Electronic Supplementary Information

Visible-light-promoted C-S cross-coupling reaction between alkyl mercaptan and aryl halide

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1. Experiment Information and Product Data

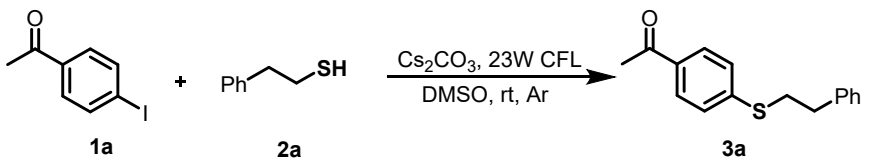
1.1 General Information.

Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. Unless otherwise indicated, all experiments were carried out under argon atmosphere. Irradiation of photochemical reactions was carried out using 18 W blue LED bulb (from Philips company, 450nm~470nm) and 23W CFL (from Philips company, 6000 K~6500 K, 400 nm~760 nm). The silica gel (200-300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof).

1.2 General Procedure for the Visible Light-Induced Oxidative Dehydrogenative Coupling of Glycine Esters.

In a 10 mL storage flask was charged with a stir bar, Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), aryl halide compounds **1** (0.2 mmol, 1 eq.), the reaction mixture was evacuated and purged with argon three times. Then thiol derivatives **2** (0.3 mmol, 1.5 eq.) were dissolved in DMSO (2 mL) and injected into the system using a syringe. The mixed solution was irradiated with 23 W CFL at room temperature. After completion of the reaction as monitored by TLC, the reaction mixture was washed with water and extracted with EtOAc for three times. Then the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with PE/EA = 64/1 to 16/1 as eluent) to afford the product.

1.3 Gram Scale Experiment.

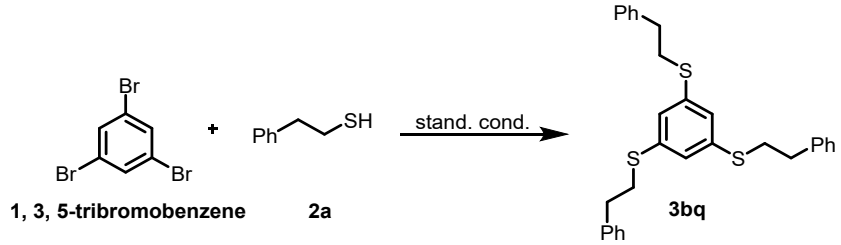


1a 2a 3a

In a 300 mL round-bottom flask was charged with a stir bar, Cs_2CO_3 (50 mmol,

1.5 eq.), **1a** (75 mmol, 1 eq.), the reaction mixture was evacuated and purged with argon three times. Then **2a** (75 mmol, 1.5 eq.) were dissolved in DMSO (200 mL) and injected into the system using a syringe. The mixed solution was irradiated with 23 W CFL at room temperature. After completion of the reaction as monitored by TLC, the reaction mixture was washed with water and extracted with EtOAc for three times. Then the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with PE/EA = 64/1 to 16/1 as eluent) to afford the product.

1.4 Synthesis of multiple reaction site products (take 3bq for example).

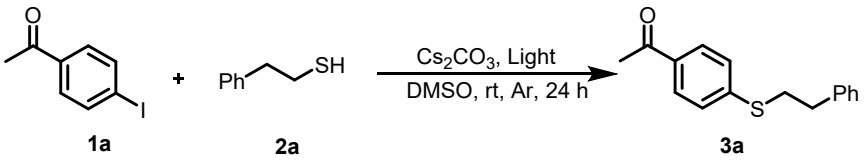


1, 3, 5-tribromobenzene **2a** **3bq**

In a 10 mL storage flask was charged with a stir bar, Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 eq.), 1, 3, 5-tribromobenzene (0.2 mmol, 1 eq.), 2-phenylethane-1-thiol (0.9 mmol, 4.5 eq.) and 2.0 mL DMSO. The reaction mixture was evacuated and purged with argon three times. the mixed solution was irradiated with 23 W CFL at room temperature. After completion of the reaction as monitored by TLC, the reaction mixture was washed with water and extracted with EtOAc. Then the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with PE/EA = 32/1 to 16/1 as eluent) to afford the product.

2. Optimization of Reaction Conditions

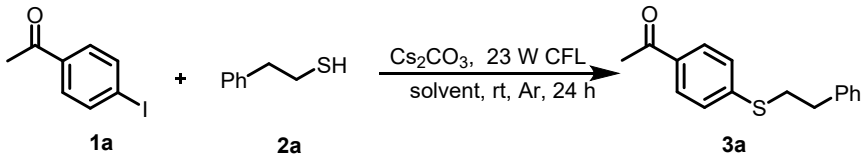
Table S1. Screening of light source [a]



Entry	Light Source	Yield (%) [b]
1	Blue LED	80
2	Purple LED	62
3	Green LED	51
4	**CFL**	**96**

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Cs_2CO_3 (0.15 mmol), DMSO (1.0 mL), with light irradiation under argon atmosphere at room temperature. [b] Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

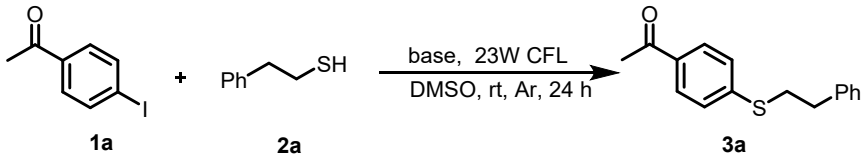
Table S2. Screening of solvents [a]



Entry	Solvent	Yield (%) [b]
1 [c]	DMSO	30
2 [d]	DMSO	74
3 [e]	DMSO	48
4	DMAc	55
5	DMF	50
6	1,4-dioxane	NR
7	CH_3CN	trace
8	CH_3OH	trace
9	CH_3CH_2OH	trace
10	DCE	trace
11	DCM	trace
12	THF	trace
13	Diethyl ether	NR
14	$CHCl_3$	trace
15	EtOAc	trace
16	Toluene	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Cs_2CO_3 (0.15 mmol), solvent (1.0 mL), with 23 W CFL irradiation under argon atmosphere at room temperature for 24 h. [b] Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] 2 mL DMSO was used. [d] 3 mL DMSO was used. [e] 4 mL DMSO was used.

Table S3. Screening of additive [a]



1a 2a 3a

Entry	Additive	Yield (%) [b]
1	K_2CO_3	33
2	Na_2CO_3	NR
3	KOH	70
4	Et_2NH	NR
5	Et_3N	NR
6	DIPEA	NR
7	BDU	51
8	NaOAc	NR
9	K^{t}BuO	40

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Cs_2CO_3 (0.15 mmol), DMSO (1.0 mL), with LED light irradiation under argon atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

3. Mechanistic Investigation

3.1 UV/Vis absorption spectra of EDA complex

The UV/Vis absorption spectra were recorded in 1 cm path quartz cuvettes by using a Varian Cary 300 Conc UV/Vis spectrometer, respectively.

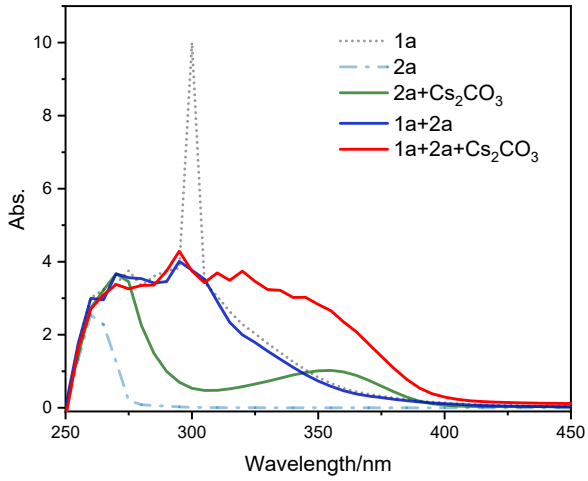
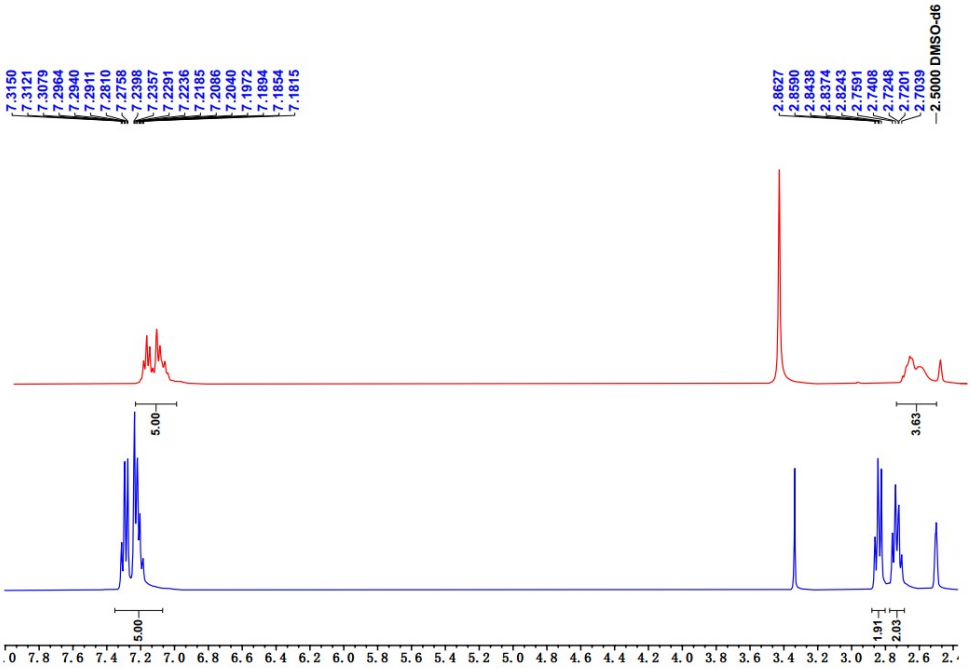


Fig. S1. Absorption spectra of EDA complex.



3.2 NMR study of EDA complex

Fig. S2. NMR spectra of **2a**$^{-}$.

3.2 Free radical trapping experiment

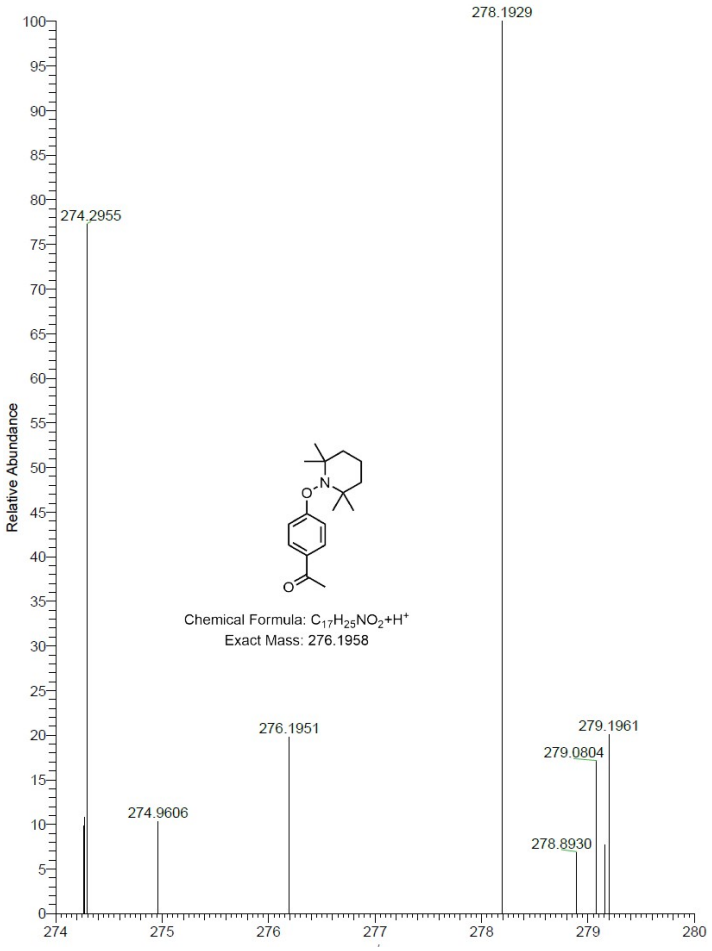


Fig. S3. HRMS spectrum from the trapping experiment of **1a-radical**.

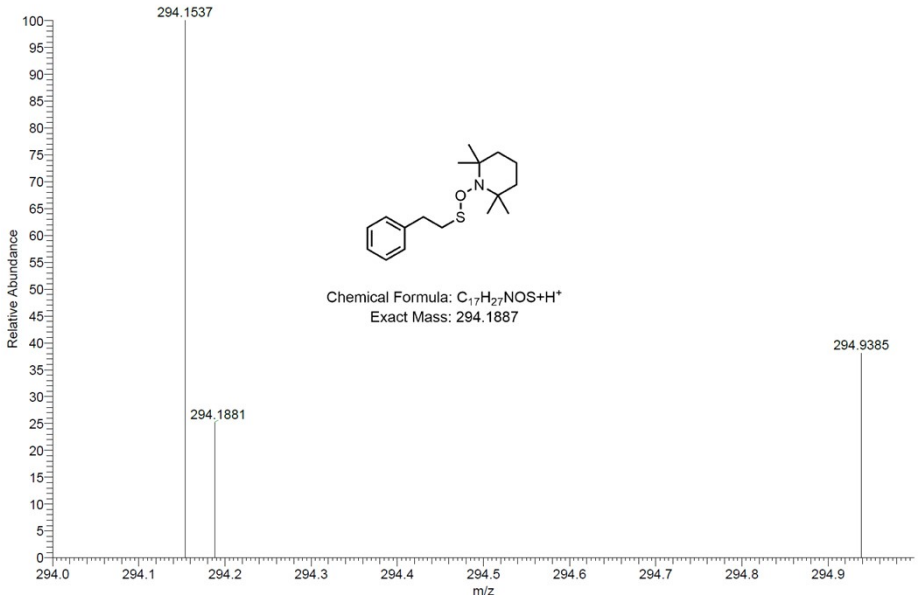


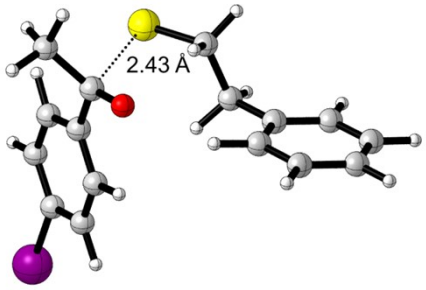
Fig. S4. HRMS spectrum from the trapping experiment of **2a-radical**.

4. Computational Study

4.1 Computational methods

All calculations were carried out with the Gaussian 09 D.01programs[1]. Ground state geometry were fully optimized by using density functional theory (DFT)[2] and the B3LYP[3]-D3 method with the 6-31G(d,p) basis set for C, H, O, S atoms and Lanl2DZ for I atom. Frequency calculations have been performed. The 3D molecular structures were generated using the CYL-View[4]. Using this geometry, single point time dependent density functional theory (TD-DFT) calculation was then performed using the CAM-B3LYP-D3/6-31G(d,p)/Lanl2DZ level of theory. The effect of solvent is considered from Truhlar and co-workers' universal solvation model (SMD[5]-DMSO).

4.2 Optimized structure of EDA complex



Binding energy: -14.3 kcal/mol

Fig. S5. Structure of EDA complex predicted by DFT.

4.3 Theory predicts UV/Vis spectrum of EDA complex

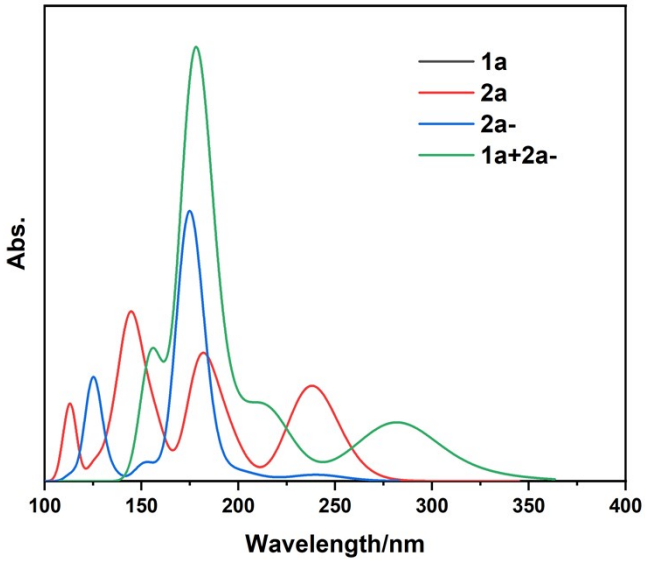


Fig. S6. UV/Vis spectra predicted by TD-DFT theory

4.4 Interaction between 1a and $2a^-$

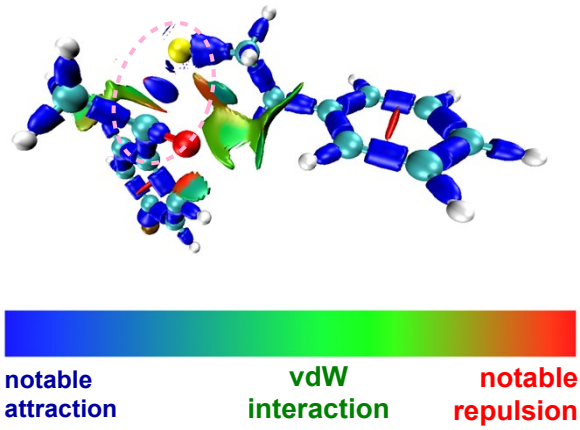


Fig. S7. Interaction in EDA complex

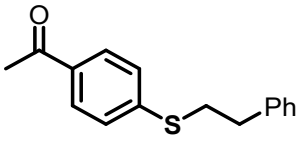
4.5 The Cartesian Coordinates

0 1

C	-2.53604600	-1.23881100	0.41946900
C	-1.35678200	-1.94725300	0.22397100
C	-0.31263100	-1.42144100	-0.54386500
C	-0.47877600	-0.15677000	-1.10841300
C	-1.64767100	0.57869900	-0.91530300
C	-2.66698500	0.02171400	-0.15796700
H	-3.33472000	-1.65617600	1.02338600
H	-1.23005100	-2.91041100	0.70922500
H	0.33830100	0.23869500	-1.70407800
H	-1.75865900	1.56384300	-1.35594700
C	0.96633100	-2.17638400	-0.87598200
O	1.84855300	-1.55882400	-1.50658100
C	0.79390300	-3.66531700	-1.16435000
H	1.78325500	-4.12367400	-1.18284600
H	0.17959300	-4.18399800	-0.42620100
H	0.33059500	-3.77163600	-2.15652000
C	3.93846900	1.01740200	-0.88916900
C	4.91158400	1.81748800	-1.47790200
C	5.71244600	2.64889800	-0.69326600
C	5.53084100	2.66948800	0.68614300
C	4.55316700	1.86689900	1.27379900
C	3.74254600	1.03528400	0.49925600
H	3.31218400	0.35399800	-1.48425900
H	5.04868000	1.79441500	-2.55596400
H	6.47169000	3.27431400	-1.15514700
H	6.14956500	3.31204600	1.30760200
H	4.41189900	1.88566800	2.35231600

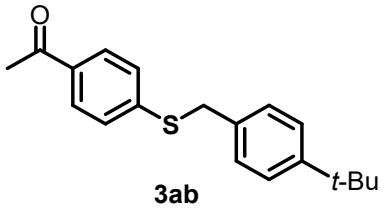
C	2.69599700	0.13350400	1.10287700
H	2.48854100	0.41495000	2.14189000
H	1.76038800	0.24164400	0.54423500
C	3.09931200	-1.34875300	1.03748400
H	3.94437200	-1.53895700	1.71005200
H	3.42678300	-1.56385500	0.01285200
S	1.72161200	-2.45982900	1.41374700
I	-4.47794100	1.12243600	0.13493200

5. Product Data.



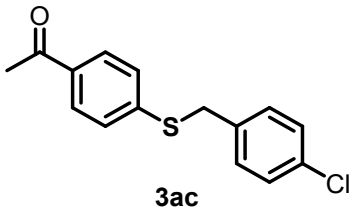
3aa

***1-(4-(phenethylthio)phenyl)ethan-1-one* (*3aa*)[6].** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89-7.85 (m, 2H), 7.35-7.34(m, 4H), 7.33-7.22 (m, 3H), 3.27-3.23 (m, 2H), 3.00-2.96 (m, 2H), 2.58 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3, 144.4, 139.8, 134.1, 129.0, 128.8, 128.6, 126.8, 126.7, 35.3, 33.6, 26.6.



3ab

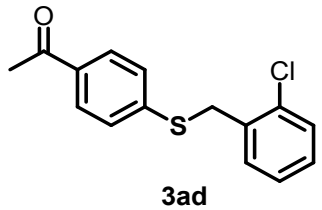
***1-(4-((4-(tert-butyl)benzyl)thio)phenyl)ethan-1-one* (*3ab*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.83 (m, 2H), 7.37-7.30 (m, 6H), 4.20 (s, 2H), 2.56 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3, 150.7, 144.8, 134.2, 133.2, 128.9, 128.6, 126.7, 125.8, 36.8, 34.7, 31.4, 26.6. HRMS (ESI) calcd for $C_{19}H_{23}OS$ ($M+H^+$) 299.1464, found 299.1463.



3ac

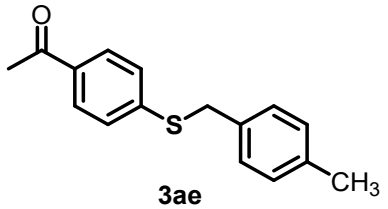
***1-(4-((4-chlorobenzyl)thio)phenyl)ethan-1-one* (*3ac*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow

liquid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85-7.82 (m, 2H), 7.31-7.26 (m, 6H), 4.17 (s, 2H), 2.56(s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3 143.6, 135.0, 134.6, 133.5, 130.2, 129.0, 128.9, 127.4, 36.8, 26.6. HRMS (ESI) calcd for $C_{15}H_{14}ClOS$ ($M+H^+$) 277.0448, found 277.0450.



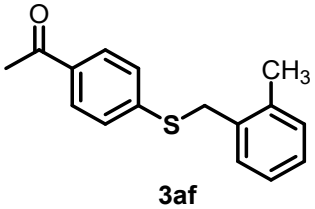
3ad

1-(4-((2-chlorobenzyl)thio)phenyl)ethan-1-one **(*3ad*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.83 (m, 2H), 7.40-7.34 (m, 2H), 7.35-7.31 (m, 2H), 7.24-7.17 (m, 2H), 4.32 (s, 2H), 2.56 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3, 143.7, 134.6, 134.3, 134.2, 130.7, 129.9, 129.1, 128.9, 127.7, 127.2, 35.1, 26.6. HRMS (ESI) calcd for $C_{15}H_{14}ClOS$ ($M+H^+$) 277.0448, found 277.0449.



