Supporting Information

Solvent controlled highly regio-selective thieno[2,3-*b*]indole formation under metal-free conditions

Penghui Ni,[a] Bin Li, [a] Huawen Huang, [a] Fuhong Xiao[a]* and Guo-Jun Deng [a]*

Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China
E-mail: fhxiao@xtu.edu.cn; gjdeng@xtu.edu.cn

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1. General information

All reactions were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed using aluminum oxide (neutral) (100-200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at the Institute of Chemistry, Chinese Academy of Sciences. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. All reagents were obtained from commercial suppliers and used without further purification.

2. General procedure for 8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole synthesis

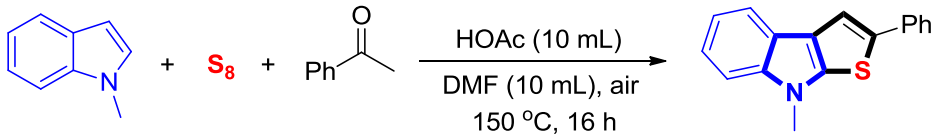
1-Methyl-1*H*-indole (75.0 μL, 0.6 mmol), acetophenone (58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol), and sulfur powder (32.0 mg, 1.0 mmol) were added to an oven-dried reaction vessel (20 mL). The reaction vessel was sealed and HI (50 mol %, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid) and CF_3Ph/1,4-dioxane (1.0 mL, 2:3) were added by syringe. The reaction vessel was stirred at 130 ^{o}C for 4 h under air atmosphere. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3aa** as yellow oily liquid (106.5 mg, 81% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

3. General procedure for 8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole synthesis

1-Methyl-1*H*-indole (25.0 μL, 0.2 mmol), acetophenone (47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol) were added to an oven-dried reaction vessel (20 mL). The reaction vessel was sealed and HOAc (0.1 mL) and DMF (0.3 mL) were added by syringe. The reaction vessel was stirred at 150 ^{o}C for 16 h under air atmosphere. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum

ether/EtOAc = 300:1) to yield the desired product **4aa** as white solid (41.1 mg, 78% yield), mp 137-139 °C. R_f = 0.75 (100:1 petroleum ether/EtOAc).

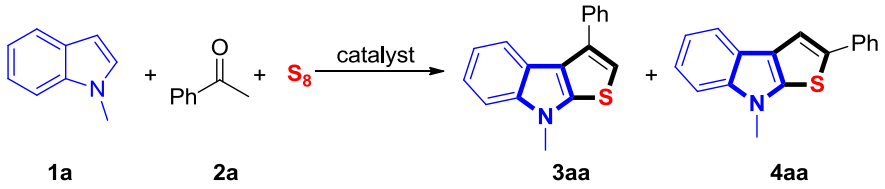
4. Procedure for gram-scale reaction



1-Methyl-1*H*-indole (2.5. mL, 0.02 mol), acetophenone (4.7 mL, 0.04 mol) and sulfur powder (3.2 g, 0.1 mol) were added to a round bottomed flask (50 mL). The reaction vessel was open and HOAc (10 mL) and DMF (10 mL) were added by measuring cylinder. The reaction mixture was stirred at 150 °C under air condition to reflux for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (15 mL) and washed with saturated salt water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4aa** as white solid (3.73 g, 71% yield).

5. Supporting tables S1-S8

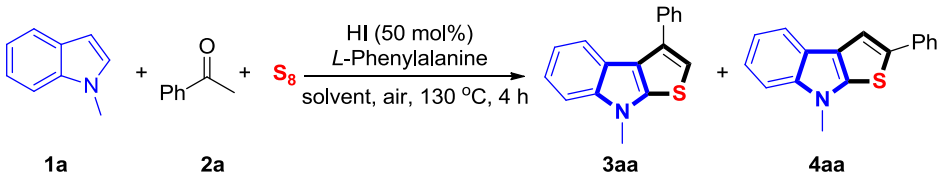
Table S1. Catalyst screening of **3aa**[a]



entry	catalyst (50 mol %)	yield (**3aa**/**4aa**) (%)[b]
1	I_2	13 (>99 : 1))
2	HI	75 (>99 : 1)
3	NH_4I	trace
4	ICl	35 (>99 : 1)
5	NIS	27 (>99 : 1)
6	[Hydroxy(tosyloxy)iodo]benzene	trace
7	(Diacetoxyiodo)benzene	9 (>99 : 1)
8	[Bis(trifluoroacetoxy)iodo]benzene	17 (>99 : 1)

[a] *Conditions*: **1a** (0.6 mmol), **2a** (0.5 mmol), S (1.0 mmol), *L*-phenylalanine (1 equiv), $PhCF_3$: 1,4-dioxane = 2:3 (1.0 mL), 130 °C, 4 h, under air atmosphere.
[b] GC yield based on **2a**.

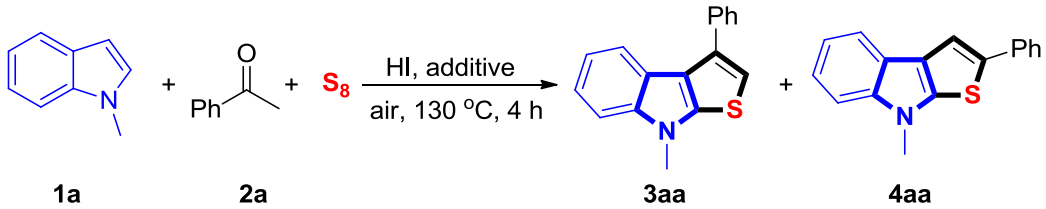
Table S2. Solvent screening of **3aa**[a]



entry	solvent (1.0 mL)	yield (**3aa**/**4aa**) (%)[b]
1	toluene	11 (60 : 1)
2	chlorobenzene	19 (80 : 1)
3	$PhCF_3$	22 (85 : 1)
4	*o*-xylene	27 (60 : 1)
5	anisole	26 (60 : 1)
6	1,4-dioxane	35 (>99 : 1)
7	mesitylene	12 (65 : 1)
8	$PhCF_3$:1,4-dioxane = 2:3	73 (>99 : 1)
9	$PhCF_3$:1,4-dioxane = 3:2	52 (>99 : 1)
10	DMF	9 (7 : 1)
11	DMSO	trace

[a] *Conditions*: **1a** (0.6 mmol), **2a** (0.5 mmol), S (1.0 mmol), *L*-phenylalanine (1 equiv), HI (50 mol%), 130 °C, 4 h, under air atmosphere.
[b] GC yield based on **2a**.

Table S3. Additive screening of **3aa**[a]

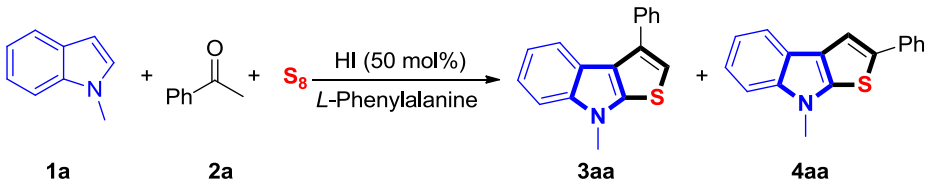


entry	additive (1 equiv)	yield (**3aa**/**4aa**) (%)[b]
1	pyrrolidine	trace
2	piperidine	trace
3	piperazine	trace
4	cyclohexanamine	trace
5	ethane-1,2-diamine	7 (20:1)
6	dibutylamine	9 (15:1)
7	*L*-phenylalanine	75 (>99:1)
8	*L*-histidine	41 (>99:1)
9	*L*-cysteine	27 (>99:1)
10	*L*-methionine	6 (>99:1)
11	*L* -tryptophan	48 (>99:1)
12	*L* -proline	56 (>99:1)
13	*L* -asparagine	67 (>99:1)

14	*L* -glutamine	64 (>99:1)
15	*L* -alanine	59 (>99:1)
16	*L* -leucine	63 (>99:1)
17	*L* -tyrosine	70 (>99:1)
18	*L* -valine	18 (>99:1)
19 [c]	*L*-phenylalanine	49 (>99:1)
20 [d]	*L*-phenylalanine	70 (>99:1)

[a] *Conditions*: **1a** (0.6 mmol), **2** (0.5 mmol), S (1.0 mmol), $PhCF_3$: 1,4-dioxane = 2:3 (1.0 mL), HI (50 mol%), 130 °C, 4 h, under air atmosphere.
[b] GC yield based on **2a**.
[c] *L*-Phenylalanine 0.1 mmol.
[d] *L*-Phenylalanine 0.3 mmol.

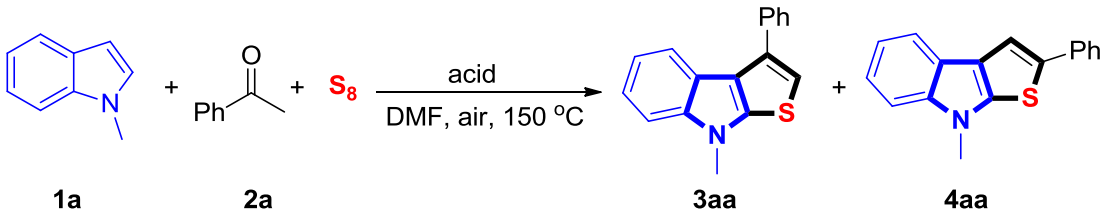
Table S4. Optimization on reaction temperature and atmosphere of **3aa**[a]



entry	temperature (°C)	atmosphere	yield (%)[b]
1	120	air (opened tube)	53 (60 : 1)
2	130	air (opened tube)	78 (>99: 1)
3	140	air (opened tube)	73 (>99: 1)
4[c]	150	air (opened tube)	75 (>99: 1)
5	130	O_2 (sealed tube)	75 (>99: 1)
6	130	Ar (sealed tube)	76 (>99: 1)

[a] *Conditions*: **1a** (0.6 mmol), **2** (0.5 mmol), S (1.0 mmol), *L*-phenylalanine (1 equiv), $PhCF_3$: 1,4-dioxane = 2:3 (1.0 mL), HI (50 mol%).
[b] GC yield based on **2a**.
[c] 2 h.

Table S5. Acid screening of **4aa**[a]

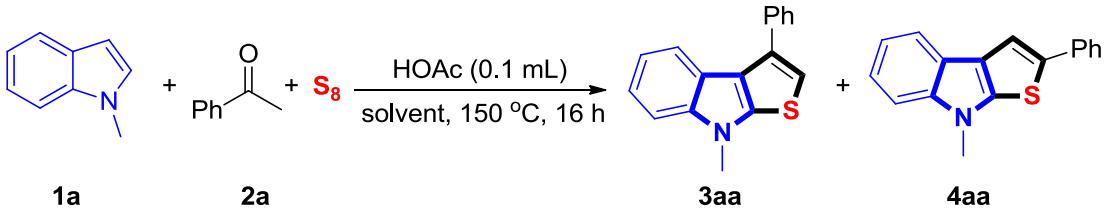


entry	acid (5 equiv)	yield (**3aa**/**4aa**) (%)[b]
1	formic acid	52 (1 : 20)
2	TsOH	63 (1 : 2)
3	TfOH	67 (1 : 2)
4	isobutyric acid	73 (1 : 15)

5	pivalic acid	75 (1 : 20)
6	cyclopropanecarboxylic acid	75 (1 : 15)
7	cyclohexanecarboxylic acid	46 (1 : 10)
8	tetrafluoroboric acid	52 (1 : 5)
9	*p*-hydroxybenzoic acid	10 (1 : 1)
10	*p*-nitrobenzoic acid	74 (1 : 55)
11	acetic anhydride	41 (1 : 4)
12	nicotinic acid	73 (1 : 70)

[a] *Conditions*: **1a** (0.2 mmol), **2** (0.4 mmol), S (1.0 mmol), acid (5 equiv), DMF (0.3 mL), 150 °C, 16 h, under air atmosphere.
[b] GC yield based on **1a**.

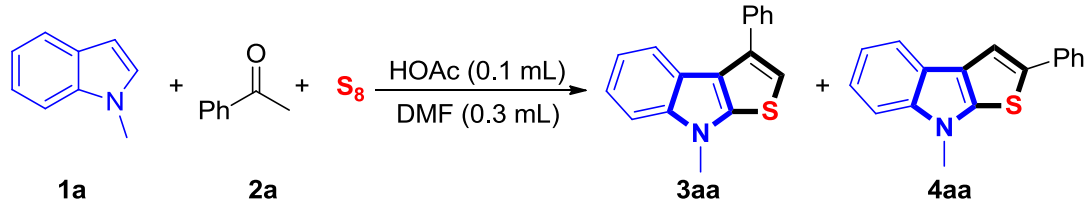
Table S6. Solvent screening of **4aa**[a]



entry	solvent (0.3 mL)	yield (**3aa**/**4aa**) (%)[b]
1	1,2-dichlorobenzene	trace
2	1,4-dioxane	trace
3	(trifluoromethyl)benzene	trace
4	toluene	trace
5	DMSO	trace
6	DMF	87 (1 : 80)
7	DMAc	54 (1 : 60)
8	DEF	19 (1 : 35)
9	DMF (3eq.)	trace
10	DMF (5eq.)	trace
11	DMF (7eq.)	23 (1 : 65)
12	DMF (0.2 mL)	76 (1 : 80)
13	DMF (0.4 mL)	83 (1 : 80)

[a] *Conditions*: **1a** (0.2 mmol), **2a** (0.4 mmol), S (1.0 mmol), HOAc (0.1 mL), 150 °C,16 h, under air atmosphere, DMAc = dimethylacetamide, DEF = N,N-Diethylformamide.
[b] GC yield based on **1a**.

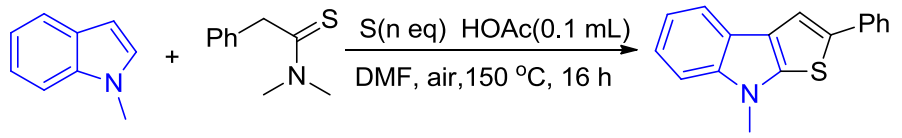
Table S7. Optimization on reaction temperature of **4aa**[a]



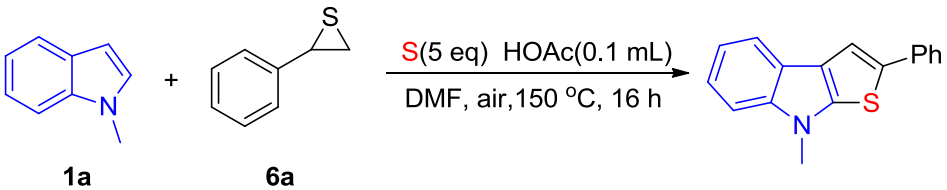
entry	temperature (°C)	yield (%)[b]
1	100	15 (1:15)
2	120	56 (1:25)
3	130	67 (1:40)
4	140	80 (1:70)
5	150	84 (1:80)

[a] *Conditions*: **1a** (0.2 mmol), **2a** (0.4 mmol), S (1.0 mmol), HOAc (0.1 mL), 16 h.
[b] GC yield based on **1a**.

Table S8. Control experiments under various conditions.

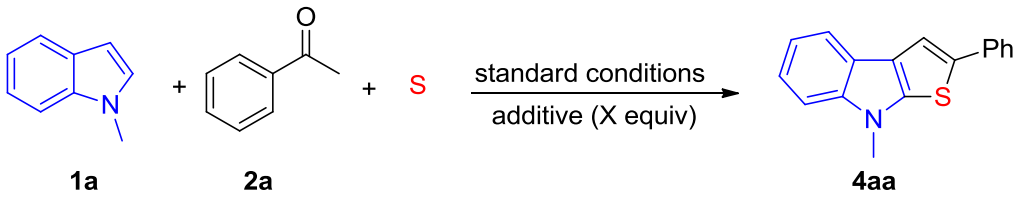


with n = 0 **4aa**, trace
with n = 1 **4aa**, 13%
with n = 3 **4aa**, 31%
with n = 5 **4aa**, 49%



4**aa**, 45%
4**aa**, 82%
4**aa**, 85%

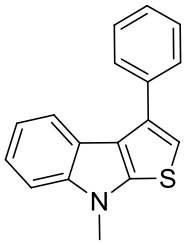
with n = 0 **4aa**, trace
with n = 1 **4aa**, 43%
with n = 2 **4aa**, 58%
with n = 3 **4aa**, 80%
with n = 5 **4aa**, 82%



BHT (1 eq.)	80%
BHT (2 eq.)	81%
ethene-1,1-diyldibenzene (1 eq.)	78%
ethene-1,1-diyldibenzene (2 eq.)	74%

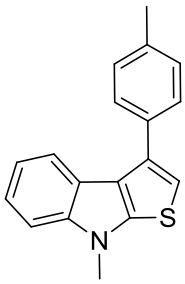
6. Characterization data of products

8-Methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3aa)



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.40-7.33 (m, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.78 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, ppm) δ 145.0, 142.5, 136.7, 135.9, 128.6, 128.0, 127.4, 121.9, 120.8, 119.4, 119.0, 112.2, 109.0, 32.0； HRMS calcd. for $C_{17}H_{14}NS$ $[M+H]^+$ 264.08415, found 264.08423.

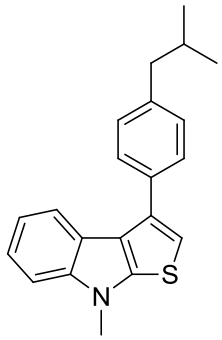
8-Methyl-3-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (3ab)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-methylacetophenone (**3b**, 67.5 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ab** as yellow oily liquid (113.6 mg, 82% yield). R_f = 0.80 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.2 Hz, 1H), 7.32-7.29 (m, 3H), 7.11 (t, J = 7.1 Hz, 1H), 6.76 (s, 1H), 3.86 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.9, 142.5, 137.2, 135.9, 133.8, 129.3, 127.9, 122.0, 121.9, 120.9, 119.5, 119.0, 111.7, 108.9, 32.1, 21.3; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09970.

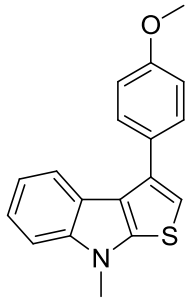
3-(4-Isobutylphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ac)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-(2-methylpropyl)acetophenone (**3c**, 93.8 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ac** as yellow oily liquid (97.3 mg, 61% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (d, J = 7.9 Hz, 1H), 7.71-7.69 (m, 2H), 7.37 (d, J = 8.2 Hz, 1H), 7.30-7.27 (m, 3H), 7.14-7.10 (m, 1H), 6.77 (s, 1H), 3.87 (s, 3H), 2.56 (d, J = 7.2 Hz, 2H), 1.95 (dt, J = 13.5 Hz, 6.8 Hz, 1H), 0.97 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.9 , 142.5, 141.0, 136.0, 134.1, 129.3, 127.7, 122.0, 121.9, 120.8, 119.5, 119.5, 111.7, 108.9, 45.2, 32.0, 30.2, 22.5; HRMS calcd. for $C_{21}H_{22}NS^+$ $(M+H)^+$ 320.14675, found 320.14664.

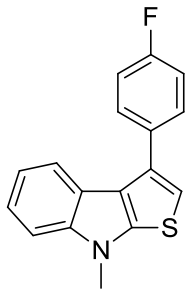
3-(4-Methoxyphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ad)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-methoxyacetophenone (**3d**, 76.3 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) to yield the desired product **3ad** as yellowish solid (121.6 mg, 83% yield), mp 147-149 ^{o}C. R_f = 0.65 (50:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, J = 7.9 Hz, 1H), 7.73-7.71 (m, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.31-7.27 (m, 1H), 7.14-7.10 (m, 1H), 7.06-7.03 (m, 2H), 6.72 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.1, 144.9, 142.5, 135.6, 129.3, 129.1, 122.0, 121.9, 120.9, 119.3, 119.0, 114.0, 111.2, 109.0, 55.4, 32.1; HRMS calcd. For $C_{18}H_{16}NOS^{+}$ $(M+H)^{+}$ 294.09471, found 294.09479.

3-(4-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ae)

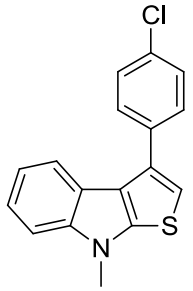


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-fluoroacetophenone (**3e**, 60.6 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ae** as yellowish solid (91.3 mg, 65% yield), mp 121-123 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79-7.73 (m, 3H), 7.39 (d, J = 8.3 Hz, 1H), 7.33-7.29 (m, 1H), 7.22-7.17 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.76 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$, ppm) δ 162.3 (d, J = 246.3 Hz), 145.0, 142.5, 134.8, 132.8 (d, J = 3.3 Hz), 129.5 (d, J = 8.0 Hz), 122.0, 121.8, 120.7, 119.1, 115.5 (d, J = 21.4 Hz), 112.1, 109.1, 32.1; HRMS calcd. for $C_{17}H_{13}FNS^+$ $(M+H)^+$ 282.07472, found 282.07495.

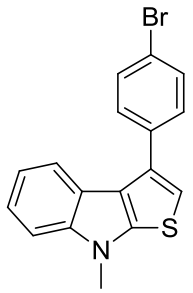
3-(4-Chlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3af)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-chloroacetophenone (**3f**, 65.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3af** as white solid (82.8 mg, 63% yield), mp 117-119 ^oC. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, J = 7.9 Hz, 1H), 7.72-7.70 (m, 2H), 7.48-7.46 (m, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.32-7.28 (m, 1H), 7.14-7.10 (m, 1H), 6.78 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.1, 142.6, 135.2, 134.7, 133.3, 129.2, 128.8, 122.1, 121.8, 120.6, 119.20, 119.18, 112.5, 109.1, 32.1; HRMS calcd. for $C_{17}H_{13}ClNS^+$ $(M+H)^+$ 298.04517, found 298.04578.

3-(4-Bromophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ag)

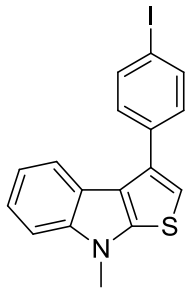


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-bromoacetophenone (**3g**, 100.0 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur

powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ag** as white solid (104.0 mg, 61% yield), mp 123-124 ^{o}C. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 8.0 Hz, 1H), 7.66-7.60 (m, 4H), 7.37 (d, J = 8.2 Hz, 1H), 7.32-7.28 (m, 1H), 7.14-7.10 (m, 1H), 6.78 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.1, 142.6, 135.6, 134.7, 131.8, 129.6, 122.1, 121.7, 121.4, 120.5, 119.20, 119.19, 112.5, 109.1, 32.1; HRMS calcd. for $C_{17}H_{13}BrNS^{+}$ $(M+H)^{+}$ 341.99466, found 341.99454.

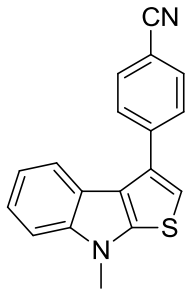
3-(4-Iodophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ah)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-iodoacetophenone (**3h**, 123.2 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ah** as white solid (136.2 mg, 70% yield), mp 158-160 ^{o}C. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88-7.82 (m, 3H), 7.57 (dd, J = 8.1 Hz, 1.4 Hz, 2H), 7.42 (d, J = 8.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 6.83 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.1, 142.5, 137.7, 136.2, 134.8, 129.8, 122.1, 121.7, 120.4, 119.23, 119.18, 112.6, 109.1, 92.9, 32.1; HRMS calcd. for $C_{17}H_{13}INS^{+}$ $(M+H)^{+}$ 389.98079, found 389.98111.

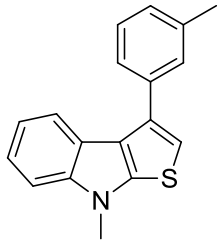
4-(8-Methyl-8*H*-thieno[2,3-*b*]indol-3-yl)benzonitrile (3ai)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 4'-cyanoacetophenone (**3i**, 72.5 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ai** as yellowish solid (95.0 mg, 66% yield), mp 169-171 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.90-7.88 (m, 2H), 7.80-7.74 (m, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.35-7.31 (m, 1H), 7.17-7.13 (m, 1H), 6.89 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.3, 142.6, 141.3, 134.1, 132.5, 128.5, 122.4, 121.5, 120.1, 119.4, 119.1, 119.0, 114.2, 110.9, 109.3, 32.2; HRMS calcd. for $C_{18}H_{13}N_2S^+$ $(M+H)^+$ 289.07940, found 289.07977.

8-Methyl-3-(*m*-tolyl)-8*H*-thieno[2,3-*b*]indole (3aj)

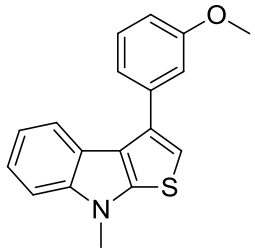


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-methylacetophenone (**3j**, 66.3 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3aj** as yellow liquid (115.0 mg, 83% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, J = 7.9 Hz, 1H), 7.61-7.59 (m, 2H), 7.41-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.22-7.20 (m, 1H), 7.14-7.10 (m, 1H), 6.77 (s, 1H), 3.83 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.0, 142.6, 138.2, 136.6, 136.1, 128.7, 128.5, 128.2, 125.1, 122.0, 121.9, 120.9, 119.4, 119.0, 112.1, 109.0, 32.1, 21.5; HRMS calcd. for $C_{18}H_{16}NS^+$

$(M+H)^+$ 278.09980, found 278.10028.

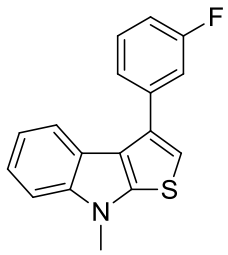
3-(3-Methoxyphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ak)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-methoxyacetophenone (**3k**, 68.8 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ak** as yellow solid (108.4 mg, 74% yield), mp 122-125 ^oC. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.89 (d, J = 7.9 Hz, 1H), 7.42-7.37 (m, 2H), 7.35-7.33 (m, 2H), 7.30-7.26 (m, 1H), 7.14-7.10 (m, 1H), 6.96-6.93 (m, 1H), 6.79 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 145.0, 142.5, 138.1, 135.8, 129.6, 121.95, 121.92, 120.7, 120.5, 119.5, 119.1, 113.3, 113.3, 112.4, 109.0, 55.3, 32.0; HRMS calcd. for $C_{18}H_{16}NOS^+$ $(M+H)^+$ 294.09471, found 294.09467.

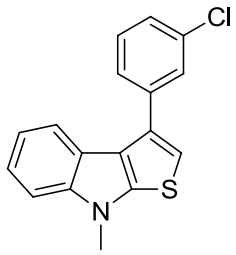
3-(3-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3al)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-fluoroacetophenone (**3l**, 60.6 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3al** as brown liquid (113.8 mg, 81% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (d, J = 8.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.49-7.43 (m, 2H), 7.38-7.36 (m, 1H), 7.32-7.28 (m, 1H), 7.16-7.07 (m, 2H), 6.81 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.0 (d, J = 245.8 Hz), 145.1, 142.6, 138.9 (d, J = 8.1 Hz), 134.7 (d, J = 2.3 Hz), 130.1 (d, J = 8.5 Hz), 123.7 (d, J = 2.8 Hz), 122.1, 121.8, 120.5, 119.3 (d, J = 8.7 Hz), 114.8 (d, J = 21.9 Hz), 114.3 (d, J = 21.2 Hz), 112.9, 109.1, 32.1; HRMS calcd. for $C_{17}H_{13}FNS^+$ $(M+H)^+$ 282.07472, found 282.07458.

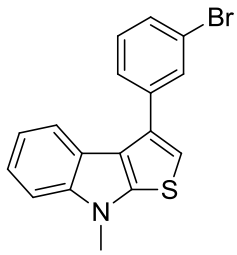
3-(3-Chlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3am)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-chloroacetonenone (**3m**, 65.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3am** as yellowish solid (105.4 mg, 71% yield), mp 125-127 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, J = 8.0 Hz, 1H), 7.77 (t, J = 1.8 Hz, 1H), 7.69-7.66 (m, 1H), 7.45-7.41 (m, 1H), 7.39-7.36 (m, 2H), 7.33-7.29 (m, 1H), 7.17-7.13 (m, 1H), 6.82 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.0, 142.5, 138.4, 134.5, 134.4, 129.8, 127.9, 127.4, 126.1, 122.1, 121.7, 120.4, 119.22, 119.20, 113.0, 109.1, 32.0; HRMS calcd. for $C_{17}H_{13}ClNS^+$ $(M+H)^+$ 298.04517, found 298.04480.

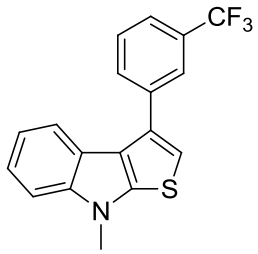
3-(3-Bromophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3an)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-bromoacetophenones (**3n**, 68.8 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3an** as yellowish solid (80.1 mg, 47% yield), mp 115-117 ^{o}C. R_f = 0.40 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (t, J = 1.7 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.73-7.70 (m, 1H), 7.54-7.51 (m, 1H), 7.38-7.34 (m, 2H), 7.33-7.28 (m, 1H), 7.17-7.13 (m, 1H), 6.80 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.0, 142.5, 138.7, 134.3, 130.9, 130.3, 130.1, 126.5, 122.7, 122.1, 121.7, 120.4, 119.3, 119.2, 113.0, 109.1, 32.1; HRMS calcd. for $C_{17}H_{13}BrNS^{+}$ $(M+H)^{+}$ 341.99466, found 341.99451.

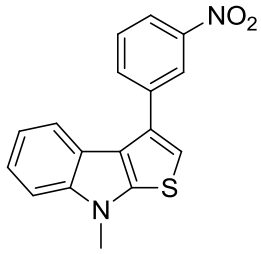
8-Methyl-3-(3-(trifluoromethyl)phenyl)-8*H*-thieno[2,3-*b*]indole (3ao)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-(trifluoromethyl)acetophenone (**3o**, 73.8 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ao** as yellow solid (124.1 mg, 75% yield), mp 94-95 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.66-7.57 (m, 2H), 7.38-7.28 (m, 2H), 7.16-7.12 (m, 1H), 6.83 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.2, 142.7, 137.6, 134.4, 131.2, 129.2, 124.8 (q, J = 3.6 Hz), 124.1 (q, J = 3.8 Hz), 122.3, 121.7, 120.5, 119.4, 119.1, 113.3, 109.2, 32.2; HRMS calcd. for $C_{18}H_{13}F_3NS^{+}$ $(M+H)^{+}$ 332.07153, found 332.07187.

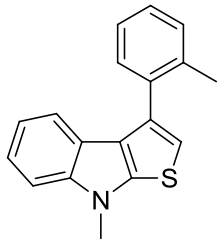
8-Methyl-3-(3-nitrophenyl)-8*H*-thieno[2,3-*b*]indole (3ap)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3'-nitroacetophenone (**3p**, 82.6 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ap** as yellow solid (100.1 mg, 65% yield), mp 115-117 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.64 (t, J = 1.9 Hz, 1H), 8.26-8.24 (m, 1H), 8.12 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.9 Hz, 1H), 7.42-7.40 (m, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.92 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 148.6, 145.3, 142.6, 138.4, 133.8, 133.4, 129.6, 122.7, 122.4, 122.1, 121.5, 120.2, 119.5, 119.0, 113.9, 109.3, 32.2; HRMS calcd. for $C_17H_{13}N_2O_2S^+$ $(M+H)^+$ 309.06922, found 309.06927.

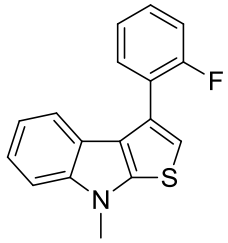
8-Methyl-3-(*o*-tolyl)-8*H*-thieno[2,3-*b*]indole (3aq)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 2'-methylacetophenone (**3q**, 66.3 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3aq** as yellow liquid (51.2 mg, 37% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (d, J = 7.2, 1H), 7.37-7.33 (m, 3H), 7.31-7.23 (m, 3H), 7.04 (t, J = 7.5, 1H), 6.68 (s, 1H), 3.88 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 142.4, 136.7, 136.4, 134.7, 130.2, 130.0, 127.7, 125.7, 122.6, 122.1, 121.8, 119.1, 118.9, 113.0, 108.9, 32.1, 20.2; HRMS calcd. for $C_{18}H_{16}NS^+$ $(M+H)^+$ 278.09980, found 278.10004.

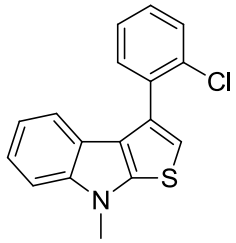
3-(2-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3ar)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 2'-fluoroacetophenone (**3r**, 60.8 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ar** as yellow solid (91.3 mg, 65% yield), mp 90-92 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.75-7.71 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.39-7.36 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.22 (m, 1H), 7.13-7.09 (m, 1H), 6.93 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.9 (d, J = 248.2 Hz), 144.4, 142.5, 131.1 (d, J = 3.4 Hz), 129.1 (d, J = 8.1 Hz), 128.4, 124.4, 124.3, 124.1 (d, J = 3.6 Hz), 122.0, 121.9, 121.6, 119.4 (d, J = 2.1 Hz), 119.1, 116.1 (d, J = 22.1 Hz), 114.6 (d, J = 3.4 Hz), 108.9, 32.1; HRMS calcd. for $C_{17}H_{13}NFS^{+}$ $[M+H]^{+}$ 282.07472, found 282.07483.

3-(2-Chlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3as)

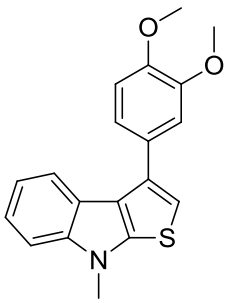


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 2'-chloroacetophenone (**3s**, 65.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3as** as yellow liquid (91.7 mg, 63% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61-7.59 (m, 1H), 7.56-7.54 (m, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.37-7.34 (m, 3H), 7.29-7.24 (m, 1H), 7.10-7.05 (m, 1H), 6.87 (s, 1H), 3.86 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 142.4, 135.5, 133.3, 131.9, 131.6, 130.0, 128.9, 126.7, 122.2, 122.0, 121.9, 119.4, 119.1, 114.6, 108.9, 32.1; HRMS calcd. for $C_{17}H_{13}ClNS^+$ $(M+H)^+$ 298.04517, found 298.04523.

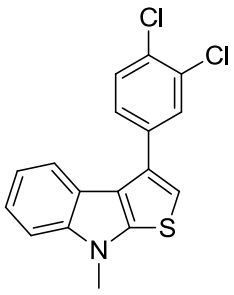
3-(3,4-Dimethoxyphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3at)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3',4'-dimethoxyacetophenone (**3t**, 90.1 μL, 0.5mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3at** as yellowish solid (126.0 mg, 78% yield), mp 170-172 ^oC. R_f = 0.30 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.89 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.35-7.28 (m, 3H), 7.15-7.11 (m, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.75 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 148.9, 148.6, 145.0, 142.6, 135.7, 129.6, 122.0, 121.9, 120.9, 120.3, 119.3, 119.0, 111.4, 111.3, 109.0, 56.0, 55.9, 32.1; HRMS calcd. for $C_{19}H_{18}NO_2S^+$ $(M+H)^+$ 324.10528, found 324.10535.

3-(3,4-Dichlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3au)

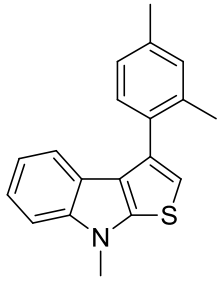


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 3',4'-dichloroacetophenone (**3u**, 95.0 mg, 0.4 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and

sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3au** as yellowish solid (102.6 mg, 62% yield), mp 165-167 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.61-7.59 (m, 1H), 7.56-7.54 (m, 1H), 7.38-7.36 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.79 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.1, 142.5, 136.7, 133.4, 132.7, 131.3, 130.5, 129.7, 127.2, 122.2, 121.5, 120.2, 119.4, 119.1, 113.2, 109.2, 32.1; HRMS calcd. for $C_{17}H_{12}Cl_2NS^+$ $(M+H)^+$ 332.00620, found 332.00635.

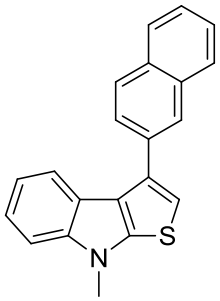
3-(2,4-Dimethylphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (3av)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 2',4'-dimethylacetophenone (**3v**, 74.4 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3av** as yellow liquid (88.8 mg, 61% yield). R_f = 0.50 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36-7.34 (m, 3H), 7.27-7.23 (m, 1H), 7.17 (s, 1H), 7.10 (dd, J = 7.9 Hz, 0.9 Hz, 1H), 7.06-7.02 (m, 1H), 6.65 (s, 1H), 3.87 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 142.4, 137.3, 136.4, 134.7, 133.4, 131.0, 129.9, 126.4, 122.6, 122.1, 121.8, 119.1, 119.0, 112.8, 108.8, 32.1, 21.2, 20.1; HRMS calcd. for $C_{19}H_{18}NS^+$ $(M+H)^+$ 292.11545, found 292.11526.

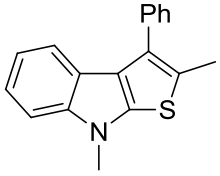
8-Methyl-3-(naphthalen-2-yl)-8*H*-thieno[2,3-*b*]indole (3aw)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 2-acetylnaphthalene (**3w**, 91.0 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3aw** as yellowish solid (51.7 mg, 33% yield), mp 179-180 ^{o}C. R_f = 0.40 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.26 (s, 1H), 8.00-7.97 (m, 1H), 7.94-7.87 (m, 4H), 7.55-7.50 (m, 2H), 7.40-7.39 (m, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.1, 142.6, 135.9, 134.2, 133.6, 132.8, 128.2, 128.1, 127.8, 126.51, 126.49, 126.3, 125.9, 122.0, 121,0, 119.5, 119.2, 112.6, 109.0, 32.1; HRMS calcd. for $C_{21}H_{16}NS$ $[M+H]^+$ 314.09980, found 314.10004.

2,8-Dimethyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ax)

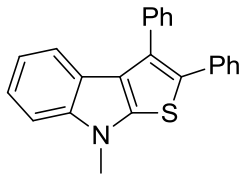


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.5 mmol), propiophenone (**3x**, 66.5 μL, 0.4 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ax** as yellow liquid (126.0 mg, 91% yield). R_f = 0.70 (500:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59-7.58 (m, 2H), 7.51-7.48 (m, 3H), 7.41-7.37 (m, 1H), 7.31 (d, *J* = 8.2, 1H), 7.22 (t, *J* = 7.5, 1H), 7.01 (t, *J* = 7.5, 1H), 3.80 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.8, 140.8, 136.0, 131.1, 129.6, 128.3, 127.1, 125.9, 122.0, 121.4, 118.8, 108.8, 32.1, 14.6; HRMS calcd. for $C_{18}H_{16}NS^+$ $(M+H)^+$ 278.09980, found

278.10037.

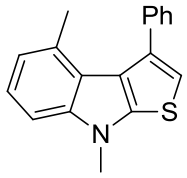
8-Methyl-2,3-diphenyl-8*H*-thieno[2,3-*b*]indole (3ay)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 75.0 μL, 0.6 mmol), 1,2-diphenylethanone (**3y**, 98.0 mg, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ay** as yellow solid (55.9 mg, 33% yield), mp = 121-123 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.54-7.49 (m, 3H), 7.43-7.34 (m, 4H), 7.31-7.28 (m, 2H), 7.26-7.16 (m, 4H), 7.06-7.01 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.6, 142.0, 136.2, 135.2, 131.1, 130.0, 129.8, 129.2, 128.5, 128.3, 127.3, 126.6, 123.5, 122.4, 122.0, 119.14, 119.09, 108.9, 32.2; HRMS calcd. for$C_{23}H_{18}NS^{+}$ $(M+H)^{+}$ 340.11545, found 340.11545.

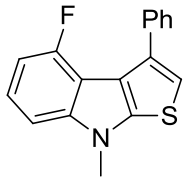
4,8-Dimethyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ba)



The reaction was conducted with 1,4-dimethyl-1*H*-indole (**1b**, 87.0 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ba** as yellow solid (66.5 mg, 48% yield), mp 286-288 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52-7.49 (m, 2H), 7.41-7.39 (m, 3H), 7.21-7.14 (m, 2H), 6.84 (d, J = 7.5 Hz, 1H), 6.64 (s, 1H), 3.86 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.7, 142.5, 139.2, 136.5, 130.8, 129.9, 127.7, 127.5, 125.1, 122.8, 122.1, 121.1, 113.1, 106.3, 32.2, 22.3; HRMS calcd. for $C_{18}H_{16}NS^{+}$ $(M+H)^{+}$ 278.09980, found 278.09995.

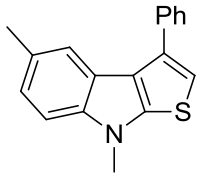
4-Fluoro-8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ca)



The reaction was conducted with 4-fluoro-1-methyl-1*H*-indole (**1c**, 89.4 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ca** as brown liquid (39.3 mg, 28% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.66-7.63 (m, 2H), 7.47-7.40 (m, 3H), 7.21-7.14 (m, 2H), 6.82-6.79 (m, 1H), 6.77 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.8 (d, J = 249.0 Hz), 144.9, 144.9, 144.8, 136.81, 136.79, 136.4, 129.0 (d, J = 3.4 Hz), 127.7, 127.4, 122.6 (d, J = 8.0 Hz), 119.1, 113.3, 110.9, 110.6, 105.4 (d, J = 20.5 Hz), 104.9 (d, J = 3.5 Hz), 32.5; HRMS calcd. for $C_{17}H_{13}FNS^+$ $(M+H)^+$ 282.07472, found 282.07480.

5,8-Dimethyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3da)

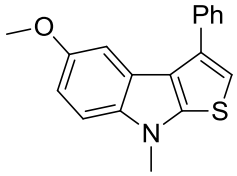


The reaction was conducted with 1,5-dimethyl-1*H*-indole (**1d**, 87.0 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3da** as yellowish liquid (88.6 mg, 64% yield), mp 107-108 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 7.7 Hz, 2H), 7.62 (s, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 6.76 (s, 1H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.1, 141.0, 136.8, 136.0, 128.6, 128.3, 128.0, 127.4, 123.3, 122.1, 120.4, 119.4, 112.0, 108.6, 32.1, 21.5; HRMS calcd. for $C_{18}H_{16}NS^+$

$(M+H)^+$ 278.09980, found 278.09995.

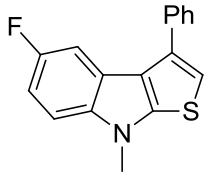
5-Methoxy-8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ea)



The reaction was conducted with 5-methoxy-1-methyl-1*H*-indole (**1e**, 96.6 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) to yield the desired product **3ea** as yellow liquid (96.7 mg, 66% yield. R_f = 0.65 (20:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79-7.77 (m, 2H), 7.52-7.48 (m, 2H), 7.41-7.37 (m, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 6.94 (dd, *J* = 8.9 Hz, 2.5 Hz, 1H), 6.76 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 153.5, 145.6, 137.9, 136.7, 135.8, 128.6, 128.0, 127.5, 122.3, 120.4, 111.9, 110.7, 109.5, 103.1, 56.0, 32.2; HRMS calcd. for $C_{18}H_{16}NOS^+$ $(M+H)^+$ 294.09471, found 294.09473.

5-Fluoro-8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3fa)

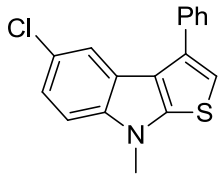


The reaction was conducted with 5-fluoro-1-methyl-1*H*-indole (**1f**, 89.4 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3fa** as yellow brown liquid (84.3 mg, 60% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (d, *J* = 7.2, 2H), 7.52-7.47 (m, 3H), 7.40 (t, *J* = 7.4, 1H), 7.25-7.21 (m, 1H), 7.04-6.98 (m, 1H), 6.77 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.3 (d, *J* = 234.4 Hz), 146.4, 139.1, 136.4, 135.8, 128.8, 127.8, 127.6, 122.0 (d, *J* = 10.2

Hz), 120.49, 120.45, 112.4, 109.8, 109.5 (d, J = 17.4 Hz), 109.3, 105.1 (d, J = 24.8 Hz), 32.3; HRMS calcd. for $C_{17}H_{13}FNS^+$ $(M+H)^+$ 282.07472, found 282.07410.

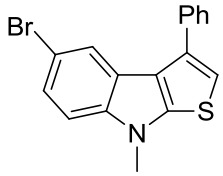
5-Chloro-8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ga)



The reaction was conducted with 5-chloro-1-methyl-1*H*-indole (**1g**, 99.0 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-Phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ga** as yellow liquid (93.6 mg, 63% yield). R_f = 0.65 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.77-7.72 (m, 3H), 7.52 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 7.4 Hz, 1H), 7.24 (s, 2H), 6.79 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.1, 140.9, 136.3, 135.8, 128.8, 127.8, 127.7, 124.8, 122.7, 122.0, 120.1, 118.9, 112.8, 109.8, 32.2; HRMS calcd. for $C_{17}H_{13}ClNS^+$ $(M+H)^+$ 298.04517, found 298.04483.

5-Bromo-8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ha)

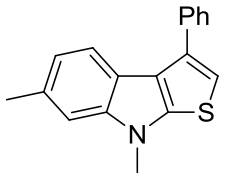


The reaction was conducted with 5-bromo-1-methyl-1*H*-indole (**1h**, 125.5 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ha** as yellow liquid (97.2 mg, 57% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.93 (d, J = 1.9 Hz, 1H), 7.74-7.72 (m, 2H), 7.54-7.50 (m, 2H), 7.44 -7.40 (m, 1H), 7.37 (dd, J = 8.7 Hz, 1.9 Hz, 1H), 7.24-7.21 (m, 1H), 6.80 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.9, 141.2, 136.3, 135.8, 128.8, 127.8, 127.7, 124.7,

123.4, 121.9, 120.1, 112.8, 112.3, 110.3, 32.2; HRMS calcd. for $C_{17}H_{13}BrNS^+$ $(M+H)^+$ 341.99466, found 341.99451

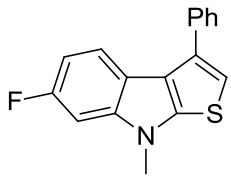
6,8-Dimethyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ia)



The reaction was conducted with 1,6-dimethyl-1*H*-indole (**1i**, 87.0 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ia** as yellowy liquid (85.9 mg, 62% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80-7.78 (m, 2H), 7.72 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.42-7.38 (m, 1H), 7.17 (s, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.78 (s, 1H), 3.83 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 143.0, 136.8, 135.8, 131.9, 128.6, 127.9, 127.4, 120.7, 120.5, 119.8, 119.1, 111.9, 109.2, 32.0, 21.9; HRMS calcd for $C_{18}H_{16}NS^+$ $(M+H)^+$ 278.09980, found 278.09991.

6-Fluoro-8-methyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ja)

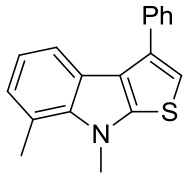


The reaction was conducted with 6-fluoro-1*H*-indole (**1j**, 81.0 mg, 0.6 mmol), acetophenone (58.0 μL, 0.5 mmol), *L*-phenylalanine (**3a**, 82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ja** as yellowish-brown liquid (91.3 mg, 65% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76-7.71 (m, 3H), 7.51-7.48 (m, 2H), 7.42-7.38 (m, 1H), 7.03 (dd, J = 9.8 Hz, 2.3 Hz, 1H), 6.91-6.82 (m, 1H), 6.79 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$, ppm) δ 159.72 (d, J = 238.9 Hz), 144.9, 142.8 (d, J = 11.7 Hz), 136.5, 135.7, 128.7, 127.9, 127.5, 120.7, 120.0 (d, J = 10.0 Hz), 118.5, 112.6, 107.1 (d, J = 23.8 Hz), 96.0 (d, J = 26.6 Hz), 32.3; HRMS calcd. for $C_{17}H_{13}FNS^+$ $(M+H)^+$ 282.07472, found 282.07492.

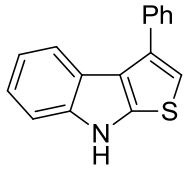
7,8-Dimethyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ka)



The reaction was conducted with 1,7-dimethyl-1*H*-indole (**1k**, 78.6 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ka** as yellow solid (92.8 mg, 67% yield), mp 153-155^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76-7.73 (m, 2H), 7.67 (t, J = 4.6 Hz, 1H), 7.50-7.46 (m, 2H), 7.40-7.37 (m, 1H), 6.97-6.96 (m, 2H), 6.76 (s, 1H), 4.08 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.4, 141.2, 136.8, 136.1, 128.6, 128.1, 127.4, 125.0, 122.9, 121.0, 120.5, 119.3, 117.6, 112.4, 36.3, 19.7; HRMS calcd. For $C_{18}H_{16}NS^+$ $(M+H)^+$ 278.09980, found 278.09988.

3-Phenyl-8*H*-thieno[2,3-*b*]indole (3la)

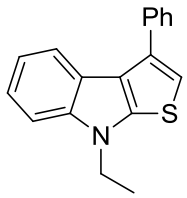


The reaction was conducted with 1*H*-indole (**1l**, 70.2 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **3la** as yellow solid (71.0 mg, 57% yield), mp 154-157^{o}C. R_f = 0.60 (10:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.34 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.4 Hz,

2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43-7.39(m, 2H), 7.27-7.23 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.3, 141.4, 136.6, 135.4, 128.6, 128.0, 127.5, 123.3, 122.5, 122.2, 119.7, 119.4, 113.2, 111.2; HRMS calcd. for $C_{16}H_{12}NS^+$ $(M+H)^+$ 250.06850, found 250.06863.

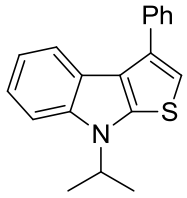
8-Ethyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3ma)



The reaction was conducted with 1-ethyl-1*H*-indole (**1m**, 87.0 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3ma** as yellow liquid (98.4 mg, 71% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.80-7.78 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41-7.38 (m, 2H), 7.30-7.26 (m, 1H), 7.13-7.09 (m, 1H), 6.78 (s, 1H), 4.29 (q, *J* = 7.3 Hz, 2H), 1.51 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.6, 141.5, 136.7, 135.9, 128.6, 128.0, 127.4, 122.0, 121.9, 121.1, 119.5, 118.9, 112.3, 109.0, 40.7, 13.8; HRMS calcd. for $C_{18}H_{16}NS^+$ $(M+H)^+$ 278.09980, found 278.10007.

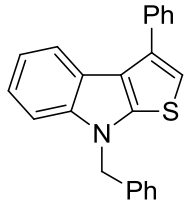
8-Isopropyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3na)



The reaction was conducted with 1-isopropyl-1*H*-indole (**1n**, 95.4 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3na** as yellowy liquid (97.5 mg, 67% yield). R_f = 0.7 (100:1 petroleum ether/EtOAc).

^{1}H NMR (100 MHz, $CDCl_3$, ppm) δ 7.83 (d, J = 8.0 Hz, 1H), 7.78-7.76 (m, 2H), 7.51-7.47 (m, 2H), 7.44-7.37 (m, 2H), 7.29-7.25 (m, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.77 (s, 1H), 4.89 (dt, J = 13.6 Hz, 6.8 Hz, 1H), 1.65 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.6, 140.7, 136.7, 135.4, 128.6, 128.1, 127.4, 122.0, 121.9, 121.8, 119.4, 118.9, 113.2, 109.3, 47.7, 20.8; HRMS calcd. for $C_{19}H_{18}NS^+$ $(M+H)^+$ 292.11545, found 292.11563.

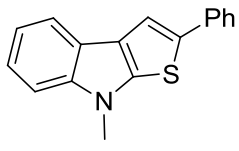
8-Benzyl-3-phenyl-8*H*-thieno[2,3-*b*]indole (3oa)



The reaction was conducted with 1-benzyl-1*H*-indole (**1o**, 124.2 mg, 0.6 mmol), acetophenone (**3a**, 58.0 μL, 0.5 mmol), *L*-phenylalanine (82.5 mg, 0.5 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **3oa** as yellow solid (105.1 mg, 62% yield), mp 124-125^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (100 MHz, $CDCl_3$, ppm) δ 7.87 (d, J = 7.9 Hz, 1H), 7.79-7.77 (m, 2H), 7.51-7.48 (m, 2H), 7.42-7.38 (m, 2H), 7.33-7.24 (m, 6H), 7.16-7.11(m, 1H), 6.75 (s, 1H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.2, 142.3, 136.7, 135.7, 135.7, 128.9, 128.6, 128.0, 127.5, 127.4, 122.2, 122.1, 121.5, 119.5, 119.3, 112.9, 109.4, 49.7; HRMS calcd. for $C_{23}H_{18}NS^+$ $(M+H)^+$ 340.11545, found 340.11597.

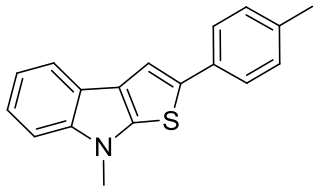
8-Methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4aa, CAS: 22315-09-9) [1]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (d, J = 7.8 Hz, 1H), 7.64-7.62 (m, 3H), 7.37 (dd, J = 15.7 Hz, 7.7 Hz, 3H), 7.31-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.21-7.17 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, ppm) δ 144.0, 141.9, 135.72, 135.67, 128.9, 126.5, 125.1, 123.5, 122.2, 122.0, 119.5, 119.3, 114.2, 109.1, 32.2; HRMS calcd. for $C_{17}H_{14}NS$ $[M+H]^+$ 264.08415, found

264.08377.

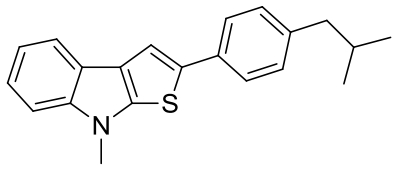
8-Methyl-2-(*p*-tolyl)-8*H*-thieno[2,3-*b*]indole (4ab)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-methylacetophenone (**4b**, 54.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ab** as white solid (43.3 mg, 78% yield), mp 150-152 ^{o}C. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 7.8 Hz, 1H), 7.55 (s, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.33-7.31 (m, 1H), 7.29-7.25 (m, 1H), 7.20-7.16 (m, 3H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.7, 141.9, 136.4, 135.9, 132.9, 129.6, 125.0, 123.4, 122.2, 121.8, 119.4, 119.2, 113.6, 109.0, 32.2, 21.1; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09964.

2-(4-Isobutylphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ac)

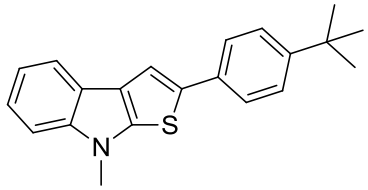


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-(2-methylpropyl)acetophenone (**4c**, 75.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ac** as yellowish solid (42.1 mg, 66% yield), mp 132-134 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, J = 7.7 Hz, 1H), 7.57 (s, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.35-7.33 (m, 1H), 7.30-7.26 (m, 1H), 7.20-7.14 (m, 3H), 3.84 (s, 3H), 2.48 (d, J = 7.2 Hz, 2H), 1.88 (dt, J = 13.5 Hz, 6.8 Hz, 1H), 0.93 (d, J = 6.6, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ

143.7, 141.9, 140.3, 136.0, 133.2, 129.6, 124.9, 123.4, 122.2, 121.9, 119.4, 119.3, 113.7, 109.0, 45.1, 32.3, 30.2, 22.4; HRMS calcd. for $C_{21}H_{22}NS$ $[M+H]^+$ 320.14675, found 320.14672.

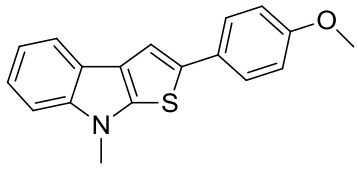
2-(4-(tert-Butyl)phenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ad)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-tert-butylacetophenone (**4d**, 75.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ad** as golden solid (54.1 mg, 84% yield), mp 143-145 ^oC. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, J = 7.7 Hz, 1H), 7.57-7.55 (m, 3H), 7.41-7.39 (m, 2H), 7.34-7.32 (m, 1H), 7.29-7.25 (m, 1H), 7.20-7.16 (m, 1H), 3.83 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.7, 143.8, 141.9, 135.8, 132.9, 125.8, 124.9, 123.4, 122.2, 121.9, 119.4, 119.3, 113.7, 109.0, 34.5, 32.3, 31.3; HRMS calcd. for $C_{21}H_{22}NS$ $[M+H]^+$ 320.14675, found 320.14622.

2-(4-Methoxyphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ae, CAS: 22315-10-2) [1]

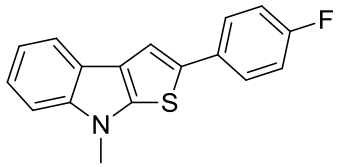


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-methoxyacetophenone (**4e**, 61.0 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to yield the desired product **4ae** as brown solid (49.9 mg, 85% yield), mp 173-175 ^oC. R_f = 0.30 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, J = 7.8 Hz, 1H), 7.56-7.54 (m, 2H), 7.49 (s, 1H), 7.36-7.34 (m, 1H), 7.30-7.26 (m, 1H), 7.18 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 3.85 (s,

3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.7, 143.4, 141.9, 135.8, 128.6, 126.5, 123.4, 122.2, 121.8, 119.4, 119.2, 114.4, 113.2, 109.0, 55.4, 32.3; HRMS calcd. for $C_{18}H_{15}ONS$ [M] 293.08689, found 293.08699.

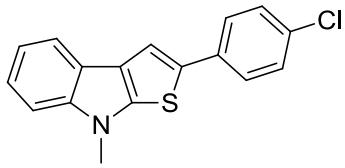
2-(4-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4af)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-fluoroacetophenone (**4f**, 48.5 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4af** as white solid (37.1 mg, 66% yield), mp 143-144 ^{o}C. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 7.8 Hz, 1H), 7.56-7.52 (m, 2H), 7.50 (s, 1H), 7.34-7.25 (m, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 8.6 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.8 (d, J = 246.0 Hz), 143.8, 141.9, 134.5, 131.99, 131.96, 126.7 (d, J = 7.8 Hz), 123.5, 122.1, 122.0, 119.4 (d, J = 27.5 Hz), 115.8 (d, J = 21.8 Hz), 114.3, 109.1, 32.3; HRMS calcd. for $C_{17}H_{12}NFS$ [M] 281.06690, found 281.06658.

2-(4-Chlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ag)

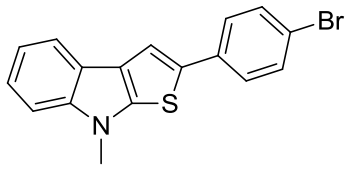


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-chloroacetophenone (**4g**, 52.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ag** as white solid (36.3 mg, 61% yield), mp 163-165 ^{o}C. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (dd, J = 7.8 Hz, 0.9 Hz, 1H), 7.59 (s, 1H), 7.54-7.52 (m, 2H), 7.36-7.34 (m, 2H), 7.33-7.28 (m, 2H), 7.22-7.18 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$, ppm) δ 144.1, 142.0, 134.24, 134.21, 132.0, 129.0, 126.1, 123.5, 122.1, 122.1, 119.6, 119.3, 114.7, 109.1, 32.3; HRMS calcd. for $C_{17}H_{13}NClS$ $[M+H]^+$ 298.04517, found 298.04507.

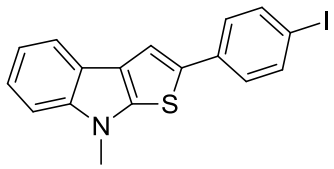
2-(4-Bromophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ah, CAS: 22315-11-3) [1]



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-bromoacetophenone (**4h**, 80 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ah** as white solid (48.0 mg, 70% yield), mp 158-160 ^oC. R_f = 0.80 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (d, J = 7.7 Hz, 1H), 7.61 (s, 1H), 7.48 (s, 4H), 7.36-7.35 (m, 1H), 7.32-7.28 (m, 1H), 7.22-7.18 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.2, 142.0, 134.7, 134.3, 132.0, 126.5, 123.6, 122.2, 122.1, 120.1, 119.7, 119.3, 114.8, 109.1, 32.3; HRMS calcd. for $C_{17}H_{13}NBrS$ $[M+1]^+$ 341.99466, found 341.99445.

2-(4-Iodophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ai)

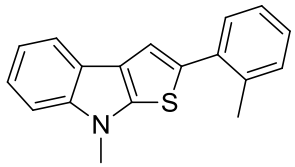


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 4'-iodoacetophenone (**4i**, 98.5 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ai** as yellowish solid (31.9 mg, 41% yield), mp 169-171 ^oC. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 7.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.60 (s, 1H), 7.35-7.33 (m, 3H), 7.31-7.27 (m, 1H), 7.20 (t, J = 7.3 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$, ppm) δ 144.1, 142.0, 137.8, 135.3, 134.3, 126.6, 123.6, 122.2, 122.1, 119.7, 119.3, 114.8, 109.1, 91.1, 32.3; HRMS calcd. for $C_{17}H_{13}NIS$ $[M+H]^+$ 389.98079, found 389.98038.

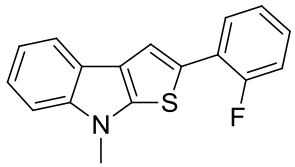
8-Methyl-2-(*o*-tolyl)-8*H*-thieno[2,3-*b*]indole (4aj)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 2'-methylacetophenone (**4j**, 53.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4aj** as yellow liquid (31.6 mg, 57% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, J = 7.7 Hz, 1H), 7.49-7.47 (m, 1H), 7.38-7.36 (m, 1H), 7.33 (s, 1H), 7.31-7.27 (m, 2H), 7.25-7.23 (m, 2H), 7.21-7.17 (m, 1H), 3.87 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 141.8, 136.4, 135.1, 134.2, 130.8, 130.7, 127.4, 125.9, 122.9, 122.2, 121.9, 119.4, 119.2, 117.6, 109.0, 32.3, 21.4; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09959.

2-(2-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ak)

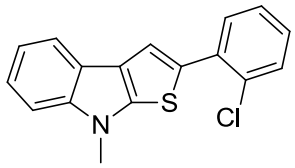


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 2'-fluoroacetophenone (**4k**, 48.6 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ak** as yellow solid (23.6 mg, 41% yield), mp 122-125 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83-7.81 (m, 2H), 7.67-7.63 (m, 1H), 7.37-7.35 (m, 1H), 7.32-7.29 (m, 1H), 7.23-7.14 (m, 4H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.9 (d,

J = 249.0 Hz), 144.8, 142.1, 128.4, 127.8 (d, *J* = 3.7 Hz), 127.4 (d, *J* = 8.4 Hz), 124.5, 124.4, 123.6, 123.5, 122.2, 122.1, 119.5 (d, *J* = 19.7 Hz), 117.9 (d, *J* = 7.8 Hz), 116.3 (d, *J* = 22.6 Hz), 109.1, 32.4; HRMS calcd. for $C_{17}H_{13}NFS$ $[M+H]^+$ 282.07472, found 282.07489.

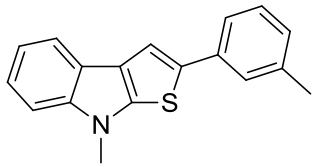
2-(2-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4al)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 2'-chloroacetophenone (**4l**, 52.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4al** as brown liquid (32.1 mg, 54% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.70 (s, 1H), 7.60 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.48 (dd, *J* = 7.9 Hz, 1.3 Hz, 1H), 7.37-7.36 (m, 1H), 7.32-7.28 (m, 2H), 7.24-7.18 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.2, 142.0, 134.0, 132.1, 131.3, 131.1, 130.6, 127.9, 127.0, 122.9, 122.2, 122.1, 119.5, 119.4, 119.1, 109.0, 32.4; HRMS calcd. for $C_{17}H_{13}NClS$ $[M+H]^+$ 298.04517, found 298.04498.

8-Methyl-2-(*m*-tolyl)-8*H*-thieno[2,3-*b*]indole (4am)

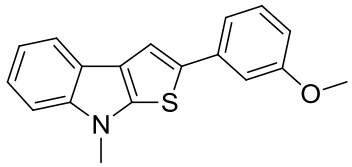


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3'-methylacetophenone (**4m**, 55.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4am** as yellowish solid (38.8 mg, 70% yield), mp 125-127 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 7.44-7.42 (m, 2H), 7.34-7.32 (m, 1H), 7.30-7.28 (m, 1H), 7.24-7.22 (m, 1H), 7.21-7.17 (m, 1H), 7.05 (d, *J* = 7.3 Hz,

1H), 3.82 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 141.9, 138.5, 135.8, 135.6, 128.8, 127.4, 125.8, 123.4, 122.24, 122.15, 121.9, 119.5, 119.2, 114.1, 109.0, 32.3, 21.5; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09971.

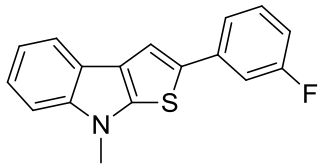
2-(3-Methoxyphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4an)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3'-methoxyacetophenone (**4n**, 55.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4an** as yellowish solid (44.0 mg, 75% yield), mp 115-117 ^{o}C. R_f = 0.40 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 7.7 Hz, 1H), 7.60 (s, 1H), 7.33-7.25 (m, 3H), 7.22-7.15 (m, 3H), 6.79-6.77 (m, 1H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.0, 144.0, 141.9, 137.0, 135.4, 129.9, 123.3, 122.1, 122.0, 119.5, 119.3, 117.7, 114.5, 112.0, 110.7, 109.0, 55.3, 32.2; HRMS calcd. for $C_{18}H_{16}ONS$ $[M+H]^+$ 294.09471, found 294.09436.

2-(3-Fluorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ao)

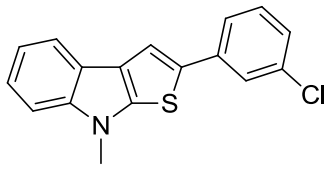


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3'-fluoroacetophenone (**4o**, 50.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ao** as golden solid (36.6 mg, 65% yield), mp 94-95 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (d, J = 7.7 Hz, 1H), 7.63 (s, 1H), 7.40-7.37 (m, 1H), 7.36-7.34 (m, 1H), 7.33-7.28 (m, 3H), 7.22-7.18 (m, 1H), 6.94-6.89 (m, 1H), 3.85 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$, ppm) δ 163.3 (d, J = 245.4 Hz), 144.3, 142.0, 137.9 (d, J = 8.3 Hz), 134.1 (d, J = 2.8 Hz), 130.4 (d, J = 8.7 Hz), 123.5, 122.2, 122.1, 120.6, 120.6, 119.5 (d, J = 33.5 Hz), 115.1, 113.2 (d, J = 21.4 Hz), 111.7 (d, J = 23.0 Hz), 109.1, 32.3; HRMS calcd. for $C_{17}H_{13}NFS$ $[M+H]^+$ 282.07472, found 282.07428.

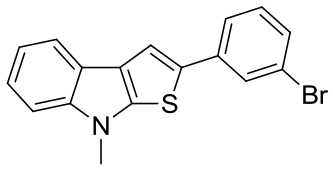
2-(3-Chlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ap)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3'-chloroacetonenone (**4p**, 52.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ap** as golden solid (37.5 mg, 63% yield), mp 115-117 ^oC. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, J = 7.8 Hz, 1H), 7.65 (s, 1H), 7.61 (t, J = 1.9 Hz, 1H), 7.50-7.48 (m, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.33-7.27 (m, 2H), 7.21-7.18 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.3, 142.1, 137.5, 134.8, 133.8, 130.1, 126.3, 124.9, 123.5, 123.1, 122.2, 122.1, 119.7, 119.4, 115.2, 109.1, 32.3; HRMS calcd. for $C_{17}H_{13}NClS$ $[M+1]^+$ 298.04517, found 298.04459.

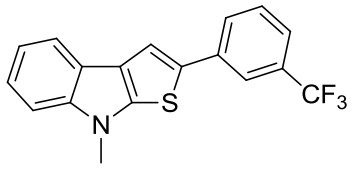
2-(3-Bromophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4aq)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3'-bromoacetophenones (**4q**, 55.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4aq** as yellow liquid (45.7 mg, 67% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 1.8 Hz, 1H), 7.61 (s, 1H), 7.53-7.50 (m, 1H), 7.36-7.28 (m, 3H), 7.24-7.18 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 142.1, 137.8, 133.7, 131.0, 130.4, 129.3, 127.8, 123.6, 123.1, 122.3, 122.1, 119.8, 119.4, 115.3, 109.2, 32.4; HRMS calcd. for $C_{17}H_{13}NBrS$ $[M+H]^+$ 341.99466, found 341.99417.

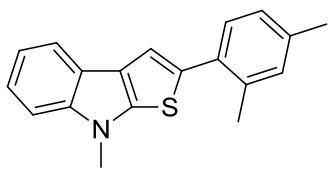
8-Methyl-2-(3-(trifluoromethyl)phenyl)-8*H*-thieno[2,3-*b*]indole (4ar)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3'-(trifluoromethyl)acetophenone (**4r**, 59.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ar** as golden solid (37.8 mg, 57% yield), mp 90-92 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (s, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.76-7.30 (m, 1H), 7.67 (s, 1H), 7.46-7.45 (m, 2H), 7.35-7.28 (m, 2H), 7.24-7.19 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.3 (d, J = 234.6 Hz), 136.5, 133.7, 122.9 (q, J = 3.8 Hz), 123.6, 122.9, 122.93, 122.90, 122.8, 122.3, 122.1, 121.5 (q, J = 3.6 Hz), 119.6 (d, J = 38.5 Hz), 115.5, 109.2, 32.3; HRMS calcd. for $C_{18}H_{13}NF_3S$ $[M+H]^+$ 332.07153, found 332.07101.

2-(2,4-Dimethylphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4as)

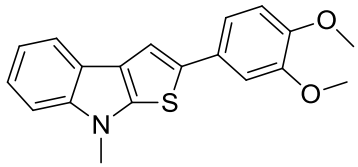


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 2',4'-dimethylacetophenone (**4s**, 59.5 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4as** as yellow liquid (42.5 mg, 73% yield). R_f = 0.60 (100:1 petroleum

ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7 .80 (d, J = 7.8 Hz, 1H), 7.38-7.35 (m, 2H), 7.30-7.27 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.11 (s, 1H), 7.05 (d, J = 7.8 Hz, 1H), 3.86 (s, 3H), 2.48 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.3, 141.8, 137.3, 136.2, 134.4, 132.2, 131.6, 130.6, 126.7, 122.9, 122.2, 121.8, 119.4, 119.2, 117.4, 109.0, 32.4, 21.2, 21.1; HRMS calcd. for $C_{19}H_{18}NS$ $[M+H]^+$ 292.11545, found 292.11508.

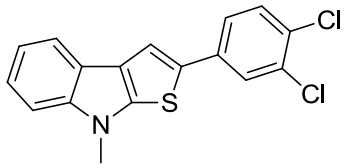
2-(3,4-Dimethoxyphenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4at)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3',4'-dimethoxyacetophenone (**4t**, 72.1 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4at** as yellowish solid (53.0 mg, 82% yield), mp 170-172 ^{o}C. R_f = 0.30 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80 (d, J = 7.7 Hz, 1H), 7.50 (s, 1H), 7.36-7.34 (m, 1H), 7.30-7.27 (m, 1H), 7.21-7.14 (m, 3H), 6.89 (d, J = 8.2 Hz, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.2, 148.2, 143.4, 141.8, 135.8, 128.9, 123.3, 122.1, 121.8, 119.4, 119.2, 117.8, 113.4, 111.6, 109.0, 108.8, 56.0, 55.9, 32.3; HRMS calcd. for $C_{19}H_{17}O_2NS$ [M] 323.09745, found 323.09704.

