Oxidative thiocyanation of allylic alcohols: an easy access to allylic thiocyanate within $K_2S_2O_8$ and NH_4SCN

Keyuan Zhang,[a] Tianbing Liang,[a] Yulong Wang,[a] Chonglong He,[a] Mingyou Hu,[a] Xin-Hua Duan[a] and Le Liu*[a]

[a] School of Chemistry, Xi'an Key Laboratory of Sustainable Energy Material Chemistry, and MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi’an Jiaotong University, Xi’an 710049, China.

Supplementary information

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1. General information

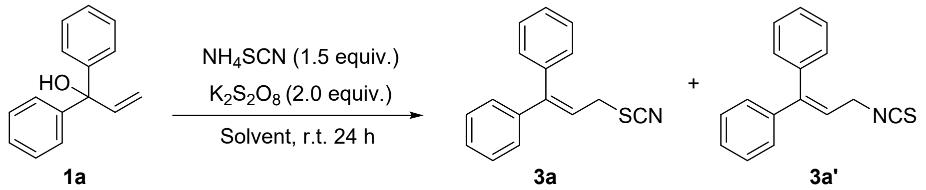
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance and JEOL III–400 spectrometer at 25 °C in solvents as indicated. Chemical shift values are reported in ppm with the solvent resonance refereed to the standard position ($CDCl_3$: ^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.00$). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants *J* are reported in Hertz (Hz). HRMS were obtained on a QTOF micro spectrometer. Melting points were measured using open glass capillaries in SGW® X-4A apparatus.

All reactions were conducted in oven–dried Round bottom flask under an atmosphere of air. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Conversion of the reactions was monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh). All the allylic alcohols were prepared according to reported method.[1]

2. Optimization of the reaction conditions

2.1 Optimization of reaction conditions for tertiary allylic alcohol

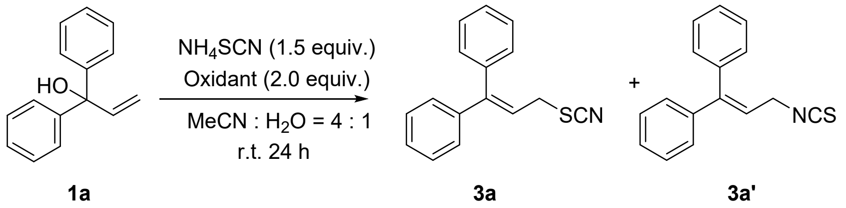
Table S1: Screening of the solvents



Entry[a]	**Solvent**	Yield of **3a**[b] (%)	Yield of **3a'**[b] (%)
1	DCE/H_2O (4:1, v/v)	51	8
2	Dioxane/H_2O (4:1)	74	17
3	Toluene/H_2O (4:1)	36	trace
4	$PhCF_3$/H_2O (4:1)	45	13
5	EtOH/H_2O (4:1)	25	trace
6	MeCN/H_2O (4:1)	87	8
7	MeCN	41	13
8	HFIP/H_2O (4:1)	57	26

[a] All the reactions were carried out with 1,1-diphenylprop-2-en-1-ol **1a** (0.2 mmol), NH_4SCN (0.3 mmol) and $K_2S_2O_8$ (0.4 mmol) in the indicated solvent (2.0 mL) under air at r.t. for 24 h. [b] Isolated yield.

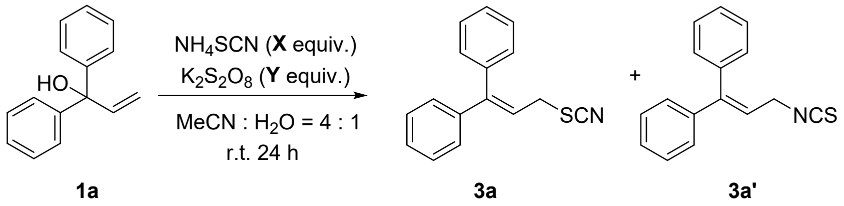
Table S2: Screening of the oxidants



Entry[a]	**Oxidant**	Yield of **3a**[b] (%)	Yield of **3a'** [b] (%)
1	$K_2S_2O_8$	87	8
2	PIDA	66	23
3	PIFA	62	14

[a] All the reactions were carried out with 1,1-diphenylprop-2-en-1-ol **1a** (0.2 mmol), NH_4SCN (0.3 mmol) and the indicated oxidant (0.4mmol) in MeCN/H_2O (4:1, v/v) (2.0 mL) under air at r.t. for 24 h. [b] Isolated yield.

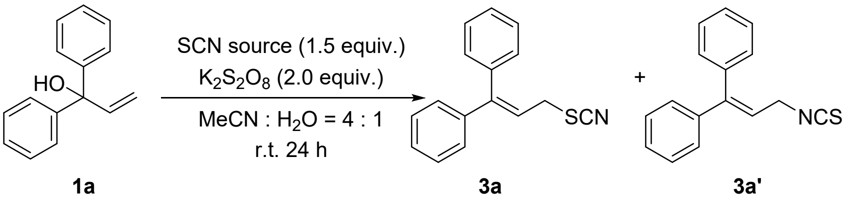
Table S3: Optimization of loading of NH_4SCN and oxidant



Entry^{a}	**X**	**Y**	Yield of **3a**^{b} (%)	Yield of **3a'** ^{b} (%)
1	1.5	2.0	87	8
2	1.5	1.5	69	14
3	2.0	2.0	70	20

^{a} All the reactions were carried out with 1,1-diphenylprop-2-en-1-ol **1a** (0.2 mmol), NH_4SCN (**X** equiv.) and K_2S_2O8 (**Y** equiv.) in MeCN/H_2O (4:1, v/v) (2.0 mL) under air at r.t. for 24 h. ^{b} Isolated yield.

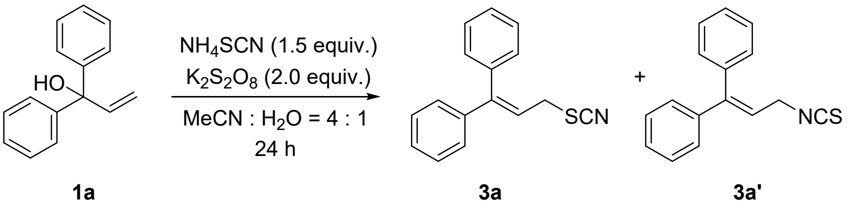
Table S4: Optimization of SCN source



Entry^{a}	**XSCN**	Yield of **3a**^{b} (%)	Yield of **3a'** ^{b} (%)
1	NaSCN	20	trace
2	KSCN	77	trace
3	NH_4SCN	87	8

^{a} All the reactions were carried out with 1,1-diphenylprop-2-en-1-ol **1a** (0.2 mmol), SCN source (0.3 mmol) and $K_2S_2O_8$ (0.4 mmol) in MeCN/H_2O (4:1, v/v) (2.0 mL) under air at rt for 24 h. ^{b} Isolated yield.

Table S5: Evaluation of the reaction temperature

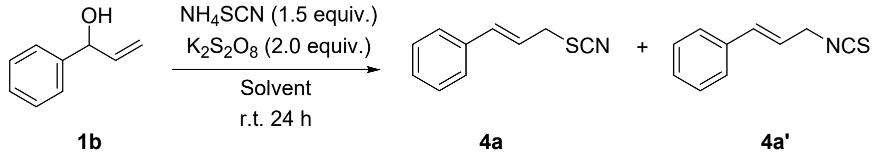


Entry^{a}	**Temperature**	Yield of **3a**^{b} (%)	Yield of **3a'** ^{b} (%)
1	25 °C	87	8
2	45 °C	76	21

^{a} All the reactions were carried out with 1,1-diphenylprop-2-en-1-ol **1a** (0.2 mmol), NH_4SCN (0.3 mmol) and $K_2S_2O_8$ (0.4 mmol) in MeCN/H_2O (4:1, v/v) (2.0 mL) under air at r.t. for 24 h. ^{b} Isolated yield.

2.2 Optimization of reaction conditions for secondary allylic alcohol

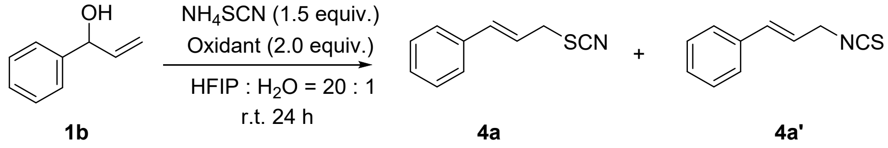
Table S6: Screening of the solvents



Entry[a]	**Solvent**	Yield of **4a**[b] (%)	Yield of **4a'**[b] (%)
1	DCE/H_2O (4:1, v/v)	43 (E/Z = 2 : 1)	11 (E/Z = 2 : 1)
2	Dioxane/H_2O (4:1)	26 (E/Z > 20 : 1)	17 (E/Z > 20 : 1)
3	Toluene/H_2O (4:1)	27 (E/Z > 20 : 1)	15 (E/Z > 20 : 1)
4	THF/H_2O (4:1)	trace	trace
5	EtOH/H_2O (4:1)	34 (E/Z > 20 : 1)	12 (E/Z > 20 : 1)
6	MeCN/H_2O (4:1)	17 (E/Z > 20 : 1)	trace
7	DMSO/H_2O (4:1)	trace	trace
8	HFIP/H_2O (4:1)	66 (E/Z > 20 : 1)	33 (E/Z > 20 : 1)
9	HFIP	54 (E/Z > 20 : 1)	12 (E/Z > 20 : 1)
10	HFIP/MeCN/H_2O (4:4:1)	39 (E/Z > 20 : 1)	22 (E/Z > 20 : 1)
11	TFE/H_2O (4:1)	54 (E/Z > 20 : 1)	31 (E/Z > 20 : 1)
12	$CHCl_3$/H_2O (4:1)	trace	trace
13	HFIP/H_2O (20:1)	70 (E/Z > 20 : 1)	25 (E/Z > 20 : 1)

[a] All the reactions were carried out with 1-phenylprop-2-en-1-ol **1b** (0.2 mmol), NH_4SCN (0.3 mmol) and $K_2S_2O_8$ (0.4 mmol) in the indicated solvent (2.0 mL) under air at r.t. for 24 h. [b] Isolated yield and the E/Z selectivity was determined by crude ^{1}HNMR spectroscopy.

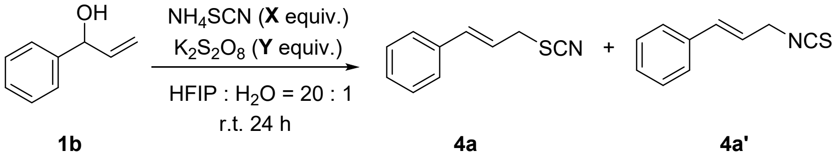
Table S7: Screening of the oxidant



Entry[a]	**Oxidant**	Yield of **4a**[b] (%)	Yield of **4a'**[b] (%)
1	$K_2S_2O_8$	70 (E/Z > 20 : 1)	25 (E/Z > 20 : 1)
2	PIDA	40 (E/Z > 20 : 1)	8 (E/Z > 20 : 1)
3	PIFA	trace	trace

[a] All the reactions were carried out with 1-phenylprop-2-en-1-ol **1b** (0.2 mmol), NH_4SCN (0.3 mmol) and the indicated oxidant (0.4 mmol) in HFIP/H_2O (20:1, v/v) (2.0 mL) under air at r.t. for 24 h. [b] Isolated yield and the E/Z selectivity was determined by crude ^{1}HNMR spectroscopy.

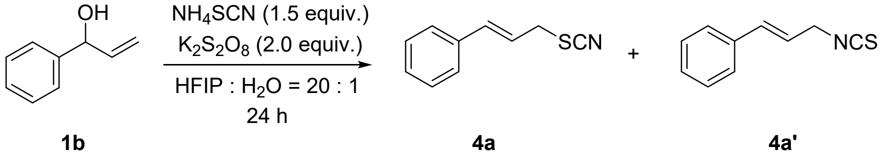
Table S8: Optimization of loading of NH_4SCN and Oxidant



Entry[a]	X	Y	Yield of **4a**[b] (%)	Yield of **4a'**[b] (%)
1	1.5	2.0	70 (E/Z > 20 : 1)	25 (E/Z > 20 : 1)
2	1.5	1.5	49 (E/Z > 20 : 1)	45 (E/Z > 20 : 1)
3	2.0	2.0	58 (E/Z > 20 : 1)	31 (E/Z > 20 : 1)

[a] All the reactions were carried out with 1-phenylprop-2-en-1-ol **1b** (0.2 mmol), NH_4SCN (**X** equiv.) and K_2S_2O8 (**Y** equiv.) in HFIP/H_2O (20:1, v/v) (2.0 mL) under air at rt for 24 h. [b] Isolated yield and the *E/Z* selectivity was determined by crude ^{1}HNMR spectroscopy.

Table S9: Evaluation of reaction temperature



Entry[a]	temperature	Yield of **3a**[b] (%)	Yield of **3a'**[b] (%)
1	25 °C	70 (E/Z > 20 : 1)	25 (E/Z > 20 : 1)
2	45 °C	45 (E/Z > 20 : 1)	41 (E/Z > 20 : 1)
3	55 °C	trace	trace

[a] All reactions were carried out with 1-phenylprop-2-en-1-ol **1b** (0.2 mmol), NH_4SCN (0.3 mmol), $K_2S_2O_8$ (0.4 mmol) in HFIP/H_2O (20:1, v/v) (2.0 mL) under air at r.t. for 24 h. [b] Isolated yield and the *E/Z* selectivity was determined by crude ^{1}HNMR spectroscopy.

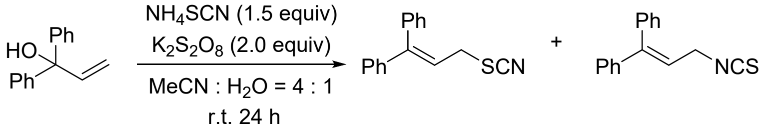
3. General Procedures

General procedure for preparation of allyl alcohols[1]

Scheme to show the reaction for the preparation of allylic alcohols

To a solution of aldehyde/ketone (5 mmol) in dry THF was added vinylmagnesium bromide (1 M in THF, 1.2 equiv.) under nitrogen by a syringe over 5 min at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with a saturated NH_4Cl aqueous solution (20 mL) and extracted with ethyl acetate (3×70 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduce pressure to give the crude allylic alcohols which was purified by a flash chromatograph (PE/EA) on silica gel to afford the corresponding pure ones.

General procedure for $K_2S_2O_8$ promoted thiocyanation of α,α-diaryl allylic alcohols with NH_4SCN

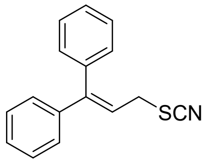


1 **3a** **3a'**

To a solution of α,α-diaryl allylic alcohols (**1**, 0.2 mmol) and NH_4SCN (0.3 mmol) in $MeCN/H_2O$ (4:1, v/v) (2 mL), $K_2S_2O_8$ (0.4 mmol) were added at 25 °C under air atmosphere. The reaction was then stirred for 24 hours and the progress was monitored by TLC. After the reactions were completed, the reaction mixture was diluted with water (10 mL) and extracted with EA (3×10 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduce pressure to give crude product which was purified by a flash chromatograph (PE/EA) on silica gel to afford the corresponding pure allylic thiocyanate.

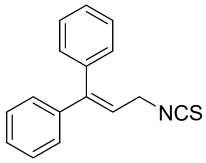
4. Characterization of products

(3-Thiocyanatoprop-1-ene-1,1-diyl) dibenzene (3a)



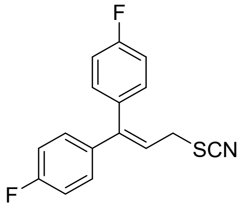
87% yield, 43.7 mg; white soild, mp. 66–68 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.39 (m, 3H), 7.32 – 7.26 (m, 5H), 7.23 – 7.20 (m, 2H), 6.22 (t, *J* = 8.0 Hz, 1H), 3.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 140.6, 137.8, 129.7, 128.7, 128.3 (two peaks overlapped), 128.1, 127.6, 119.9, 111.9, 33.6; HRMS (ESI) m/z calcd for $C_{15}H_{13}^+$ [M -SCN]$^+$ m/z 193.1012, found m/z 193.1007.

(3-Isothiocyanatoprop-1-ene-1,1-diyl) dibenzene (3a')



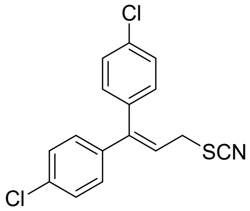
73% yield, 36,7 mg; yellow oil;^1H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 3H), 7.32 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 7.17 – 7.15 (m, 2H), 6.14 (t, *J* = 7.1 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 140.7, 137.9, 129.4, 128.6, 128.3, 128.2, 128.1, 127.6, 120.2 (two peaks overlapped), 44.4; HRMS (ESI) m/z calcd for $C_{16}H_{14}NS^+$ [M + H]$^+$ m/z 252.0842, found m/z 252.0870.

4,4'-(3-Thiocyanatoprop-1-ene-1,1-diyl) bis(fluorobenzene) (3b)



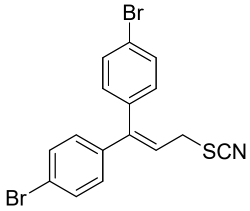
86% yield, 49.4 mg; yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 – 7.10 (m, 6H), 7.03 – 6.97 (m, 2H), 6.16 (t, J = 8.0 Hz, 1H), 3.67 (d, J = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, CDCl$_3$) δ -112.8(9) – -112.9(5) (m, 1F), 112.9(7) – 113.0 (m, 1F); ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.9 (d, $J_{C–F}$ = 34.5 Hz), 161.5 (d, $J_{C–F}$ = 34.0 Hz), 146.4, 136.7 (d, $J_{C–F}$ = 3.3 Hz), 133.5 (d, $J_{C–F}$ = 3.6 Hz), 131.4 (d, $J_{C–F}$ = 8.1 Hz), 129.3 (d, $J_{C–F}$ = 8.2 Hz), 120.3, 115.8 (d, $J_{C–F}$ = 21.5 Hz), 115.3 (d, $J_{C–F}$ = 21.6 Hz), 111.6, 33.4; HRMS (ESI) m/z calcd for $C_{15}H_{12}F_2^+$ [M - SCN]$^+$ m/z 229.0824, found m/z 229.0832.

4,4'(3-Thiocyanatoprop-1-ene-1,1-diyl) bis(chlorobenzene) (3c)



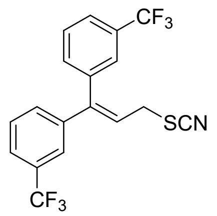
70% yield, 44.8 mg; White solid; mp. 60–62 °C;^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 - 7.40 (m, 2H), 7.30 – 7.26 (m, 2H), 7.19 – 7.12 (m, 4H), 6.21 (t, J = 8.0 Hz, 1H), 3.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.1, 138.7, 135.7, 134.6, 134.4, 131.0, 129.1, 128.8, 128.6, 121.0, 111.5, 33.2; HRMS (ESI) m/z calcd for $C_{15}H_{11}{}^{35}Cl_2$ [M - SCN]$^+$ m/z 261.0233, found m/z 261.0238.

4,4'-(3-Thiocyanatoprop-1-ene-1,1-diyl) bis(bromobenzene) (3d)



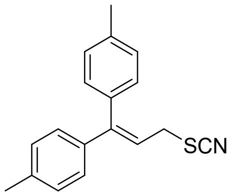
68% yield, 55.5 mg; white soild, mp. 93–95 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 - 7.55 (m, 2H), 7.45 – 7.42 (m, 2H), 7.13 – 7.06 (m, 4H), 6.22 (t, J = 8.0 Hz, 1H), 3.65 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.2, 139.0, 136.1, 132.1, 131.6, 131.3, 129.1, 122.8, 122.6, 121.0, 111.5, 33.2; HRMS (ESI) m/z calcd for $C_{15}H_{11}{}^{79}Br_2$ [M - SCN]$^+$ m/z 348.9223, found m/z 348.9231.

3,3'-(3-Thiocyanatoprop-1-ene-1,1-diyl) bis ((trifluoromethyl)benzene) (3e)



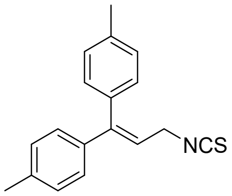
71% yield, 54.7 mg; yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (d, J = 7.9 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.51 – 7.44 (m, 4H), 7.39 (d, J = 7.9 Hz, 1H), 6.34 (t, J = 7.9 Hz, 1H), 3.65 (d, J = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, CDCl$_3$) δ -62.8(5) (S, 3F), -62.8(7) (S, 3F); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.7, 140.7, 137.8, 133.1, 131.5 (q, $J_{C–F}$ = 32.7 Hz), 131.4 (q, $J_{C–F}$ = 33.0 Hz), 130.9, 129.6, 129.2, 126.3(q, $J_{C–F}$ = 3.8 Hz), 125.4(q, $J_{C–F}$ = 3.8 Hz), 125.4(q, $J_{C–F}$ = 3.7 Hz), 124.0(q, $J_{C–F}$ = 3.7 Hz), 123.8(q, $J_{C–F}$ = 271.1 Hz), 123.7(q, $J_{C–F}$ = 270.5 Hz), 123.0, 111.3, 32.9; HRMS (ESI) m/z calcd for $C_{18}H_{11}F_6NSNa^+$ [M + Na]$^+$ m/z 410.0409, found m/z 410.0418.

4,4'-(3-Thiocyanatoprop-1-ene-1,1-diyl) bis(methylbenzene) (3f)



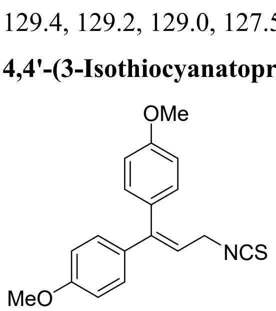
34% yield, 19.0 mg; yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 (d, J = 7.8 Hz, 2H), 7.17 – 7.07 (m, 6H), 6.15 (t, J = 8.0 Hz, 1H), 3.71 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.4, 138.3, 138.0, 137.8, 135.0, 129.6, 129.3, 129.0, 127.5, 118.7, 112.0, 33.9, 21.2, 21.1; HRMS (ESI) m/z calcd for $C_{17}H_{17}$ [M - SCN]$^+$ m/z 221.1325, found m/z 221.1331.

4,4'-(3-Isothiocyanatoprop-1-ene-1,1-diyl) bis(methylbenzene) (3f')



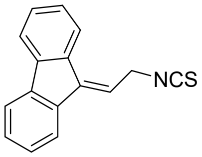
43% yield, 24.0 mg; white soild, mp. 90–92 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 (d, J = 7.8 Hz, 2H), 7.15 – 7.09 (m, 4H), 7.03 (d, J = 8.0 Hz, 2H), 6.08 (t, J = 7.1 Hz, 1H), 4.14 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.7, 138.1 (two peaks overlapped), 137.8, 135.1, 129.4, 129.2, 129.0, 127.5, 119.0 (two peaks overlapped), 44.5, 21.2, 21.1.

4,4'-(3-Isothiocyanatoprop-1-ene-1,1-diyl) bis(methoxybenzene) (3g')



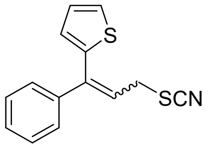
47% yield, 29.2 mg; yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 - 7.16 (m, 2H), 7.08 – 7.06 (m, 2H), 6.94 – 6,92 (m, 2H), 6.84 – 6,82 (m, 2H), 6.00 (t, J = 7.2 Hz, 1H), 4.14 (d, J = 7.0 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.7, 159.3, 146.1, 133.7, 130.9, 130.7, 130.4, 128.9, 118.0, 113.9, 113.6, 55.3, 44.6, 29.7; HRMS (ESI) m/z calcd for $C_{18}H_{18}NO_2S^+$ [M + H]$^+$ m/z 312.1053, found m/z 312.1058.

9-(2-Isothiocyanatoethylidene)-9H-fluorene (3h')



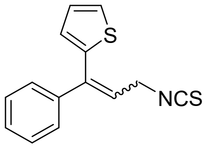
58% yield, 28.9 mg; white soild, mp. 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.71 (m, 2H), 7.67 – 7.65 (m, 2H), 7.44 – 7.28 (m, 4H), 6.68 (t, *J* = 8.4 Hz, 1H), 4.41 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.0, 139.4, 138.1, 135.7, 129.4, 129.2, 127.5, 127.4, 125.2, 120.6, 120.3, 119.7, 118.3, 111,6, 32.5; HRMS (ESI) m/z calcd for $C_{16}H_{11}NSNa^+$ [M + Na]$^+$ m/z 272.0505, found m/z 272.0516.

2-(1-Phenyl-3-thiocyanatoprop-1-en-1-yl) thiophene (3i)



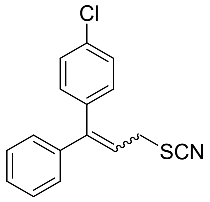
37% yield, 19.4 mg; yellow oil; *E/Z* = 3 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, E/Z mixture) δ major isomer 7.48 - 7.40 (overlapped, 3H), 7.34 (overlapped, 1H), 7.26– 7.25 (m, 2H), 6.93 (q, *J* = 3.6 Hz, 1H), 6.69 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 6.24 (t, *J* = 8.1 Hz, 1H), 3.62 (d, *J* = 8.1 Hz, 2H); minor isomer 7.48 - 7.40 (overlapped, 3H), 7.34 (overlapped, 1H), 7.31– 7.28 (m, 2H), 7.11 (q, *J* = 3.5 Hz, 1H), 7.04 (dd, J_1 = 3.6 Hz, J_2 = 1.3 Hz, 1H), 6.18 (t, *J* = 8.0 Hz, 1H), 3.90 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 144.7, 142.1, 136.8, 129.4, 128.7, 128.4, 127.7, 127.4, 126.0, 117.9 (two peaks overlapped), 33.7; minor isomer 143.4, 138.8, 134.9, 128.9, 128.3, 127.5, 127.2, 127.1(8), 122.2, 111.8 (two peaks overlapped), 33.6; HRMS (ESI) m/z calcd for $C_{14}H_{12}NS_2^+$ [M + H]$^+$ m/z 258.0406, found m/z 258.0423.

2-(3-isothiocyanato-1-phenylprop-1-en-1-yl) thiophene (3i')



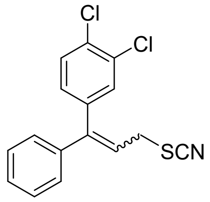
21% yield, 10.8 mg; yellow oil; *E/Z* = 5 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, E/Z mixture) δ major isomer 7.46 - 7.40 (overlapped, 3H), 7.26-7.23 (m, 3H), 6.93 (dd, J_1 = 5.1 Hz, J_2 = 3.6 Hz, 1H), 6.69 (dd, J_1 = 3.7 Hz, J_2 = 1.2 Hz, 1H), 6.17 (t, *J* = 7.2 Hz, 1H), 4.06 (d, *J* = 7.2 Hz, 2H); minor isomer 7.46 - 7.40 (overlapped, 3H), 7.34– 7.33 (m, 3H), 7.09 (dd, J_1 = 5.2 Hz, J_2 = 3.5 Hz, 1H), 6.97 (dd, J_1 = 3.5 Hz, J_2 = 1.2 Hz, 1H), 6.07 (t, *J* = 7.0 Hz, 1H), 4.37 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 144.7, 140.6, 137.0, 129.1, 128.6, 128.4(5), 127.5, 127.2, 125.7, 118.2 (two peaks overlapped), 44.0 (overlapped); 142.5, 138.0, 128.7, 128.5(4), 128.3, 127.8, 127.1(3), 127.1(0) 122.4 (two peaks overlapped), 44.0 (overlapped); HRMS (ESI) m/z calcd for $C_{14}H_{12}NS_2^+$ [M + H]$^+$ m/z 258.0406, found m/z 258.0423.

1-Chloro-4-(1-phenyl-3-thiocyanatoprop-1-en-1-yl) benzene (3j)



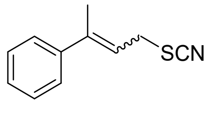
77% yield, 44.0 mg; yellow oil; *E/Z* = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, E/Z mixture) δ first isomer 7.46 - 7.40 (overlapped, 3H), 7.32 - 7.24 (overlapped, 3H), 7.29 – 6,24 (overlapped, 3H), 6.25 - 6.19 (overlapped, 1H), 3.69 - 3.66 (overlapped, 2H); second isomer 7.46 - 7.40 (overlapped, 2H), 7.32 - 7.24 (overlapped, 4H), 7.29 - 6,24 (overlapped, 3H), 6.25 - 6.19 (overlapped, 1H), 3.69 - 3.66 (overlapped, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ first isomer 147.2 (overlapped, 1C), 139.1, 136.2, 134.3, 131.1, 128.8(3), 128.7(5), 128.4(8), 127.5, 120.4, 111.7, 33.3(9); second isomer 147.2 (overlapped, 1C), 140.2, 137.3, 134.1, 129.6, 128.9, 128.5(3), 128.4, 128.3, 120.5, 111.6, 33.3(6); HRMS (ESI) m/z calcd for $C_{16}H_{12}{}^{35}ClNSNa^+$ $[M + Na]^+$ m/z 308.0272, found m/z 308.0283.

1,2-Dichloro-4-(1-phenyl-3-thiocyanatoprop-1-en-1-yl) benzene (3k)



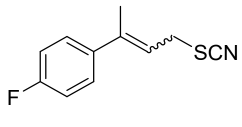
63% yield, 40.6 mg; yellow oil; *E/Z* = 1 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, E/Z mixture) δ first isomer 7.47 - 7.41 (overlapped, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.31 (overlapped, 2H), 7.26 - 7.23 (overlapped, 1H), 7.19 - 7.17 (overlapped, 1H), 7.11 - 7.08 (overlapped, 1H), 6.27 - 6.20 (overlapped, 1H), 3.68 - 3.66 (overlapped, 2H); second isomer 7.52 (d, *J* = 8.1 Hz, 1H), 7.47 - 7.41 (overlapped, 2H), 7.34 – 7.31 (overlapped, 2H), 7.26 - 7.23 (overlapped, 1H), 7.19 - 7.17 (overlapped, 1H), 7.11 - 7.08 (overlapped, 1H), 6.27 - 6.20 (overlapped, 1H), 3.68 - 3.66 (overlapped, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ first isomer 146.2, 140.6, 136.7, 132.6, 132.4, 130.3, 129.6, 129.3, 128.9, 128.6(overlapped, 1C), 127.5, 121.6, 111.5(4), 33.2; second isomer 146,1, 139.6, 137.8, 133.0, 132.5, 131.5, 130.8, 129.2, 128.8, 128.6 (overlapped, 1C), 126.8, 121.2, 111.4(5), 33.1(5); HRMS (ESI) m/z calcd for $C_{16}H_{11}NS^{35}Cl_2Na^+$ $[M + Na]^+$ m/z 341.9882, found m/z 341.9891.

(4-Thiocyanatobut-2-en-2-yl) benzene (3l)



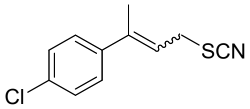
64% yield, 24.4 mg; yellow oil; *E/Z* = 3 : 1; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.37 – 7.30 (m, 3H), 5.93 – 5.88 (m, 1H), 3.86 (d, *J* = 8.2 Hz, 2H), 2.18 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 142.0, 128.4, 128.0, 126.0, 119.0, 112.1, 32.6, 16.3; HRMS (ESI) m/z calcd for $C_{10}H_{11}^+$ $[M – SCN]^+$ m/z 131.0856, found m/z 131.0869.

1-Fluoro-4-(4-thiocyanatobut-2-en-2-yl) benzene (3m)



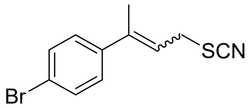
62% yield, 25.9 mg; yellow oil; *E/Z* = 2 : 1; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.35 (m, 2H), 7.06 – 7.00 (m, 2H), 5.89 – 5.83 (m, 1H), 3.84 (d, *J* = 8.2 Hz, 2H), 2.15 (d, *J* = 1.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2 – -114.3 (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, $J_{C–F}$ = 246.0 Hz), 142.2, 138.0 (d, $J_{C–F}$ = 3.3 Hz), 127.6 (d, $J_{C–F}$ = 8.1 Hz), 119.0, 115.2 (d, $J_{C–F}$ = 21.3 Hz), 112.0, 32.5, 16.4; HRMS (ESI) m/z calcd for $C_{10}H_{10}F$ [M – SCN]$^+$ m/z 149.0762, found m/z 149.0772 .

1-Chloro-4-(4-thiocyanatobut-2-en-2-yl) benzene (3n)



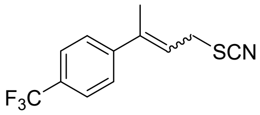
64% yield, 28.6 mg; yellow oil; *E/Z* = 4 : 1; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.28 (m, 4H), 5.92 – 5.87 (m, 1H), 3.83 (dd, J_1= 8.2 Hz J_2= 0.5 Hz, 2H), 2.15 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 140.3, 133.8, 128.5, 127.3, 119.5, 111.9, 32.4, 16.2; HRMS (ESI) m/z calcd for $C_{10}H_{10}{}^{35}Cl$ [M – SCN]$^+$ m/z 165.0466, found m/z 165.0477.

1-Bromo-4-(4-thiocyanatobut-2-en-2-yl) benzene (3o)



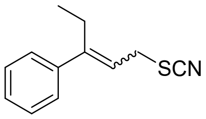
57% yield, 30.9 mg; yellow oil; *E/Z* = 3 : 1; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.45 (m, 2H), 7.29 – 7.26 (m, 2H), 5.92 – 5.87 (m, 1H), 3.83 (d, *J* = 8.2 Hz, 2H), 2.14 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.8, 131.5, 127.6, 122.0, 119.6, 111.9, 32.4, 16.2; HRMS (ESI) m/z calcd for $C_{10}H_{10}{}^{79}Br$ [M – SCN]$^+$ m/z 208.9961, found m/z 208.9976.

1-(4-Thiocyanatobut-2-en-2-yl)-4-(trifluoromethyl) benzene (3p)



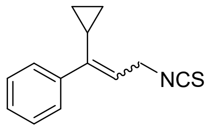
65% yield, 33.5 mg; yellow oil; *E/Z* = 4 : 1; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 5.99 – 5.94 (m, 1H), 3.84 (d, *J* = 8.2 Hz, 2H), 2.19 (d, *J* = 1.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5 (S, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 142.0, 130.0 (q, $J_{C–F}$ = 32.2 Hz), 126.4, 125.4 (q, $J_{C–F}$ = 3.8 Hz), 122.7, 121.1, 111.7, 32.2, 16.3; HRMS (ESI) m/z calcd for $C_{11}H_{10}F_3{}^+$ [M - SCN]$^+$ m/z 199.0730, found m/z 199.0739.

(1-Thiocyanatopent-2-en-3-yl) benzene (3q)



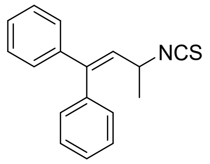
60% yield, 24.5 mg; yellow oil; *E/Z* = 1 : 1; specture date of the major one; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 4H), 7.34 – 7.31 (m, 1H), 5.75 (t, *J* = 8.3 Hz, 1H), 3.85 (d, *J* = 8.2 Hz, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 140.9, 128.4, 127.9, 126.6, 118.6, 112.1, 32.3, 23.2, 13.7; HRMS (ESI) m/z calcd for $C_{11}H_{13}{}^+$ [M – SCN]$^+$ m/z 145.1012, found m/z 145.1024 .

(1-Cyclopropyl-3-isothiocyanatoprop-1-en-1-yl) benzene (3r')



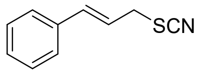
57% yield, 24.5 mg; yellow oil; *E/Z* = 5 : 1; ^{1}H NMR (400 MHz, $CDCl_3$, E/Z mixture)δ major isomer 7.42 - 7.26 (overlapped, 4H), 7.13 - 7.10 (overlapped, 1H), 6.60 - 6.54 (m, 1H), 5.69 (t, *J* = 7.4 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 4.76 (d, *J* = 17.3 Hz, 1H), 2.93 (t, *J* = 5.0 Hz, 2H), 2.46 (q, *J* = 7.2 Hz, 2H); minor isomer 7.42 - 7.26 (overlapped, 4H), 7.13 - 7.10 (overlapped, 1H), 6.86 - 6.80 (m, 1H), 5.51 (t, *J* = 7.6 Hz, 1H), 5.39 - 5.35 (m, 1H), 5.16 (dd, J_1 = 17.7 Hz, J_2 = 1.6 Hz, 1H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.85 (q, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ major isomer 145.0, 139.8, 132.3, 129.2, 128.4, 127.4, 126.3 (overlapped, 1C), 116.8, 112.2, 33.7(1), 33.7(0), 29.2(4), 29.2(3); minor isomer 143.3, 140.6, 136.6, 128.7, 128.1, 127.5, 126.3 (overlapped, 1C), 119.8, 112.1, 33.7(4), 33.7(3), 28.4(3) 28.4(2); HRMS (ESI) m/z calcd for $C_{13}H_{14}NS^+$ [M + H]$^+$ m/z 216.0842, found m/z 216.0832.

