Supporting Information

Redox Reaction Between *N*-heterocyclic Carbenes and Sulfonates: Insights into Unproductive Catalytic Paths

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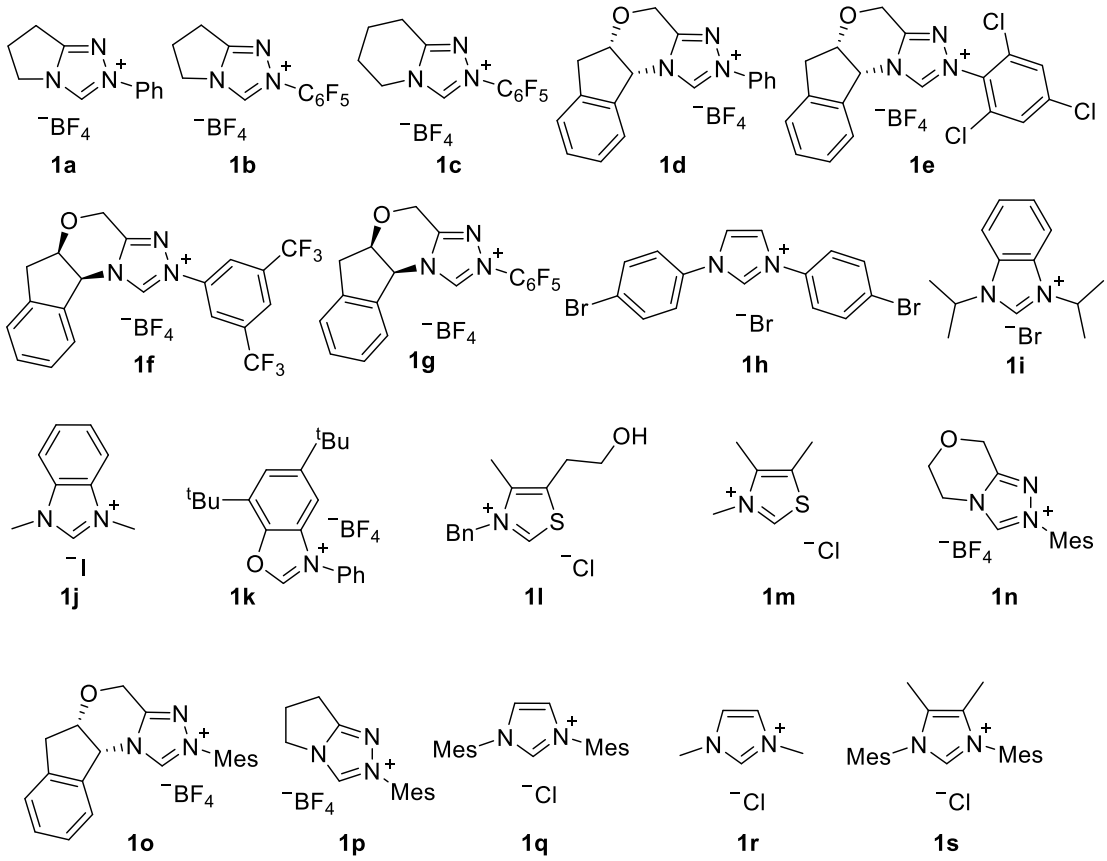
Content

I. General information

Commercially available materials and solvents purchased from Energy Chemical, Aladdin and J&K were used as received. All reactions and manipulations involving air-sensitive compounds were carried out using standard Schlenk techniques, unless otherwise stated. Anhydrous CH_2Cl_2 was distilled from CaH_2 under an atmosphere of nitrogen. Thin-layer chromatography (TLC) was conducted using silica gel GF254, visualized under ultraviolet light (at 254 nm). 200–300 mesh silica gel was used for column chromatography separation. ^1H NMR spectra were recorded on a Bruker BBFO (400 MHz) or ECA400SL (396 MHz) instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). ^{13}C NMR spectra were recorded on a Bruker BBFO (101 MHz) or ECA400SL (100 MHz) instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.16 ppm). ^{19}F NMR spectra were recorded on a Bruker BBFO (377 MHz) instrument. High resolution mass spectra (HRMS) were obtained from the Agilent 6546 LC/Q-TOF with electrospray ionization (ESI). Meanwhile, there action process was also monitored using Agilent 8890-5977B-IP-7693A GC/MSD gas chromatography-mass spectrometry (GC-MS).

