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Supplemental Information

Non-transition Metal-Mediated Diverse Aryl–Heteroatom Bond Formation of Arylammonium Salts

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Supplementary Information

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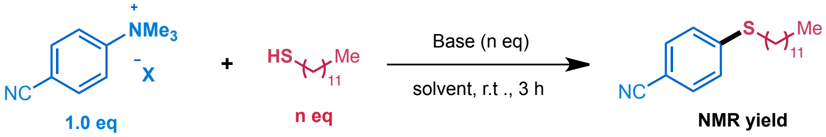
1. General Methods for Experiments

All solvents and chemical reagents were obtained from commercial sources such as *Strem Chemicals, Adamas-beta, Sigma-Aldrich, J&K, Accela* and *TCI,* which were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal reference. Low and high-resolution mass spectra were recorded on EI-TOF (electrospray ionization-time of flight) or ESI-TOF. Normal-phase column chromatography was performed with silica gel 60 (230–400 mesh) from Merck and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254). DNA headpiece HP-NH2 (5'-/5phos/GAGTCA/iSp9/iUniAmM/iSp9/TGACTCCC-3') was obtained from Biosearch Technologies, Novato, CA.

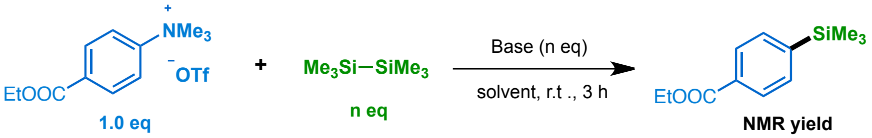
2. Optimization for Reaction Conditions

Table S1. Screening of Thioetherification Conditions, related to **Scheme 2a**.



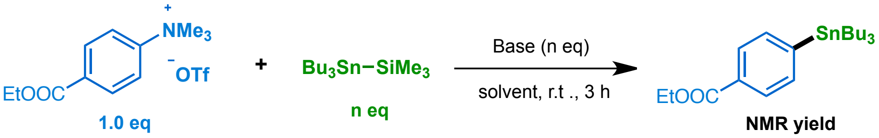
Entry	X	Base	n	solvent	NMR Yield
1	OTf	NaO^{t}Bu	2.0	DMF	46%
2	OTf	KO^{t}Bu	2.0	DMF	90%
3	OTf	KHMDS	2.0	DMF+THF	87%
4	OTf	K_2CO_3	2.0	DMF	98%
5	I	K_2CO_3	2.0	DMF	90%
6	BF_4	K_2CO_3	2.0	DMF	85%
7	OTf	Li_2CO_3	2.0	DMF	trace
8	OTf	Na_2CO_3	2.0	DMF	35%
9	OTf	Cs_2CO_3	2.0	DMF	93%
10	OTf	K_3PO_4	2.0	DMF	82%
11	OTf	K_2CO_3	2.0	THF	88%
12	OTf	K_2CO_3	2.0	DMSO	45%
13	OTf	K_2CO_3	2.0	DMA	78%
14	OTf	K_2CO_3	2.0	NMP	53%
15	OTf	K_2CO_3	2.0	DCM	38%
16	OTf	K_2CO_3	1.5	DMF	96%
17	OTf	K_2CO_3	1.1	DMF	80%
18	OTf	KO^{t}Bu (with 2.0eq. TEMPO)	1.5	DMF	92%

Table S2. Screening of Silylation Conditions, related to **Scheme 2b**.



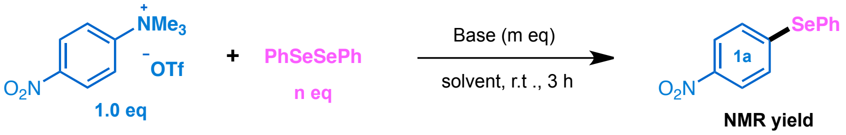
Entry	Base	n	solvent	NMR
1	KO^{t}Bu	2.0	NMP	0%
2	KF	2.0	NMP	25%
3	KOAc	2.0	NMP	0%
4	NaOEt	2.0	NMP	0%
5	TBAF	2.0	NMP	32%
6	CsF	2.0	DMF	65%
7	CsF	2.0	DMSO	42%
8	CsF	2.0	CH_3CN	trace
9	CsF	2.0	DCM	trace
10	CsF	1.5	NMP	88%
11	CsF	1.1	NMP	55%
12	CsF (with 2.0eq. TEMPO)	1.5	NMP	72%

Table S3. Screening of Stannylation Conditions, related to **Scheme 2c**.



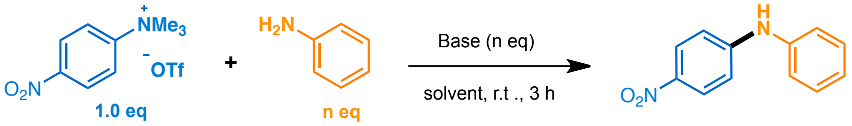
Entry	Base	n	solvent	NMR Yield
1	KF	2.0	DMF	83%
2	CsF	2.0	DMF	92%
3	NaOMe	2.0	DMF	76%
4	TBAF	2.0	DMF	80%
5	CsF	2.0	THF	75%
6	CsF	2.0	DMSO	47%
7	CsF	2.0	CH_3CN	62%
8	CsF	2.0	NMP	83%
9	CsF	1.5	DMF	90%
10	CsF	1.1	DMF	77%
11	CsF (with 2.0eq. TEMPO)	1.5	DMF	85%

Table S4. Screening of Selenation Conditions, related to **Scheme 2e**.



Entry	Base	n	m	solvent	NMR Yield
1	KO^tBu	1.5	1.5	DMF	0%
2	NaH	1.5	1.5	DMF	trace
3	KH	1.5	1.5	DMF	65%
4	KHMDS	1.5	1.5	DMF+THF	trace
5	$NaBH_4$	1.5	3.0	$THF+H_2O+DMF$	80%
6	KBH_4	1.5	3.0	$THF+H_2O+DMF$	98%
7	KBH_4	1.0	2.0	$THF+H_2O+DMF$	95%
8	KBH_4	0.6	1.2	$THF+H_2O+DMF$	55%

Table S5. Screening of Amination Conditions, related to **Scheme 2f**.



Entry	Base	n	solvent	NMR Yield
1	KO^tBu	2.0	DMF	15%
2	K_2CO_3	2.0	DMF	0%
3	Cs_2CO_3	2.0	DMF	0%
4	KH	2.0	DMF	35%
5	KOH	2.0	DMF	40%
6	KHMDS	2.0	DMF	83%
7	KHMDS	2.0	DMSO	42%
8	KHMDS	1.5	DMF	80%
9	KHMDS	1.1	DMF	56%

3. Transparent Methods

3.1 General Procedure for Preparations of Aryltrimethylammonium Salts.

3.1.1 Preparations of $ArNMe_3OTf$: To a stirred solution of *N*,*N*–dimethylaniline (10 mmol) in CH_2Cl_2 (10 mL) was added dropwise methyl trifluoromethanesulfonate (1.24 mL, 11.0 mmol, 1.1 equiv.) at 25°C. The resulting solution was stirred for 4 h or 12 h at room temperature (r.t.). For some anilines bearing strong electron-withdrawing groups, the reactions may need heating up to 70 ˚C in MeCN in stead of CH_2Cl_2. Solvent was then removed in vacuum and the residue was washed with Et_2O, dried under vacuum to give a white solid. (Wang et al., 2016)

3.1.2 Preparations of $ArNMe_3Cl$: To a stirred solution of aryl chloride (10 mmol) in CH_2Cl_2 (10 mL) was added dropwise NMe_3 (2M in THF, 6 mL, 12.0 mmol, 1.2 equiv.; For **1s**, 0.7 equiv.) at 25°C. The resulting solution was stirred for 2 h at room temperature (r.t.). Solvent was then removed in vacuum and the residue was washed with Et_2O, dried under vacuum to give a white solid.

3.2 General Procedure for the Reactions of Aryltrimethylammonium Salts with Thiols (Fig. S1)

A flask was charged with aryltrimethylammonium triflates (0.2 mmol), thiols (0.3 mmol), K_2CO_3 (0.3 or 0.6 mmol) and DMF (3 mL). The reaction mixture was stirred at r.t. for 3 h to give a colorless or (pale) yellow suspended solution. Then water (30 mL) was added to remove DMF. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified on column chromatography or preparative TLC (silica gel) or preparative HPLC (for **3ir**) to give the product and NMR yields with mesitylene as an internal standard.

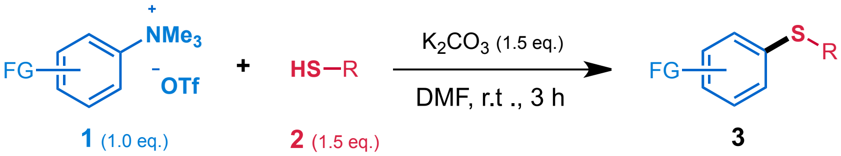
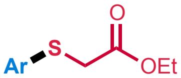


Fig.S1, related to **Scheme 2a.**



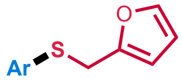
3aa: White solid, isolated yield 71%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 2H), 1.28 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.60, 145.73, 145.46, 126.89, 124.07, 62.14, 34.67, 14.10.; All spectral data match those previously reported. (Nagao et al., 2006)

3ab: Yellow solid, isolated yield 78%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 3.14 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 5.9 Hz, 2H), 1.52 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.94, 145.24, 126.63, 124.02, 40.68, 36.12. HRMS (EI) *m/z*: calcd for $C_8H_{10}N_2O_2S$ [M^+] 198.0458, found 198.0462.

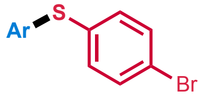
3ac: Yellow solid, isolated yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 3.89 (t, *J* = 6.1 Hz, 2H), 3.25 (t, *J* = 6.1 Hz, 2H), 2.04 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.30, 145.41, 126.88, 124.04, 60.54, 35.12.; All spectral data match those previously reported. (Irie et al., 1980)

3ad: Colorless oil, isolated yield 80%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 9.0 Hz, 2H), 3.57 (s, 9H), 3.07 – 3.01 (m, 2H), 1.83 (dt, *J* = 15.2, 7.7 Hz, 2H), 0.85 – 0.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.85, 144.92, 126.12, 123.94, 50.61, 34.47, 22.28, 8.69. HRMS (EI) *m/z*: calcd for $C_{12}H_{19}NO_5SSi$ [M$^+$] 317.0748, found 317.0760.

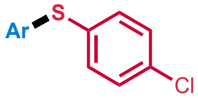
3ae: Yellow solid, isolated yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.1 Hz, 2H), 7.34 (d, *J* = 9.1 Hz, 2H), 5.89 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.26 (ddd, *J* = 13.5, 11.2, 1.1 Hz, 2H), 3.68 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.83, 145.23, 131.96, 126.81, 123.86, 119.04, 35.21.; All spectral data match those previously reported. (Pace et al., 2012)



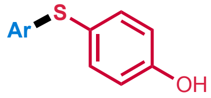
3af: Colorless oil, isolated yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 9.1 Hz, 2H), 7.36 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.24 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.24 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.04, 145.79, 145.11, 142.23, 126.83, 123.52, 110.29, 108.11, 29.18.



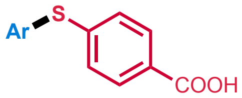
3ag: White solid, isolated yield 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.86, 145.07, 135.43, 132.69, 129.31, 126.52, 123.63.; All spectral data match those previously reported. (Taniguchi et al., 2017)



3ah: White solid, isolated yield 80%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.1 Hz, 2H), 7.45 (q, *J* = 8.6 Hz, 4H), 7.21 – 7.15 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.59, 145.66, 136.08, 135.84, 130.29, 129.20, 127.00, 124.17.; All spectral data match those previously reported. (Taniguchi et al., 2017)

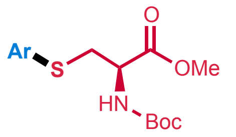


3ai: White solid, isolated yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.53 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.37, 150.07, 144.96, 137.38, 125.57, 123.96, 120.29, 117.19.; All spectral data match those previously reported. (Tian et al., 2014)

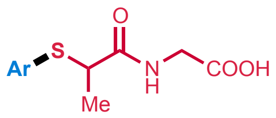


3aj: Yellow solid, isolated yield 88%; ^{1}H NMR (300 MHz, DMSO) δ 8.19 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 166.58, 145.85, 144.77, 136.88, 132.45, 131.03, 130.71, 129.09, 124.48. HRMS (ESI) *m/z*: calcd for $C_{13}H_8NO_4S$ [M-H]$^-$ 274.0180, found

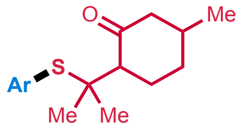
274.0182.



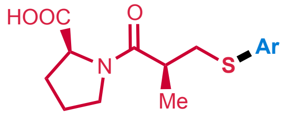
3ak: White solid, isolated yield 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 5.34 (d, *J* = 6.7 Hz, 1H), 4.65 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.70 (s, 3H), 3.57 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.44 (dd, *J* = 14.0, 4.8 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.52, 154.88, 145.61, 127.60, 123.97, 80.52, 53.16, 52.79, 35.01, 28.21. HRMS (EI) *m/z*: calcd for $C_{15}H_{20}N_2O_6S$ [M^+] 356.1037, found 356.1043.



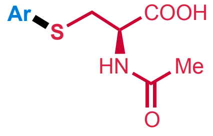
3al: White solid, isolated yield 83%; ^{1}H NMR (300 MHz, DMSO) δ 12.61 (s, 1H), 8.61 (t, *J* = 5.8 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 2H), 7.55 (d, *J* = 9.1 Hz, 2H), 4.29 (q, *J* = 7.0 Hz, 1H), 3.79 (dd, *J* = 5.9, 2.2 Hz, 2H), 1.46 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 171.44, 171.39, 146.23, 145.43, 128.20, 124.35, 44.28, 41.39, 18.53. HRMS (ESI) *m/z*: calcd for $C_{11}H_{13}N_2O_5S$ $[M+H]^{+\cdot}$ 285.0540, found 285.0544.



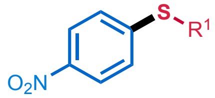
3am: White solid, isolated yield 80%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 2.66 (d, *J* = 13.2 Hz, 1H), 2.40 – 2.26 (m, 2H), 1.97 (d, *J* = 11.7 Hz, 3H), 1.64 (dd, *J* = 13.1, 3.1 Hz, 2H), 1.43 (d, *J* = 11.1 Hz, 6H), 1.02 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.98, 148.02, 141.38, 137.50, 123.39, 57.98, 52.93, 52.26, 36.75, 34.54, 29.78, 28.20, 24.67, 22.19. HRMS (EI) *m/z*: calcd for $C_{16}H_{21}NO_3S$ [M^+] 307.1237, found 307.1236.



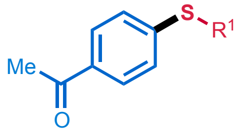
3an: Colorless oil, isolated yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.56 (d, *J* = 5.5 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.42 (dd, *J* = 12.6, 8.9 Hz, 2H), 3.10 (dd, *J* = 13.0, 5.3 Hz, 1H), 2.92 (dd, *J* = 14.5, 6.0 Hz, 1H), 2.01 (s, 2H), 1.33 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.45, 172.92, 146.58, 145.38, 126.55, 124.10, 59.72, 47.66, 38.11, 35.16, 27.72, 24.80, 17.53. HRMS (ESI) *m/z*: calcd for $C_{15}H_{19}N_2O_5S$ $[M+H]^+$ 339.1009, found 339.1007.



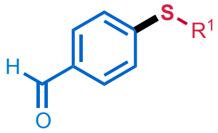
3ao: Colorless oil, isolated yield 85%; ^{1}H NMR (500 MHz, DMSO) δ 12.99 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 9.1 Hz, 2H), 7.54 (d, *J* = 9.1 Hz, 2H), 4.47 (td, *J* = 8.4, 4.9 Hz, 1H), 3.54 (dd, *J* = 13.6, 5.0 Hz, 1H), 3.33 (d, *J* = 5.1 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 171.55, 169.52, 146.60, 144.68, 126.62, 123.95, 51.15, 32.73, 22.29. HRMS (ESI) *m/z*: calcd for $C_{11}H_{11}N_2O_5S$ $[M-H]^-$ 283.0394, found 283.0393.



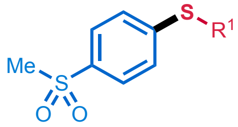
3ap: White solid, isolated yield 91%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 3.04 – 2.96 (m, 2H), 1.76 – 1.65 (m, 2H), 1.50 – 1.40 (m, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.16, 144.72, 125.86, 123.84, 31.85, 29.57, 29.50, 29.41, 29.29, 29.06, 28.82, 28.41, 22.64, 14.07.; All spectral data match those previously reported. (Kondoh et al., 2006)



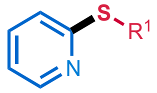
3bp: White solid, isolated yield 71%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 3.02 – 2.94 (m, 2H), 2.57 (s, 3H), 1.74 – 1.65 (m, 2H), 1.44 (s, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.15, 145.03, 133.75, 128.74, 126.28, 32.01, 31.92, 29.63, 29.63, 29.57, 29.48, 29.34, 29.15, 28.90, 28.76, 26.41, 22.69, 14.11.; All spectral data match those previously reported. (Xu et al., 2013)



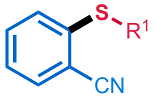
3cp: Colorless oil, isolated yield 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.03 – 2.96 (m, 2H), 1.70 (dd, *J* = 15.0, 7.6 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.18, 147.17, 133.13, 130.00, 126.31, 31.92, 31.84, 29.63, 29.63, 29.56, 29.48, 29.34, 29.14, 28.91, 28.66, 22.69, 14.12.; All spectral data match those previously reported. (Kondoh et al., 2006)



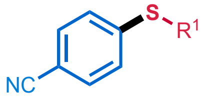
3dp: White solid, isolated yield 77%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 3.03 (s, 3H), 2.99 (t, *J* = 7.4 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.45 (s, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.43, 136.45, 127.67, 126.66, 44.67, 31.96, 31.91, 29.62, 29.56, 29.47, 29.34, 29.13, 28.88, 28.58, 22.69, 14.11. HRMS (EI) *m/z*: calcd for $C_{19}H_{23}O_2S_2$ $[M^+]$ 356.1838, found 356.1834.



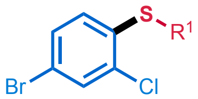
3ep: Colorless oil, isolated yield 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (ddd, *J* = 5.0, 1.8, 0.9 Hz, 1H), 7.46 (ddd, *J* = 8.1, 7.4, 1.9 Hz, 1H), 7.16 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.95 (ddd, *J* = 7.3, 4.9, 1.1 Hz, 1H), 3.21 – 3.09 (m, 2H), 1.69 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.25 (s, 16H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.65, 149.42, 135.75, 122.11, 119.12, 31.91, 30.14, 29.65, 29.62, 29.59, 29.51, 29.33, 29.31, 29.20, 28.96, 22.68, 14.11.; All spectral data match those previously reported. (Kanemura et al., 2008)



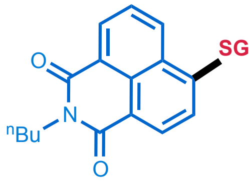
3fp: Colorless oil, isolated yield 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 9.3 Hz, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 1.74 – 1.59 (m, 2H), 1.44 (s, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.31, 133.65, 132.73, 128.66, 125.69, 117.19, 113.38, 33.56, 31.92, 29.63, 29.62, 29.56, 29.46, 29.34, 29.12, 28.82, 28.77, 22.69, 14.12. HRMS (EI) *m/z*: calcd for $C_{19}H_{29}NS$ [M$^+$] 303.2015, found 303.2022.



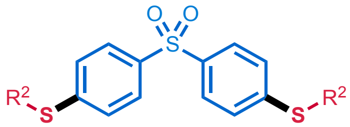
3gp: White solid, isolated yield 90%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 3.01 – 2.92 (m, 2H), 1.75 – 1.62 (m, 2H), 1.49 – 1.37 (m, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.35, 132.19, 126.68, 118.97, 107.91, 31.92, 29.62, 29.55, 29.46, 29.34, 29.12, 28.87, 28.57, 22.69, 14.11.; All spectral data match those previously reported. (Kondoh et al., 2006)



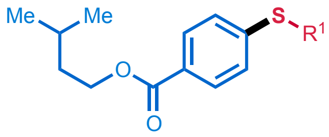
3hp: Colorless oil, isolated yield 46%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 2.92 – 2.88 (m, 2H), 1.67 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.48 – 1.41 (m, 2H), 1.26 (s, 16H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.02, 133.94, 132.12, 130.14, 128.89, 118.54, 32.55, 31.92, 29.63, 29.56, 29.46, 29.34, 29.15, 28.91, 28.50, 22.69, 14.12.



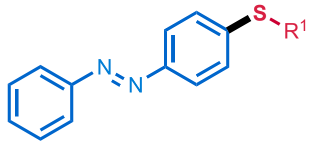
3ir: Yellow solid, isolated yield 70%; ^{1}H NMR (500 MHz, D_2O) δ 7.88 – 7.78 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 4.74 – 4.69 (m, 1H), 3.83 – 3.74 (m, 3H), 3.71 – 3.64 (m, 2H), 3.59 (d, *J* = 9.5 Hz, 1H), 3.35 (s, 1H), 2.54 – 2.43 (m, 2H), 2.10 – 2.01 (m, 2H), 1.57 (s, 2H), 1.43 (dd, *J* = 13.8, 6.7 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, D_2O) δ 176.01, 175.56, 174.92, 170.97, 164.30, 164.17, 143.71, 131.29, 130.27, 129.95, 127.83, 126.50, 125.99, 123.38, 120.52, 117.24, 54.42, 52.36, 43.41, 40.44, 33.28, 31.63, 30.10, 29.47, 27.12, 19.91, 13.17. HRMS (ESI) *m/z*: calcd for $C_{26}H_{31}N_4O_8S$ [M+H]$^+$ 559.1857, found 559.1848.



3jq: White solid, isolated yield 45%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.7 Hz, 4H), 7.30 (d, *J* = 8.7 Hz, 4H), 2.99 (q, *J* = 7.4 Hz, 4H), 1.35 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.33, 137.81, 127.84, 126.72, 26.05, 13.79. HRMS (EI) *m/z*: calcd for $C_{16}H_{18}O_2S_3$ [M$^+$] 338.0463, found 338.0458.



3kp: White solid, isolated yield 66%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.7 Hz, 2H), 3.01 – 2.92 (m, 2H), 1.79 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.71 – 1.59 (m, 4H), 1.44 (s, 2H), 1.25 (s, 16H), 0.97 (d, *J* = 6.5 Hz, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.40, 144.29, 129.83, 126.90, 126.30, 63.52, 37.42, 32.10, 31.89, 29.61, 29.61, 29.55, 29.46, 29.32, 29.13, 28.88, 28.76, 25.21, 22.67, 22.51, 14.10. HRMS (EI) *m/z*: calcd for $C_{24}H_{40}O_2S$ [M$^+$] 392.2744, found 392.2748.



3lp: Yellow solid, isolated yield 85%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94 – 7.81 (m, 4H), 7.56 – 7.44 (m, 3H), 7.39 (d, *J* = 8.6 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.70 (dd, *J* = 14.8, 7.5 Hz, 2H), 1.45 (d, *J* = 5.6 Hz, 2H), 1.27 (s, 16H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 152.69, 150.18, 141.86, 130.76, 129.05, 127.56, 123.33, 122.73, 32.67, 31.90, 29.63, 29.62, 29.56, 29.48, 29.33, 29.15, 28.89, 22.68, 14.11. HRMS (EI) *m/z*: calcd for $C_{24}H_{34}N_2S$ [M$^+$] 382.2437, found 382.2435.

3.3 General Procedure for the C-Si/Sn/Ge Bond-forming Reaction of Arylammonium Salts (Fig. S2, S3, S4)

A Schlenk tube was charged with aryltrimethylammonium triflate (0.2 mmol), Si/Sn/Ge reagents (0.3 mmol), CsF (0.28 mmol), and DMF (3 mL) under a argon atmosphere. The reaction mixture was stirred at r.t. or 50°C for 8 hours to give a colorless or (pale) yellow transparent solution (slightly suspended for some cases). Then water (30 mL) was added to remove DMF. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product and NMR yields with mesitylene as an internal standard.

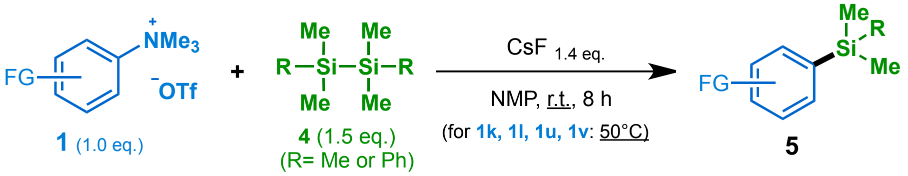
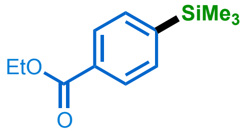
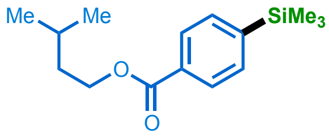


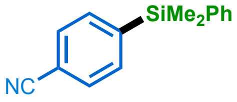
Fig.S2, related to **Scheme 2b.**



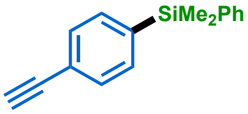
5a: Colorless oil, isolated yield 84%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 0.29 (s, 9H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.82, 146.70, 133.27, 130.67, 128.49, 60.91, 14.37, -1.29.; All spectral data match those previously reported. (Tobisu et al., 2008)



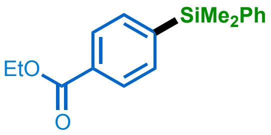
5b: Colorless oil, isolated yield 88%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 4.36 (t, *J* = 6.7 Hz, 2H), 1.81 (dt, *J* = 13.6, 6.5 Hz, 1H), 1.66 (q, *J* = 6.7 Hz, 2H), 0.97 (d, *J* = 6.5 Hz, 6H), 0.29 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.87, 146.71, 133.27, 130.67, 128.47, 63.59, 37.44, 25.25, 22.54, -1.31.



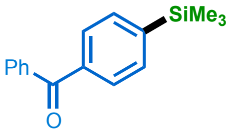
5c: Colorless oil, isolated yield 71%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (s, 4H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.43 – 7.35 (m, 3H), 0.58 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.41, 136.48, 134.62, 134.11, 131.04, 129.65, 128.09, 118.97, 112.71, -2.74. All spectral data match those previously reported. (Guo et al., 2015)



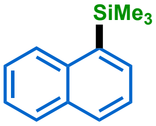
5d: Colorless oil, isolated yield 52%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.47 (d, *J* = 1.5 Hz, 4H), 7.39 – 7.34 (m, 3H), 3.09 (s, 1H), 0.55 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 139.55, 137.60, 134.12, 134.01, 131.25, 129.26, 127.88, 122.68, 83.70, 77.66, -2.56. HRMS (EI) *m/z*: calcd for $C_{16}H_{16}Si$ [M$^+$] 236.1016, found 236.1009.



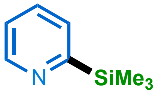
5e: Colorless oil, isolated yield 80%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.37 (d, *J* = 5.9 Hz, 3H), 4.38 (d, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.58 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.76, 144.51, 137.40, 134.15, 134.14, 130.96, 129.36, 128.53, 127.94, 60.95, 14.35, -2.55.; All spectral data match those previously reported. (Hamze et al., 2006)



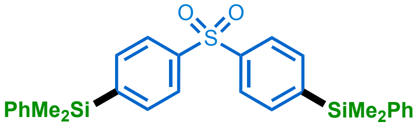
5f: Colorless oil, isolated yield 60%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 0.32 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 196.88, 146.29, 137.69, 137.63, 133.16, 132.38, 130.07, 129.00, 128.24, -1.30. All spectral data match those previously reported. (McNeill et al., 2007)



5g: Colorless oil, isolated yield 75%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 7.8, 5.9 Hz, 2H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.52 (ddd, *J* = 21.9, 15.0, 6.7 Hz, 3H), 0.53 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.12, 136.89, 133.41, 133.15, 129.71, 129.11, 128.12, 125.56, 125.26, 125.08, 0.24.; All spectral data match those previously reported. (Tobisu et al., 2008)



5h: Colorless oil, isolated yield 62%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, *J* = 4.5 Hz, 1H), 7.58 (td, *J* = 7.6, 1.7 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.9, 1.4 Hz, 1H), 0.32 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.89, 149.60, 133.63, 128.31, 122.28, -2.25. All spectral data match those previously reported. (Chau et al., 2008)



5i: Colorless oil, isolated yield 60%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.3 Hz, 4H), 7.62 (d, *J* = 8.3 Hz, 4H), 7.48 (dd, *J* = 7.8, 1.6 Hz, 4H), 7.41 – 7.33 (m, 6H), 0.55 (s, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.70, 141.92, 136.51, 134.86, 134.06, 129.57, 128.02, 126.54, -2.73. HRMS (EI) *m/z*: calcd for $C_{28}H_{30}O_2Si_2S$ [M$^+$] 486.1500, found 486.1503.

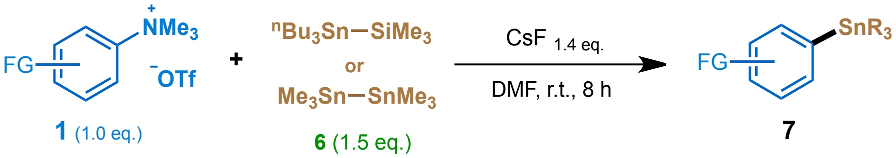
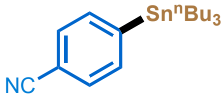
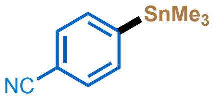


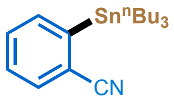
Fig.S3, related to **Scheme 2c.**



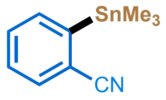
7a: Colorless oil, isolated yield 82%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 2.59 (s, 3H), 1.59 – 1.48 (m, 6H), 1.33 (dd, *J* = 14.6, 7.3 Hz, 6H), 1.20 – 0.98 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 198.66, 150.30, 136.64, 136.59, 127.10, 29.04, 27.33, 26.55, 13.66, 9.68.; All spectral data match those previously reported. (Komeyama et al., 2015)



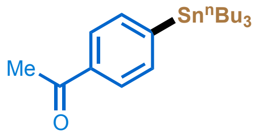
7b: Colorless oil, isolated yield 85%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.66 – 7.50 (m, 4H), 0.33 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.28, 136.31, 130.87, 119.13, 111.85, -9.49.; All spectral data match those previously reported. (Chen et al., 2016)



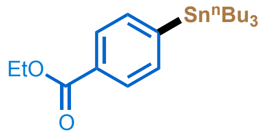
7c: Colorless oil, isolated yield 60%;^{1}H NMR (300 MHz, CDCl$_3$) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.43 (m, 2H), 7.36 (td, *J* = 7.5, 1.5 Hz, 1H), 1.63 – 1.48 (m, 6H), 1.41 – 1.26 (m, 6H), 1.26 – 1.17 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 148.37, 136.96, 132.89, 131.37, 128.27, 120.60, 120.28, 28.98, 27.23, 13.63, 10.05.; All spectral data match those previously reported. (Shirakawa et al., 2003)



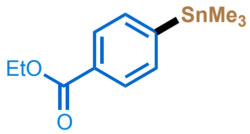
7d: Colorless oil, isolated yield 76%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.66 (ddd, *J* = 7.6, 1.3, 0.7 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.39 (td, *J* = 7.5, 1.6 Hz, 1H), 0.44 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 148.03, 136.40, 132.79, 131.51, 128.59, 120.31, 120.03, -9.02.; All spectral data match those previously reported. (Chen et al., 2016)



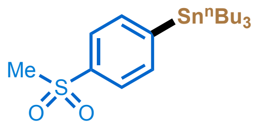
7e: Colorless oil, isolated yield 60%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.56 (s, 4H), 1.51 (d, *J* = 7.7 Hz, 6H), 1.32 (d, *J* = 7.2 Hz, 6H), 1.19 – 0.99 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.37, 136.89, 130.73, 119.26, 111.57, 28.98, 27.30, 13.64, 9.75.; All spectral data match those previously reported. (Komeyama et al., 2015)



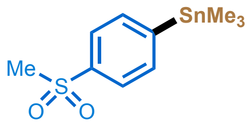
7f: Colorless oil, isolated yield 82%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.63 – 1.47 (m, 6H), 1.35 (dd, *J* = 16.0, 7.3 Hz, 10H), 1.14 – 1.01 (m, 5H), 0.88 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.10, 149.49, 136.39, 129.93, 128.35, 60.83, 29.04, 27.33, 14.36, 13.66, 9.66.; All spectral data match those previously reported. (Reed et al., 2012)



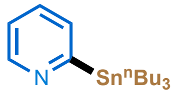
7g: Colorless oil, isolated yield 61%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.32 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.94, 149.44, 135.72, 130.16, 128.47, 60.85, 14.33, -9.55.; All spectral data match those previously reported. (Chen et al., 2016)



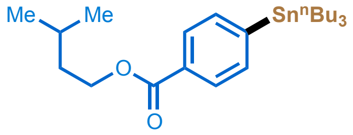
7h: Colorless oil, isolated yield 60%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 3.05 (s, 3H), 1.59 – 1.46 (m, 6H), 1.33 (dq, *J* = 14.2, 7.1 Hz, 6H), 1.15 – 1.04 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 151.36, 140.01, 137.16, 125.88, 44.50, 28.98, 27.30, 13.63, 9.79. All spectral data match those previously reported. (Tang et al., 2010)



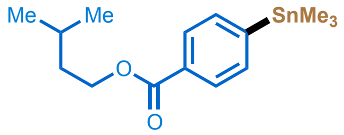
7i: Colorless oil, isolated yield 83%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 3.04 (s, 3H), 0.35 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 151.29, 140.30, 136.60, 126.06, 44.53, -9.45. HRMS (EI) *m/z*: calcd for $C_{10}H_{16}O_2SSn$ [M$^+$] 319.9888, found 319.9896.



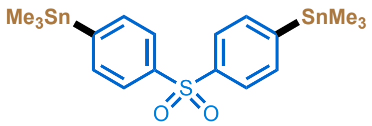
7j: Colorless oil, isolated yield 52%; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.73 (ddd, *J* = 4.9, 1.6, 1.0 Hz, 1H), 7.49 (td, *J* = 7.5, 1.8 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.11 (ddd, *J* = 7.6, 4.9, 1.4 Hz, 1H), 1.59 – 1.52 (m, 6H), 1.33 (dq, *J* = 14.6, 7.3 Hz, 6H), 1.14 – 1.10 (m, 6H), 0.88 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 174.09, 150.51, 133.24, 132.36, 121.97, 29.06, 27.33, 13.66, 9.76. All spectral data match those previously reported. (Fargeas et al., 2003)



7k: Colorless oil, isolated yield 70%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 1.85 – 1.75 (m, 1H), 1.66 (q, *J* = 6.8 Hz, 2H), 1.52 (dd, *J* = 15.7, 8.1 Hz, 5H), 1.37 – 1.28 (m, 7H), 1.14 – 1.02 (m, 6H), 0.97 (d, *J* = 6.6 Hz, 6H), 0.88 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.12, 149.47, 136.38, 129.93, 128.33, 63.49, 37.45, 29.04, 27.33, 25.22, 22.53, 13.66, 9.66. HRMS (EI) *m/z*: calcd for $C_{24}H_{42}O_2Sn$ [M$^+$] 482.2201, found 482.2197.



7l: Colorless oil, isolated yield 76%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.35 (t, *J* = 6.7 Hz, 2H), 1.79 (tt, *J* = 12.9, 6.4 Hz, 1H), 1.66 (q, *J* = 6.7 Hz, 2H), 0.97 (d, *J* = 6.5 Hz, 6H), 0.31 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.01, 149.46, 135.76, 130.22, 128.50, 63.57, 37.45, 25.26, 22.53, -9.55. HRMS (EI) *m/z*: calcd for $C_{15}H_{24}O_2Sn$ [M$^+$] 356.0793, found 356.0793.



7m: Colorless oil, isolated yield 77%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 4H), 7.62 (d, *J* = 8.2 Hz, 4H), 0.30 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.43, 141.45, 136.46, 126.33, -9.52. All spectral data match those previously reported. (Jeon et al., 2014)

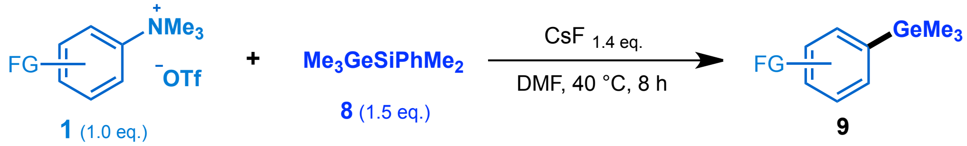
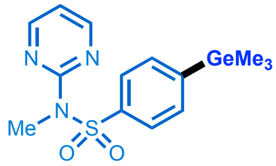


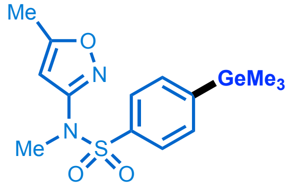
Fig.S4, related to **Scheme 2d.**

Procedure for the Preparation of $Me_3GeSiPhMe_2$:

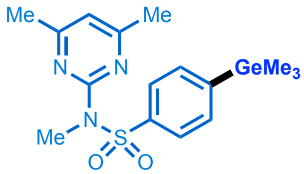
To a solution of naphthalene (0.4 mmol) in THF (16 mL), were added lithium clippings (24 mmol). The resulting mixture started turning dark green and was stirred at room temperature for 1 h under an argon atmosphere. Then chlorodimethylphenylsilane (4 mmol) was added dropwise and the mixture was stirred at room temperature for 3 h. The resulting solution was added into a stirred a solution of Me_3GeCl (4 mmol) in THF at 0°C. The reaction was stirred at room temperature for 8 h followed by extraction with hexane and H_2O. The organic phase was washed with brine and dried over Na_2SO_4. The residue was purified on column chromatography to give the product **8** as colorless oil**:** isolated yield 78%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.39 – 7.29 (m, 3H), 0.39 (s, 6H), 0.15 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.25, 133.64, 128.53, 127.78, -3.09, -3.39.



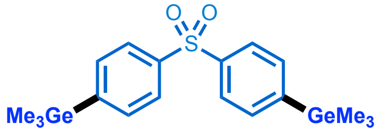
9a: Colorless oil, isolated yield 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 6.88 (t, *J* = 4.8 Hz, 1H), 3.68 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.78, 157.46, 149.73, 140.12, 132.97, 127.28, 115.38, 34.23, -1.91. HRMS (EI) *m/z*: calcd for $C_{14}H_{19}N_3O_2GeS$ [M^+] 367.0404, found 367.0404.



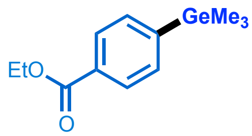
9b: Colorless oil, isolated yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 6.51 (s, 1H), 3.26 (s, 3H), 2.38 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.33, 160.86, 150.80, 136.55, 133.79, 126.05, 97.58, 35.12, 12.67, -1.96. HRMS (EI) *m/z*: calcd for $C_{13}H_{17}O_3N_2GeS$ $[M-CH_3]^+$ 355.0166, found 355.0136.



9c: Colorless oil, isolated yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 6.57 (s, 1H), 3.66 (s, 3H), 2.31 (s, 6H), 0.39 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.24, 158.20, 149.33, 140.59, 132.59, 127.74, 114.45, 33.85, 23.62, -1.89. HRMS (ESI) *m/z*: calcd for $C_{16}H_{24}N_3O_2SGe$ $[M+H]^+$ 396.0801, found 396.0811.



9d: Colorless oil, isolated yield 70%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 4H), 7.59 (d, *J* = 8.2 Hz, 4H), 0.38 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.14, 141.47, 133.76, 126.58, -1.95. HRMS (EI) *m/z*: calcd for $C_{17}H_{21}O_2Ge_2S$ $[M-CH_3]^+$ 436.9680, found 436.9686.



9e: Colorless oil, isolated yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.89, 149.20, 132.91, 130.25, 128.60, 60.87, 14.34, -1.90. All spectral data match those previously reported. (Komami et al., 2018)

3.4 General Procedure for the Selenation Reaction of Arylammonium Salts (Fig. S5)

A flask was charged with RSeSeR (0.2 mmol) and 1mL THF, KBH_4 (0.4 mmol) in 1mL H_2O was added. The reaction mixture was stirred at r.t. for 10 minutes and then aryltrimethylammonium triflates (0.2 mmol) in 1mL DMF was added. After 3 h, the water (30 mL) was added to remove DMF. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product and NMR yields with mesitylene as an internal standard.

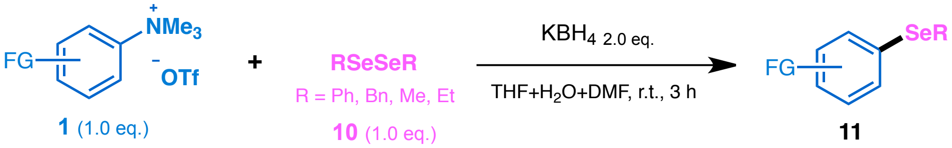
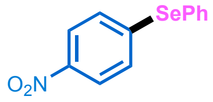
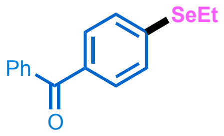


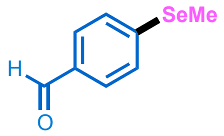
Fig.S5, related to **Scheme 2e.**



11a: Yellow oil, isolated yield 90%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, *J* = 9.0 Hz, 2H), 7.64 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.42 (dt, *J* = 14.2, 7.0 Hz, 3H), 7.36 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.22, 143.94, 135.89, 130.06, 129.74, 129.39, 127.24, 123.98.; All spectral data match those previously reported. (Maity et al., 2017)

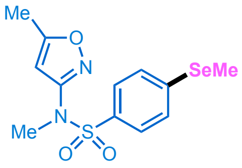


11b: Colorless oil, isolated yield 56%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.52 (dd, *J* = 15.6, 7.7 Hz, 4H), 3.06 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 196.08, 138.04, 137.64, 135.15, 132.32, 130.57, 130.16, 129.89, 128.28, 20.58, 15.19. HRMS (EI) *m/z*: calcd for $C_{15}H_{14}OSe$ [M$^+$] 290.0204, found 290.0196.

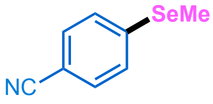


11c: Colorless oil, isolated yield 81%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.93 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 191.45, 142.40, 133.95, 129.95, 128.85, 6.43.; All spectral data match those previously reported. (Sugiura et al., 1990)

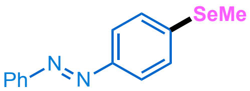
11d: Colorless oil, isolated yield 85%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.54 (d, *J* = 4.8 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 12.6, 5.7 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.03 (t, *J* = 4.2 Hz, 1H), 4.49 (s, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 170.72, 157.24, 138.58, 129.06, 128.48, 126.93, 117.27, 30.32.; All spectral data match those previously reported. (Ma et al., 2017)



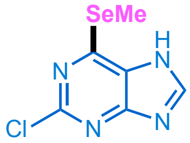
11f: Colorless oil, isolated yield 65%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.48 (s, 1H), 3.25 (s, 3H), 2.38 (d, *J* = 2.0 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.39, 160.79, 141.28, 133.69, 129.11, 127.39, 97.60, 35.15, 12.68, 6.54. HRMS (ESI) *m/z*: calcd for $C_{15}H_{19}N_2O_5S$ [M+H]$^+$ 339.1009, found 339.1007. HRMS (ESI) *m/z*: calcd for $C_{12}H_{15}N_2O_3SSe$ [M+H]$^+$ 346.9969, found 346.9973.



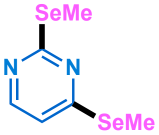
11g: Colorless oil, isolated yield 41%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 140.28, 132.17, 129.19, 118.90, 108.98, 6.58. All spectral data match those previously reported. (Lewis et al., 1987)



11h: Yellow solid, isolated yield 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.45 (m, 5H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.23, 150.35, 136.38, 130.44, 129.29, 128.65, 122.92, 122.34, 6.46. HRMS (ESI) *m/z*: calcd for $C_{13}H_{13}N_2Se$ $[M+H]^+$ 277.0244, found 277.0249.



11i: White solid, isolated yield 80%; ^{1}H NMR (400 MHz, DMSO) δ 13.75 (s, 1H), 8.52 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 174.33, 152.18, 144.70, 129.62, 123.99. HRMS (ESI) *m/z*: calcd for $C_{15}H_{19}N_2O_5S$ $[M+H]^+$ 339.1009, found 339.1007. HRMS (ESI) *m/z*: calcd for $C_6H_6ClN_4Se$ $[M+H]^+$ 248.9446, found 248.9451.



11j: Colorless oil, isolated yield 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 5.3 Hz, 1H), 6.97 (d, *J* = 5.3 Hz, 1H), 2.45 (d, *J* = 1.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.84, 168.20, 154.00, 117.84, 6.79, 5.27. All spectral data match those previously reported. (Dhau et al., 2014)

11k: Yellow oil, isolated yield 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.35 (d, *J* = 8.6 Hz, 1H), 2.93 – 2.87 (m, 2H), 2.62 – 2.57 (m, 2H), 2.41 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.83, 143.75, 140.41, 127.48, 123.43, 121.60, 58.82, 45.37, 33.25, 6.74. HRMS (ESI) *m/z*: calcd for $C_{11}H_{17}N_2O_2Se$ $[M+H]^+$ 289.0455, found 289.0448.

3.5 General Procedure for the Amination Reaction of Arylammonium Salts (Fig. S6)

A Schlenk tube was charged with $ArNH_2$ (0.3 mmol), KHMDS (0.28 mL, 1M in THF) and DMF (3mL). The reaction mixture was stirred at r.t. for 5 minutes and then aryltrimethylammonium triflates (0.2 mmol) was added. After 3 h, the water (30 mL) was added to remove DMF. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified on column chromatography or preparative TLC (silica gel) to give the product and NMR yields with mesitylene as an internal standard.

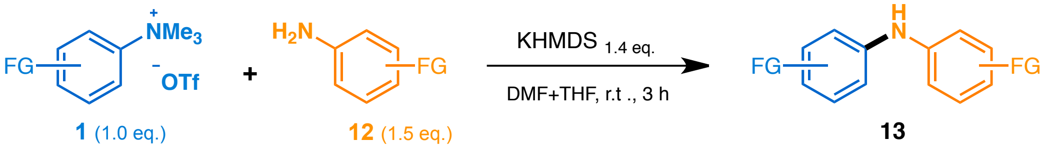
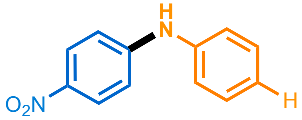
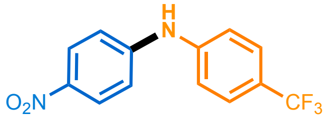


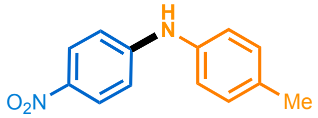
Fig.S6, related to **Scheme 2f.**



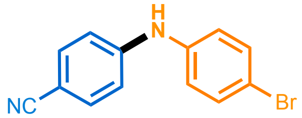
13a: Yellow oil, isolated yield 75%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.12 (d, *J* = 9.2 Hz, 2H), 7.39 (dd, *J* = 8.4, 7.5 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.31 (s, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.16, 139.77, 139.48, 129.72, 126.22, 124.65, 121.91, 113.67.; All spectral data match those previously reported. (Ding et al., 2017)



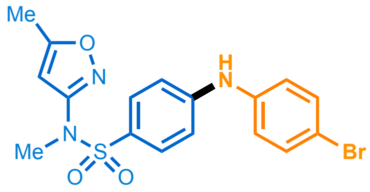
13b: Yellow oil, isolated yield 78%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, *J* = 9.1 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 9.2 Hz, 2H), 6.47 (s, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 148.29, 143.18, 141.02, 127.01 (q, $^{3}J_{\text{C-F}}$ = 3.7 Hz), 126.13, 125.40 (q, $^{2}J_{\text{C-F}}$ = 33.0 Hz), 124.05 (q, $^{1}J_{\text{C-F}}$ = 271.4 Hz), 119.59, 115.31. HRMS (EI) *m/z*: calcd for $C_{13}H_9N_2O_2F_3$ [M^{+}] 282.0611, found 282.0606.



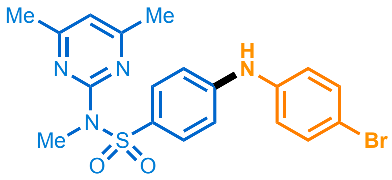
13c: White solid, isolated yield 40%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10 (d, *J* = 9.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 6.22 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.83, 139.48, 136.73, 134.86, 130.31, 126.28, 122.71, 113.22, 20.93.; All spectral data match those previously reported. (Fors et al., 2009)



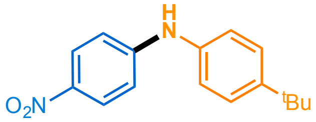
13d: Colorless oil, isolated yield 70%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.07 (s, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.42, 139.25, 133.85, 132.66, 122.56, 119.65, 116.29, 115.28, 102.28. All spectral data match those previously reported. (Miti et al., 2011)



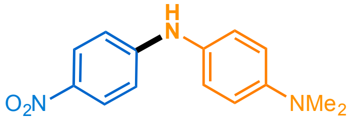
13e: Colorless oil, isolated yield 80%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 0.7 Hz, 1H), 6.11 (s, 1H), 3.24 (s, 3H), 2.37 (d, *J* = 0.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.21, 161.05, 148.39, 139.14, 132.65, 129.33, 126.67, 122.81, 116.47, 114.78, 97.69, 35.02, 12.67. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_3O_3SBr$ [M+H]+ 422.0169, found 422.0177.



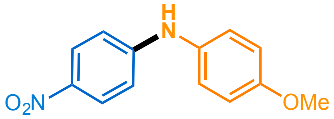
13f: Colorless oil, isolated yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.04 – 6.99 (m, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.57 (s, 1H), 6.07 (s, 1H), 3.64 (s, 3H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.17, 158.31, 147.32, 139.71, 132.55, 131.06, 130.92, 122.10, 115.71, 114.26, 114.10, 33.82, 23.69. HRMS (ESI) *m/z*: calcd for $C_{19}H_{20}N_4O_2BrS$ $[M+H]^+$ 447.0485, found 447.0482.



13g: Yellow oil, isolated yield 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.2 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 6.27 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.63, 148.00, 139.45, 136.67, 126.56, 126.24, 122.03, 113.30, 34.48, 31.34. All spectral data match those previously reported. (Kayama et al., 2016)



13h: Yellow solid, isolated yield 62%; ^{1}H NMR (400 MHz, DMSO) δ 9.02 (s, 1H), 8.02 (d, *J* = 9.2 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.79 (dd, *J* = 15.7, 7.7 Hz, 4H), 2.89 (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ 152.74, 147.92, 136.62, 128.58, 126.35, 124.22, 113.30, 111.94, 40.41. All spectral data match those previously reported. (Novak et al., 1989)

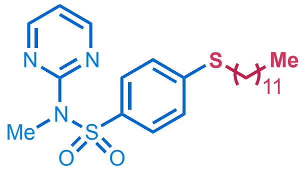


13i: Yellow solid, isolated yield 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.2 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.18 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 157.43, 151.69, 139.09, 131.97, 126.30, 125.49, 114.95, 112.60, 55.53. All spectral data match those previously reported. (McNulty et al., 2007)

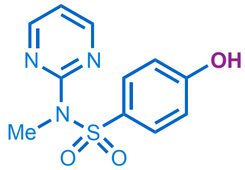
3.6 Procedure for the Late-stage Diversification of Pharmaceutical Ammonium Derivative (Fig. 4)

Various aryl-heteroatom bonds formation products **3mp**, **5j**, **7o**, **9a**, **11h**, **13h** were prepared following a similar procedure above. **14b**, **14c**, **14d** were prepared with previously reported methods. (Lang et al., 2009)

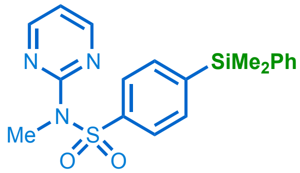
Procedure for the Preparation of 14a: A flask was charged with aryltrimethylammonium triflates (0.2 mmol), 2-mercaptoethanol (0.3 mmol), KHMDS (0.6 mmol, 2M in THF) and DMF (3 mL). The reaction mixture was stirred at r.t. for 3 h to give a yellow suspended solution. Then 1M HCl (30 mL) was added and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified on column chromatography to give the product and NMR yields with mesitylene as an internal standard.



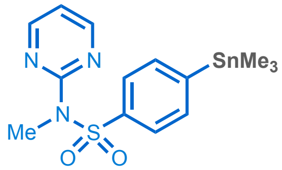
3mp: Colorless oil, isolated yield 73%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (t, *J* = 4.8 Hz, 1H), 3.67 (s, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.68 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.48 – 1.36 (m, 2H), 1.25 (s, 16H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.71, 157.44, 145.16, 136.23, 128.77, 125.87, 115.37, 34.15, 32.01, 31.91, 29.62, 29.56, 29.47, 29.33, 29.13, 28.89, 28.63, 22.69, 14.11. HRMS (EI) *m/z*: calcd for $C_{23}H_{36}N_3O_2S_2$ [M$^+$] 450.2243, found 450.2268.



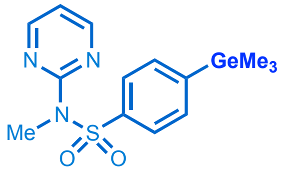
14a: Colorless oil, isolated yield 78%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.45 (d, *J* = 4.8 Hz, 2H), 7.97 – 7.90 (m, 2H), 6.90 – 6.83 (m, 3H), 3.65 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.23, 158.69, 157.48, 131.33, 130.86, 115.39, 115.25, 34.20. HRMS (ESI) *m/z*: calcd for $C_{11}H_{12}N_3O_3S$ [M+H]$^+$ 266.0594, found 266.0594.



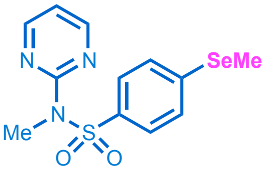
5j: Colorless oil, isolated yield 75%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.46 (d, *J* = 4.8 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.40 – 7.32 (m, 3H), 6.88 (t, *J* = 4.8 Hz, 1H), 3.68 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.76, 157.47, 145.15, 140.86, 136.78, 134.14, 129.53, 128.01, 127.19, 115.44, 34.25, -2.63. HRMS (EI) *m/z*: calcd for $C_{19}H_{22}N_3O_2SSi$ [M$^+$] 384.1197, found 384.1195.



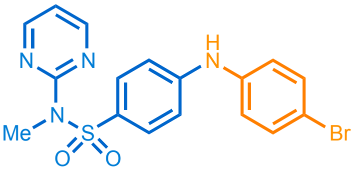
7o: Colorless oil, isolated yield 43%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 6.87 (t, *J* = 4.8 Hz, 1H), 3.68 (s, 3H), 0.31 (s, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.77, 157.46, 150.06, 140.10, 135.72, 127.10, 115.39, 34.23, -9.46. HRMS (EI) *m/z*: calcd for $C_{14}H_{20}O_2N_3SnS$ [M$^+$] 414.0293, found 414.0300.



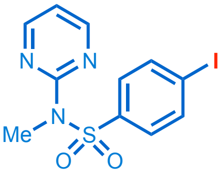
9a: Colorless oil, isolated yield 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 6.88 (t, *J* = 4.8 Hz, 1H), 3.68 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.78, 157.46, 149.73, 140.12, 132.97, 127.28, 115.38, 34.23, -1.91. HRMS (EI) *m/z*: calcd for $C_{14}H_{19}N_3O_2GeS$ [M^+] 367.0404, found 367.0404.



11h: Colorless oil, isolated yield 43%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.88 (t, *J* = 4.8 Hz, 1H), 3.67 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.67, 157.46, 140.03, 137.37, 128.73, 128.39, 115.43, 34.16, 6.54. HRMS (ESI) *m/z*: calcd for $C_{12}H_{14}N_3O_2SSe$ $[M+H]^+$ 343.9972, found 343.9994.

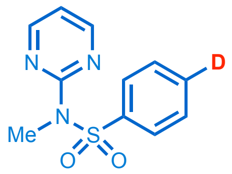


13h: Colorless oil, isolated yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.87 (t, *J* = 4.8 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.85, 157.42, 147.64, 139.53, 132.57, 130.66, 130.33, 122.34, 115.95, 115.19, 114.27, 34.16. HRMS (ESI) m/z: calcd for $C_{17}H_{16}N_4O_2SBr$ [M+H]+ 419.0172, found 419.0169.



14b: Colorless oil, isolated yield 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 6.90 (s, 1H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.51, 157.48, 140.12, 137.68, 129.81, 115.62, 100.38, 34.15. HRMS (ESI) *m/z*: calcd for $C_{11}H_{11}N_3O_2SI$ $[M+H]^+$ 375.9611, found 375.9618.

14c: Colorless oil, isolated yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 6.90 (t, *J* = 4.8 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.50, 157.53, 139.38, 131.74, 130.01, 127.94, 115.69, 34.20. HRMS (ESI) *m/z*: calcd for $C_{11}H_{11}N_3O_2SBr$ $[M+H]^+$ 327.9750, found 327.9751.



14d: Colorless oil, isolated yield 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 6.87 (t, *J* = 4.8 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.71, 157.45, 140.43, 128.45, 128.34, 128.32, 115.44, 34.19. HRMS (ESI) *m/z*: calcd for $C_{11}H_{11}N_3O_2SD$ $[M+H]^+$ 251.0708, found 251.0712.

3.7 Procedure for Click Reaction of NBD-ammonium Salt and Biological Thiols (Fig. 5)

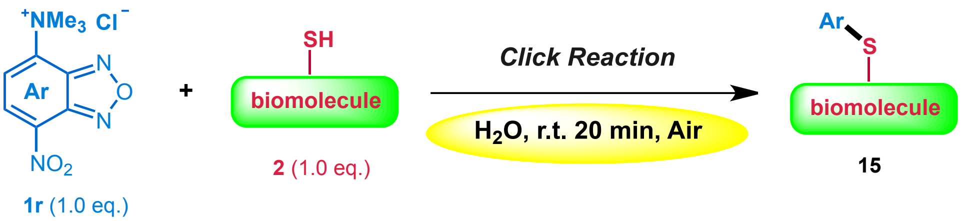


Fig.S7, related to **Scheme 4a.**

3.7.1 An open-air vial was charged with NBD-ammonium salt **1r** (0.01 mmol; for **15d**: 0.005mmol), biological thiols (0.01 mmol; for **15d**: 0.005mmol) and H_2O (1 mL). The reaction mixture was stirred at r.t. for 20 minutes and then determined by LCMS.

3.7.2 An open-air vial was charged with NBD-ammonium salt **1r** (0.05 mmol), biological thiols (**2r, 2v, 2w**) (0.05 mmol) and D_2O (0.5 mL). The reaction mixture was stirred at r.t. for 20 minutes and then was analyzed by ^{1}H-NMR in DMSO-d_6–D_2O (4:1, v/v). When Cys or Hcy was the reactant, the H^a and H^b protons of the product NBD moiety showed upfield shifts, especially for H^a, which were different from NBD-SR (GSH as reactant) was being formed. (Chen et al., 2016) **(Fig. S8)**

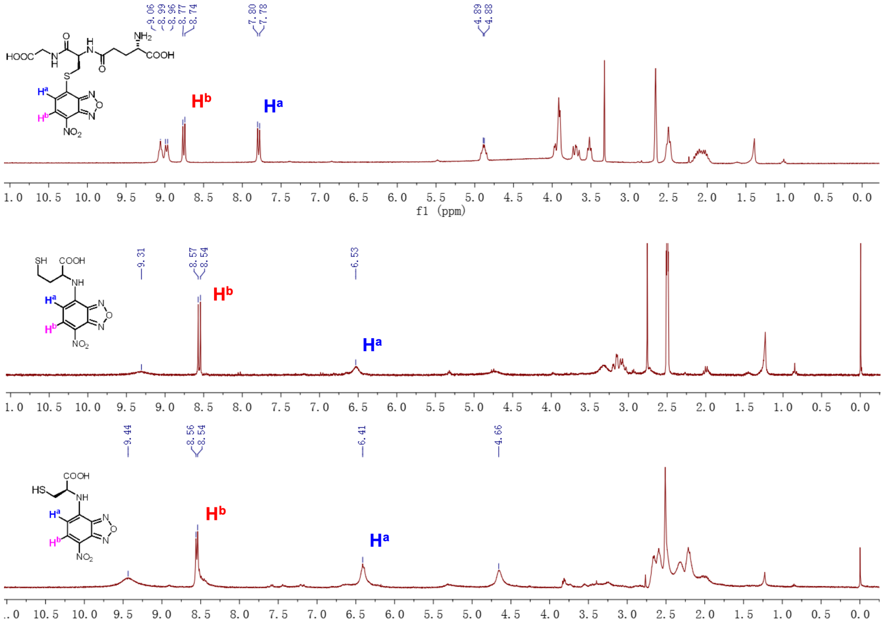


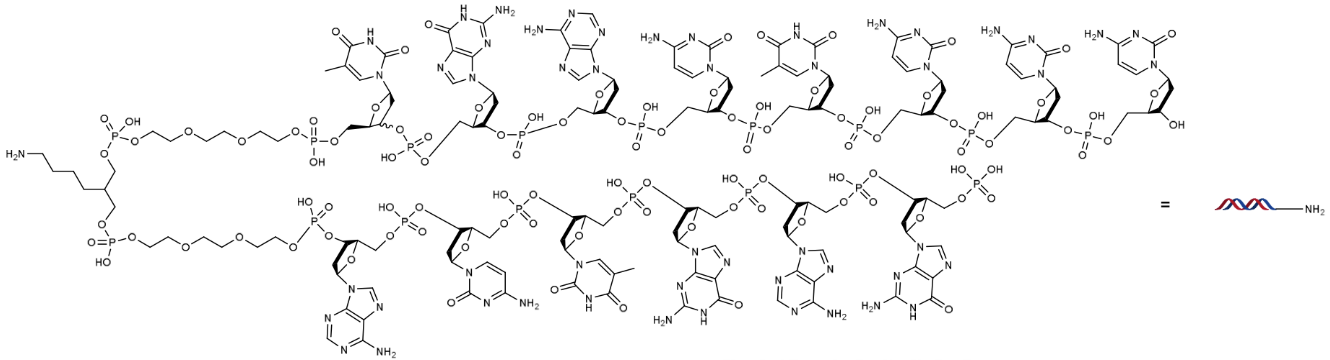
Fig.S8, related to **Scheme 4a.**

3.7.3 For the procedure of fluorescence measurement: stock solutions of probe (**1r**) and biological thiols were freshly prepared in H_2O prior to each experiment. 5eq. biological thiols (250μM) were added to separate portions of the probe (50μM) solution and mixed thoroughly. The reaction mixture was shaken uniformly before absorption and fluorescence spectra were measured.

3.8 Procedure for on-DNA Reactions

3.8.1 Headpiece Structure (Fig. S9)

DNA headpiece HP-NH_2 (5'-/5phos/GAGTCA/iSp9/iUniAmM/iSp9/TGACTCCC-3', Figure 1) was obtained from Biosearch Technologies, Novato, CA.



Chemical Formula: $C_{154}H_{215}N_{52}O_{101}P_{17}$
Molecular Weight: 4937.23

Fig.S9, related to **Scheme 5.**

3.8.2 Preparation of HP-Ar-$N^+Me_3Cl^-$

Materials

Headpiece: 2 mM in water
B: 200 mM in water
K_2CO_3: 200 mM in water

Procedure

1) To the headpiece in H_2O (100 nmol, 50 µL), was added 100 eq. of K_2CO_3 (in 50 µL H_2O) and 60 eq. of ammonium salt **1s** (in 30 µL H_2O) . The mixture was vortexed.

2) React at room temperature for 10 h.

3) Add 5 M NaCl solution (10 % by volume) and cold ethanol (2.5 times by volume, ethanol stored at -20°C). The mixture was stored at a -80°C freezer for more than 30 minutes.

4) Centrifuge the sample for around 30 minutes at 4°C in a microcentrifuge at 10000 rpm. The above supernatant was removed and the pellet (precipitate) was cooled in liquid nitrogen and then placed on a lyophilizer. After lyophilization, the dry pellet was recovered.

5) To gain a higher yield, the dry pellet was solute in water（50 µL）, then repeat step1-4.

Molecular Weight: 5151.65

68% conversion determined by LCMS.

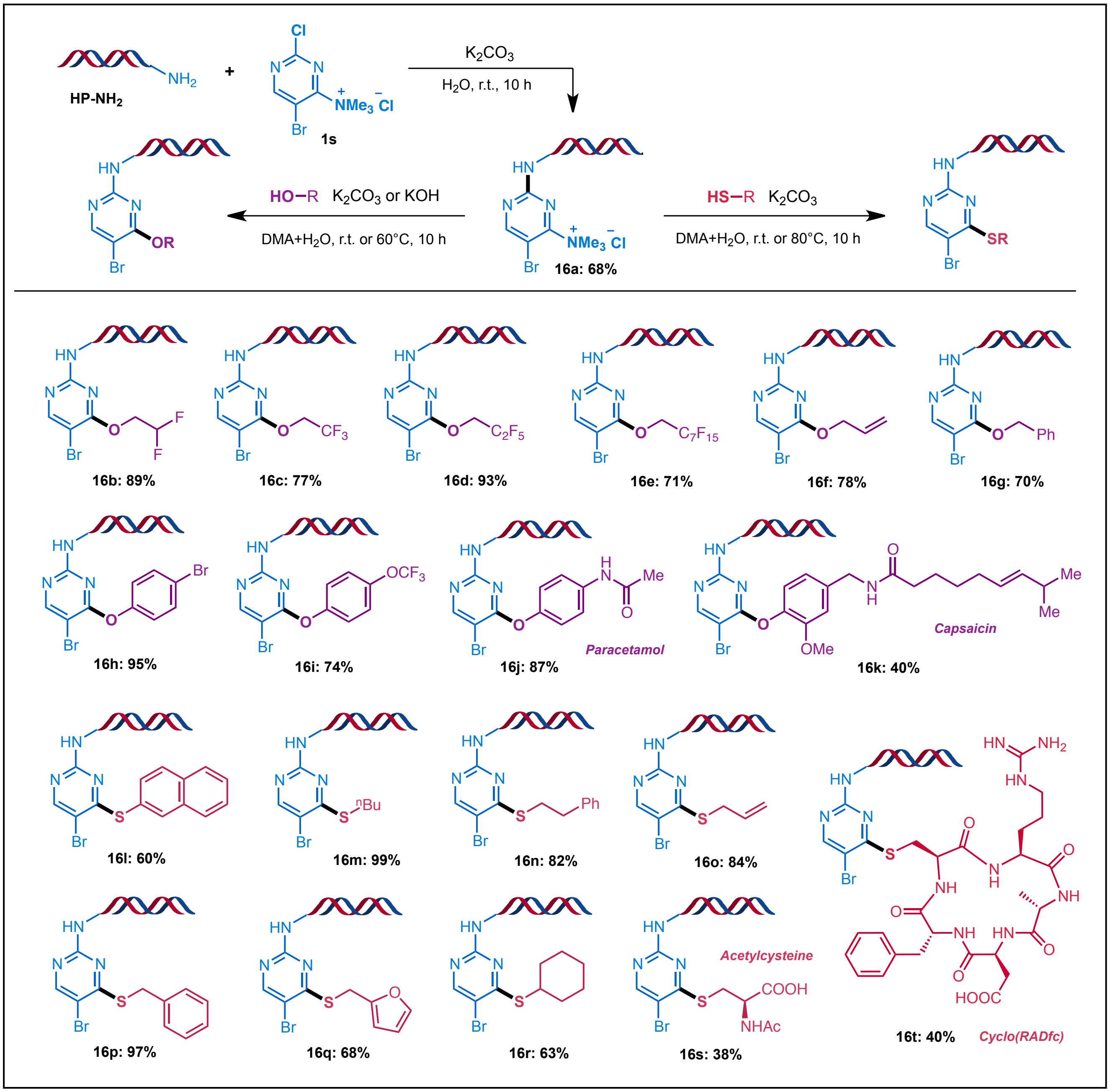


Fig.S10, related to **Scheme 5.**

3.8.3 C–O bond formations of arylammonium salts on DNA

Materials

16a: 1 mM in water

ROH: 200 mM in DMA

K_2CO_3 (or KOH): 1M in water

Procedure

1) To **16a** solution (5 nmol, 5 µL), was added 35µL H_2O, 1000 eq. of ROH (25 µL) and 1000 eq. of K_2CO_3 (for

16c–f, **16i–k**) or KOH (for **16b**, **16g–h**) (5 μL). The mixture was vortexed.

2) React at room temperature (or 60°C for **16h–k**) for 10 h.

3) Add 5 M NaCl solution (10 % by volume) and cold ethanol (2.5 times by volume, ethanol stored at -20°C). The mixture was stored at a -80°C freezer for more than 30 minutes.

4) Centrifuge the sample for around 30 minutes at 4 °C in a microcentrifuge at 10000 rpm. The abovesupernatant was removed and the pellet (precipitate) was cooled in liquid nitrogen and then placedon a lyophilizer. After lyophilization, the dry pellet was recovered.

Conversion determined by LCMS.

3.8.4 C–S bond formations of arylammonium salts on DNA

Materials

16a: 1 mM in water

RSH: 200 mM in DMA

K_2CO_3: 200 mM in water

Procedure

1) To **16a** solution (5 nmol, 5 μL), was added 35μL H_2O, 1000 eq. of RSH (25 μL) and 200 eq. of K_2CO_3 (5 μL). The mixture was vortexed.

2) React at room temperature (or 80°C for **16s**, **16t**) for 10 h.

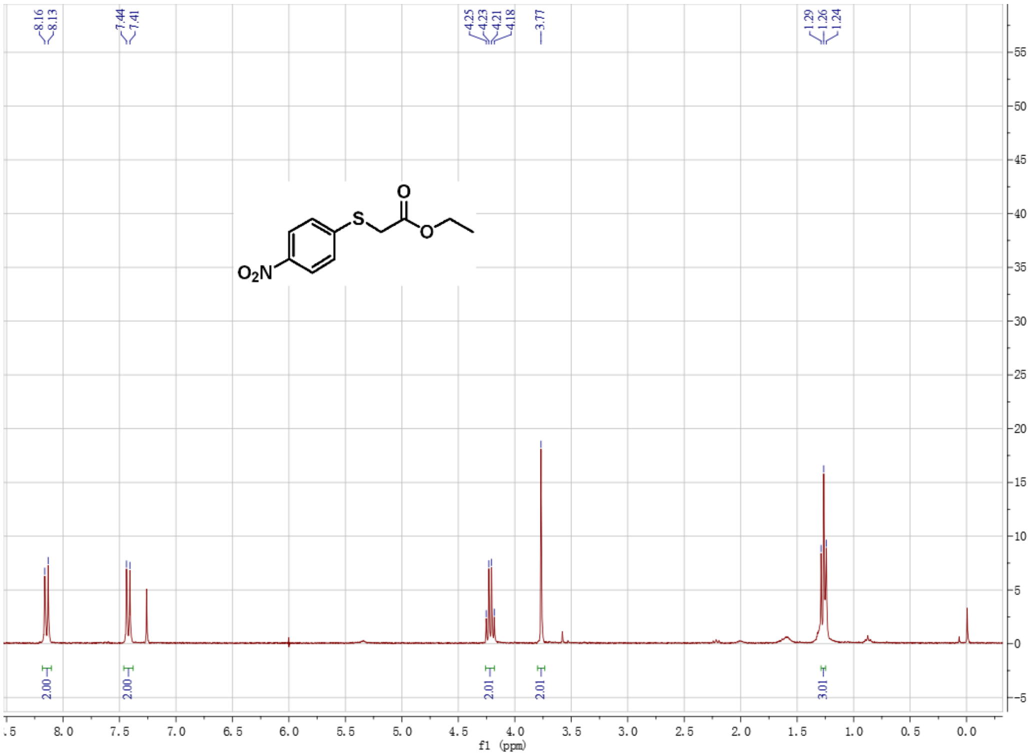
3) Add 5 M NaCl solution (10 % by volume) and cold ethanol (2.5 times by volume, ethanol stored at -20°C). The mixture was stored at a -80°C freezer for more than 30 minutes.

