

Supplementary Information

Visible-light-promoted synthesis of secondary and tertiary thiocarbamates from thiosulfonates and *N*-substituted formamides

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1. General information

All reagents and solvents were purchased from commercial suppliers without further purification. All reactions were studied in borosilicate glass vessels irradiated by 5 W blue LED light from a photo reactor manufactured by Beijing Roger Technology Co., Ltd. without using filters with magnetic stirring apparatus. The progress of the reactions were monitored by thin-layer chromatography under 254 nm UV light. ^1H NMR and ^{13}C NMR spectra were recorded at Bruker Avance 400 MHz spectrometer operating at 400.13 MHz and 100.61 MHz, respectively. NMR spectra were recorded in CDCl_3 at room temperature (20 ± 2 °C). High-resolution mass spectra (HRMS) of the products were obtained on a Thermo TNG Orbitrap Fusion using the ESI technique and Agilent Technologies 6530 Accuratmass Q-TOF LC/MS with ESI as ion source. Melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Fluorescence quenching experiments were performed by Hitachi F7000 fluorescence spectrometer.

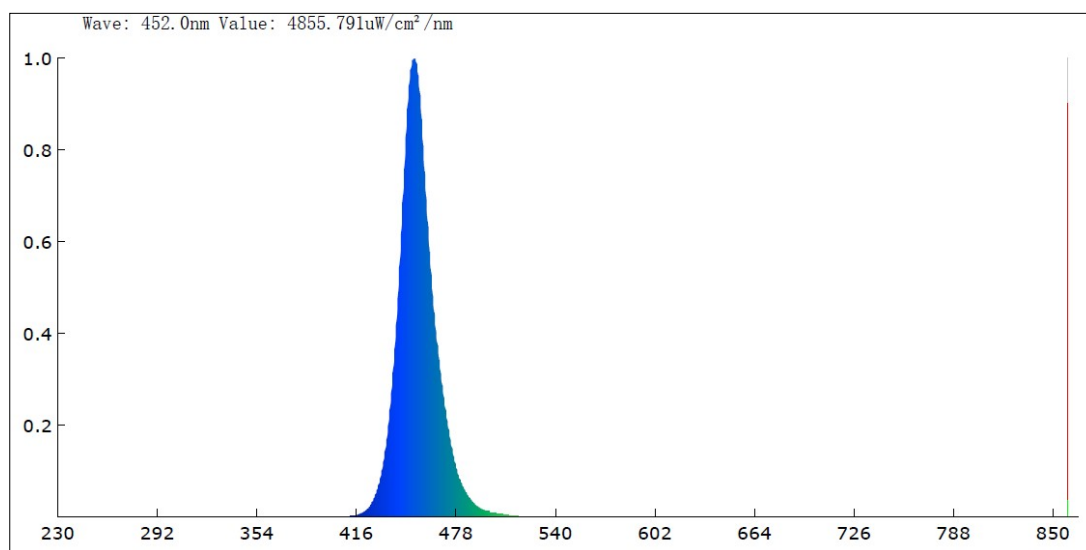
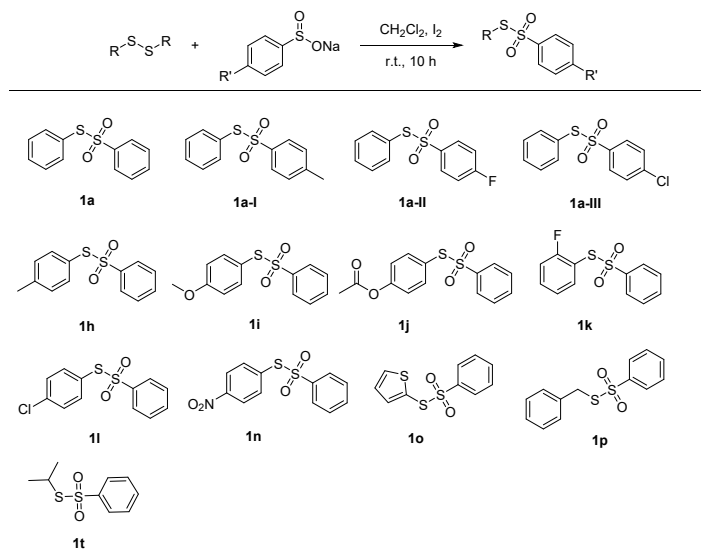


Figure S1 The emission spectrum of blue LEDs ($\lambda_{\text{max}} = 452.0$ nm)

2. General procedure for the synthesis of thiosulfonates

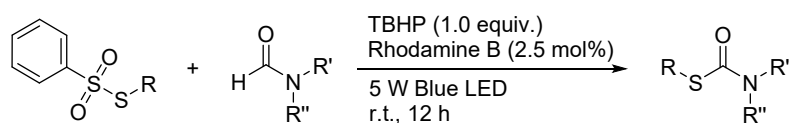
Disulfides (0.5 mmol, 1.0 equiv.), sodium benzenesulfonates (12 mmol, 2.4 equiv.), iodine (7.5 mmol, 1.5 equiv.) were mixed in CH_2Cl_2 (20 mL) in a 250 mL round bottom flask. The mixture was stirred at room temperature for 10 h. After completion of the reaction, sodium thiosulfate was added to the above mixture to remove the excess iodine. Then, the mixture was extracted with brine (20 mL \times 3). The organic phase were combined and dried over anhydrous Na_2SO_4 . After filtration, the solvent

ra was evaporated and the crude product was purified by silica gel (petroleum ether : ethyl acetate = 10 : 1, v/v) to give the desired products.



3. General procedure for the synthesis of products 3 and 5

Thiosulfonates (0.4 mmol), TBHP (0.4 mmol, 70% aqueous solution), rhodamine B (2.5 mol%) were dissolved in corresponding formamides (2.0 mL) in a 25 mL reaction tube, and then the mixture was stirred with the irradiation of 5 W blue LED under N₂ at room temperature for 12 h. After reaction, the mixture was diluted with brine and extracted with petroleum ether (15 mL × 3). The organic layers were collected and dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the desired products.



4. Mechanism Study

4.1 Experiment interfered with radical scavenger

In a 25 mL reaction tube, *S*-phenyl benzenethiosulfonate (0.4 mmol), TBHP (0.4 mmol, 70% aqueous solution), rhodamine B (2.5 mol%) and 2.0 equiv. of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) or 2,6-di-tert-butyl-4-methylphenol (BHT) were dissolved in DMF (2.0 mL), respectively. The mixtures were stirred under standard reaction conditions for 12 h and then detected by HRMS.

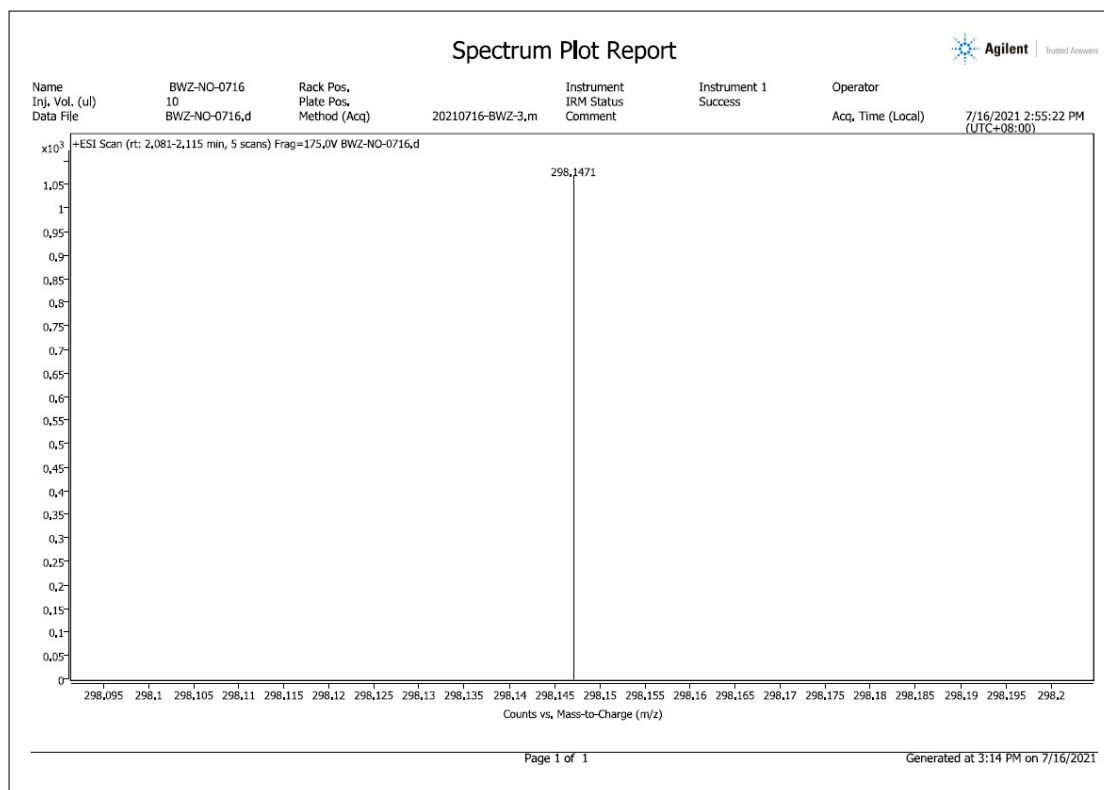


Figure S2 HRMS spectrum of the benzenesulfonyl radical/TEMPO adduct **7**

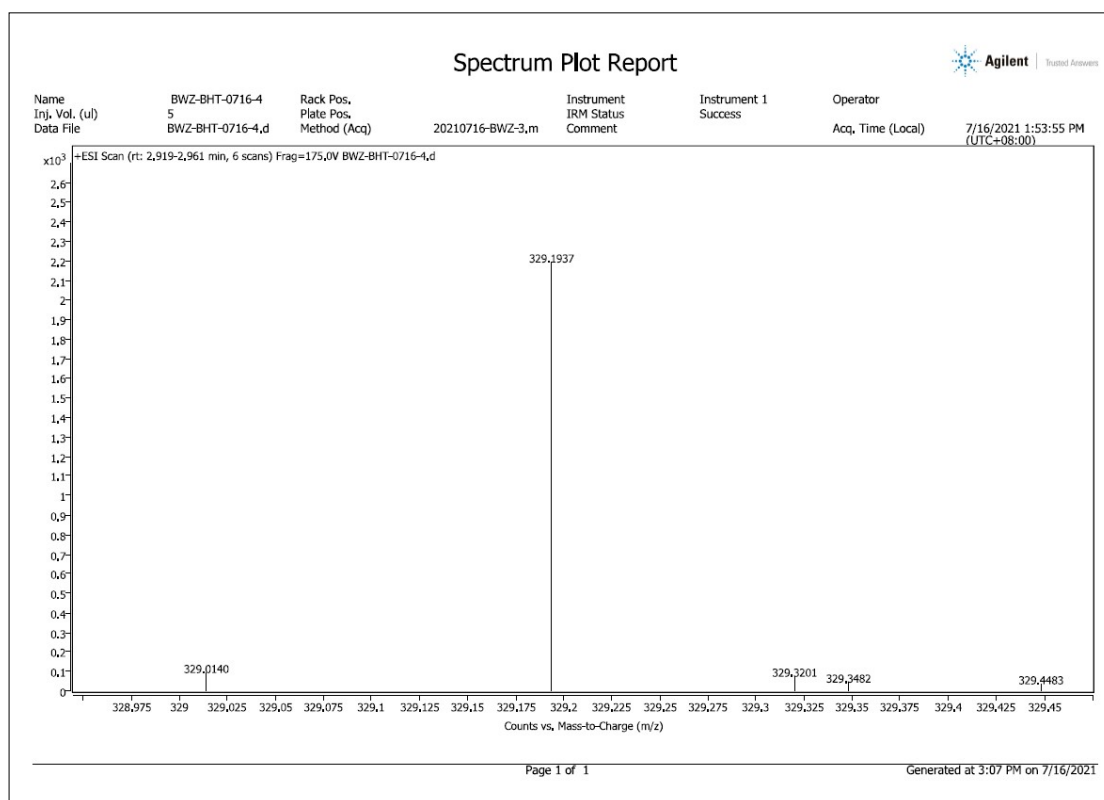


Figure S3 HRMS Spectrum of the benzenesulfonyl radical/BHT adduct **8**

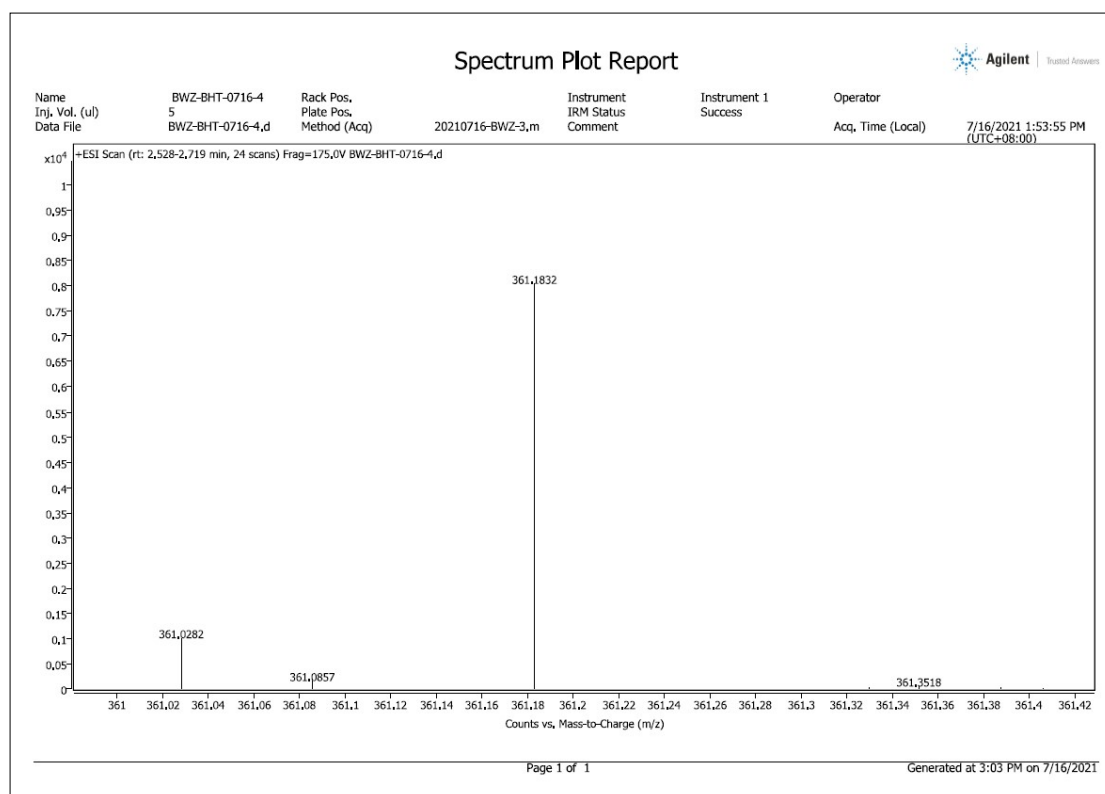


Figure S4 HRMS spectrum of the benzenesulfonyl radical/BHT adduct **9**

4.2 Fluorescence quenching experiments

A stock solution of RhB (rhodamine B) (5 mM in dry DMF) was prepared for the quenching experiment. 20 μ L RhB stock solution was added in 2.0 mL of DMF in a quartz cuvette (1 cm \times 1 cm). The fluorescence excitation and emission spectra were firstly recorded as shown below. The maximum excitation/emission wavelength were detected as 325/566 nm. Then, quenching experiments were performed with addition of TBHP (5 mM in DMF) or **1a** (0, 1, 2, 3, 4, 5 mM in DMF) by a HPLC needle, respectively.

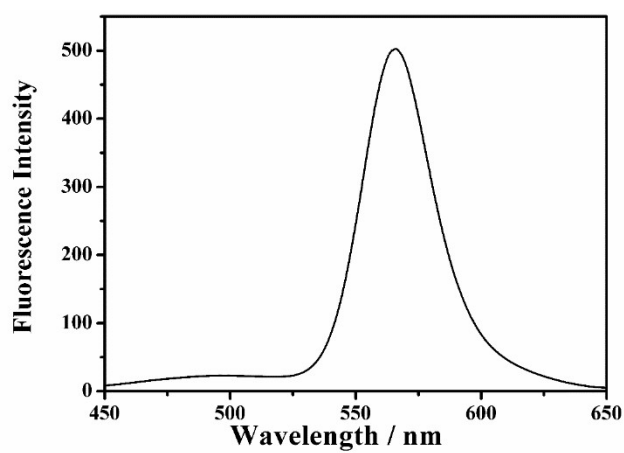
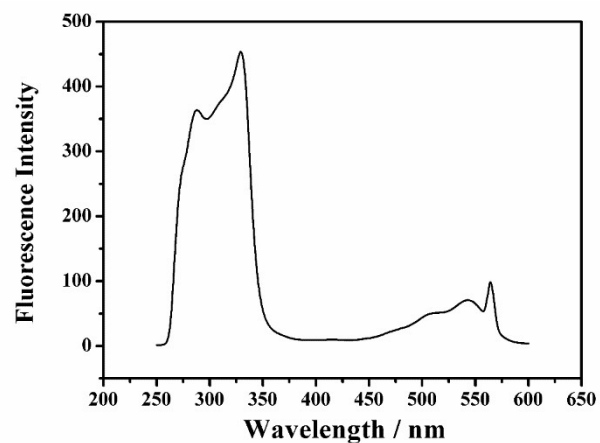


Figure S5 Fluorescence excitation (up) and emission (down) spectra of RhB (5×10^{-4} M) in DMF

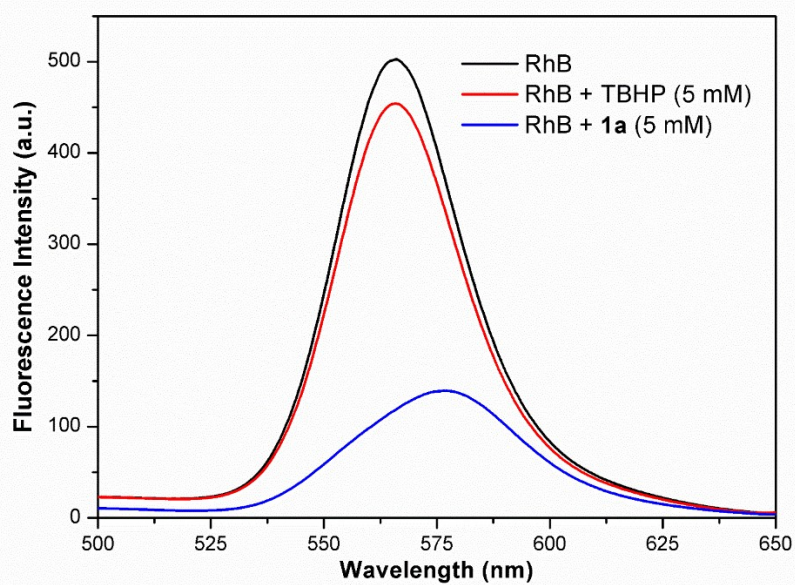


Figure S6 Fluorescence emission spectra of RhB (5×10^{-4} M) in DMF with TBHP or **1a** (5 mM)

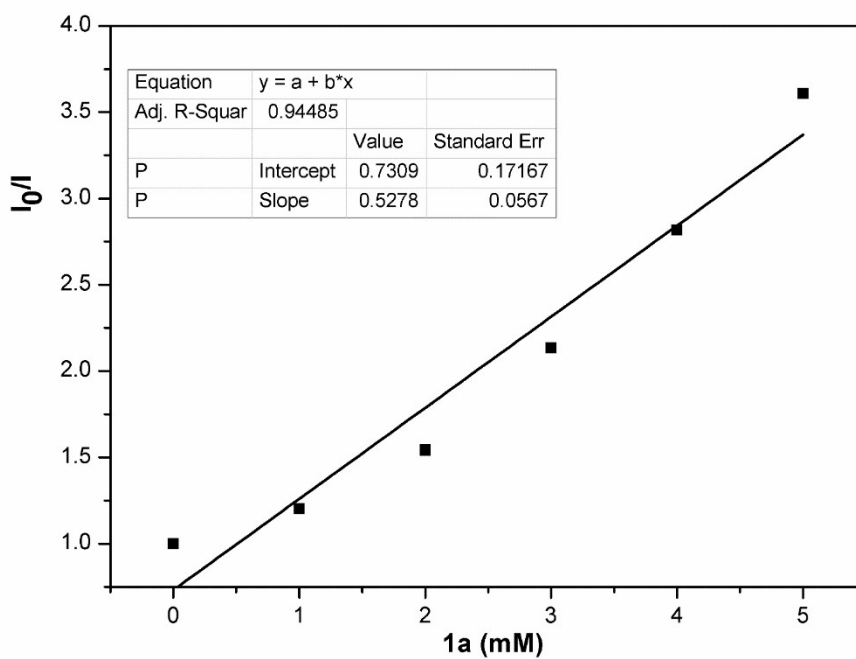
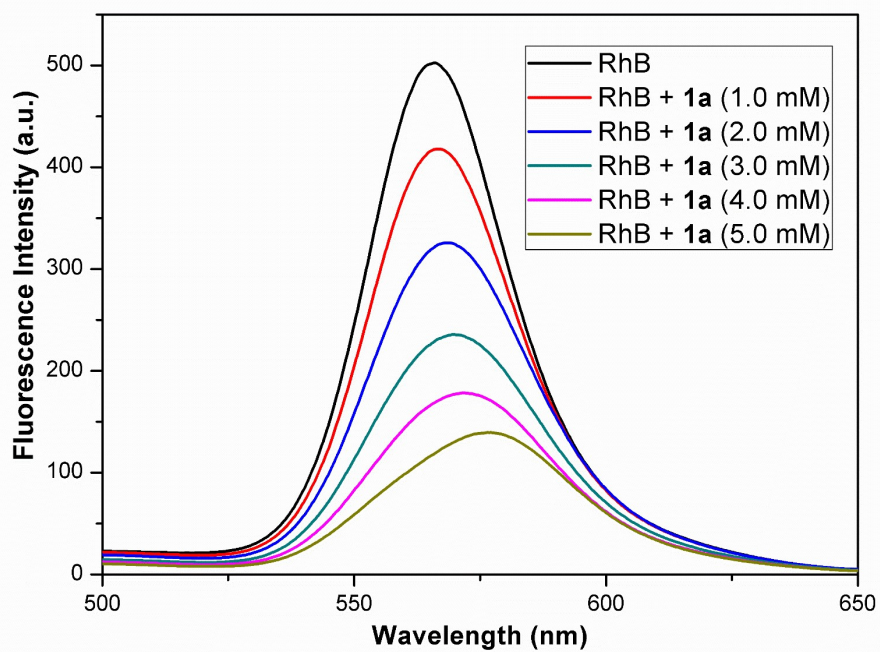
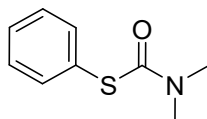


Figure S7 Fluorescence emission spectra of RhB in DMF with **1a** (up) and the linear relationship between I_0/I and the concentration of **1a** (down)

5. Characterization data of compounds 3a-h, 3j-r and 5a-j

S-phenyl dimethylcarbamothioate (**3a**)



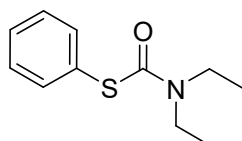
Colourless oil, yield: 80%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.51-7.48 (m, 2H, Ar-H), 7.40-7.37 (m, 3H, Ar-H), 3.09 (s, 3H, CH_3), 3.03 (s, 3H, CH_3).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 166.9, 135.7, 129.1, 128.9, 128.8, 36.9.

HRMS: $\text{C}_9\text{H}_{12}\text{NOS}$ [$\text{M} + \text{H}$] $^+$ 182.0634, found 182.0633.

S-phenyl diethylcarbamothioate (**3b**)



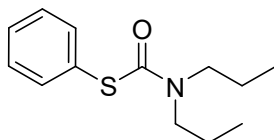
Colourless oil, yield: 75%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.52-7.50 (m, 2H, Ar-H), 7.39-7.37 (m, 3H, Ar-H), 3.46-3.41 (m, 4H, $(\text{CH}_2)_2$), 1.26-1.17 (m, 6H, $(\text{CH}_3)_2$).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 165.7, 135.8, 129.6, 129.0, 128.9, 42.4, 13.2.

HRMS: $\text{C}_{11}\text{H}_{16}\text{NOS}$ [$\text{M} + \text{H}$] $^+$ 210.0947, found 210.0946.

S-phenyl dipropylcarbamothioate (**3c**)



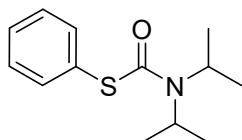
Colourless oil, yield: 74%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.50-7.49 (m, 2H, Ar-H), 7.38-7.36 (m, 3H, Ar-H), 3.34-3.30 (m, 4H, $\text{N}(\text{CH}_2)_2$), 1.72-1.56 (m, 4H, $(\text{CH}_2)_2$), 0.98-0.88 (m, 6H, $(\text{CH}_3)_2$).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 166.3, 135.7, 129.0, 128.84, 128.80, 49.7, 21.8, 11.3.

HRMS: $\text{C}_{13}\text{H}_{20}\text{NOS}$ [$\text{M} + \text{H}$] $^+$ 238.1260, found 238.1260.

S-phenyl diisopropylcarbamothioate (**3d**)



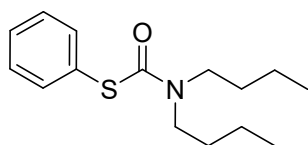
White solid, yield: 73%, M.p.: 100-102 °C.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.51-7.49 (m, 2H, Ar-H), 7.38-7.37 (m, 3H, Ar-H), 4.20 (s, 1H, CH), 3.51 (s, 1H, CH), 1.33 (s, 12H, $(\text{CH}_3)_4$).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 164.1, 136.0, 129.3, 128.9, 128.8, 63.2, 20.7.

HRMS: $\text{C}_{13}\text{H}_{20}\text{NOS}$ [$\text{M} + \text{H}$] $^+$ 238.1260, found 238.1261.

S-phenyl dibutylcarbamothioate (**3e**)



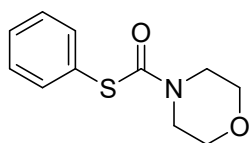
Colourless oil, yield: 65%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.51-7.49 (m, 2H, Ar-H), 7.38-7.36 (m, 3H, Ar-H), 3.37-3.33 (m, 4H, N(CH₂)₂), 1.62 (m, 4H, (CH₂)₂), 1.39-1.26 (m, 4H, (CH₂)₂), 1.00-0.89 (m, 6H, (CH₃)₂).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 166.1, 135.7, 128.99, 128.96, 128.8, 47.9, 29.9, 20.1, 13.8.

HRMS: C₁₅H₂₄NOS [M + H]⁺ 266.1573, found 266.1572.