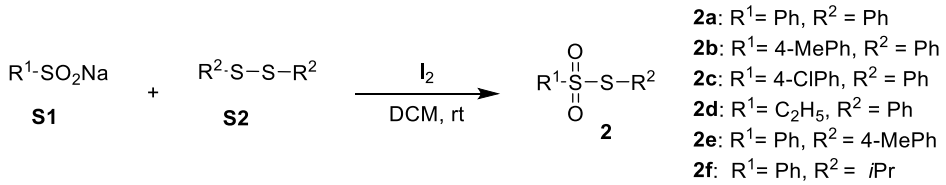


Scheme S1. Substrate scope of pre-NHC.

Pre-NHC **1f, 1h-1m, 1q-1s** are commercially available substrates. **1a-1e, 1g, 1n-1p** are known compounds and prepared according to reported methods [1].

II. Experimental procedures.

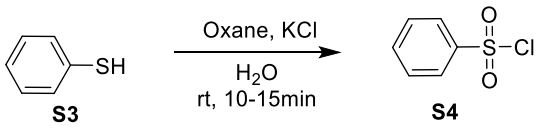
2.1 Benzenesulfonyl sulfide 2a-2f.



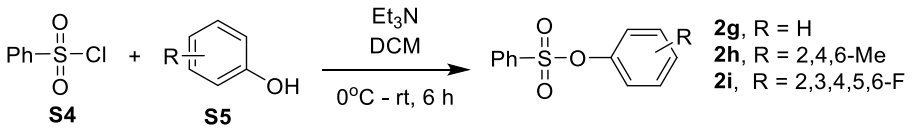
To a stirred solution of sodium sulfinate (6.4 mmol) and disulfide (2 mmol, 436 mg) in CH_2Cl_2 (20 mL) was added I_2 (4 mmol, 1.02 g) at room temperature. The reaction was detected by TLC until the disulfide was consumed, then CH_2Cl_2 (50 mL) was added, followed by aqueous $Na_2S_2O_3$ (1 M, 10 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with water and dried over Na_2SO_4. The mixture was filtered and the filtrate was concentrated *in vacuo*, then the resulting mixture was purified by flash column chromatography to give **2a-2f** in excellent yields. Sulfonothioates (**2a** [2] **2b** [2], **2c** [2], **2d** [3], **2e** [4], **2f** [4]) were prepared following reported procedures.

2.2 Aryl benzenesulfonates.

General procedure for the preparation of sulfonyl chlorides from thiophenol [6].

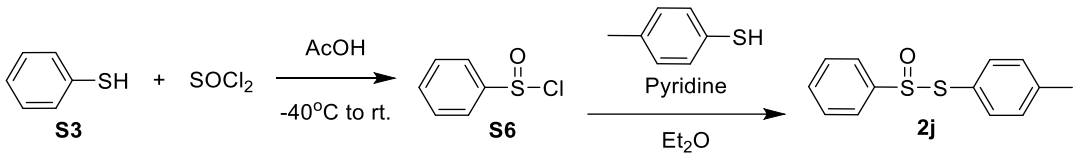


A mixture of thiophenol (1.7 mmol), oxone (3.5 mmol) KCl (3.5 mmol), and water (10 mL) was taken in a round bottomed flask and stirred at room temperature. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (4 × 5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product obtained was purified by normal column chromatography (silica gel 60-120 mesh, *n*-hexane) to obtain the corresponding sulfonyl chloride.



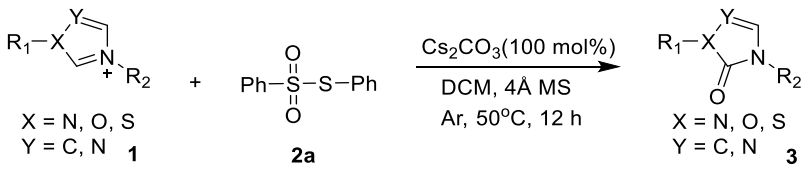
To a stirred solution of phenol **S5** (5.00 g, 53.1 mmol) in CH_2Cl_2 (100 mL) at 0°C, benzenesulfonyl chloride **S4** (8.21 mL, 63.8 mmol) and Et_3N (8.83 mL, 63.8 mmol) were added. The reaction mixture was warmed to room temperature and stirred for 6 h. The mixture was quenched with 1 M HCl solution, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by SiO_2, flash column chromatography (hexane: EtOAc =9:1 ≈ 3:1) to give aryl benzenesulfonate **2g-2i** [7].

