Supporting information for

Palladium-Catalyzed Benzothieno[2,3-*b*]indole Formation via Dehydrative-Dehydrogenative Double C-H Sulfuration with Sulfur Powder, Indoles and Cyclohexanones

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General information:

All reactions were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 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 was measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra were recorded at Institute of Chemistry, Chinese Academy of Sciences. The structure 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.

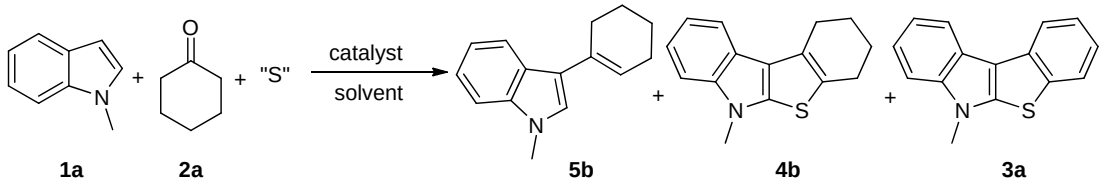
General procedure (for 0.5 mmol scale):

PdI_2 (9.0 mg, 0.025 mmol), 5*H*-cyclopenta[1,2-*b*:5,4-*b′*]dipyridin-5-one (9.0 mg, 0.05 mmol) and sulfur powder (32 mg, 1.0 mmol) were added to a 25 mL oven-dried reaction vessel. The reaction vessel was purged with oxygen for three times and then was added 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol), cyclohexanone (**2a**, 103.6 μL, 1.0 mmol) and 1,2-dichlorobenzene (2.0 mL) by syringe. The reaction vessel was stirred at 125 ^{o}C for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3a** as pale yellow solid (83.0 mg, 70%).

General procedure (for 5.0 mmol scale):

PdI_2 (90 mg, 0.25 mmol), 5*H*-cyclopenta[1,2-*b*:5,4-*b′*]dipyridin-5-one (90 mg, 0.5 mmol) and sulfur powder (320 mg, 10 mmol) were added to a 100 mL round-bottom flask. The reaction flask was purged with oxygen for three times and was added 1-methyl-1*H*-indole (**1a,** 0.64 mL, 5 mmol), cyclohexanone (**2a**, 1.04 mL, 10 mmol) and 1,2-dichlorobenzene (20 mL) by syringe. The reaction flask with an oxygen balloon was stirred at 125 ^{o}C for 16 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3a** as pale yellow solid (805 mg, 68%).

Table S1. Optimization of the Reaction Conditions[a]

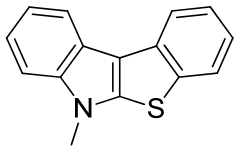


1a **2a** **5b** **4b** **3a**

Entry	Catalyst	Ligand	S source	Yield (%)[b]		
				4b	**5b**	**3a**
1			S_8	0	15	trace
2	I_2		S_8	2	trace	35
3	NIS		S_8	trace	1	24
4	KI		S_8	8	12	trace
5	CuI		S_8	17	trace	13
6	PdI_2		S_8	2	trace	42
7	PdI_2	1,10-phen	S_8	2	2	10
8	PdI_2	CPDO	S_8	trace	trace	62
9	PdI_2	DMAP	S_8	trace	trace	trace
10	PdI_2	CPDO	sublimed sulfur	26	4	43
11	PdI_2	CPDO	KSCN	trace	trace	trace
12	PdI_2	CPDO	$Na_2S \cdot 9H_2O$	trace	trace	trace
13[c]	**PdI_2**	**CPDO**	**S_8**	**2**	**2**	**80**
14[c]	$PdBr_2$	CPDO	S_8	trace	7	10
15[c]	$PdCl_2$	CPDO	S_8	3	2	trace
16[c]	$Pd(CH_3CN)_2Cl_2$	CPDO	S_8	3	6	trace
17[c]	$Pd(OAc)_2/I_2$	CPDO	S_8	1	2	75
18[c,d]	PdI_2	CPDO	S_8	33	4	40
19[c,e]	PdI_2	CPDO	S_8	3	2	70

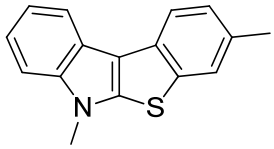
[a] conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), S source (0.4 mmol), catalyst (0.01 mmol), ligand (0.02 mmol), *o*-dichlorobenzene (1.0 mL) under oxygen unless otherwise noted, 125 °C, 16 h. [b] GC yield based on **1a**. [c] **2a** (0.4 mmol)**.** [d] 115 °C. [e] Under air. 1,10-phen = 1,10-phenanthroline, CPDO = 5*H*-cyclopenta[1,2-*b*:5,4-*b*']dipyridin-5-one, DMAP = 4-dimethylaminopyridine.

6-Methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3a, CAS: 1269621-22-8)[1]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.50-7.41 (m, 2H), 7.34-7.23 (m, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.3, 141.7, 137.9, 133.2, 125.0, 123.6, 122.5, 121.7, 121.4, 120.4, 119.9, 118.7, 116.6, 109.1, 32.0; MS (EI) *m/z* (%) 237 (100), 222, 195, 152, 119.

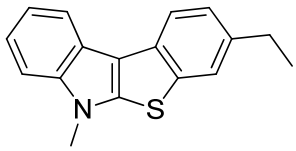
3,6-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3b)



The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 4-methylcyclohexanone (**2b**, 122.5 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3b** as pale yellow solid (106.7 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00-7.95 (m, 2H), 7.62 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.32-7.28 (m, 3H), 3.89 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 141.6, 138.3, 131.5, 130.9, 126.4, 123.7, 122.5, 121.2, 120.1, 119.8, 118.7, 116.5, 109.1, 32.1, 21.4; HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NS$ $[M]^+$ 251.0763, found 251.0767.

3-Ethyl-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3c)

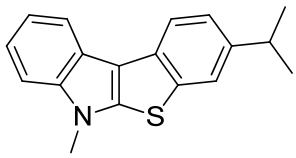


The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 4-ethylcyclohexanone (**2c**, 141 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3c** as white solid (106 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00-7.97 (m, 2H), 7.64 (s, 1H), 7.40 (d, J = 7.6 Hz, 1H),

7.32-7.27 (m, 3H), 3.89 (s, 3H), 2.79 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 141.6, 138.3, 138.1, 131.1, 125.3, 122.5, 121.2, 120.2, 119.8, 118.7, 116.5, 113.9, 109.1, 32.0, 28.9, 16.0; HRMS (ESI, m/z): calcd. for $C_{17}H_{15}NS$ $[M]^+$ 265.0920, found 265.0924.

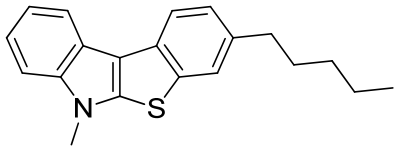
3-Isopropyl-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3d)



The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 4-isopropylcyclohexanone (**2d**, 155 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3d** as white solid (102 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.99 (d, J = 7.6 Hz, 2H), 7.67 (s, 1H), 7.41-7.27 (m, 4H), 3.89 (s, 3H), 3.09-3.02 (m, 2H), 1.34 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.9, 141.6, 138.3, 131.1, 128.2, 124.0, 122.6, 121.2, 121.1, 120.3, 119.8, 118.7, 116.5, 109.1, 34.2, 32.1, 24.3; HRMS (ESI, m/z): calcd. for $C_{18}H_{17}NS$ $[M]^+$ 279.1076, found 279.1080.

6-Methyl-3-pentyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3e)

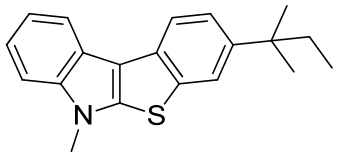


The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 4-pentylcyclohexanone (**2e**, 190 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3e** as pale yellow solid (133.5 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (t, J = 6.2 Hz, 2H), 7.62 (s, 1H), 7.40 (d, J = 6.0 Hz, 1H), 7.32-7.27 (m, 3H), 3.89 (s, 3H), 2.74 (t, J = 6.2 Hz, 2H), 1.73-1.67 (m, 2H), 1.38-1.35 (m, 4H), 0.91 (t, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 141.6, 138.2, 136.7, 131.0, 125.8, 123.1, 122.5, 121.2, 120.1, 119.7, 118.7, 116.5, 109.1, 36.0, 32.0, 31.9, 31.5, 22.6, 14.1;

HRMS (ESI, m/z): calcd. for $C_{20}H_{21}NS$ $[M]^+$ 307.1389, found 307.1393.

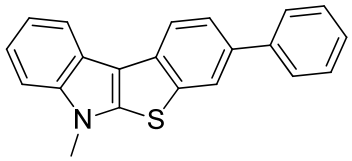
6-Methyl-3-(*tert*-pentyl)-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3f)



The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 4-(*tert*-pentyl)cyclohexanone (**2f**, 183 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3f** as white solid (130.5 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01-7.99 (m, 2H), 7.76 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.32-7.27 (m, 2H), 3.89 (s, 3H), 1.73 (q, *J* = 7.3 Hz, 2H), 1.38 (s, 6H), 0.72 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.5, 143.0, 141.6, 138.3, 130.8, 123.5, 122.6, 121.2, 120.9, 119.9, 119.8, 118.7, 116.5, 109.1, 38.1, 37.1, 32.1, 28.8, 9.2; HRMS (ESI, m/z): calcd. for $C_{20}H_{21}NS$ $[M]^+$ 307.1389, found 307.1393.

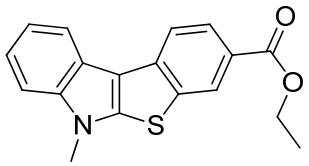
6-Methyl-3-phenyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3g)



The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 4-phenylcyclohexanone (**2g**, 174 mg, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100:1) afforded the product **3g** as pale yellow solid (126.8 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.04-8.03 (m, 2H), 7.73-7.68 (m, 3H), 7.49-7.42 (m, 3H), 7.37-7.29 (m, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.7, 141.8, 141.2, 138.8, 135.1, 132.4, 128.8, 127.1, 126.9, 124.5, 122.6, 122.1, 121.6, 120.6, 120.1, 118.9, 116.4, 109.3, 32.3; HRMS (ESI, m/z): calcd. for $C_{21}H_{15}NS$ $[M]^+$ 313.0920, found 313.0924.

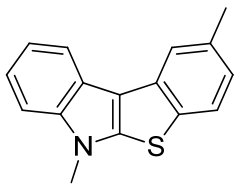
Ethyl 6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole-3-carboxylate (3h)



The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and ethyl 4-oxocyclohexanecarboxylate (**2h**, 159.3 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) afforded the product **3h** as pale yellow solid (114.3 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.53 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.07-8.02 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37-7.30 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.6, 145.9, 141.8, 137.3, 136.5, 126.4, 125.4, 123.5, 122.3, 121.9, 120.3, 119.5, 118.9, 116.4, 109.2, 60.8, 32.1, 14.4; HRMS (ESI, m/z): calcd. for $C_{18}H_{15}NO_2S$ $[M+H]^+$ 310.0896, found 310.0900.

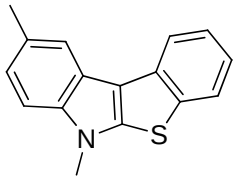
2,6-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3i)



The reaction was conducted with 1-methyl-1*H*-indole (**1a,** 64 μL, 0.5 mmol) and 3-methylcyclohexanone (**2i**, 121.7 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3i** as pale yellow solid (75.3 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.89 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.33-7.28 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.7, 141.7, 135.0, 134.9, 133.4, 125.2, 123.2, 122.6, 121.3, 120.9, 119.8, 118.8, 118.1, 109.1, 32.1, 21.6; HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NS$ $[M]^+$ 251.0763, found 251.0767.

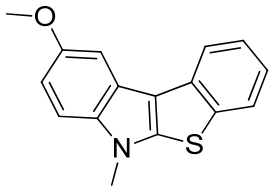
6,9-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3k)



The reaction was conducted with 1,5-dimethyl-1*H*-indole (**1b,** 72.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3k** as pale yellow solid (75.4 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.81 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.30-7.12 (m, 3H), 3.86 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.5, 140.3, 138.0, 133.5, 129.3, 125.0, 123.6, 122.9, 122.8, 121.6, 120.5, 118.8, 116.4, 108.8, 32.1, 21.5. HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NS$ $[M]^+$ 251.0763, found 251.0759.

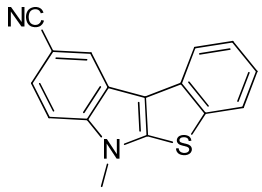
9-Methoxy-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3l)



The reaction was conducted with 5-methoxy-1-methyl-1*H*-indole (**1c,** 80.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3l** as pale yellow solid (68.1 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.48-7.45 (m, 2H), 7.30-7.22 (m, 2H), 6.97-6.94 (m, 1H), 3.96 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.5, 143.9, 137.9, 137.1, 133.3, 125.1, 123.6, 123.0, 121.7, 120.3, 116.3, 110.4, 109.7, 102.2, 56.1, 32.3; HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NOS$ $[M]^+$ 267.0712, found 267.0715.

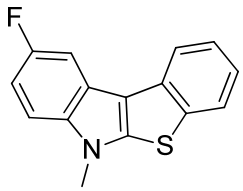
6-Methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole-9-carbonitrile (3m)



The reaction was conducted with Palladium(II) iodide (18 mg, 0.05 mmol), 5H-cyclopenta[1,2-*b*:5,4-*b'*]dipyridin-5-one (18 mg, 0.1 mmol), 1-methyl-1*H*-indole-5-carbonitrile (**1d,** 78 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 150 ^{o}C, 24 h. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) afforded the product **3m** as white solid (68.2 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.27 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.4, 142.9, 138.1, 132.2, 125.5, 124.5, 123.7, 123.3, 122.8, 122.0, 120.7, 120.4, 116.7, 109.7, 102.9, 32.3; HRMS (ESI, m/z): calcd. for $C_{16}H_{10}N_2S$ $[M]^+$ 262.0559, found 262.0557.

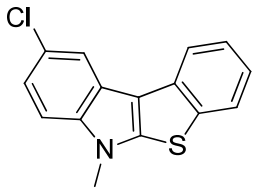
9-Fluoro-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3n)



The reaction was conducted with 5-fluoro-1-methyl-1*H*-indole (**1f,** 74.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3n** as pale yellow solid (79.1 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.64-7.61 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.29-7.23 (m, 2H), 7.06-7.01 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.8 (d, *J* = 234.0 Hz), 144.8, 138.1, 137.7, 132.8, 125.1, 123.6, 122.5 (d, *J* = 10.4 Hz), 122.0, 120.3, 116.2, 109.5 (d, *J* = 9.8 Hz), 109.0 (d, *J* = 15.7 Hz), 104.2 (d, *J* = 24.0 Hz), 32.2; HRMS (ESI, m/z): calcd. for $C_{15}H_{10}FNS$ $[M]^+$ 255.0513, found 255.0515.

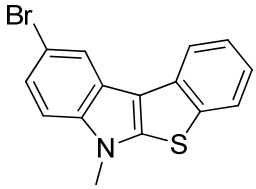
9-Chloro-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3o)



The reaction was conducted with 5-chloro-1-methyl-1*H*-indole (**1g,** 82.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3o** as white solid (85.4 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.30-7.28 (m, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 139.9, 137.8, 132.6, 125.6, 125.2, 123.6, 123.1, 122.1, 121.3, 120.4, 118.2, 115.9, 109.9, 32.1; HRMS (ESI, m/z): calcd. for $C_{15}H_{10}ClNS$ $[M]^+$ 271.0217, found 271.0218.

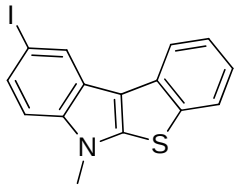
9-Bromo-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3p)



The reaction was conducted with 5-bromo-1-methyl-1*H*-indole (**1h,** 104.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3p** as white solid (94.5 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.11 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.4, 140.3, 137.9, 132.7, 125.2, 124.0, 123.9, 123.6, 122.3, 121.3, 120.5, 116.0, 113.3, 110.4, 32.2; HRMS (ESI, m/z): calcd. for $C_{15}H_{10}BrNS$ $[M]^+$ 314.9712, found 314.9712.

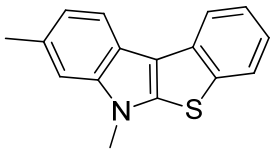
9-Iodo-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3q)



The reaction was conducted with 5-iodo-1-methyl-1*H*-indole (**1i,** 128.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3q** as white solid (96.2 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.31 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.1, 140.8, 137.9, 132.7, 129.7, 127.5, 125.3, 124.7, 123.7, 122.2, 120.6, 115.7, 111.0, 83.4, 32.2; HRMS (ESI, m/z): calcd. for $C_{15}H_{10}INS$ $[M]^+$ 362.9573, found 362.9567.

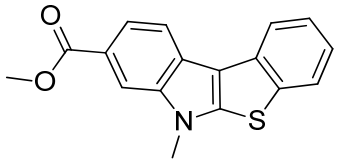
6,8-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3r)



The reaction was conducted with 1,6-dimethyl-1*H*-indole (**1j,** 72.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3r** as pale yellow solid (87.9 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.23-7.20 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 142.2, 137.9, 133.3, 131.3, 125.0, 123.6 (2C), 121.6, 121.4, 120.4, 118.4, 116.5, 109.5, 32.2, 21.9; HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NS$ $[M]^+$ 251.0763, found 251.0765.

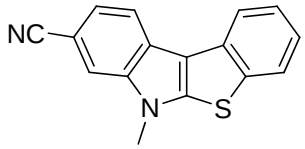
Methyl 6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole-8-carboxylate (3s)



The reaction was conducted with methyl 1-methyl-1*H*-indole-6-carboxylate (**1k,** 94.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) afforded the product **3s** as white solid (95.9 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.16 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.99 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 8.2 Hz, 1H), 3.99 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.0, 146.7, 141.2, 138.1, 132.9, 125.9, 125.4, 123.8, 123.0, 122.6, 121.4, 120.8, 120.4, 118.1, 111.3, 52.0, 32.5; HRMS (ESI, m/z): calcd. for $C_{17}H_{13}NO_2S$ $[M]^+$ 295.0662, found 295.0664.

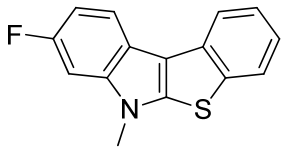
6-Methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole-8-carbonitrile (3t)



The reaction was conducted with Palladium(II) iodide (18 mg, 0.05 mmol), 5H-cyclopenta[1,2-*b*:5,4-*b'*]dipyridin-5-one (18 mg, 0.1 mmol), methyl 1-methyl-1*H*-indole-6-carbonitrile (**1k,** 78 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3t** as white solid (62.9 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.50 (t, *J* = 6.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.2, 140.5, 138.1, 132.3, 125.6, 125.1, 123.8, 123.3, 123.0, 120.8, 120.4, 119.1, 117.1, 113.4, 103.7, 32.4; HRMS (ESI, m/z): calcd. for $C_{16}H_{10}N_2S$ $[M]^+$ 262.0559, found 262.0556.

8-Fluoro-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3u)

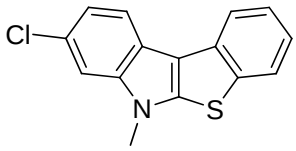


The reaction was conducted with 6-fluoro-1-methyl-1*H*-indole (**1l,** 74.5 mg, 0.5 mmol) and

cyclohexanone (**2a**, 103.6 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3u** as pale yellow solid (91.8 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.91-7.88 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.28-7.24 (m, 1H), 7.11-7.01 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.5 (d, *J* = 237.1 Hz), 143.3, 141.9 (d, *J* = 11.7 Hz), 138.0, 132.9, 125.1, 123.6, 121.9, 120.4, 119.2, 119.2 (d, *J* = 9.9 Hz), 116.5, 108.4 (d, *J* = 24.0 Hz), 96.3 (d, *J* = 26.7 Hz), 32.2; HRMS (ESI, m/z): calcd. for $C_{15}H_{10}FNS$ $[M]^+$ 255.0513, found 255.0515.

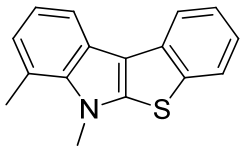
8-Chloro-6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3v)



The reaction was conducted with 6-chloro-1-methyl-1*H*-indole (**1m,** 82.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3v** as white solid (89.4 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (s, 3H), 7.28-7.23 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 142.0, 138.0, 132.8, 127.4, 125.2, 123.7, 122.1, 121.0, 120.5, 120.4, 119.3, 116.5, 109.4, 32.2; HRMS (ESI, m/z): calcd. for $C_{15}H_{10}ClNS$ $[M]^+$ 271.0217, found 271.0219.

6,7-Dimethyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3w)

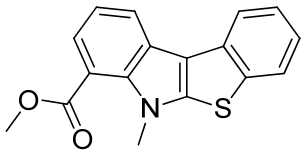


The reaction was conducted with 1,7-dimethyl-1*H*-indole (**1n,** 72.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3w** as white solid (76.6 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* =

8.0 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 4.14 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 144.7, 140.4, 137.9, 133.4, 125.0, 124.5, 123.6 (2C), 121.8, 121.2, 120.5, 120.2, 117.0, 116.3, 36.4, 19.6; HRMS (ESI, m/z): calcd. for $C_{16}H_{13}NS$ $[M]^+$ 251.0763, found 251.0765.

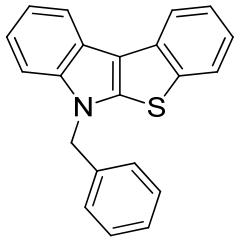
Methyl 6-methyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole-7-carboxylate (3x)



The reaction was conducted with Palladium(II) iodide (18 mg, 0.05 mmol), 5H-cyclopenta[1,2-*b*:5,4-*b′*]dipyridin-5-one (18 mg, 0.1 mmol), methyl 1-methyl-1*H*-indole-7-carboxylate (**1o,** 94.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol), 24 h. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) afforded the product **3x** as white solid (56.1 mg, 38%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.17 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.31-7.27 (m, 2H), 4.01 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.7, 146.5, 139.2, 138.3, 133.0, 125.3, 125.0, 124.5, 123.7, 122.8, 122.4, 120.6, 119.3, 116.7, 116.3, 52.2, 37.2; HRMS (ESI, m/z): calcd. for $C_{17}H_{13}NO_2S$ $[M]^+$ 295.0662, found 295.0658.

