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Supporting Information

for

Nickel-Catalyzed Decarbonylative Thioetherification of Acyl Fluorides via C-F Bond Activation

Jingwen You,[a] Qiang Chen,[a] and Yasushi Nishihara*[b]

[a] *Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*

[b] *Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*

Phone: +81-86-251-7855
Fax: +81-86-251-7855
Email: ynishiha@okayama-u.ac.jp

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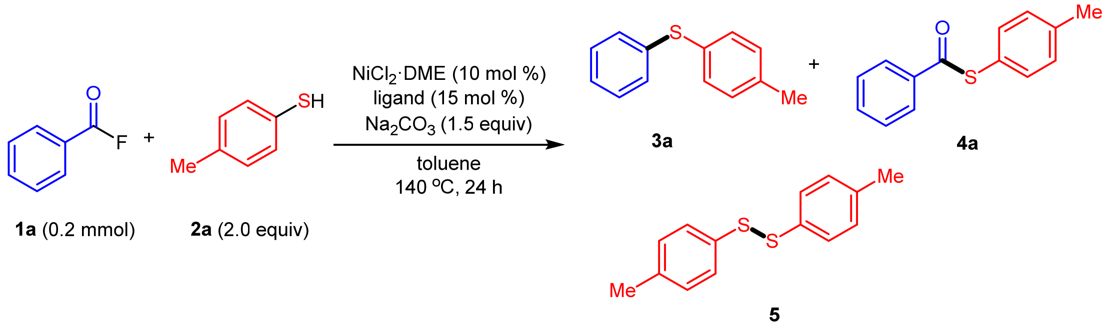
1. Optimization of Reaction Conditions

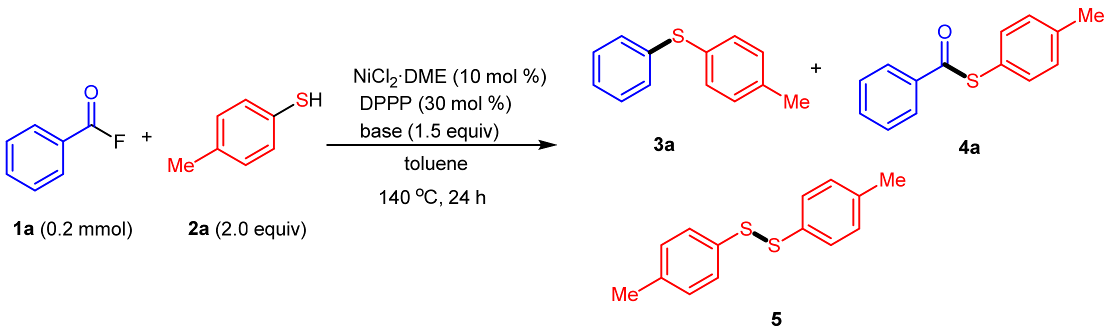
Table S1. Screening of the Ligand[a]



entry	**ligand (x mol %)**	yield (%)[b]		
		3a	**4a**	**5**
1	DPPE (30 mol %)	44	15	26
2	**DPPP (30 mol %)**	**84**	**0**	**24**
3	DPPF (30 mol %)	50	16	26
4	DCYPE (30 mol %)	0	52	27
5	PPh_3 (30 mol %)	1	60	37
6[c]	DPPP (15 mol %)	1	0	43
7	DPPP (15 mol %)	32	35	57
8[d]	DPPP (40 mol %)	84	trace	8

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) and $NiCl_2$·DME (0.02 mmol, 10 mol %), Na_2CO_3 (0.3 mmol, 1.5 equiv). [b]GC yields, using n-dodecane as an internal standard. [c]$Pd(OAc)_2$ (10 mol %). [d]**2a** (0.3 mmol, 1.5 equiv).

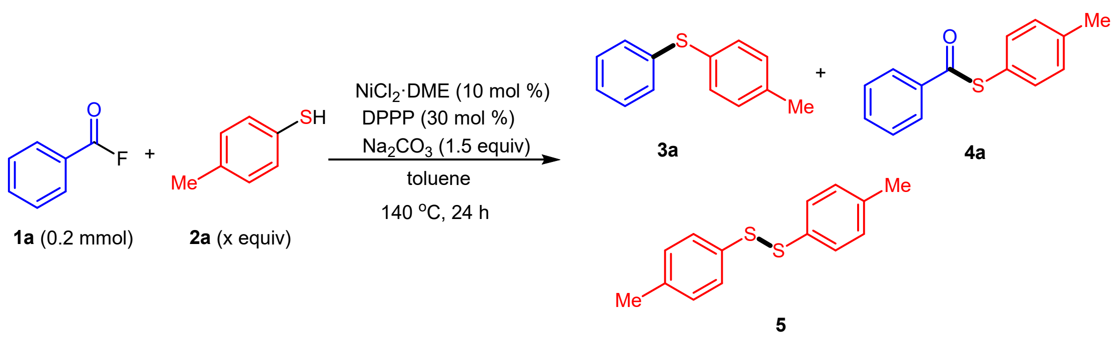
Table S2. Screening of the Base[a]



entry	base (1.5 equiv)	yield (%)[b]		
		3a	4a	5
1	**Na_2CO_3**	**84**	**0**	**24**
2	K_2CO_3	57	1	15
3[c]	Na_2CO_3	81	trace	18
4	NaOAc	60	trace	31
5	K_3PO_4	63	1	23

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv) and $NiCl_2$·DME (0.02 mmol, 10 mol %), DPPP (0.06 mmol, 30 mol %), base (0.3 mmol, 1.5 equiv) in toluene at 140 °C for 24 h. [b]GC yields, using n-dodecane as an internal standard. [c]Base (3.0 equiv).

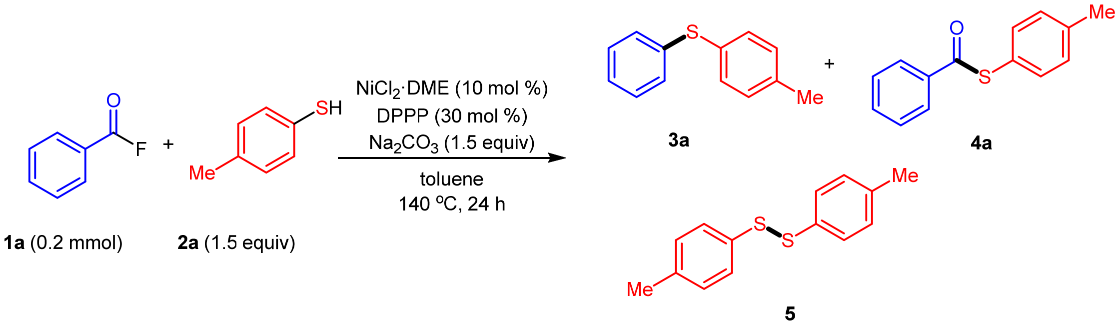
Table S3. Screening of the Amount of Compound 2a[a]



entry	2a (x equiv)	yield (%)[b]		
		3a	4a	5
1	2.0	84	0	24
2	**1.5**	**90**	**0**	**8**
3	1.2	69	0	trace
4[c]	1.5	30	39	20
5[d]	1.5	83	3	6

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv), $NiCl_2$·DME (0.02 mmol, 10 mol %), DPPP (0.06 mmol, 30 mol %), Na_2CO_3 (0.3 mmol, 1.5 equiv) in toluene at 140 °C for 24 h. [b]GC yields, using n-dodecane as an internal standard. [c]120 °C. [d]12 h.

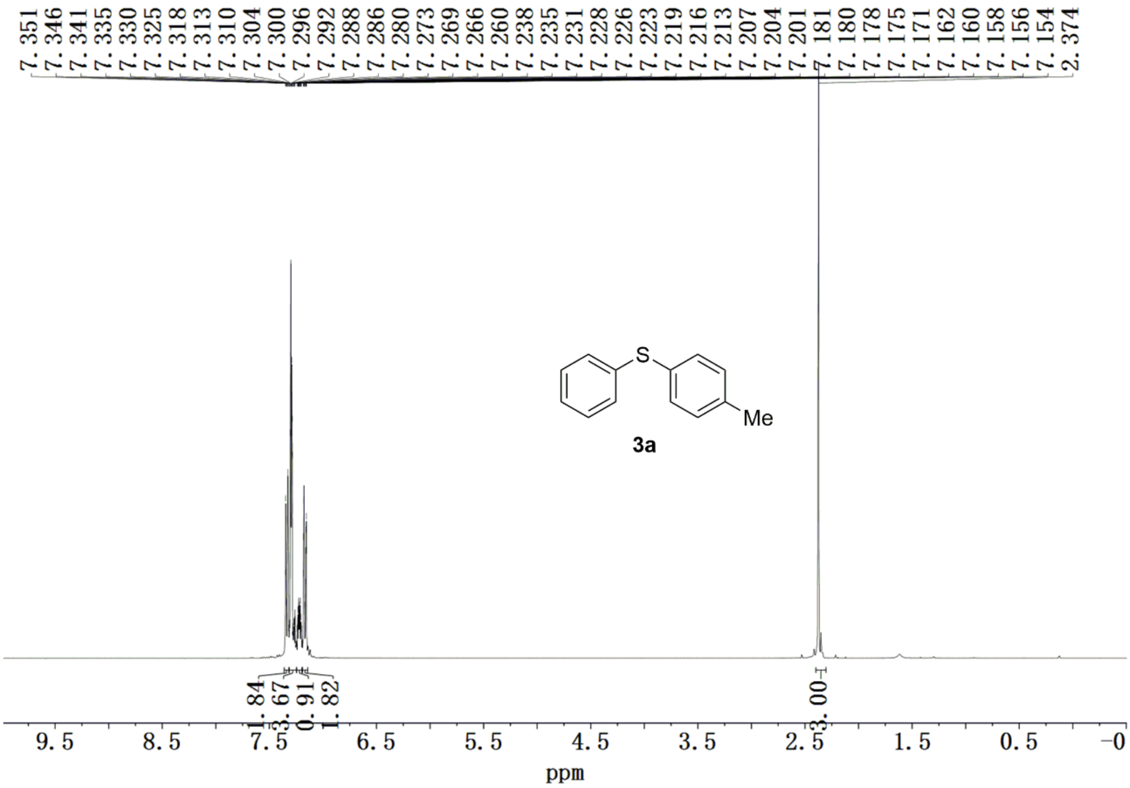
Table S4. Control Experiments[a]

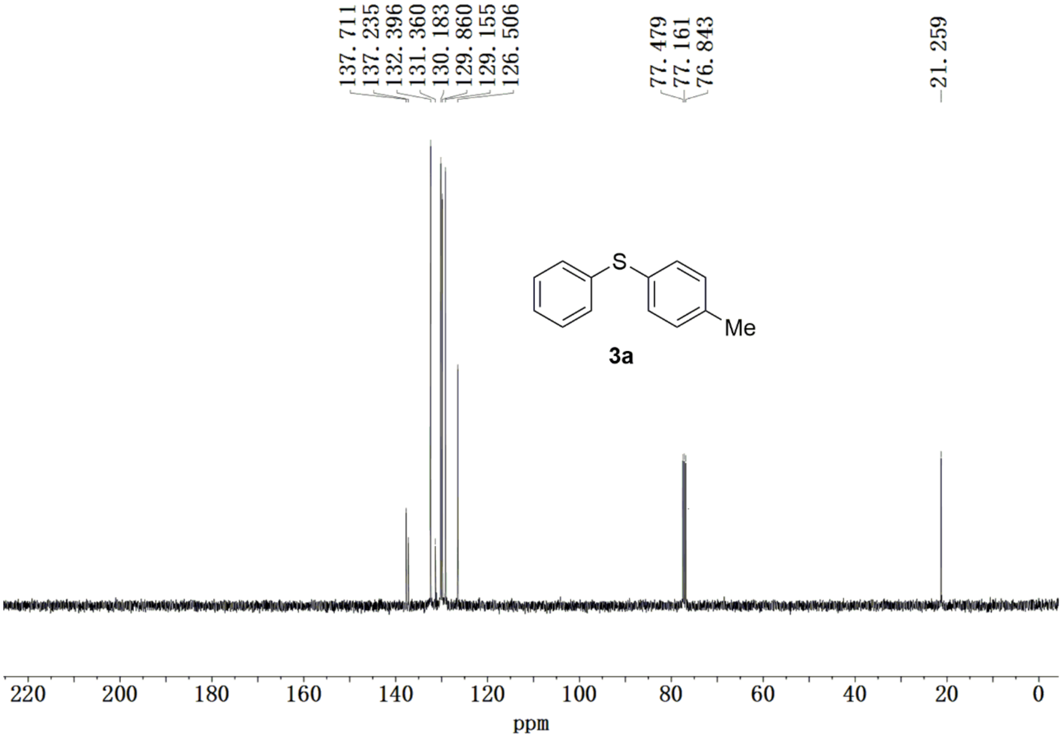


entry	Deviations from standard condition	yield (%)[b]		
		3a	**4a**	**5**
1	**none**	**90**	**0**	**8**
2	Without Na_2CO_3	45	24	8
3	Without $NiCl_2$·DME and DPPP	0	68	24
4	Benzoyl chloride instead of **1a**	0	67	trace

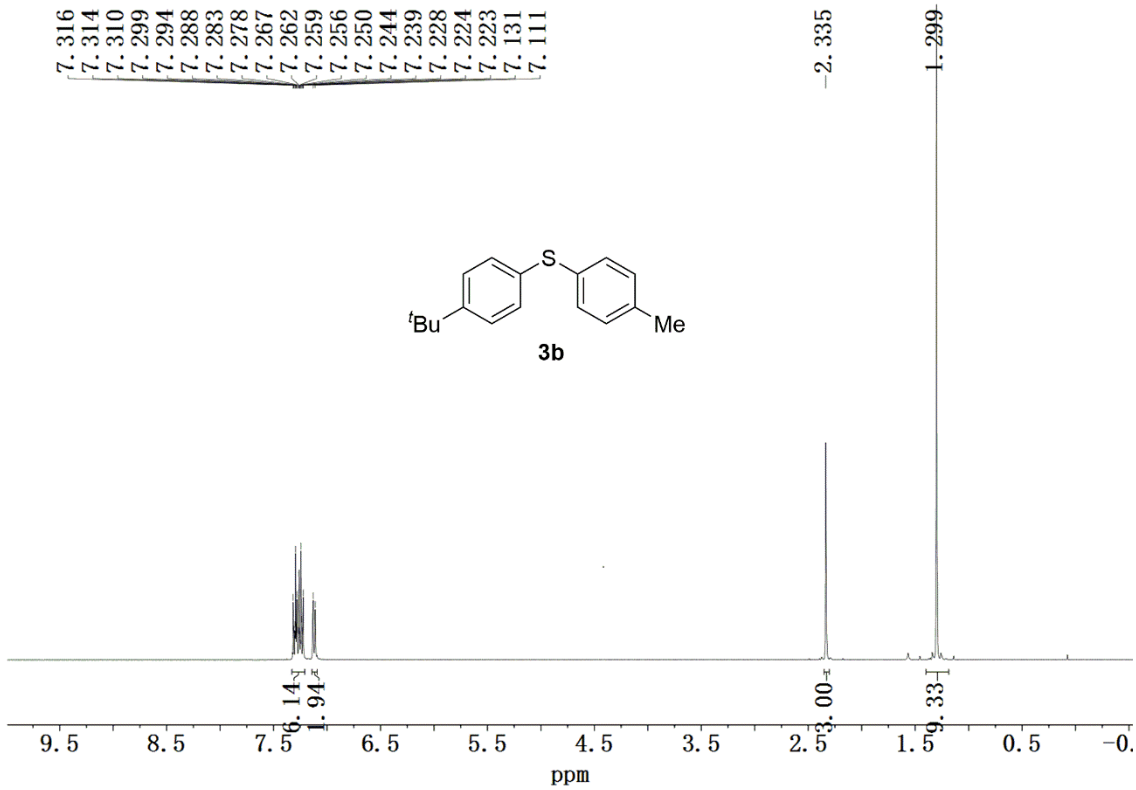
[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), $NiCl_2$·DME (0.02 mmol, 10 mol %), DPPP (0.06 mmol, 30 mol %), Na_2CO_3 (0.3 mmol, 1.5 equiv) in toluene at 140 °C for 24 h. [b]GC yields, using n-dodecane as an internal standard.