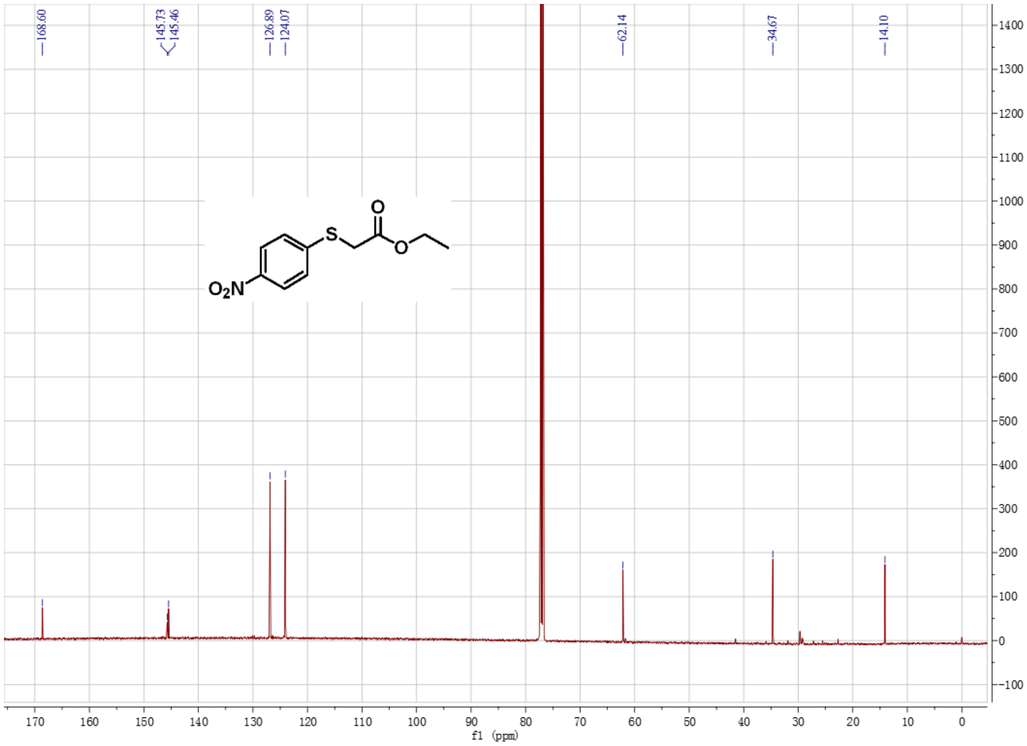
4) Centrifuge the sample for around 30 minutes at 4 °C in a microcentrifuge at 10000 rpm. The abovesupernatant was removed and the pellet (precipitate) was cooled in liquid nitrogen and then placedon a lyophilizer. After lyophilization, the dry pellet was recovered.

Conversion determined by LCMS.

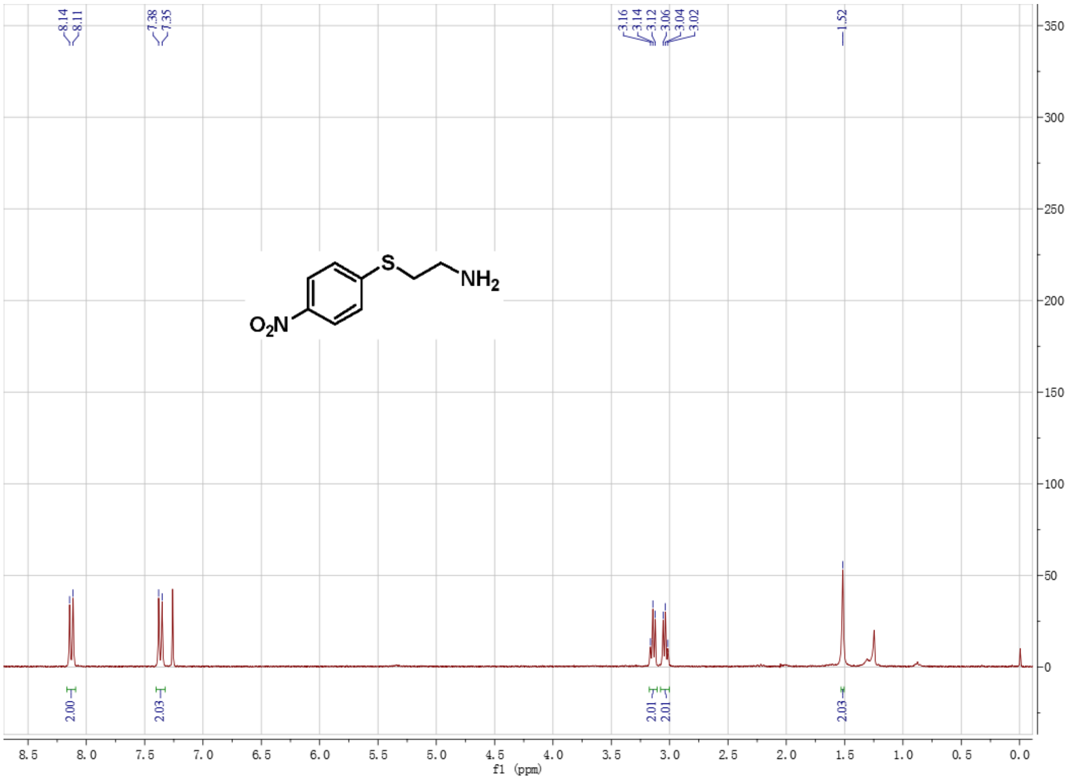
4. Copies of NMR Spectrums for All Compounds

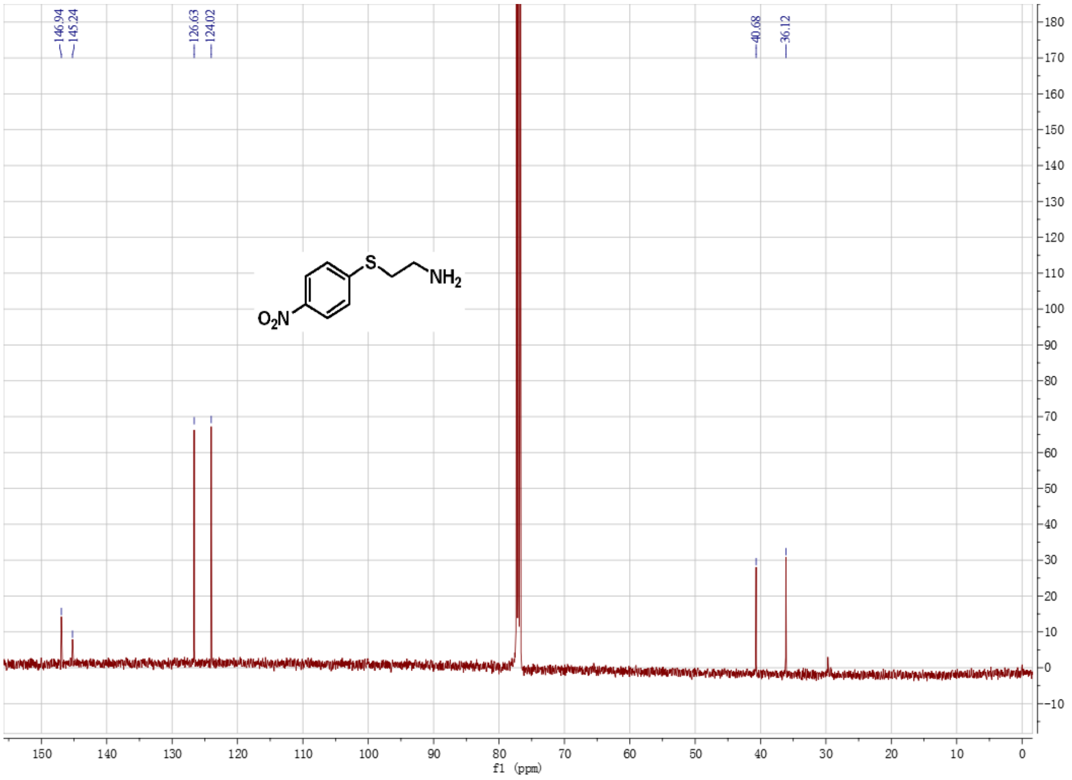
Compound **3aa**



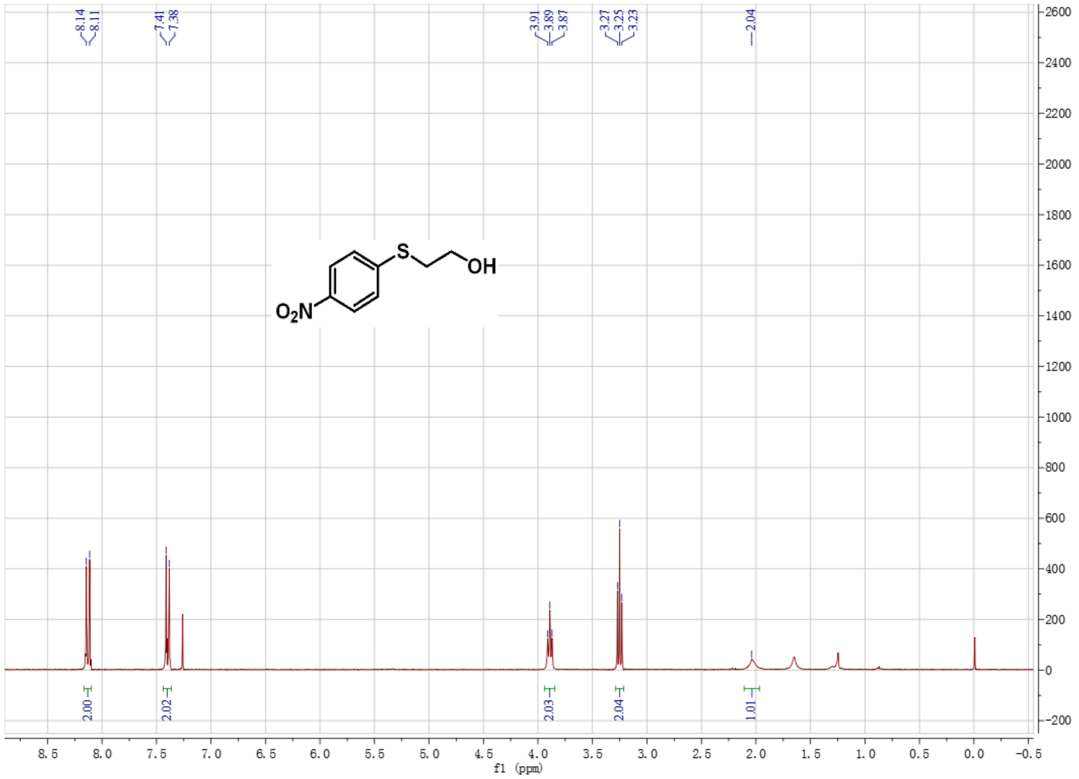


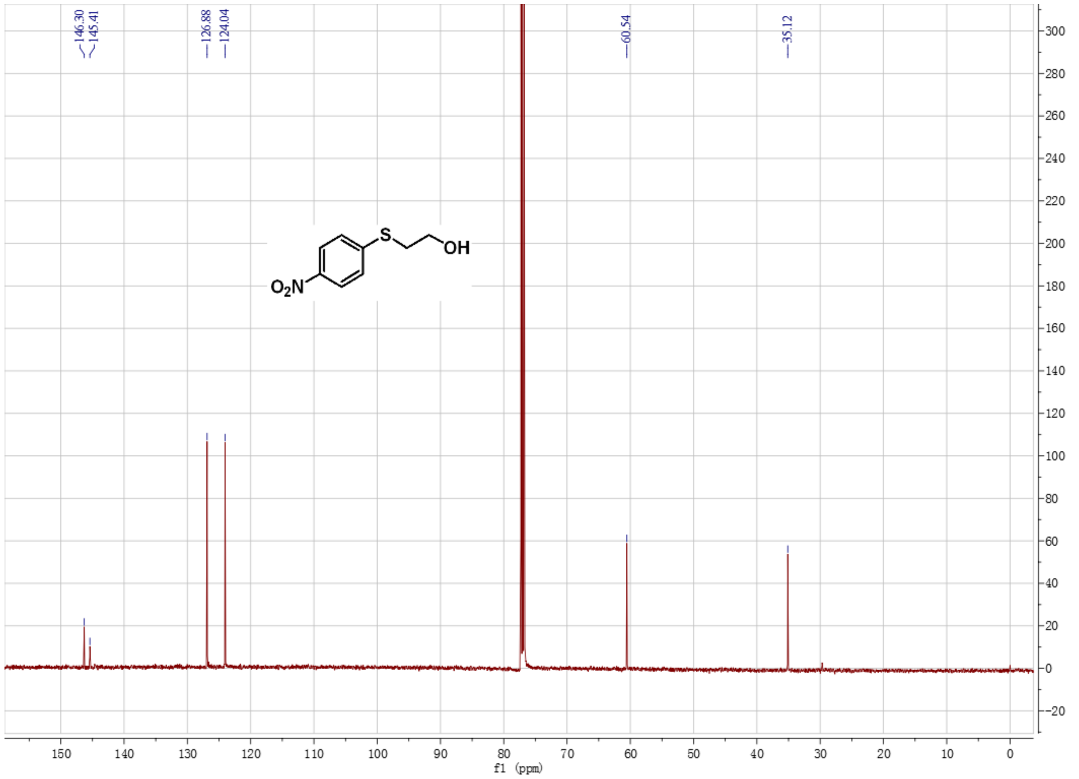
Compound **3ab**



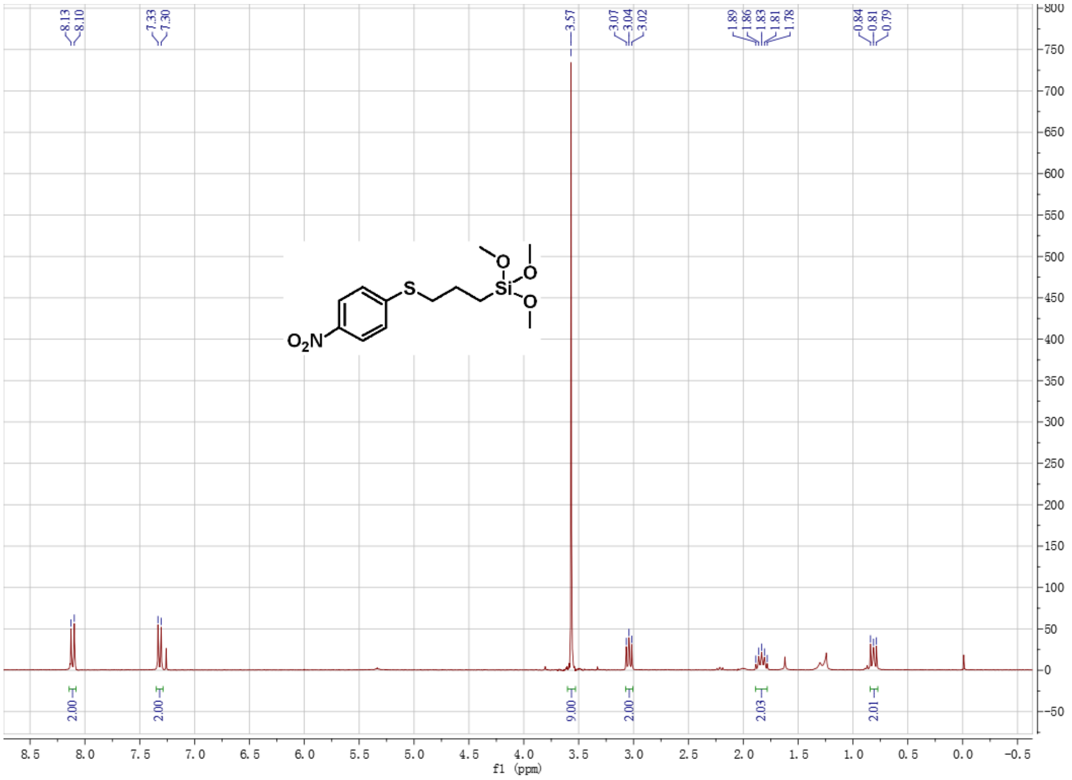


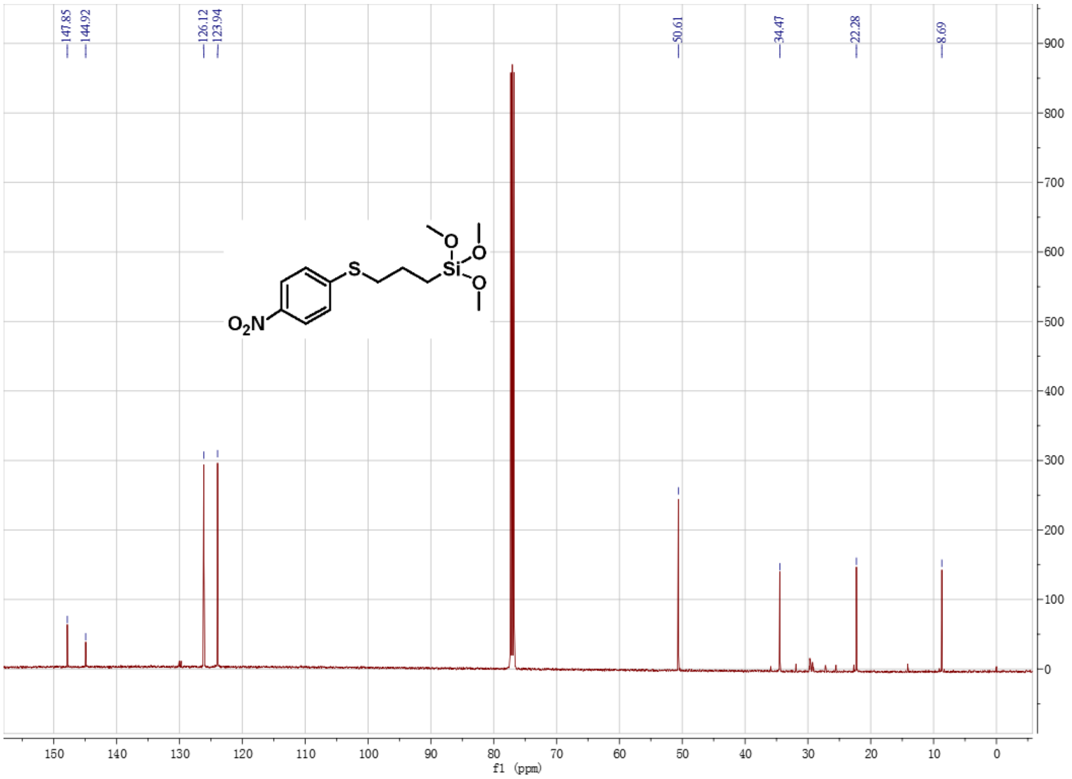
Compound **3ac**



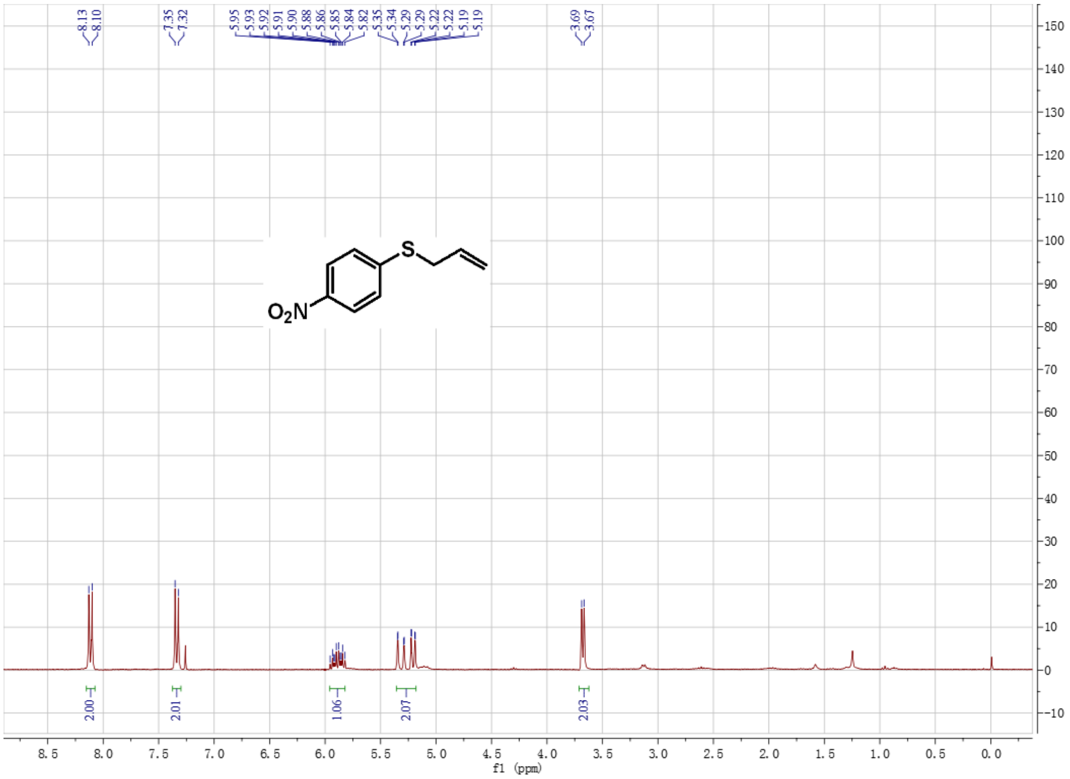


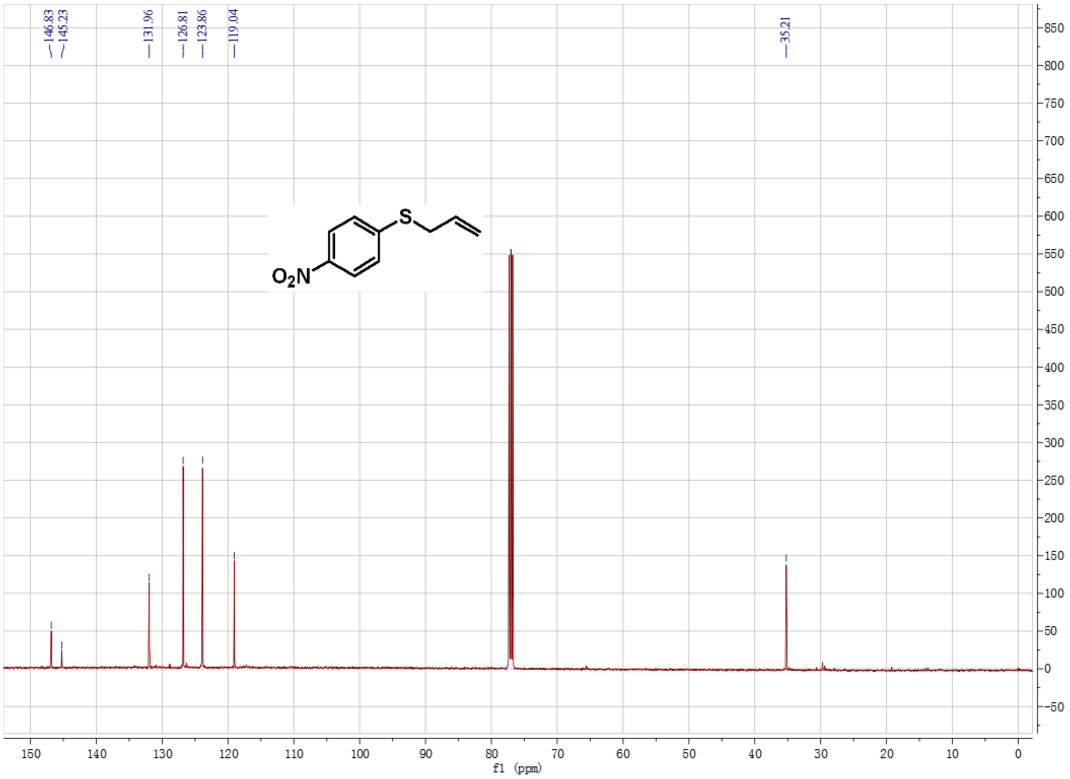
Compound **3ad**





Compound **3ae**





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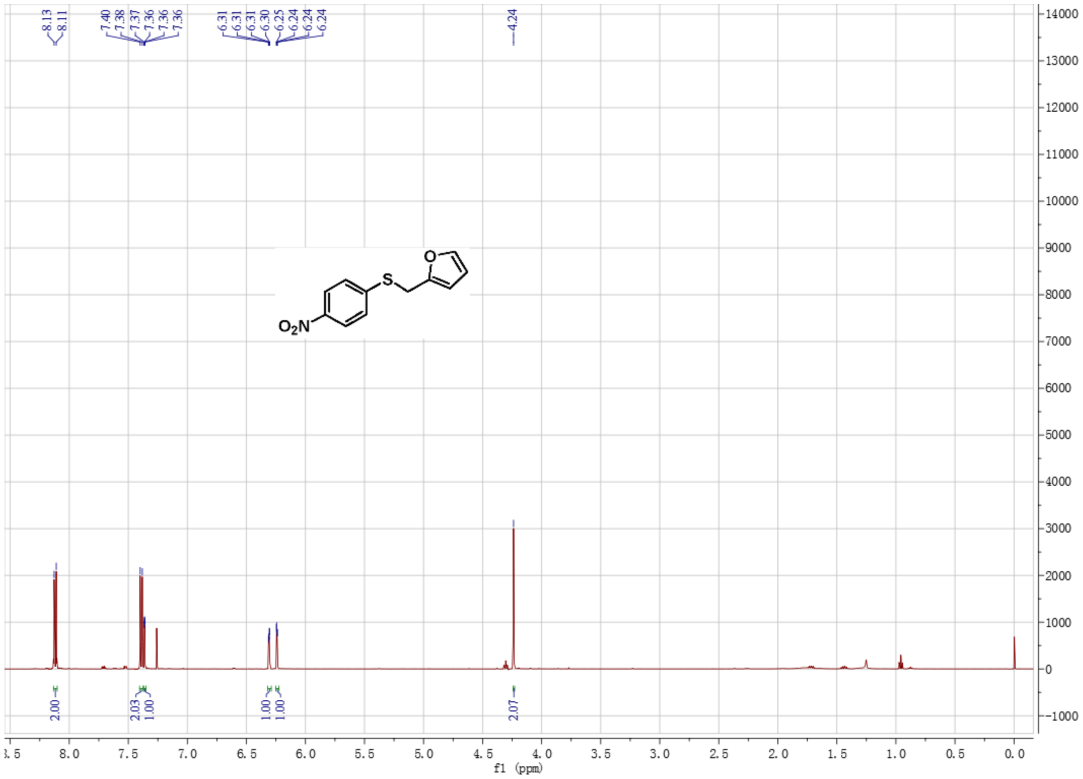

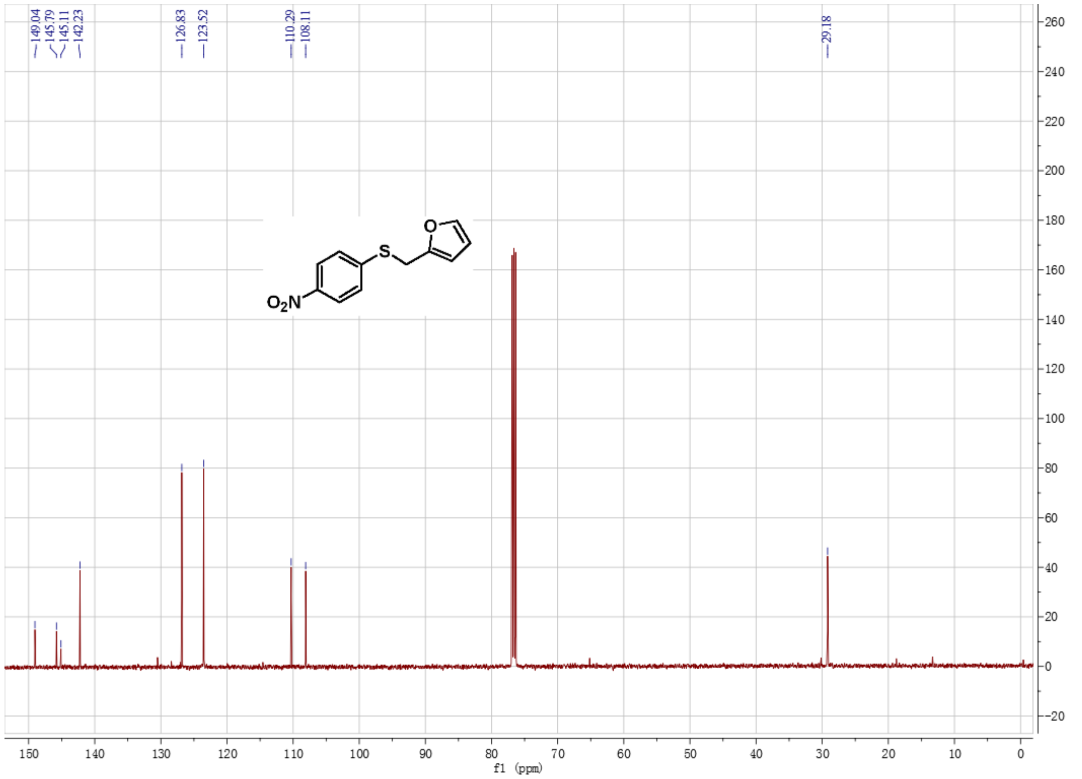

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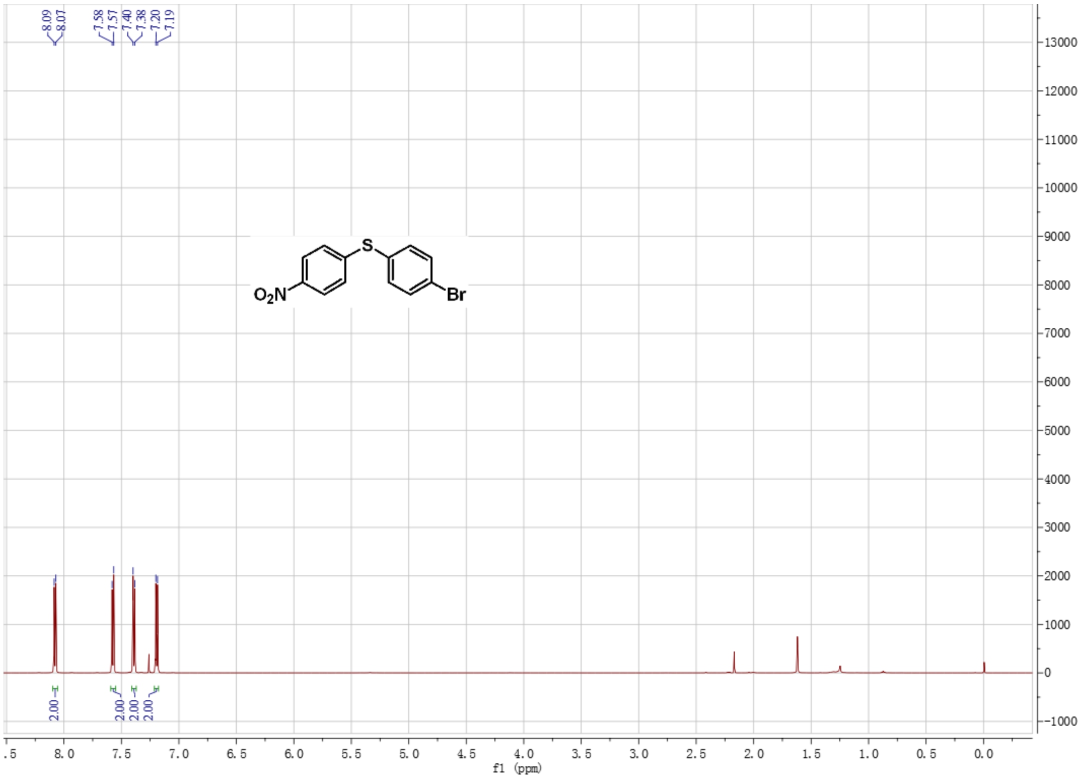

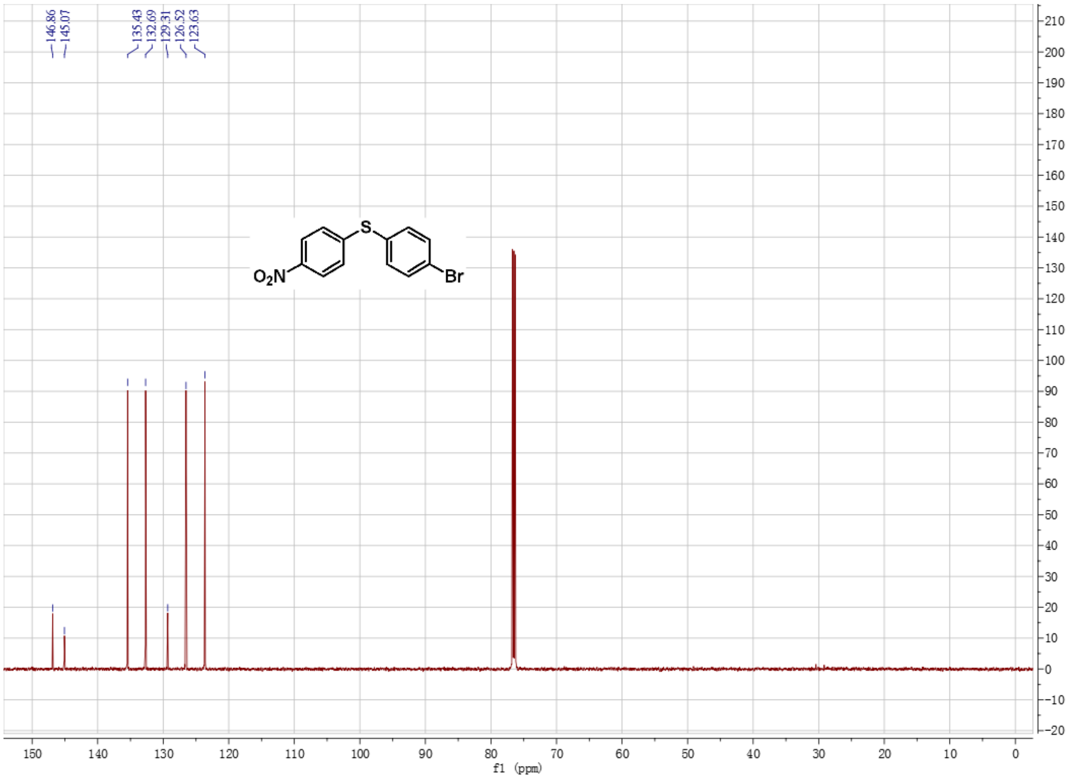

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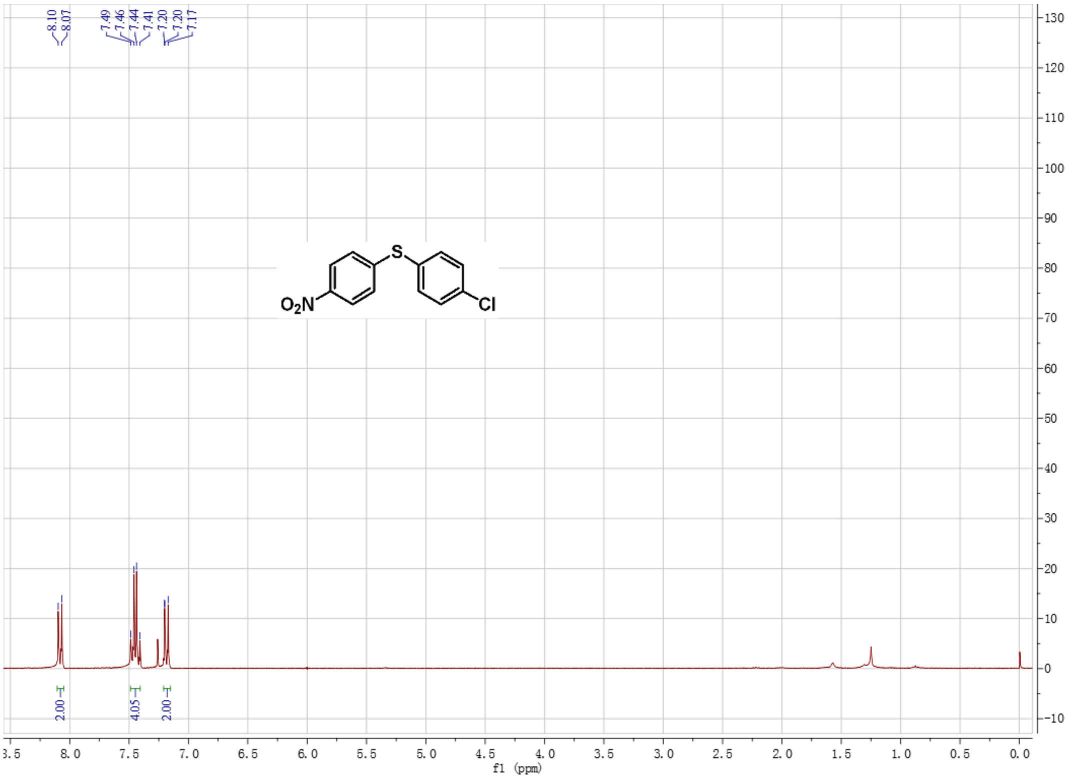

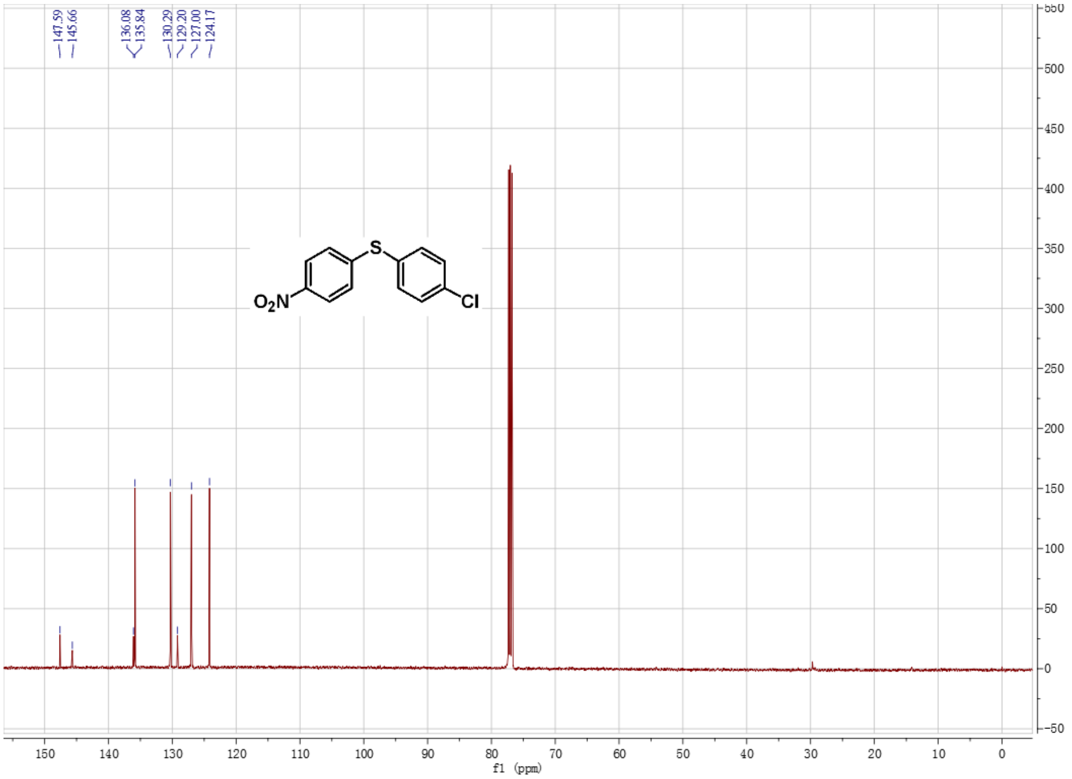

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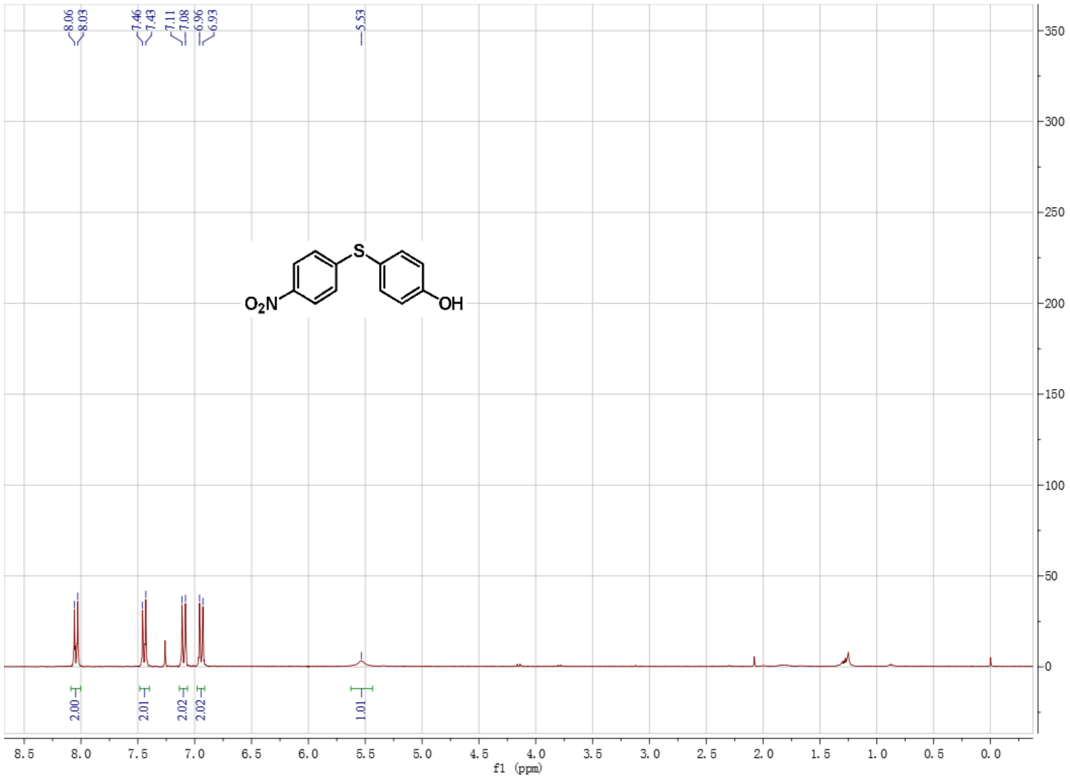

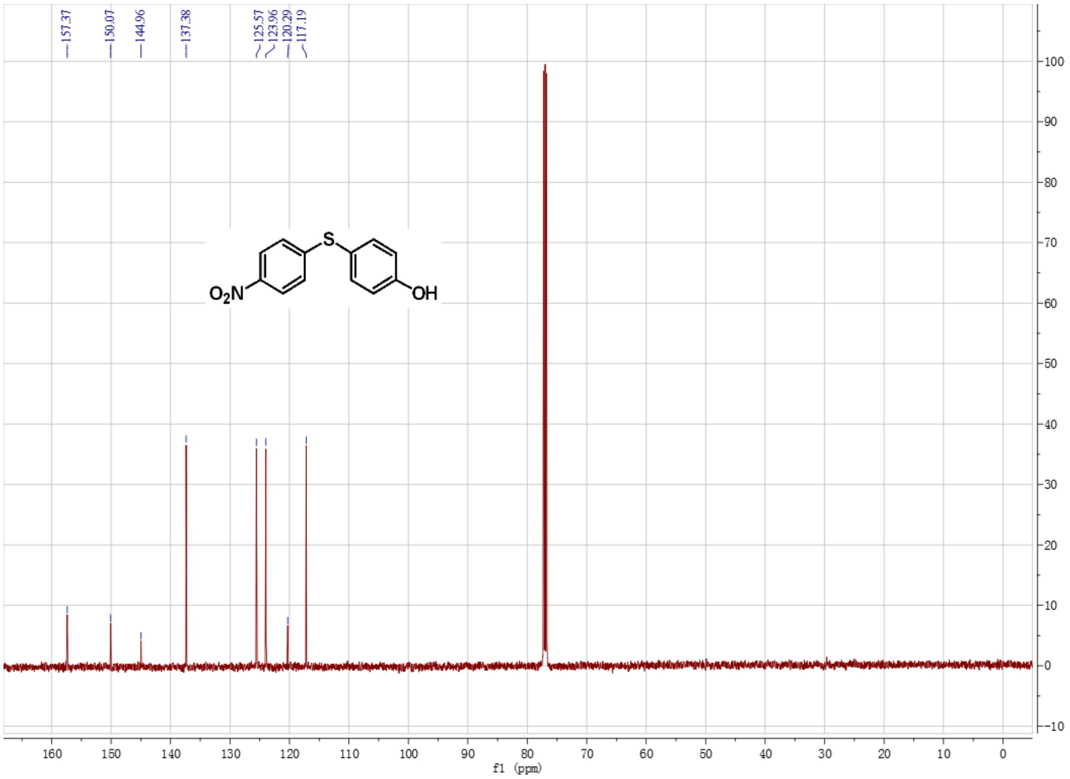

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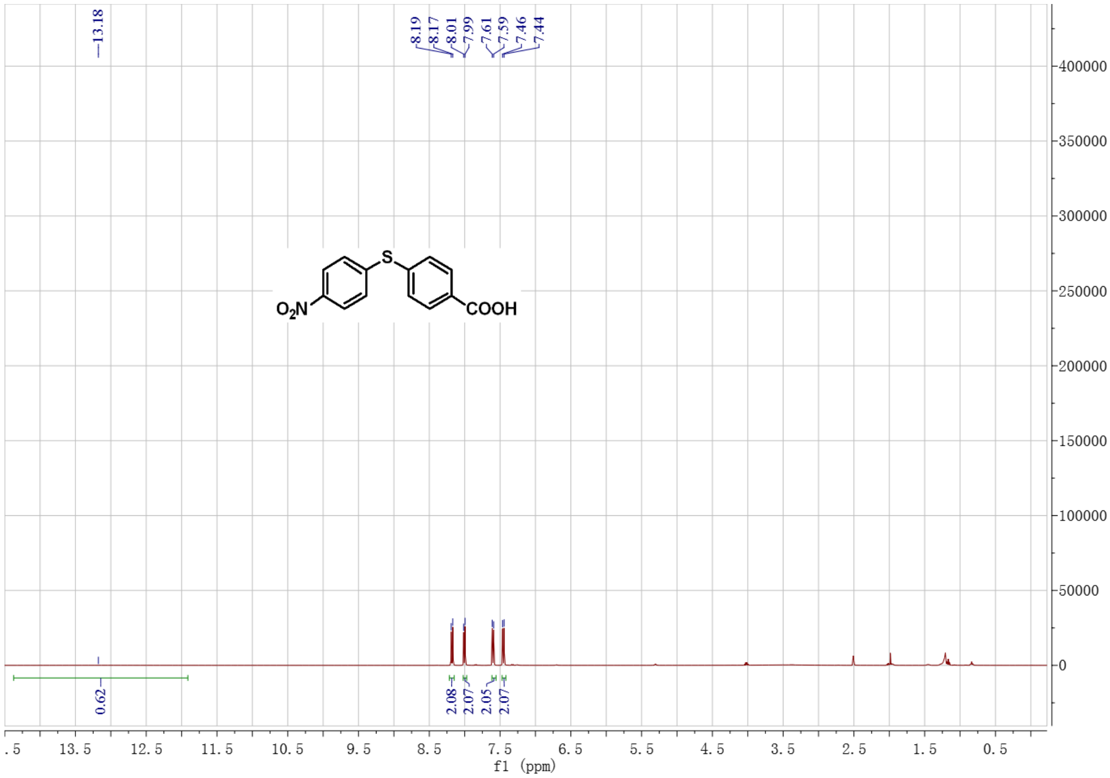

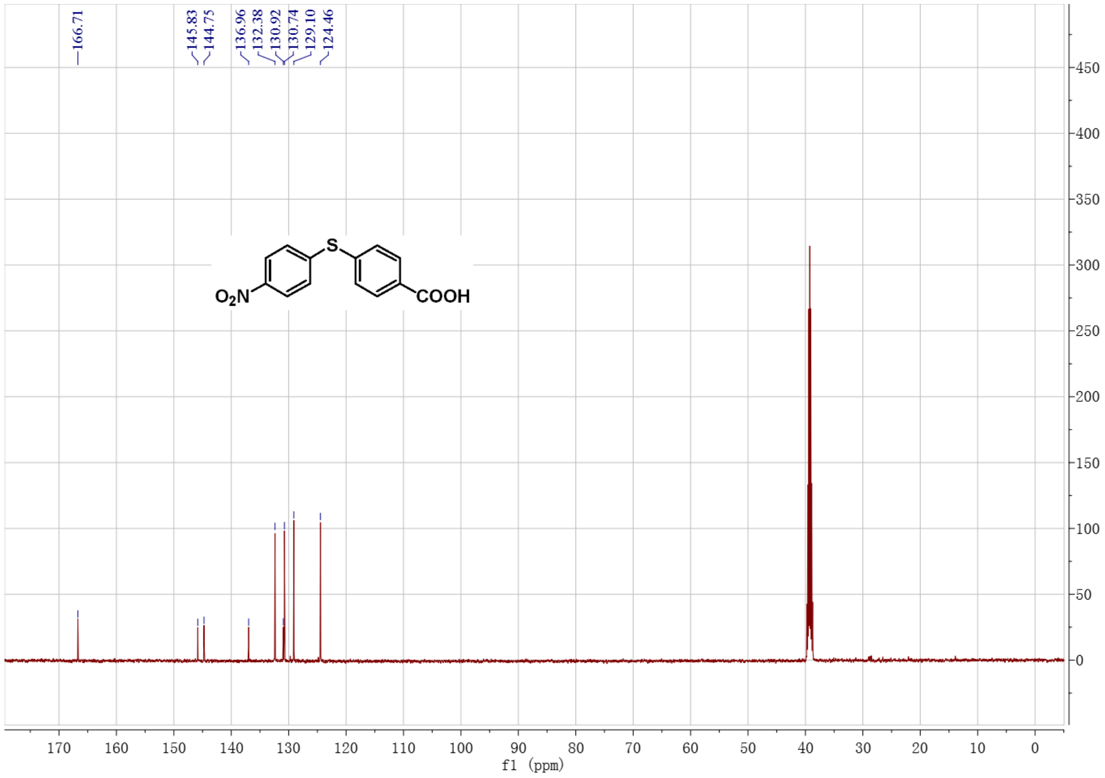

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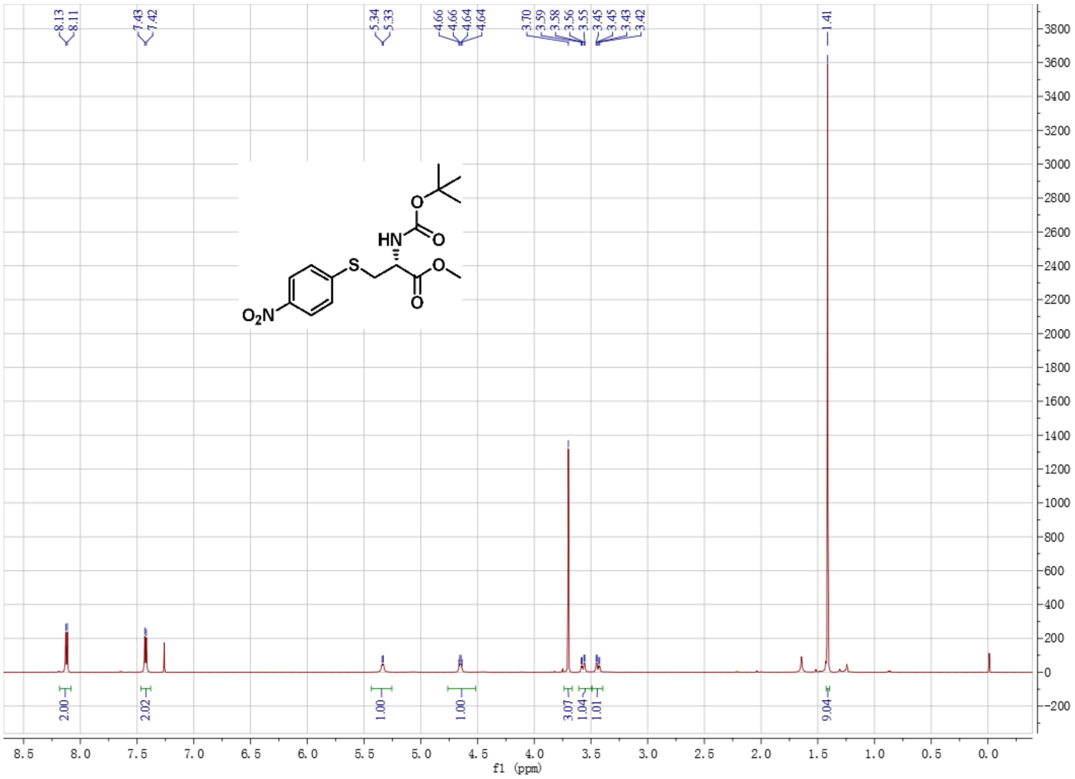
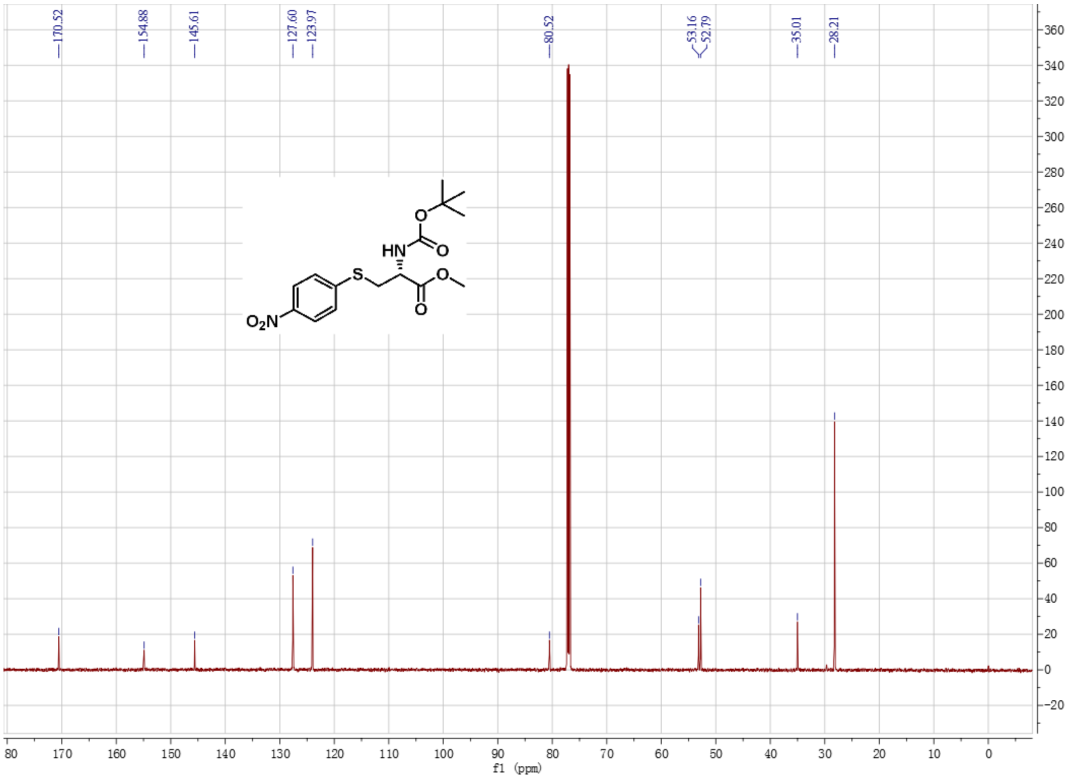
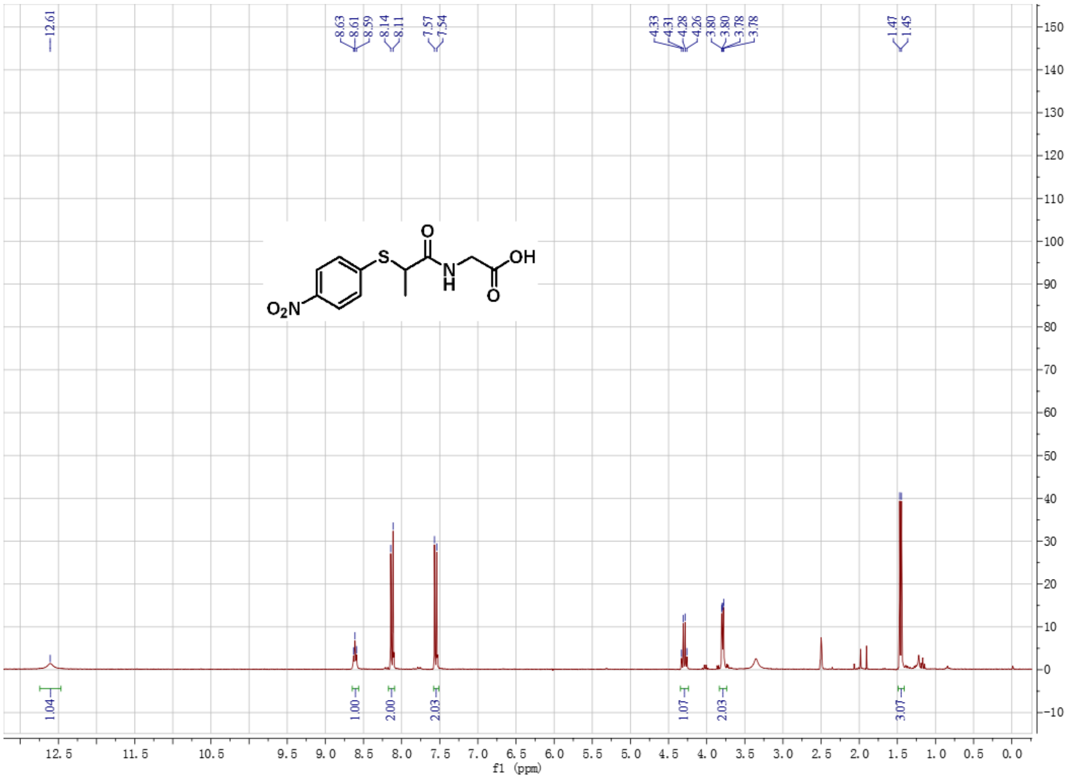
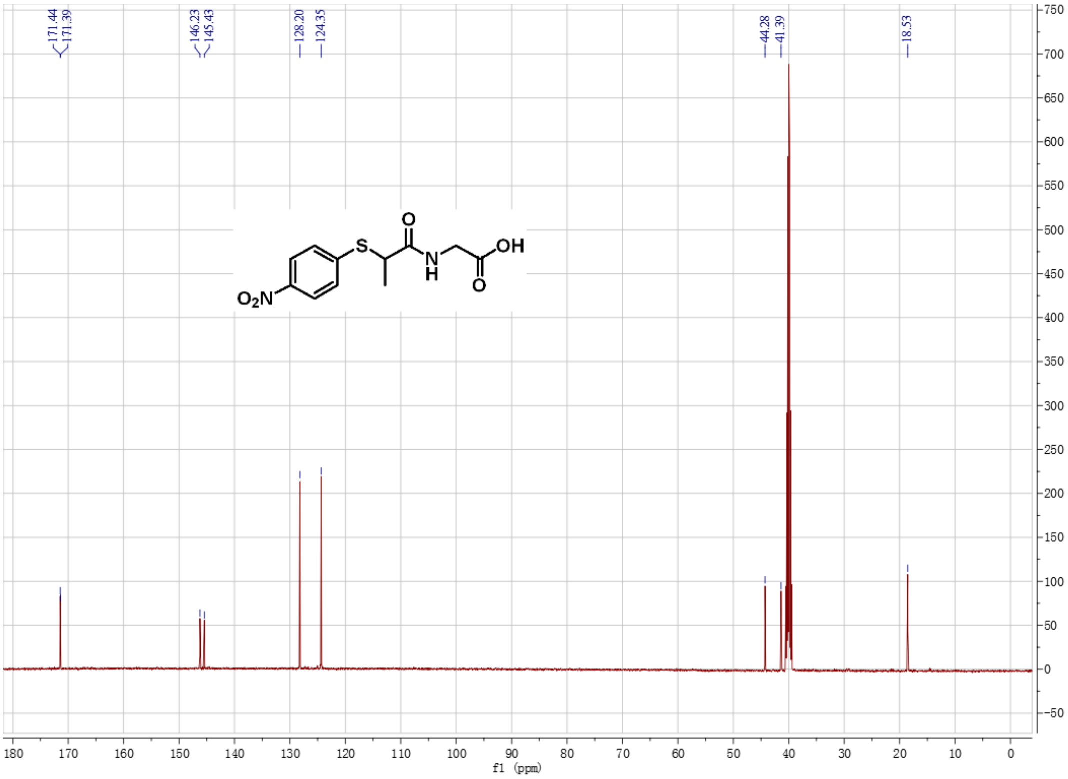


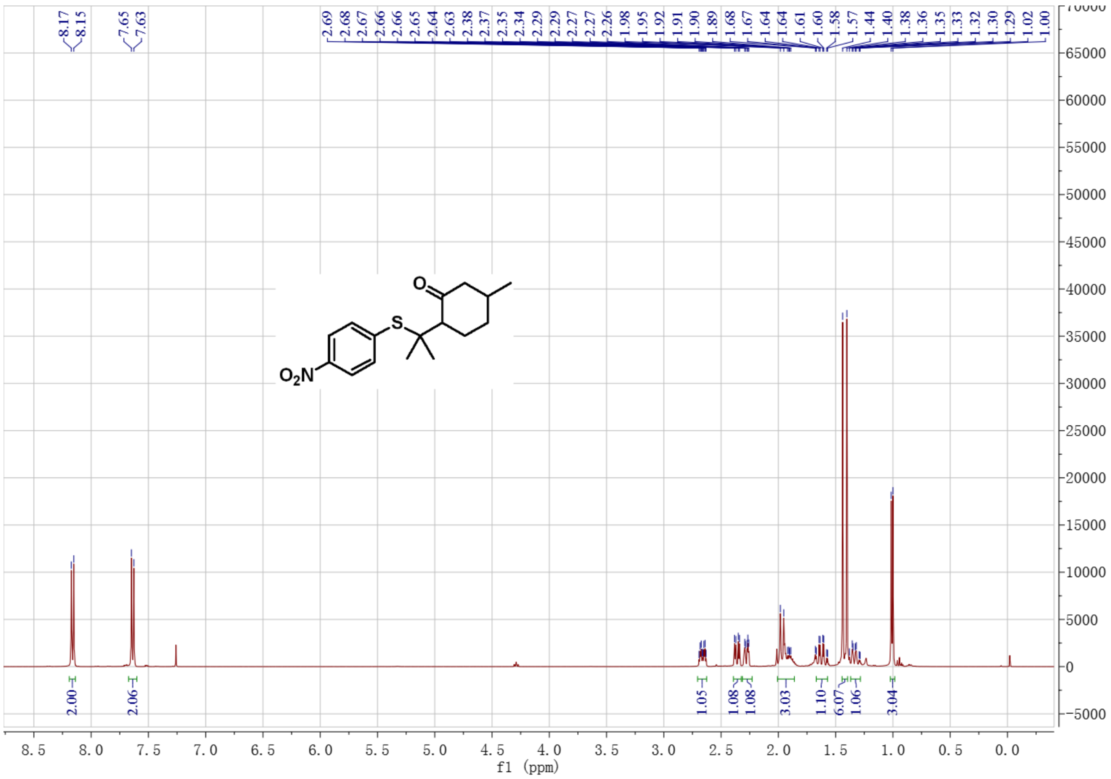


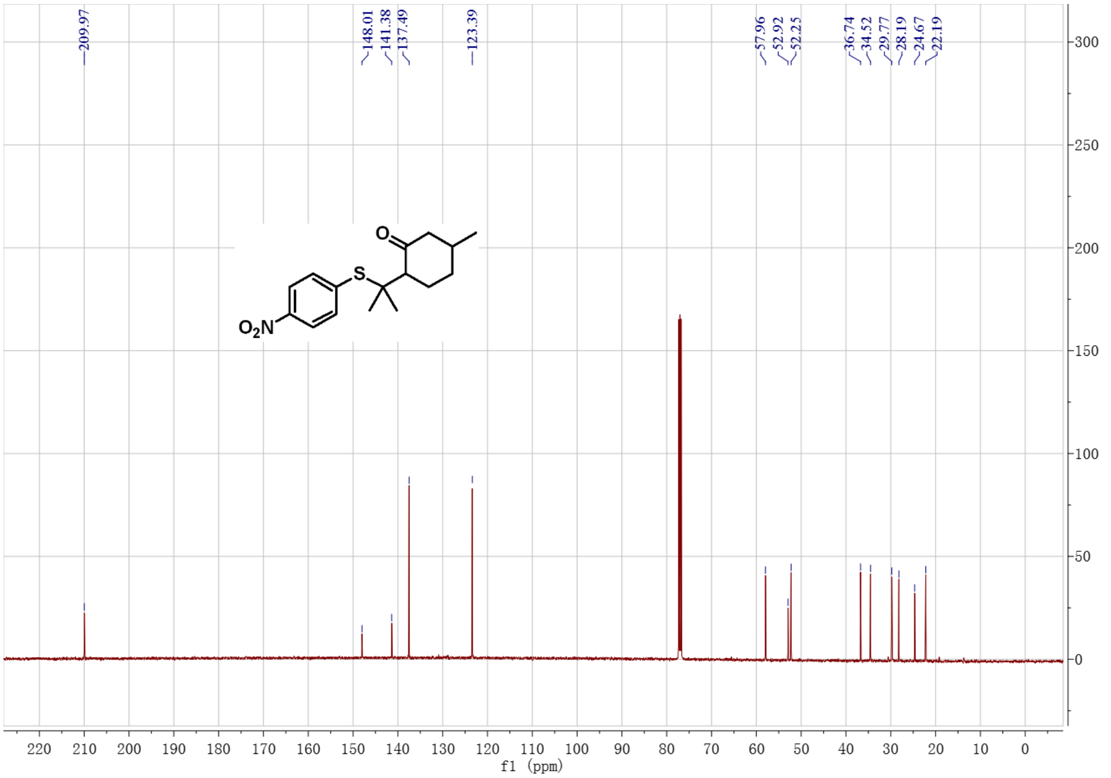
Compound **3al**





Compound **3am**





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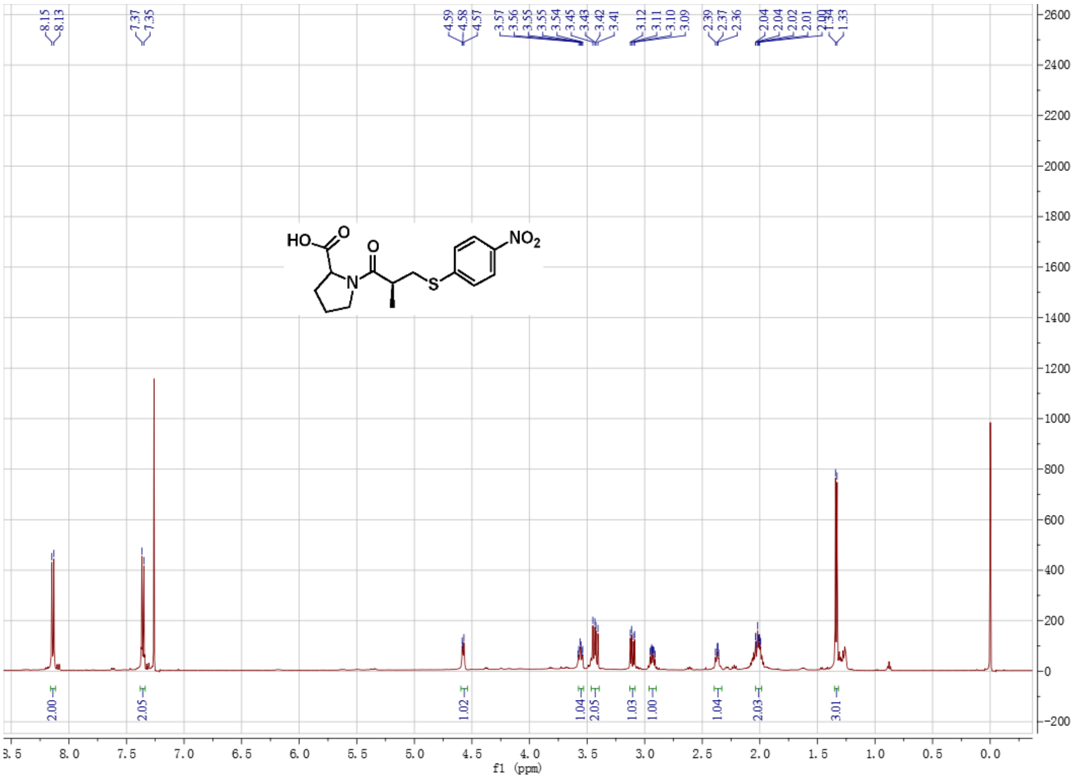