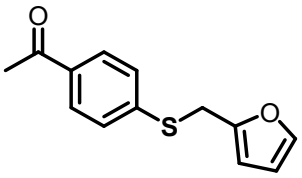
3ae

1-(4-((4-methylbenzyl)thio)phenyl)ethan-1-one **(*3ae*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84-7.82 (m, 2H), 7.32-7.30 (m, 2H), 7.27-7.25 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.18 (s, 2H), 2.55 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.2, 144.5, 137.3, 134.1, 133.1, 129.4, 128.7, 128.7, 126.8, 36.9, 26.4, 21.1. HRMS (ESI) calcd for $C_{16}H_{17}OS$ ($M+H^+$) 257.0995, found 257.0991. IR (film)ν_{max}:3858, 3728, 3441,2955, 2920, 2852, 2378, 2350, 2310, 1675, 1650, 1457, 1397, 1098, 1028, 817, 743, 590, 567 cm^{-1}.



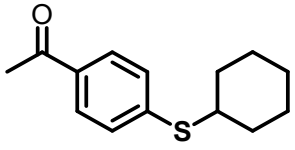
3af

1-(4-((2-methylbenzyl)thio)phenyl)ethan-1-one **(*3af*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87-7.84 (m, 2H), 7.35-7.32 (m, 2H), 7.28-7.26 (m, 1H), 7.20-7.18 (m, 2H), 7.17-7.12 (m, 1H), 4.20 (s, 2H), 2.57 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3, 144.8, 137.0, 134.4, 133.9, 130.8, 129.8, 128.9, 128.0, 127.2, 126.4, 35.7, 26.6, 19.4. HRMS (ESI) calcd for $C_{16}H_{17}OS$ ($M+H^+$) 257.0995, found 257.0997.



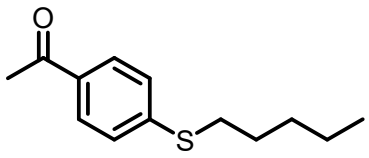
3ag

1-(4-((furan-2-ylmethyl)thio)phenyl)ethan-1-one **(*3ag*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.84 (m, 2H), 7.37-7.34 (m, 3H), 6.29 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.20 (dd, *J* = 3.3, 0.9 Hz, 1H), 4.20 (d, *J* = 0.8 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3, 150.2, 143.3, 142.5, 134.6, 128.9, 127.7, 110.7, 108.3, 29.9, 26.6. HRMS (ESI) calcd for $C_{13}H_{13}O_2S$ ($M+H^+$) 233.0631, found 233.0635.



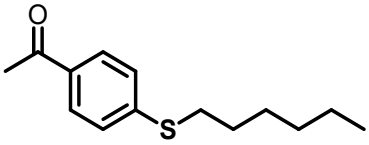
3ah

1-(4-(cyclohexylthio)phenyl)ethan-1-one(3ah) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.32-3.30 (m, 1H), 2.57 (s, 3H), 2.09-1.98 (m, 2H), 1.84-1.74 (m, 2H), 1.69-1.56 (m, 2H), 1.49-1.31 (m, 5H), 1.31-1.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.4, 143.7, 134.4, 128.8, 128.6, 45.1, 33.2, 29.8, 26.6, 26.1, 25.8. HRMS (ESI) calcd for $C_{14}H_{19}OS$ ($M+H^+$) 235.1151, found 235.1147. IR (film)ν_{max}:3857, 3745, 3442, 2953, 2926, 2852, 2350, 2310, 1678, 1589, 1263, 1097, 761, 592, 518, cm^{-1}.



3ai

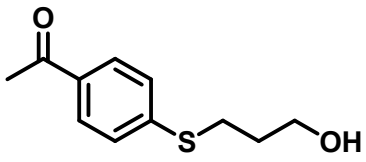
1-(4-(pentylthio)phenyl)ethan-1-one(3ai) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87-7.84 (m, 2H), 7.30-7.28 (m, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.57 (s, 3H), 1.70 (p, *J* = 7.4 Hz, 2H), 1.47-1.39 (m, 2H), 1.38-1.30 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H).); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.3, 145.1, 133.8, 128.9, 126.3, 32.0, 31.2, 28.5, 26.6, 22.4, 14.1. HRMS (ESI) calcd for $C_{13}H_{19}OS$ ($M+H^+$) 223.1151, found 223.1148.



3aj

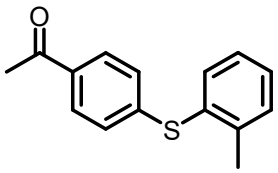
***1-(4-(hexylthio)phenyl)ethan-1-one* (*3ai*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.83 (m, 2H), 7.30-7.28 (m, 2H), 2.98 (t, *J*=7.4,

2H), 2.56 (s, 3H), 1.70 (pent, *J*=7.4, 2H), 1.47-1.23 (m, 6H), 0.90 (t, *J*=7.2, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.4, 145.2, 133.8, 128.9, 126.3, 32.1, 31.5, 28.8, 28.7, 26.6, 22.6, 14.2. HRMS (ESI) calcd for $C_{14}H_{21}OS$ ($M+H^+$) 237.1307, found 237.1304.



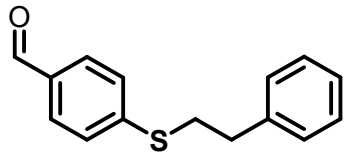
3ak

1-(4-((3-hydroxypropyl)thio)phenyl)ethan-1-one (3ak) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 66 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.81 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.78 (t, *J* = 5.9 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.98-1.91 (m, 2H), 1.90 (Br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.5, 144.5, 134.0, 128.9, 126.6, 61.2, 31.5, 28.60, 26.5. HRMS (ESI) calcd for $C_{11}H_{15}O_2S$ ($M+H^+$) 211.0787, found 211.0781. IR (film)ν_{max}: 3743, 3441, 2953, 2921, 2851, 2310, 1658, 1585, 1553, 1420, 1397, 1357, 1265, 1184, 1097, 1047, 956, 816, 761, 617, 590, 519 cm^{-1}.



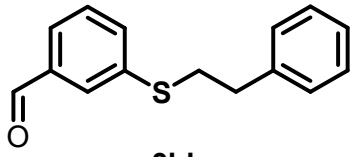
3al

1-(4-(o-tolylthio)phenyl)ethan-1-one (3al) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70–7.66 (m, 2H), 7.42–7.38 (m, 1H), 7.26–7.21 (m, 2H), 7.16–7.09 (m, 1H), 6.99–6.94 (m, 2H), 2.42 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.2, 145.1, 142.2, 136.0, 134.2, 131.2, 130.4, 129.8, 129.0, 127.2, 126.4, 26.5, 20.8. HRMS (ESI) calcd for $C_{15}H_{14}OS$ ($M+H^+$) 243.0848, found 243.0844.



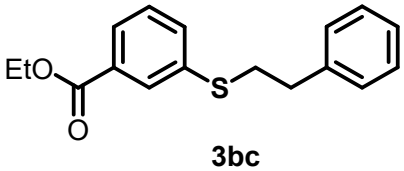
3ba

4-(phenethylthio)benzaldehyde (3ba) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 86 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.84 (s, 1H), 7.71-7.65 (m, 2H), 7.30-7.21 (m, 4H), 7.19-7.12 (m, 3H), 3.20-3.16 (m, 2H), 2.93-2.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 146.5, 139.7, 133.4, 130.2, 128.8, 128.6, 126.9, 126.7, 35.2, 33.4. HRMS (ESI) calcd for $C_{15}H_{15}OS$ ($M+H^+$) 243.0838, found 243.0834. IR (film)ν_{max}:3856, 3746, 3745, 3441, 2922, 2852, 1700, 1650, 1457, 1384, 1275, 1198, 1093, 1030, 750, 517 cm^{-1}.



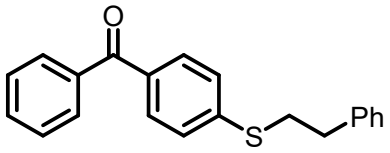
3bb

3-(phenethylthio)benzaldehyde (**3bb**)[7] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 72 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.97 (s, 1H), 7.80 (t, J = 1.8 Hz, 1H), 7.66 (dt, J = 7.5, 1.4 Hz, 1H), 7.56 (dt, J = 7.9, 1.5 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.33-7.28 (m, 2H), 7.27-7.17 (m, 3H), 3.26-3.22 (m, 2H), 2.98-2.94(m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.5, 139.4, 138.8, 137.3, 131.6, 128.8, 128.7, 126.9, 35.5, 35.3. HRMS (ESI) calcd for $C_{15}H_{15}OS$ ($M+H^+$) 243.0838, found 243.0834. IR (film)ν_{max}:3857, 3746, 3441, 2955, 2922, 2851, 2377, 2310, 1693, 1651, 1588, 1455, 1212, 1087, 1030, 835, 810, 750, 695, 517, 513 cm^{-1}.



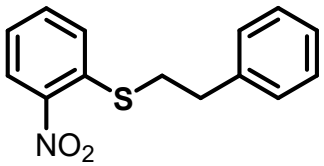
3bc

ethyl 3-(phenethylthio)benzoate (3bc) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 71 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (t, *J* = 1.8 Hz, 1H), 7.87 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.52 (ddd, *J* = 7.8, 2.0, 1.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.35-7.30 (m, 2H), 7.27-7.20 (m, 3H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.28-3.17 (m, 2H), 2.98-2.94 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.3, 140.0, 137.4, 133.2, 131.4, 129.6, 129.0, 128.7, 128.7, 127.1, 126.7, 61.3, 35.6, 35.0, 14.5. HRMS (ESI) calcd for $C_{17}H_{19}O_2S$ ($M+H^+$) 287.1100, found 287.1086.



3bd

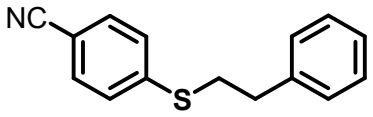
(4-(phenethylthio)phenyl)(phenyl)methanone(3bd) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71-7.60 (m, 4H), 7.50-7.46 (m, 1H), 7.40-7.36 (m, 2H), 7.28-7.19 (m, 4H), 7.18-7.10 (m, 3H), 3.16 (m, 2H), 2.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.8, 143.6, 139.7, 137.8, 134.2, 132.3, 130.7, 129.9, 128.7, 128.5, 128.3, 126.7, 126.5, 35.3, 33.6. HRMS (ESI) calcd for $C_{21}H_{19}OS$ ($M+H^+$) 319.1151, found 319.1138. IR (film)ν_{max}: 3744, 3442, 2954, 2921, 2851, 2310, 1650, 1585, 1454, 1316, 1280, 1089, 1029, 936, 921, 730, 697, 517 cm^{-1}.



3be

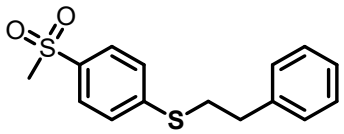
(2-nitrophenyl)(phenethyl)sulfane(3be)[8] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 73 %

yield ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.55-7.51 (m, 1H), 7.41 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.36-7.28 (m, 2H), 7.26-7.21 (m, 4H), 3.23-3.19 (m, 2H), 3.03-2.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.2, 139.7, 137.6, 133.5, 128.7, 128.5, 126.8, 126.7, 126.2, 124.6, 77.4, 77.1, 76.8, 34.3, 33.9. HRMS (ESI) calcd for $C_{14}H_{14}NO_2S$ ($M+H^+$) 260.0740, found 260.0730. IR (film)ν_{max}:3856, 3804, 3737,3677, 3360, 2921, 2852, 1655, 1590, 1562, 1510, 1453, 1334, 1302, 1101, 1029, 851, 730, 696, 503 cm^{-1}.



3bf

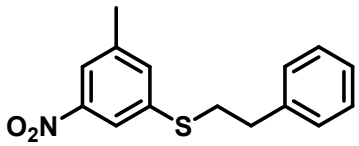
4-(phenethylthio)benzonitrile(3df)[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 83 % yield ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.39 (m, 2H), 7.30-7.21 (m, 4H), 7.21-7.11 (m, 3H), 3.18-3.14 (m, 2H), 2.93-2.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.7, 139.5, 132.3, 128.8, 128.6, 127.0, 126.9, 118.9, 108.3, 35.1, 33.5. HRMS (ESI) calcd for $C_{15}H_{13}NNaS$ ($M+Na^+$) 262.0660, found 262.0651. IR (film)ν_{max}:3744, 3442, 2921, 2851, 2310, 2222, 1650, 1590, 1485, 1453, 1398, 1086, 1029, 816, 749, 696, 542 cm^{-1}.



3bg

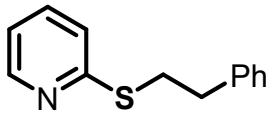
(4-(methylsulfonyl)phenyl)(phenethyl)sulfane(3bg) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 -7.62 (m, 2H), 7.26-7.20 (m, 2H), 7.19-7.15(m, 2H), 7.12-7.01 (m, 3H), 3.12-3.18 (m, 2H), 2.88 (s, 3H), 2.86-2.79 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.7, 139.5, 136.8, 128.7, 128.6, 127.8,

127.0, 126.8, 44.6, 35.0, 33.5. HRMS (ESI) calcd for $C_{15}H_{17}O_2S_2$ ($M+H^+$) 293.0664, found 293.0650. IR (film)ν_{max}:3442, 2955, 2921, 2851, 1640, 1580, 1304, 1149, 1080, 772, 528 cm^{-1}.



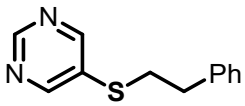
3bh

(3-methyl-5-nitrophenyl)(phenethyl)sulfane (3bh) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 73% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.79 (s, 1H), 7.36 (s, 1H), 7.29 (m, 2H), 7.24-7.17 (m, 3H), 3.25-3.21 (m, 2H), 2.98-2.92 (m, 2H), 2.40 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.3, 139.7, 139.5, 134.7, 128.8, 128.7, 126.9, 121.2, 119.7, 35.4, 34.7, 21.4. HRMS (ESI) calcd for $C_{15}H_{16}NO_2S$ ($M+H^+$) 274.0931, found 274.0945. IR (film)ν_{max}:3745, 3442, 2955, 2921, 2921, 2851, 2310, 1650, 1527, 1455, 1347, 1092, 1030, 743, 518 cm^{-1}.



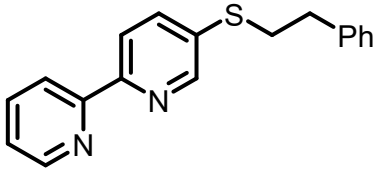
3bi

***1-(4-(hexylthio)phenyl)ethan-1-one* (*3bi*)[10].** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.44 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.45 (td, *J* = 7.7, 1.9 Hz, 1H), 7.34-7.24 (m, 4H), 7.24-7.19 (m, 1H), 7.16 (dt, *J* = 8.1, 1.1 Hz, 1H), 6.96 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 3.48-3.37 (m, 2H), 3.04-2.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.0, 149.6, 140.7, 135.9, 128.8, 128.7, 128.6, 128.5, 126.5, 122.5, 119.4, 35.9, 31.5.



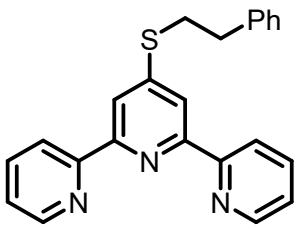
3bj

***5-(phenethylthio)pyrimidine* (*3bj*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.01 (s, 1H), 8.65 (s, 2H), 7.33-7.30 (m, 2H), 7.29-7.22 (m, 1H), 7.20-7.17 (m, 2H), 3.23-3.20 (m, 2H), 2.97-2.94 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.1, 156.1, 139.1, 132.9, 128.8, 128.6, 127.0, 35.7, 35.1. HRMS (ESI) calcd for $C_{12}H_{13}N_2S$ ($M+H^+$) 217.0740, found 217.0742.



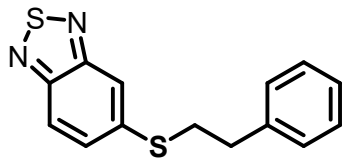
3bk

5-(phenethylthio)-2,2'-bipyridine(3bk) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.62 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 8.59 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.42-8.11 (m, 2H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.70 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.42-7.04 (m, 6H), 3.33-3.08 (m, 2H), 2.93-2.89 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.7, 153.7, 149.2, 139.7, 137.3, 137.0, 133.9, 128.6, 128.6, 126.67, 123.7, 121.0, 120.9, 35.6, 35.0. HRMS (ESI) calcd for $C_{18}H_{17}N_2S$ ($M+H^+$) 293.1107, found 293.1102. IR (film)ν_{max}:3745, 3421, 3060, 3027, 2923, 2852, 1586, 1572, 1541, 1495, 1451, 1432, 1360, 1270, 1107, 1014, 848, 791, 744, 696, 638, 568, 505 cm^{-1}.



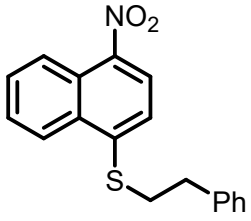
3bl

4'-(phenethylthio)-2,2':6',2''-terpyridine（3bl） Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.61 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.51 (dt, *J* = 8.0, 1.2 Hz, 2H), 8.29 (s, 2H), 7.74 (td, *J* = 7.7, 1.8 Hz, 2H), 7.33-7.11 (m, 7H), 3.39-3.25 (m, 2H), 3.00-2.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.9, 155.1, 151.1, 149.1, 139.9, 136.8, 128.8, 128.7, 126.7, 123.9, 121.4, 117.7, 35.0, 32.4. HRMS (ESI) calcd for $C_{23}H_{20}N_3S$ ($M+H^+$) 370.1372, found 370.1357. IR (film)ν_{max}:3443, 3060, 2924, 2852, 1650, 1576, 1556, 1464, 1433, 1390, 1327, 1265, 1093, 1070, 1040, 987, 871, 818, 789, 742, 697, 679, 657, 620, 577 cm^{-1}.



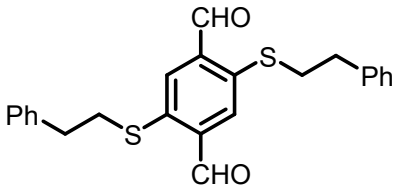
3bm

5-(phenethylthio)benzo[c][1,2,5]thiadiazole(3bm) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.7 Hz, 1H), 7.50 (dd, *J* = 8.7, 7.1 Hz, 1H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.19 (m, 3H), 3.45-3.38 (m, 2H), 3.09-3.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.9, 153.6, 139.8, 131.2, 129.6, 128.6, 128.5, 126.7, 125.4, 118.2, 35.3, 33.5. HRMS (ESI) calcd for $C_{14}H_{13}N_2S_2$ ($M+H^+$) 273.0515, found 273.0505. IR (film)ν_{max}:3745, 3421, 2954, 2921, 2852, 2379, 2310, 1651, 1515, 1495, 1453, 1311, 1268, 1205, 1090, 1029, 963, 891, 852, 826, 795, 744, 696, 596, 570, 518 cm^{-1}.



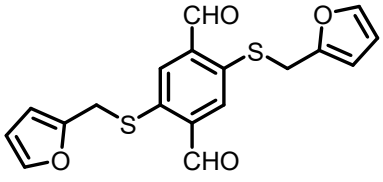
3bn

(4-nitronaphthalen-1-yl)(phenethyl)sulfane(3bn) Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69-8.60 (m, 1H), 8.41-8.27 (m, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.73-7.69 (m, 1H), 7.62-7.58 (m, 1H), 7.40-7.28 (m, 3H), 7.27-7.19 (m, 3H), 3.37-3.33 (m, 2H), 3.07-3.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.9, 143.8, 139.4, 131.8, 129.7, 128.7, 128.5, 127.3, 126.9, 125.3, 124.7, 124.0, 123.9, 120.5, 34.8, 33.9. HRMS (ESI) calcd for $C_{18}H_{16}NO_2S$ ($M+H^+$) 310.0896, found 310.0894. IR (film)ν_{max}:3744, 3420, 3026, 2922, 2857, 2379, 2351, 2310, 1650, 1555, 1495, 1453, 1364, 1190, 1093, 1030, 990, 819, 756, 696, 518, 503 cm^{-1}.



3bo

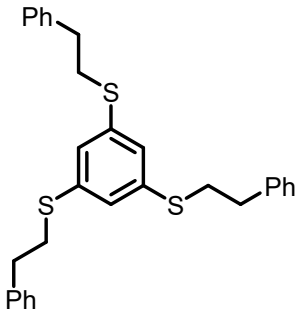
***2,5-bis(phenethylthio)terephthalaldehyde*(*3bo*)** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.43 (s, 2H), 7.88 (s, 2H), 7.35-7.33 (m, 6H), 7.31-7.23 (m, 10H), 3.31-3.27 (m, 4H), 3.02-2.98 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.6, 139.5, 138.9, 137.3, 131.6, 128.9, 128.7, 127.0, 35.6, 35.3. HRMS (ESI) calcd for $C_{24}H_{22}NaO_2S_2$ ($M+Na^+$) 429.0953, found 429.0936. IR (film)ν_{max}:3858, 3740, 3421, 2955, 2922, 2851, 2378, 2310, 1651, 1459, 1378, 1092, 1028, 748, 518 cm^{-1}.



3bp

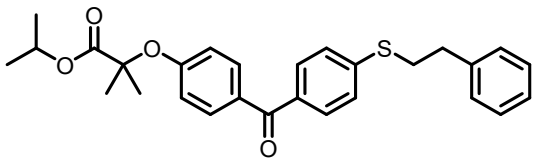
2,5-bis((furan-2-ylmethyl)thio)terephthalaldehyde（3bp） Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow

liquid, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.24 (s, 2H), 7.94 (s, 2H), 7.33 (dd, *J* = 1.9, 0.9 Hz, 2H), 6.25 (dd, *J* = 3.2, 1.9 Hz, 2H), 6.08 (dd, *J* = 3.2, 0.8 Hz, 2H), 4.16 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.6 149.2, 142.9, 138.4, 138.4 133.8 110.8, 109.29, 31.9 HRMS (ESI) calcd for $C_{18}H_{14}NaO_4S_2$ ($M+Na^+$)381.0226, found 381.0209.



3bq

1,3,5-tris(phenethylthio)benzene **(*3bq*).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.38-7.14 (m, 18H), 3.17-3.13 (m, 3H), 3.01-2.87 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.2, 139.8, 139.7, 128.7, 128.7, 128.6, 128.6, 128.2, 126.8, 126.7, 126.7, 126.5, 123.1, 40.3, 35.9, 35.5, 34.8. HRMS (ESI) calcd for $C_{30}H_{31}S_3$ ($M+H^+$) 487.1582, found 487.1582.



4aa

isopropyl 2-methyl-2-(4-(4-(phenethylthio)benzoyl)phenoxy)propanoate **(4aa).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 32/1 to 16/1 as eluent). Yellow liquid, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78-7.66 (m, 4H), 7.39-7.28 (m, 4H), 7.26-7.22 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.09 (hept, *J* = 6.3 Hz, 1H), 3.28-3.24 (m, 2H), 3.01-2.97 (m, 2H), 1.66 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.7 173.3 159.5, 142.9, 139.9 134.9, 131.9, 130.8, 130.5, 128.7, 128.6, 126.8 126.7, 117.3, 79.5 69.4 35.4 33.8, 25.5 21.6. HRMS

(ESI) calcd for $C_{28}H_{31}O_4S$ ($M+H^+$) 463.1938, found 463.1920. IR (film)ν_{max}:3745, 3421, 2924, 2852, 2310, 1726, 1648, 1593, 1501, 1455, 1383, 1283, 1247, 1175, 1145, 1100, 926, 850, 760, 697, 517 cm^{-1}.