S-phenyl morpholine-4-carbothioate (**3f**)



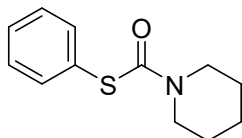
White solid, yield: 68%, M.p.: 105-107 °C.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.51-7.49 (m, 2H, Ar-H), 7.41-7.39 (m, 3H, Ar-H), 3.74-3.72 (m, 4H, (CH₂)₂), 3.62-3.60 (m, 4H, (CH₂)₂).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 166.4, 135.8, 129.4, 129.0, 128.0, 66.5, 45.3.

HRMS: C₁₁H₁₄NO₂S [M + H]⁺ 224.0740, found 224.0740.

S-phenyl piperidine-1-carbothioate (**3g**)



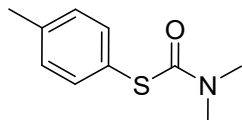
White solid, yield: 78%, M.p.: 58-60 °C.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.51-7.49 (m, 2H, Ar-H), 7.39-7.36 (m, 3H, Ar-H), 3.53 (s, 4H, (CH₂)₂), 1.63 (m, 6H, (CH₂)₃).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 165.4, 135.8, 129.1, 128.9, 46.8, 45.5, 25.8, 24.5.

HRMS: C₁₂H₁₆NOS [M + H]⁺ 222.0947, found 222.0947.

S-*p*-tolyl dimethylcarbamothioate (**3h**)



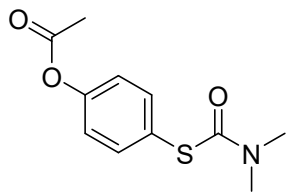
Colourless oil, yield: 53%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.37 (d, J = 8.0 Hz, 2H, Ar-H), 7.19 (d, J = 8.0 Hz, 2H, Ar-H), 3.06-3.02 (m, 6H, (CH₃)₂), 2.36 (s, 3H, CH₃).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ (ppm) 167.3, 139.4, 135.7, 129.8, 125.3, 36.9, 21.3.

HRMS: C₁₀H₁₄NOS [M + H]⁺ 196.0791, found 196.0790.

S-4-(dimethylcarbamoylthio)phenyl acetate (**3j**)



White solid, yield: 75%, M.p.: 71.2-73.6 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.49 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.12 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.06 (s, 6H, N(CH₃)₂), 2.30 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 169.0, 166.6, 151.5, 136.8, 126.0, 122.1, 36.9, 21.1.

HRMS: C₁₁H₁₄NO₃S [M + H]⁺ 240.0689, found 240.0685.

S-2-fluorophenyl dimethylcarbamothioate (**3k**)



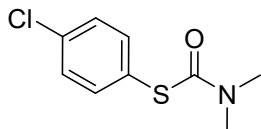
Colourless oil, yield: 77%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.51-7.46 (m, 1H, Ar-H), 7.42-7.40 (s, 1H, Ar-H), 7.18-7.13 (m, 2H, Ar-H), 3.13 (s, 3H, CH₃), 3.03 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 165.1, 164.2, 137.8, 131.9 (d, *J* = 8.2 Hz), 124.4 (d, *J* = 3.8 Hz), 116.2, 115.9, 37.0.

HRMS: C₉H₁₁FNOS [M + H]⁺ 200.0540, found 200.0540.

S-4-chlorophenyl dimethylcarbamothioate (**3l**)



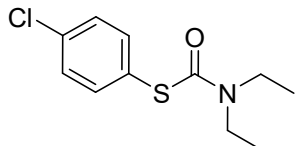
Colourless oil, yield: 83%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.41 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.34 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.07 (s, 3H, CH₃), 3.02 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.3, 136.9, 135.6, 129.1, 127.4, 36.9.

HRMS: C₉H₁₁ClNOS [M + H]⁺ 216.0244, found 216.0241.

S-4-chlorophenyl diethylcarbamothioate (**3m**)



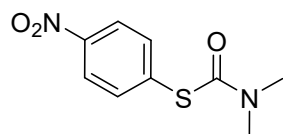
Colourless oil, yield: 81%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.43 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.34 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.45-3.40 (s, 4H, (CH₂)₂), 1.22 (m, 6H, (CH₃)₂).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 165.1, 136.9, 135.4, 129.1, 127.4, 42.4, 13.8, 13.2.

HRMS: C₁₁H₁₅ClNOS [M + H]⁺ 244.0557, found 244.0551.

S-4-nitrophenyl dimethylcarbamothioate (**3n**)



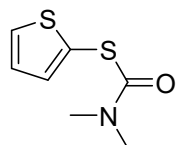
Yellow oil, yield: 68%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.22 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.68 (d, *J* = 9.2 Hz, 2H, Ar-H), 3.12 (s, 3H, CH₃), 3.06 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 164.5, 148.0, 137.6, 135.8, 123.5, 37.1.

HRMS: C₉H₁₀N₂NaO₃S [M + Na]⁺ 249.0304, found 249.0312.

S-thiophen-2-yl dimethylcarbamothioate (**3o**)



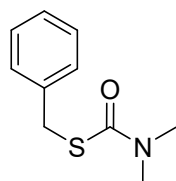
Colourless oil, yield: 57%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.53 (d, *J* = 5.2 Hz, 1H, Ar-H), 7.20 (d, *J* = 3.2 Hz, 1H, Ar-H), 7.08-7.06 (m, 1H, Ar-H), 3.08 (s, 3H, CH₃), 3.04 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.2, 136.8, 132.1, 127.5, 126.0, 37.1.

HRMS: C₇H₁₀NOS₂ [M + H]⁺ 188.0198, found 188.0204.

S-benzyl dimethylcarbamothioate (**3p**)



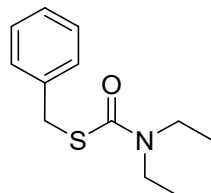
Colourless oil, yield: 66%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.35 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.31-7.27 (m, 2H, Ar-H), 7.24-7.21 (m, 1H, Ar-H), 4.16 (s, 2H, CH₂), 2.99 (s, 6H, (CH₃)₂).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 167.8, 138.4, 128.9, 128.5, 127.1, 36.7, 34.8.

HRMS: C₁₀H₁₄NOS [M + H]⁺ 196.0791, found 196.0796.

S-benzyl diethylcarbamothioate (**3q**)



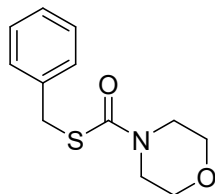
Colourless oil, yield: 62%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.35 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.30 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 4.16 (s, 2H, CH₂), 3.42-3.34 (m, 4H, (CH₂)₂), 1.18-1.14 (m, 6H, (CH₃)₂).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.7, 138.3, 129.0, 128.5, 127.1, 42.1, 34.6, 13.3.

HRMS: C₁₂H₁₃NOS [M + H]⁺ 224.1104, found 224.1103.

S-benzyl morpholine-4-carbothioate (**3r**)



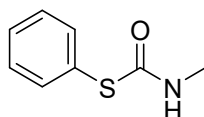
Colourless oil, yield: 55%.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.23-7.22 (m, 3H, Ar-H), 7.18-7.17 (m, 2H, Ar-H), 4.27 (s, 2H, CH₂), 1.56 (s, 2H, CH₂), 1.26 (s, 2H, CH₂).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.8, 133.5, 129.2, 128.8, 126.9, 53.3, 40.4, 29.6.

HRMS: C₁₂H₁₅KNO₂S [M + K]⁺ 276.0455, found 276.0440.

S-phenyl methylcarbamothioate (**5a**)



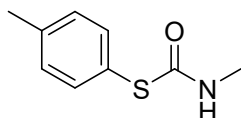
White solid, yield: 75%, M.p.: 138-140 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.58-7.56 (m, 2H, Ar-H), 7.43-7.41 (m, 3H, Ar-H), 5.30 (s, 1H, NH), 2.84 (d, *J* = 4.4 Hz, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.8, 135.5, 129.7, 129.5, 128.6, 28.1.

HRMS: C₈H₁₀NOS [M + H]⁺ 168.0478, found 168.0484.

S-*p*-tolyl methylcarbamothioate (**5b**)



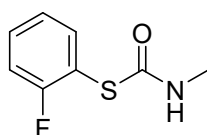
White solid, yield: 60%, M.p.: 79-81 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.44 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.21 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.44 (s, 1H, NH), 2.80 (d, *J* = 4.4 Hz, 3H, CH₃), 2.37 (s, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 167.3, 140.1, 135.6, 130.4, 125.1, 28.0, 21.3.

HRMS: C₉H₁₂NOS [M + H]⁺ 182.0634, found 182.0636.

S-2-fluorophenyl methylcarbamothioate (**5c**)



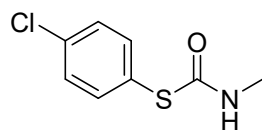
White solid, yield: 78%, M.p.: 95-97 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.56-7.52 (m, 1H, Ar-H), 7.44-7.41 (m, 1H, Ar-H), 7.20-7.15 (m, 2H, Ar-H), 5.40 (s, 1H, NH), 2.87 (d, *J* = 4.0 Hz, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 164.3 (d, *J* = 98.8 Hz), 161.3, 137.6, 132.2 (d, *J* = 8.1 Hz), 124.7 (d, *J* = 3.9 Hz), 116.4, 116.2, 28.2.

HRMS: C₈H₉FNOS [M + H]⁺ 186.0383, found 186.0392.

S-4-chlorophenyl methylcarbamothioate (**5d**)



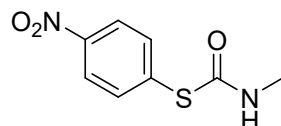
White solid, yield: 82%, M.p.: 121-123 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.47 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.37 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.41 (s, 1H, NH), 2.85 (d, *J* = 4.4 Hz, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.0, 136.6, 136.0, 129.6, 127.0, 28.2.

HRMS: C₈H₉CINOS [M + H]⁺ 202.0088, found 202.0098.

S-4-nitrophenyl methylcarbamothioate (**5e**)



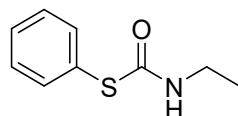
Yellow solid, yield: 76%, M.p.: 126-128 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.22 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.70 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.48 (s, 1H, NH), 2.93 (d, *J* = 4.8 Hz, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 163.8, 147.9, 137.4, 134.7, 123.8, 28.3.

HRMS: C₈H₉N₂O₃S [M + H]⁺ 213.0328, found 213.0340.

S-phenyl ethylcarbamothioate (**5f**)



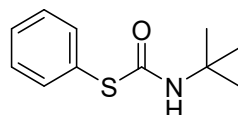
White solid, yield: 73%, M.p.: 80-82 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.56-7.54 (m, 2H, Ar-H), 7.41-7.40 (m, 3H, Ar-H), 5.46 (s, 1H, NH), 3.32-3.26 (m, 2H, CH₂), 1.12-1.08 (m, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 165.9, 135.5, 129.6, 129.4, 128.7, 36.5, 14.8.

HRMS: C₉H₁₂NOS [M + H]⁺ 182.0634, found 182.0634.

S-phenyl tert-butylcarbamothioate (**5g**)



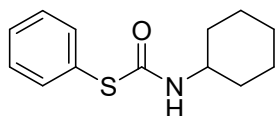
White solid, yield: 70%, M.p.: 110-112 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.54-7.52 (m, 2H, Ar-H), 7.39-7.38 (m, 3H, Ar-H), 5.24 (s, 1H, NH), 1.32 (s, 9H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 164.0, 135.4, 129.3, 129.24, 129.21, 53.5, 28.8.

HRMS: C₁₁H₁₆NOS [M + H]⁺ 210.0947, found 210.0943.

S-phenyl cyclohexylcarbamothioate (**5h**)



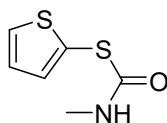
White solid, yield: 64%, M.p.: 107-109 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.56-7.54 (m, 2H, Ar-H), 7.42-7.40 (m, 3H, Ar-H), 5.18 (s, 1H, NH), 3.73 (s, 1H, CH), 1.89 (d, *J* = 9.6 Hz, 2H, CH₂), 1.63-1.56 (m, 2H, CH₂), 1.34-1.09 (m, 6H, (CH₂)₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 165.0, 135.7, 135.4, 129.5, 129.4, 50.5, 32.9, 25.4, 24.6.

HRMS: C₁₃H₁₈NOS [M + H]⁺ 236.1104, found 236.1104.

S-thiophen-2-yl methylcarbamothioate (**5i**)



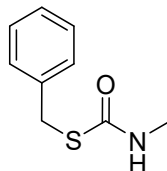
White solid, yield: 53%, M.p.: 119-121 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.58 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.30 (d, *J* = 2.8 Hz, 1H, Ar-H), 7.13-7.11 (m, 1H, Ar-H), 5.42 (s, 1H, NH), 2.84 (d, *J* = 4.4 Hz, 3H, CH₃).

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 166.4, 137.6, 133.1, 128.4, 126.4, 28.2.

HRMS: C₆H₈NOS₂ [M + H]⁺ 174.0042, found 174.0046.

S-benzyl methylcarbamothioate (**5j**)



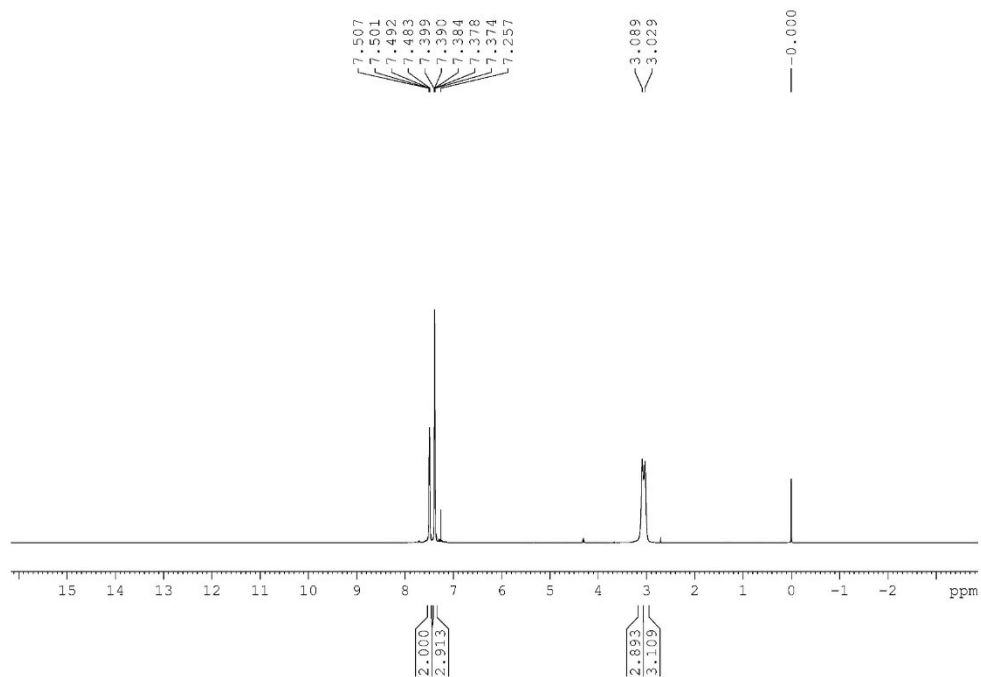
White solid, yield: 54%, M.p.: 35-37 °C.

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.34-7.29 (m, 3H, Ar-H), 7.25-7.23 (m, 2H, Ar-H), 5.36 (s, 1H, NH), 4.16 (s, 2H, CH₂), 2.87 (d, *J* = 4.8 Hz, 3H, CH₃).

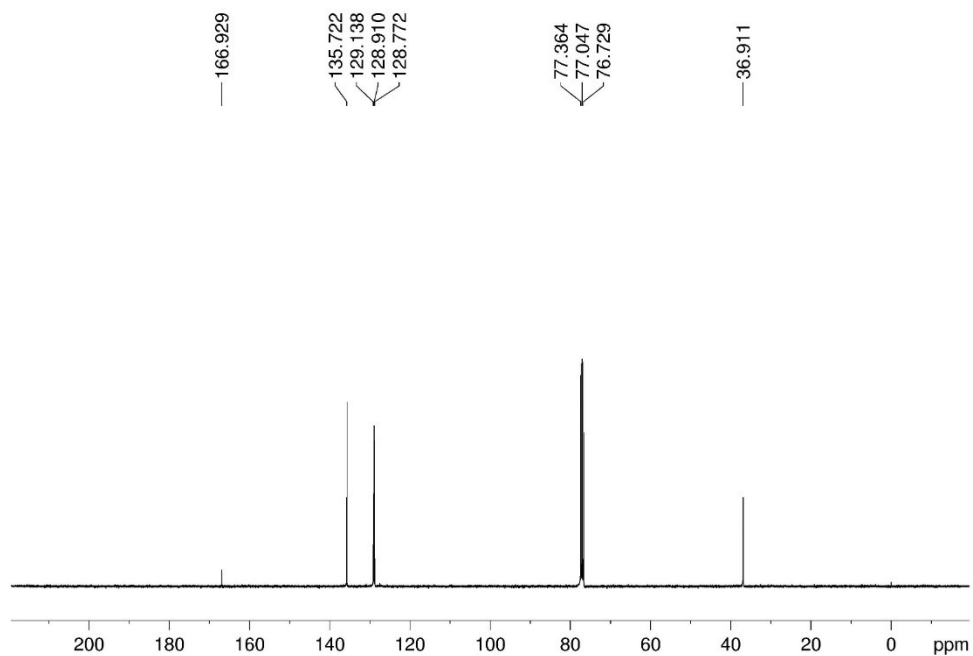
¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 167.4, 138.4, 128.8, 128.6, 127.2, 34.2, 28.0.

HRMS: C₉H₁₂NOS [M + H]⁺ 182.0634, found 182.0640.

6. ^1H NMR, ^{13}C NMR and HRMS copies of compounds 3a-h, 3j-r and 5a-j

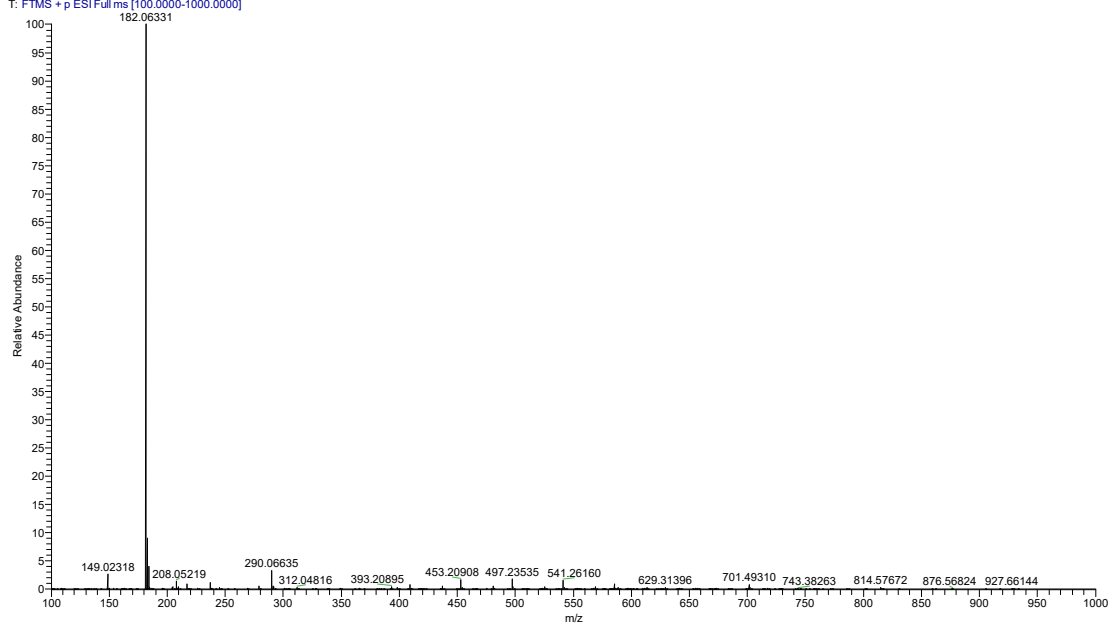


^1H NMR spectrum of compound **3a**

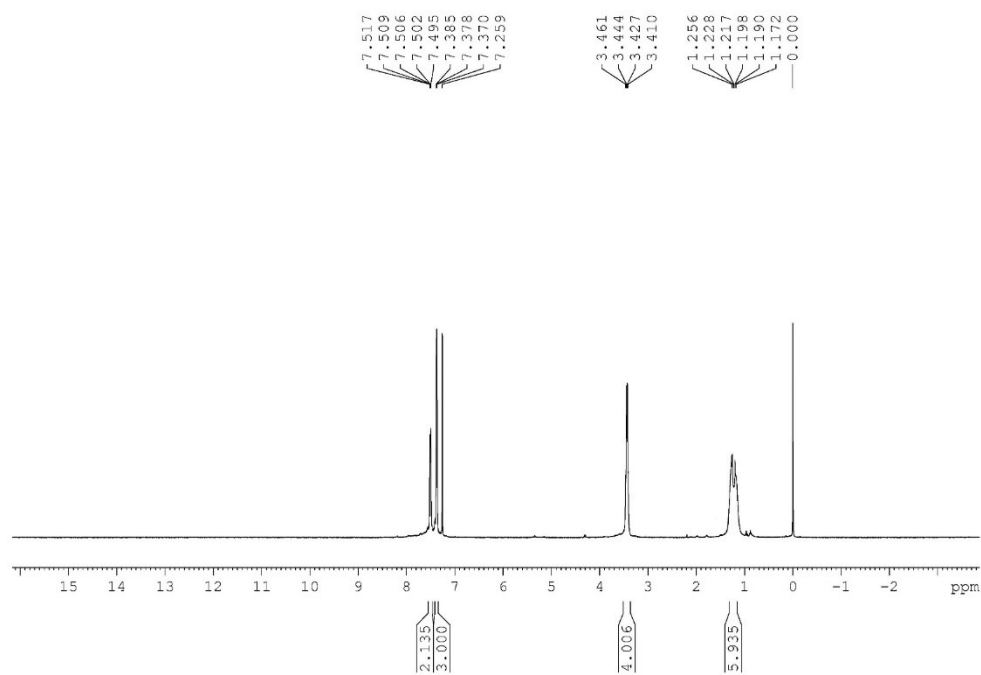


^{13}C NMR spectrum of compound **3a**

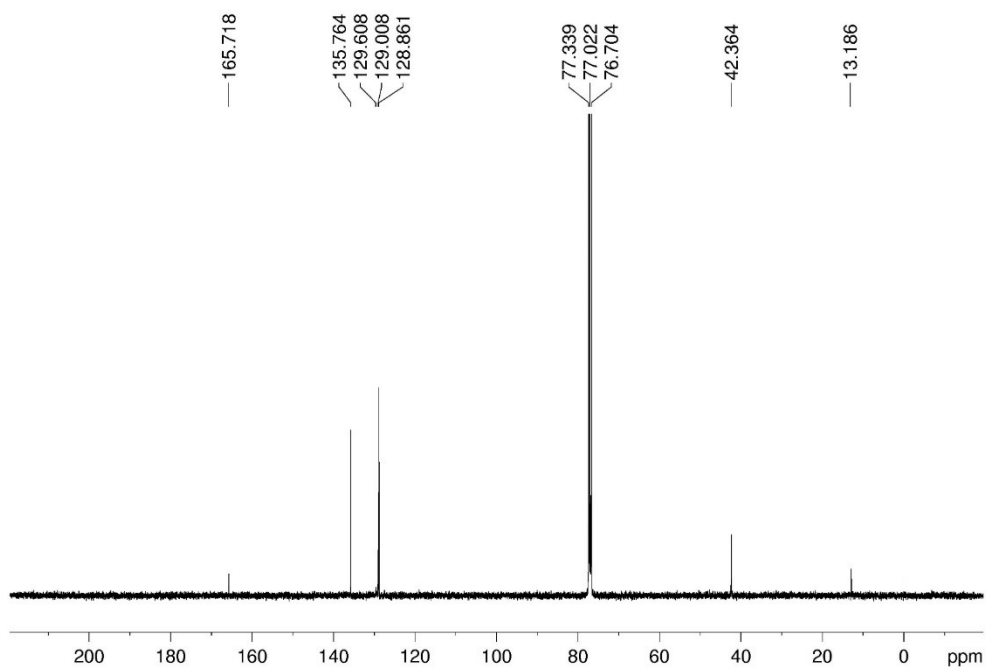
Rawdata_20210401115906 #42 RT: 0.29 AV: 1 NL: 3.18E6
T: FTMS + p ESI Full ms [100.0000-1000.0000]



