Supporting Information

Electrochemical formal [3+2] cycloaddition of azobenzenes with hexahydro-1,3,5-triazines

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1. General Considerations

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 600 MHz Bruker FT-NMR spectrometer (600 MHz and 151 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) and a Thermo Fisher Scientific LTQ FTICR-MS instrument. GC data were recorded on a Gas Chromatography instrument (9790 II) that provided by FULI Instrument Company in China. Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

The starting materials, such as azobenzenes,[1] and hexahydro-1,3,5-triazines reagents,[2] are prepared according to the reported methods, and all materials are known. All the solvents are commercially available from Chemical Reagent Company in China, such as Energy, Titan, and Macklin Chemical Company, and directly used in this electrochemical system. Products were purified by flash chromatography on silica gels, eluting with petroleum ether/ethyl acetate (100:1 to 50:1).

2. General Procedure for the Reactions

2.1 Graphical Guide for the Set-Up

As experimental setup, we used a carbon rod anode (Φ 6 mm) and a platinum plate electrode (10 mm×10 mm×0.3 mm), rubber stoppers, an undivided 15 mL single-necked flask, a DC adjustable power supply regulator (HY3005MT) (Made in China) and a magnetic stirrer.

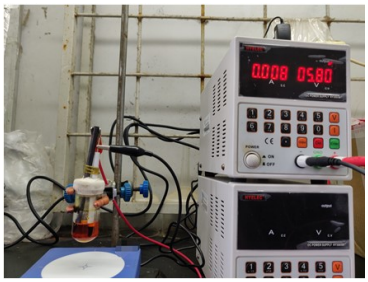
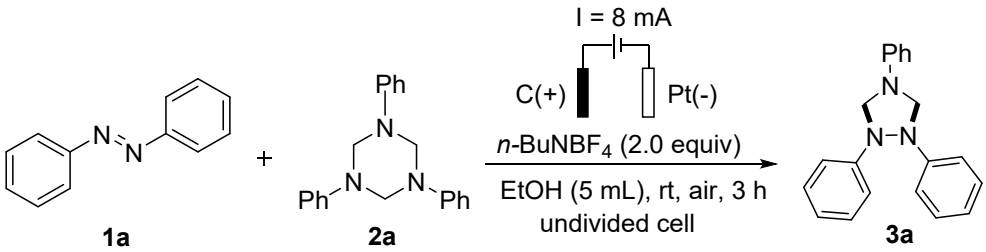


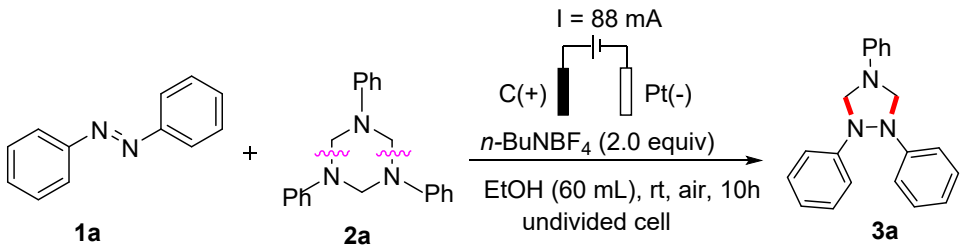
Figure S1 Experiment setup for the [3+2] cycloaddition of azobenzenes with hexahydro-1,3,5-triazines.

2.2 Typical Procedure for the Synthesis of 3a



Azobenzene (**1a**, 0.20 mmol， 1.0 equiv), hexahydro-1,3,5-triazine (**2a**, 0.20 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (0.40 mmol, 2.0 equiv) and EtOH (95%, 5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A carbon rod (Φ 6 mm) anode and a platinum electrode (10 mm×10 mm×0.3 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 3 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1) to give the desired product **3a**.

2.3 Gram-Scale Synthesis of 3a



Azobenzene (**1a**, 1.0 g, 5.5 mmol, 1.0 equiv), hexahydro-1,3,5-triazine (**2a**, 1.73 g, 5.5 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (3.62 g, 11.0 mmol, 2.0 equiv), EtOH (95%, 60 mL) was sequentially added to a 100 mL oven-dried undivided three neck bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A carbon rod (Φ 6 mm) anode and a platinum electrode (10 mm×10 mm×0.3 mm) were used as the cathode in the bottle. The reaction mixture was stirred and electrolyzed at a constant current of 88 mA under air at room temperature for 10 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography to give the desired product **3a (**1.19 g, 72% yield).

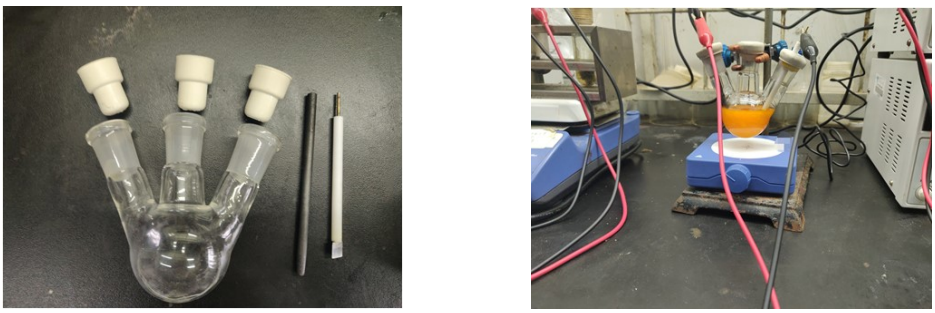


Figure S2 Experiment setup for the gram-scale synthesis of **3a**.

2.4 Late-Stage Transformation of 4o by Click Chemistry

1,2-Diphenyl-4-(prop-2-yn-1-yl)-1,2,4-triazolidine (**4o**, 52.67 mg, 0.20 mmol, 1.0 equiv), NaN_3 (19.5 mg, 0.30 mmol, 1.5 equiv), benzyl bromide (35.6 μL, 0.30 mmol,

1.5 equiv), CuI (1.9 mg, 0.01 mmol, 5 mol%), THF (1.0 mL) and H_2O (1.0 mL) were sequentially added to a 10 mL Pressure-resistant tubes that equipped with a magnetic stirrer bar. The reaction mixture was stirred under air at room temperature for 10 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1) to give the desired product **5** (59.5 mg, 75% yield).

3. Mechanistic Experiments

3.1 Cyclic Voltammetry Studies

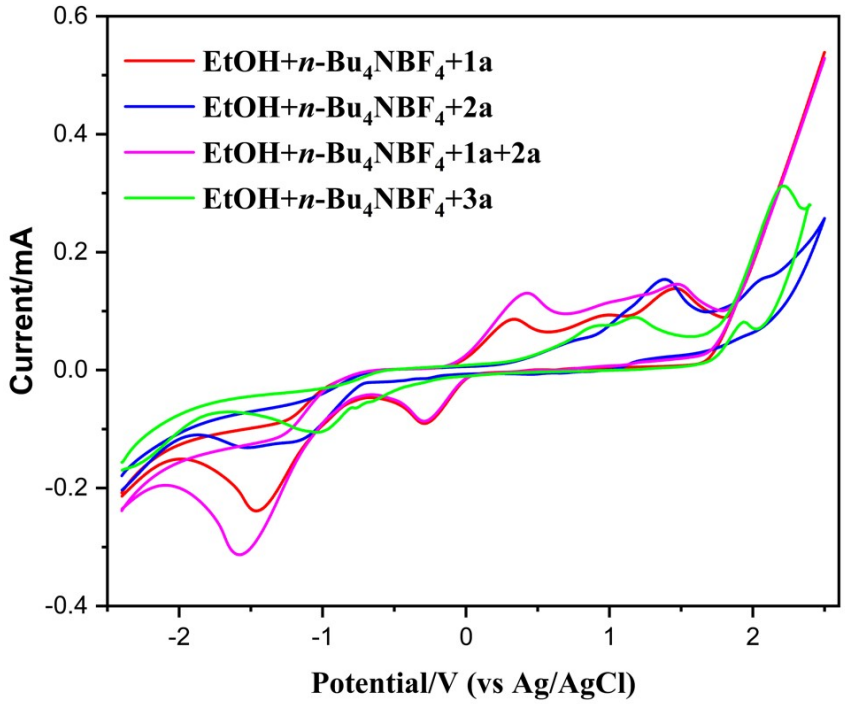


Figure S3 The cyclic voltammograms recorded in EtOH with 0.1 M *n*-Bu_4NBF_4 as the supporting electrolyte [**1a** (1 mM), **2a** (1 mM), **1a**+**2a** (1 mM), **3a** (1 mM)]. Applied potential range: -2.0 to 2.5 V; Scan direction: from negative to positive; Scan rate: 0.1 V/s.

Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum electrode. The reference was an Ag/AgCl wire,

and EtOH (95%, 10 mL) containing 0.1 M *n*-Bu_4NBF_4 was poured into the electrochemical cell in all experiments. Under ambient conditions, the LK98C electrochemical workstation was used with an applied potential range of -2.0 to 2.5 V, a scan direction of Positive and a scan rate of 0.1 V/s. The test concentrations of **1a**, **2a, 1a+2a** and **3a** are 1 mM, respectively.

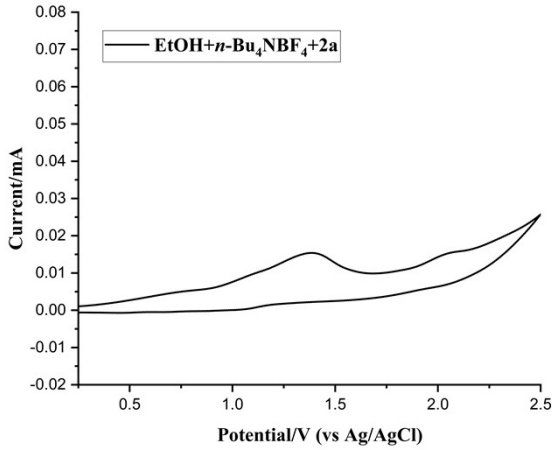


Figure S4 Cyclic voltammogram of **2a** (10 mM) in EtOH solution (10 mL) with $^{n}Bu_4NBF_4$ (0.1 M) as electrolyte. Black curve: E_p = 1.37V. Applied potential range: -2.0 to 2.5 V; Scan direction: from negative to positive; Scan rate: 0.1 V/s.

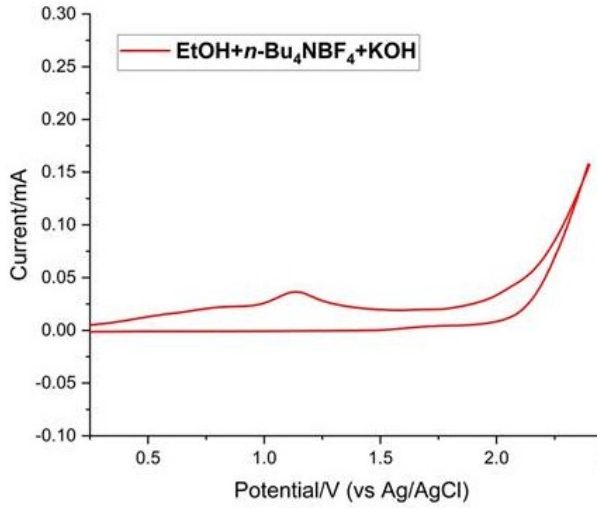


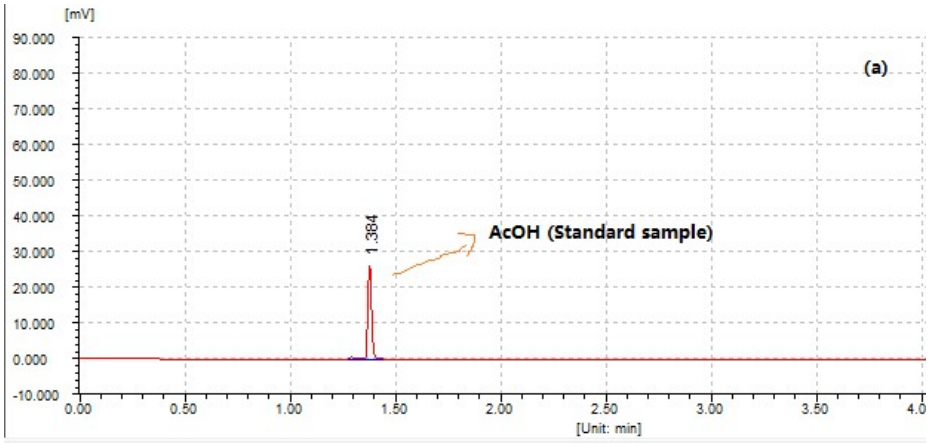
Figure S5 Cyclic voltammogram of KOH (10 mM) in EtOH solution (10 mL) with $^{n}Bu_4NBF_4$ (0.1 M) as electrolyte. Red curve: E_p = 1.14 V for EtO^-. Applied potential

range: -2.0 to 2.5 V; Scan direction: from negative to positive; Scan rate: 0.1 V/s.

The cyclic voltammograms in Figures S4–5 were recorded in an electrolyte of $^{n}Bu_4NBF_4$ (0.1 M) in EtOH (10 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate is 0.1V/s.

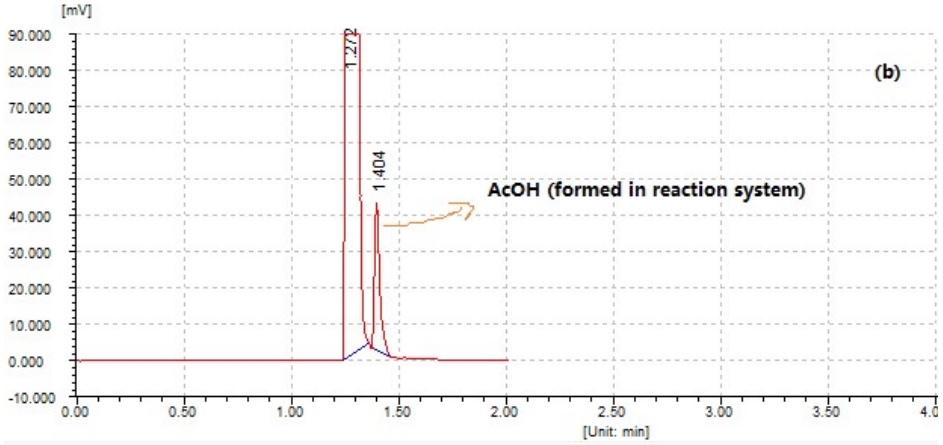
3.2 Detection of AcOH by Gas Chromatography (GC)

In order to detect the formation of AcOH as the oxidation product, a gas chromatography (GC) analysis of AcOH was recorded on a GC instrument (9790 II, FULI company, China). The procedure is as follows: An oven-dried undivided three-necked flask equipped with a magnetic stirrer bar was recharged with pure N_2 for three times. Then, azobenzene (**1a**, 0.20 mmol, 1.0 equiv), hexahydro-1,3,5-triazine (**2a**, 0.20 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (0.40 mmol, 2.0 equiv) and EtOH (95%, 5.0 mL) were sequentially added into the flask and sealed with rubber plugs. Particularly, a balloon filled with N_2 was used to protect the reaction system until the completion of the electrochemical reaction. A carbon rod (Φ 6 mm) anode and a platinum electrode (10 mm×10 mm×0.3 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at room temperature for 3 h. After the completion of the reaction, the detection of AcOH was recorded by GC. By comparing to the GC data of standard AcOH sample, it is indicated that there is AcOH formed during the reaction system.



峰序	组分名	保留时间[min]	半峰宽[min]	峰高[uV]	峰面积[uV*s]	峰面积[%]	含量[%]	峰类型
1		1.384	0.019	26448.3	35236.1	100.0000	100.0000	BB
			总计:	26448.3	35236.1	100.0000	100.0000	

Peak sequence	Component name	Retention time [min]	Peak width at half height [min]	Peak height [uV]	Peak area [uV*s]	Peak area [%]	Content [%]	Peak type
1		1.384	0.019	26448.3	35236.1	100	100	BB
			Total:	26448.3	35236.1	100	100	



峰序	组分名	保留时间[min]	半峰宽[min]	峰高[uV]	峰面积[uV*s]	峰面积[%]	含量[%]	峰类型
1		1.272	0.043	1331815.7	3531610.1	98.0513	98.0513	BB
2		1.404	0.025	40812.8	70187.4	1.9487	1.9487	BB
			总计:	1372628.4	3601797.6	100.0000	100.0000	

Peak sequence	Component name	Retention time [min]	Peak width at half height [min]	Peak height [uV]	Peak area [uV*s]	Peak area [%]	Content [%]	Peak type
1		1.272	0.043	1331815.7	3531610.1	98.0513	98.0513	BB
2		1.404	0.025	40812.8	70187.4	1.9487	1.9487	BB
			Total:	1372628.4	3601797.6	100.00	100.00	

Figure S6 (a) Detection of AcOH (Standard sample) by GC; Retention time = 1.38 min. (b) Detection of AcOH by GC analysis (after the completion of the reaction); Retention time = 1.40 min.

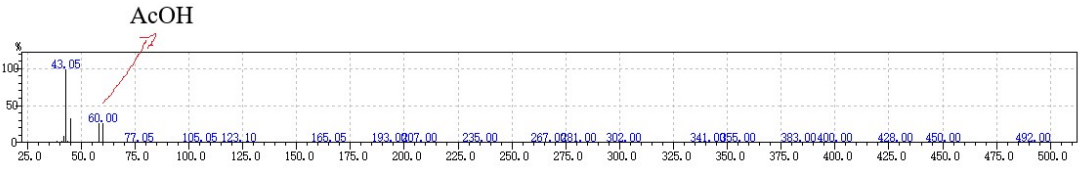
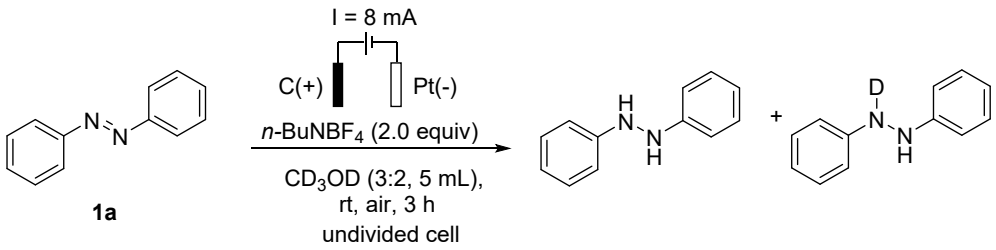


Figure S7 MS spectra of AcOH

3.3 Reaction of 1,2-Diphenylhydrazine with Hexahydro-1,3,5-triazine

1,2-Diphenylhydrazine (0.20 mmol, 1.0 equiv), hexahydro-1,3,5-triazine (**2a**, 0.20 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (0.40 mmol, 2.0 equiv) and EtOH (5.0 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A carbon rod (Φ 6 mm) anode and a platinum electrode (10 mm×10 mm×0.3 mm) were used as the cathode in the bottle. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA under air at room temperature for 3 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1) to give the desired product **3a** (13.26 mg, 22% yield). Yield of 28% can be obtained without electric current.

3.4 Isotope-Labeling Experiment



Azobenzene (**1a**, 0.20 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (0.40 mmol, 2.0 equiv) and CD_3OD (5 mL) were sequentially added into a 15.0 mL oven-dried undivided single necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. A carbon rod (Φ 6 mm) anode and a platinum electrode (10 mm×10 mm×0.3 mm) were used as the cathode in the bottle. About 1.0 cm of the carbon rod was under the solution. The reaction mixture was stirred and electrolyzed

at a constant current of 8 mA under air at room temperature for 3 h. And then, without any treatment, the reaction mixture was detected by HRMS (data of $[M+H]^+$ are showed).

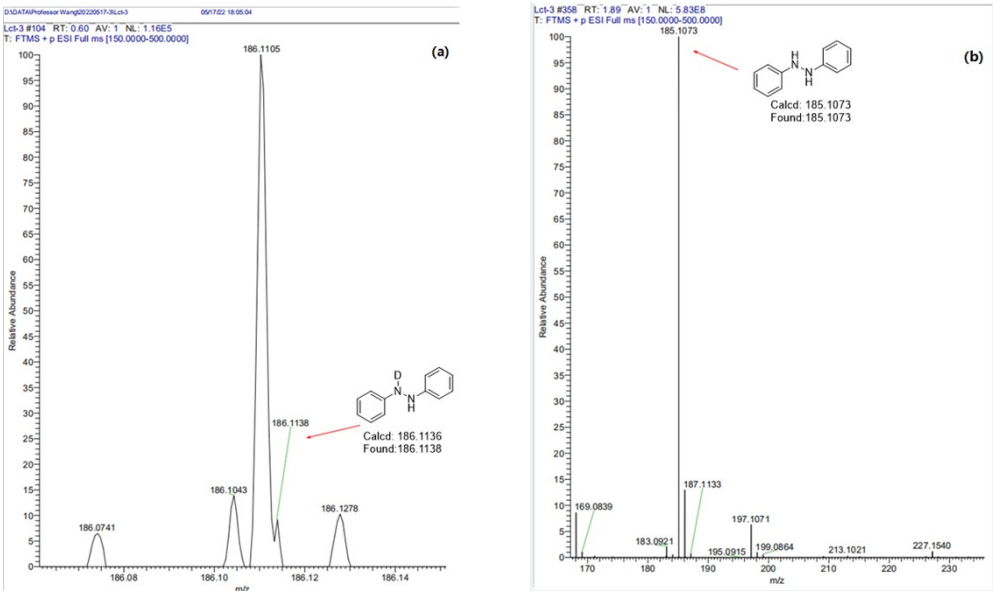
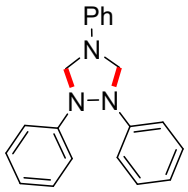


Figure S8 Isotope-Labeling Experiment

4. Characterization Data for the Products



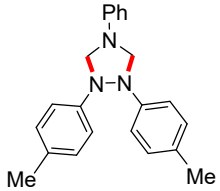
3a

1,2,4-Triphenyl-1,2,4-triazolidine (3a)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3a** (47.6 mg, 79% yield). White solid; m.p.: 132~134 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.25 (m, 4H), 7.22–7.19 (m, 2H), 7.16 (d, J = 7.2 Hz, 4H), 6.94 (t, J = 6.6 Hz, 2H), 6.76 (t, J = 6.6 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 4.85 (s, 2H), 4.66 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 145.1, 129.4, 129.2, 121.6, 118.4, 115.0, 113.3, 67.1.

HRMS (ESI) calcd for $C_{20}H_{19}N_3Na^+$ $[M+Na]^+$ 324.1471, found 324.1471.



3b

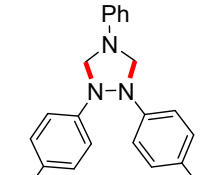
4-Phenyl-1,2-di-p-tolyl-1,2,4-triazolidine (3b)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3b** (55.3 mg, 84% yield).

White solid; m.p.: 130~132 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 2H), 7.09 (s, 8H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 4.83 (s, 2H), 4.66 (s, 2H), 2.29 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 145.2, 130.9, 129.7, 129.4, 118.2, 115.1, 113.2, 67.1, 20.5.

HRMS (ESI) calcd for $C_{22}H_{23}N_3Na^+$ $[M+Na]^+$ 352.1784, found 352.1784.



3c

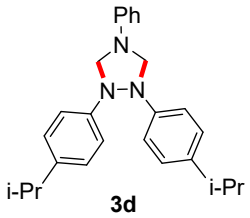
1,2-bis(4-Ethylphenyl)-4-phenyl-1,2,4-triazolidine (3c): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3c** (60.8 mg, 85% yield).

White solid; m.p.: 124~126 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 2H), 7.12 (s, 8H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.83 (s, 2H), 4.65 (s, 2H), 2.58 (q, *J* = 7.8 Hz, 4H), 1.20 (t, *J* = 7.8 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 145.2, 137.4, 129.3, 128.5, 118.1, 115.1, 113.1, 67.1, 28.0, 15.8.

HRMS (ESI) calcd for $C_{24}H_{27}N_3Na^+$ $[M+Na]^+$ 380.2097, found 380.2098.



3d

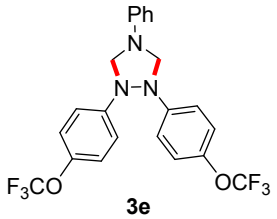
1,2-bis(4-Isopropylphenyl)-4-phenyl-1,2,4-triazolidine (3d): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3d** (66.3 mg, 86% yield).

White solid; m.p.: 113~115 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 4H),7.12 (d, *J* = 8.4 Hz, 4H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 4.84 (s, 2H), 4.66 (s, 2H), 2.88–2.83 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 145.1, 142.1, 129.3, 127.1, 118.1, 115.1, 113.1, 67.1, 33.3, 24.2.

HRMS (ESI) calcd for $C_{26}H_{32}N_3^+$ $[M+H]^+$ 386.2591, found 386.2590.



3e

4-Phenyl-1,2-bis(4-(trifluoromethoxy)phenyl)-1,2,4-triazolidine (3e)[3]: Prepared following general procedure and the reaction mixture was purified by flash column

chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **3e** (58.2 mg, 62% yield).

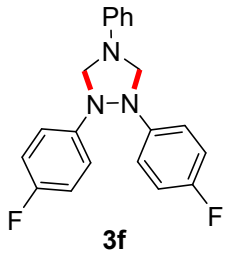
Colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 2H), 7.04 (s, 8H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 2H), 4.70 (s, 2H), 4.59 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 143.8, 142.8, 128.5, 120.8 (d, *J* = 113.7 Hz), 118.4 (d, *J* = 105.7 Hz), 114.9, 112.5, 66.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ –58.2.

HRMS (ESI) calcd for $C_{22}H_{18}F_6N_3O_2^+$ $[M+H]^+$ 470.1298, found 470.1295.



3f

1,2-bis(4-Fluorophenyl)-4-phenyl-1,2,4-triazolidine (3f)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3f** (45.2 mg, 67% yield).

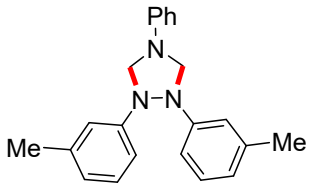
White solid; m.p.: 118~119 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 9.6, 4.8 Hz, 4H), 6.96 (t, *J* = 8.4 Hz, 4H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 4.74 (s, 2H), 4.67 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3 (d, *J* = 240.8 Hz), 145.7 (d, *J* = 213.5 Hz), 129.5, 118.7, 116.6, 116.5, 115.8, 115.7, 113.4, 67.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -122.8.

HRMS (ESI) calcd for $C_{20}H_{18}F_2N_3^+$ $[M+H]^+$ 338.1463, found 338.1463.



3h

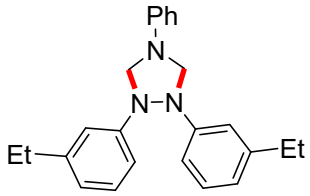
4-Phenyl-1,2-di(*m*-tolyl)-1,2,4-triazolidine (3h)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3h** (46.8 mg, 71% yield).

White solid; m.p.: 52~54 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.24 (m, 4H), 7.10–7.04 (m, 4H), 6.84 (s, 3H), 6.64 (s, 2H), 4.91 (s, 2H), 4.71 (s, 2H), 2.40 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 145.1, 139.0, 129.3, 129.0, 122.3, 118.2, 115.5, 113.1, 112.0, 67.0, 21.7.

HRMS (ESI) calcd for $C_{22}H_{24}N_3^+$ $[M+H]^+$ 330.1965, found 330.1964.



3i

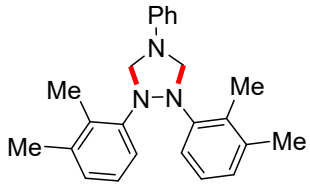
1,2-bis(3-Ethylphenyl)-4-phenyl-1,2,4-triazolidine (3i): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3i** (52.9 mg, 74% yield).

Yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, J = 7.8 Hz, 2H), 7.11 (s, 8H), 6.75 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 4.83 (s, 2H), 4.65 (s, 2H), 2.58 (q, J = 7.8 Hz, 4H), 1.20 (t, J = 7.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 145.2, 137.4, 129.3, 128.5, 118.1, 115.1, 113.1, 67.1, 28.0, 15.8.

HRMS (ESI) calcd for $C_{24}H_{28}N_3^+$ $[M+H]^+$ 358.2278, found 358.2276.



3j

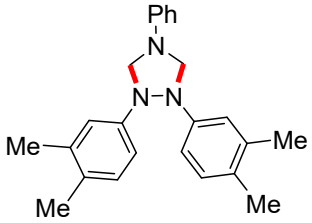
1,2-bis(2,3-Dimethylphenyl)-4-phenyl-1,2,4-triazolidine (3j): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3j** (55.8 mg, 78% yield).

White solid; m.p.: 124~125 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.8 Hz, 2H), 7.06 (t, J = 7.8 Hz, 2H), 6.90 (d, J = 7.2 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 6.51 (d, J = 7.8 Hz, 2H), 4.94 (s, 2H), 4.47 (s, 2H), 2.31 (s, 6H), 2.29 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4, 144.7, 138.0, 129.3, 128.5, 125.6, 125.3, 117.6, 115.9, 112.7, 69.7, 20.5, 15.3.

HRMS (ESI) calcd for $C_{24}H_{27}N_3Na^+$ $[M+Na]^+$ 380.2097, found 380.2101.



3k

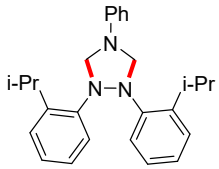
1,2-bis(3,4-Dimethylphenyl)-4-phenyl-1,2,4-triazolidine (3k)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3k** (57.9 mg, 81% yield).

White solid; m.p.: 142~144 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.2 Hz, 2H), 7.0 (d, *J* = 8.4 Hz, 2H), 6.99 (s, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 2H), 4.62 (s, 2H), 2.23 (s, 6H), 2.18 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 145.2, 137.3, 130.2, 129.5, 129.2, 118.0, 116.4, 113.1, 112.3, 67.0, 20.1, 18.8.

HRMS (ESI) calcd for $C_{24}H_{28}N_3^+$ $[M+H]^+$ 358.2278, found 358.2275.



3l

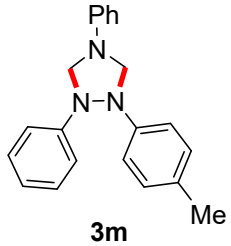
1,2-bis(2-Isopropylphenyl)-4-phenyl-1,2,4-triazolidine (3l): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3l** (64.0 mg, 83% yield).

White solid; m.p.: 106~108 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 4.96 (s, 2H), 4.55 (s, 2H), 3.46–3.41 (m, 1H), 1.32 (s, 6H), 1.14 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 144.7, 141.6, 129.5, 126.6, 126.2, 124.5, 118.9, 117.71, 112.7, 70.1, 27.7.

HRMS (ESI) calcd for $C_{26}H_{32}N_3^+$ $[M+H]^+$ 386.2591, found 386.2591.



3m

1,4-Diphenyl-2-(*p*-tolyl)-1,2,4-triazolidine (3m)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography

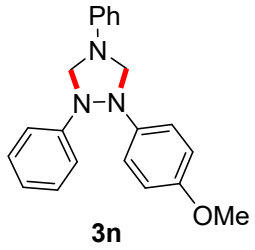
with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3m** (52.4 mg, 83% yield).

White solid; m.p.: 104~106 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (s, 4H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 4.82 (s, 2H), 4.64 (d, *J* = 53.4 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 148.0, 145.2, 131.2, 129.8, 129.4, 129.2, 121.4, 118.3, 115.3, 114.9, 113.3, 67.4, 67.0, 20.6.

HRMS (ESI) calcd for $C_{21}H_{21}N_3Na^+$ $[M+Na]^+$ 338.1628, found 338.1629.



3n

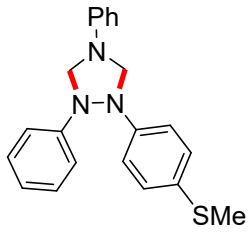
1-(4-Methoxyphenyl)-2,4-diphenyl-1,2,4-triazolidine (3n)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **3n** (53.0 mg, 80% yield).

White solid; m.p.: 91~93 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 4.79 (s, 2H), 4.58 (s, 2H), 3.76 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1, 150.1, 145.1, 144.1, 129.4, 129.2, 121.2, 118.2, 117.0, 114.7, 114.5, 113.2, 67.8, 66.9, 55.6.

HRMS (ESI) calcd for $C_{21}H_{22}N_3O^+$ $[M+H]^+$ 332.1757, found 332.1755.



3o

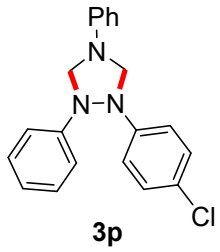
1-(4-(Methylthio)phenyl)-2,4-diphenyl-1,2,4-triazolidine (3o): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3o** (52.8 mg, 76% yield).

White solid; m.p.: 101~103 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 5.4 Hz, 2H), 4.65 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 148.4, 144.9, 129.8, 129.6, 129.3, 129.1, 121.6, 118.4, 115.7, 114.9, 113.2, 67.1, 67.0, 17.7.

HRMS (ESI) calcd for $C_{21}H_{22}N_3S^+$ $[M+H]^+$ 348.1529, found 348.1528.



3p

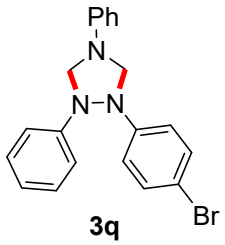
1-(4-Chlorophenyl)-2,4-diphenyl-1,2,4-triazolidine (3p)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3p** (47.0 mg, 70% yield).

White solid; m.p.: 117~119 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 4H),7.15 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 4.84 (d, *J* = 33.0 Hz, 2H), 4.69 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 148.8, 145.0, 129.5, 129.3, 129.1, 126.5, 121.9, 118.7, 116.3, 115.0, 113.4, 67.3, 67.2.

HRMS (ESI) calcd for $C_{20}H_{18}ClN_3Na^+$ $[M+Na]^+$ 358.1081, found 358.1079.



3q

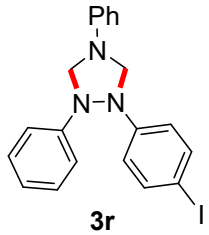
1-(4-Bromophenyl)-2,4-diphenyl-1,2,4-triazolidine (3q)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3q** (57.0 mg, 75% yield).

White solid; m.p.: 153~155 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 9.0 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 2H), 4.80 (d, *J* = 42.6 Hz, 2H), 4.66 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 149.3, 145.0, 132.0, 129.5, 129.3, 121.9, 118.7, 116.7, 115.1, 113.8, 113.4, 67.4, 67.1.

HRMS (ESI) calcd for $C_{20}H_{19}BrN_3^+$ $[M+H]^+$ 380.0757, found 380.0753.



3r

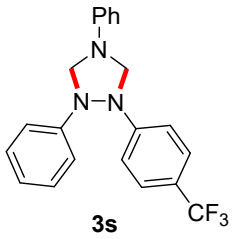
1-(4-Iodophenyl)-2,4-diphenyl-1,2,4-triazolidine (3r)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3r** (61.5 mg, 72% yield).

White solid; m.p.: 173~175 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 4.83 (d, *J* = 44.4 Hz, 2H), 4.67 (d, *J* = 28.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 149.8, 144.9, 137.9, 129.4, 129.2, 121.9, 118.7, 117.0, 115.0, 113.3, 83.6, 67.3, 66.9.

HRMS (ESI) calcd for $C_{20}H_{19}IN_3^+$ $[M+H]^+$ 428.0618, found 428.0618.



3s

1,4-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,4-triazolidine (3s): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3s** (42.8 mg, 58% yield).

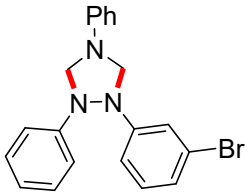
Colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 2H), 7.18 (s, 2H), 7.12 (s, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.88 (s, 1H), 6.69 (s, 1H), 6.48 (d, *J* = 7.8 Hz, 2H), 4.80 (s, 1H), 4.68 (s, 2H), 4.47 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.3, 149.7, 144.8, 129.4, 129.3, 126.5 (q, *J* = 4.2 Hz), 124.5 (q, *J* = 270.6 Hz), 122.9 (q, *J* = 2.4 Hz), 122.3, 118.9, 115.3, 114.0, 113.4, 67.7, 66.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.3.

HRMS (ESI) calcd for $C_{21}H_{19}F_3N_3^+$ $[M+H]^+$ 370.1526, found 370.1522.



3t

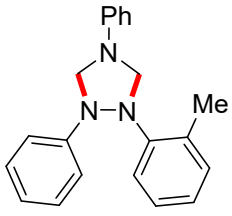
1-(3-Bromophenyl)-2,4-diphenyl-1,2,4-triazolidine (3t): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **3t** (47.2 mg, 62% yield).

White solid; m.p.: 145~147 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.16–7.09 (m, 3H), 7.03 (dd, *J* = 15.6, 7.8 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 2H), 4.80 (d, *J* = 49.8 Hz, 2H), 4.64 (d, *J* = 34.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 149.9, 145.0, 130.6, 129.5, 129.3, 124.4, 123.3, 122.1, 118.8, 117.9, 115.2, 113.5, 113.4, 67.5, 67.0.

HRMS (ESI) calcd for $C_{20}H_{19}BrN_3^+$ $[M+H]^+$ 380.0757, found 380.0755.



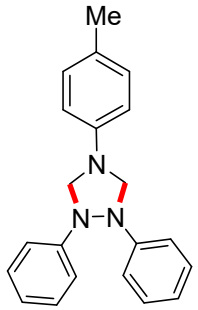
3u

1,4-Diphenyl-2-(*o*-tolyl)-1,2,4-triazolidine (3u): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **3u** (51.1 mg, 81% yield).

White solid; m.p.: 121~122 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.24 (m, 3H), 7.23–7.17 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 6.6 Hz, 1H), 6.91 (t, *J* = 6.6 Hz, 1H), 6.76 (t, *J* = 6.0 Hz, 1H), 6.54 (d, *J* = 6.0 Hz, 2H), 4.93–4.79 (m, 2H), 4.56 (d, *J* = 4.2 Hz, 2H), 2.47 (d, *J* = 5.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 149.4, 145.0, 131.4, 130.5, 129.5, 129.2, 126.5, 124.3, 121.1, 118.5, 118.3, 115.0, 113.2, 68.6, 70.0, 19.2. HRMS (ESI) calcd for $C_{21}H_{22}N_3^+$ $[M+H]^+$ 316.1808, found 316.1810.



4a

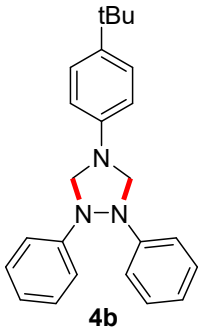
1,2-Diphenyl-4-(p-tolyl)-1,2,4-triazolidine (4a)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4a** (50.5 mg, 80% yield).

White solid; m.p.: 93~95 °C.

^{1}H NMR (600 MHz, DMSO) δ 7.23 (t, *J* = 7.8 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 4H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.89 (s, 2H), 4.49 (s, 2H), 2.13 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 150.0, 143.2, 129.5, 129.1, 127.0, 121.0, 114.7, 113.9, 67.3, 20.0.

HRMS (ESI) calcd for $C_{21}H_{22}N_3^+$ $[M+H]^+$ 316.1808, found 316.1807.



4b

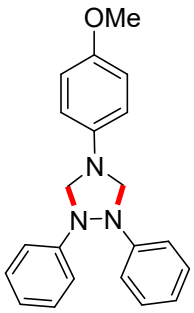
4-(4-(*tert*-Butyl)phenyl)-1,2-diphenyl-1,2,4-triazolidine (4b)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **4b** (53.6 mg, 75% yield).

White solid; m.p.: 92~94 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (q, *J* = 8.4 Hz, 6H), 7.17 (d, *J* = 8.4 Hz, 4H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.86 (s, 2H), 4.68 (s, 2H), 1.27 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 142.8, 141.1, 129.1, 126.1, 121.4, 114.9, 113.0, 67.3, 33.9, 31.4.

HRMS (ESI) calcd for $C_{24}H_{28}N_3^+$ $[M+H]^+$ 358.2278, found 358.2276.



4c

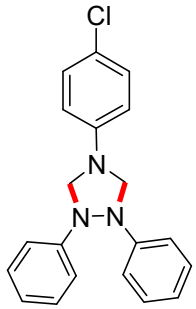
4-(4-Methoxyphenyl)-1,2-diphenyl-1,2,4-triazolidine (4c)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4c** (41.8 mg, 63% yield).

White solid; m.p.: 73~75 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.22 (t, J = 7.2 Hz, 4H), 7.08 (d, J = 7.8 Hz, 4H), 6.86 (t, J = 7.2 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 4.84 (s, 2H), 4.49 (s, 2H), 3.61 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 152.5, 150.1, 139.8, 129.0, 121.0, 115.3, 114.6, 114.6, 68.0, 55.3.

HRMS (ESI) calcd for $C_{21}H_{22}ON_3^+$ $[M+H]^+$ 332.1757, found 332.1756.



4d

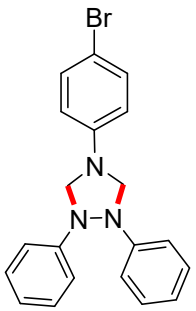
4-(4-Chlorophenyl)-1,2-diphenyl-1,2,4-triazolidine (4d)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4d** (56.4 mg, 84% yield).

White solid; m.p.: 130~132 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.22 (t, J = 7.2 Hz, 4H), 7.17 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 4H), 6.87 (t, J = 7.2 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 4.95 (s, 2H), 4.47 (s, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 149.8, 144.0, 129.1, 128.8, 121.7, 121.2, 115.0, 114.7, 66.7.

HRMS (ESI) calcd for $C_{20}H_{19}N_3Cl^+$ $[M+H]^+$ 336.1262, found 336.1261.



4e

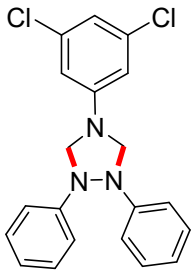
4-(4-Bromophenyl)-1,2-diphenyl-1,2,4-triazolidine (4e)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4e** (62.4 mg, 82% yield).

White solid; m.p.: 135~136 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.27 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.8 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H), 6.85 (t, J = 7.2 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 4.93 (s, 2H), 4.44 (s, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 149.8, 144.3, 131.7, 129.2, 121.3, 115.5, 114.7, 109.3, 66.6.

HRMS (ESI) calcd for $C_{20}H_{18}BrN_3^+$ $[M]^+$ 379.0679, found 379.0678.



4f

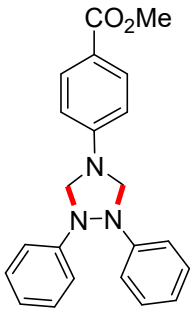
4-(3,5-Dichlorophenyl)-1,2-diphenyl-1,2,4-triazolidine (4f): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4f** (63.7 mg, 85% yield).

White solid; m.p.: 171~173 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.22 (t, J = 7.8 Hz, 4H), 7.12 (d, J = 8.4 Hz, 4H), 6.88 (t, J = 7.2 Hz, 2H), 6.74 (d, J = 7.2 Hz, 3H), 5.06 (s, 2H), 4.43 (s, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 149.5, 146.4, 134.7, 129.2, 121.4, 116.5, 114.7, 111.6, 65.8.

HRMS (ESI) calcd for $C_{20}H_{16}Cl_2N_3^+$ $(M-H)^+$ 368.0716, found 368.0717.



4g

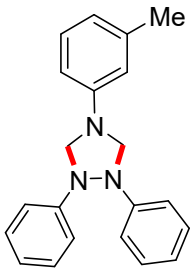
Methyl 4-(1,2-diphenyl-1,2,4-triazolidin-4-yl)benzoate (4g): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4g** (61.8 mg, 86% yield).

White solid; m.p.: 173~175 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.74 (d, J = 7.8 Hz, 2H), 7.24 (t, J = 7.8 Hz, 4H), 7.17 (d, J = 8.4 Hz, 4H), 6.90 (t, J = 7.2 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 5.12 (s, 2H), 4.53 (s, 2H), 3.72 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 166.1, 149.5, 148.0, 130.9, 129.2, 121.5, 117.9, 114.8, 112.4, 65.6, 51.5.

HRMS (ESI) calcd for $C_{22}H_{20}N_3O_2^+$ $[M-H]^+$ 358.1550, found 358.1547.



4h

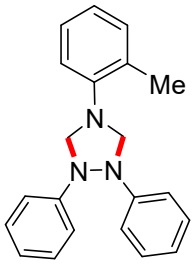
1,2-Diphenyl-4-(m-tolyl)-1,2,4-triazolidine (4h)[3]: Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4h** (33.4 mg, 53% yield).

White solid; m.p.: 116~117 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.2 Hz, 4H), 7.23 (d, *J* = 7.2 Hz, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.66 (d, *J* = 6.6 Hz, 1H), 6.46 (s, 2H), 4.91 (s, 2H), 4.72 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.1, 139.1, 129.2, 129.1, 121.5, 119.2, 114.9, 113.9, 110.4, 67.1, 21.7.

HRMS (ESI) calcd for $C_{21}H_{22}N_3^+$ $[M+H]^+$ 316.1808, found 316.1806.



4i

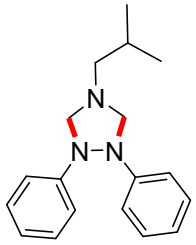
1,2-Diphenyl-4-(*o*-tolyl)-1,2,4-triazolidine (4i): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 100:1) to afford the product **4i** (29.6 mg, 47% yield).

White solid; m.p.: 108~109 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 4H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 6.6 Hz, 2H), 4.88 (s, 2H), 4.70 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.1, 139.2, 129.2, 129.1, 121.5, 119.2, 115.0, 114.0, 110.4, 67.1, 21.7.

HRMS (ESI) calcd for $C_{21}H_{22}N_3^+$ $[M+H]^+$ 316.1808, found 316.1807.



4j

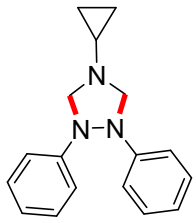
4-Isobutyl-1,2-diphenyl-1,2,4-triazolidine (4j): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4j** (40.5 mg, 72% yield).

Pale yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.2 Hz, 4H), 6.95 (d, *J* = 7.8 Hz, 4H), 6.88 (t, *J* = 7.2 Hz, 2H), 4.36 (s, 2H), 4.27 (s, 2H), 2.24 (t, *J* = 8.4 Hz, 2H), 1.65–1.58 (m, 1H), 0.83 (d, *J* = 13.2 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 129.0, 120.3, 114.5, 74.2, 63.7, 28.5, 20.5 (d, *J* = 9.45 Hz).

HRMS (ESI) calcd for $C_{18}H_{24}N_3^+$ $[M+H]^+$ 282.1965, found 282.1963.



4k

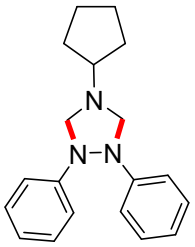
4-Cyclopropyl-1,2-diphenyl-1,2,4-triazolidine (4k): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4k** (60.6 mg, 83% yield).

White solid; m.p.: 97~98 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.4 Hz, 4H), 7.02 (d, *J* = 7.8 Hz, 4H), 6.93 (t, *J* = 7.8 Hz, 2H), 4.56 (d, *J* = 8.4 Hz, 2H), 4.44 (d, *J* = 8.4 Hz, 2H), 2.04–2.01 (m, 1H), 0.53 (s, 2H), 0.45–0.42 (m, 1H), 0.37–0.34 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 129.0, 120.3, 114.4, 74.2, 36.3, 7.3, 6.5.

HRMS (ESI) calcd for $C_{17}H_{20}N_3^+$ $[M+H]^+$ 266.1652, found 266.1650.



4l

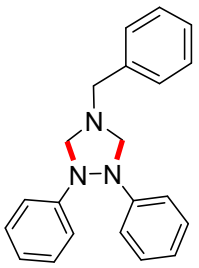
4-Cyclopentyl-1,2-diphenyl-1,2,4-triazolidine (4l): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4l** (35.8 mg, 61% yield).

Pale green liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.2 Hz, 4H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.89 (t, *J* = 7.2 Hz, 2H), 4.41 (s, 2H), 4.31 (s, 2H), 2.77–2.72 (m, 1H), 1.79–1.64 (m, 4H)，1.45–1.25 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 129.0, 120.4, 114.4, 72.4, 62.5, 32.7, 32.1, 24.1.

HRMS (ESI) calcd for $C_{19}H_{24}N_3^+$ $[M+H]^+$ 294.1965, found 294.1963.



4m

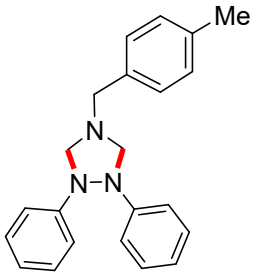
4-Benzyl-1,2-diphenyl-1,2,4-triazolidine (4m): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4m** (51.1 mg, 81% yield).

