

## Supporting Information

### Rapid assembly of structurally diverse cyanamides and disulfanes *via* base-mediated aminoalkylation of aryl thiourea

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## 1. Materials and Methods

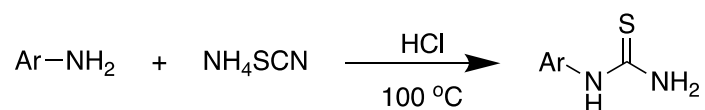
### Materials

Commercially available reagents and solvents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was conducted using silica gel (200-300 mesh) with the indicated solvent system. All the reaction temperatures reported are oil bath temperatures. Unless otherwise noted, purchased chemicals were used without further purification.

### Methods

Melting points were measured using a melting point instrument and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV 400 spectrometer. The chemical shifts are reported in ppm from the solvent resonance as the internal reference ( $\text{CDCl}_3$ )  $\delta_{\text{H}} = 7.26$  ppm, downfield from TMS,  $\delta_{\text{C}} = 77.0$  ppm. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF).

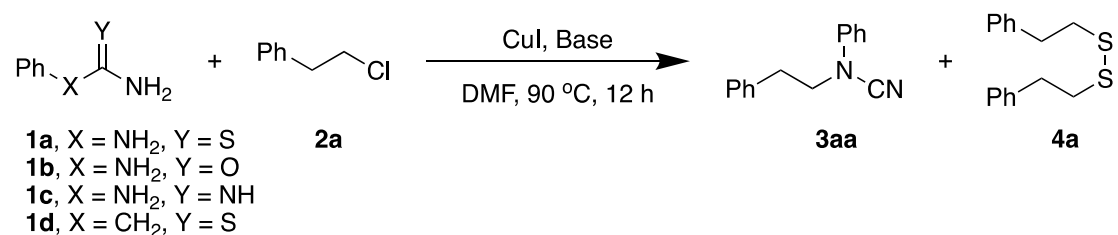
## 2. Typical procedure for the preparation of aryl thiourea



$\text{NH}_4\text{SCN}$  (10 mmol) was added to a stirred solution of arylamine (5 mmol) in 2M HCl (5 mL) and the solution stirred at 100 °C for 5 h. The solution was diluted with water (50 mL) and cooled to room temperature. The precipitate was filtered, washed with water (100 mL) and petroleum ether (50 mL) in sequence, and then dried. All products were isolated in a yield varying from 70-90% and were used directly for the preparation of cyanamide without further purification.

### 3. Detailed Reaction Condition Optimization

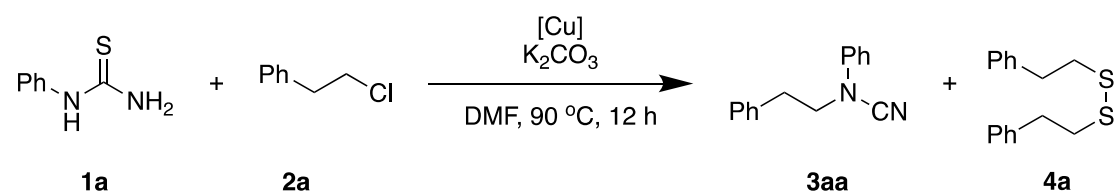
**Table S1.** Optimization of substrates and bases



Entry	Sub	Base	Conv. of <b>2a</b>	Yield of <b>3aa</b>	Yield of <b>4</b>
1	<b>1a</b>	K <sub>2</sub> CO <sub>3</sub>	100	65	20
2	<b>1b</b>	K <sub>2</sub> CO <sub>3</sub>	0	ND	ND
3	<b>1c</b>	K <sub>2</sub> CO <sub>3</sub>	0	ND	ND
4	<b>1d</b>	K <sub>2</sub> CO <sub>3</sub>	0	ND	ND
5	<b>1a</b>	Na <sub>2</sub> CO <sub>3</sub>	100	64	22
<b>6</b>	<b>1a</b>	Cs <sub>2</sub> CO <sub>3</sub>	100	64	32
7	<b>1a</b>	NaOAc	ND	ND	ND
8	<b>1a</b>	NaHCO <sub>3</sub>	90	44	34
9	<b>1a</b>	Et <sub>3</sub> N	<5	Trace	ND
10	<b>1a</b>	K <sub>3</sub> PO <sub>4</sub>	<5	Trace	ND
11	<b>1a</b>	<sup>t</sup> BuOK	<5	Trace	ND

Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol), CuI (10 mol%), Base (1.0 equiv), DMF (0.5 mL), under air, 90 °C, 12 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard. ND: not detected.

**Table S2.** Optimization of copper salt



Entry	[Cu]	Yield of <b>3aa</b>	Yield of <b>4a</b>
1	CuCl	50	42
2	CuBr <sub>2</sub> ·3Cu(OH) <sub>2</sub>	60	40
3	CuI	54	35
4	CuCl <sub>2</sub>	54	41
5	CuOAc	50	44
6	Cu(OAc) <sub>2</sub>	44	50
<b>7</b>	<b>Cu(OH)<sub>2</sub></b>	<b>62</b>	<b>38</b>
8	Cu(OTf) <sub>2</sub>	51	44
9	Cu(OCCF <sub>3</sub> ) <sub>2</sub>	ND	ND

10	Cu(acac) <sub>2</sub>	ND	ND
11	CuTc	53	35
12	Cu	50	33
13	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	54	26
14	CuO	ND	ND

Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [Cu] (10 mol%), K<sub>2</sub>CO<sub>3</sub> (1.5 equiv), DMF (0.5 mL), under air, 90 °C, 12 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard. ND: not detected.

**Table S3.** Optimization the ratio of substrates

Entry	Equiv of <b>2a</b>	Yield of <b>3aa</b>	Yield of <b>4a</b>
1	1	48	33
2	1.5	70	49
3	1.9	83	56
4	1.95	82	60
5	2.0	81	57
<b>6</b>	<b>2.5</b>	<b>94</b>	<b>64</b>
7	3.0	92	70
8 <sup>a</sup>	2.5	0	0
9 <sup>b</sup>	2.5	81	26
10 <sup>c</sup>	2.5	0	0

Reaction conditions: **1a** (0.2 mmol), **2a** (as shown in the table), Cu(OH)<sub>2</sub> (10 mol%), K<sub>2</sub>CO<sub>3</sub> (equiv same as **2a**), DMF (0.5 mL), under air, 90 °C, 12 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard. ND: not detected. <sup>a</sup> without K<sub>2</sub>CO<sub>3</sub>; <sup>b</sup> without Cu(OH)<sub>2</sub>; <sup>c</sup> without K<sub>2</sub>CO<sub>3</sub> and Cu(OH)<sub>2</sub>;

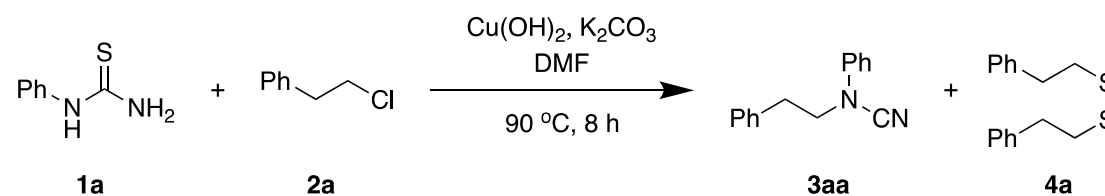
**Table S4.** Optimization the amount of base (without of Cu salt)

Entry	Equiv of K <sub>2</sub> CO <sub>3</sub>	Yield of <b>3aa</b>	Yield of <b>4a</b>
1	0.1	6	0

2	0.5	33	16
3	1.0	65	30
4	1.5	74	26
5	2.0	77	25
6	2.5	78	26
7	3.0	79	24

Reaction conditions: **1a** (0.2 mmol), **2a** (2.4 equiv), K<sub>2</sub>CO<sub>3</sub> (as shown in the table), DMF (0.5 mL), under air, 90 °C, 8 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

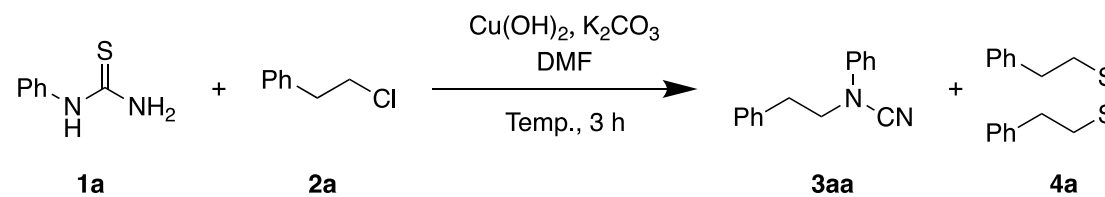
**Table S5.** Optimization the amount of Copper salt



Entry	Cu(OH) <sub>2</sub> /mol%	Yield of <b>3aa</b>	Yield of <b>4a</b>
<b>1</b>	<b>10</b>	<b>93</b>	<b>60</b>
2	20	90	47
3	50	86	19
4	100	95	trace

Reaction conditions: **1a** (0.2 mmol), **2a** (2.4 equiv), K<sub>2</sub>CO<sub>3</sub> (2.5 equiv), Cu(OH)<sub>2</sub> (as shown in the table), DMF (0.5 mL), under air, 90 °C, 8 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

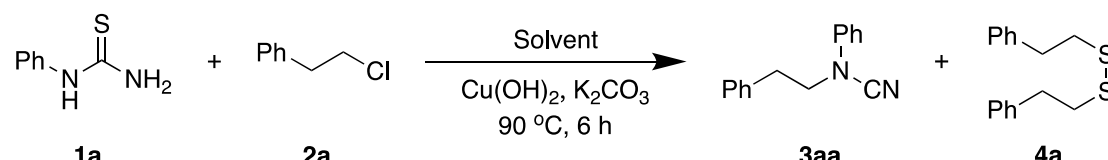
**Table S6.** Optimization of reaction temperature



Entry	Temp/°C	Yield of <b>3aa</b>	Yield of <b>4a</b>
1	RT	ND	ND
2	40	Trace	Trace
3	60	Trace	Trace
4	80	75	48
5	90	89	65
6	100	82	62
7	110	90	74

Reaction conditions: **1a** (0.2 mmol), **2a** (2.4 equiv), K<sub>2</sub>CO<sub>3</sub> (2.5 equiv), Cu(OH)<sub>2</sub> (10 mol%), DMF (0.5 mL), under air, temperature (as shown in the table), 3 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

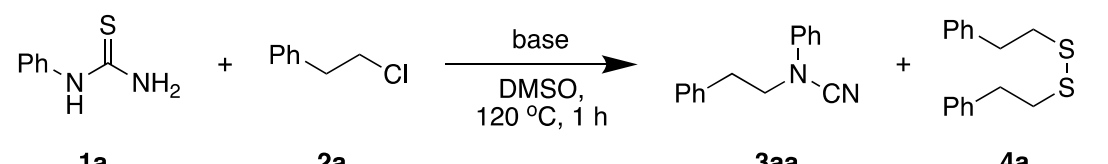
**Table S7.** Optimization of solvents



Entry	Solvent	Yield of <b>3aa</b>	Yield of <b>4a</b>
<b>1</b>	<b>DMSO</b>	<b>94</b>	<b>75</b>
2	glycol	56	45
3	1,4-dioxane	0	0
4	Toluene	0	0
5	THF	0	0
6	DME	<10	0
7	Acetone	<10	0
8	DMAc	79	62
9	DMF	91	71
10	Chlorobenzene	0	0
11	IPA	44	24
12	PhOPh	0	0
13	BnOBn	0	0
14	[Bmim]OAc	0	0

Reaction conditions: **1a** (0.2 mmol), **2a** (2.5 equiv), Base (2.5 equiv), Cu(OH)<sub>2</sub> (10 mol%), solvent (0.5 mL), under air, 90 °C, 6 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard. THF: Tetrahydrofuran; DME: 1,2-Dimethoxyethane; DMAc: N,N-Dimethylacetamide; IPA: Isopropyl alcohol.

**Table S8.** Optimization of the kinds of bases



Entry	Solvent	Yield of <b>3aa</b>	Yield of <b>4a</b>
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1	Na <sub>2</sub> CO <sub>3</sub>	95	79
2	K <sub>2</sub> CO <sub>3</sub>	97	70
3	Cs <sub>2</sub> CO <sub>3</sub>	72	50
4	CaCO <sub>3</sub>	0	Trace
5	KHCO <sub>3</sub>	92	79
6	NaHCO <sub>3</sub>	90	75
7	LiOH	58	44

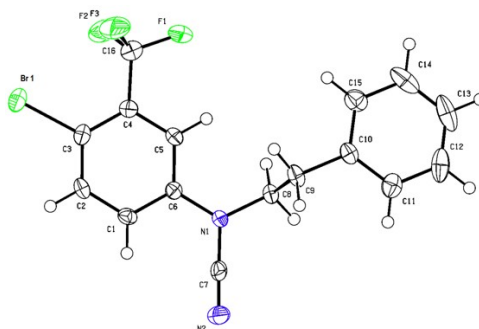
Reaction conditions: **1a** (0.2 mmol), **2a** (2.5 equiv), base (2.5 equiv), Cu(OH)<sub>2</sub> (10 mol%), DMSO (0.5 mL), under air, 120 °C, 1 h. Yield Determined by <sup>1</sup>H NMR analysis of the crude product with CH<sub>2</sub>Br<sub>2</sub> as an internal standard.

#### 4. General procedure for the preparation of products

Aryl thiourea (0.2 mmol), halide (0.5 mmol, 2.5 equiv), Cu(OH)<sub>2</sub> (10 mol%) and K<sub>2</sub>CO<sub>3</sub> (2.5 equiv) were added into a reaction tube (25 mL) which contained with a stirred bar, and then DMSO (0.5 mL) was added. The mixture was stirred at 120 °C for 1 h. After completion of the reaction and quenched by diluted HCl (5 mL, 2M), the mixture was extracted with ethyl acetate (3 × 5 mL). The combined ethyl acetate layer was then dried over anhydrous sodium sulfate and concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure products.

## 5. X-ray Crystallographic analysis for product **3bba**

The CCDC number of the compound **3bba** is 2241702.



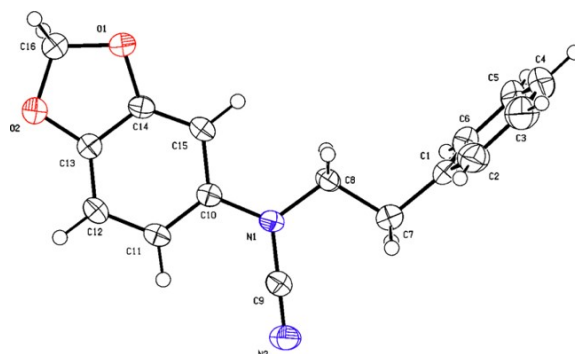
Crystal Data and Structure Refinement for Product **3bba**

Empirical formula	$C_{16}H_{12}BrF_3N_2$
Formula weight	369.19
Temperature/K	170
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 12.1120(5) \text{ \AA} \quad \alpha = 90^\circ$
	$b = 7.3561(3) \text{ \AA} \quad \beta = 99.730(2)^\circ$
	$c = 18.2597(6) \text{ \AA} \quad \gamma = 90^\circ$
Volume/ $\text{\AA}^3$	1603.48(11)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.529
$\mu/\text{mm}^{-1}$	2.591
F(000)	736
Crystal size/ $\text{mm}^3$	$0.19 \times 0.08 \times 0.05$
Radiation	$\text{MoK}\alpha (\lambda = 0.71073)$
$2\theta$ range for data collection/ $^\circ$	5.188 to 52.794
Index ranges	$-15 \leq h \leq 15, -9 \leq k \leq 9, -20 \leq l \leq 22$
Reflections collected	11895
Independent reflections	3232 [ $R_{\text{int}} = 0.0502, R_{\text{sigma}} = 0.0496$ ]
Data/restraints/parameters	3232/0/199
Goodness-of-fit on $F^2$	1.037
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0330, wR_2 = 0.0693$
Final R indexes [all data]	$R_1 = 0.0485, wR_2 = 0.0772$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.29/-0.47



## 6. X-ray Crystallographic analysis for product 3bea

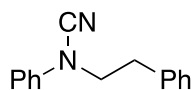
The CCDC number of the compound **3bea** is 2241703.



Crystal Data and Structure Refinement for Product **3bea**

Empirical formula	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	266.29
Temperature/K	170
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
Unit cell dimensions	$a = 6.5729(5)\text{\AA}$ $\alpha = 90^\circ$
	$b = 29.957(2)\text{\AA}$ $\beta = 100.913(3)^\circ$
	$c = 6.9575(5)\text{\AA}$ $\gamma = 90^\circ$
Volume/ $\text{\AA}^3$	1345.19(17)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.315
$\mu/\text{mm}^{-1}$	0.088
F(000)	560
Crystal size/ $\text{mm}^3$	0.12 × 0.08 × 0.05
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	5.44 to 52.714
Index ranges	$-8 \leq h \leq 8, -37 \leq k \leq 37, -8 \leq l \leq 8$
Reflections collected	10375
Independent reflections	2743 [ $R_{\text{int}} = 0.0670, R_{\text{sigma}} = 0.0628$ ]
Data/restraints/parameters	2743/0/181
Goodness-of-fit on F <sup>2</sup>	1.071
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0505, wR_2 = 0.1056$
Final R indexes [all data]	$R_1 = 0.0923, wR_2 = 0.1288$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.20/-0.23

## 7. Analysis Data for the Products



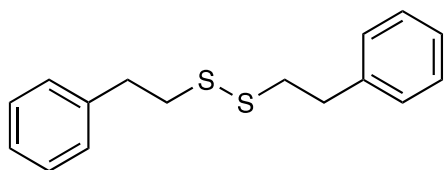
### ***N*-phenethyl-*N*-phenylcyanamide (3aa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aa** as yellow oil. The yield for **3aa** is 90% (40.0 mg) when using (2-chloroethyl)benzene as substrate or 80% (35.6 mg) with (2-bromoethyl)benzene.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.30 (m, 4H), 7.29-7.20 (m, 3H), 7.15-7.04 (m, 3H), 3.84-3.76 (m, 2H), 3.15-3.06 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 136.9, 129.7, 128.9, 128.8, 127.1, 123.7, 116.0, 113.4, 50.9, 33.8.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{15}\text{N}_2$ , 223.1230; found, 223.1226.



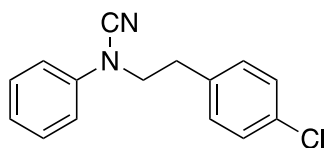
### **1,2-diphenethyl disulfane (4a)<sup>1</sup>**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4a** as colorless oil. The yield for **4a** is 79% (21.9 mg) when using (2-chloroethyl)benzene or 78% yield with (2-bromoethyl)benzene.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.26 (m, 4H), 7.25-7.15 (m, 6H), 3.04-2.96 (m, 4H), 2.96-2.88 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 128.6, 128.6, 126.4, 40.2, 35.8.

GC-MS (EI+)  $m/z$  = 77 (10%), 91 (17%), 105 (100%), 274 (18%).



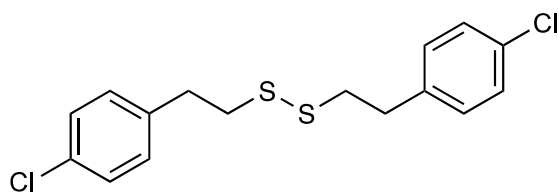
### ***N*-(4-chlorophenethyl)-*N*-phenylcyanamide (3ab)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ab** (46.8 mg, 91% yield) as pale yellow solid, m.p.: 56.5-57.0 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.14-7.06 (m, 3H), 3.79 (t, *J* = 7.2 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.7, 135.4, 133.0, 130.2, 129.8, 129.0, 123.9, 116.1, 113.3, 50.7, 33.1.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>ClN<sub>2</sub>, 257.0840; found, Y.



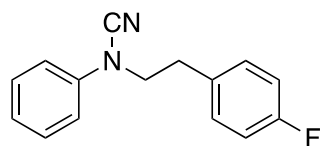
#### 1,2-bis(4-chlorophenethyl)disulfane (**4b**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4b** (26.3 mg, 76% yield) as yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 (d, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H), 2.98-2.92 (m, 4H), 2.91-2.84 (m, 4H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.3, 132.3, 130.0, 128.7, 39.9, 34.9.

GC-MS (EI+) *m/z* = 103 (32%), 125 (22%), 139 (100%), 141 (32%).



#### *N*-(4-fluorophenethyl)-*N*-phenylcyanamide (**3ac**)

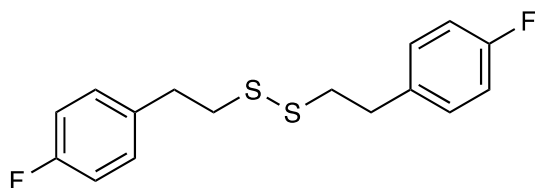
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ac** (32.9 mg, 68% yield) as yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.33 (m, 2H), 7.23-7.16 (m, 2H), 7.14-7.06 (m, 3H), 7.04-6.98 (m, 2H), 3.79 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 (d,  $J_{\text{C-F}} = 245.5$  Hz), 139.7, 132.6 (d,  $J_{\text{C-F}} = 3.3$  Hz), 130.4 (d,  $J_{\text{C-F}} = 8.0$  Hz), 129.78, 123.83, 116.05, 115.8 (d,  $J_{\text{C-F}} = 21.4$  Hz), 113.38, 50.90, 50.89, 32.96.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.5 (tt,  $J = 8.8, 5.3$  Hz).

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{14}\text{FN}_2$ , 241.1136; found, 241.1132.



### 1,2-bis(4-fluorophenethyl)disulfane (4c)

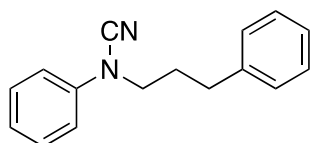
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4c** (26.3 mg, 59% yield, **4c:5c** = 93:7) as yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 (d,  $J = 5.2$  Hz, 1H), 7.12 (d,  $J = 5.2$  Hz, 1H), 6.98 (d,  $J = 8.8$  Hz, 2H), 6.96 (d,  $J = 8.8$  Hz, 2H), 2.99-2.92 (m, 2H), 2.92-2.85 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6 (d,  $J_{\text{C-F}} = 244.3$  Hz), 135.6 (d,  $J_{\text{C-F}} = 3.3$  Hz), 130.0 (d,  $J_{\text{C-F}} = 7.9$  Hz), 115.3 (d,  $J_{\text{C-F}} = 21.3$  Hz), 40.2, 34.80.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.6 (ddd,  $J = 14.1, 8.7, 5.1$  Hz).

GC-MS (EI+)  $m/z = 109$  (24%), 123 (100%), 310 (6%).



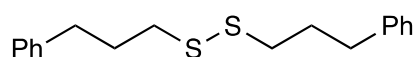
### N-phenyl-N-(3-phenylpropyl)cyanamide (3ad)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ad** (39.7 mg, 84% yield) as yellow solid, m.p.: 69.7-70.5 °C .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.28 (m, 4H), 7.25-7.16 (m, 3H), 7.14-7.05 (m, 3H), 3.59 (t,  $J = 7.2$  Hz, 2H), 2.79 (t,  $J = 7.2$  Hz, 2H), 2.17 (tt,  $J = 7.2, 7.2$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 139.9, 129.7, 128.6, 128.4, 126.4, 123.6, 115.9, 48.5, 32.6, 28.9.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_2$ , 237.1386; found, 237.1382.



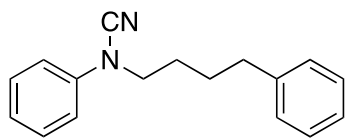
### 1,2-bis(3-phenylpropyl)disulfane (4d)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4d** (22.3 mg, 73% yield) as yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.24 (m, 4H), 7.23-7.14 (m, 6H), 2.76-2.63 (m, 8H), 2.08-1.94 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 128.5, 128.4, 126.0, 38.2, 34.4, 30.6.

GC-MS (EI+)  $m/z$  = 91 (100%), 119 (10%), 150 (29%), 302 (41%).



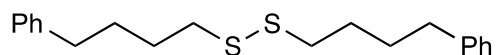
### N-phenyl-N-(4-phenylbutyl)cyanamide (3ae)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ae** (47.6 mg, 95% yield) as yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.33 (m, 2H), 7.33-7.27 (m, 2H), 7.24-7.16 (m, 2H), 7.14-7.06 (m, 3H), 3.56 (t,  $J$  = 7.2 Hz, 2H), 2.69 (t,  $J$  = 7.2 Hz, 2H), 1.94-1.84 (m, 2H), 1.84-1.74 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 140.0, 129.7, 128.5, 128.4, 126.1, 123.6, 115.9, 113.7, 77.4, 77.1, 76.8, 49.3, 35.3, 28.2, 27.0.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_2$ , 251.1543; found, 251.1537.



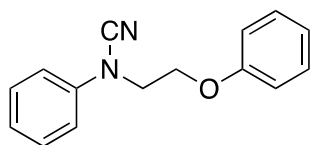
### 1,2-bis(4-phenylbutyl)disulfane (4e)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4e** (31.7 mg, 95% yield) as yellow oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.27 (m, 4H), 7.23-7.14 (m, 6H), 2.73-2.67 (m, 4H), 2.67-2.60 (m, 4H), 1.80-1.65 (m, 8H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.1, 128.4, 128.4, 128.4, 125.8, 39.0, 35.5, 30.2, 28.8.

GC-MS (EI+)  $m/z$  = 91 (100%), 133 (23%), 330 (13%).



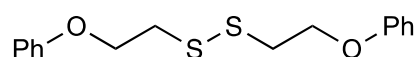
### ***N*-(2-phenoxyethyl)-*N*-phenylcyanamide (3af)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3af** (42.0 mg, 88% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (dd,  $J$  = 8.8, 7.2 Hz, 2H), 7.27 (dd,  $J$  = 8.4, 7.6 Hz, 2H), 7.20 (dd,  $J$  = 8.8, 1.2 Hz, 2H), 7.12 (dt,  $J$  = 7.2, 1.2 Hz, 1H), 6.97 (dt,  $J$  = 7.2, 1.2 Hz, 1H), 6.90 (dd,  $J$  = 8.8, 1.2 Hz, 2H), 4.29 (t,  $J$  = 5.6 Hz, 2H), 4.00 (t,  $J$  = 5.6 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 139.8, 129.7, 129.6, 124.0, 121.6, 116.3, 114.7, 113.5, 77.4, 77.1, 76.8, 64.5, 49.3.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}$ , 239.1179; found, 239.1175.

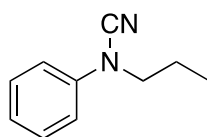


### **1,2-bis(2-phenoxyethyl)disulfane (4f)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4f** (15.4 mg, 67% yield) as white solid, m.p.: 89.5-90.5 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (dd,  $J$  = 8.8, 7.2 Hz, 4H), 6.96 (dt,  $J$  = 7.6, 1.2 Hz, 2H), 6.91 (dd,  $J$  = 8.8, 1.2 Hz, 4H), 4.25 (t,  $J$  = 5.4 Hz, 4H), 3.09 (t,  $J$  = 5.4 Hz, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 129.6, 129.6, 121.2, 114.7, 66.1, 37.9.



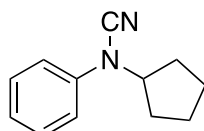
### ***N*-phenyl-*N*-propylcyanamide (3ag)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ag** as yellow oil. The yield for **3ag** is 70% (22.5 mg) when using 1-chloropropane or 66% yield with 1-iodopropane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.32 (m, 2H), 7.14-7.05 (m, 3H), 3.55 (t,  $J = 7.2$  Hz, 2H), 1.86 (tq,  $J = 7.6, 7.2$  Hz, 2H), 1.06 (t,  $J = 7.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 129.7, 123.5, 115.9, 51.1, 20.9, 11.1.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{10}\text{H}_{13}\text{N}_2$ , 161.1073; found, 161.1070.



#### ***N*-cyclopentyl-*N*-phenylcyanamide (3ah)**

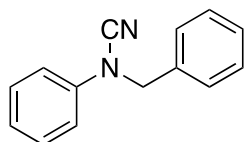
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ah** (22.3 mg, 60% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.32 (m, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.09 (d,  $J = 7.6$  Hz, 2H), 4.17-4.06 (m, 1H), 2.18-2.04 (m, 2H), 2.03-1.80 (m, 4H), 1.75-1.63 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 129.6, 123.6, 116.9, 59.5, 31.5, 23.8.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{12}\text{H}_{15}\text{N}_2$ , 187.1230; found, 187.1226.

GC-MS (EI+) for **4ah**,  $m/z = 69$  (100%), 134 (56%), 202 (22%).



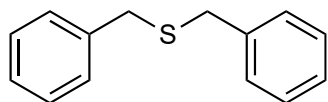
#### ***N*-benzyl-*N*-phenylcyanamide (3ai)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ai** as yellow solid, m.p.: 60.0-61.0 °C; The yield for **3ai** is 81% (41.6 mg) when using benzyl chloride or 56% yield with Benzyl bromide.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.37 (m, 4H), 7.37-7.30 (m, 3H), 7.18-7.12 (m, 2H), 7.12-7.06 (m, 1), 4.80 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 134.3, 129.7, 129.1, 128.6, 127.4, 123.7, 116.1, 114.0, 53.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{14}\text{H}_{13}\text{N}_2$ , 209.1073; found, 209.1069.



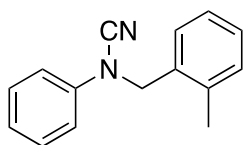
### dibenzylsulfane (**5i**)<sup>2</sup>

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5i** as colorless oil in 95% yield (24.6 mg) using benzyl chloride. **4i:5i** = 4:96

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.25 (m, 10H), 3.65 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 129.0, 128.5, 127.0, 35.6.

GC-MS (EI+)  $m/z$  = 91 (100%), 123 (30%), 214 (22%).



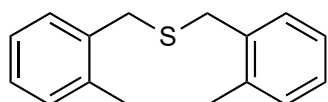
### *N*-(2-methylbenzyl)-*N*-phenylcyanamide (**3aj**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aj** (19.3 mg, 43% yield) as brown solid, m.p.: 99.8-100.3 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.32 (m, 2H), 7.32-7.18 (m, 4H), 7.16-7.06 (m, 3H), 4.73 (s, 2H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 136.3, 131.7, 130.9, 129.7, 128.8, 128.2, 126.6, 123.8, 116.0, 113.4, 51.8, 19.2.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{15}\text{N}_2$ , 223.1230; found, 223.1228.



### bis(2-methylbenzyl)sulfane (**5j**)<sup>2</sup>

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5j**

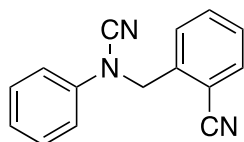


(23.0 mg, 83% yield) as pale white solid, m.p.: 79.3-80.4 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27-7.08 (m, 8H), 3.66 (s, 4H), 2.30 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.9, 135.8, 130.6, 129.6, 127.3, 125.8, 34.3, 19.1.

GC-MS (EI+) *m/z* = 105 (100%), 242 (21%).



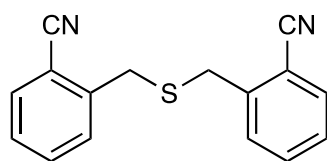
### *N*-(2-cyanobenzyl)-*N*-phenylcyanamide (**3ak**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ak** (27.3 mg, 99% yield) as yellow solid, m.p.: 119.6-120.5 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.63 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.56 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.47 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.41-7.33 (m, 2H), 7.17-7.09 (m, 3H), 5.03 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.2, 137.8, 133.6, 133.5, 129.9, 129.2, 128.1, 124.4, 116.7, 116.1, 113.3, 111.6, 51.7.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>, 234.1026; found, 234.1021.



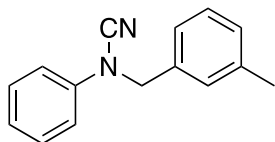
### 2,2'-(thiobis(methylene))dibenzonitrile (**5k**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5k** (29.3 mg, 87% yield) as yellow solid, m.p.: 112.2-112.7 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.55 (dt, *J* = 8.0, 1.6 Hz, 2H), 7.51 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.34 (dt, *J* = 7.6, 1.6 Hz, 2H), 3.90 (s, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.5, 133.1, 133.0, 130.1, 127.8, 117.4, 112.7, 34.5.

GC-MS (EI+) *m/z* = 169 (100%), 171 (97%), 372 (16%), 374 (8%).



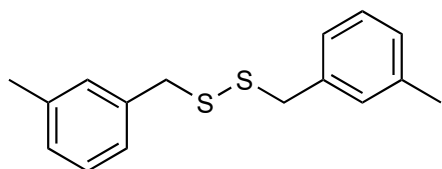
***N*-(3-methylbenzyl)-*N*-phenylcyanamide (3al)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3al** (24.5 mg, 98% yield) as brown solid, m.p.: 82.1-83.5 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.22-7.14 (m, 5H), 7.14-7.06 (m, 1H), 4.79 (s, 2H), 2.38 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.9, 138.9, 134.3, 129.6, 129.3, 129.0, 128.0, 124.4, 123.6, 116.0, 114.0, 53.8, 21.4.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>, 223.1230; found, 223.1225.



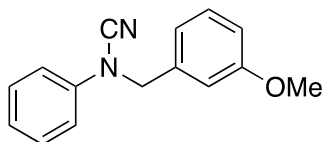
**1,2-bis(3-methylbenzyl)disulfane (4l)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4l** (24.2 mg, 87% yield) as yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25-7.16 (m, 2H), 7.12-7.00 (m, 6H), 3.57 (s, 4H), 2.34 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.1, 129.8, 128.4, 127.8, 126.1, 35.7, 21.4.

GC-MS (EI+) *m/z* = 105 (100%), 274 (5%).



***N*-(3-methoxybenzyl)-*N*-phenylcyanamide (3am)**

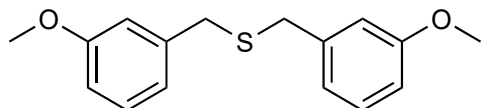
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3am** (38.5 mg, 81% yield) as yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38-7.22 (m, 3H), 7.15-7.03 (m, 3H), 6.98-6.92 (m,

1H), 6.90-6.82 (m, 2H), 4.76 (s, 2H), 3.78 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.1, 139.8, 135.9, 130.2, 129.7, 123.7, 119.5, 116.0, 114.0, 113.8, 113.0, 55.3, 53.7.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O, 239.1179; found, 239.1174.



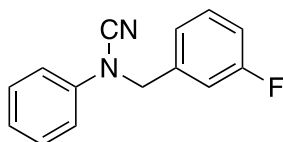
### 1,2-bis(3-methoxybenzyl)sulfane (**5m**)<sup>2</sup>

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5m** (30.4 mg, 99% yield, **5m**:**4m** = 94:6) as yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.20 (m, 2H), 6.95-6.85 (m, 4H), 6.81 (d, *J* = 8.0, 2.4 Hz, 2H), 3.83 (s, 4H), 3.62 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.7, 139.7, 129.4, 121.4, 114.4, 112.7, 55.2, 35.7.

GC-MS (EI+) *m/z* = 121 (43%), 122 (100%), 274 (8%).



### *N*-(3-fluorobenzyl)-*N*-phenylcyanamide (**3an**)

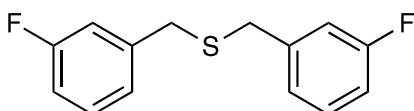
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3an** (34.0 mg, 75% yield) as white solid, m.p.: 59.4-60.3 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.30 (m, 3H), 7.18-6.97 (m, 6H), 4.80 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.1 (d, *J*<sub>C-F</sub> = 247.7 Hz), 139.5, 136.9 (d, *J*<sub>C-F</sub> = 7.1 Hz), 130.8 (d, *J*<sub>C-F</sub> = 8.3 Hz), 129.8, 124.0, 122.8 (d, *J*<sub>C-F</sub> = 3.0 Hz), 116.0, 115.6 (d, *J*<sub>C-F</sub> = 21.1 Hz), 114.3 (d, *J*<sub>C-F</sub> = 22.2 Hz), 113.7, 53.2 (d, *J*<sub>C-F</sub> = 2.1 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -111.56 (dt, *J* = 9.0, 5.6 Hz).

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>12</sub>FN<sub>2</sub>, 227.0979; found, 227.0975.



### bis(3-fluorobenzyl)sulfane (**5n**)

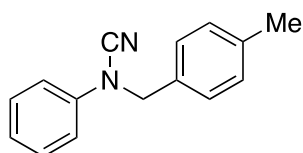
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5n** (15.5 mg, 57% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.25 (m, 2H), 7.08-7.01 (m, 2H), 6.98 (dt,  $J = 8.0$ , 2.4 Hz, 2H), 3.61 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9 (d,  $J_{\text{C-F}} = 246.2$  Hz), 140.5 (d,  $J_{\text{C-F}} = 7.3$  Hz), 130.0 (d,  $J_{\text{C-F}} = 8.3$  Hz), 124.6 (d,  $J_{\text{C-F}} = 2.9$  Hz), 115.8 (d,  $J_{\text{C-F}} = 21.8$  Hz), 114.1 (d,  $J_{\text{C-F}} = 21.2$  Hz), 35.2 (d,  $J_{\text{C-F}} = 1.8$  Hz).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.0 (dt,  $J_{\text{C-F}} = 9.2$ , 5.8 Hz).

GC-MS (EI+)  $m/z = 109$  (100%), 141 (33%), 250 (21%).



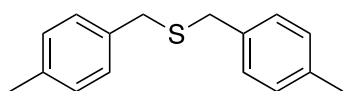
### *N*-(4-methylbenzyl)-*N*-phenylcyanamide (**3ao**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ao** (23.2 mg, 52% yield) as pale yellow solid, m.p.: 99.7-101.5 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (dt,  $J = 7.2$ , 1.6 Hz, 2H), 7.25 (d,  $J = 7.6$  Hz, 2H), 7.17 (d,  $J = 7.6$  Hz, 2H), 7.11 (dd,  $J = 7.2$ , 1.2 Hz, 2H), 7.07 (dt,  $J = 8.0$ , 1.2 Hz, 2H), 4.74 (s, 2H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 138.4, 131.2, 129.8, 129.6, 127.5, 123.6, 116.1, 114.0, 53.5, 21.2.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{15}\text{N}_2$ , 223.1230; found, 223.1226.



### bis(4-methylbenzyl)sulfane (**5o**)<sup>2</sup>

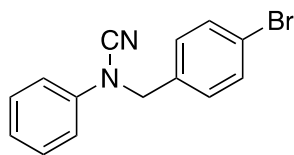
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5o** (28.2 mg, 57% yield, **5o:4o** 91:9) as brown solid, m.p.: 72.6-73.7 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J = 8.0$  Hz, 4H), 7.15 (d,  $J = 8.0$  Hz, 4H), 3.60

(s, 4H), 2.37 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 135.1, 129.2, 128.9, 35.3, 21.1.

GC-MS (EI+)  $m/z$  = 105 (100%), 242 (16%).



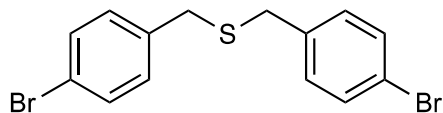
### ***N*-(4-bromobenzyl)-*N*-phenylcyanamide (3ap)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ap** (46.5 mg, 81% yield) as brown solid, m.p.: 94.8-95.8 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J$  = 8.4 Hz, 2H), 7.41-7.32 (m, 2H), 7.26 (d,  $J$  = 8.4 Hz, 2H), 7.17-7.08 (m, 3H), 4.77 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 133.3, 132.3, 129.8, 129.1, 124.0, 122.6, 116.1, 113.7, 53.2.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{14}\text{H}_{12}\text{BrN}_2$ , 287.0178; found, 287.0171.



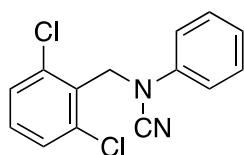
### **bis(4-bromobenzyl)sulfane (5p)<sup>2</sup>**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5p** (38.2 mg, 94% yield) as pale pink solid, m.p.: 53.7-55.0 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J$  = 8.0 Hz, 4H), 7.13 (d,  $J$  = 8.0 Hz, 4H), 3.52 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 131.6, 130.7, 120.9, 34.9.

GC-MS (EI+)  $m/z$  = 169 (100%), 171 (95%), 372 (14%), 374 (7%).



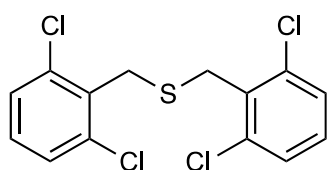
### ***N*-(2,6-dichlorobenzyl)-*N*-phenylcyanamide (3aq)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aq** (55.0 mg, 99% yield) as white solid, m.p.: 109.6-110.8 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.34 (m, 4H), 7.27 (dd, *J* = 8.8, 7.2 Hz, 1H), 7.25-7.20 (m, 2H), 7.23 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.93 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.3, 137.3, 131.3, 129.7, 129.0, 128.8, 124.2, 116.6, 112.1, 48.1.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>11</sub>C<sub>12</sub>N<sub>2</sub>, 277.0294; found, 277.0290.



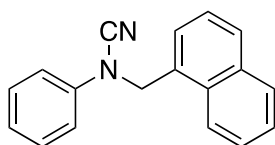
#### bis(2,6-dichlorobenzyl)sulfane (**4q**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4q** (37.5 mg, 97% yield) as white crystal, m.p.: 128.6-129.2 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 8.0 Hz, 4H), 7.11 (t, *J* = 8.0 Hz, 2H), 4.18 (s, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.7, 134.4, 128.7, 128.4, 32.4.

GC-MS (EI+) *m/z* = 159 (100%), 161 (62%), 350 (15%), 352 (20%).



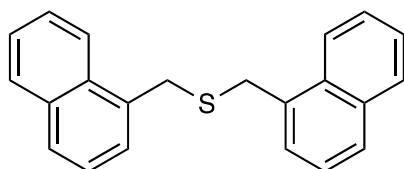
#### *N*-(naphthalen-1-ylmethyl)-*N*-phenylcyanamide (**3ar**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ar** (25.8 mg, 50% yield) as white solid, m.p.: 116.7-117.7 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00-7.80 (m, 3H), 7.65-7.42 (m, 4H), 7.40-7.30 (m, 2H), 7.24-7.06 (m, 3H), 5.24 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 133.9, 130.9, 129.8, 129.4, 129.2, 128.9, 127.0, 126.3, 126.1, 125.4, 123.9, 122.3, 116.0, 113.5, 51.6, 29.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{18}\text{H}_{15}\text{N}_2$ , 259.1230; found, 259.1227.



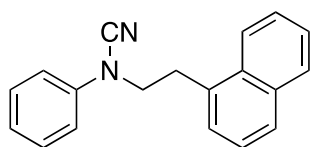
### bis(naphthalen-1-ylmethyl)sulfane (**5r**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5r** (34.6 mg, 98% yield) as green solid, m.p.: 98.6-99.4 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.4$  Hz, 2H), 7.85 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.78 (d,  $J = 8.4$  Hz, 2H), 7.57-7.46 (m, 4H), 7.36 (dd,  $J = 8.4, 6.8$  Hz, 2H), 7.12 (d,  $J = 6.8$  Hz, 2H), 3.96 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0, 132.7, 131.3, 128.8, 128.5, 128.2, 126.2, 125.9, 125.2, 124.1, 41.3.

GC-MS (EI+)  $m/z = 141$  (100%), 173 (19%), 314 (20%).



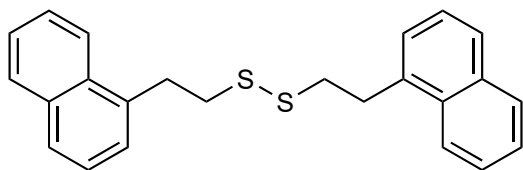
### *N*-(2-(naphthalen-1-yl)ethyl)-*N*-phenylcyanamide (**3as**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3as** (44.7 mg, 82% yield) as yellow solid, m.p.: 84.6-86.1 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.90 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.80 (d,  $J = 7.2$  Hz, 1H), 7.63-7.49 (m, 2H), 7.46-7.33 (m, 4H), 7.16-7.07 (m, 3H), 3.98-3.88 (m, 2H), 3.65-3.54 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 134.0, 132.9, 131.6, 129.8, 129.2, 128.0, 127.2, 126.6, 125.9, 125.6, 123.8, 122.9, 116.0, 50.0, 31.0.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2$ , 273.1386; found, 273.1379.

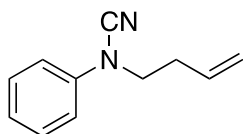


#### 1,2-bis(2-(naphthalen-1-yl)ethyl)disulfane (**4s**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4s** (28.0 mg, 74% yield) as green solid, m.p.: 98.6-100.0 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 7.6$  Hz, 2H), 7.85 (dd,  $J = 7.6, 2.0$  Hz, 2H), 7.73 (d,  $J = 8.0$  Hz, 2H), 7.55-7.43 (m, 4H), 7.39 (dd,  $J = 6.8, 1.2$  Hz, 2H), 7.34 (dd,  $J = 6.8, 1.2$  Hz, 2H), 3.48 (dt,  $J = 5.2, 2.8$  Hz, 4H), 3.08 (dt,  $J = 5.2, 2.8$  Hz, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 134.0, 131.7, 128.9, 127.3, 126.6, 126.2, 125.7, 125.6, 123.4, 39.3, 33.3.



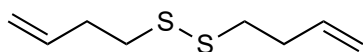
#### *N*-(but-3-en-1-yl)-*N*-phenylcyanamide (**3at**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3at** as yellow liquid. The yield for **3at** is 71% (24.5 mg) when 4-chlorobut-1-ene as substrate or 89% yield (30.8 mg) with 4-bromobut-1-ene.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.24 (m, 2H), 7.22-7.08 (m, 3H), 5.98 (ddt,  $J = 15.6, 10.4, 5.6$  Hz, 1H), 5.51-5.36 (m, 2H), 4.24 (dt,  $J = 5.6, 1.6$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 133.1, 129.7, 123.6, 118.6, 116.0, 113.5, 48.8, 31.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{11}\text{H}_{13}\text{N}_2$ , 173.1073; found, 173.1071.



#### 1,2-di(but-3-en-1-yl)disulfane (**4t**)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4t** as yellow liquid. The yield for **4t** is 50% (8.8 mg) when 4-chlorobut-1-ene as substrate

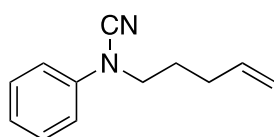


or 34% yield (12.0 mg) with 4-bromobut-1-ene.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.85 (ddt,  $J = 16.8, 10.4, 6.8$  Hz, 1H), 5.12 (dd,  $J = 16.8, 1.6$  Hz, 1H), 5.08 (dd,  $J = 10.4, 1.6$  Hz, 1H), 2.78 (t,  $J = 7.2$  Hz, 2H), 2.46 (ddt,  $J = 9.2, 7.2, 1.6$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 116.3, 38.2, 33.4, 29.7.

GC-MS (EI+)  $m/z = 55$  (100%), 87 (19%), 174 (15%).



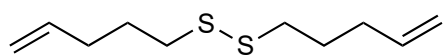
### ***N*-(pent-4-en-1-yl)-*N*-phenylcyanamide (3au)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3au** (30.0 mg, 87% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.33 (m, 2H), 7.15-7.06 (m, 3H), 5.80 (ddt,  $J = 16.8, 10.4, 6.8$  Hz, 1H), 5.14-5.01 (m, 2H), 3.95 (t,  $J = 7.6$  Hz, 2H), 2.27-2.16 (m, 2H), 1.93 (p,  $J = 7.2$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 136.5, 129.7, 123.6, 116.3, 115.9, 48.7, 30.4, 26.5.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{12}\text{H}_{15}\text{N}_2$ , 187.1230; found, 187.1226.



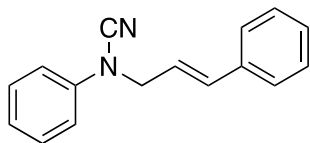
### **1,2-di(pent-4-en-1-yl)disulfane (4u)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4u** (6.7 mg, 38% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.85 (ddt,  $J = 16.8, 10.4, 6.8$  Hz, 2H), 5.04 (dd,  $J = 16.8, 1.6$  Hz, 2H), 5.00 (dd,  $J = 10.4, 1.6$  Hz, 2H), 2.69 (t,  $J = 7.2$  Hz, 4H), 2.22-2.10 (m, 4H), 1.78 (p,  $J = 7.2$  Hz, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 116.3, 38.2, 33.4, 29.7.

GC-MS (EI+)  $m/z = 69$  (19%), 101 (100%).



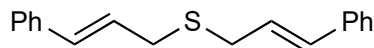
***N*-cinnamyl-*N*-phenylcyanamide (3av)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3av** (13.8 mg, 40% yield) as yellow solid, m.p.: 68.6-69.5 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.27 (m, 7H), 7.23-7.17 (m, 2H), 7.17-7.10 (m, 1H), 6.75 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.33 (dt, *J* = 16.0, 6.4 Hz, 1H), 4.41 (dd, *J* = 6.4, 1.6 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.8, 135.7, 135.2, 129.7, 128.7, 128.4, 126.8, 123.7, 121.1, 116.0, 113.6, 52.0.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>, 235.1230; found, 235.1225.



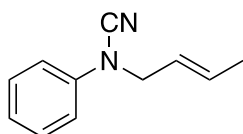
**dicinnamylsulfane (5v)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5v** (7.1 mg, 40% yield) as yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44-7.32 (m, 8H), 7.31-7.25 (m, 2H), 6.47 (d, *J* = 15.6 Hz, 2H), 6.22 (dt, *J* = 15.6, 7.2 Hz, 2H), 3.34 (dd, *J* = 7.6, 1.2 Hz, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.8, 132.5, 128.6, 127.6, 126.3, 126.0, 33.2.

GC-MS (EI+) *m/z* = 91 (25%), 115 (89%), 117 (100%), 149 (61%), 266 (8%).



**(*E*)-*N*-(but-2-en-1-yl)-*N*-phenylcyanamide (3aw)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aw** (24.2 mg, 70% yield, E/Z = 5.84:1) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.30 (m, 2H), 7.15-7.05 (m, 3H), 5.94-5.81 (m, 2H), 5.68-5.56 (m, 1H), 4.11 (dt,  $J$  = 6.4, 1.2 Hz, 2H), 1.76 (dd,  $J$  = 6.4, 1.2 Hz, 3H).

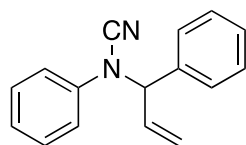
**(E)-1-(but-2-en-1-yl)-1H-benzo[d]imidazole (3aw)**

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 132.6, 129.6, 123.5, 122.9, 115.9, 51.6, 17.8.

**(Z)-1-(but-2-en-1-yl)-1H-benzo[d]imidazole (3aw)**

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.3, 129.6, 123.6, 122.5, 117.1, 113.6, 46.2, 13.3.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{11}\text{H}_{13}\text{N}_2$ , 173.1073; found, 173.1071.



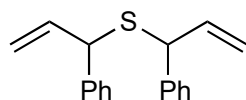
**N-phenyl-N-(1-phenylvinyl)cyanamide (3ax)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ax** (36.7 mg, 78% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.35 (m, 2H), 7.35-7.22 (m, 4H), 7.16-7.05 (m, 3H), 6.69 (ddd,  $J$  = 17.6, 6.8, 1.6 Hz, 1H), 5.75 (dt,  $J$  = 17.6, 1.2 Hz, 1H), 5.27 (ddd,  $J$  = 10.8, 4.4, 0.8 Hz, 1H), 4.78 (d,  $J$  = 4.8 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 139.8, 138.5, 137.9, 136.2, 136.1, 134.7, 133.7, 129.7, 129.7, 129.3, 127.6, 126.9, 126.6, 126.3, 125.2, 123.8, 116.1, 116.0, 114.9, 114.7, 113.9, 77.4, 77.1, 76.8, 53.7, 53.5.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{15}\text{N}_2$ , 235.1230; found, 235.1225.



**bis(1-phenylallyl)sulfane (5x)**

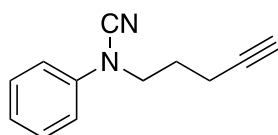
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **5x**

(22.3 mg, 74% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.33 (m, 2H), 7.32-7.14 (m, 6H), 6.70 (ddd,  $J = 17.6, 10.8, 3.2$  Hz, 2H), 5.74 (dd,  $J = 17.6, 2.8$  Hz, 2H), 5.24 (ddd,  $J = 10.8, 6.8, 0.8$  Hz, 2H), 3.61-3.55 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 137.8, 137.7, 136.7, 136.7, 136.5, 136.4, 129.2, 128.7, 128.5, 128.5, 126.9, 126.3, 125.0, 124.9, 114.1, 114.1, 113.7, 77.4, 77.0, 76.7, 35.5, 35.5, 35.4, 35.3.

GC-MS (EI+)  $m/z = 117$  (100%), 266 (18%).



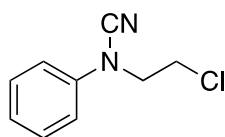
### ***N*-(pent-4-yn-1-yl)-*N*-phenylcyanamide (3ay)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ay** (29.5 mg, 80% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.33 (m, 2H), 7.20-7.07 (m, 3H), 3.75 (t,  $J = 7.2$  Hz, 2H), 2.38 (dt,  $J = 6.8, 2.4$  Hz, 2H), 2.12-1.99 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 129.4, 123.8, 116.0, 82.2, 70.1, 48.1, 26.1, 15.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{12}\text{H}_{13}\text{N}_2$ , 185.1073; found, 185.1070.



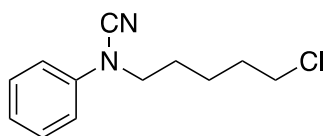
### ***N*-(2-chloroethyl)-*N*-phenylcyanamide (3az)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3az** (14.5 mg, 40% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.36 (m, 2H), 7.23-7.17 (m, 3H), 3.98 (t,  $J = 6.4$  Hz, 2H), 3.38 (dt,  $J = 6.4, 2.4$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 129.9, 124.4, 116.3, 113.1, 51.1, 39.8.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_9\text{H}_{10}\text{ClN}_2$ , 181.0527; found, 181.0524.



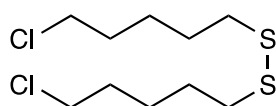
### ***N*-(5-chloropentyl)-*N*-phenylcyanamide (3aaa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aaa** (42.4 mg, 95% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.33 (m, 2H), 7.15-7.06 (m, 3H), 3.60 (t,  $J = 7.2$  Hz, 2H), 3.55 (t,  $J = 6.4$  Hz, 2H), 1.92-1.79 (m, 4H), 1.66-1.55 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 129.7, 123.6, 115.9, 113.5, 49.2, 44.5, 32.0, 26.8, 23.9.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{12}\text{H}_{16}\text{ClN}_2$ , 223.0997; found, 223.0993.

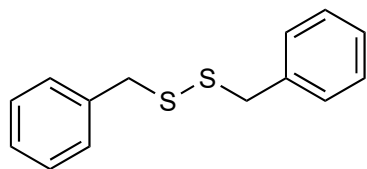


### **1,2-bis(5-chloropentyl)disulfane (4aa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4aa** (13.9 mg, 50% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.57 (t,  $J = 6.8$  Hz, 4H), 2.71 (t,  $J = 6.8$  Hz, 4H), 1.88-1.79 (m, 4H), 1.78-1.69 (m, 4H), 1.57-1.52 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  44.8, 38.7, 32.2, 28.5, 25.8.



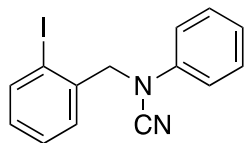
### **1,2-dibenzyl disulfane (4i)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4i** (14.3 mg, 50% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.22 (m, 10H), 3.63 (s, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 129.4, 128.5, 127.5, 43.3.

GC-MS (EI+)  $m/z$  = 91 (100%), 246 (13%).



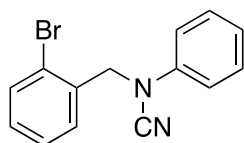
***N*-(2-iodobenzyl)-*N*-phenylcyanamide (3aab)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aab** (29.5 mg, 44% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.41-7.31 (m, 4H), 7.16-7.02 (m, 4H), 4.80 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 139.6, 136.0, 130.2, 129.8, 128.9, 128.3, 123.9, 115.8, 113.3, 97.9, 58.4.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{14}\text{H}_{12}\text{IN}_2$ , 335.0040; found, 335.0032.



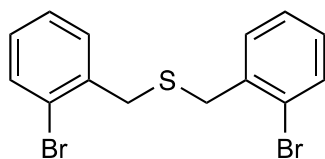
***N*-(2-bromobenzyl)-*N*-phenylcyanamide (3aac)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aac** (39.1 mg, 68% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.41-7.28 (m, 4H), 7.22 (dt,  $J$  = 8.0, 2.0 Hz, 1H), 7.15-7.07 (m, 3H), 4.88 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 133.3, 133.2, 130.1, 129.8, 128.8, 128.1, 123.9, 123.0, 115.8, 113.4, 53.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{14}\text{H}_{12}\text{BrN}_2$ , 287.0178; found, 287.0172.



**bis(2-bromobenzyl)sulfane (5ac)<sup>2</sup>**

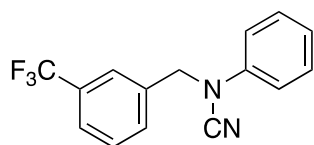
This reaction was conducted on a 0.2 mmol scale with the general procedure to give

**4ac** (9.3 mg, 23% yield) as pink solid, m.p.: 82.5-83.7 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.30-7.24 (m, 4H), 7.18-7.09 (m, 2H), 3.80 (s, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.7, 133.1, 131.7, 129.1, 127.4, 124.6, 77.3, 77.0, 76.7, 43.8.

GC-MS (EI+) *m/z* = 169 (100%), 171 (94%), 215 (62%), 217 (57%), 369 (21%), 371 (42%), 373 (23%).



#### ***N*-phenyl-*N*-(3-(trifluoromethyl)benzyl)cyanamide (3aad)**

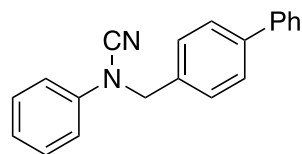
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aad** (32.6 mg, 59% yield) as yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.39 (m, 1H), 7.39-7.28 (m, 3H), 7.24-7.16 (m, 2H), 7.15-7.07 (m, 3H), 4.83 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.7, 139.5, 136.7, 130.7, 129.8, 125.5, 124.1, 120.3 (q, *J*<sub>C-F</sub> = 102.7 Hz), 116.1, 113.6, 53.2.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -57.80.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>, 277.0947; found, 227.0941.



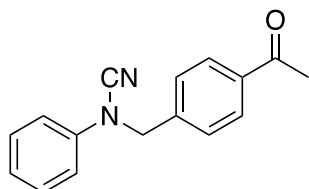
#### ***N*-([1,1'-biphenyl]-4-ylmethyl)-*N*-phenylcyanamide (3aae)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aae** (40.0 mg, 70% yield) as white solid, m.p.: 131.3-132.4 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65-7.54 (m, 4H), 7.48-7.408 (m, 4H), 7.39-7.32 (m, 3H), 7.20-7.14 (m, 2H), 7.10 (dt, *J* = 7.2, 1.2 Hz, 1H), 4.83 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 140.3, 139.8, 133.2, 129.7, 128.9, 127.8, 127.8, 127.6, 127.1, 123.8, 116.1, 114.0, 53.5.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_2$ , 285.1386; found, 285.1380.



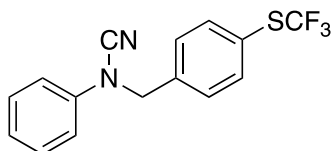
### ***N*-(4-acetylbenzyl)-*N*-phenylcyanamide (3aaf)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aaf** (23.6 mg, 43% yield) as orange solid, m.p.: 106.1-107.2 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.4$  Hz, 1H), 7.46 (d,  $J = 8.4$  Hz, 1H), 7.39-7.29 (m, 2H), 7.15-7.05 (m, 3H), 4.87 (s, 2H), 2.59 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 139.5, 139.4, 137.2, 129.8, 129.1, 127.4, 124.0, 116.0, 113.7, 53.4, 26.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}$ , 251.1179; found, 251.1174.



### ***N*-phenyl-*N*-(4-((trifluoromethyl)thio)benzyl)cyanamide (3aag)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aag** (38.3 mg, 62% yield) as yellow liquid.

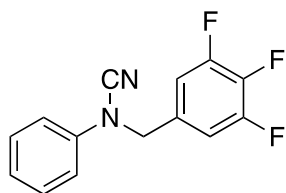
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 8.4$  Hz, 1H), 7.42 (d,  $J = 8.4$  Hz, 1H), 7.39-7.29 (m, 2H), 7.15-7.06 (m, 3H), 4.85 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.4, 137.5, 136.9, 129.8, 129.2, 128.2, 127.9, 124.8 (q,  $J = 2.0$  Hz), 124.1, 115.9, 113.6, 53.2.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -42.49.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{12}\text{F}_3\text{N}_2\text{S}$ , 309.0668; found, 309.0660.





### ***N*-phenyl-*N*-(3,4,5-trifluorobenzyl)cyanamide (3aah)**

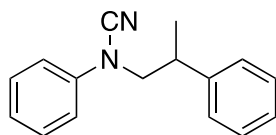
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aah** (37.4 mg, 72% yield) as pale yellow solid, m.p.: 78.5-79.4 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.13 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00 (dt, *J* = 7.2, 1.2 Hz, 2H), 4.75 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.9 (dd, *J*<sub>C-F</sub> = 10.1, 4.0 Hz), 150.4 (dd, *J*<sub>C-F</sub> = 10.2, 4.0 Hz), 139.1, 130.7 (ddd, *J*<sub>C-F</sub> = 11.6, 7.0, 4.6 Hz), 129.9, 124.4, 116.0, 113.3, 111.6 (d, *J*<sub>C-F</sub> = 6.3 Hz), 111.5 (d, *J*<sub>C-F</sub> = 6.3 Hz).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -132.0 (d, *J* = 7.6 Hz), -132.0 (d, *J* = 7.6 Hz), -159.5 (tt, *J* = 20.6, 6.3 Hz).

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>, 263.0791; found, 263.0786.



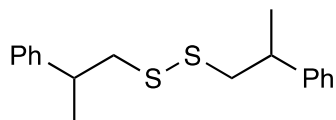
### ***N*-phenyl-*N*-(2-phenylpropyl)cyanamide (3aai)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aai** (31.3 mg, 66% yield) as yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.33 (m, 4H), 7.32-7.24 (m, 3H), 7.14-7.08 (m, 3H), 3.79 (dd, *J* = 14.0, 7.2 Hz, 1H), 3.71 (dd, *J* = 14.0, 7.6 Hz, 1H), 3.33 (tq, *J* = 14.0, 6.8 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.4, 139.9, 129.7, 128.9, 127.3, 127.2, 123.7, 116.2, 113.8, 56.7, 38.2, 18.7.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>, 237.1386; found, 237.1380.



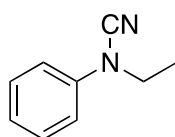
#### 1,2-bis(2-phenylpropyl)disulfane (4ai)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **4ai** (10.0 mg, 16% yield) as yellow oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.28 (m, 4H), 7.25-7.16 (m, 6H), 3.15-3.02 (m, 2H), 1.96 (ddd,  $J = 12.8, 6.4, 2.4$  Hz, 2H), 2.82 (ddd,  $J = 12.8, 8.0, 5.6$  Hz, 2H), 1.35 (d,  $J = 6.8$  Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 128.5, 127.1, 126.5, 47.4, 47.4, 39.4, 39.4, 20.8, 20.8.

GC-MS (EI+)  $m/z = 91$  (100%), 105 (35%), 119 (74%), 302 (14%).



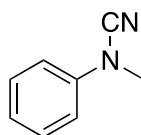
#### *N*-ethyl-*N*-phenylcyanamide (3aaj)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aaj** (26.4 mg, 90% yield) as yellow oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.33 (m, 2H), 7.16-7.03 (m, 3H), 3.63 (q,  $J = 7.2$  Hz, 2H), 1.46 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 129.7, 123.5, 115.8, 113.3, 44.2, 12.7.

HRMS (ESI)  $[M+H]^+$  Calcd. for  $\text{C}_9\text{H}_{11}\text{N}_2$ , 147.0917; found, 147.0914.



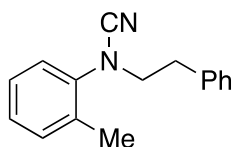
#### *N*-methyl-*N*-phenylcyanamide (3aak)

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3aak** (18.6 mg, 70% yield) as yellow oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.34 (m, 2H), 7.16-7.05 (m, 3H), 3.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 129.6, 123.4, 114.9, 114.1, 36.8.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_8\text{H}_9\text{N}_2$ , 133.0760; found, 133.0759.



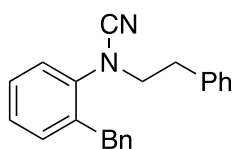
### ***N*-phenethyl-*N*-(*o*-tolyl)cyanamide (3ba)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ba** (25.7 mg, 54% yield) as yellow liquid and **4a** (19.4 mg, 70% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.27 (m, 2H), 7.26-7.16 (m, 6H), 7.13-7.06 (m, 1H), 3.70-3.60 (m, 2H), 3.10-3.00 (m, 2H), 2.26 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 137.2, 134.0, 131.8, 128.9, 128.8, 127.7, 127.3, 127.0, 124.6, 115.4, 55.1, 34.2, 17.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_2$ , 237.1386; found, 237.1381.



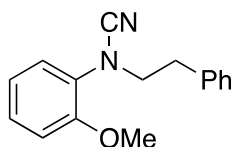
### ***N*-(2-benzylphenyl)-*N*-phenethylcyanamide (3ca)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ca** (37.5 mg, 60% yield) as yellow liquid and **4a** (21.9 mg, 79% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.05 (m, 14H), 4.04 (s, 2H), 3.42-3.31 (m, 2H), 2.88-2.77 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 139.3, 137.3, 137.2, 131.8, 128.9, 128.8, 128.7, 128.6, 128.1, 127.9, 126.9, 126.5, 125.5, 115.4, 55.4, 37.2, 34.0.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{22}\text{H}_{21}\text{N}_2$ , 313.1699; found, 313.1691.



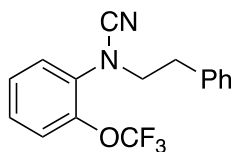
***N*-(2-methoxyphenyl)-*N*-phenethylcyanamide (3ea)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ea** (48.5 mg, 96% yield) as yellow liquid and **4a** (19.6 mg, 71% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.26 (m, 2H), 7.26-7.16 (m, 4H), 7.13 (dd,  $J = 8.0$ , 1.6 Hz, 1H), 6.96-6.88 (m, 2H), 3.86 (s, 3H), 3.73-3.64 (m, 2H), 3.07-2.98 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 137.5, 129.1, 128.9, 128.6, 128.3, 126.8, 125.2, 121.1, 115.8, 112.4, 55.8, 54.7, 34.4.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}$ , 253.1335; found, 253.1329.



***N*-phenethyl-*N*-(2-(trifluoromethoxy)phenyl)cyanamide (3fa)**

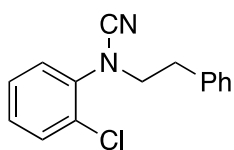
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3fa** (59.0 mg, 96% yield) as yellow liquid and **4a** (23.0 mg, 83% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.15 (m, 9H), 3.77-3.68 (m, 2H), 3.11-3.02 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.6, 136.8, 133.2, 128.8, 128.8, 128.1, 127.9, 127.0, 125.4, 122.1 (q,  $J_{\text{C-H}} = 1.7$  Hz), 121.7, 119.1, 114.3, 55.1, 34.2.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.46.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ , 307.1053; found, 307.1046.



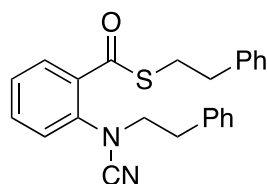
***N*-(2-chlorophenyl)-*N*-phenethylcyanamide (3ga)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ga** (41.1 mg, 80% yield) as yellow liquid and **4a** (22.5 mg, 81% yield) as colorless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47-7.40 (m, 1H), 7.34-7.28 (m, 2H), 7.27-7.16 (m, 6H), 3.76-3.67 (m, 2H), 3.12-3.05 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.8, 137.0, 131.1, 130.5, 128.9, 128.9, 128.8, 128.1, 127.0, 126.9, 114.7, 55.3, 34.2.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>ClN<sub>2</sub>, 257.0840; found, 257.0833.



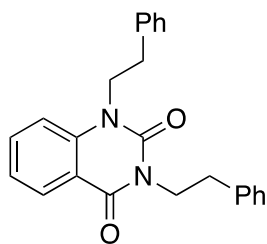
### **S-phenethyl 2-(N-phenethylcyanamido)benzothioate (3ha)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ha** (41.7 mg, 54% yield) as white solid (m.p.: 79.1-79.7 °C) and **3ha'** (30.0 mg, 40% yield) as yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05-7.99 (m, 1H), 7.78-7.69 (m, 2H), 7.39 (ddd, *J* = 8.0, 6.0, 2.0 Hz, 1H), 7.35-7.18 (m, 10H), 4.75 (t, *J* = 7.2 Hz, 2H), 3.50-3.42 (m, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 3.14-3.06 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.7, 165.8, 151.9, 140.8, 137.9, 133.8, 129.1, 128.7, 128.6, 128.5, 126.7, 126.4, 126.3, 125.4, 123.8, 114.3, 67.7, 36.3, 35.3, 32.4.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>OS, 387.1526; found, 387.1519.



### **1,3-diphenethylquinazoline-2,4(1H,3H)-dione (3ha')**

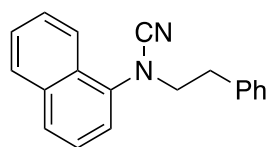
This reaction was conducted on a 0.2 mmol scale with the general procedure to give

**3ha** (41.7 mg, 54% yield) as white solid (m.p.: 79.1-79.7 °C) and **3ha'** (30.0 mg, 40% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.71 (ddd,  $J = 8.4, 7.2, 1.6$  Hz, 1H), 7.60 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.42-7.36 (m, 1H), 7.36-7.30 (m, 7H), 7.29-7.22 (m, 2H), 4.36-4.25 (m, 2H), 3.57-3.49 (m, 2H), 3.15-3.07 (m, 2H), 3.07-2.99 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 156.0, 147.6, 140.1, 138.0, 134.3, 129.0, 128.8, 128.7, 128.6, 127.0, 126.8, 126.7, 126.2, 125.7, 119.5, 46.1, 35.5, 34.2, 33.4.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_2$ , 371.1754; found, 371.1740.



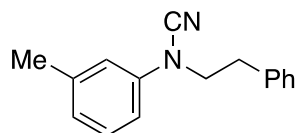
#### ***N*-(naphthalen-1-yl)-*N*-phenethylcyanamide (**3ia**)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ga** (31.7 mg, 58% yield) as yellow liquid and **4a** (22.5 mg, 81% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93-7.81 (m, 2H), 7.79 (d,  $J = 8.0$  Hz, 1H), 7.55-7.48 (m, 2H), 7.45-7.35 (m, 2H), 7.34-7.20 (m, 5H), 3.82-3.75 (m, 2H), 3.19-3.11 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2, 137.0, 134.7, 129.0, 128.8, 128.6, 128.6, 128.6, 127.2, 127.0, 126.8, 125.5, 122.6, 122.1, 116.2, 56.1, 34.3.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2$ , 273.1386; found, 273.1381.



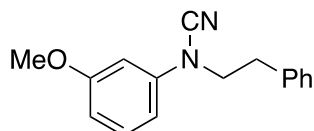
#### ***N*-phenethyl-*N*-(*p*-tolyl)cyanamide (**3ja**)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ja** (43.5 mg, 92% yield) as yellow liquid and **4a** (19.4 mg, 70% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.30 (m, 2H), 7.30-7.16 (m, 3H), 6.95-6.84 (m, 2H), 3.84-3.72 (m, 2H), 3.17-3.03 (m, 2H), 2.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 139.8, 137.0, 129.5, 128.9, 128.8, 127.1, 124.6, 116.9, 113.6, 113.0, 50.9, 33.8, 21.6.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_2$ , 237.1386; found, 237.1381.



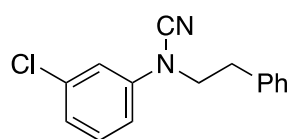
### ***N*-(3-methoxyphenyl)-*N*-phenethylcyanamide (3ka)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ka** (35.0 mg, 69% yield) as yellow liquid and **4a** (15.8 mg, 57% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.30 (m, 2H), 7.30-7.19 (m, 3H), 6.73-6.60 (m, 2H), 3.82-3.76 (m, 2H), 3.80 (s, 3H), 3.15-3.07 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 141.1, 136.9, 130.5, 128.9, 128.8, 127.1, 113.3, 109.1, 108.3, 102.5, 55.4, 51.0, 33.8.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}$ , 253.1335; found, 253.1330.



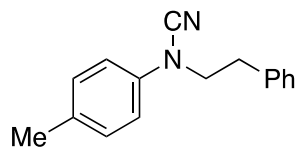
### ***N*-(3-chlorophenyl)-*N*-phenethylcyanamide (3la)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3la** (37.0 mg, 70% yield) as yellow liquid and **4a** (11.4 mg, 41% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.22 (m, 6H), 7.13-7.06 (m, 2H), 7.04-6.98 (m, 1H), 3.87-3.78 (m, 2H), 3.18-3.09 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1, 136.6, 135.7, 130.7, 129.0, 128.8, 127.3, 123.8, 116.2, 114.2, 112.6, 51.0, 33.7.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>14</sub>CIN<sub>2</sub>, 257.0840; found, 257.0835.



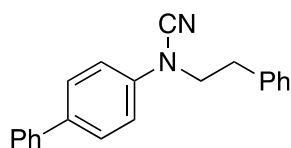
### ***N*-phenethyl-*N*-(*p*-tolyl)cyanamide (3ma)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ma** (30.0 mg, 64% yield) as yellow liquid and **4a** (21.3 mg, 77% yield) as colorless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.32 (m, 2H), 7.32-7.24 (m, 3H), 7.22-7.16 (m, 2H), 7.06-6.98 (m, 2H), 3.85-3.76 (m, 2H), 3.17-3.07 (m, 2H), 2.35 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.4, 137.0, 133.5, 130.2, 128.9, 128.8, 127.1, 116.3, 113.8, 51.2, 33.8, 20.6.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>, 237.1386; found, 237.1382.



### **1-phenethyl-6-phenyl-1*H*-benzo[*d*]imidazole (3na)**

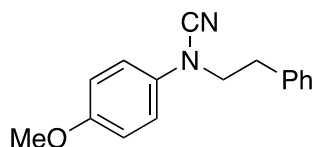
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3na** (41.5 mg, 68% yield) as pale yellow solid (m.p.: 96.8-97.5 °C) and **4a** (20.3 mg, 73% yield) as colorless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63-7.53 (m, 4H), 7.46-7.40 (m, 2H), 7.38-7.30 (m, 2H), 7.30-7.22 (m, 2H), 7.19-7.12 (m, 2H), 3.90-3.78 (m, 2H), 3.20-3.08 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.9, 139.0, 136.9, 136.8, 128.9, 128.9, 128.8, 128.3, 127.4, 127.2, 126.8, 116.4, 113.4, 51.0, 33.8.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>, 299.1543; found, 299.1537.





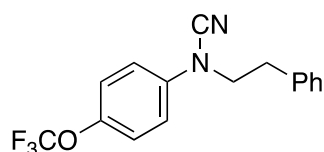
***N*-(4-methoxyphenyl)-*N*-phenethylcyanamide (30a)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **30a** (50.0 mg, 99% yield) as orange solid (m.p.: 70.0-70.7 °C) and **4a** (21.8 mg, 79% yield) as colorless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.22 (m, 5H), 7.08-7.02 (m, 2H), 6.95-6.88 (m, 2H), 3.81 (s, 3H), 3.80-3.74 (m, 2H), 3.14-3.06 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.4, 137.1, 133.2, 128.9, 128.8, 127.1, 118.5, 115.0, 114.4, 55.6, 52.0, 33.9.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O, 253.1335; found, 253.1330.



***N*-phenethyl-*N*-(4-(trifluoromethoxy)phenyl)cyanamide (3pa)**

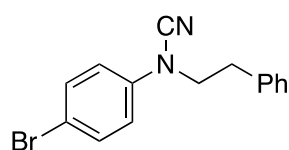
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3pa** (60.6 mg, 99% yield) as yellow liquid and **4a** (24.3 mg, 88% yield) as colorless liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39-7.30 (m, 2H), 7.30-7.26 (m, 1H), 7.26-7.18 (m, 4H), 7.11-7.04 (m, 2H), 3.86-3.74 (m, 2H), 3.17-3.06 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.0 (d, *J*<sub>C-H</sub> = 3.0 Hz), 138.6, 136.6, 129.0, 128.8, 127.3, 122.6, 121.7, 119.2, 117.2, 112.9, 51.3, 33.8.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -58.3.

HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub>O, 307.1053; found, 307.1048.



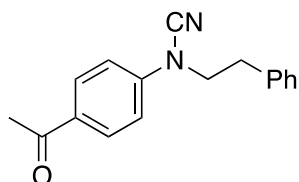
***N*-(4-bromophenyl)-*N*-phenethylcyanamide (3qa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3qa** (37.0 mg, 61% yield) as yellow liquid and **4a** (22.8 mg, 82% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 8.8$  Hz, 2H), 7.36-7.18 (m, 5H), 6.94 (d,  $J = 8.8$  Hz, 2H), 3.81-3.72 (m, 2H), 3.14-3.04 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 136.6, 132.7, 129.0, 128.8, 127.3, 117.7, 116.5, 112.9, 51.1, 33.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{14}\text{BrN}_2$ , 301.0335; found, 301.0327.



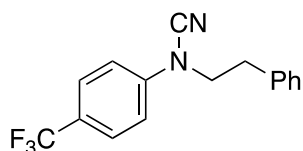
#### ***N*-(4-acetylphenyl)-*N*-phenethylcyanamide (**3ra**)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ra** (28.4 mg, 54% yield) as yellow solid (m.p.: 81.0-82.0 °C) and **4a** (20.8 mg, 75% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.8$  Hz, 2H), 7.40-7.22 (m, 5H), 7.16 (d,  $J = 8.8$  Hz, 2H), 3.95-3.86 (m, 2H), 3.21-3.11 (m, 2H), 2.60 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.4, 143.8, 136.4, 132.5, 130.4, 129.0, 128.8, 127.3, 115.2, 112.2, 50.8, 33.7, 26.4.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}$ , 265.1335; found, 265.1329.



#### ***N*-phenethyl-*N*-(4-(trifluoromethyl)phenyl)cyanamide (**3sa**)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3sa** (25.0 mg, 43% yield) as yellow solid (m.p.: 65.0-66.5 °C) and **4a** (18.0 mg, 65% yield) as colorless liquid.

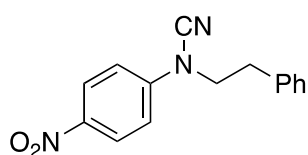
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (dd,  $J = 6.4, 2.4$  Hz, 2H), 7.36-7.30 (m, 2H), 7.30-

7.26 (m, 1H), 7.26-7.21 (m, 2H), 7.16 (dd,  $J = 6.4, 2.4$  Hz, 2H), 3.90-3.82 (m, 2H), 3.17-3.09 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 136.4, 129.0, 128.8, 127.4, 127.0 (q,  $J_{\text{C-H}} = 3.7$  Hz), 125.9, 125.6, 125.2, 122.5, 115.6, 112.2, 50.9, 33.7.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.1.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_2$ , 291.1104; found, 291.1097.



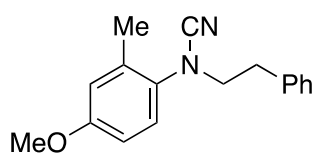
### ***N*-(4-nitrophenyl)-*N*-phenethylcyanamide (3ta)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ta** (39.5 mg, 74% yield) as yellow liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 9.2$  Hz, 2H), 7.38-7.21 (m, 5H), 7.16 (d,  $J = 9.2$  Hz, 2H), 3.95-3.88 (m, 2H), 3.20-3.12 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 143.4, 136.1, 129.1, 128.8, 127.5, 125.7, 115.4, 111.4, 51.1, 33.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_2$ , 268.1081; found, 268.1072.