HRMS spectrum of compound 3a



¹H NMR spectrum of compound 3b

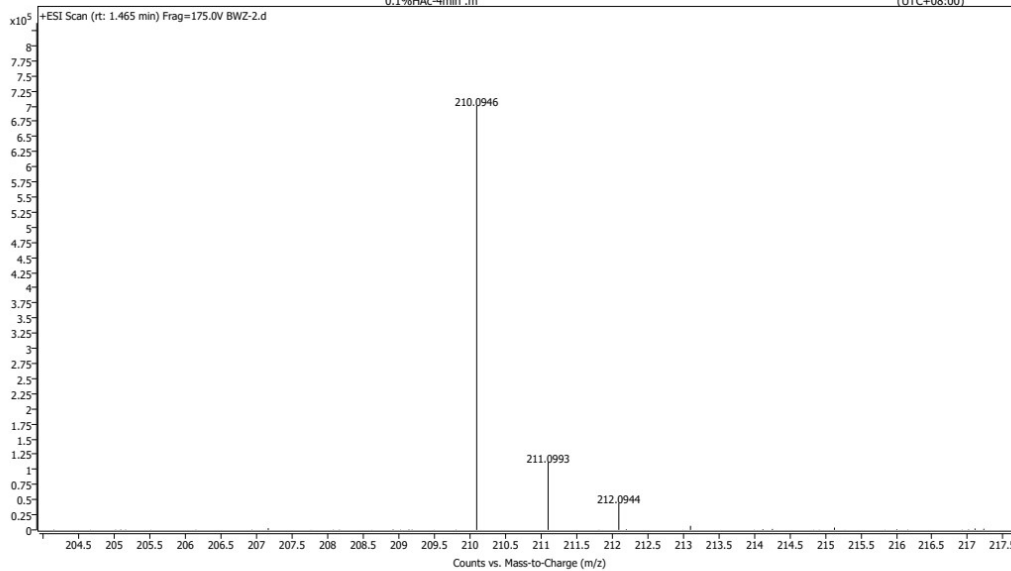


^{13}C NMR spectrum of compound **3b**

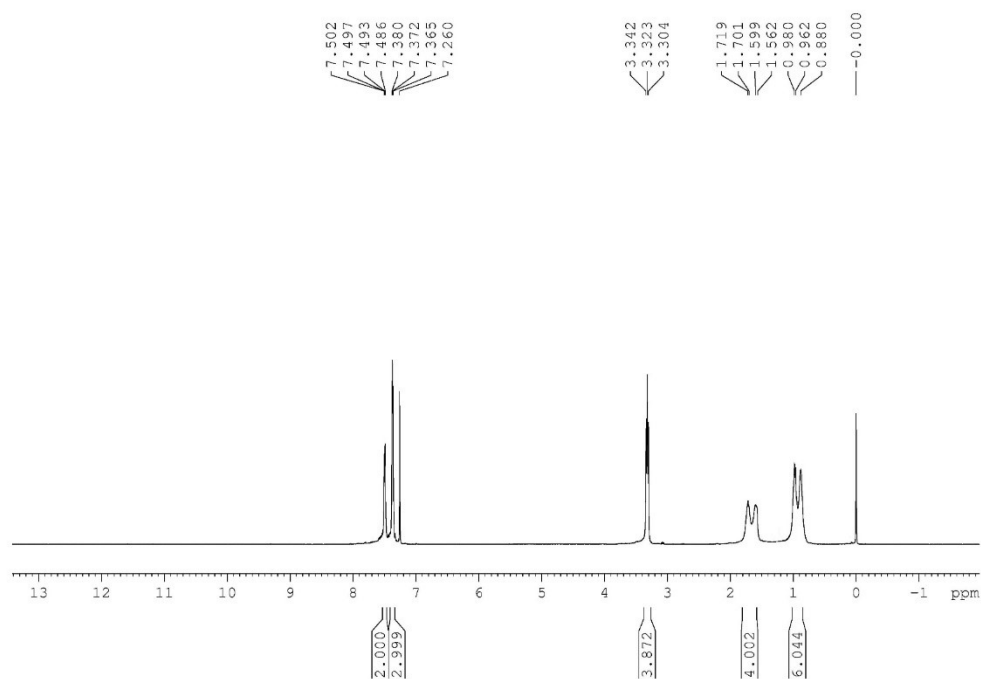
Spectrum Plot Report

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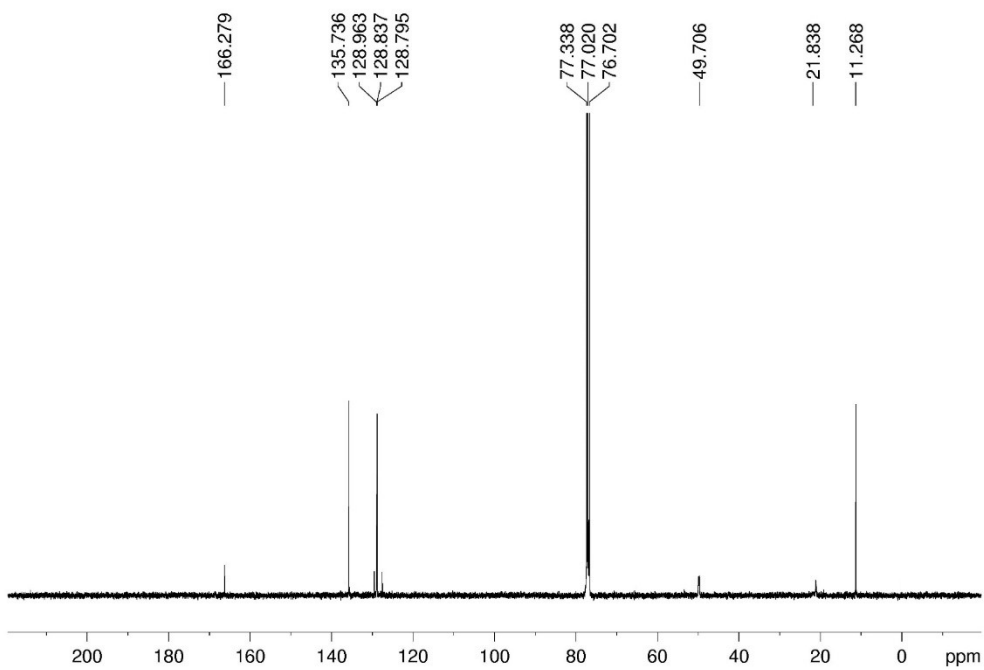
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					7/7/2021 12:58:27 PM (UTC+08:00)



HRMS spectrum of compound **3b**



^1H NMR spectrum of compound **3c**

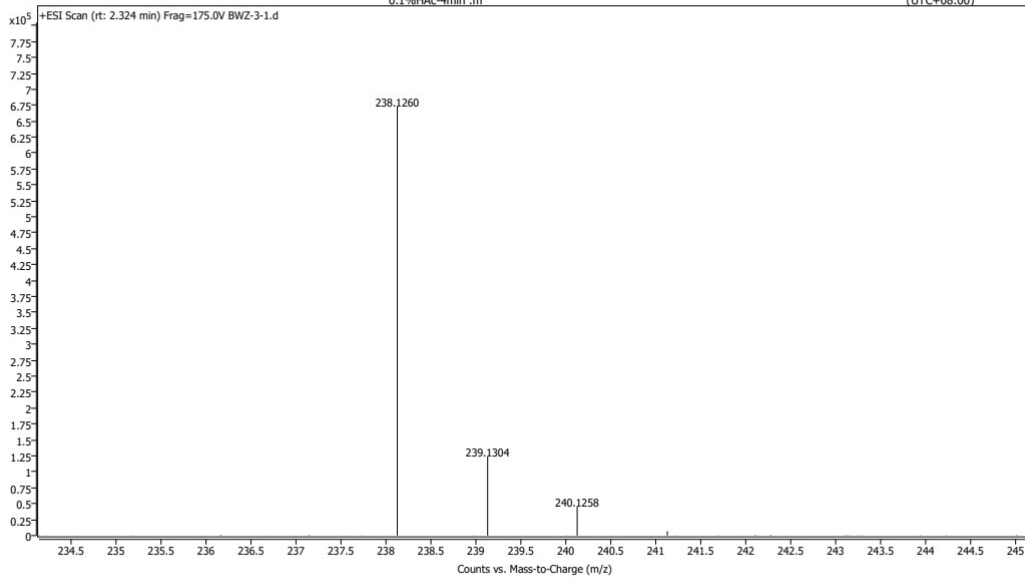


^{13}C NMR spectrum of compound **3c**

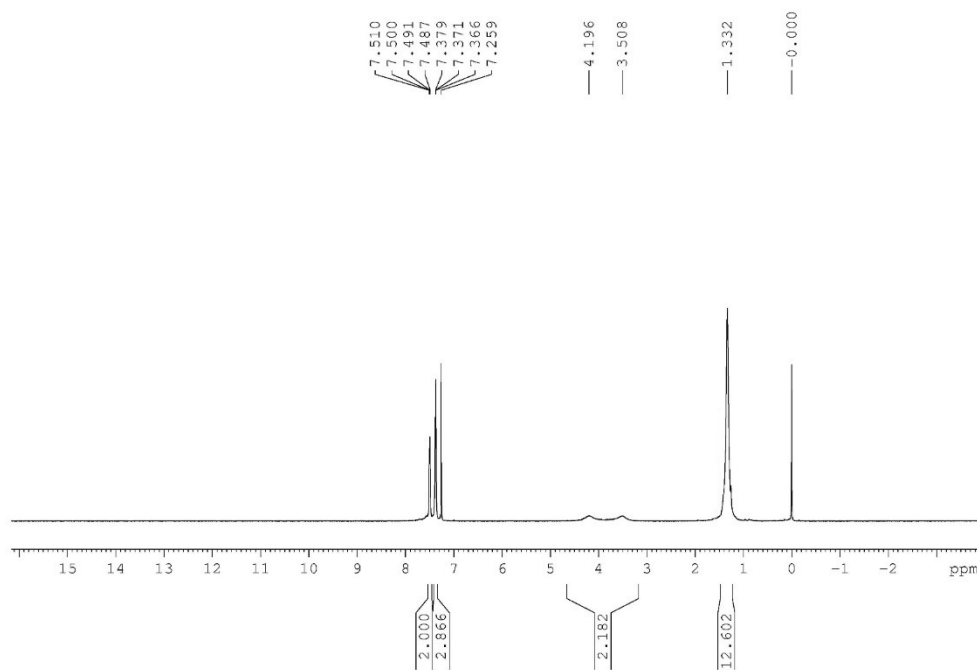
Spectrum Plot Report



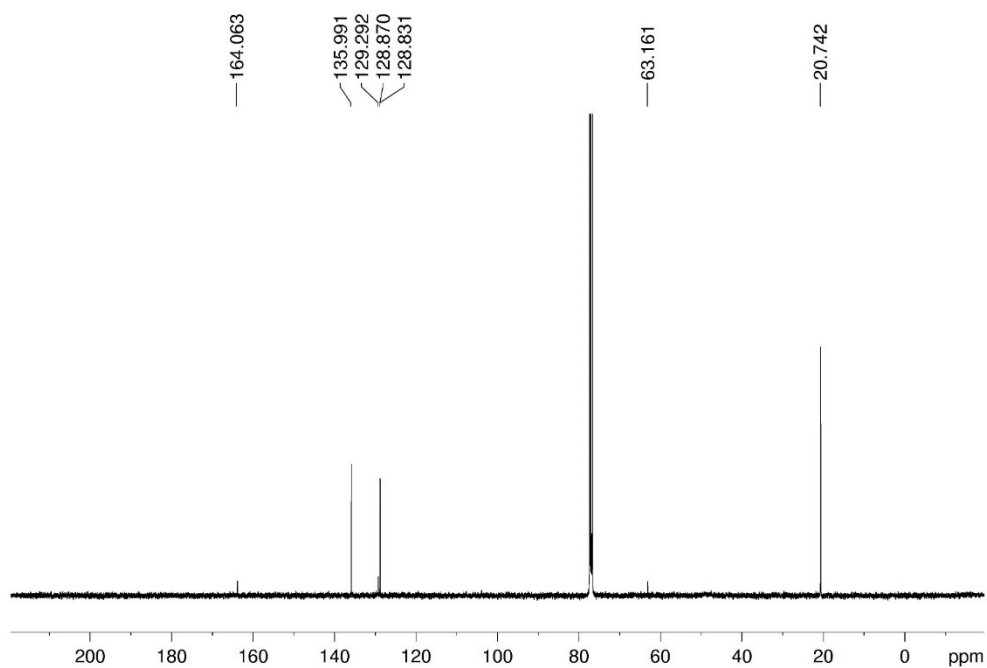
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Inj. Vol. (ul): 5
Data File: BWZ-3-1.d
Rack Pos.:
Plate Pos.:
Method (Acq): BWZ20210707-0.1%*n*Ac-4min.m
Instrument: Instrument 1
IRM Status: Success
Comment:
Operator: Operator
Acq. Time (Local): 7/7/2021 1:27:14 PM (UTC+08:00)



HRMS spectrum of compound 3c



¹H NMR spectrum of compound 3d

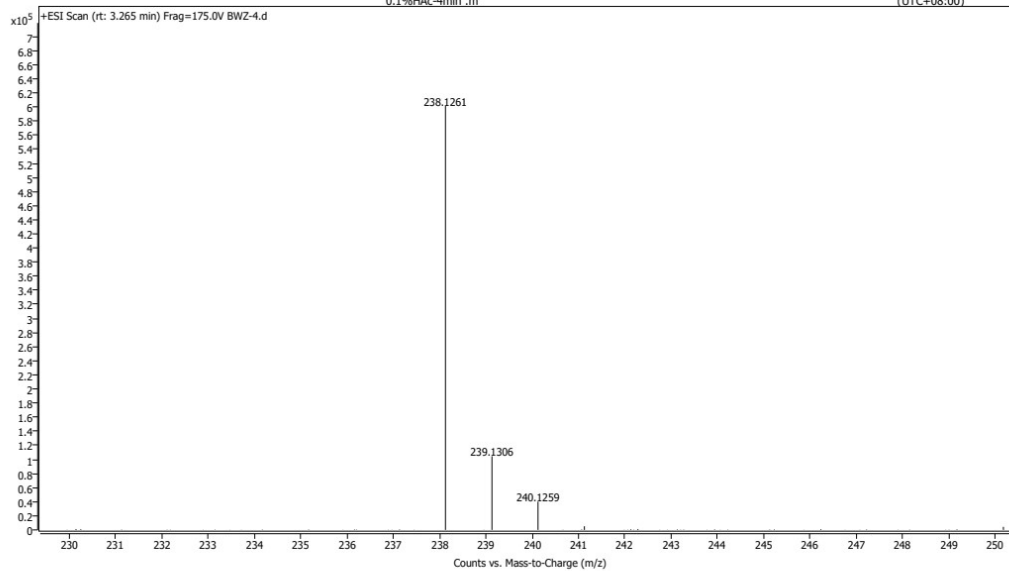


^{13}C NMR spectrum of compound **3d**

Spectrum Plot Report

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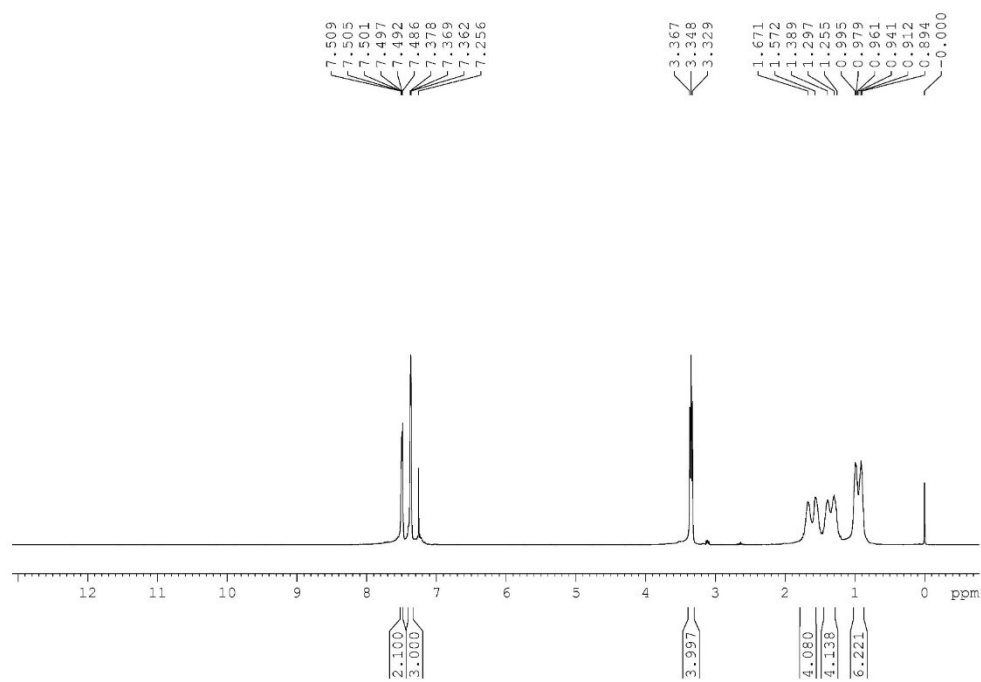
Name	BWZ-4	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-4.d	Method (Acq)	BWZ20210707-0.1% <i>Ac</i> -4min.m		Acq. Time (Local) 7/7/2021 1:20:59 PM (UTC+08:00)



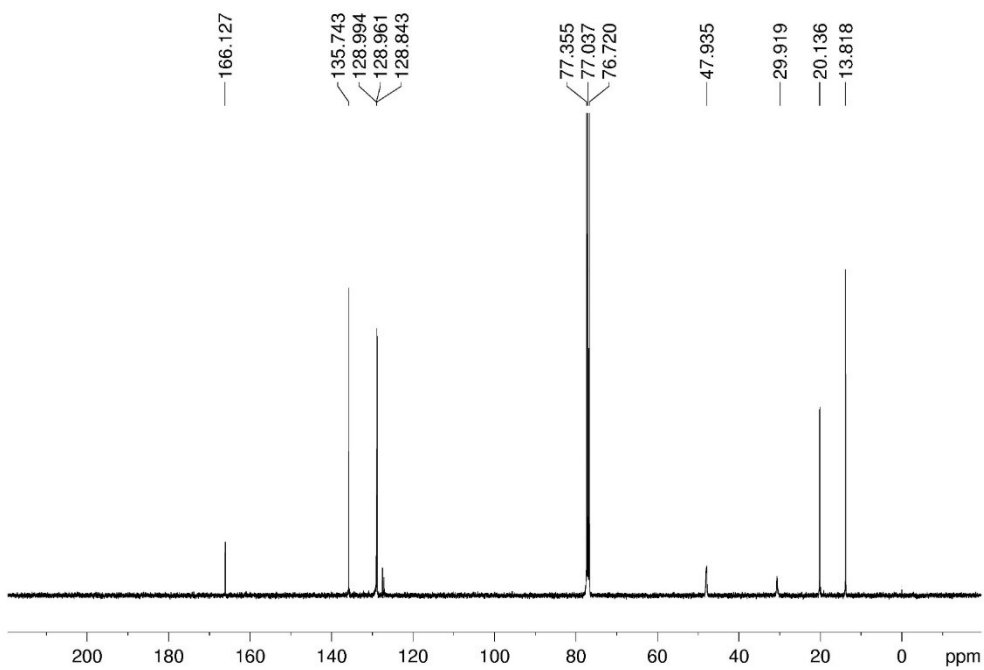
Page 1 of 1

Generated at 1:29 PM on 7/7/2021

HRMS spectrum of compound **3d**



¹H NMR spectrum of compound **3e**

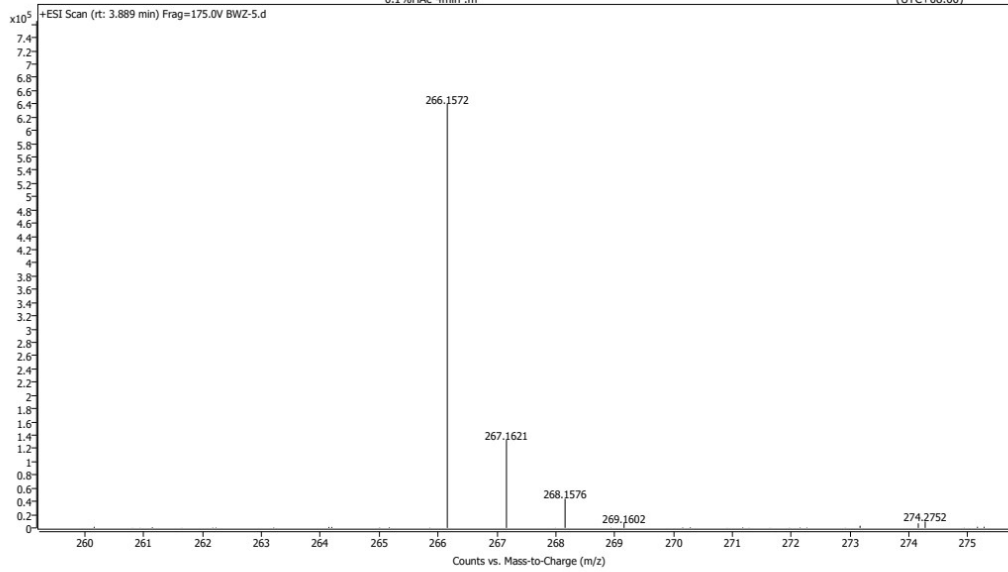


¹³C NMR spectrum of compound **3e**

Spectrum Plot Report



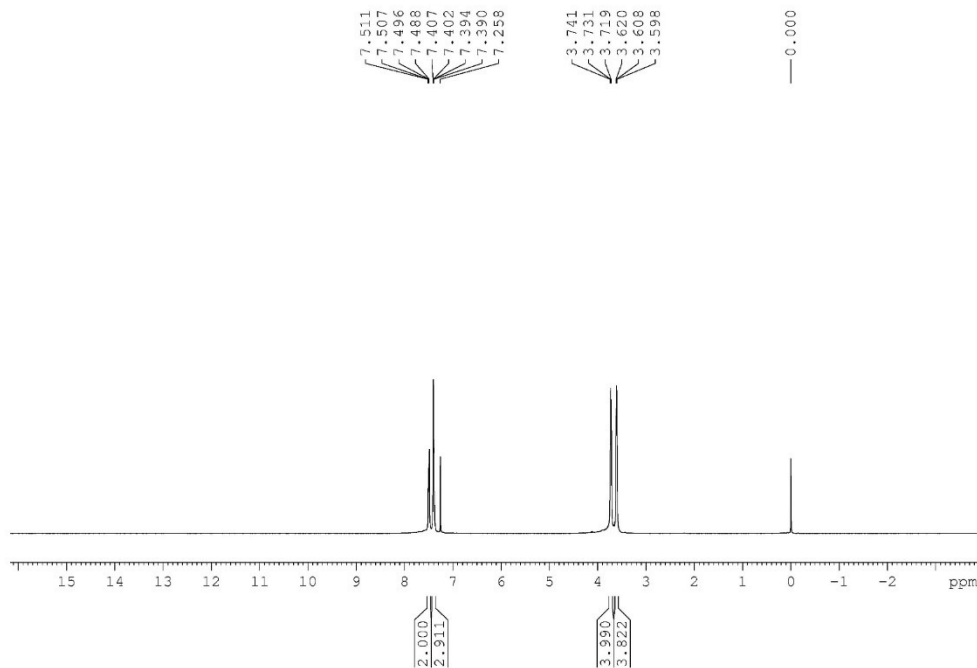
Name	BWZ-5	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	5	Plate Pos.		IRM Status	Success		
Data File	BWZ-5.d	Method (Acq)	BWZ20210707-0.1% ¹⁸ HAc-4min.m	Comment		Acq. Time (Local)	7/7/2021 1:44:29 PM (UTC+08:00)



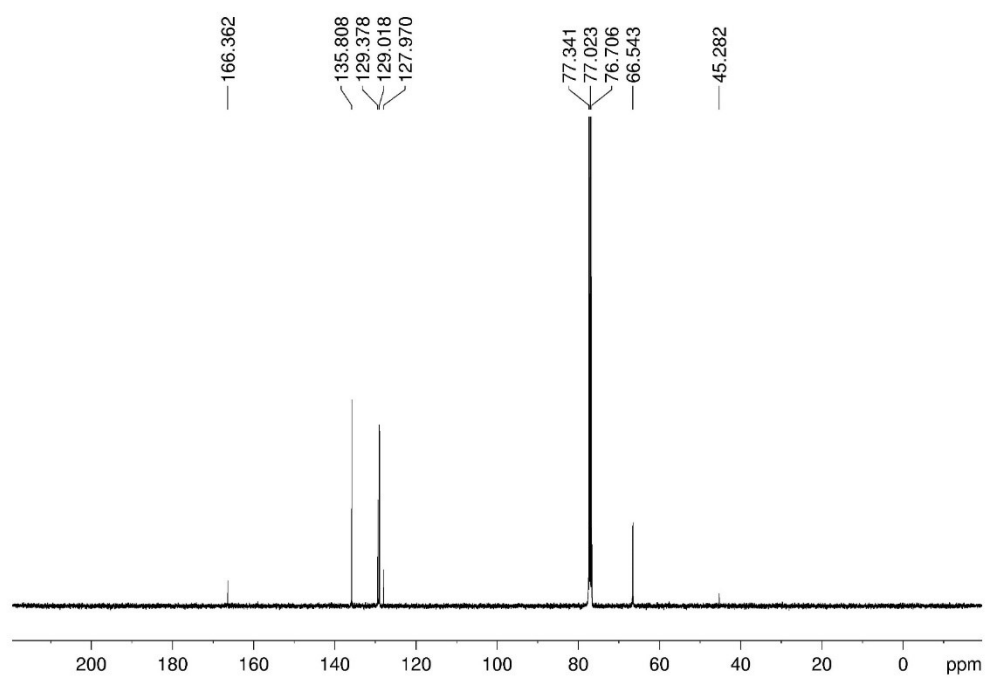
Page 1 of 1

Generated at 3:32 PM on 7/7/2021

HRMS spectrum of compound 3e



¹H NMR spectrum of compound 3f



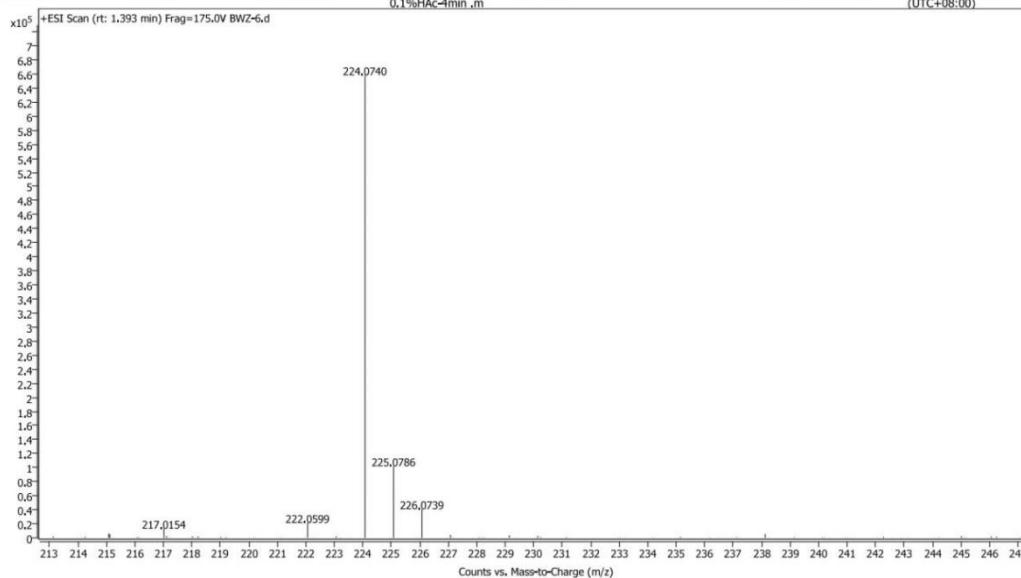
^{13}C NMR spectrum of compound **3f**

Spectrum Plot Report

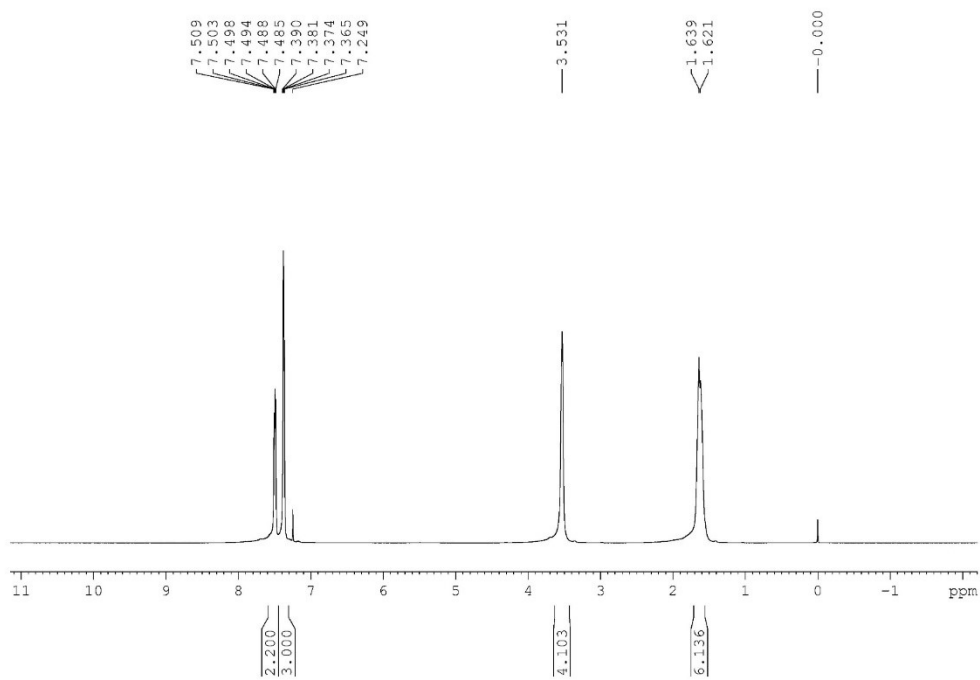


Name	BWZ-6	Rack Pos.	Instrument	Instrument 1	Operator
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Data File	BWZ-6.d	Method (Acq)	Comment		Acq. Time (Local)

