Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Azobenzene-Benzoylphenylureas as Photoswitchable Chitin Synthesis Inhibitors

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1. Materials and General Methods

Instruments and Chemicals. ^{1}H NMR spectra were recorded on Bruker AM-400 spectrometer. Chemical shifts are reported in δ (ppm) values with TMS as internal standard, using DMSO-d_6 as the solvent. Melting points were recorded on Büchi Melting Point B-540 and were uncorrected. High-resolution mass spectrometry (HRMS) data were recorded on a MicroMass GCT CA 055 instrument under electron impact (70 eV) condition. The UV-Vis spectra was recorded with Lambda 650 UV-Vis spectrophotometer (PerkinElmer). The *cis*/*trans* ratio was recorded with ACQUITY UPLC H-Class. In experiments of affinity binding to SUR, processes of chopping and homogenization were completed with Tissuelyser-24 homogenizer. Centrifugation was completed with Allegra 64R Centrifuge (Beckman Coulter). Fluorescence polarization was conducted on Synergy H1 microplate reader (Bio-Tek). All reagents were analytically or chemically pure and solvents were dried before reactions when necessary.

Optical Properties: UV-Vis spectra, *cis/trans* ratio, half-life time.

Test of UV-Vis spectra. A 2×10^{-5} M solution of the target compound was prepared with acetonitrile as the solvent, and saved in the dark for 24 h at room temperature. The prepared solution was added in a 1 cm×1 cm cuvette and irradiated with 365 nm light. Meanwhile, its absorbance of 600-200 nm was recorded until the absorbance had no changes.

Test of cis/trans ratio. A 50 mg L^{-1} acetonitrile solution of the target compound was prepared, saved in the dark for 24 h at room temperature. The *cis/trans* ratio was recorded with Ultra Performance Liquid Chromatography. Then the solution was irradiated with 365 nm light, and the *cis/trans* ratio was recorded.

Test of half-life. A 25 mg L^{-1} acetonitrile solution of the target compound was prepared, saved in the dark for 24 h at room temperature. Its absorbance at $\lambda_{trans\text{-}max}$ was recorded. Then the solution was fully irradiated with 365 nm light to make the *trans* configuration convert to the *cis* configuration at the most extent. Subsequently, the solution was saved in the dark and its absorbance was recorded at intervals.

Insecticidal Activity against Armyworm (*Mythimna separate*).

All bioassays were performed on representative test organisms raised in the laboratory. Each experiment was repeated three times at 25 ± 1 ^oC according to the statistical requirements. Mortality rates were evaluated on the basis of a percentage scale of 0 to 100, 0 means no activity while 100

means total kill. If the mortality rates of the blank control was less than 5%, the results could be directly used. If the mortality rates was more than 5% and less than 20%, the results should be corrected by V = ((X − Y) / X) × 100 (V = value of corrected mortality; X = livability of the blank control; Y = livability of the treat).[1] LC_{50} was calculated by Poloplus.

The insecticidal activities of target compounds before and after 365 nm light against third-instar armyworm were measured by a leaf-dipping method.[2] Different concentrations of compounds were prepared and divided in two. One was irradiated by 365 nm UV light for 30 min. Moderate corn leaves were fully immersed in the solutions of different concentrations, allowed to dry naturally in the dark and placed in dishes. Ten third-instar armyworm larvae were placed. Percentage mortalities were analyzed 72 h after treatment. Teflubenzuron was tested under same conditions as a control.

Binding Affinity to SUR.

Preparation of SUR. SUR was prepared by the reported method with minor modifications.[3,4] The German cockroach was purchased from the National Institute of Parasitic Diseases, Chinese Center for Disease Control and Prevention (China CDC). The integuments of German cockroach (*Blattlla germanica*) were chopped and homogenized in MES-sucrose buffer. After centrifugation, the buffer of SUR was obtained.

Experiments of binding to SUR. To confirm the proper concentration of the fluorescence probe, N-Phenyl-1-naphthylamine (1-NPN) was added to the buffer of SUR to make its eventual concentration was respectively 1.0, 1.5, 2.0, 4.0, 6.0 μM. The mixture was incubated for 1 h at room temperature. Then the affinity of 1-NPN binding to SUR was measured by FP. The excitation wavelength and emission wavelength were 337 nm and 410 nm, respectively.

To compare the binding affinity of compound **B3** before and after 365 nm light irradiation, 1-NPN and SUR were added to 96-well plates. Ligands such as glibenclamide and compound **B3** before and after exposure to 365 nm light were added to 96-well plates to make the eventual concentrations of ligands were respectively 3, 6, 9, 12, 15 μM. Then the mixture was incubated for 1 h at room temperature, and the fluorescence polarization values were collected using Synergy H1 microplate reader (Bio-Tek).

2. General Synthetic Procedure for Compounds A1−A3.

*Synthesis of nitrosobenzene **3**.* Aniline **1** (10 mmol, 0.93 g) was added into dichloromethane (30

mL) and stirred at 25 °C. Potassium peroxomonosulfate (oxone, 10 mmol, 6.15 g) dissolved in water (30 mL) was added dropwise into the reaction mixture. The mixture was stirred for about 0.5 h and then was extracted with dichloromethane (3×30 mL). The organic layer was dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure to give nitrosobenzene **3** *as* a black-green oil (0.696 g, yield 65%).

*Synthesis of (E)-2-(phenyldiazenyl)benzamide **5***. Nitrosobenzene **3** (8 mmol, 0.856 g) was dissolved in toluene (40 mL), then 2-aminobenzamide **4** (8 mmol, 1.088 g) and acetic acid (32 mmol, 1.92 g) were added orderly. The reaction was protected with argon, stirred for 48 h at 60 °C and monitored by TLC. The mixture was extracted with dichloromethane (3×70 mL) and water (70 mL). The organic layer was dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was then purified by silica gel column chromatography with petroleum ether and ethyl acetate (v/v = 3:1) to give product **5** as an orange solid (0.468 g, yield 26%).

*Synthesis of (E)-N-(phenylcarbamoyl)-2-(phenyldiazenyl)benzamide (**A1**)*. Triphosgene (2 mmol, 0.594 g) was dissolved in toluene (20 mL) and stirred. Aniline (6 mmol, 0.558 g) was added dropwise into the reaction solution at 0 °C. The mixture was refluxed for 4 h under the protection of argon to produce phenyl isocyanate **2**. After the reaction solution cooled to room temperature, (*E*)-2-(phenyldiazenyl)benzamide **5** (1 mmol, 0.225 g) was added. The mixture was stirred, refluxed for 24 h and monitored by TLC. After completion, the mixture was filtered and the residue was washed with methanol. Target product **A1** was obtained as an orange solid (0.162 g, yield 47%). mp = 152.4-153.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 10.58 (s, 1H), 7.90-7.81 (m, 4H), 7.76-7.66 (m, 2H), 7.64-7.57 (m, 5H), 7.40-7.34 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.61, 151.76, 150.43, 148.53, 137.56, 133.04, 132.18, 131.73, 131.34, 129.59, 128.98, 128.95, 123.78, 122.80, 119.82, 117.62; HRMS (ESI): calcd for $C_{20}H_{16}N_4O_2Na$ $[M + Na]^+$, 367.1273, found 367.1171.

Compound **A2** and **A3** were synthesized according to the similar method for **A1** with the structure of azobenzene at different locations.

*Data for (E)-N-(phenylcarbamoyl)-3-(phenyldiazenyl)benzamide (**A2**)*. Orange solid; yield 54%. mp = 217.6-218.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.26 (s, 1H), 10.77 (s, 1H), 8.51 (t, J = 1.8 Hz, 1H), 8.22-8.14 (m, 2H), 7.98-7.94 (m, 2H), 7.78 (t, J = 7.8 Hz, 1H), 7.67-7.59 (m, 5H),

7.41-7.35 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.01, 151.79, 151.74, 150.90, 137.57, 133.76, 132.00, 130.85, 129.84, 129.56, 128.98, 126.80, 123.79, 122.71, 122.15, 119.84; HRMS (ESI): calcd for $C_{20}H_{16}N_4O_2Na$ $[M + Na]^+$, 367.1273, found 367.1171.

*Data for (E)-N-(phenylcarbamoyl)-4-(phenyldiazenyl)benzamide (**A3**).* Yellow solid; yield 50%. mp = 258.0-258.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 10.78 (s, 1H), 8.24 (d, J = 8.4 Hz, 2H), 8.03-7.93 (m, 4H), 7.67-7.59 (m, 5H), 7.40-7.35 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H); HRMS (ESI): calcd for $C_{20}H_{15}N_4O_2$ $[M - H]^-$, 343.1273, found 343.1195.

3. General Synthetic Procedure for Compounds B1−B7.

*Synthesis of (E)-2-(phenyldiazenyl)aniline **9**.* *O*-phenylenediamine **8** (6.5 mmol, 0.702 g) was dissolved in toluene (30 mL), and then nitrosobenzene **3** (6.5 mmol, 0.696 g) and acetic acid (26 mmol, 1.56 g) were added orderly. The reaction was protected under argon and stirred for 48 h at 60 °C. The mixture was extracted with dichloromethane (3×60 mL) and water. The organic layer was dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was then purified by silica gel column chromatography with petroleum ether and ethyl acetate (v/v = 10:1) to give product **9** an orange solid (0.395 g, yield 31%).

