220
77.000
76.789
66.707
33.473
21.620
X : parts per Million : Carbon13

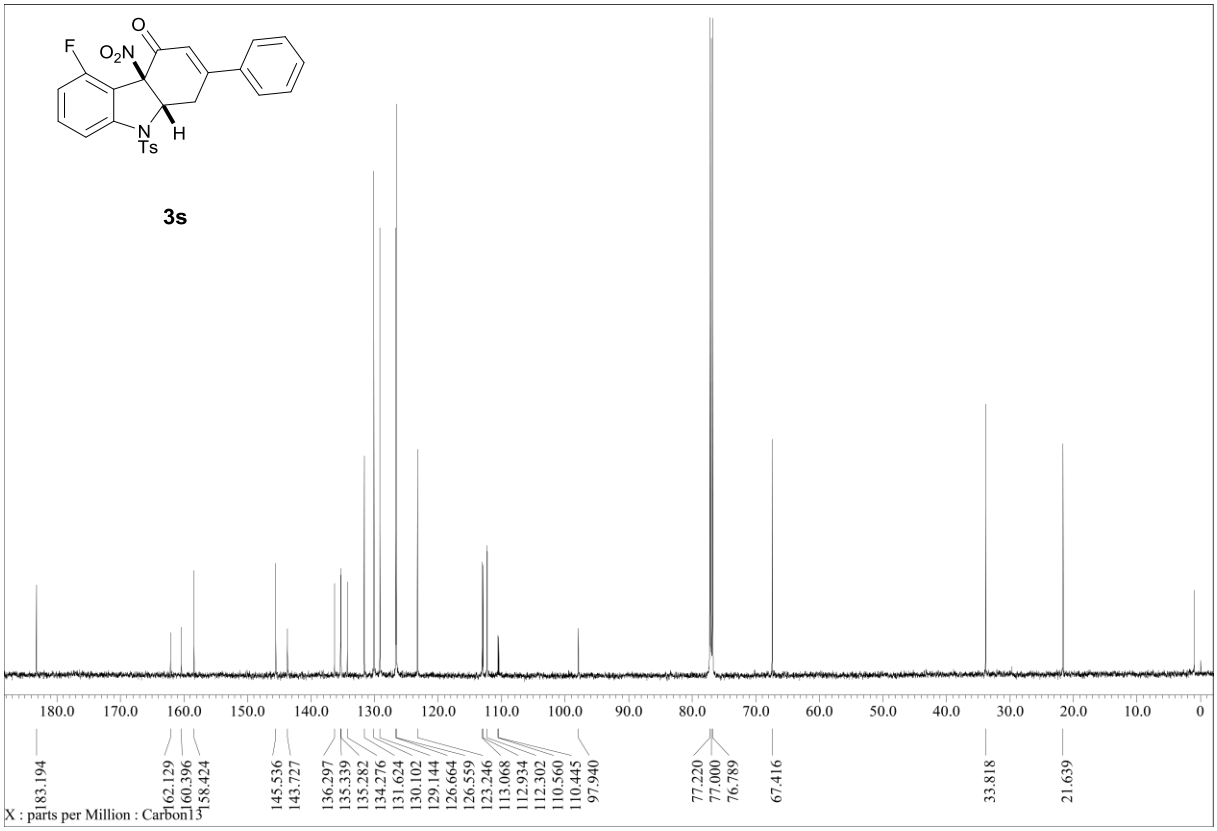

O
O2N
O
N
Ts
H
3q
3.02
2.06
1.53
1.00
0.98
0.98
0.98
0.94
0.98
1.03
0.99
1.05
3.14
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.798
7.629
7.528
7.515
7.245
7.177
7.164
7.008
7.002
6.702
6.698
6.598
6.595
6.592
6.589
5.514
5.502
5.499
5.486
3.710
3.698
3.682
3.669
2.735
2.720
2.706
2.690
2.356
X : parts per Million : Proton

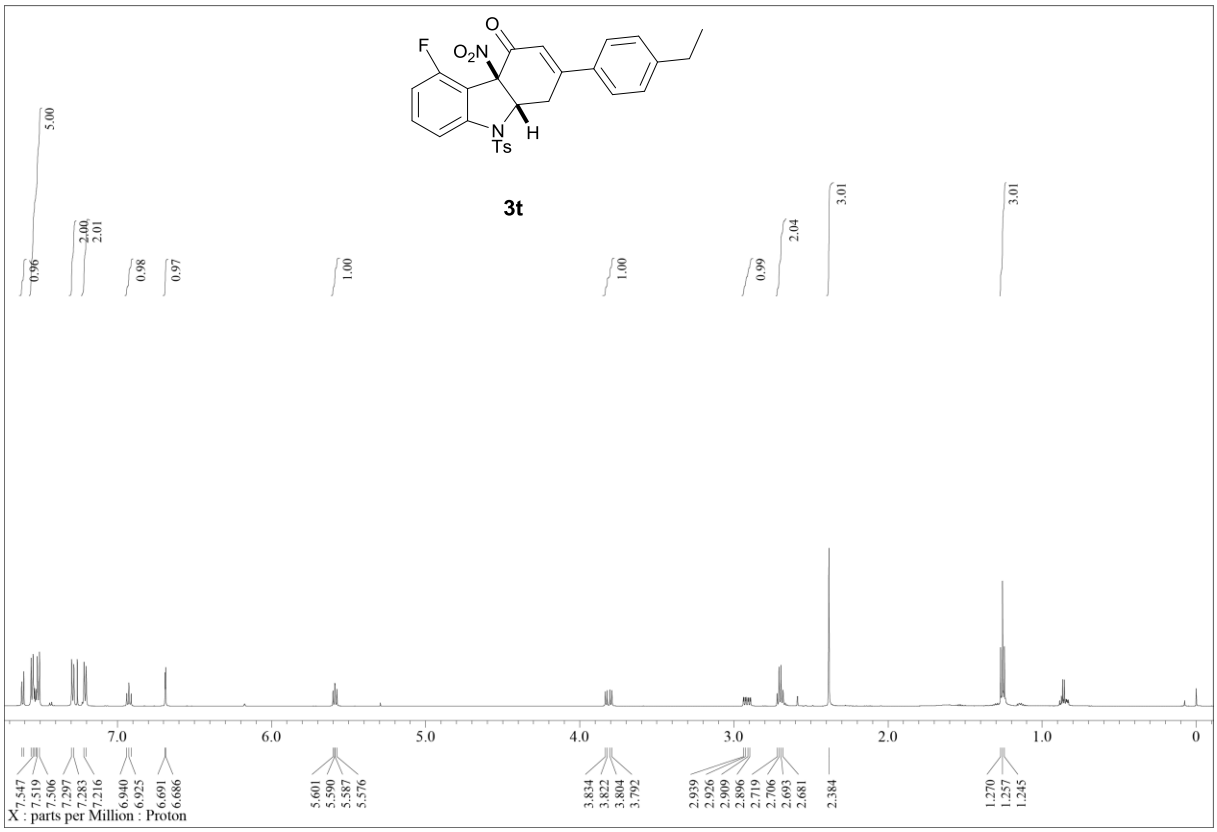

O
O2N
O
N
H
Ts
3q
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.151
150.343
147.087
145.699
145.220
141.859
134.200
133.156
129.987
128.551
126.607
125.678
123.045
118.535
116.783
116.247
113.288
96.848
77.211
77.000
76.789
66.171
30.677
21.591
X : parts per Million : Carbon13

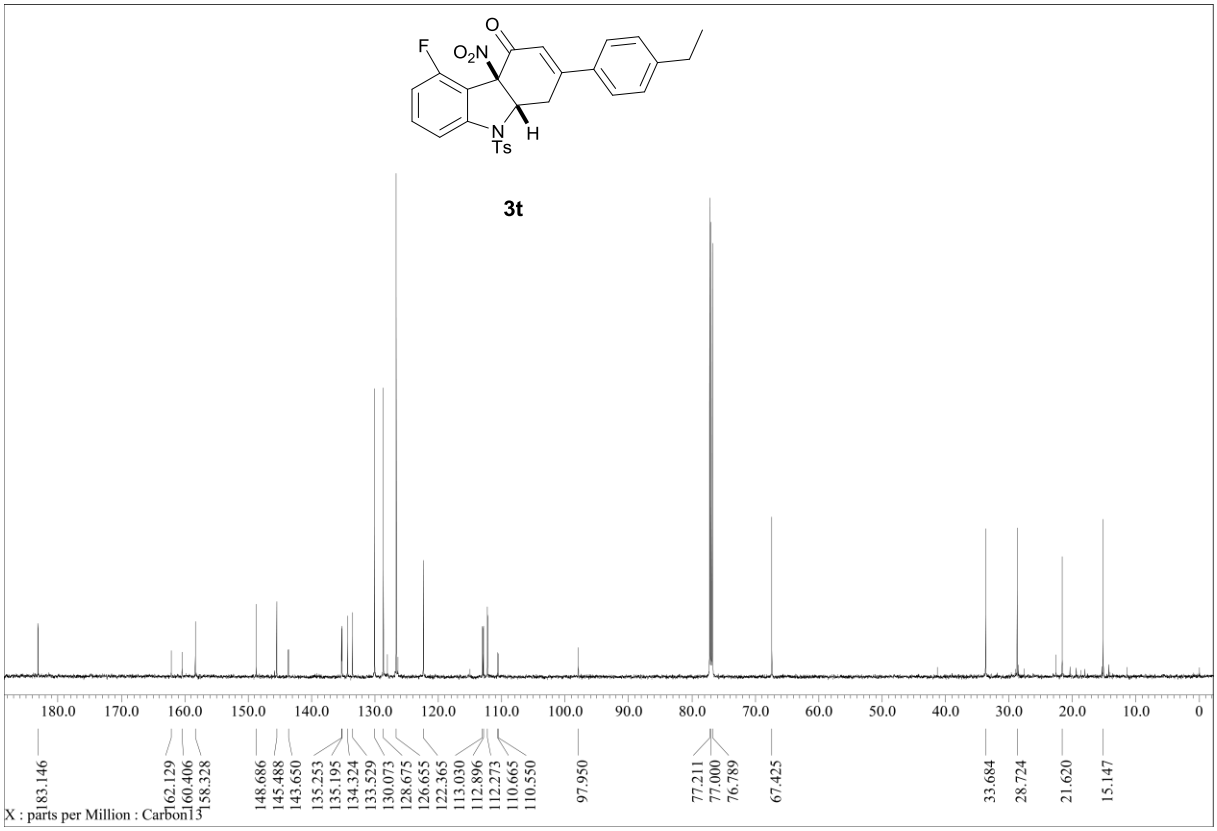

O
O2N
S
N
H
Ts
3r
3.02
2.16
3.04
0.99
0.96
0.98
1.03
1.00
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.596
7.586
7.562
7.554
7.526
7.512
7.253
7.247
7.177
7.166
6.630
6.627
5.545
5.532
5.529
5.517
3.863
3.850
3.833
3.822
2.858
2.843
2.829
2.813
2.358
X : parts per Million : Proton

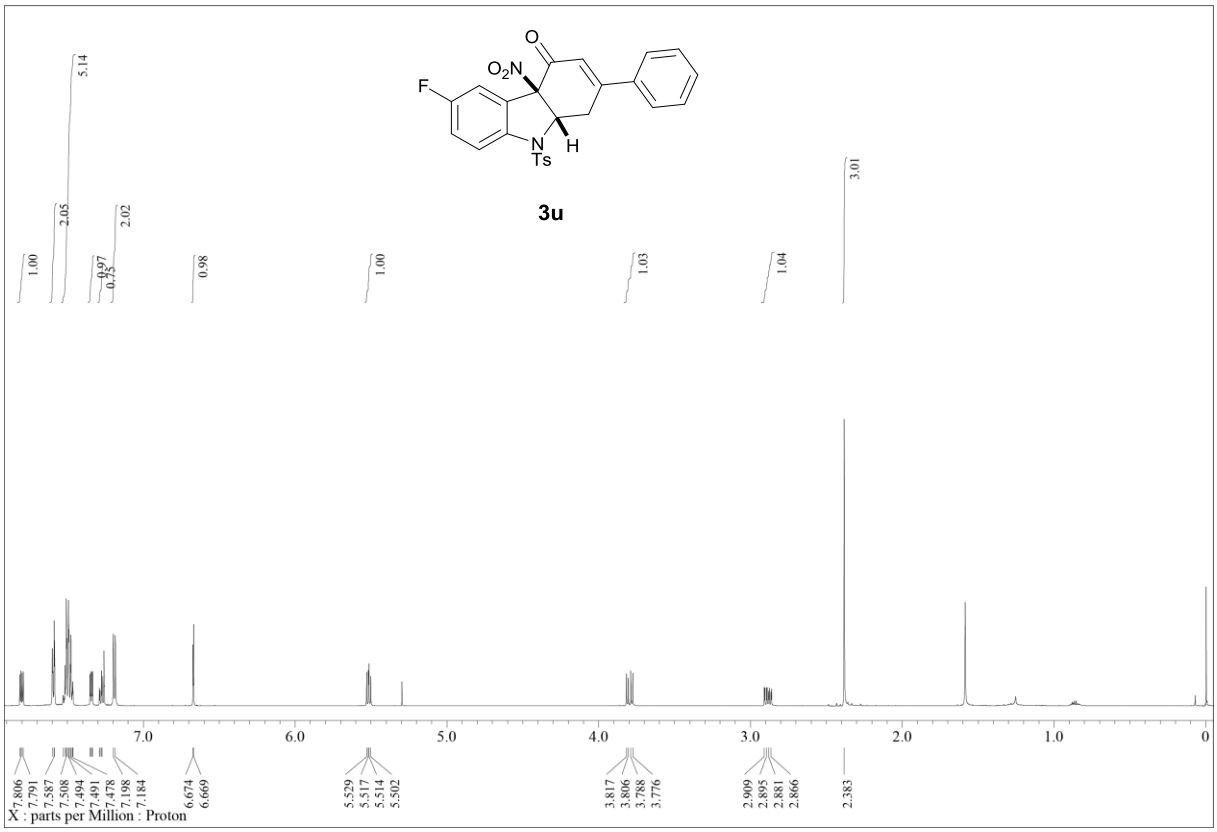

O
O2N
S
N
H
Ts
3r
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.103
151.760
145.268
141.850
140.529
134.171
133.223
131.739
130.044
130.015
129.029
128.522
126.626
125.736
123.016
120.211
116.869
96.657
77.211
77.000
76.780
66.238
33.224
21.620
X : parts per Million : Carbon13

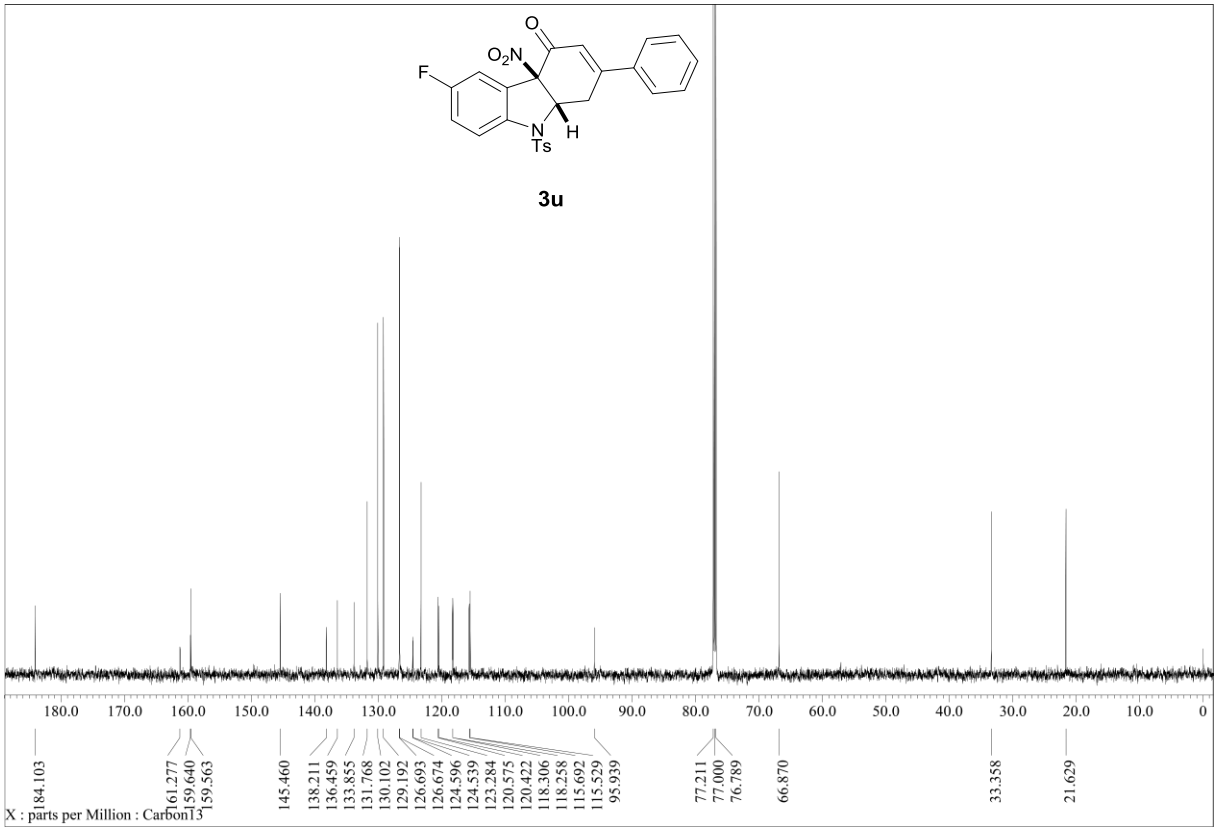

F
O
O2N
N
H
Ts
3s
5.04
2.99
2.08
1.05
1.00
0.99
1.00
1.08
1.04
3.02
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.626
7.612
7.582
7.571
7.561
7.547
7.536
7.532
7.523
7.512
7.500
7.488
7.475
7.462
7.450
7.219
7.205
6.947
6.932
6.917
6.696
6.691
5.610
5.599
5.585
3.832
3.819
3.802
3.789
2.973
2.958
2.943
2.928
2.386
X : parts per Million : Proton


F
O2N
O
N
Ts
H
3s
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
183.194
162.129
160.396
158.424
145.536
143.727
136.297
135.339
135.282
134.276
131.624
130.102
129.144
126.664
126.559
123.246
113.068
112.934
112.302
110.560
110.445
97.940
77.220
77.000
76.789
67.416
33.818
21.639
X : parts per Million : Carbon13

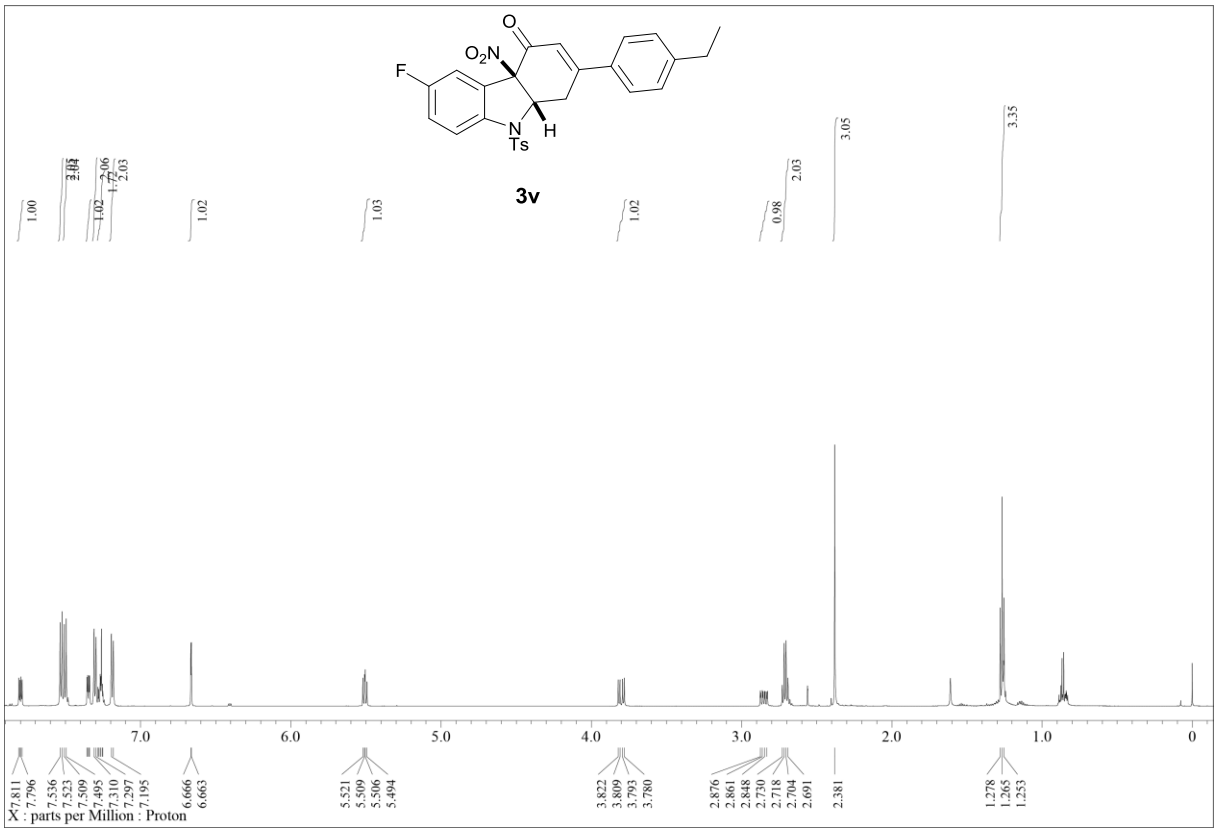

F
O2N
O
N
Ts
H
3t
5.00
2.00
2.01
0.96
0.98
0.97
1.00
1.00
0.99
2.04
3.01
3.01
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.547
7.519
7.506
7.297
7.283
7.216
6.940
6.925
6.691
6.686
5.601
5.590
5.587
5.576
3.834
3.822
3.804
3.792
2.939
2.926
2.909
2.896
2.719
2.706
2.693
2.681
2.384
1.270
1.257
1.245
X : parts per Million : Proton


F
O2N
O
N
Ts
H
3t
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
183.146
162.129
160.406
158.328
148.686
145.488
143.650
135.253
135.195
134.324
133.529
130.073
128.675
126.655
122.365
113.030
112.896
112.273
110.665
110.550
97.950
77.211
77.000
76.789
67.425
33.684
28.724
21.620
15.147
X : parts per Million : Carbon13