6. References

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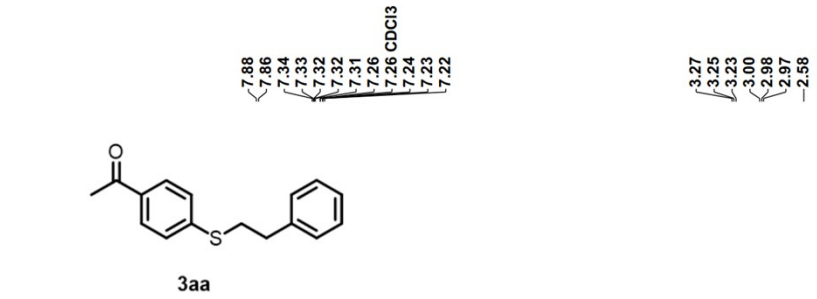
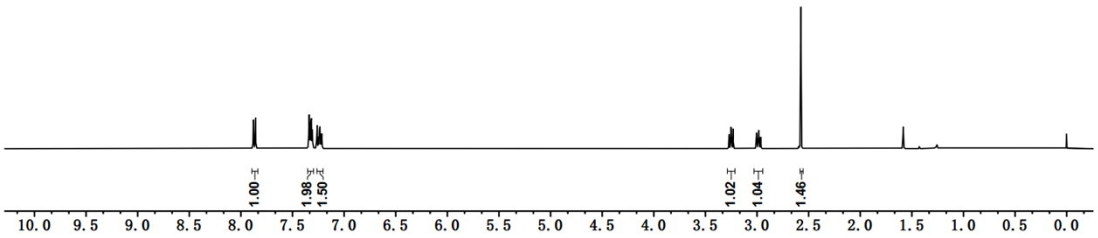
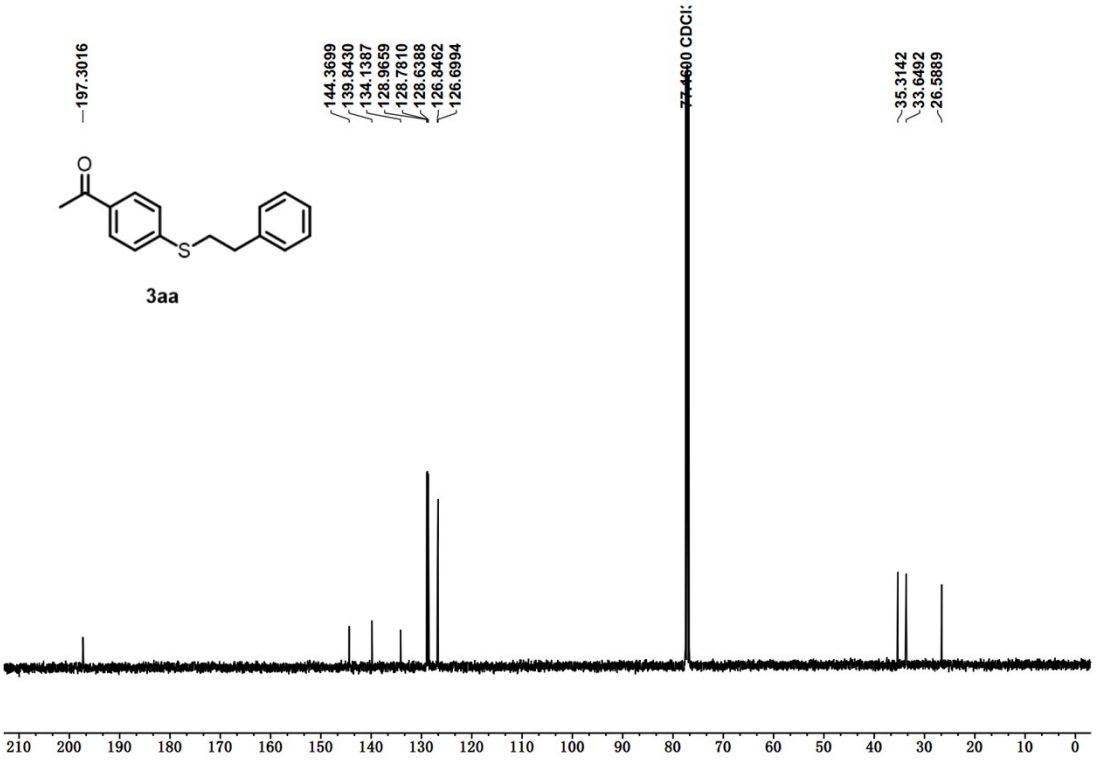
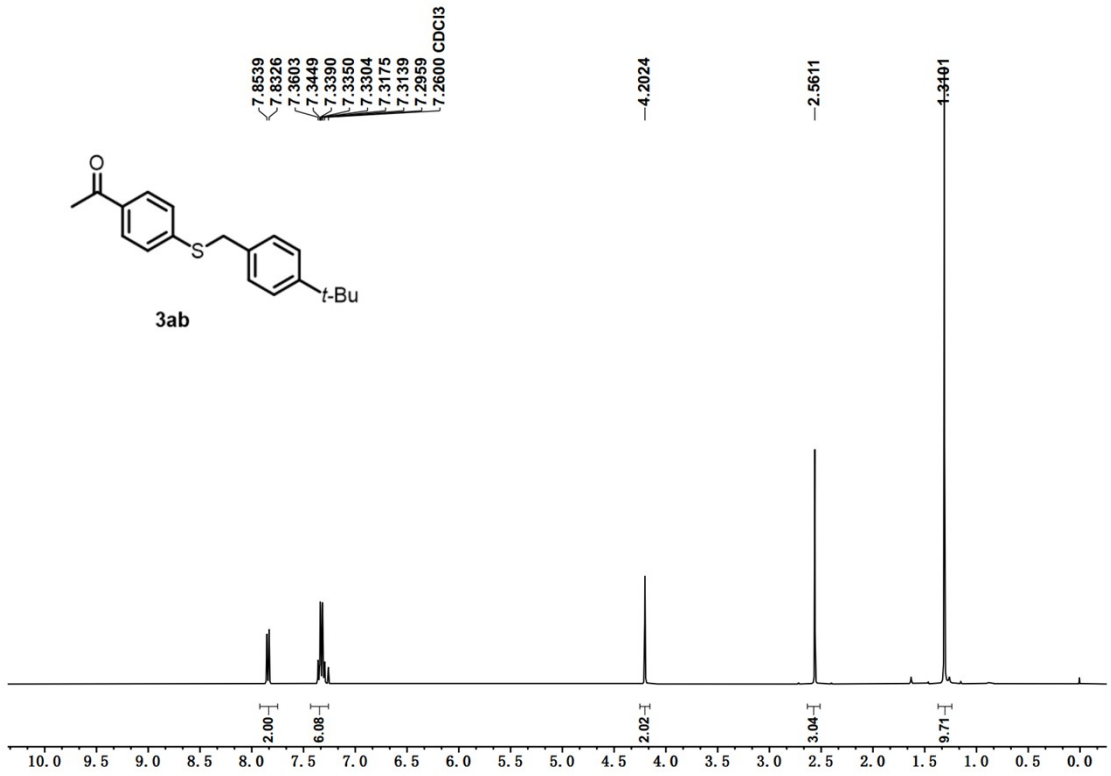
7. Copies of ^{1}H and ^{13}C NMR Spectra





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S
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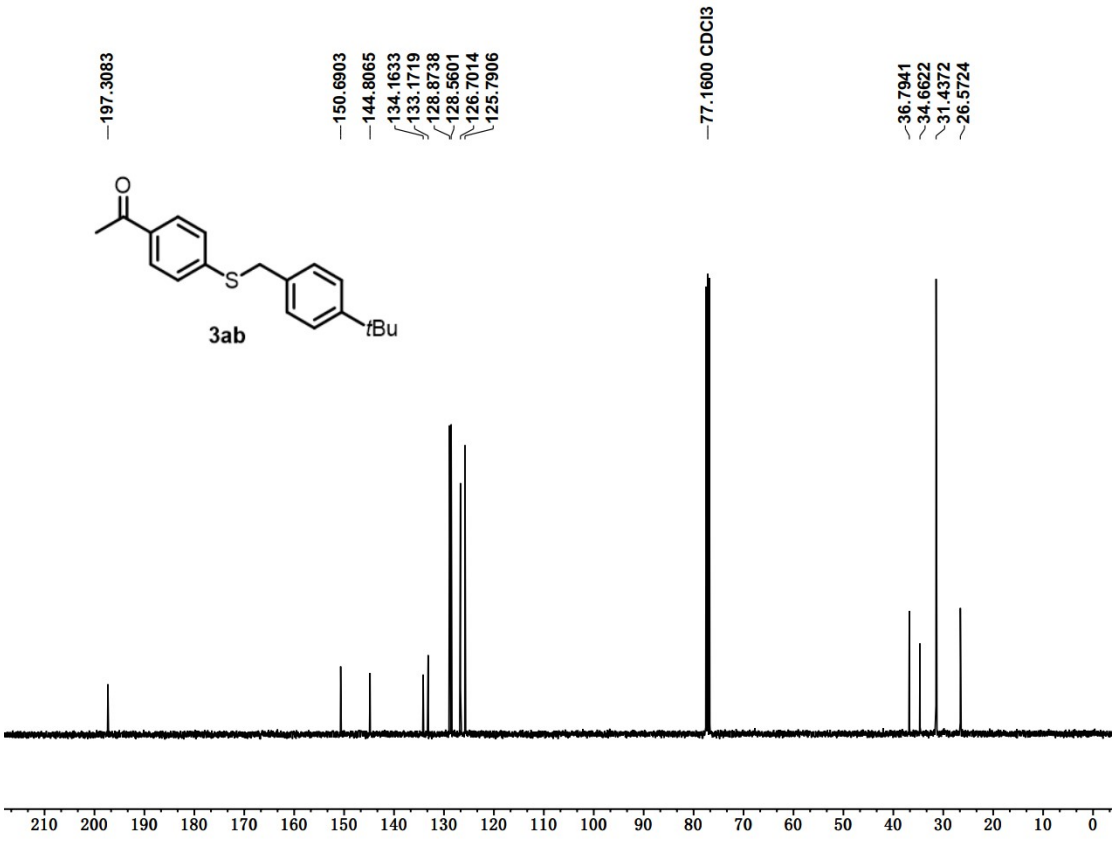
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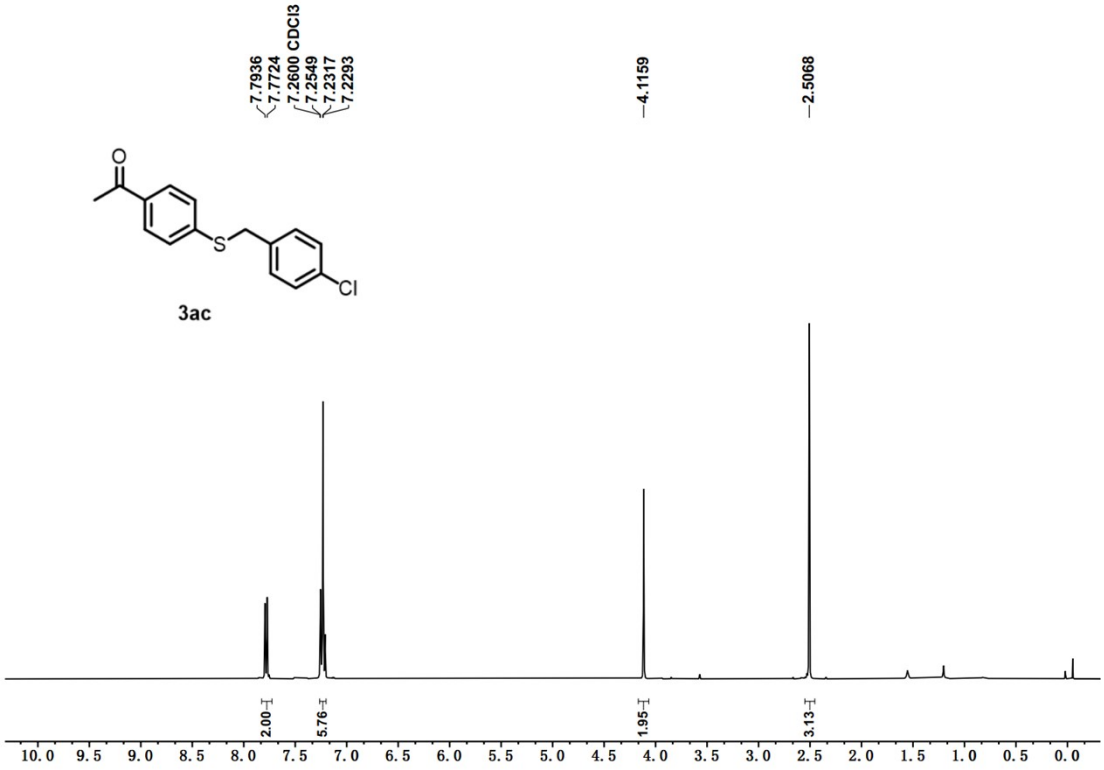
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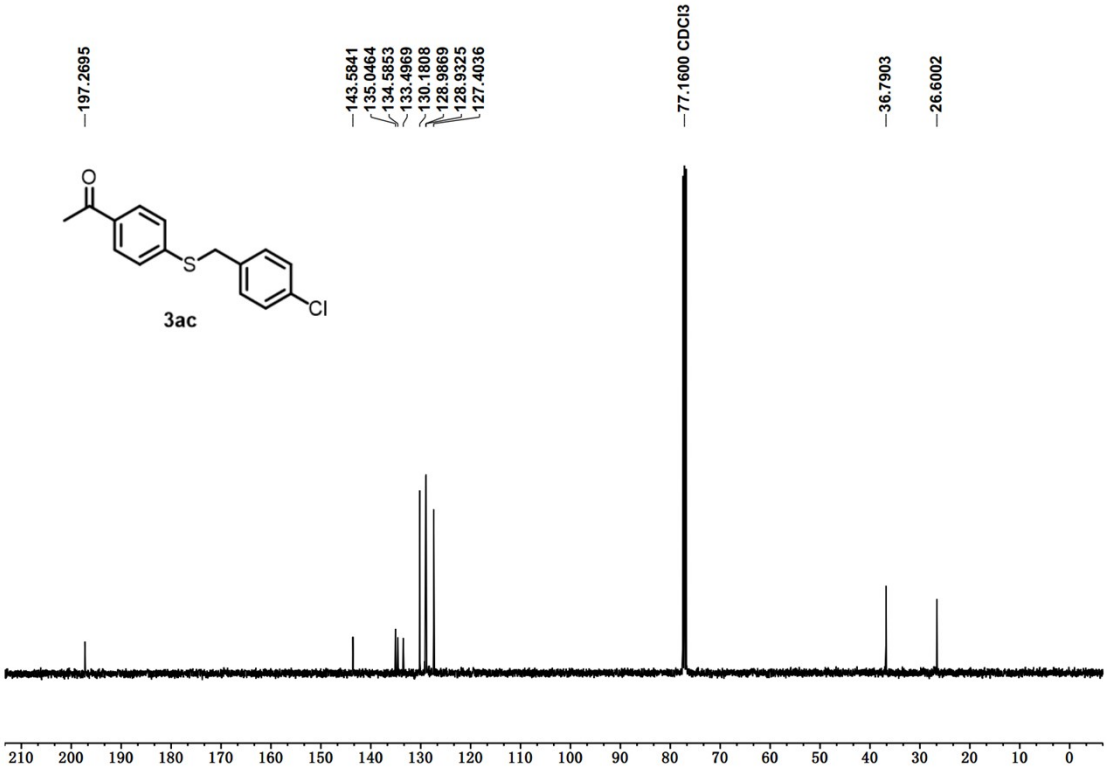
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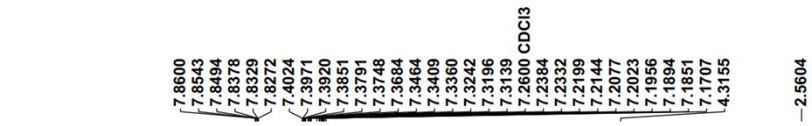
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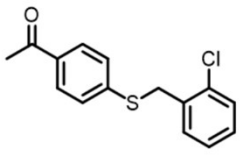
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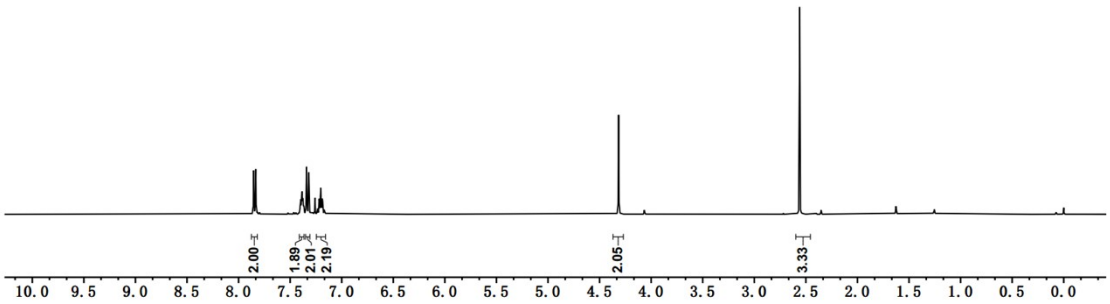
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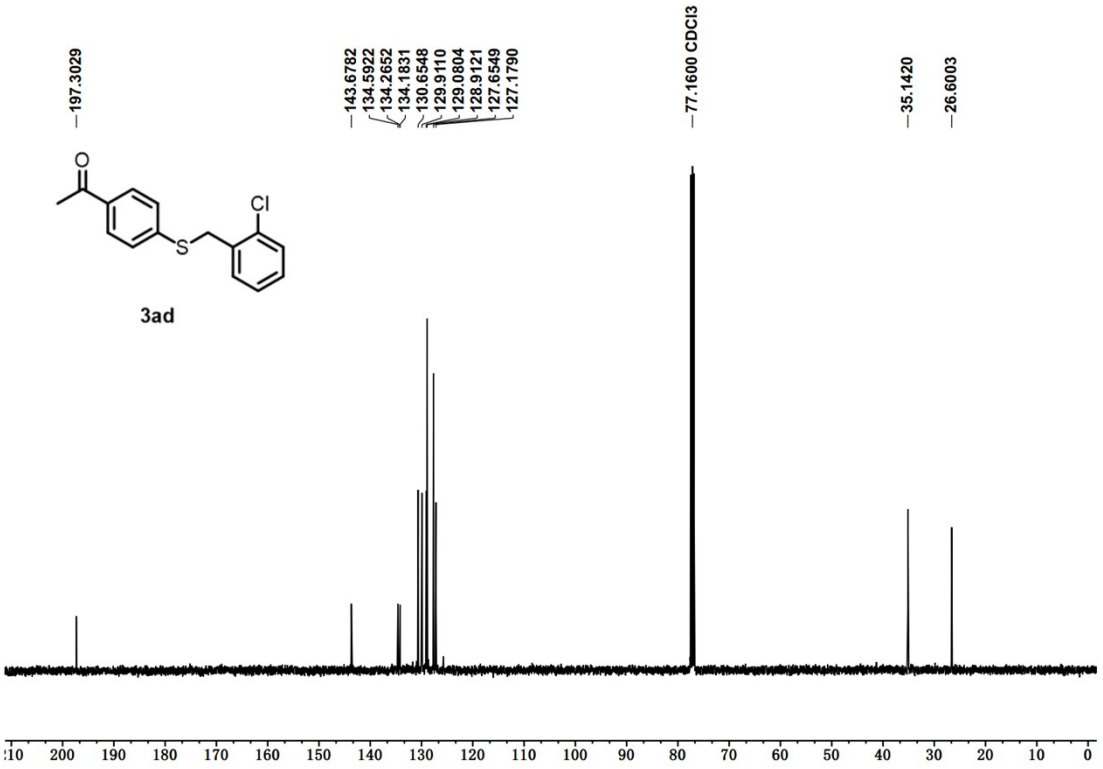
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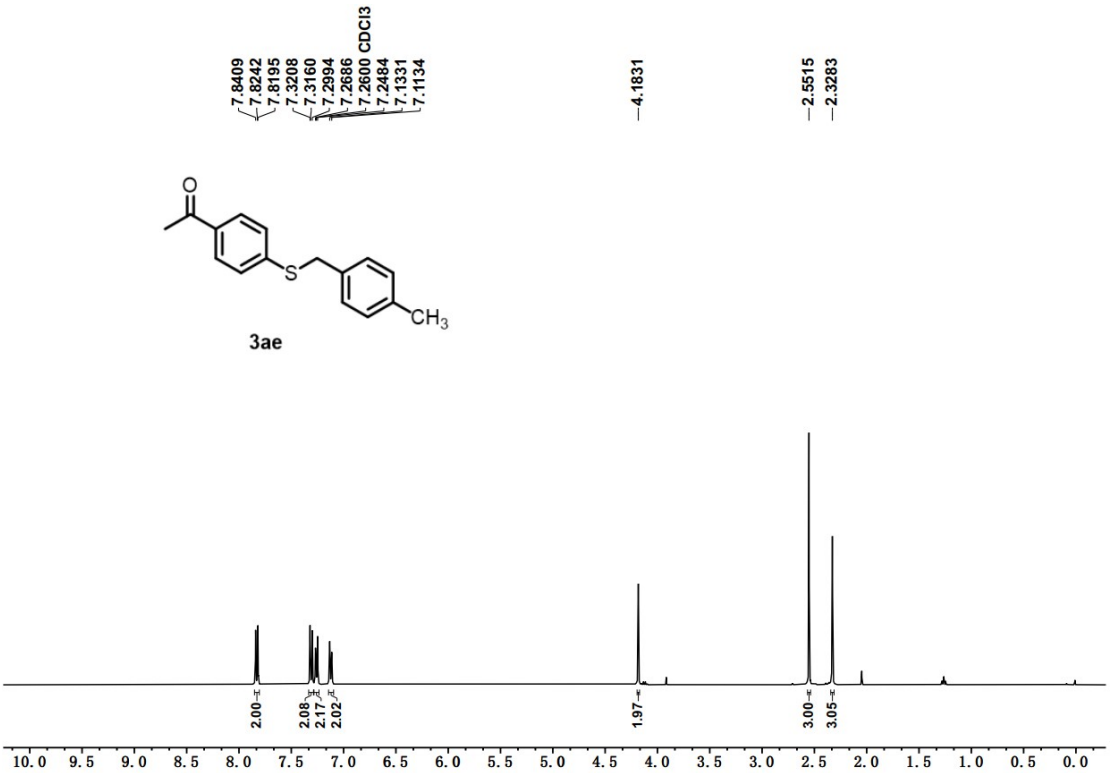
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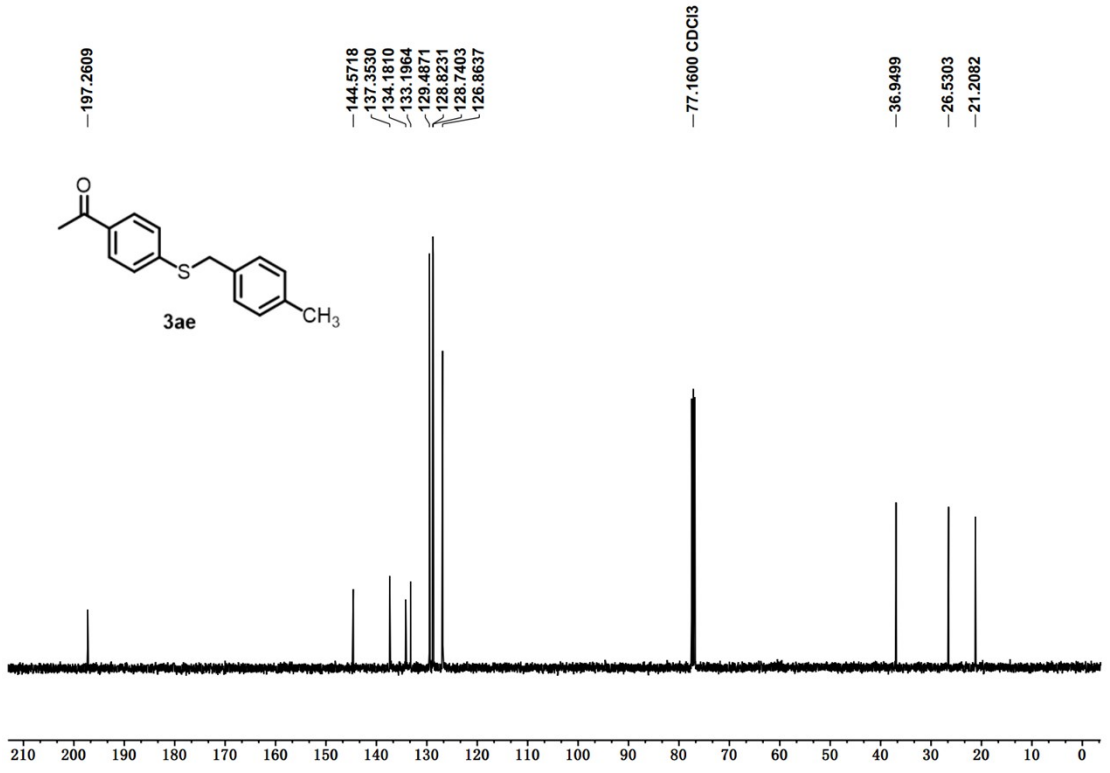
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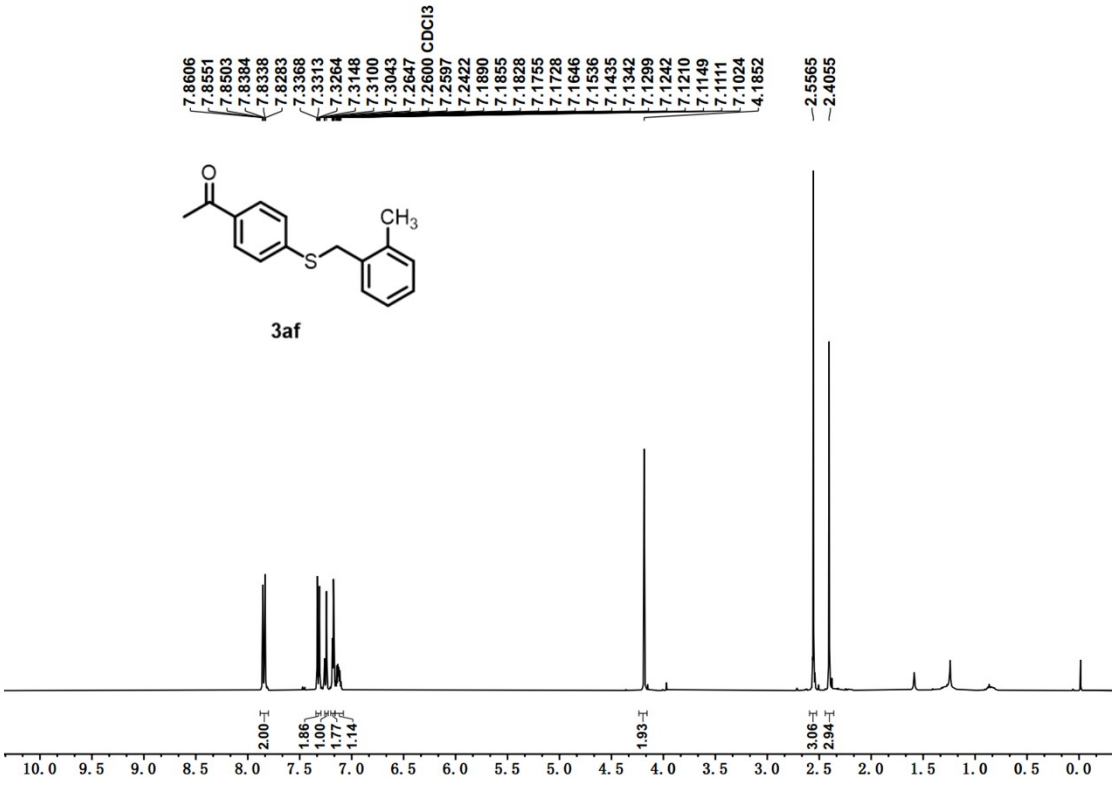
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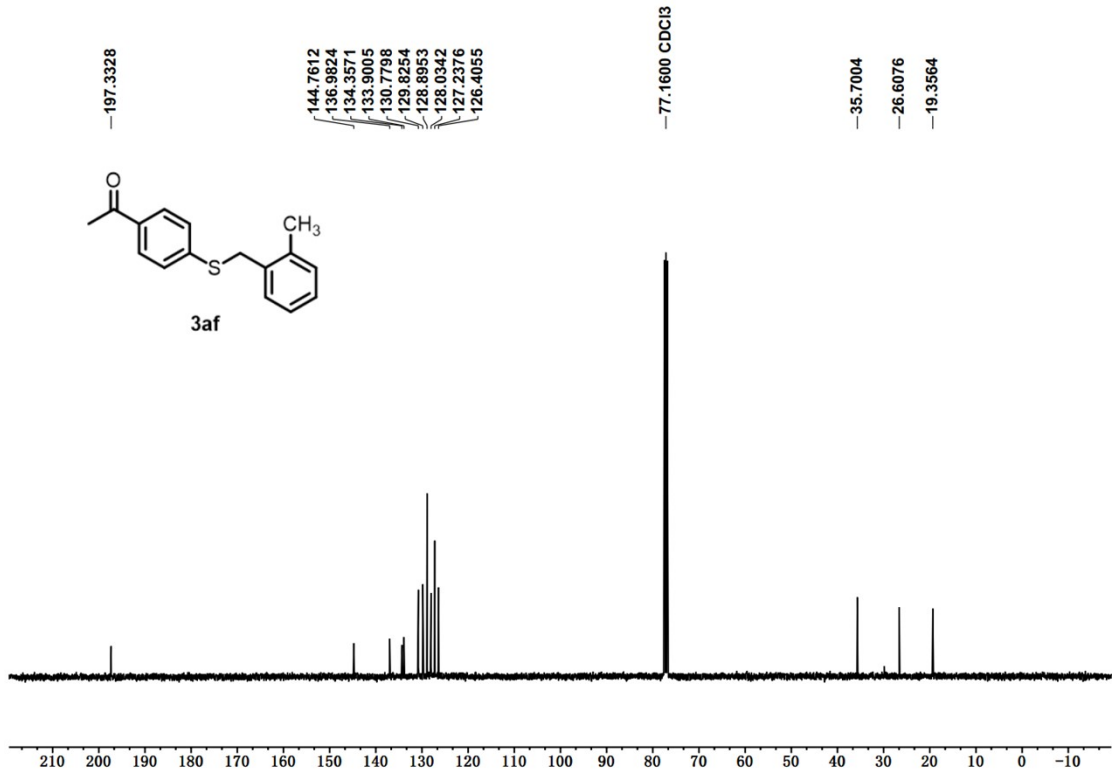
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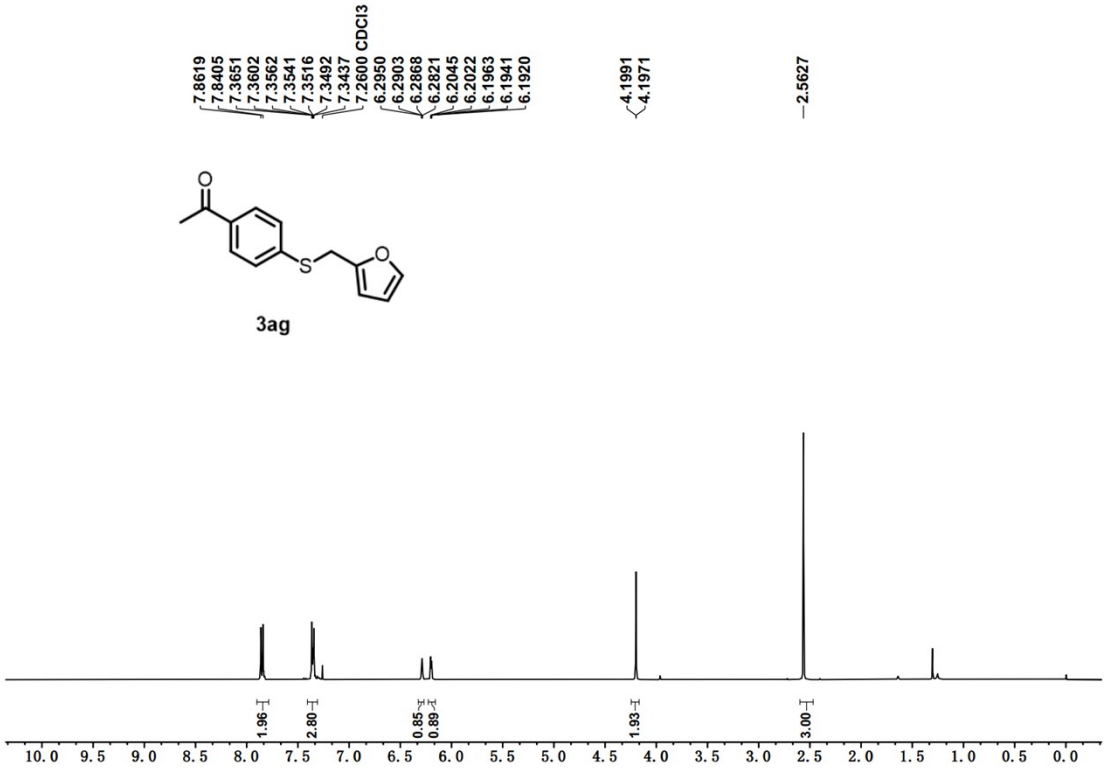
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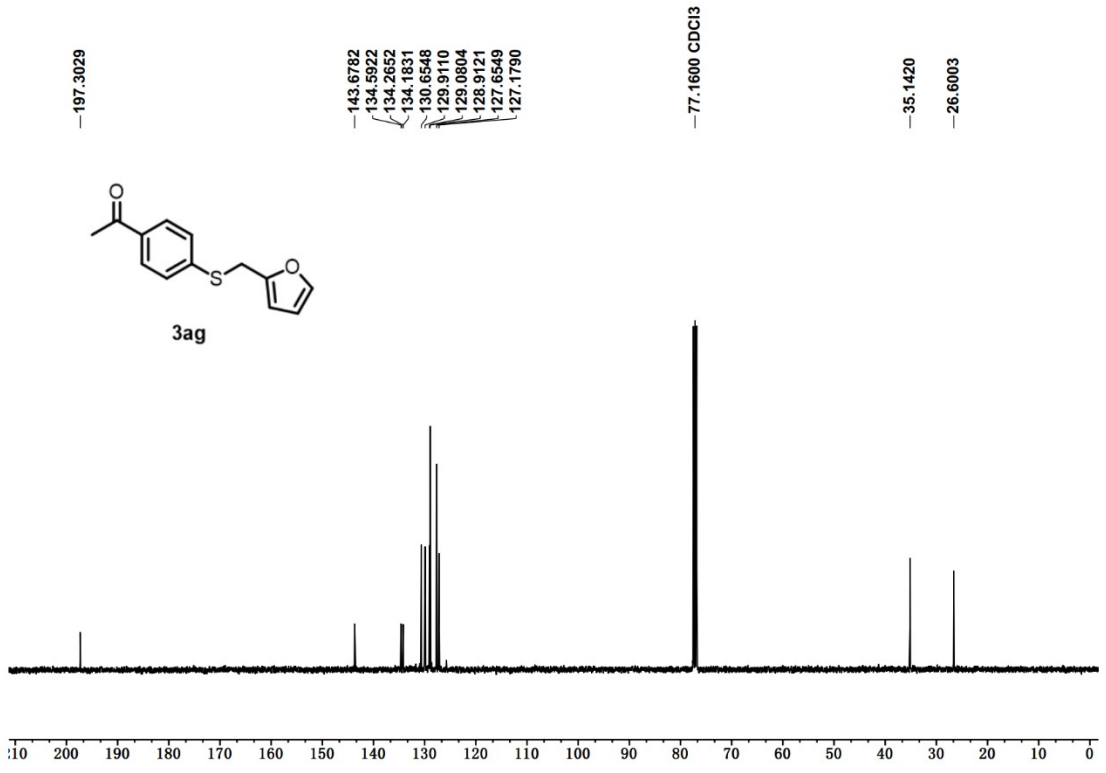
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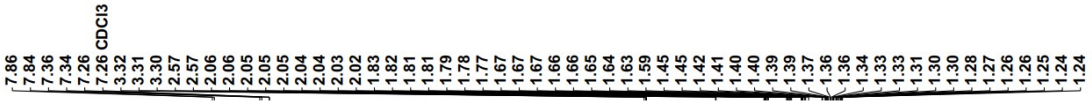
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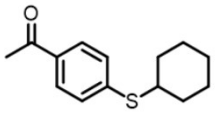