(3-Isothiocyanatobut-1-ene-1,1-diyl) dibenzene (3s')



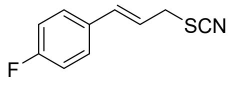
62% yield, 32.8 mg; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.32 – 7.28 (m, 3H), 7.24 – 7.22 (m, 2H), 7.19 – 7.17 (m, 2H), 6.04 (d, *J* = 9.6 Hz, 1H), 4.37– 4.29 (m, 1H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 140.6, 138.3, 129.4, 128.6, 128.3, 128.2, 128.0, 127.5, 126.6(overlapped, 1C), 52.7, 23.1; HRMS (ESI) m/z calcd for $C_{16}H_{15}^+$ [M - NCS]$^+$ m/z 207.1169, found m/z 207.1155.

(*E*)-(3-Thiocyanatoprop-1-en-1-yl) benzene (4a)



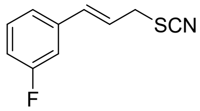
70% yield, 24.5 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.37 – 7.29 (m, 3H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.31 – 6.23 (m, 1H), 3.77 (dd, *J* = 7.7 Hz *J* = 1.1 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 136.5, 135.4, 128.7, 128.6, 126.8, 121.2, 111.8, 37.0; HRMS (ESI) m/z calcd for $C_{10}H_{10}NS^+$ [M + H]$^+$ m/z 176.0529, found m/z 176.0533.

(*E*)-1-Fluoro-4-(3-thiocyanatoprop-1-en-1-yl) benzene (4b)



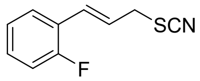
60% yield, 23.0 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.06 – 7.01 (m, 2H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.22 – 6.14 (m, 1H), 3.75 (dd, *J* = 7.6 Hz *J* = 1.1 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9 – -113.0 (m, 1F)^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{–}F}$ = 247.2 Hz), 135.3, 131.6 (d, $J_{C\text{–}F}$ = 3.4 Hz), 128.5 (d, $J_{C\text{–}F}$ = 8.2 Hz), 121.0 (d, $J_{C\text{–}F}$ = 2.3 Hz), 115.7 (d, $J_{C\text{–}F}$ = 21.7 Hz), 111.8, 36.8; HRMS (ESI) m/z calcd for $C_9H_8F^+$ [M – SCN]$^+$ m/z 135.0605, found m/z 135.0615.

(*E*)-1-Fluoro-3-(3-thiocyanatoprop-1-en-1-yl) benzene (4c)



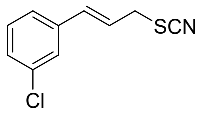
42% yield, 16.4 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.28 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.02 – 6.97 (m, 1H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.31 – 6.23 (m, 1H), 3.75 (dd, *J* = 7.6 Hz, *J* = 1.1 Hz, 2H); ^{19}F NMR (376 MHz, CDCl$_3$) δ -113.6(6) – -113.7(2) (m, 1F); ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.0 (d, $J_{C–F}$ = 244.6 Hz), 137.7 (d, $J_{C–F}$ = 7.8 Hz), 135.2 (d, $J_{C–F}$ = 2.7 Hz), 130.2 (d, $J_{C–F}$ = 8.3 Hz), 122.8 (d, $J_{C–F}$ = 2.8 Hz), 122.7, 115.4 (d, $J_{C–F}$ = 21.3 Hz), 113.2 (d, $J_{C–F}$ = 21.9 Hz), 111.6, 36.6; HRMS (ESI) m/z calcd for $C_9H_8F^+$ [M – SCN]$^+$ m/z 135.0605, found m/z 135.0616.

(*E*)-1-Fluoro-2-(3-thiocyanatoprop-1-en-1-yl) benzene (4d)



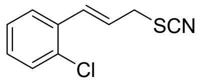
35% yield, 13.8 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.44 (m, 1H), 7.30 - 7.22 (m, 1H), 7.14 – 7.10 (m, 1H), 7.08 – 7.03 (m, 1H), 6.83 (d, *J* = 15.8 Hz, 1H), 6.41 – 6.33 (m, 1H), 3.78 (dd, *J* = 7.6 Hz *J* = 1.1 Hz, 2H); ^{19}F NMR (376 MHz, CDCl$_3$) δ -112.3 – -112.4 (m, 1F); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.4 (d, $J_{C–F}$ = 249.5 Hz), 129.9 (d, $J_{C–F}$ = 8.6 Hz), 129.1 (d, $J_{C–F}$ = 3.1 Hz), 127.9 (d, $J_{C–F}$ = 3.4 Hz), 124.3 (d, $J_{C–F}$ = 3.5 Hz), 123.9 (d, $J_{C–F}$ = 5.7 Hz), 123.3 (d, $J_{C–F}$ = 11.9 Hz), 115.9 (d, $J_{C–F}$ = 21.8 Hz), 111.7, 37.1; HRMS (ESI) m/z calcd for $C_{10}H_8FNSNa^+$ [M + Na]$^+$ m/z 216.0254, found m/z 216.0273.

(*E*)-1-Chloro-3-(3-thiocyanatoprop-1-en-1-yl) benzene (4e)



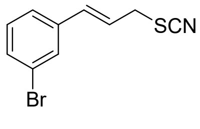
46% yield, 19.2 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.39 (m, 1H), 7.29 – 7.25 (m, 3H), 6.64 (d, *J* = 15.6 Hz, 1H), 6.32 – 6.24 (m, 1H), 3.75 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.2, 135.0, 134.7, 129.9, 128.6, 126.7, 125.1, 122.8, 111.6, 36.6; HRMS (ESI) m/z calcd for $C_{10}H_9ClNS^+$ [M + H]$^+$ m/z 210.0139, found m/z 210.0151.

(*E*)-1-Chloro-2-(3-thiocyanatoprop-1-en-1-yl) benzene (4f)



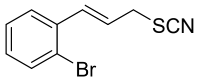
54% yield, 22.7 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.54 (m, 1H), 7.38 – 7.36 (m, 1H), 7.28 – 7.21 (m, 2H), 7.08 (d, *J* = 15.6 Hz, 1H), 6.39 – 6.22 (m, 1H), 3.79 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 133.7, 133.4, 132.6, 129.8, 129.6, 127.2, 127.0, 124.1, 111.6, 36.6; HRMS (ESI) m/z calcd for $C_{10}H_8{}^{35}ClNSNa^+$ [M + Na]$^+$ m/z 231.9959, found m/z 231.9971.

(*E*)-1-Bromo-3-(3-thiocyanatoprop-1-en-1-yl) benzene (4g)



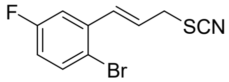
44% yield, 22.5 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (t, *J* = 1.9 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.33 – 7.31 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.31 – 6.23 (m, 1H), 3.75 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 137.5, 134.9, 131.4 (two peaks overlapped), 130.2, 129.6, 125.5, 122.8, 111.7, 36.6; HRMS (ESI) m/z calcd for $C_9H_8{}^{79}Br^+$ [M - SCN]$^+$ m/z 194.9804, found m/z 194.9817.

(*E*)-1-Bromo-2-(3-thiocyanatoprop-1-en-1-yl) benzene (4h)



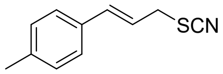
51% yield, 26 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.32 – 7.28 (m, 1H), 7.18 – 7.14 (m, 1H), 7.04 (d, *J* = 15.5 Hz, 1H), 6.25 – 6.18 (m, 1H), 3.79 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 135.1, 133.1, 129.8, 127.6, 127.4, 124.2, 123.8, 111.5, 36.5; HRMS (ESI) m/z calcd for $C_9H_8{}^{79}Br^+$ [M - SCN]$^+$ m/z 194.9804, found m/z 194.9816.

(*E*)-1-Bromo-4-fluoro-2-(3-thiocyanatoprop-1-en-1-yl) benzene (4i)



40% yield, 21.9 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J_1= 8.8 Hz J_2= 5.3 Hz, 1H), 7.25 (dd, J_1= 9.5 Hz J_2= 3.0 Hz, 1H), 6.99 (dd, J_1= 15.6 Hz J_2= 1.4 Hz, 1H), 6.93 – 6.88(m, 1H), 6.26 – 6.18 (m, 1H), 3.79 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9(8) – -115.0(4) (m, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, $J_{C–F}$ = 245.9 Hz), 137.1 (d, $J_{C–F}$ = 7.8 Hz), 134.3 (d, $J_{C–F}$ = 3.7 Hz), 134.3(d, $J_{C–F}$ = 2.0 Hz), 125.4, 117.9 (d, $J_{C–F}$ = 2.9 Hz), 117.1 (d, $J_{C–F}$ = 22.6 Hz), 114.1 (d, $J_{C–F}$ = 23.8 Hz), 111.3, 36.2; HRMS (ESI) m/z calcd for $C_9H_7BrF^+$ [M -SCN]$^+$ m/z 212.9710, found m/z 212.9722.

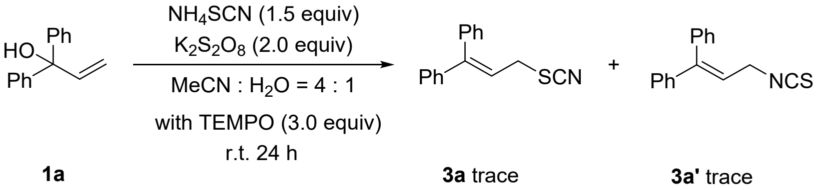
(*E*)-1-Methyl-4-(3-thiocyanatoprop-1-en-1-yl) benzene (4j)



26% yield, 9.7 mg; yellow oil; *E/Z* > 20 : 1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 15.5 Hz, 1H), 6.25 – 6.17 (m, 1H), 3.76 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.4, 132.6, 129.4, 126.7, 120.1, 111.9, 37.2, 21.2; HRMS (ESI) m/z calcd for $C_{11}H_{11}NSNa^+$ [M + Na]$^+$ m/z 212.0505, found m/z 212.0522.

5. Control experiments

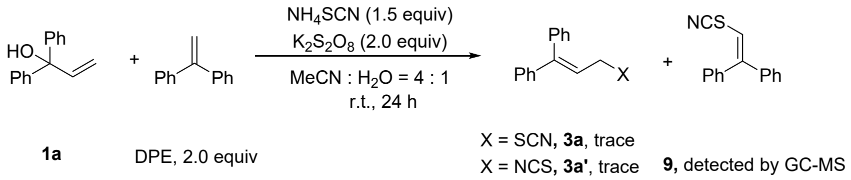
5.1 TEMPO inhibition

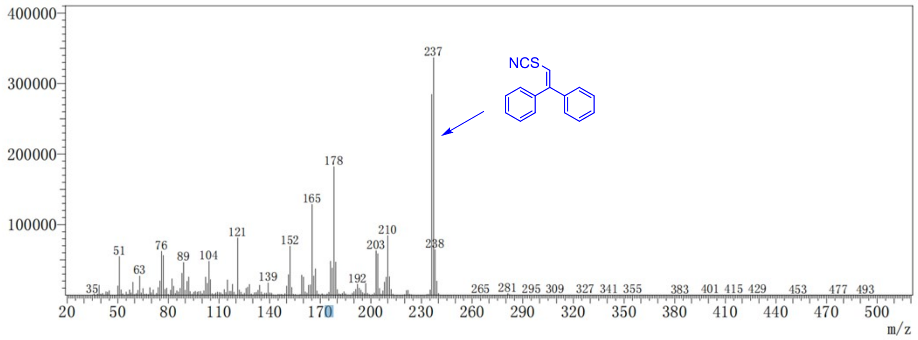


To a solution of 1,1-diphenylprop-2-en-1-ol (**1a**, 0.2 mmol) and NH_4SCN (0.3 mmol, 1.5 equiv.) in MeCN/H_2O (4:1, v/v) (2 mL) was added $K_2S_2O_8$ (0.4 mmol) at 25 °C under efficient stirring, followed by the addition of TEMPO (0.6 mmol, 3.0 equiv.). The reaction mixture was stirred for 24 hours. Afterwards, the reaction mixture was diluted with water (10 mL) and extracted with EA (3×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure to give crude residue, which was subjected to ^{1}HNMR analysis with trimethoxy benzene as internal standard. The results indicted that only trace amount of the target product **3a** and **3a'** was observed. And the original thiohydantoin process was completely inhibited

5.2 Ethene-1,1-diyldibenzene Inhibition

To a solution of 1,1-diphenylprop-2-en-1-ol (1a, 0.2 mmol) and NH_4SCN (0.3 mmol, 1.5 equiv.) in $MeCN/H_2O$ (4:1, v/v) (2 mL) was added $K_2S_2O_8$ (0.4 mmol) at 25 °C, followed by the addition of ethene-1,1-diyldibenzene (0.4 mmol, 2.0 equiv.). The reaction mixture was then stirred for 24 hours. Afterwards, the reaction mixture was diluted with water (10 mL and extracted with EA (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure to give crude residue, which was subjected to GC-MS and H-NMR analysis. The DPE-adduct **9** could be detected by GC-MS.

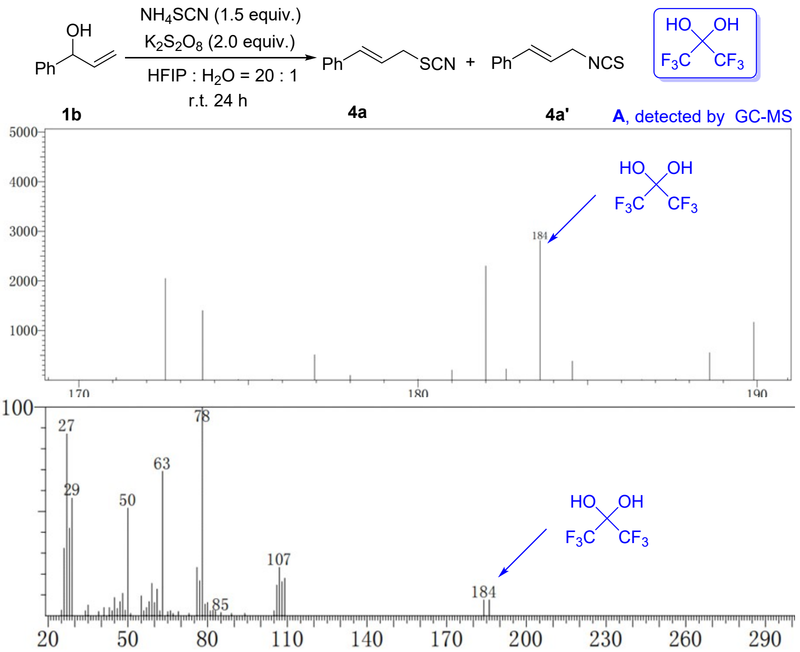




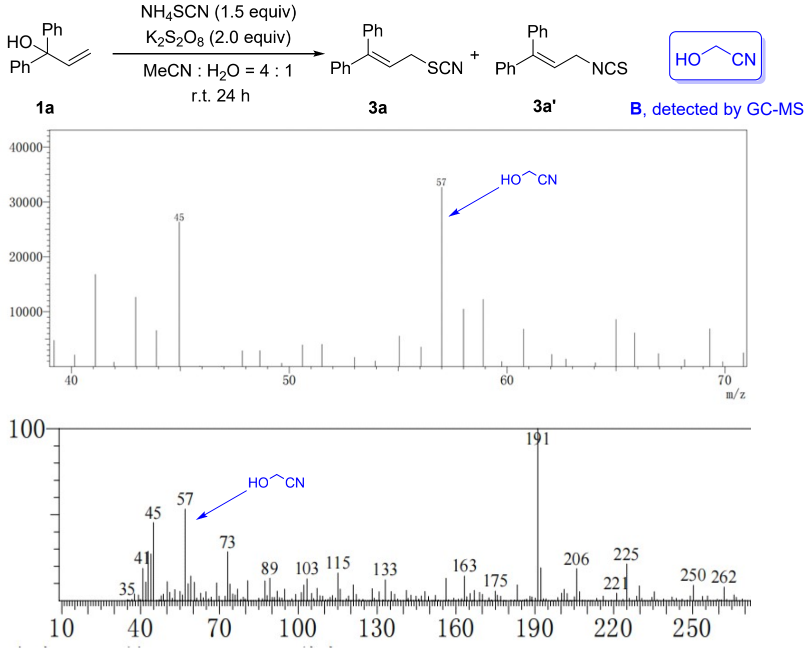
Note: these results indicated that a radical mechanistic pathway was involved in this oxidative thiocyanation reaction.

5.3 By-products A and B detection

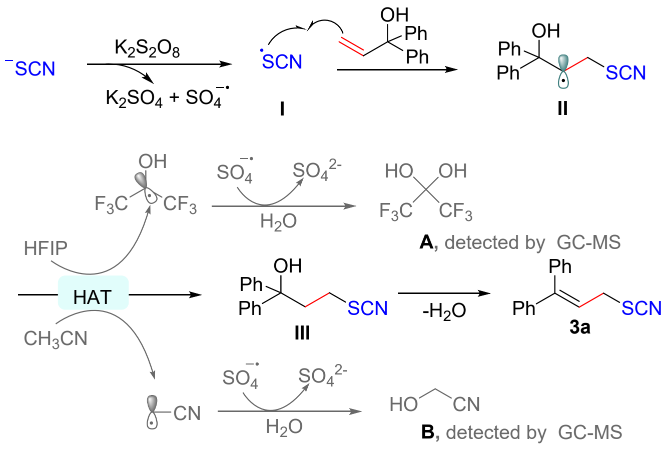
To a solution of 1-phenylprop-2-en-1-ol (**1a**, 0.2 mmol) and NH_4SCN (0.3 mmol, 1.5 equiv.) in $HFIP/H_2O$ (20:1, v/v) (2 mL) was added $K_2S_2O_8$ (0.4 mmol) at 25 °C under efficient stirring. The reaction mixture was stirred for 24 hours. Then, the reaction mixture was filtered and subjected to GC-MS analysis. The by-products **A** could be detected by GC-MS.



To a solution of 1,1-diphenylprop-2-en-1-ol (**1a**, 0.2 mmol) and NH$_4$SCN (0.3 mmol, 1.5 equiv.) in MeCN/H$_2$O (4:1, v/v) (2 mL) was added K$_2$S$_2$O$_8$ (0.4 mmol) at 25 ^{o}C under efficient stirring. The reaction mixture was stirred for 24 hours. The reaction mixture was stirred for 24 hours. Then, the reaction mixture was filtered and subjected to GC-MS analysis. The by-products **B** could be detected by GC-MS.



Base on these results, we proposed the following possible mechanistic pathway for this reaction.



Scheme S1 Proposed echanistic pathway

6. NMR study of the thermal isomerization process of thiocyanate

Temperature dependent NMR study of the isomerization of 3a

A solution of (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (**3a**, 0.05 mmol) in MeCN (1 mL) was stirred at indicated temperature under nitrogen. After 21 hours, the mixture was concentrated under reduce pressure and subjected to NMR analysis. Temperature dependent NMR study of the thermal isomerization of thiocyanate **3a** was observed in Figure S1. With the increase of temperature, the proportion of **3b** gradually increases.

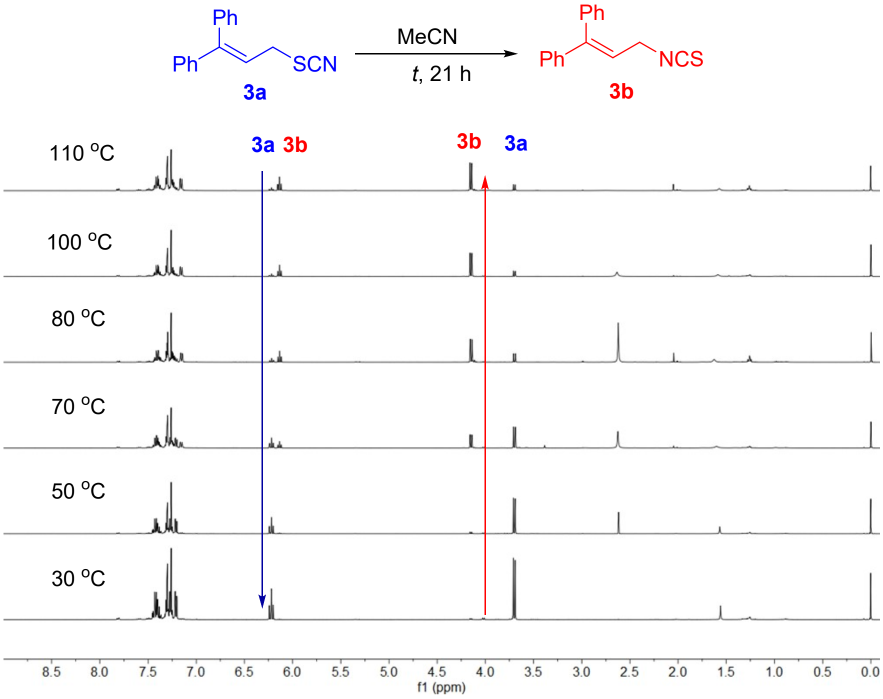


Figure S1 Temperature dependent NMR study of the thermal isomerization of **3a**

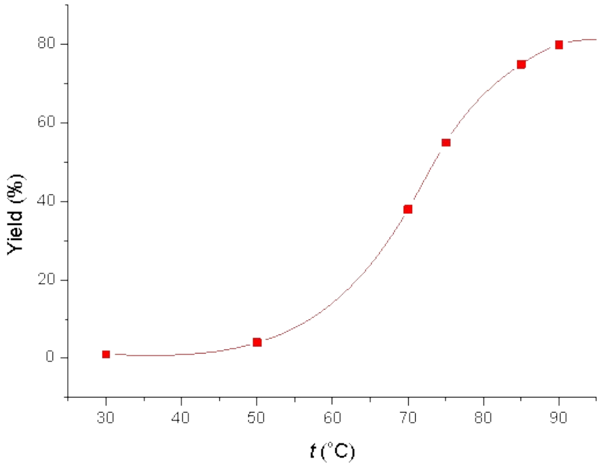


Figure S2 Plot of thermal isomerization of process **3a** in MeCN at different temperature

Time dependent NMR study of the isomerization of 3a

A solution of (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (3a, 0.05 mmol) in MeCN (1 mL) was stirred at 90 °C under nitrogen. After the indicated reaction time the mixture was concentrated under reduce pressure and subjected to NMR analysis. The relationship between the product formation and time can be proved. With the increase of time, the proportion of **3b** gradually increases.

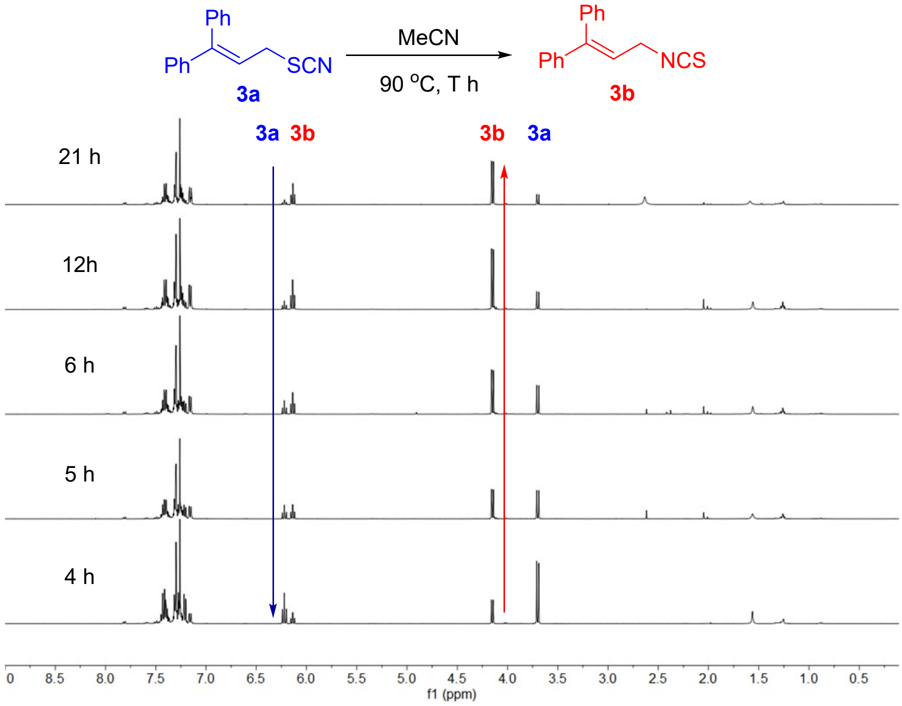


Figure S3 Time dependent NMR study of the thermal isomerization of **3a**

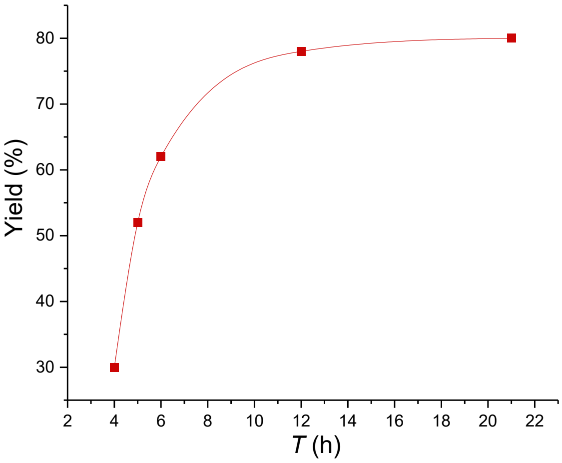


Figure S4 Plot of thermal isomerization of process **3a** within different reaction time at 90 ^oC

In order to know the isomerization process in the standard reaction conditions, the temperature dependent NMR study was also performed for the reaction running in MeCN/H_2O (4:1, v/v).

To a solution of (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (3a, 0.1 mmol) in MeCN/H_2O (4:1, v/v) (1 mL) were stirred at different temperature. After 12 hours, concentrated under reduce pressure to give crude residue, which was subjected to NMR analysis. The relationship between the product formation and temperature can be proved. With the increase of temperature, the proportion of **3b** gradually increases and changes significantly at 50 ^oC.

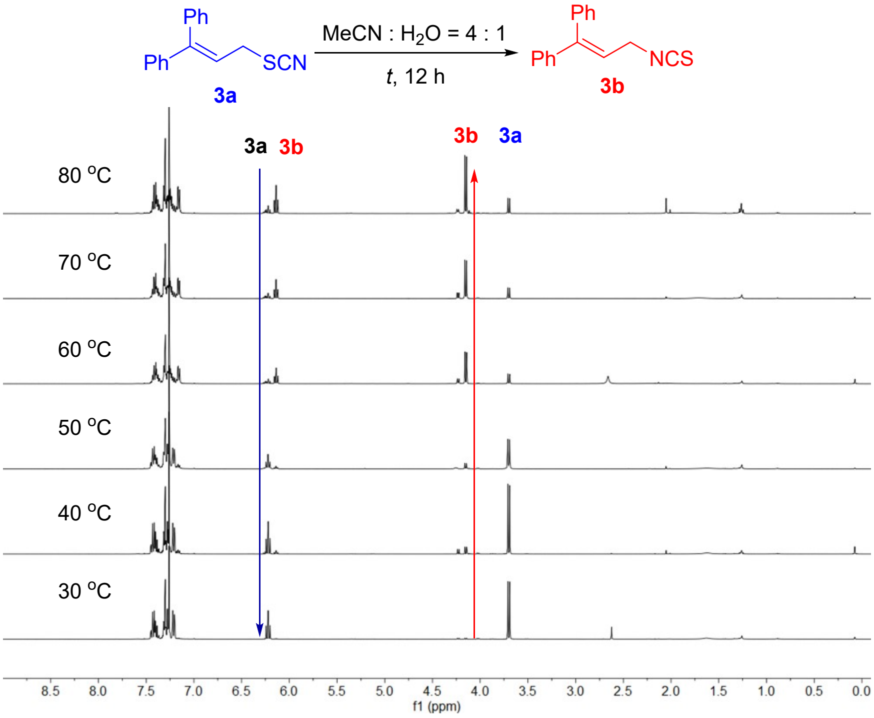


Figure S5 Temperature dependent NMR study of the thermal isomerization of **3a**

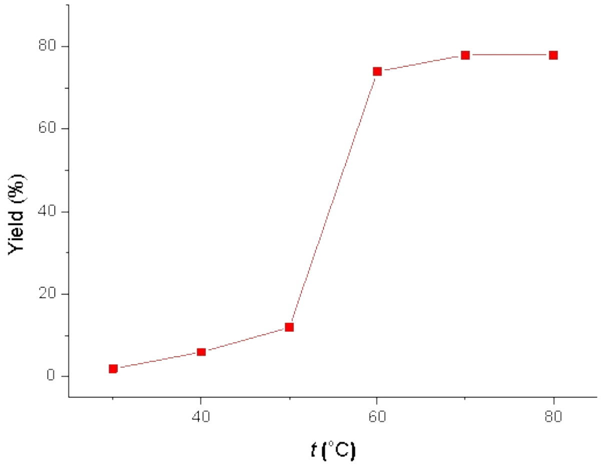
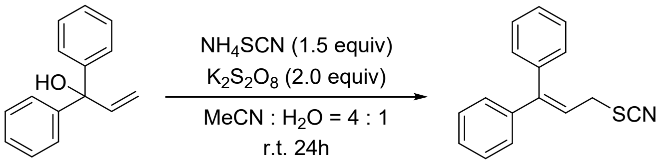


Figure S6 Plot of thermal isomerization of process **3a** in MeCN/H_2O (4:1, v/v) at different temperature

7. Synthetic application of the product

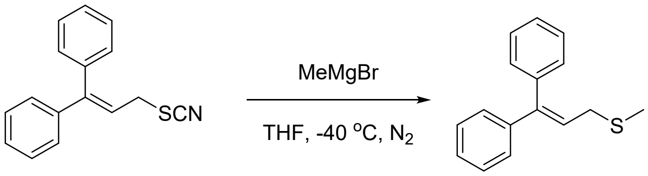
7.1 Scale-up experiments



1a **3a**, 75 % yield, 0.94g

To a solution of 1,1-diphenylprop-2-en-1-ol (**1a**, 5.0 mmol, 1.05g) and NH_4SCN (7.5 mmol, 0.571 g, 1.5 equiv.) in MeCN/H_2O (4:1, v/v) (50 mL), $K_2S_2O_8$ (10.0 mmol, 2.70 g, 2.0 equiv.) were added at 25 °C. The reaction was under an air atmosphere and stirred for 24 hours. The reaction progress was monitored by TLC. After the reactions were completed, the reaction mixture was diluted with water (70 mL) and washed with EA (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The reaction was concentrated under reduce pressure, and the crude material was purified by a flash chromatograph (PE/EA) on silica gel to yield the product **3a** as a white solid (0.94 g, 75%).

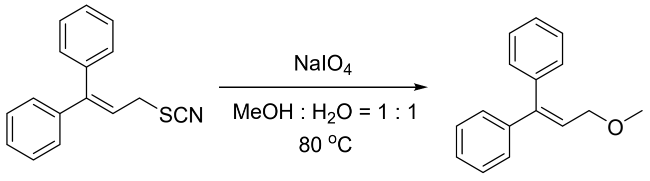
7.2 Application of the product 3a



3a **5**

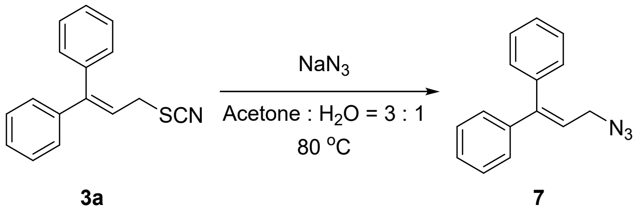
Following the reported procedure,[5] a 5 mL Shlenck tube containing a PTFE-coated stirring bar was charged with (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (0.2 mmol, 1.0 equiv.). The vessel was then evacuated and filled with nitrogen three times. Then, dry THF (2 mL) was added under nitrogen flow. The solution was cooled down to -40 °C and stirred for 10 minutes. Then, methylmagnesium bromide

(1M in THF, 0.6 mmol, 3.0 equiv.) was added and the reaction was stirred at -40 °C for 2 hours. The reaction progress was monitored by TLC. After the reactions were completed, the reaction was warmed to r.t, and diluted with CH_2Cl_2 (30 mL). The organic phase was washed with H_2O (15 mL) and brine (15 mL). Then, it was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The product was purified by silica gel column chromatography to yield the product **5** as a yellow oil (38.4 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 3H), 7.30 – 7.23 (m, 5H), 7.19 – 7.17 (m, 2H), 6.14 (t, *J* = 7.8 Hz, 1H), 3.21 (d, *J* = 7.8 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 141.8, 139.1, 130.0, 128.3, 128.1, 127.4, 127.4, 127.3, 124.9, 32.8, 14.8. The spectra data are consistent with the reported reference.[2]



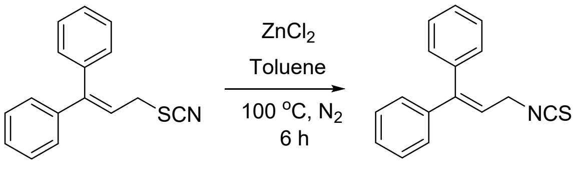
3a **6**

To a solution of (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (0.2 mmol, 1.0 equiv.) in $MeOH/H_2O$ (1 : 1, v/v) (2 mL), $NaIO_4$ (0.4 mmol, 2.0 equiv.) was added at 25 °C. The reaction was then exposed to 80 °C under an air atmosphere and stirred for 16 hours. After cooling down to 25 °C, the reaction mixture was diluted with water (10 mL) and extracted with EA (3×10 mL). The combined organic layers dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The product was purified by silica gel column chromatography to yield the product **6** as a yellow oil (19.7 mg, 44%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.34 (m, 3H), 7.29 – 7.26 (m, 5H), 7.19 – 7.17 (m, 2H), 6.22 (t, *J* = 6.7 Hz, 1H), 4.00 (d, *J* = 6.7 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.8, 139.2, 129.7, 128.3, 128.1, 127.6, 127.5, 127.5, 125.4, 70.2, 58.1. The spectra data are consistent with the reported reference.[3]



3a **7**

To a solution of (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (0.2 mmol, 1.0 equiv.), in acetone/H_2O (3 : 1, v/v) (2 mL), NaN_3 (0.4 mmol, 2.0 equiv.) was added at 25 °C. The reaction was then exposed to 80 °C under an air atmosphere and stirred for 30 min. After cooling down to 25 °C, the reaction mixture was diluted with CH_2Cl_2 (30 mL), and washed with H_2O (15 mL) and brine (15 mL). The combined organic layers dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The products were purified by silica gel column chromatography to yield the product **7** as a yellow oil (37.2 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.37 (m, 3H), 7.31 – 7.26 (m, 5H), 7.19 – 7.17 (m, 2H), 6.18 (t, *J* = 7.4 Hz, 1H), 3.86 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 141.2, 138.4, 129.8, 128.4, 128.3, 128.0, 127.8, 127.6, 121.3, 49.7. The spectra data are consistent with the reported reference[4]



3a **3a'**

General procedure for preparation of 3a'

A 5 mL Shlenck tube containing a PTFE-coated stirring bar was charged with (3-thiocyanatoprop-1-ene-1,1-diyl) dibenzene (0.2 mmol, 1.0 equiv.) and $ZnCl_2$ (0.2 mmol, 1.0 equiv.). The vessel was then evacuated and filled with nitrogen three times. Then, toluene (4 mL) was added under nitrogen flow. Finally the mixture was heated at 100 °C for 6 hours. After cooling down to 25 °C, he reaction mixture was quenched with H_2O (30 mL). The mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The products were purified by silica gel column chromatography to yield the product **3a'** as a yellow oil (36.7 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 3H), 7.32 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 7.17 – 7.15 (m, 2H), 6.14 (t, *J* = 7.1 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 140.7, 137.9, 129.4, 128.6, 128.3, 128.2, 128.1, 127.6, 120.2 (two peaks overlapped), 44.4; HRMS (ESI) m/z calcd for $C_{16}H_{14}NS^+$ $[M + H]^+$ m/z 252.0842, found m/z 252.0870.

8. Reference

1 X. Liu, F. Xiong, X. Huang, L. Xu, P. Li and X. Wu, Copper-catalyzed trifluoromethylation-initiated radical 1,2-aryl migration in α,α-diaryl allylic alcohols, *Angew. Chem. Int. Ed.*, 2013, **52**, 6962-6966.