6-Benzyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (3z, CAS: 1269621-18-2)[1]

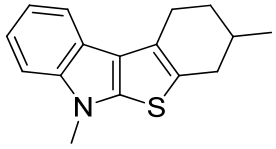


The reaction was conducted with methyl 1-benzyl-1*H*-indole (**1q,** 103.5 mg, 0.5 mmol) and cyclohexanone (**2a**, 103.6 μL, 1.0 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) afforded the product **3z** as white solid (114.3 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (d, *J* = 6.4 Hz, 1H), 8.05-8.03 (m, 1H), 7.75 (d, *J* = 6.4 Hz, 1H), 7.48-7.42 (m, 2H), 7.32-7.22 (m, 8H), 5.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ

142.8, 141.4, 138.3, 135.6, 132.9, 128.8, 128.0, 127.4, 125.0, 123.5, 122.8, 122.0, 121.6, 120.5, 120.2, 118.9, 117.3, 109.6, 49.7; MS (EI) *m/z* (%) 313 (100), 222, 195, 177, 91.

3,6-Dimethyl-2,3,4,6-tetrahydro-1*H*-benzo[4,5]thieno[2,3-*b*]indole (4a)

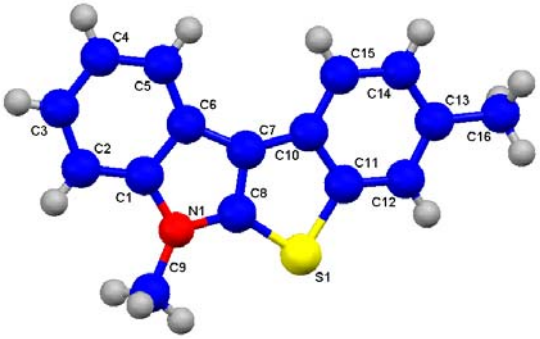


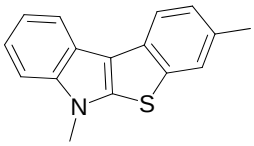
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.74 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.13-3.09 (m, 1H), 2.96-2.87 (m, 2H), 2.54-2.50 (m, 1H), 2.05-1.98 (m, 2H), 1.62 (m, 1H), 1.13 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.7, 141.5, 127.3, 126.9, 122.4, 121.7, 121.0, 118.9, 118.6, 108.8, 34.0, 32.0, 31.0, 30.2, 24.9, 21.5; HRMS (ESI, m/z): calcd. for $C_{16}H_{17}NS$ $[M]^+$ 255.1076, found 255.1077.

References

[1] M. Kienle, A. J. Wagner, C. Dunst, and P. Knochel. *Chem. Asian J.* **2011**, *6*, 517 – 523.

Crystal data and structure refinement for 3b





3b

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

Identification code	**3b**	
Empirical formula		
Formula weight	251.33	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 5.7076(11) Å	α= 90°.
	b = 20.718(4) Å	β= 90°.
	c = 21.125(4) Å	γ = 90°.
Volume	2498.0(9) $Å^3$	
Z	8	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.238 mm^{-1}	
F(000)	1056	
Crystal size	0.32 x 0.13 x 0.11 mm^3	
Theta range for data collection	3.498 to 27.507°.	
Index ranges	-7<=h<=7, -26<=k<=26, -27<=l<=26	
Reflections collected	15510	
Independent reflections	2862 [R(int) = 0.0728]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6337	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2862 / 0 / 165	
Goodness-of-fit on F^2	1.304	
Final R indices [I>2sigma(I)]	R1 = 0.0835, wR2 = 0.1728	
R indices (all data)	R1 = 0.0930, wR2 = 0.1774	

Extinction coefficient	n/a
Largest diff. peak and hole	0.425 and -0.358 e.Å^{-3}

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

	x	y	z	U(eq)
S1	7919(1)	451(1)	4550(1)	32(1)
N1	5090(4)	1576(1)	4572(1)	32(1)
C1	5094(5)	2141(1)	4218(2)	33(1)
C2	3464(6)	2641(2)	4229(2)	44(1)
C3	3787(7)	3137(2)	3803(2)	55(1)
C4	5666(7)	3141(2)	3380(2)	51(1)
C5	7290(7)	2647(2)	3372(2)	42(1)
C6	7026(5)	2134(1)	3795(2)	33(1)
C7	8229(5)	1535(1)	3907(1)	30(1)
C8	6977(5)	1222(1)	4374(1)	30(1)
C9	3433(6)	1403(2)	5064(2)	39(1)
C10	10122(5)	1144(2)	3677(1)	29(1)
C11	10130(5)	530(1)	3972(1)	30(1)
C12	11747(5)	55(2)	3814(2)	35(1)
C13	13441(6)	184(2)	3362(2)	36(1)
C14	13498(6)	798(2)	3090(2)	37(1)
C15	11888(6)	1270(2)	3236(1)	34(1)
C16	15175(7)	-326(2)	3165(2)	48(1)

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

S1-C8	1.725(3)
S1-C11	1.764(3)
N1-C1	1.390(4)
N1-C8	1.369(4)
N1-C9	1.449(4)
C1-C2	1.391(4)
C1-C6	1.419(5)
C2-C3	1.379(6)

C3-C4	1.396(6)
C4-C5	1.381(5)
C5-C6	1.397(5)
C6-C7	1.439(4)
C7-C8	1.380(4)
C7-C10	1.435(4)
C10-C11	1.417(4)
C10-C15	1.398(4)
C11-C12	1.389(4)
C12-C13	1.385(4)
C13-C14	1.396(5)
C13-C16	1.507(5)
C14-C15	1.375(5)

C8-S1-C11	89.27(14)
C1-N1-C9	126.5(3)
C8-N1-C1	106.6(3)
C8-N1-C9	126.9(3)
N1-C1-C2	128.1(3)
N1-C1-C6	109.3(3)
C2-C1-C6	122.5(3)
C3-C2-C1	117.1(4)
C2-C3-C4	121.6(3)
C5-C4-C3	121.3(4)
C4-C5-C6	118.9(4)
C1-C6-C7	106.0(3)
C5-C6-C1	118.6(3)
C5-C6-C7	135.3(3)
C8-C7-C6	106.1(3)
C8-C7-C10	111.5(3)
C10-C7-C6	142.2(3)
N1-C8-S1	132.5(2)
N1-C8-C7	111.9(3)
C7-C8-S1	115.4(2)
C11-C10-C7	111.1(3)
C15-C10-C7	131.7(3)
C15-C10-C11	117.2(3)
C10-C11-S1	112.7(2)

C12-C11-S1	125.1(2)
C12-C11-C10	122.2(3)
C13-C12-C11	119.5(3)
C12-C13-C14	118.5(3)
C12-C13-C16	120.9(3)
C14-C13-C16	120.7(3)
C15-C14-C13	122.6(3)
C14-C15-C10	120.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3b**. 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	34(1)	32(1)	29(1)	2(1)	5(1)	1(1)
N1	32(1)	34(1)	31(1)	-4(1)	2(1)	0(1)
C1	34(2)	29(2)	35(2)	-4(1)	-6(1)	-2(1)
C2	41(2)	35(2)	55(2)	-9(2)	-9(2)	4(1)
C3	50(2)	37(2)	76(3)	-4(2)	-19(2)	8(2)
C4	61(2)	35(2)	59(3)	9(2)	-17(2)	-3(2)
C5	48(2)	38(2)	41(2)	6(2)	-8(2)	-6(2)
C6	35(2)	30(2)	34(2)	-1(1)	-10(1)	-4(1)
C7	32(2)	33(2)	25(2)	-2(1)	-3(1)	-5(1)
C8	32(2)	31(2)	26(1)	-2(1)	-1(1)	-2(1)
C9	34(2)	43(2)	40(2)	-7(2)	6(1)	-4(1)
C10	31(2)	35(2)	22(1)	-3(1)	-2(1)	-5(1)
C11	32(2)	34(2)	24(1)	-2(1)	2(1)	-2(1)
C12	36(2)	37(2)	31(2)	-3(1)	0(1)	4(1)
C13	34(2)	48(2)	28(2)	-8(1)	0(1)	-1(1)
C14	32(2)	56(2)	25(2)	-4(2)	4(1)	-6(1)
C15	37(2)	43(2)	23(2)	2(1)	1(1)	-6(1)
C16	44(2)	60(2)	41(2)	-11(2)	5(2)	7(2)

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

	x	y	z	U(eq)
H2	2212	2639	4510	52
H3	2727	3478	3797	66
H4	5826	3483	3098	62
H5	8540	2656	3090	51
H9A	3651	1681	5423	58
H9B	3684	963	5188	58
H9C	1866	1451	4905	58
H12	11692	-346	4011	42
H14	14671	892	2799	45
H15	11975	1671	3040	41
H16A	15339	-638	3499	72
H16B	16665	-129	3082	72
H16C	14623	-537	2789	72

Table 6. Torsion angles [°] for **3b**.

S1-C11-C12-C13	-178.2(2)
N1-C1-C2-C3	-176.4(3)
N1-C1-C6-C5	177.0(3)
N1-C1-C6-C7	-0.2(3)
C1-N1-C8-S1	-173.6(3)
C1-N1-C8-C7	0.4(3)
C1-C2-C3-C4	-0.1(5)
C1-C6-C7-C8	0.5(3)
C1-C6-C7-C10	174.5(4)
C2-C1-C6-C5	-0.3(5)
C2-C1-C6-C7	-177.5(3)
C2-C3-C4-C5	-0.3(6)
C3-C4-C5-C6	0.4(5)
C4-C5-C6-C1	-0.1(5)
C4-C5-C6-C7	176.1(3)
C5-C6-C7-C8	-176.0(4)
C5-C6-C7-C10	-2.0(7)
C6-C1-C2-C3	0.4(5)

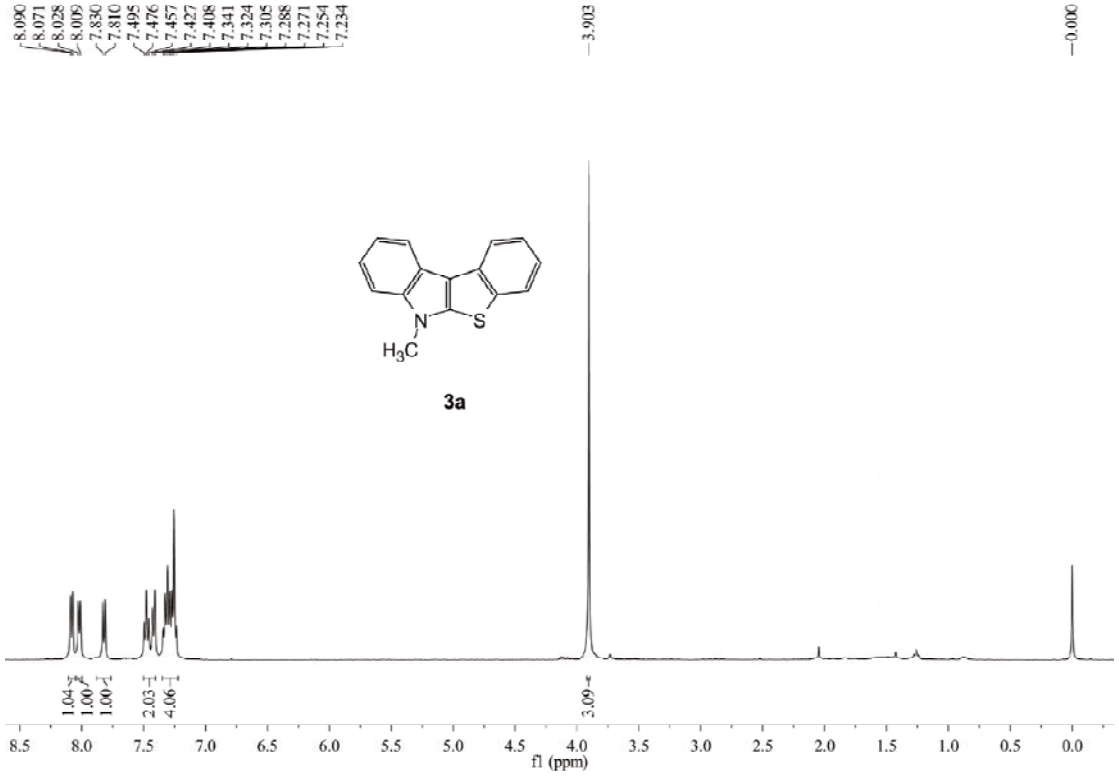
C6-C7-C8-S1	174.6(2)
C6-C7-C8-N1	-0.6(3)
C6-C7-C10-C11	-171.1(4)
C6-C7-C10-C15	9.6(7)
C7-C10-C11-S1	-2.8(3)
C7-C10-C11-C12	177.8(3)
C7-C10-C15-C14	-178.9(3)
C8-S1-C11-C10	1.7(2)
C8-S1-C11-C12	-179.0(3)
C8-N1-C1-C2	177.0(3)
C8-N1-C1-C6	-0.1(3)
C8-C7-C10-C11	2.7(4)
C8-C7-C10-C15	-176.6(3)
C9-N1-C1-C2	-4.1(5)
C9-N1-C1-C6	178.8(3)
C9-N1-C8-S1	7.5(5)
C9-N1-C8-C7	-178.4(3)
C10-C7-C8-S1	-1.5(3)
C10-C7-C8-N1	-176.7(2)
C10-C11-C12-C13	1.1(5)
C11-S1-C8-N1	173.8(3)
C11-S1-C8-C7	-0.1(2)
C11-C10-C15-C14	1.9(4)
C11-C12-C13-C14	1.6(5)
C11-C12-C13-C16	-178.1(3)
C12-C13-C14-C15	-2.5(5)
C13-C14-C15-C10	0.7(5)
C15-C10-C11-S1	176.6(2)
C15-C10-C11-C12	-2.8(4)
C16-C13-C14-C15	177.1(3)

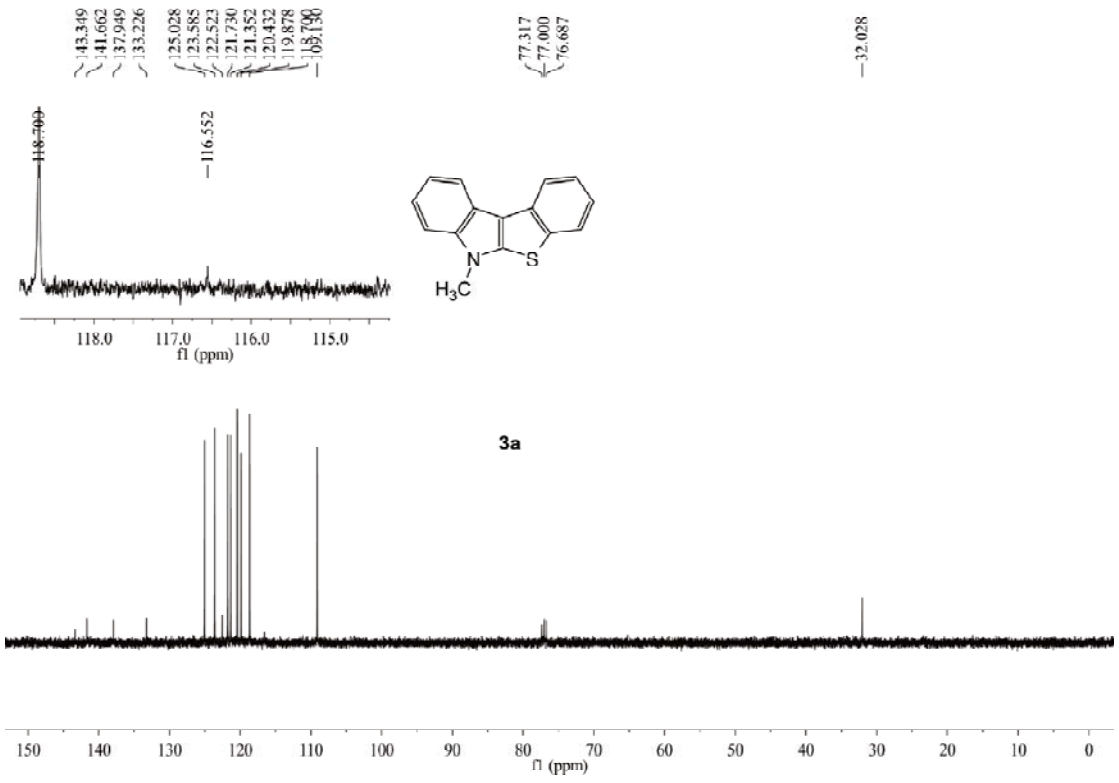
Symmetry transformations used to generate equivalent atoms:

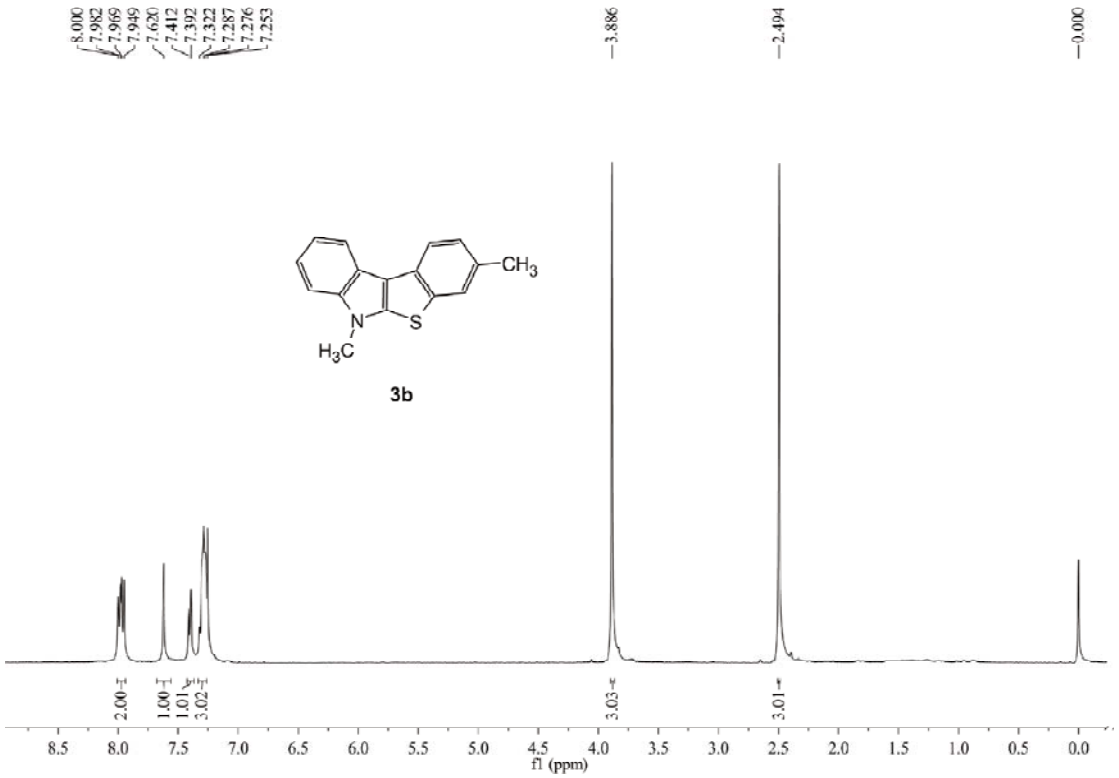
Table 7. Hydrogen bonds for **3b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