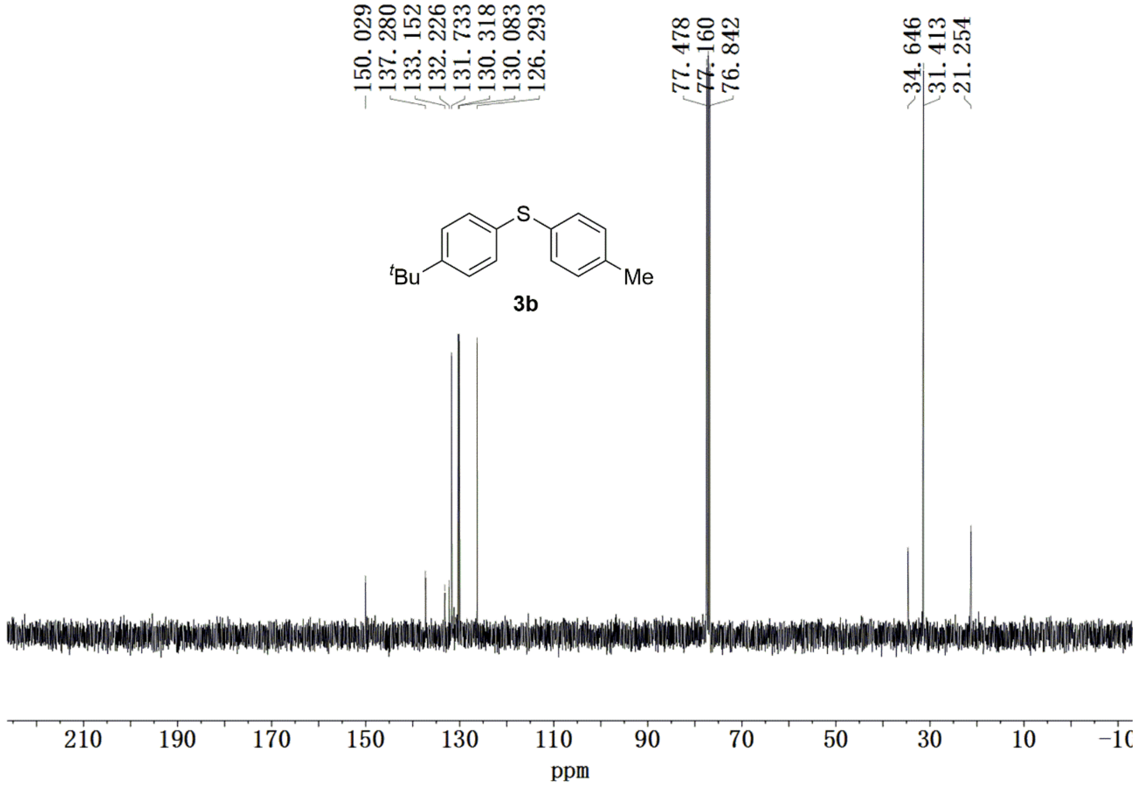
2. *Copies of ¹H, ¹³C{¹H}, and ¹⁹F{¹H} NMR Charts for the Products*



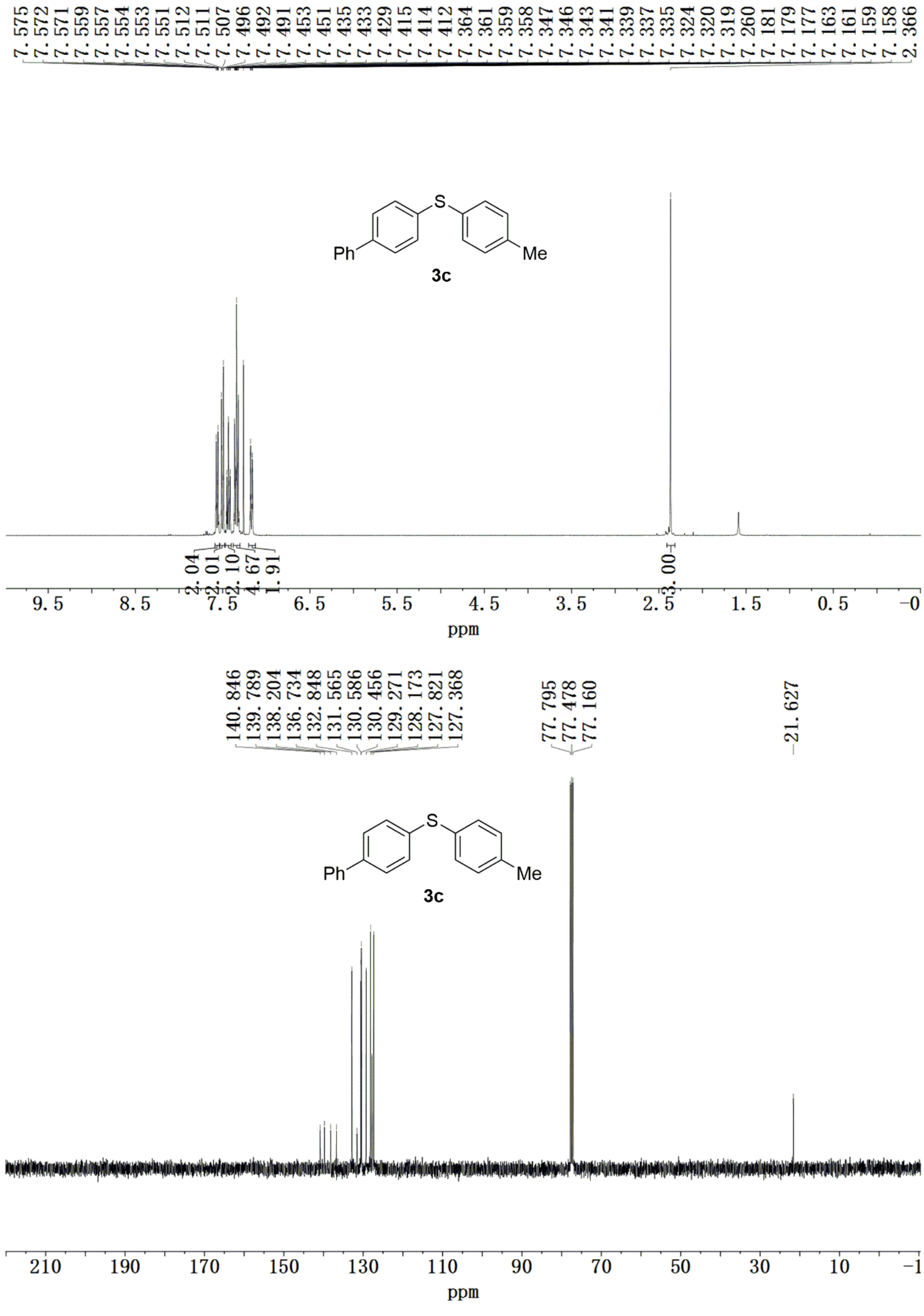


¹H NMR (400 MHz) and ¹³C{¹H} NMR (101 MHz) spectra of **3a** (rt, $CDCl_3$).

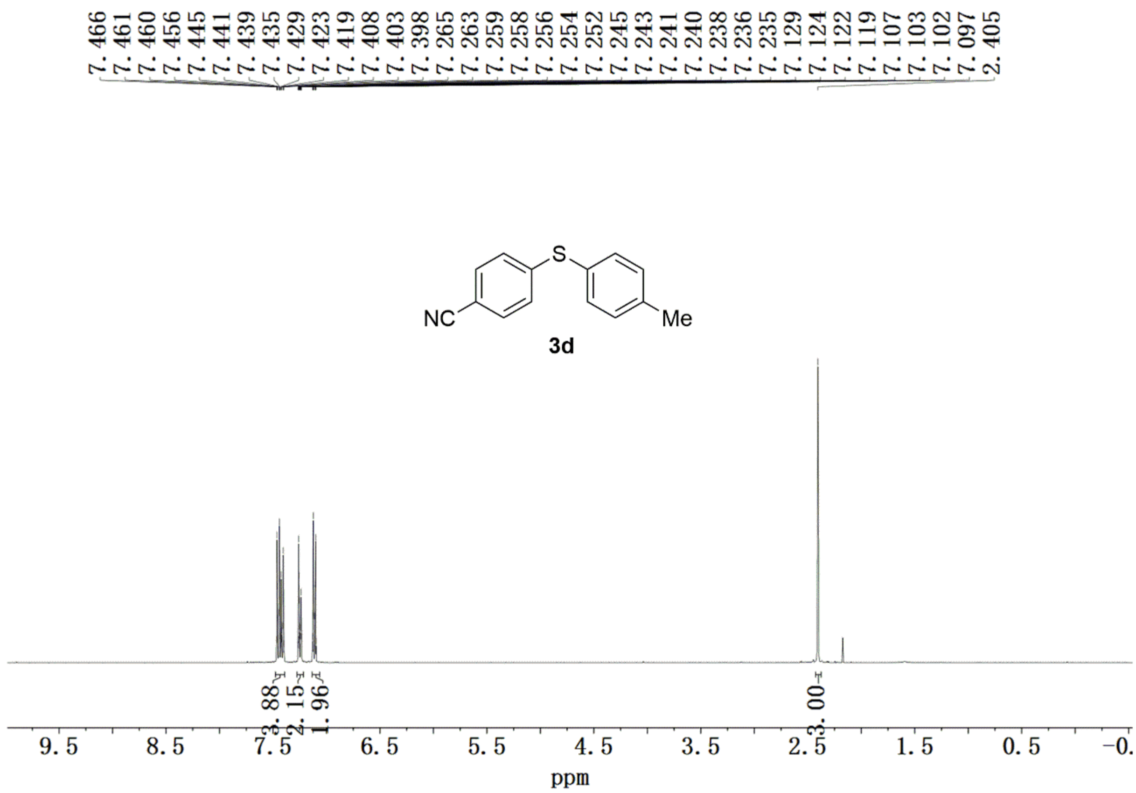


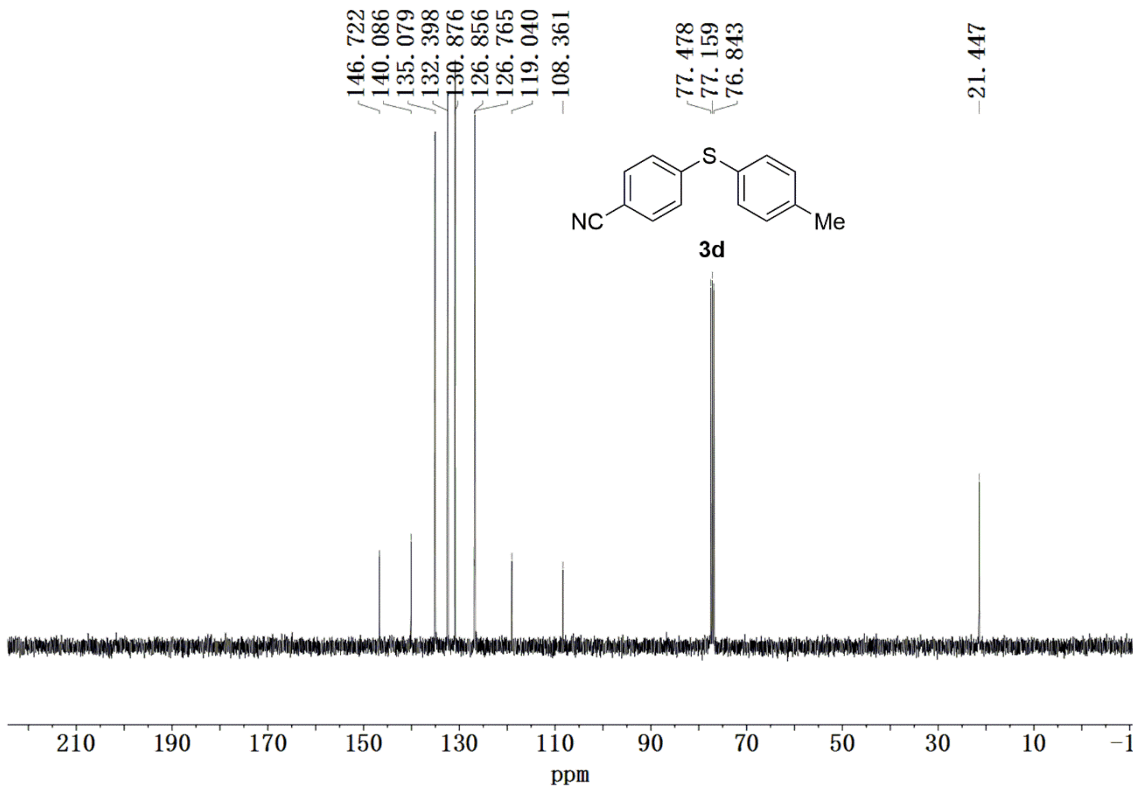


^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3b** (rt, $CDCl_3$).