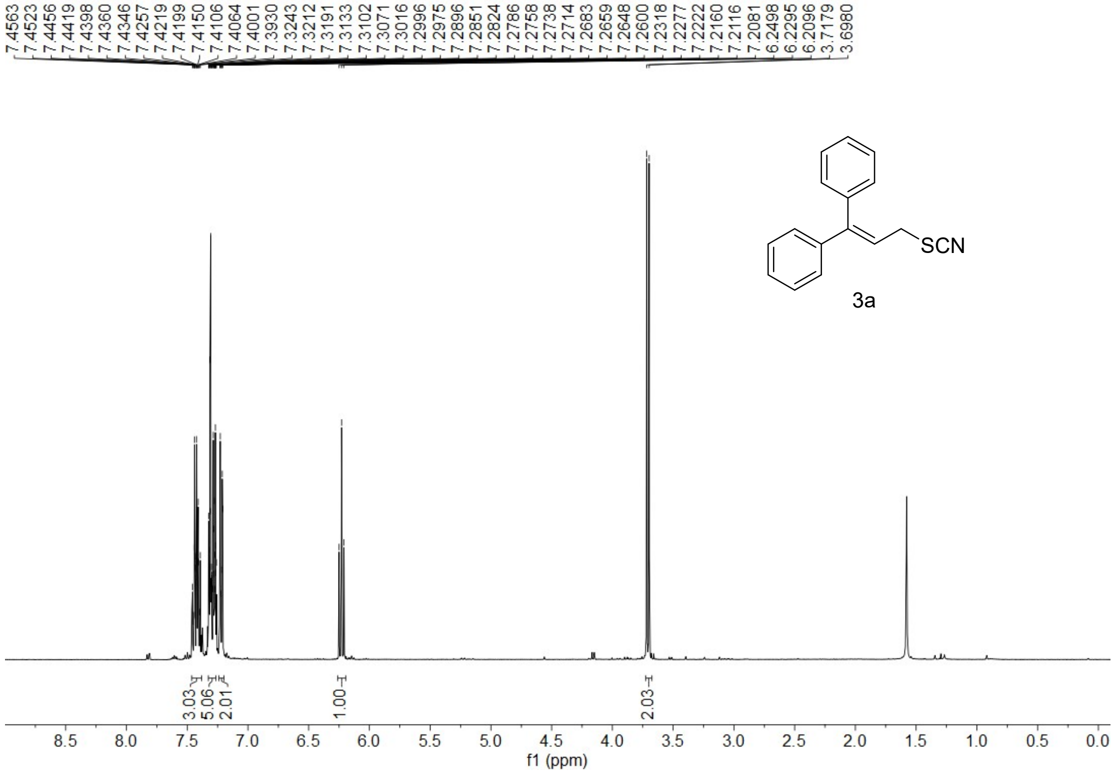
2 H. Cao, D. Liu, C. Liu, X. Hu and A. Lei, Copper-catalyzed oxidative alkenylation of thioethers via Csp^3–H functionalization, *Org. Biomol. Chem.*, 2015, **13**, 2264–2266.

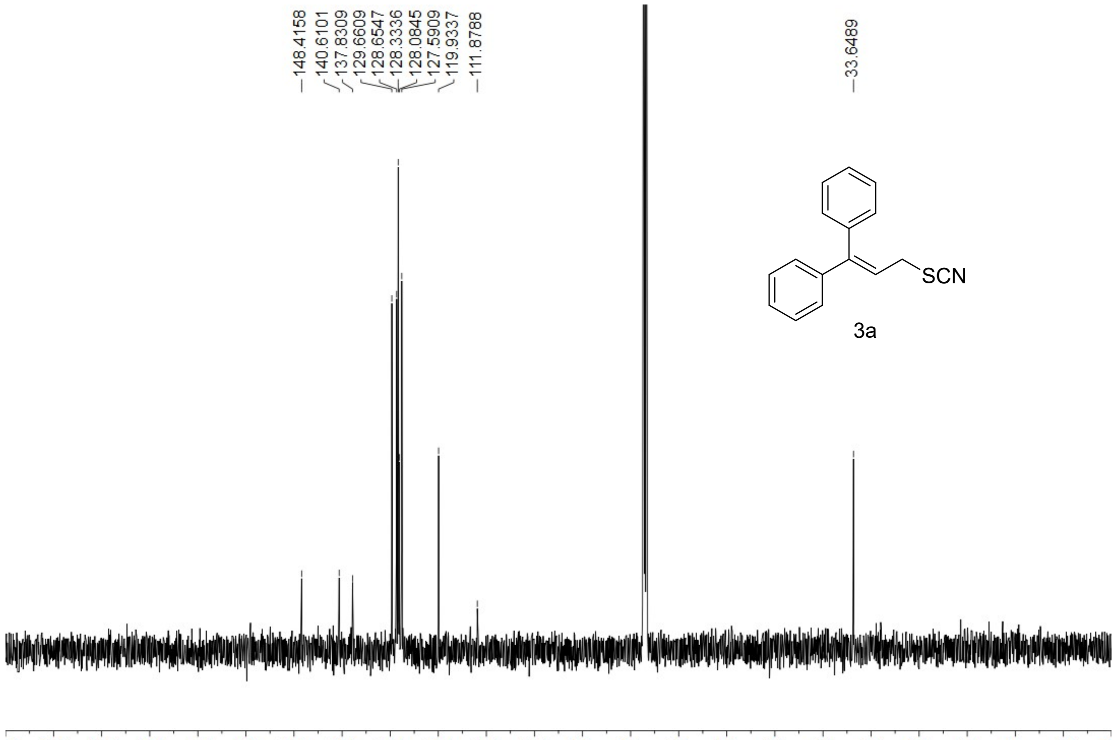
3 L. Hu, M. Hussain, Q. Deng, Q. Liu, Y. Feng, X. Zhang, Y. Xiong, I_2/Li_2CO_3-promoted cyanation of diarylalcohols through a dual activation process, *Tetrahedron,* 2019, **75**, 308-314.

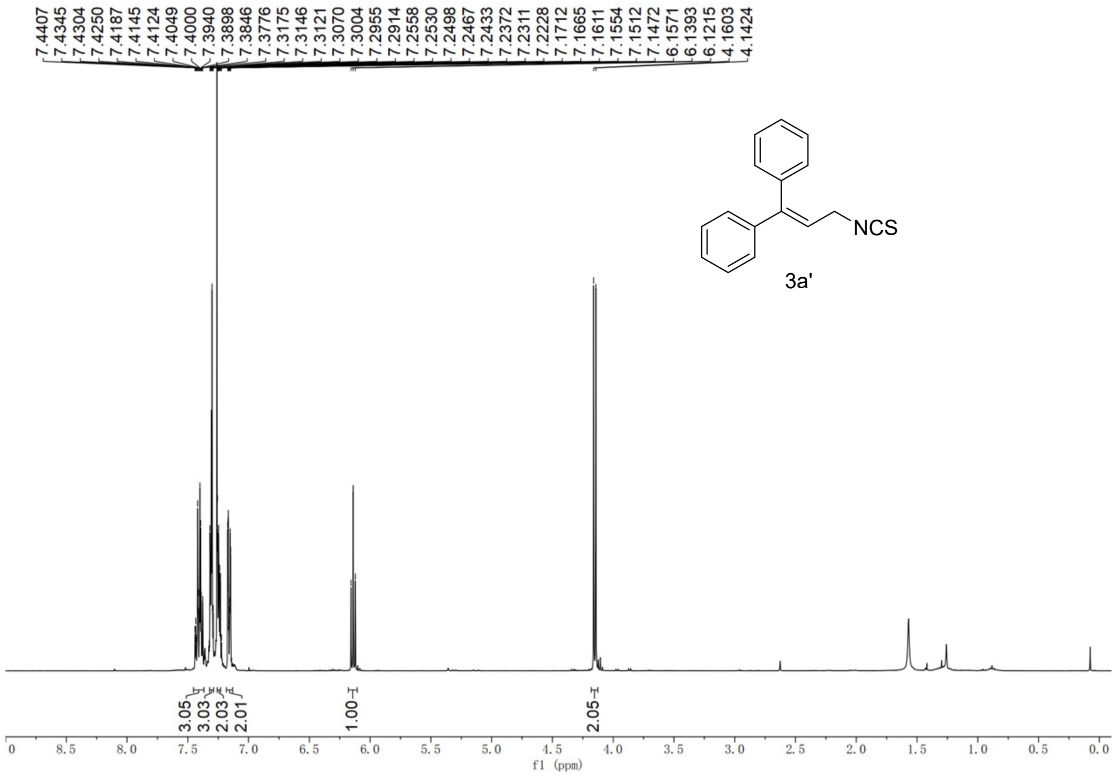
4 M. Rueping, C. Vila, and U. Uria, Direct catalytic azidation of allylic alcohols, *Org. Lett.*, 2012, **14**, 768-771.

5 Adams, R.; Bramlet, H. B.; Tendick, F. H, The action of the grigard reagent on thiocyanates, *J. Am. Chem. Soc.*, 1920, **42**, 2369–2374.

9. NMR Spectra







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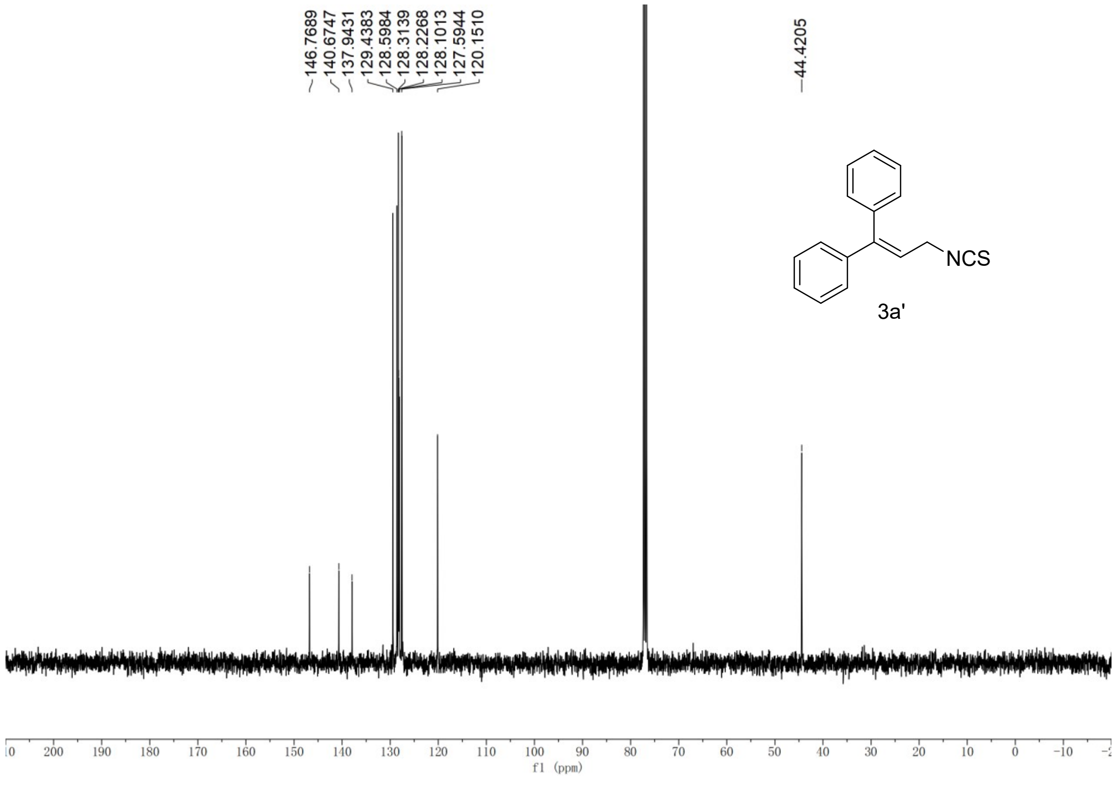