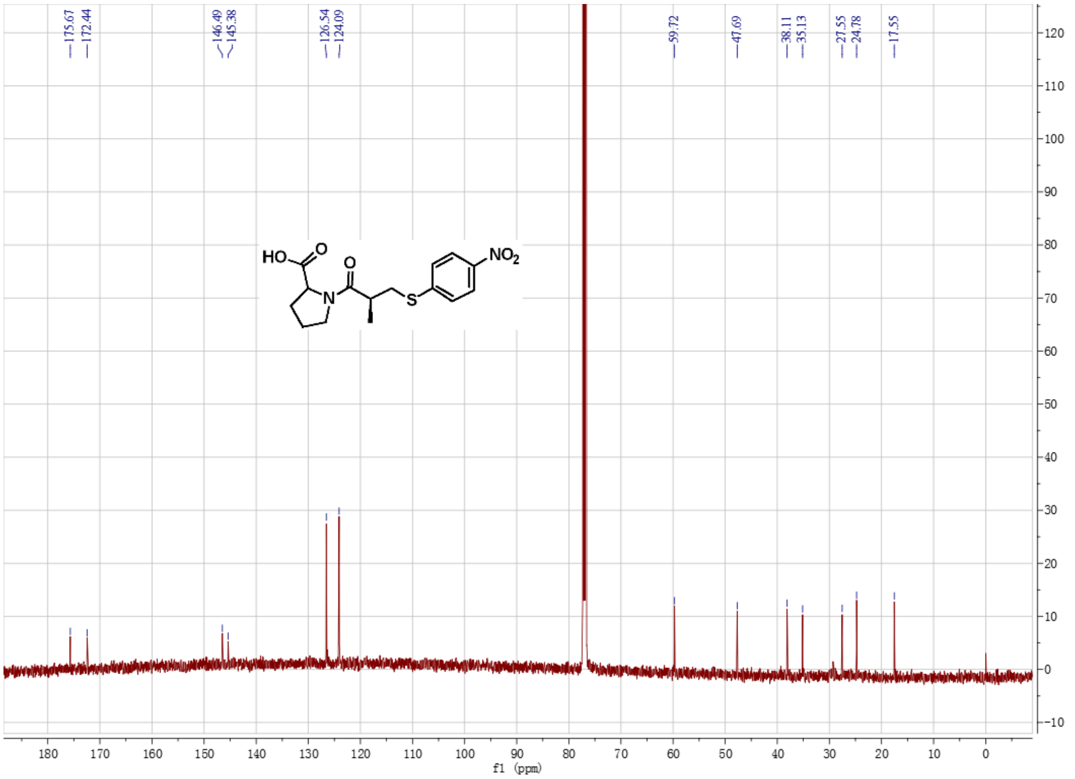

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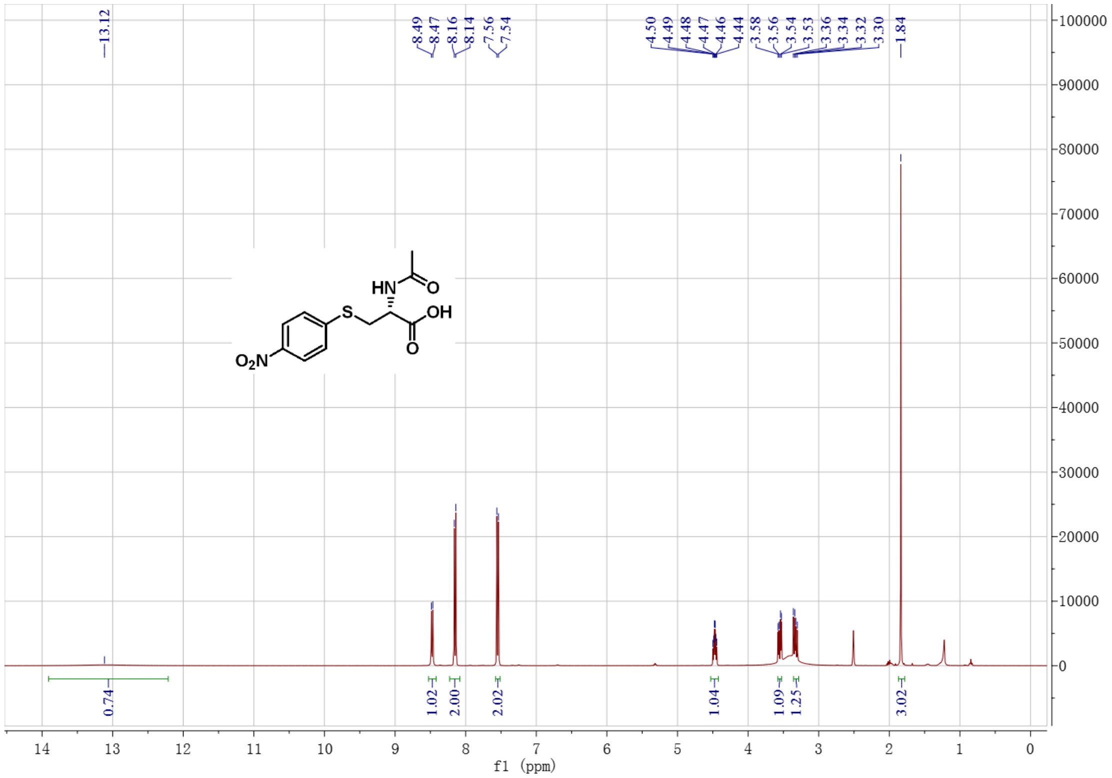

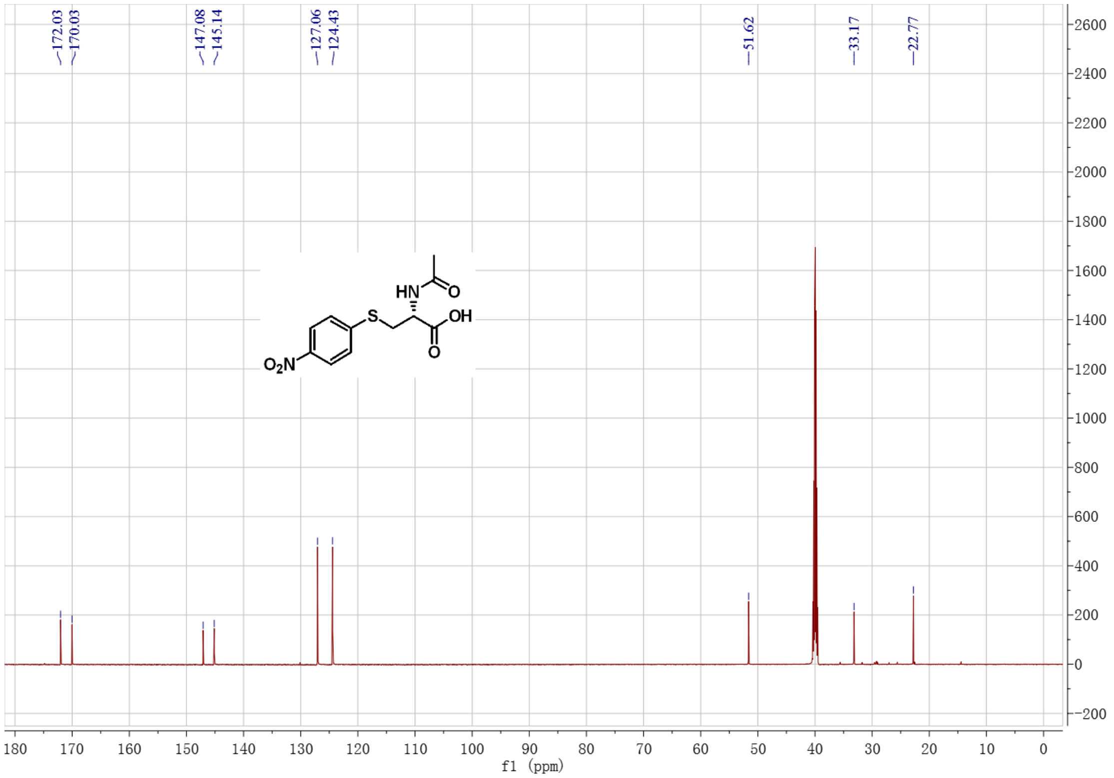

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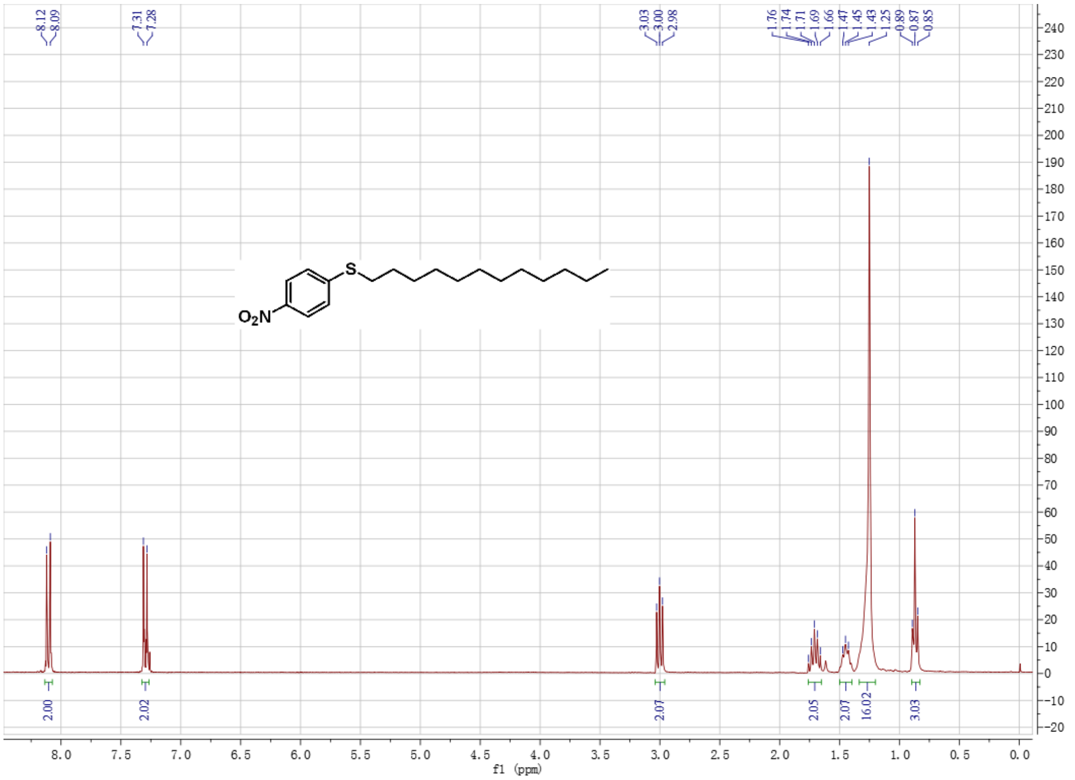

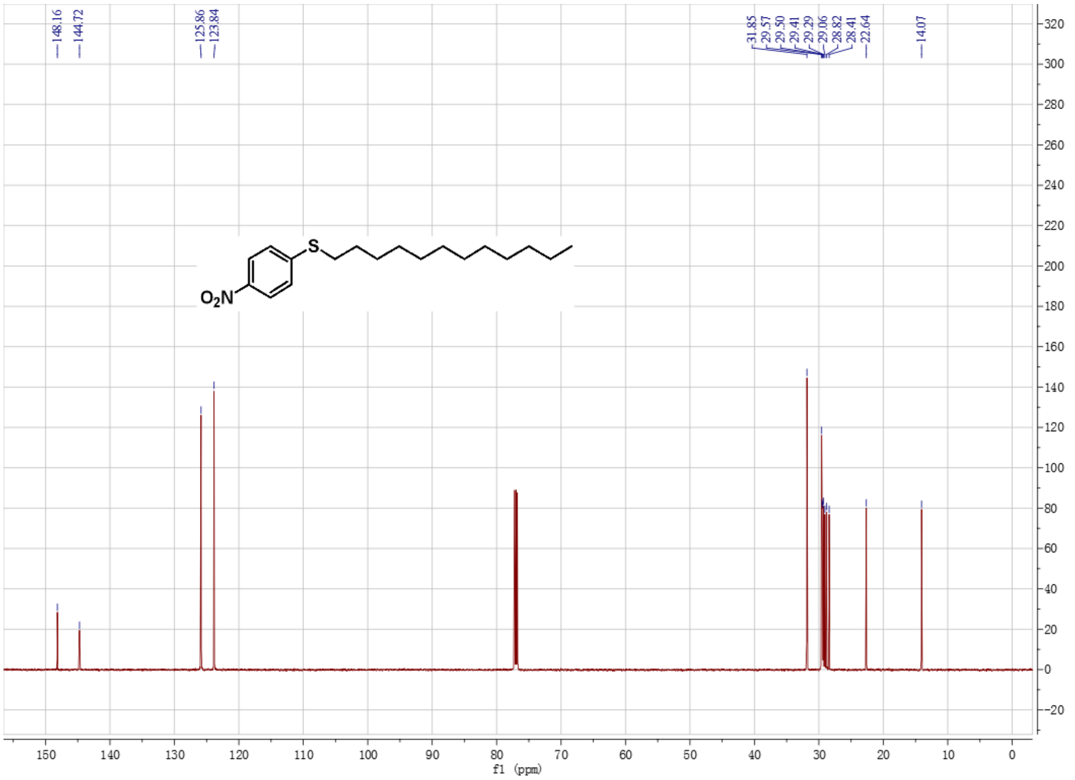

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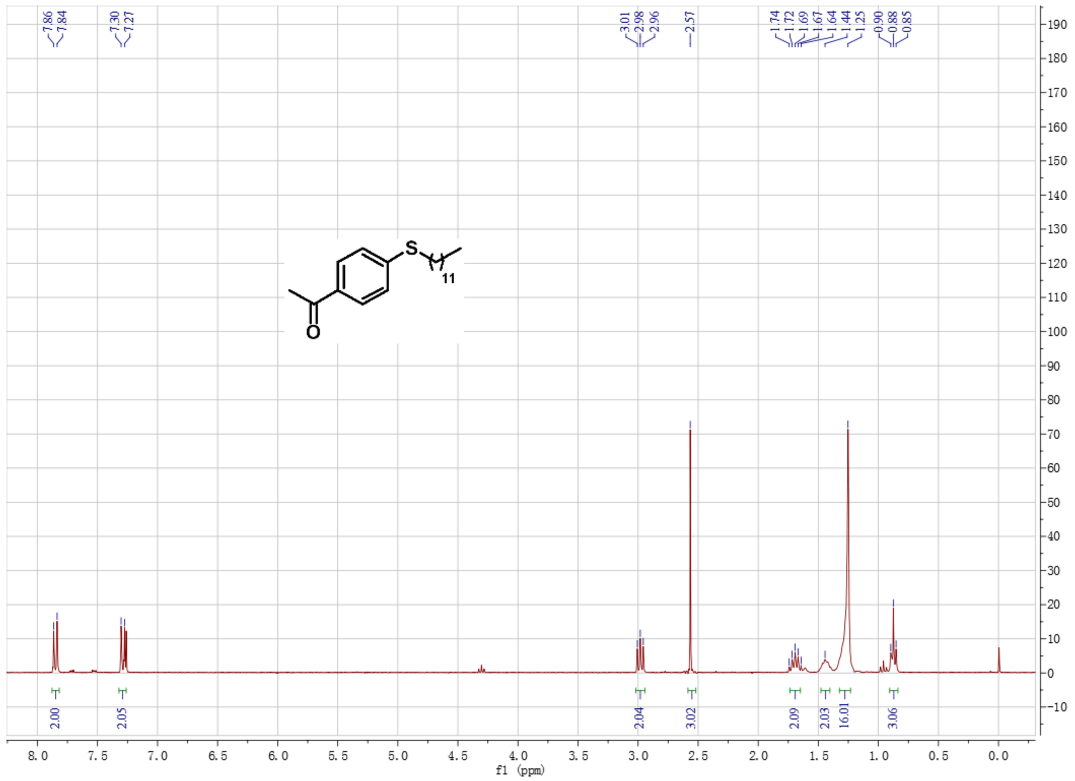

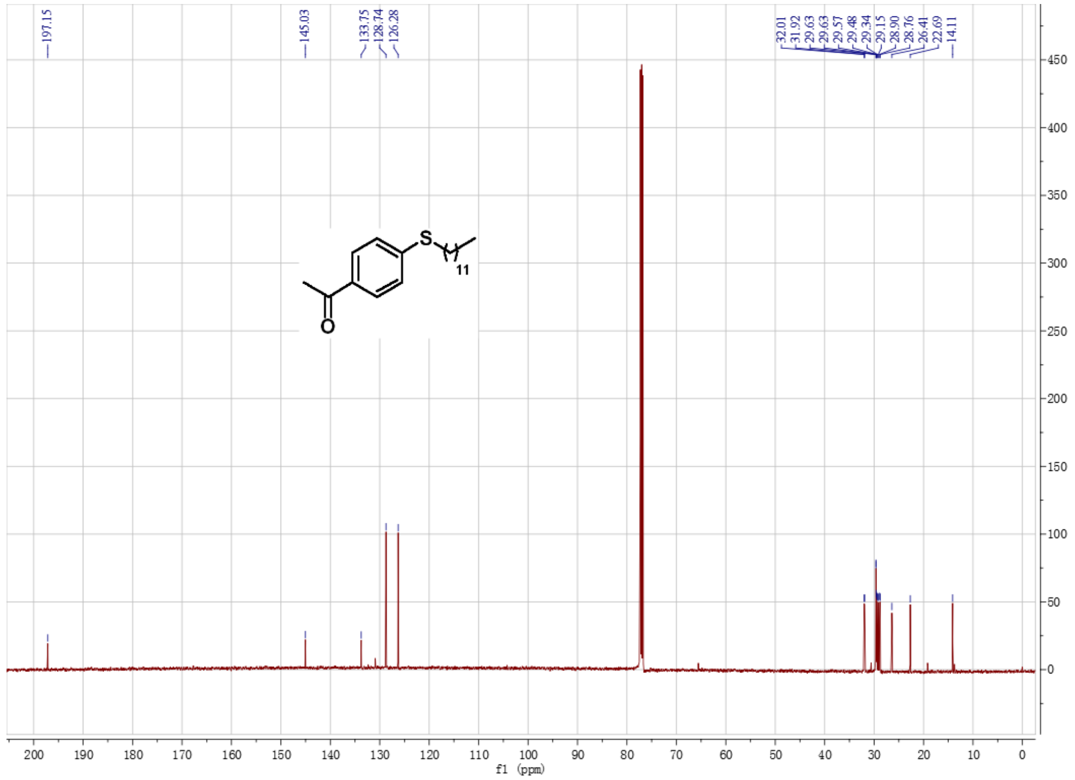

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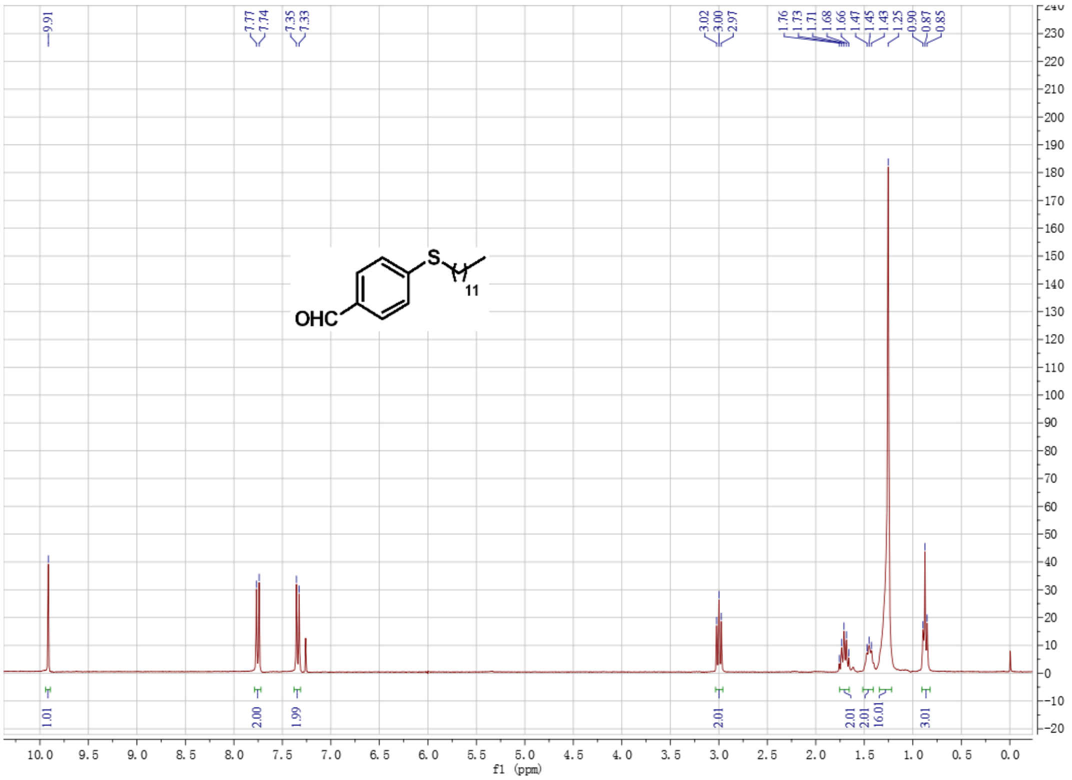

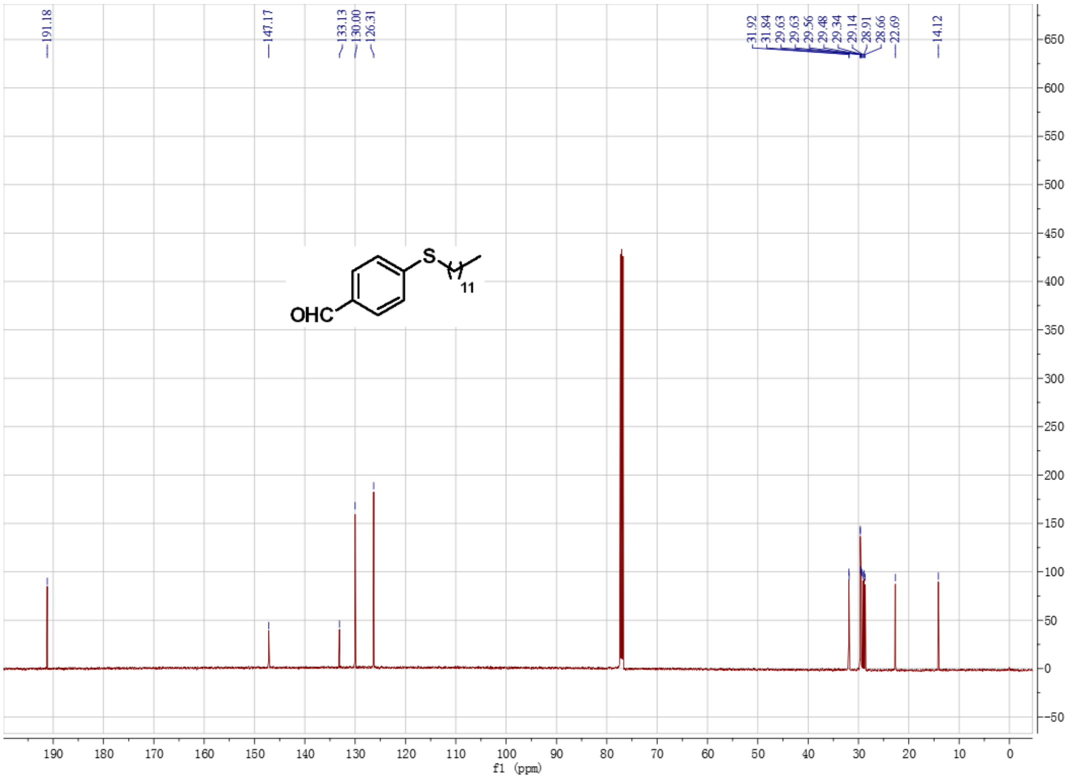

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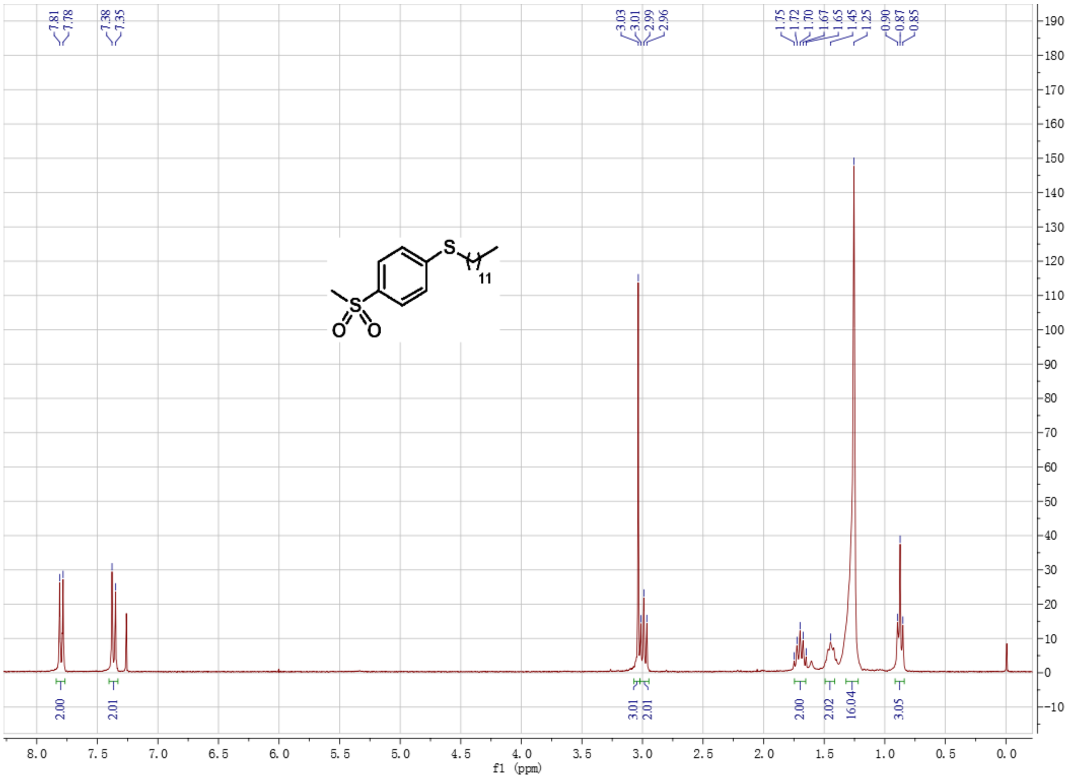

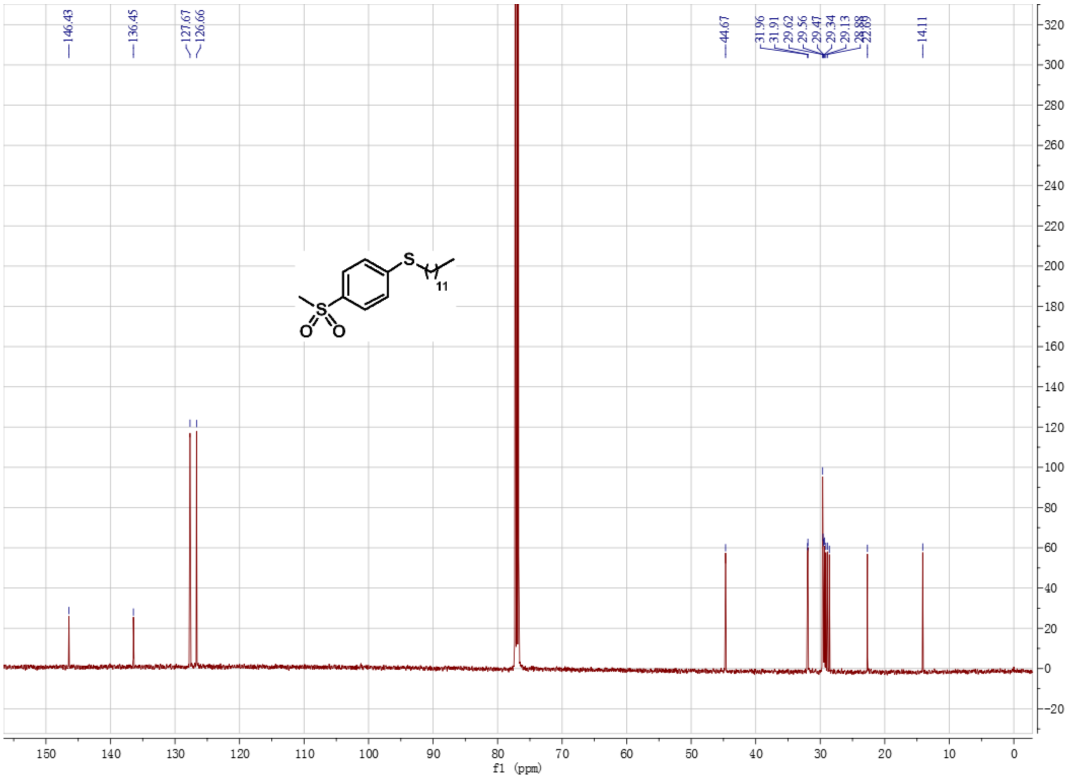

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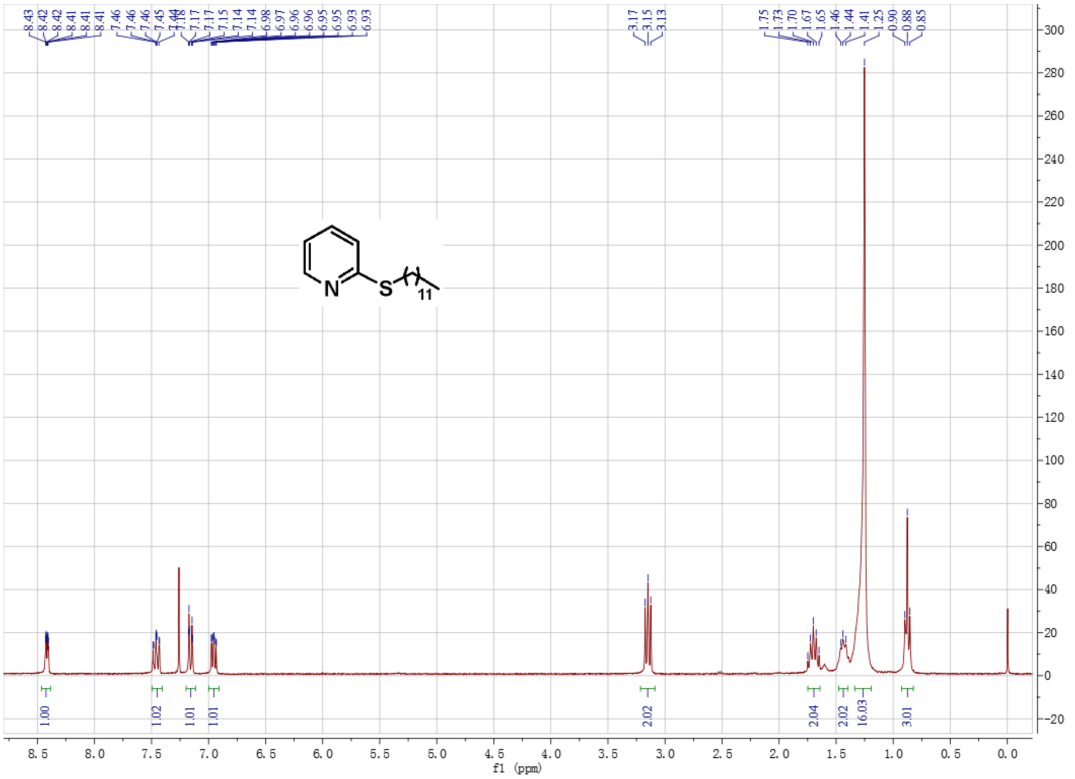

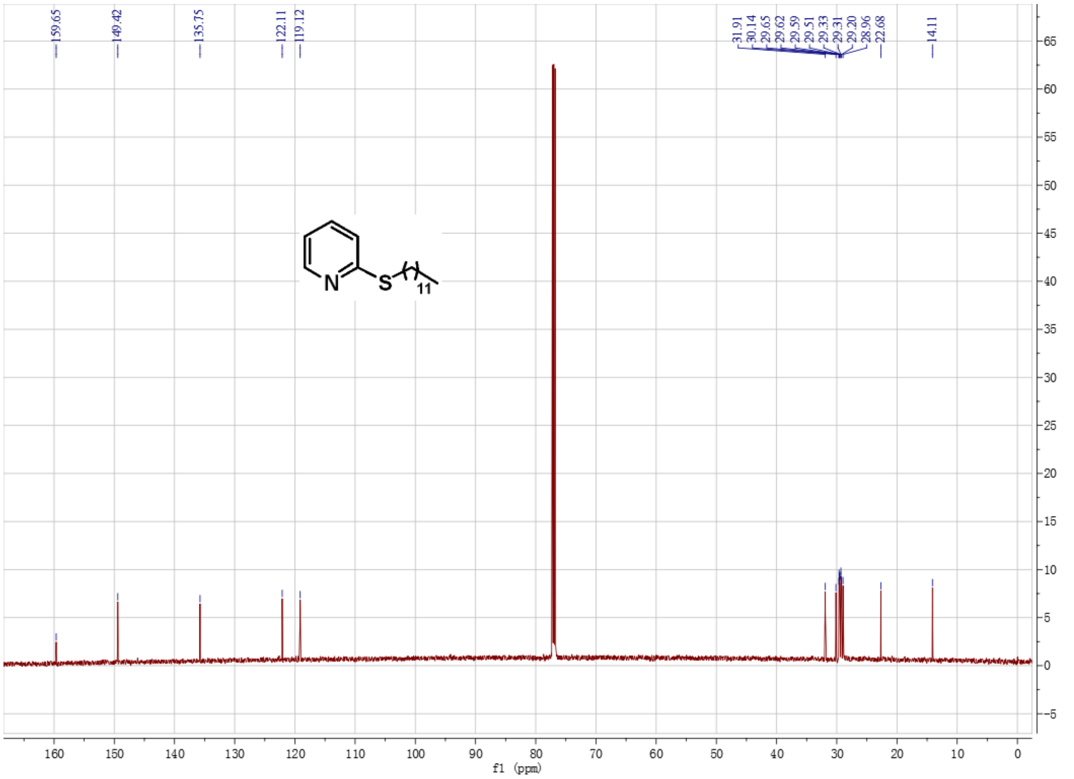

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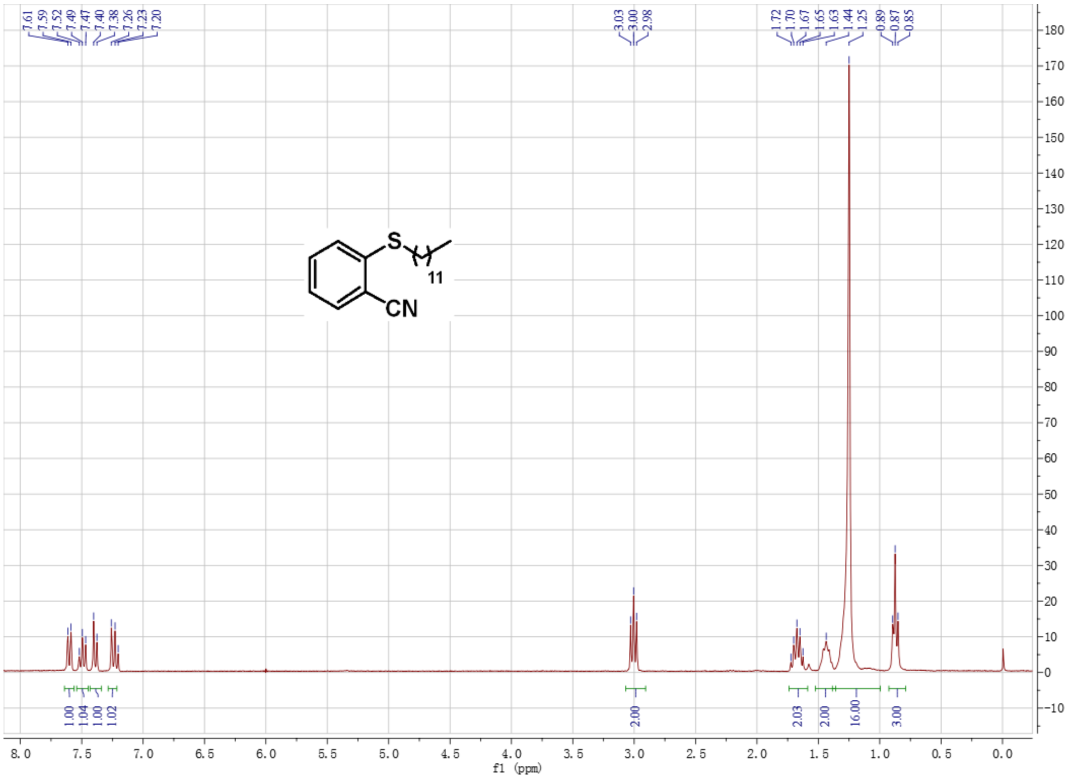

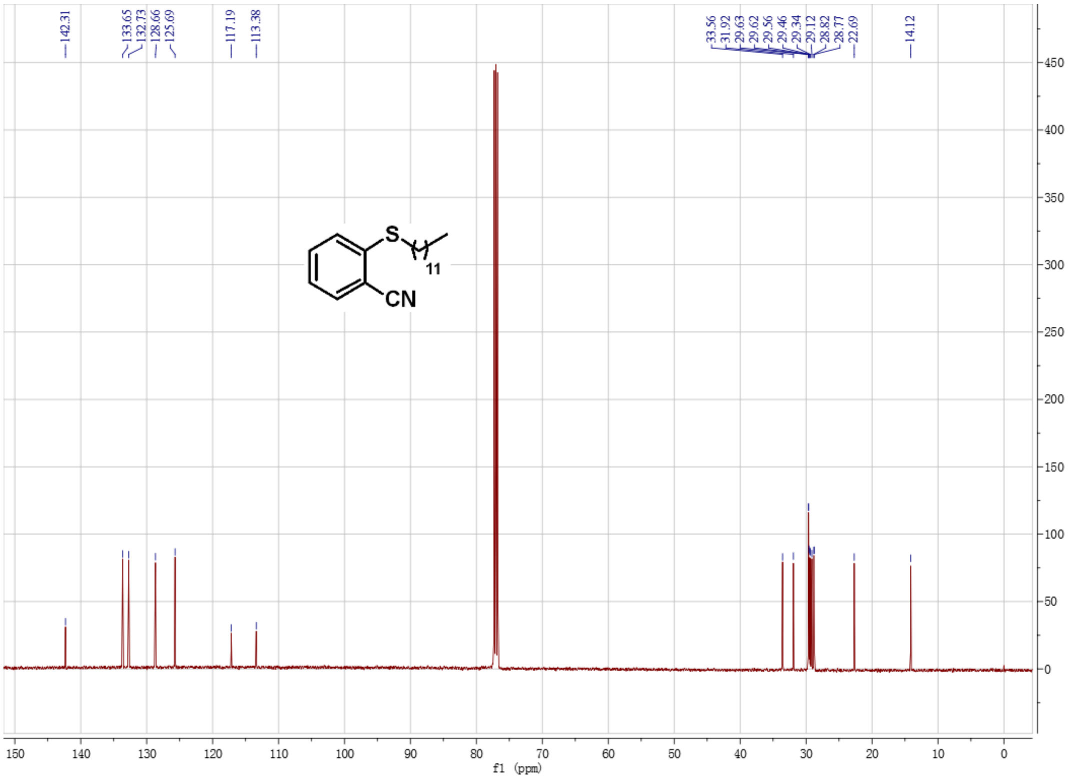

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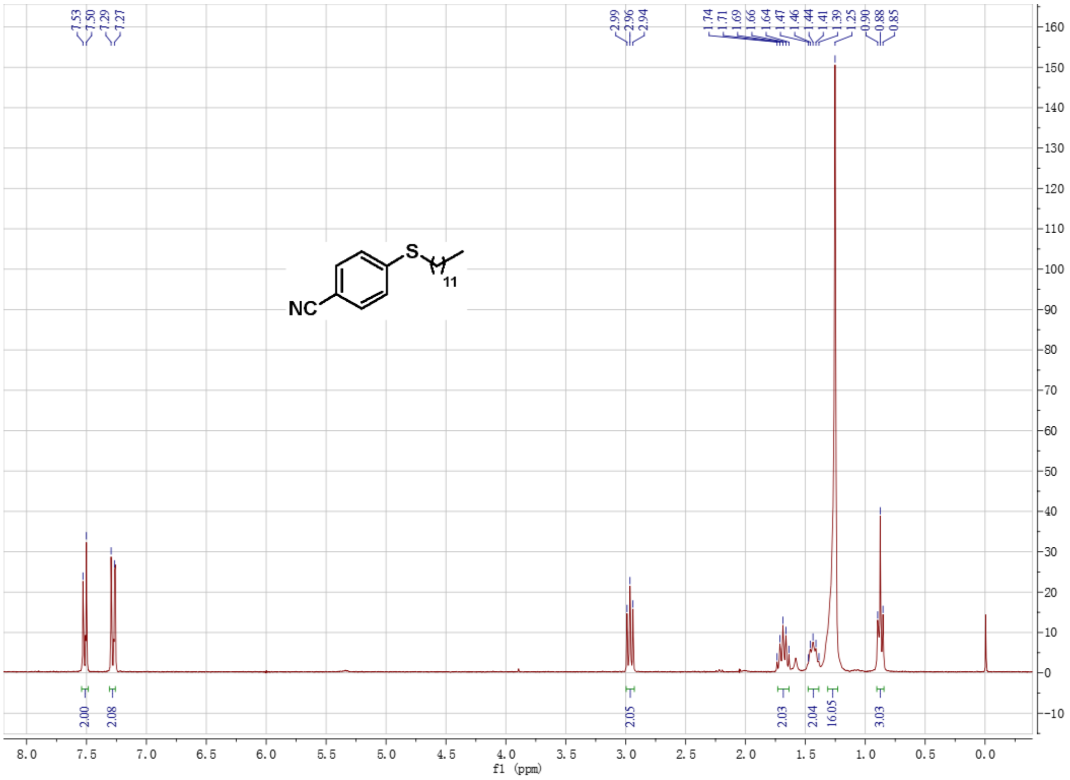

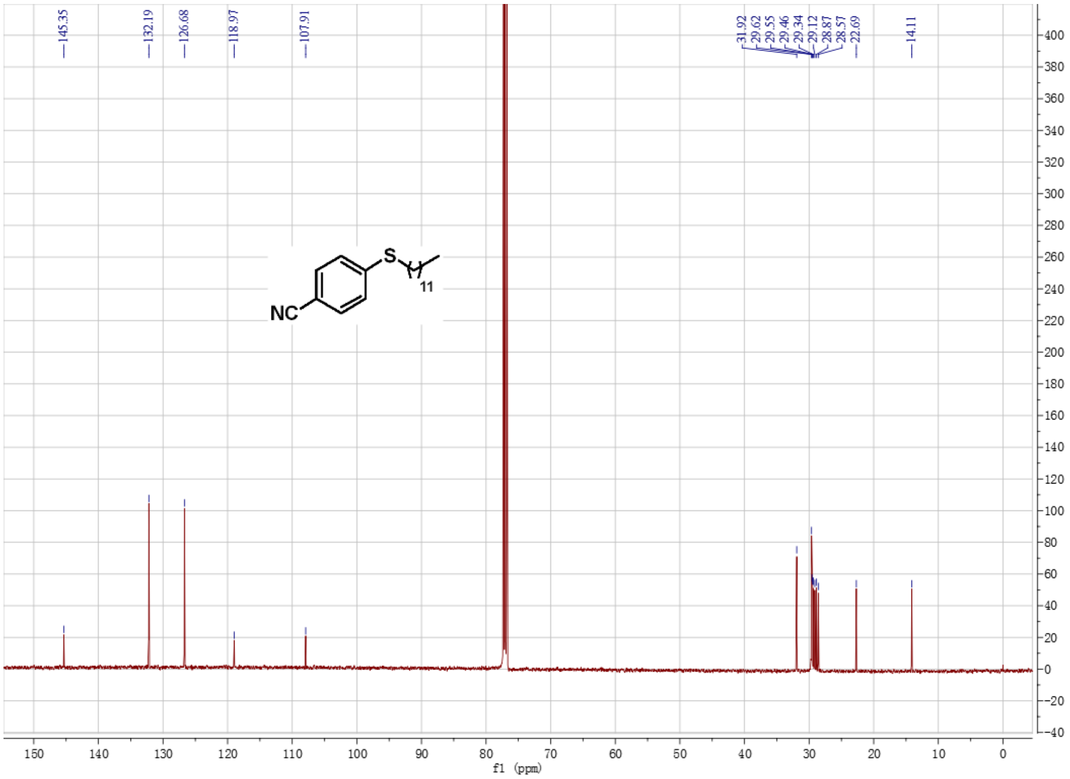

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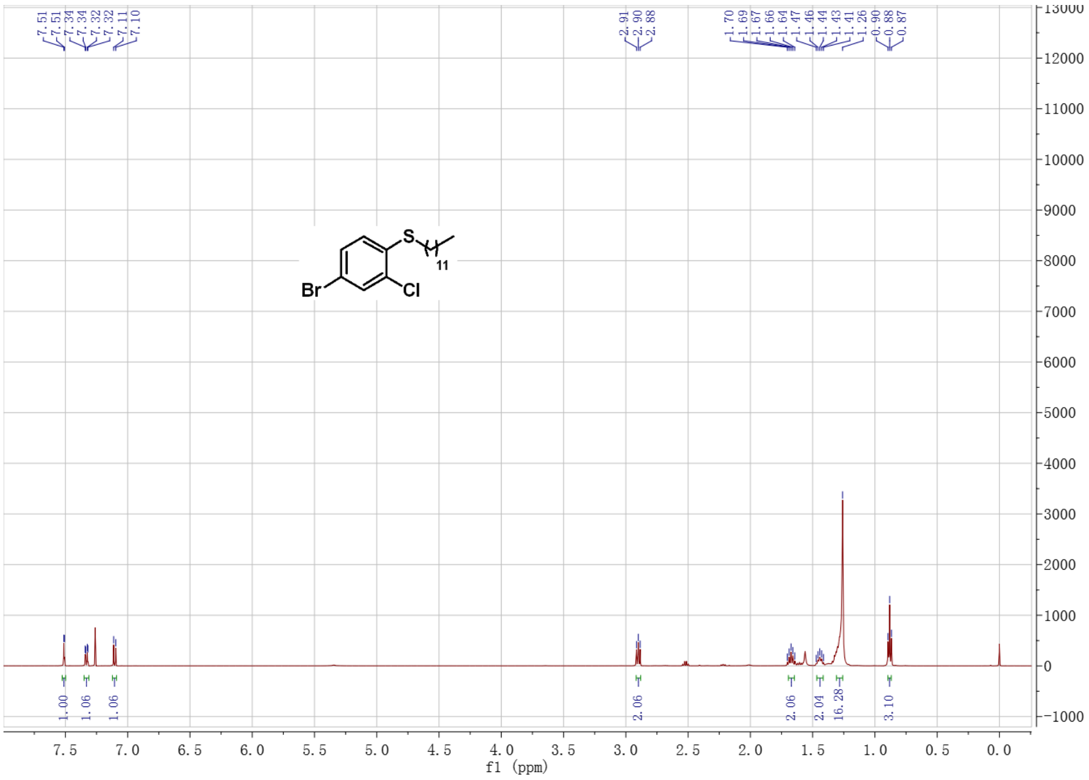

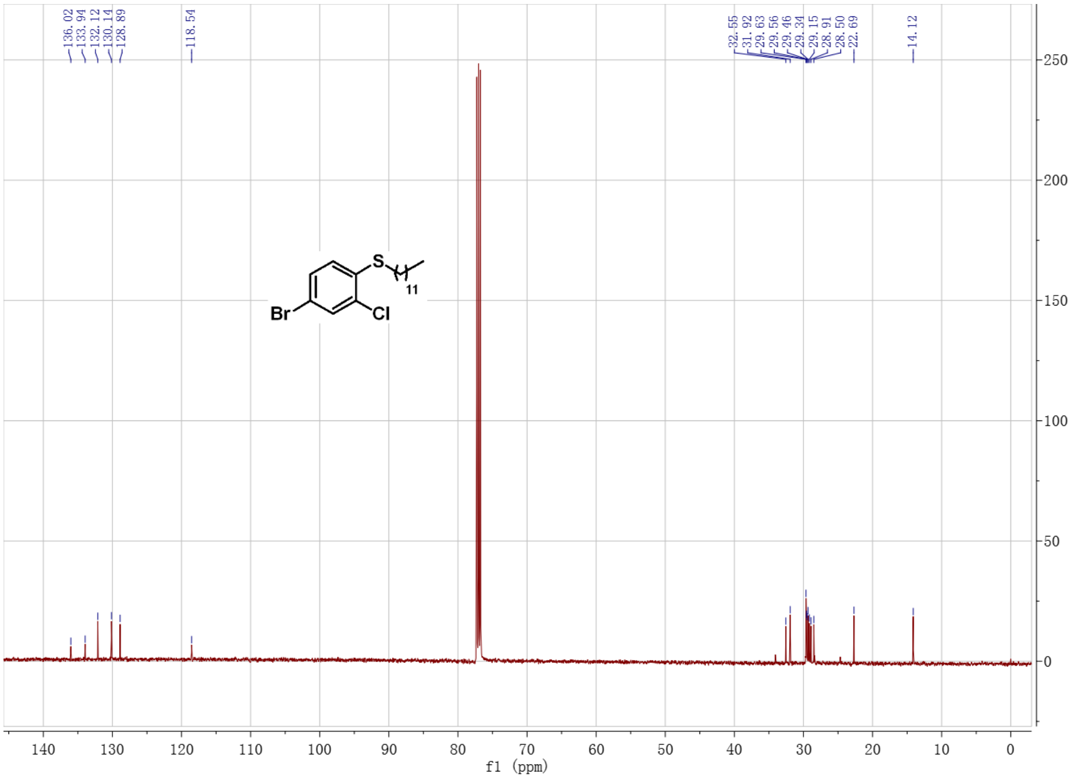

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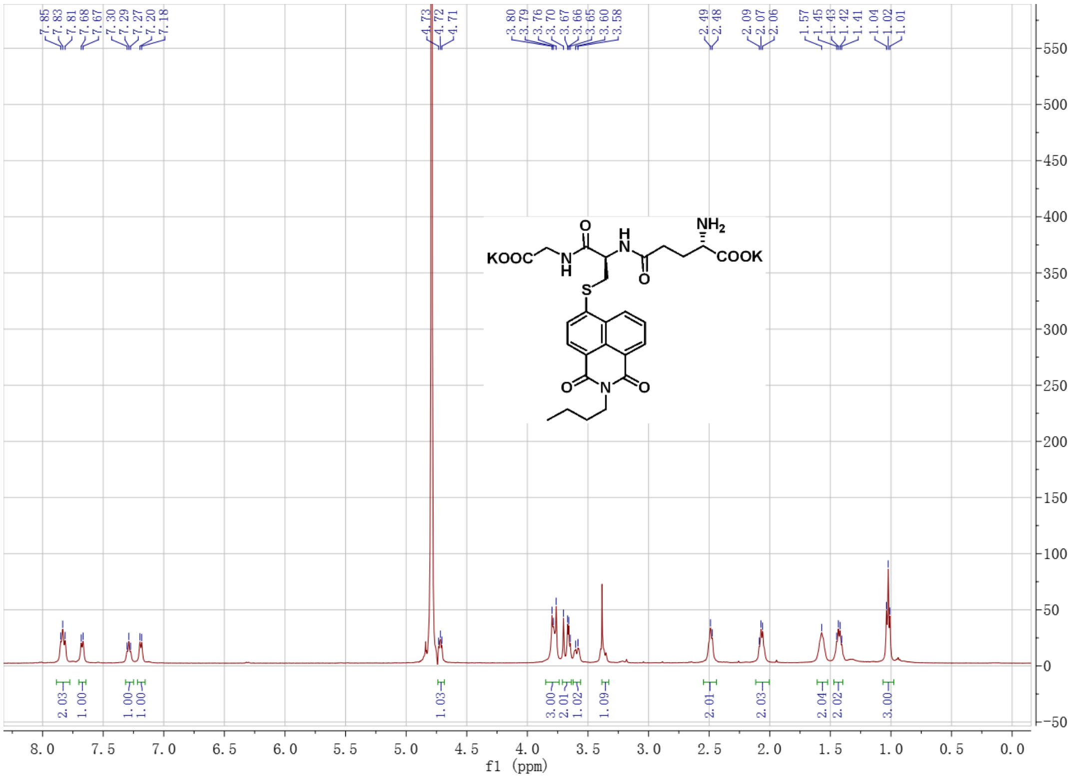

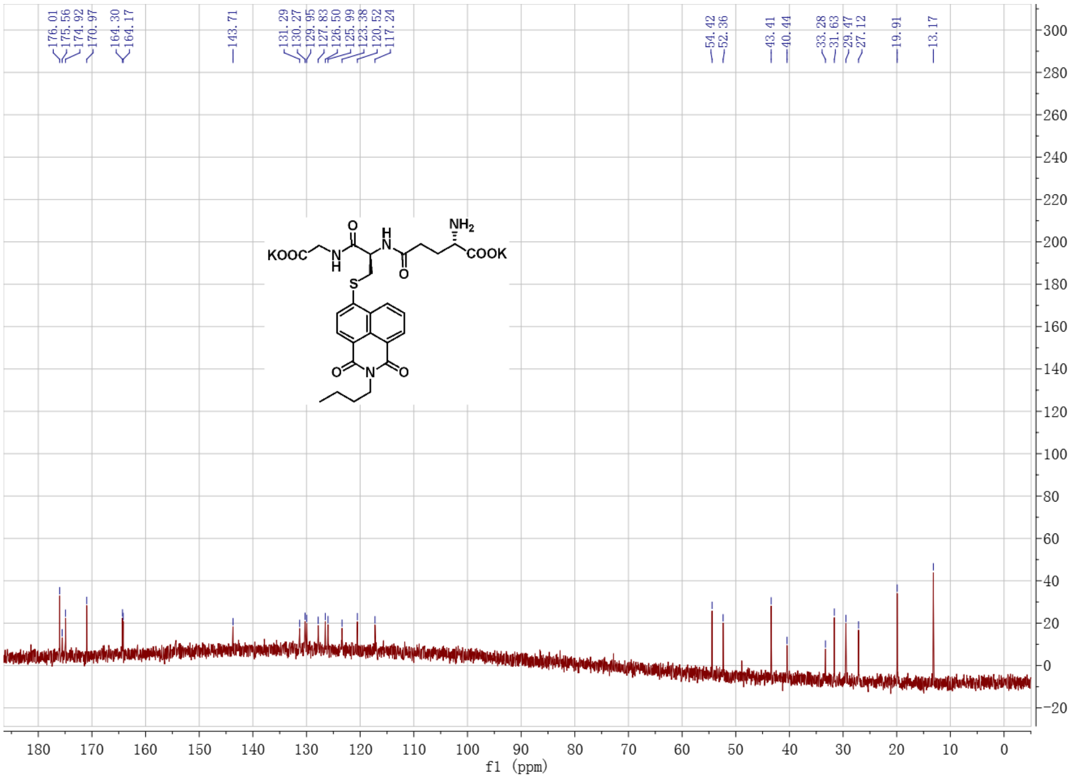

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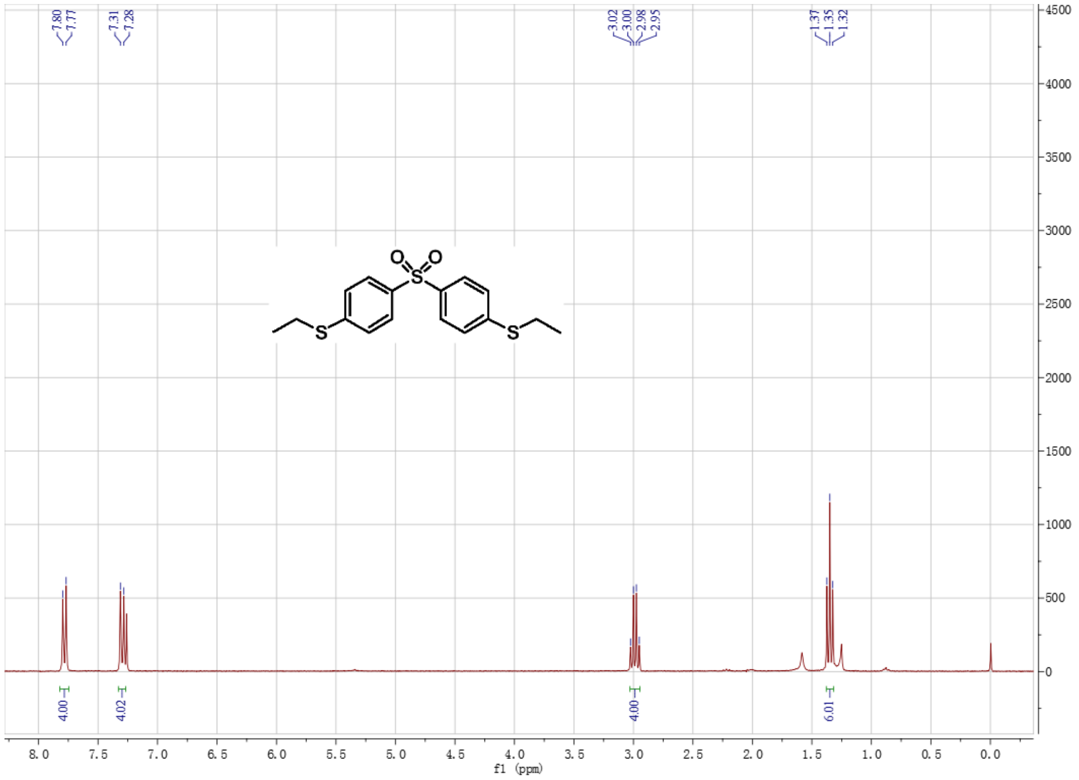

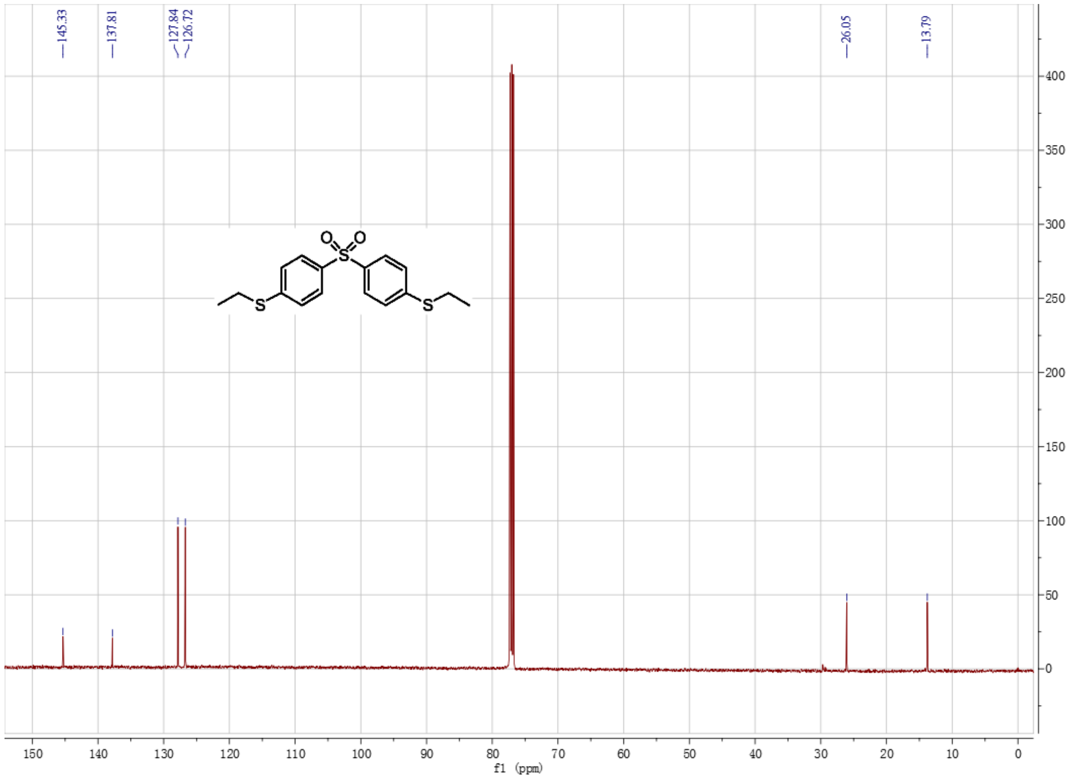

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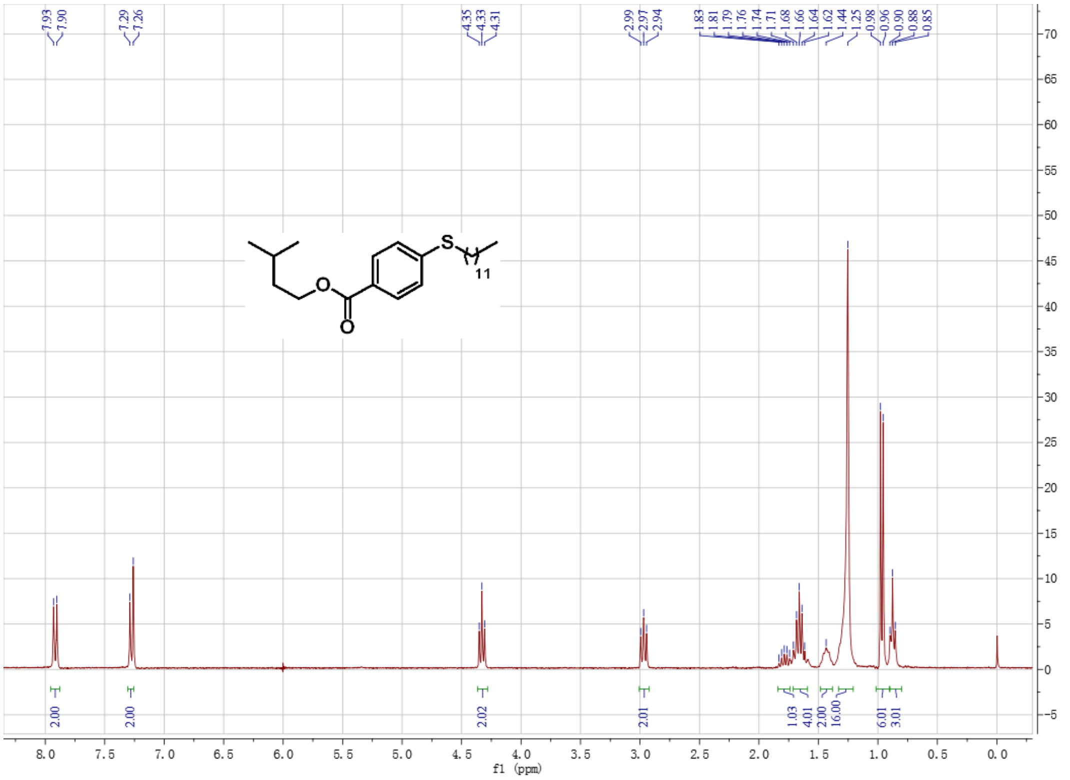

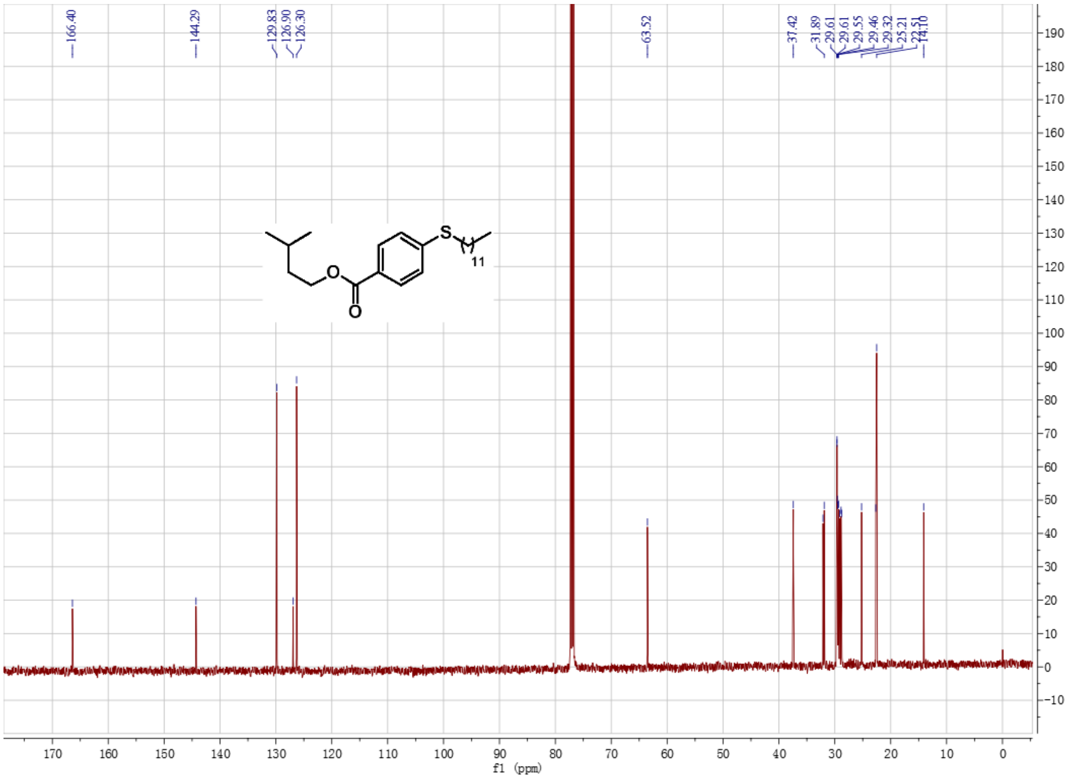

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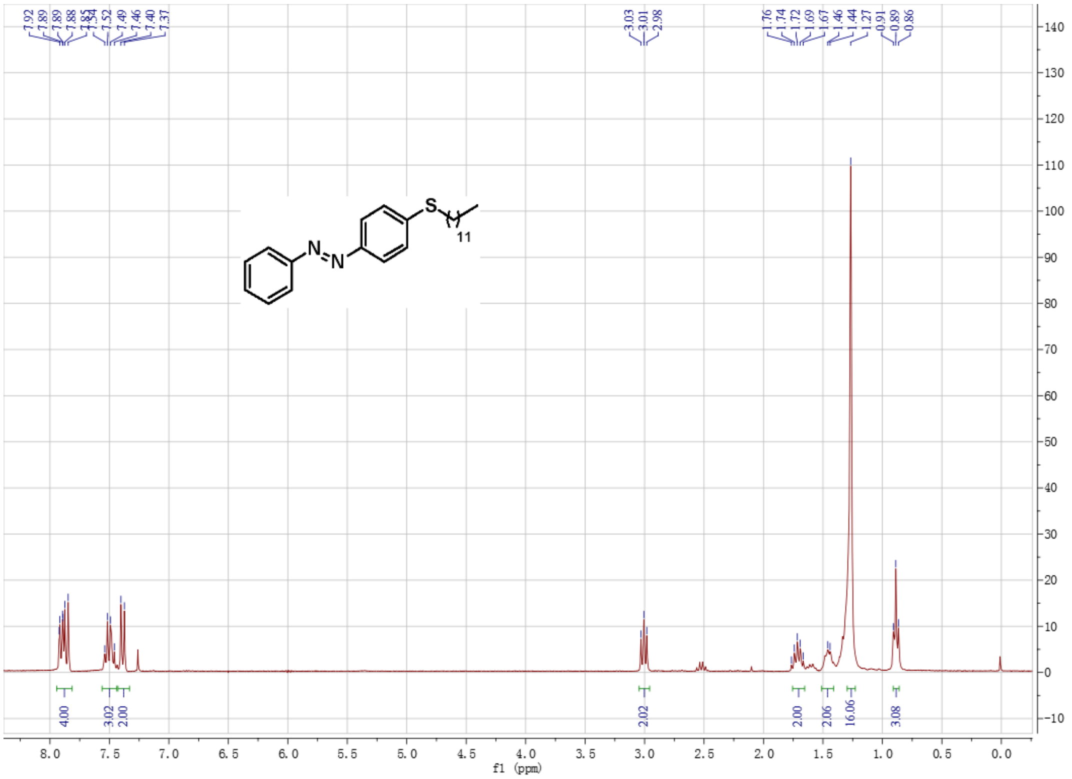
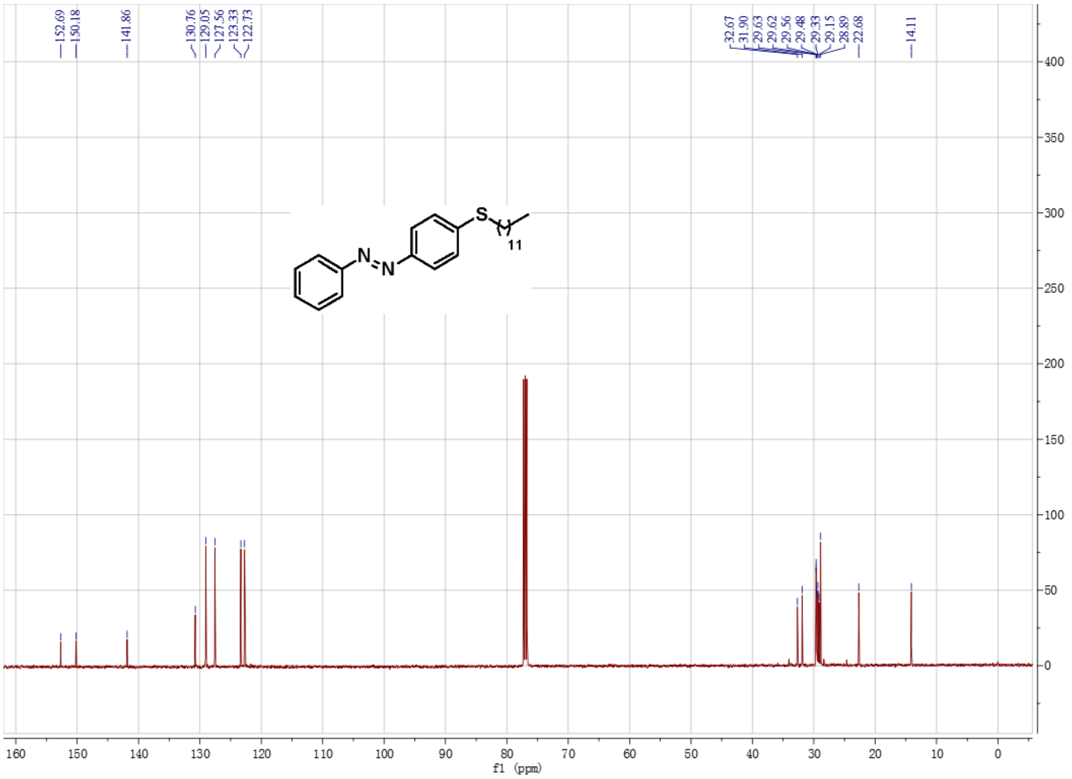
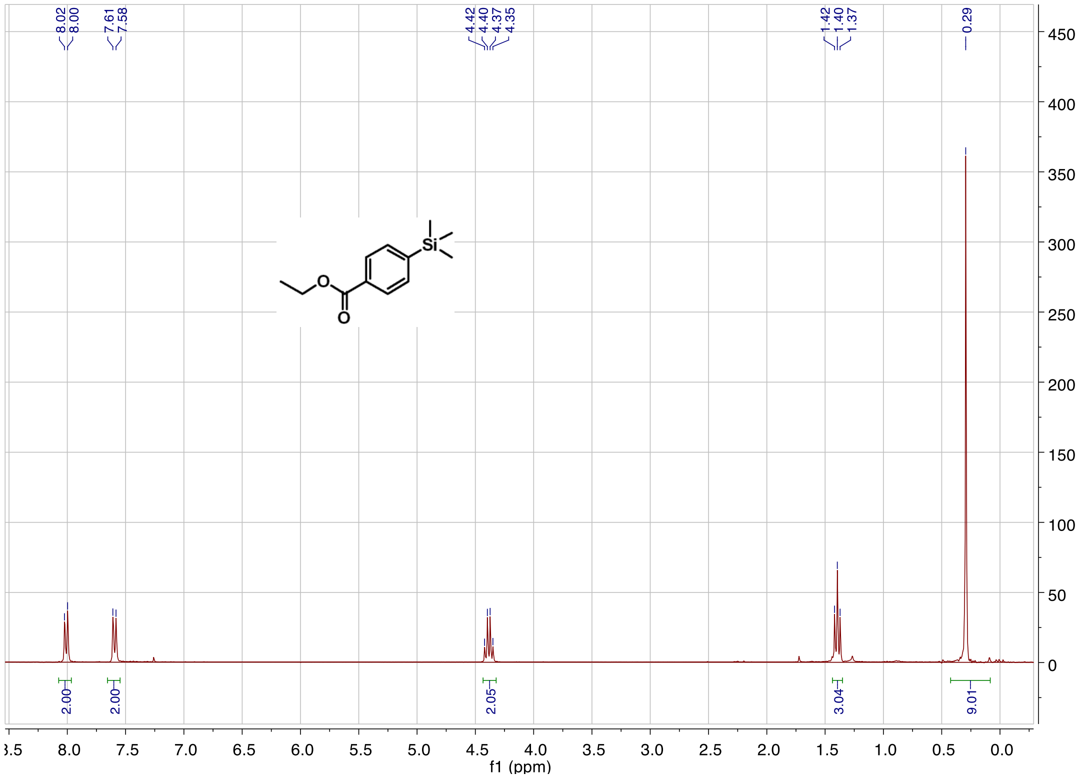
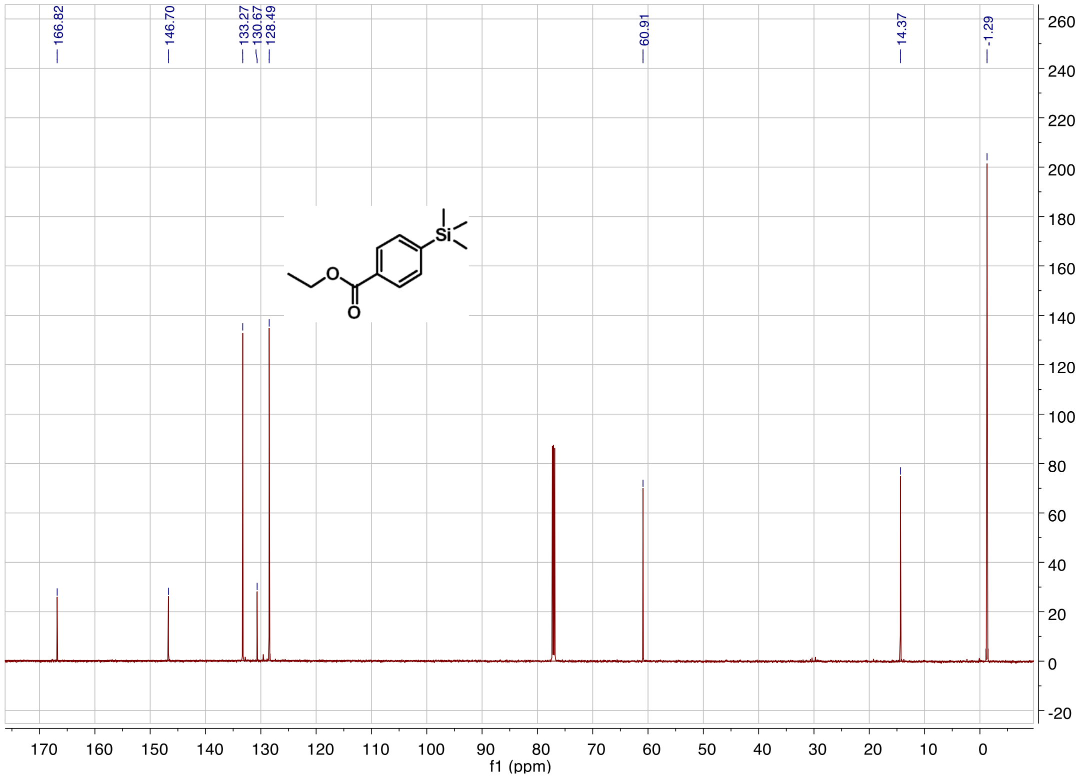