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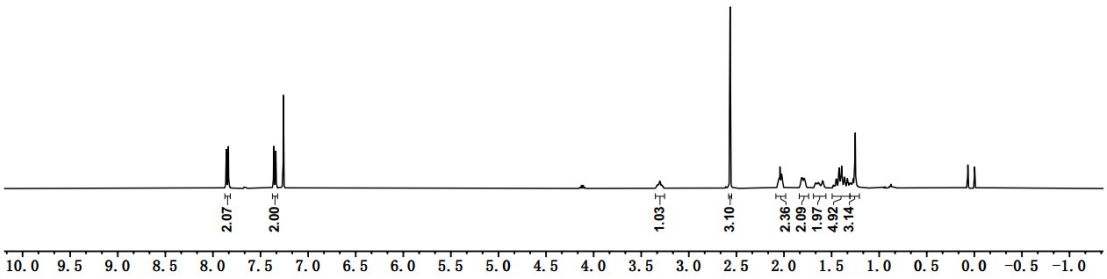
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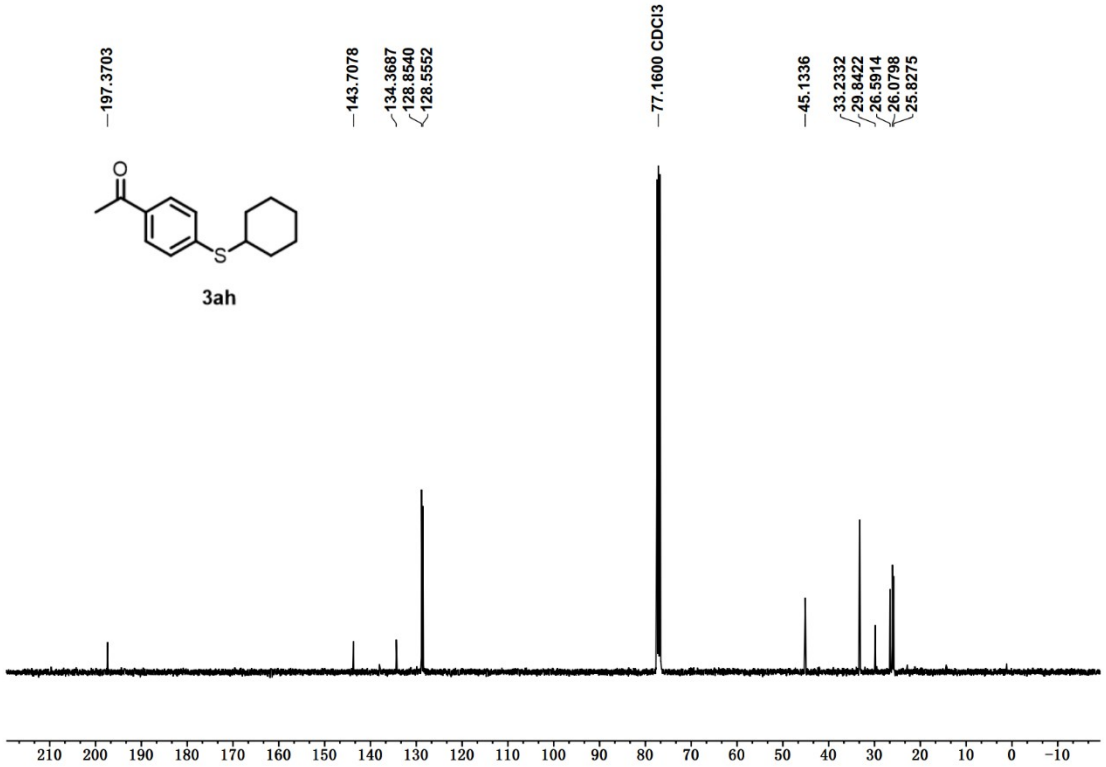
4.92
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0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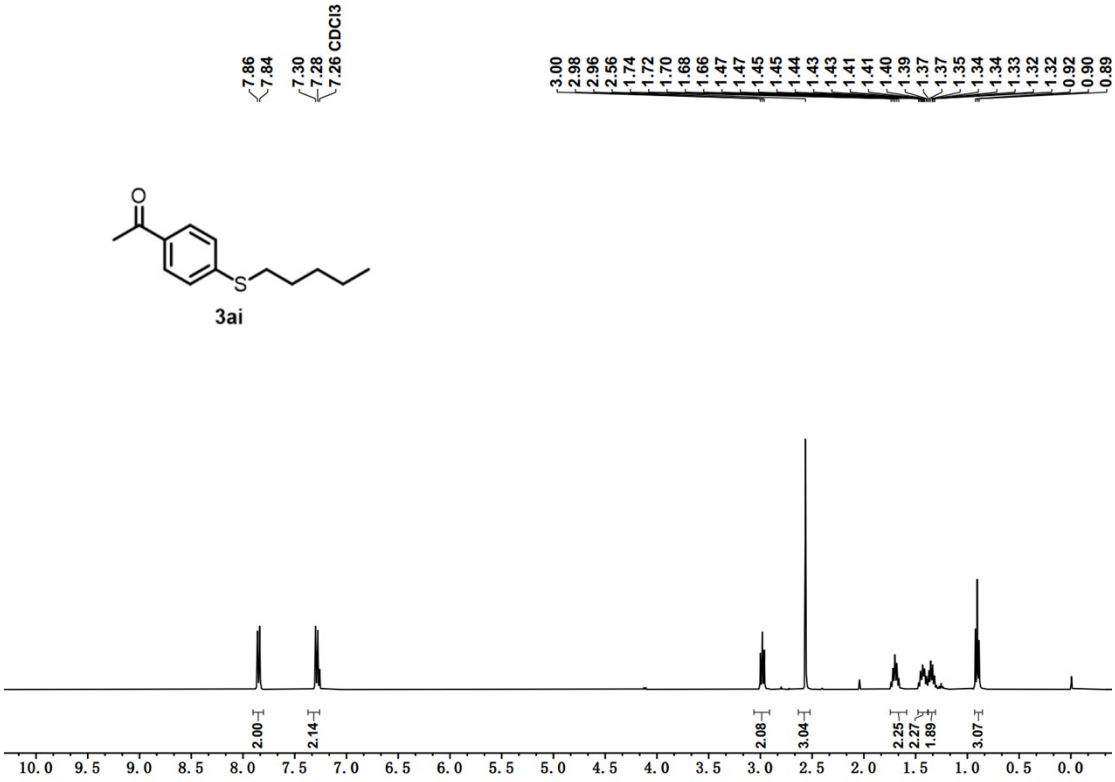
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1.43
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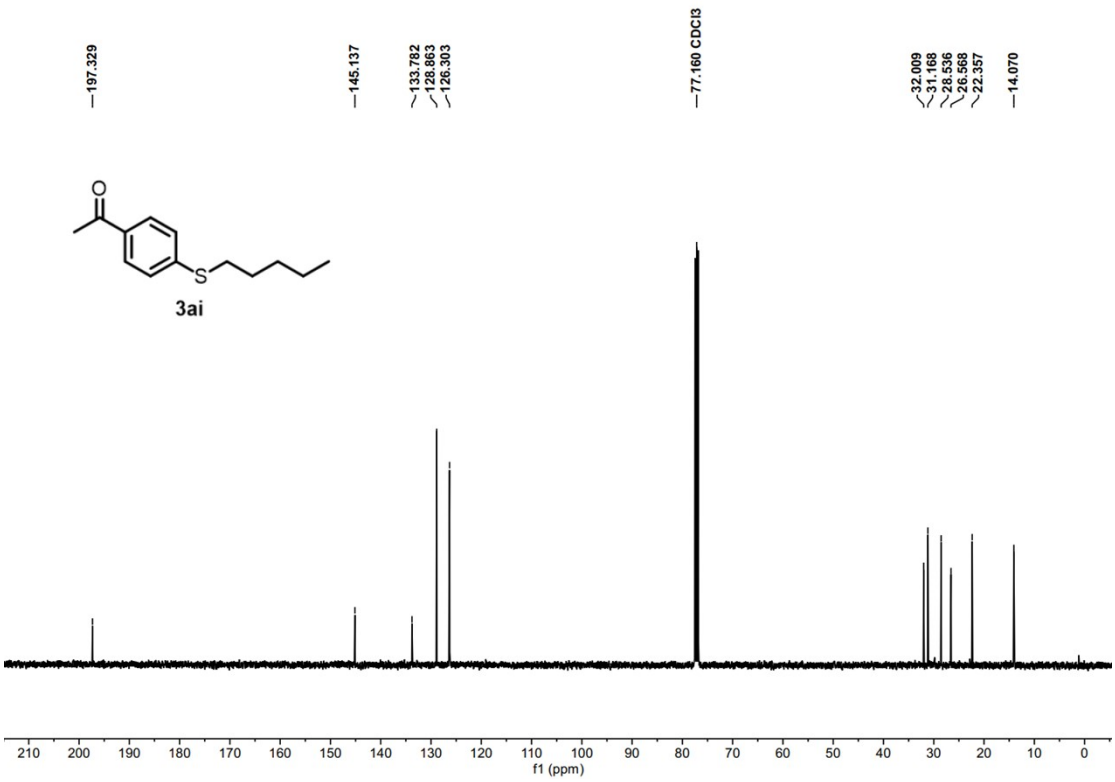
1.40
1.39
1.37
1.37
1.35
1.34
1.34
1.33
1.32
1.32
0.92
0.90
0.89
3ai
2.00
2.14
2.08
3.04
2.25
2.27
1.89
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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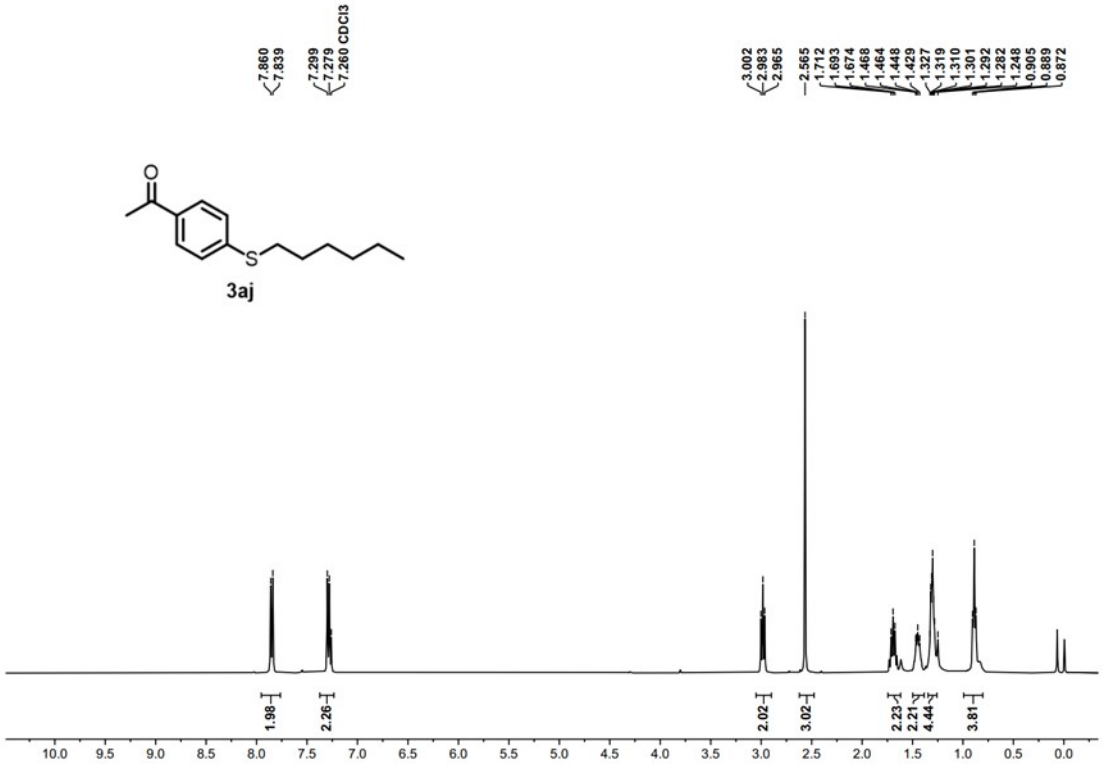
f1 (ppm)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1.319
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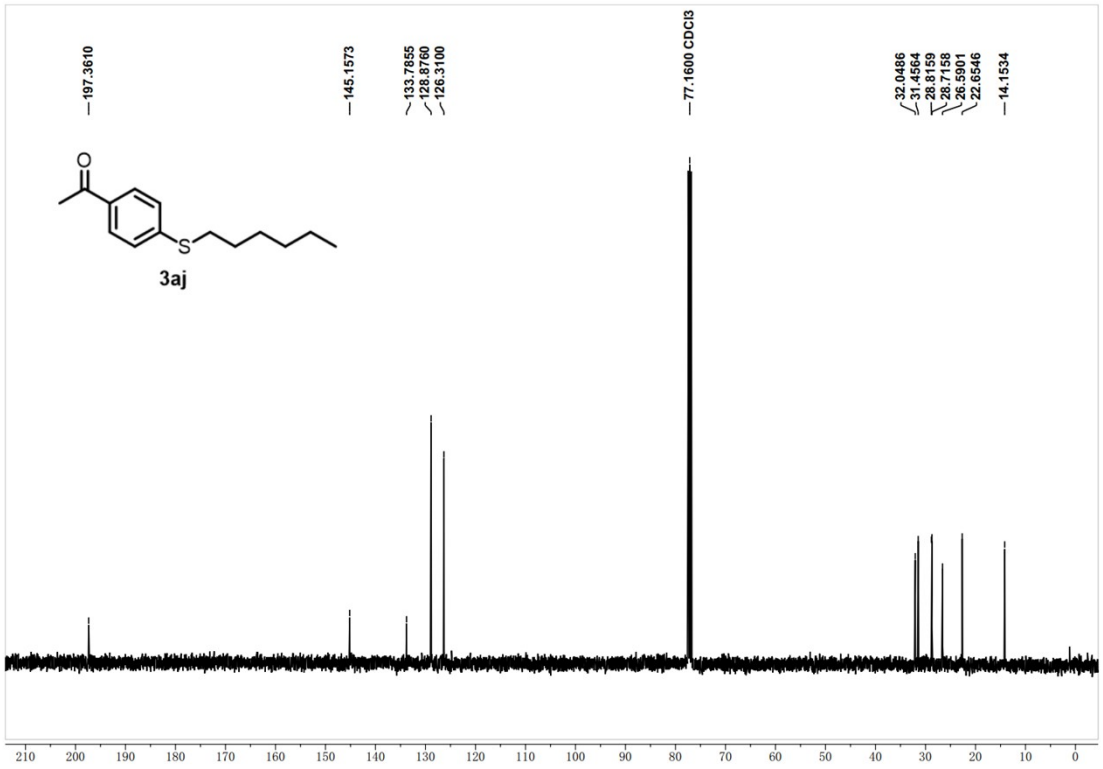
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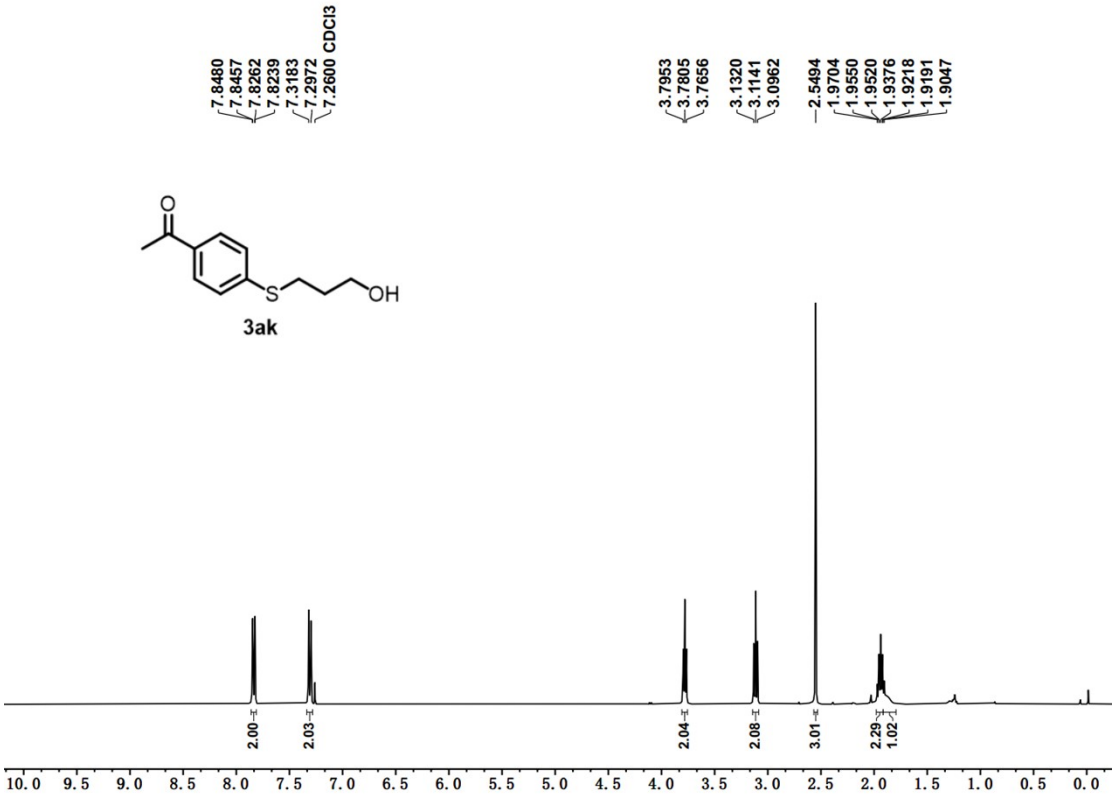
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O
S
OH
3ak
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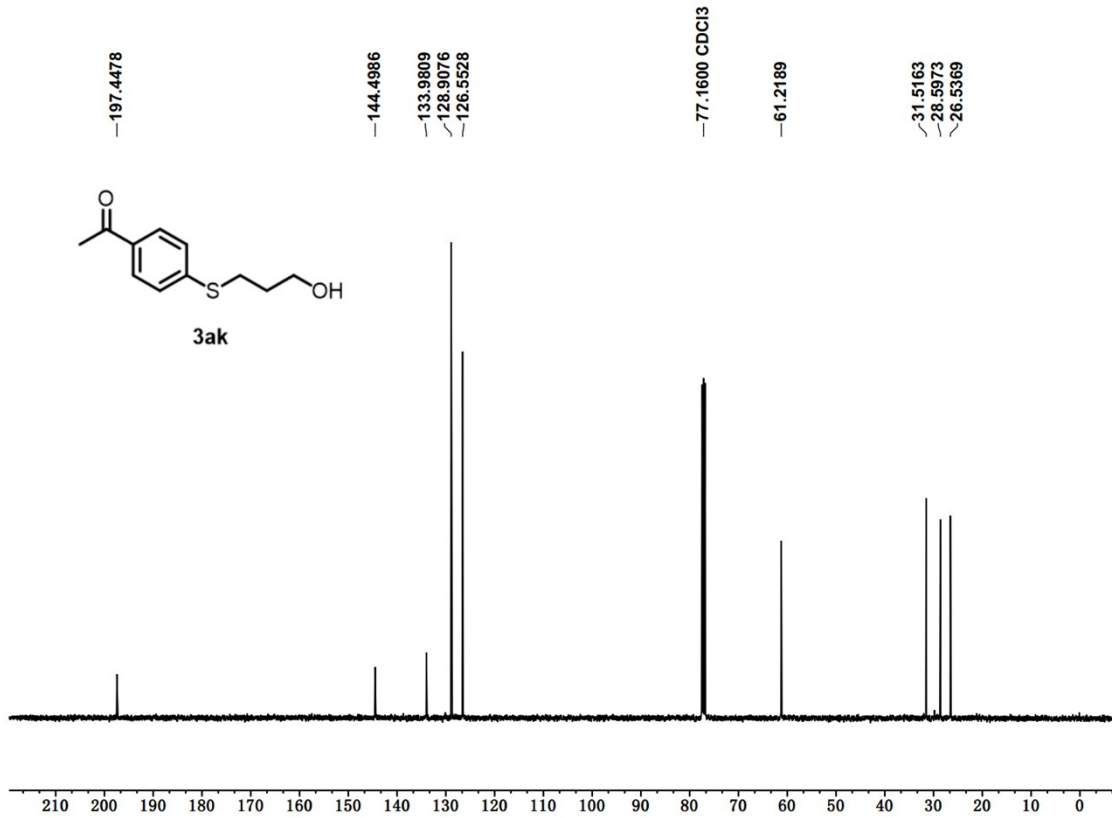
2.03
2.04
2.08
3.01
2.29
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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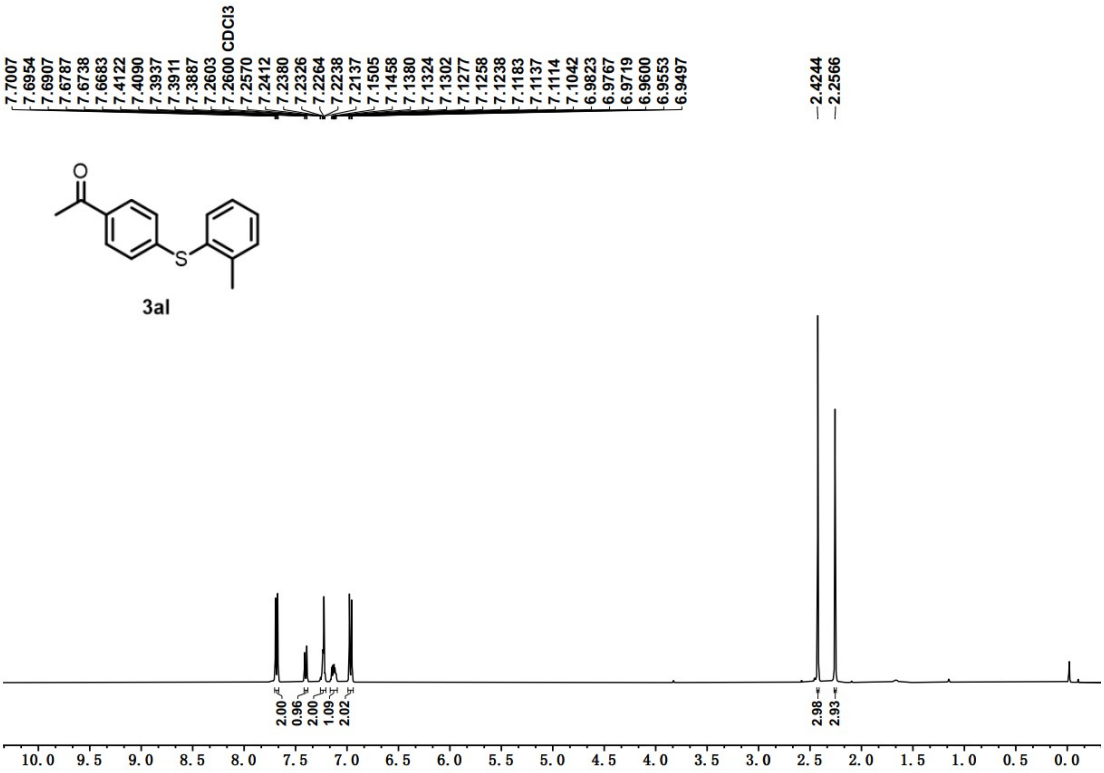
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2.2566
3al
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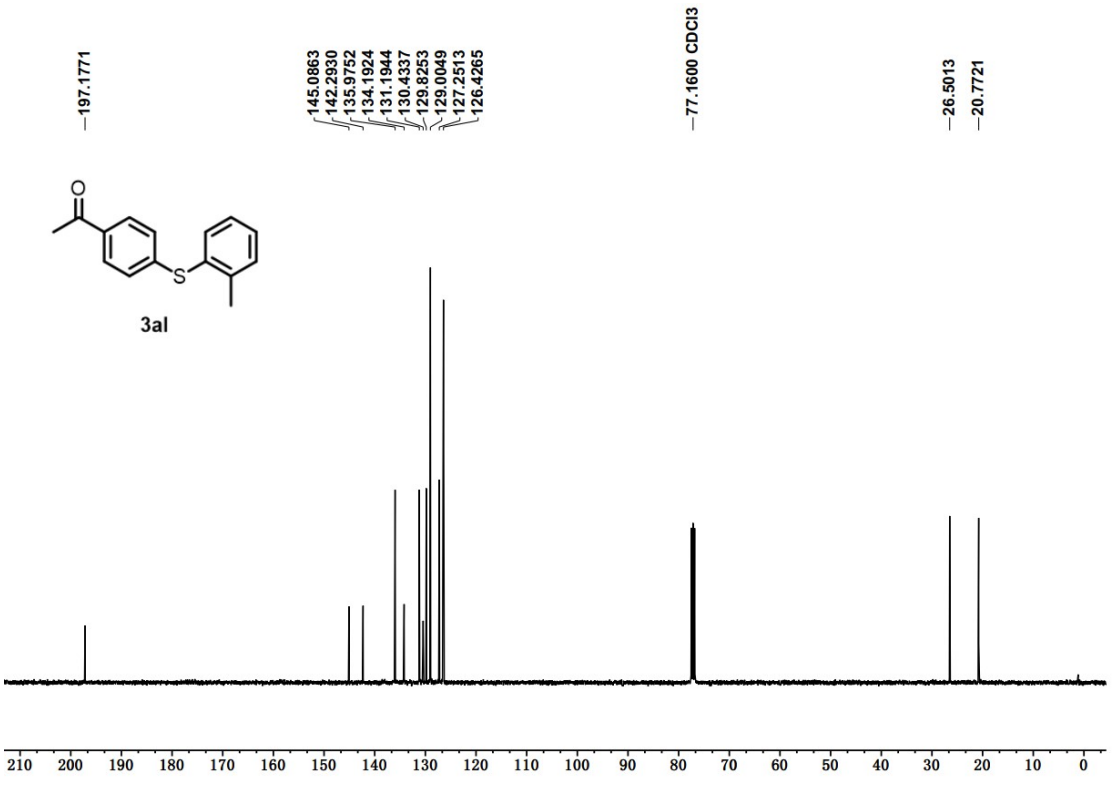
0.96
2.00
1.09
2.02
2.98
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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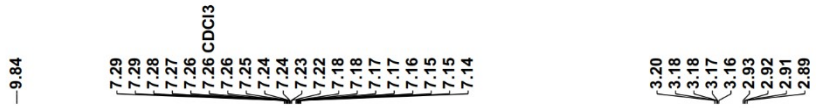
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7.18
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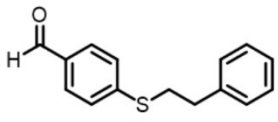
2.91
2.89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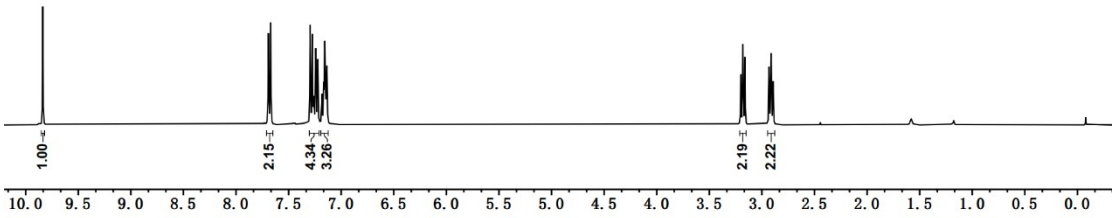
S