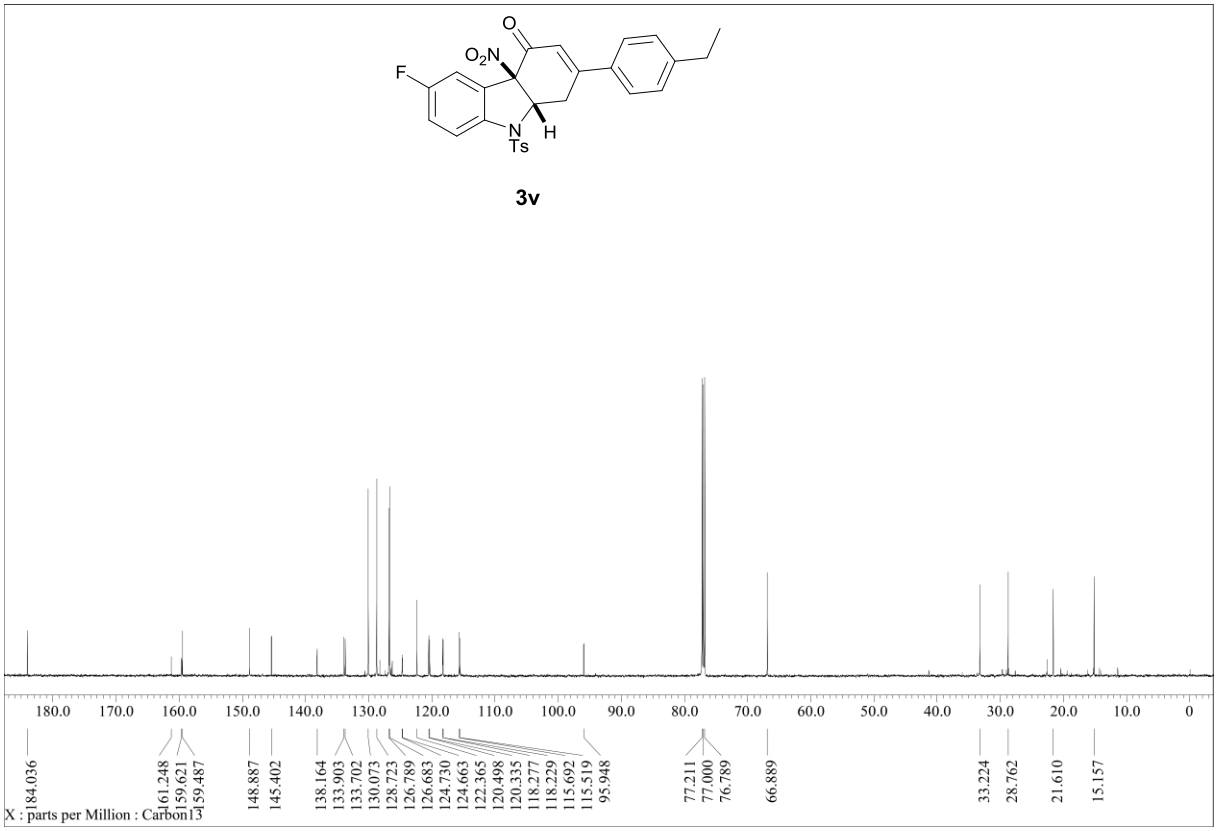

F
O2N
O
N
Ts
H
3u
1.00
2.05
5.14
2.02
0.97
0.98
1.00
1.03
1.04
3.01
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.806
7.791
7.587
7.508
7.494
7.491
7.478
7.198
7.184
6.674
6.669
5.529
5.517
5.514
5.502
3.817
3.806
3.788
3.776
2.909
2.895
2.881
2.866
2.383
X : parts per Million : Proton

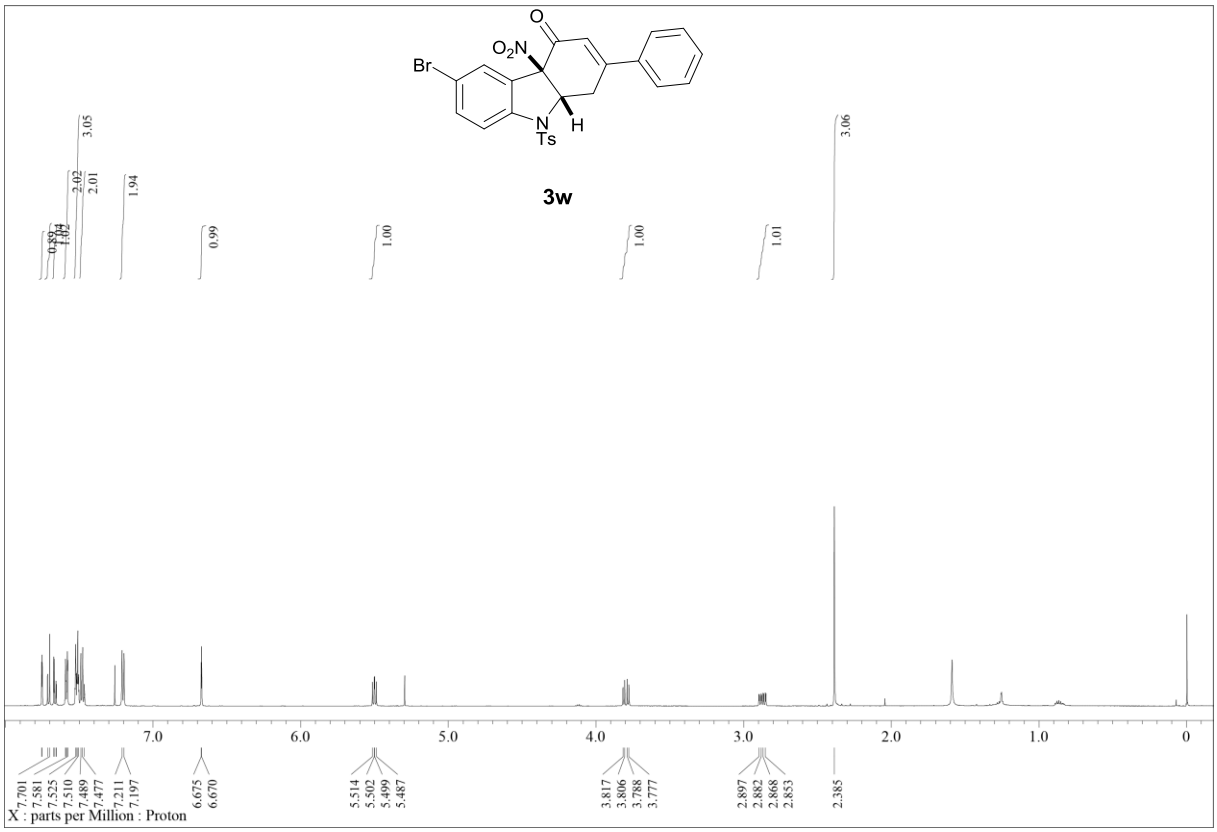

O
O2N
F
N
H
Ts
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.103
161.277
159.640
159.563
145.460
138.211
136.459
133.855
131.768
130.102
129.192
126.693
126.674
124.596
124.539
123.284
120.575
120.422
118.306
118.258
115.692
115.529
95.939
77.211
77.000
76.789
66.870
33.358
21.629
X : parts per Million : Carbon13

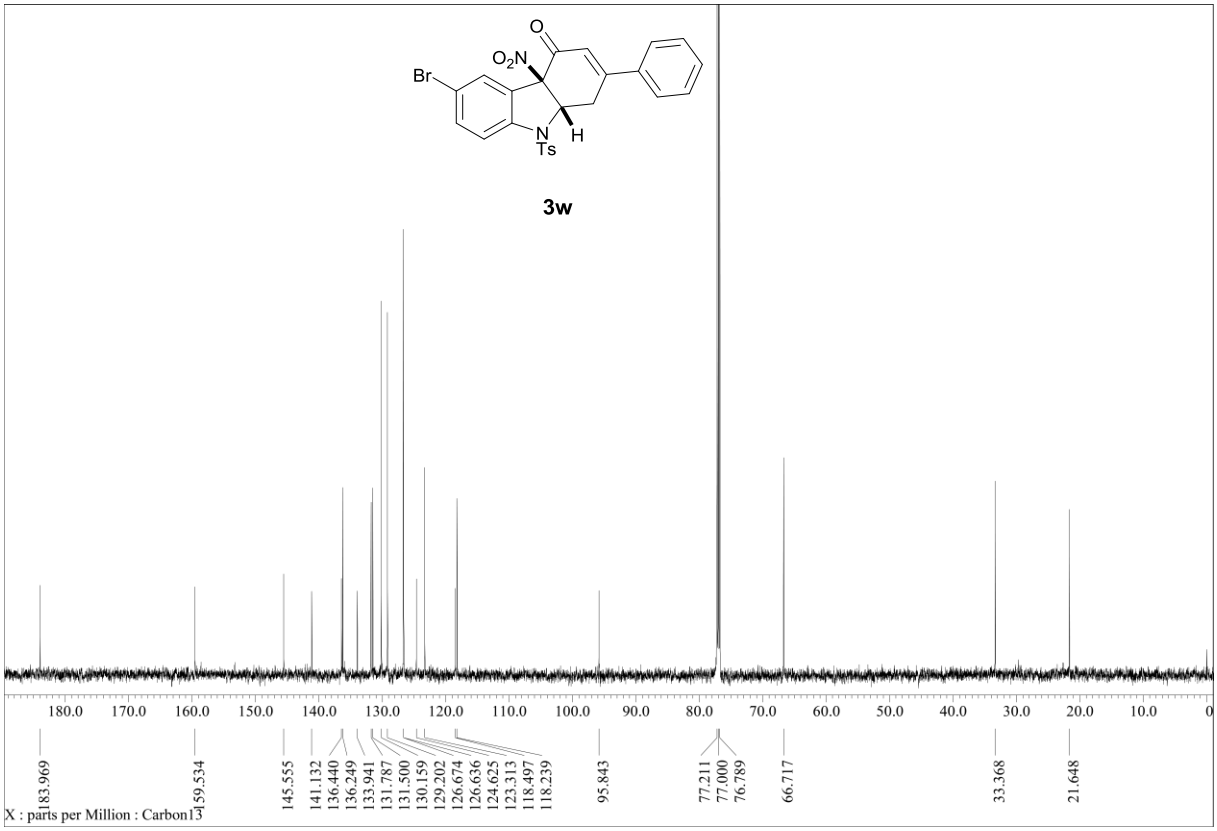
3u

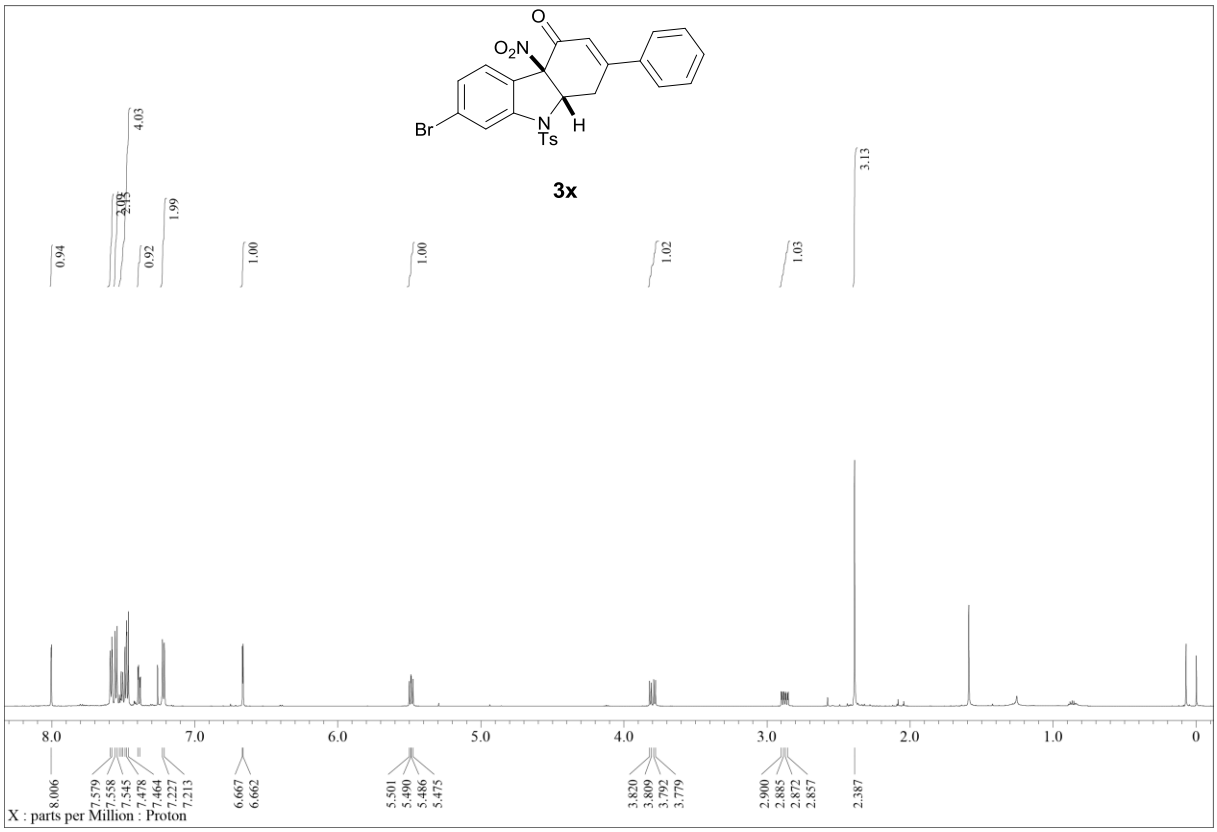

O
O2N
F
N
H
Ts
1.00
2.04
2.05
1.02
2.06
1.77
2.03
1.02
1.03
1.02
0.98
2.03
3.05
3.35
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.811
7.796
7.536
7.523
7.509
7.495
7.310
7.297
7.195
6.666
6.663
5.521
5.509
5.506
5.494
3.822
3.809
3.793
3.780
2.876
2.861
2.848
2.730
2.718
2.704
2.691
2.381
1.278
1.265
1.253
X : parts per Million : Proton

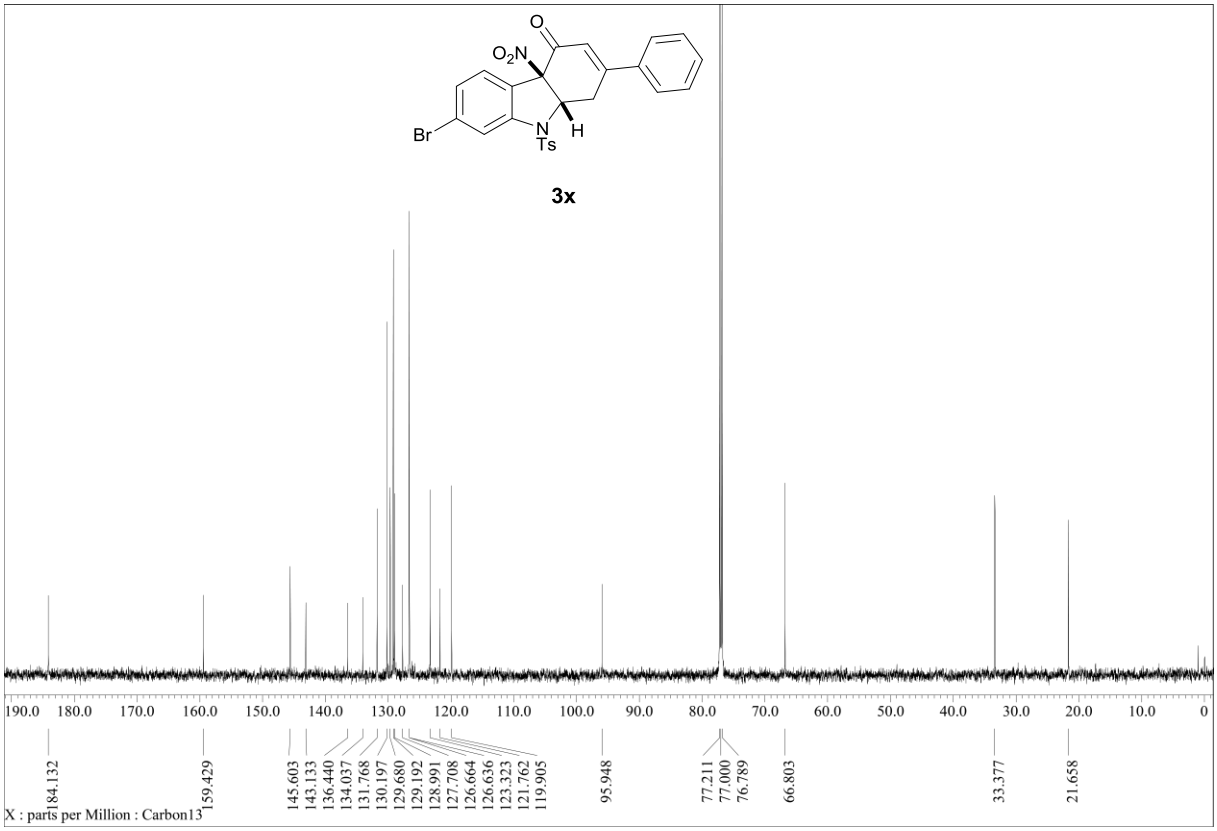
3v

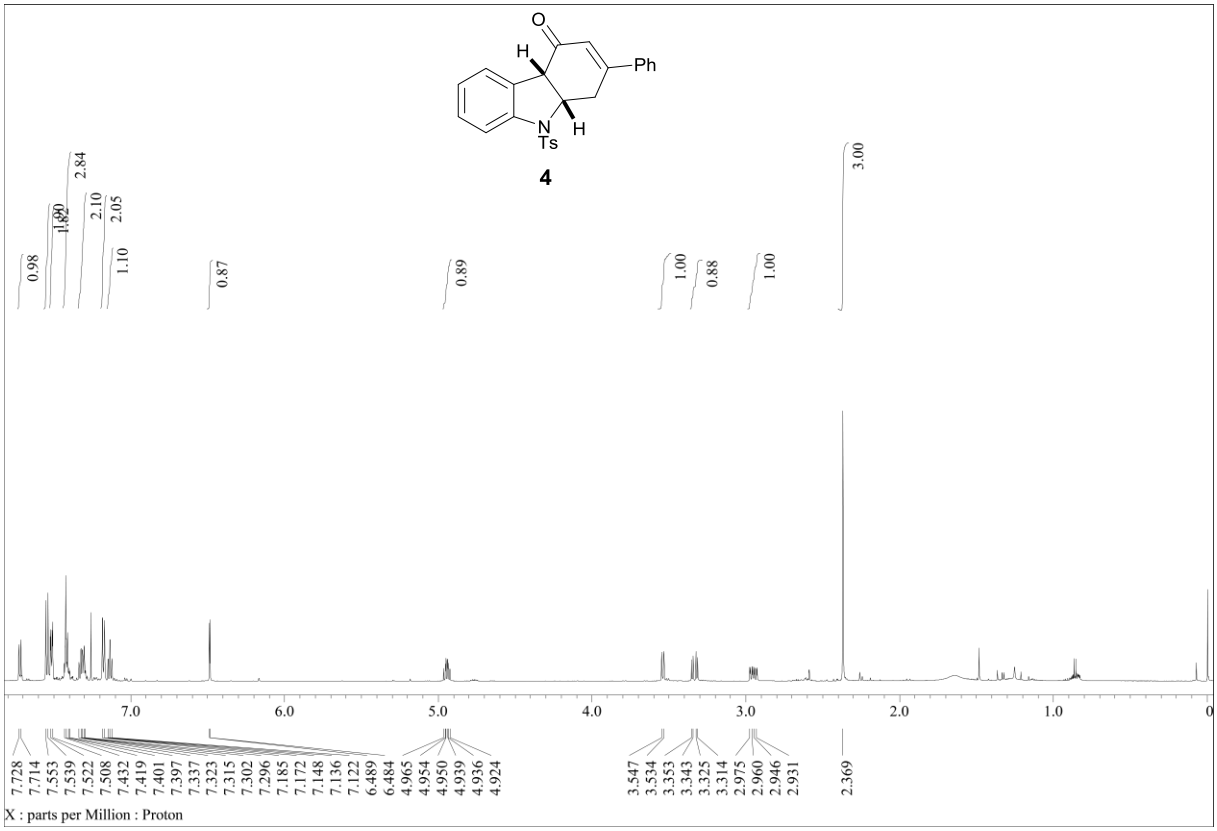

O
O2N
F
N
H
Ts
3v
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.036
161.248
159.621
159.487
148.887
145.402
138.164
133.903
133.702
130.073
128.723
126.789
126.683
124.730
124.663
122.365
120.498
120.335
118.277
118.229
115.692
115.519
95.948
77.211
77.000
76.789
66.889
33.224
28.762
21.610
15.157
X : parts per Million : Carbon13

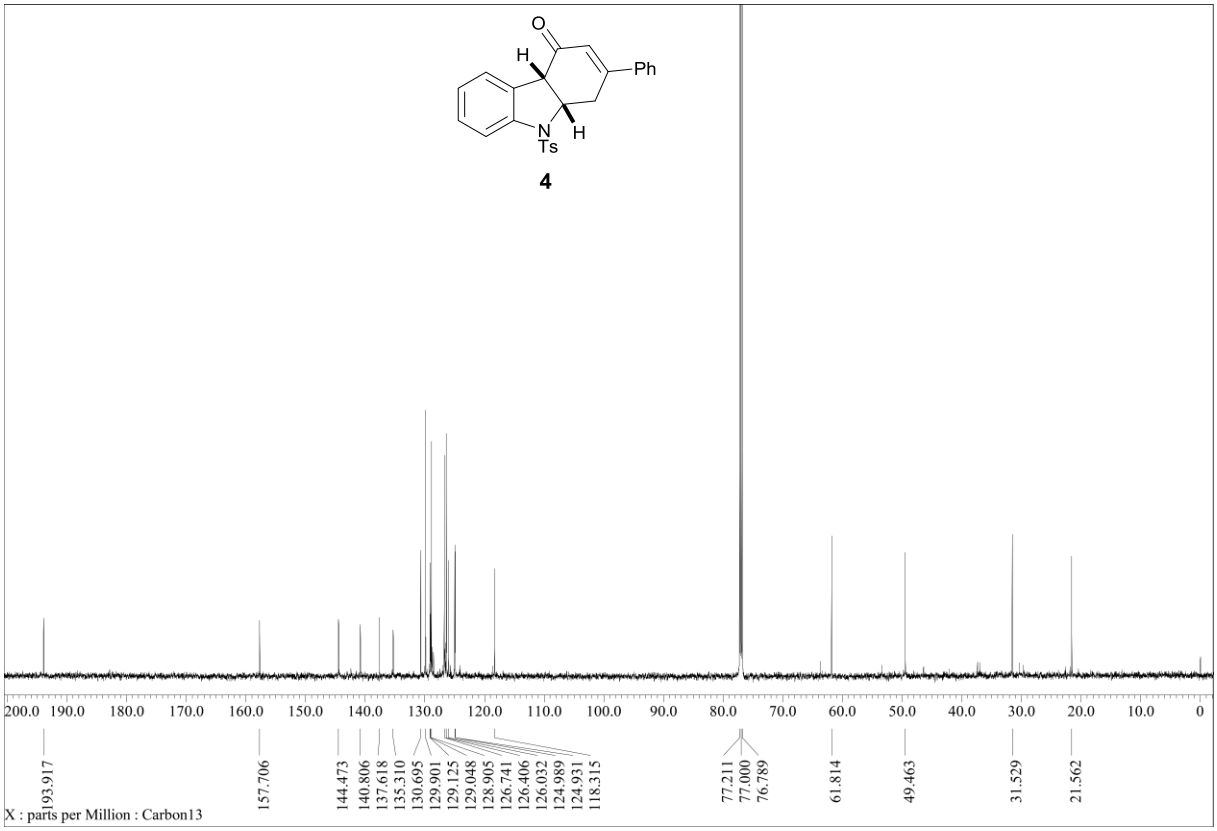

O
O2N
Br
N
H
Ts
3w
3.05
2.02
2.01
1.94
0.99
1.00
1.00
1.01
3.06
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.701
7.581
7.525
7.510
7.489
7.477
7.211
7.197
6.675
6.670
5.514
5.502
5.499
5.487
3.817
3.806
3.788
3.777
2.897
2.882
2.868
2.853
2.385
X : parts per Million : Proton