*Synthesis of (E)-2,6-difluoro-N-((2-(phenyldiazenyl)phenyl)carbamoyl)benzamide (**B1**).* Triphosgene (2 mmol, 0.594 g) was dissolved in toluene (15 mL), and then 2,6-difluorobenzamide **6** (8 mmol, 1.256 g) dissolved in toluene (15 mL) was added dropwise into the reaction mixture. The reaction was protected with argon and refluxed until the mixture was clear to produce 2,6-difluorobenzoyl isocyanate **7**. When the reaction solution cooled to room temperature, (*E*)-2-(phenyldiazenyl)aniline **9** (2 mmol, 0.394 g) was added. The mixture was stirred, refluxed for 48 h and monitored by TLC. The mixture was filtered, the filtrate was concentrated under reduced pressure and purified by silica gel column chromatography with petroleum ether and ethyl acetate (v/v = 3:1) to give target product **B1** as an orange solid (0.18 g, yield 24%). mp = 238.1-239.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.01 (s, 1H), 11.77 (s, 1H), 8.55 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 7.6 Hz, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.70-7.54 (m, 5H), 7.32-7.23 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.65, 159.94, 158.45, 152.03, 149.59, 139.40, 137.10, 133.14, 131.92, 129.49, 123.69, 123.15, 120.21, 115.45, 112.35-112.21, 112.15-111.98; HRMS (ESI): calcd for $C_{20}H_{13}F_2N_4O_2$ $[M - H]^-$, 379.1085, found 379.1010.

Compounds **B2**−**B7** were synthesized according to the similar method for **B1**. Corresponding nitrobenzene containing different substituents and phenylenediamine were used to prepare azobenzene intermediates. Then target compounds were obtained with reactions of azobenzene intermediates and 2,6-difluorobenzoyl isocyanate.

*Data for (E)-2,6-difluoro-N-((3-(phenyldiazenyl)phenyl)carbamoyl)benzamide (**B2**).* Orange solid; yield 36%. mp = 185.4-186.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 10.36 (s, 1H), 8.19 (s, 1H), 7.92 (dd, J_1 = 7.8 Hz, J_2= 1.8 Hz, 2H), 7.68-7.54 (m, 7H), 7.27 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.09, 159.90, 157.41, 152.35, 151.85, 150.05, 138.46, 131.65, 129.89, 129.47, 122.91, 122.59, 118.96, 113.15, 112.27-112.15, 112.08-111.94; HRMS (ESI): calcd for $C_{20}H_{13}F_2N_4O_2$ [M - H]$^-$, 379.1085, found 379.1007.

*Data for (E)-2,6-difluoro-N-((4-(phenyldiazenyl)phenyl)carbamoyl)benzamide (**B3**).* Orange solid; yield 51%. mp = 244.7-245.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (s, 1H), 10.42 (s, 1H), 7.95-7.86 (m, 4H), 7.81 (d, J = 8.8 Hz, 2H), 7.65-7.54 (m, 4H), 7.27 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.12, 159.89, 157.39, 151.97, 149.86, 148.00, 140.44, 131.18, 129.42, 123.69, 122.37, 120.22, 112.30-112.12, 112.09-111.91; HRMS (ESI): calcd for $C_{20}H_{13}F_2N_4O_2$ [M - H]$^-$, 379.1085, found 379.1006.

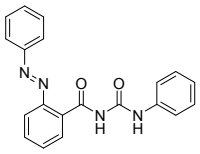
*Data for (E)-4-((4-(3-(2,6-difluorobenzoyl)ureido)phenyl)diazenyl)benzoic acid ethyl ester (**B4**).* Orange solid; yield 59%. mp = 241.8-242.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.56 (s, 1H), 10.48 (s, 1H), 8.15 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 7.2 Hz, 4H), 7.84 (d, J = 7.6 Hz, 2H), 7.69-7.70 (m, 1H), 7.27 (t, J = 8.0 Hz, 2H), 4.39-4.32 (m, 2H), 1.36 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.11, 162.12, 159.90, 157.41, 154.50, 149.87, 147.98, 141.16, 131.44, 130.43, 124.12, 122.49, 120.21, 112.30-112.16, 112.11-111.93, 61.04, 14.11; HRMS (ESI): calcd for $C_{23}H_{18}F_2N_4O_4Na$ [M + Na]$^+$, 475.1296, found 475.1194.

*Data for (E)-2-((2-(3-(2,6-difluorobenzoyl)ureido)phenyl)diazenyl)benzoic acid ethyl ester (**B5**).* Orange solid; yield 32%. mp = 167.7-168.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (s, 1H), 11.78 (s, 1H), 8.55 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 6.8 Hz, 1H), 7.72-7.60 (m, 5H), 7.31-7.23 (m, 3H), 4.39-4.32 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.73, 162.60, 159.92, 157.43, 150.33, 149.62, 139.60, 137.37, 133.66, 132.07, 131.36, 131.09, 129.27, 123.73, 120.30, 116.83, 115.85, 112.35-112.17, 112.15-111.97, 61.27, 14.15; HRMS (ESI): calcd for $C_{23}H_{18}F_2N_4O_4Na$ [M + Na]$^+$, 475.1296, found 475.1196.

*Data for (E)-2,6-difluoro-N-((4-((4-nitrophenyl)diazenyl)phenyl)carbamoyl)- benzamide (**B6**).* Orange solid; yield 81%. mp = 268.9-269.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.56 (s, 1H), 10.50 (s, 1H), 8.44 (d, J = 7.2 Hz, 2H), 8.16-7.76 (m, 6H), 7.70-7.61 (m, 1H), 7.28 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.10, 159.92, 157.43, 155.27, 149.86, 148.21, 147.97, 141.71, 133.27, 125.06, 124.48, 123.30, 120.24, 112.26-112.216, 112.07-112.02; HRMS (ESI): calcd for $C_{20}H_{13}F_2N_5O_4Na$ $[M + Na]^+$, 448.0936, found 448.0836.

*Data for (E)-2,6-difluoro-N-((3-((3-nitrophenyl)diazenyl)phenyl)carbamoyl)- benzamide (**B7**).* Yellow solid; yield 55%. mp = 214.9-215.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.53 (s, 1H), 10.41 (s, 1H), 8.58 (t, J = 2.0 Hz, 1H), 8.45-8.36 (m, 2H), 8.28 (s, 1H), 7.92 (t, J = 8.0 Hz, 1H), 7.80-7.74 (m, 2H), 7.68-7.58 (m, 2H), 7.28 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.11, 159.92, 157.41, 152.04, 150.08, 148.64, 138.57, 133.26, 131.13, 130.03, 129.83, 125.55, 123.87, 119.54, 115.69, 113.38, 112.32-112.14, 112.193-111.93; HRMS (ESI): calcd found $C_{20}H_{13}F_2N_5O_4Na$ $[M + Na]^+$, 448.0936, found 448.0831.

4. Copies of NMR Spectra of Compounds



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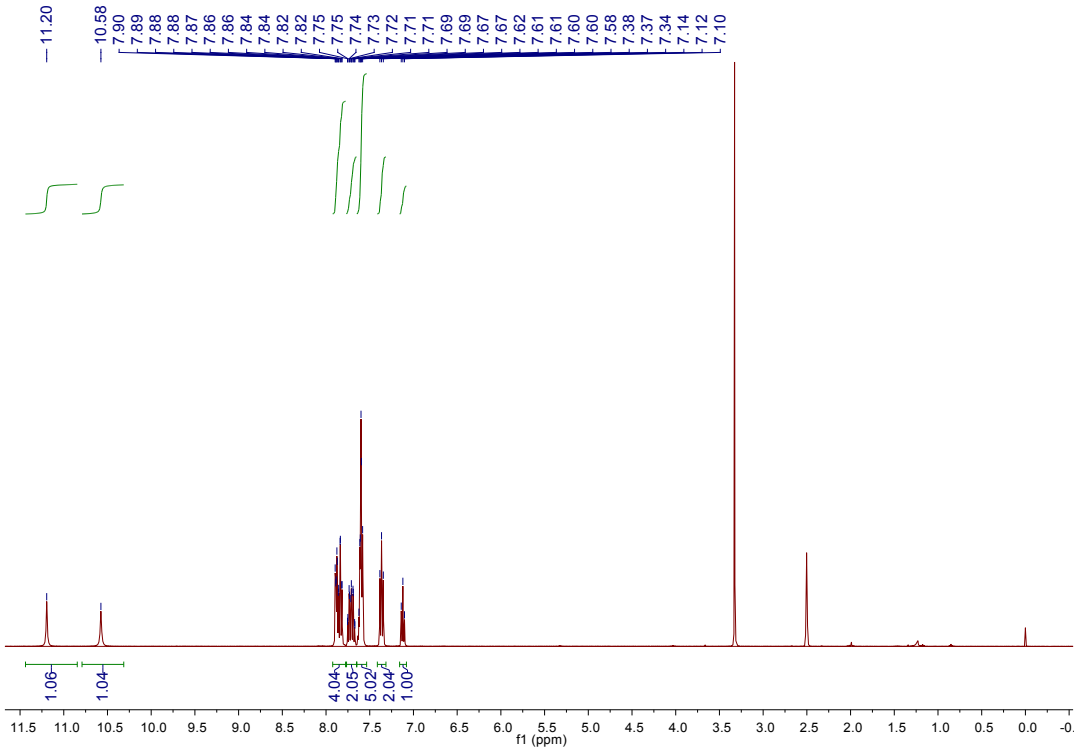