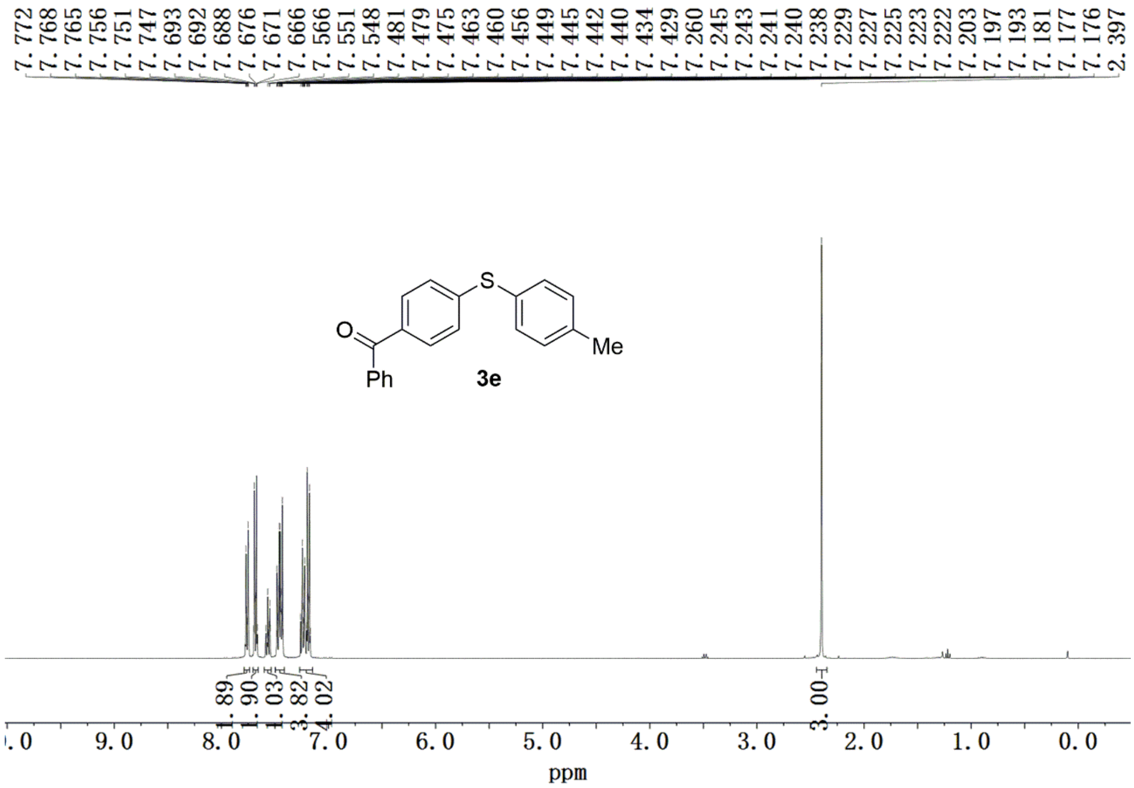


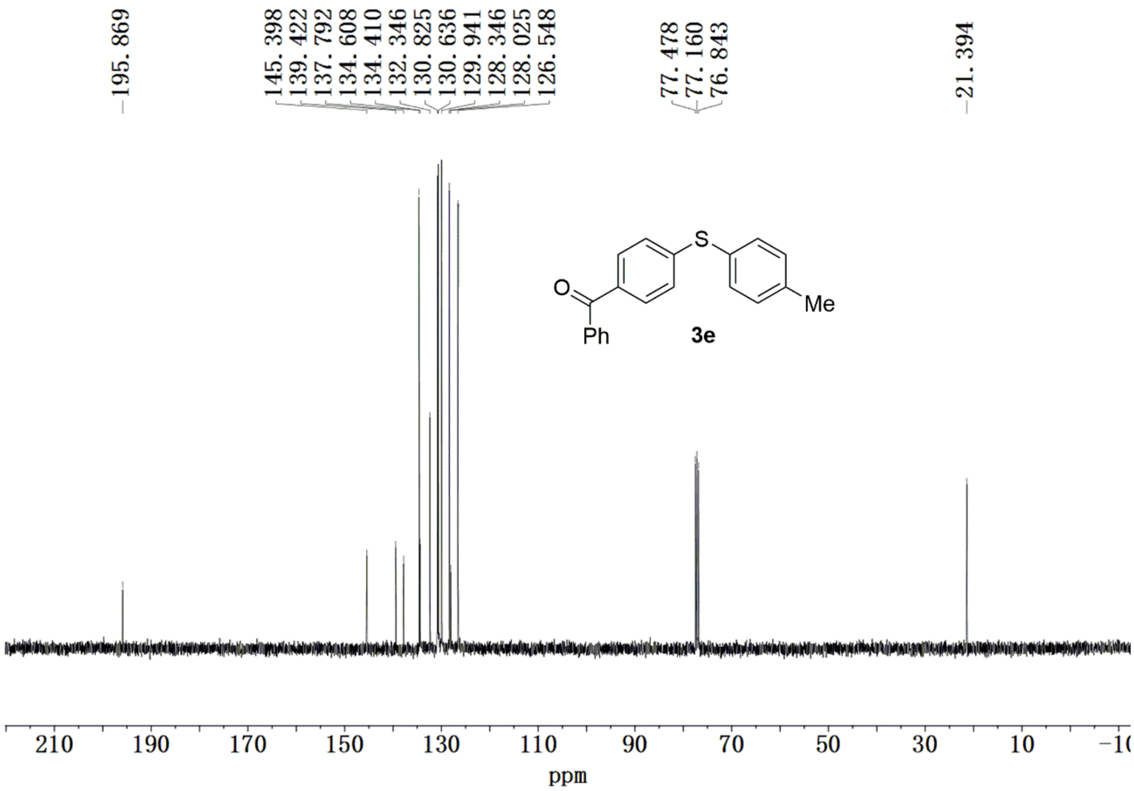
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3c** (rt, $CDCl_3$).



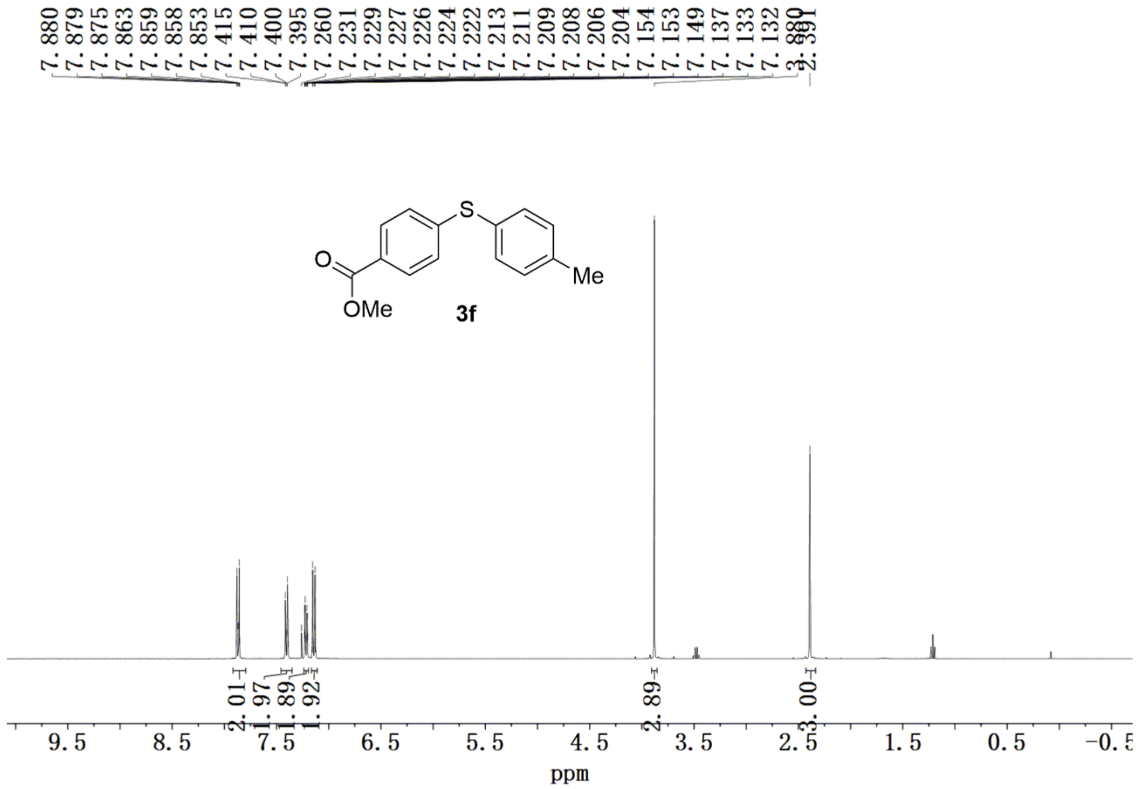


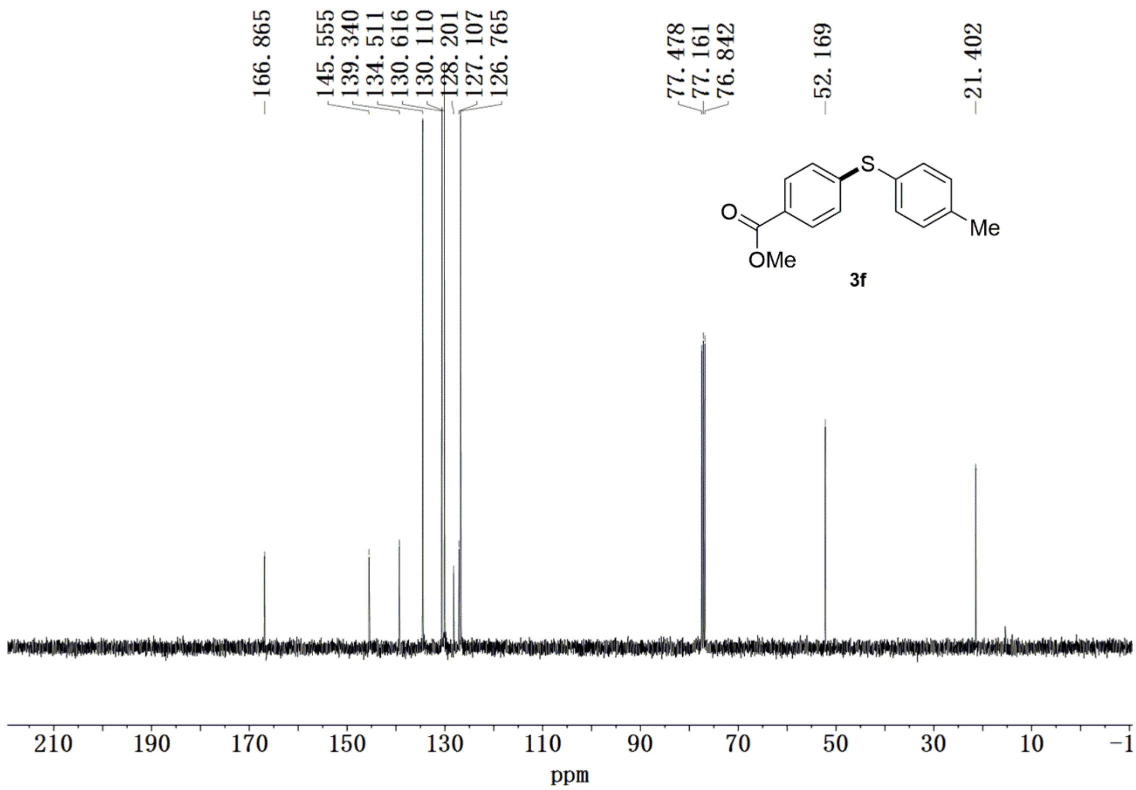
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3d** (rt, $CDCl_3$).



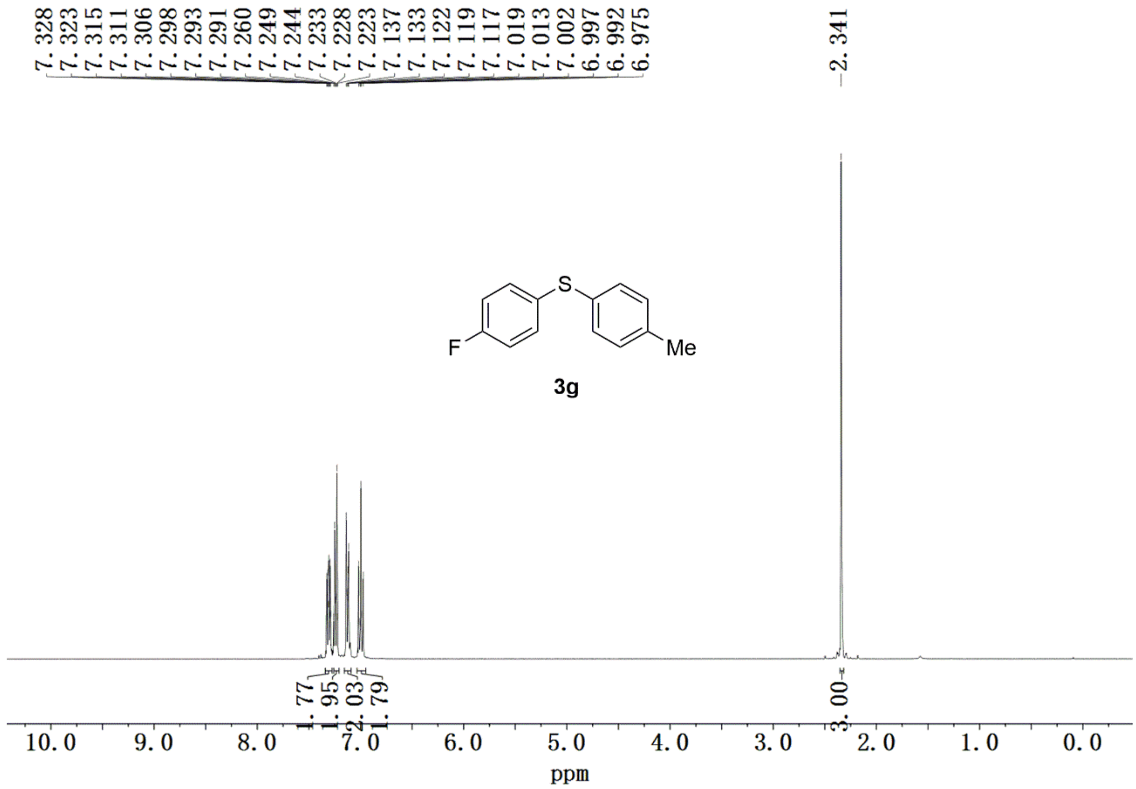


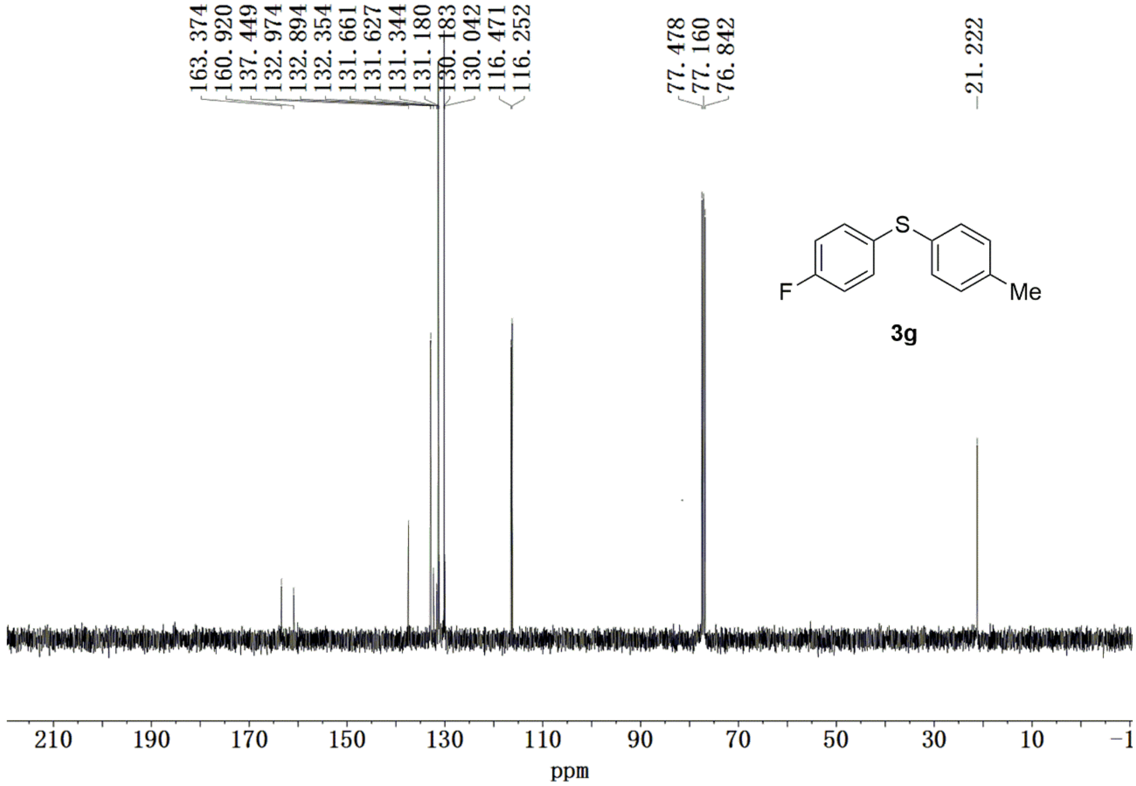
[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3e** (rt, $CDCl_3$).