White solid; m.p.: 112~114 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.25 (m, 7H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 4H), 6.93 (t, *J* = 7.2 Hz, 2H), 4.43 (d, *J* = 8.4 Hz, 2H), 4.34 (d, *J* = 9.0 Hz, 2H), 3.68 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 138.2, 129.1, 128.9, 128.4, 127.4, 120.5, 114.5, 73.2, 58.9.

HRMS (ESI) calcd for $C_{21}H_{21}N_3^+$ $[M]^+$ 315.1730, found 315.1731.



4n

4-(4-Methylbenzyl)-1,2-diphenyl-1,2,4-triazolidine (4n): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 30:1) to afford the product **4n** (52.1 mg, 79% yield).

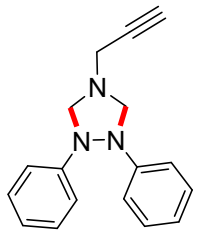
White solid; m.p.: 104~105 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.19 (t, *J* = 7.2 Hz, 4H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 4H), 6.83 (t, *J* = 7.2 Hz, 2H), 4.31 (d, *J* =

9.0 Hz, 2H), 4.26 (d, J = 8.4 Hz, 2H), 3.54 (d, J = 12.6 Hz, 1H), 3.44 (d, J = 13.2 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 151.3, 136.3, 135.3, 129.0, 128.9, 128.5, 120.1, 114.3, 72.8, 57.4, 20.7.

HRMS (ESI) calcd for $C_{22}H_{23}N_3^+$ $[M]^+$ 329.1886, found 329.1889.



4o

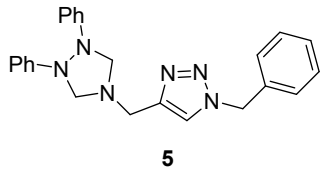
1,2-Diphenyl-4-(prop-2-yn-1-yl)-1,2,4-triazolidine (4o): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 50:1) to afford the product **4o** (33.7 mg, 64% yield).

White solid; m.p.: 98~100 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, J = 7.2 Hz, 4H), 6.99 (d, J = 8.4 Hz, 4H), 6.93 (t, J = 7.2 Hz, 2H), 4.53 (d, J = 7.8 Hz, 2H), 4.38 (d, J = 7.2 Hz, 2H), 3.39–3.31 (m, 2H), 2.22 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0, 129.1, 120.7, 114.4, 79.5, 72.6, 72.3, 43.2.

HRMS (ESI) calcd for $C_{17}H_{18}N_3^+$ $[M+H]^+$ 264.1495, found 264.1493.



5

1-Benzyl-4-((1,2-diphenyl-1,2,4-triazolidin-4-yl)methyl)-1*H*-1,2,3-triazole (5): Prepared following general procedure and the reaction mixture was purified by flash column chromatography with petroleum ether and ethylacetate (PE/EA = 5:1) to afford the product **5** (59.5 mg, 75 % yield).

Pale yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 6.6 Hz, 2H), 7.26–7.24 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 4H), 7.17 (s, 1H), 6.94 (d, *J* = 7.8 Hz, 4H), 6.89 (t, *J* = 7.2 Hz, 2H), 5.48 (d, *J* = 7.8 Hz, 2H), 4.45 (s, 2H), 4.37 (s, 2H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.69 (d, *J* = 12.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 145.5, 134.5, 129.1, 129.1, 128.8, 128.1, 122.4, 120.6, 114.5, 73.2, 54.1, 49.9.

HRMS (ESI) calcd for $C_{24}H_{25}N_6^+$ $[M+H]^+$ 397.2135, found 397.2132.

5. References

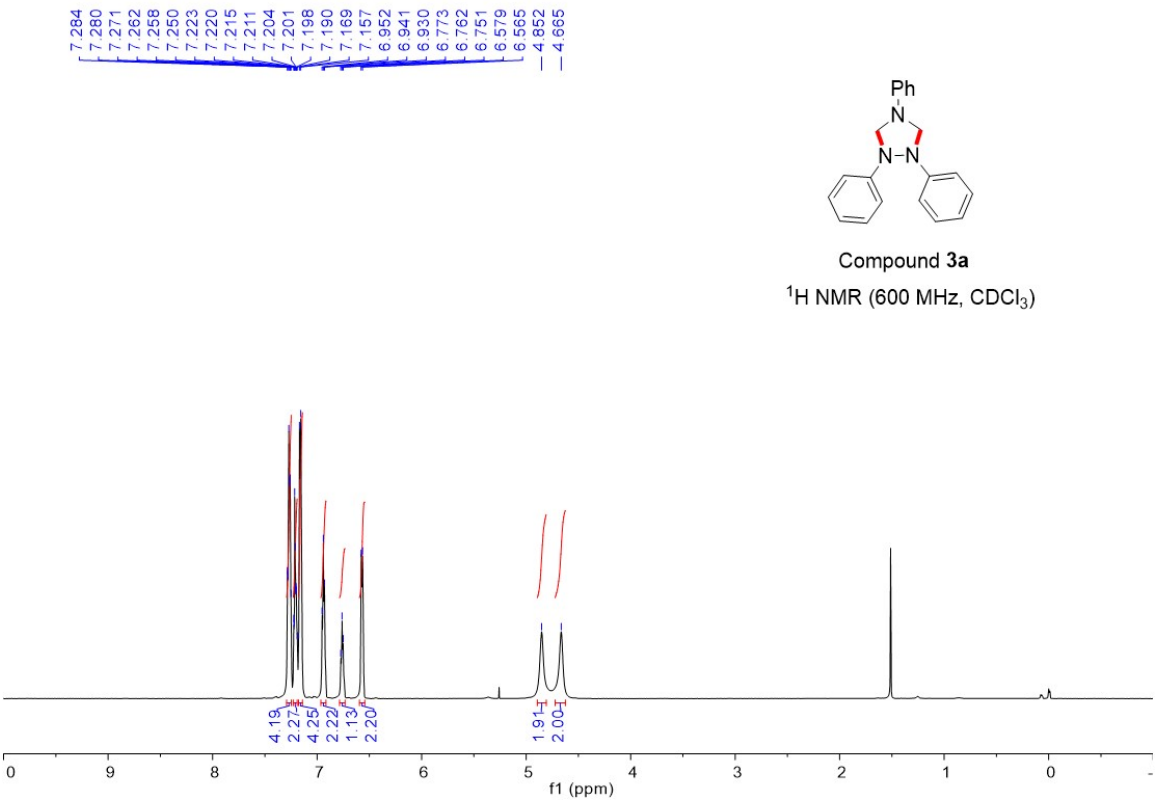
[1] Zhang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 6174–6177.

[2] (a) Guranova, N.; Dar'in, D.; Krasavin, M. *Synthesis* **2018**, *50*, 2001–2008. (b) Giumanini, A. G.; Verardo, G.; Zangrando, E.; Lassiani, L. *J. Prakt. Chem.* **1987**, *329*, 1087–1103.

[3] Yang, J.; Song, M.; Zhou, H.; Qi, Y.; Ma, B. Wang, X.-C. *Green Chem.* **2021***, 23,* 5806–5811.

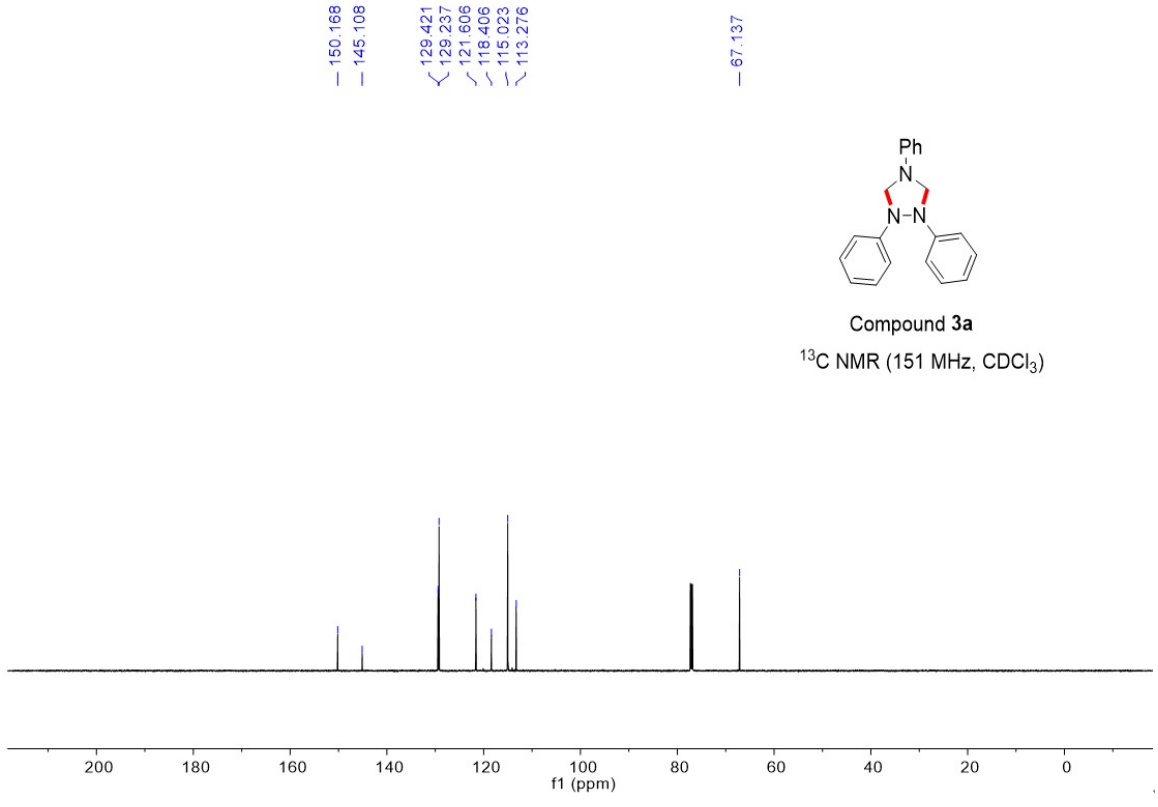
6. NMR Spectra of the Products

NMR spectra of 1,2,4-triphenyl-1,2,4-triazolidine (**3a**)



Compound **3a**

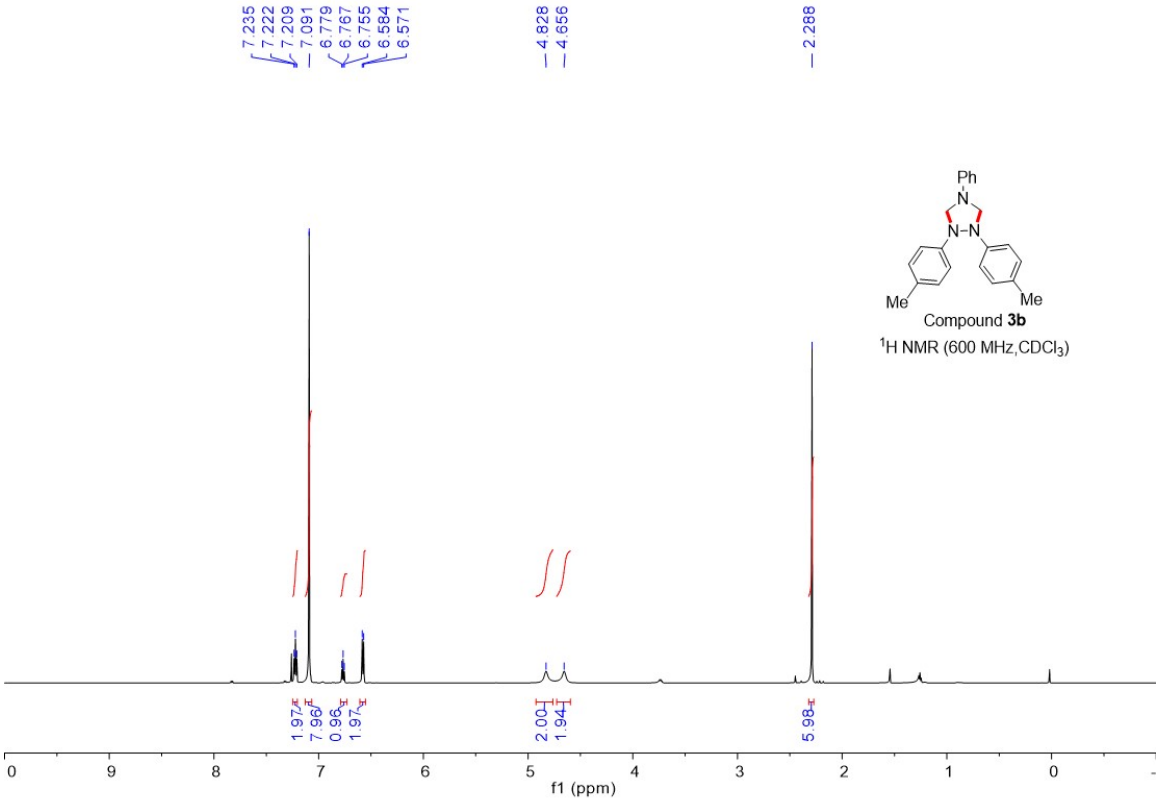
^{1}H NMR (600 MHz, $CDCl_3$)

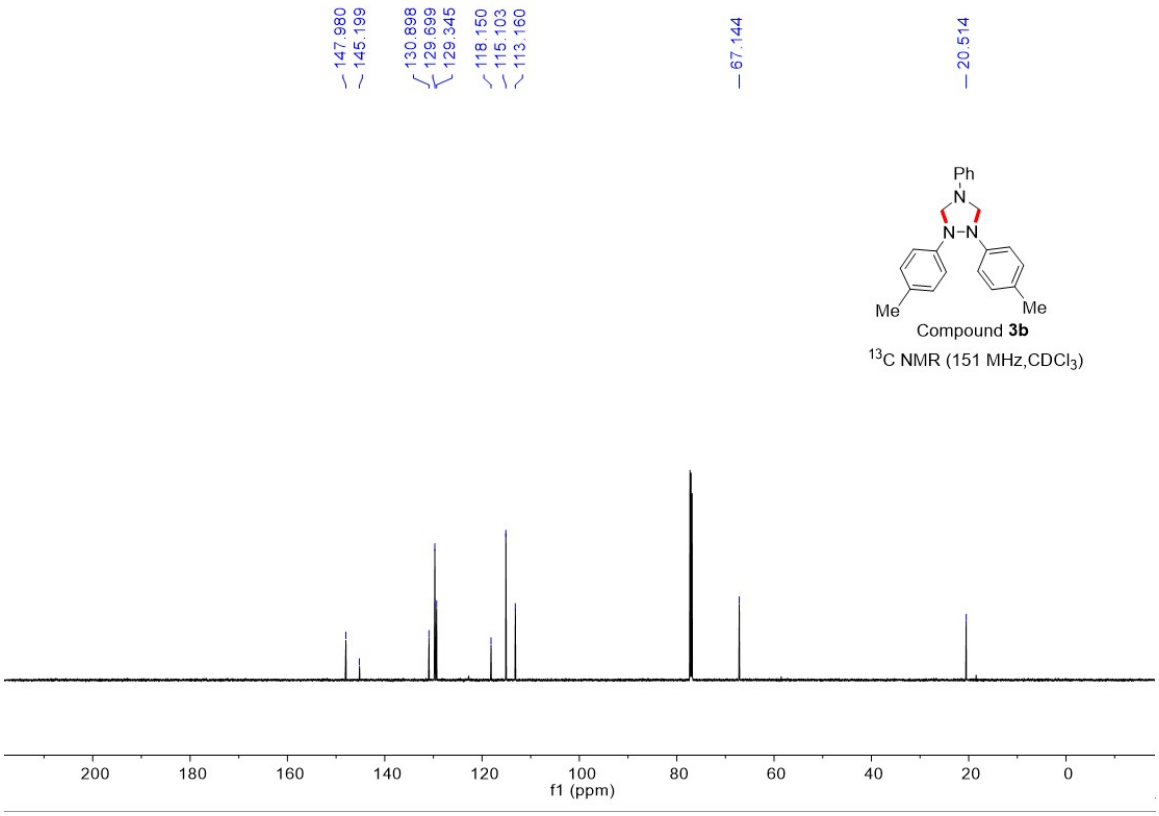


Compound **3a**

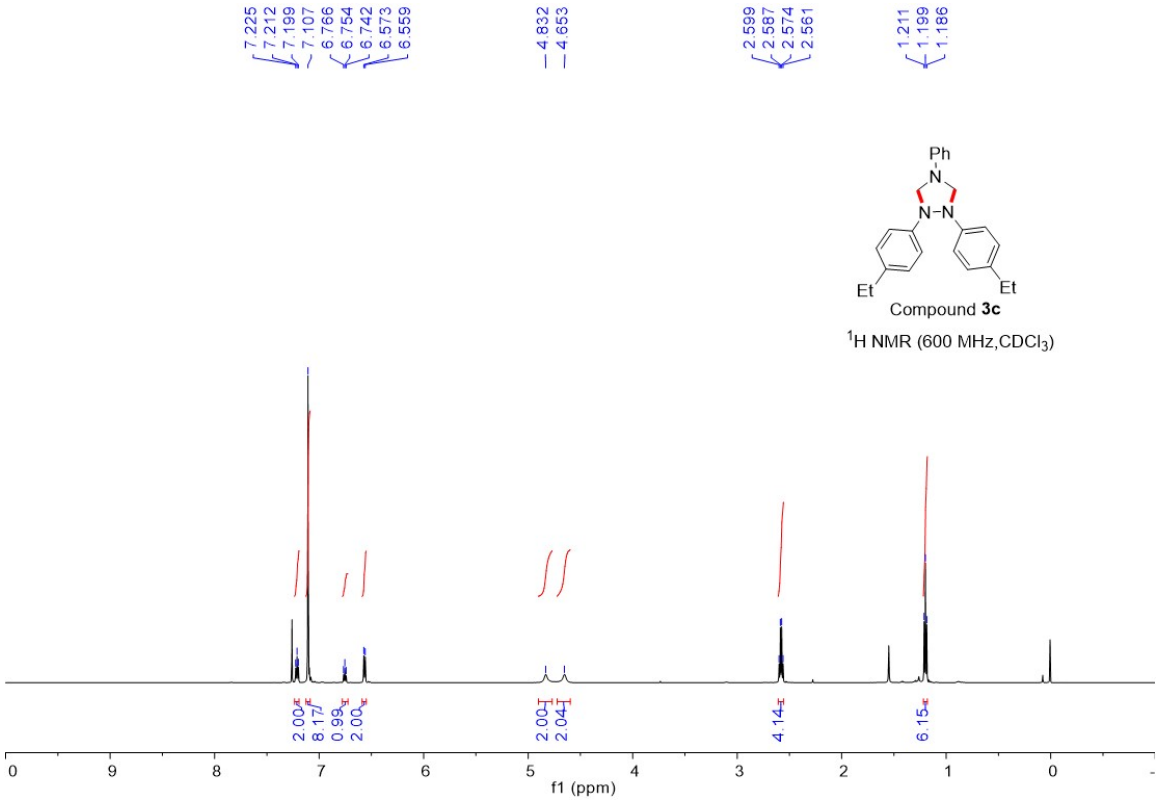
^{13}C NMR (151 MHz, $CDCl_3$)

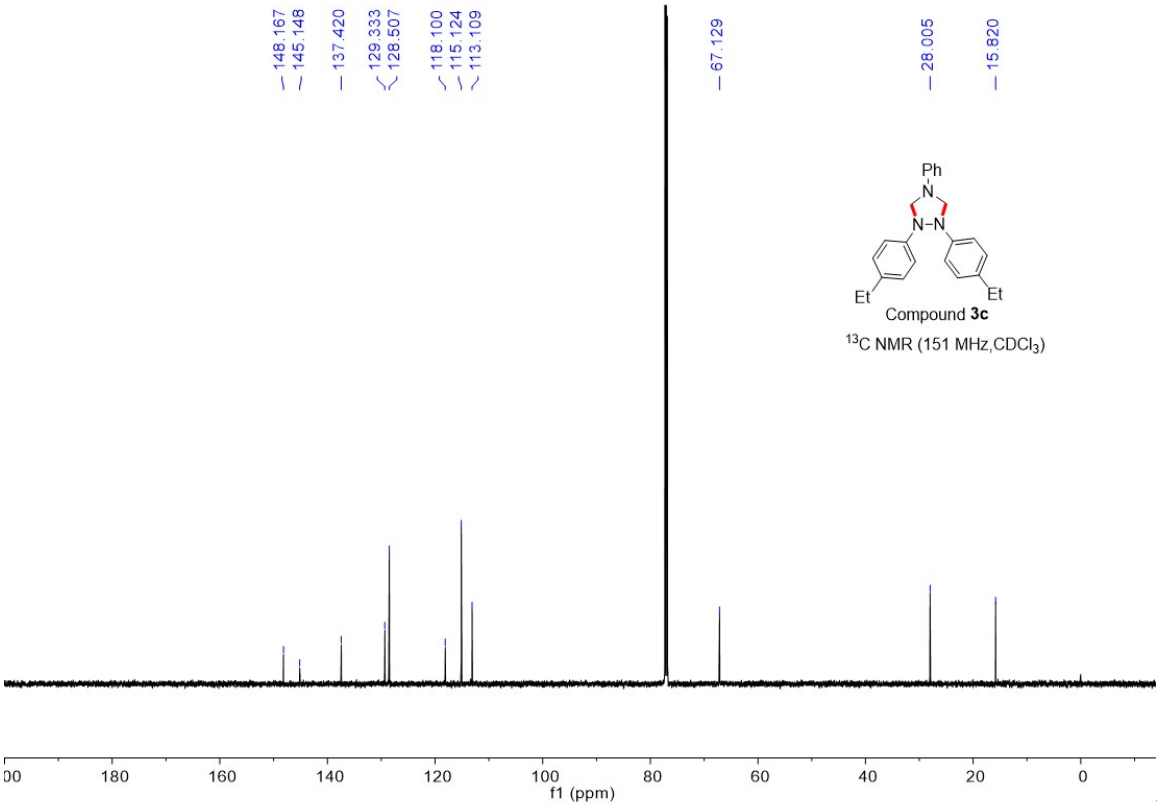
NMR spectra of 4-phenyl-1,2-di(*p*-tolyl)-1,2,4-triazolidine (**3b**)



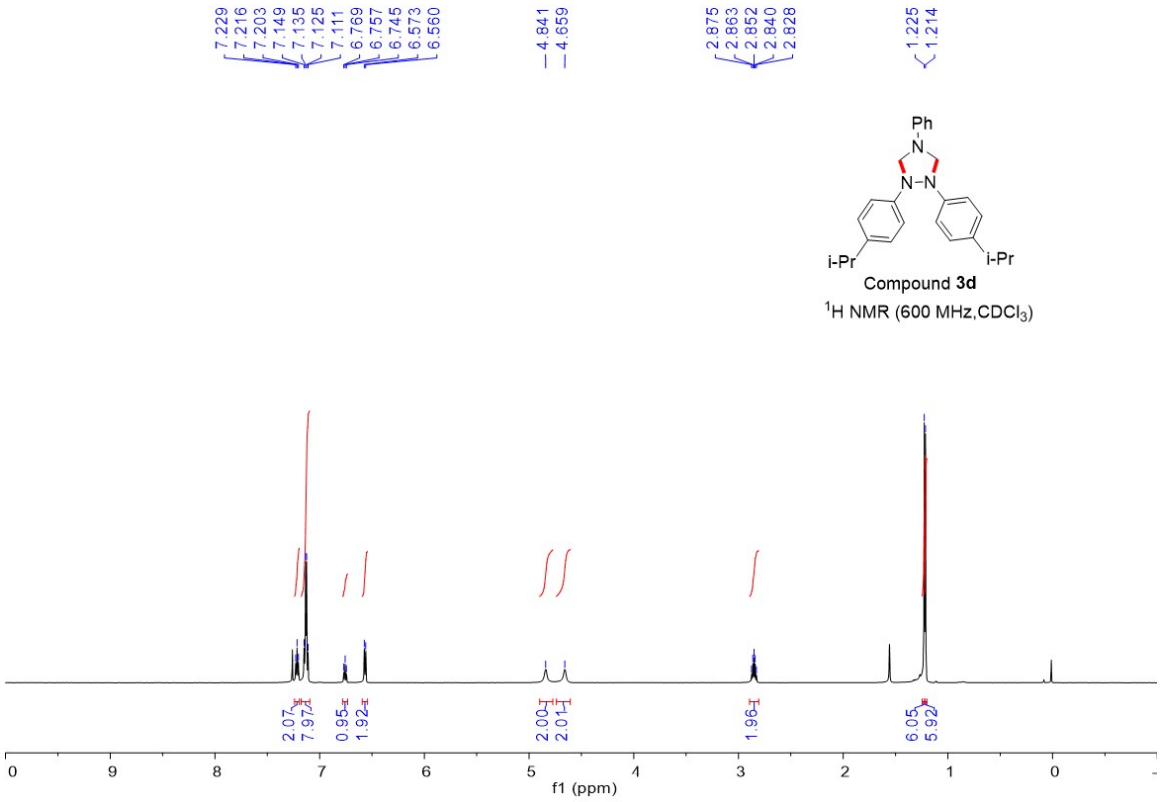


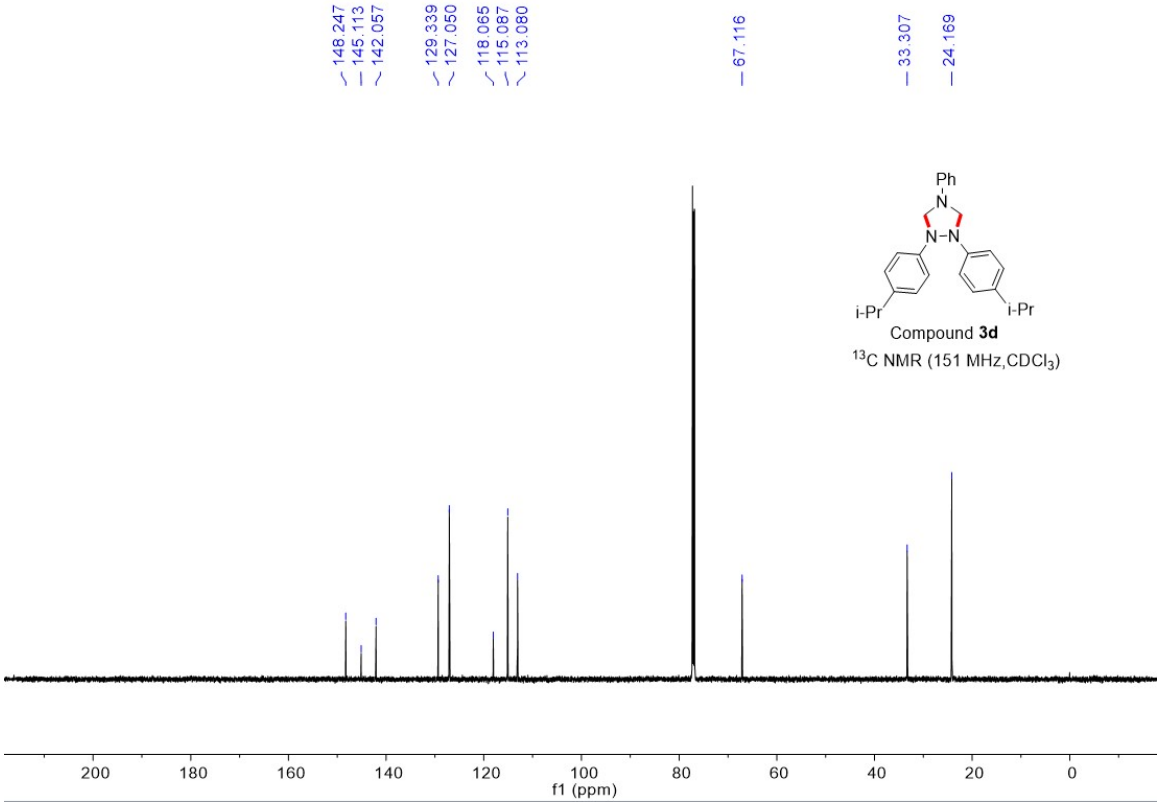
NMR spectra of 1,2-bis(4-ethylphenyl)-4-phenyl-1,2,4-triazolidine (**3c**)



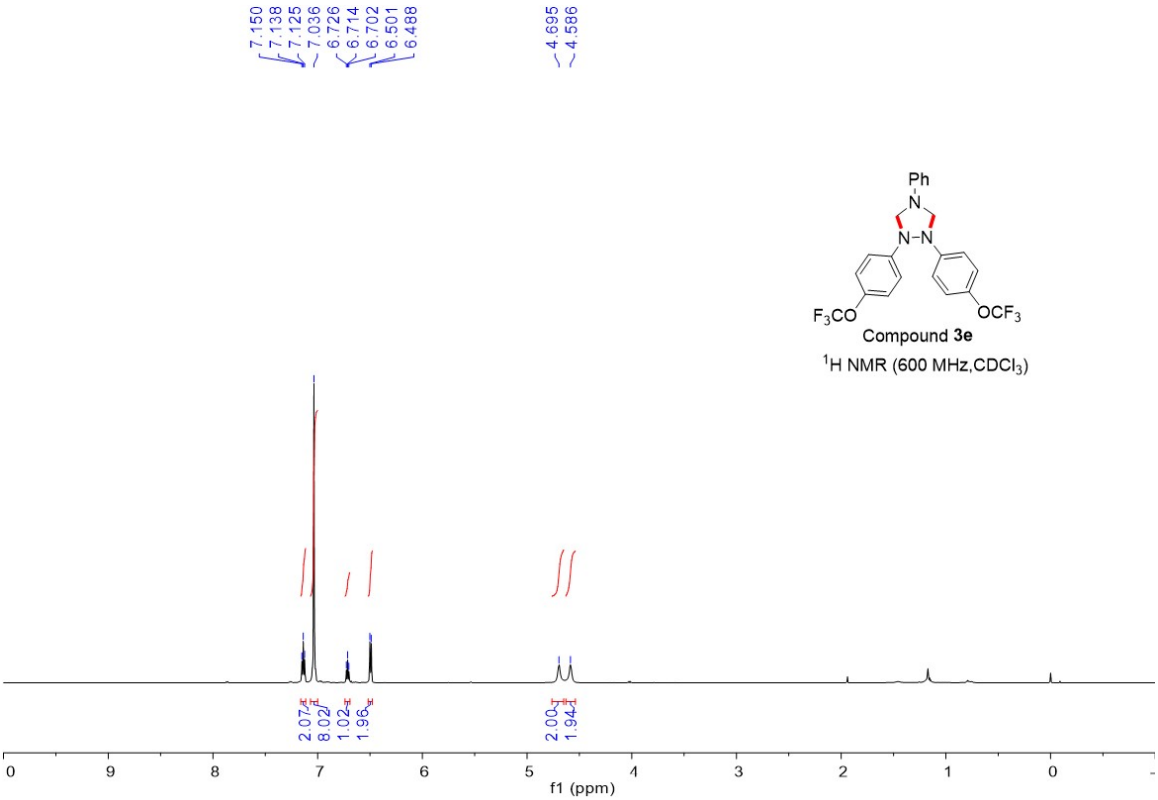


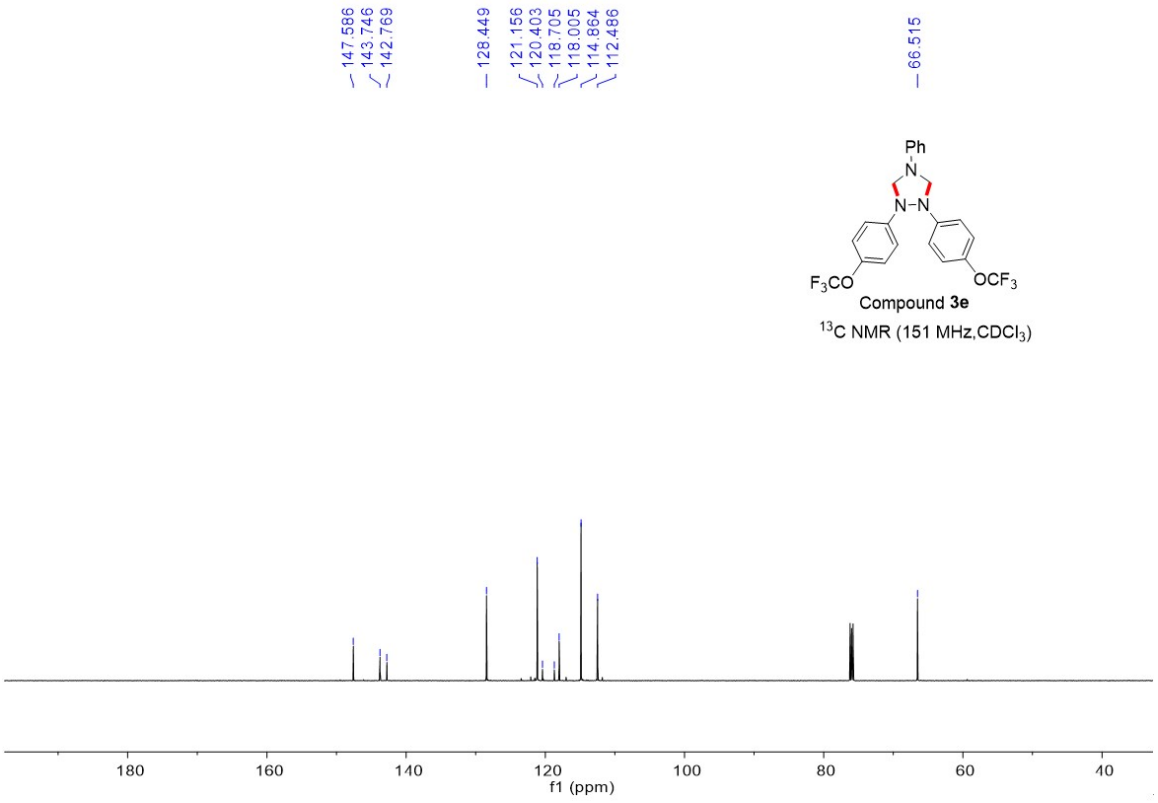
NMR spectra of 1,2-bis(4-isopropylphenyl)-4-phenyl-1,2,4-triazolidine (**3d**)

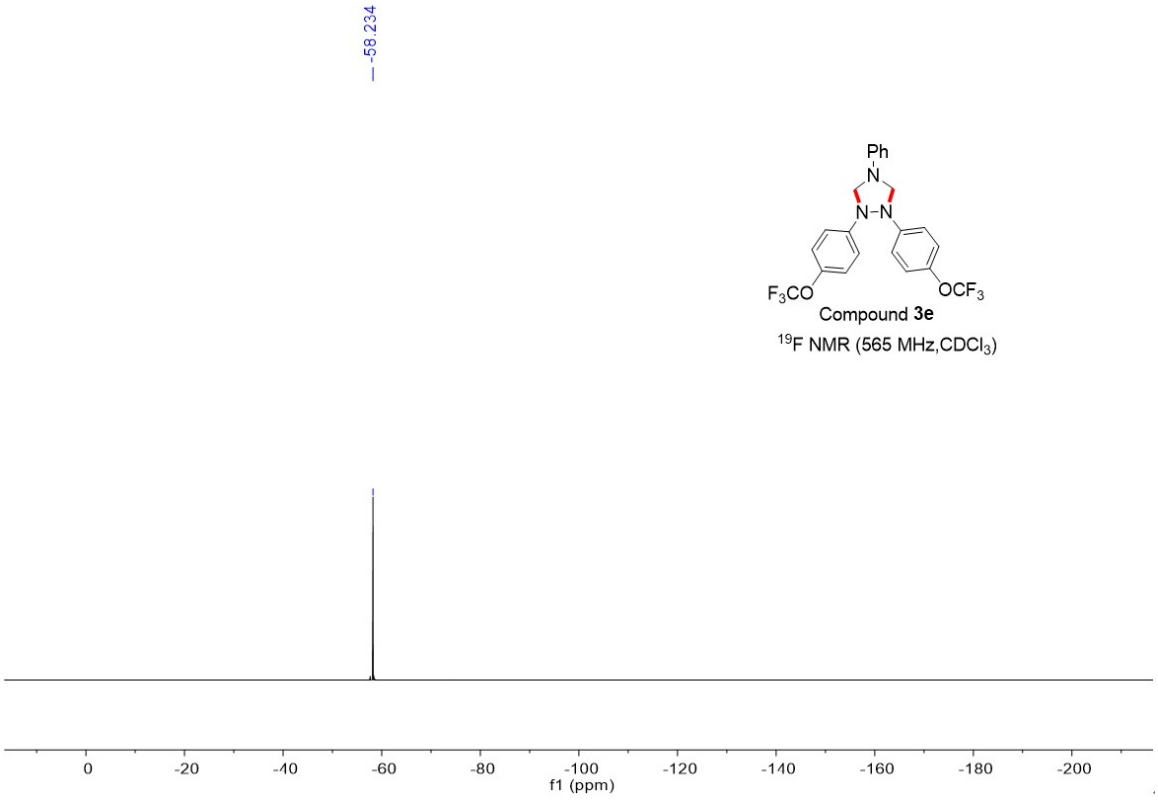




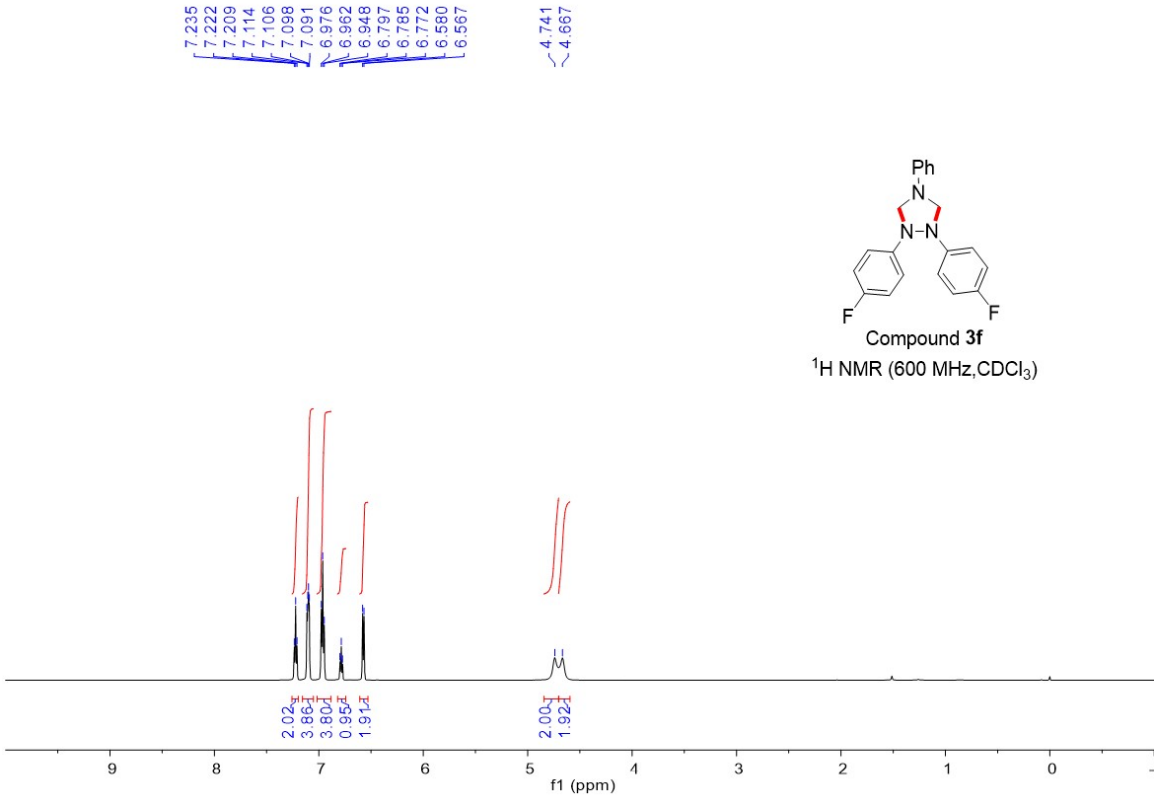
NMR spectra of 4-phenyl-1,2-bis(4-(trifluoromethoxy)phenyl)-1,2,4-triazolidine (**3e**)

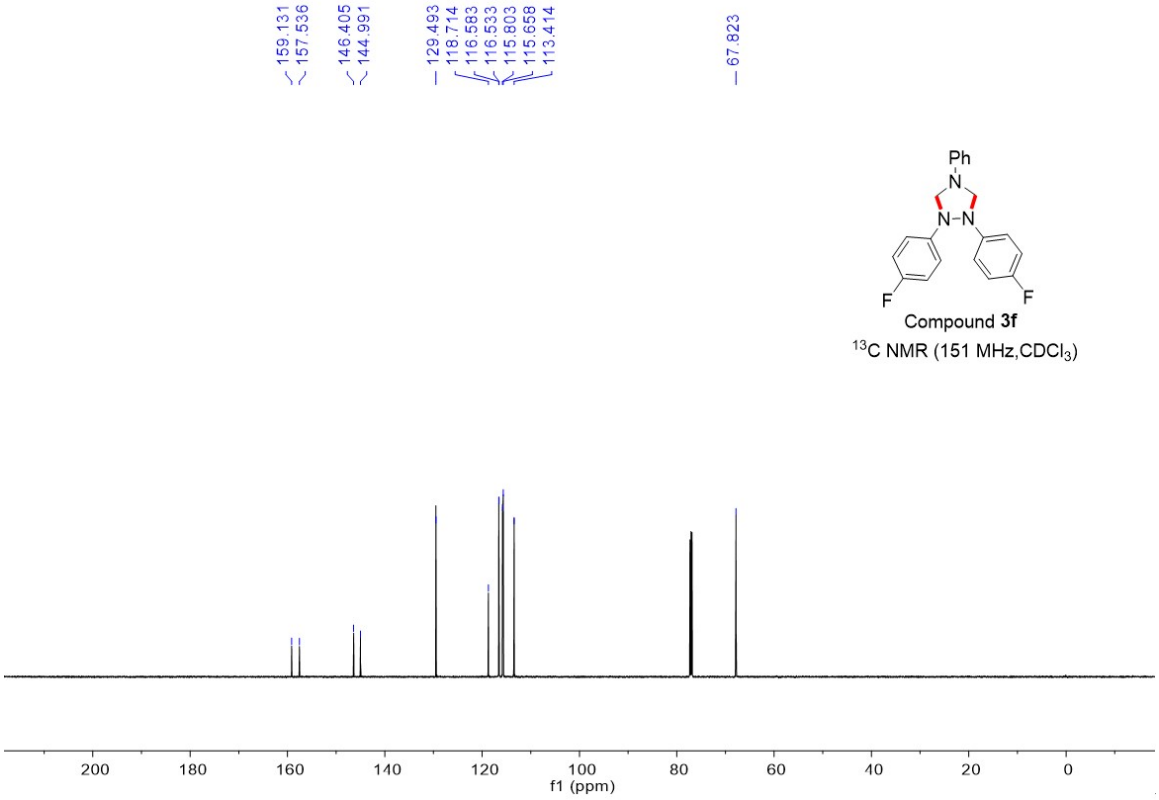






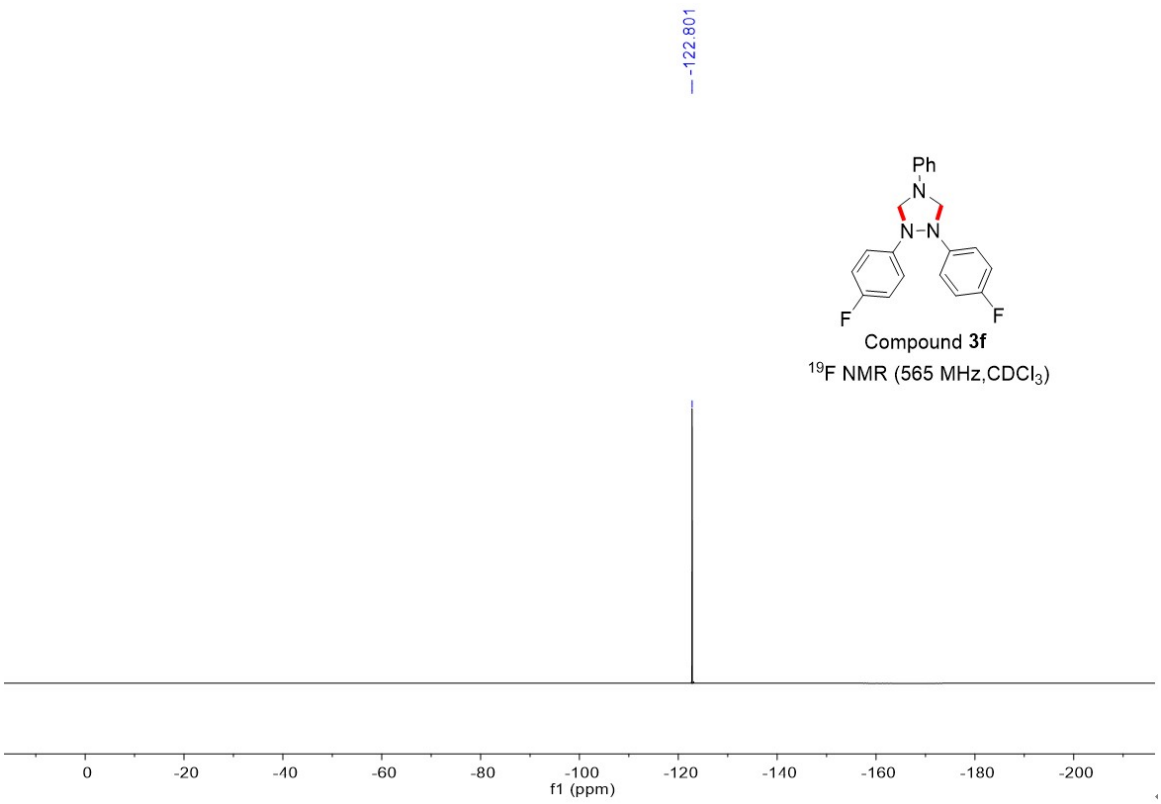
NMR spectra of 1,2-bis(4-fluorophenyl)-4-phenyl-1,2,4-triazolidine (**3f**)





Compound **3f**

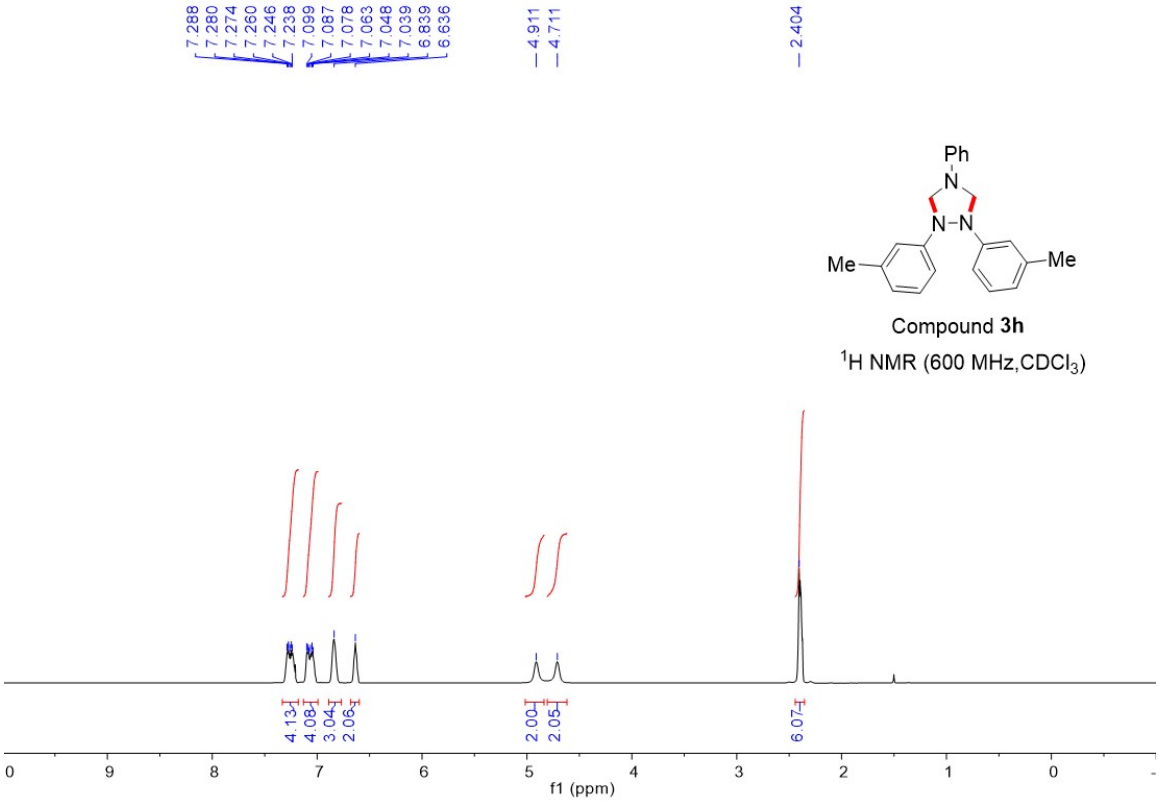
^{13}C NMR (151 MHz,$CDCl_3$)