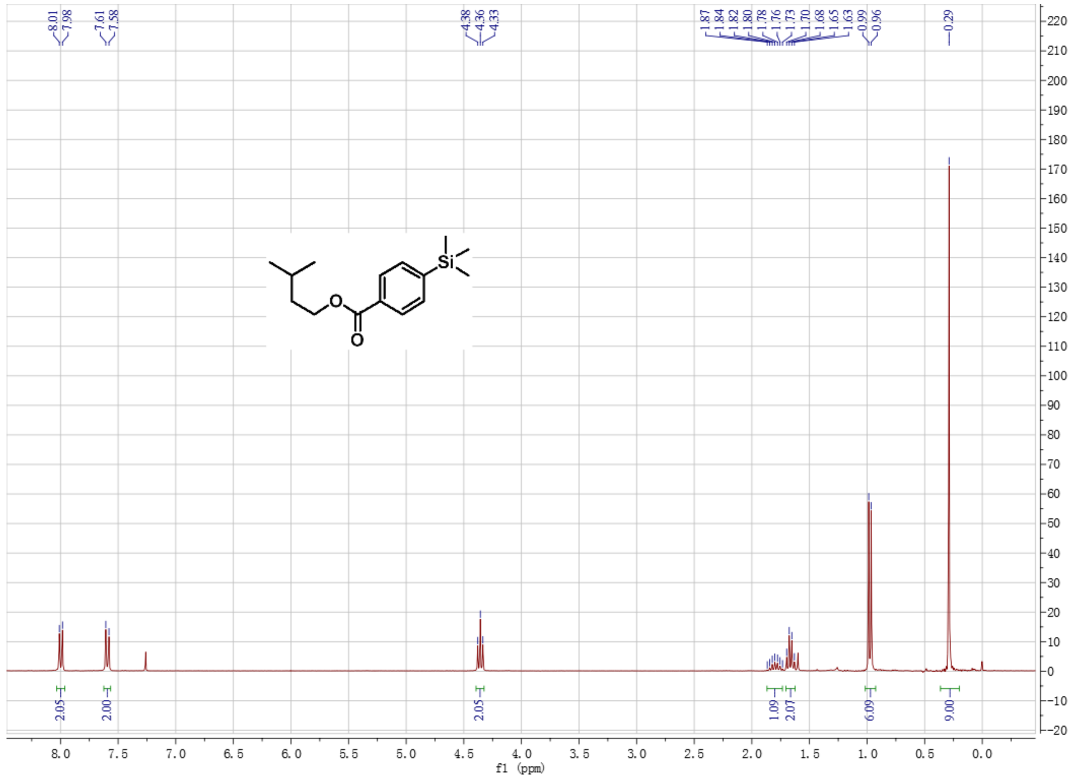


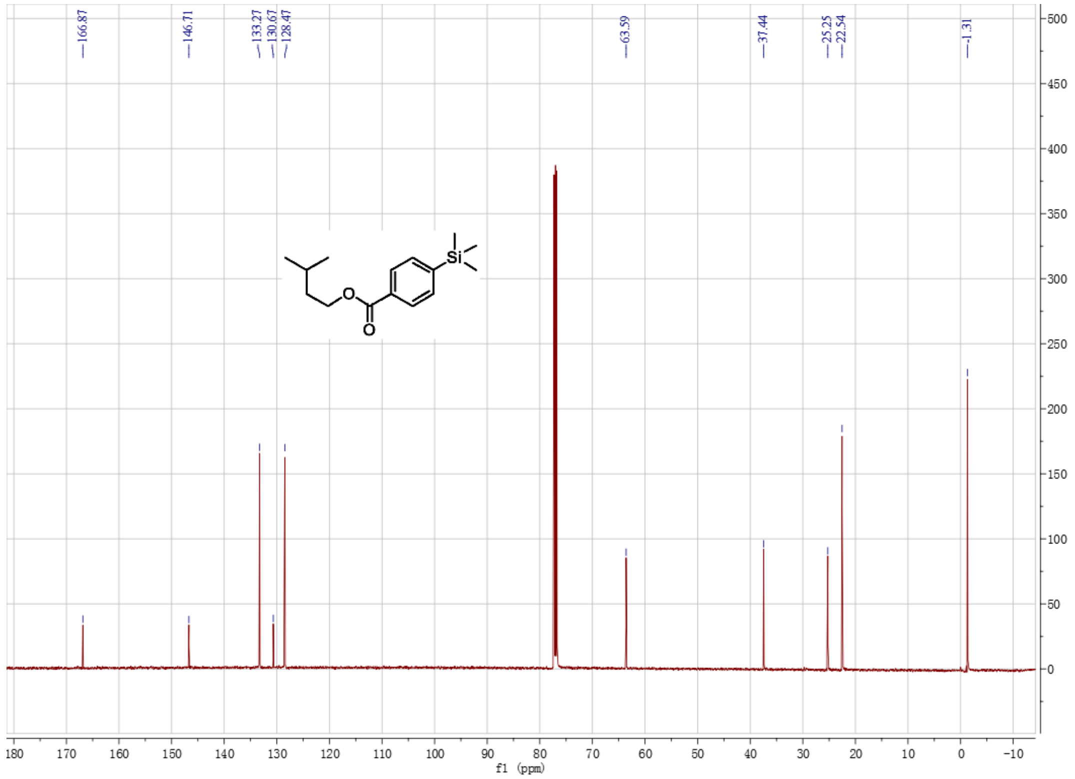
Compound **5a**


8.02
8.00
7.61
7.58
4.42
4.40
4.37
4.35
1.42
1.40
1.37
0.29
Si
O
O
2.00
2.00
2.05
3.04
9.01
450
400
350
300
250
200
150
100
50
0
.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)


166.82
146.70
133.27
130.67
128.49
60.91
14.37
-1.29
Si
O
O
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound **5b**


8.01
7.98
7.61
7.58
4.38
4.36
4.33
1.87
1.84
1.82
1.80
1.78
1.76
1.73
1.70
1.68
1.65
1.63
0.99
0.96
0.29
Si
O
O
2.05
2.00
2.05
1.09
2.07
6.09
9.00
f1 (ppm)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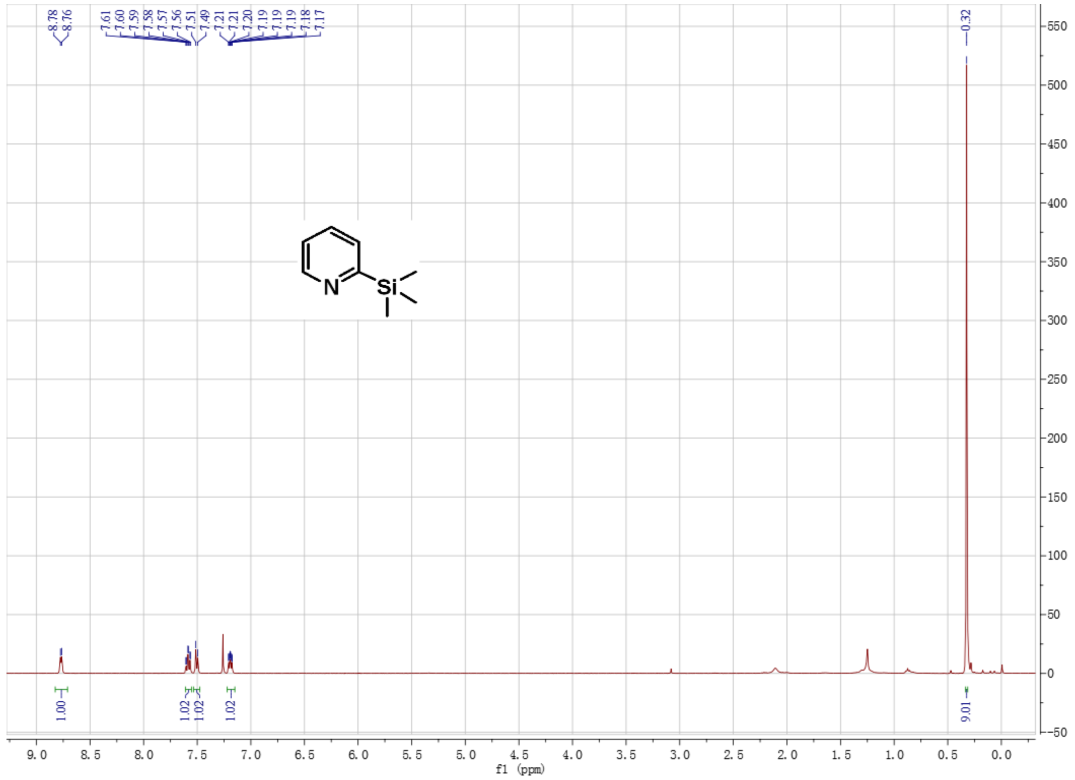
25.25
22.54
-1.31
Si
O
O
f1 (ppm)

Compound **5h**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8.76
7.61
7.60
7.59
7.58
7.57
7.56
7.51
7.49
7.21
7.21
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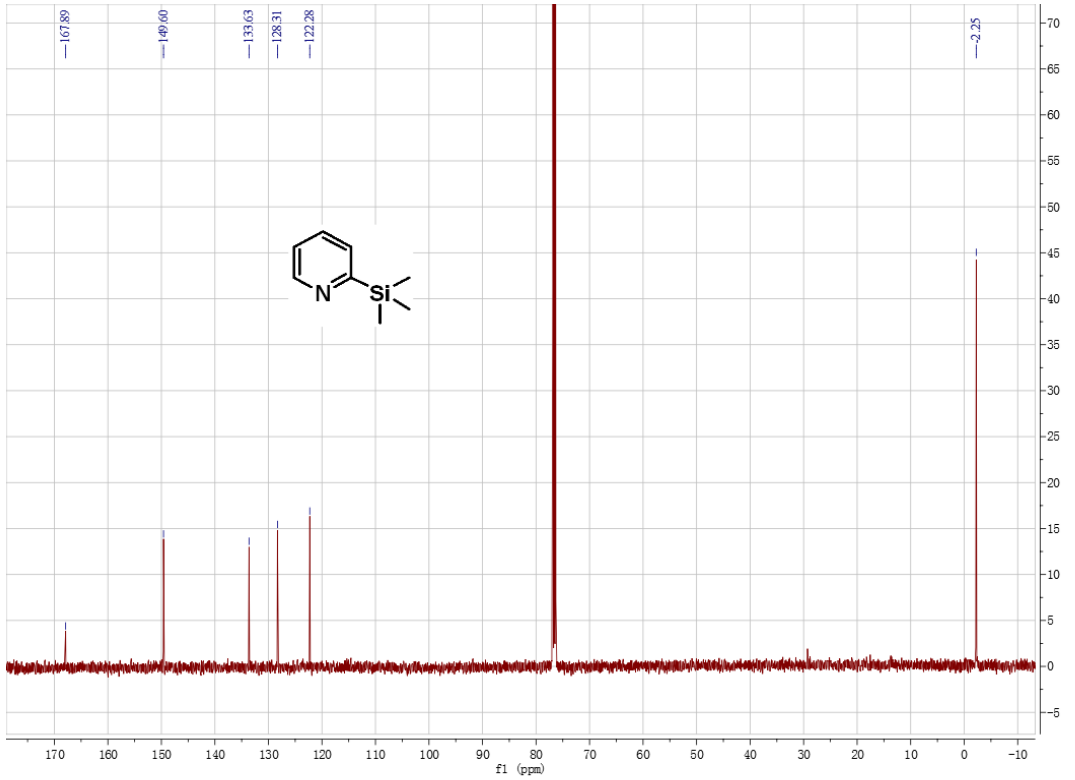
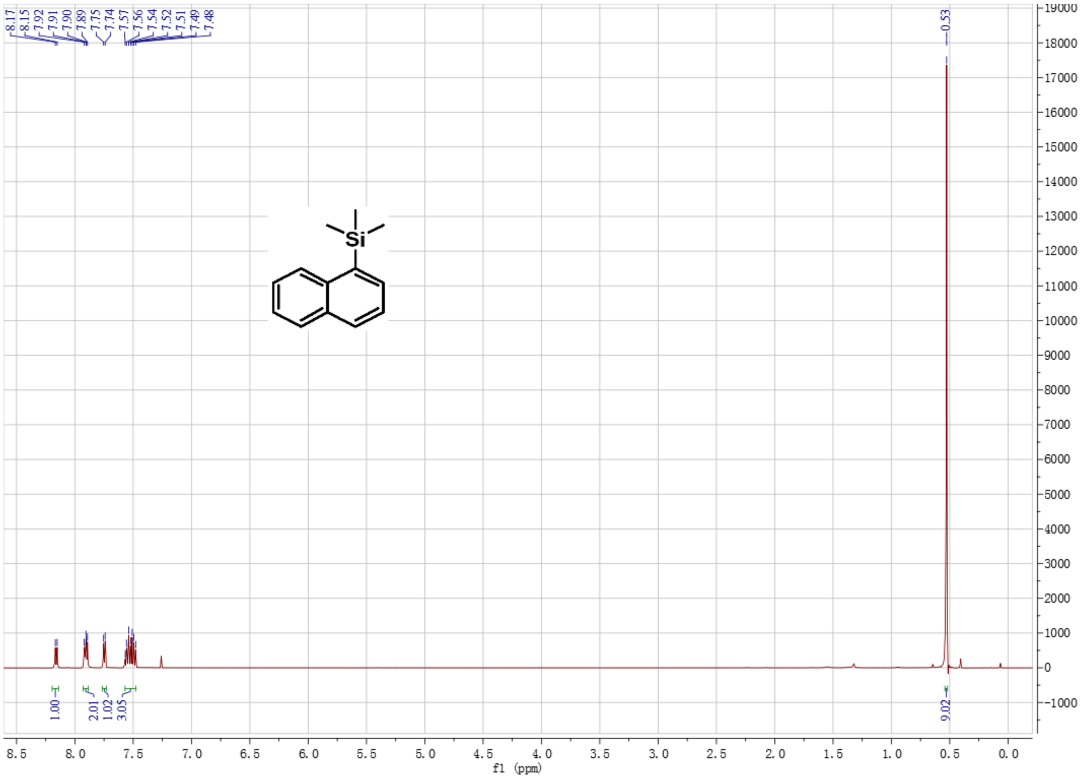
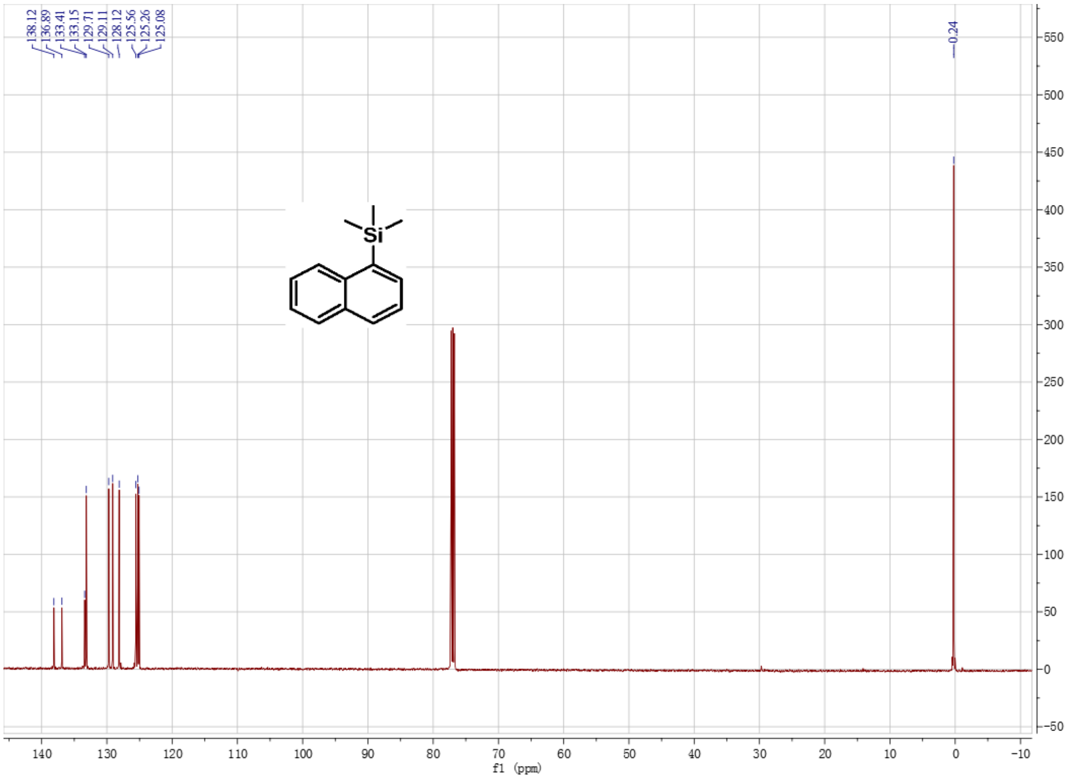
7.19
7.19
7.19
7.18
7.17
0.32
N
Si
1.00
1.02
1.02
1.02
9.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
550 500 450 400 350 300 250 200 150 100 50 0 -50

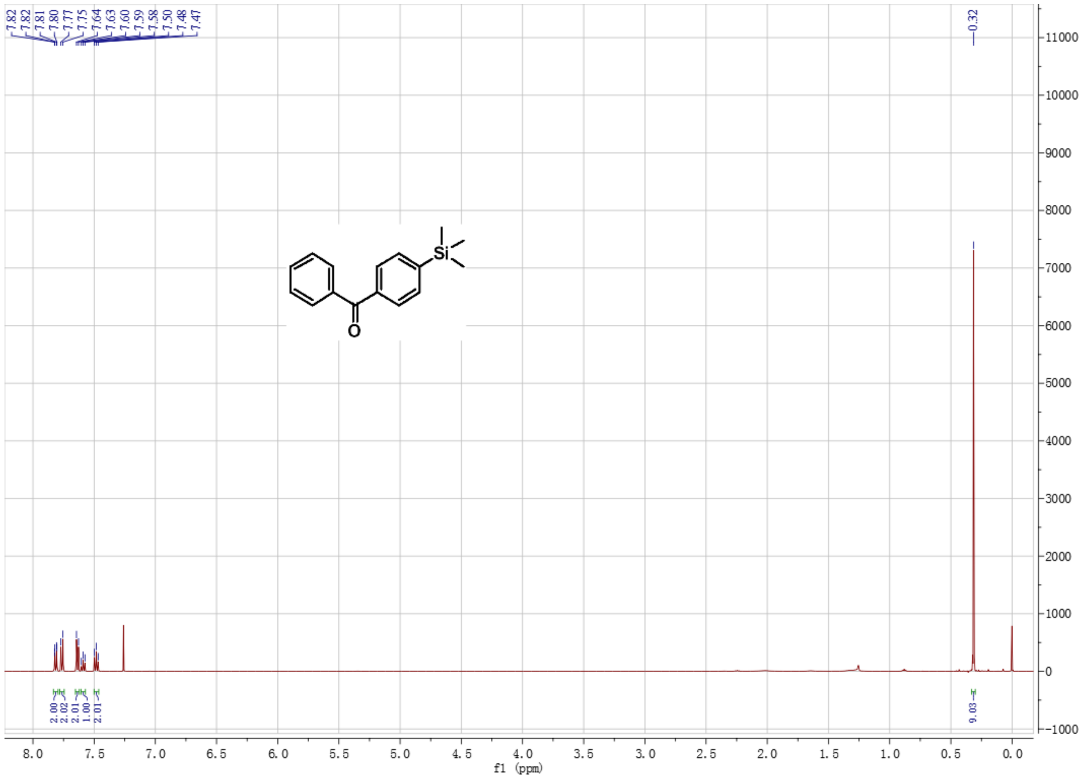

167.89
149.60
133.63
128.31
122.28
-2.25
N
Si
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5

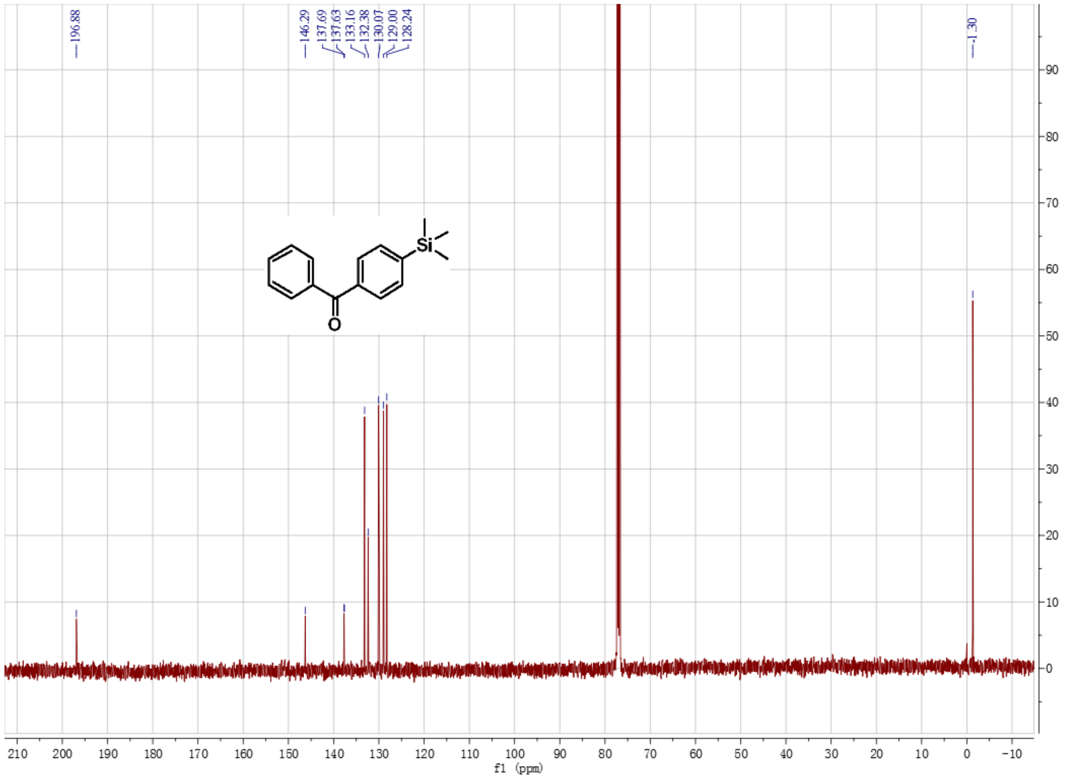
Compound **5g**


8.17
8.15
7.92
7.91
7.90
7.89
7.75
7.74
7.57
7.56
7.54
7.52
7.51
7.49
7.48
0.53
Si
1.00
2.01
1.02
3.05
9.02
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)
19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000

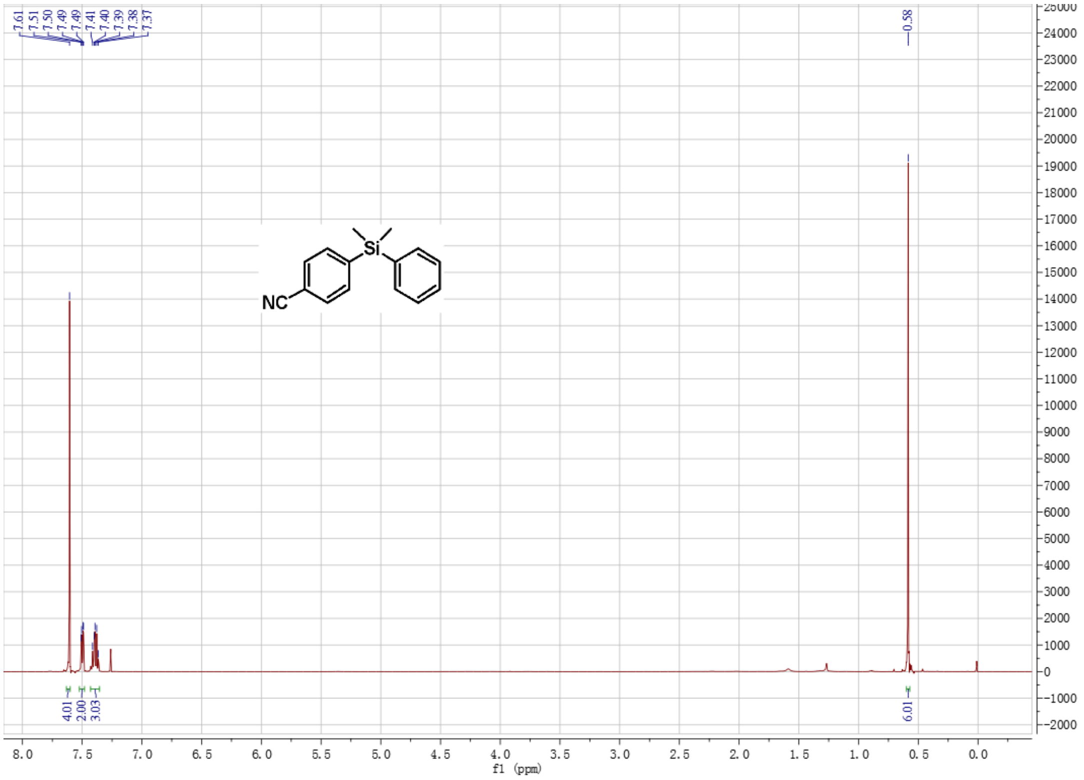

138.12
136.89
133.41
133.15
129.71
129.11
128.12
125.56
125.26
125.08
0.24
Si
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
550 500 450 400 350 300 250 200 150 100 50 0 −50

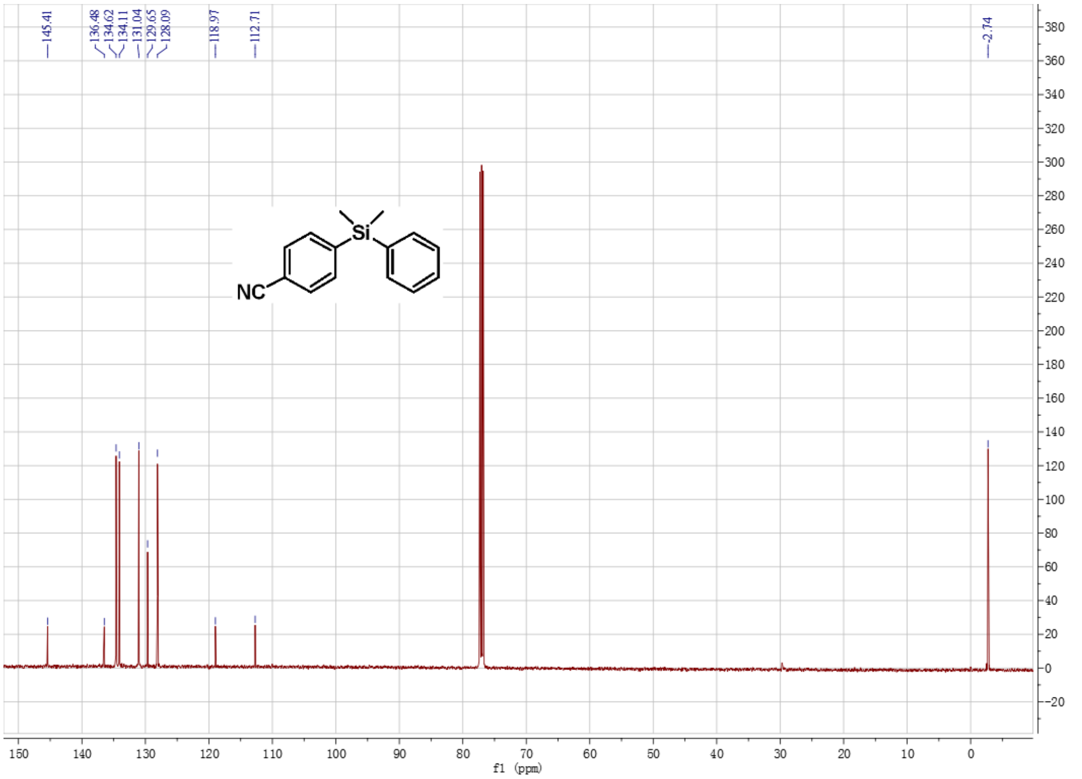
Compound **5f**


7.82
7.82
7.81
7.80
7.77
7.75
7.64
7.63
7.60
7.59
7.58
7.50
7.48
7.47
0.32
Si
O
2.00
2.02
2.01
1.00
2.01
9.03
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)


196.88
146.29
137.69
137.63
133.16
132.38
130.07
129.00
128.24
-1.30
Si
O
90
80
70
60
50
40
30
20
10
0
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)

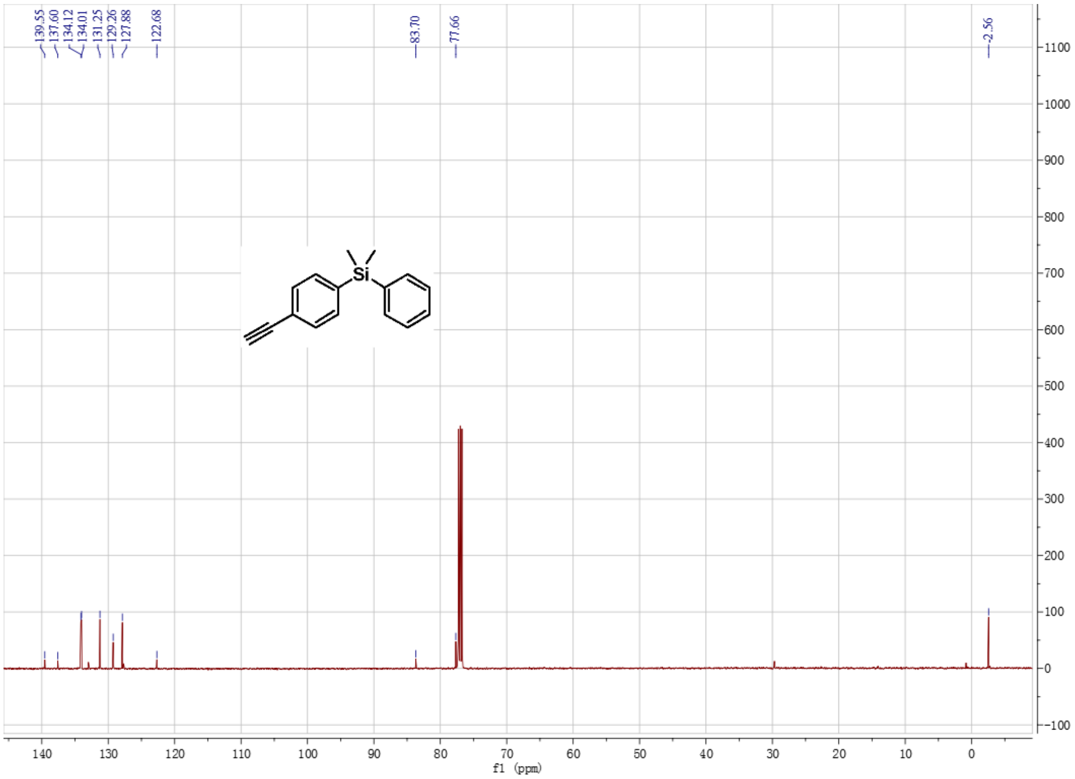
Compound **5c**


7.61
7.51
7.50
7.49
7.49
7.41
7.40
7.39
7.38
7.37
0.58
4.01
2.00
3.03
6.01
NC
Si
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)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

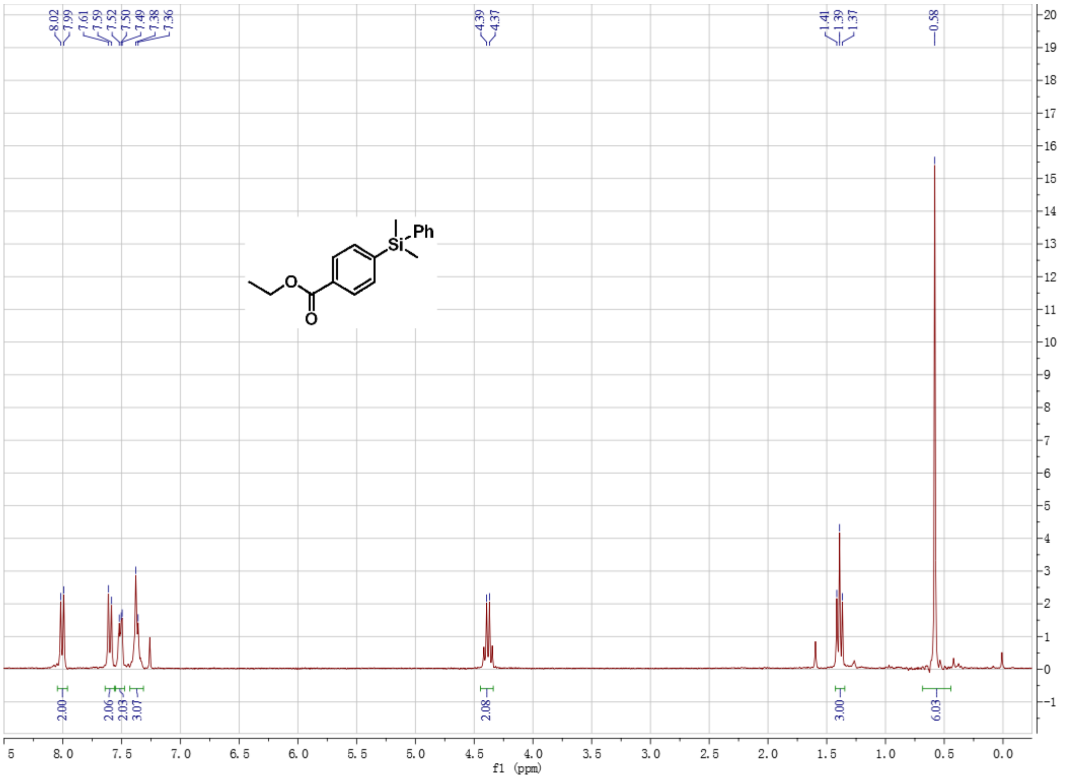

145.41
136.48
134.62
134.11
131.04
129.65
128.09
118.97
112.71
-2.74
NC
Si
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

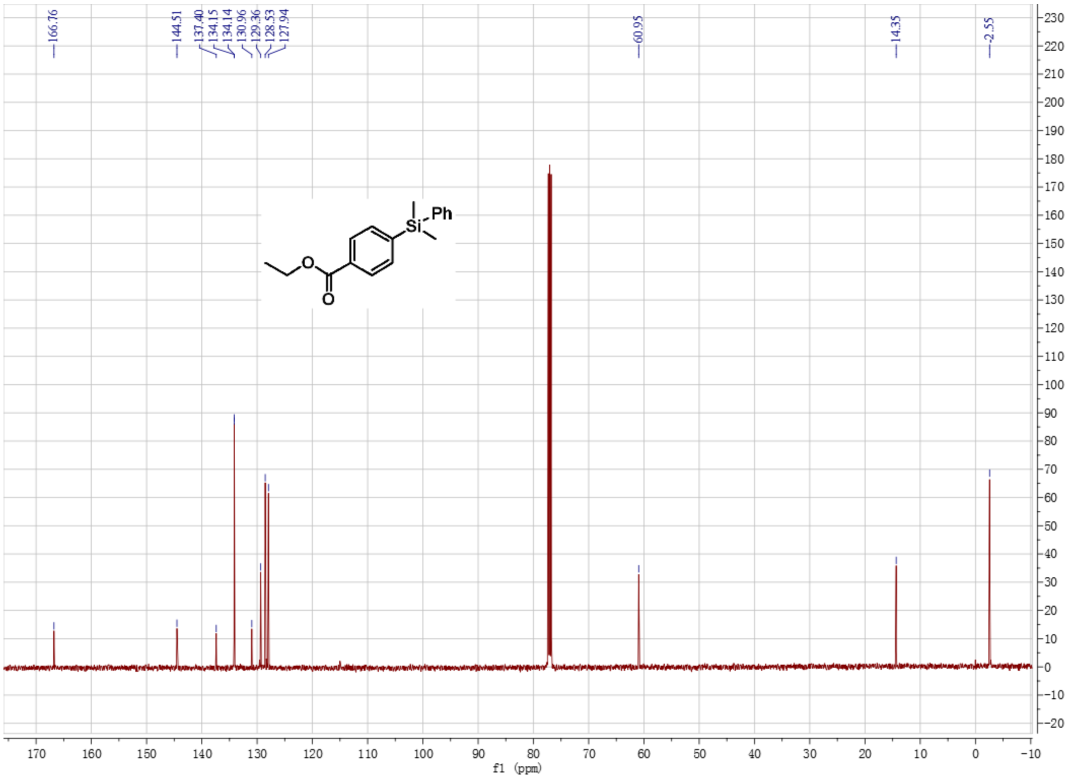
Compound **5d**


7.51
7.51
7.50
7.49
7.47
7.47
7.38
7.38
7.37
7.37
7.35
3.09
0.55
Si
2.04
4.00
3.02
1.00
6.01
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
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

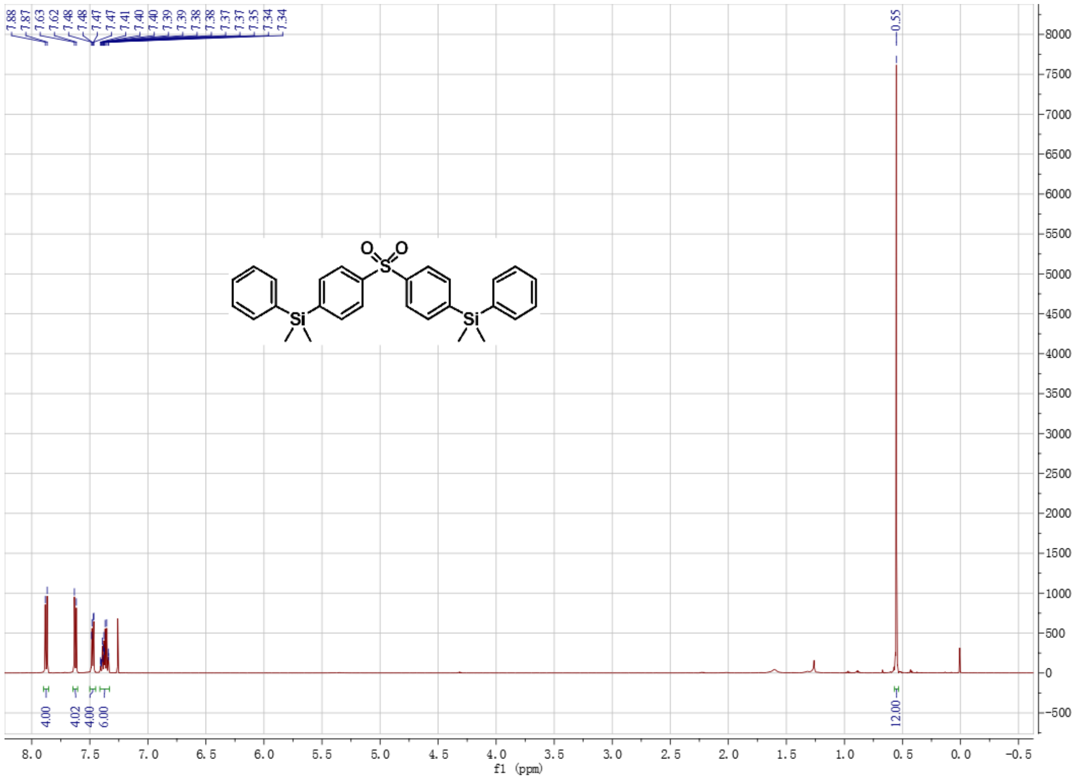

139.55
137.60
134.12
134.01
131.25
129.26
127.88
122.68
83.70
77.66
-2.56
Si
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

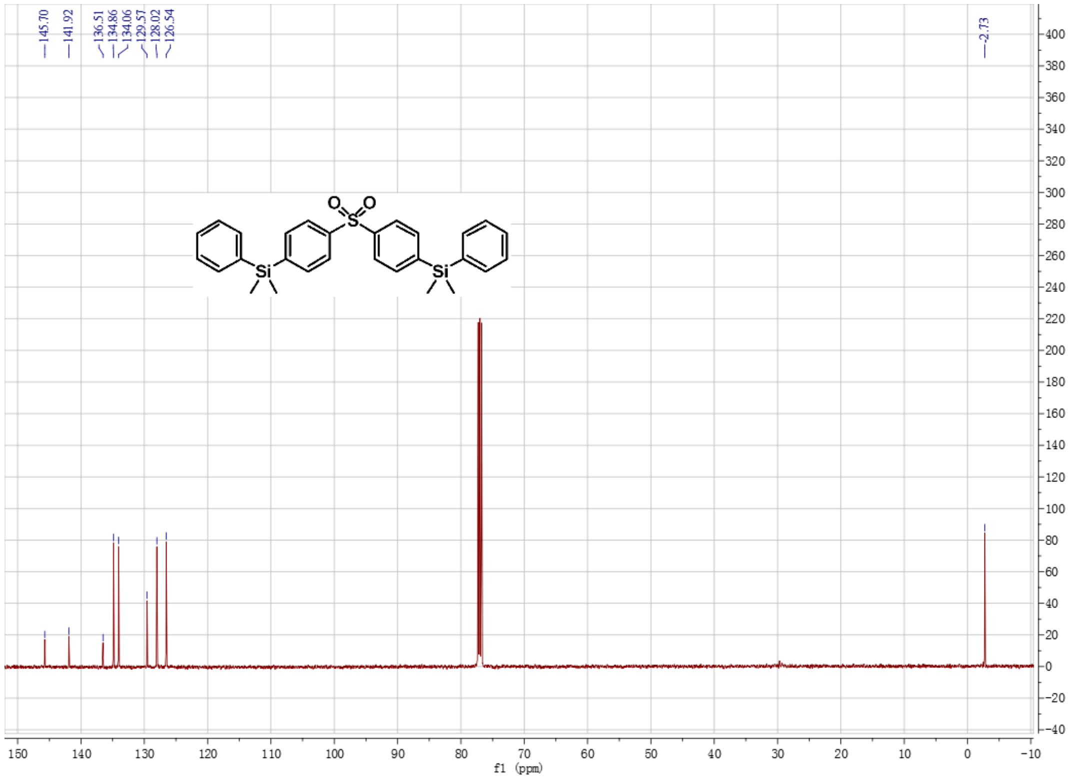
Compound **5e**


8.02
7.99
7.61
7.59
7.52
7.50
7.49
7.38
7.36
4.39
4.37
1.41
1.39
1.37
0.58
2.00
2.06
2.03
3.07
2.08
3.00
6.03
Si
Ph
O
O
f1 (ppm)

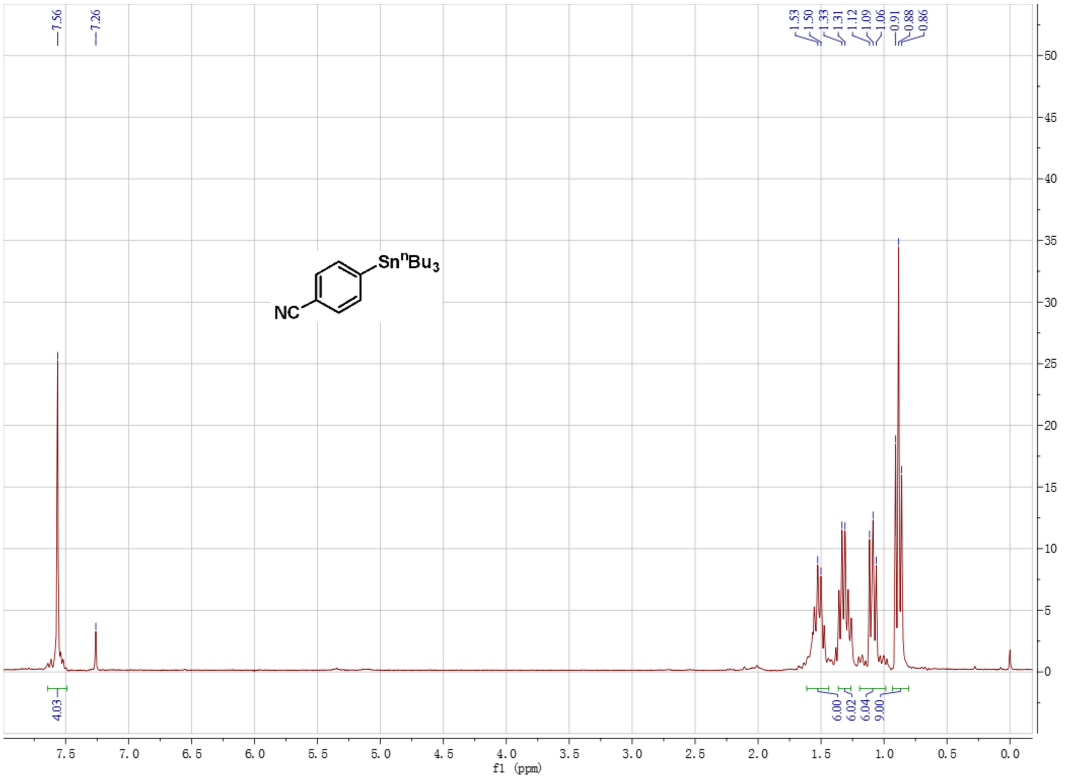

166.76
144.51
137.40
134.15
134.14
130.96
129.36
128.53
127.94
60.95
14.35
-2.55
Si
Ph
O
O
f1 (ppm)

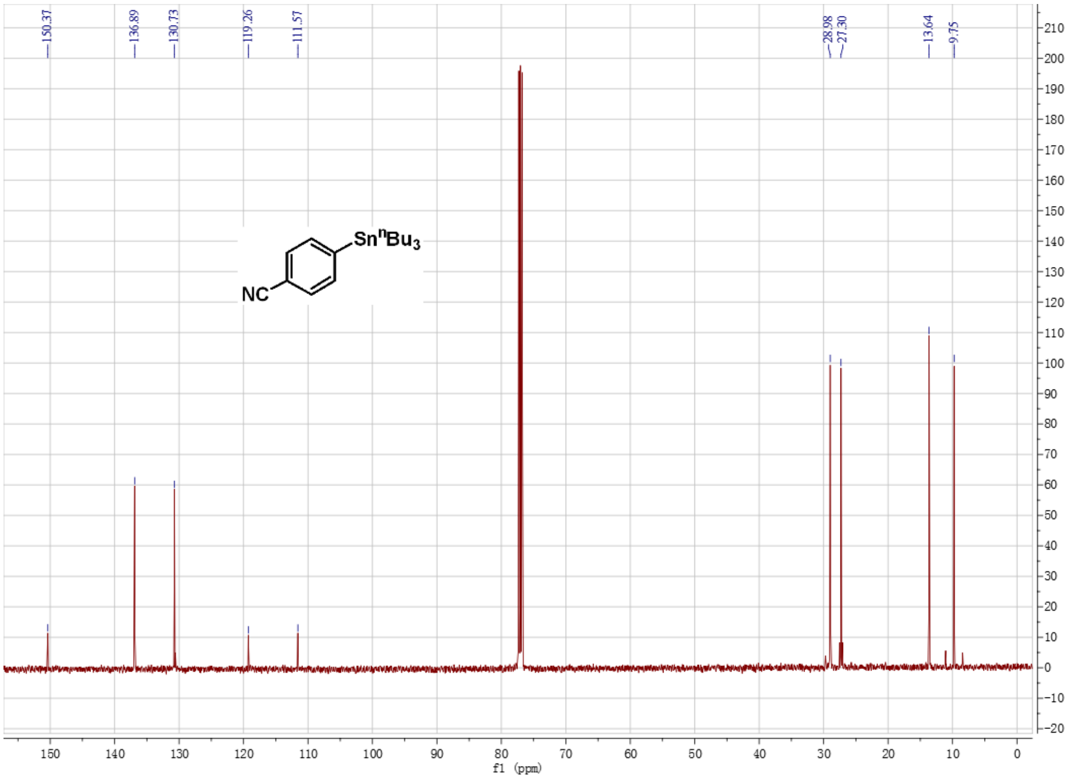
Compound **5i**


7.88
7.87
7.63
7.62
7.48
7.48
7.47
7.47
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.35
7.34
7.34
0.55
4.00
4.02
4.00
6.00
12.00
O
O
S
Si
Si
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)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

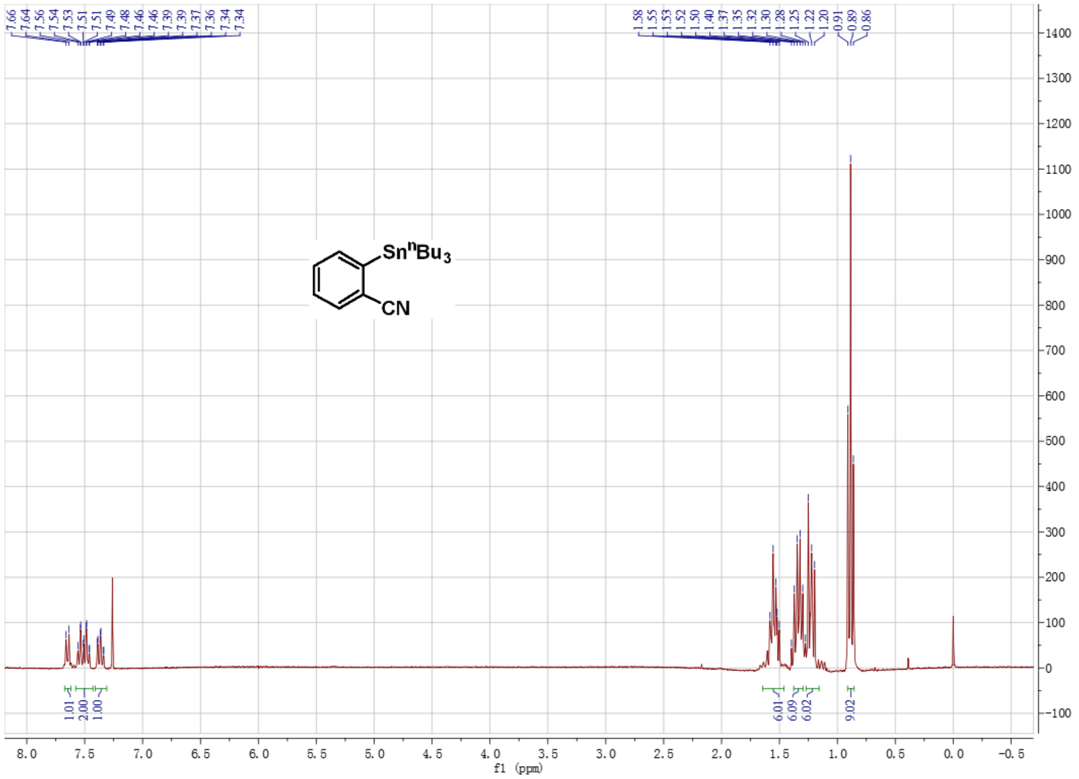

145.70
141.92
136.51
134.86
134.06
129.57
128.02
126.54
-2.73
O
O
S
Si
Si
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40

Compound **7a**

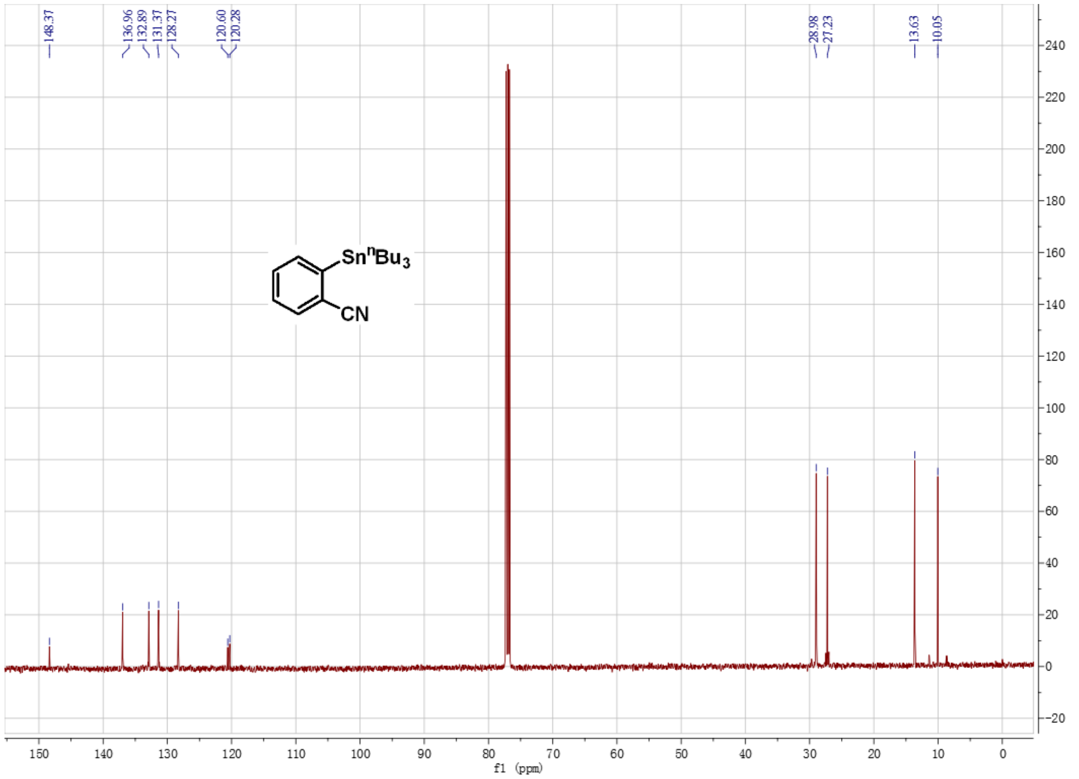

7.56
7.26
1.53
1.50
1.33
1.31
1.12
1.09
1.06
0.91
0.88
0.86
Sn^{n}Bu$_3$
NC
4.03
6.00
6.02
6.04
9.00
f1 (ppm)


150.37
136.89
130.73
119.26
111.57
28.98
27.30
13.64
9.75
Sn^{n}Bu$_3$
NC
f1 (ppm)

Compound **7c**

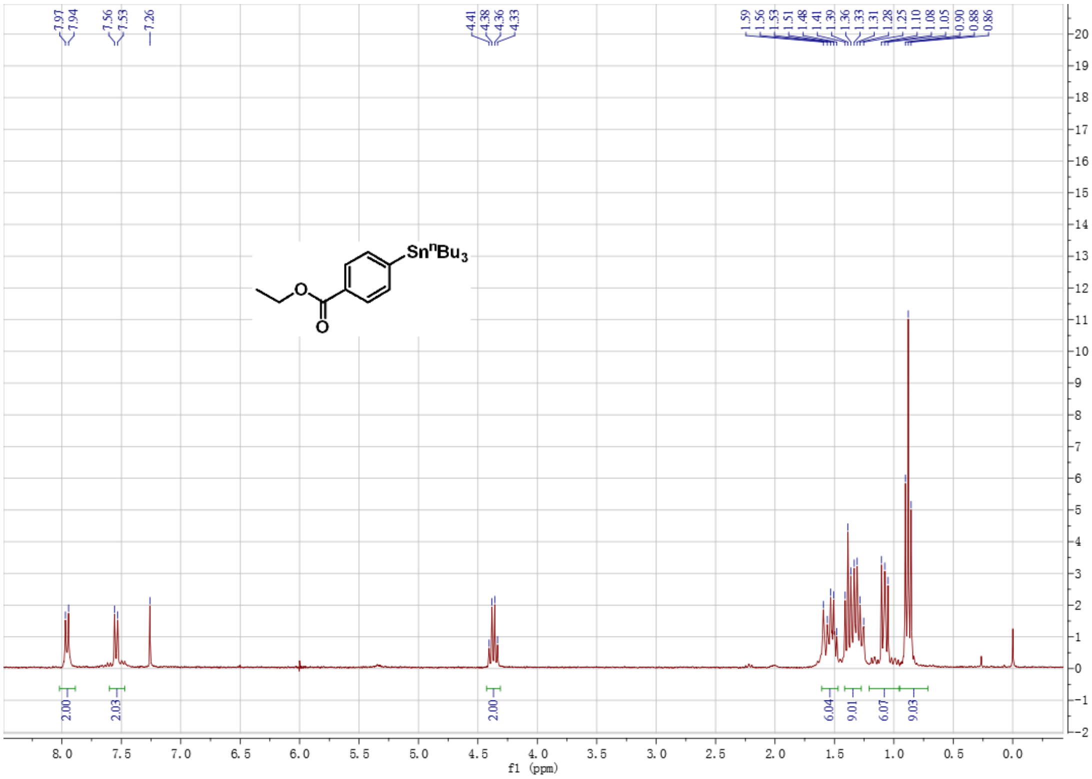


7.66
7.64
7.56
7.54
7.53
7.51
7.51
7.49
7.48
7.46
7.46
7.39
7.39
7.37
7.36
7.34
7.34
1.58
1.55
1.53
1.52
1.50
1.40
1.37
1.35
1.32
1.30
1.28
1.25
1.22
1.20
0.91
0.89
0.86
Sn^{n}Bu$_3$
CN
1.01
2.00
1.00
6.01
6.09
6.02
9.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

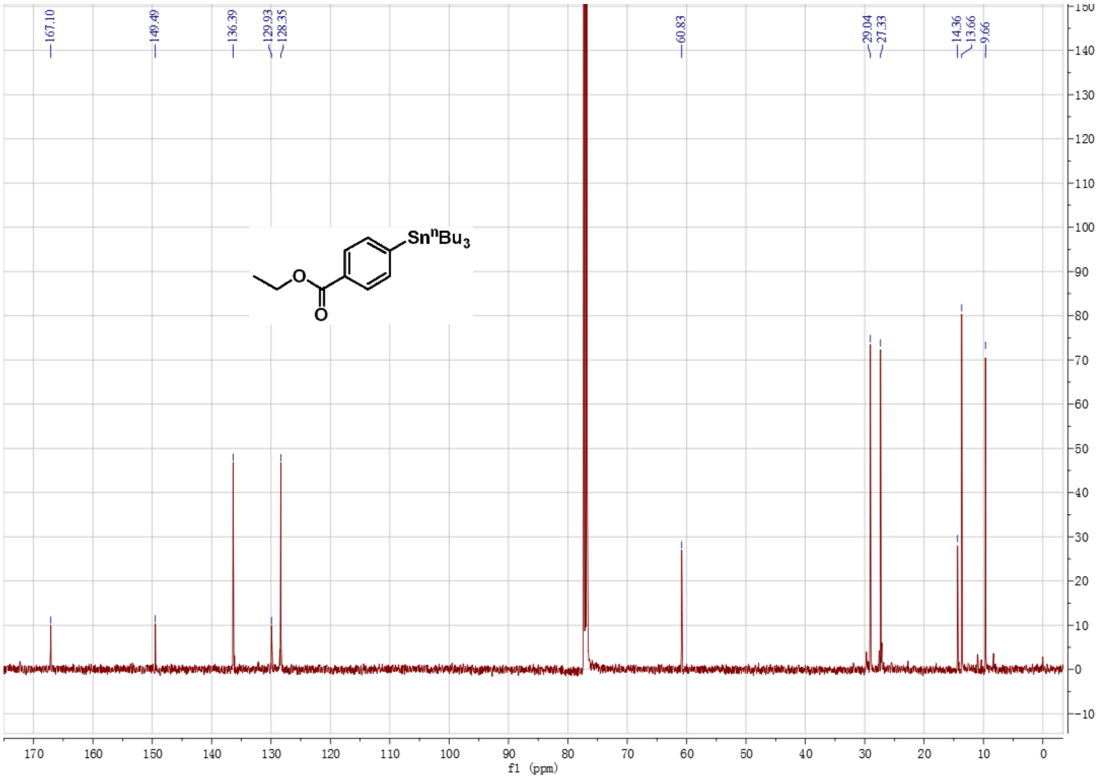


148.37
136.96
132.89
131.37
128.27
120.60
120.28
28.98
27.23
13.63
10.05
Sn^{n}Bu$_3$
CN
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

Compound **7f**

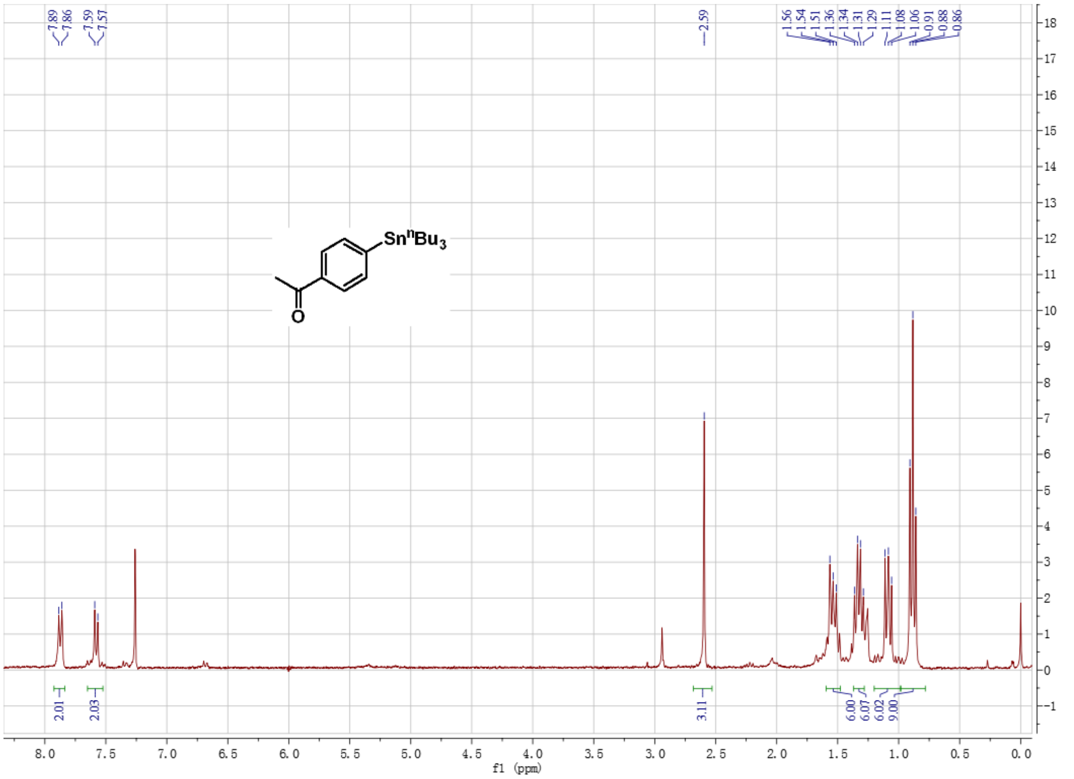


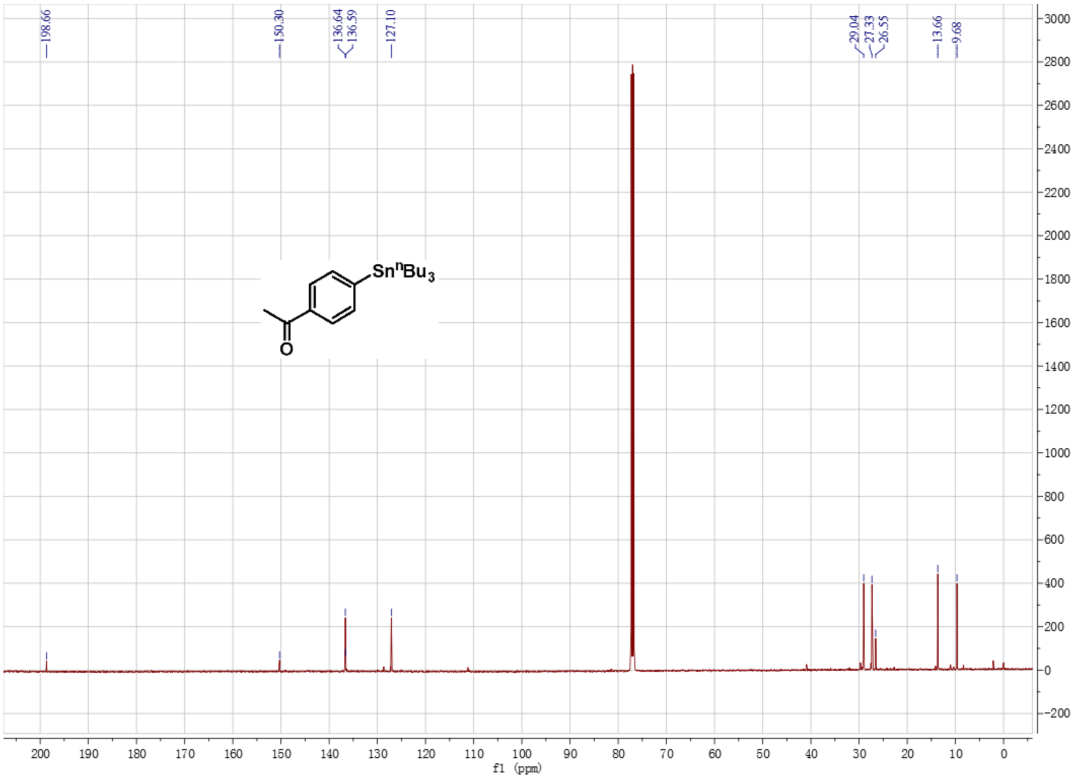
7.97
7.94
7.56
7.53
7.26
4.41
4.38
4.36
4.33
1.59
1.56
1.53
1.51
1.48
1.41
1.39
1.36
1.33
1.31
1.28
1.25
1.10
1.08
1.05
0.90
0.88
0.86
Sn^{n}Bu$_3$
O
O
2.00
2.03
2.00
6.04
9.01
6.07
9.03
f1 (ppm)



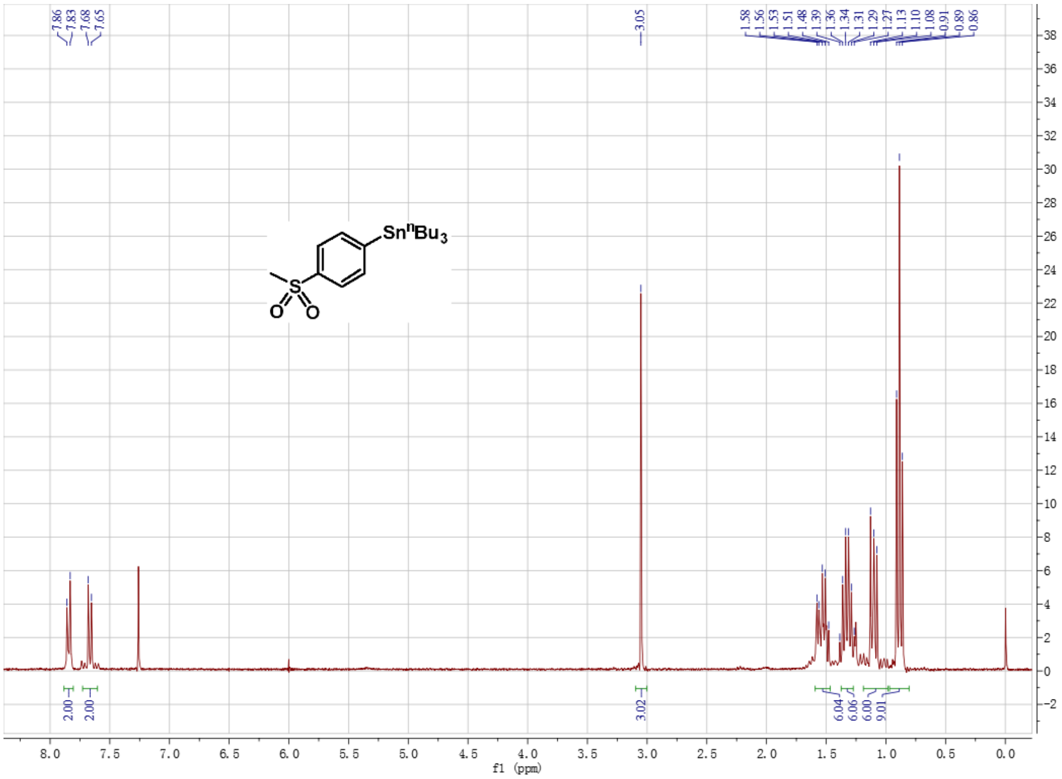
167.10
149.49
136.39
129.93
128.35
60.83
29.04
27.33
14.36
13.66
9.66
Sn^{n}Bu$_3$
O
O
f1 (ppm)