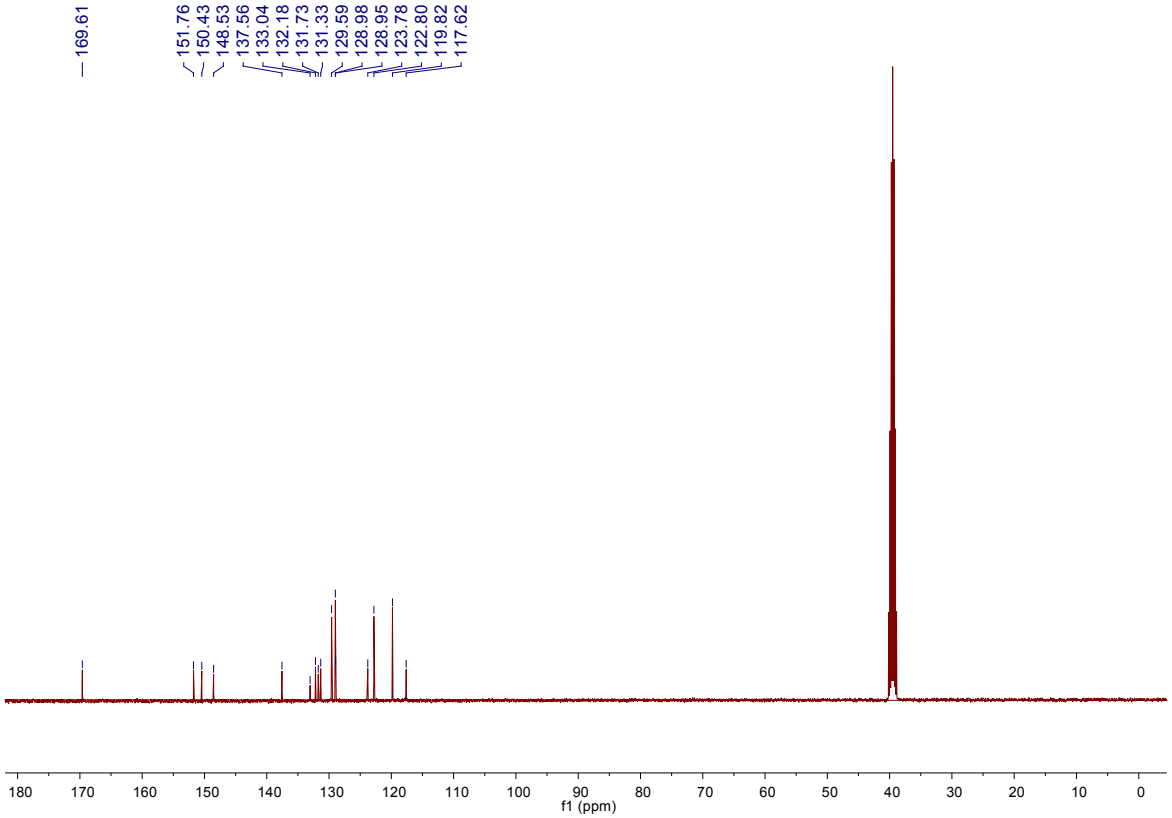
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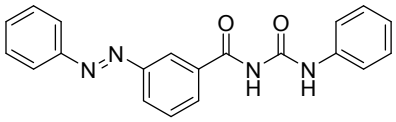
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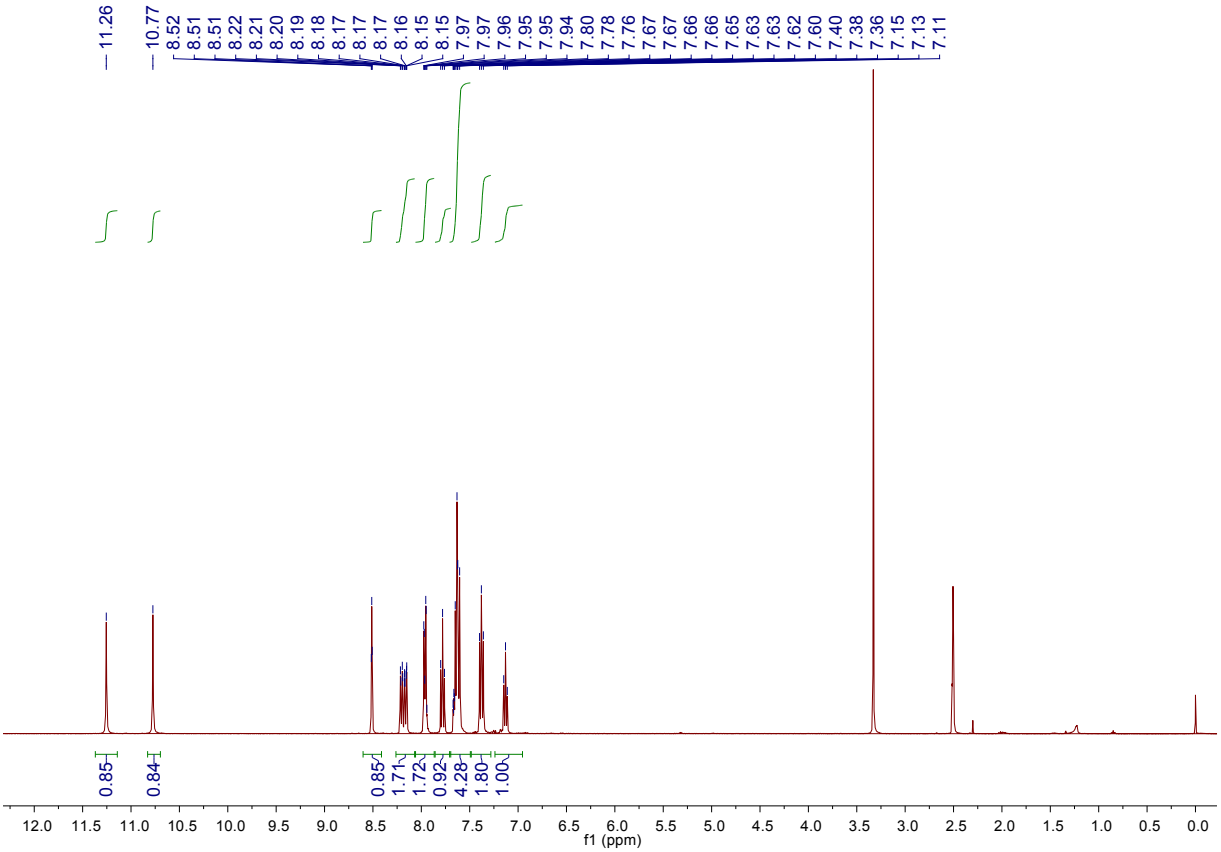
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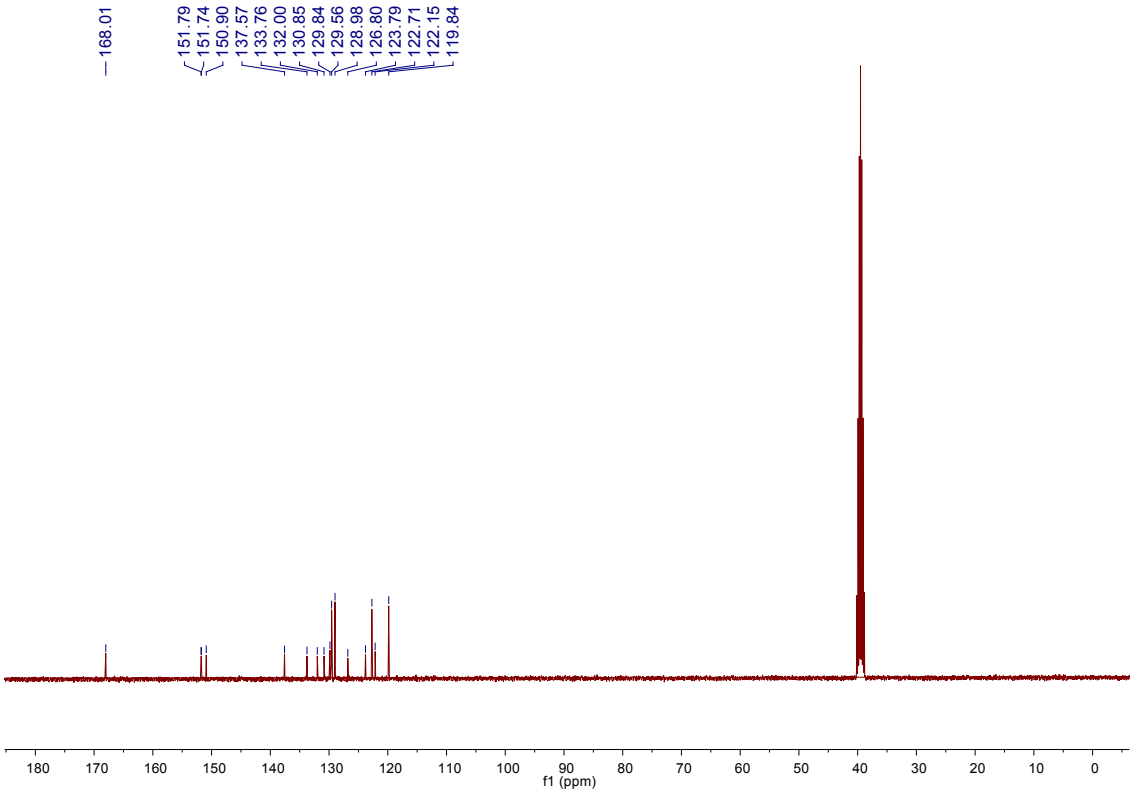
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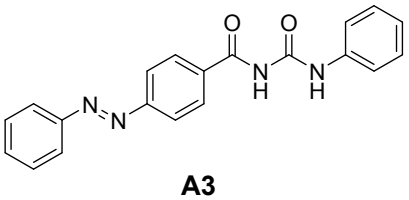