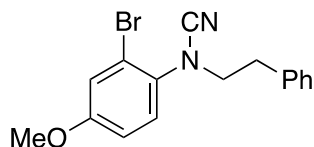
### ***N*-(4-methoxy-2-methylphenyl)-*N*-phenethylcyanamide (3ua)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ua** (32.0 mg, 60% yield) as yellow liquid and **4a** (20.7 mg, 75% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.28 (m, 2H), 7.27-7.19 (m, 3H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.76-6.64 (m, 2H), 3.77 (s, 3H), 3.62-3.54 (m, 2H), 3.07-3.00 (m, 2H), 3.23 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 137.3, 136.0, 132.1, 128.9, 128.7, 126.9, 126.6, 116.5, 116.0, 112.4, 55.5, 55.5, 34.2, 17.8.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}$ , 267.1492; found, 267.1487.



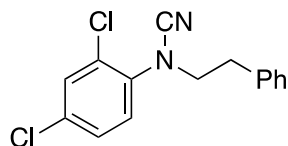
### ***N*-(2-bromo-4-methoxyphenyl)-*N*-phenethylcyanamide (3va)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3va** (44.0 mg, 66% yield) as yellow liquid and **4a** (19.1 mg, 75% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.27 (m, 2H), 7.27-7.19 (m, 3H), 7.12 (d,  $J = 2.8$  Hz, 1H), 7.05 (d,  $J = 8.8$  Hz, 1H), 3.78 (s, 3H), 3.66-3.56 (m, 2H), 3.10-3.00 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 137.2, 132.0, 128.9, 128.7, 128.6, 126.9, 122.0, 118.9, 115.1, 114.4, 55.9, 55.8, 34.2.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{16}\text{BrN}_2\text{O}$ , 331.0441; found, 331.0434.



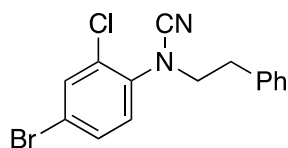
### ***N*-(2,4-dichlorophenyl)-*N*-phenethylcyanamide (3wa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3wa** (28.0 mg, 48% yield) as yellow solid (m.p.: 58.5-59.2 °C) and **4a** (19.8 mg, 71% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 2.4$  Hz, 1H), 7.35-7.28 (m, 2H), 7.28-7.24 (m, 1H), 7.24-7.17 (m, 3H), 7.05 (d,  $J = 8.4$  Hz, 1H), 3.75-3.64 (m, 2H), 3.14-2.99 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 136.6, 134.1, 131.4, 130.8, 128.9, 128.8, 128.3, 127.6, 127.1, 114.2, 55.4, 34.2.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{N}_2$ , 291.0450; found, 291.0445.



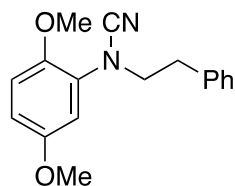
***N*-(4-bromo-2-chlorophenyl)-*N*-phenethylcyanamide (3xa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3xa** (54.0 mg, 80% yield) as yellow liquid and **4a** (21.4 mg, 77% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 2.0$  Hz, 1H), 7.39-7.19 (m, 6H), 6.98 (d,  $J = 8.4$  Hz, 1H), 3.76-3.62 (m, 2H), 3.12-3.00 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 136.7, 133.7, 131.5, 131.3, 128.9, 128.8, 127.8, 127.1, 121.6, 114.1, 55.3, 34.2.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{13}\text{BrClN}_2$ , 334.9945; found, 334.9940.



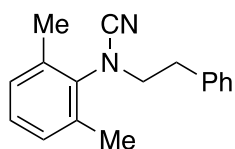
***N*-(2,5-dimethoxyphenyl)-*N*-phenethylcyanamide (3ya)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ya** (44.1 mg, 80% yield) as yellow liquid and **4a** (20.5 mg, 74% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.18 (m, 5H), 6.84 (d,  $J = 9.2$  Hz, 1H), 6.73 (dd,  $J = 9.2, 2.8$  Hz, 1H), 6.65 (d,  $J = 2.8$  Hz, 1H), 3.81 (s, 3H), 3.73-3.67 (m, 2H), 3.71 (s, 3H), 3.08-2.98 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 147.4, 137.5, 129.7, 128.9, 128.7, 126.8, 115.6, 113.7, 112.9, 110.8, 56.5, 55.8, 54.7, 34.3.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2$ , 283.1441; found, 283.1434.

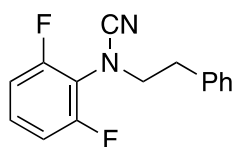


***N*-(2,6-dimethylphenyl)-*N*-phenethylcyanamide (3za)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ya** (44.1 mg, 60% yield) as yellow liquid and **4a** (20.5 mg, 74% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.20 (m, 5H), 7.17-7.10 (m, 1H), 7.09-7.04 (m, 2H), 3.53-3.44 (m, 2H), 3.17-3.07 (m, 2H), 2.30 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 137.2, 136.2, 129.2, 128.9, 128.8, 128.6, 127.0, 115.3, 54.6, 34.5, 18.0.



***N*-(2,6-difluorophenyl)-*N*-phenethylcyanamide (3baa)**

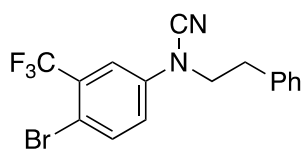
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3ya** (44.1 mg, 62% yield) as yellow liquid and **4a** (20.5 mg, 74% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.20 (m, 6H), 7.05-6.94 (m, 2H), 3.78-3.67 (m, 2H), 3.15-3.05 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3 (d,  $J_{\text{C-F}} = 3.9$  Hz), 156.8 (d,  $J_{\text{C-F}} = 3.8$  Hz), 136.6, 129.2 (t,  $J_{\text{C-F}} = 9.8$  Hz), 128.8, 128.7, 127.0, 112.6 (d,  $J_{\text{C-F}} = 5.0$  Hz), 112.4 (d,  $J_{\text{C-F}} = 5.0$  Hz), 55.7 (d,  $J = 5.0$  Hz), 34.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.03 (d,  $J = 6.3$  Hz), -118.05 (d,  $J = 6.3$  Hz).

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{13}\text{F}_2\text{N}_2$ , 259.1041; found, 259.1036.



***N*-(4-bromo-3-(trifluoromethyl)phenyl)-*N*-phenethylcyanamide (3bba)**

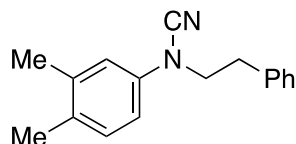
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3za** (34.8 mg, 47% yield) as yellow solid (m.p.: 84.5-85.2 °C) and **4a** (19.5 mg, 71% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.8$  Hz, 1H), 7.37-7.19 (m, 6H), 7.09 (dd,  $J = 8.8, 3.2$  Hz, 1H), 3.90-3.76 (m, 2H), 3.17-3.05 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 136.3, 136.2, 131.8 (q,  $J_{\text{C-F}} = 31.8$  Hz), 129.1, 128.8, 127.4, 123.7, 121.0, 120.2, 115.2 (q,  $J_{\text{C-F}} = 5.7$  Hz), 113.7 (d,  $J_{\text{C-F}} = 1.7$  Hz), 112.0, 51.2, 33.7.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.0.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{13}\text{BrClF}_3\text{N}_2$ , 369.0209; found, 369.0201.



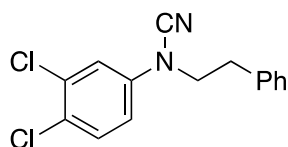
#### ***N*-(3,4-dimethylphenyl)-*N*-phenethylcyanamide (3bca)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3bca** (34.0 mg, 68% yield) as yellow liquid and **4a** (17.4 mg, 63% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.18 (m, 5H), 7.09 (d,  $J = 8.0$  Hz, 1H), 6.88 (d,  $J = 2.4$  Hz, 1H), 6.80 (dd,  $J = 8.0, 2.4$  Hz, 1H), 3.80-3.70 (m, 2H), 3.13-3.03 (m, 2H), 2.24 (s, 3H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 137.6, 137.1, 132.2, 130.6, 128.9, 128.8, 127.1, 117.8, 114.0, 113.5, 51.1, 33.9, 20.0, 19.0.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_2$ , 251.1543; found, 251.1538.



#### ***N*-(3,4-dichlorophenyl)-*N*-phenethylcyanamide (3bda)**

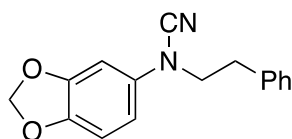
This reaction was conducted on a 0.2 mmol scale with the general procedure to give

**3bda** (28.0 mg, 48% yield) as yellow liquid and **4a** (21.0 mg, 76% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.8$  Hz, 1H), 7.37-7.18 (m, 5H), 7.13 (d,  $J = 2.8$  Hz, 1H), 6.91 (dd,  $J = 8.8, 2.8$  Hz, 1H), 3.85-3.72 (m, 2H), 3.18-3.04 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 136.4, 133.8, 131.2, 129.0, 128.8, 127.4, 117.8, 115.4, 77.4, 77.1, 76.7, 51.2, 33.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{N}_2$ , 291.0450; found, 291.0444.



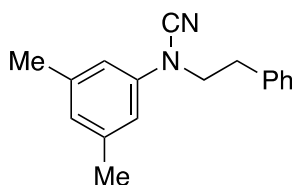
### ***N*-(benzo[*d*][1,3]dioxol-5-yl)-*N*-phenethylcyanamide (3bea)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3bea** (50.5 mg, 95% yield) as brown solid (m.p.: 76.6-77.8 °C) and **4a** (13.9 mg, 50% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.20 (m, 5H), 6.78 (d,  $J = 8.4$  Hz, 1H), 6.65 (d,  $J = 2.4$  Hz, 1H), 6.55 (dd,  $J = 8.4, 2.4$  Hz, 1H), 5.99 (s, 2H), 3.80-3.70 (m, 2H), 3.15-3.01 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.8, 144.5, 137.0, 134.7, 128.9, 128.8, 127.1, 114.1, 109.9, 108.6, 101.7, 99.7, 52.2, 33.8, 29.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2$ , 267.1128; found, 267.1123.



### ***N*-(3,5-dimethylphenyl)-*N*-phenethylcyanamide (3bfa)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3baa** (40.5 mg, 81% yield) as yellow liquid and **4a** (17.5 mg, 63% yield) as colorless liquid.

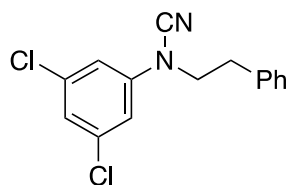
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.24 (m, 5H), 6.82-6.70 (m, 3 H), 3.87-3.75 (m,



2H), 3.21-3.08 (m, 2H), 2.34 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 139.6, 137.1, 128.9, 128.9, 127.1, 125.5, 113.9, 113.8, 50.9, 33.9, 21.5.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_2$ , 251.1543; found, 251.1536.



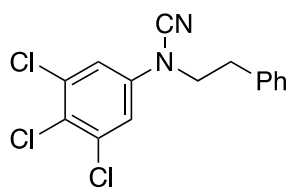
### ***N*-(3,5-dichlorophenyl)-*N*-phenethylcyanamide (3bga)**

This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3bga** (28.2 mg, 48% yield) as yellow liquid and **4a** (19.3 mg, 70% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.20 (m, 5H), 7.07 (t,  $J = 1.6$  Hz, 1H), 6.95 (d,  $J = 1.6$  Hz, 2H), 3.83-3.72 (m, 2H), 3.16-3.05 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 136.3, 136.3, 129.0, 128.8, 127.4, 123.8, 114.5, 111.8, 51.0, 33.7, 29.7.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{N}_2$ , 291.0450; found, 291.0442.



### ***N*-phenethyl-*N*-(3,4,5-trichlorophenyl)cyanamide (3bha)**

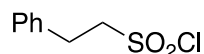
This reaction was conducted on a 0.2 mmol scale with the general procedure to give **3bga** (26.0 mg, 40% yield) as white solid (m.p.: 84.5-85.5 °C) and **4a** (21.0 mg, 76% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.21 (m, 5H), 7.01 (s, 2H), 3.84-3.75 (m, 2H), 3.18-3.10 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 136.2, 135.3, 129.1, 128.8, 127.5, 126.3, 116.2, 111.6, 51.2, 33.7.

HRMS (ESI)  $[M+H]^+$  Calcd. for  $C_{15}H_{12}Cl_3N_2$ , 325.0061; found, 325.0053.

### 2-phenylethane-1-sulfonyl chloride (5)



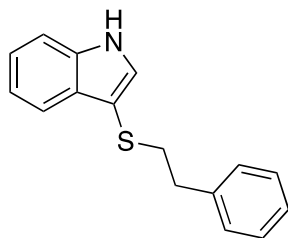
This reaction was conducted on a 0.1 mmol scale to give **5** (90% yield) as yellowish oil.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43-7.23 (m, 5H), 7.01 (s, 2H), 3.98-3.89 (m, 2H), 3.42-3.32 (m, 2H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  135.6, 129.2, 128.5, 127.7, 66.2, 30.4.

HRMS (ESI)  $[M+H]^+$  Calcd. for  $C_8H_{10}ClO_2 S$ , 205.0085; found, 204.9900.

### 3-(phenethylthio)-1H-indole (6)



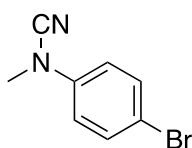
This reaction was conducted on a 0.1 mmol scale to give **5** (85% yield) as yellowish oil.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.27-8.13 (br, 1H), 7.77 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.36 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.29 (d,  $J = 2.8$  Hz, 1H), 7.28-7.14 (m, 5H), 7.11 (dd,  $J = 8.4, 1.2$  Hz, 1H), 2.99-2.91 (m, 2H), 2.88-2.80 (m, 2H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  140.6, 136.4, 129.5, 129.4, 128.6, 128.4, 126.2, 122.8, 120.5, 119.4, 111.5, 105.7, 37.5, 36.6.

HRMS (ESI)  $[M+H]^+$  Calcd. for  $C_{16}HNS$ , 254.0998; found, 254.0992.

### N-(4-bromophenyl)-N-methylcyanamide (7)



This reaction was conducted on a 0.1 mmol scale to give **7** (90% yield) as yellowish

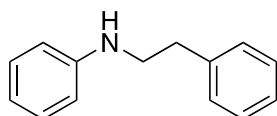
oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.8$  Hz, 2H), 6.98 (d,  $J = 8.8$  Hz, 2H), 3.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 132.6, 116.6, 116.2, 113.6, 37.0.

HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd. for  $\text{C}_8\text{H}_7\text{BrN}_2$ , 210.9865; found, 210.9860.

### ***N*-phenethylaniline (8)**



This reaction was conducted on a 0.1 mmol scale to give **8** (90% yield) as colorless liquid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 7.2$  Hz, 2H), 7.27-7.12 (m, 5H), 6.70 (tt,  $J = 7.2, 1.2$  Hz, 1H), 6.60 (dd,  $J = 8.8, 1.2$  Hz, 2H), 3.64 (br, 1H), 3.38 (t,  $J = 7.2$  Hz, 2H), 2.90 (t,  $J = 7.2$  Hz, 2H).

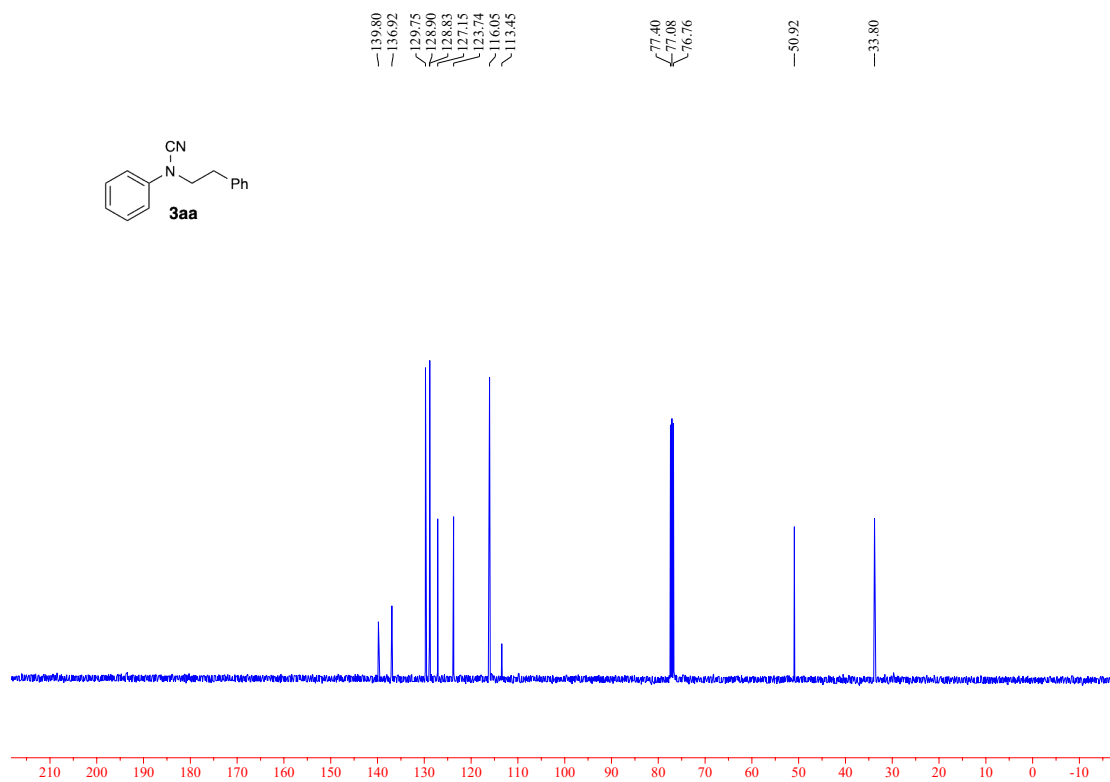
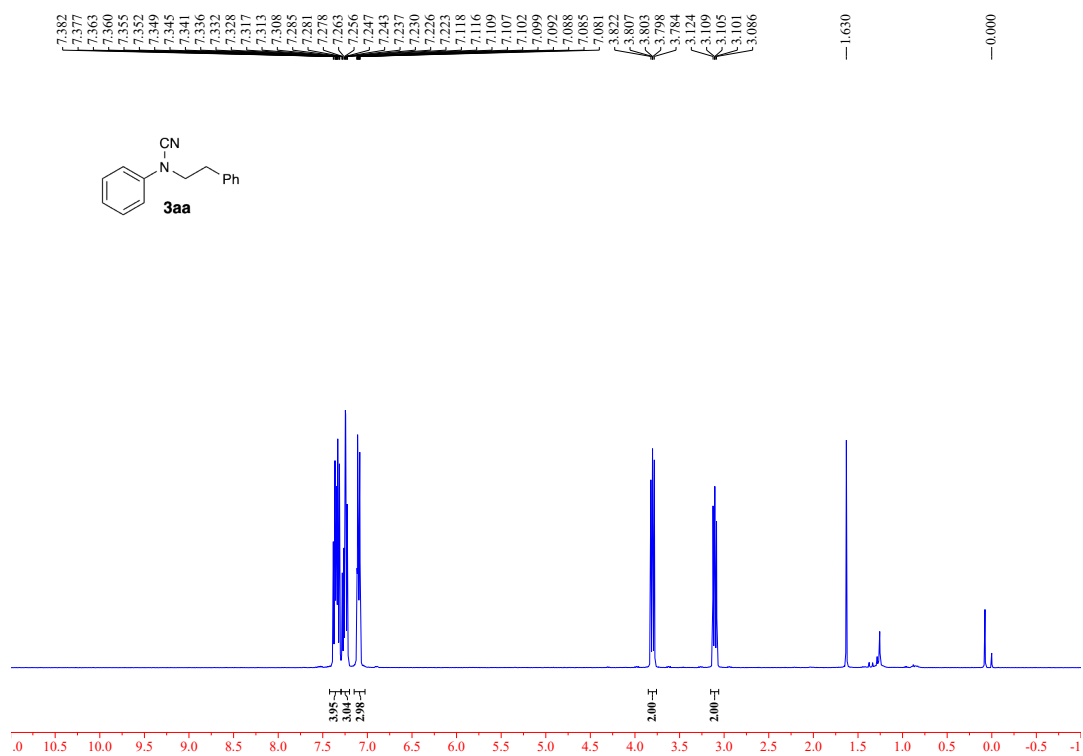
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.1, 139.4, 129.4, 128.9, 128.7, 126.5, 117.5, 113.1, 77.4, 77.1, 76.8, 45.1, 35.6.

### **Uncategorized References**

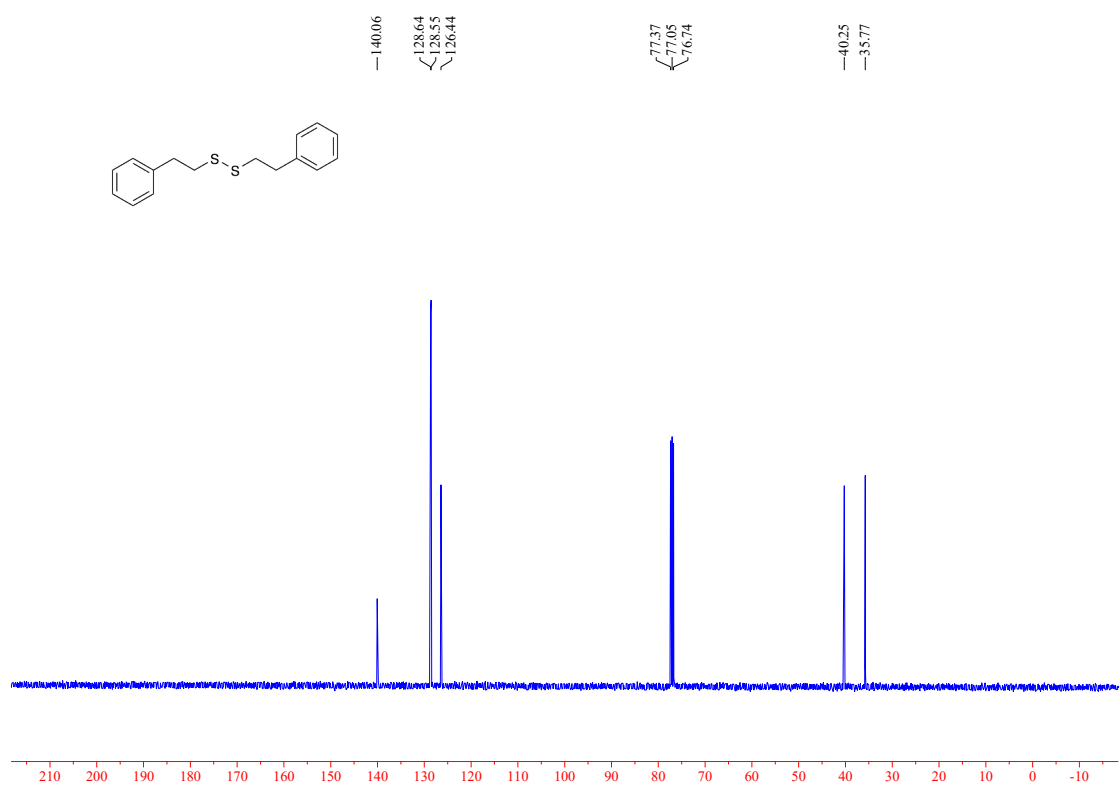
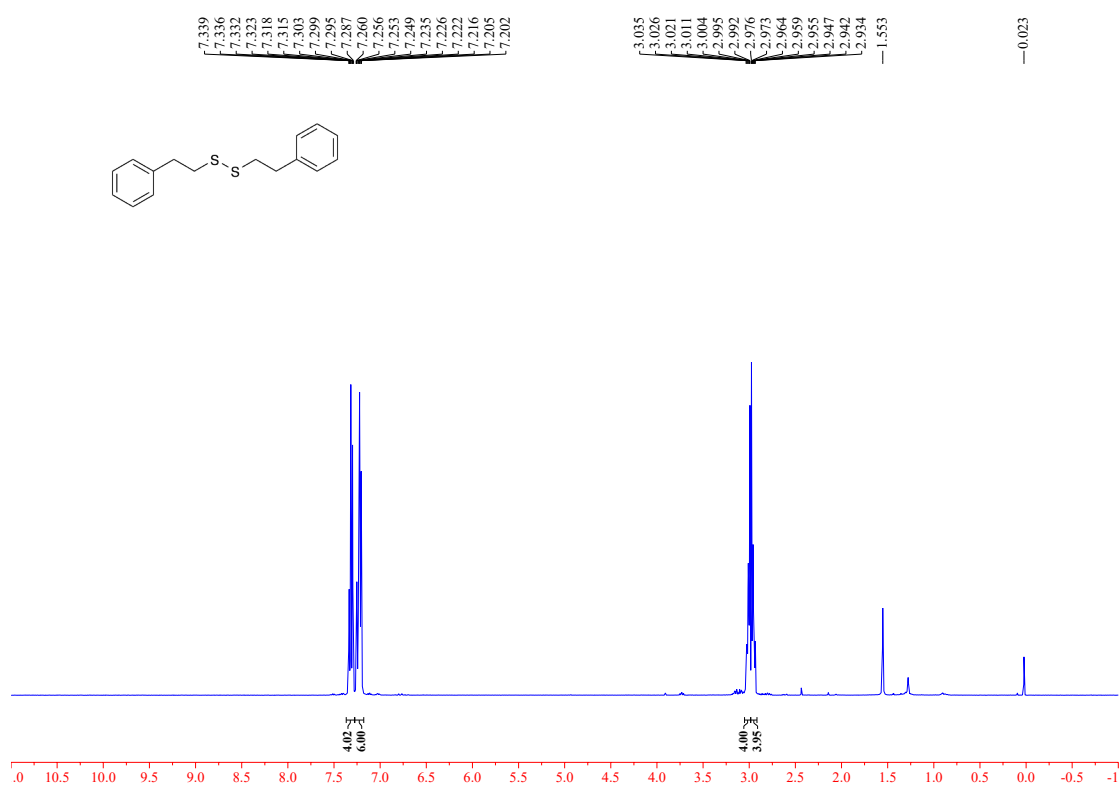
1. H. Yue, J. Wang, Z. Xie, J. Tian, D. Sang and S. Liu, *ChemistrySelect*, 2020, **5**, 4273-4277.
2. T. Miyazaki, K. Nishino, S. Yoshimoto, Y. Ogiwara and N. Sakai, *European Journal of Organic Chemistry*, 2015, **2015**, 1991-1994.

## 8. NMR Spectra for products

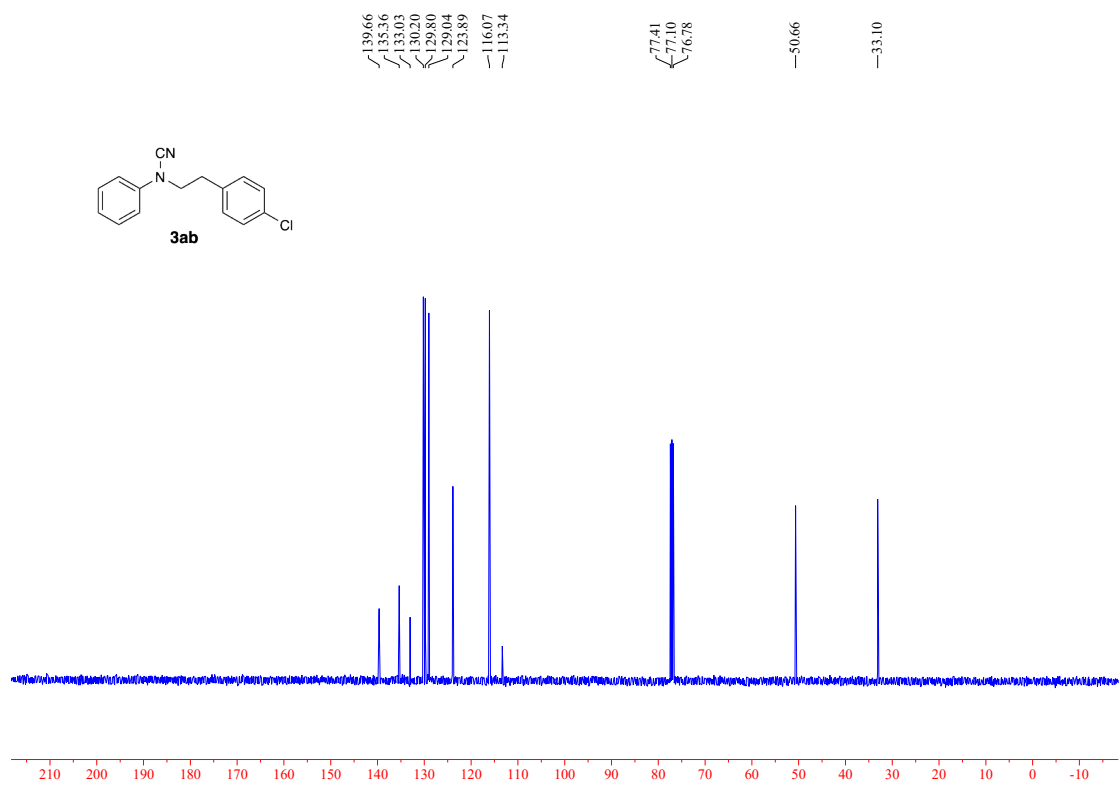
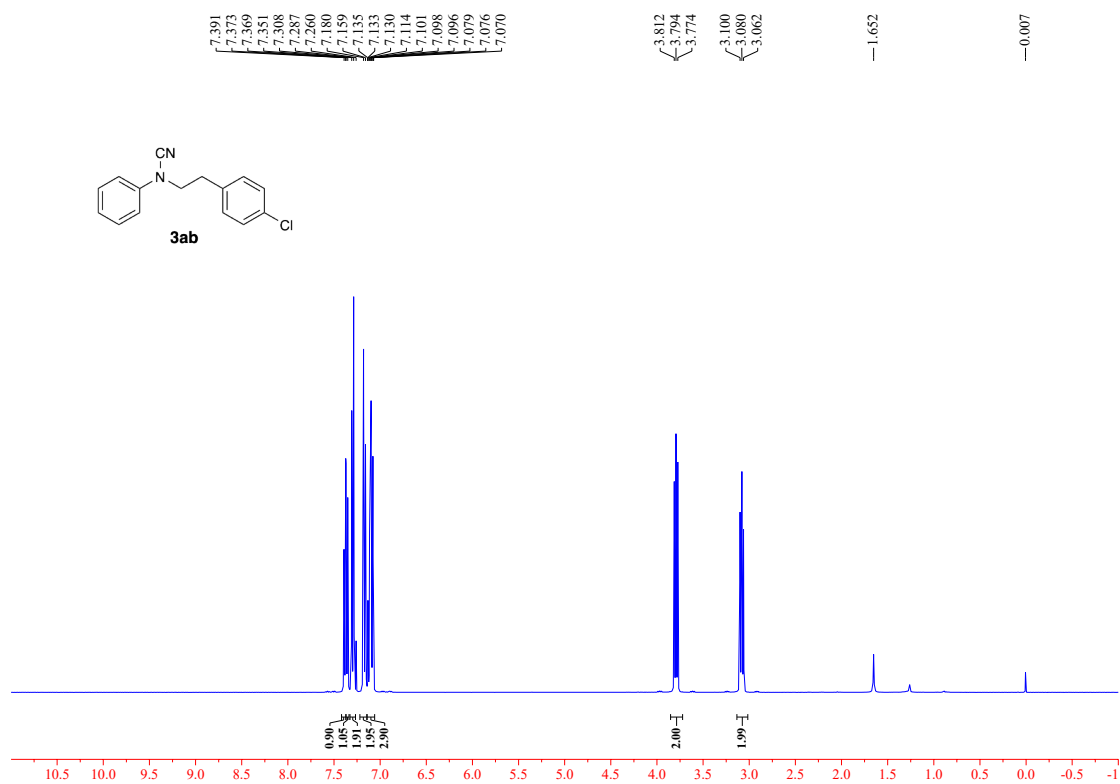
### *N*-phenethyl-*N*-phenylcyanamide (3aa)



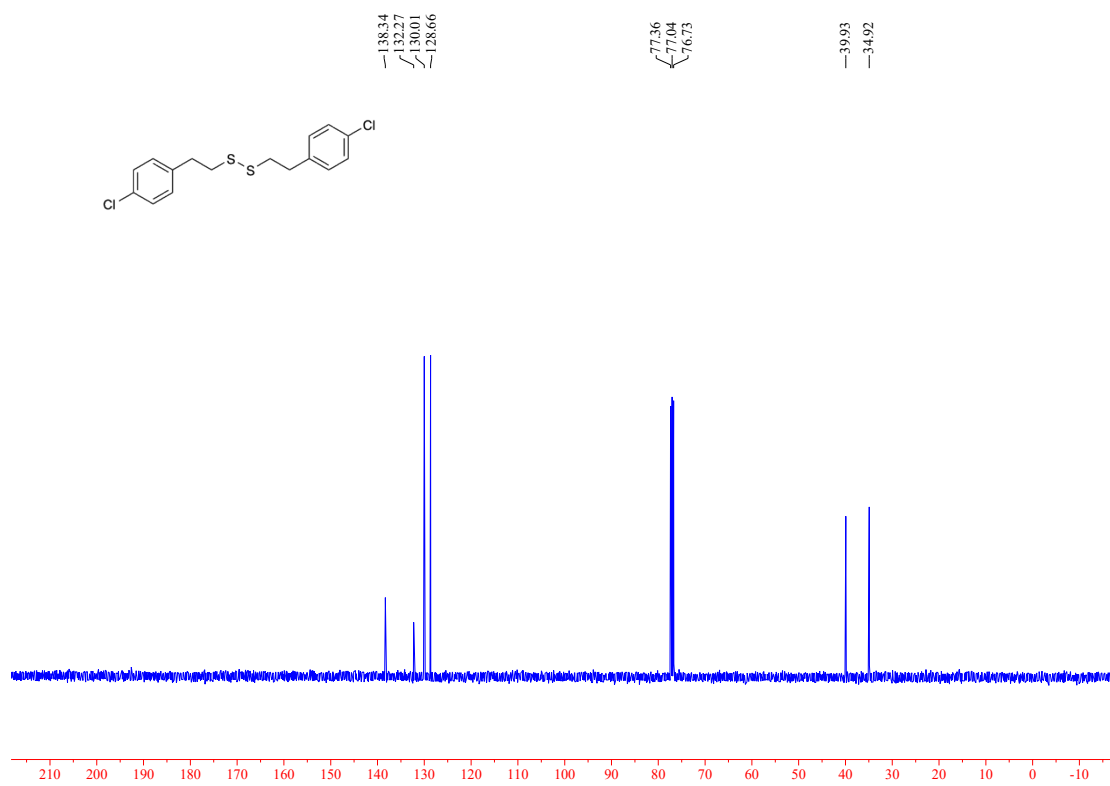
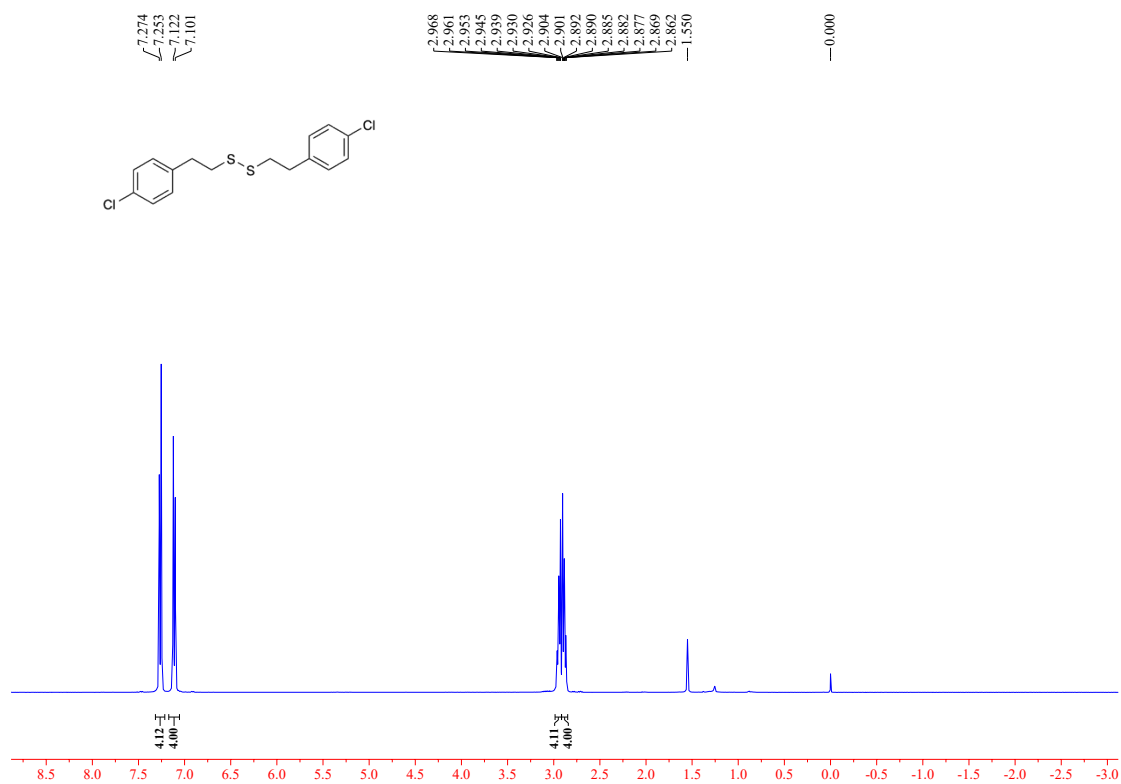
# 1,2-diphenethylsulfane (4a)



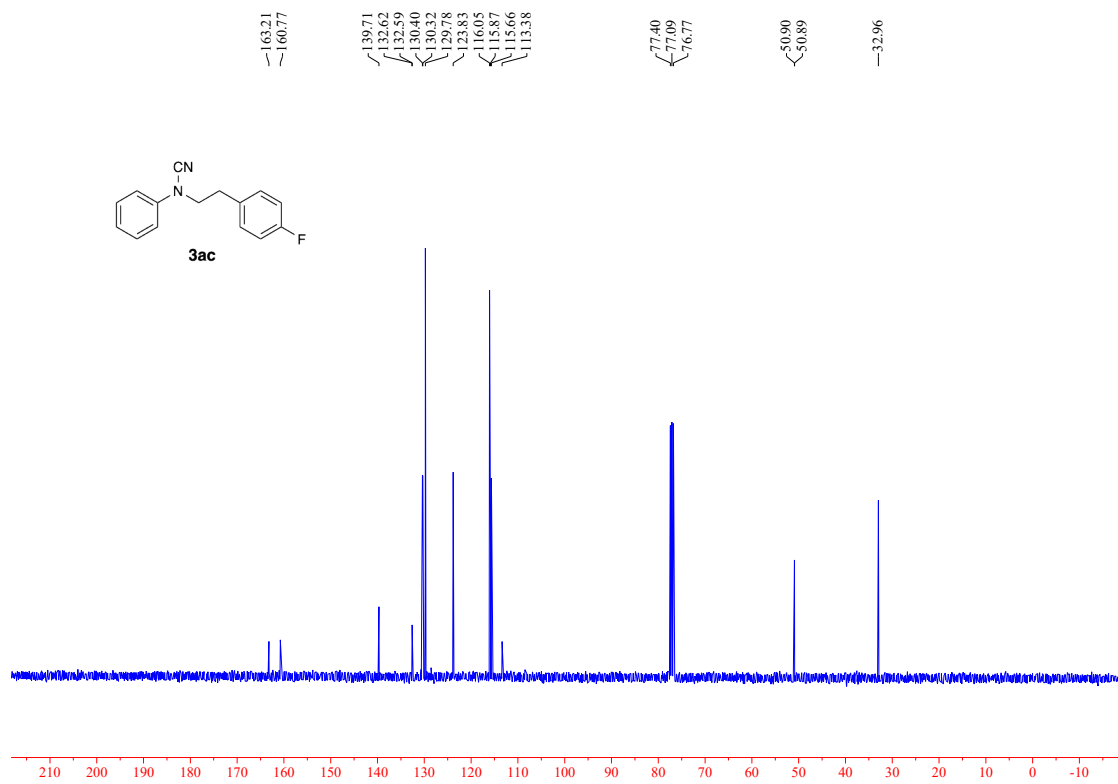
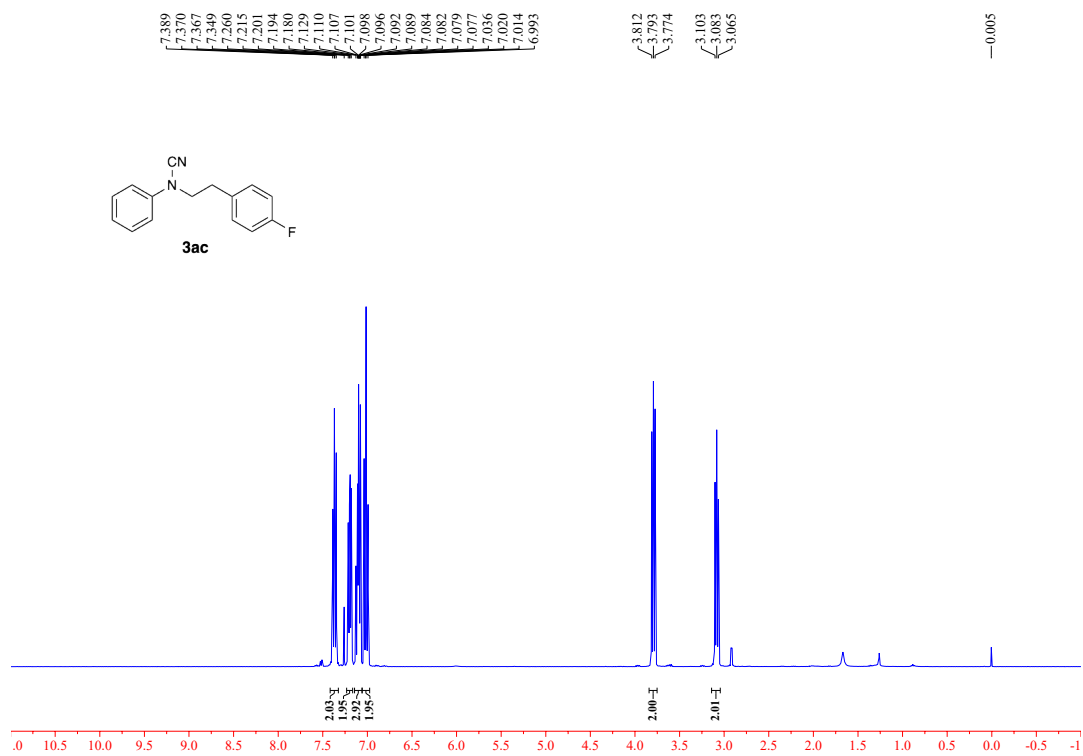
# *N*-(4-chlorophenethyl)-*N*-phenylcyanamide (**3ab**)



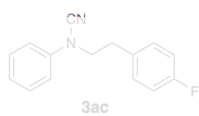
# 1,2-bis(4-chlorophenethyl)disulfane (4b)



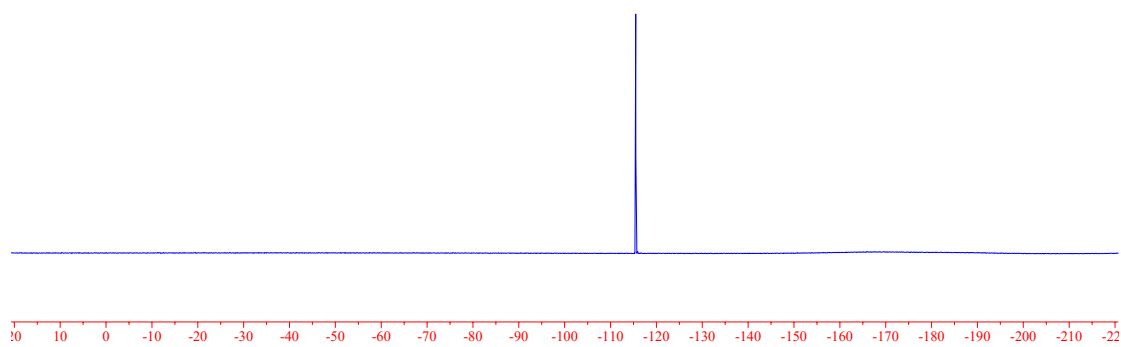
# *N*-(4-fluorophenethyl)-*N*-phenylcyanamide (**3ac**)





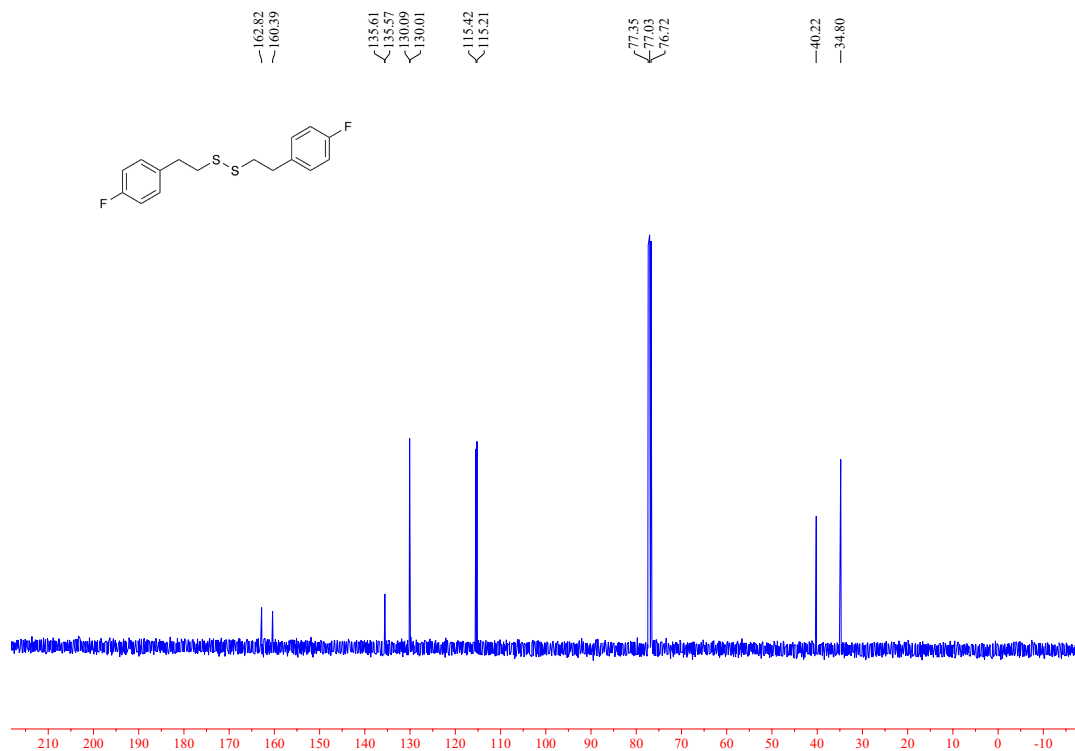
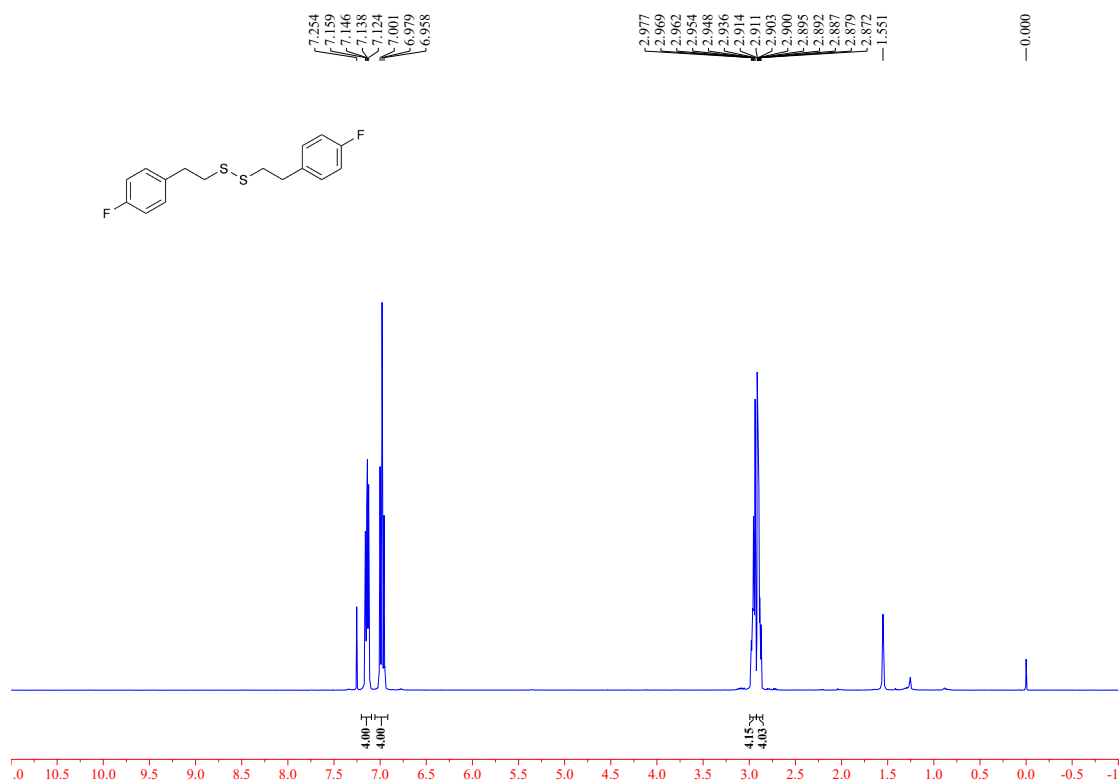


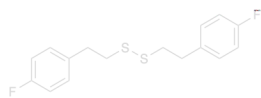
115.45  
115.46  
115.47  
115.48  
115.49  
115.50  
115.51  
115.52



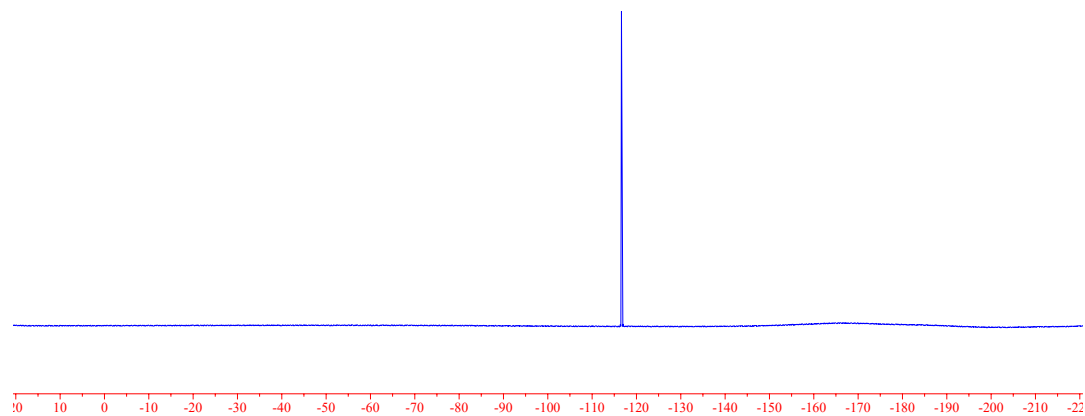
# 1,2-bis(4-fluorophenethyl)disulfane

(4c)

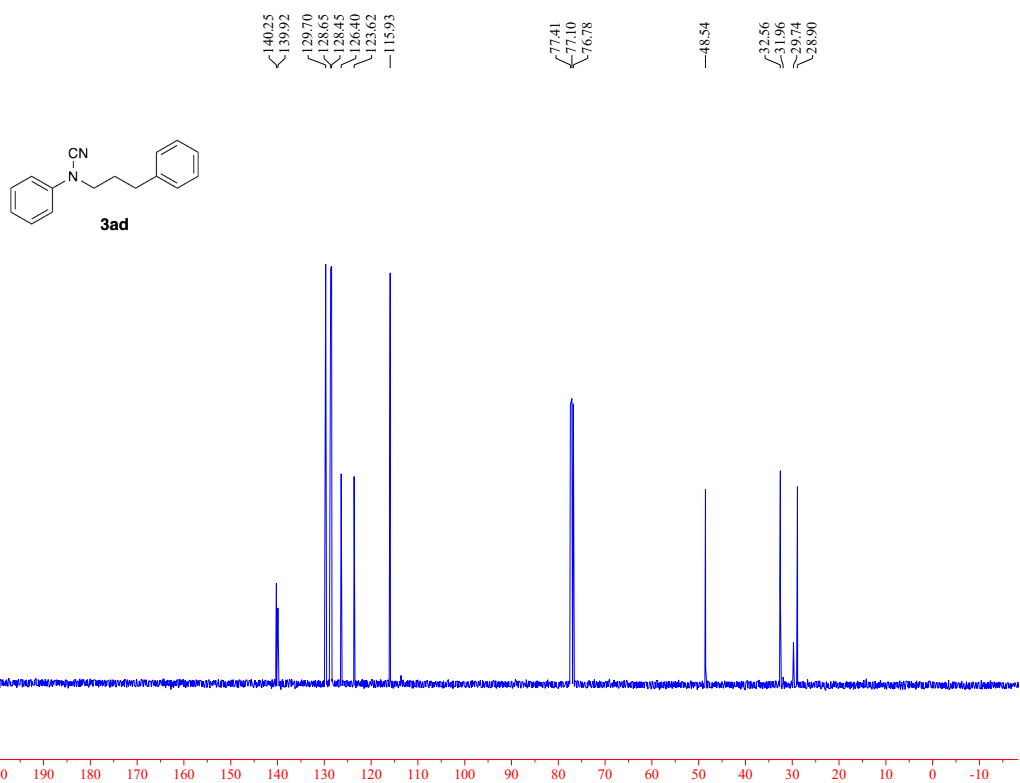
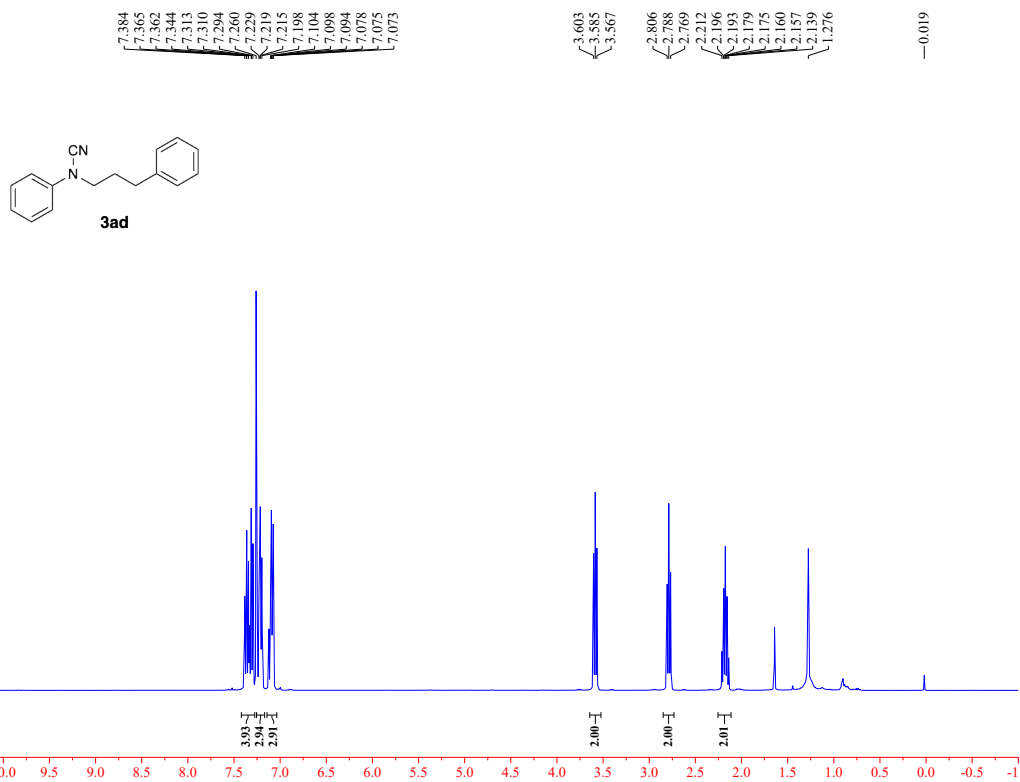




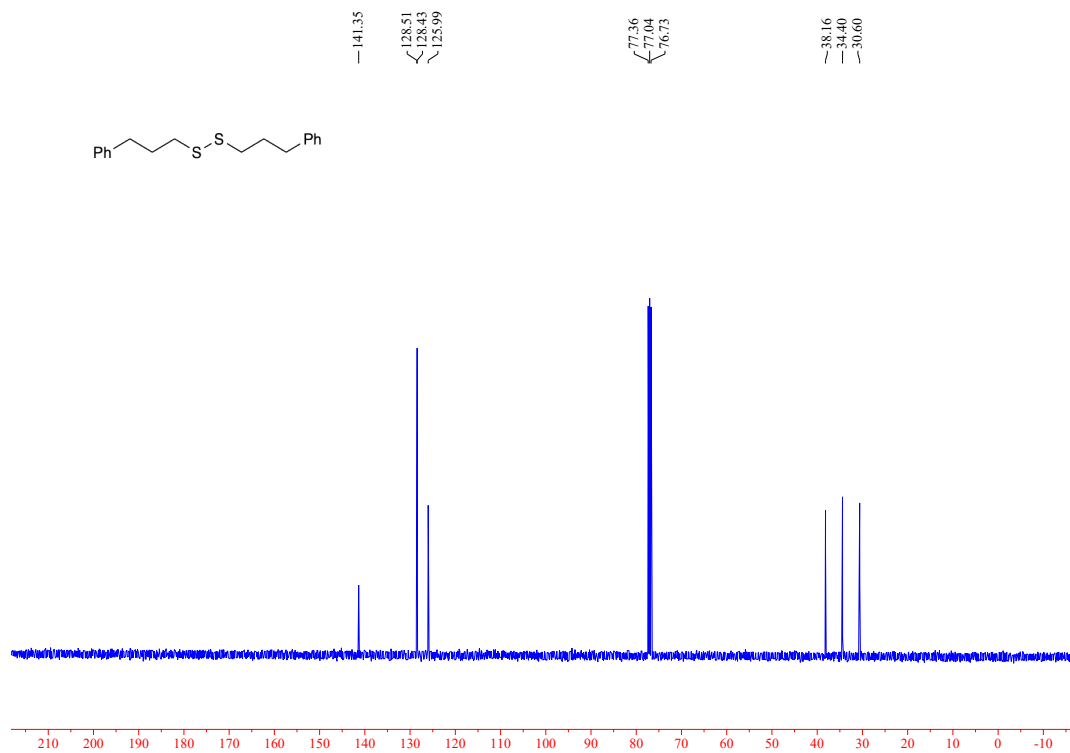
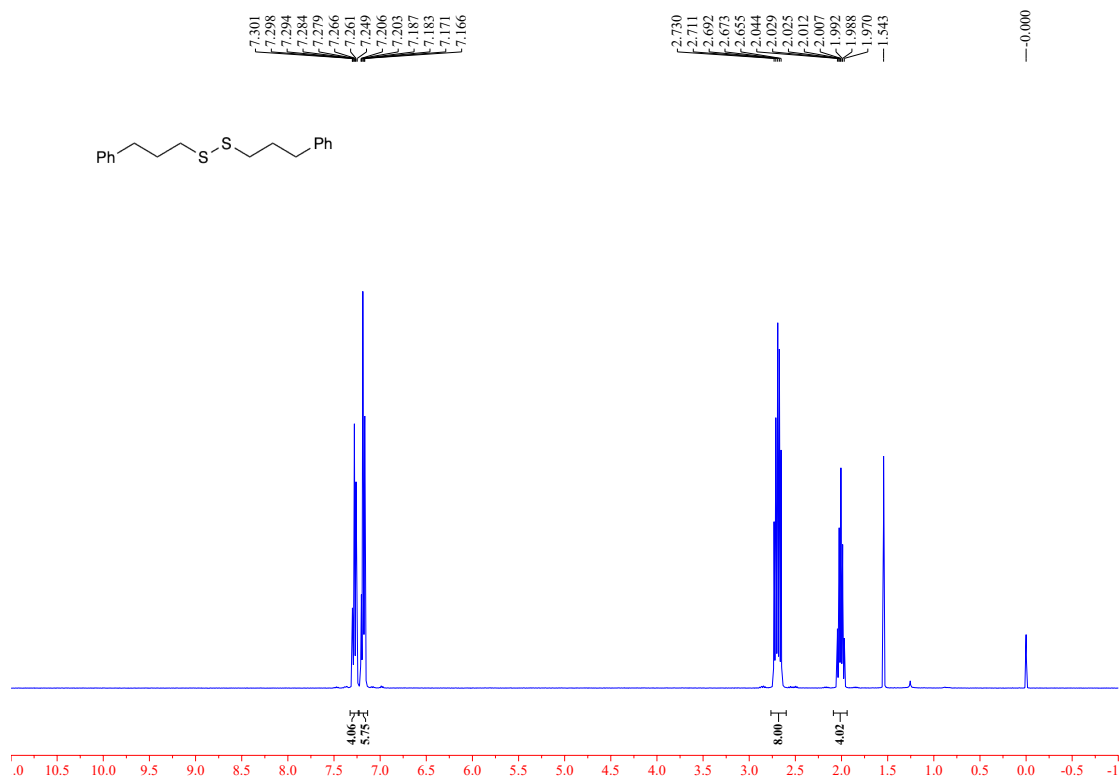
116.59  
116.60  
116.61  
116.62  
116.64  
116.65  
116.66



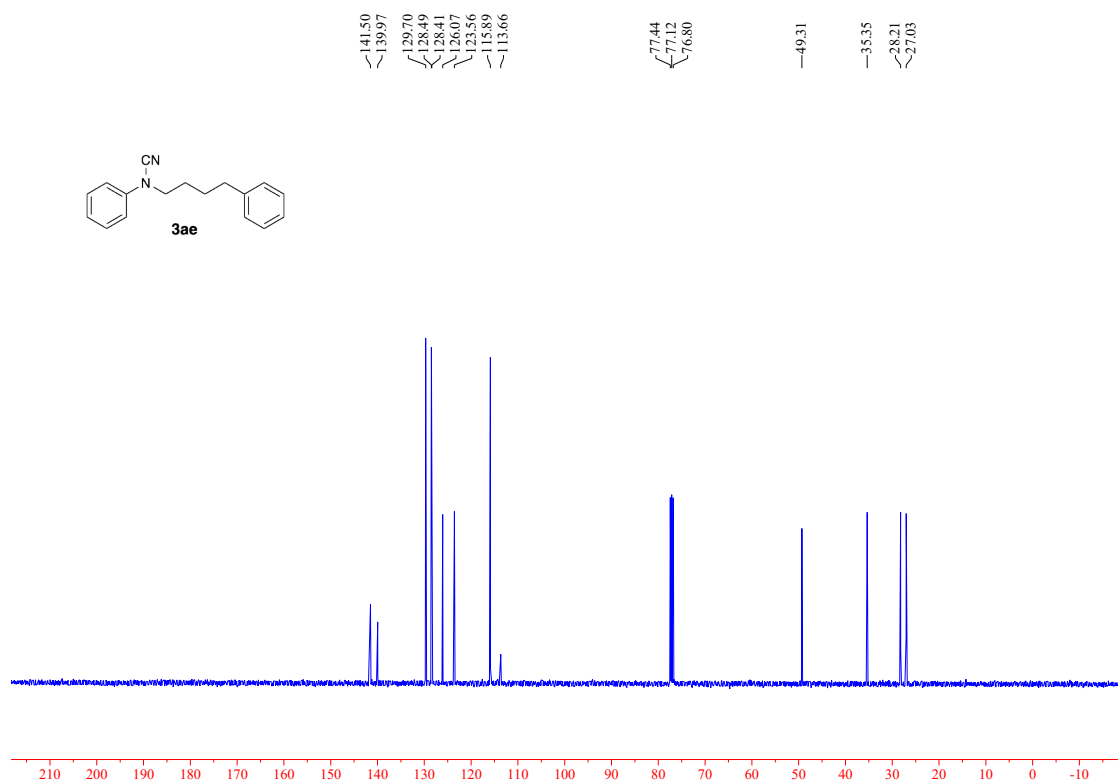
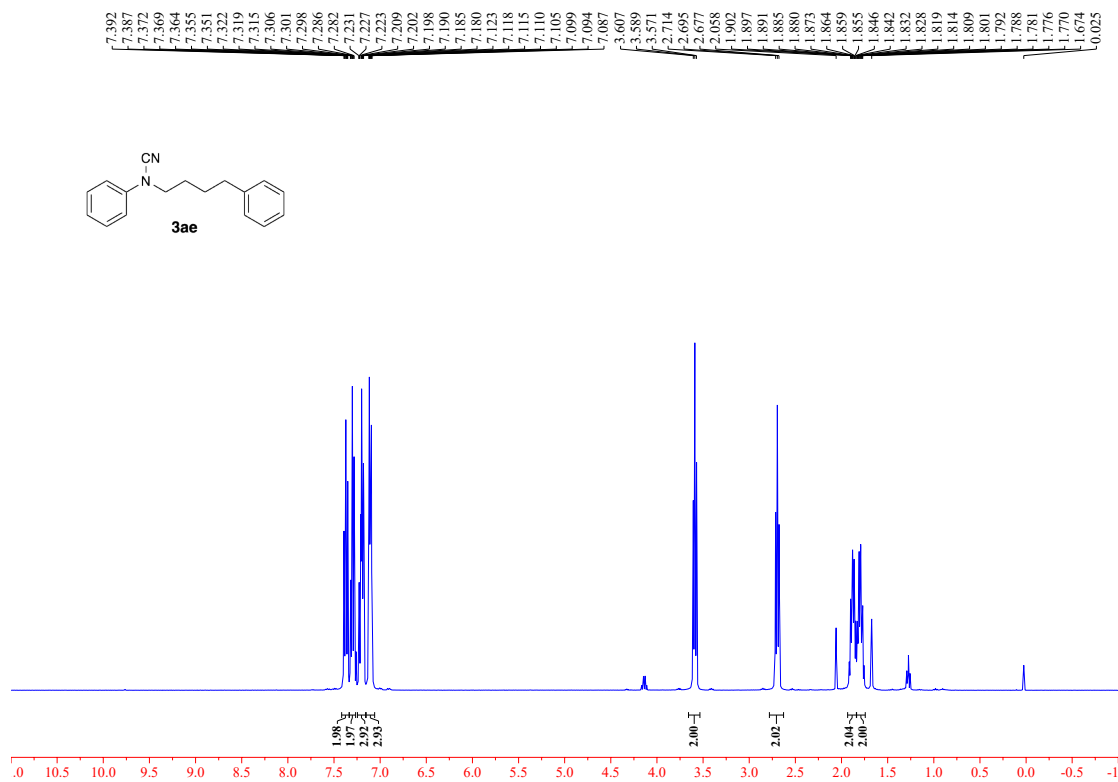
# *N*-phenyl-*N*-(3-phenylpropyl)cyanamide (**3ad**)



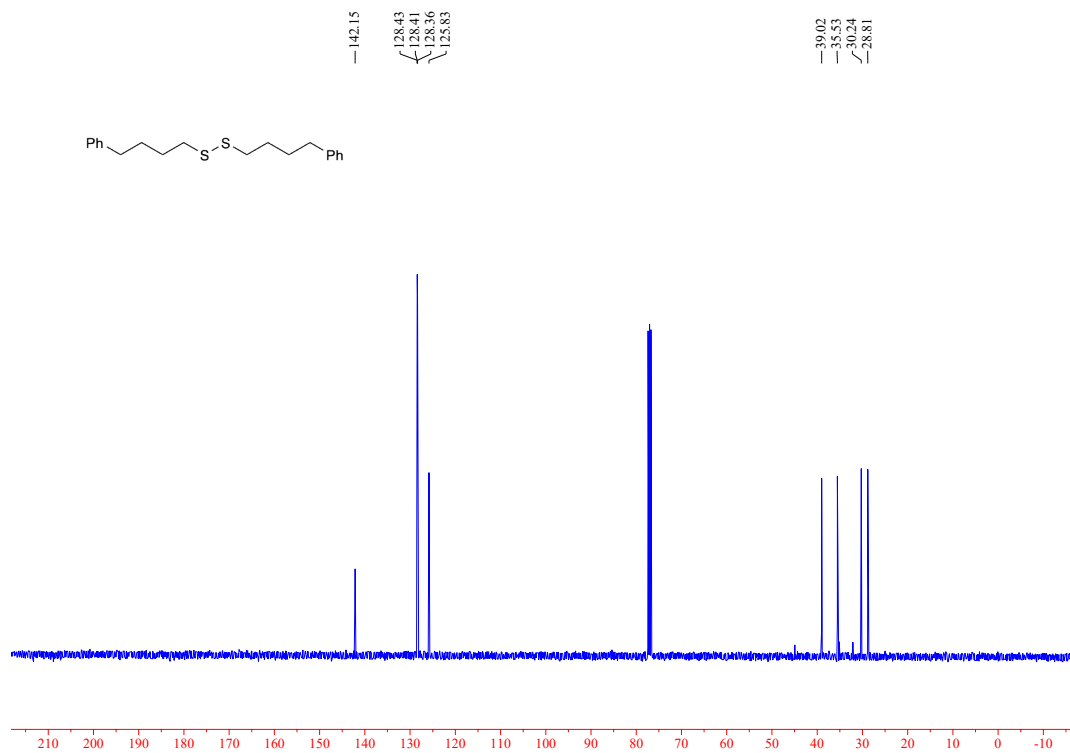
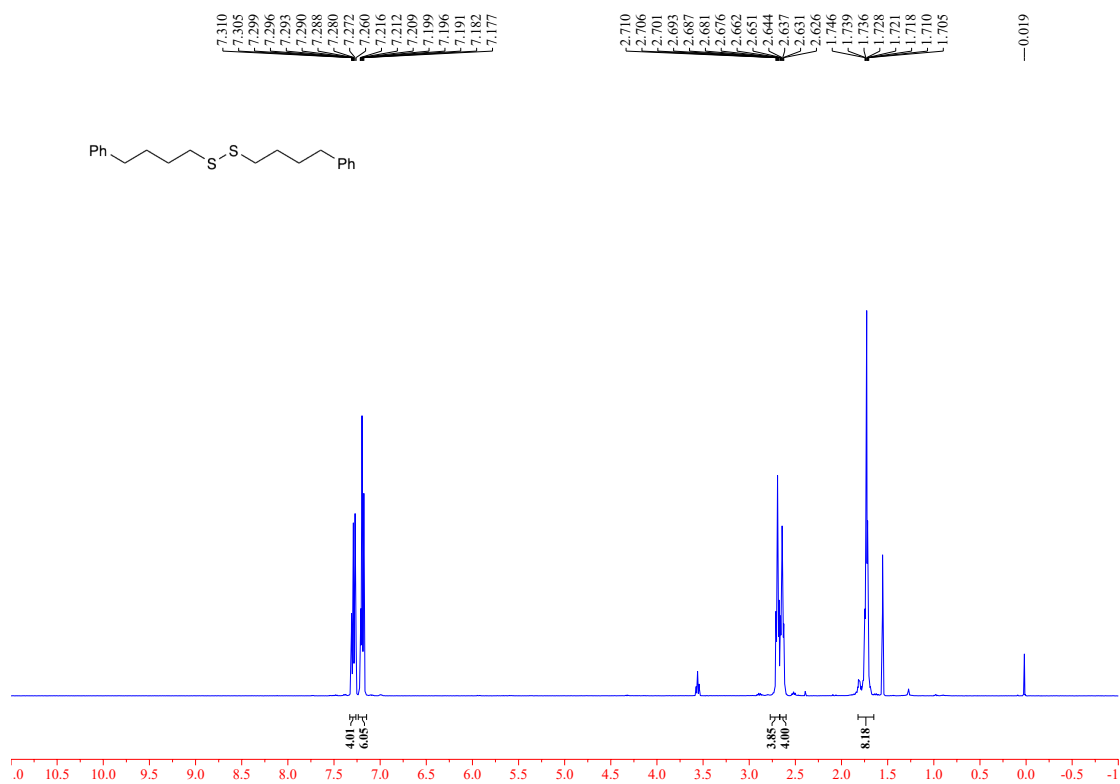
# 1,2-bis(3-phenylpropyl)disulfane (4d)



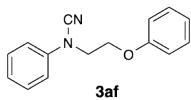
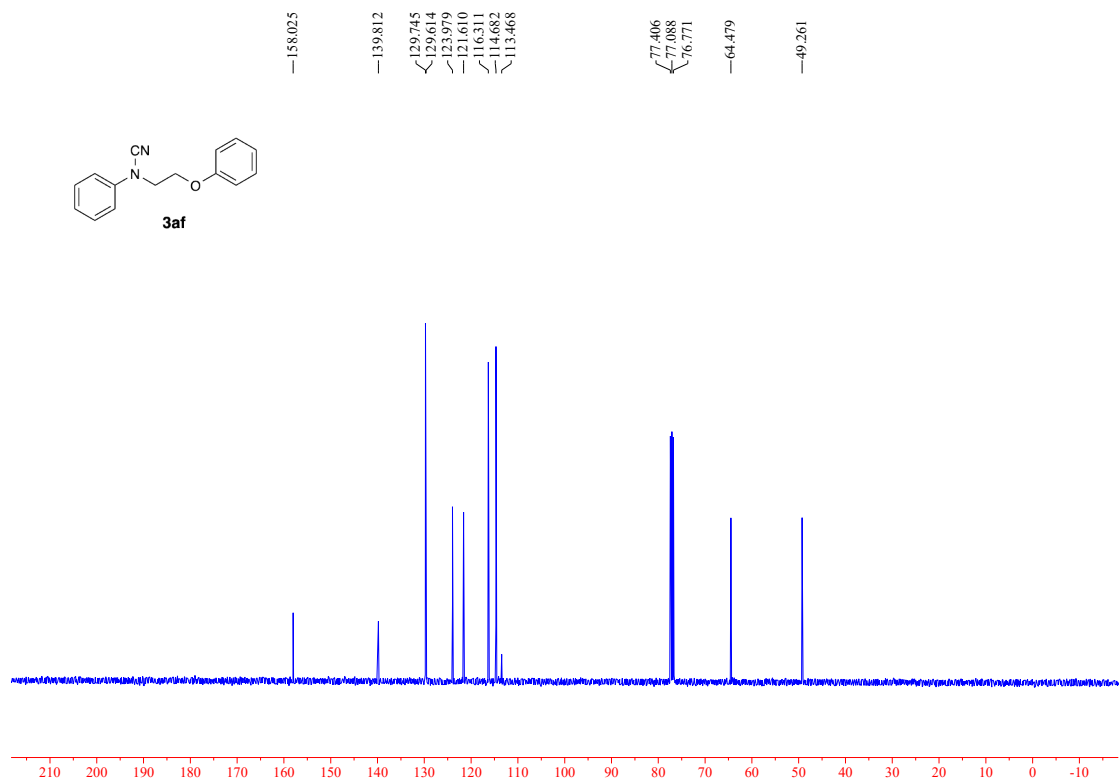
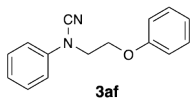
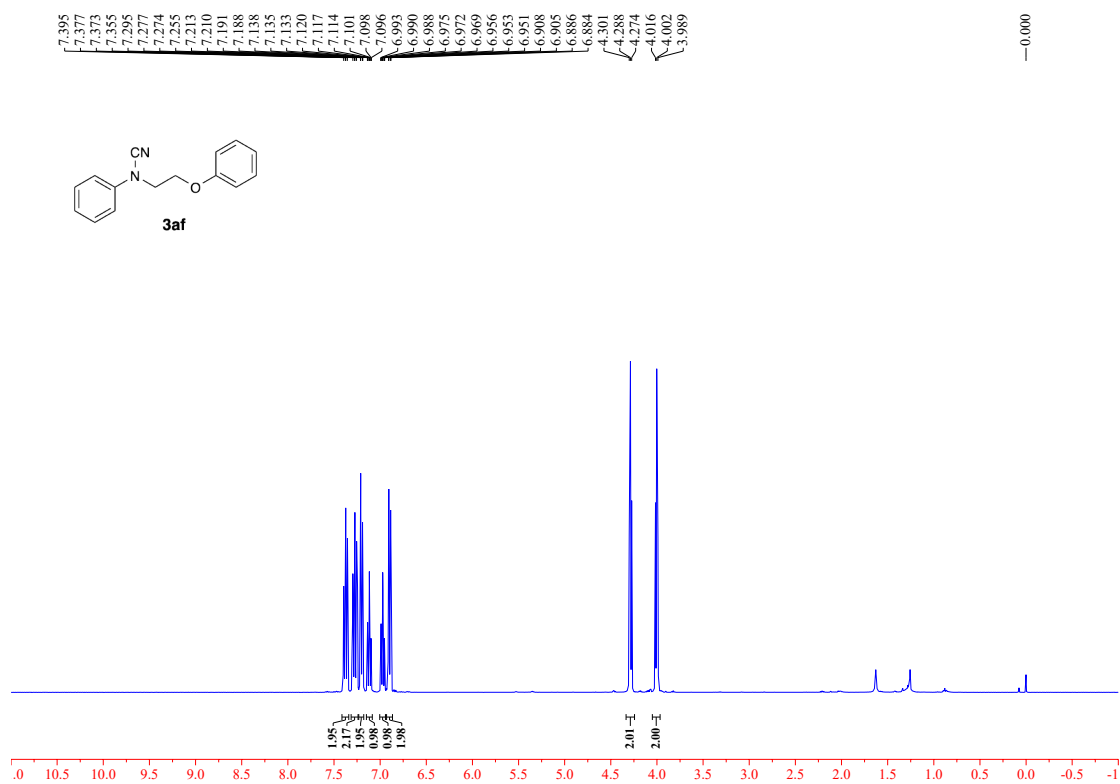
# *N*-phenyl-*N*-(4-phenylbutyl)cyanamide (3ae)



# 1,2-bis(4-phenylbutyl)disulfane (4e)

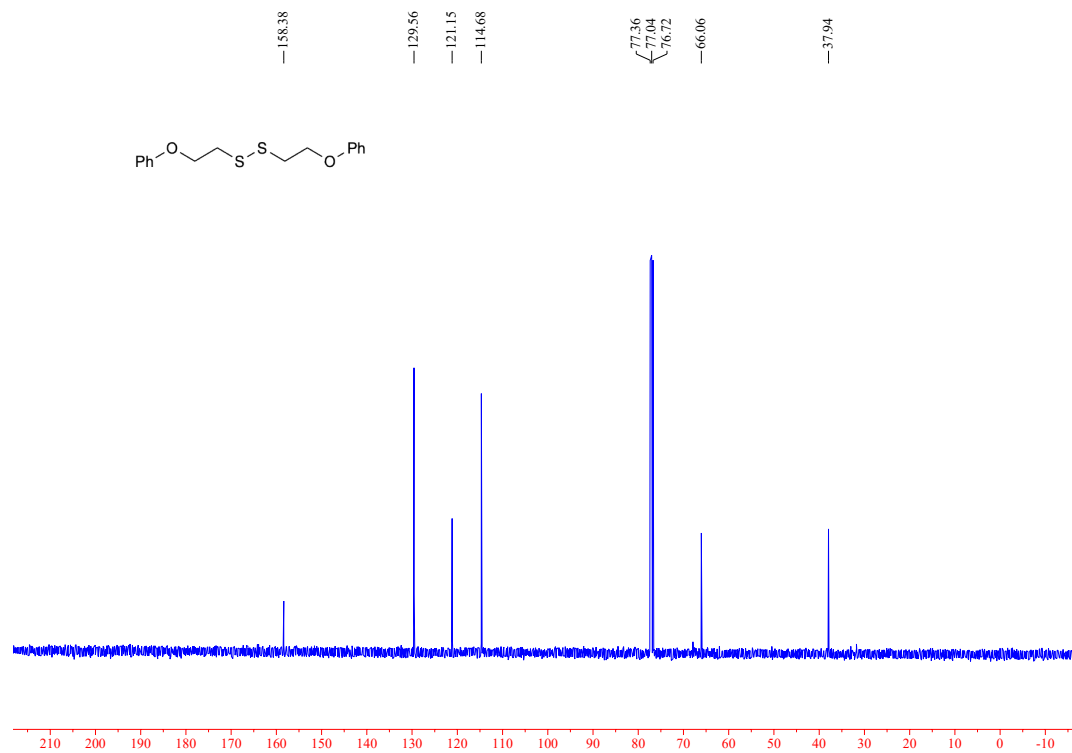
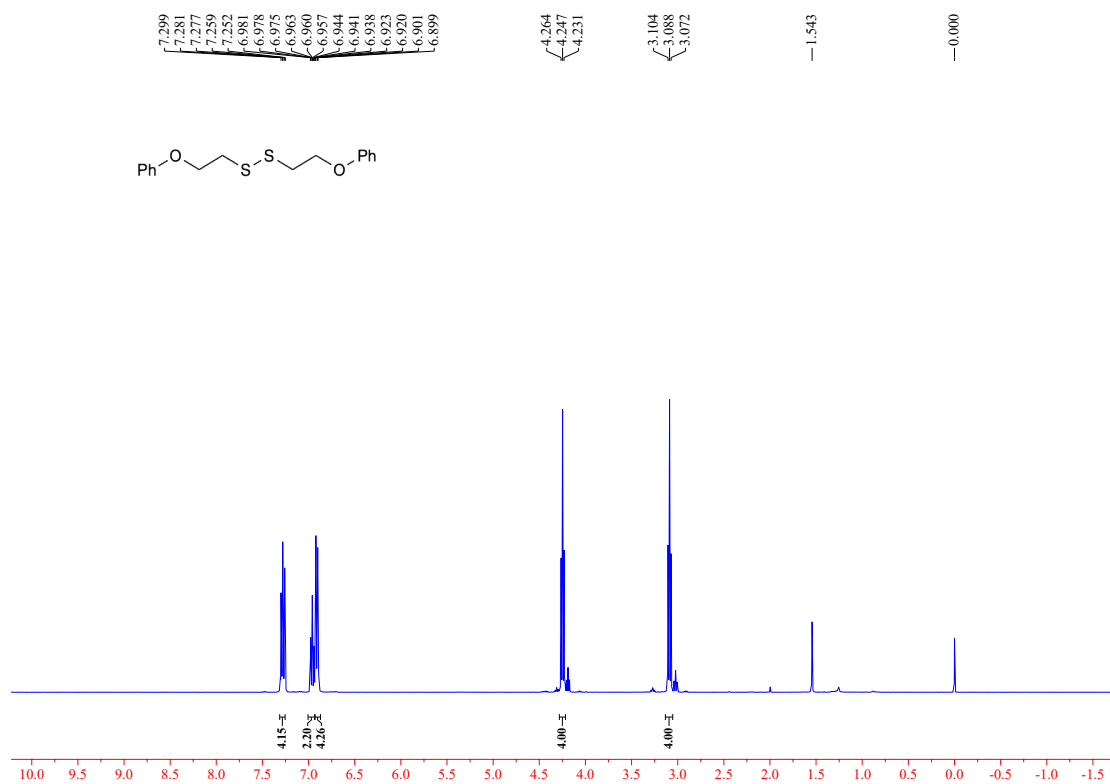