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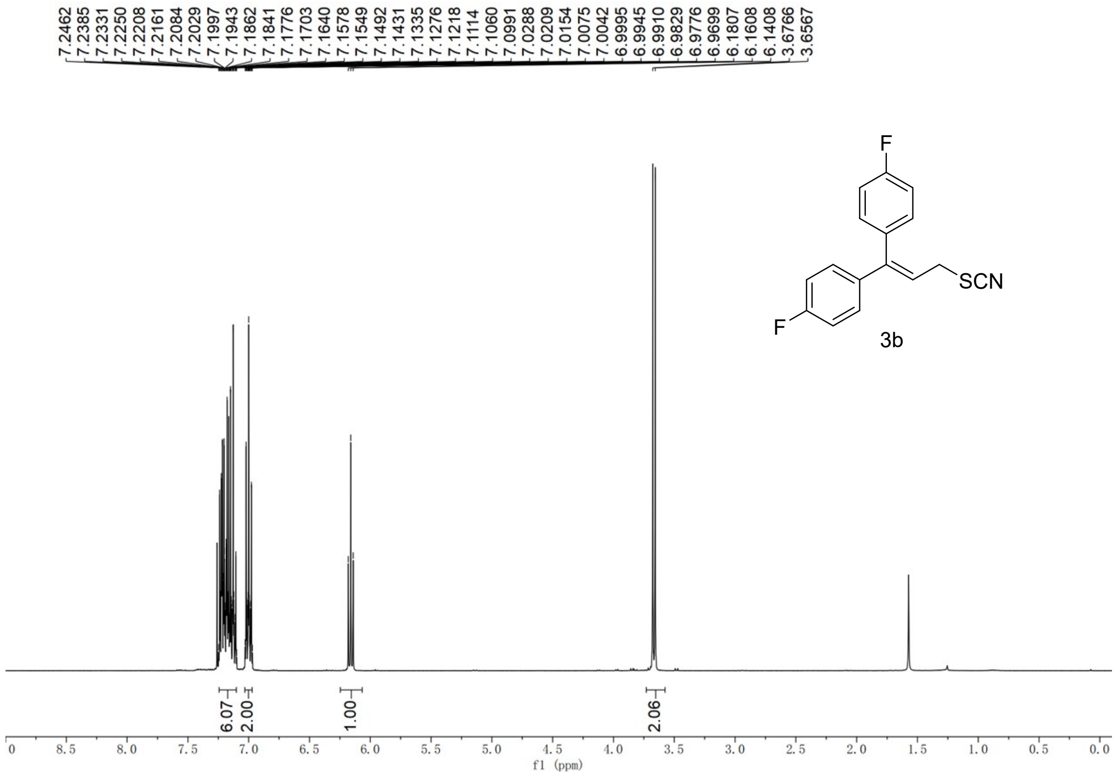
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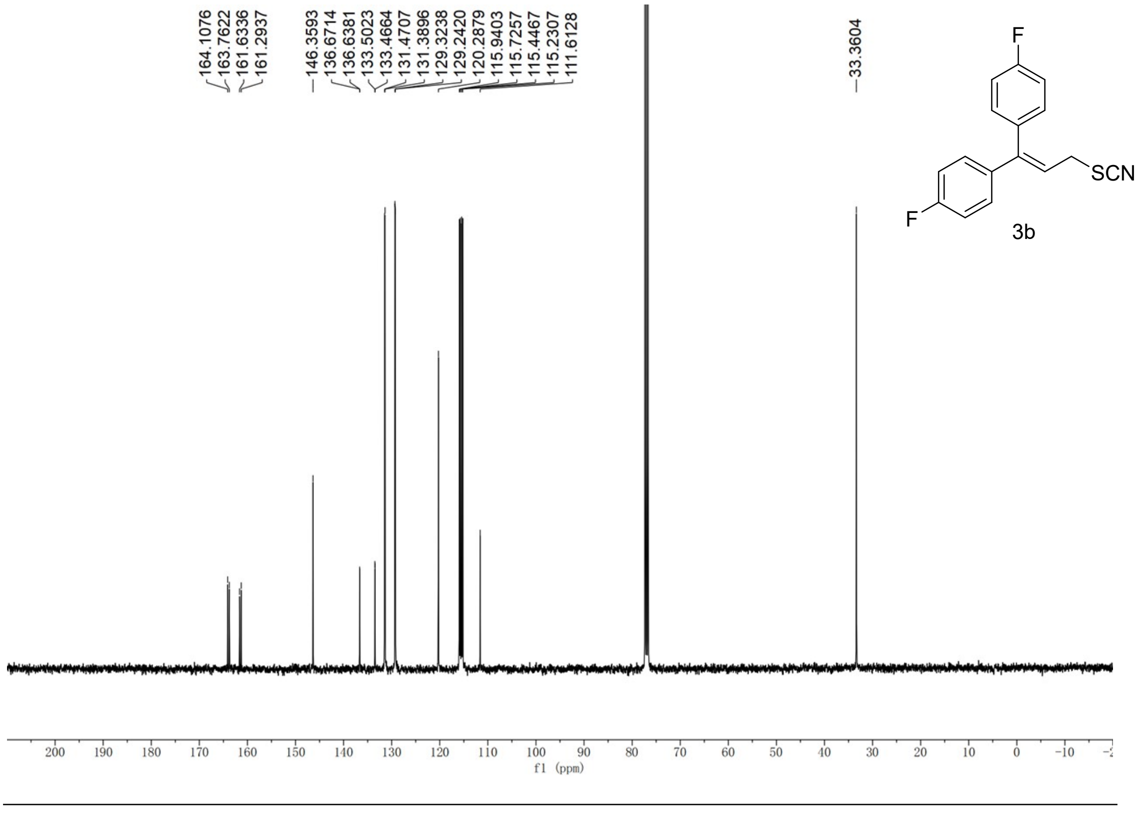
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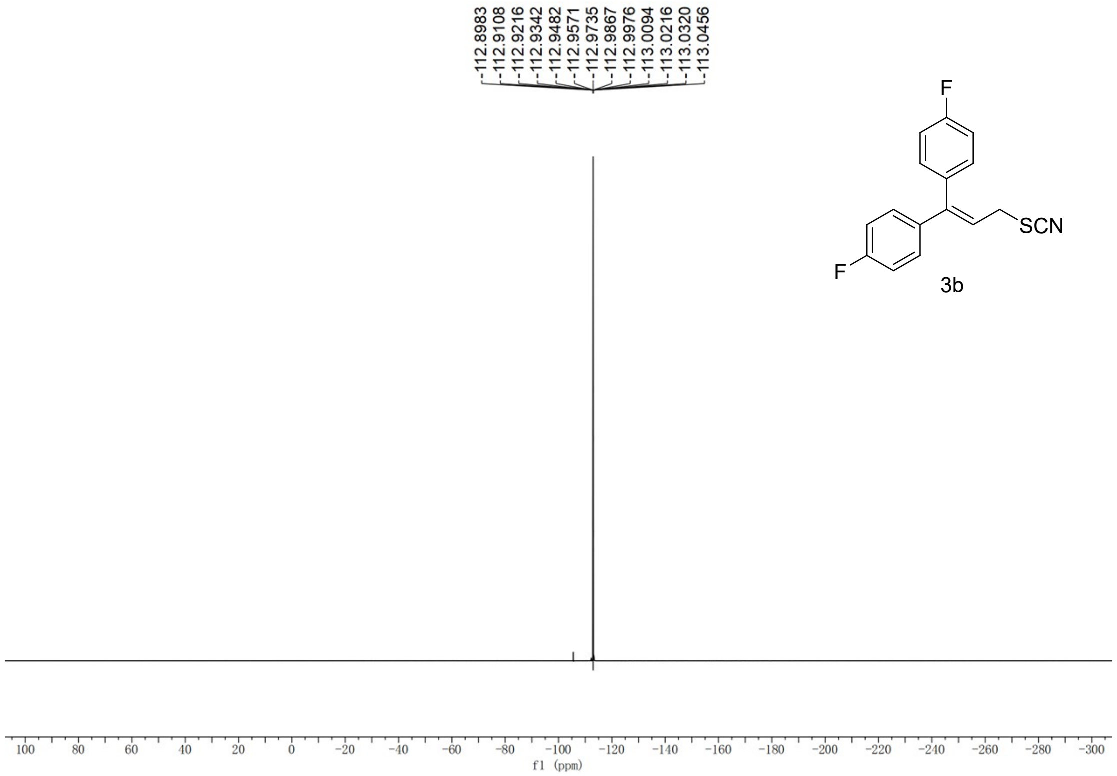
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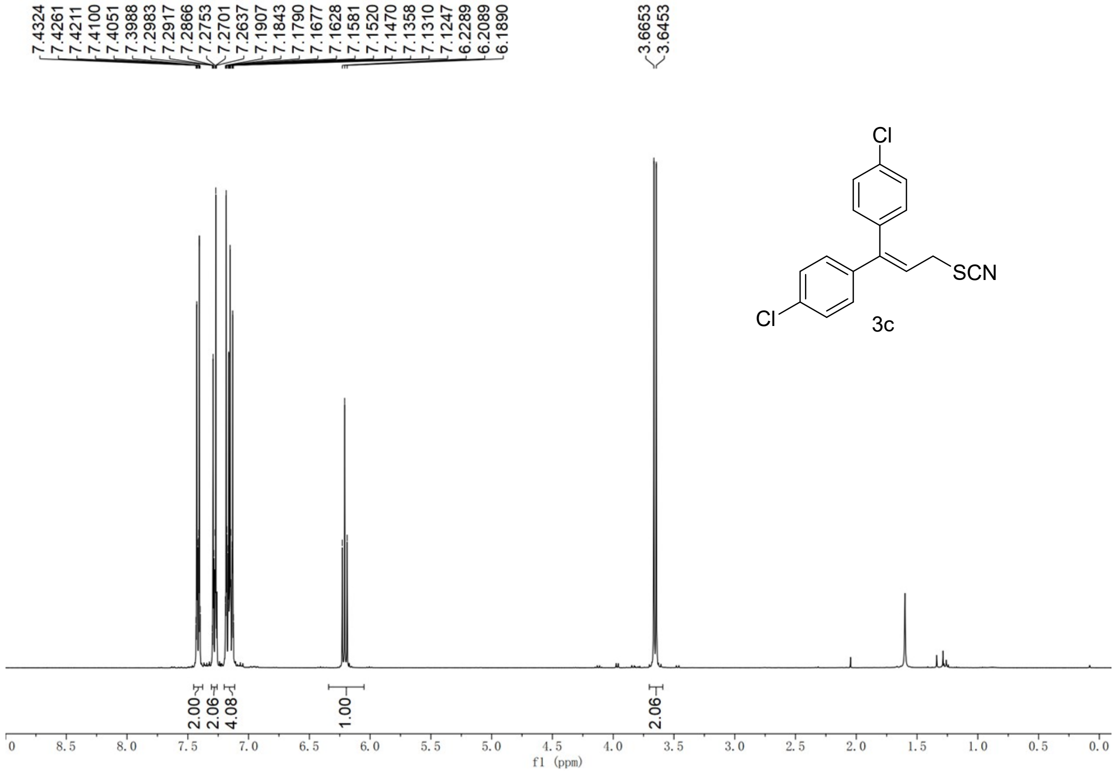
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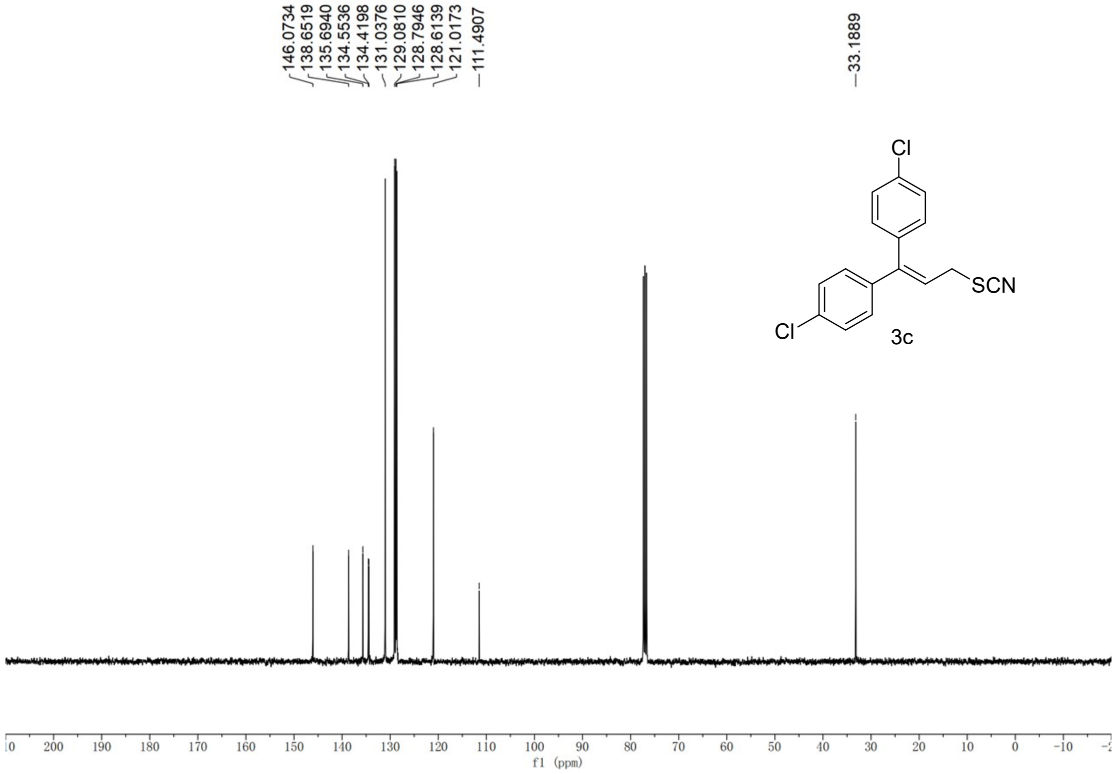
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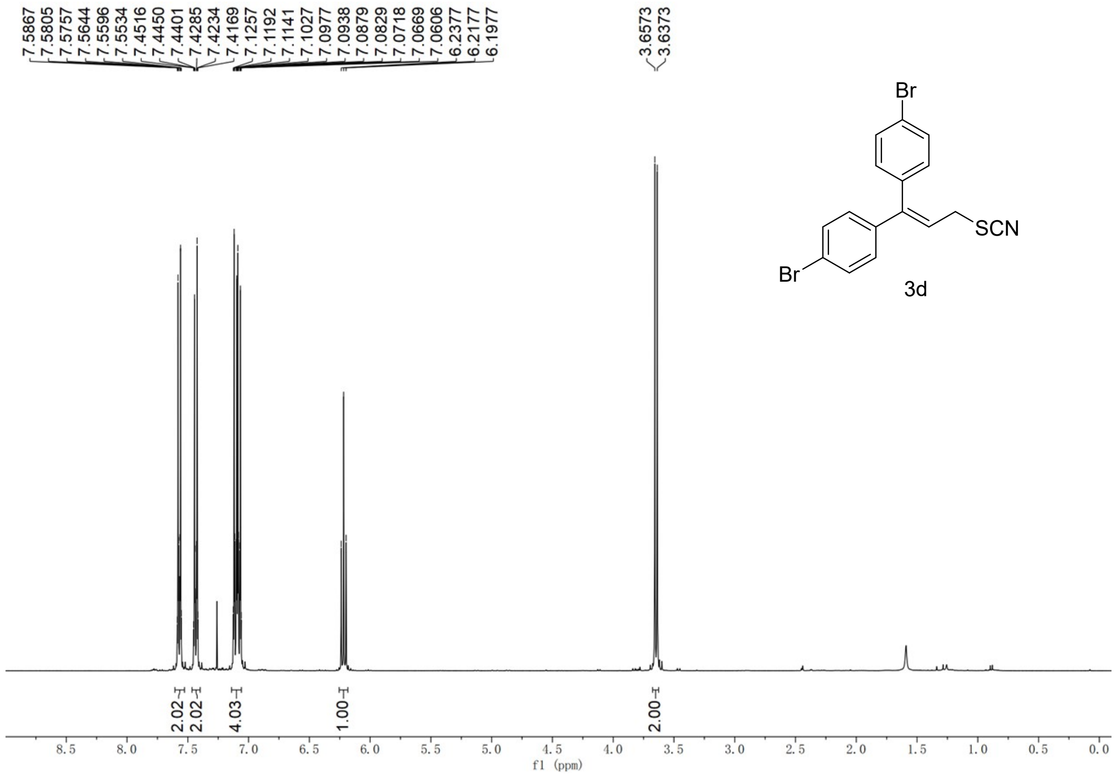
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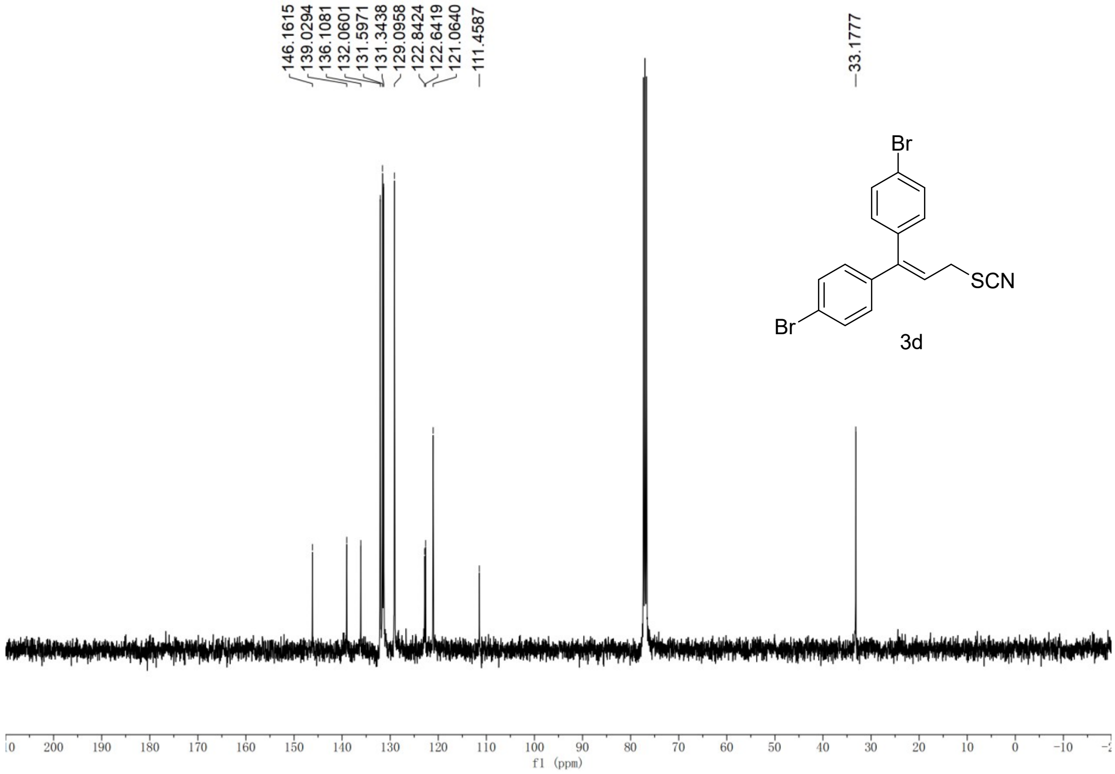
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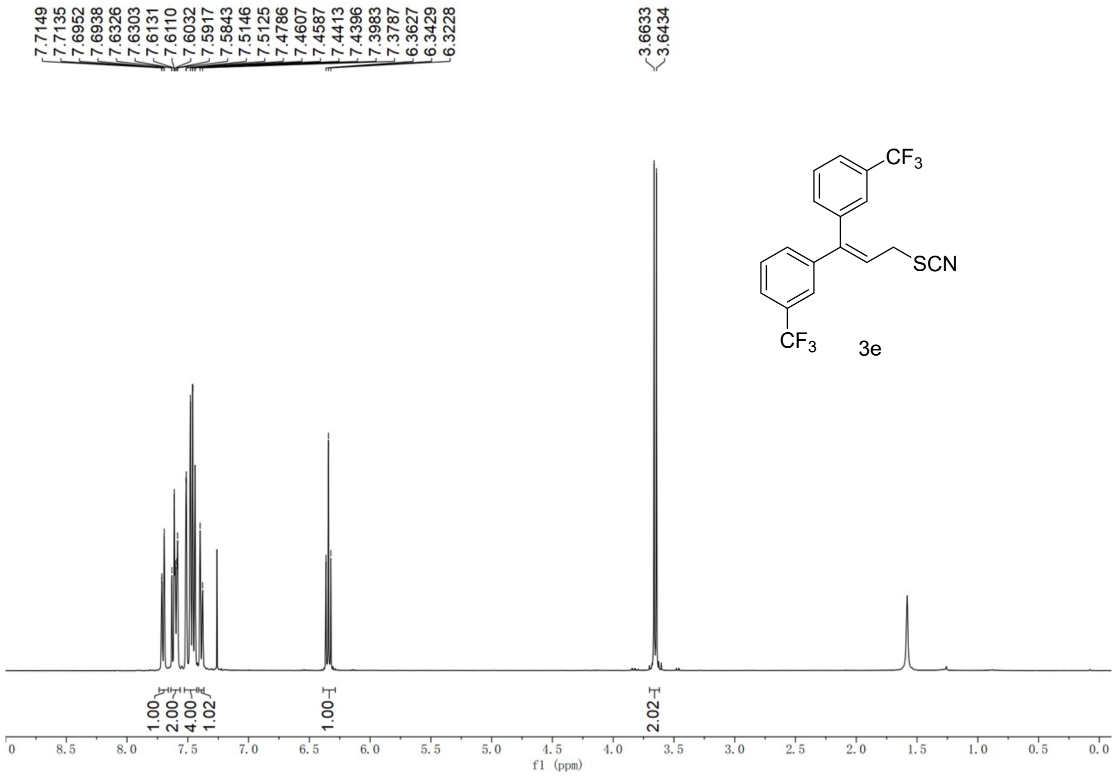
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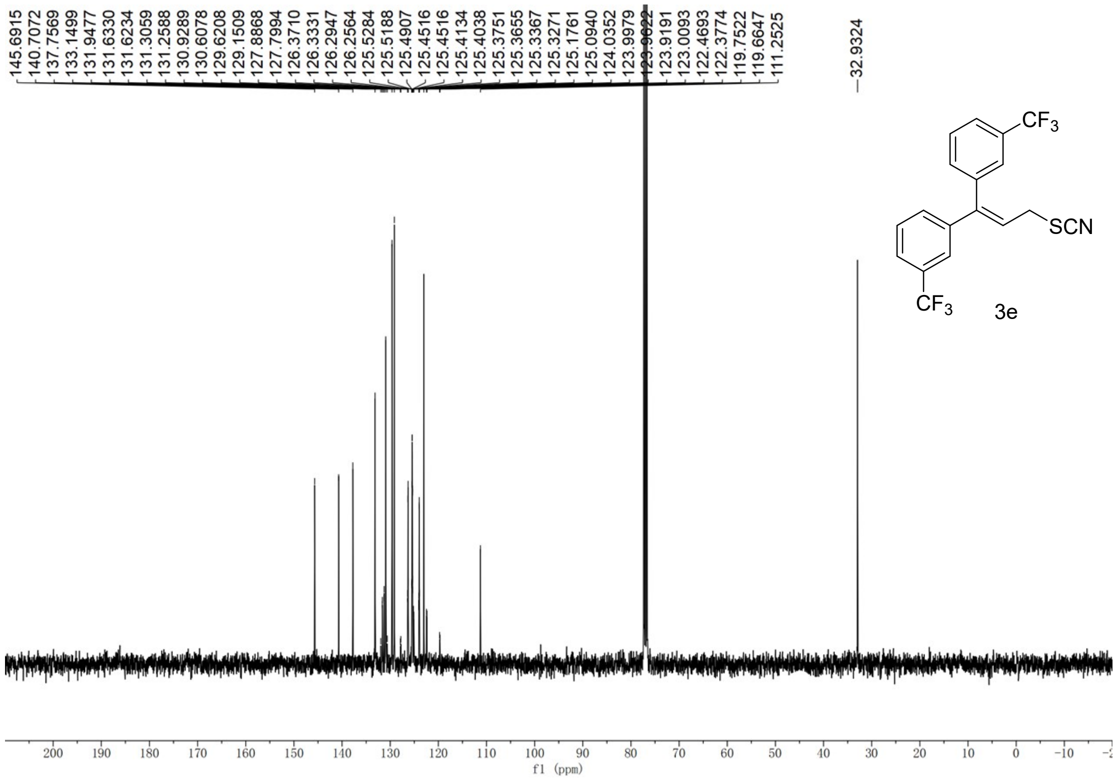
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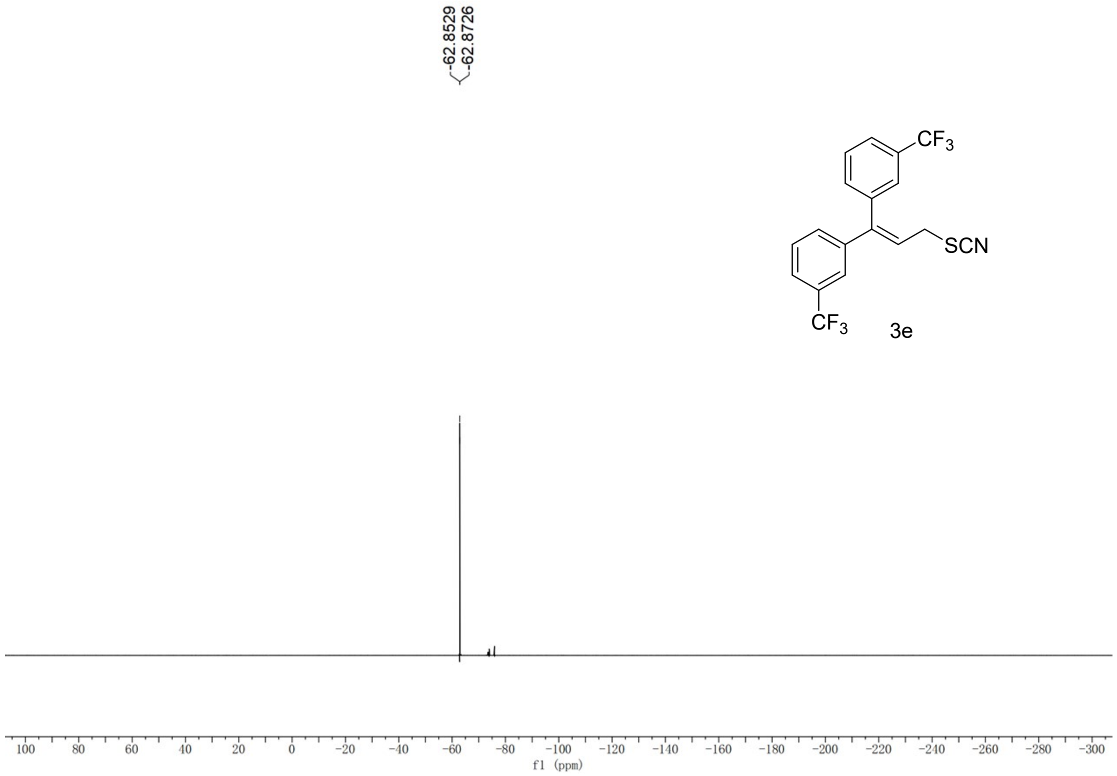
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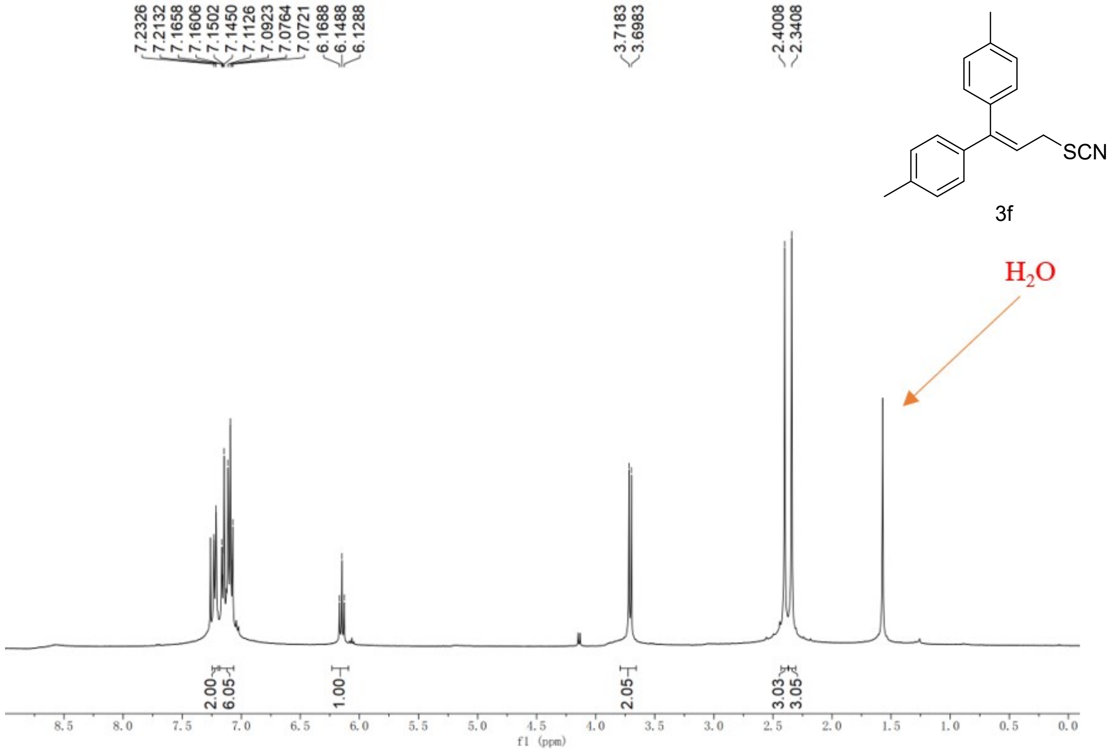
3e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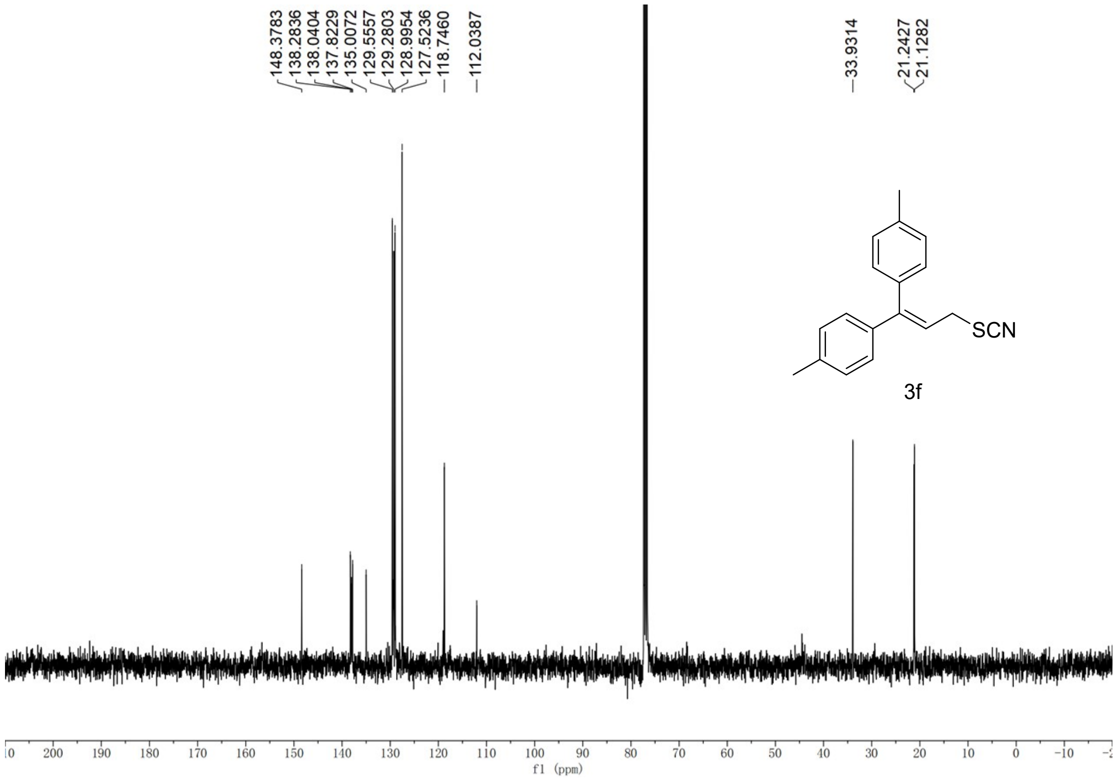
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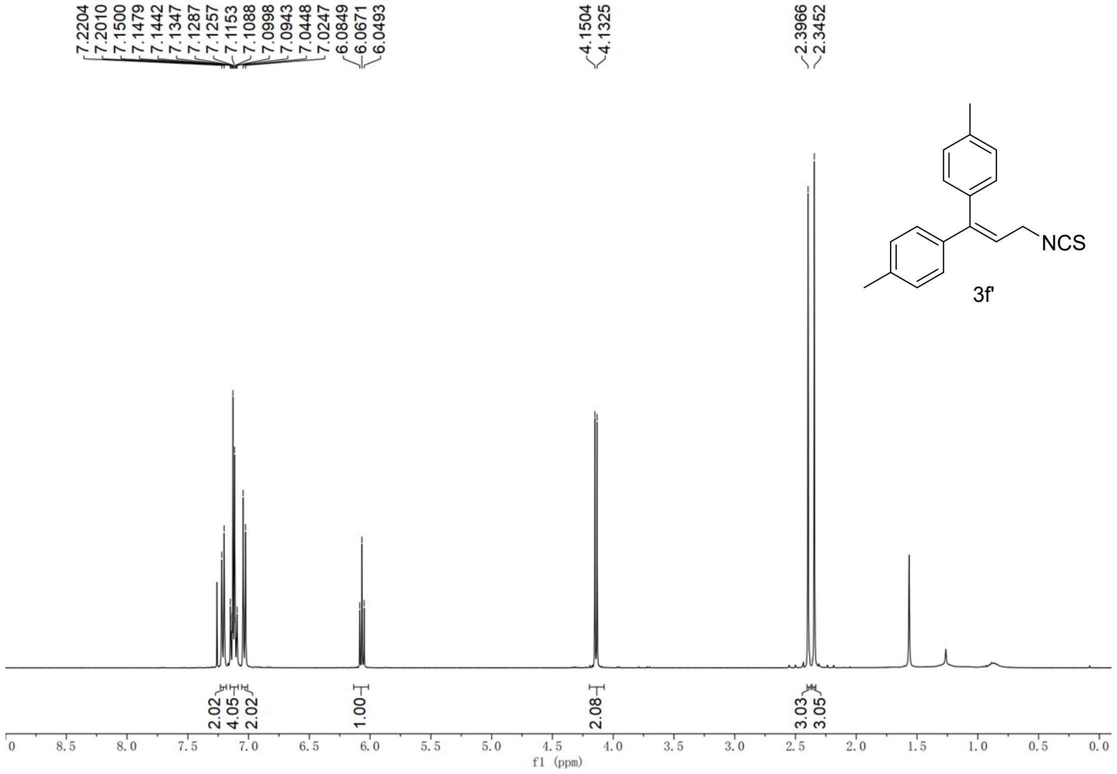
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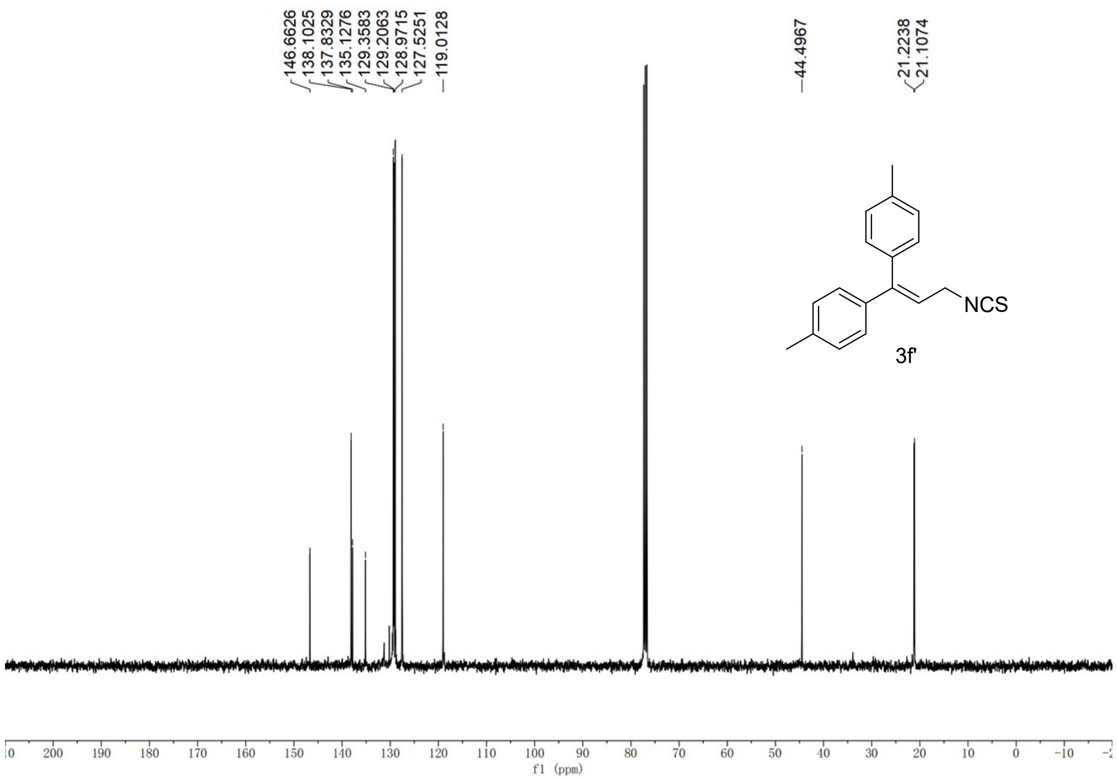
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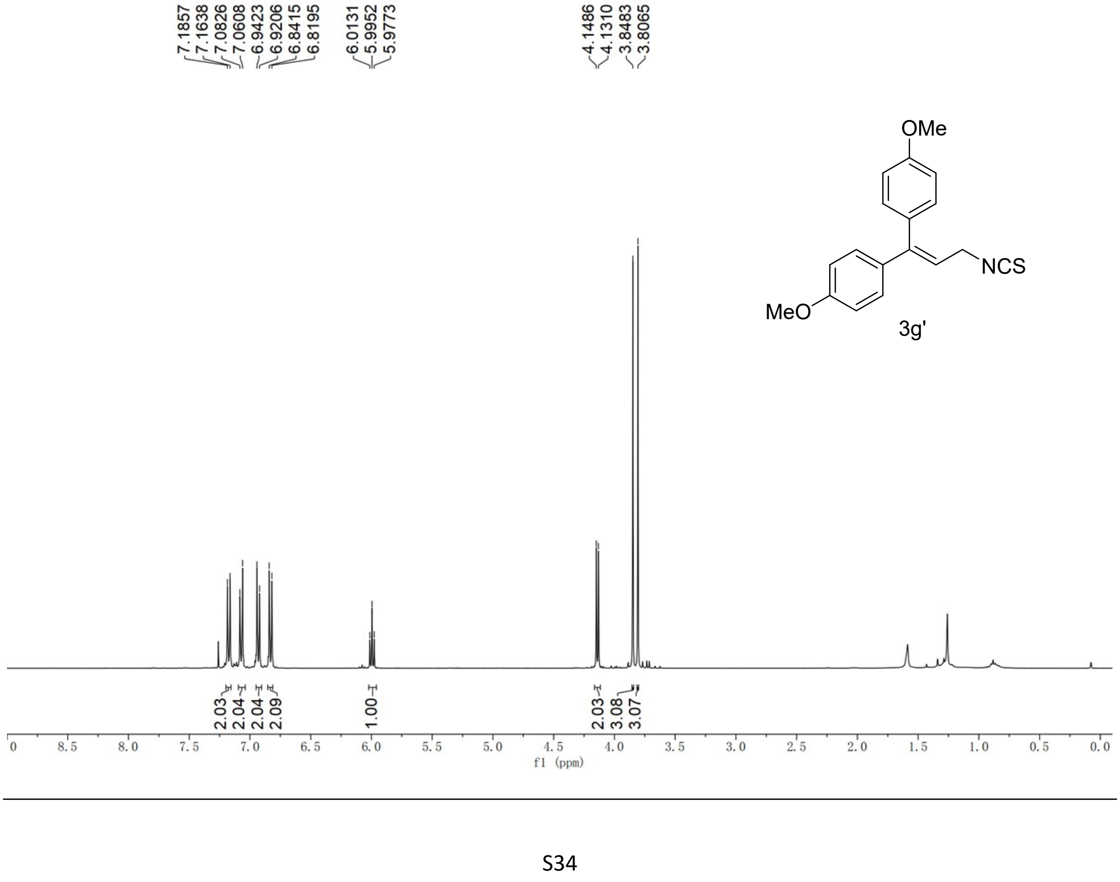
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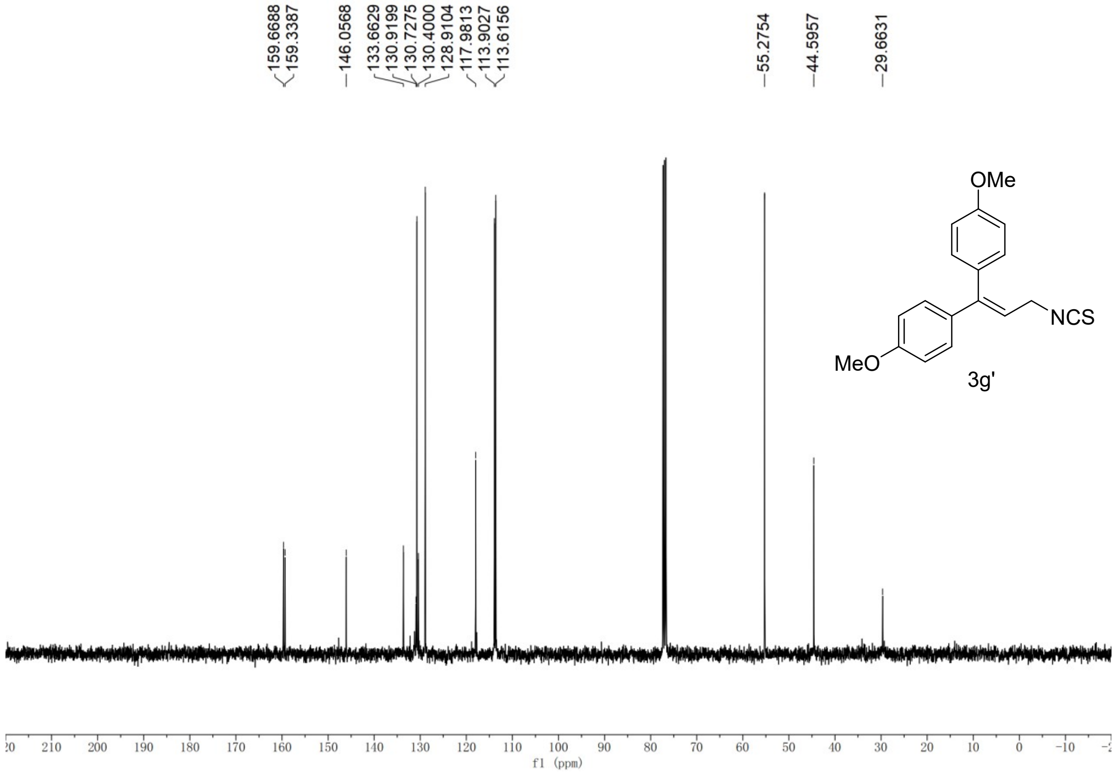
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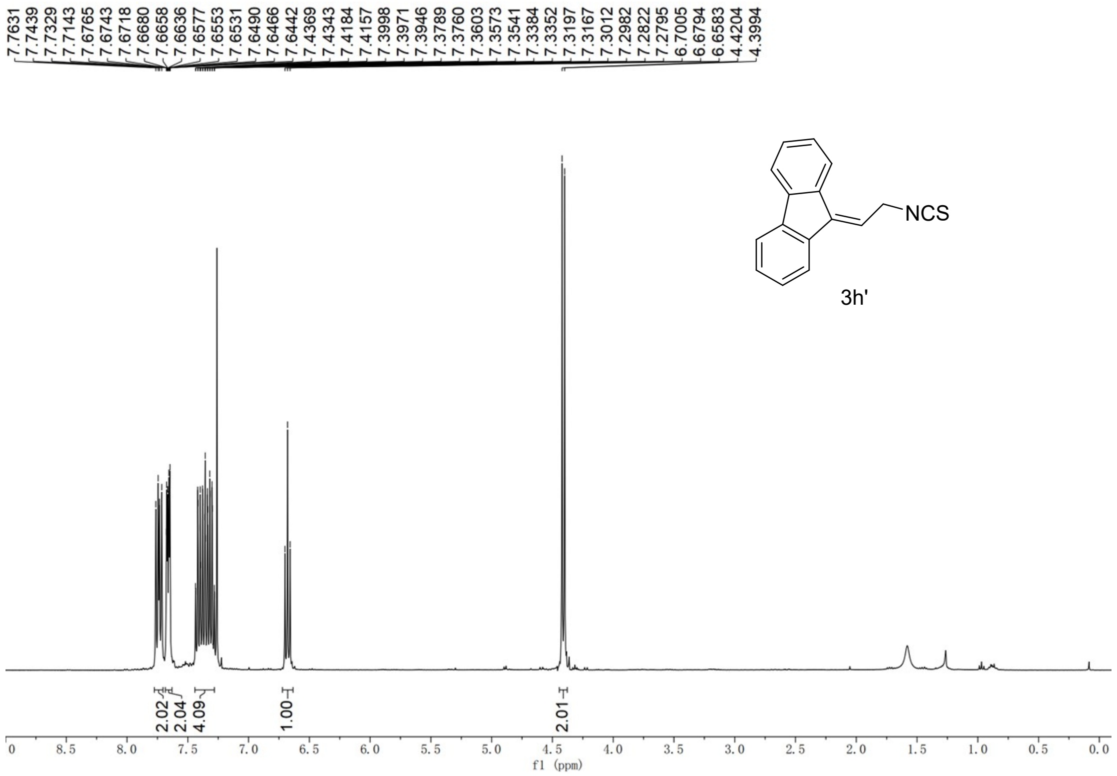
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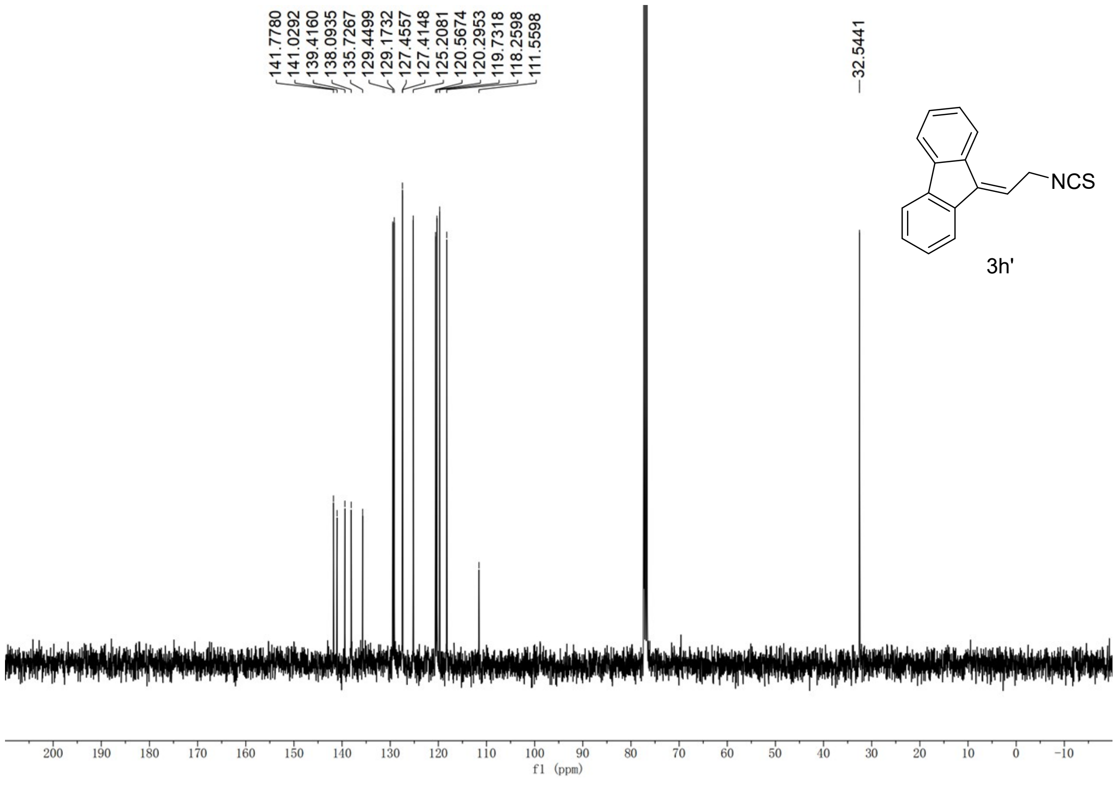
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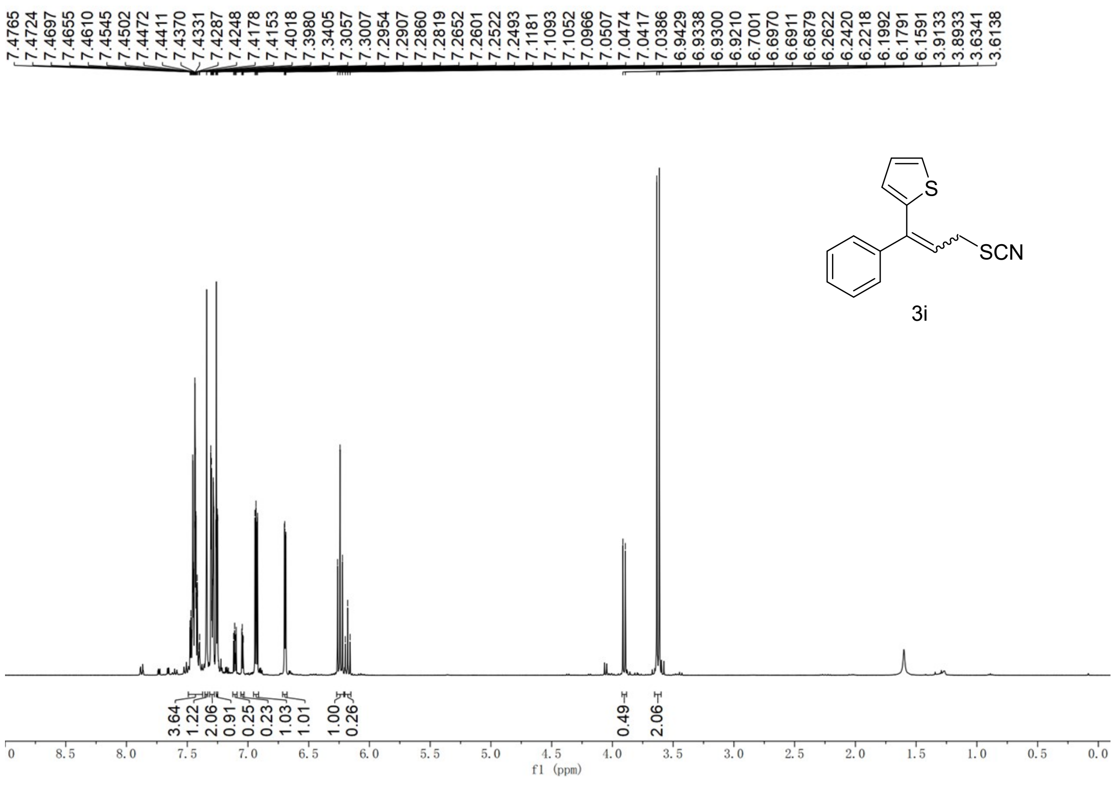
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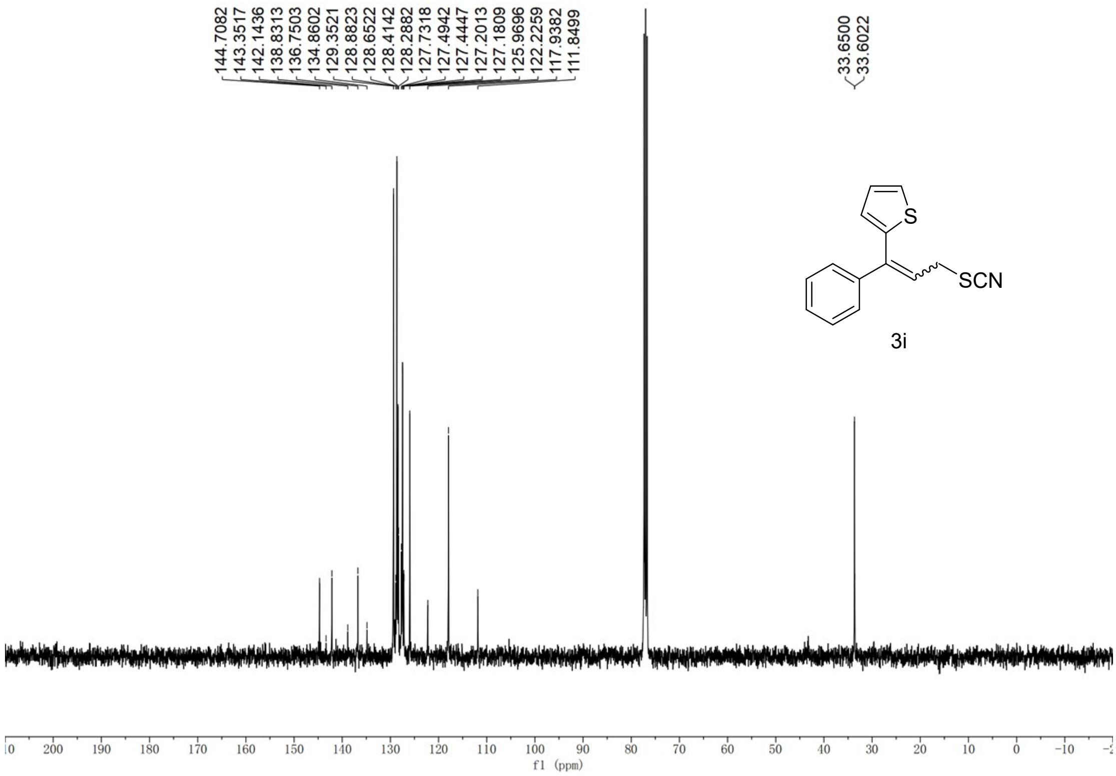
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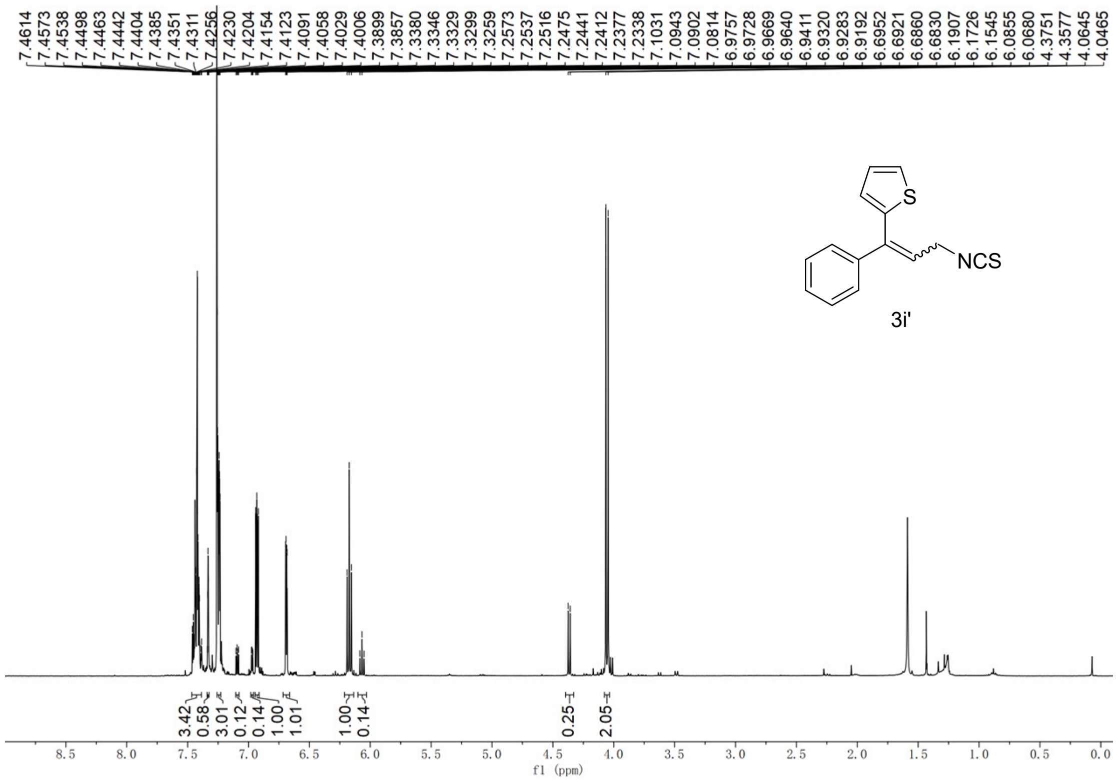
f1 (ppm)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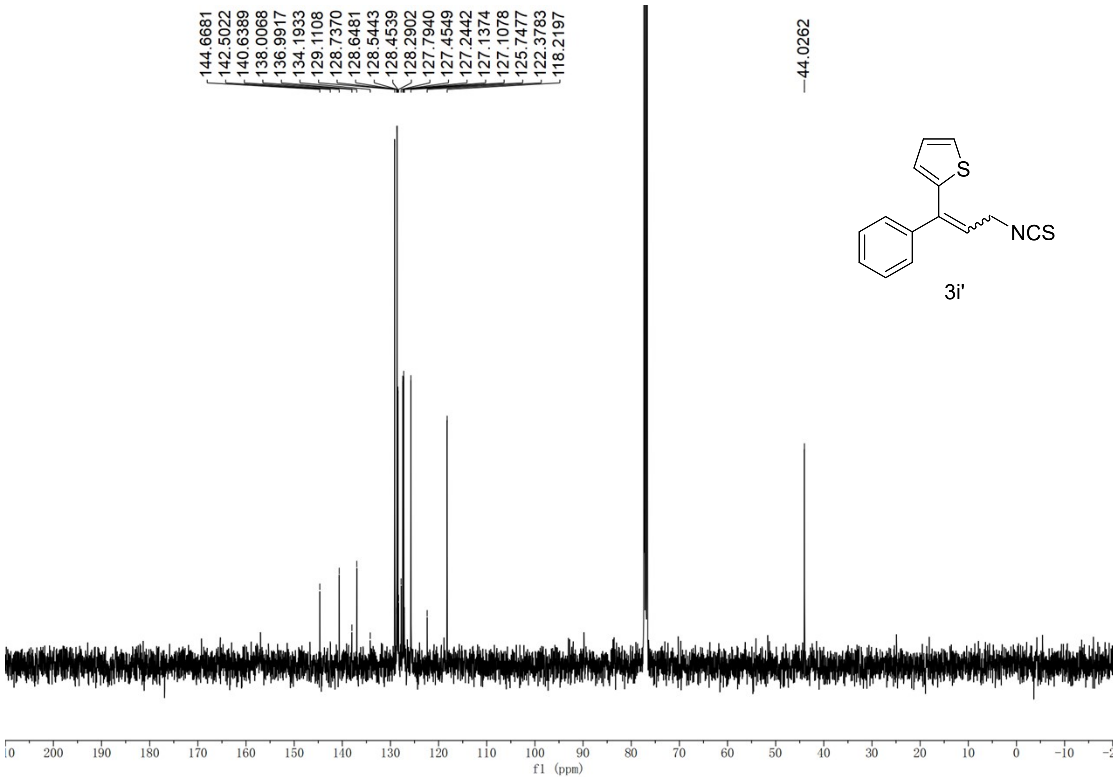
7.4256
7.4230
7.4204
7.4154
7.4123
7.4091
7.4058
7.4029
7.4006
7.3899
7.3857
7.3380
7.3346
7.3329
7.3299
7.3259
7.2573
7.2537
7.2516
7.2475
7.2441
7.2412
7.2377
7.2338
7.1031
7.0943
7.0902
7.0814
6.9757
6.9728
6.9669
6.9640
6.9411
6.9320
6.9283
6.9192
6.6952
6.6921
6.6860
6.6830
6.1907
6.1726
6.1545
6.0855
6.0680
4.3751
4.3577
4.0645
4.0465
S
NCS
3i'
3.42
0.58
3.01
0.12
0.14
1.00
1.01
1.00
0.14
0.25
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.2902
127.7940
127.4549
127.2442
127.1374
127.1078
125.7477
122.3783
118.2197
44.0262
S
NCS
3i'
200
190
180
170
160
150
140
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120
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100
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80
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30
20
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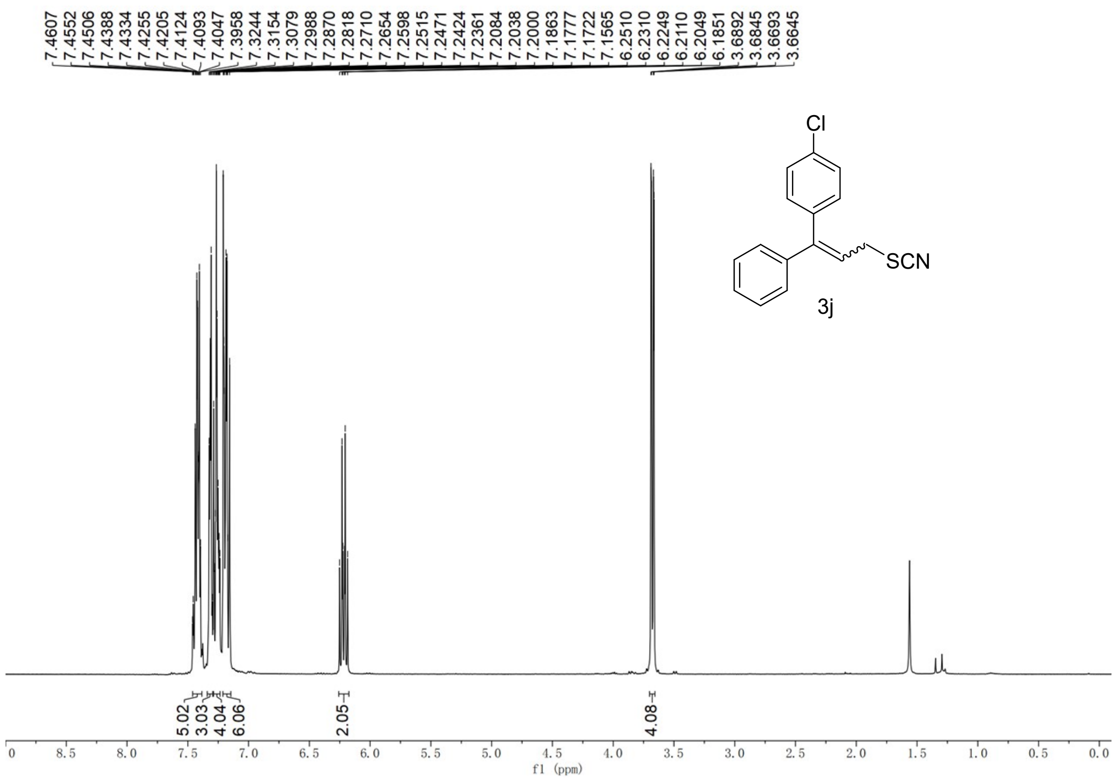
-10
f1 (ppm)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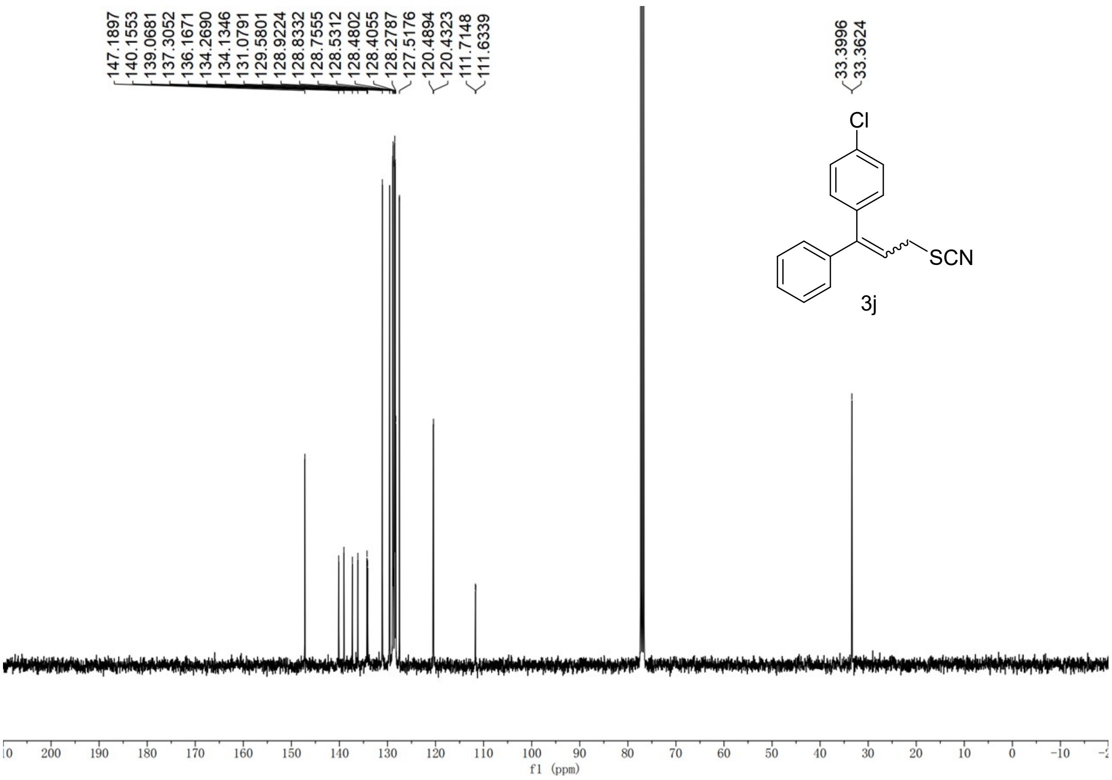
7.4047
7.3958
7.3244
7.3154
7.3079
7.2988
7.2870
7.2818
7.2710
7.2654
7.2598
7.2515
7.2471
7.2424
7.2361
7.2084
7.2038
7.2000
7.1863
7.1777
7.1722
7.1565
6.2510
6.2310
6.2249
6.2110
6.2049
6.1851
3.6892
3.6845
3.6693
3.6645
Cl
SCN
3j
5.02
3.03
4.04
6.06
2.05
4.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.7555
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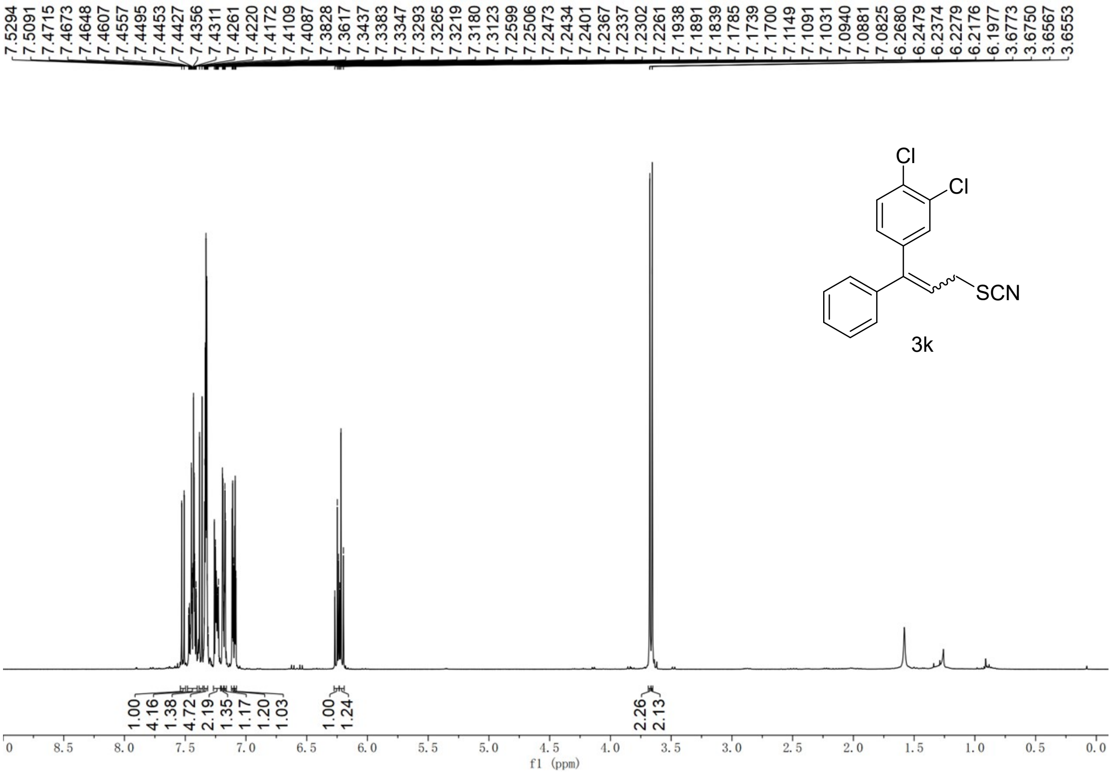
128.4802
128.4055
128.2787
127.5176
120.4894
120.4323
111.7148
111.6339
33.3996
33.3624
Cl
SCN
3j
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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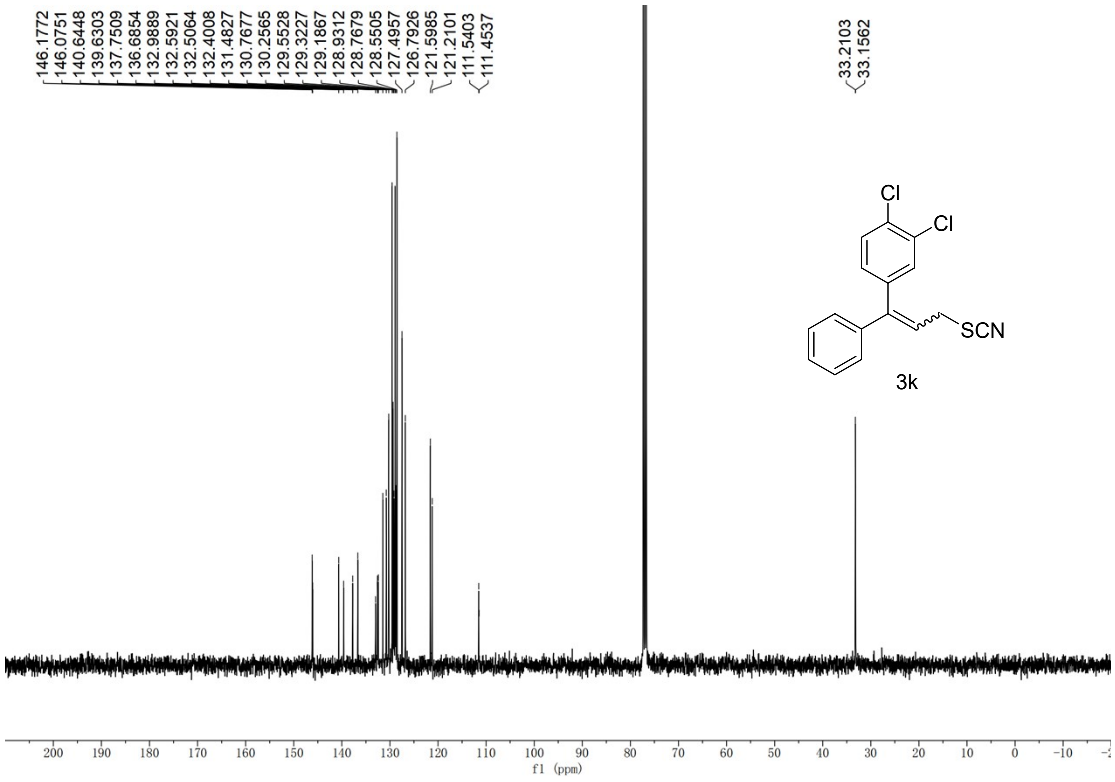
7.4311
7.4261
7.4220
7.4172
7.4109
7.4087
7.3828
7.3617
7.3437
7.3383
7.3347
7.3293
7.3265
7.3219
7.3180
7.3123
7.2599
7.2506
7.2473
7.2434