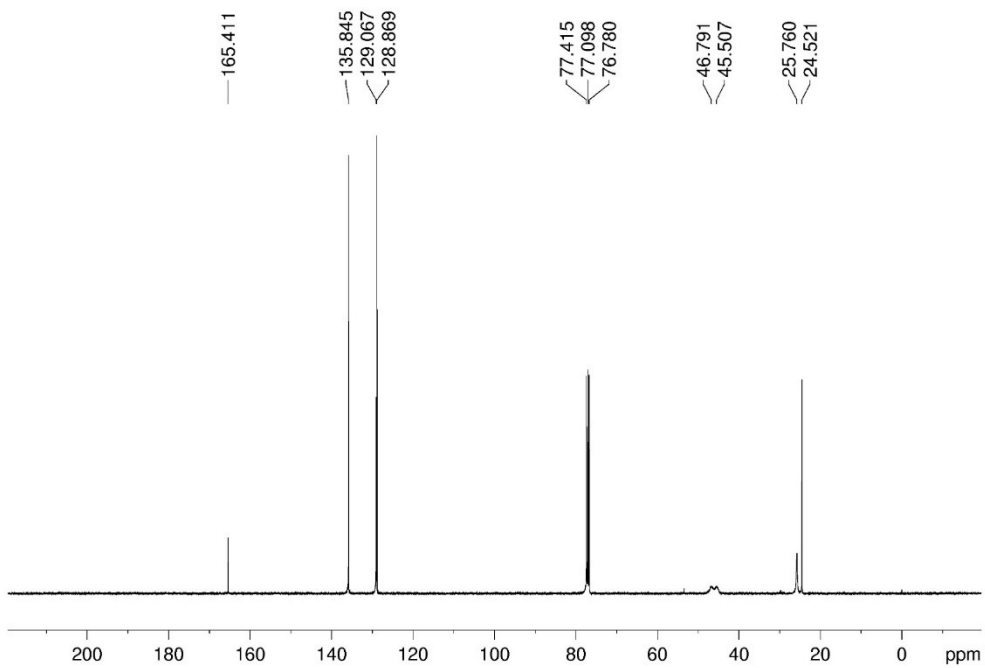
BWZ20210707-0.1%HAc-4min.m
7/7/2021 1:50:05 PM (UTC+08:00)



HRMS spectrum of compound **3f**



^1H NMR spectrum of compound **3g**

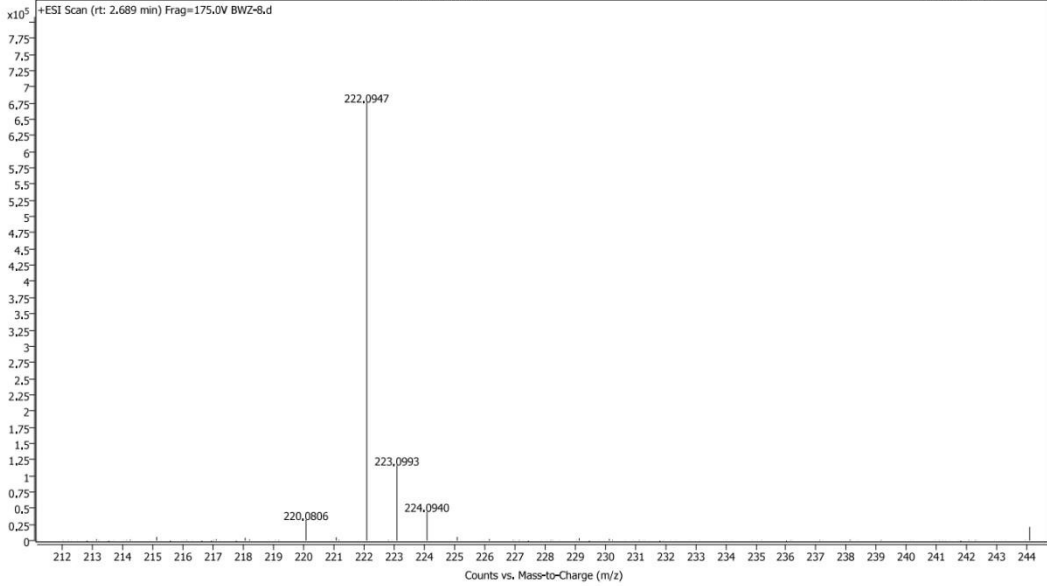


^{13}C NMR spectrum of compound **3g**

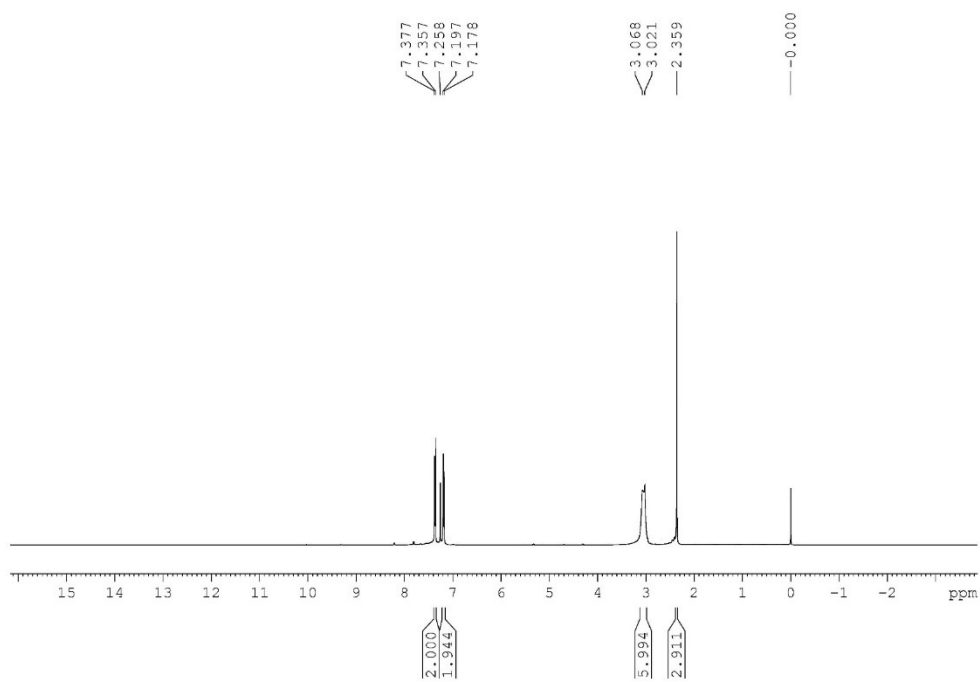
Spectrum Plot Report



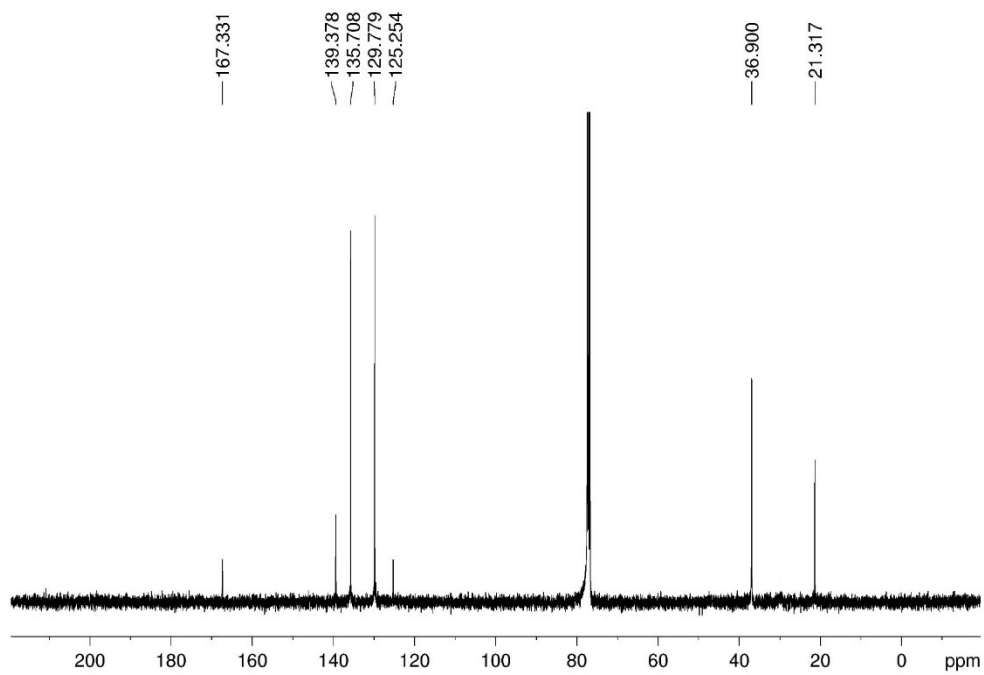
Name	BWZ-8	Rack Pos.	Instrument	Instrument 1	Operator
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Data File	BWZ-8.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707-0.1% ⁹⁴ HAc-tmin.m		7/7/2021 2:01:33 PM (UTC+08:00)



HRMS spectrum of compound **3g**



^1H NMR spectrum of compound **3h**

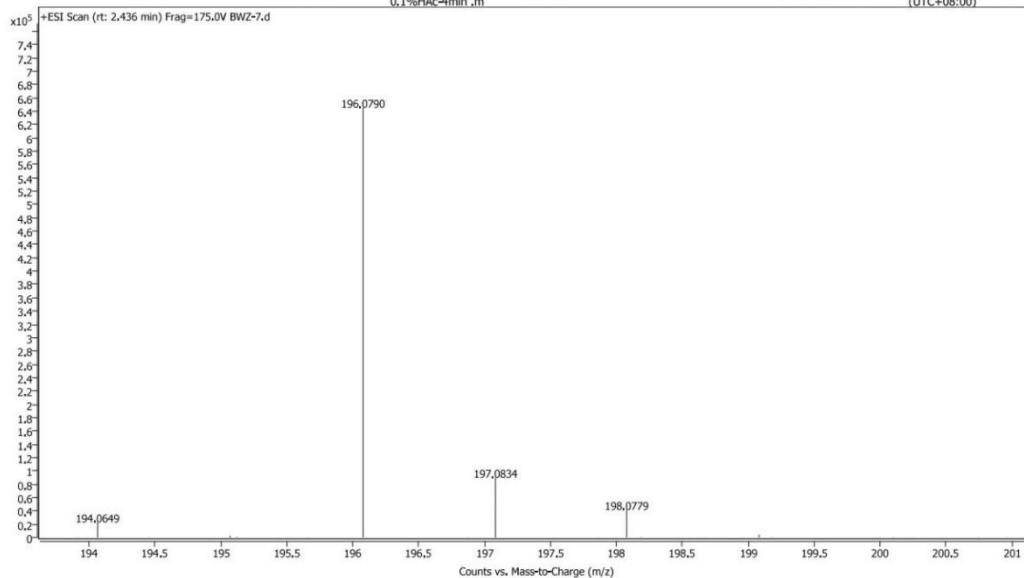


^{13}C NMR spectrum of compound **3h**

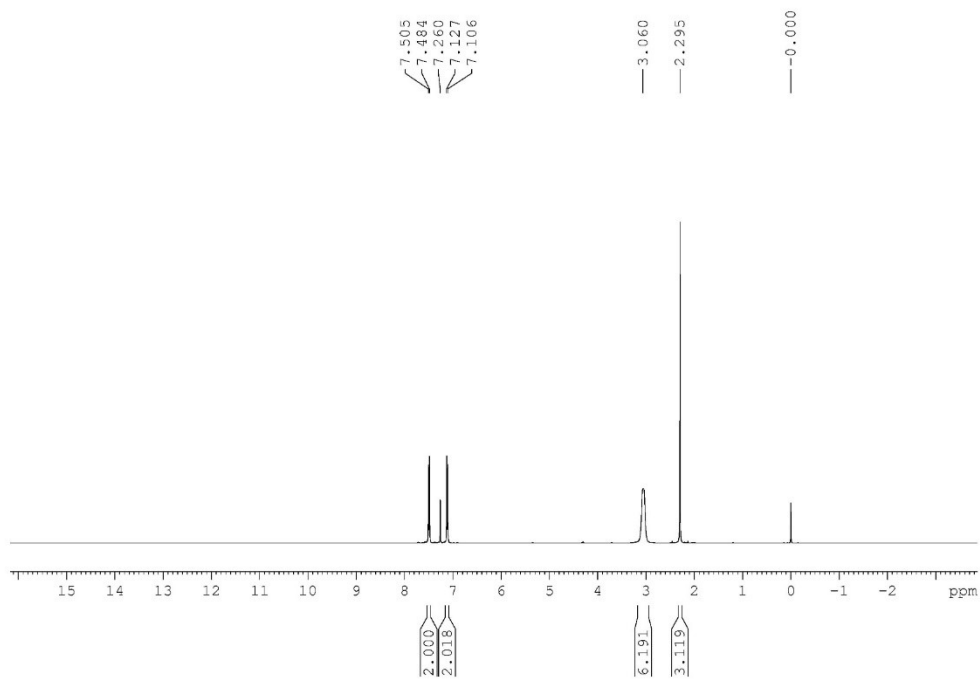
Spectrum Plot Report



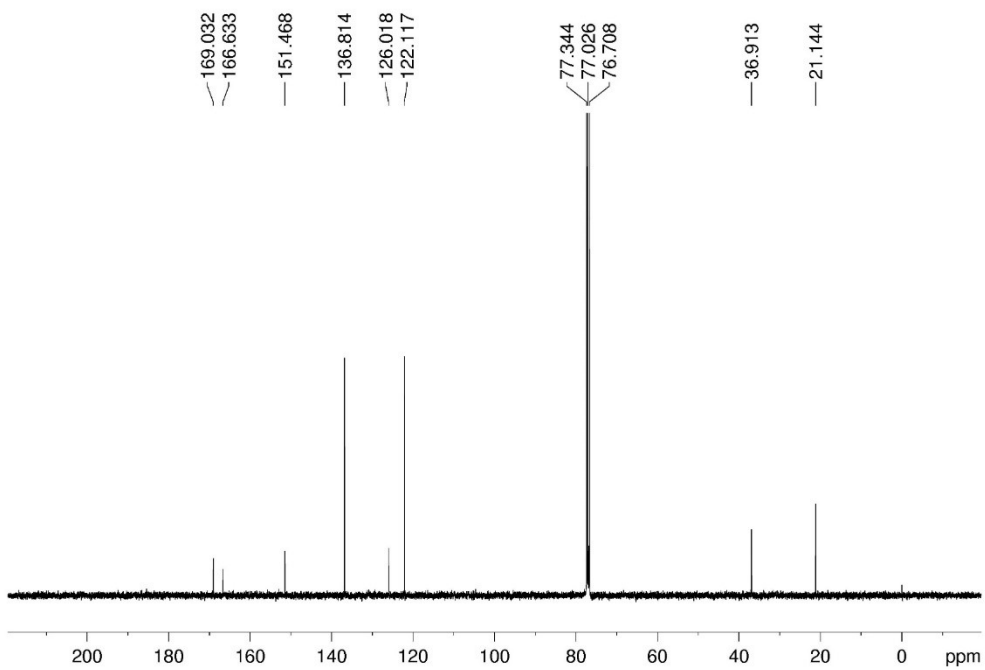
Name: Inj. Vol. (ul) Data File: BWZ-7 5 BWZ-7.d Rack Pos. Plate Pos. Method (Acq): BWZ20210707-0,1%HAc-4min.m Instrument IRM Status Comment: Instrument 1 Success Operator: Acq. Time (Local) 7/7/2021 1:56:00 PM (UTC+08:00)



HRMS spectrum of compound **3h**



^1H NMR spectrum of compound **3j**

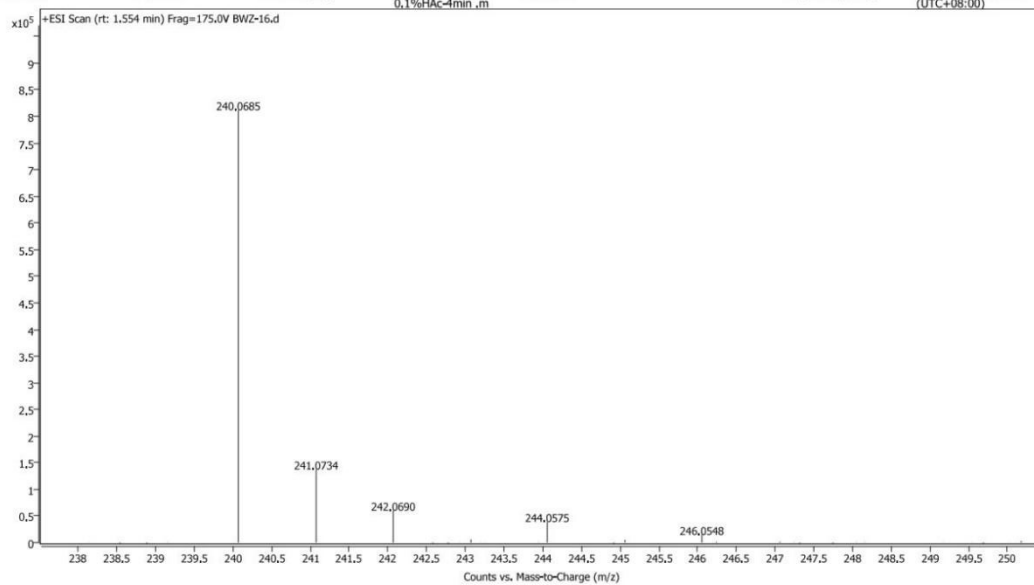


^{13}C NMR spectrum of compound **3j**

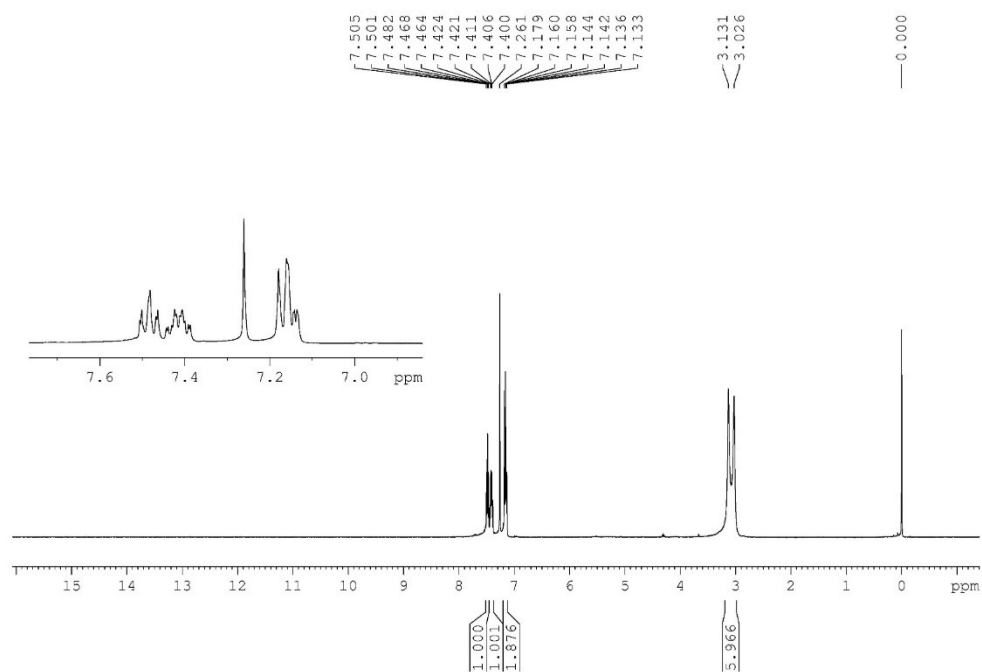
Spectrum Plot Report



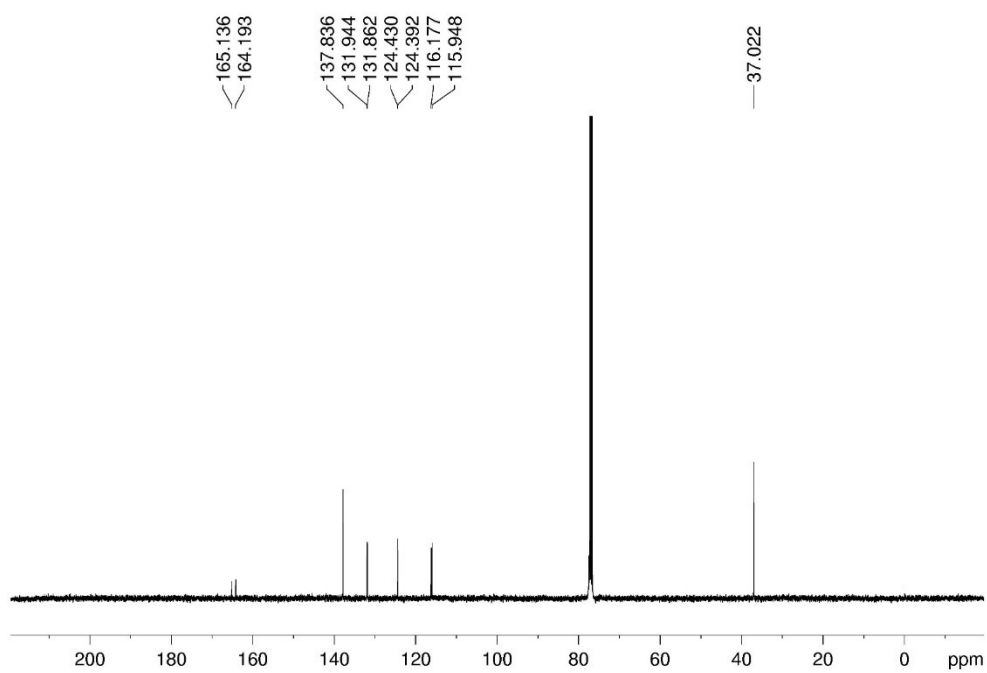
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Instrument: Instrument 1 Success
IRM Status Comment
Operator: Acq. Time (Local) 7/7/2021 2:52:08 PM (UTC+08:00)



HRMS spectrum of compound **3j**



^1H NMR spectrum of compound **3k**

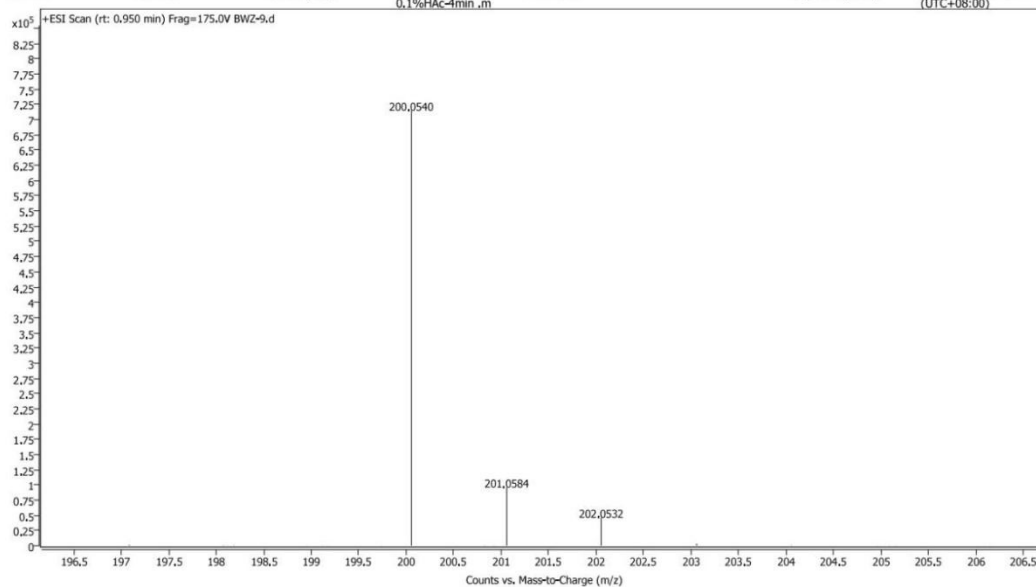


^{13}C NMR spectrum of compound **3k**

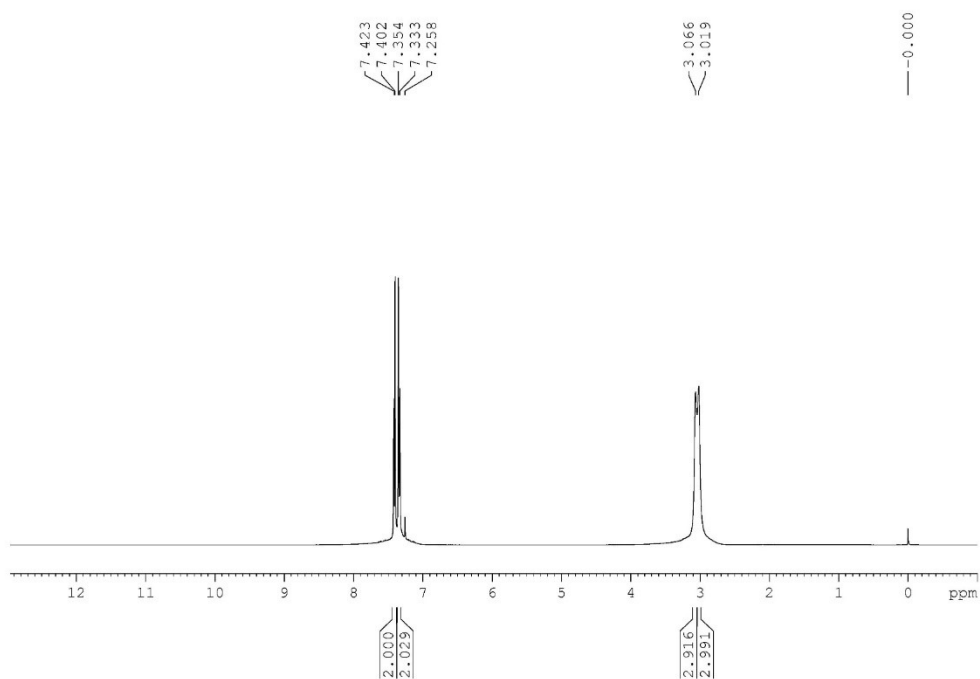
Spectrum Plot Report



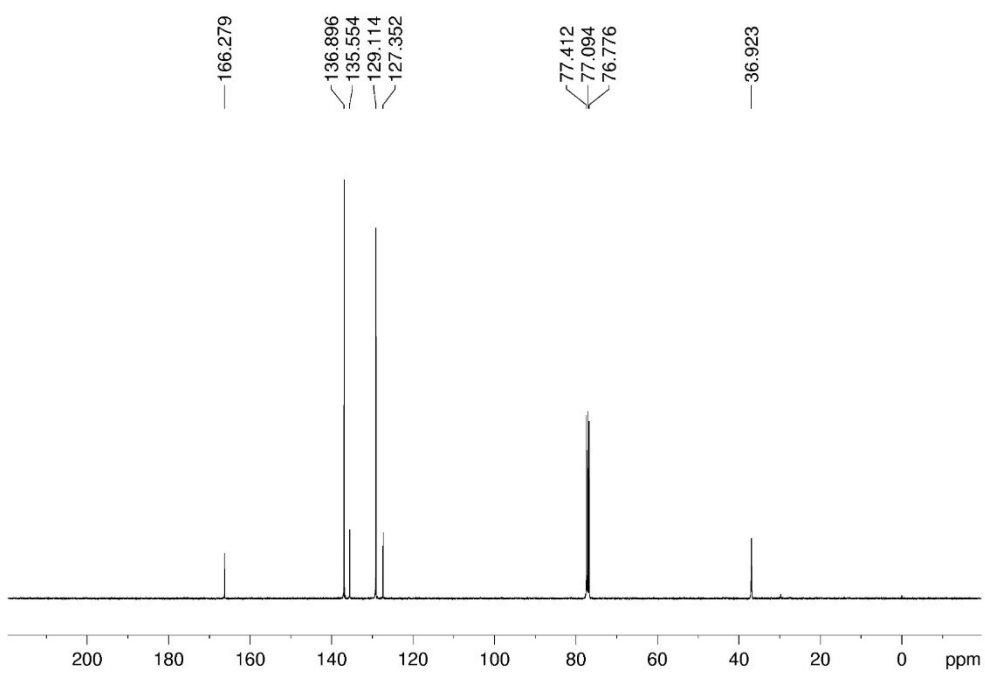
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HRMS spectrum of compound **3k**