# *N*-(2-phenoxyethyl)-*N*-phenylcyanamide (3af)

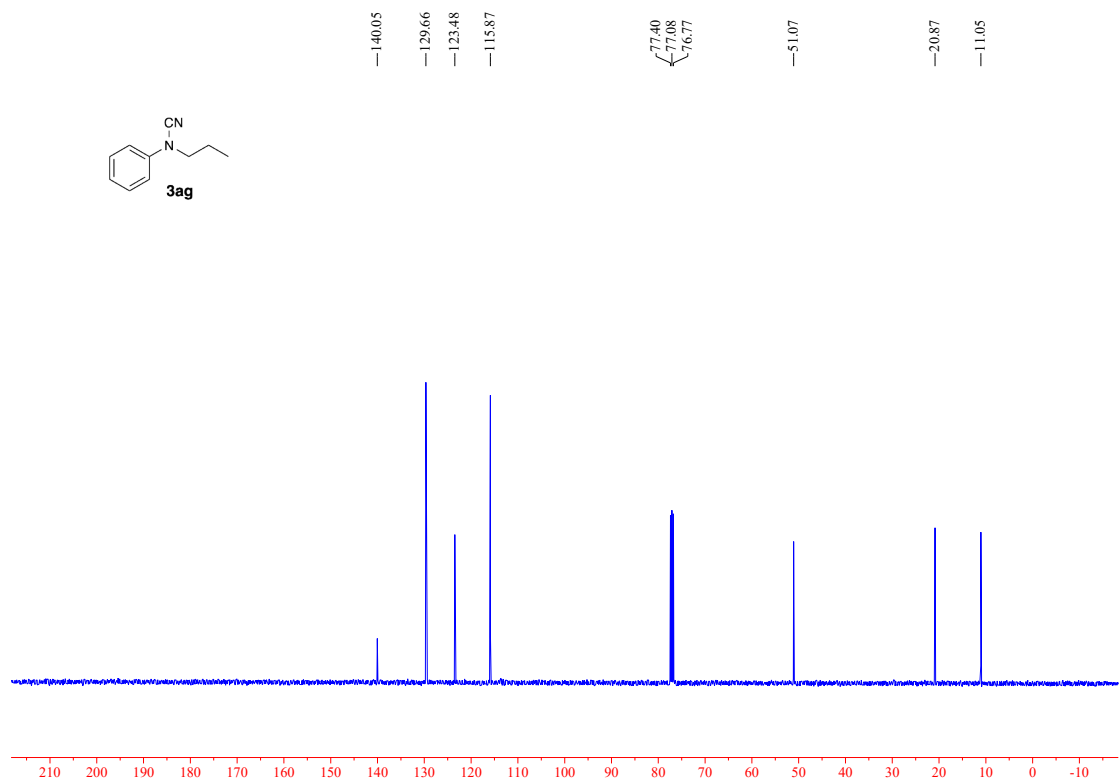
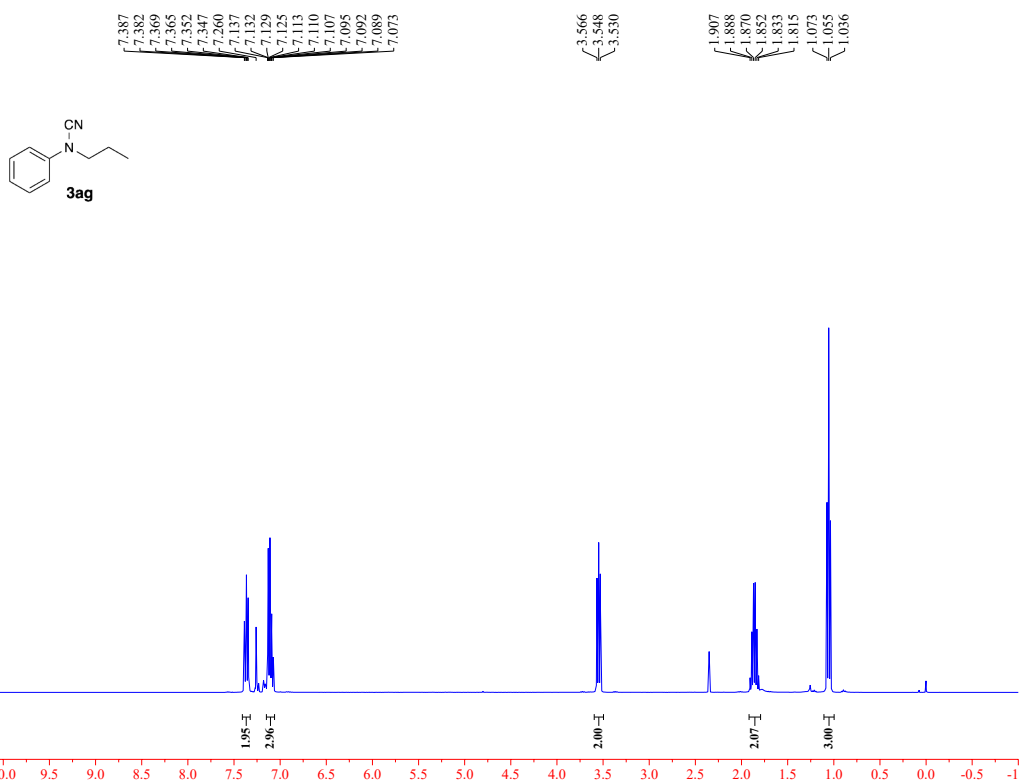




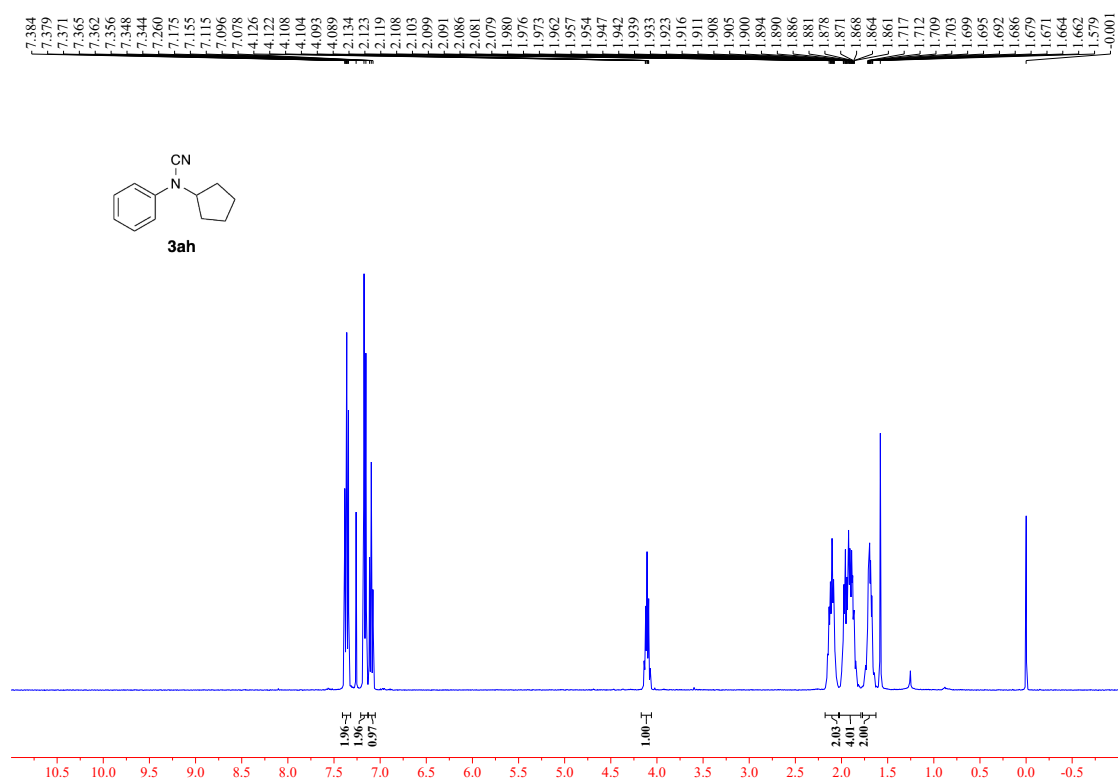
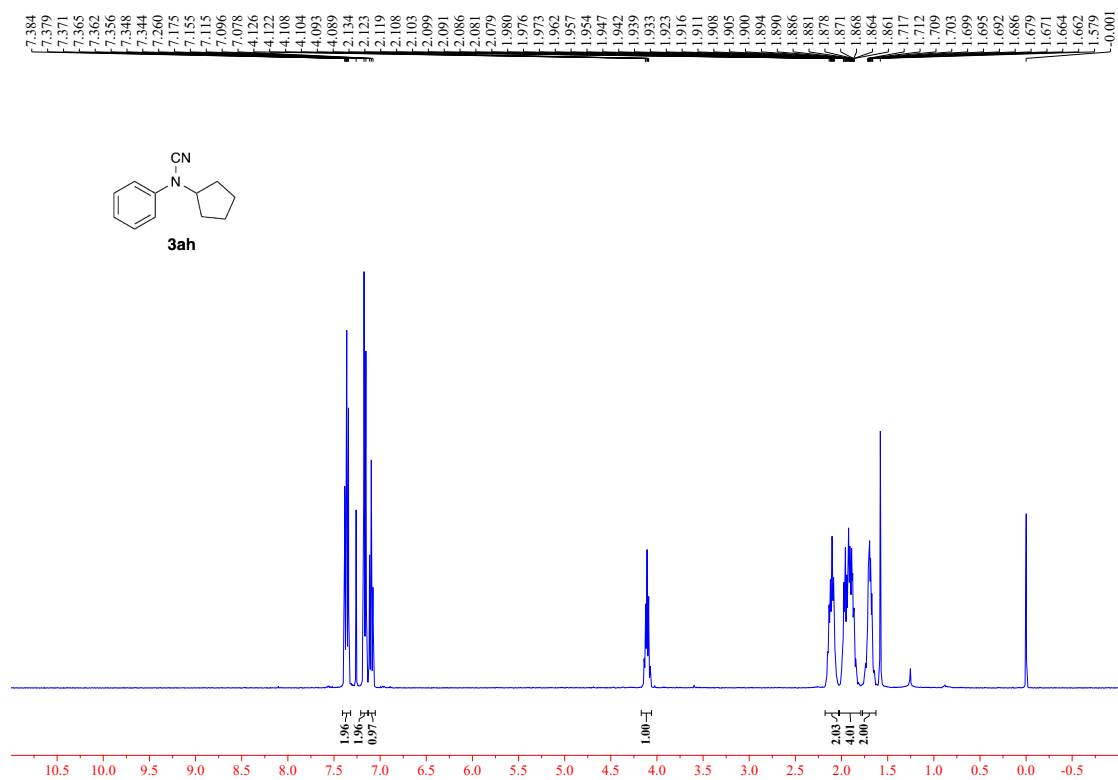
# 1,2-bis(2-phenoxyethyl)disulfane (4f)



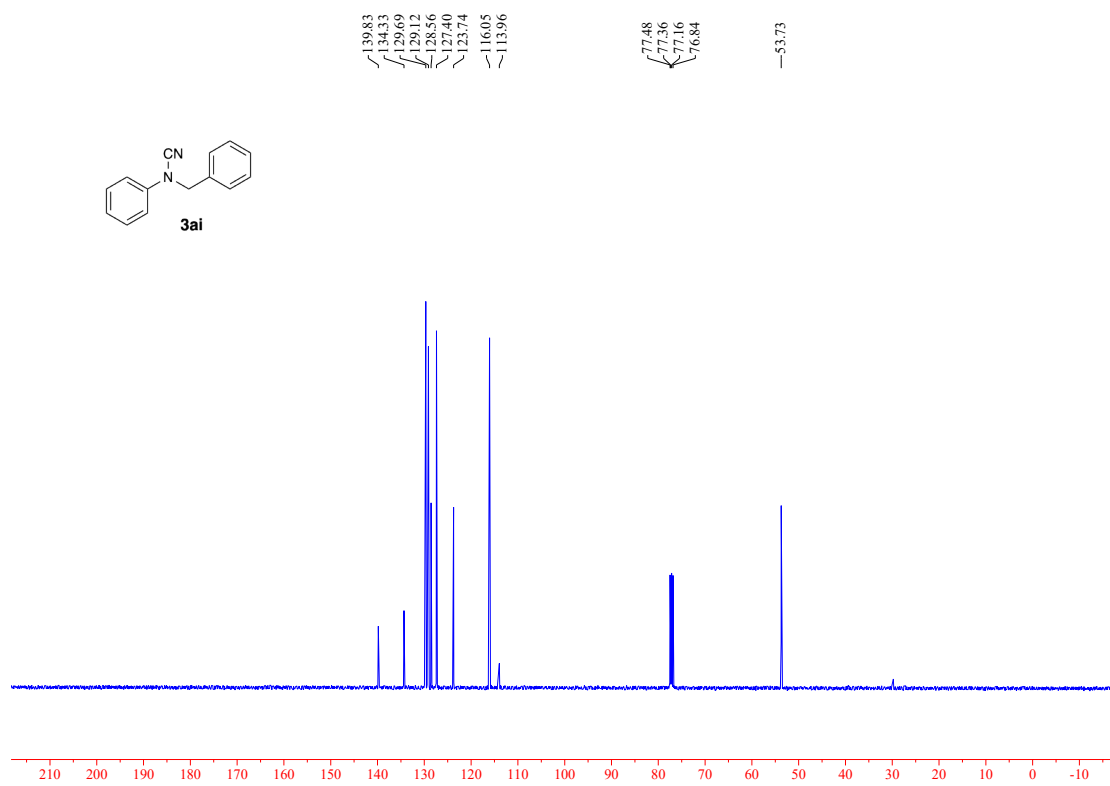
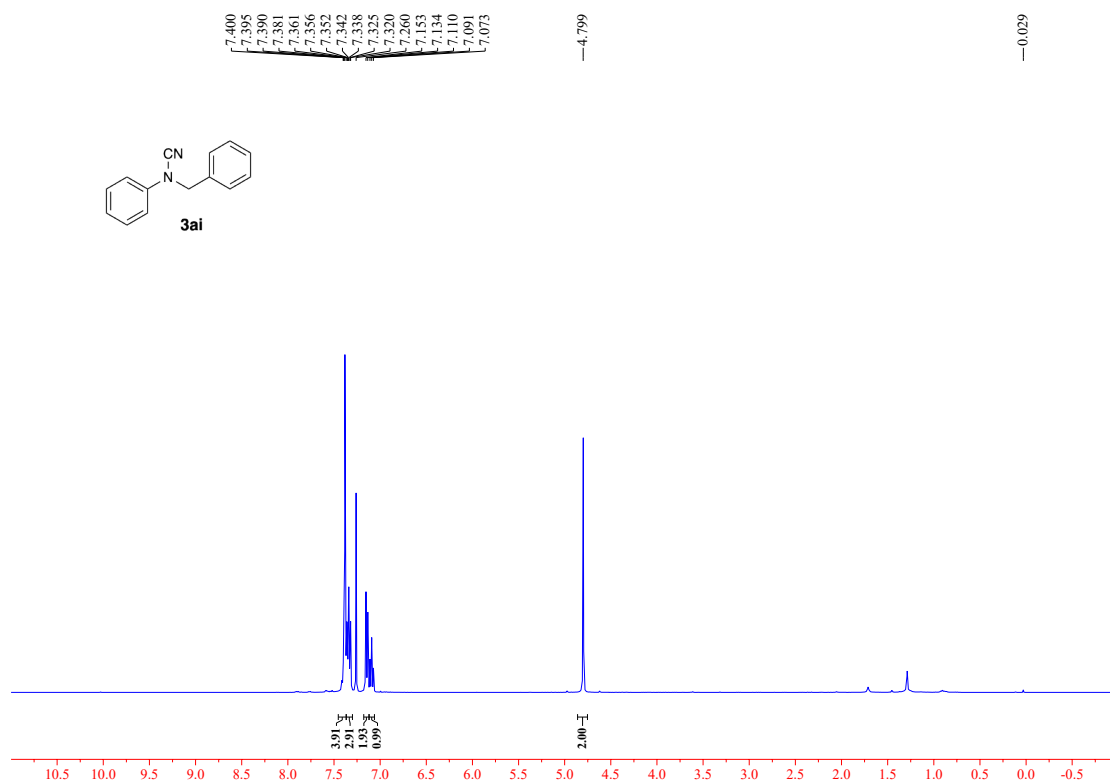
# *N*-phenyl-*N*-propylcyanamide (**3ag**)



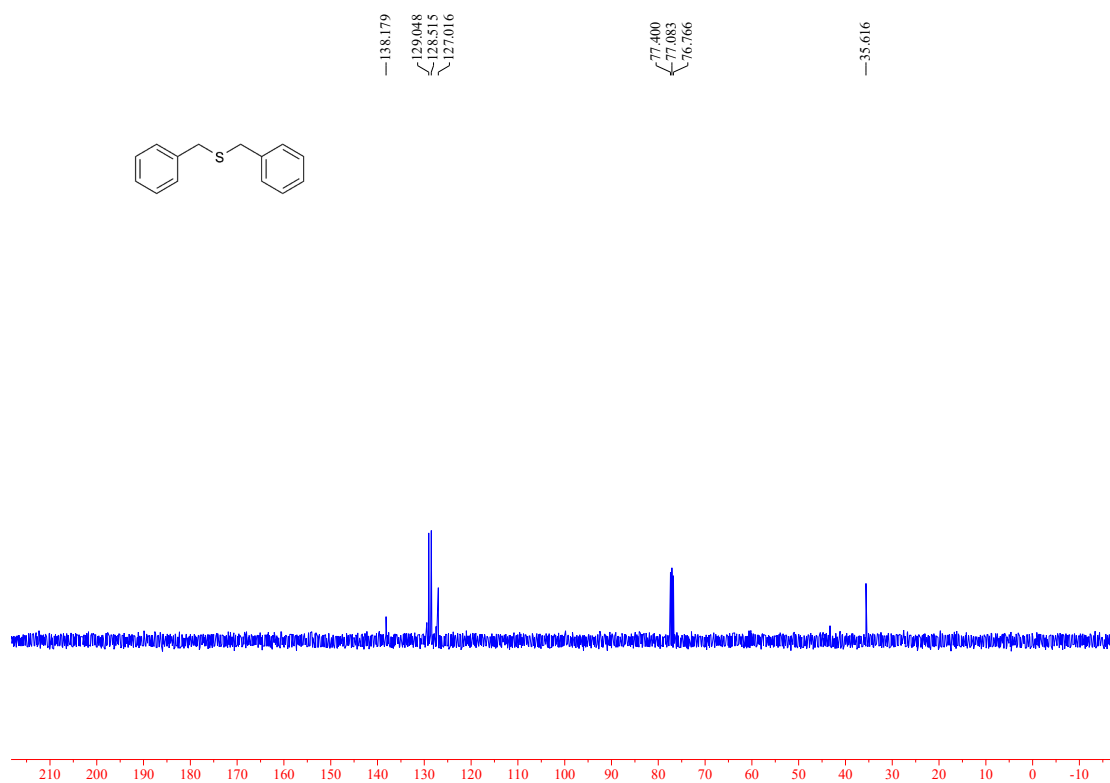
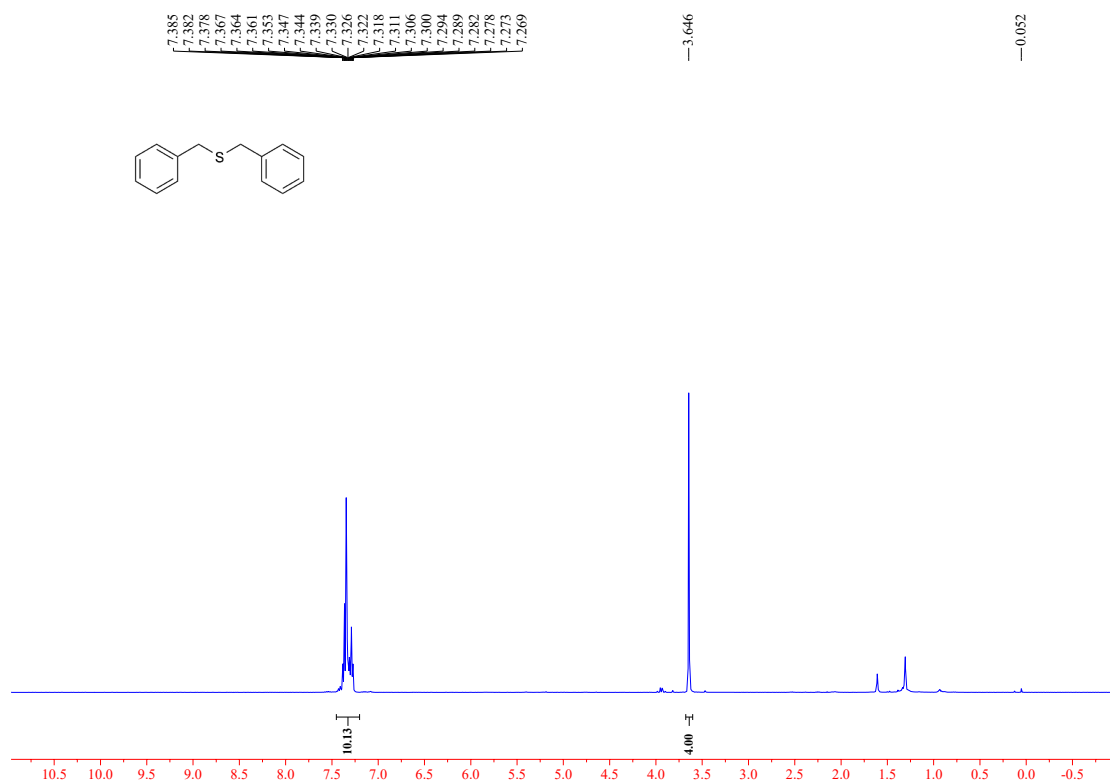
# *N*-cyclopentyl-*N*-phenylcyanamide (3ah)



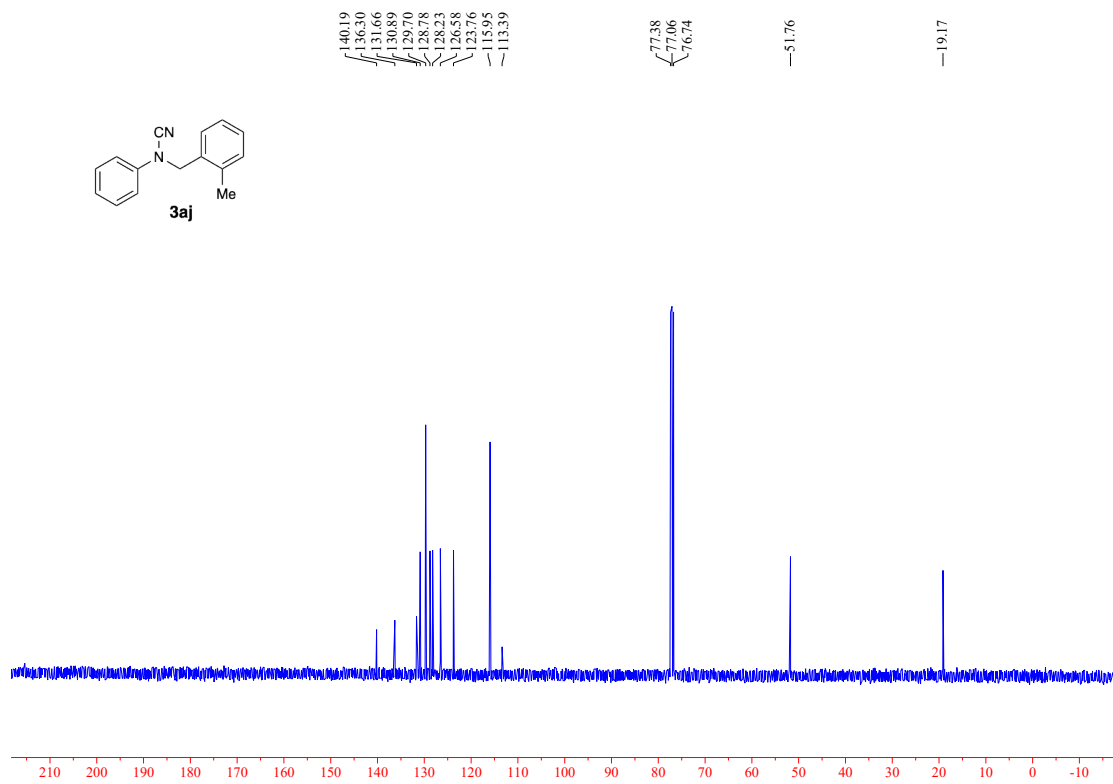
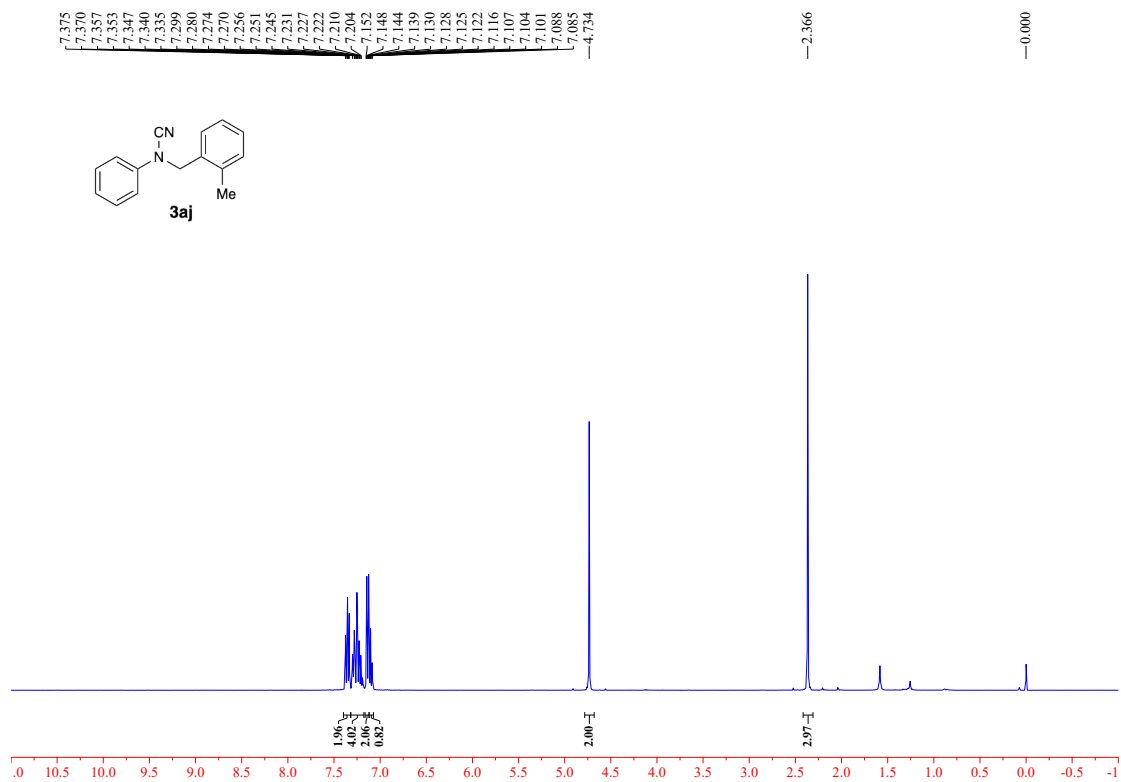
# *N*-benzyl-*N*-phenylcyanamide (**3ai**)



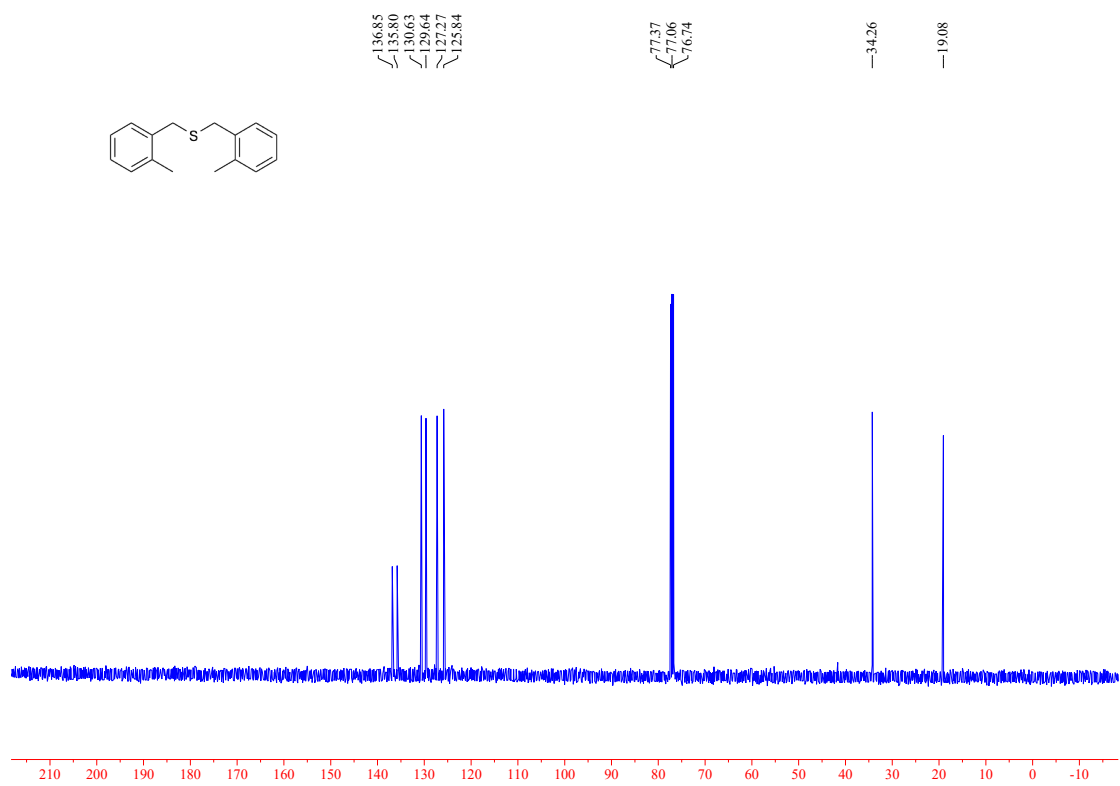
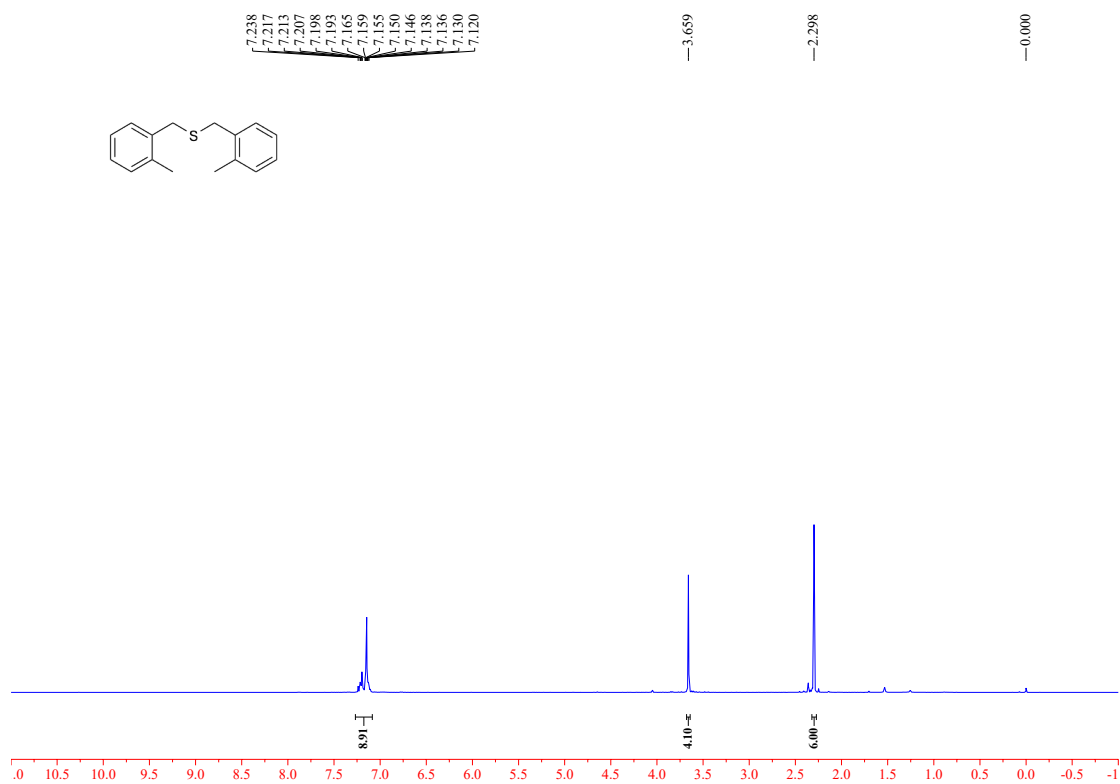
# dibenzylsulfane (5i)



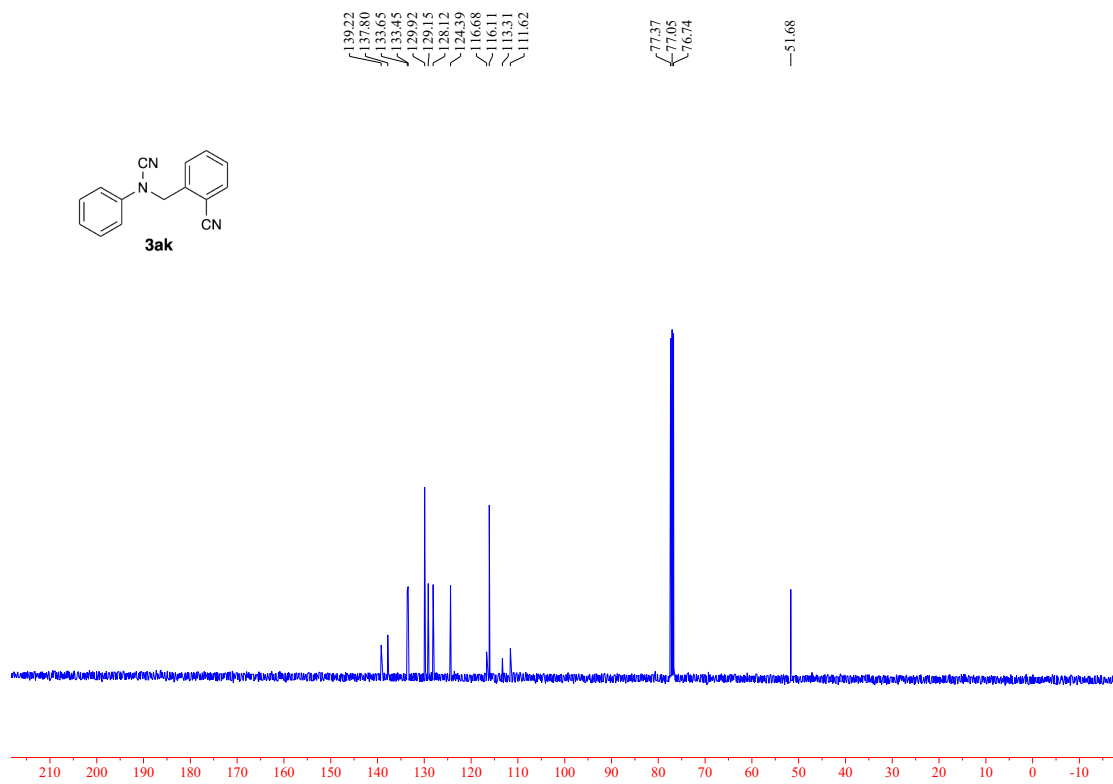
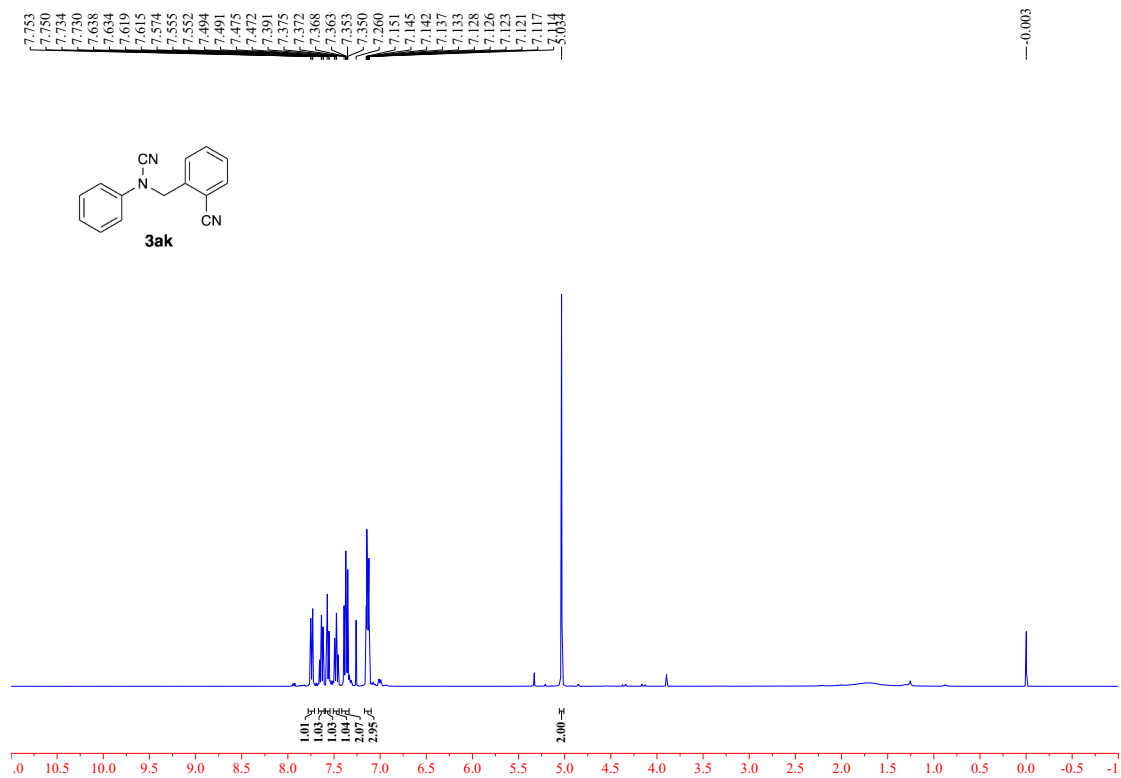
# *N*-(2-methylbenzyl)-*N*-phenylcyanamide (**3aj**)



# 1,2-bis(2-methylbenzyl)sulfane (5j)

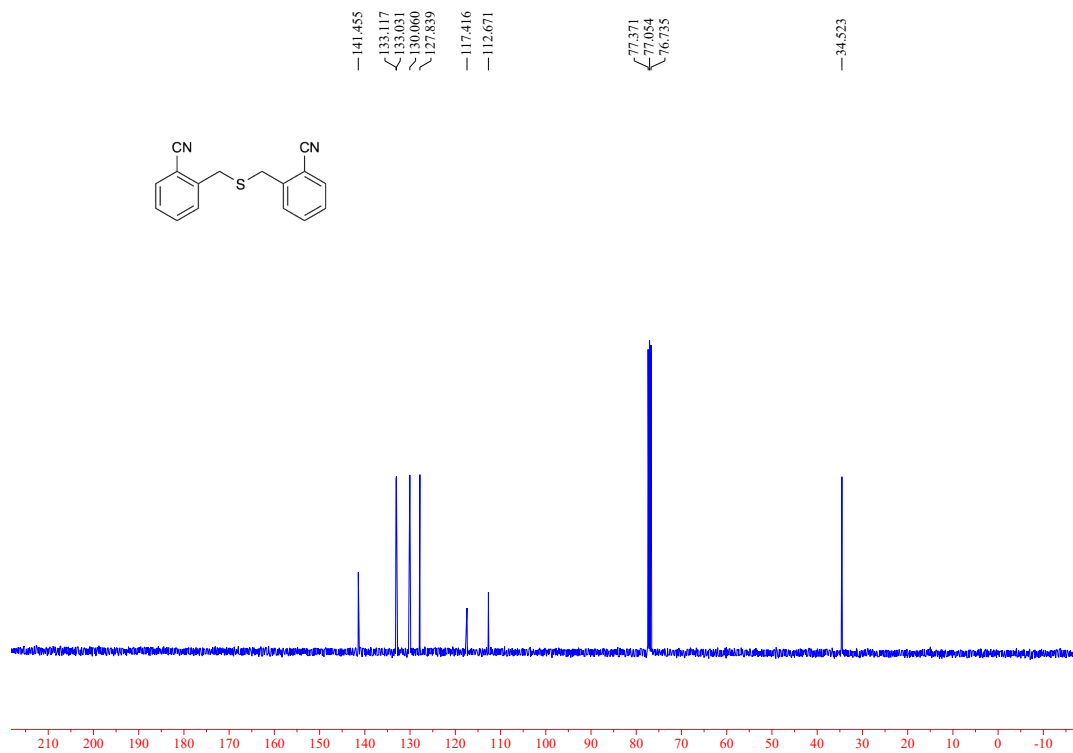
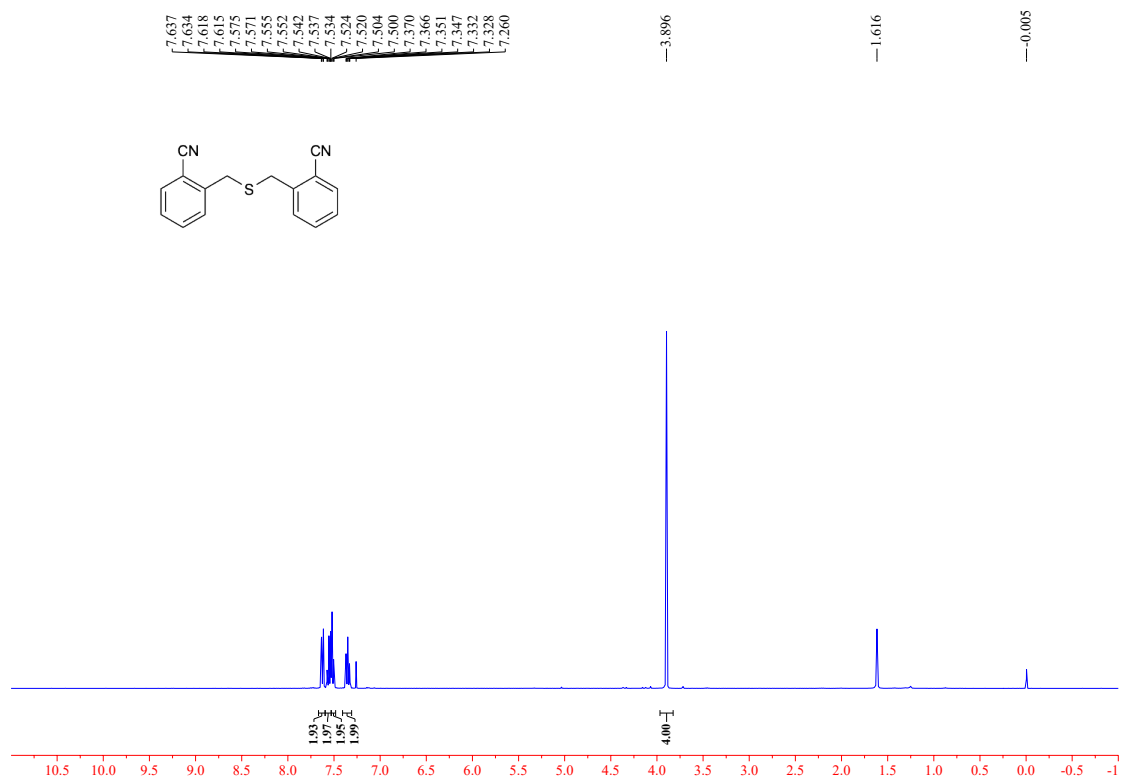


***N*-(2-cyanobenzyl)-*N*-phenylcyanamide (3ak)**

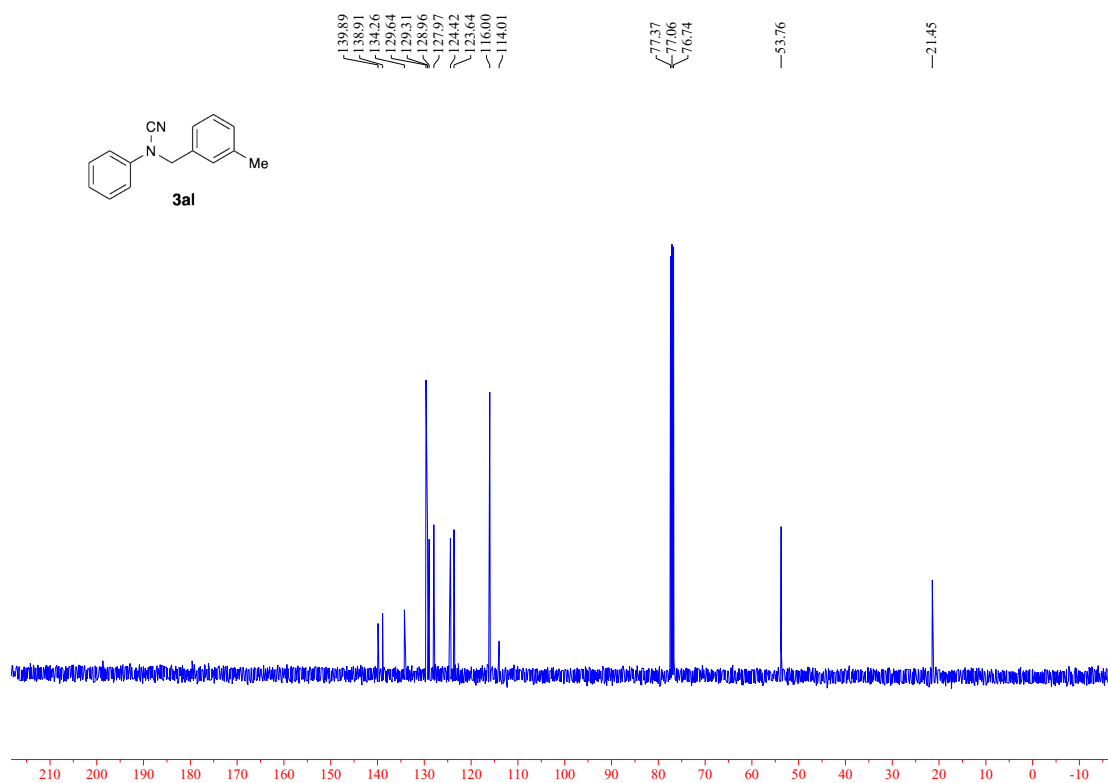
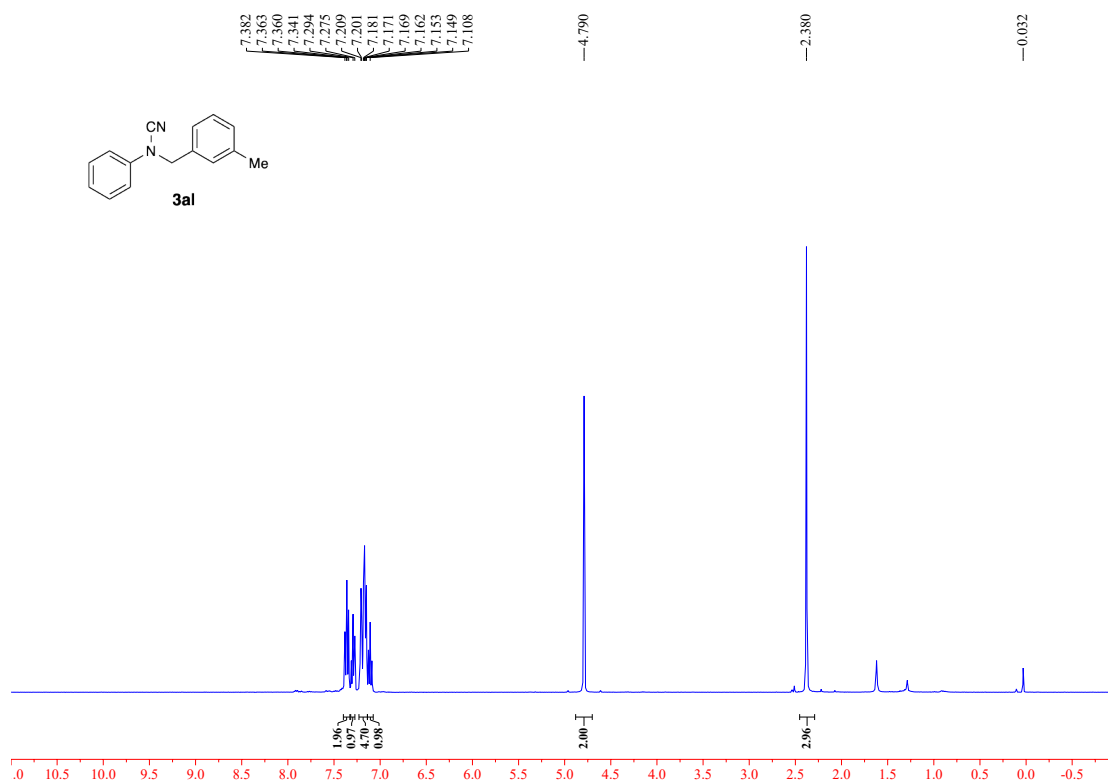




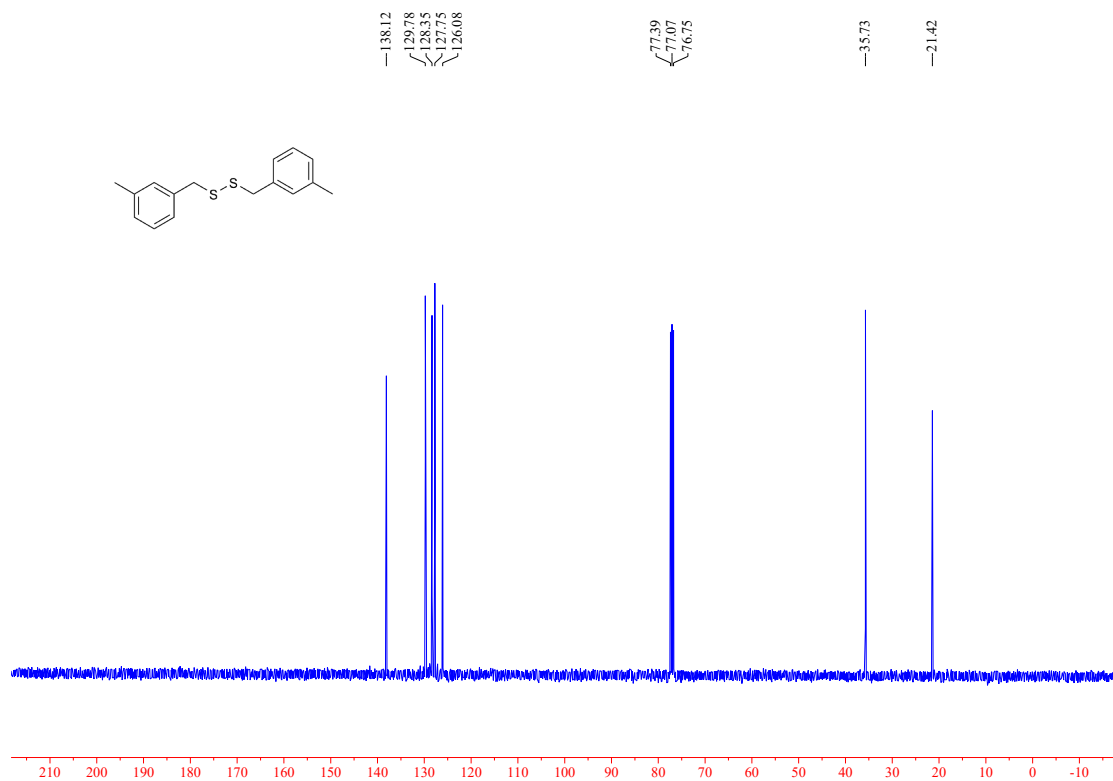
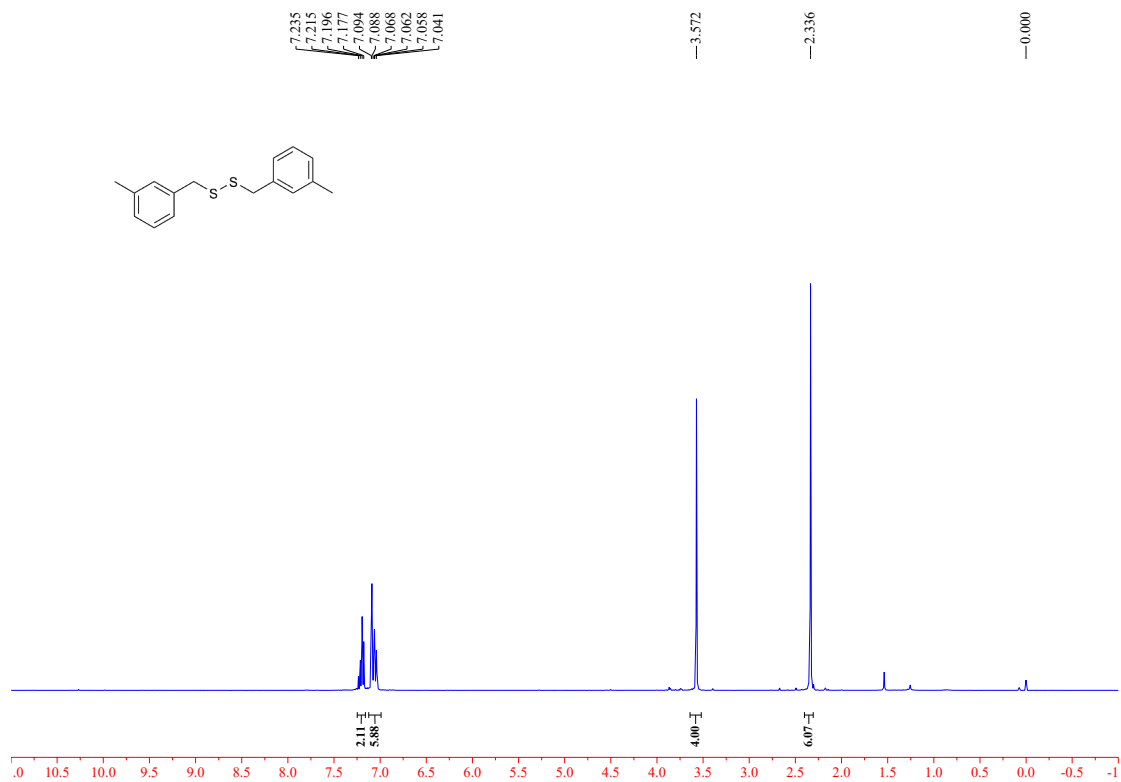
## 2,2'-(thiobis(methylene))dibenzonitrile (5k)



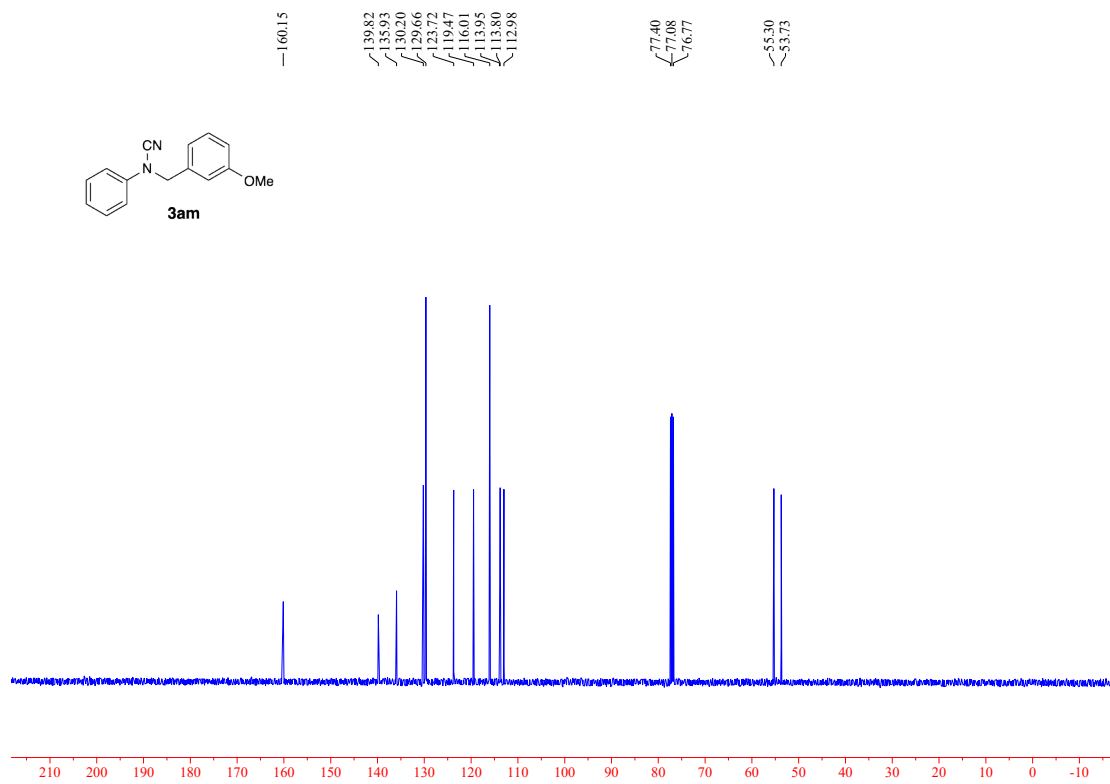
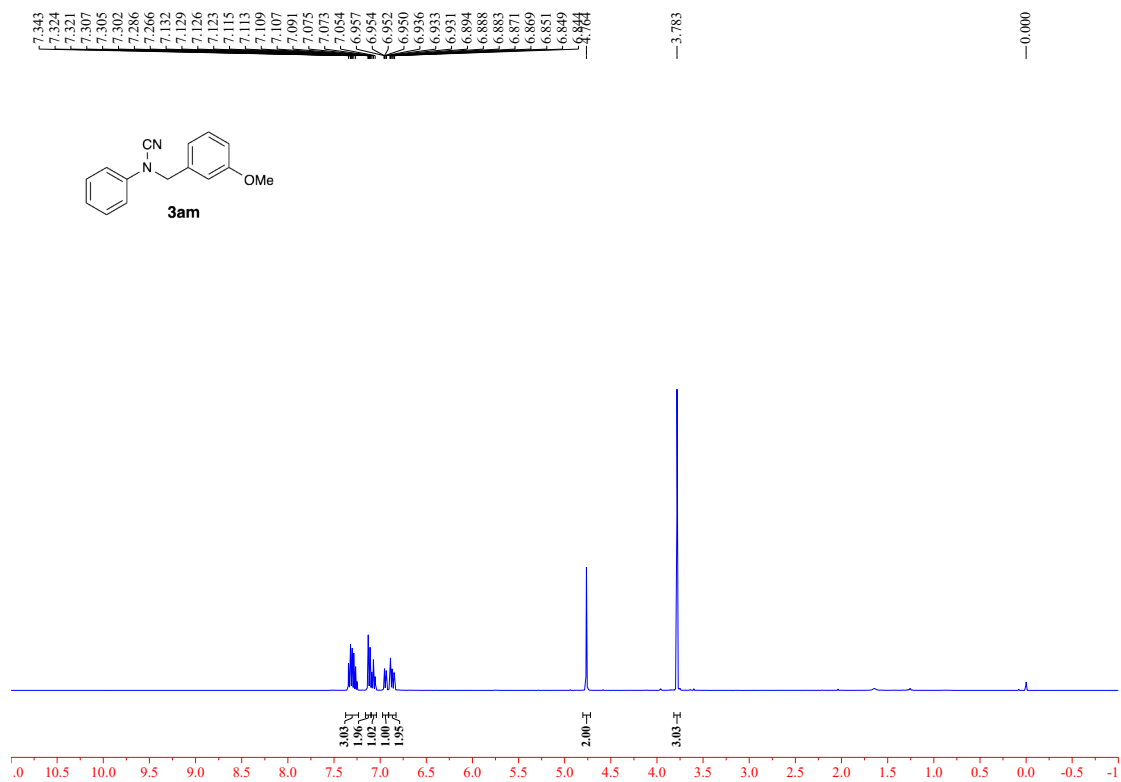
# *N*-(3-methylbenzyl)-*N*-phenylcyanamide (**3al**)



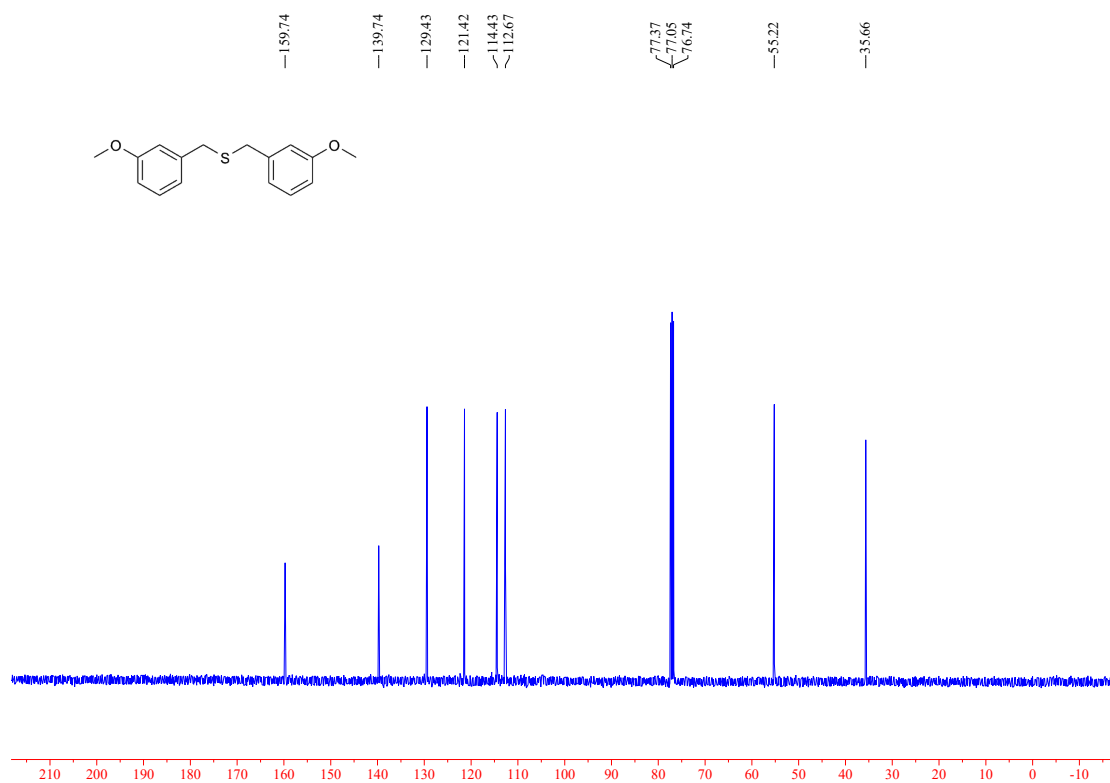
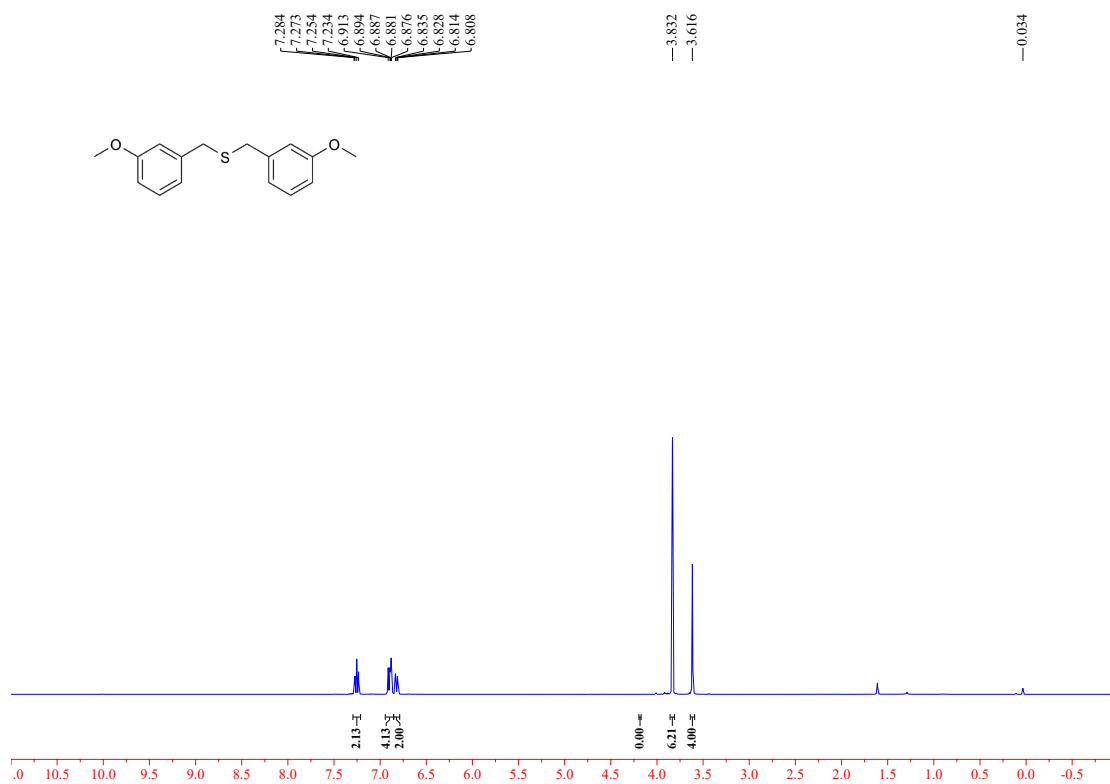
# 1,2-bis(3-methylbenzyl)disulfane (4I)



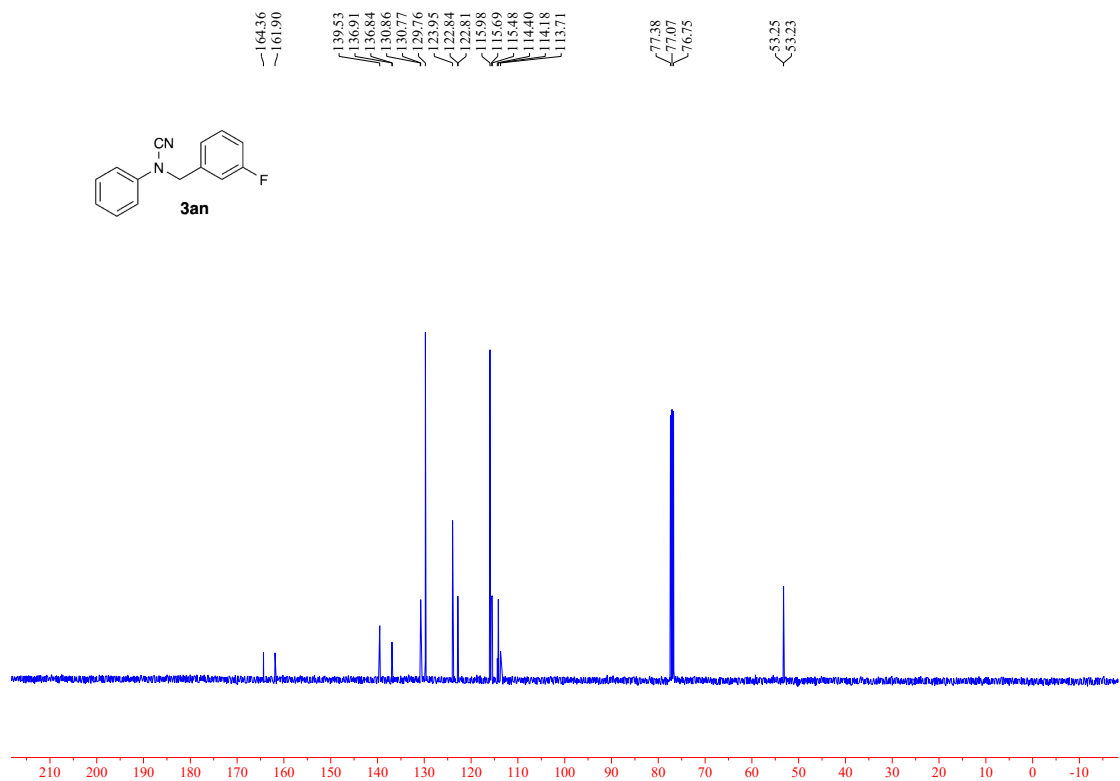
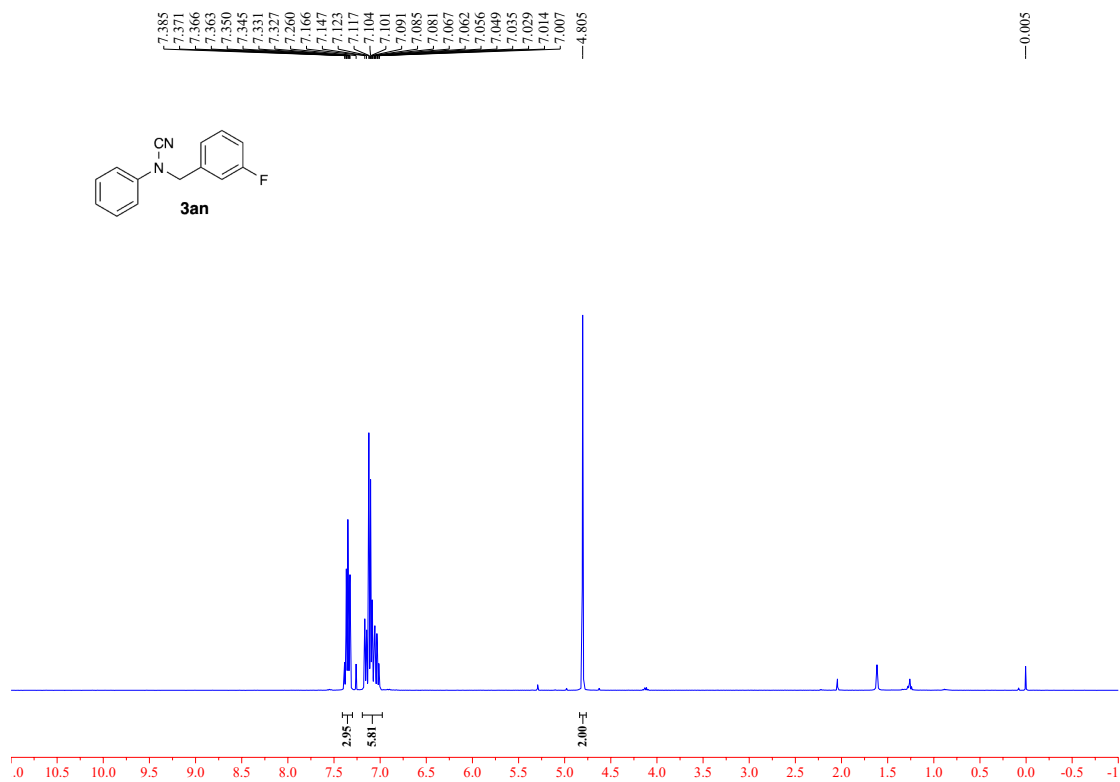
# N-(3-methoxybenzyl)-N-phenylcyanamide (3am)

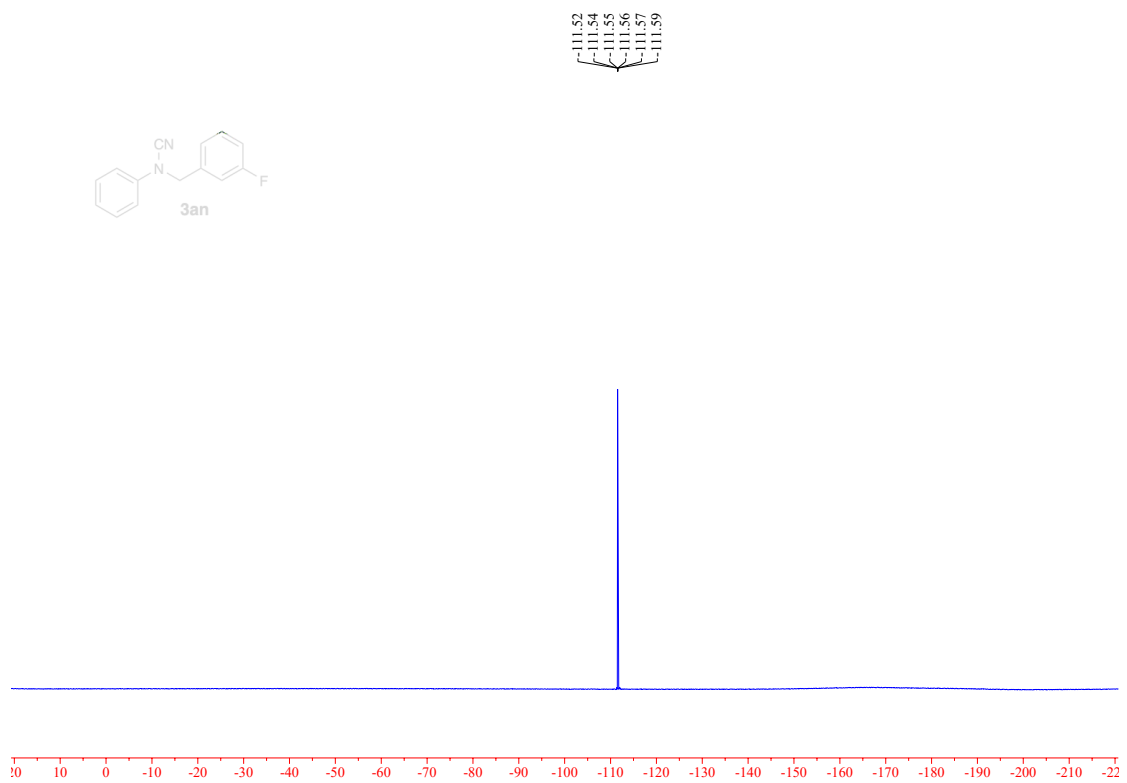


# 1,2-bis(3-methoxybenzyl)sulfane (5m)

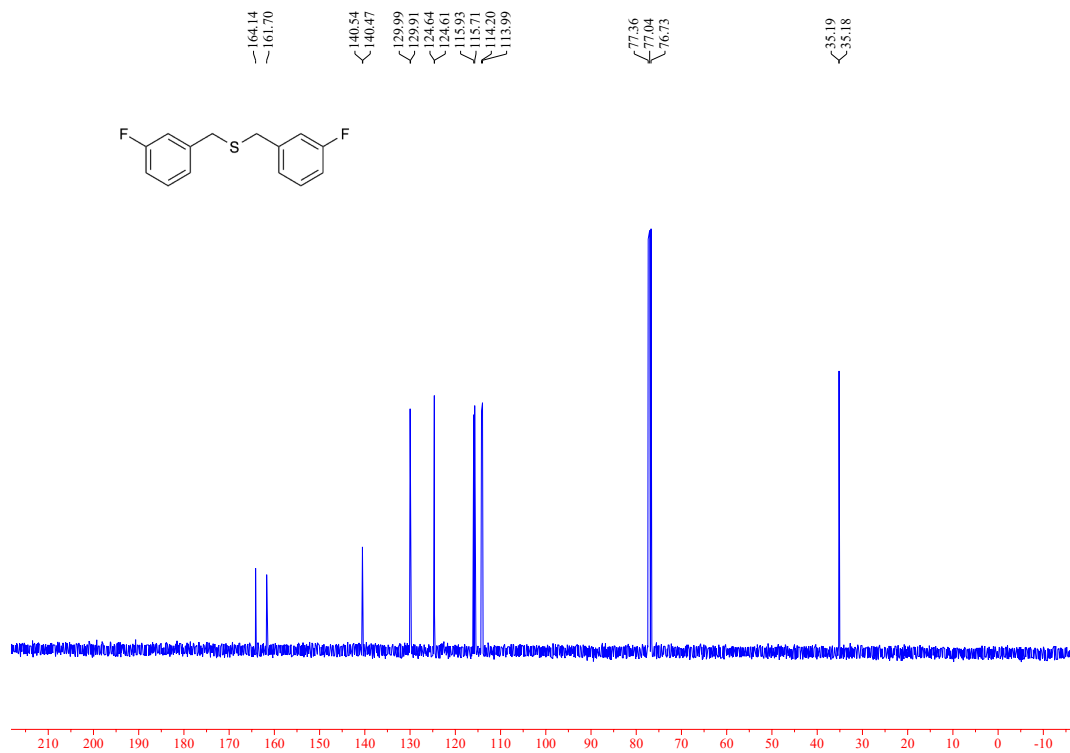
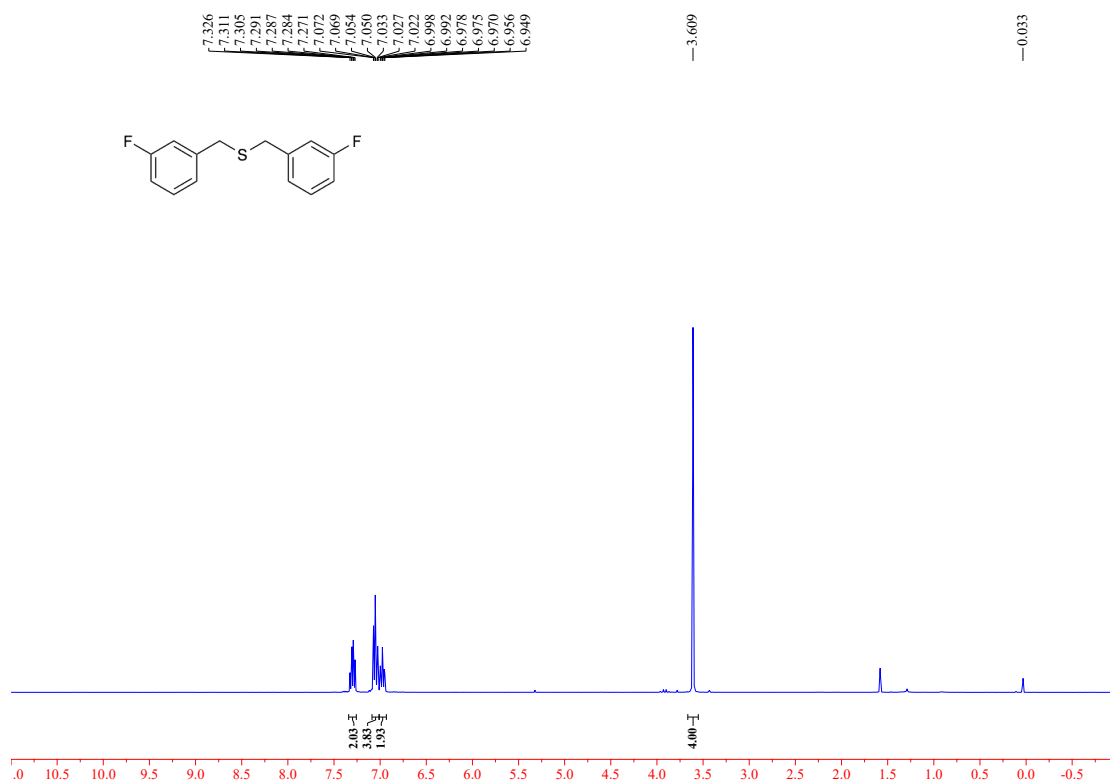