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



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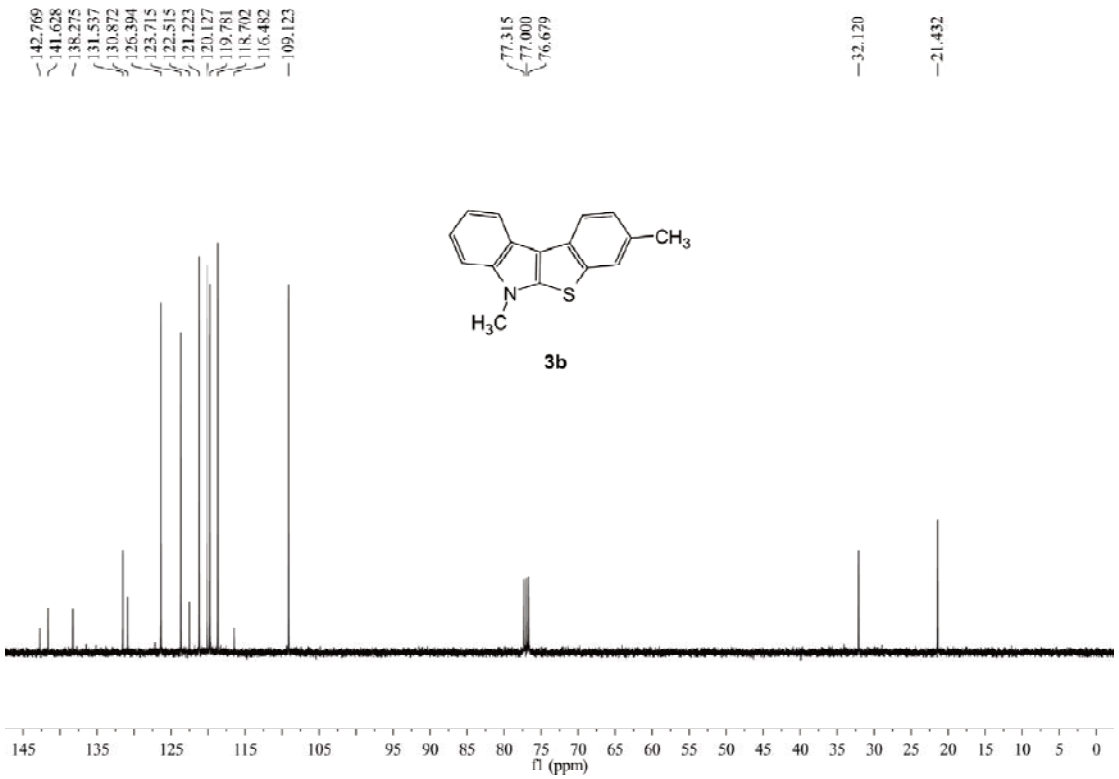
0.000
CH3
N
S
H3C
3b
2.00
1.00
1.01
3.02
3.03
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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116.482
109.123
77.315
77.000
76.679
32.120
21.432
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S
H3C
3b
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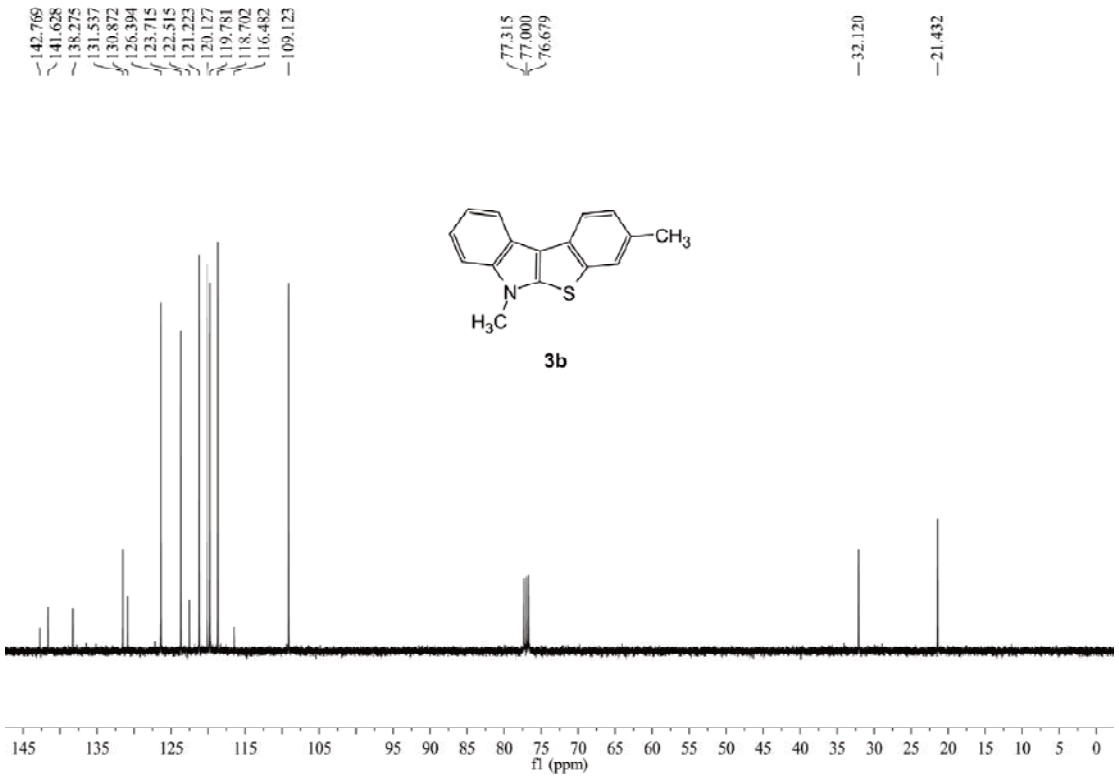
f1 (ppm)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120.127
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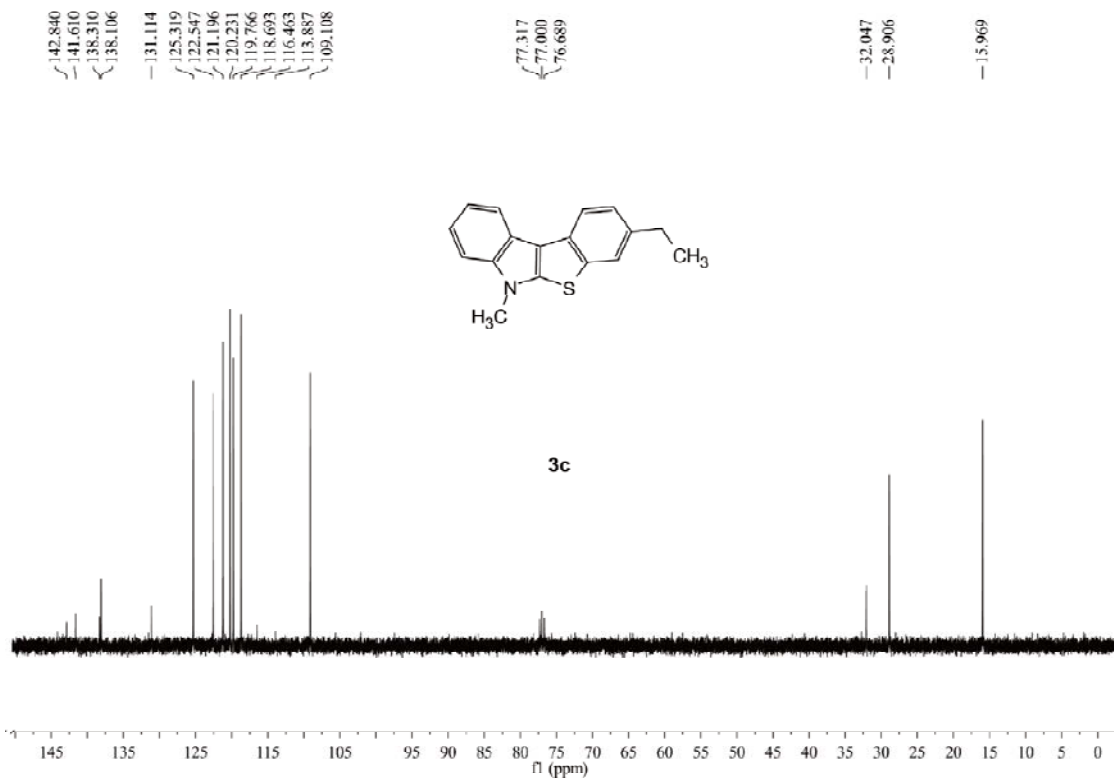
116.482
109.123
77.315
77.000
76.679
32.120
21.432
CH3
N
S
H3C
3b
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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77.317
77.000
76.689
32.047
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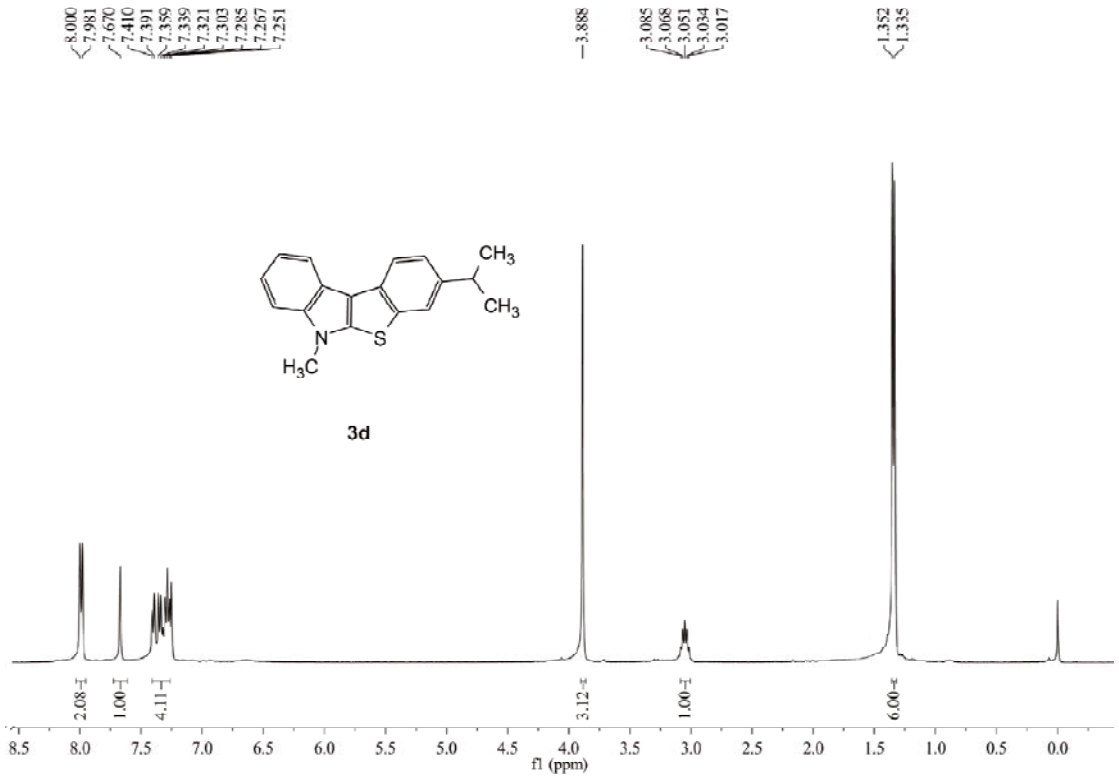
N
S
H3C
3c
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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3.085
3.068
3.051
3.034
3.017
1.352
1.335
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CH3
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S
H3C
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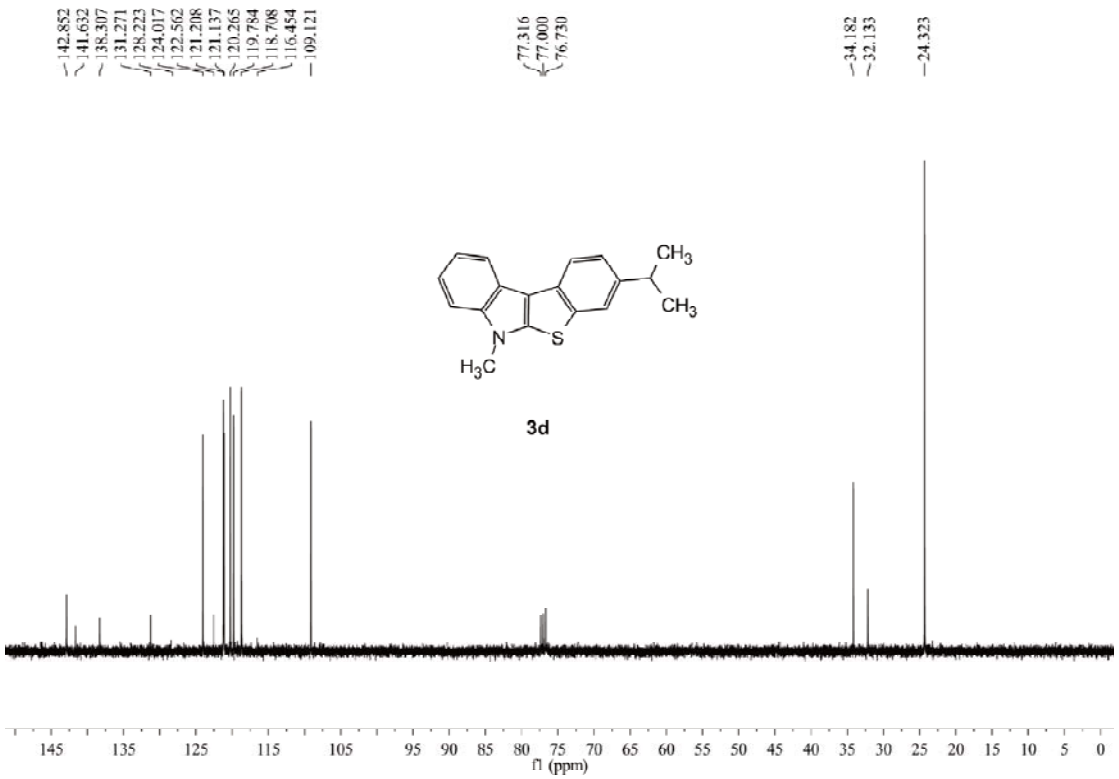
1.00
6.00
f1 (ppm)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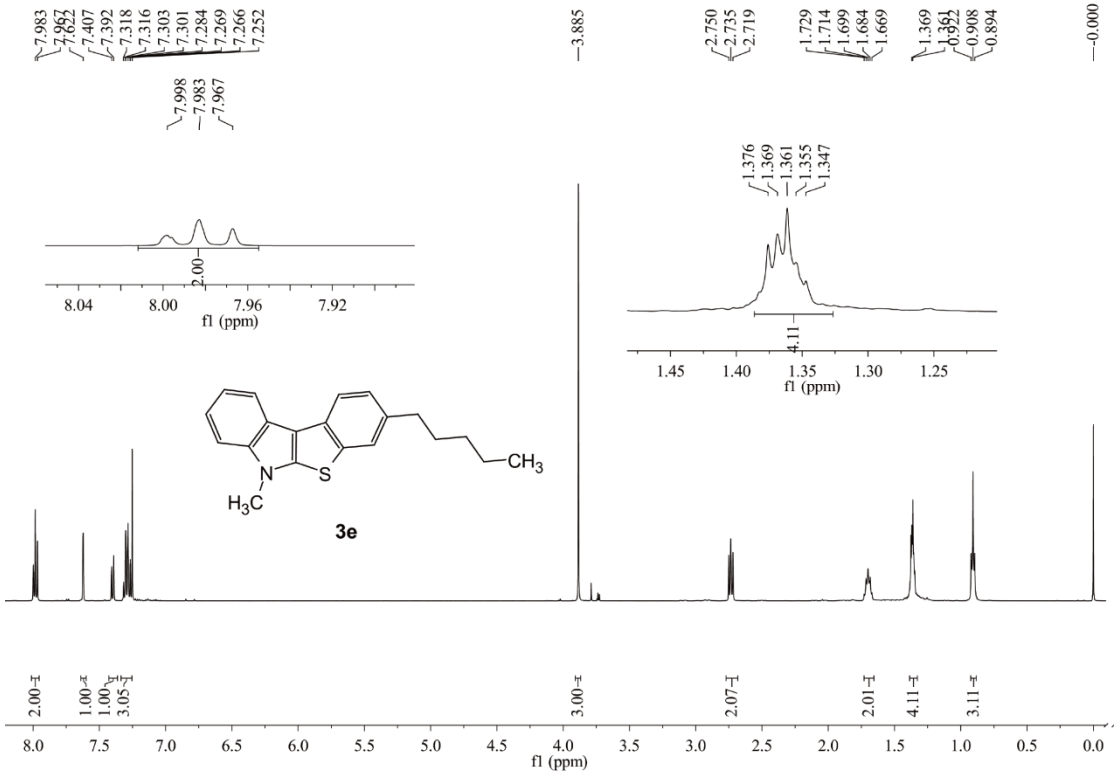
CH3
CH3
N
S
H3C
3d
f1 (ppm)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1.714
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1.369
1.361
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0.908
0.894
0.000
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8.04
8.00
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7.92
f1 (ppm)
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1.361
1.355
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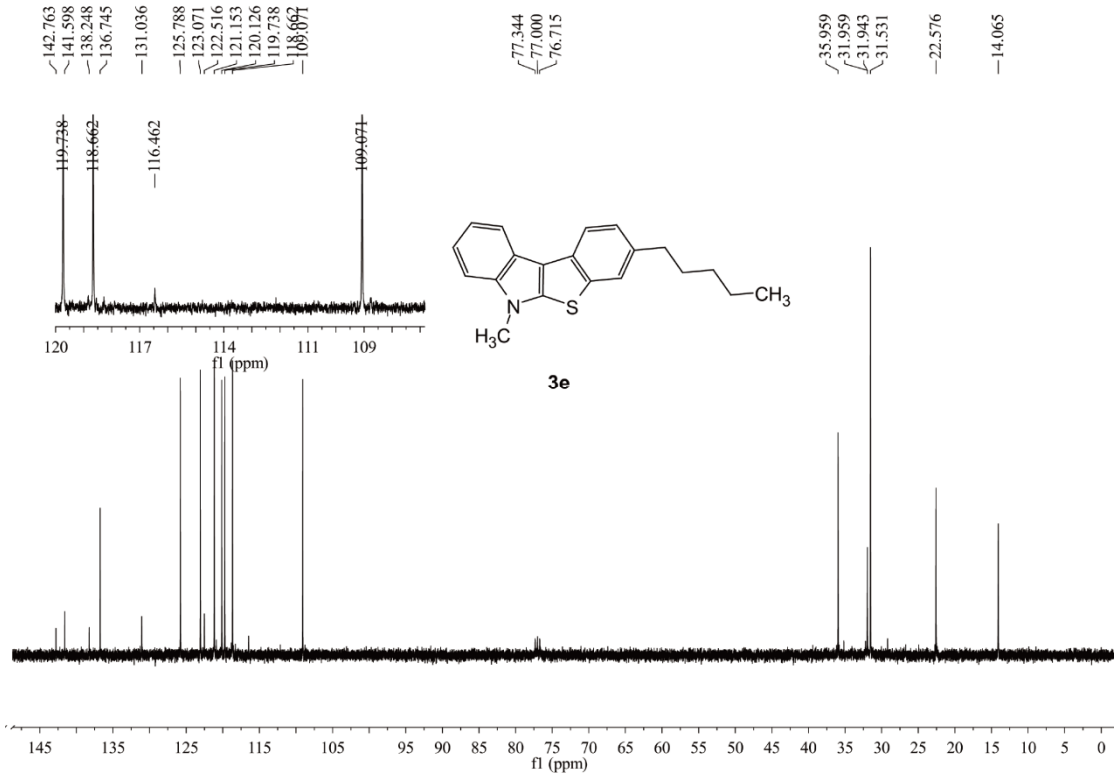
1.45
1.40
1.35
1.30
1.25
f1 (ppm)
N
S
H3C
CH3
3e
2.00
1.00
1.00
3.05
3.00
2.07
2.01
4.11
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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120
117
114
111
109
f1 (ppm)
N
S
H3C
CH3
3e
145
135
125
115
105
95
90
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65
60
55
50
45
40
35
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25
20
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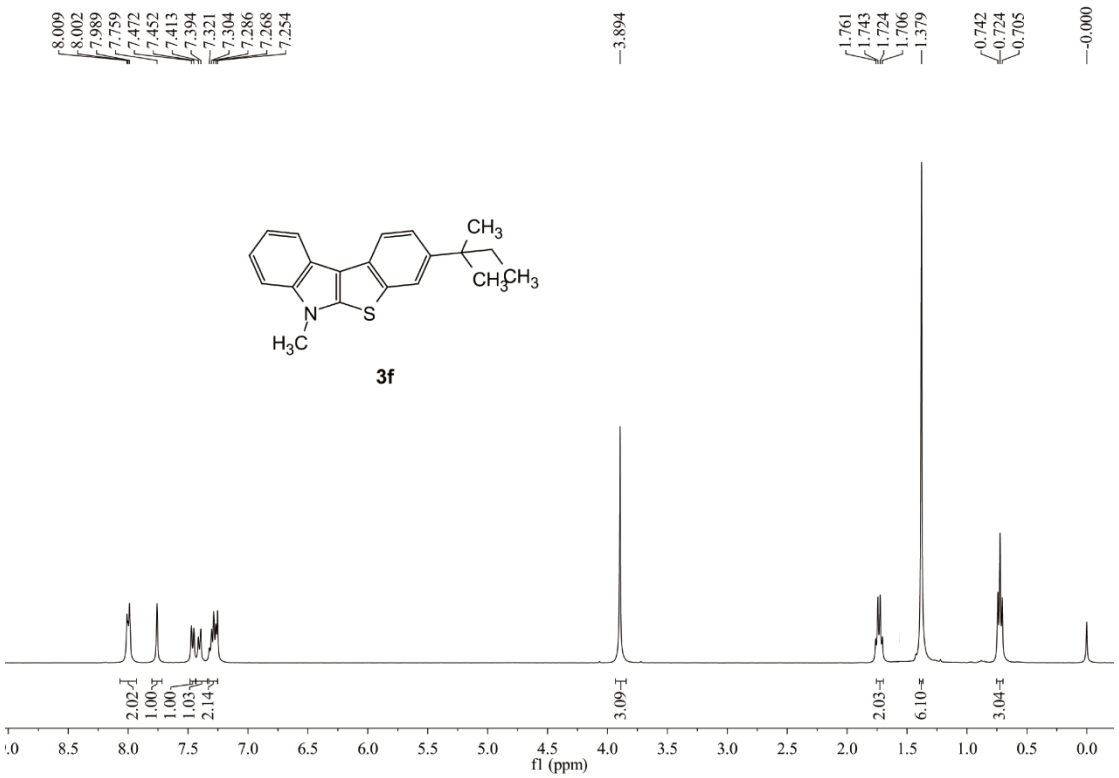