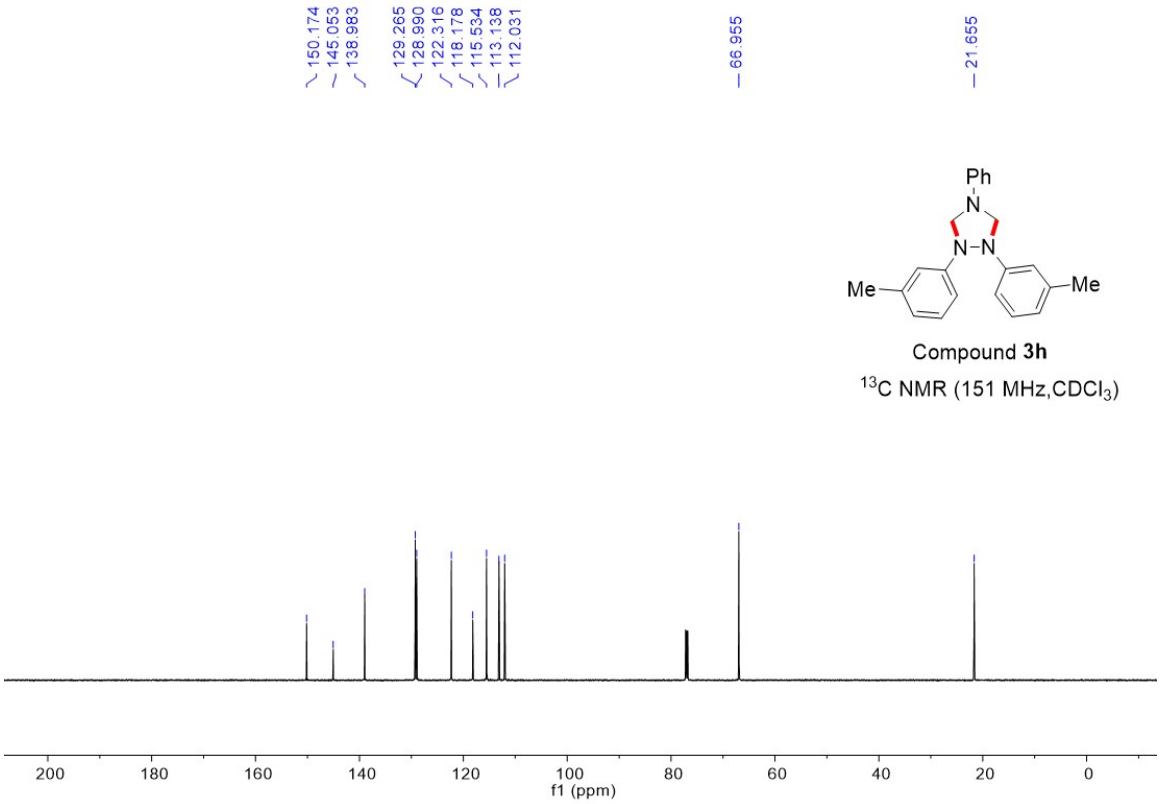


Compound **3f**

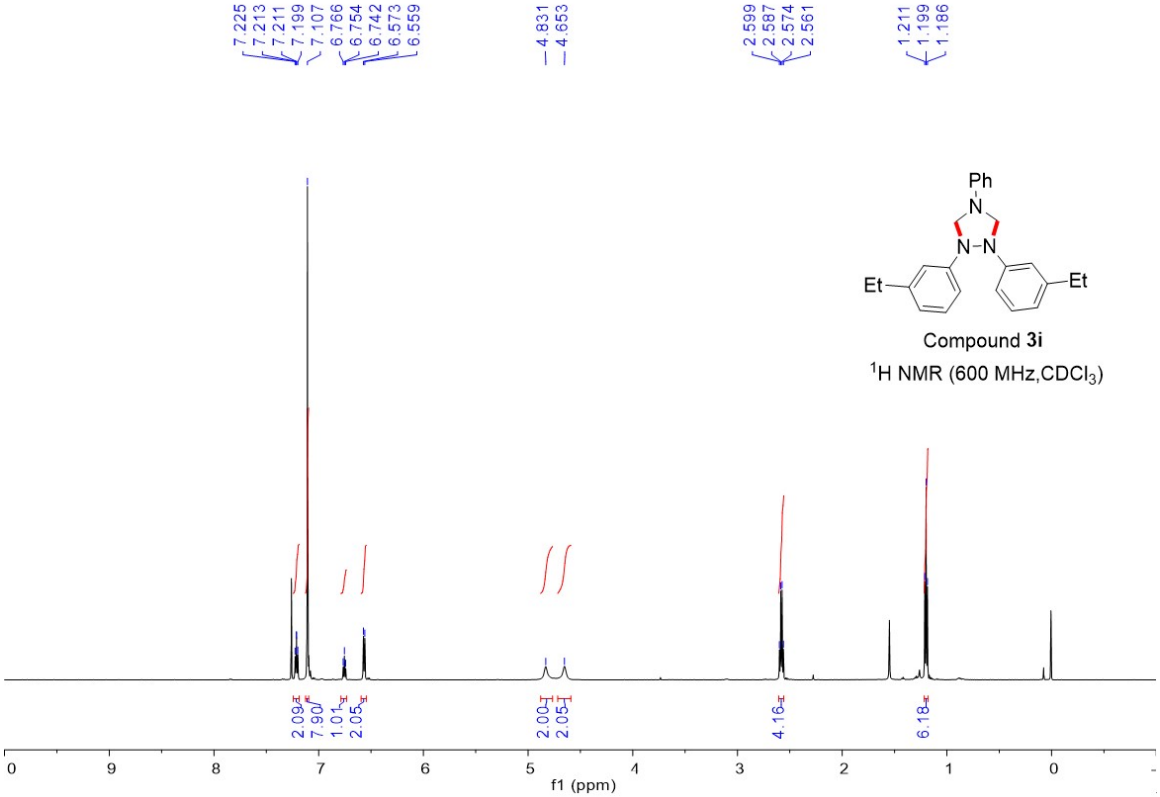
^{19}F NMR (565 MHz,$CDCl_3$)

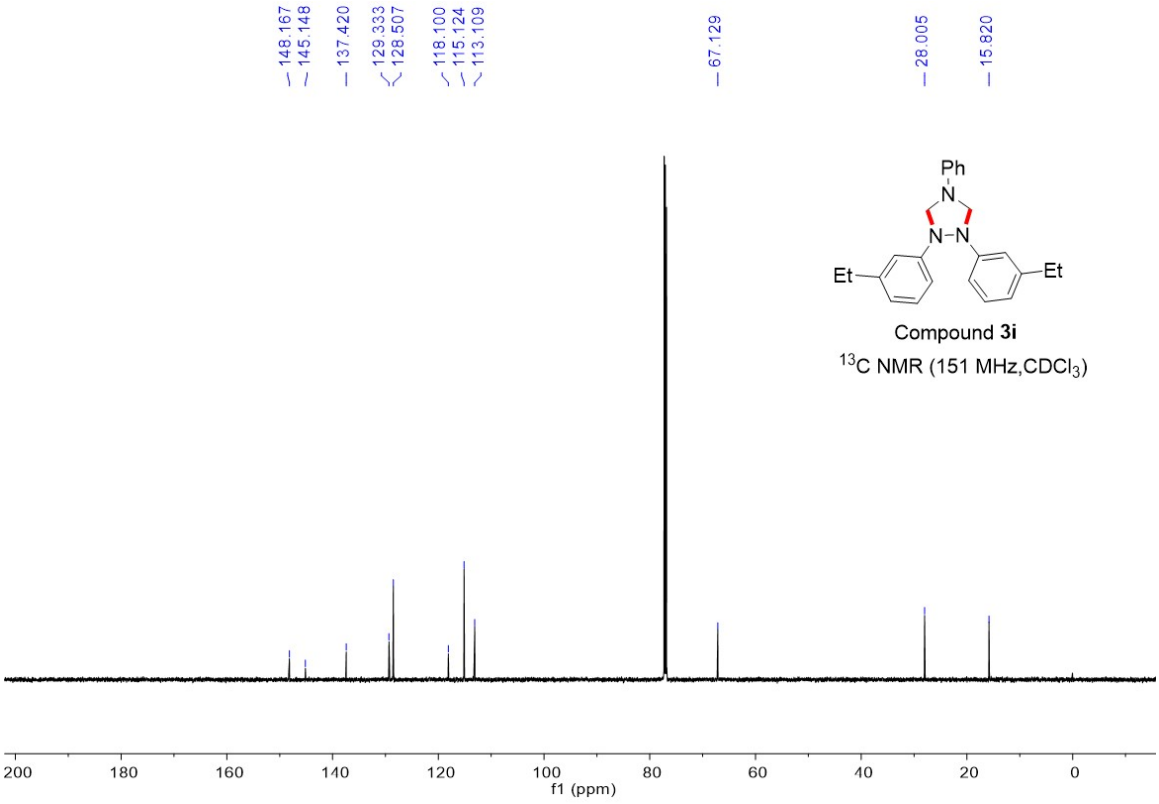
NMR spectra of 4-phenyl-1,2-di(*m*-tolyl)-1,2,4-triazolidine (**3h**)



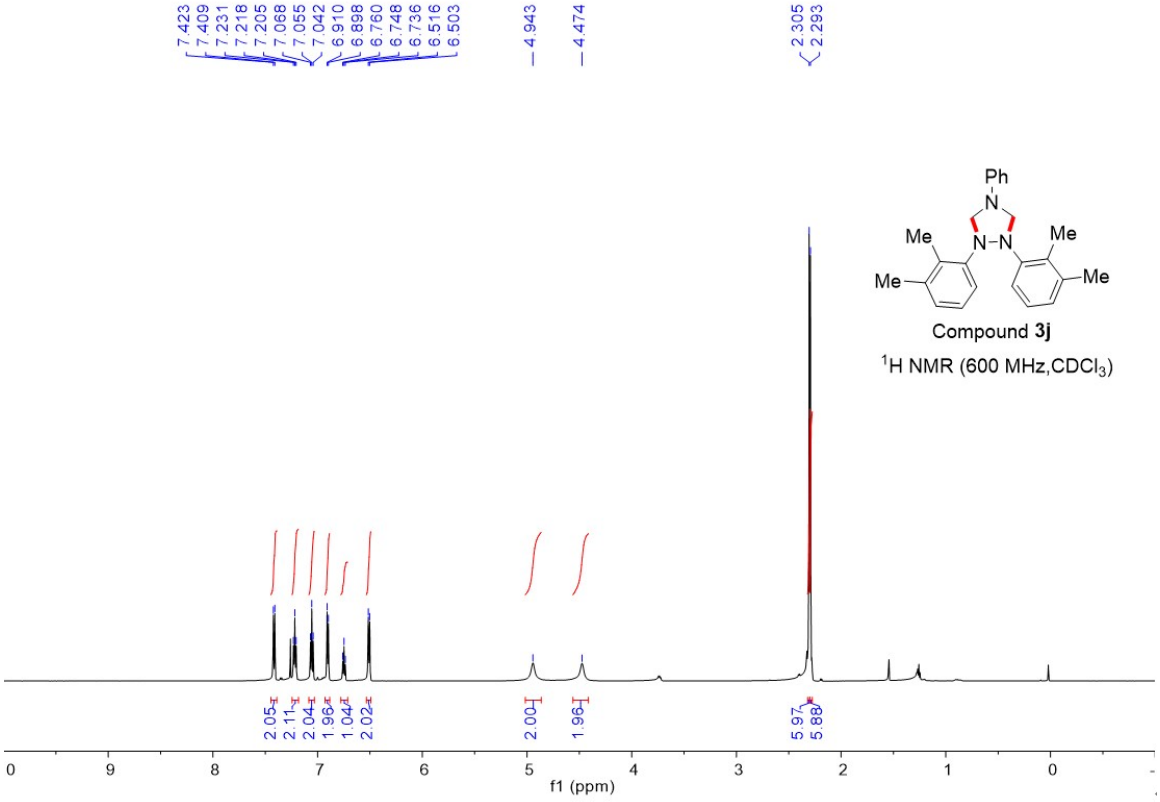


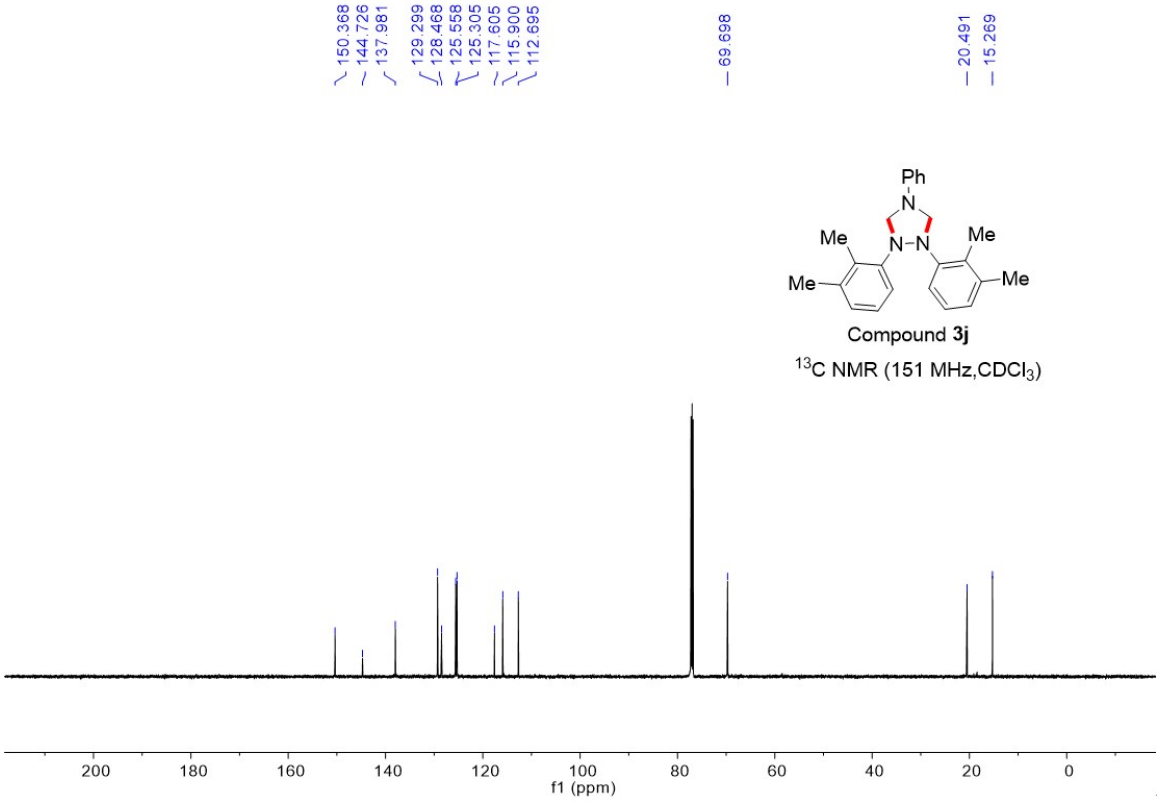
NMR spectra of 1,2-bis(3-ethylphenyl)-4-phenyl-1,2,4-triazolidine (**3i**)



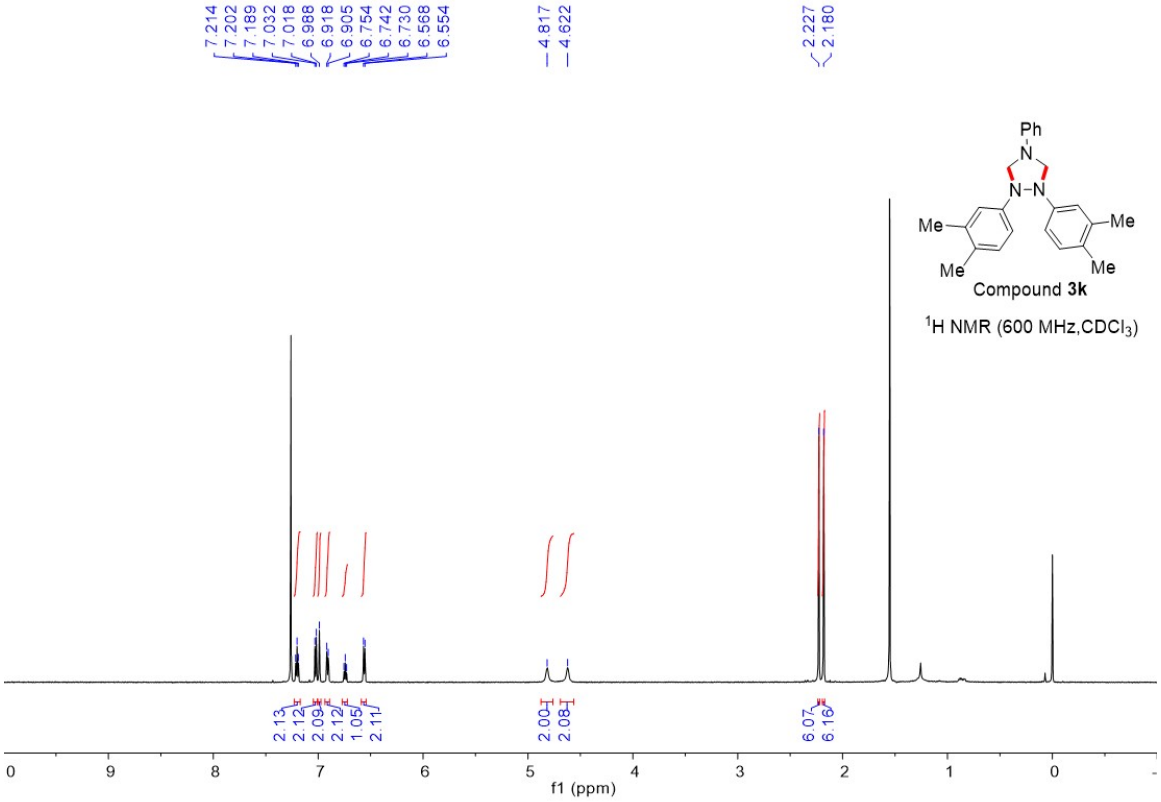


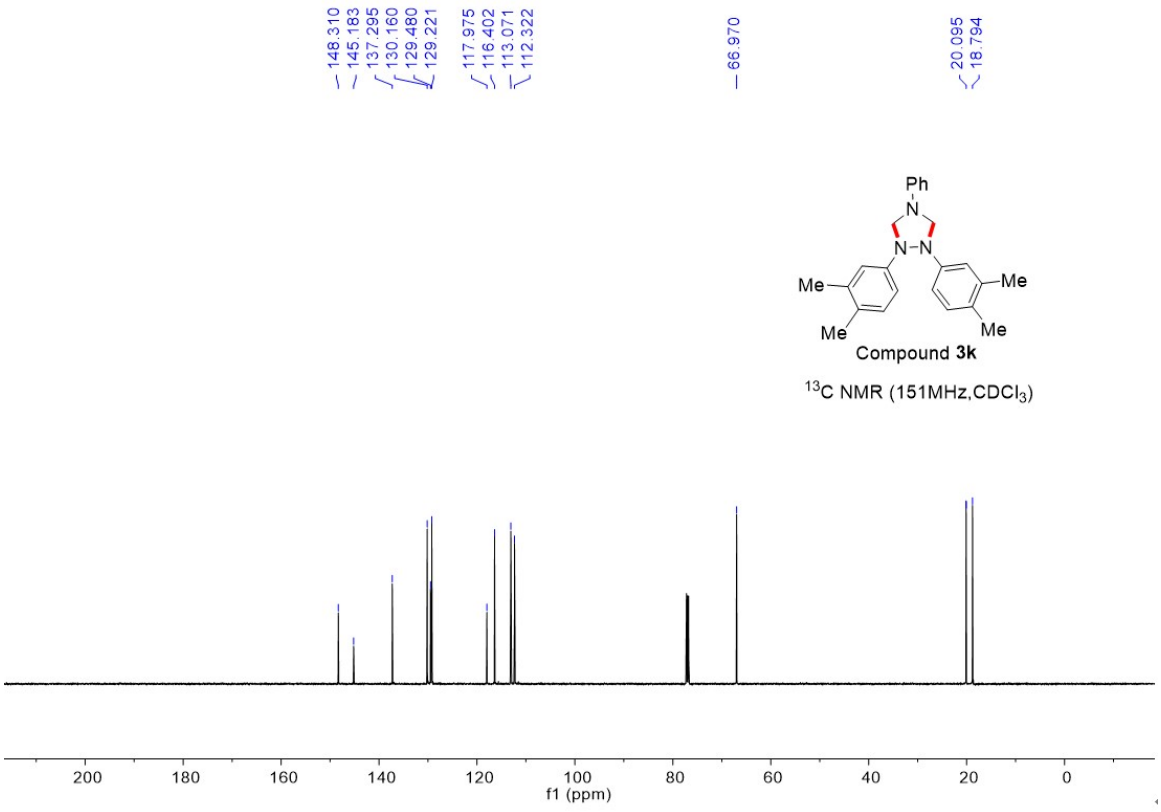
NMR spectra of 1,2-bis(2,3-dimethylphenyl)-4-phenyl-1,2,4-triazolidine (**3j**)



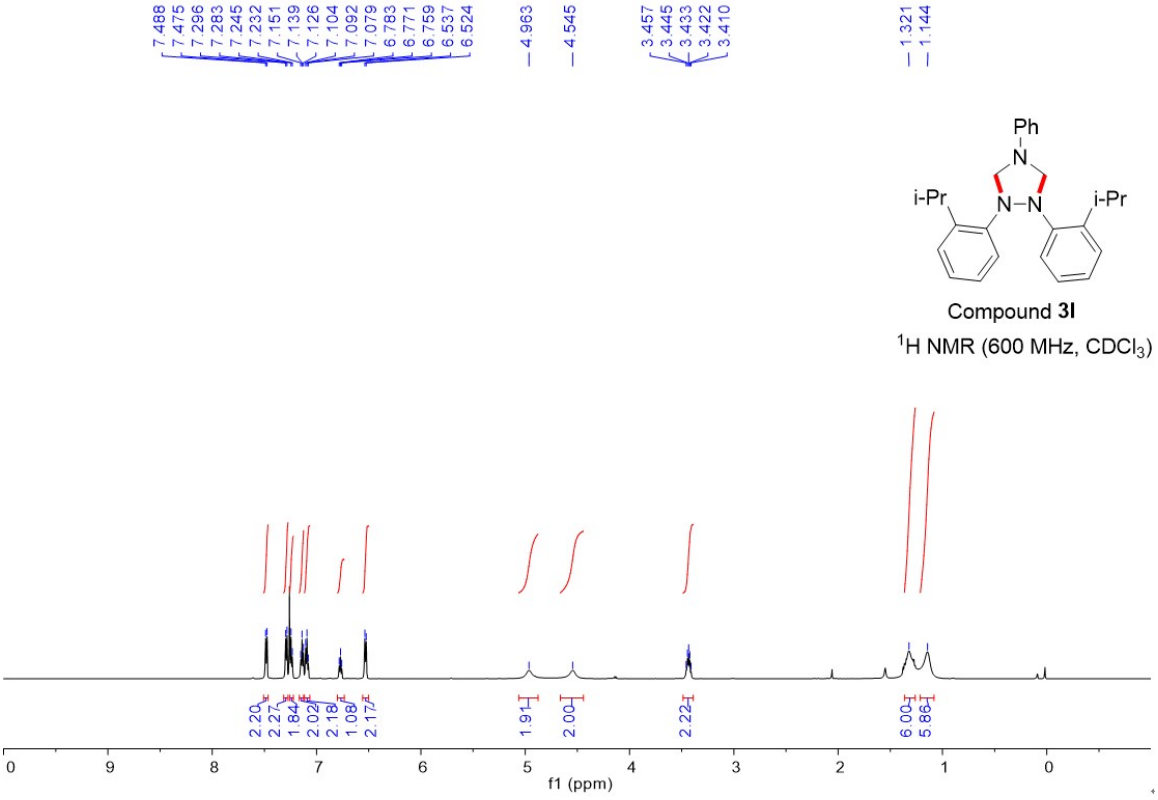


NMR spectra of 1,2-bis(3,4-dimethylphenyl)-4-phenyl-1,2,4-triazolidine (**3k**)



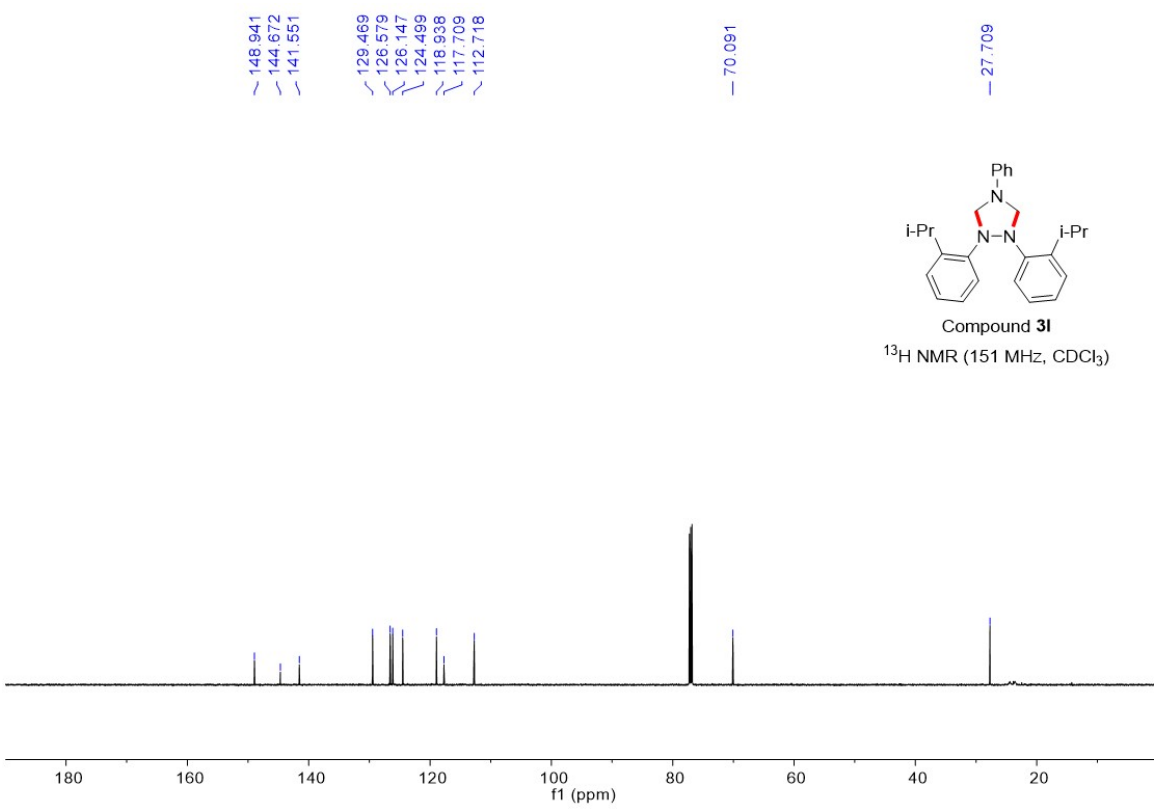


NMR spectra of 1,2-bis(2-isopropylphenyl)-4-phenyl-1,2,4-triazolidine (**3l**)



Compound **3l**

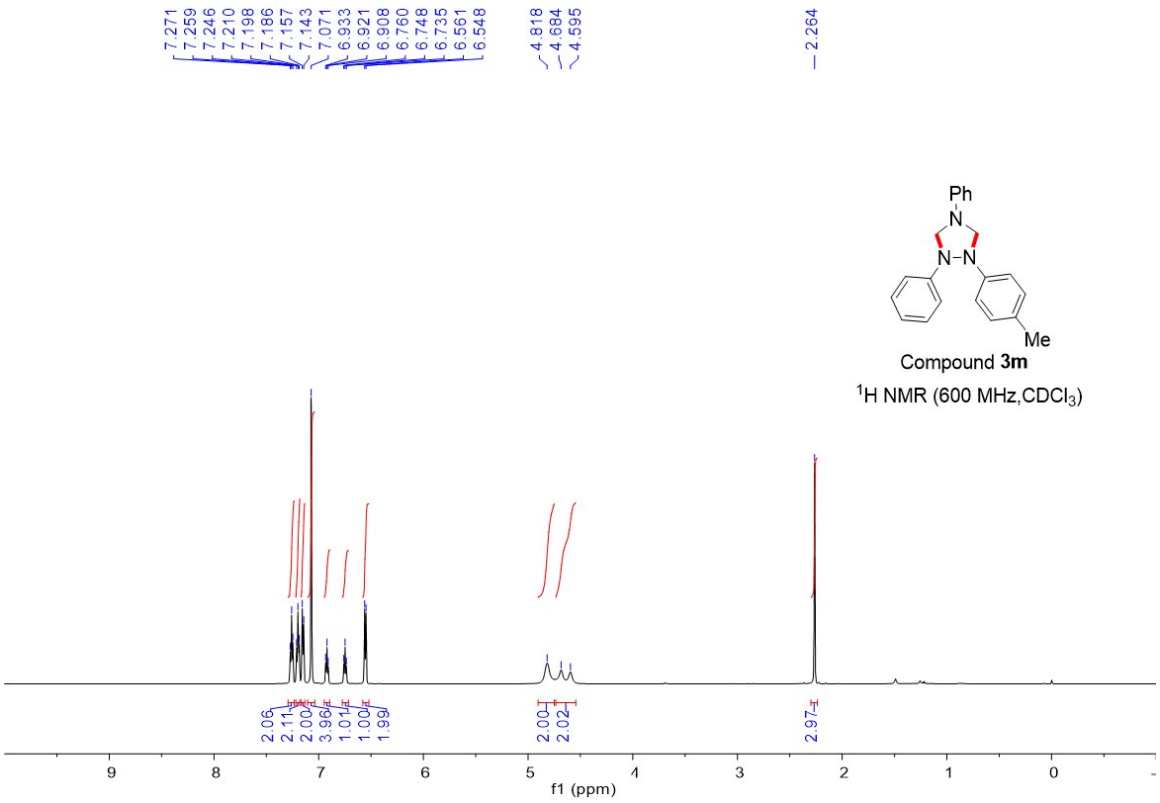
^{1}H NMR (600 MHz, $CDCl_3$)

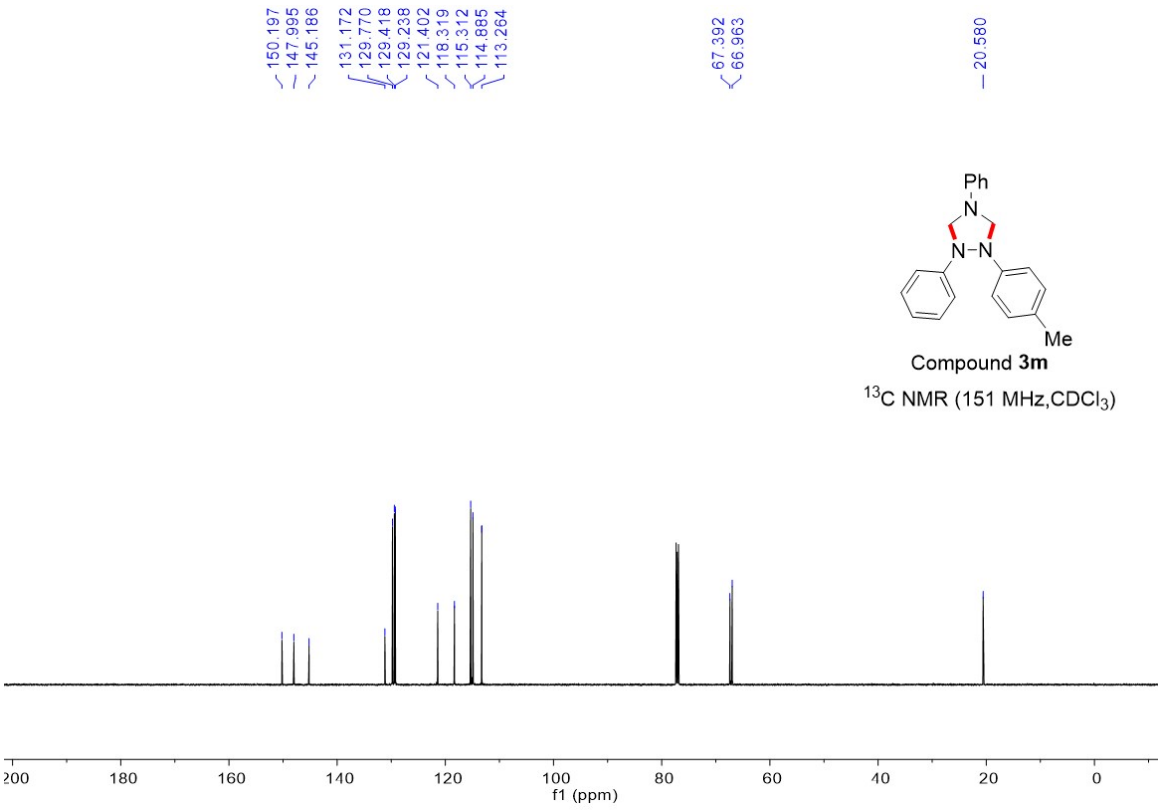


Compound **3l**

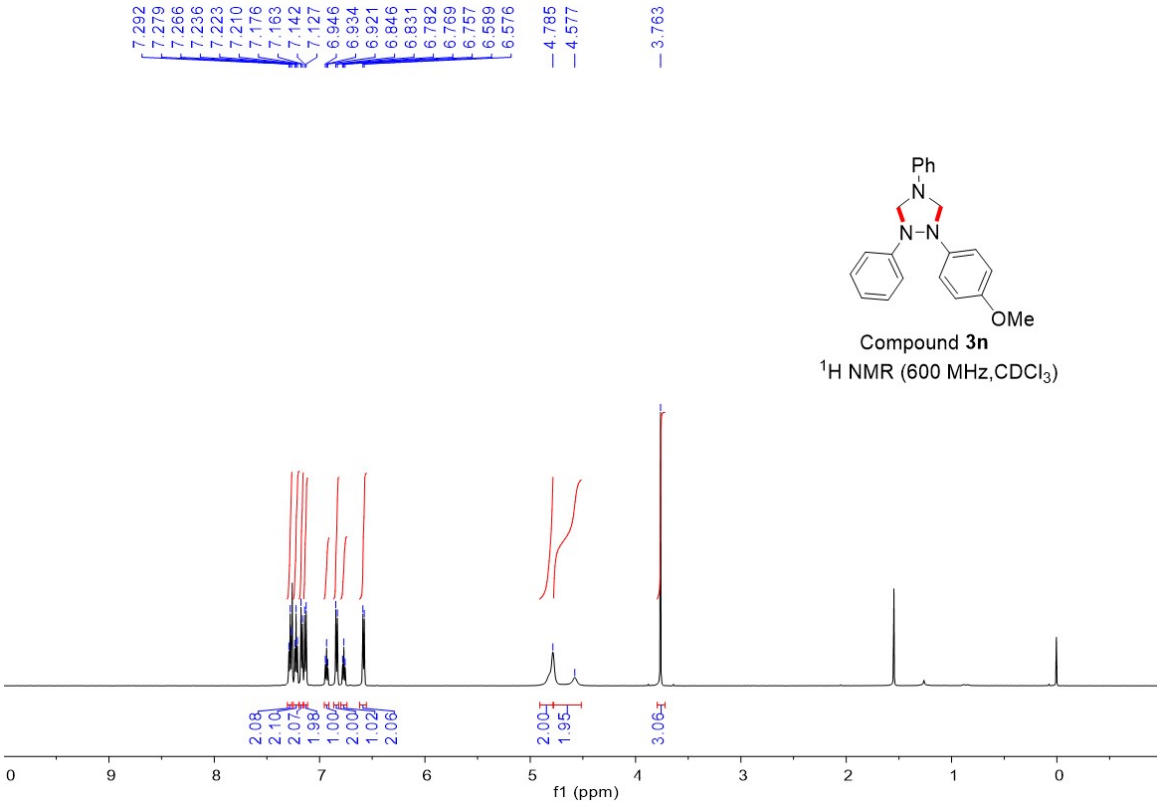
^{13}H NMR (151 MHz, $CDCl_3$)

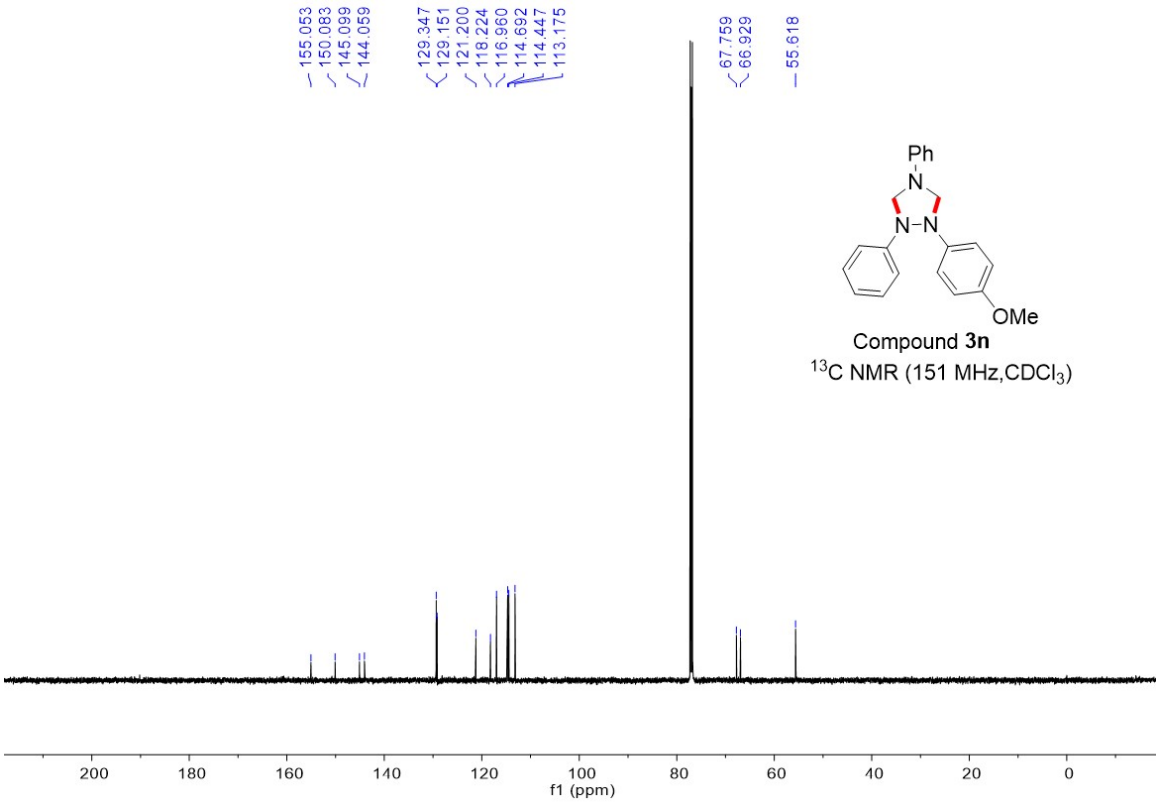
NMR spectra of 1,4-diphenyl-2-(*p*-tolyl)-1,2,4-triazolidine (**3m**)



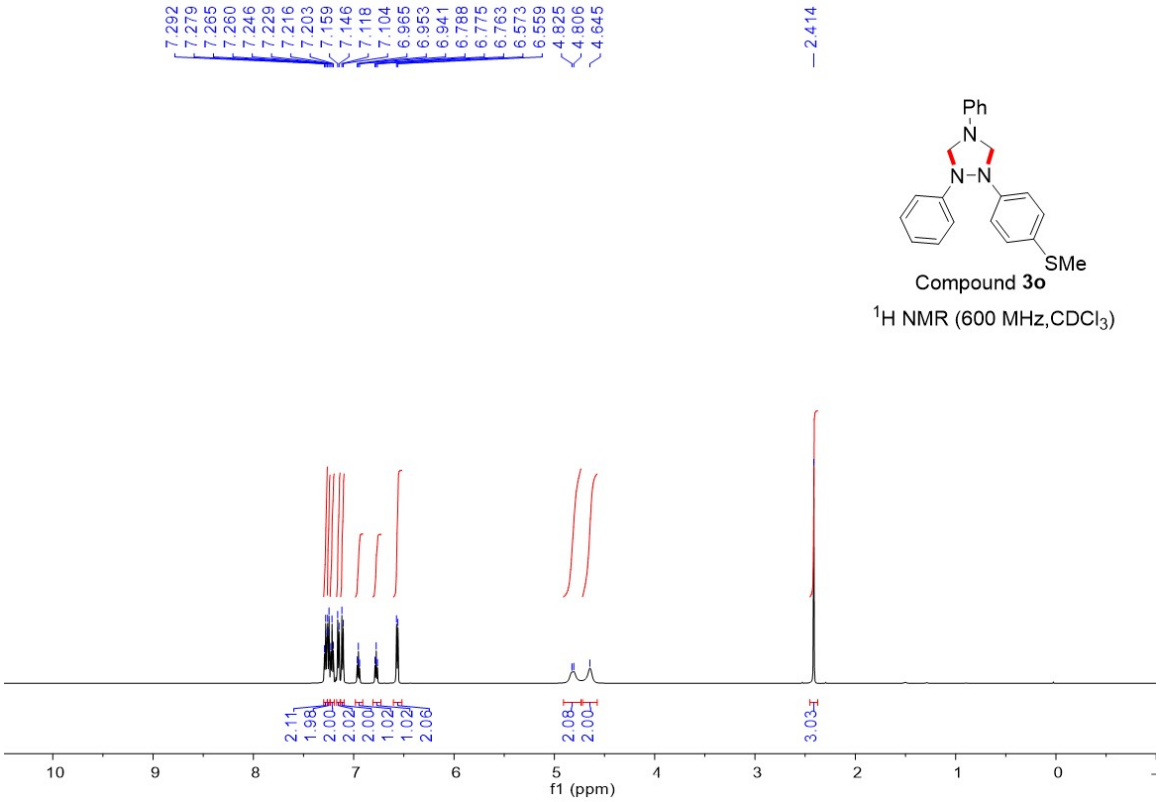


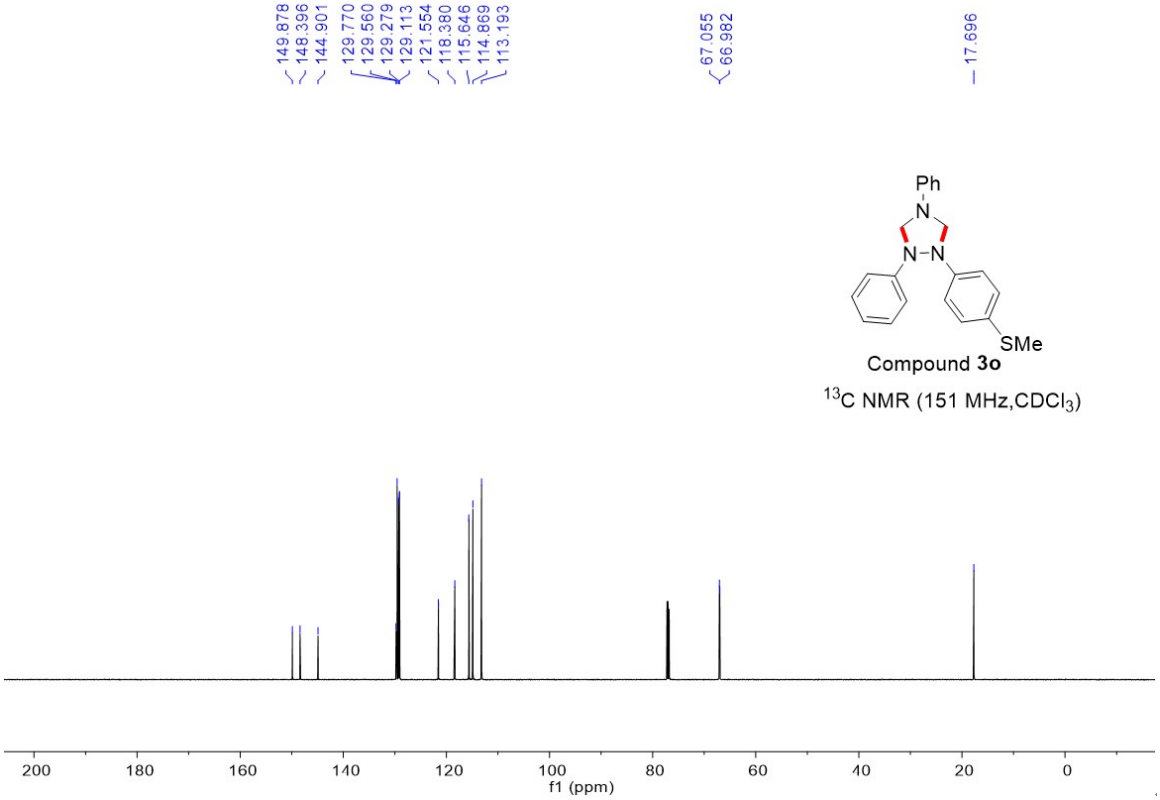
NMR spectra of 1-(4-methoxyphenyl)-2,4-diphenyl-1,2,4-triazolidine (**3n**)



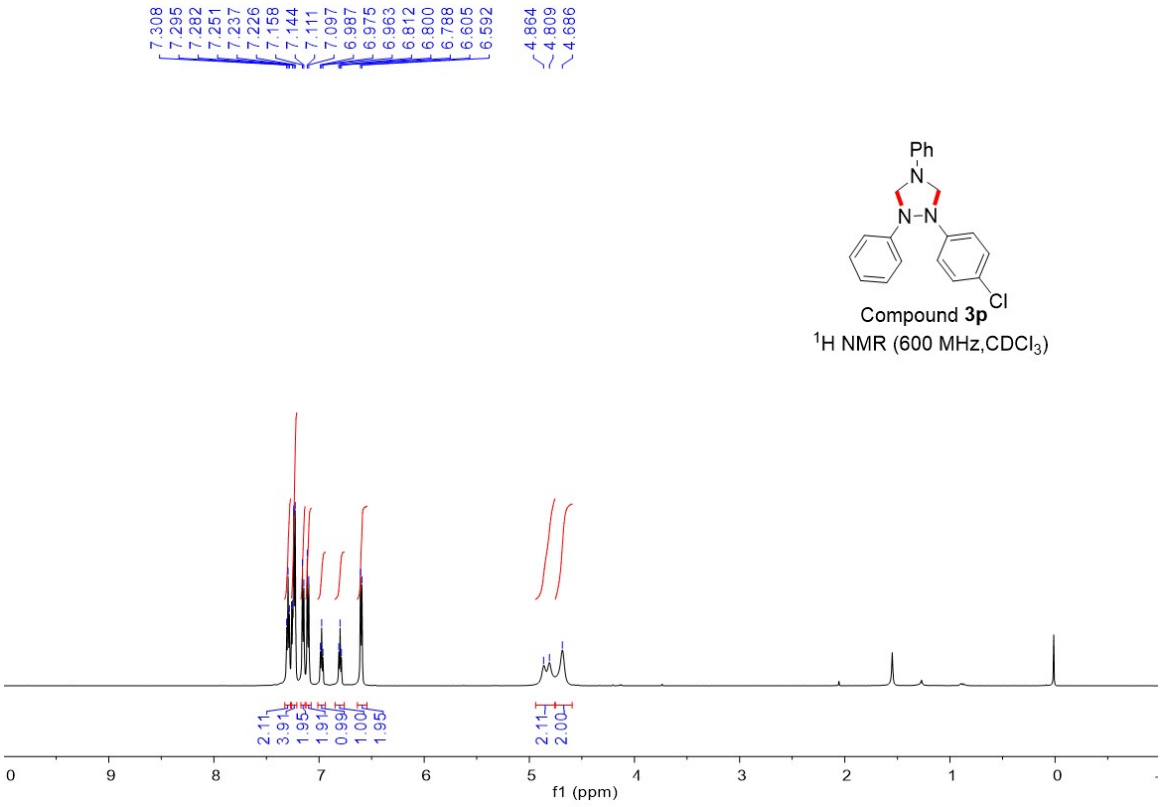


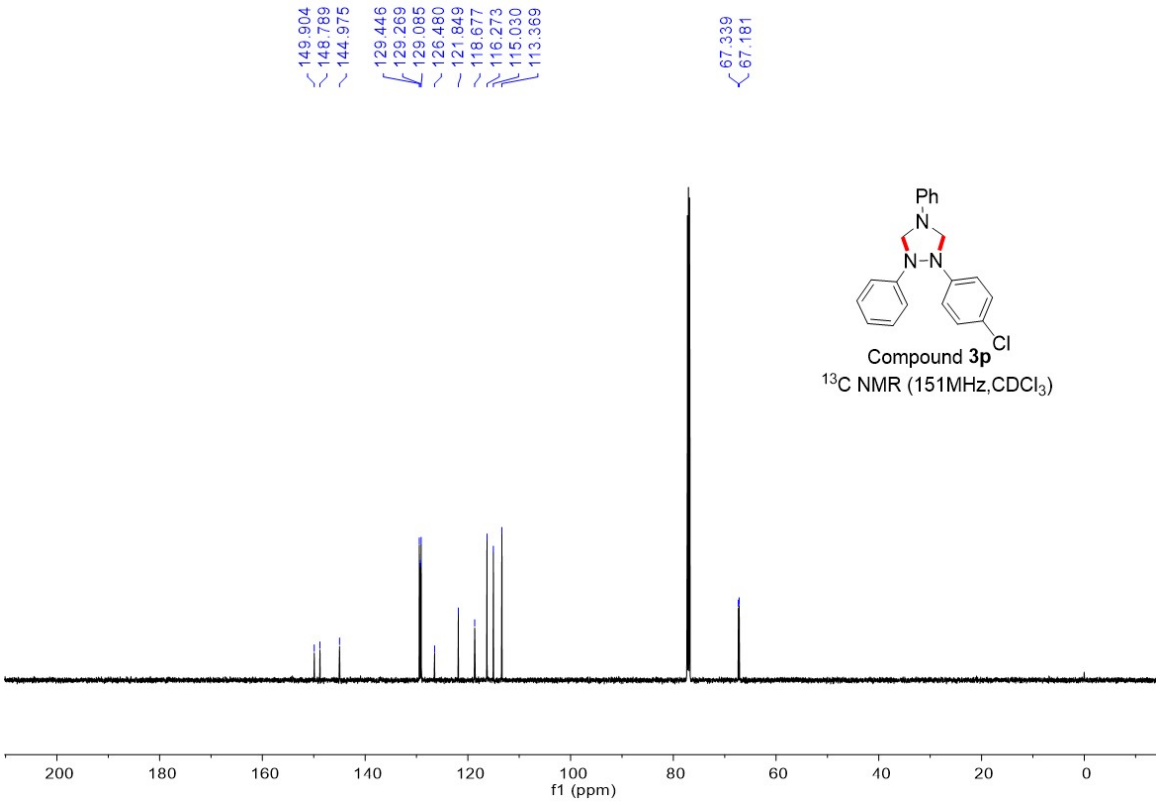
NMR spectra of 1-(4-(methylthio)phenyl)-2,4-diphenyl-1,2,4-triazolidine (**3o**)