2-(3,4-Dichlorophenyl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4au)

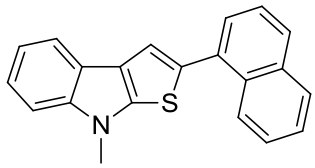


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3',4'-dichloroacetophenone (**4u**, 76.0 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to

yield the desired product **4au** as yellowish solid (34.5 mg, 52% yield), mp 165-167 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, J = 7.8 Hz, 1H), 7.68 (t, J = 1.2 Hz, 1H), 7.61 (s, 1H), 7.41 (d, J = 1.2 Hz, 2H), 7.37-7.35 (m, 1H), 7.33-7.29 (m, 1H), 7.23-7.19 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 142.1, 135.8, 132.9, 132.6, 130.7, 129.9, 126.4, 124.0, 123.6, 122.4, 122.0, 119.8, 119.4, 115.5, 109.2, 32.3; HRMS calcd. for $C_{17}H_{12}NCl_2S$ $[M+H]^+$ 332.00620, found 332.00590.

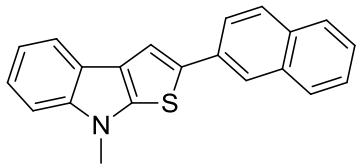
8-Methyl-2-(naphthalen-1-yl)-8*H*-thieno[2,3-*b*]indole (4av)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 1-acetylnaphthalene (**4v**, 72.8 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4av** as yellowish solid (32.0 mg, 51% yield), mp 138-141 ^{o}C. R_f = 0.50 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.43-8.41 (m, 1H), 7.92-.90 (m, 1H), 7.86-7.84 (m, 2H), 7.65 (dd, J = 7.1 Hz, 1.2 Hz, 1H), 7.54-7.49 (m, 4H), 7.41-7.38 (m, 1H), 7.34-7.30 (m, 1H), 7.24-7.20 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.6, 141.9, 134.0, 133.3, 132.7, 132.2, 128.4, 128.3, 128.1, 126.4, 125.99, 125.95, 125.3, 123.1, 122.2, 122.0, 119.5, 119.3, 118.7, 109.0, 32.4； HRMS calcd. for $C_{21}H_{16}NS$ $[M+H]^+$ 314.09980, found 314.09911.

8-Methyl-2-(naphthalen-2-yl)-8*H*-thieno[2,3-*b*]indole (4aw)

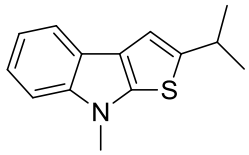


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 2-acetylnaphthalene (**4w**, 72.8 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue

was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4aw** as yellowish solid (29.5 mg, 47% yield), mp 179-180 ^{o}C. R_f = 0.40 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, J = 1.0 Hz, 1H), 7.85-7.79 (m, 4H), 7.75 (s, 1H), 7.50-7.40 (m, 3H), 7.37-7.35 (m, 1H), 7.32-7.28 (m, 1H), 7.23-7.19 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.2, 142.0, 135.8, 133.8, 133.2, 132.3, 128.5, 127.74, 127.70, 126.53, 125.50, 123.9, 123.6, 122.8, 122.2, 122.0, 119.6, 119.3, 114.8, 109.1, 32.3; HRMS calcd. for $C_{21}H_{16}NS$ $[M+H]^+$ 314.09980, found 314.09930.

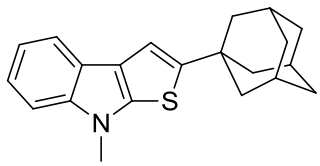
2-Isopropyl-8-methyl-8*H*-thieno[2,3-*b*]indole (4ax)



The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 3-methylbutan-2-one (**4x**, 49.7 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ax** as yellow liquid (17.0 mg, 37% yield). R_f = 0.70 (500:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.26-7.22 (m, 1H), 7.16-7.13 (m, 1H), 7.07 (d, J = 1.0 Hz, 1H), 3.81 (s, 3H), 3.26-3.20 (m, 1H), 1.40 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.3, 142.4, 141.6, 122.1, 121.6, 121.3, 119.0, 118.9, 112.5, 108.8, 32.2, 30.9, 24.9; HRMS calcd. for $C_{14}H_{16}NS^+$ $(M+H)^+$ 230.09980, found 230.09972.

2-((1*r*,3*r*,5*r*,7*r*)-Adamantan-2-yl)-8-methyl-8*H*-thieno[2,3-*b*]indole (4ay)

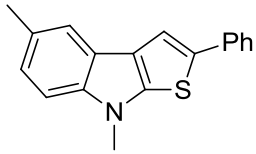


The reaction was conducted with 1-methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol), 1-acetyladamantan (**4y**, 71.3 mg, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by

column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ay** as yellow liquid (27.7 mg, 43% yield). R_f = 0.90 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.73 (d, J = 7.7 Hz, 1H), 7.32-7.30 (m, 1H), 7.24-7.21 (m, 1H), 7.16-7.12 (m, 1H), 7.07 (s, 1H), 3.81 (s, 3H), 2.11 (s, 3H), 2.05-2.04 (m, 6H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.6, 142.2, 141.7, 122.2, 121.6, 121.2, 119.0, 118.9, 111.0, 108.8, 45.2, 36.9, 36.7, 32.2, 29.0; HRMS calcd. for $C_{21}H_{24}NS$ $[M+H]^+$ 322.16240, found 322.16190.

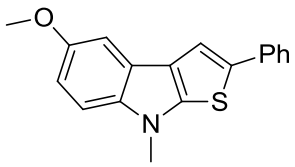
5,8-Dimethyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ba)



The reaction was conducted with 1,5-dimethyl-1*H*-indole (**1b**, 29.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ba** as yellowish solid (46.0 mg, 83% yield), mp 124-126 ^{o}C. R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.635-7.627 (m, 1H), 7.61-7.59 (m, 3H), 7.40-7.36 (m, 2H), 7.25-7.21 (m, 2H), 7.11 (dd, J = 8.3 Hz, 1.3 Hz, 1H), 3.84 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.1, 140.4, 135.8, 135.3, 128.9, 128.8, 126.5, 125.0, 123.3, 123.1, 122.3, 119.3, 114.2, 108.7, 32.3, 21.4; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09958.

5-Methoxy-8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ca)

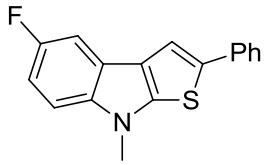


The reaction was conducted with 5-methoxy-1-methyl-1*H*-indole (**1c**, 32.5 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ca** as golden solid (46.5 mg, 79% yield), mp 163-164 ^{o}C. R_f = 0.30 (100:1

petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.63-7.61 (m, 2H), 7.59 (s, 1H), 7.39-7.36 (m, 2H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.24-7.21 (m, 2H), 6.93 (dd, *J* = 8.9 Hz, 2.5 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.1, 144.5, 137.2, 135.7, 135.2, 128.9, 126.5, 125.0, 123.1, 122.5, 114.1, 111.1, 109.7, 102.3, 56.0, 32.4; HRMS calcd. for $C_{18}H_{16}ONS$ $[M+H]^+$ 294.09471, found 29409487.

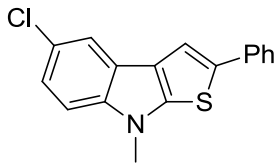
5-Fluoro-8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4da)



The reaction was conducted with 5-fluoro-1-methyl-1*H*-indole (**1d**, 30.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4da** as yellowish solid (38.8 mg, 69% yield), mp 107-108 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.63-7.60 (m, 2H), 7.55 (s, 1H), 7.45 (dd, *J* = 9.3 Hz, 2.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.27-7.22 (m, 3H), 7.02 (td, *J* = 9.1 Hz, 2.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.8 (d, *J* = 235.3 Hz), 145.4, 138.5, 136.0, 135.5, 129.0, 126.8, 125.2, 123.1 (d, *J* = 4.2 Hz), 122.3 (d, *J* = 10.2 Hz), 114.0, 109.9, 109.6 (d, *J* = 6.0 Hz), 109.5, 104.9 (d, *J* = 24.3 Hz), 32.6; HRMS calcd. for $C_{17}H_{12}NFS$ [M] 281.06690, found 281.06684.

5-Chloro-8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ea)

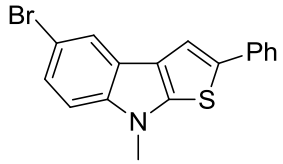


The reaction was conducted with 5-chloro-1-methyl-1*H*-indole (**1e**, 33.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was

purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ea** as yellowish liquid (31.5 mg, 53% yield. R_f = 0.65 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 (t, J = 1.3 Hz, 1H), 7.62-7.59 (m, 2H), 7.53 (s, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.27-7.25 (m, 1H), 7.22 (d, J = 1.3 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.0, 140.2, 136.3, 135.4, 129.0, 126.8, 125.2, 125.2, 122.9, 122.7, 122.0, 118.9, 113.9, 109.9, 32.4; HRMS calcd. for $C_{17}H_{13}NClS$ [M] 298.04517, found 298.04485.

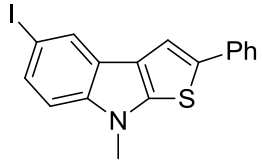
5-Bromo-8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4fa)



The reaction was conducted with 5-bromo-1-methyl-1*H*-indole (**1f**, 42.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4fa** as yellowish solid (37.5 mg, 55% yield), mp 165-166 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.91 (d, J = 1.8 Hz, 1H), 7.62-7.60 (m, 2H), 7.55 (s, 1H), 7.41-7.35 (m, 3H), 7.22-7.20(m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.9, 140.6, 136.5, 135.4, 129.0, 126.9, 125.2, 124.7, 123.6, 122.7, 122.0, 113.9, 112.7, 110.4, 32.5; HRMS calcd. for $C_{17}H_{13}NBrS$ $[M+H]^+$ 341.99466, found 341.99434.

5-Iodo-8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ga)

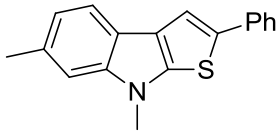


The reaction was conducted with 5-iodo-1-methyl-1*H*-indole (**1g**, 51.4 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the

desired product **4ga** as yellowish solid (31.9 mg, 41% yield), mp 126-129 ^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, J = 1.6 Hz, 1H), 7.62-7.59 (m, 2H), 7.54-7.51 (m, 2H), 7.41-7.37 (m, 2H), 7.27-7.23 (m, 2H), 7.10 (d, J = 8.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.5, 141.0, 136.5, 135.4, 130.2, 129.0, 128.1, 126.9, 125.2, 124.3, 122.4, 113.9, 111.0, 82.7, 32.4; HRMS calcd. for $C_{17}H_{13}NIS$ $[M+H]^+$ 389.98079, found 389.98080.

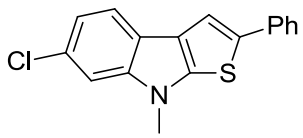
6,8-Dimethyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ha)



The reaction was conducted with 1,6-dimethyl-1*H*-indole (**1h**, 29.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ha** as yellowish solid (37.2 mg, 67% yield), mp 143-145^{o}C. R_f = 0.70 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, J = 8.0 Hz, 1H), 7.63-7.61 (m, 2H), 7.59 (s, 1H), 7.39-7.35 (m, 2H), 7.24-7.20 (m, 1H), 7.14 (s, 1H), 7.02 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.5, 142.4, 135.8, 135.3, 131.9, 128.9, 126.4, 125.0, 123.4, 121.0, 120.0, 118.9, 114.2, 109.3, 32.2, 21.9; HRMS calcd. for $C_{18}H_{15}NS$ [M] 277.09197, found 277.09180.

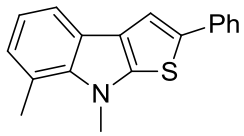
6-Chloro-8-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ia)



The reaction was conducted with 1,6-dimethyl-1*H*-indole (**1i**, 33.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ia** as yellowish solid (30.9 mg, 52% yield), mp 84-86^{o}C. R_f = 0.65 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.69 (d, J = 8.4 Hz, 1H), 7.63-7.61 (m, 2H), 7.57 (s, 1H), 7.41-7.34 (m, 4H), 7.16 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 142.2, 136.5, 135.4, 128.9, 128.0, 126.8, 125.2, 123.3, 120.7, 119.98, 119.95, 114.0, 109.3, 32.4; HRMS calcd. for $C_{17}H_{13}NClS$ $[M+H]^+$ 298.04517, found 298.04487.

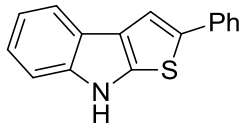
7,8-Dimethyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ja)



The reaction was conducted with 1,7-dimethyl-1*H*-indole (**1j**, 29.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ja** as yellowish solid (40.5 mg, 73% yield), mp 183-185^{o}C. R_f = 0.65 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64-7.60 (m, 3H), 7.57 (s, 1H), 7.39-7.35 (m, 2H), 7.24-7.20 (m, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.1 Hz, 1H), 4.08 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.3, 140.6, 135.7, 135.6, 128.9, 126.5, 125.05, 125.03, 123.3, 123.1, 121.1, 119.8, 117.4, 114.2, 36.4, 19.5; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09968.

2-Phenyl-8*H*-thieno[2,3-*b*]indole (4ka, 22315-06-6) [1]

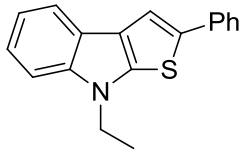


The reaction was conducted with 1*H*-indole (**1k**, 23.5 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to yield the desired product **4ka** as yellowish solid (37.4 mg, 75% yield), mp 265-267^{o}C. R_f = 0.60 (10:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, Acetone, ppm) δ 10.76 (s, 1H), 7.84-7.82 (m, 2H), 7.70-7.68 (m, 2H), 7.52 (d, J = 8.1 Hz, 1H), 7.42-7.38 (m, 2H), 7.27-7.20 (m, 2H), 7.16-7.12 (m, 1H); ^{13}C NMR (100 MHz, Acetone, ppm) δ 142.0, 141.0, 135.8, 135.6, 129.0, 126.6, 125.3, 124.8, 122.3, 122.1, 119.5, 118.9,

113.9, 111.6; HRMS calcd. for $C_{16}H_{12}NS$ $[M+H]^+$ 250.06850, found 250.06824.

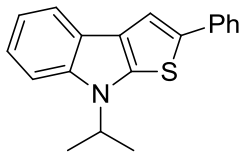
8-Ethyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4la)



The reaction was conducted with 1-ethyl-1*H*-indole (**1l**, 29.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4la** as yellow liquid (39.9 mg, 72% yield). R_f = 0.60 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86 (d, J = 7.7 Hz, 1H), 7.69-7.66 (m, 3H), 7.45-7.41 (m, 3H), 7.35-7.33 (m, 1H), 7.31-7.28 (m, 1H), 7.27-7.22 (m, 1H), 4.32 (q, J = 7.3 Hz, 2H), 1.57 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.5, 141.0, 135.70, 135.69, 128.9, 126.5, 125.1, 123.9, 122.3, 121.9, 119.41, 119.36, 114.1, 109.1, 40.9, 13.8; HRMS calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.09980, found 278.09973.

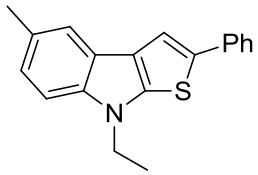
8-Isopropyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4ma)



The reaction was conducted with 1-isopropyl-1*H*-indole (**1m**, 31.8 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4ma** as yellow liquid (49.5 mg, 78% yield). R_f = 0.65 (100:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.81 (d, J = 7.6 Hz, 1H), 7.65-7.63 (m, 3H), 7.42-7.35 (m, 3H), 7.29-7.25 (m, 2H), 7.20-7.16 (m, 1H), 4.86 (dt, J = 13.5 Hz, 6.8 Hz, 1H), 1.64 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.0, 139.7, 136.2, 135.6, 128.9, 126.6, 125.1, 124.8, 122.2, 121.9, 119.4, 119.3, 113.6, 109.4, 47.8, 20.9; HRMS calcd. for $C_{19}H_{18}NS$ $[M+H]^+$ 292.11545, found 292.11517.

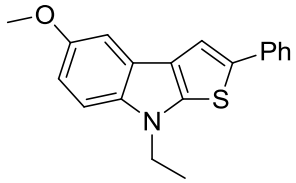
8-Ethyl-5-methyl-2-phenyl-8*H*-thieno[2,3-*b*]indole (4na)



The reaction was conducted with 1-ethyl-5-methyl-1H-indole (**1n**, 31.8 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4na** as gold solid (43.7 mg, 75% yield), mp 107-109^{o}C. R_f = 0.65 (100:1 petroleum ether/EtOAc).

^{1}H NMR (100 MHz, $CDCl_3$, ppm) δ 7.63-7.61 (m, 3H), 7.59 (s, 1H), 7.39-7.35 (m, 2H), 7.26-7.22 (m, 2H), 7.09 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 4.24 (q, *J* = 7.3 Hz, 2H), 2.50 (s, 3H), 1.49 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.6, 139.4, 135.8, 135.3, 128.9, 128.7, 126.5, 125.0, 123.5, 123.2, 122.5, 119.3, 114.1, 108.8, 40.9, 21.4, 13.8; HRMS calcd. for $C_{19}H_{18}NS$ $[M+H]^+$ 292.11545, found 292.11531.

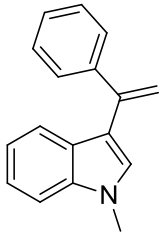
8-Ethyl-5-methoxy-2-phenyl-8*H*-thieno[2,3-*b*]indole (4oa)



The reaction was conducted with 1-ethyl-5-methoxy-1*H*-indole (**1o**, 35.0 mg, 0.2 mmol), acetophenone (**4a**, 47.0 μL, 0.4 mmol) and sulfur powder (32.0 mg, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 300:1) to yield the desired product **4oa** as brown solid (47.9 mg, 78% yield), mp 163-164^{o}C. R_f = 0.40 (100:1 petroleum ether/EtOAc).

^{1}H NMR (100 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.59 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.24-7.21 (m, 2H), 6.92 (dd, *J* = 8.9 Hz, 2.5 Hz, 1H), 4.23 (q, *J* = 7.3 Hz, 2H), 3.90 (s, 3H), 1.50 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.0, 143.0, 136.2, 135.7, 135.3, 128.9, 126.5, 125.1, 123.5, 122.6, 114.0, 111.1, 109.7, 102.4, 56.0, 41.0, 13.8; HRMS calcd. for $C_{20}H_{19}ONS$ [M] 321.11819, found 321.11728.

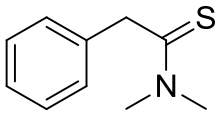
1-methyl-3-(1-phenylvinyl)-1H-indole (3a, CAS: 112122-42-6)[3]



1-Methyl-1*H*-indole (38.0 μL, 0.3 mmol), acetophenone (24.0 μL, 0.2 mmol) and *L*-phenylalanine (33.0 mg, 0.2 mmol) were added to an oven-dried reaction vessel (20 mL). The reaction vessel was sealed and HI (50 mol %, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid) and CF_3Ph/1,4-dioxane (1.0 mL, 2:3) were added by syringe. The reaction vessel was stirred at 115 ^oC for 1.5 h under air atmosphere. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on neutral alum (petroleum ether/EtOAc = 50:1) to yield the desired product **3a** as white solid (9.8 mg, 21% yield). R_f = 0.70 (100:1 petroleum ether/EtOAc).

^1H NMR (100 MHz, $CDCl_3$, ppm) δ 7.56 (d, J = 8.1 Hz, 1H), 7.49-7.46 (m, 2H), 7.34-7.33 (m, 5H), 7.11-7.08 (m, 1H), 6.97 (s, 1H), 5.56 (d, J = 1.4 Hz, 1H), 5.37 (d, J = 1.5 Hz, 1H), 3.77 (s, 3H).

***N,N*-Dimethyl-2-phenylethanethioamide (4a, CAS: 17709-95-4) [4]**

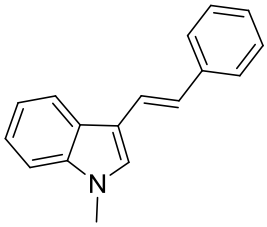


Acetophenone (**2a**, 23.0 μL, 0.2 mmol) and sulfur powder (32.0 mg, 1.0 mmol) were added to a oven-dried reaction vessel (20 mL). HOAc(0.1 mL) and DMF (0.3 mL) were added by syringe. The sealed reaction vessel was stirred at 150 ^oC for 16 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **4a** as white solid (23.3 mg, 65% yield).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.29 (m, 4H), 7.28-7.22 (m, 1H), 4.32 (s, 2H), 3.50 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 200.6, 135.6, 128.8, 128.0, 126.9, 50.9,

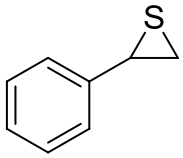
44.8, 42.2.

***(E)*-1-Methyl-3-styryl-1*H*-indole (5a, CAS: 72228-54-7)** [5]



1-Methyl-1*H*-indole (**1a**, 25.0 μL, 0.2 mmol) and styrene (28.0 μL, 1.2 mmol) were added to a oven-dried reaction vessel (20 mL), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (1.8 equiv) and DMF/DMSO (9:1, 0.4 mL) by syringe. The reaction vessel under air atmosphere was stirred at 70 ^oC for 18 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (5 mL) and washed with saturated salt water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over sodium sulfate, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **5a**.

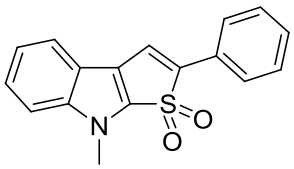
2-Phenylthiirane (6a, CAS: 1498-99-3) [6]



A solution of styrene oxide (230.0 μL, 2.0 mmol) and KSCN (778.0 mg, 8.0 mmol) in water (5.0 mL) was heated to 45 ℃ and stirred for 24 h at the same temperature. The resulting mixture was diluted with EtOAc and washed with brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE) to give 2-phenylthiirane **6a**.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40-7.03 (m, 5H), 4.05-3.66 (m, 1H), 2.86 (dd, J = 6.6 Hz, 1.5 Hz, 1H), 2.64 (dd, J = 5.6 Hz, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.1, 128.5, 127.6, 126.7, 36.1, 27.3.

8-Methyl-2-phenyl-8H-thieno[2,3-b]indole 1,1-dioxide (4aa')



A solution of **4aa** (0.53 g, 2.0 mmol) and *m*-CPBA(1.73 g, 10.0 mmol) in trichloromethane (10.0 mL) was heated to 40 ℃ and stirred for 24 h at the same temperature. The resulting mixture was diluted with EtOAc and volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to yield the desired product **4aa'** as white solid (0.52 g, 87% yield). R_f = 0.60 (5:1 petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.75 (dd, J = 7.7 Hz, 1.7 Hz, 2H), 7.50-7.43 (m, 5H), 7.16 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.9 Hz, 1H), 6.64 (s, 1H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.5, 143.9, 140.3, 132.5, 131.2, 129.4, 127., 126.4, 125.8, 125.0, 124.1, 122.7, 109.4, 84.6, 27.1.

7. References

[1] G. Kobayashi, S. Furukawa, Y. Matsuda, R. Natsuki, *Yakugaku Zasshi* **1969**, *89*, 58-63.

[2] R. A. Irgashev, A. A. Karmatsky, G. L. Rusinov, V. N. Charushin, *Beilstein J. Org. Chem.* **2015**, *11*, 1000-1007.

[3] U. Pindur, G. Lutz, D. Schollmeyer, W. Massa, L. Schöder, *Tetrahedron* **1993**, *49*, 2863-2872.

[4] S. Kumar, R. Vanjari, T. Guntreddi, K. N. Singh, *Tetrahedron* **2016**, *72*, 2012-2017.

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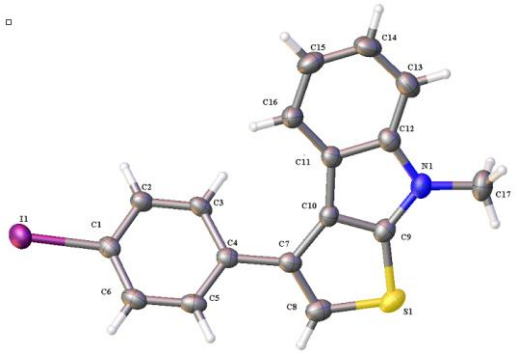
[6] X. P. Chen, J. X. Xu, *Tetrahedron Lett*. **2017**, *58*, 1651-1654.

8. Crystal data and structure refinement for 3ah and 4aa



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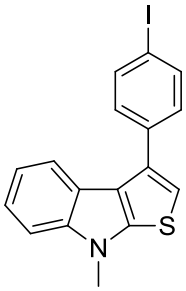


3ah

Table 1. Crystal data and structure refinement for **3ah**.

Identification code	**3ah**	
Empirical formula	C17 H12 I N S	
Formula weight	389.24	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 6.2817(13) Å	α= 90 °.
	b = 19.730(4) Å	β= 90 °.
	c = 23.695(5) Å	γ = 90 °.
Volume	2936.7(10) $Å^3$	
Z	8	
Density (calculated)	1.761 Mg/m^3	
Absorption coefficient	2.311 mm^{-1}	
F(000)	1520	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.064 to 27.487 °.	
Index ranges	-8<=h<=8, -24<=k<=16, -30<=l<=30	
Reflections collected	12514	
Independent reflections	3329 [R(int) = 0.0426]	
Completeness to theta = 25.242 °	99.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3329 / 0 / 182	
Goodness-of-fit on F^2	1.162	
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.0900	

R indices (all data)	R1 = 0.0514, wR2 = 0.0923
Extinction coefficient	n/a
Largest diff. peak and hole	0.483 and -0.659 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3ah**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I1	9666(1)	1718(1)	3106(1)	37(1)
S1	1249(2)	5339(1)	3279(1)	35(1)
N1	-1065(6)	4821(2)	4217(1)	32(1)
C17	-2754(8)	5320(2)	4271(2)	42(1)
C1	7630(6)	2559(2)	3193(2)	28(1)
C2	5572(6)	2449(2)	3385(2)	28(1)
C3	4245(6)	2999(2)	3471(2)	27(1)
C4	4924(6)	3660(2)	3368(2)	26(1)
C5	6996(6)	3753(2)	3160(2)	30(1)
C6	8347(7)	3206(2)	3069(2)	31(1)
C7	3454(6)	4234(2)	3453(2)	26(1)
C8	3320(7)	4790(2)	3111(2)	34(1)
C9	527(7)	4811(2)	3825(2)	29(1)
C10	1826(6)	4253(2)	3883(2)	26(1)
C11	1014(6)	3892(2)	4366(2)	27(1)
C12	-787(7)	4256(2)	4555(2)	31(1)
C13	-2011(7)	4045(2)	5016(2)	40(1)
C14	-1362(8)	3470(2)	5302(2)	41(1)
C15	461(8)	3117(2)	5136(2)	40(1)
C16	1633(7)	3314(2)	4672(2)	32(1)

Table 3. Bond lengths [Å] and angles [°] for **3ah**.

I1-C1	2.105(4)
S1-C8	1.739(5)
S1-C9	1.722(4)
N1-C17	1.453(5)
N1-C9	1.366(5)

N1-C12	1.384(5)
C17-H17A	0.9600
C17-H17B	0.9600
C17-H17C	0.9600
C1-C2	1.388(5)
C1-C6	1.386(6)
C2-H2	0.9300
C2-C3	1.384(6)
C3-H3	0.9300
C3-C4	1.394(6)
C4-C5	1.404(5)
C4-C7	1.475(6)
C5-H5	0.9300
C5-C6	1.389(6)
C6-H6	0.9300
C7-C8	1.368(6)
C7-C10	1.444(5)
C8-H8	0.9300
C9-C10	1.377(5)
C10-C11	1.442(5)
C11-C12	1.412(6)
C11-C16	1.407(6)
C12-C13	1.399(6)
C13-H13	0.9300
C13-C14	1.381(7)
C14-H14	0.9300
C14-C15	1.398(7)
C15-H15	0.9300
C15-C16	1.377(6)
C16-H16	0.9300
C9-S1-C8	89.6(2)
C9-N1-C17	127.1(4)
C9-N1-C12	106.9(3)
C12-N1-C17	126.0(4)
N1-C17-H17A	109.5
N1-C17-H17B	109.5
N1-C17-H17C	109.5
H17A-C17-H17B	109.5

H17A-C17-H17C	109.5
H17B-C17-H17C	109.5
C2-C1-I1	118.3(3)
C6-C1-I1	120.5(3)
C6-C1-C2	121.1(4)
C1-C2-H2	120.4
C3-C2-C1	119.1(4)
C3-C2-H2	120.4
C2-C3-H3	119.2
C2-C3-C4	121.6(4)
C4-C3-H3	119.2
C3-C4-C5	117.8(4)
C3-C4-C7	120.2(3)
C5-C4-C7	121.9(4)
C4-C5-H5	119.3
C6-C5-C4	121.3(4)
C6-C5-H5	119.3
C1-C6-C5	119.0(4)
C1-C6-H6	120.5
C5-C6-H6	120.5
C8-C7-C4	125.0(4)
C8-C7-C10	110.7(4)
C10-C7-C4	124.0(4)
S1-C8-H8	122.9
C7-C8-S1	114.2(3)
C7-C8-H8	122.9
N1-C9-S1	134.1(3)
N1-C9-C10	112.2(4)
C10-C9-S1	113.7(3)
C9-C10-C7	111.7(4)
C9-C10-C11	105.3(3)
C11-C10-C7	143.0(4)
C12-C11-C10	106.6(3)
C16-C11-C10	135.4(4)
C16-C11-C12	118.0(4)
N1-C12-C11	109.1(4)
N1-C12-C13	128.5(4)
C13-C12-C11	122.4(4)

C12-C13-H13	121.2
C14-C13-C12	117.7(4)
C14-C13-H13	121.2
C13-C14-H14	119.6
C13-C14-C15	120.8(4)
C15-C14-H14	119.6
C14-C15-H15	119.2
C16-C15-C14	121.5(4)
C16-C15-H15	119.2
C11-C16-H16	120.3
C15-C16-C11	119.4(4)
C15-C16-H16	120.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3ah**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

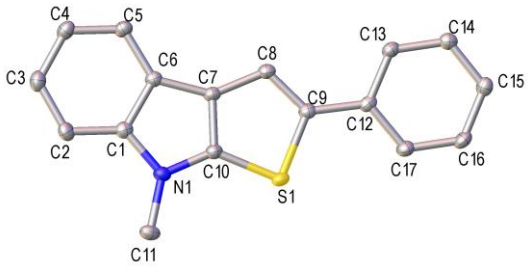
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I1	28(1)	41(1)	43(1)	2(1)	3(1)	4(1)
S1	48(1)	26(1)	32(1)	3(1)	-6(1)	-2(1)
N1	33(2)	29(2)	33(2)	-3(2)	-2(2)	4(2)
C17	43(3)	35(2)	49(3)	-9(2)	-3(2)	11(2)
C1	25(2)	35(2)	24(2)	1(2)	0(2)	0(2)
C2	29(2)	29(2)	28(2)	-3(2)	4(2)	-6(2)
C3	23(2)	34(2)	26(2)	-5(2)	5(2)	-6(2)
C4	29(2)	28(2)	21(2)	-3(2)	1(2)	-4(2)
C5	29(2)	36(2)	23(2)	2(2)	-2(2)	-12(2)
C6	24(2)	42(2)	27(2)	3(2)	1(2)	-5(2)
C7	30(2)	28(2)	22(2)	-3(2)	1(2)	-6(2)
C8	46(2)	31(2)	26(2)	-1(2)	-1(2)	-8(2)
C9	36(2)	26(2)	26(2)	-3(2)	-4(2)	0(2)
C10	28(2)	23(2)	27(2)	-4(2)	-1(2)	0(2)
C11	30(2)	26(2)	25(2)	-6(2)	2(2)	-2(2)
C12	31(2)	34(2)	29(2)	-5(2)	1(2)	-1(2)
C13	34(2)	45(3)	43(3)	-7(2)	10(2)	-1(2)
C14	47(3)	41(3)	34(2)	0(2)	14(2)	-8(2)

C15	54(3)	28(2)	36(2)	6(2)	2(2)	-4(2)
C16	35(2)	28(2)	32(2)	-1(2)	5(2)	1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3ah**.

	x	y	z	U(eq)
H17A	-2462	5697	4027	63
H17B	-2828	5475	4654	63
H17C	-4088	5118	4167	63
H2	5091	2011	3455	34
H3	2866	2926	3601	33
H5	7475	4189	3082	35
H6	9710	3274	2927	37
H8	4255	4868	2813	41
H13	-3220	4282	5126	49
H14	-2149	3317	5609	49
H15	893	2741	5342	48
H16	2823	3066	4563	38

Crystal data and structure refinement for 4aa



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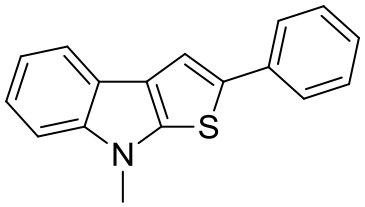


4aa

Table S1. Crystal data and structure refinement for **4aa**.

Table 1. Crystal data and structure refinement for **4aa**.

Identification code	**4aa**	
Empirical formula	$C_{17}H_{13}NS$	
Formula weight	263.34	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.4797(4) Å	α= 90 °.
	b = 9.5670(7) Å	β= 90 °.
	c = 24.6309(17) Å	γ = 90 °.
Volume	1291.26(16) $Å^3$	
Z	4	
Density (calculated)	1.355 Mg/m^3	
Absorption coefficient	0.234 mm^{-1}	
F(000)	552	
Crystal size	0.389 x 0.324 x 0.171 mm^3	
Theta range for data collection	3.270 to 27.468 °.	
Index ranges	-6<=h<=6, -12<=k<=11, -15<=l<=31	
Reflections collected	5038	
Independent reflections	2767 [R(int) = 0.0268]	
Completeness to theta = 26.000 °	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85076	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2767 / 0 / 173	
Goodness-of-fit on F^2	1.132	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0857	

R indices (all data)	R1 = 0.0417, wR2 = 0.0878
Absolute structure parameter	0.09(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.189 and -0.177 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	1630(1)	3575(1)	5361(1)	30(1)
N1	2871(4)	2420(2)	6390(1)	30(1)
C1	4697(5)	2730(3)	6763(1)	28(1)
C2	5173(5)	2100(3)	7262(1)	33(1)
C3	7137(5)	2600(3)	7558(1)	35(1)
C4	8607(5)	3686(3)	7365(1)	34(1)
C5	8141(5)	4303(3)	6867(1)	30(1)
C6	6148(5)	3848(3)	6560(1)	27(1)
C7	5124(5)	4208(3)	6037(1)	26(1)
C8	5413(5)	5130(3)	5586(1)	27(1)
C9	3700(5)	4922(3)	5193(1)	27(1)
C10	3156(5)	3321(3)	5963(1)	27(1)
C11	1011(5)	1350(3)	6436(1)	34(1)
C12	3433(5)	5657(3)	4672(1)	26(1)
C13	5160(5)	6658(3)	4514(1)	28(1)
C14	4992(5)	7344(3)	4017(1)	30(1)
C15	3080(6)	7037(3)	3665(1)	32(1)
C16	1352(5)	6069(3)	3817(1)	34(1)
C17	1506(5)	5389(3)	4314(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for **4aa**.

S1-C9	1.766(3)
S1-C10	1.719(3)
N1-C1	1.391(4)
N1-C10	1.368(3)
N1-C11	1.449(3)

C1-C2	1.394(4)
C1-C6	1.423(4)
C2-H2	0.9300
C2-C3	1.385(4)
C3-H3	0.9300
C3-C4	1.398(4)
C4-H4	0.9300
C4-C5	1.386(4)
C5-H5	0.9300
C5-C6	1.399(4)
C6-C7	1.446(4)
C7-C8	1.427(4)
C7-C10	1.384(4)
C8-H8	0.9300
C8-C9	1.363(4)
C9-C12	1.472(4)
C11-H11A	0.9600
C11-H11B	0.9600
C11-H11C	0.9600
C12-C13	1.402(4)
C12-C17	1.398(4)
C13-H13	0.9300
C13-C14	1.392(4)
C14-H14	0.9300
C14-C15	1.392(4)
C15-H15	0.9300
C15-C16	1.376(4)
C16-H16	0.9300
C16-C17	1.391(4)
C17-H17	0.9300
C10-S1-C9	89.62(13)
C1-N1-C11	127.2(2)
C10-N1-C1	106.9(2)
C10-N1-C11	125.9(2)
N1-C1-C2	128.7(3)
N1-C1-C6	109.3(2)
C2-C1-C6	122.0(3)
C1-C2-H2	121.3

C3-C2-C1	117.4(3)
C3-C2-H2	121.3
C2-C3-H3	119.2
C2-C3-C4	121.7(3)
C4-C3-H3	119.2
C3-C4-H4	119.6
C5-C4-C3	120.8(3)
C5-C4-H4	119.6
C4-C5-H5	120.3
C4-C5-C6	119.4(3)
C6-C5-H5	120.3
C1-C6-C7	106.0(2)
C5-C6-C1	118.7(2)
C5-C6-C7	135.3(2)
C8-C7-C6	142.8(2)
C10-C7-C6	105.9(2)
C10-C7-C8	111.3(2)
C7-C8-H8	123.6
C9-C8-C7	112.7(2)
C9-C8-H8	123.6
C8-C9-S1	112.5(2)
C8-C9-C12	128.2(3)
C12-C9-S1	119.30(19)
N1-C10-S1	134.1(2)
N1-C10-C7	112.0(2)
C7-C10-S1	113.92(19)
N1-C11-H11A	109.5
N1-C11-H11B	109.5
N1-C11-H11C	109.5
H11A-C11-H11B	109.5
H11A-C11-H11C	109.5
H11B-C11-H11C	109.5
C13-C12-C9	120.0(2)
C17-C12-C9	122.5(2)
C17-C12-C13	117.5(2)
C12-C13-H13	119.3
C14-C13-C12	121.4(2)
C14-C13-H13	119.3

C13-C14-H14	120.0
C13-C14-C15	119.9(3)
C15-C14-H14	120.0
C14-C15-H15	120.3
C16-C15-C14	119.3(3)
C16-C15-H15	120.3
C15-C16-H16	119.6
C15-C16-C17	120.9(3)
C17-C16-H16	119.6
C12-C17-H17	119.5
C16-C17-C12	121.0(3)
C16-C17-H17	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	24(1)	35(1)	31(1)	-4(1)	-2(1)	-5(1)
N1	27(1)	31(1)	31(1)	-2(1)	2(1)	-6(1)
C1	28(1)	29(1)	29(1)	-5(1)	3(1)	2(1)
C2	37(2)	35(2)	27(1)	1(1)	7(1)	1(1)
C3	41(2)	40(2)	26(1)	0(1)	1(1)	7(1)
C4	37(2)	33(1)	32(1)	-7(1)	-7(1)	5(1)
C5	31(2)	27(1)	33(1)	-5(1)	-2(1)	-1(1)
C6	25(1)	25(1)	30(1)	-3(1)	0(1)	2(1)
C7	23(1)	26(1)	30(1)	-5(1)	0(1)	-1(1)
C8	23(1)	27(1)	32(1)	-3(1)	0(1)	-1(1)
C9	23(1)	27(1)	31(1)	-4(1)	2(1)	1(1)
C10	24(1)	29(1)	28(1)	-3(1)	0(1)	-2(1)
C11	31(2)	31(1)	39(2)	-6(1)	6(1)	-8(1)
C12	22(1)	28(1)	27(1)	-8(1)	-1(1)	5(1)
C13	26(1)	30(1)	30(1)	-6(1)	-2(1)	1(1)
C14	29(2)	28(1)	33(1)	-4(1)	3(1)	1(1)
C15	36(2)	29(1)	30(1)	-1(1)	-3(1)	6(1)
C16	28(2)	41(2)	34(1)	-4(1)	-8(1)	1(1)

C17	25(2)	35(1)	35(1)	-1(1)	-2(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4aa**.

	x	y	z	U(eq)
H2	4209	1373	7391	39
H3	7486	2203	7894	43
H4	9912	3998	7574	40
H5	9144	5014	6738	36
H8	6637	5801	5563	33
H11A	1522	530	6243	50
H11B	-490	1689	6284	50
H11C	769	1122	6812	50
H13	6445	6870	4747	34
H14	6157	8006	3921	36
H15	2970	7482	3330	38
H16	65	5867	3583	41
H17	309	4746	4411	38

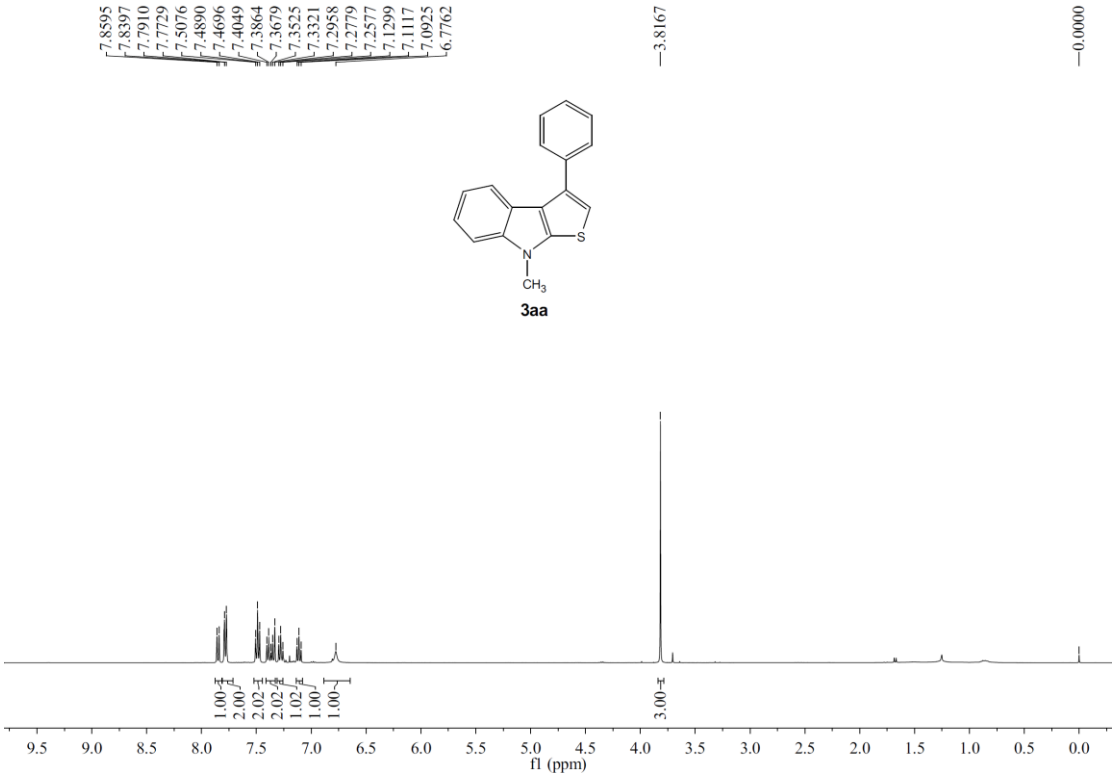
Table 6. Torsion angles [°] for **4aa**.

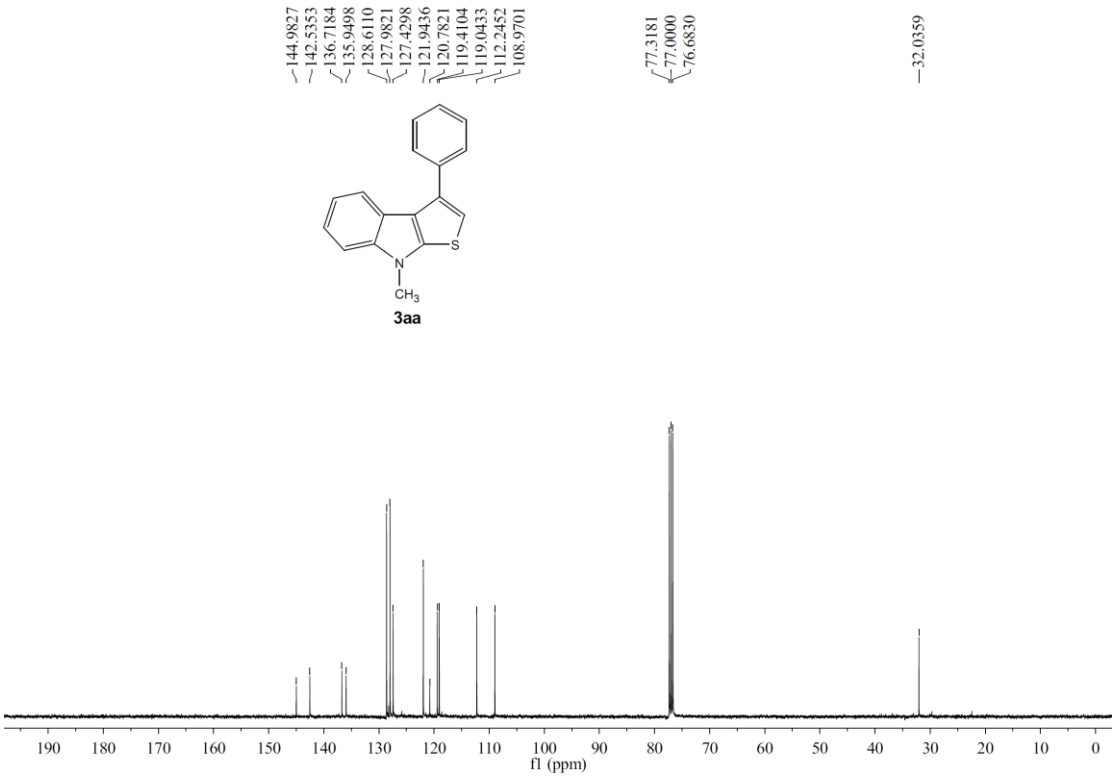
S1-C9-C12-C13	-175.45(19)
S1-C9-C12-C17	3.9(3)
N1-C1-C2-C3	179.4(3)
N1-C1-C6-C5	-178.3(2)
N1-C1-C6-C7	-0.3(3)
C1-N1-C10-S1	-179.9(2)
C1-N1-C10-C7	0.7(3)
C1-C2-C3-C4	-0.5(4)
C1-C6-C7-C8	-179.7(3)
C1-C6-C7-C10	0.7(3)
C2-C1-C6-C5	1.4(4)
C2-C1-C6-C7	179.4(2)
C2-C3-C4-C5	0.0(4)

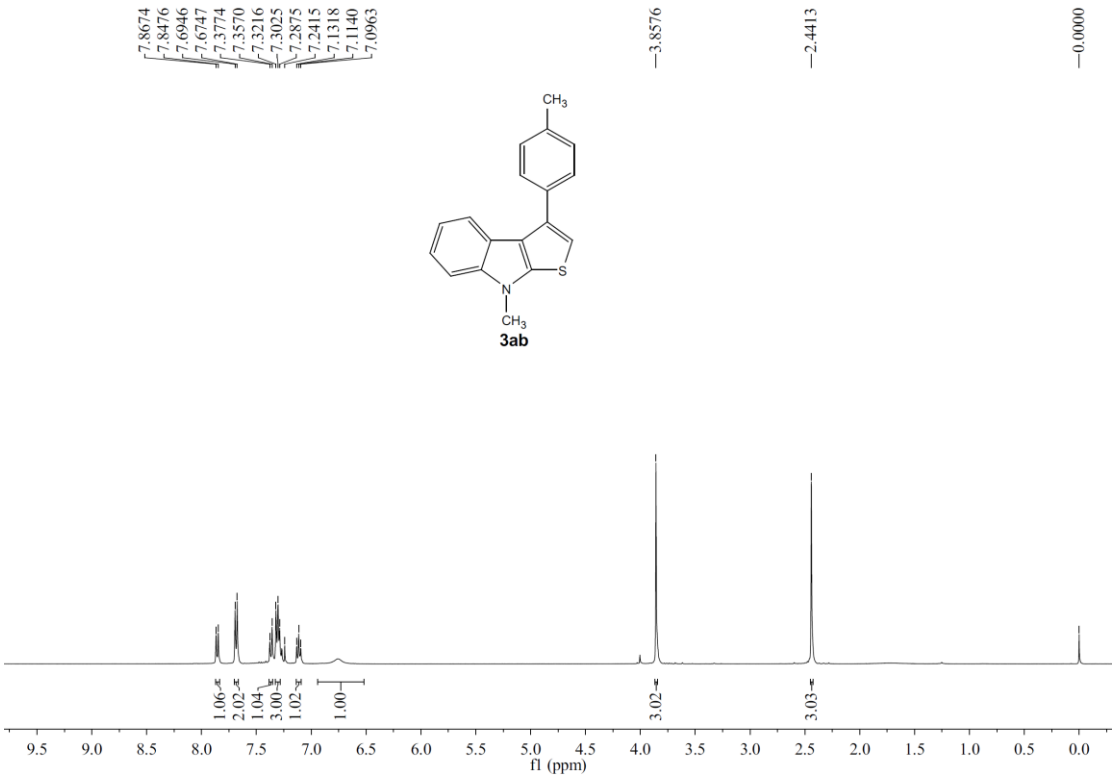
C3-C4-C5-C6	1.2(4)
C4-C5-C6-C1	-1.8(4)
C4-C5-C6-C7	-179.1(3)
C5-C6-C7-C8	-2.1(6)
C5-C6-C7-C10	178.2(3)
C6-C1-C2-C3	-0.2(4)
C6-C7-C8-C9	-179.6(3)
C6-C7-C10-S1	179.57(18)
C6-C7-C10-N1	-0.9(3)
C7-C8-C9-S1	0.2(3)
C7-C8-C9-C12	-179.3(2)
C8-C7-C10-S1	-0.2(3)
C8-C7-C10-N1	179.4(2)
C8-C9-C12-C13	4.0(4)
C8-C9-C12-C17	-176.6(3)
C9-S1-C10-N1	-179.2(3)
C9-S1-C10-C7	0.3(2)
C9-C12-C13-C14	178.3(2)
C9-C12-C17-C16	-177.8(2)
C10-S1-C9-C8	-0.3(2)
C10-S1-C9-C12	179.3(2)
C10-N1-C1-C2	-179.9(3)
C10-N1-C1-C6	-0.2(3)
C10-C7-C8-C9	0.0(3)
C11-N1-C1-C2	0.0(5)
C11-N1-C1-C6	179.7(2)
C11-N1-C10-S1	0.3(4)
C11-N1-C10-C7	-179.2(2)
C12-C13-C14-C15	-0.1(4)
C13-C12-C17-C16	1.6(4)
C13-C14-C15-C16	0.9(4)
C14-C15-C16-C17	-0.5(4)
C15-C16-C17-C12	-0.8(4)
C17-C12-C13-C14	-1.1(4)

Symmetry transformations used to generate equivalent atoms:

9. Copies of ^{1}H and ^{13}C NMR spectra of all products



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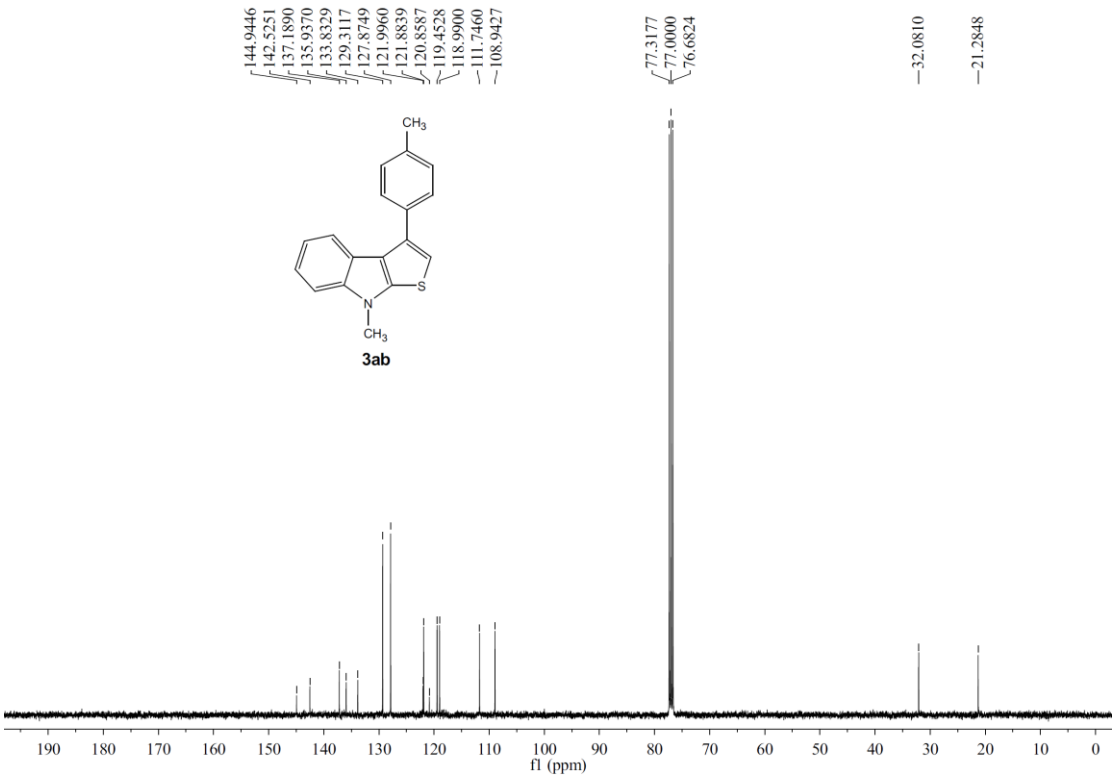
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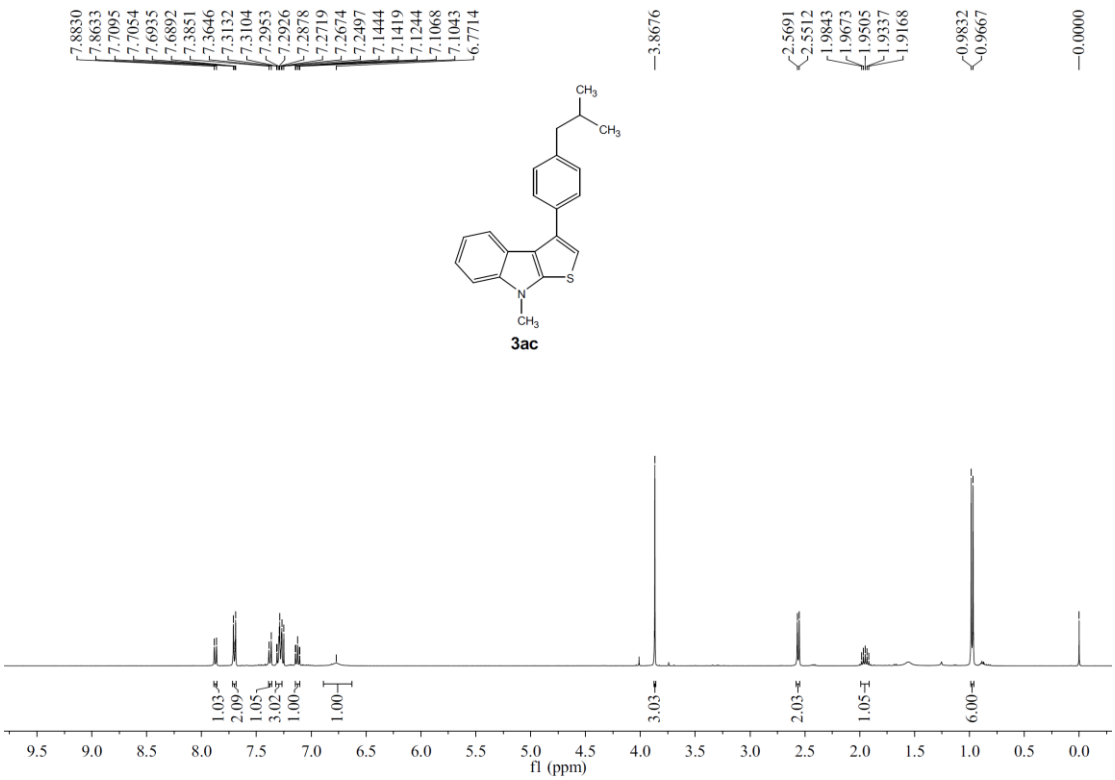
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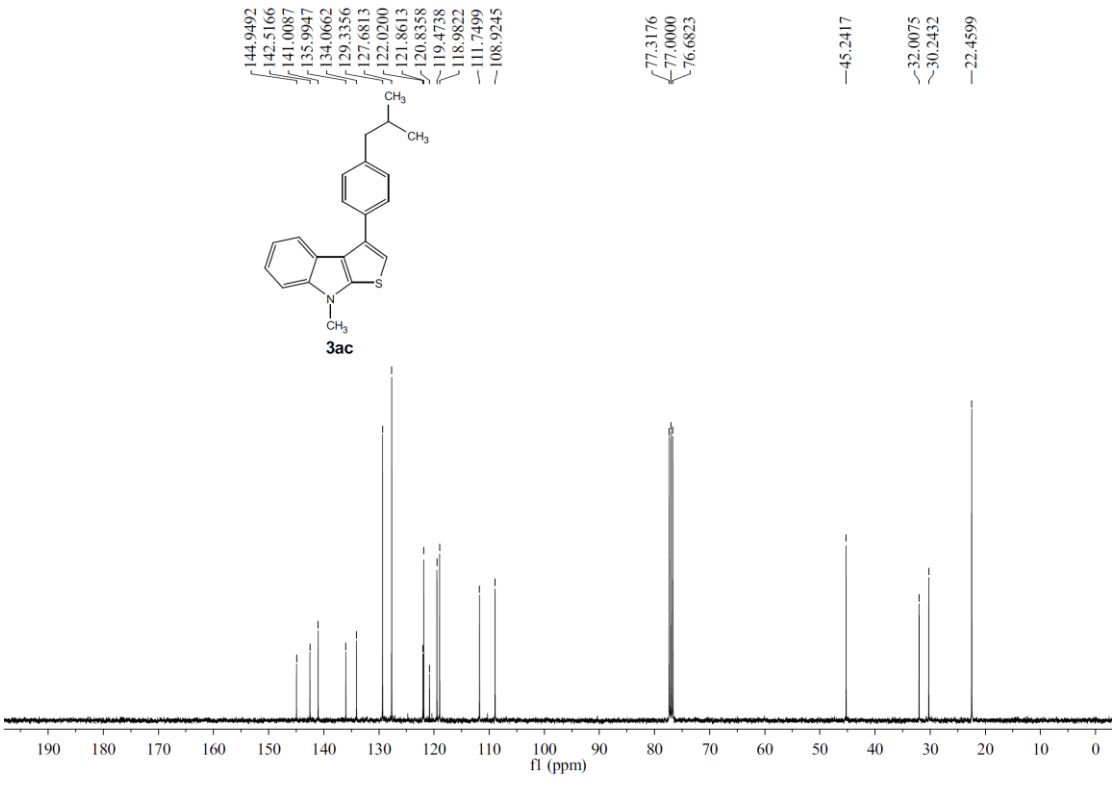
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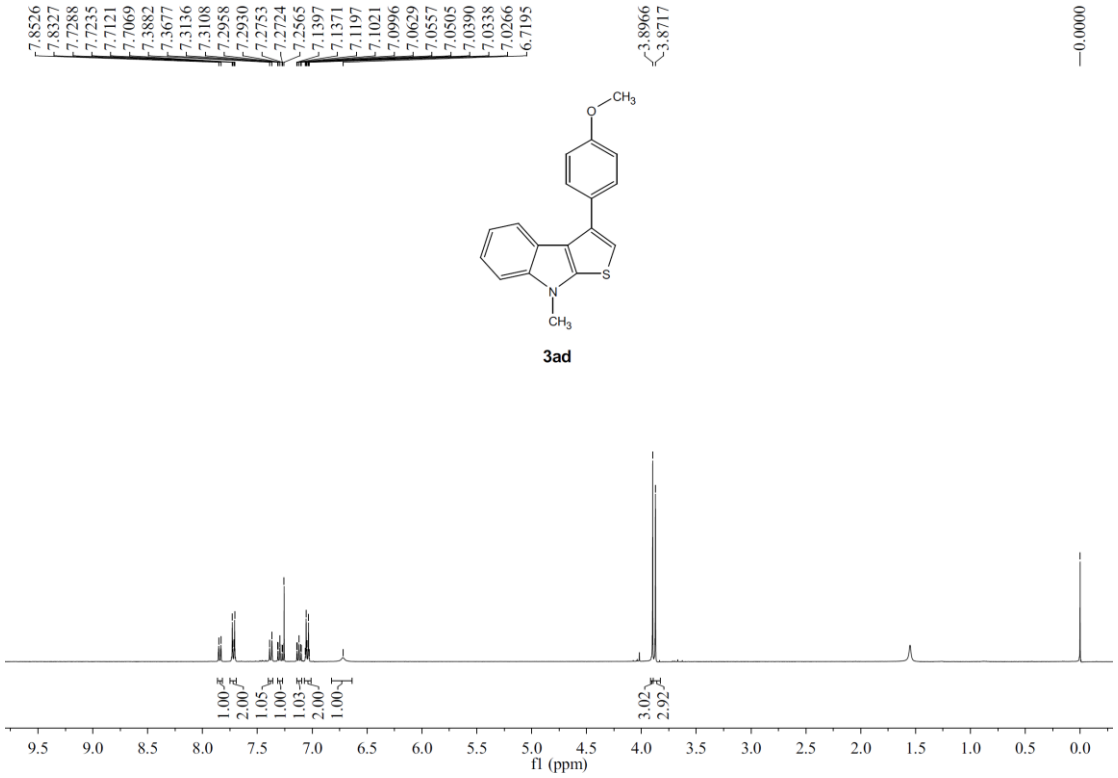
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1.00
3.02
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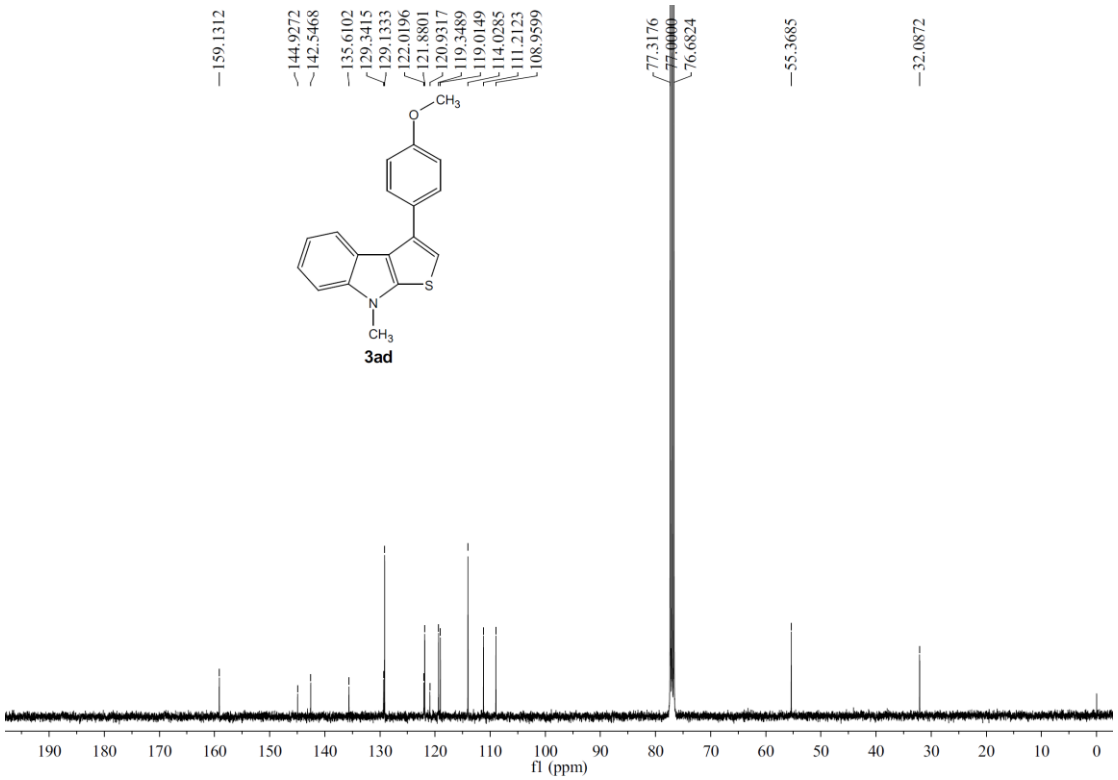
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CH3
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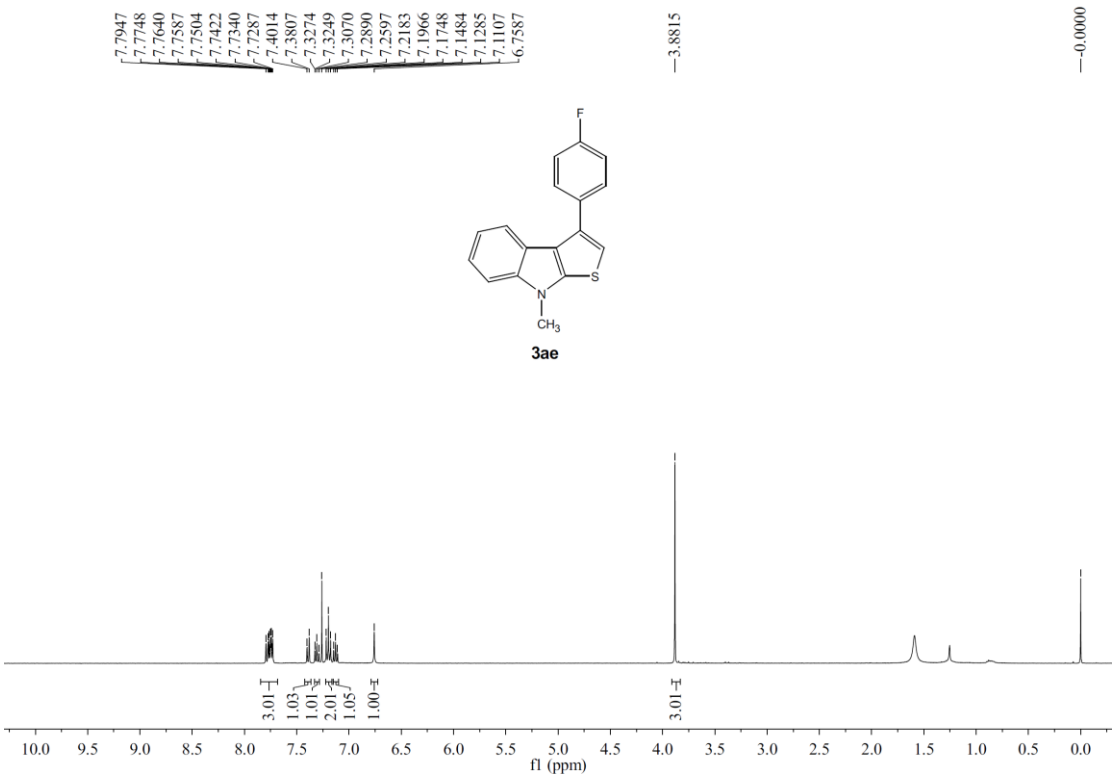
f1 (ppm)