f1 (ppm)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1.743
1.724
1.706
1.379
0.742
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0.705
0.000
CH3
CH3CH3
N
S
H3C
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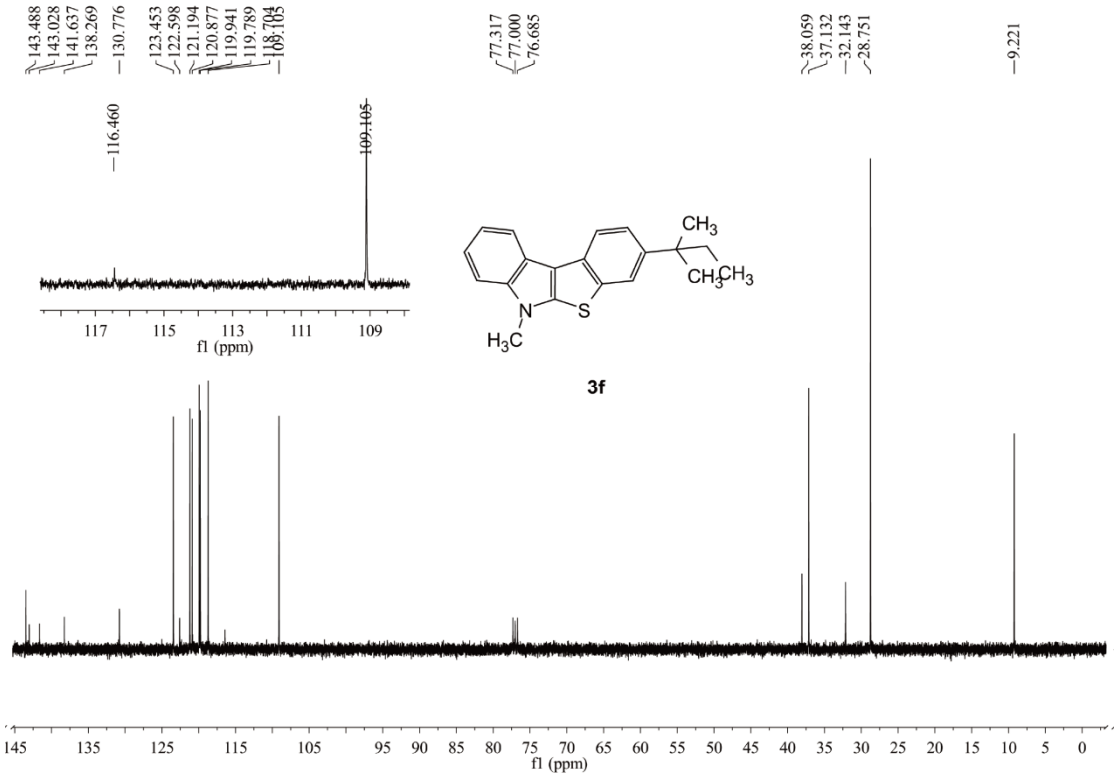
1.00
1.03
2.14
3.09
2.03
6.10
3.04
fl (ppm)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76.685
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37.132
32.143
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9.221
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109.105
117
115
113
111
109
fl (ppm)
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CH3CH3
N
S
H3C
3f
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135
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115
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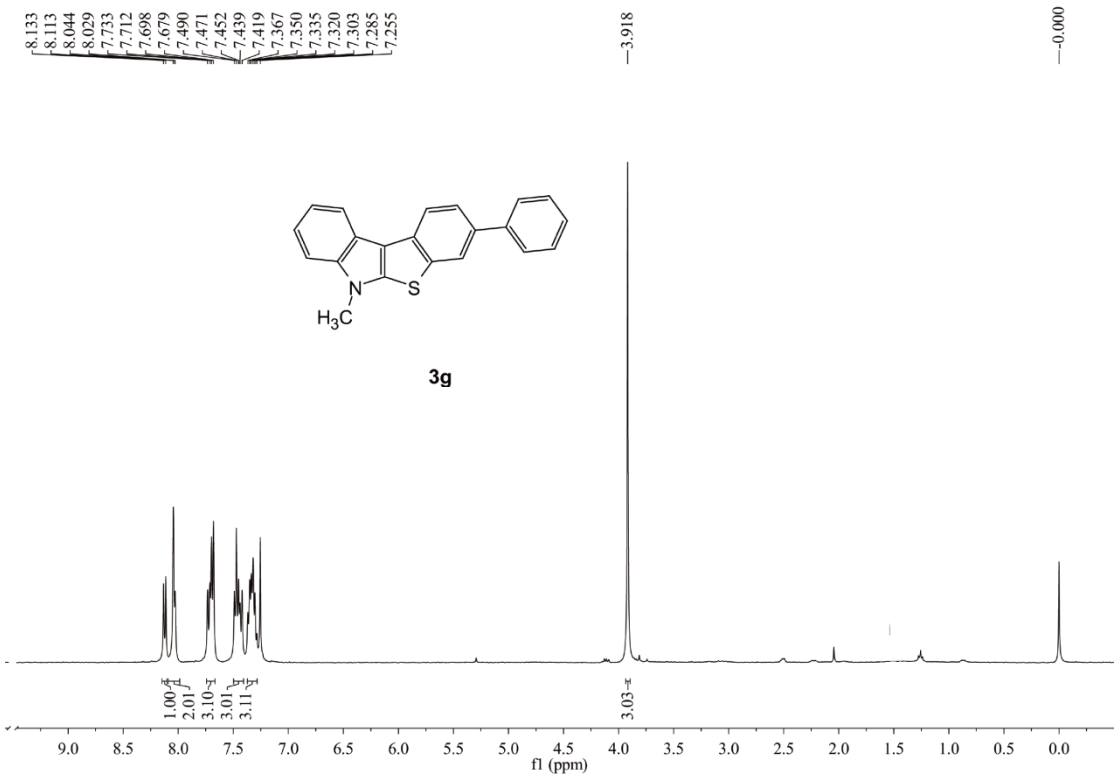
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7.335
7.320
7.303
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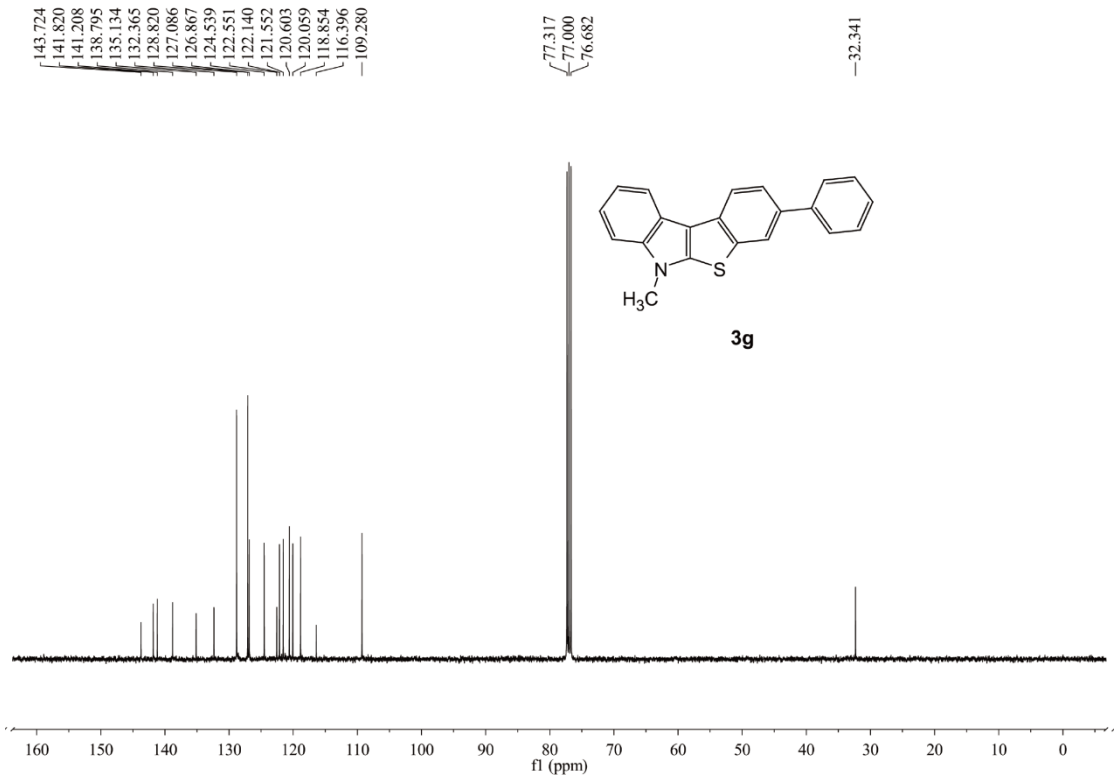
7.255
3.918
0.000
N
S
H3C
3g
1.00
2.01
3.10
3.01
3.11
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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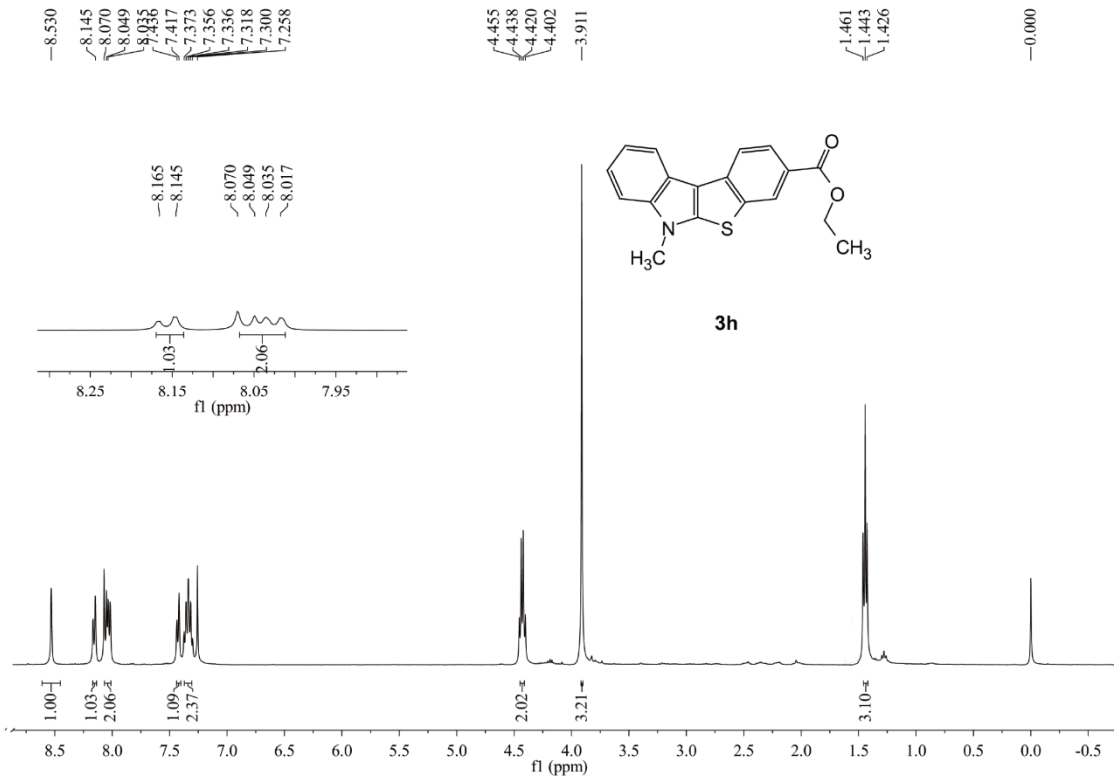
N
S
H3C
3g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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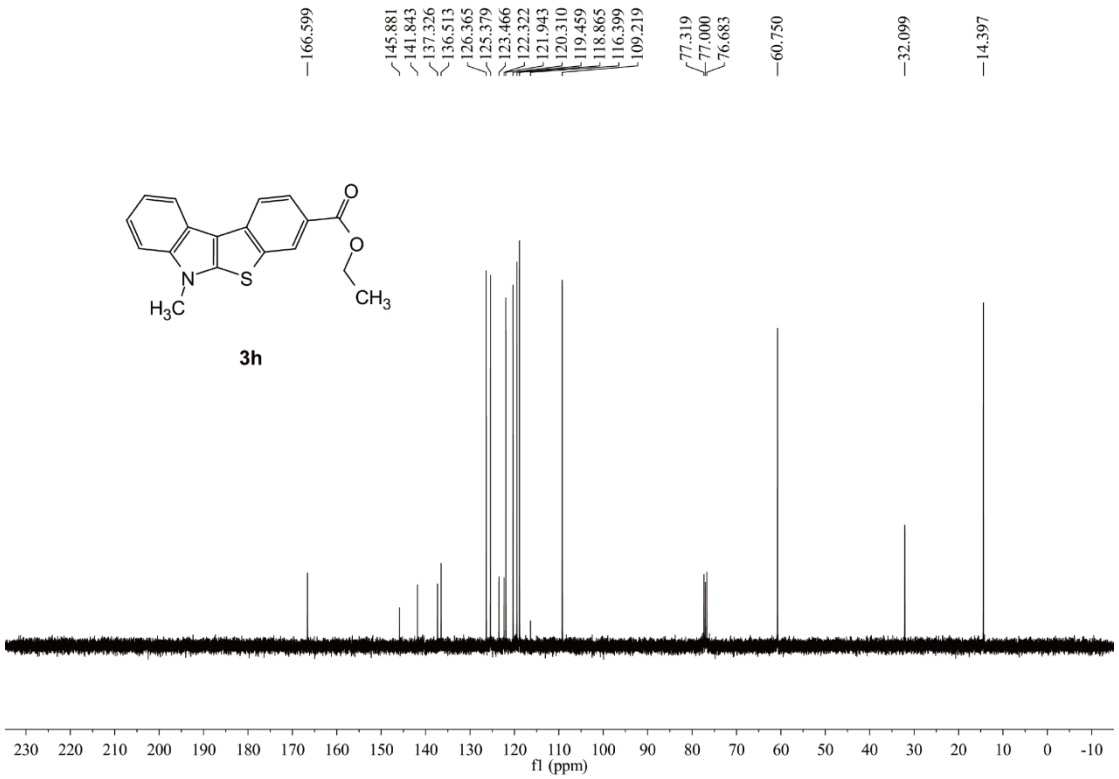
4.455
4.438
4.420
4.402
3.911
1.461
1.443
1.426
0.000
8.165
8.145
8.070
8.049
8.035
8.017
1.03
2.06
8.25
8.15
8.05
7.95
f1 (ppm)
O
O
N
S
H3C
CH3
3h
1.00
1.03
2.06
1.09
2.37
2.02
3.21
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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O
N
S
H3C
CH3
3h
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220
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200
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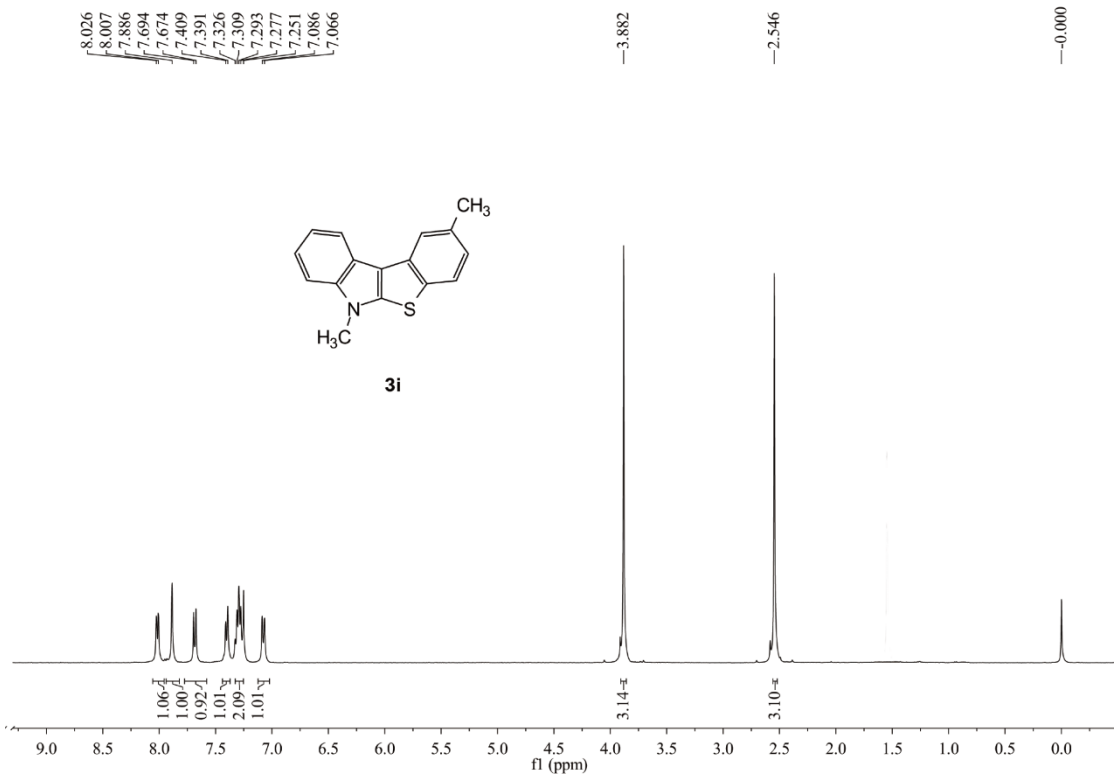
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.391
7.326
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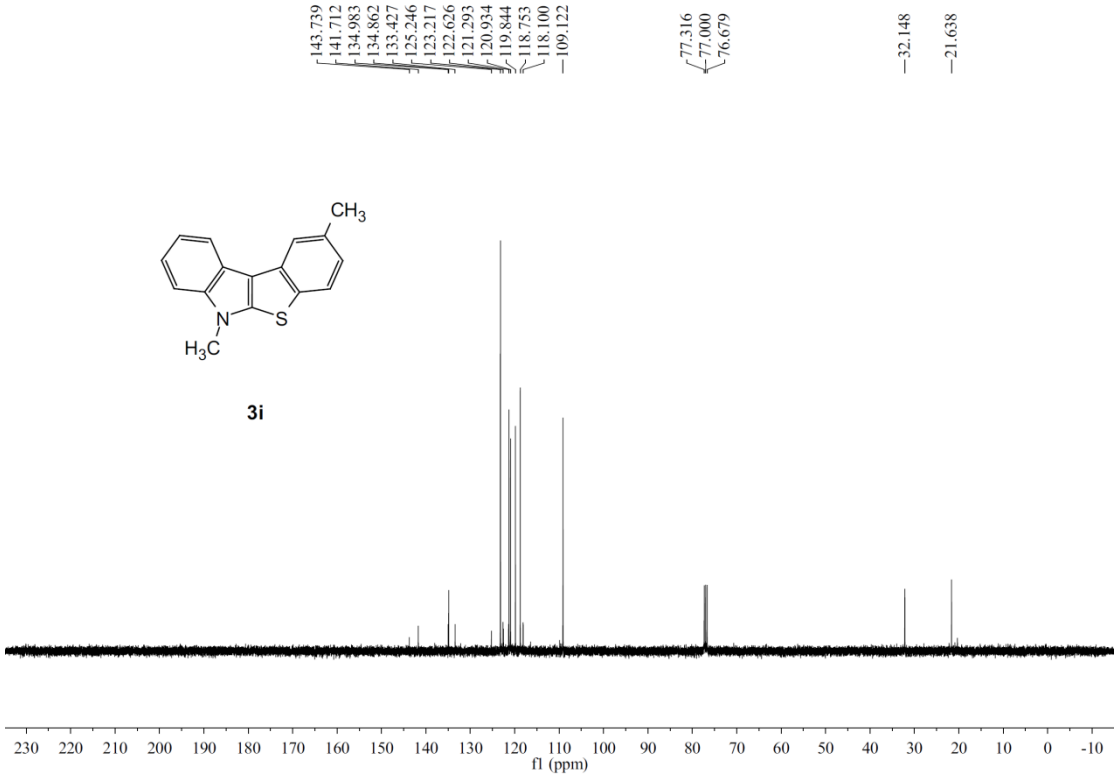
7.293
7.277
7.251
7.086
7.066
3.882
2.546
0.000
CH3
N
S
H3C
3i
1.06
1.00
0.92
1.01
2.09
1.01
3.14
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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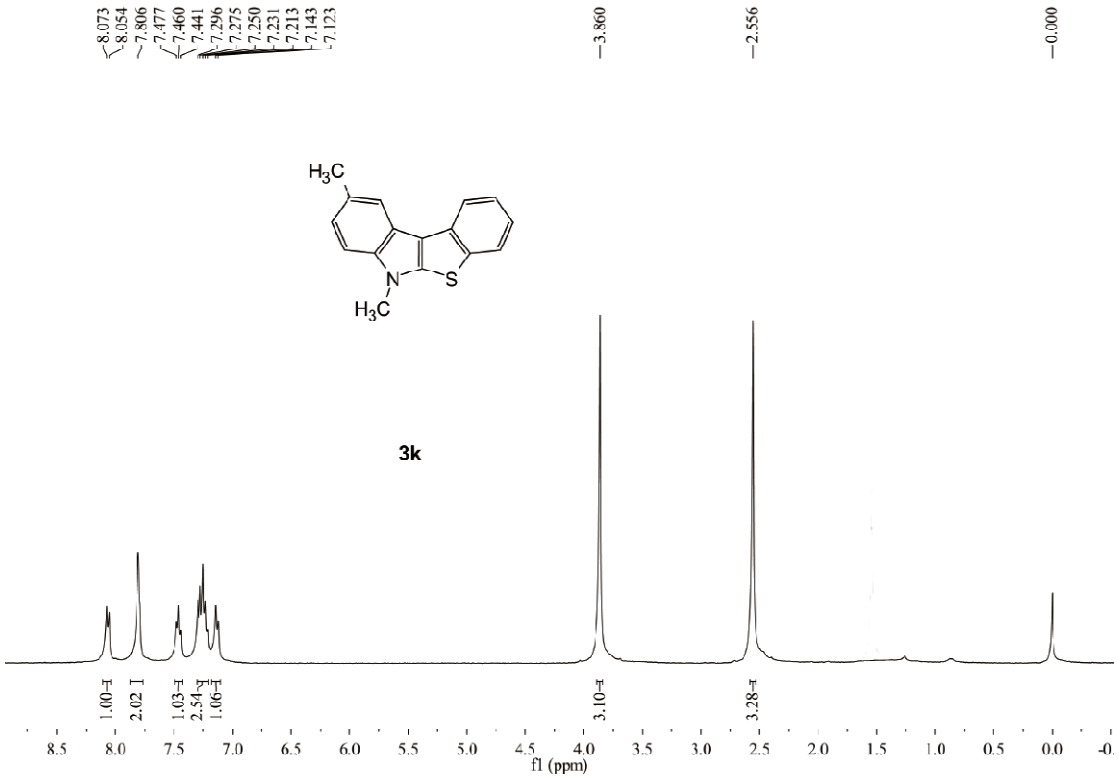
125.246
123.217
122.626
121.293
120.934
119.844
118.753
118.100
109.122
77.316
77.000
76.679
32.148
21.638
CH3