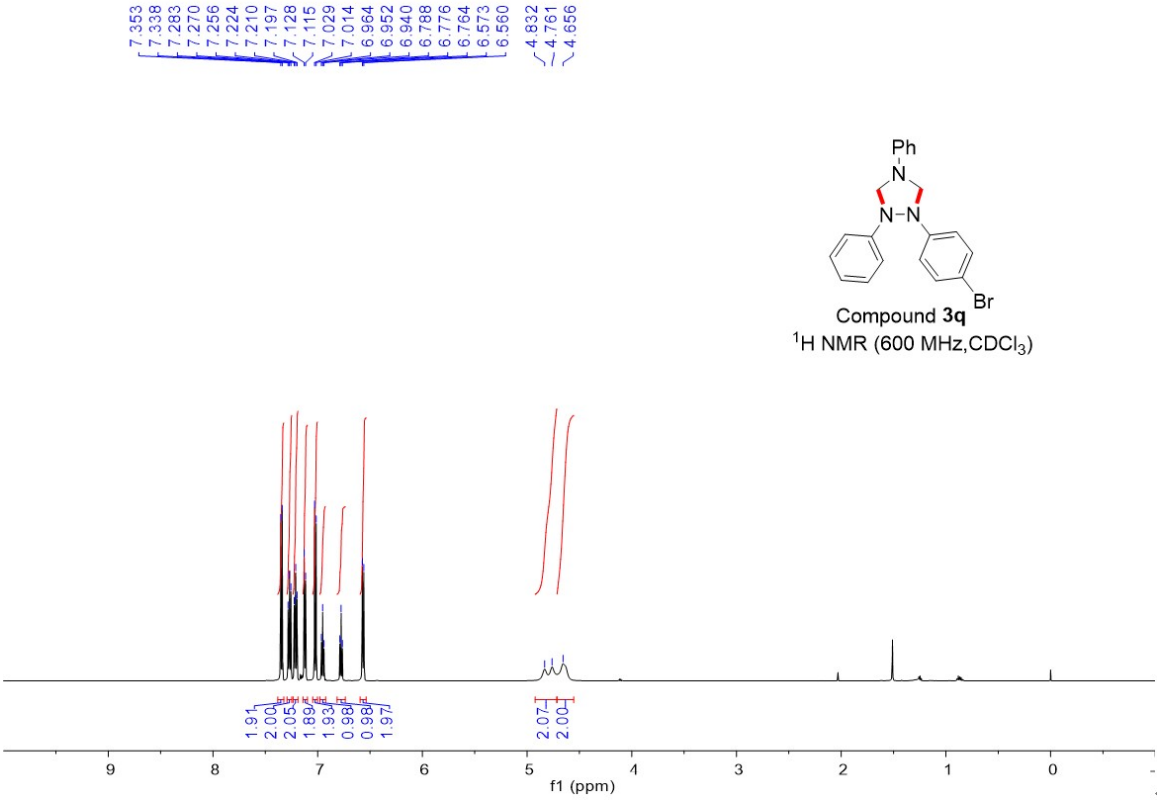


NMR spectra of 1-(4-chlorophenyl)-2,4-diphenyl-1,2,4-triazolidine (**3p**)



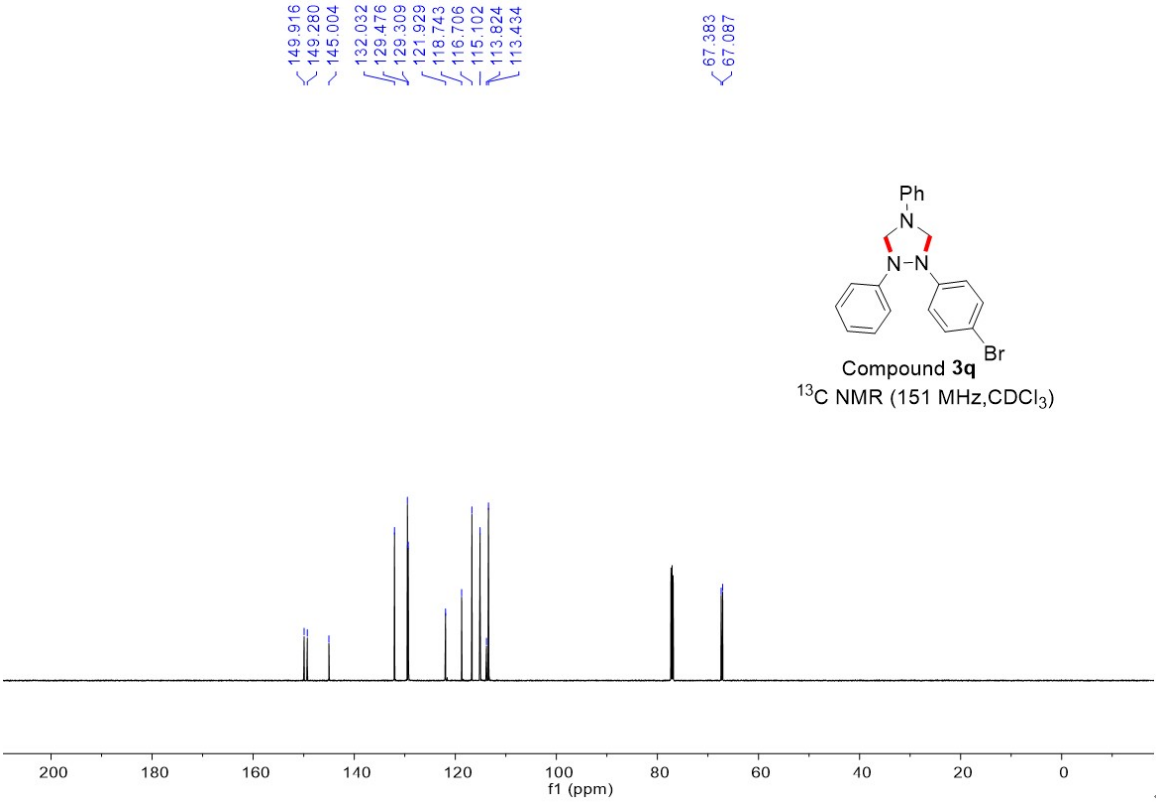


NMR spectra of 1-(4-bromophenyl)-2,4-diphenyl-1,2,4-triazolidine (**3q**)



Compound **3q**

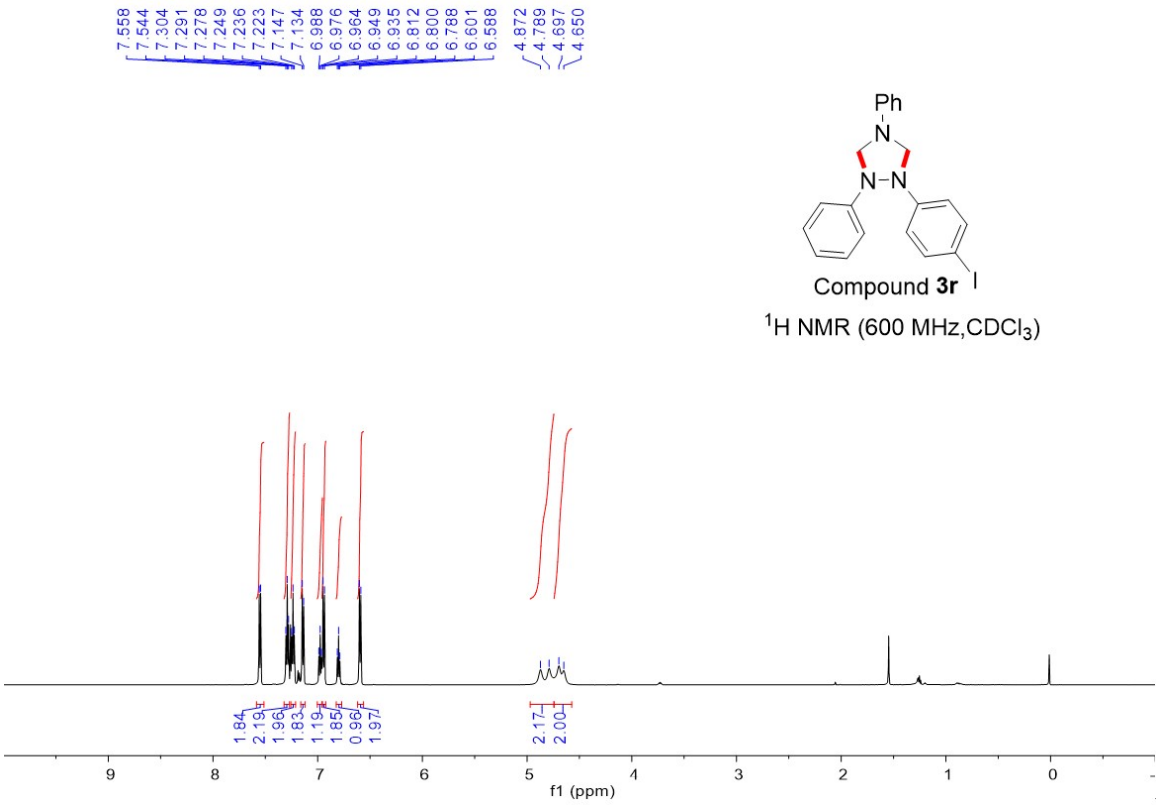
^{1}H NMR (600 MHz,$CDCl_3$)

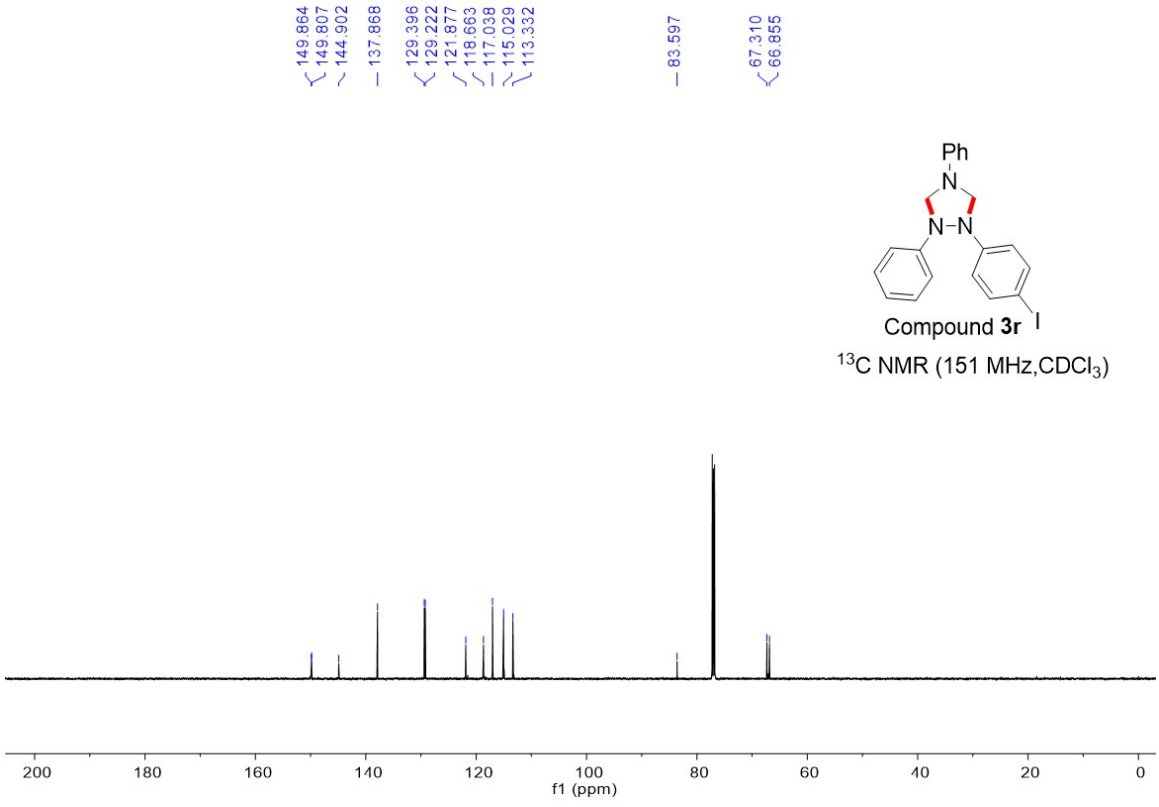


Compound **3q**

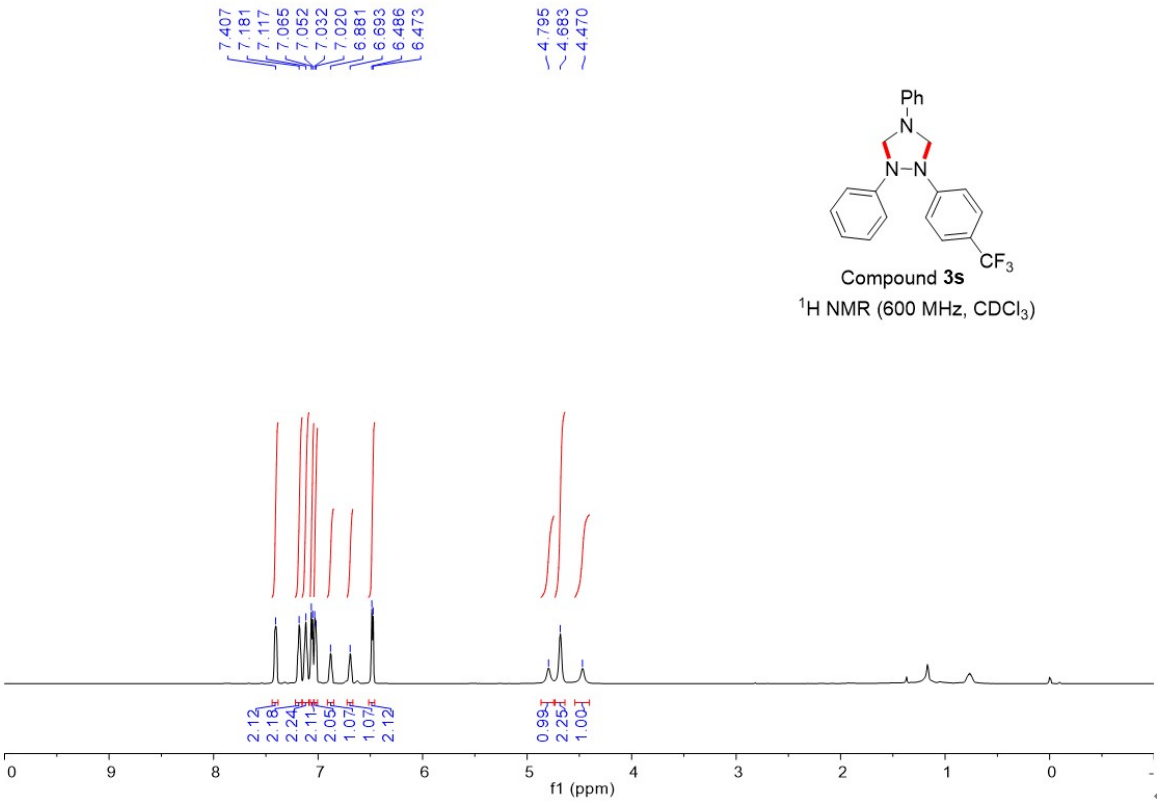
^{13}C NMR (151 MHz,$CDCl_3$)

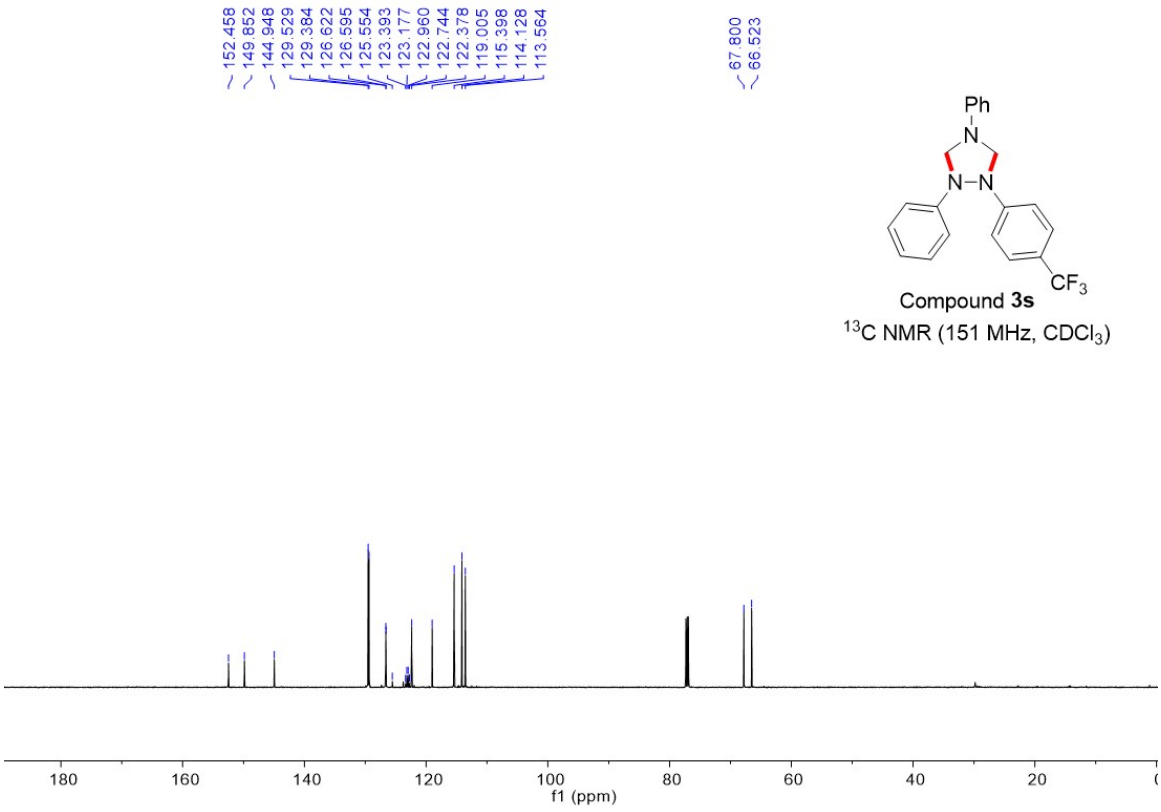
NMR spectra of 1-(4-iodophenyl)-2,4-diphenyl-1,2,4-triazolidine (**3r**)

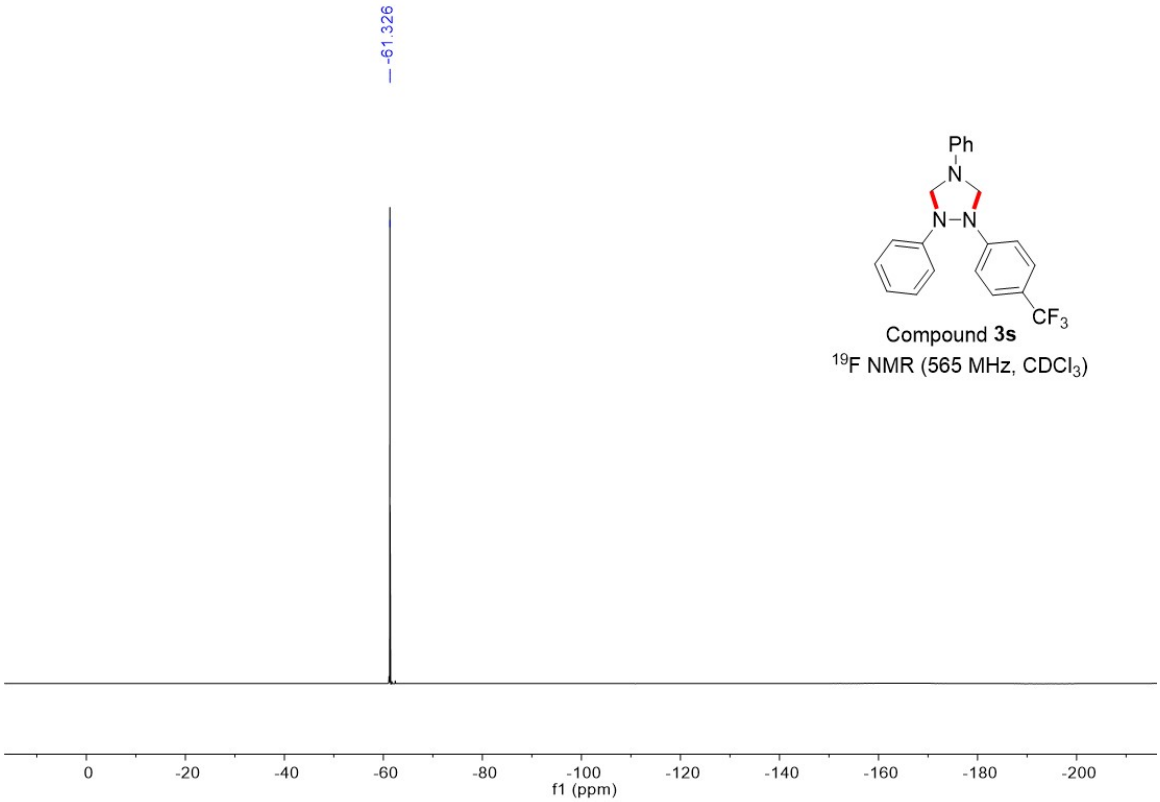




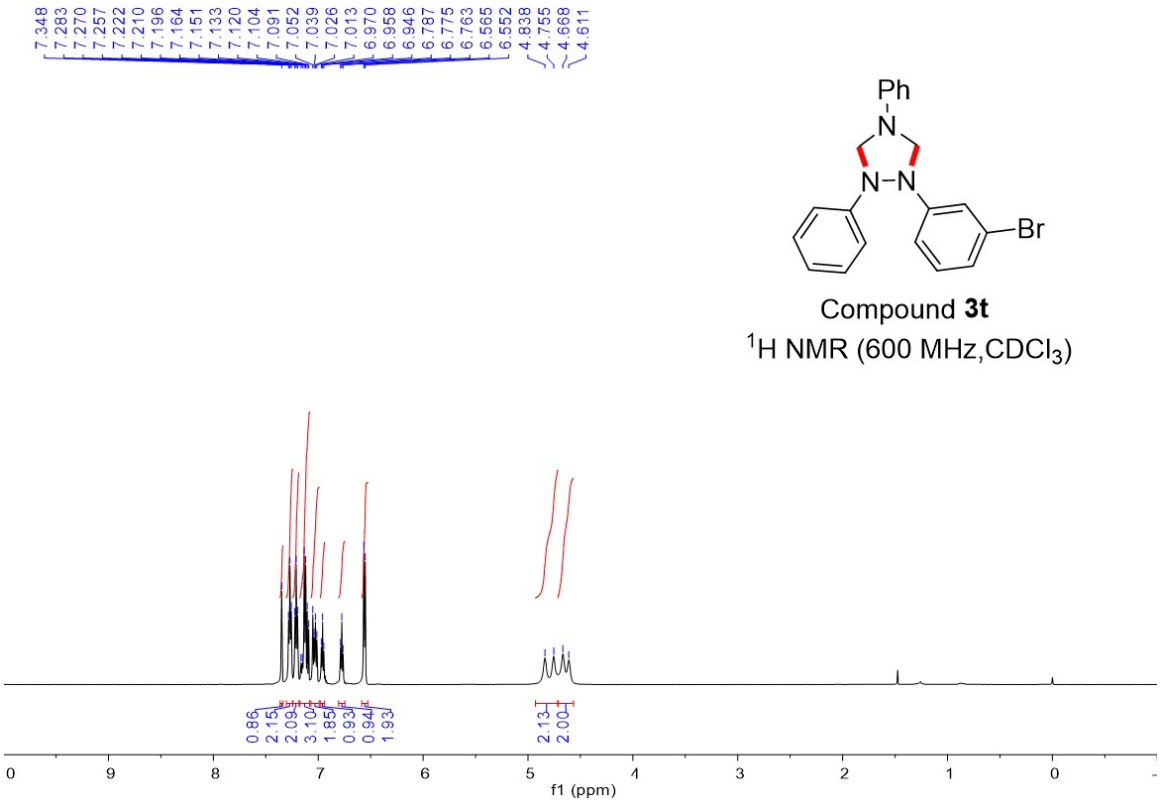
NMR spectra of 1,4-diphenyl-2-(4-(trifluoromethyl)phenyl)-1,2,4-triazolidine (**3s**)

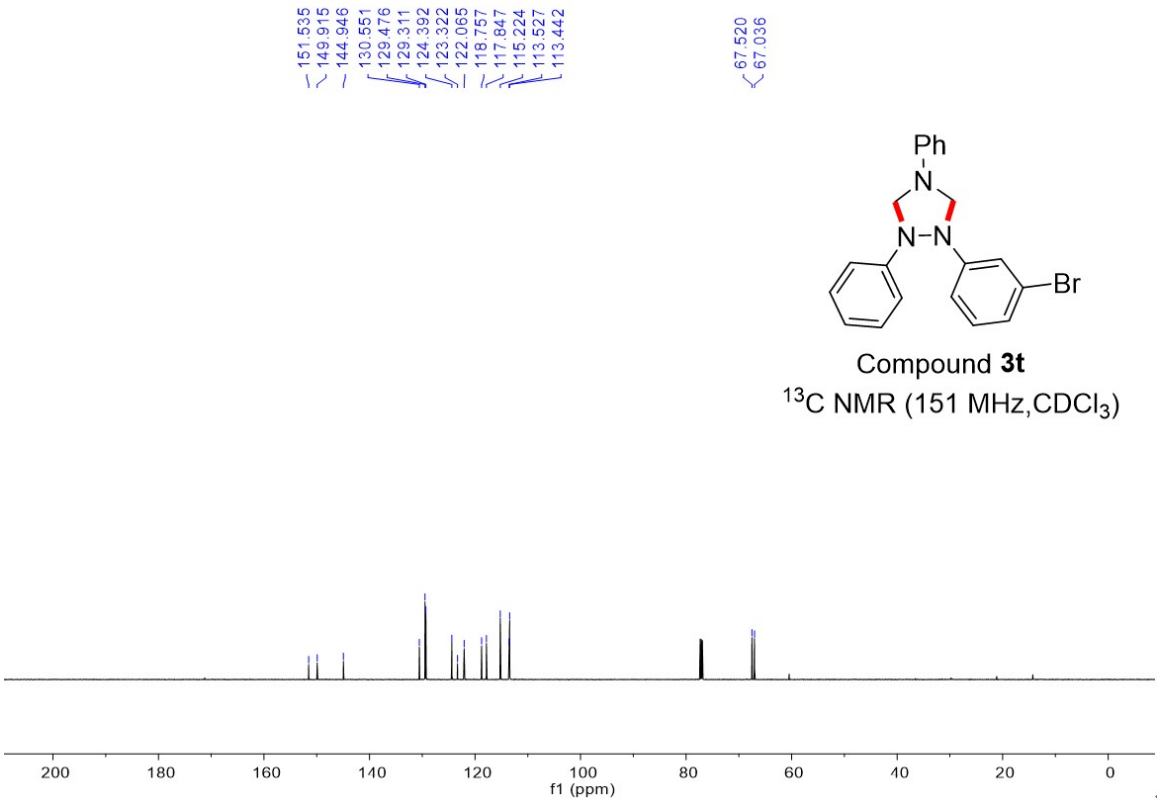




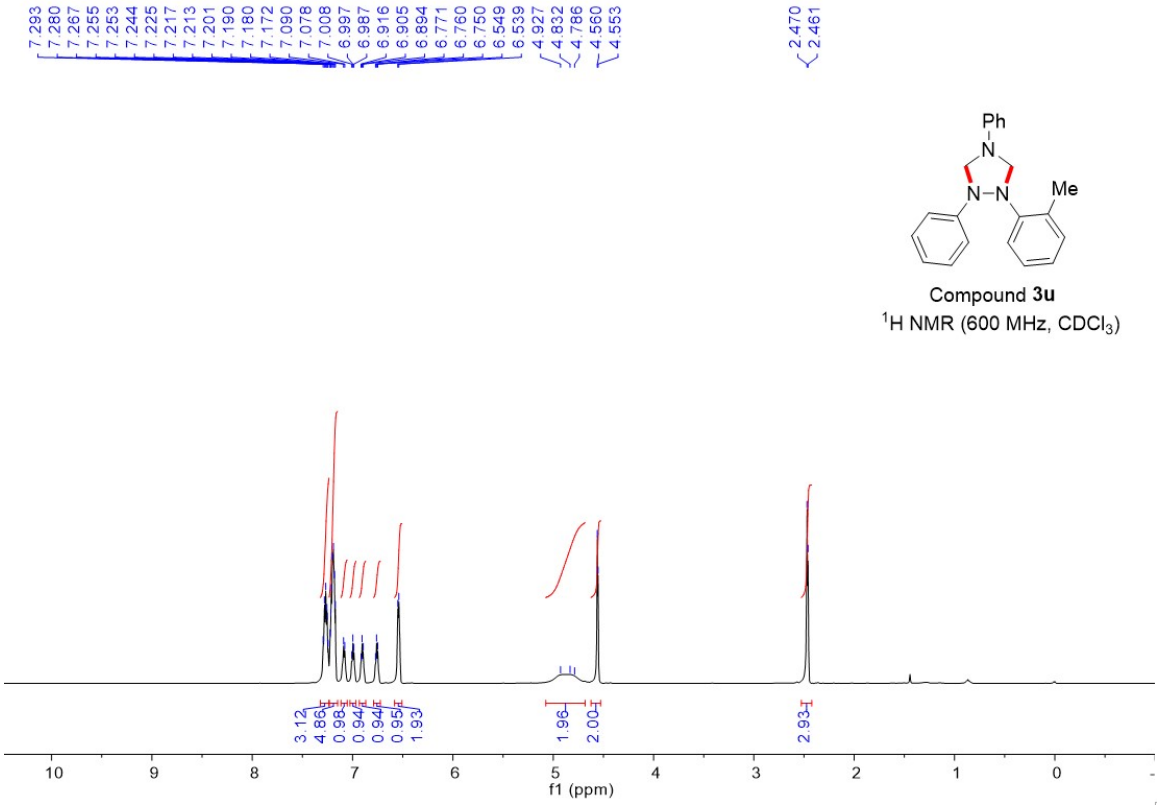


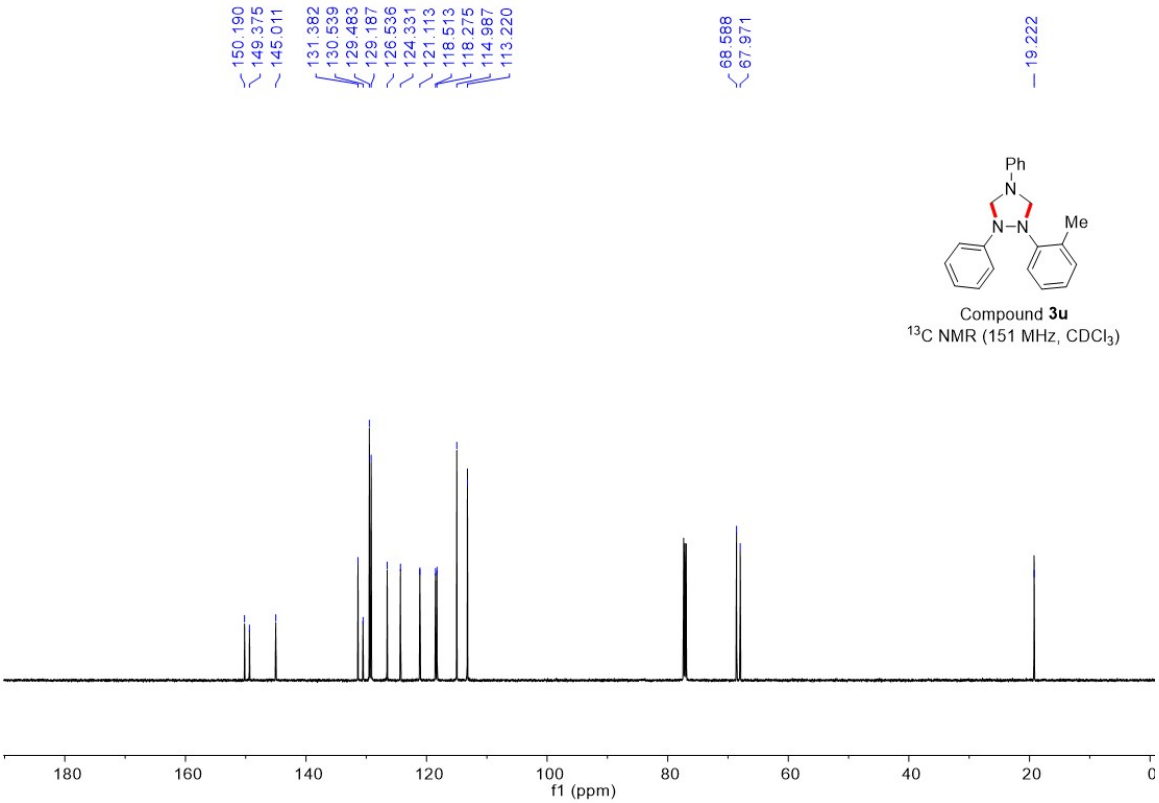
NMR spectra of 1-(3-bromophenyl)-2,4-diphenyl-1,2,4-triazolidine (**3t**)



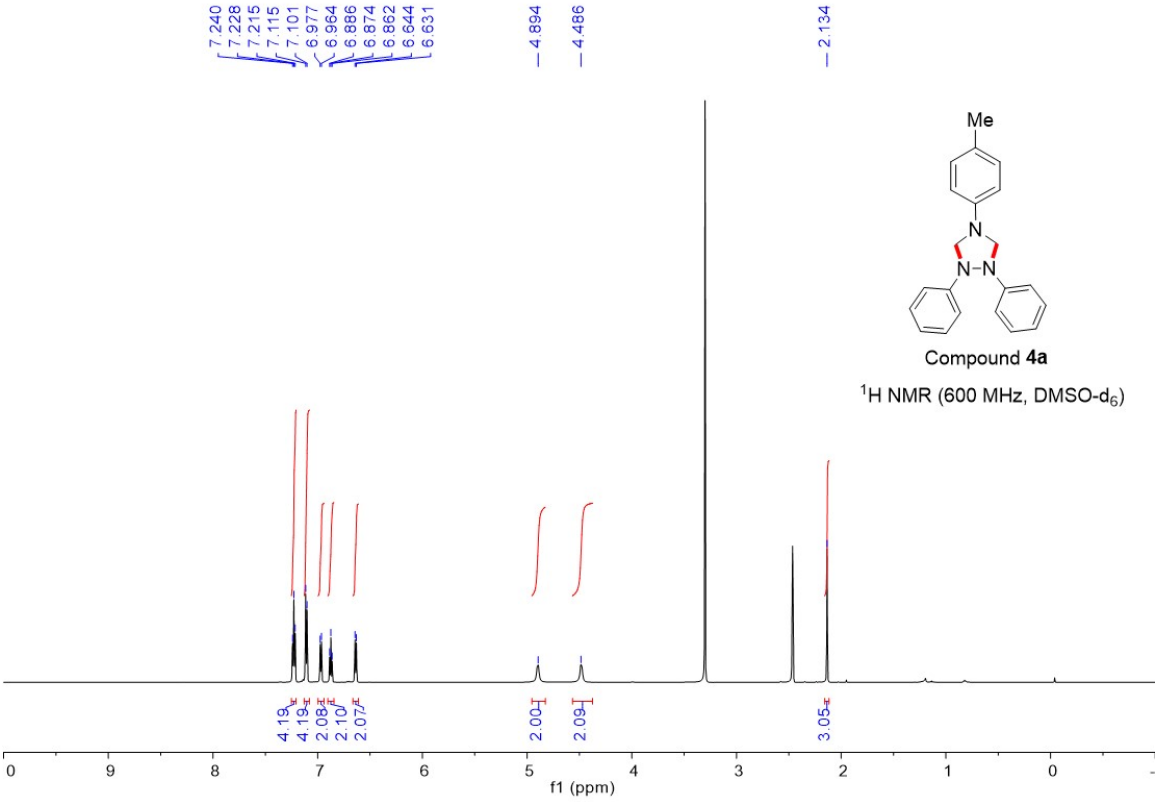


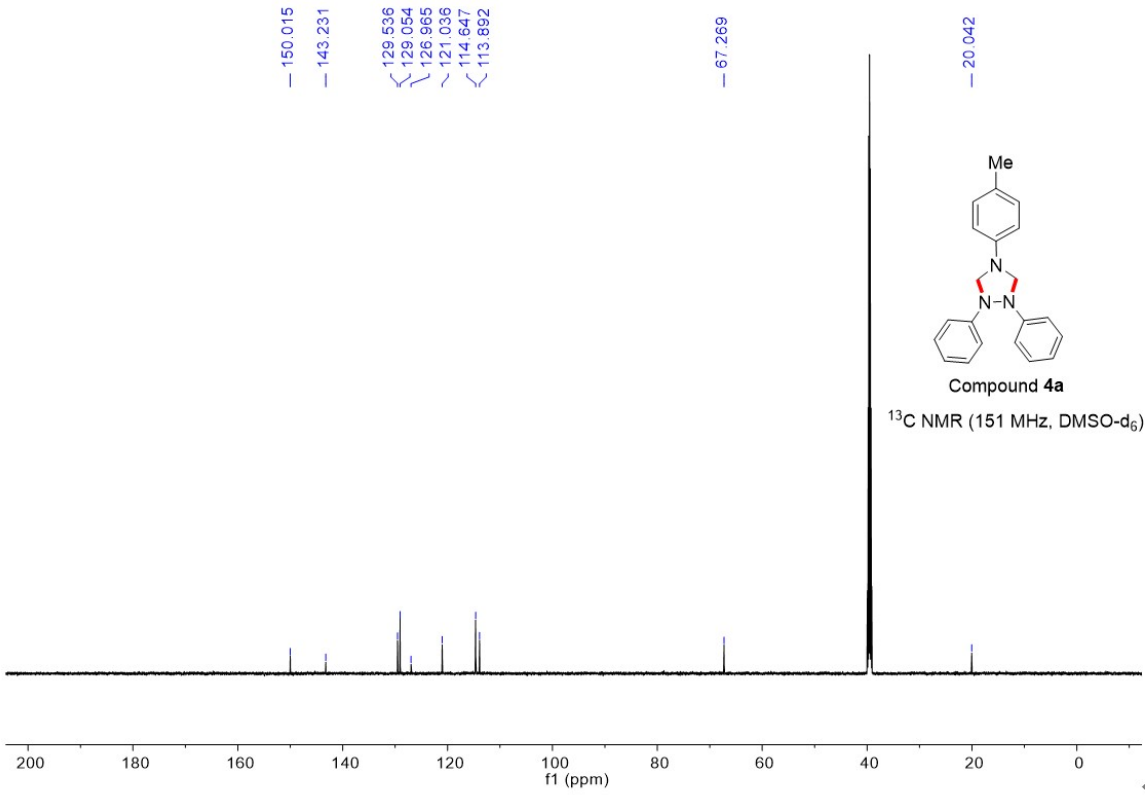
NMR spectra of 1,4-diphenyl-2-(*o*-tolyl)-1,2,4-triazolidine (**3u**)



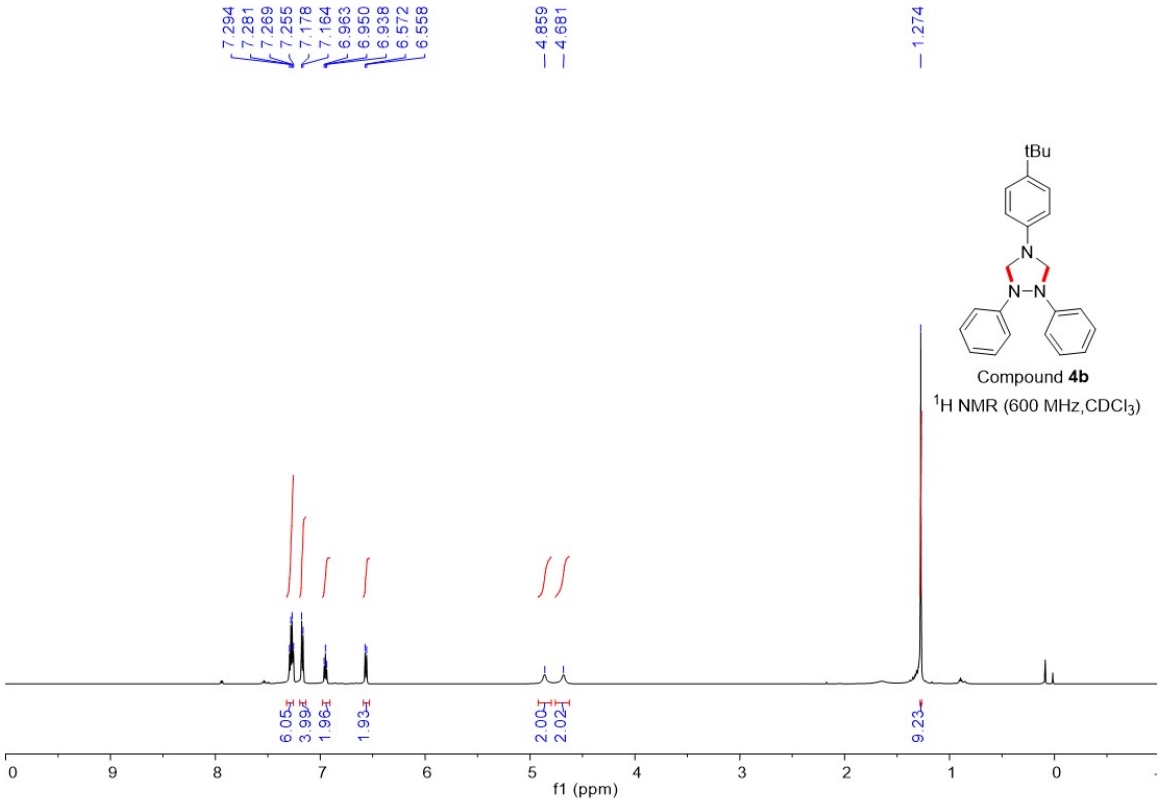


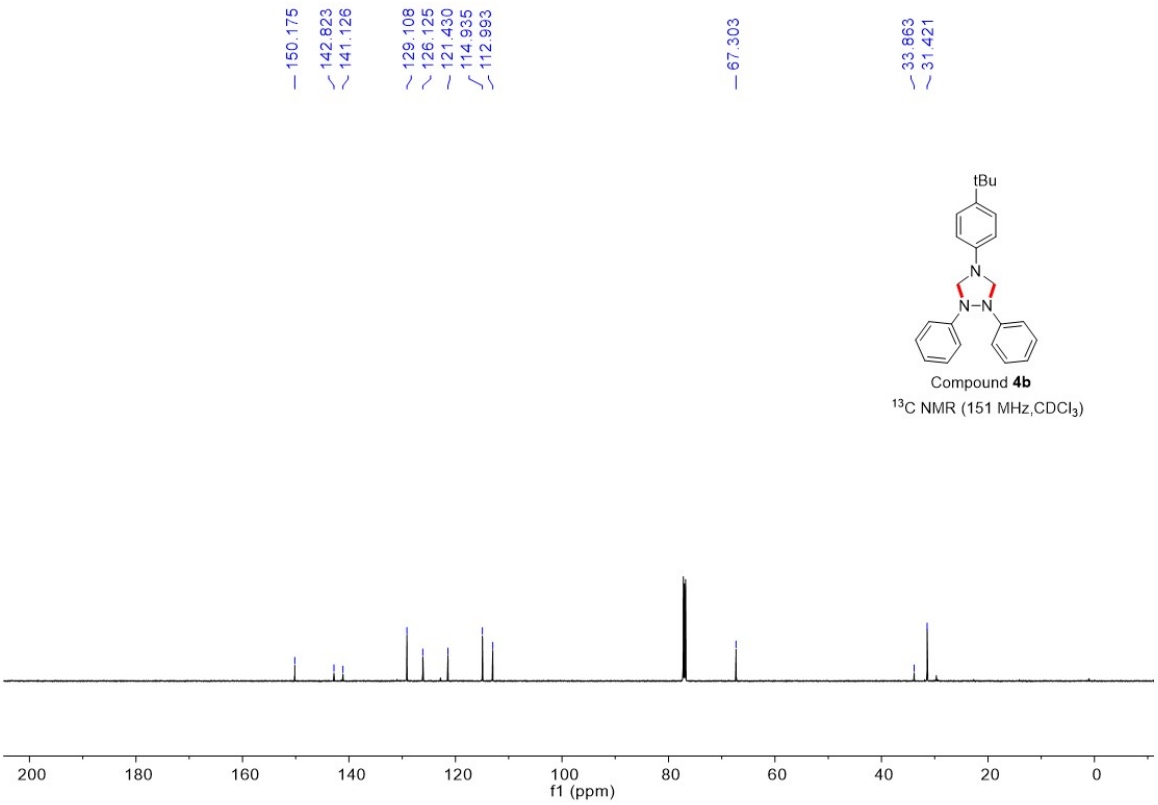
NMR spectra of 1,2-diphenyl-4-(*p*-tolyl)-1,2,4-triazolidine (**4a**)