# *N*-(3-fluorobenzyl)-*N*-phenylcyanamide (**3an**)

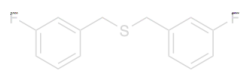




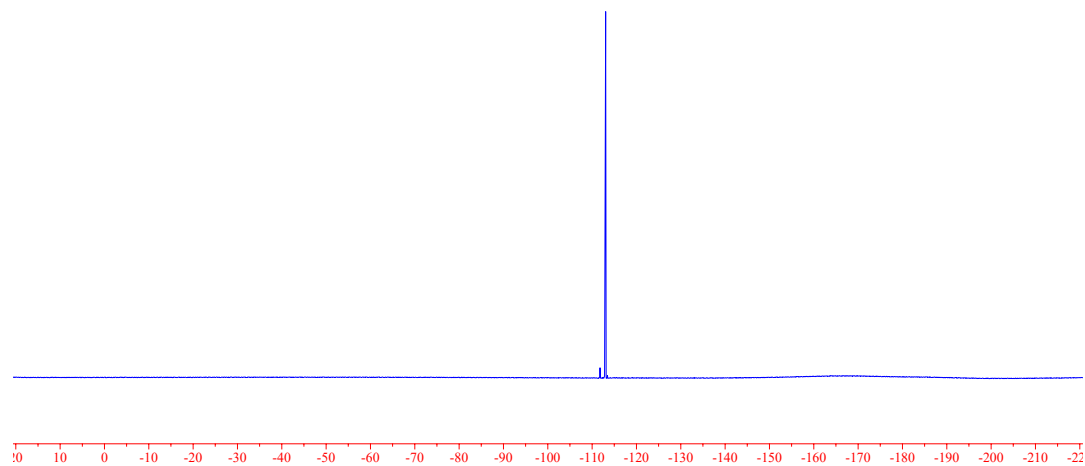
# bis(3-fluorobenzyl)sulfane (5n)



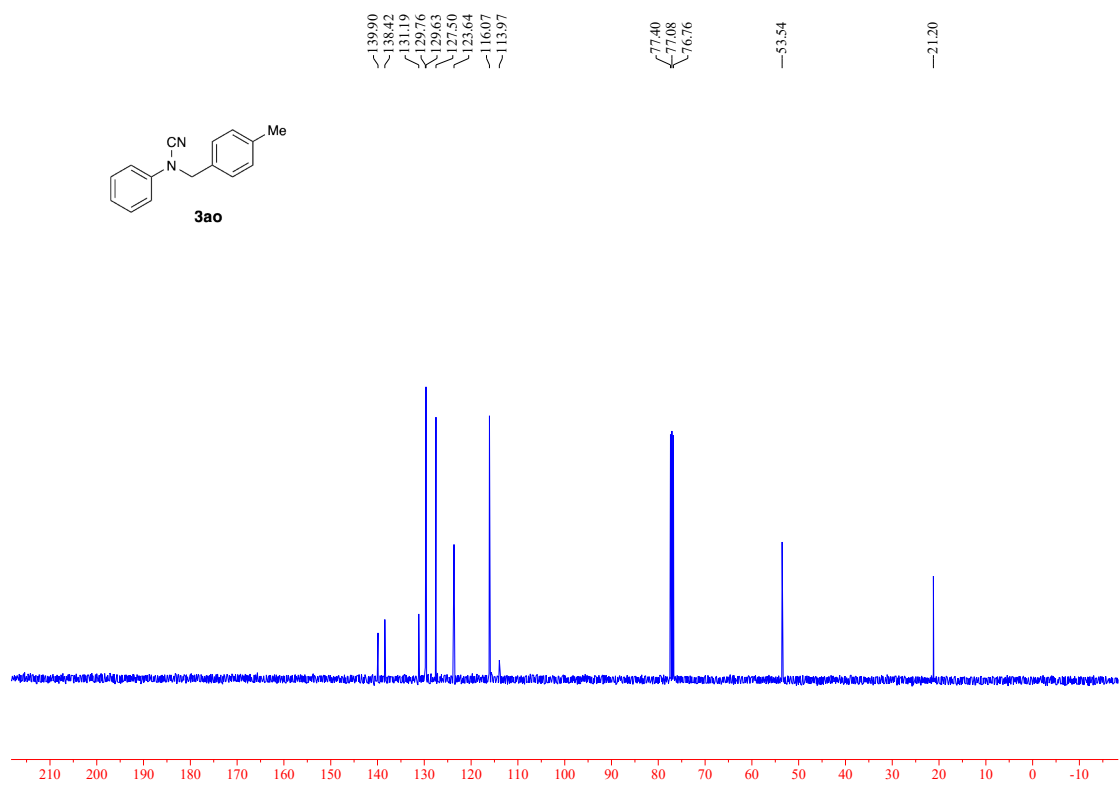
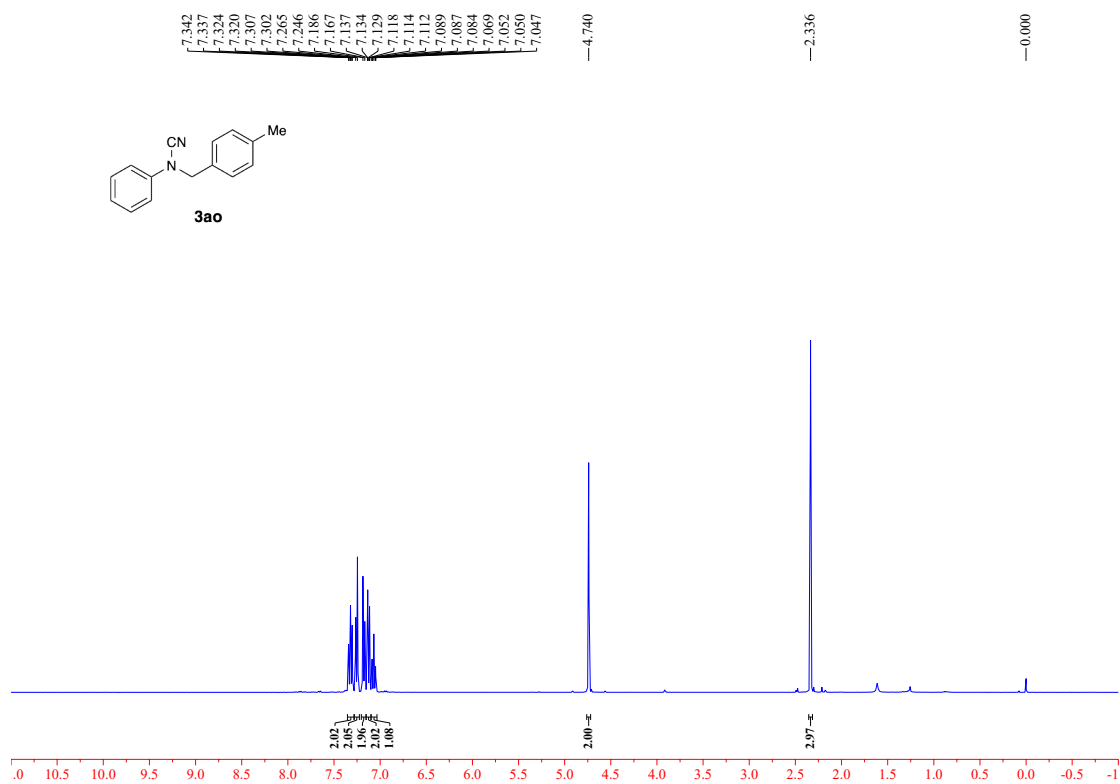




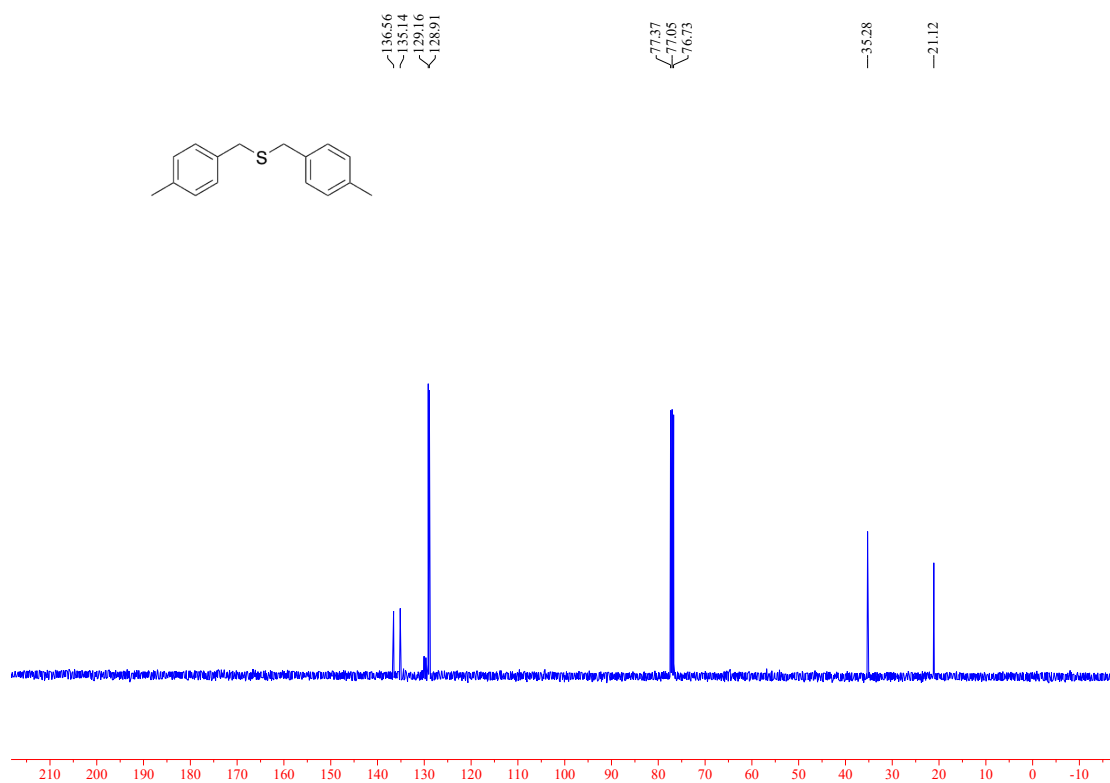
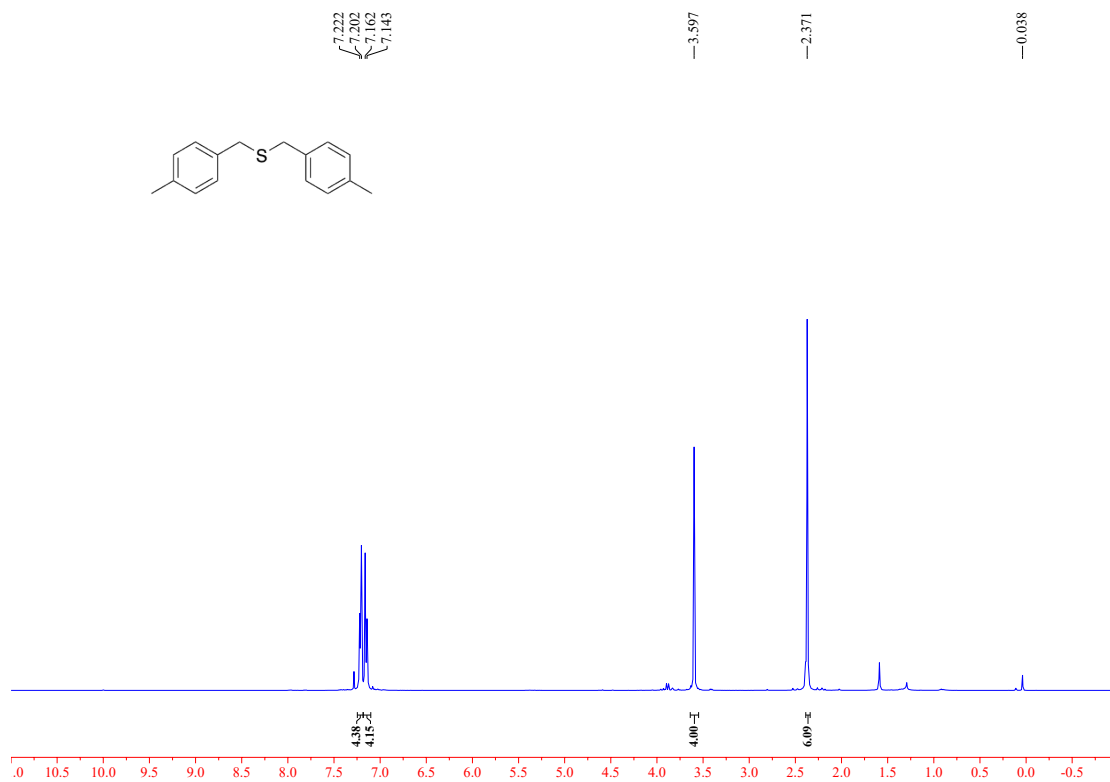
-113.02  
-113.03  
-113.04  
-113.06  
-113.08



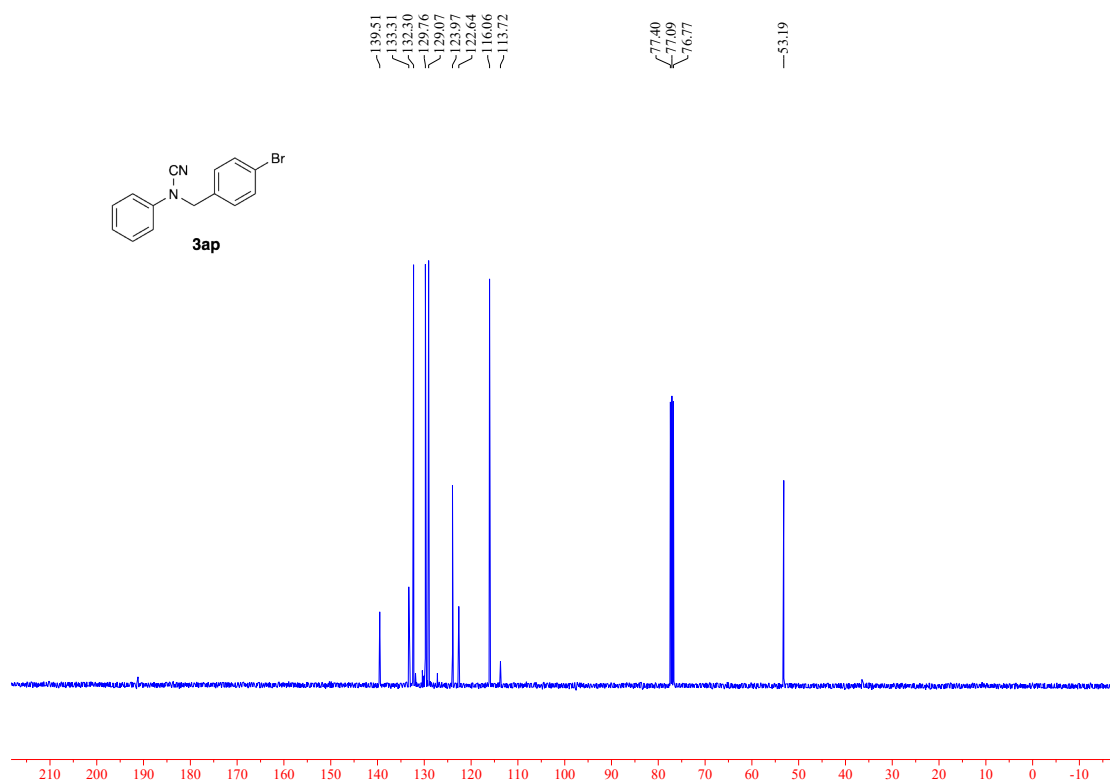
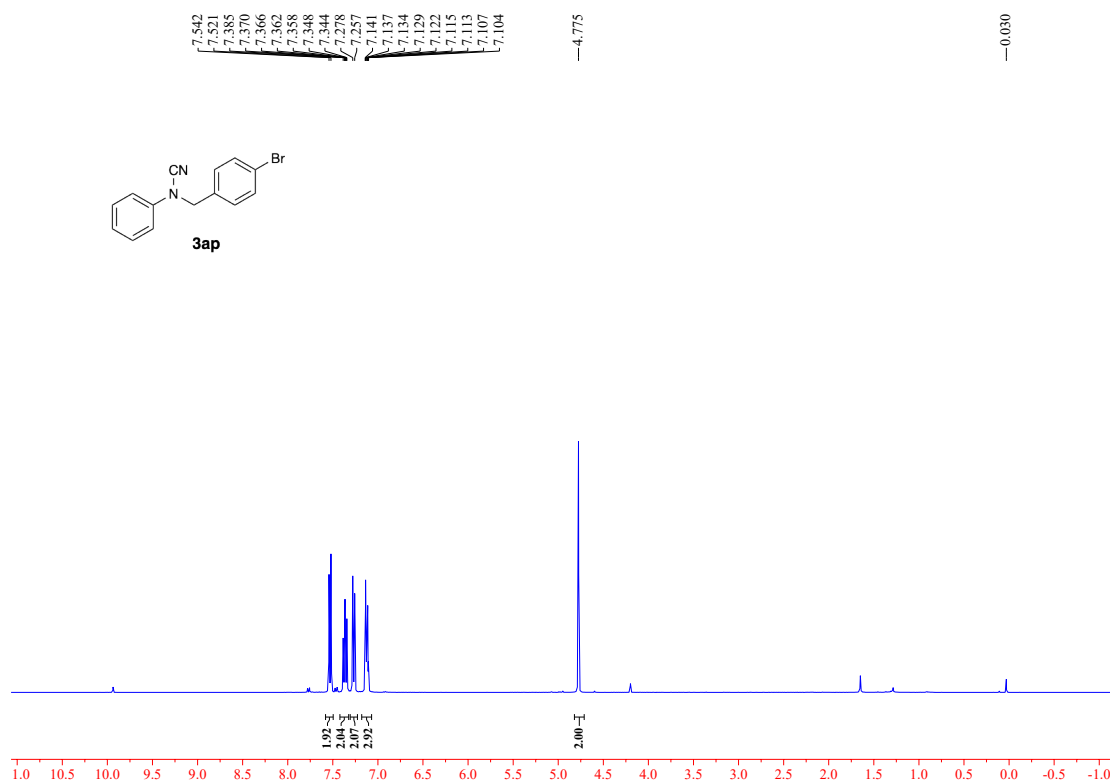
# *N*-(4-methylbenzyl)-*N*-phenylcyanamide (**3ao**)



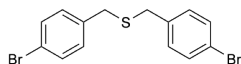
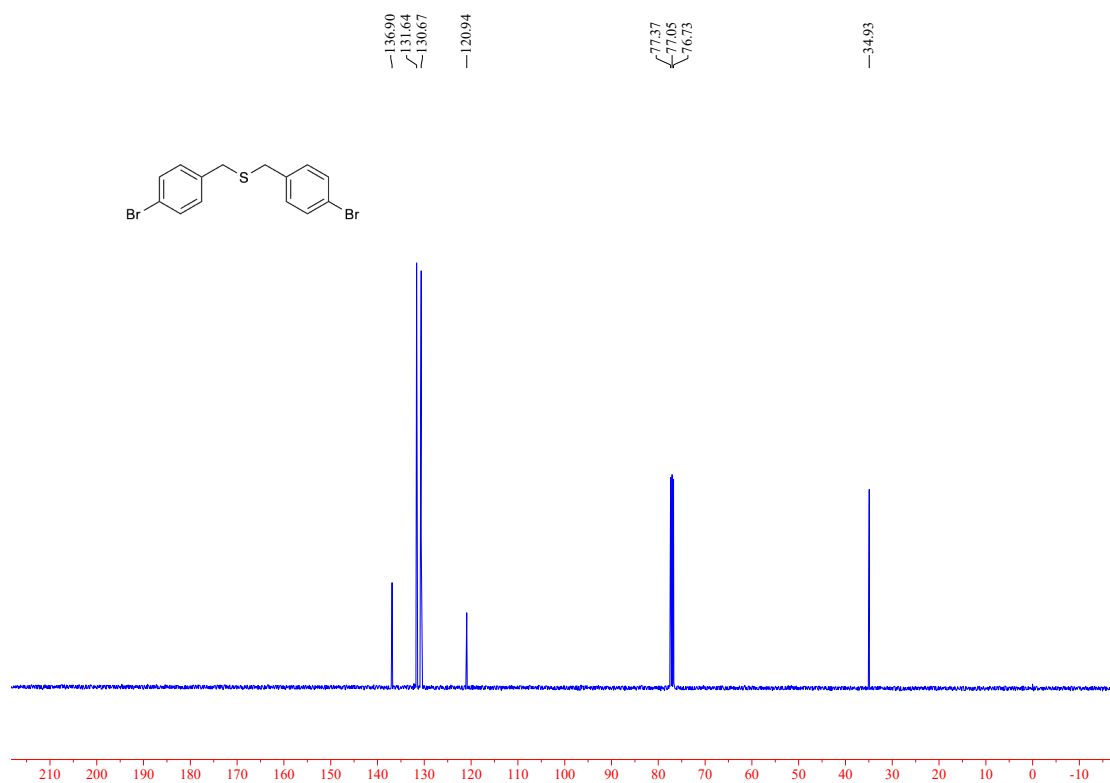
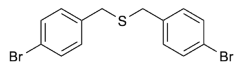
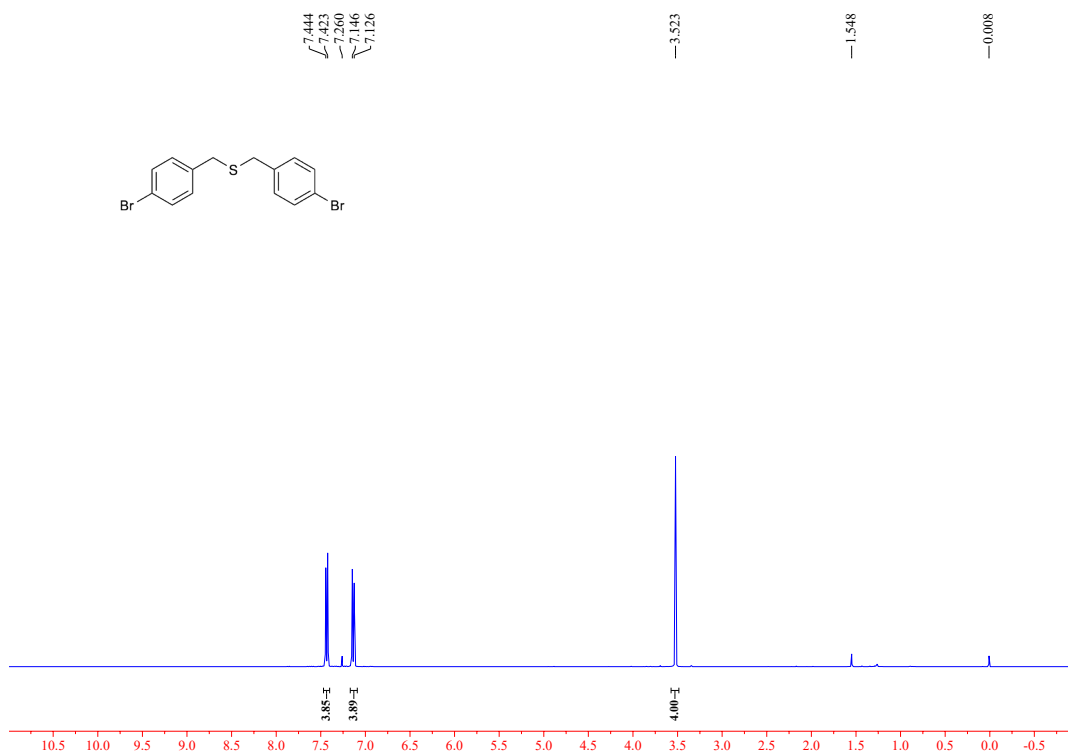
# bis(4-methylbenzyl)sulfane (5o)



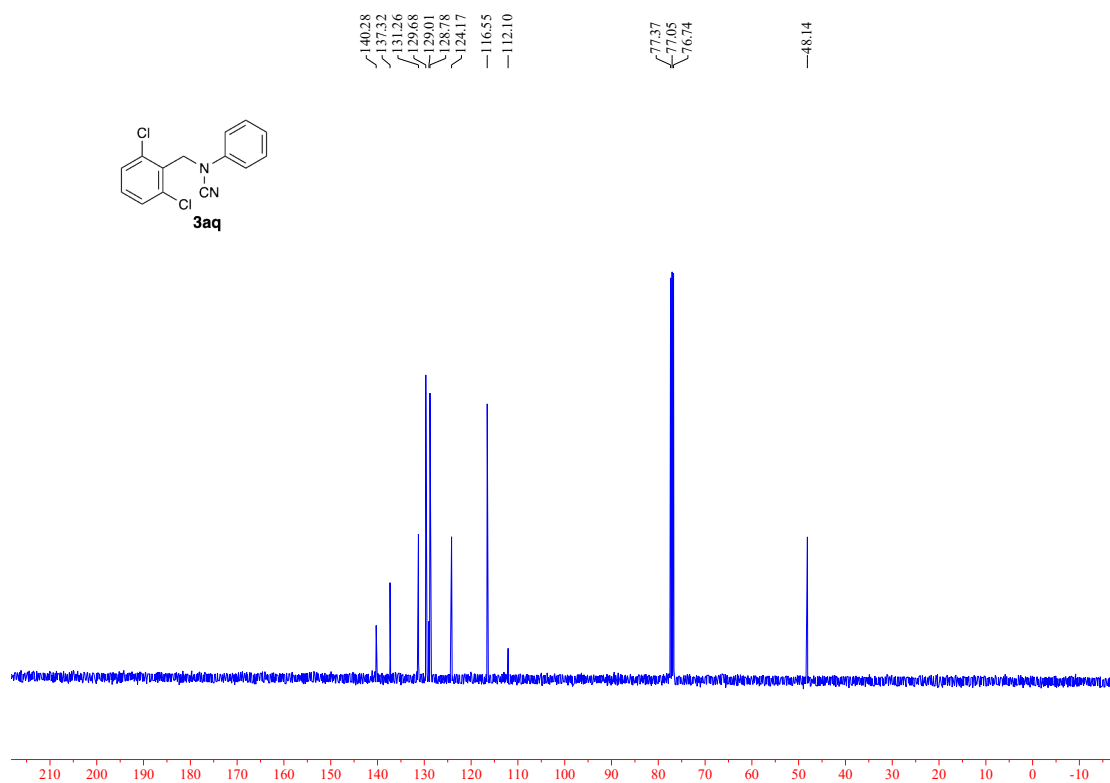
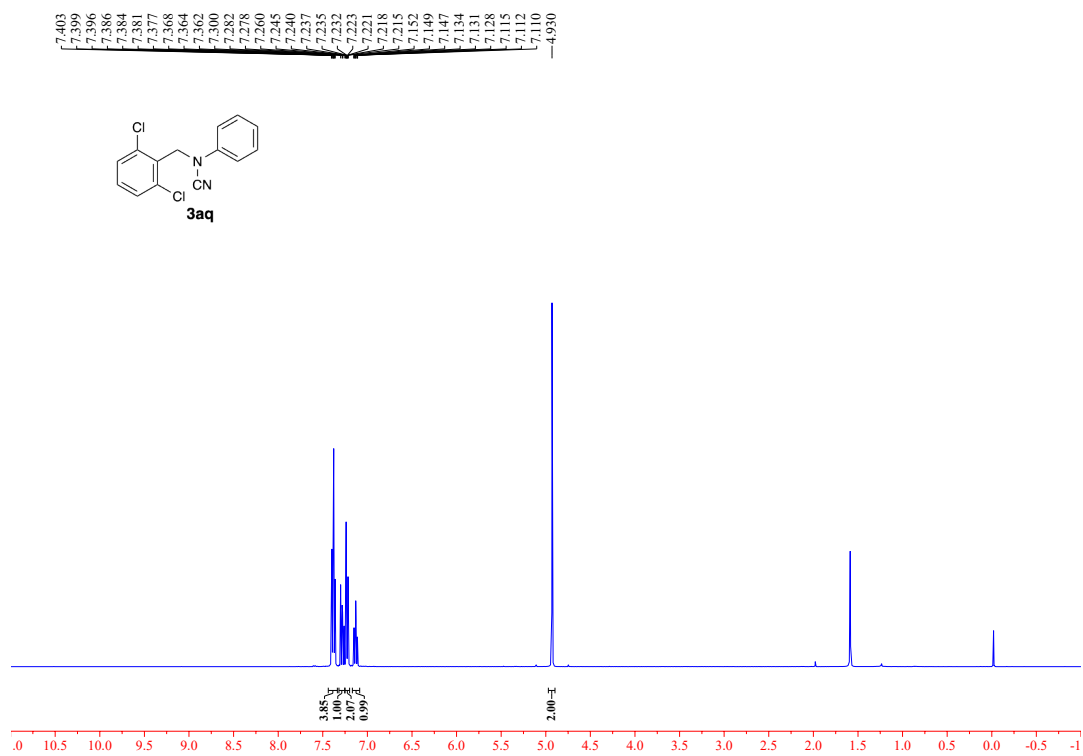
# *N*-(4-bromobenzyl)-*N*-phenylcyanamide (**3ap**)



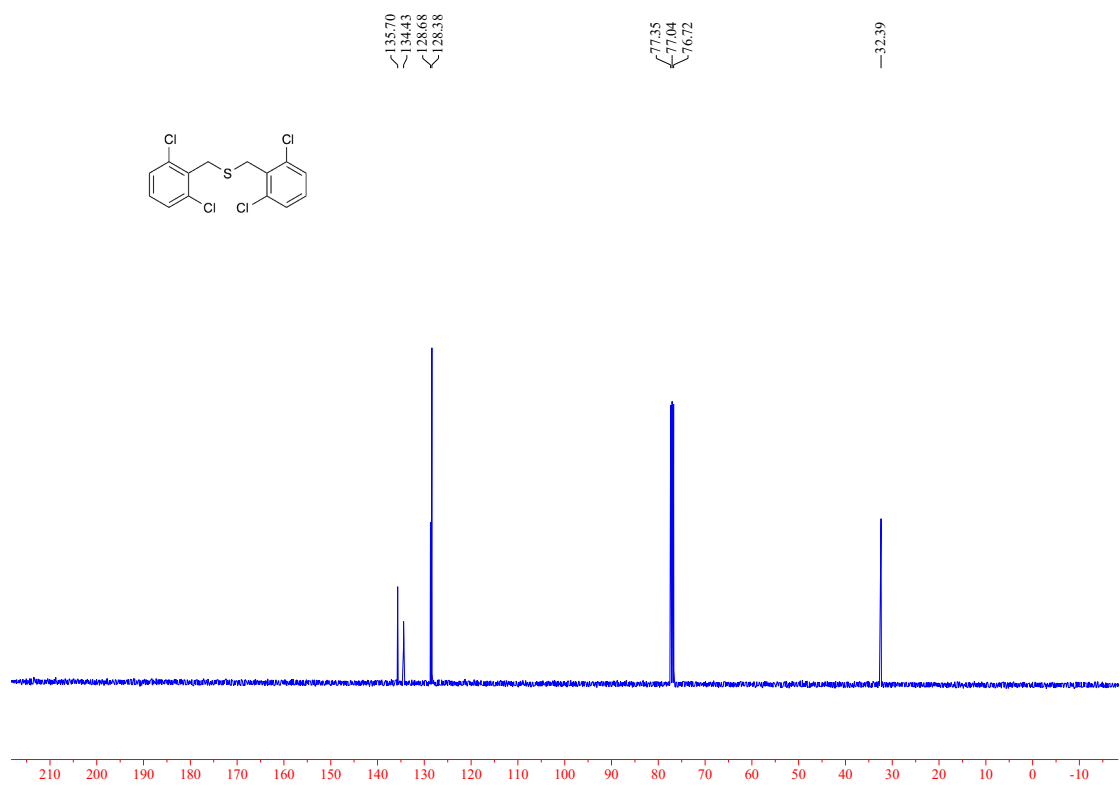
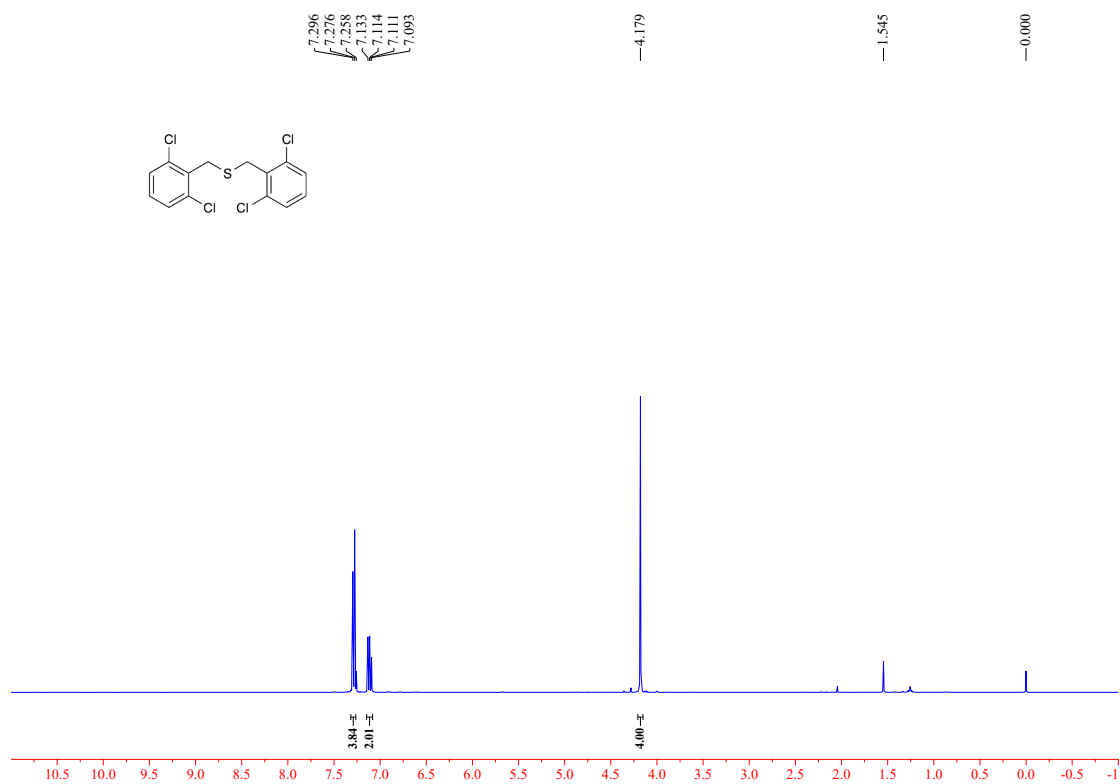
# bis(4-bromobenzyl)sulfane (5p)



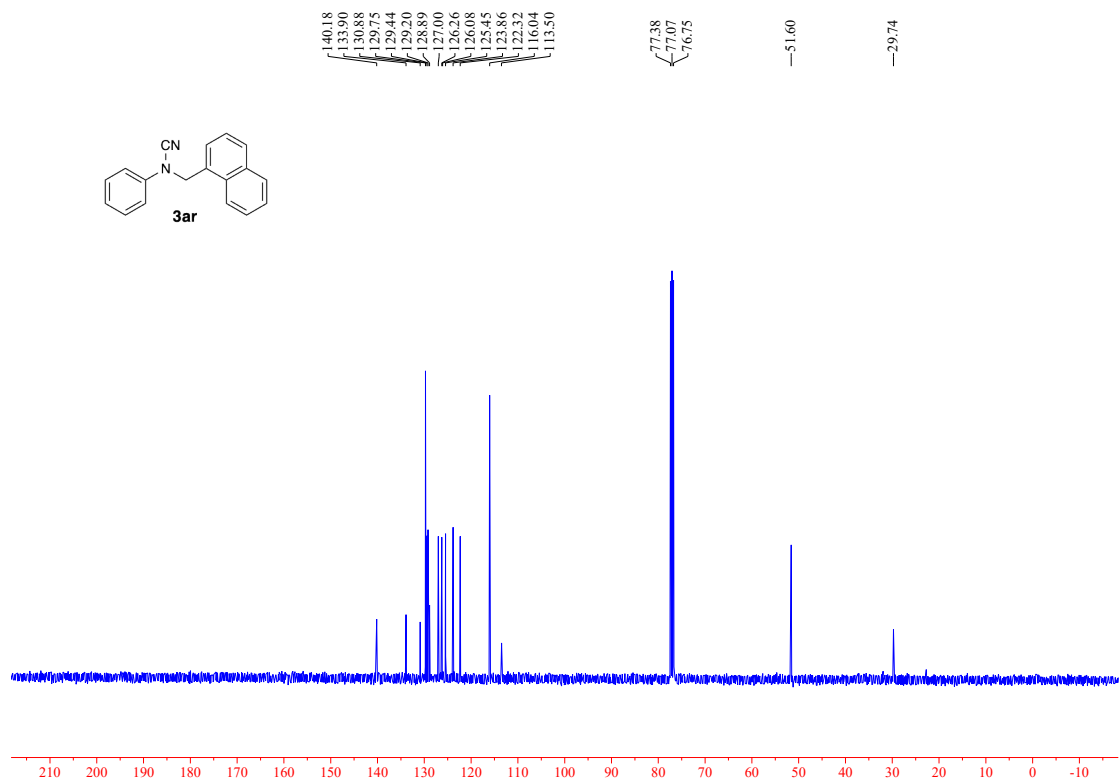
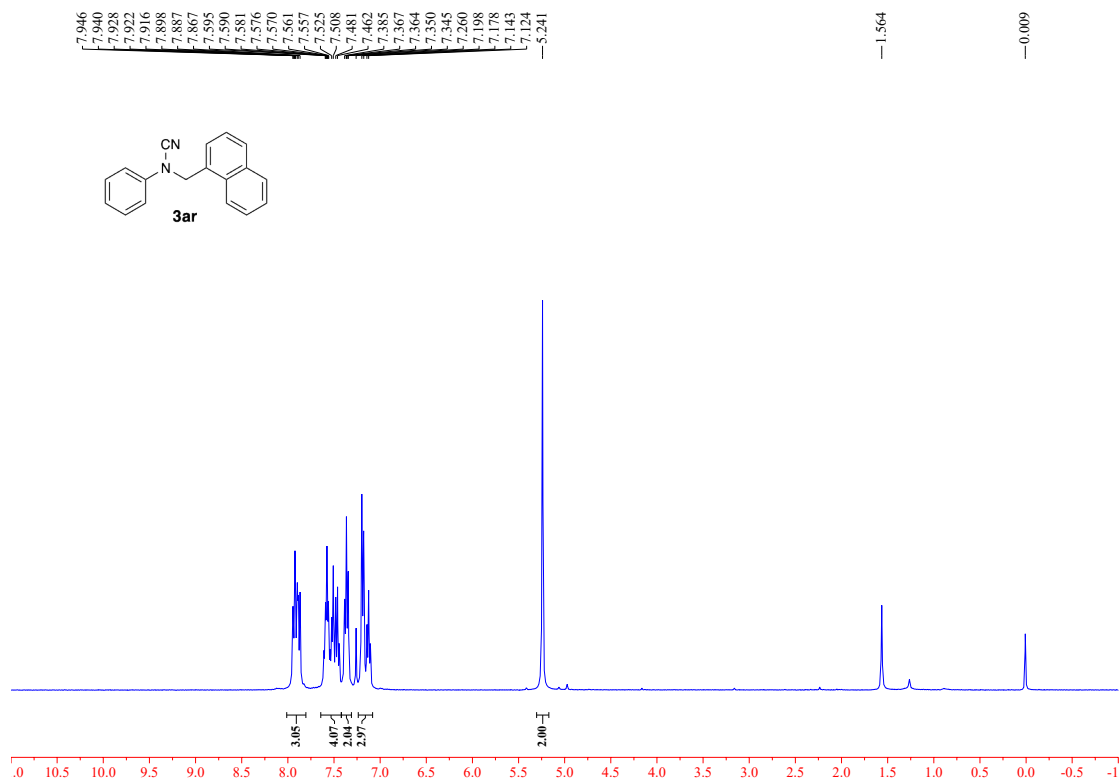
# *N*-(2,6-dichlorobenzyl)-*N*-phenylcyanamide (**3aq**)



# bis(2,6-dichlorobenzyl)sulfane (5q)

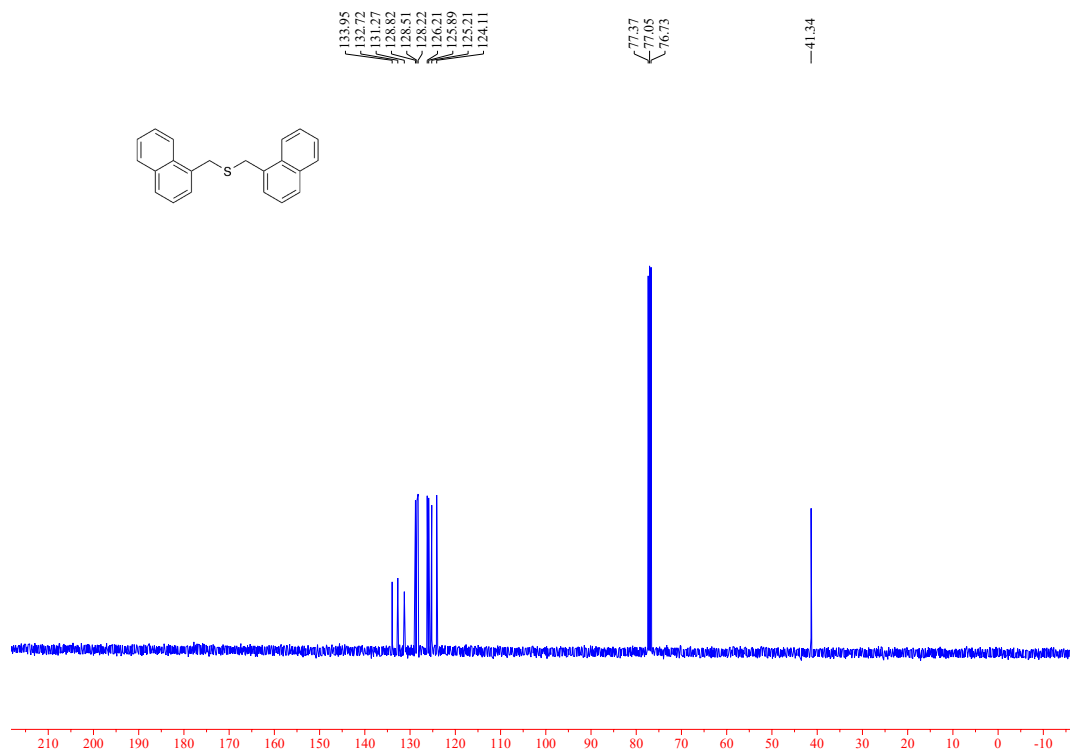
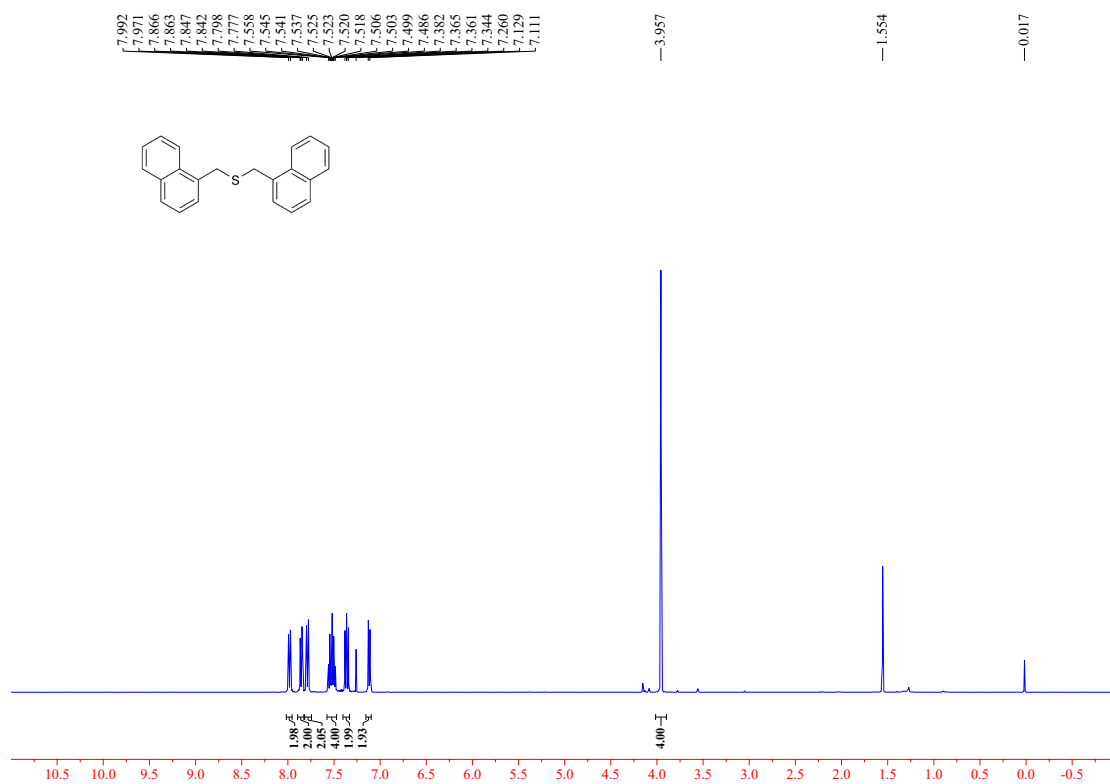


# *N*-(naphthalen-1-ylmethyl)-*N*-phenylcyanamide (**3ar**)

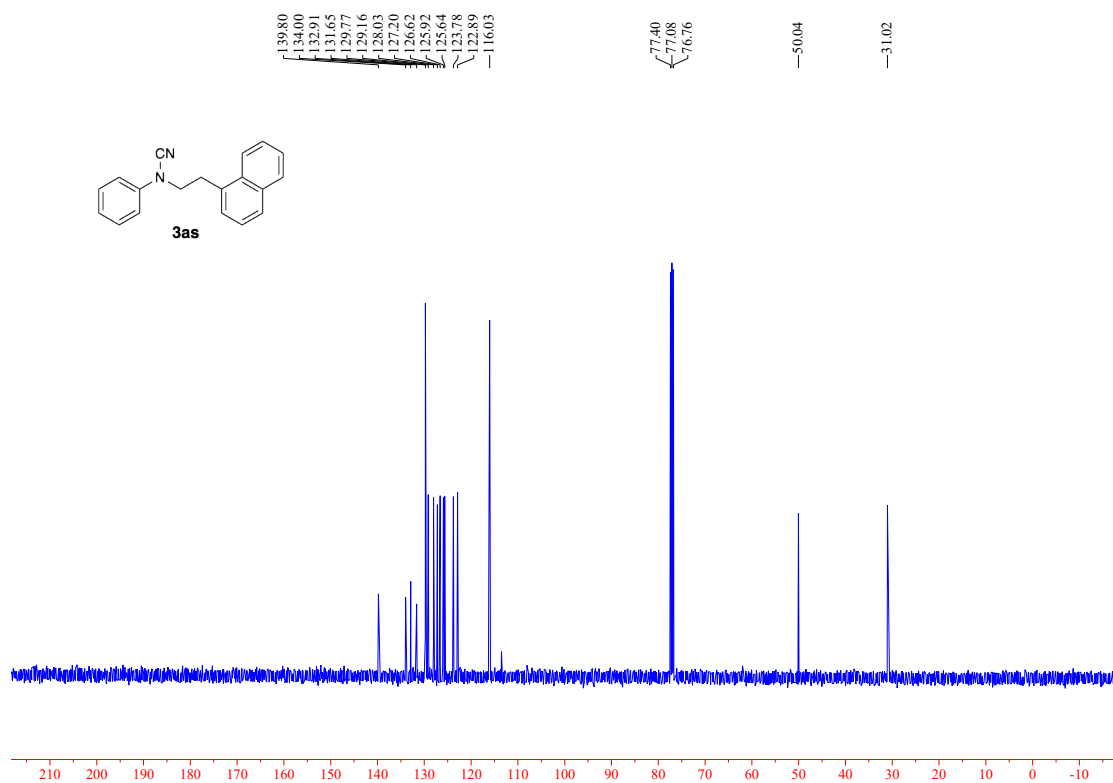
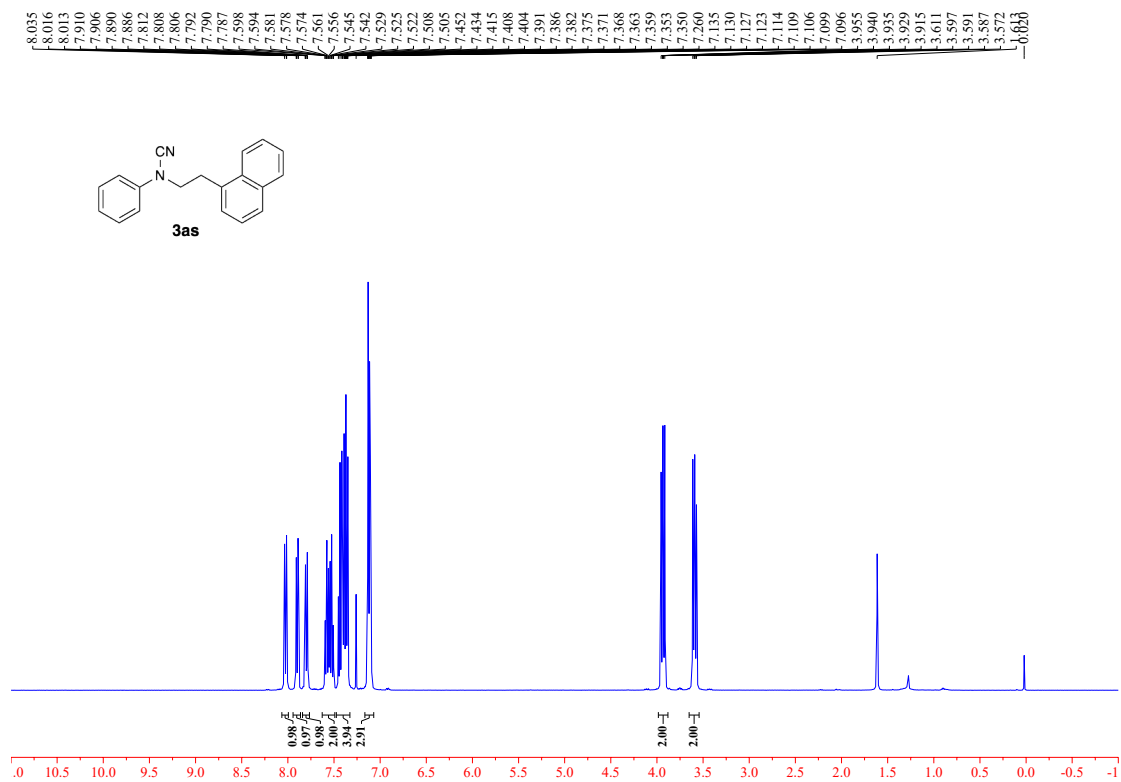




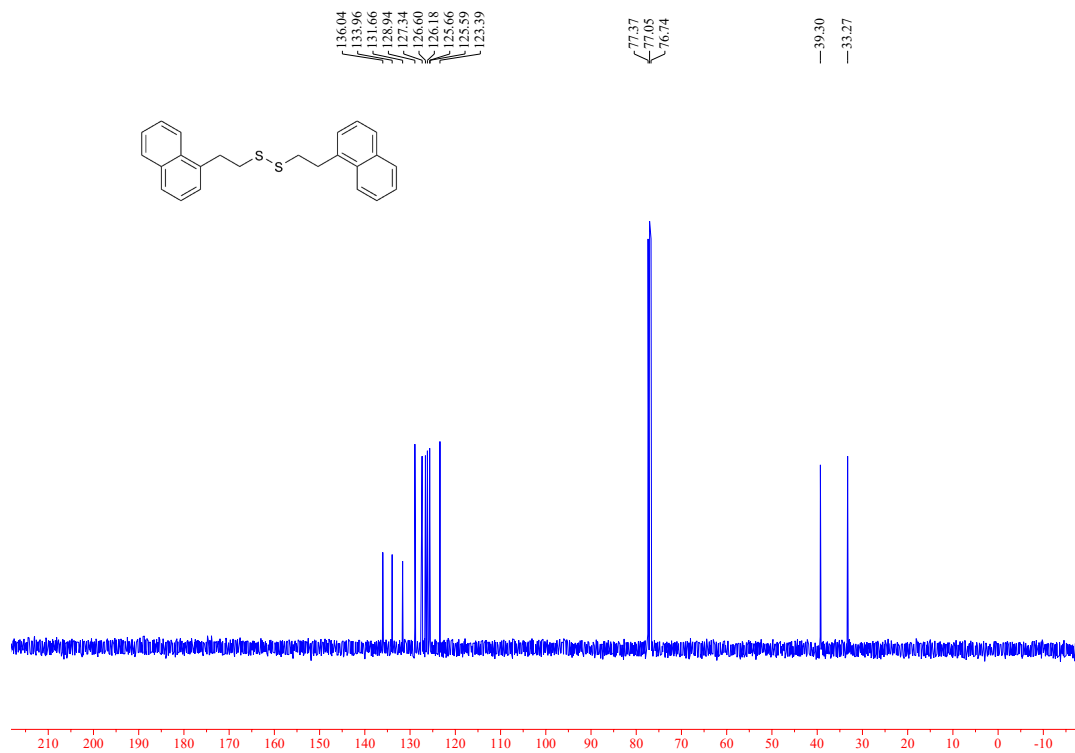
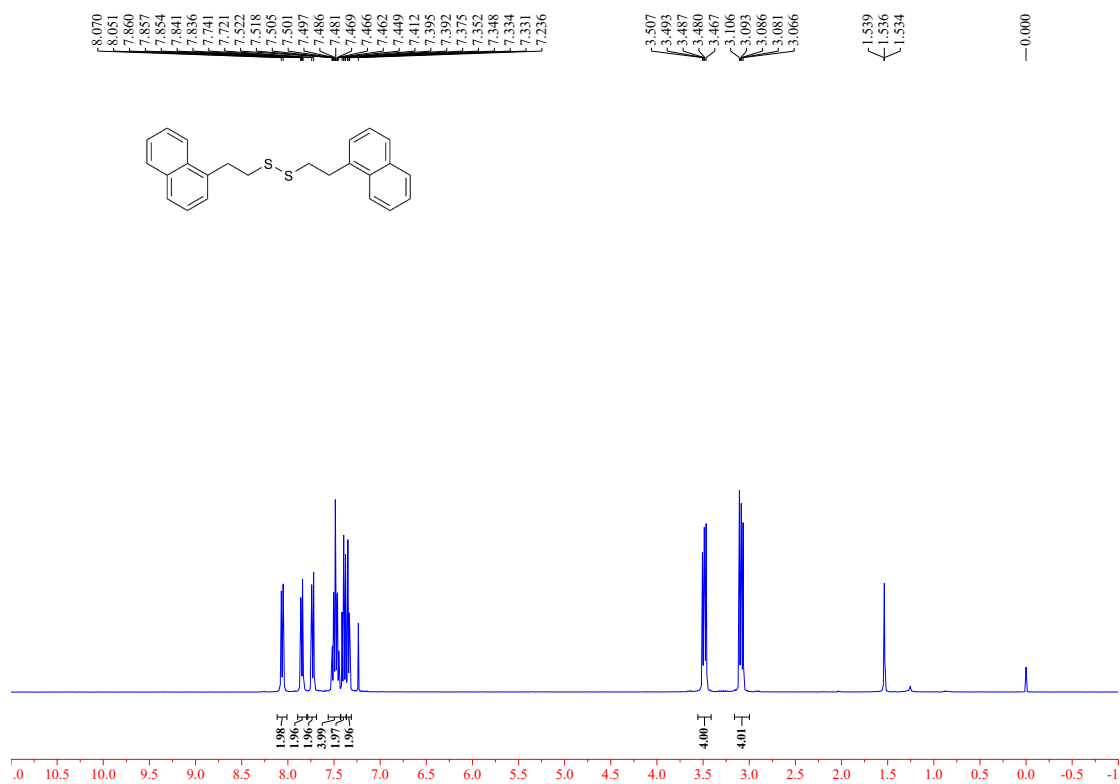
# bis(naphthalen-1-ylmethyl)sulfane (5r)



# *N*-(2-(naphthalen-1-yl)ethyl)-*N*-phenylcyanamide (3as)

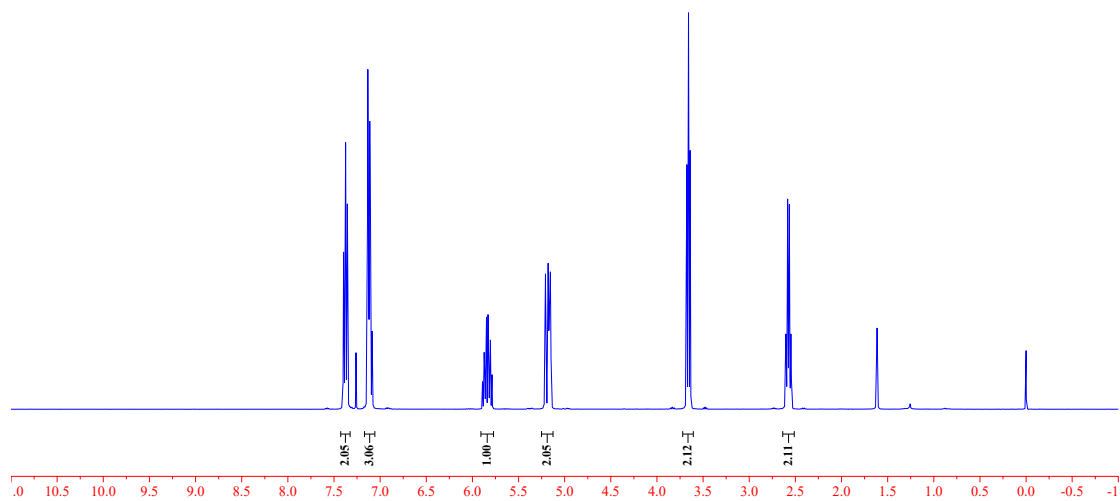
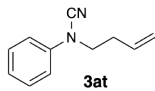


# 1,2-bis(2-(naphthalen-1-yl)ethyl)disulfane (4s)



***N*-(but-3-en-1-yl)-*N*-phenylcyanamide (3at)**

7.396  
7.390  
7.378  
7.374  
7.361  
7.356  
7.349  
7.261  
7.126  
7.123  
7.112  
7.105  
7.089  
7.087  
5.890  
5.873  
5.865  
5.856  
5.848  
5.830  
5.822  
5.813  
5.805  
5.788  
5.216  
5.212  
5.208  
5.204  
5.183  
5.180  
5.177  
5.173  
5.169  
5.165  
5.161  
5.155  
5.151  
3.677  
3.658  
3.640  
2.605  
2.601  
2.598  
2.588  
2.584  
2.569  
2.565  
2.562  
2.551  
2.548  
2.544  
1.615  
-0.000

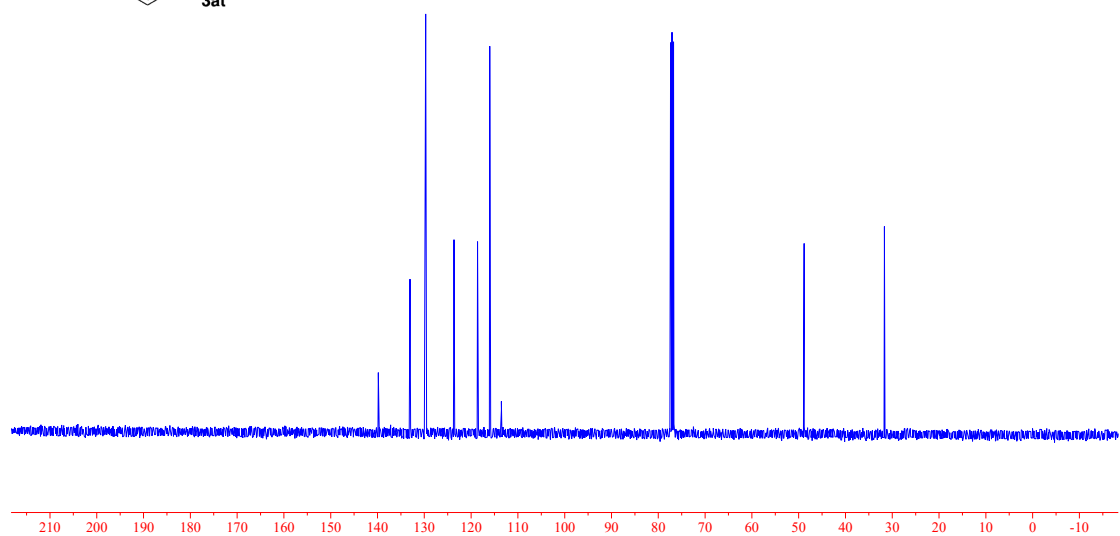
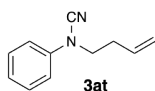


139.83  
133.06  
129.71  
123.65  
118.61  
116.01  
113.53

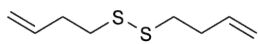
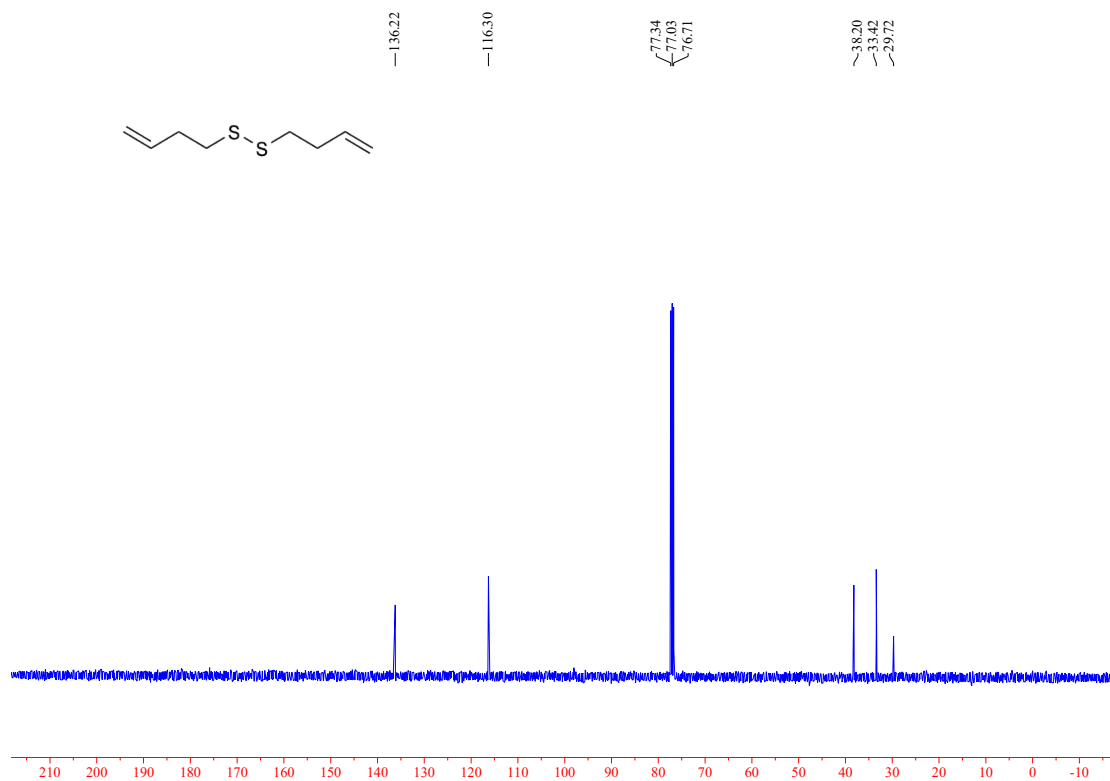
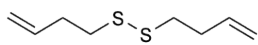
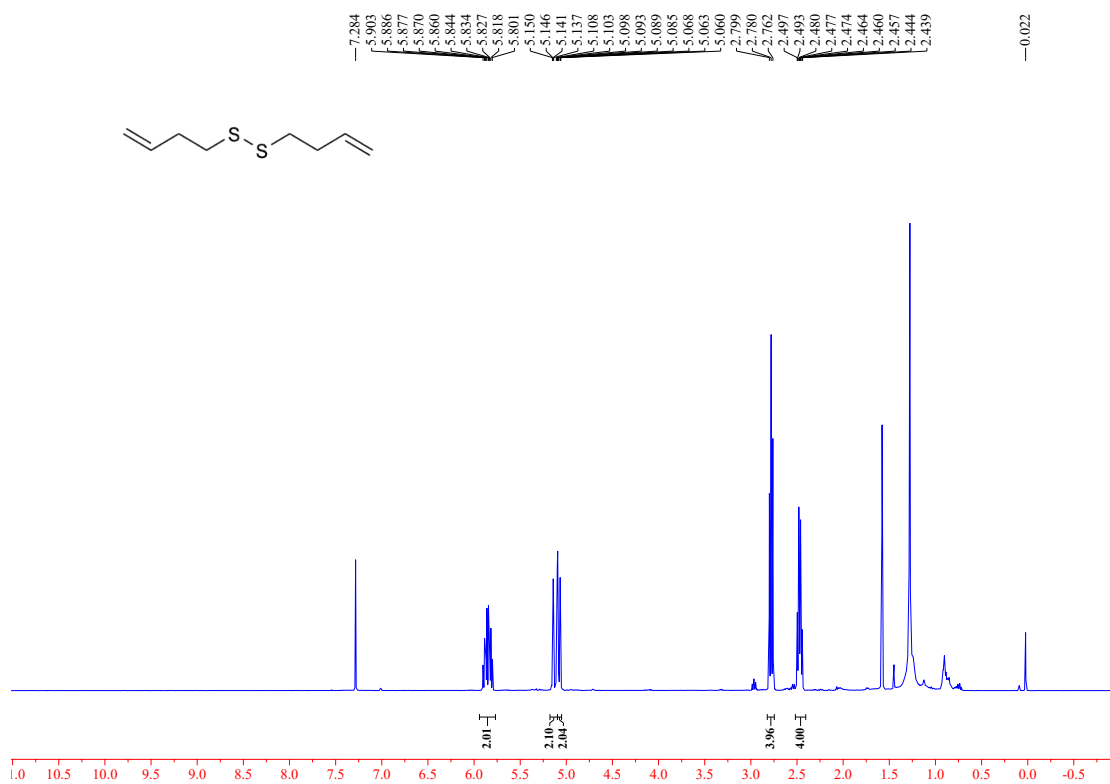
77.37  
77.06  
76.74

48.83

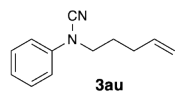
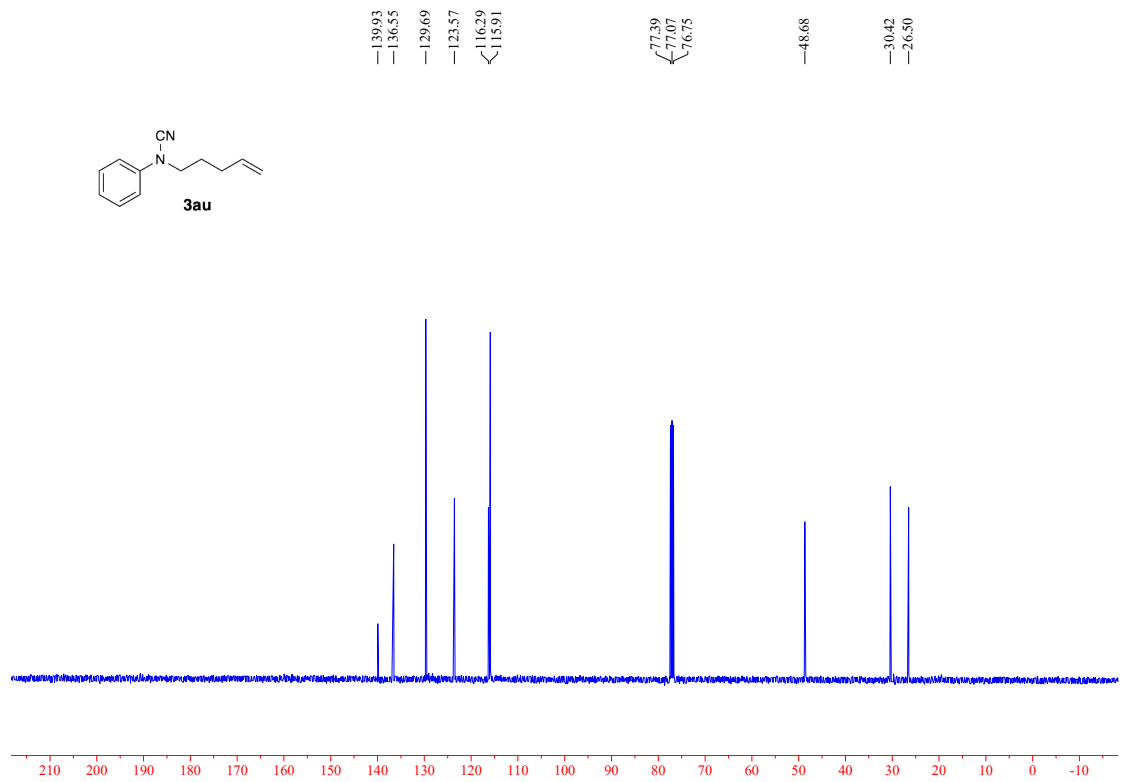
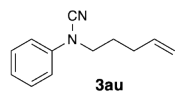
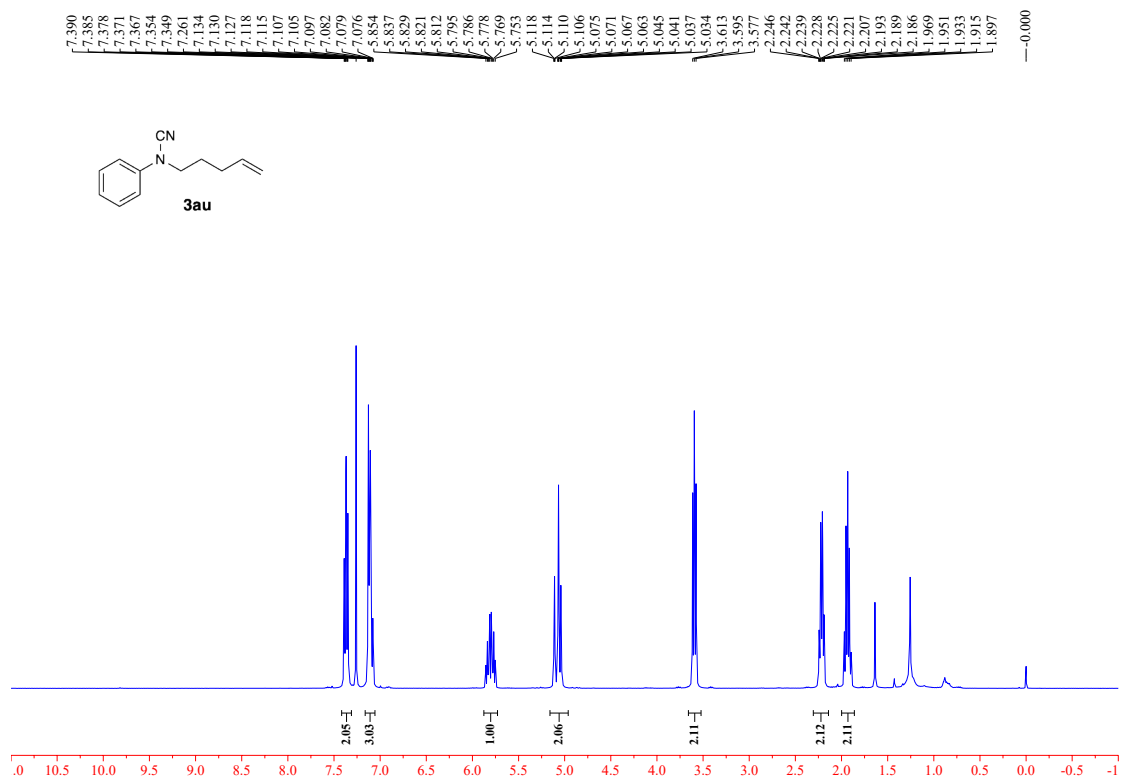
31.68



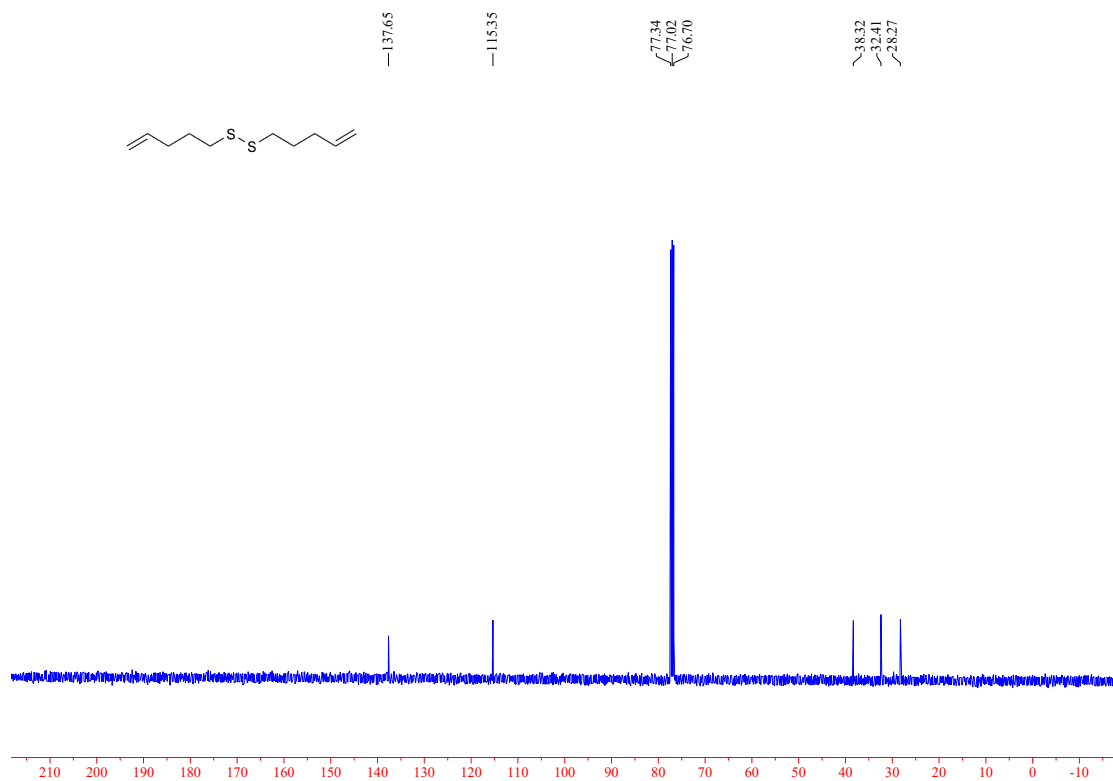
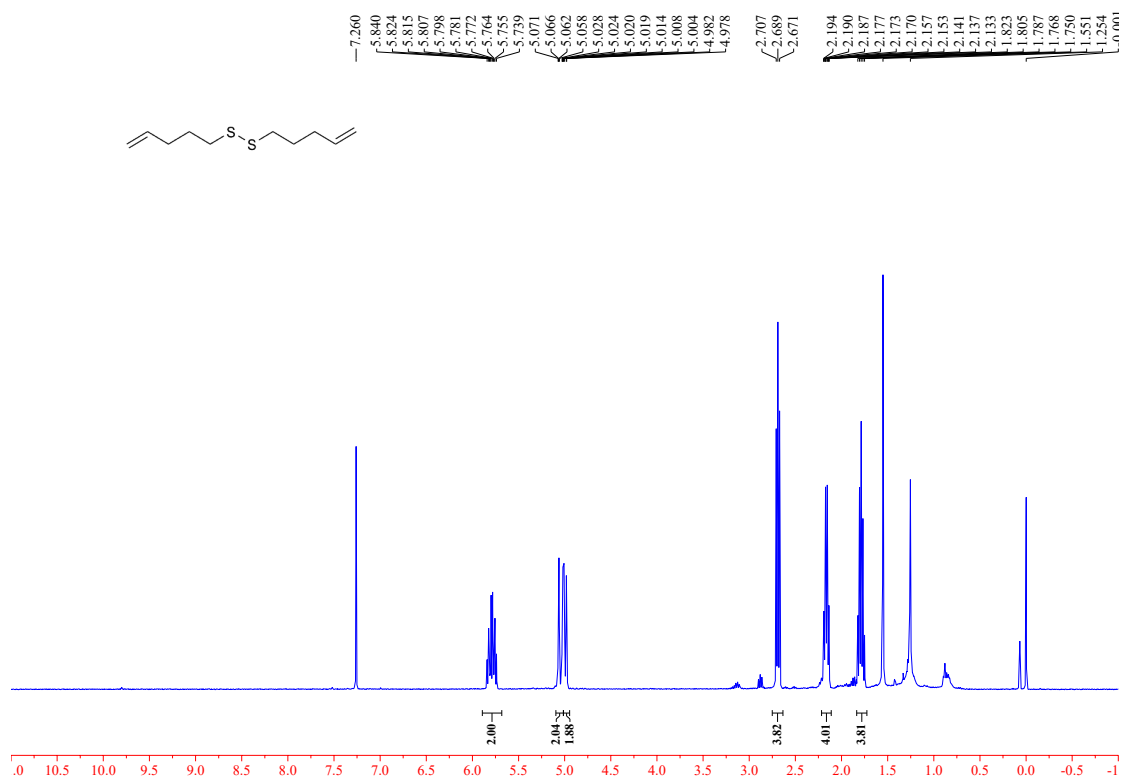
# 1,2-di(but-3-en-1-yl)disulfane (4t)