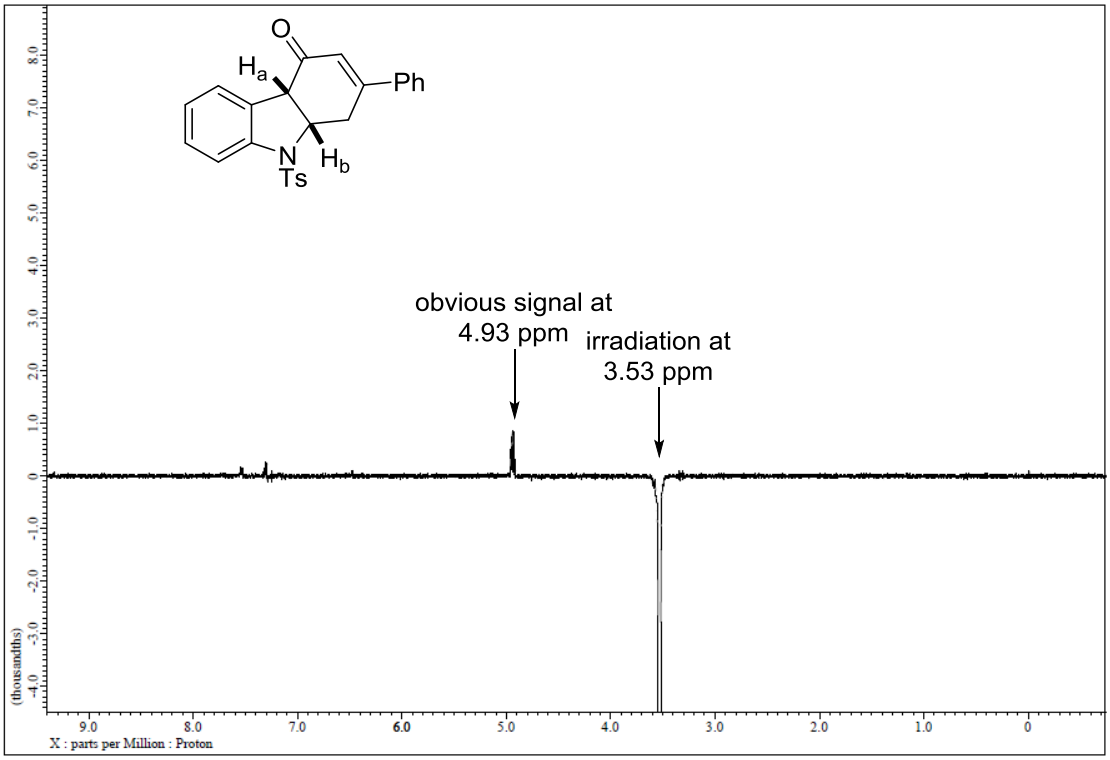

O
O2N
Br
N
H
Ts
3w
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
183.969
159.534
145.555
141.132
136.440
136.249
133.941
131.787
131.500
130.159
129.202
126.674
126.636
124.625
123.313
118.497
118.239
95.843
77.211
77.000
76.789
66.717
33.368
21.648
X : parts per Million : Carbon13

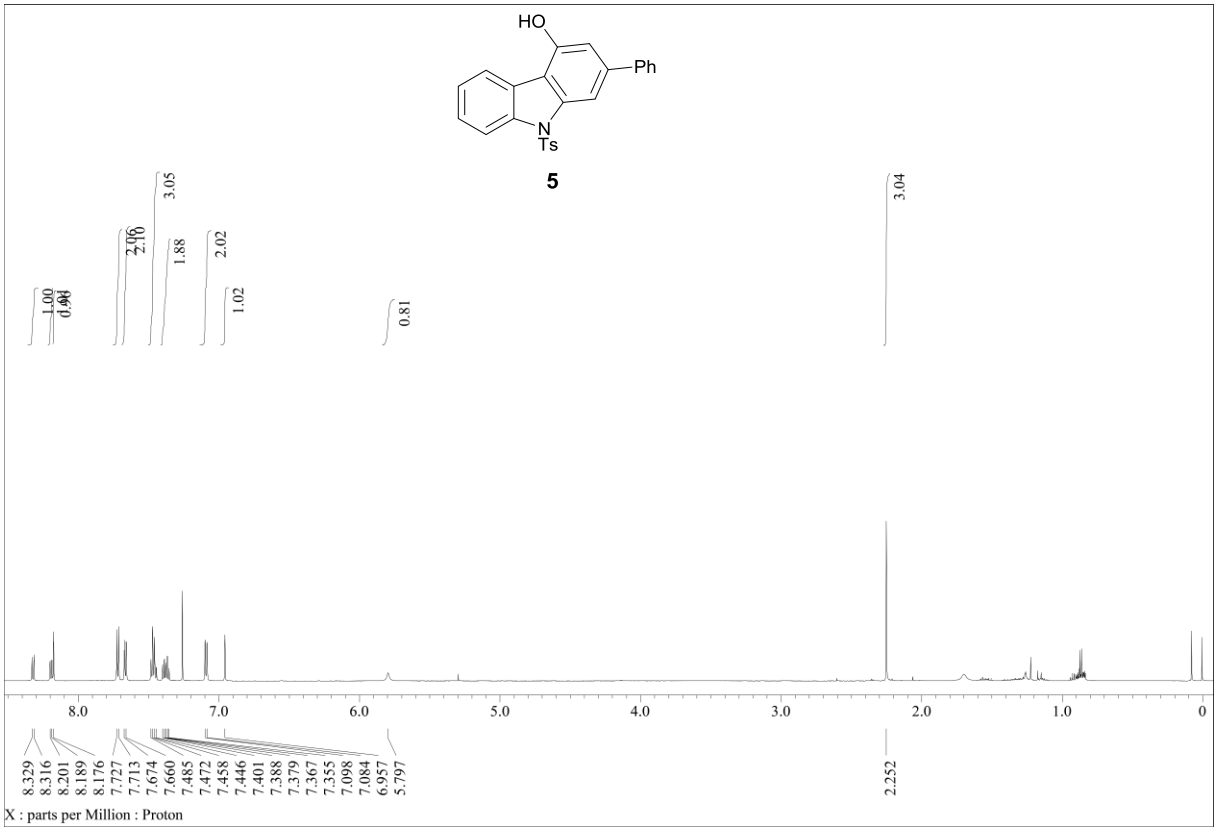

O
O2N
Br
N
H
Ts
3x
4.03
2.08
2.15
1.99
0.94
0.92
1.00
1.00
1.02
1.03
3.13
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.006
7.579
7.558
7.545
7.478
7.464
7.227
7.213
6.667
6.662
5.501
5.490
5.486
5.475
3.820
3.809
3.792
3.779
2.900
2.885
2.872
2.857
2.387
X : parts per Million : Proton

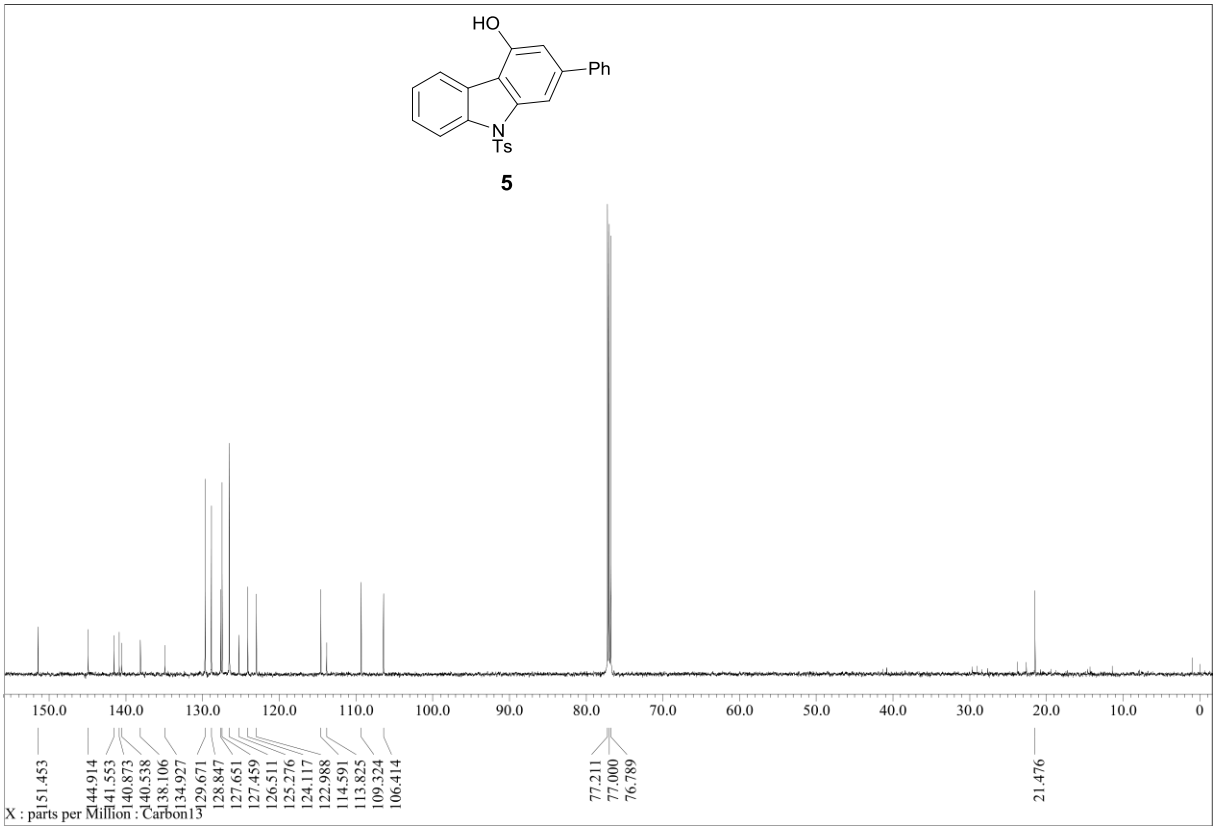

O
O2N
Br
N
Ts
H
3x
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
184.132
159.429
145.603
143.133
136.440
134.037
131.768
130.197
129.680
129.192
128.991
127.708
126.664
126.636
123.323
121.762
119.905
95.948
77.211
77.000
76.789
66.803
33.377
21.658
X : parts per Million : Carbon13

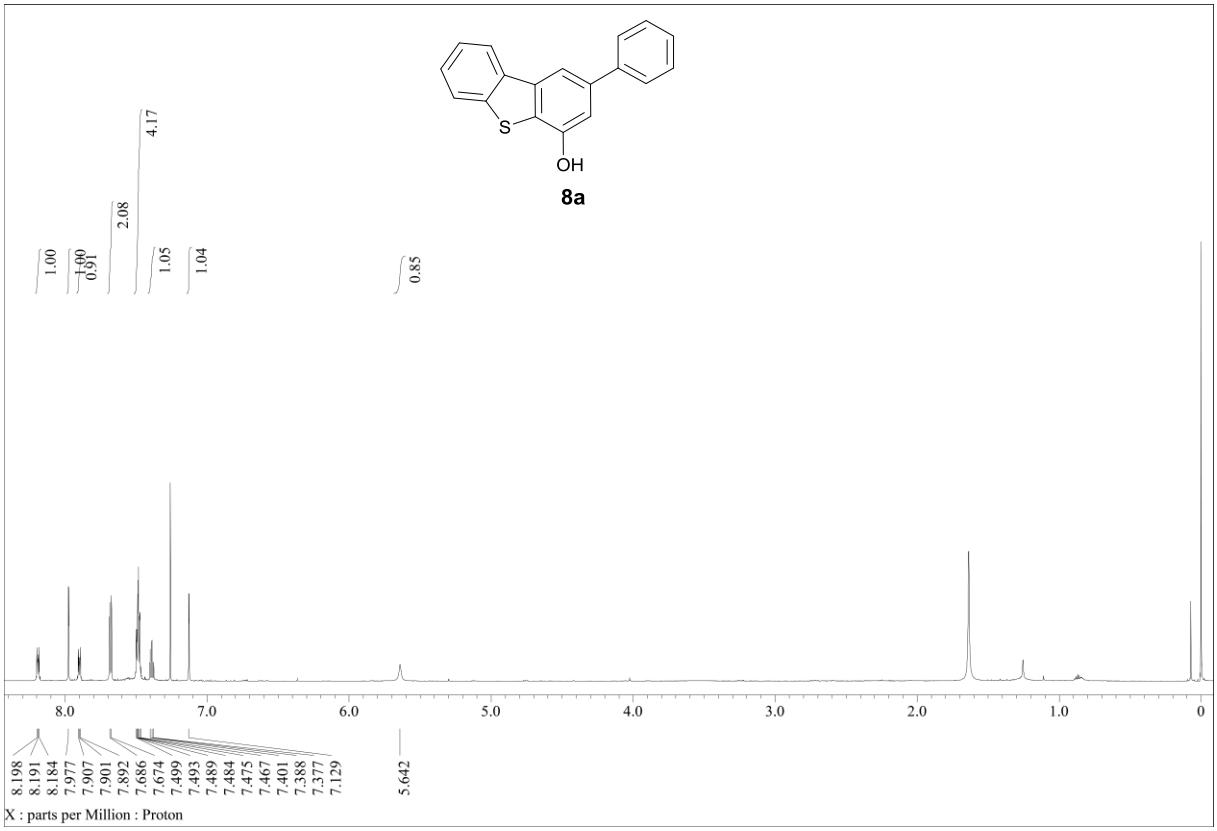

O
H
Ph
N
Ts
H
4
0.98
1.00
1.82
2.84
2.10
2.05
1.10
0.87
0.89
1.00
0.88
1.00
3.00
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.728
7.714
7.553
7.539
7.522
7.508
7.432
7.419
7.401
7.397
7.337
7.323
7.315
7.302
7.296
7.185
7.172
7.148
7.136
7.122
6.489
6.484
4.965
4.954
4.950
4.939
4.936
4.924
3.547
3.534
3.353
3.343
3.325
3.314
2.975
2.960
2.946
2.931
2.369
X : parts per Million : Proton

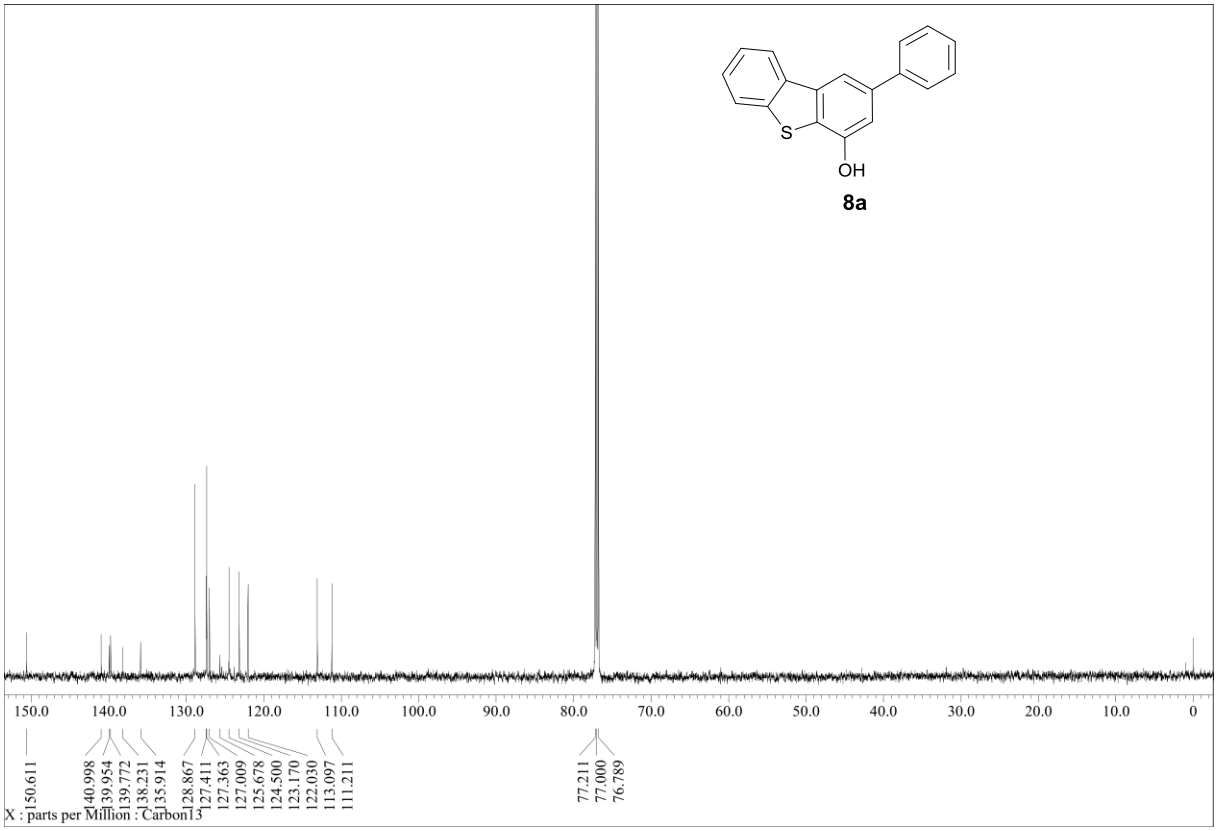

O
H
Ph
N
H
Ts
4
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
193.917
157.706
144.473
140.806
137.618
135.310
130.695
129.901
129.125
129.048
128.905
126.741
126.406
126.032
124.989
124.931
118.315
77.211
77.000
76.789
61.814
49.463
31.529
21.562
X : parts per Million : Carbon13

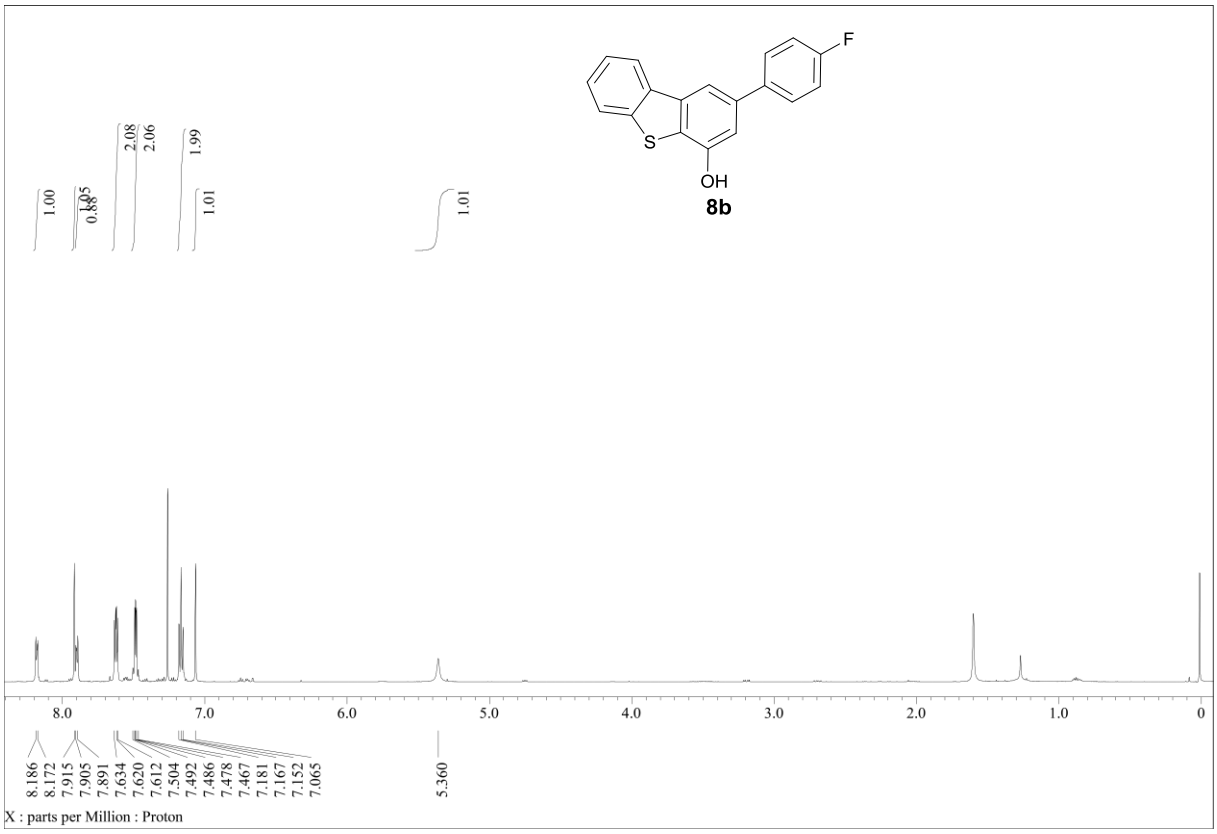

O
Ha
Ph
N
Hb
Ts
obvious signal at
4.93 ppm
irradiation at
3.53 ppm
(thousandths)
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
X : parts per Million : Proton