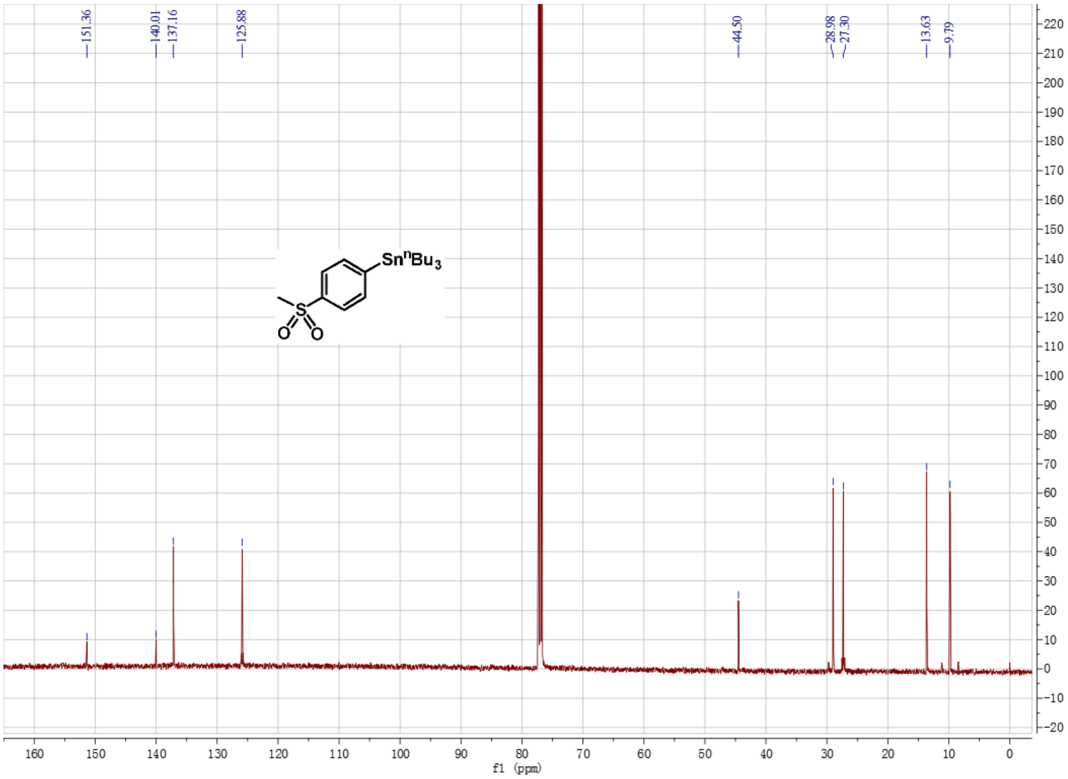
Compound **7e**


7.89
7.86
7.59
7.57
2.59
1.56
1.54
1.51
1.36
1.34
1.31
1.29
1.11
1.08
1.06
0.91
0.88
0.86
Sn^{n}Bu$_3$
O
2.01
2.03
3.11
6.00
6.07
6.02
9.00
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)
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1

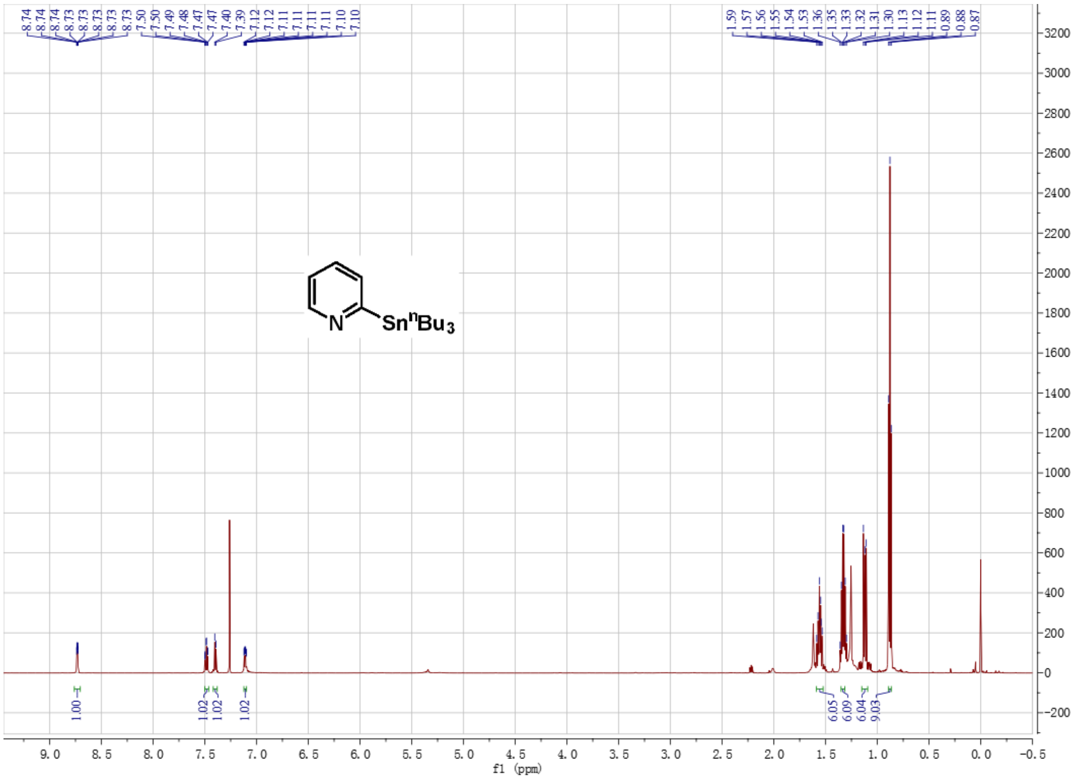

198.66
150.30
136.64
136.59
127.10
29.04
27.33
26.55
13.66
9.68
Sn^{n}Bu$_3$
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 −200

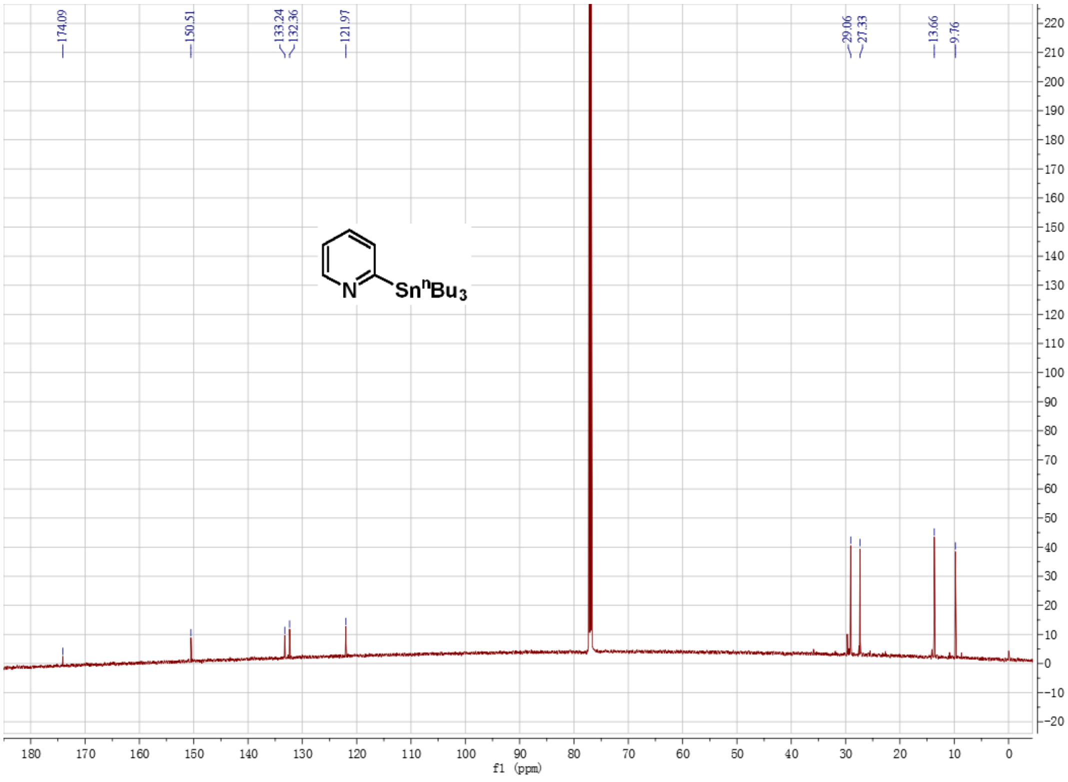
Compound **7h**


7.86
7.83
7.68
7.65
3.05
1.58
1.56
1.53
1.51
1.48
1.39
1.36
1.34
1.31
1.29
1.27
1.13
1.10
1.08
0.91
0.89
0.86
Sn^{n}Bu$_3$
S
O
O
2.00
2.00
3.02
6.04
6.06
6.00
9.01
f1 (ppm)

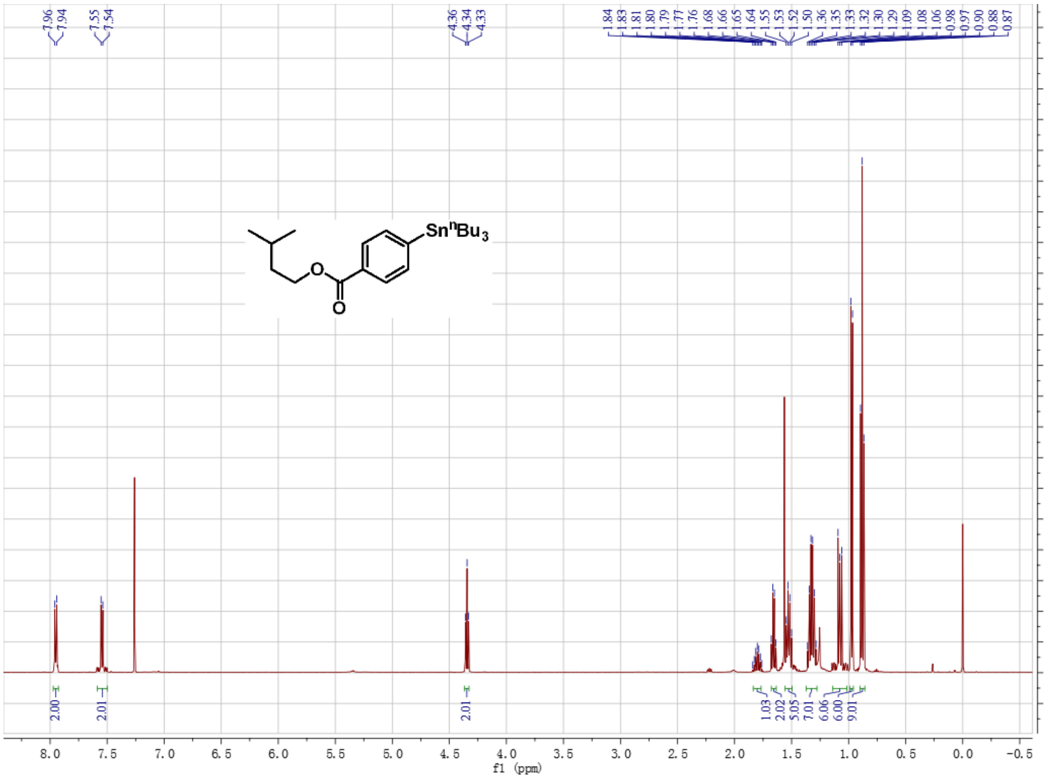

151.36
140.01
137.16
125.88
44.50
28.98
27.30
13.63
9.79
Sn^{n}Bu$_3$
S
O
O
f1 (ppm)

Compound **7j**

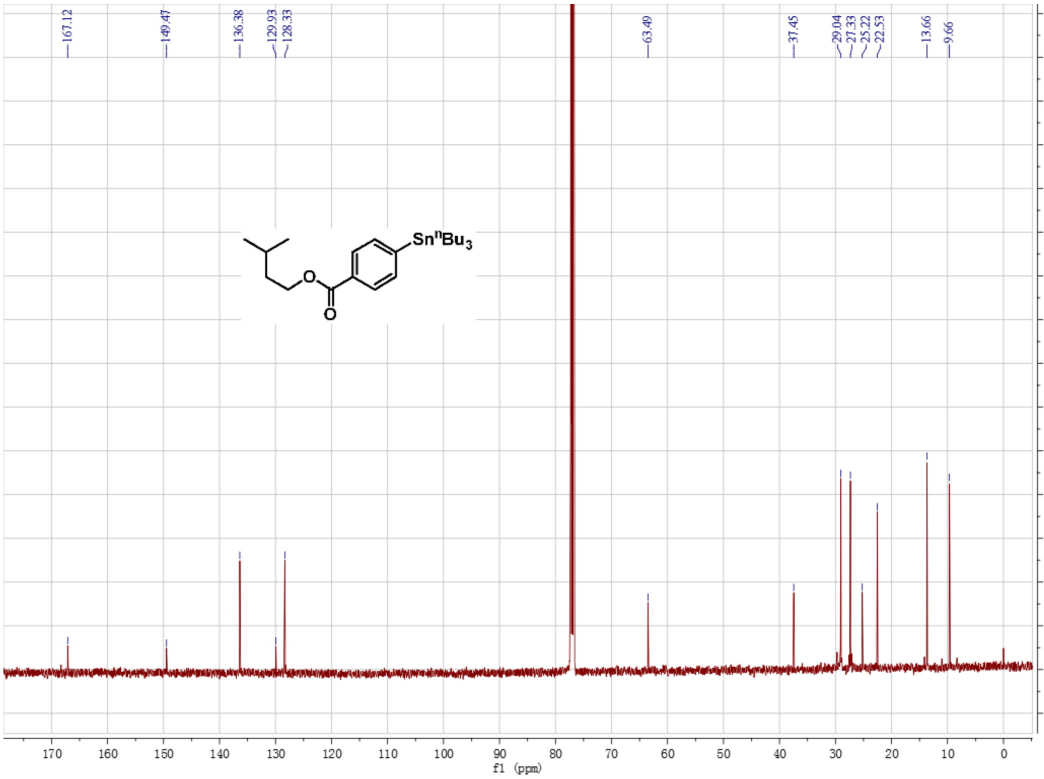

8.74
8.74
8.74
8.73
8.73
8.73
8.73
8.73
7.50
7.50
7.49
7.48
7.47
7.47
7.40
7.39
7.12
7.12
7.11
7.11
7.11
7.11
7.10
7.10
1.59
1.57
1.56
1.55
1.54
1.53
1.36
1.35
1.33
1.32
1.31
1.30
1.13
1.12
1.11
0.89
0.88
0.87
N
Sn^nBu3
1.00
1.02
1.02
1.02
6.05
6.09
6.04
9.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200


174.09
150.51
133.24
132.36
121.97
29.06
27.33
13.66
9.76
N
Sn^nBu3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

Compound **7k**

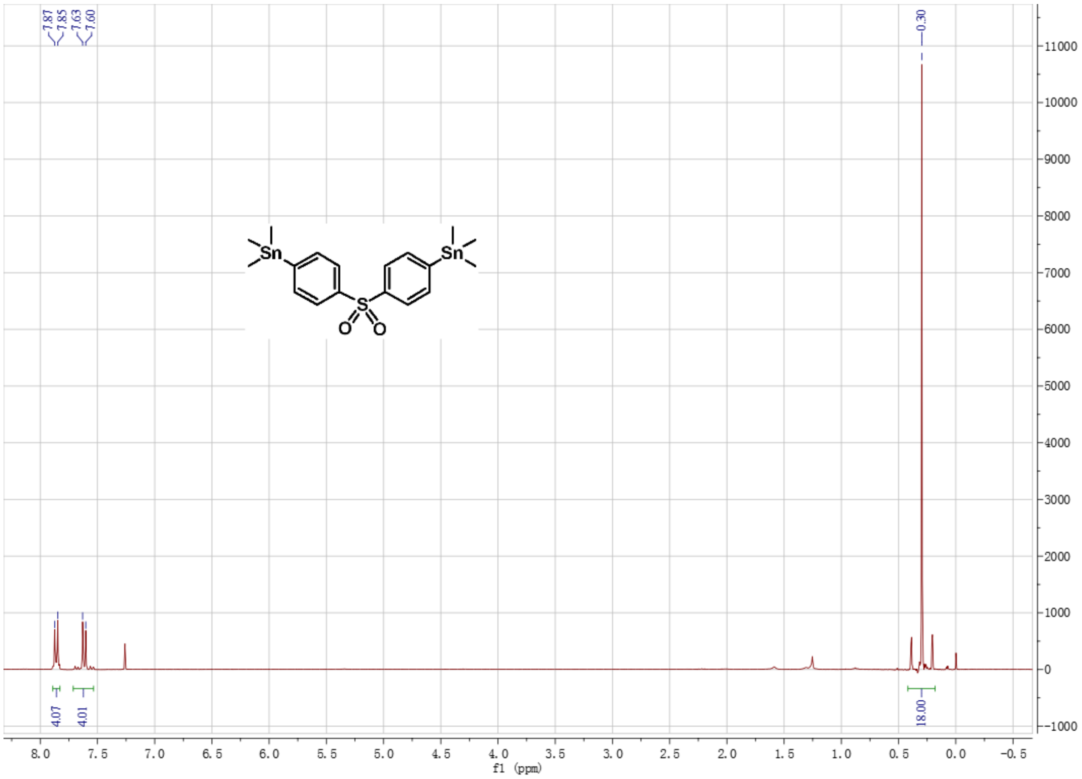


7.96
7.94
7.55
7.54
4.36
4.34
4.33
1.84
1.83
1.81
1.80
1.79
1.77
1.76
1.68
1.66
1.65
1.64
1.55
1.53
1.52
1.50
1.36
1.35
1.33
1.32
1.30
1.29
1.09
1.08
1.06
0.98
0.97
0.90
0.88
0.87
Sn^nBu_3
O
O
2.00
2.01
2.01
1.03
2.02
5.05
7.01
6.06
6.00
9.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

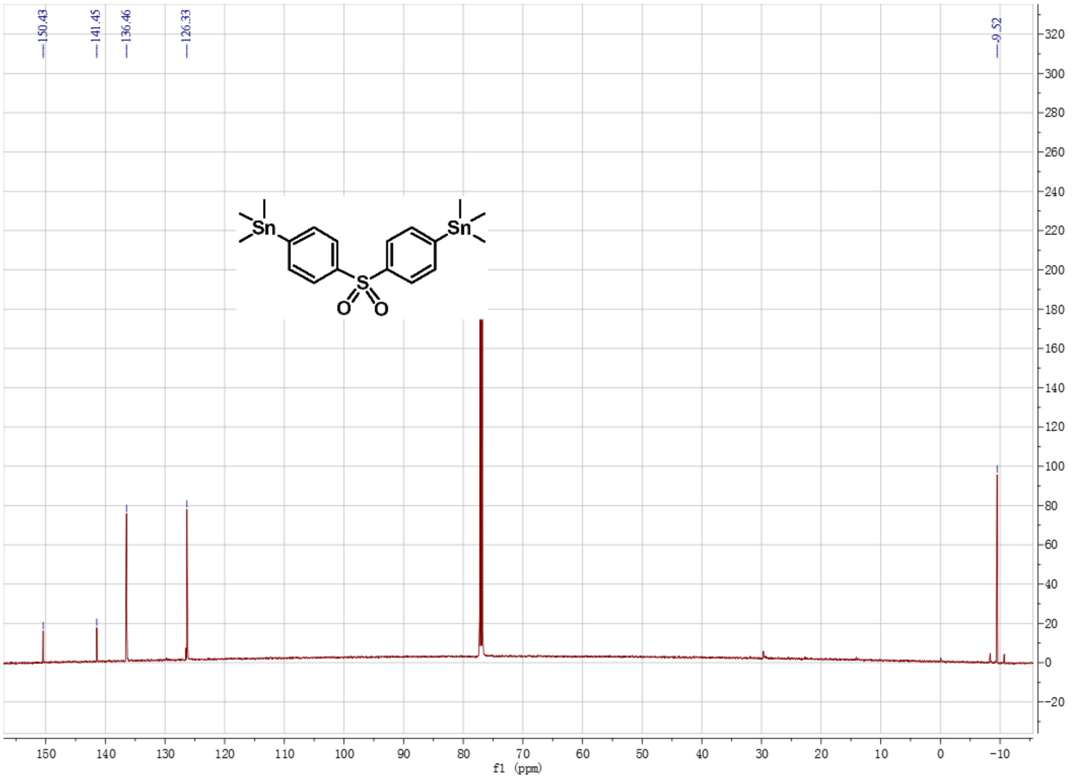


167.12
149.47
136.38
129.93
128.33
63.49
37.45
29.04
27.33
25.22
22.53
13.66
9.66
Sn^nBu_3
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

Compound **7m**

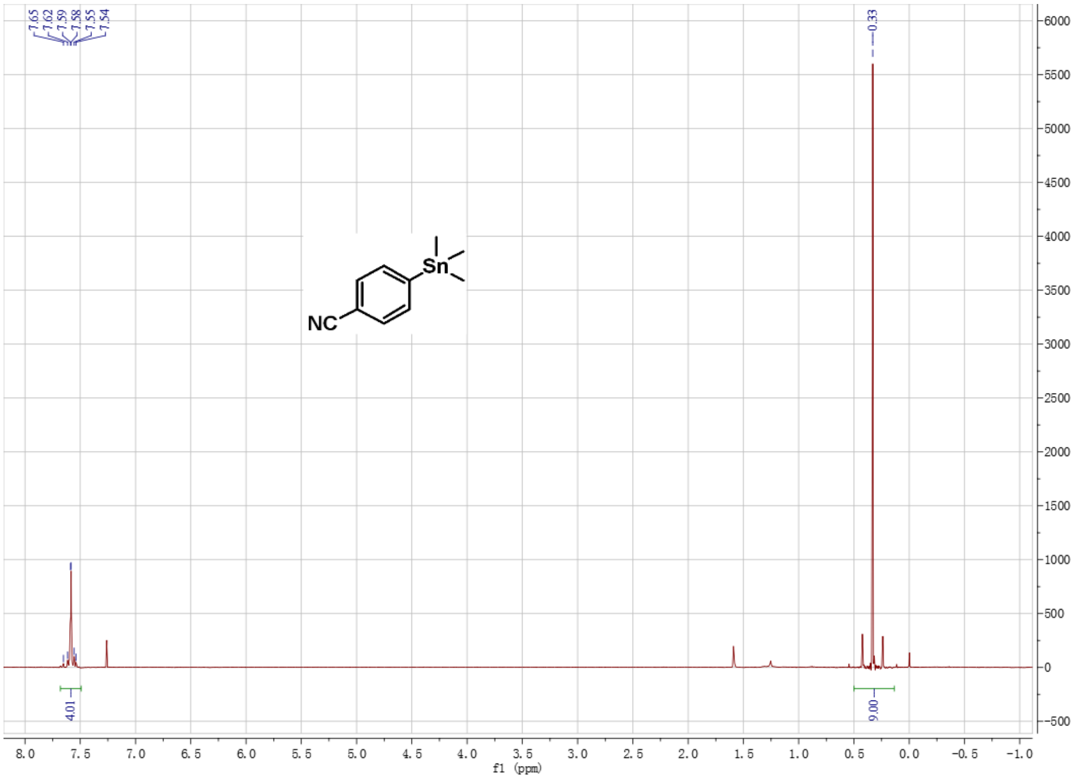


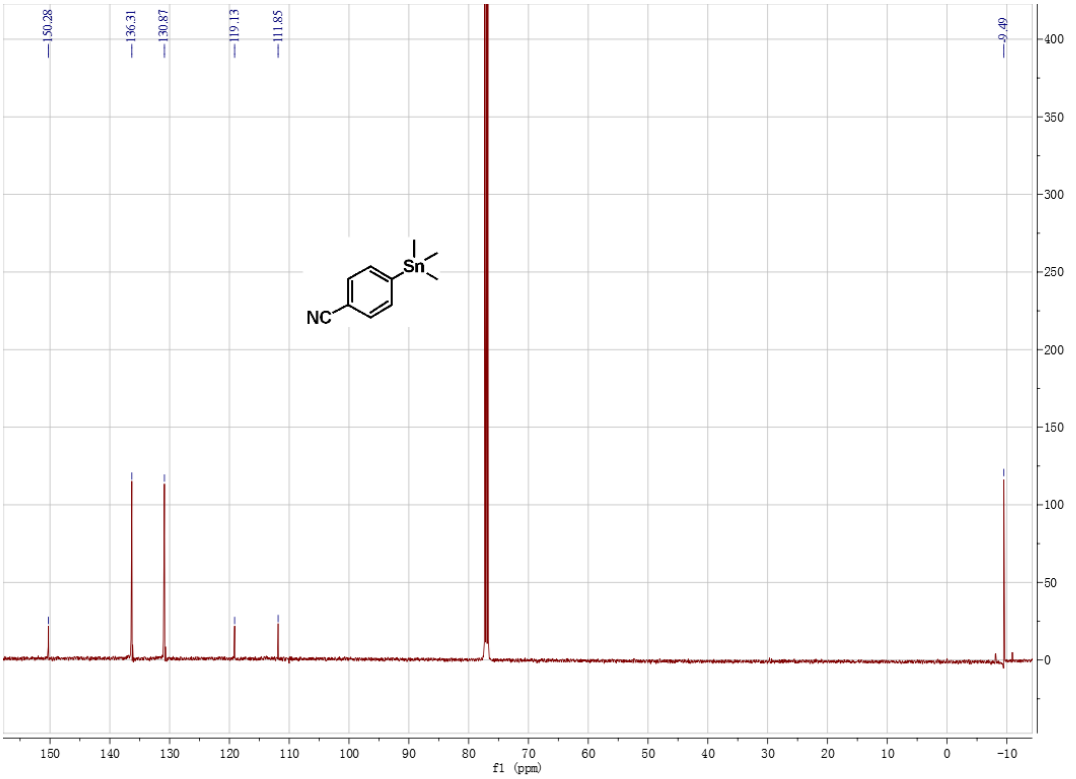
7.87
7.85
7.63
7.60
0.30
4.07
4.01
18.00
Sn
Sn
S
O
O
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



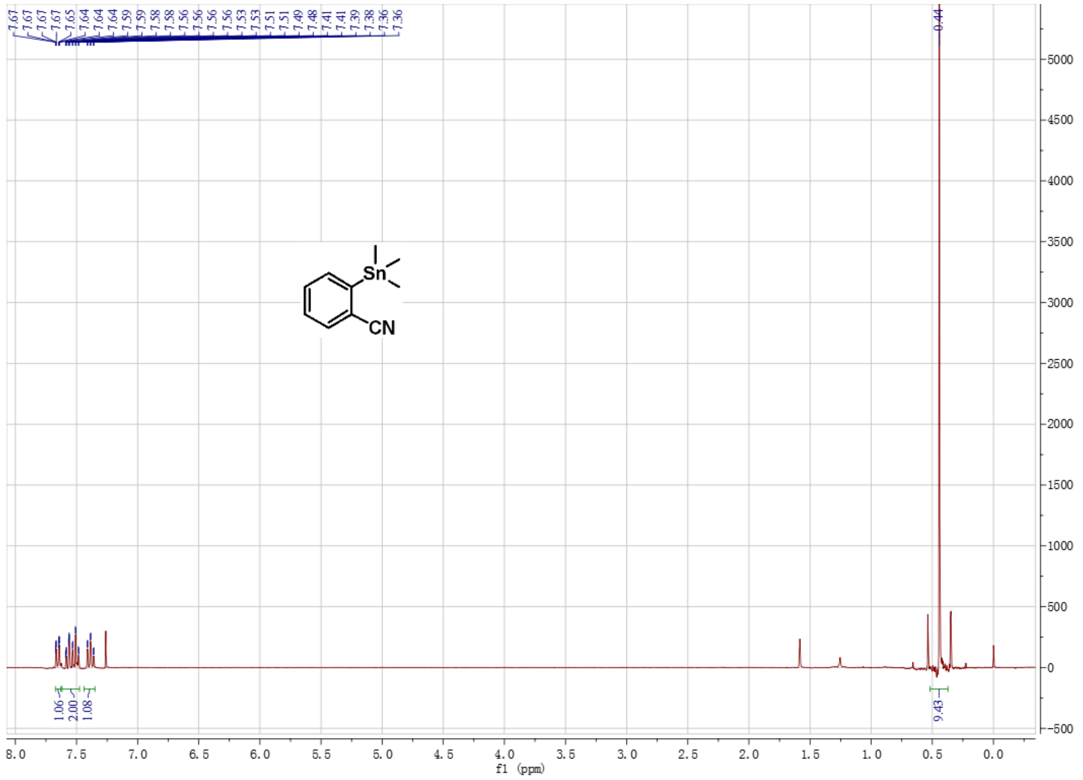
150.43
141.45
136.46
126.33
-9.52
Sn
Sn
S
O
O
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

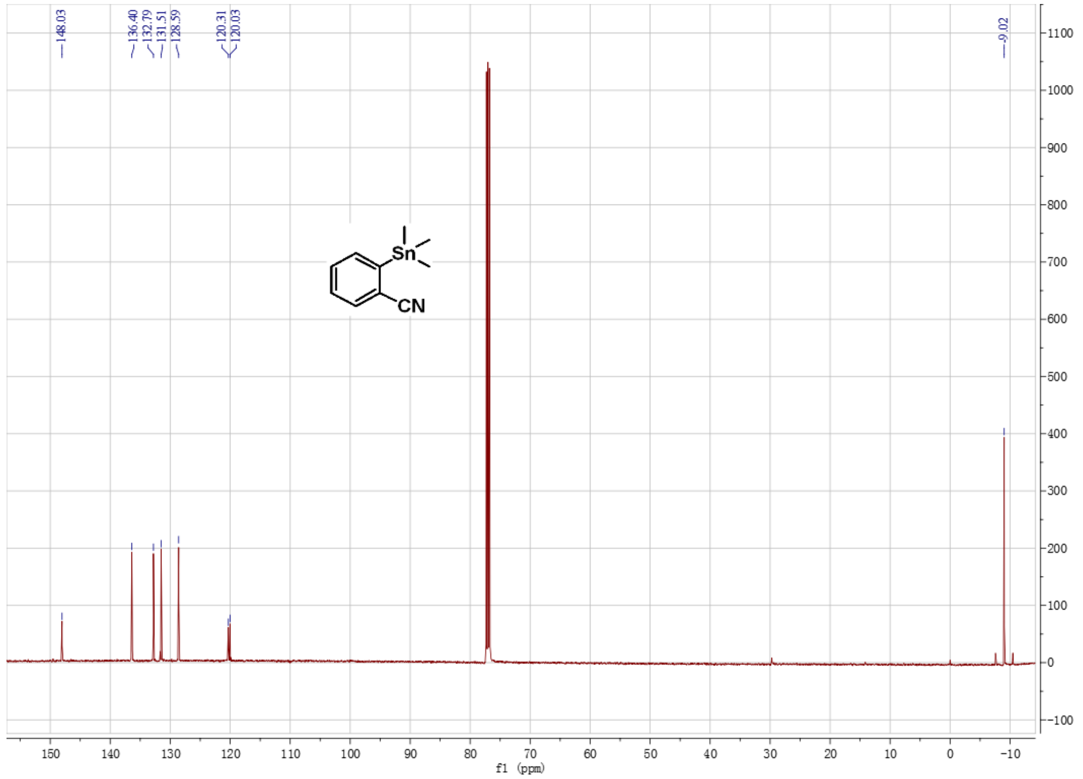
Compound **7b**


7.65
7.62
7.59
7.58
7.55
7.54
0.33
NC
Sn
4.01
9.00
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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
f1 (ppm)

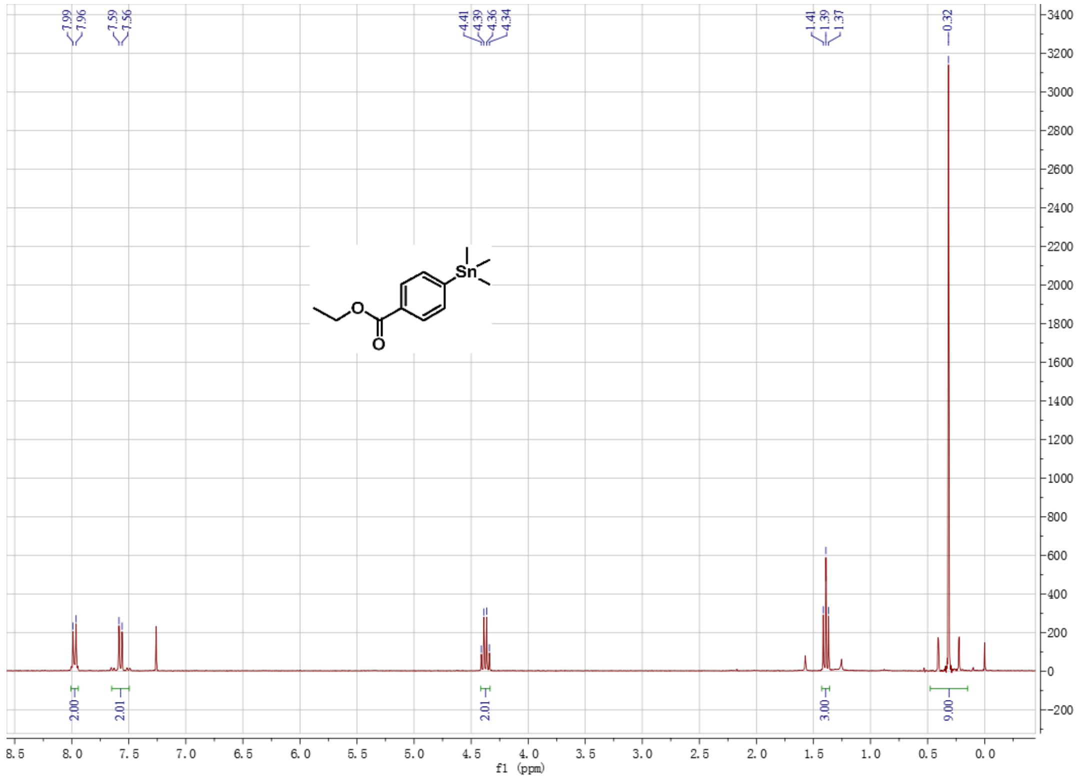

150.28
136.31
130.87
119.13
111.85
-9.49
NC
Sn
400
350
300
250
200
150
100
50
0
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

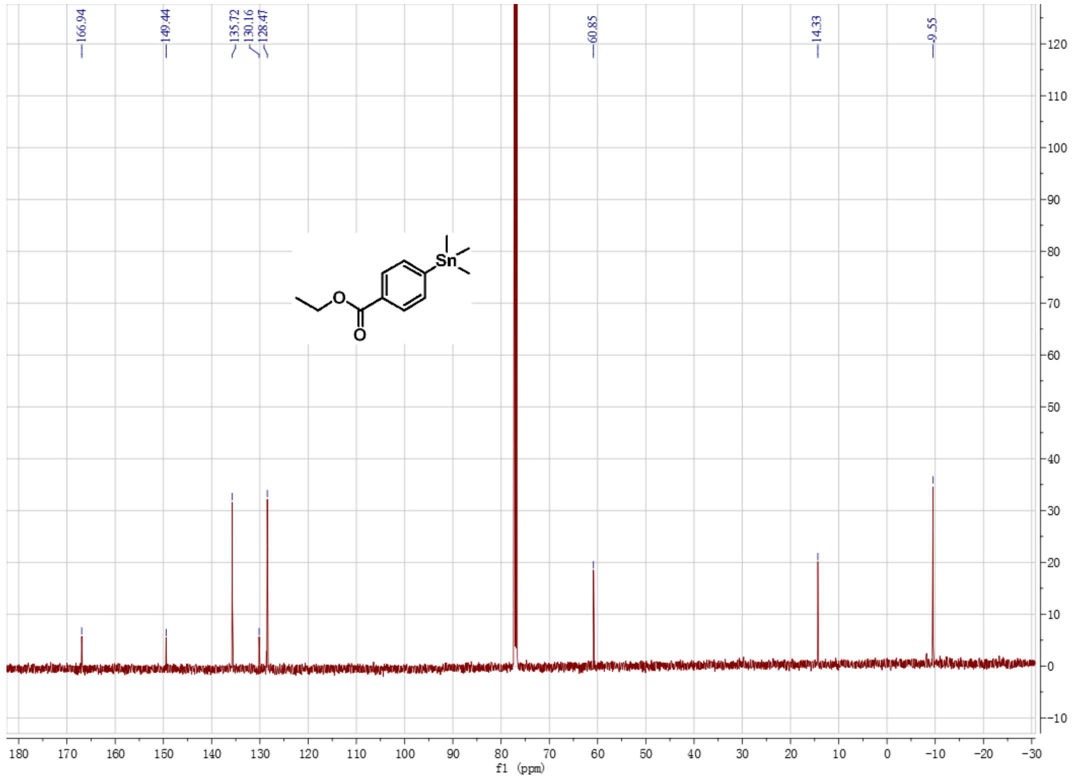
Compound **7d**


7.67
7.67
7.67
7.67
7.65
7.64
7.64
7.64
7.59
7.59
7.58
7.58
7.56
7.56
7.56
7.56
7.53
7.53
7.51
7.51
7.49
7.48
7.41
7.41
7.39
7.38
7.36
7.36
0.44
Sn
CN
1.06
2.00
1.08
9.43
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)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

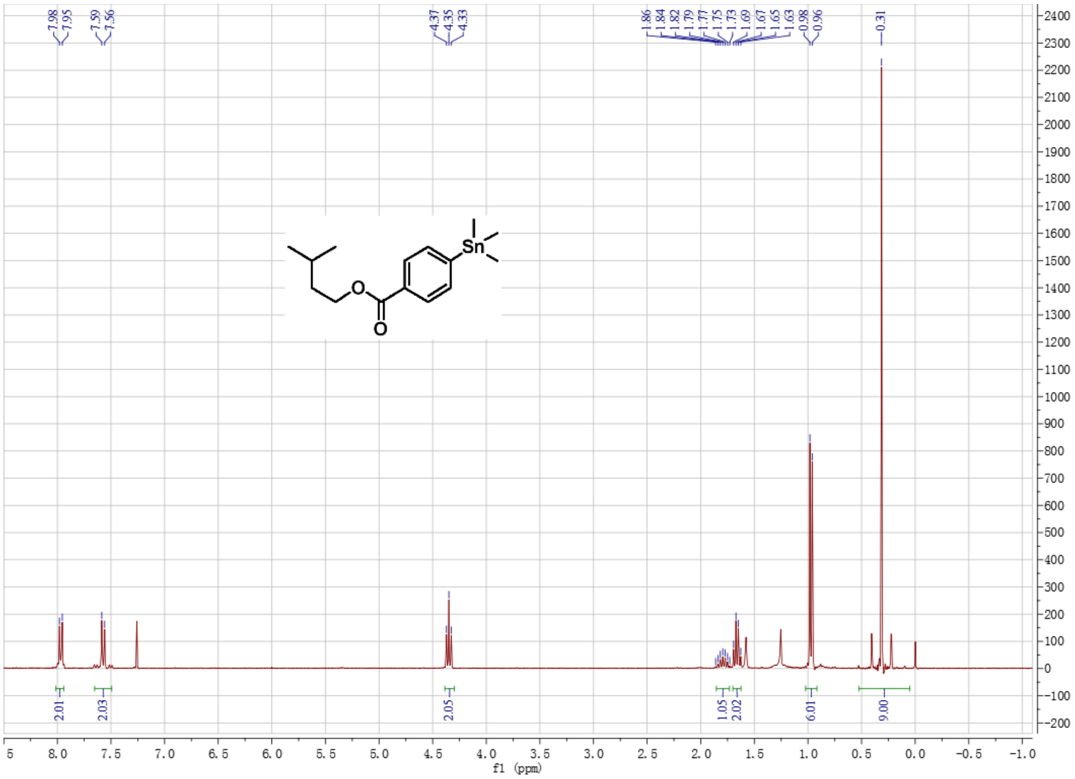

148.03
136.40
132.79
131.51
128.59
120.31
120.03
-9.02
Sn
CN
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

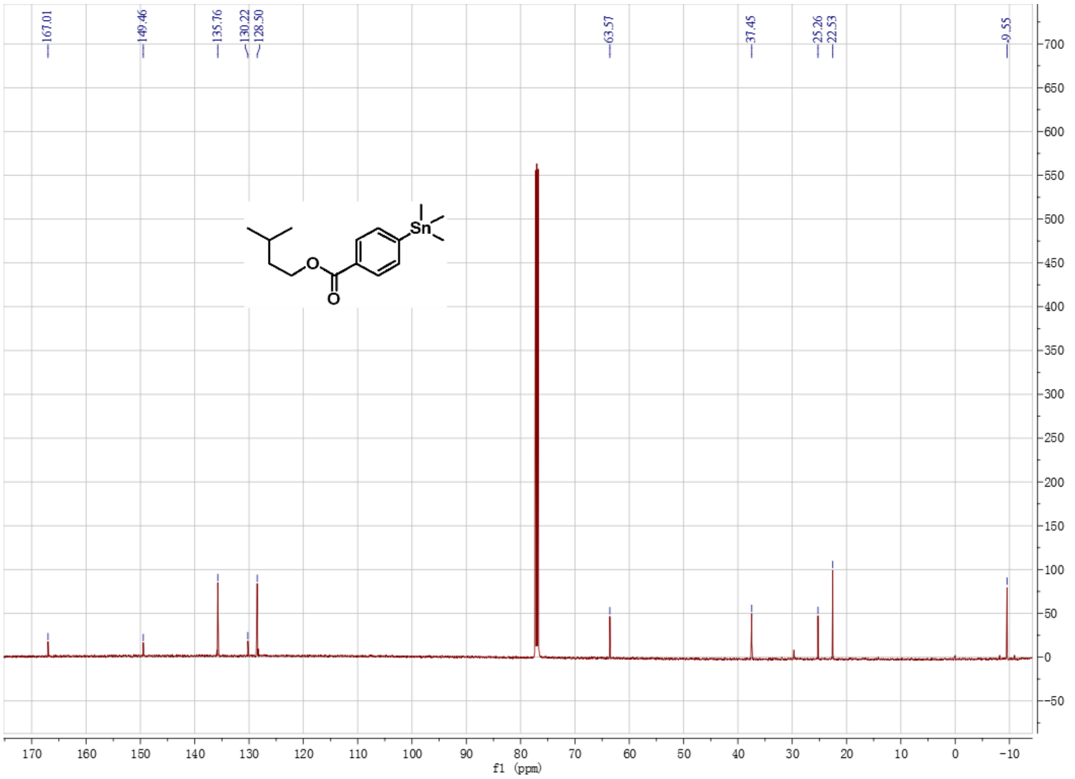
Compound **7g**


7.99
7.96
7.59
7.56
4.41
4.39
4.36
4.34
1.41
1.39
1.37
0.32
Sn
O
O
2.00
2.01
2.01
3.00
9.00
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)
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 −200

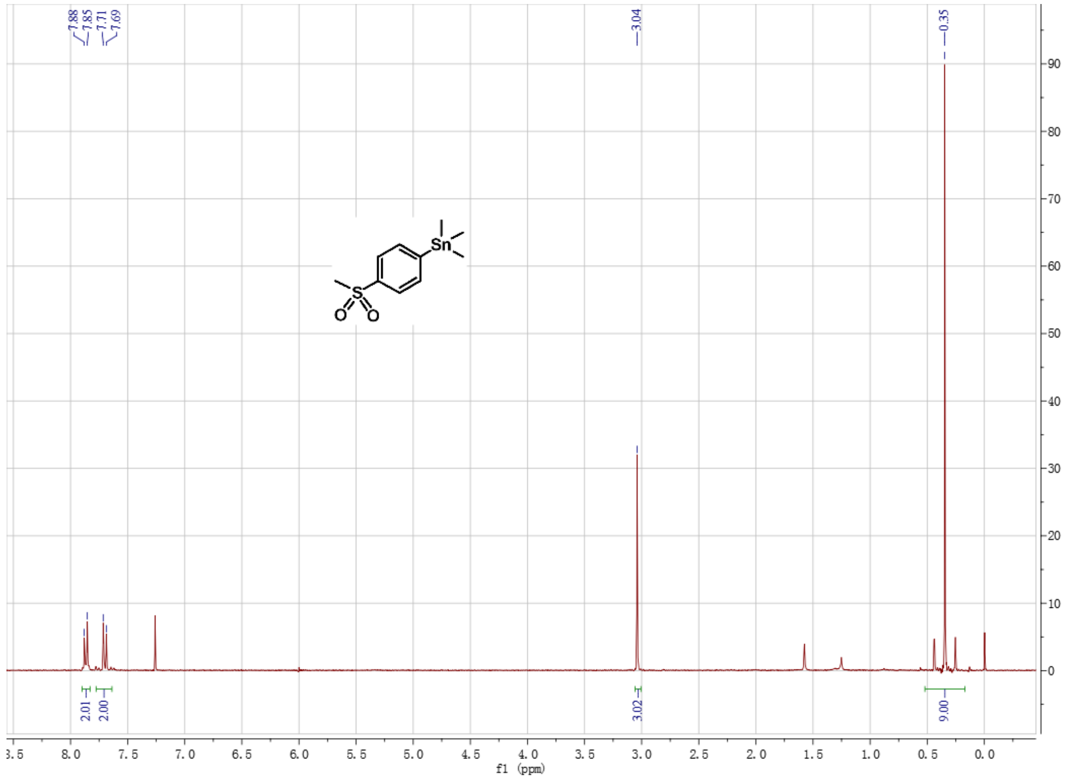

166.94
149.44
135.72
130.16
128.47
60.85
14.33
−9.55
Sn
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)
120 110 100 90 80 70 60 50 40 30 20 10 0 −10

Compound **7l**

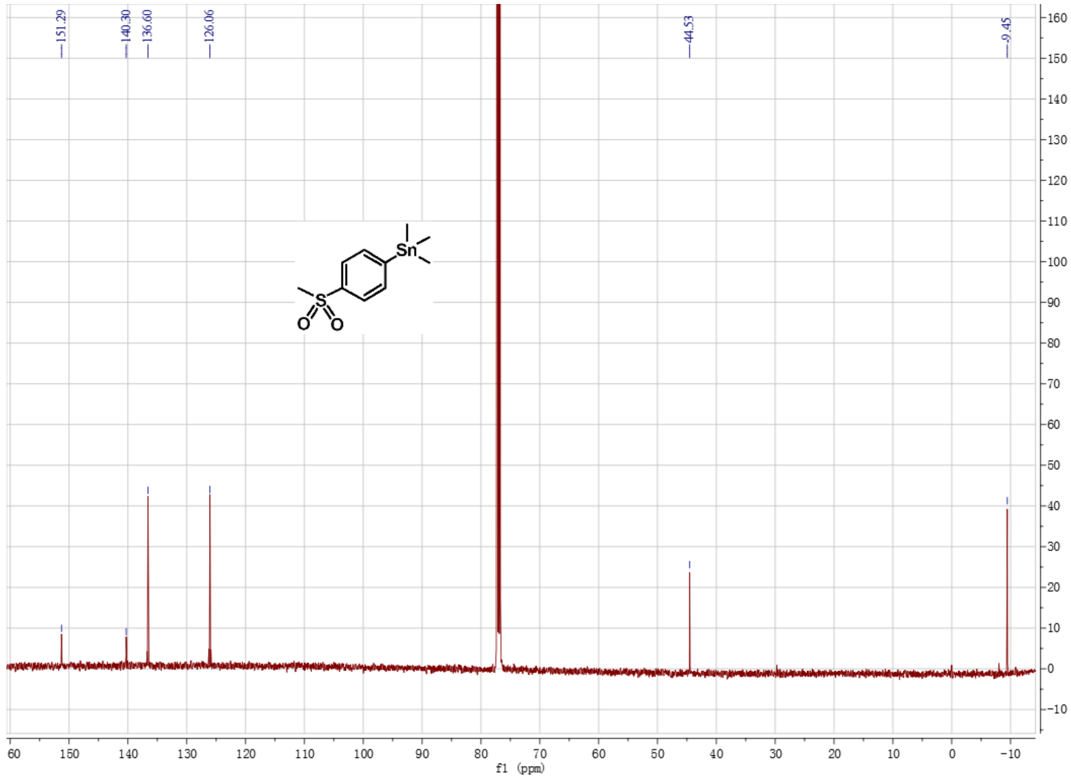

7.98
7.95
7.59
7.56
4.37
4.35
4.33
1.86
1.84
1.82
1.79
1.77
1.75
1.73
1.69
1.67
1.65
1.63
0.98
0.96
0.31
Sn
O
O
2.01
2.03
2.05
1.05
2.02
6.01
9.00
f1 (ppm)


167.01
149.46
135.76
130.22
128.50
63.57
37.45
25.26
22.53
-9.55
Sn
O
O
f1 (ppm)

Compound **7i**

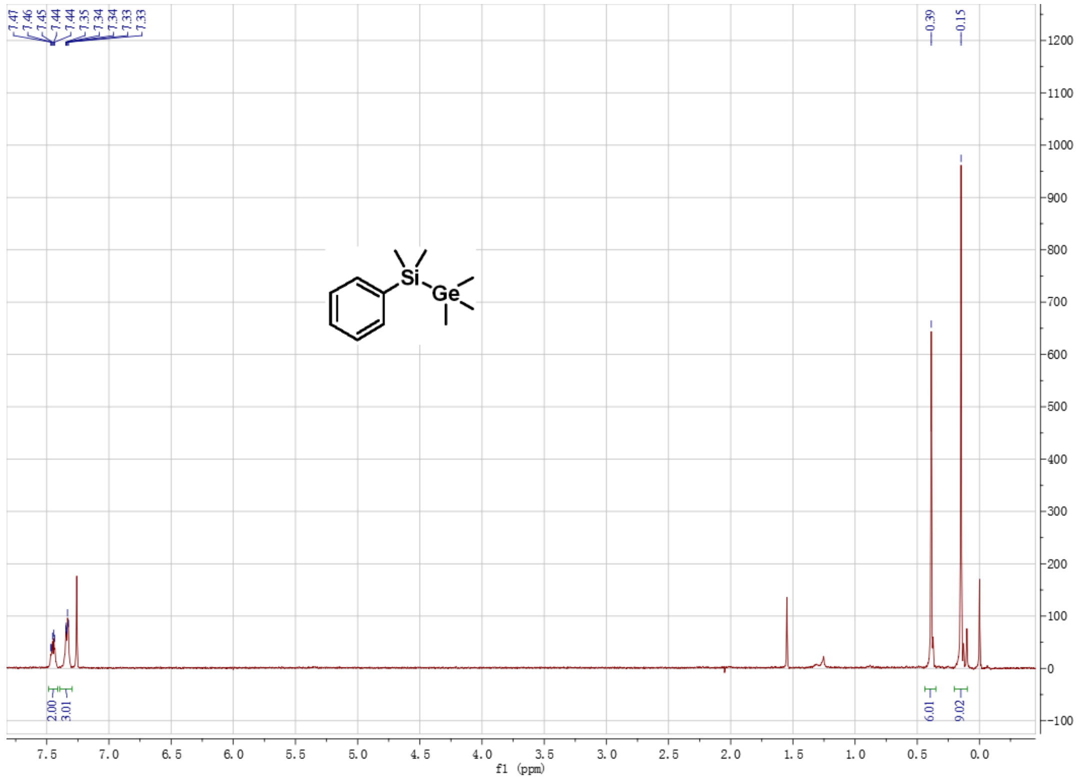


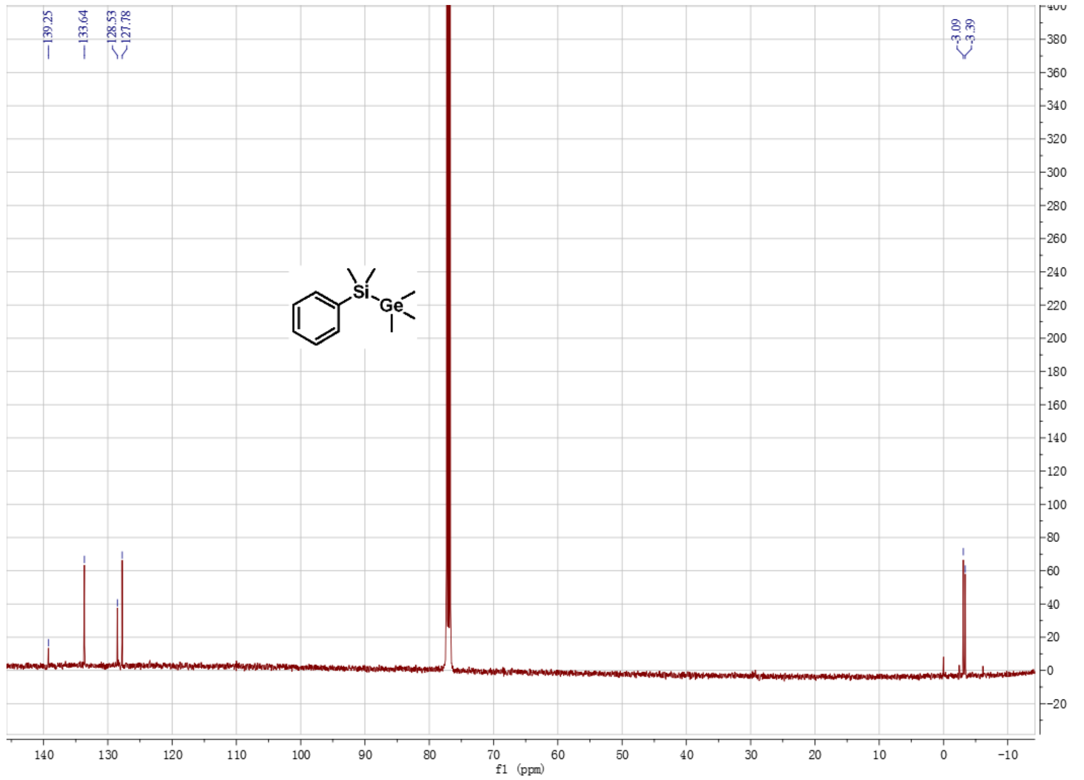
7.88
7.85
7.71
7.69
3.04
0.35
Sn
S
O
O
2.01
2.00
3.02
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
90
80
70
60
50
40
30
20
10
0



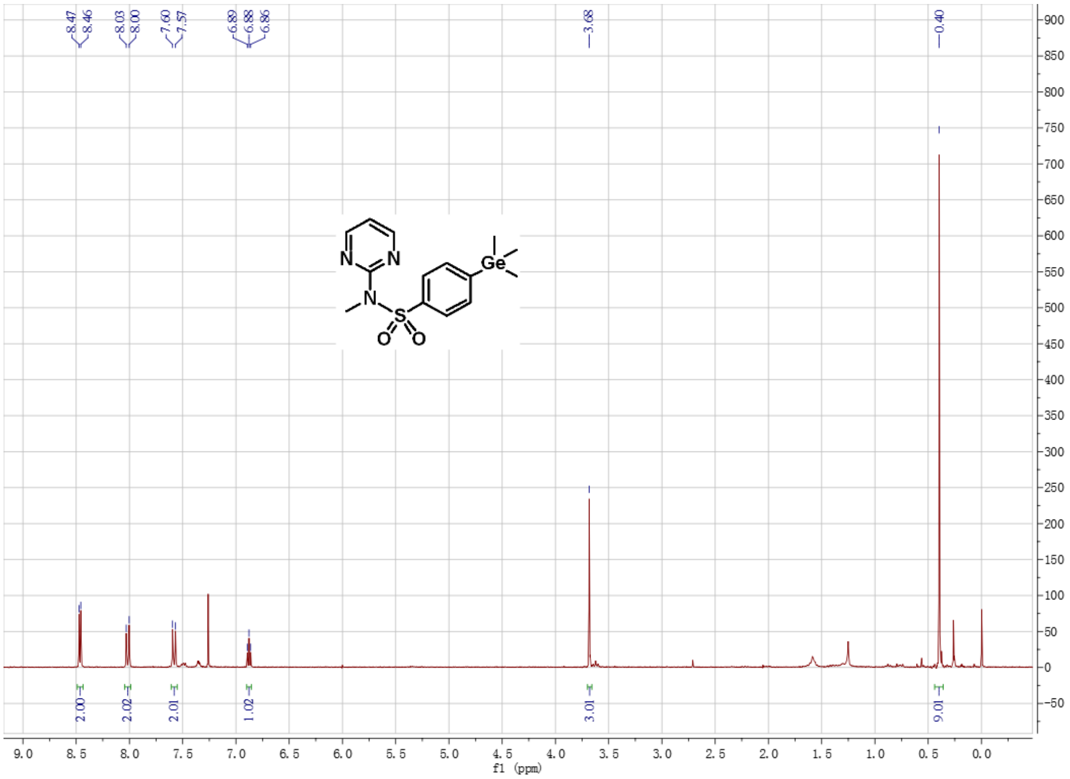
151.29
140.30
136.60
126.06
44.53
-9.45
Sn
S
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

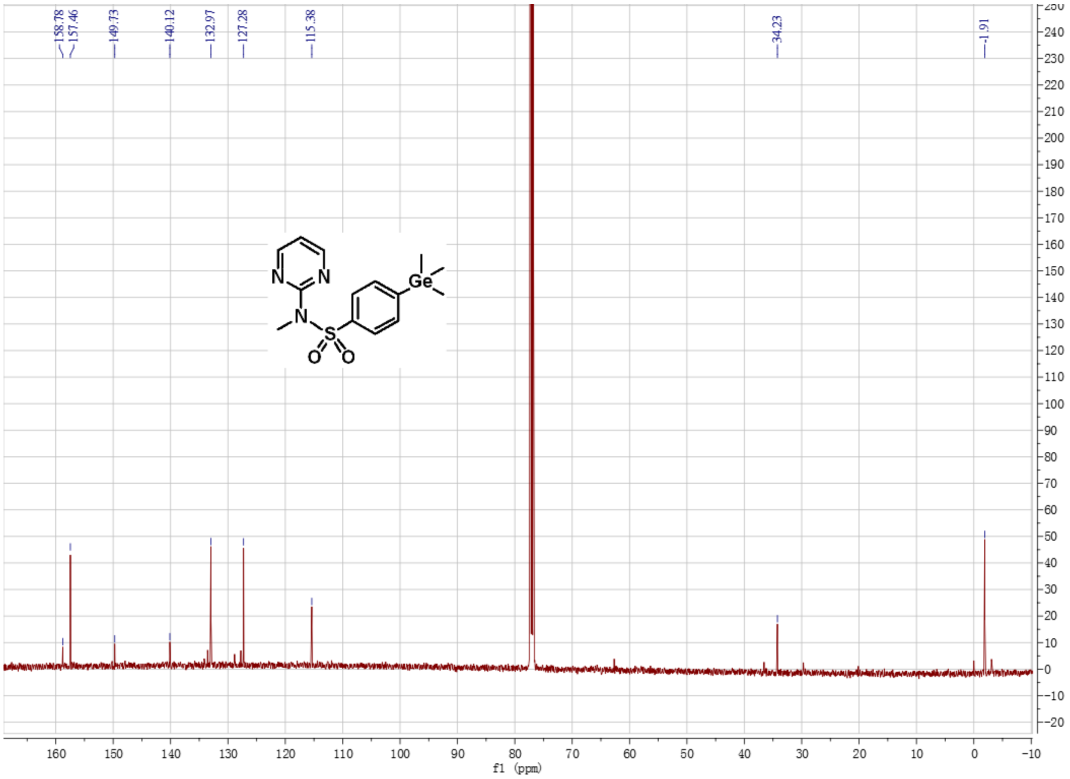
Compound **8**


7.47
7.46
7.45
7.44
7.44
7.35
7.34
7.34
7.33
7.33
0.39
0.15
Si
Ge
2.00
3.01
6.01
9.02
f1 (ppm)

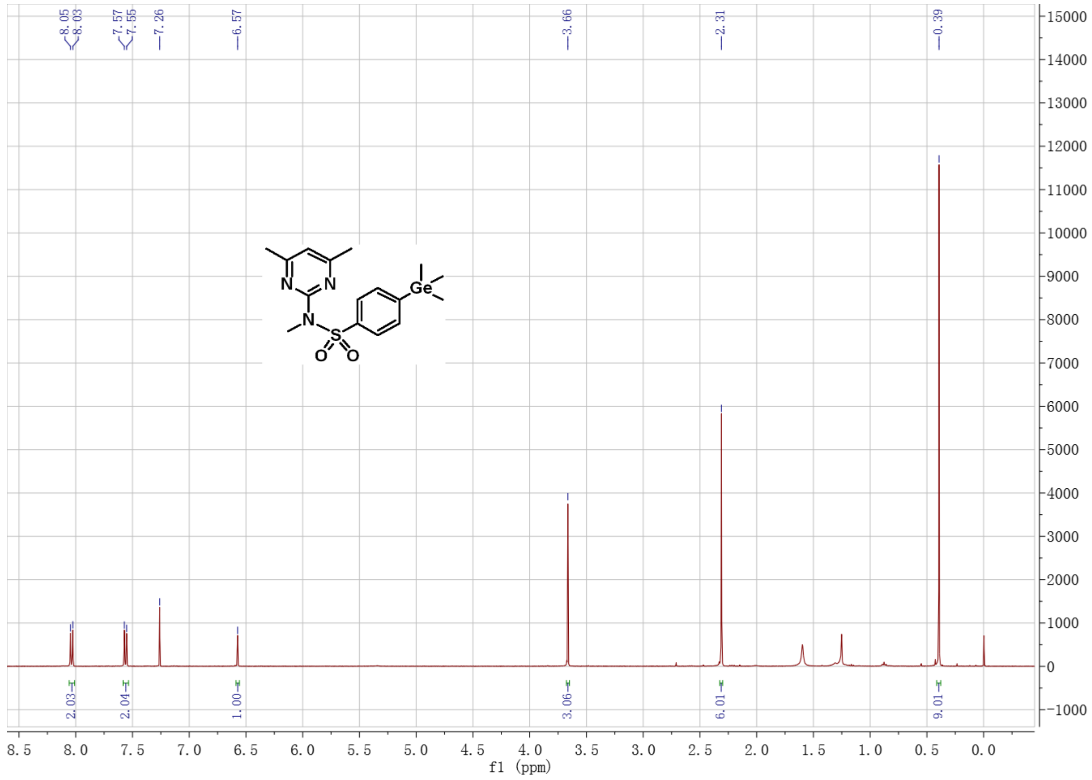

139.25
133.64
128.53
127.78
-3.09
-3.39
Si
Ge
f1 (ppm)

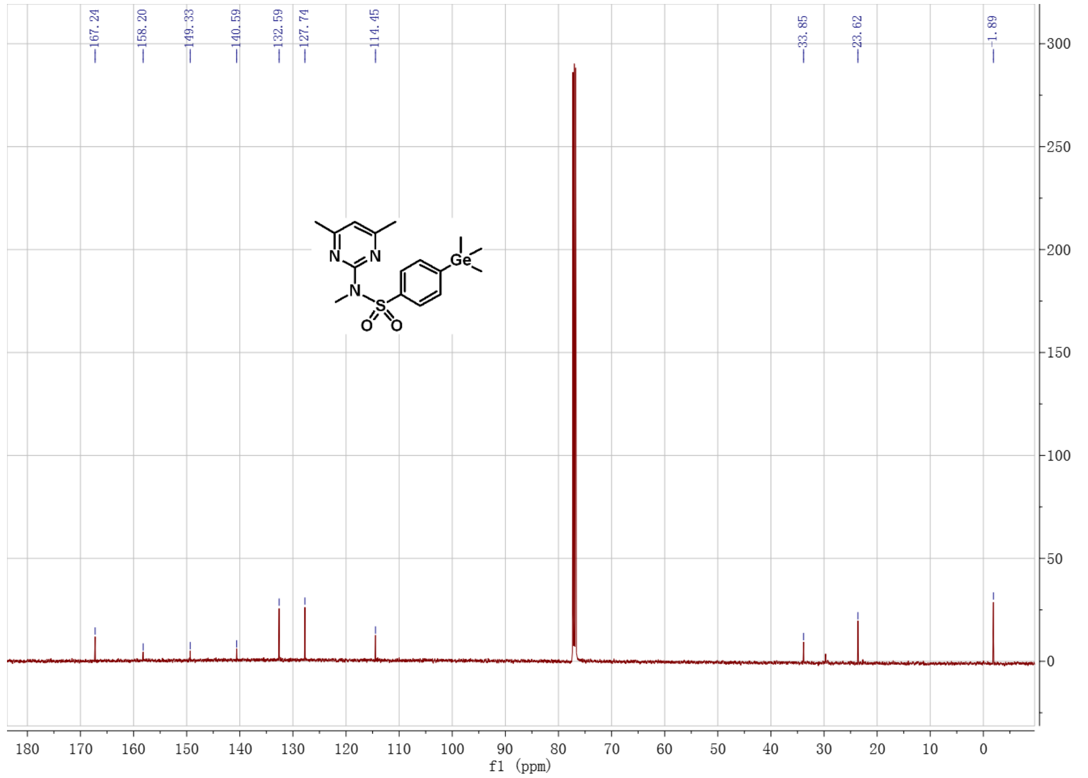
Compound **9a**


8.47
8.46
8.03
8.00
7.60
7.57
6.89
6.88
6.86
3.68
0.40
2.00
2.02
2.01
1.02
3.01
9.01
N
N
N
S
O
O
Ge
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)
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

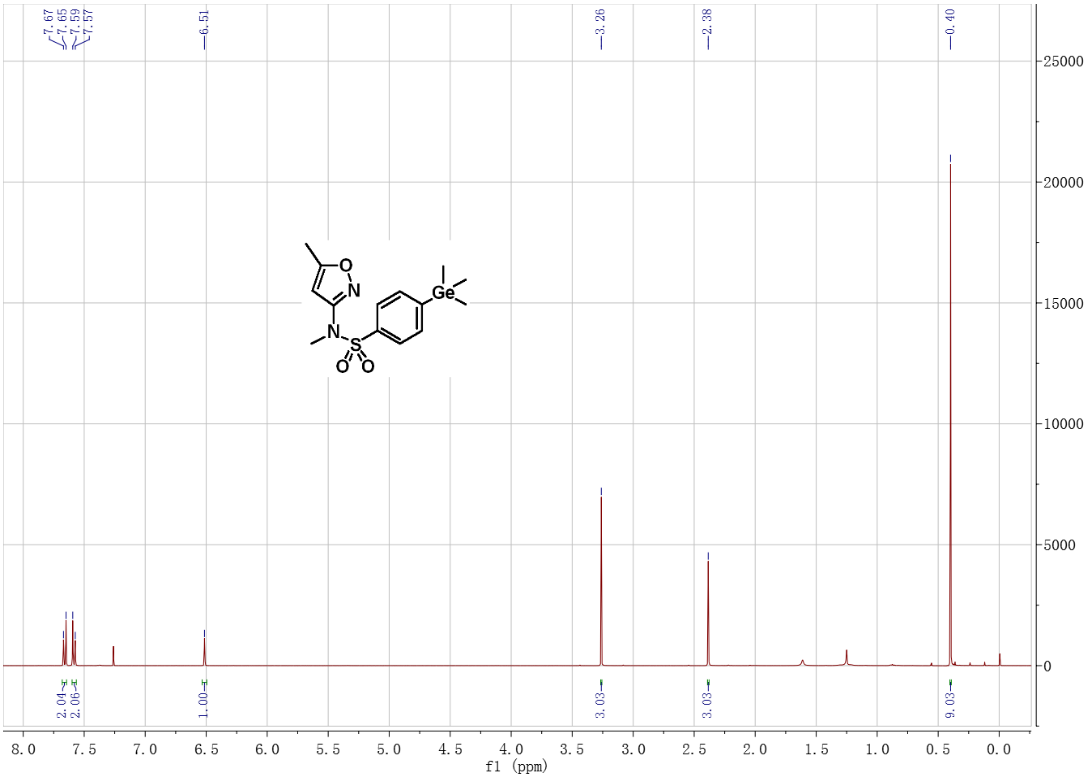

158.78
157.46
149.73
140.12
132.97
127.28
115.38
34.23
-1.91
N
N
N
S
O
O
Ge
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

Compound **9c**

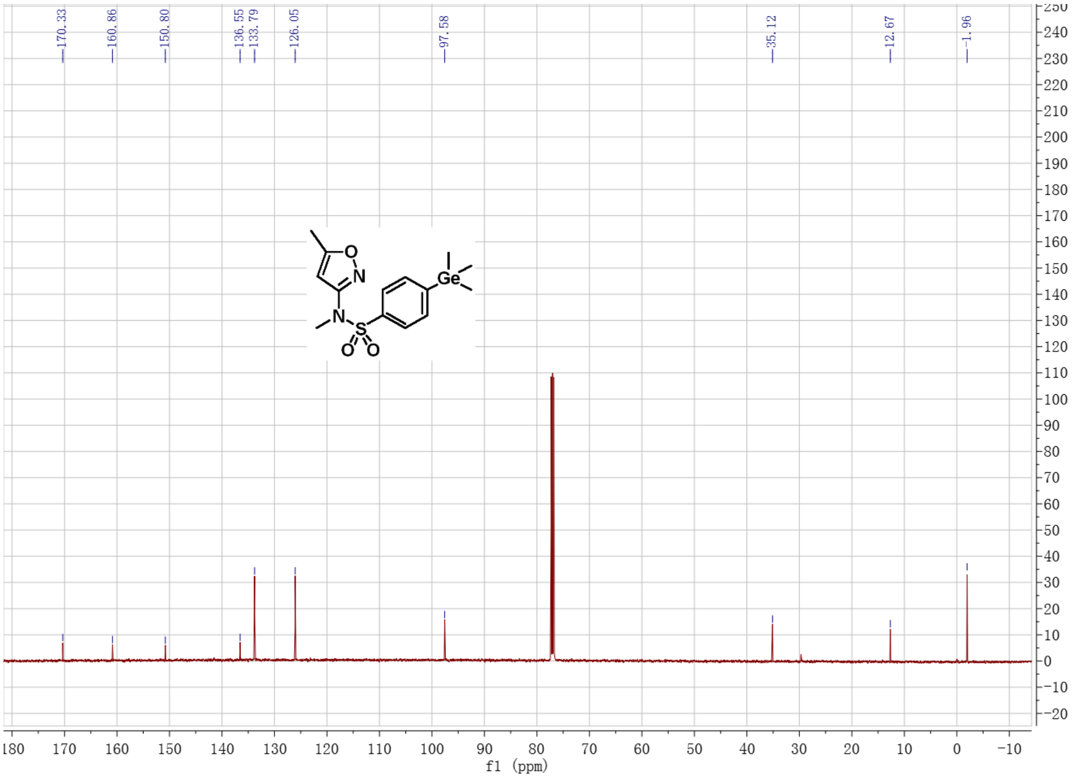

8.05
8.03
7.57
7.55
7.26
6.57
3.66
2.31
0.39
2.03
2.04
1.00
3.06
6.01
9.01
N
N
N
S
O
O
Ge
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.24
158.20
149.33
140.59
132.59
127.74
114.45
33.85
23.62
−1.89
N
N
N
S
O
O
Ge
300
250
200
150
100
50
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound **9b**

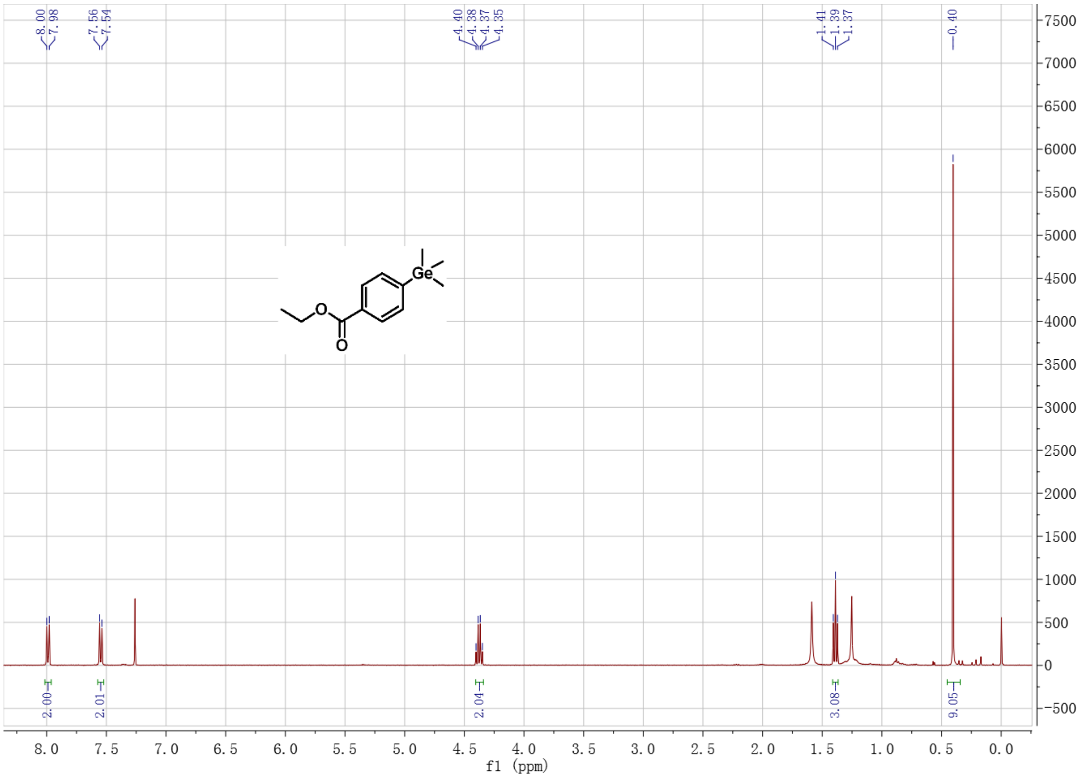


7.67
7.65
7.59
7.57
6.51
3.26
2.38
0.40
2.04
2.06
1.00
3.03
3.03
9.03
O
N
N
S
O
O
Ge
25000
20000
15000
10000
5000
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