^1H NMR spectrum of compound **31**

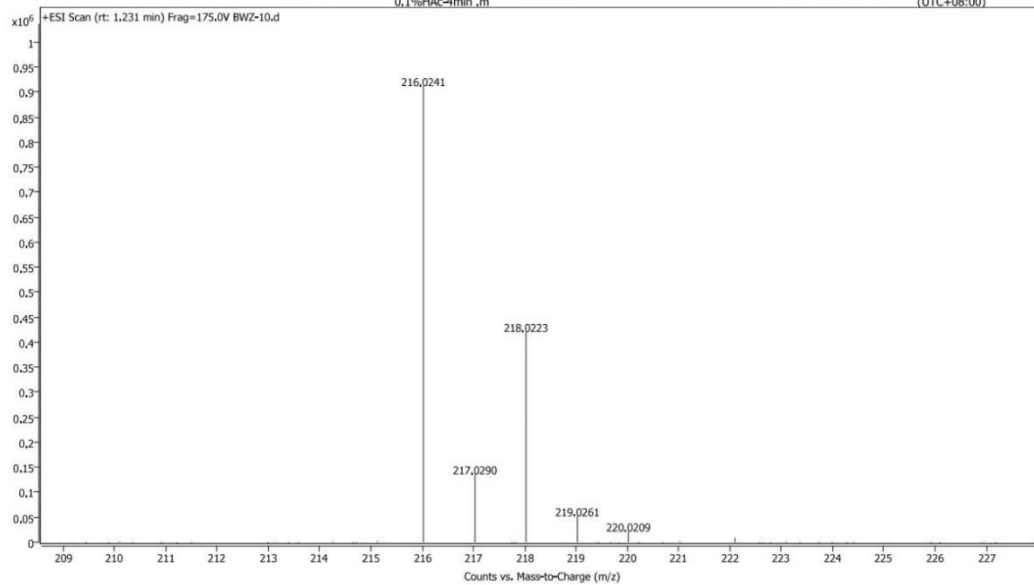


^{13}C NMR spectrum of compound **31**

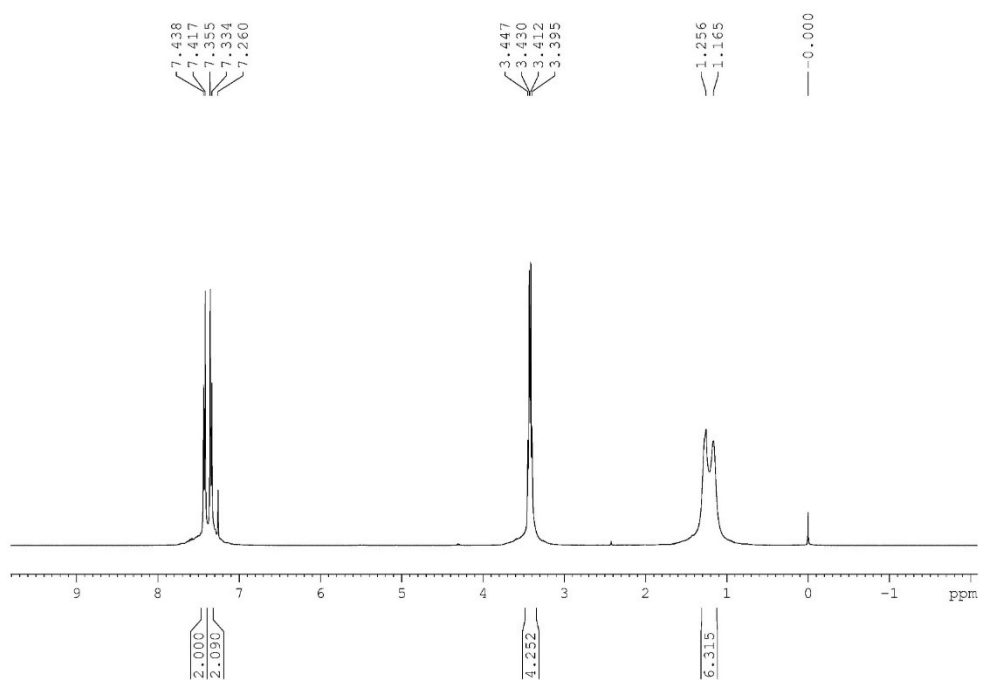
Spectrum Plot Report



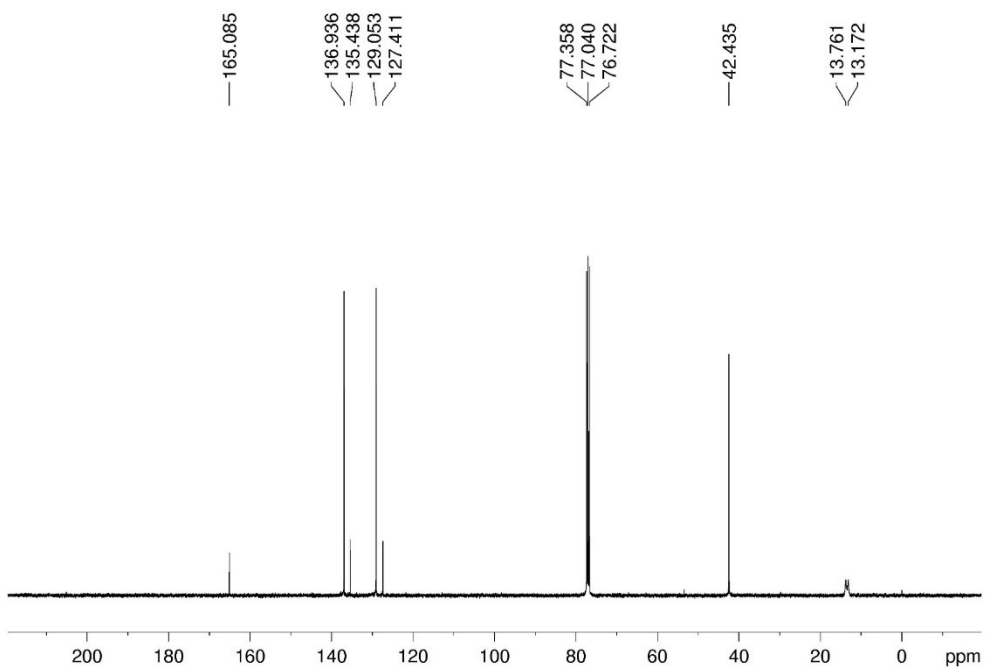
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			BWZ20210707-0,1%HAc-4min.m		7/7/2021 2:17:17 PM (UTC+08:00)



HRMS spectrum of compound **31**



^1H NMR spectrum of compound **3m**

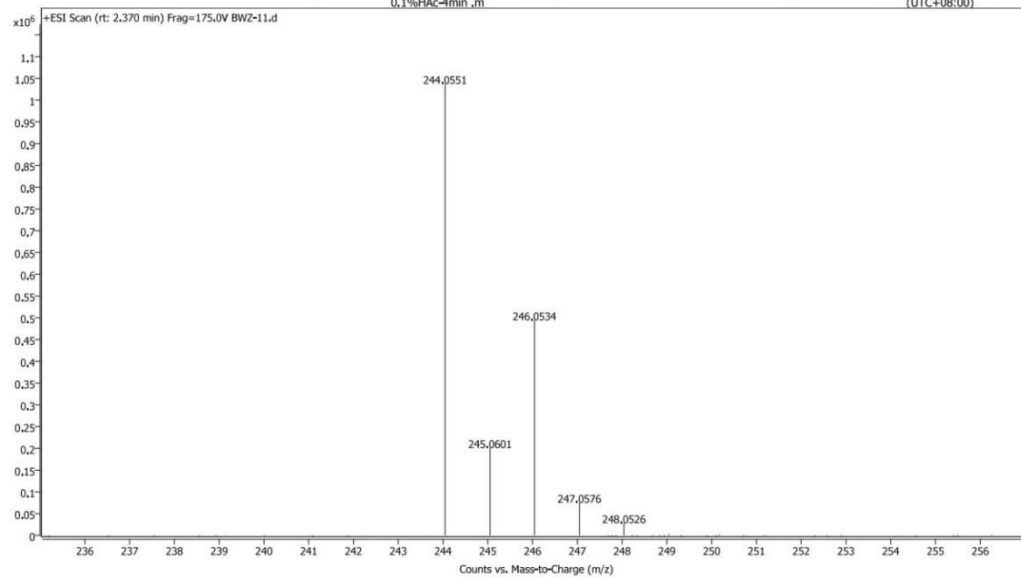


^{13}C NMR spectrum of compound **3m**

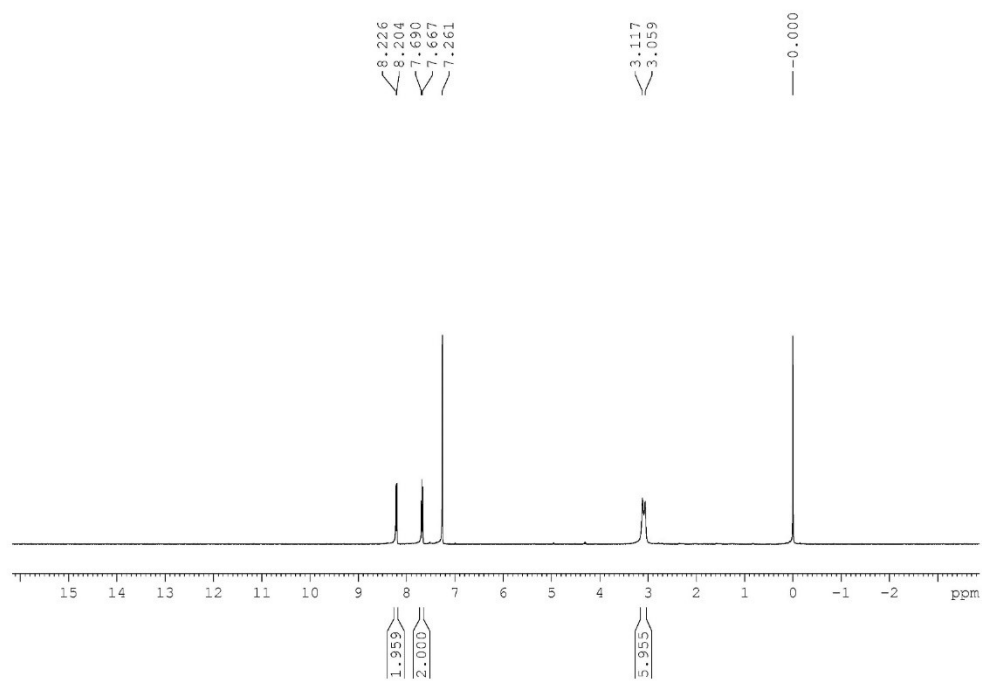
Spectrum Plot Report



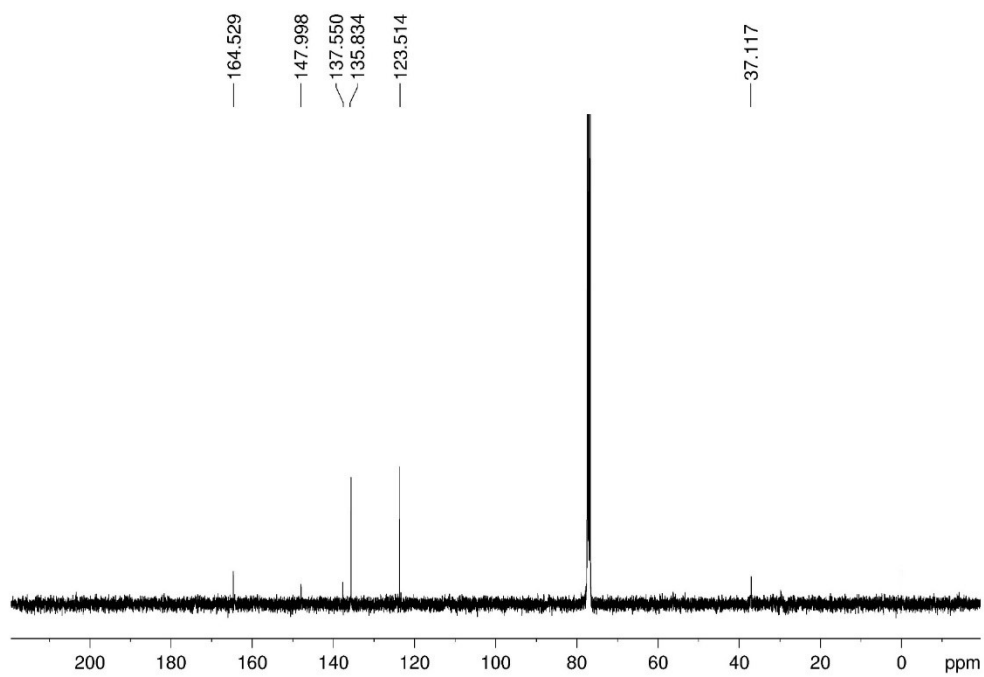
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HRMS spectrum of
compound **3m**



^1H NMR spectrum of compound **3n**

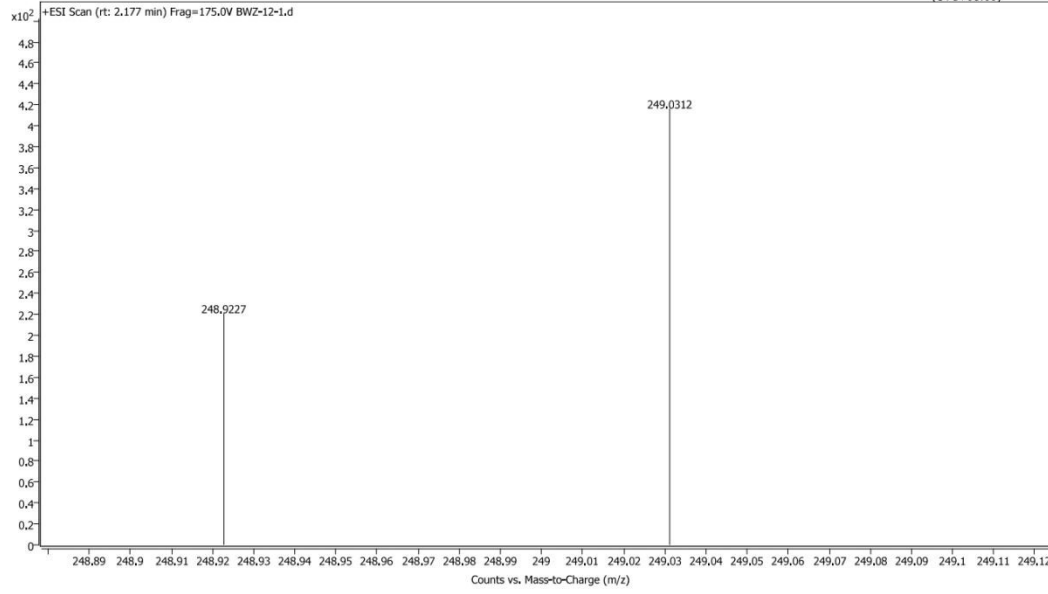


^{13}C NMR spectrum of compound **3n**

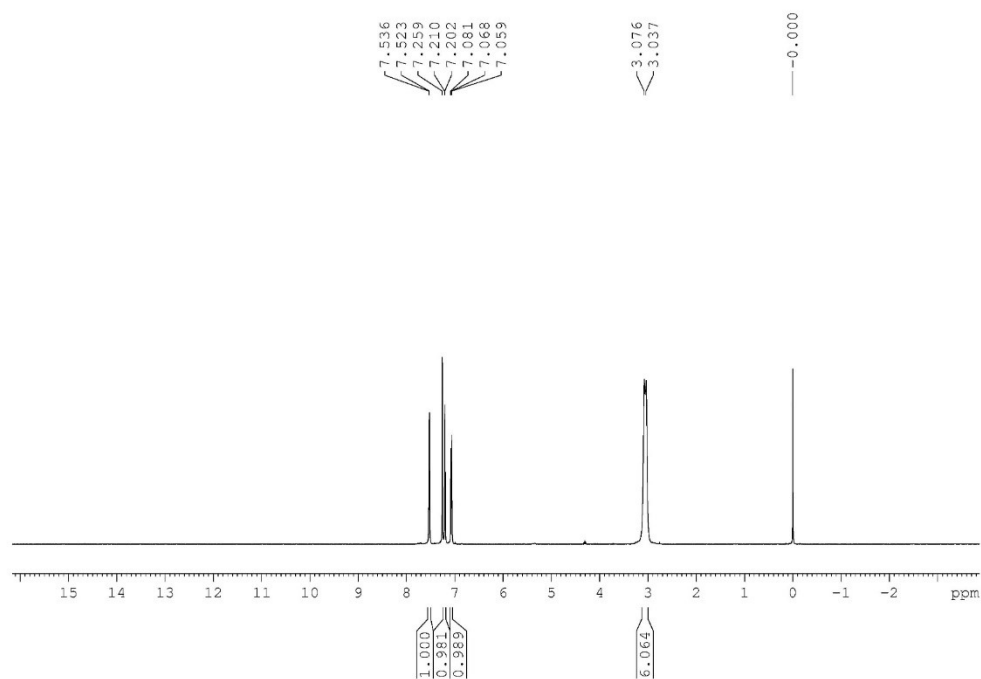
Spectrum Plot Report



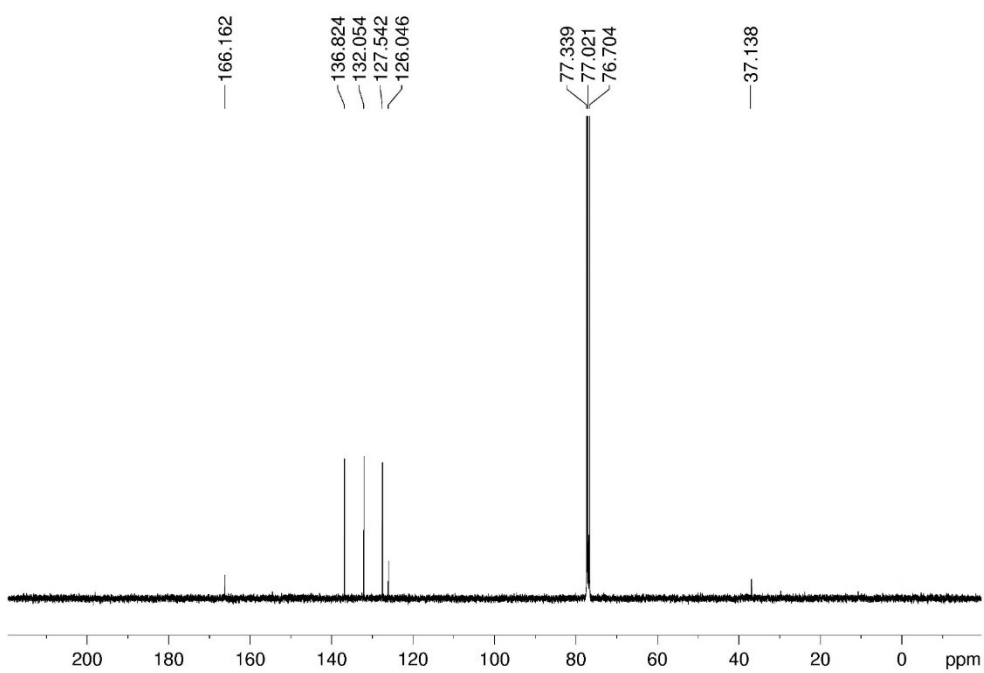
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HRMS spectrum of compound **3n**



^1H NMR spectrum of compound **30**

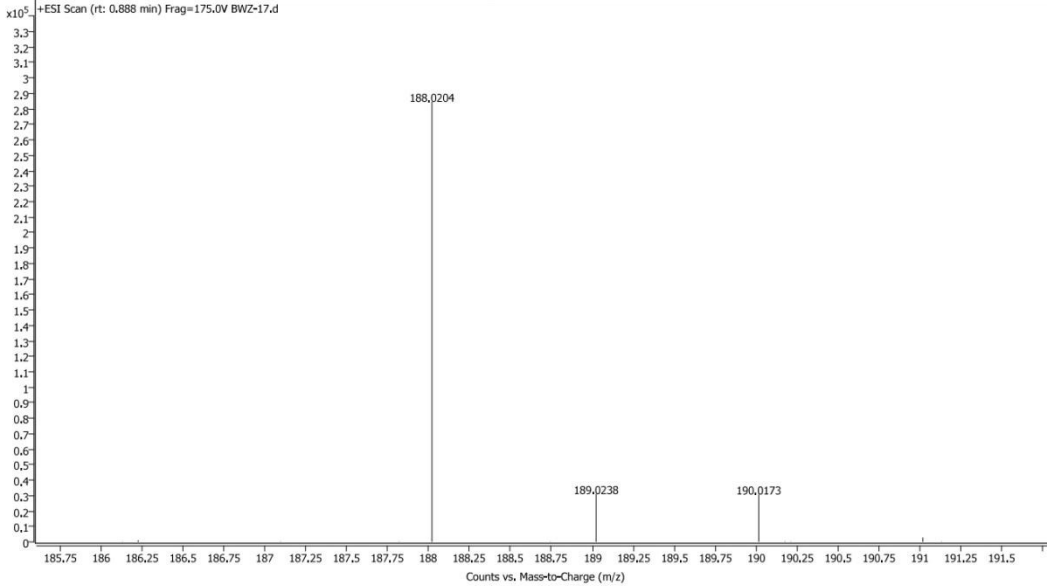


^{13}C NMR spectrum of compound **30**

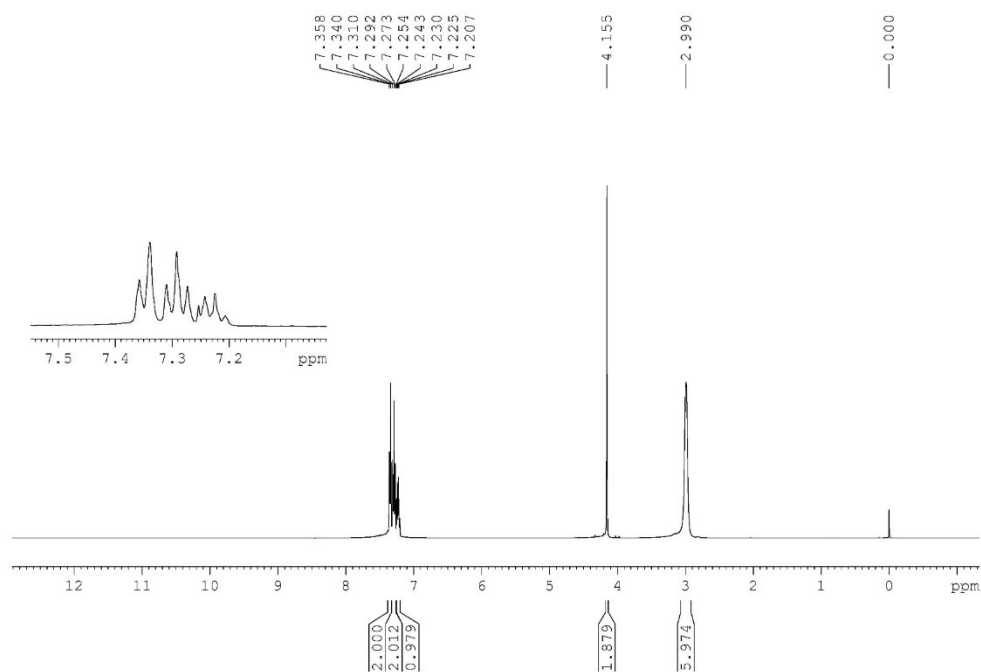
Spectrum Plot Report



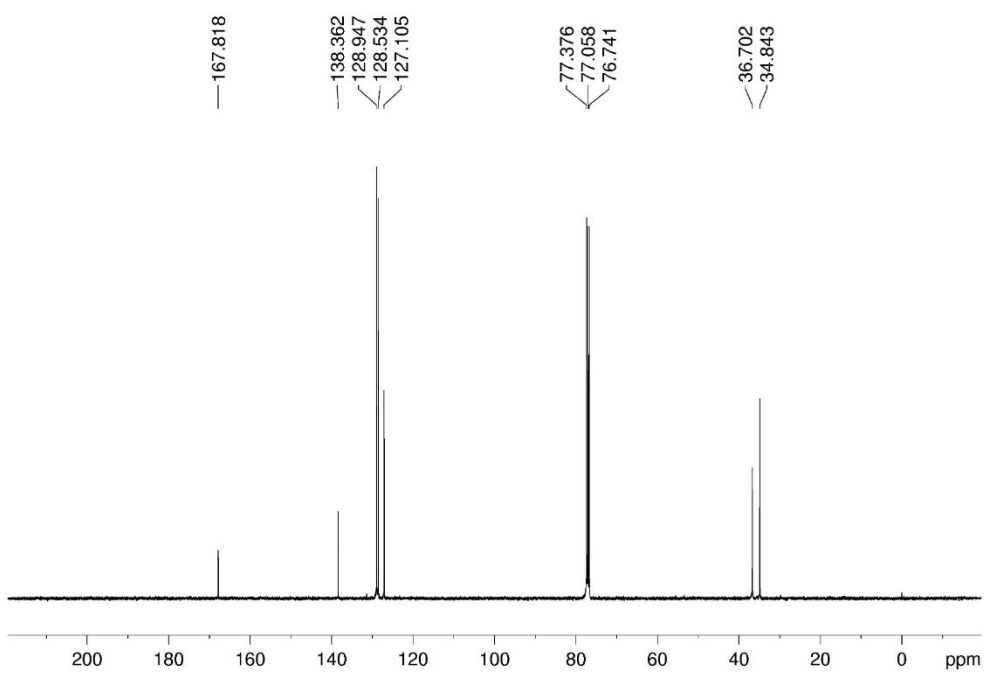
Name	BWZ-17	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-17.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707-0.1%tAc-4min.m		7/7/2021 2:57:15 PM (UTC+08:00)