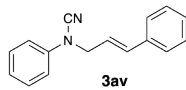
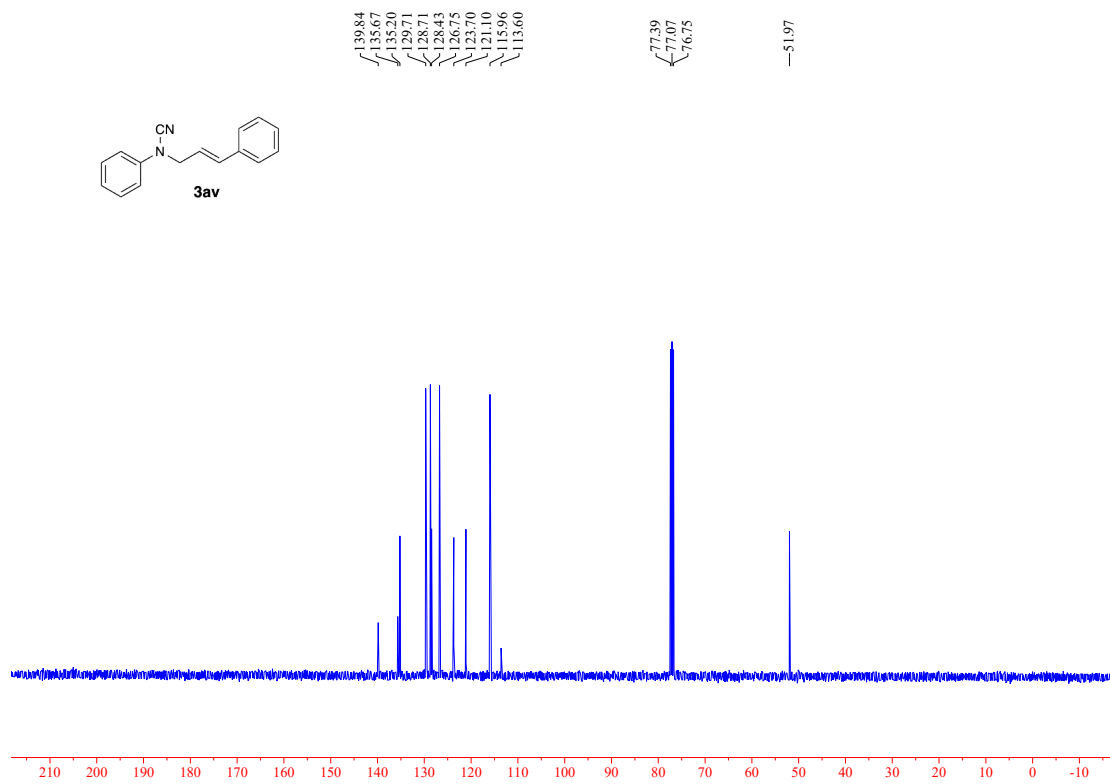
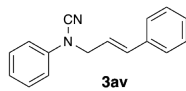
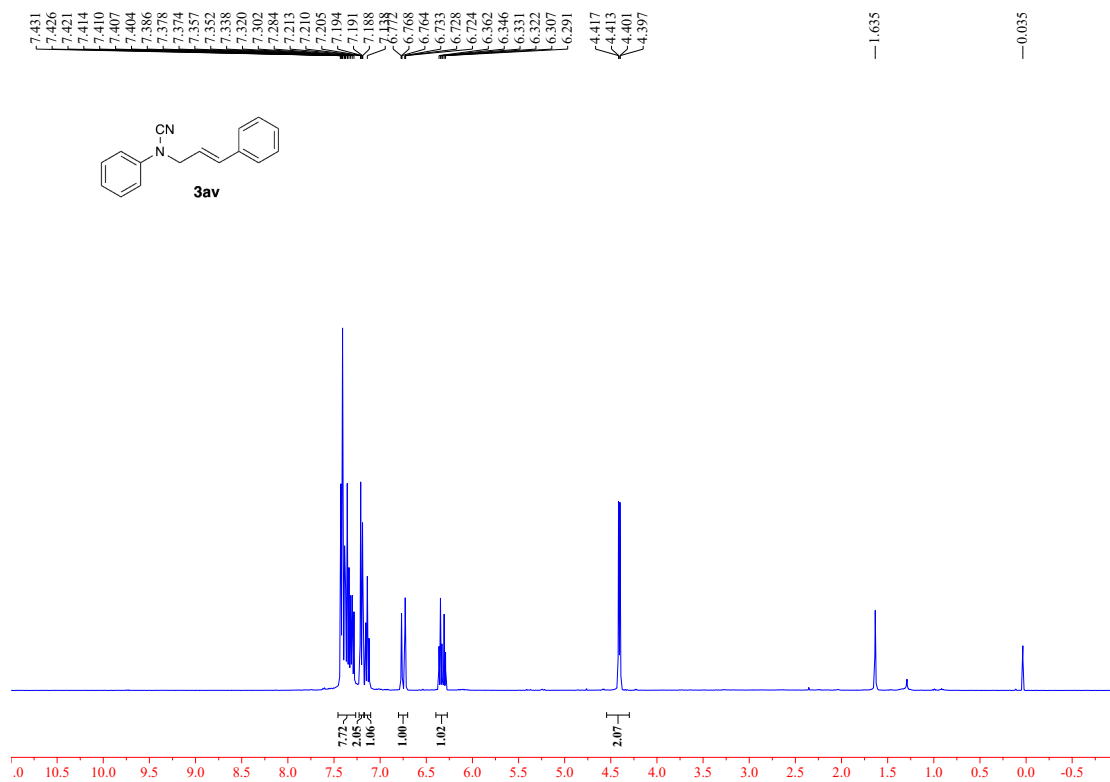
***N*-(pent-4-en-1-yl)-*N*-phenylcyanamide (3au)**



# 1,2-di(pent-4-en-1-yl)disulfane (4u)



# *N*-cinnamyl-*N*-phenylcyanamide (**3av**)





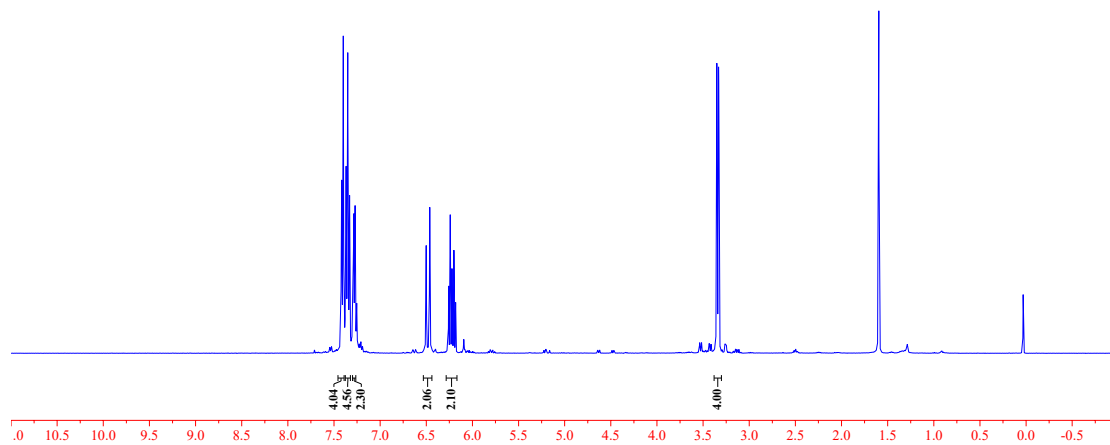
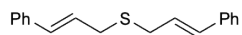
# dicinnamylsulfane (5v)

7.421  
7.417  
7.412  
7.404  
7.400  
7.397  
7.391  
7.369  
7.351  
7.346  
7.335  
7.331  
7.326  
7.293  
7.289  
7.284  
7.277  
7.271  
7.265  
7.253  
6.501  
6.462  
6.258  
6.240  
6.222  
6.219  
6.201  
6.182

3.351  
3.348  
3.333  
3.330

1.596

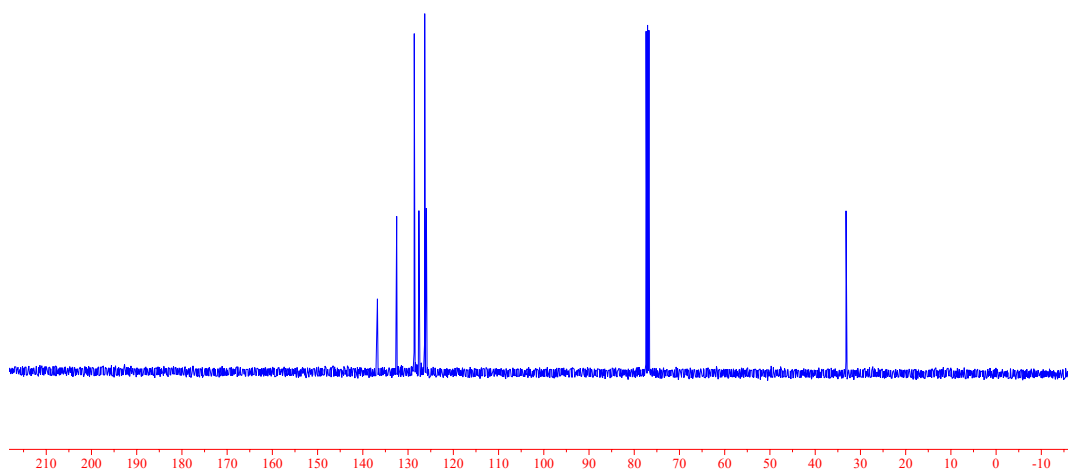
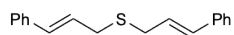
-0.032



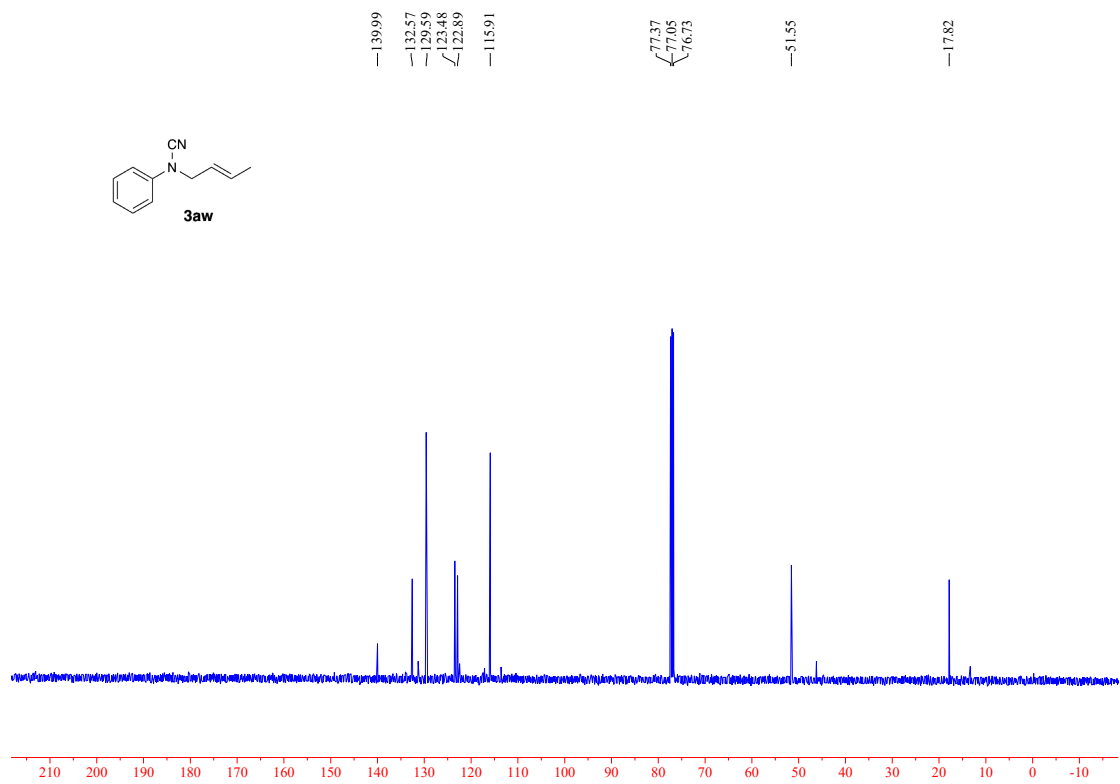
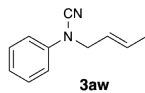
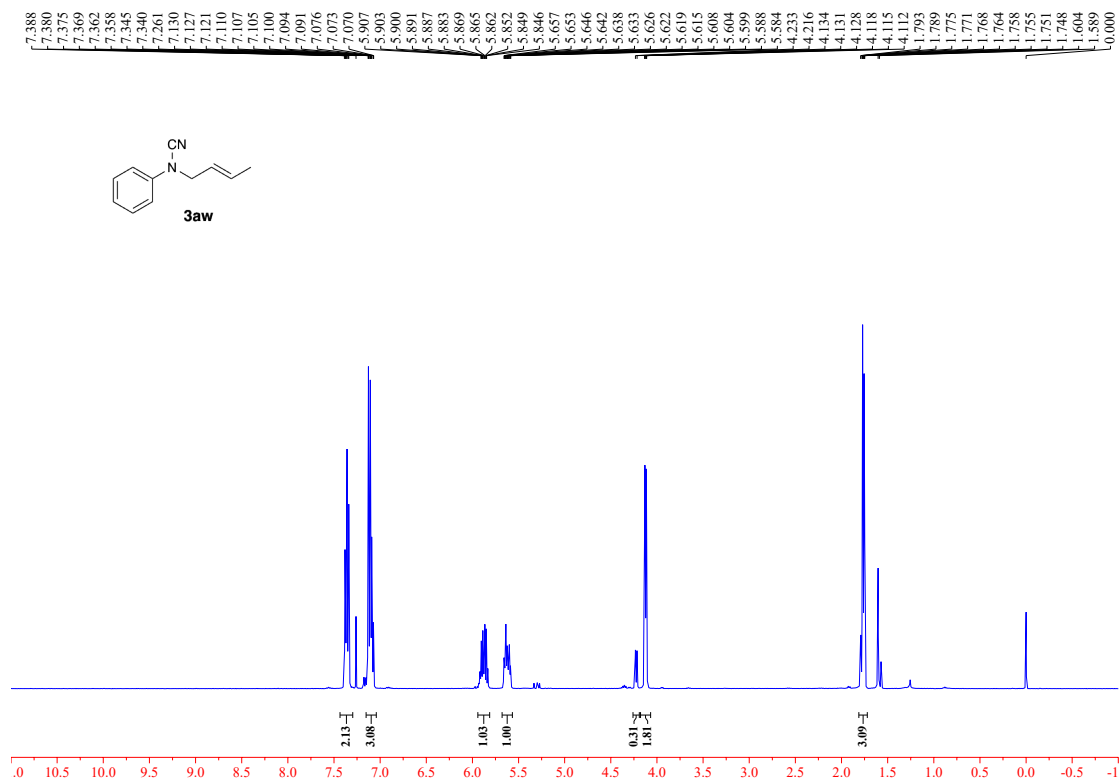
136.77  
132.52  
128.64  
127.60  
126.32  
125.95

77.37  
77.06  
76.74

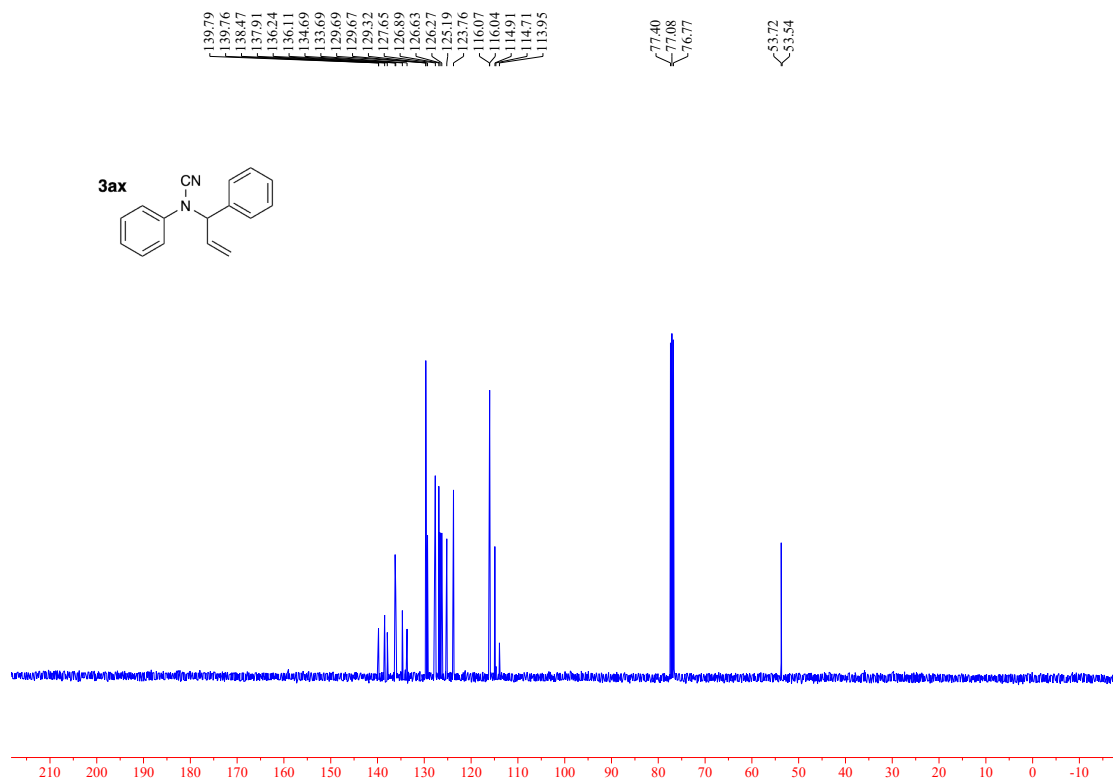
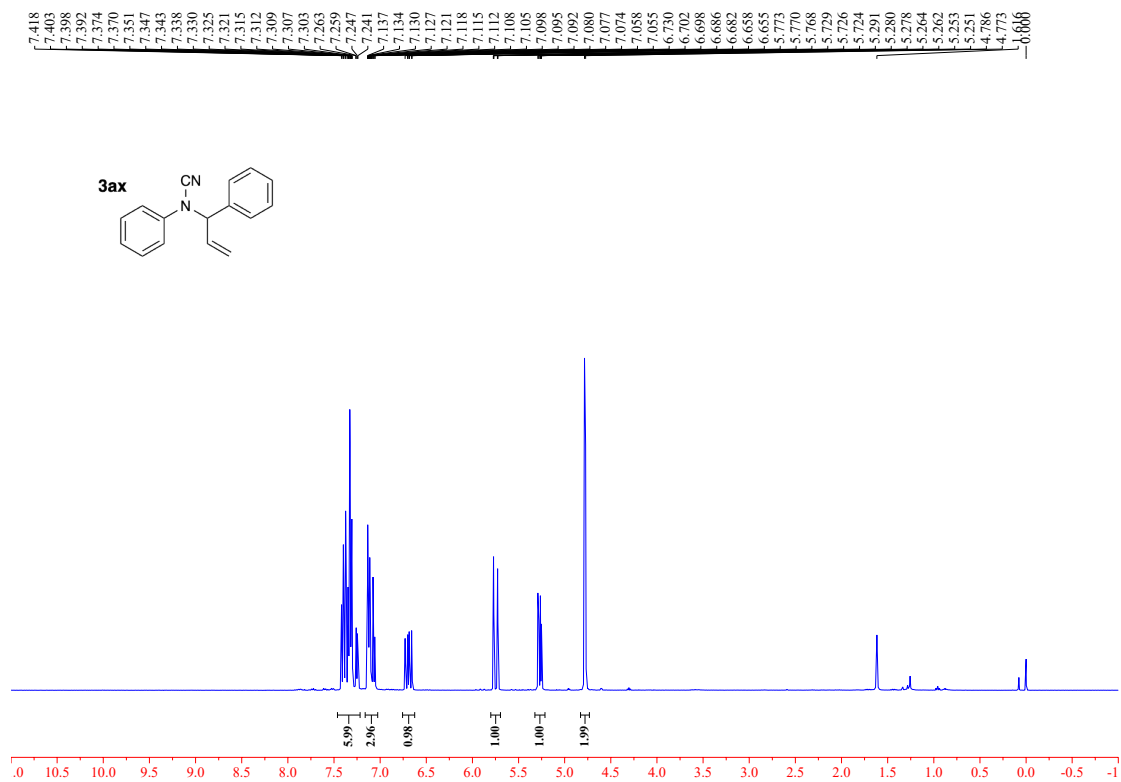
33.19



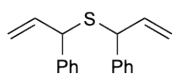
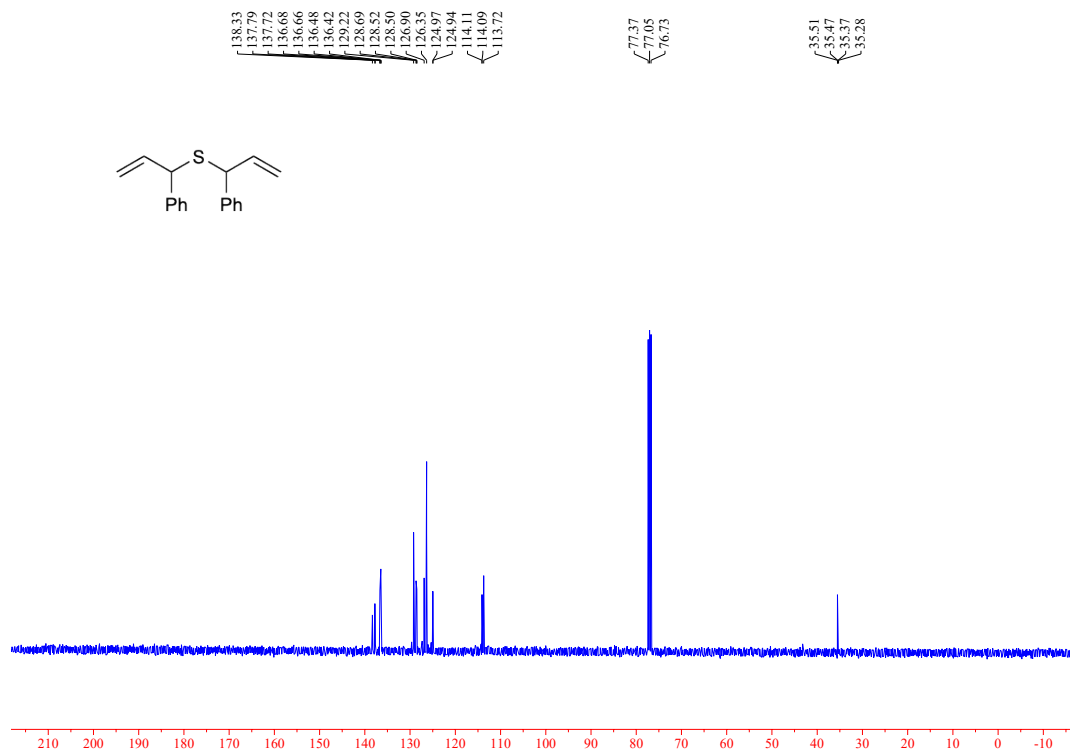
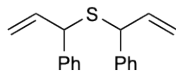
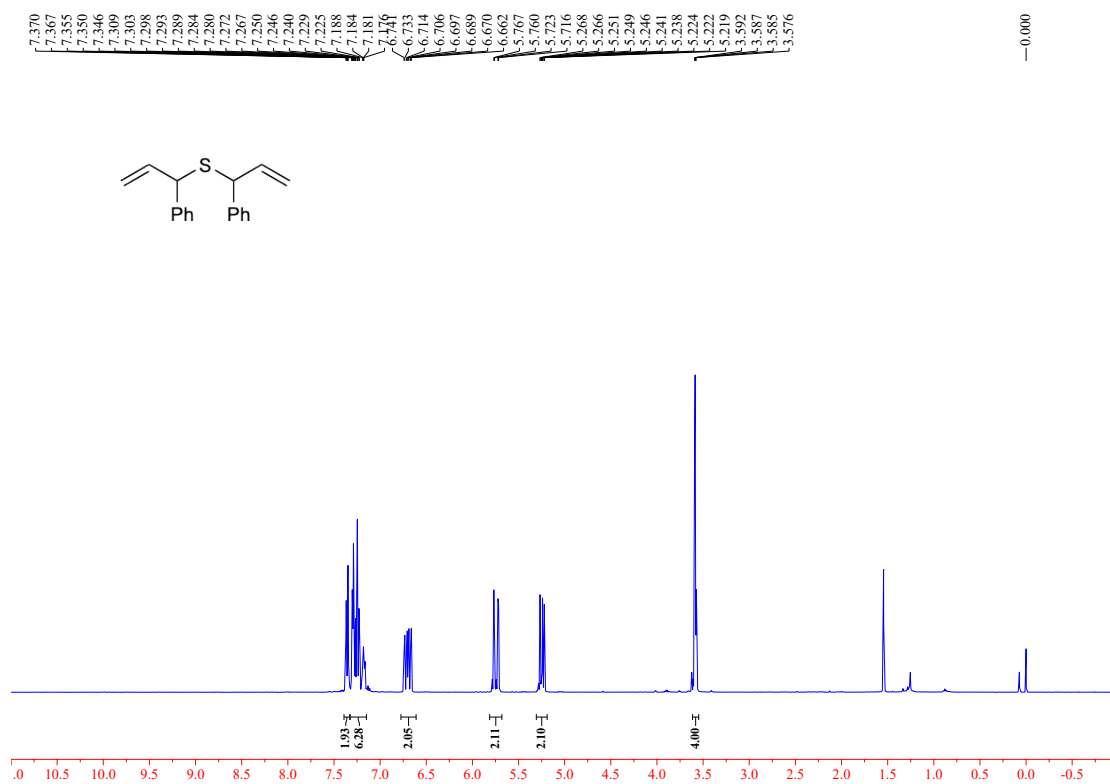
**(E)-N-(but-2-en-1-yl)-N-phenylcyanamide (3aw)**



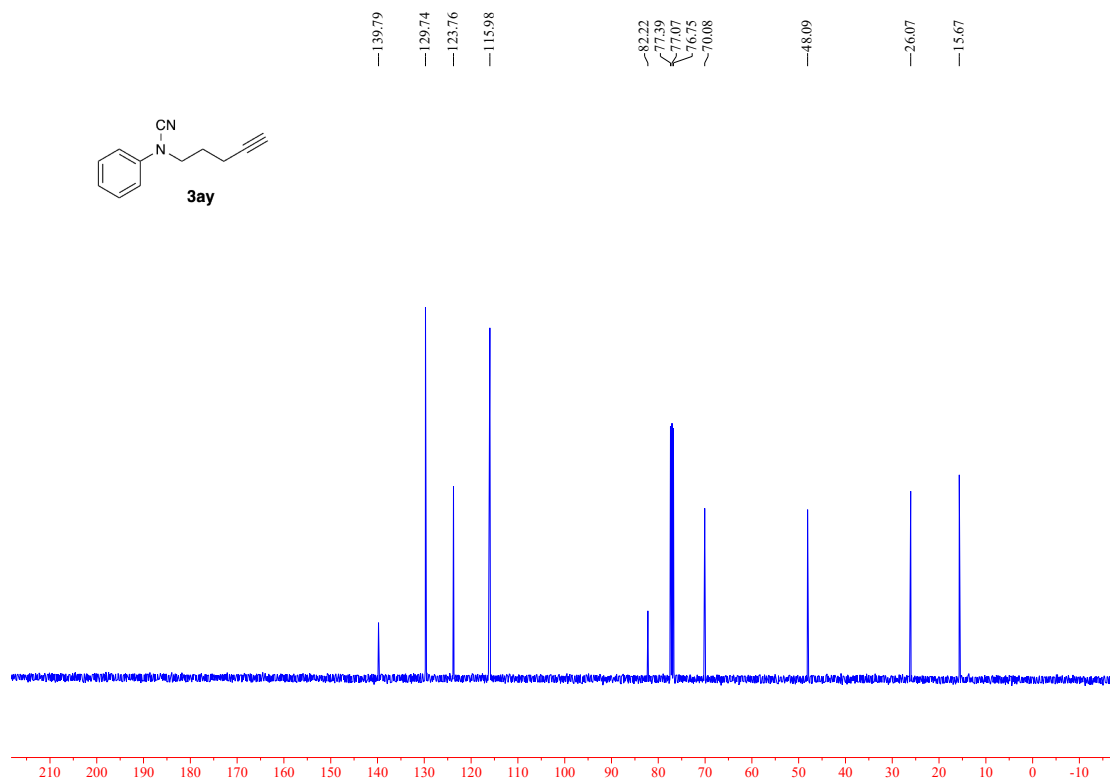
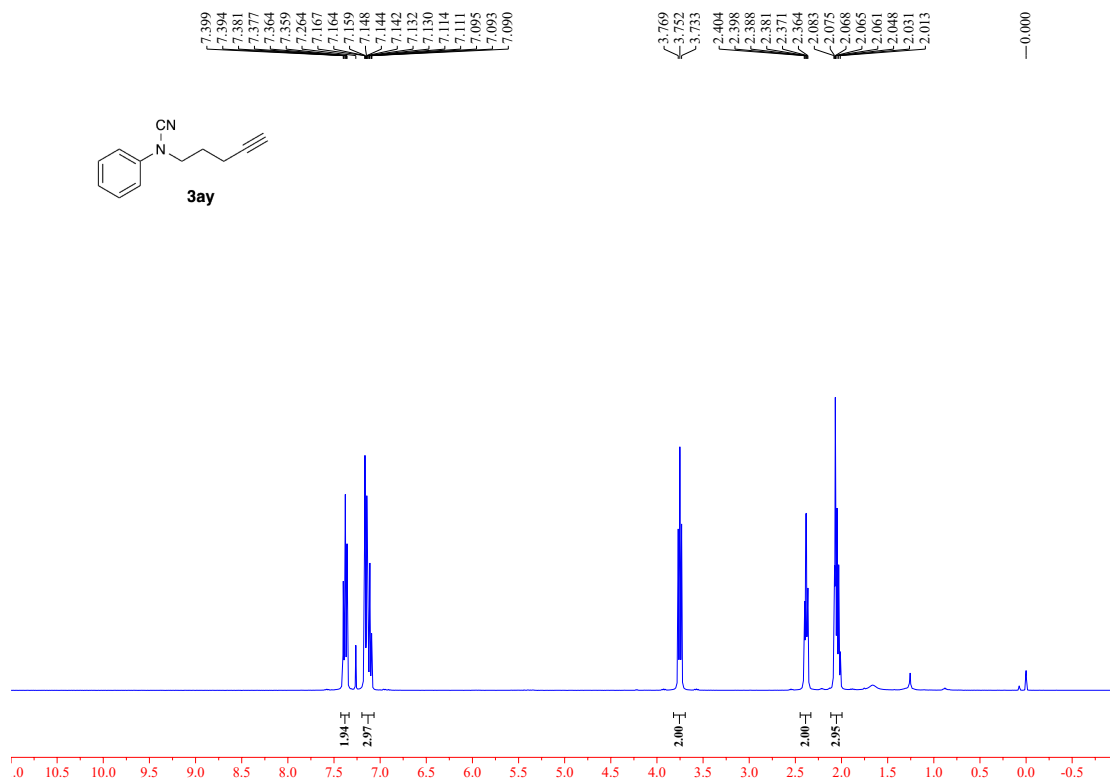
# N-phenyl-N-(1-phenylvinyl)cyanamide (3ax)



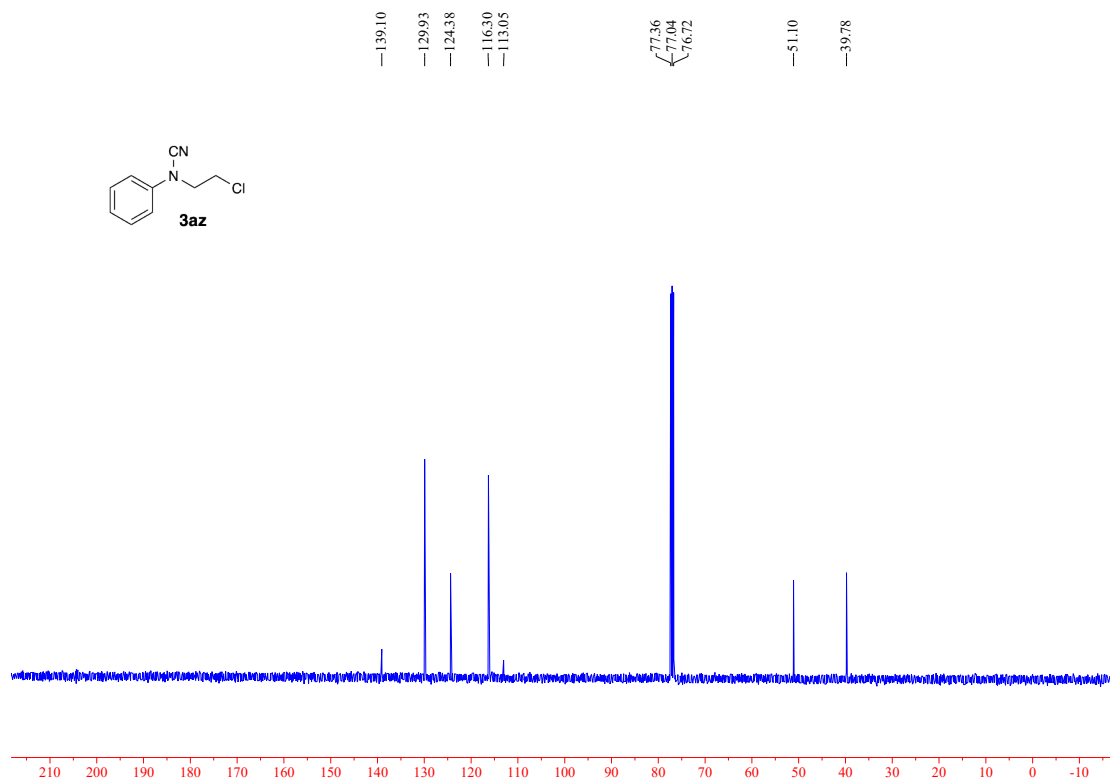
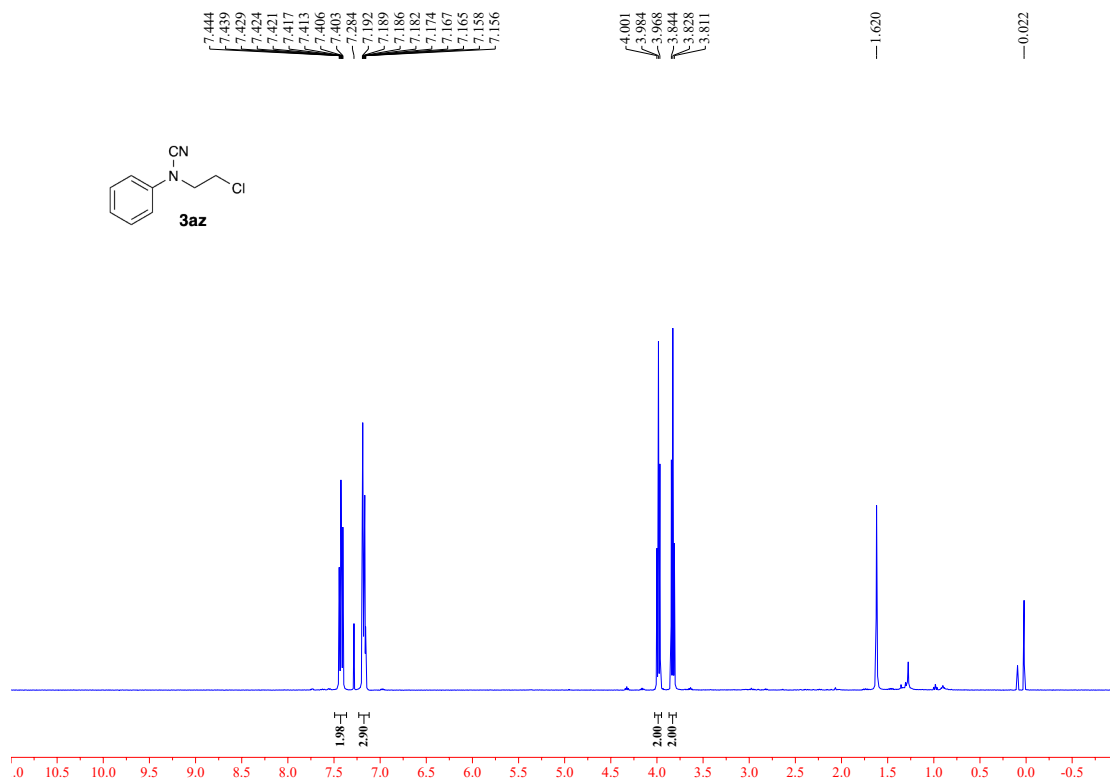
**bis(1-phenylallyl)sulfane (5x)**



# *N*-(pent-4-yn-1-yl)-*N*-phenylcyanamide (**3ay**)

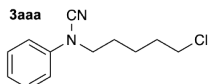


# *N*-(2-chloroethyl)-*N*-phenylcyanamide (3az)

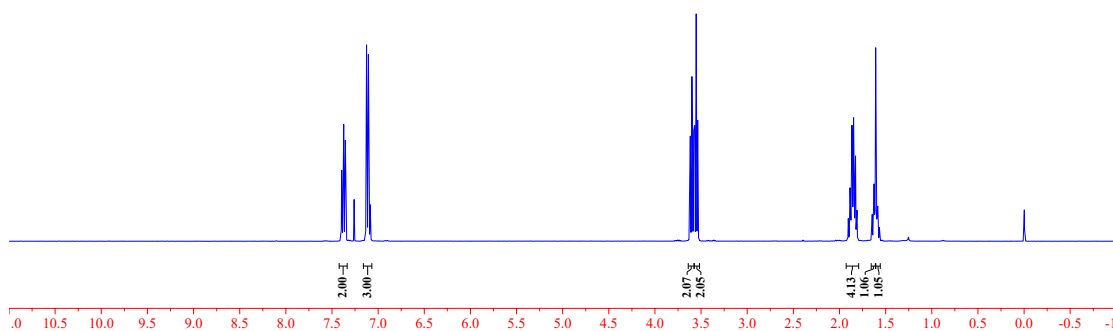


# *N*-(5-chloropentyl)-*N*-phenylcyanamide (3aaa)

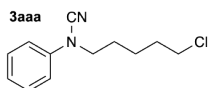
7.395, 7.390, 7.378, 7.373, 7.368, 7.361, 7.355, 7.260, 7.133, 7.126, 7.121, 7.106, 7.104, 7.089, 7.086, 7.084, 3.618, 3.599, 3.581, 3.560, 3.549, 3.537, 3.505, 1.900, 1.886, 1.881, 1.885, 1.887, 1.847, 1.843, 1.840, 1.835, 1.833, 1.829, 1.810, 1.810, 1.647, 1.645, 1.633, 1.626, 1.622, 1.617, 1.608, 1.594, 1.584, 1.580, 1.583, -0.003



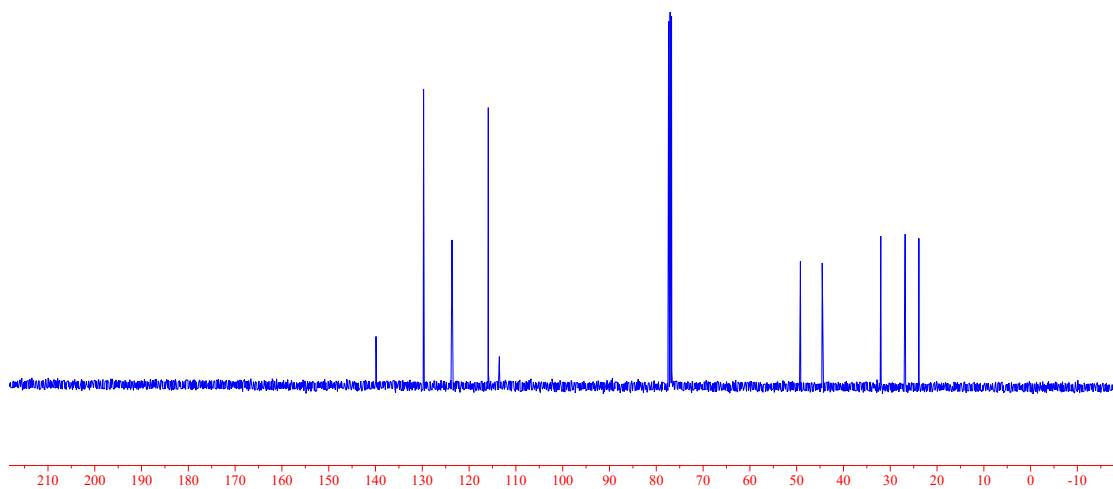
Chemical Formula: C<sub>12</sub>H<sub>15</sub>ClN<sub>2</sub>  
Exact Mass: 222.0924



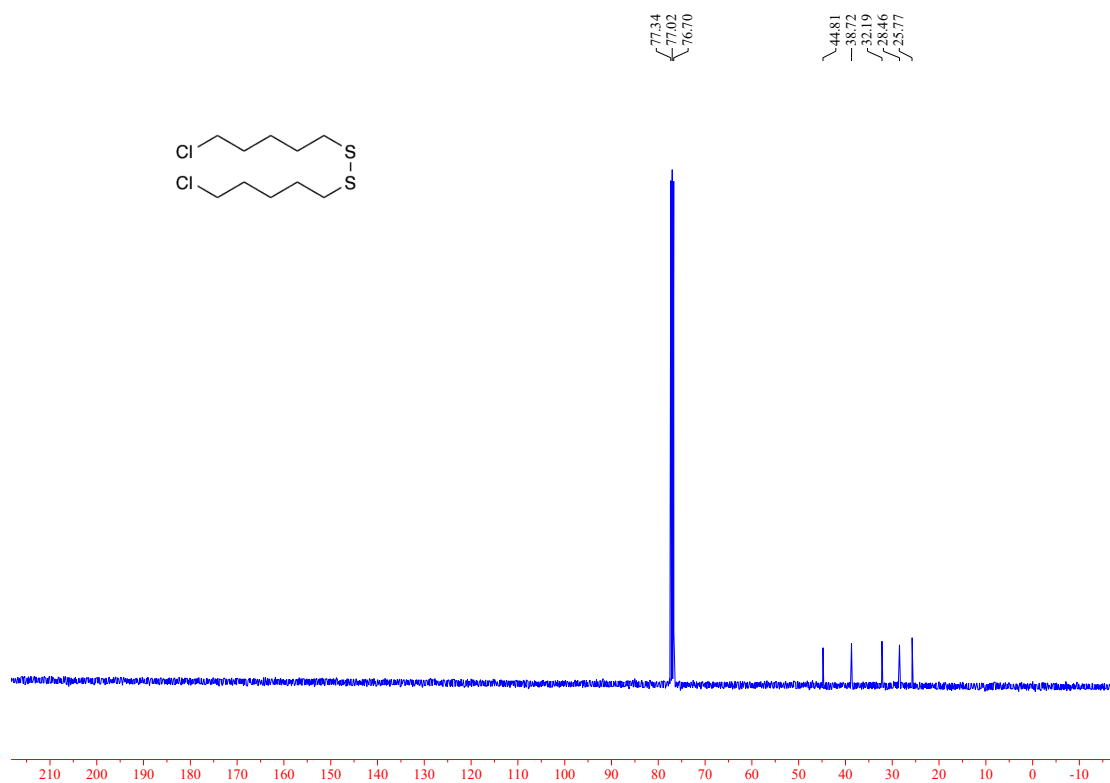
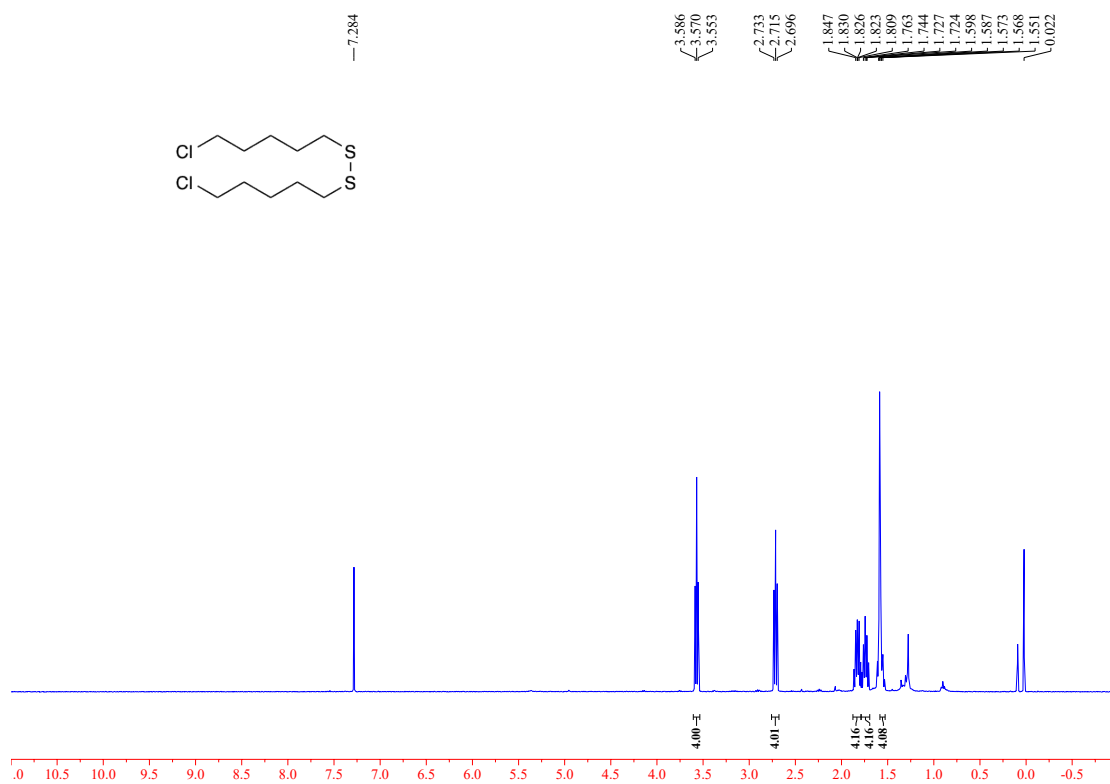
139.885, 129.731, 123.654, 115.894, 113.540, 77.371, 77.053, 76.736, 49.209, 44.539, 32.018, 26.818, 23.874



Chemical Formula: C<sub>12</sub>H<sub>15</sub>ClN<sub>2</sub>  
Exact Mass: 222.0924

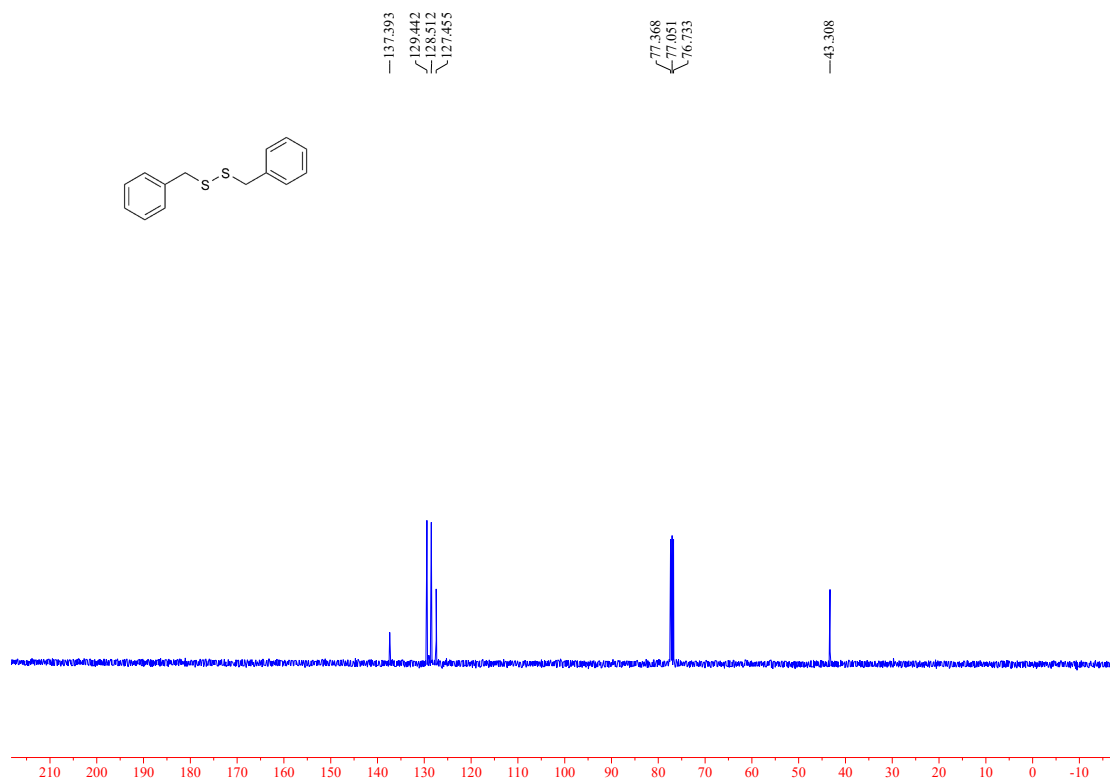
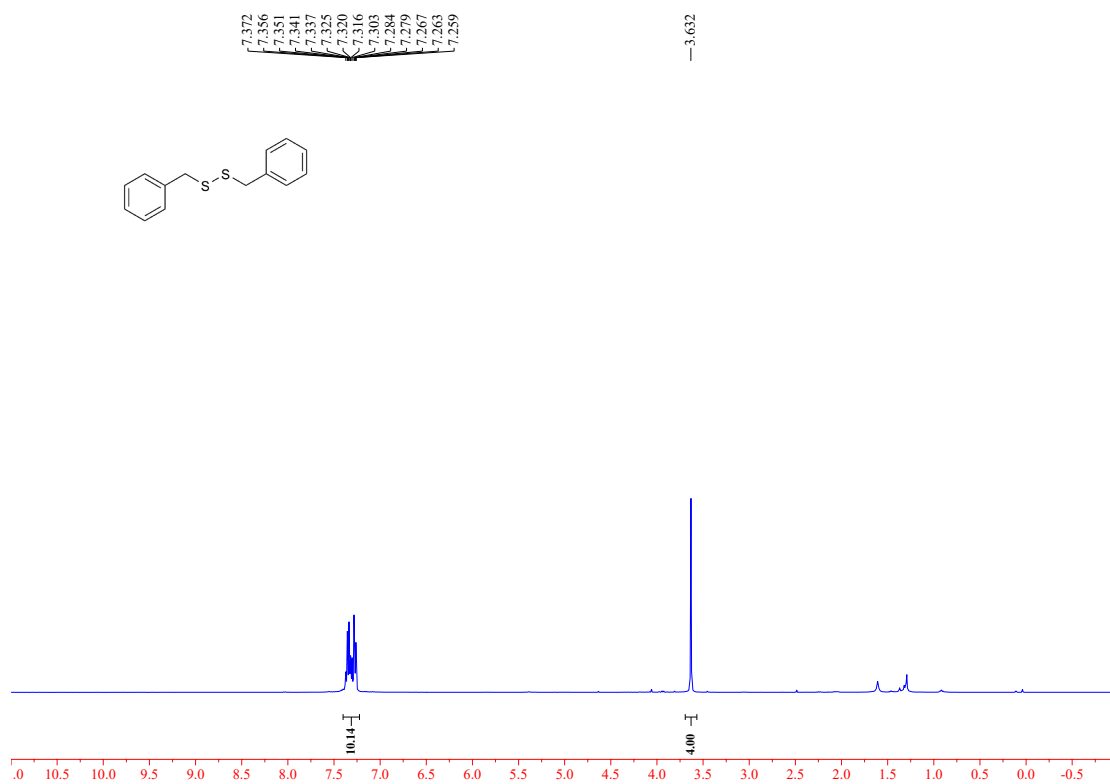


# 1,2-bis(5-chloropentyl)disulfane (4aa)

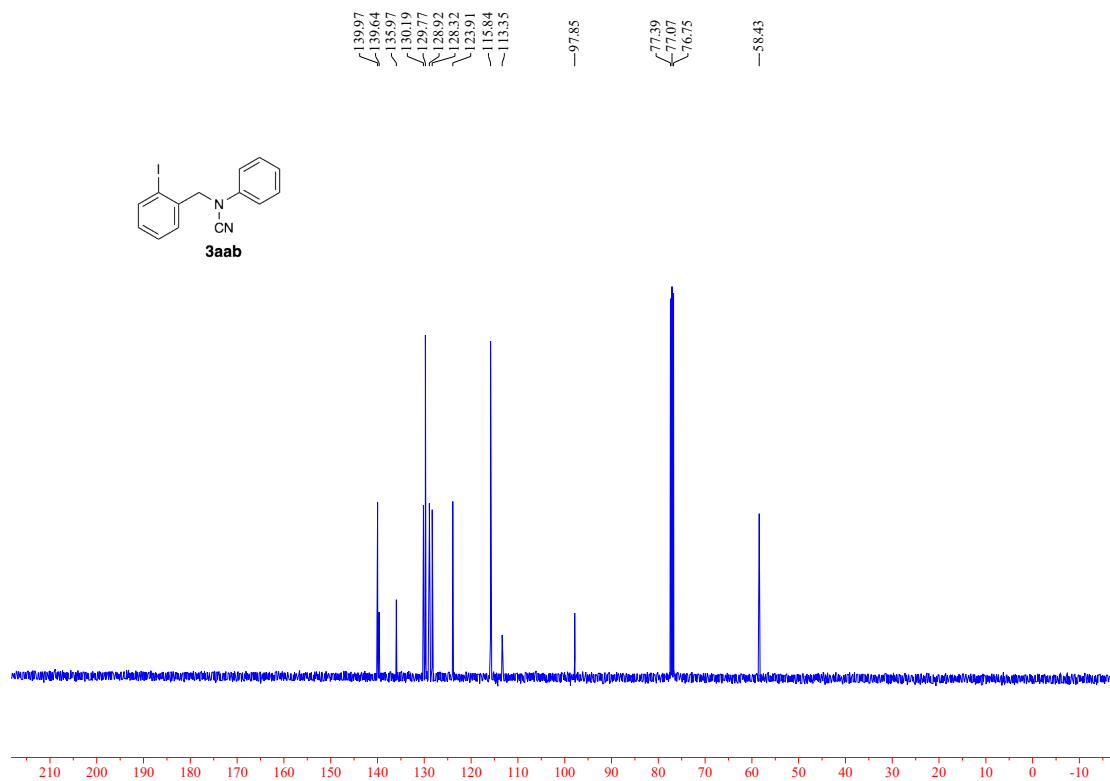
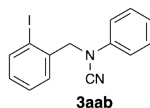
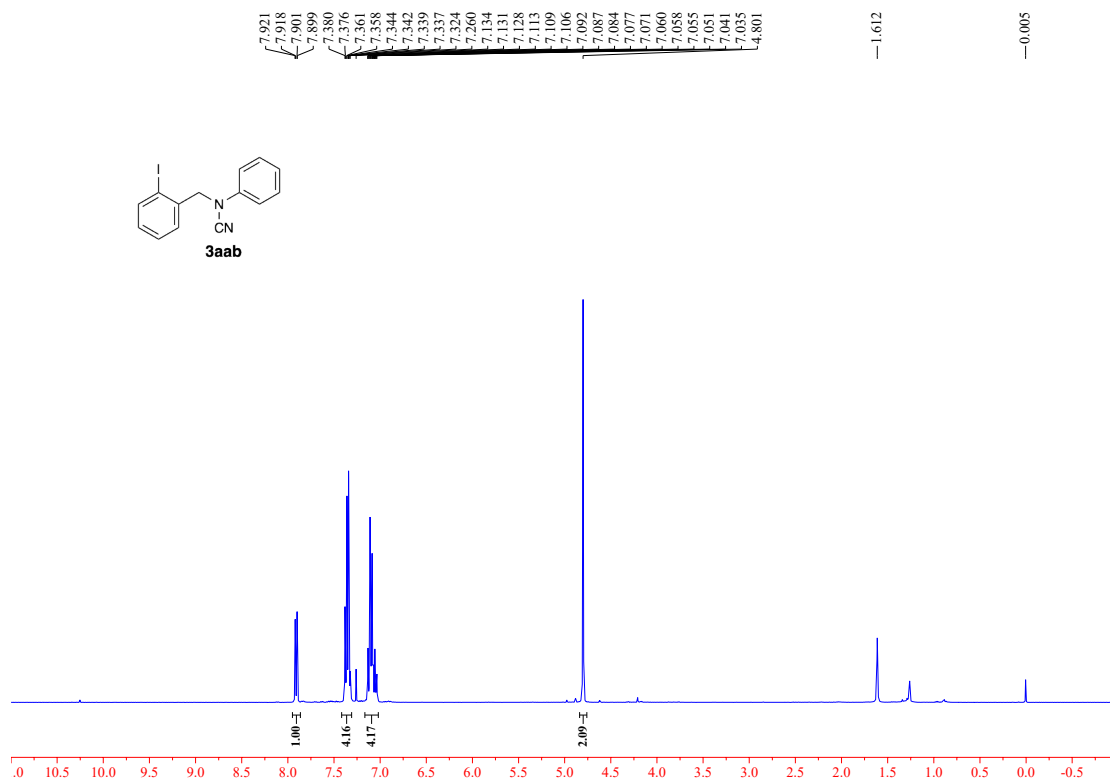
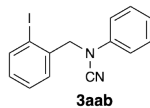




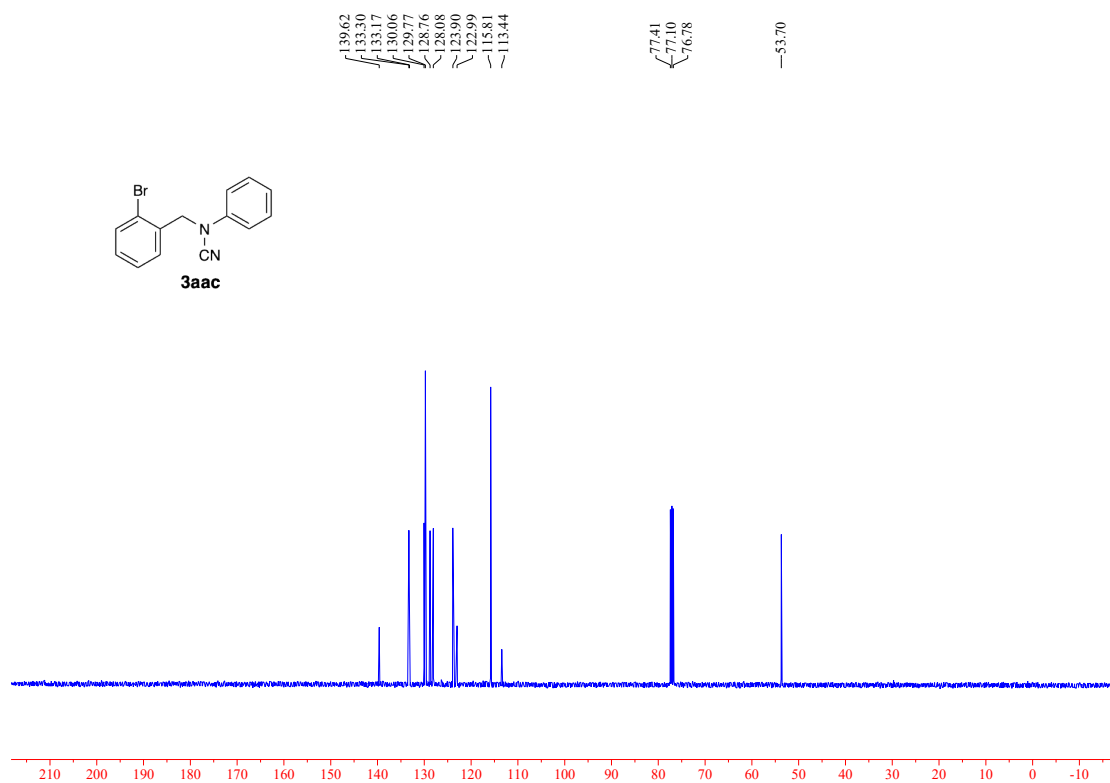
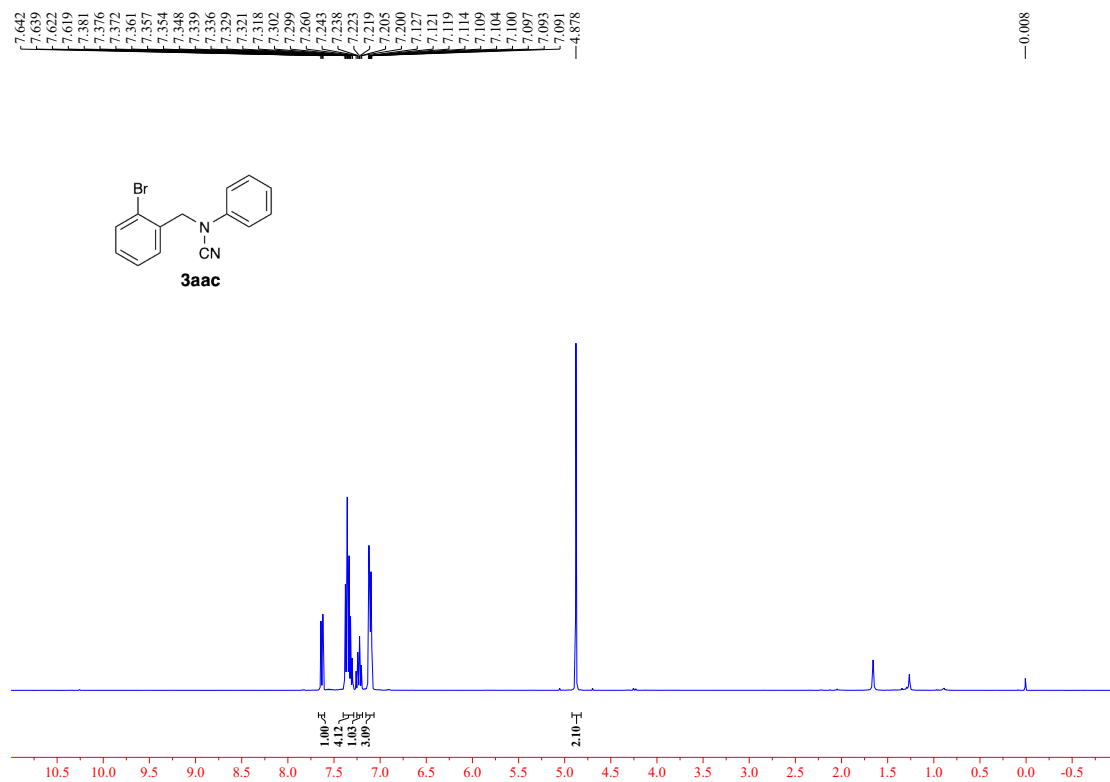
# 1,2-dibenzylsulfane (4i)



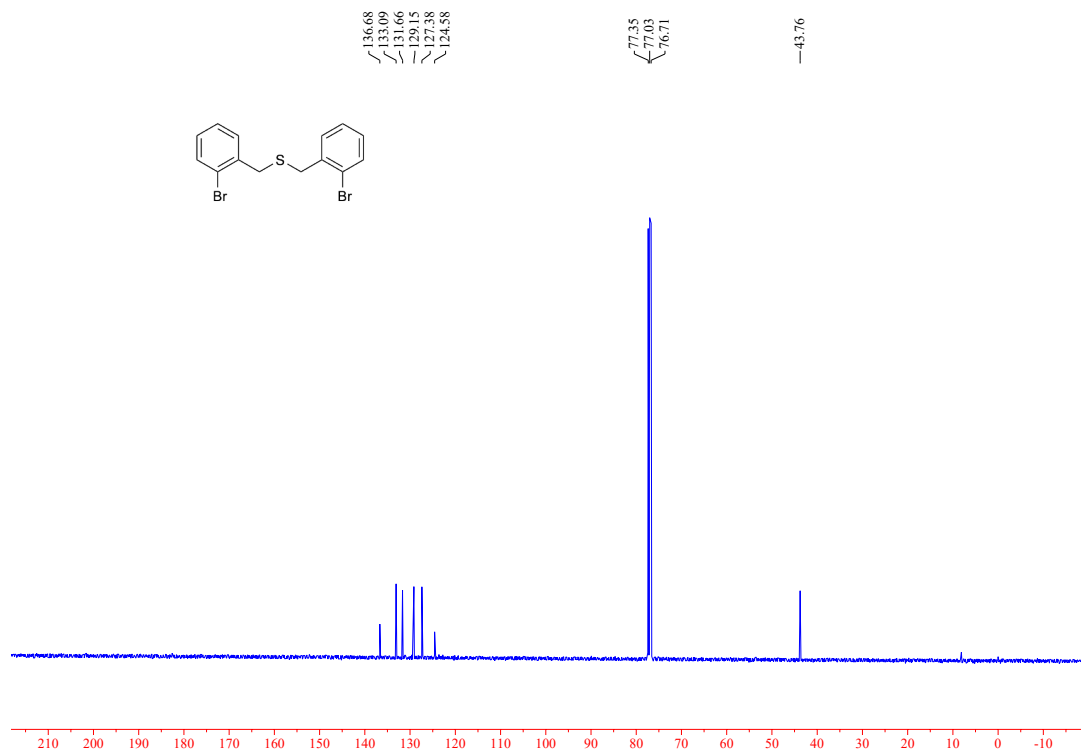
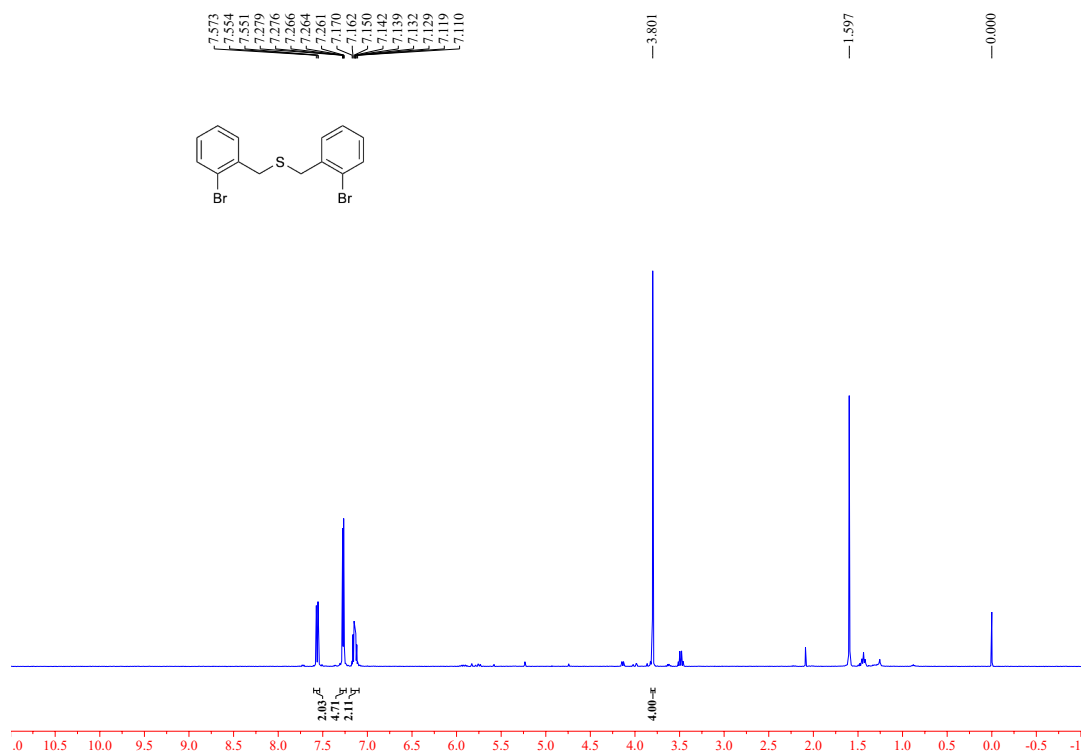
***N*-(2-iodobenzyl)-*N*-phenylcyanamide (3aab)**



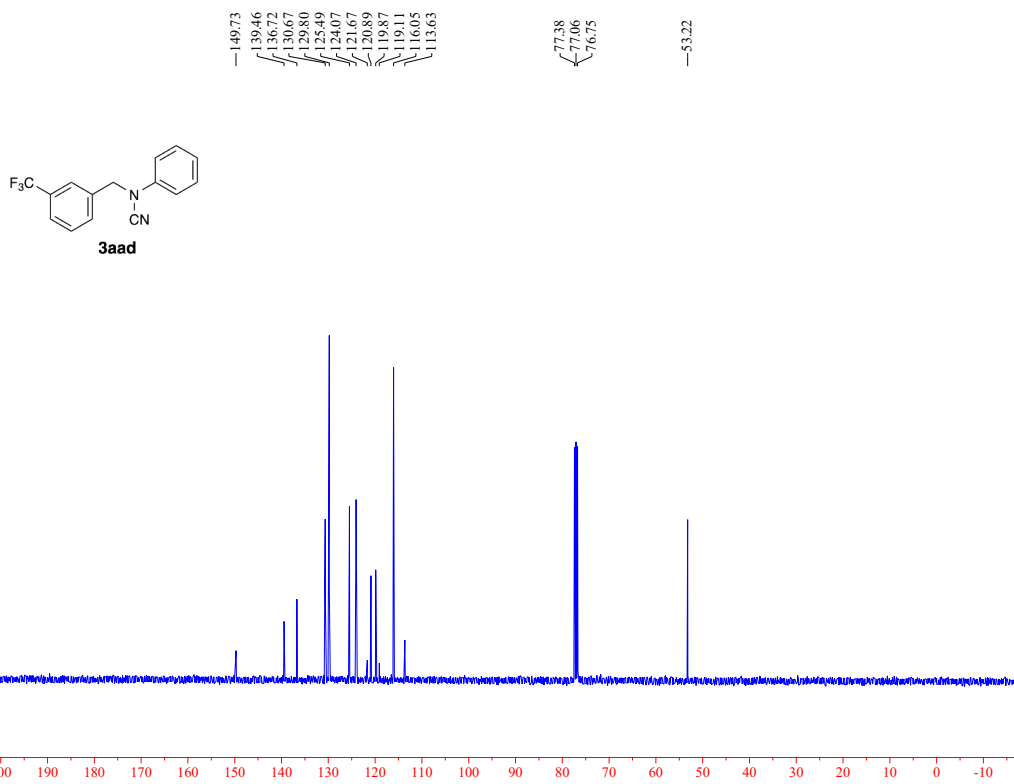
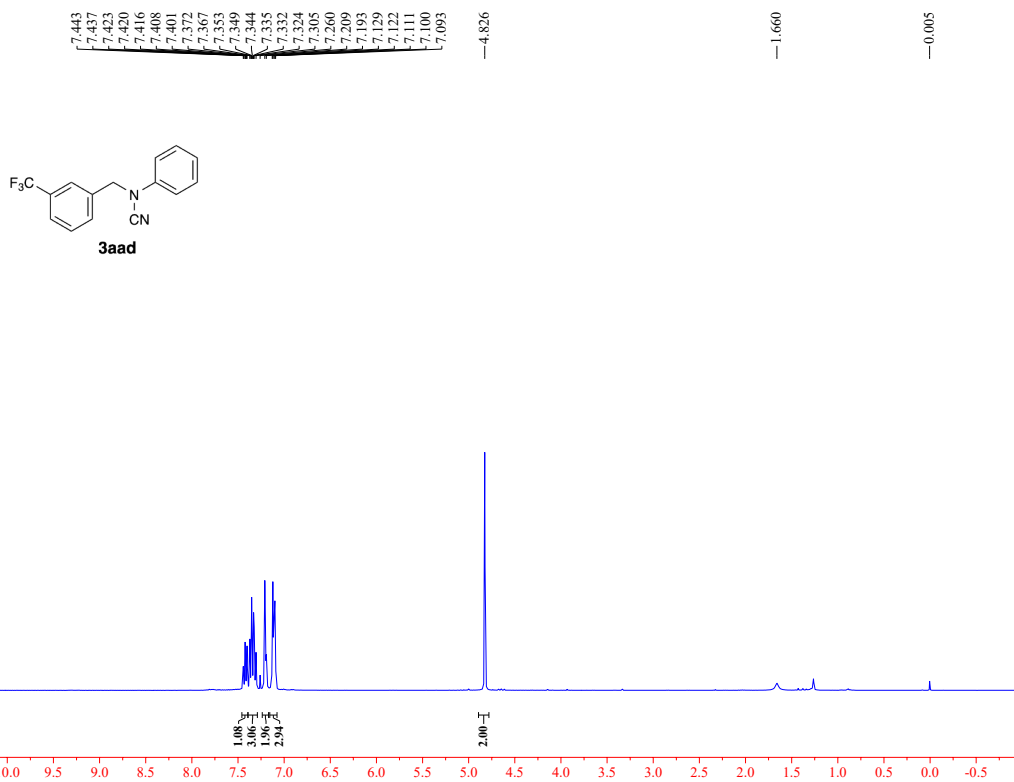
# *N*-(2-bromobenzyl)-*N*-phenylcyanamide (3aac)



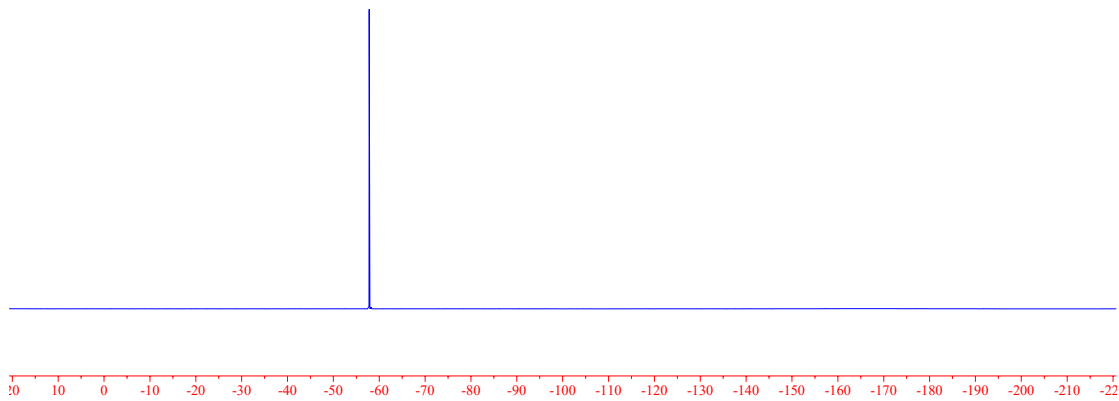
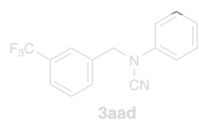
**bis(2-bromobenzyl)sulfane (5ac)**



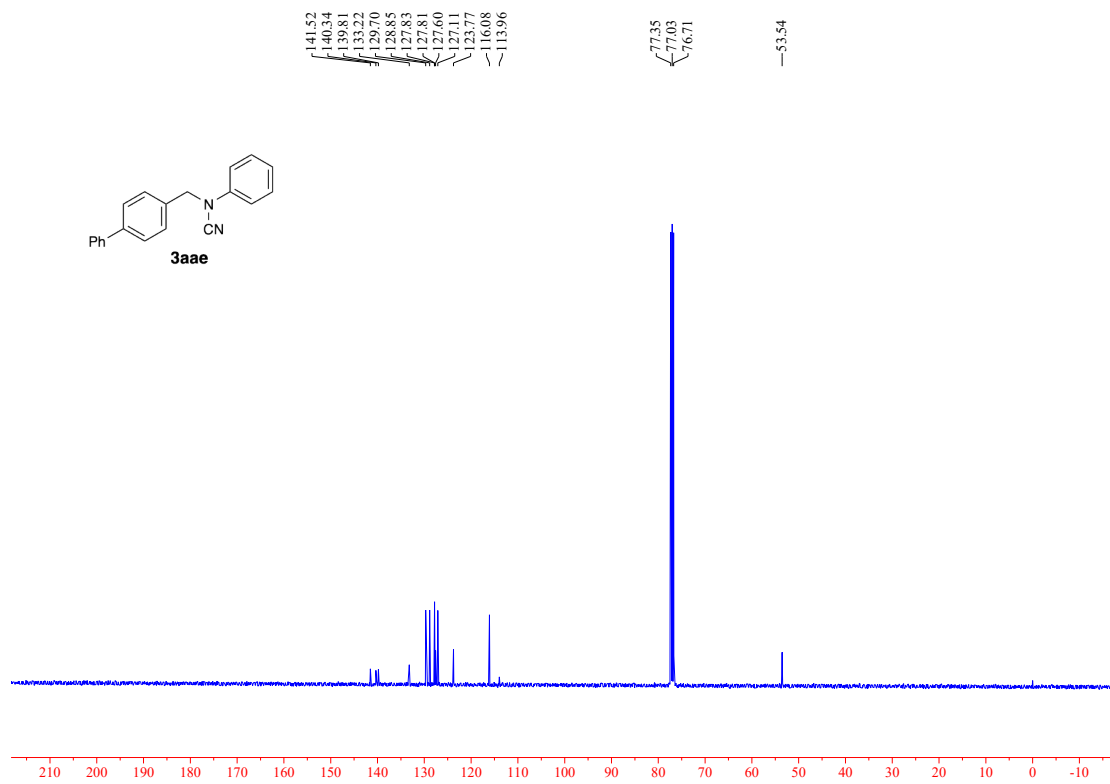
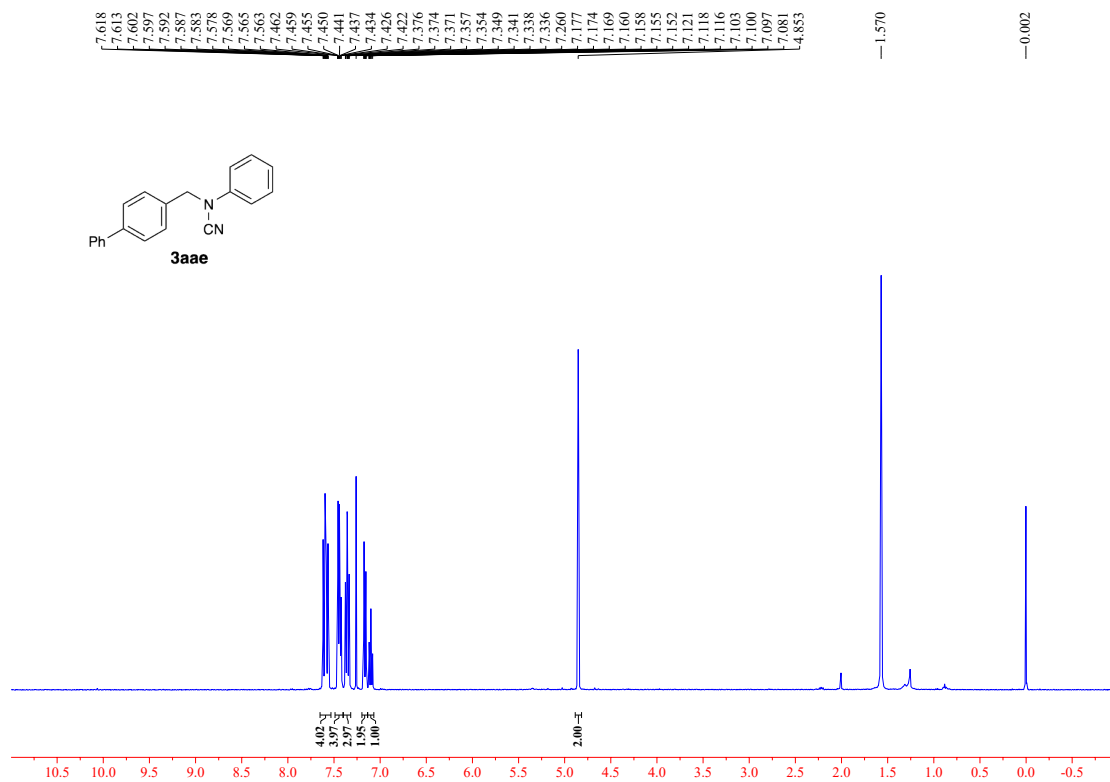
***N*-phenyl-*N*-(3-(trifluoromethyl)benzyl)cyanamide (3aad)**



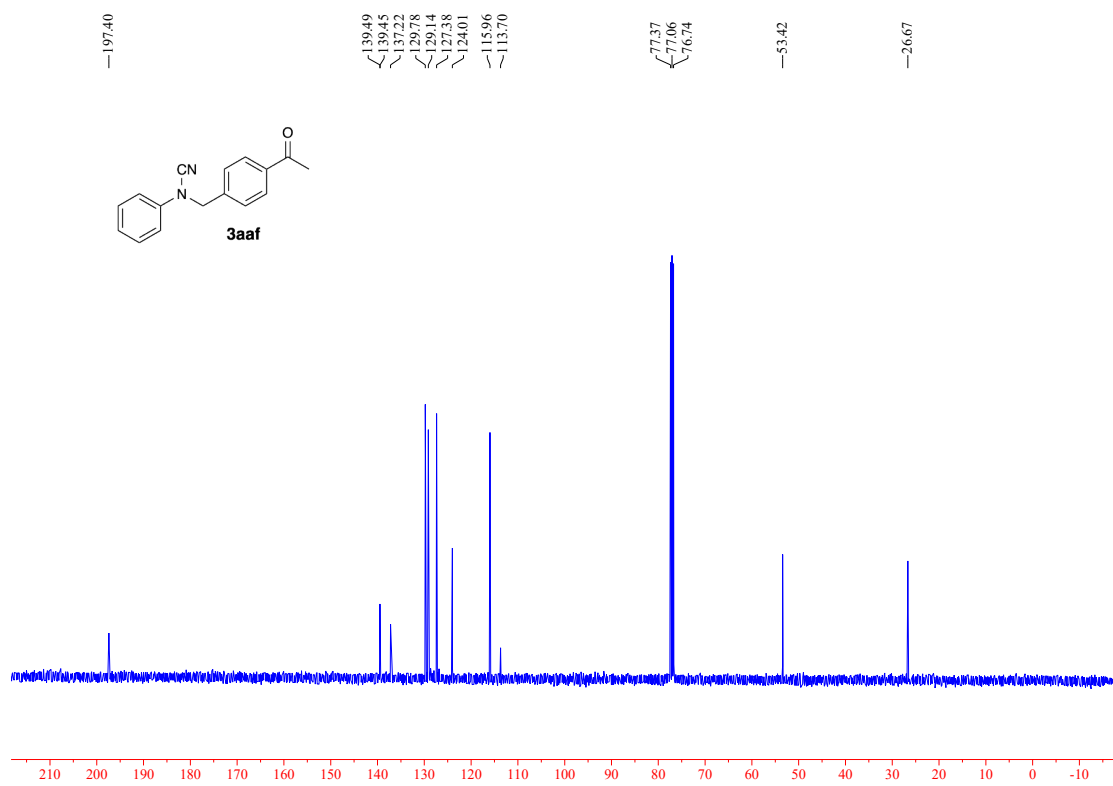
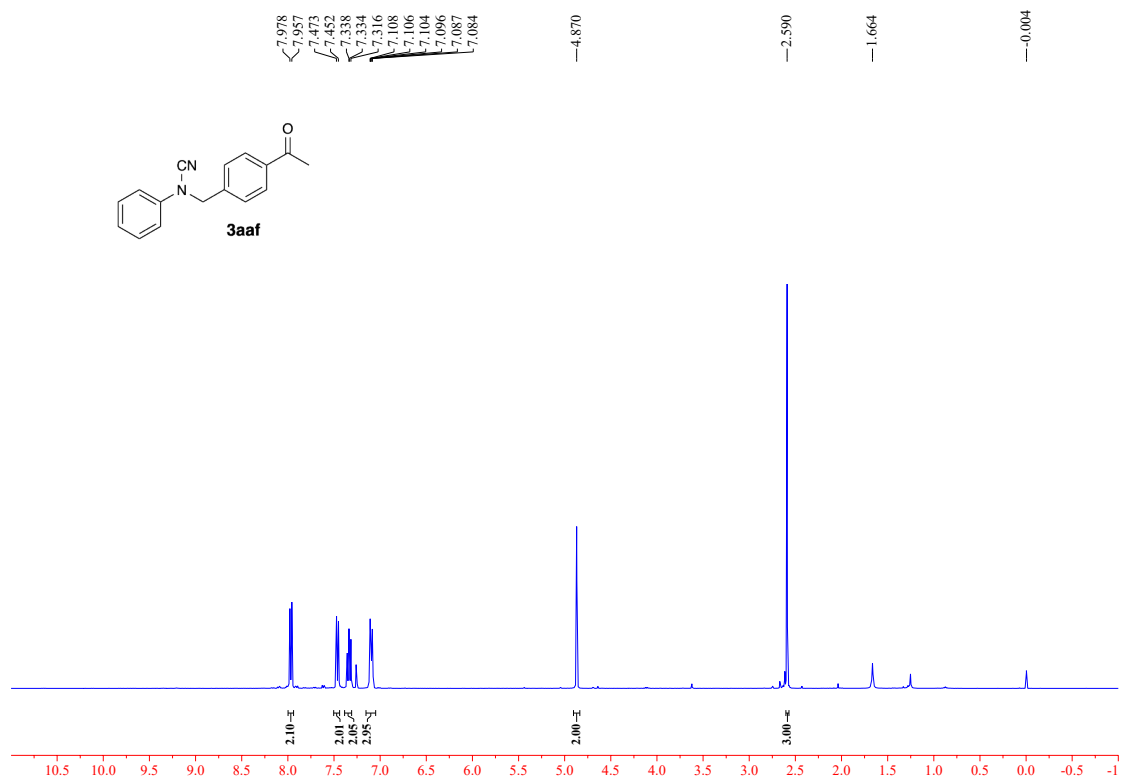
—57.802