7.2401
7.2367
7.2337
7.2302
7.2261
7.1938
7.1891
7.1839
7.1785
7.1739
7.1700
7.1149
7.1091
7.1031
7.0940
7.0881
7.0825
6.2680
6.2479
6.2374
6.2279
6.2176
6.1977
3.6773
3.6750
3.6567
3.6553
Cl
Cl
SCN
3k
1.00
4.16
1.38
4.72
2.19
1.35
1.17
1.20
1.03
1.00
1.24
2.26
2.13
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.7509
136.6854
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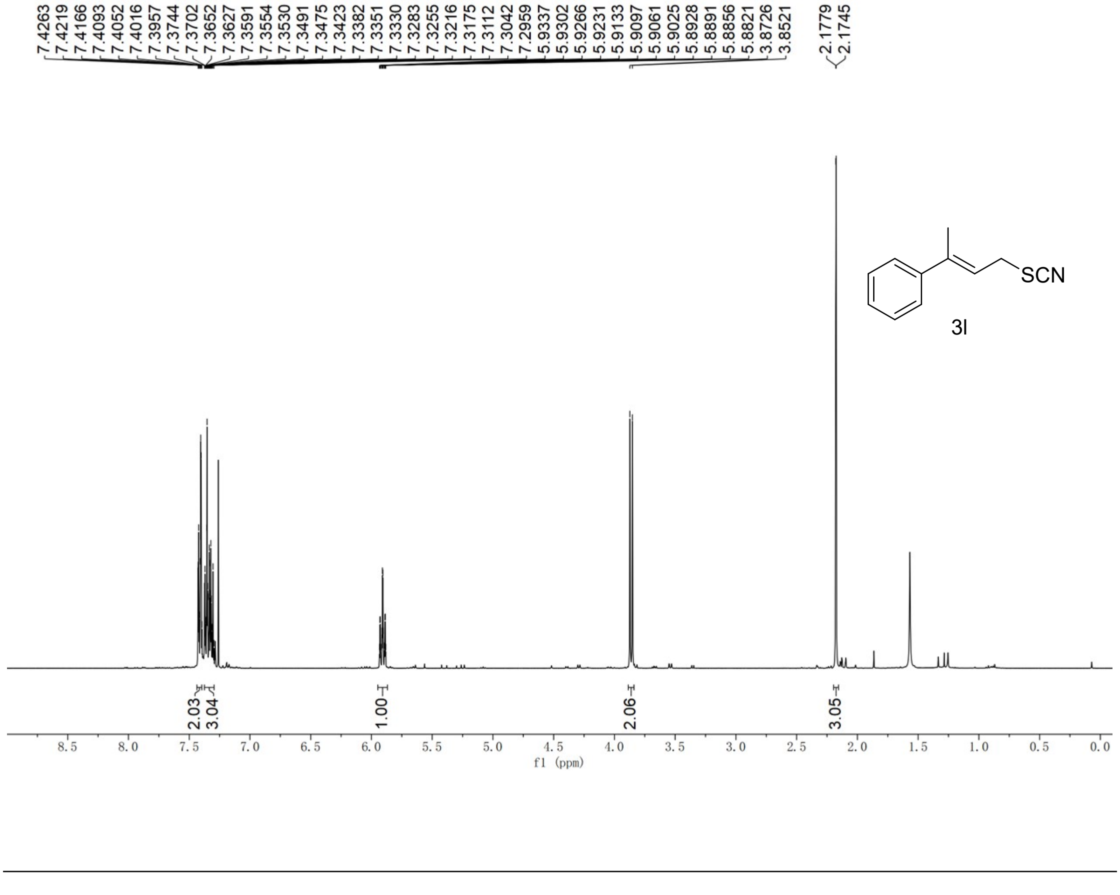
132.5064
132.4008
131.4827
130.7677
130.2565
129.5528
129.3227
129.1867
128.9312
128.7679
128.5505
127.4957
126.7926
121.5985
121.2101
111.5403
111.4537
33.2103
33.1562
Cl
Cl
SCN
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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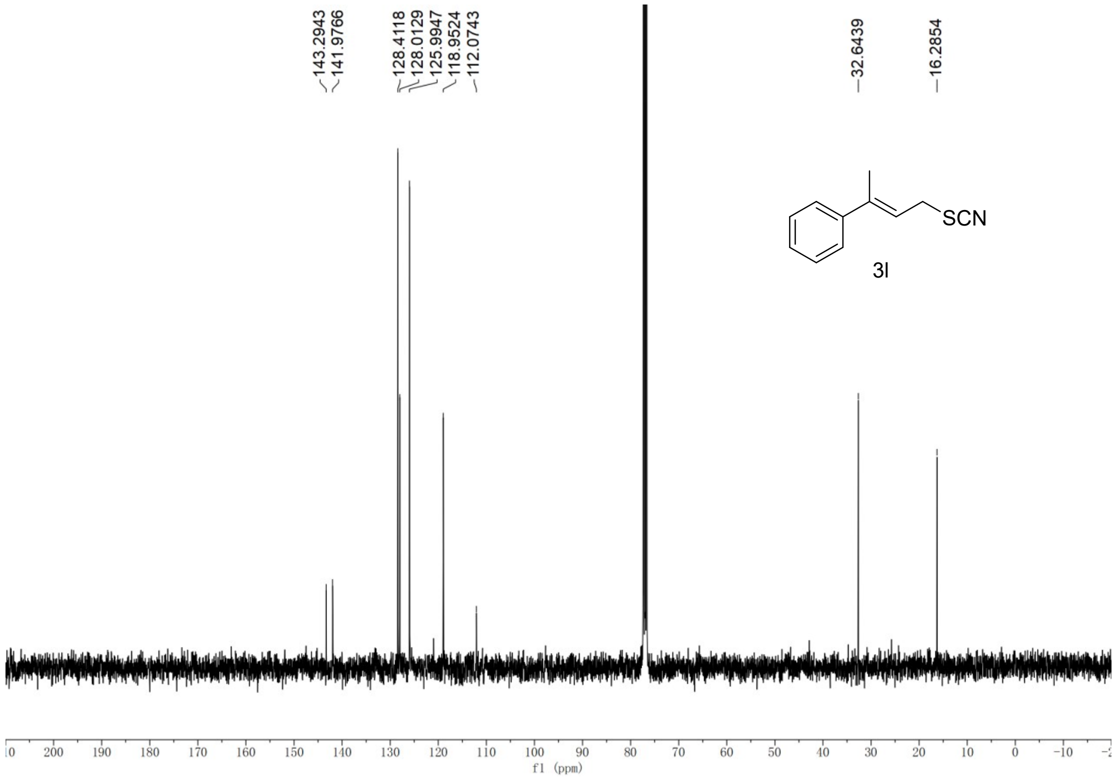
7.3957
7.3744
7.3702
7.3652
7.3627
7.3591
7.3554
7.3530
7.3491
7.3475
7.3423
7.3382
7.3351
7.3330
7.3283
7.3255
7.3216
7.3175
7.3112
7.3042
7.2959
5.9337
5.9302
5.9266
5.9231
5.9133
5.9097
5.9061
5.9025
5.8928
5.8891
5.8856
5.8821
3.8726
3.8521
2.1779
2.1745
SCN
3l
2.03
3.04
1.00
2.06
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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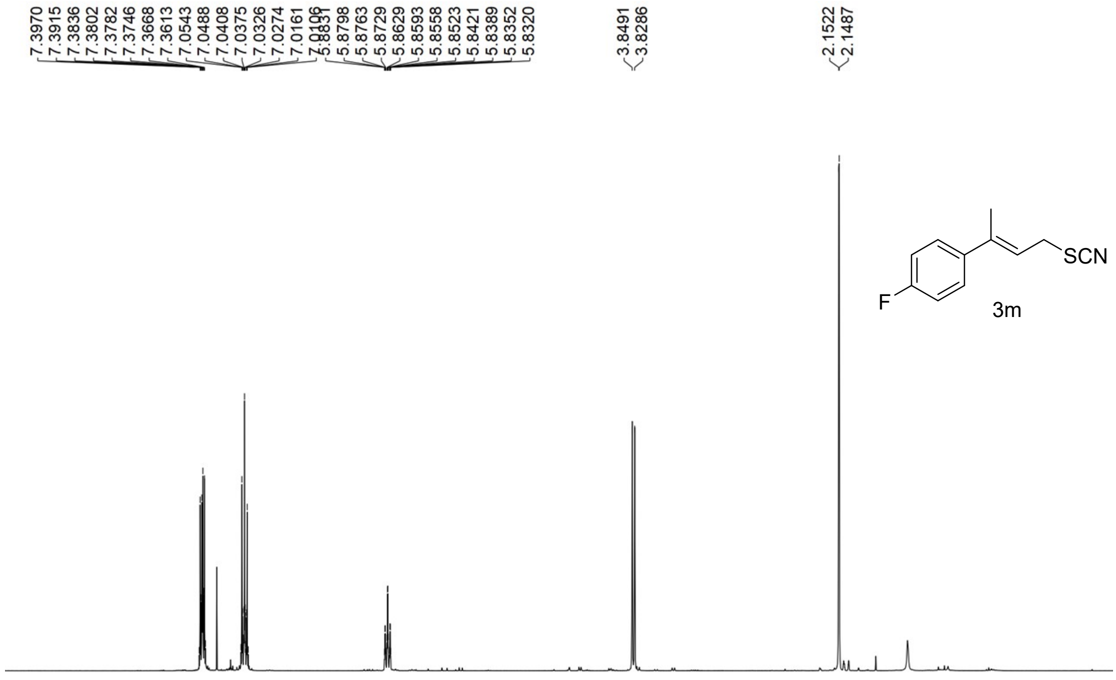
128.4118
128.0129
125.9947
118.9524
112.0743
32.6439
16.2854
SCN
3l
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.3668
7.3613
7.0543
7.0488
7.0408
7.0375
7.0326
7.0274
7.0161
7.0106
5.8831
5.8798
5.8763
5.8729
5.8629
5.8593
5.8558
5.8523
5.8421
5.8389
5.8352
5.8320
3.8491
3.8286
2.1522
2.1487
SCN
F
3m
2.08
2.04
1.00
2.07
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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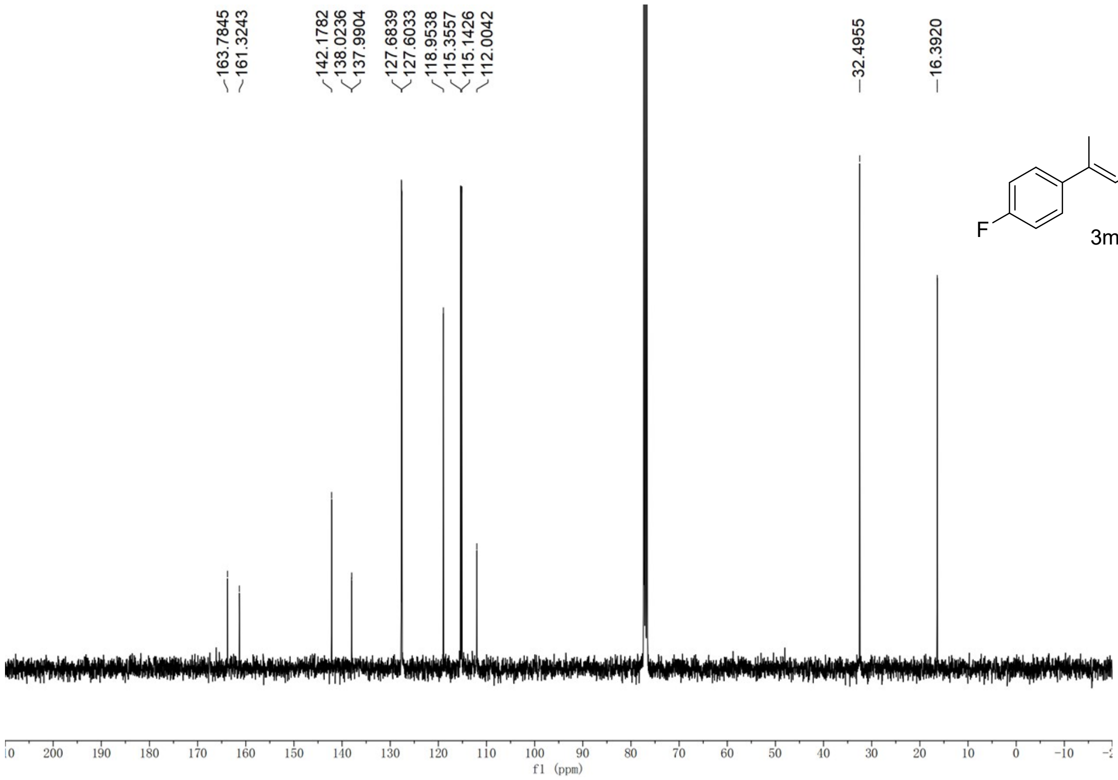
0.0
f1 (ppm)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127.6839
127.6033
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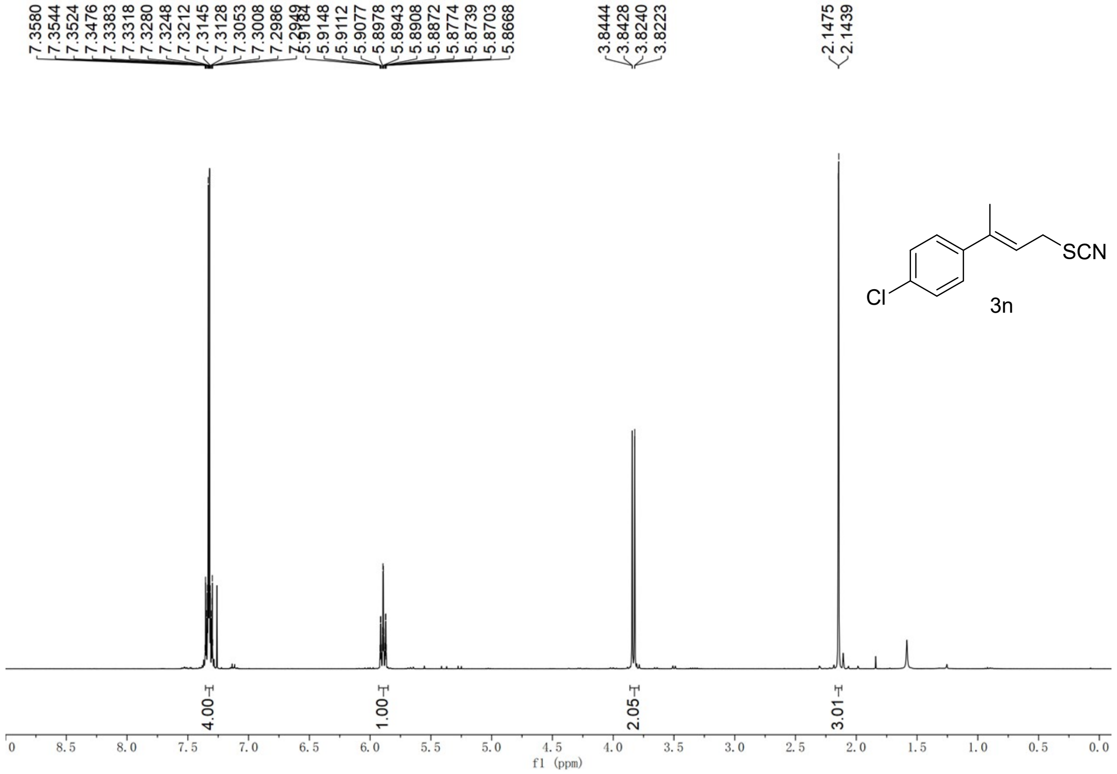
115.3557
115.1426
112.0042
32.4955
16.3920
SCN
F
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-114.2211
-114.2344
-114.2453
-114.2578
-114.2706
-114.2810
-114.2956
SCN
F
3m
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
−260
−280
−300
f1 (ppm)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7.3280
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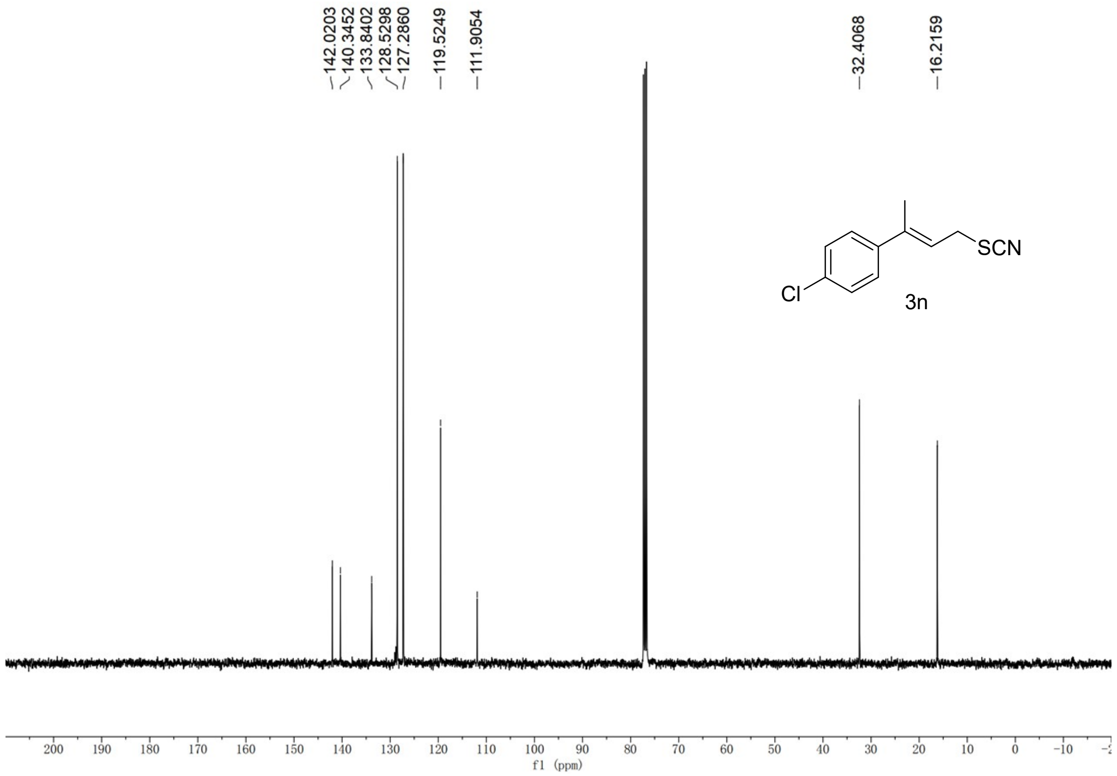
7.3212
7.3145
7.3128
7.3053
7.3008
7.2986
7.2949
5.9184
5.9148
5.9112
5.9077
5.8978
5.8943
5.8908
5.8872
5.8774
5.8739
5.8703
5.8668
3.8444
3.8428
3.8240
3.8223
2.1475
2.1439
SCN
Cl
3n
4.00
1.00
2.05
3.01
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.2860
119.5249
111.9054
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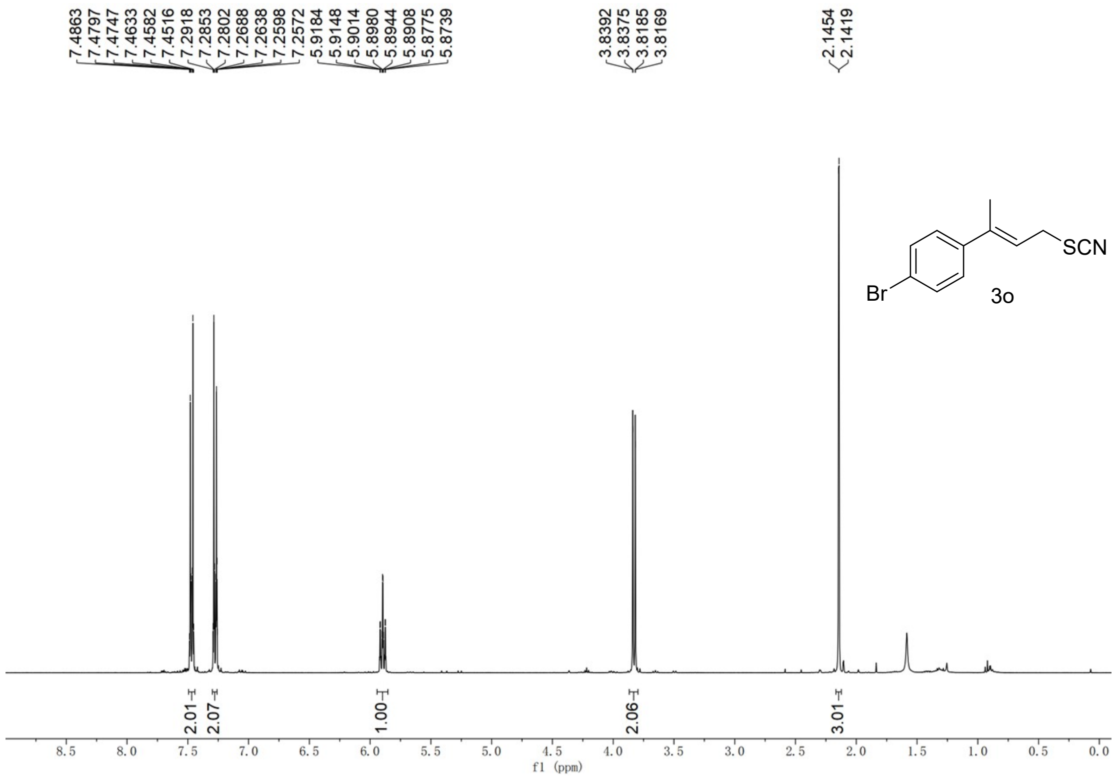
16.2159
SCN
Cl
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −2
f1 (ppm)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7.4516
7.2918
7.2853
7.2802
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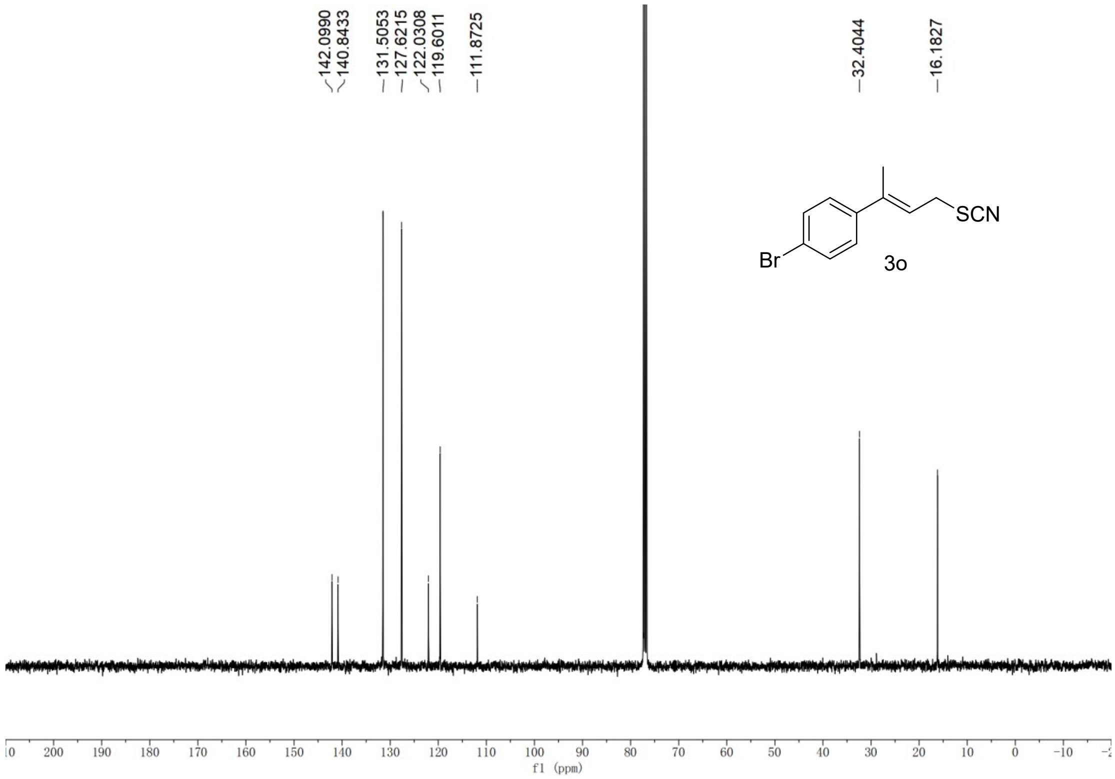
7.2638
7.2598
7.2572
5.9184
5.9148
5.9014
5.8980
5.8944
5.8908
5.8775
5.8739
3.8392
3.8375
3.8185
3.8169
2.1454
2.1419
SCN
Br
3o
2.01
2.07
1.00
2.06
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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111.8725
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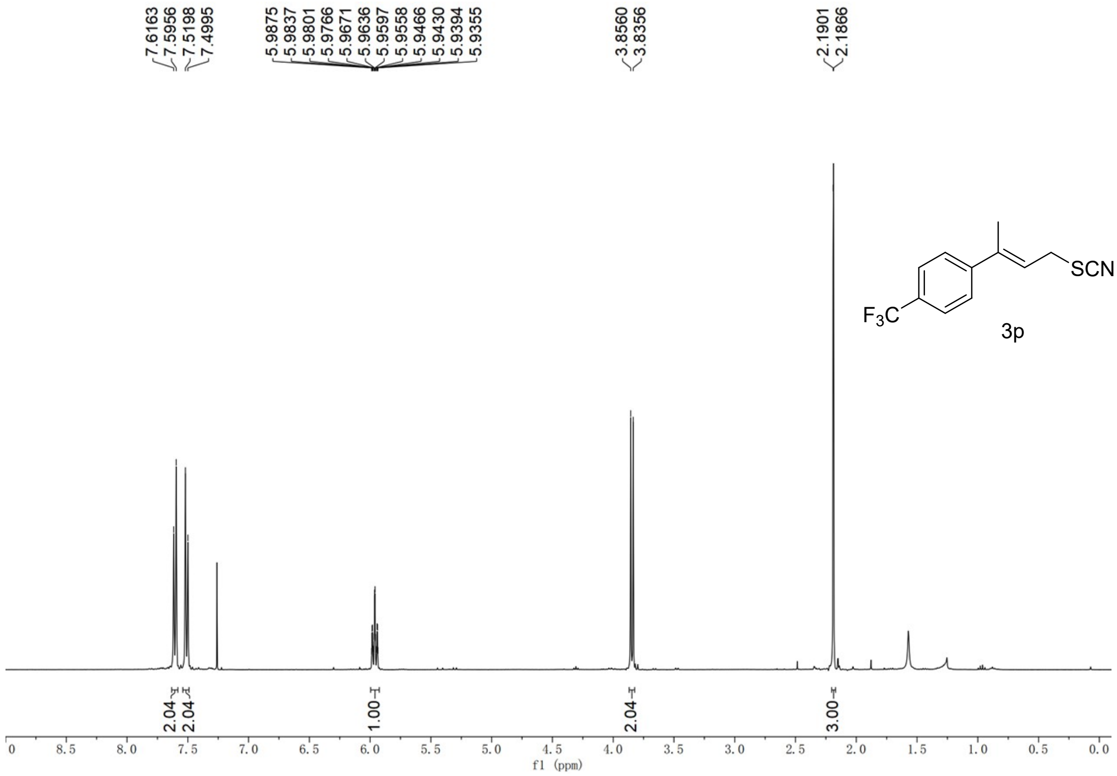
16.1827
Br
SCN
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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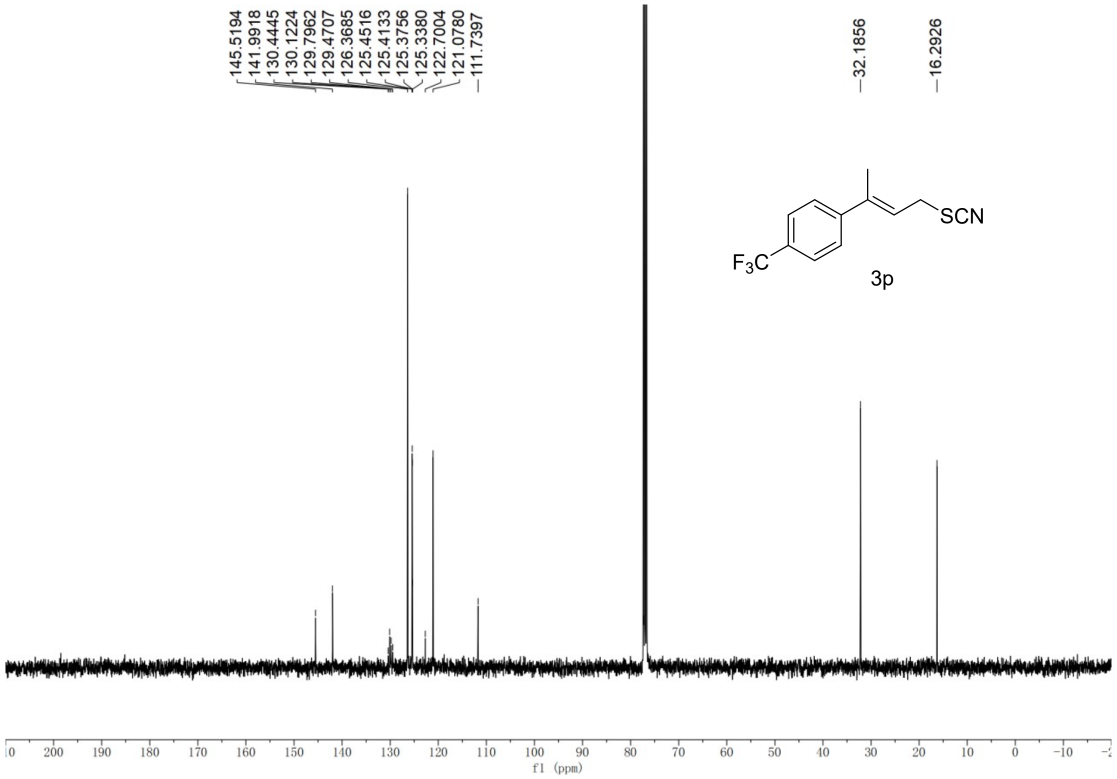
5.9597
5.9558
5.9466
5.9430
5.9394
5.9355
3.8560
3.8356
2.1901
2.1866
SCN
F3C
3p
2.04
2.04
1.00
2.04
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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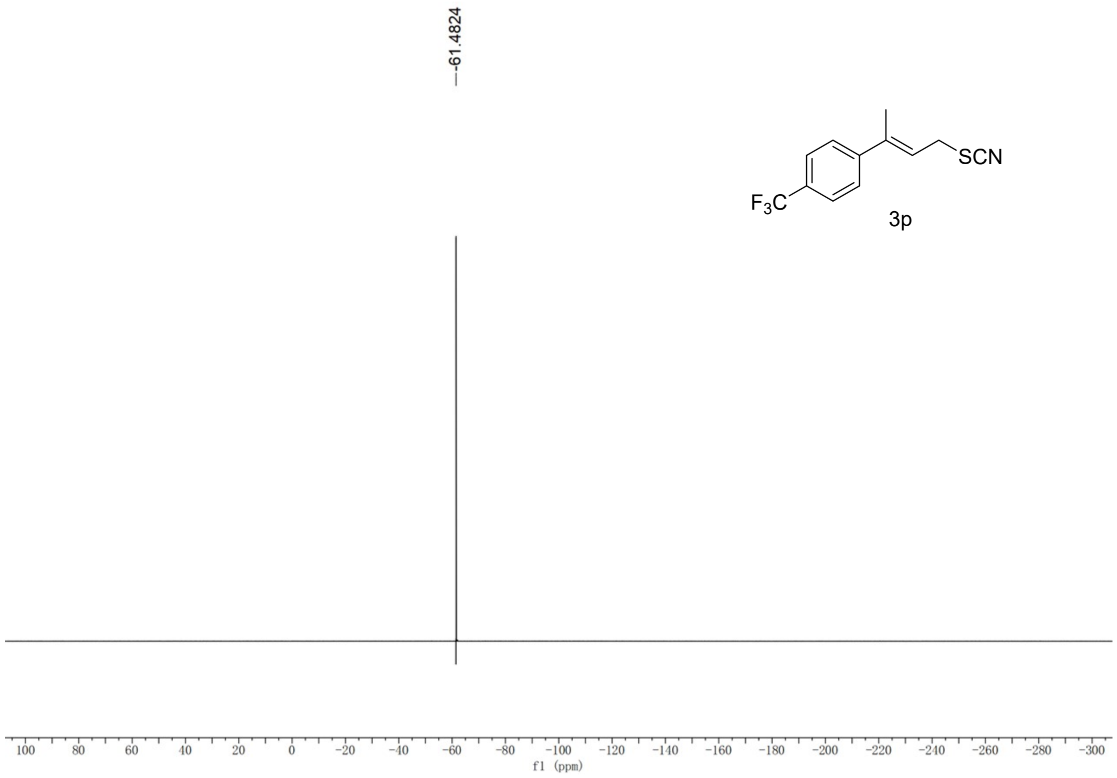
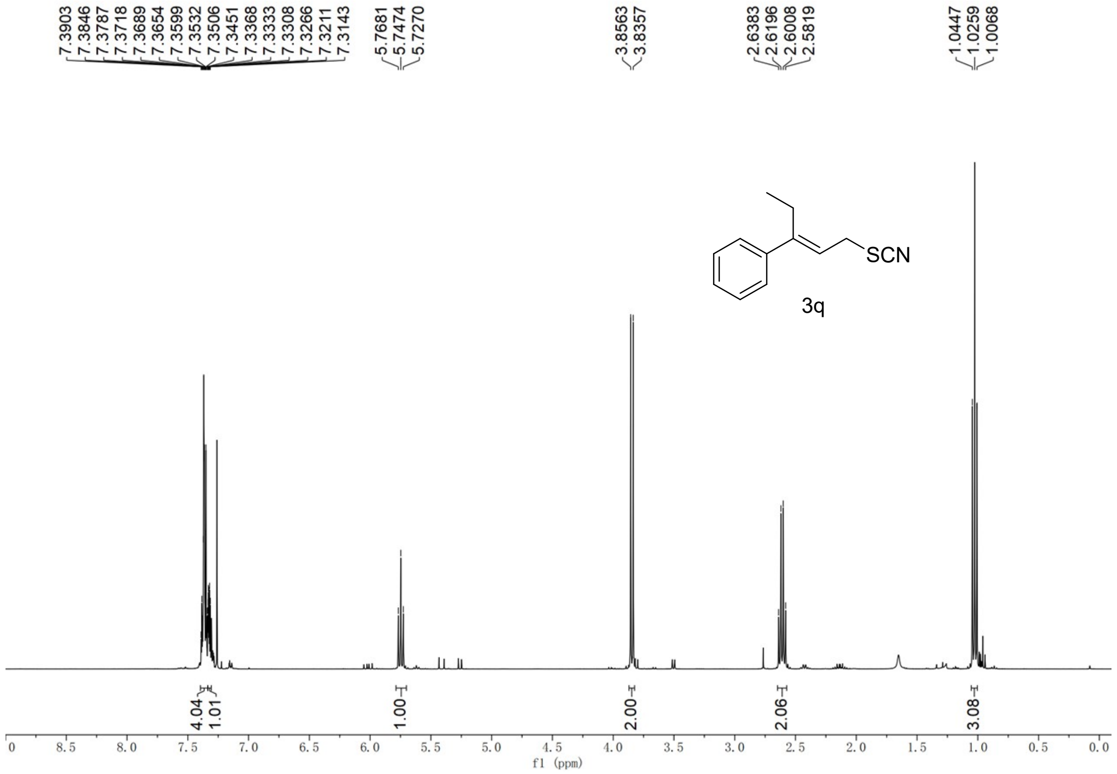
125.3380
122.7004
121.0780
111.7397
32.1856
16.2926
SCN
F3C
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-61.4824
SCN
F3C
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)