3ad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3.01
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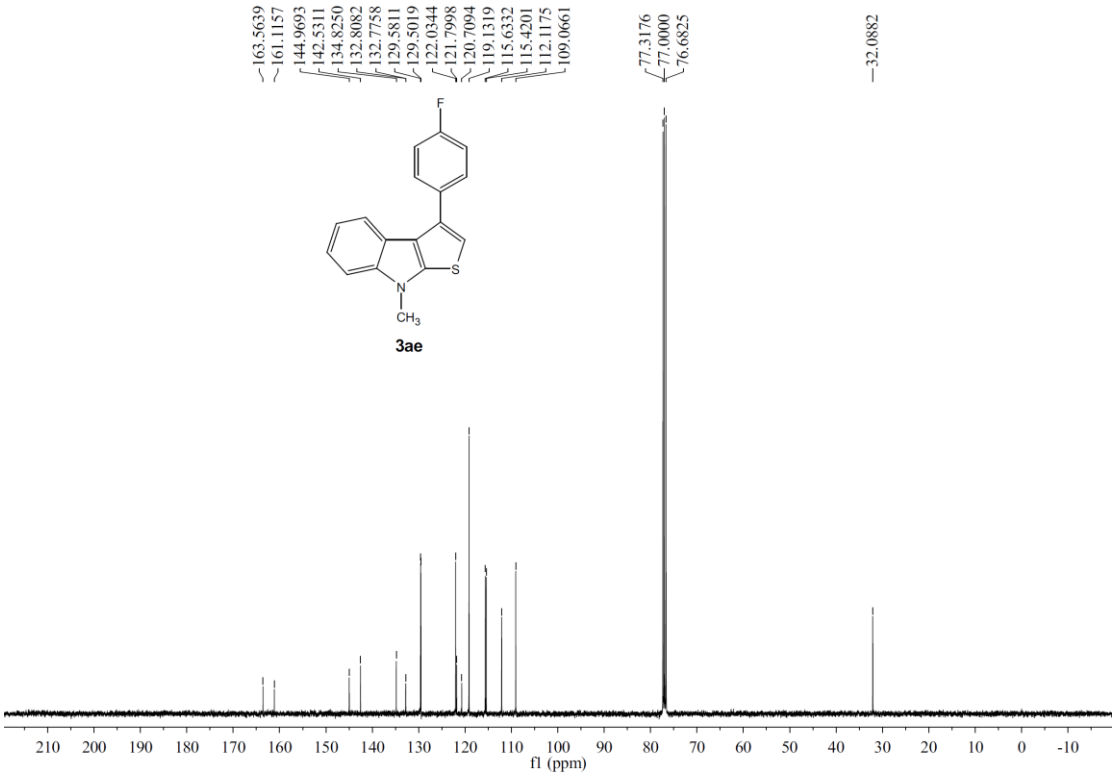
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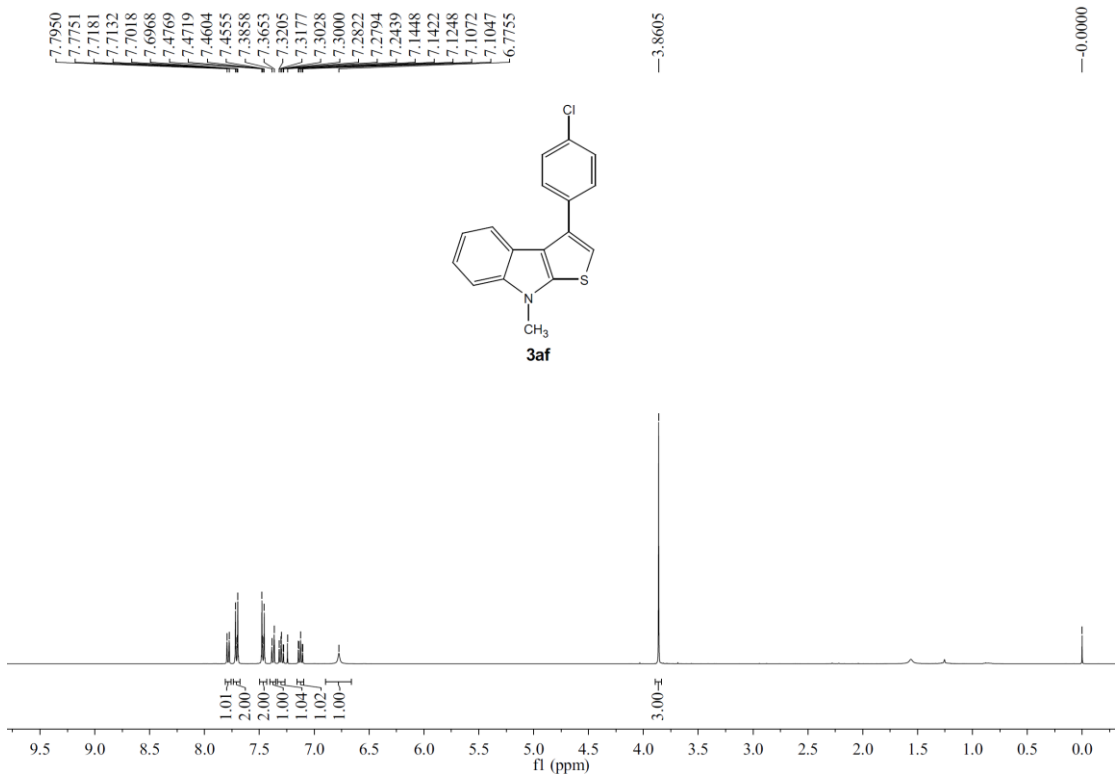
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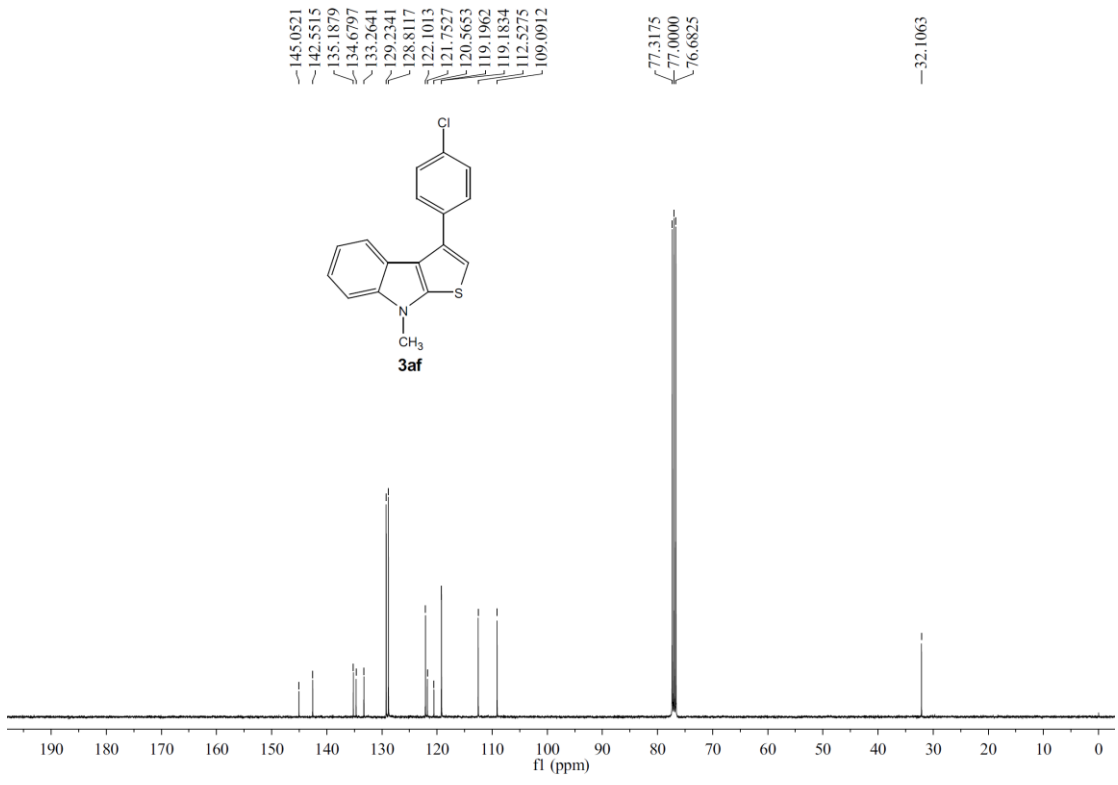
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S
N
CH3
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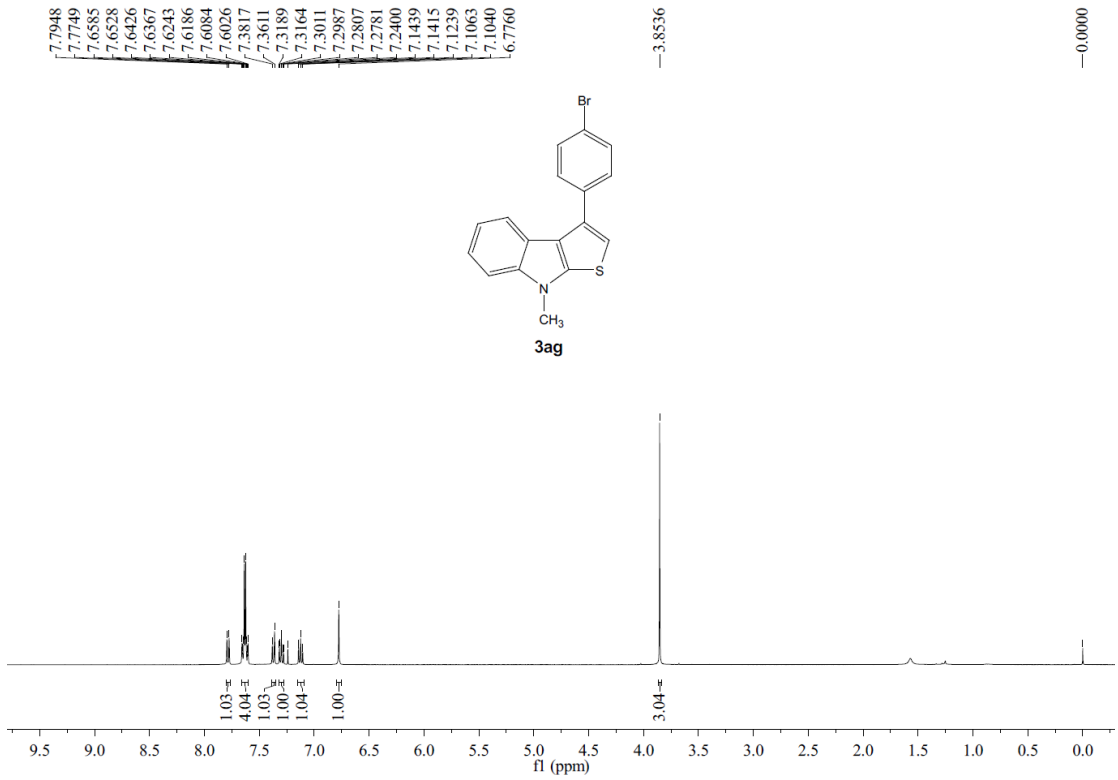
f1 (ppm)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7.3164
7.3011
7.2987
7.2807
7.2781
7.2400
7.1439
7.1415
7.1239
7.1063
7.1040
6.7760
3.8536
0.0000
Br
S
N
CH3
3ag
1.03
4.04
1.03
1.00
1.04
1.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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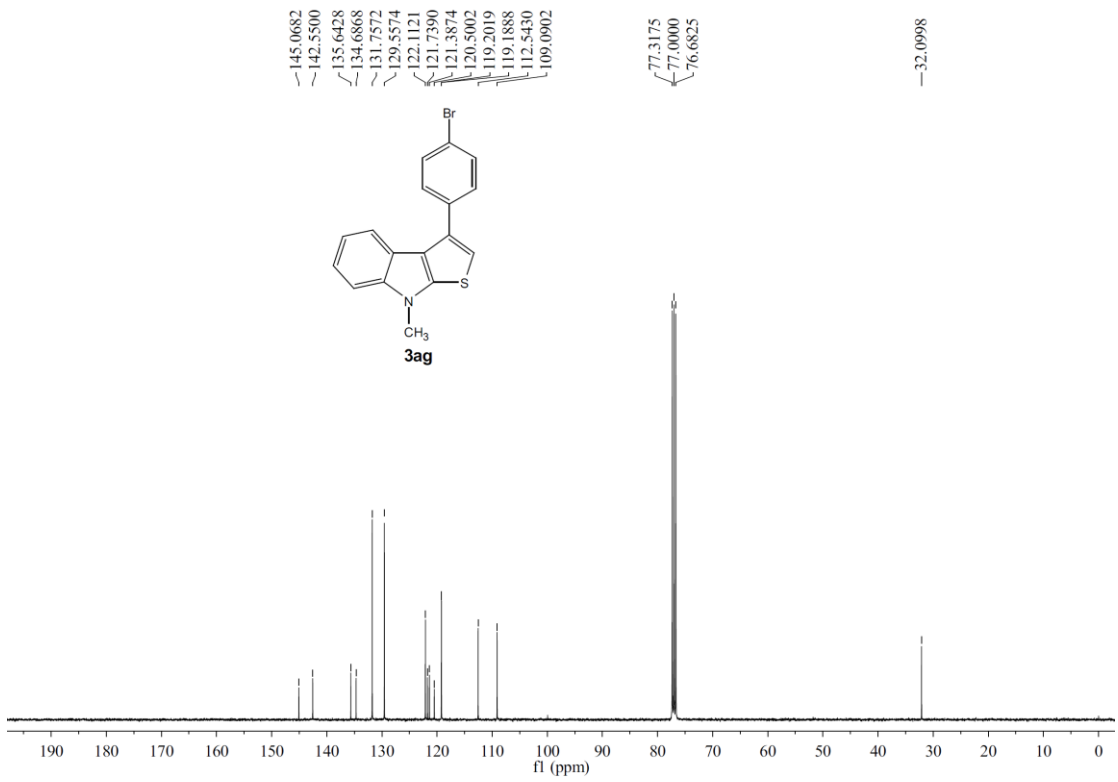
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112.5430
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77.3175
77.0000
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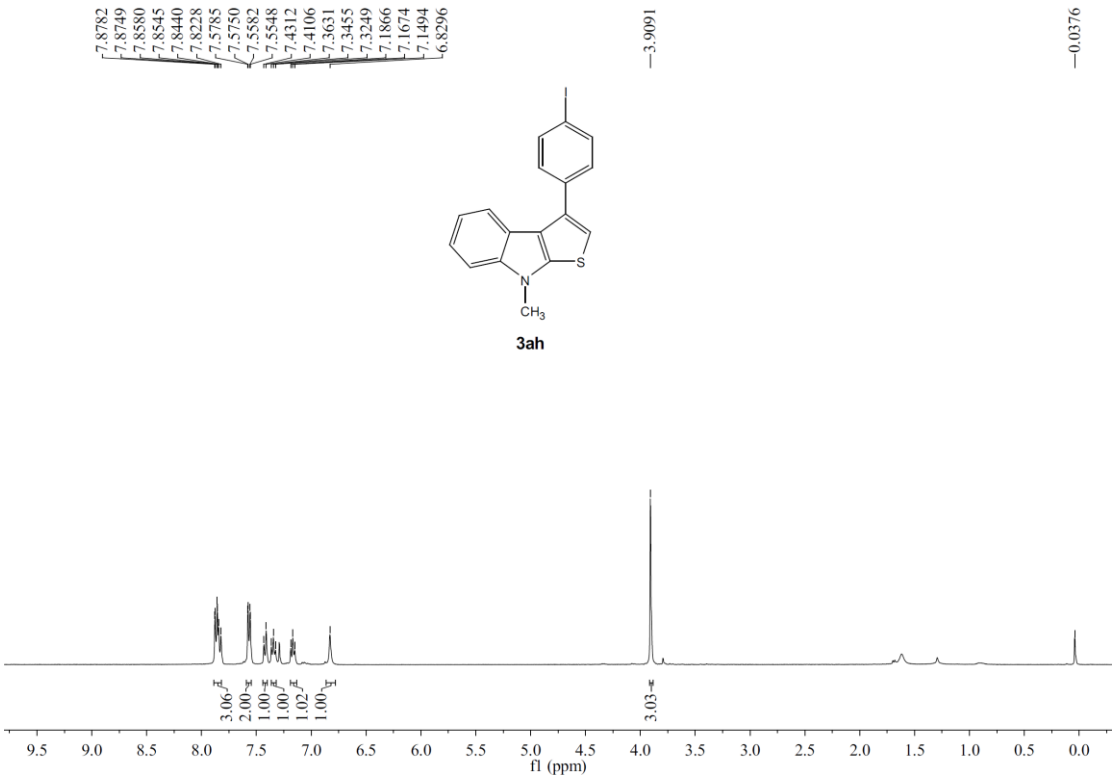
S
N
CH3
3ag
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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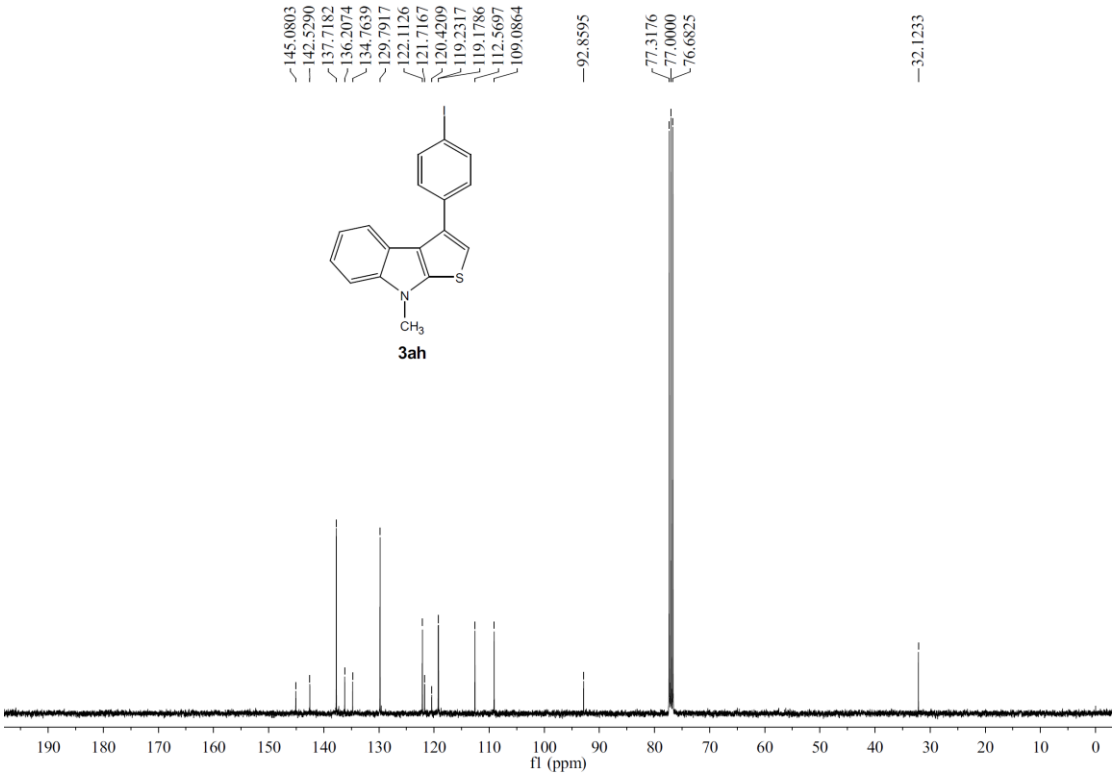
7.4312
7.4106
7.3631
7.3455
7.3249
7.1866
7.1674
7.1494
6.8296
3.9091
0.0376
3.06
2.00
1.00
1.00
1.02
1.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ah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112.5697
109.0864
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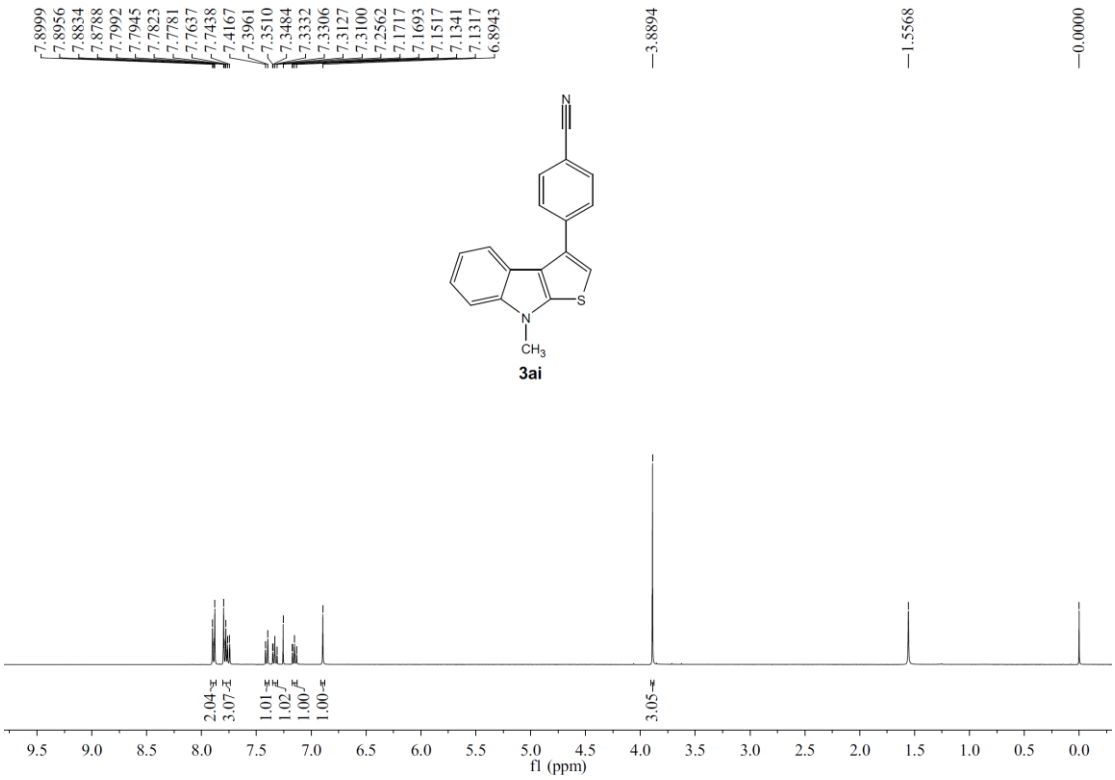
f1 (ppm)

3ah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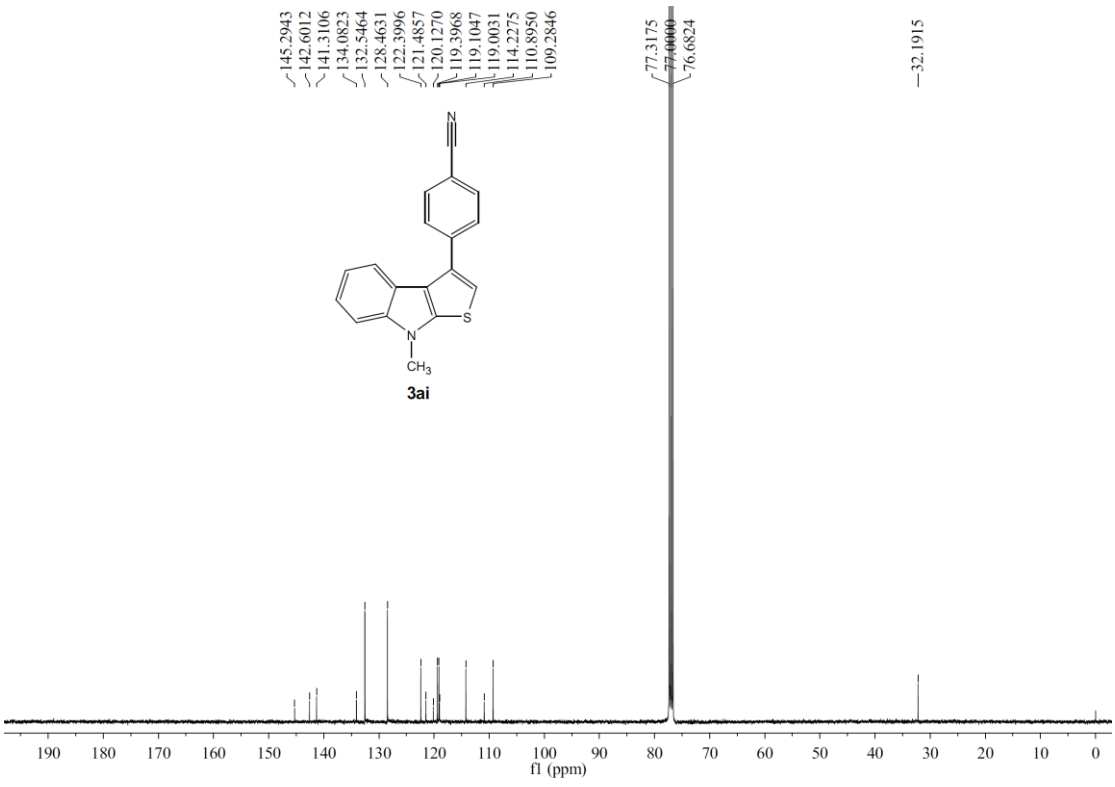
7.3961
7.3510
7.3484
7.3332
7.3306
7.3127
7.3100
7.2562
7.1717
7.1693
7.1517
7.1341
7.1317
6.8943
3.8894
1.5568
0.0000
N
S
N
CH3
3ai
2.04
3.07
1.01
1.02
1.00
1.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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110.8950
109.2846
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S
N
CH3
3ai
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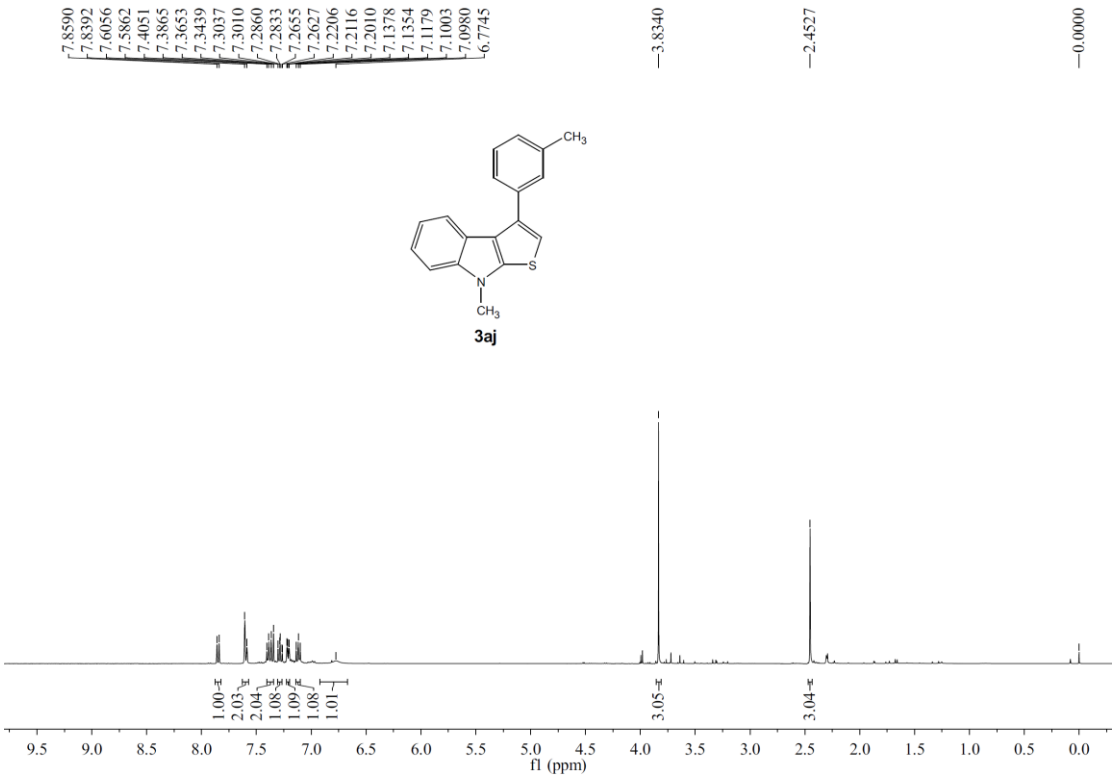
f1 (ppm)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7.2627
7.2206
7.2116
7.2010
7.1378
7.1354
7.1179
7.1003
7.0980
6.7745
3.8340
2.4527
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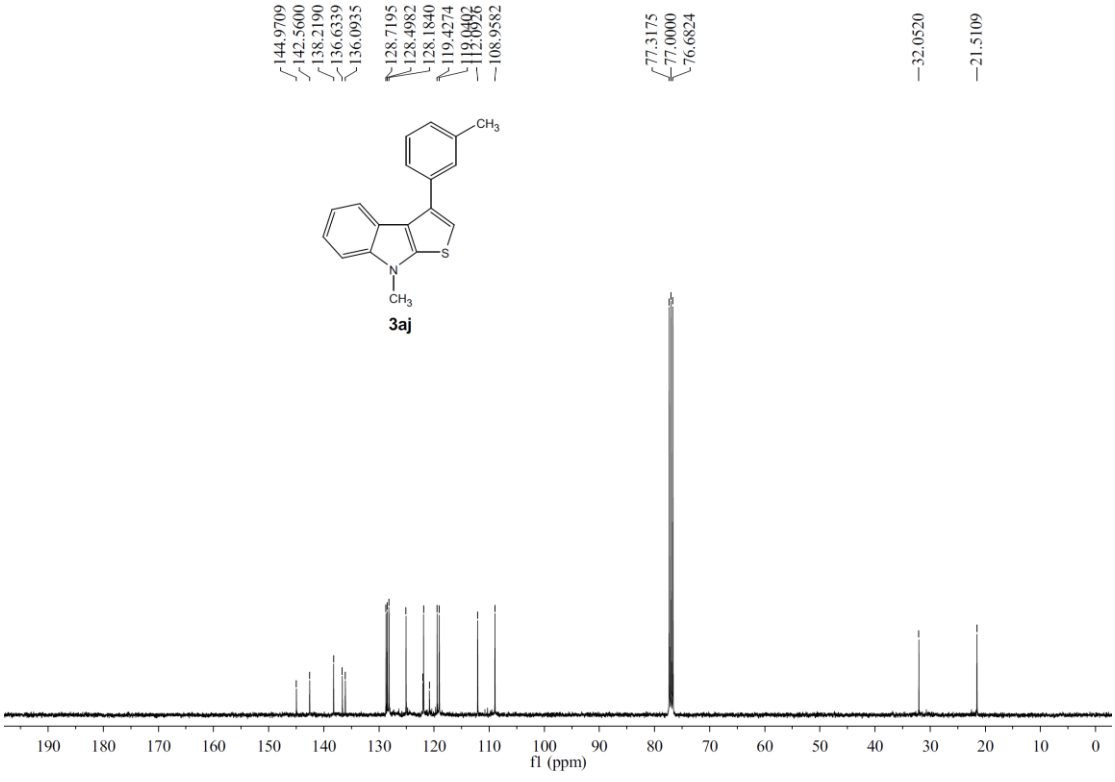
CH3
S
N
CH3
1.00
2.03
2.04
1.08
1.09
1.08
1.01
3.05
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3aj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112.0926
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77.3175
77.0000
76.6824
32.0520
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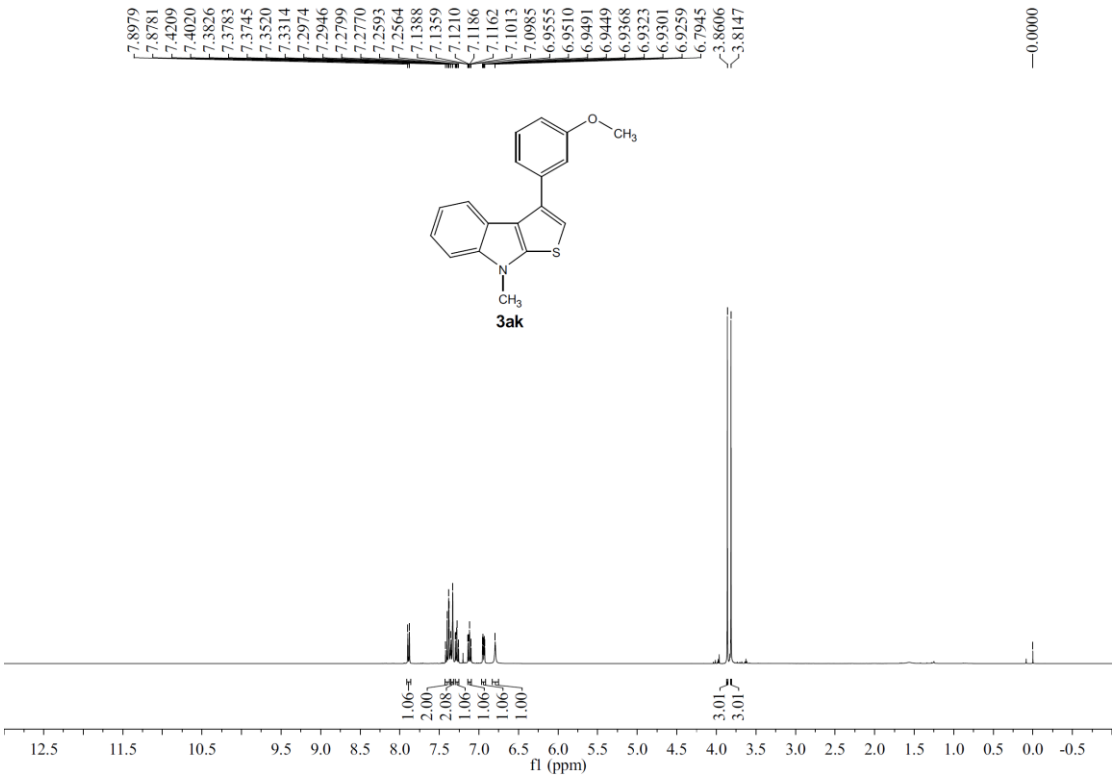
CH3
S
N
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3aj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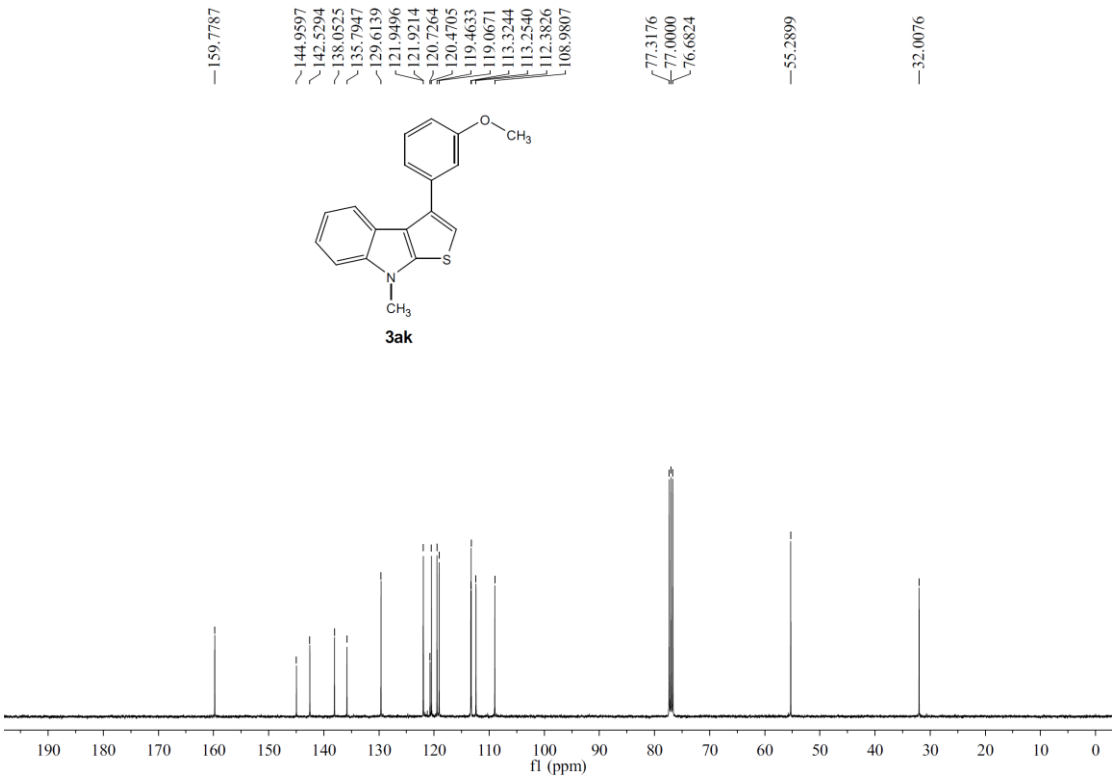
7.2974
7.2946
7.2799
7.2770
7.2593
7.2564
7.1388
7.1359
7.1210
7.1186
7.1162
7.1013
7.0985
6.9555
6.9510
6.9491
6.9449
6.9368
6.9323
6.9301
6.9259
6.7945
3.8606
3.8147
0.0000
O
CH3
S
N
CH3
1.06
2.00
2.08
1.06
1.06
1.06
1.00
3.01
3.01
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3ak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112.3826
108.9807
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77.0000
76.6824
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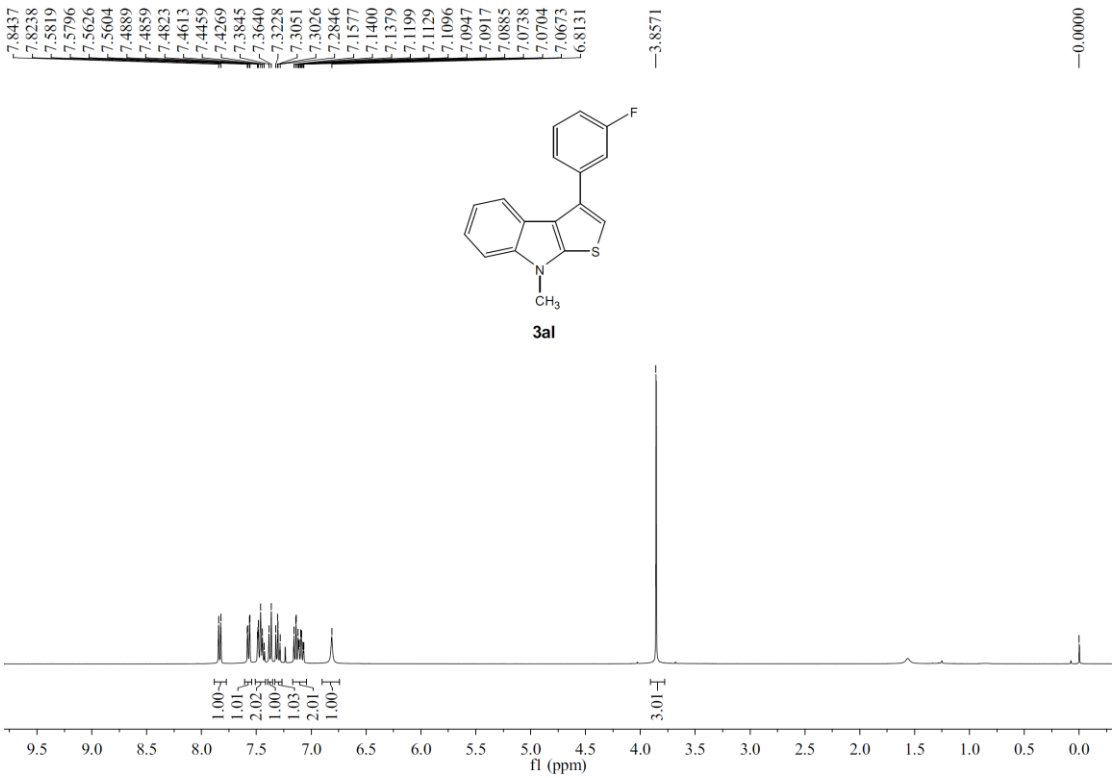
O
CH3
S
N
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ak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7.0917
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7.0704
7.0673
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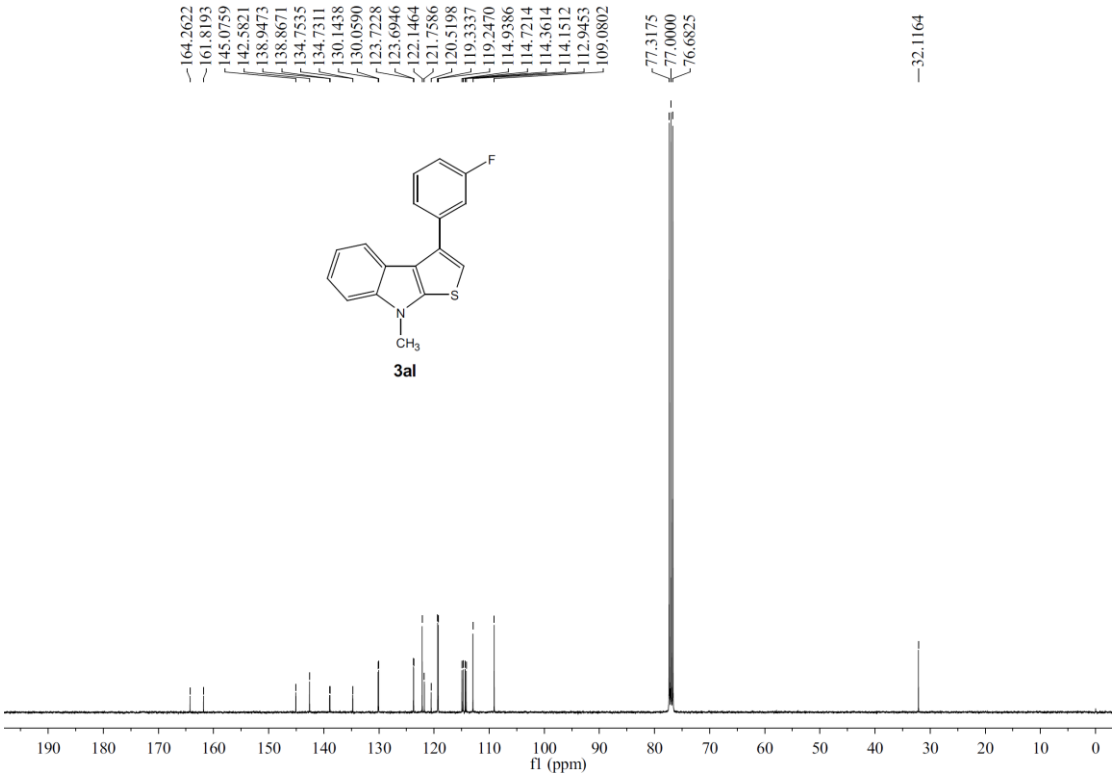
S
N
CH3
3al
1.00
1.01
2.02
1.00
1.03
2.01
1.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.6946
122.1464
121.7586
120.5198
119.3337
119.2470
114.9386
114.7214
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114.1512
112.9453
109.0802
77.3175
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F
S
N
CH3
3al
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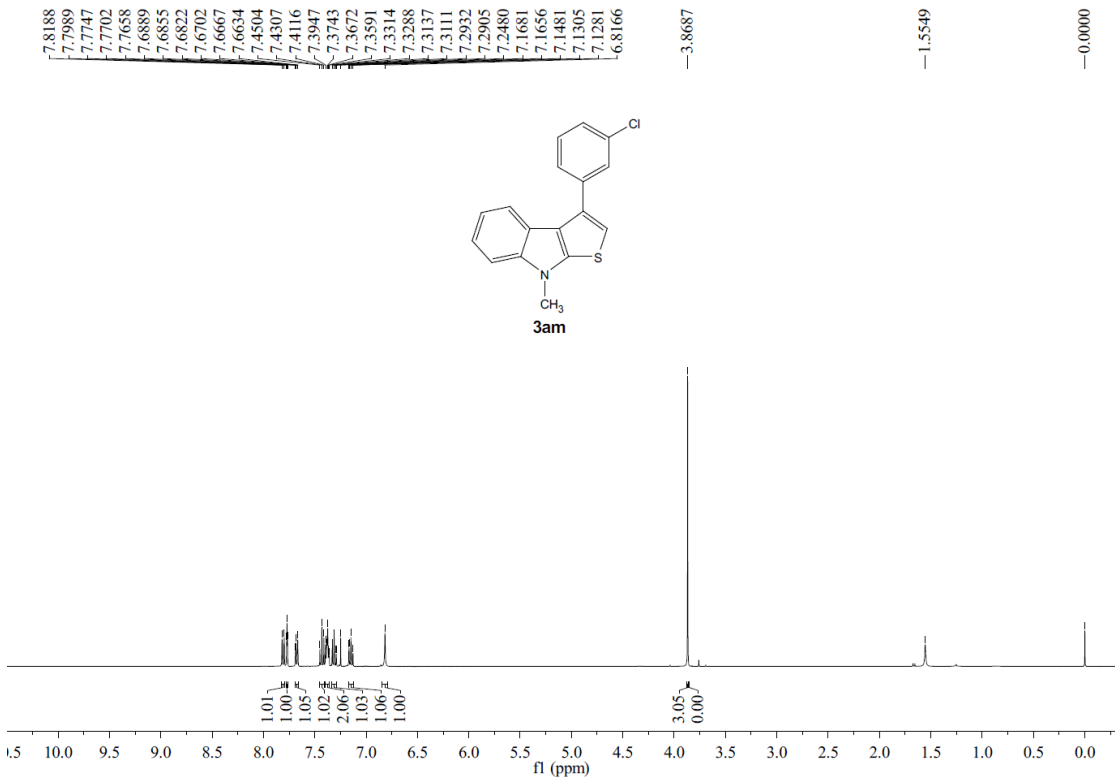
f1 (ppm)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7.4504
7.4307
7.4116
7.3947
7.3743
7.3672
7.3591
7.3314
7.3288
7.3137
7.3111
7.2932
7.2905
7.2480
7.1681
7.1656
7.1481
7.1305
7.1281
6.8166
3.8687
1.5549
0.0000
Cl
S
N
CH3
1.01
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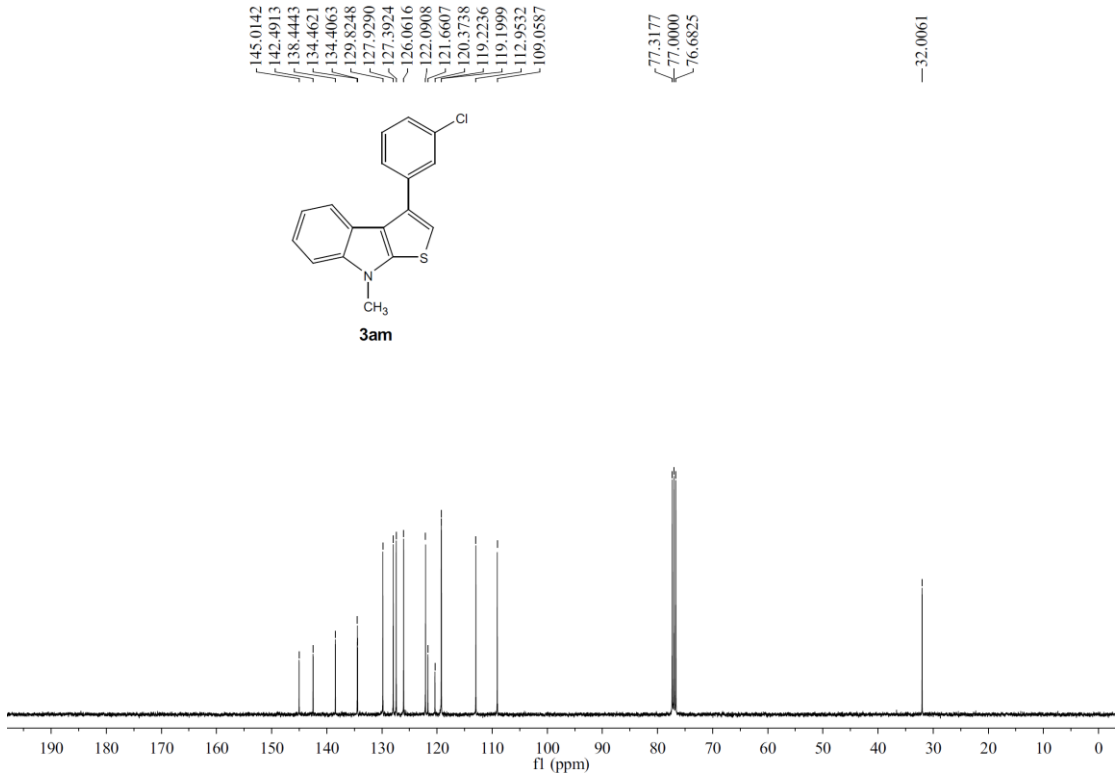
1.02
2.06
1.03
1.06
1.00
3.05
0.00
f1 (ppm)

3am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120.3738
119.2236
119.1999
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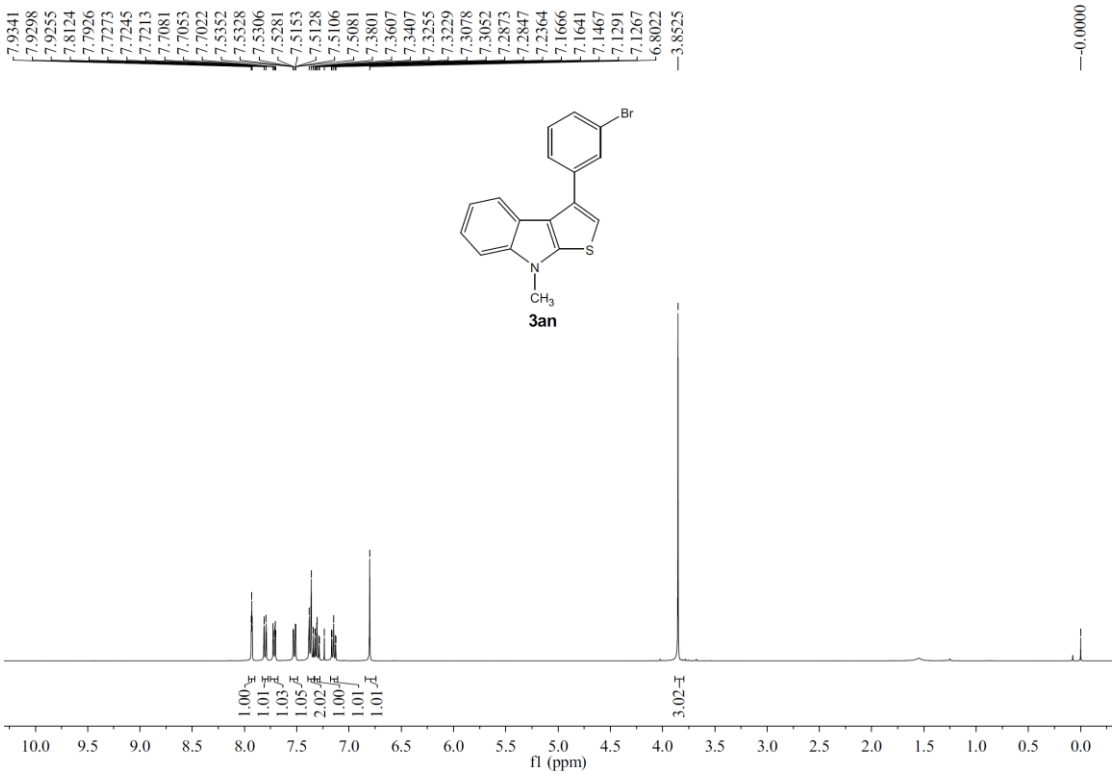
76.6825
32.0061
Cl
S
N
CH3
f1 (ppm)

3am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7.7245
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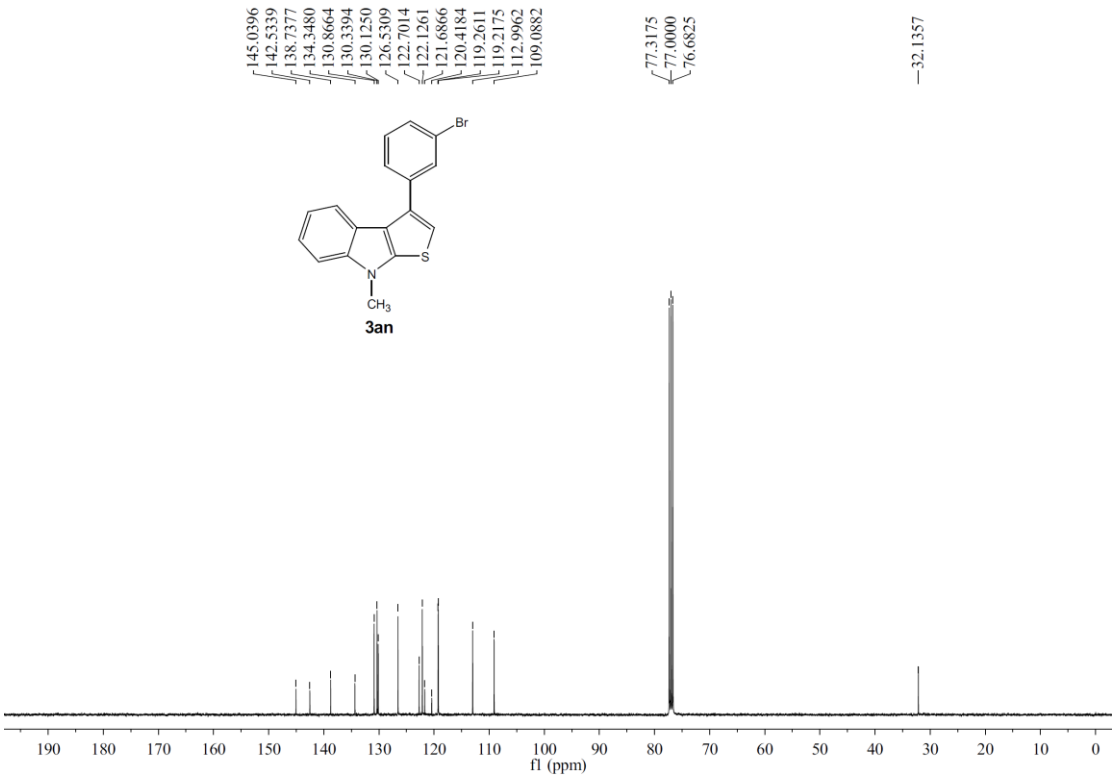
7.5352
7.5328
7.5306
7.5281
7.5153
7.5128
7.5106
7.5081
7.3801
7.3607
7.3407
7.3255
7.3229
7.3078
7.3052
7.2873
7.2847
7.2364
7.1666
7.1641
7.1467
7.1291
7.1267
6.8022
3.8525
0.0000
Br
N
S
CH3
3an
1.00
1.01
1.03
1.05
2.02
1.00
1.01
1.01
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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S
CH3
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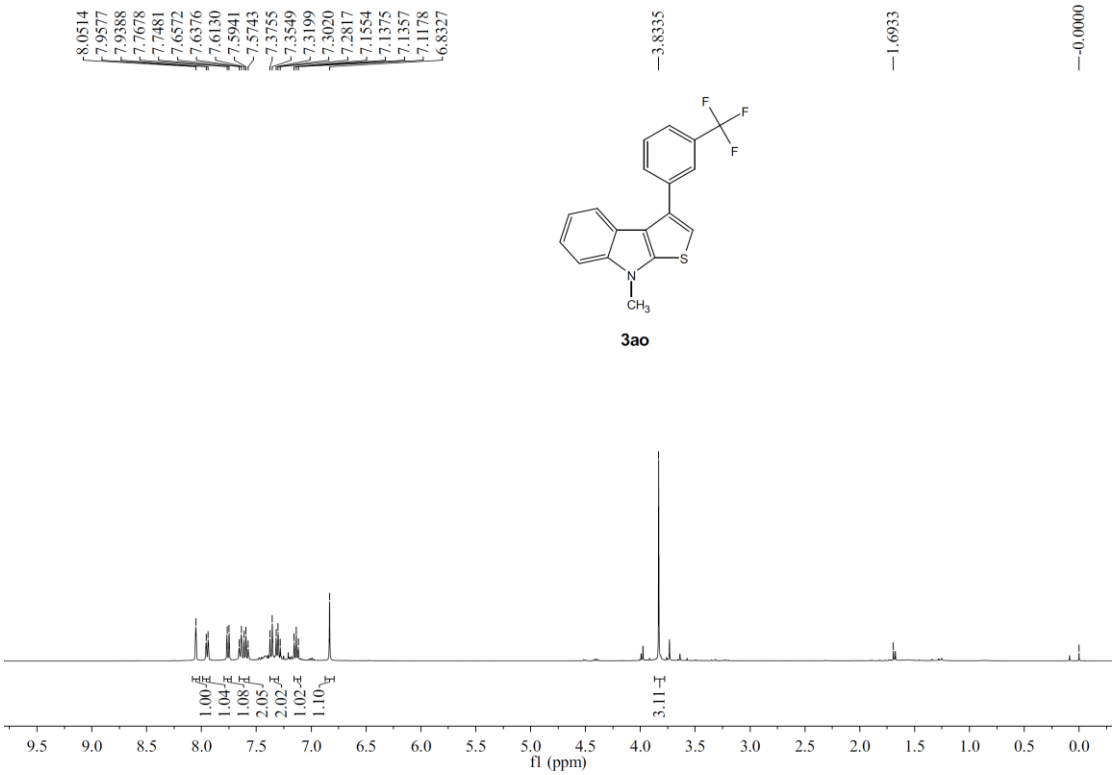
f1 (ppm)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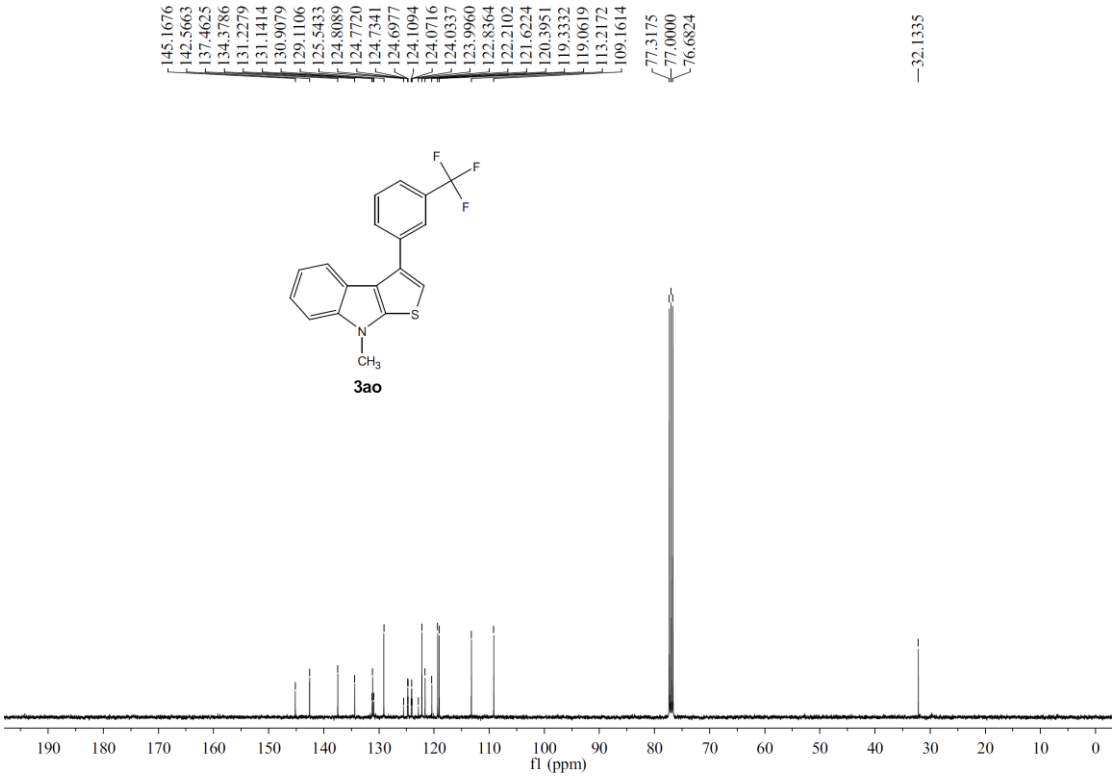
7.3549
7.3199
7.3020
7.2817
7.1554
7.1375
7.1357
7.1178
6.8327
3.8335
1.6933
0.0000
F
F
F
S
N
CH3
1.00
1.04
1.08
2.05
2.02
1.02
1.10
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ao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124.6977
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119.3332
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77.3175
77.0000
76.6824
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F
F
S
N
CH3
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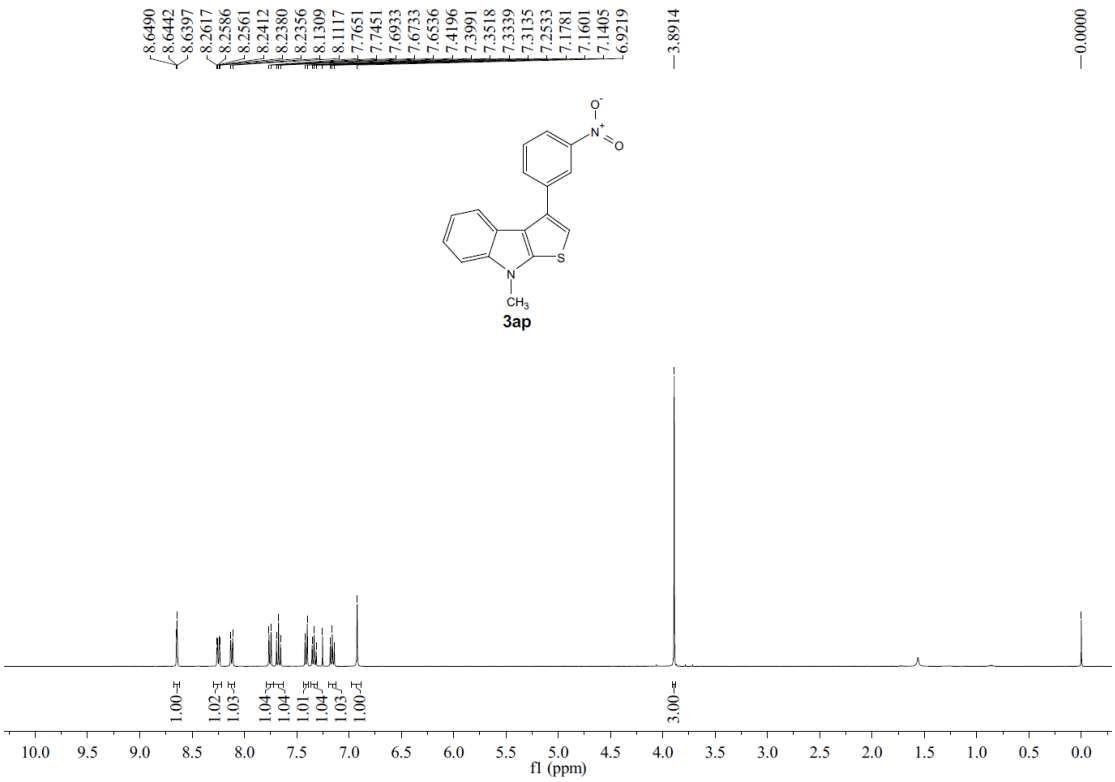
f1 (ppm)