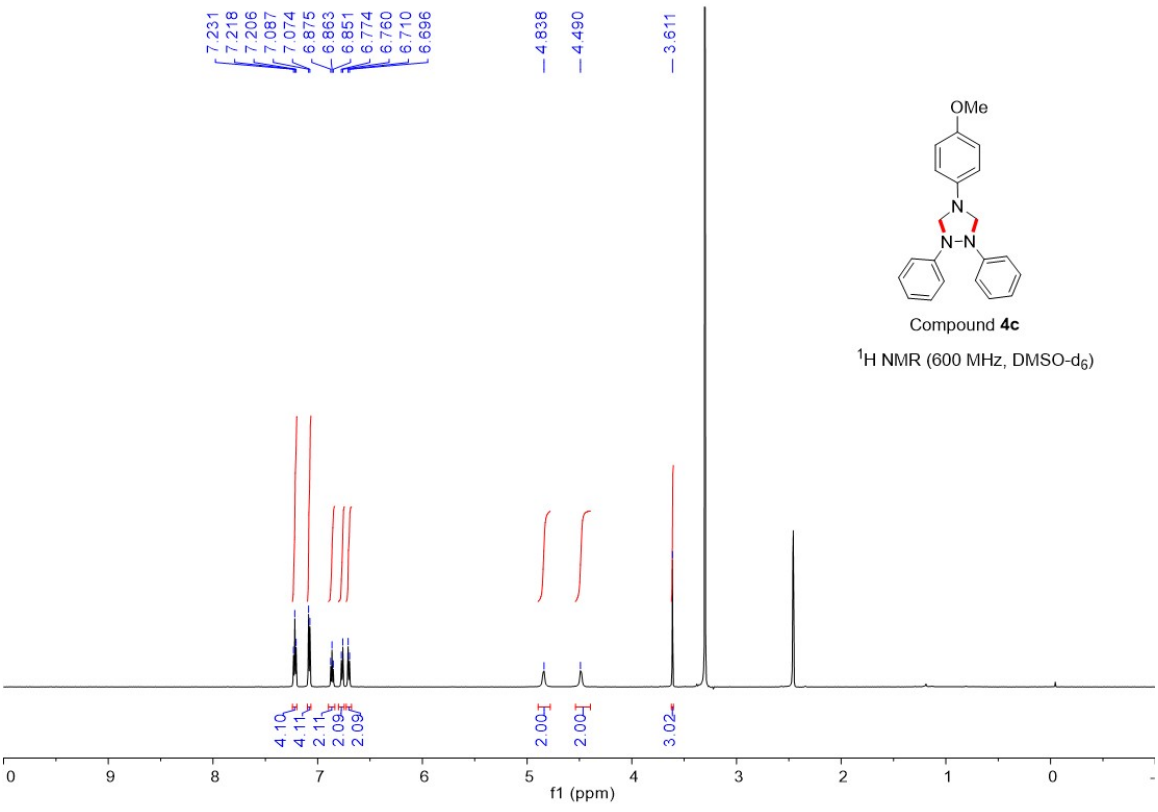


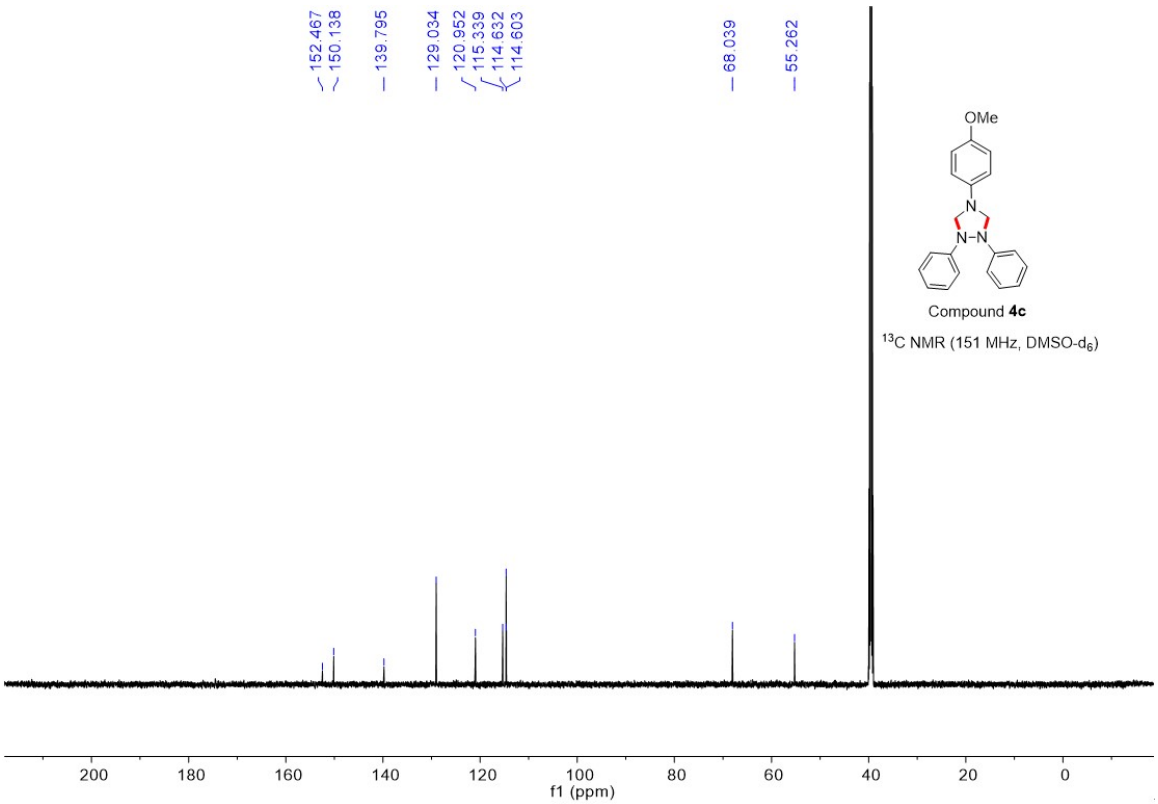
NMR spectra of 4-(4-(*tert*-butyl)phenyl)-1,2-diphenyl-1,2,4-triazolidine (**4b**)



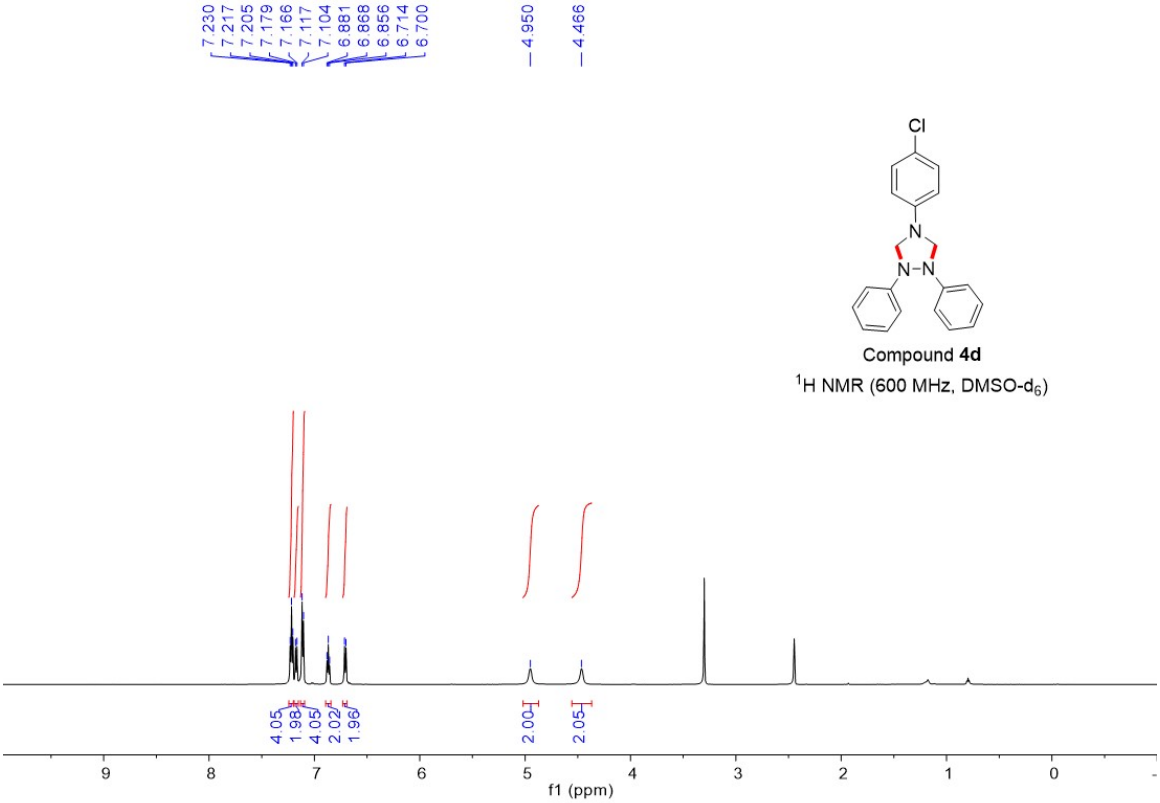


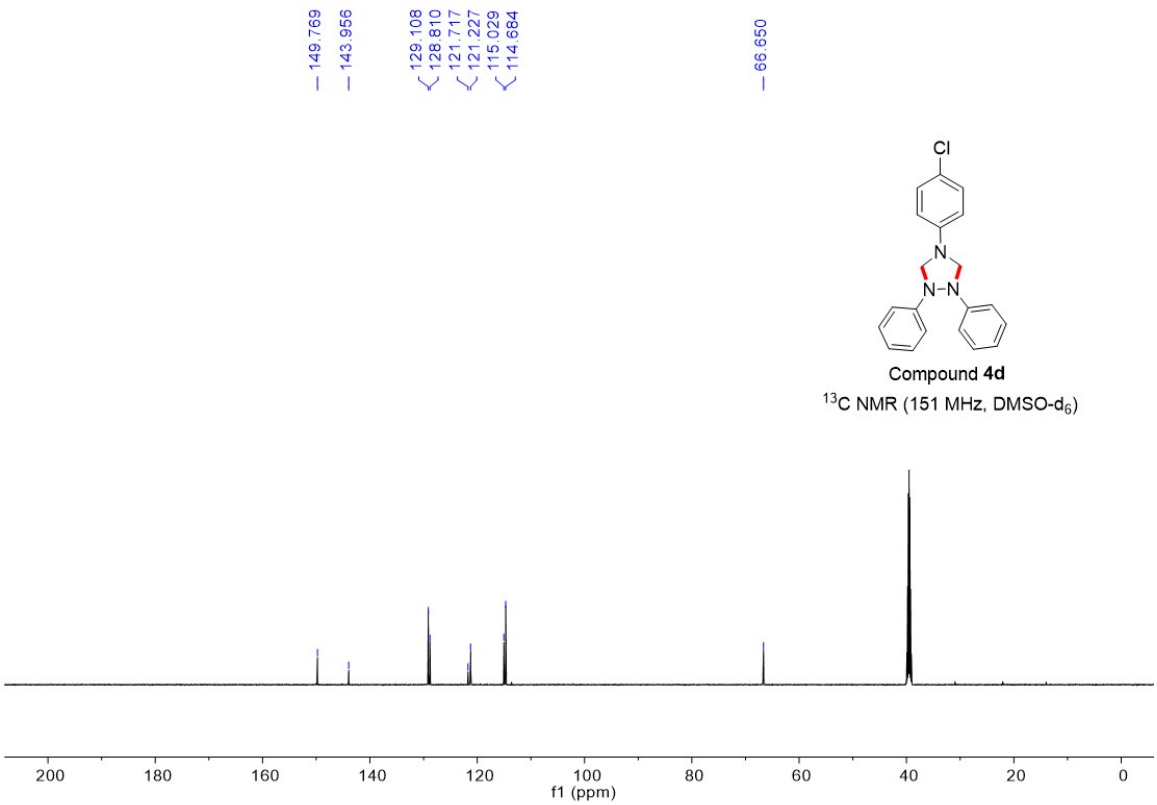
NMR spectra of 4-(4-methoxyphenyl)-1,2-diphenyl-1,2,4-triazolidine (**4c**)



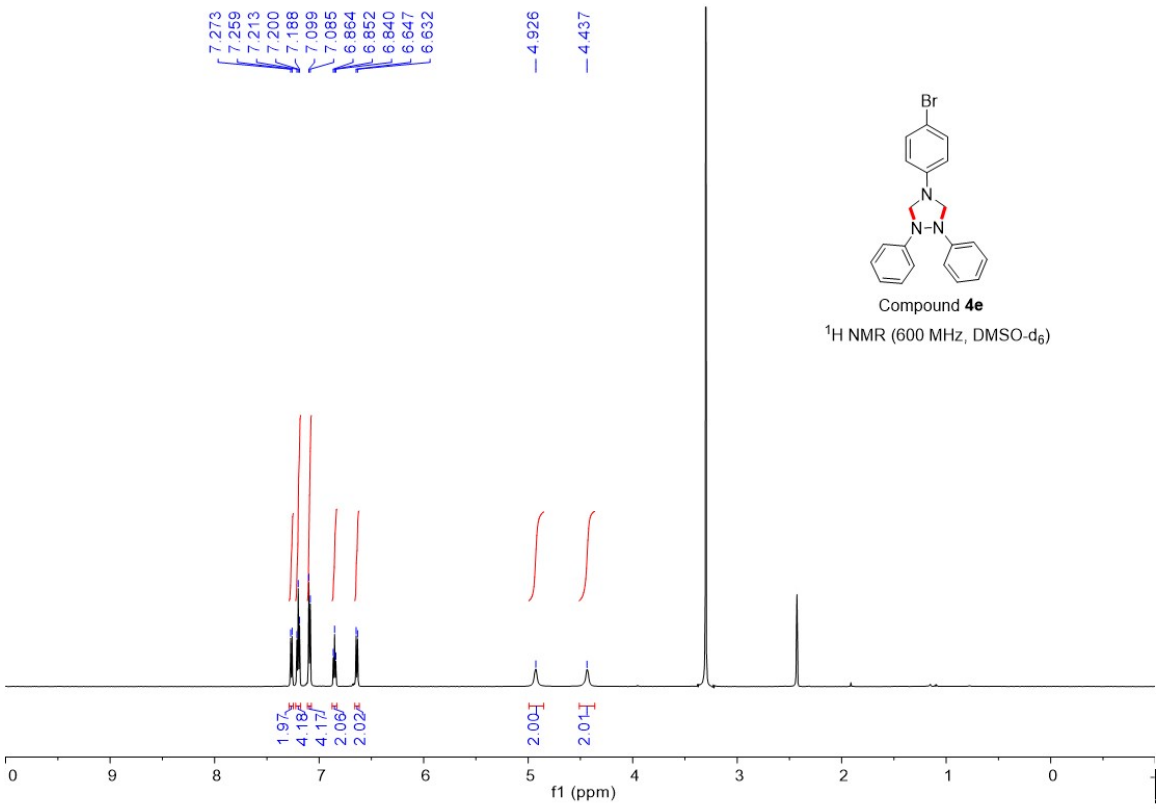


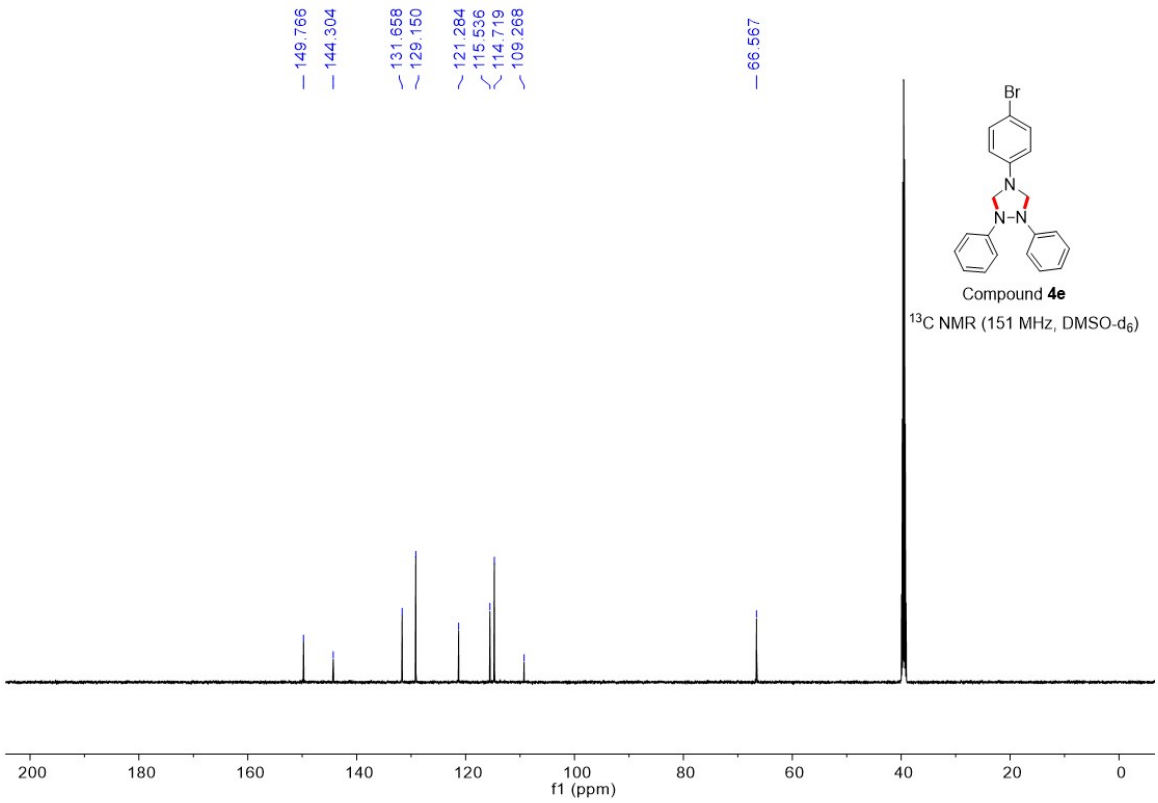
NMR spectra of 4-(4-chlorophenyl)-1,2-diphenyl-1,2,4-triazolidine (**4d**)



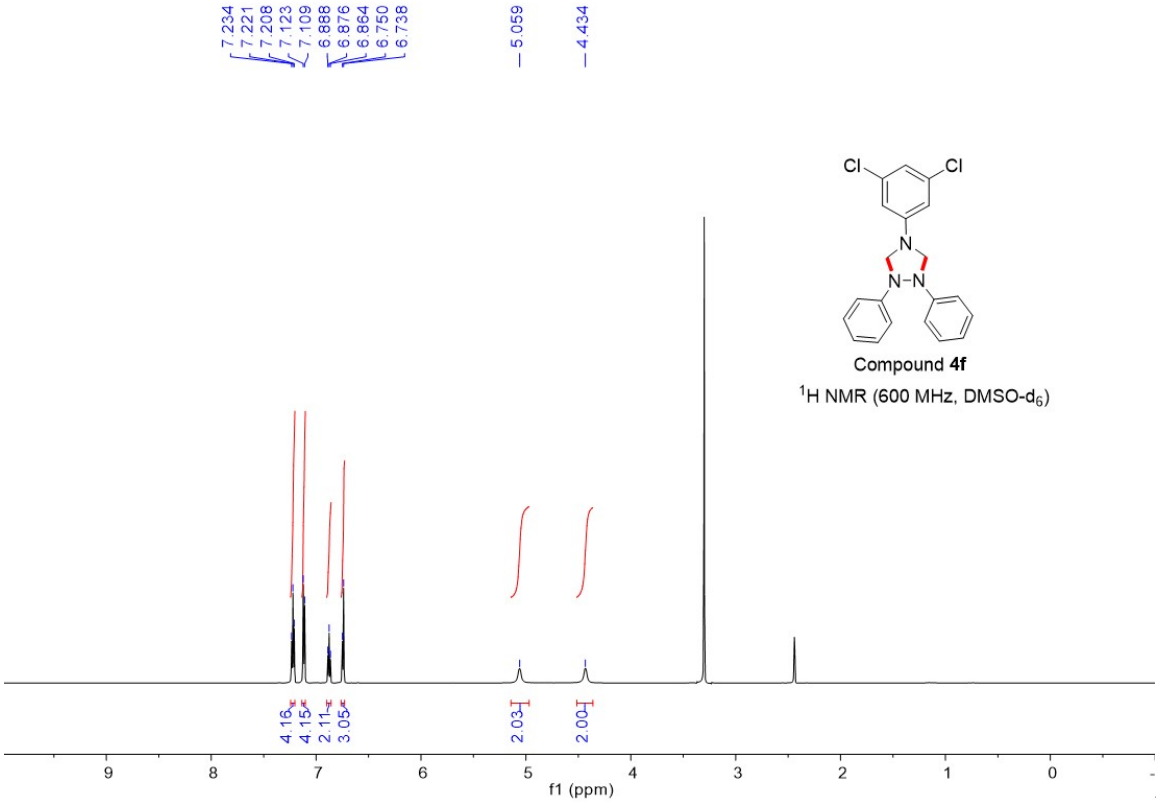


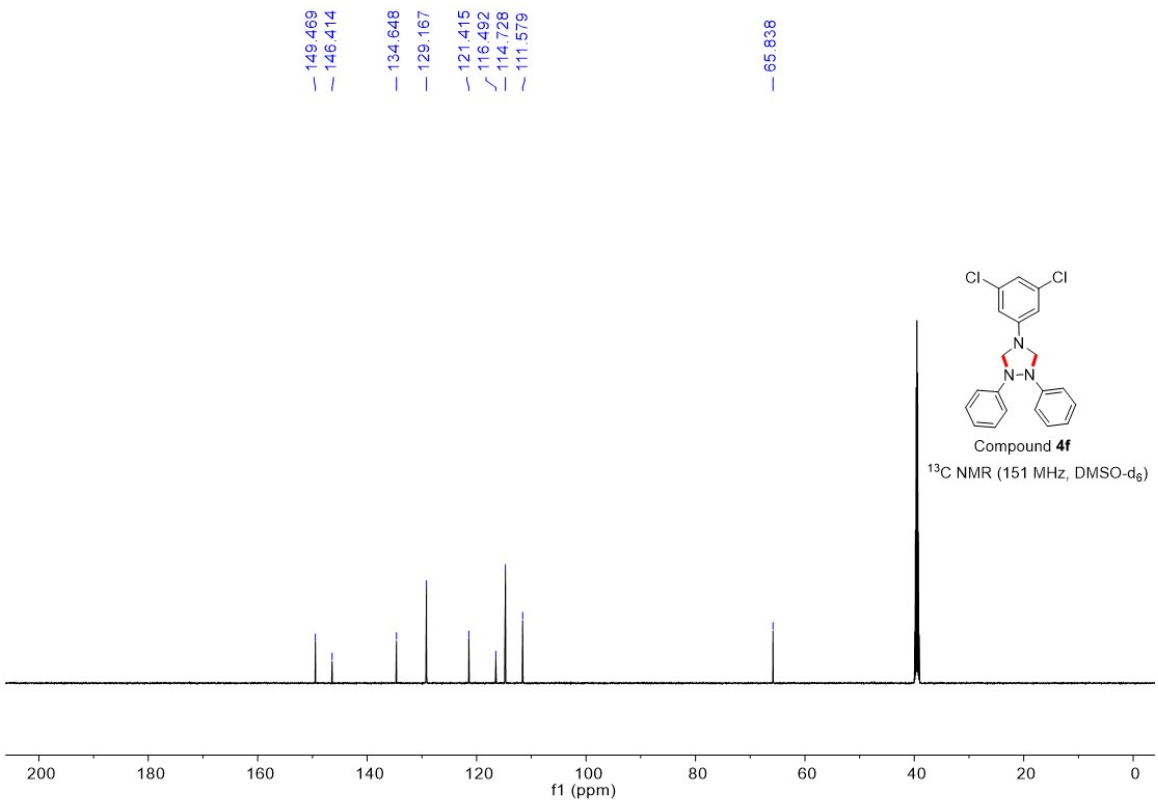
NMR spectra of 4-(4-bromophenyl)-1,2-diphenyl-1,2,4-triazolidine (**4e**)



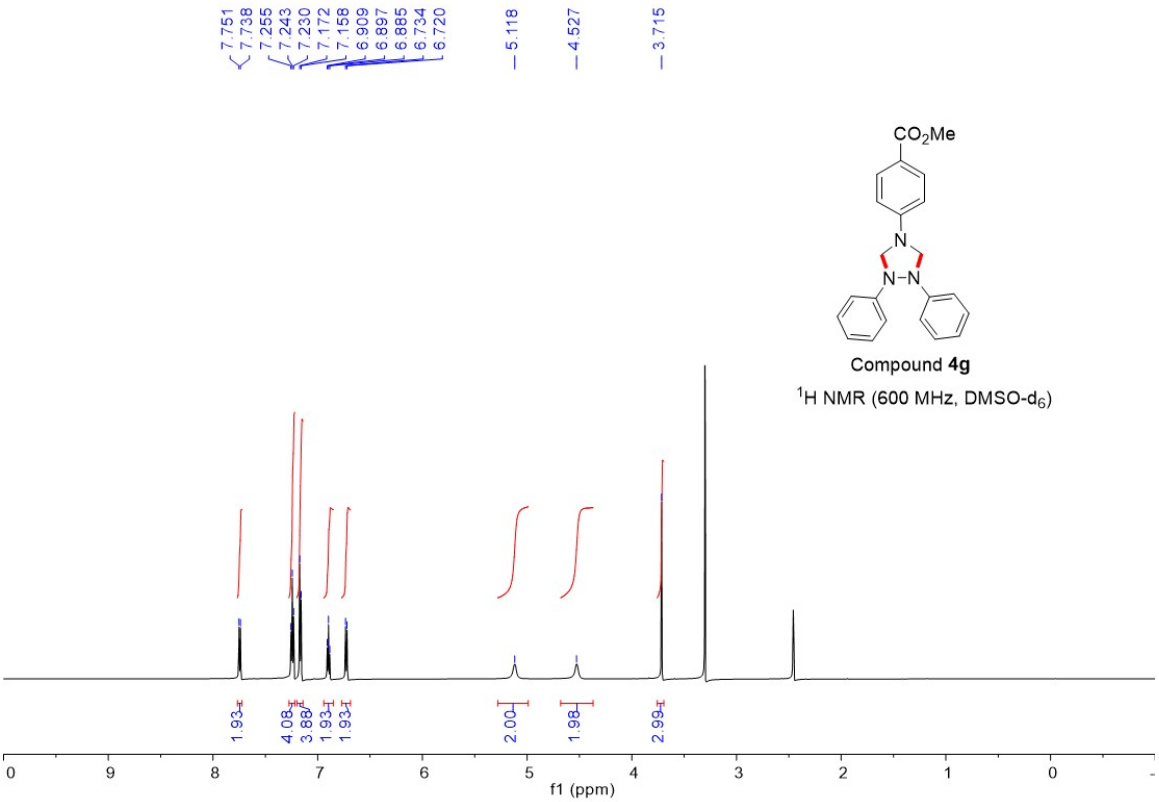


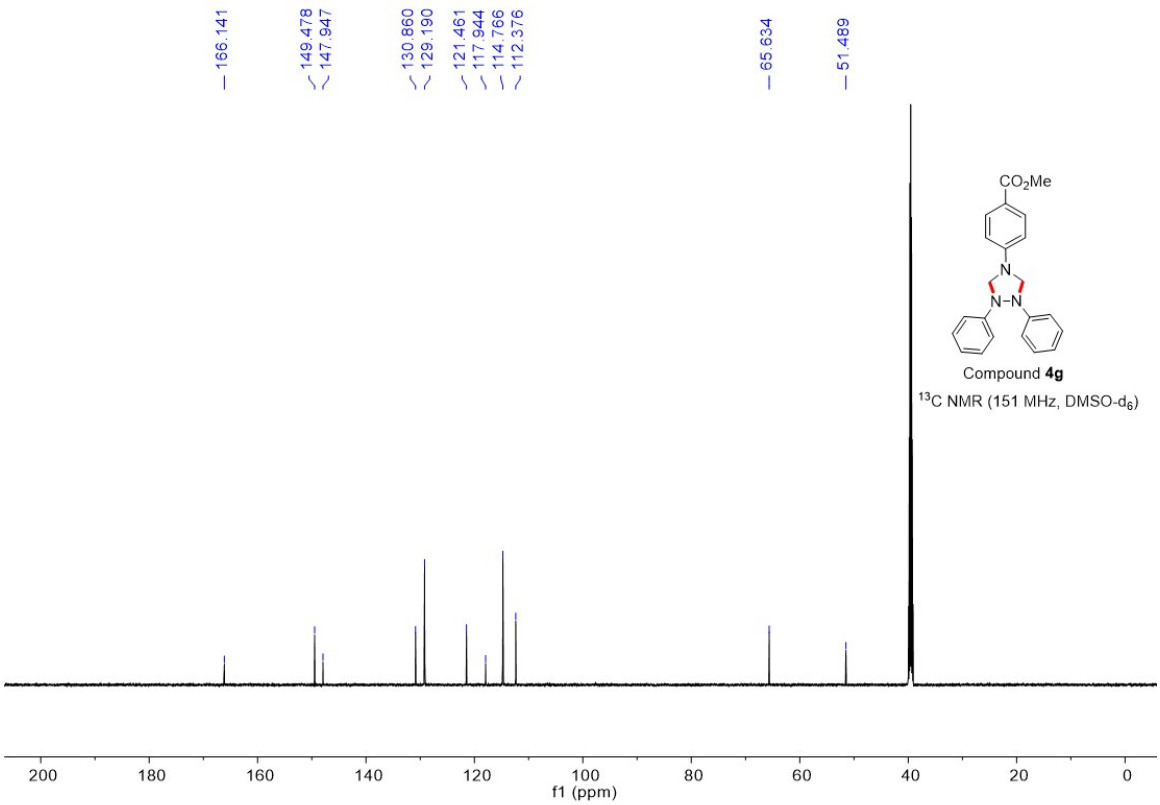
NMR spectra of 4-(3,5-dichlorophenyl)-1,2-diphenyl-1,2,4-triazolidine (**4f**)



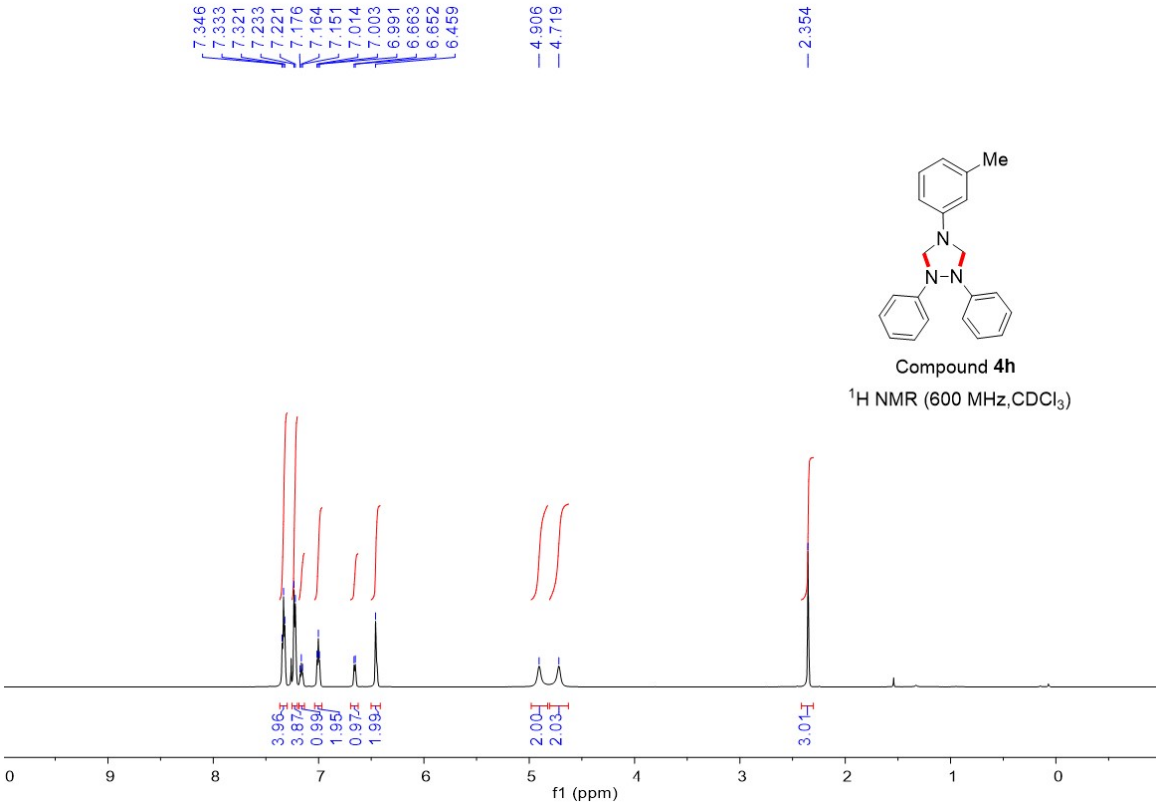


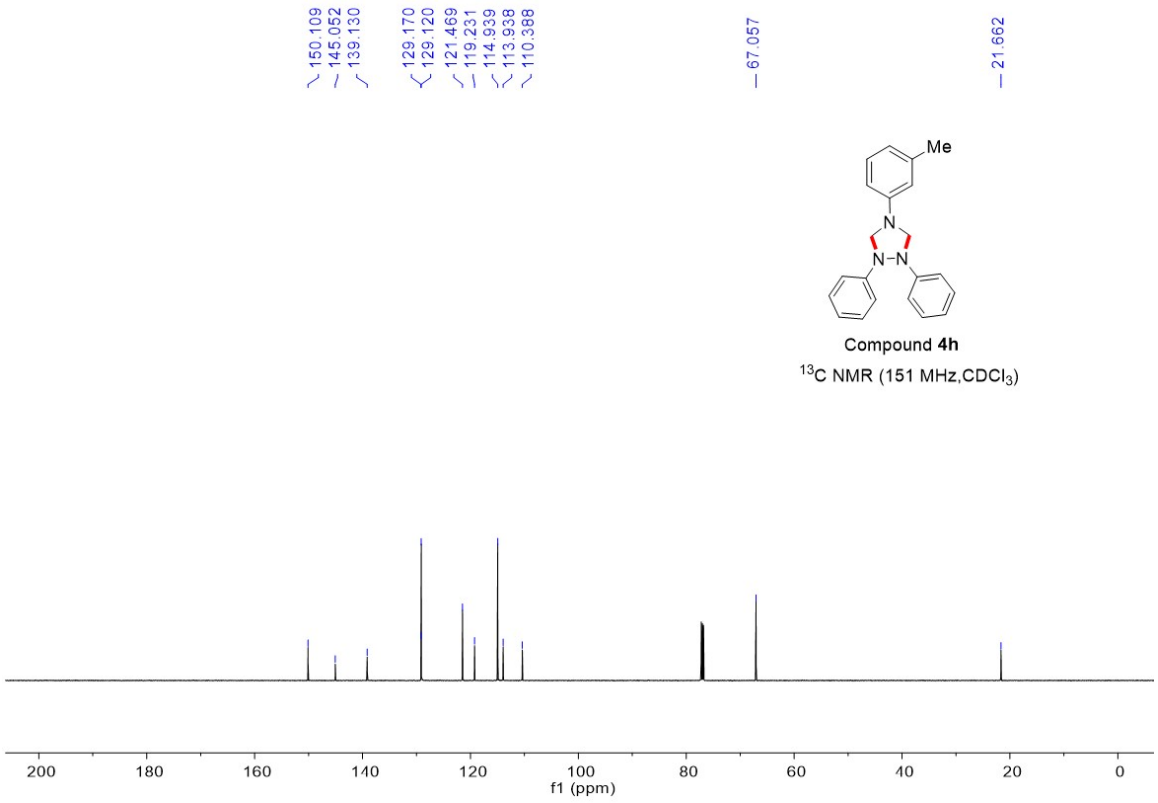
NMR spectra of methyl 4-(1,2-diphenyl-1,2,4-triazolidin-4-yl)benzoate (**4g**)



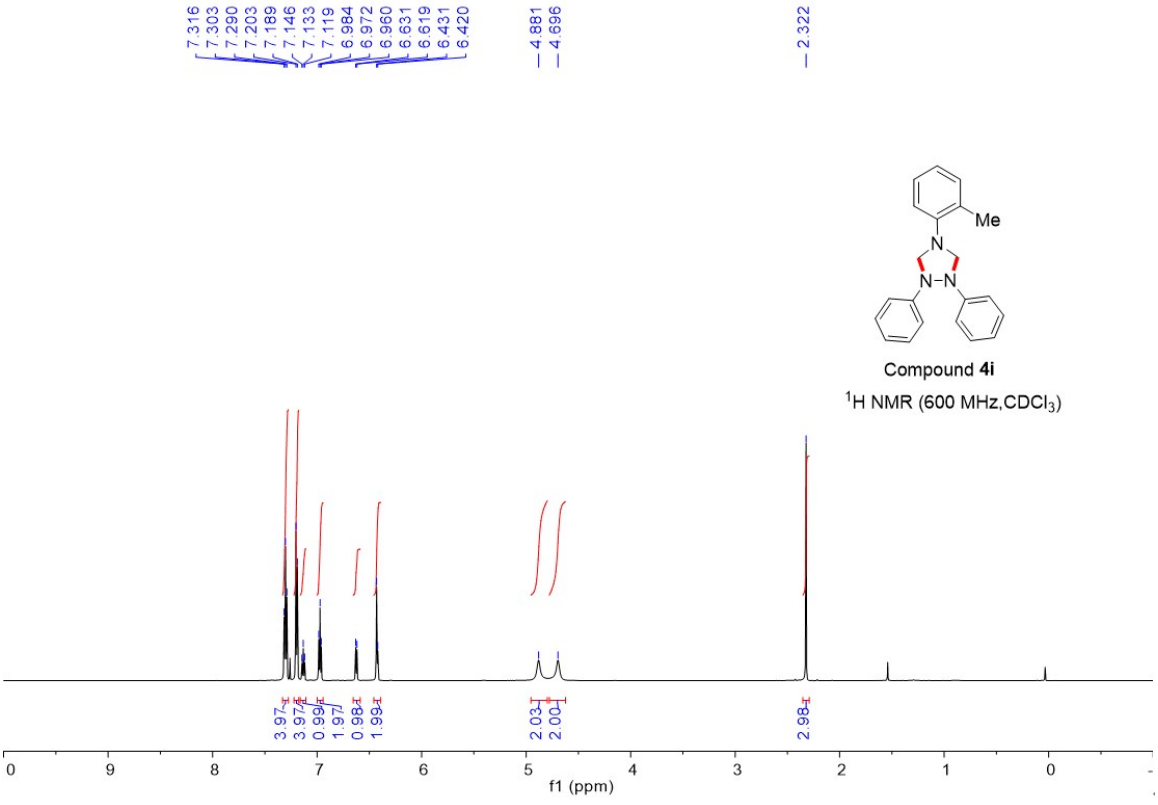


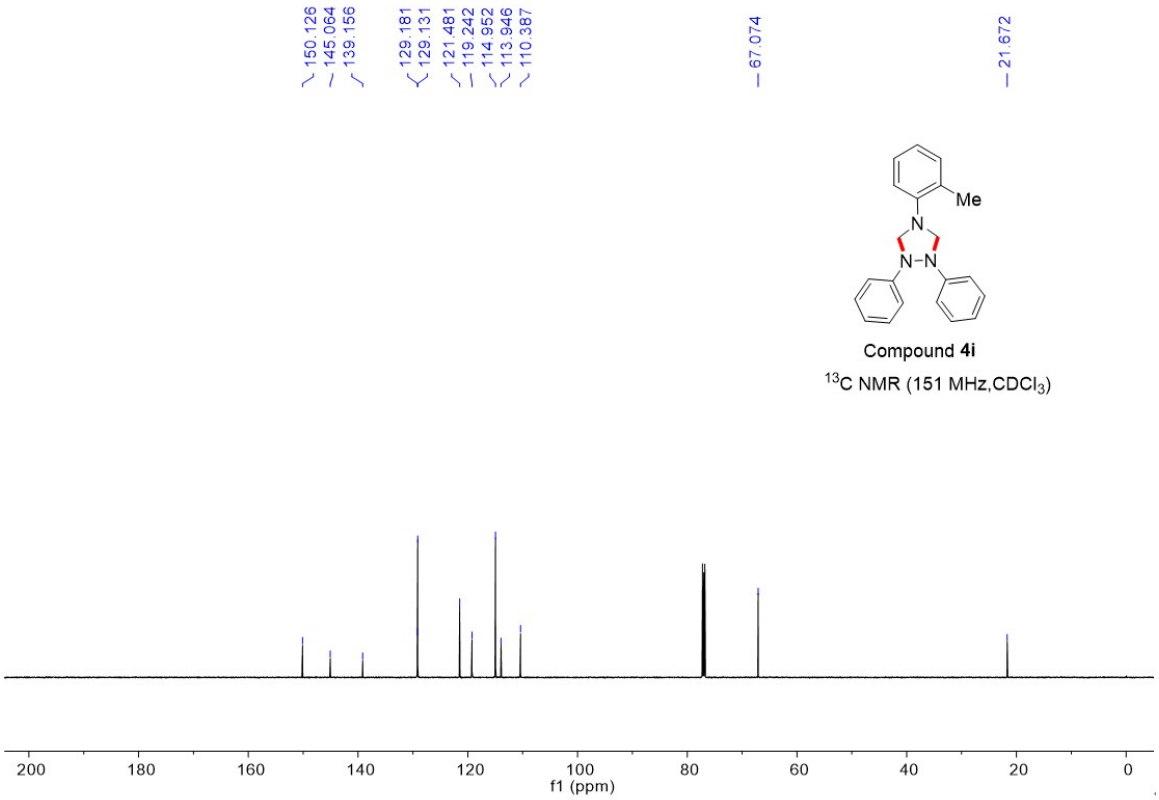
NMR spectra of 1,2-diphenyl-4-(*m*-tolyl)-1,2,4-triazolidine (**4h**)



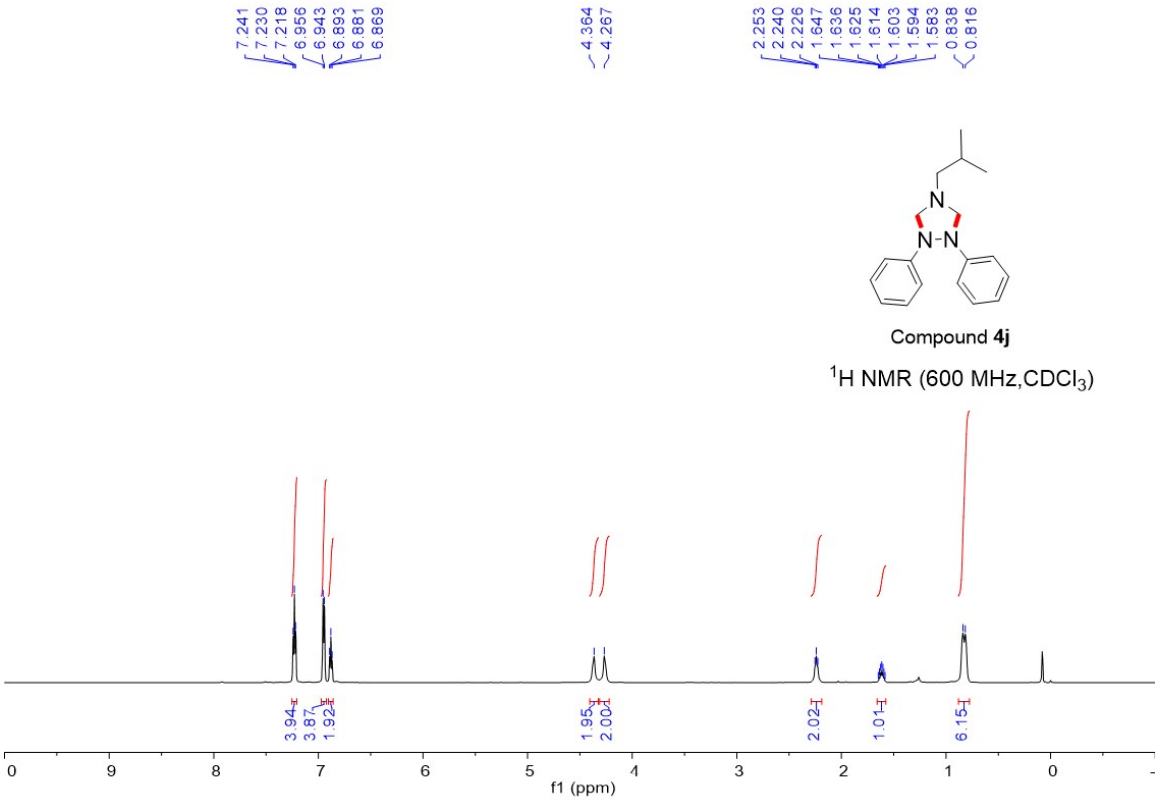


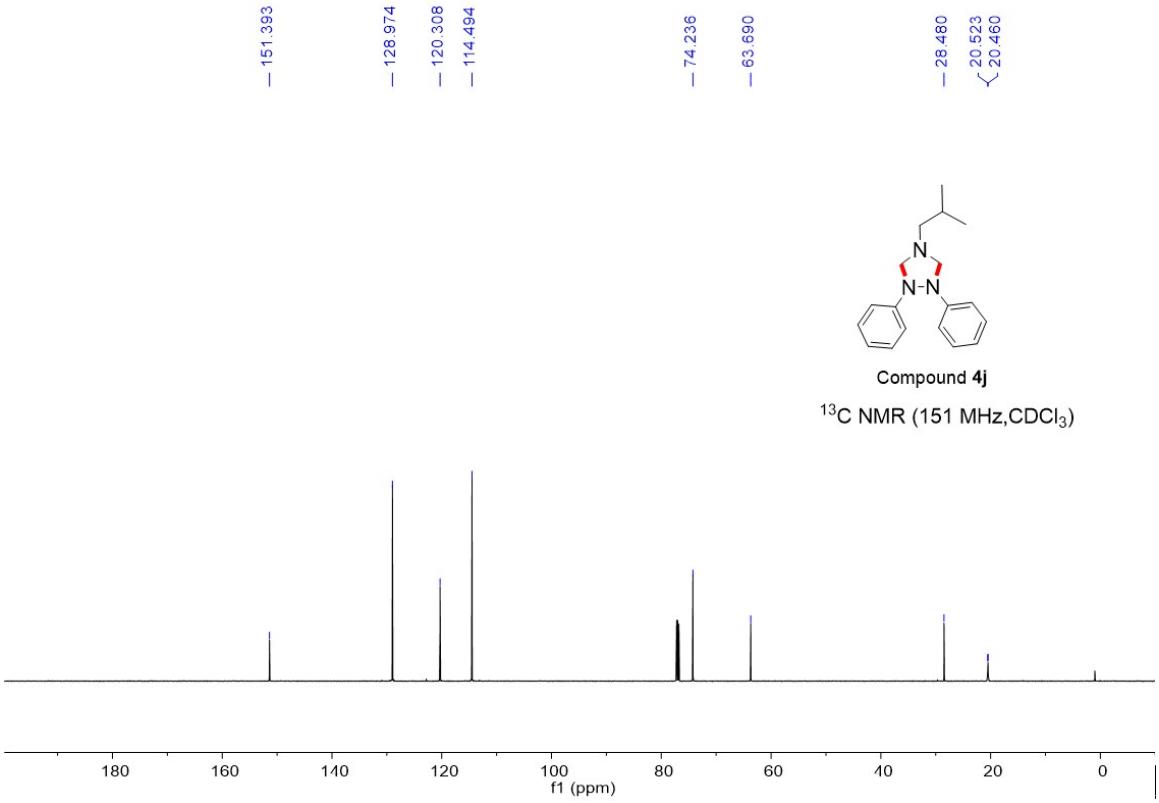
NMR spectra of 1,2-diphenyl-4-(*o*-tolyl)-1,2,4-triazolidine (**4i**)