HRMS spectrum of compound **3o**



^1H NMR spectrum of compound **3p**

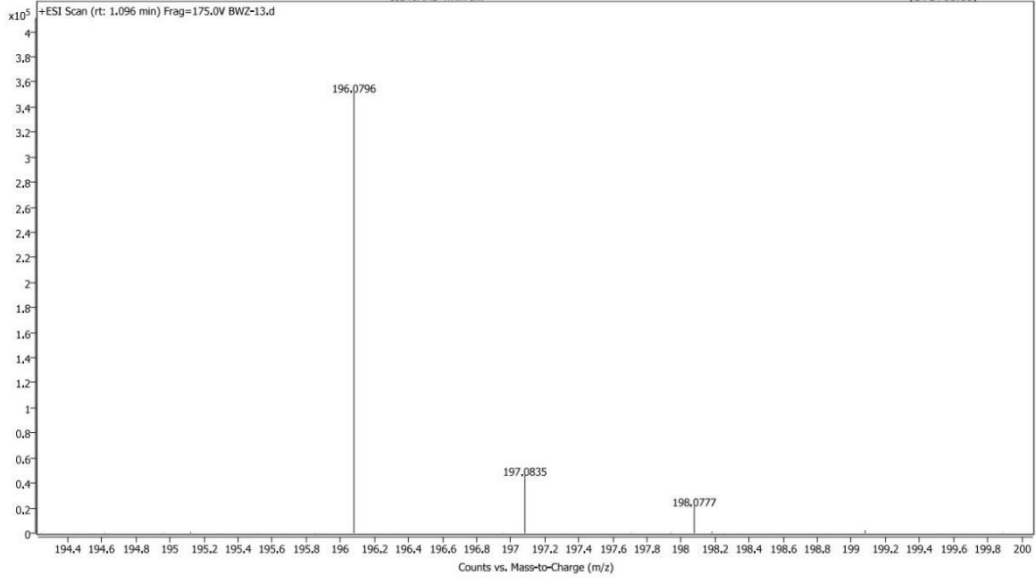


^{13}C NMR spectrum of compound **3p**

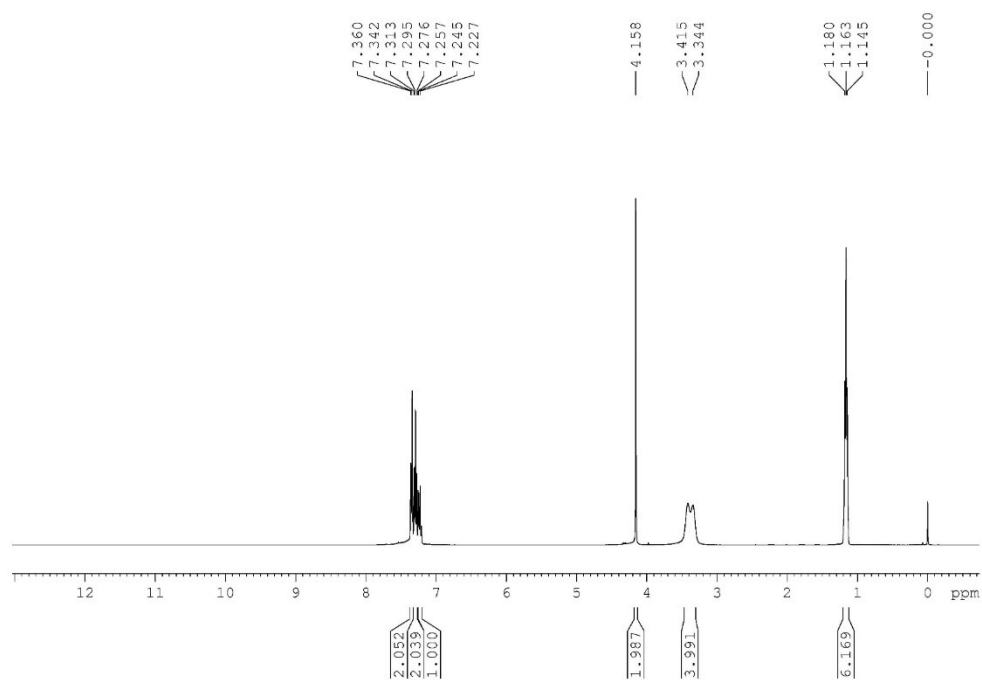
Spectrum Plot Report



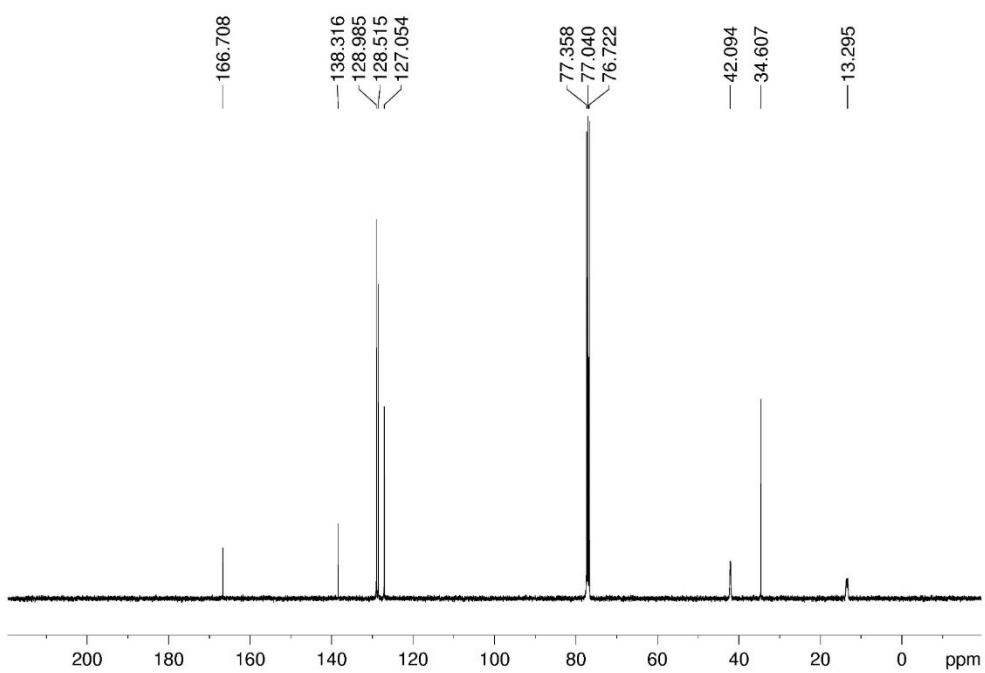
Name	BWZ-13	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-13.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707-0.1% <i>HAc</i> -4min.m		7/7/2021 2:36:08 PM (UTC+08:00)



HRMS spectrum of compound **3p**



^1H NMR spectrum of compound **3q**

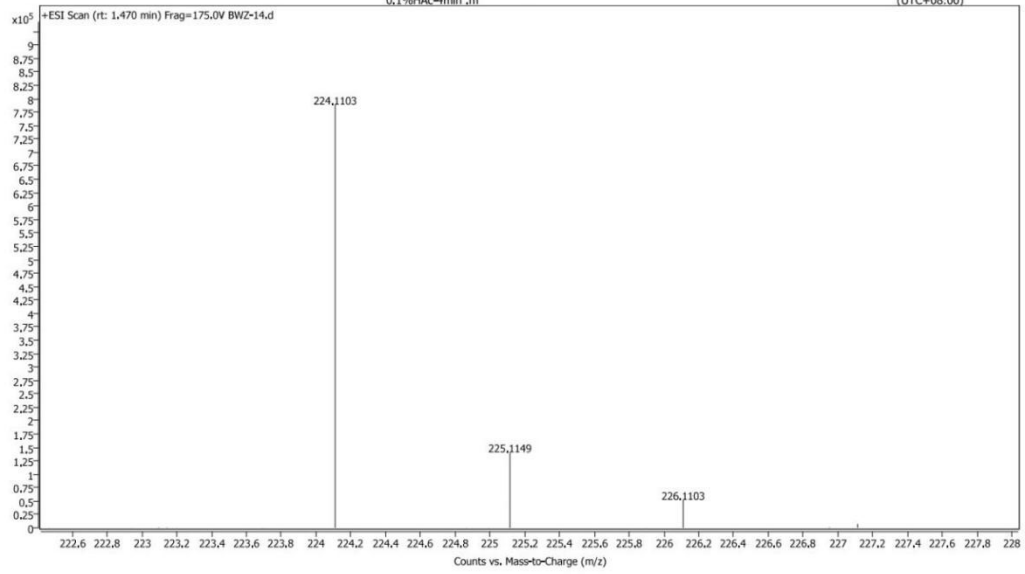


^{13}C NMR spectrum of compound **3q**

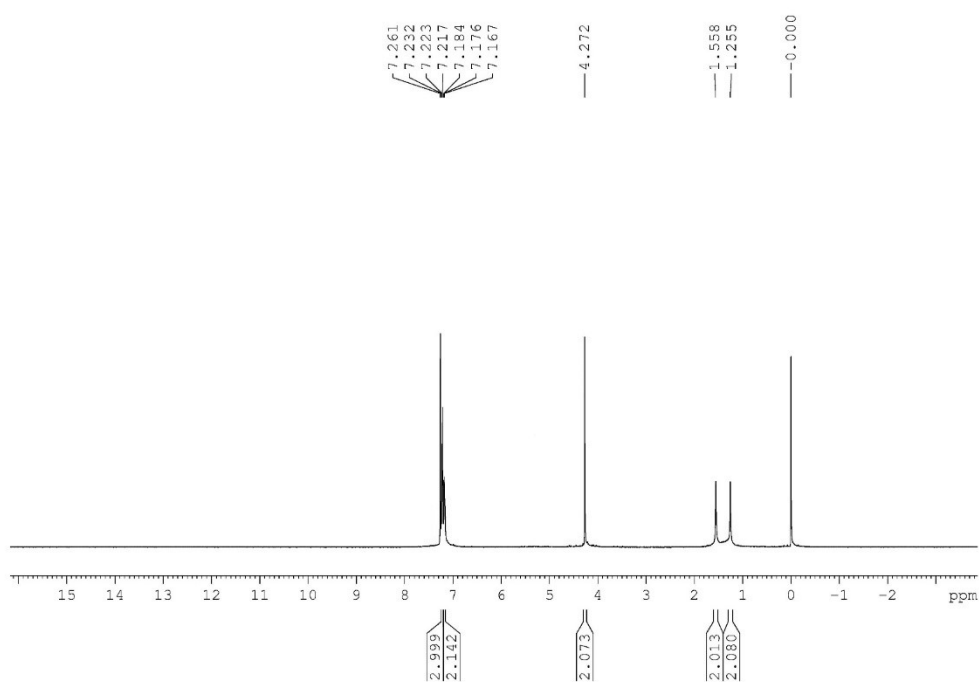
Spectrum Plot Report



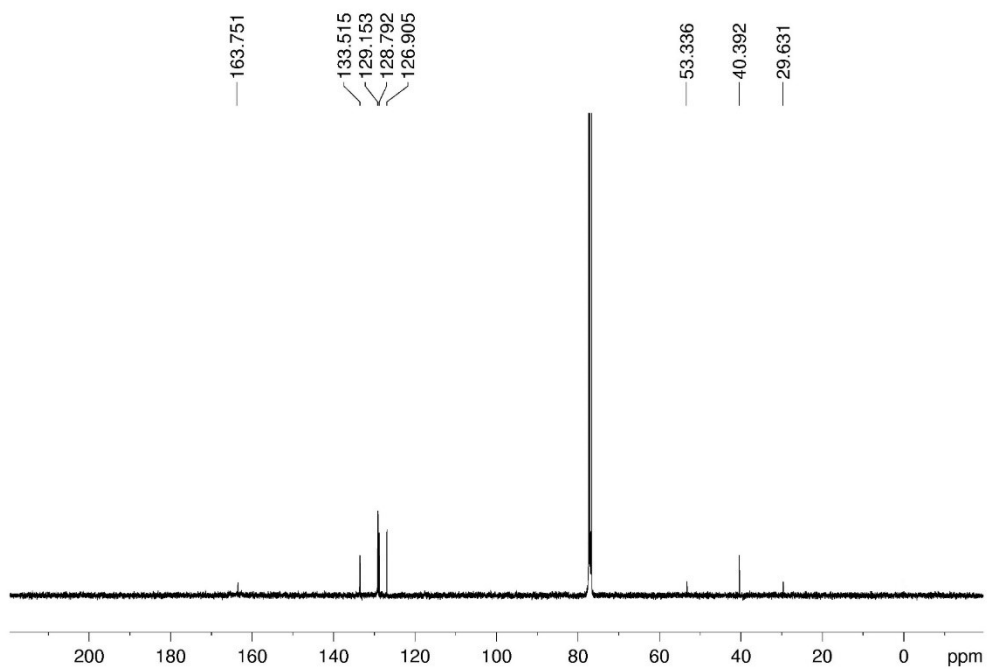
Name	BWZ-14	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-14.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707-0.1%tAC-4min.m		7/7/2021 2:41:38 PM (UTC+08:00)



HRMS spectrum of compound **3q**



¹H NMR spectrum of compound **3r**

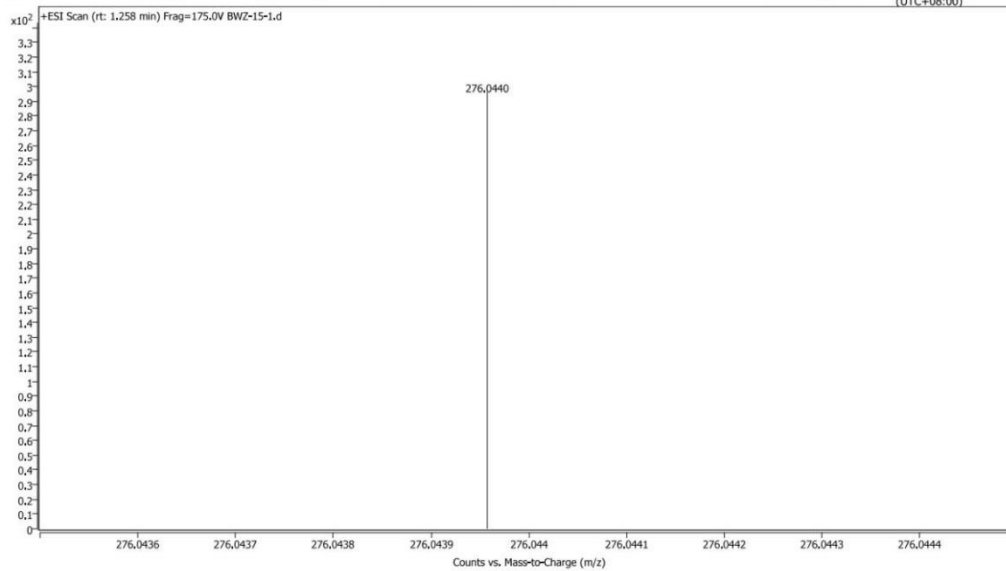


¹³C NMR spectrum of compound **3r**

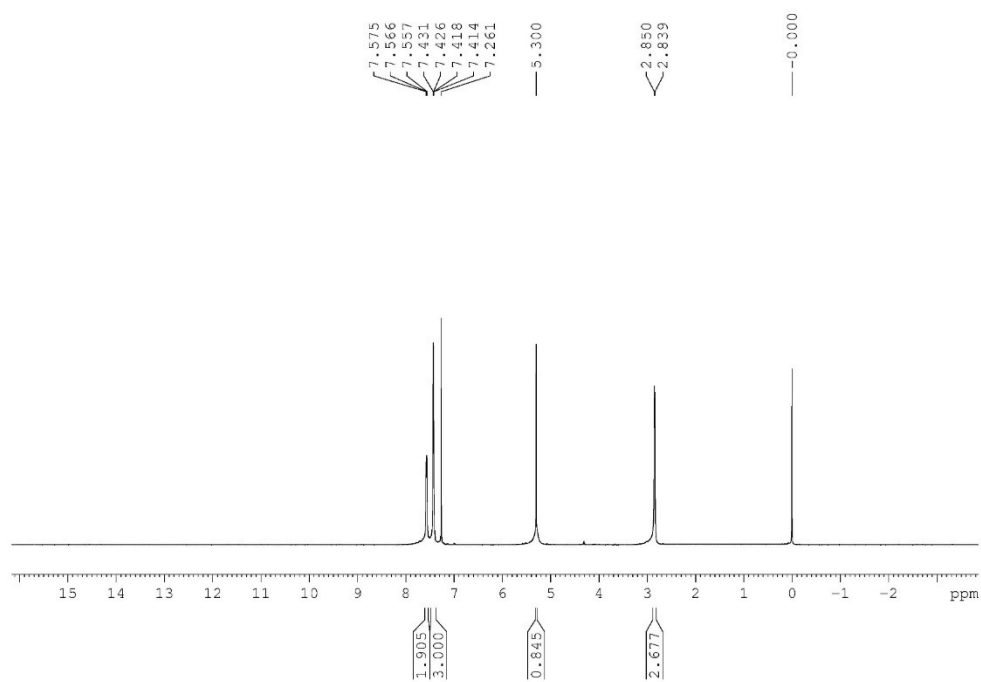
Spectrum Plot Report



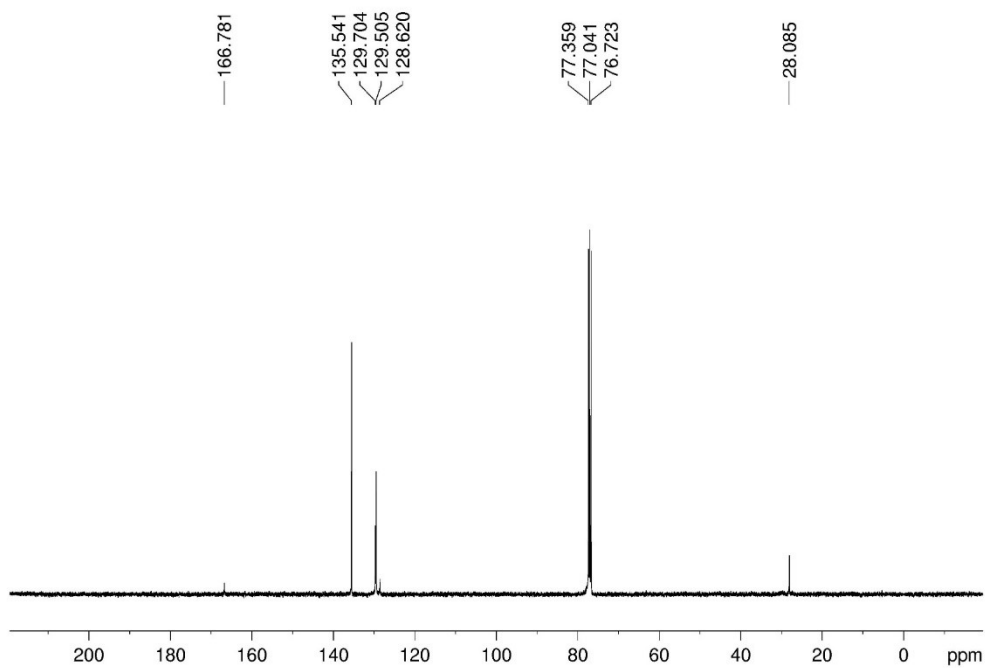
Name	BWZ-15-1	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-15-1.d	Method (Acq)	LZH20210707.m	Comment	Acq. Time (Local)
					7/8/2021 10:12:20 AM (UTC+08:00)



HRMS spectrum of compound **3r**



^1H NMR spectrum of compound **5a**

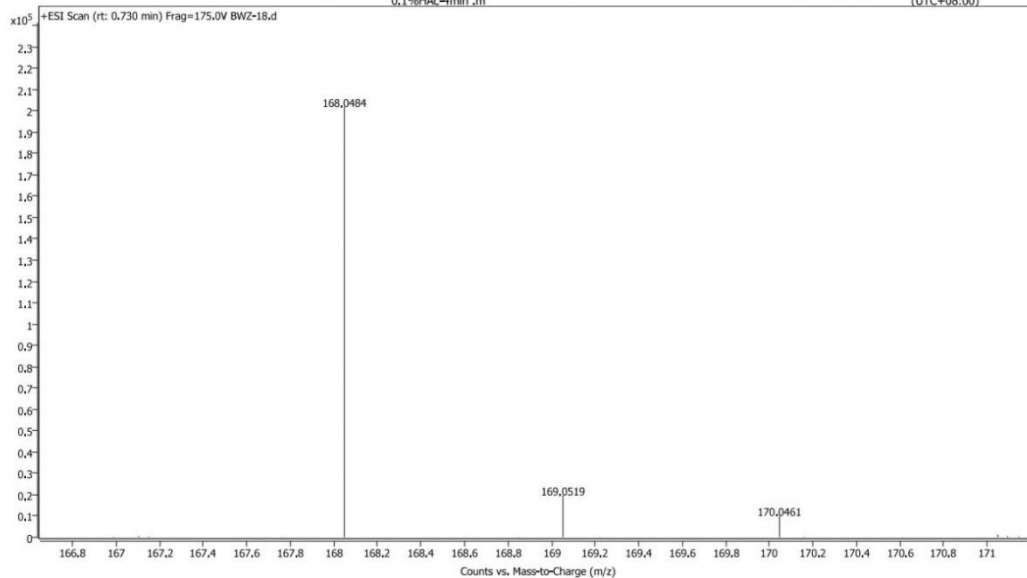


^{13}C NMR spectrum of compound **5a**

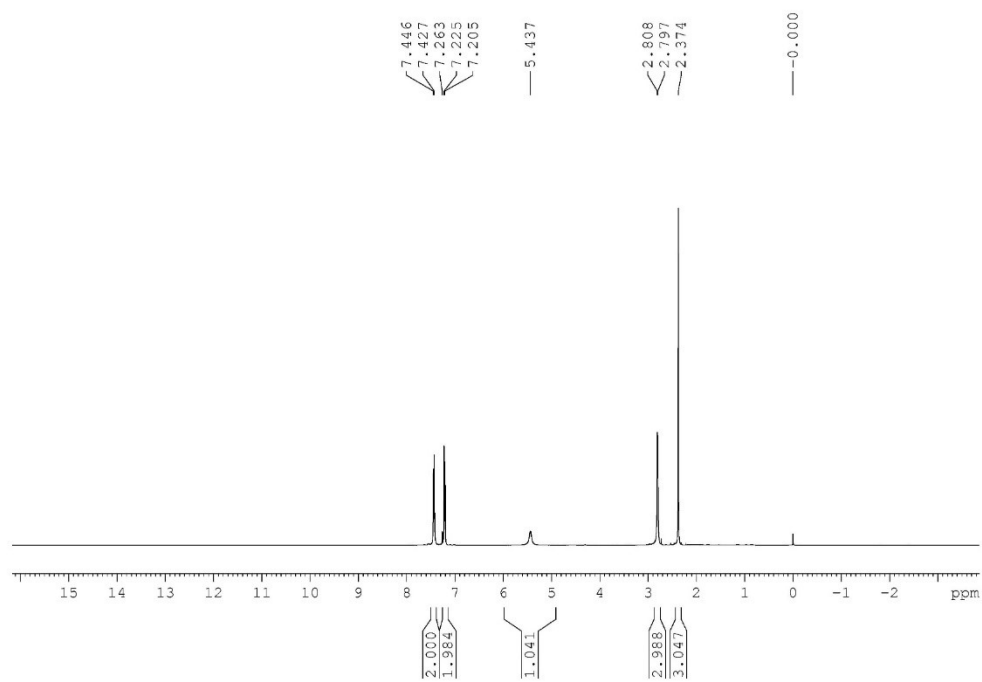
Spectrum Plot Report



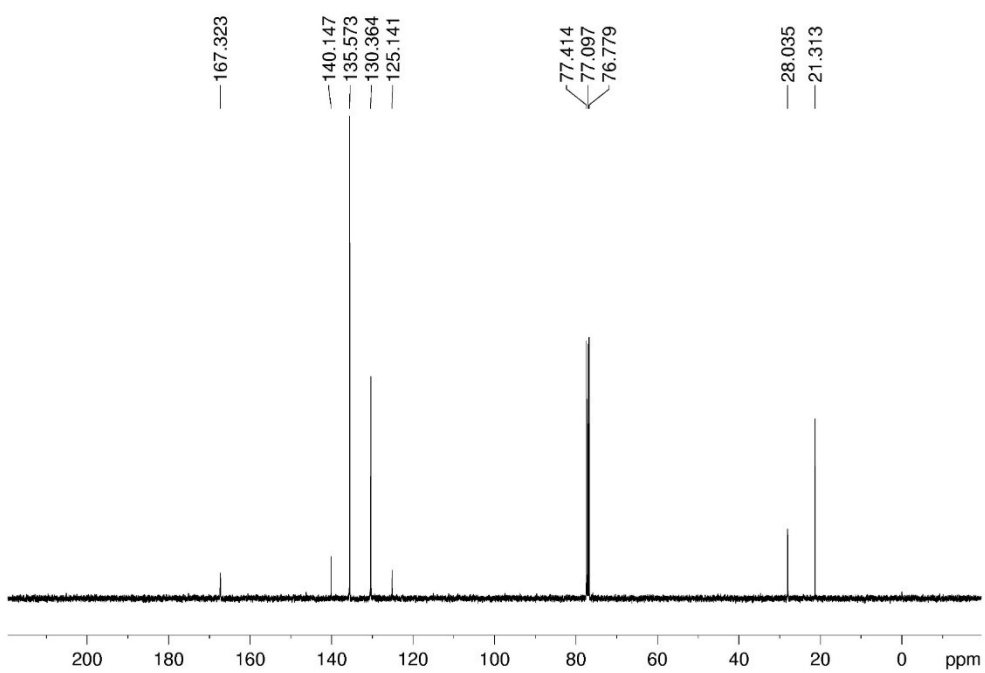
Name	BWZ-18	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-18.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707- 0.15eHAc-1min.m		7/7/2021 3:07:58 PM (UTC+08:00)