3p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7.3333
7.3308
7.3266
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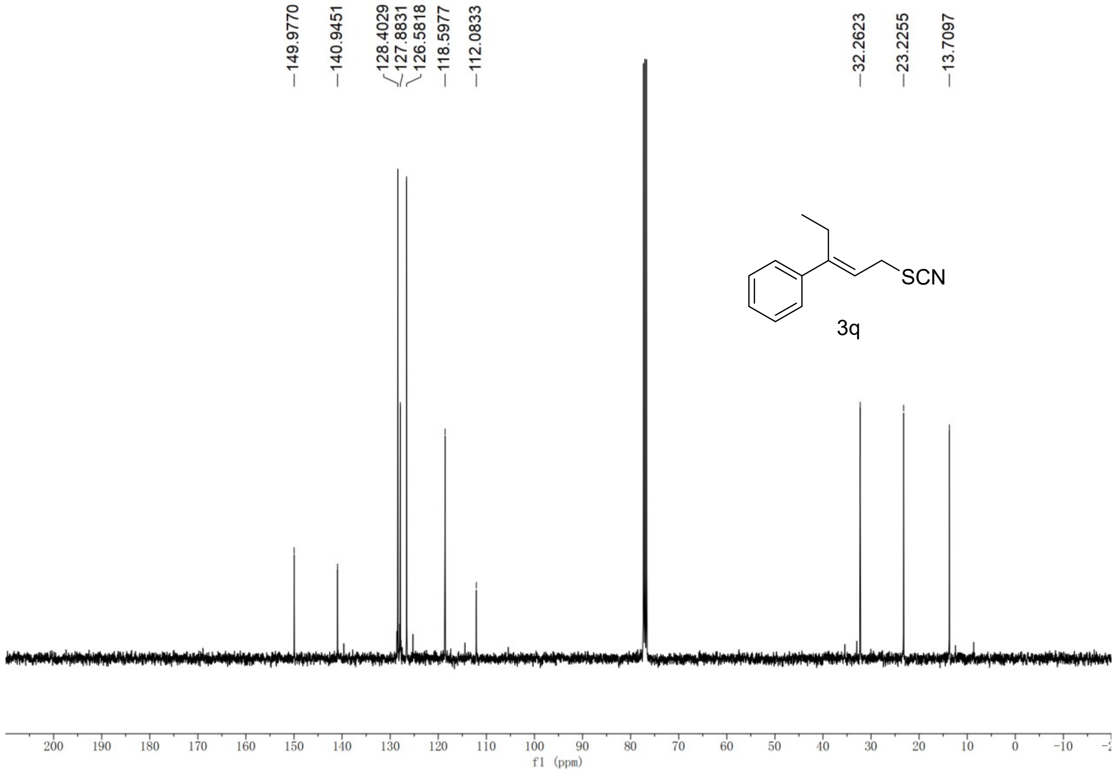
7.3143
5.7681
5.7474
5.7270
3.8563
3.8357
2.6383
2.6196
2.6008
2.5819
1.0447
1.0259
1.0068
SCN
4.04
1.01
1.00
2.00
2.06
3.08
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3q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128.4029
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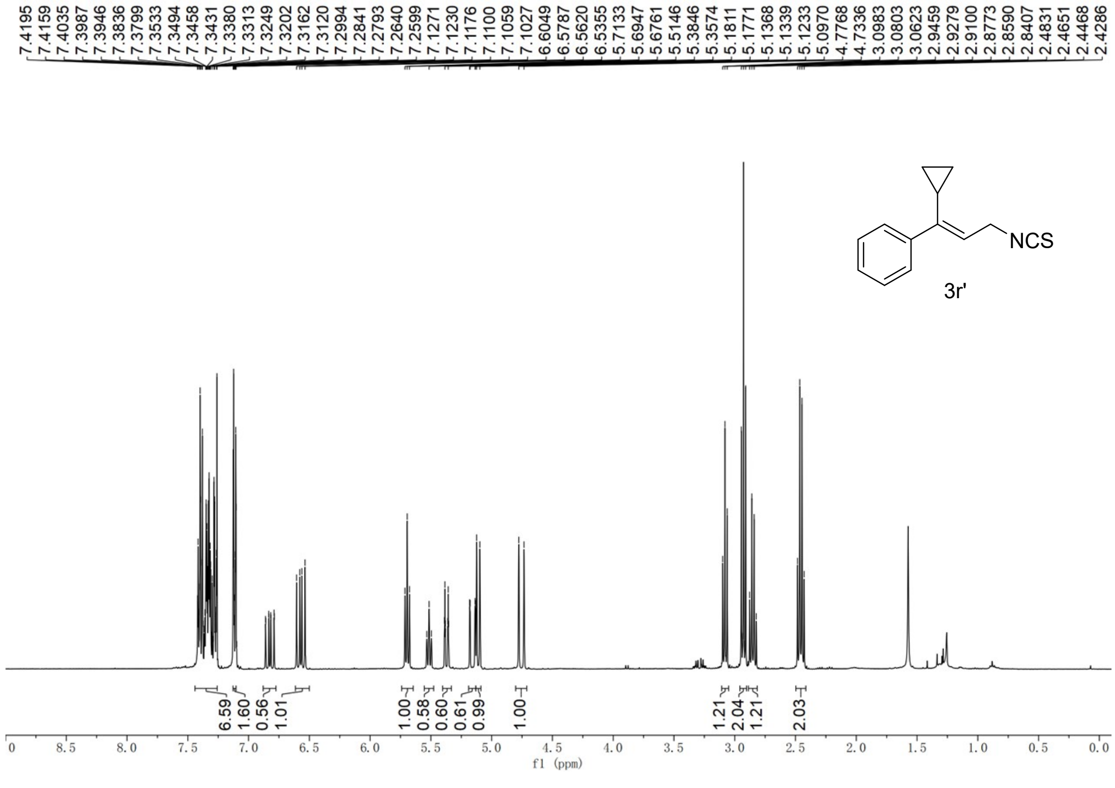
126.5818
118.5977
112.0833
32.2623
23.2255
13.7097
SCN
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.3380
7.3313
7.3249
7.3202
7.3162
7.3120
7.2994
7.2841
7.2793
7.2640
7.2599
7.1271
7.1230
7.1176
7.1100
7.1059
7.1027
6.6049
6.5787
6.5620
6.5355
5.7133
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5.6761
5.5146
5.3846
5.3574
5.1811
5.1771
5.1368
5.1339
5.1233
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3.0803
3.0623
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2.9279
2.9100
2.8773
2.8590
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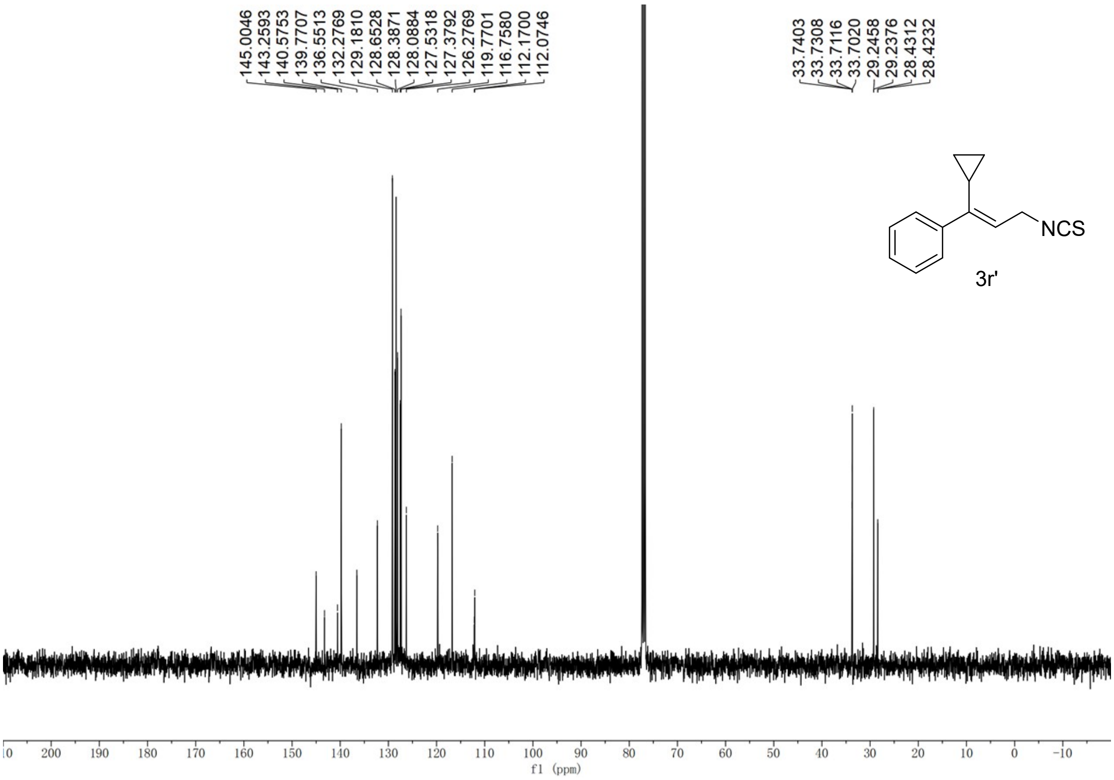
2.4831
2.4651
2.4468
2.4286
NCS
3r'
6.59
1.60
0.56
1.01
1.00
0.58
0.60
0.61
0.99
1.00
1.21
2.04
1.21
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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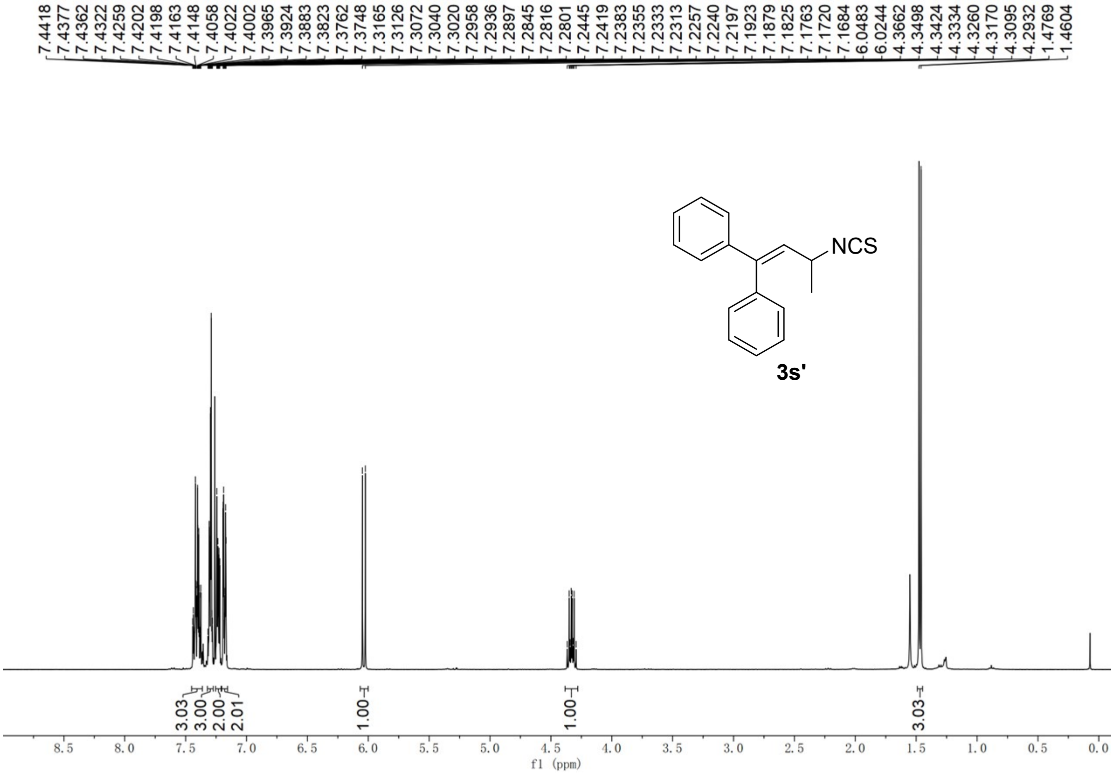
128.0884
127.5318
126.2769
119.7701
116.7580
112.1700
112.0746
33.7403
33.7308
33.7116
33.7020
29.2458
29.2376
28.4312
28.4232
NCS
3r'
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3924
7.3883
7.3823
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7.3748
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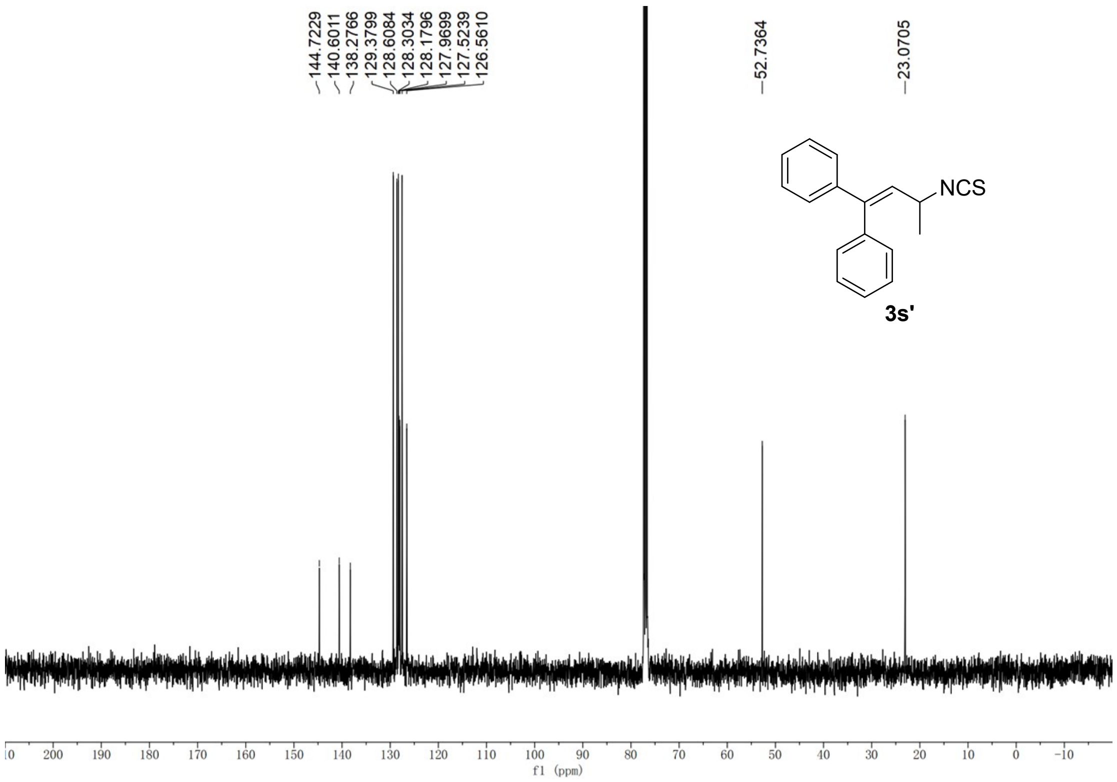
7.3126
7.3072
7.3040
7.3020
7.2958
7.2936
7.2897
7.2845
7.2816
7.2801
7.2445
7.2419
7.2383
7.2355
7.2333
7.2313
7.2257
7.2240
7.2197
7.1923
7.1879
7.1825
7.1763
7.1720
7.1684
6.0483
6.0244
4.3662
4.3498
4.3424
4.3334
4.3260
4.3170
4.3095
4.2932
1.4769
1.4604
NCS
3s'
3.03
3.00
2.00
2.01
1.00
1.00
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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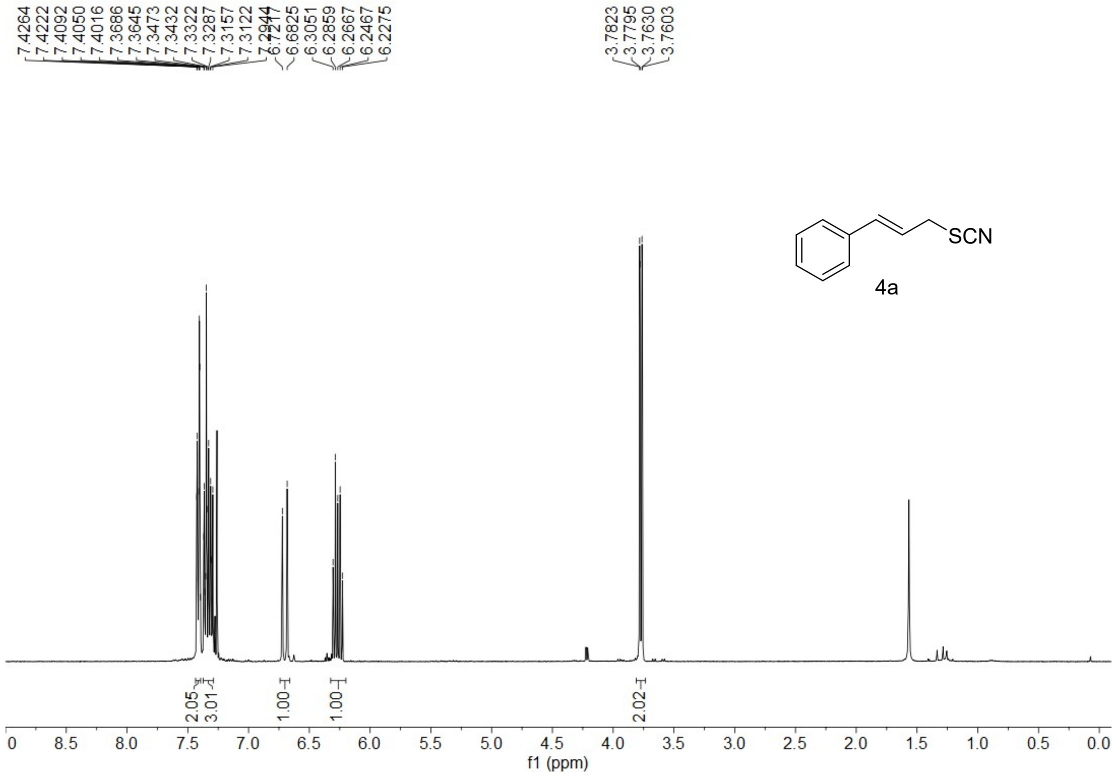
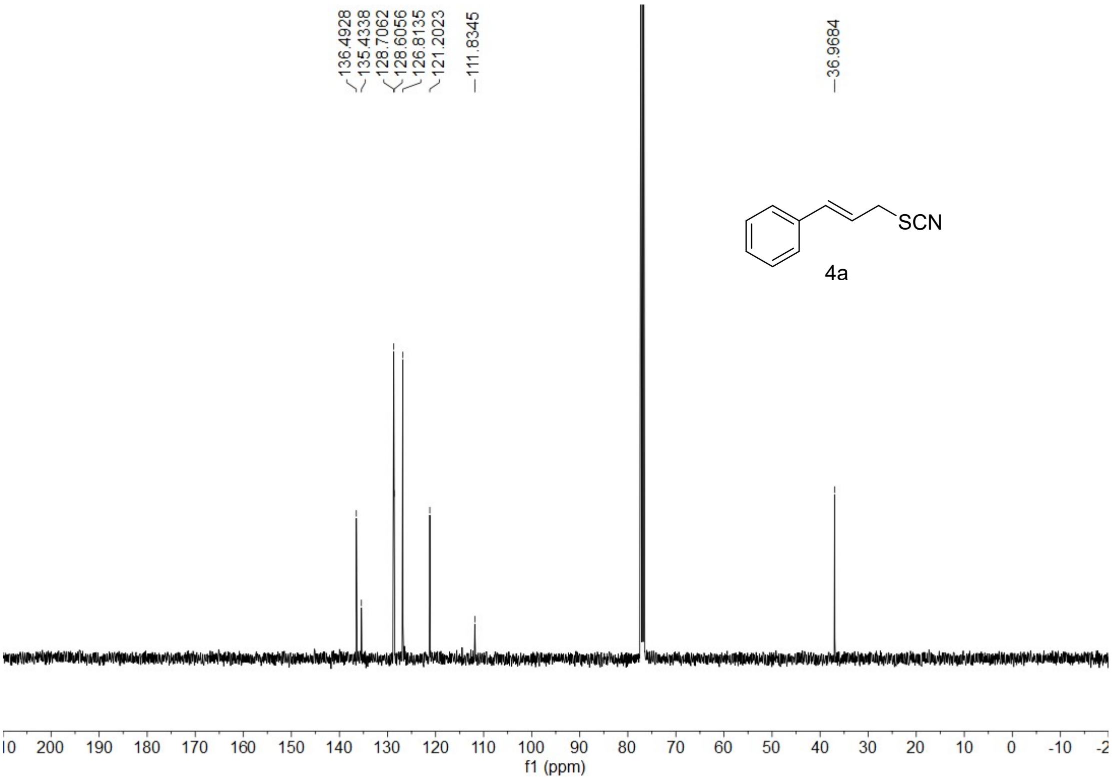
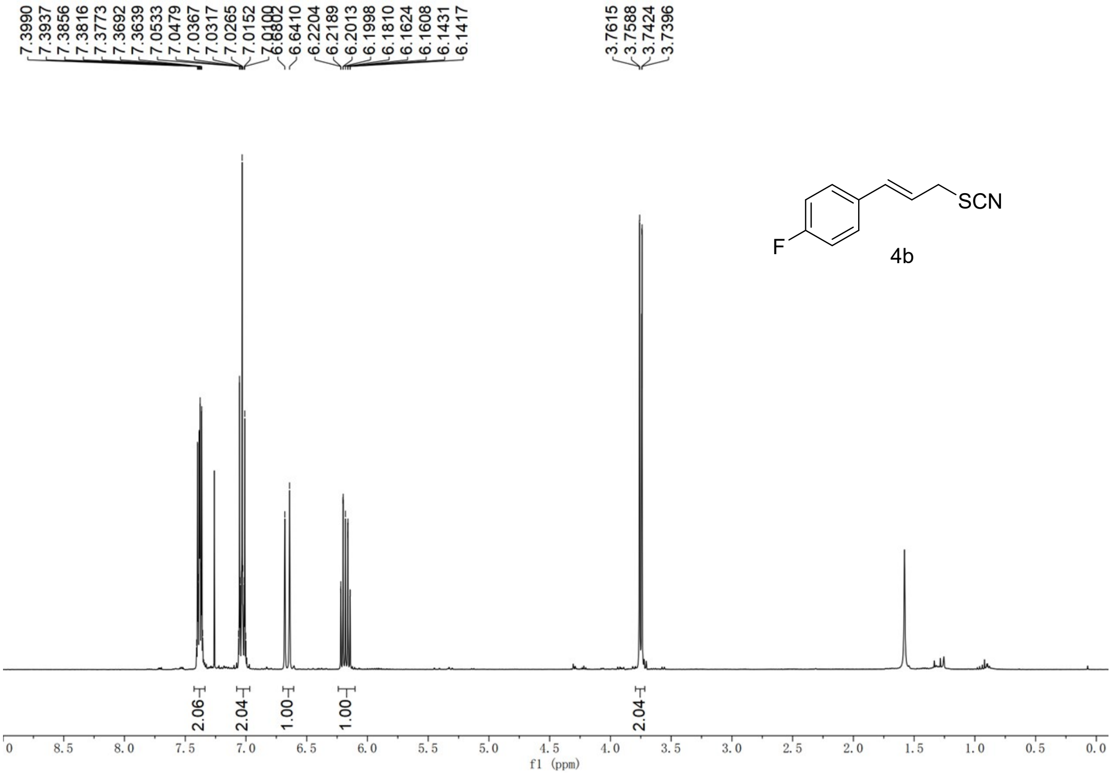
138.2766
129.3799
128.6084
128.3034
128.1796
127.9699
127.5239
126.5610
52.7364
23.0705
NCS
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