***N*-([1,1'-biphenyl]-4-ylmethyl)-*N*-phenylcyanamide (3aae)**

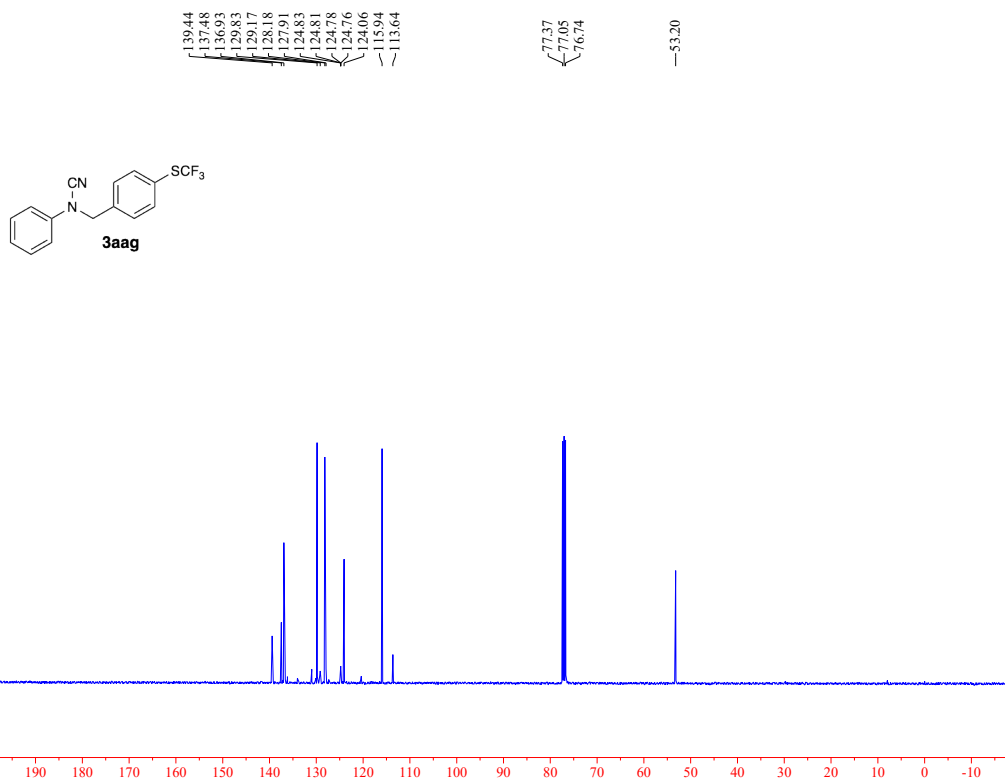
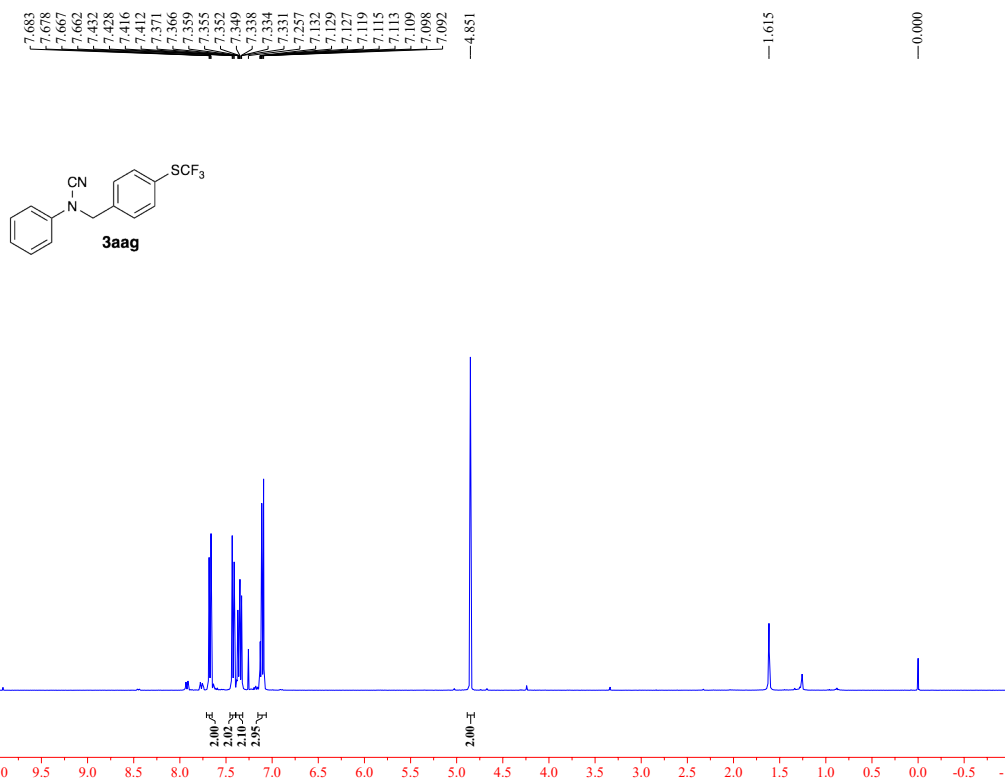


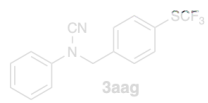
# *N*-(4-acetylbenzyl)-*N*-phenylcyanamide (3aaf)





***N*-phenyl-*N*-(4-((trifluoromethyl)thio)benzyl)cyanamide (3aag)**

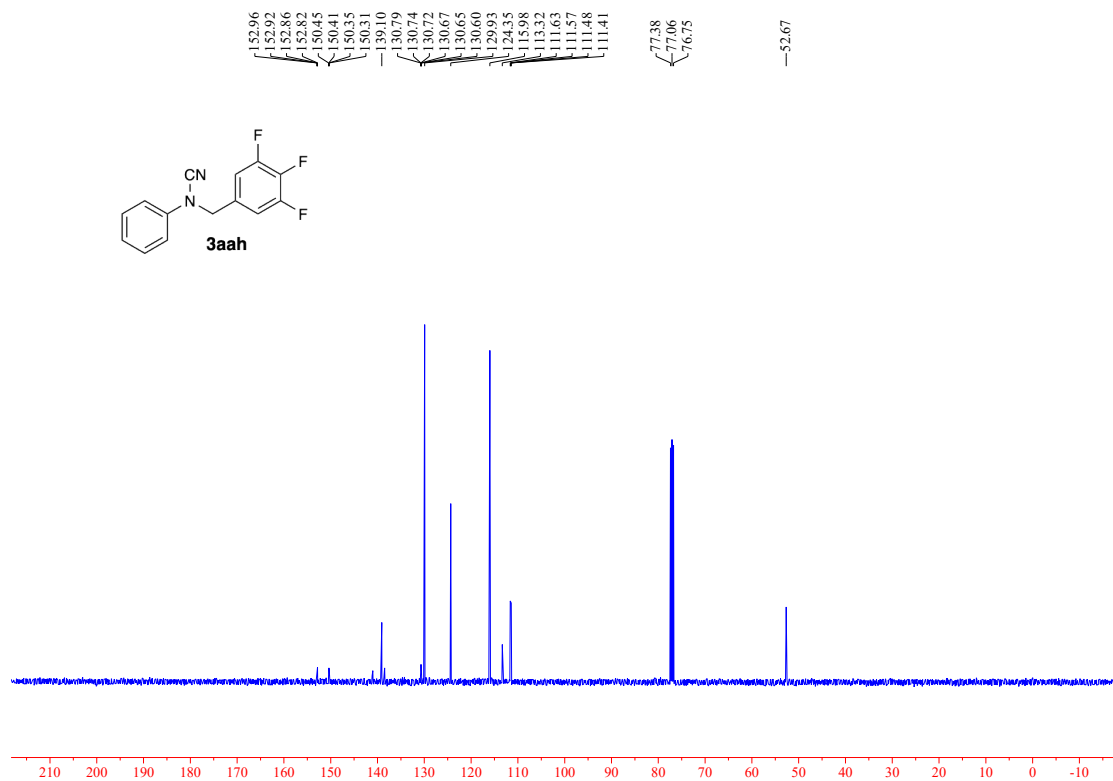
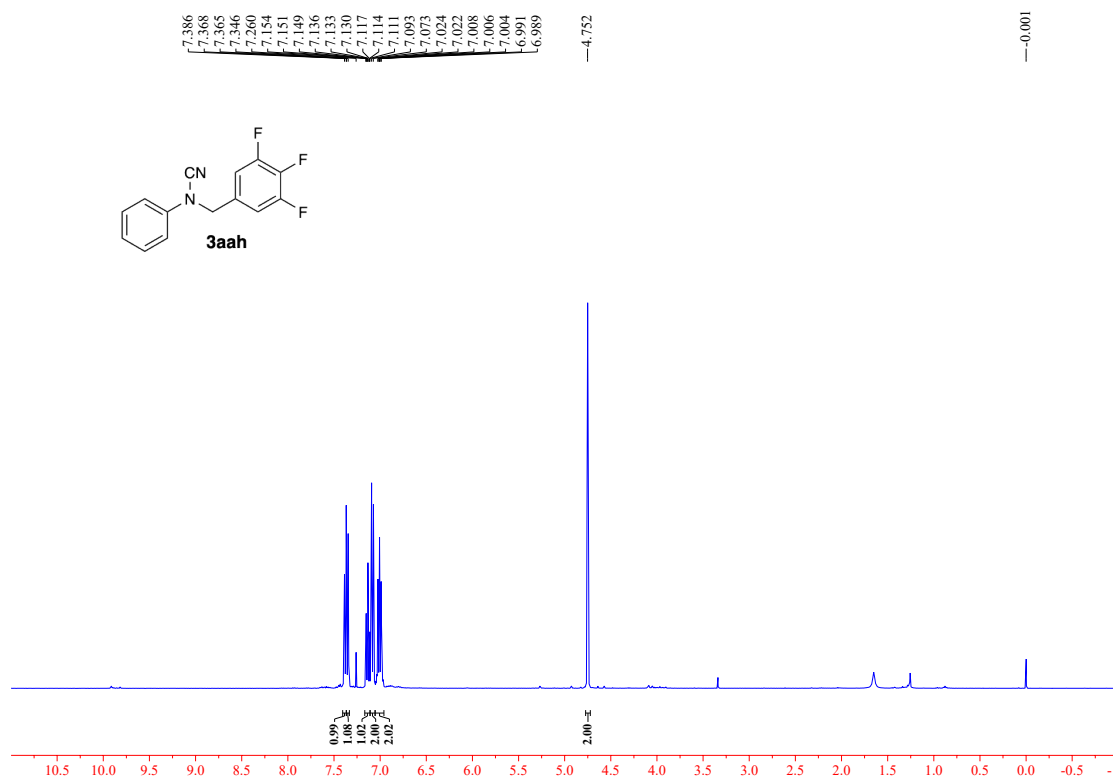


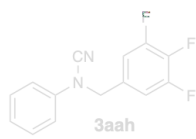


—42.49



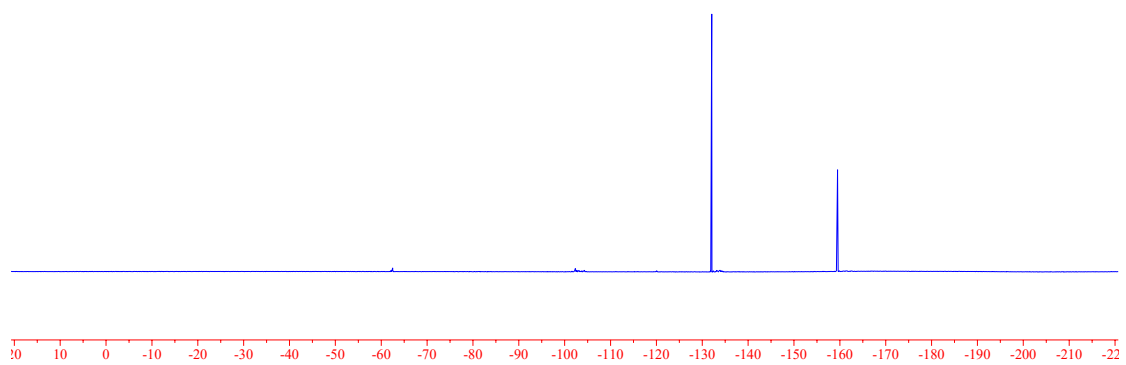
# *N*-phenyl-*N*-(3,4,5-trifluorobenzyl)cyanamide (3aah)





131.98  
132.00  
132.04  
132.06

159.43  
159.44  
159.46  
159.48  
159.50  
159.51  
159.54  
159.55  
159.57

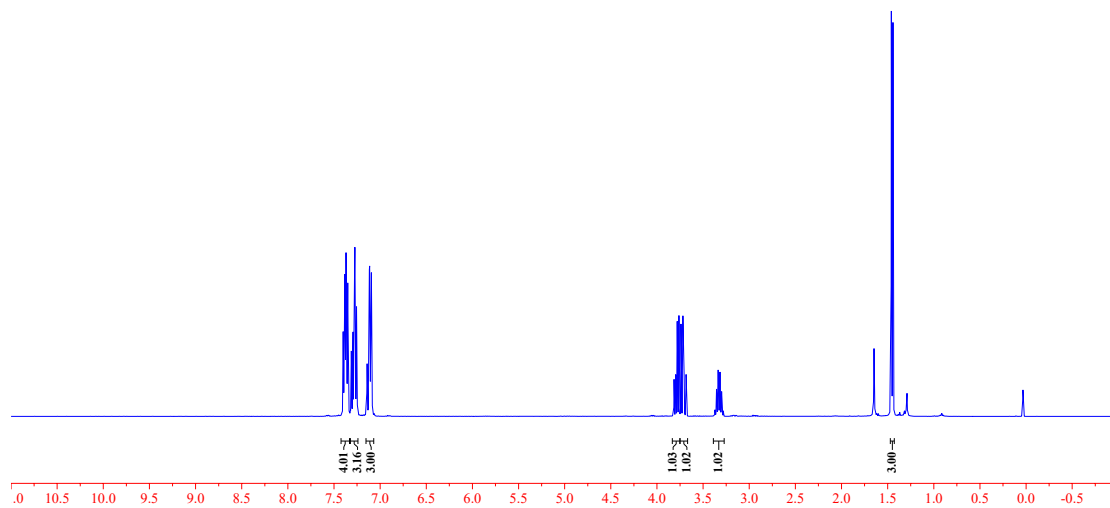
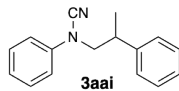


# N-phenyl-N-(2-phenylpropyl)cyanamide (3aai)

7.401  
7.398  
7.390  
7.387  
7.382  
7.379  
7.374  
7.370  
7.366  
7.360  
7.355  
7.351  
7.349  
7.342  
7.312  
7.308  
7.294  
7.284  
7.277  
7.273  
7.267  
7.260  
7.256  
7.253  
7.141  
7.138  
7.123  
7.121  
7.117  
7.114  
7.111  
7.108  
7.104  
7.101  
7.098  
7.095  
3.872  
3.871  
3.797  
3.780  
3.762  
3.739  
3.719  
3.705  
3.684  
3.354  
3.337  
3.334  
3.319  
3.316  
3.299

1.460  
1.443

-0.034



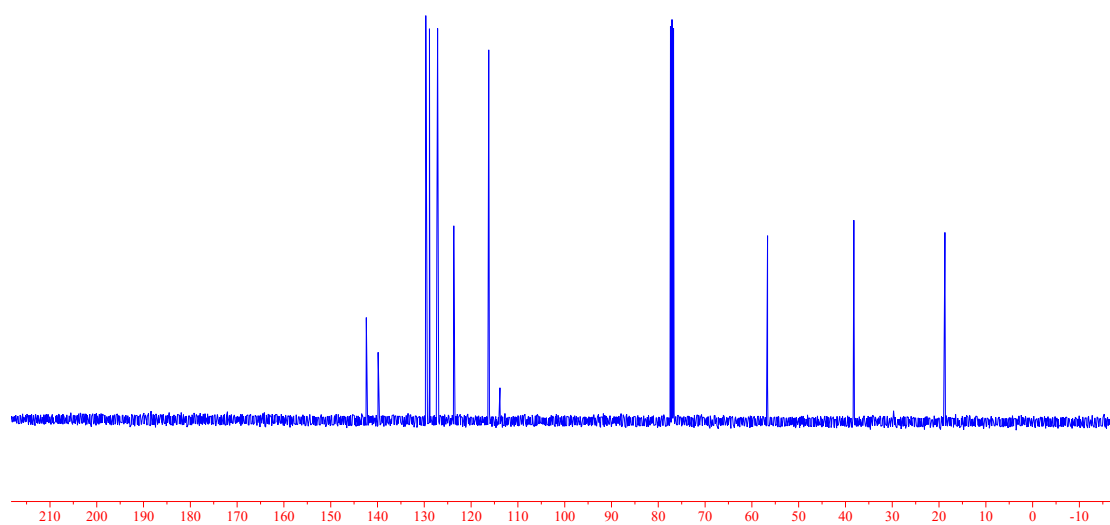
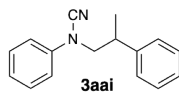
142.39  
139.86  
129.69  
128.90  
127.31  
127.17  
126.60  
126.22  
113.84

77.39  
77.07  
76.75

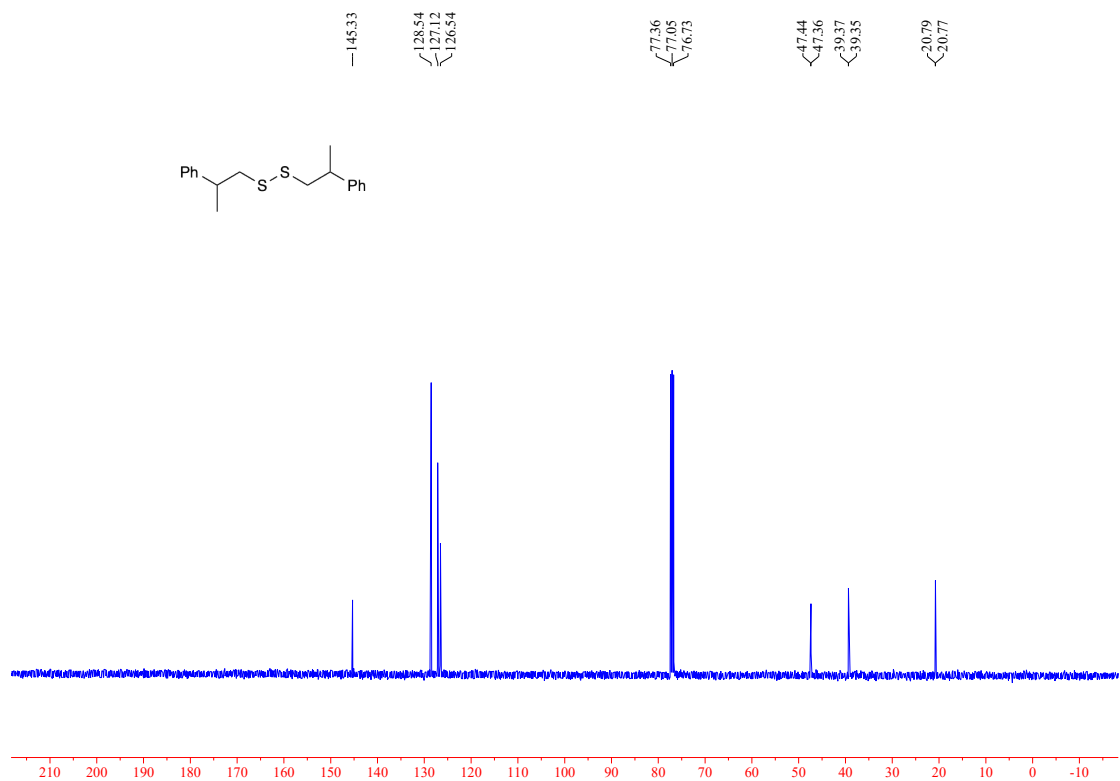
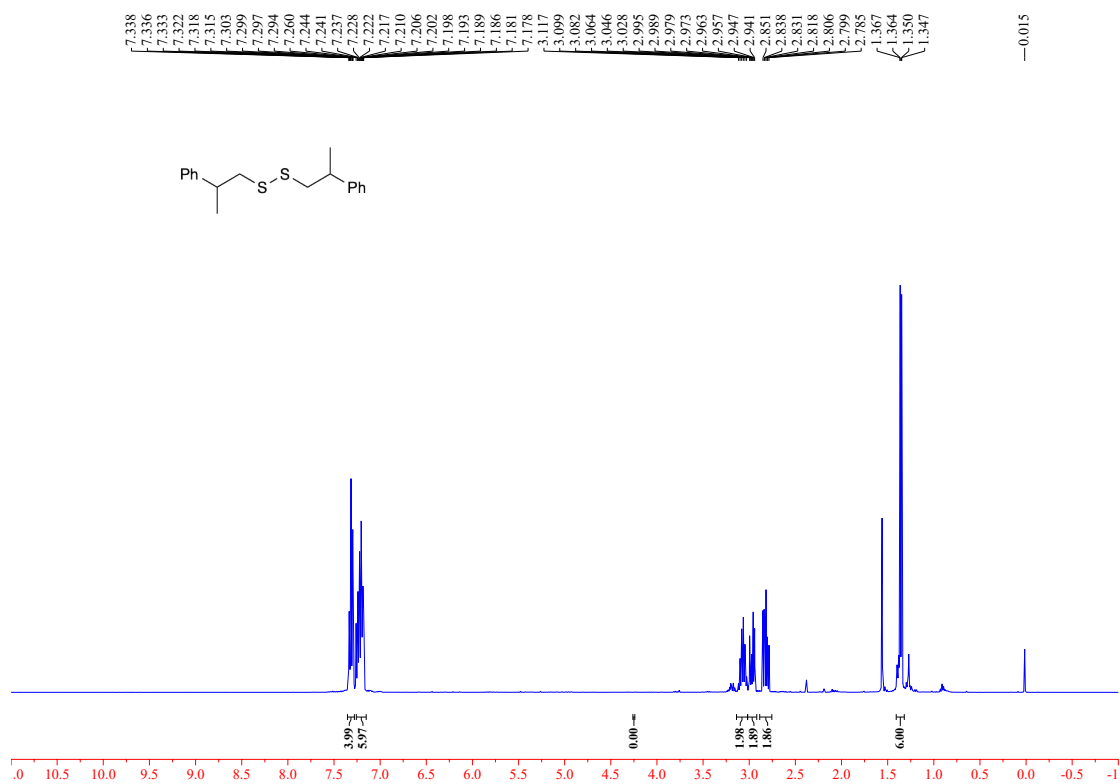
-56.66

-38.20

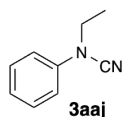
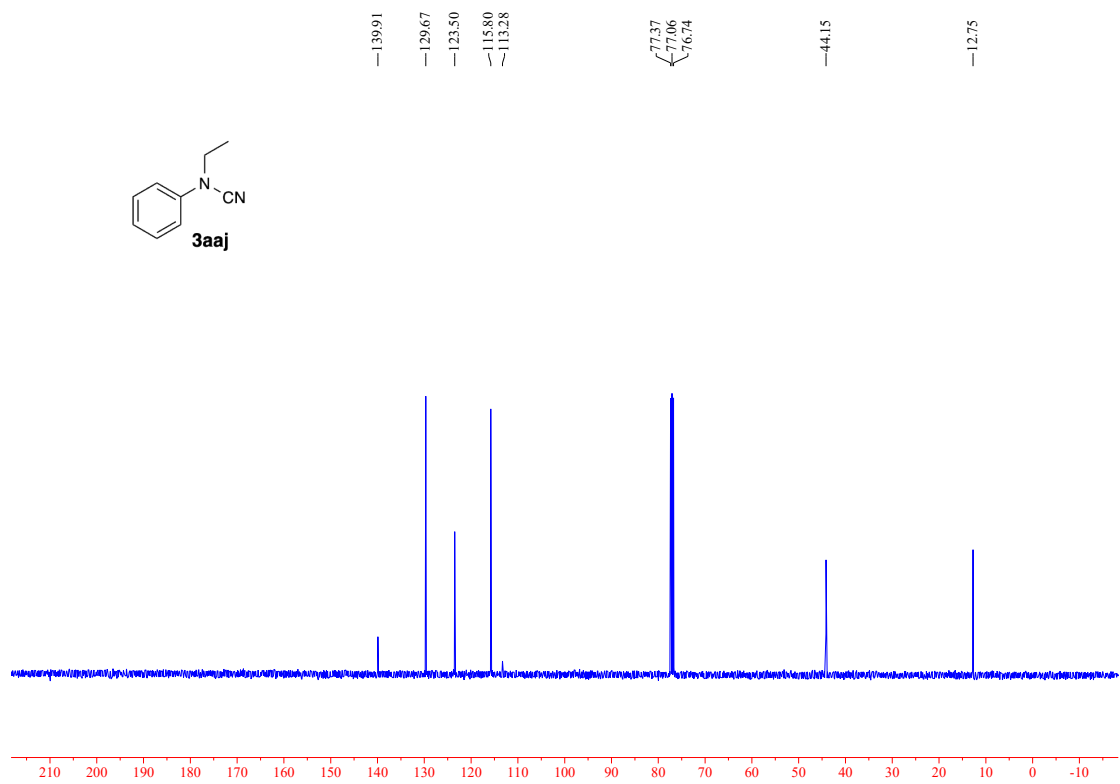
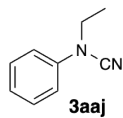
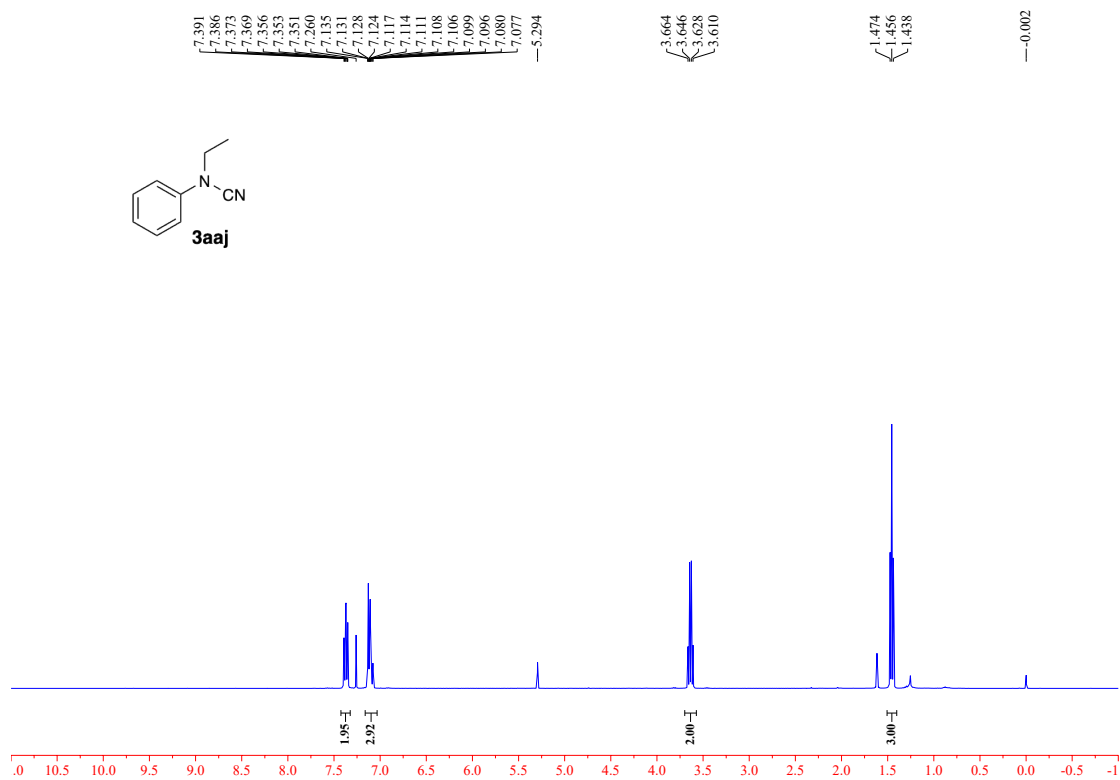
-18.74



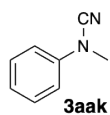
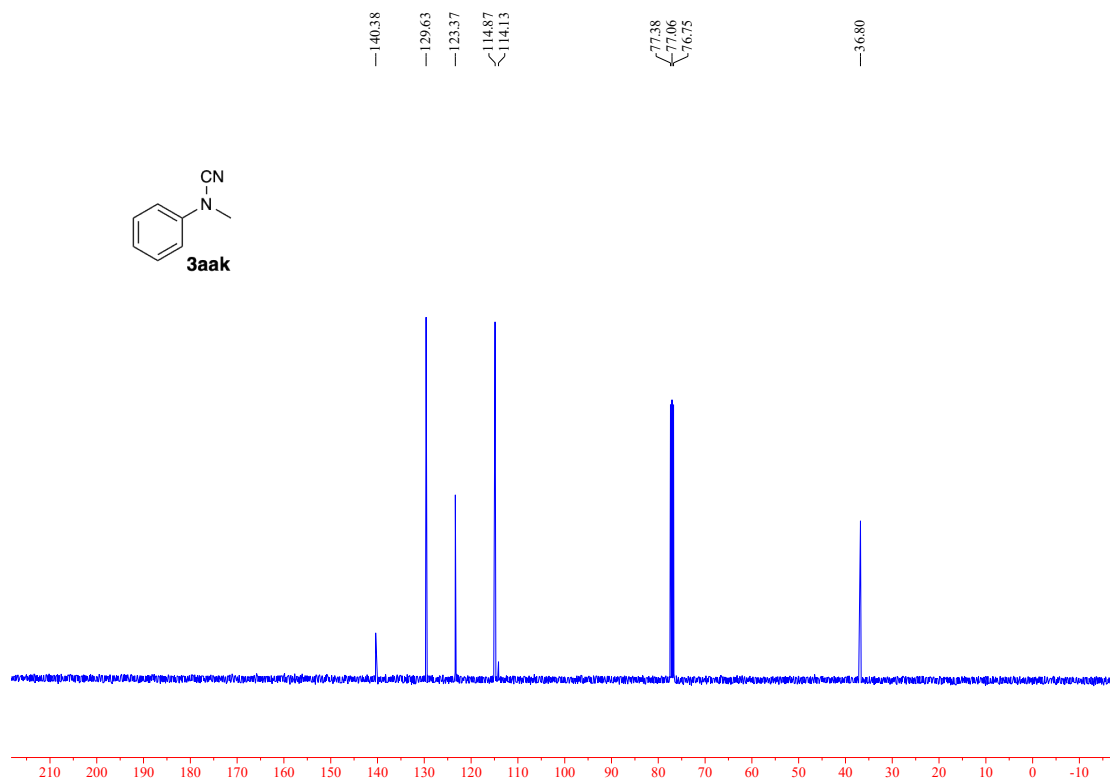
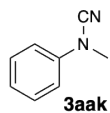
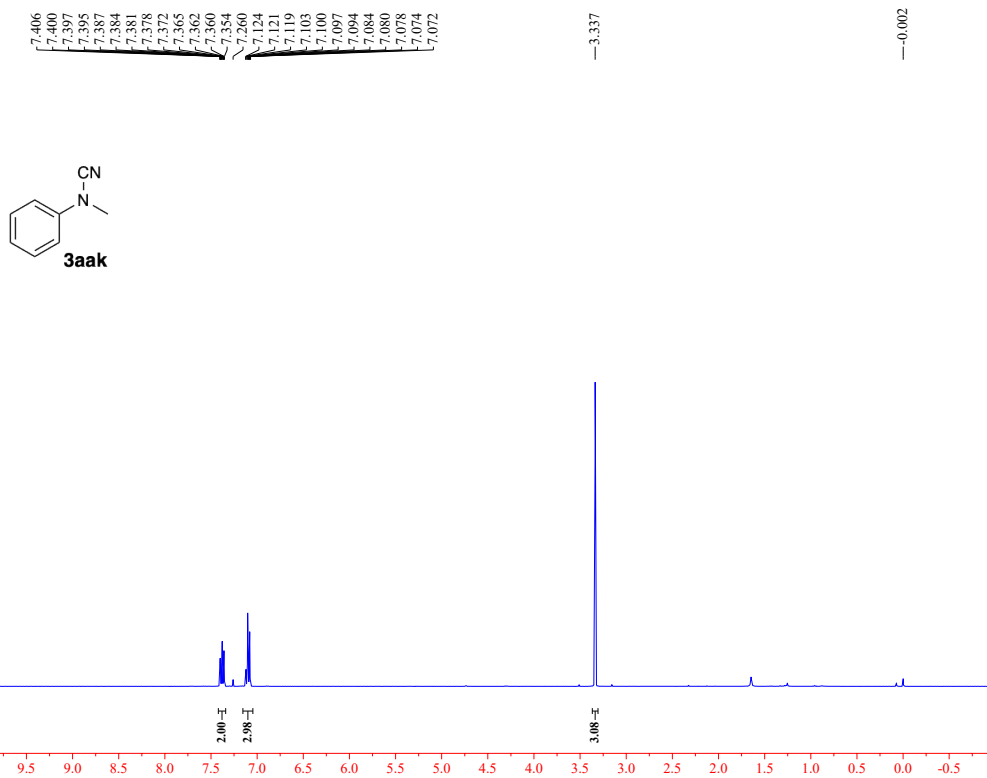
# 1,2-bis(2-phenylpropyl)disulfane (4ai)



# N-ethyl-N-phenylcyanamide (3aaj)

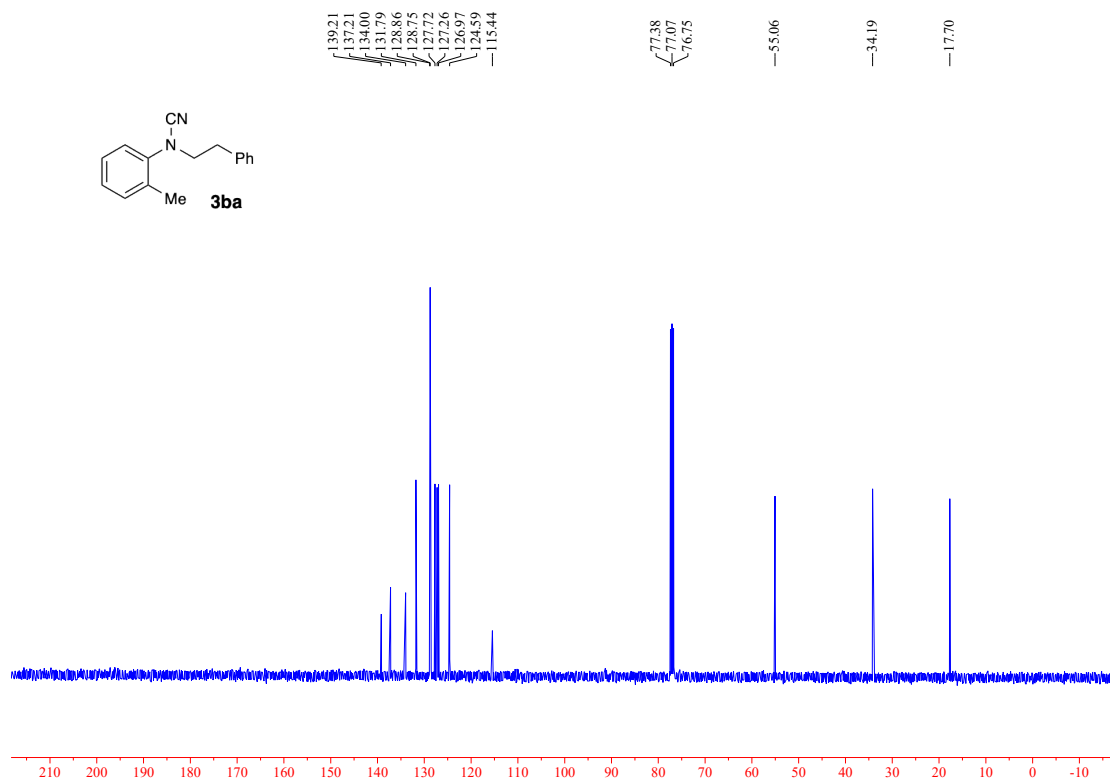
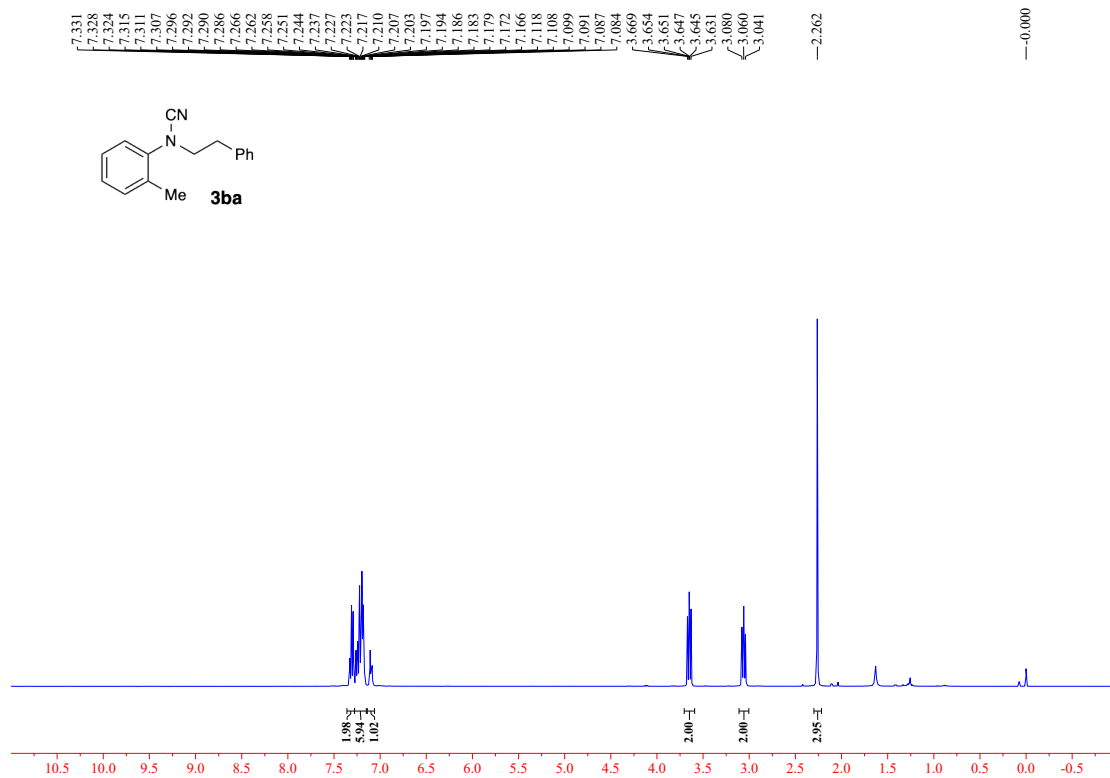


# *N*-methyl-*N*-phenylcyanamide (3aak)

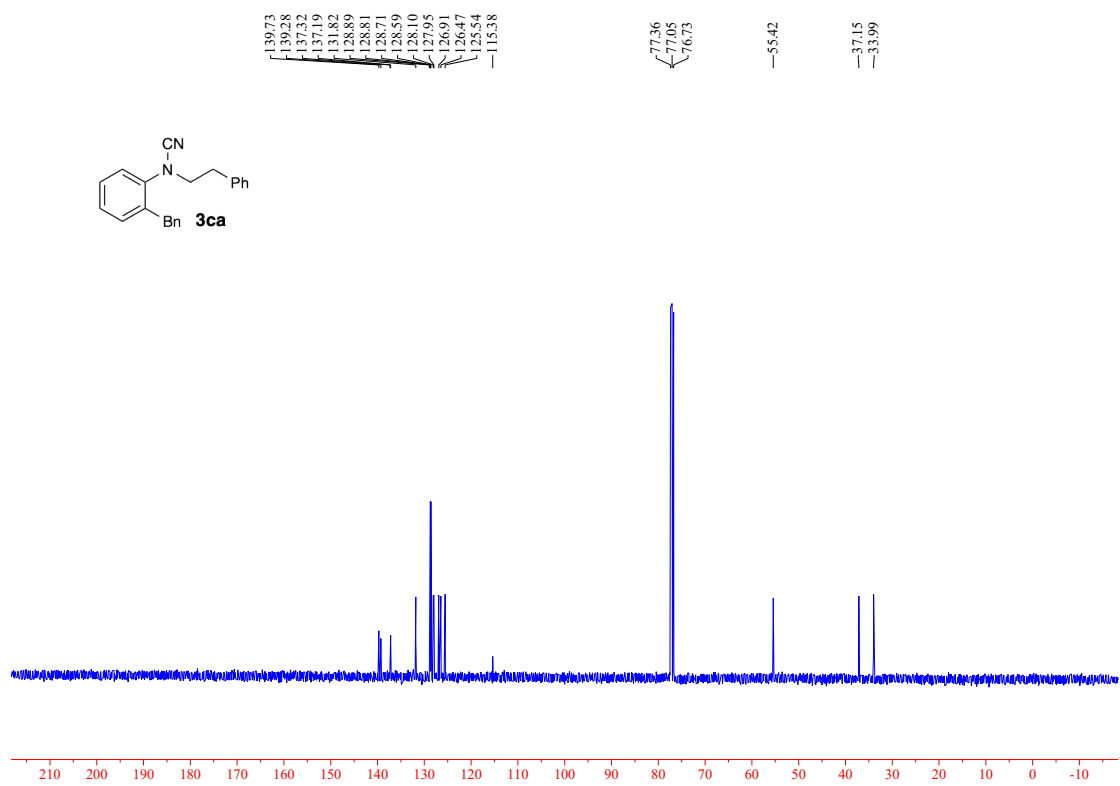
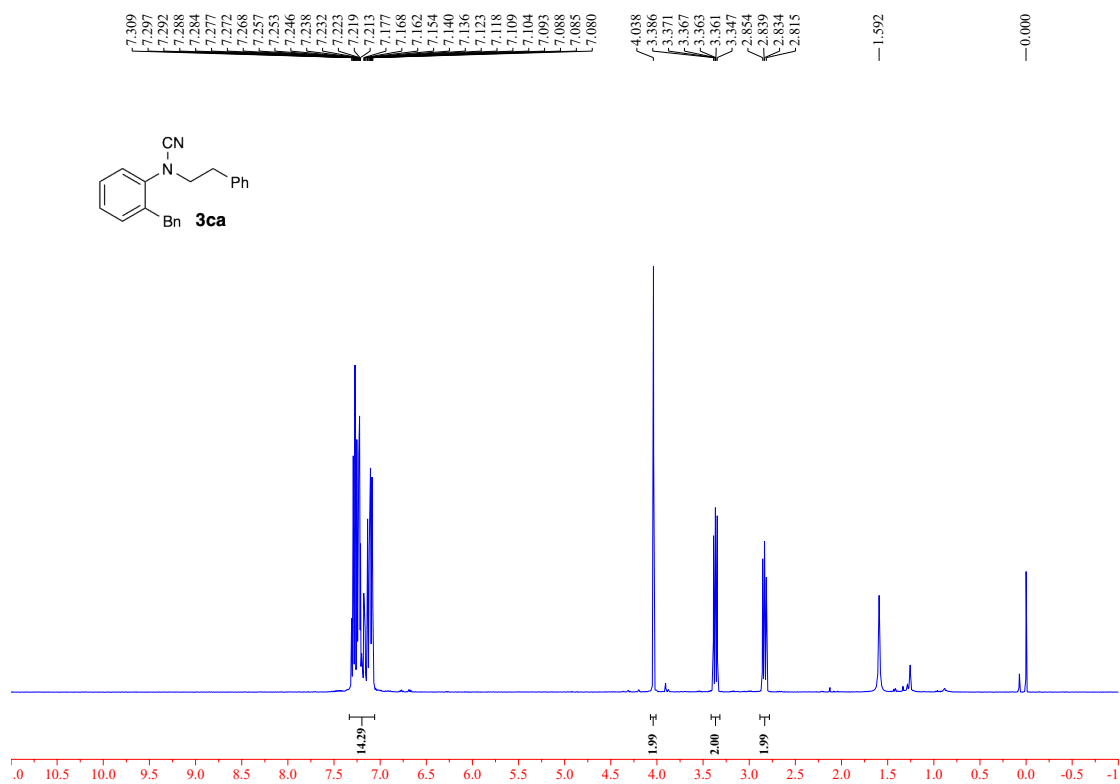




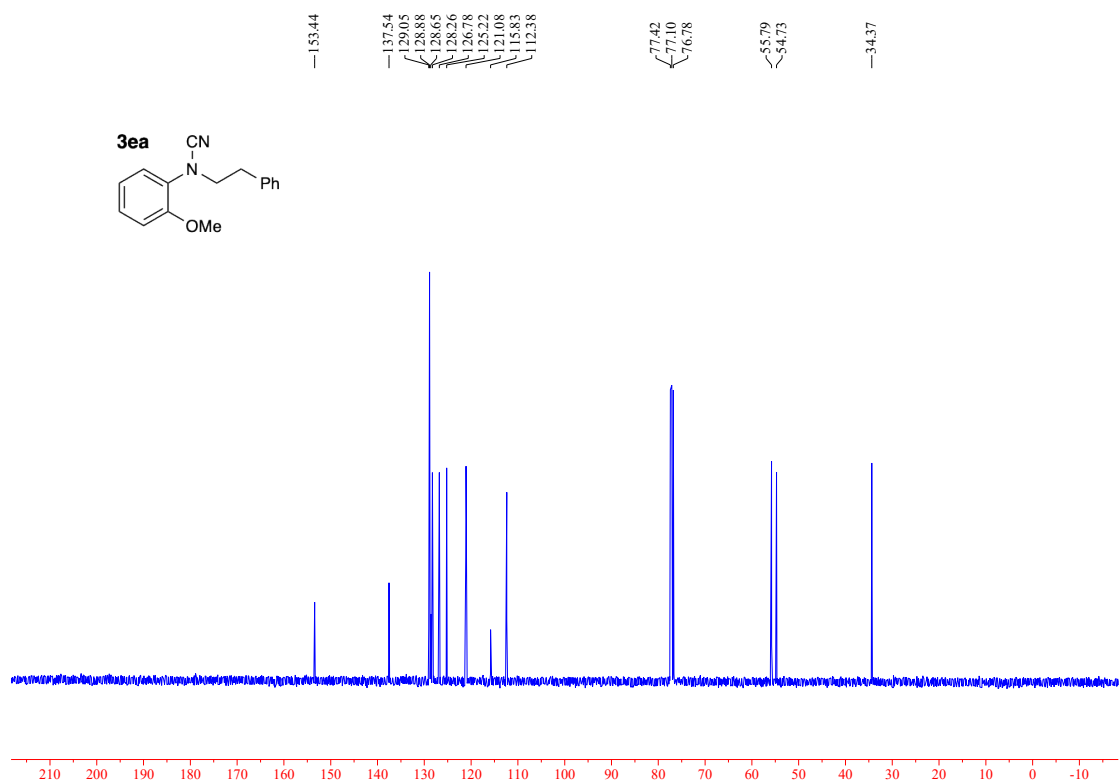
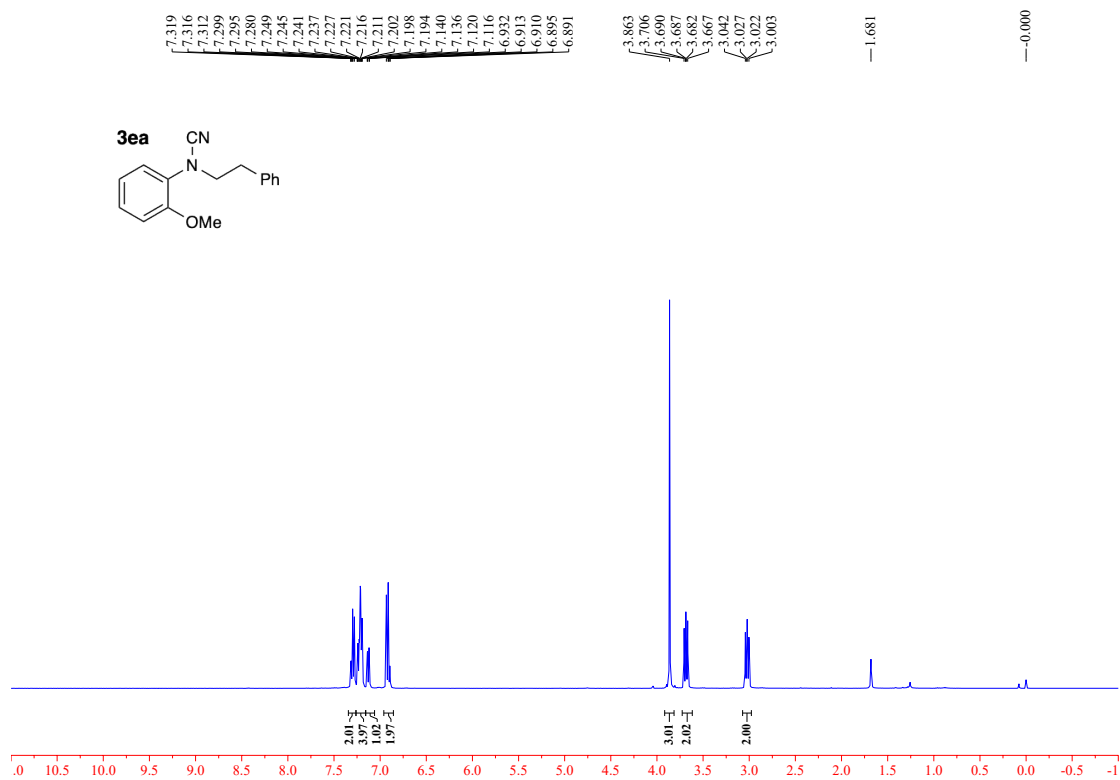
# *N*-phenethyl-*N*-(*o*-tolyl)cyanamide (3ba)



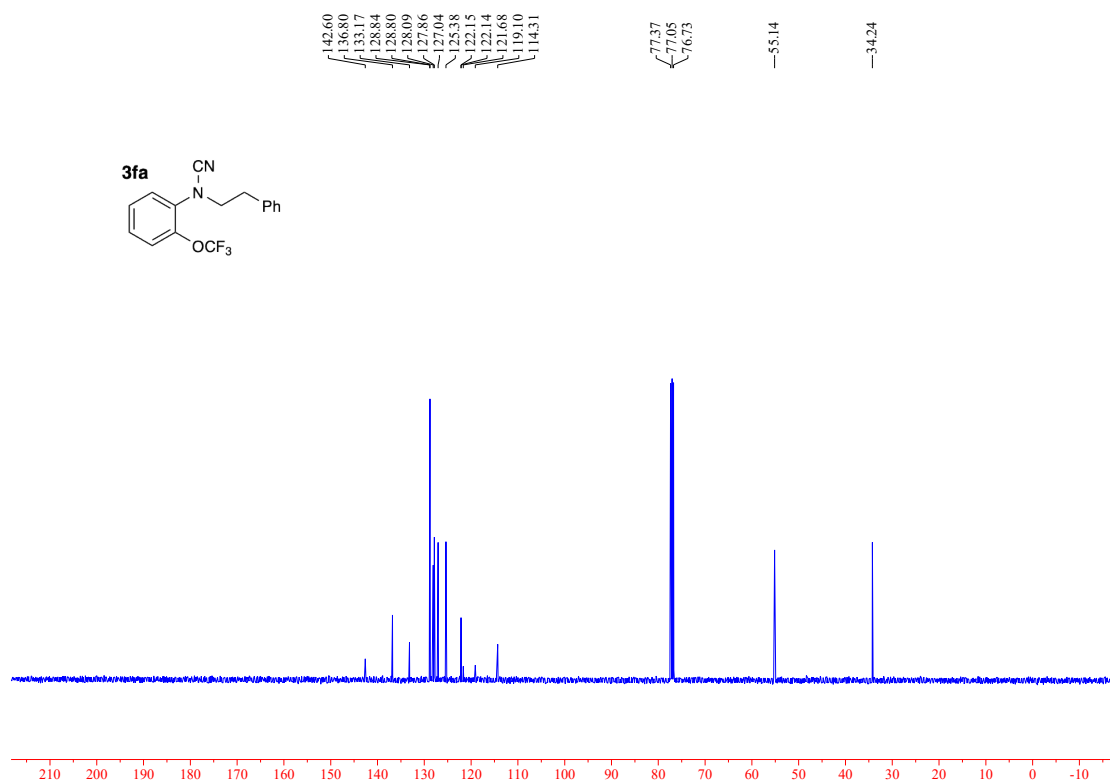
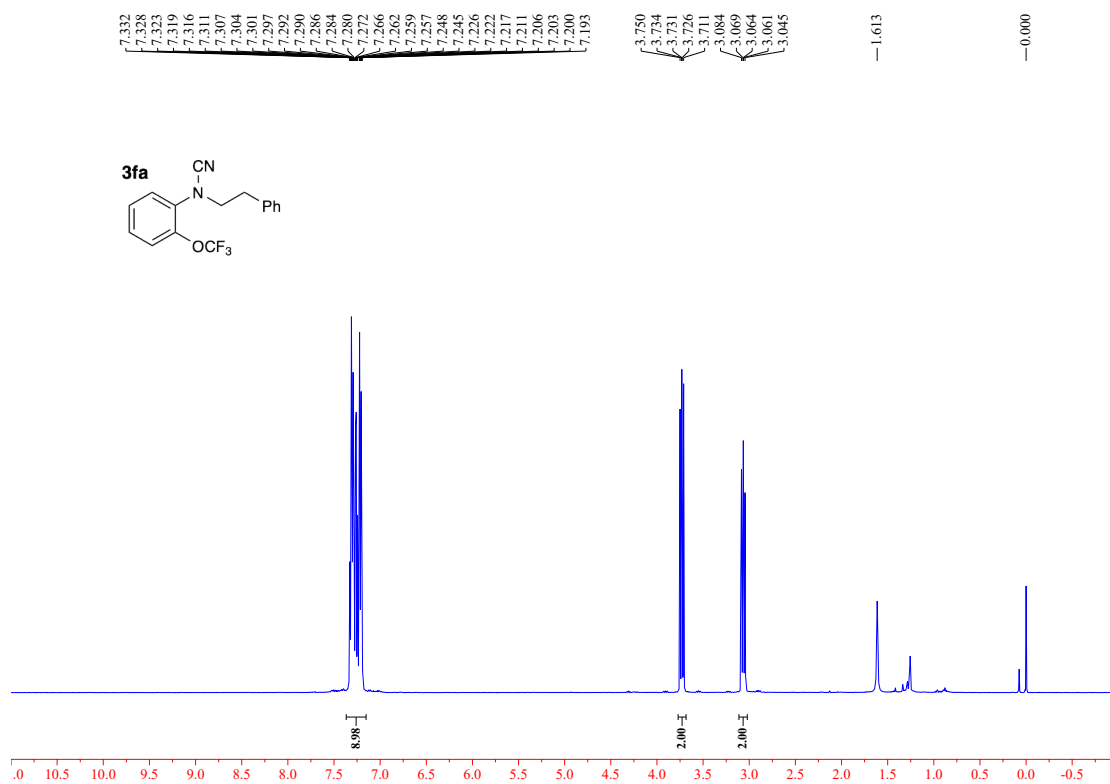
# *N*-(2-benzylphenyl)-*N*-phenethylcyanamide (**3ca**)

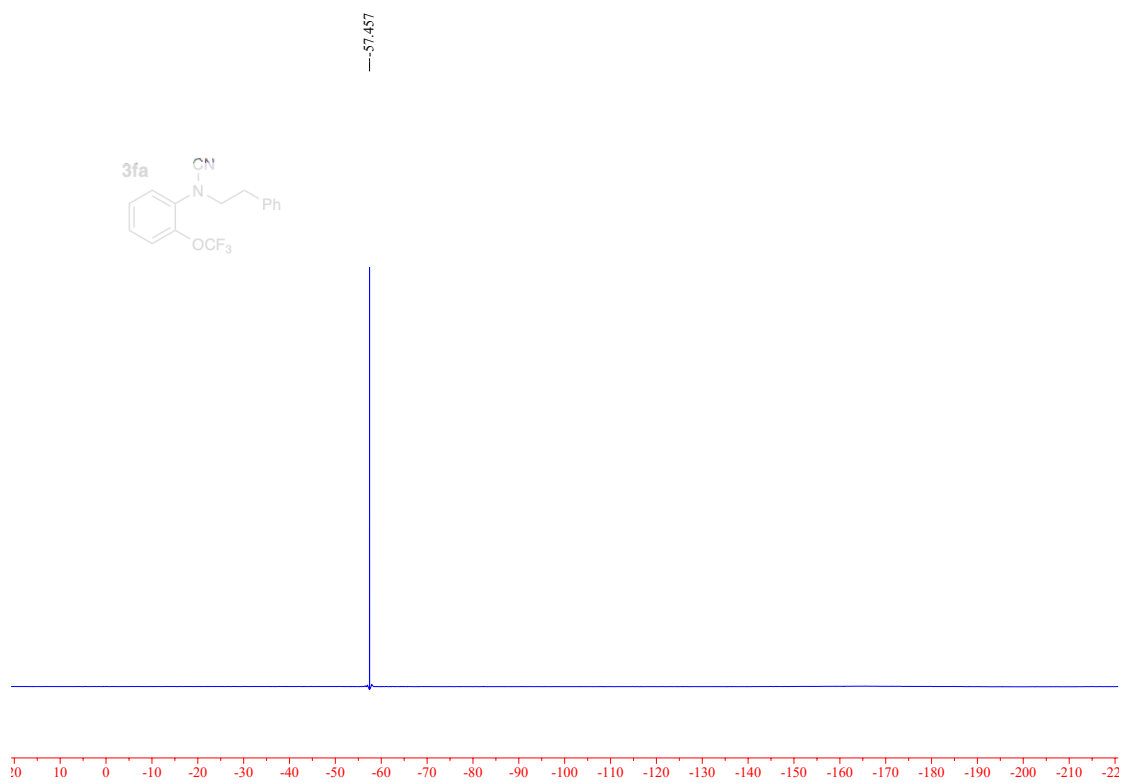


### *N*-(2-methoxyphenyl)-*N*-phenethylcyanamide (**3ea**)

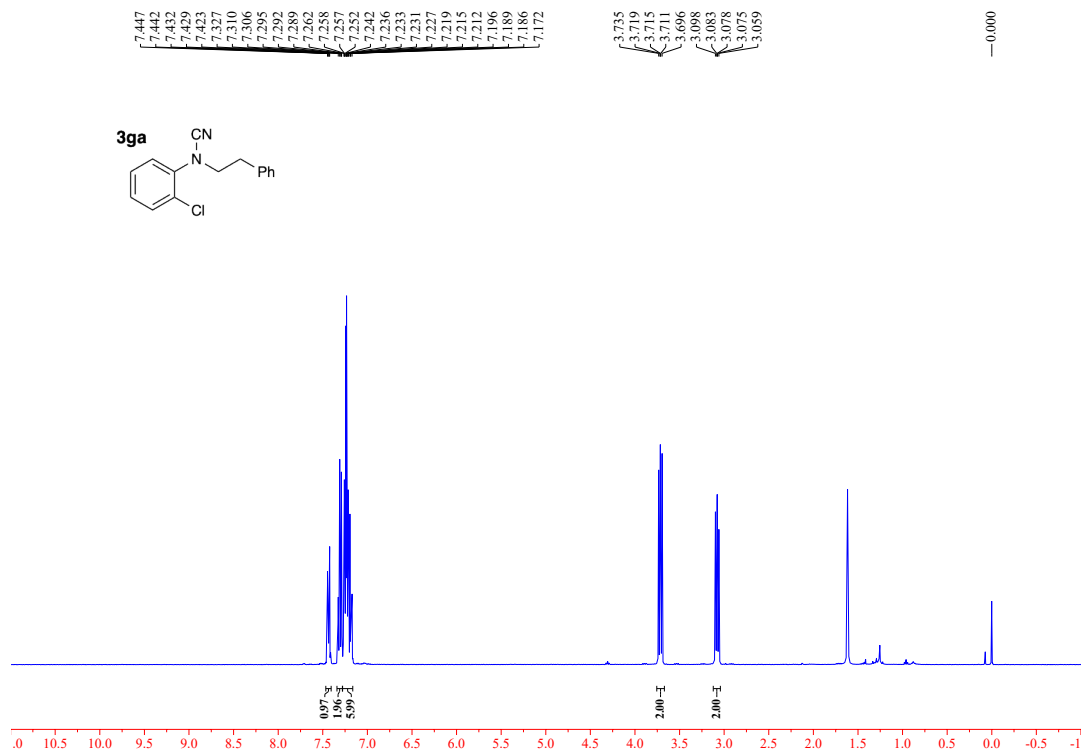
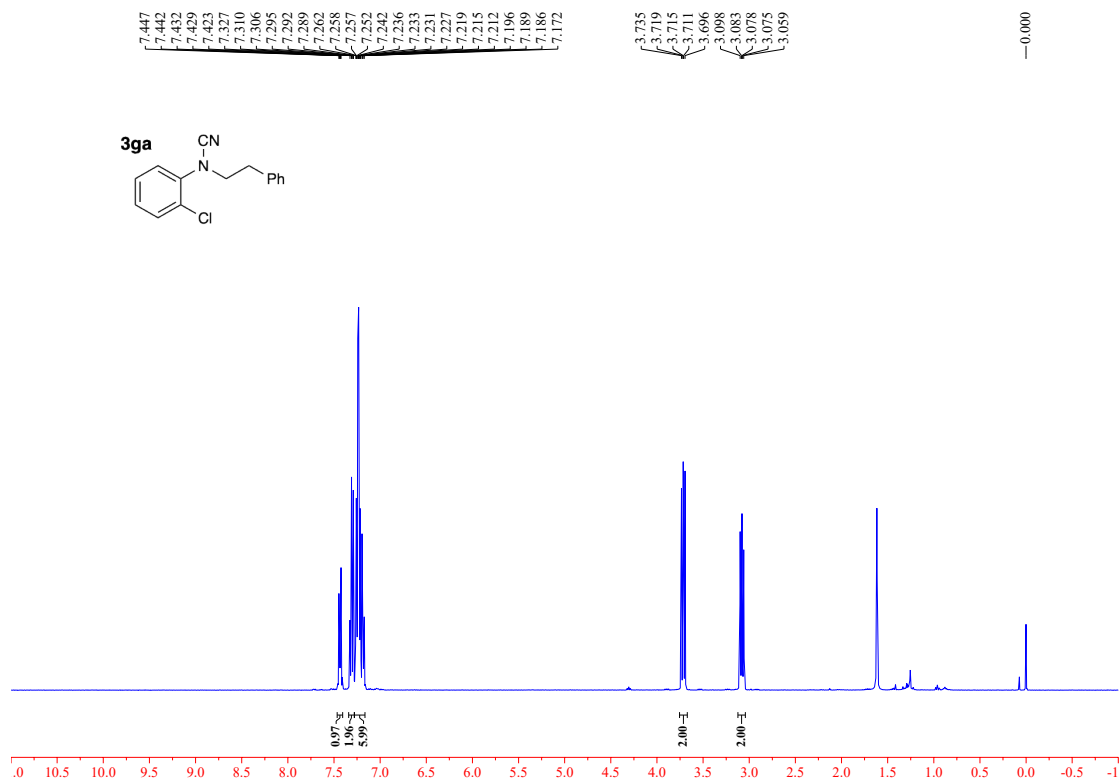


***N*-phenethyl-*N*-(2-(trifluoromethoxy)phenyl)cyanamide (3fa)**

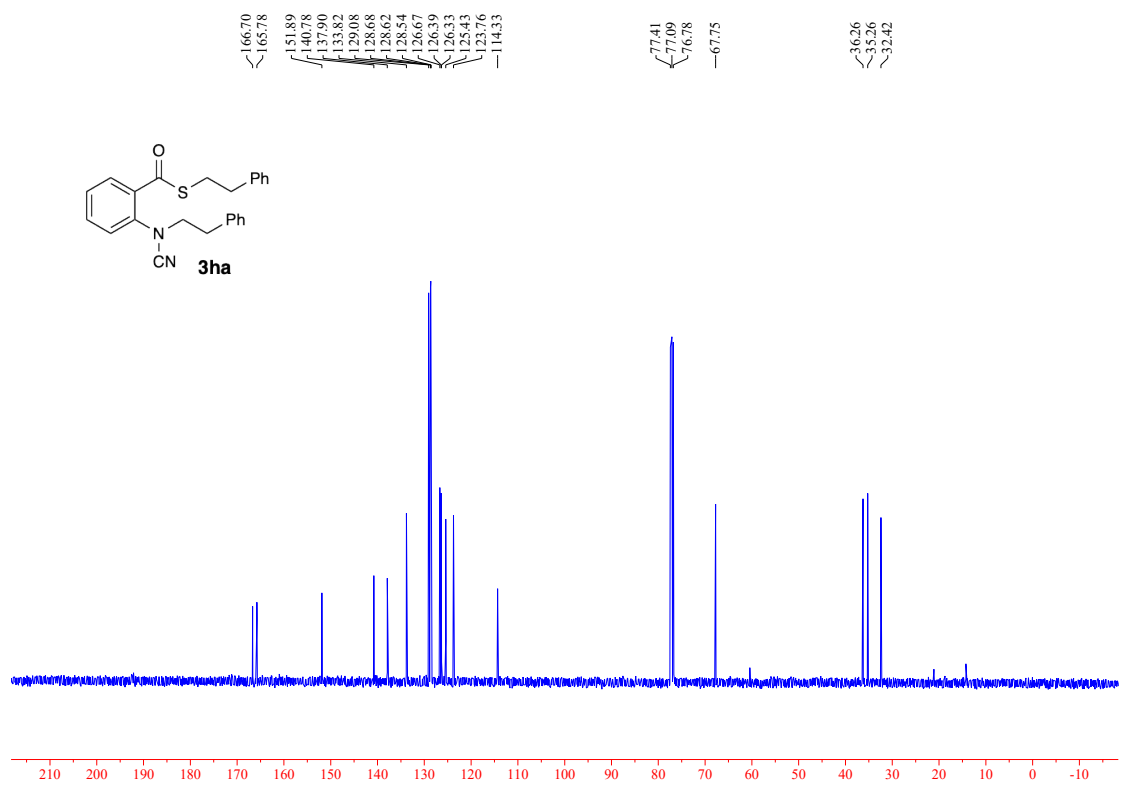
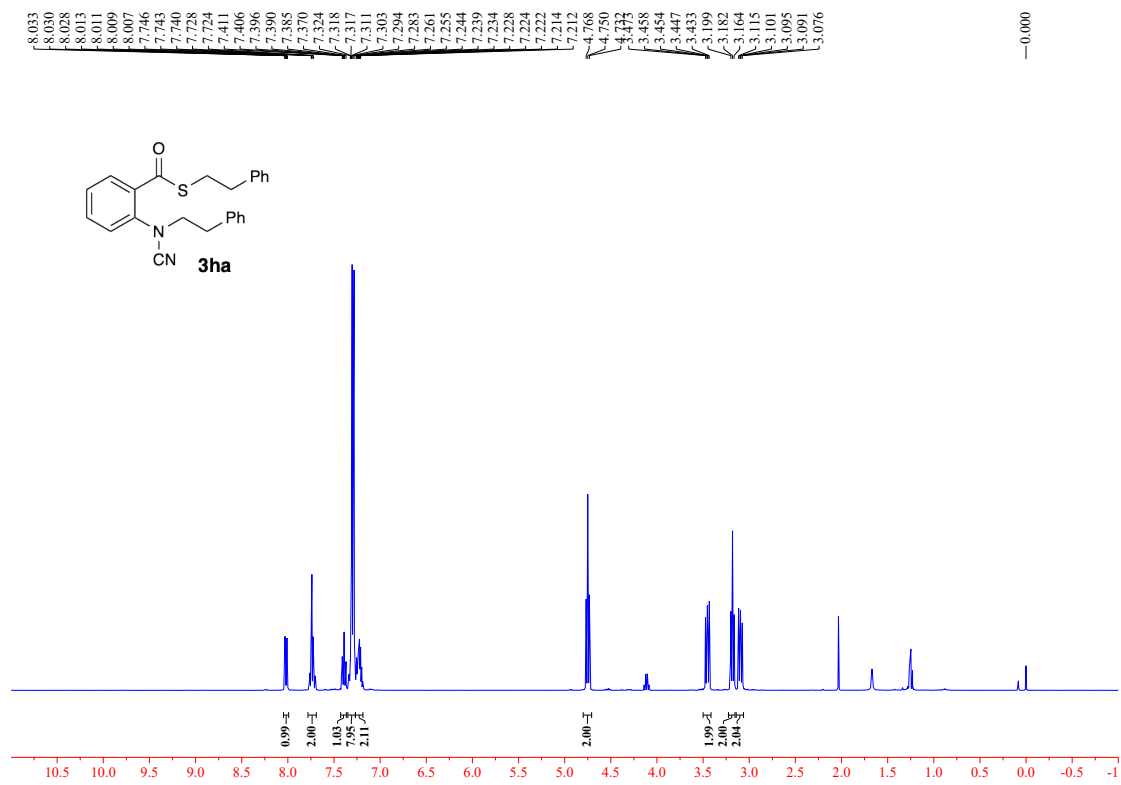




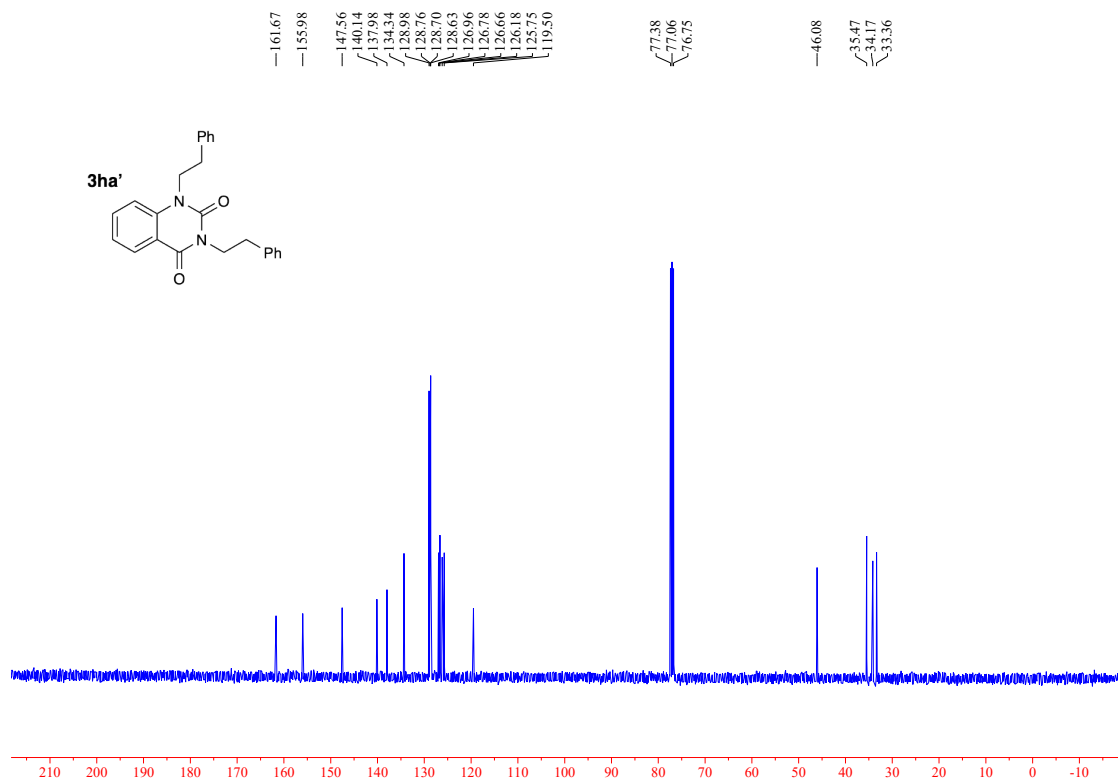
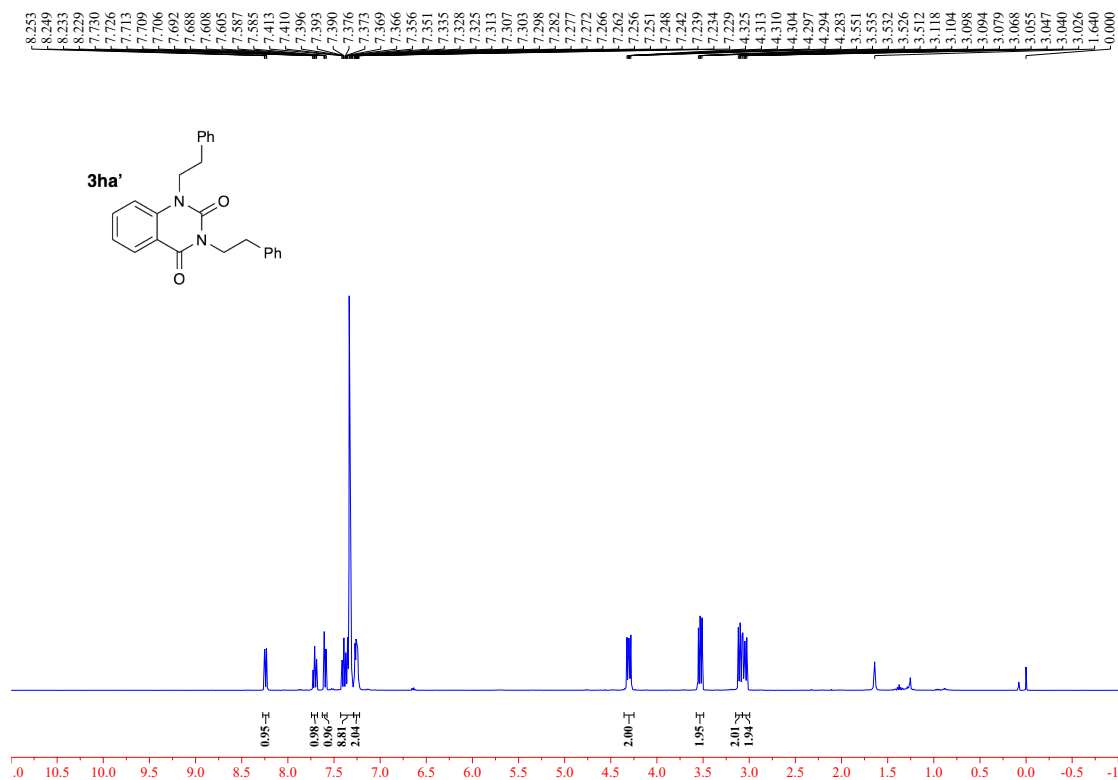
# *N*-(2-chlorophenyl)-*N*-phenethylcyanamide (3ga)



# phenethyl 2-(N-phenethylcyanamido)benzoate (3ha)

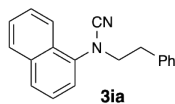
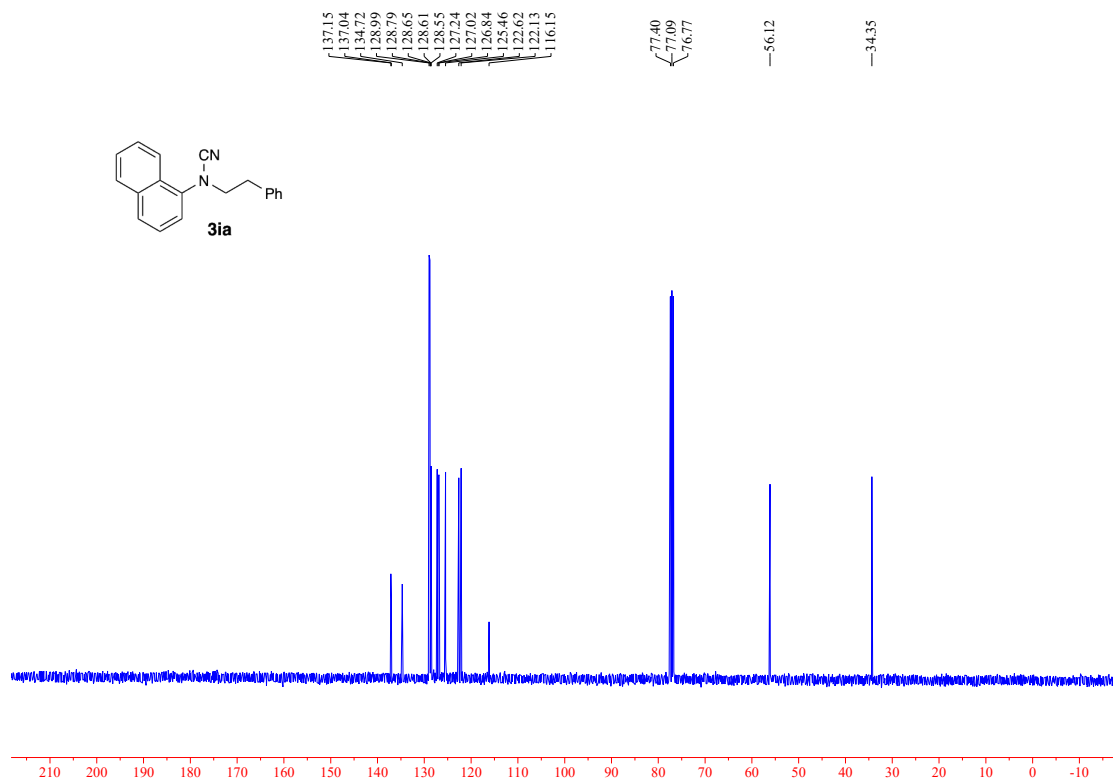
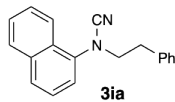
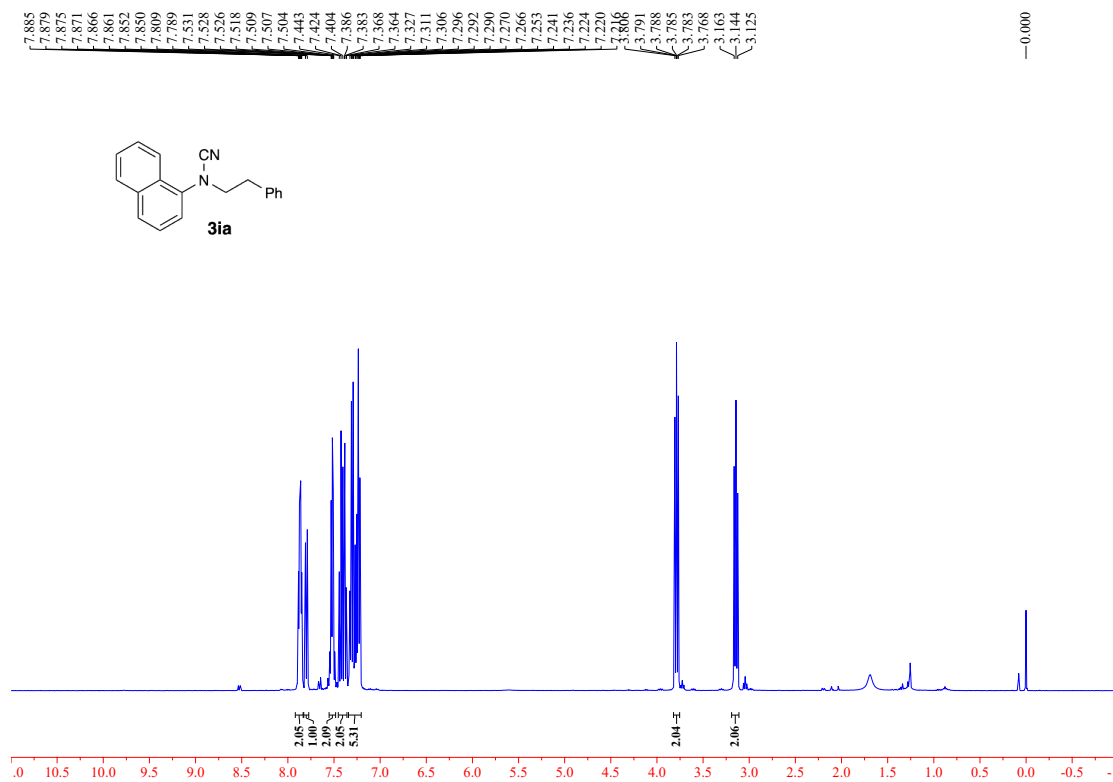


phenethyl 2-phenethyl-1*H*-benzo[*d*]imidazole-4-carboxylate (3ha')