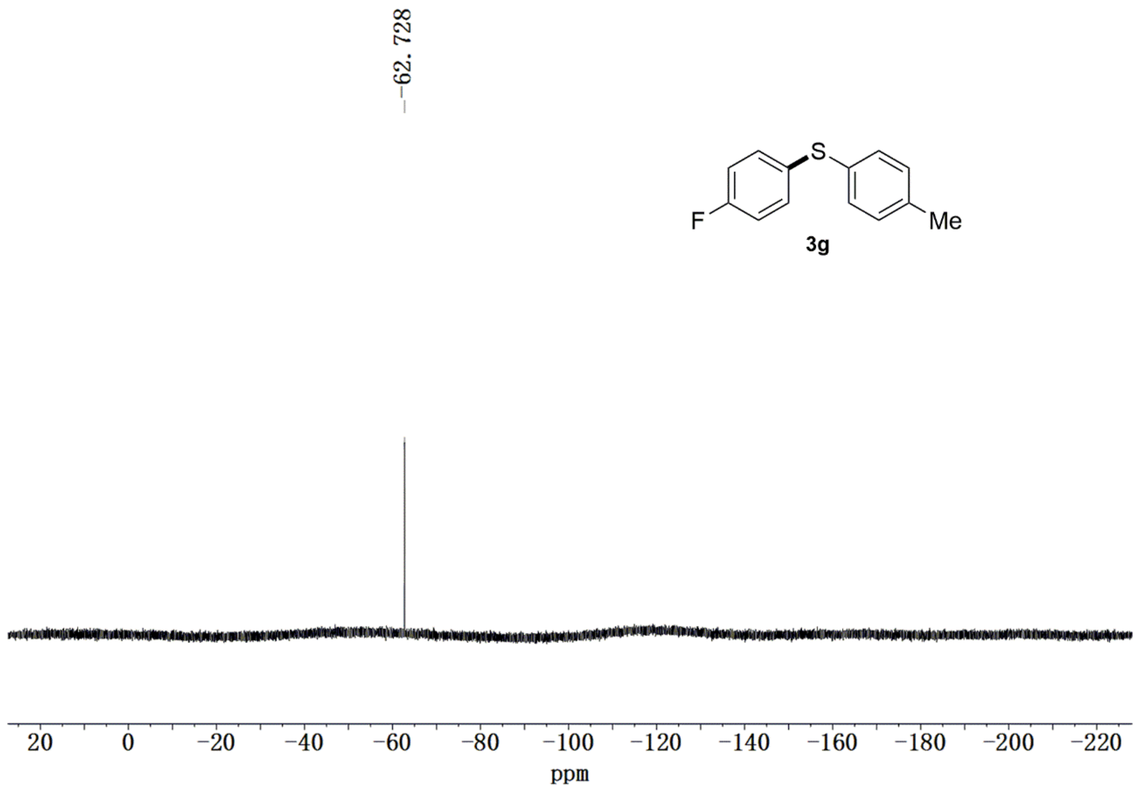


^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3f** (rt, $CDCl_3$).

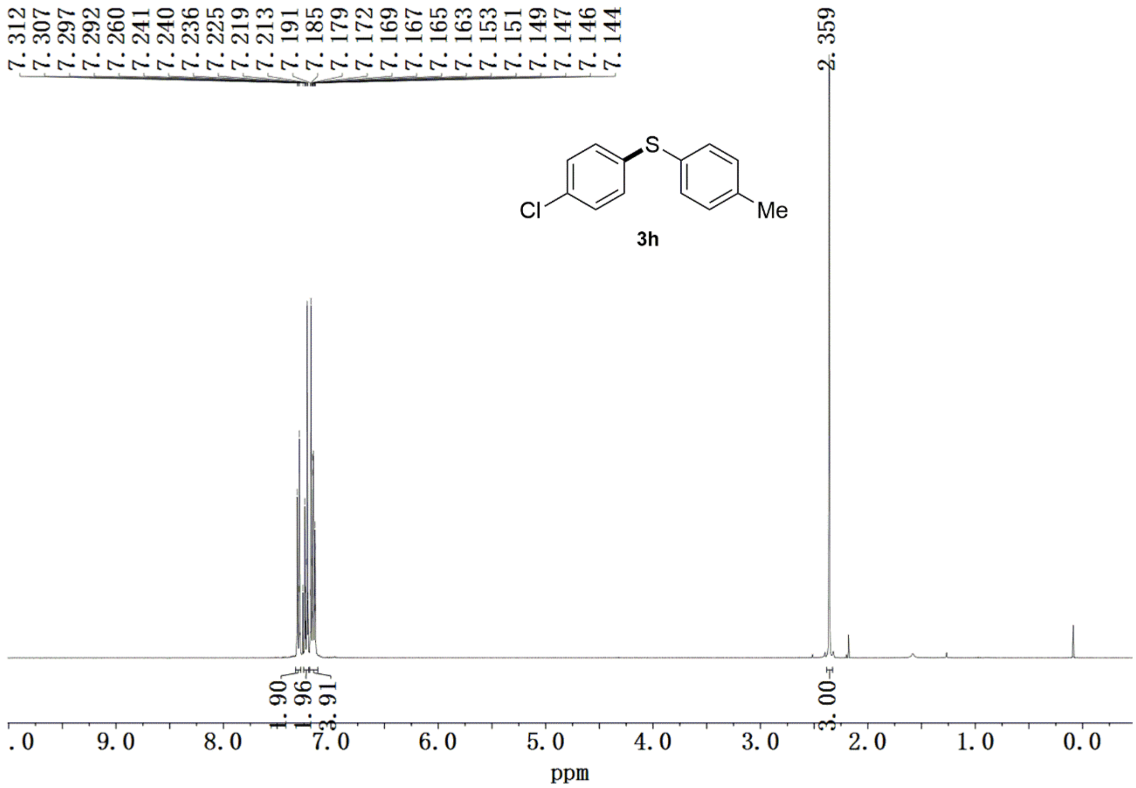


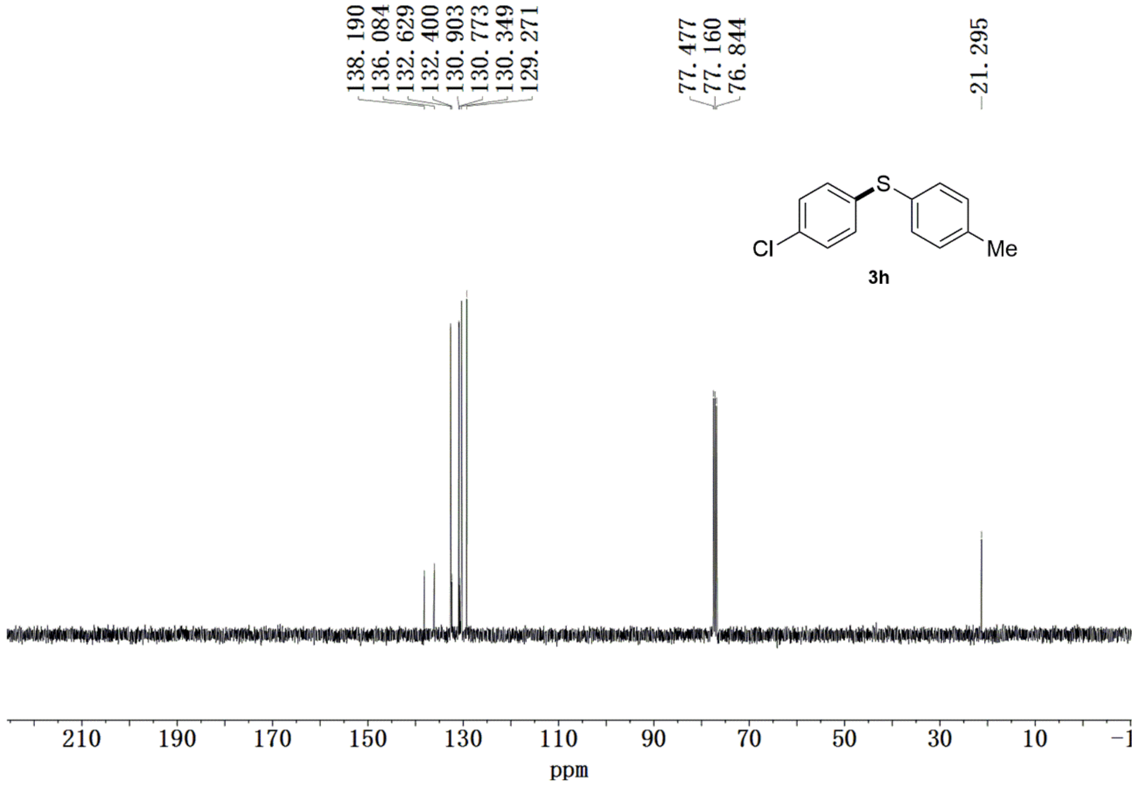


[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3g** (rt, $CDCl_3$).

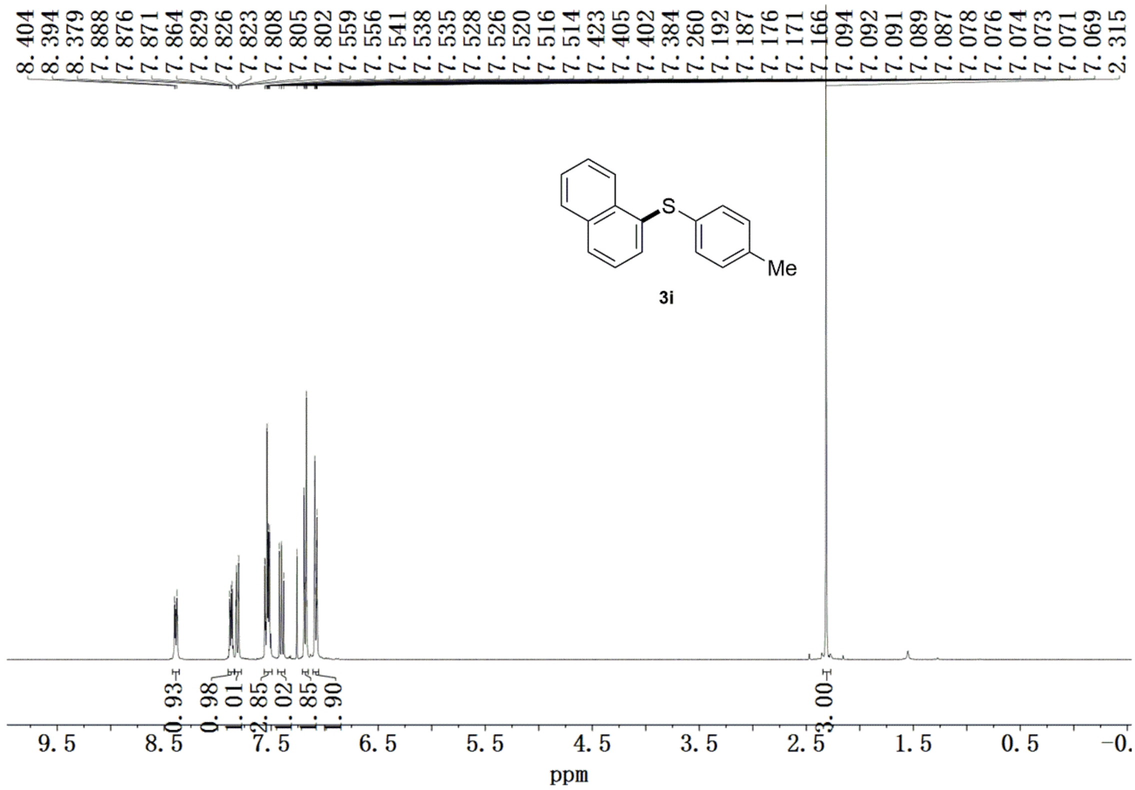


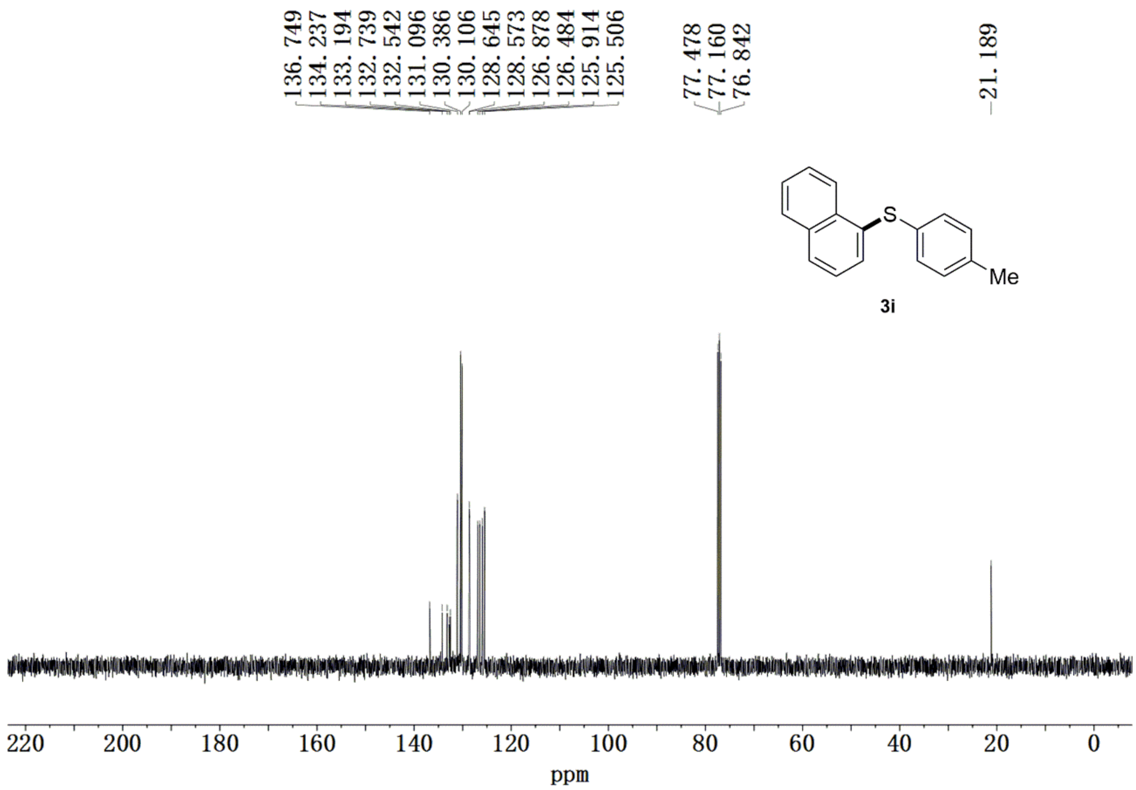
$^{19}F\{^1H\}$ NMR (376 MHz) spectrum of **3g** (rt, $CDCl_3$).