N
S
H3C
3i
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.477
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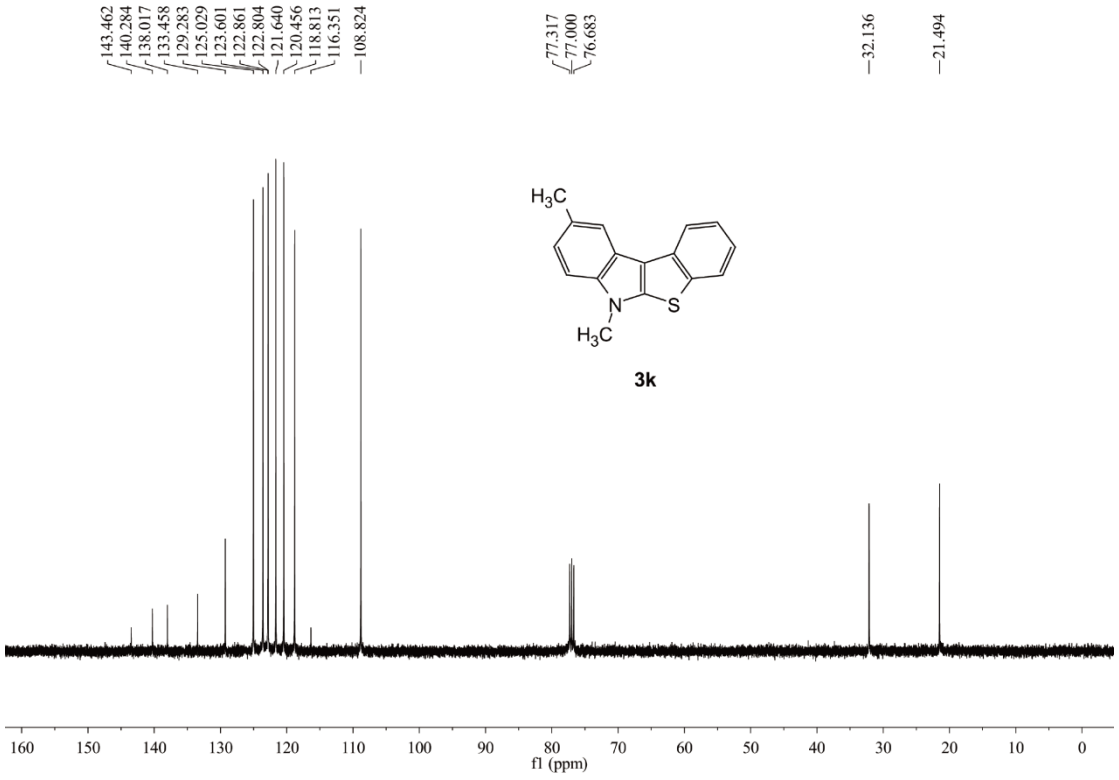
7.441
7.296
7.275
7.250
7.231
7.213
7.143
7.123
3.860
2.556
0.000
H3C
N
S
H3C
3k
1.00
2.02
1.03
2.54
1.06
3.10
3.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.017
133.458
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125.029
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121.640
120.456
118.813
116.351
108.824
77.317
77.000
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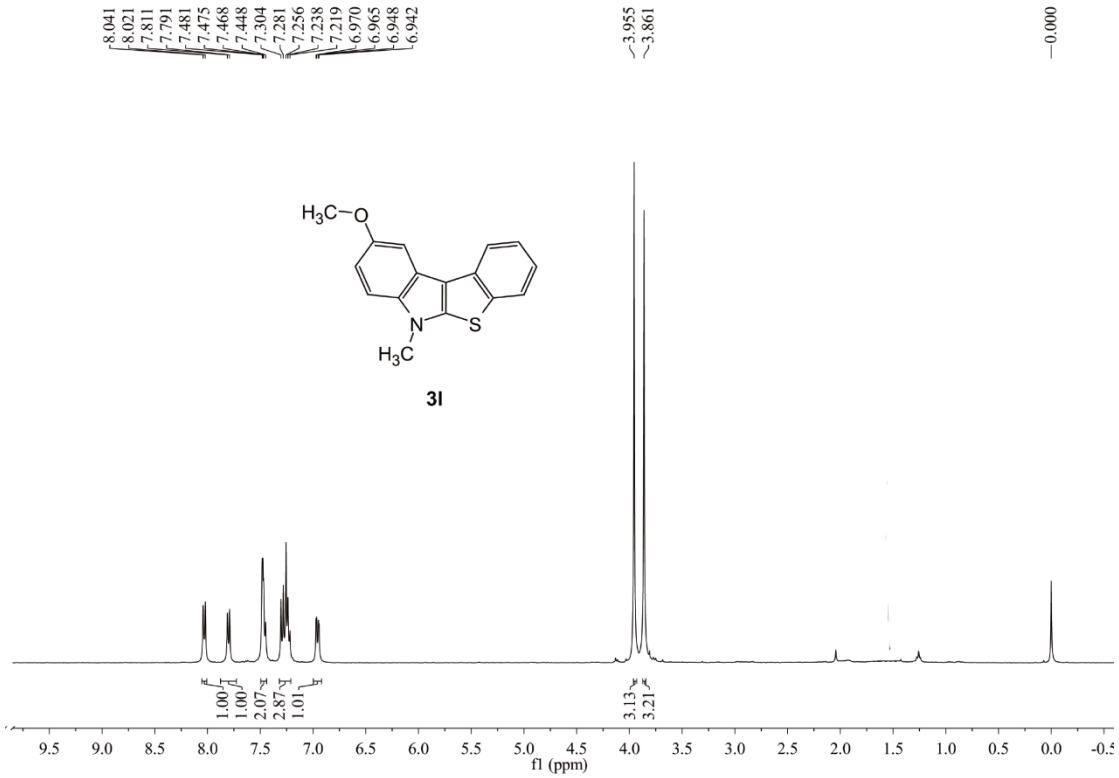
H3C
N
S
H3C
3k
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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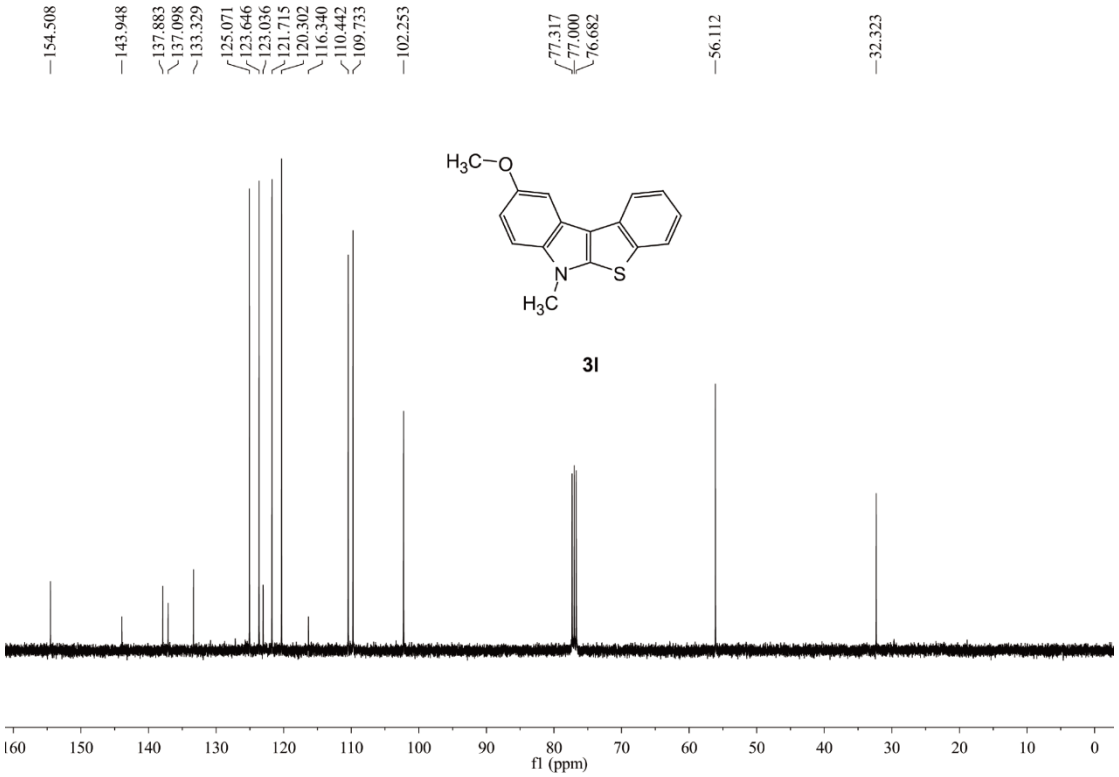
7.811
7.791
7.481
7.475
7.468
7.448
7.304
7.281
7.256
7.238
7.219
6.970
6.965
6.948
6.942
3.955
3.861
0.000
H3C—O
N
S
H3C
3l
1.00
1.00
2.07
2.87
1.01
3.13
3.21
fl (ppm)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123.036
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120.302
116.340
110.442
109.733
102.253
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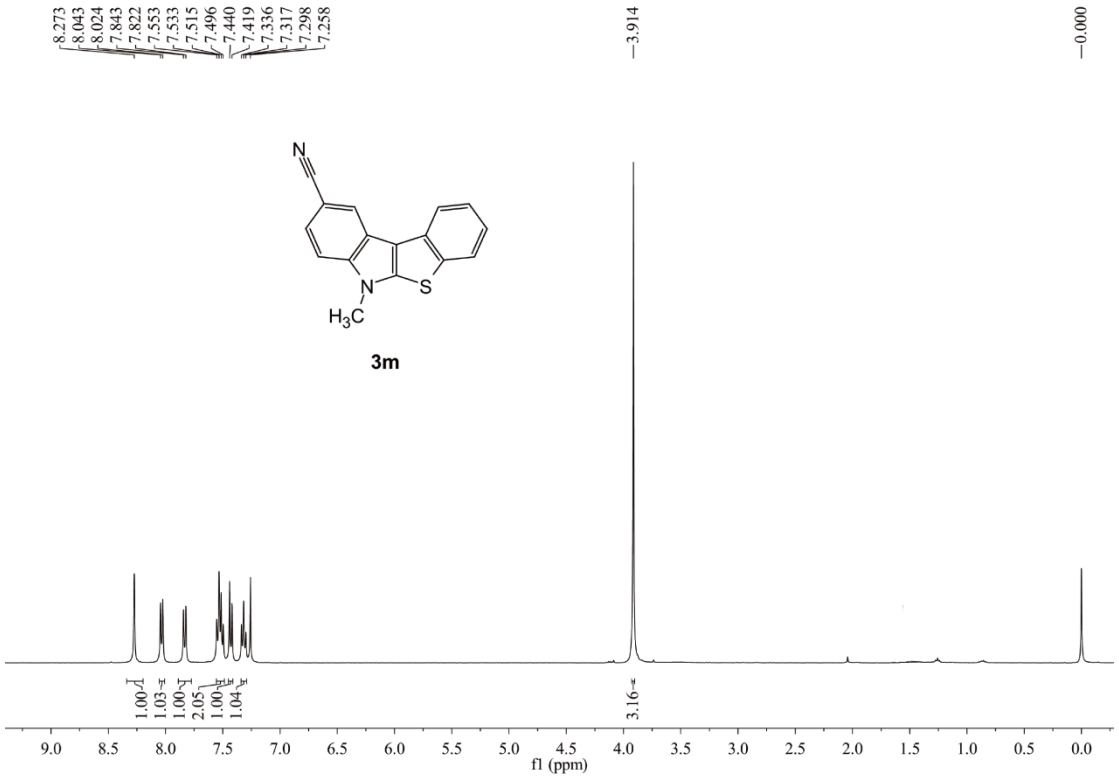
77.000
76.682
56.112
32.323
H3C—O
N
S
H3C
3l
fl (ppm)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7.843
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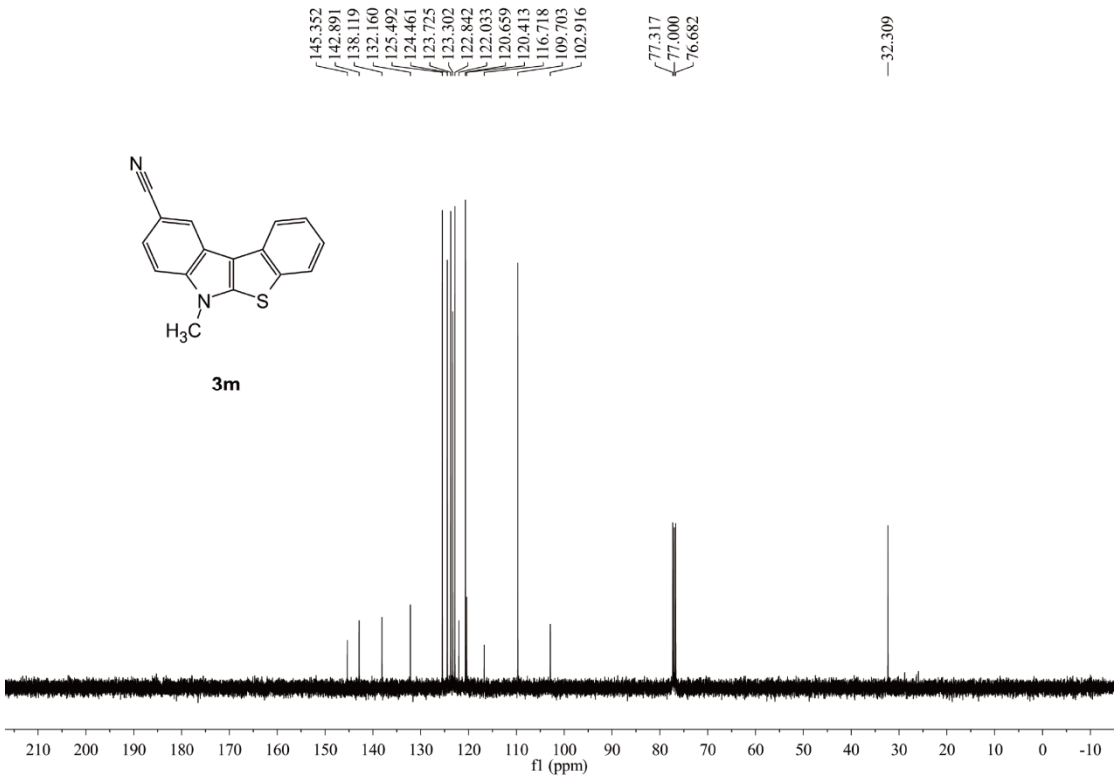
7.515
7.496
7.440
7.419
7.336
7.317
7.298
7.258
3.914
0.000
N
N
S
H3C
3m
1.00
1.03
1.00
2.05
1.00
1.04
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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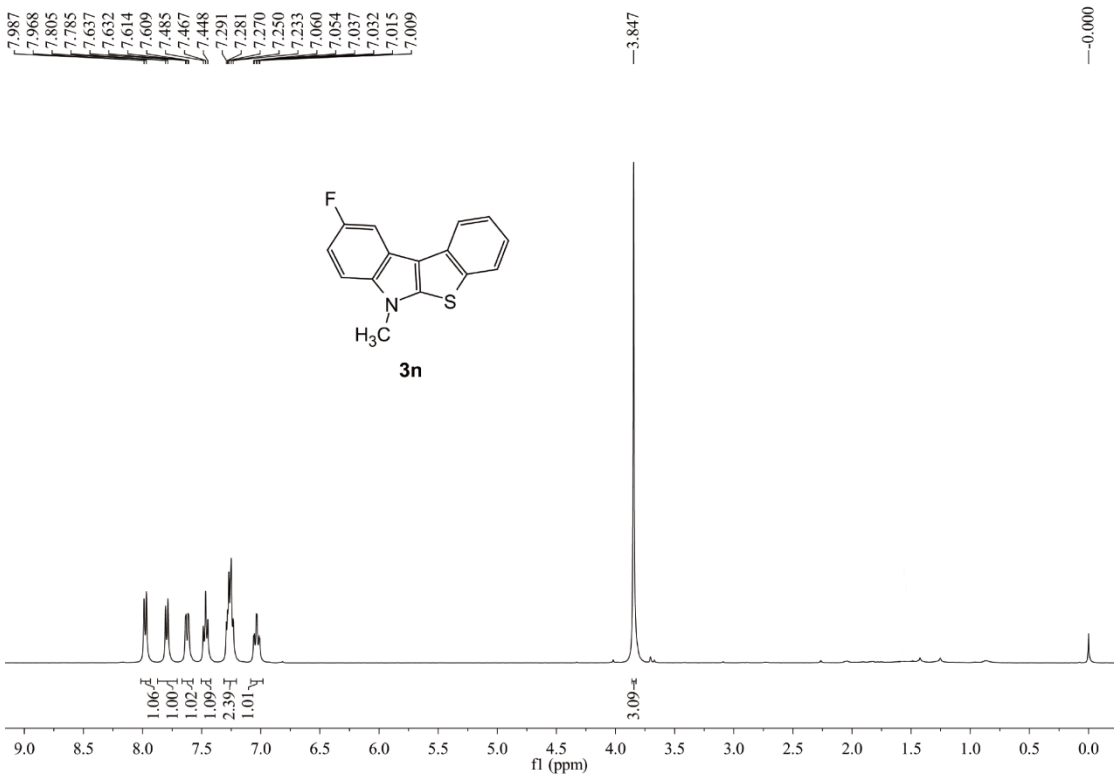
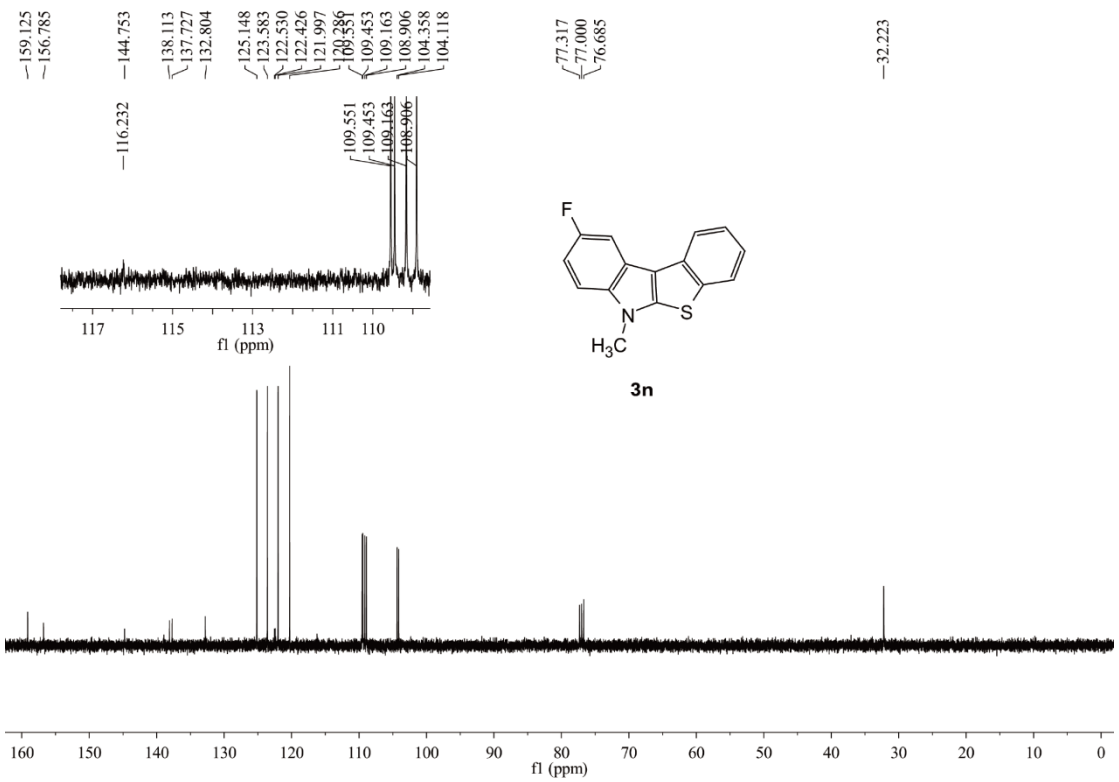
138.119
132.160
125.492
124.461
123.725
123.302
122.842
122.033
120.659
120.413
116.718
109.703
102.916
77.317
77.000
76.682
32.309
N
N
S
H3C
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.987
7.968
7.805
7.785
7.637
7.632
7.614
7.609
7.485
7.467
7.448
7.291
7.281
7.270
7.250
7.233
7.060
7.054
7.037
7.032
7.015
7.009
3.847
0.000
F
N
S
H3C
3n
1.06
1.00
1.02
1.09
2.39
1.01
3.09
fl (ppm)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144.753
138.113
137.727
132.804
125.148
123.583
122.530
122.426
121.997
109.551
109.453
109.163
108.906
104.358
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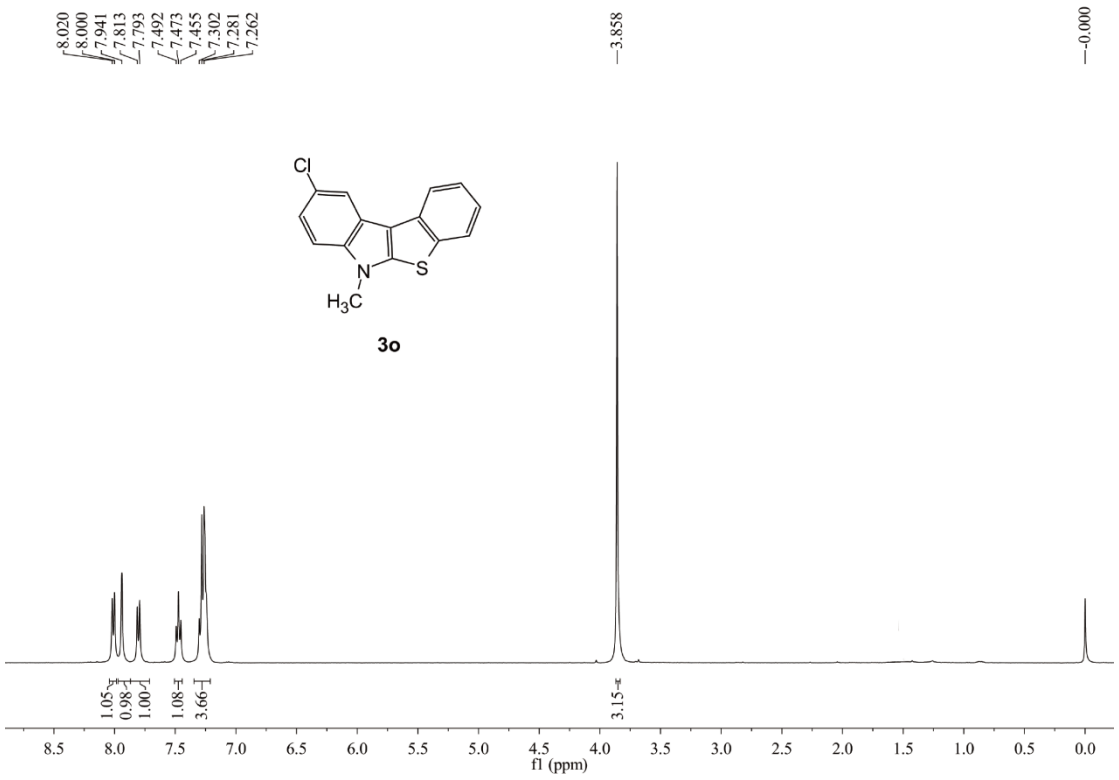
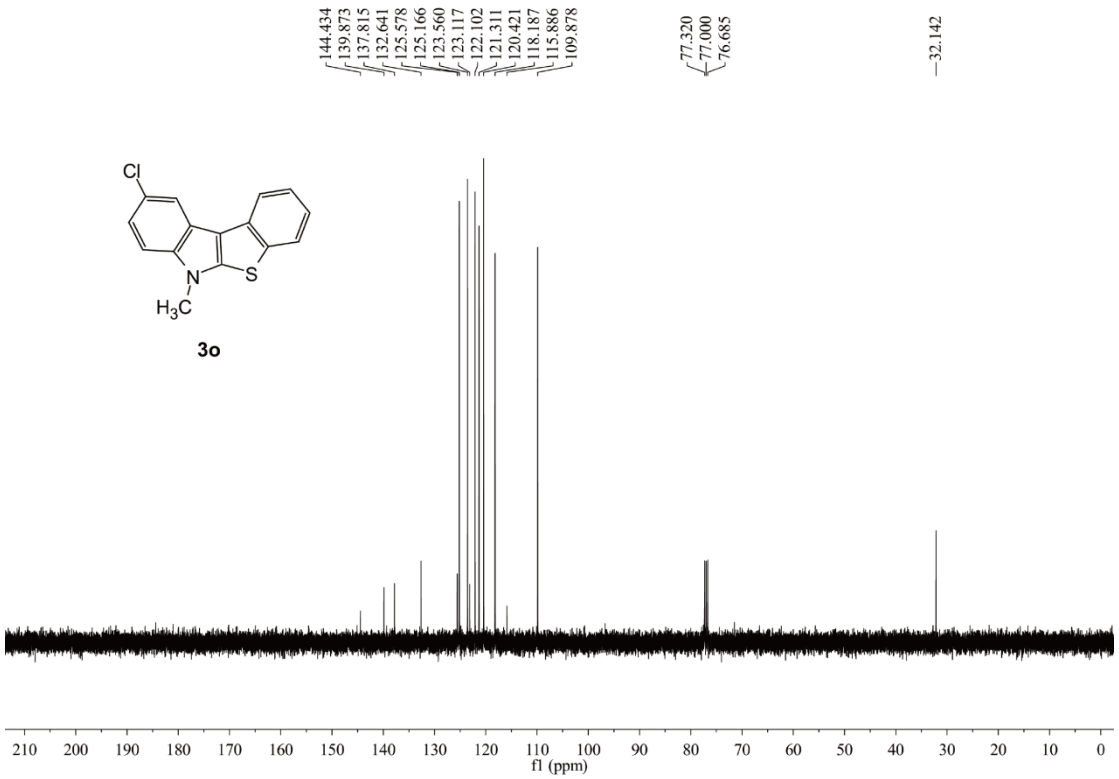
77.317
77.000
76.685
32.223
116.232
F
N
S
H3C
3n
fl (ppm)