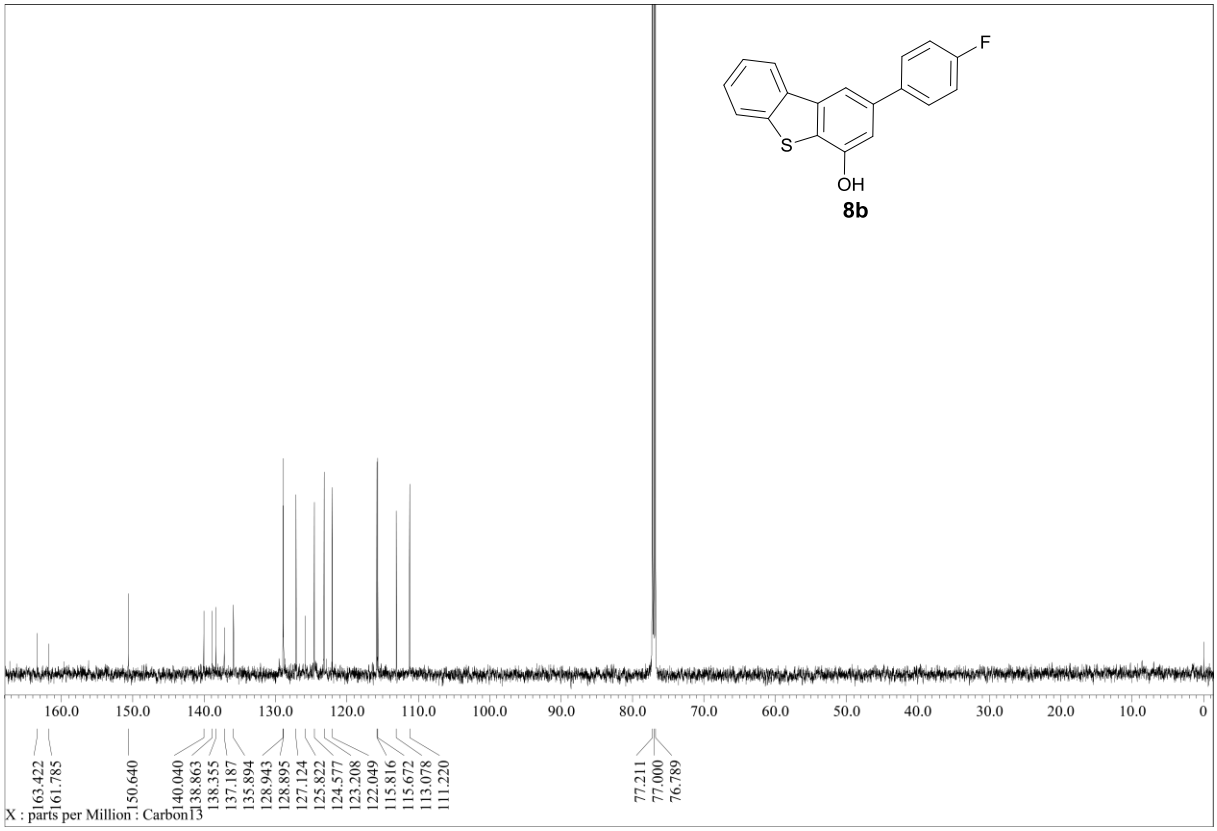

HO
Ph
N
Ts
5
3.05
2.16
2.10
1.88
2.02
1.02
1.00
0.81
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.329
8.316
8.201
8.189
8.176
7.727
7.713
7.674
7.660
7.485
7.472
7.458
7.446
7.401
7.388
7.379
7.367
7.355
7.098
7.084
6.957
5.797
2.252
X : parts per Million : Proton

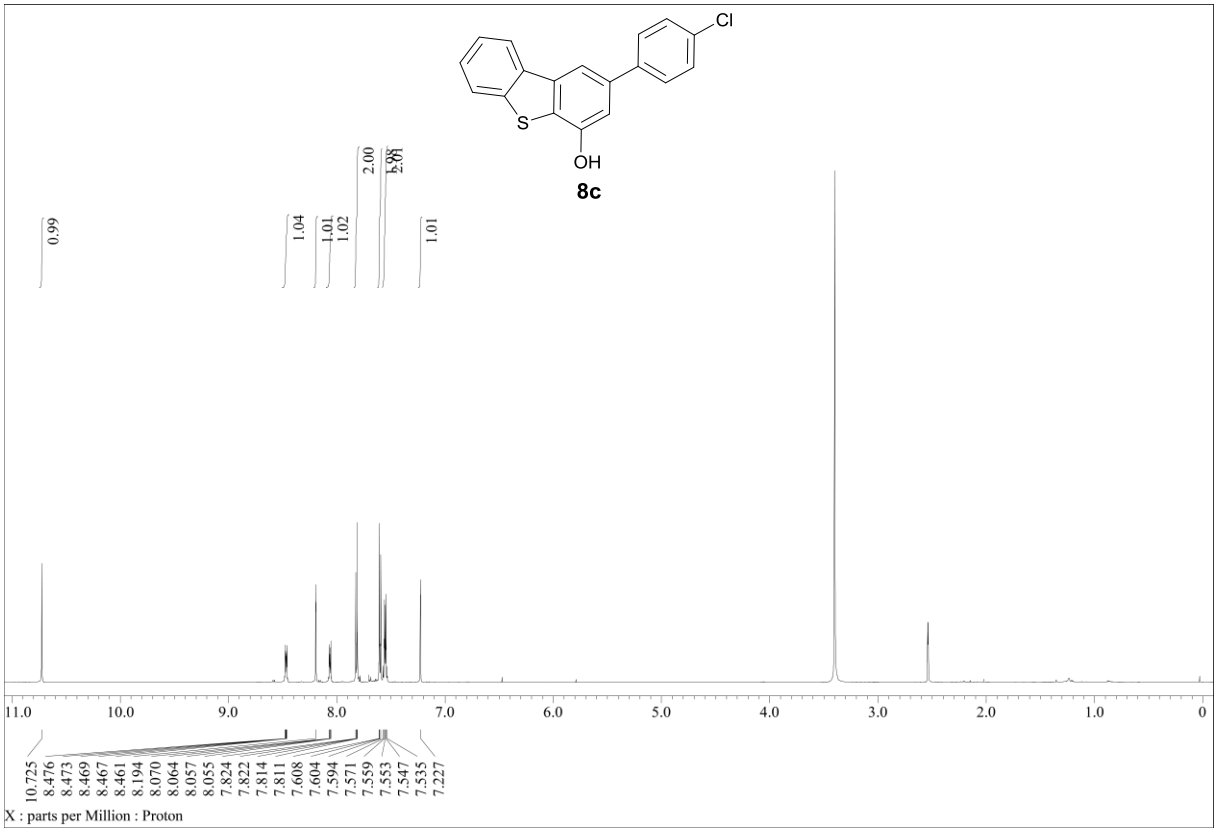

HO
Ph
N
Ts
5
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.453
144.914
141.553
140.873
140.538
138.106
134.927
129.671
128.847
127.651
127.459
126.511
125.276
124.117
122.988
114.591
113.825
109.324
106.414
77.211
77.000
76.789
21.476
X : parts per Million : Carbon13

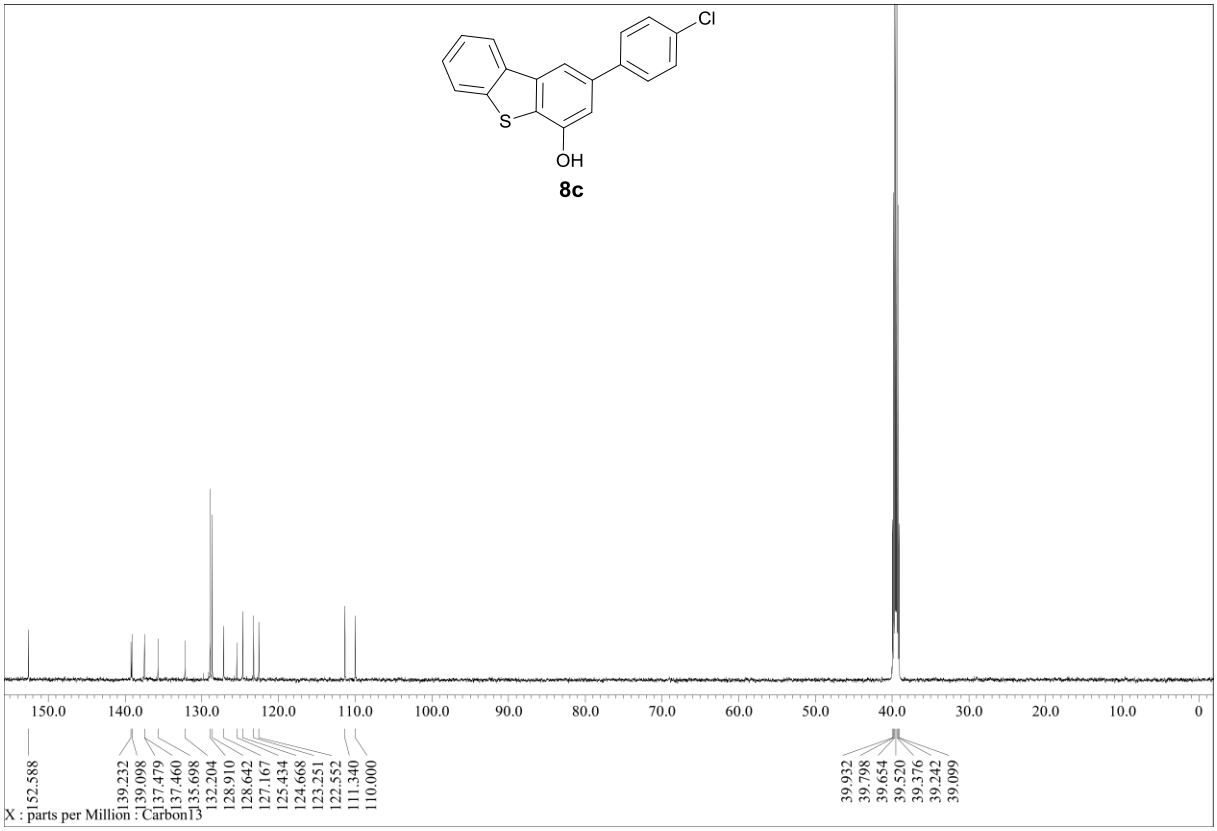

S
OH
8a
4.17
2.08
1.05
1.04
1.00
1.00
0.91
0.85
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.198
8.191
8.184
7.977
7.907
7.901
7.892
7.686
7.674
7.499
7.493
7.489
7.484
7.475
7.467
7.401
7.388
7.377
7.129
5.642
X : parts per Million : Proton

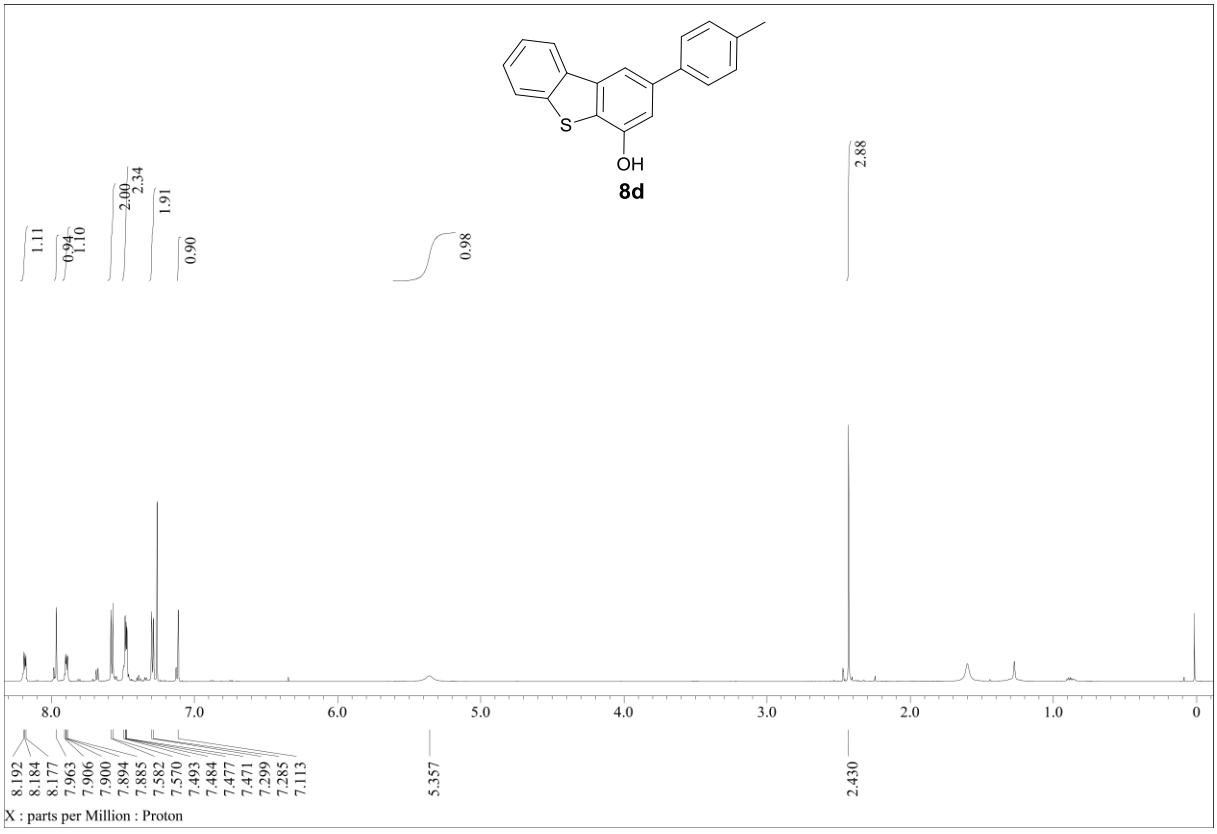

S
OH
8a
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
150.611
140.998
139.954
139.772
138.231
135.914
128.867
127.411
127.363
127.009
125.678
124.500
123.170
122.030
113.097
111.211
77.211
77.000
76.789
X : parts per Million : Carbon13

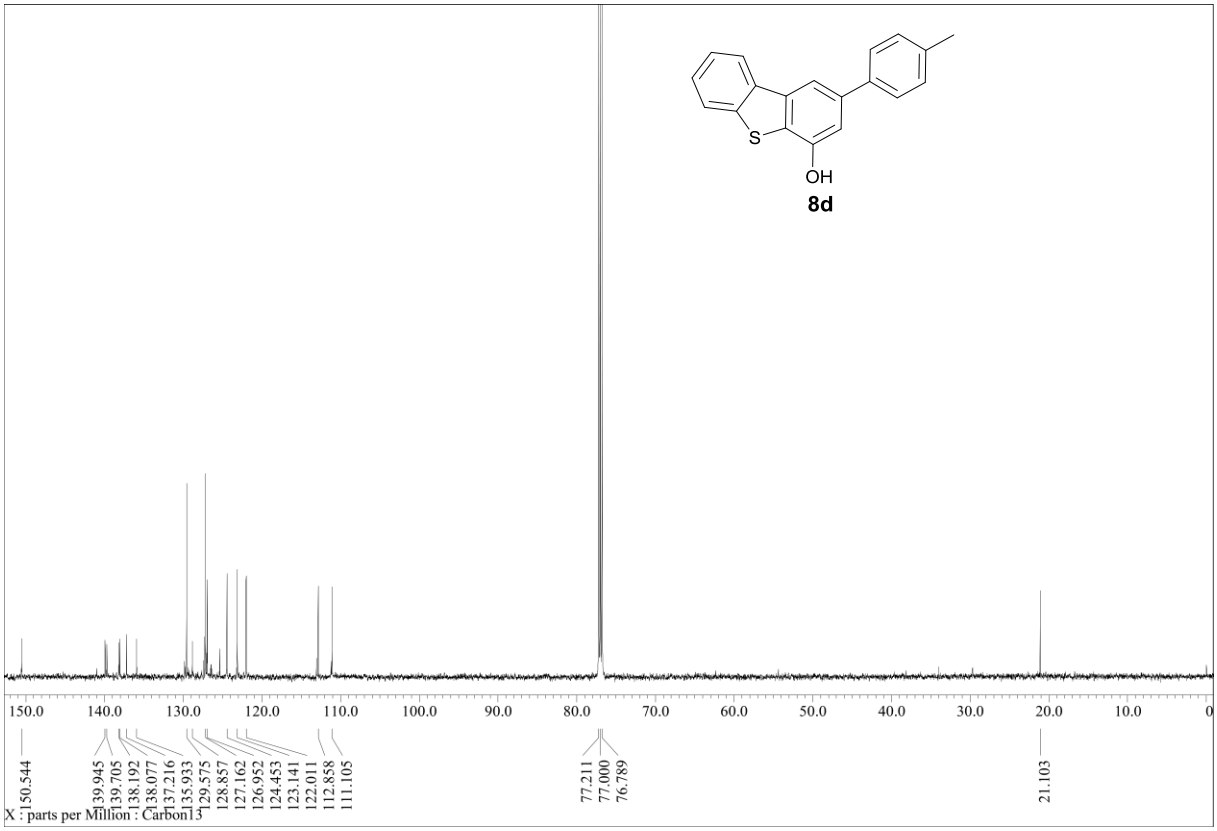

F
S
OH
8b
1.00
1.05
0.88
2.08
2.06
1.99
1.01
1.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.186
8.172
7.915
7.905
7.891
7.634
7.620
7.612
7.504
7.492
7.486
7.478
7.467
7.181
7.167
7.152
7.065
5.360
X : parts per Million : Proton

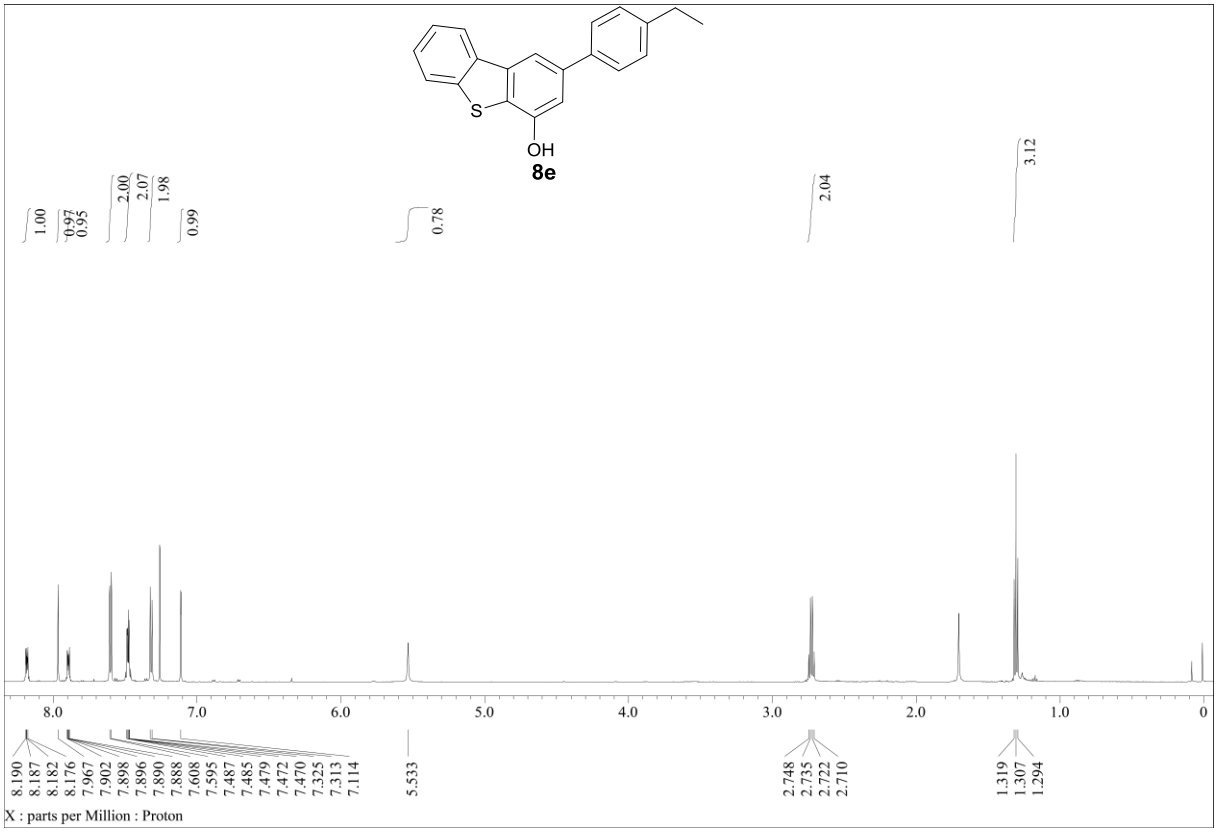

F
S
OH
8b
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
163.422
161.785
150.640
140.040
138.863
138.355
137.187
135.894
128.943
128.895
127.124
125.822
124.577
123.208
122.049
115.816
115.672
113.078
111.220
77.211
77.000
76.789
X : parts per Million : Carbon13

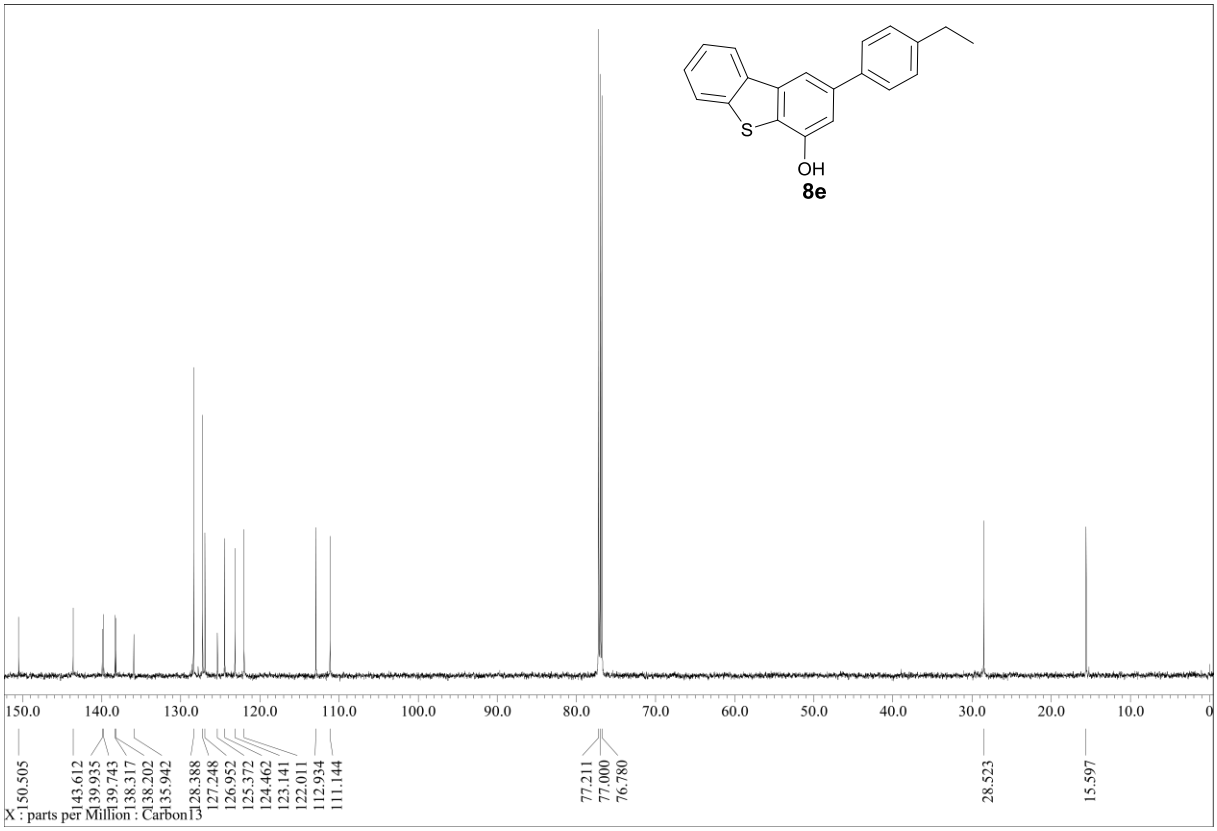

Cl
S
OH
8c
0.99
1.04
1.01
1.02
2.00
1.98
1.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.725
8.476
8.473
8.469
8.467
8.461
8.194
8.070
8.064
8.057
8.055
7.824
7.822
7.814
7.811
7.608
7.604
7.594
7.571
7.559
7.553
7.547
7.535
7.227
X : parts per Million : Proton