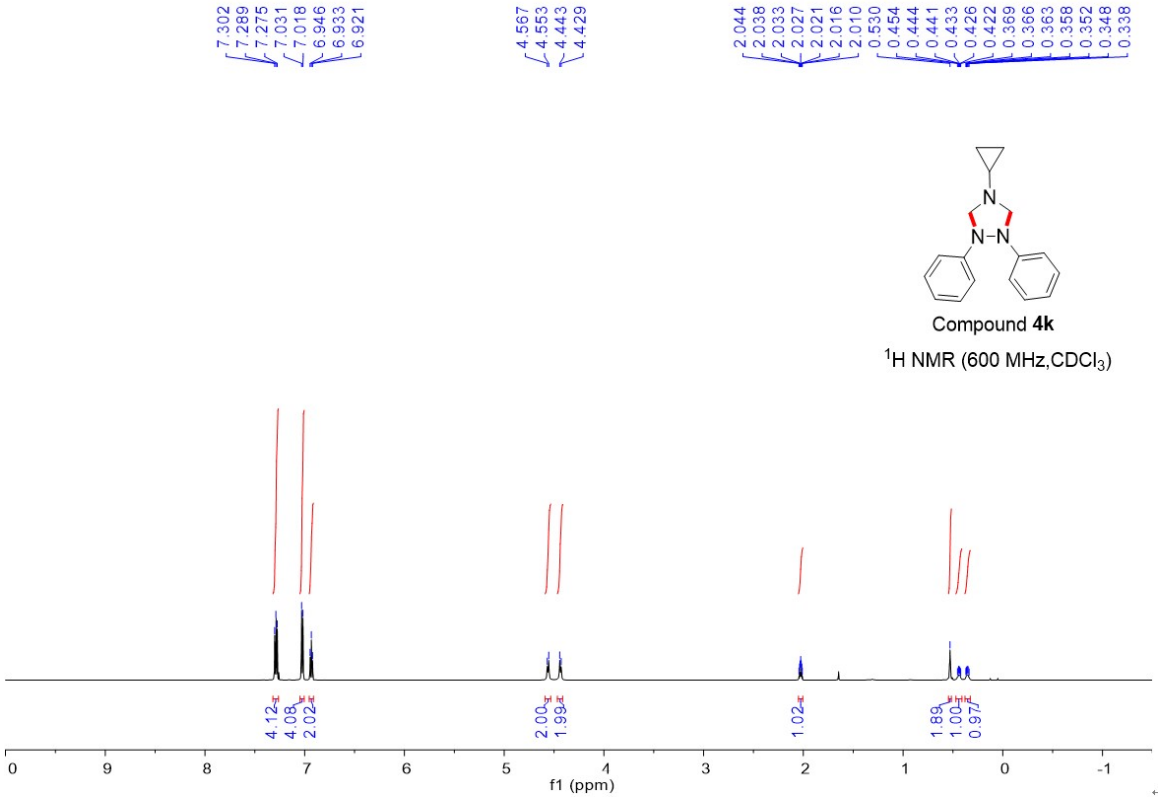


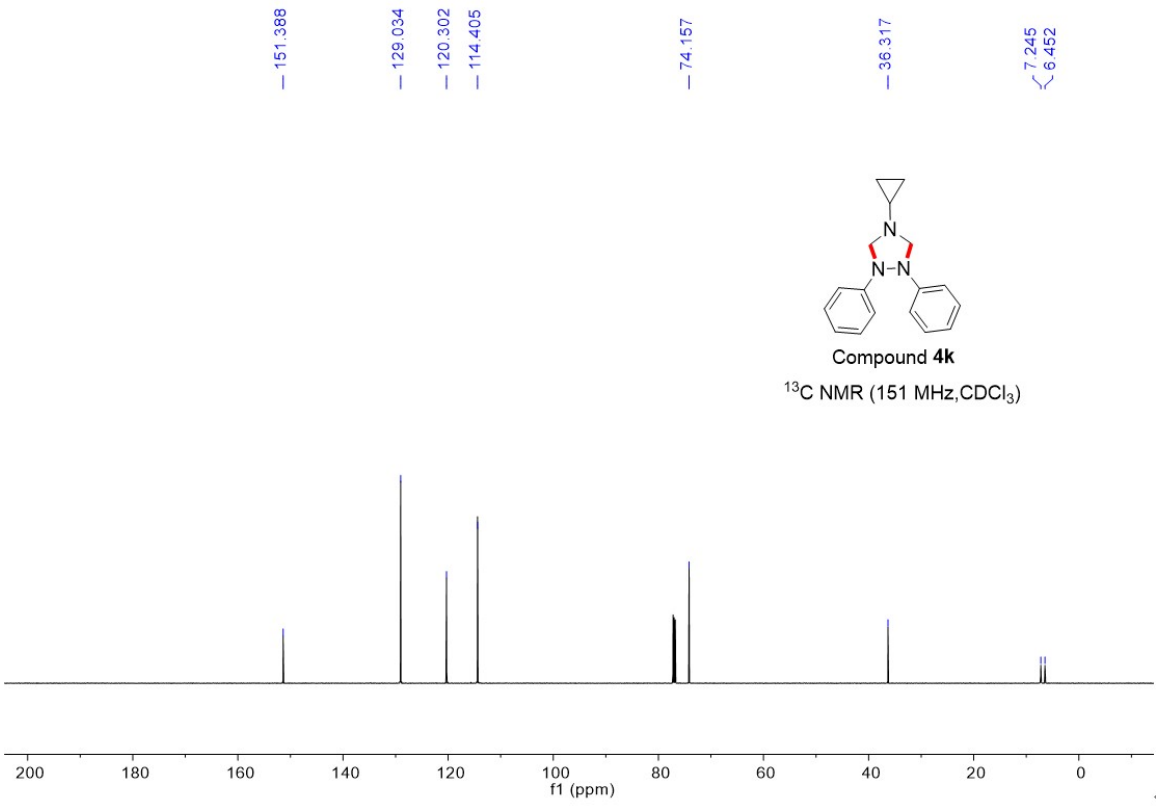
NMR spectra of 4-isobutyl-1,2-diphenyl-1,2,4-triazolidine (**4j**)



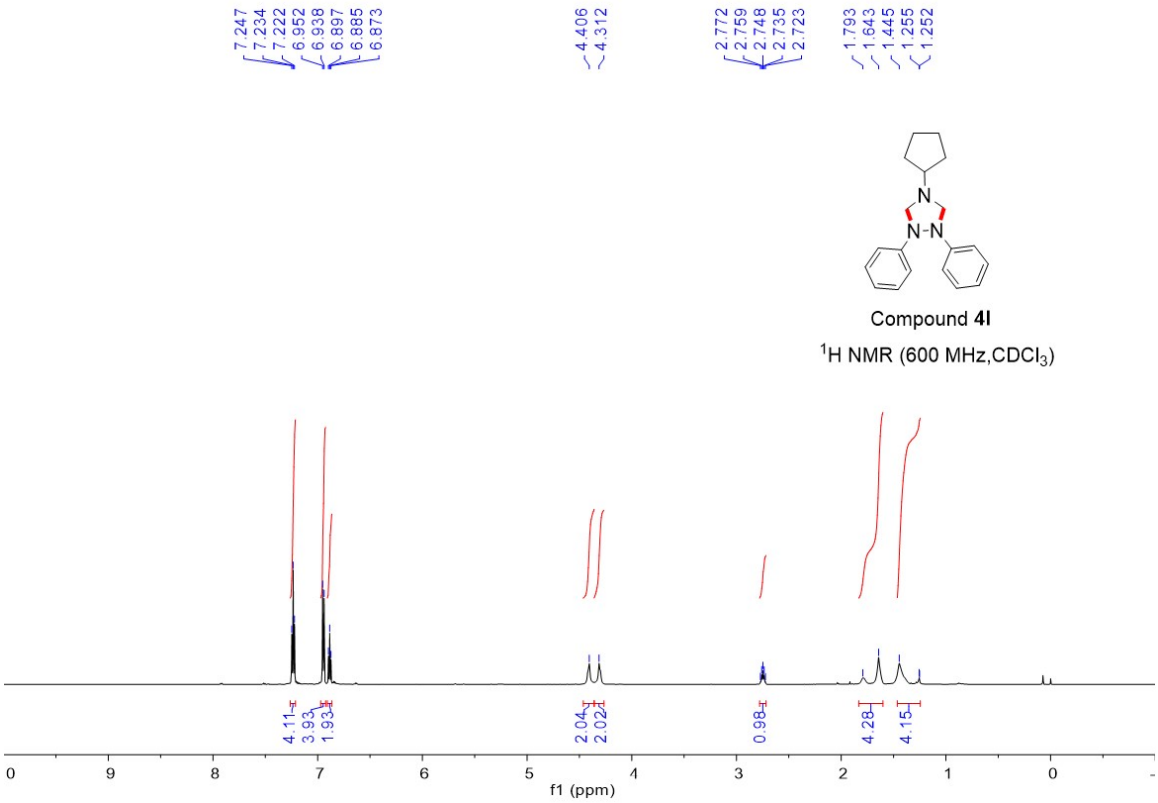


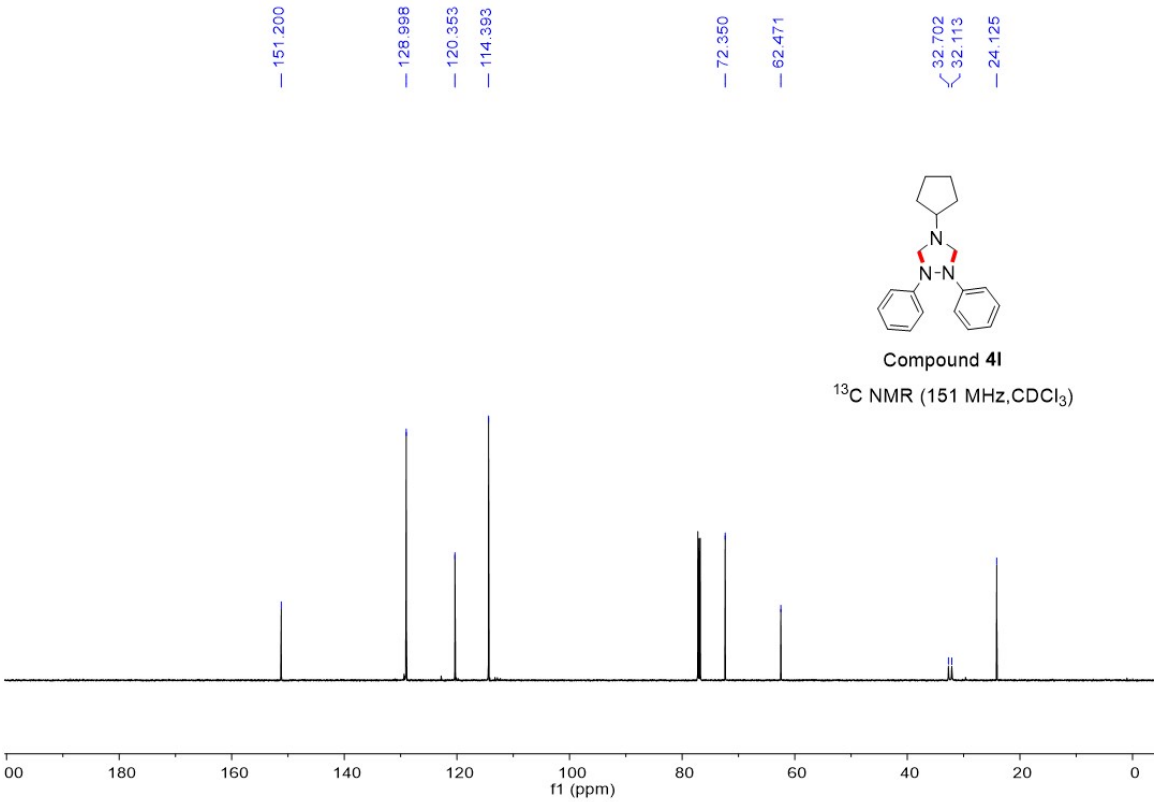
NMR spectra of 4-cyclopropyl-1,2-diphenyl-1,2,4-triazolidine (**4k**)



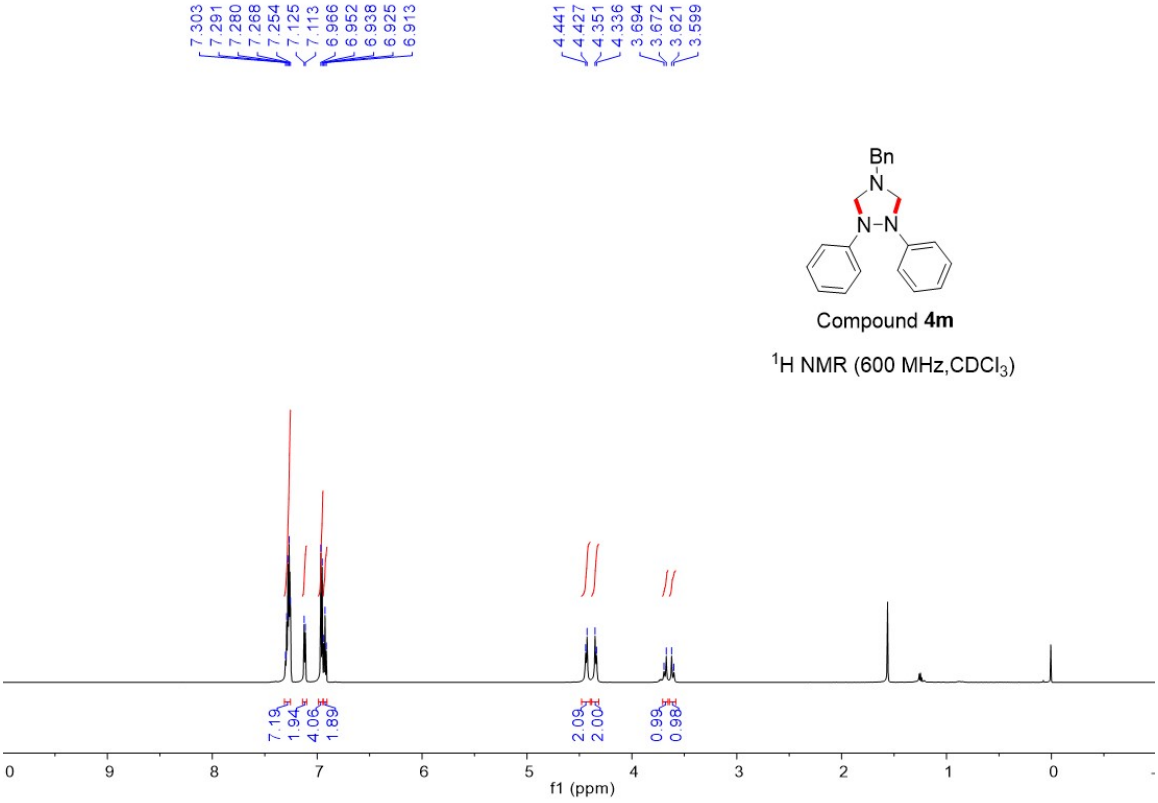


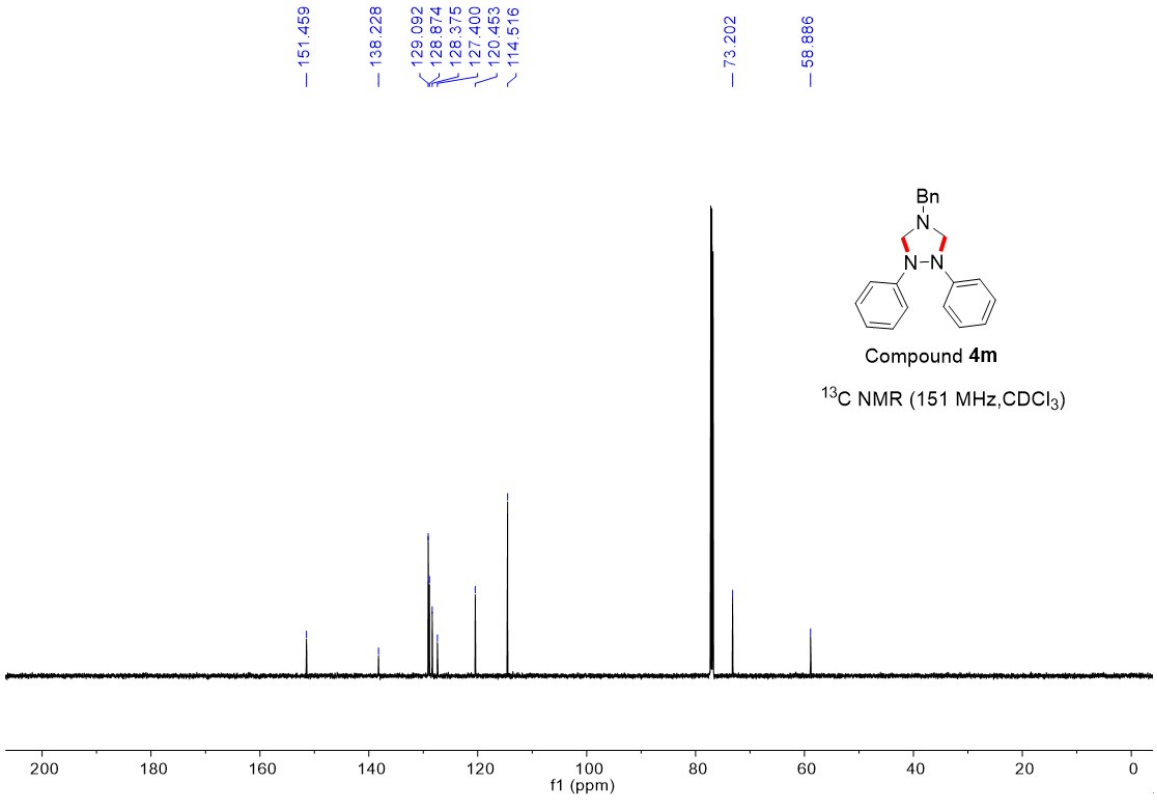
NMR spectra of 4-cyclopentyl-1,2-diphenyl-1,2,4-triazolidine (**4l**)



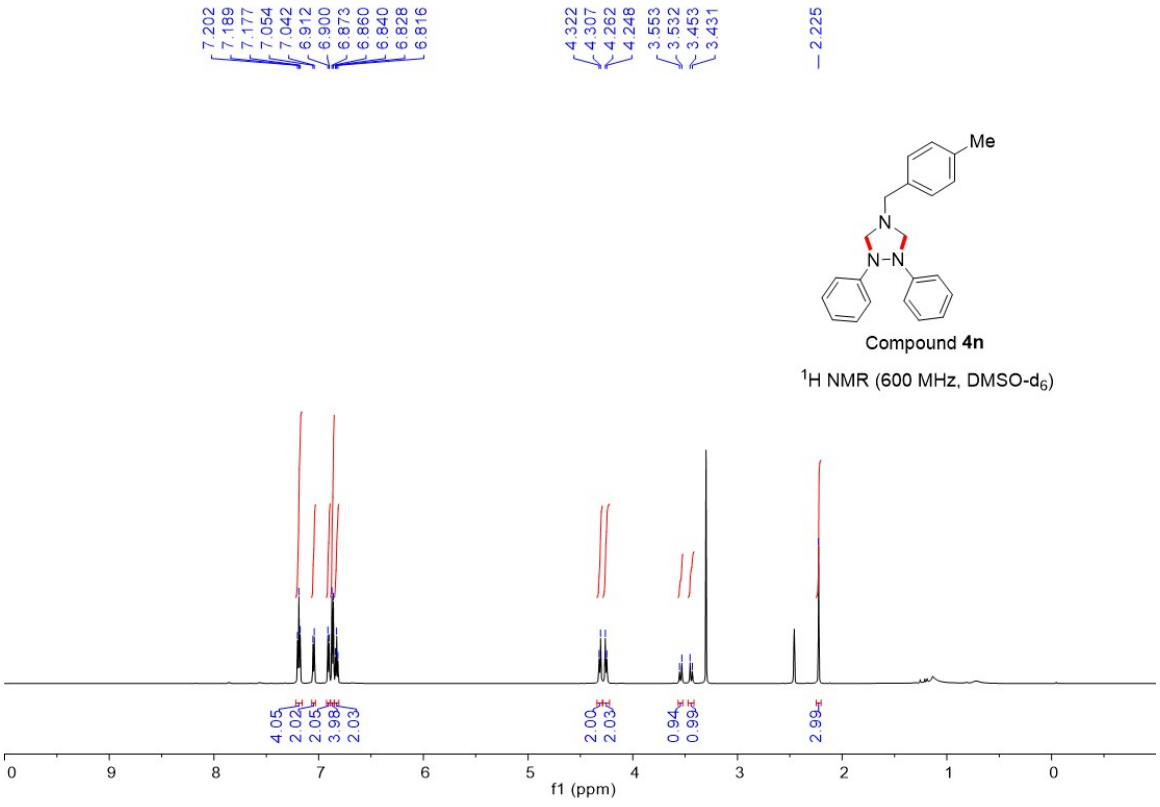


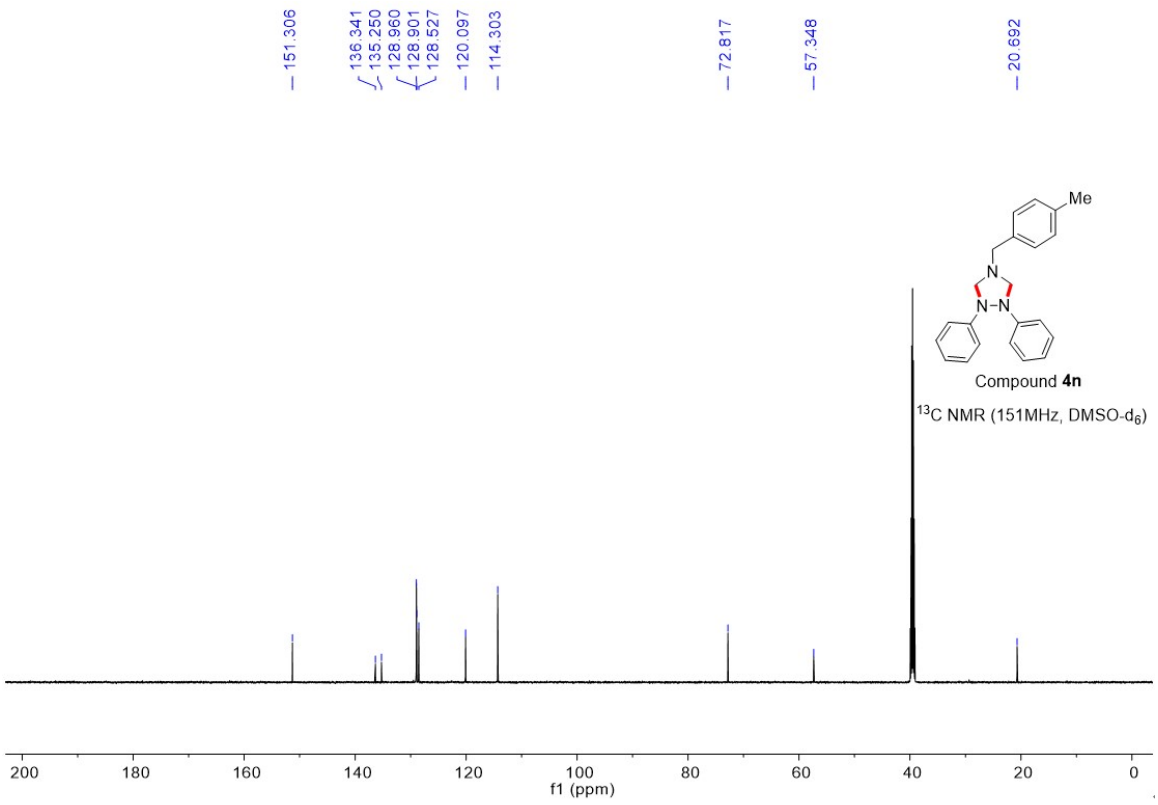
NMR spectra of 4-benzyl-1,2-diphenyl-1,2,4-triazolidine (**4m**)



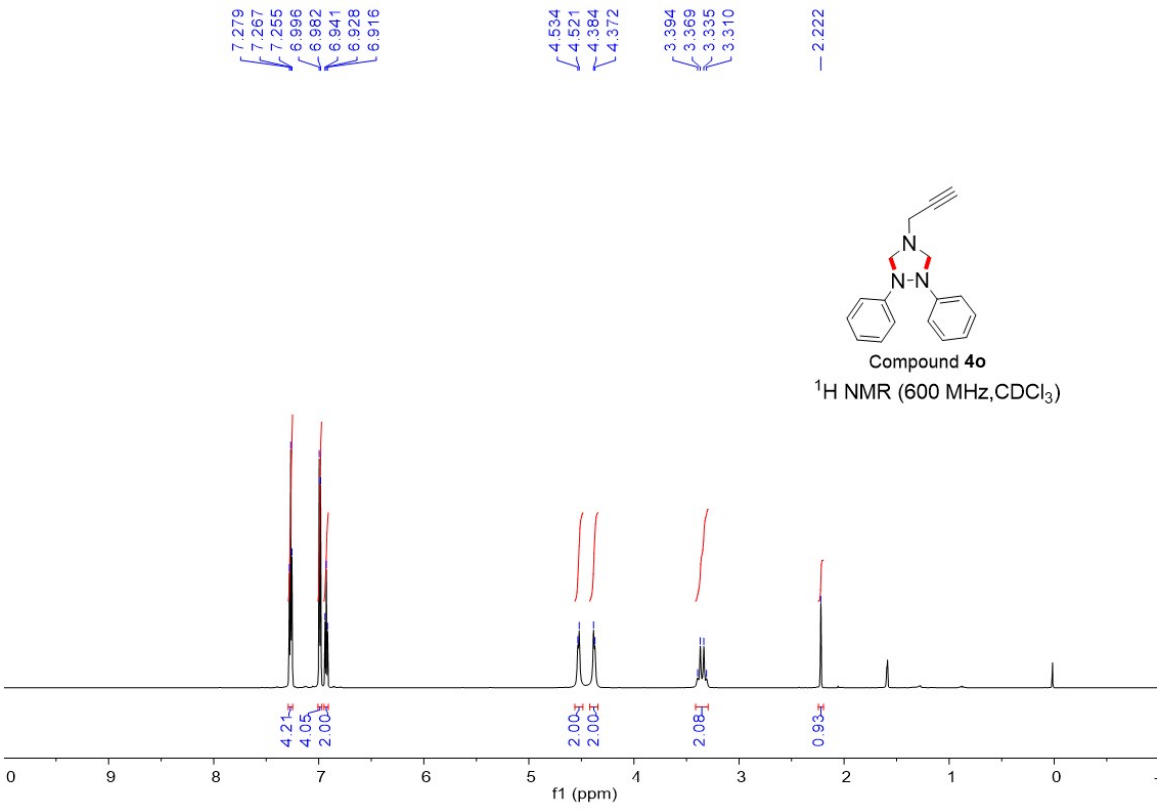


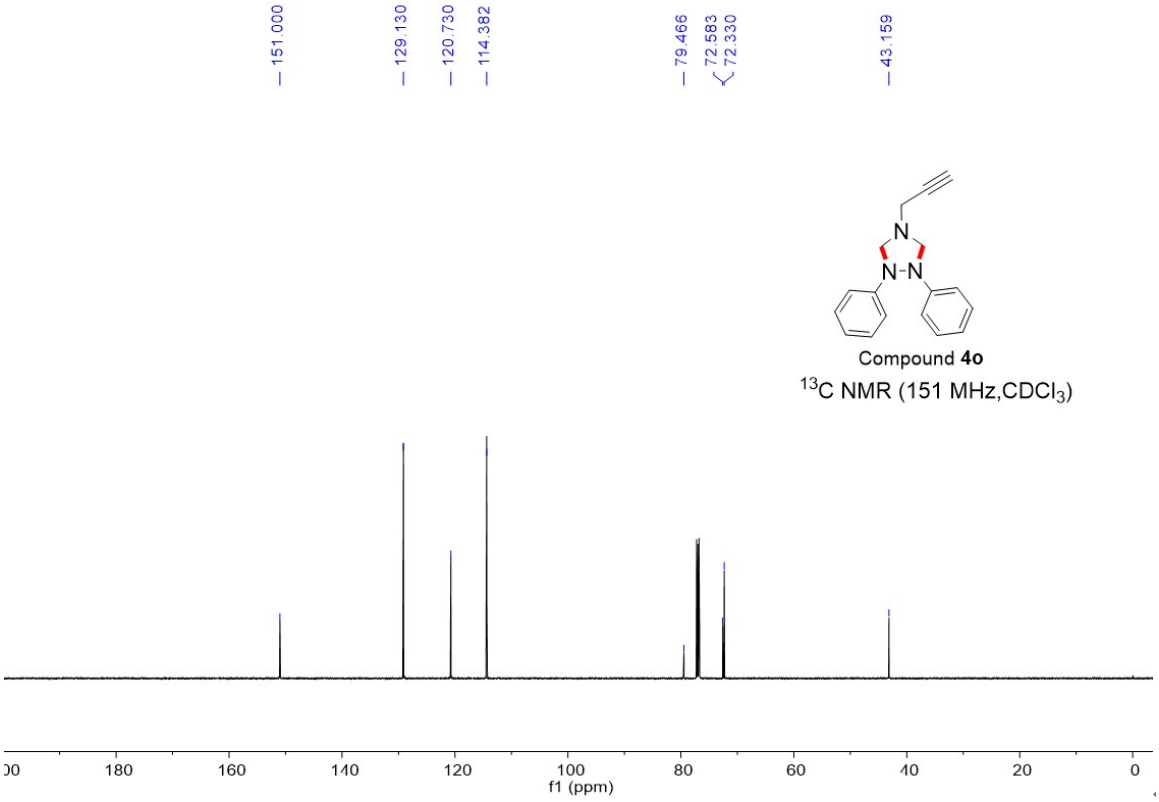
NMR spectra of 4-(4-methylbenzyl)-1,2-diphenyl-1,2,4-triazolidine (**4n**)



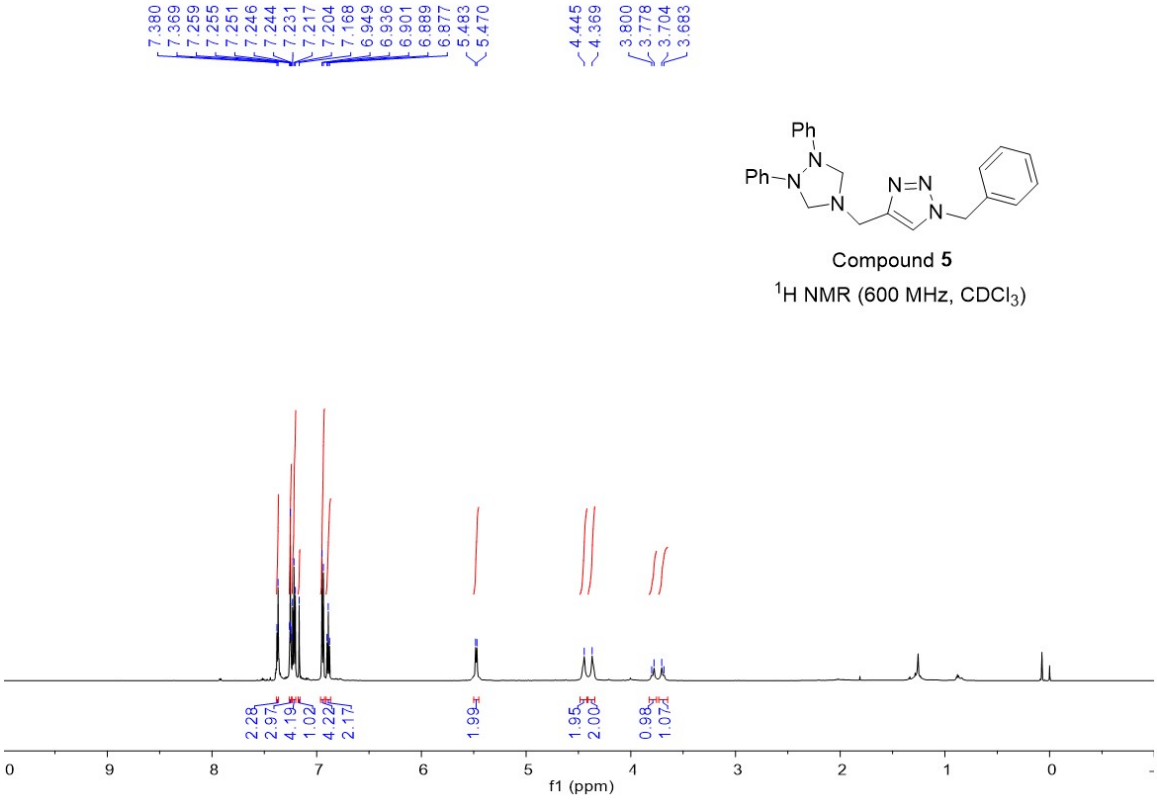


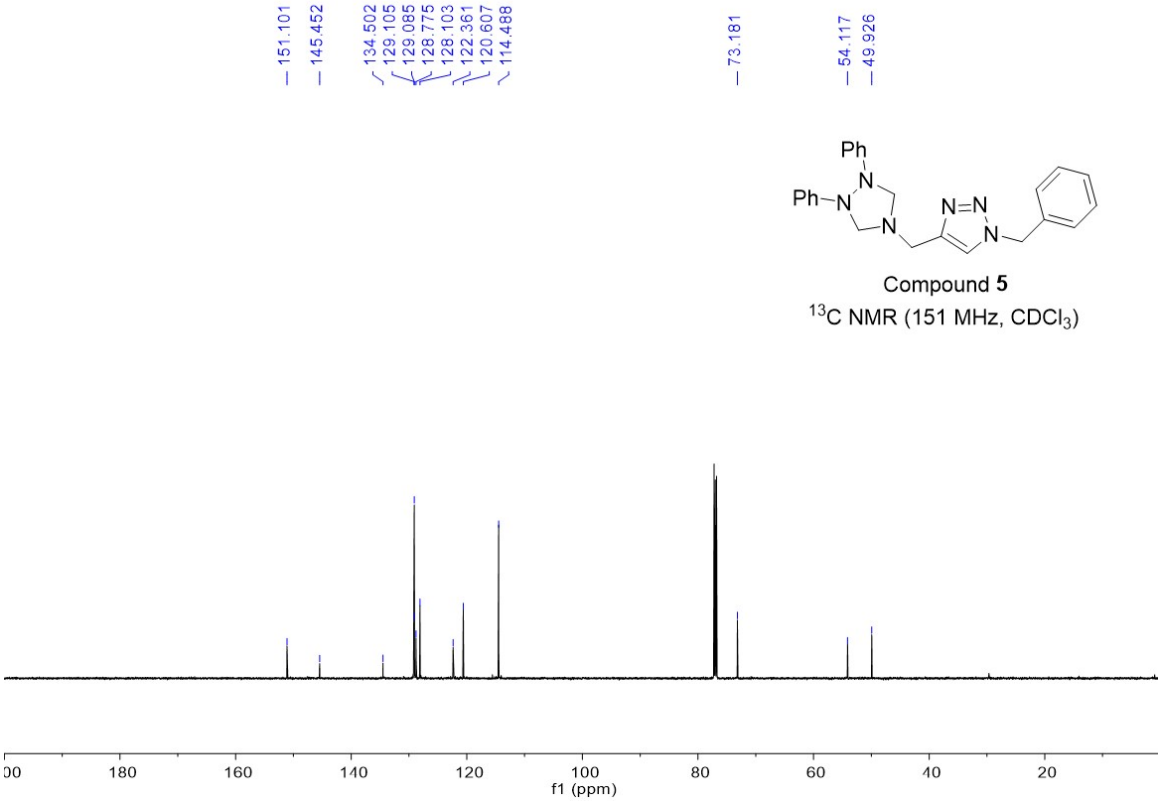
NMR spectra of 1,2-diphenyl-4-(prop-2-yn-1-yl)-1,2,4-triazolidine (**4o**)





NMR spectra of 1-benzyl-4-((1,2-diphenyl-1,2,4-triazolidin-4-yl)methyl)-1*H*-1,2,3-triazole (**5**)

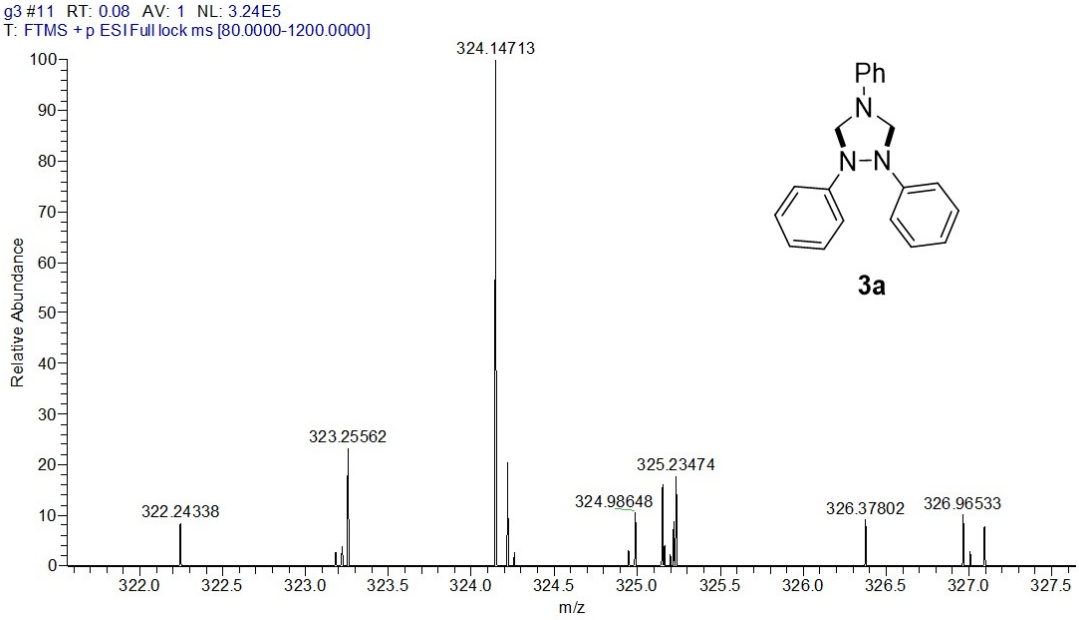




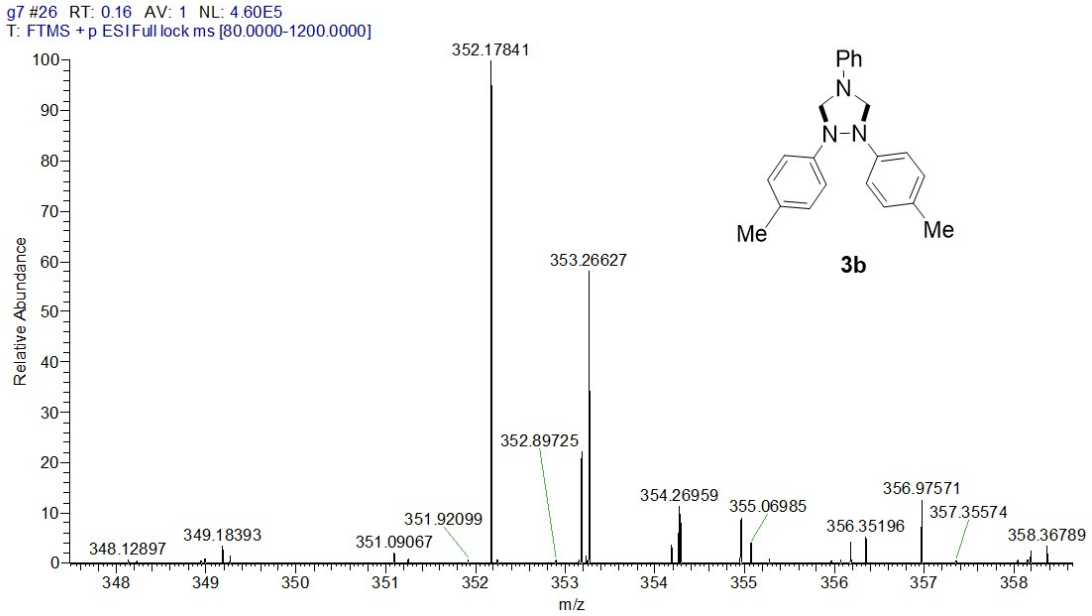
Compound **5**

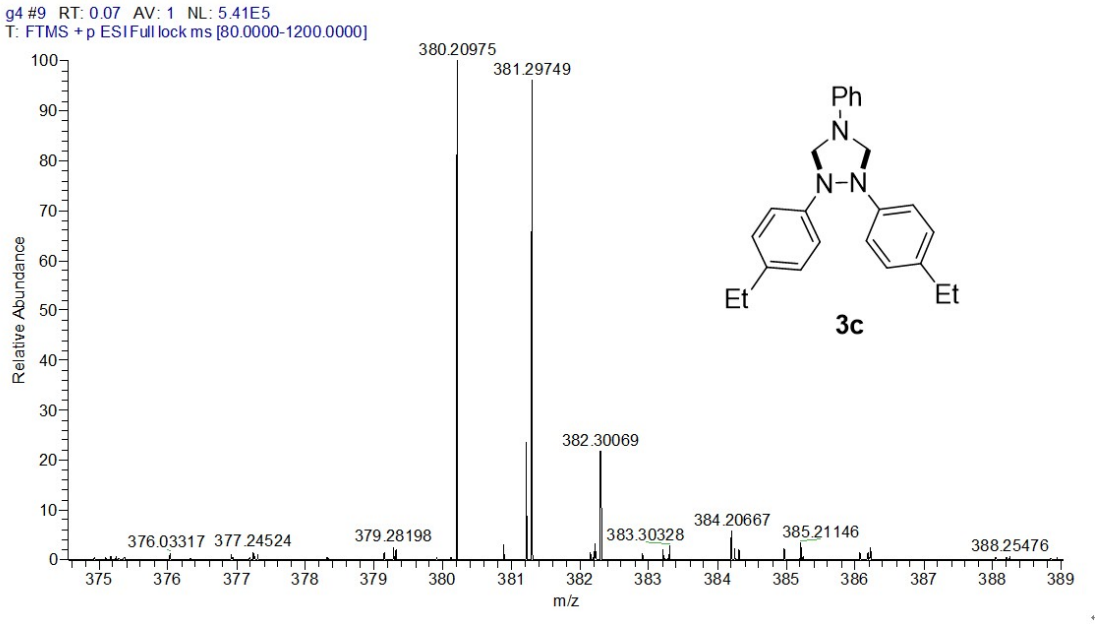
^{13}C NMR (151 MHz, $CDCl_3$)

7. HRMS Analysis Reports for All Compounds

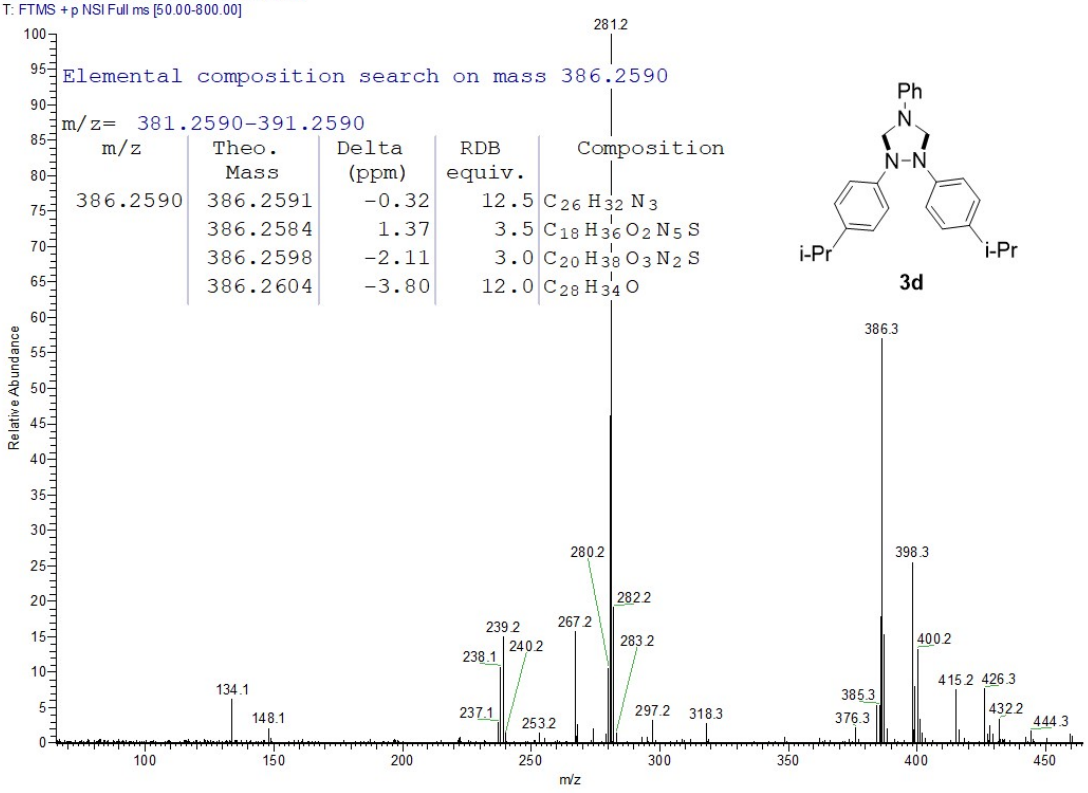


3a

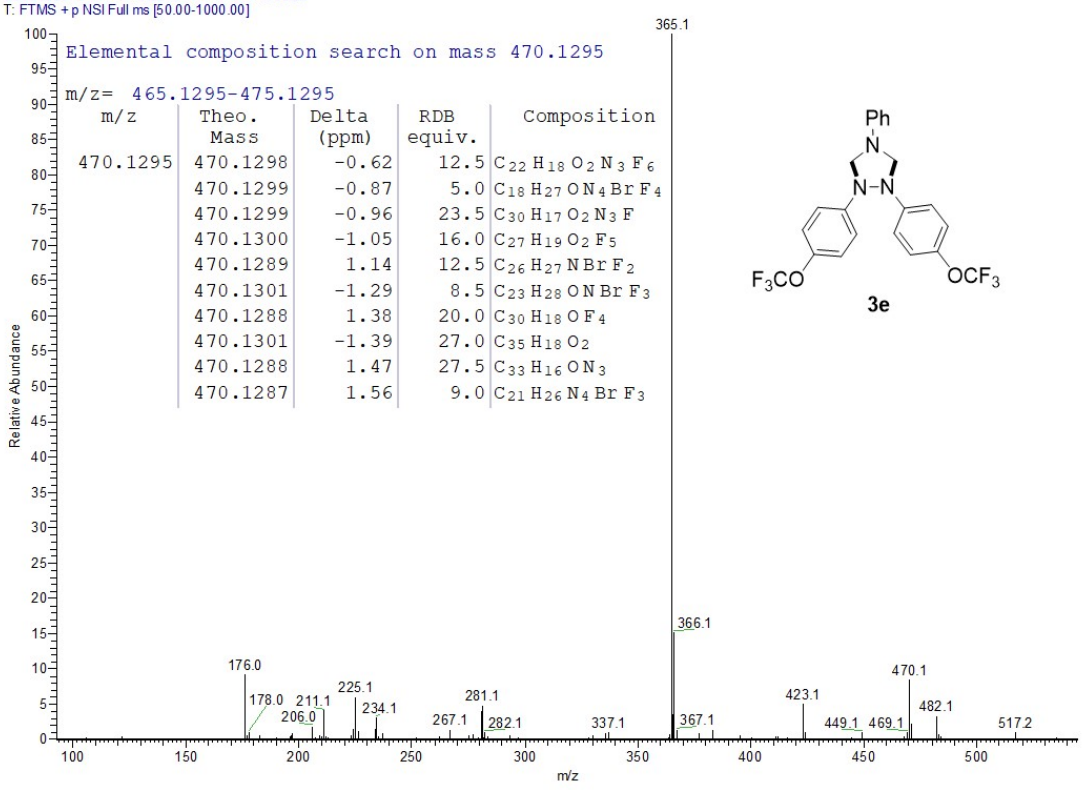

g7 #26 RT: 0.16 AV: 1 NL: 4.60E5
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
Relative Abundance
m/z
352.17841
353.26627
352.89725
354.26959
355.06985
356.97571
357.35574
356.35196
358.36789
351.92099
349.18393
348.12897
351.09067
Ph
N
N–N
Me
Me
3b

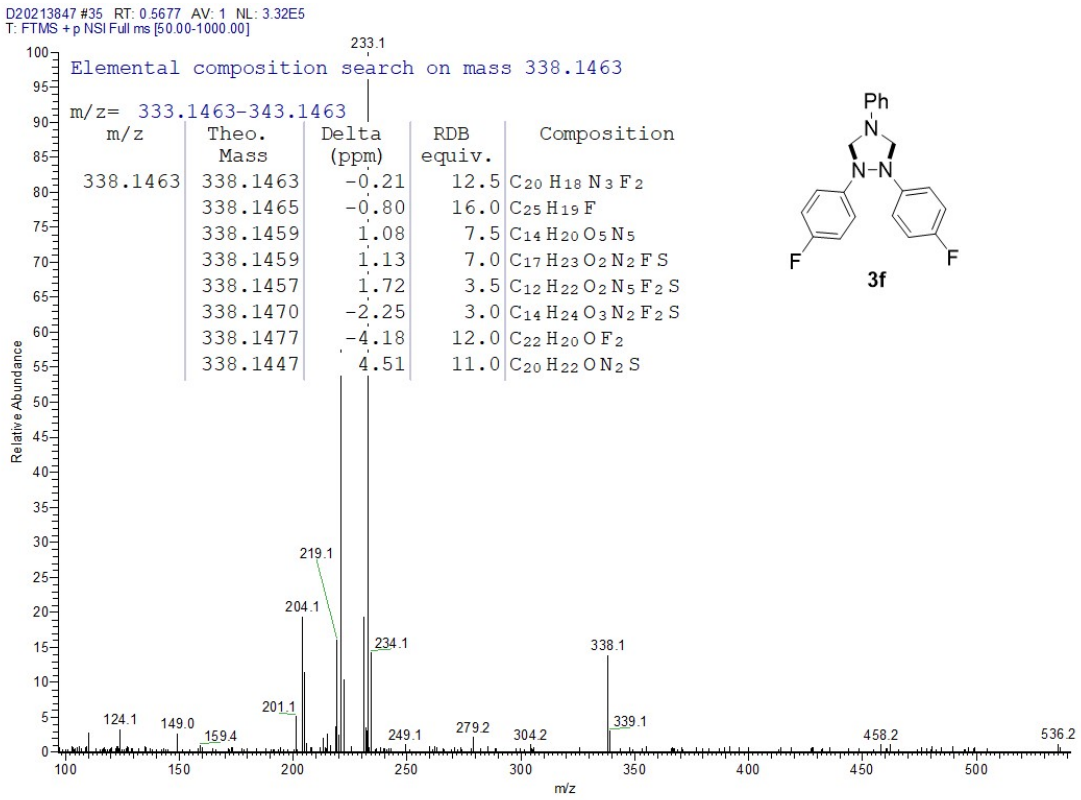

g4 #9 RT: 0.07 AV: 1 NL: 5.41E5
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
Relative Abundance
m/z
380.20975
381.29749
382.30069
384.20667
383.30328
385.21146
388.25476
379.28198
376.03317
377.24524
Ph
N
N–N
Et
Et
3c