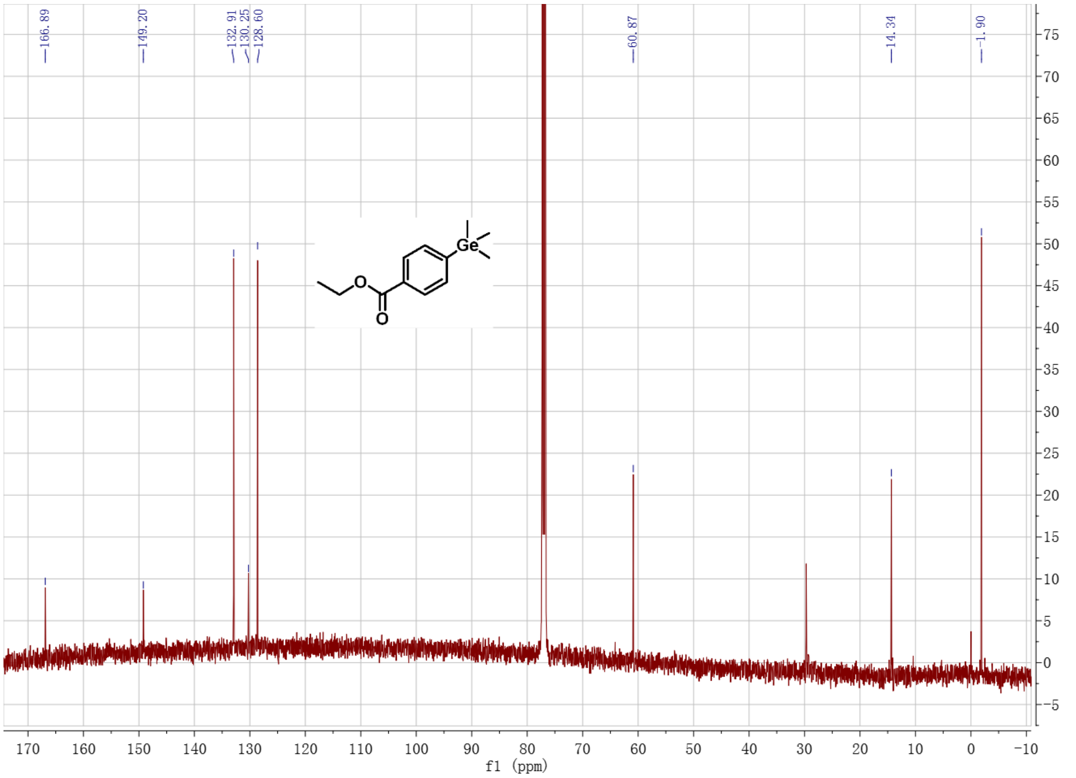


170.33
160.86
150.80
136.55
133.79
126.05
97.58
35.12
12.67
-1.96
O
N
N
S
O
O
Ge
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound **9e**

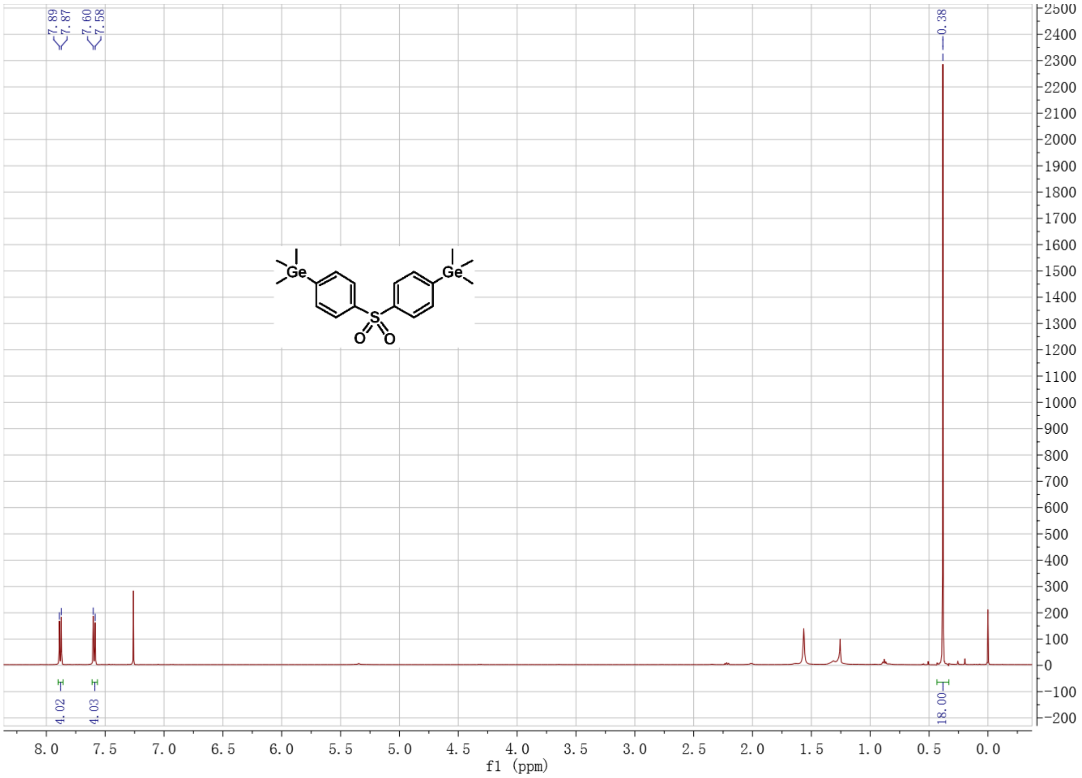


8.00
7.98
7.56
7.54
4.40
4.38
4.37
4.35
1.41
1.39
1.37
0.40
Ge
O
O
2.00
2.01
2.04
3.08
9.05
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

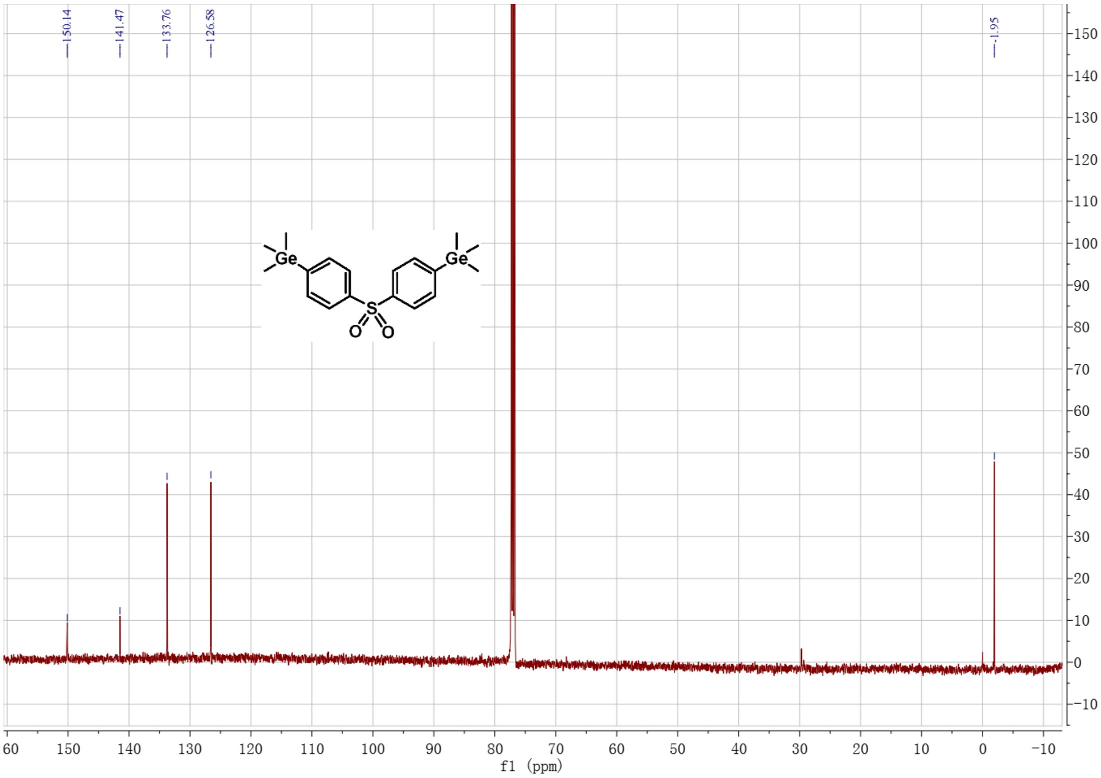


166.89
149.20
132.91
130.25
128.60
60.87
14.34
−1.90
Ge
O
O
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Compound **9d**

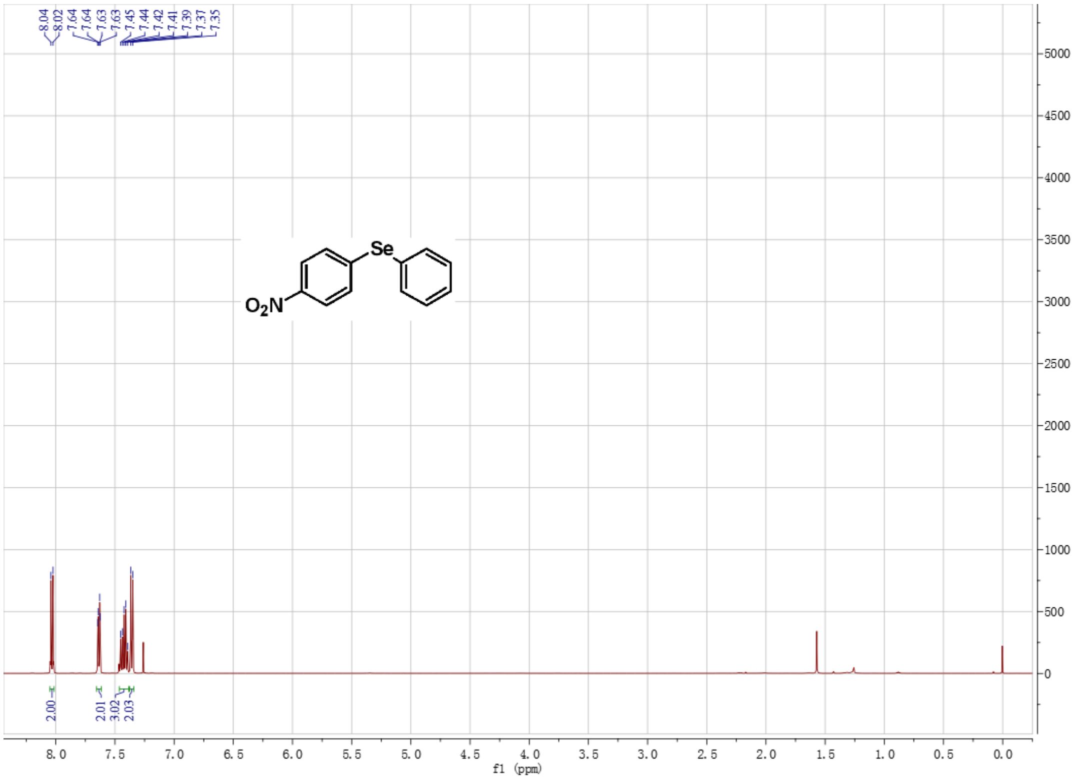


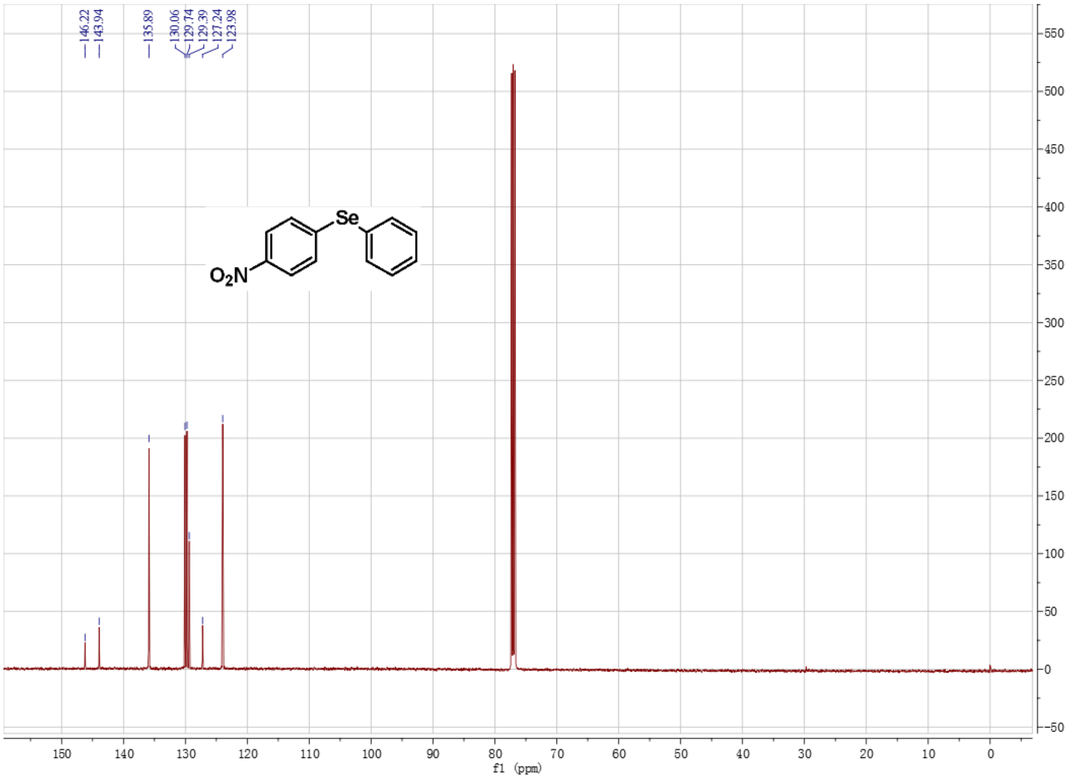
7.89
7.87
7.60
7.58
0.38
4.02
4.03
18.00
Ge
Ge
S
O
O
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



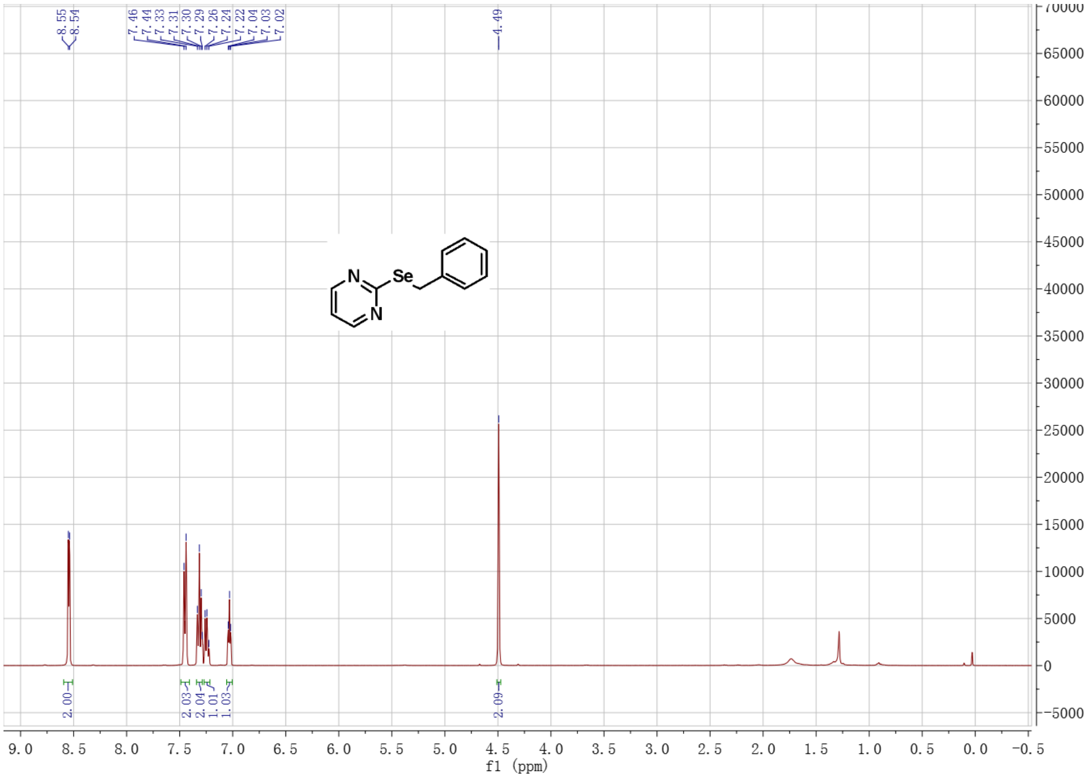
150.14
141.47
133.76
126.58
-1.95
Ge
Ge
S
O
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