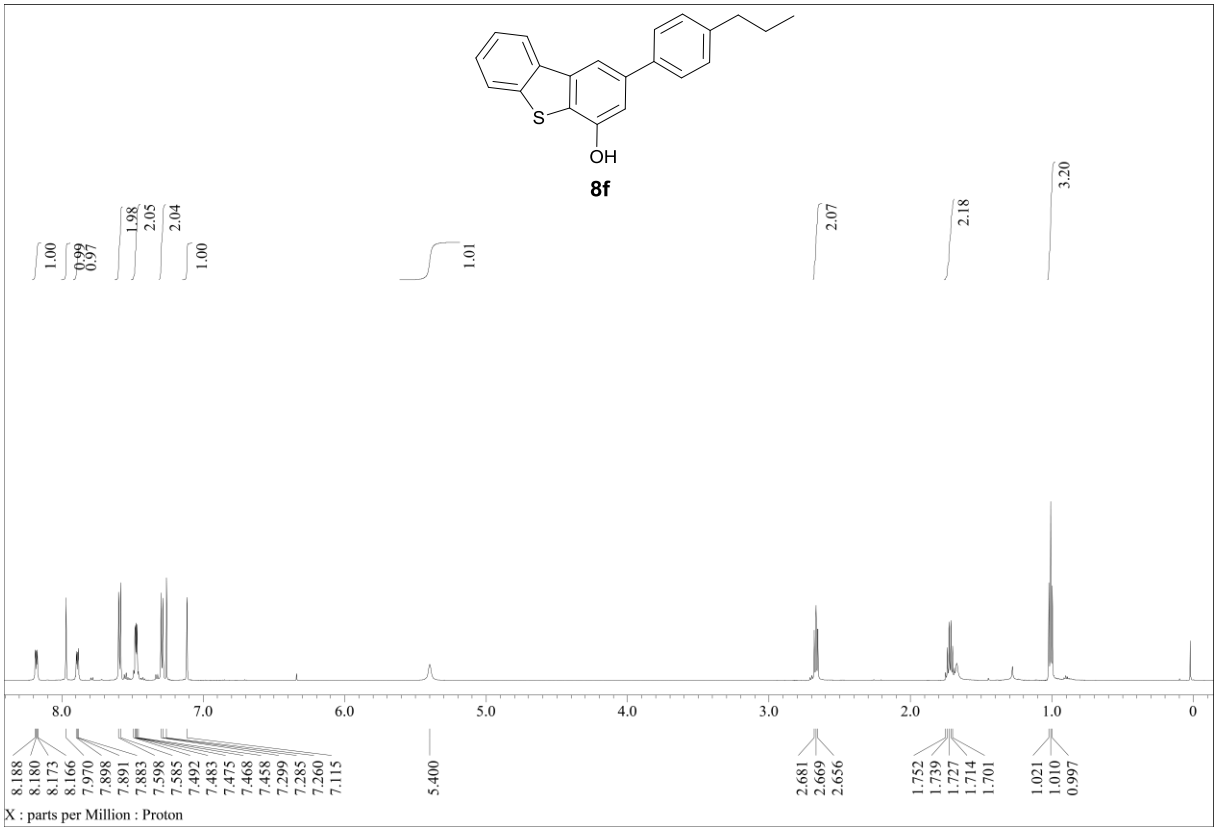

Cl
S
OH
8c
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.588
139.232
139.098
137.479
137.460
135.698
132.204
128.910
128.642
127.167
125.434
124.668
123.251
122.552
111.340
110.000
39.932
39.798
39.654
39.520
39.376
39.242
39.099
X : parts per Million : Carbon13

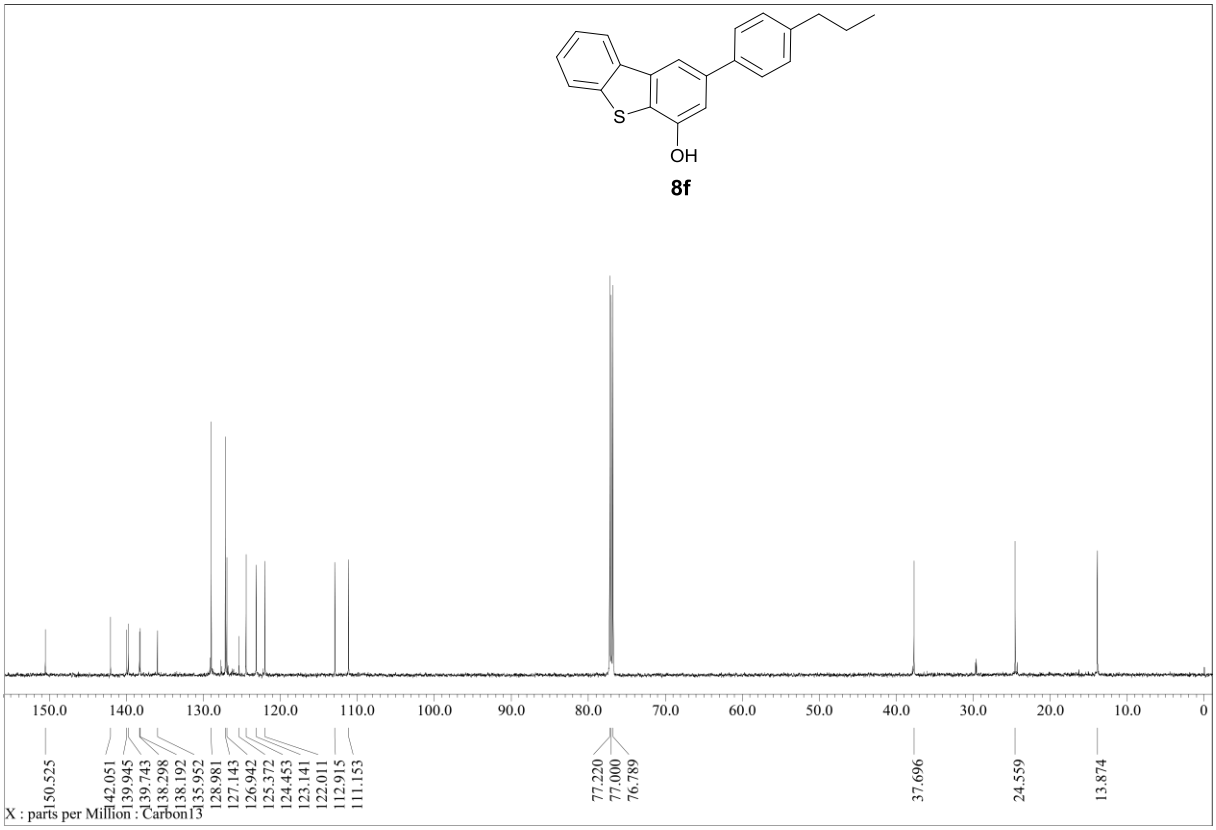

S
OH
8d
1.11
0.94
1.10
2.00
2.34
1.91
0.90
0.98
2.88
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.192
8.184
8.177
7.963
7.906
7.900
7.894
7.885
7.582
7.570
7.493
7.484
7.477
7.471
7.299
7.285
7.113
5.357
2.430
X : parts per Million : Proton

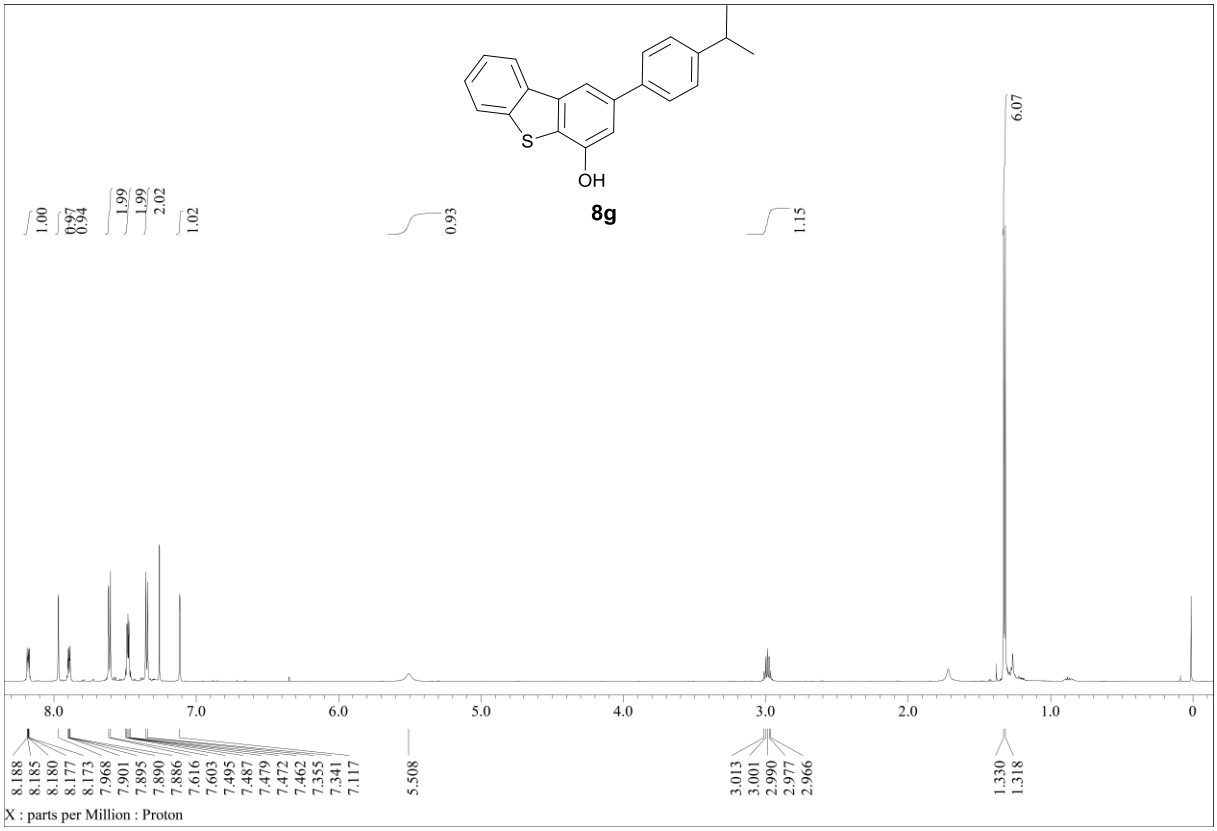

S
OH
8d
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
150.544
139.945
139.705
138.192
138.077
137.216
135.933
129.575
128.857
127.162
126.952
124.453
123.141
122.011
112.858
111.105
77.211
77.000
76.789
21.103
X : parts per Million : Carbon13

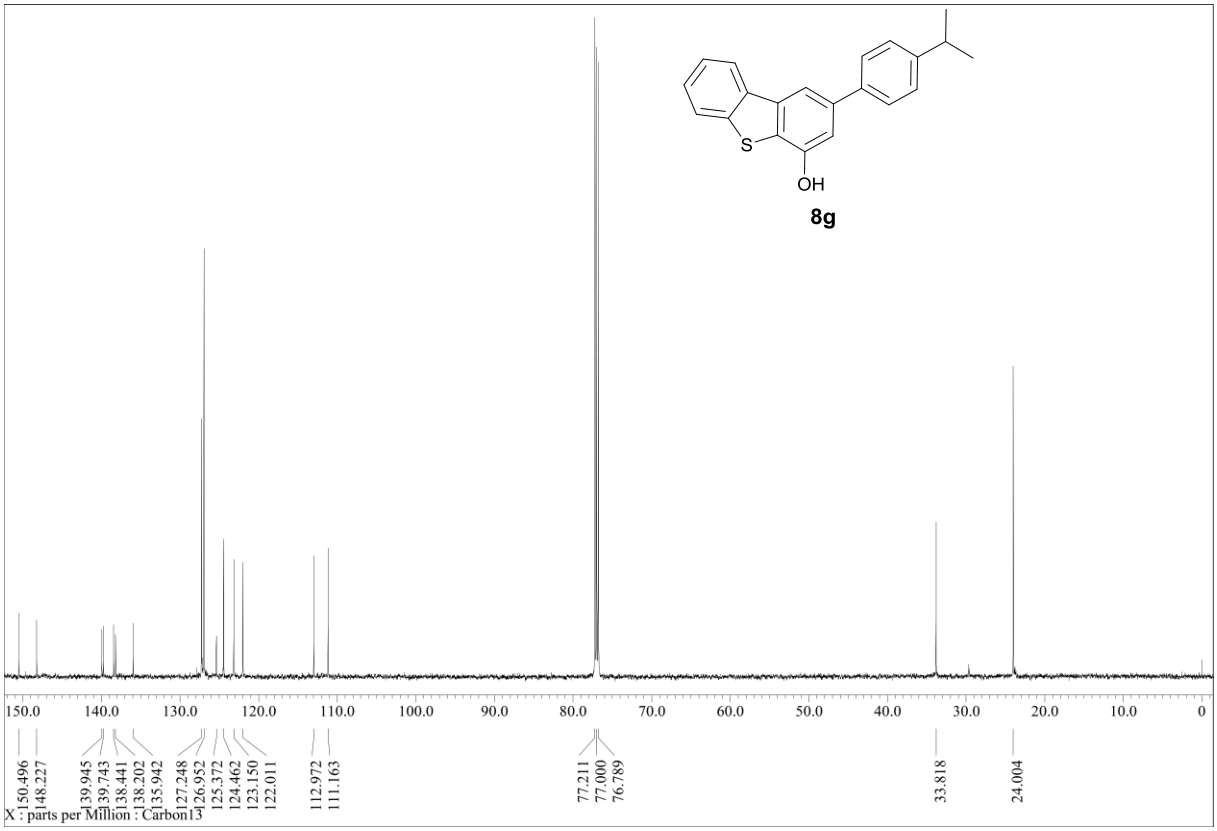

S
OH
8e
1.00
0.97
0.95
2.00
2.07
1.98
0.99
0.78
2.04
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.190
8.187
8.182
8.176
7.967
7.902
7.898
7.896
7.890
7.888
7.608
7.595
7.487
7.485
7.479
7.472
7.470
7.325
7.313
7.114
5.533
2.748
2.735
2.722
2.710
1.319
1.307
1.294
X : parts per Million : Proton


S
OH
8e
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
150.505
143.612
139.935
139.743
138.317
138.202
135.942
128.388
127.248
126.952
125.372
124.462
123.141
122.011
112.934
111.144
77.211
77.000
76.780
28.523
15.597
X : parts per Million : Carbon13

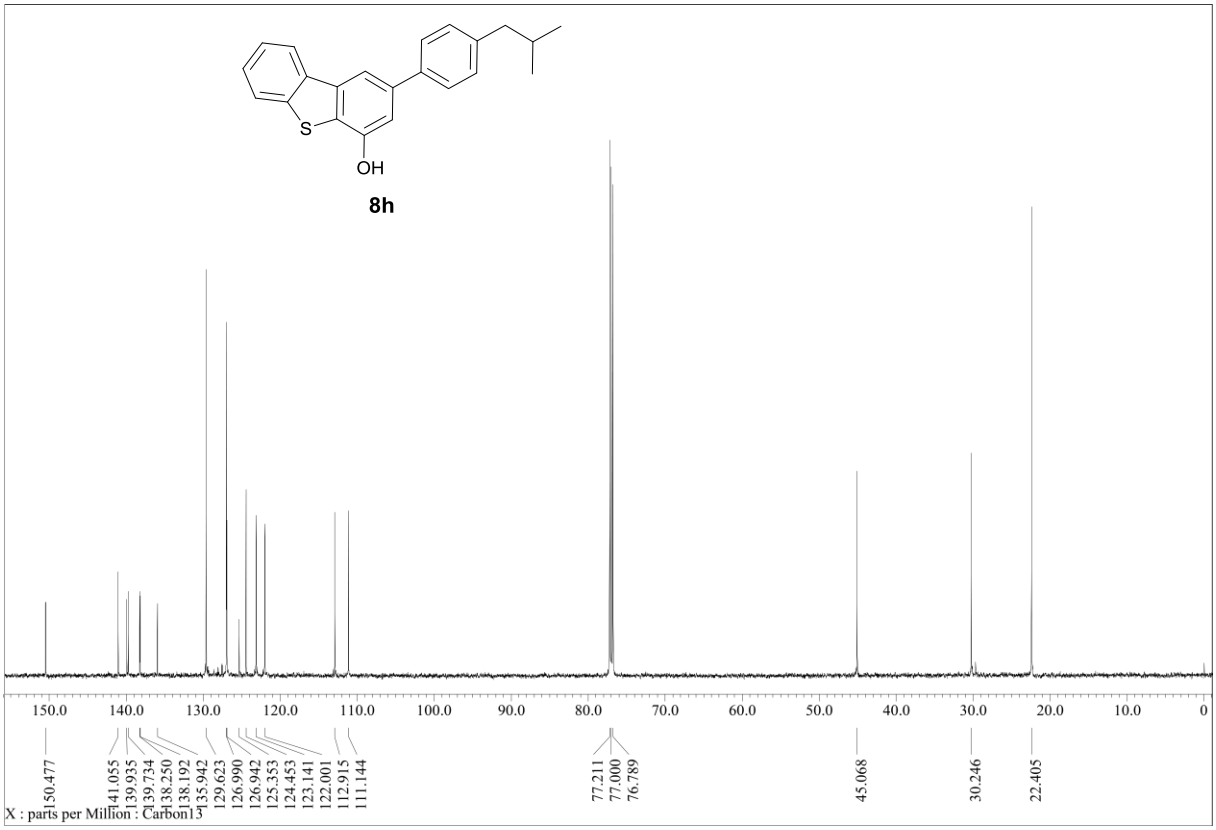

S
OH
8f
1.00
0.99
0.97
1.98
2.05
2.04
1.00
1.01
2.07
2.18
3.20
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.188
8.180
8.173
8.166
7.970
7.898
7.891
7.883
7.598
7.585
7.492
7.483
7.475
7.468
7.458
7.299
7.285
7.260
7.115
5.400
2.681
2.669
2.656
1.752
1.739
1.727
1.714
1.701
1.021
1.010
0.997
X : parts per Million : Proton


S
OH
8f
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
150.525
142.051
139.945
139.743
138.298
138.192
135.952
128.981
127.143
126.942
125.372
124.453
123.141
122.011
112.915
111.153
77.220
77.000
76.789
37.696
24.559
13.874
X : parts per Million : Carbon13

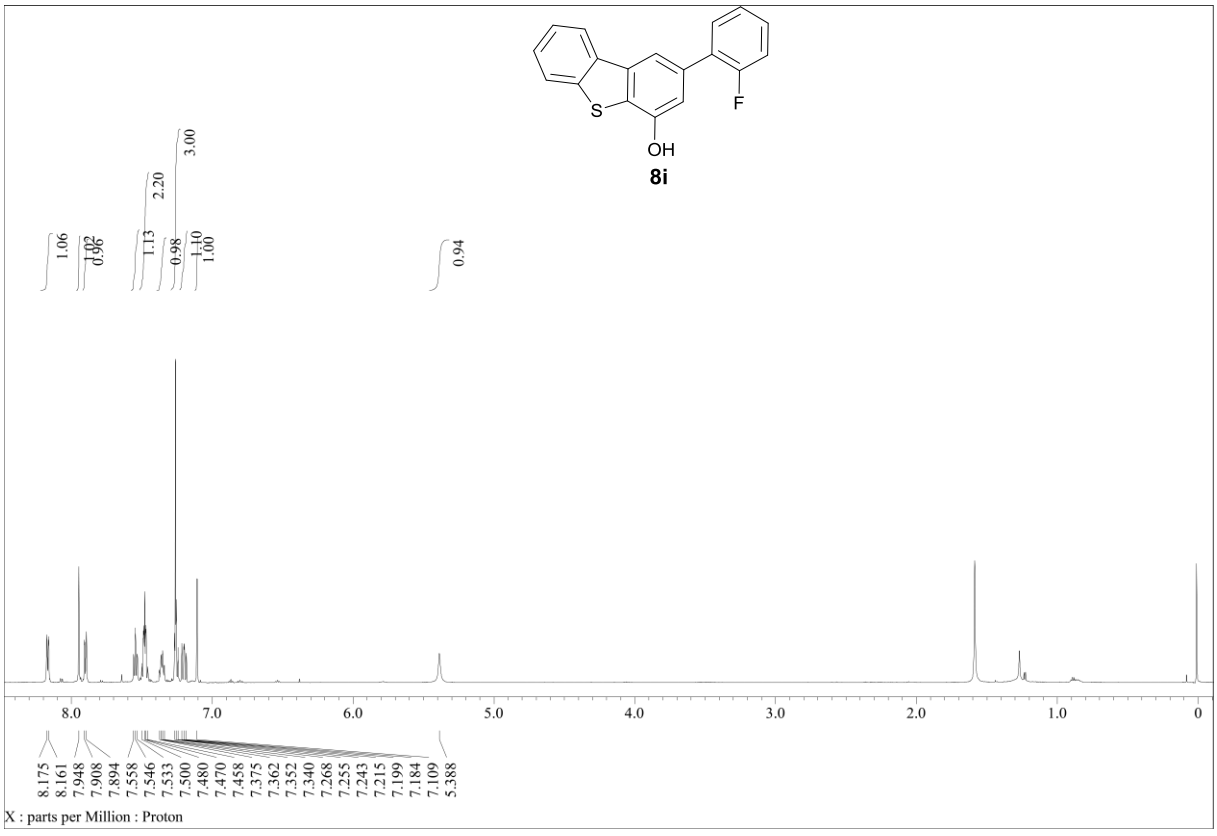

S
OH
8g
1.00
0.97
0.94
1.99
1.99
2.02
1.02
0.93
1.15
6.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.188
8.185
8.180
8.177
8.173
7.968
7.901
7.895
7.890
7.886
7.616
7.603
7.495
7.487
7.479
7.472
7.462
7.355
7.341
7.117
5.508
3.013
3.001
2.990
2.977
2.966
1.330
1.318
X : parts per Million : Proton