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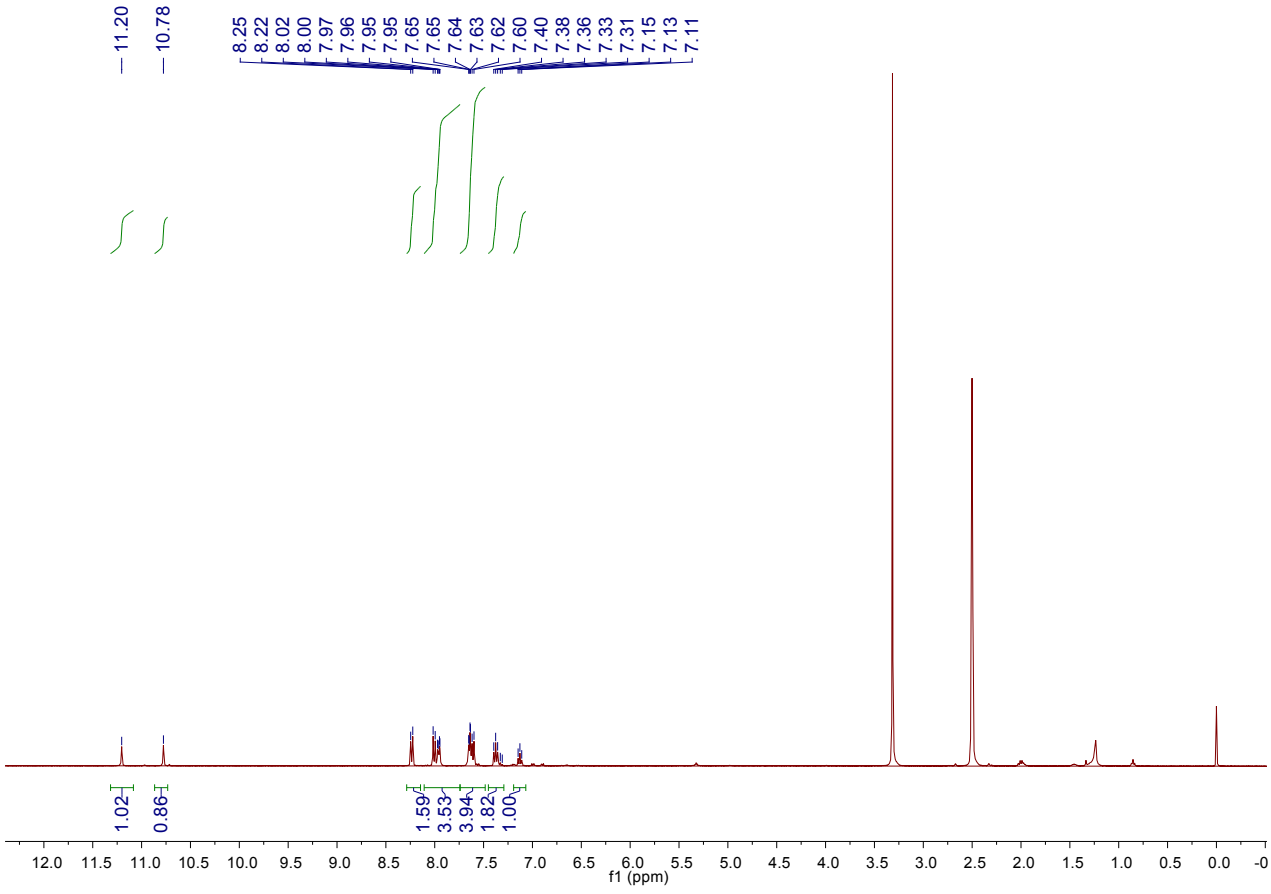
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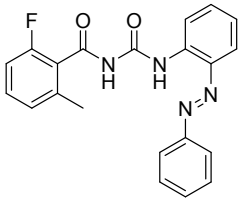

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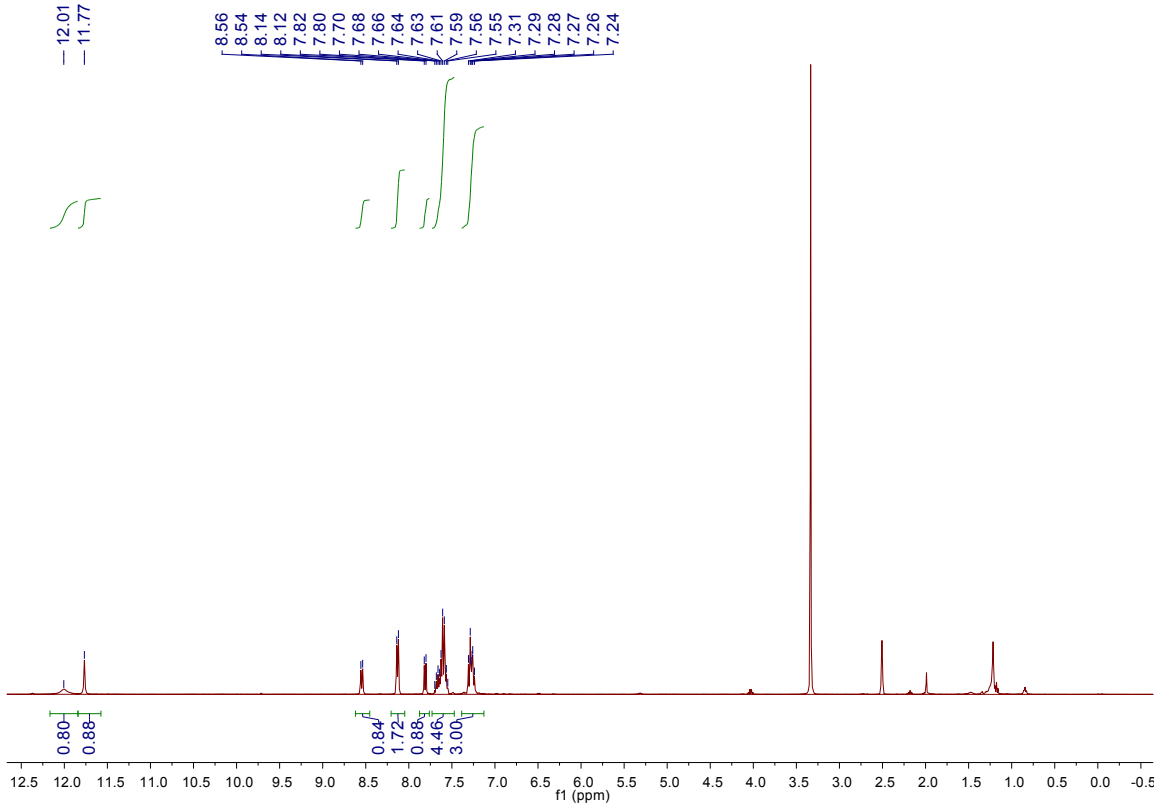
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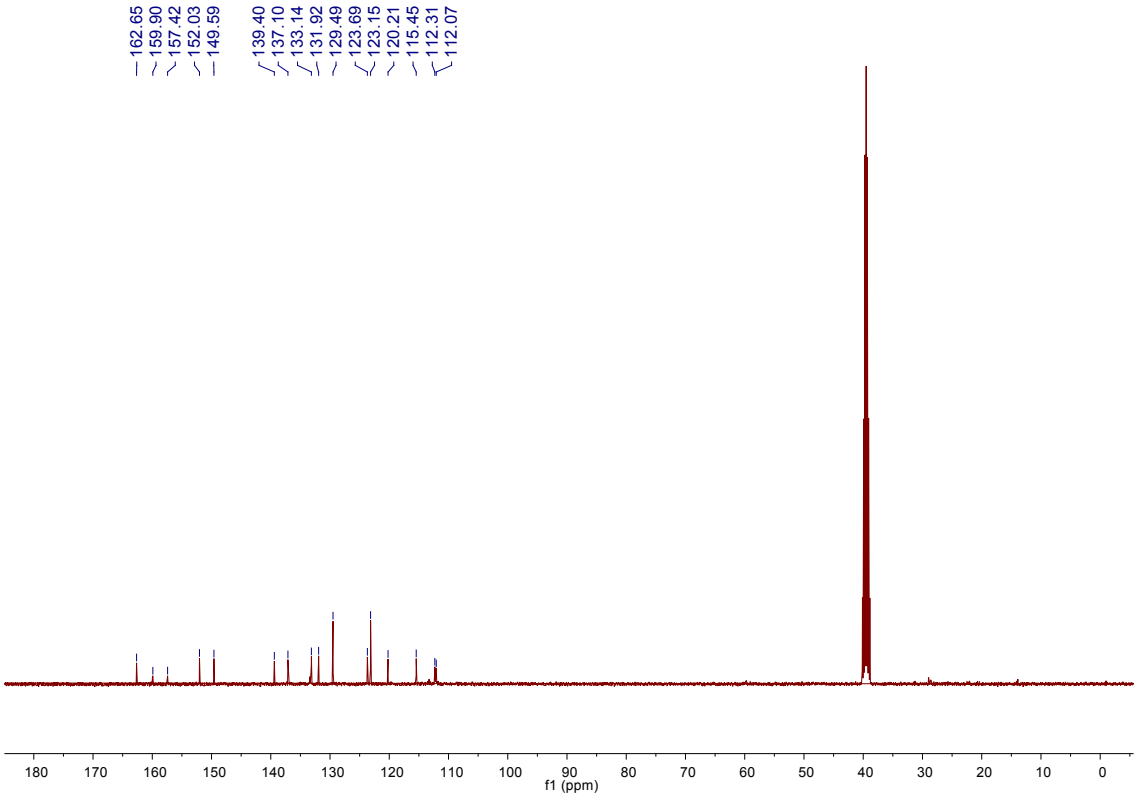
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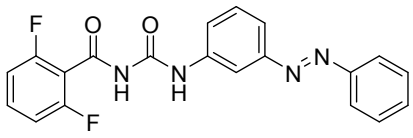