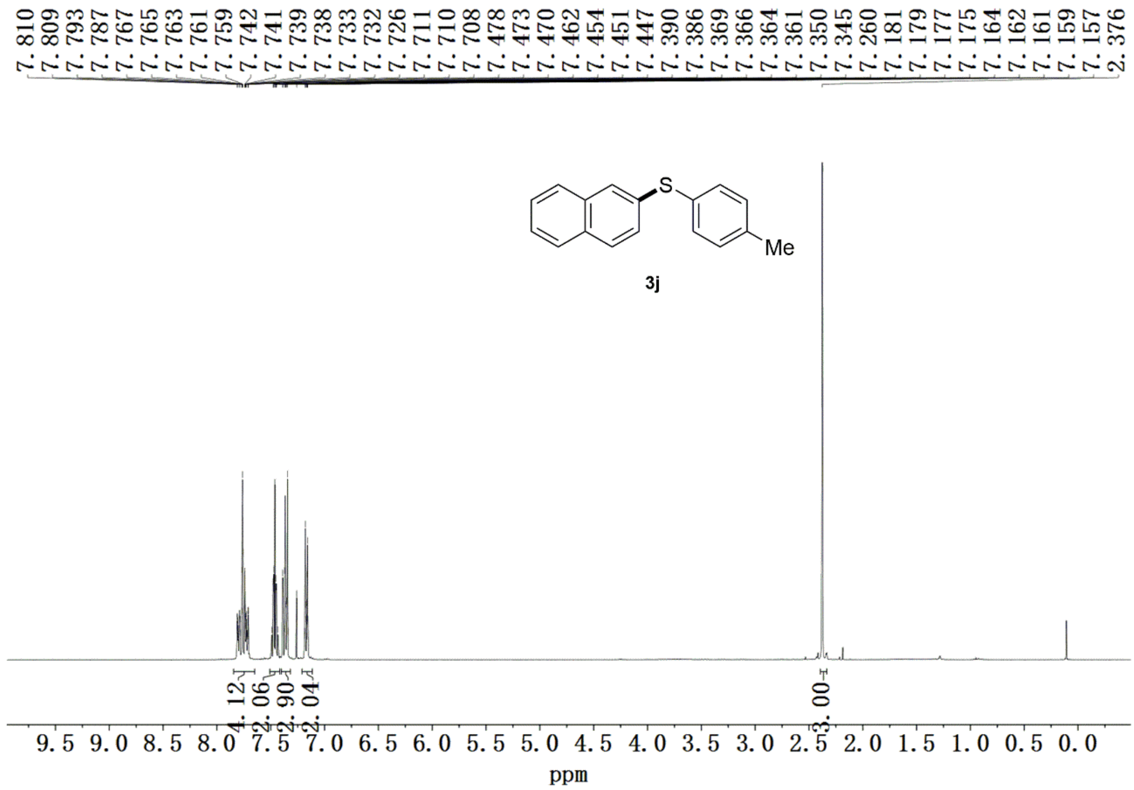


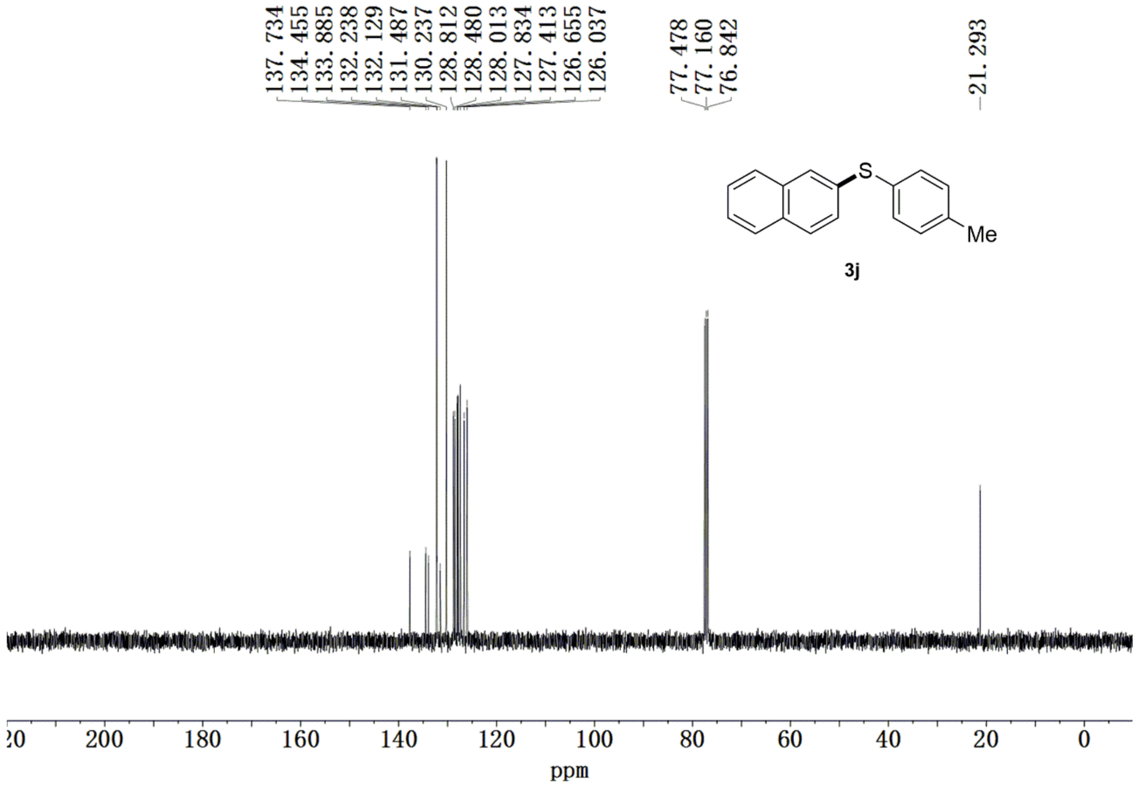
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3h** (rt, $CDCl_3$).



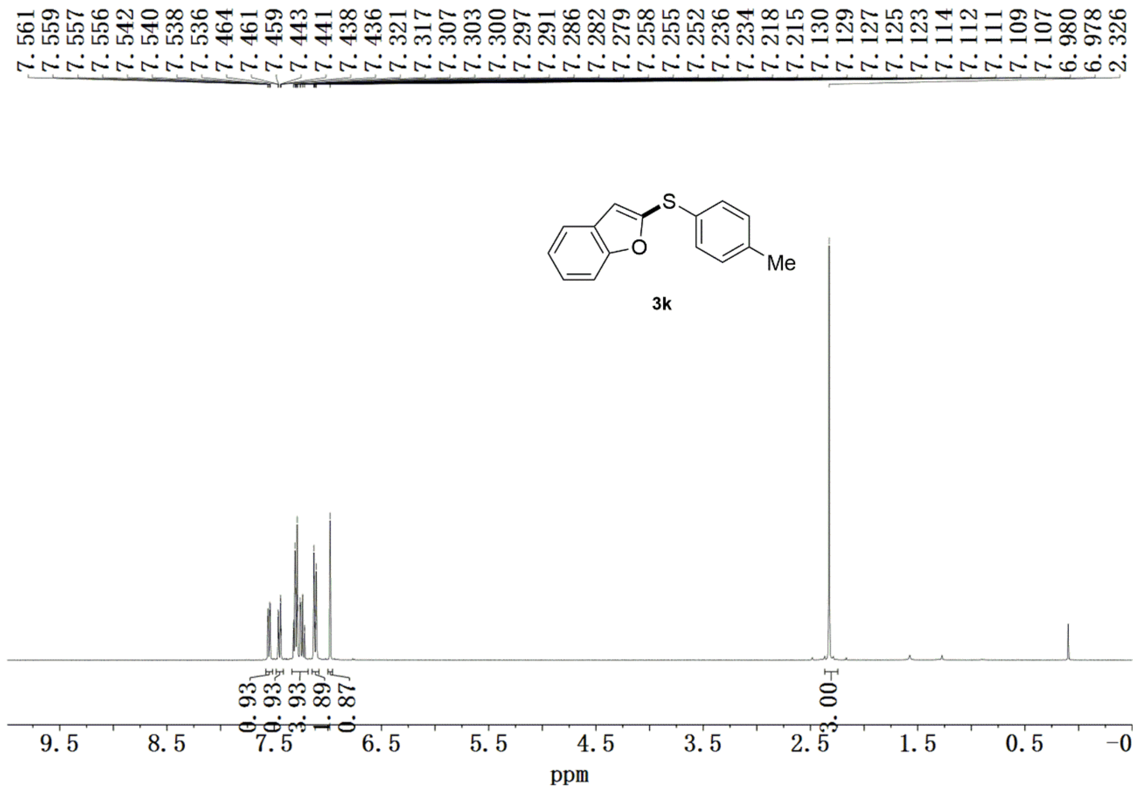


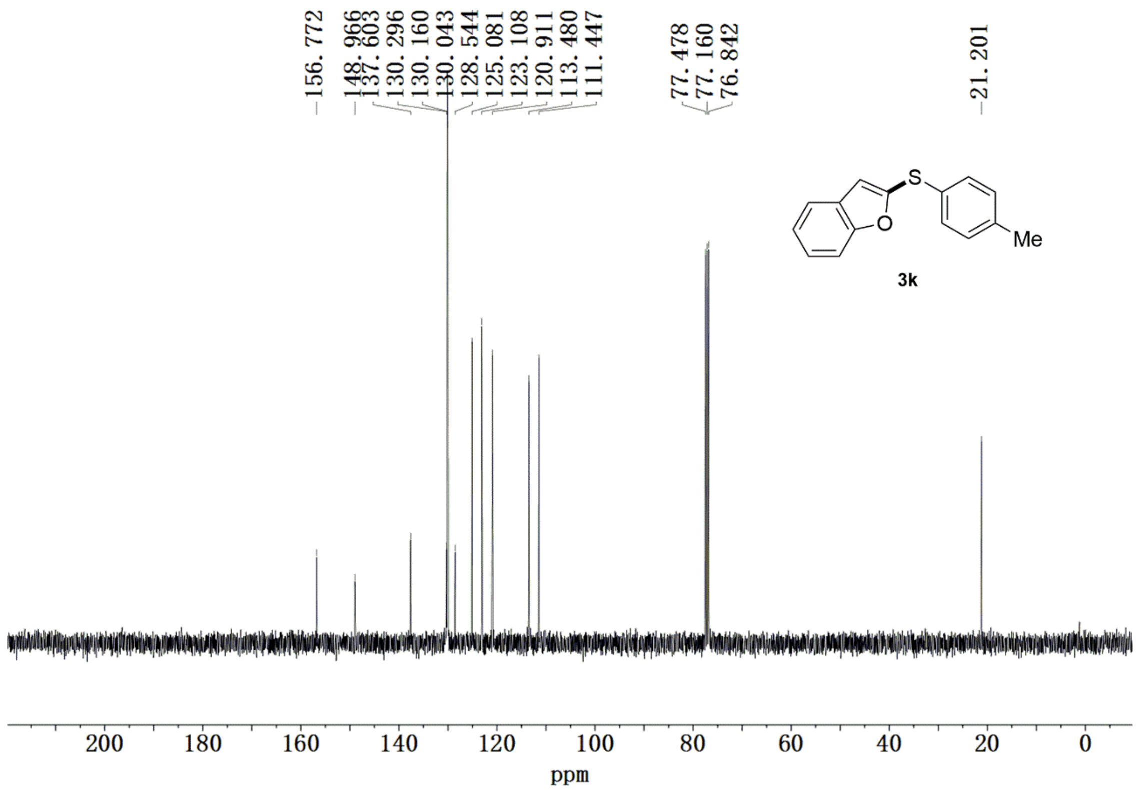
[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3i** (rt, $CDCl_3$).



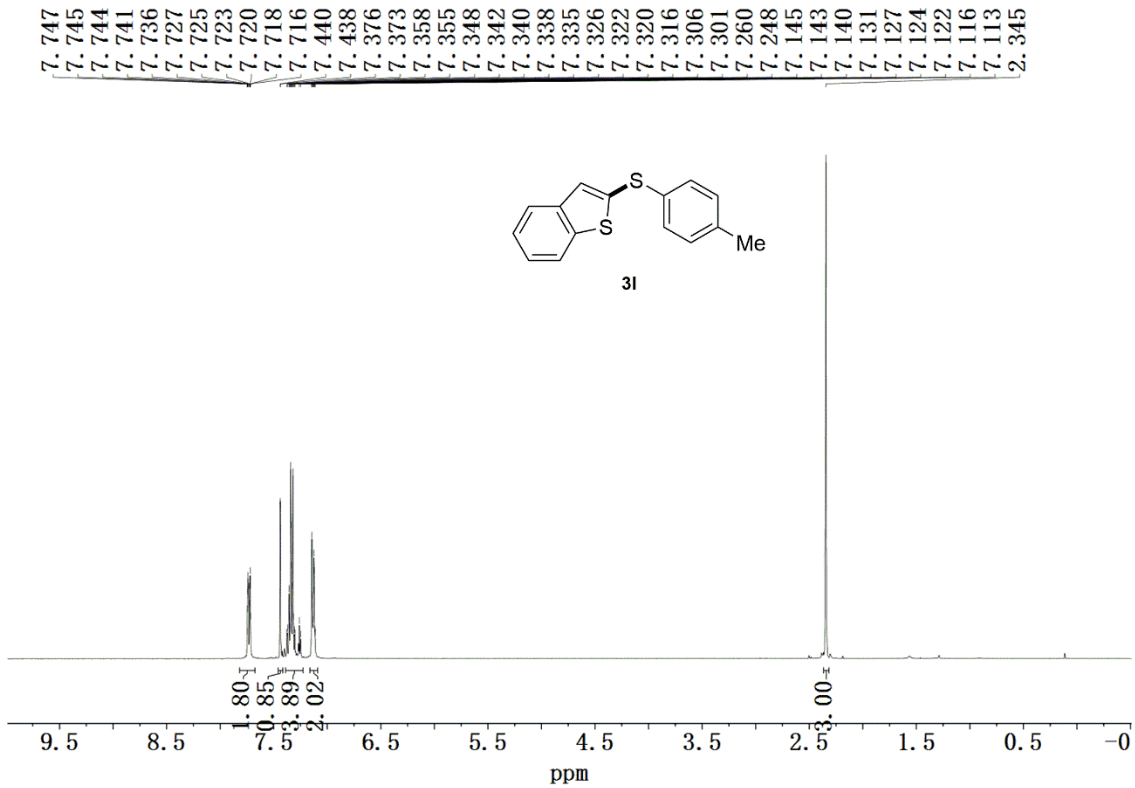


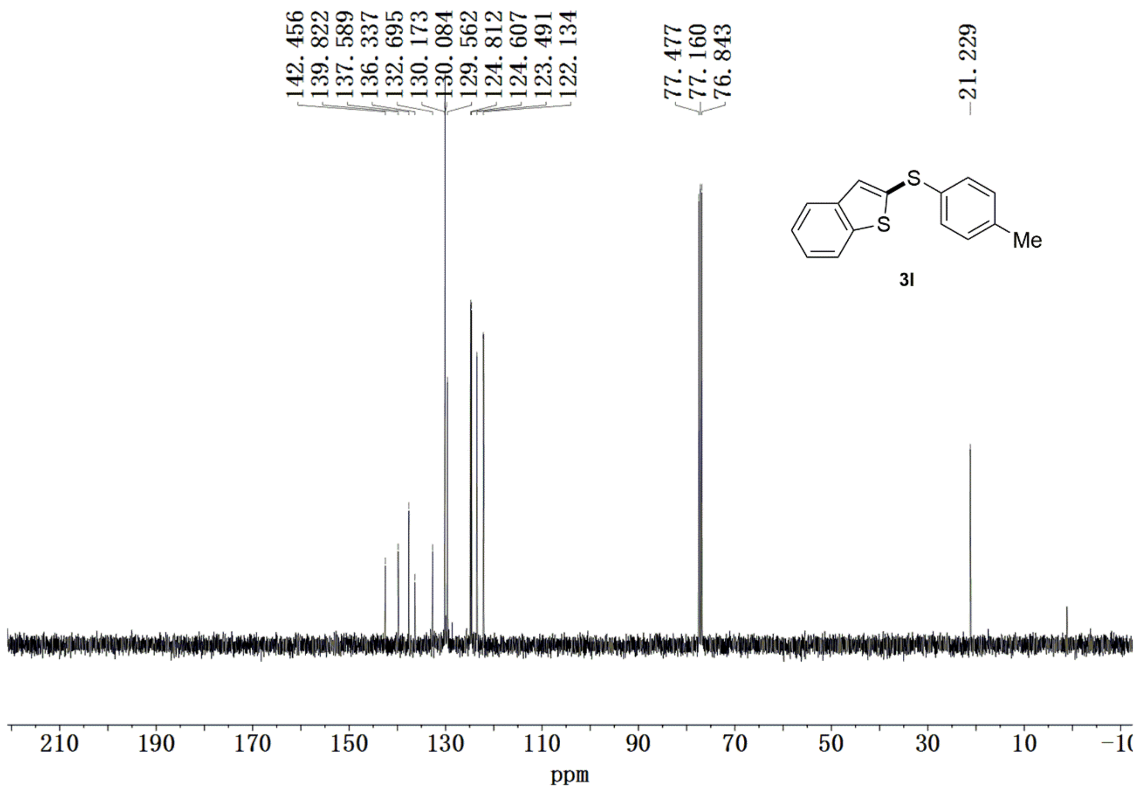
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3j** (rt, $CDCl_3$).