3s'


7.4264
7.4222
7.4092
7.4050
7.4016
7.3686
7.3645
7.3473
7.3432
7.3322
7.3287
7.3157
7.3122
7.2944
6.7217
6.6825
6.3051
6.2859
6.2667
6.2467
6.2275
3.7823
3.7795
3.7630
3.7603
SCN
2.05
3.01
1.00
1.00
2.02
f1 (ppm)
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

4a


136.4928
135.4338
128.7062
128.6056
126.8135
121.2023
111.8345
36.9684
SCN
4a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)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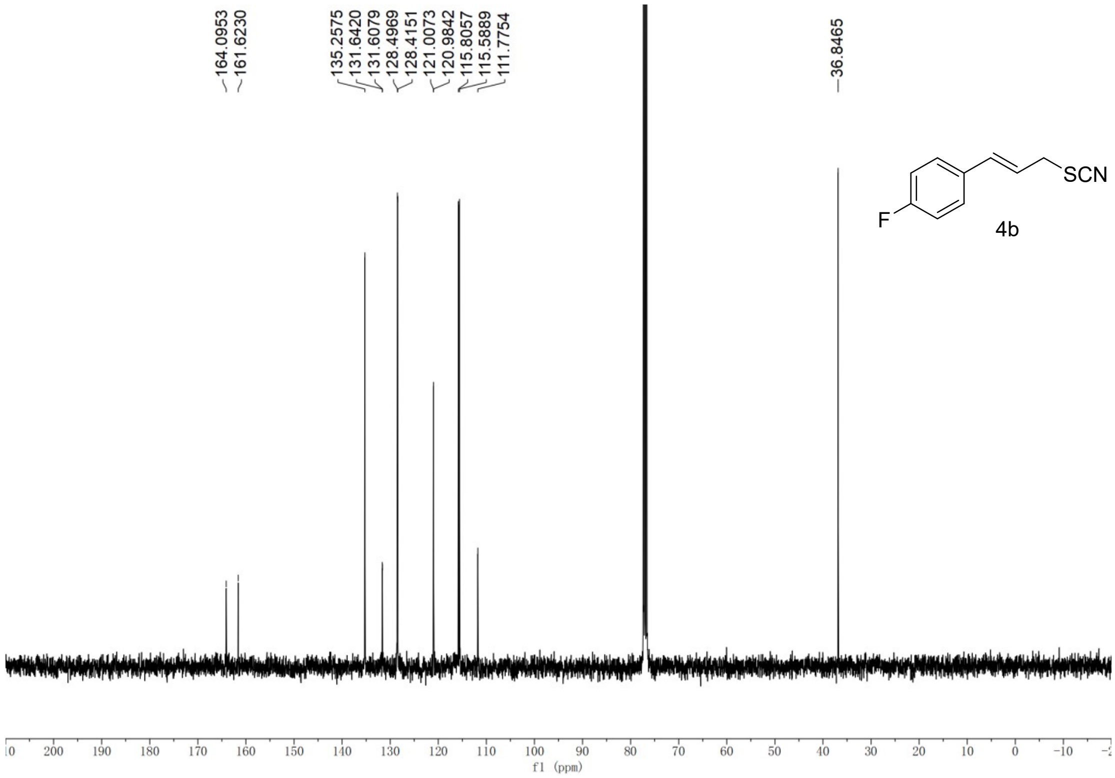
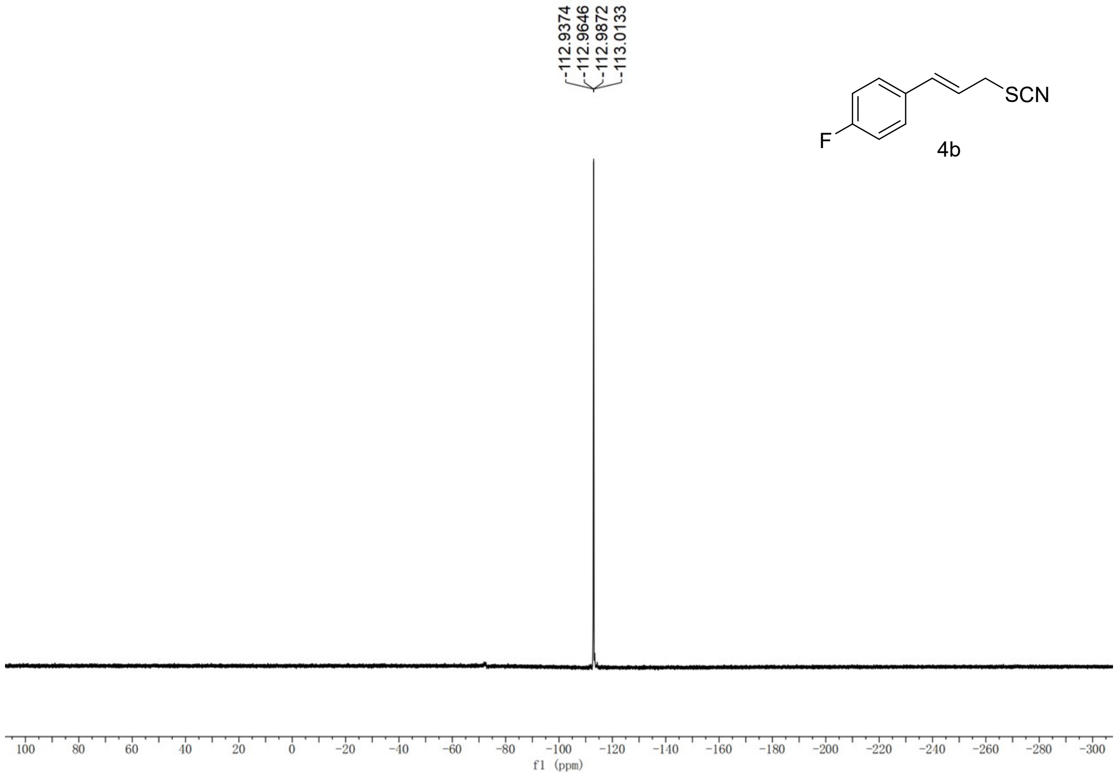
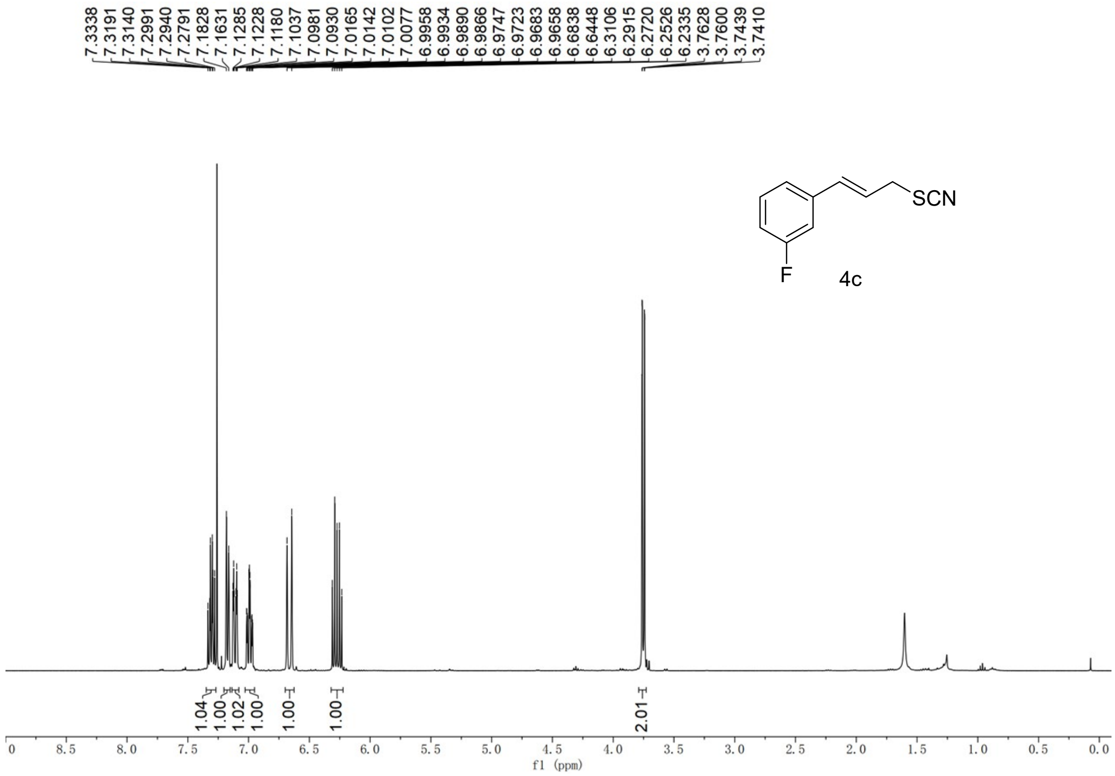
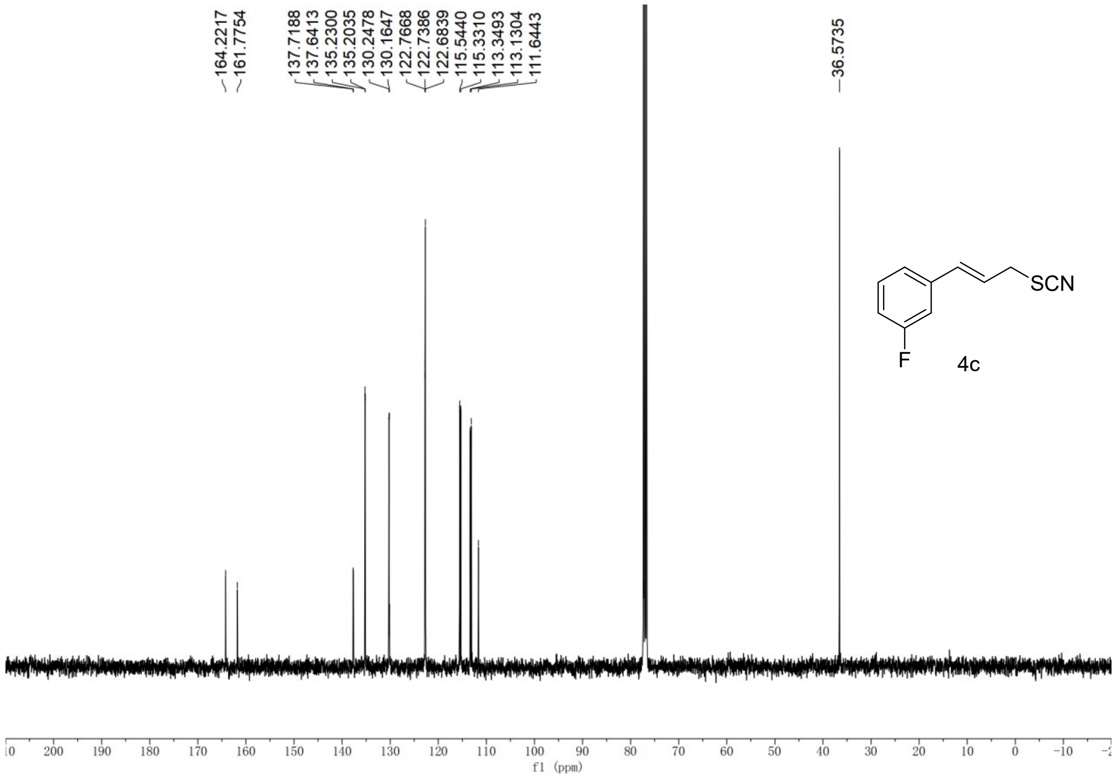
7.3937
7.3856
7.3816
7.3773
7.3692
7.3639
7.0533
7.0479
7.0367
7.0317
7.0265
7.0152
7.0100
6.6802
6.6410
6.2204
6.2189
6.2013
6.1998
6.1810
6.1624
6.1608
6.1431
6.1417
3.7615
3.7588
3.7424
3.7396
SCN
F
4b
2.06
2.04
1.00
1.00
2.04
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.0953
161.6230
135.2575
131.6420
131.6079
128.4969
128.4151
121.0073
120.9842
115.8057
115.5889
111.7754
36.8465
SCN
F
4b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-112.9374
-112.9646
-112.9872
-113.0133
SCN
F
4b
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)


7.3338
7.3191
7.3140
7.2991
7.2940
7.2791
7.1828
7.1631
7.1285
7.1228
7.1180
7.1037
7.0981
7.0930
7.0165
7.0142
7.0102
7.0077
6.9958
6.9934
6.9890
6.9866
6.9747
6.9723
6.9683
6.9658
6.6838
6.6448
6.3106
6.2915
6.2720
6.2526
6.2335
3.7628
3.7600
3.7439
3.7410
SCN
F
4c
1.04
1.00
1.02
1.00
1.00
1.00
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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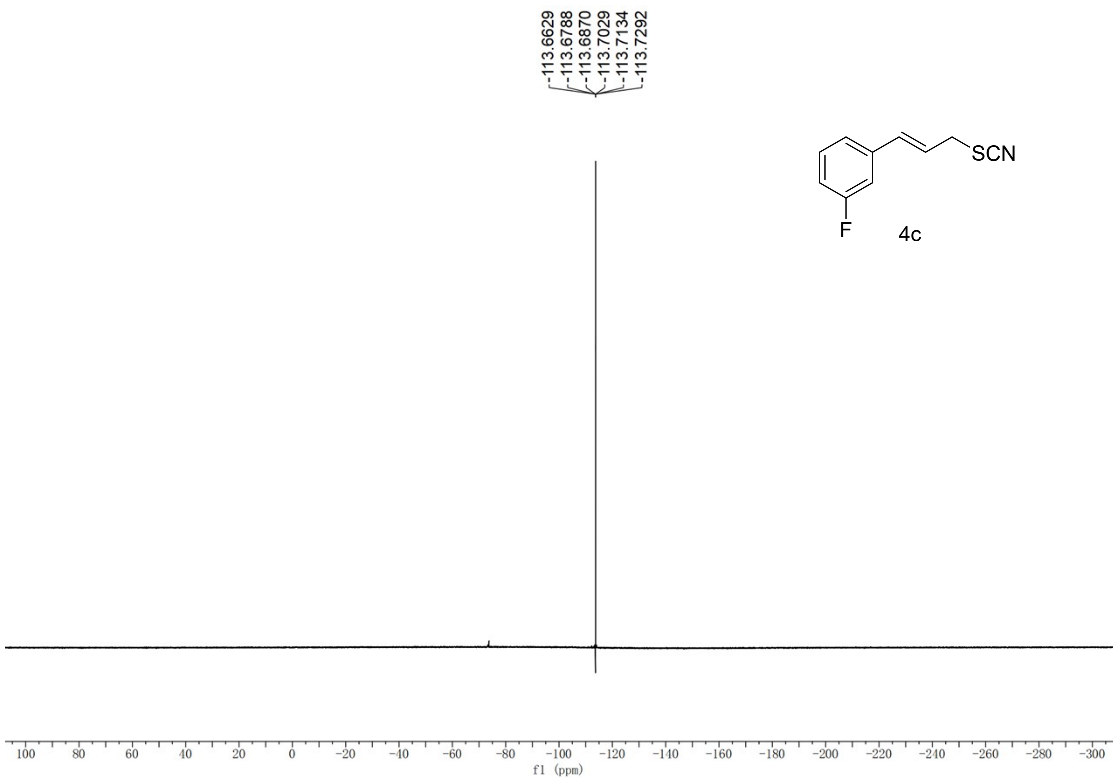
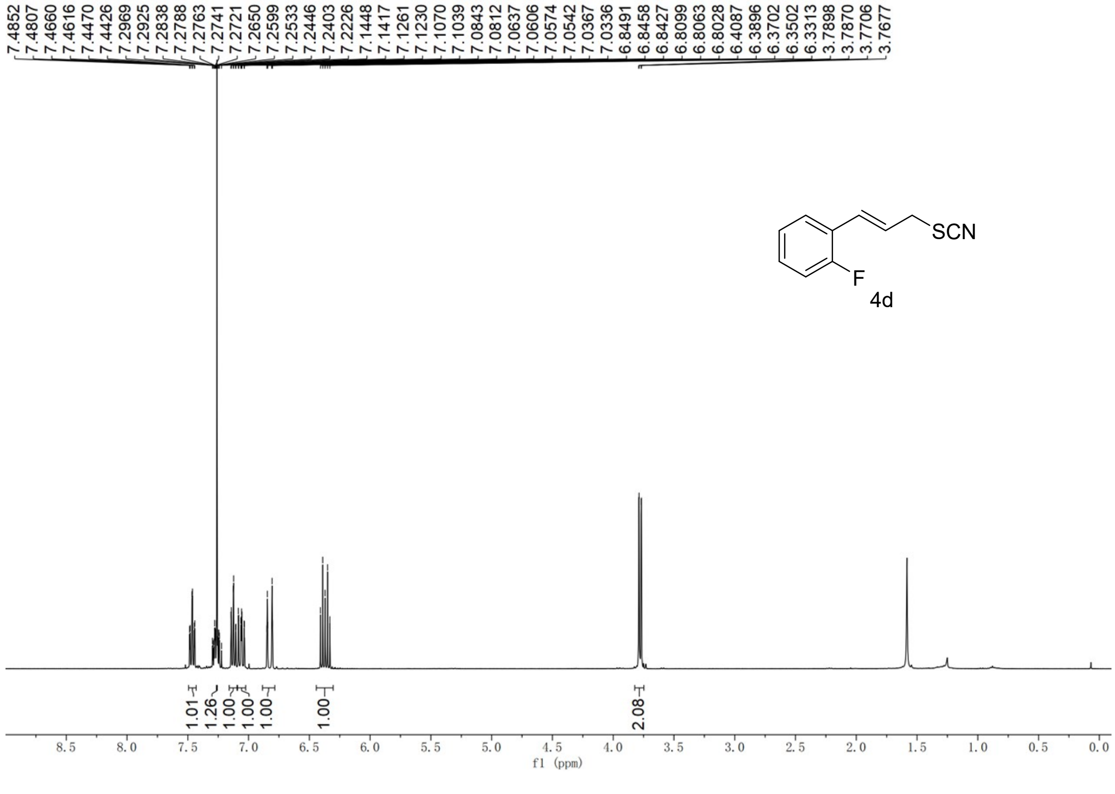
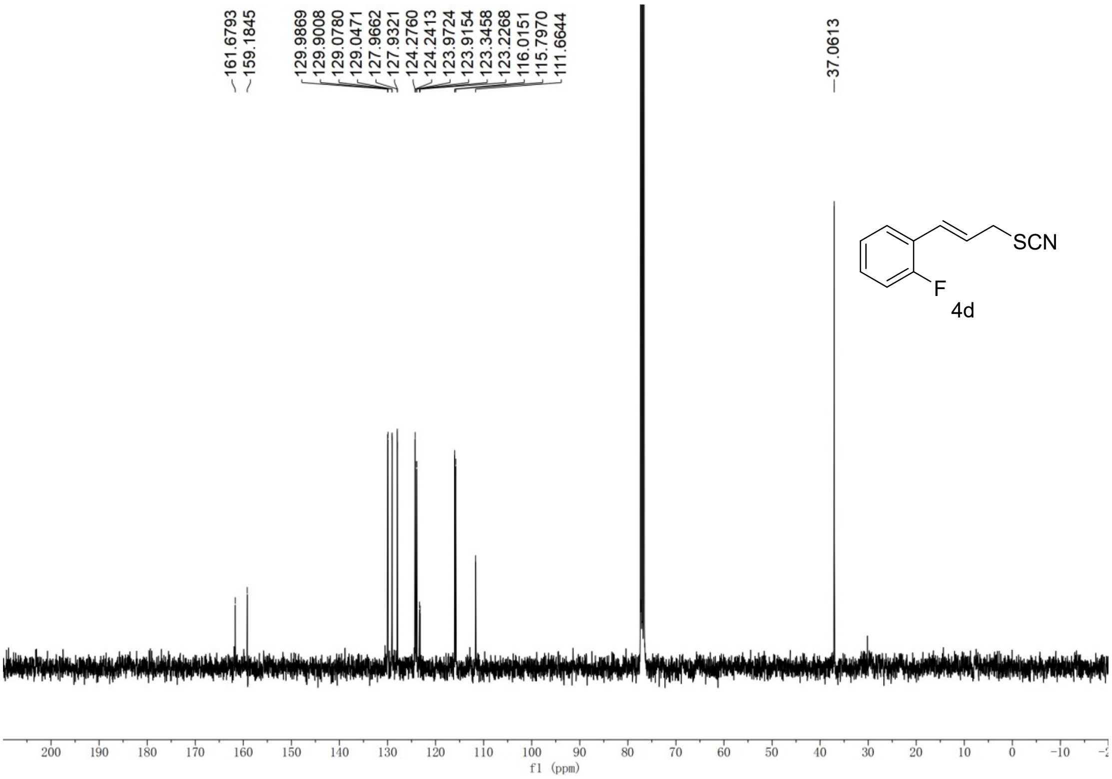
161.7754
137.7188
137.6413
135.2300
135.2035
130.2478
130.1647
122.7668
122.7386
122.6839
115.5440
115.3310
113.3493
113.1304
111.6443
36.5735
SCN
F
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-113.6629
-113.6788
-113.6870
-113.7029
-113.7134
-113.7292
SCN
F
4c
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


7.4852
7.4807
7.4660
7.4616
7.4470
7.4426
7.2969
7.2925
7.2838
7.2788
7.2763
7.2741
7.2721
7.2650
7.2599
7.2533
7.2446
7.2403
7.2226
7.1448
7.1417
7.1261
7.1230
7.1070
7.1039
7.0843
7.0812
7.0637
7.0606
7.0574
7.0542
7.0367
7.0336
6.8491
6.8458
6.8427
6.8099
6.8063
6.8028
6.4087
6.3896
6.3702
6.3502
6.3313
3.7898
3.7870
3.7706
3.7677
SCN
F
4d
1.01
1.26
1.00
1.00
1.00
1.00
2.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.9869
129.9008
129.0780
129.0471
127.9662
127.9321
124.2760
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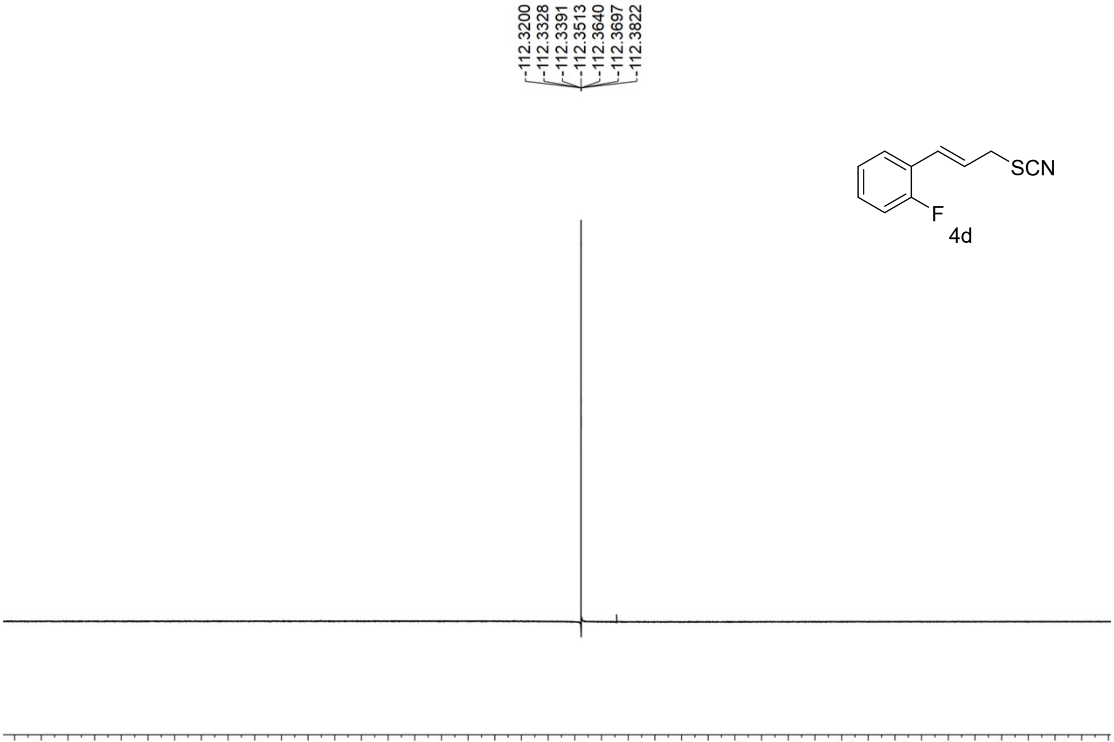
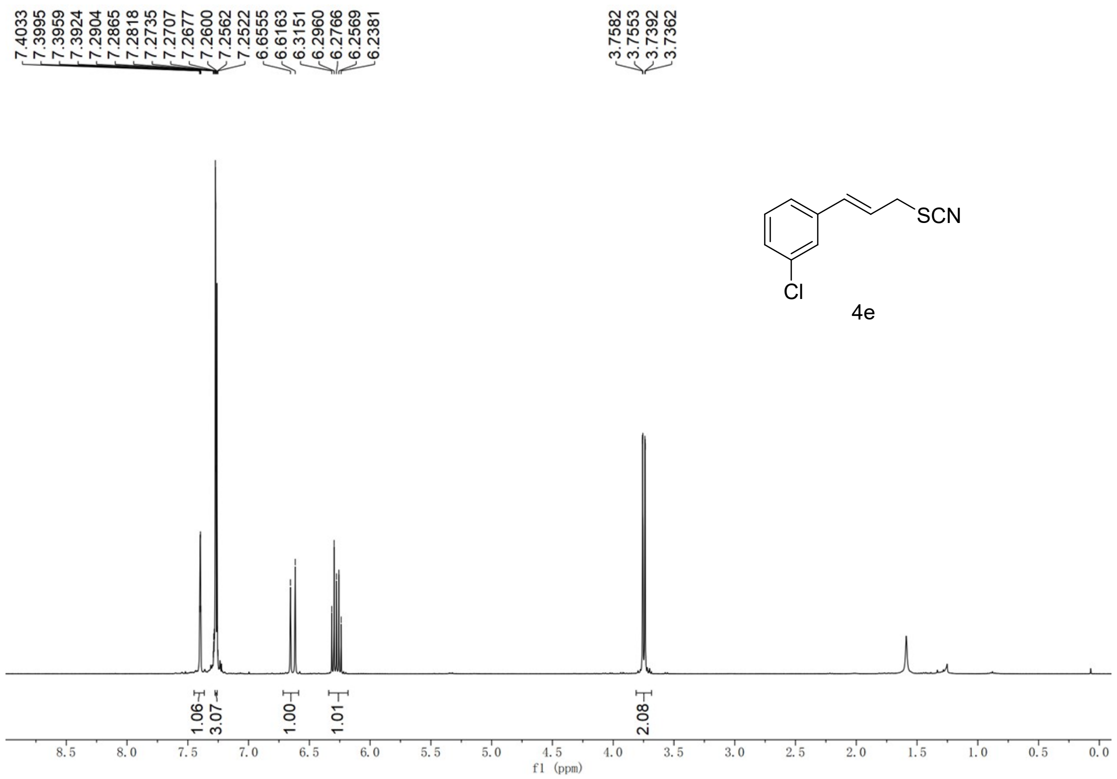
123.9724
123.9154
123.3458
123.2268
116.0151
115.7970
111.6644
37.0613
SCN
F
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-112.3200
-112.3328
-112.3391
-112.3513
-112.3640
-112.3697
-112.3822
SCN
F
4d
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−250
−270
−290
f1 (ppm)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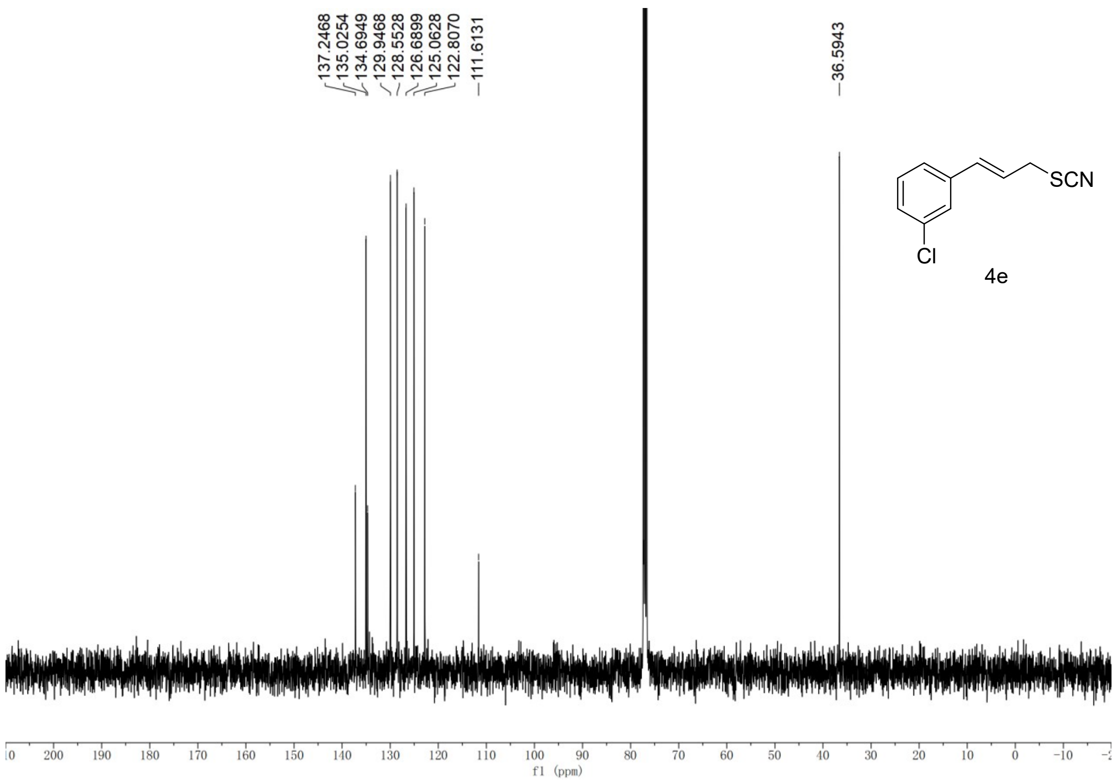
7.3995
7.3959
7.3924
7.2904
7.2865
7.2818
7.2735
7.2707
7.2677
7.2600
7.2562
7.2522
6.6555
6.6163
6.3151
6.2960
6.2766
6.2569
6.2381
3.7582
3.7553
3.7392
3.7362
SCN
Cl
1.06
3.07
1.00
1.01
2.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4e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134.6949
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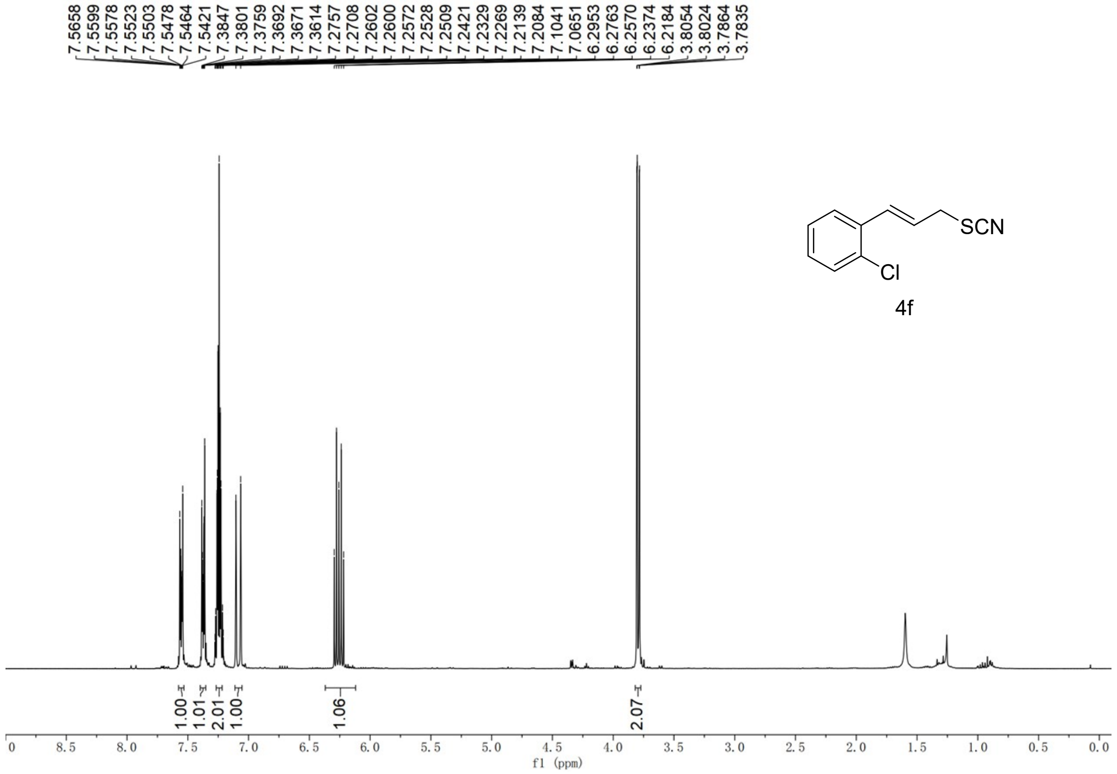
128.5528
126.6899
125.0628
122.8070
111.6131
36.5943
SCN
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4e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7.5464
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7.3847
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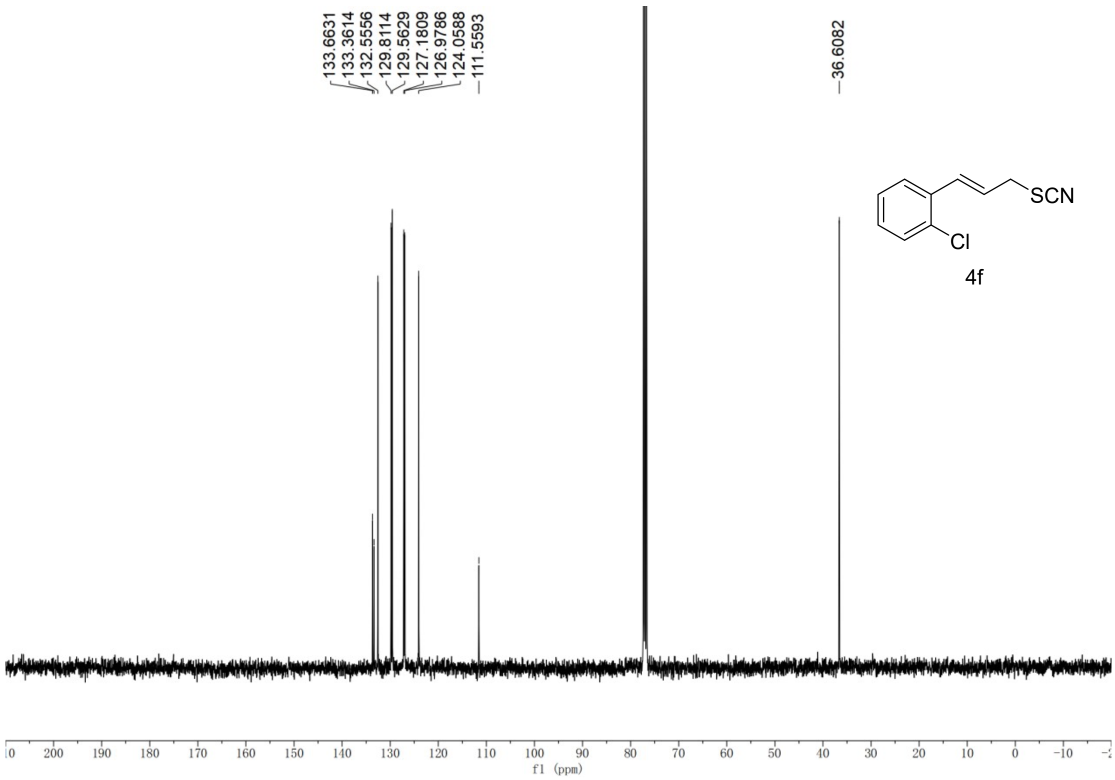
7.3692
7.3671
7.3614
7.2757
7.2708
7.2602
7.2600
7.2572
7.2528
7.2509
7.2421
7.2329
7.2269
7.2139
7.2084
7.1041
7.0651
6.2953
6.2763
6.2570
6.2374
6.2184
3.8054
3.8024
3.7864
3.7835
SCN
Cl
1.00
1.01
2.01
1.00
1.06
2.07
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4f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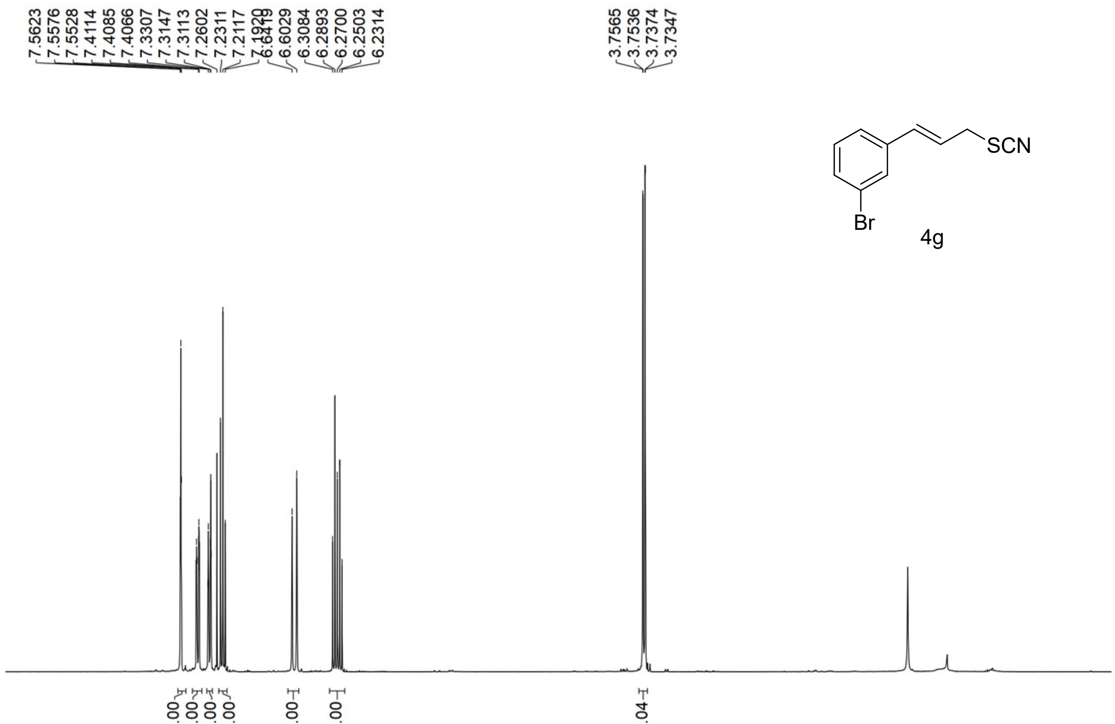
132.5556
129.8114
129.5629
127.1809
126.9786
124.0588
111.5593
36.6082
SCN
Cl
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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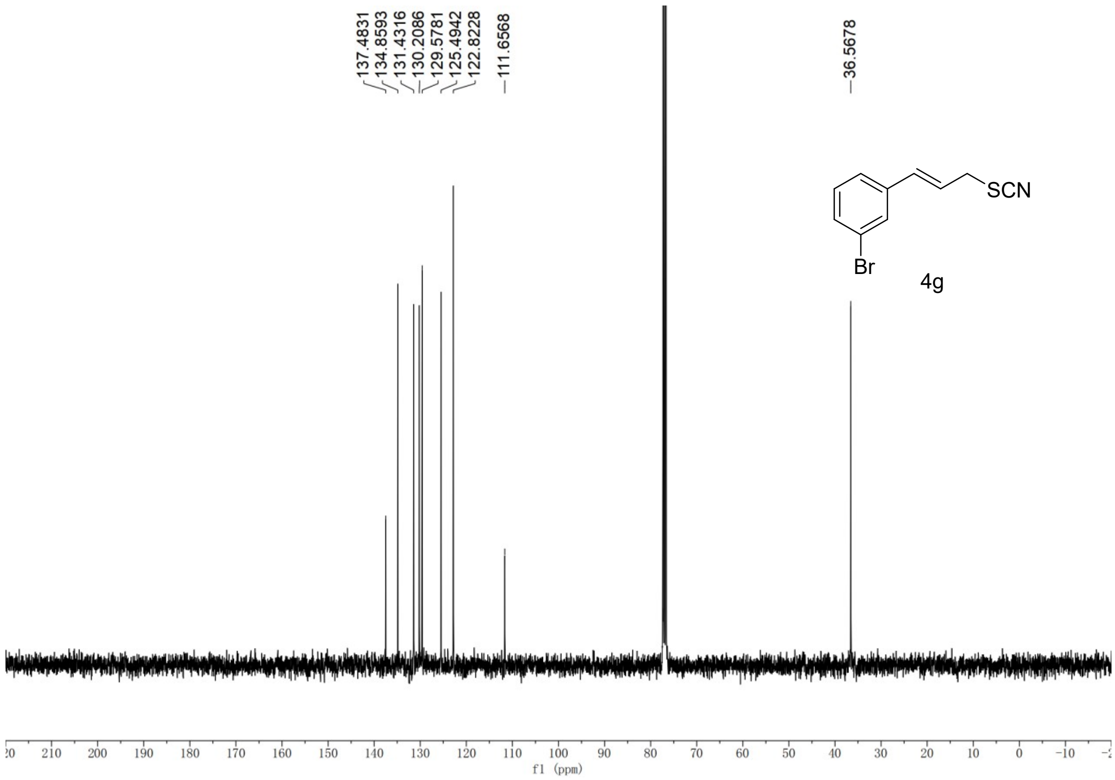
7.3307
7.3147
7.3113
7.2602
7.2311
7.2117
7.1920
6.6419
6.6029
6.3084
6.2893
6.2700
6.2503
6.2314
3.7565
3.7536
3.7374
3.7347
SCN
Br
4g
1.00
1.00
1.00
1.00
1.00
1.00
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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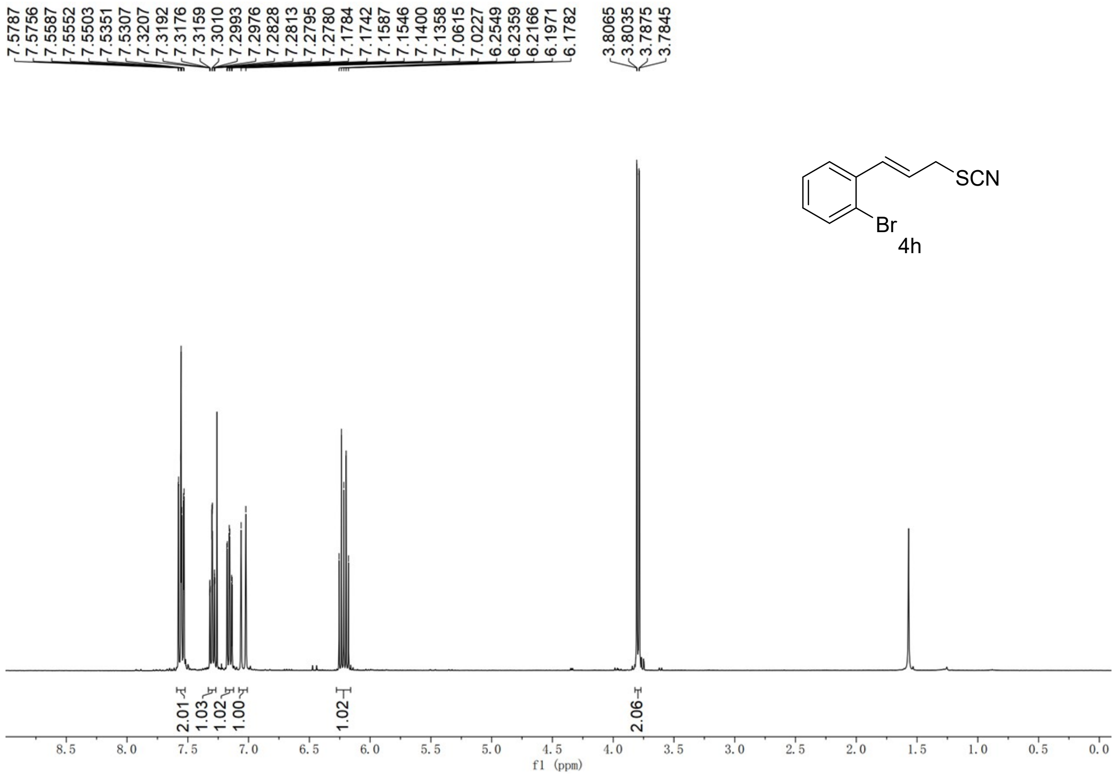
36.5678
SCN
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