3ba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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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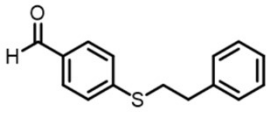
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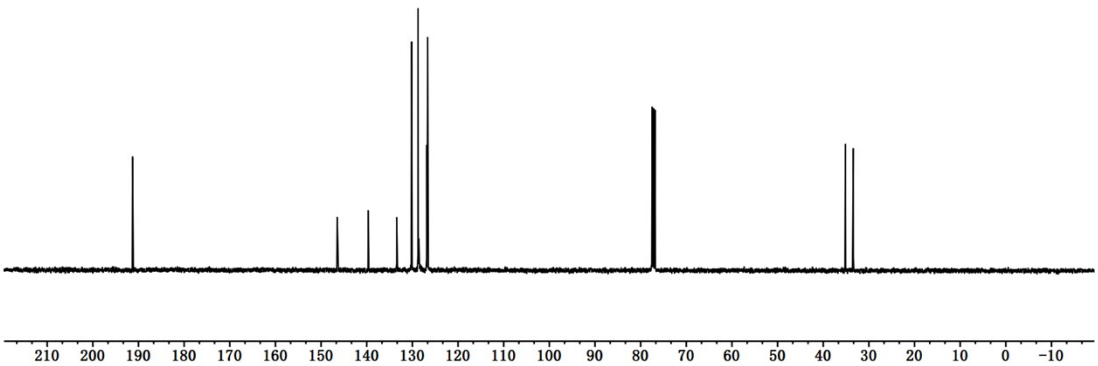
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0
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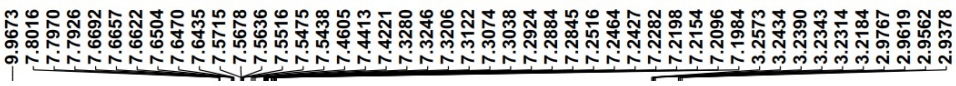
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7.2427
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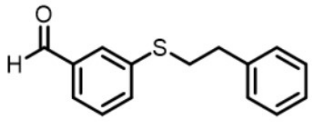
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S