S
OH
8g
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
150.496
148.227
139.945
139.743
138.441
138.202
135.942
127.248
126.952
125.372
124.462
123.150
122.011
112.972
111.163
77.211
77.000
76.789
33.818
24.004
X : parts per Million : Carbon13

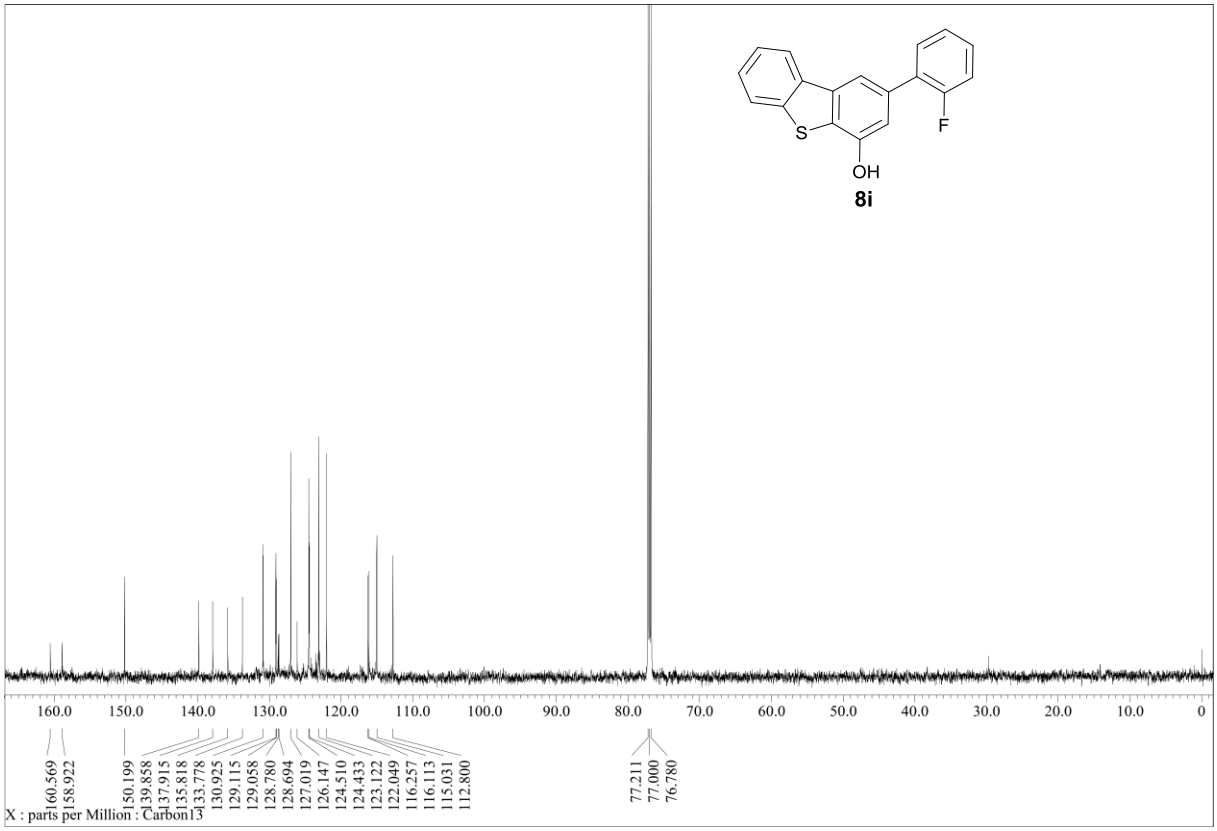

S
OH
8h
1.00
0.99
0.95
2.00
2.04
2.41
0.97
1.01
2.12
1.04
6.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.172
8.169
8.164
8.157
7.955
7.882
7.878
7.875
7.870
7.867
7.573
7.559
7.477
7.467
7.460
7.455
7.452
7.444
7.242
7.231
7.097
5.512
2.538
2.526
1.940
1.929
1.918
1.907
1.895
0.958
0.946
X : parts per Million : Proton

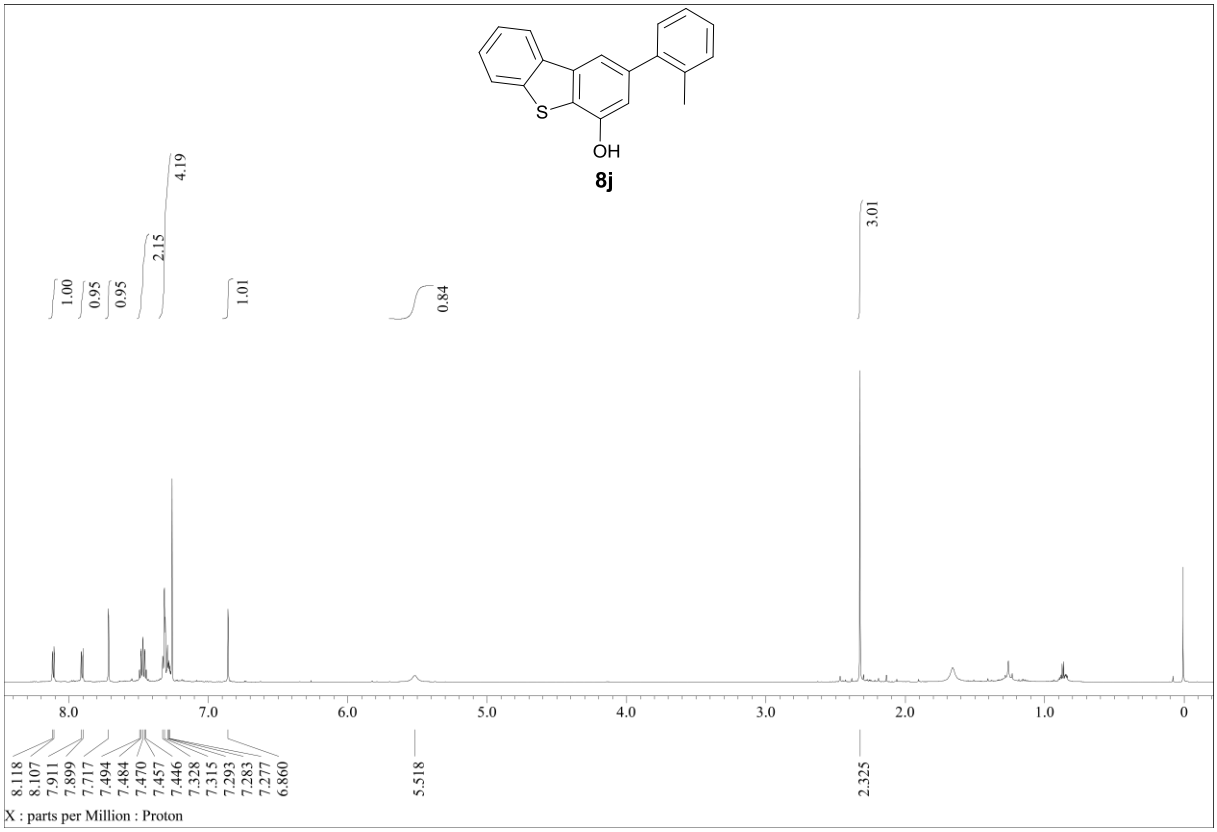

S
OH
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
150.477
141.055
139.935
139.734
138.250
138.192
135.942
129.623
126.990
126.942
125.353
124.453
123.141
122.001
112.915
111.144
77.211
77.000
76.789
45.068
30.246
22.405
X : parts per Million : Carbon13

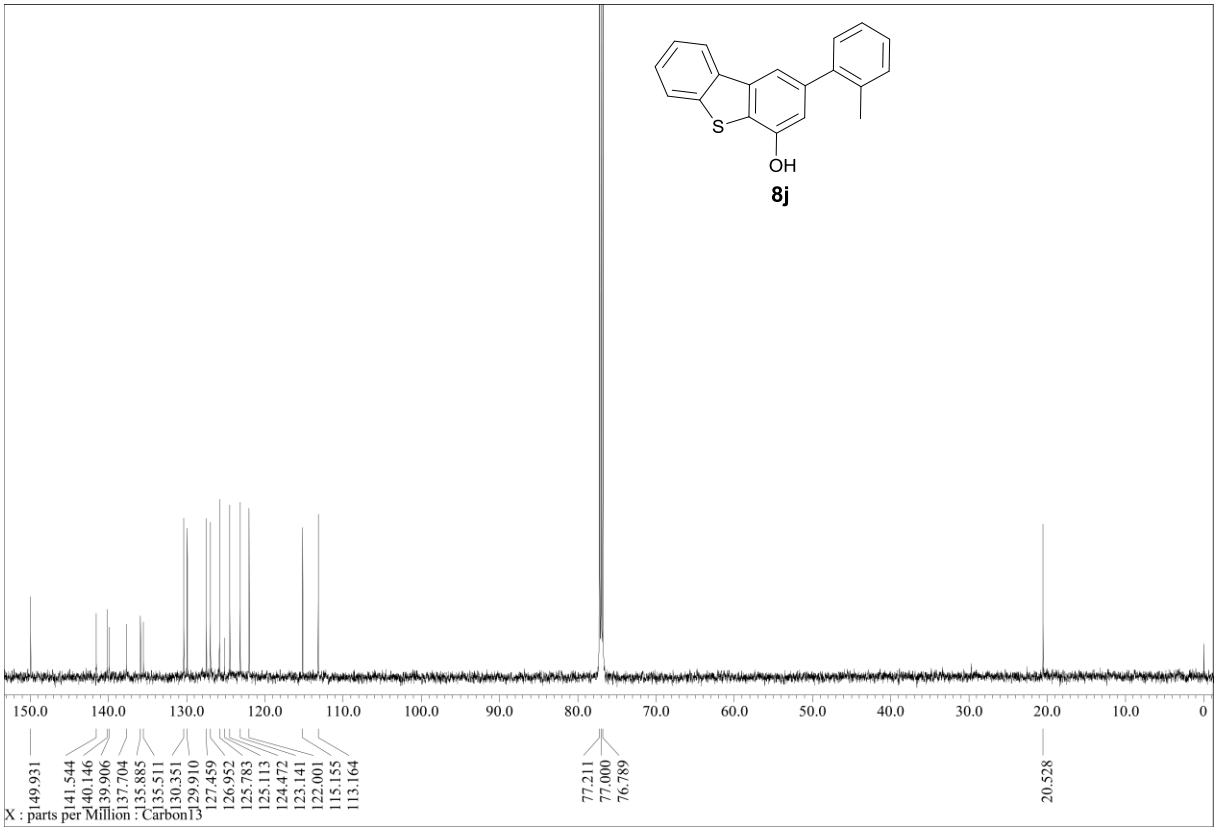
8h

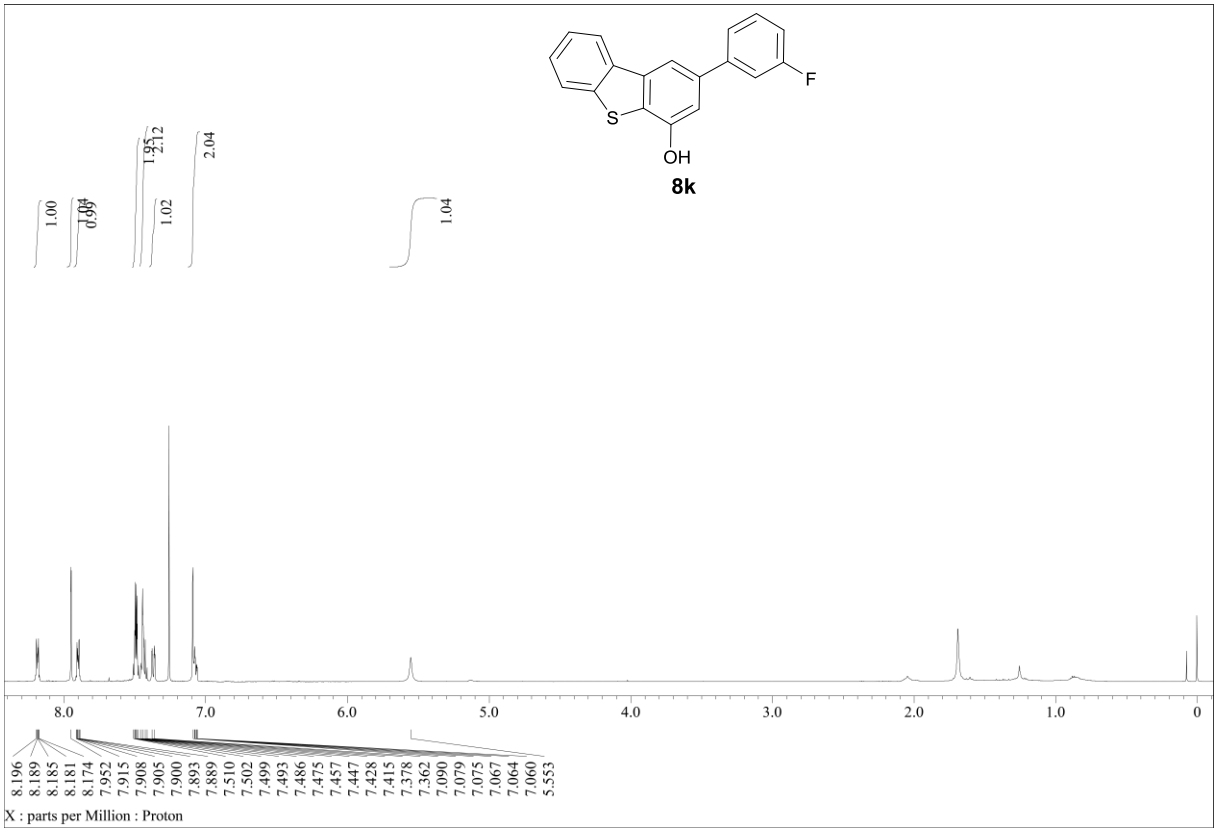

S
F
OH
1.06
1.02
0.96
1.13
2.20
0.98
1.10
1.00
3.00
0.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.175
8.161
7.948
7.908
7.894
7.558
7.546
7.533
7.500
7.480
7.470
7.458
7.375
7.362
7.352
7.340
7.268
7.255
7.243
7.215
7.199
7.184
7.109
5.388
X : parts per Million : Proton

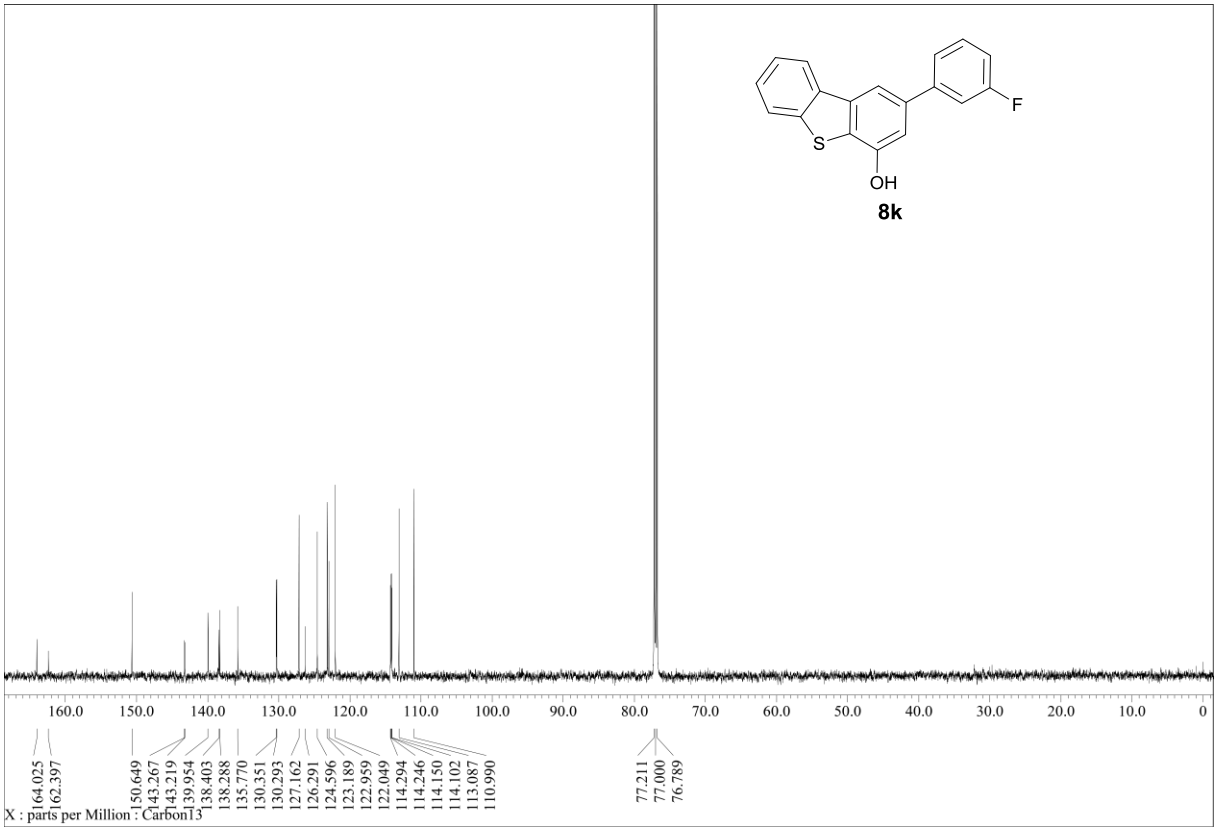
8i


S
F
OH
8i
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
160.569
158.922
150.199
139.858
137.915
135.818
133.778
130.925
129.115
129.058
128.780
128.694
127.019
126.147
124.510
124.433
123.122
122.049
116.257
116.113
115.031
112.800
77.211
77.000
76.780
X : parts per Million : Carbon13

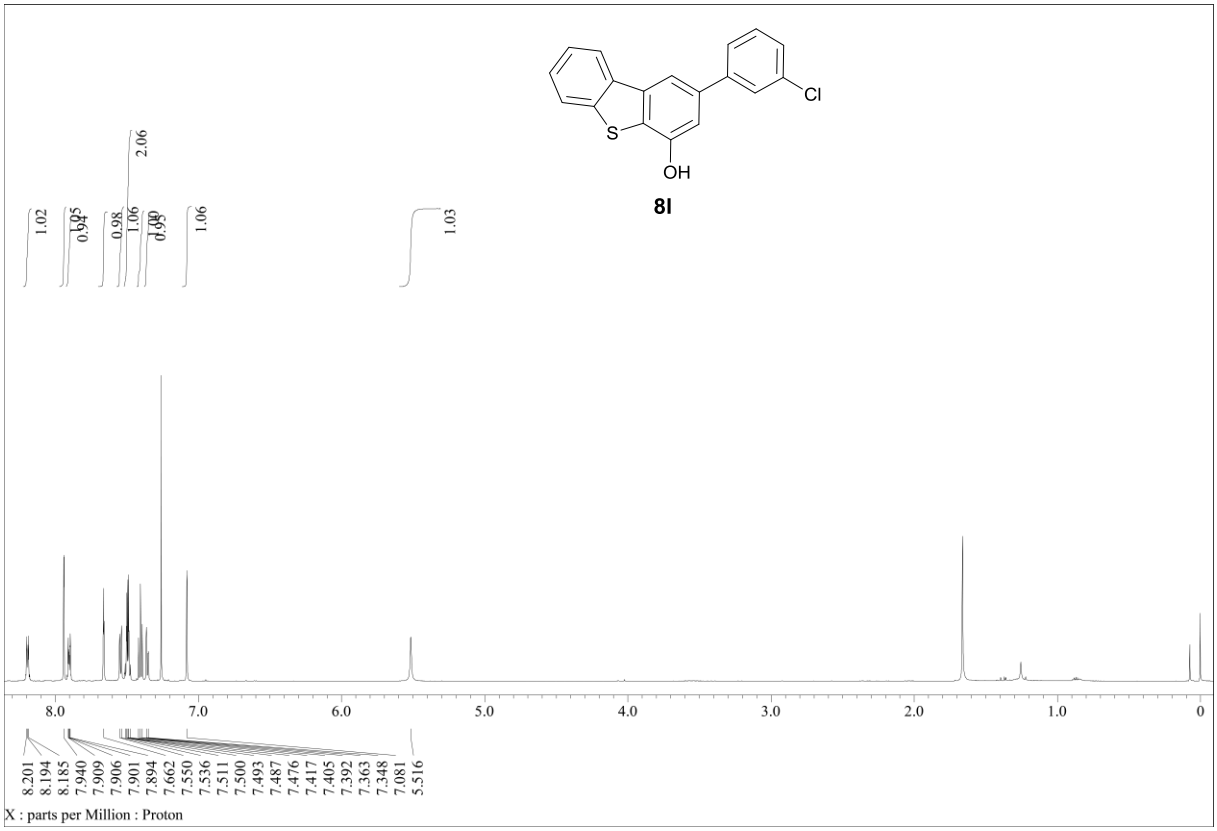

S
OH
8j
4.19
2.15
1.00
0.95
0.95
1.01
0.84
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.118
8.107
7.911
7.899
7.717
7.494
7.484
7.470
7.457
7.446
7.328
7.315
7.293
7.283
7.277
6.860
5.518
2.325
X : parts per Million : Proton


S
OH
8j
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
149.931
141.544
140.146
139.906
137.704
135.885
135.511
130.351
129.910
127.459
126.952
125.783
125.113
124.472
123.141
122.001
115.155
113.164
77.211
77.000
76.789
20.528
X : parts per Million : Carbon13