4g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7.3192
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7.3159
7.3010
7.2993
7.2976
7.2828
7.2813
7.2795
7.2780
7.1784
7.1742
7.1587
7.1546
7.1400
7.1358
7.0615
7.0227
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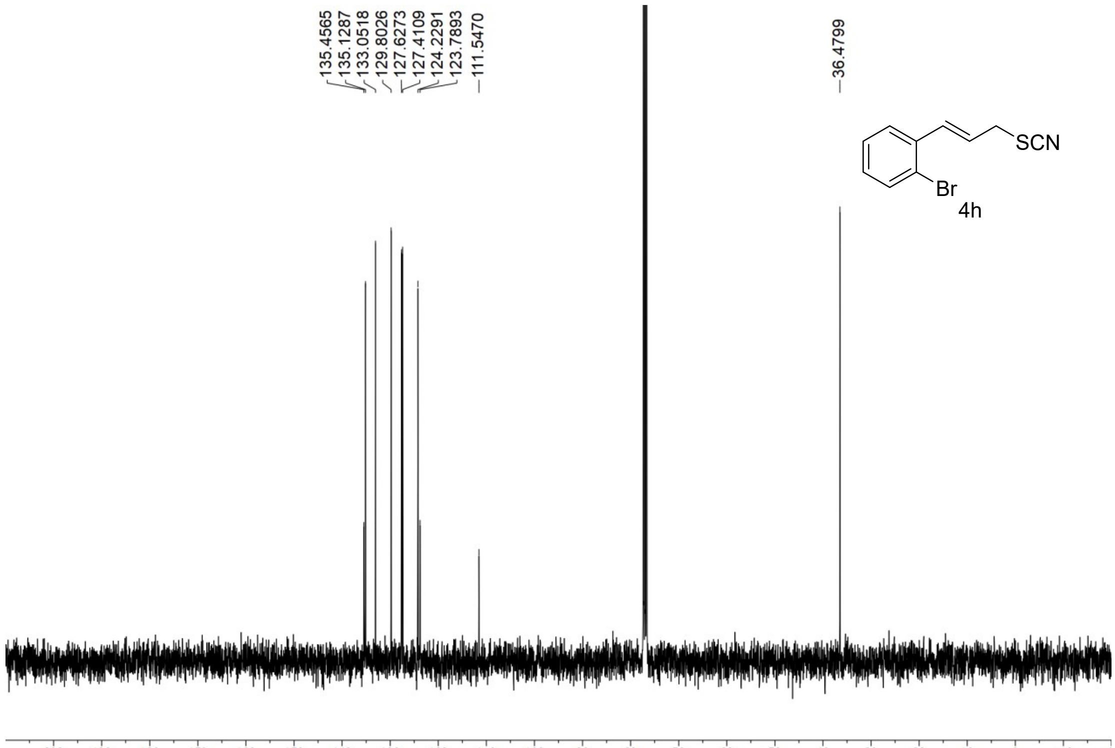
6.2359
6.2166
6.1971
6.1782
3.8065
3.8035
3.7875
3.7845
SCN
Br
4h
2.01
1.03
1.02
1.00
1.02
2.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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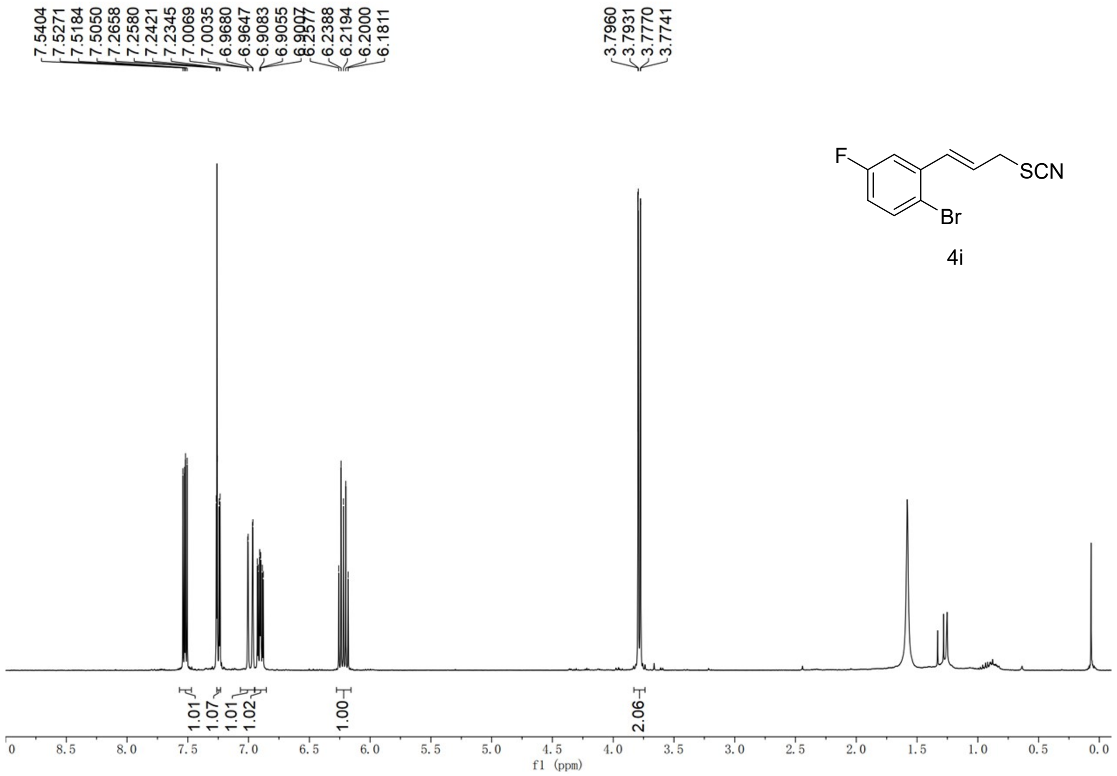
111.5470
36.4799
SCN
Br
4h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2658
7.2580
7.2421
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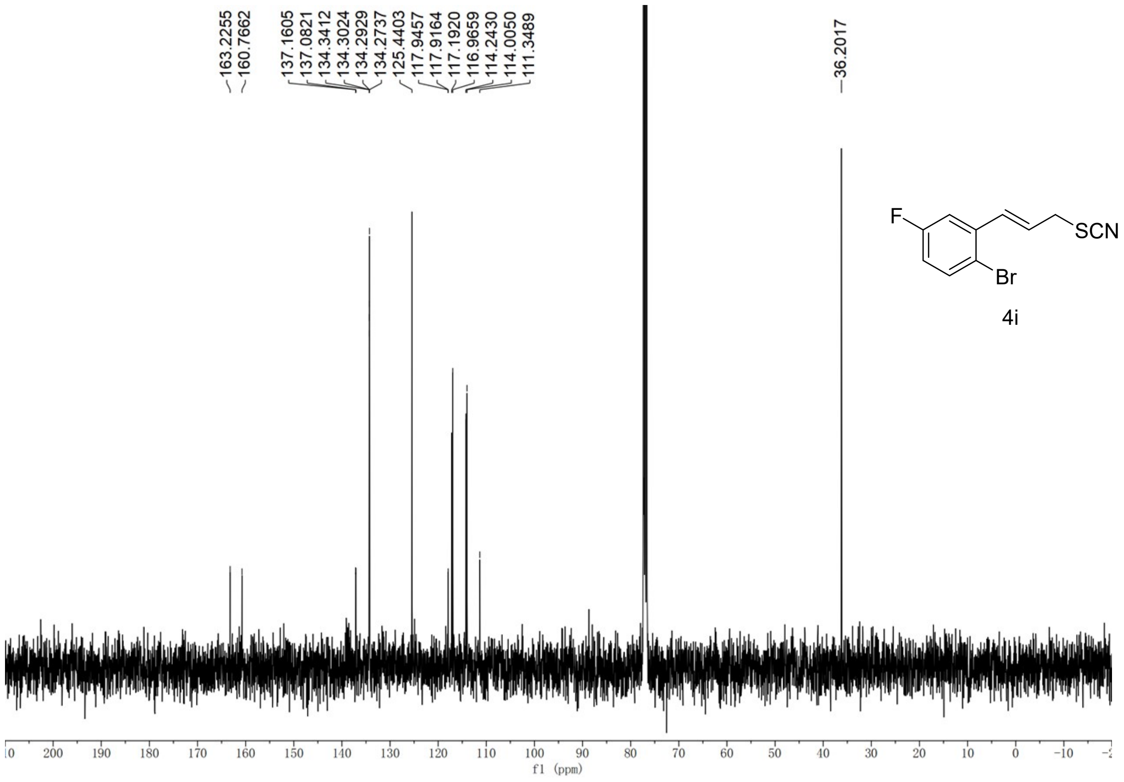
7.0069
7.0035
6.9680
6.9647
6.9083
6.9055
6.9007
6.2577
6.2388
6.2194
6.2000
6.1811
3.7960
3.7931
3.7770
3.7741
F
SCN
Br
4i
1.01
1.07
1.01
1.02
1.00
2.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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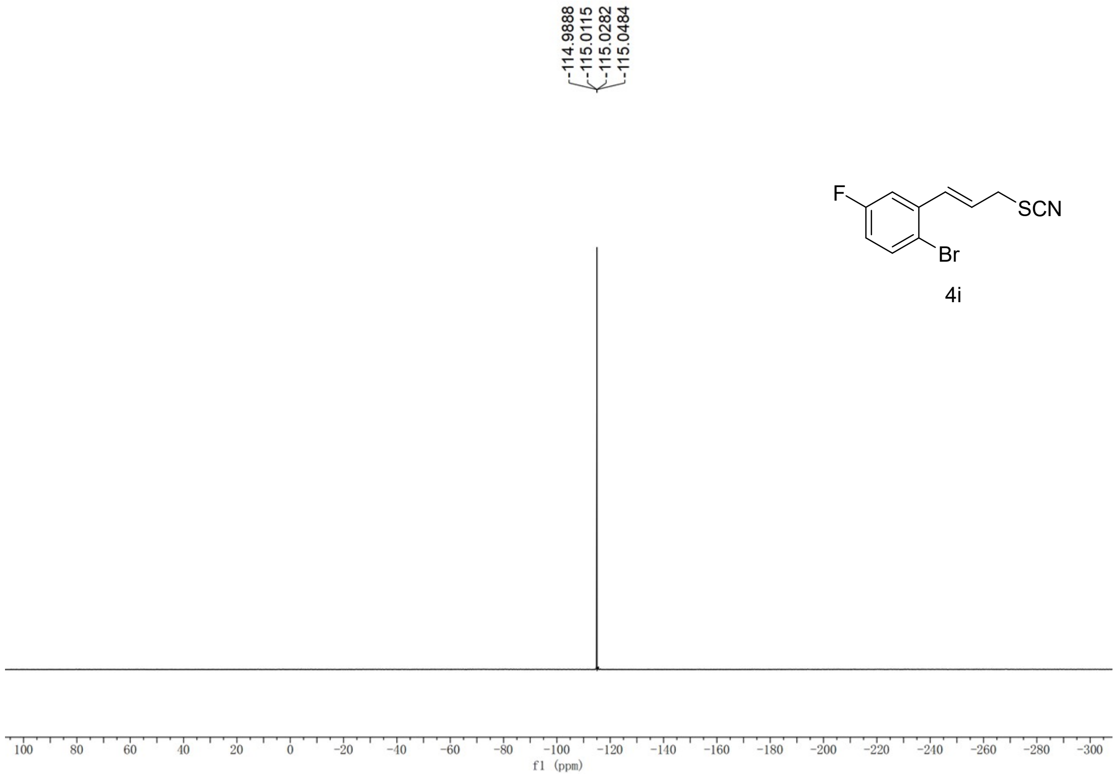
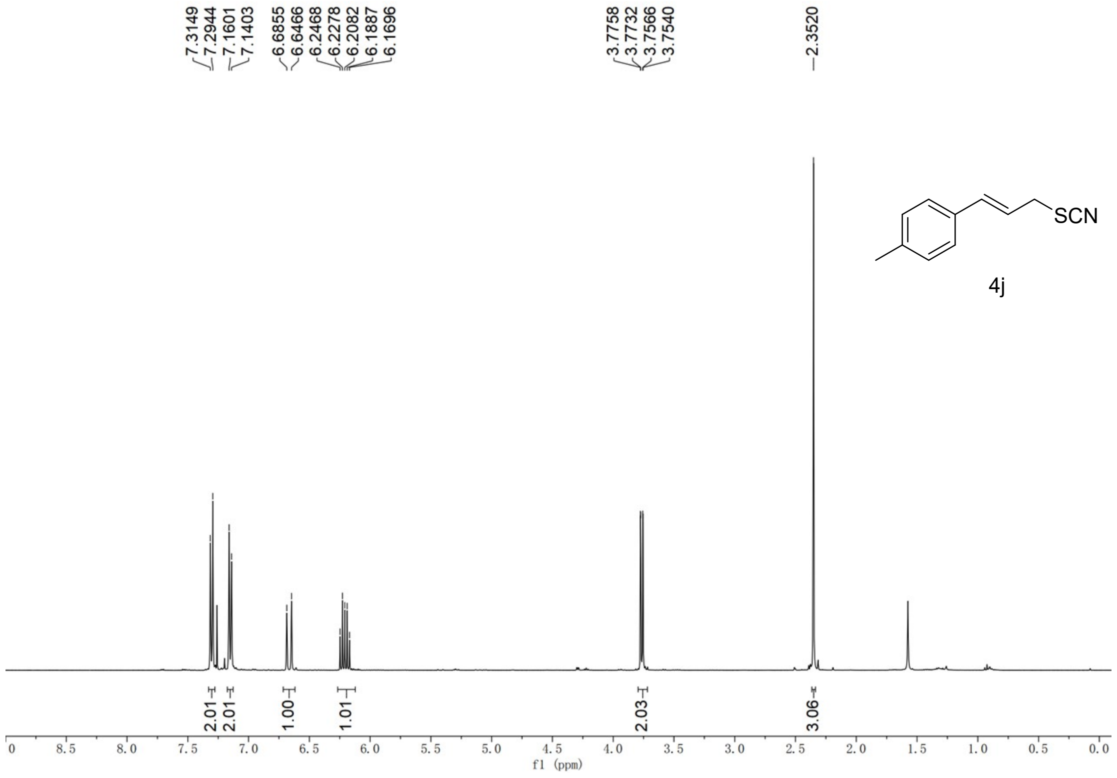
117.9457
117.9164
117.1920
116.9659
114.2430
114.0050
111.3489
36.2017
F
SCN
Br
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-114.9888
-115.0115
-115.0282
-115.0484
F
SCN
Br
4i
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)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7.1601
7.1403
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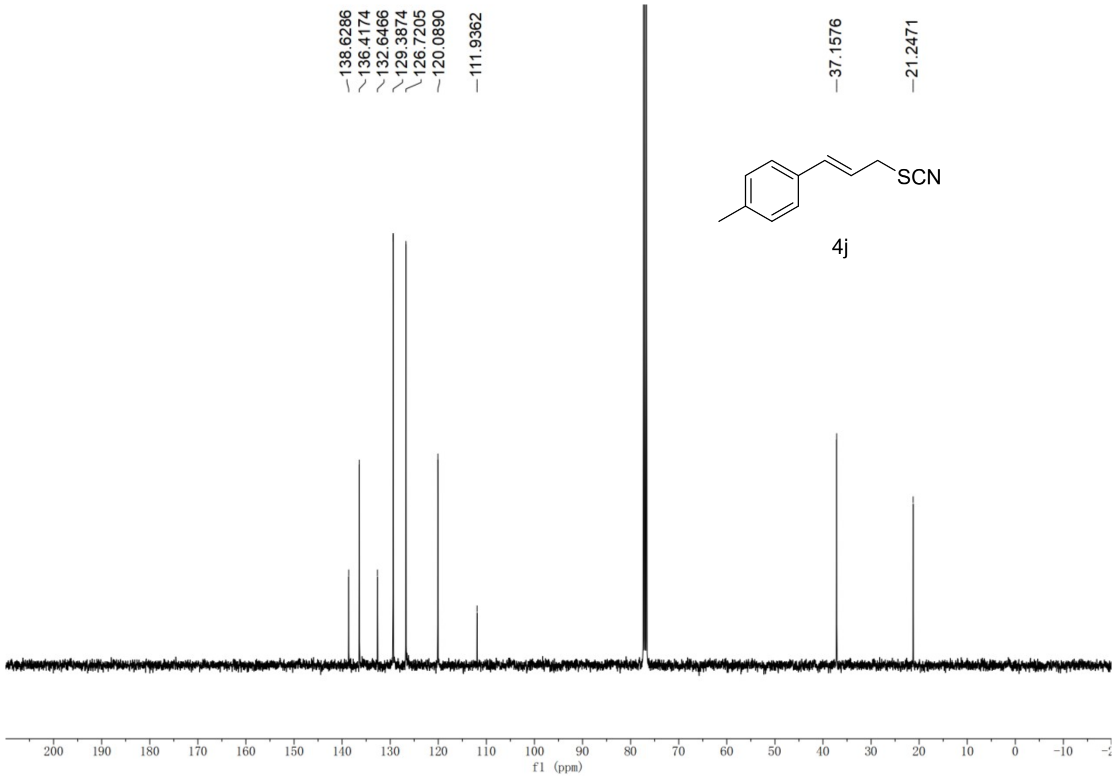
6.6466
6.2468
6.2278
6.2082
6.1887
6.1696
3.7758
3.7732
3.7566
3.7540
2.3520
SCN
4j
2.01
2.01
1.00
1.01
2.03
3.06
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



4j

138.6286
136.4174
132.6466
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126.7205
120.0890
111.9362
37.1576
21.2471
SCN
200
190
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170
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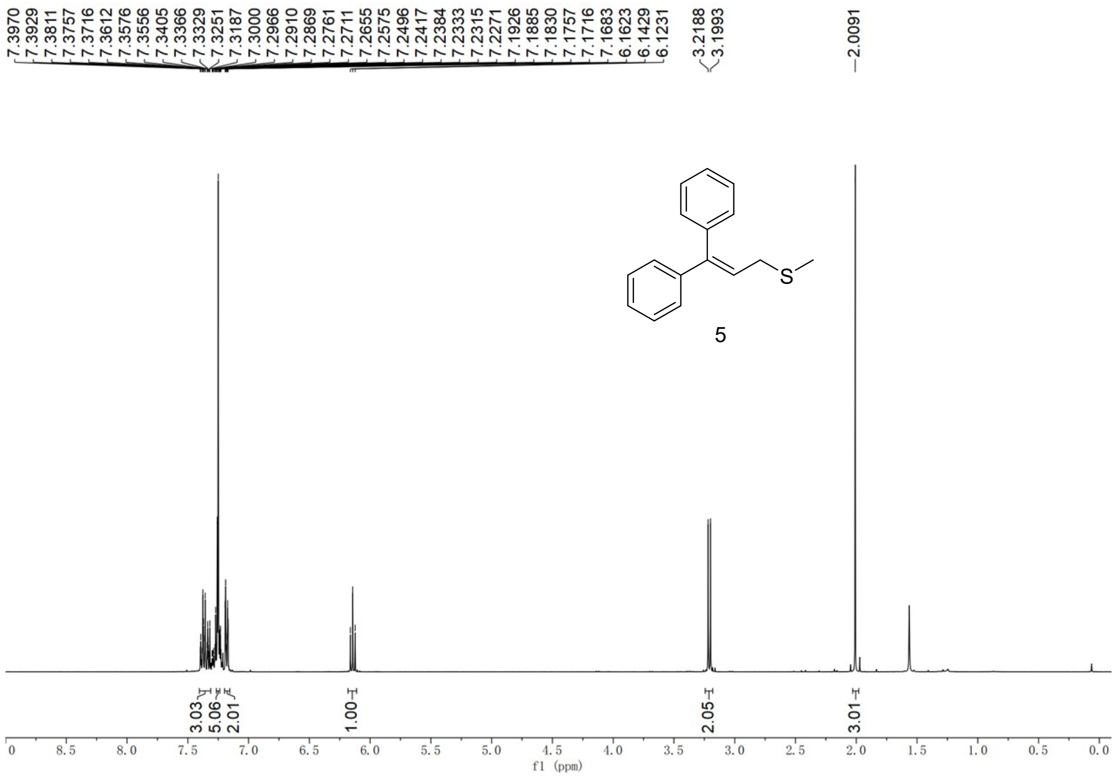

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7.3251
7.3187
7.3000
7.2966
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7.2869
7.2761
7.2711
7.2655
7.2575
7.2496
7.2417
7.2384
7.2333
7.2315
7.2271
7.1926
7.1885
7.1830
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7.1716
7.1683
6.1623
6.1429
6.1231
3.2188
3.1993
2.0091
S
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5.06
2.01
1.00
2.05
3.01
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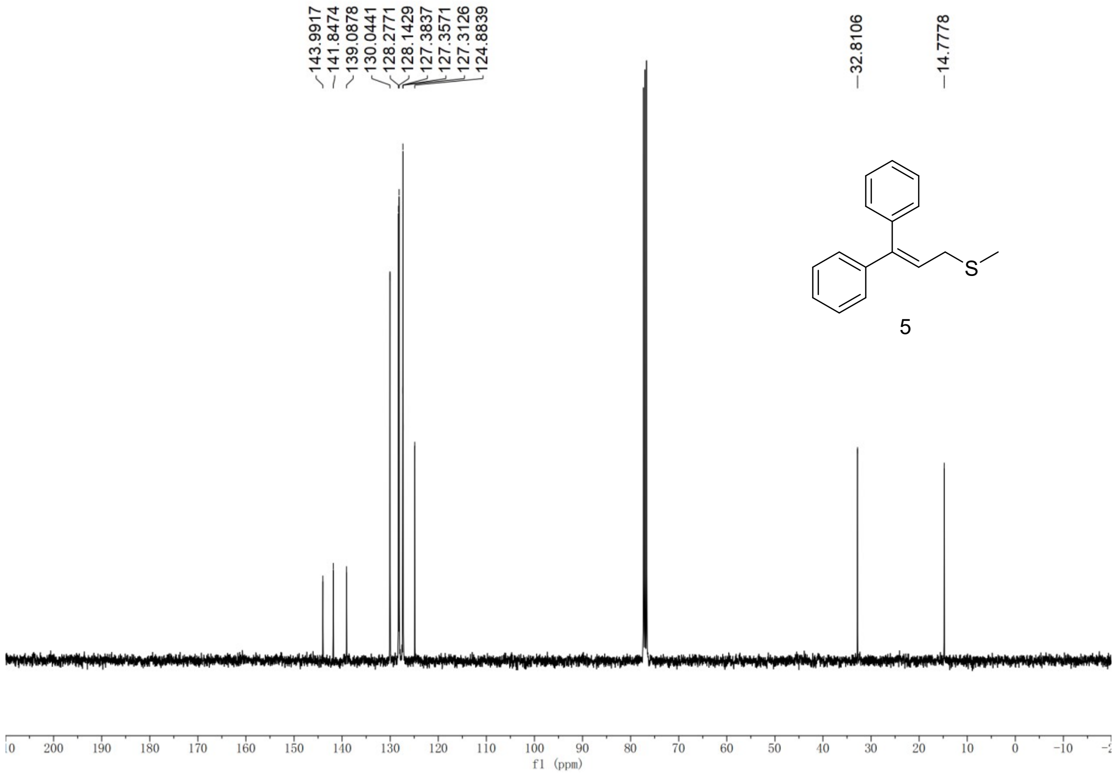
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14.7778
S
210
200
190
180
170
160
150
140
130
120
110
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90
80
70
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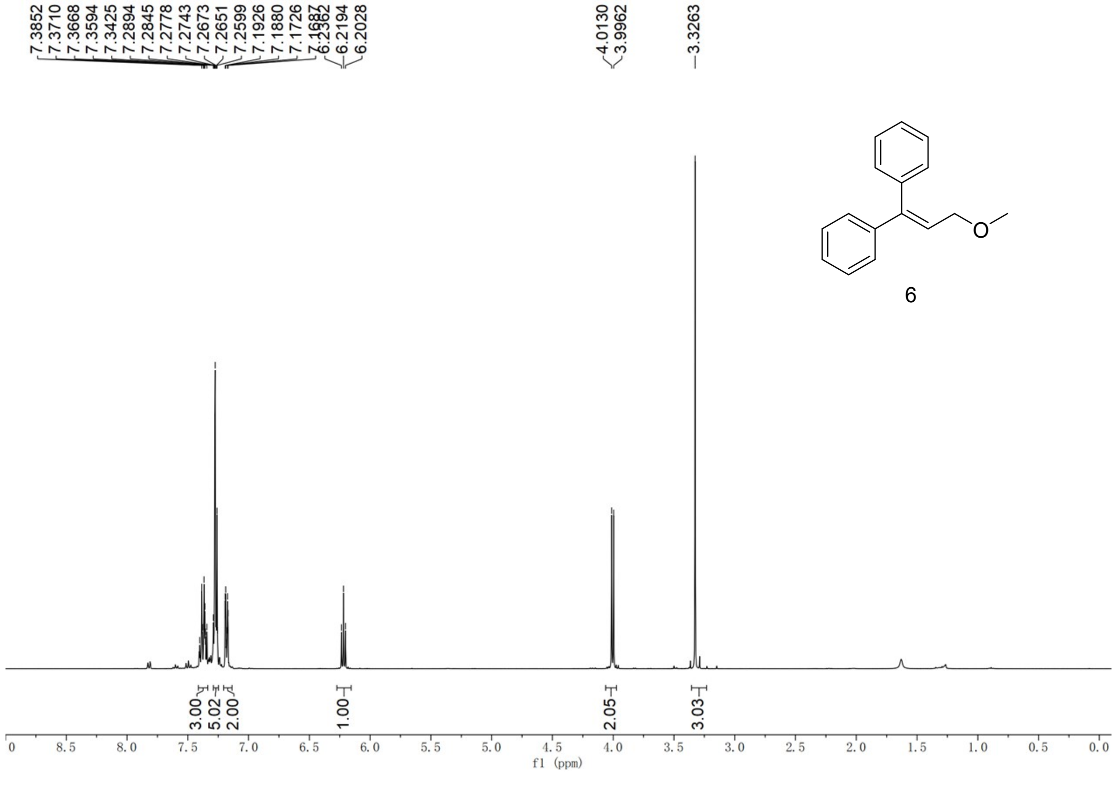
-10
-20
f1 (ppm)

5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7.2743
7.2673
7.2651
7.2599
7.1926
7.1880
7.1726
7.1687
6.2362
6.2194
6.2028
4.0130
3.9962
3.3263
O
3.00
5.02
2.00
1.00
2.05
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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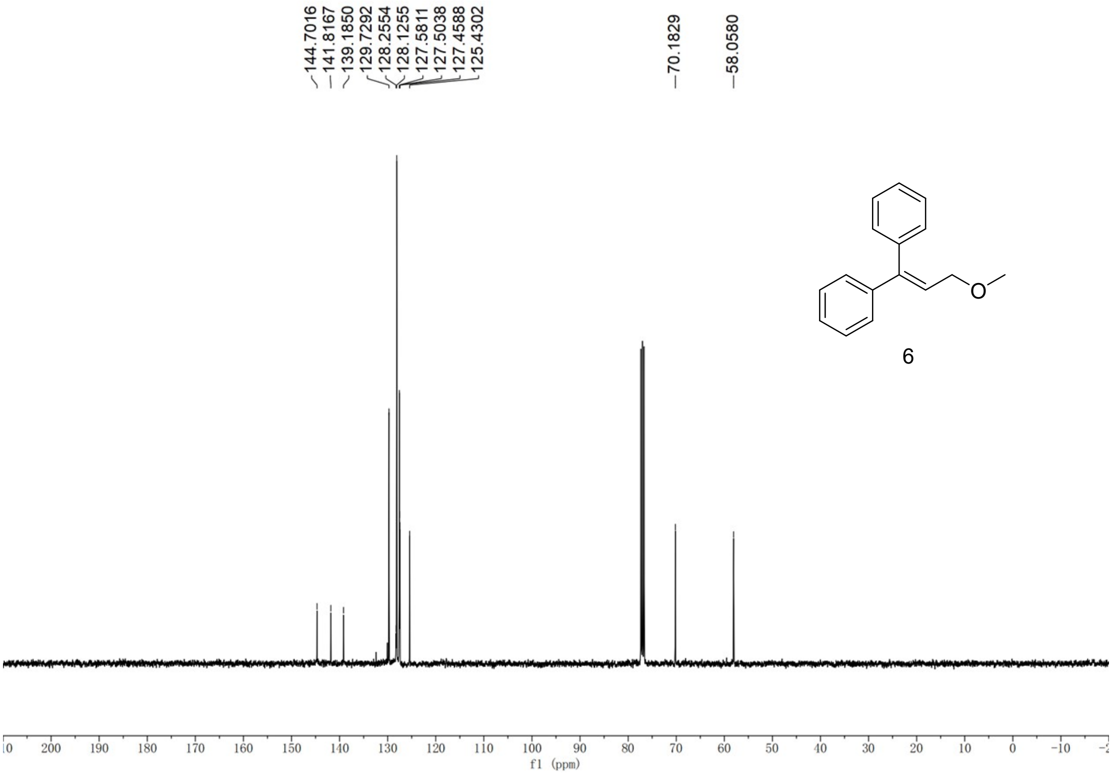
1.0
0.5
0.0
f1 (ppm)

6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139.1850
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128.2554
128.1255
127.5811
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127.4588
125.4302
70.1829
58.0580
O
200
190
180
170
160
150
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130
120
110
100
90
80
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60
50
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30
20
10
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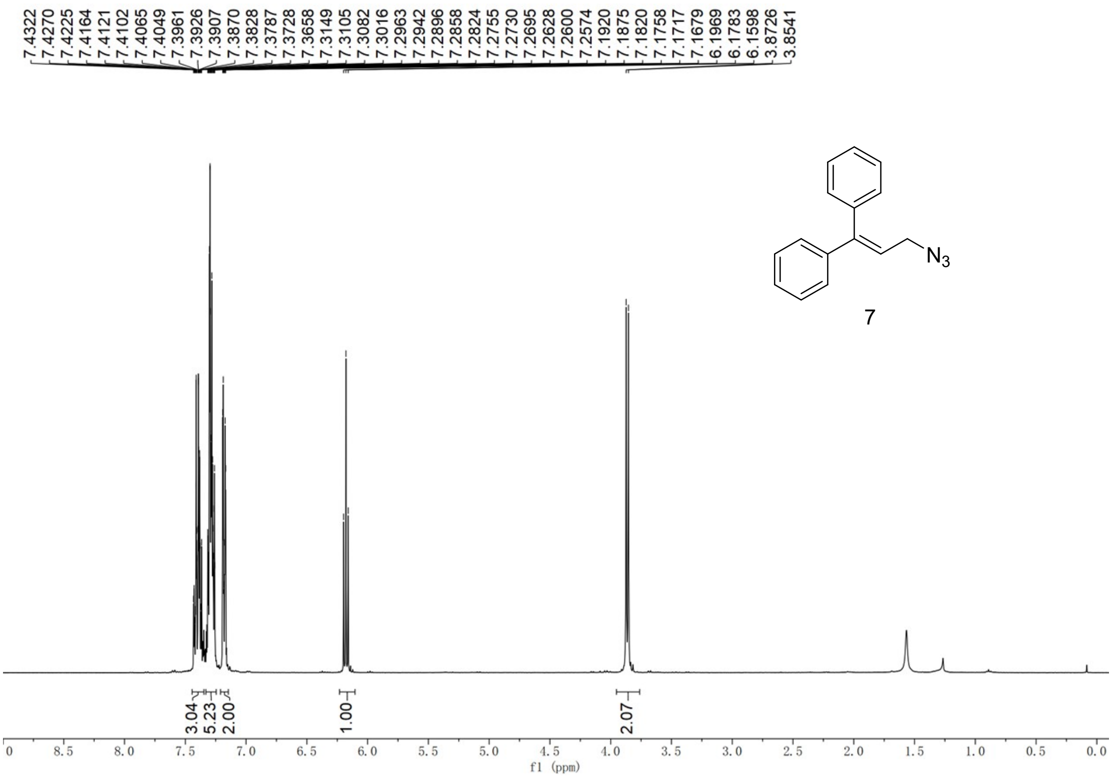
f1 (ppm)

6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7.3926
7.3907
7.3870
7.3828
7.3787
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7.3149
7.3105
7.3082
7.3016
7.2963
7.2942
7.2896
7.2858
7.2824
7.2755
7.2730
7.2695
7.2628
7.2600
7.2574
7.1920
7.1875
7.1820
7.1758
7.1717
7.1679
6.1969
6.1783
6.1598
3.8726
3.8541
N3
3.04
5.23
2.00
1.00
2.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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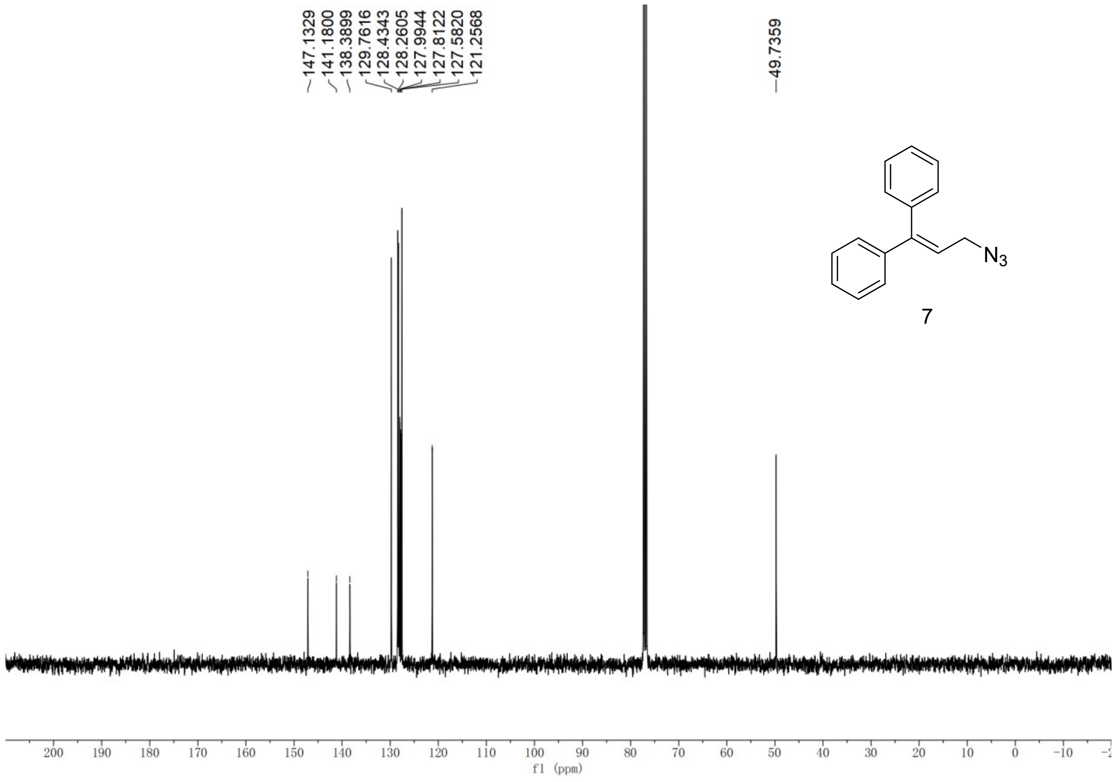
f1 (ppm)

7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N3
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)