3ao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8.1117
7.7651
7.7451
7.6933
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7.6536
7.4196
7.3991
7.3518
7.3339
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7.2533
7.1781
7.1601
7.1405
6.9219
3.8914
0.0000
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1.03
1.04
1.04
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1.03
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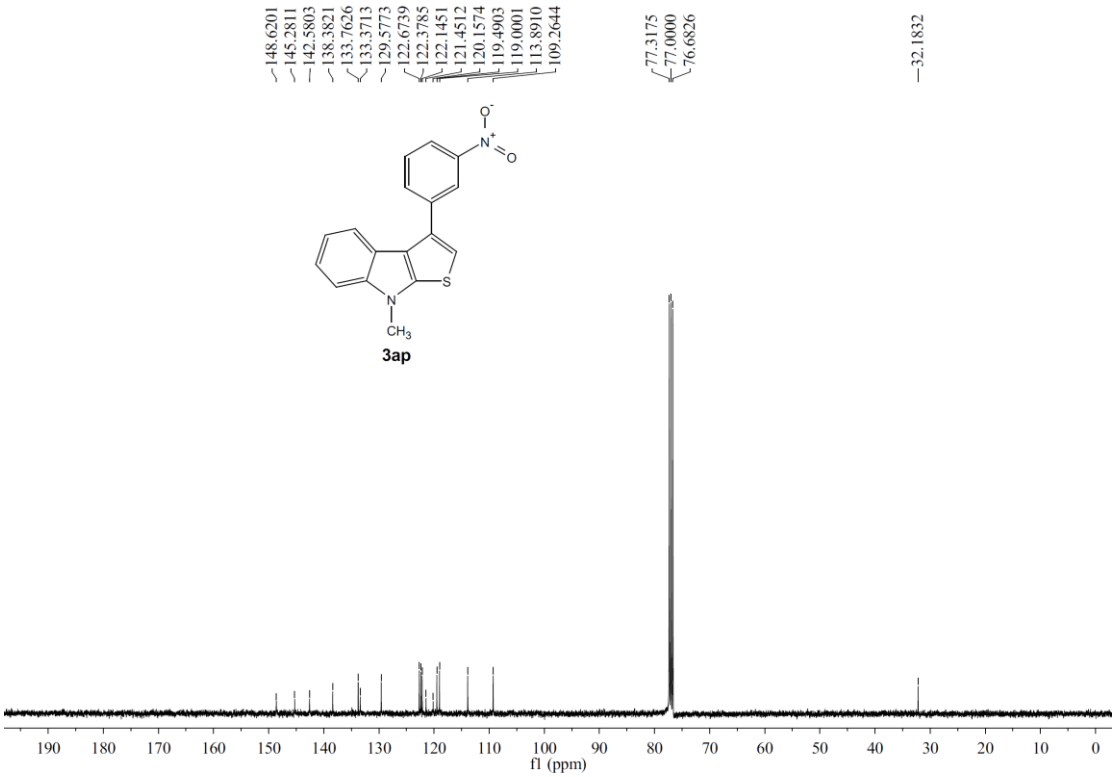
3.00
f1 (ppm)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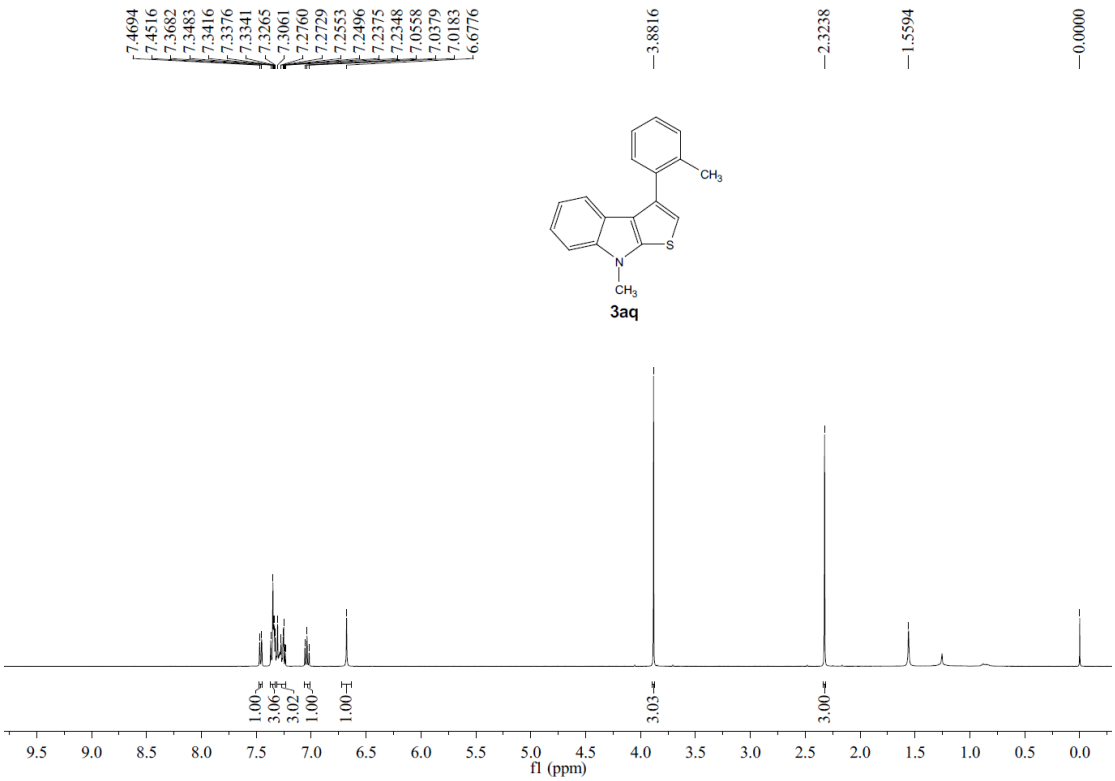
3ap
f1 (ppm)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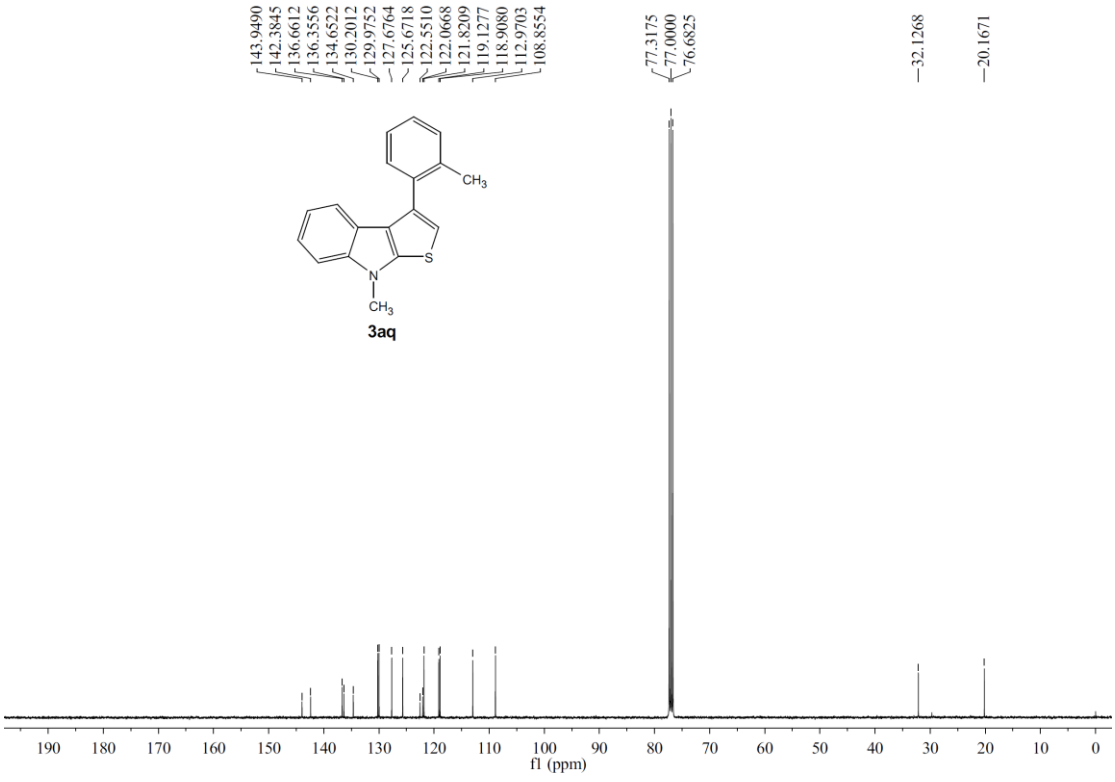
7.2496
7.2375
7.2348
7.0558
7.0379
7.0183
6.6776
3.8816
2.3238
1.5594
0.0000
CH3
S
N
CH3
3aq
1.00
3.06
3.02
1.00
1.00
3.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.3175
77.0000
76.6825
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CH3
S
N
CH3
3aq
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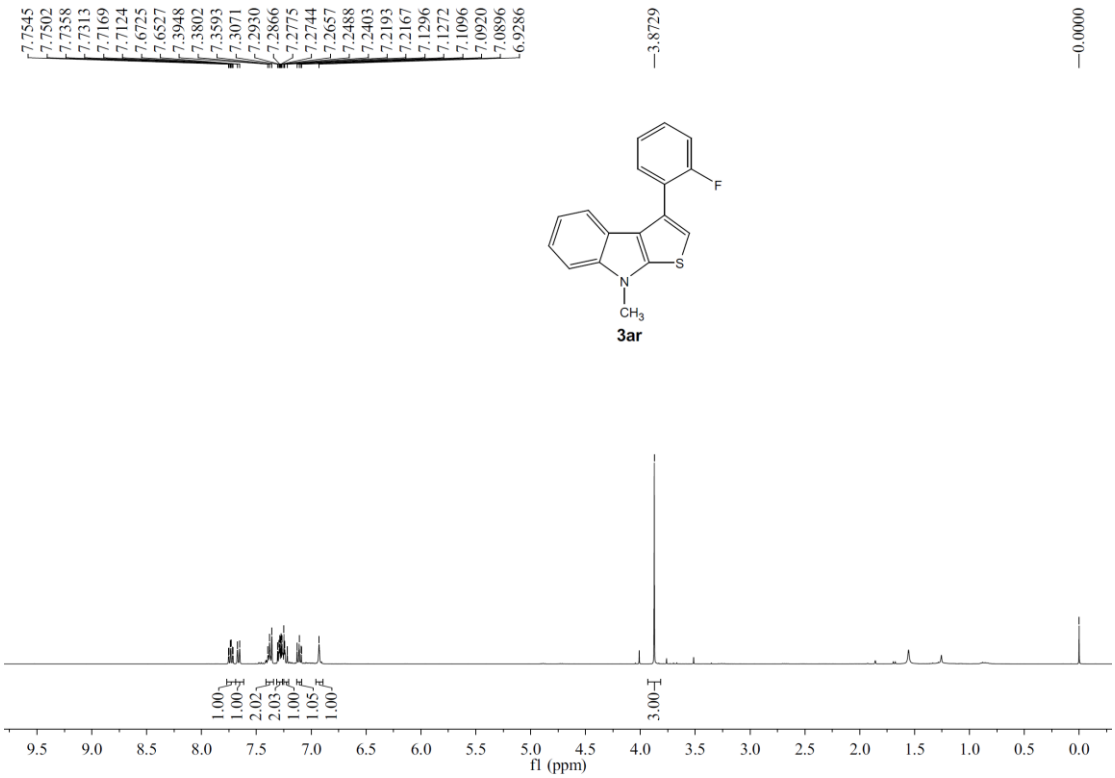
f1 (ppm)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7.1296
7.1272
7.1096
7.0920
7.0896
6.9286
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0.0000
F
S
N
CH3
3ar
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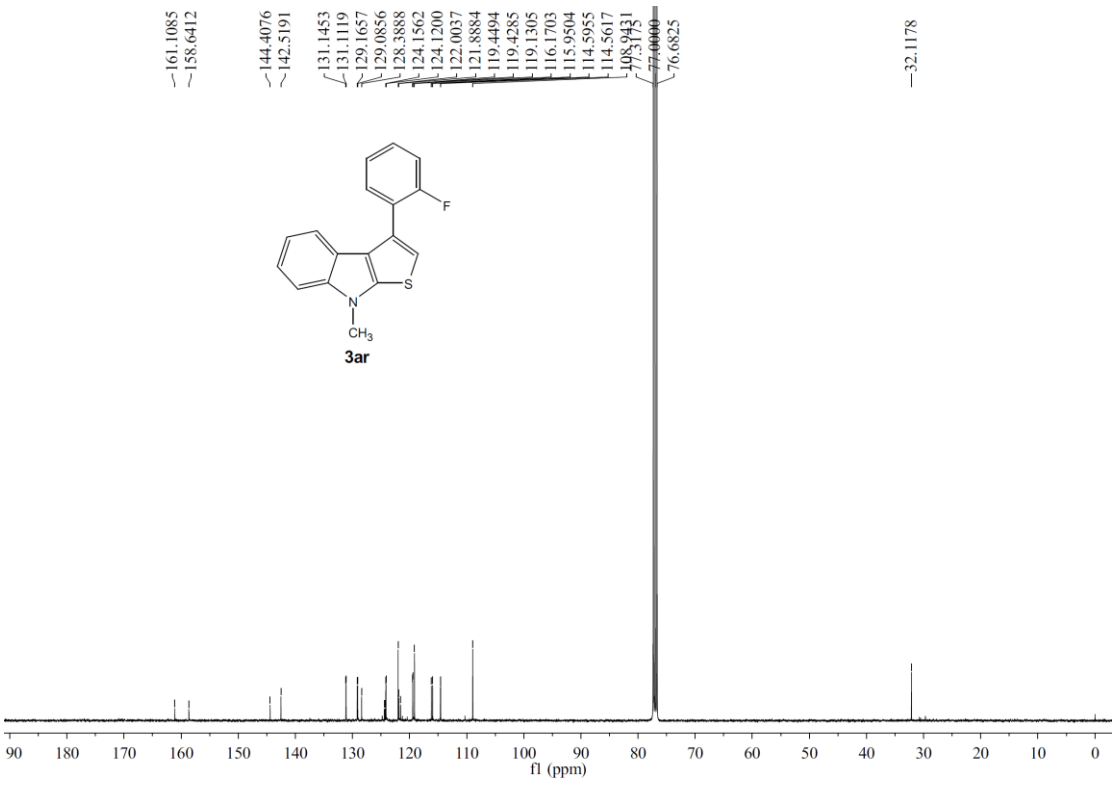
1.00
2.02
2.03
1.00
1.05
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.1200
122.0037
121.8884
119.4494
119.4285
119.1305
116.1703
115.9504
114.5955
114.5617
108.9431
77.3175
77.0000
76.6825
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F
S
N
CH3
3ar
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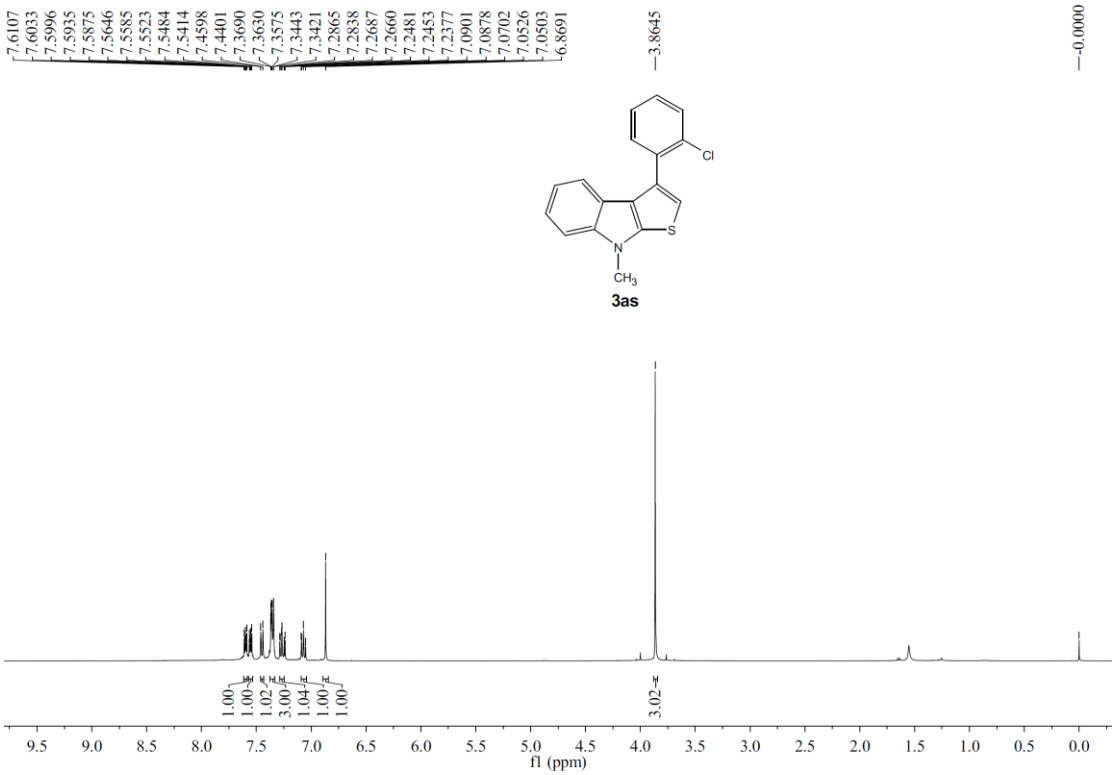
f1 (ppm)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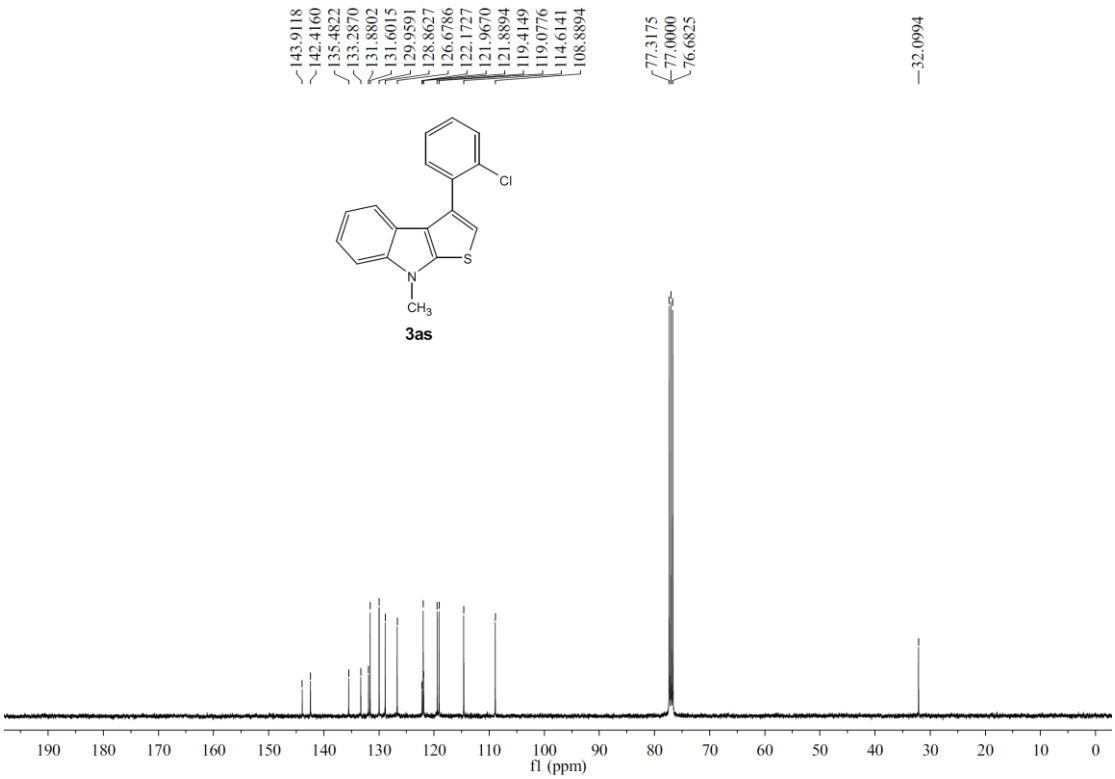
7.4401
7.3690
7.3630
7.3575
7.3443
7.3421
7.2865
7.2838
7.2687
7.2660
7.2481
7.2453
7.2377
7.0901
7.0878
7.0702
7.0526
7.0503
6.8691
3.8645
-0.0000
Cl
S
N
CH3
3as
1.00
1.00
1.02
3.00
1.04
1.00
1.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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119.4149
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114.6141
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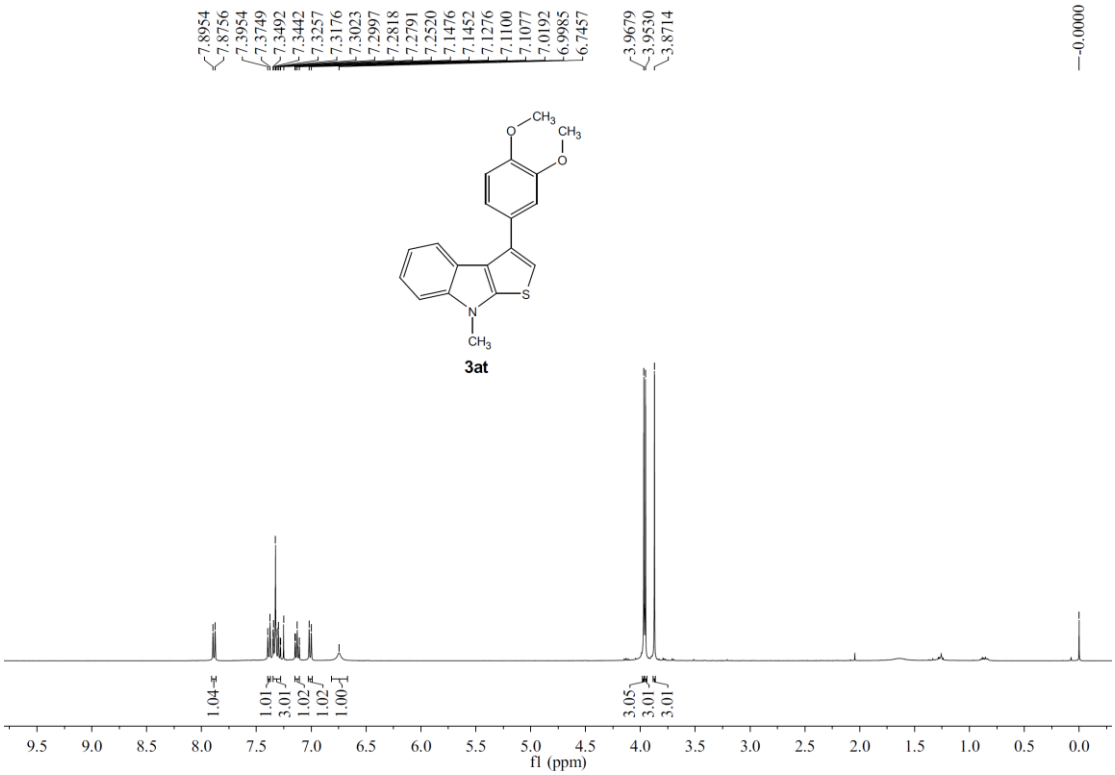
S
N
CH3
3as
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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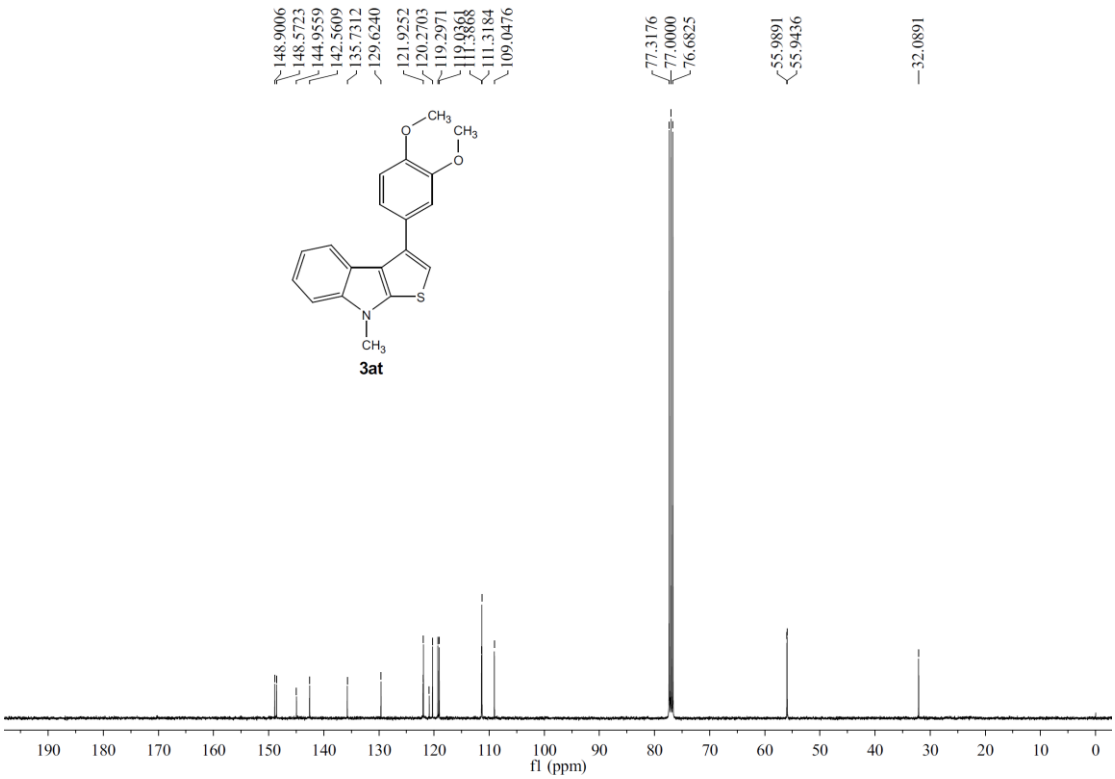
7.2791
7.2520
7.1476
7.1452
7.1276
7.1100
7.1077
7.0192
6.9985
6.7457
3.9679
3.9530
3.8714
-0.0000
3at
1.04
1.01
3.01
1.02
1.02
1.00
3.05
3.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.3176
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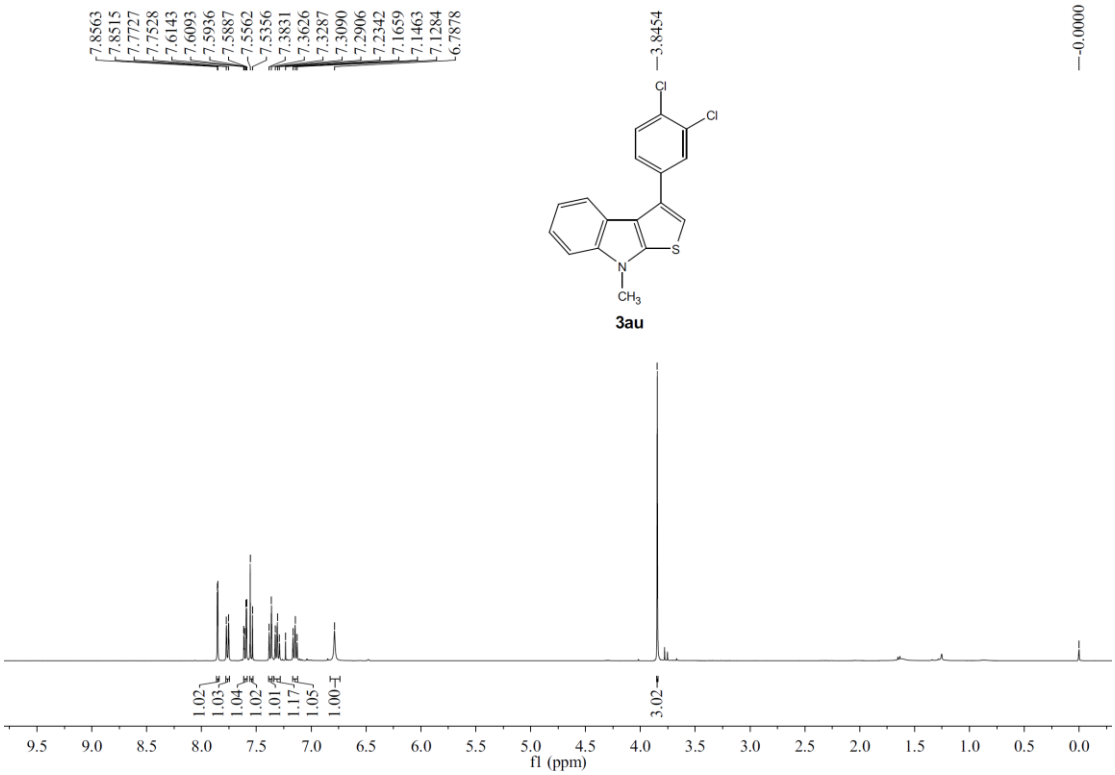
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5562
7.5356
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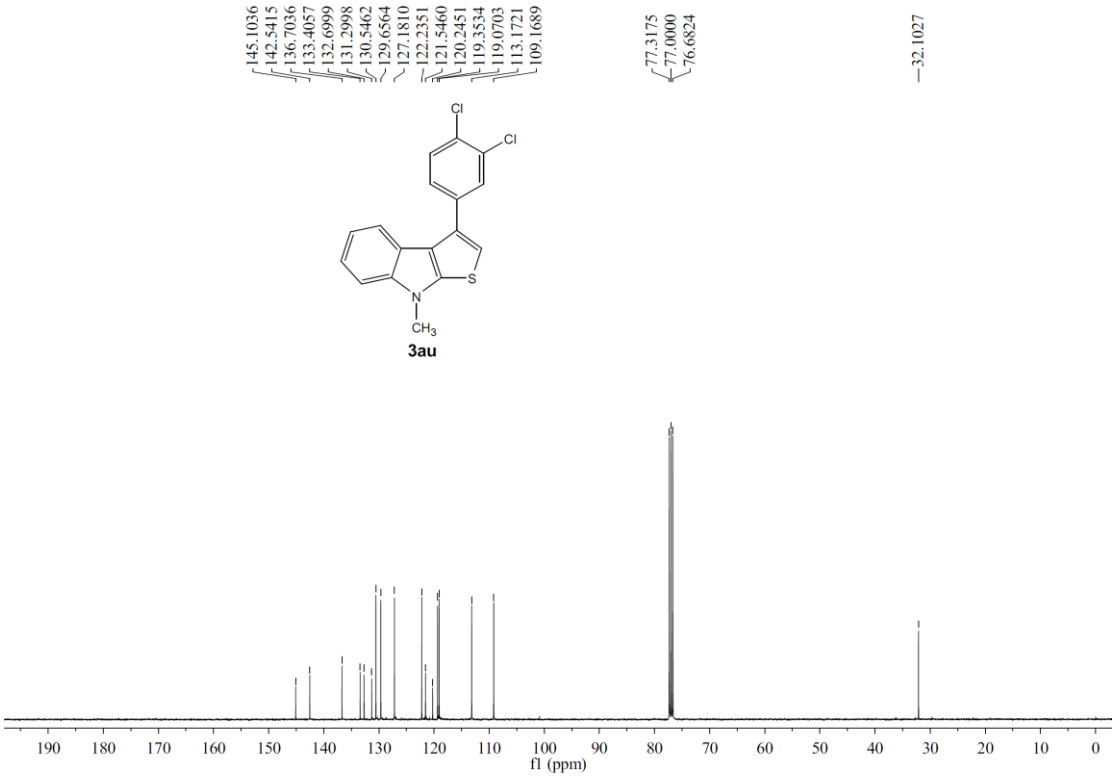
7.3626
7.3287
7.3090
7.2906
7.2342
7.1659
7.1463
7.1284
6.7878
3.8454
-0.0000
Cl
Cl
S
N
CH3
3au
1.02
1.03
1.04
1.02
1.01
1.17
1.05
1.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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120.2451
119.3534
119.0703
113.1721
109.1689
77.3175
77.0000
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32.1027
Cl
Cl
S
N
CH3
3au
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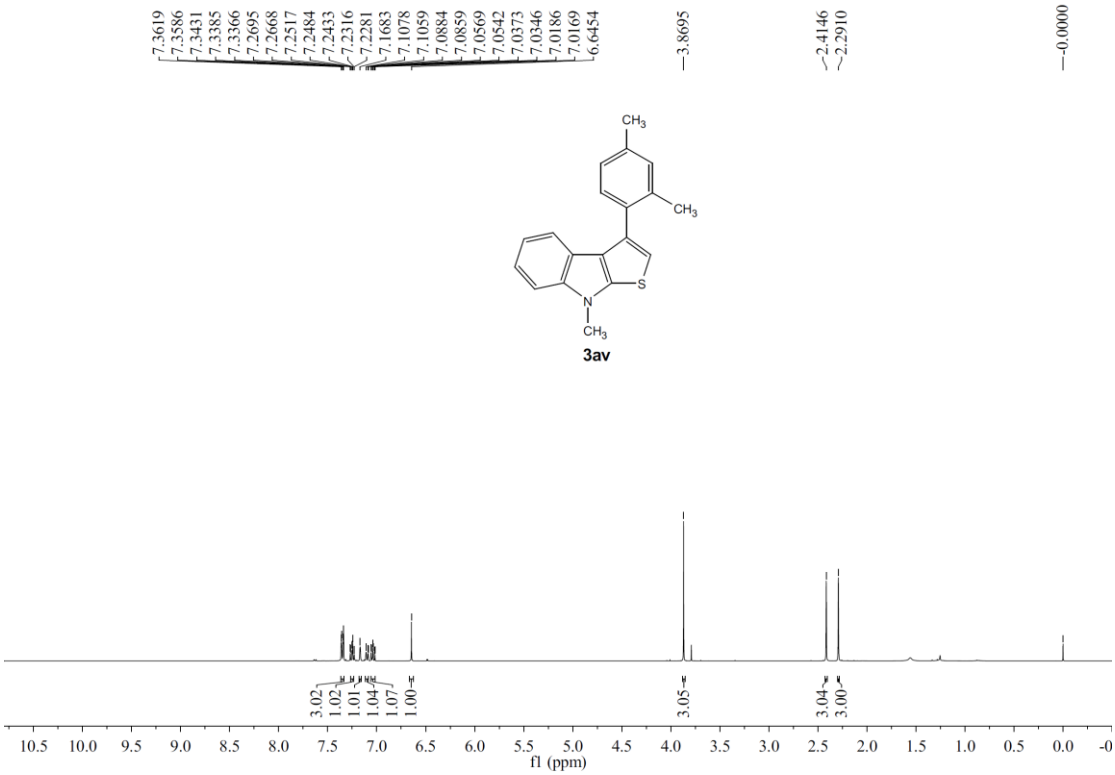
f1 (ppm)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7.3431
7.3385
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7.2695
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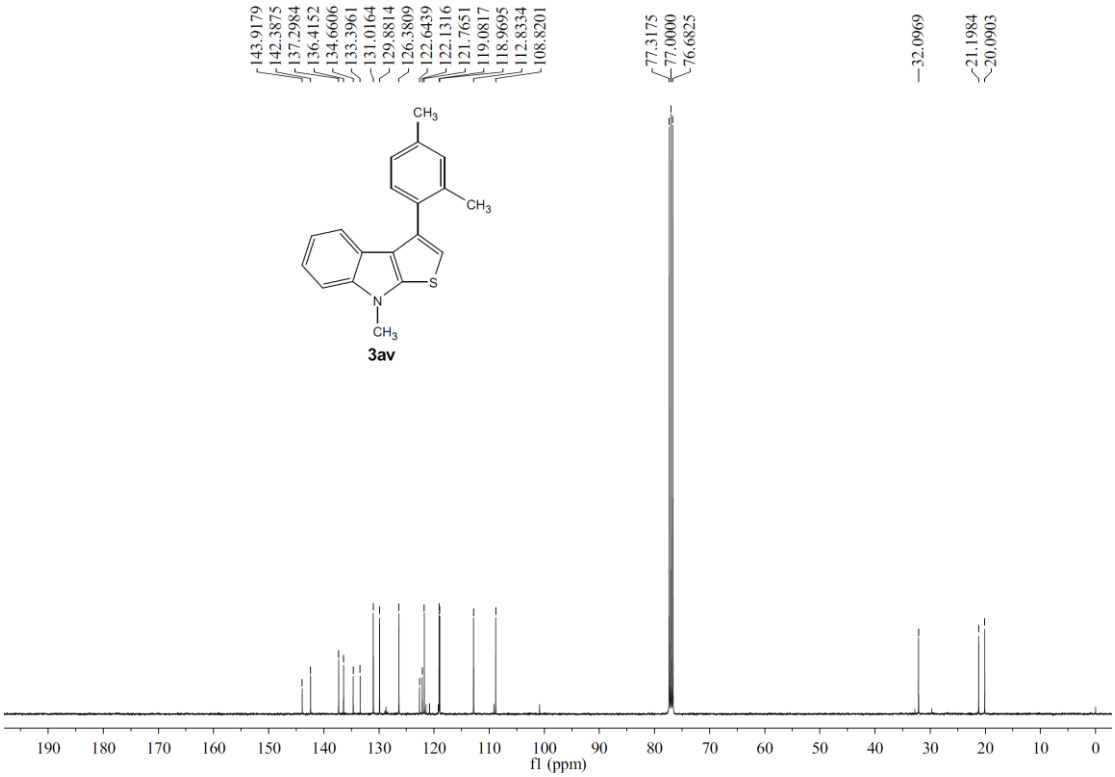
7.2517
7.2484
7.2433
7.2316
7.2281
7.1683
7.1078
7.1059
7.0884
7.0859
7.0569
7.0542
7.0373
7.0346
7.0186
7.0169
6.6454
3.8695
2.4146
2.2910
0.0000
CH3
CH3
S
N
CH3
3av
3.02
1.02
1.01
1.04
1.07
1.00
3.05
3.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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108.8201
77.3175
77.0000
76.6825
32.0969
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CH3
S
N
CH3
3av
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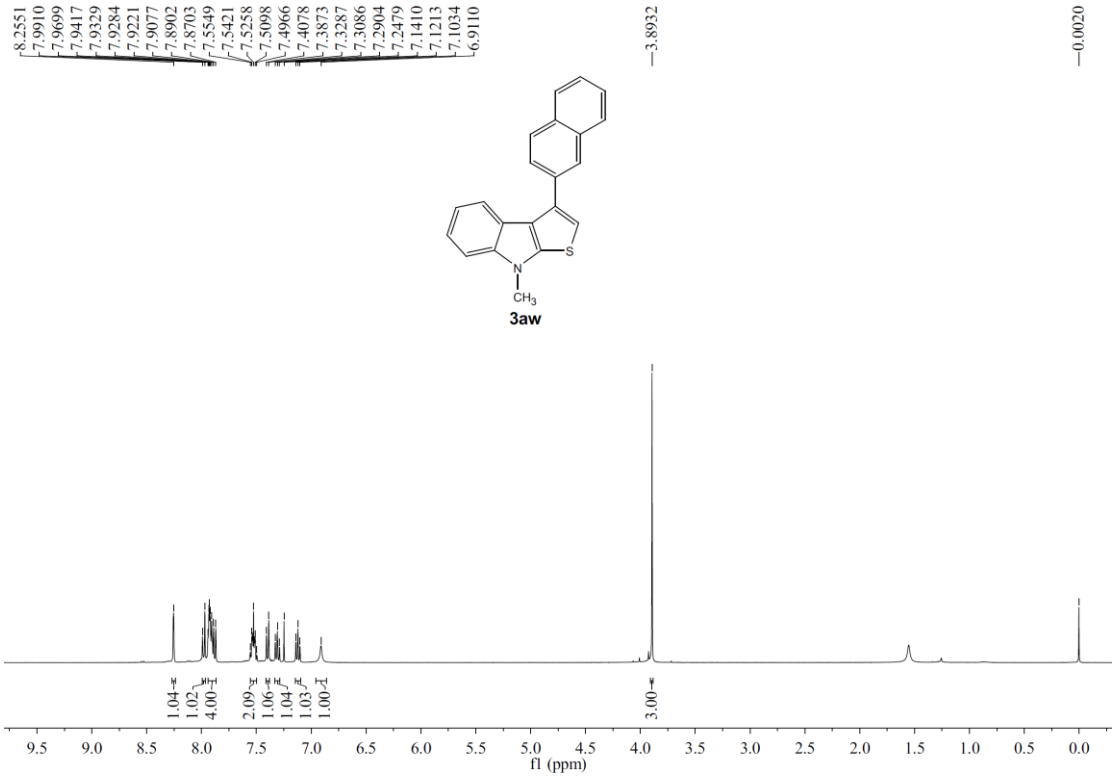
f1 (ppm)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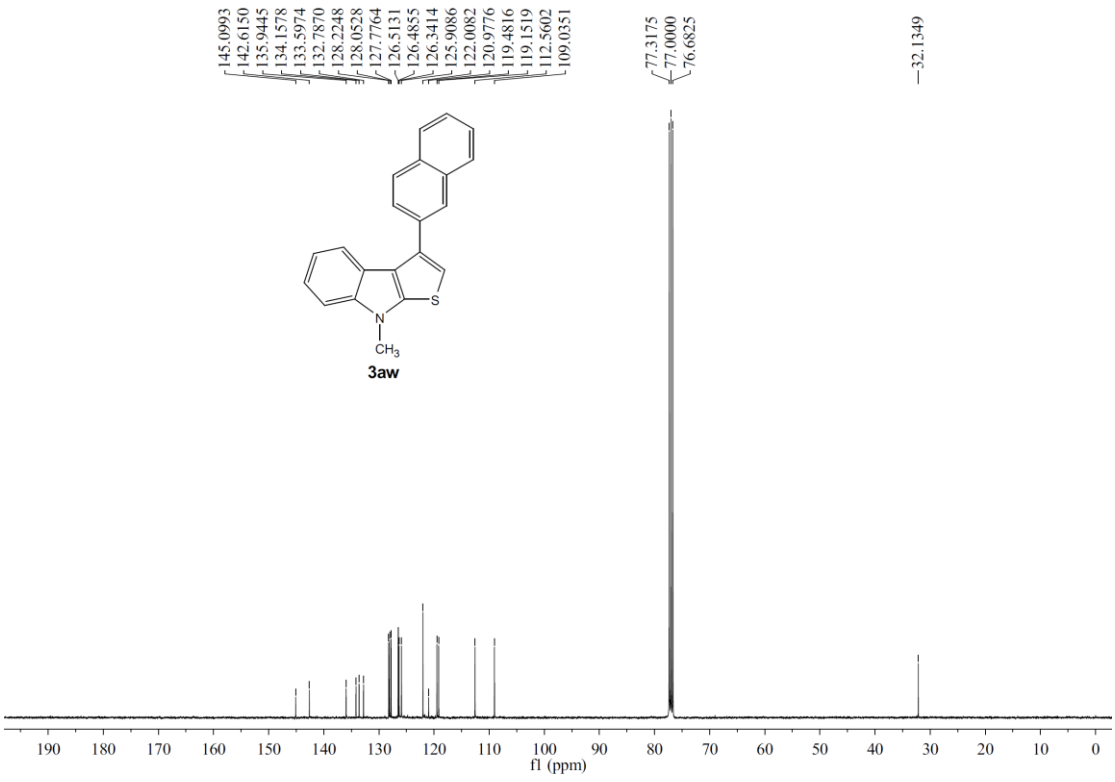
7.5421
7.5258
7.5098
7.4966
7.4078
7.3873
7.3287
7.3086
7.2904
7.2479
7.1410
7.1213
7.1034
6.9110
3.8932
0.0020
S
N
CH3
1.04
1.02
4.00
2.09
1.06
1.04
1.03
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3aw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126.3414
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112.5602
109.0351
77.3175
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S
N
CH3
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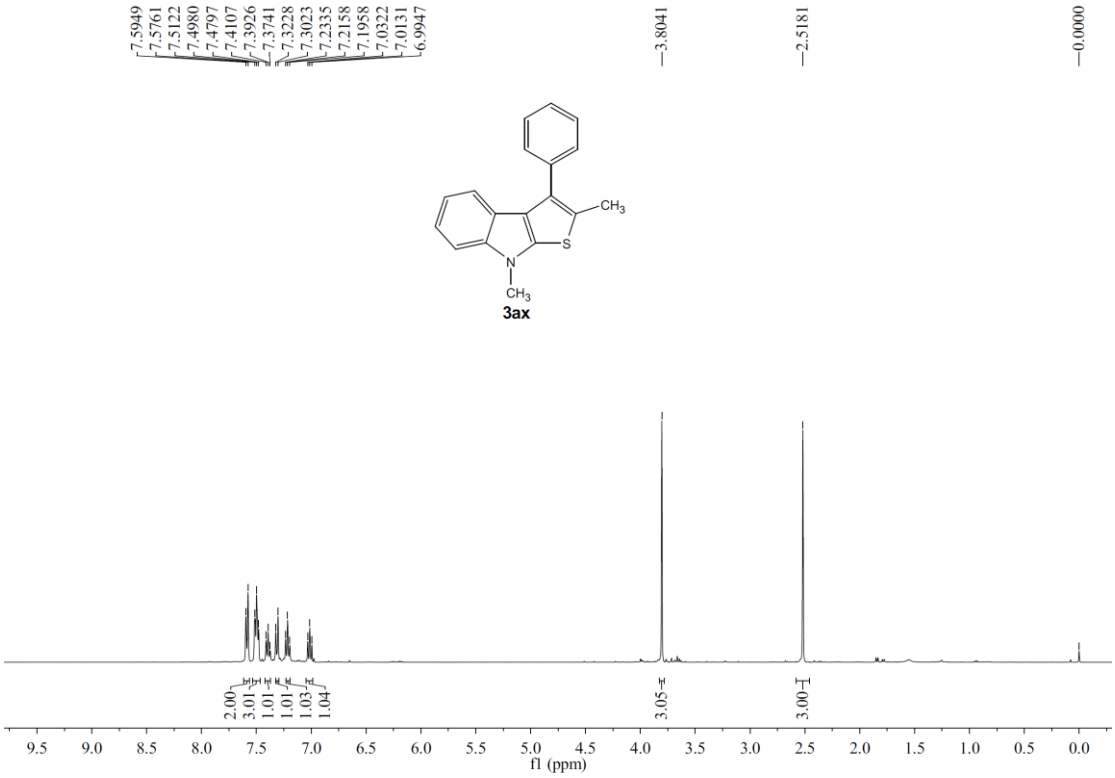
f1 (ppm)

3aw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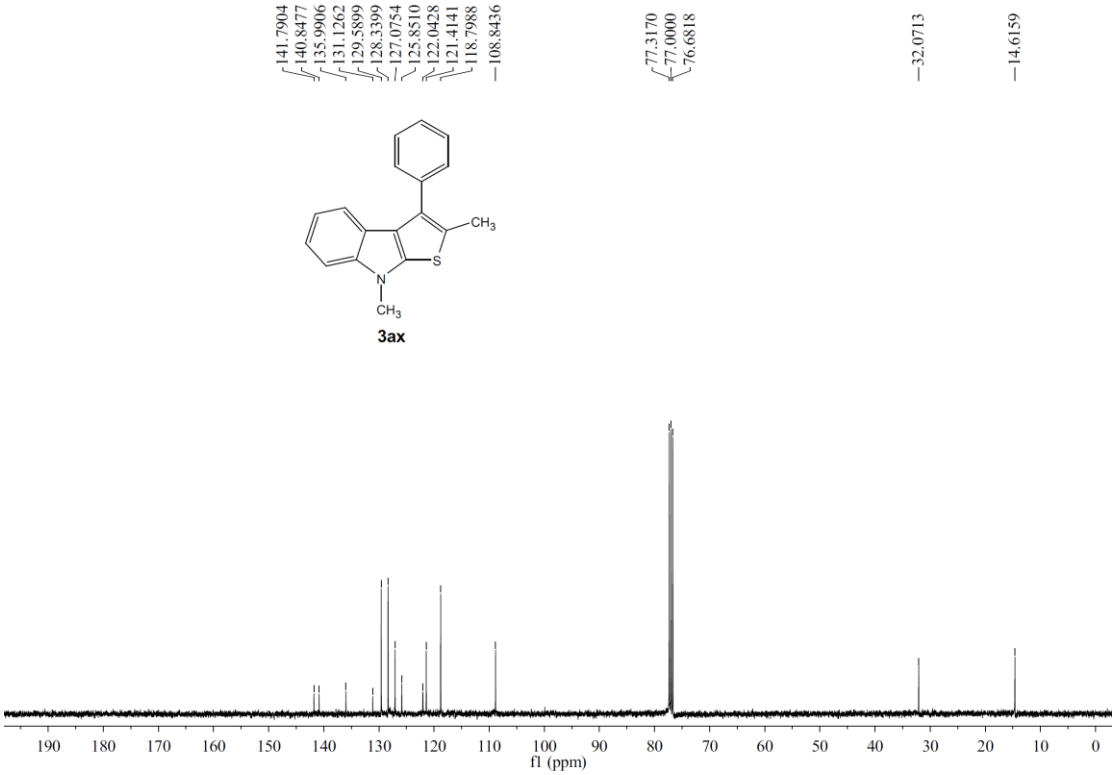
7.2335
7.2158
7.1958
7.0322
7.0131
6.9947
3.8041
2.5181
0.0000
CH3
S
N
CH3
2.00
3.01
1.01
1.01
1.03
1.04
3.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ax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127.0754
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122.0428
121.4141
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77.3170
77.0000
76.6818
32.0713
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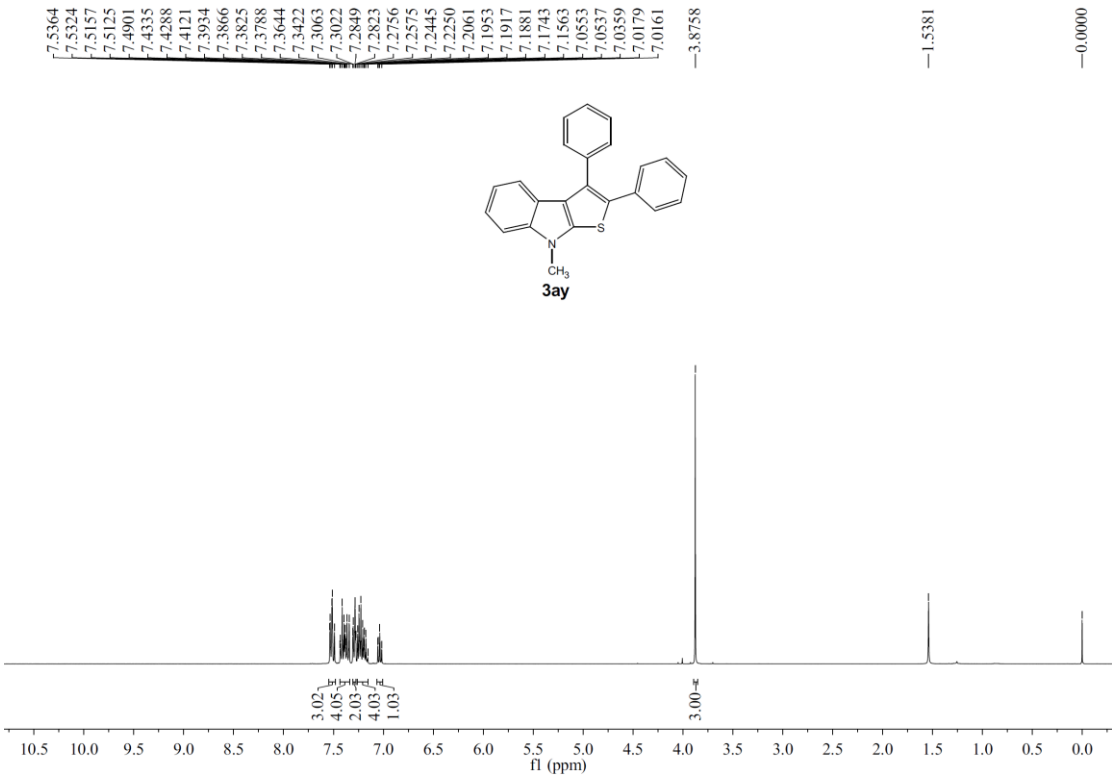
CH3
S
N
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ax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7.3644
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7.2823
7.2756
7.2575
7.2445
7.2250
7.2061
7.1953
7.1917
7.1881
7.1743
7.1563
7.0553
7.0537
7.0359
7.0179
7.0161
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S
N
CH3
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3.02
4.05
2.03
4.03
1.03
3.00
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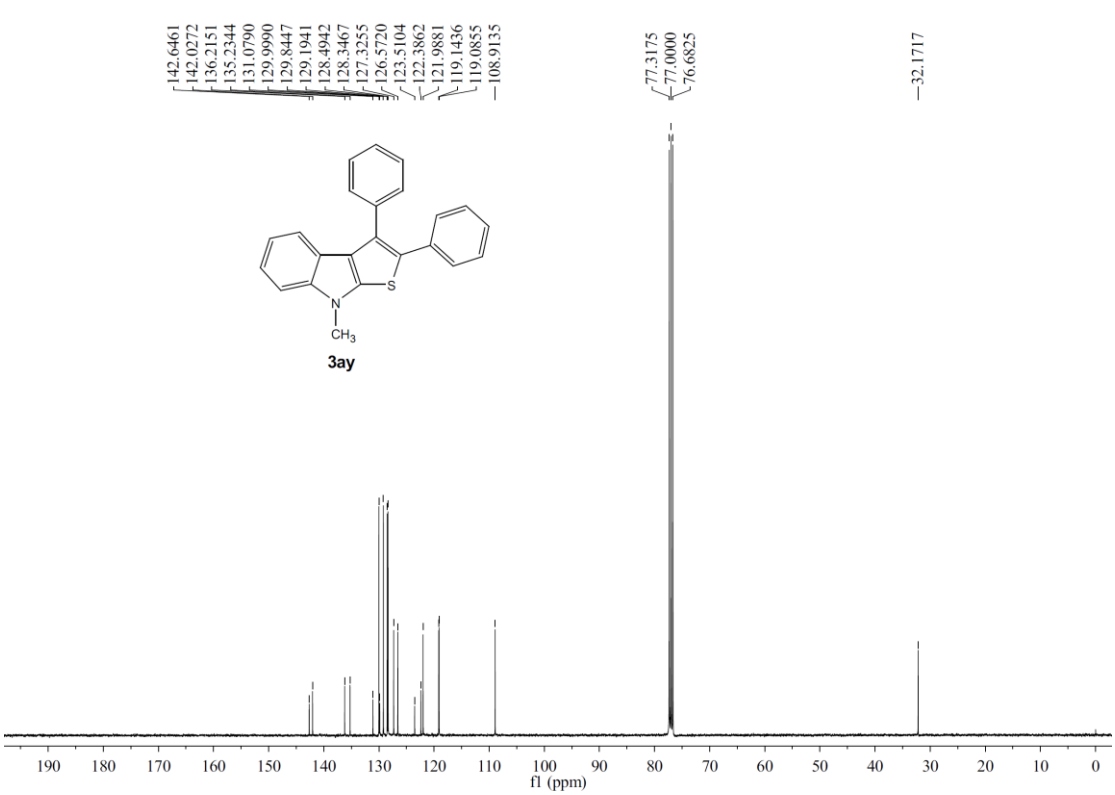
f1 (ppm)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S
N
CH3
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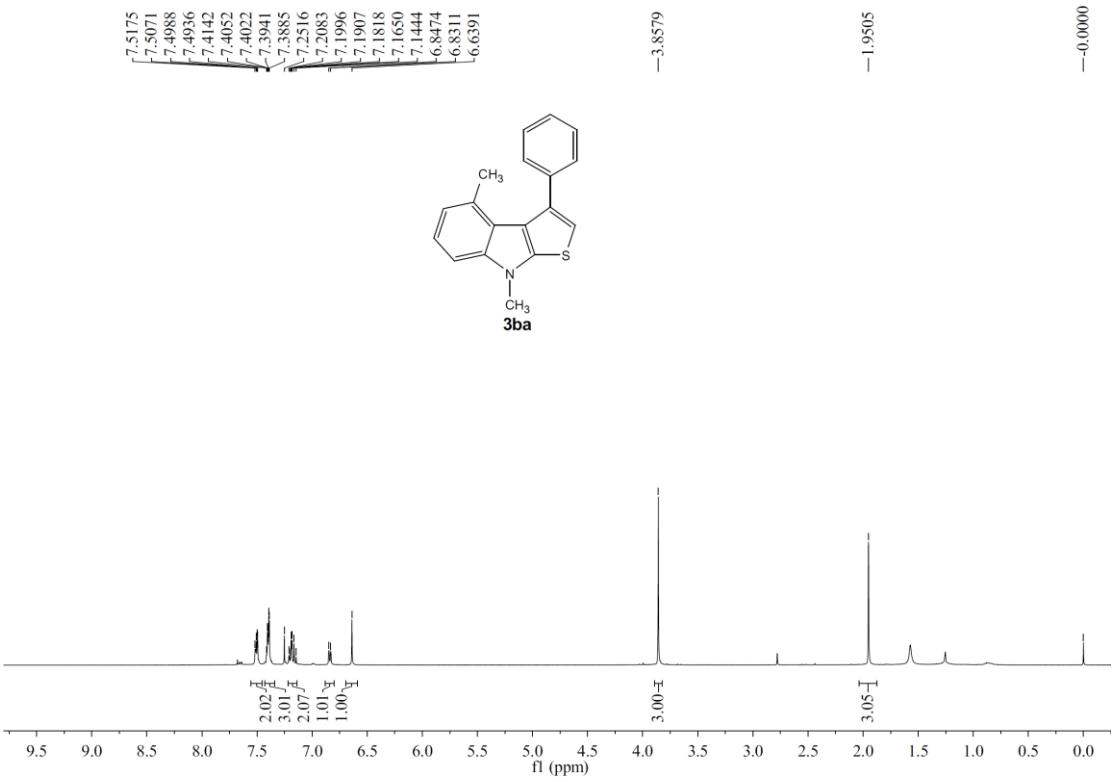
f1 (ppm)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3.8579
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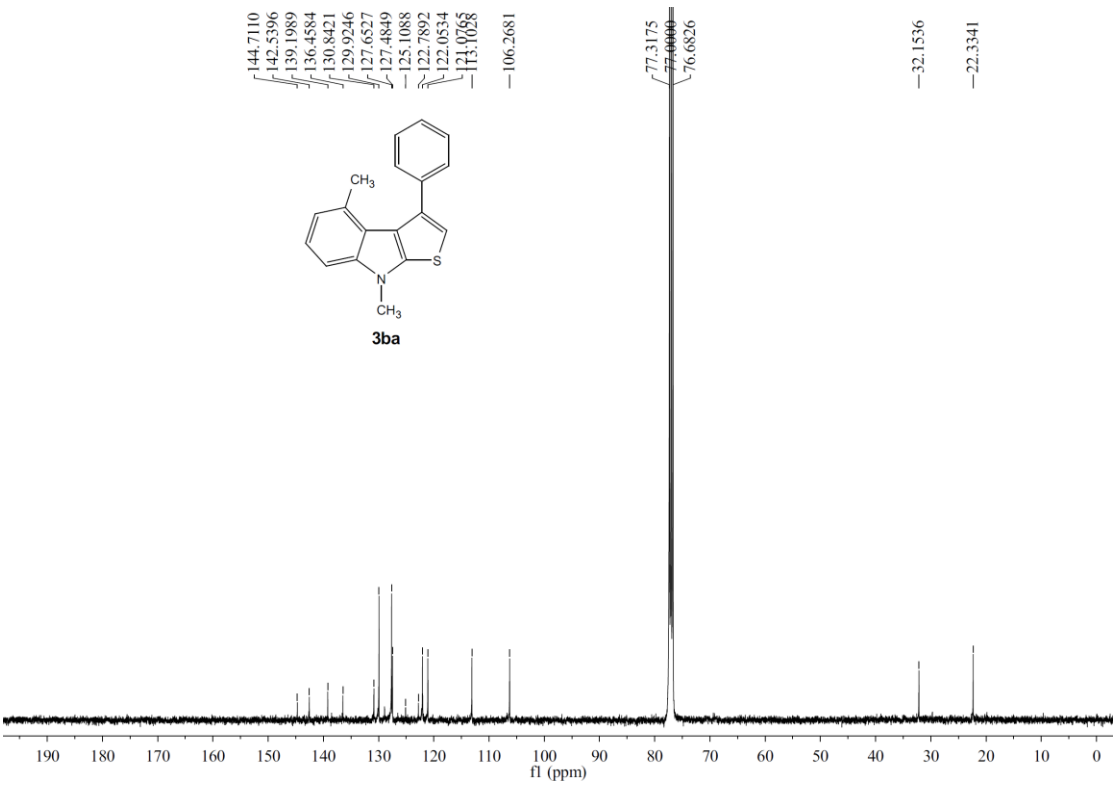
CH3
S
N
CH3
3ba
2.02
3.01
2.07
1.01
1.00
3.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
76.6826
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CH3
S
N
CH3
3ba
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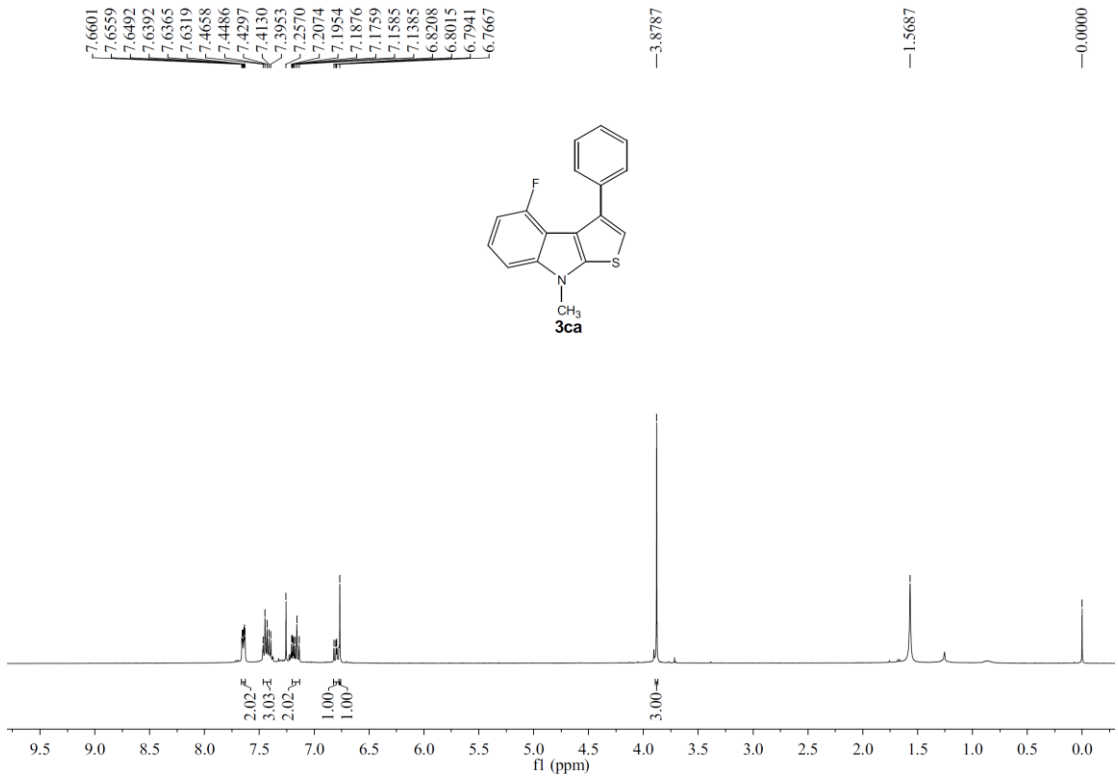
f1 (ppm)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7.2074
7.1954
7.1876
7.1759
7.1585
7.1385
6.8208
6.8015
6.7941
6.7667
3.8787
1.5687
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N
CH3
3ca
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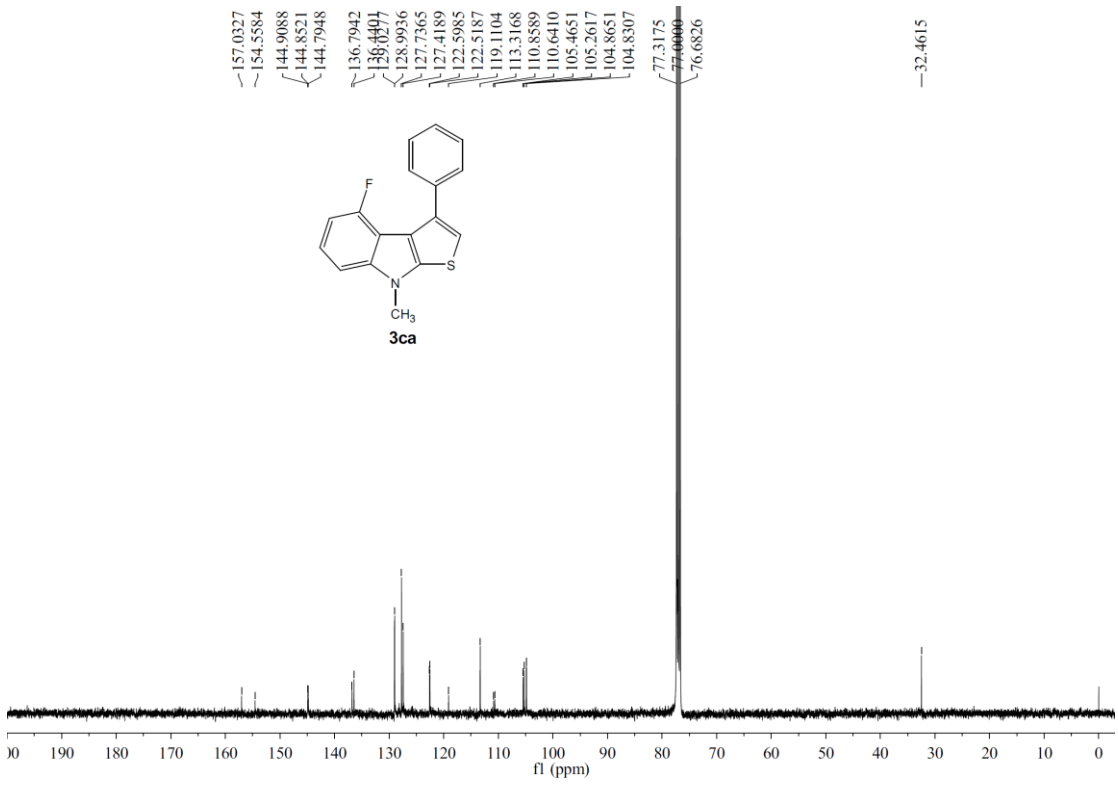
3.03
2.02
1.00
1.00
3.00
f1 (ppm)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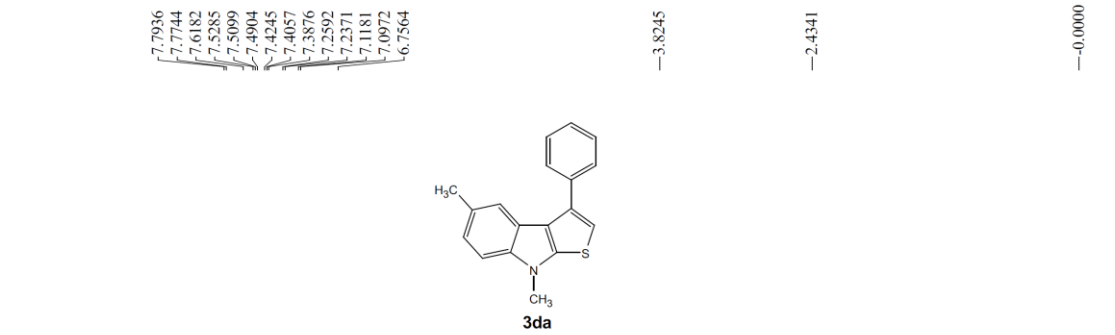
F
S
N
CH3
3ca
f1 (ppm)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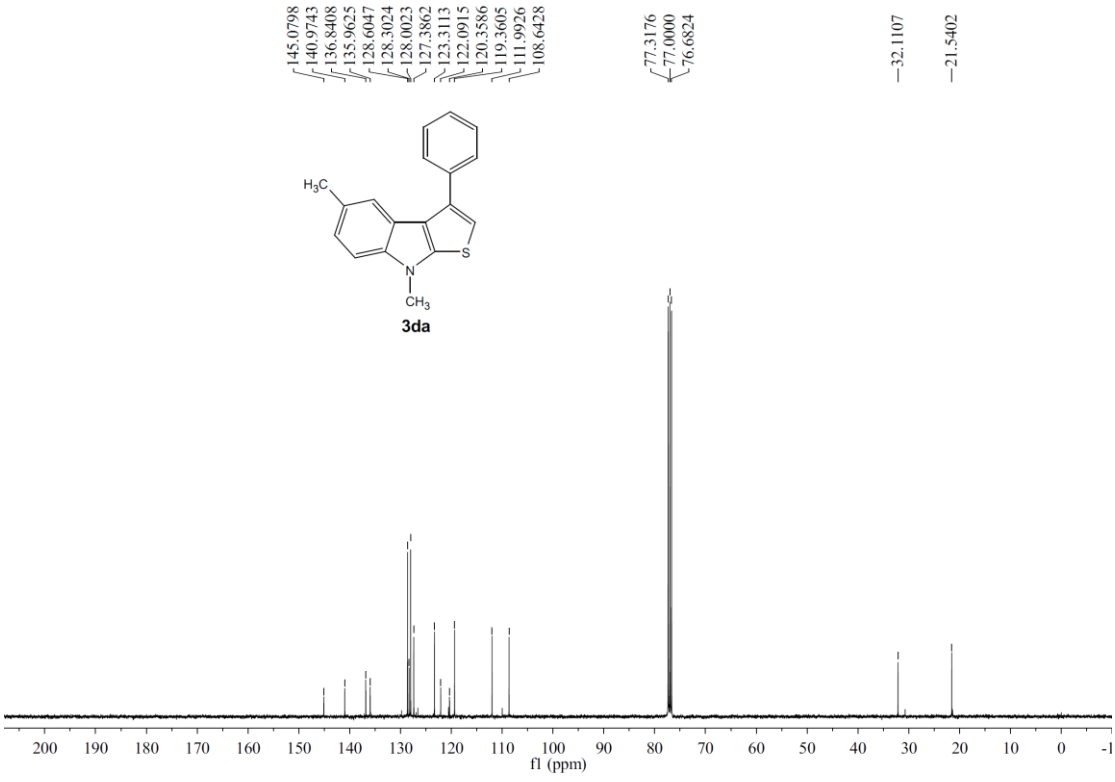
7.1181
7.0972
6.7564
3.8245
2.4341
0.0000
H3C
N
S
CH3
2.00
1.02
2.00
1.01
1.05
1.01
1.01
3.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3da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111.9926
108.6428
77.3176
77.0000
76.6824
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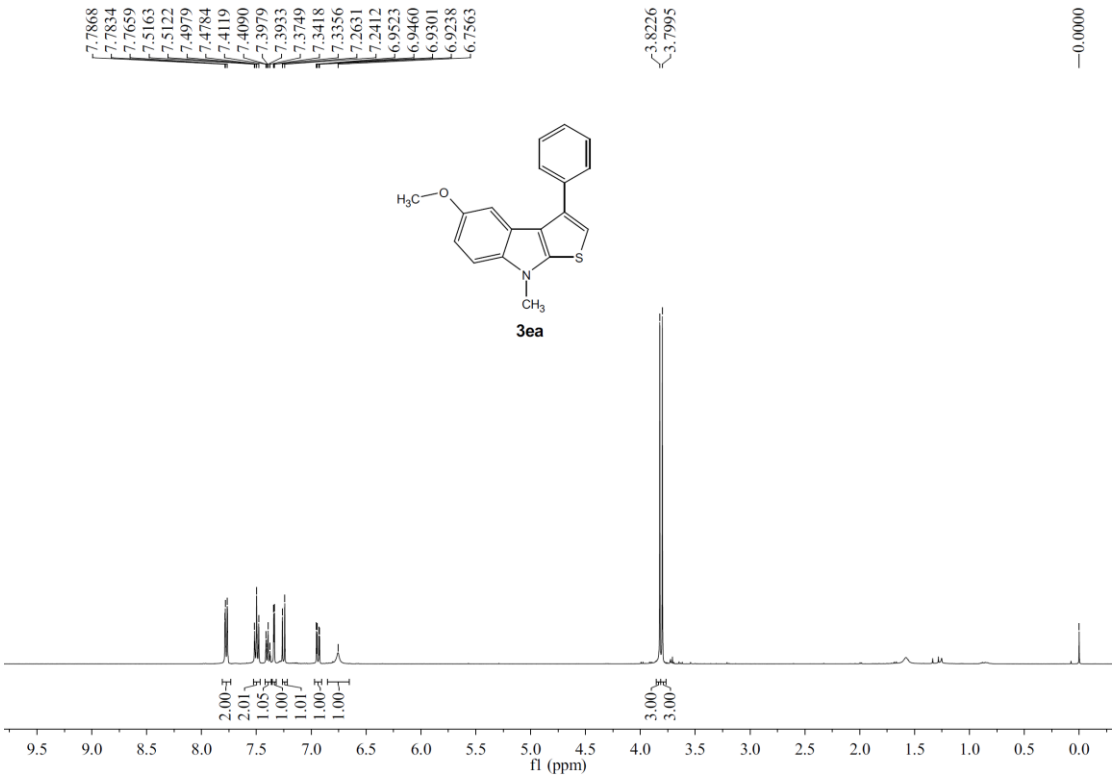
N
S
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