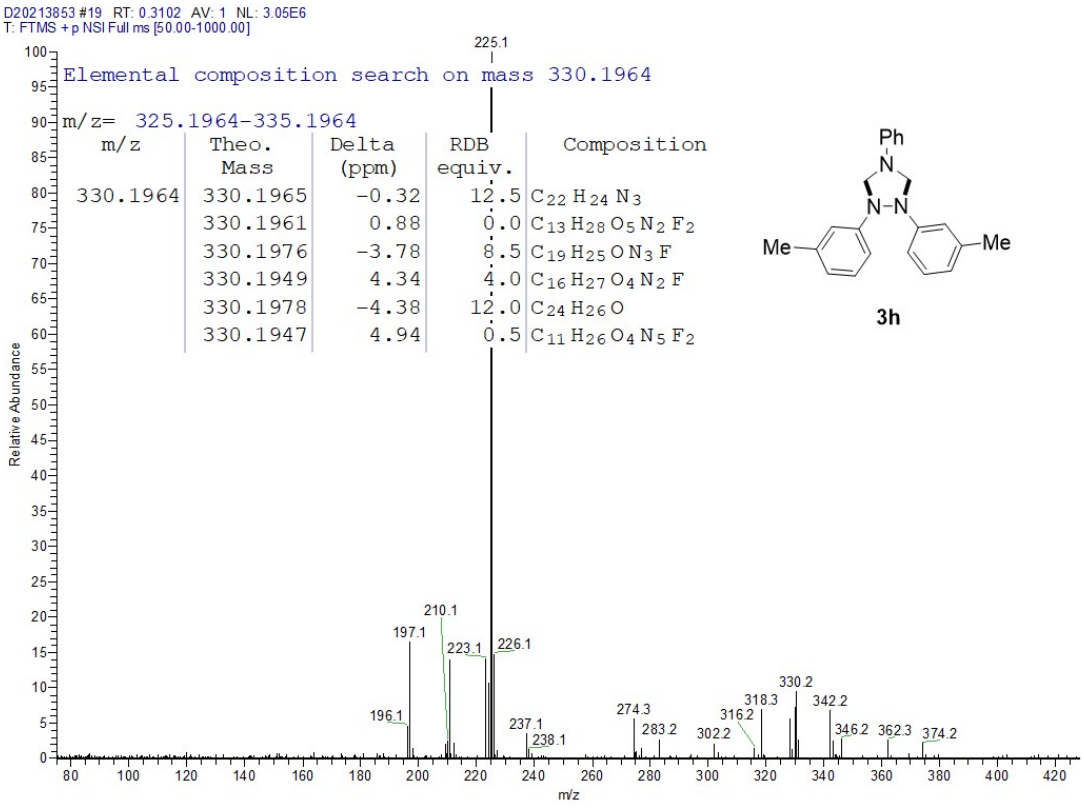
D20212788 #18 RT: 0.3186 AV: 1 NL: 7.74E5
T: FTMS + p NSI Full ms [50.00-800.00]

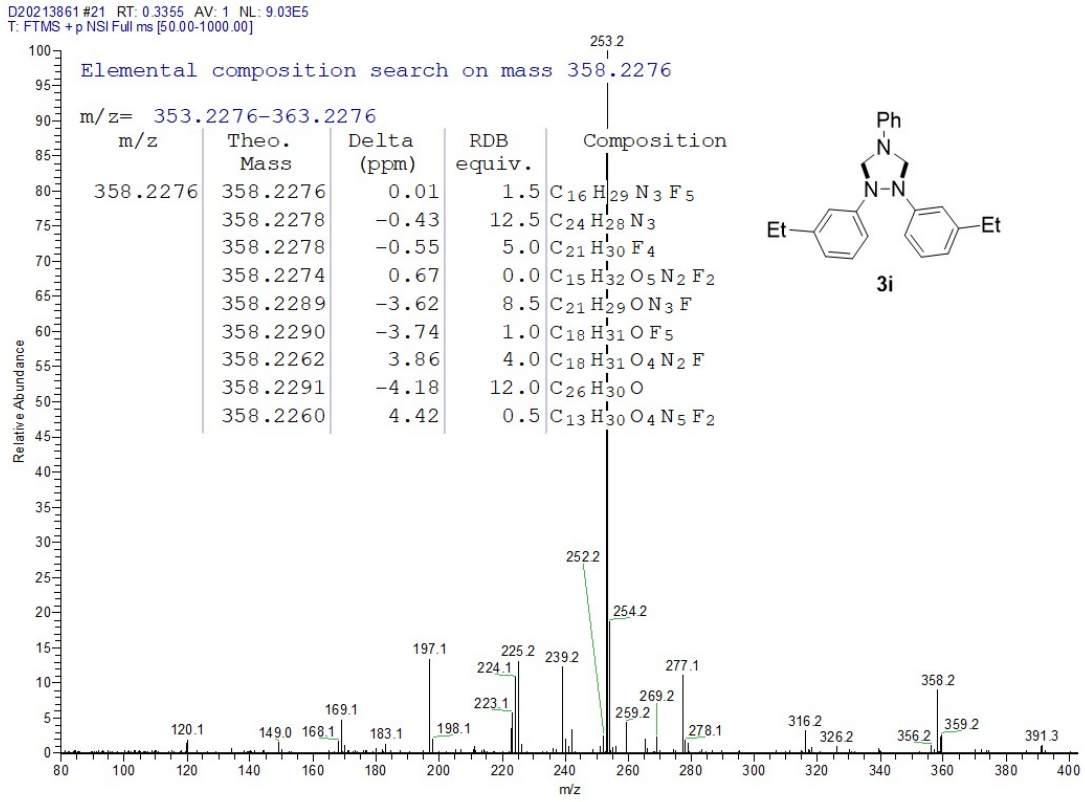


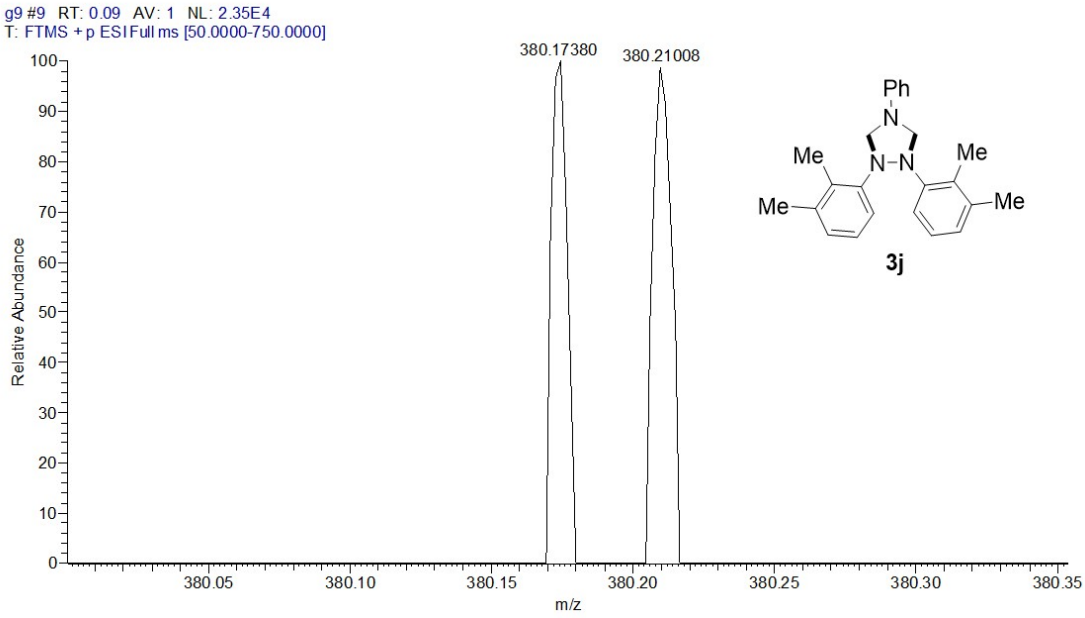
D20213857 #14 RT: 0.2249 AV: 1 NL: 6.30E6
T: FTMS + p NSI Full ms [50.00-1000.00]

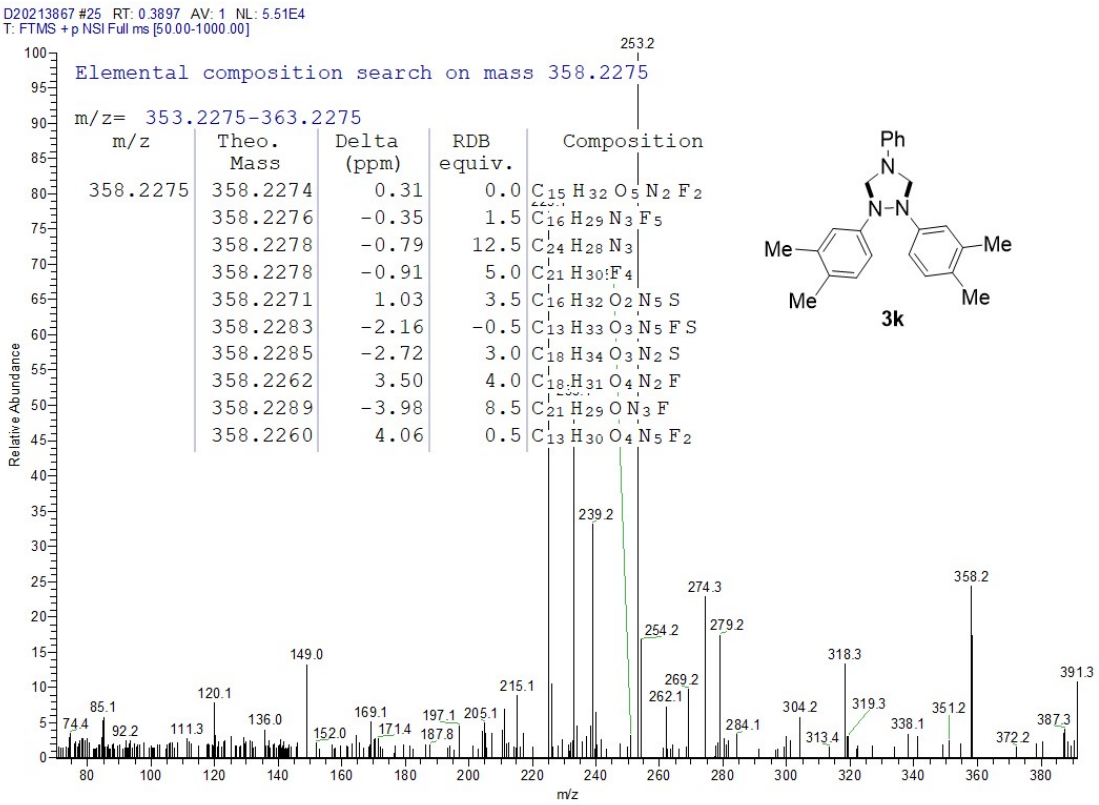


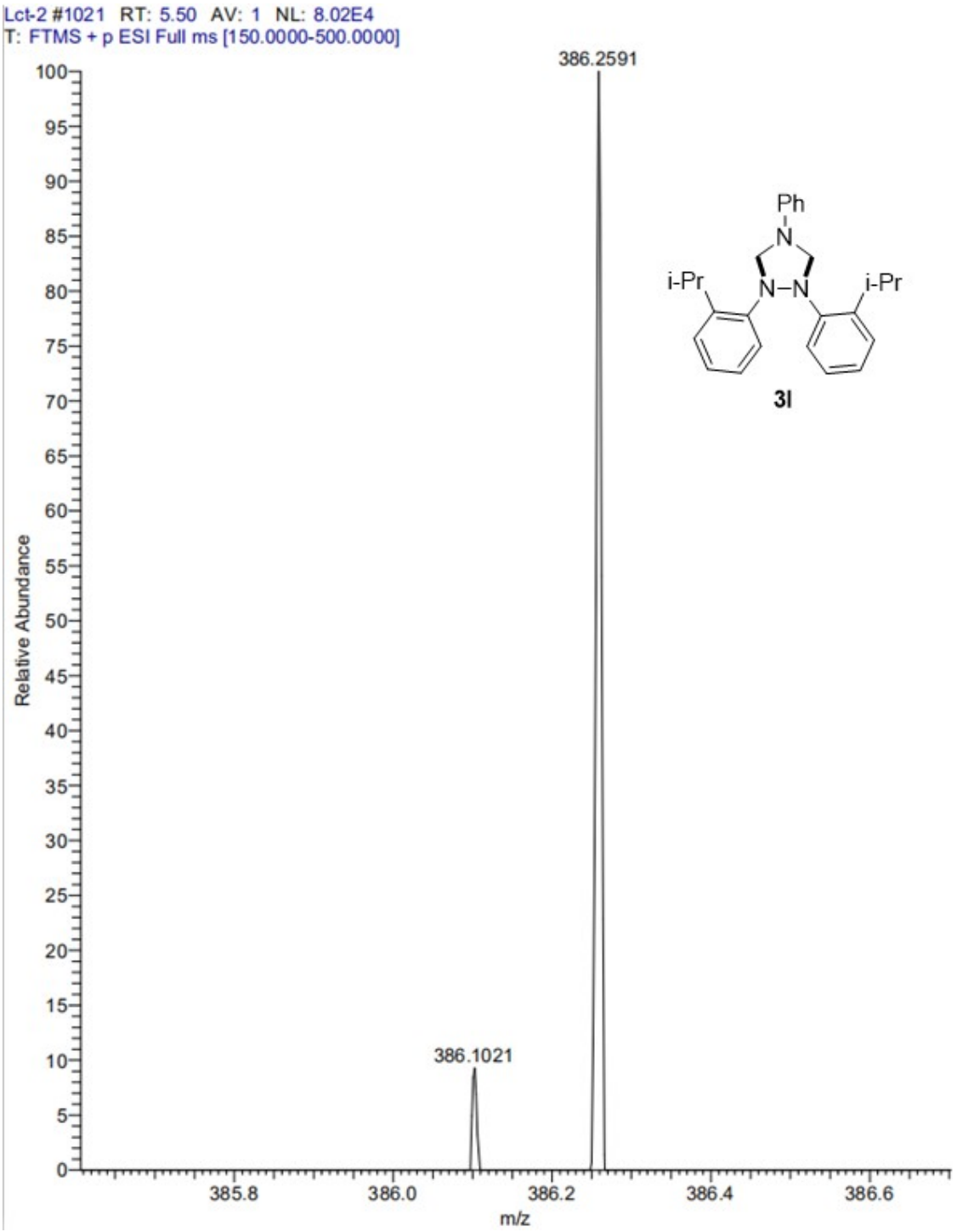

D20213847 #35 RT: 0.5677 AV: 1 NL: 3.32E5
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 338.1463
m/z= 333.1463-343.1463
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
338.1463 | 338.1463 | -0.21 | 12.5 | C20 H18 N3 F2
338.1465 | -0.80 | 16.0 | C25 H19 F
338.1459 | 1.08 | 7.5 | C14 H20 O5 N5
338.1459 | 1.13 | 7.0 | C17 H23 O2 N2 F S
338.1457 | 1.72 | 3.5 | C12 H22 O2 N5 F2 S
338.1470 | -2.25 | 3.0 | C14 H24 O3 N2 F2 S
338.1477 | -4.18 | 12.0 | C22 H20 O F2
338.1447 | 4.51 | 11.0 | C20 H22 O N2 S
Relative Abundance
m/z
Ph
N
N-N
F
F
3f


D20213853 #19 RT: 0.3102 AV: 1 NL: 3.05E6
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 330.1964
m/z= 325.1964-335.1964
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
330.1964 | 330.1965 | -0.32 | 12.5 | C22 H24 N3
330.1961 | 0.88 | 0.0 | C13 H28 O5 N2 F2
330.1976 | -3.78 | 8.5 | C19 H25 O N3 F
330.1949 | 4.34 | 4.0 | C16 H27 O4 N2 F
330.1978 | -4.38 | 12.0 | C24 H26 O
330.1947 | 4.94 | 0.5 | C11 H26 O4 N5 F2
Relative Abundance
m/z
Ph
N
N-N
Me
Me
3h

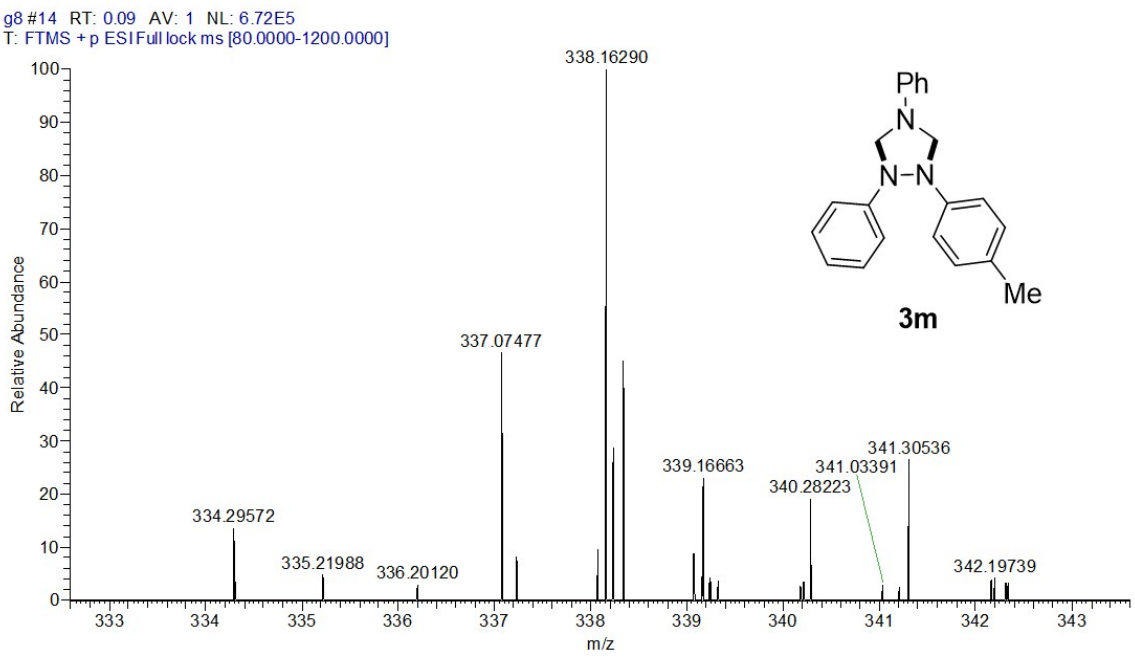

D20213861 #21 RT: 0.3355 AV: 1 NL: 9.03E5
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 358.2276
m/z= 353.2276-363.2276
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
358.2276 | 358.2276 | 0.01 | 1.5 | C16H29N3F5
358.2278 | -0.43 | 12.5 | C24H28N3
358.2278 | -0.55 | 5.0 | C21H30F4
358.2274 | 0.67 | 0.0 | C15H32O5N2F2
358.2289 | -3.62 | 8.5 | C21H29ON3F
358.2290 | -3.74 | 1.0 | C18H31OF5
358.2262 | 3.86 | 4.0 | C18H31O4N2F
358.2291 | -4.18 | 12.0 | C26H30O
358.2260 | 4.42 | 0.5 | C13H30O4N5F2
Ph
N
N-N
Et
Et
3i
Relative Abundance
m/z

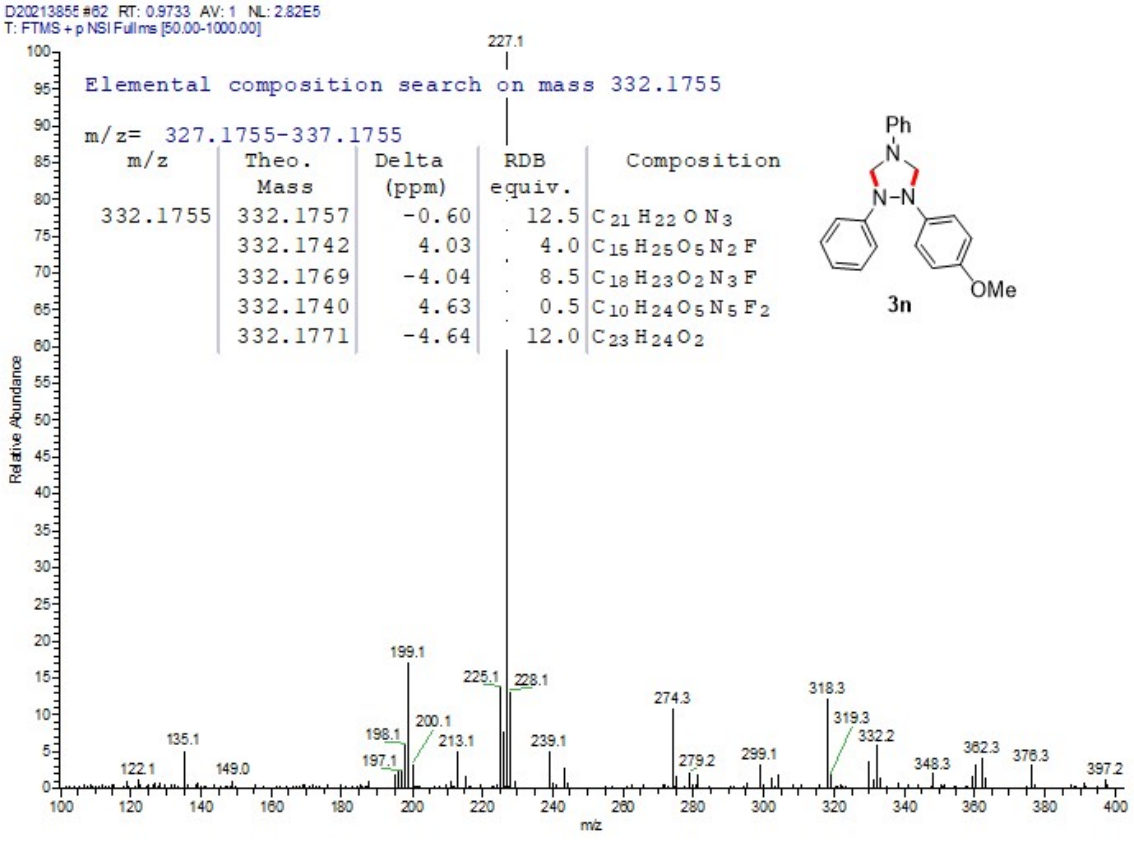

g9 #9 RT: 0.09 AV: 1 NL: 2.35E4
T: FTMS + p ESI Full ms [50.0000-750.0000]
380.17380
380.21008
Ph
N
N-N
Me
Me
Me
Me
3j
Relative Abundance
m/z


D20213867 #25 RT: 0.3897 AV: 1 NL: 5.51E4
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 358.2275
m/z= 353.2275-363.2275
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
358.2275 | 358.2274 | 0.31 | 0.0 | C15 H32 O5 N2 F2
358.2276 | -0.35 | 1.5 | C16 H29 N3 F5
358.2278 | -0.79 | 12.5 | C24 H28 N3
358.2278 | -0.91 | 5.0 | C21 H30 F4
358.2271 | 1.03 | 3.5 | C16 H32 O2 N5 S
358.2283 | -2.16 | -0.5 | C13 H33 O3 N5 F S
358.2285 | -2.72 | 3.0 | C18 H34 O3 N2 S
358.2262 | 3.50 | 4.0 | C18 H31 O4 N2 F
358.2289 | -3.98 | 8.5 | C21 H29 O N3 F
358.2260 | 4.06 | 0.5 | C13 H30 O4 N5 F2
Relative Abundance
m/z
Ph
N
N-N
Me
Me
Me
Me
3k


Lct-2 #1021 RT: 5.50 AV: 1 NL: 8.02E4
T: FTMS + p ESI Full ms [150.0000-500.0000]
386.2591
386.1021
Relative Abundance
m/z
385.8
386.0
386.2
386.4
386.6
Ph
N
i-Pr
N–N
i-Pr

3l

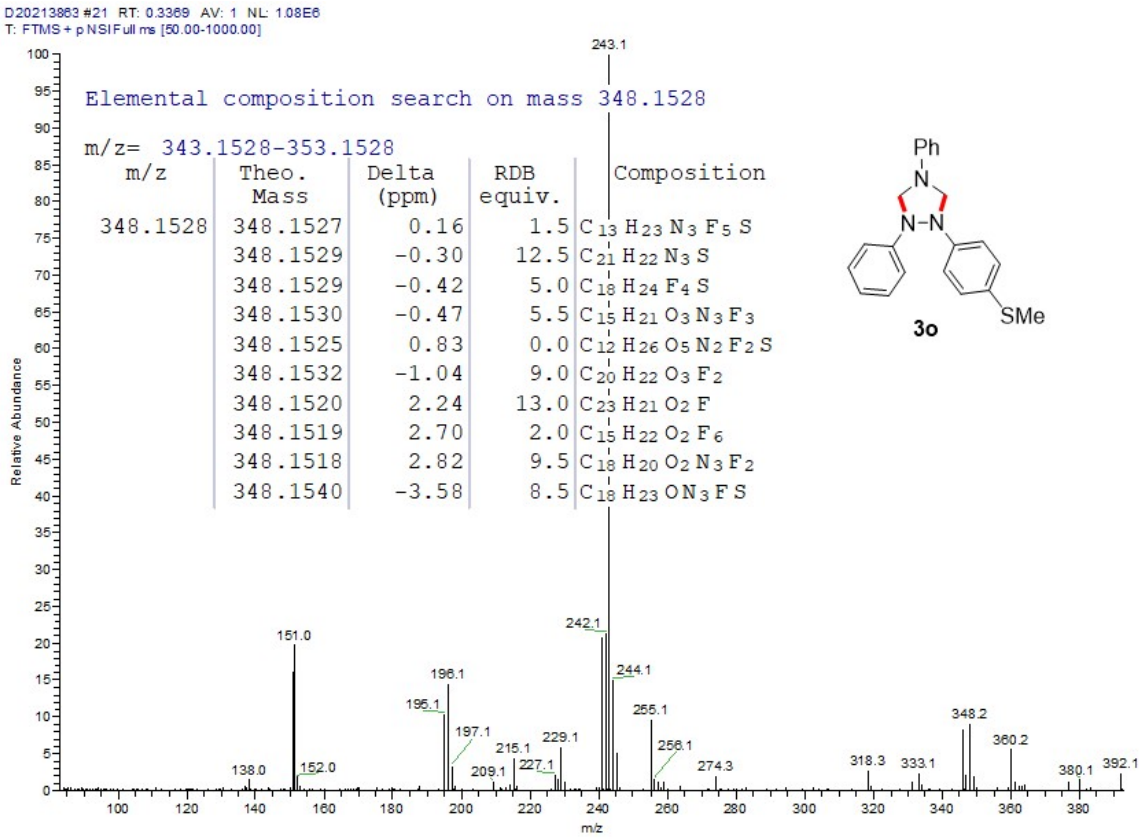


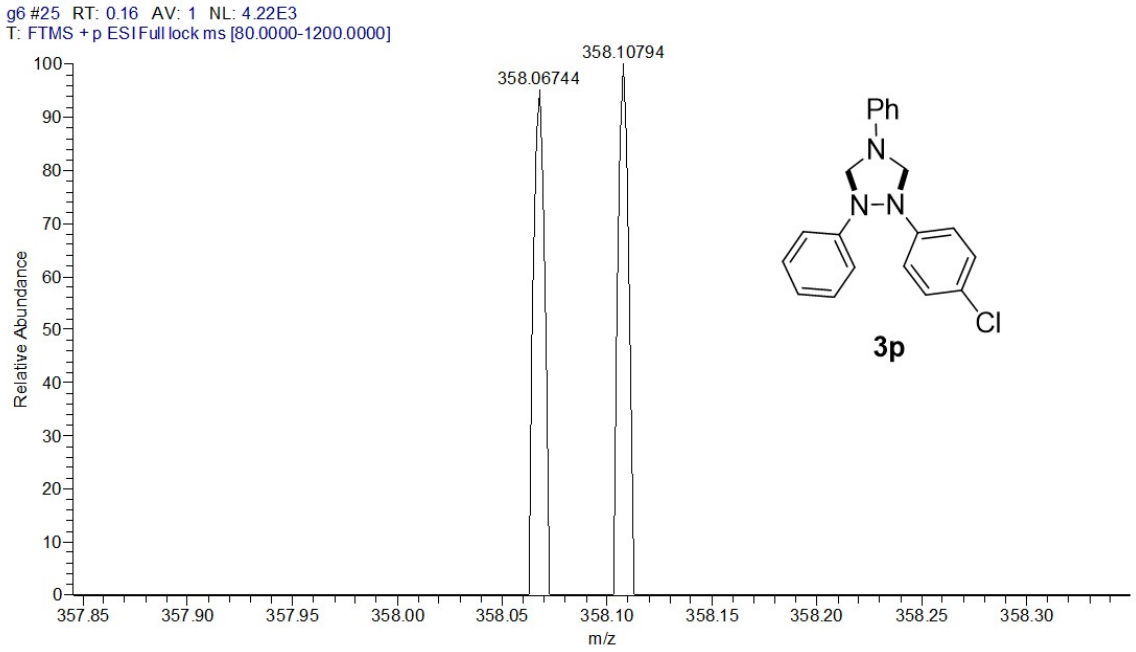


Elemental composition search on mass 332.1755

m/z= 327.1755-337.1755

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
332.1755	332.1757	-0.60	12.5	$C_{21}H_{22}ON_3$
	332.1742	4.03	4.0	$C_{15}H_{25}O_5N_2F$
	332.1769	-4.04	8.5	$C_{18}H_{23}O_2N_3F$
	332.1740	4.63	0.5	$C_{10}H_{24}O_5N_5F_2$
	332.1771	-4.64	12.0	$C_{23}H_{24}O_2$


D20213863 #21 RT: 0.3369 AV: 1 NL: 1.08E6
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 348.1528
m/z= 343.1528-353.1528
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
348.1528 | 348.1527 | 0.16 | 1.5 | C13 H23 N3 F5 S
348.1529 | -0.30 | 12.5 | C21 H22 N3 S
348.1529 | -0.42 | 5.0 | C18 H24 F4 S
348.1530 | -0.47 | 5.5 | C15 H21 O3 N3 F3
348.1525 | 0.83 | 0.0 | C12 H26 O5 N2 F2 S
348.1532 | -1.04 | 9.0 | C20 H22 O3 F2
348.1520 | 2.24 | 13.0 | C23 H21 O2 F
348.1519 | 2.70 | 2.0 | C15 H22 O2 F6
348.1518 | 2.82 | 9.5 | C18 H20 O2 N3 F2
348.1540 | -3.58 | 8.5 | C18 H23 O N3 F S
Ph
N
N-N
SMe
3o
Relative Abundance
m/z

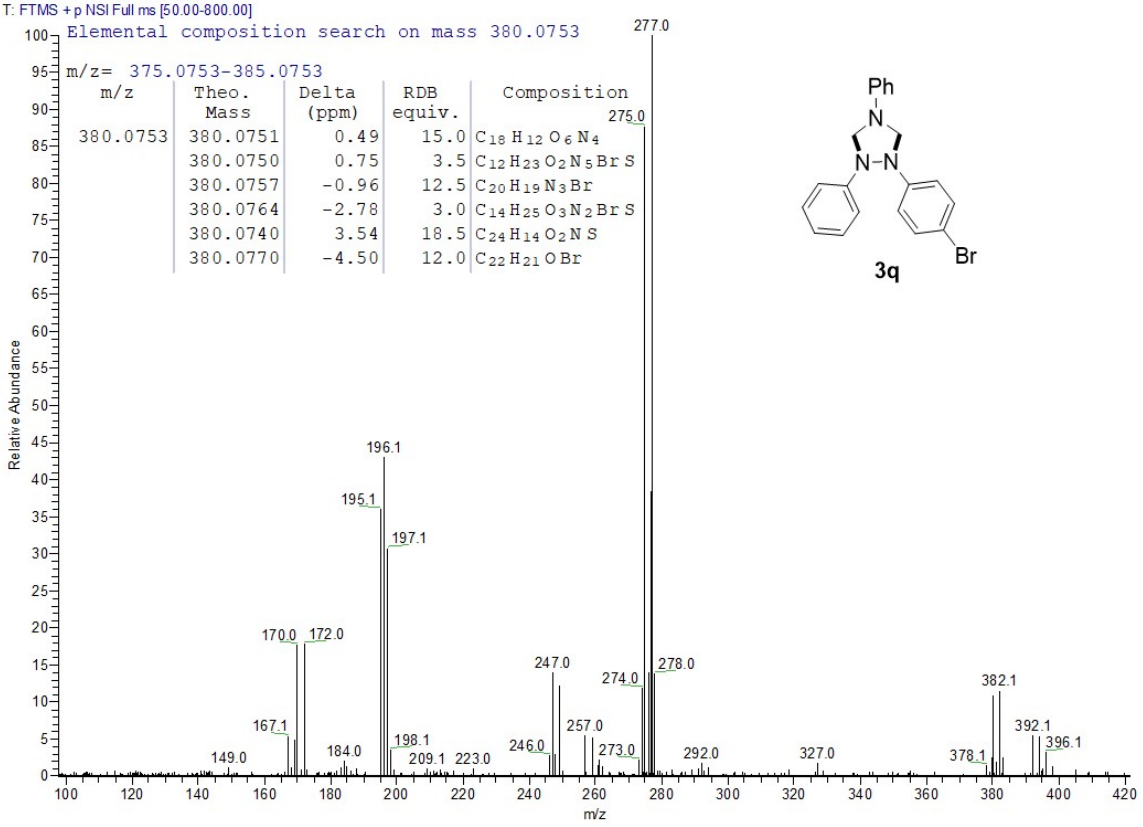

g6 #25 RT: 0.16 AV: 1 NL: 4.22E3
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
358.10794
358.06744
Ph
N
N-N
Cl
3p
Relative Abundance
m/z

D20214340 #30 RT: 0.5542 AV: 1 NL: 6.15E5
T: FTMS + p NSI Full ms [50.00-800.00]

Elemental composition search on mass 380.0753

m/z= 375.0753-385.0753

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
380.0753	380.0751	0.49	15.0	$C_{18}H_{12}O_6N_4$
	380.0750	0.75	3.5	$C_{12}H_{23}O_2N_5BrS$
	380.0757	-0.96	12.5	$C_{20}H_{19}N_3Br$
	380.0764	-2.78	3.0	$C_{14}H_{25}O_3N_2BrS$
	380.0740	3.54	18.5	$C_{24}H_{14}O_2NS$
	380.0770	-4.50	12.0	$C_{22}H_{21}OBr$



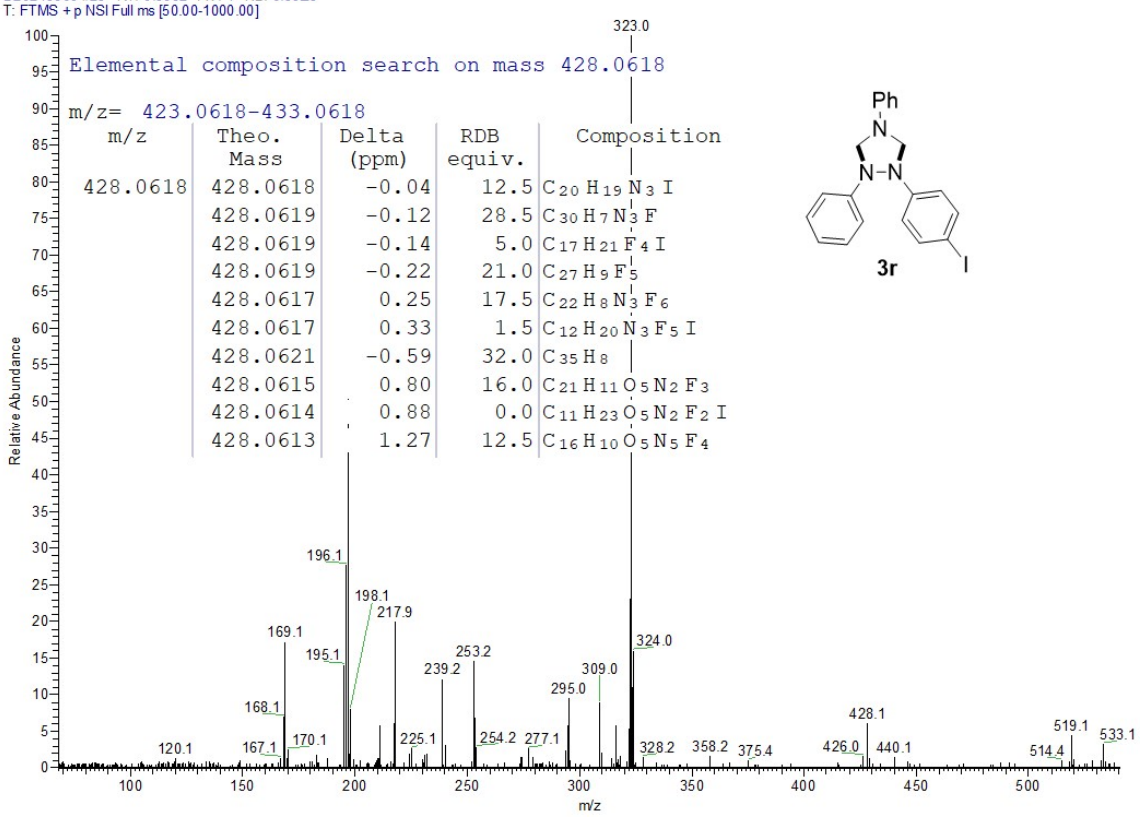
3q

D20213869 #25 RT: 0.3882 AV: 1 NL: 6.59E5
T: FTMS + p NSI Full ms [50.00-1000.00]

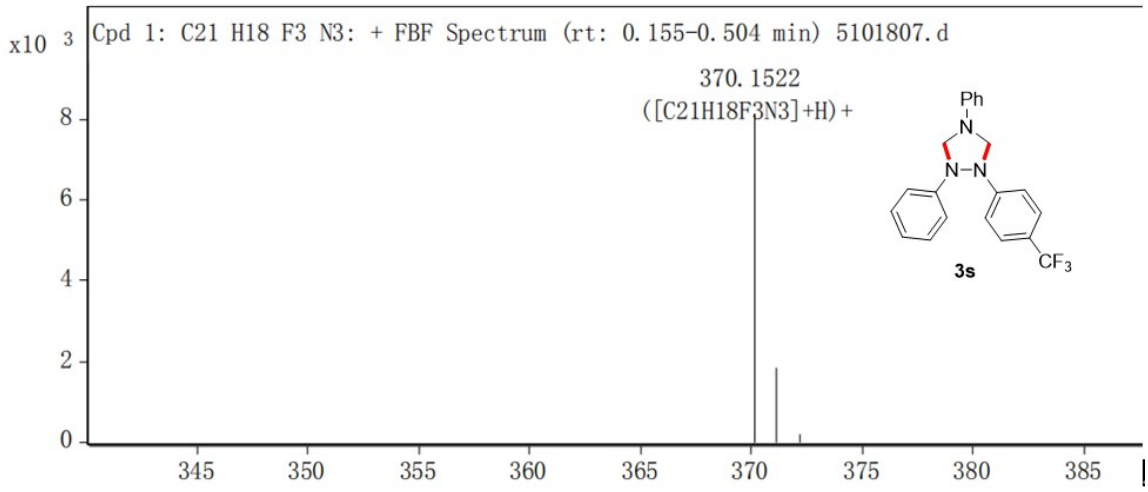
Elemental composition search on mass 428.0618

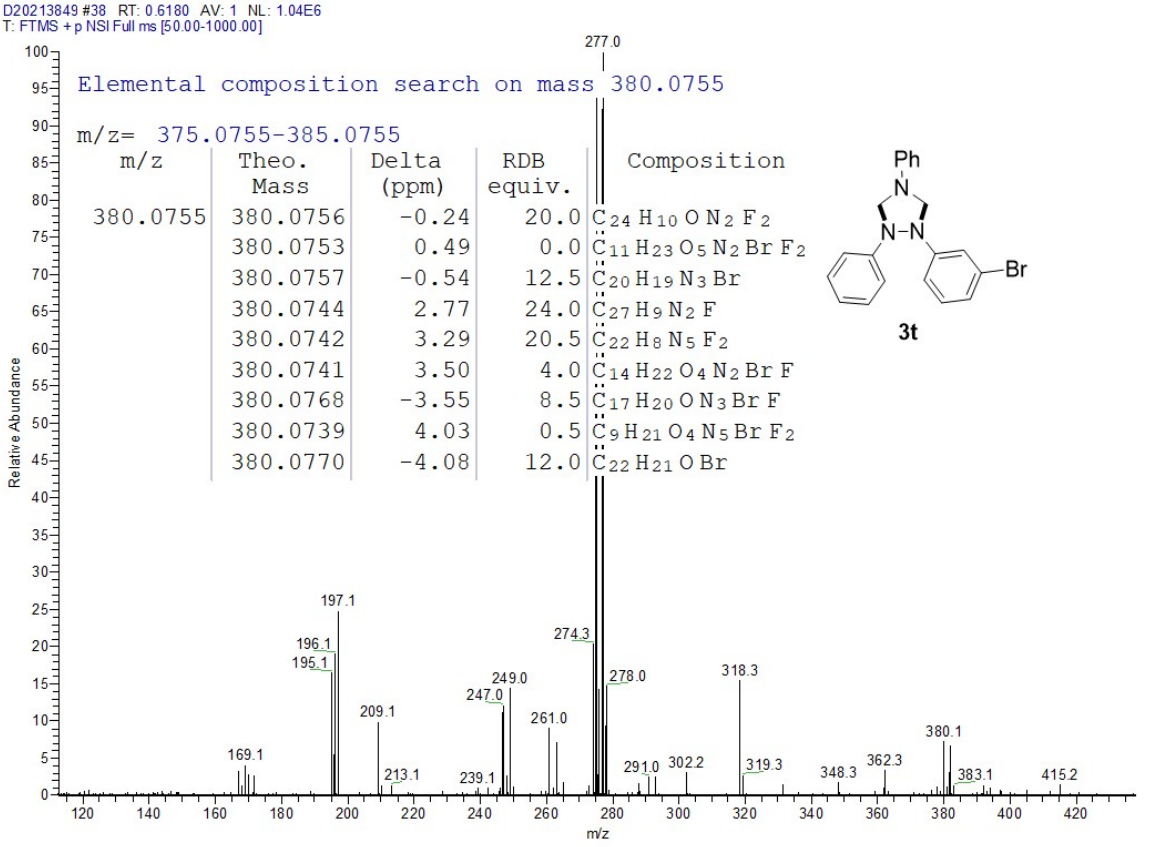
m/z= 423.0618-433.0618

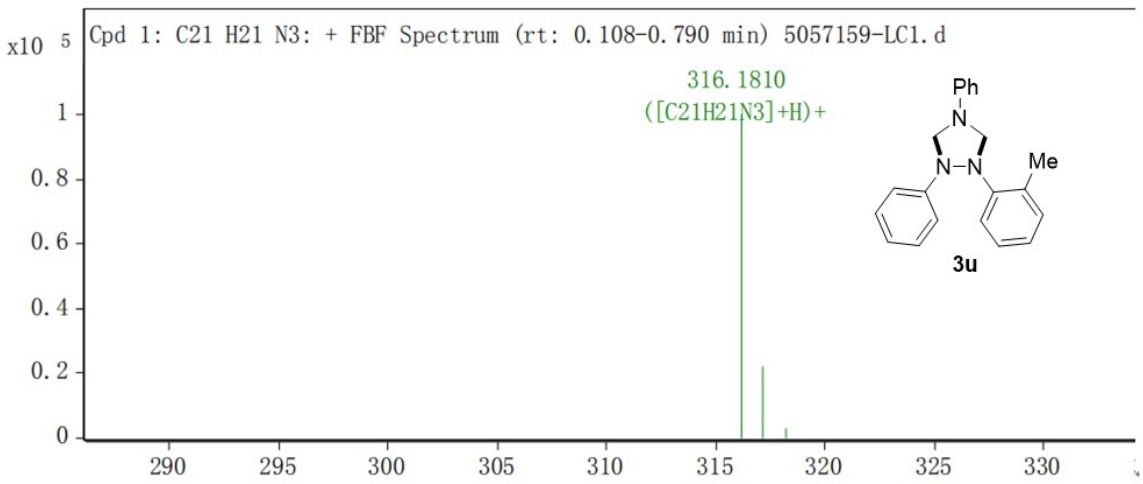
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
428.0618	428.0618	-0.04	12.5	$C_{20}H_{19}N_3I$
	428.0619	-0.12	28.5	$C_{30}H_7N_3F$
	428.0619	-0.14	5.0	$C_{17}H_{21}F_4I$
	428.0619	-0.22	21.0	$C_{27}H_9F_5$
	428.0617	0.25	17.5	$C_{22}H_8N_3F_6$
	428.0617	0.33	1.5	$C_{12}H_{20}N_3F_5I$
	428.0621	-0.59	32.0	$C_{35}H_8$
	428.0615	0.80	16.0	$C_{21}H_{11}O_5N_2F_3$
	428.0614	0.88	0.0	$C_{11}H_{23}O_5N_2F_2I$
	428.0613	1.27	12.5	$C_{16}H_{10}O_5N_5F_4$