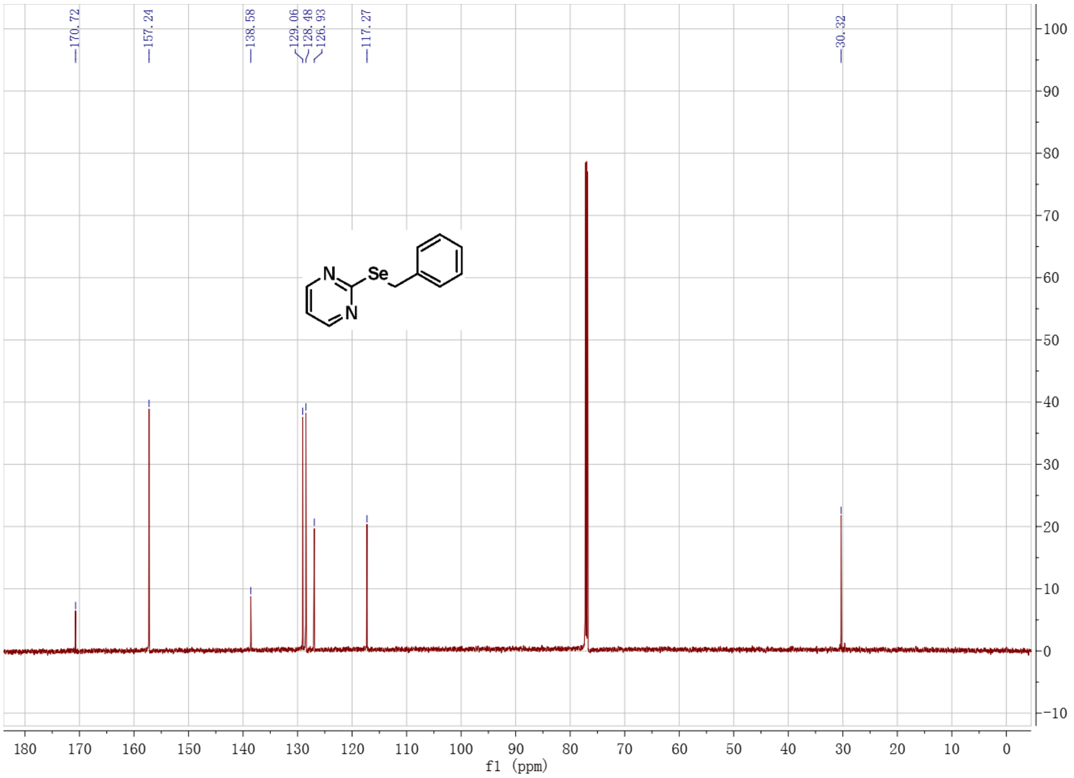
Compound **11a**



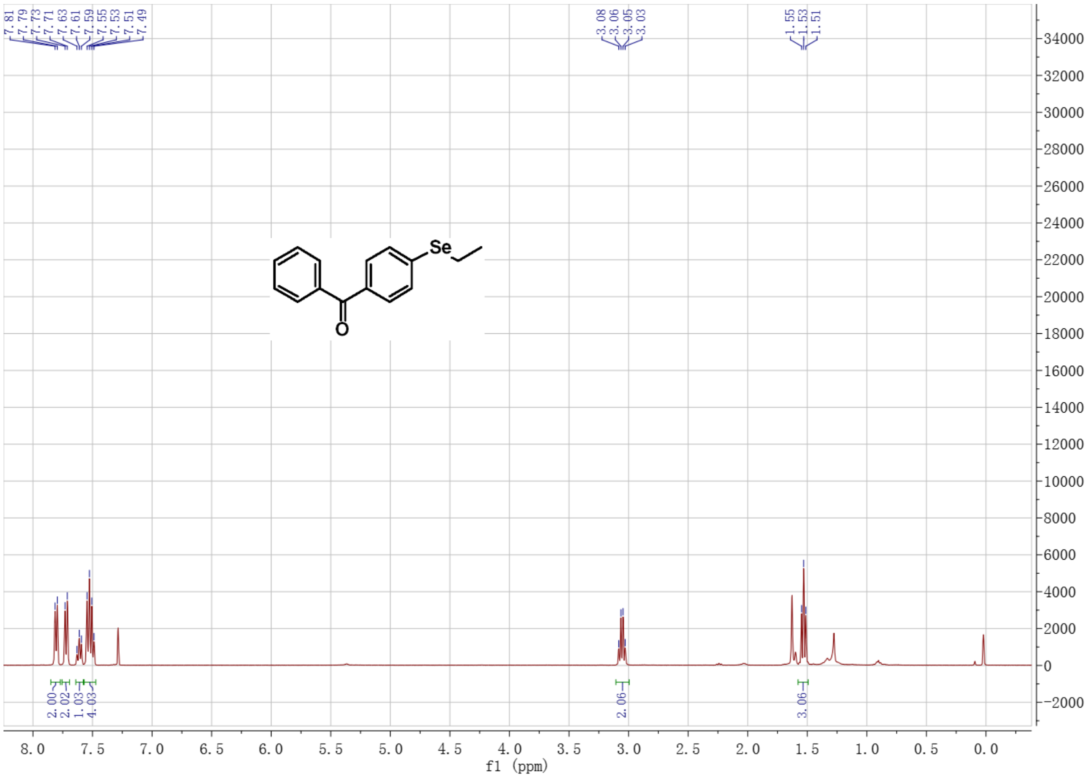


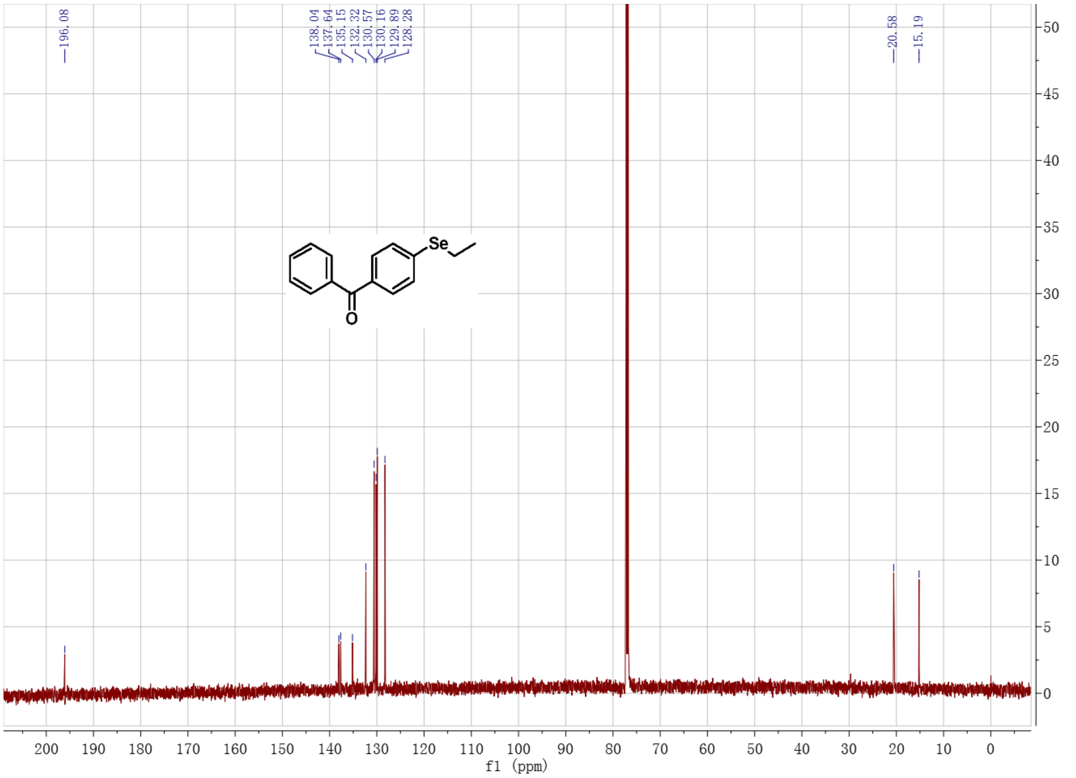
Compound **11d**



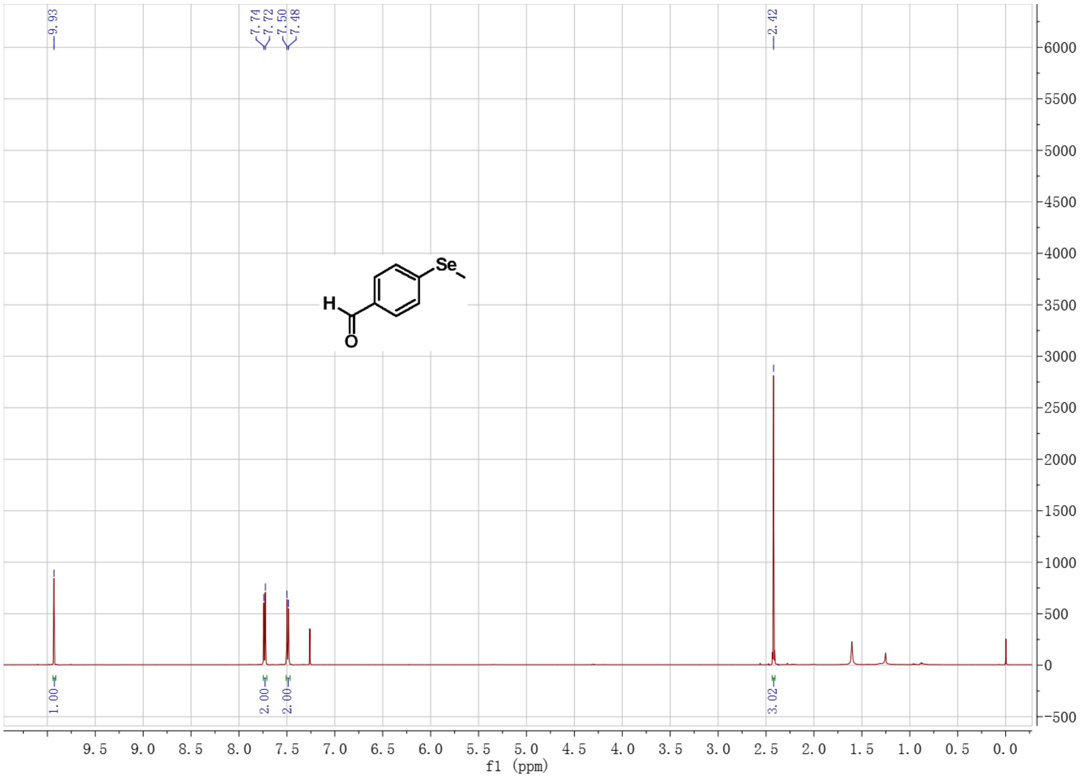


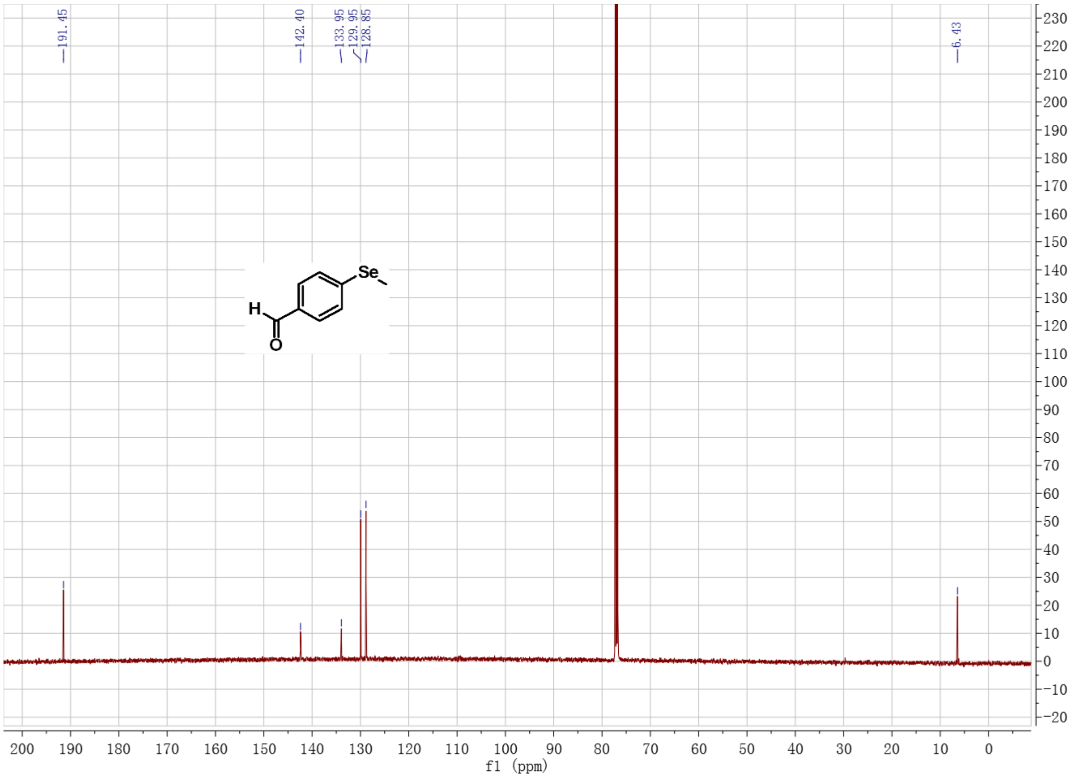
Compound **11b**



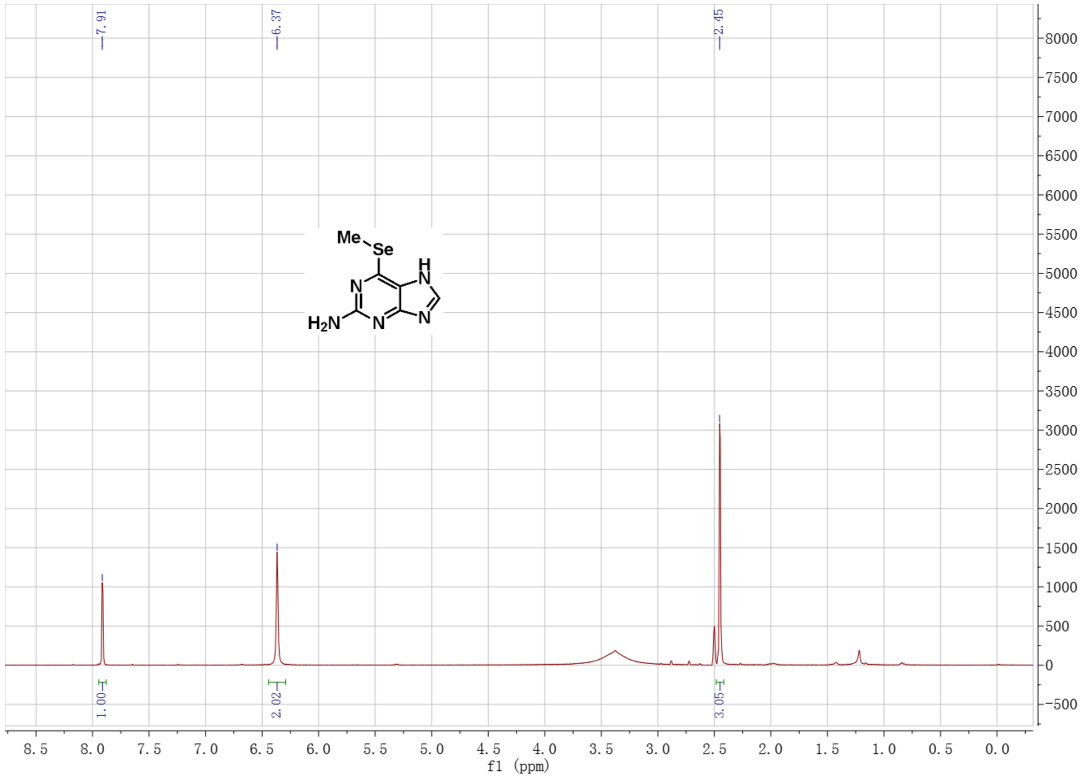


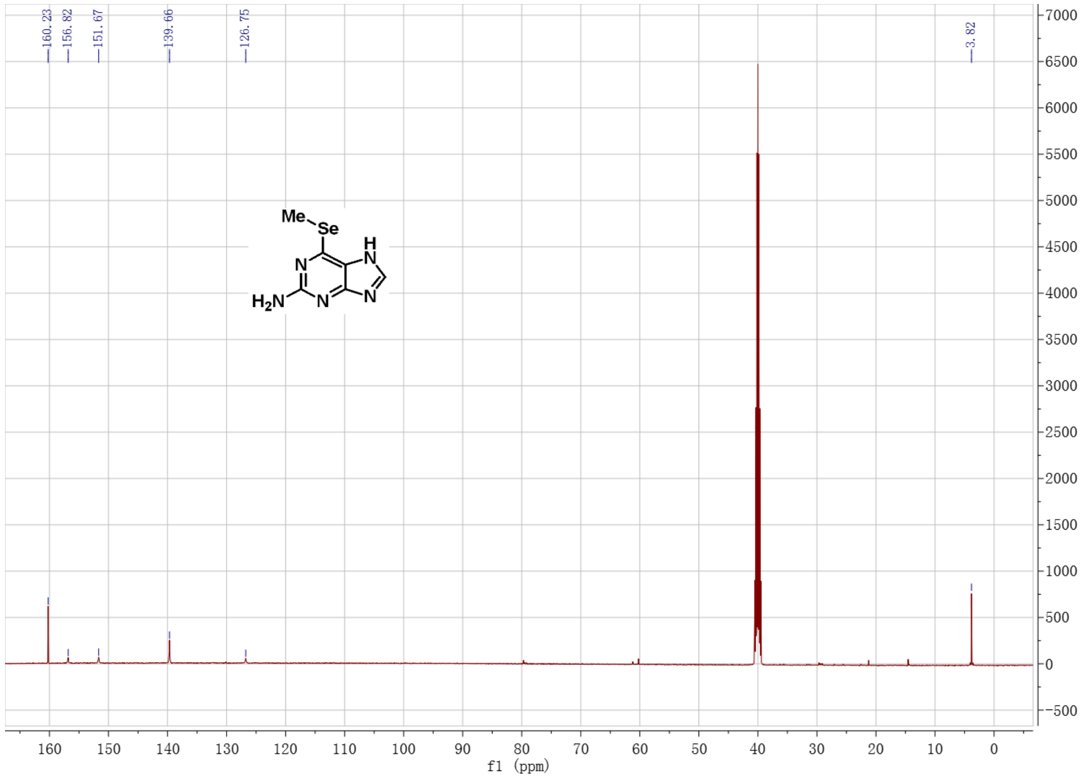
Compound **11c**



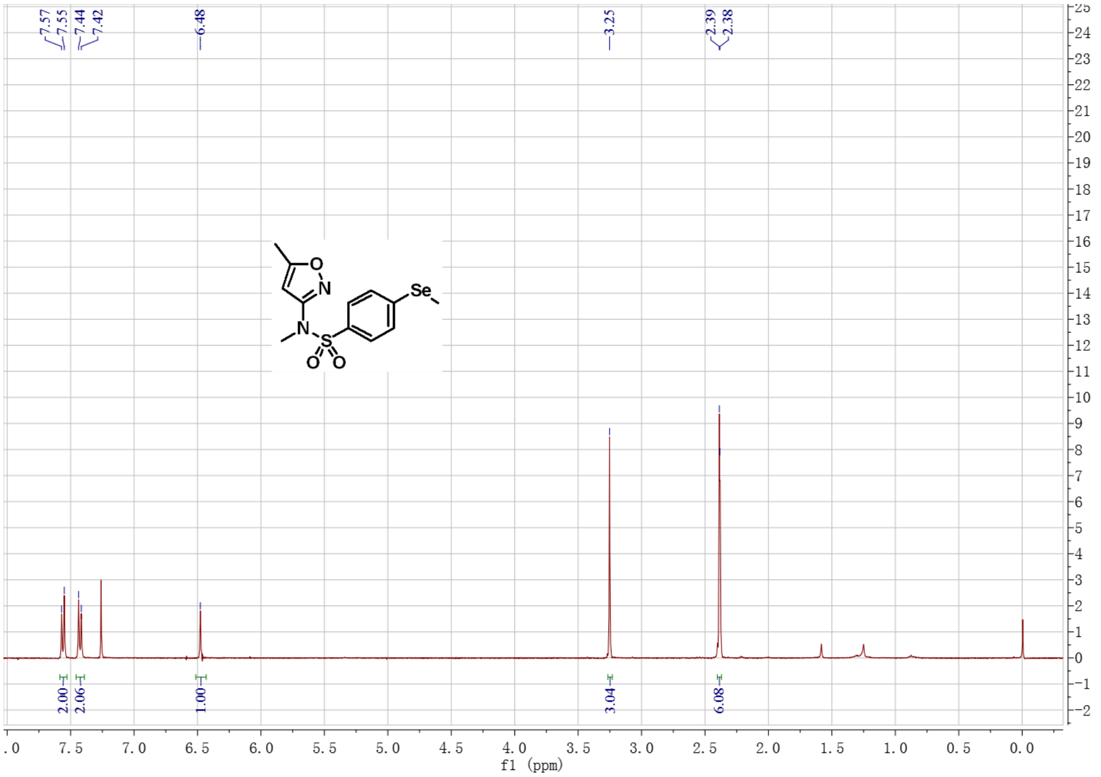


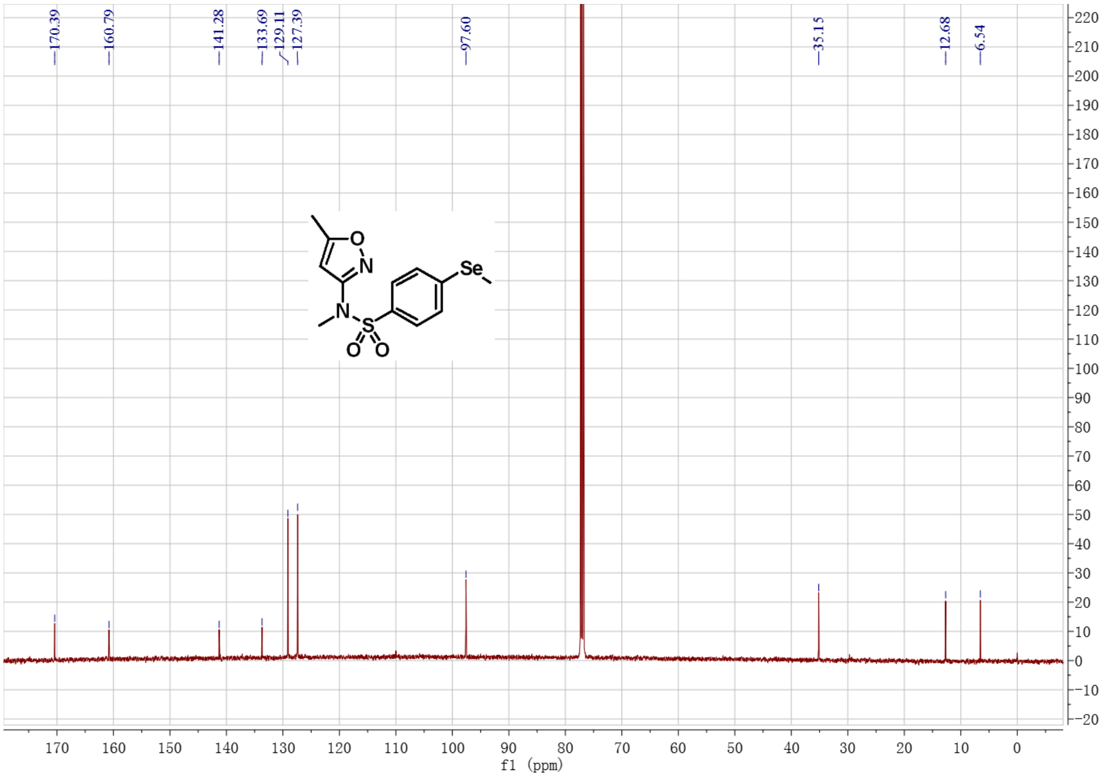
Compound **11e**



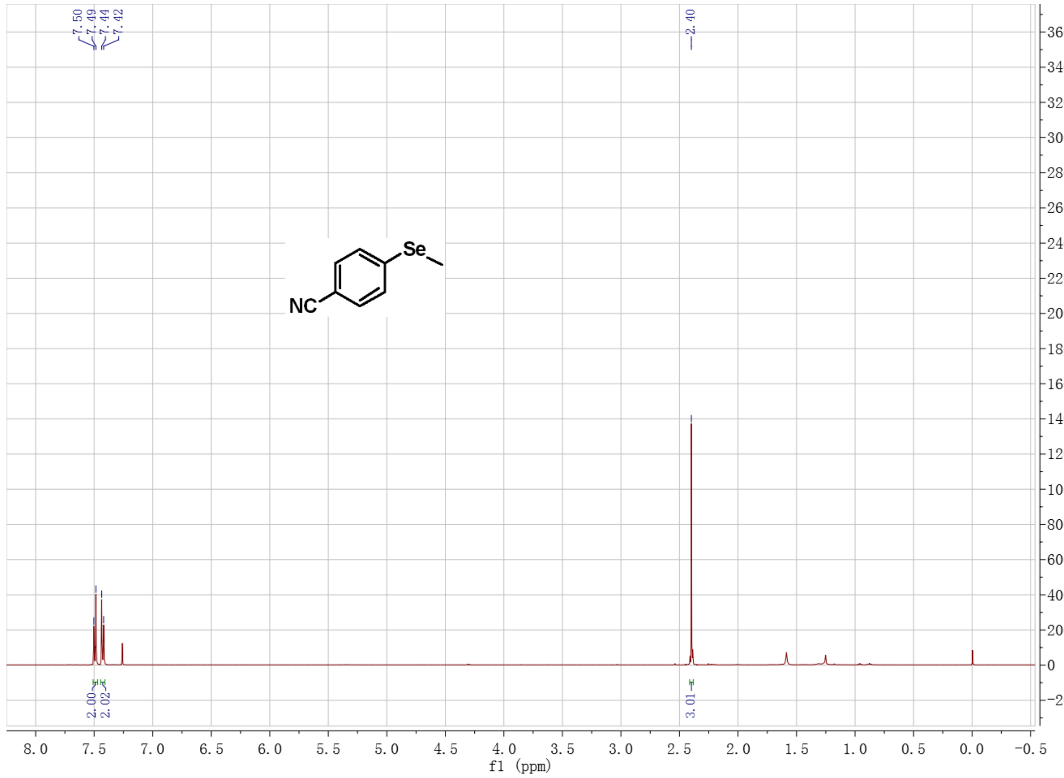


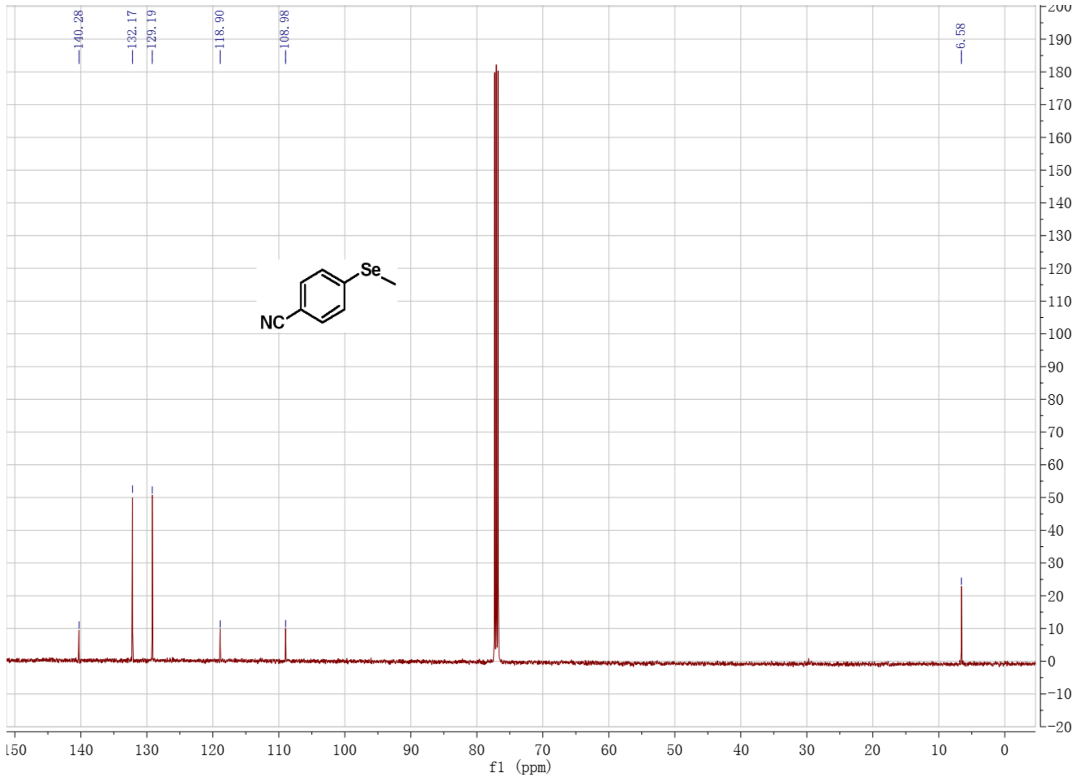
Compound **11f**



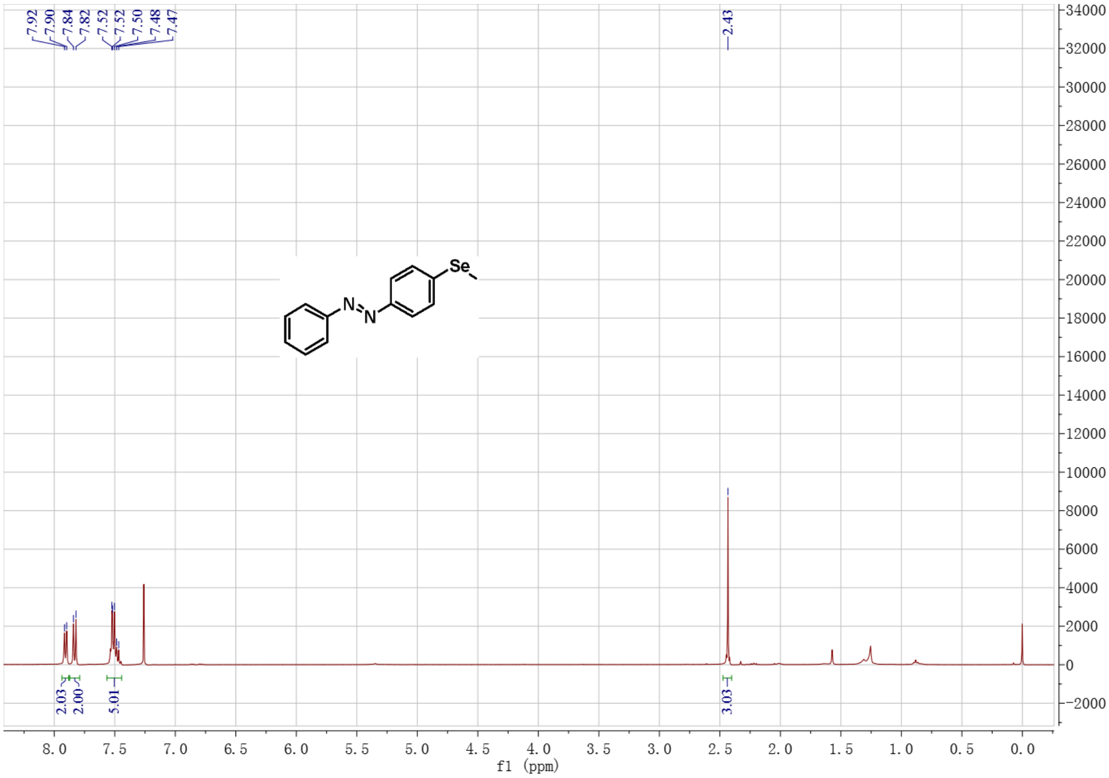


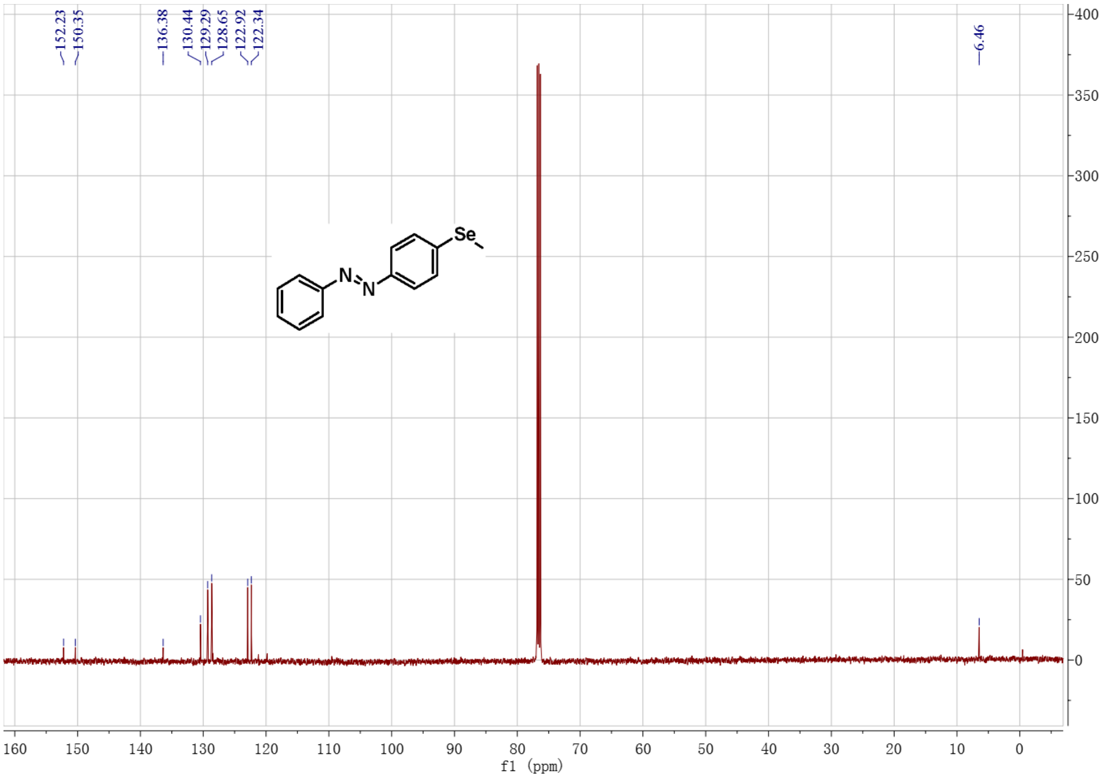
Compound **11g**



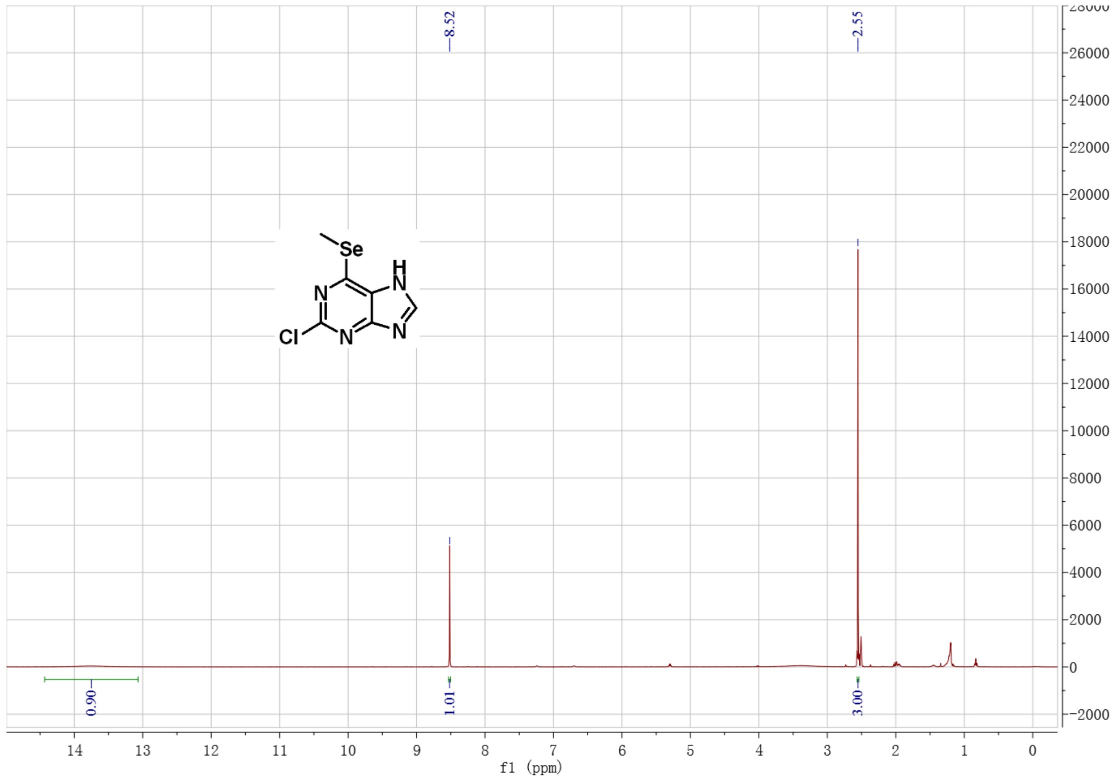


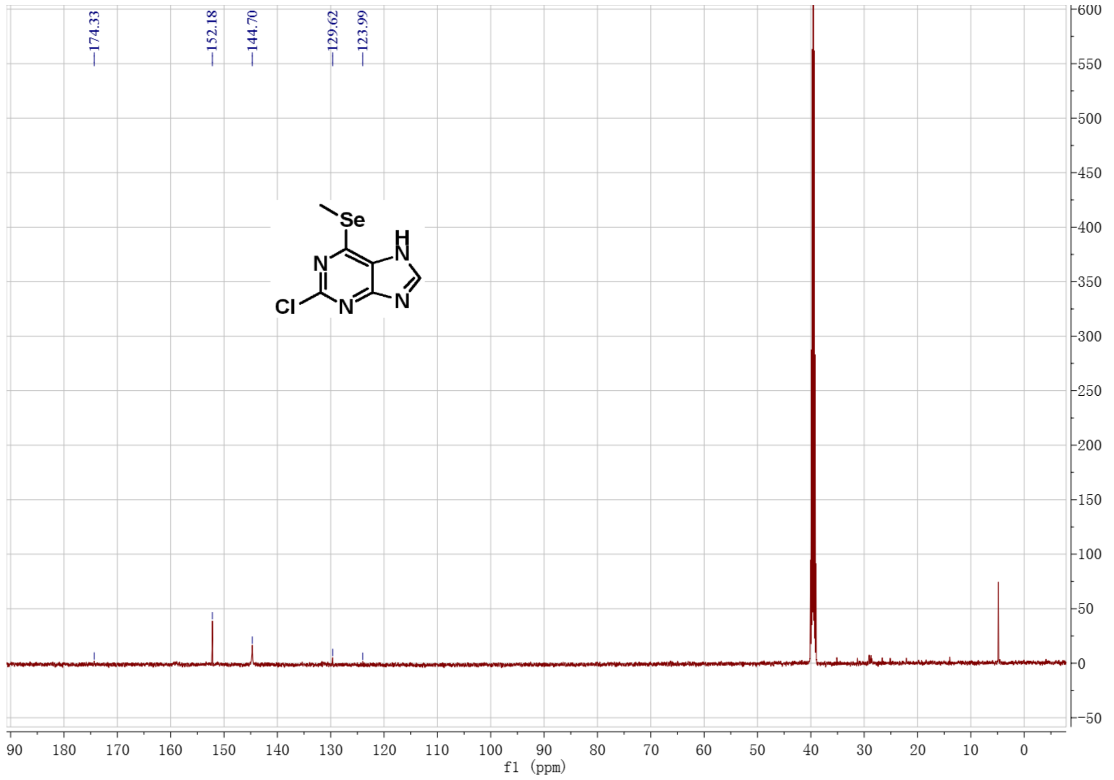
Compound **11h**



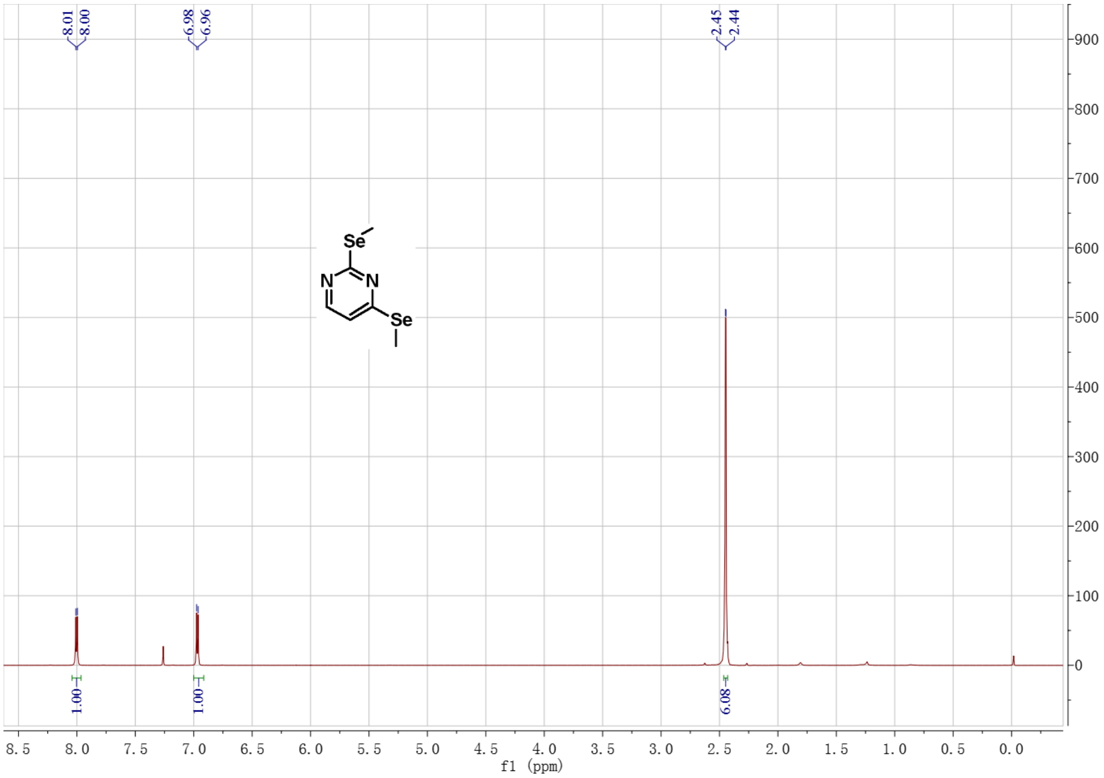


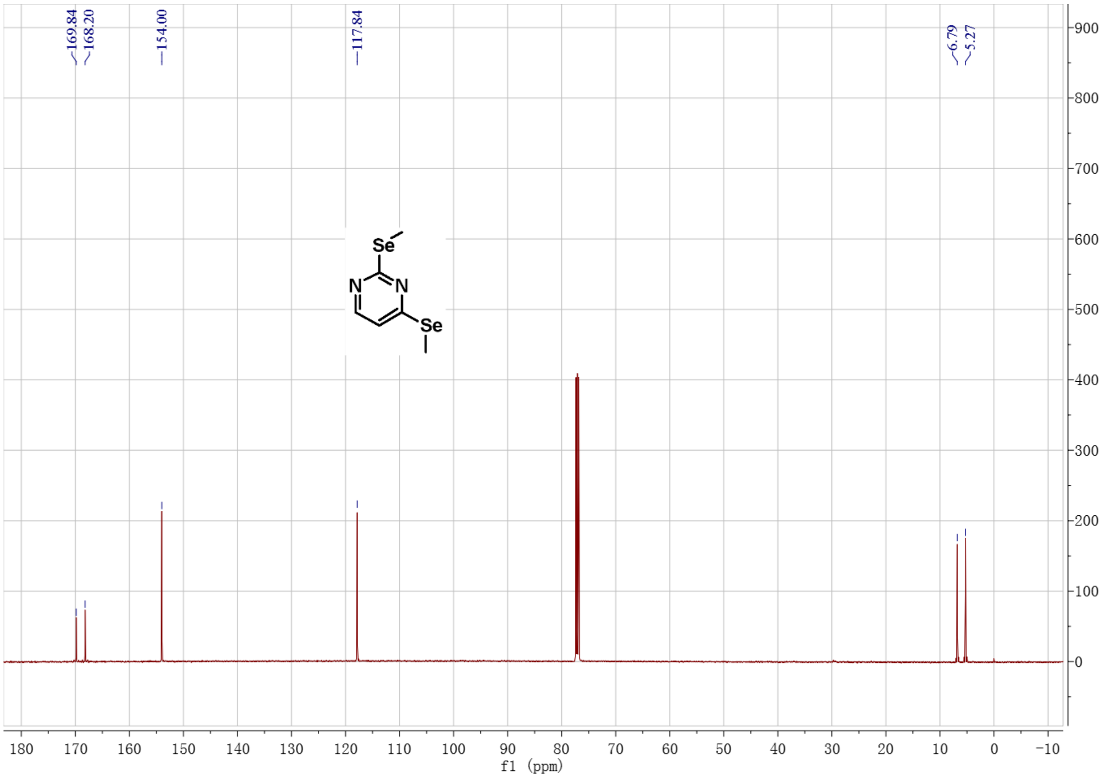
Compound **11i**



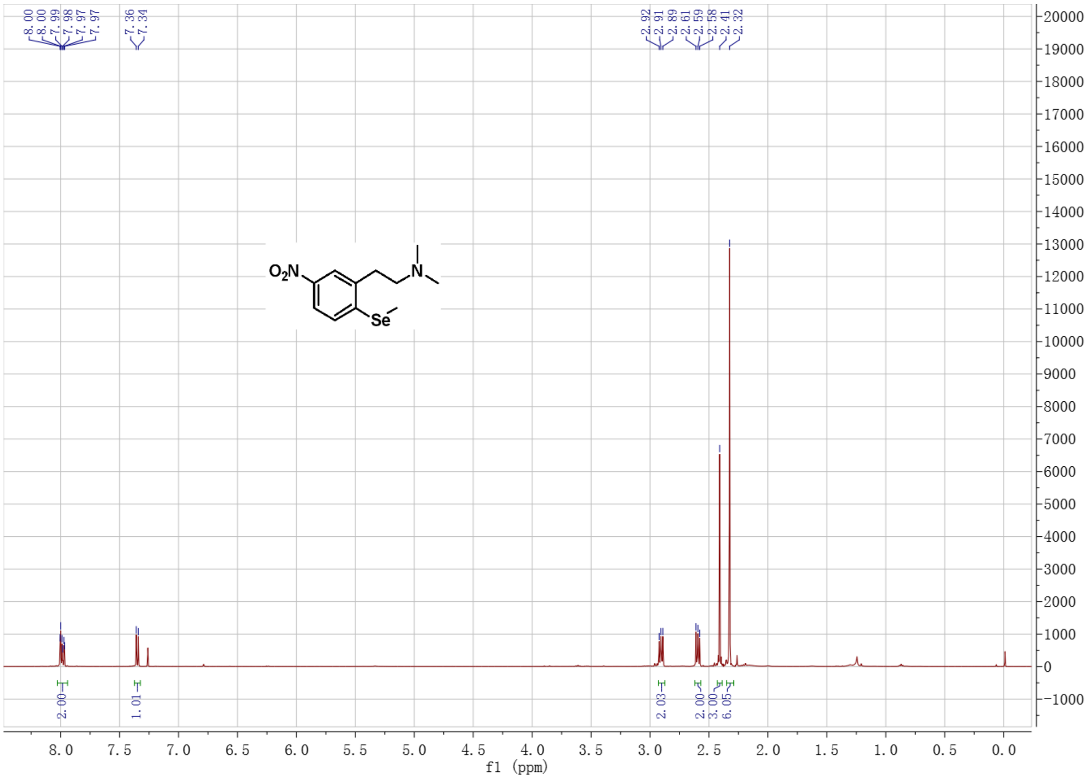


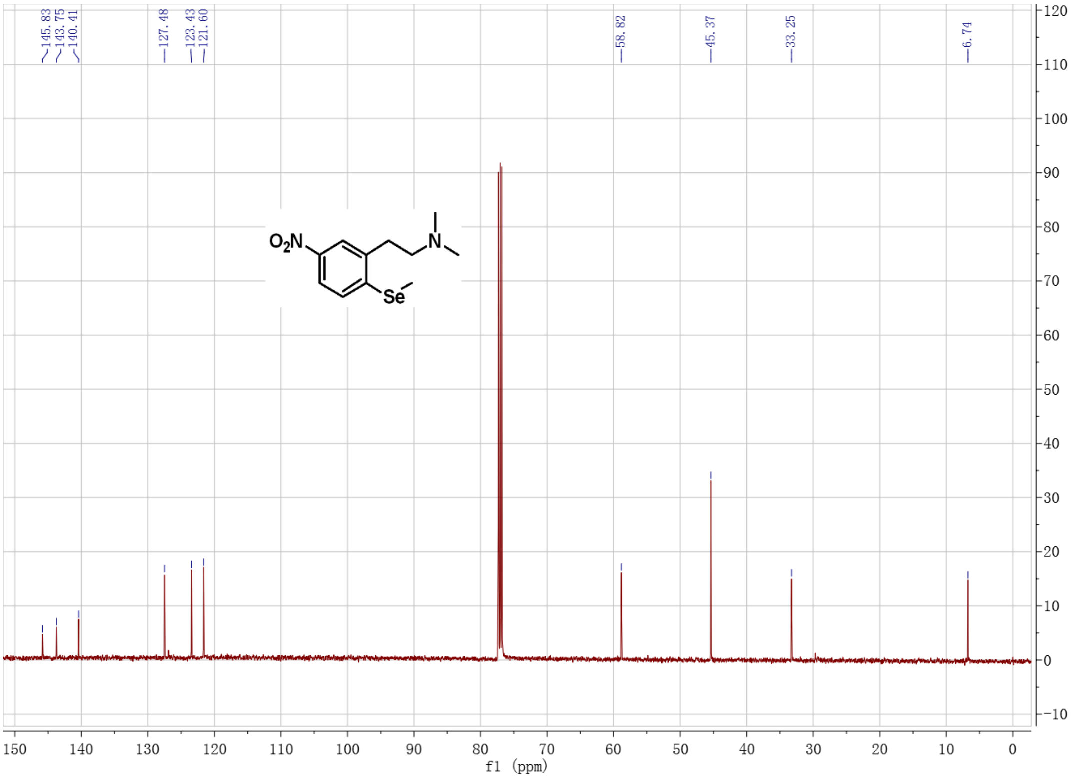
Compound **11j**



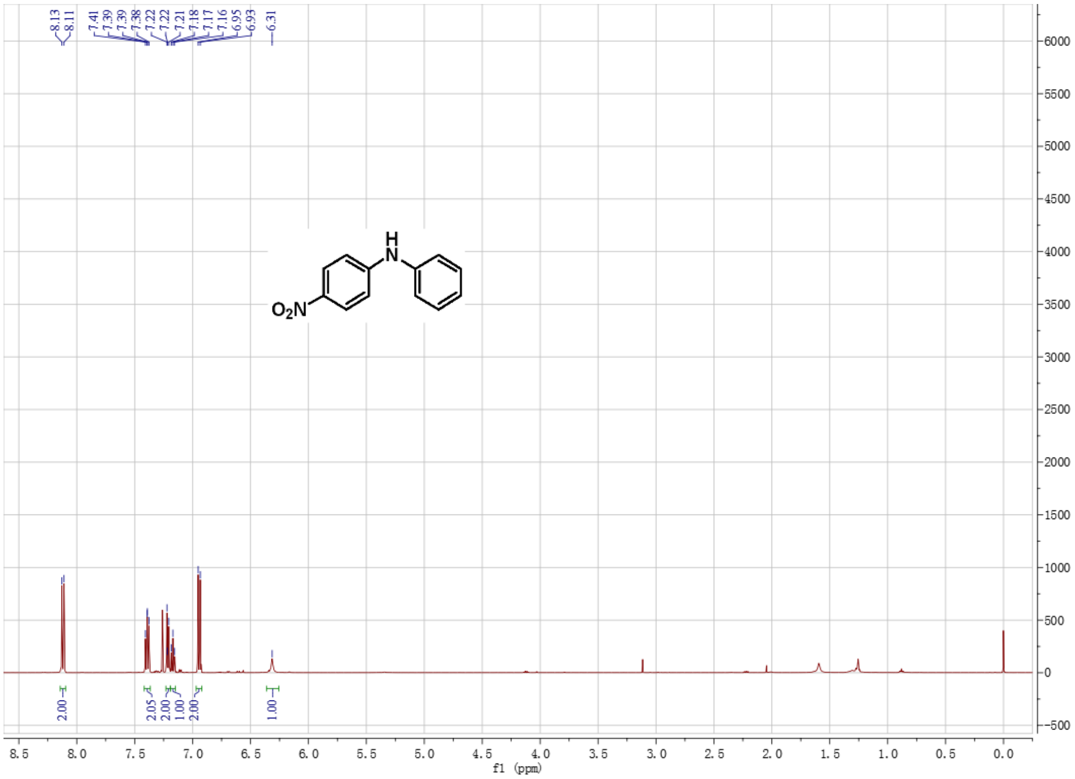


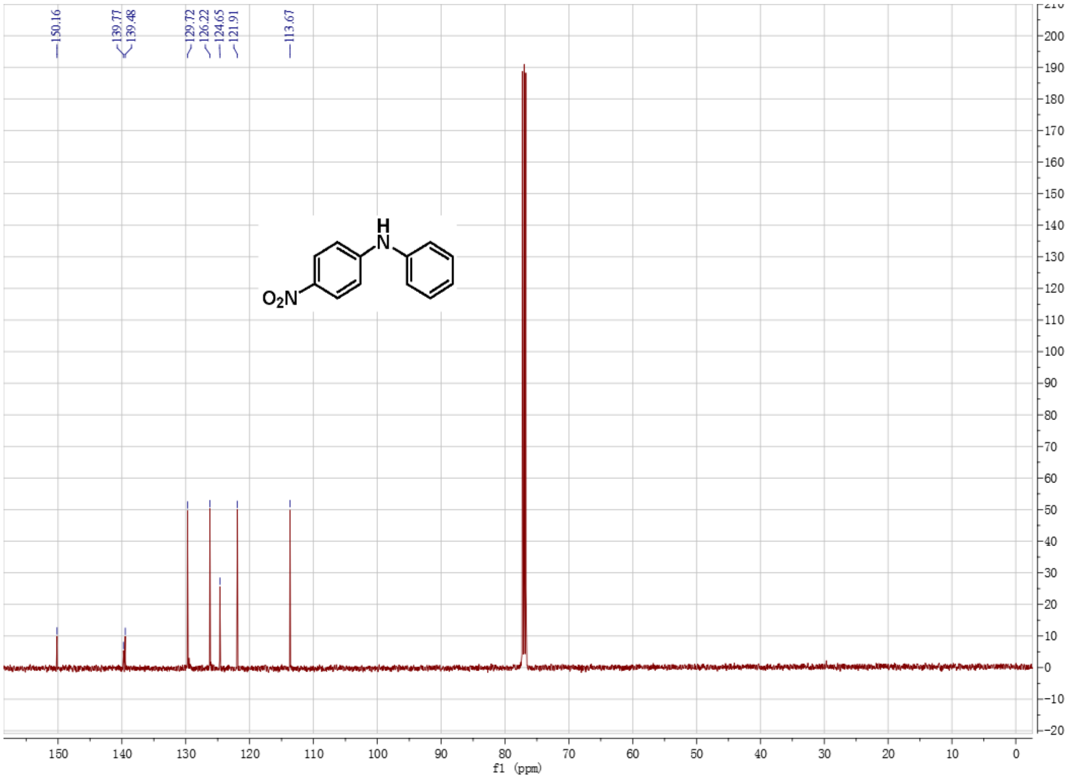
Compound **11k**



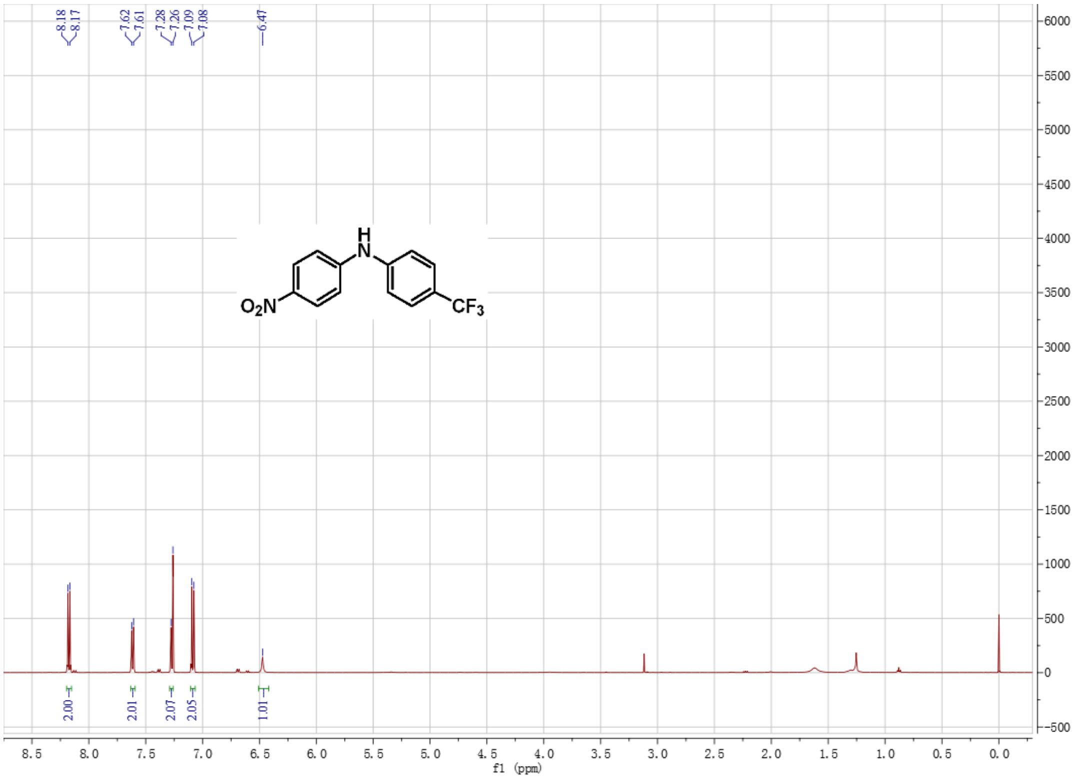


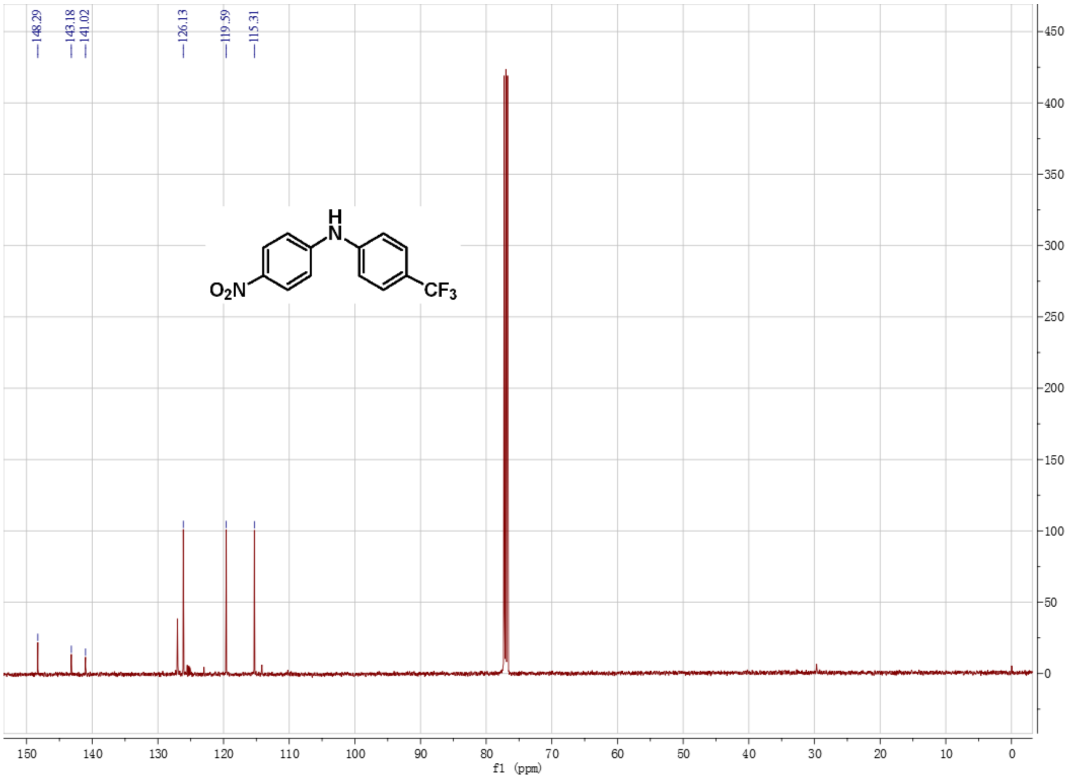
Compound **13a**



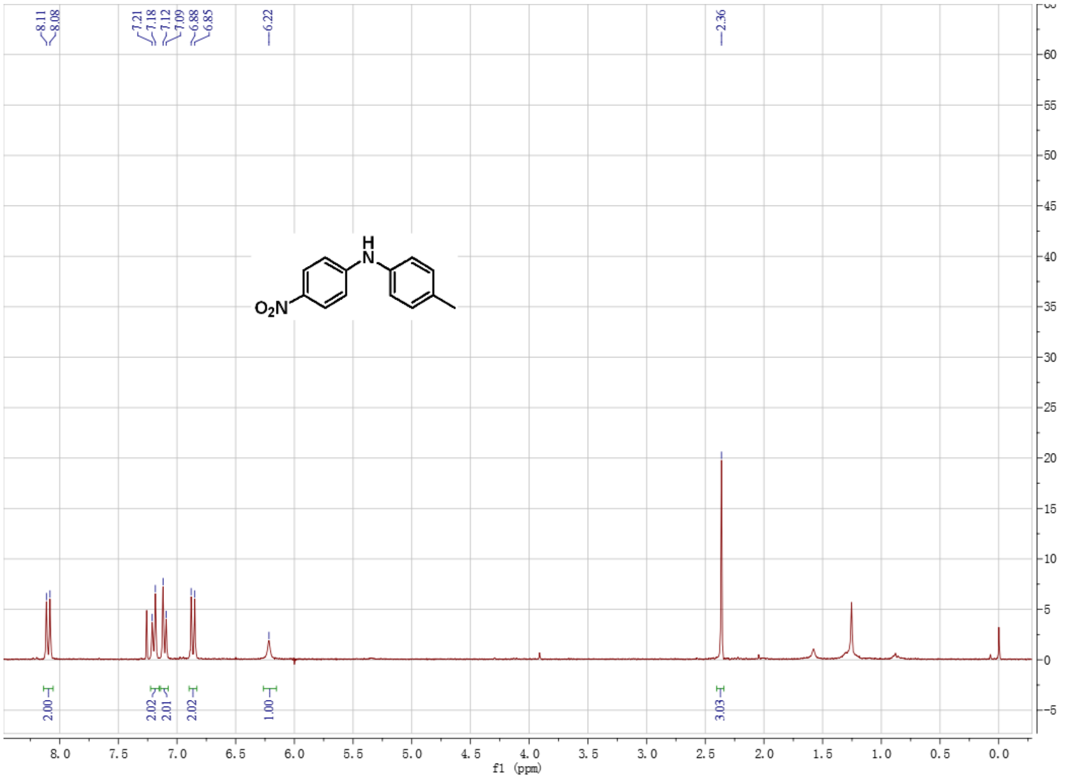


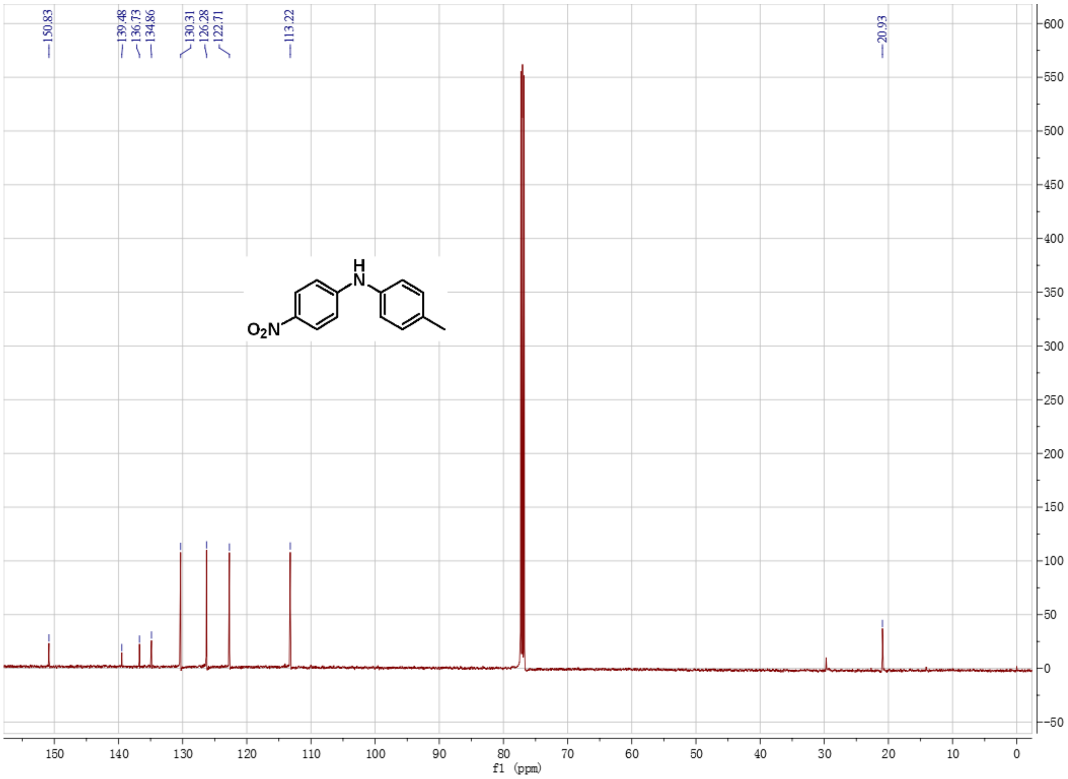
Compound **13b**



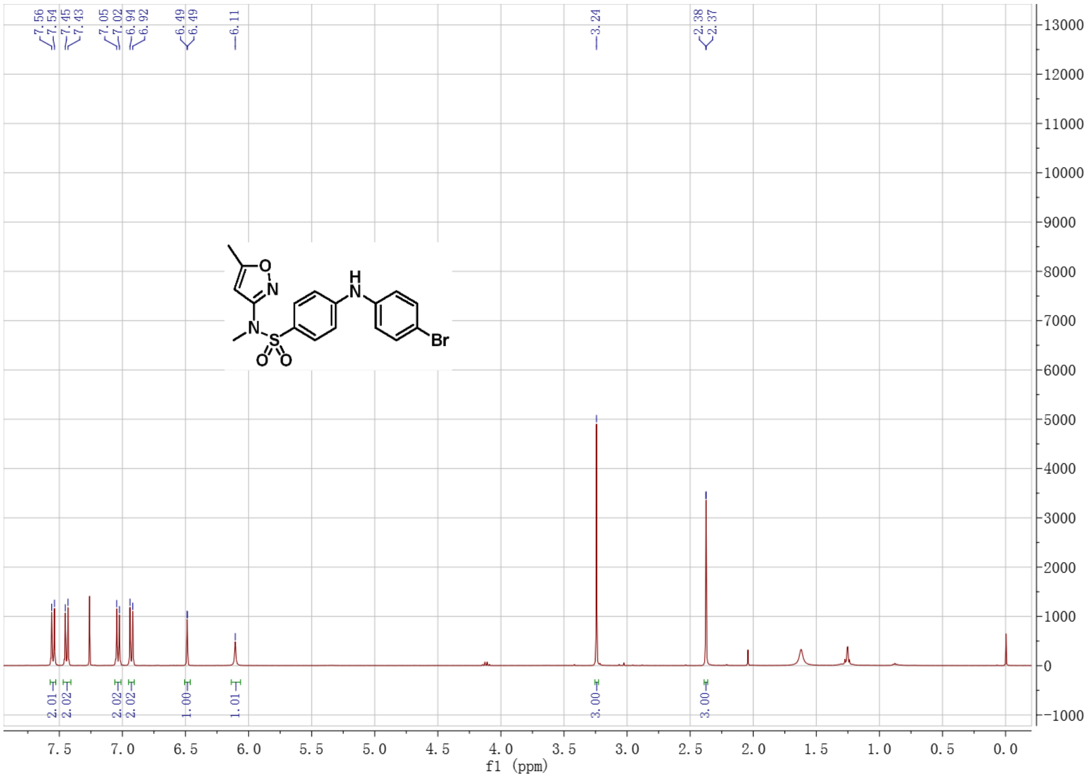


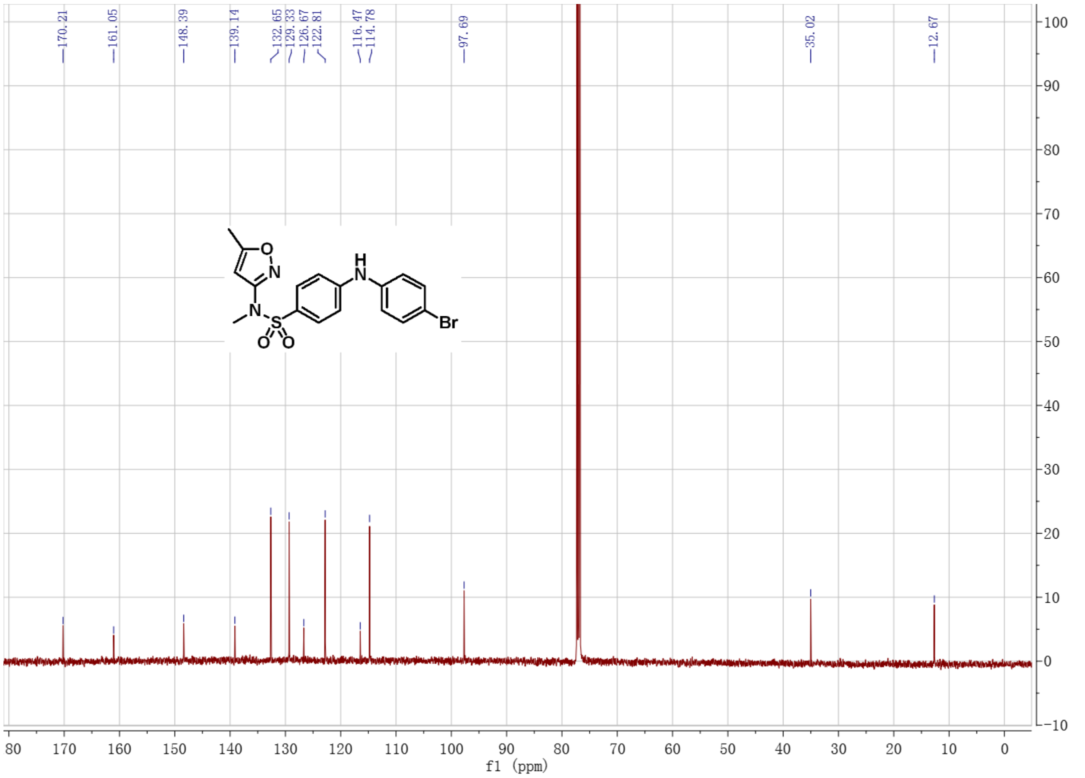
Compound **13c**



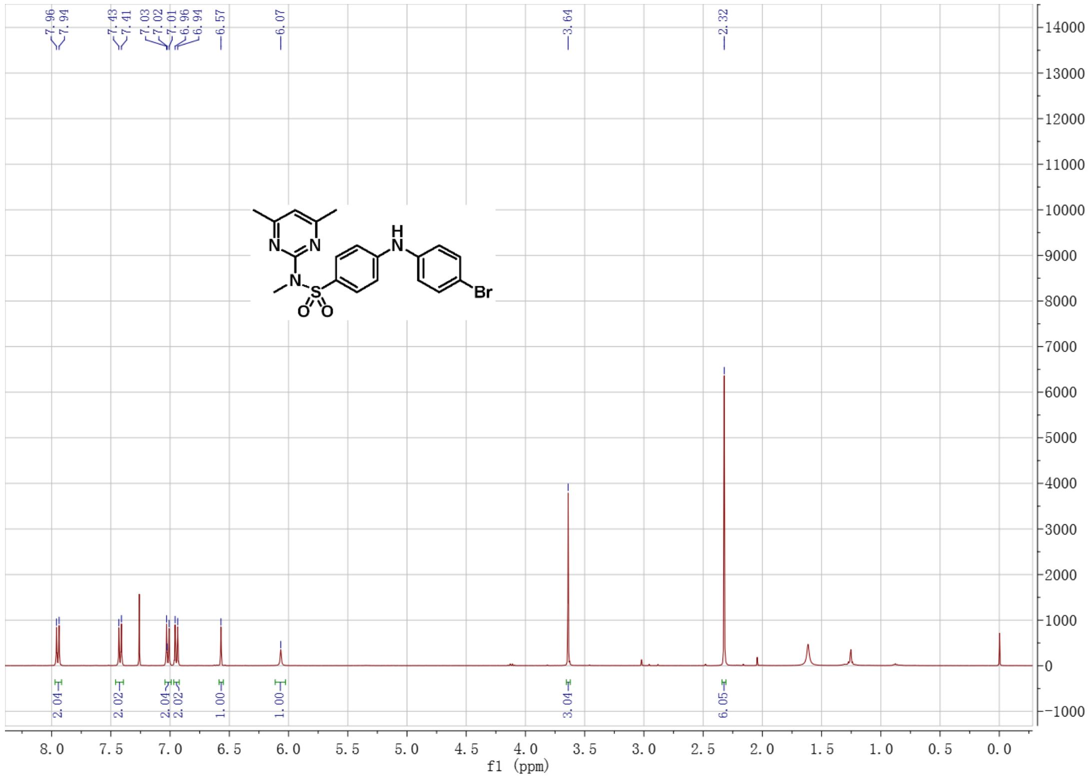


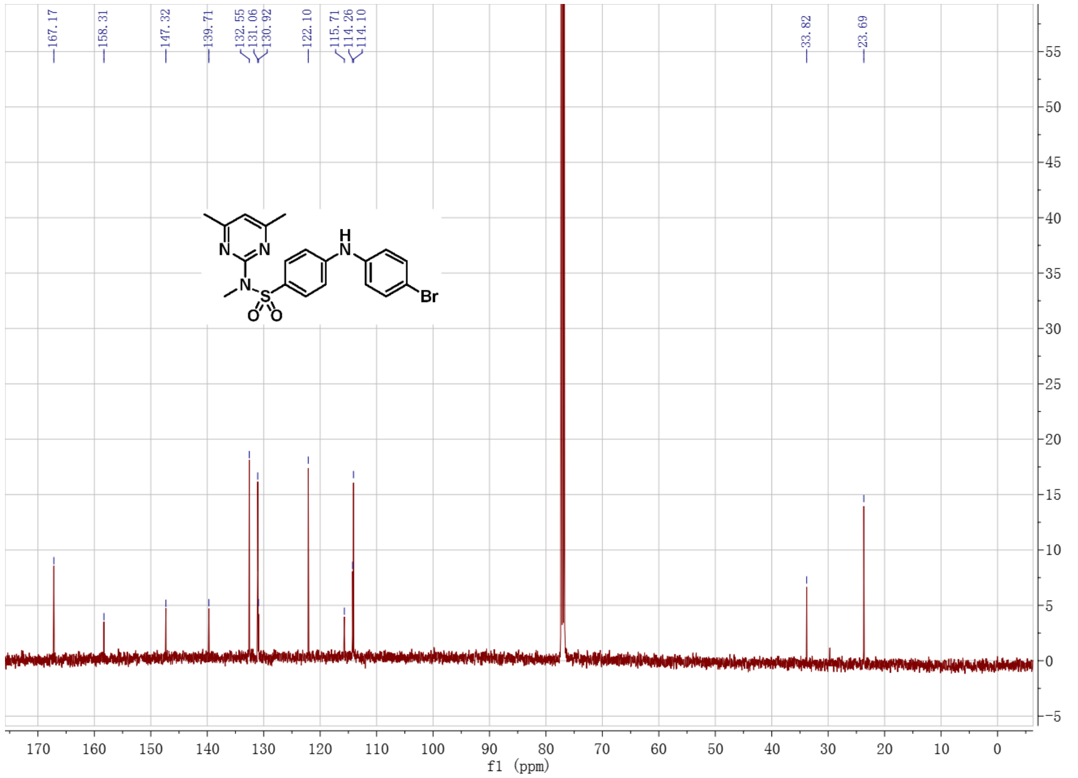
Compound **13e**



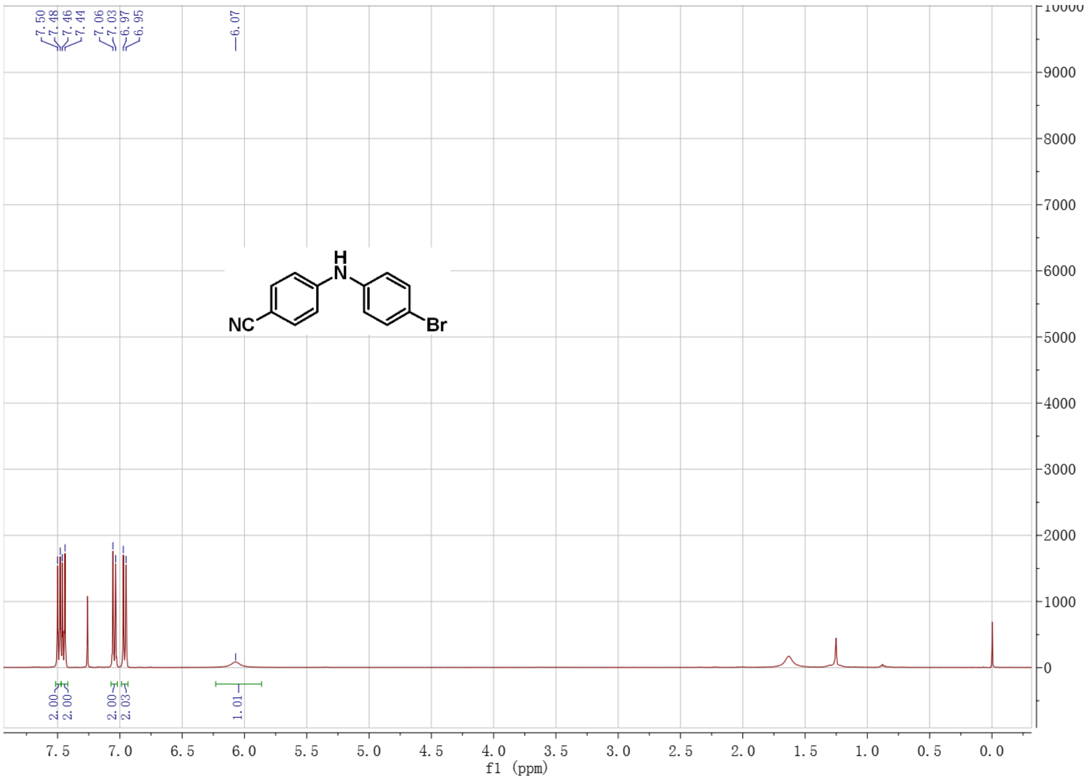


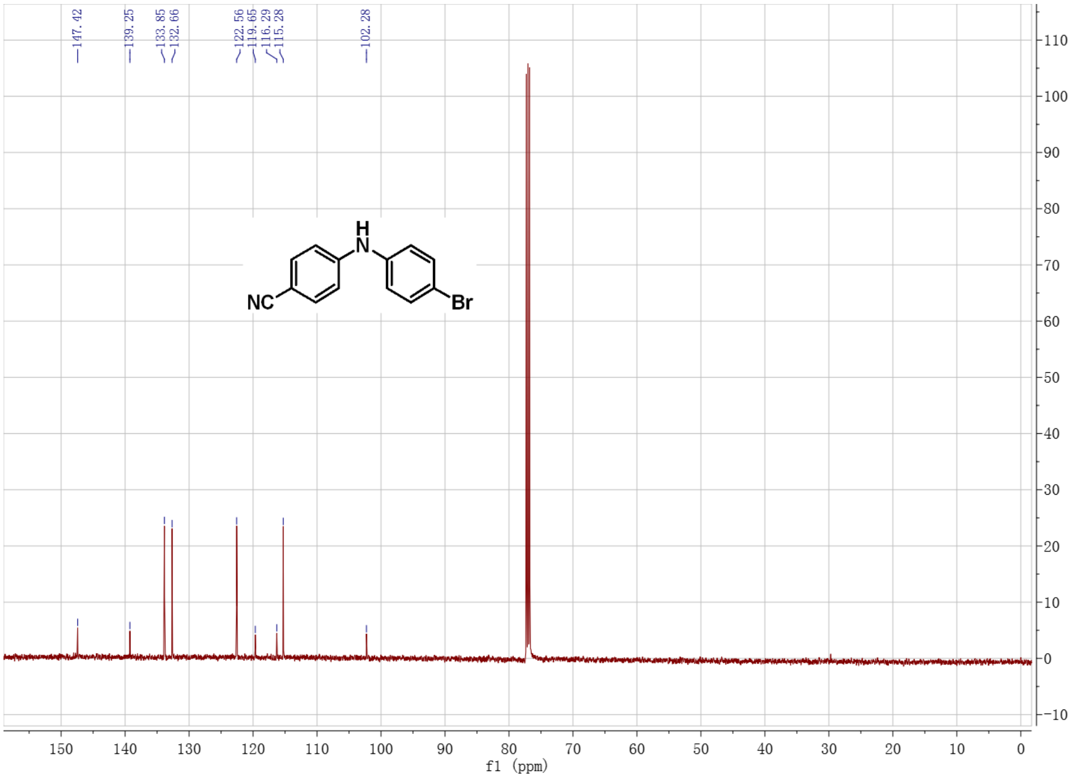
Compound **13f**



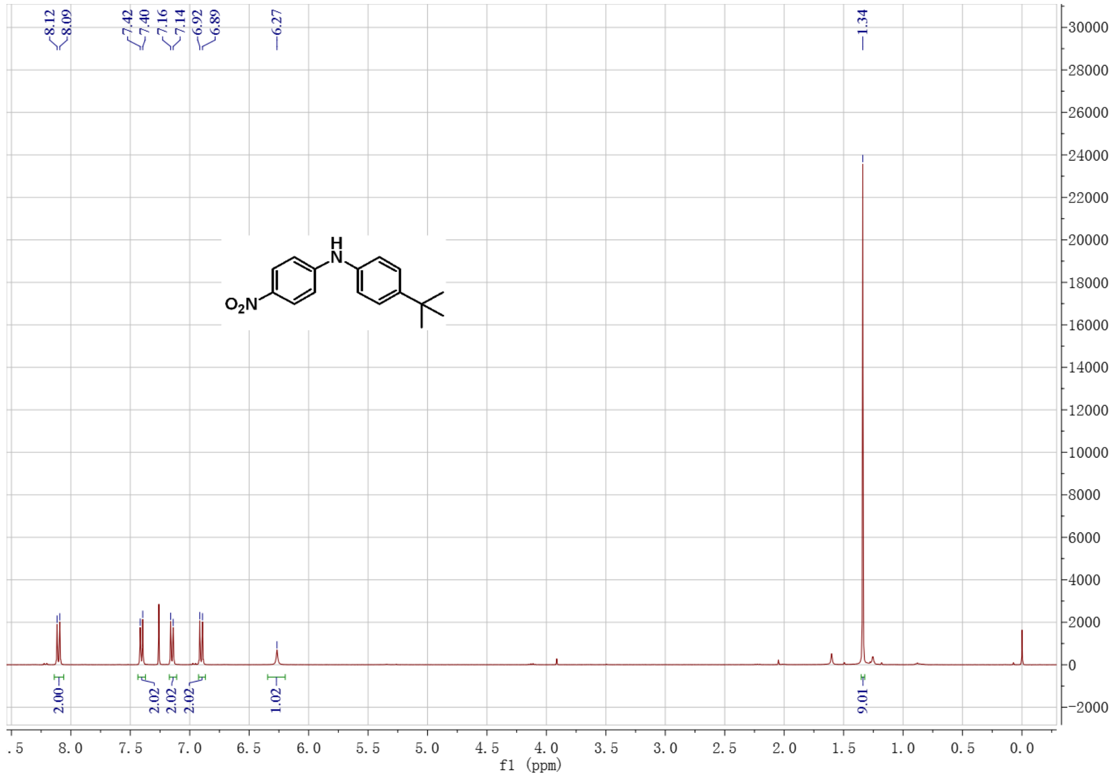


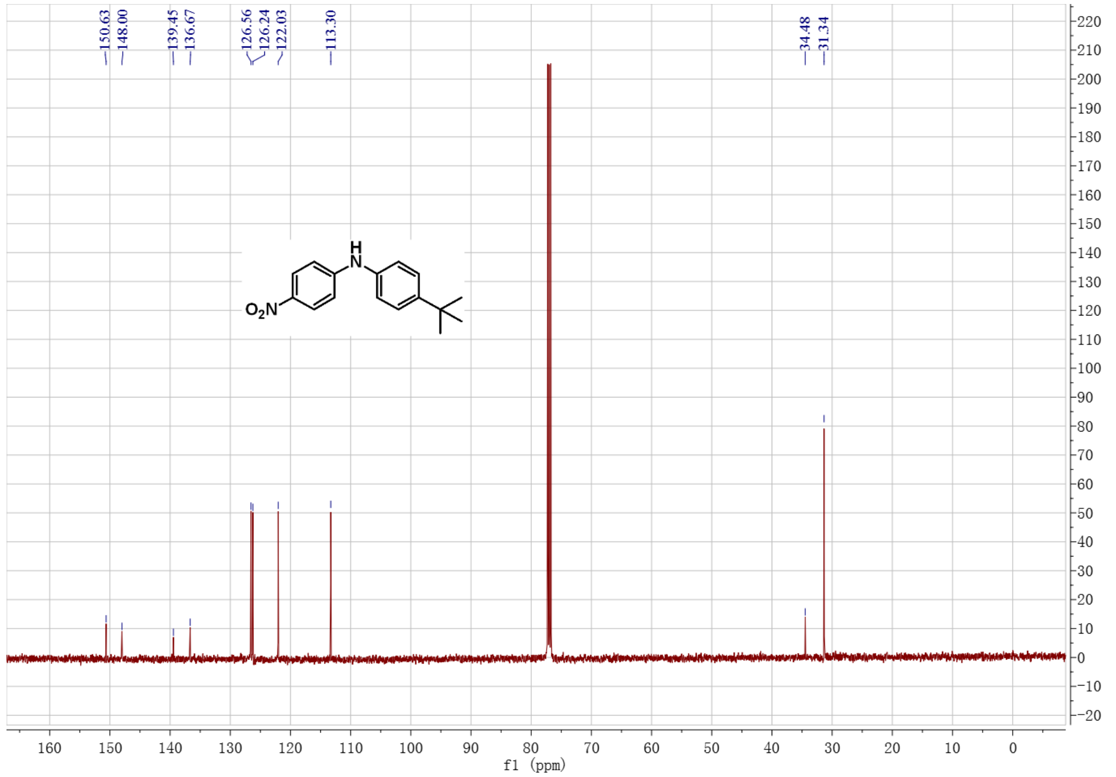
Compound **13d**



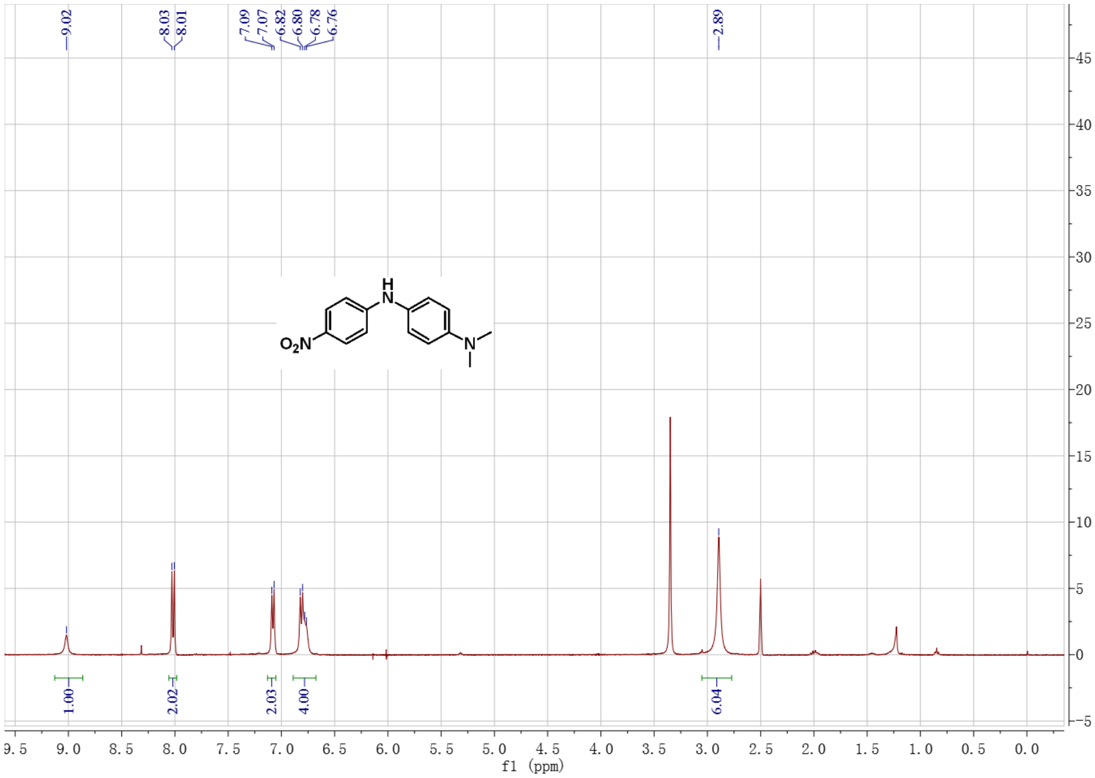


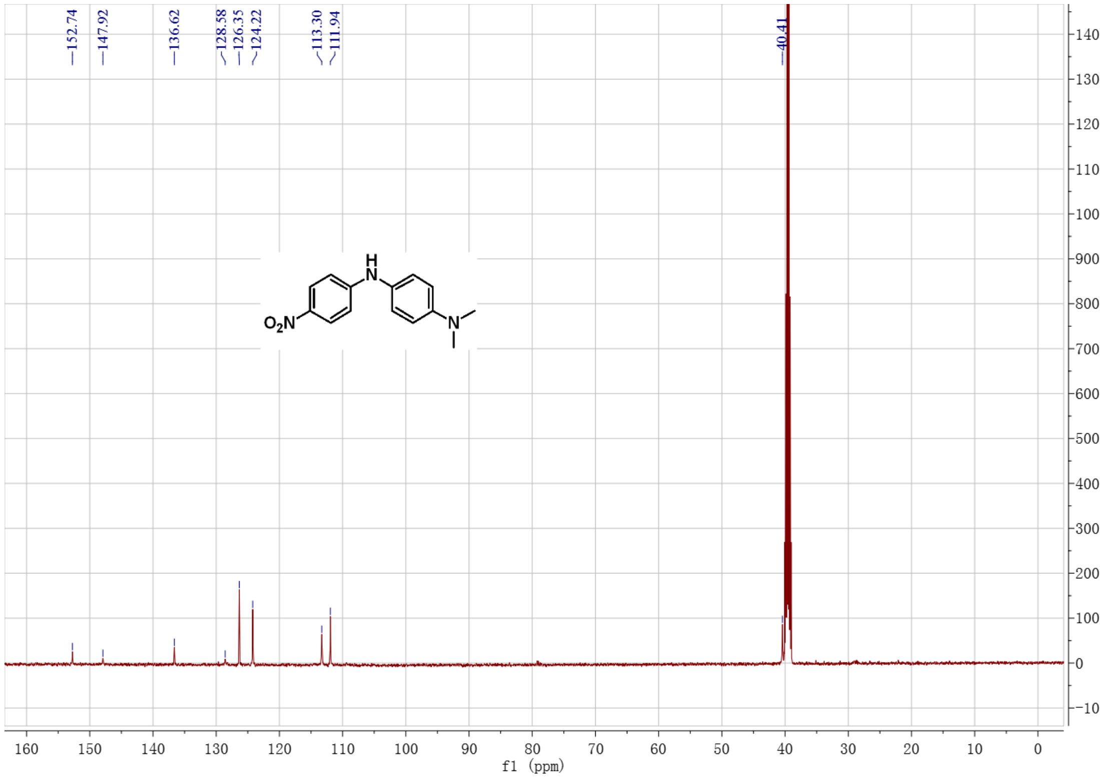
Compound **13g**



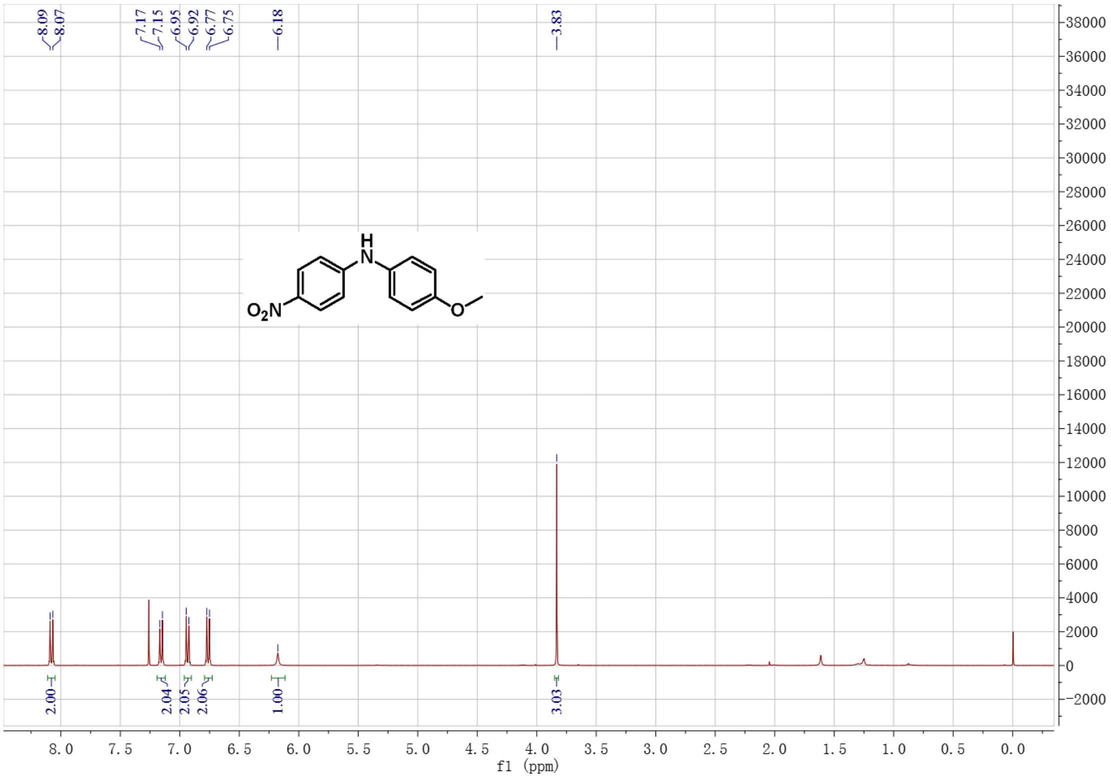


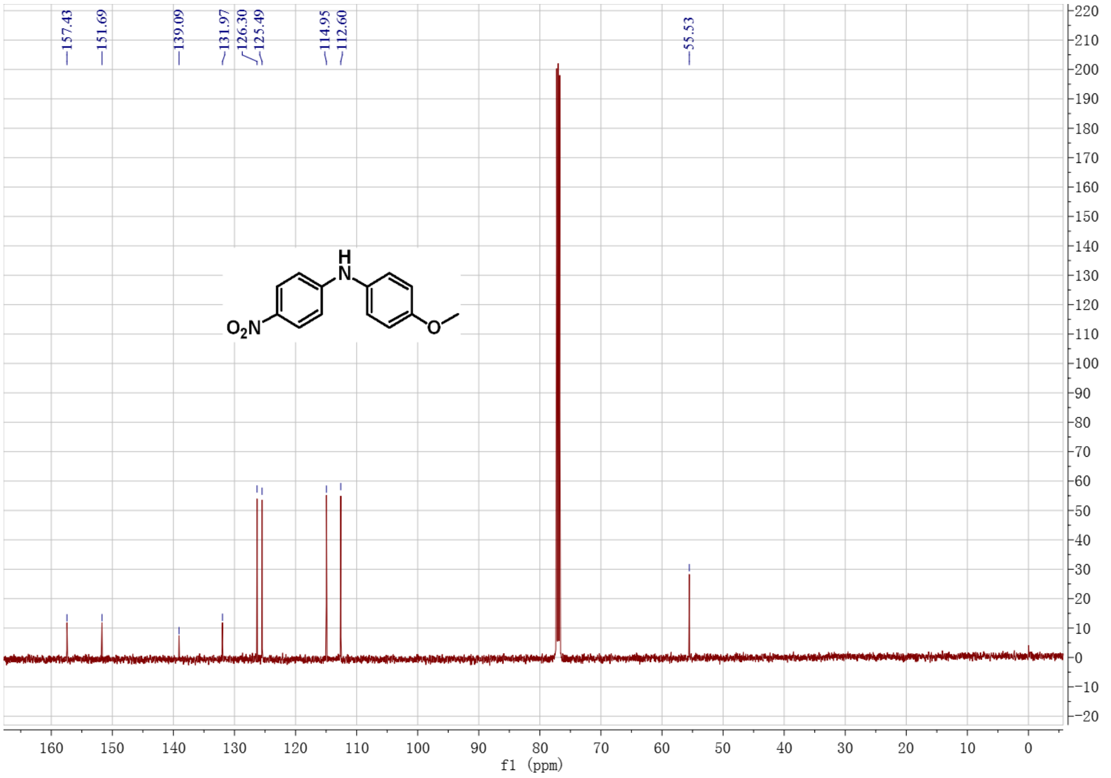
Compound **13h**



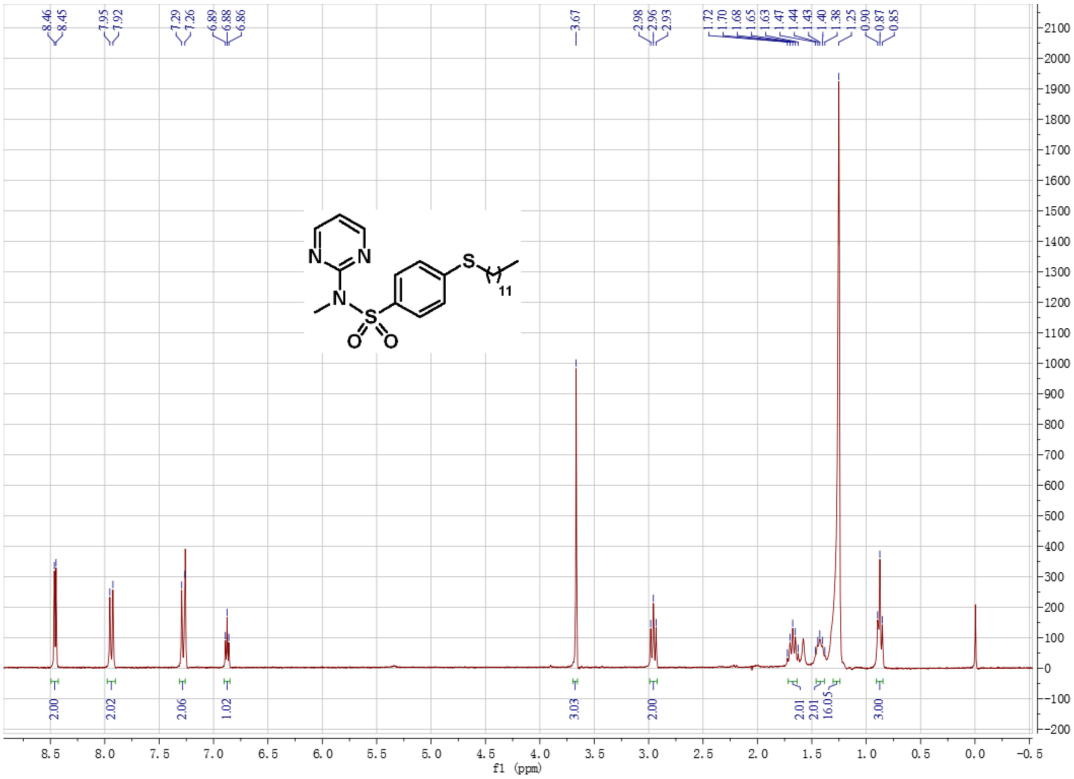


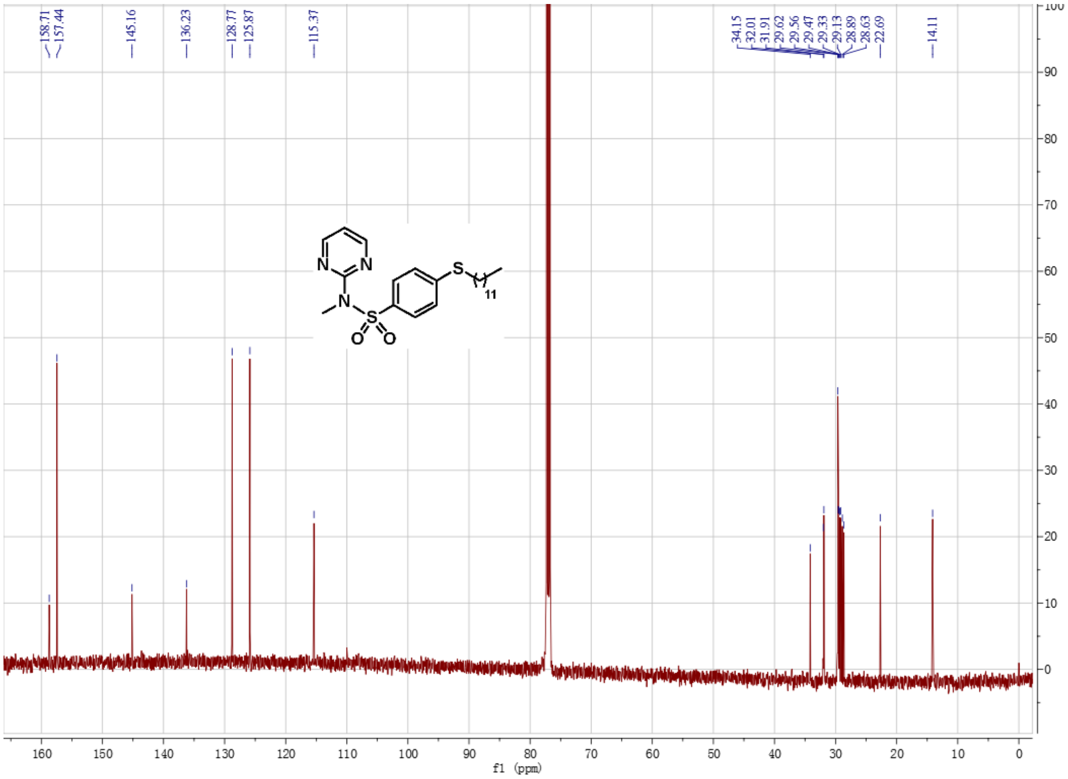
Compound **13i**



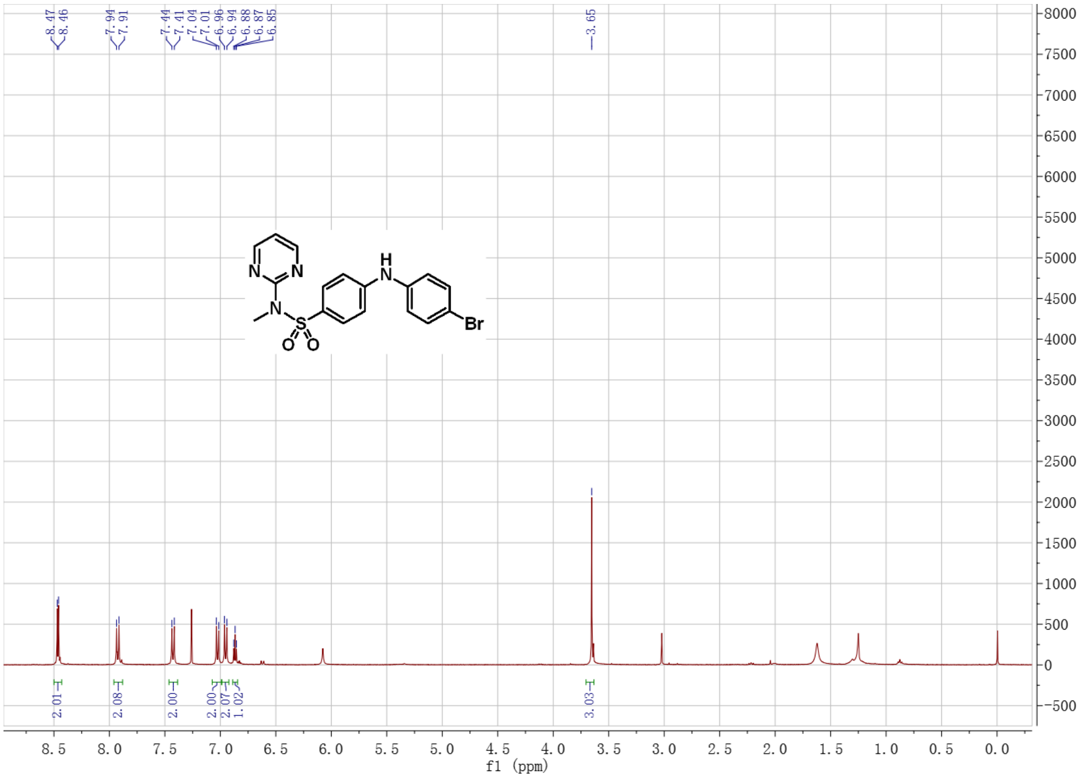


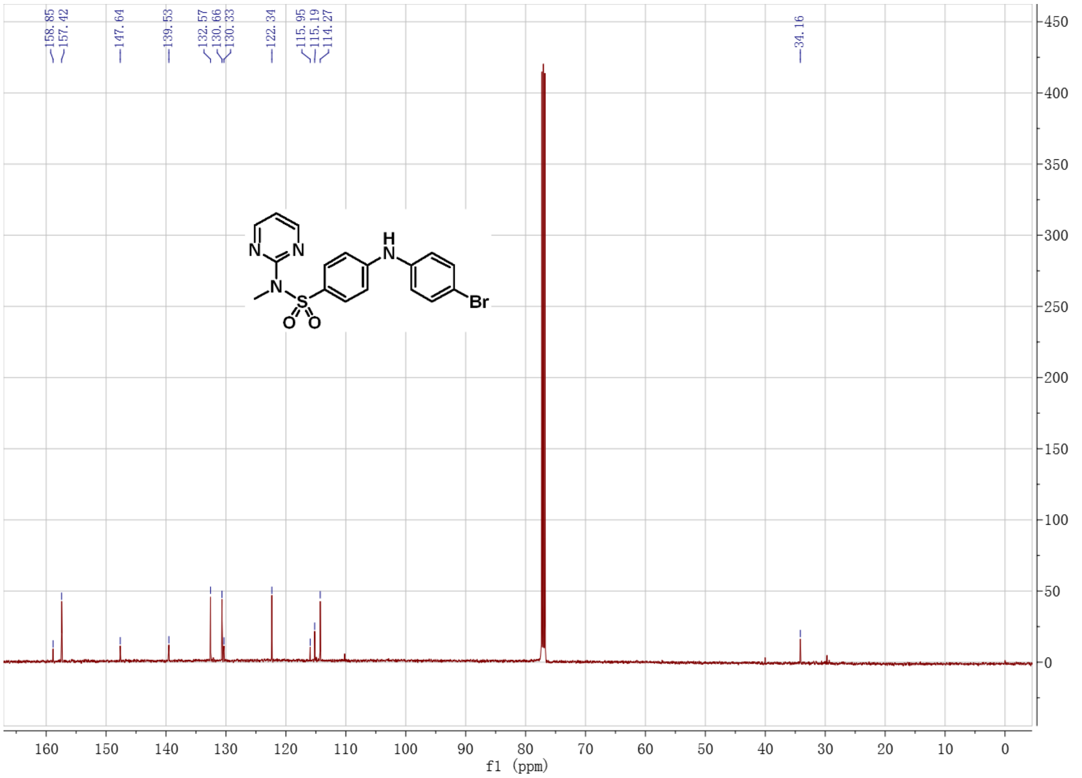
Compound **3mp**



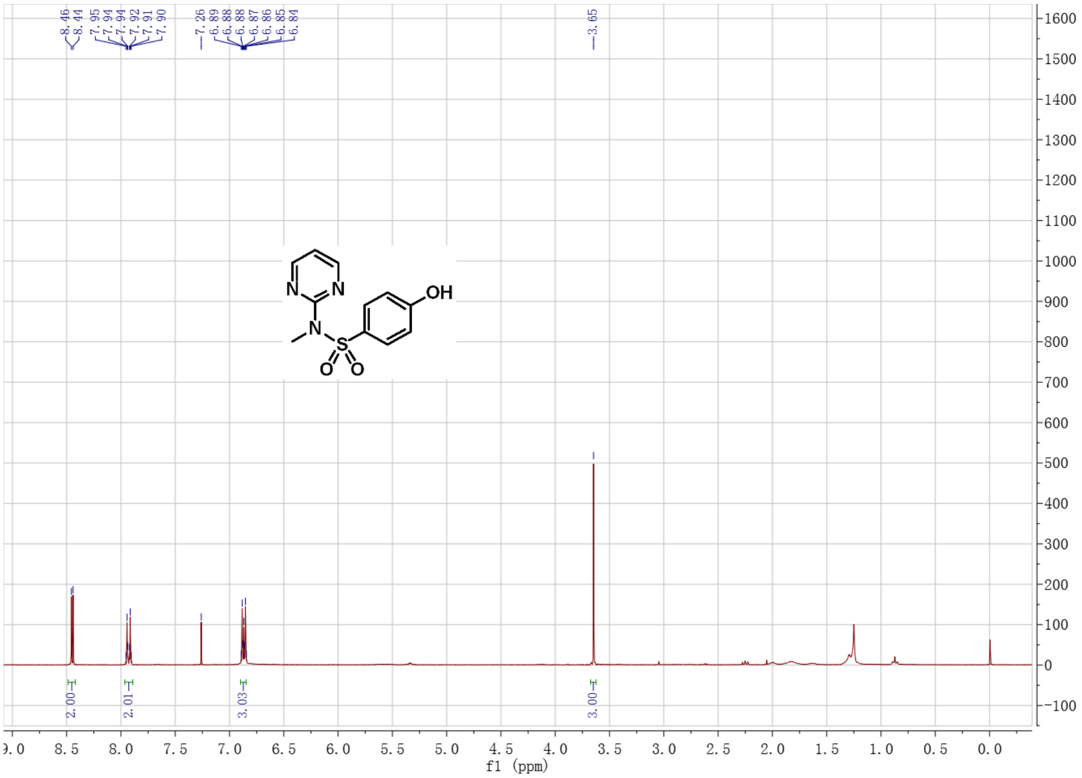


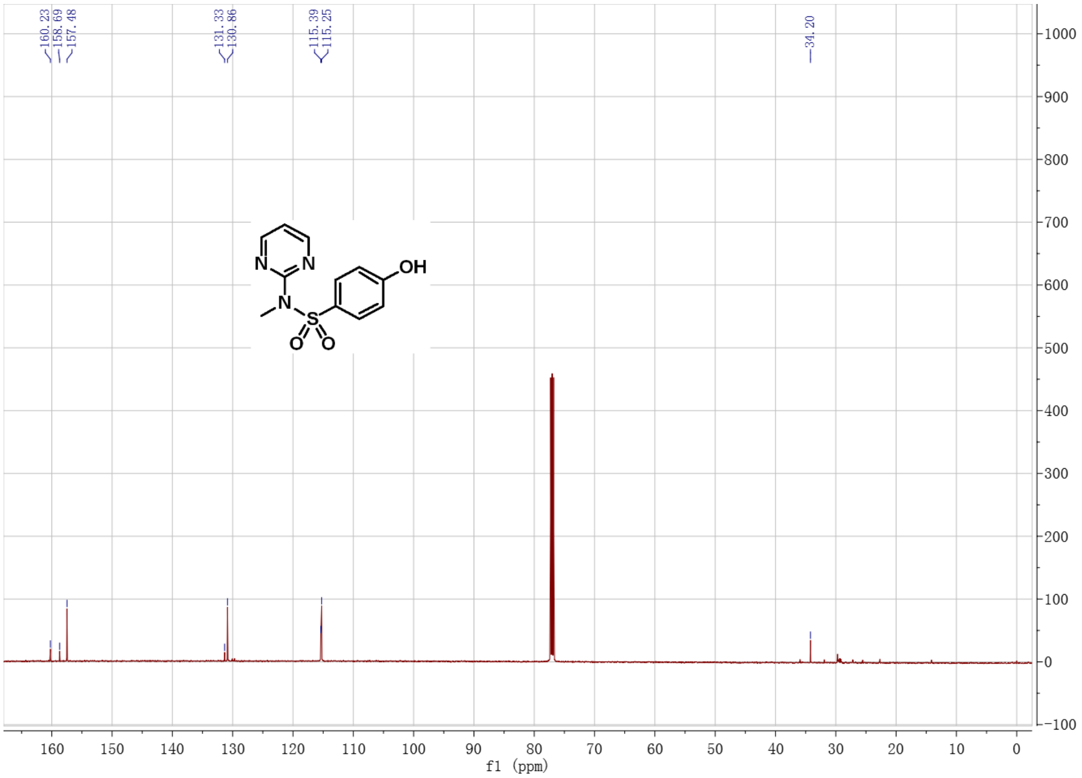
Compound **13h**



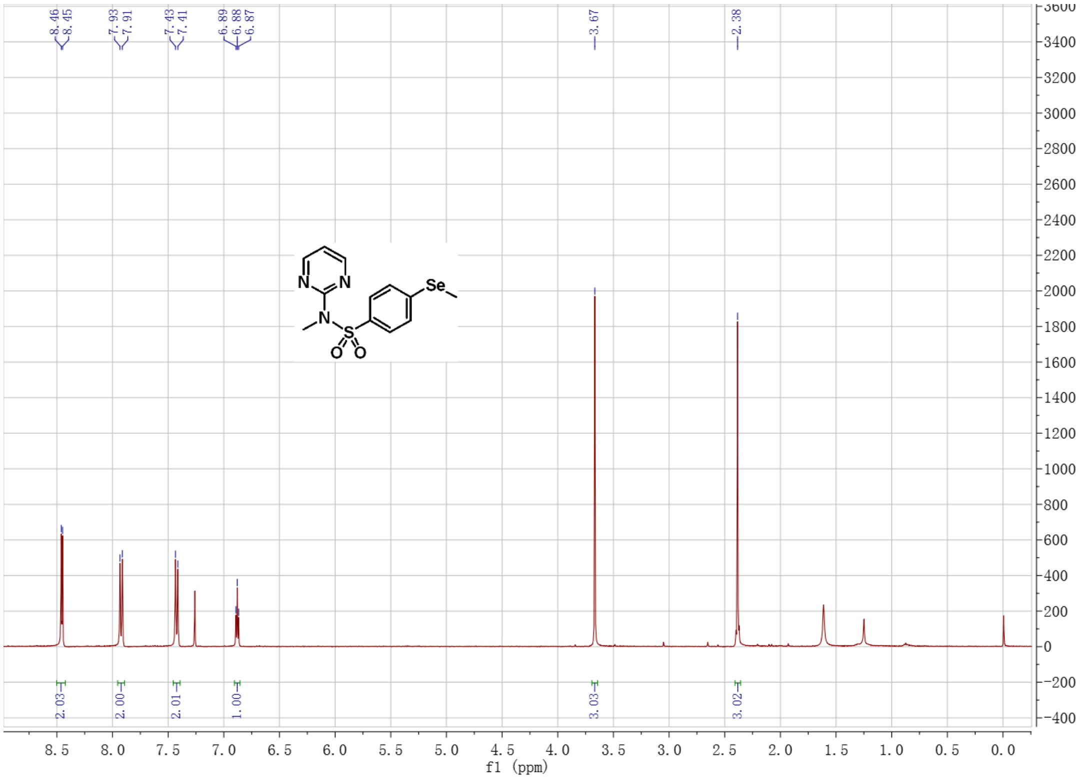


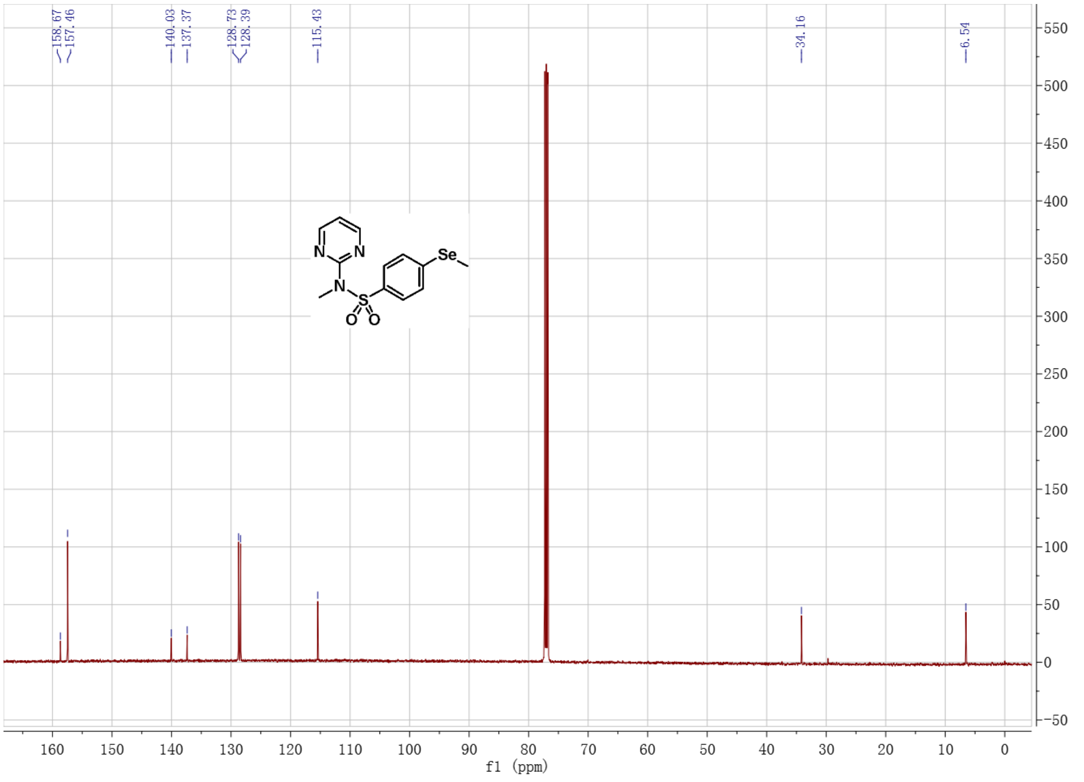
Compound **14a**



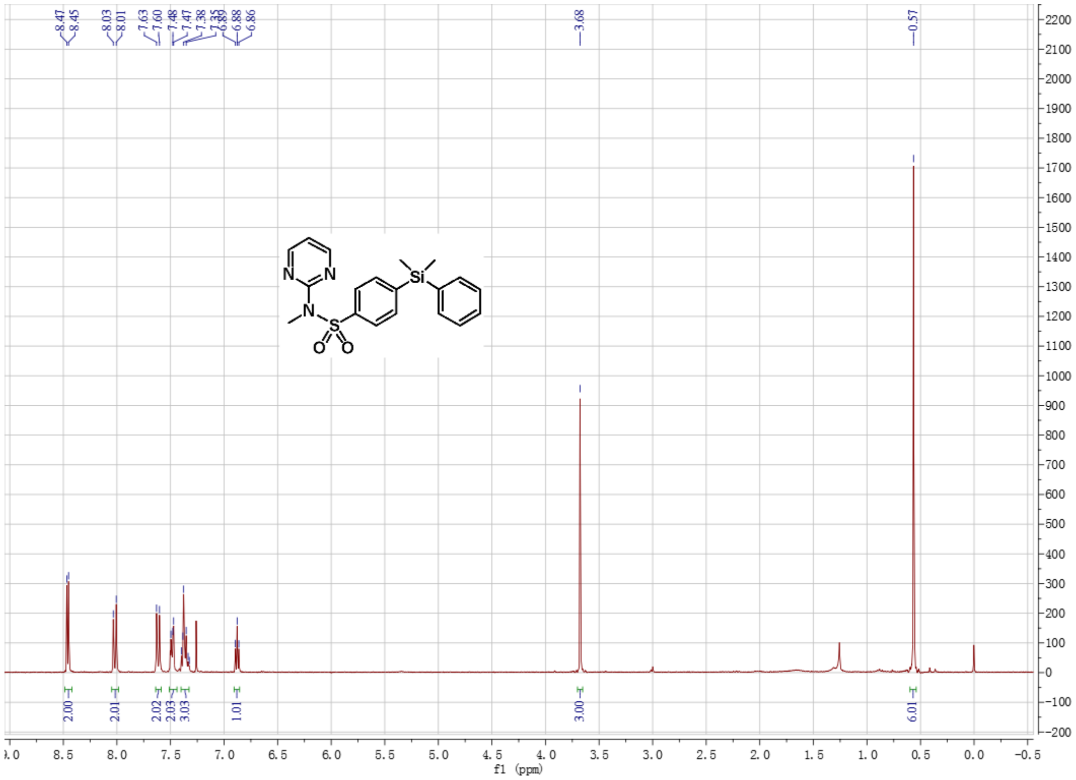


Compound **11h**

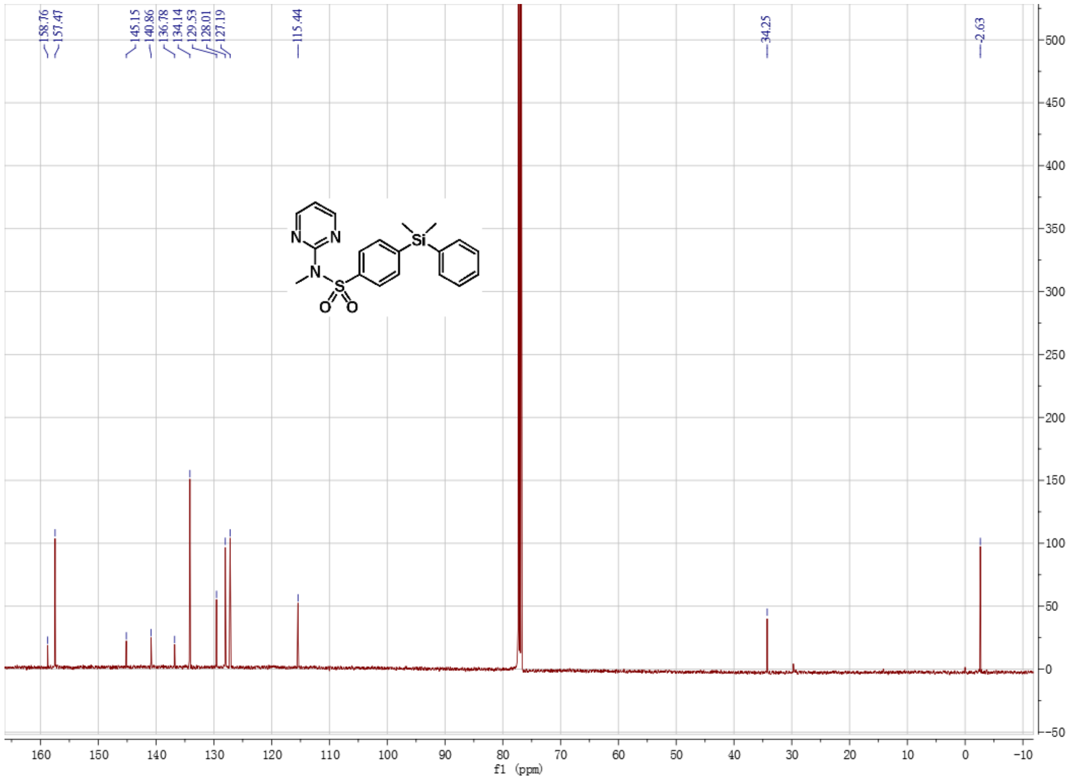




Compound **5j**

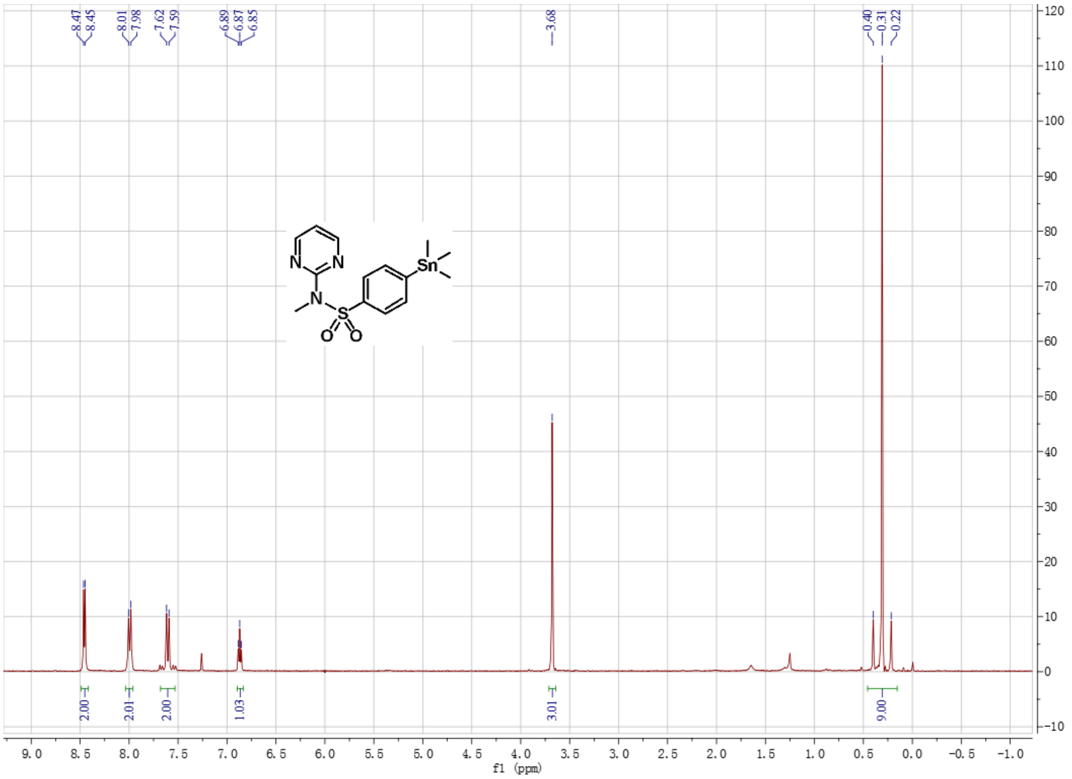


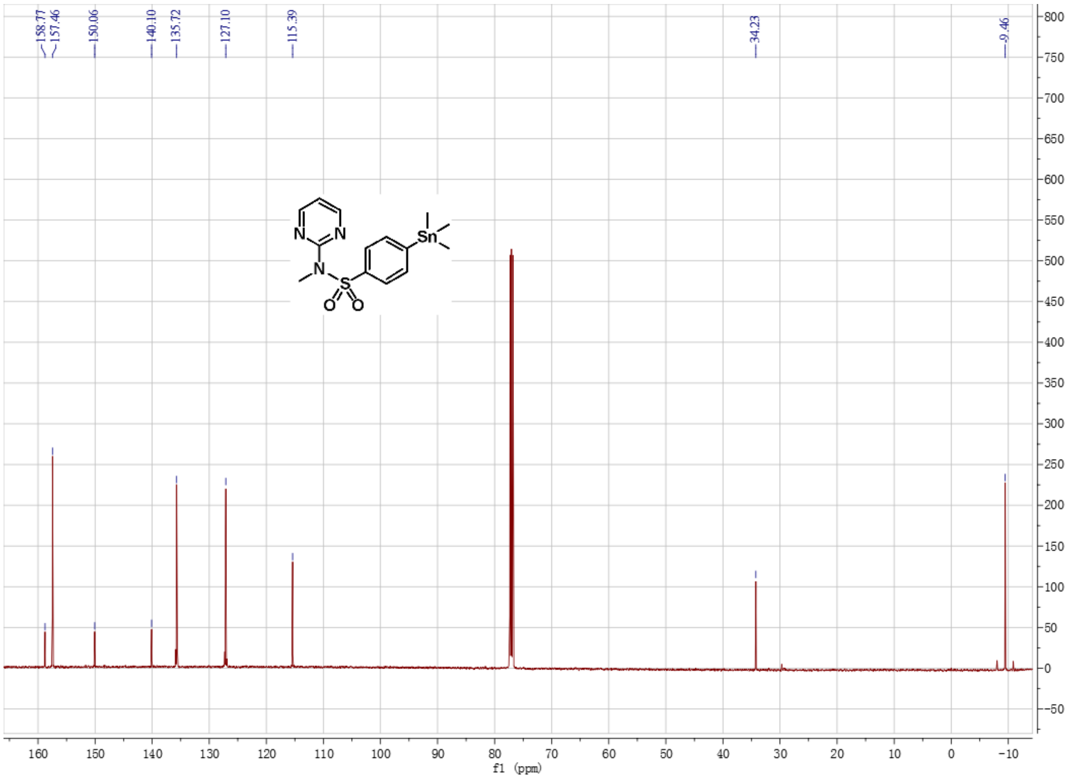
8.47
8.45
8.03
8.01
7.63
7.60
7.48
7.47
7.38
7.35
6.89
6.88
6.86
3.68
0.57
2.00
2.01
2.02
2.03
3.03
1.01
3.00
6.01
N
N
N
S
O
O
Si
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 −100 −200