3da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6.9460
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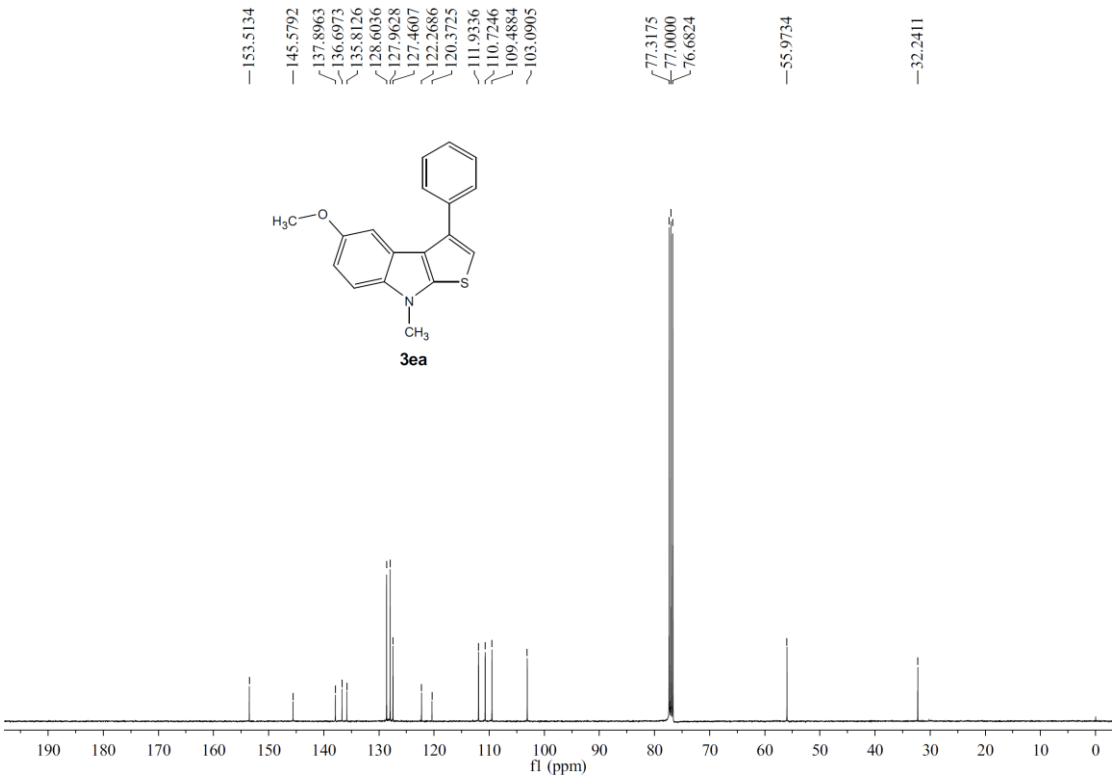
6.9238
6.7563
3.8226
3.7995
0.0000
H3C
O
S
N
CH3
3ea
2.00
2.01
1.05
1.00
1.01
1.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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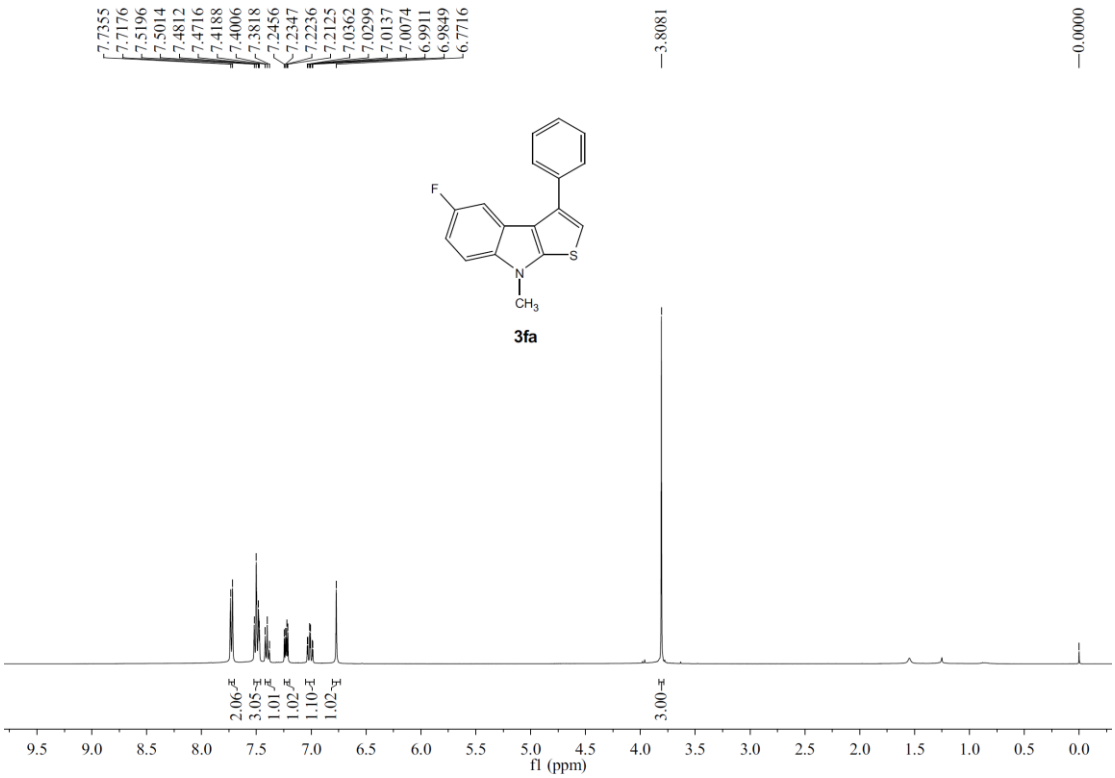
55.9734
32.2411
H3C
O
S
N
CH3
3ea
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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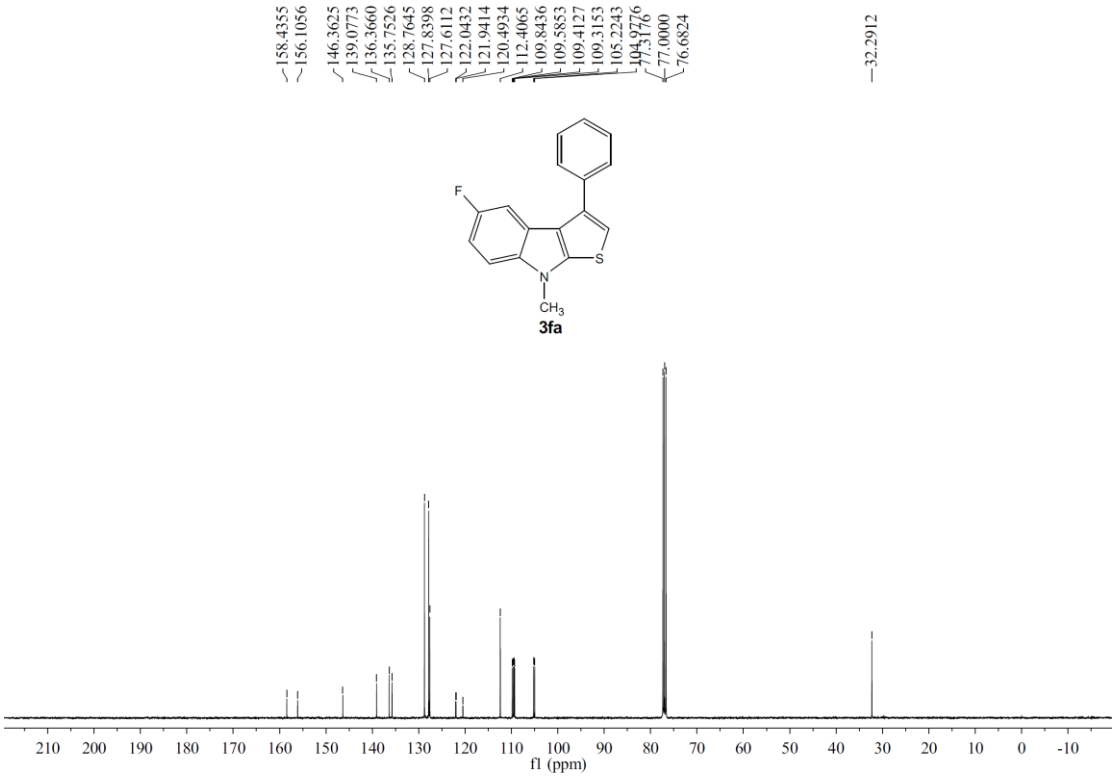
7.2236
7.2125
7.0362
7.0299
7.0137
7.0074
6.9911
6.9849
6.7716
3.8081
0.0000
F
S
N
CH3
2.06
3.05
1.01
1.02
1.10
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3fa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109.4127
109.3153
105.2243
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77.0000
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F
S
N
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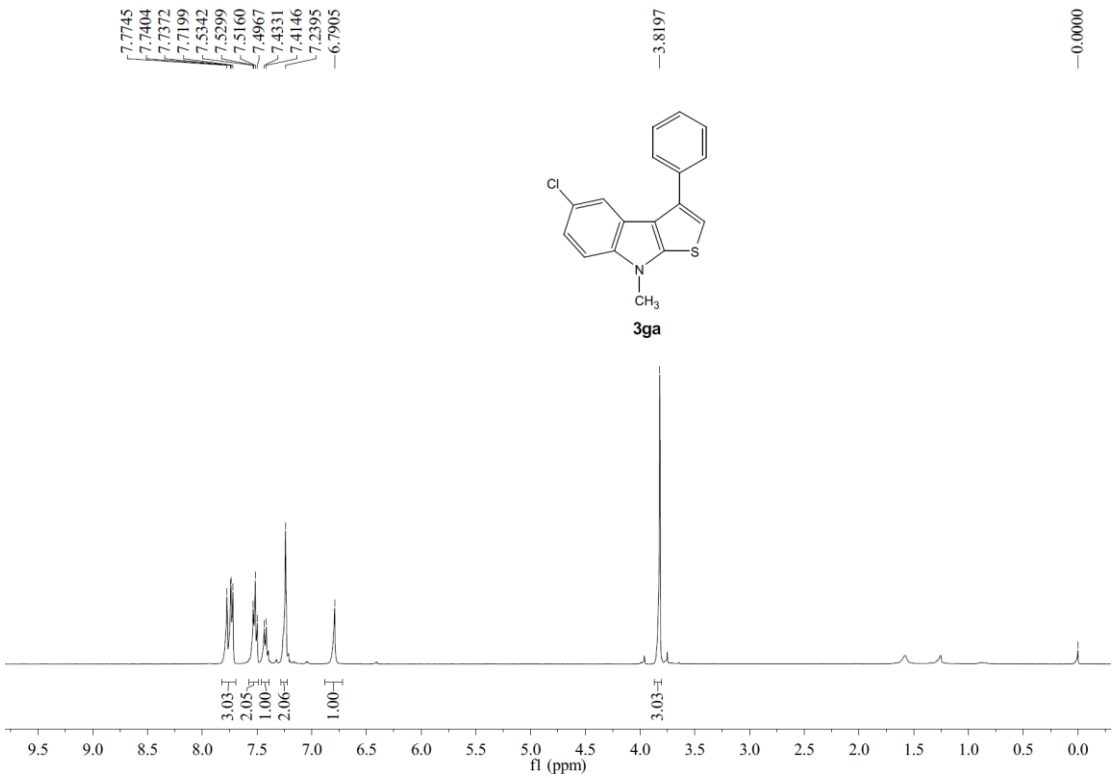
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3fa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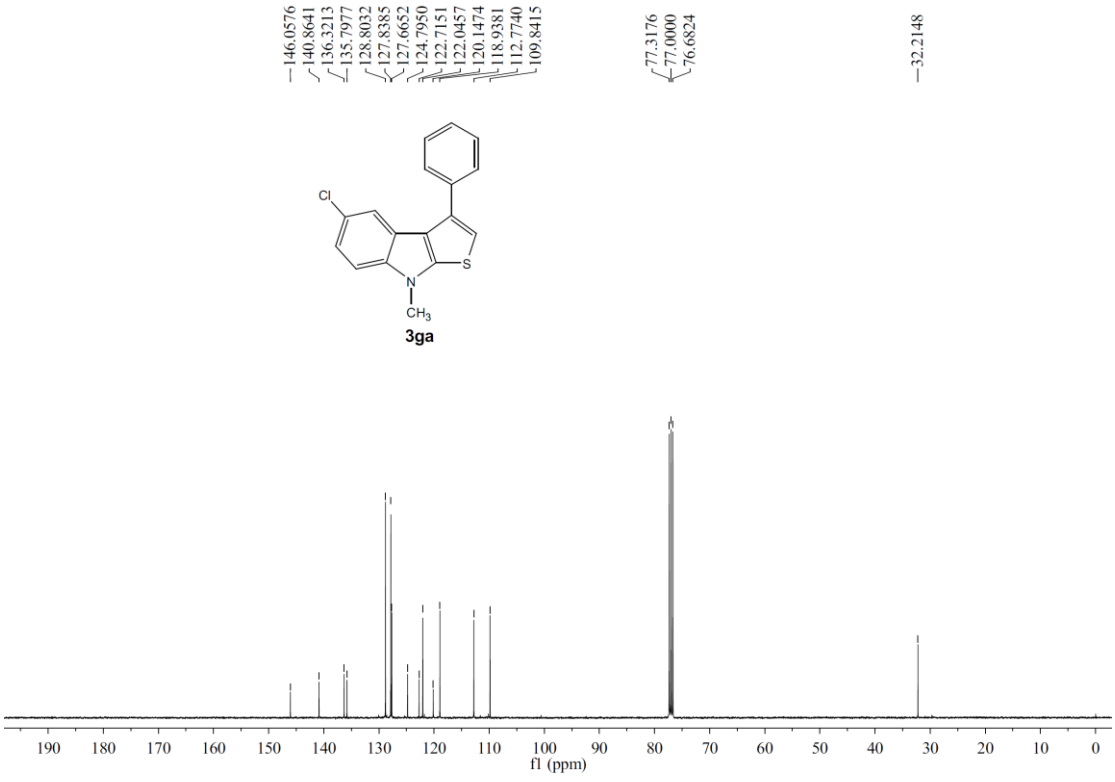
6.7905
3.8197
0.0000
Cl
S
N
CH3
3ga
3.03
2.05
1.00
2.06
1.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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S
N
CH3
3ga
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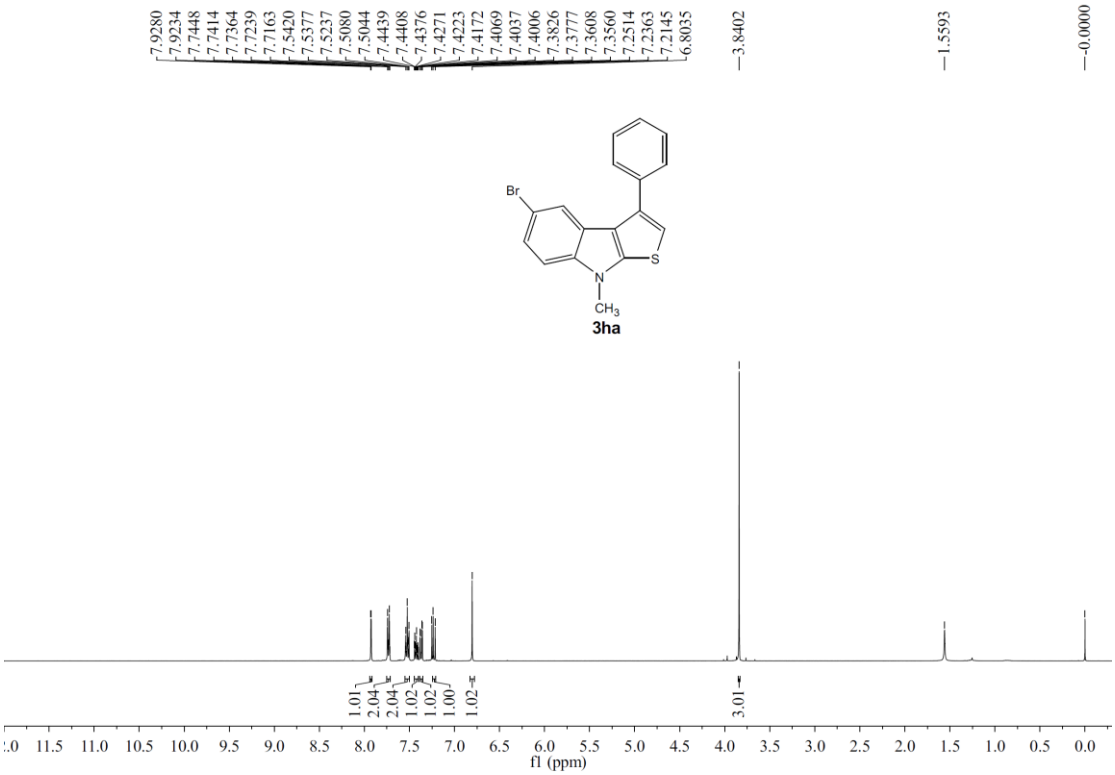
f1 (ppm)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7.5044
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7.4408
7.4376
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7.4172
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7.3826
7.3777
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7.3560
7.2514
7.2363
7.2145
6.8035
3.8402
1.5593
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Br
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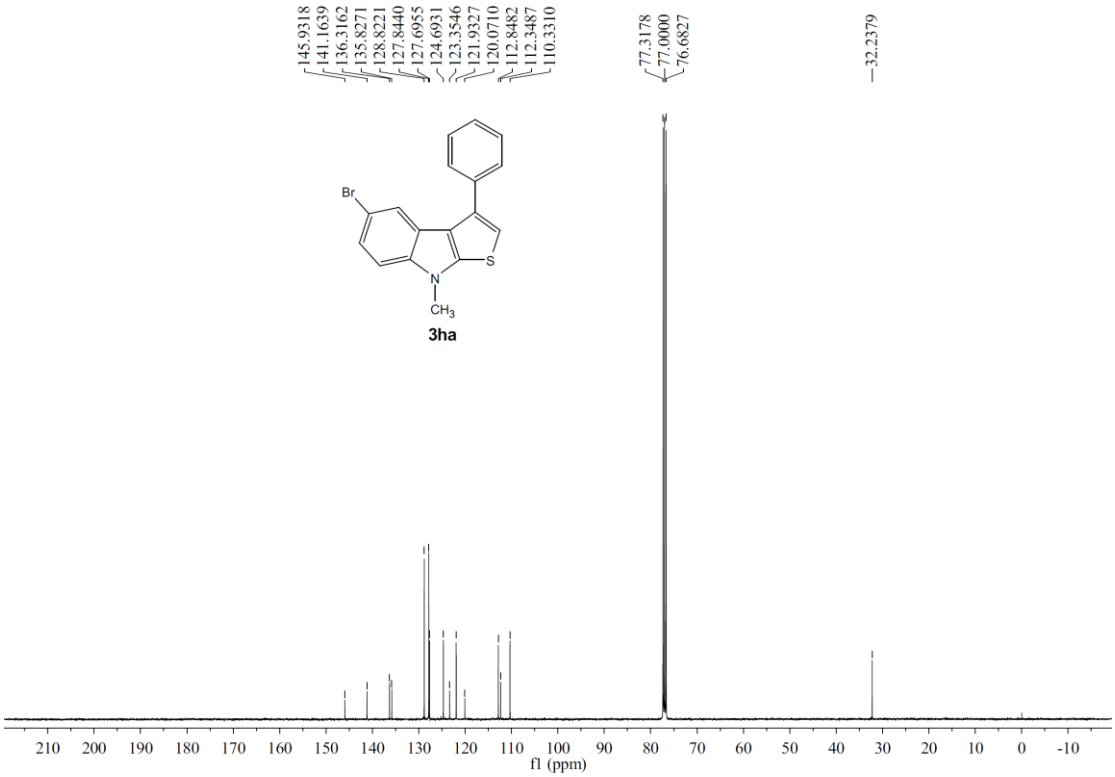
2.04
1.02
1.02
1.00
1.02
3.01
f1 (ppm)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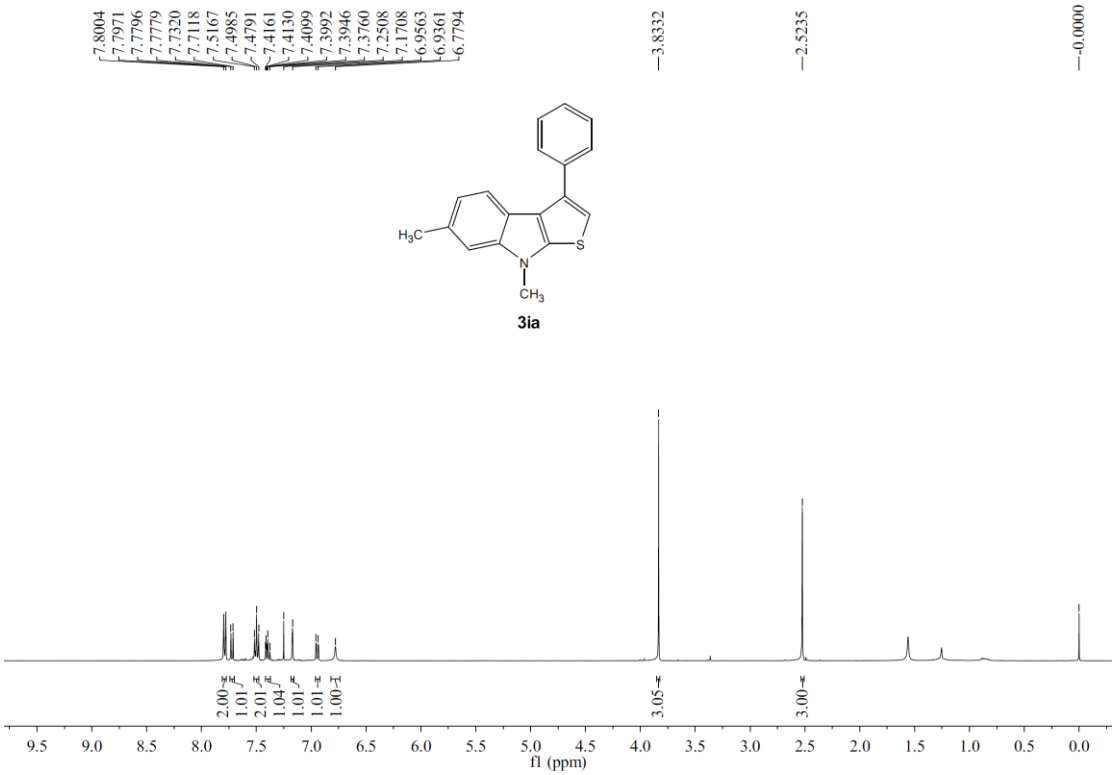
Br
S
N
CH3
3ha
f1 (ppm)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7.4099
7.3992
7.3946
7.3760
7.2508
7.1708
6.9563
6.9361
6.7794
3.8332
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H3C
S
N
CH3
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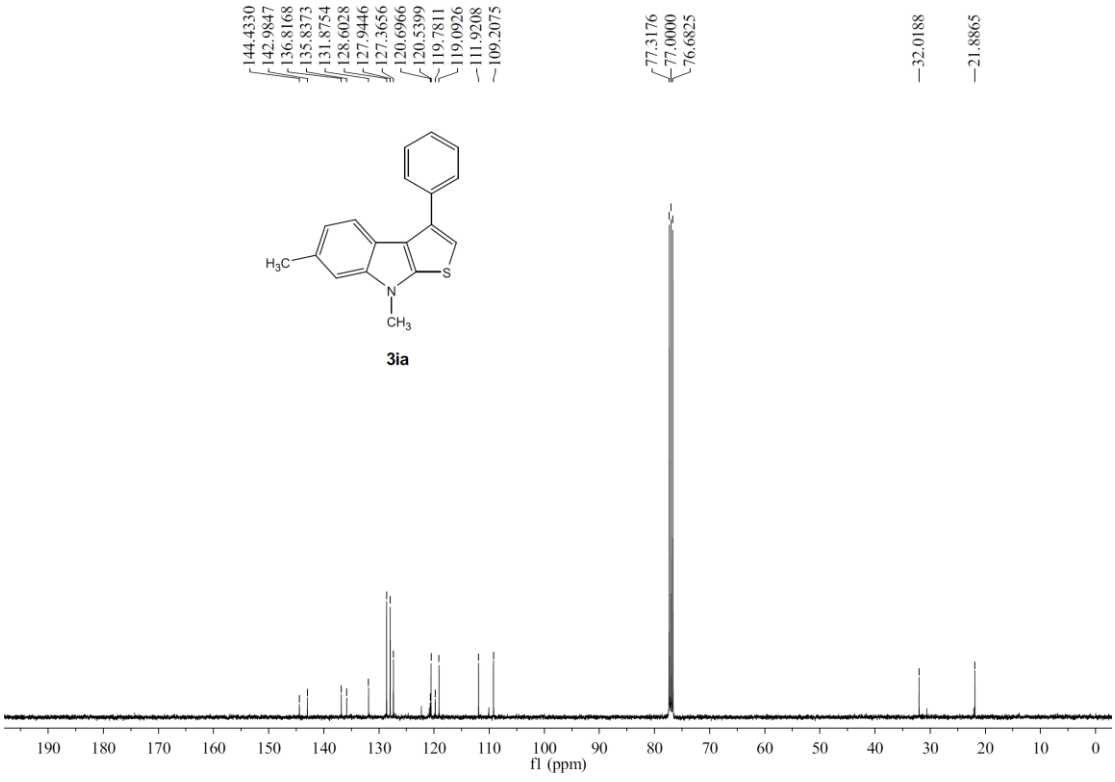
1.01
2.01
1.04
1.01
1.01
1.00
3.05
3.00
f1 (ppm)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119.0926
111.9208
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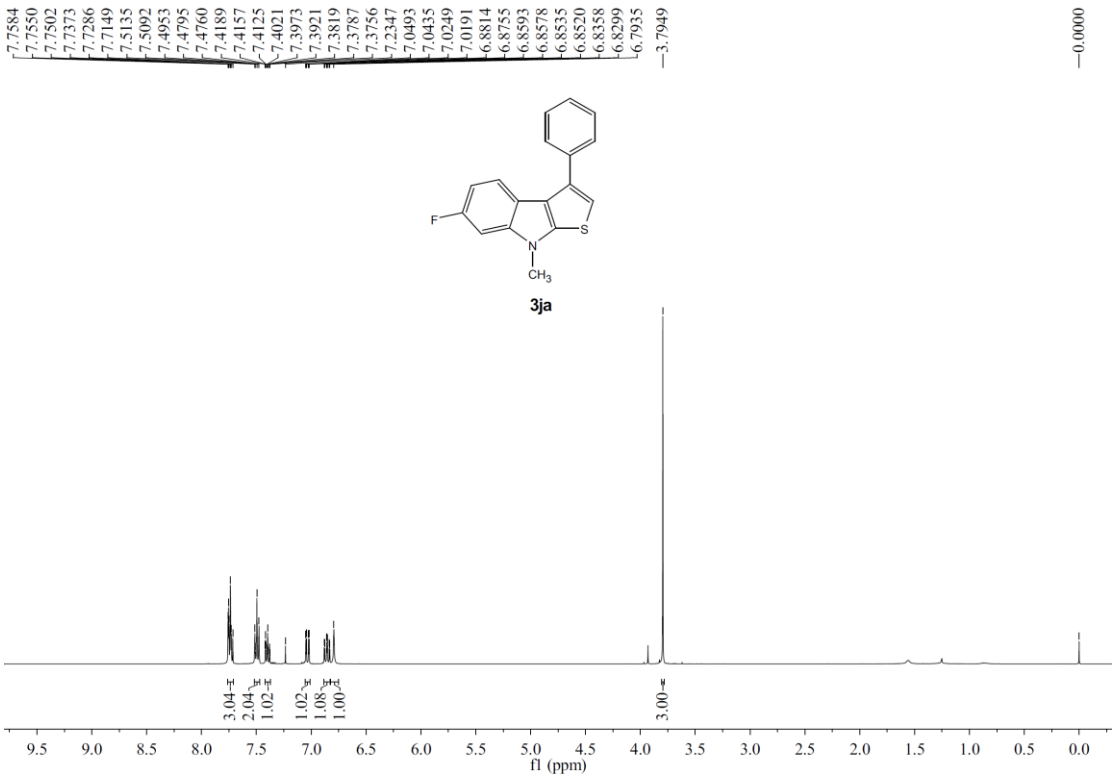
76.6825
32.0188
21.8865
H3C
S
N
CH3
3ia
f1 (ppm)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7.4189
7.4157
7.4125
7.4021
7.3973
7.3921
7.3819
7.3787
7.3756
7.2347
7.0493
7.0435
7.0249
7.0191
6.8814
6.8755
6.8593
6.8578
6.8535
6.8520
6.8358
6.8299
6.7935
3.7949
0.0000
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N
CH3
3ja
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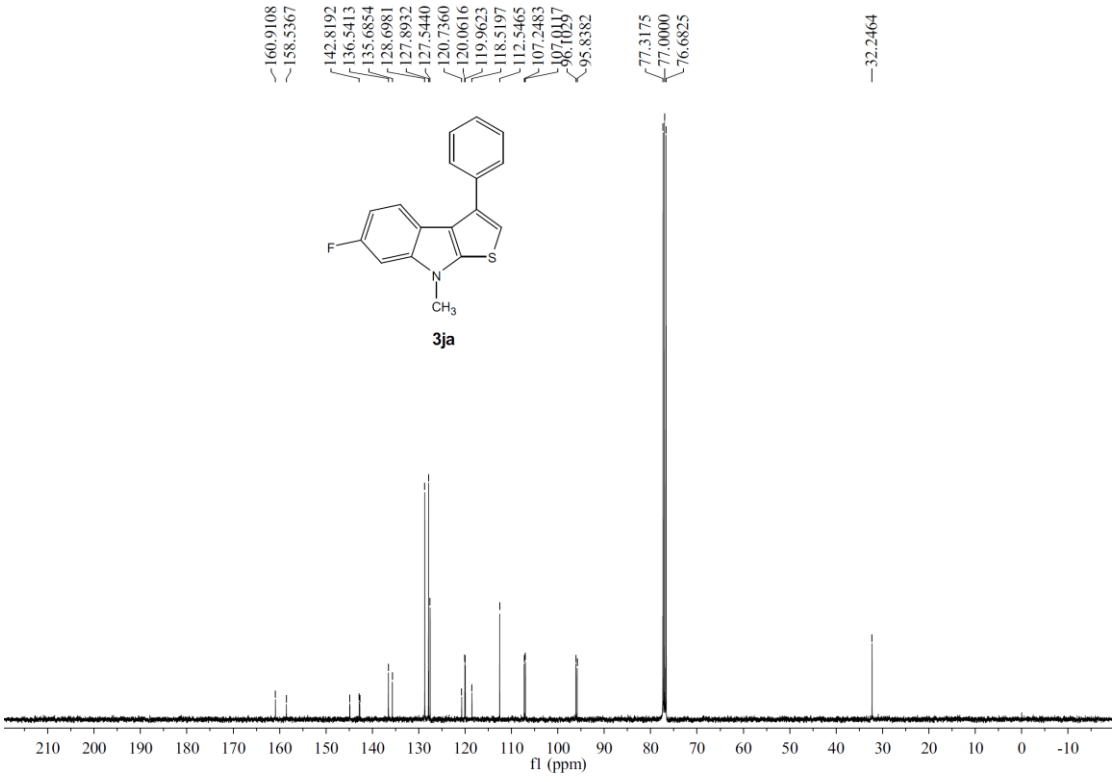
2.04
1.02
1.02
1.08
1.00
3.00
f1 (ppm)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112.5465
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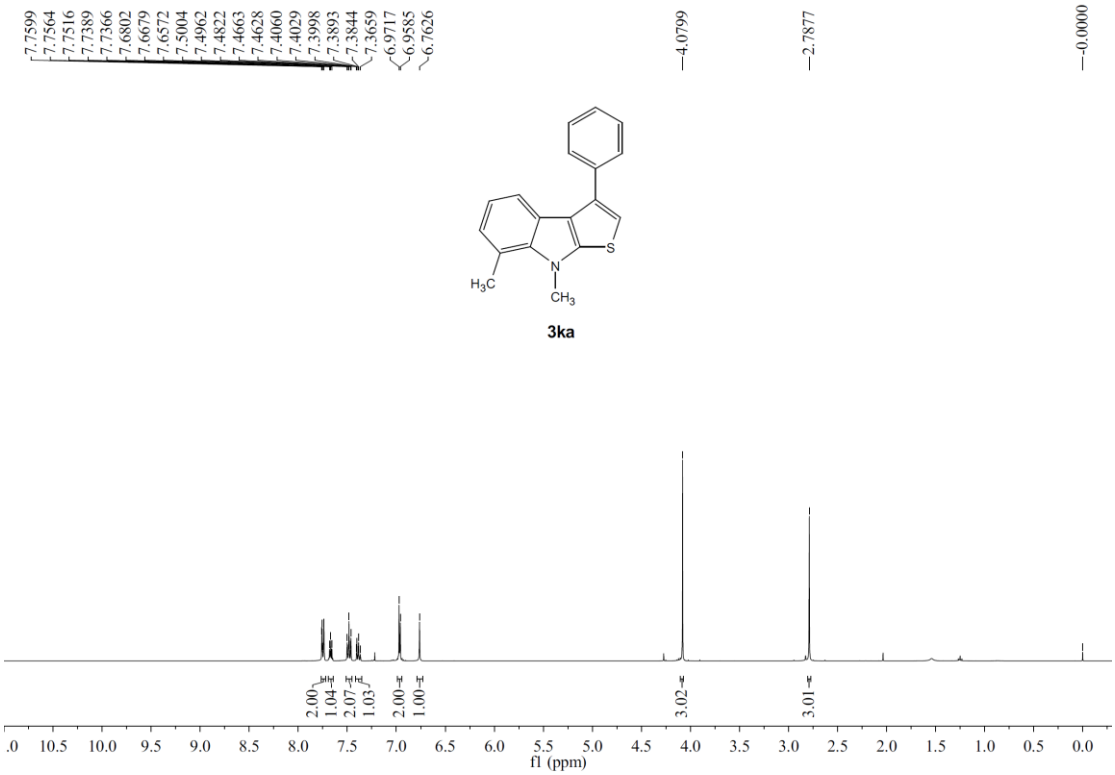
F
S
N
CH3
3ja
f1 (ppm)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7.4029
7.3998
7.3893
7.3844
7.3659
6.9717
6.9585
6.7626
4.0799
2.7877
0.0000
H3C
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CH3
S
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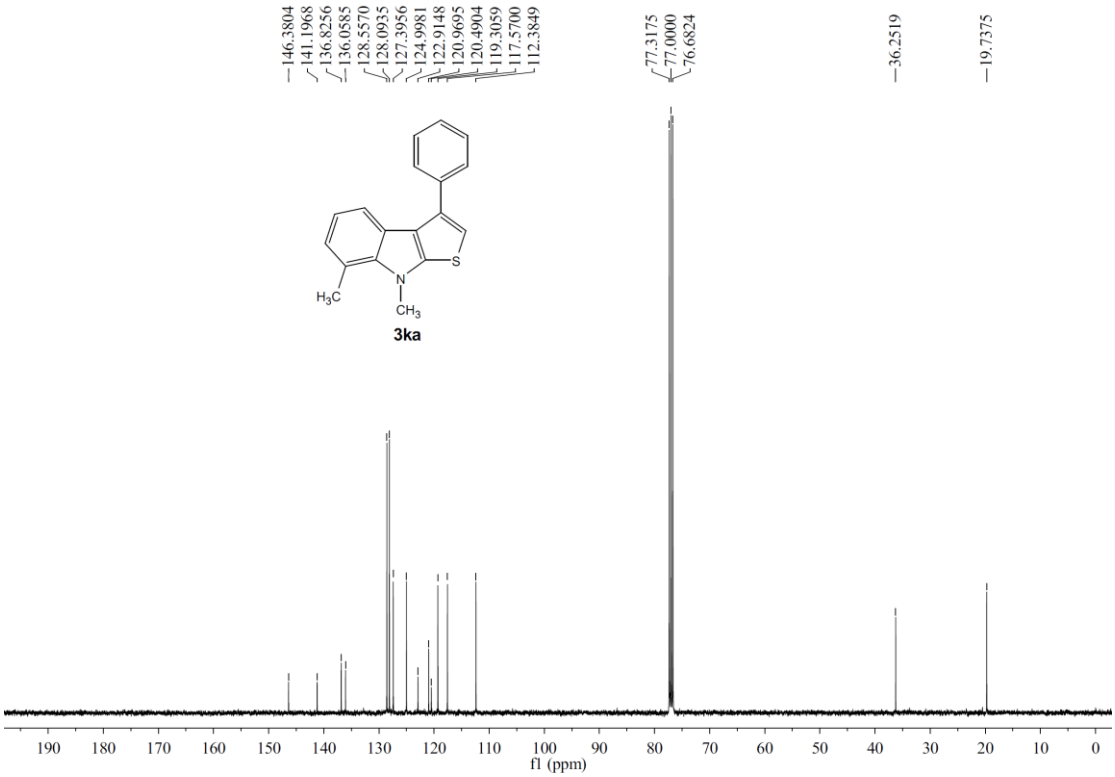
2.07
1.03
2.00
1.00
3.02
3.01
f1 (ppm)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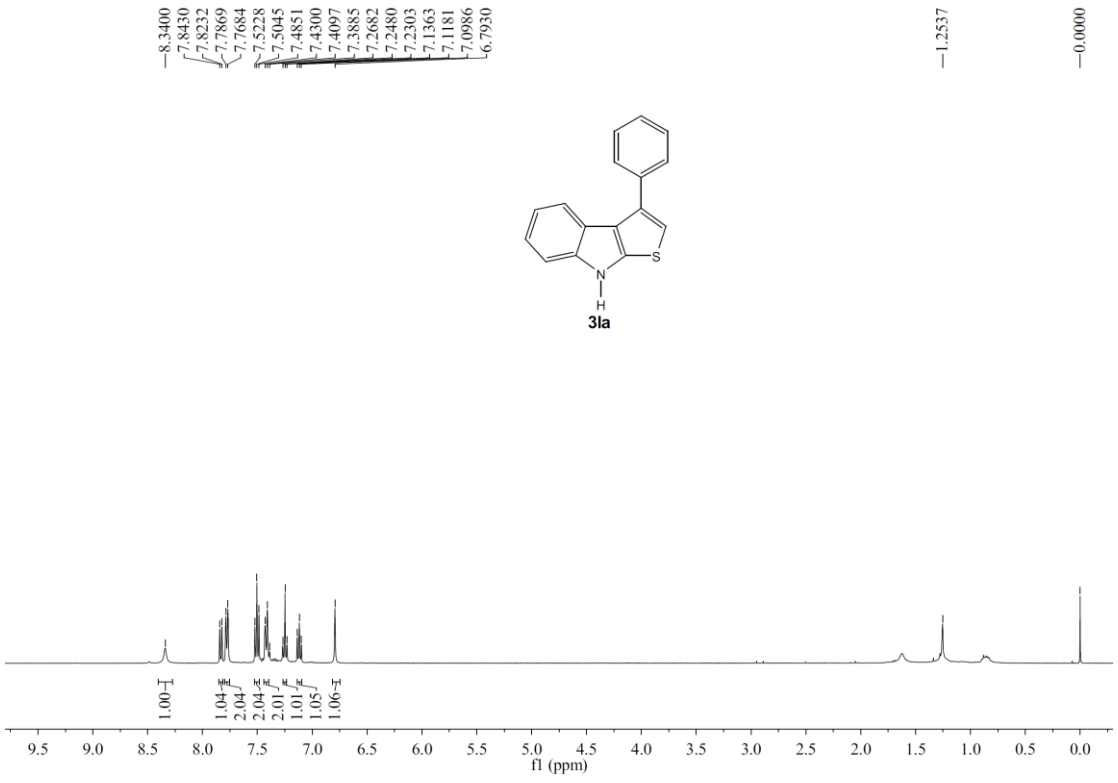
H3C
N
CH3
S
3ka
f1 (ppm)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7.3885
7.2682
7.2480
7.2303
7.1363
7.1181
7.0986
6.7930
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1.00
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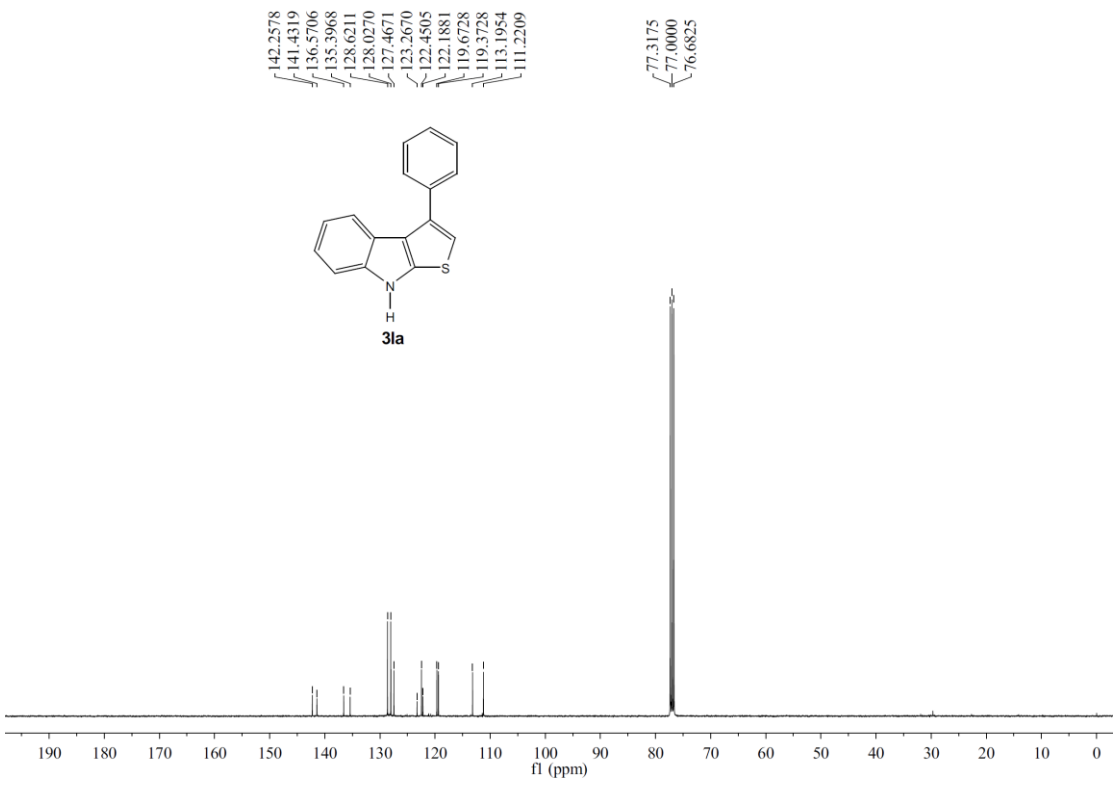
2.04
2.04
2.01
1.01
1.05
1.06
f1 (ppm)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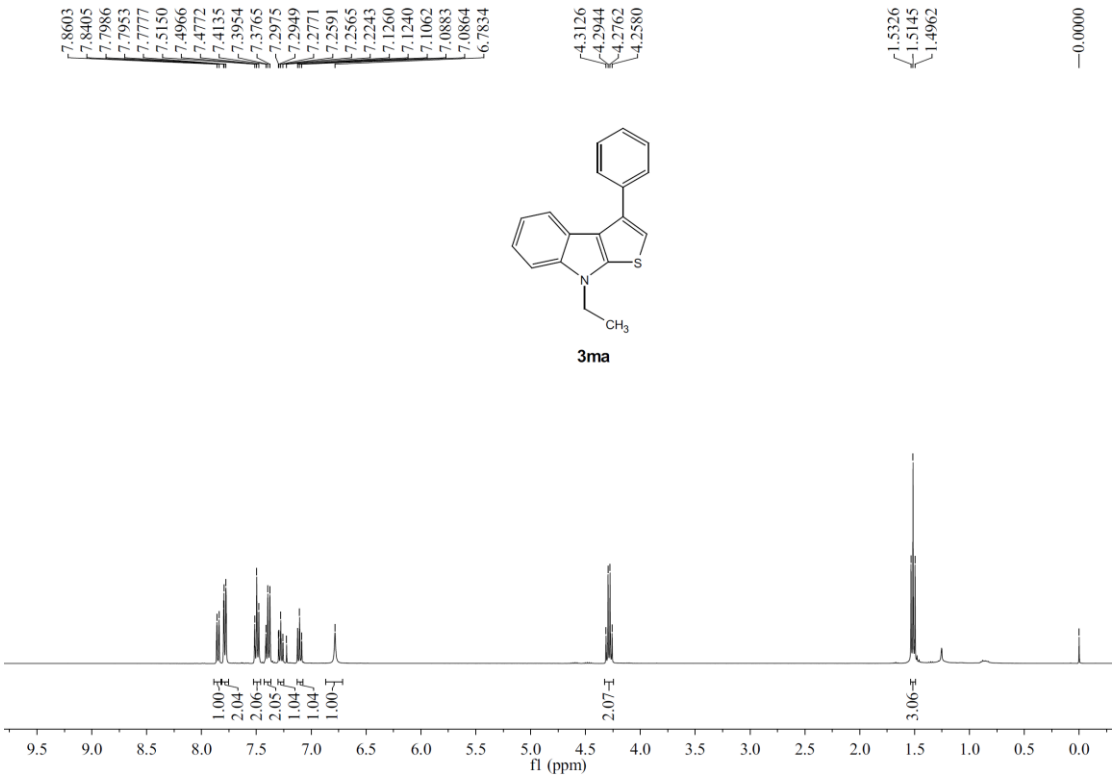
f1 (ppm)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7.2565
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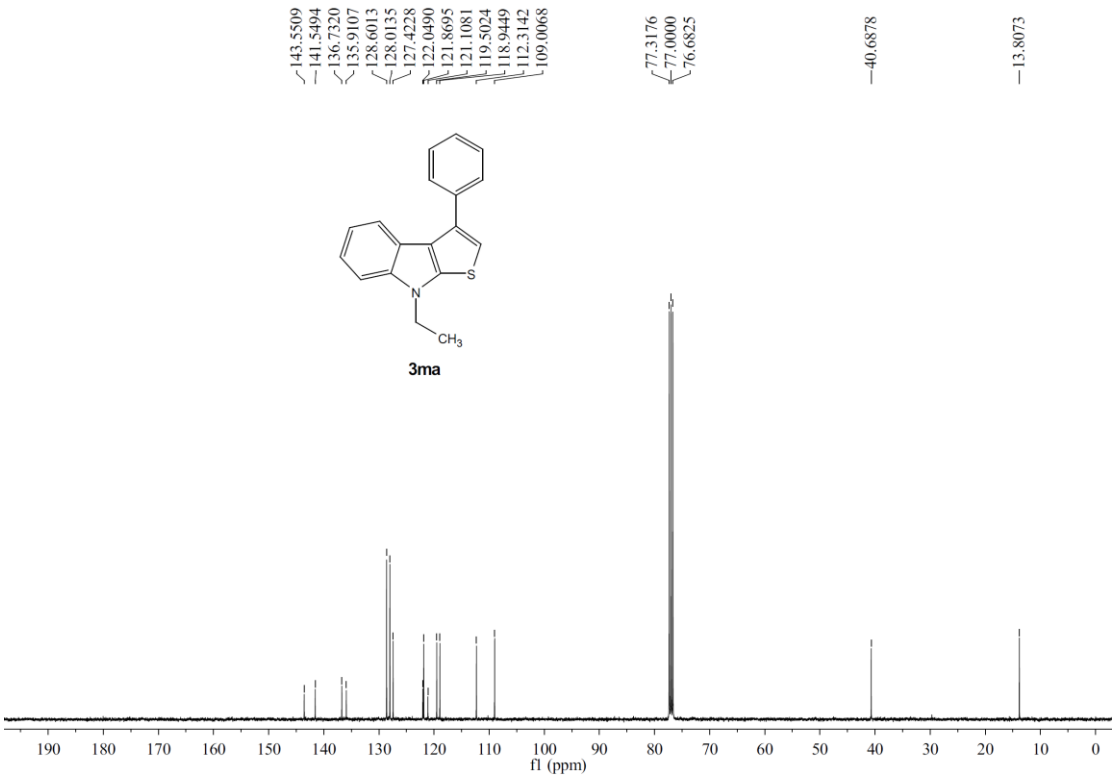
7.0883
7.0864
6.7834
4.3126
4.2944
4.2762
4.2580
1.5326
1.5145
1.4962
0.0000
S
N
CH3
1.00
2.04
2.06
2.05
1.04
1.04
1.00
2.07
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ma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77.0000
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13.8073
S
N
CH3
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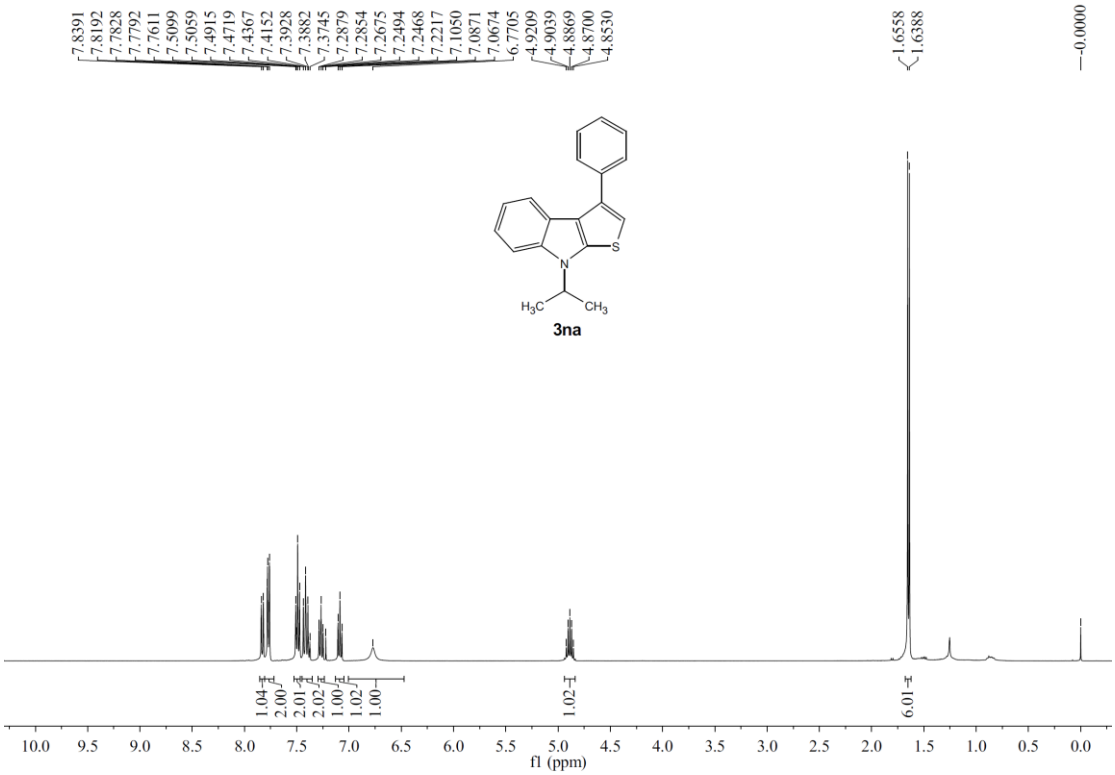
f1 (ppm)

3ma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7.3928
7.3882
7.3745
7.2879
7.2854
7.2675
7.2494
7.2468
7.2217
7.1050
7.0871
7.0674
6.7705
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4.9039
4.8869
4.8700
4.8530
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0.0000
3na
1.04
2.00
2.01
2.02
1.00
1.02
1.00
1.02
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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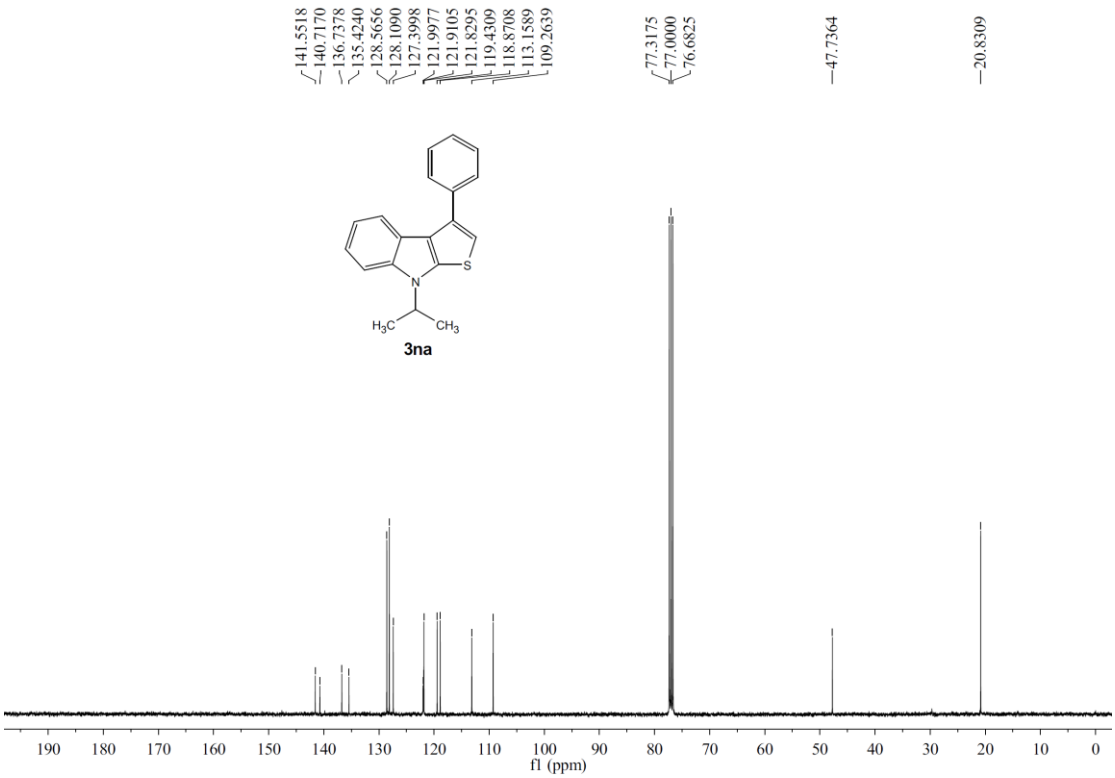
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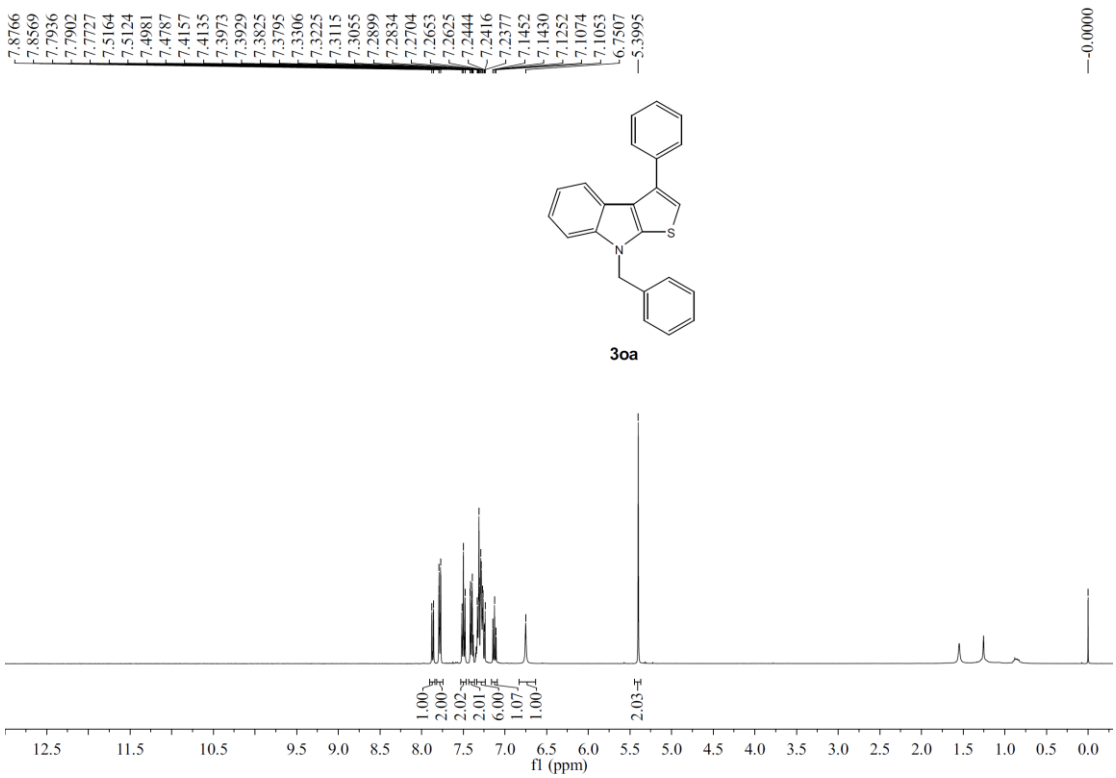
f1 (ppm)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7.2444
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7.1452
7.1430
7.1252
7.1074
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2.00
2.02
2.01
6.00
1.07
1.00
2.03
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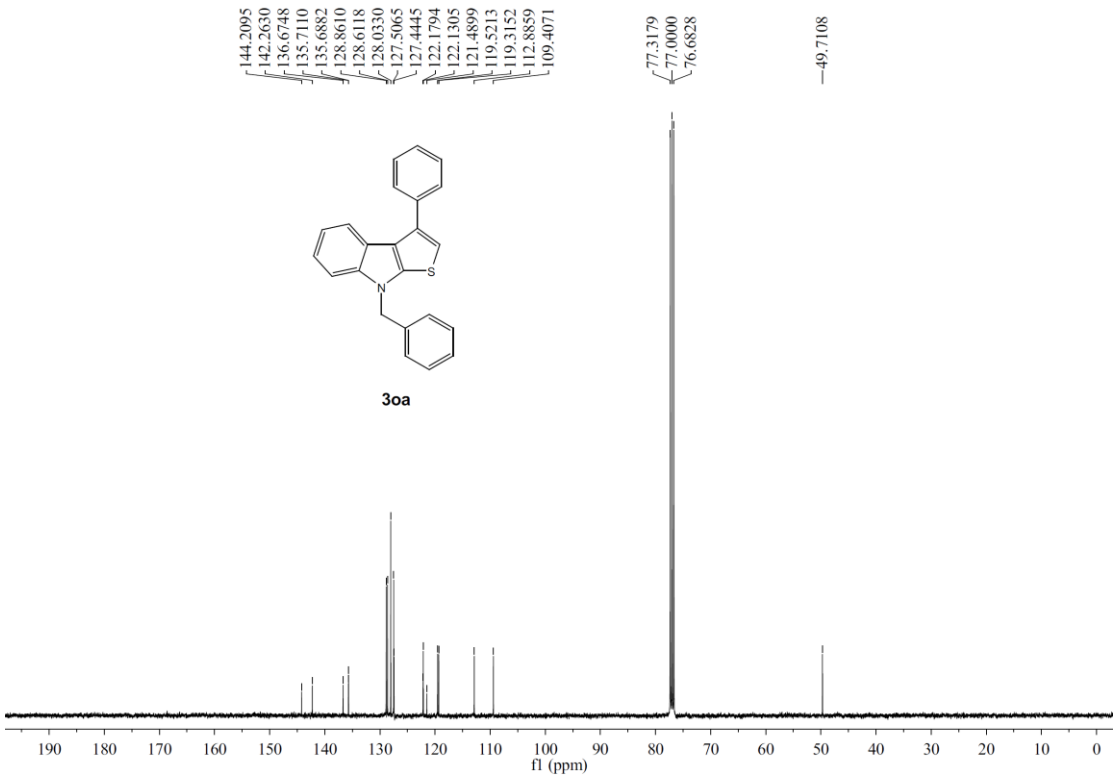
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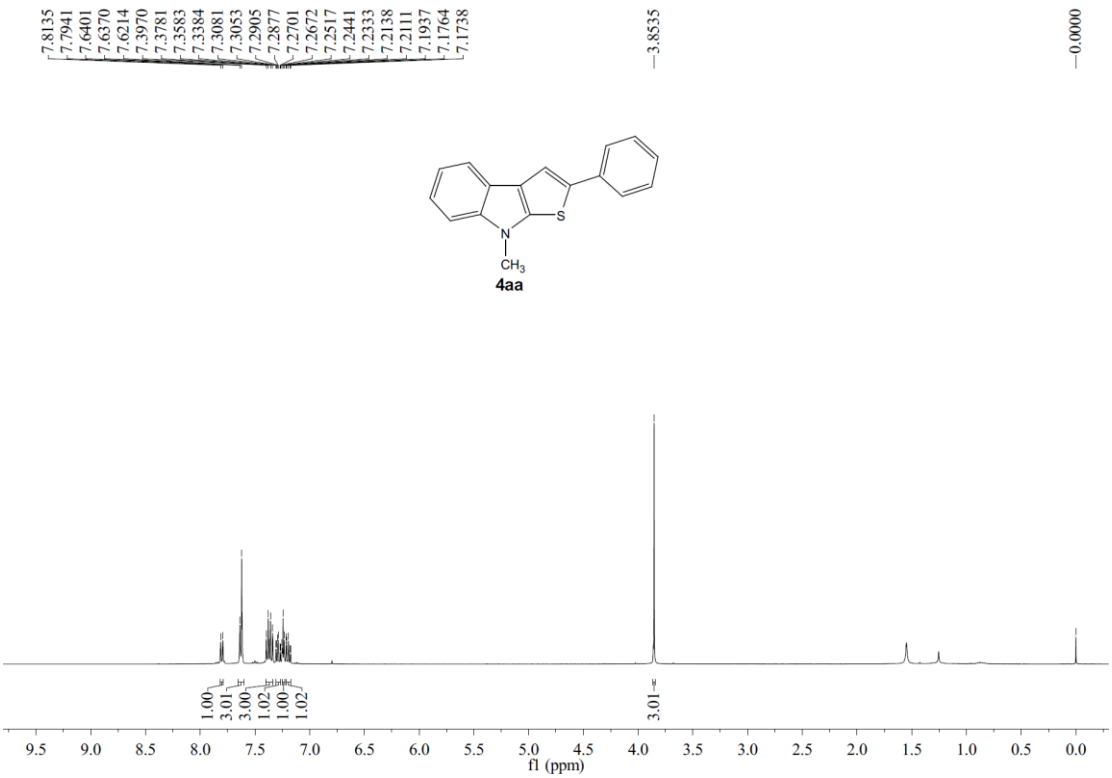
f1 (ppm)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7.2877
7.2701
7.2672
7.2517
7.2441
7.2333
7.2138
7.2111
7.1937
7.1764
7.1738
3.8535
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N
S
CH3
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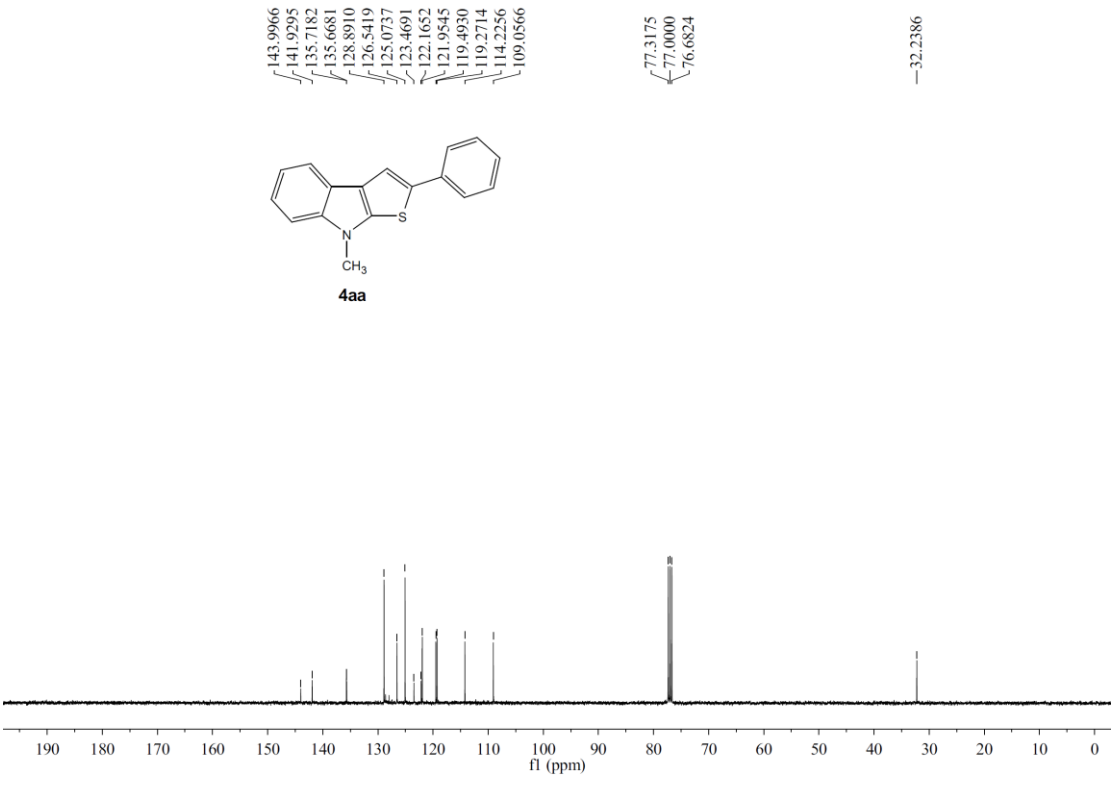
3.00
1.02
1.00
1.02
3.01
f1 (ppm)

4aa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119.4930
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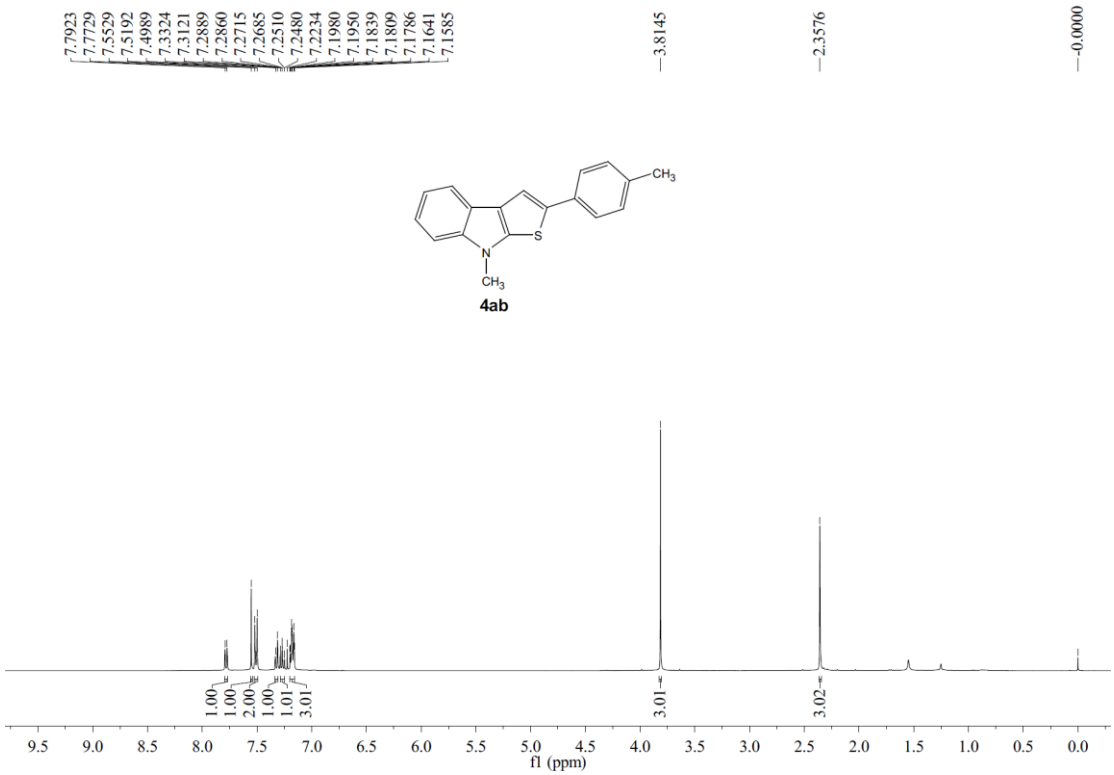
N
S
CH3
f1 (ppm)