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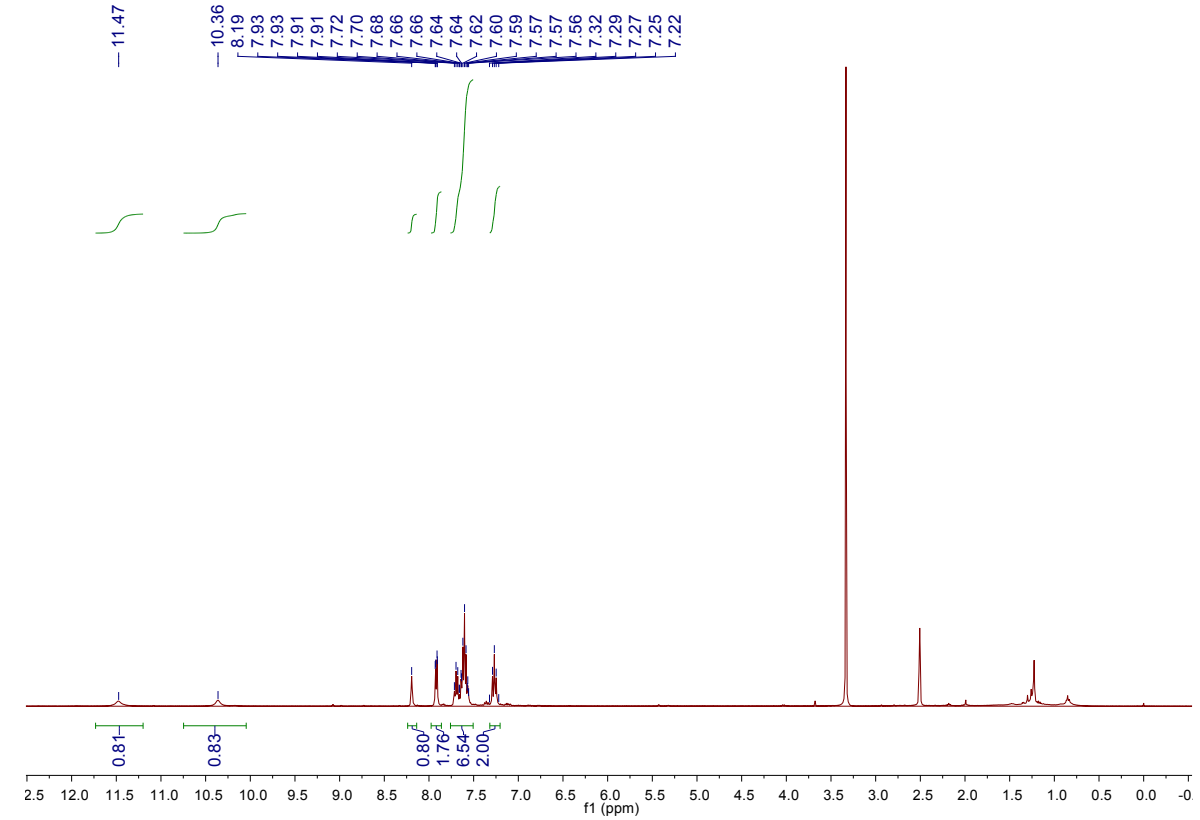
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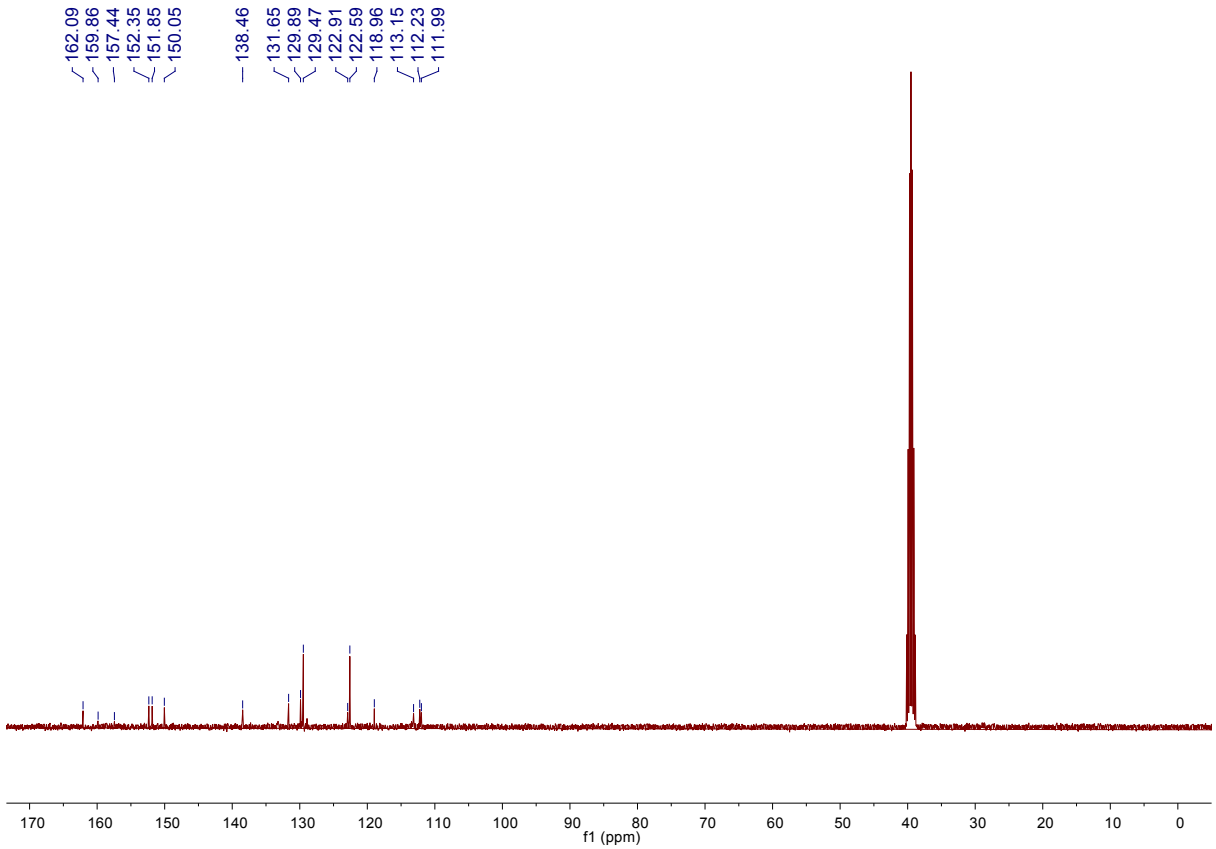
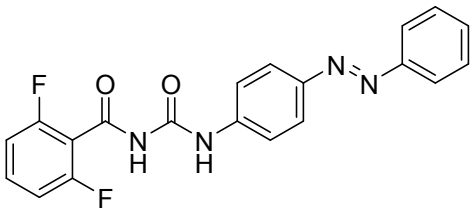
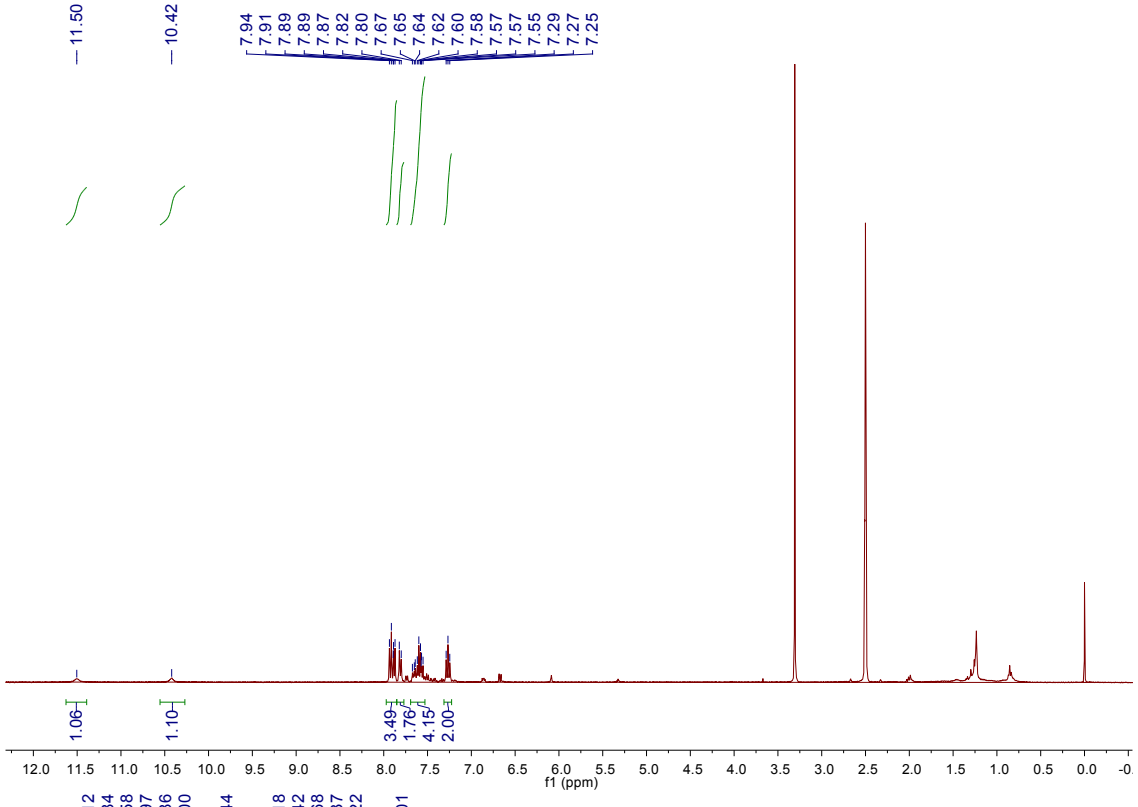
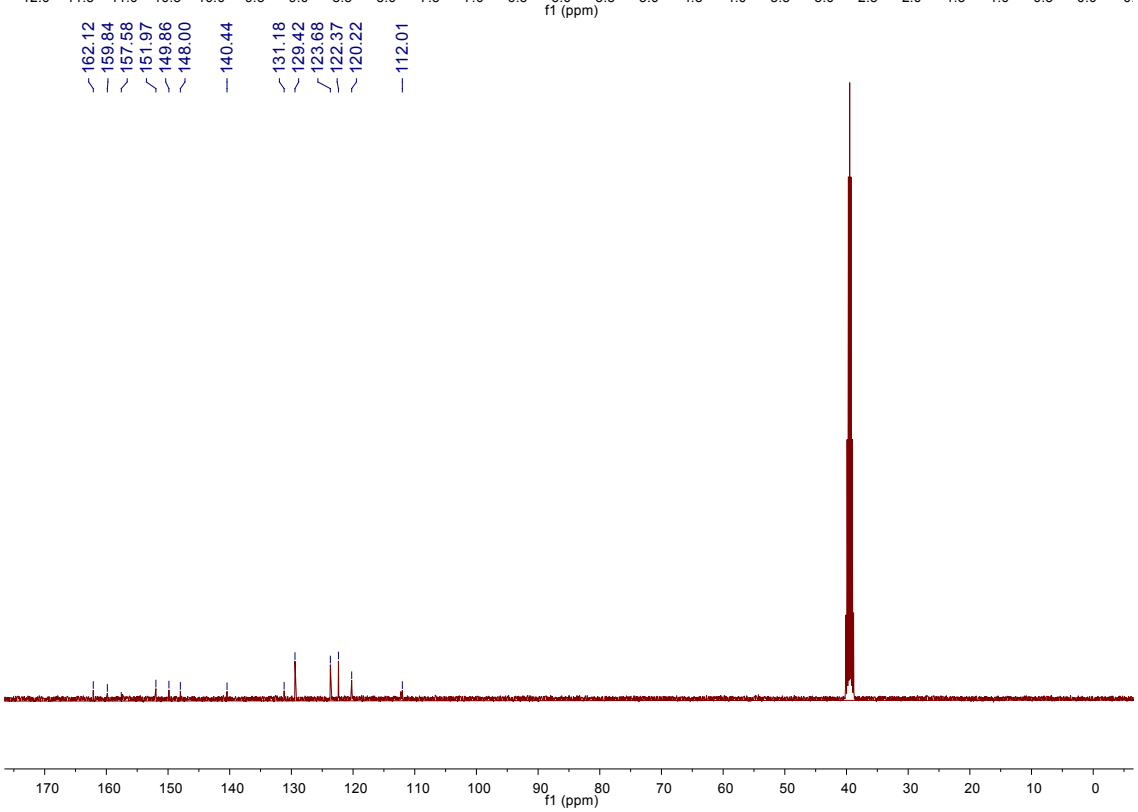
2.00
f1 (ppm)