8.020
8.000
7.941
7.813
7.793
7.492
7.473
7.455
7.302
7.281
7.262
3.858
0.000
Cl
N
S
H3C
3o
1.05
0.98
1.00
1.08
3.66
3.15
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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132.641
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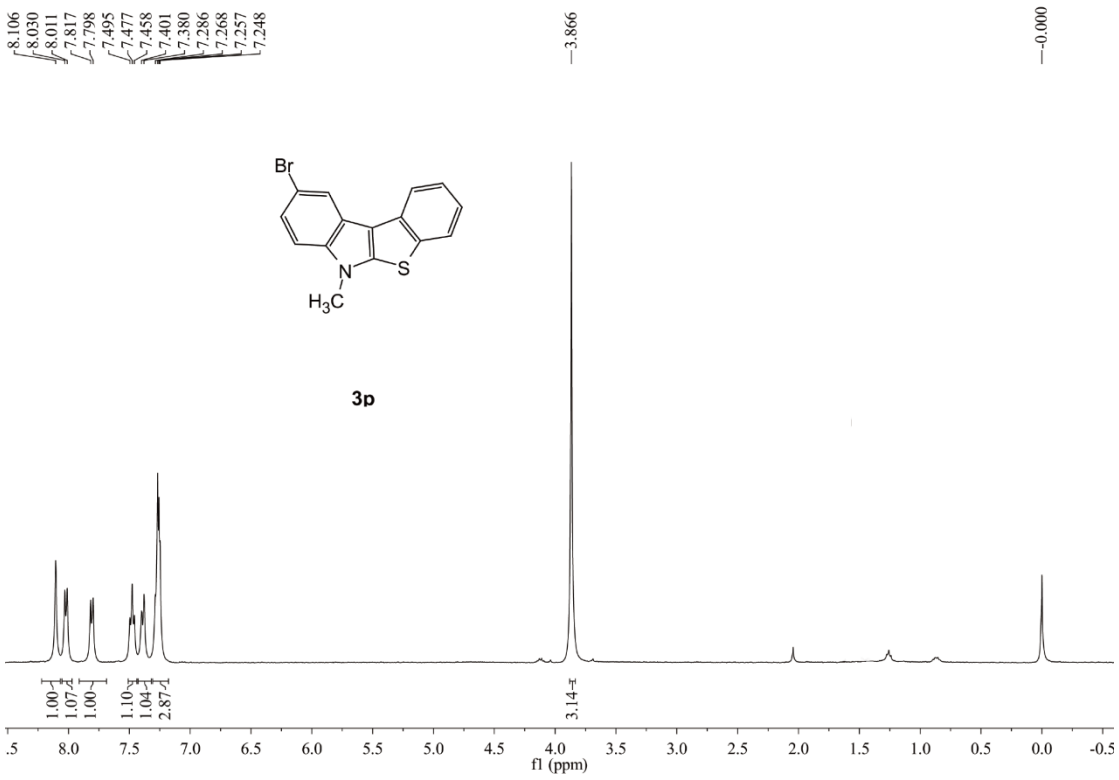
125.166
123.560
123.117
122.102
121.311
120.421
118.187
115.886
109.878
77.320
77.000
76.685
32.142
Cl
N
S
H3C
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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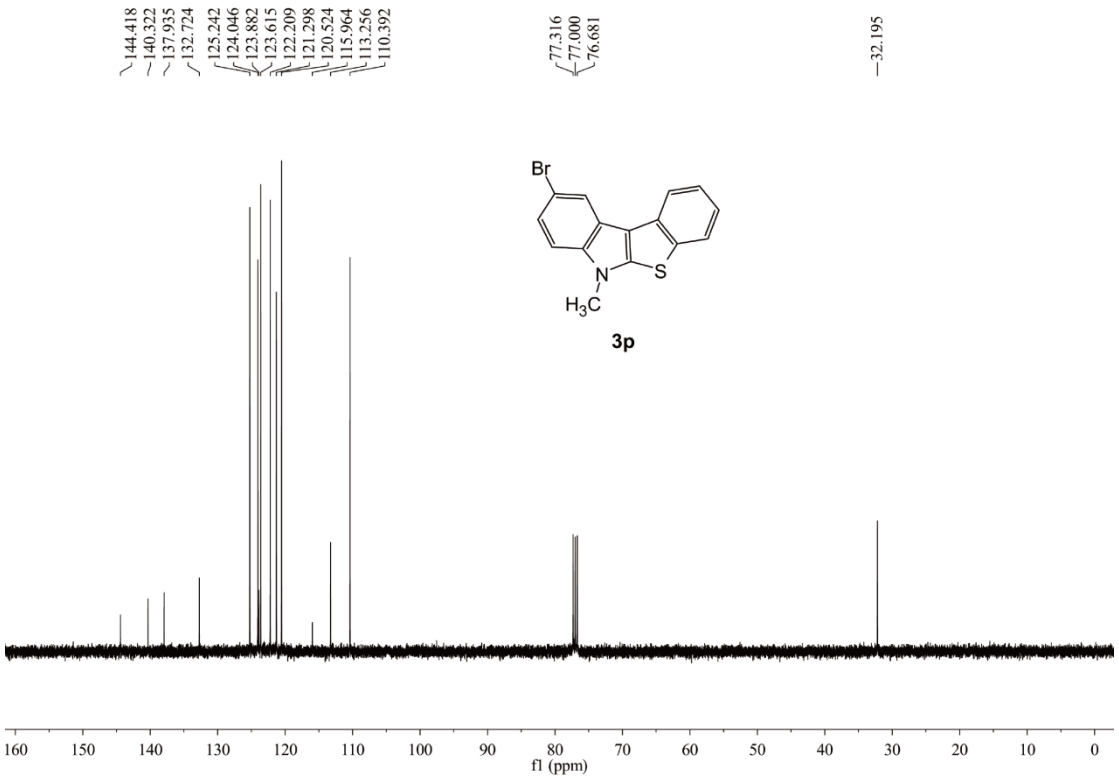
8.030
8.011
7.817
7.798
7.495
7.477
7.458
7.401
7.380
7.286
7.268
7.257
7.248
3.866
0.000
Br
N
S
H3C
3p
1.00
1.07
1.00
1.10
1.04
2.87
3.14
fl (ppm)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137.935
132.724
125.242
124.046
123.882
123.615
122.209
121.298
120.524
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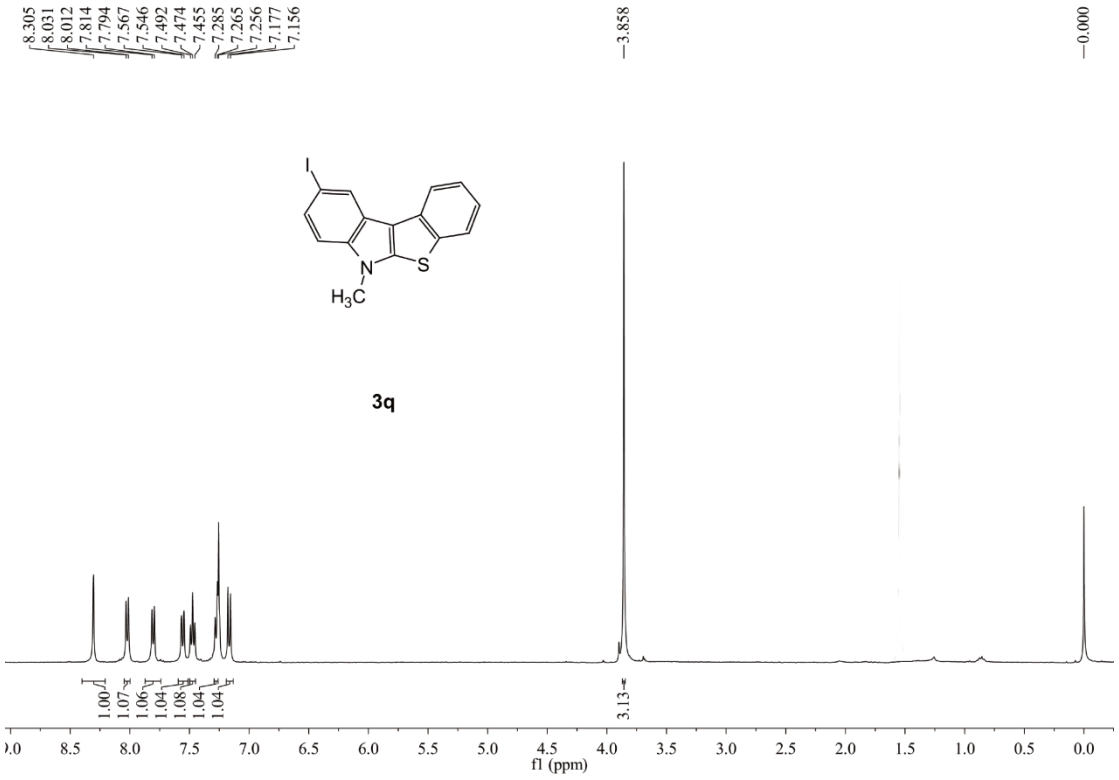
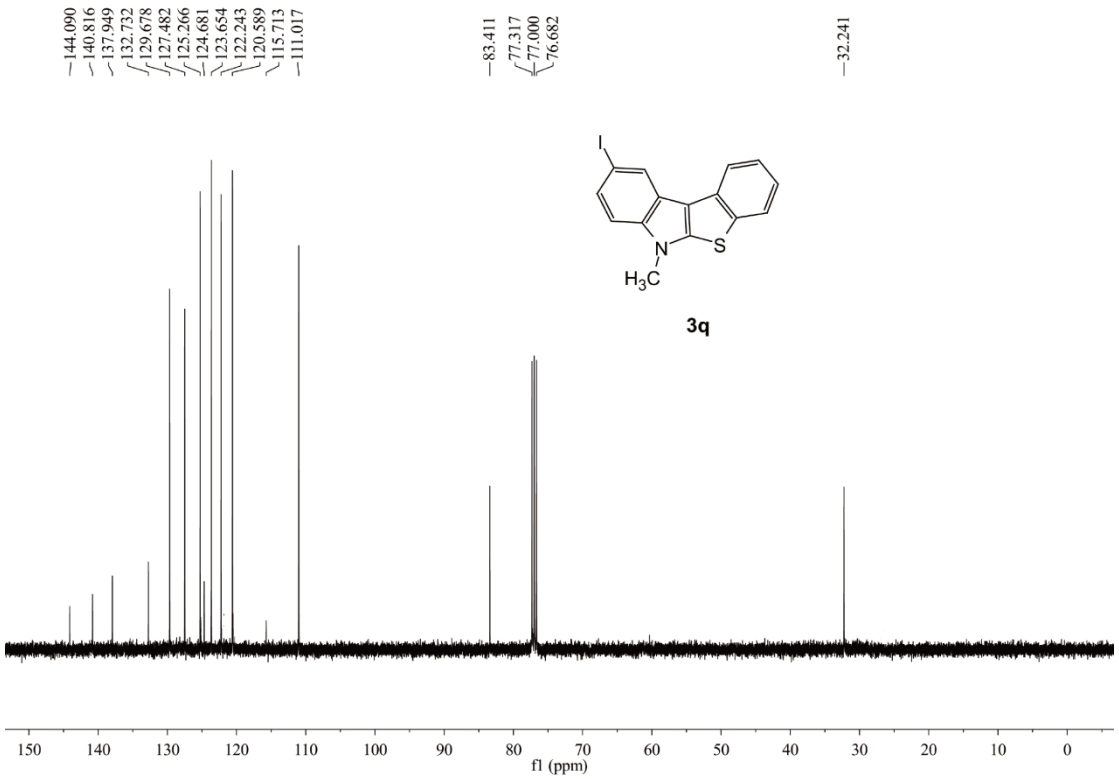
113.256
110.392
77.316
77.000
76.681
32.195
Br
N
S
H3C
3p
fl (ppm)