4aa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7.2234
7.1980
7.1950
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7.1786
7.1641
7.1585
3.8145
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S
N
CH3
4ab
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1.00
2.00
1.00
1.01
3.01
3.01
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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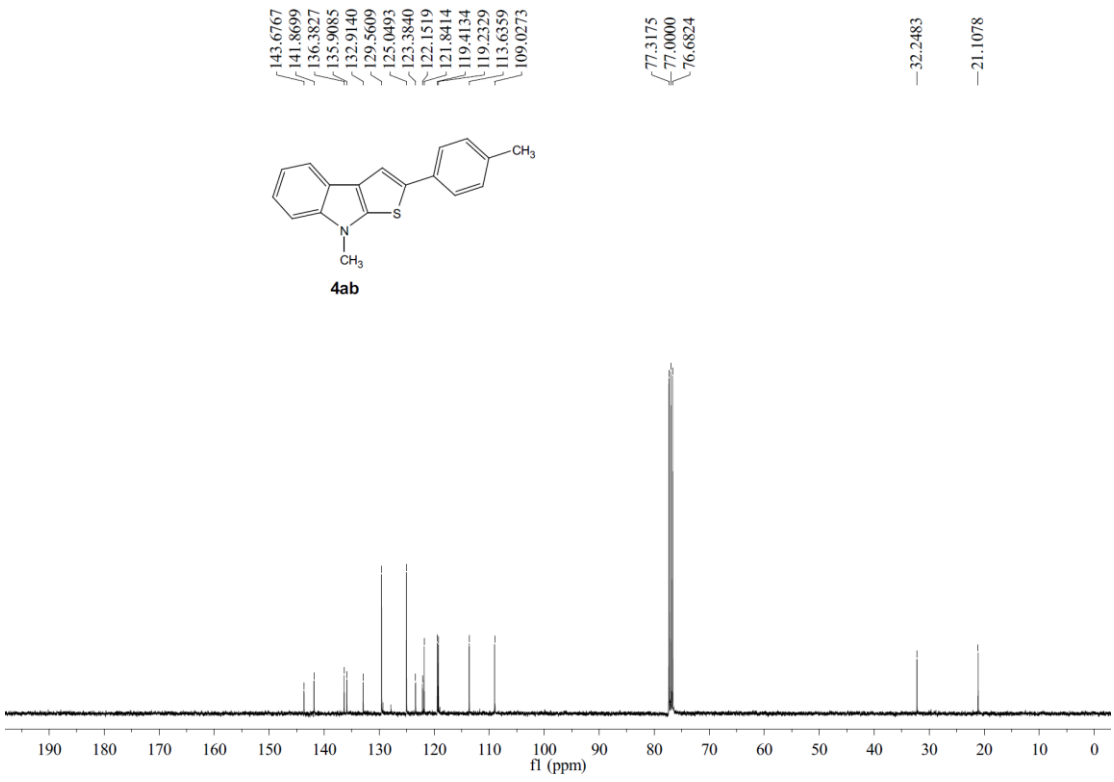
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77.0000
76.6824
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CH3
S
N
CH3
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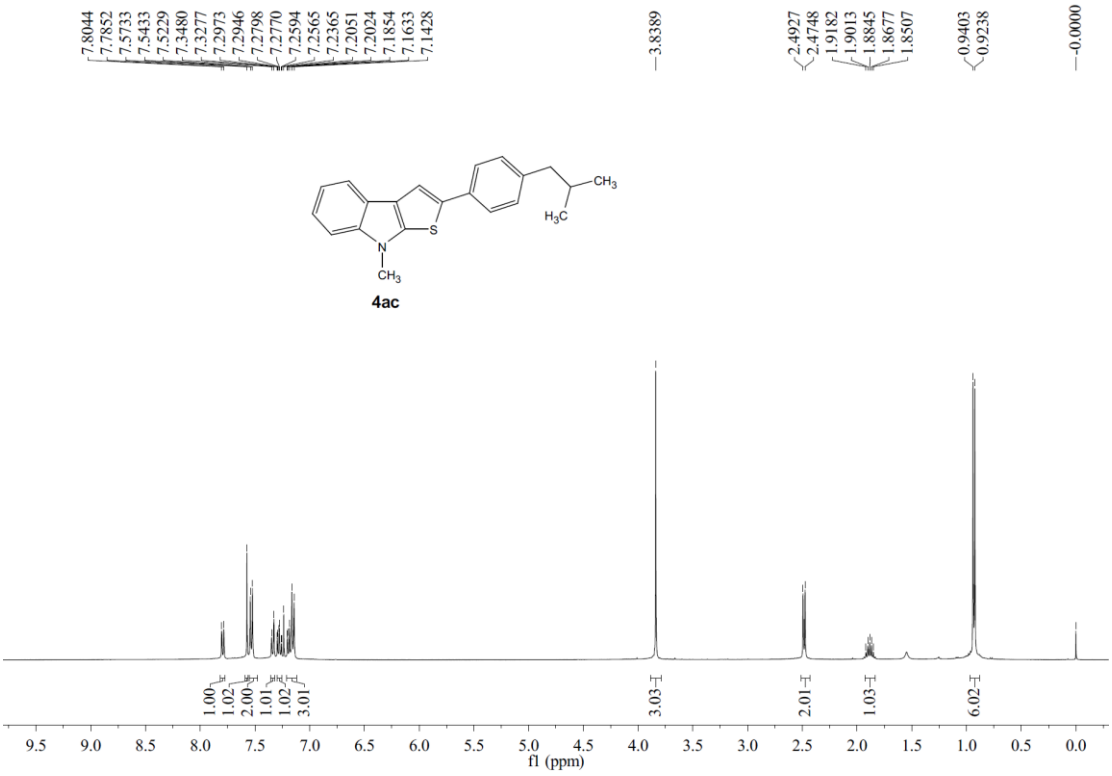
f1 (ppm)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CH3
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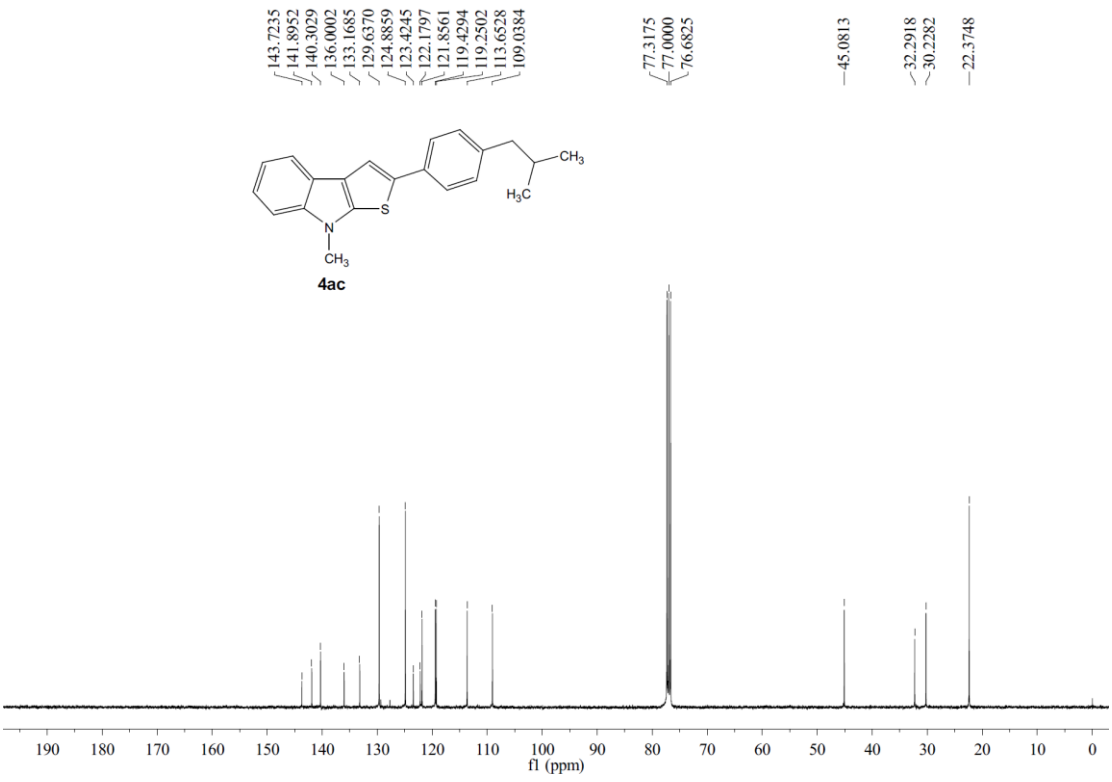
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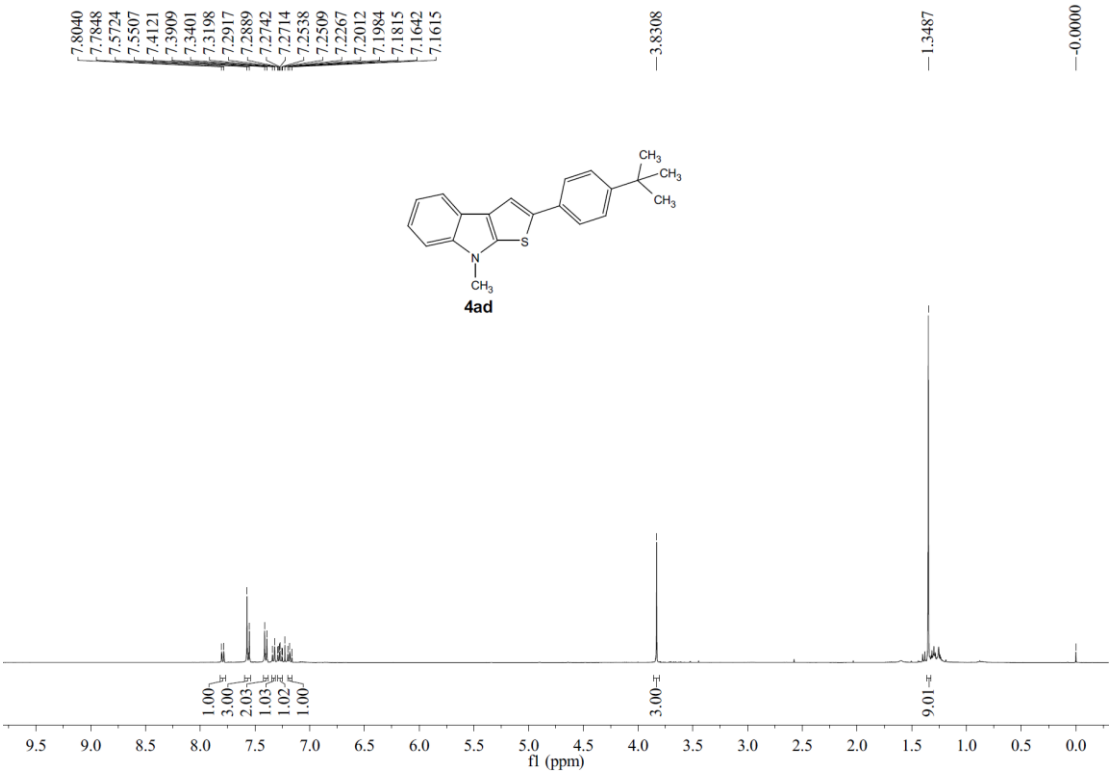
fl (ppm)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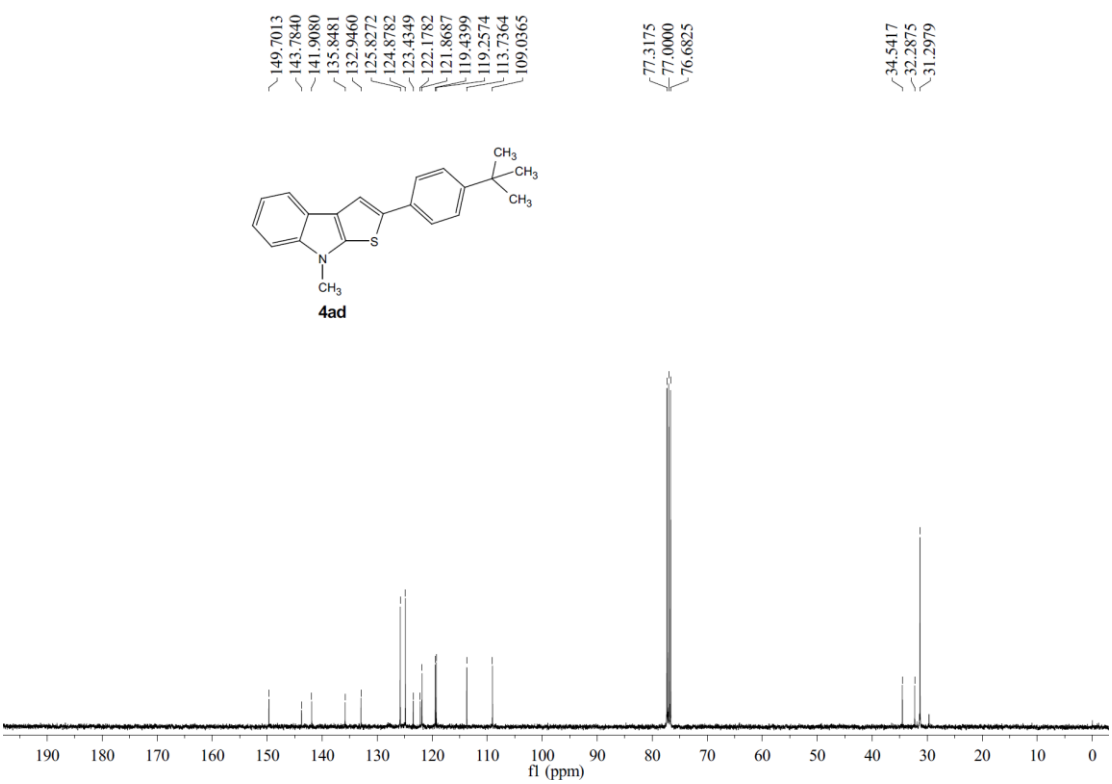
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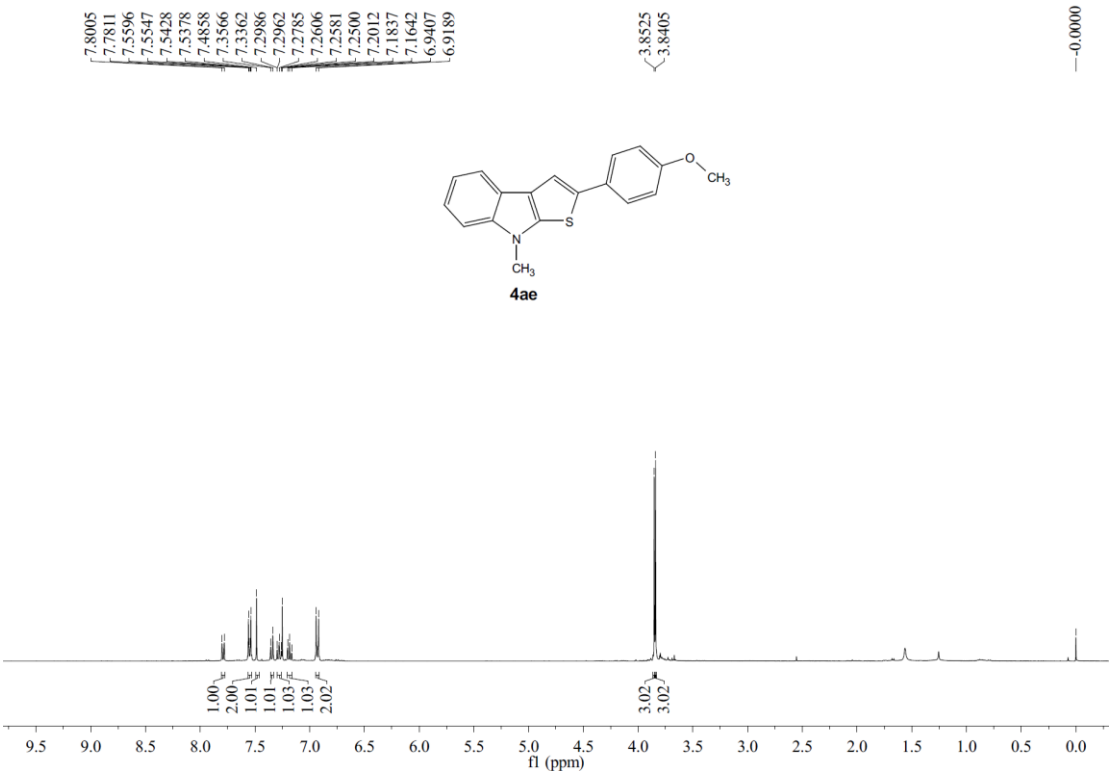
f1 (ppm)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CH3
S
N
CH3
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2.00
1.01
1.01
1.03
1.03
2.02
3.02
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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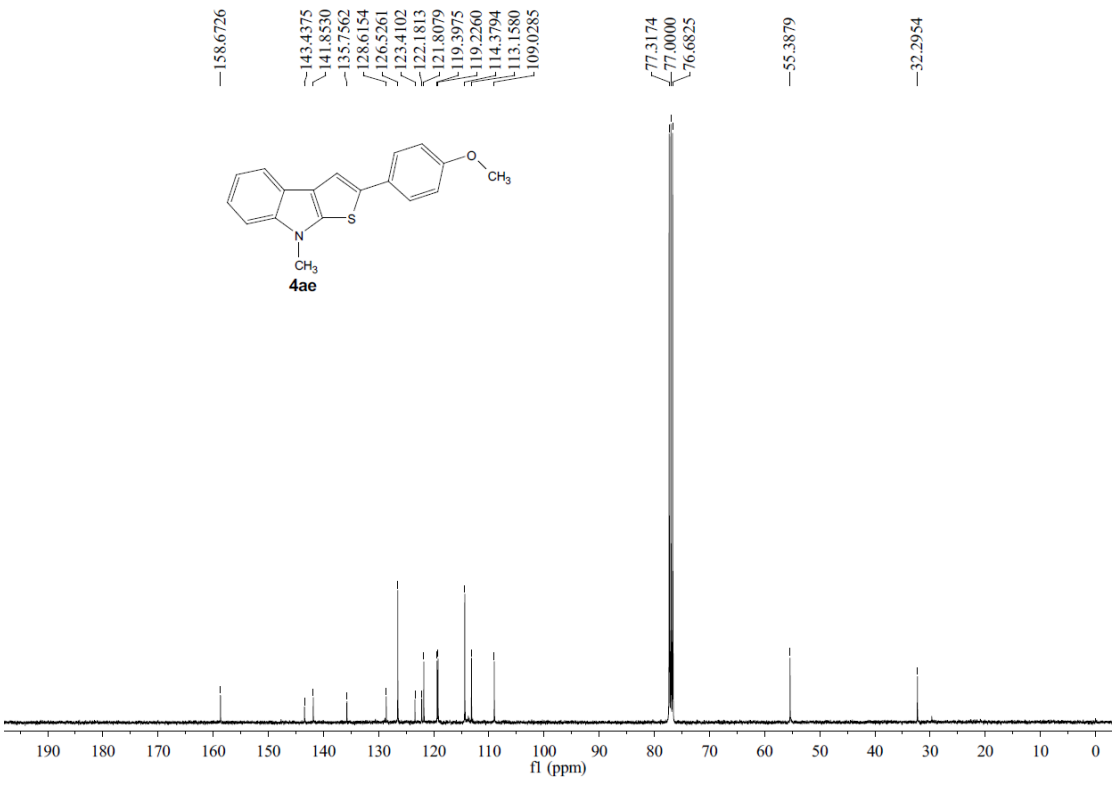
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CH3
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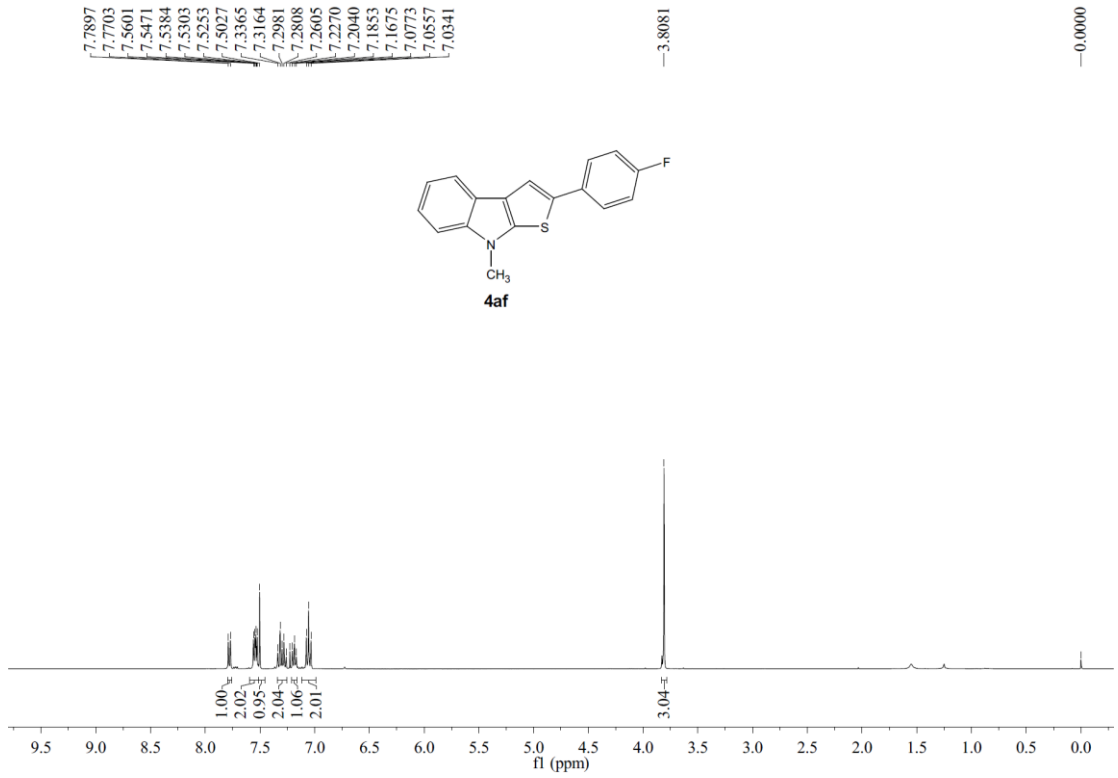
f1 (ppm)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F
S
N
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1.06
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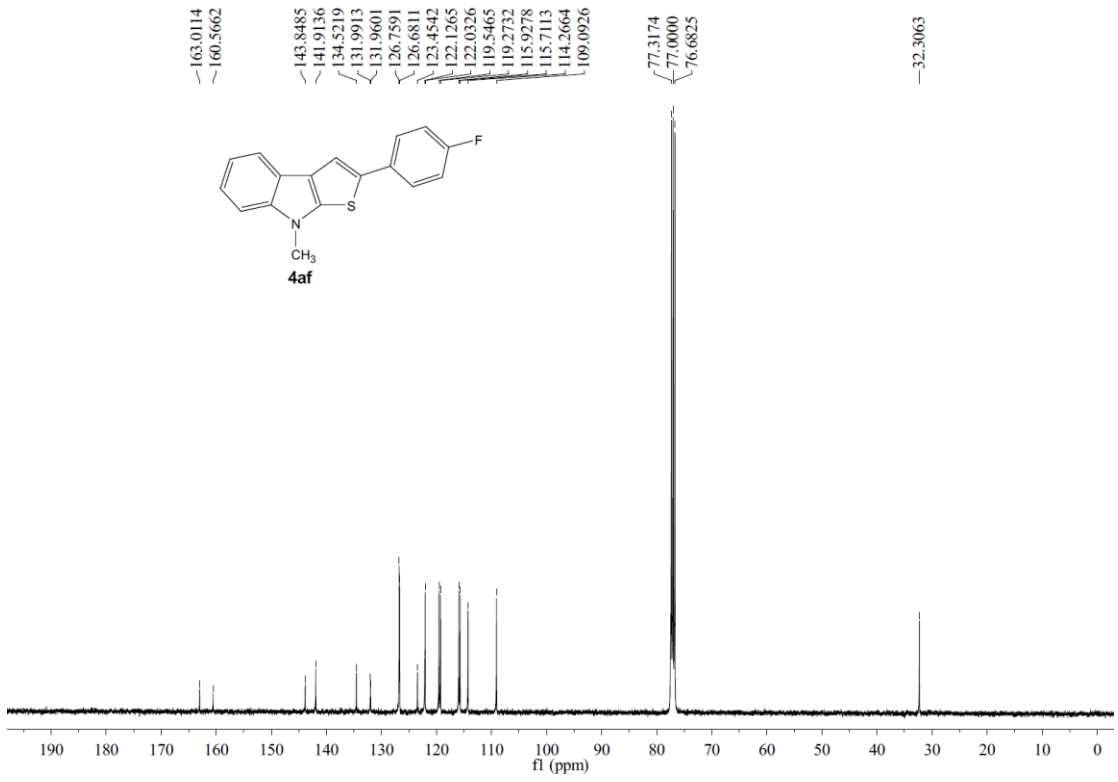
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119.5465
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S
N
CH3
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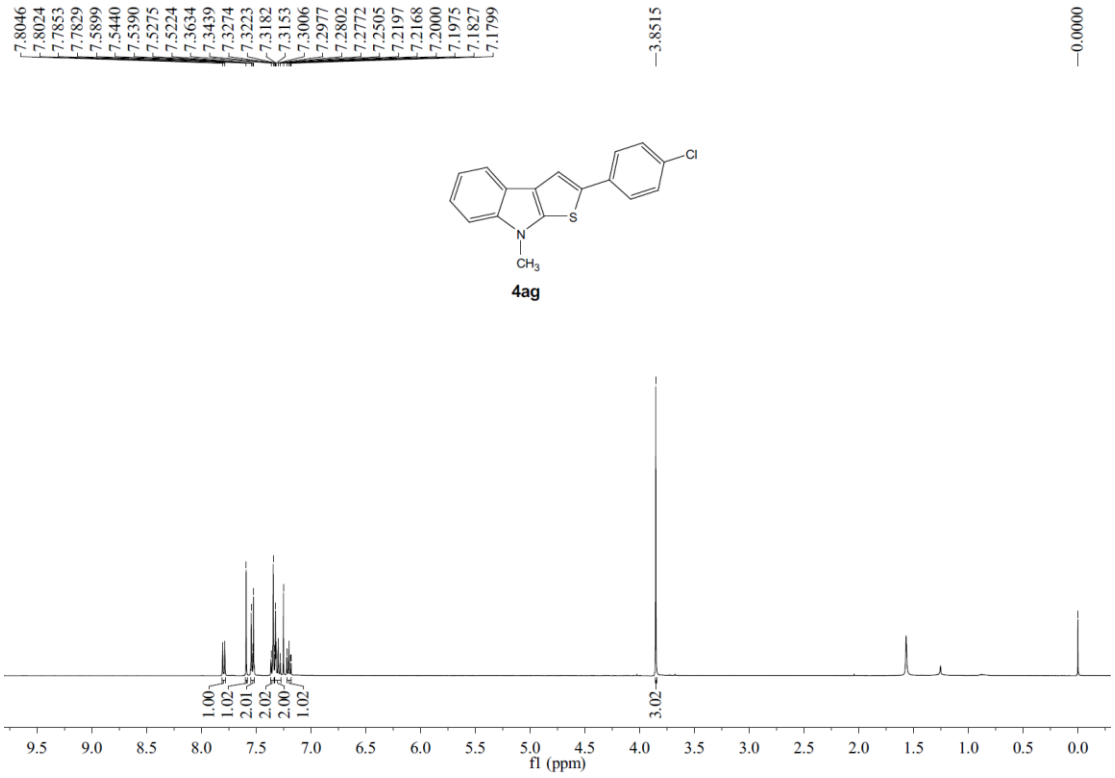
f1 (ppm)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7.3153
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7.2977
7.2802
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7.2168
7.2000
7.1975
7.1827
7.1799
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Cl
S
N
CH3
4ag
1.00
1.02
2.01
2.02
2.00
1.02
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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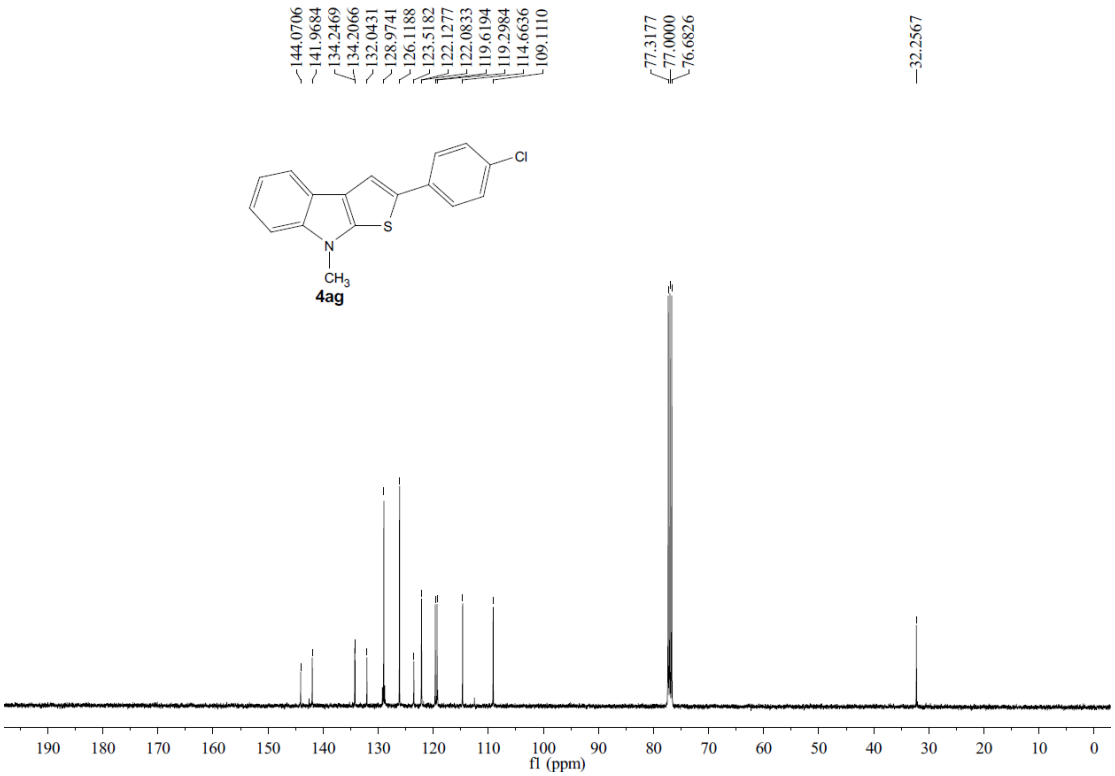
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CH3
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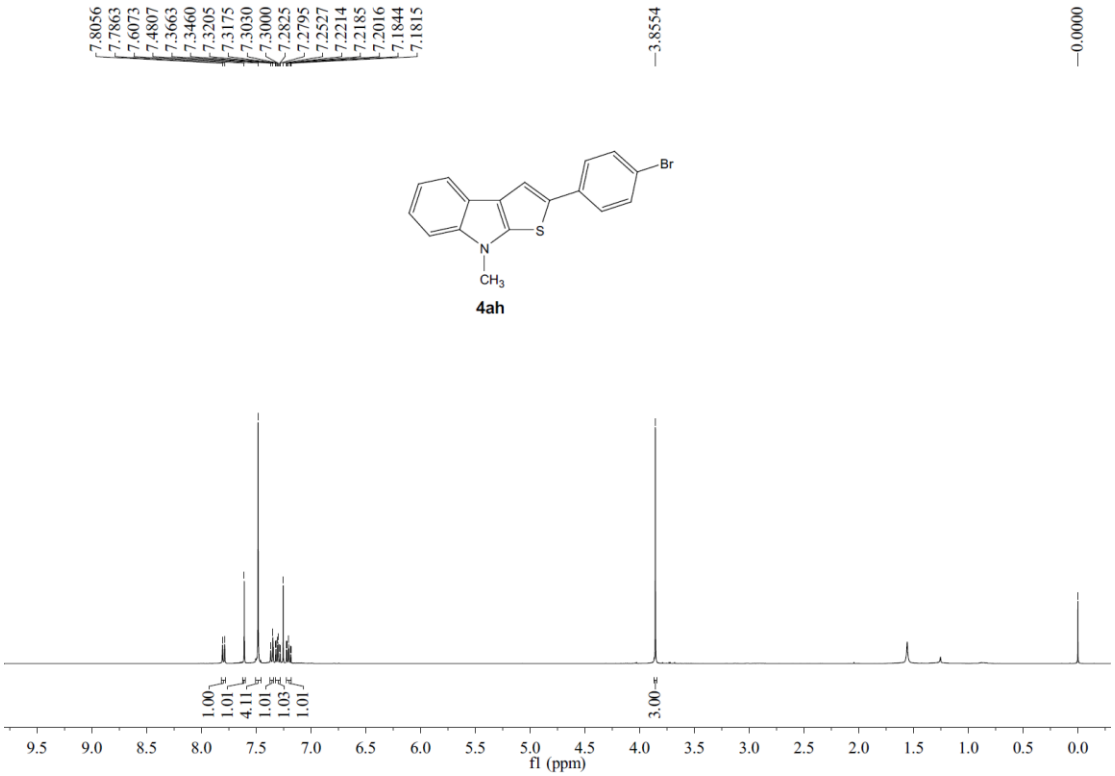
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N
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4.11
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1.03
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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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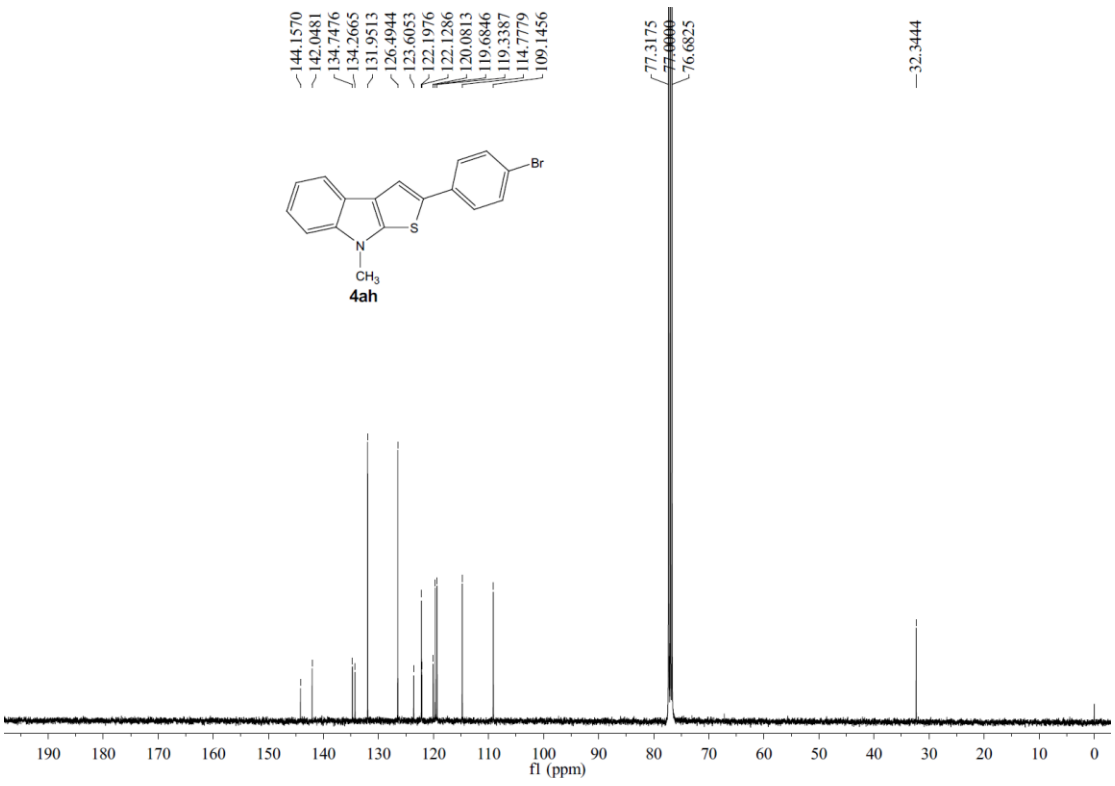
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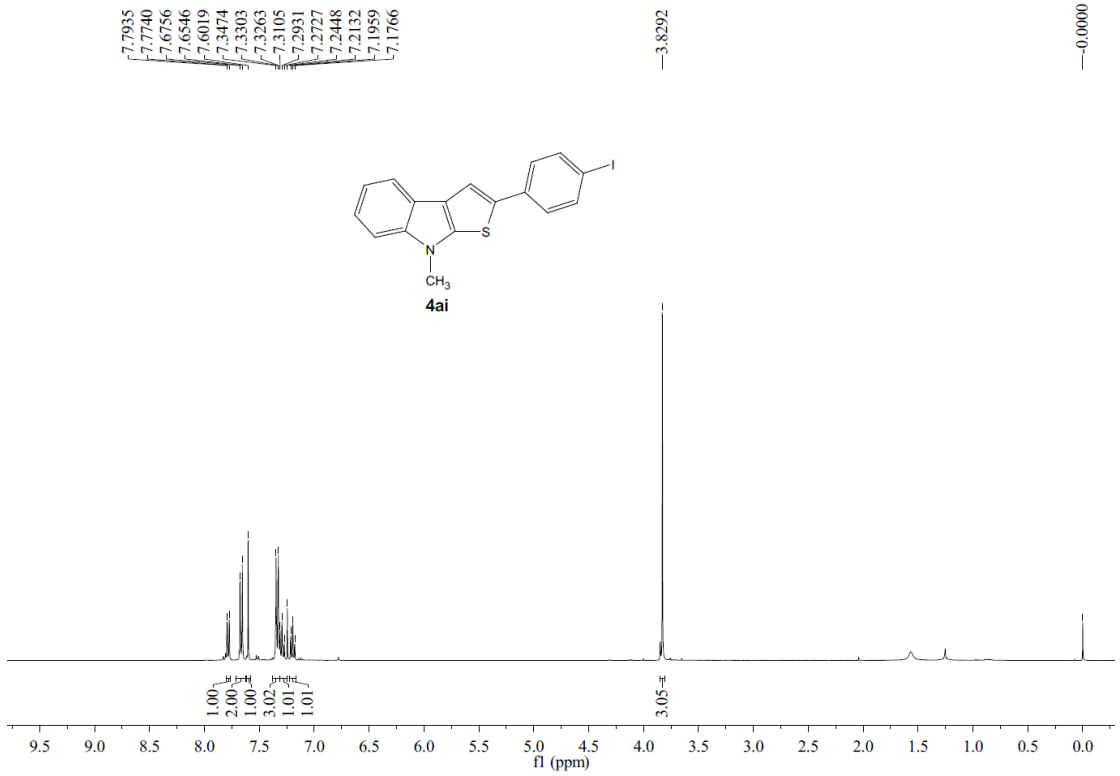
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S
N
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2.00
1.00
3.02
1.01
1.01
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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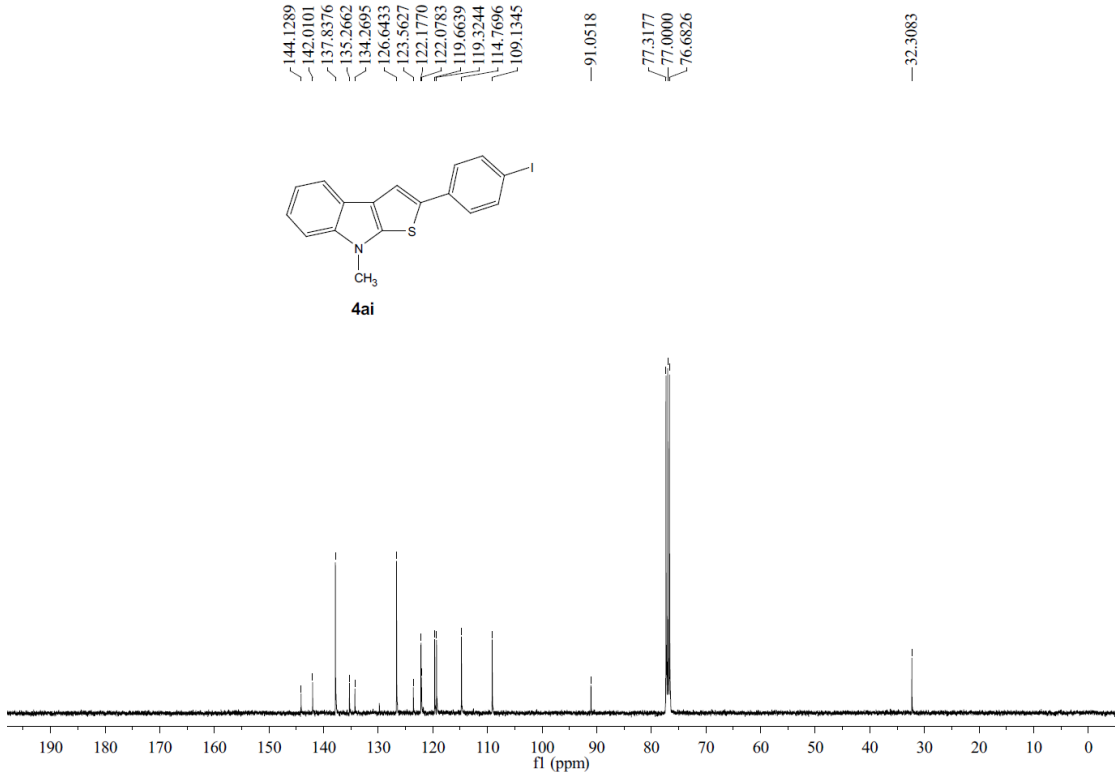
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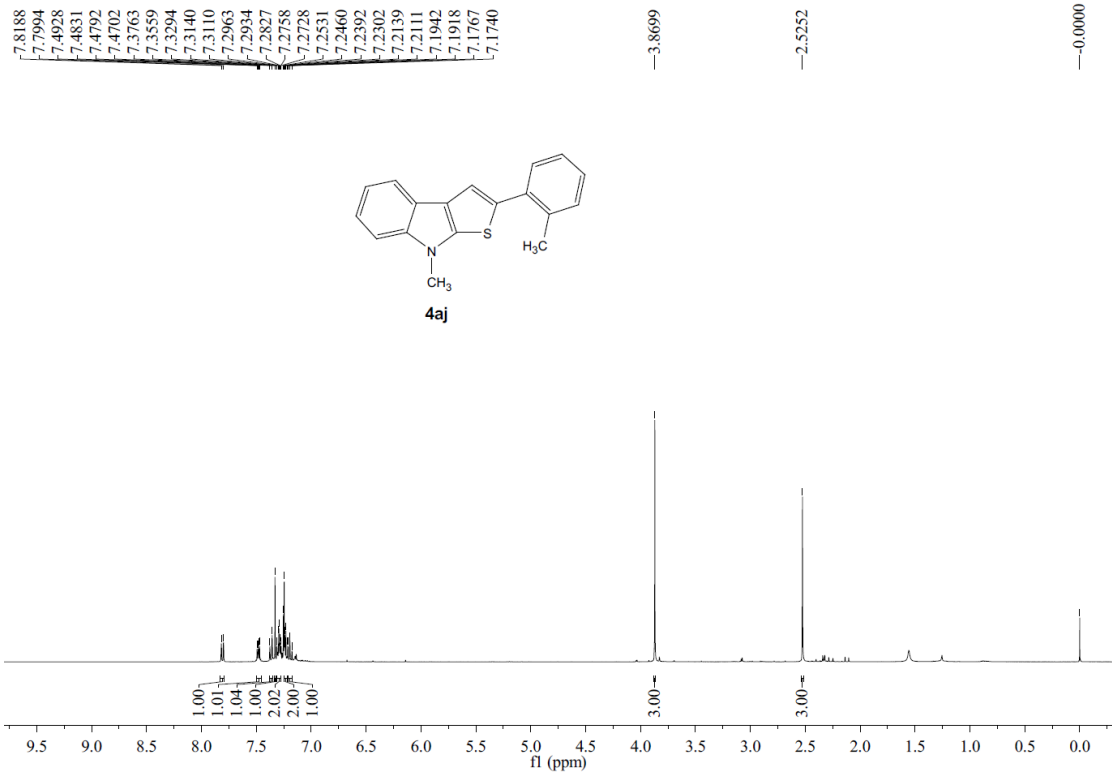
f1 (ppm)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7.2392
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7.2139
7.2111
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7.1918
7.1767
7.1740
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2.5252
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N
CH3
H3C
4aj
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1.01
1.04
1.00
2.02
2.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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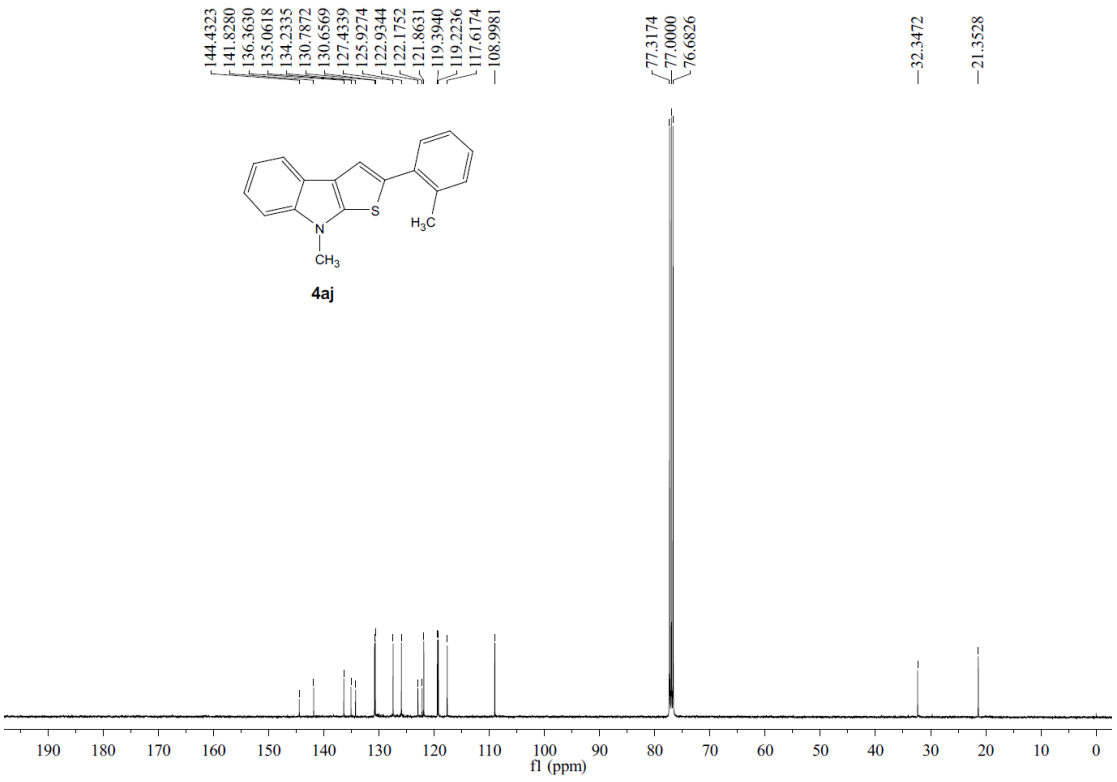
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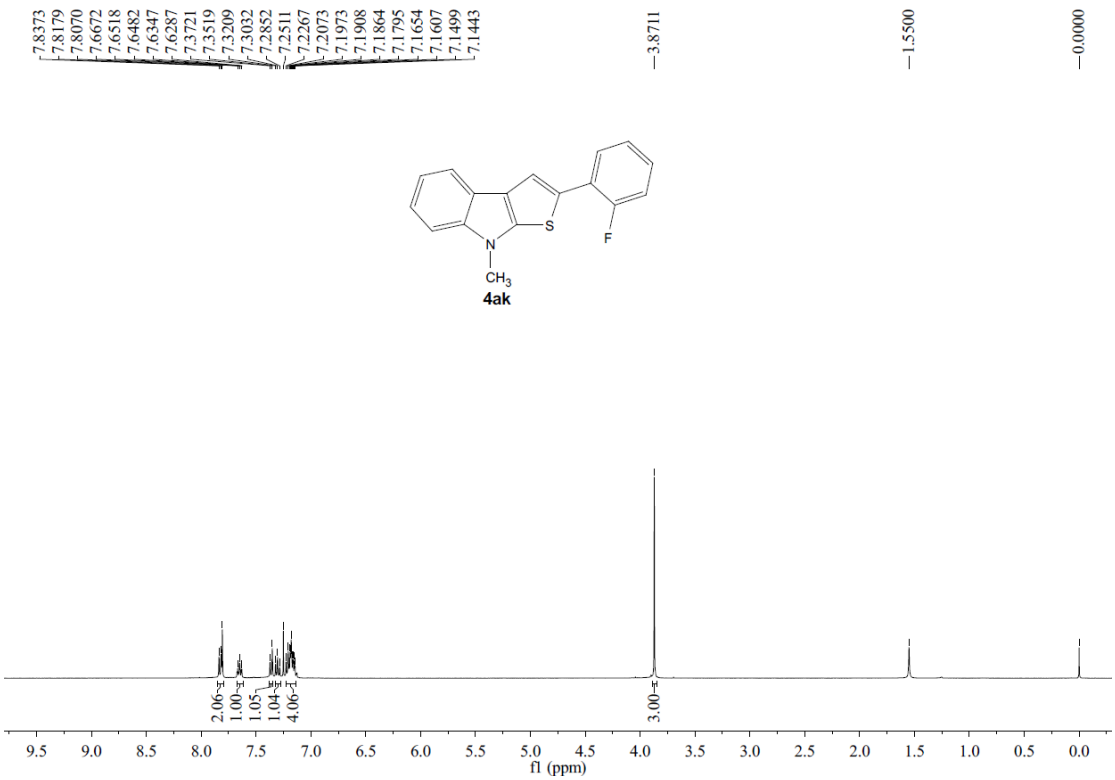
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N
F
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4.06
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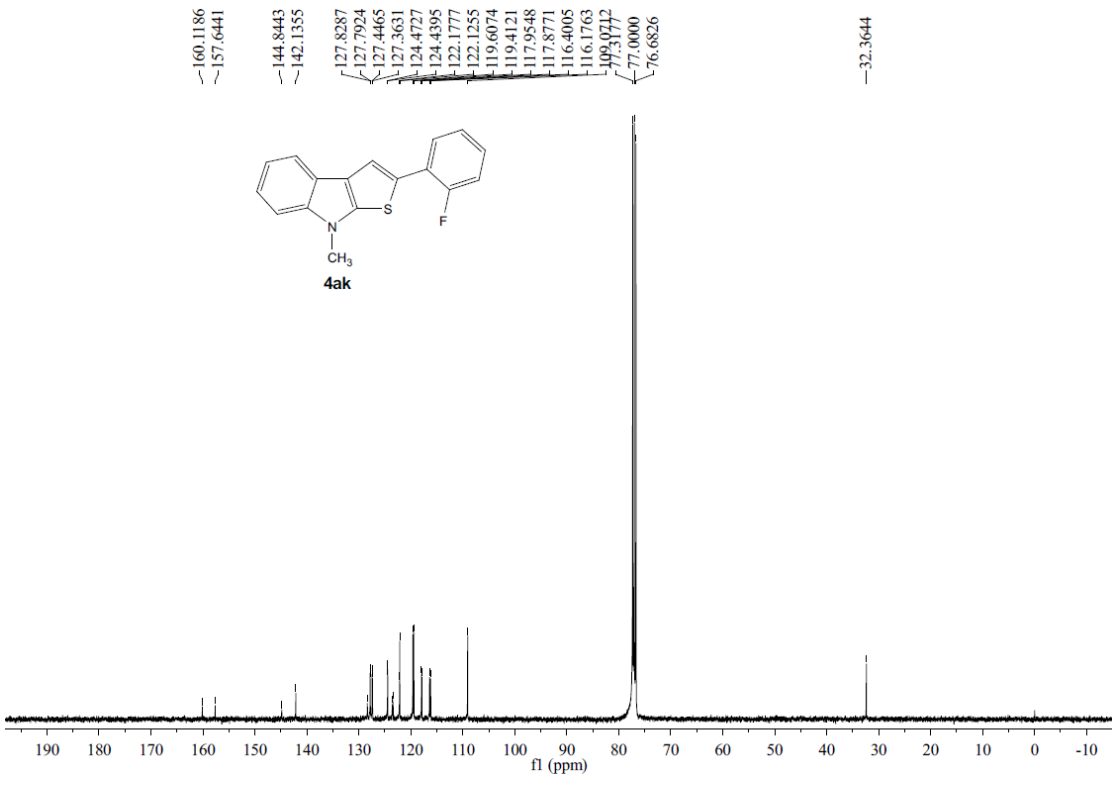
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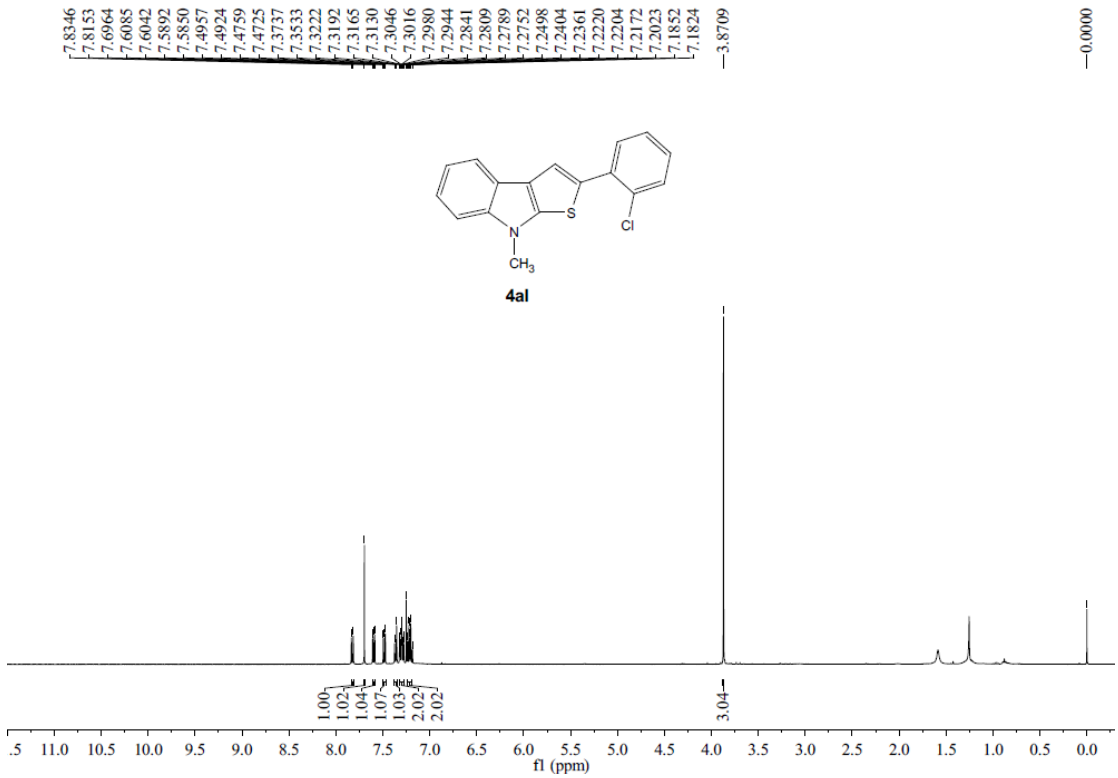
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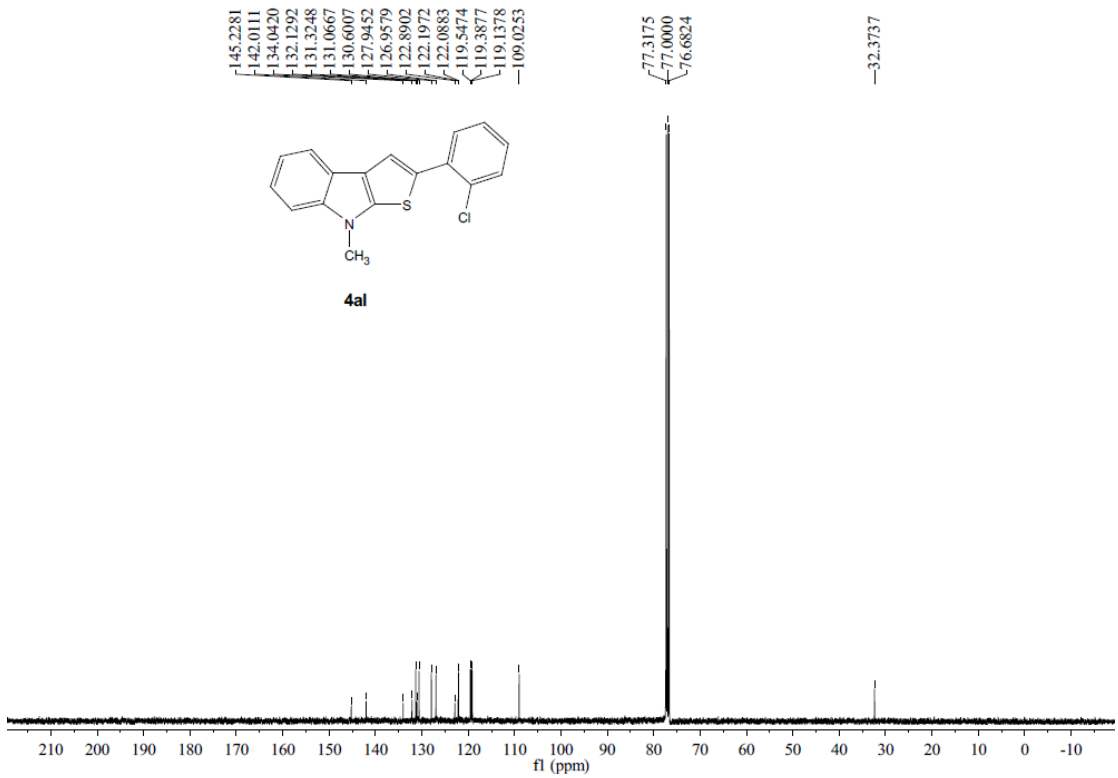
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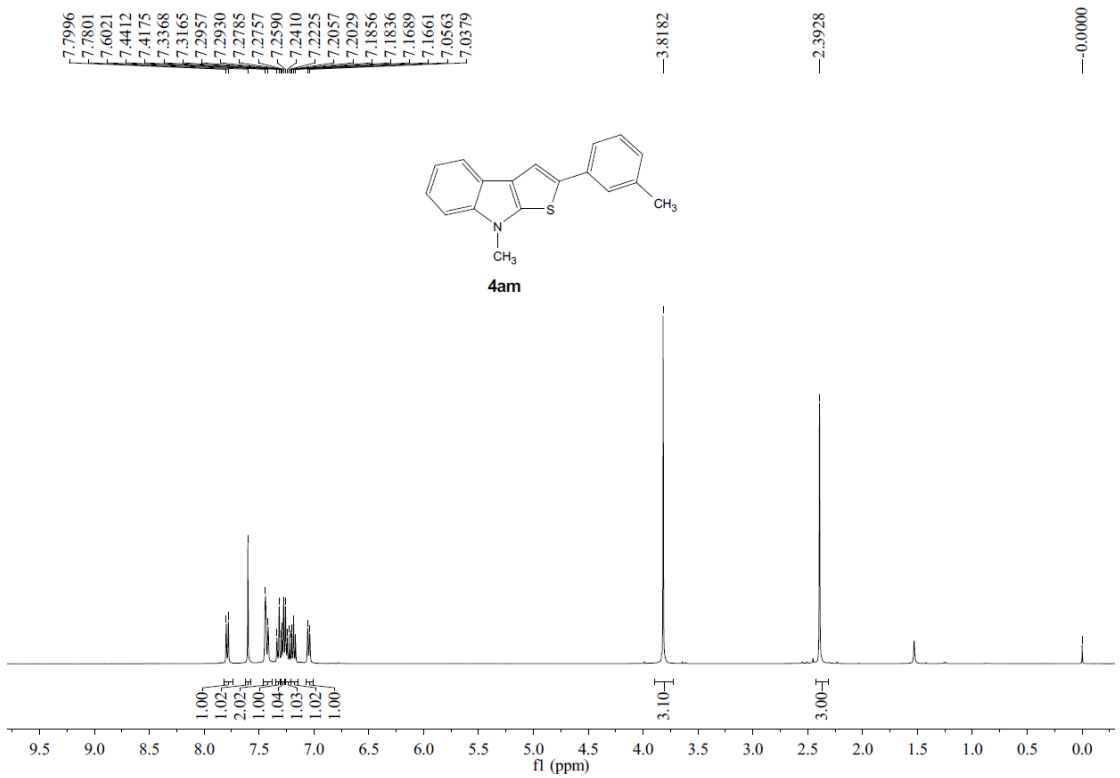
CH3
4al
f1 (ppm)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1.03
1.02
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3.10
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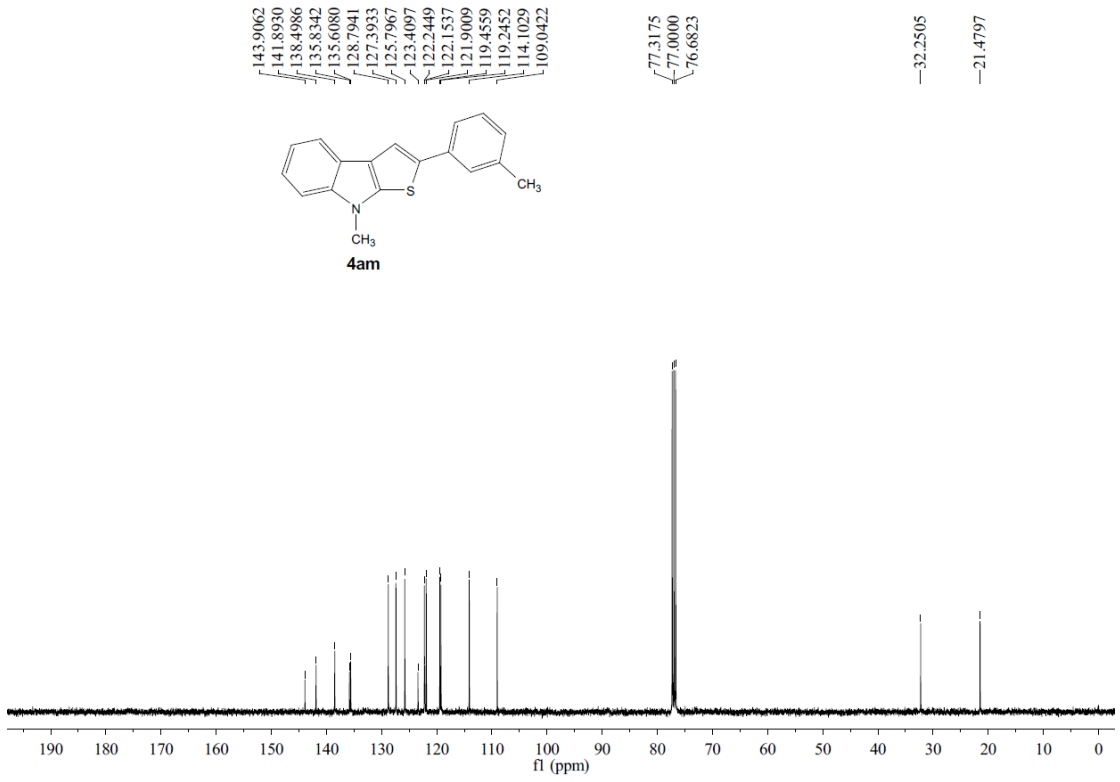
4am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S
N
CH3
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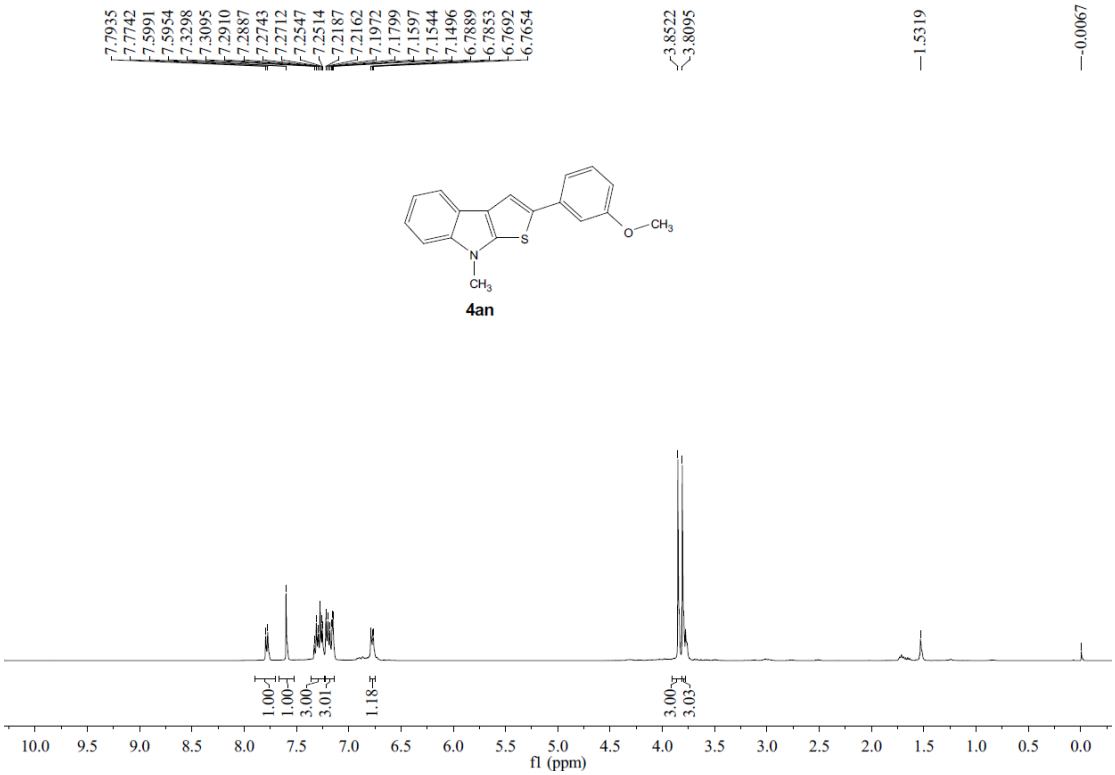
f1 (ppm)

4am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S
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3.00
3.03
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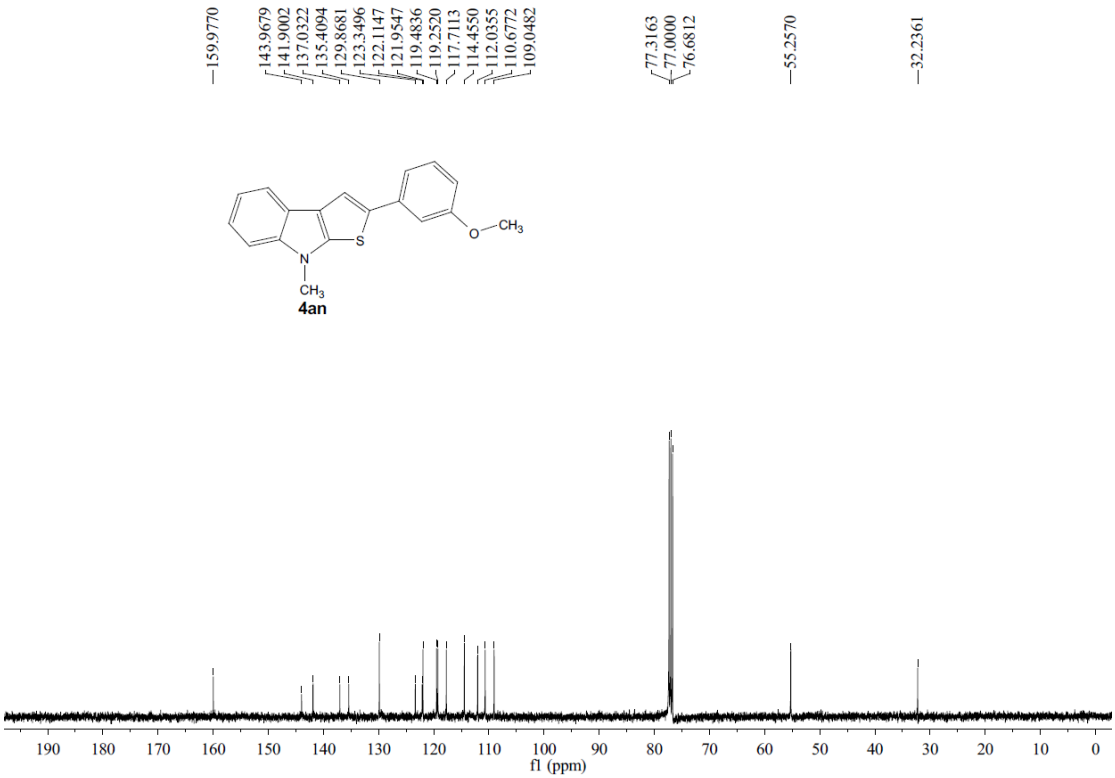
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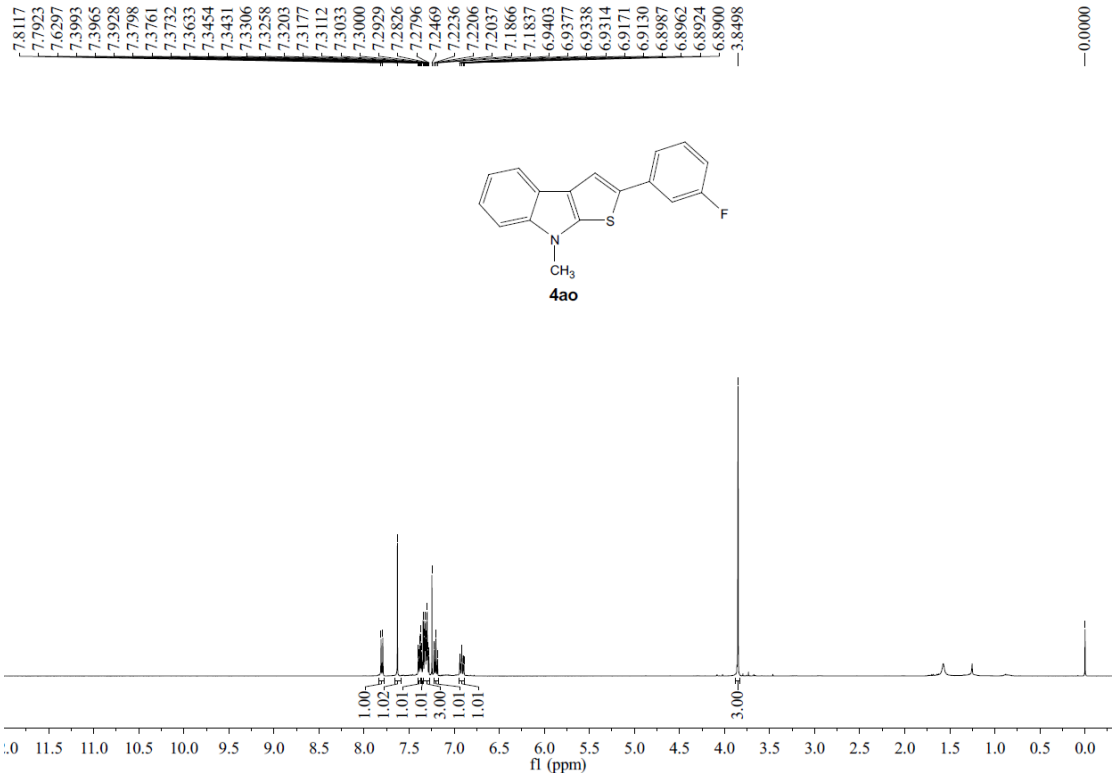
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7.3177
7.3112
7.3033
7.3000
7.2929
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7.2037
7.1866
7.1837
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6.9338
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6.9171
6.9130
6.8987
6.8962
6.8924
6.8900
3.8498
0.0000
S
N
CH3
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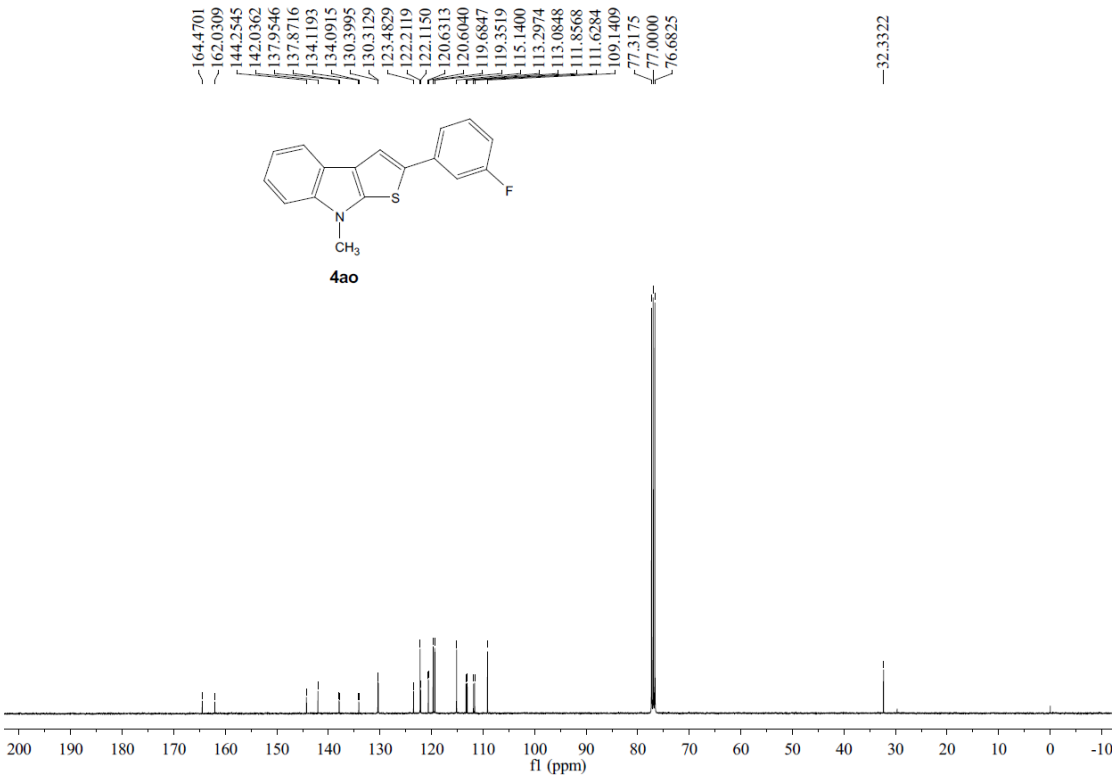
1.02
1.01
1.01
3.00
1.01
1.01
3.00
f1 (ppm)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113.0848
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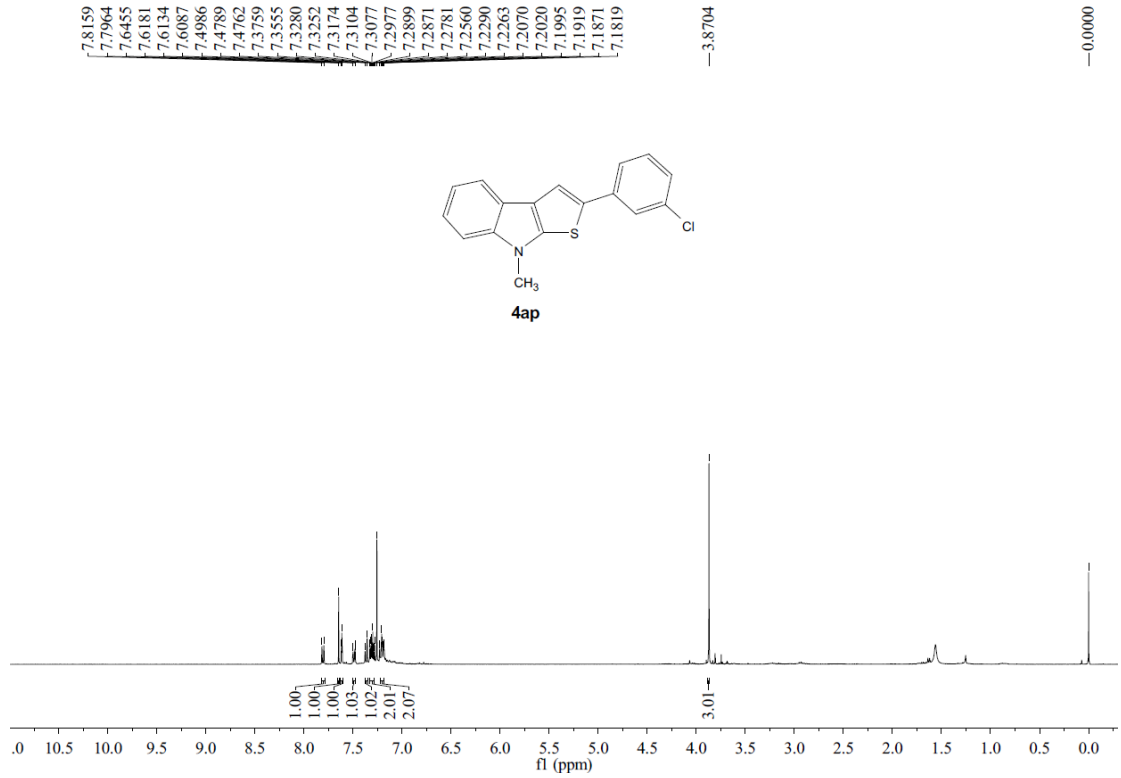
CH3
F
4ao
f1 (ppm)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7.3280
7.3252
7.3174
7.3104
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7.2977
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7.2871
7.2781
7.2560
7.2290
7.2263
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7.2020
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7.1871
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Cl
S
N
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1.02
2.01
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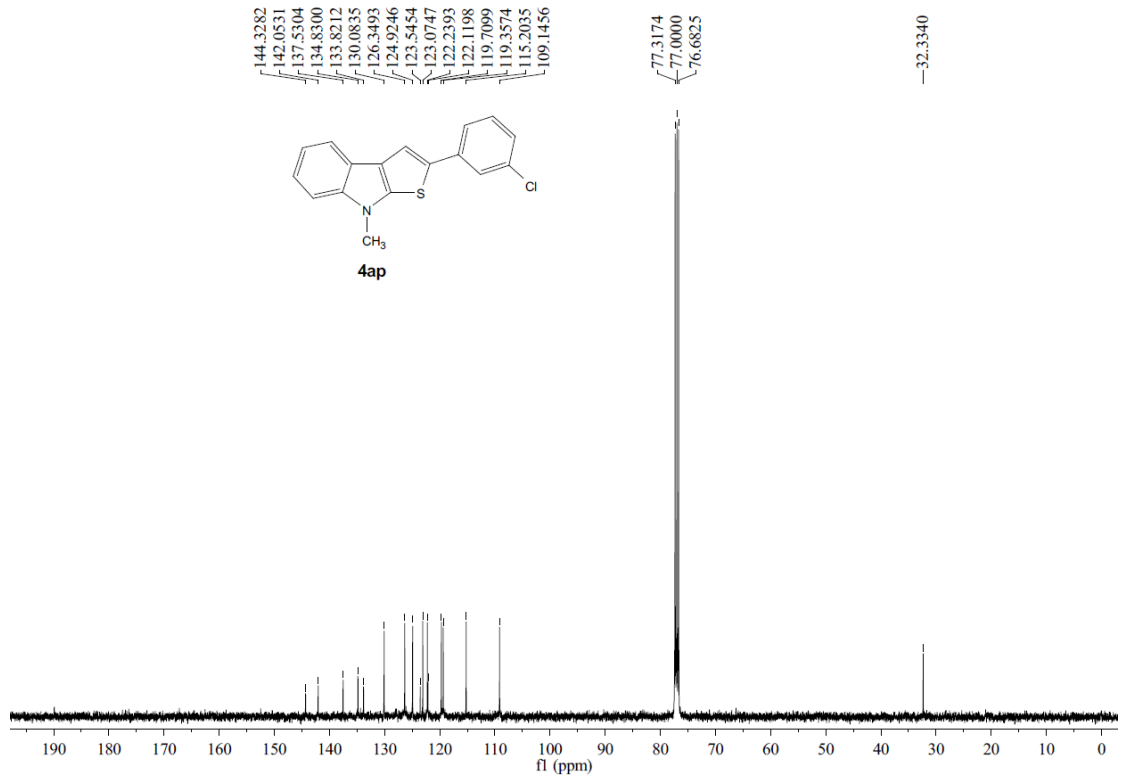
3.01
fl (ppm)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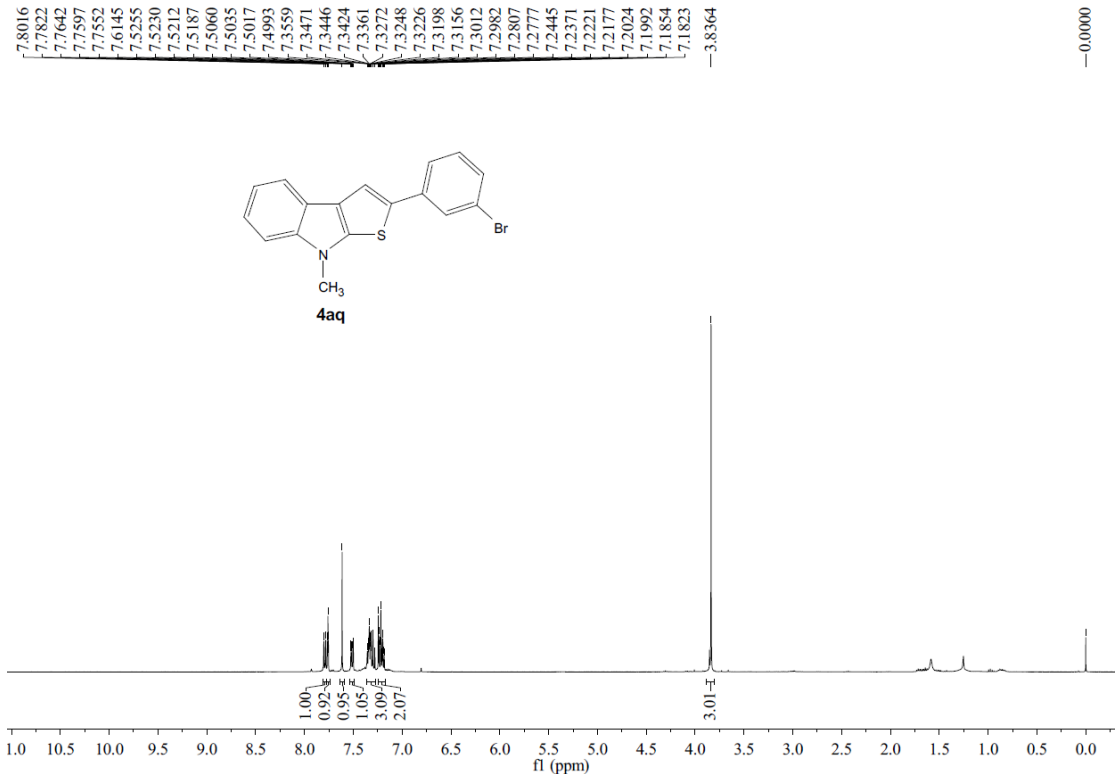
Cl
S
N
CH3
4ap
fl (ppm)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7.3471
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7.3272
7.3248
7.3226
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Br
S
N
CH3
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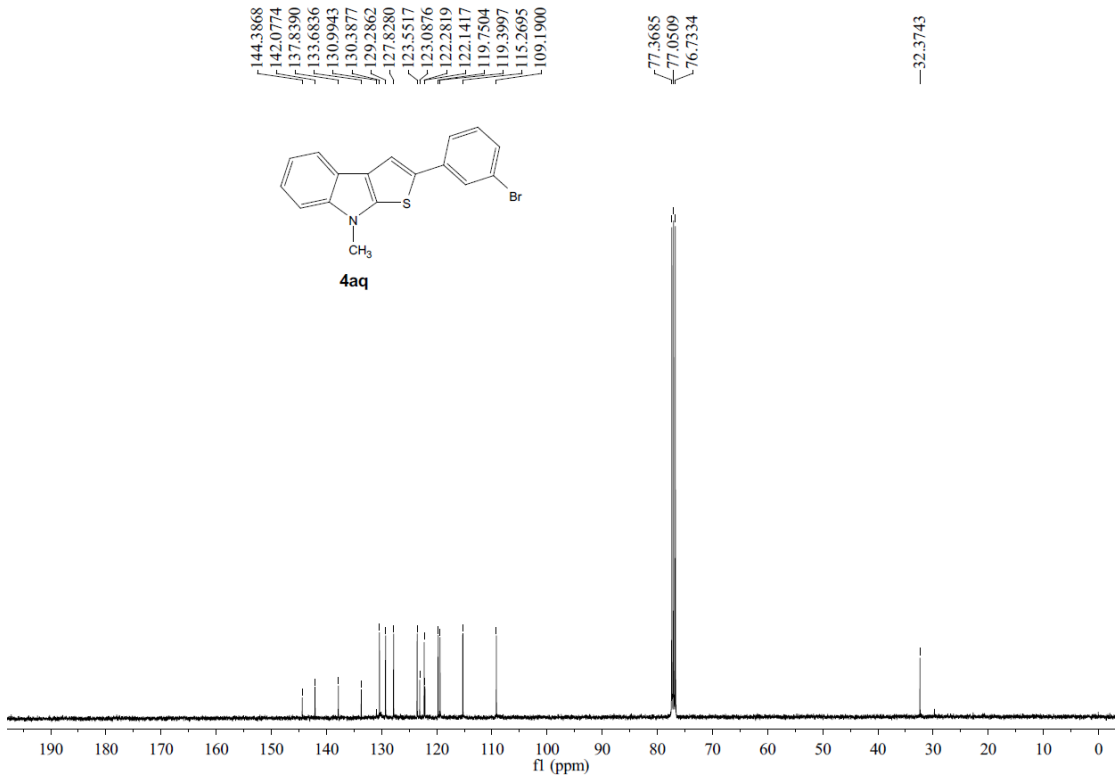
1.00
0.92
0.95
1.05
3.09
2.07
3.01
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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N
CH3
4aq
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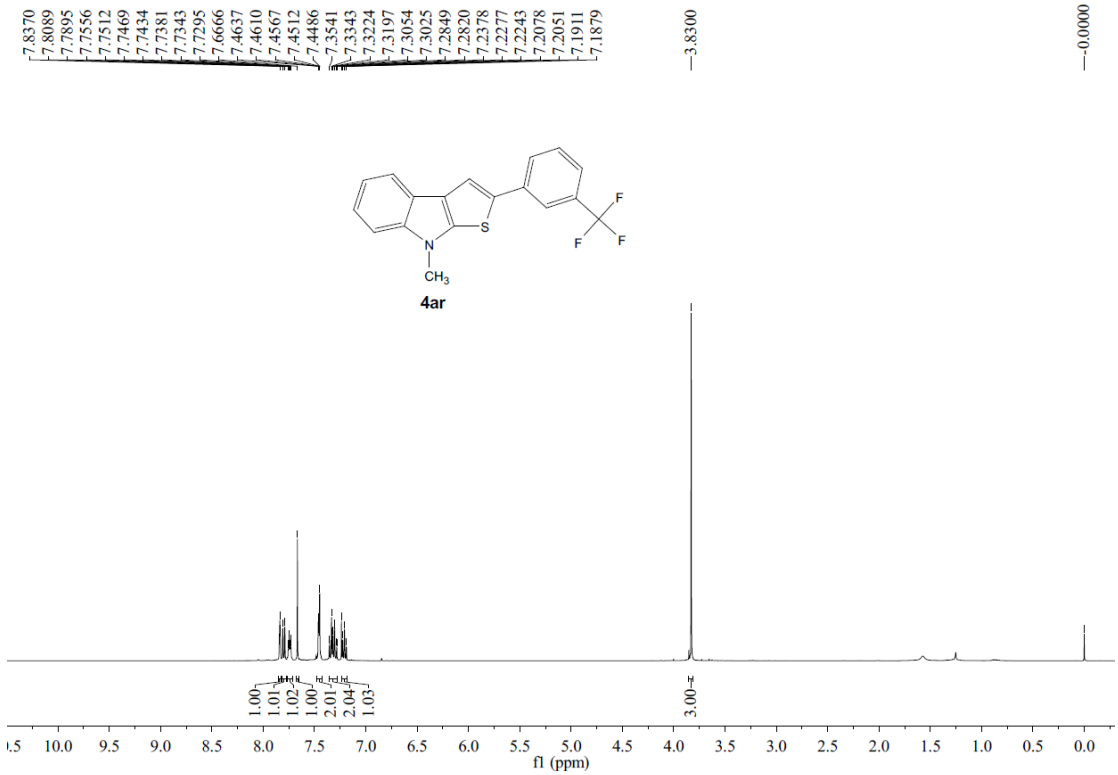
f1 (ppm)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7.4637
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7.4567
7.4512
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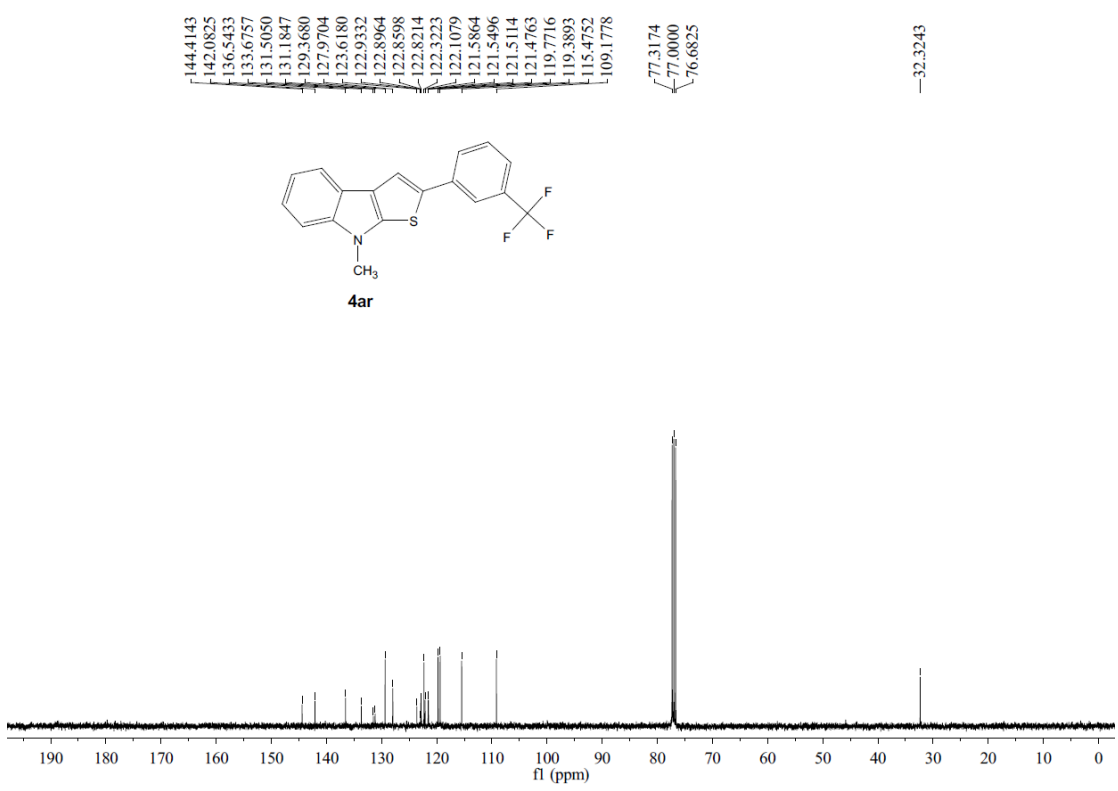
7.3541
7.3343
7.3224
7.3197
7.3054
7.3025
7.2849
7.2820
7.2378
7.2277
7.2243
7.2078
7.2051
7.1911
7.1879
3.8300
0.0000
F
F
F
S
N
CH3
4ar
1.00
1.01
1.02
1.00
2.01
2.04
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.6825
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F
F
S
N
CH3
4ar
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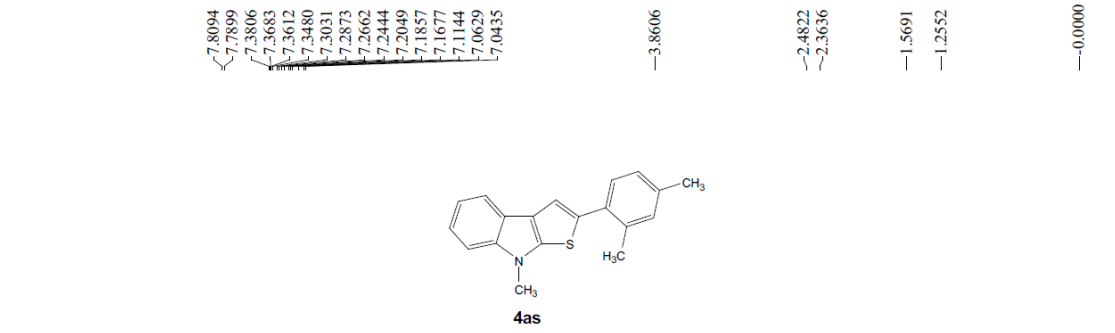
f1 (ppm)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7.1857
7.1677
7.1144
7.0629
7.0435
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2.3636
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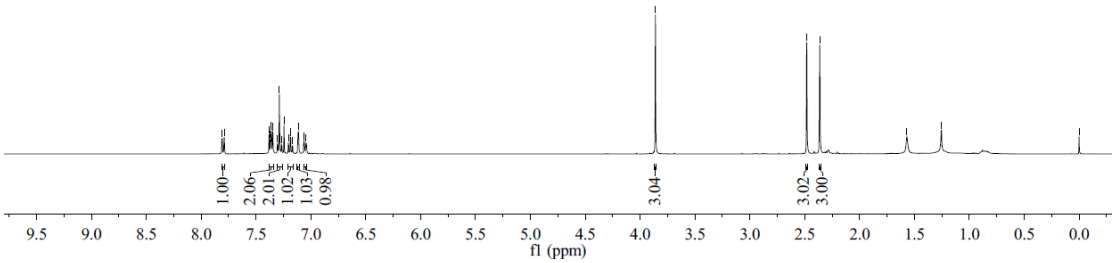
CH3
S
N
CH3
H3C