HRMS spectrum of compound **5a**



^1H NMR spectrum of compound **5b**

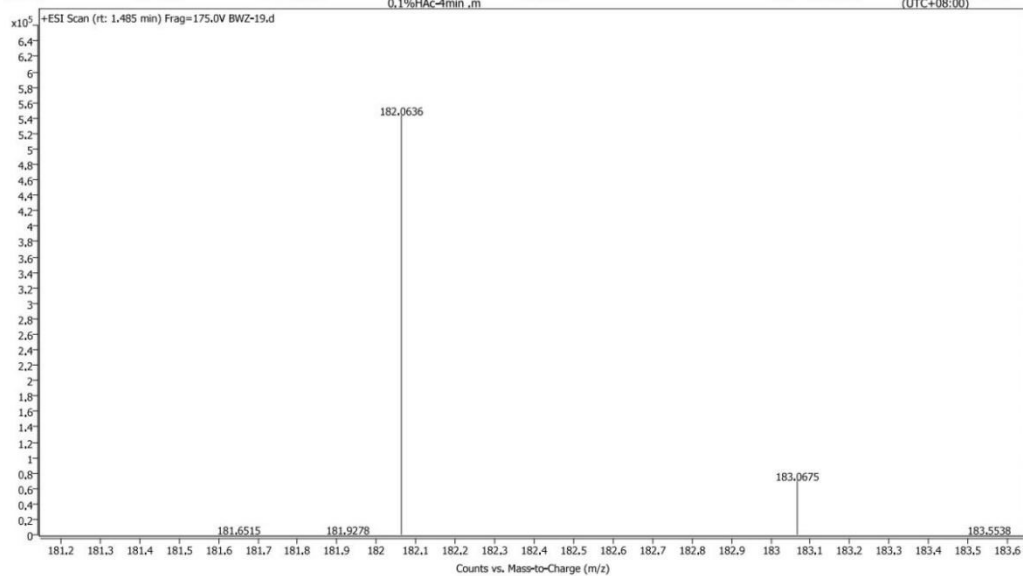


^{13}C NMR spectrum of compound **5b**

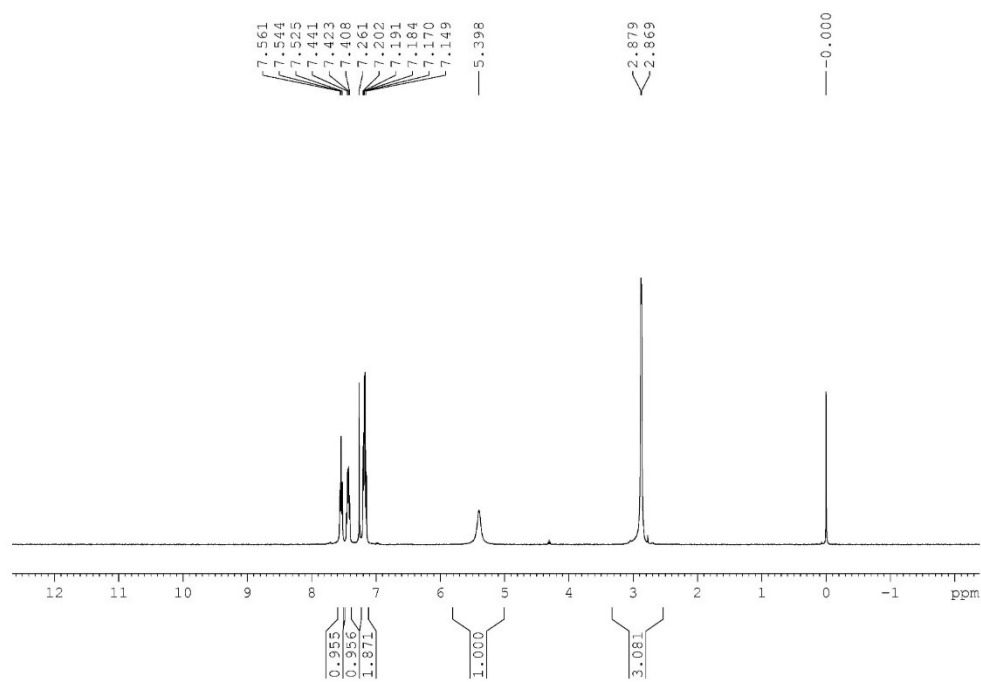
Spectrum Plot Report



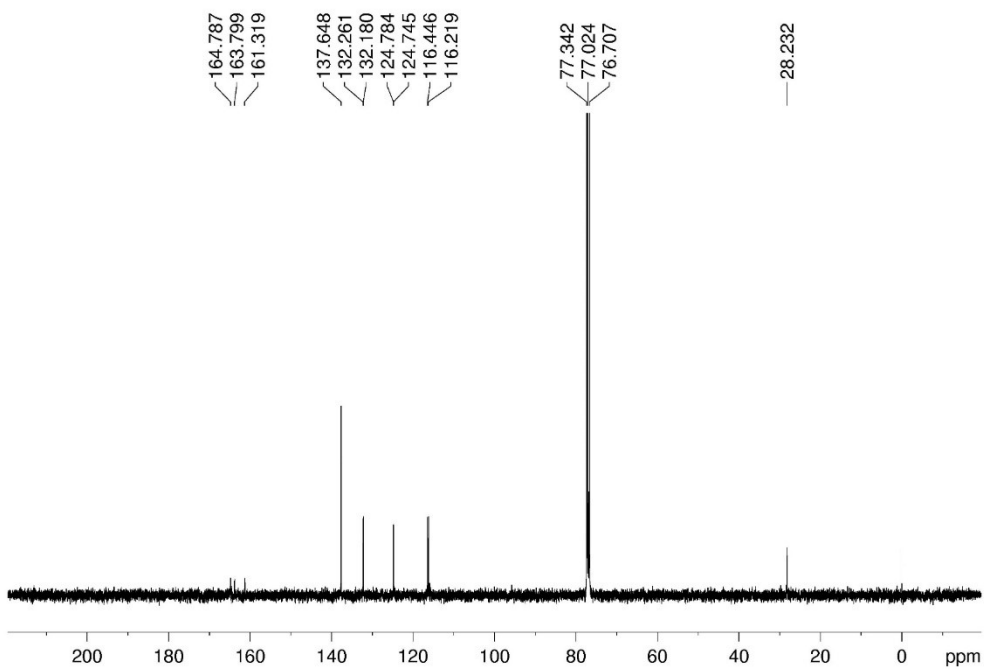
Name	BWZ-19	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (µl)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-19.d	Method (Acq)	Comment		Acq. Time (Local)
		BWZ20210707-0,1% <i>HAc</i> -1min.m			7/7/2021 3:16:46 PM (UTC+08:00)



HRMS spectrum of compound **5b**



^1H NMR spectrum of compound **5c**

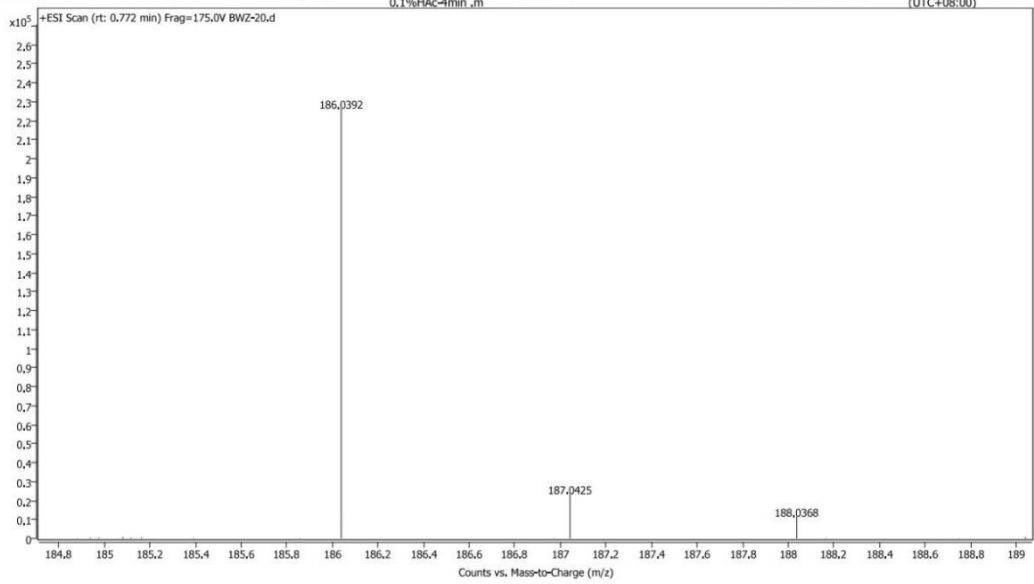


^{13}C NMR spectrum of compound **5c**

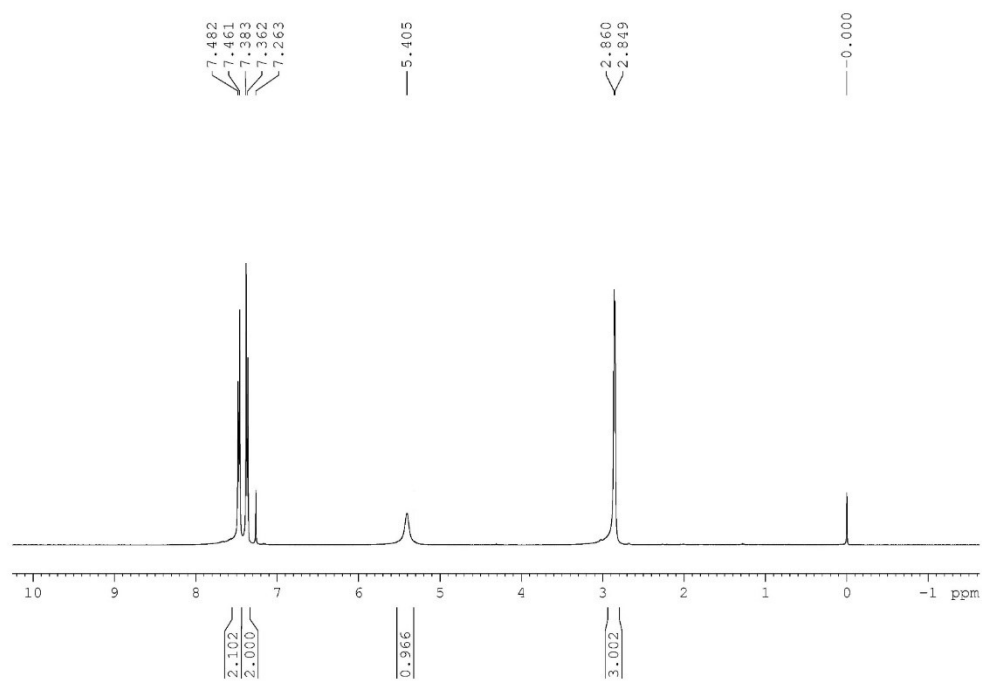
Spectrum Plot Report



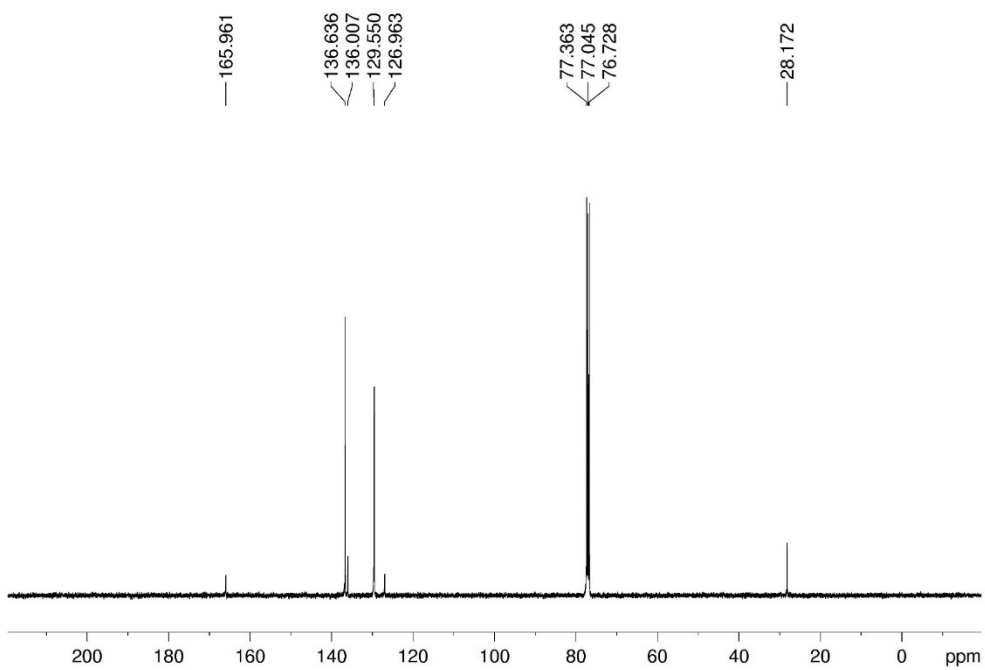
Name	BWZ-20	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-20.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707- 0.1% ¹⁴ Ac-tmin .m		7/7/2021 3:24:40 PM (UTC+08:00)



HRMS spectrum of compound **5c**



^1H NMR spectrum of compound **5d**

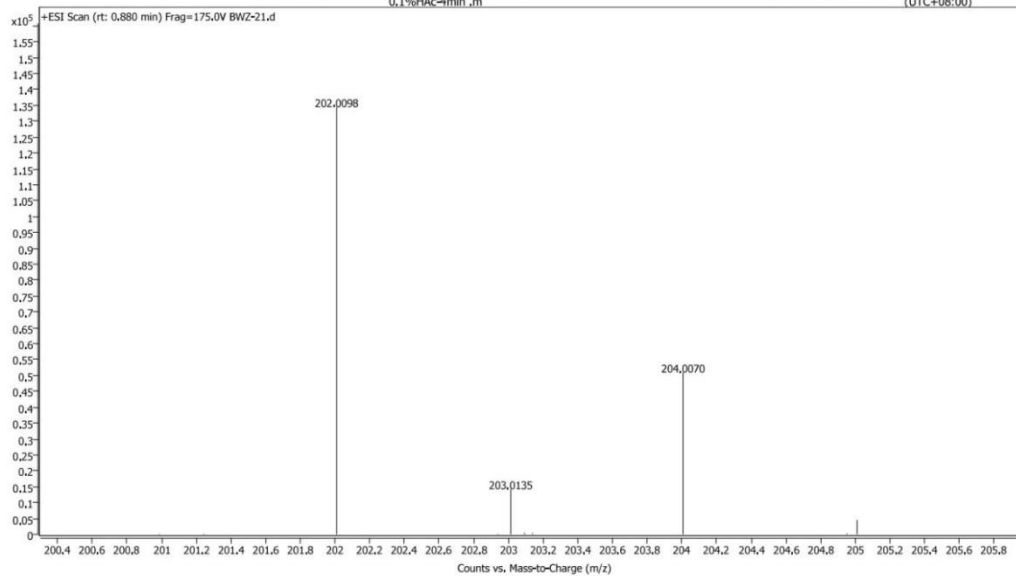


^{13}C NMR spectrum of compound **5d**

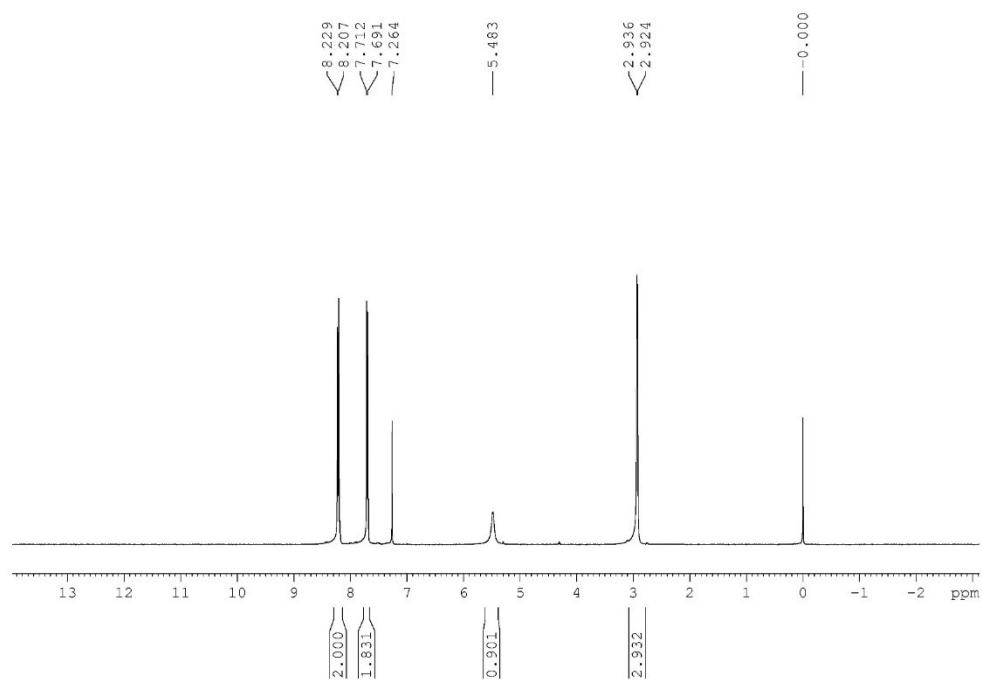
Spectrum Plot Report



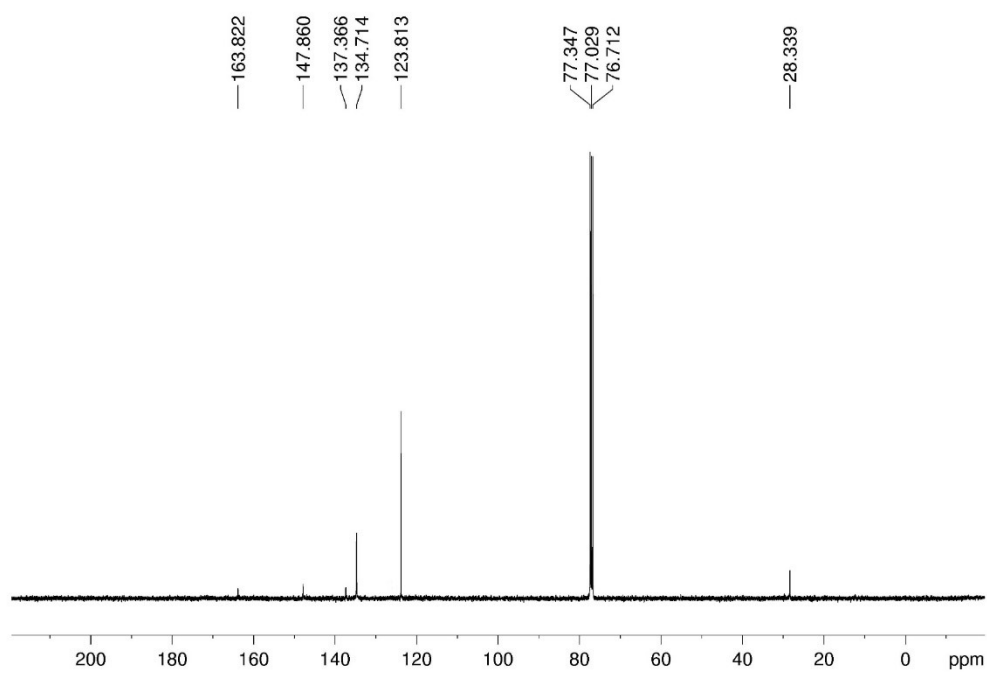
Name	BWZ-21	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (µl)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-21.d	Method (Acq)	Comment		Acq. Time (Local)
		BWZ20210707-0.1% <i>i</i> HAc- <i>t</i> min .m			7/7/2021 3:30:09 PM (UTC+08:00)



HRMS spectrum of compound **5d**



^1H NMR spectrum of compound **5e**

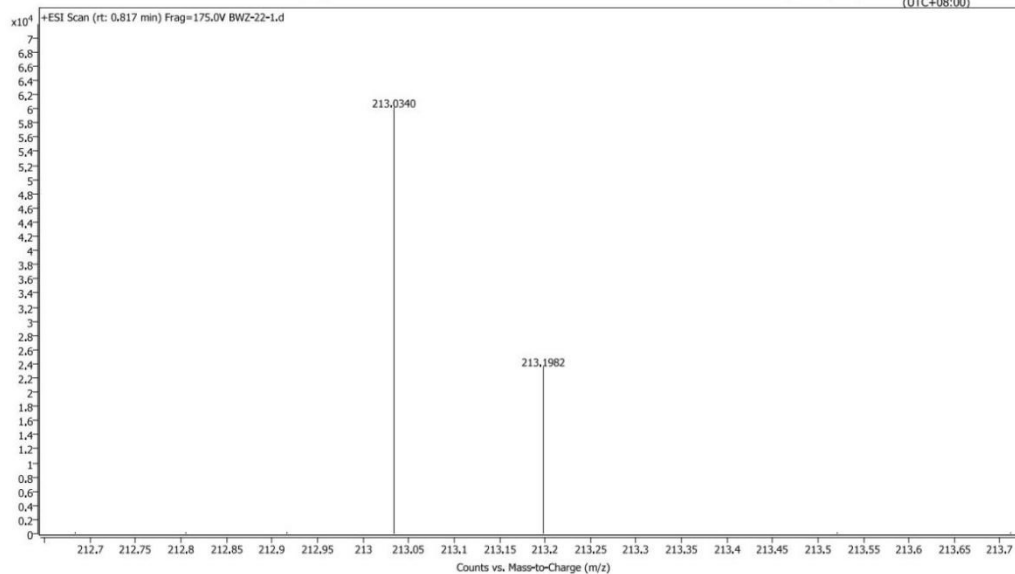


^{13}C NMR spectrum of compound **5e**

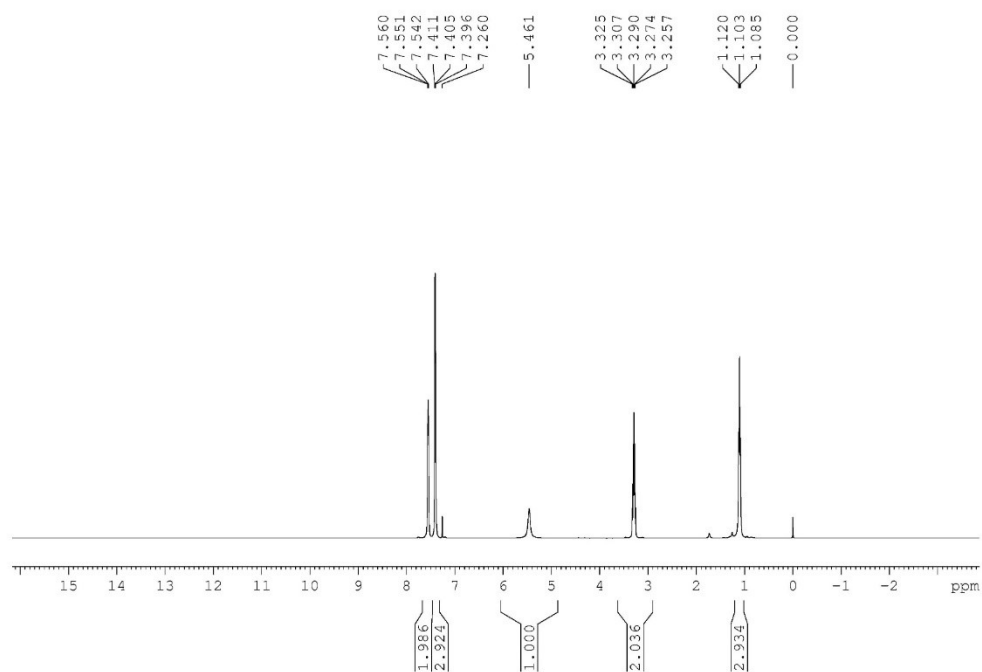
Spectrum Plot Report



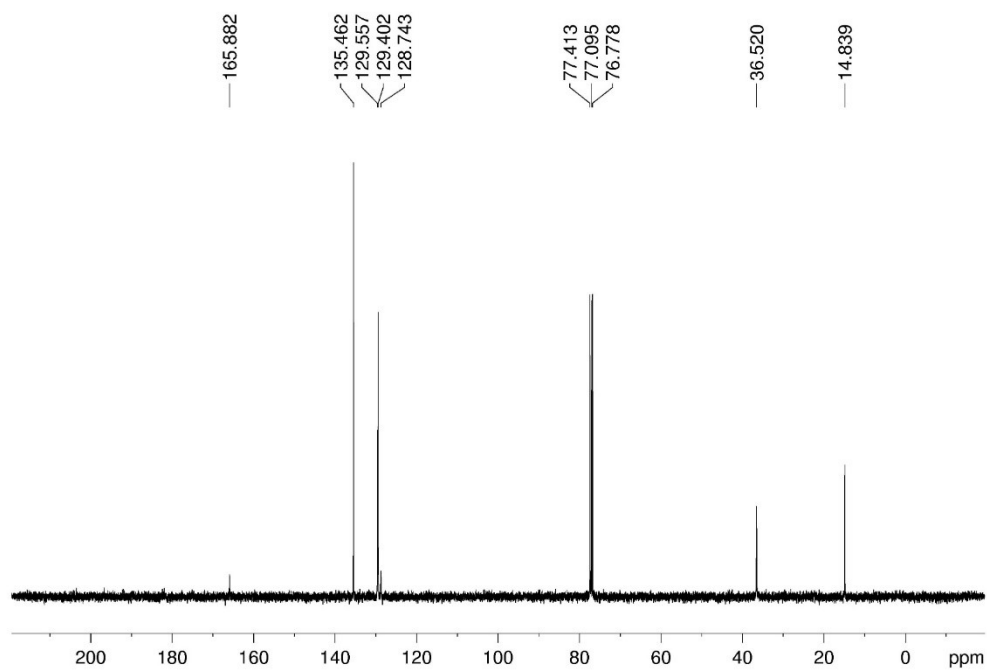
Name	BWZ-22-1	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (µl)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-22-1.d	Method (Acq)	LZH20210707.m	Comment	Acq. Time (Local)
					7/8/2021 10:19:16 AM (UTC+08:00)