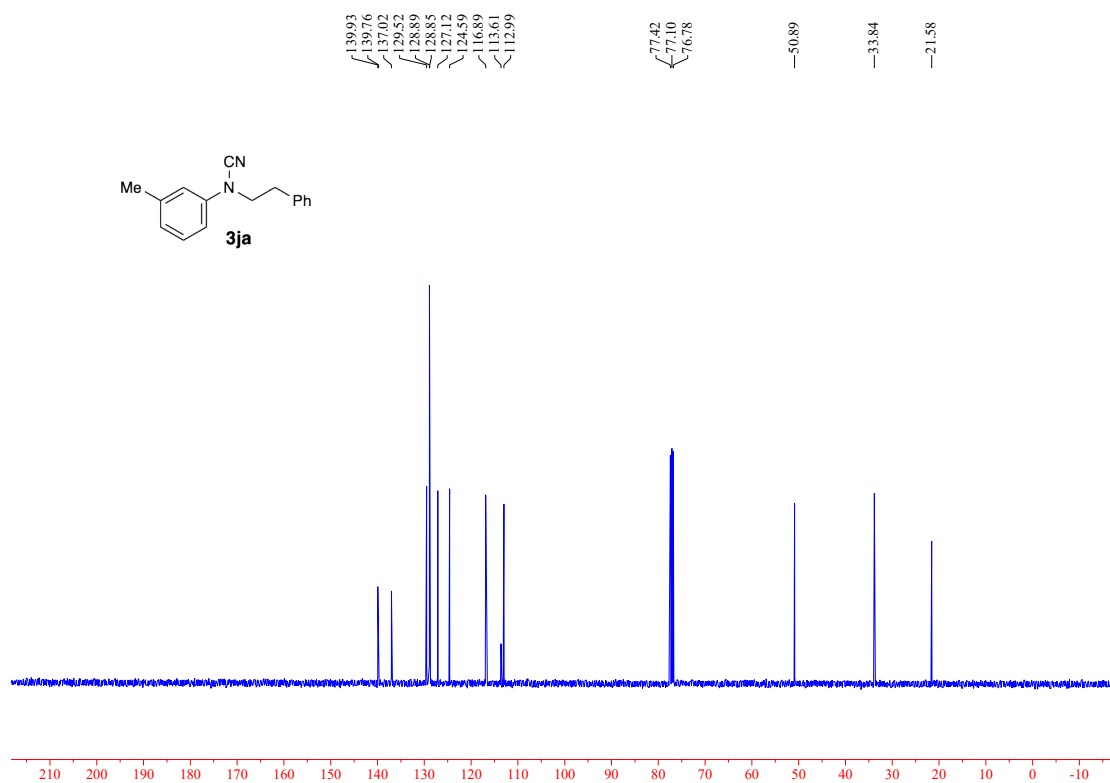
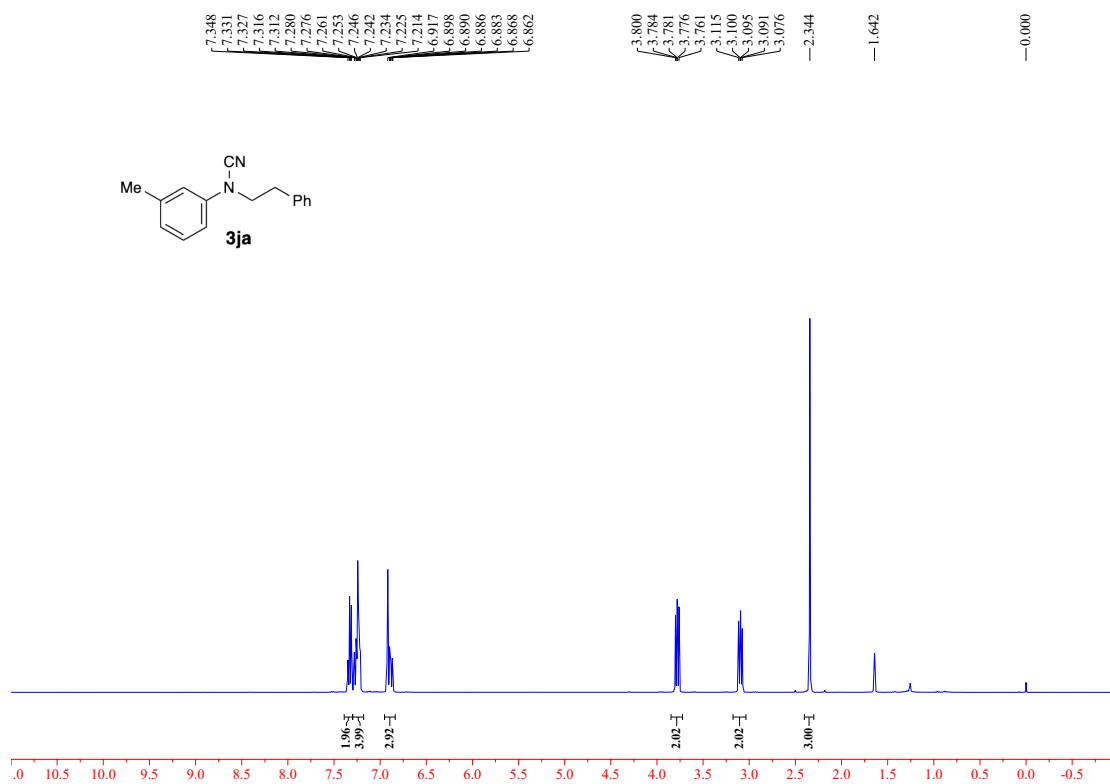




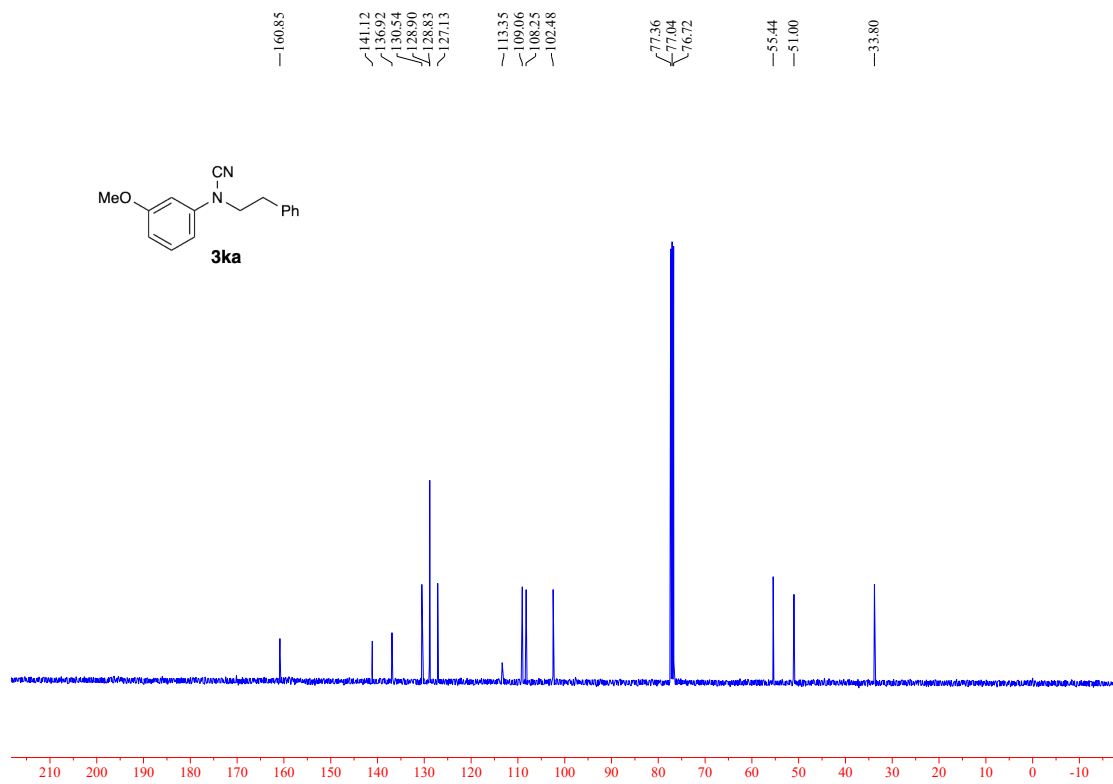
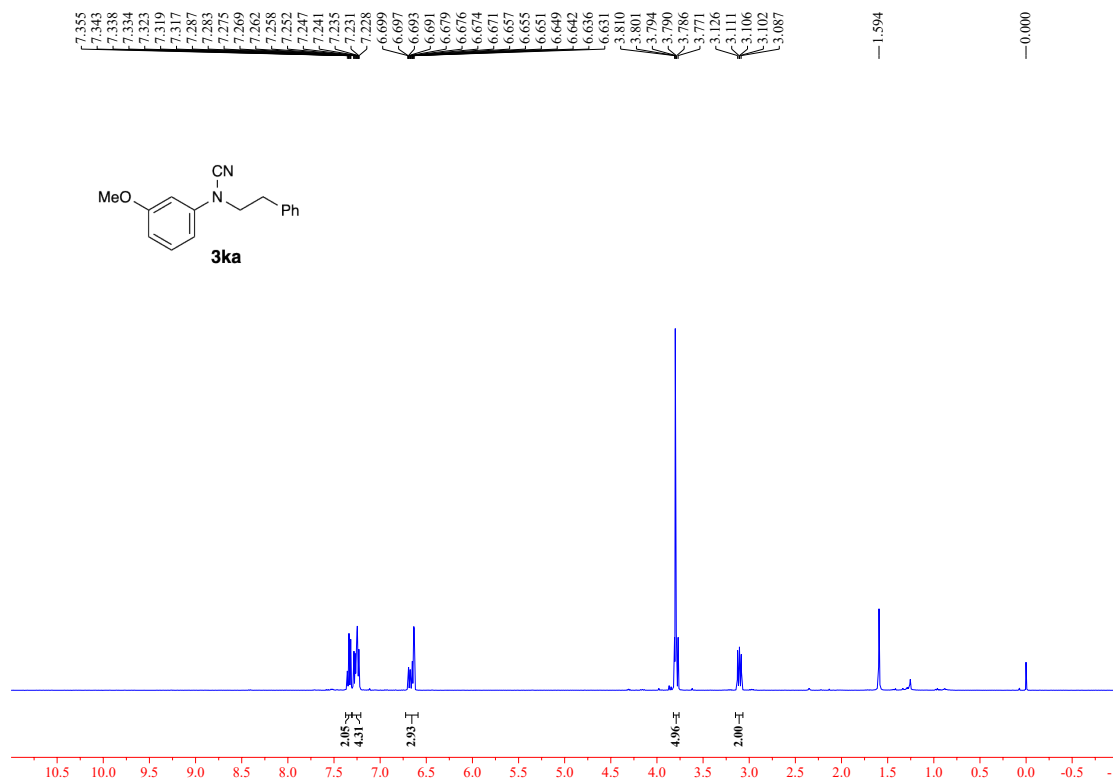
# *N*-(naphthalen-1-yl)-*N*-phenethylcyanamide (**3ia**)



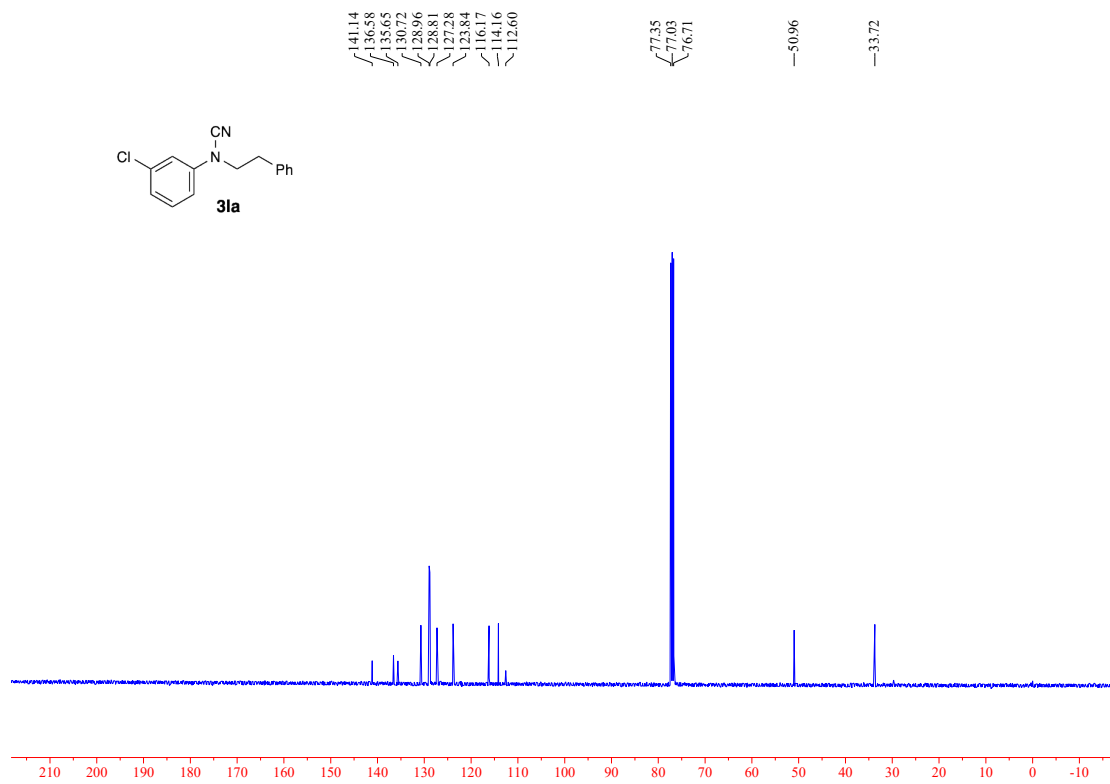
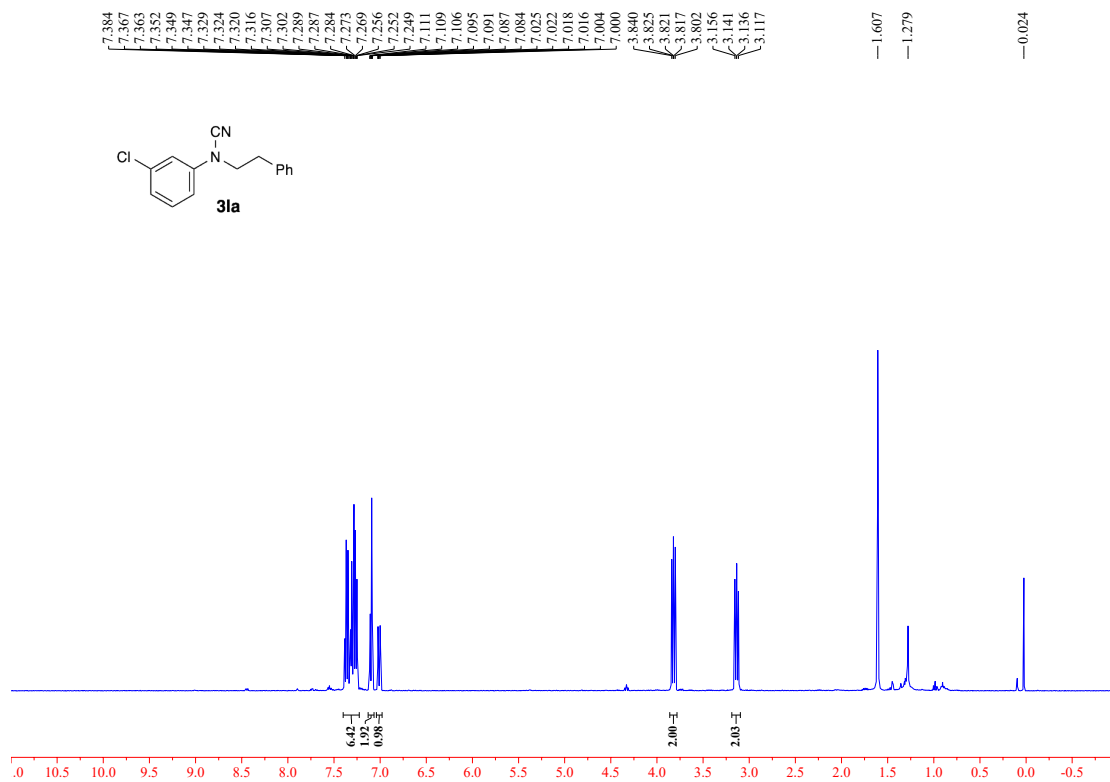
# *N*-phenethyl-*N*-(*p*-tolyl)cyanamide (**3ja**)



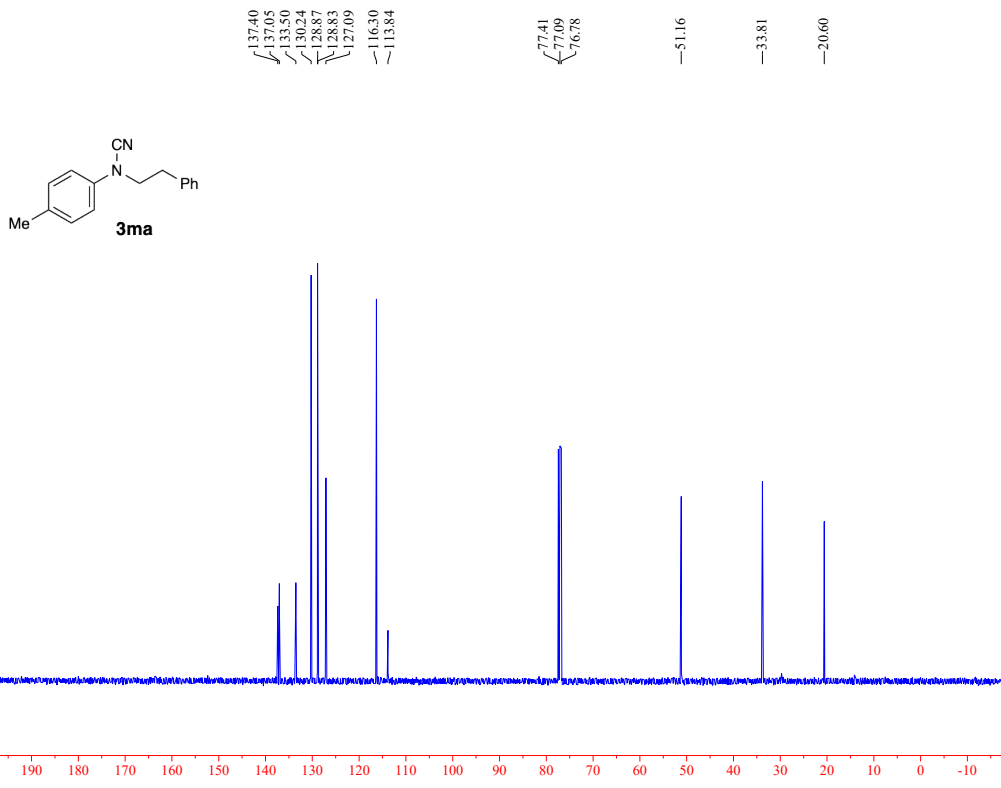
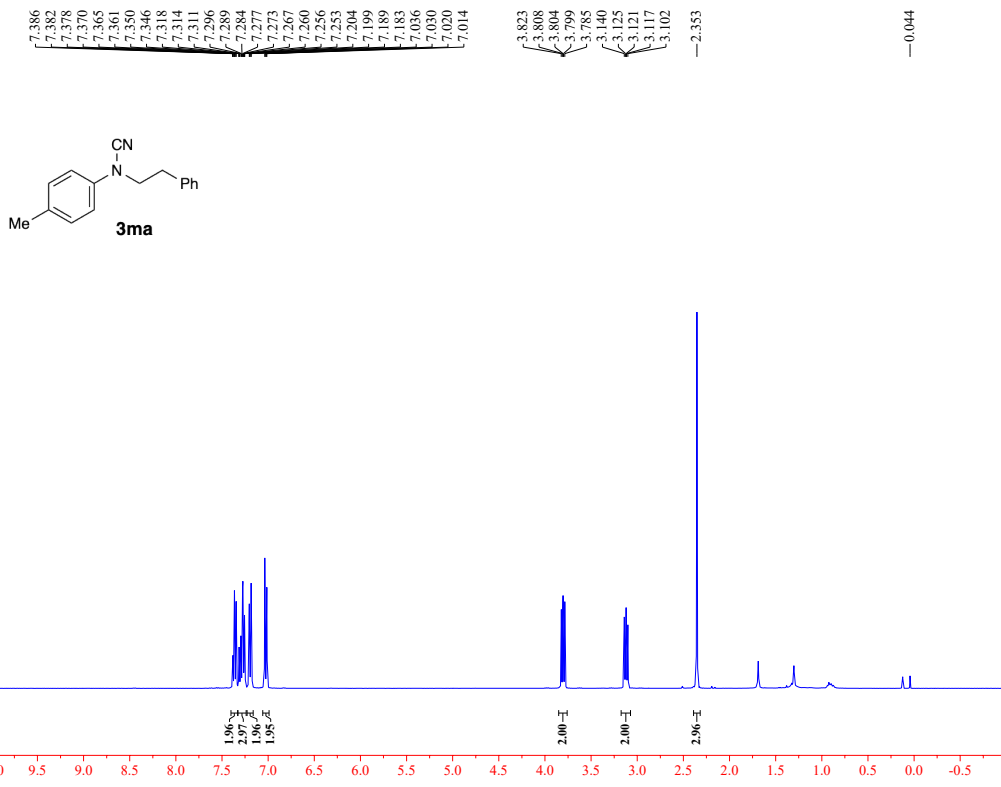
### *N*-(3-methoxyphenyl)-*N*-phenethylcyanamide (3ka)



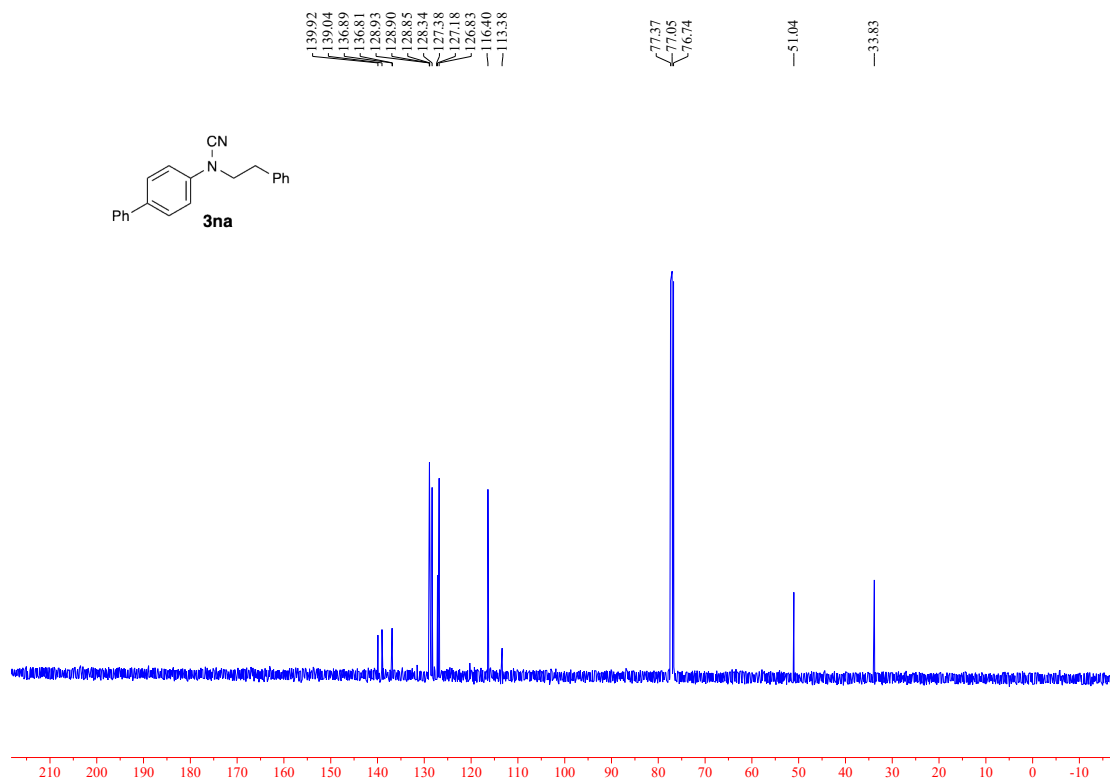
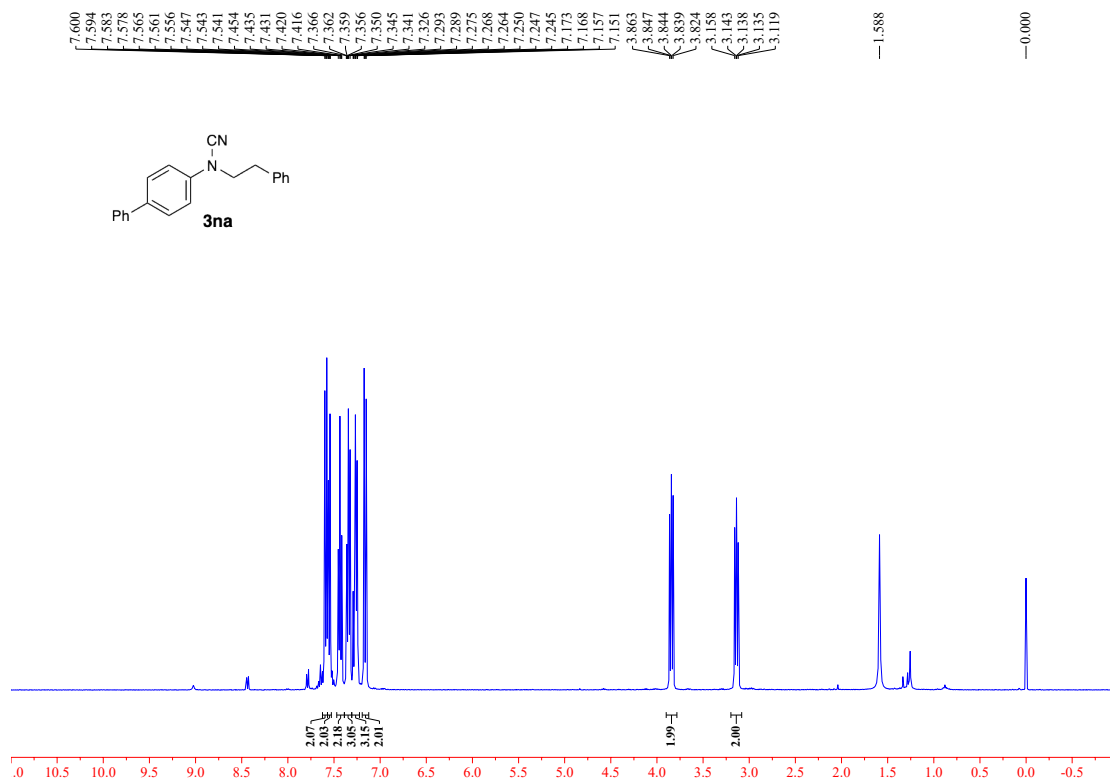
### *N*-(3-chlorophenyl)-*N*-phenethylcyanamide (**3la**)



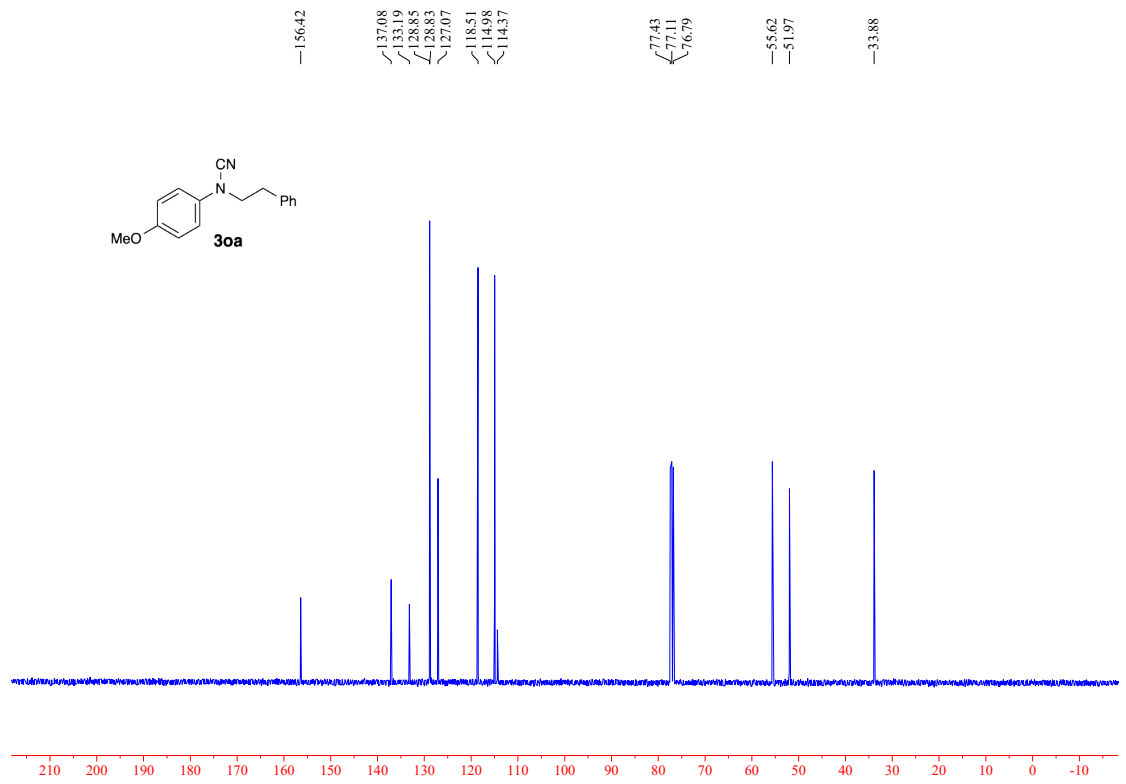
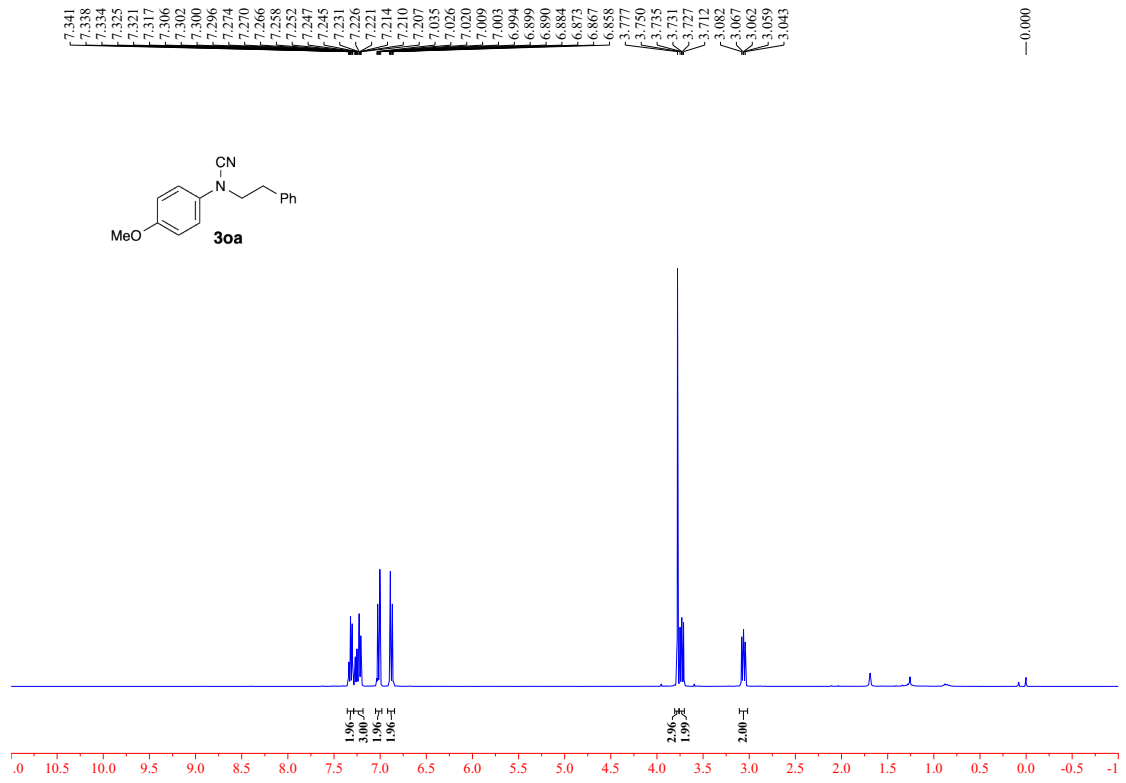
# *N*-phenethyl-*N*-(*p*-tolyl)cyanamide (3ma)



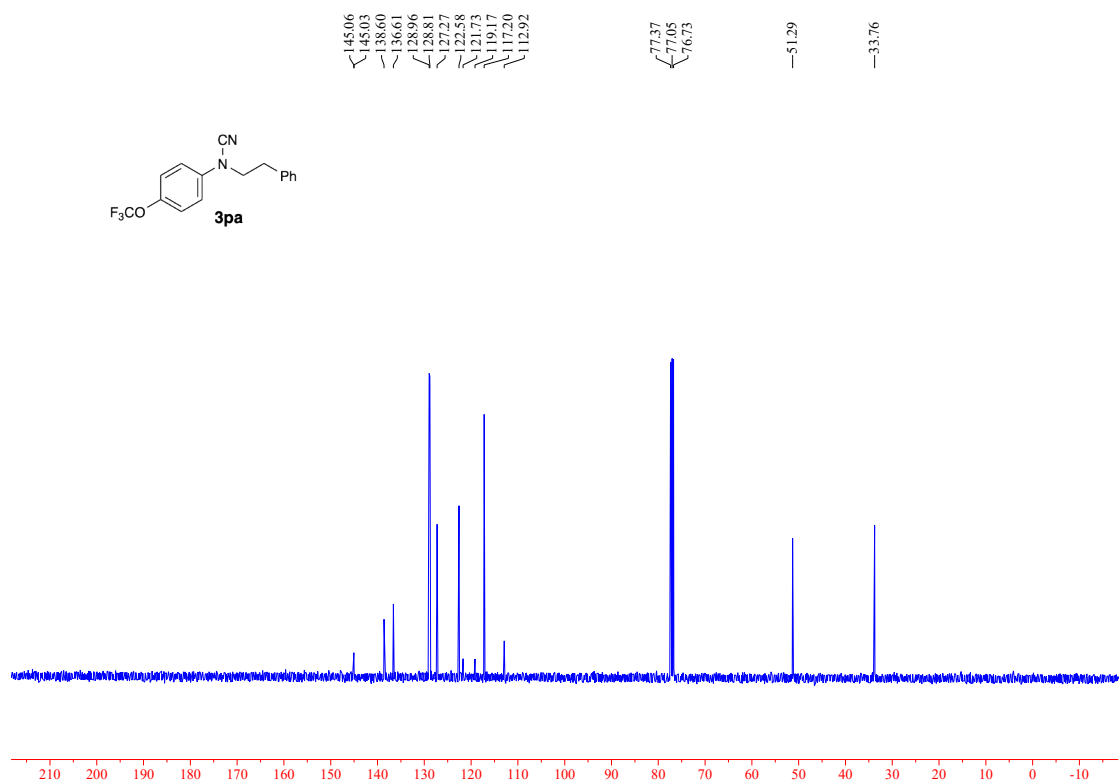
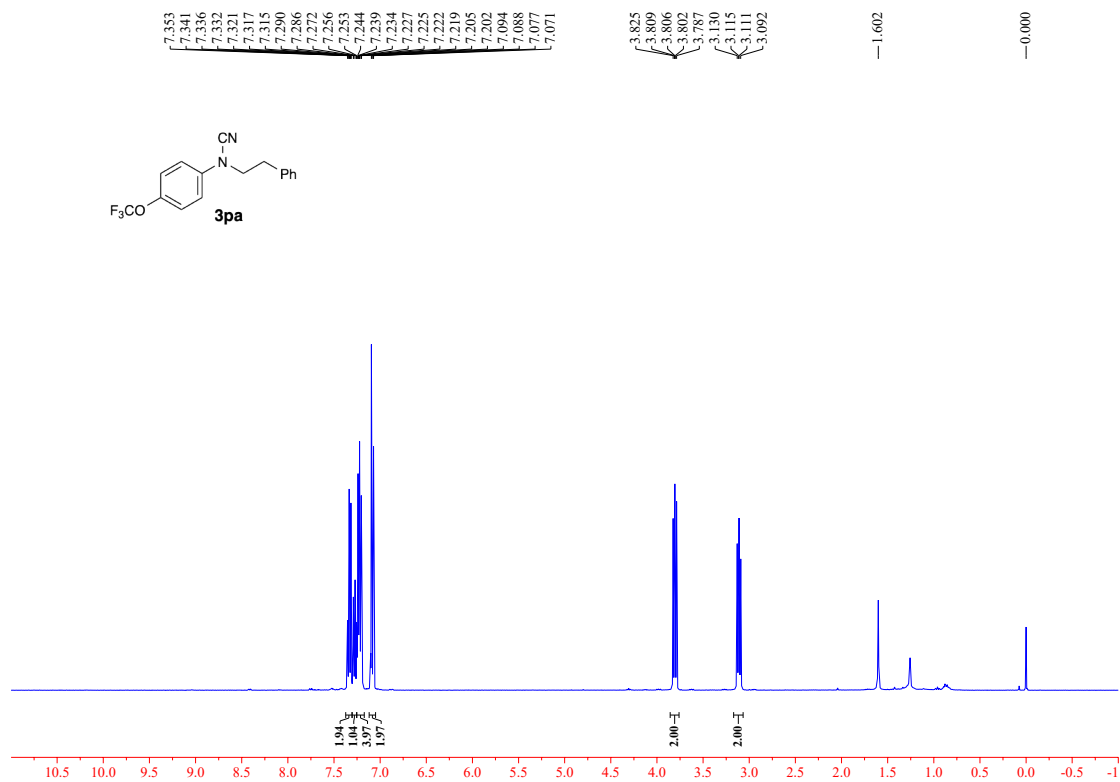
# 1-phenethyl-6-phenyl-1H-benzo[d]imidazole (3na)



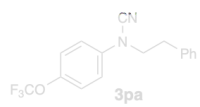
# *N*-(4-methoxyphenyl)-*N*-phenethylcyanamide (30a)



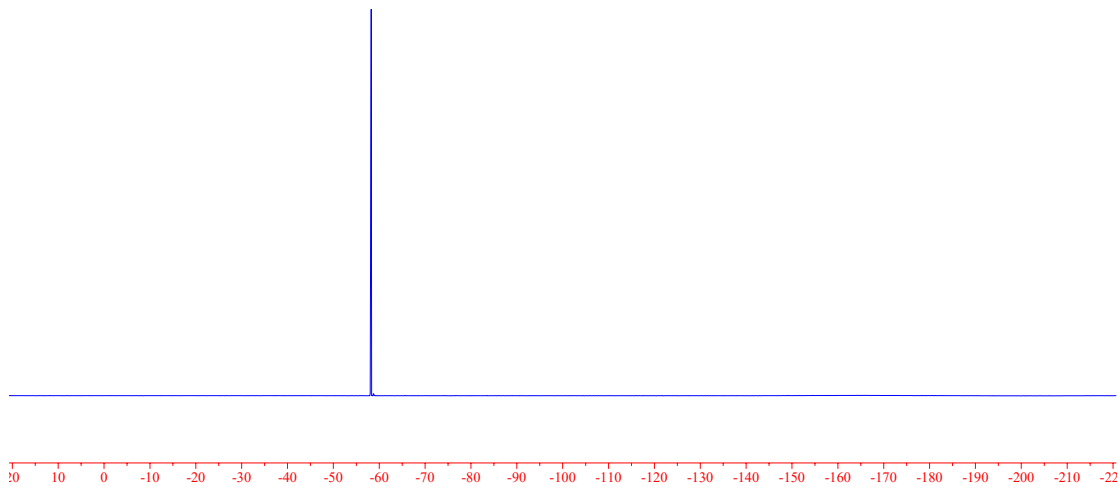
# *N*-phenethyl-*N*-(4-(trifluoromethoxy)phenyl)cyanamide (**3pa**)



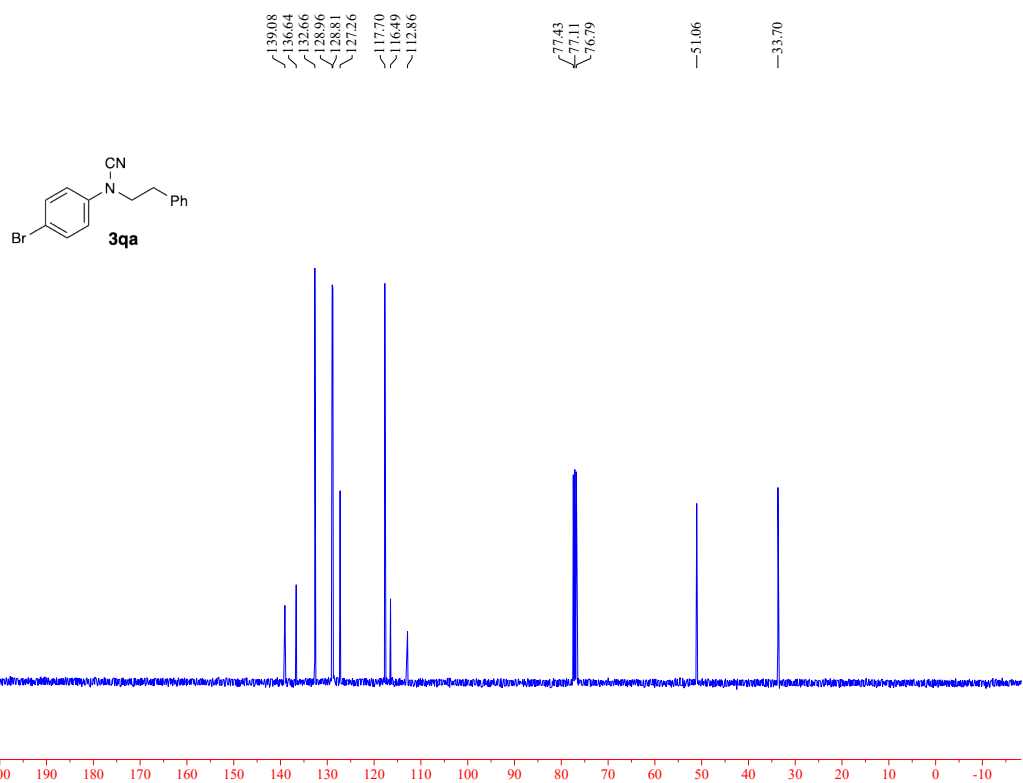
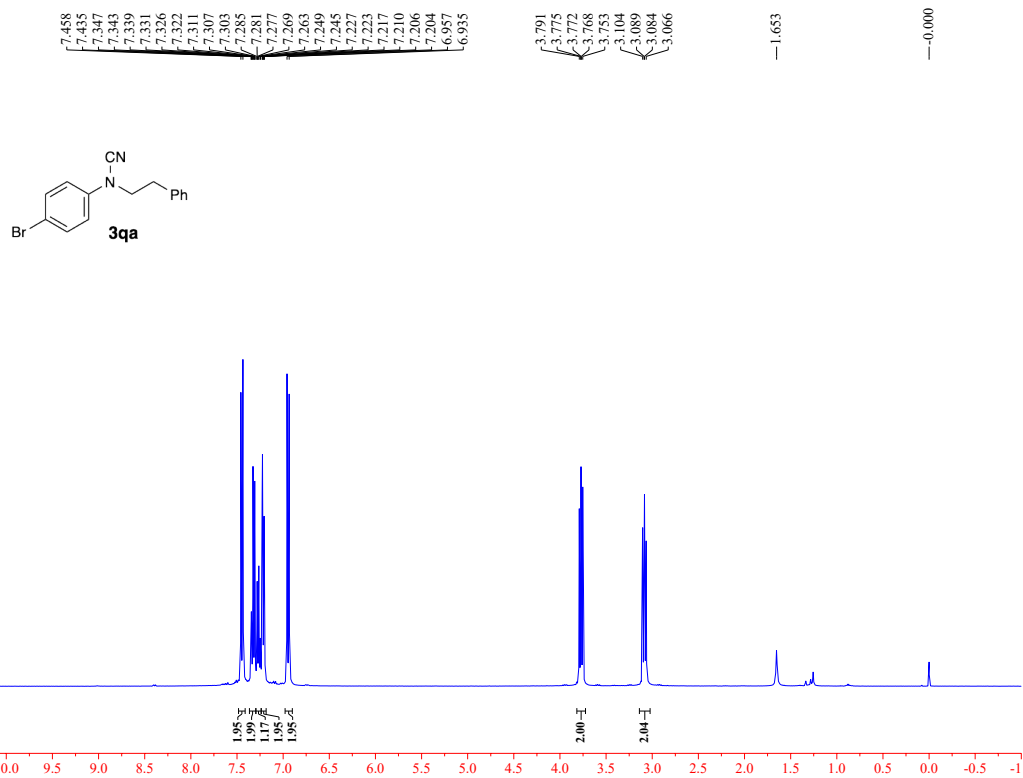




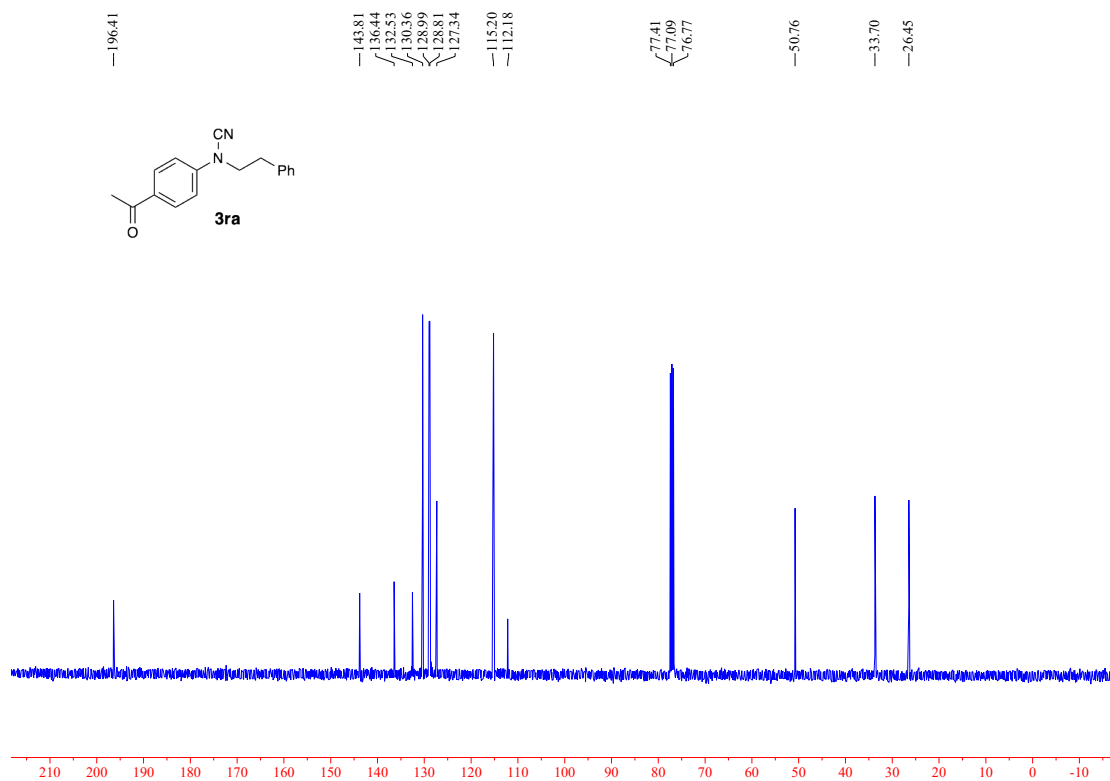
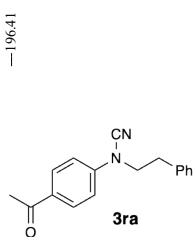
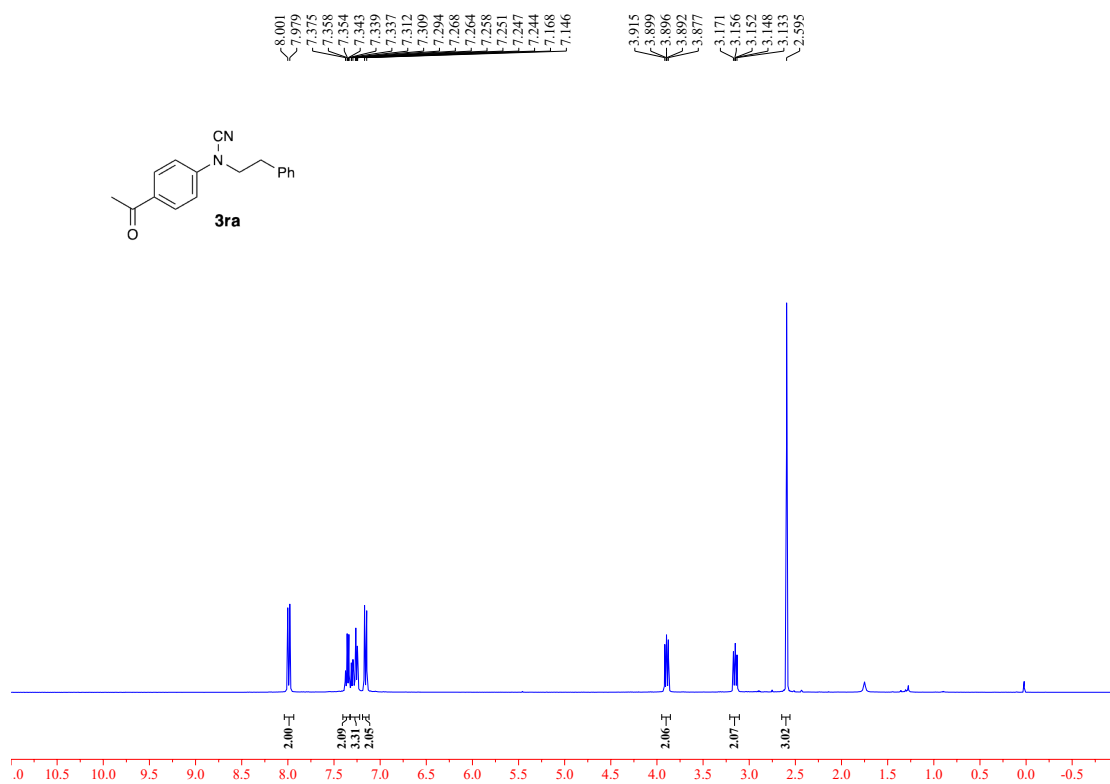
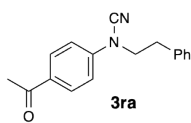
--58.26



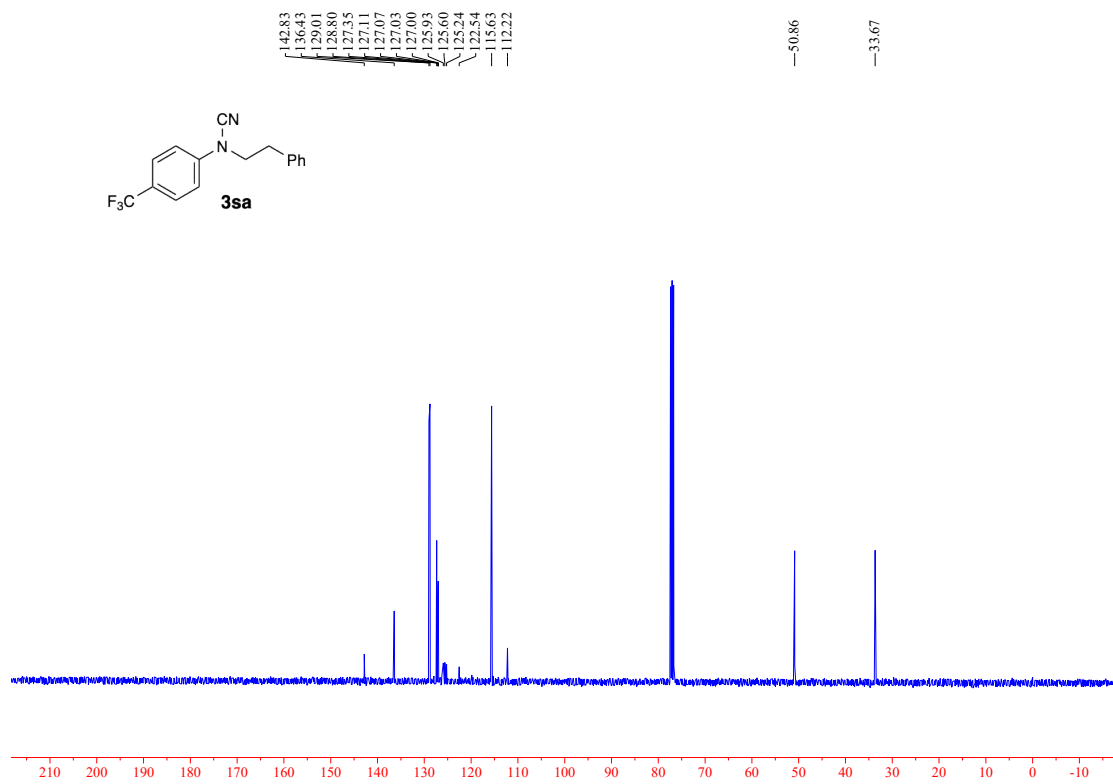
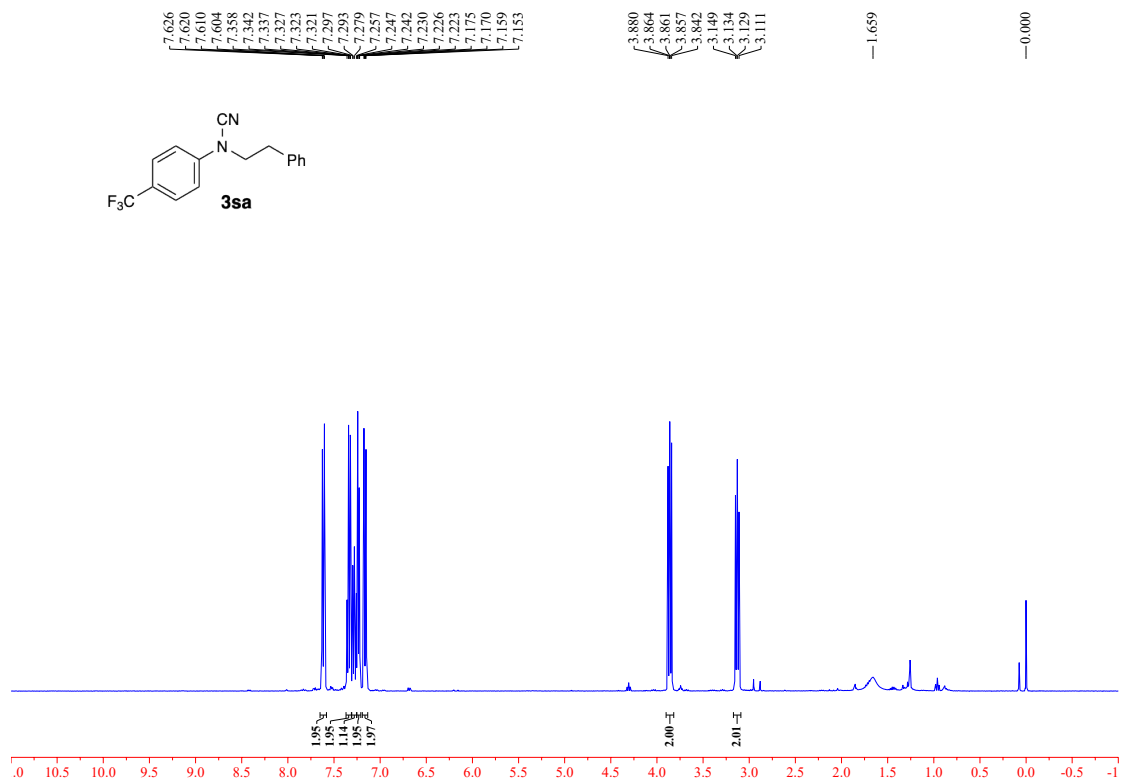
# *N*-(4-bromophenyl)-*N*-phenethylcyanamide (3qa)



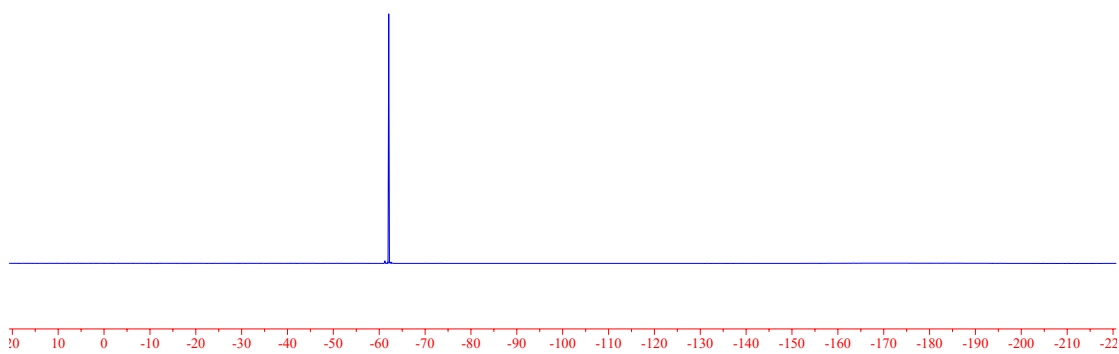
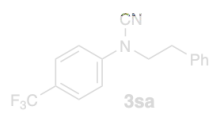
# *N*-(4-acetylphenyl)-*N*-phenethylcyanamide (3ra)



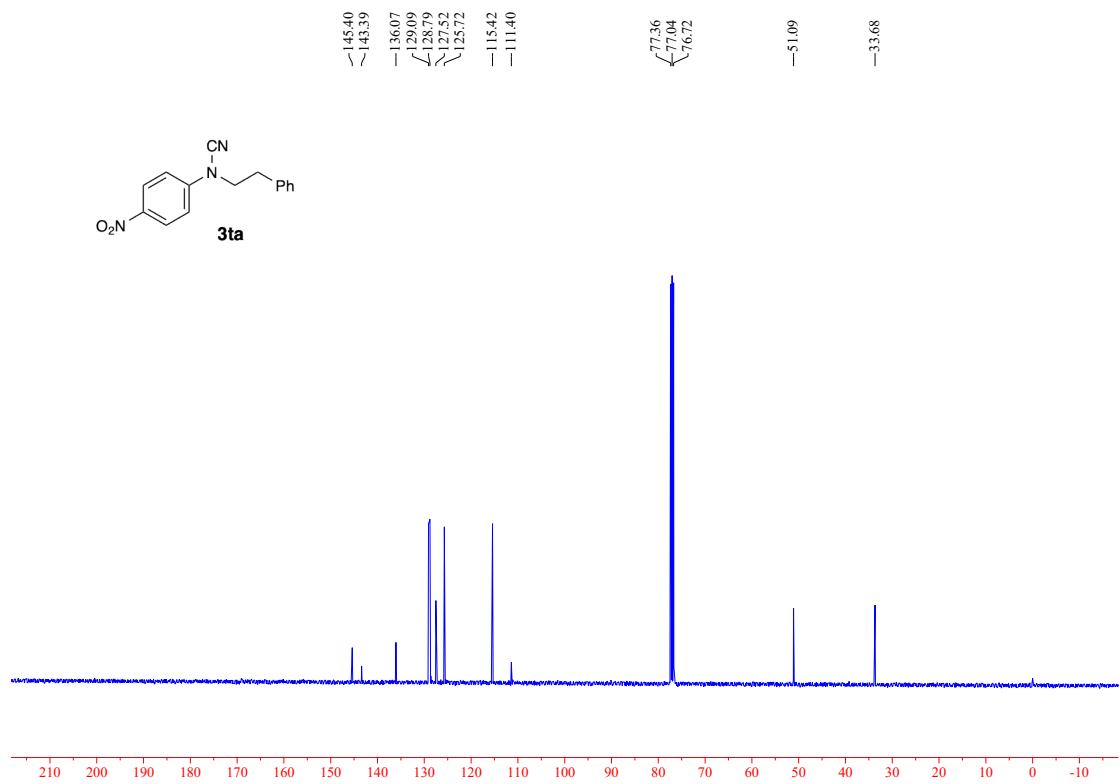
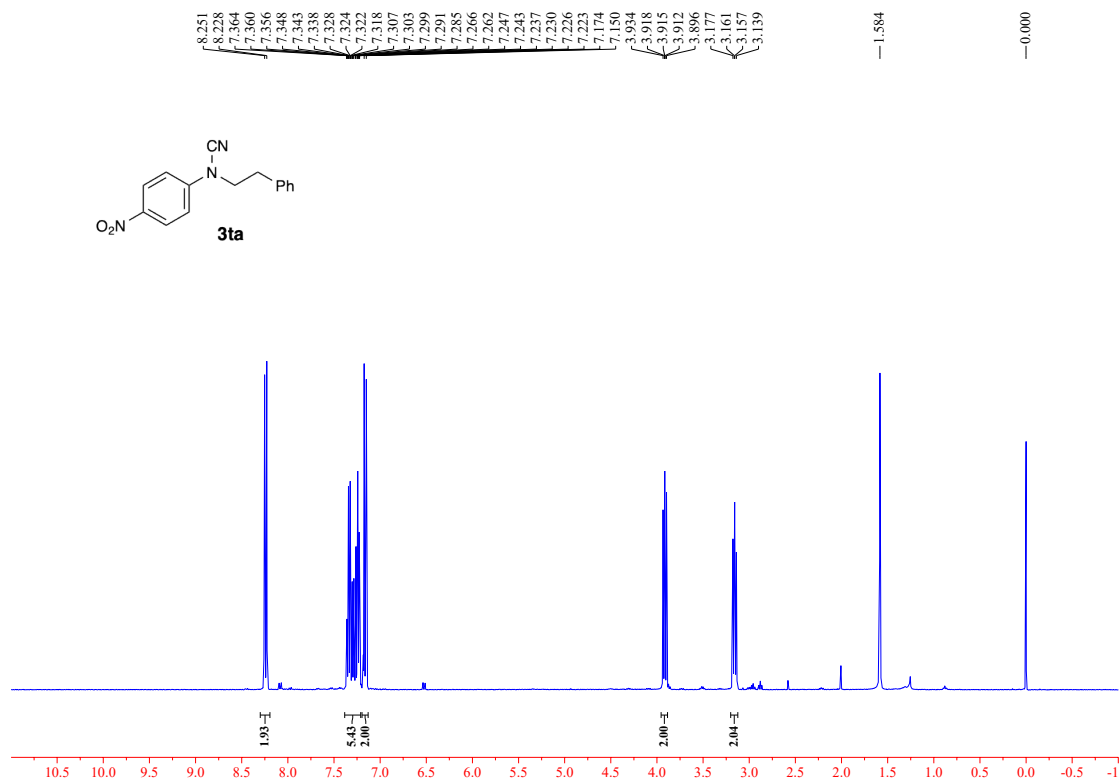
***N*-phenethyl-*N*-(4-(trifluoromethyl)phenyl)cyanamide (3sa)**



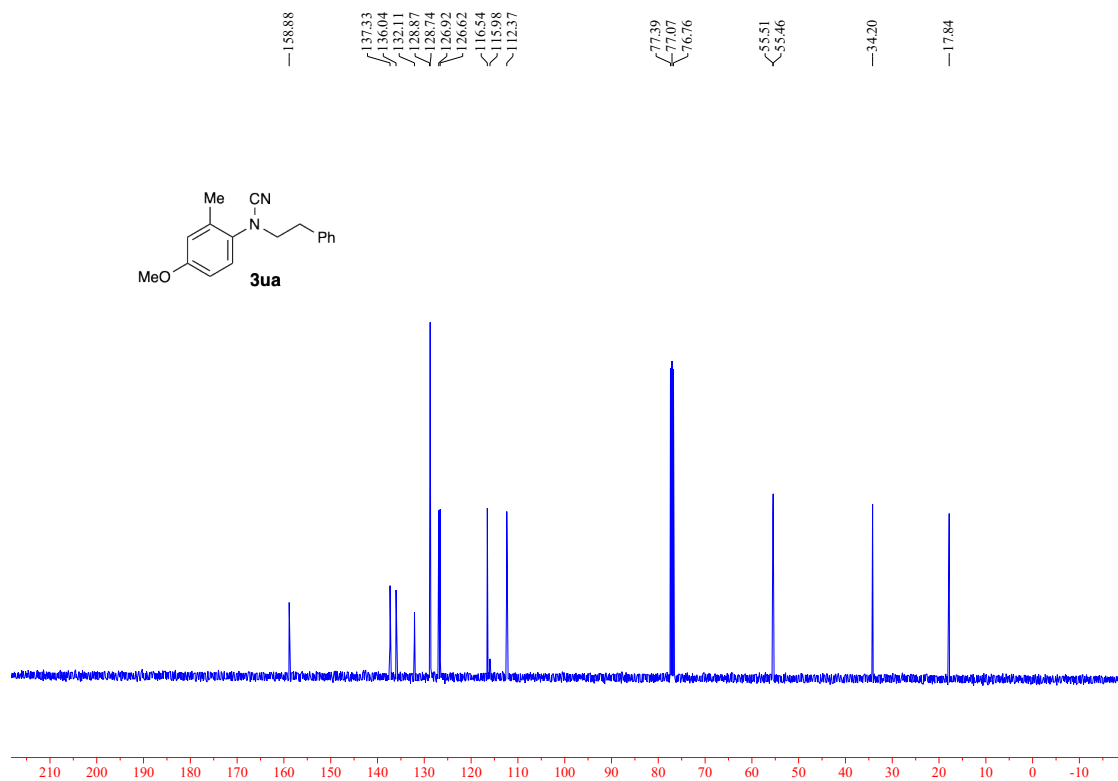
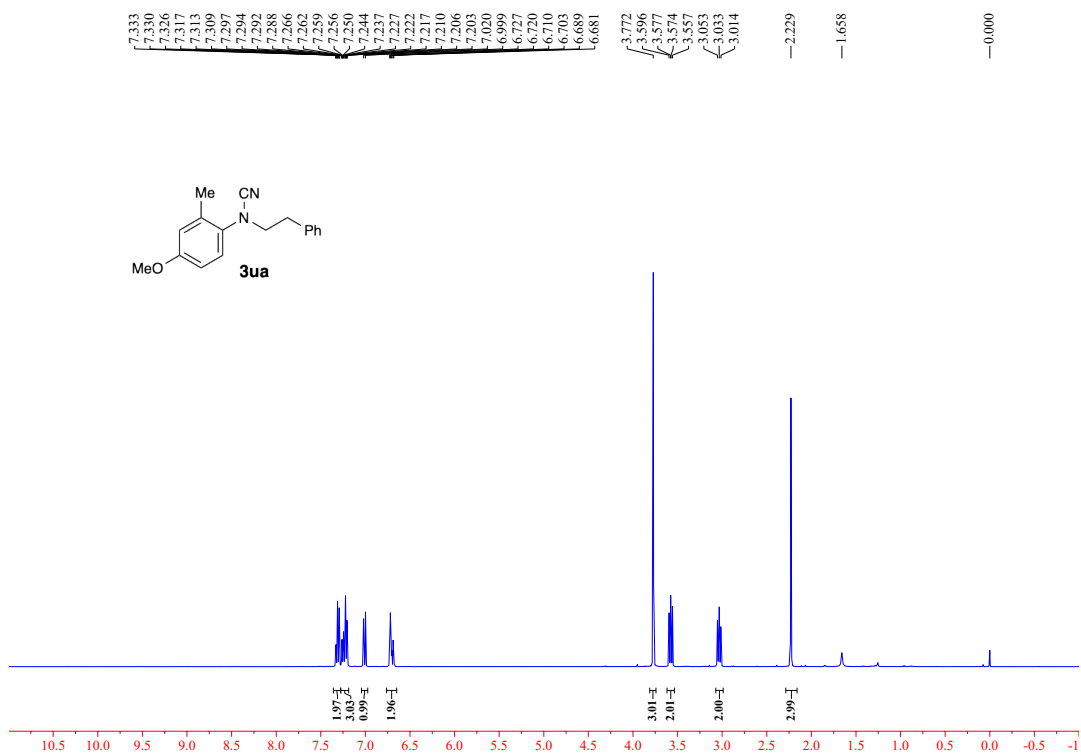
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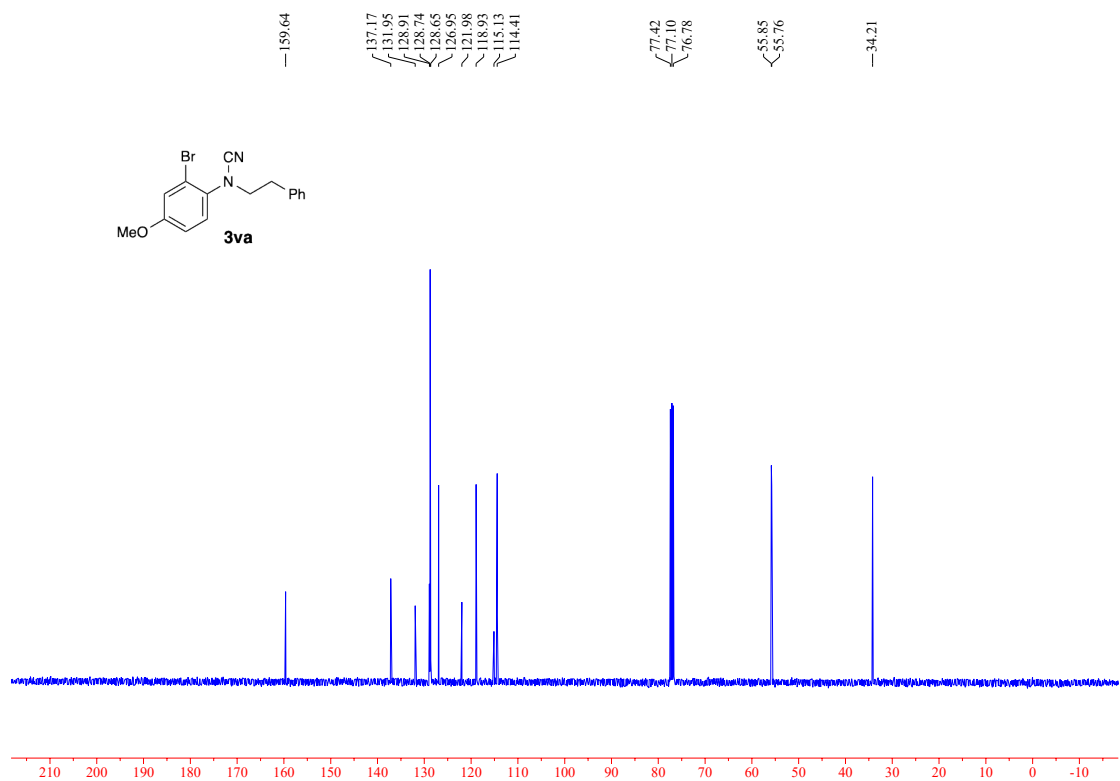
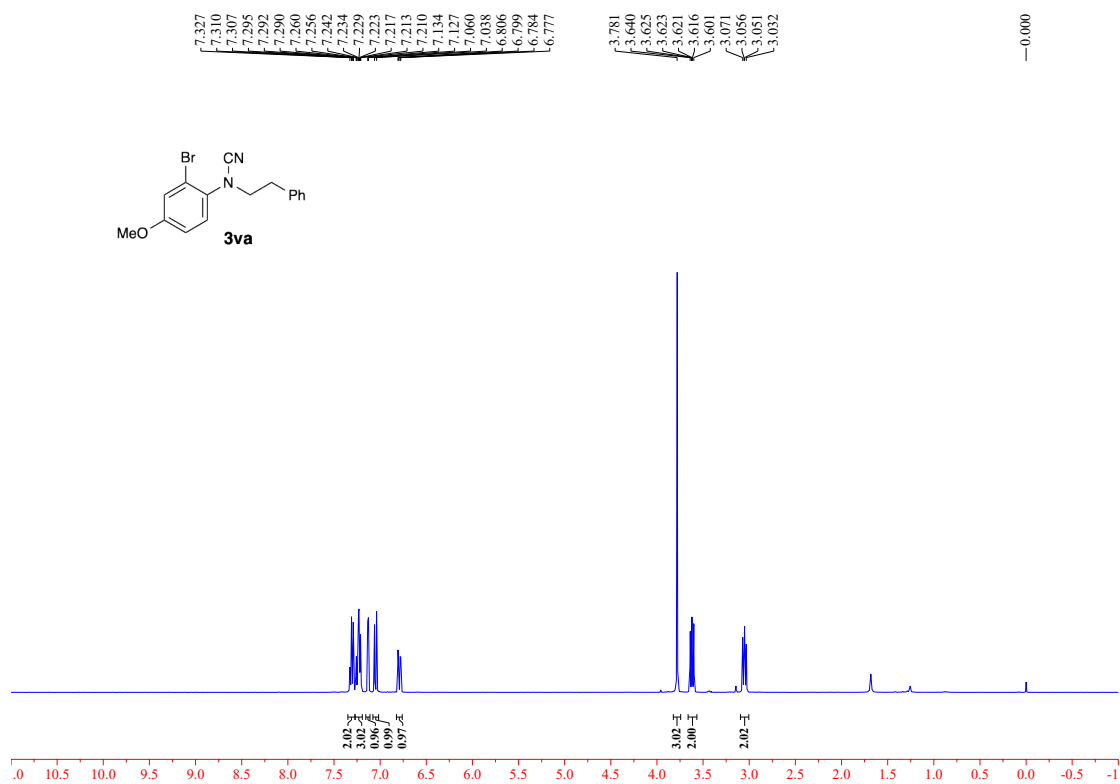
***N*-(4-nitrophenyl)-*N*-phenethylcyanamide (3ta)**



# *N*-(4-methoxy-2-methylphenyl)-*N*-phenethylcyanamide (**3ua**)

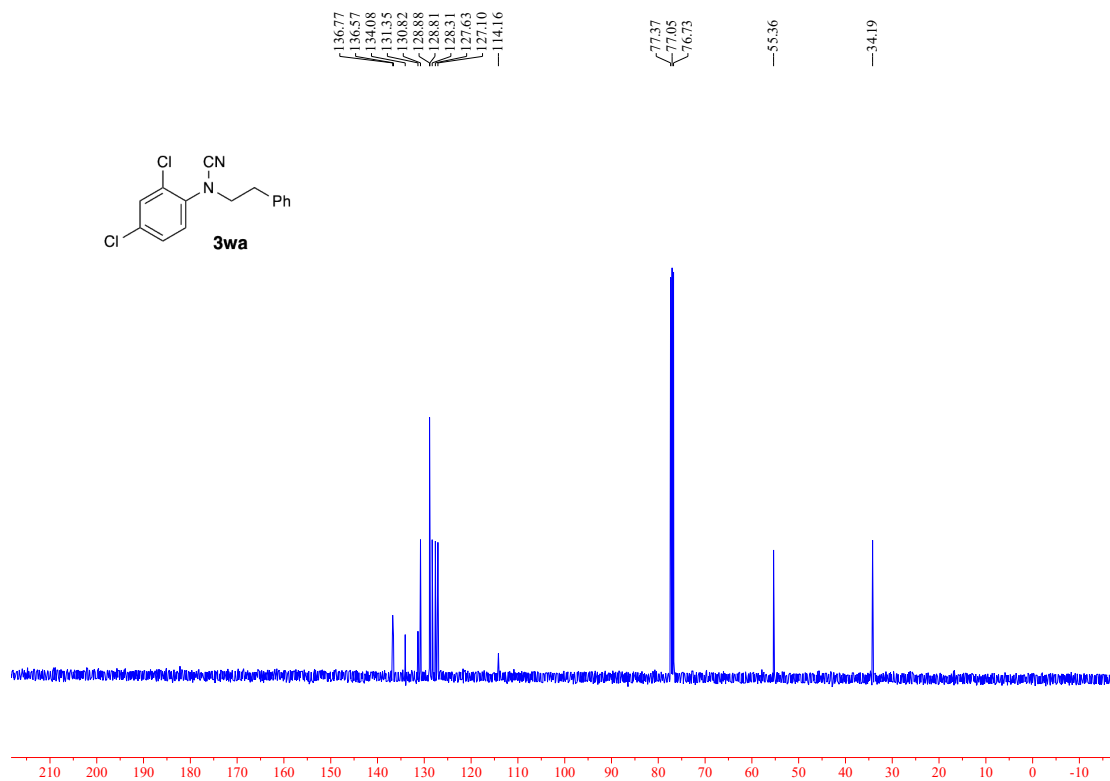
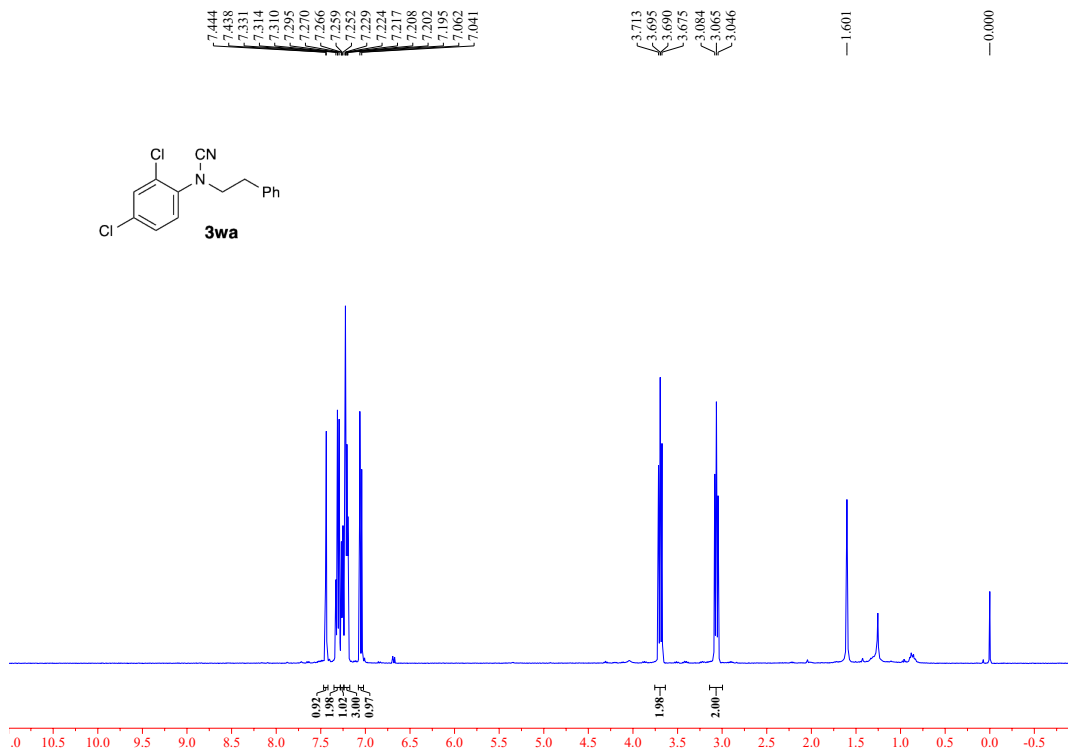