4as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3.02
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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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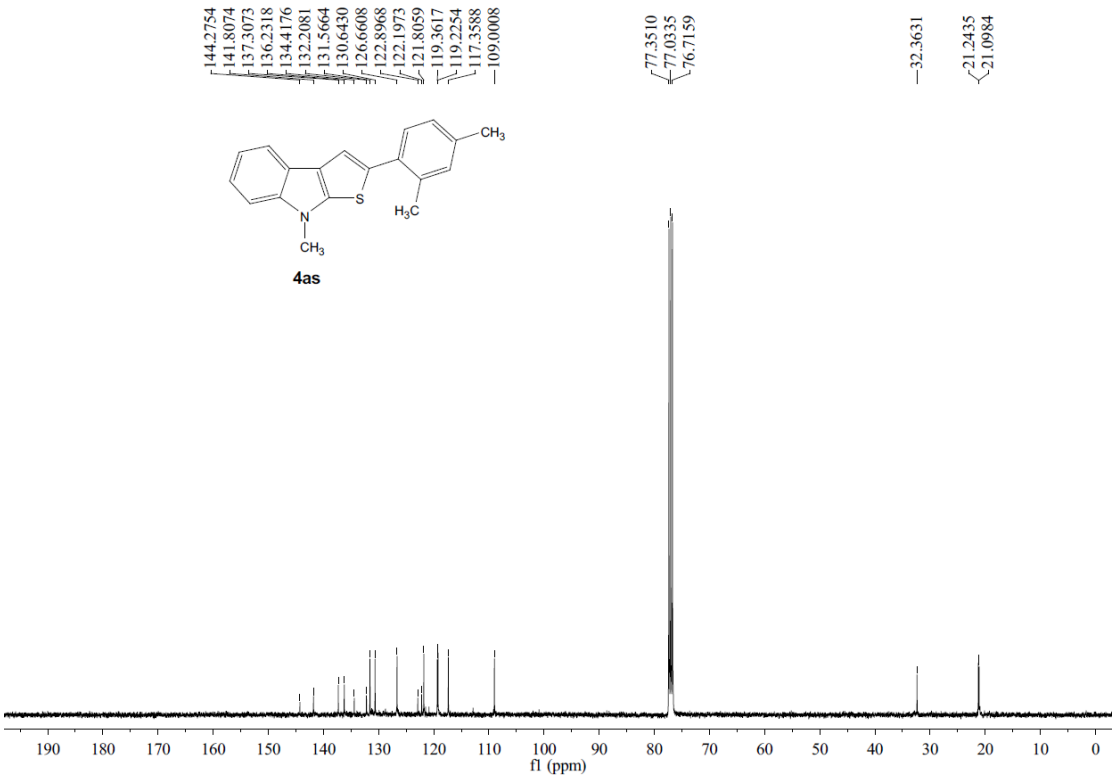
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21.2435
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S
N
CH3
H3C
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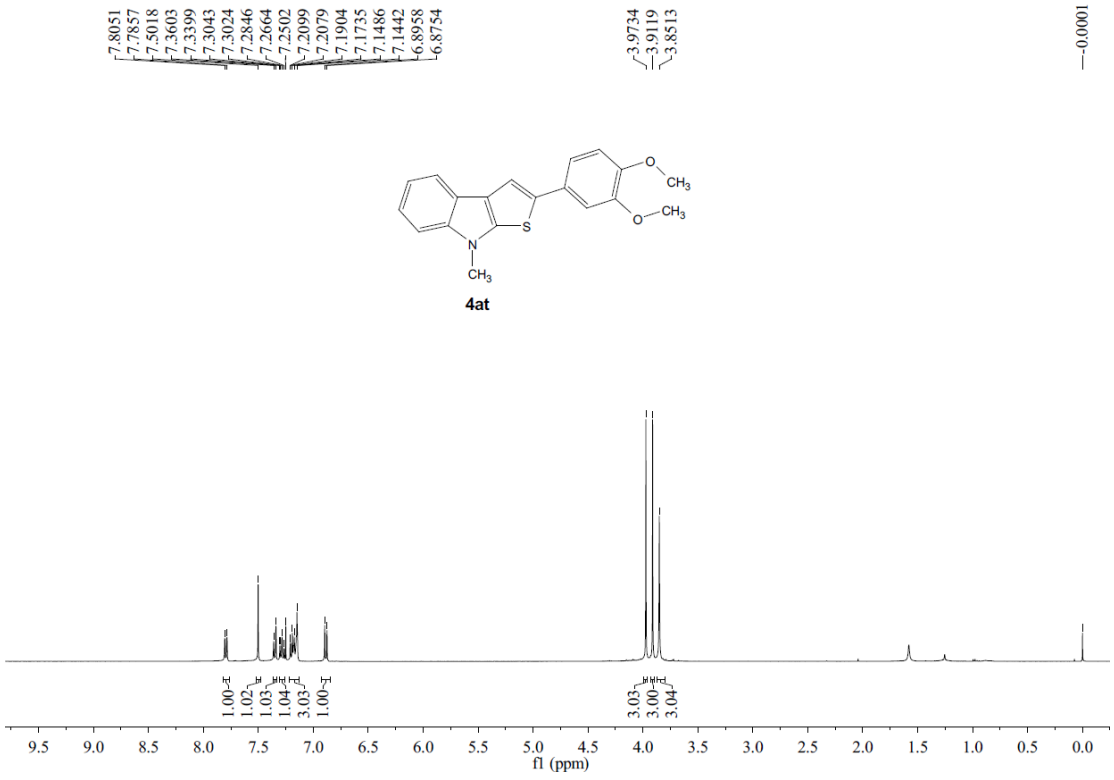
f1 (ppm)

4as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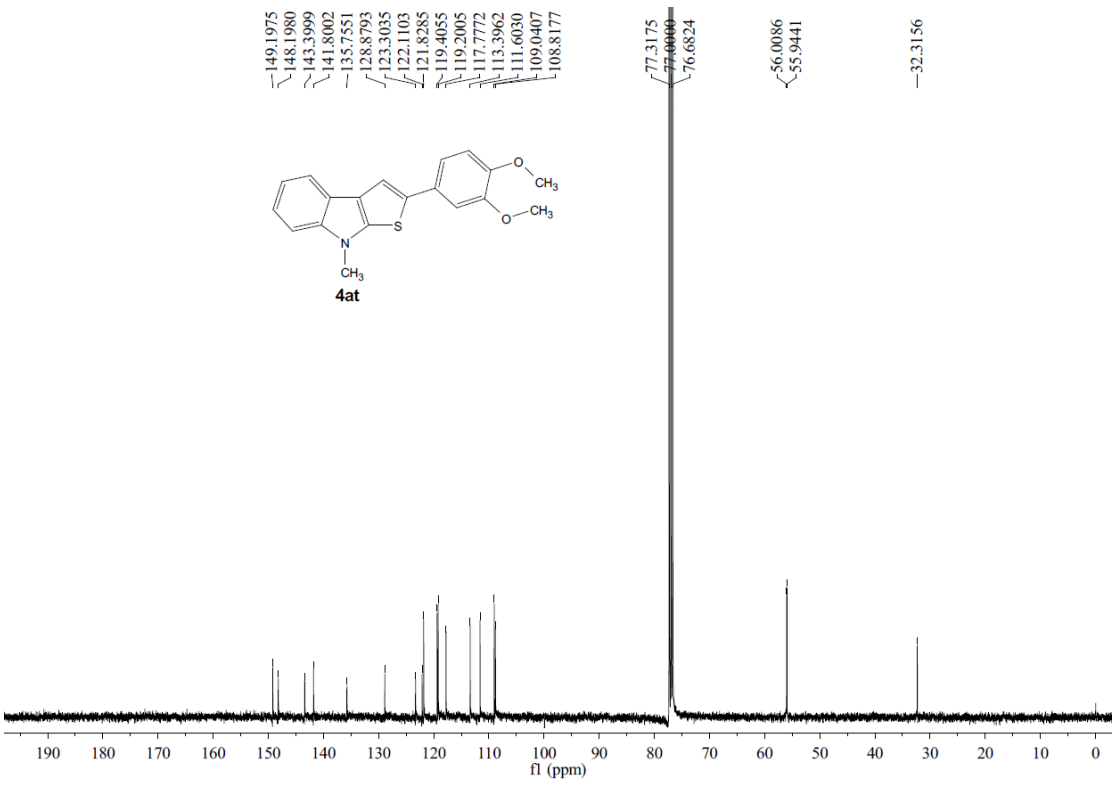
7.2079
7.1904
7.1735
7.1486
7.1442
6.8958
6.8754
3.9734
3.9119
3.8513
0.0001
O
CH3
O
CH3
S
N
CH3
4at
1.00
1.02
1.03
1.04
3.03
1.00
3.03
3.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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O
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S
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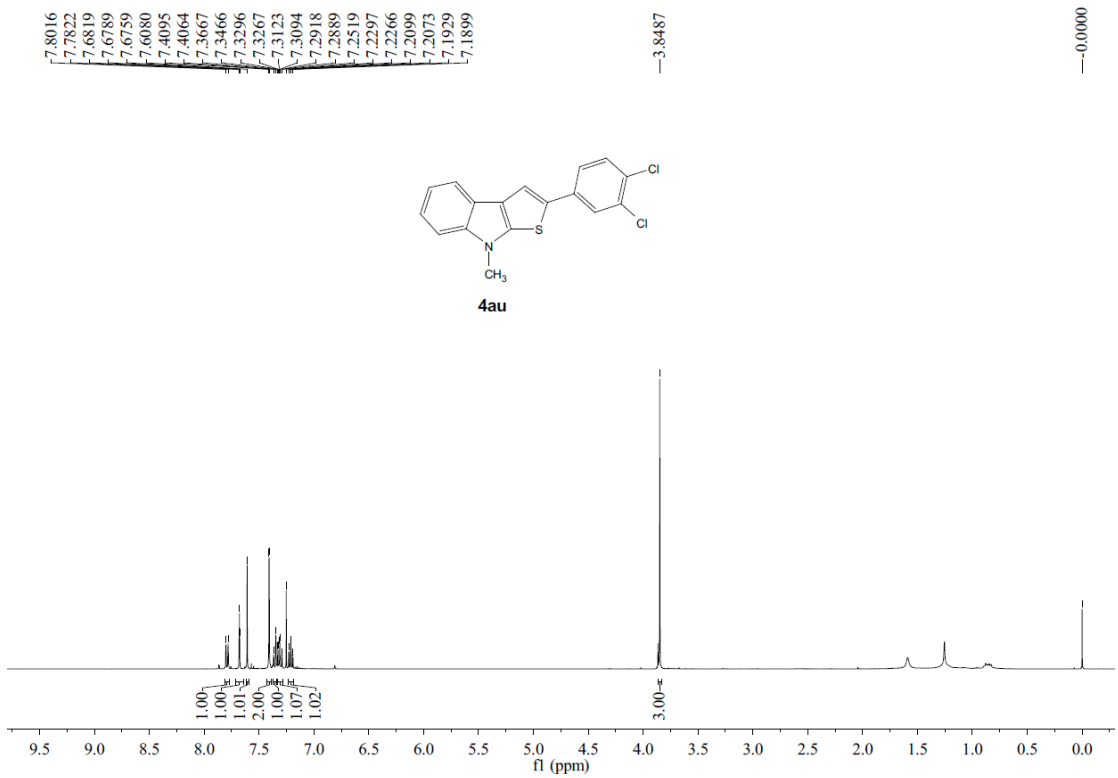
f1 (ppm)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7.2519
7.2297
7.2266
7.2099
7.2073
7.1929
7.1899
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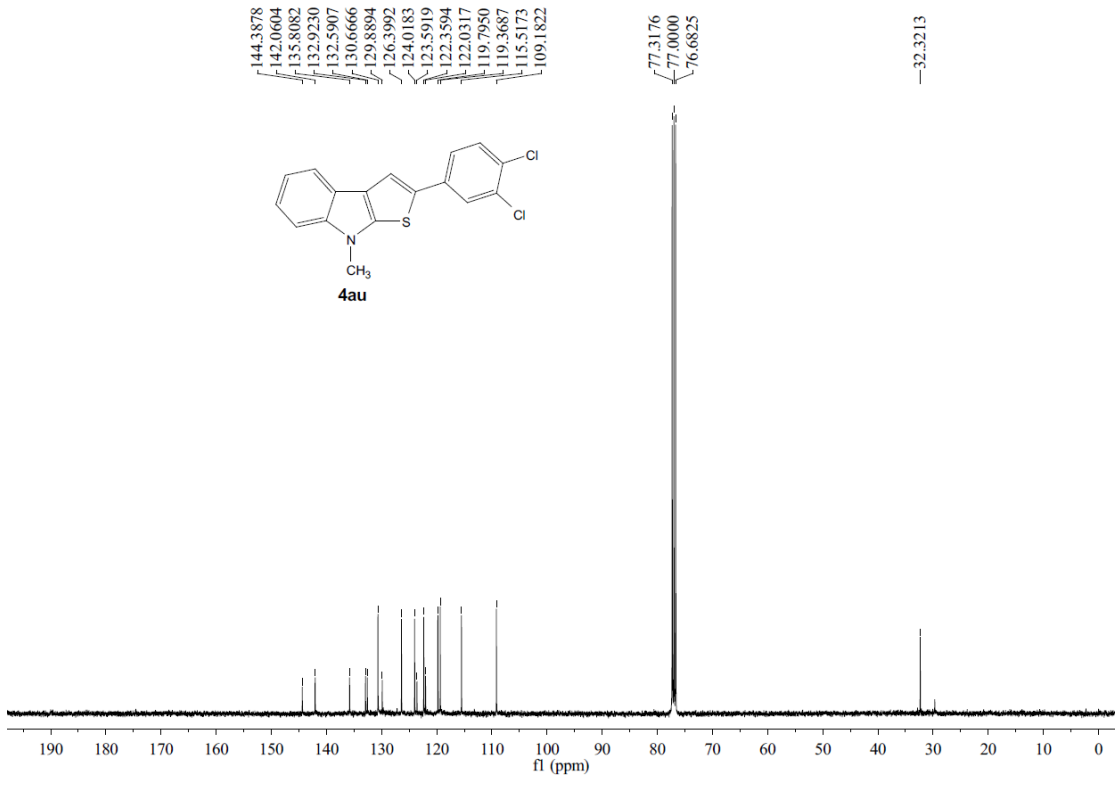
Cl
Cl
S
N
CH3
4au
1.00
1.00
1.01
2.00
1.00
1.07
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
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Cl
Cl
S
N
CH3
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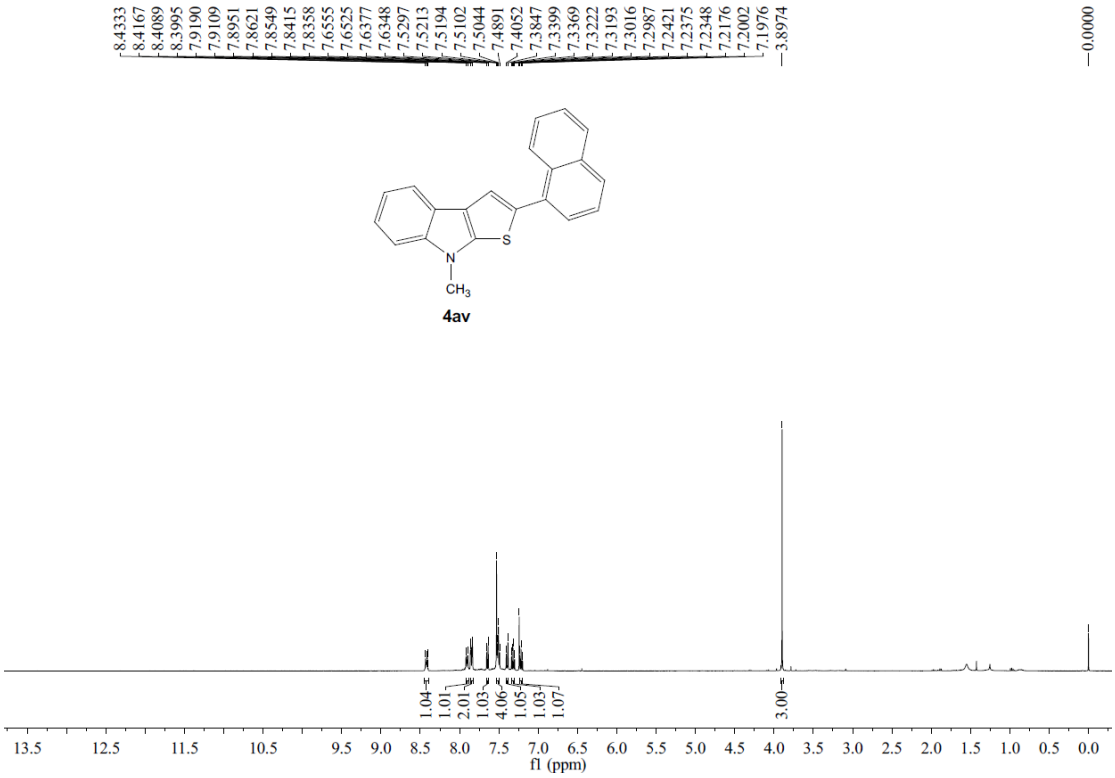
f1 (ppm)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S
CH3
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1.01
2.01
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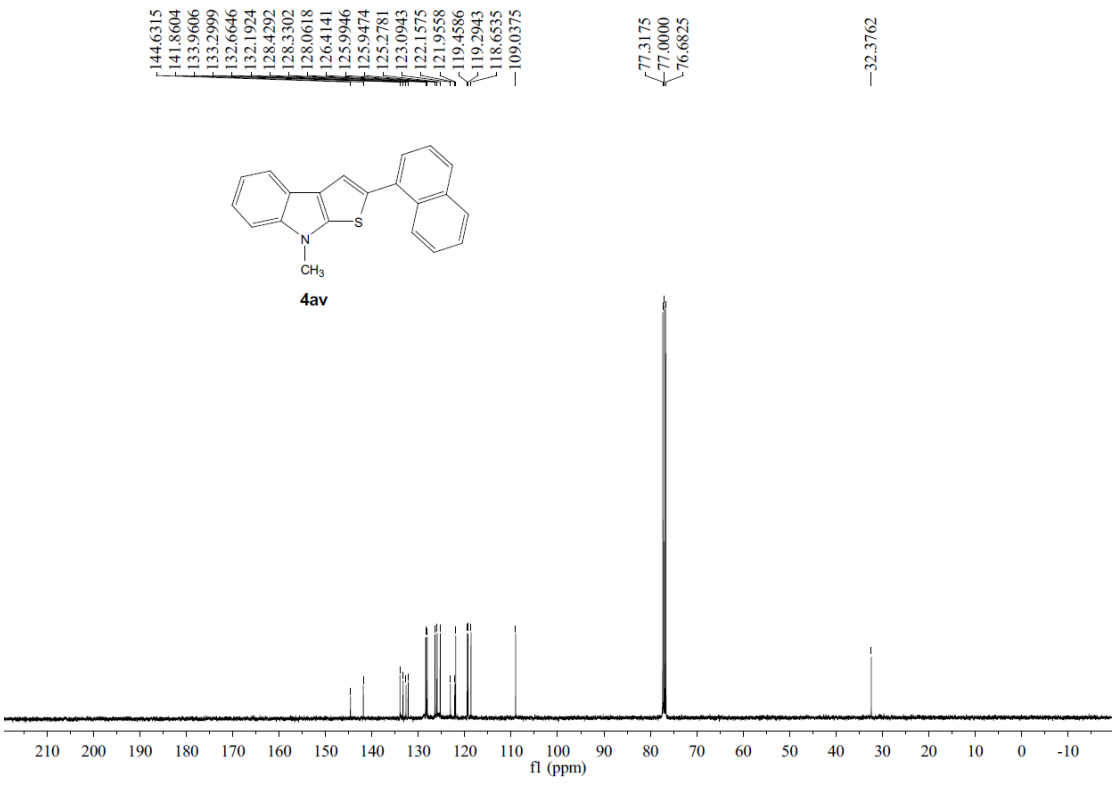
4.06
1.05
1.03
1.07
3.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
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S
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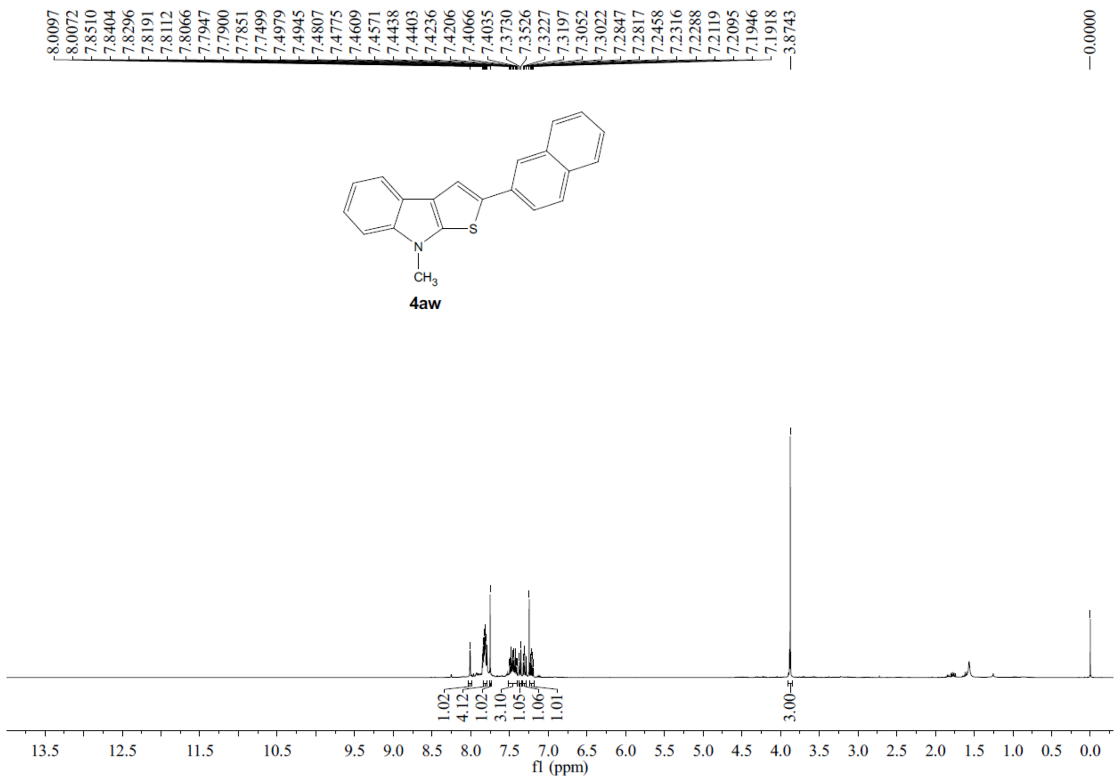
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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1.06
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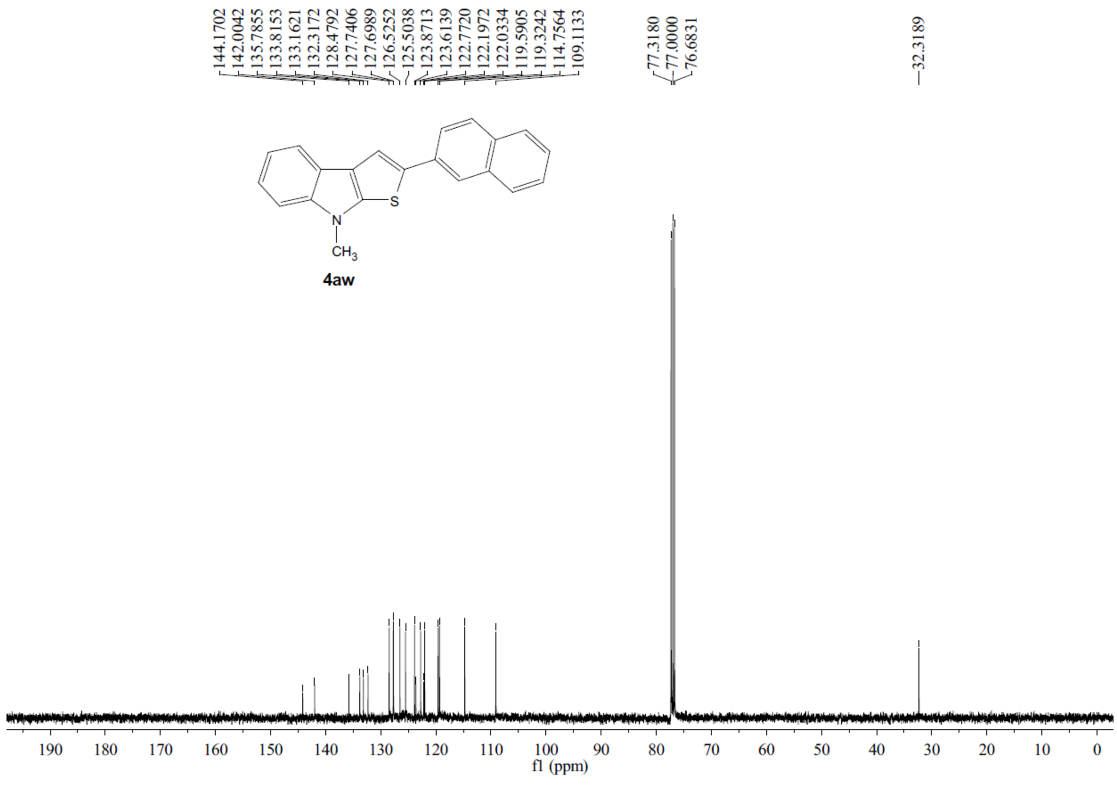
fl (ppm)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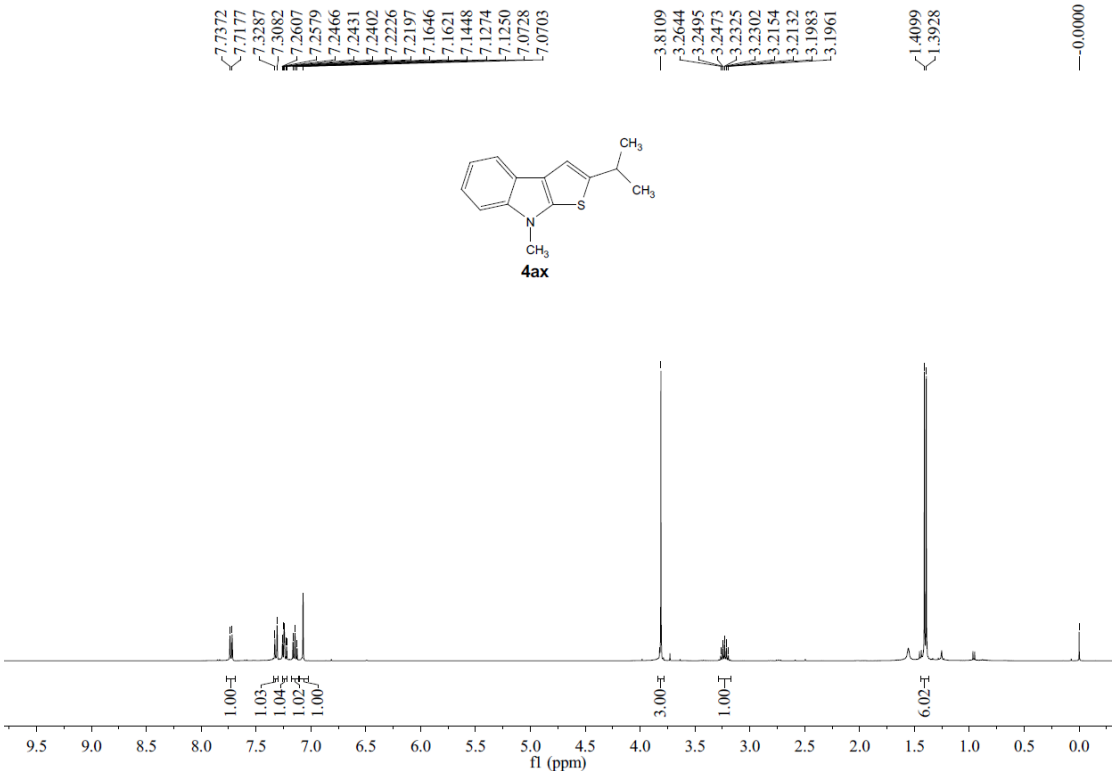
fl (ppm)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CH3
S
N
CH3
4ax
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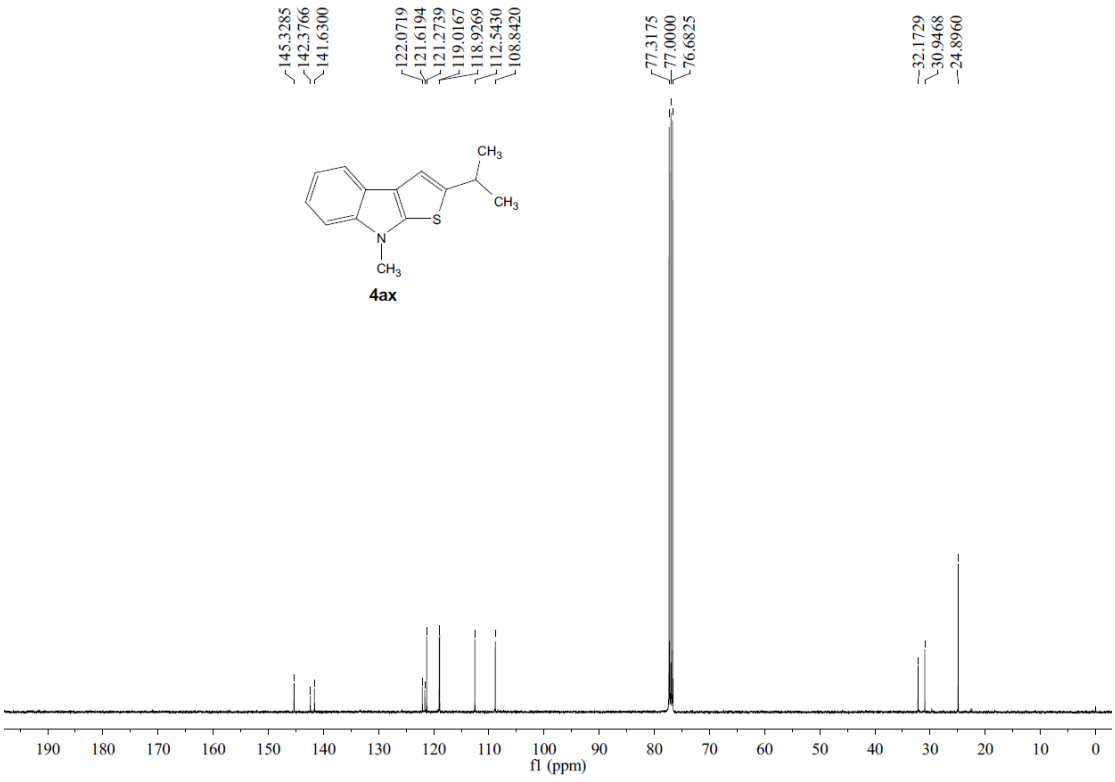
1.03
1.04
1.02
1.00
3.00
1.00
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
76.6825
32.1729
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CH3
CH3
S
N
CH3
4ax
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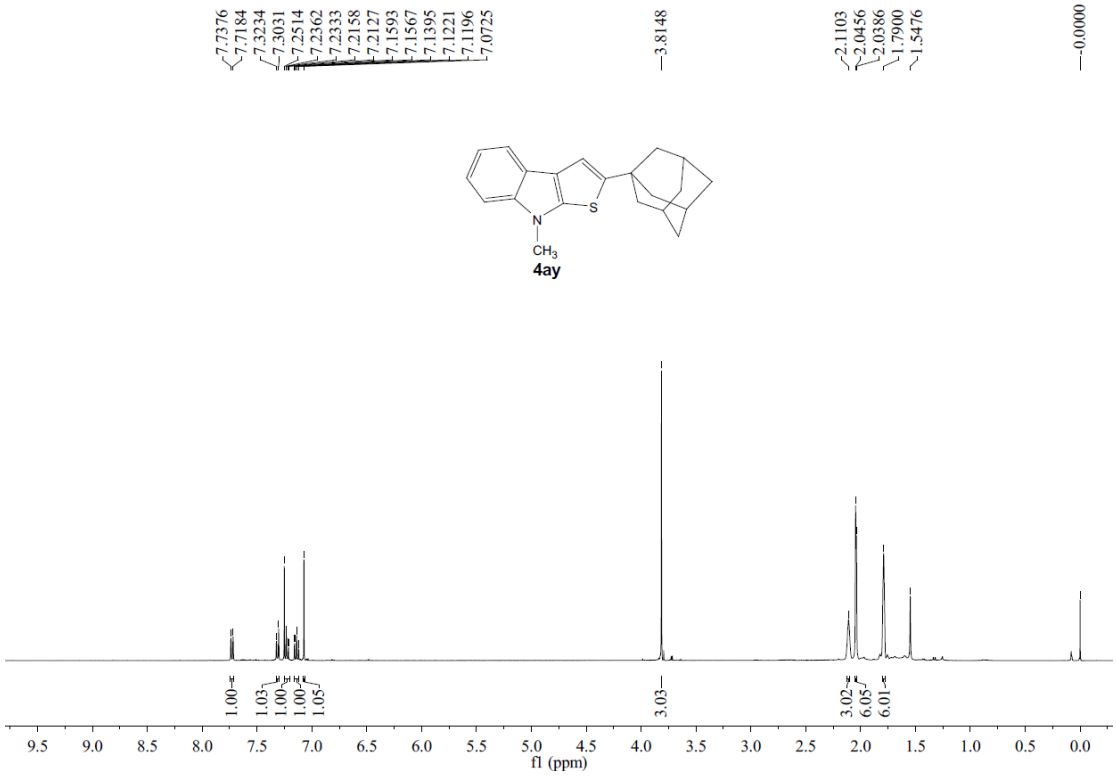
f1 (ppm)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7.1221
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7.0725
3.8148
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2.0456
2.0386
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1.5476
0.0000
N
S
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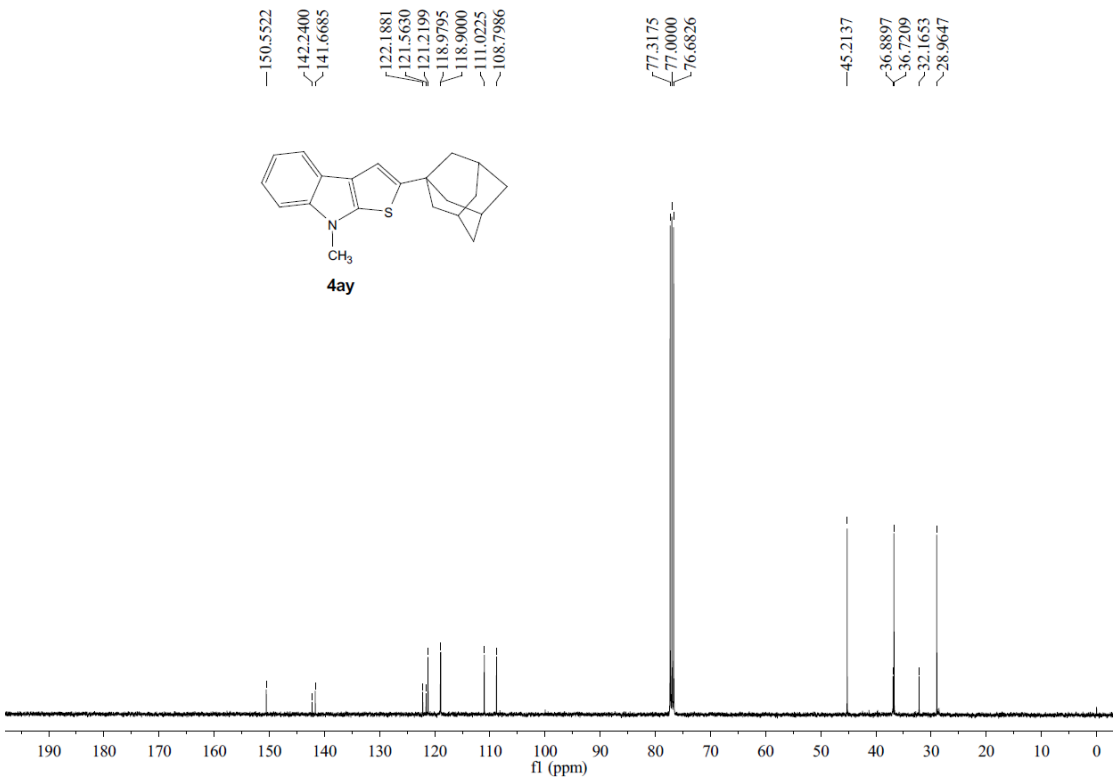
1.00
1.00
1.05
3.03
3.02
6.05
6.01
fl (ppm)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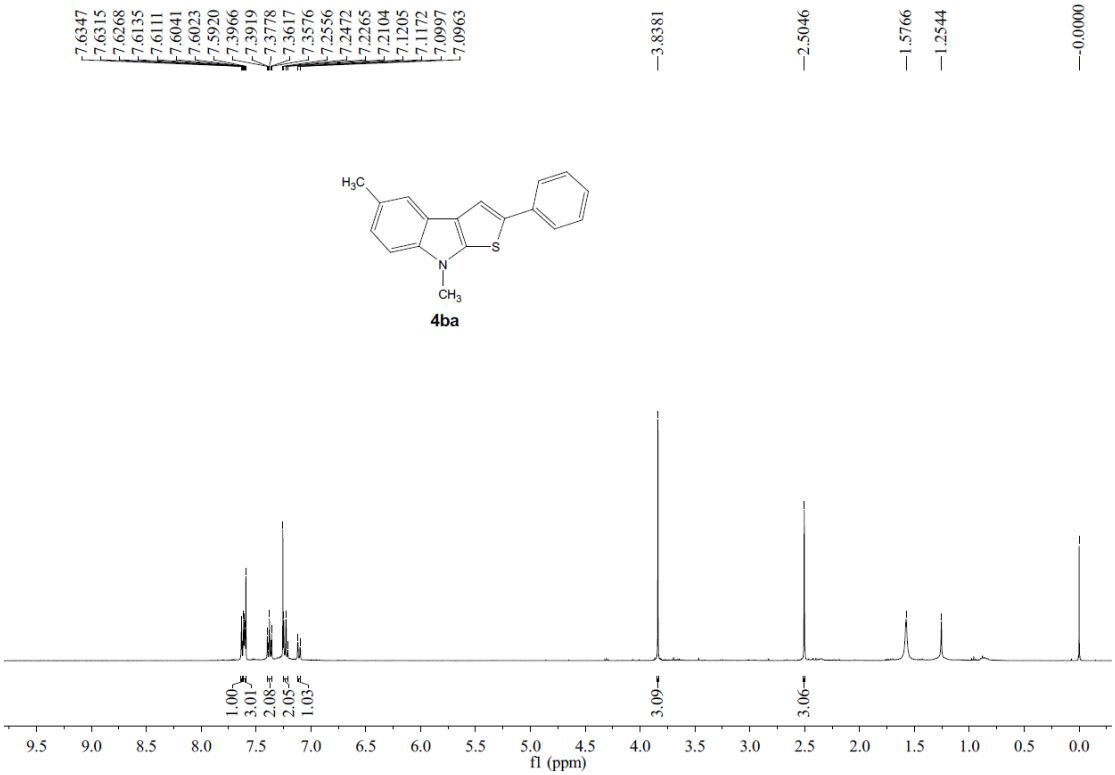
N
S
CH3
4ay
fl (ppm)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H3C
S
N
CH3
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1.00
3.01
2.08
2.05
1.03
3.09
3.06
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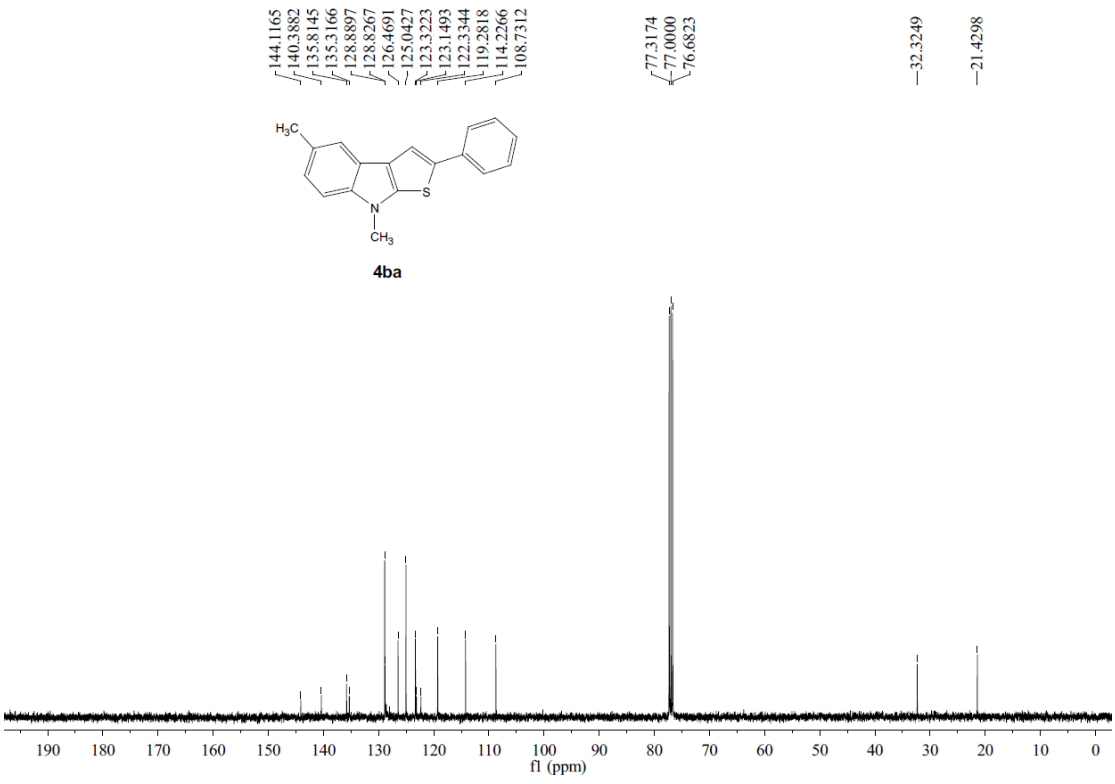
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114.2266
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77.0000
76.6823
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S
N
CH3
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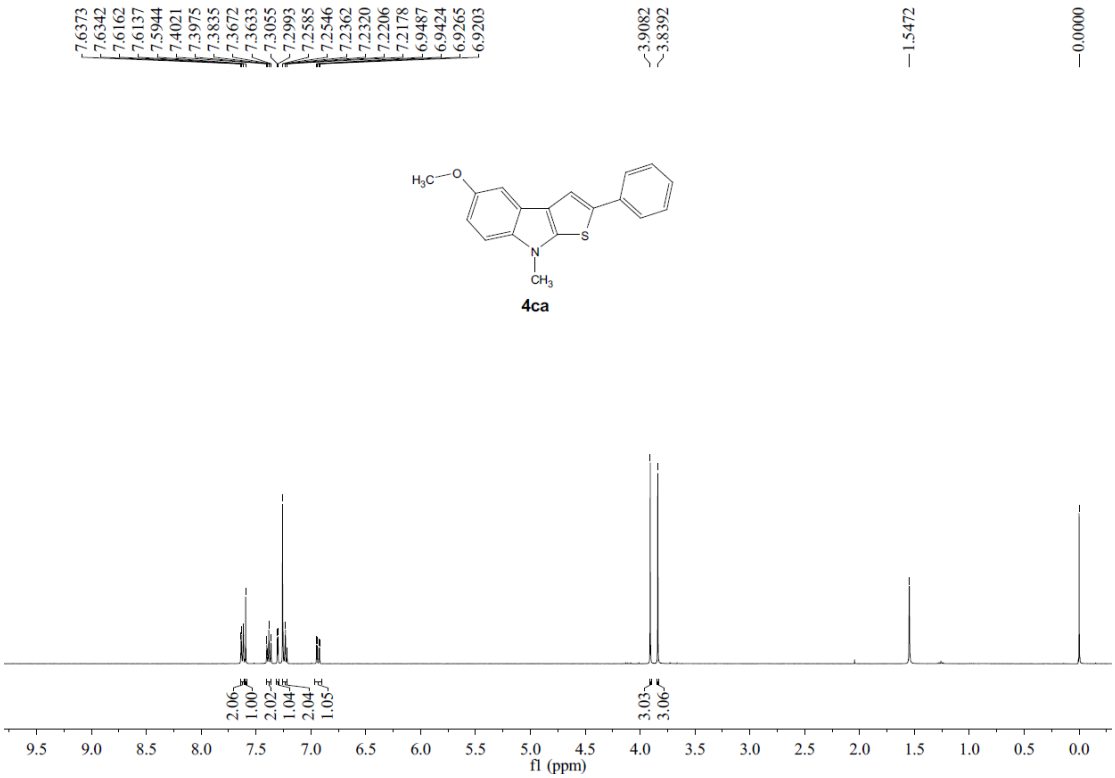
f1 (ppm)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7.2993
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7.2546
7.2362
7.2320
7.2206
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6.9424
6.9265
6.9203
3.9082
3.8392
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O
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2.02
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1.05
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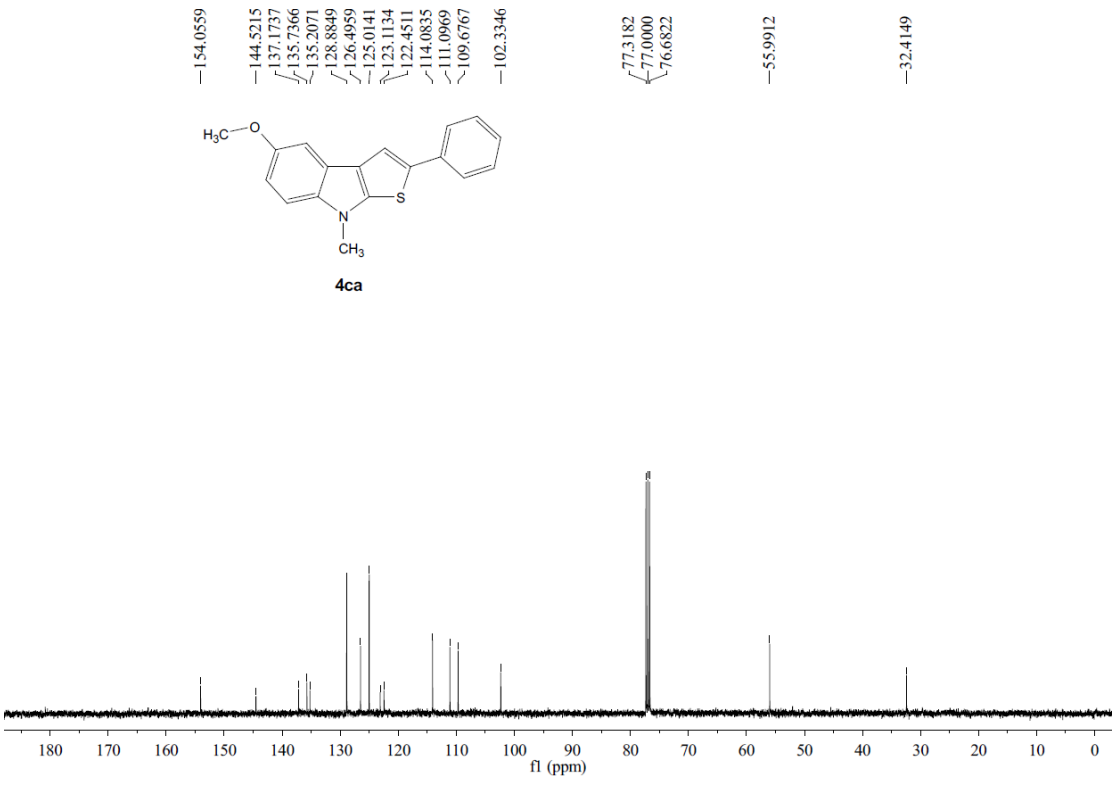
3.06
f1 (ppm)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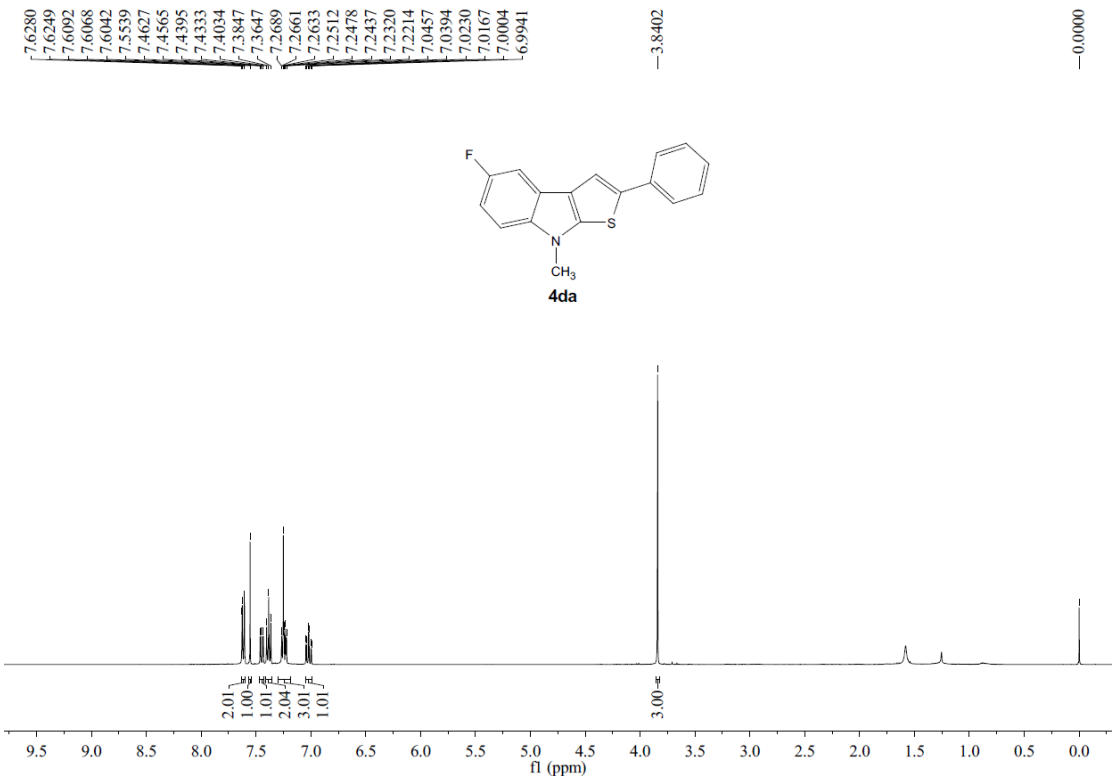
4ca
f1 (ppm)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7.2689
7.2661
7.2633
7.2512
7.2478
7.2437
7.2320
7.2214
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7.0394
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F
S
N
CH3
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1.00
1.01
2.04
3.01
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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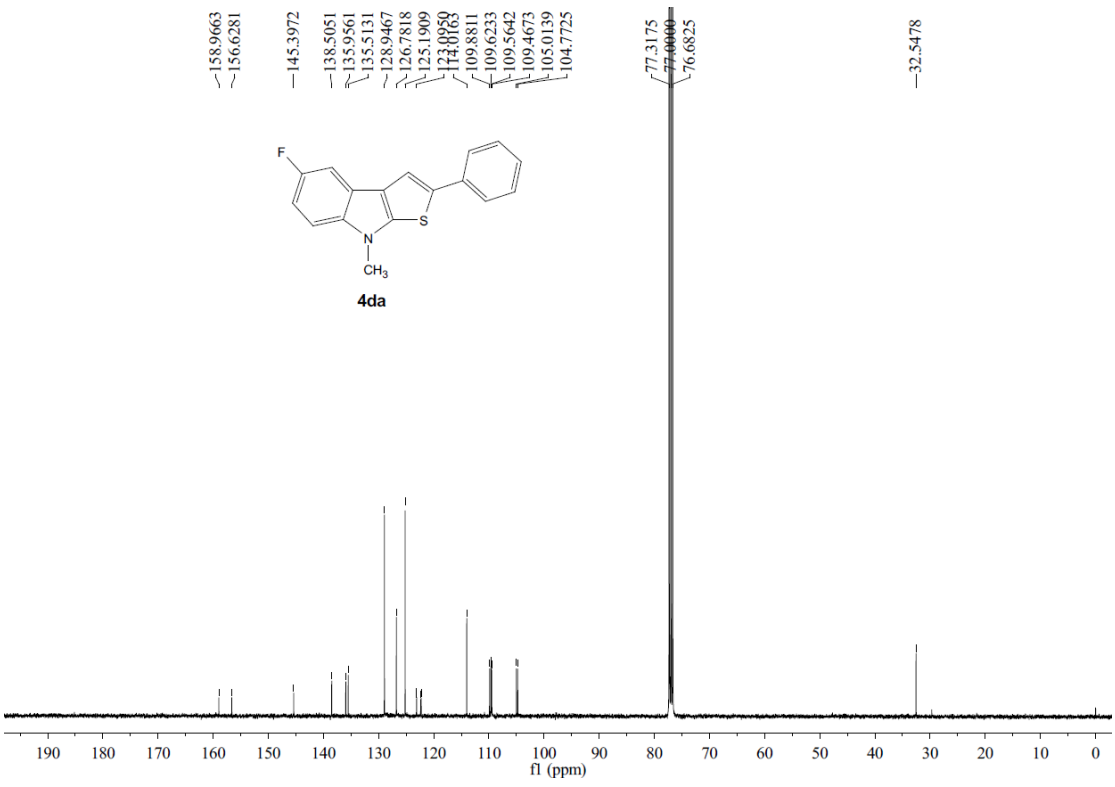
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N
CH3
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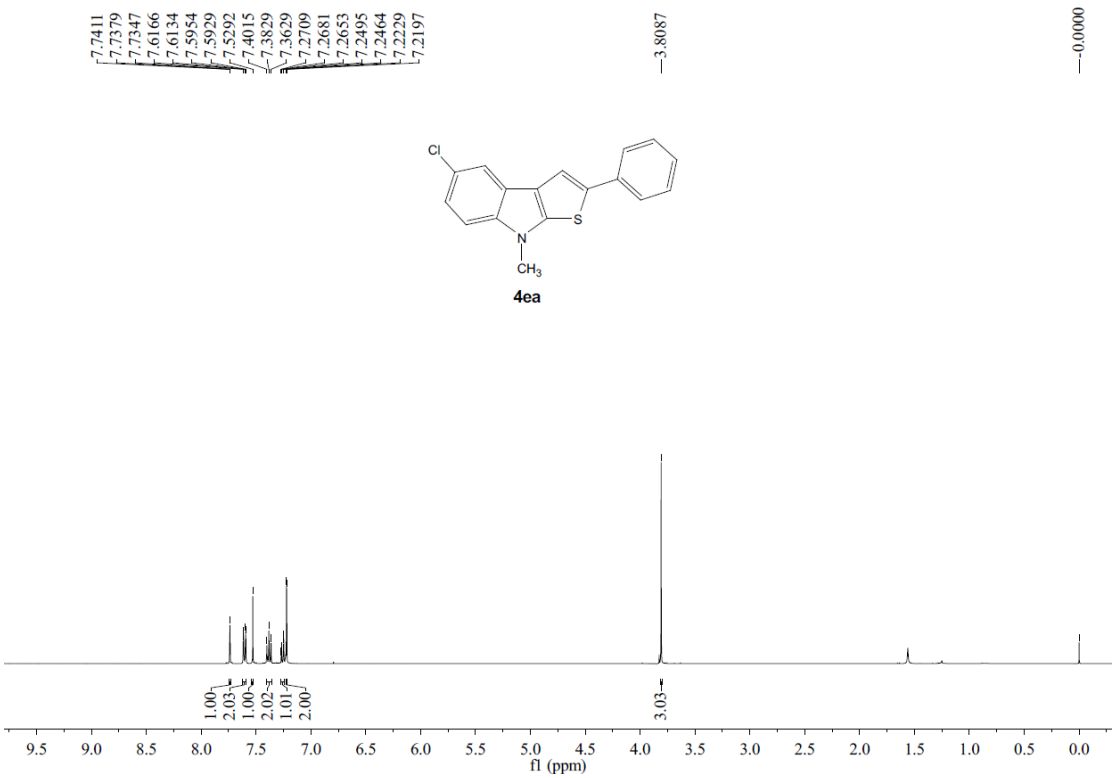
f1 (ppm)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7.2495
7.2464
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Cl
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N
CH3
4ea
1.00
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1.00
2.02
1.01
2.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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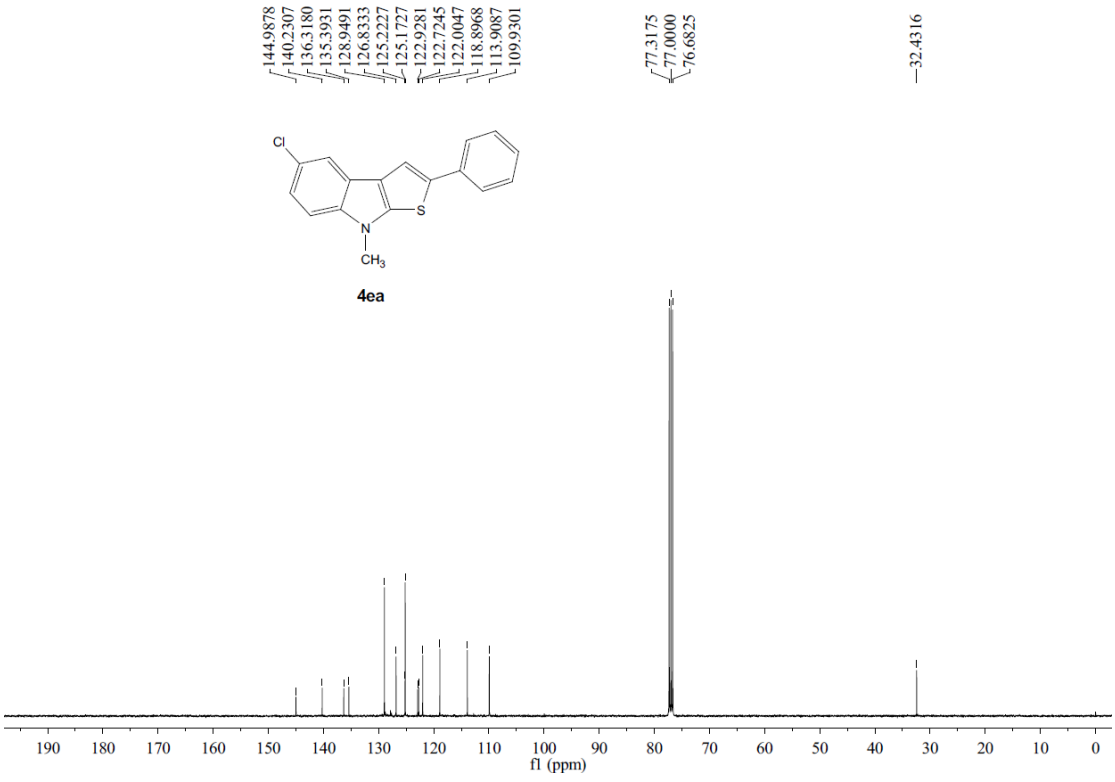
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S
N
CH3
4ea
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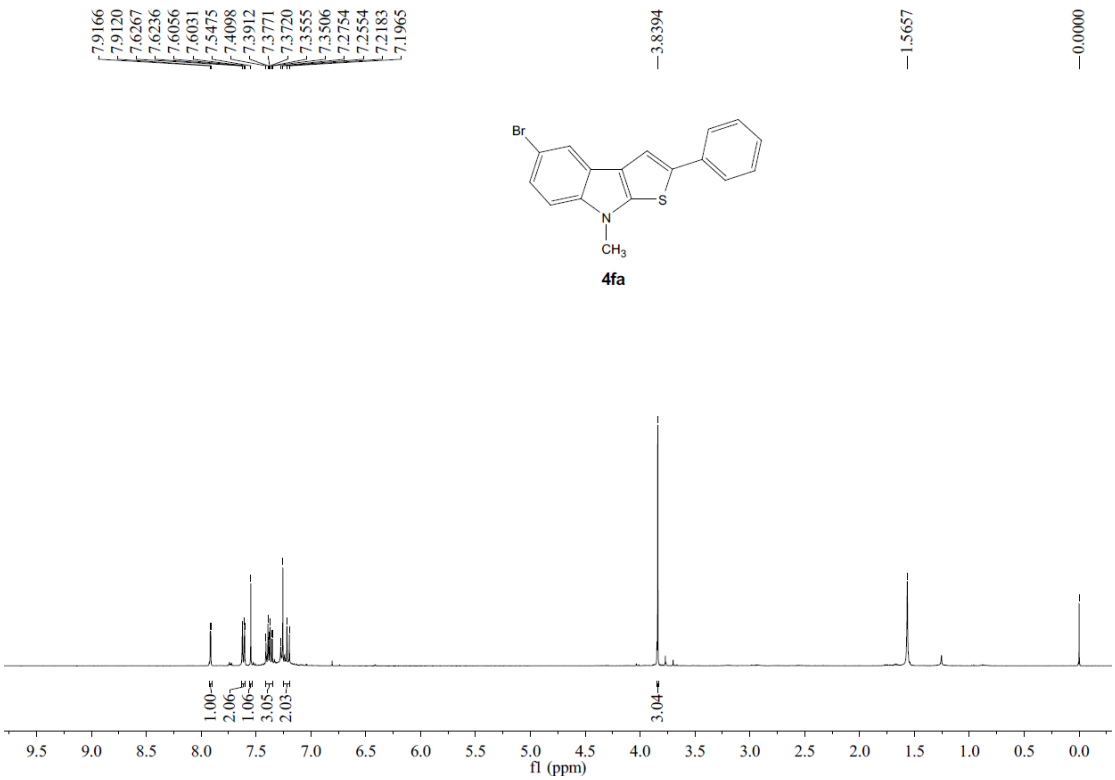
f1 (ppm)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7.3555
7.3506
7.2754
7.2554
7.2183
7.1965
3.8394
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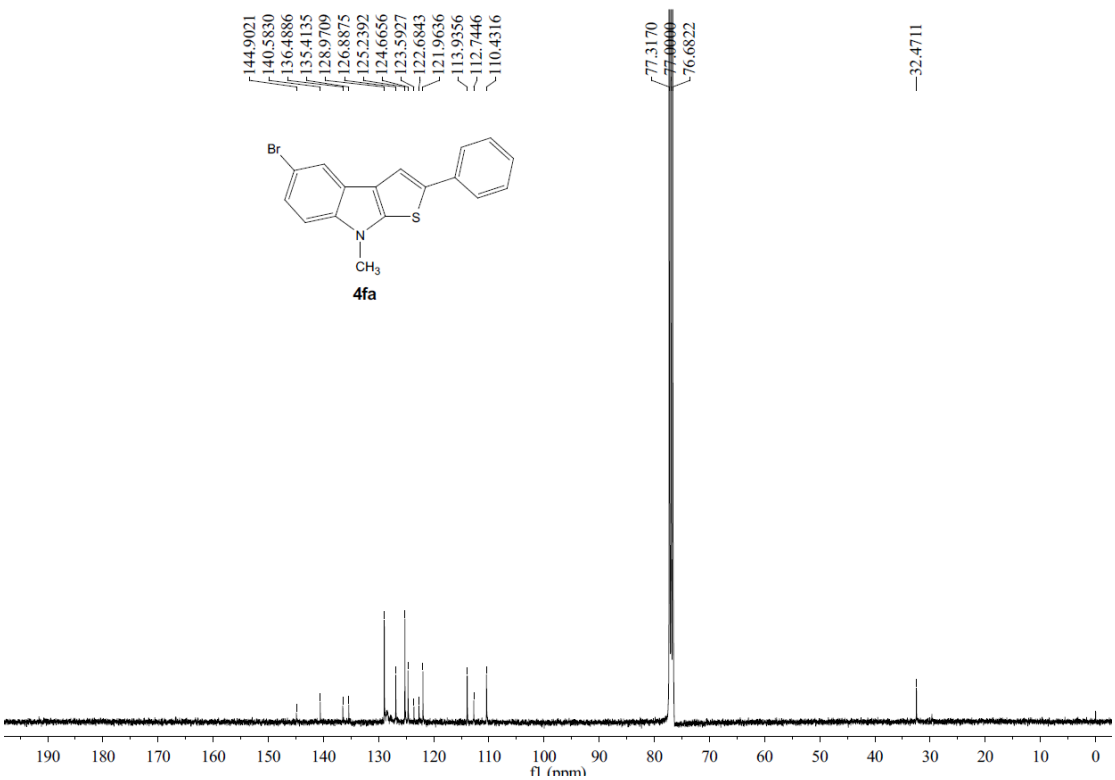
0.0000
Br
S
N
CH3
4fa
1.00
2.06
1.06
3.05
2.03
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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Br
S
N
CH3
4fa
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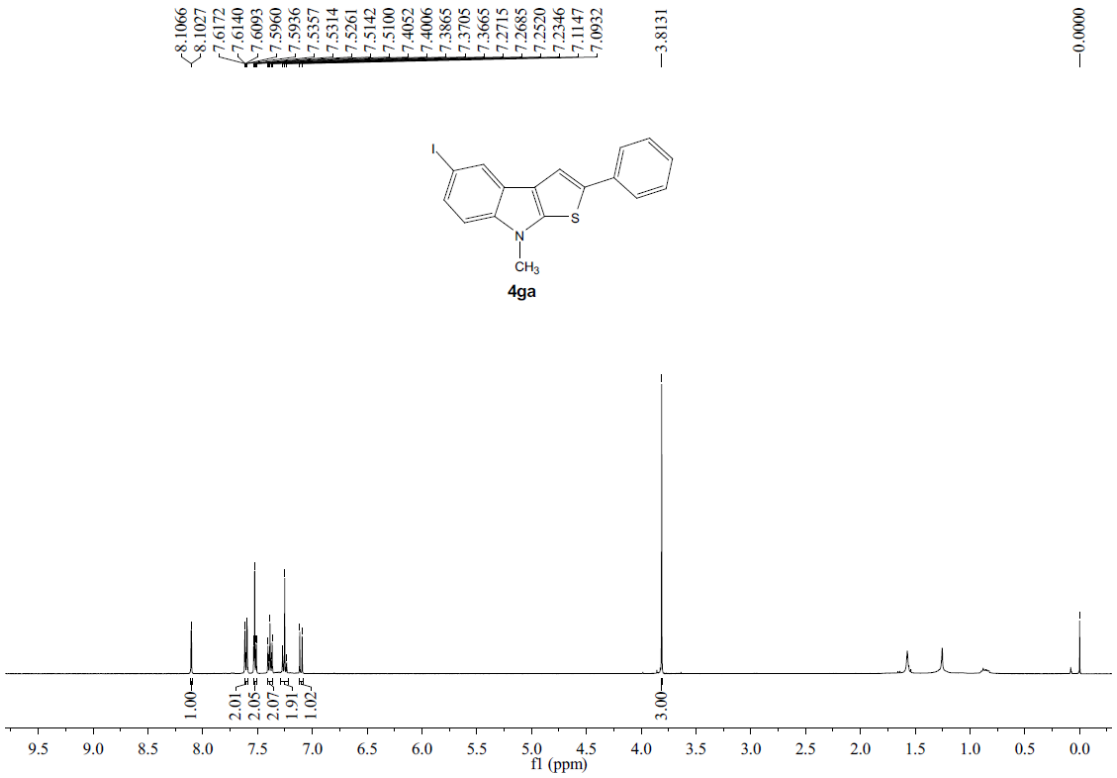
f1 (ppm)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7.3705
7.3665
7.2715
7.2685
7.2520
7.2346
7.1147
7.0932
3.8131
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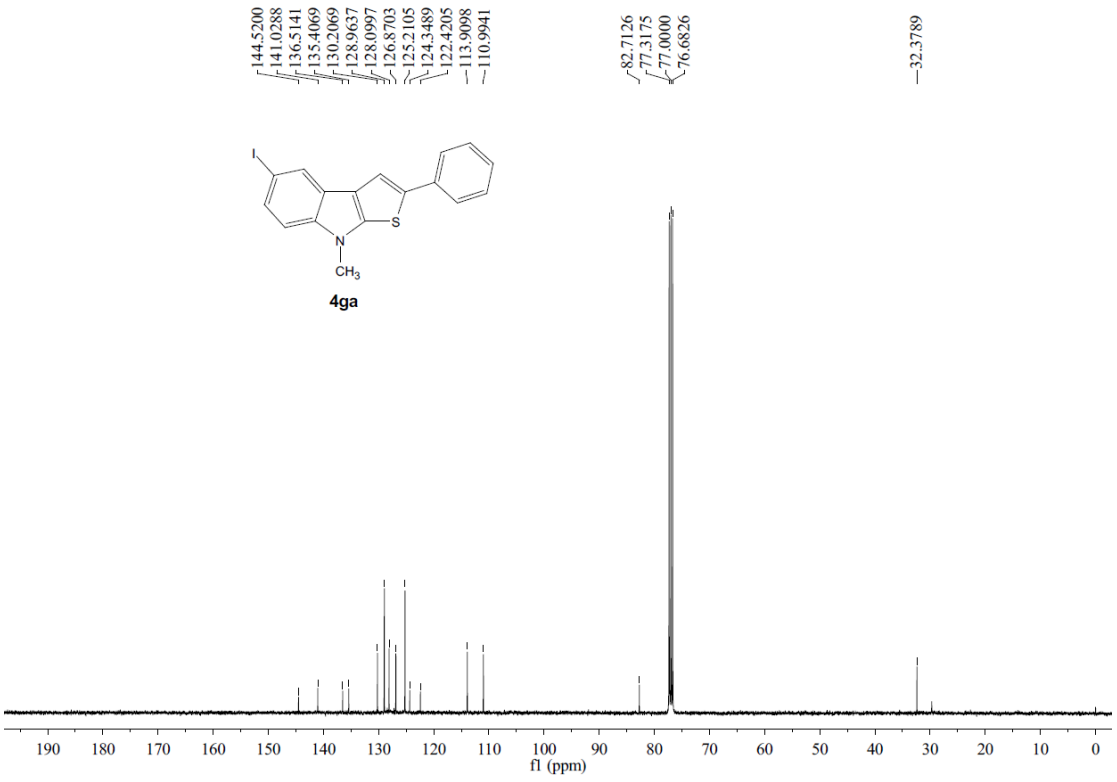
I
S
N
CH3
4ga
1.00
2.01
2.05
2.07
1.91
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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S
N
CH3
4ga
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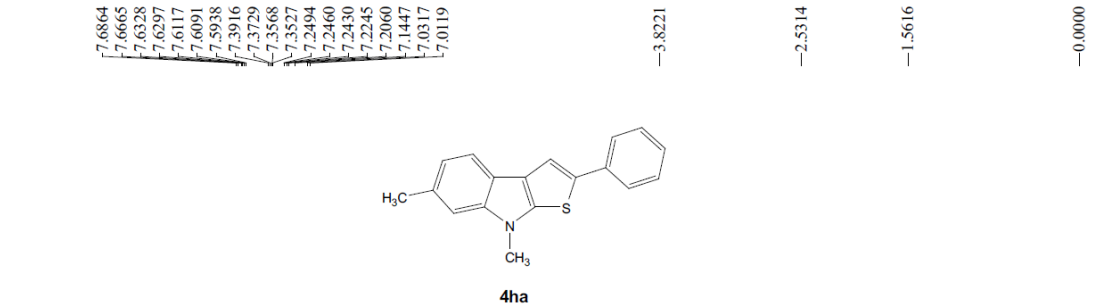
f1 (ppm)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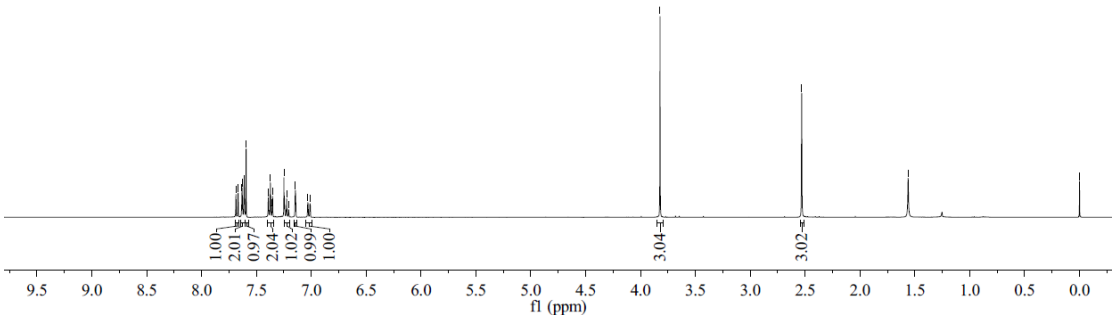
S
N
CH3