HRMS spectrum of compound **5e**



^1H NMR spectrum of compound **5f**

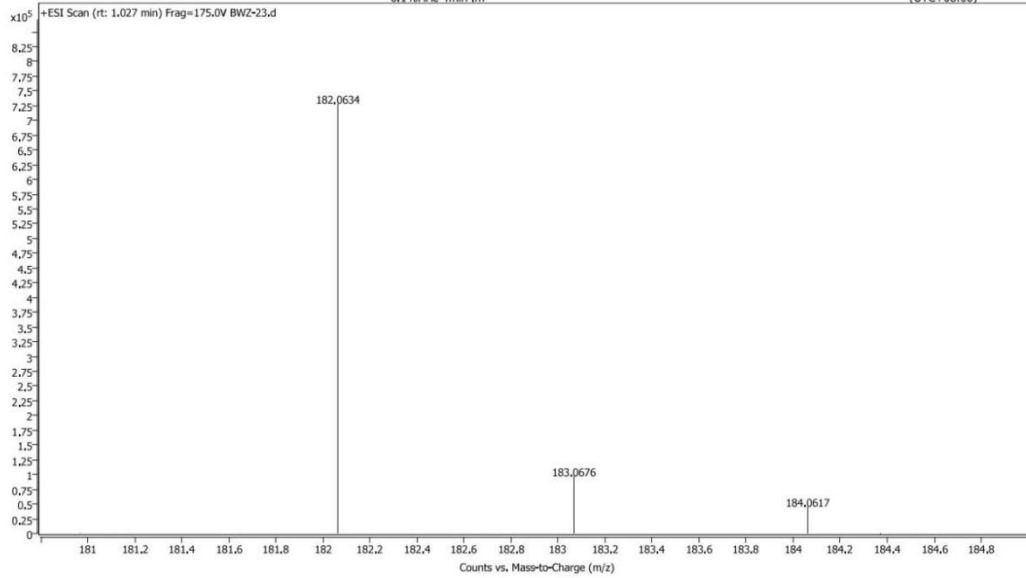


^{13}C NMR spectrum of compound **5f**

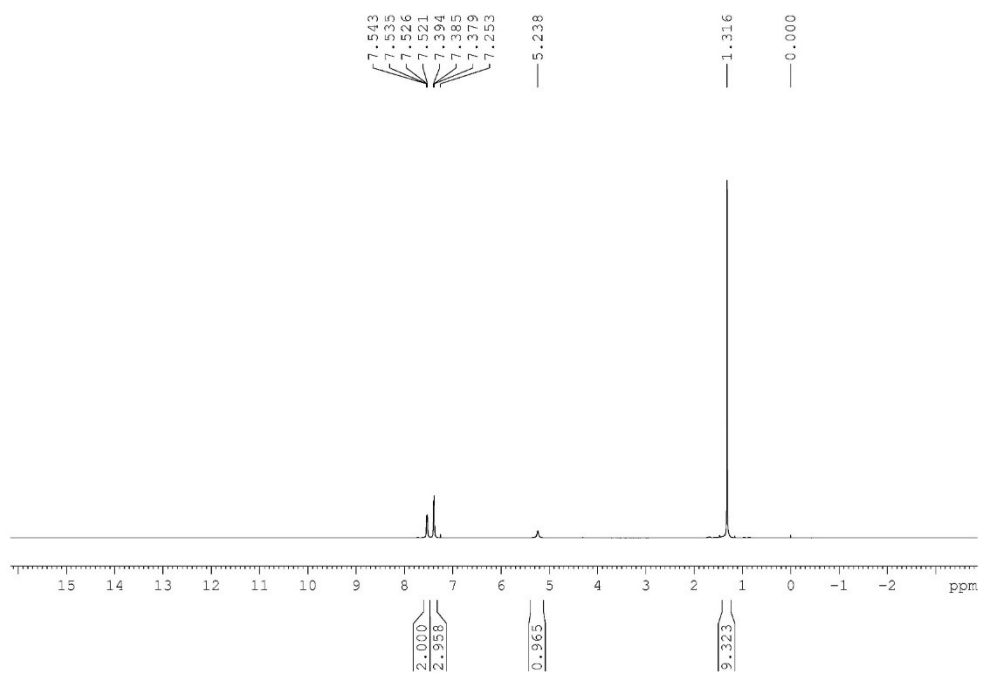
Spectrum Plot Report



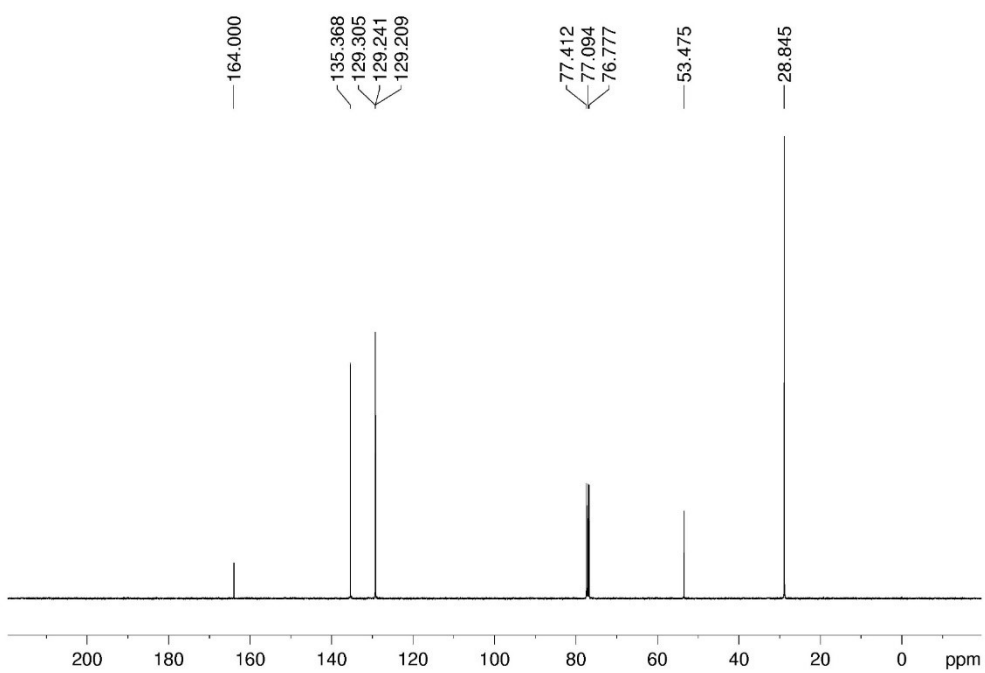
Name	BWZ-23	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (µl)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-23.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707-0.1% <i>HAc</i> -4min.m		7/7/2021 3:43:15 PM (UTC+08:00)



HRMS spectrum of compound **5f**



^1H NMR spectrum of compound **5g**

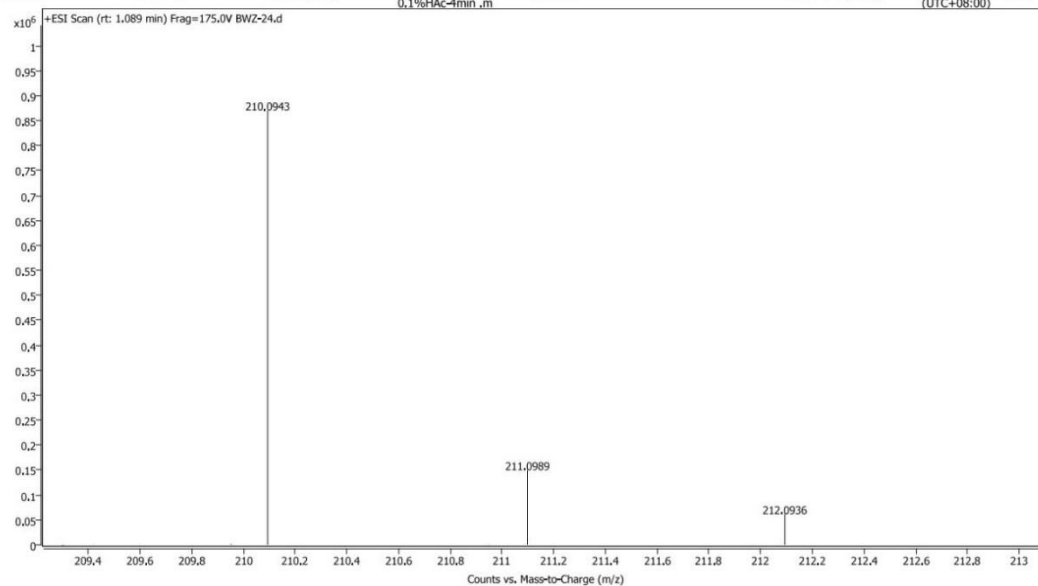


^{13}C NMR spectrum of compound **5g**

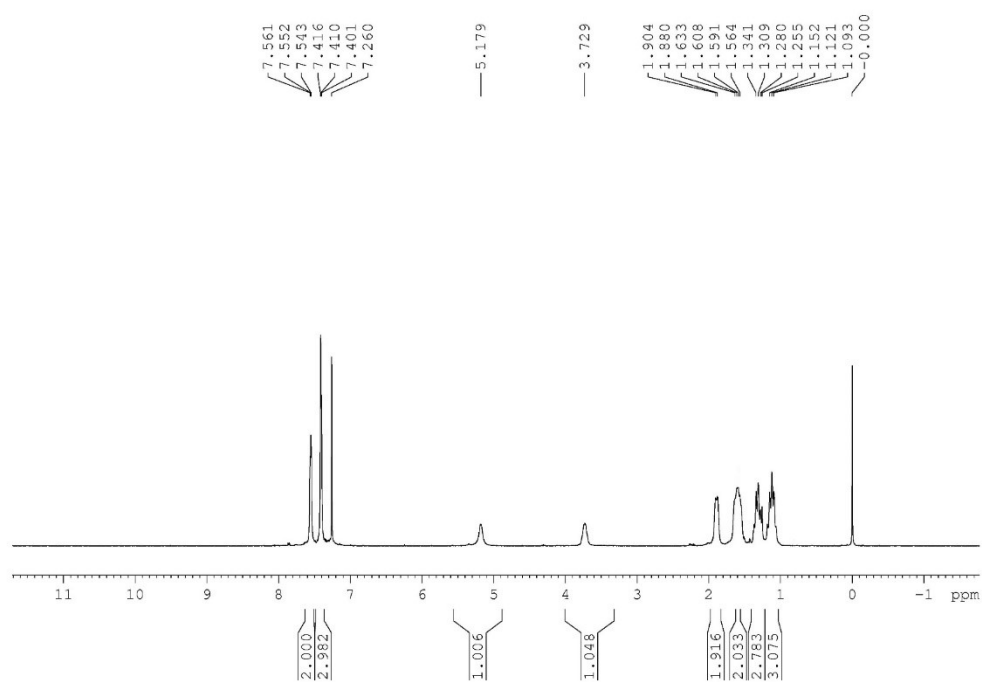
Spectrum Plot Report



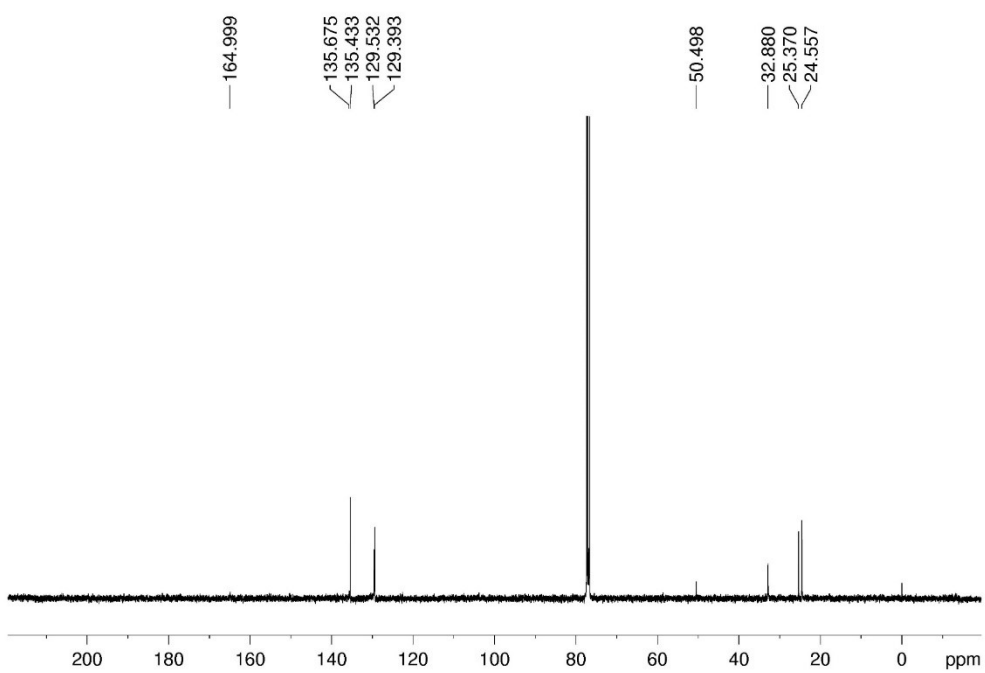
Name	BWZ-24	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-24.d	Method (Acq)	Comment	Acq. Time (Local)	7/7/2021 3:51:54 PM (UTC+08:00)



HRMS spectrum of compound **5g**



^1H NMR spectrum of compound **5h**

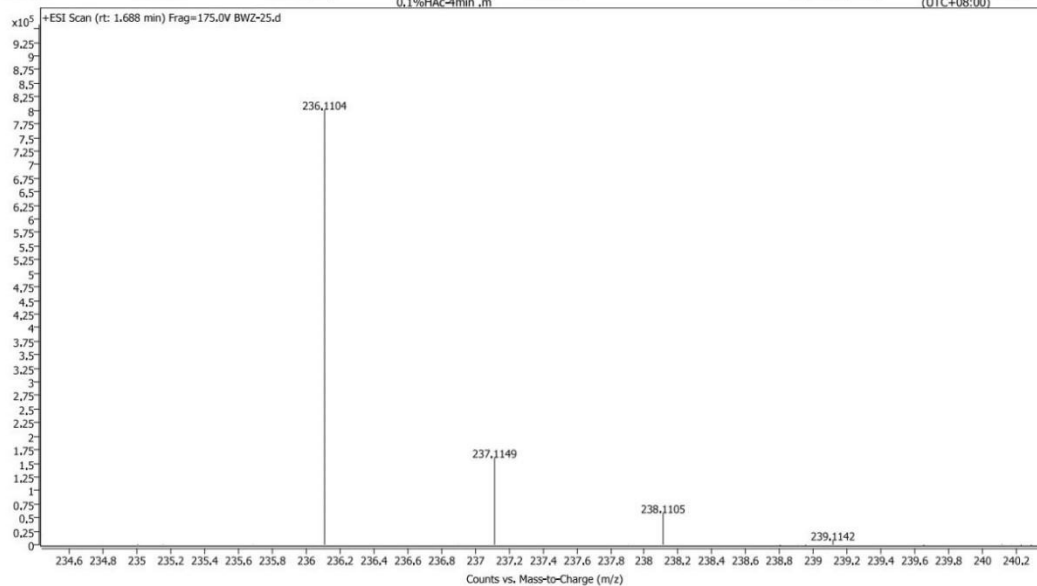


^{13}C NMR spectrum of compound **5h**

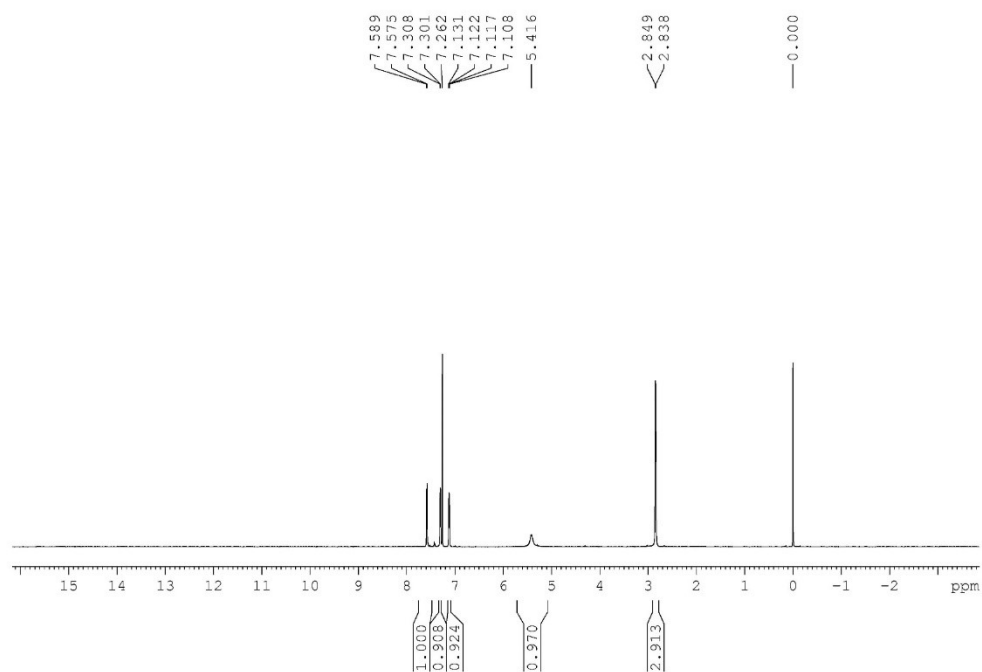
Spectrum Plot Report



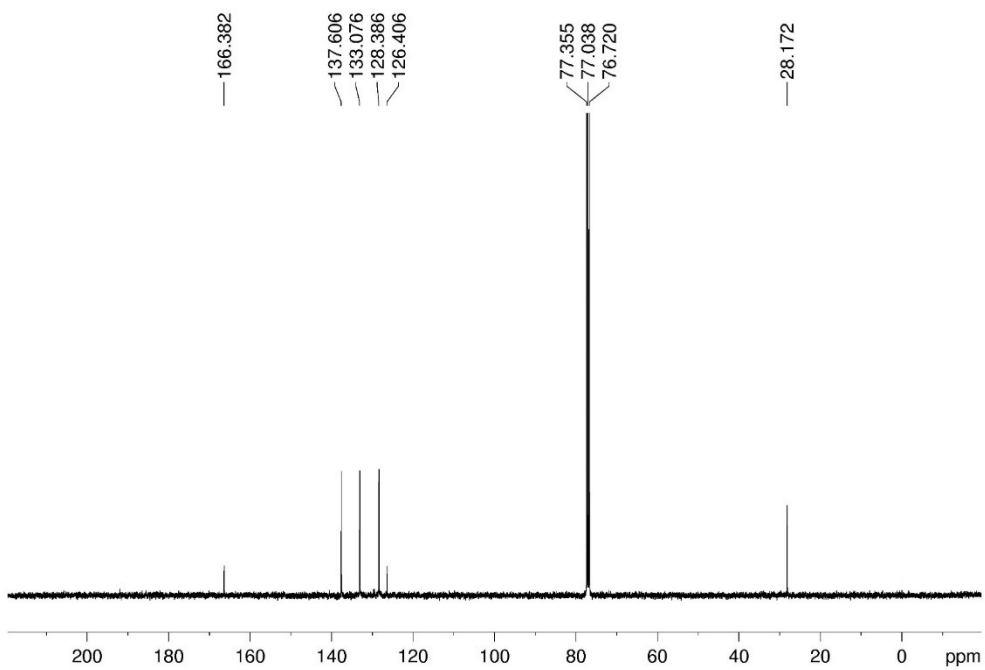
Name	BWZ-25	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (µl)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-25.d	Method (Acq)	Comment		Acq. Time (Local)
			BWZ20210707-0.1%IAC-1min.m		7/7/2021 3:57:05 PM (UTC+08:00)



HRMS spectrum of compound **5h**



^1H NMR spectrum of compound **5i**

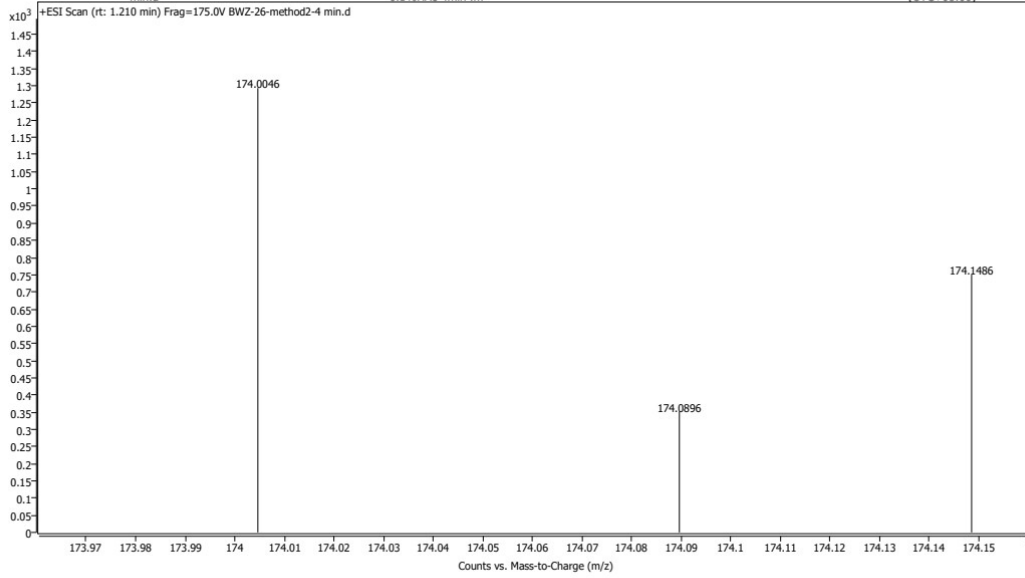


^{13}C NMR spectrum of compound **5i**

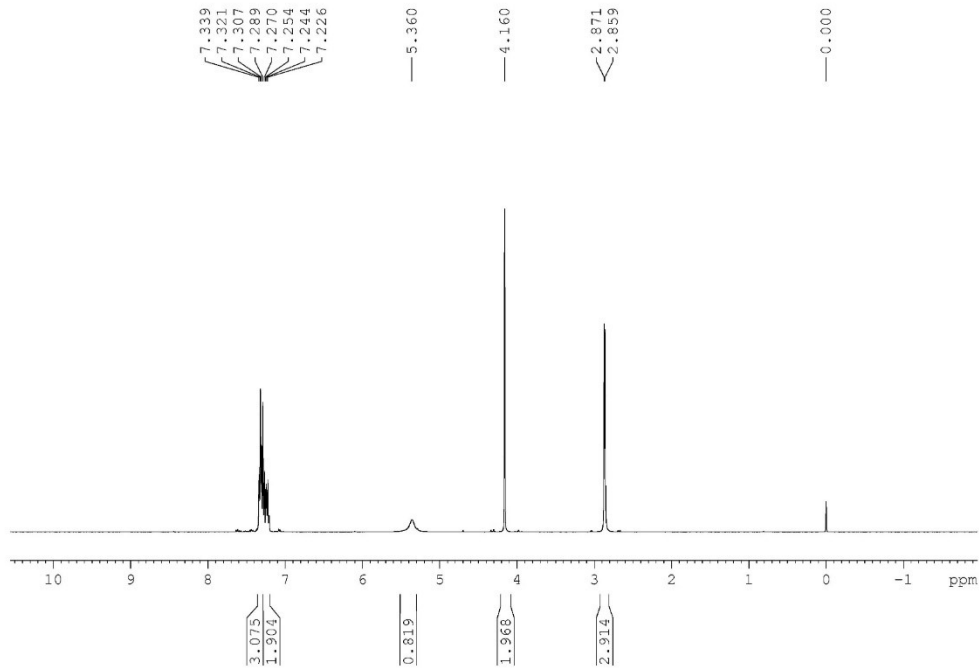
Spectrum Plot Report



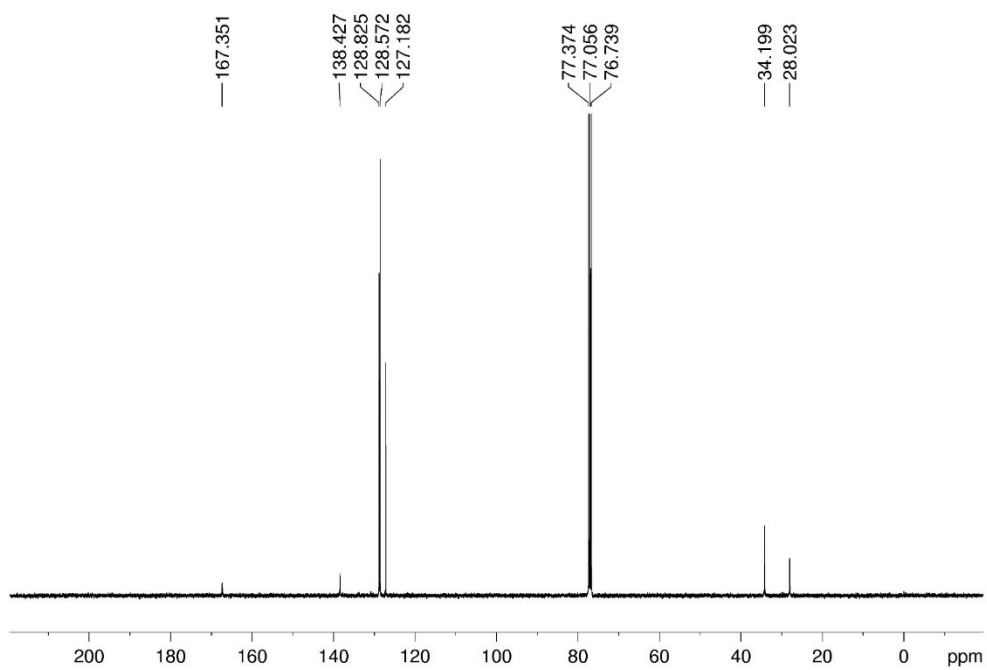
Name: BWZ-26-method2-4 min Rack Pos.
Inj. Vol. (ul): 5 Plate Pos.
Data File: BWZ-26-method2-4 min.d Method (Acq): BWZ20210707-0.1%
HAC-4min.m Instrument: Instrument 1
IRM Status: Success
Comment: Operator: 7/7/2021 12:41:28 PM (UTC+08:00)
Acq. Time (Local):



HRMS spectrum of compound **5i**



¹H NMR spectrum of compound **5j**



¹³C NMR spectrum of compound **5j**

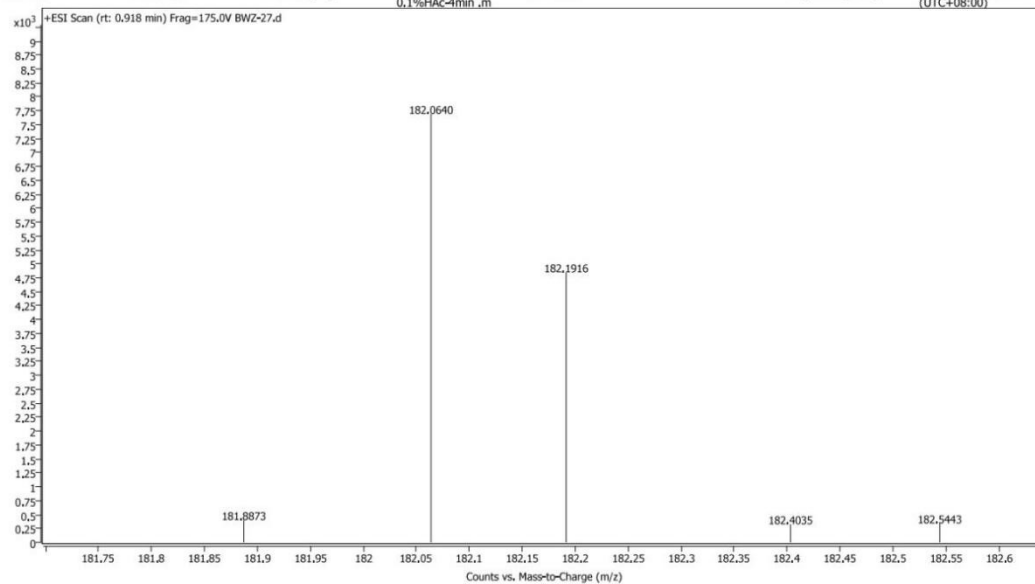
Spectrum Plot Report



Name	BWZ-27	Rack Pos.	Instrument	Instrument 1	Operator
Inj. Vol. (ul)	5	Plate Pos.	IRM Status	Success	
Data File	BWZ-27.d	Method (Acq)	Comment		Acq. Time (Local)

BWZ20210707-0.1%IAC-1min.m

7/7/2021 4:04:10 PM (UTC+08:00)



HRMS spectrum of compound **5j**