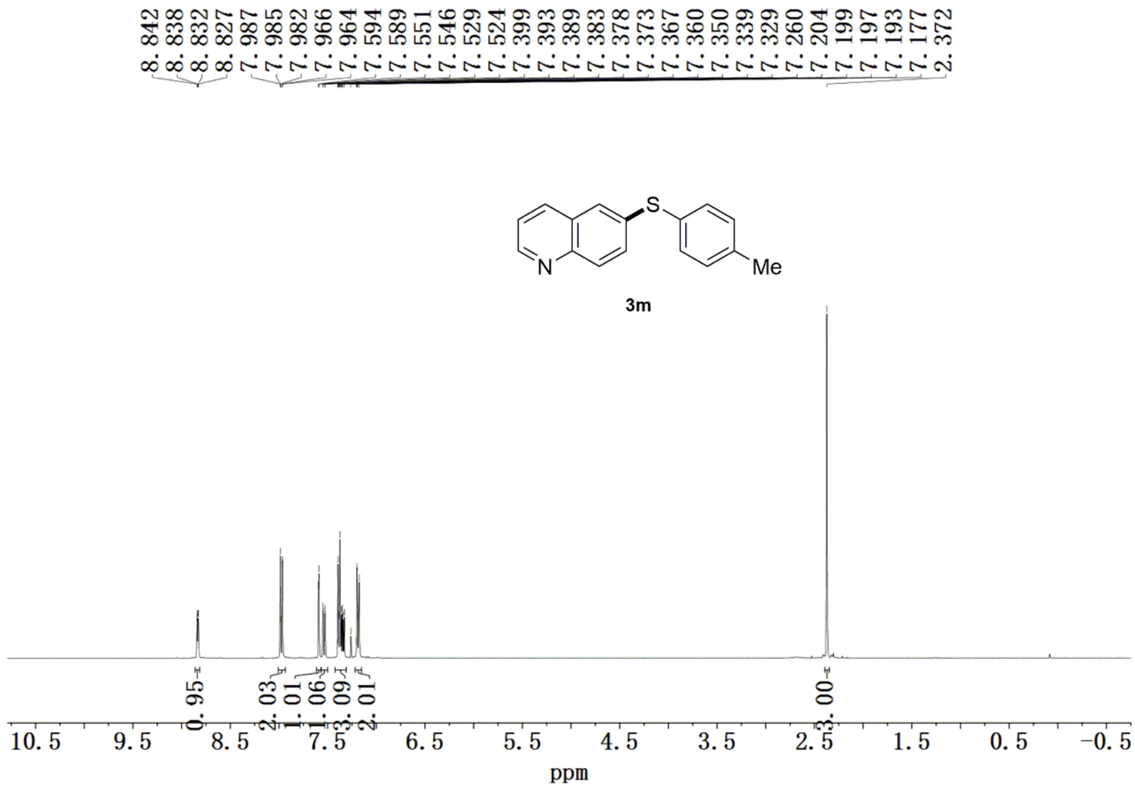


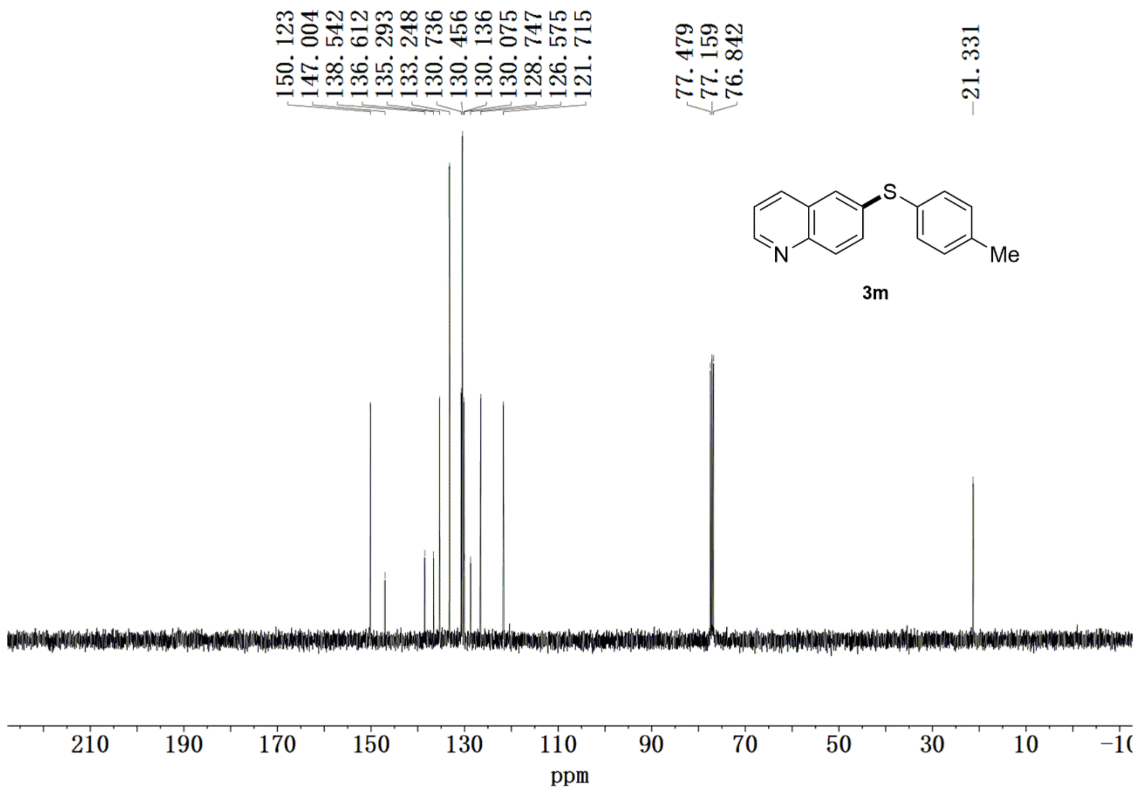
[1]H NMR (400 MHz) and [13]C{[1]H} NMR (101 MHz) spectra of **3k** (rt, $CDCl_3$).



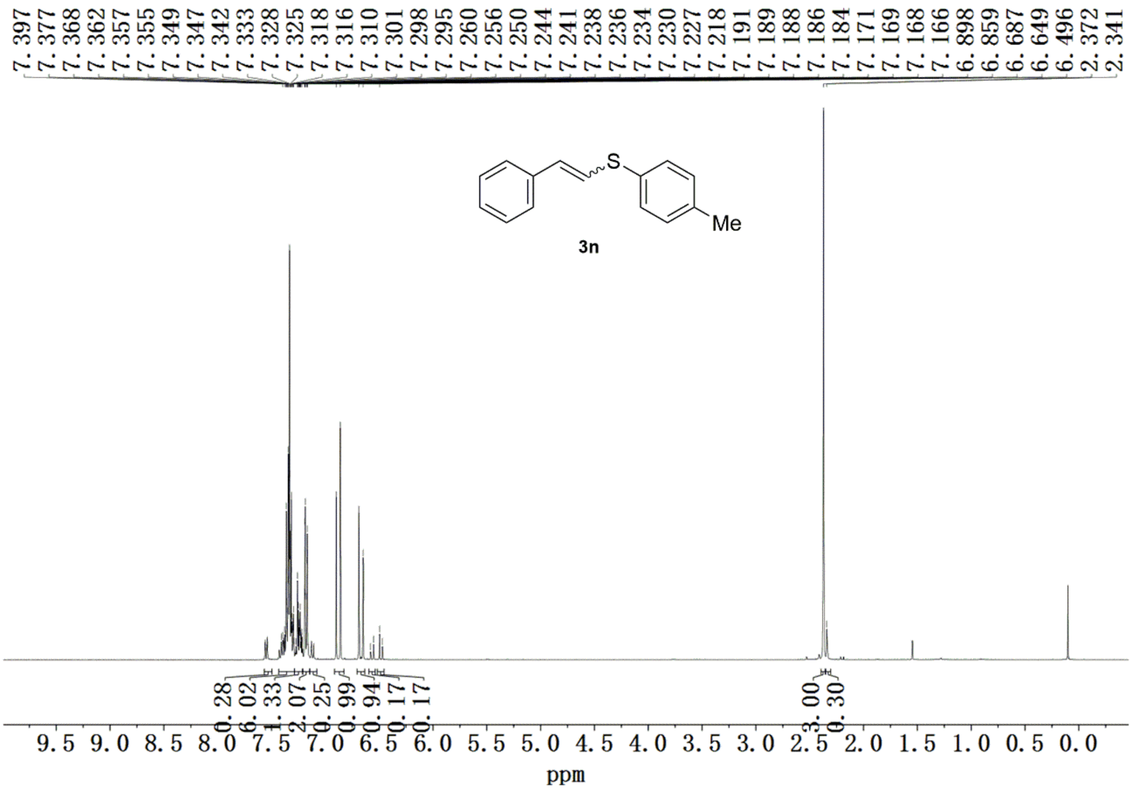


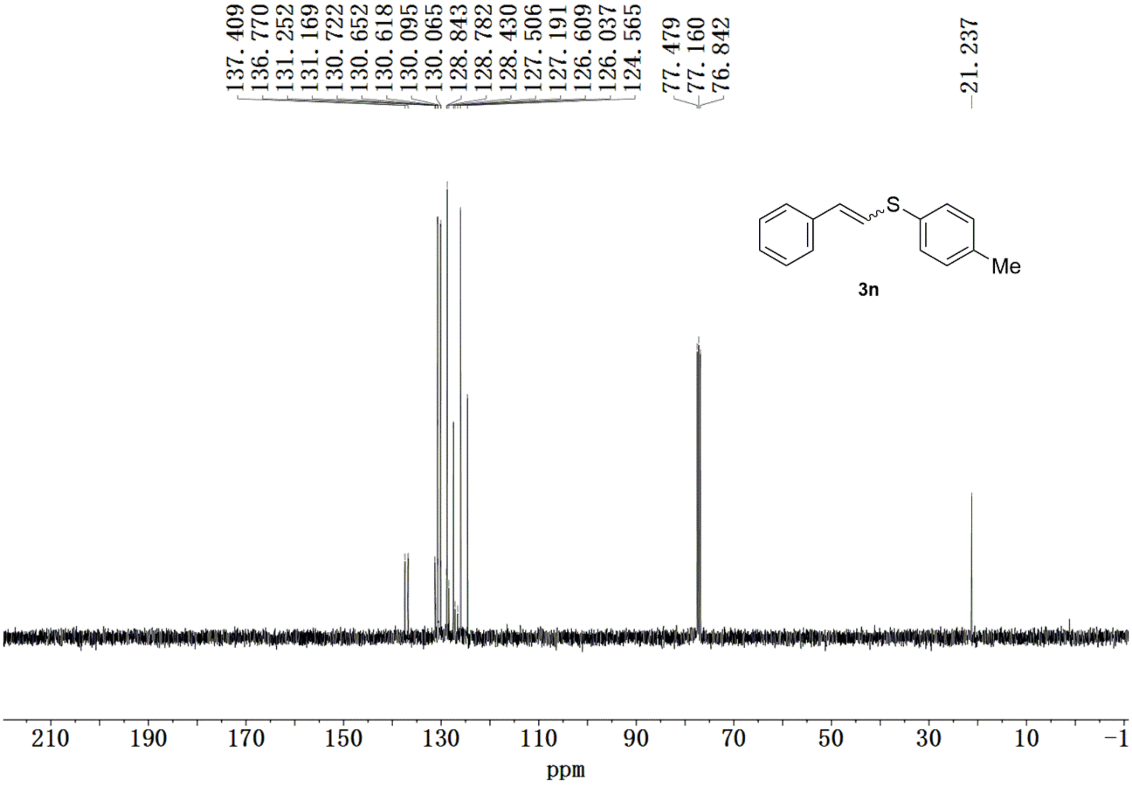
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3l** (rt, $CDCl_3$).