4ha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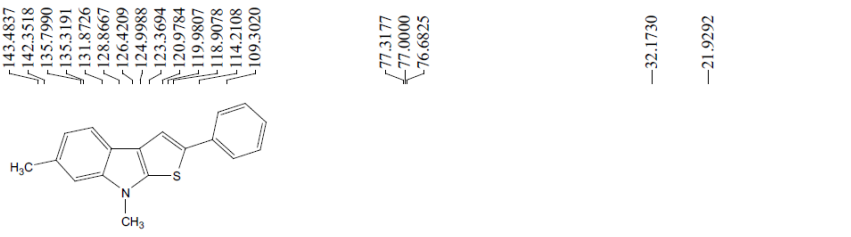
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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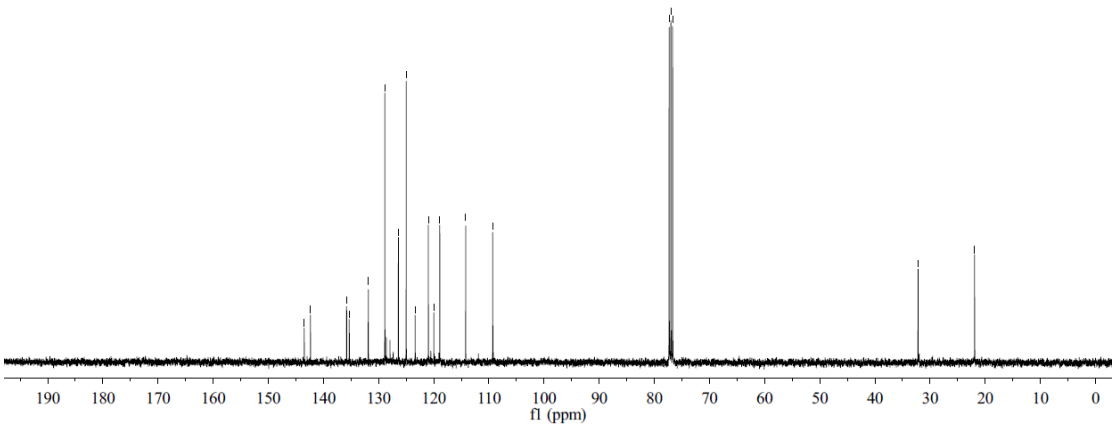
S
N
CH3

4ha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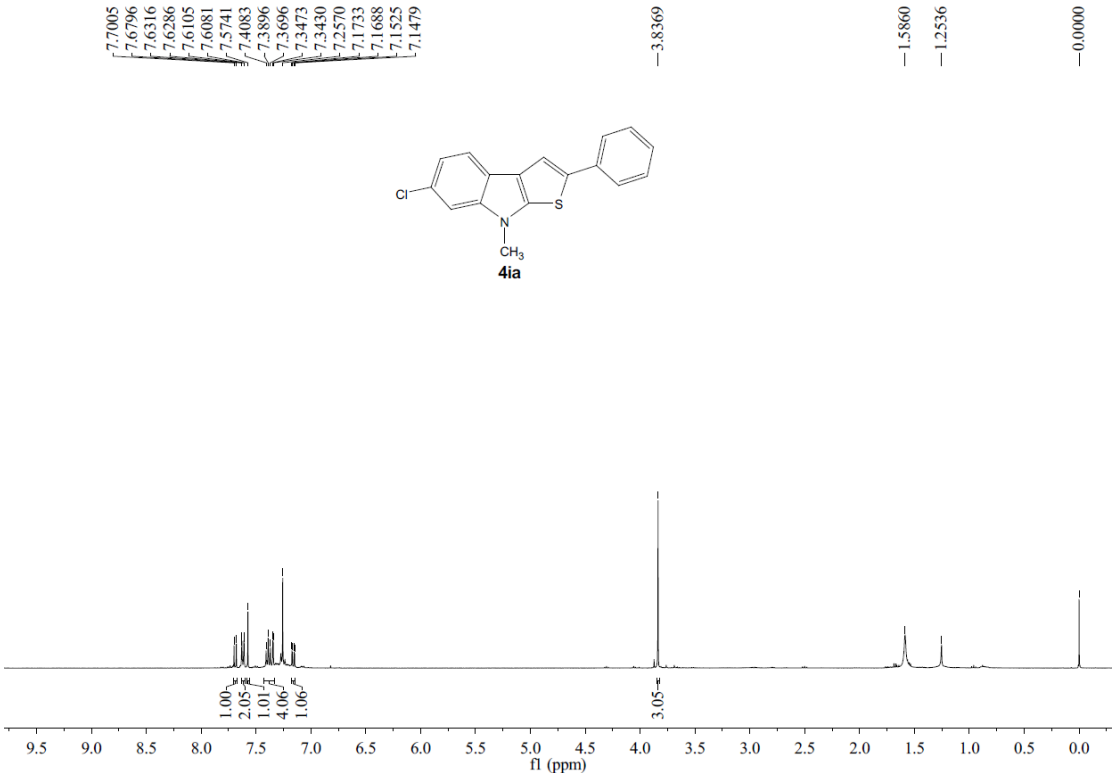
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N
CH3
4ia
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2.05
1.01
4.06
1.06
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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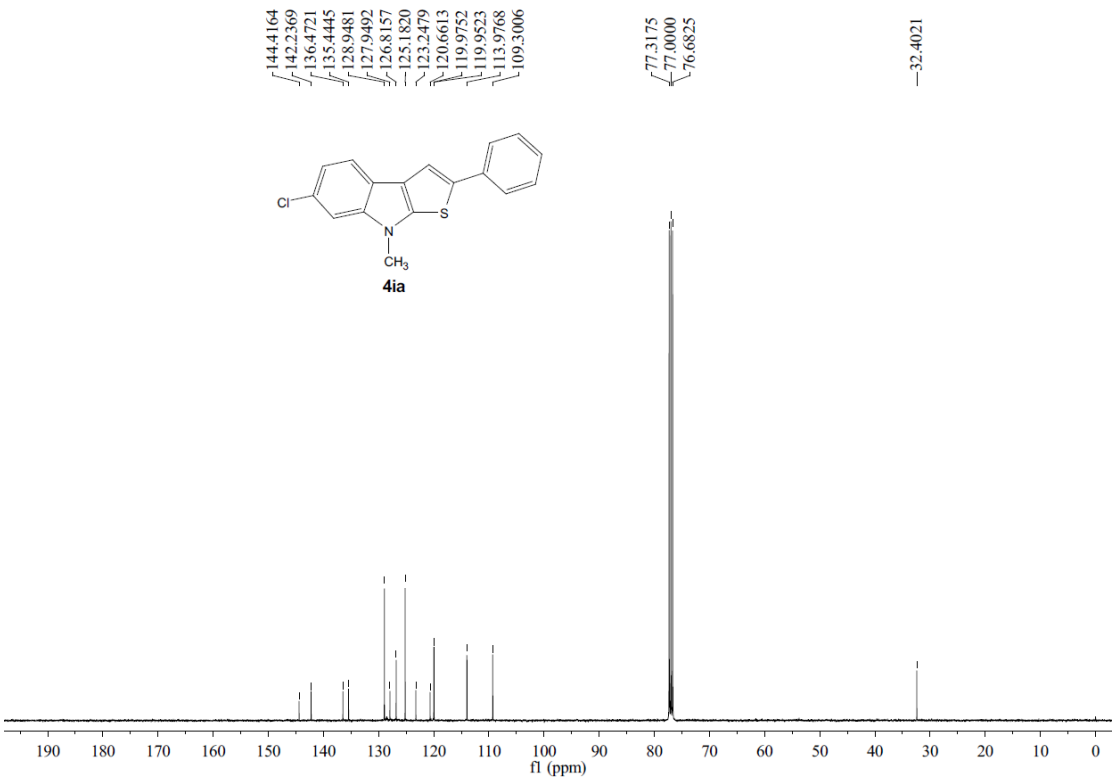
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4ia
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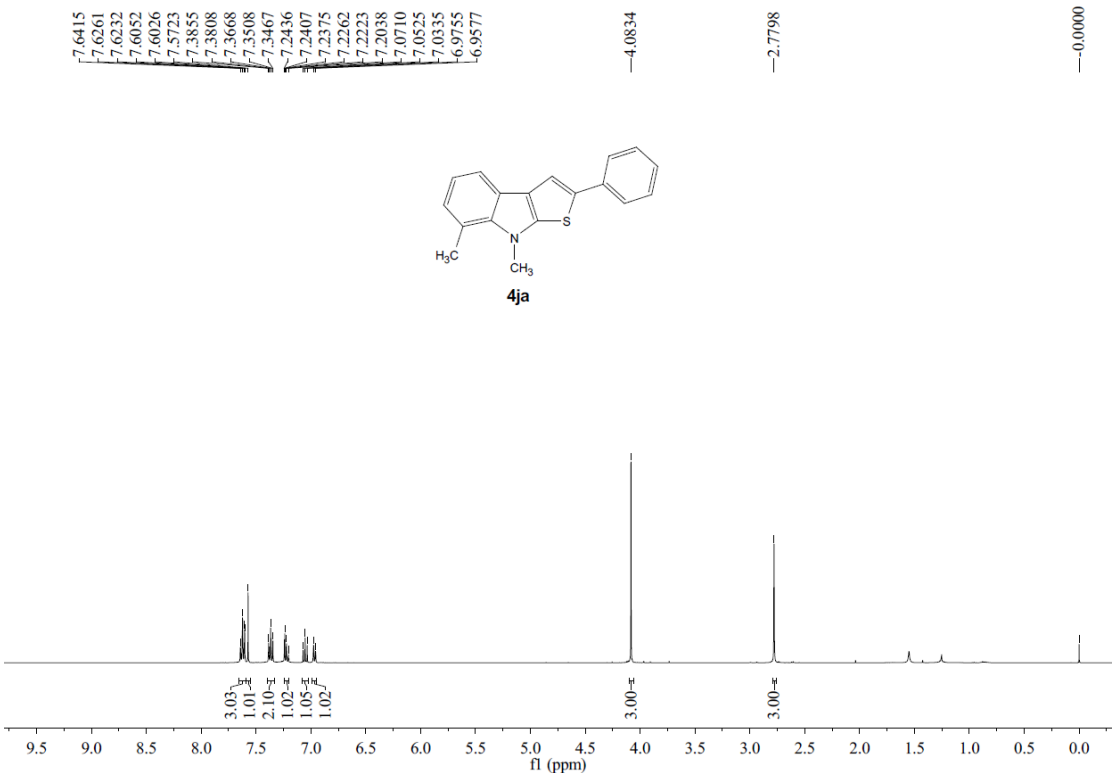
f1 (ppm)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N
H3C
CH3
4ja
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2.10
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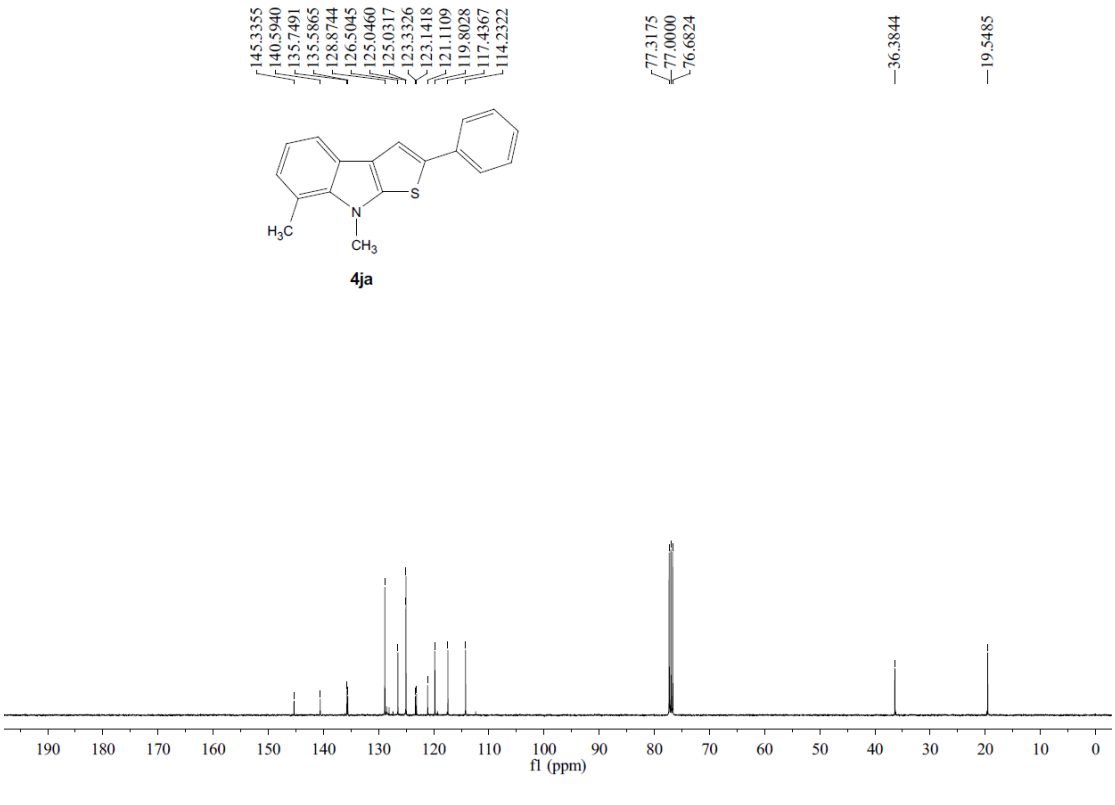
1.05
1.02
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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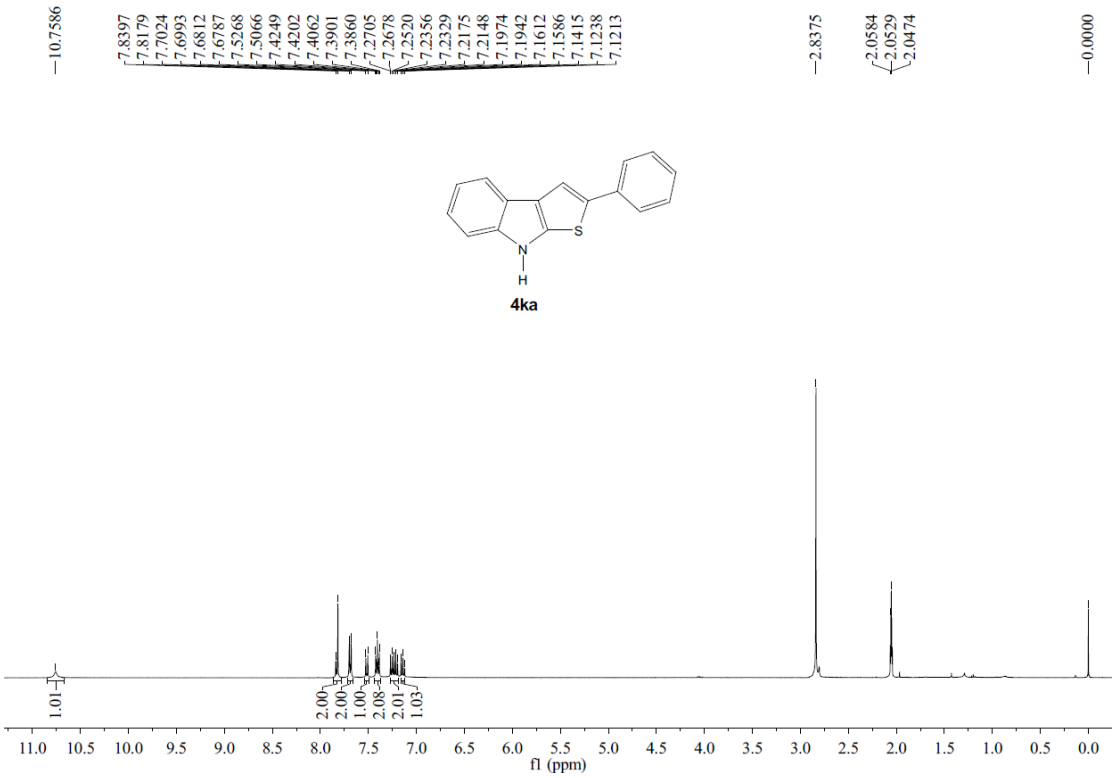
f1 (ppm)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H
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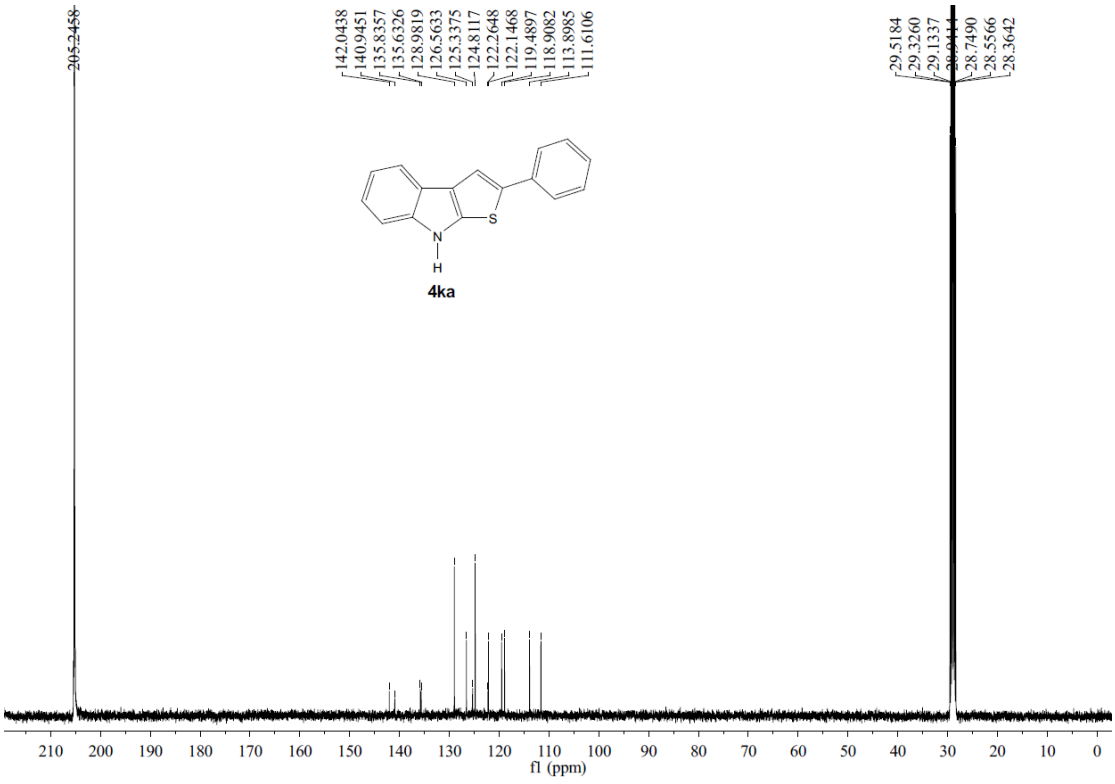
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28.9414
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H
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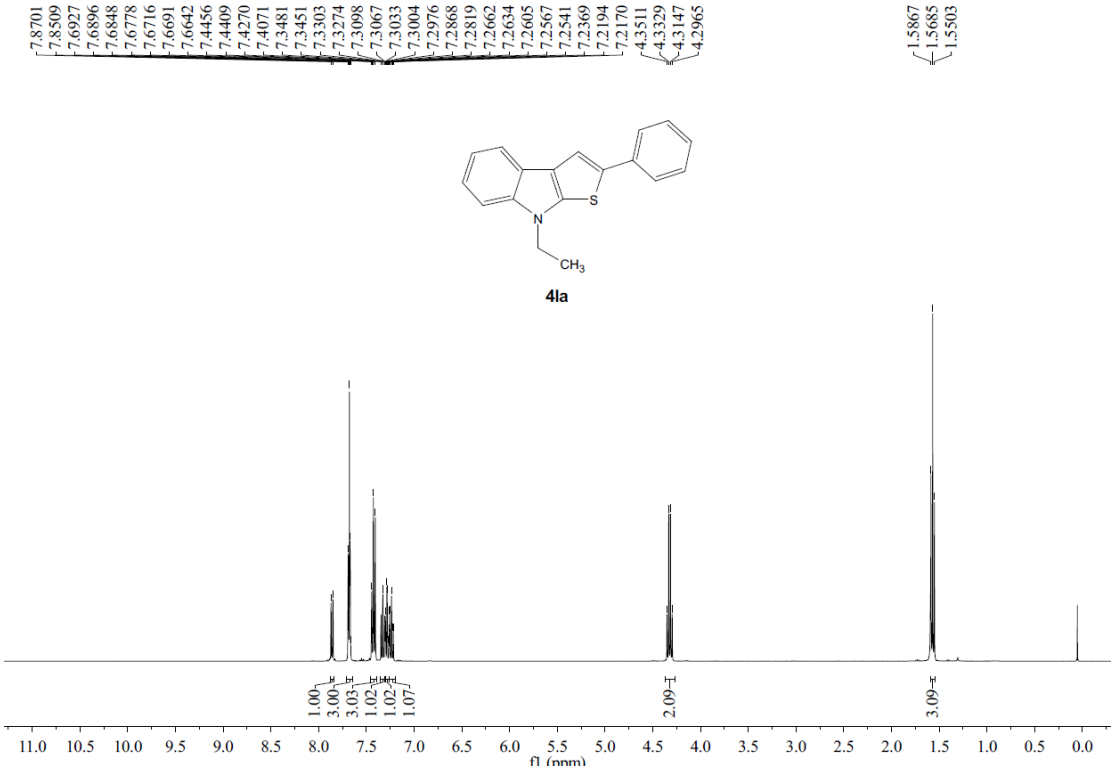
f1 (ppm)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1.5685
1.5503
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N
CH3
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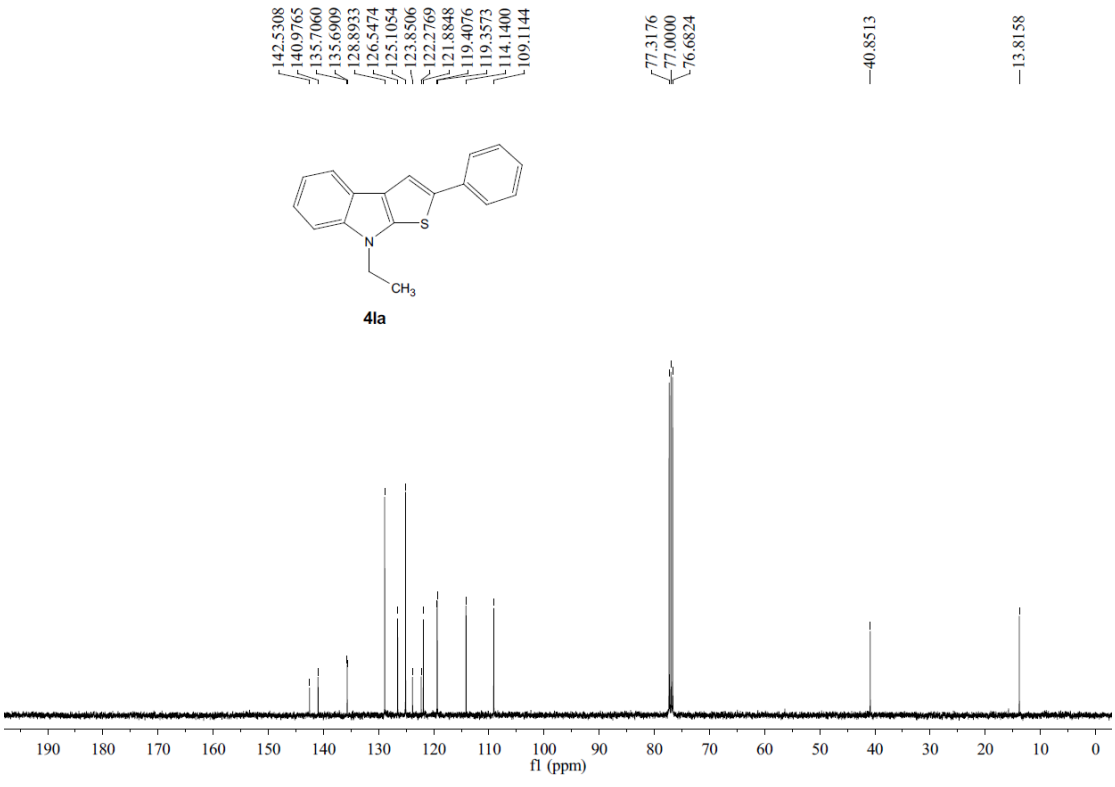
3.00
3.03
1.02
1.02
1.07
2.09
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4la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S
N
CH3
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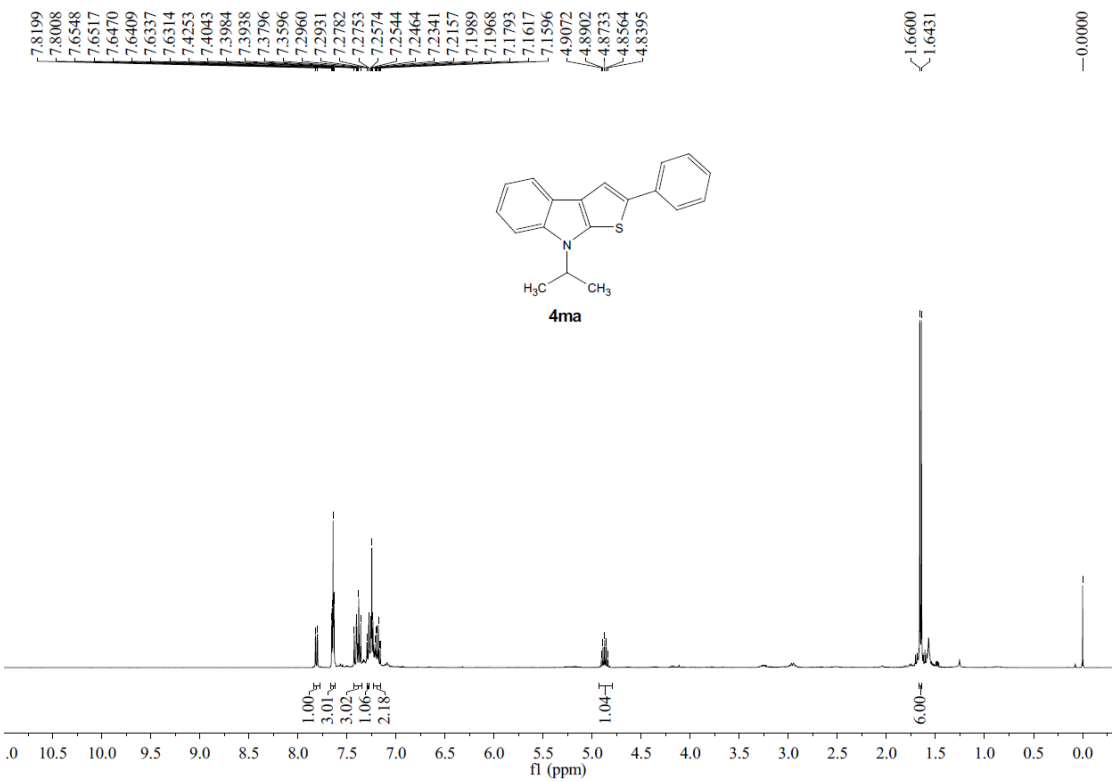
f1 (ppm)

4la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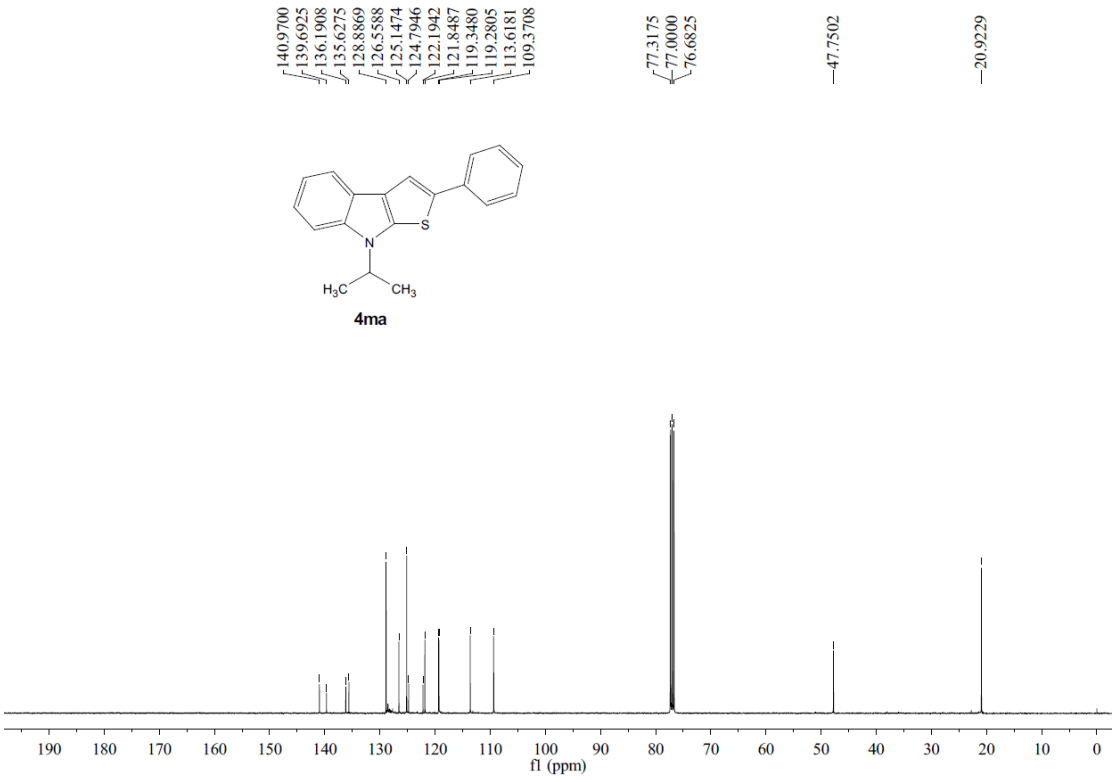
fl (ppm)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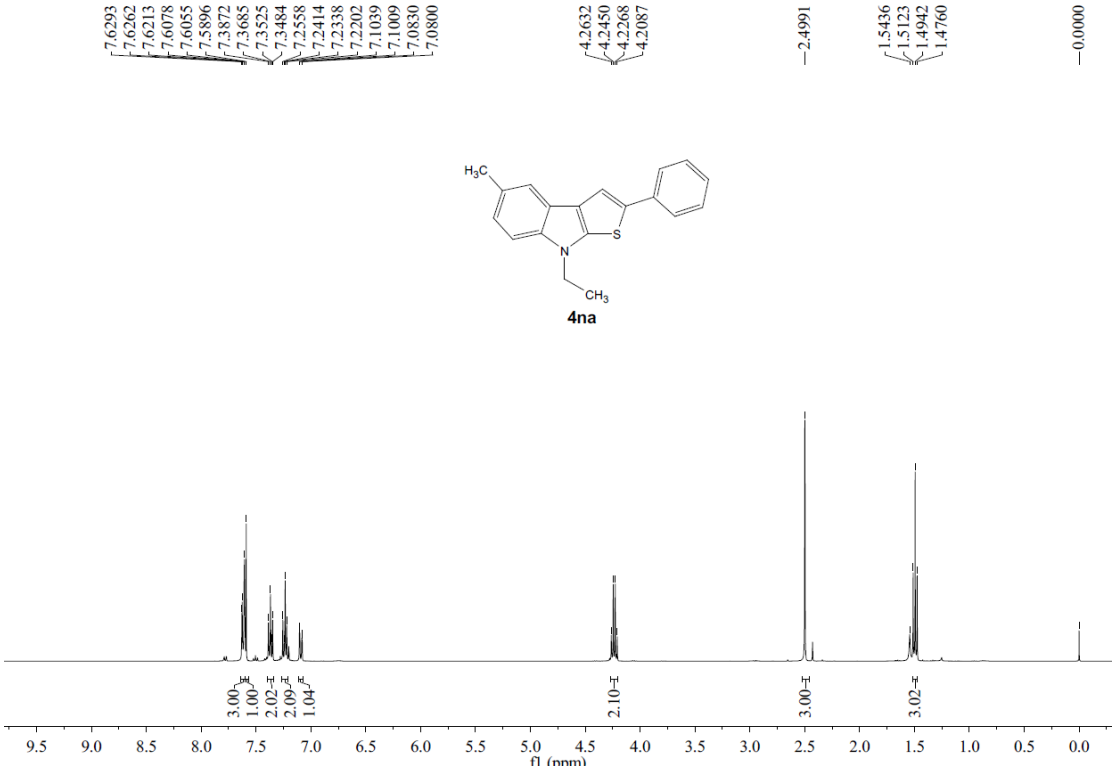
4ma
fl (ppm)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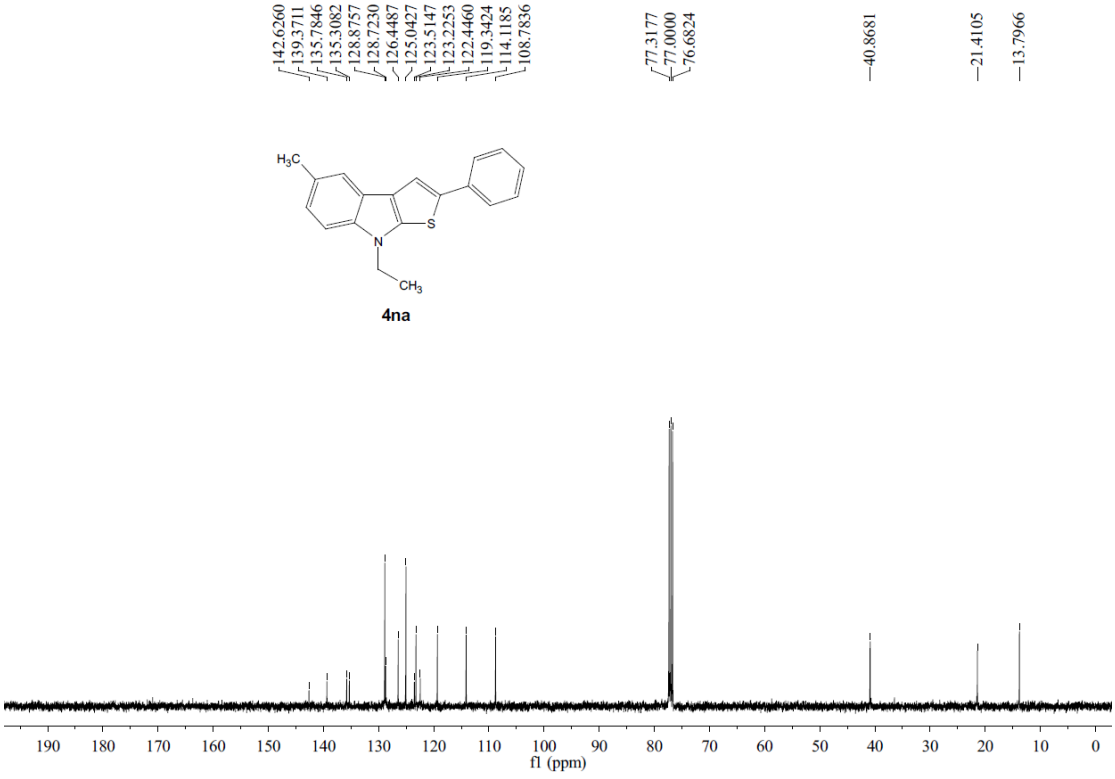
7.2558
7.2414
7.2338
7.2202
7.1039
7.1009
7.0830
7.0800
4.2632
4.2450
4.2268
4.2087
2.4991
1.5436
1.5123
1.4942
1.4760
0.0000
H3C
N
S
CH3
3.00
1.00
2.02
2.09
1.04
2.10
3.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4na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119.3424
114.1185
108.7836
77.3177
77.0000
76.6824
40.8681
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H3C
N
S
CH3
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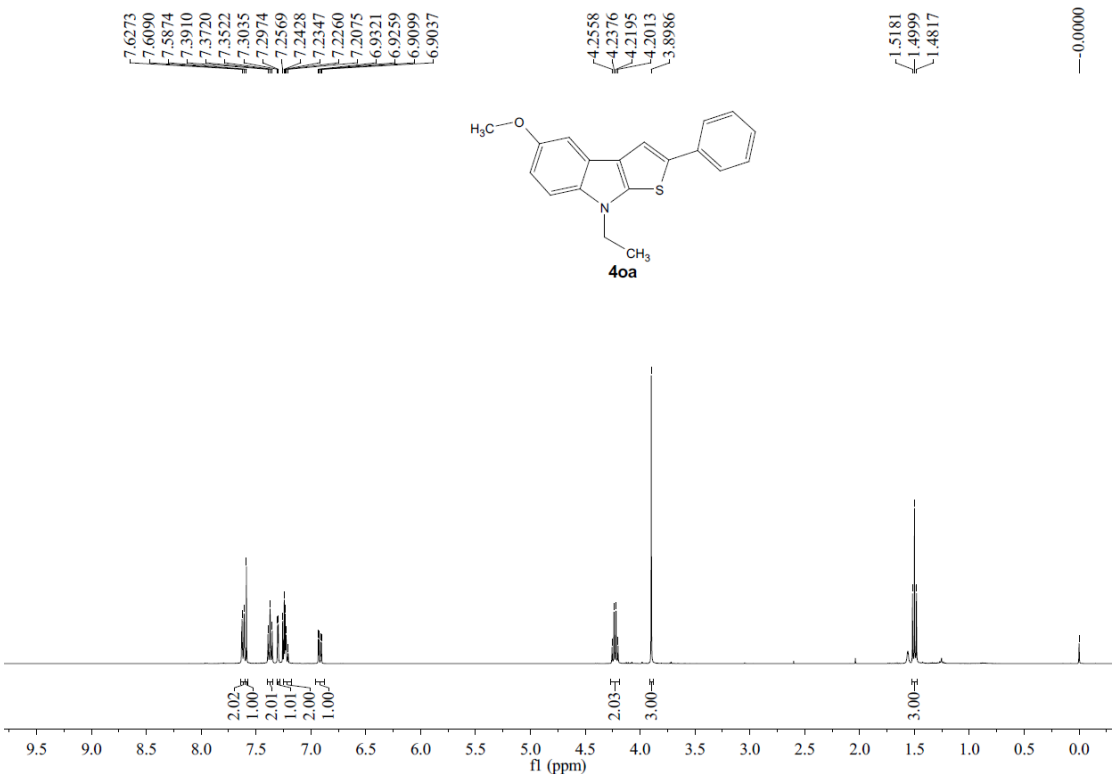
f1 (ppm)

4na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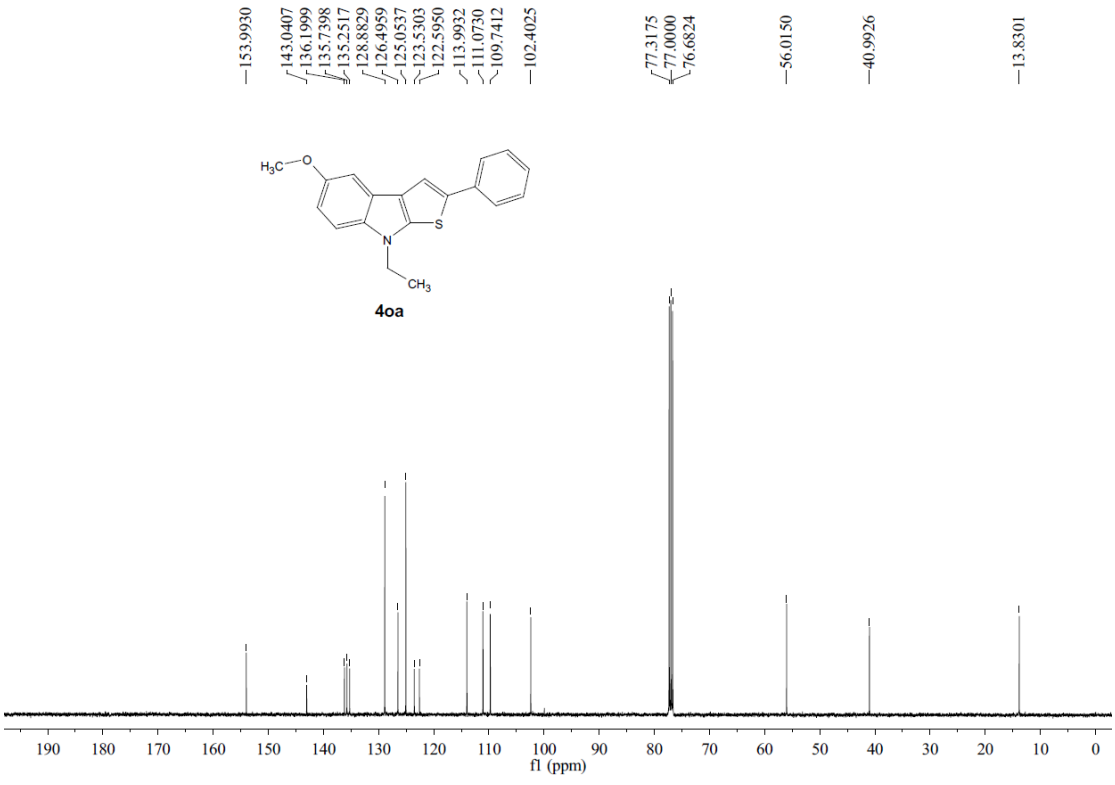
7.2260
7.2075
6.9321
6.9259
6.9099
6.9037
4.2558
4.2376
4.2195
4.2013
3.8986
1.5181
1.4999
1.4817
0.0000
H3C
O
S
N
CH3
4oa
2.02
1.00
2.01
1.01
2.00
1.00
2.03
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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111.0730
109.7412
102.4025
77.3175
77.0000
76.6824
56.0150
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O
S
N
CH3
4oa
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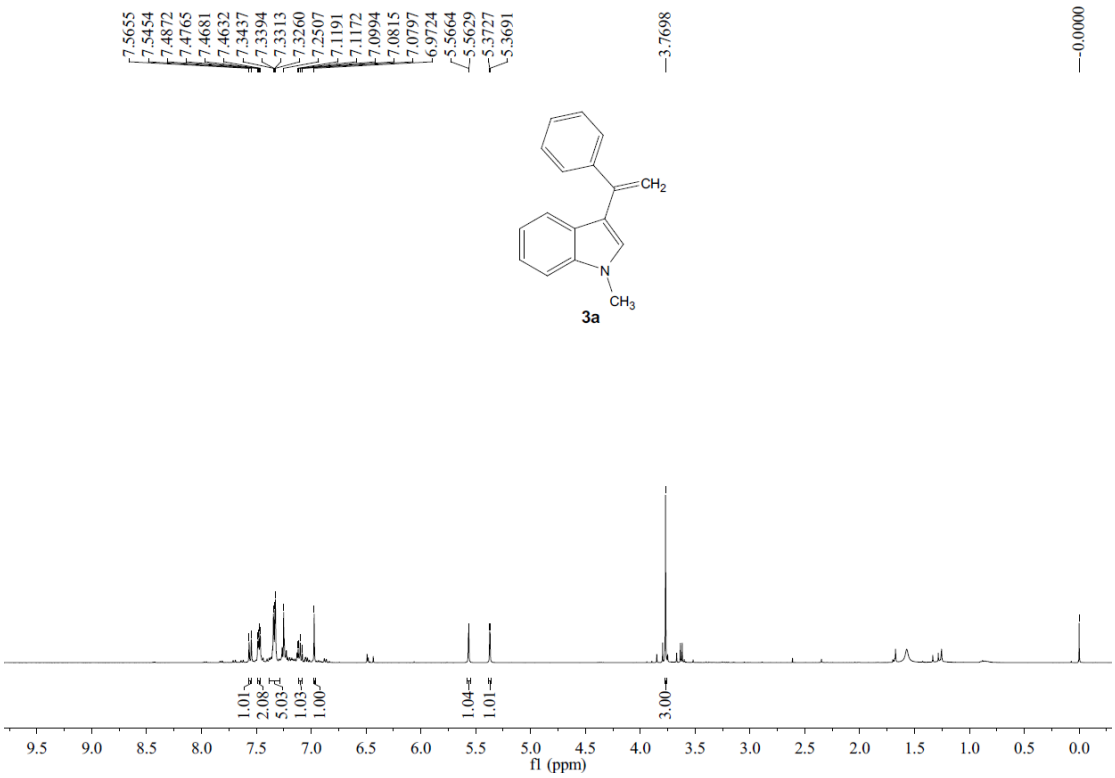
f1 (ppm)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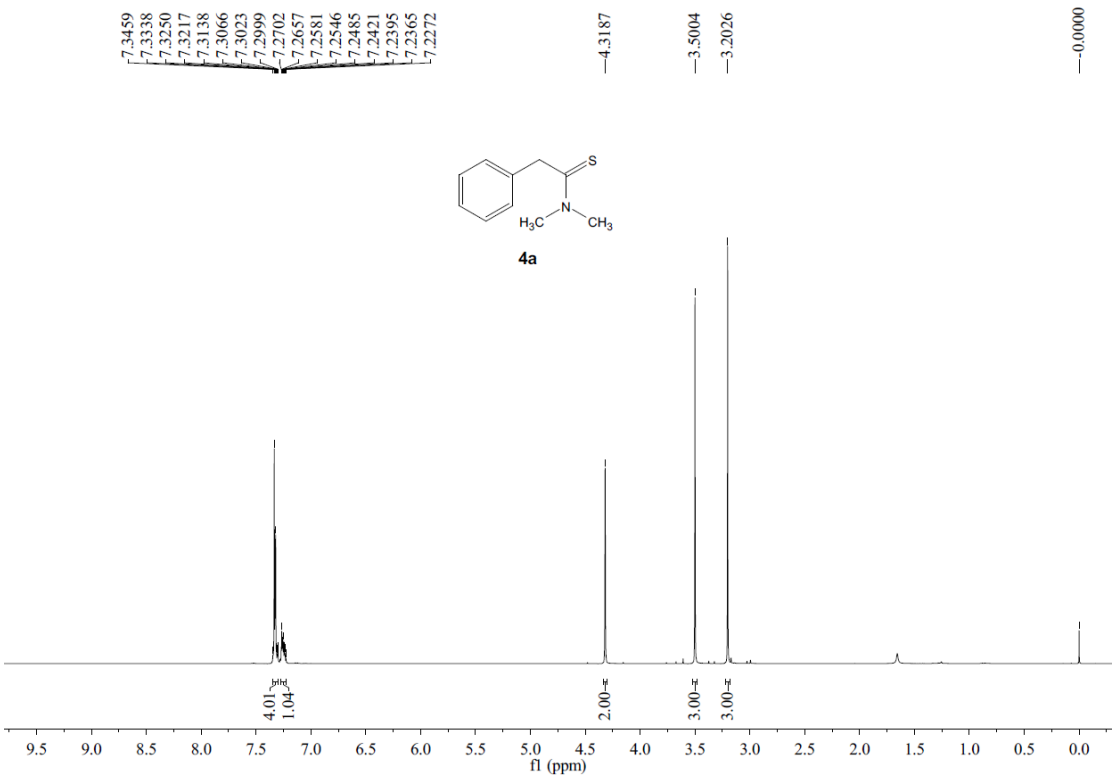
7.1191
7.1172
7.0994
7.0815
7.0797
6.9724
5.5664
5.5629
5.3727
5.3691
3.7698
0.0000
CH2
N
CH3
3a
1.01
2.08
5.03
1.03
1.00
1.04
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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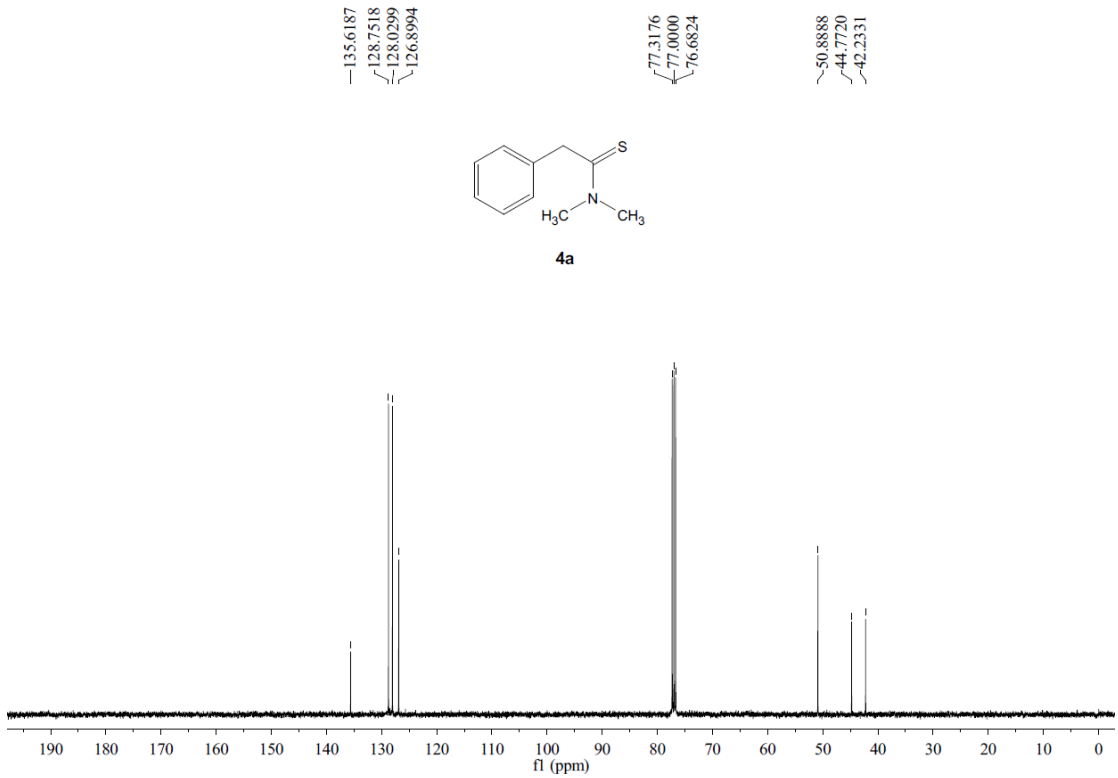
7.2581
7.2546
7.2485
7.2421
7.2395
7.2365
7.2272
4.3187
3.5004
3.2026
0.0000
S
N
H3C
CH3
4a
4.01
1.04
2.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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S
N
H3C
CH3
4a
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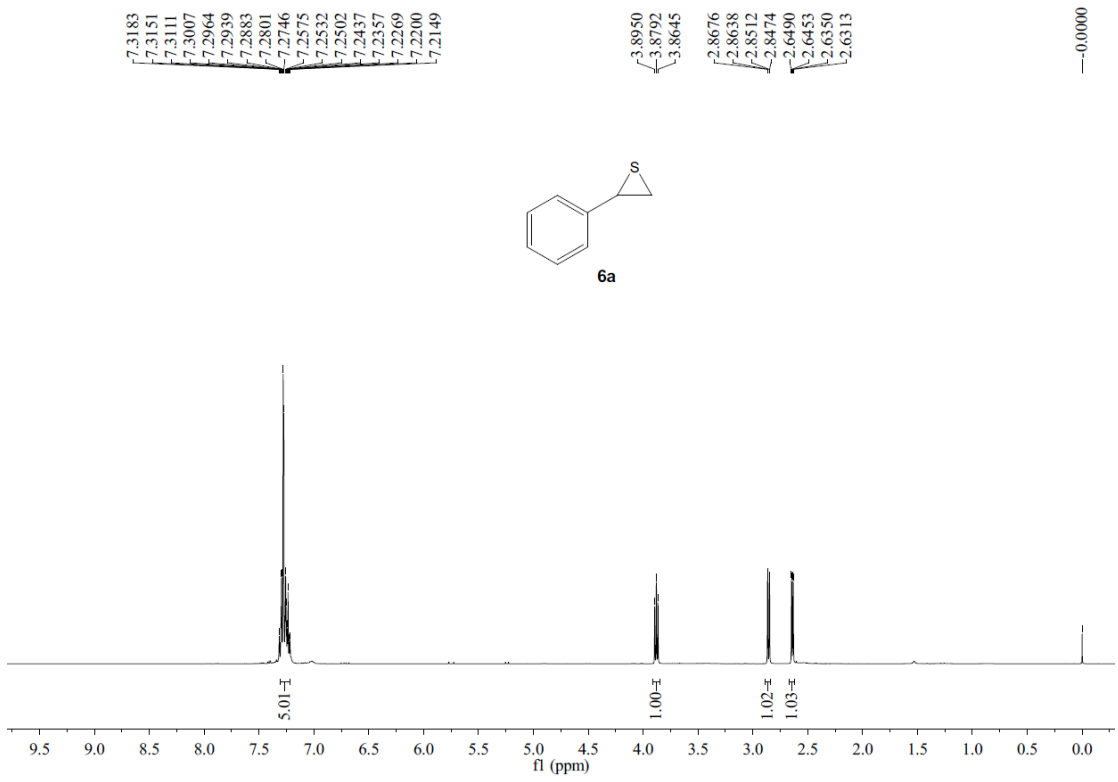
f1 (ppm)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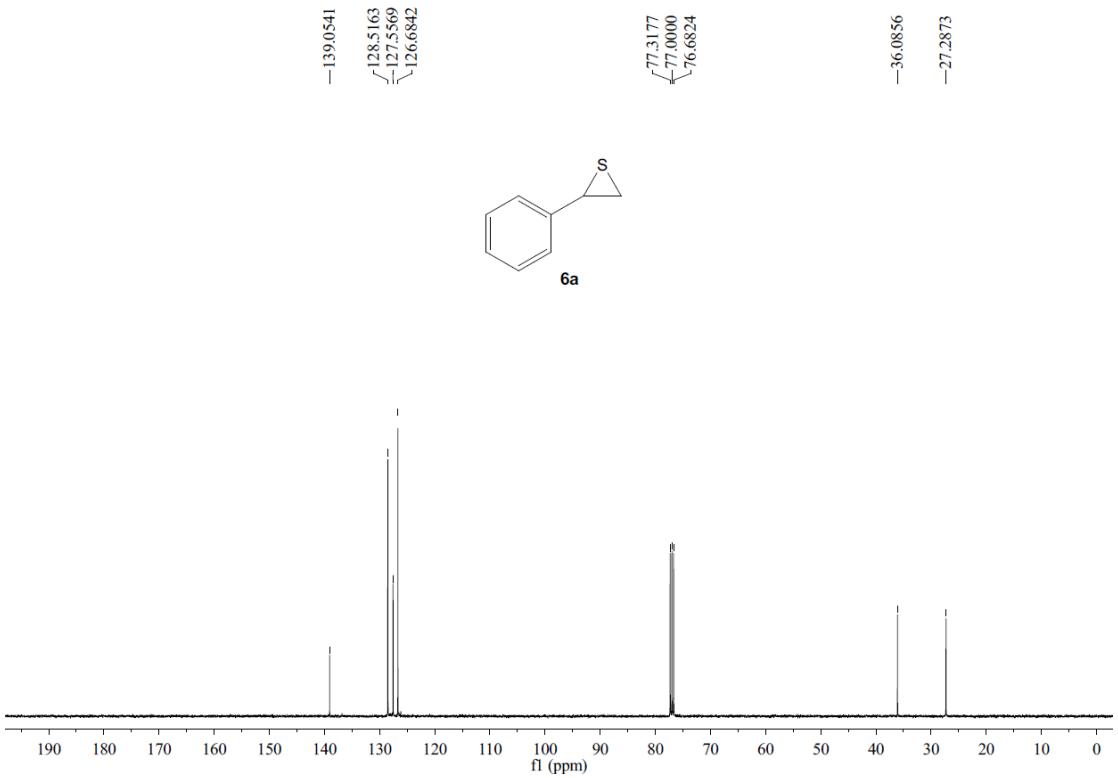
7.3007
7.2964
7.2939
7.2883
7.2801
7.2746
7.2575
7.2532
7.2502
7.2437
7.2357
7.2269
7.2200
7.2149
3.8950
3.8792
3.8645
2.8676
2.8638
2.8512
2.8474
2.6490
2.6453
2.6350
2.6313
0.0000
S
6a
5.01
1.00
1.02
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.5569
126.6842
77.3177
77.0000
76.6824
36.0856
27.2873
S
6a
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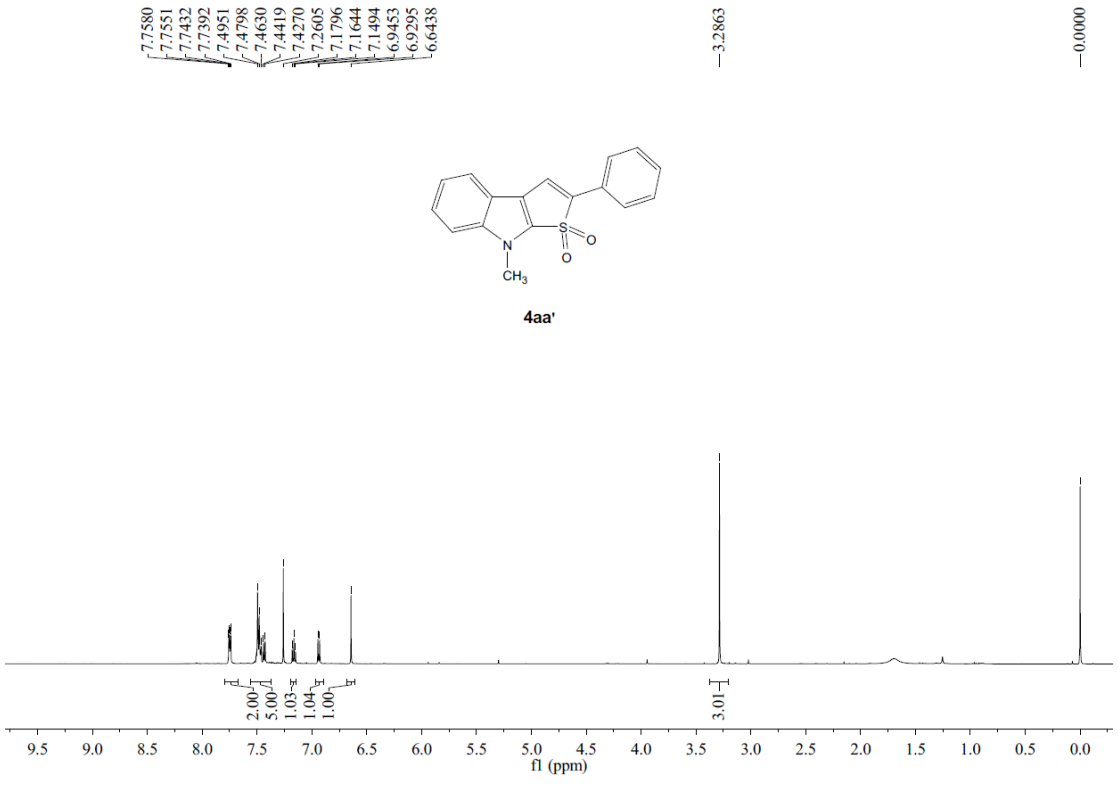
f1 (ppm)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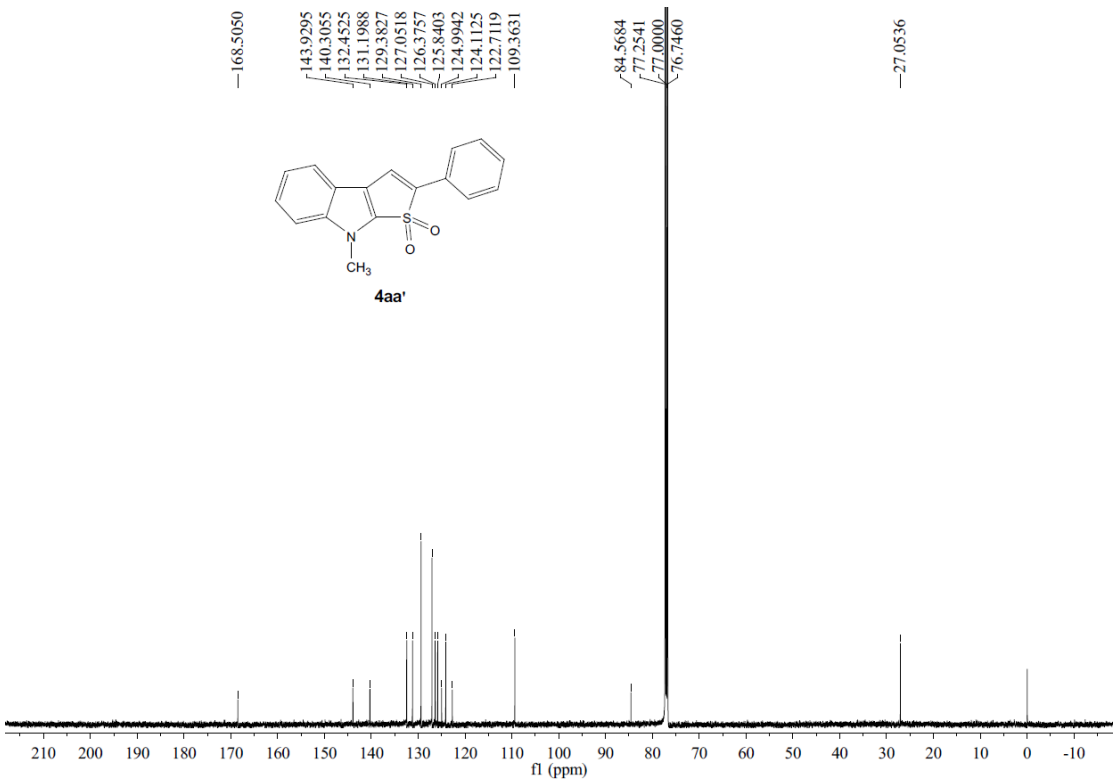
7.4630
7.4419
7.4270
7.2605
7.1796
7.1644
7.1494
6.9453
6.9295
6.6438
3.2863
0.0000
N
CH3
S
O
O
4aa'
2.00
5.00
1.03
1.04
1.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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122.7119
109.3631
84.5684
77.2541
77.0000
76.7460
27.0536
S
O
O
N
CH3
4aa'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)