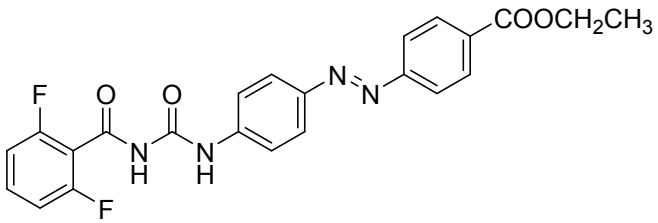

162.09
159.86
157.44
152.35
151.85
150.05
138.46
131.65
129.89
129.47
122.91
122.59
118.96
113.15
112.23
111.99
f1 (ppm)


F
O
O
N
H
N
H
N
N
F

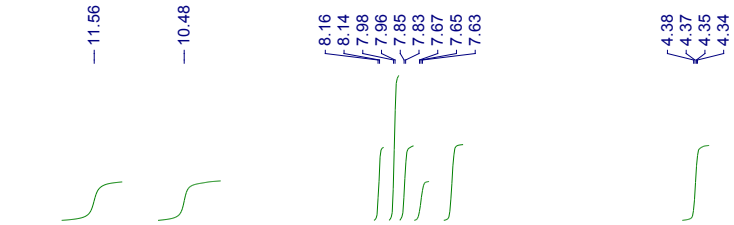
B3

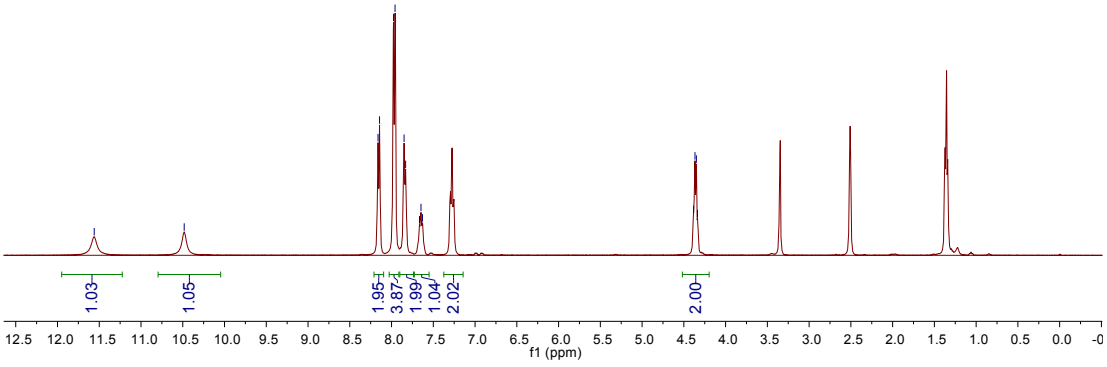

11.50
10.42
7.94
7.91
7.89
7.89
7.87
7.82
7.80
7.67
7.65
7.64
7.62
7.60
7.58
7.57
7.57
7.55
7.29
7.27
7.25
1.06
1.10
3.49
1.76
4.15
2.00
f1 (ppm)

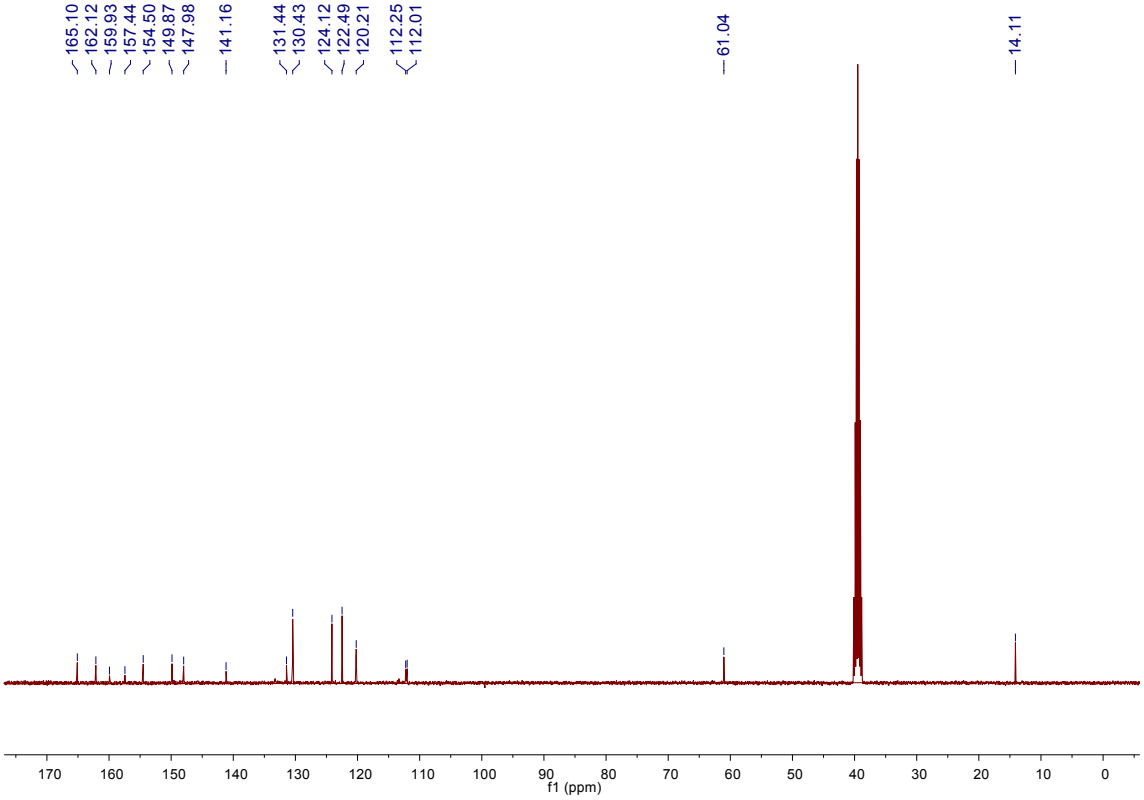

162.12
159.84
157.58
151.97
149.86
148.00
140.44
131.18
129.42
123.68
122.37
120.22
112.01
f1 (ppm)