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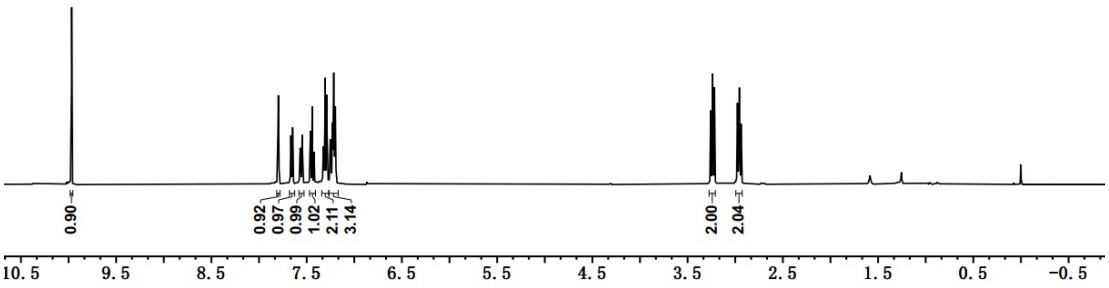
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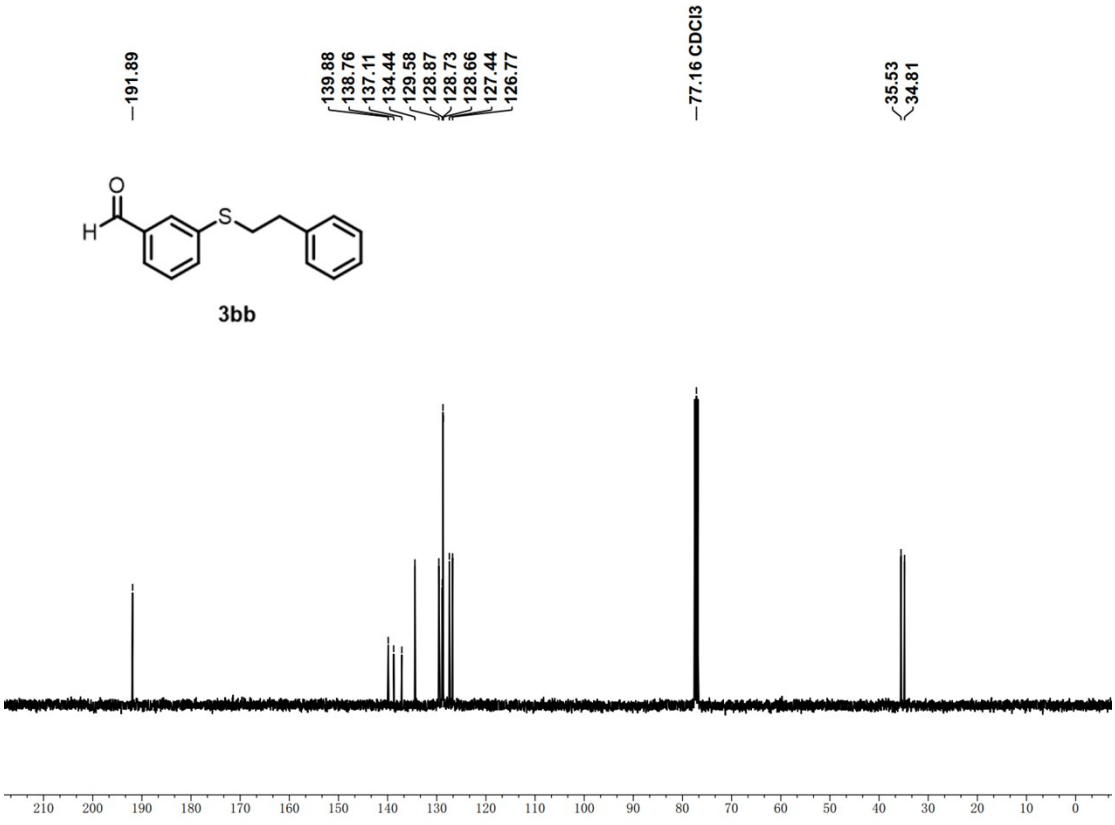
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O
H
S
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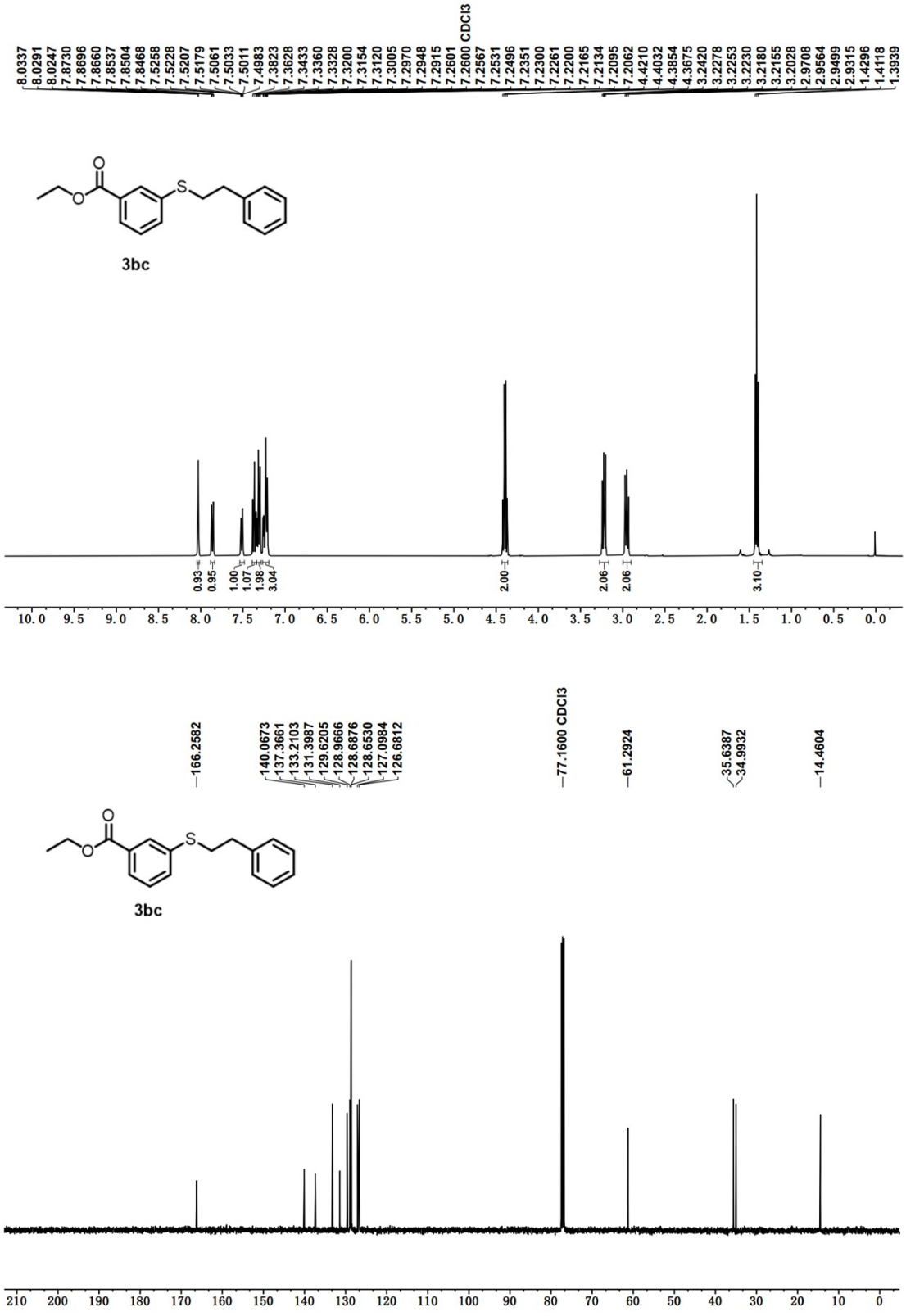
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2.00
2.06
2.06
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10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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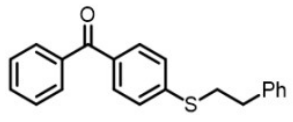
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S
Ph