8.305
8.031
8.012
7.814
7.794
7.567
7.546
7.492
7.474
7.455
7.285
7.265
7.256
7.177
7.156
3.858
0.000
I
N
S
H3C
3q
1.00
1.07
1.06
1.04
1.08
1.04
1.04
3.13
fl (ppm)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140.816
137.949
132.732
129.678
127.482
125.266
124.681
123.654
122.243
120.589
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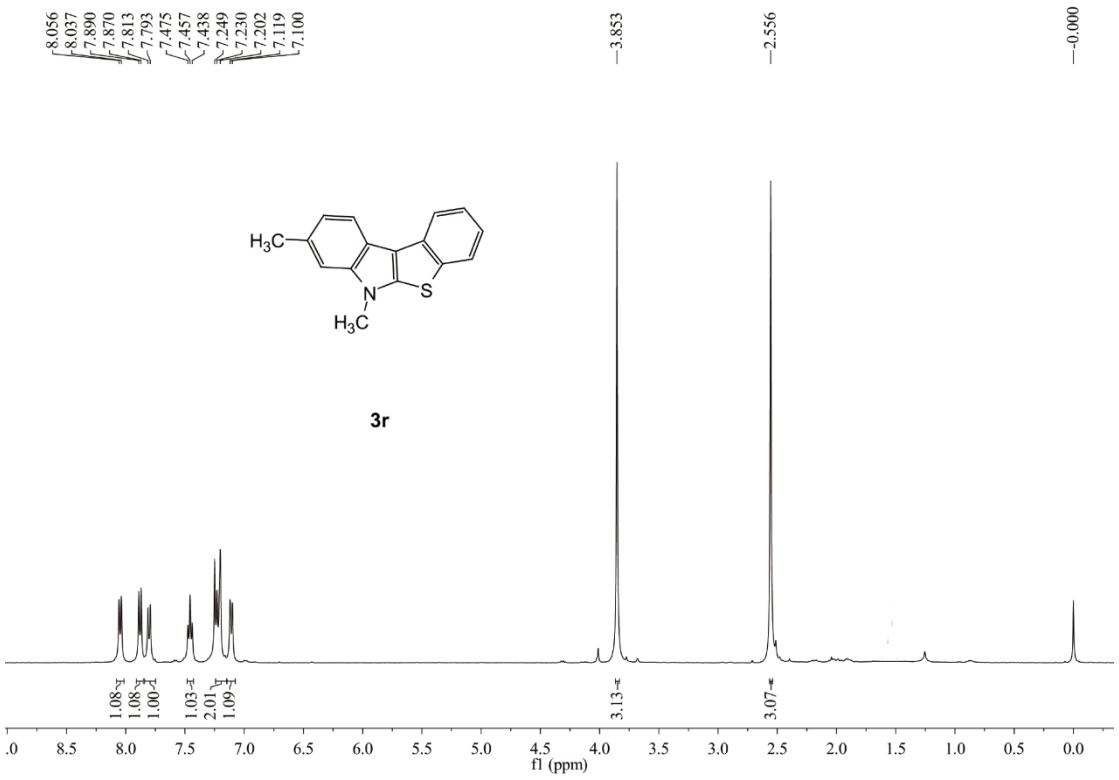
32.241
I
N
S
H3C
3q
fl (ppm)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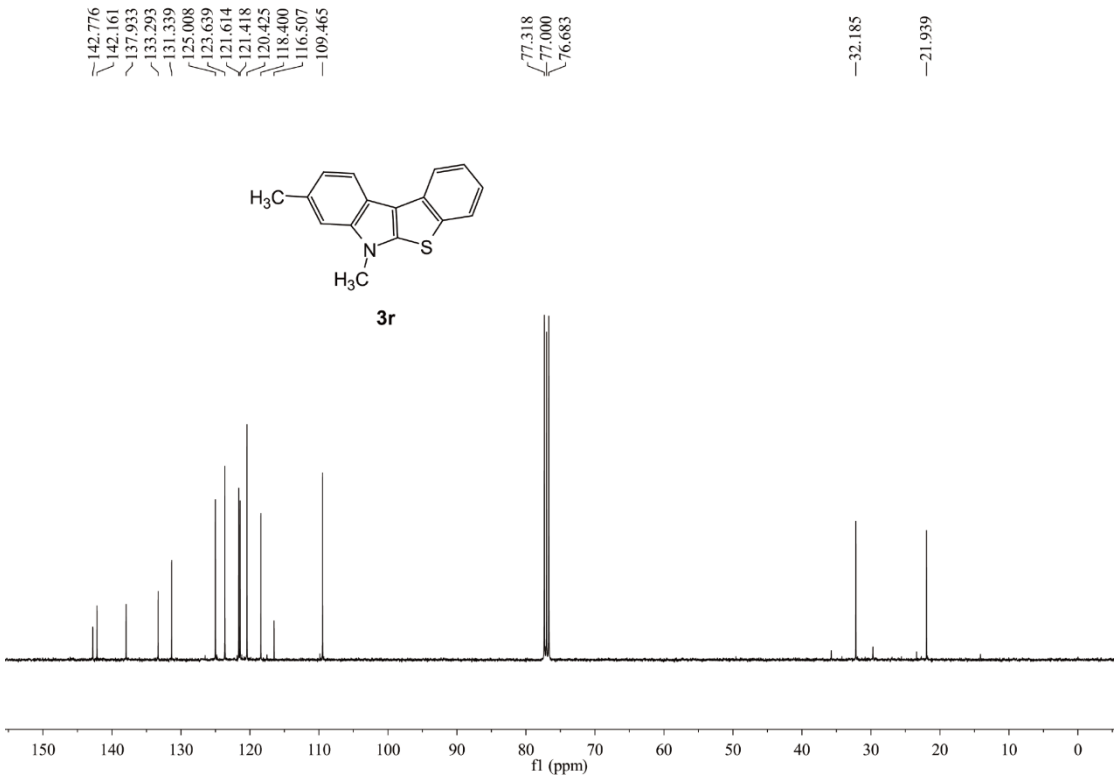
7.813
7.793
7.475
7.457
7.438
7.249
7.230
7.202
7.119
7.100
3.853
2.556
0.000
H3C
N
S
H3C
3r
1.08
1.08
1.00
1.03
2.01
1.09
3.13
3.07
fl (ppm)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137.933
133.293
131.339
125.008
123.639
121.614
121.418
120.425
118.400
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109.465
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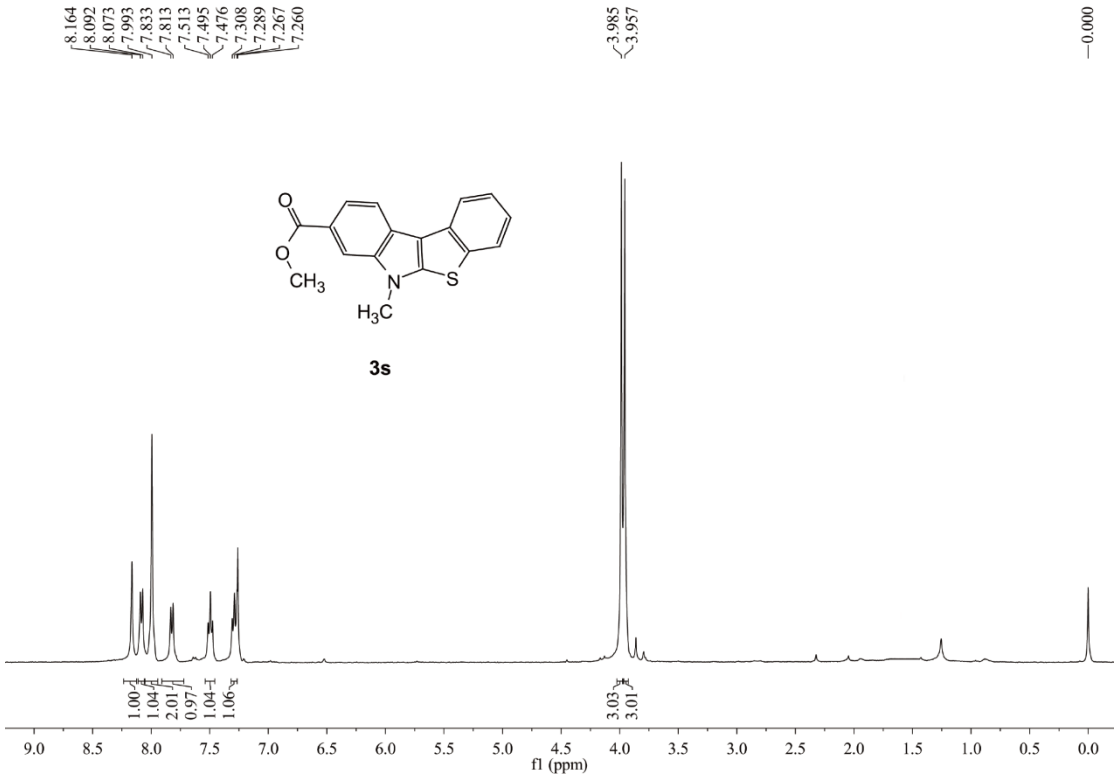
77.000
76.683
32.185
21.939
H3C
N
S
H3C
3r
fl (ppm)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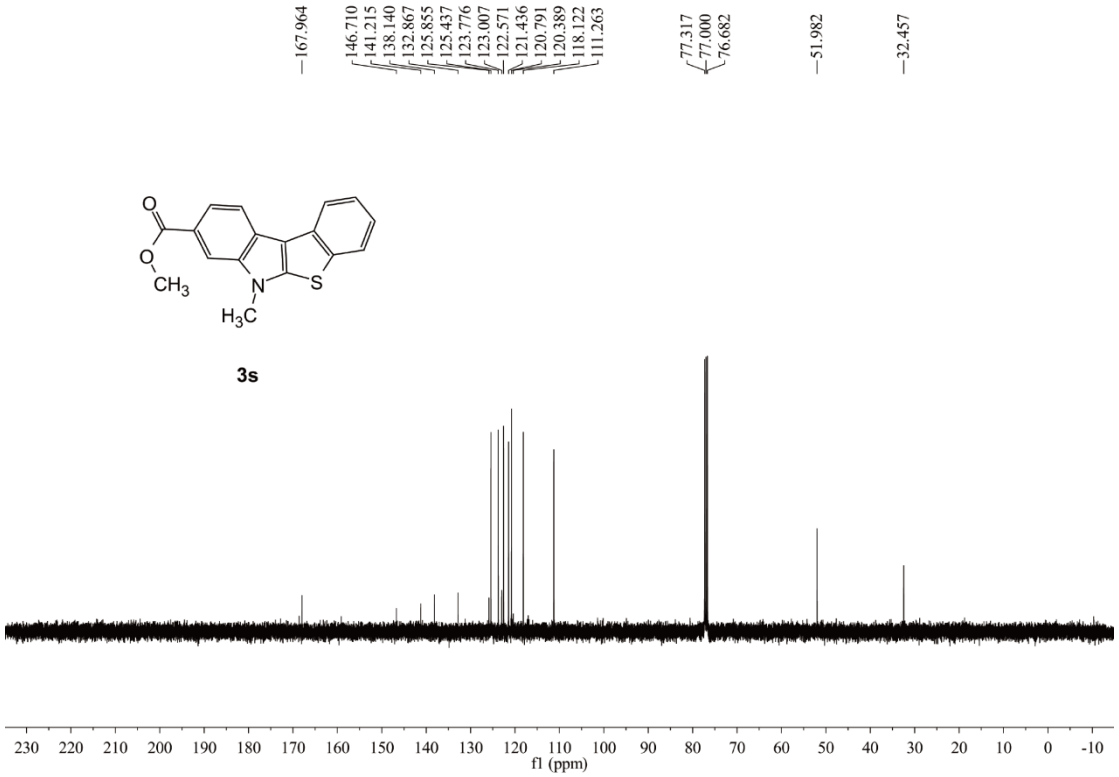
7.813
7.513
7.495
7.476
7.308
7.289
7.267
7.260
3.985
3.957
0.000
O
O
CH3
N
S
H3C
1.00
1.04
2.01
0.97
1.04
1.06
3.03
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3s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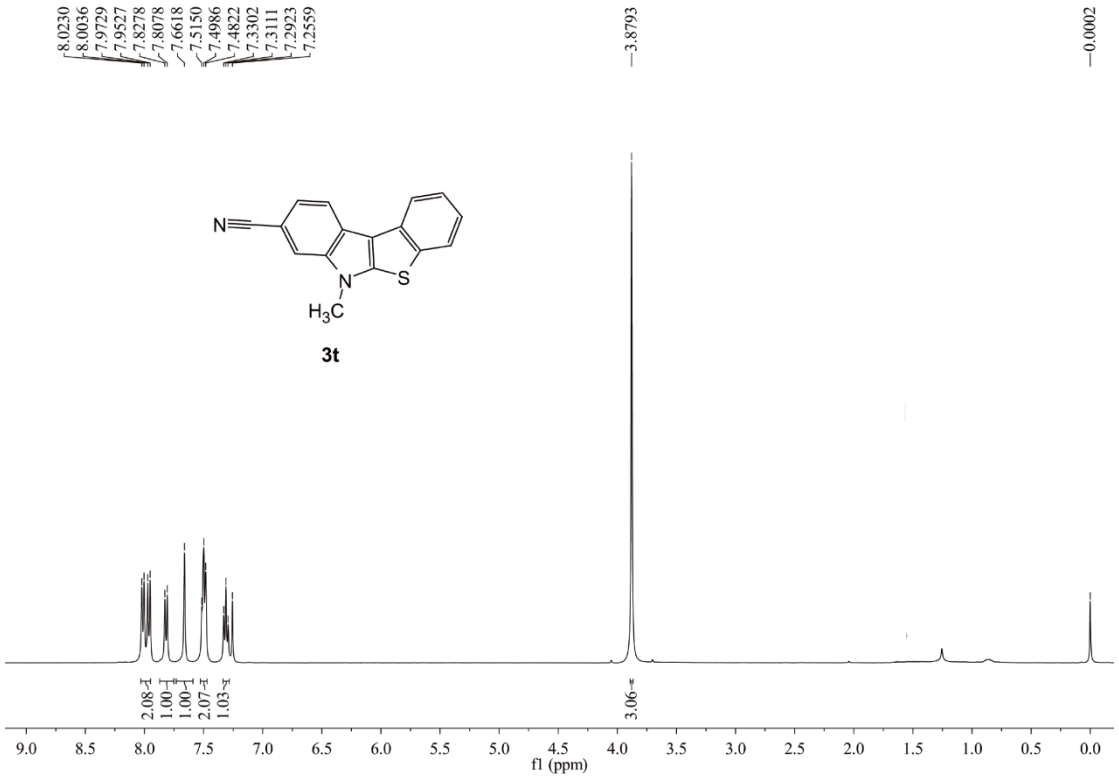
123.007
122.571
121.436
120.791
120.389
118.122
111.263
77.317
77.000
76.682
51.982
32.457
O
O
CH3
N
S
H3C
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3s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7.4986
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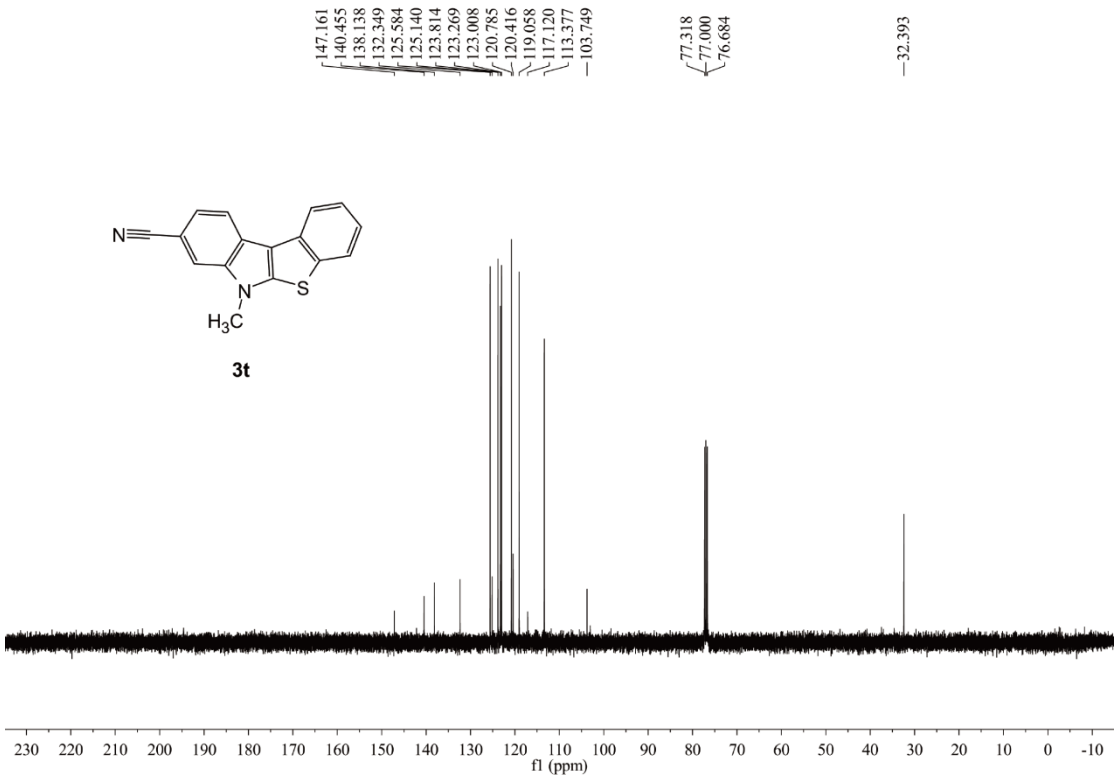
7.3302
7.3111
7.2923
7.2559
3.8793
0.0002
N
S
N
H3C
3t
2.08
1.00
1.00
2.07
1.03
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.269
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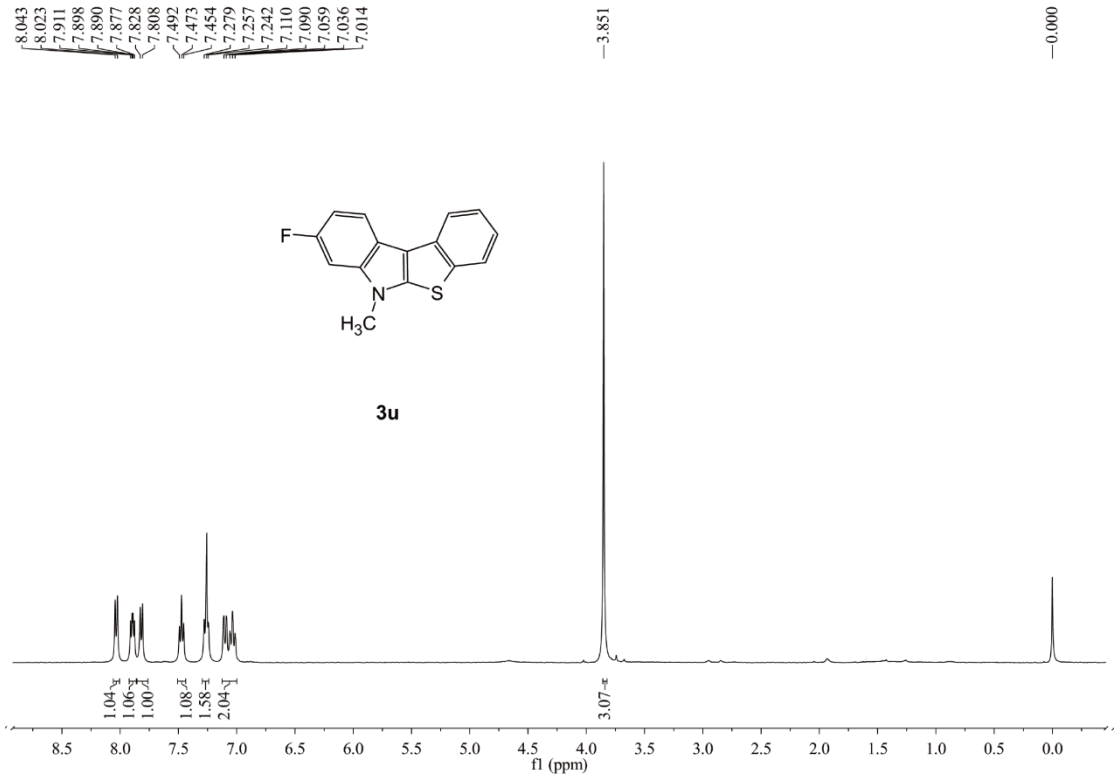
120.785
120.416
119.058
117.120
113.377
103.749
77.318
77.000
76.684
32.393
N
S
N
H3C
3t
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.023
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7.877
7.828
7.808
7.492
7.473
7.454
7.279
7.257
7.242
7.110
7.090
7.059
7.036
7.014
3.851
0.000
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N
S
H3C
3u
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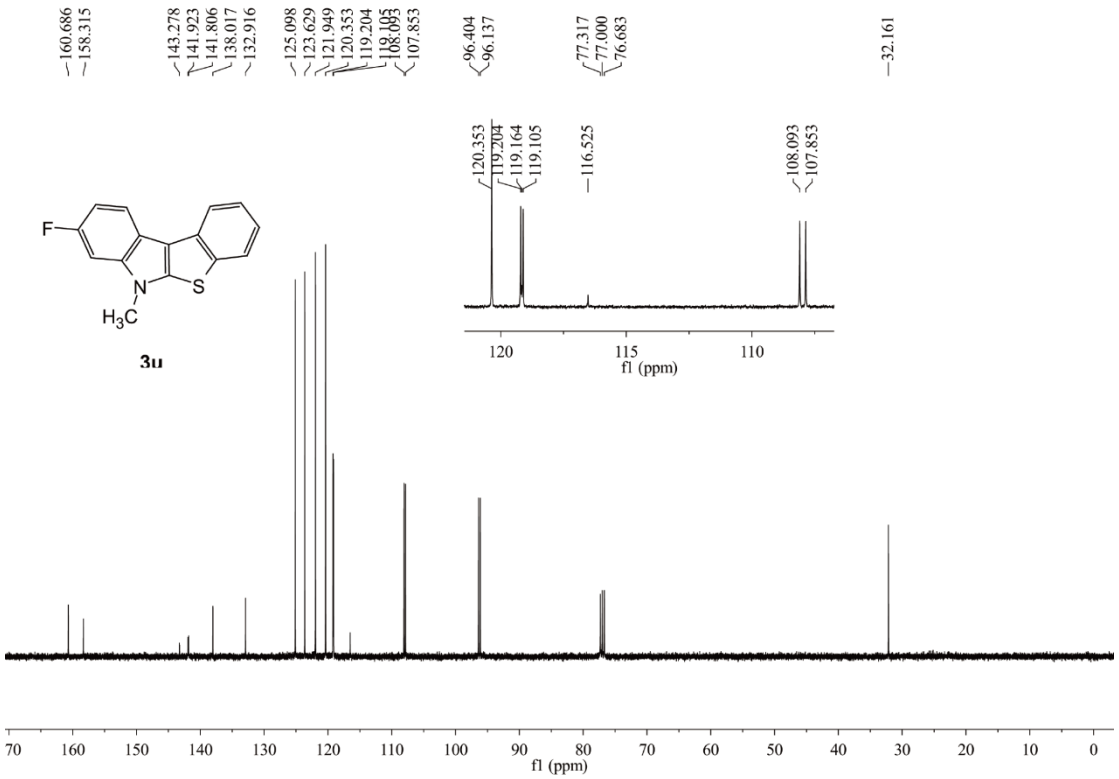
1.06
1.00
1.08
1.58
2.04
3.07
fl (ppm)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125.098
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121.949
120.353
119.204
108.093
107.853
96.404
96.137
77.317
77.000
76.683
32.161
120.353
119.204
119.164
119.105
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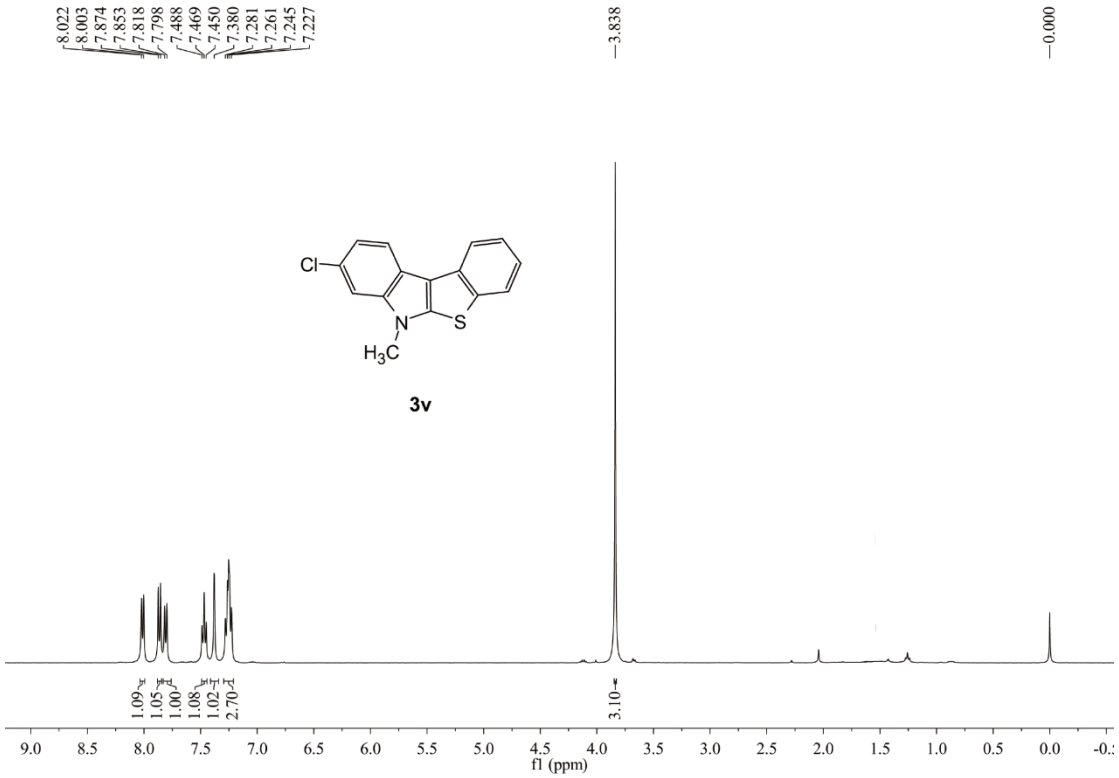
107.853
F
N
S
H3C
3u
fl (ppm)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7.488
7.469
7.450
7.380
7.281
7.261
7.245
7.227
3.838
0.000
Cl
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S
H3C
3v
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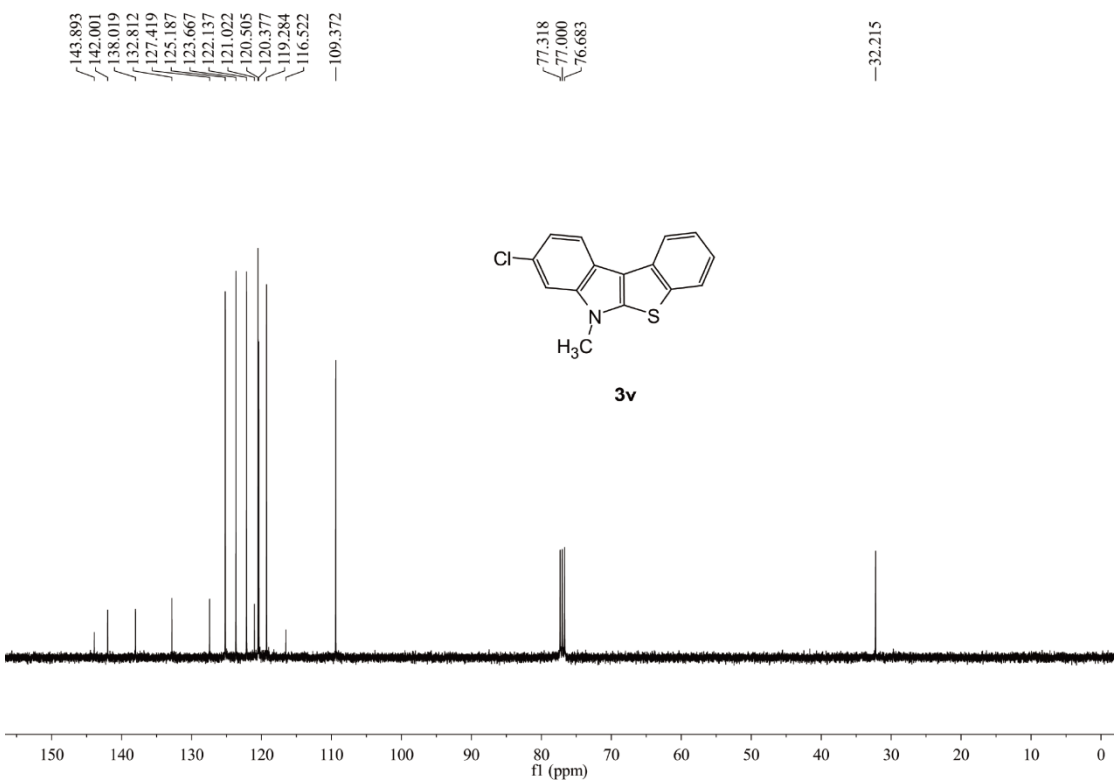
1.05
1.00
1.08
1.02
2.70
3.10
fl (ppm)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127.419
125.187
123.667
122.137
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120.505
120.377
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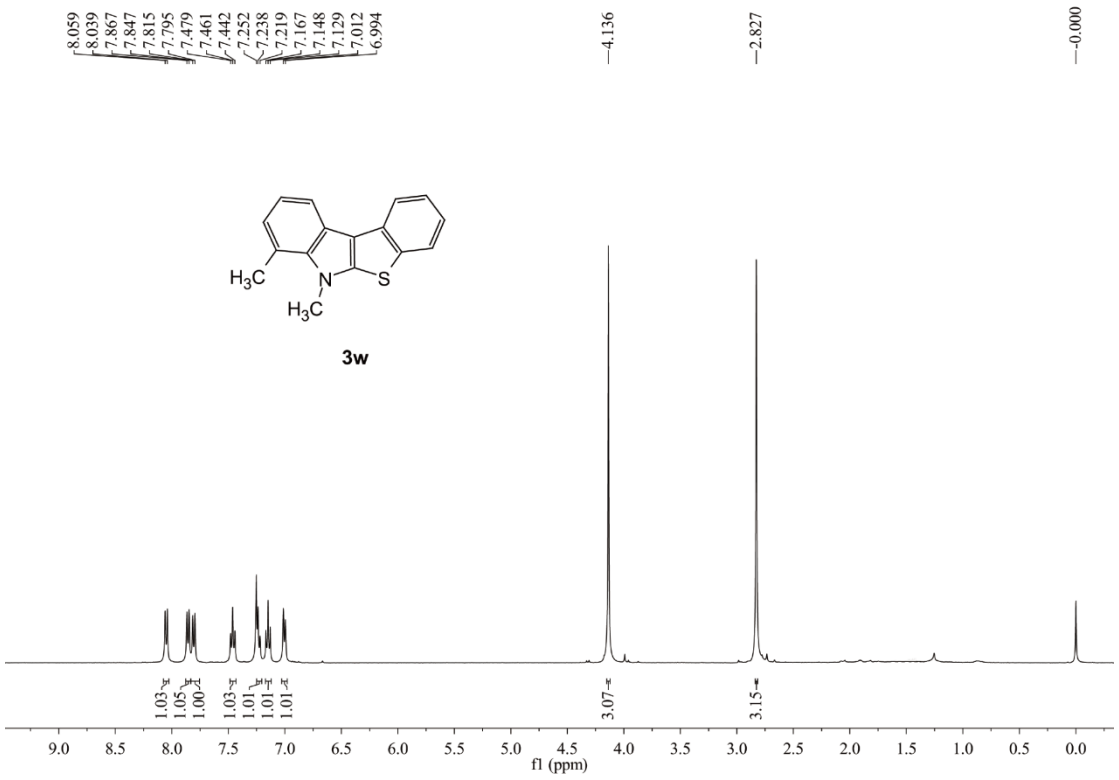
32.215
Cl
N
S
H3C
3v
fl (ppm)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7.461
7.442
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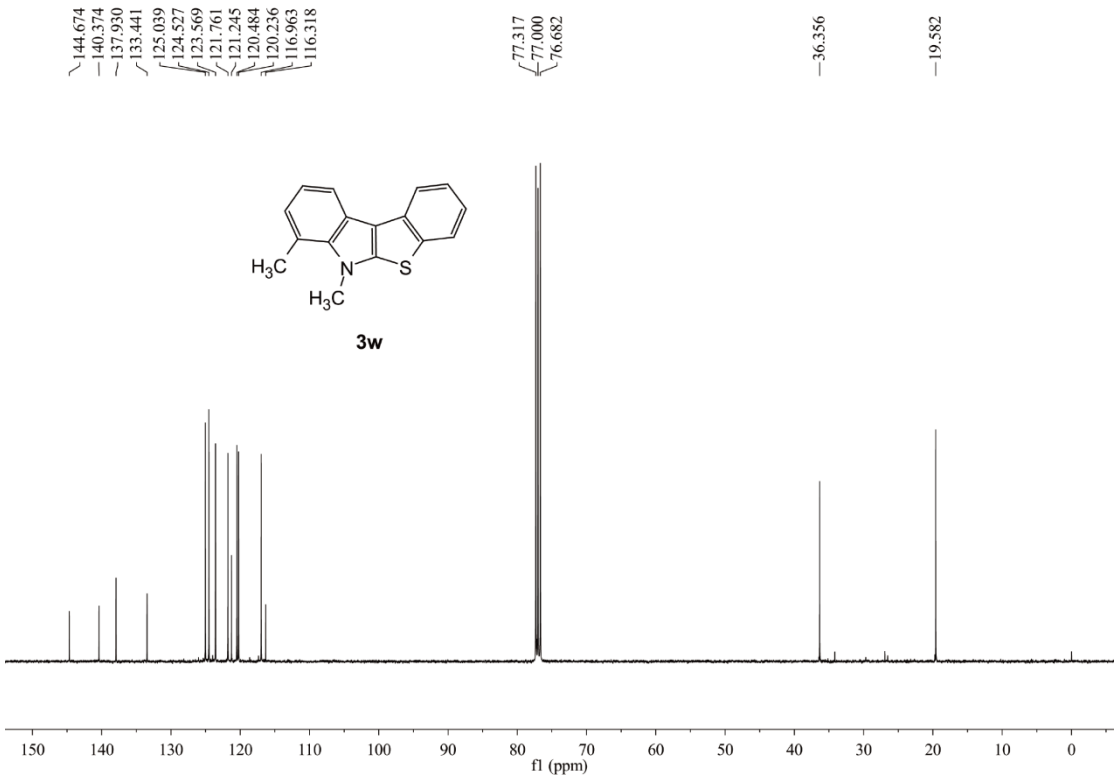
7.238
7.219
7.167
7.148
7.129
7.012
6.994
4.136
2.827
0.000
H3C
N
S
H3C
3w
1.03
1.05
1.00
1.03
1.01
1.01
1.01
3.07
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.039
124.527
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121.761
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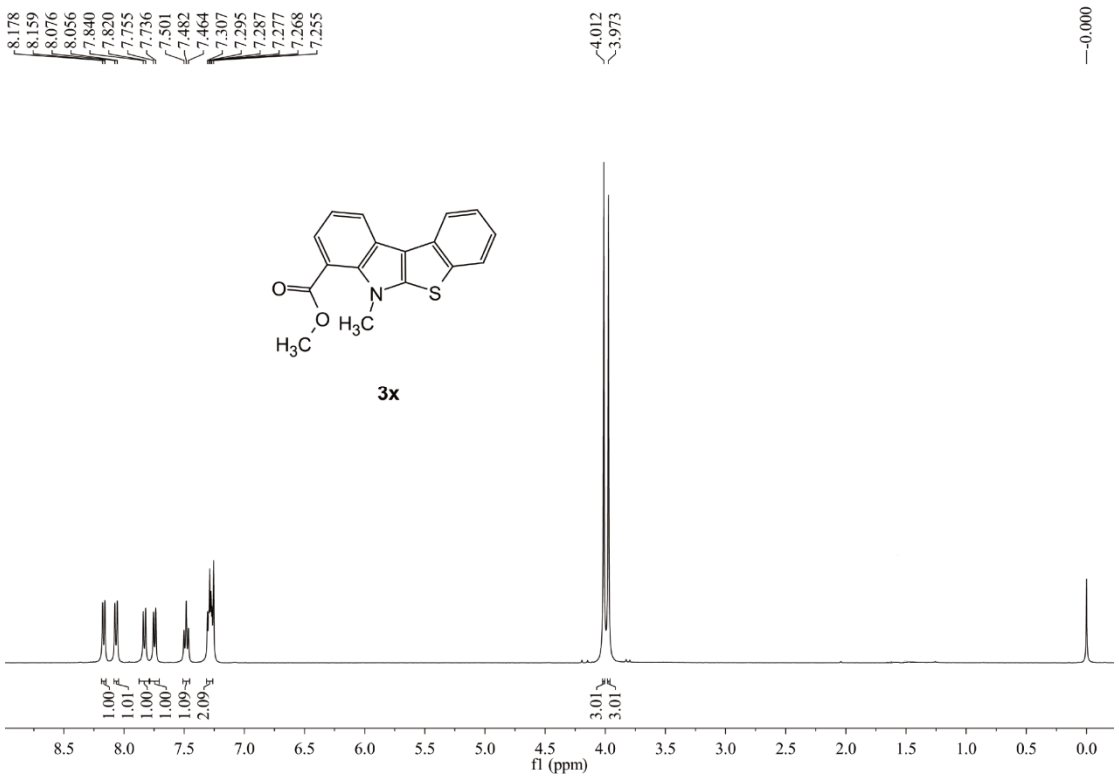
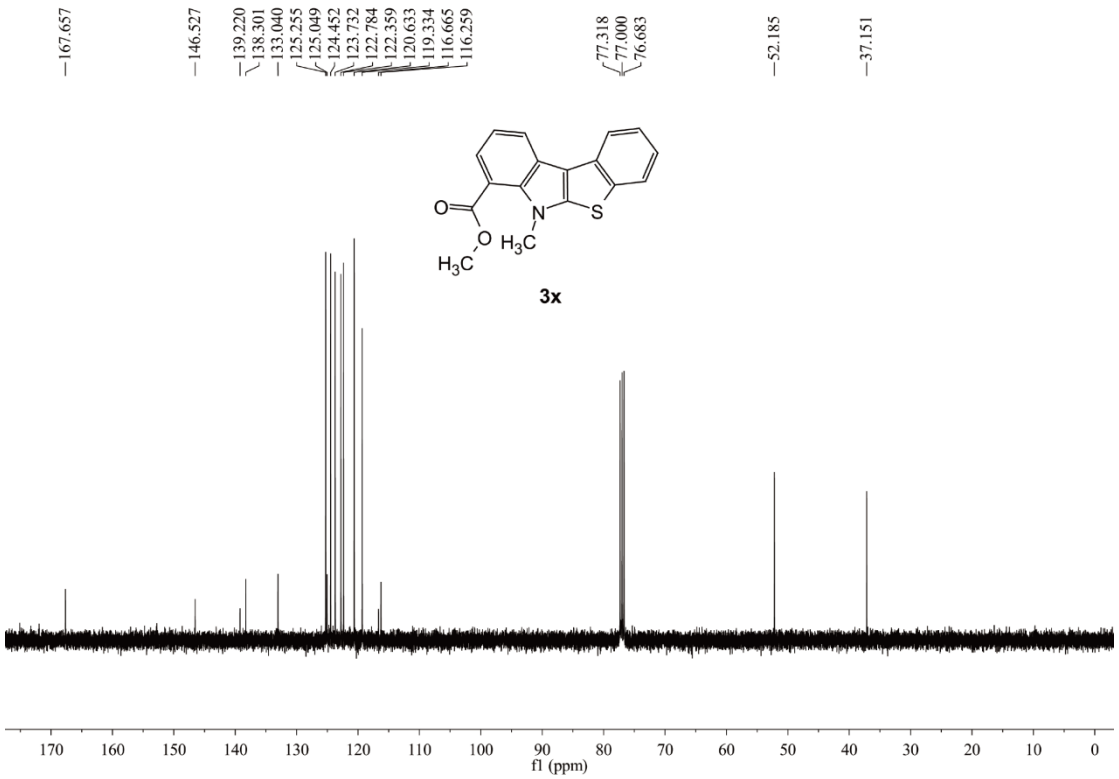
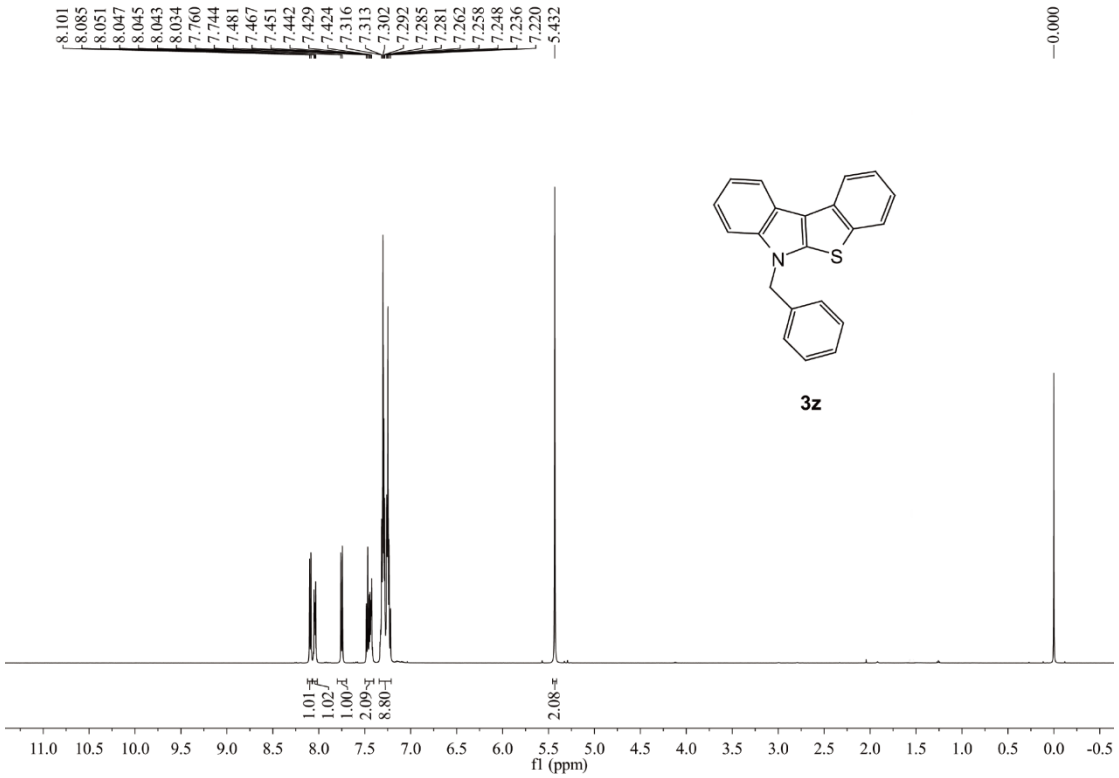
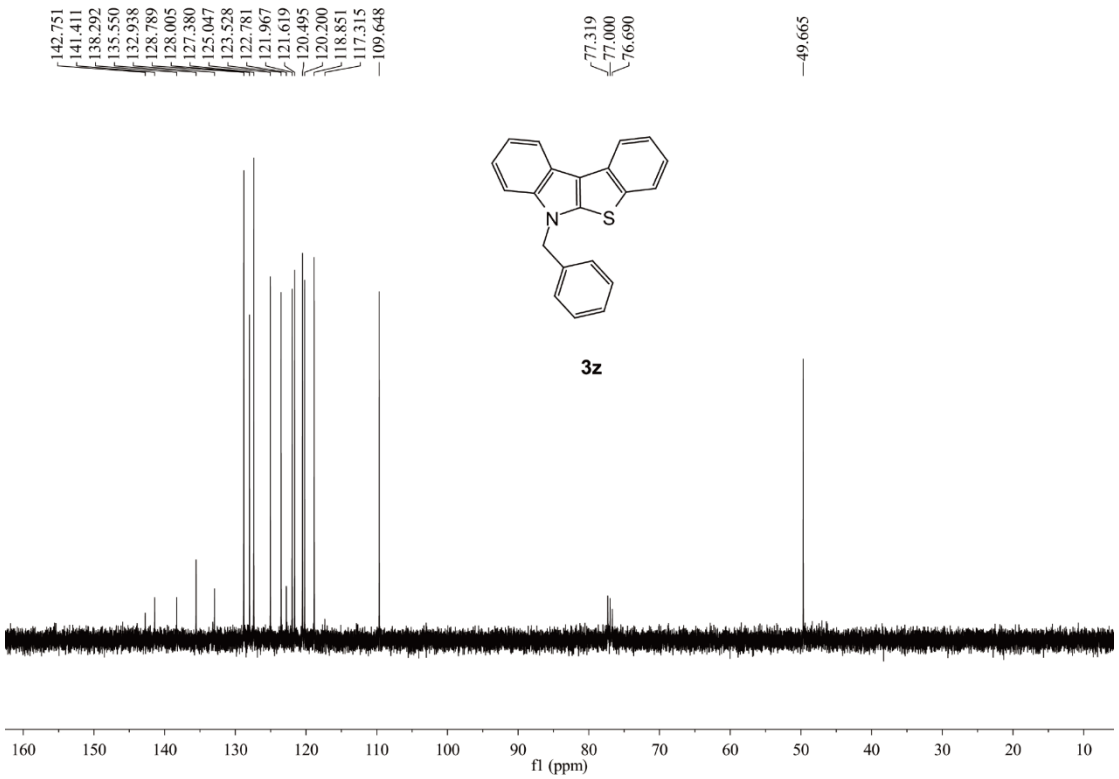
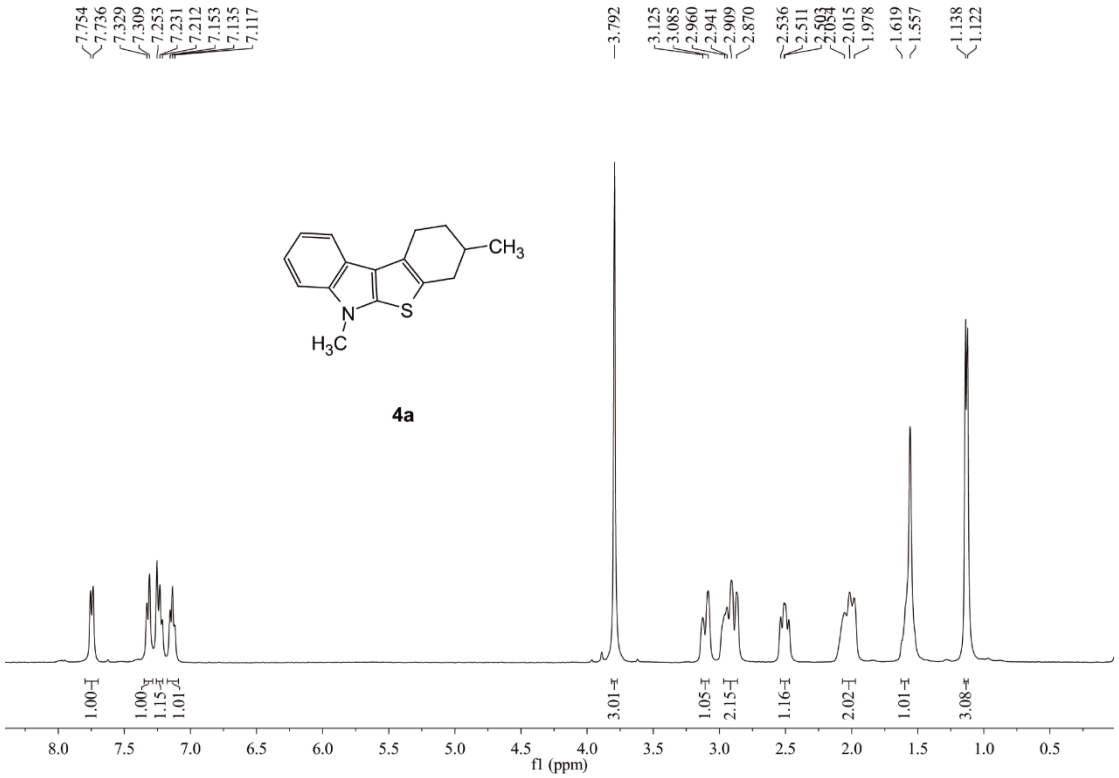
120.484
120.236
116.963
116.318
77.317
77.000
76.682
36.356
19.582
H3C
N
S
H3C
3w
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