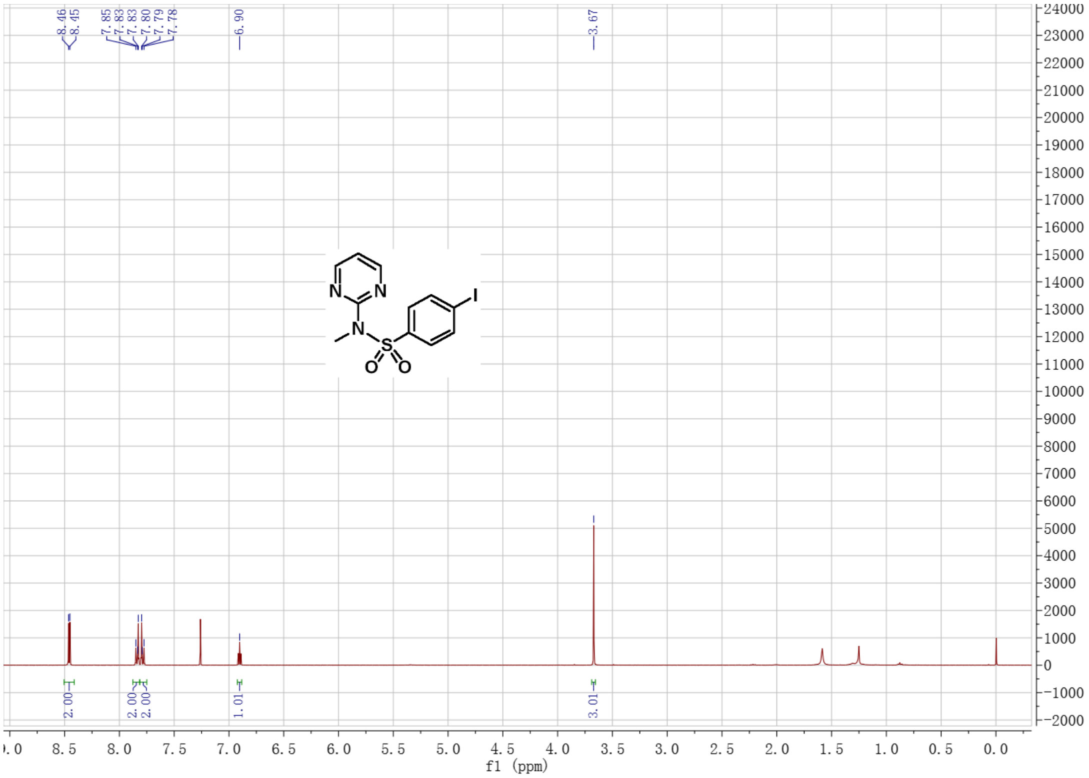
158.76
157.47
145.15
140.86
136.78
134.14
129.53
128.01
127.19
115.44
34.25
−2.63
N
N
N
S
O
O
Si
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
500 450 400 350 300 250 200 150 100 50 0 −50

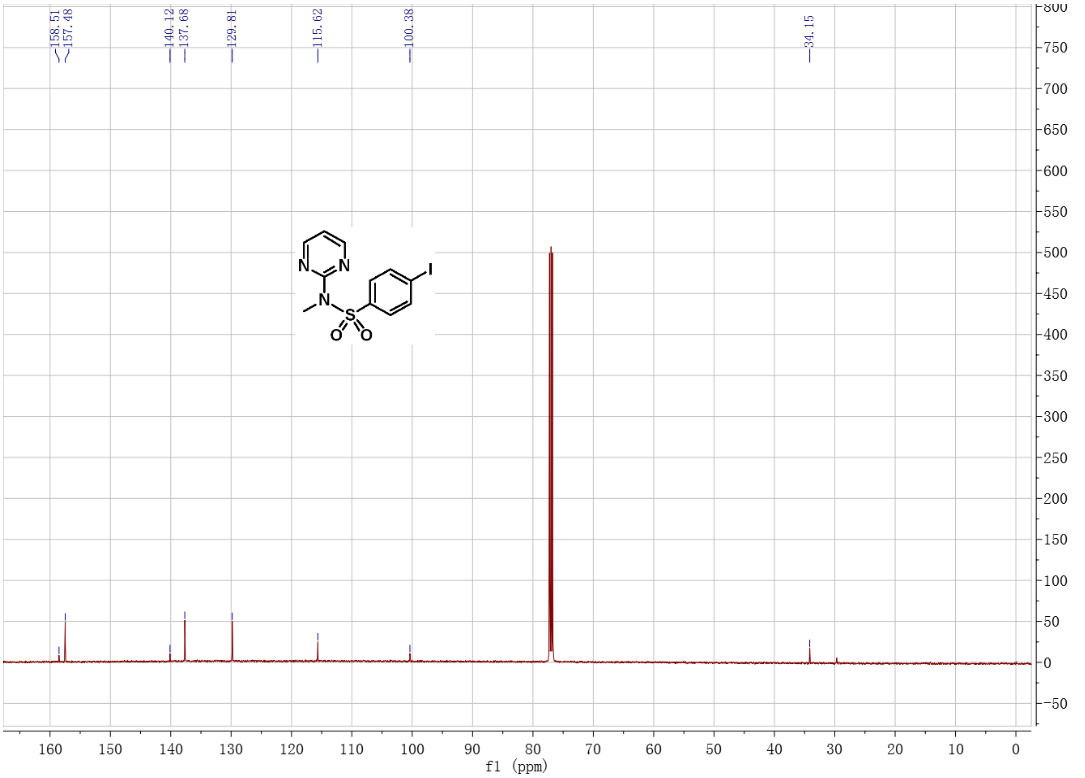
Compound **7o**


8.47
8.45
8.01
7.98
7.62
7.59
6.89
6.87
6.85
3.68
0.40
0.31
0.22
2.00
2.01
2.00
1.03
3.01
9.00
N
N
N
Sn
S
O
O
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
f1 (ppm)
120 110 100 90 80 70 60 50 40 30 20 10 0 -10

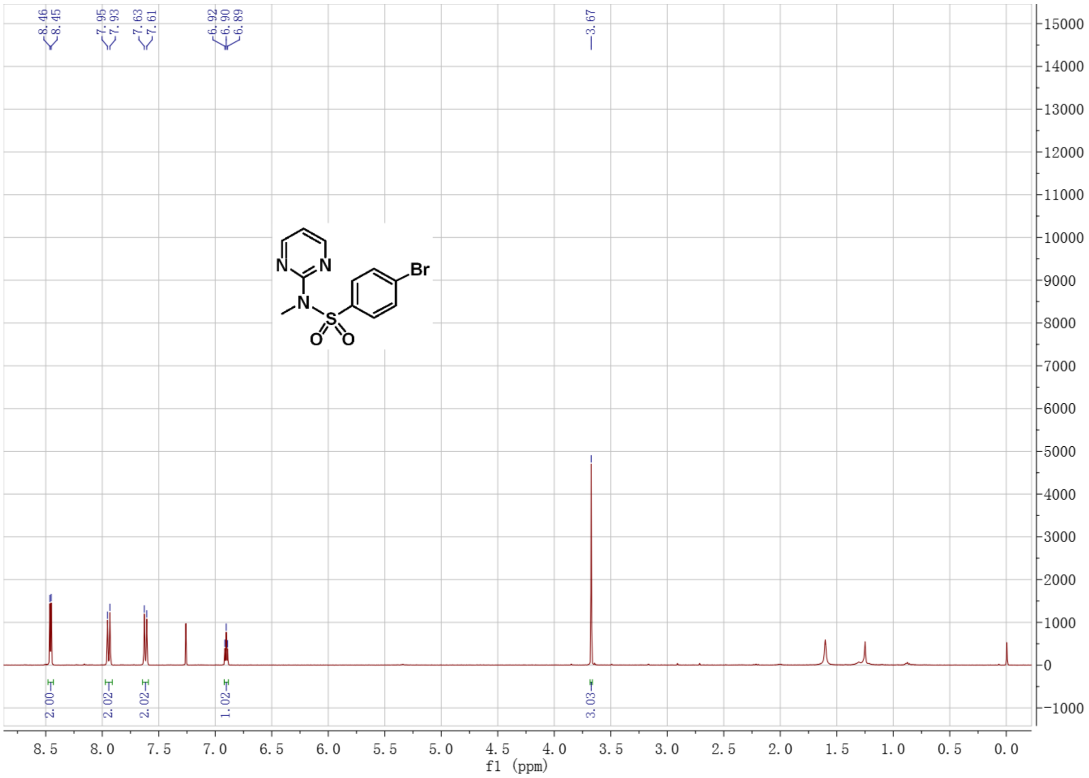

158.77
157.46
150.06
140.10
135.72
127.10
115.39
34.23
-9.46
N
N
N
Sn
S
O
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

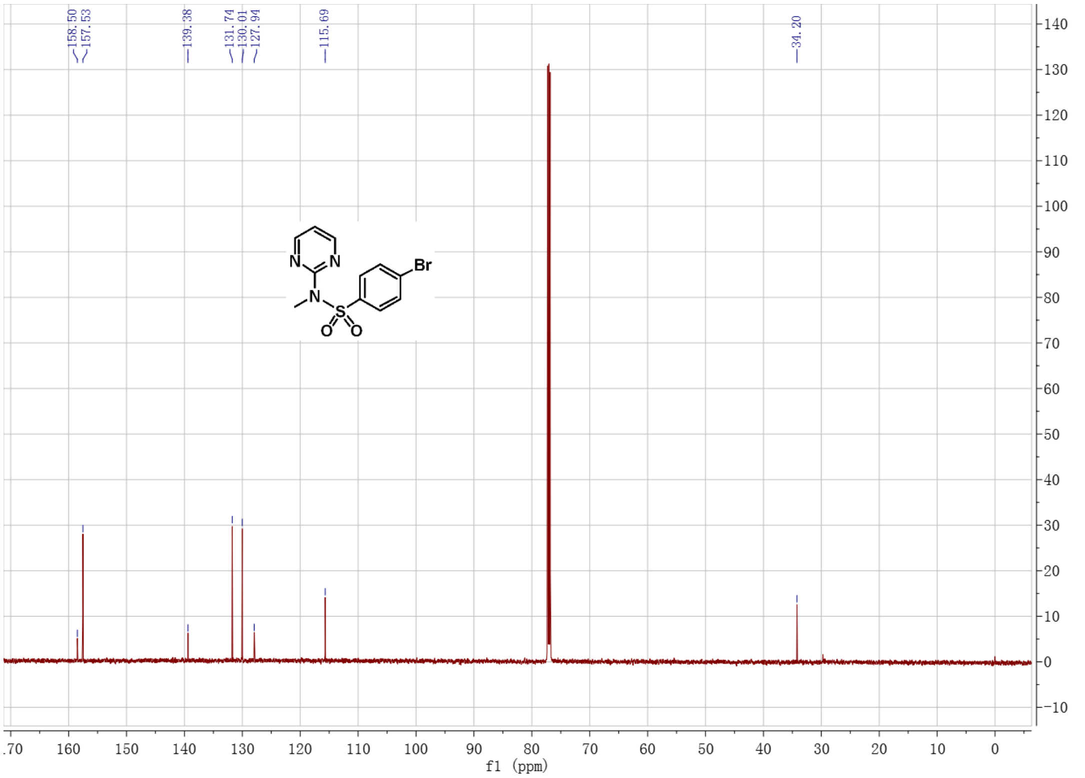
Compound **14b**



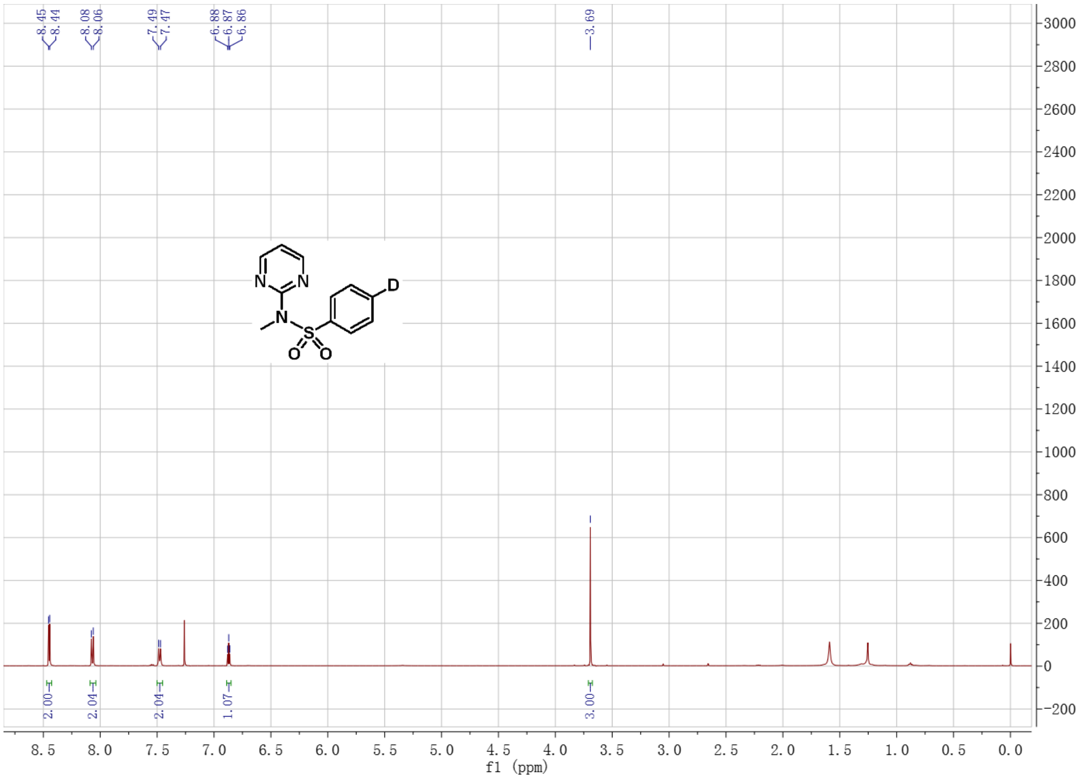


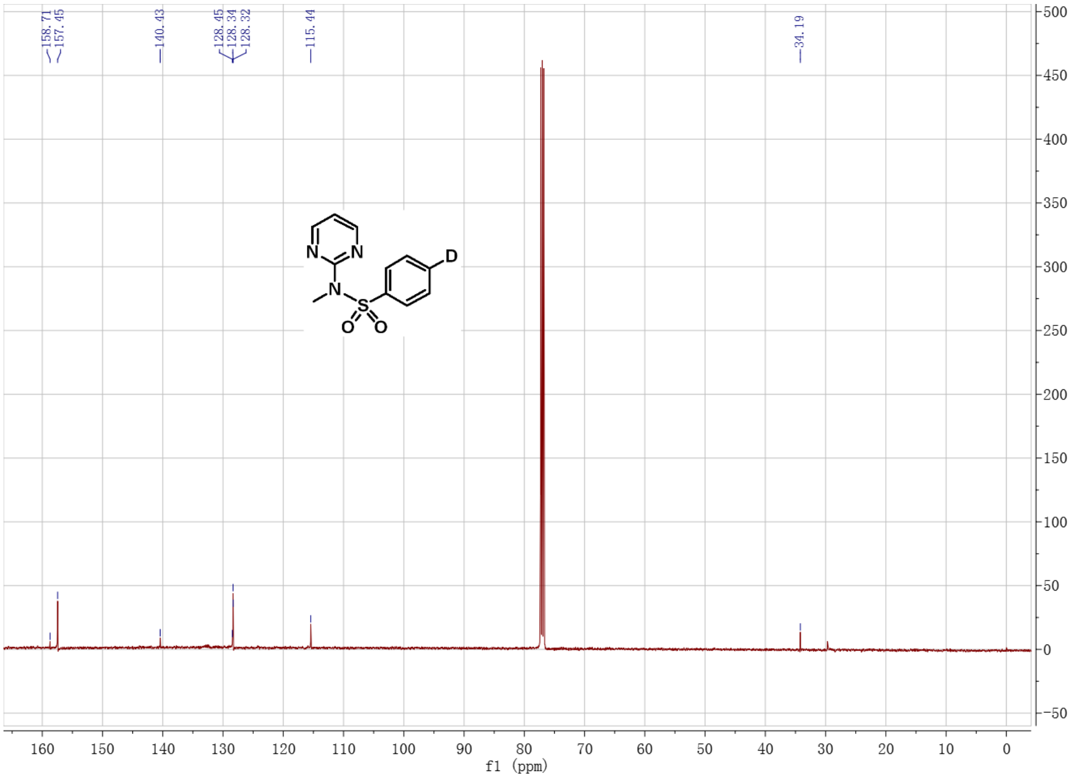
Compound **14c**





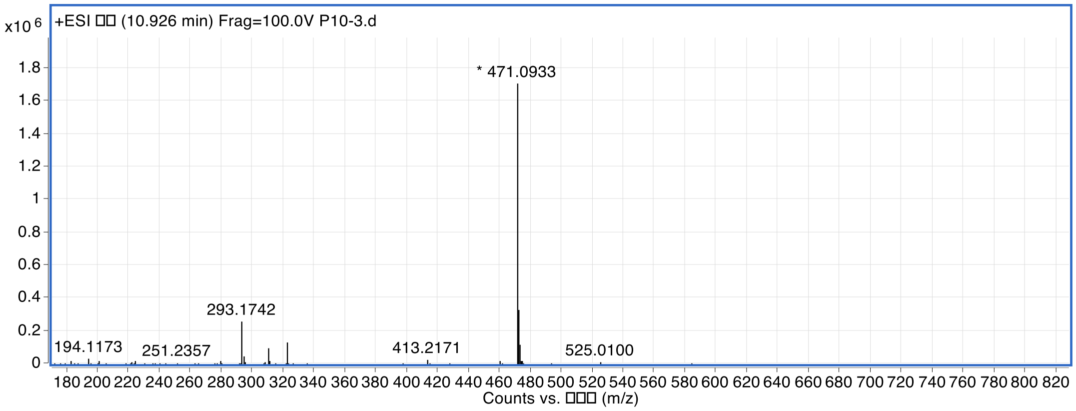
Compound **14d**



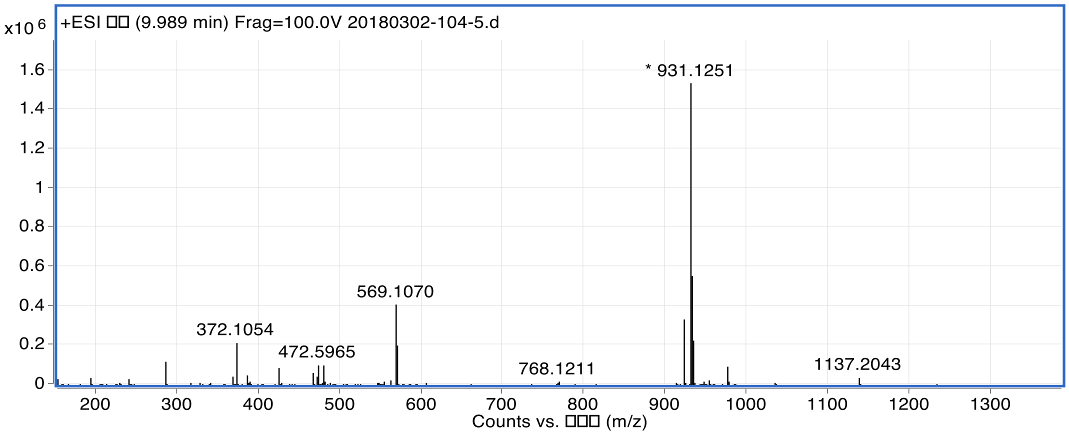


5. Copies of MS Spectrums for Compounds in Fig 5 and Fig 6.

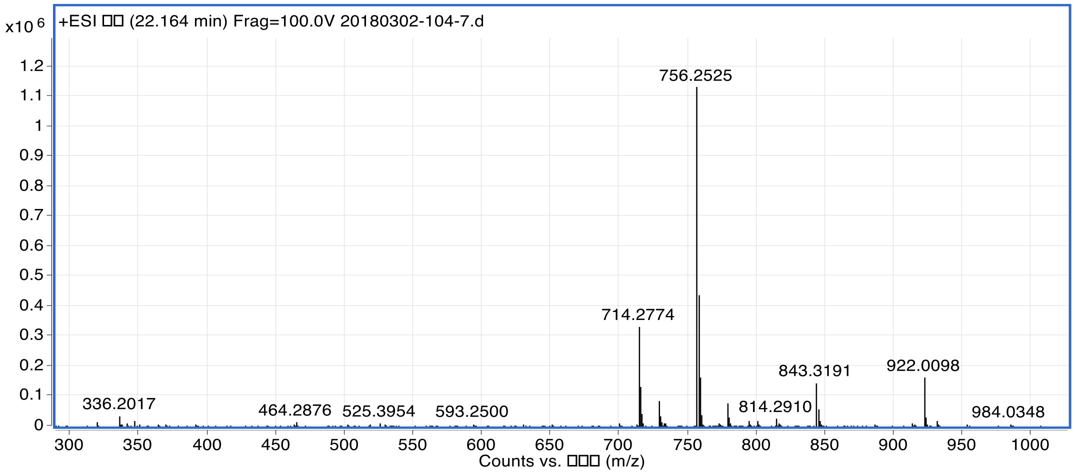
Compound **15a**



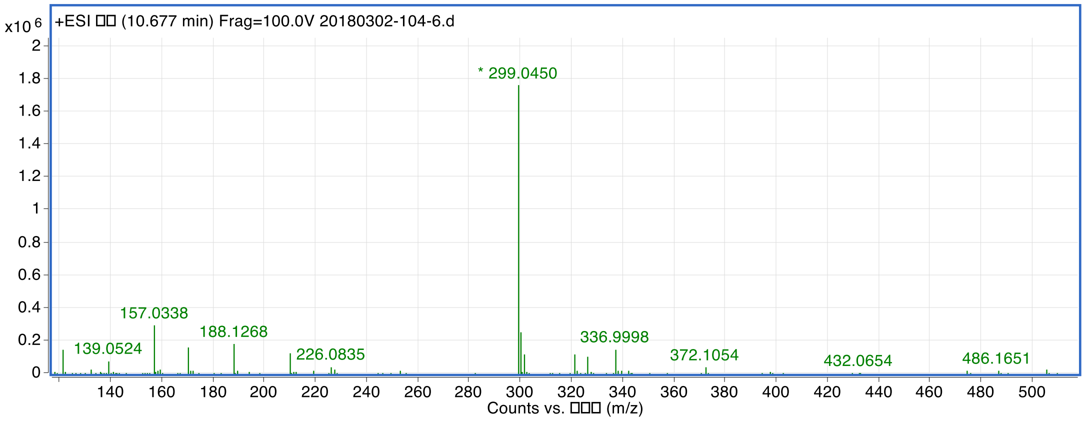
Compound **15b**



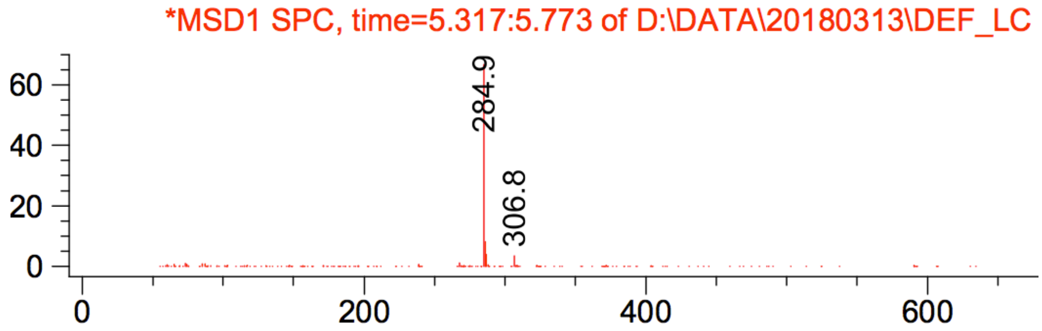
Compound **15c**



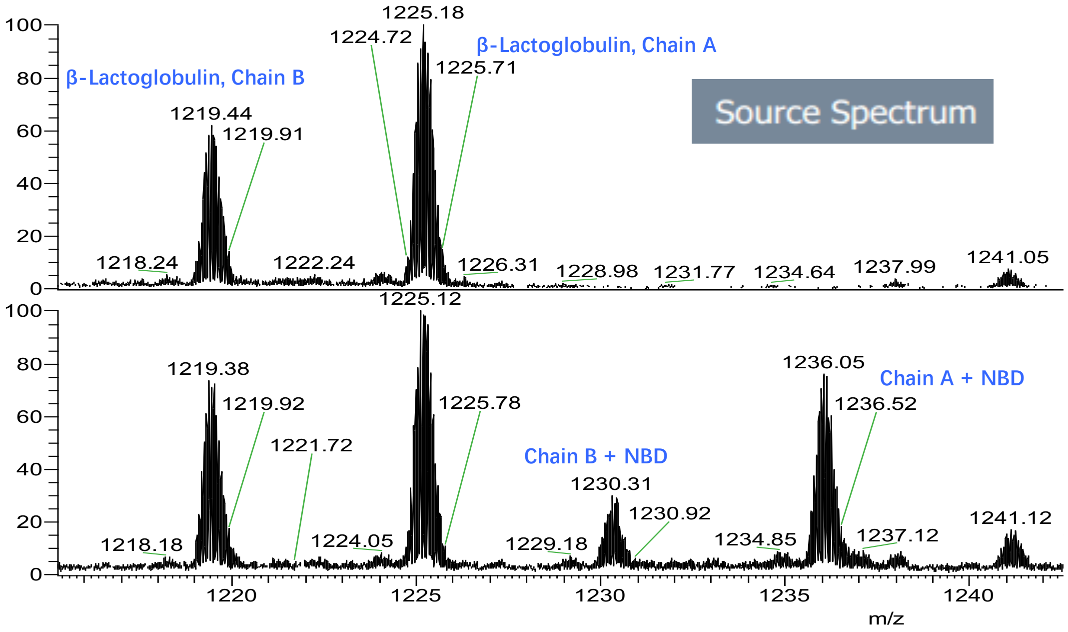
Compound **15f**



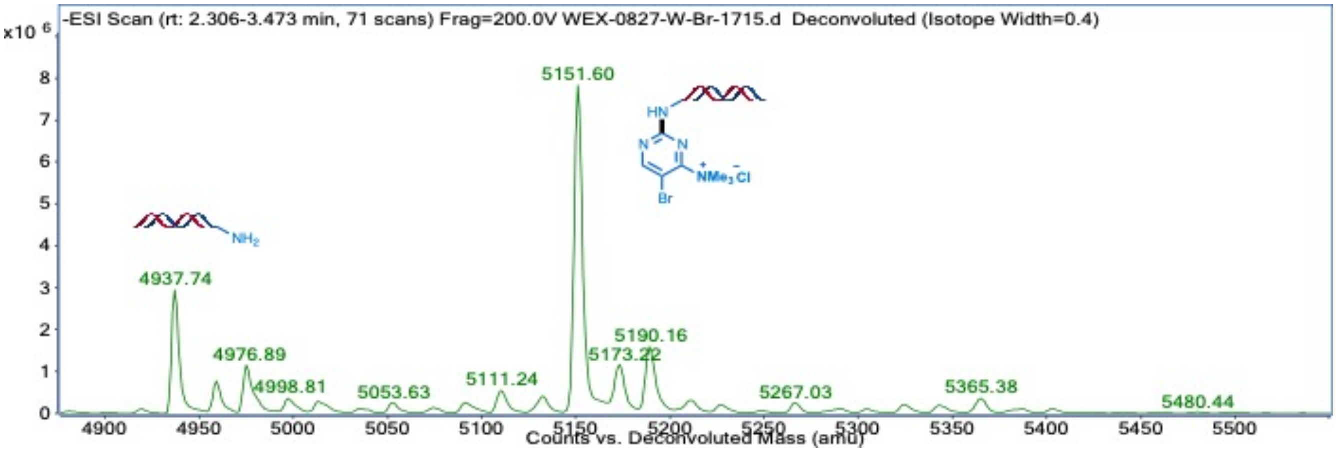
Compound **15e**



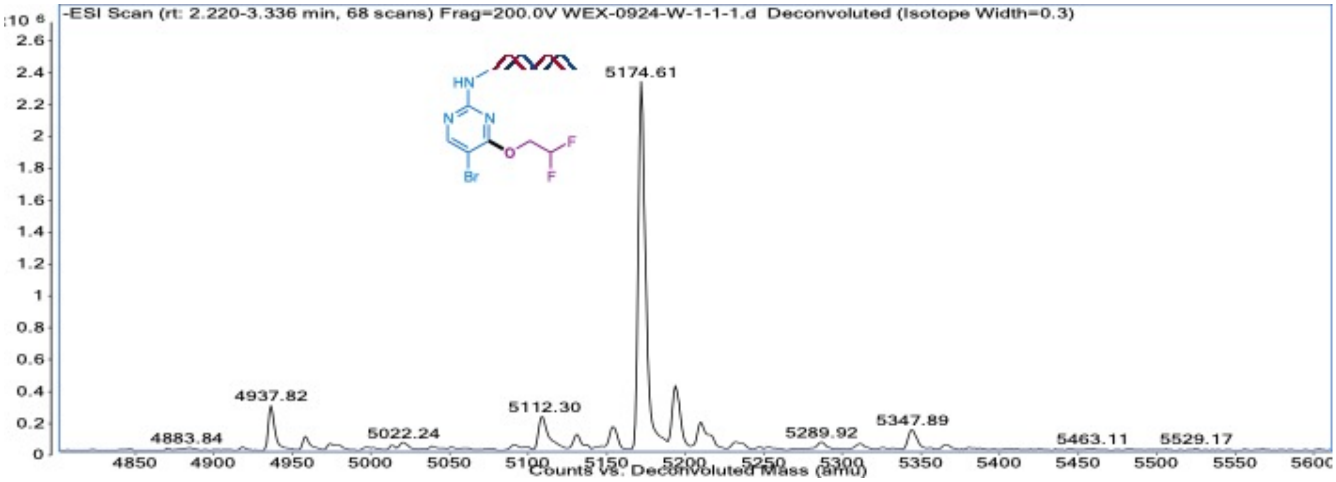
Compound **15d**



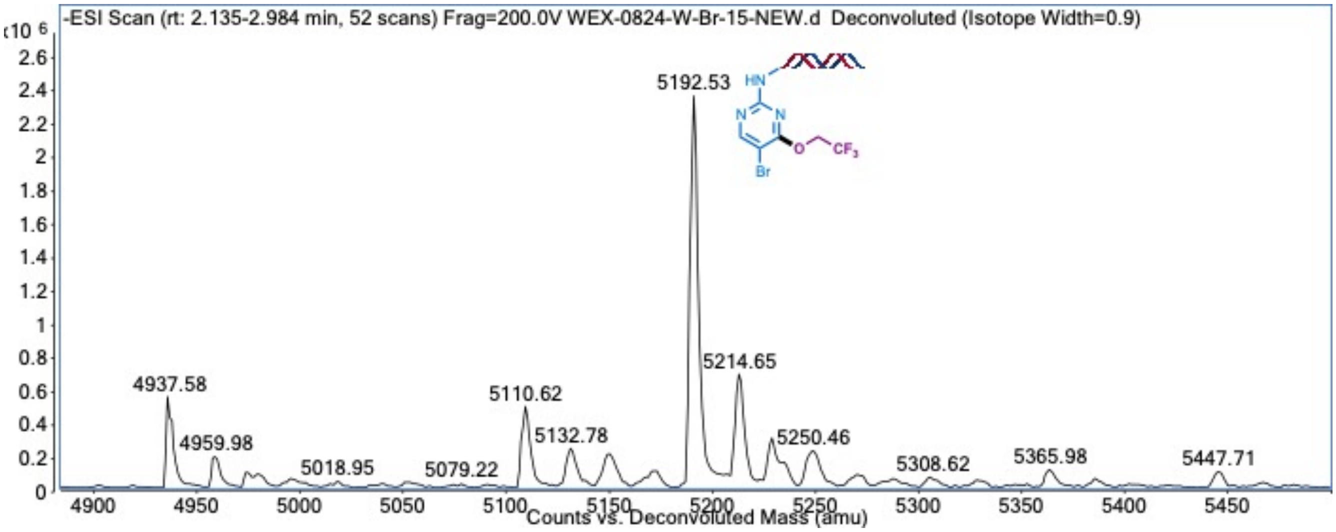
Compound **16a**



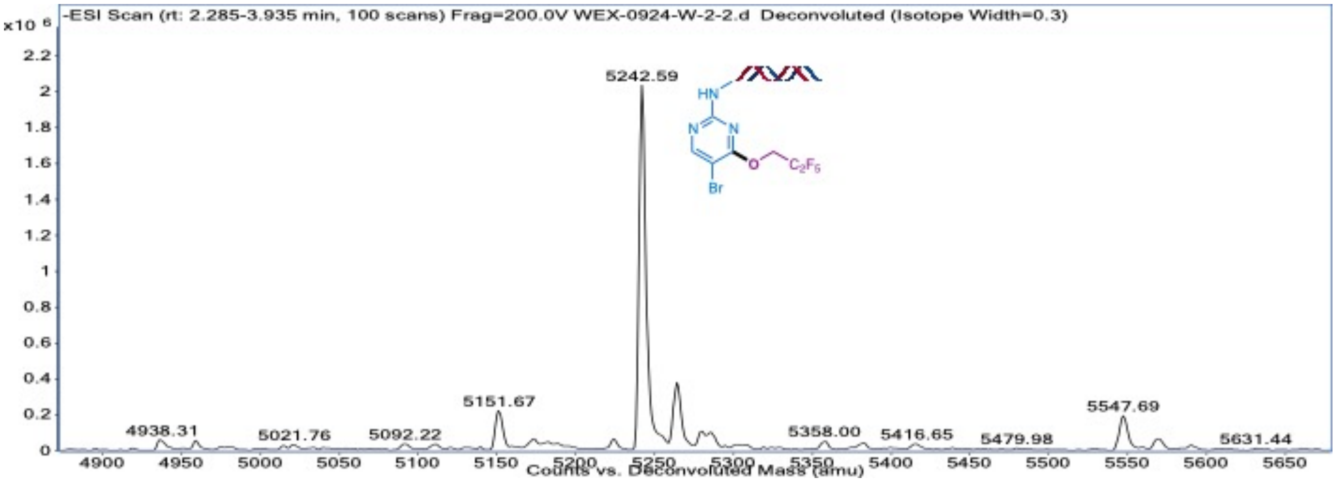
Compound **16b**



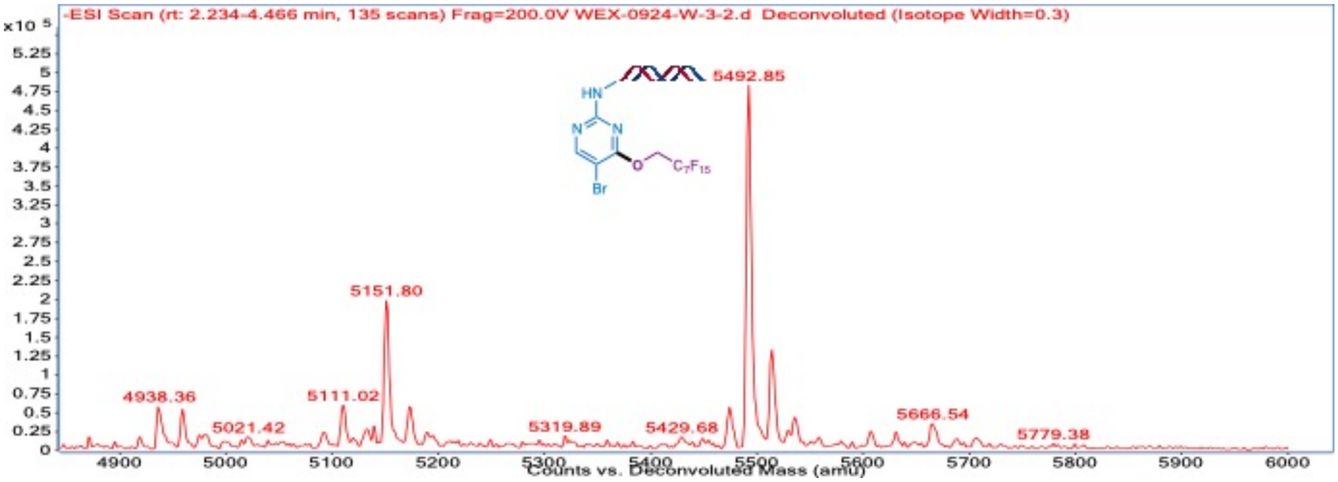
Compound **16c**



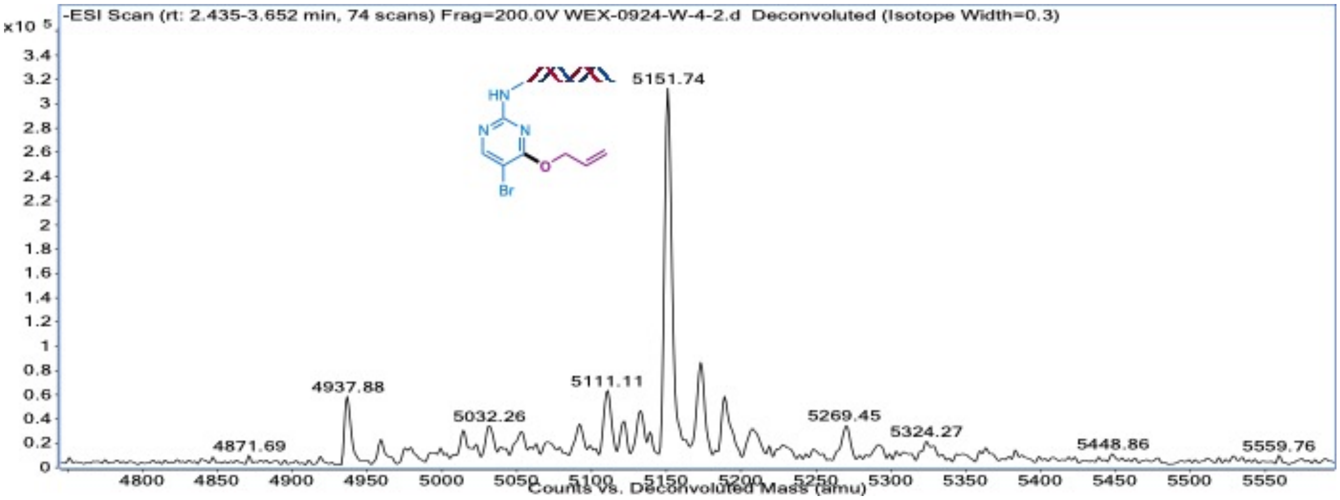
Compound **16d**



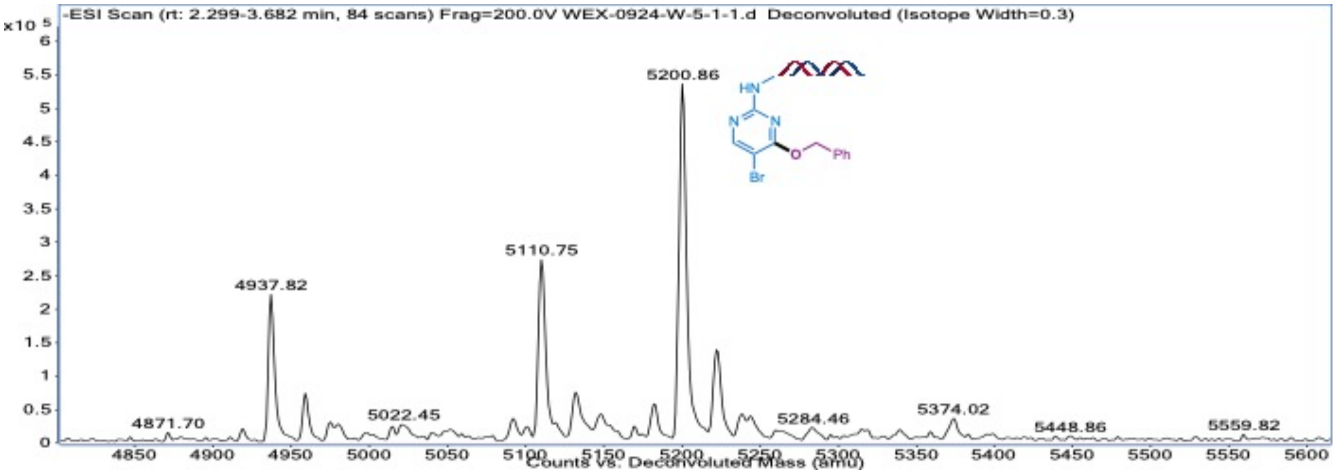
Compound **16e**



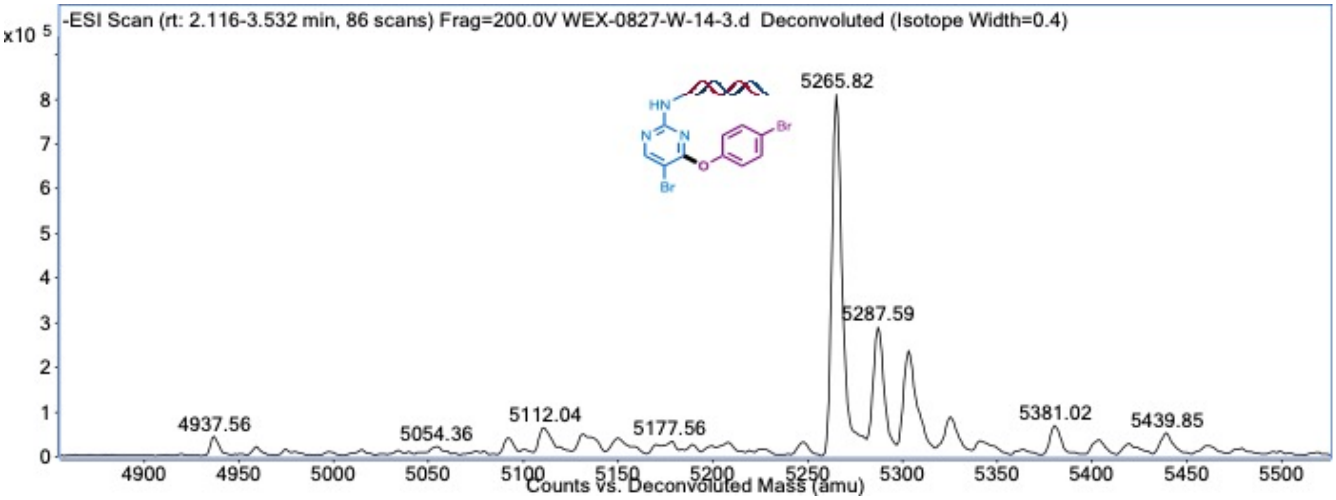
Compound **16f**



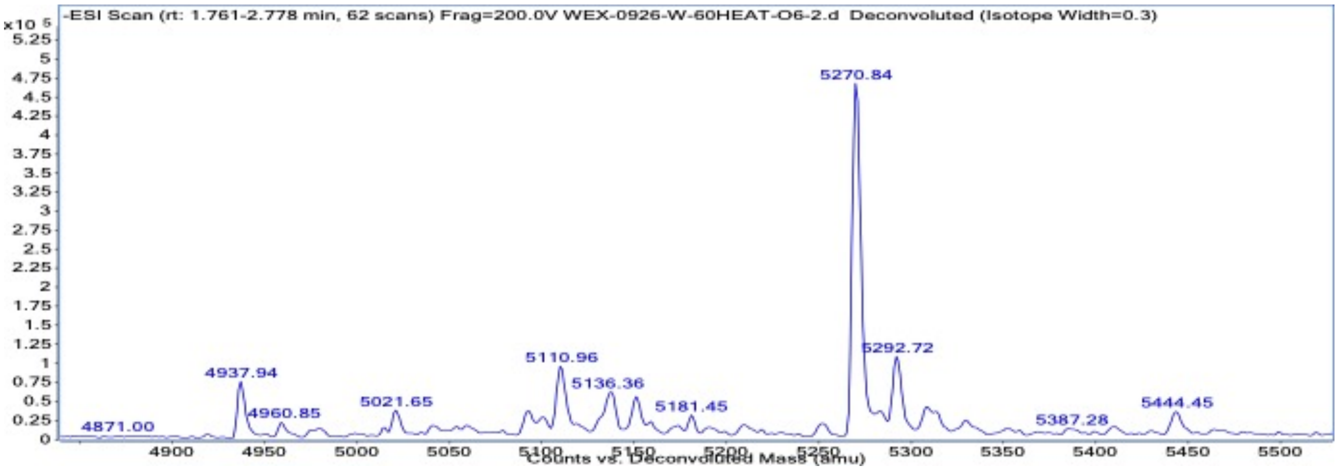
Compound **16g**



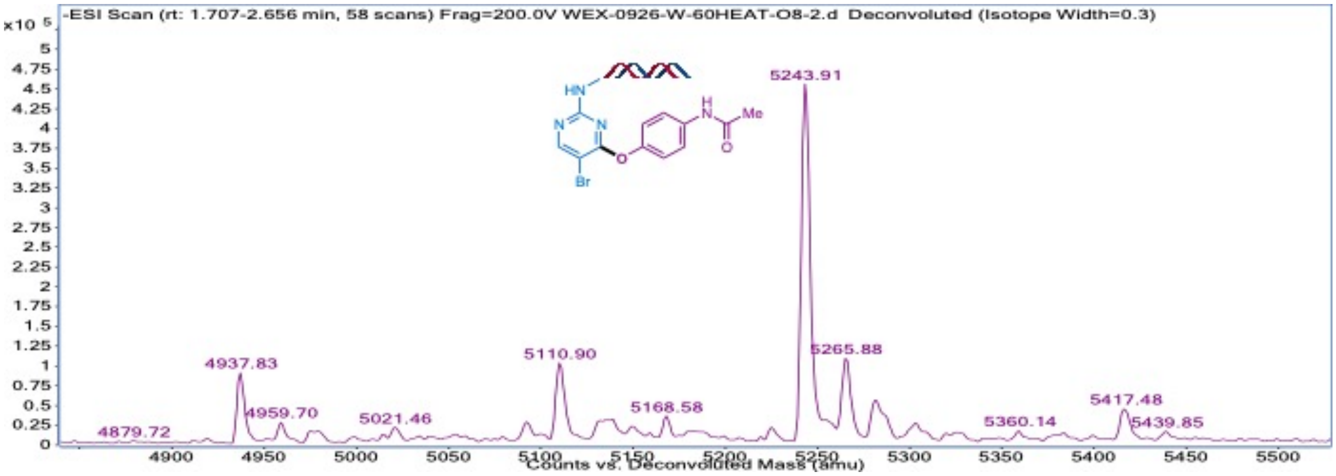
Compound **16h**



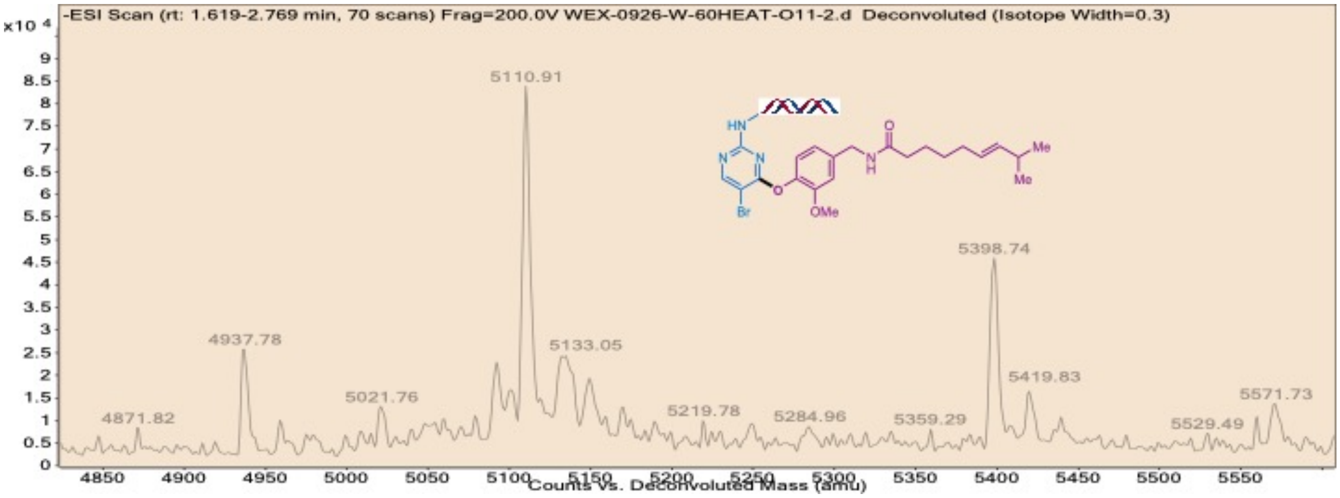
Compound **16i**



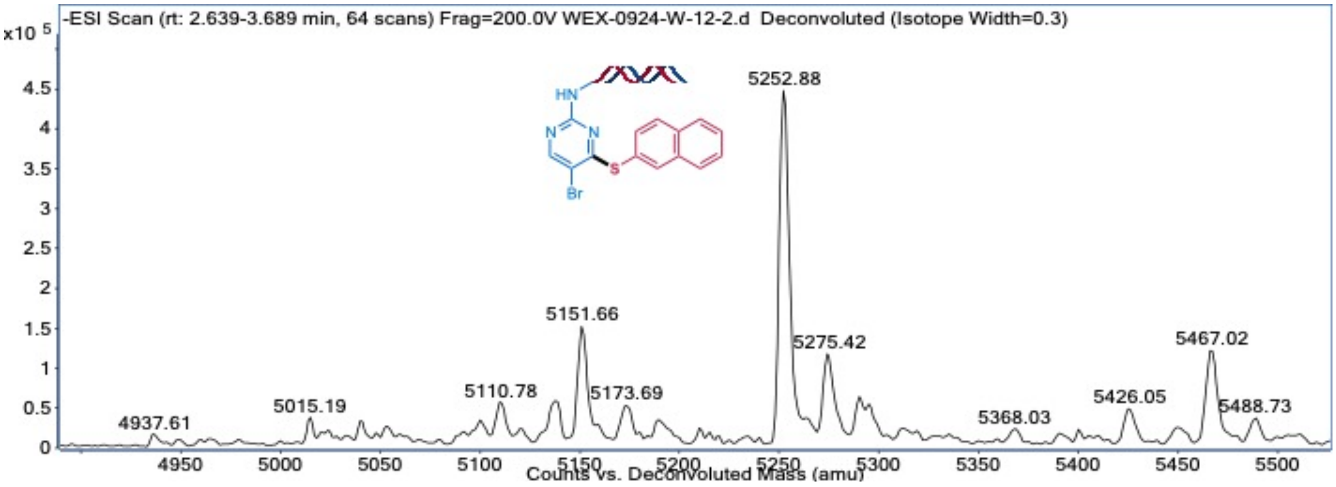
Compound **16j**



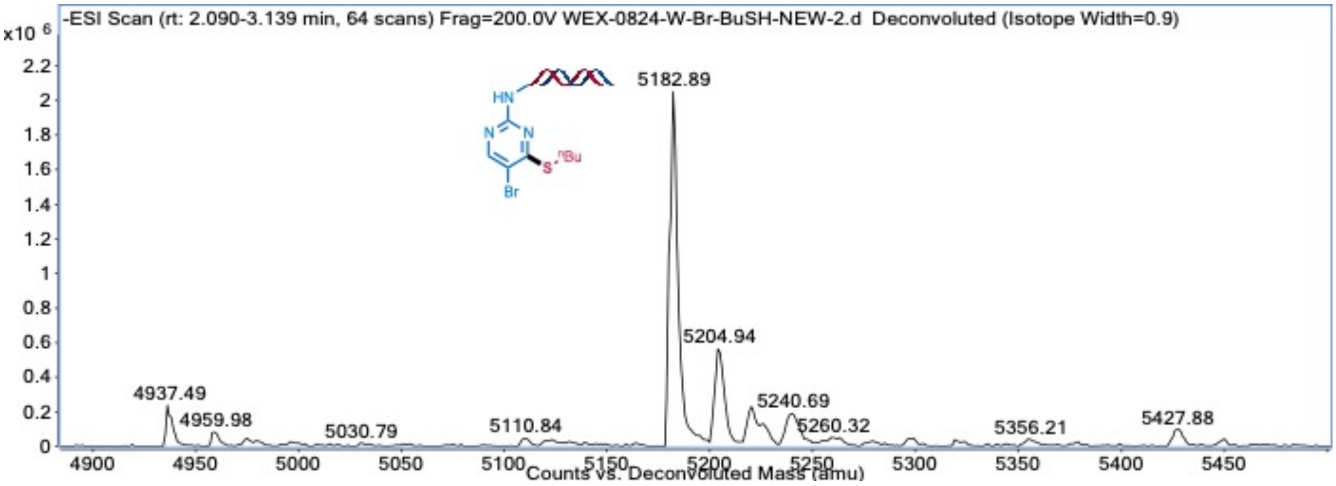
Compound **16k**



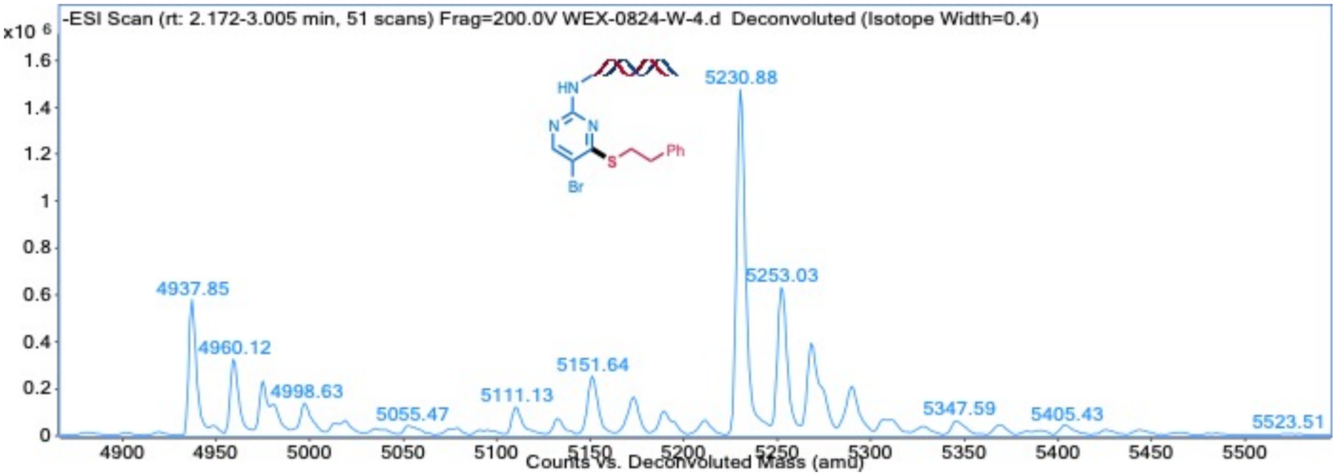
Compound **16l**



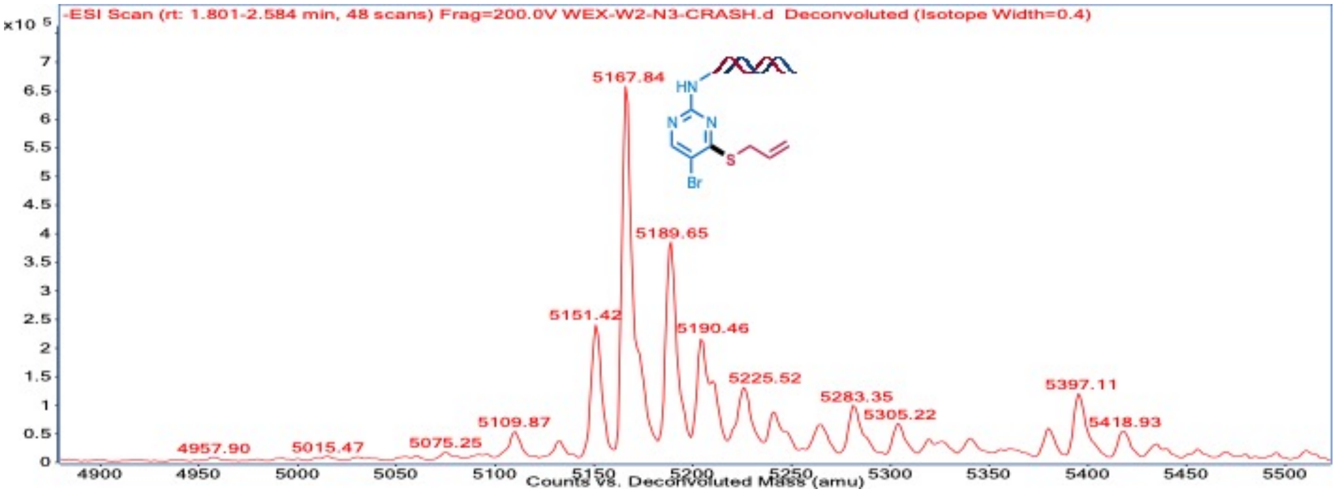
Compound **16m**



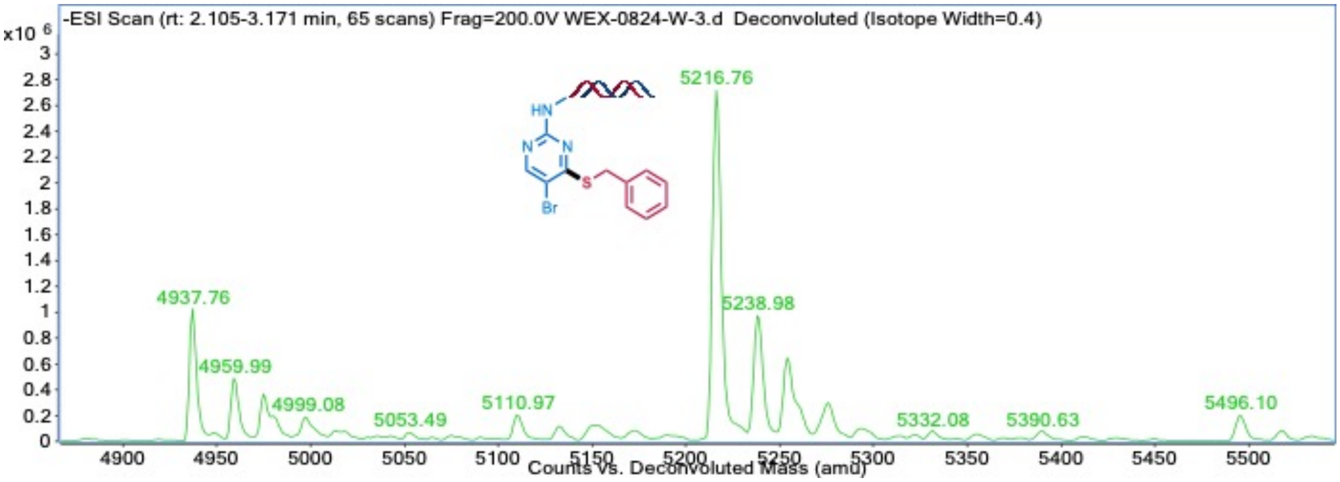
Compound **16n**



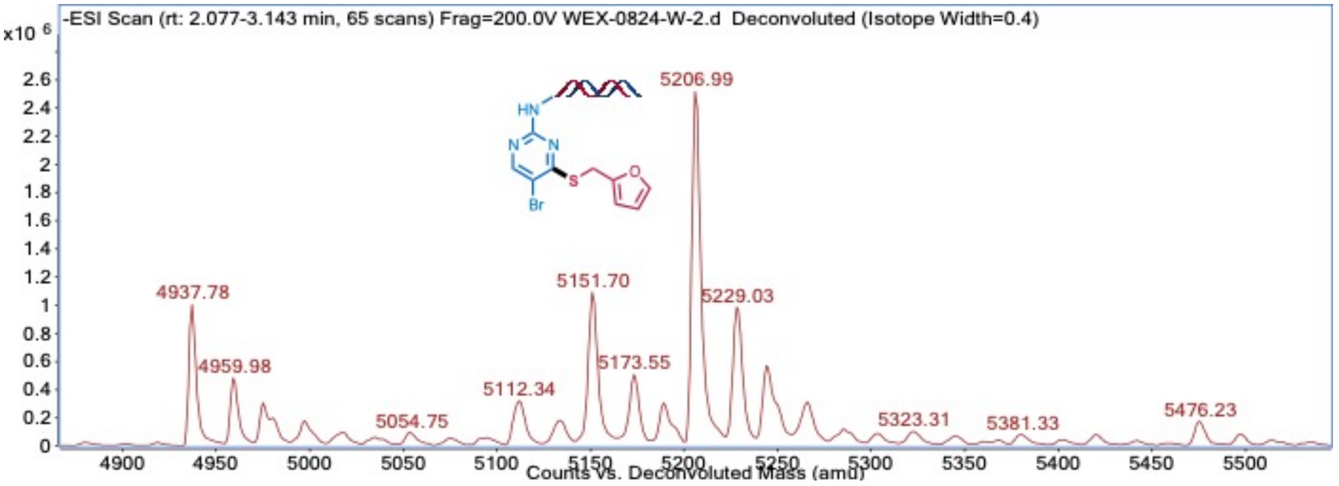
Compound **16o**



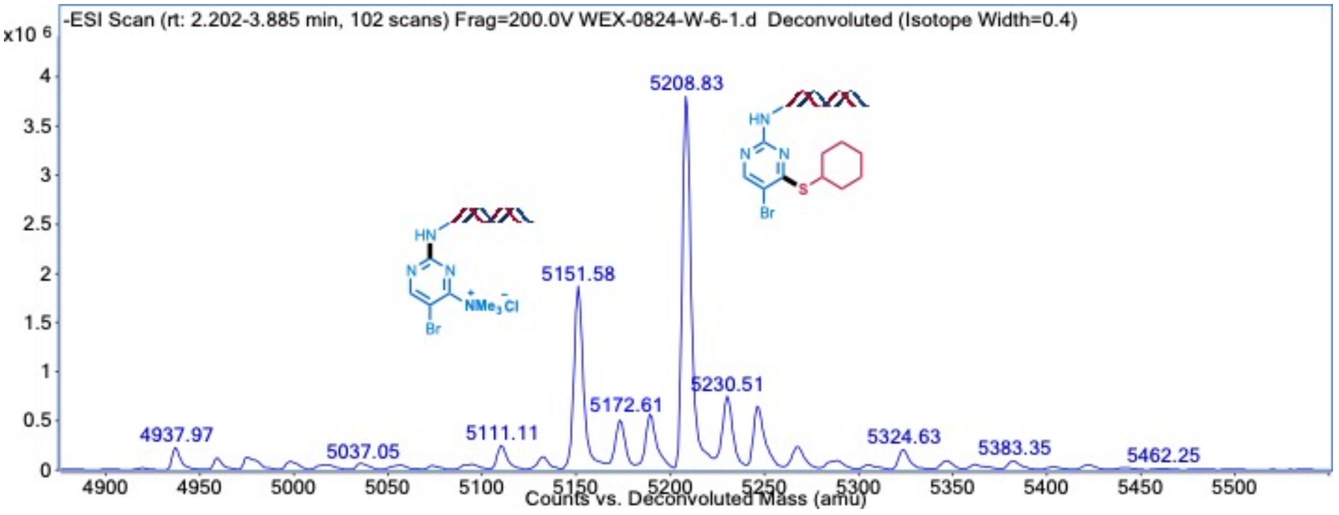
Compound **16p**



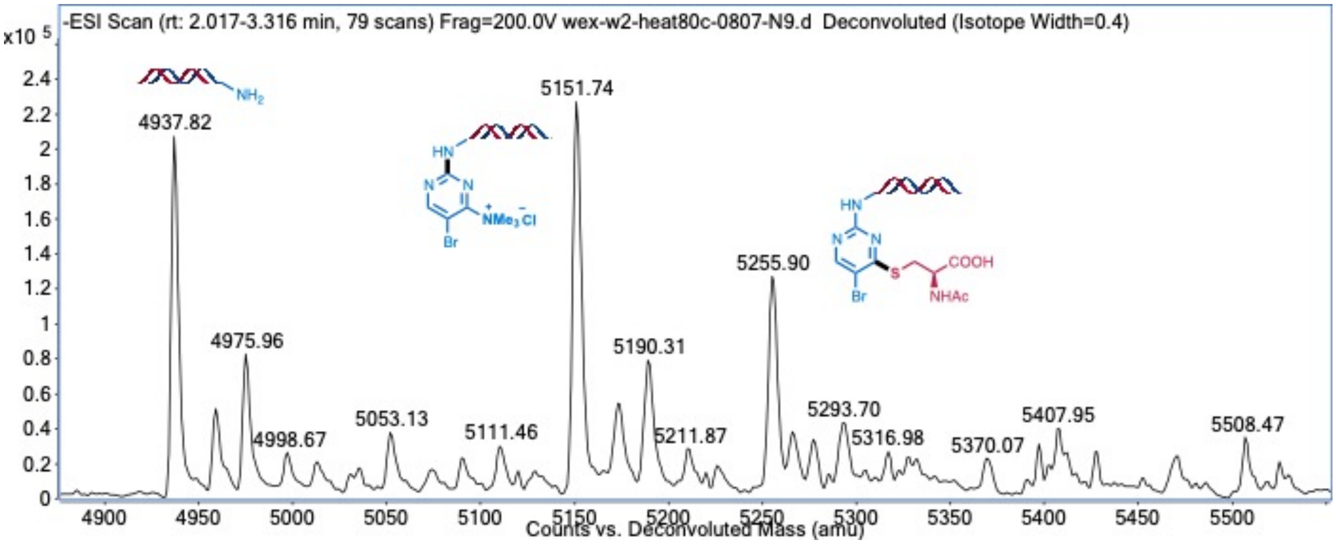
Compound **16q**



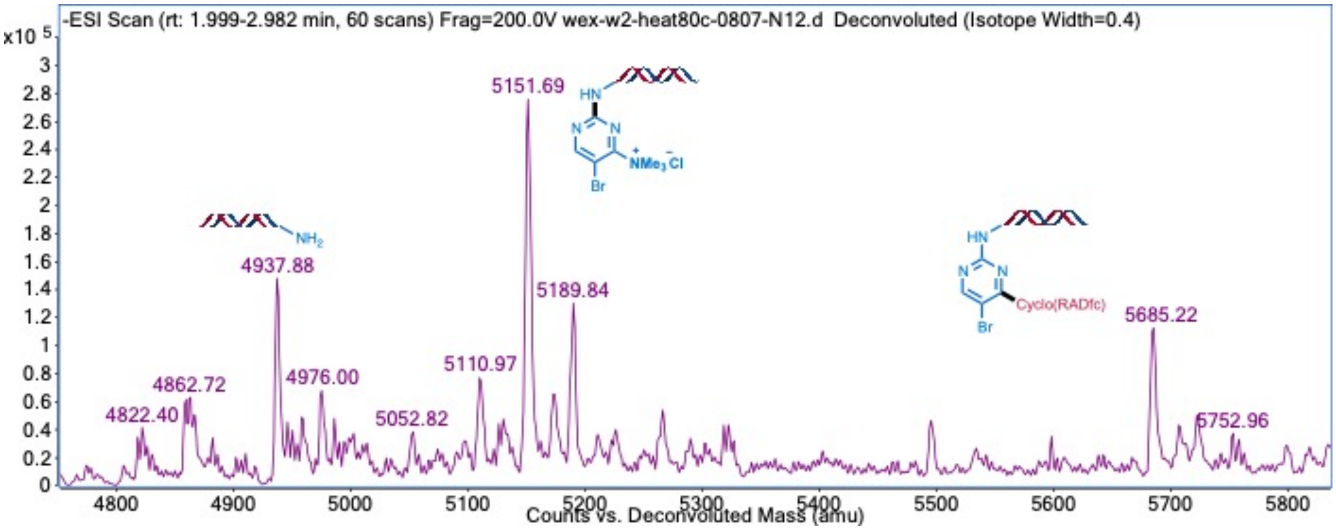
Compound **16r**



Compound **16s**



Compound **16t**



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