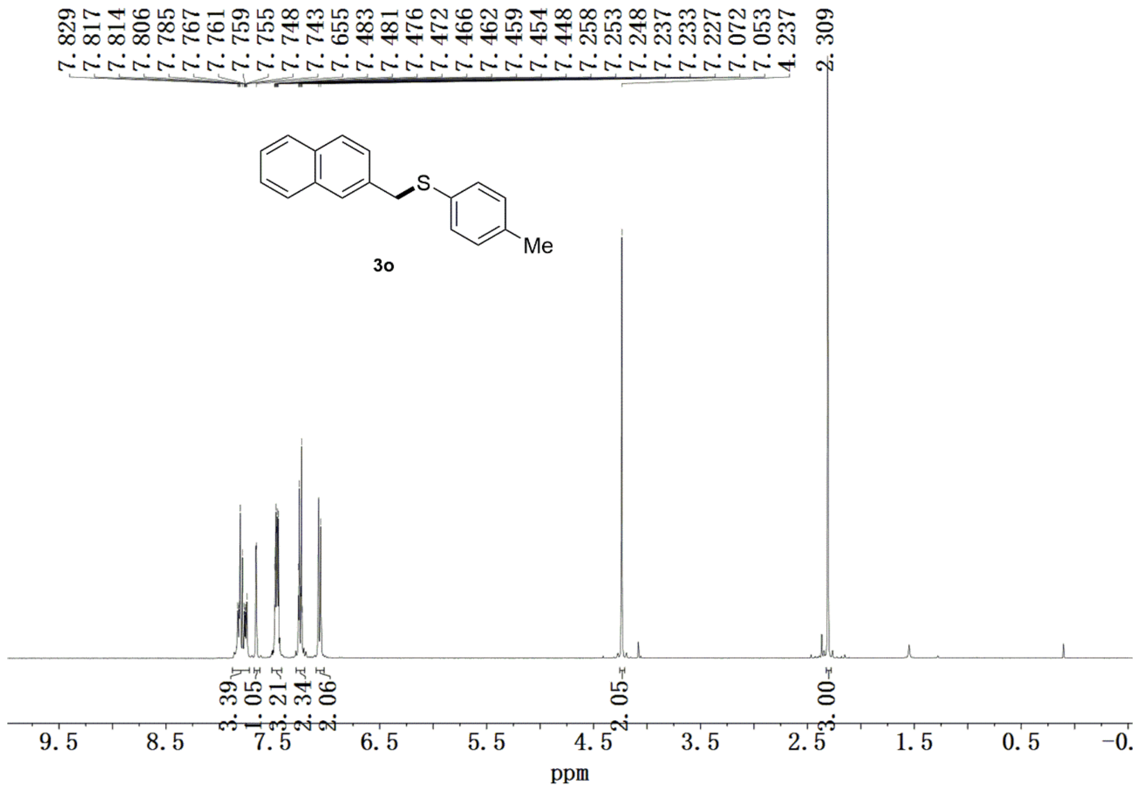


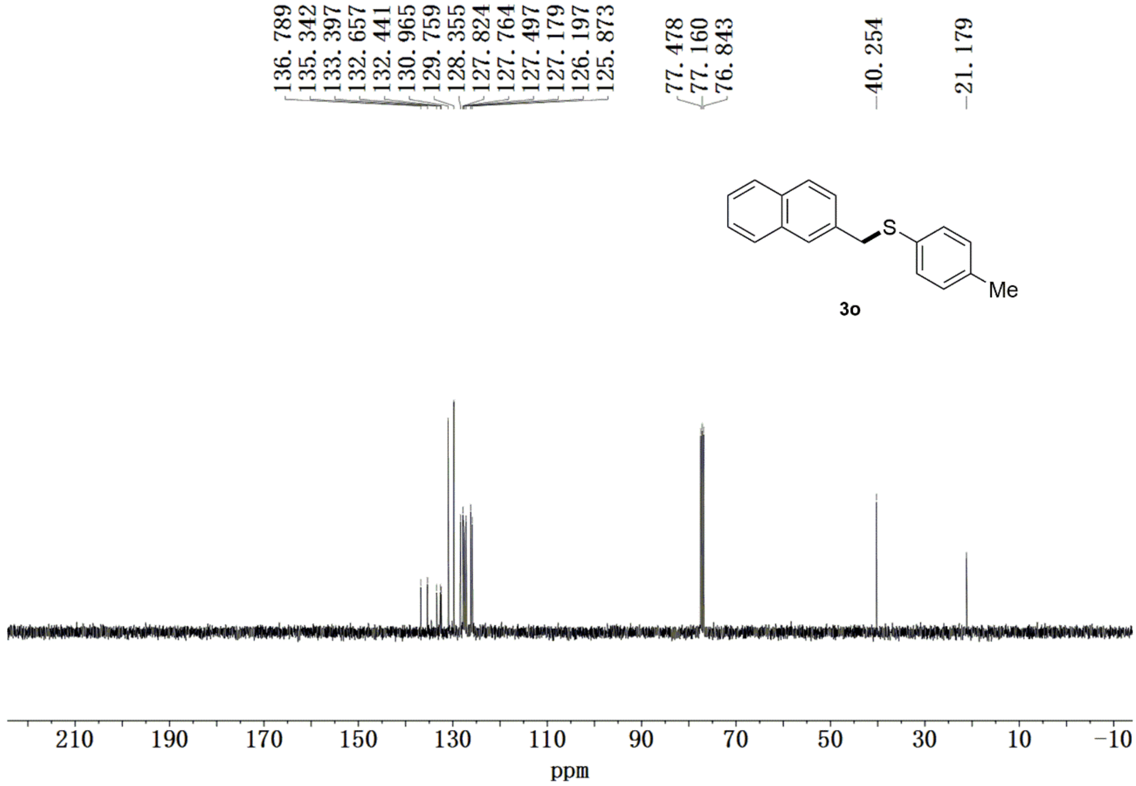
^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3m** (rt, $CDCl_3$).





^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3n** (rt, $CDCl_3$).





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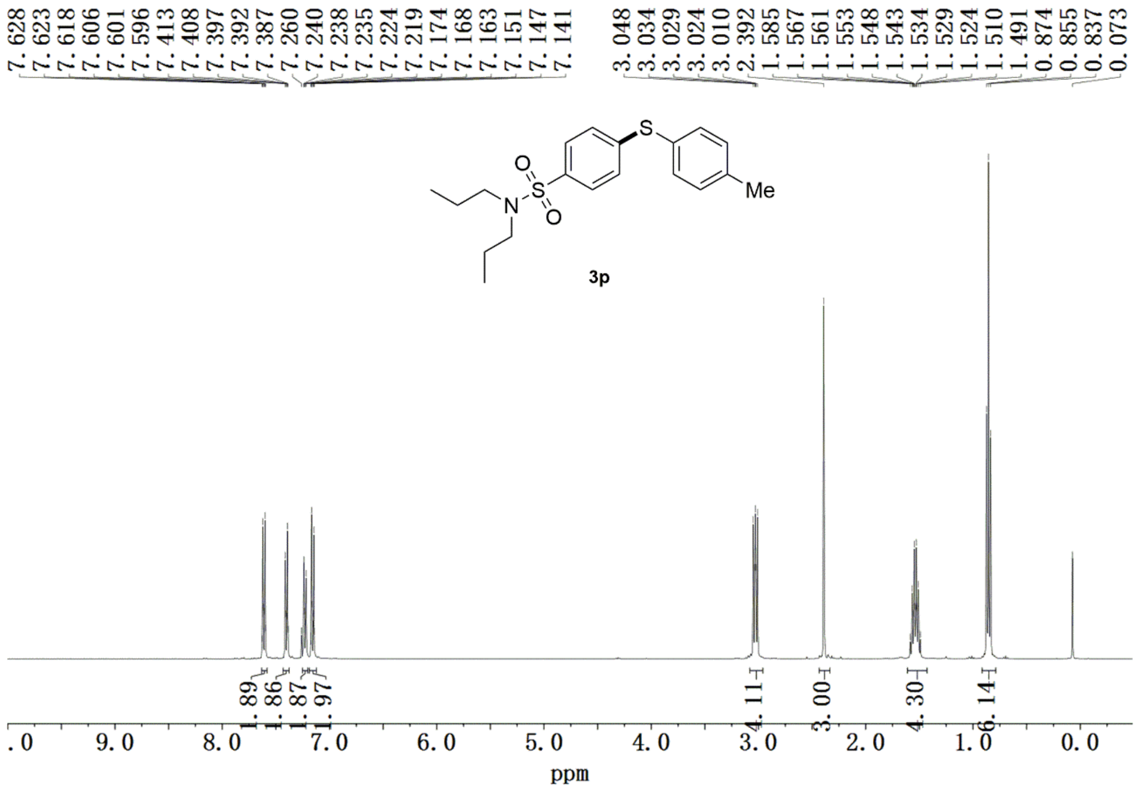