# *N*-(2-bromo-4-methoxyphenyl)-*N*-phenethylcyanamide (**3va**)

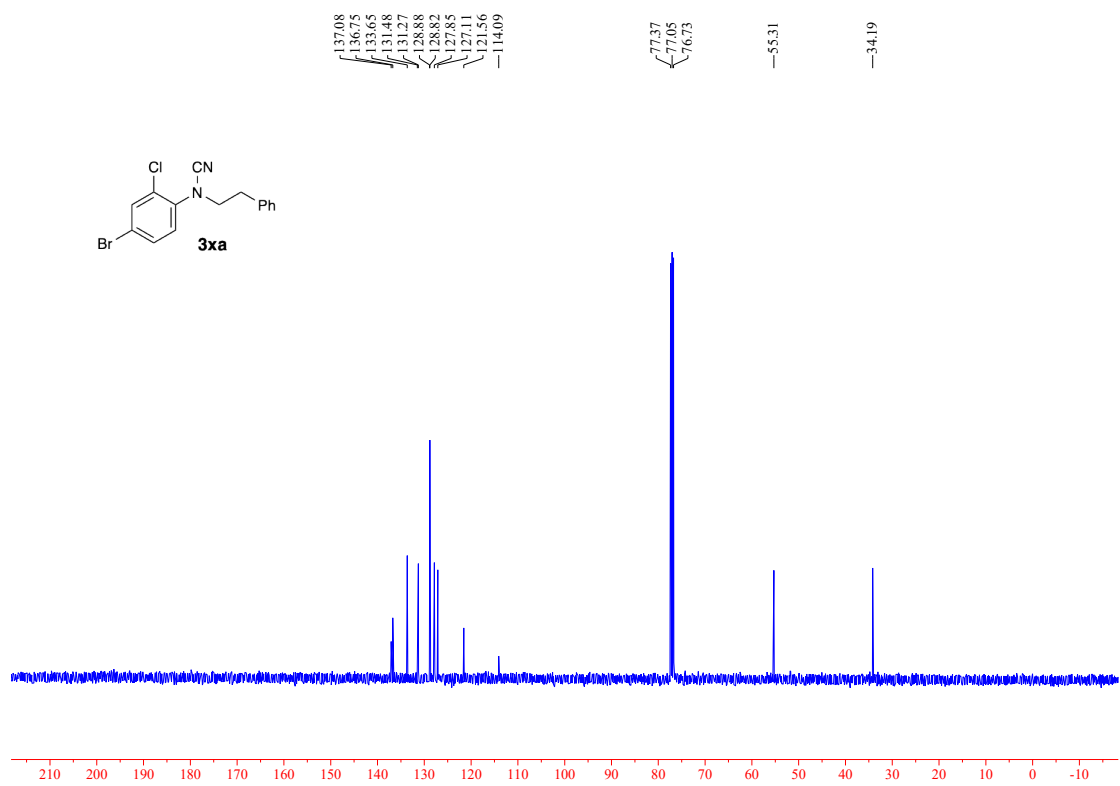
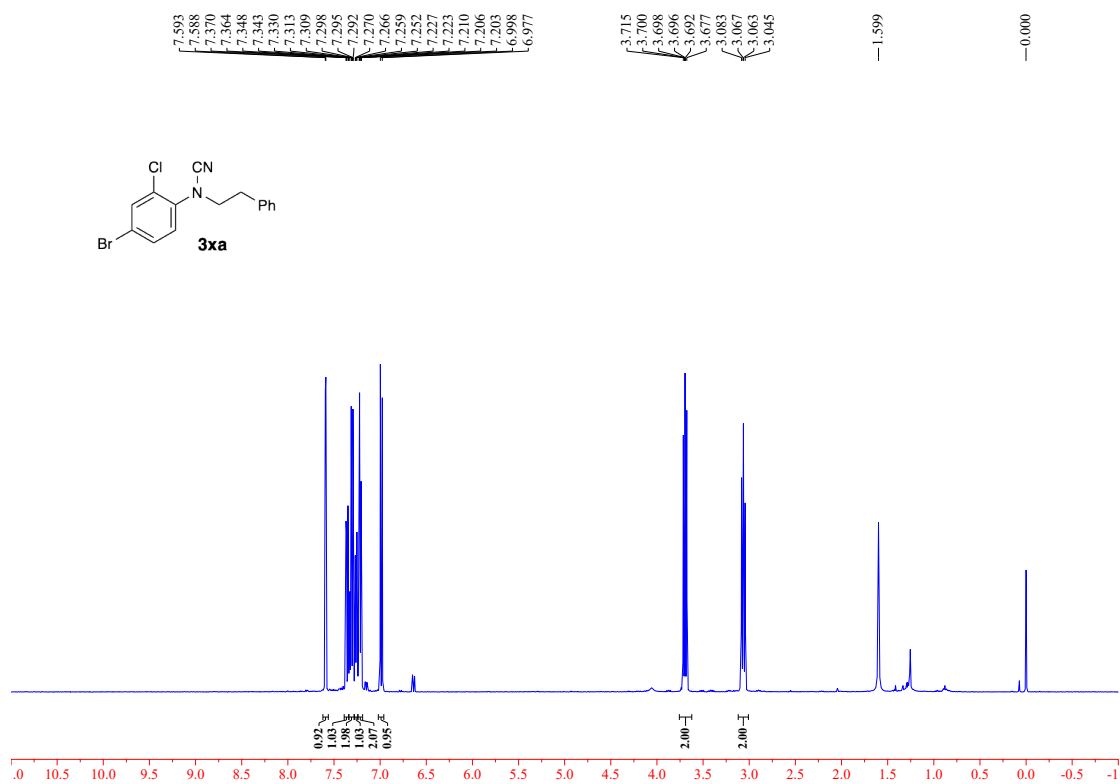




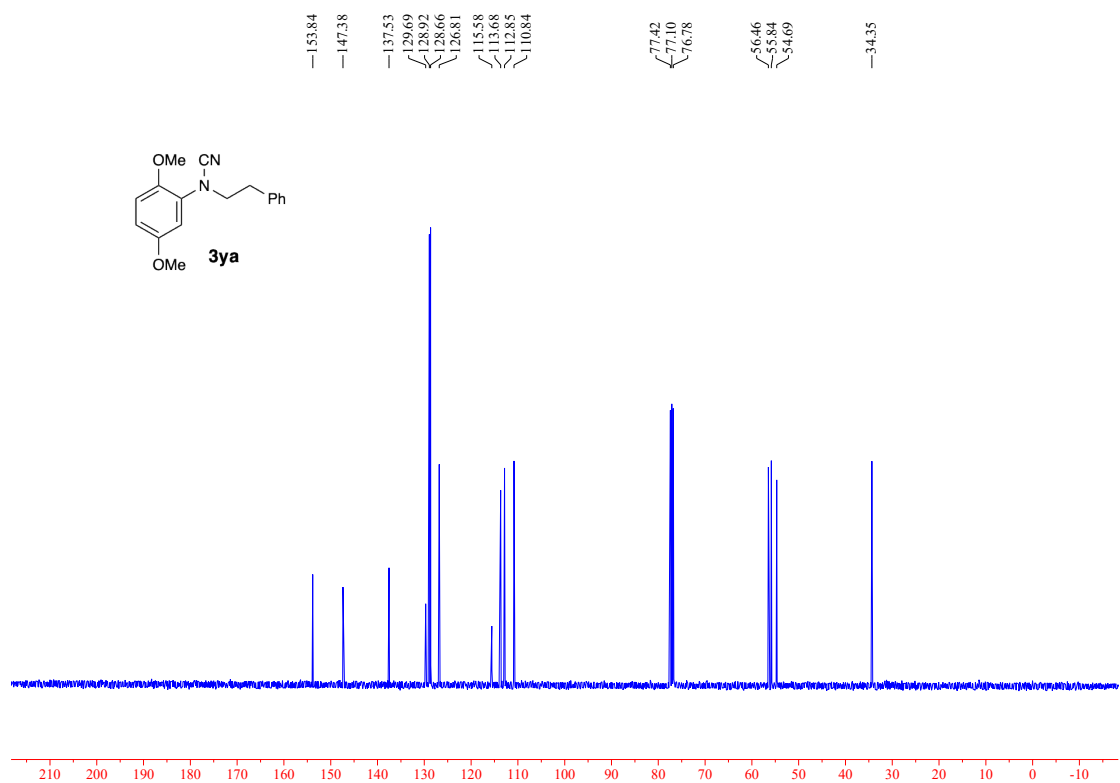
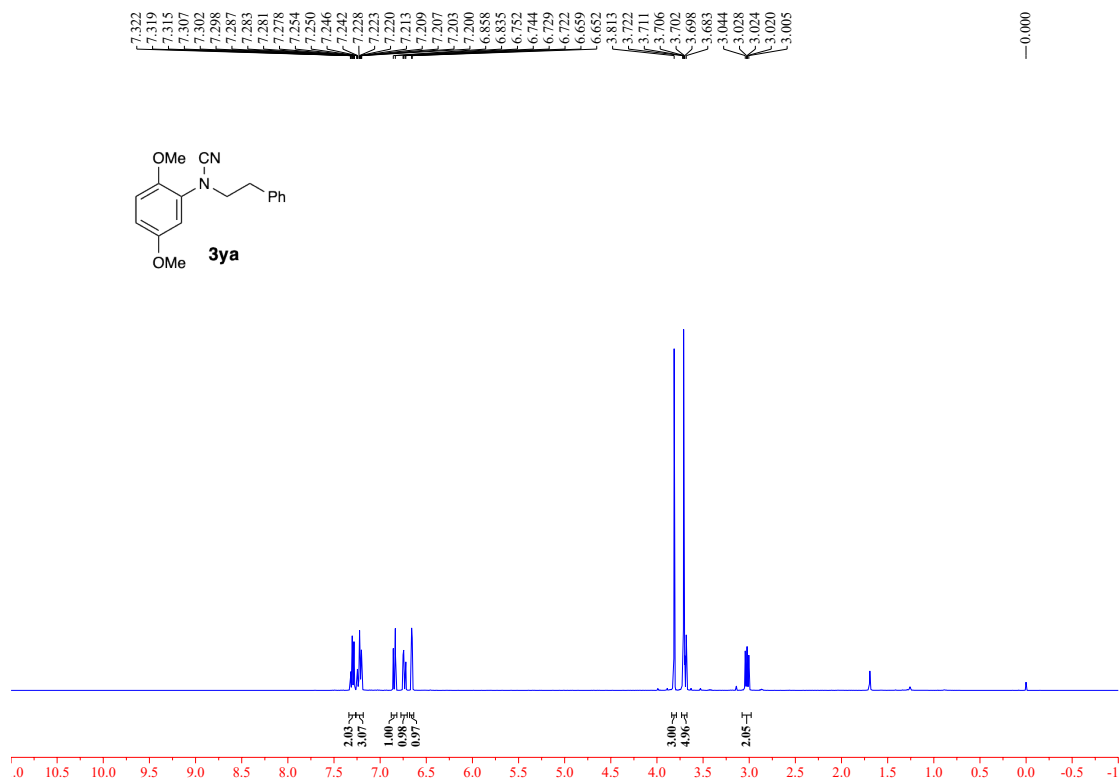
# *N*-(2,4-dichlorophenyl)-*N*-phenethylcyanamide (3wa)



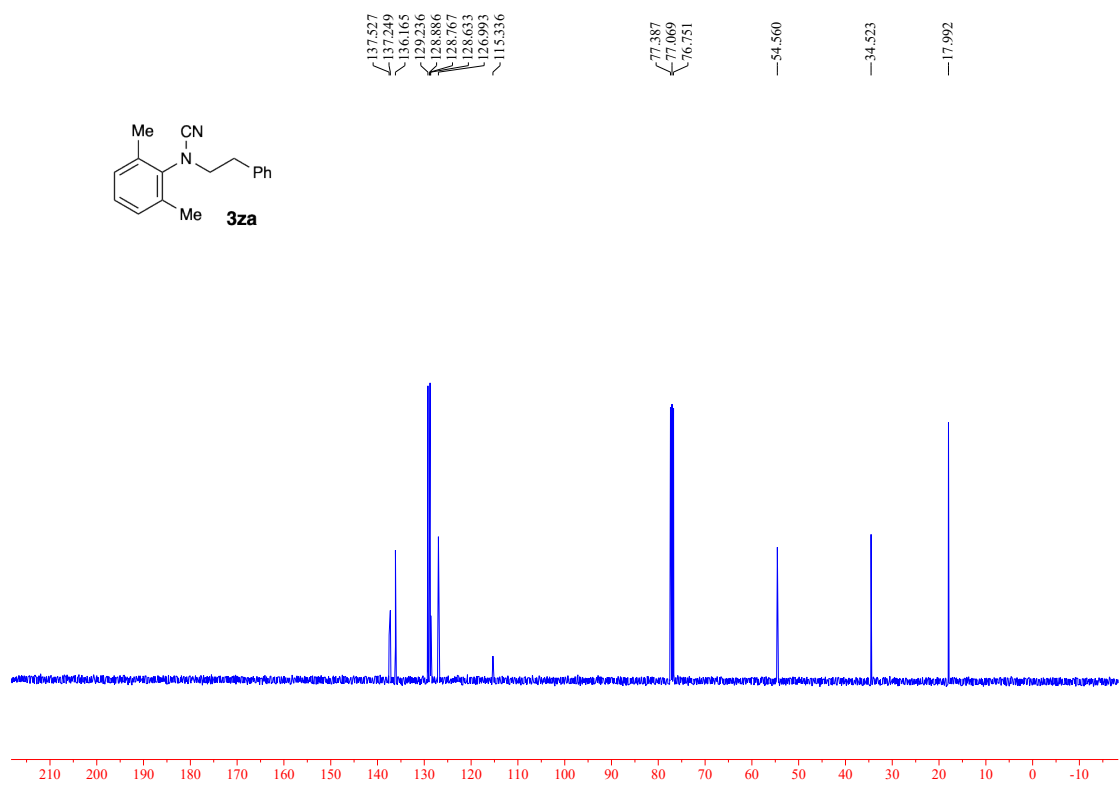
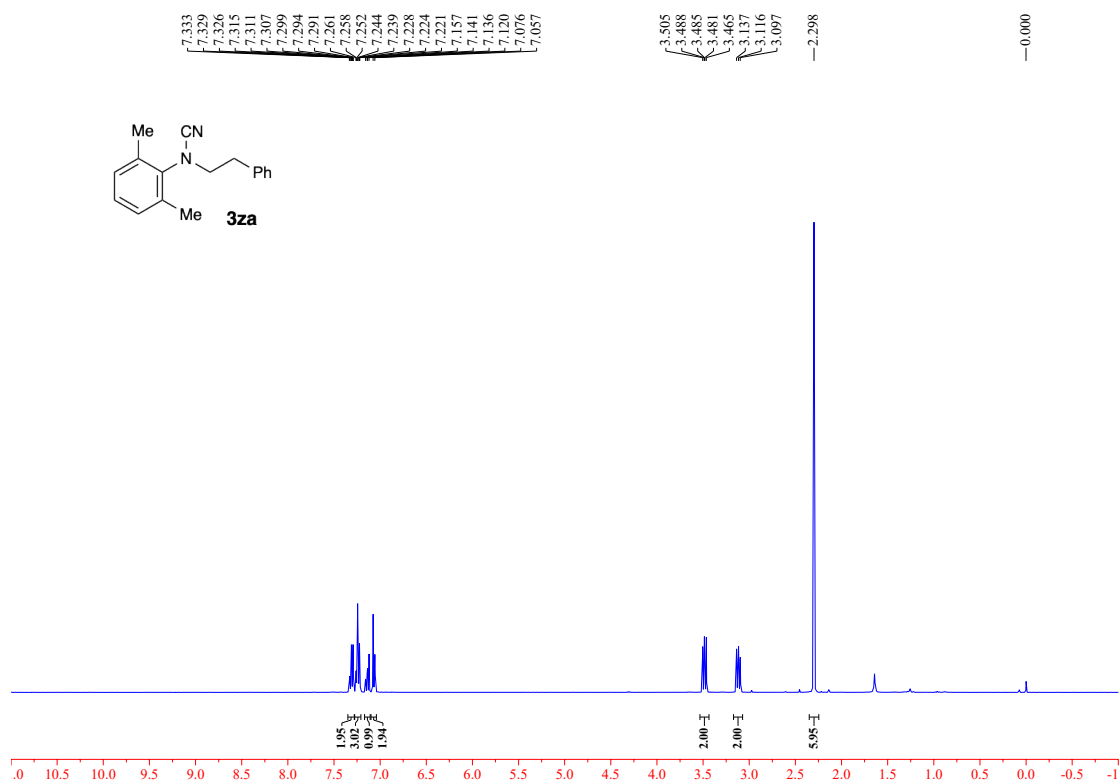
# *N*-(4-bromo-2-chlorophenyl)-*N*-phenethylcyanamide (**3xa**)



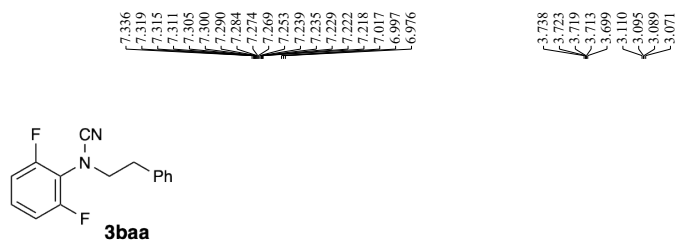
# *N*-(2,5-dimethoxyphenyl)-*N*-phenethylcyanamide (**3ya**)



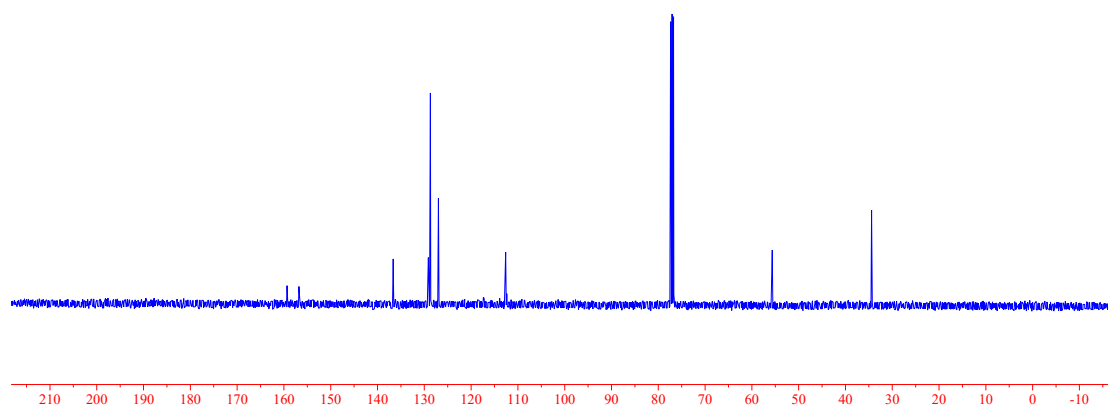
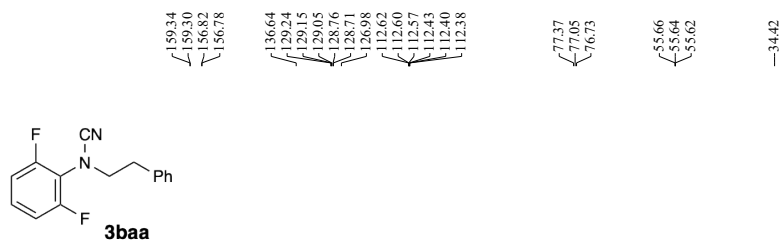
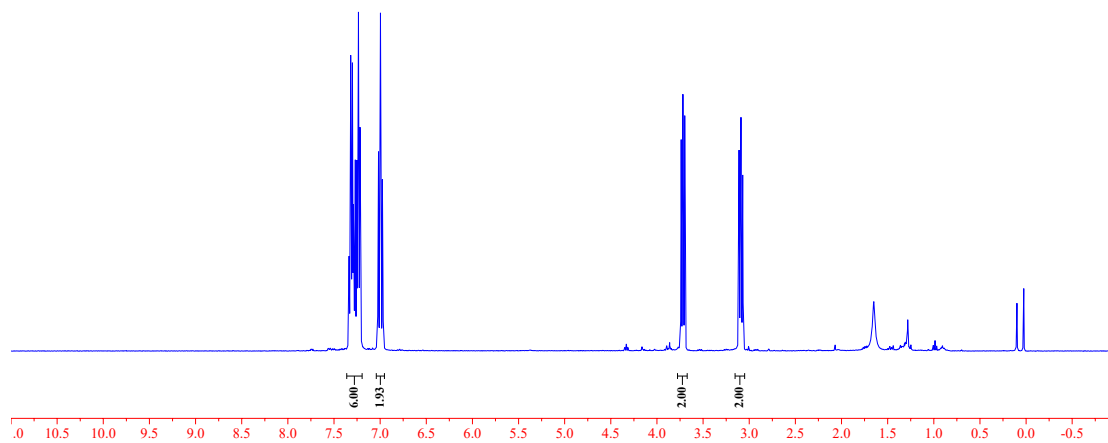
# *N*-(2,6-dimethylphenyl)-*N*-phenethylcyanamide (**3za**)

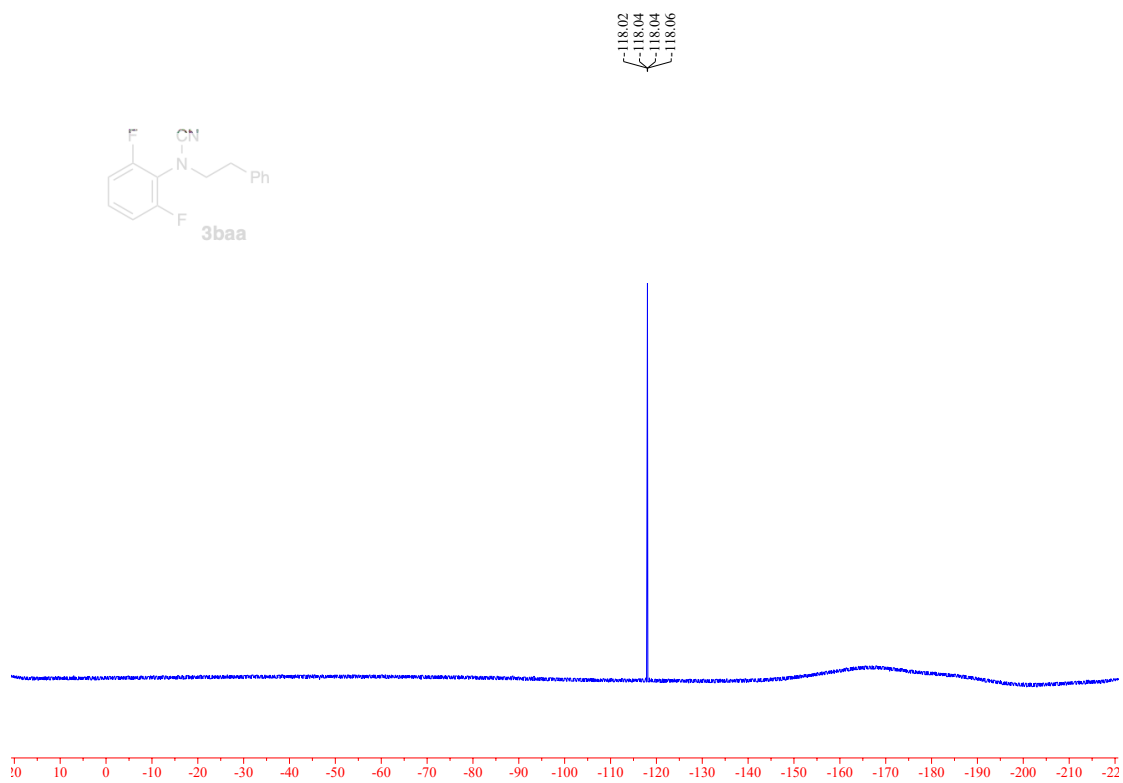
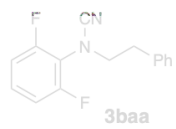


# *N*-(2,6-difluorophenyl)-*N*-phenethylcyanamide (**3baa**)

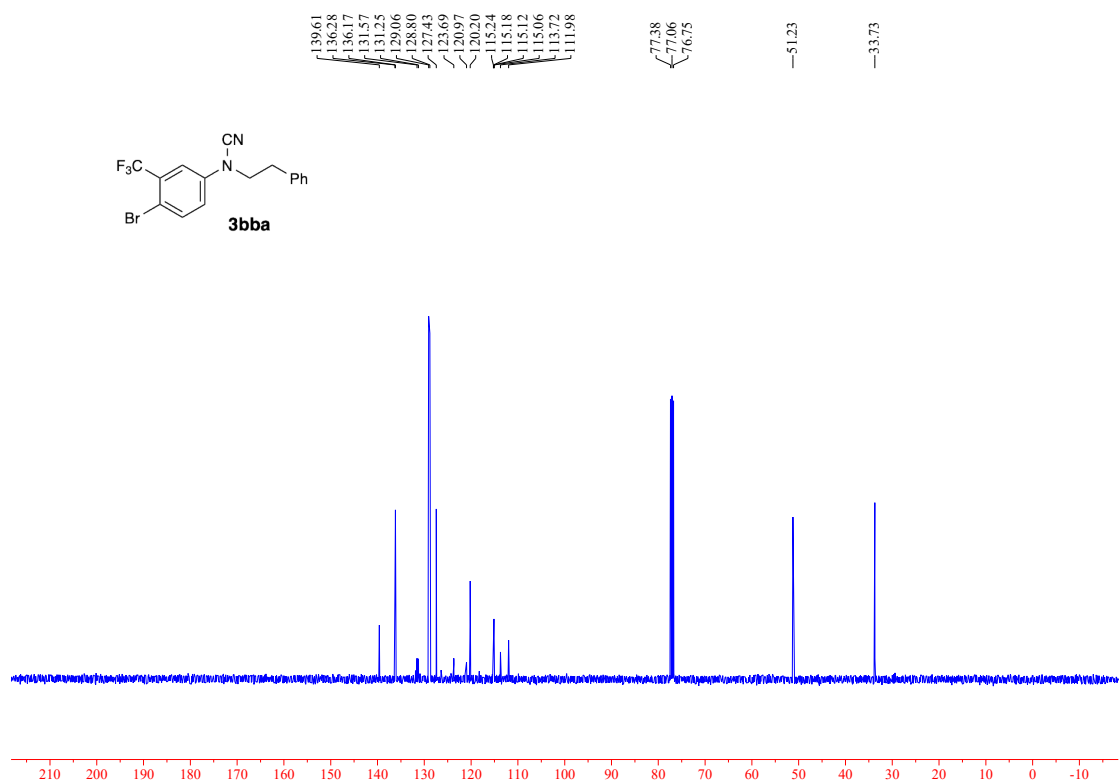
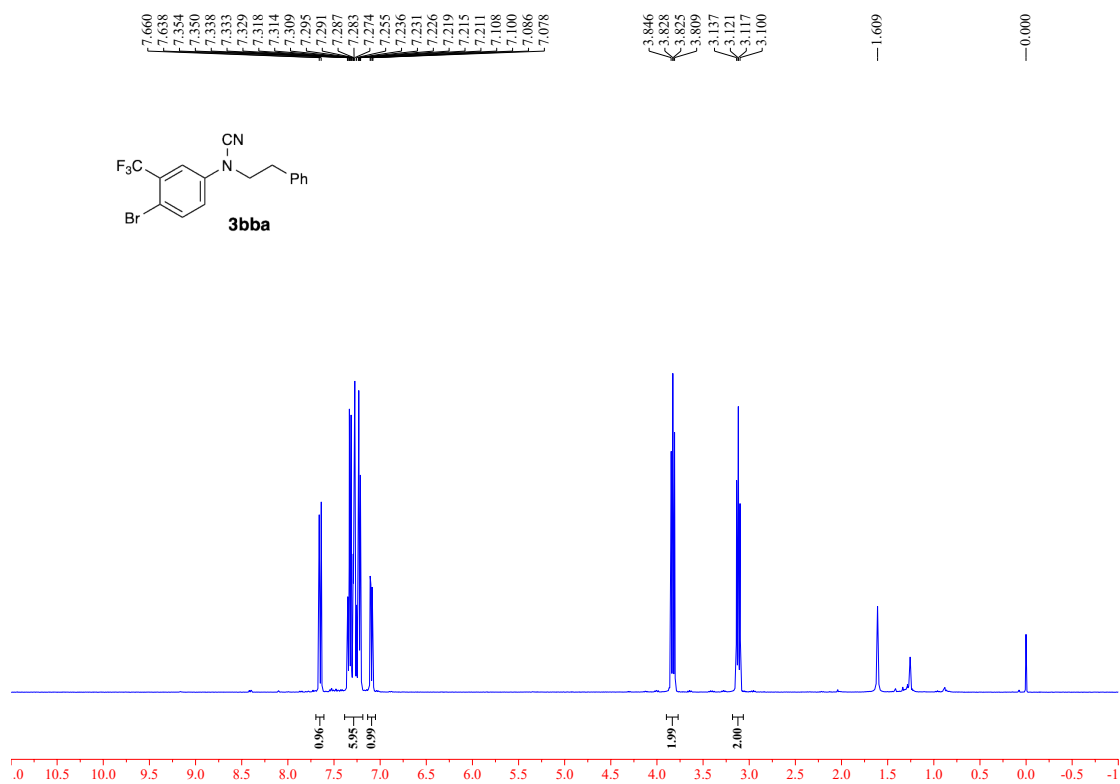


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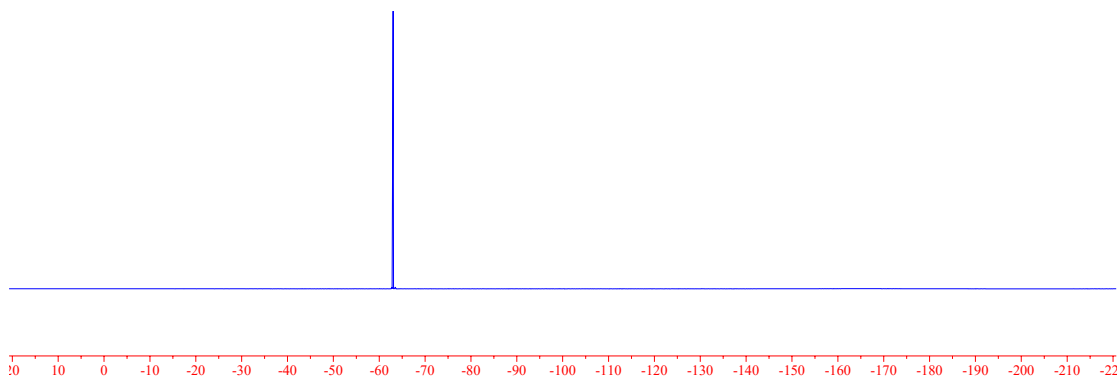
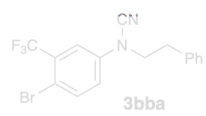




***N*-(4-bromo-3-(trifluoromethyl)phenyl)-*N*-phenethylcyanamide (3bba)**

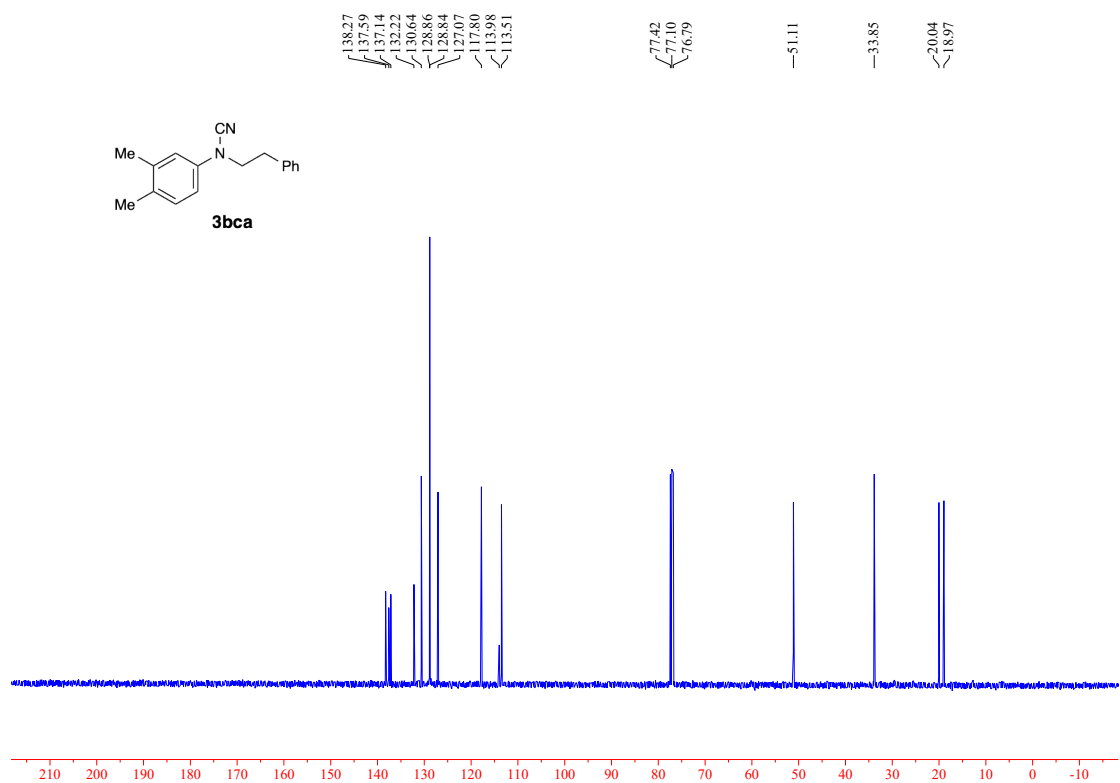
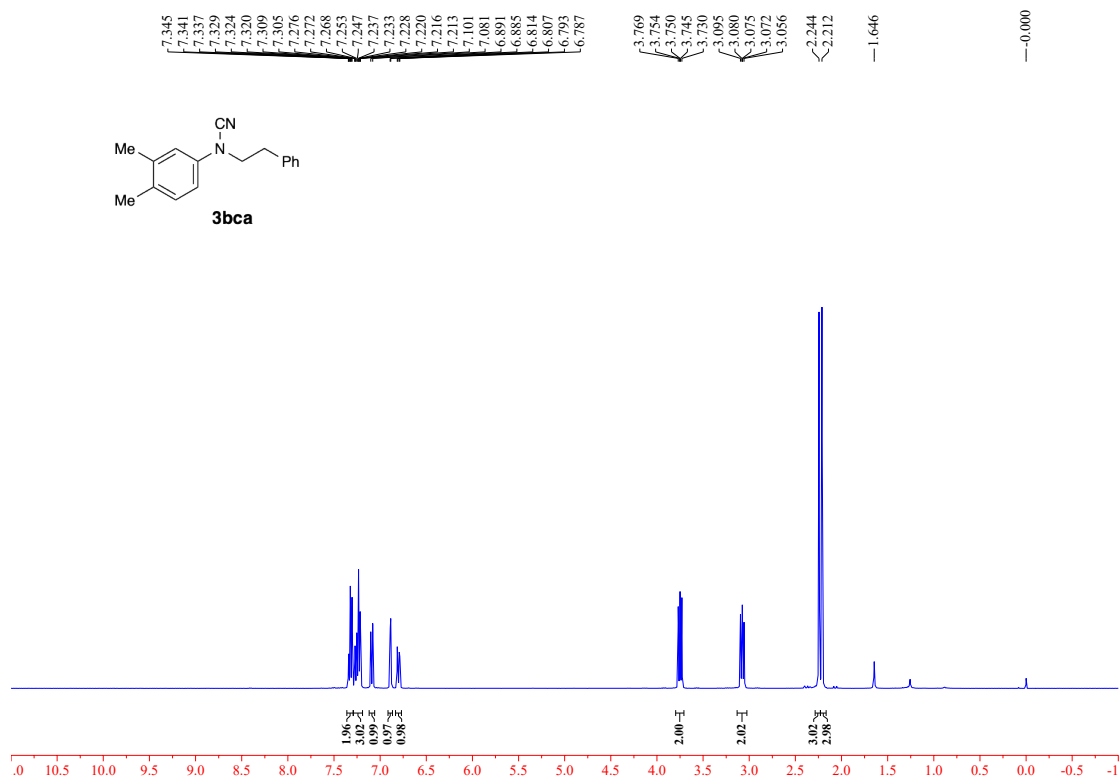


—63.02

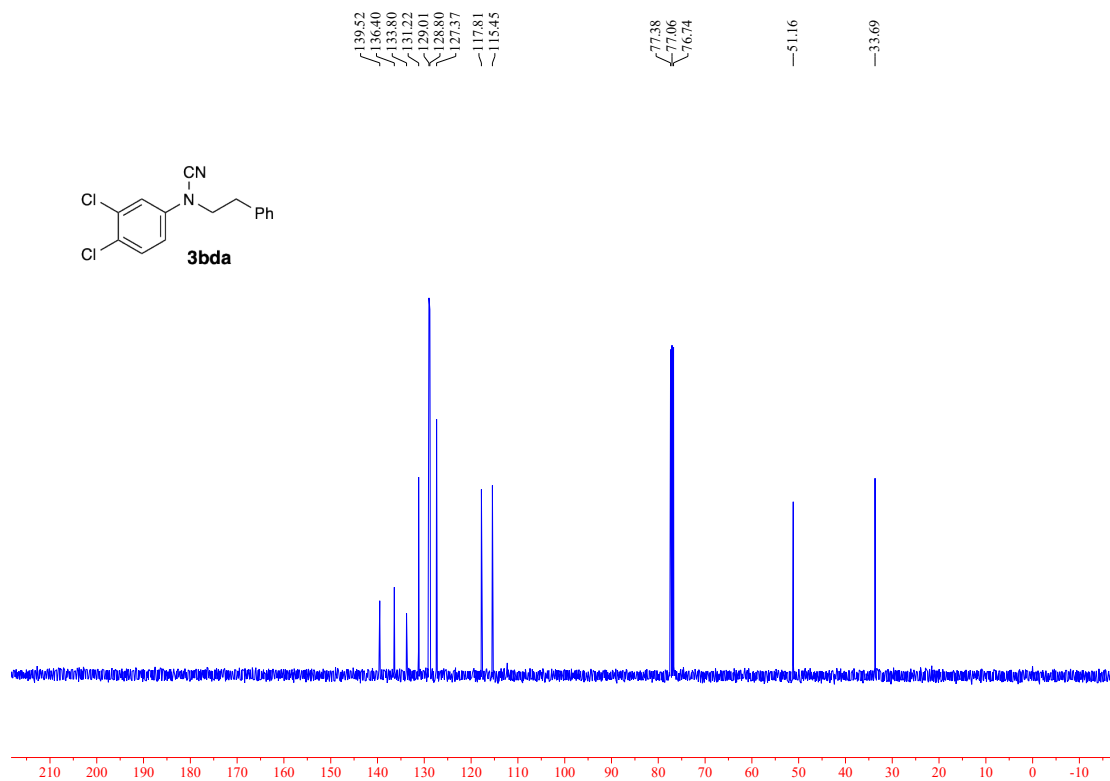
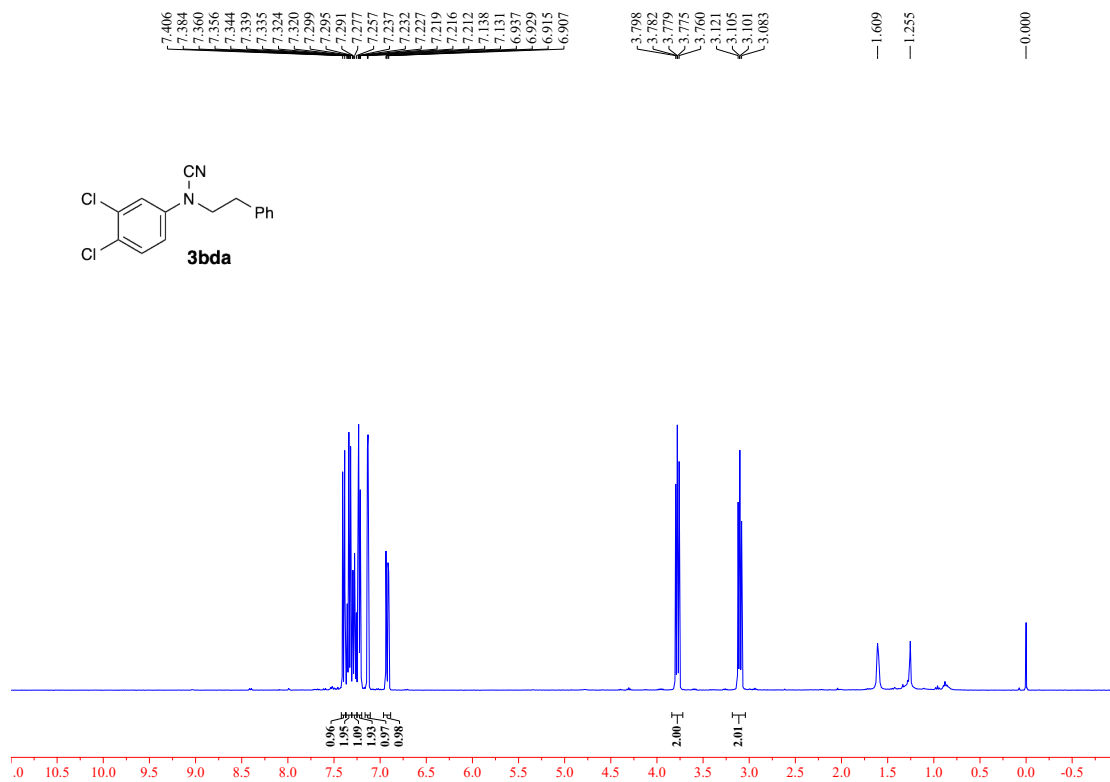




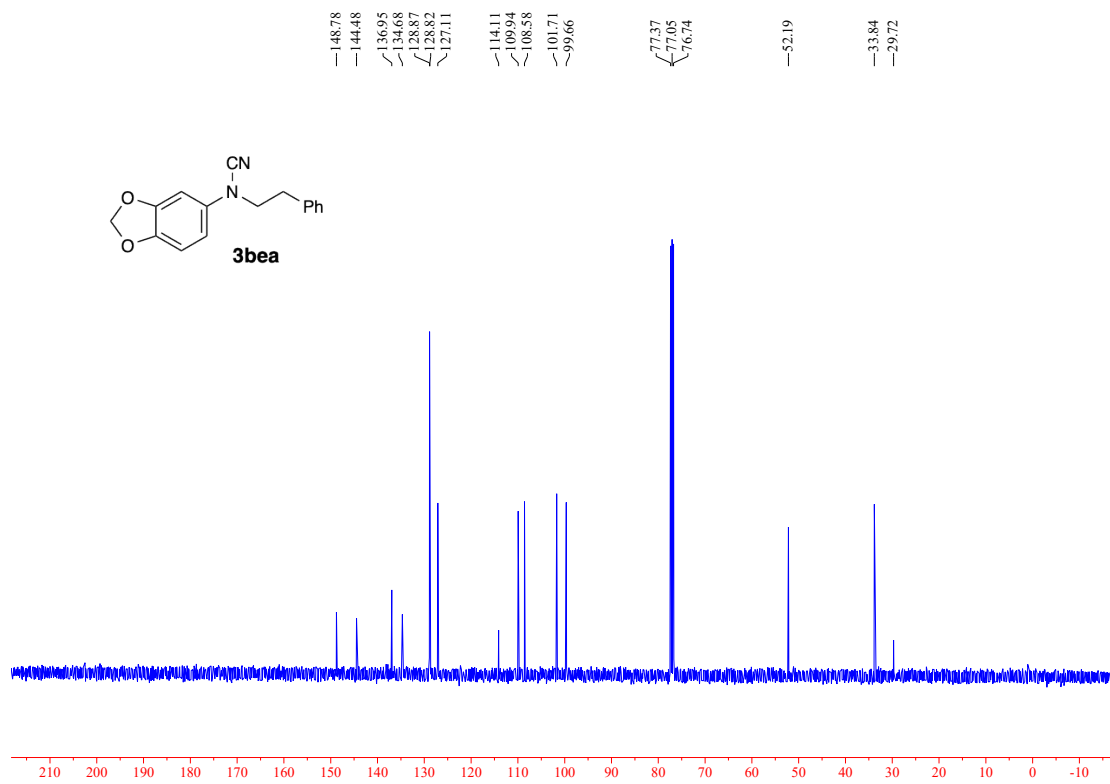
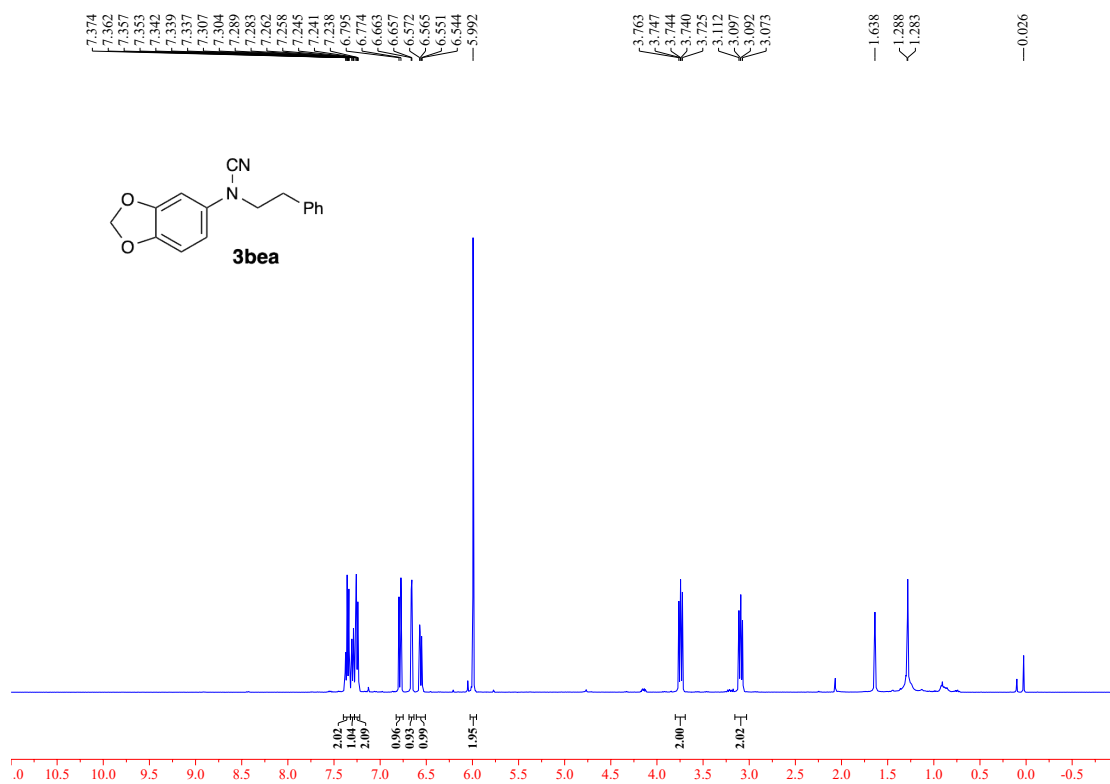
# *N*-(3,4-dimethylphenyl)-*N*-phenethylcyanamide (**3bca**)



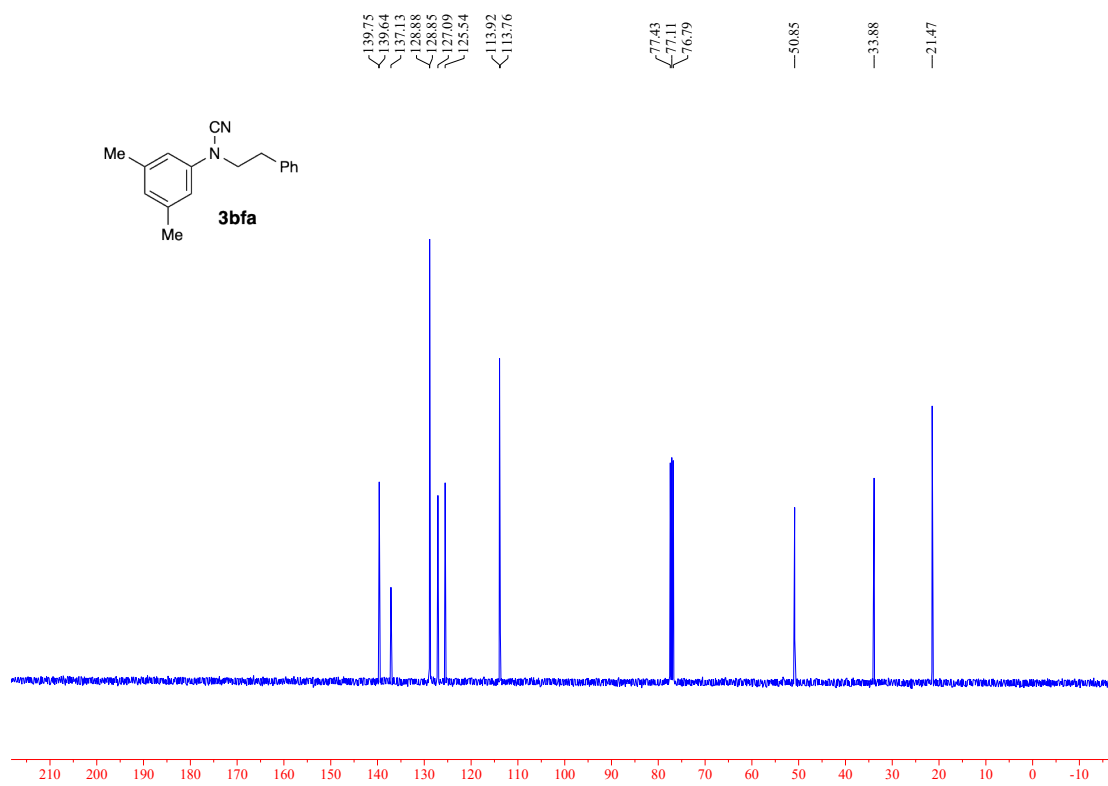
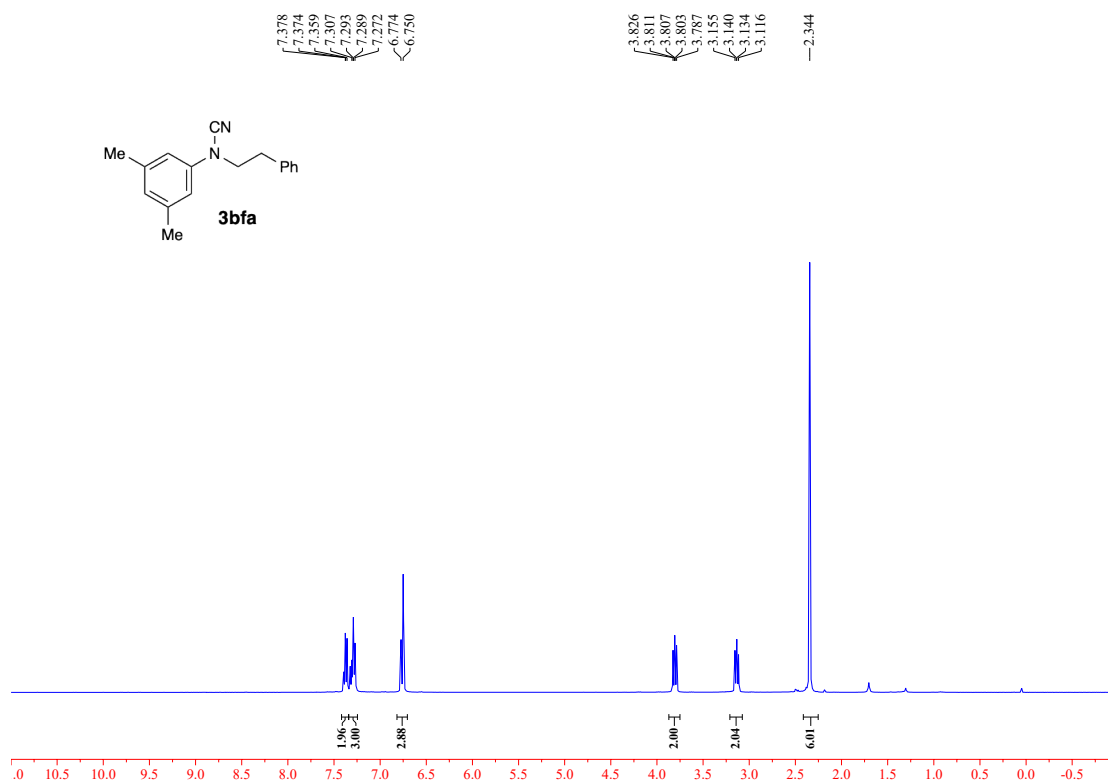
***N*-(3,4-dichlorophenyl)-*N*-phenethylcyanamide (3bda)**



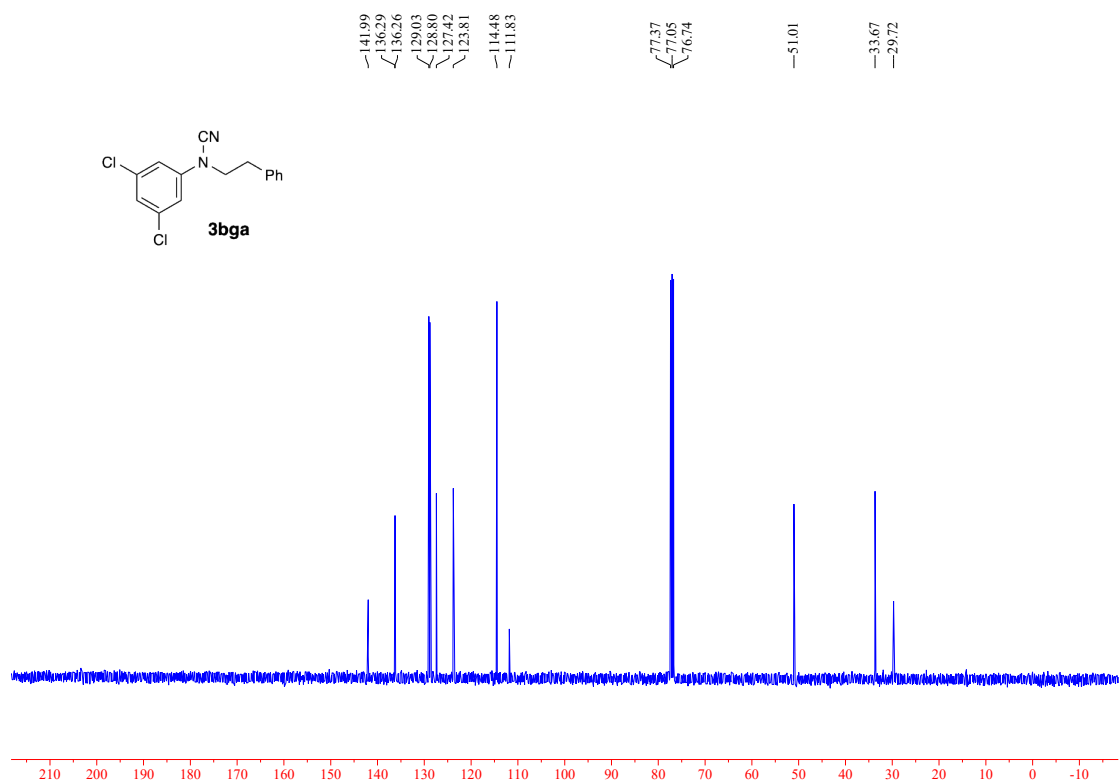
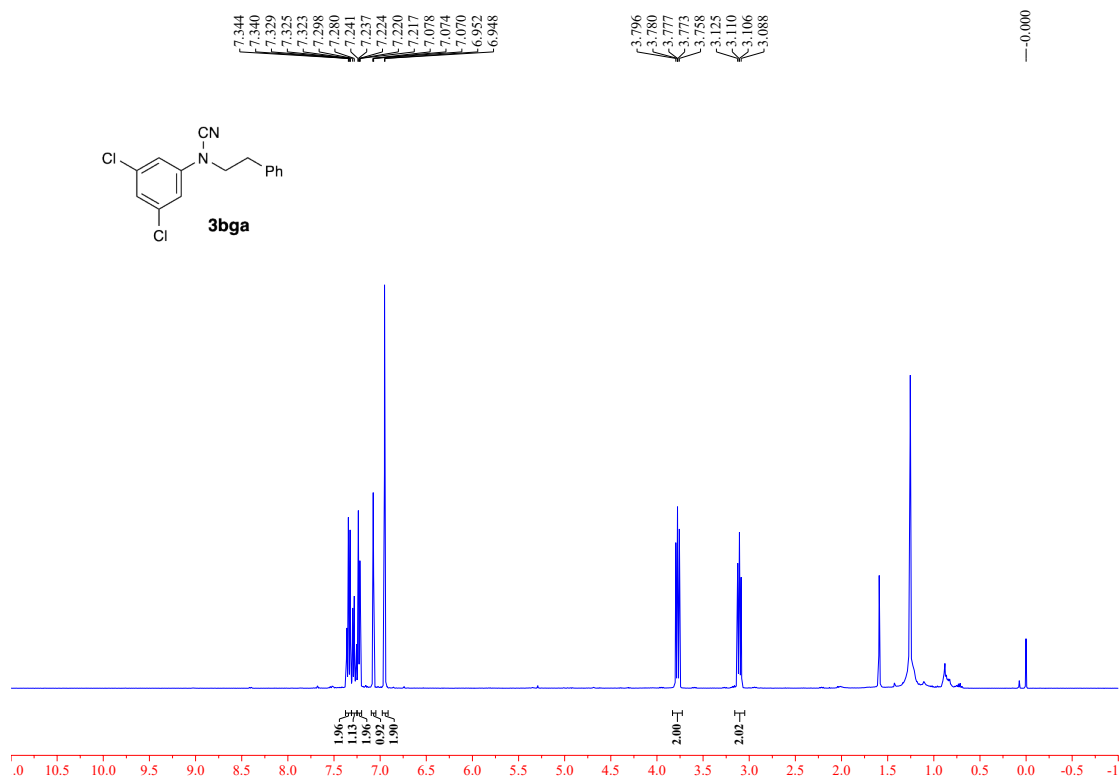
***N*-(benzo[*d*][1,3]dioxol-5-yl)-*N*-phenethylcyanamide (3bea)**



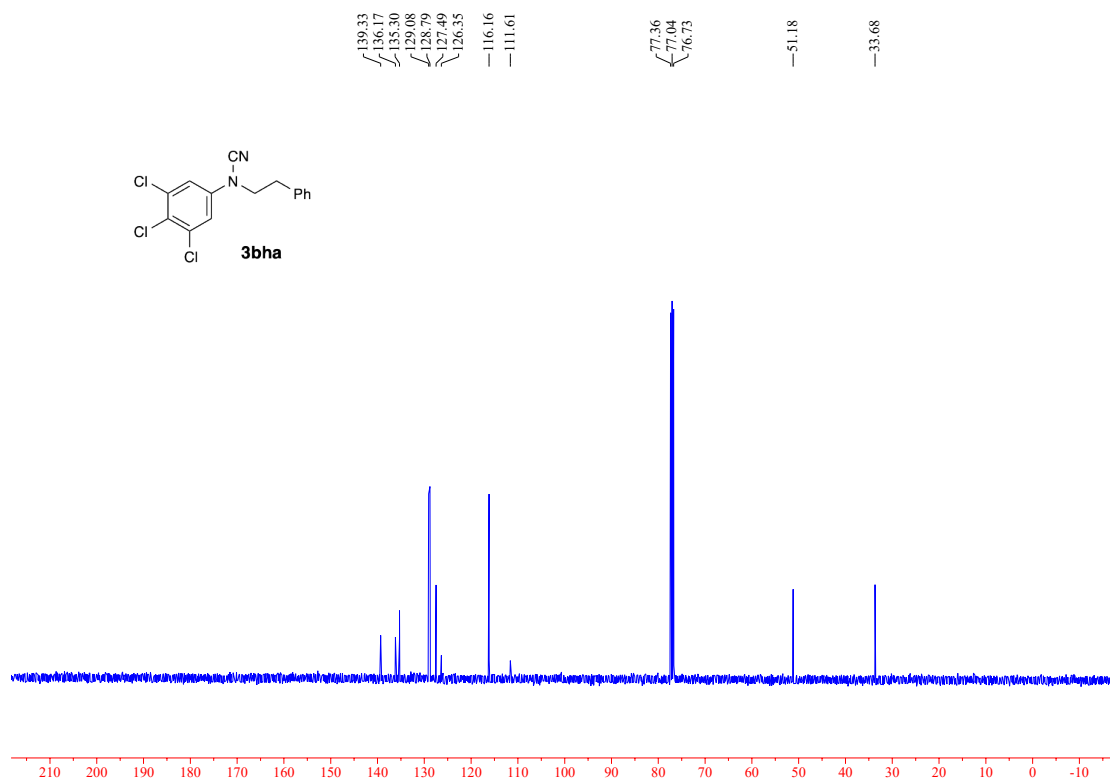
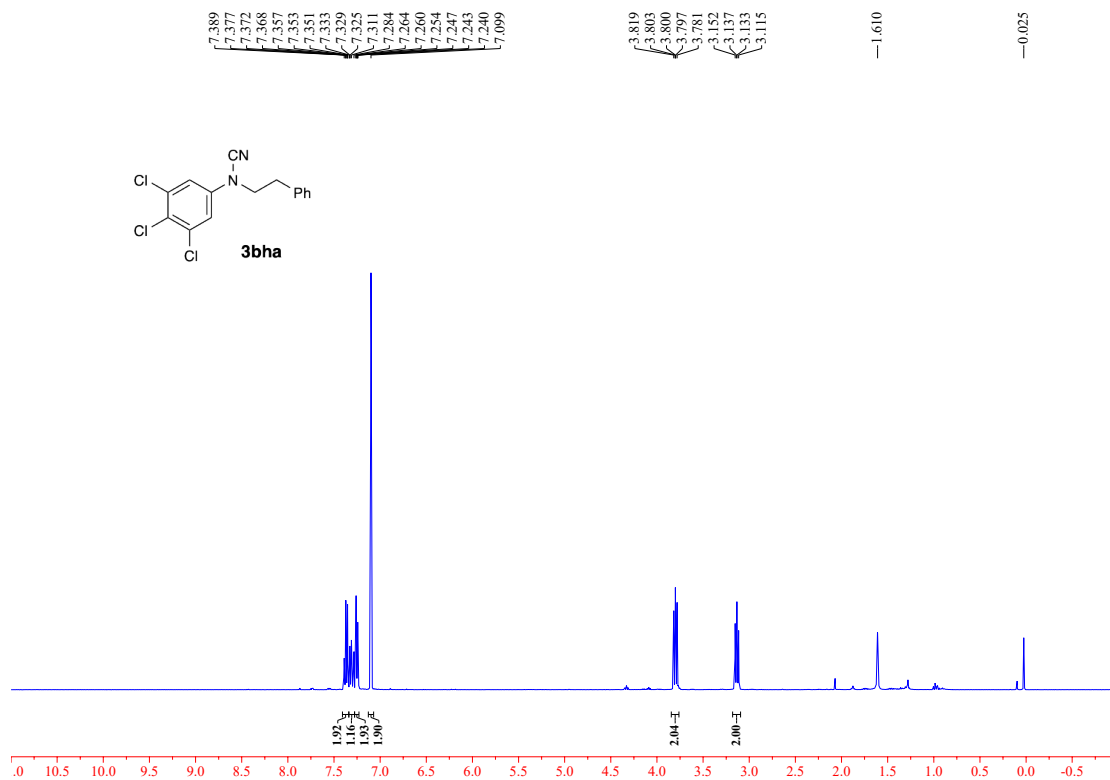
### *N*-(3,5-dimethylphenyl)-*N*-phenylethanamide (**3bfa**)



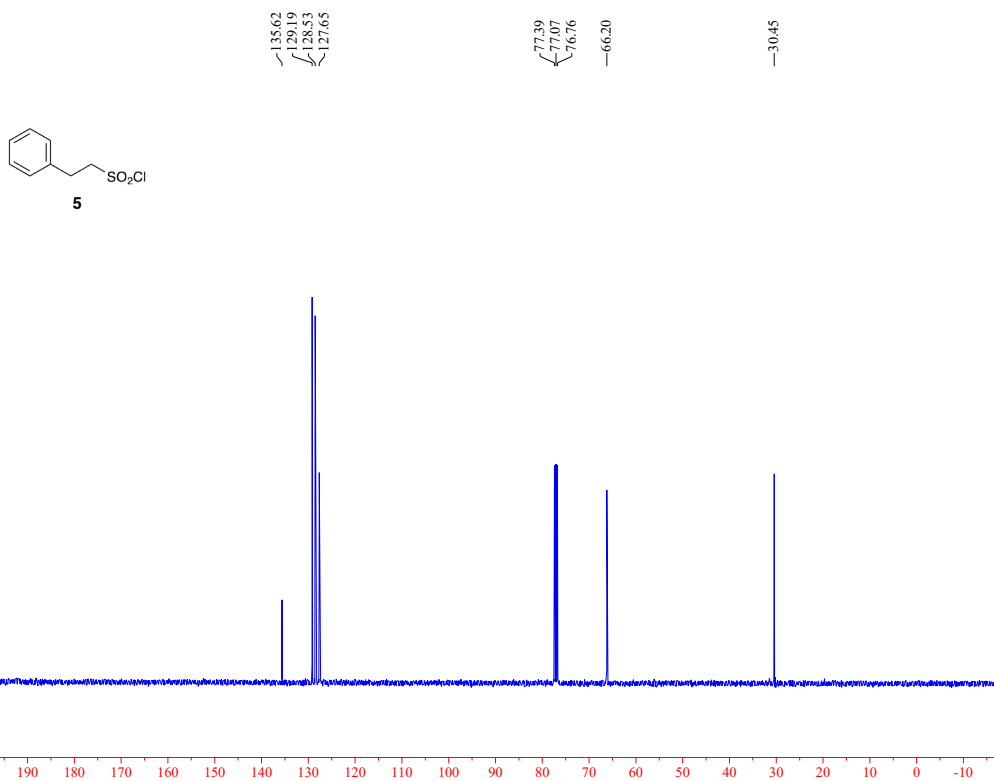
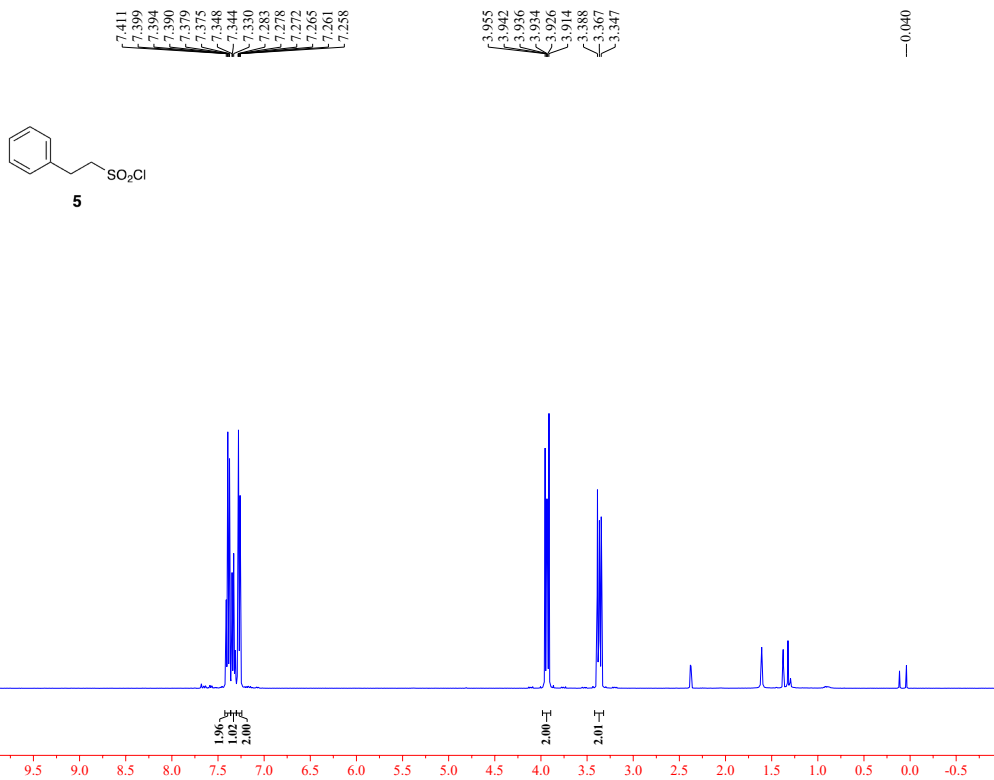
# *N*-(3,5-dichlorophenyl)-*N*-phenethylcyanamide (**3bga**)



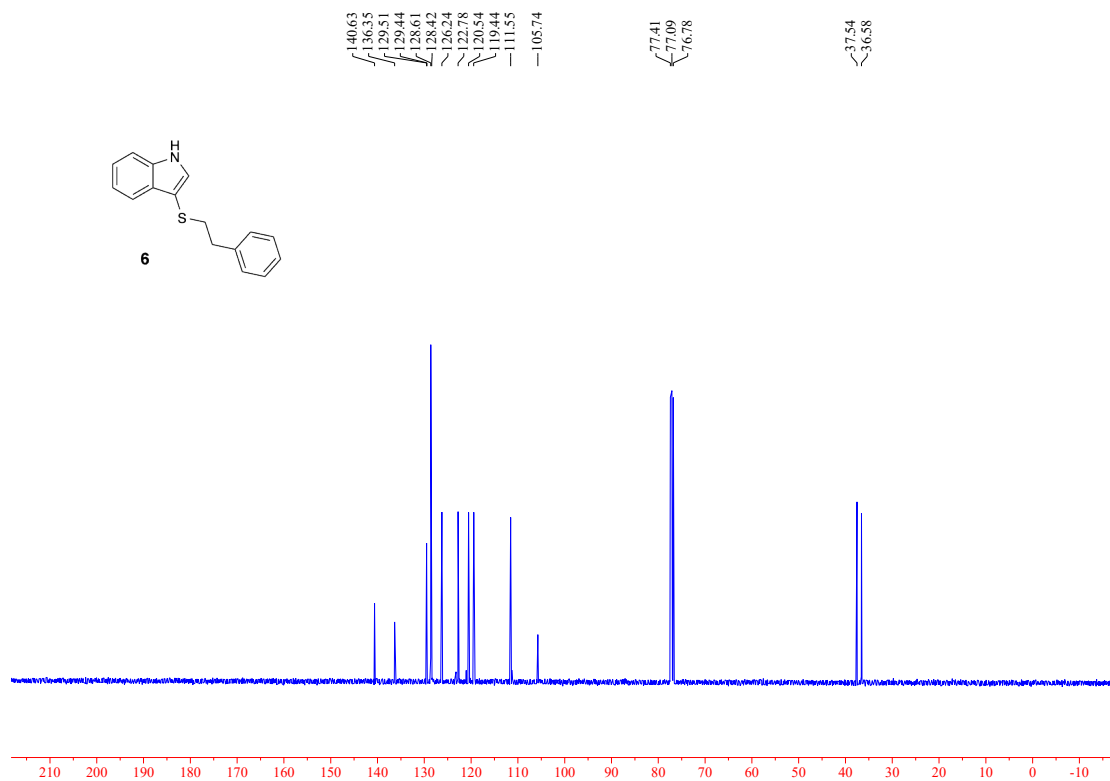
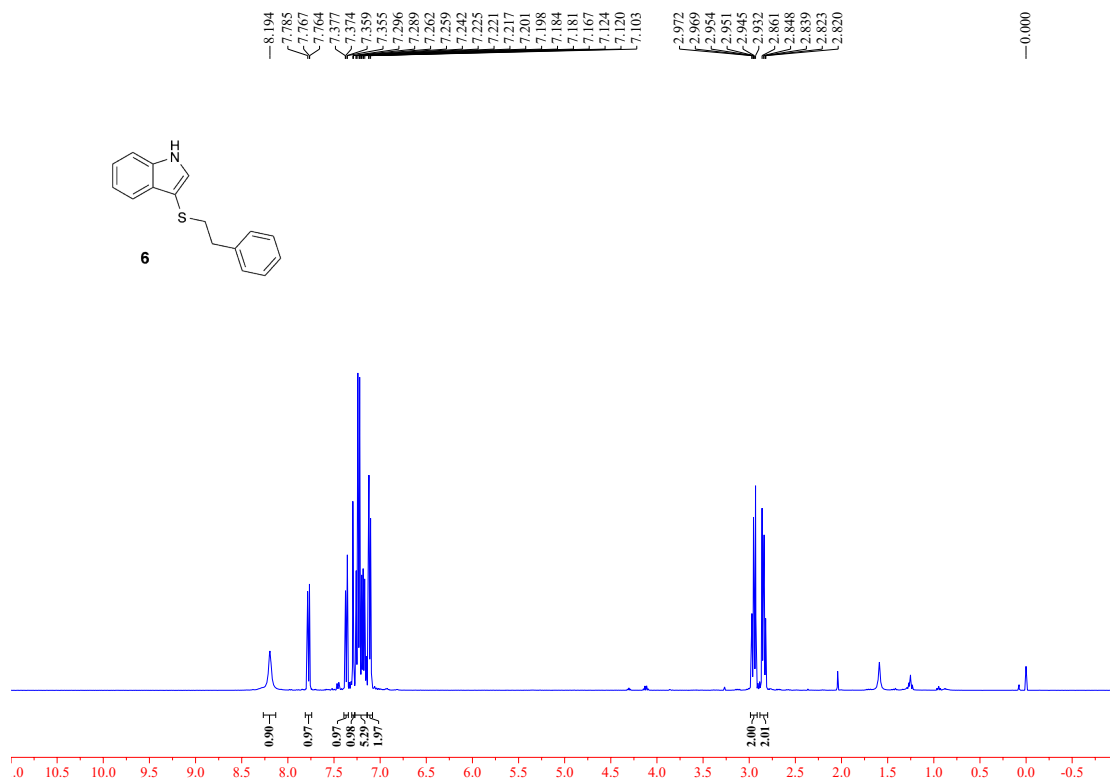
***N*-phenethyl-*N*-(3,4,5-trichlorophenyl)cyanamide (3bha)**



# 2-phenylethane-1-sulfonyl chloride (5)

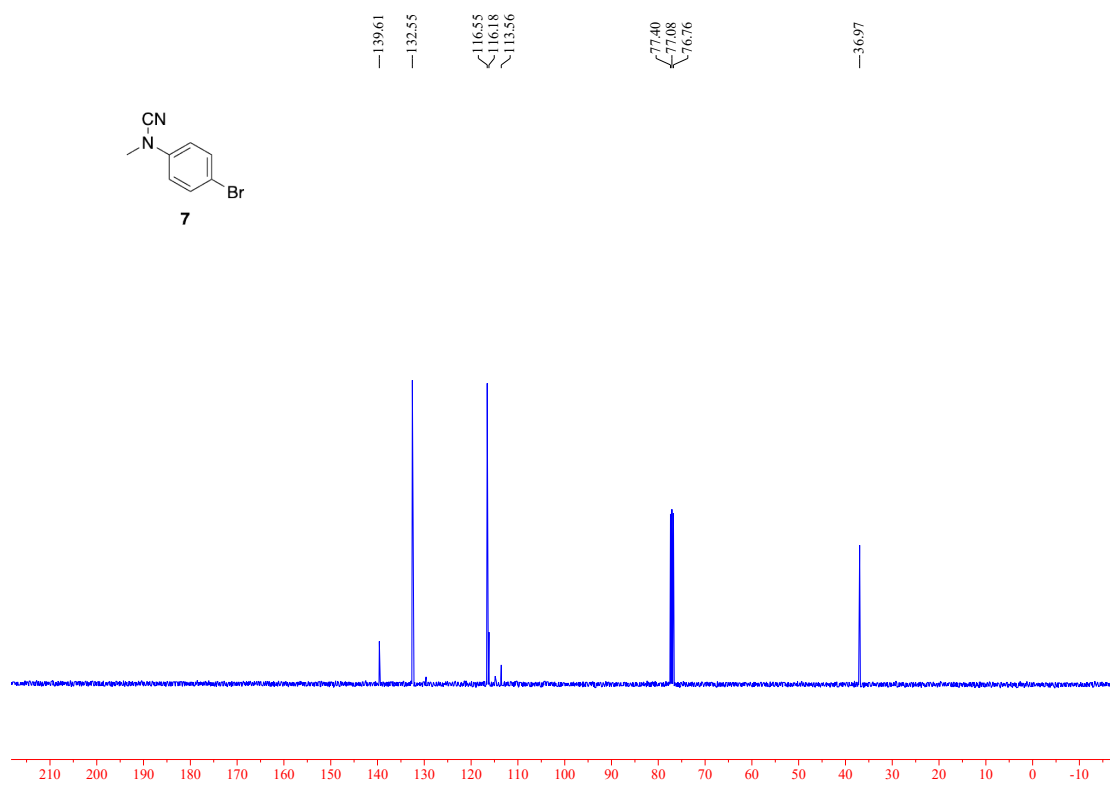
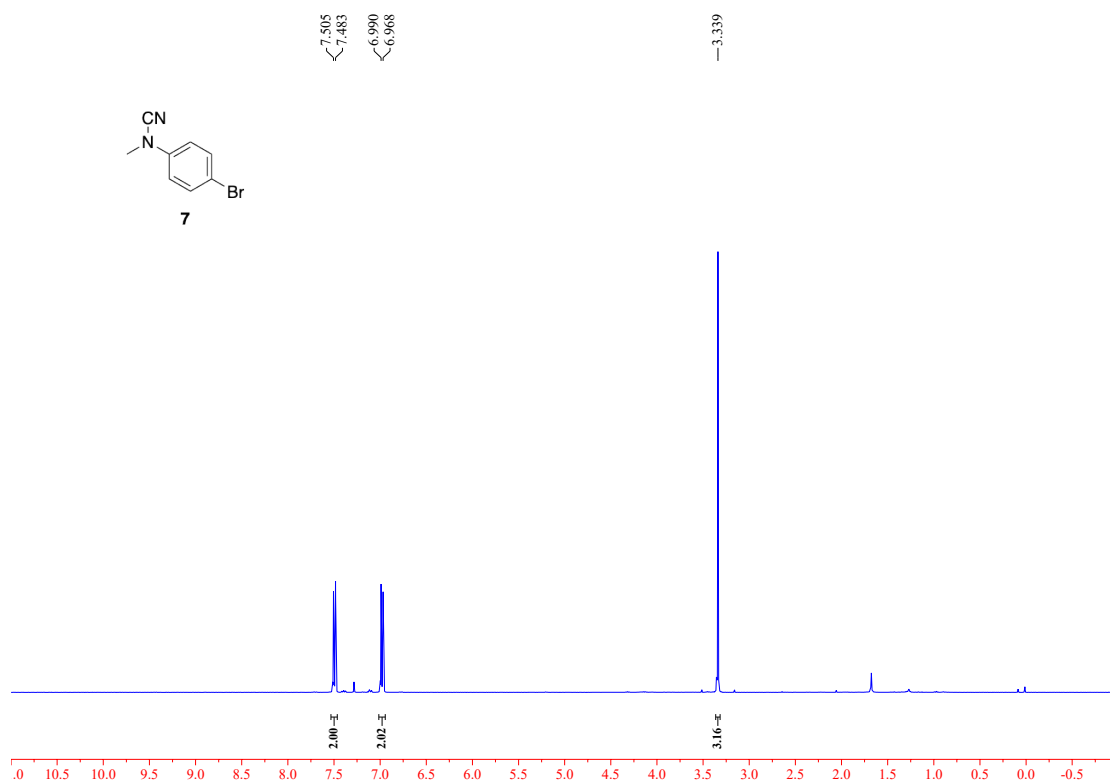


### 3-(phenethylthio)-1H-indole (6)





# *N*-(4-bromophenyl)-*N*-methylethanamide (7)



# N-phenethylamine (8)