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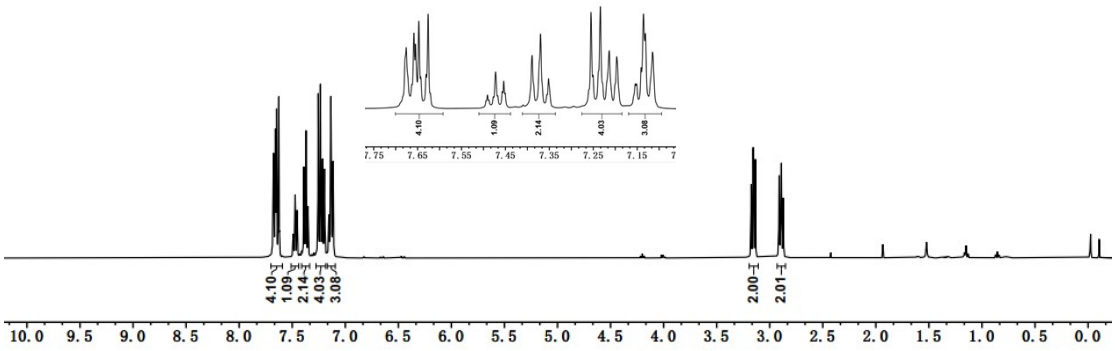
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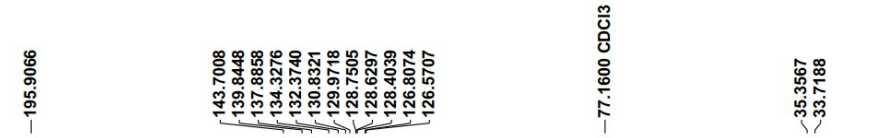
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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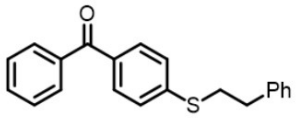
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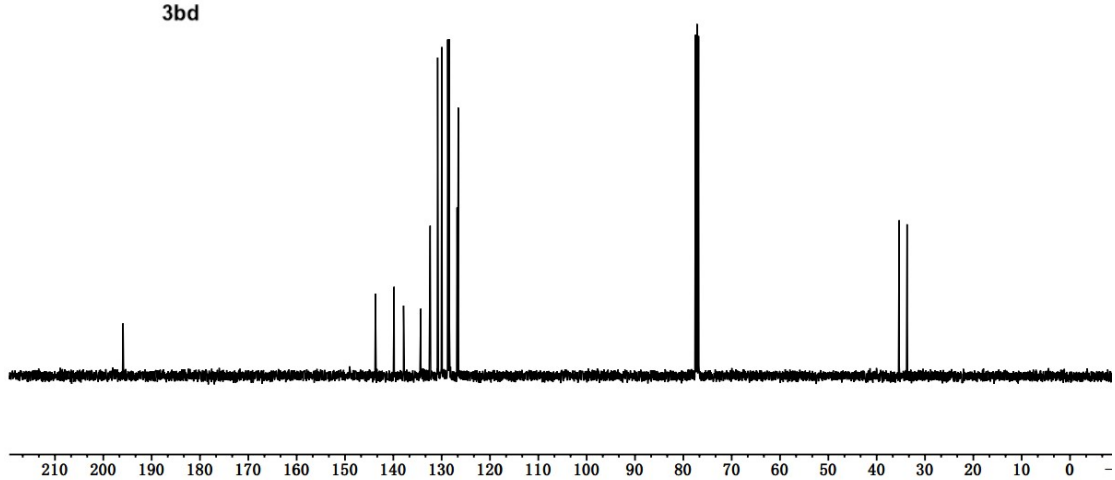
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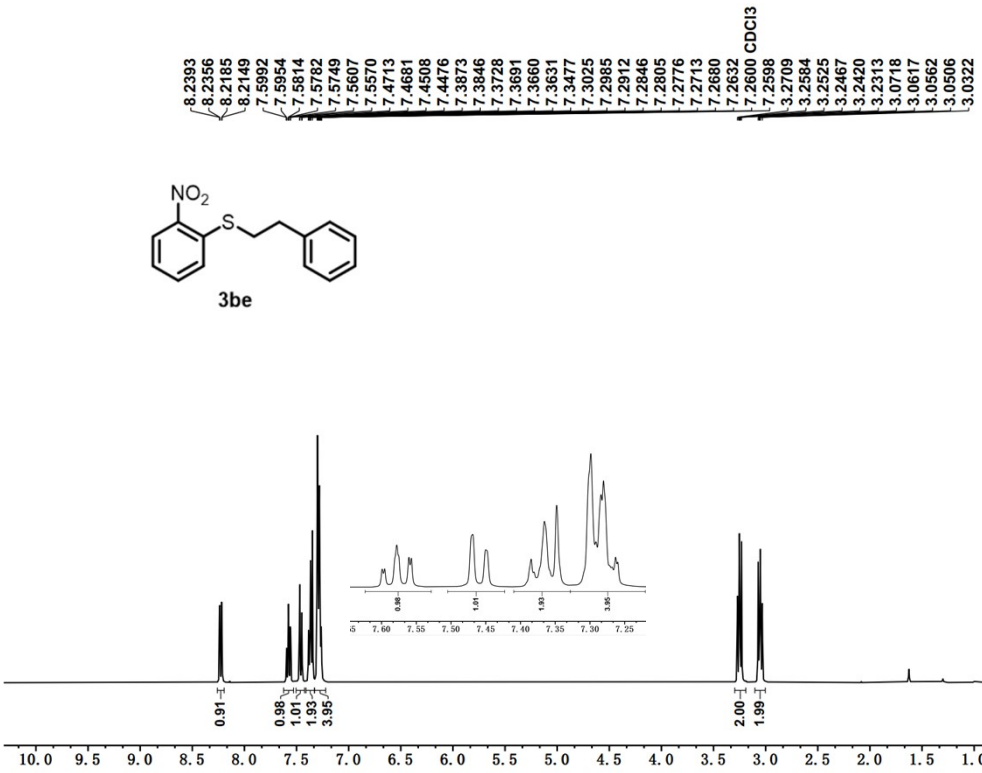
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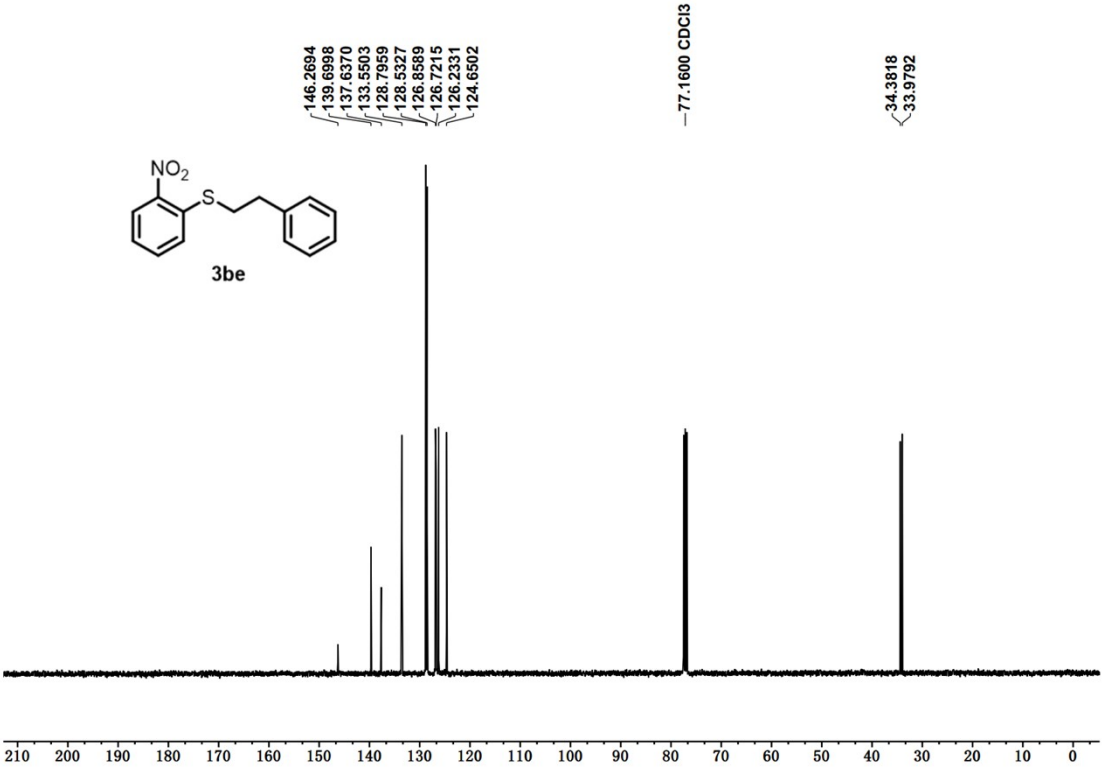
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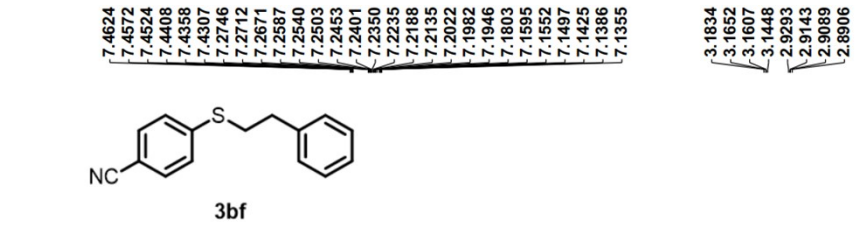
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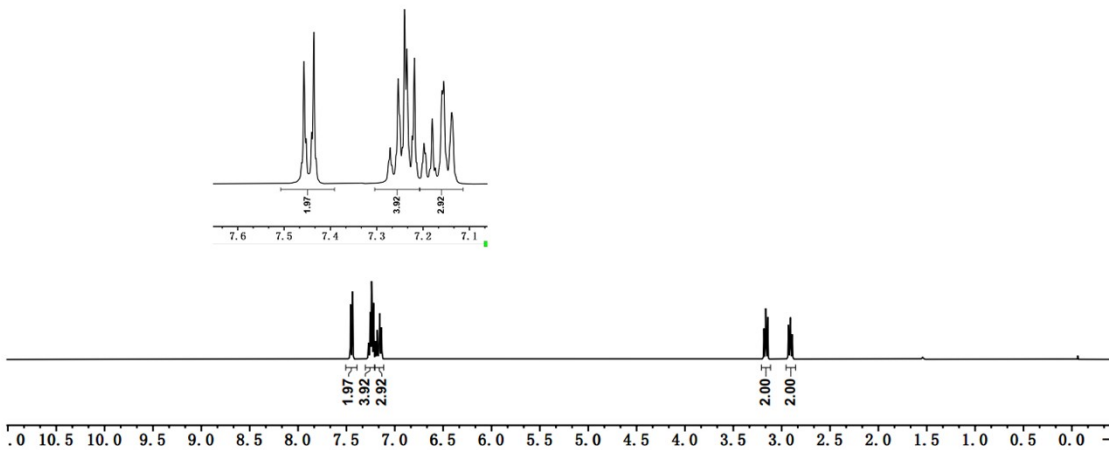
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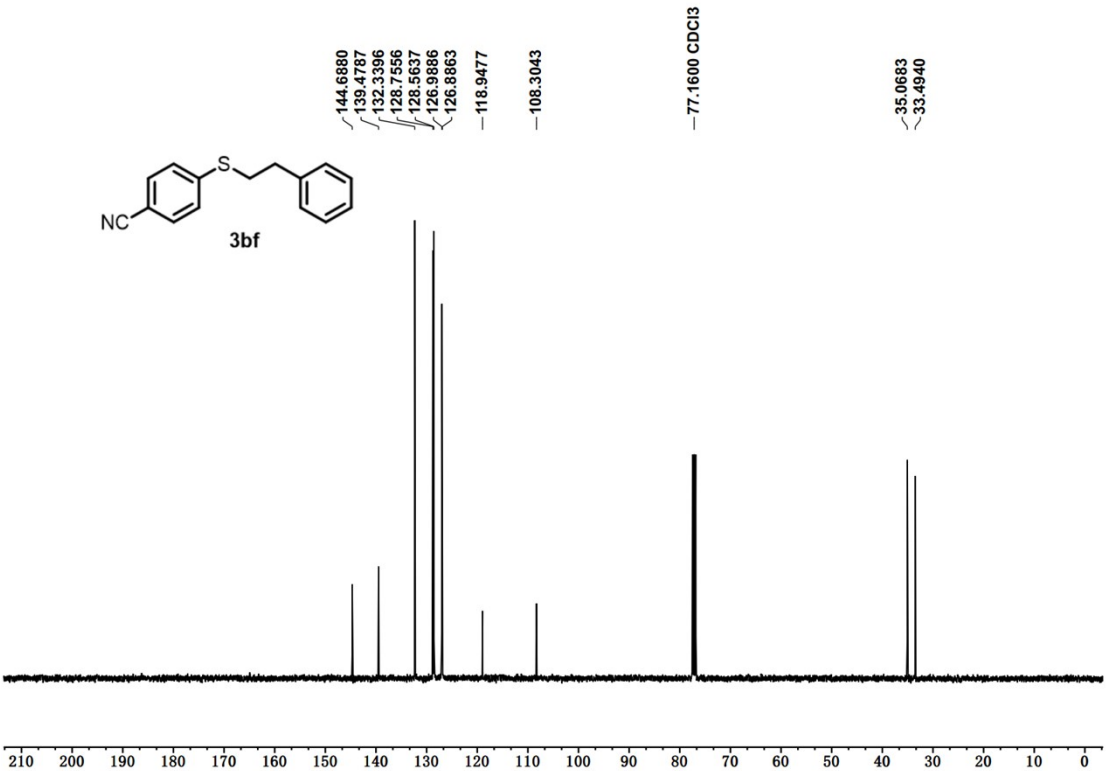
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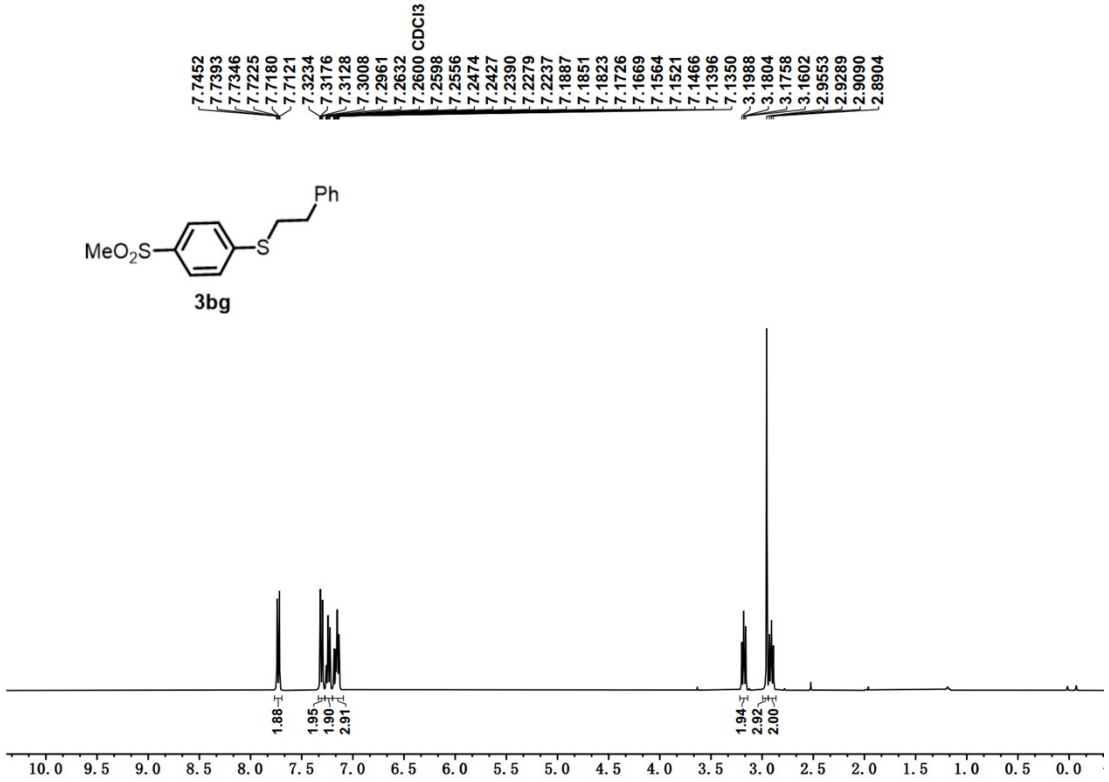
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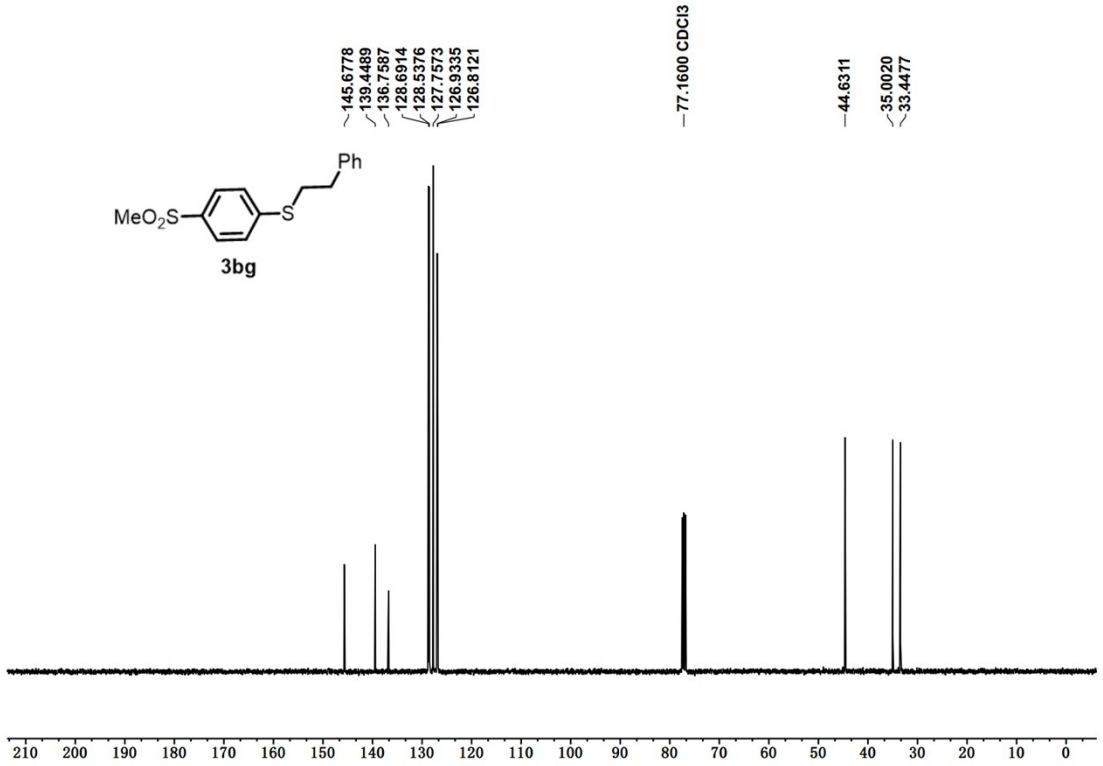
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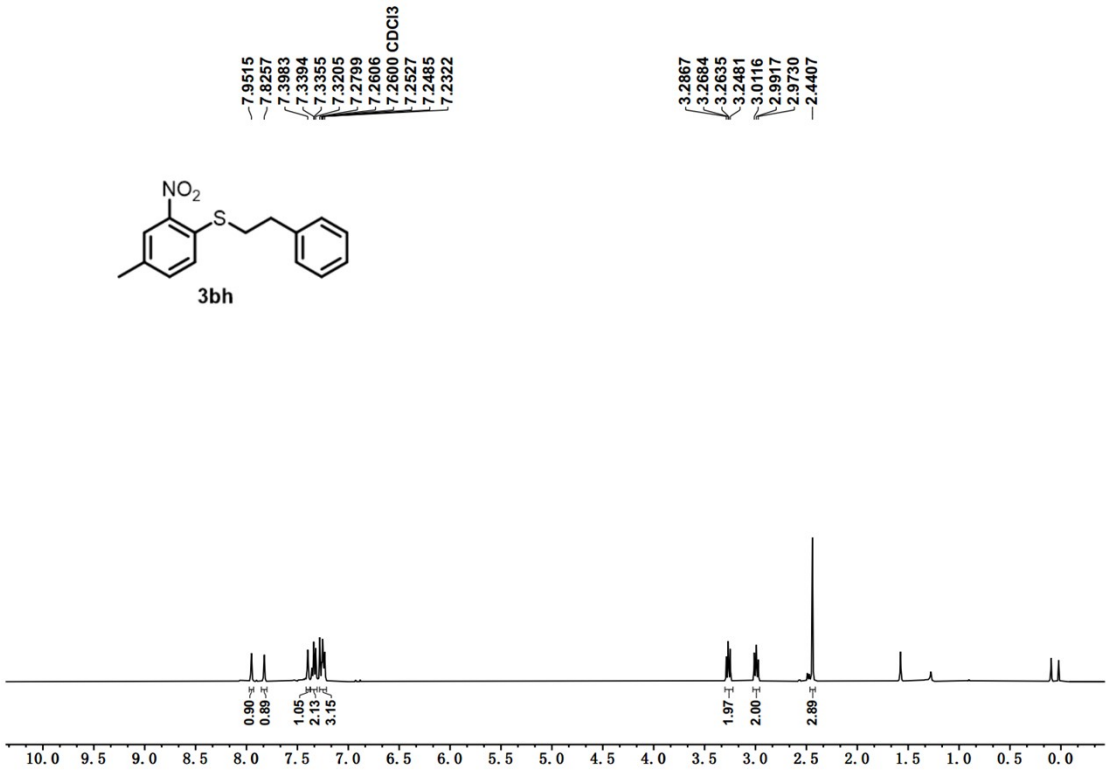
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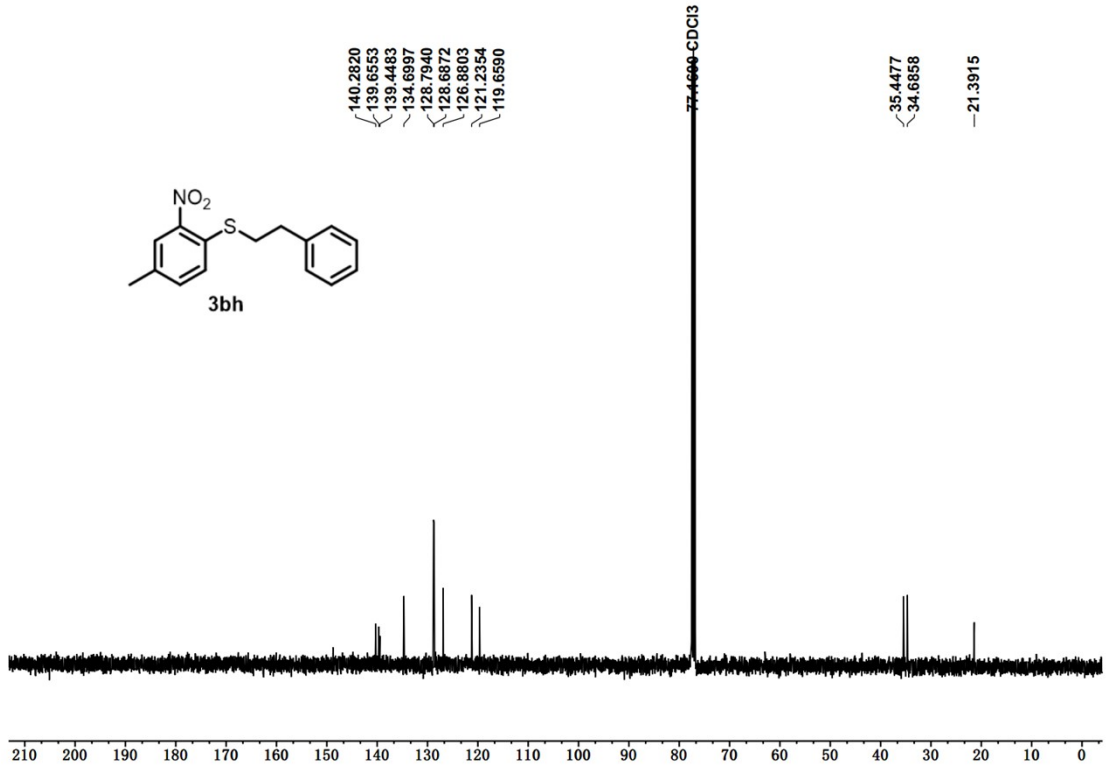
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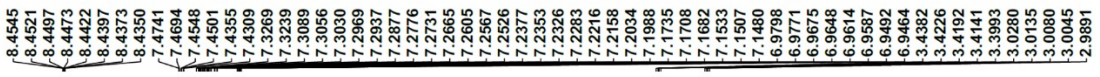
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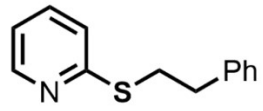
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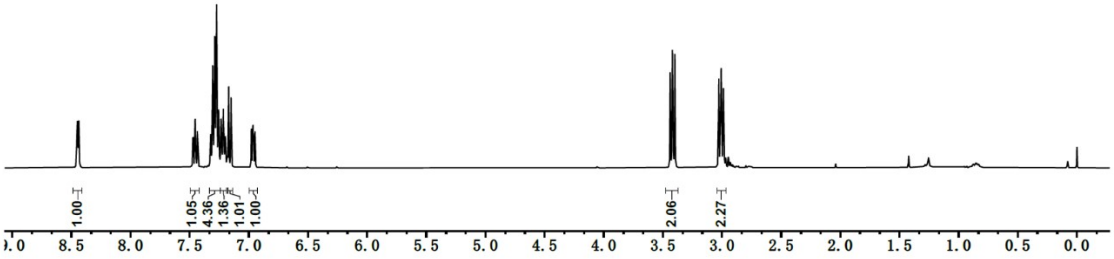
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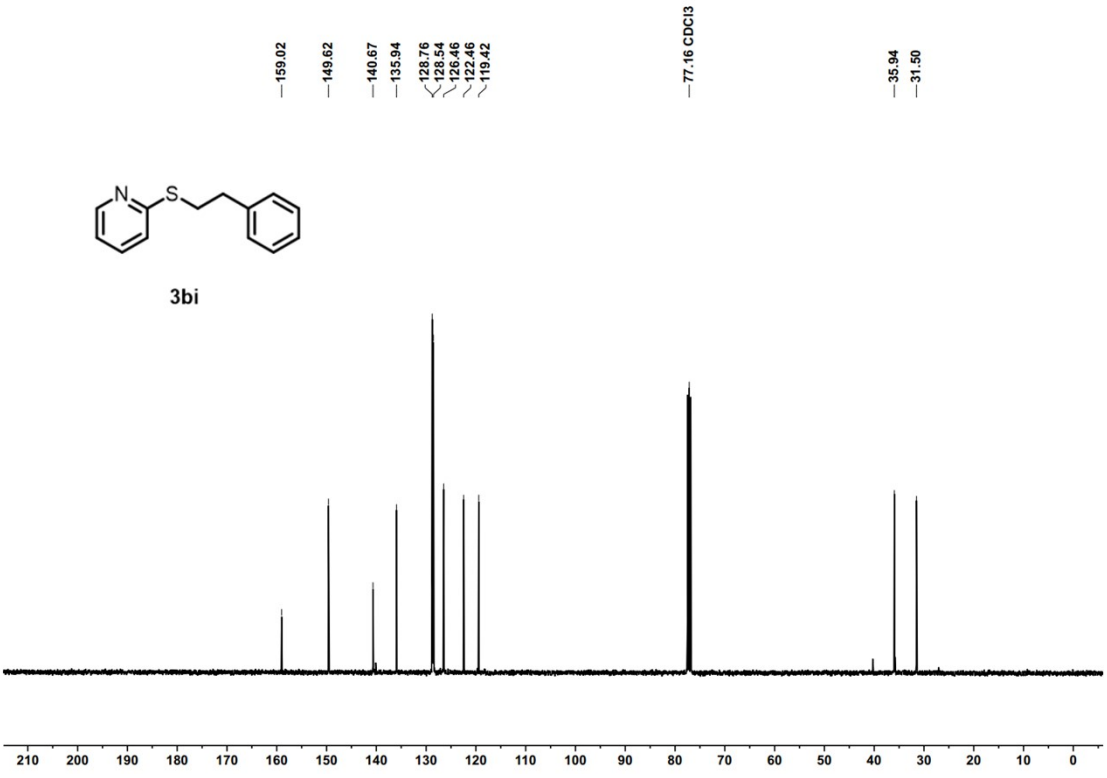
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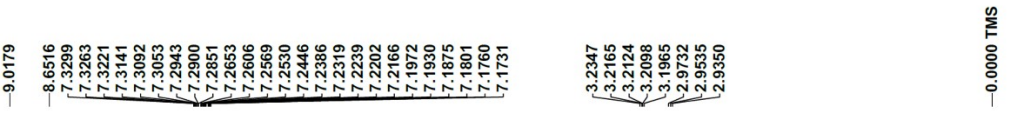
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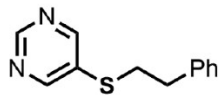
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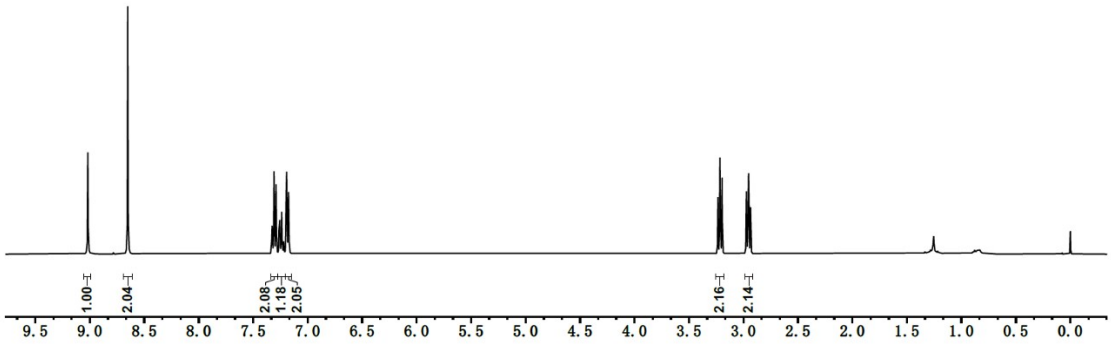
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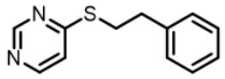
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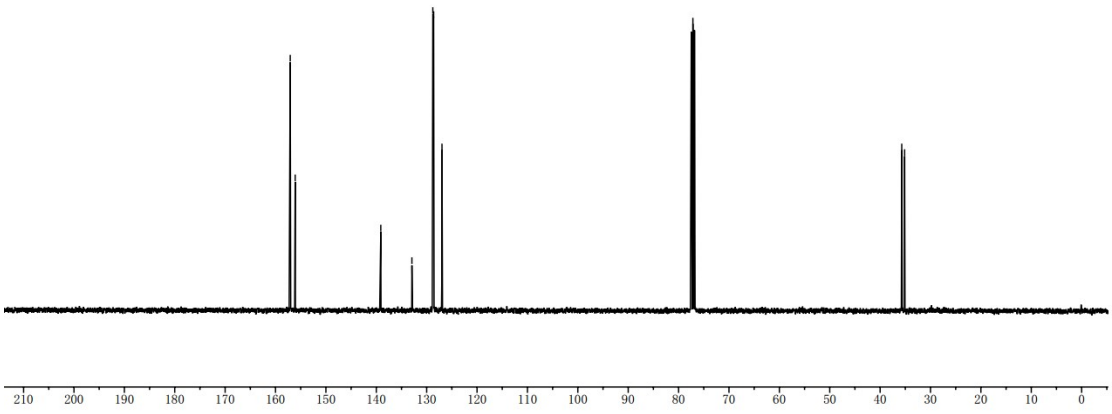
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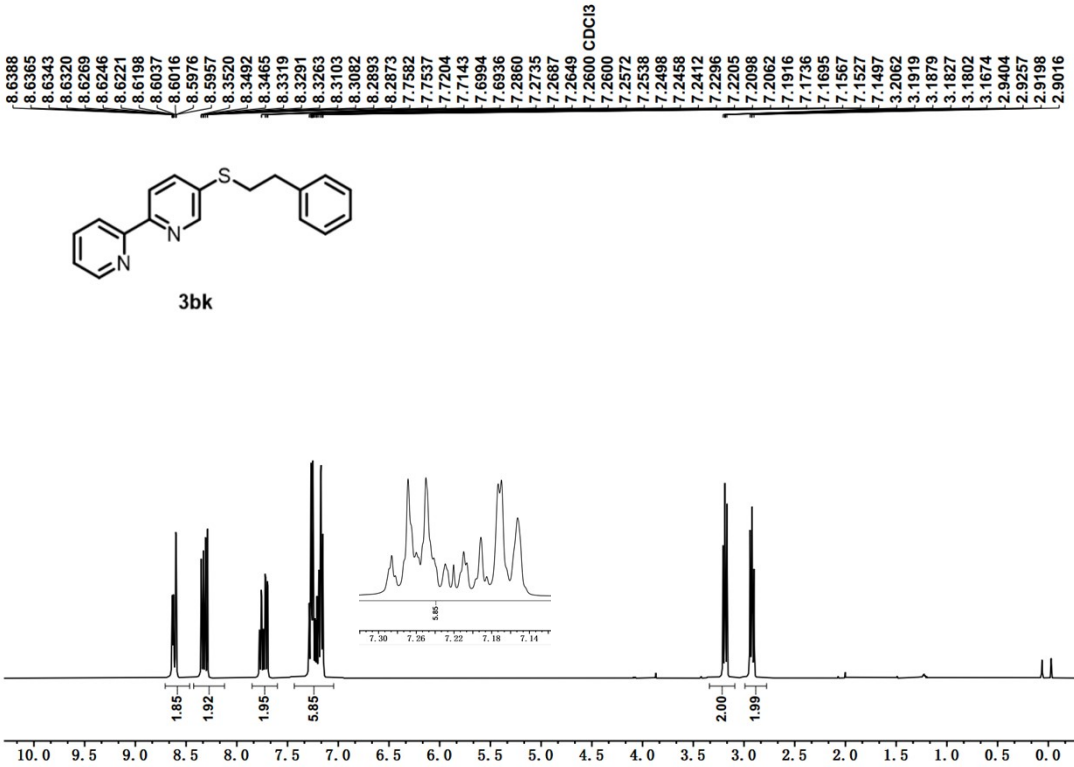
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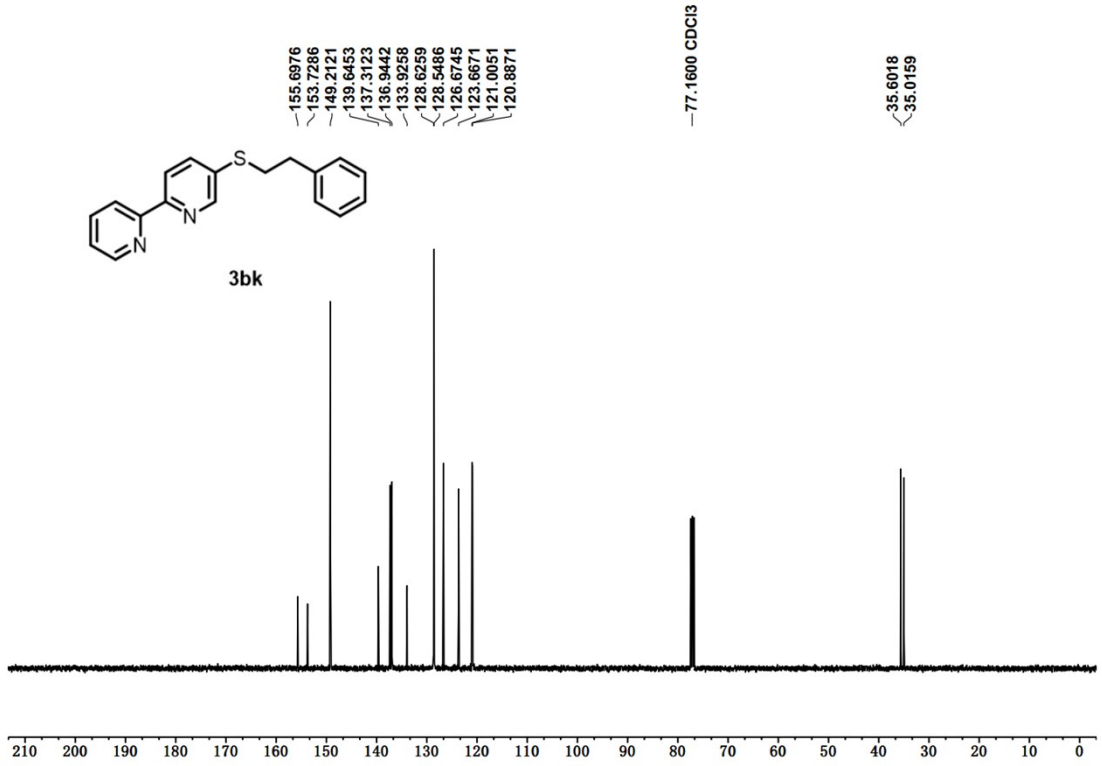
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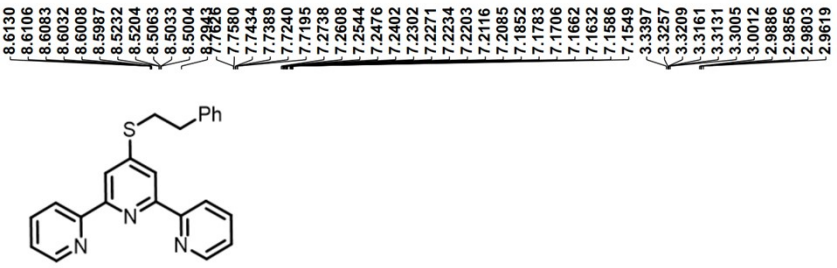
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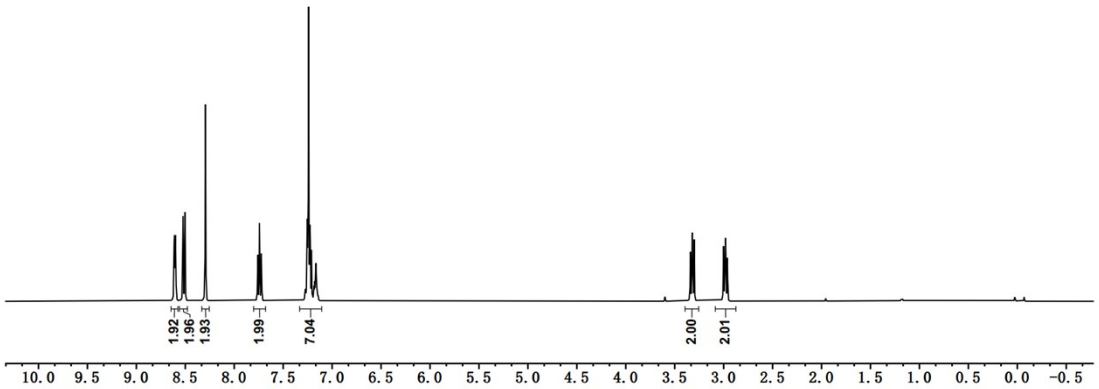
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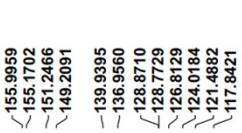
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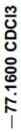
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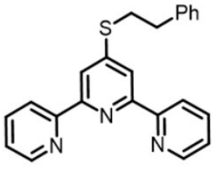
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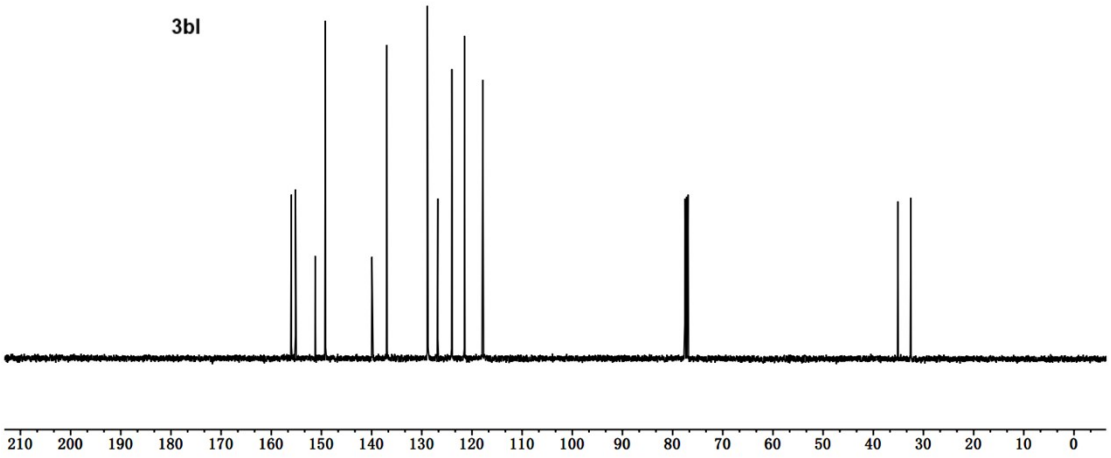
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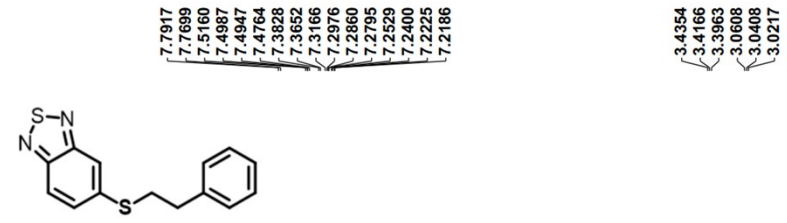
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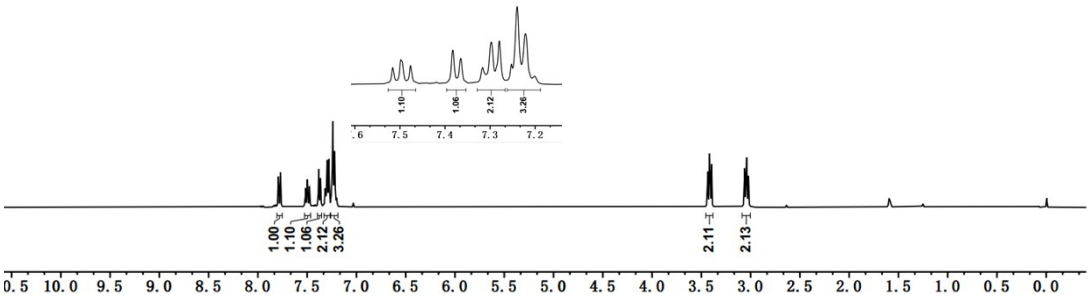
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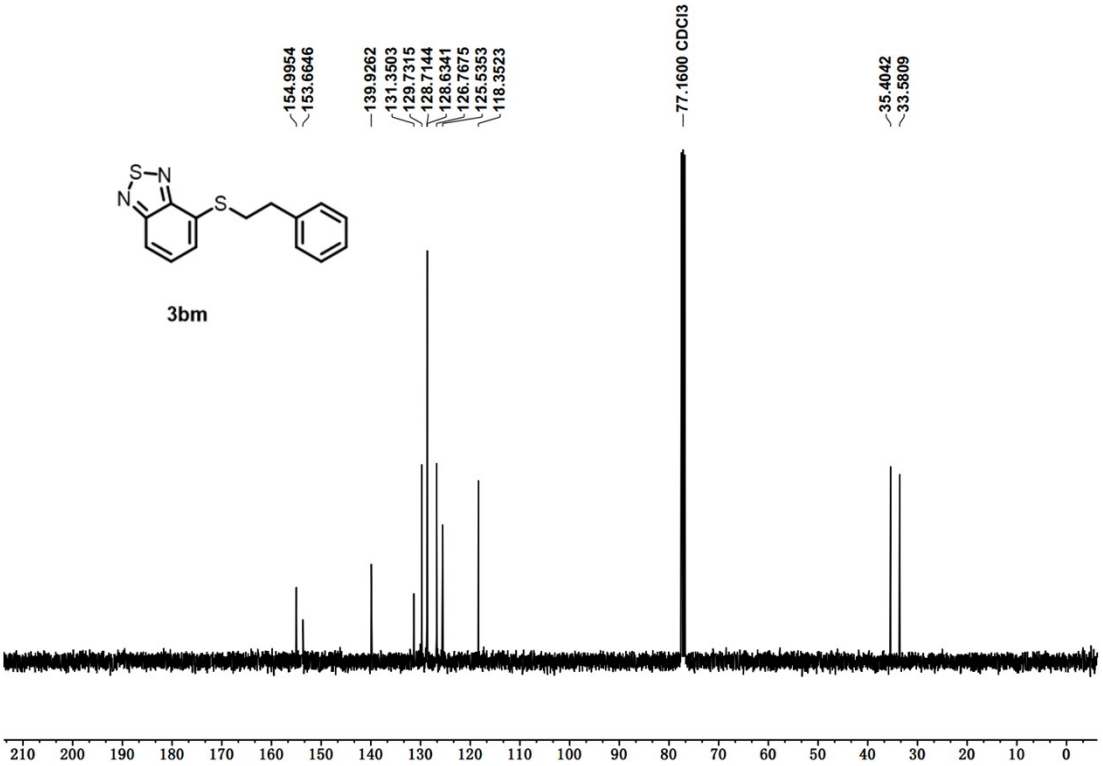
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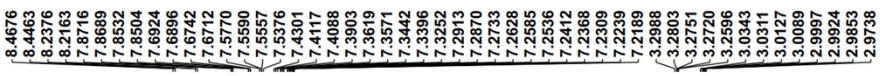
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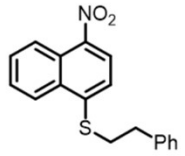
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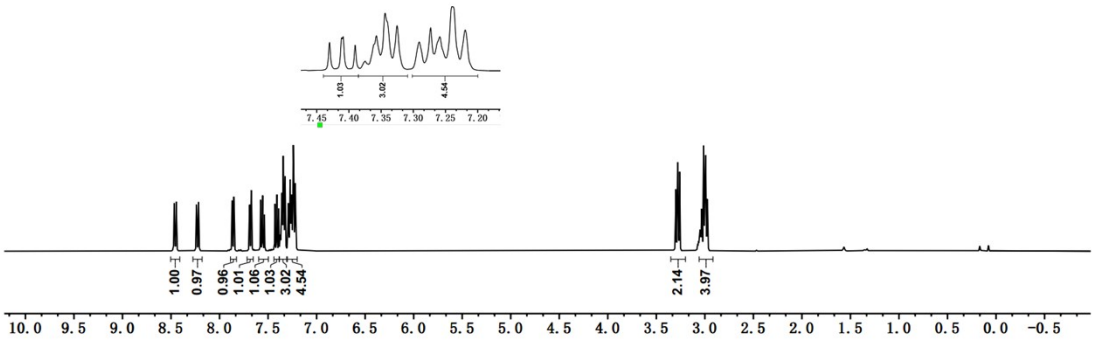
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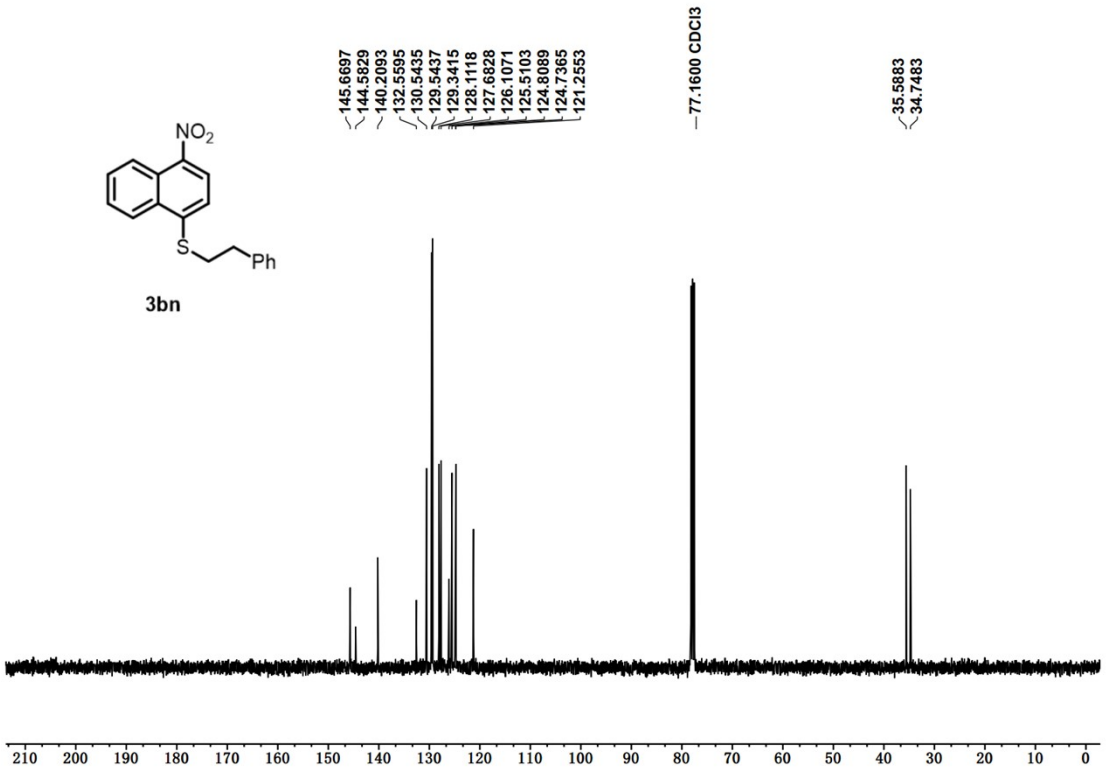
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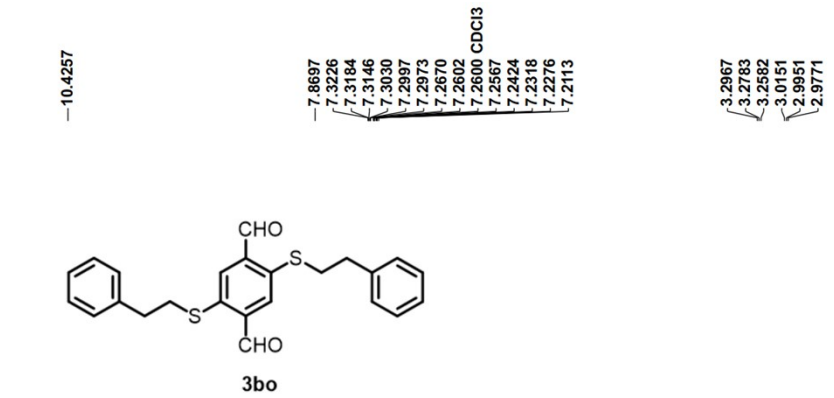
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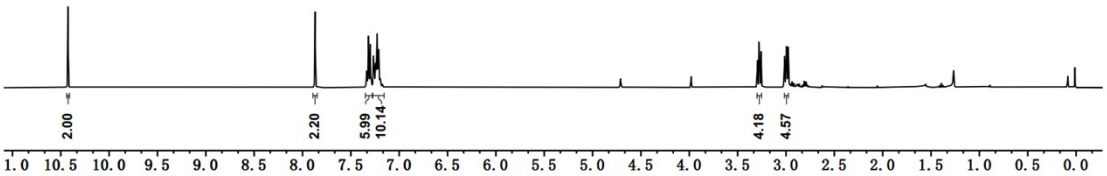
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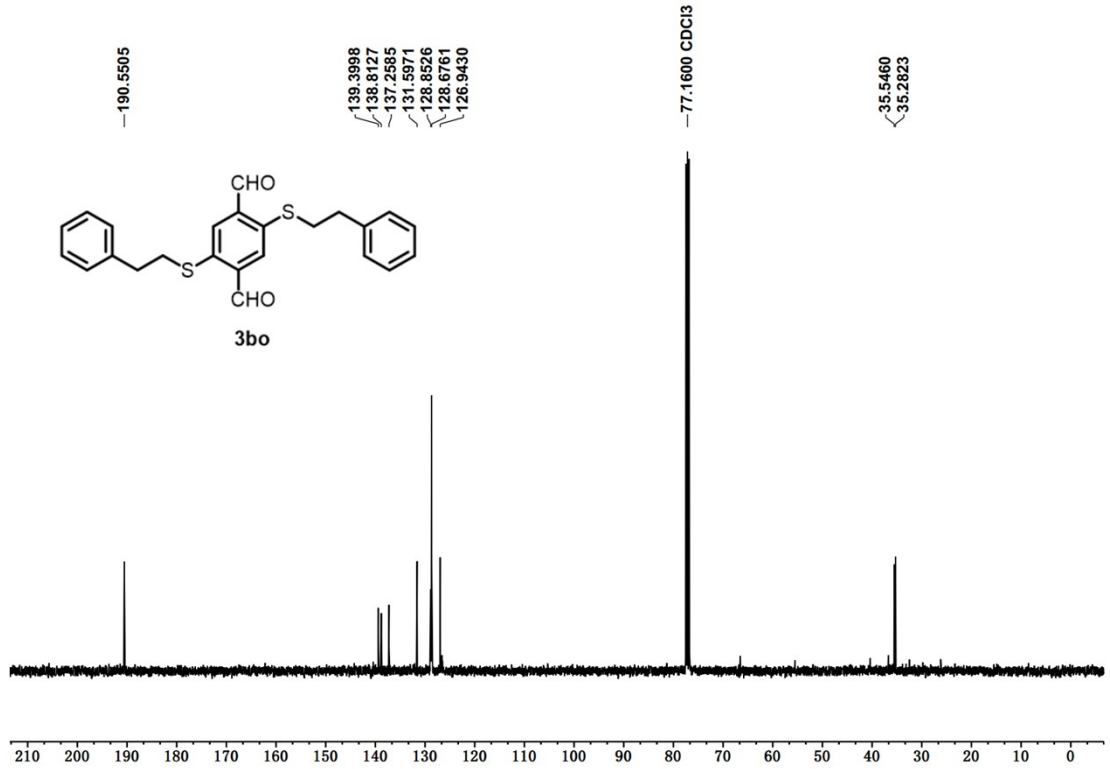
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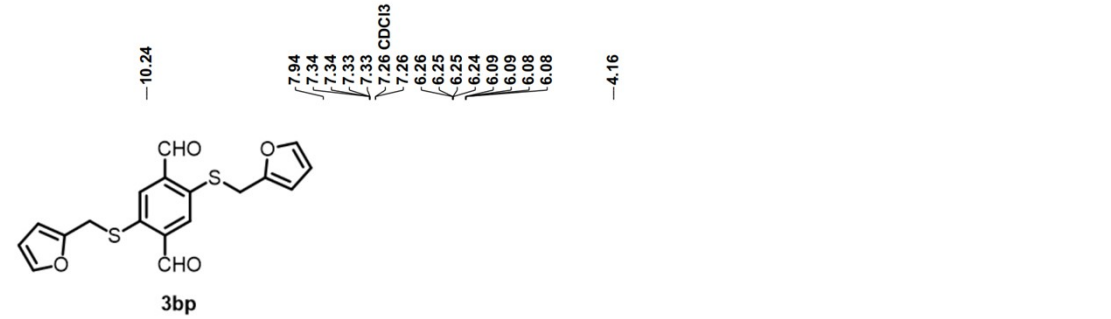
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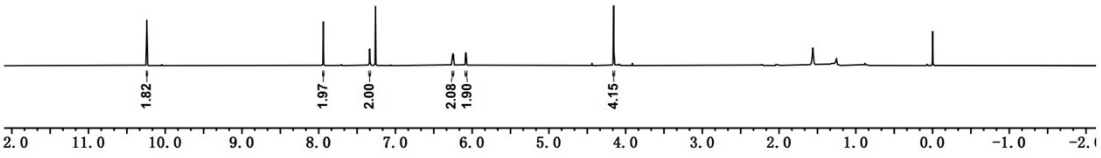
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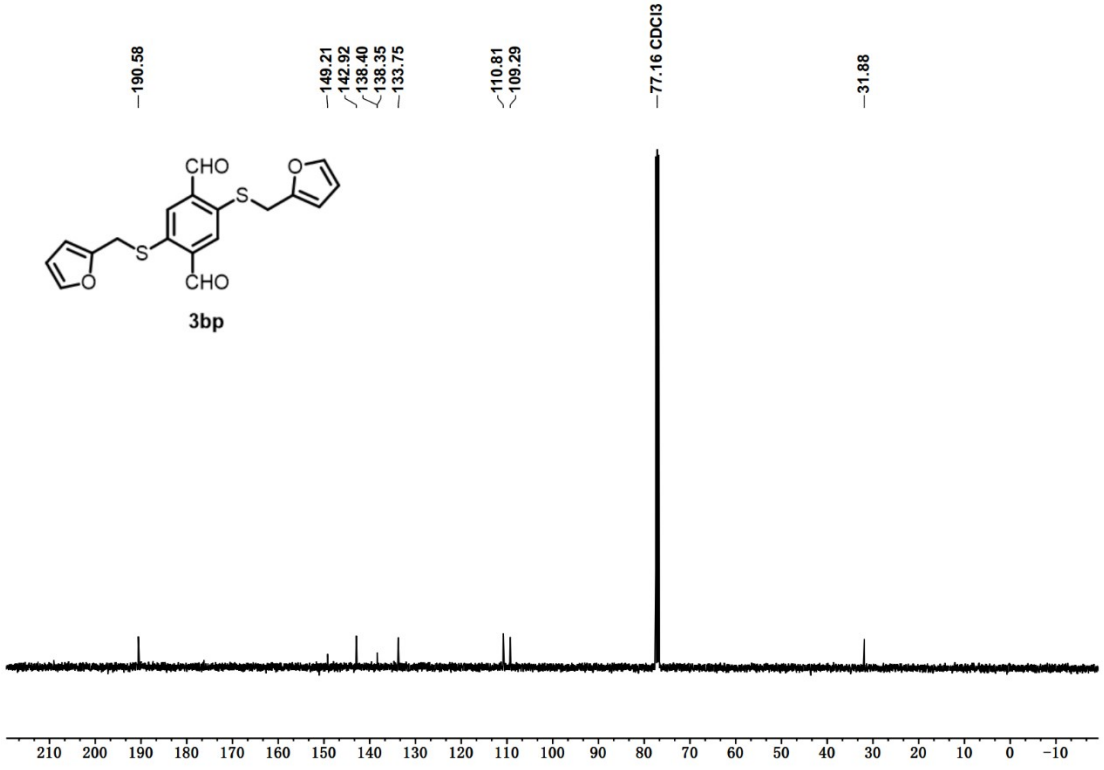
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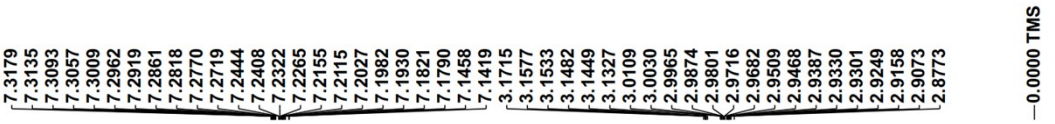
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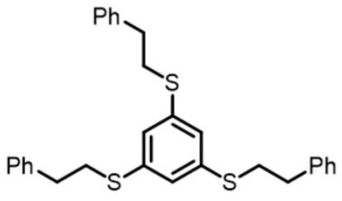
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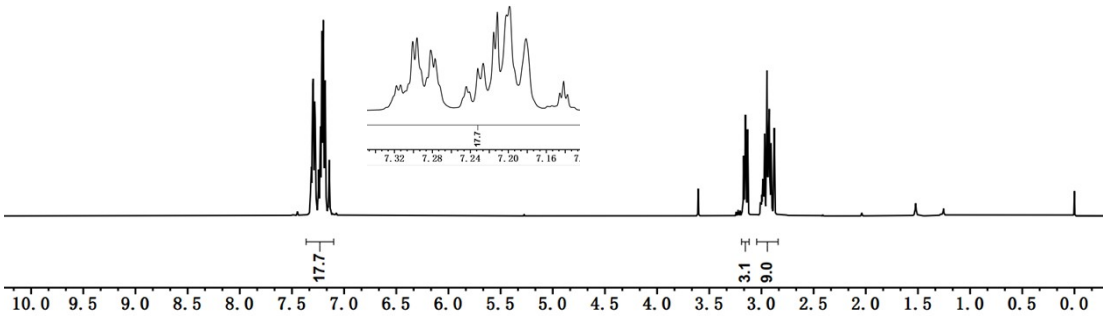
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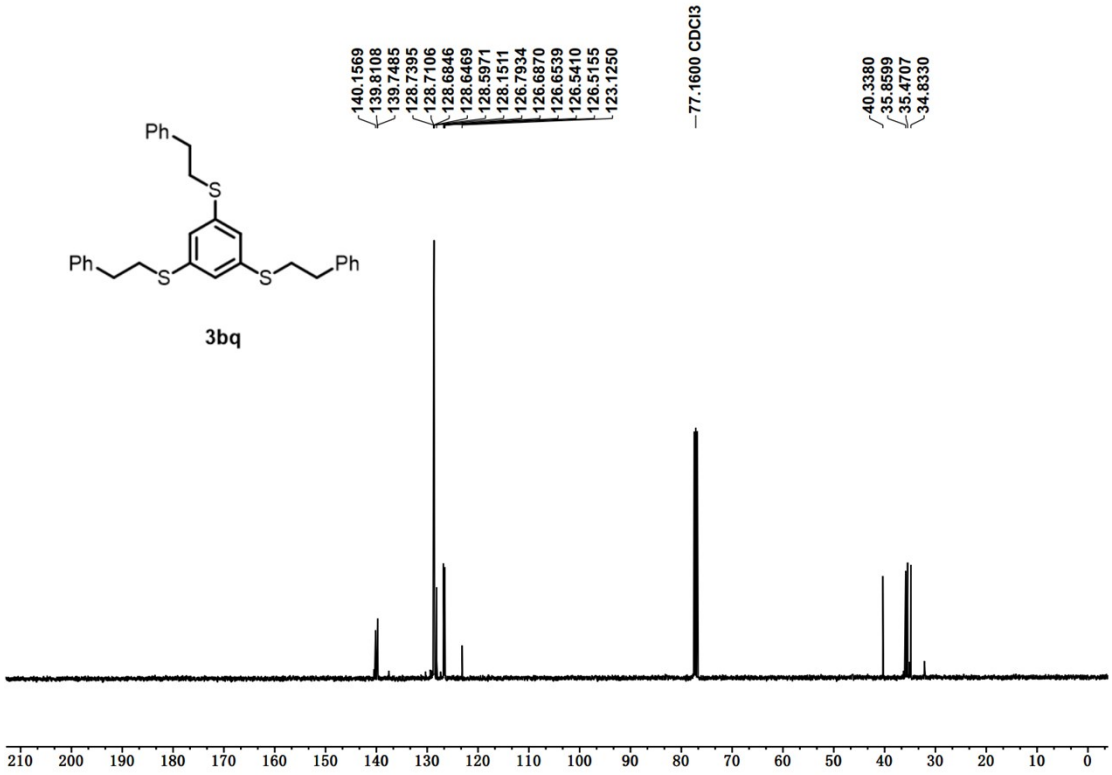
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Ph
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Ph
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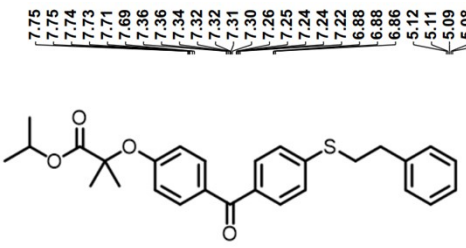
S
Ph