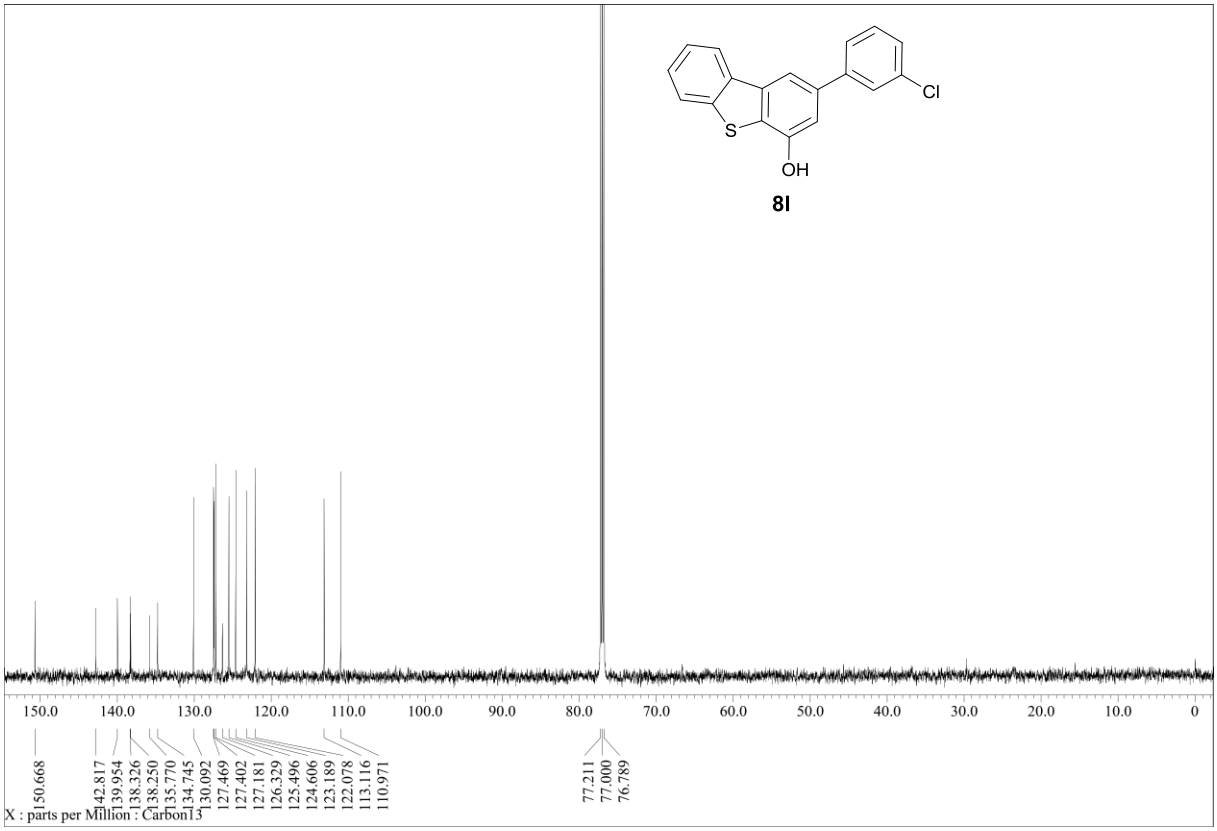

F
S
OH
8k
1.00
1.04
0.99
1.95
2.12
1.02
2.04
1.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.196
8.189
8.185
8.181
8.174
7.952
7.915
7.908
7.905
7.900
7.893
7.889
7.510
7.502
7.499
7.493
7.486
7.475
7.457
7.447
7.428
7.415
7.378
7.362
7.090
7.079
7.075
7.067
7.064
7.060
5.553
X : parts per Million : Proton

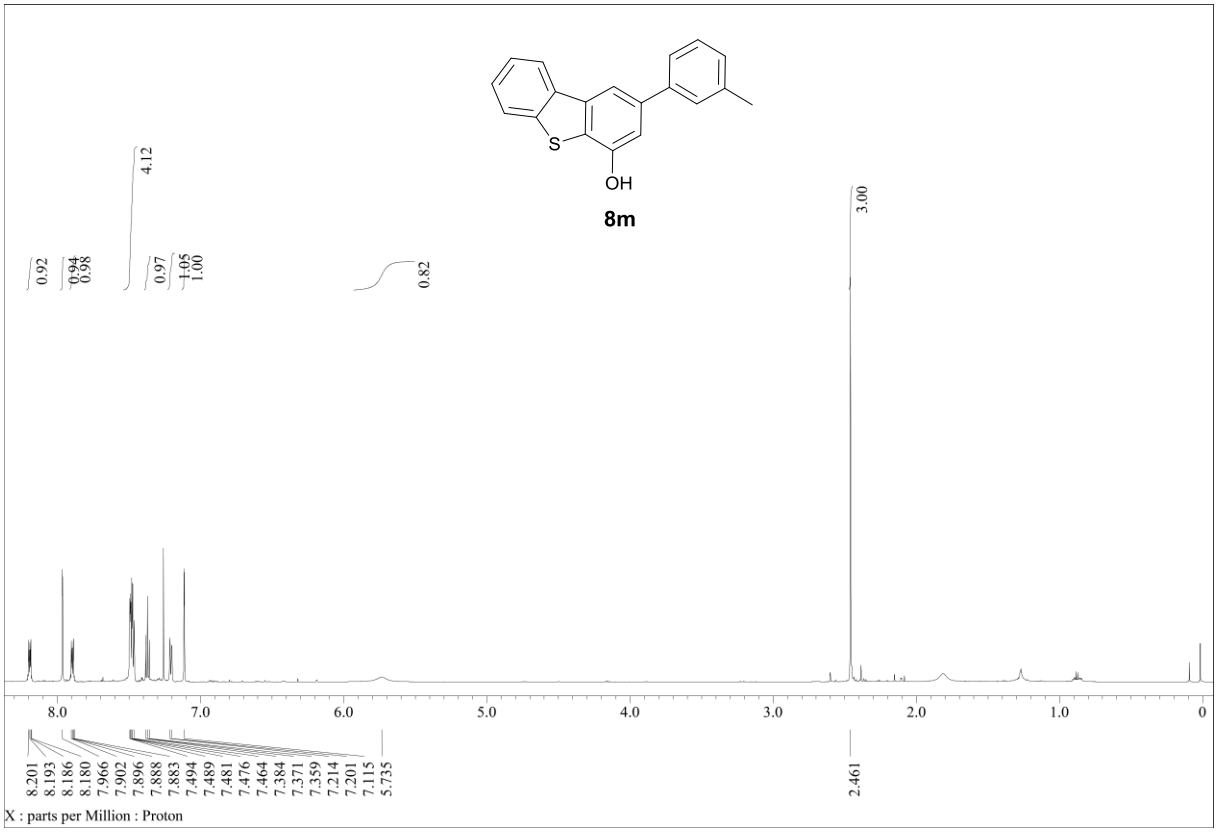

F
S
OH
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.025
162.397
150.649
143.267
143.219
139.954
138.403
138.288
135.770
130.351
130.293
127.162
126.291
124.596
123.189
122.959
122.049
114.294
114.246
114.150
114.102
113.087
110.990
77.211
77.000
76.789
X : parts per Million : Carbon13

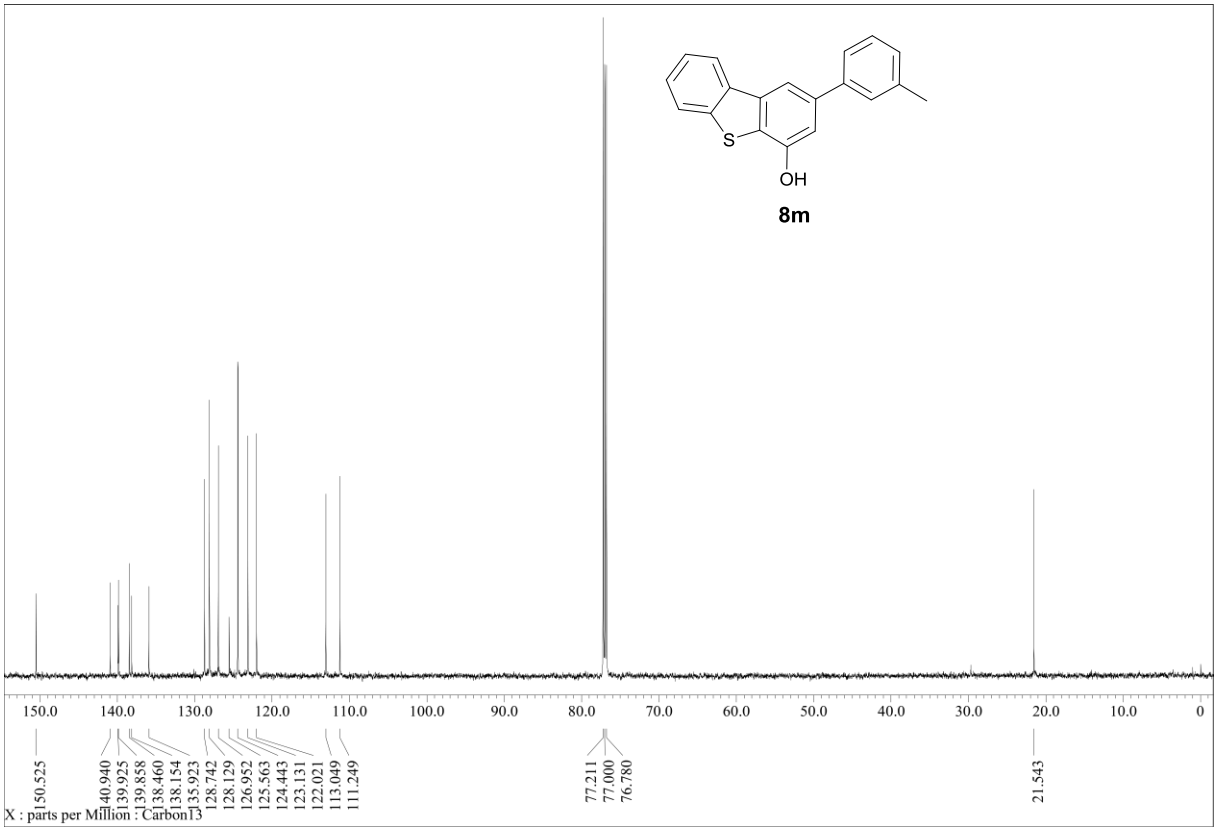
8k

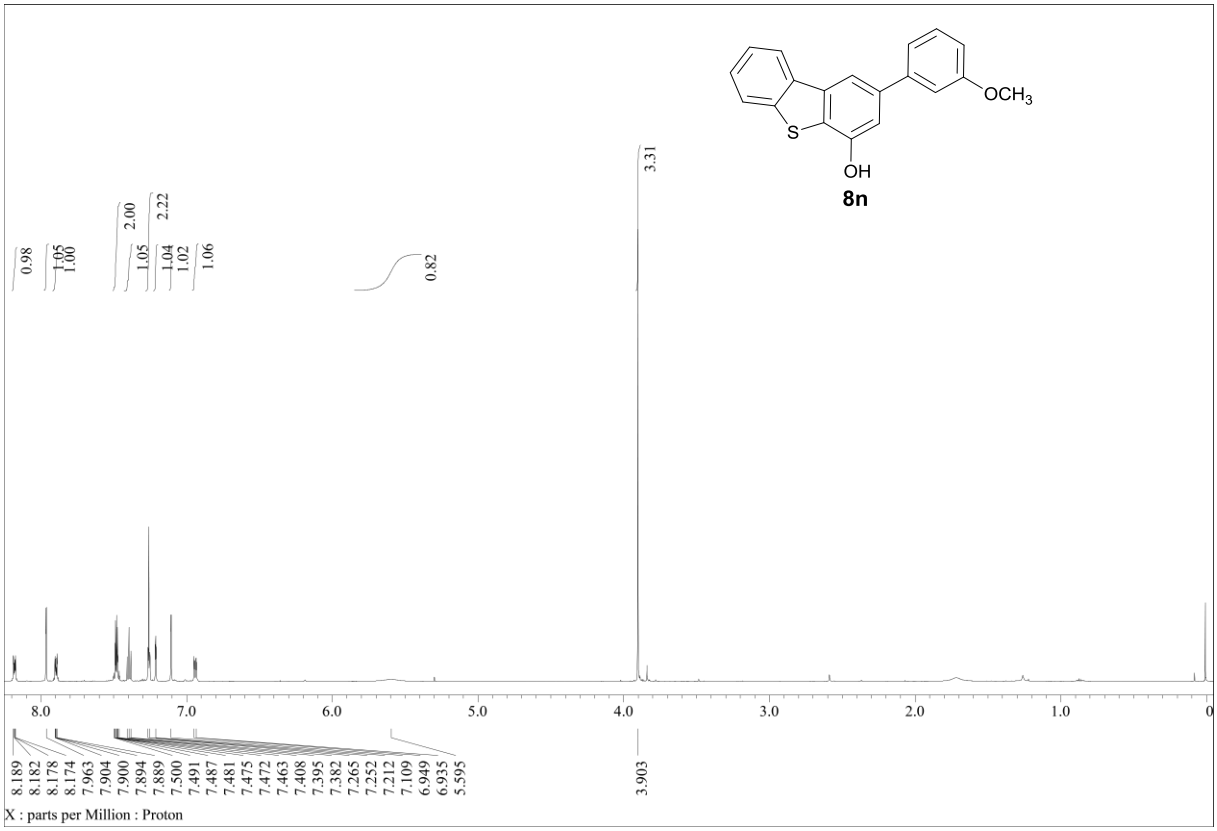

Cl
S
OH
2.06
1.02
1.05
0.97
0.98
1.06
1.00
0.95
1.06
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.201
8.194
8.185
7.940
7.909
7.906
7.901
7.894
7.662
7.550
7.536
7.511
7.500
7.493
7.487
7.476
7.417
7.405
7.392
7.363
7.348
7.081
5.516
X : parts per Million : Proton

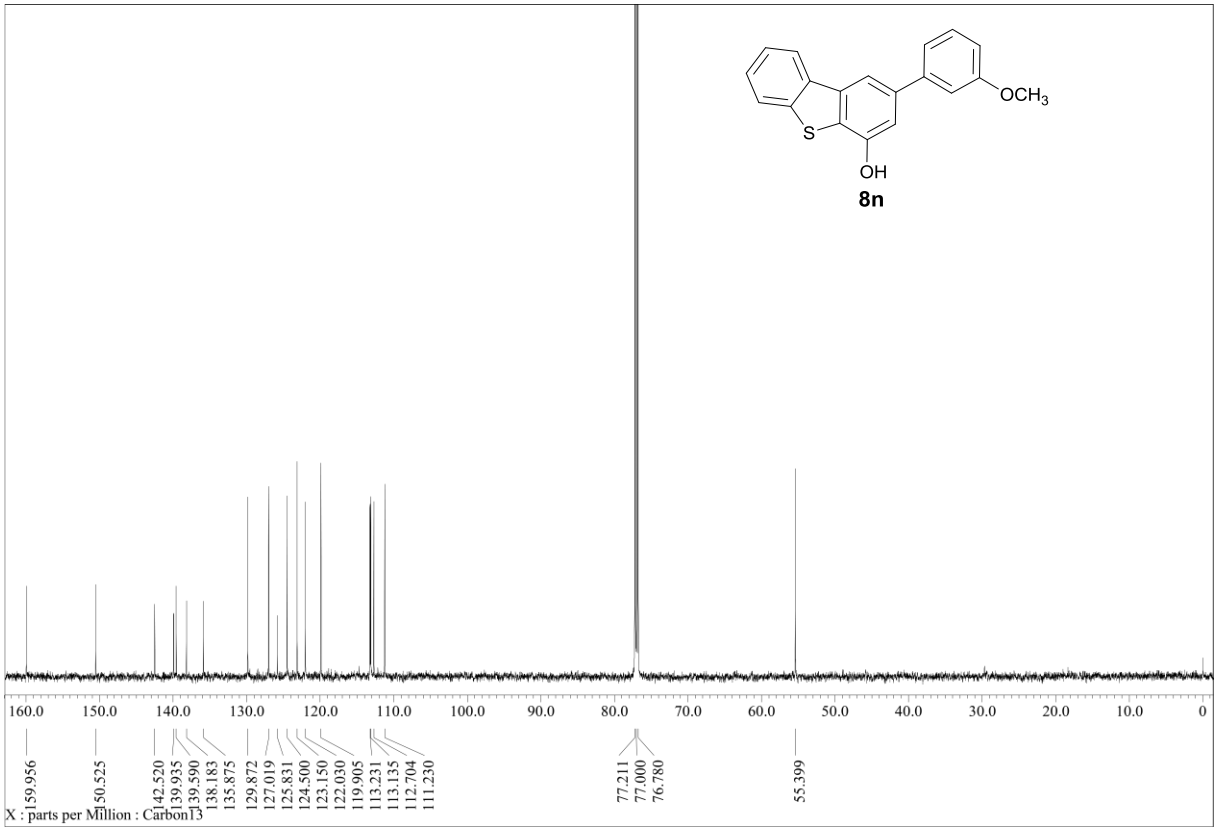
8l

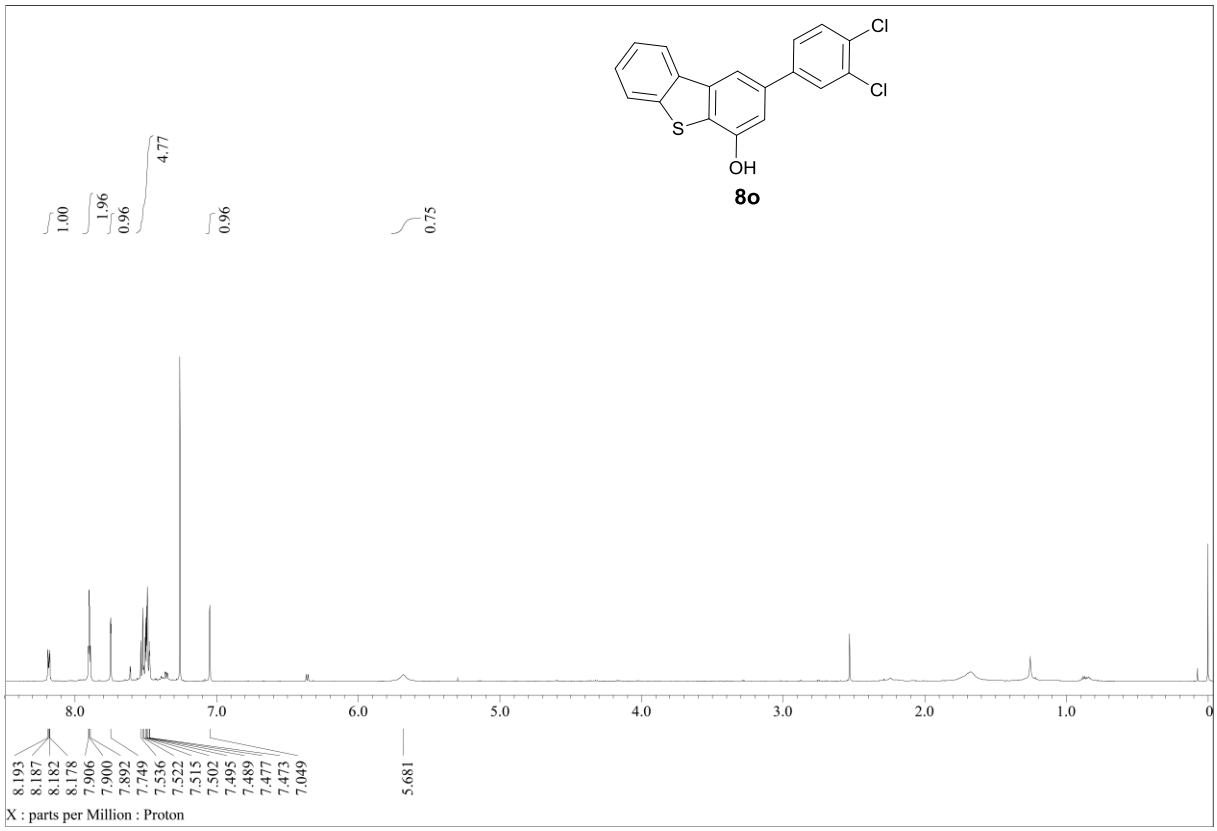

Cl
S
OH
8l
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
150.668
142.817
139.954
138.326
138.250
135.770
134.745
130.092
127.469
127.402
127.181
126.329
125.496
124.606
123.189
122.078
113.116
110.971
77.211
77.000
76.789
X : parts per Million : Carbon13

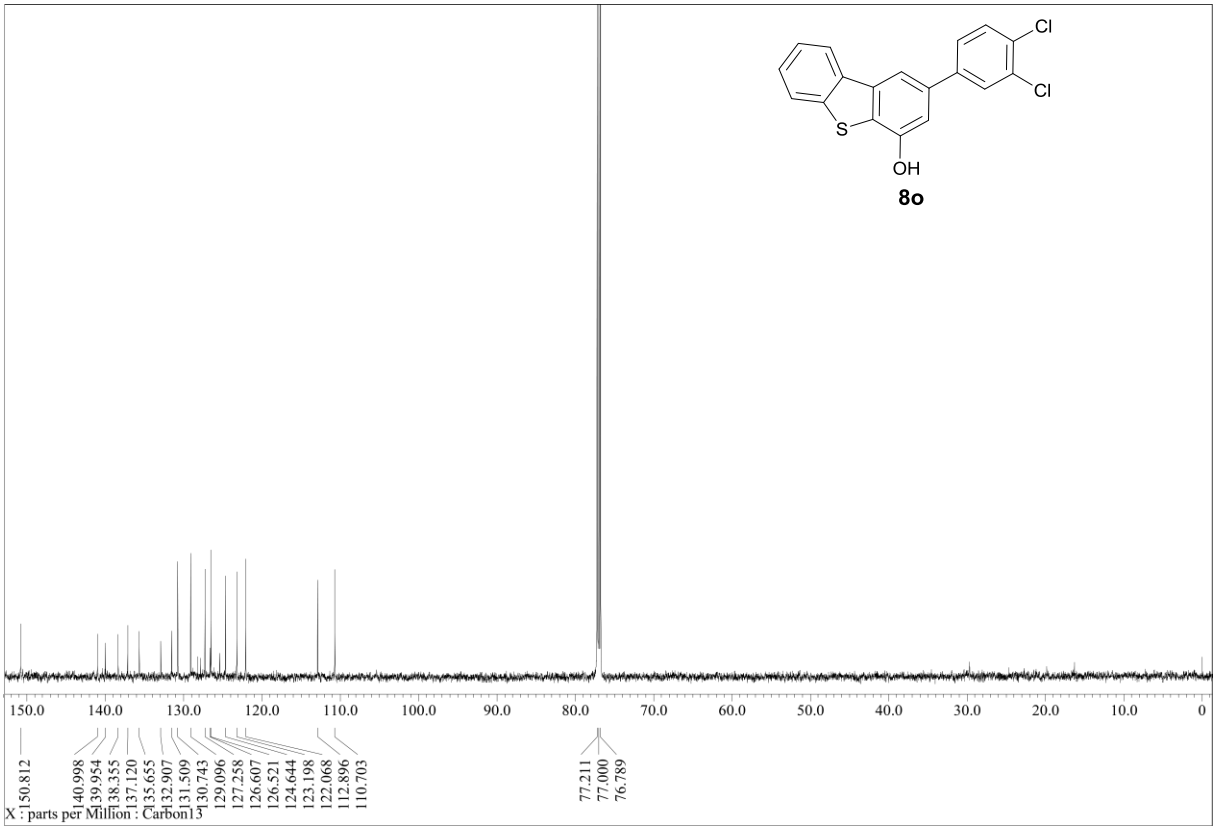

S
OH
8m
0.92
0.94
0.98
4.12
0.97
1.05
1.00
0.82
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.201
8.193
8.186
8.180
7.966
7.902
7.896
7.888
7.883
7.494
7.489
7.481
7.476
7.464
7.384
7.371
7.359
7.214
7.201
7.115
5.735
2.461
X : parts per Million : Proton