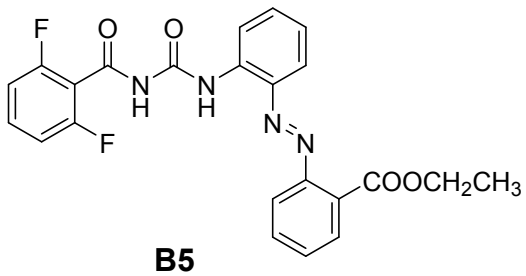

COOCH2CH3
F
O
O
N
H
N
H
N
N
F

B4

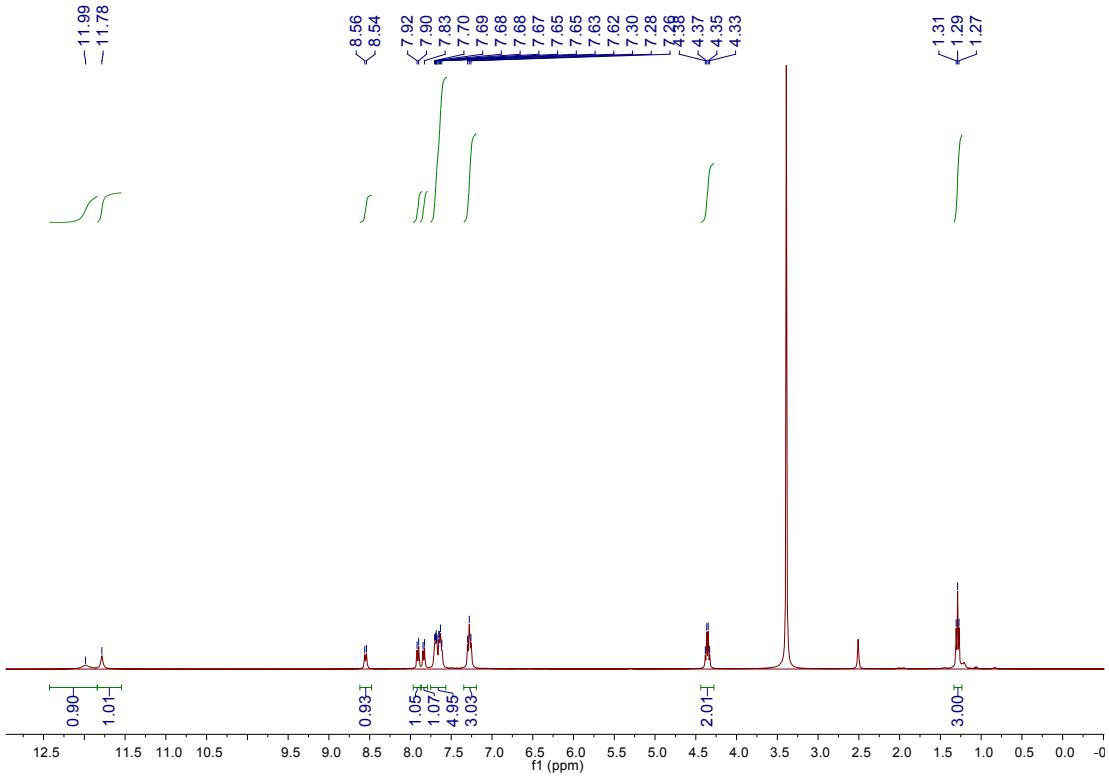

11.56
10.48
8.16
8.14
7.98
7.96
7.85
7.83
7.67
7.65
7.63
4.38
4.37
4.35
4.34

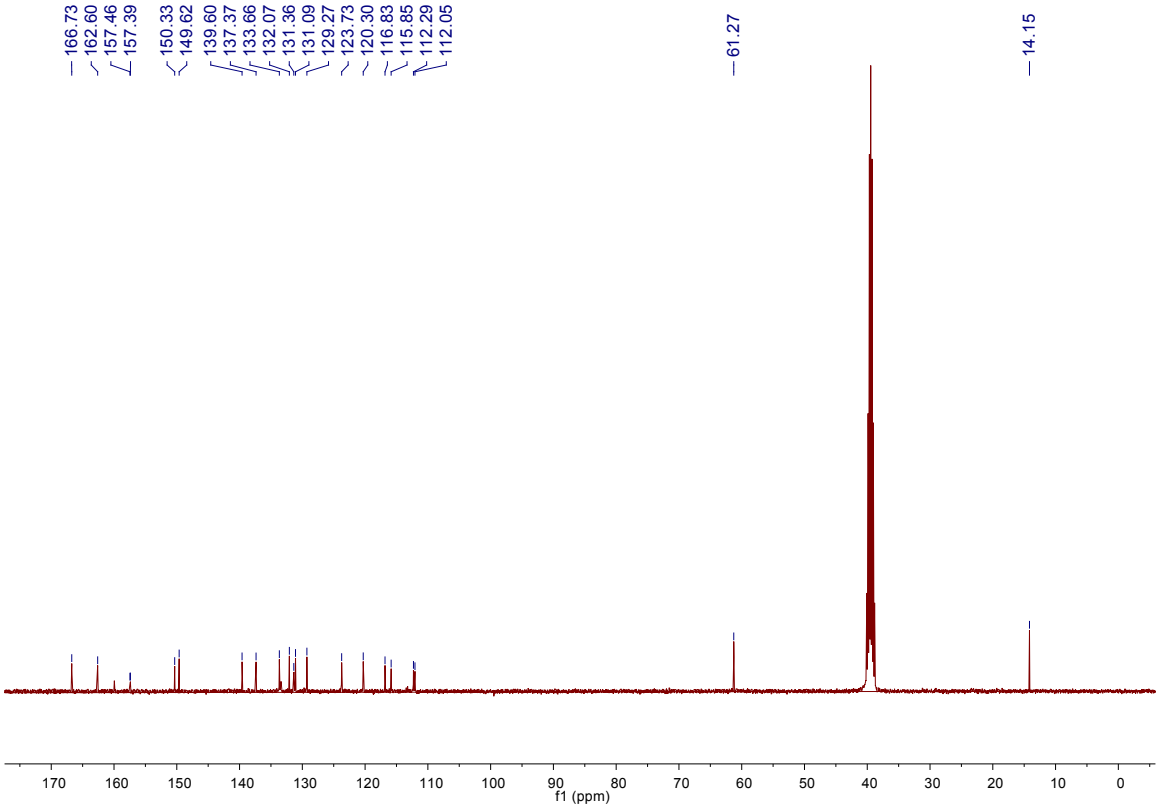

1.03
1.05
1.95
3.87
1.99
1.04
2.02
2.00
f1 (ppm)

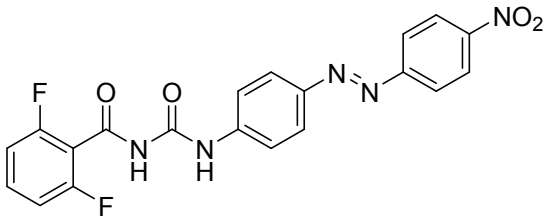

165.10
162.12
159.93
157.44
154.50
149.87
147.98
141.16
131.44
130.43
124.12
122.49
120.21
112.25
112.01
61.04
14.11
f1 (ppm)