3bq



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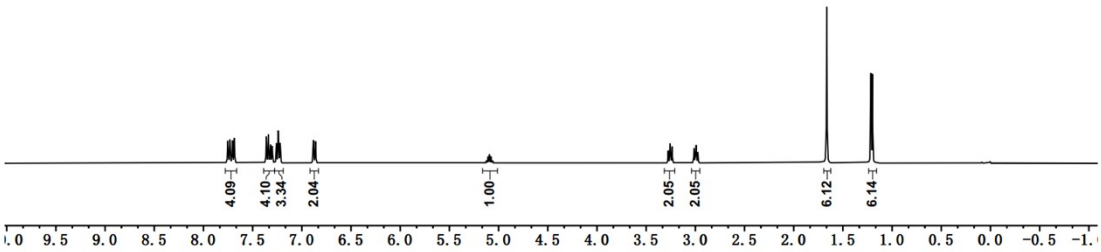

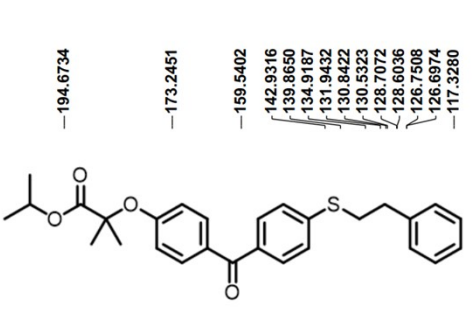

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