S
OH
8m
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
150.525
140.940
139.925
139.858
138.460
138.154
135.923
128.742
128.129
126.952
125.563
124.443
123.131
122.021
113.049
111.249
77.211
77.000
76.780
21.543
X : parts per Million : Carbon13

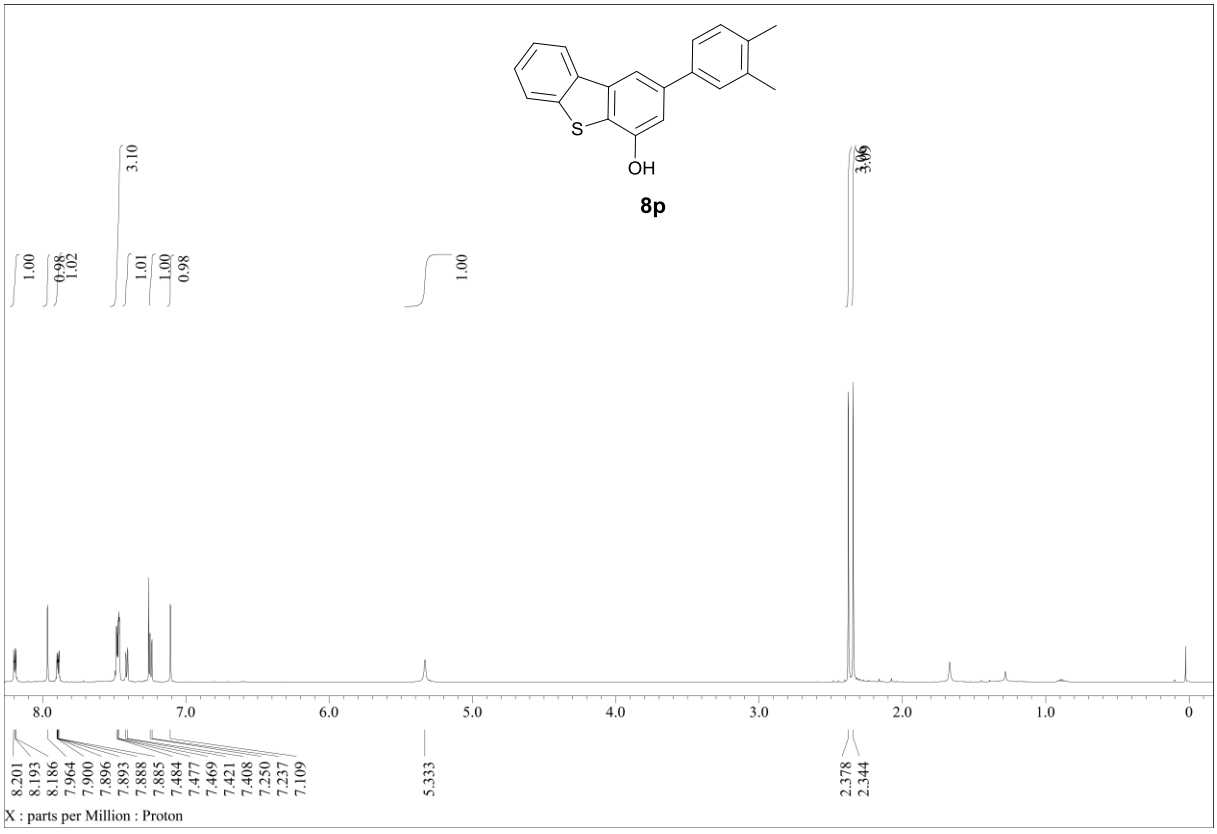

S
OH
OCH3
8n
0.98
1.05
1.00
2.00
1.05
2.22
1.04
1.02
1.06
0.82
3.31
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.189
8.182
8.178
8.174
7.963
7.904
7.900
7.894
7.889
7.500
7.491
7.487
7.481
7.475
7.472
7.463
7.408
7.395
7.382
7.265
7.252
7.212
7.109
6.949
6.935
5.595
3.903
X : parts per Million : Proton


OCH3
S
OH
8n
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
159.956
150.525
142.520
139.935
139.590
138.183
135.875
129.872
127.019
125.831
124.500
123.150
122.030
119.905
113.231
113.135
112.704
111.230
77.211
77.000
76.780
55.399
X : parts per Million : Carbon13

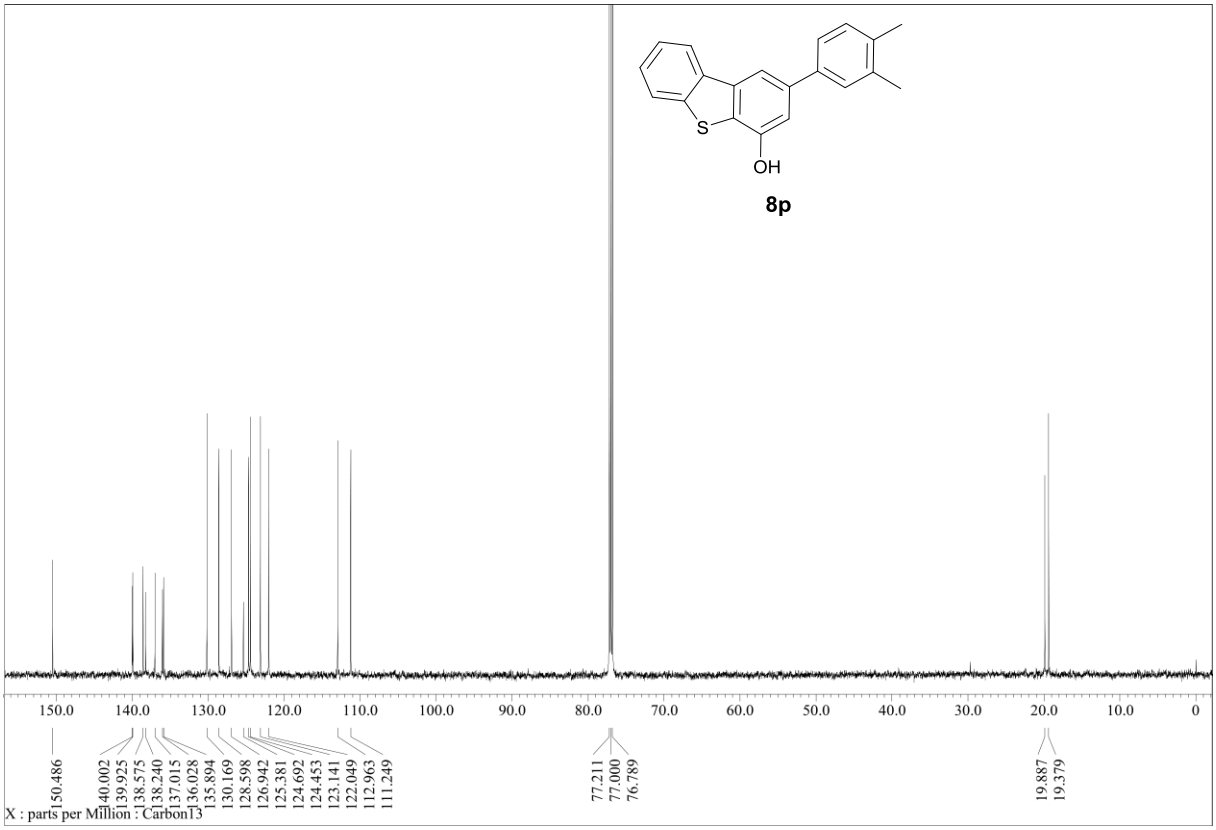

Cl
Cl
S
OH
8o
1.00
1.96
0.96
4.77
0.96
0.75
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.193
8.187
8.182
8.178
7.906
7.900
7.892
7.749
7.536
7.522
7.515
7.502
7.495
7.489
7.477
7.473
7.049
5.681
X : parts per Million : Proton

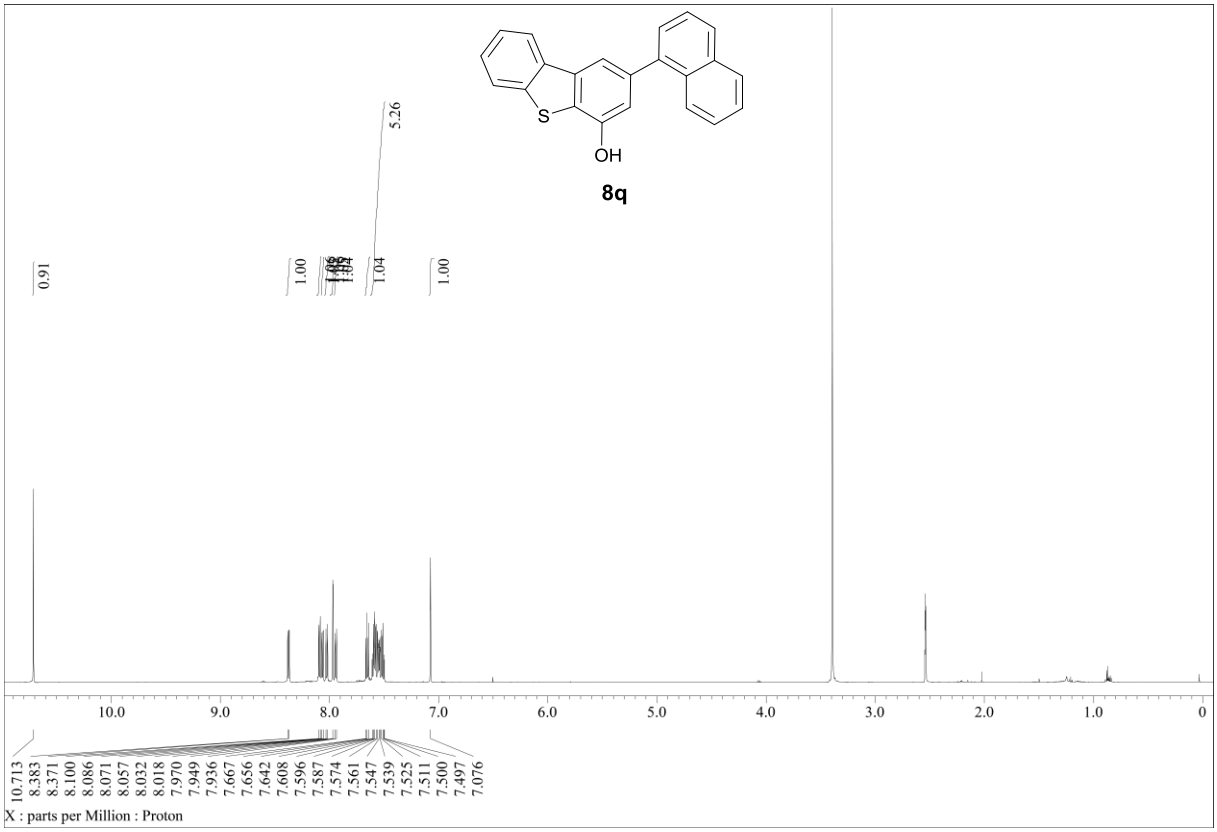

Cl
Cl
S
OH
150.812
140.998
139.954
138.355
137.120
135.655
132.907
131.509
130.743
129.096
127.258
126.607
126.521
124.644
123.198
122.068
112.896
110.703
77.211
77.000
76.789
X : parts per Million : Carbon13

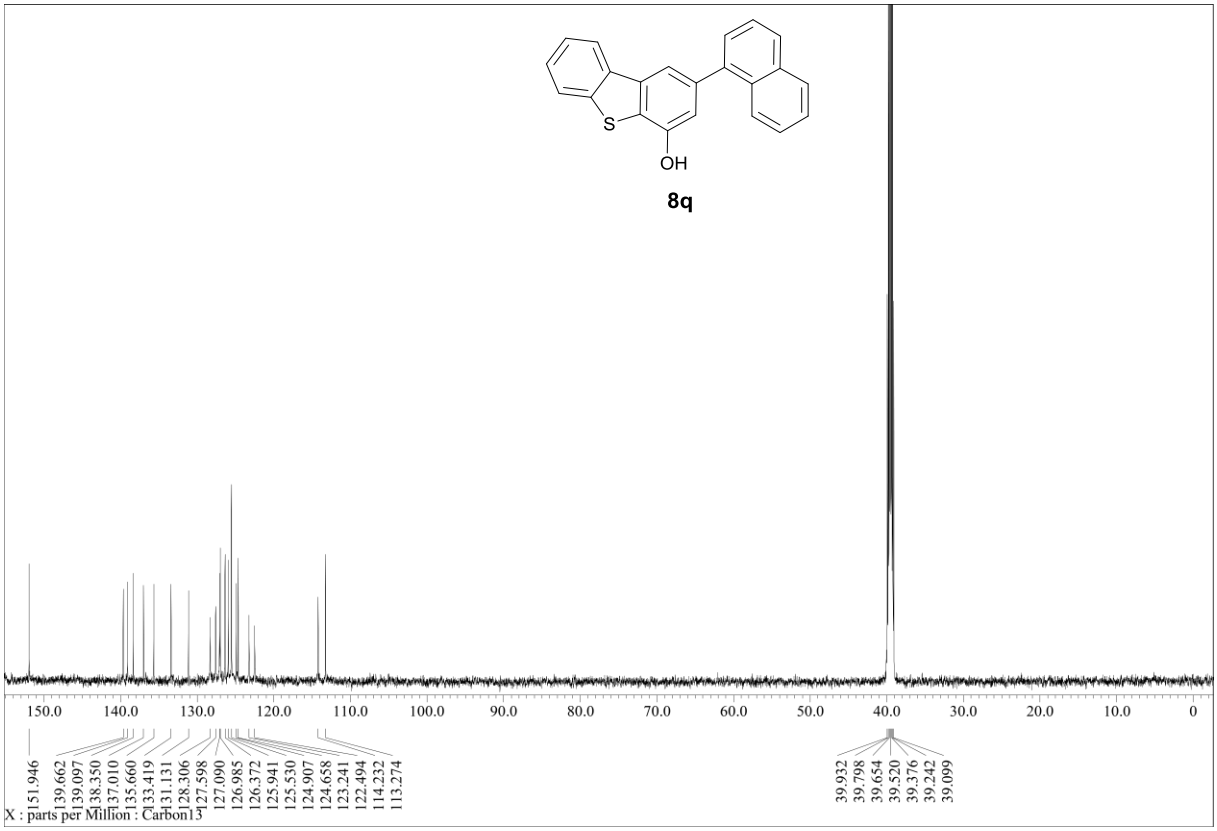
8o

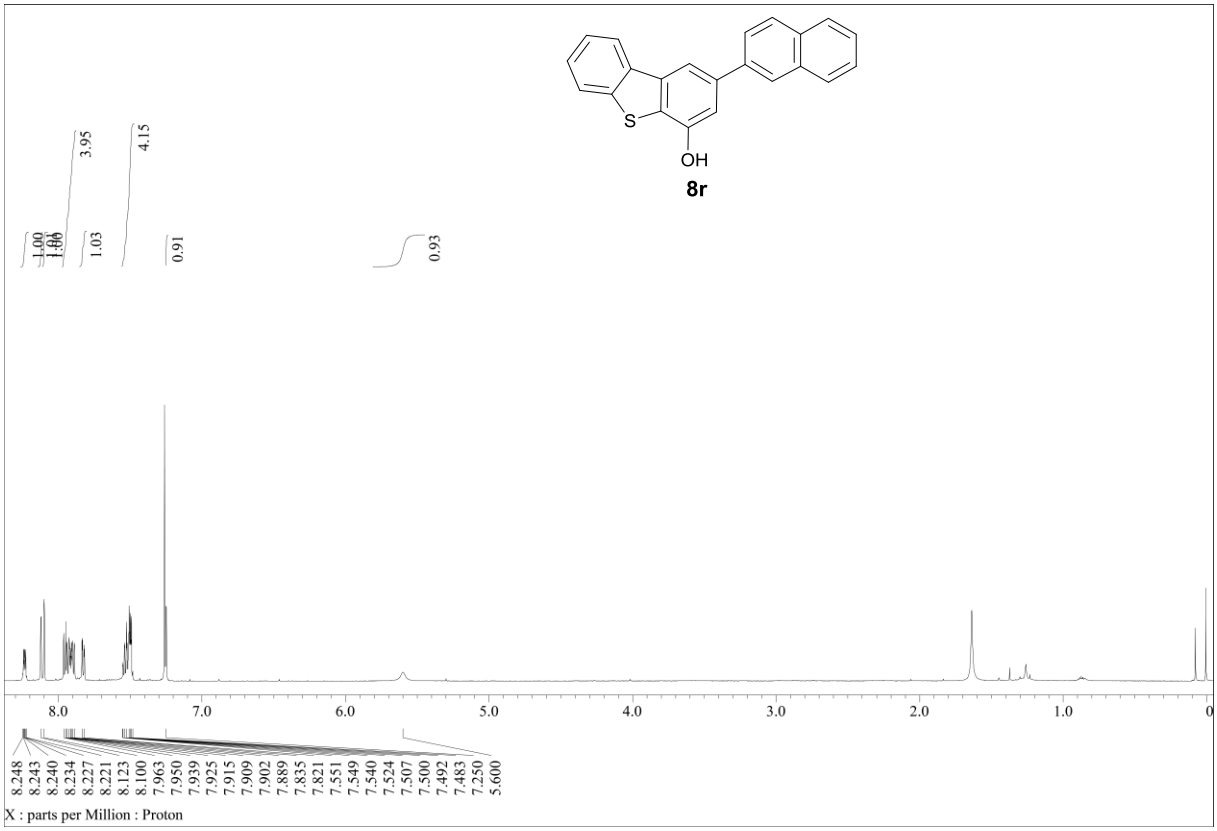

S
OH
3.10
1.00
0.98
1.02
1.01
1.00
0.98
1.00
8.201
8.193
8.186
7.964
7.900
7.896
7.893
7.888
7.885
7.484
7.477
7.469
7.421
7.408
7.250
7.237
7.109
5.333
2.378
2.344
X : parts per Million : Proton

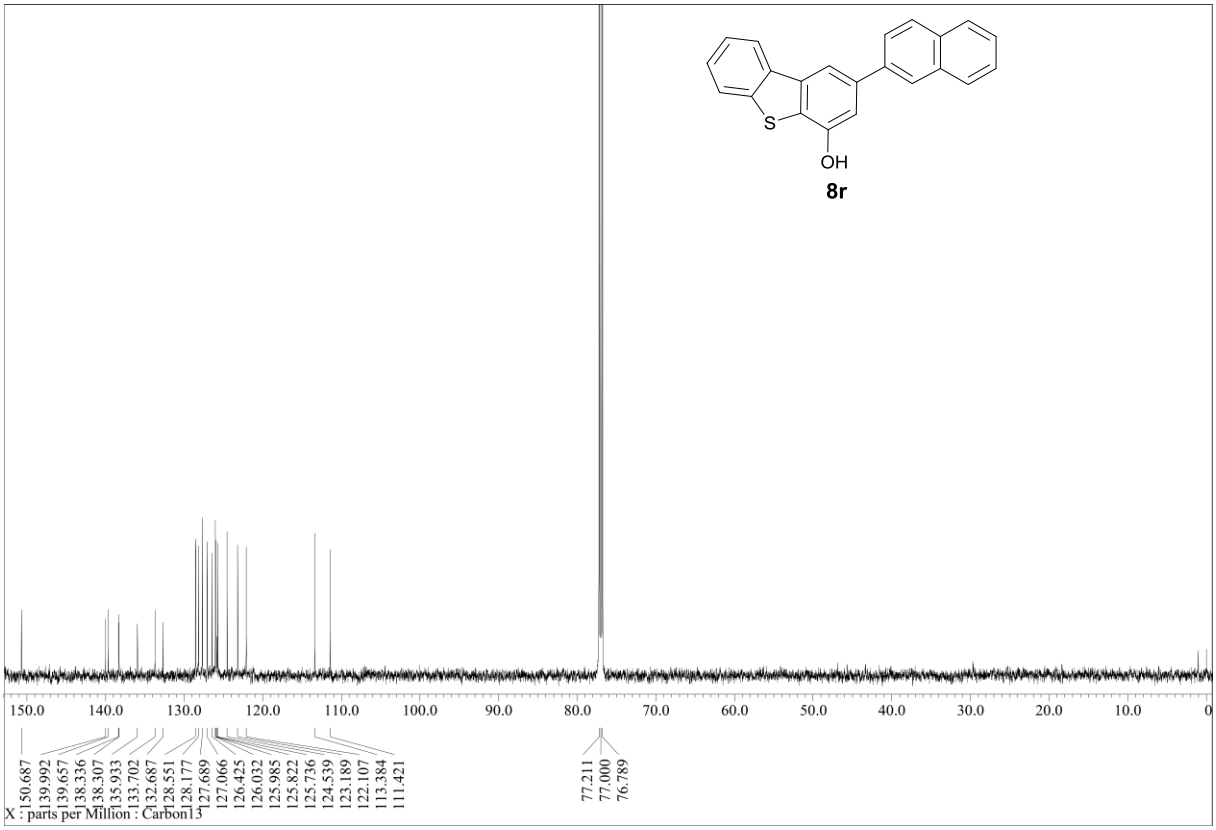
8p


S
OH
8p
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
150.486
140.002
139.925
138.575
138.240
137.015
136.028
135.894
130.169
128.598
126.942
125.381
124.692
124.453
123.141
122.049
112.963
111.249
77.211
77.000
76.789
19.887
19.379
X : parts per Million : Carbon13


S
OH
8q
5.26
0.91
1.00
1.04
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.713
8.383
8.371
8.100
8.086
8.071
8.057
8.032
8.018
7.970
7.949
7.936
7.667
7.656
7.642
7.608
7.596
7.587
7.574
7.561
7.547
7.539
7.525
7.511
7.500
7.497
7.076
X : parts per Million : Proton


S
OH
8q
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
151.946
139.662
139.097
138.350
137.010
135.660
133.419
131.131
128.306
127.598
127.090
126.985
126.372
125.941
125.530
124.907
124.658
123.241
122.494
114.232
113.274
39.932
39.798
39.654
39.520
39.376
39.242
39.099
X : parts per Million : Carbon13


S
OH
8r
3.95
4.15
1.00
1.00
1.00
1.03
0.91
0.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.248
8.243
8.240
8.234
8.227
8.221
8.123
8.100
7.963
7.950
7.939
7.925
7.915
7.909
7.902
7.889
7.835
7.821
7.551
7.549
7.540
7.524
7.507
7.500
7.492
7.483
7.250
5.600
X : parts per Million : Proton


S
OH
8r
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
150.687
139.992
139.657
138.336
138.307
135.933
133.702
132.687
128.551
128.177
127.689
127.066
126.425
126.032
125.985
125.822
125.736
124.539
123.189
122.107
113.384
111.421
77.211
77.000
76.789
X : parts per Million : Carbon13