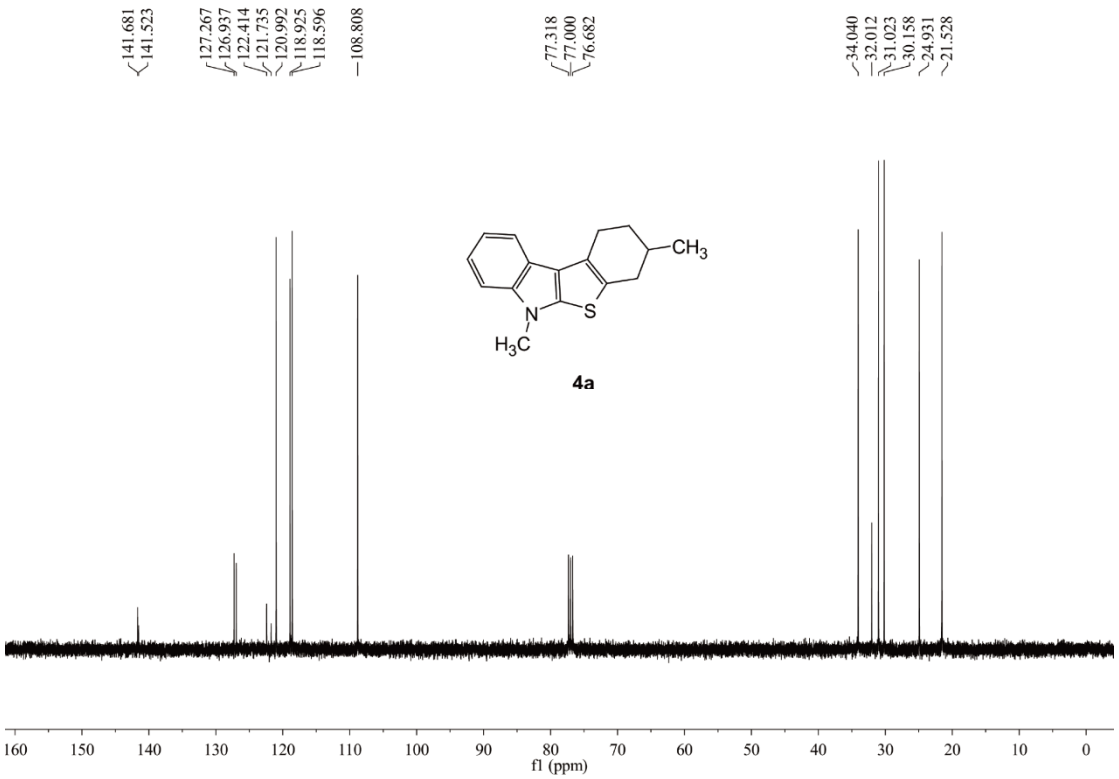

8.178
8.159
8.076
8.056
7.840
7.820
7.755
7.736
7.501
7.482
7.464
7.307
7.295
7.287
7.277
7.268
7.255
4.012
3.973
0.000
O
N
S
O
H3C
H3C
3x
1.00
1.01
1.00
1.00
1.09
2.09
3.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.657
146.527
139.220
138.301
133.040
125.255
125.049
124.452
123.732
122.784
122.359
120.633
119.334
116.665
116.259
77.318
77.000
76.683
52.185
37.151
O
N
S
O
H3C
H3C
3x
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.101
8.085
8.051
8.047
8.045
8.043
8.034
7.760
7.744
7.481
7.467
7.451
7.442
7.429
7.424
7.316
7.313
7.302
7.292
7.285
7.281
7.262
7.258
7.248
7.236
7.220
5.432
0.000
1.01
1.02
1.00
2.09
8.80
2.08
N
S
3z
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 -0.5
f1 (ppm)


142.751
141.411
138.292
135.550
132.938
128.789
128.005
127.380
125.047
123.528
122.781
121.967
121.619
120.495
120.200
118.851
117.315
109.648
77.319
77.000
76.690
49.665
N
S
3z
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.754
7.736
7.329
7.309
7.253
7.231
7.212
7.153
7.135
7.117
3.792
3.125
3.085
2.960
2.941
2.909
2.870
2.536
2.511
2.503
2.054
2.015
1.978
1.619
1.557
1.138
1.122
CH3
N
S
H3C
4a
1.00
1.00
1.15
1.01
3.01
1.05
2.15
1.16
2.02
1.01
3.08
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
f1 (ppm)


141.681
141.523
127.267
126.937
122.414
121.735
120.992
118.925
118.596
108.808
77.318
77.000
76.682
34.040
32.012
31.023
30.158
24.931
21.528
CH3
N
S
H3C
4a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)