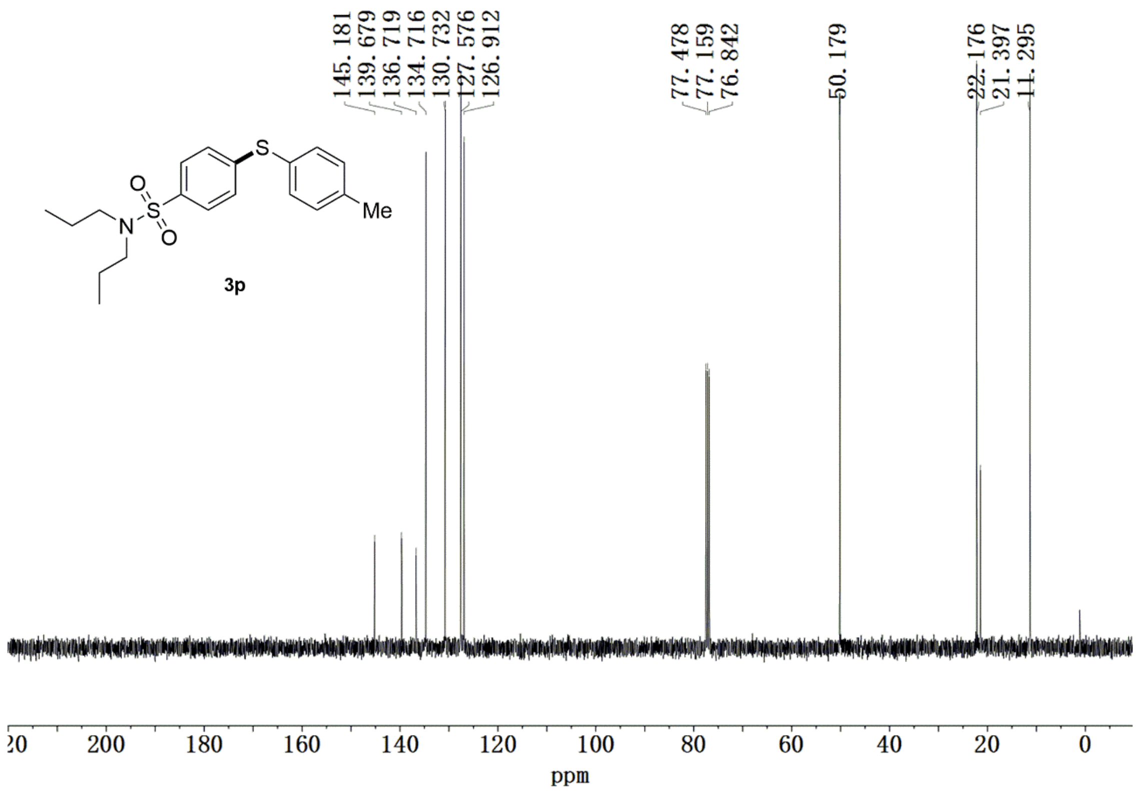

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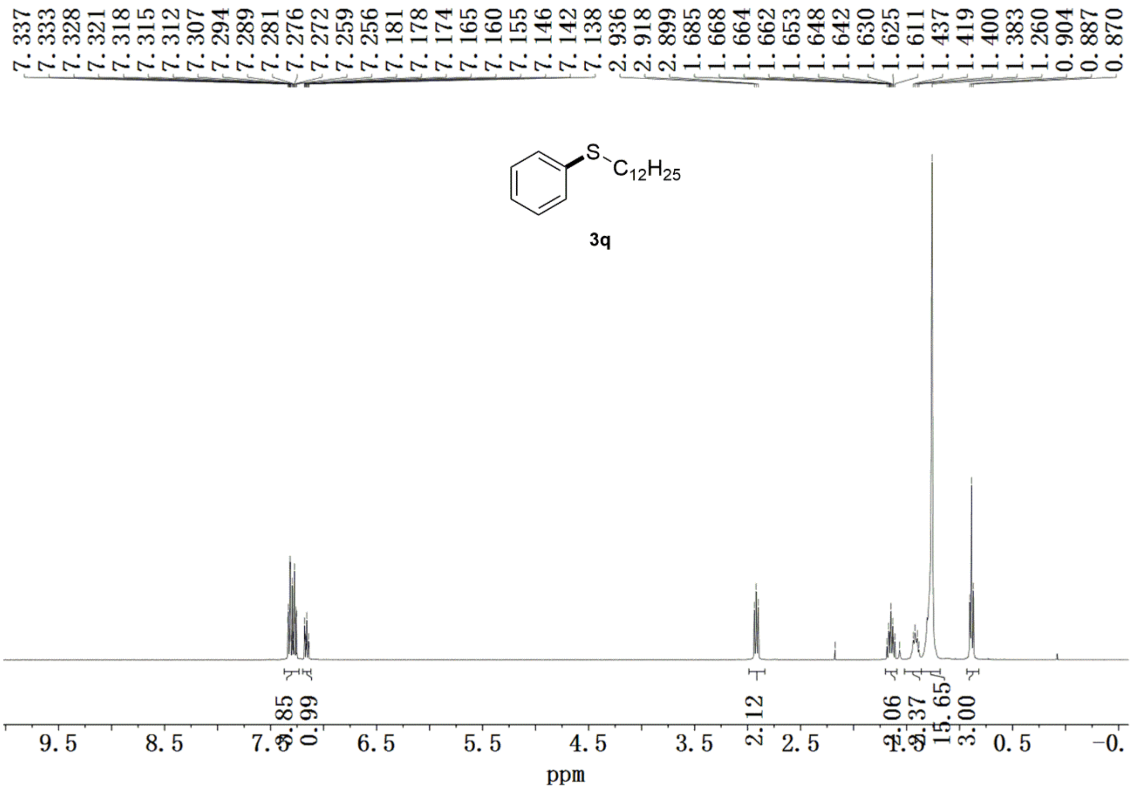
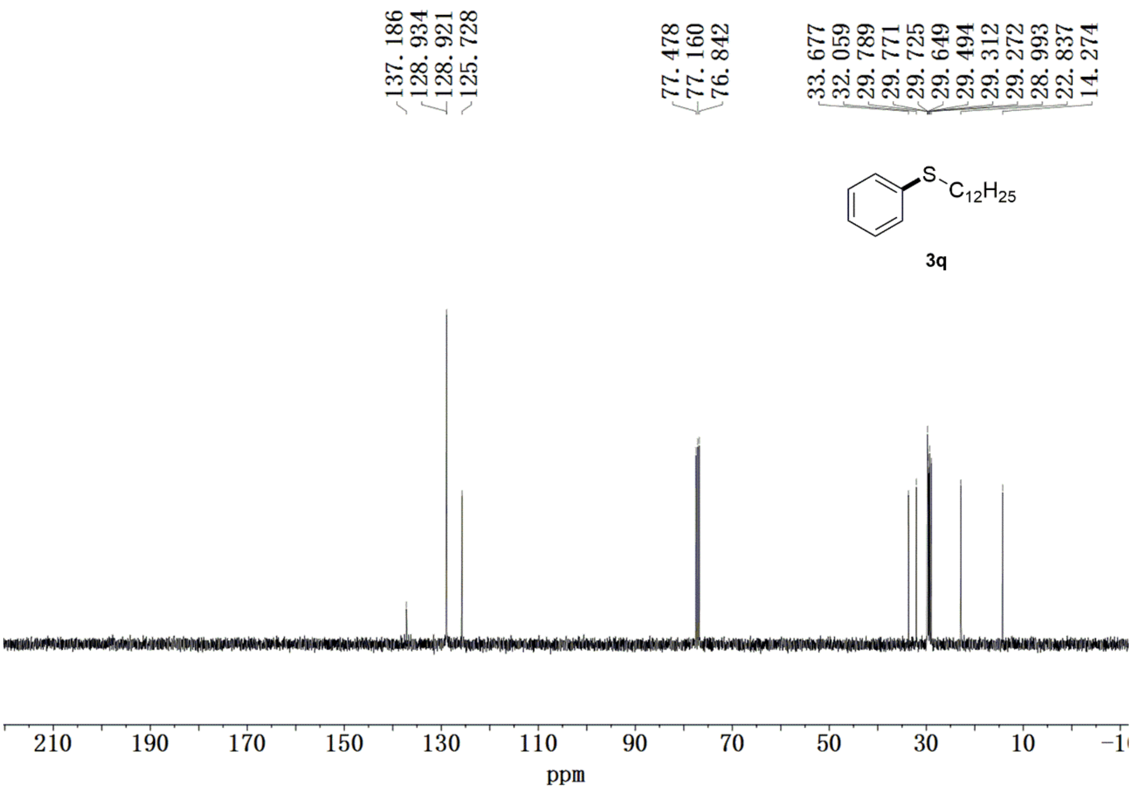
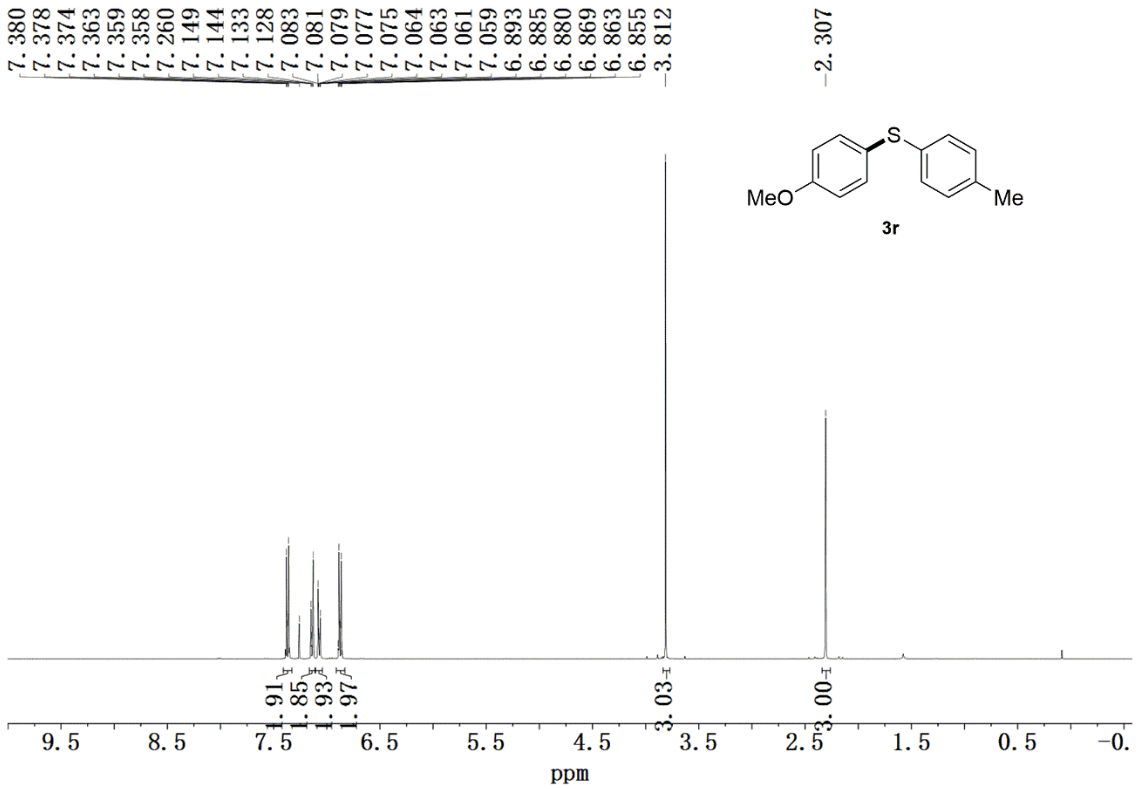
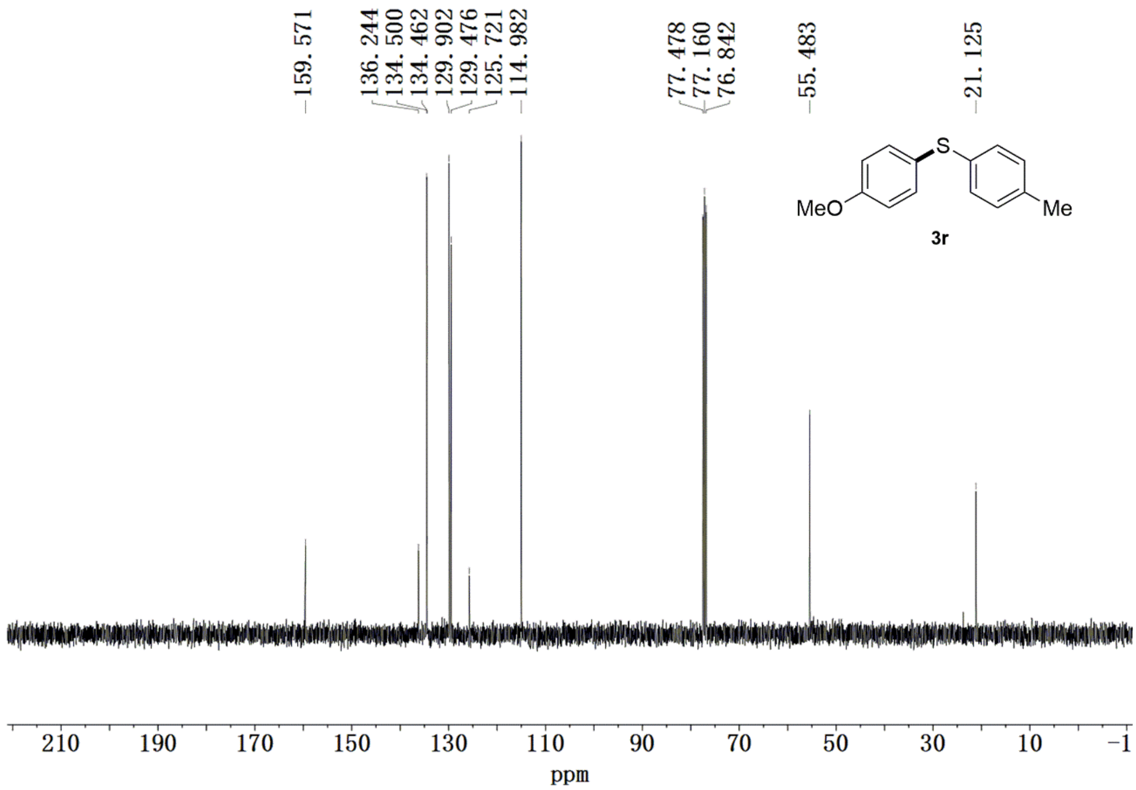


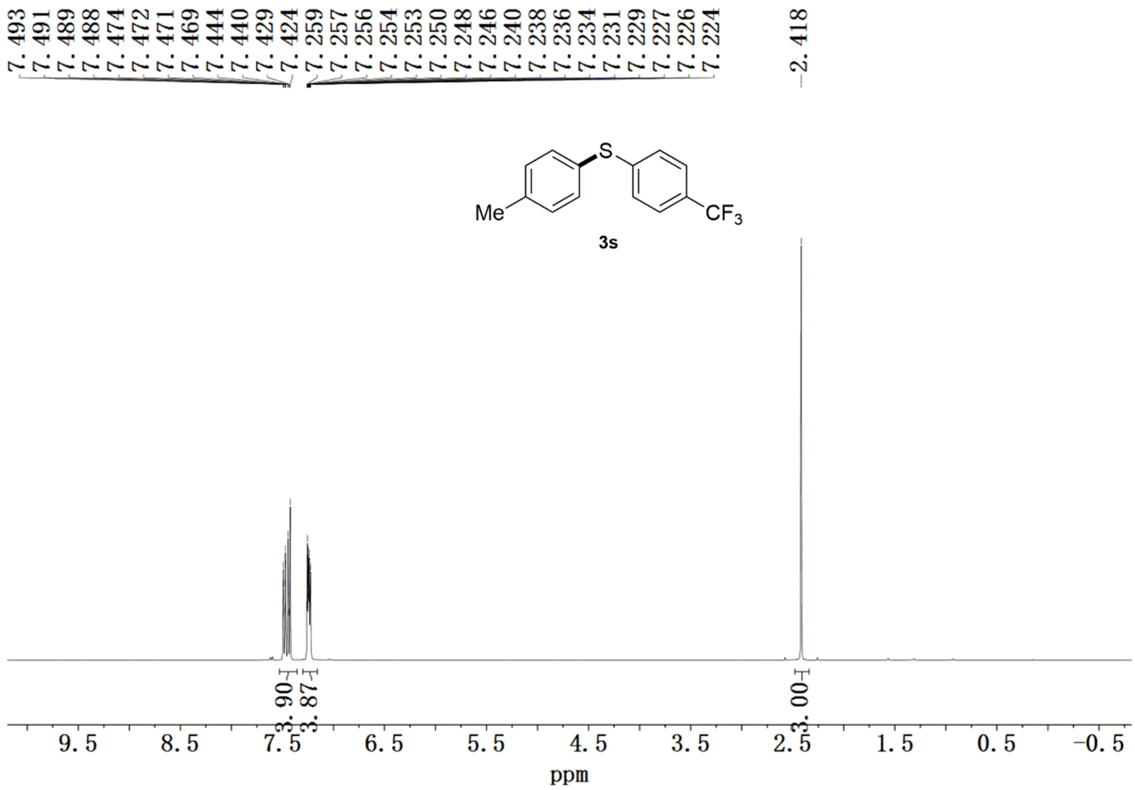


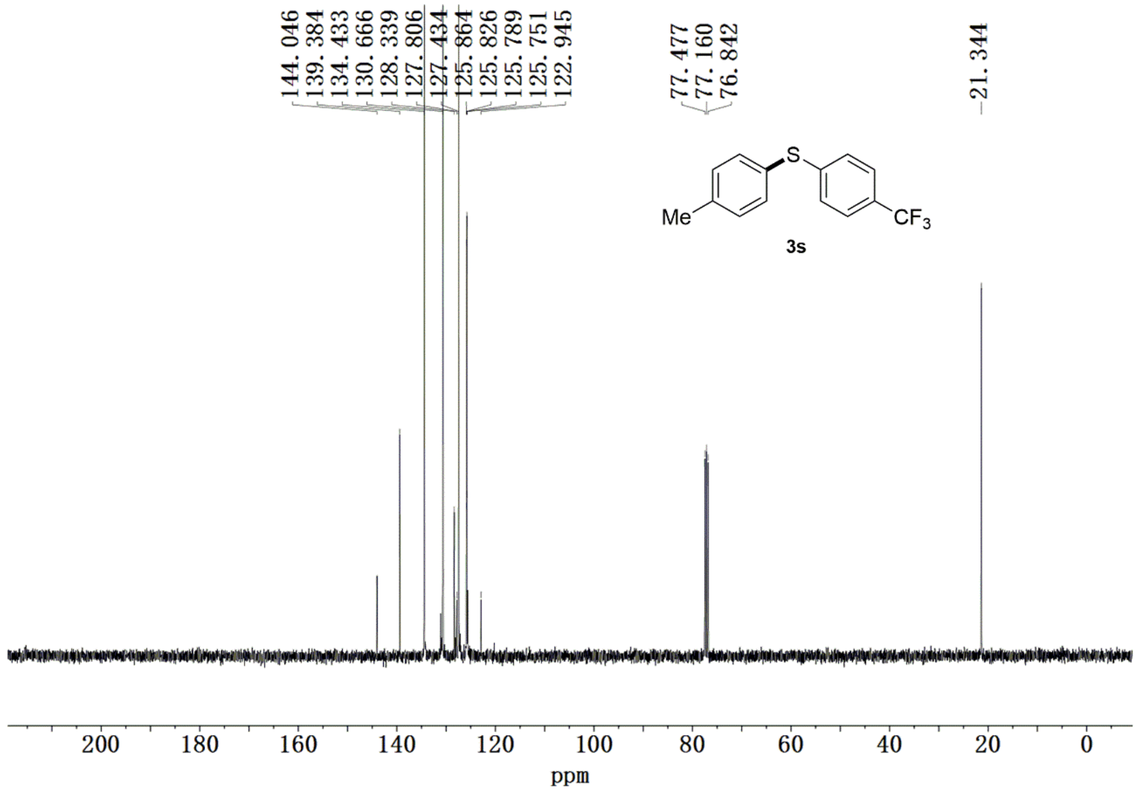
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of **3q** (rt, $CDCl_3$).





^{1}H NMR (400 MHz) and $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **3r** (rt, $CDCl_3$).





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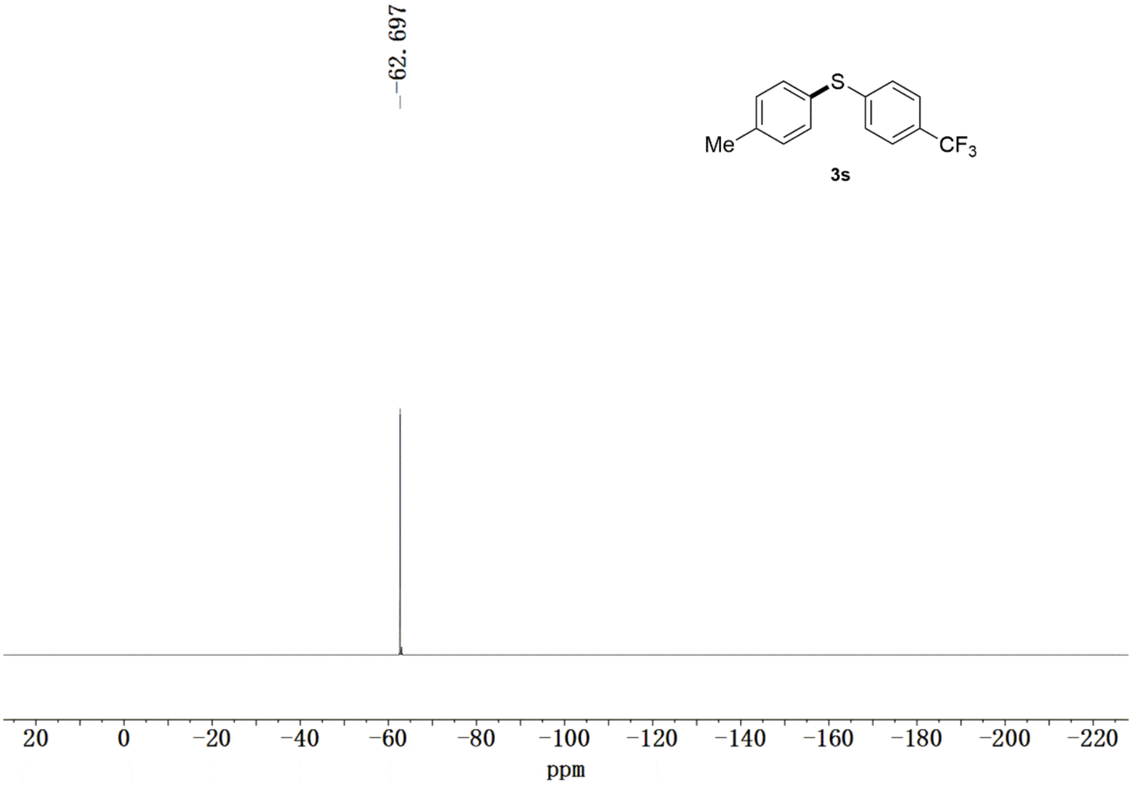

$^{19}F\{^{1}H\}$ NMR (376 MHz) spectrum of **3s** (rt, $CDCl_3$).