F
O
O
N
H
N
H
F
N
N
COOCH2CH3

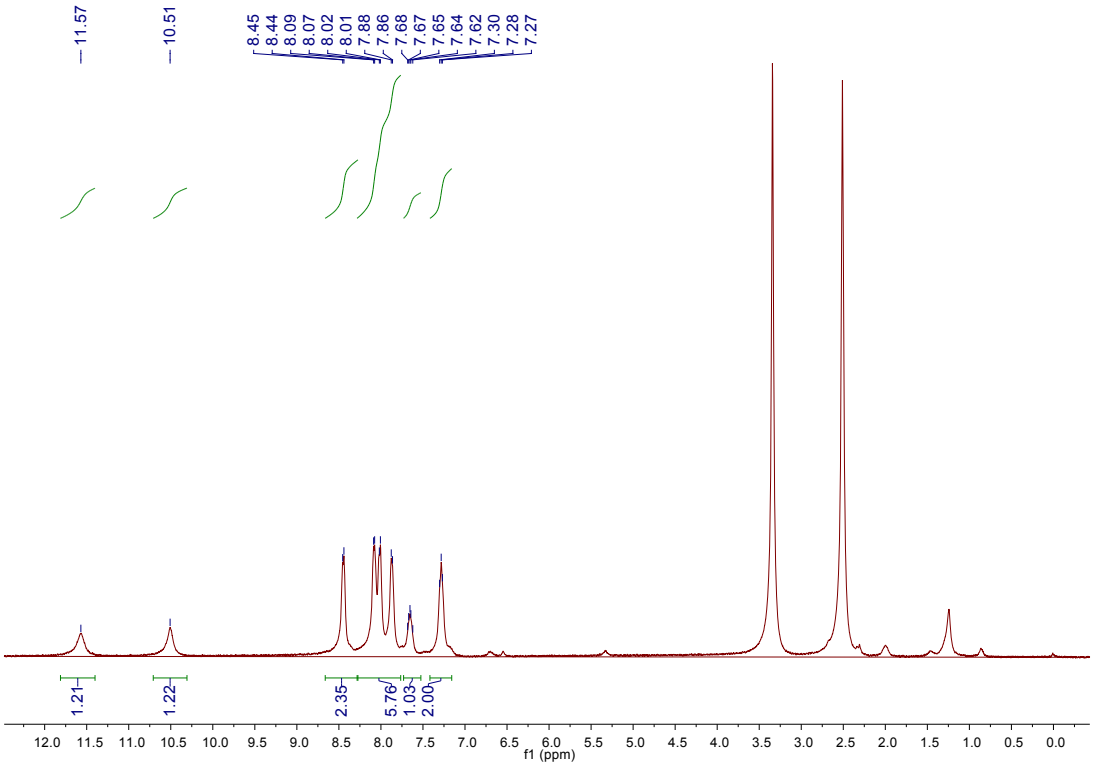
B5

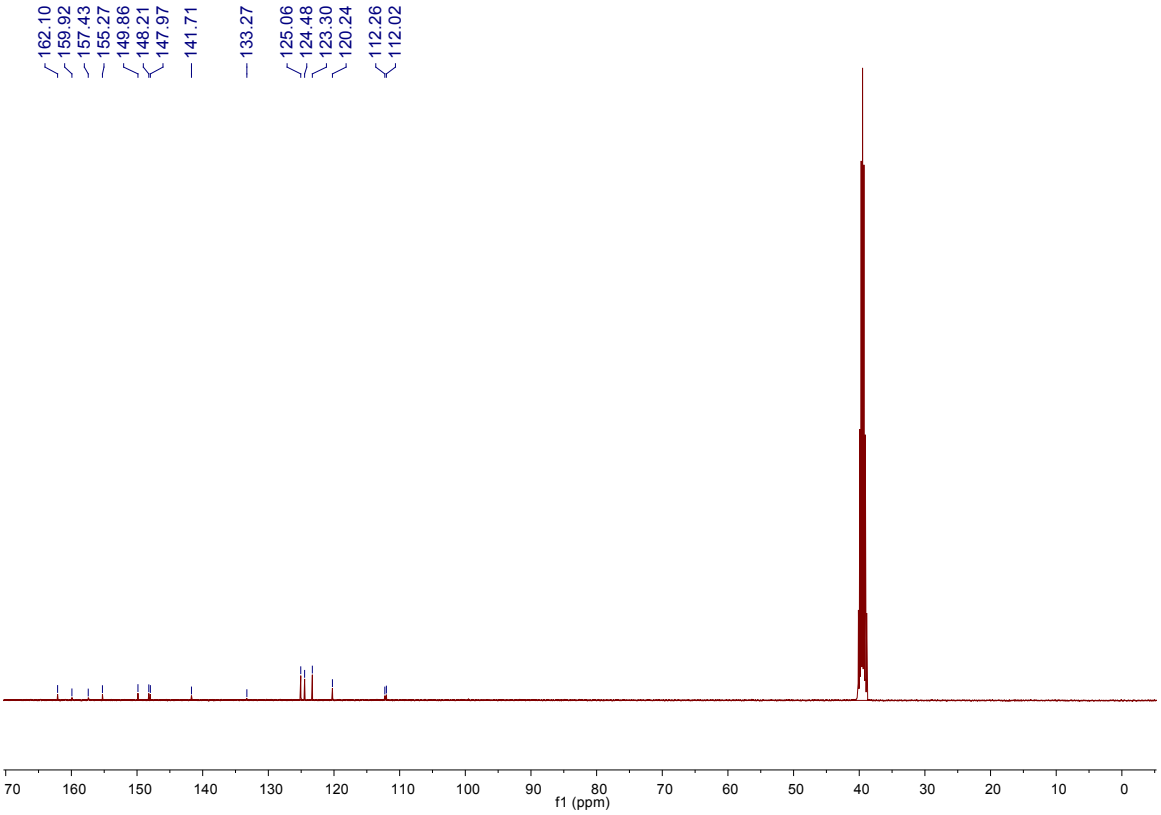

11.99
11.78
8.56
8.54
7.92
7.90
7.83
7.70
7.69
7.68
7.68
7.67
7.65
7.65
7.63
7.62
7.30
7.28
4.37
4.35
4.33
1.31
1.29
1.27
0.90
1.01
0.93
1.05
1.07
4.95
3.03
2.01
3.00
f1 (ppm)

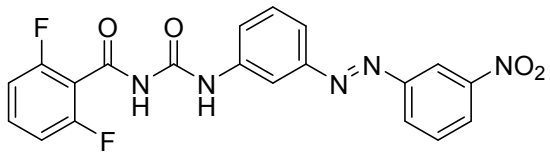

166.73
162.60
157.46
157.39
150.33
149.62
139.60
137.37
133.66
132.07
131.36
131.09
129.27
123.73
120.30
116.83
115.85
112.29
112.05
61.27
14.15
f1 (ppm)


NO2
F
O
O
N
H
N
H
N
N
F

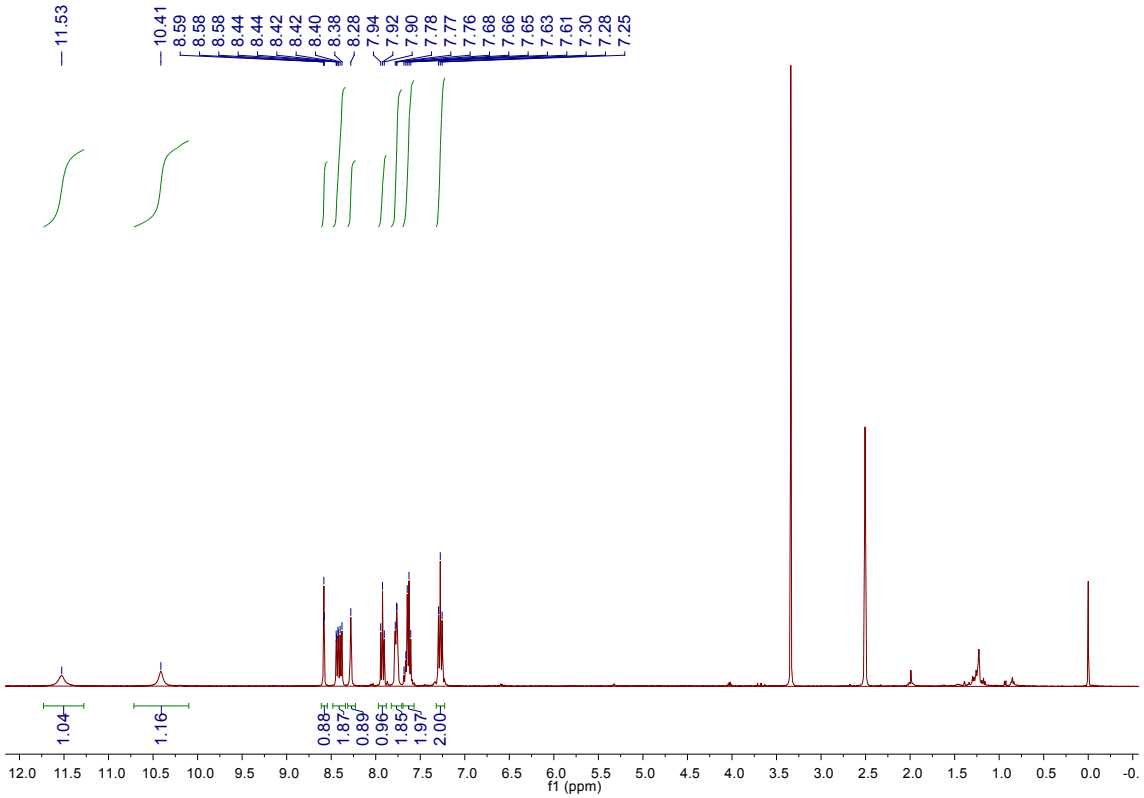
B6

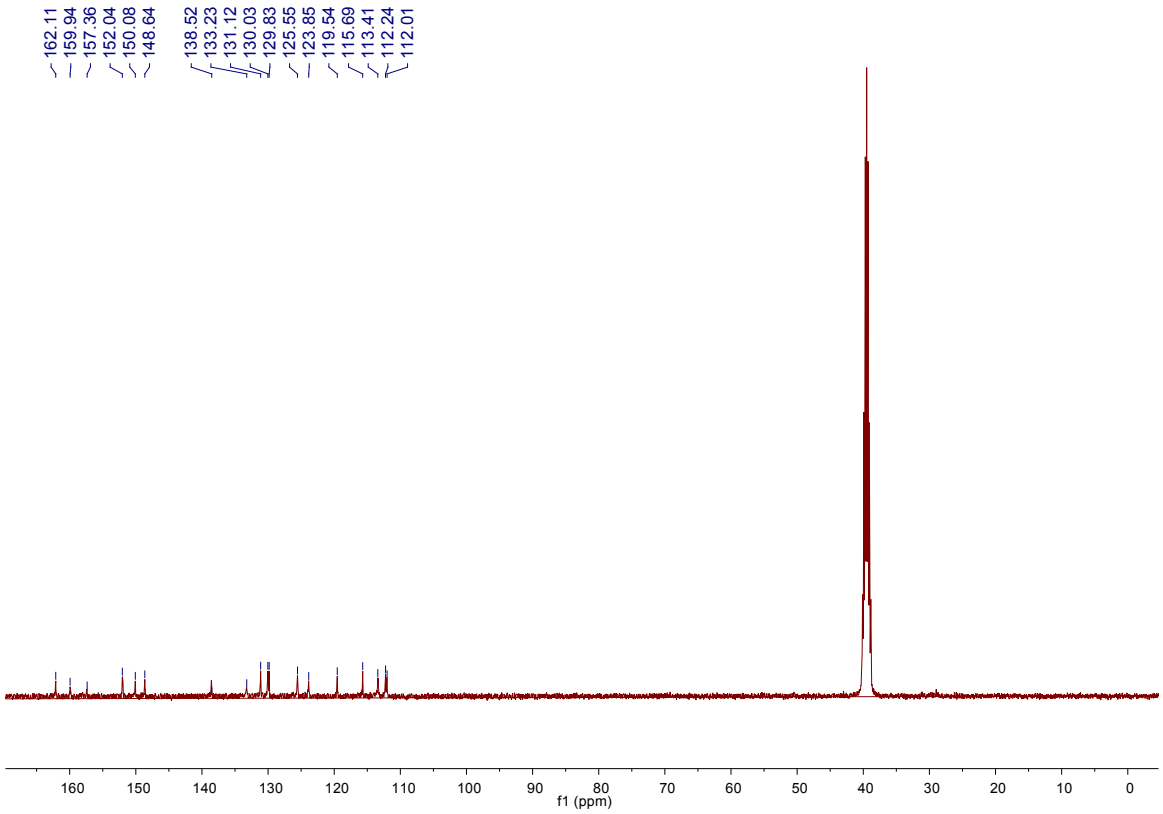

11.57
10.51
8.45
8.44
8.09
8.07
8.02
8.01
7.88
7.86
7.68
7.67
7.65
7.64
7.62
7.30
7.28
7.27
1.21
1.22
2.35
5.76
1.03
2.00
f1 (ppm)


162.10
159.92
157.43
155.27
149.86
148.21
147.97
141.71
133.27
125.06
124.48
123.30
120.24
112.26
112.02
f1 (ppm)


F
O
O
N
H
N
H
N
N
NO2
F

B7


11.53
10.41
8.59
8.58
8.58
8.44
8.44
8.42
8.42
8.40
8.38
8.28
7.94
7.92
7.90
7.78
7.77
7.76
7.68
7.66
7.65
7.63
7.61
7.30
7.28
7.25
1.04
1.16
0.88
1.87
0.89
0.96
1.85
1.97
2.00
f1 (ppm)


162.11
159.94
157.36
152.04
150.08
148.64
138.52
133.23
131.12
130.03
129.83
125.55
123.85
119.54
115.69
113.41
112.24
112.01
f1 (ppm)

5. References

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3 G. E. Abo-Elghar, P. Fujiyoshi and F. Matsumura, *Insect Biochem. Mol. Biol.*, 2004, 34, 743–752.

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