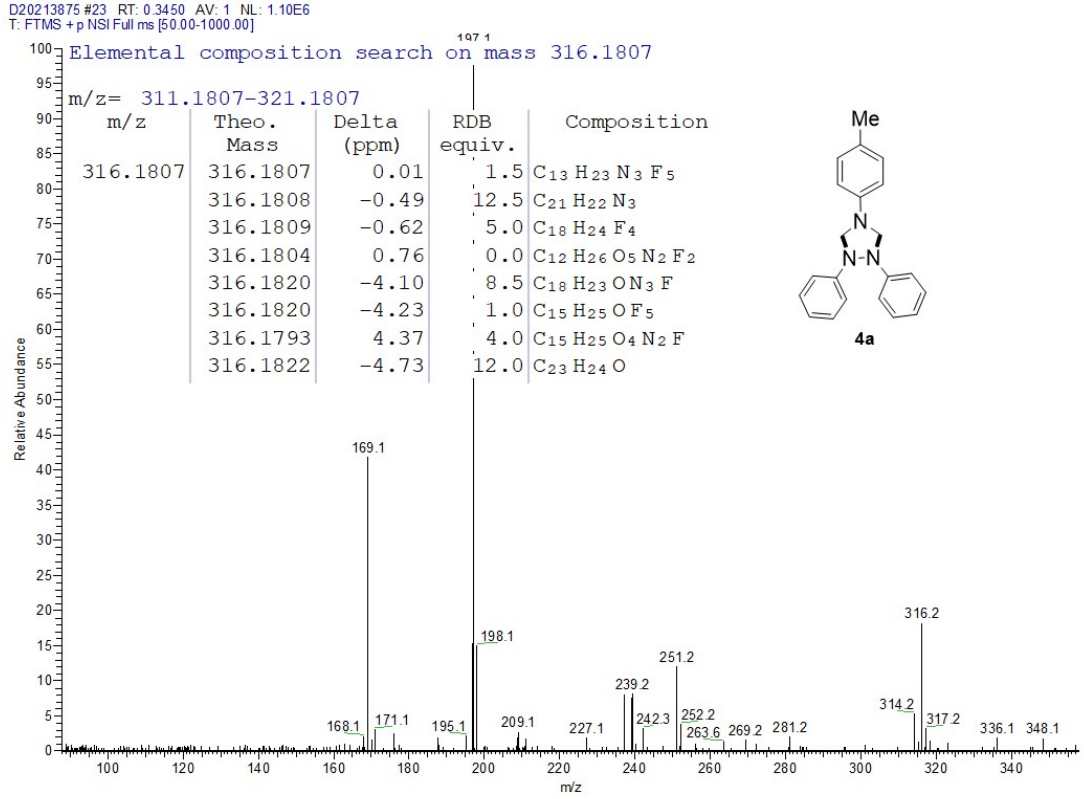


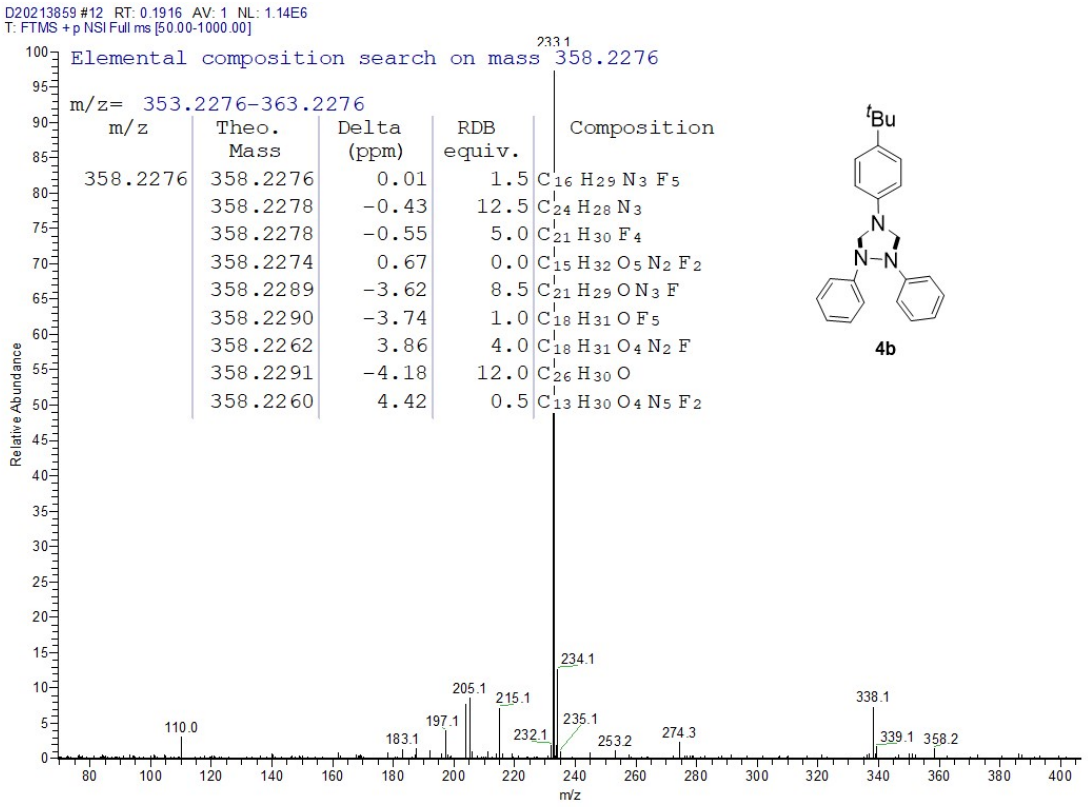
3r

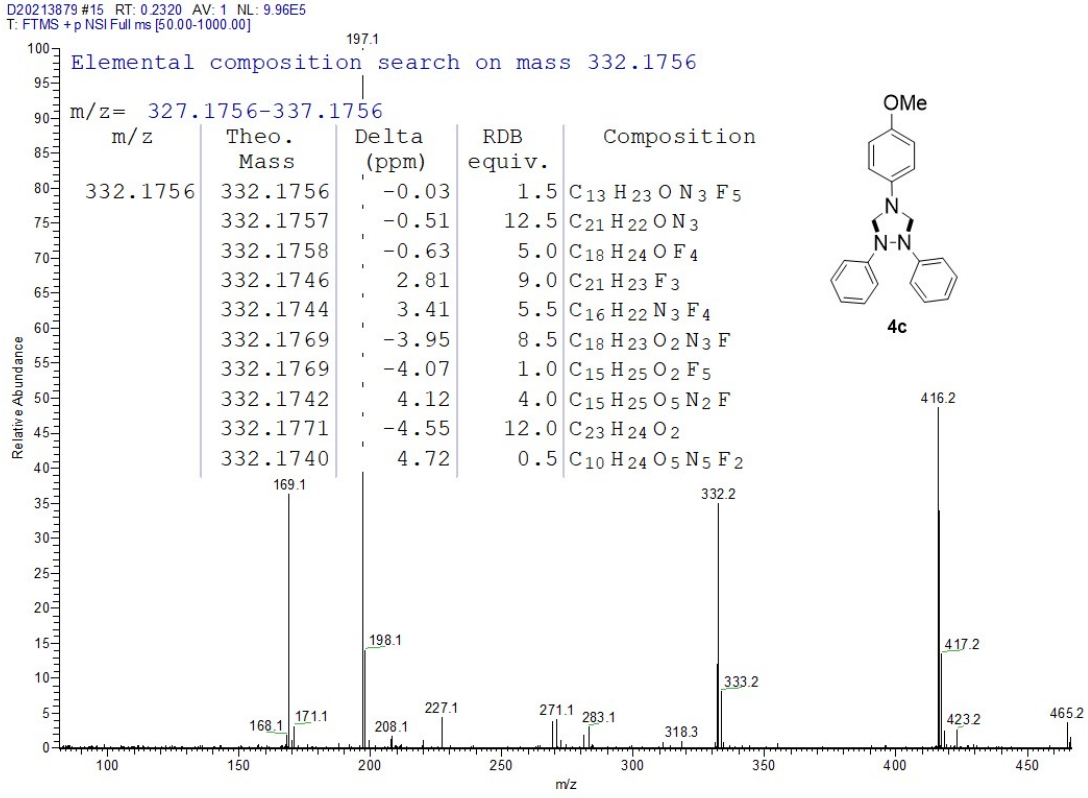

Cpd 1: C21 H18 F3 N3: + FBF Spectrum (rt: 0.155-0.504 min) 5101807.d
x10 3
370.1522
([C21H18F3N3]+H)+
Ph
N
N-N
CF3
3s


D20213849 #38 RT: 0.6180 AV: 1 NL: 1.04E6
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 380.0755
m/z= 375.0755-385.0755
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
380.0755 | 380.0756 | -0.24 | 20.0 | C24 H10 O N2 F2
380.0753 | 0.49 | 0.0 | C11 H23 O5 N2 Br F2
380.0757 | -0.54 | 12.5 | C20 H19 N3 Br
380.0744 | 2.77 | 24.0 | C27 H9 N2 F
380.0742 | 3.29 | 20.5 | C22 H8 N5 F2
380.0741 | 3.50 | 4.0 | C14 H22 O4 N2 Br F
380.0768 | -3.55 | 8.5 | C17 H20 O N3 Br F
380.0739 | 4.03 | 0.5 | C9 H21 O4 N5 Br F2
380.0770 | -4.08 | 12.0 | C22 H21 O Br
Ph
N
N-N
Br
3t
Relative Abundance
m/z

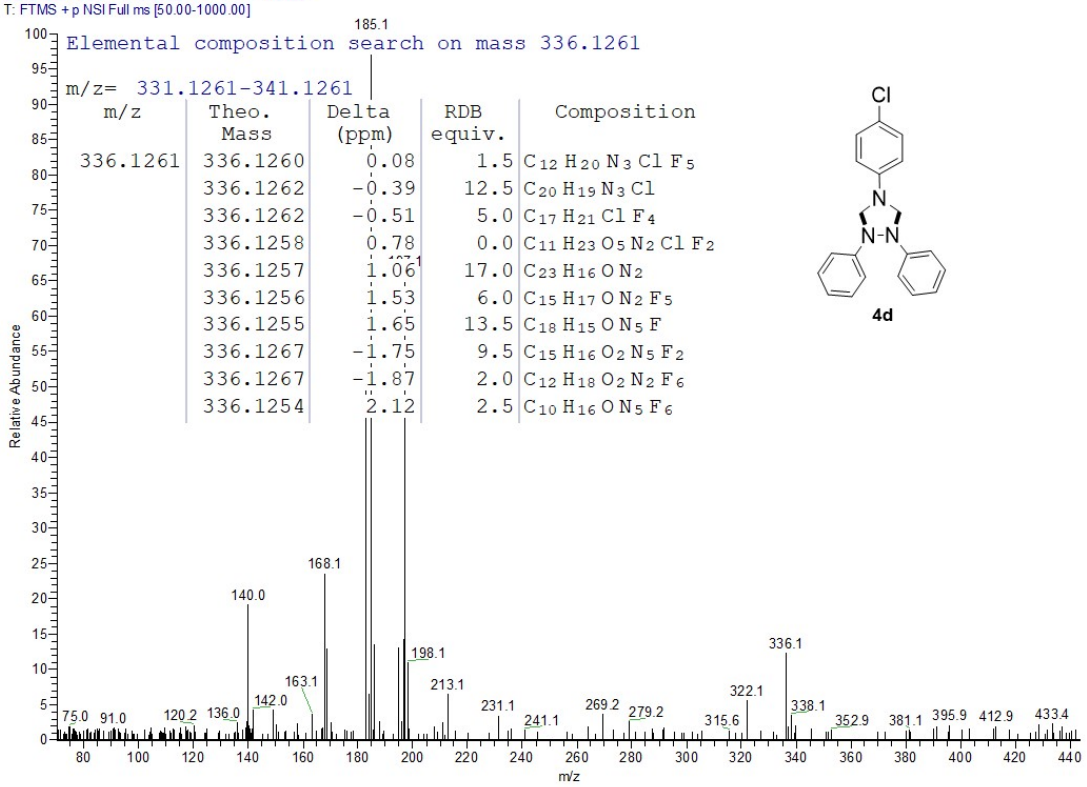

Cpd 1: C21 H21 N3: + FBF Spectrum (rt: 0.108-0.790 min) 5057159-LC1.d
x10 5
316.1810
([C21H21N3]+H)+
Ph
N
N-N
Me
3u


D20213875 #23 RT: 0.3450 AV: 1 NL: 1.10E6
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 316.1807
m/z= 311.1807-321.1807
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
316.1807 | 316.1807 | 0.01 | 1.5 | C13 H23 N3 F5
316.1808 | -0.49 | 12.5 | C21 H22 N3
316.1809 | -0.62 | 5.0 | C18 H24 F4
316.1804 | 0.76 | 0.0 | C12 H26 O5 N2 F2
316.1820 | -4.10 | 8.5 | C18 H23 O N3 F
316.1820 | -4.23 | 1.0 | C15 H25 O F5
316.1793 | 4.37 | 4.0 | C15 H25 O4 N2 F
316.1822 | -4.73 | 12.0 | C23 H24 O
Me
N
N-N
4a
Relative Abundance
m/z
169.1
198.1
316.2
251.2
239.2
314.2
317.2
168.1
171.1
195.1
209.1
227.1
242.3
252.2
263.6
269.2
281.2
336.1
348.1

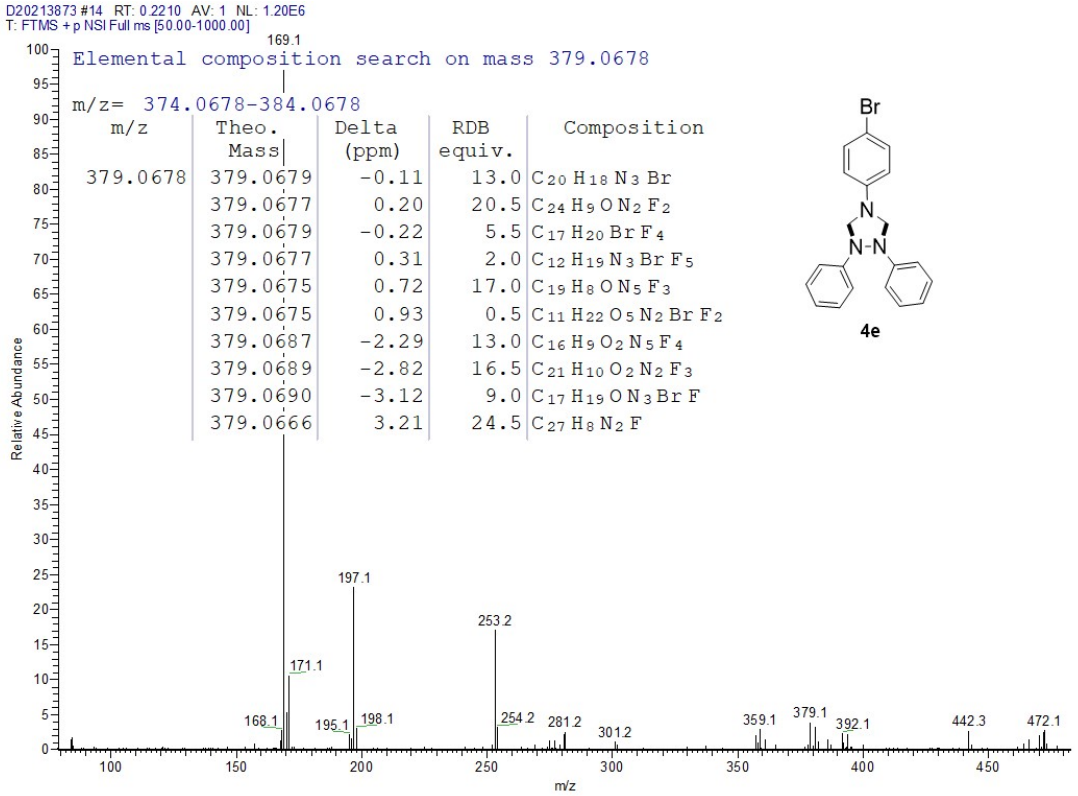

D20213859 #12 RT: 0.1916 AV: 1 NL: 1.14E6
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 358.2276
m/z= 353.2276-363.2276
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
358.2276 | 358.2276 | 0.01 | 1.5 | C16 H29 N3 F5
358.2278 | -0.43 | 12.5 | C24 H28 N3
358.2278 | -0.55 | 5.0 | C21 H30 F4
358.2274 | 0.67 | 0.0 | C15 H32 O5 N2 F2
358.2289 | -3.62 | 8.5 | C21 H29 O N3 F
358.2290 | -3.74 | 1.0 | C18 H31 O F5
358.2262 | 3.86 | 4.0 | C18 H31 O4 N2 F
358.2291 | -4.18 | 12.0 | C26 H30 O
358.2260 | 4.42 | 0.5 | C13 H30 O4 N5 F2
tBu
4b
Relative Abundance
m/z

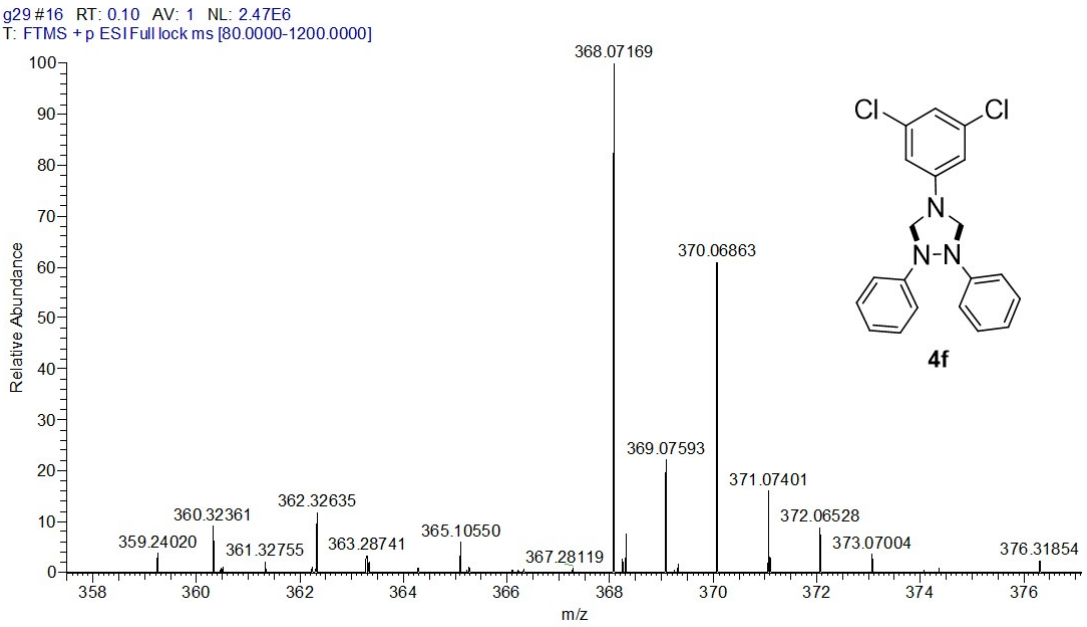

D20213879 #15 RT: 0.2320 AV: 1 NL: 9.96E5
T: FTMS + p NSI Full ms [50.00-1000.00]
Elemental composition search on mass 332.1756
m/z= 327.1756-337.1756
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
332.1756 | 332.1756 | -0.03 | 1.5 | C13 H23 O N3 F5
332.1757 | -0.51 | 12.5 | C21 H22 O N3
332.1758 | -0.63 | 5.0 | C18 H24 O F4
332.1746 | 2.81 | 9.0 | C21 H23 F3
332.1744 | 3.41 | 5.5 | C16 H22 N3 F4
332.1769 | -3.95 | 8.5 | C18 H23 O2 N3 F
332.1769 | -4.07 | 1.0 | C15 H25 O2 F5
332.1742 | 4.12 | 4.0 | C15 H25 O5 N2 F
332.1771 | -4.55 | 12.0 | C23 H24 O2
332.1740 | 4.72 | 0.5 | C10 H24 O5 N5 F2
OMe
4c
Relative Abundance
m/z

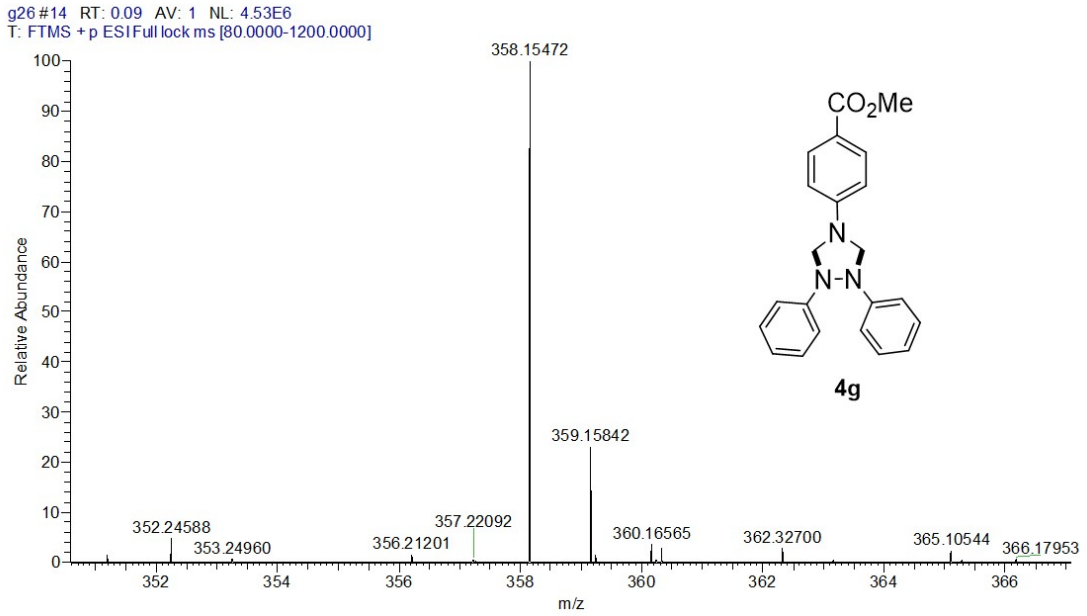
D20213871 #51 RT: 0.8052 AV: 1 NL: 1.94E5
T: FTMS + p NSI Full ms [50.00-1000.00]



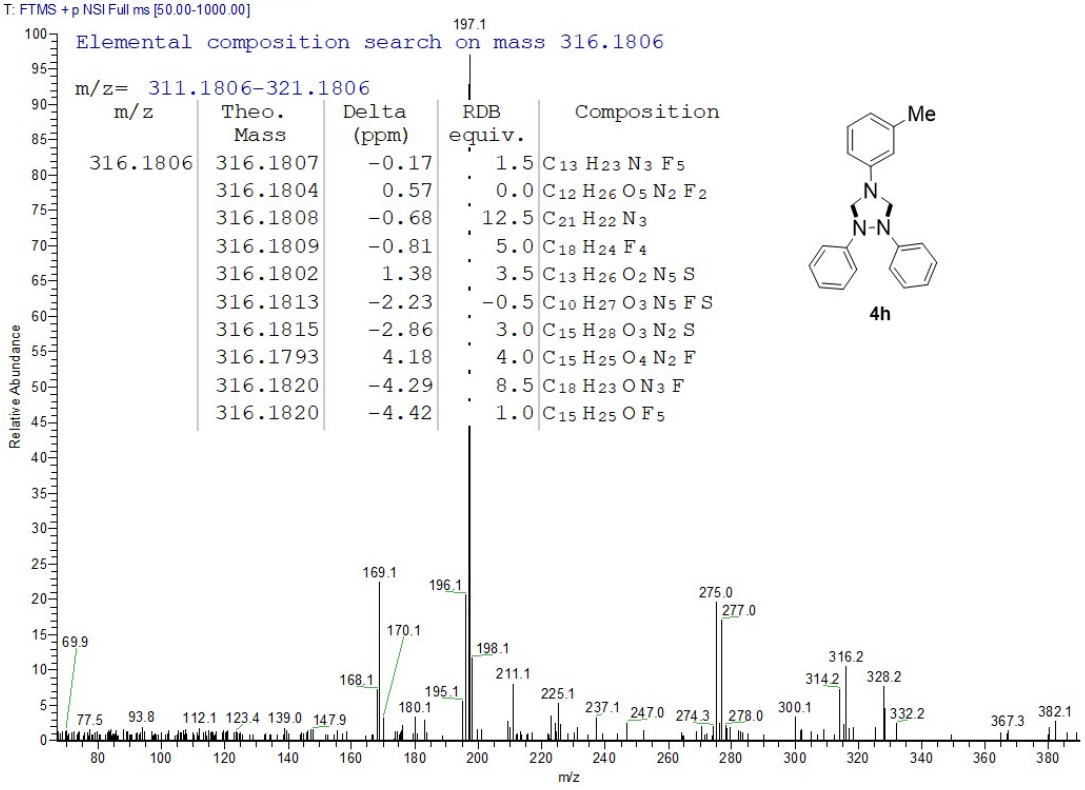
D20213873 #14 RT: 0.2210 AV: 1 NL: 1.20E6
T: FTMS + p NSI Full ms [50.00-1000.00]



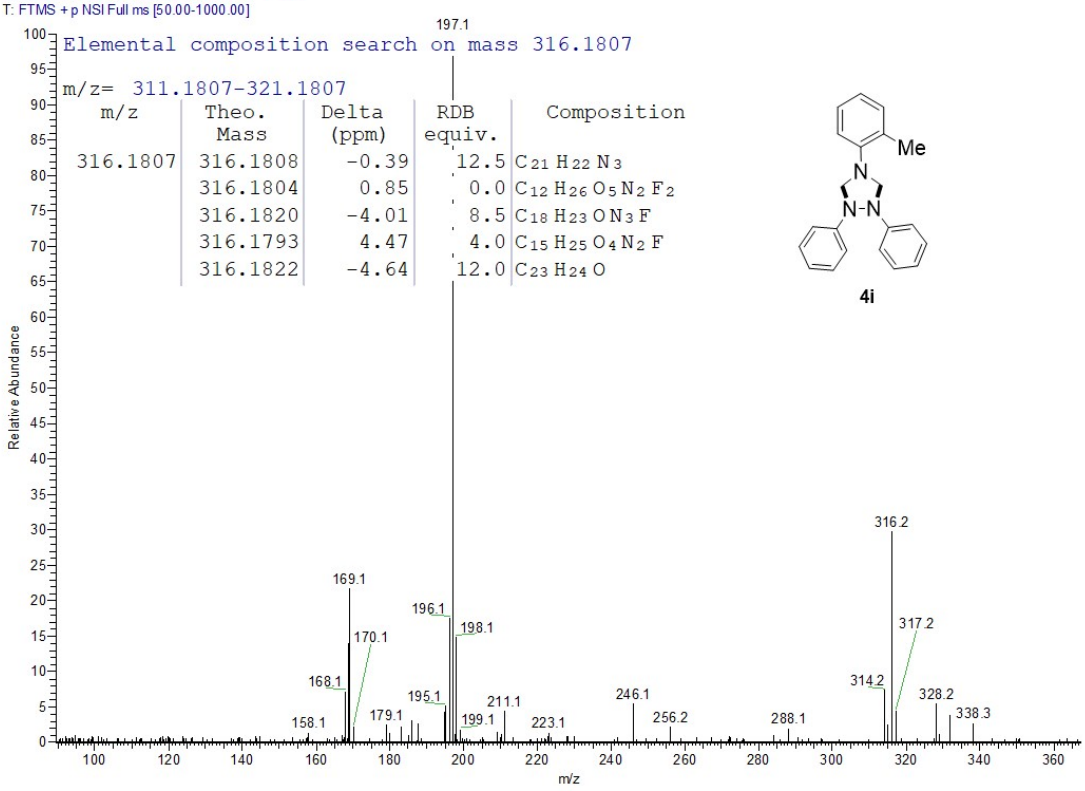

g29 #16 RT: 0.10 AV: 1 NL: 2.47E6
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
368.07169
370.06863
369.07593
371.07401
372.06528
373.07004
376.31854
362.32635
360.32361
359.24020
361.32755
363.28741
365.10550
367.28119
Relative Abundance
m/z
Cl
Cl
N
N-N
4f

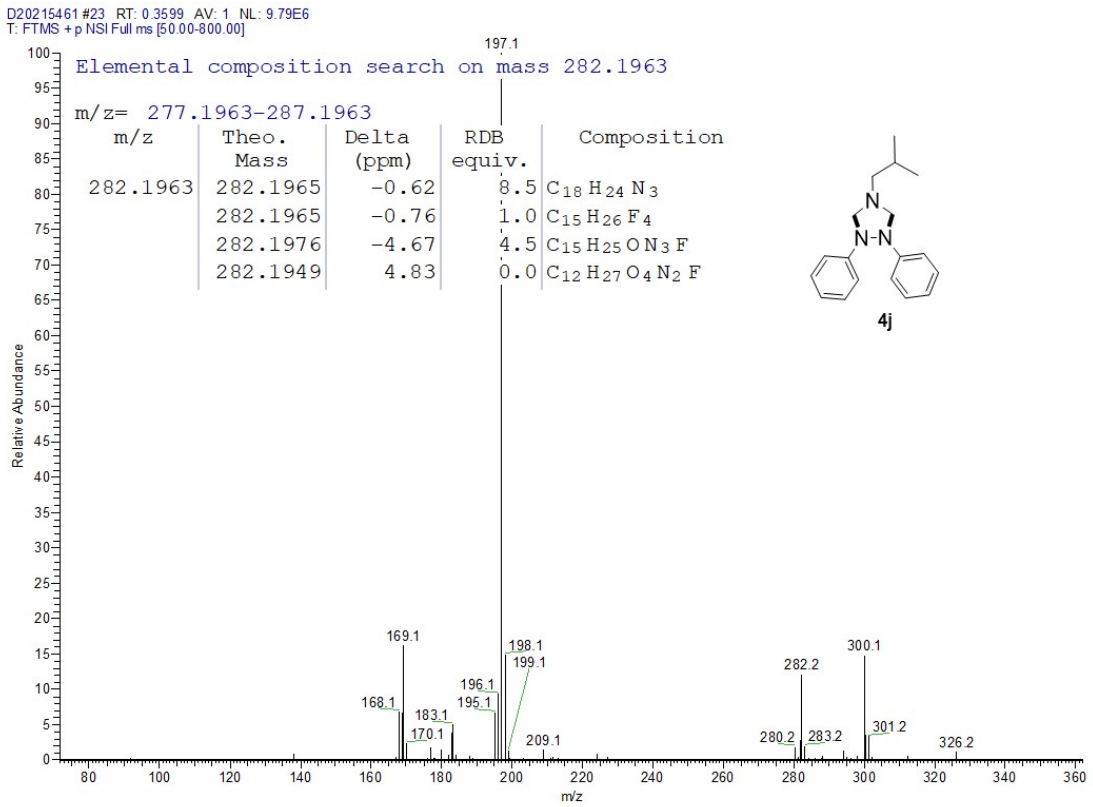

g26 #14 RT: 0.09 AV: 1 NL: 4.53E6
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
358.15472
359.15842
352.24588
353.24960
357.22092
356.21201
360.16565
362.32700
365.10544
366.17953
Relative Abundance
m/z
CO2Me
N
N-N
4g

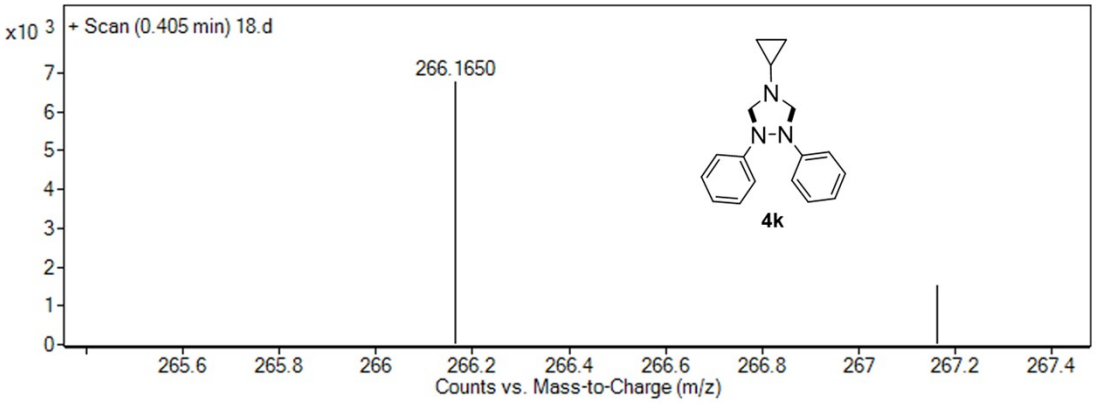
D20213865 #16 RT: 0.2535 AV: 1 NL: 8.78E5
T: FTMS + p NSI Full ms [50.00-1000.00]

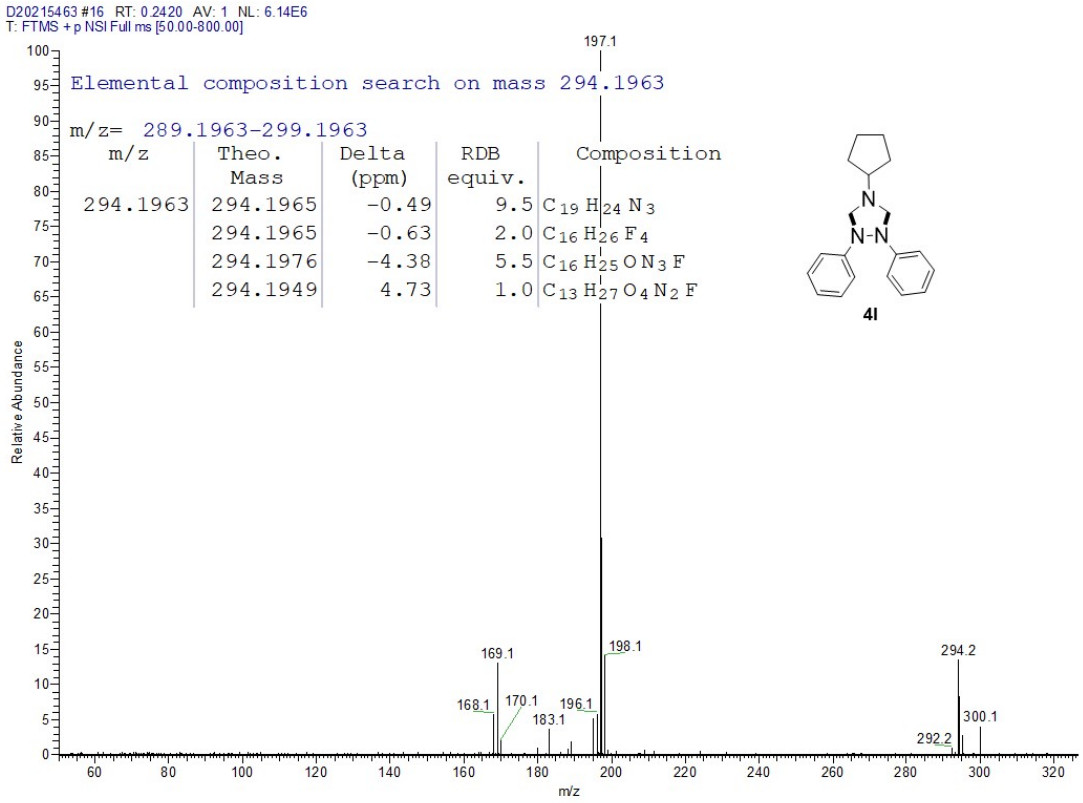


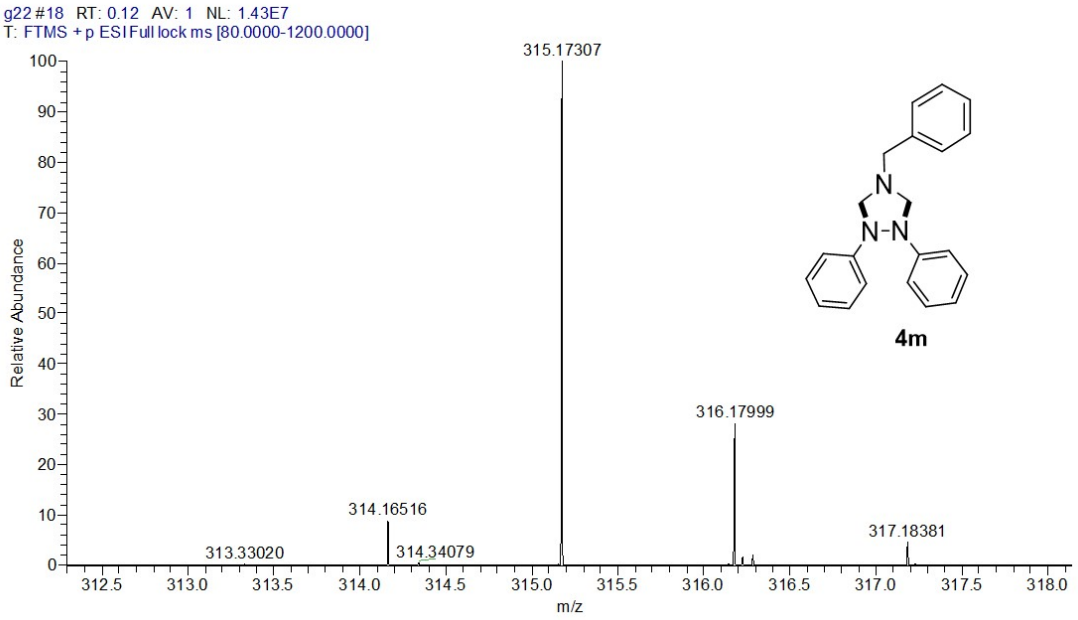
D20213851 #20 RT: 0.3175 AV: 1 NL: 7.12E5
T: FTMS + p NSI Full ms [50.00-1000.00]

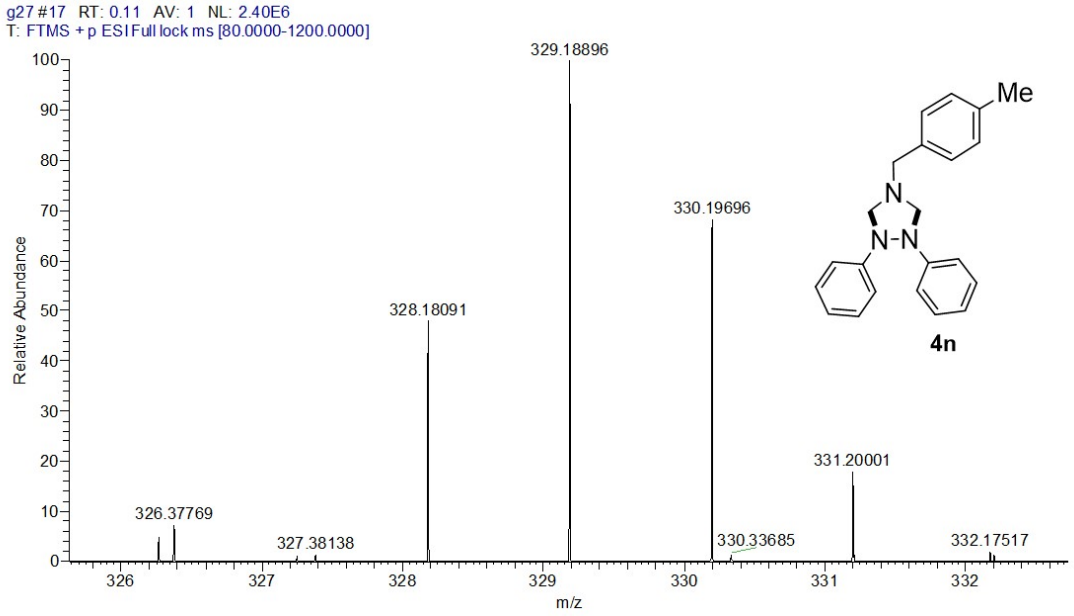


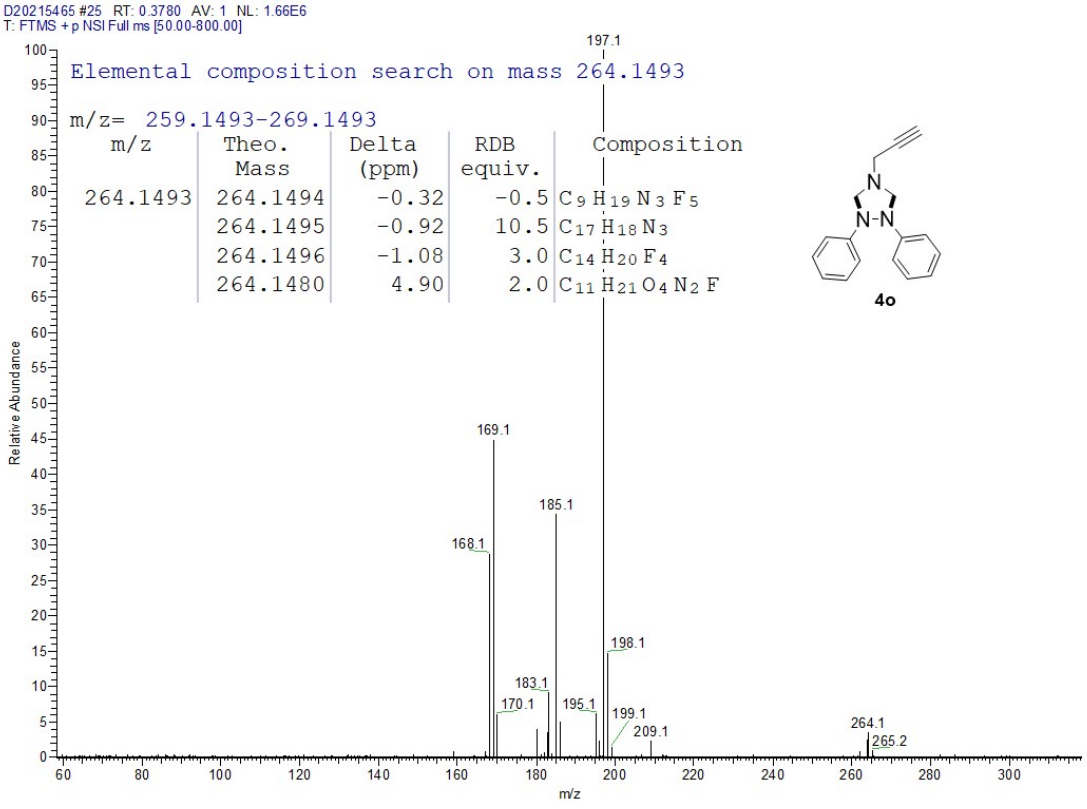

D20215461 #23 RT: 0.3599 AV: 1 NL: 9.79E6
T: FTMS + p NSI Full ms [50.00-800.00]
Elemental composition search on mass 282.1963
m/z= 277.1963-287.1963
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
282.1963 | 282.1965 | -0.62 | 8.5 | C18 H24 N3
282.1965 | -0.76 | 1.0 | C15 H26 F4
282.1976 | -4.67 | 4.5 | C15 H25 O N3 F
282.1949 | 4.83 | 0.0 | C12 H27 O4 N2 F
4j
Relative Abundance
m/z

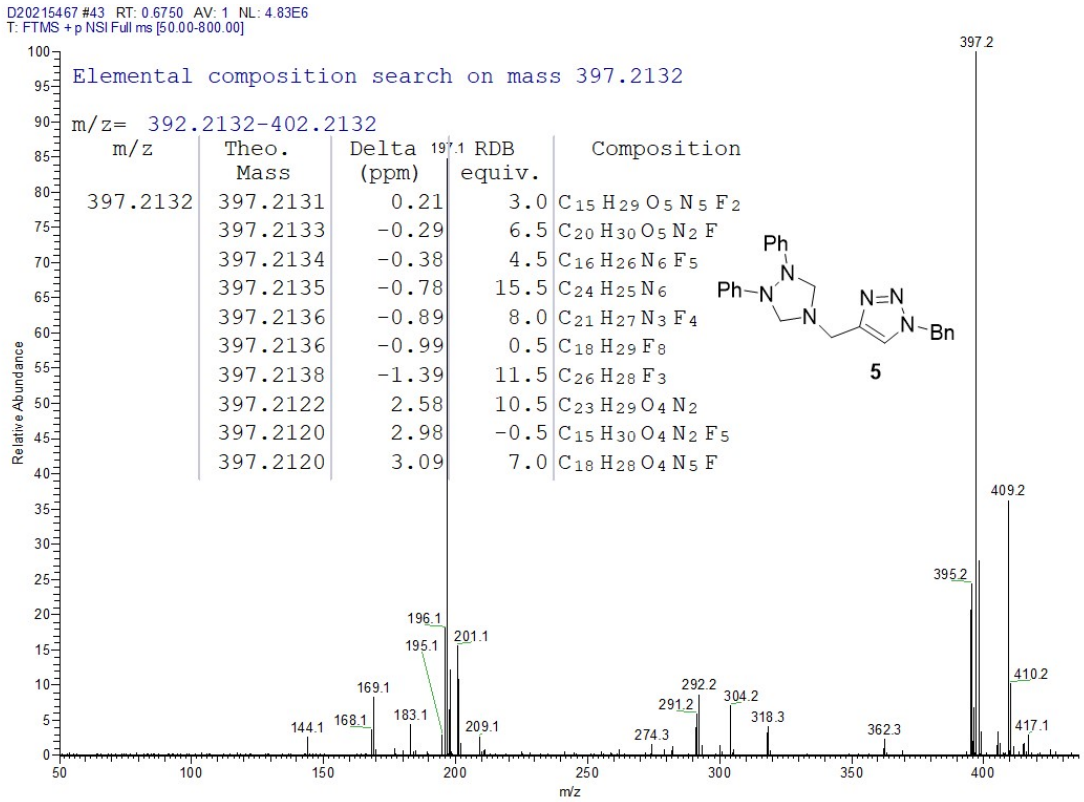

x10 3
+ Scan (0.405 min) 18.d
266.1650
4k
Counts vs. Mass-to-Charge (m/z)


D20215463 #16 RT: 0.2420 AV: 1 NL: 6.14E6
T: FTMS + p NSI Full ms [50.00-800.00]
Elemental composition search on mass 294.1963
m/z= 289.1963-299.1963
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
294.1963 | 294.1965 | -0.49 | 9.5 | C19 H24 N3
294.1965 | -0.63 | 2.0 | C16 H26 F4
294.1976 | -4.38 | 5.5 | C16 H25 O N3 F
294.1949 | 4.73 | 1.0 | C13 H27 O4 N2 F
4l
Relative Abundance
m/z
197.1
198.1
169.1
294.2
168.1
170.1
196.1
183.1
300.1
292.2


g22 #18 RT: 0.12 AV: 1 NL: 1.43E7
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
4m
Relative Abundance
m/z
315.17307
316.17999
314.16516
317.18381
313.33020
314.34079


g27 #17 RT: 0.11 AV: 1 NL: 2.40E6
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
329.18896
330.19696
328.18091
331.20001
326.37769
327.38138
330.33685
332.17517
Relative Abundance
m/z
Me
N
N-N
4n


D20215465 #25 RT: 0.3780 AV: 1 NL: 1.66E6
T: FTMS + p NSI Full ms [50.00-800.00]
197.1
Elemental composition search on mass 264.1493
m/z= 259.1493-269.1493
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
264.1493 | 264.1494 | -0.32 | -0.5 | C9 H19 N3 F5
264.1495 | -0.92 | 10.5 | C17 H18 N3
264.1496 | -1.08 | 3.0 | C14 H20 F4
264.1480 | 4.90 | 2.0 | C11 H21 O4 N2 F
169.1
185.1
168.1
198.1
183.1
170.1
195.1
199.1
209.1
264.1
265.2
Relative Abundance
m/z
N
N-N
4o


D20215467 #43 RT: 0.6750 AV: 1 NL: 4.83E6
T: FTMS + p NSI Full ms [50.00-800.00]
Elemental composition search on mass 397.2132
m/z= 392.2132-402.2132
m/z | Theo. Mass | Delta (ppm) | RDB equiv. | Composition
397.2132 | 397.2131 | 0.21 | 3.0 | C15 H29 O5 N5 F2
397.2133 | -0.29 | 6.5 | C20 H30 O5 N2 F
397.2134 | -0.38 | 4.5 | C16 H26 N6 F5
397.2135 | -0.78 | 15.5 | C24 H25 N6
397.2136 | -0.89 | 8.0 | C21 H27 N3 F4
397.2136 | -0.99 | 0.5 | C18 H29 F8
397.2138 | -1.39 | 11.5 | C26 H28 F3
397.2122 | 2.58 | 10.5 | C23 H29 O4 N2
397.2120 | 2.98 | -0.5 | C15 H30 O4 N2 F5
397.2120 | 3.09 | 7.0 | C18 H28 O4 N5 F
Ph
N
Ph
N
N
N=N
N
Bn
5
Relative Abundance
m/z
397.2
409.2
395.2
410.2
417.1
196.1
201.1
195.1
169.1
144.1
168.1
183.1
209.1
292.2
291.2
304.2
318.3
274.3
362.3

8. Crystallographic Data for 3d

The compound **3d** was crystalized over a solution of **3d** (50 mg) in CH_2Cl_2/petroleum (1 mL/1 mL) at room temperature. The mixed solvent spontaneously evaporates in open air to obtain the crystals of **3d**. Then the crystals were carefully collected and used for X-ray diffraction analysis. The crystal structure was further determined by Bruker D8 QUEST X-ray single crystal diffractometer. The CCDC number of **3d** is 2097639.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 20210401a_0m

Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=8.312(5) b=11.807(6) c=11.826(4)
alpha=71.649(17) beta=82.681(19) gamma=82.856(13)
Temperature: 293 K

	Calculated	Reported
Volume	1088.2(9)	1088.2(9)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C26 H31 N3	C26 H31 N3
Sum formula	C26 H31 N3	C26 H31 N3
Mr	385.54	385.54
Dx,g cm-3	1.177	1.177
Z	2	2
Mu (mm-1)	0.069	0.069
F000	416.0	416.0
F000'	416.13	
h,k,lmax	10,15,15	10,15,15
Nref	5165	5068
Tmin,Tmax	0.989,0.993	0.715,0.746
Tmin'	0.988	

Correction method= # Reported T Limits: Tmin=0.715 Tmax=0.746
AbsCorr = NONE

Data completeness= 0.981 Theta(max)= 27.849

R(reflections)= 0.0459(3787) wR2(reflections)= 0.1318(5068)

S = 1.045 Npar= 266

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

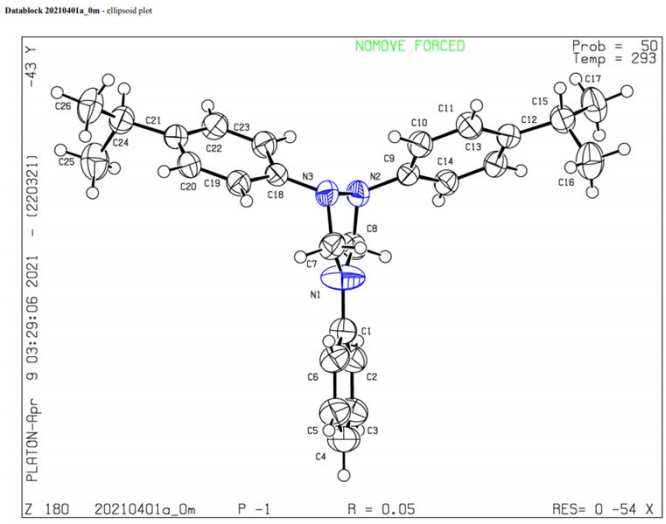


Figure S9 X-ray structure of **3d** (ORTEP diagram with ellipsoid contour 50% probability)

9. Determination of Faradaic Efficiency

$$(1)\ \text{F. E. (\%)} = \frac{n \times F \times \text{mol of product or intermediate formed}}{\text{acculumated charge (C)}} \times 100\ \%$$

$$\text{F. E. (\%)} = \frac{2 \times 96485\ \text{C mol}^{-1} \times 0.2\ \text{mmol} \times 10^{-3} \times 79\ \%}{8\ \text{mA} \times 10^{-3} \times 3\ \text{h} \times 3600} \times 100\ \%$$

$$= 35.3\ \%$$

The F.E. (%) of the product **3a** was calculated by (1). The F.E. is the proportion of electrons consumed in each electrochemical reaction of the total applied charge and represents the selectivity of the electrochemical system for each reaction. In Eq (1), F is the Faradaic constant (96485 C mol^{-1}), and n is the number of electrons required for the production of products. The yield is the proportion of reactant converted to target product.