2.3 S-(p-tolyl) benzenesulfinothioate 2j.



A solution of thiophenol **S3** (2.02 mL, 19.8 mmol) and acetic acid (1.14 mL, 19.8 mmol) was cooled to -40 °C. The yellow oil **S6** was obtained by spin drying. Then Sulfuryl chloride (0.238 mL, 2 mmol) was added dropwise to the frozen mixture of 4-Methylphenol (243 μL, 2 mmol) and anhydrous ether (3 mL), during which time gas evolution began. When the addition was completed, the reaction mixture was stirred for 30 min at -40° slowly warmed to room temperature and then stirred for a further 3 h. The solution was concentrated under reduced pressure (without warming because of explosion risks) to give the desired sulfinyl chloride **2j** [8] in quantitative yield as a yellowish solid. Because of instability, the product must be used after isolation.

2.4 NHC oxidation products were produced by pre-NHC and sulfonates.



In an Ar-filled glove box, a 4 mL vial equipped with a magnetic stir bar was charged with Pre-NHC

1 (0.1 mmol, 1.0 equiv.), Sulfonates **2** (0.1 mmol, 1.0 equiv.), Cs_2CO_3 (0.1 mmol, 1.0 equiv.), 100 mg 4Å MS and anhydrous DCM (1 mL). The 4 mL vial was sealed with a PTFE cap and was subsequently wrapped with a thin film of parafilm. The vial was then transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under the 50 °C reaction temperature for 12 h. When the reaction was complete, the reaction mixture was filtered and then concentrated in vacuo. The crude material was purified by flash column chromatography in silica gel (1:1 hexane / ethyl acetate) to afford the corresponding product.

III. References

[1] M S. Kerr, J R d Alaniz, and T Rovis, *J. Org. Chem*. **2005**, *70,* 5725-5728.

[2] P. Mampuys, Y. Zhu, S. Sergeyev, E. Ruijter, R. V. A. Orru, S. Van Doorslaer, and B. U. W. Maes, *Org. Lett*. **2016**, *18*, 2808-2811.

[3] S Duan, Y Zi, Y Du, J Cong, X Sun, H Jing, J Zhao, W Chen and X Yang, *Org. Lett*. **2023**, *25*, 3687-3692.

[4] G Y Zhang, S S Lv, A Shoberu, and J P Zou, *J. Org. Chem* **2017**, *82*, 9801-9807.

[5] M Kirihara, S Naito, Y Nishimura, Y Ishizuka, T Iwai, H Takeuchi, T Ogata, H Hanai, Y Kinoshita, M Kishida, K Yamazaki, T Noguchi, and S Yamashoji, *Tetrahedron* **2014**, *70*, 2464-2471.

[6] S Madabhushi, R Jillella, V Sriramojua and R Singh, *Green Chem*. **2014**, *16*, 3125-3131.

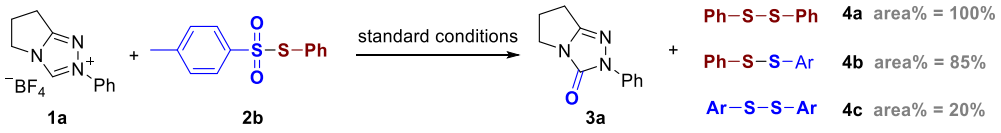
[7] M S Alama and S Koo, *Synthetic Commun*. **2018**, *48*, 247-254.

[8] S Oae, T Takata, and Y H Kim, *Tetrahedron* **1981**, *37*, 37-44.

IV. Mechanistic studies

In an Ar-filled glove box, a 25 mL vial equipped with a magnetic stir bar was charged with Pre-NHC **1a** (1 mmol, 1.0 equiv.), Sulfonates **2** (1 mmol, 1.0 equiv.), Cs_2CO_3 (1 mmol, 1 equiv.), 1 g 4Å MS and anhydrous DCM (10 mL). Seal the Shrek bottle with a rubber stopper cap and then wrap it with sealing film. The vial was then transferred out of the glovebox, and the reaction mixture was allowed to stir vigorously under the 50 ºC reaction temperature for 12 h. After the completion of the reaction was monitored by GC-MS.

4.2 symmetric/asymmetric disulfides products were produced by pre-NHC 1a and sulfonates 2b.



1a 2b 3a

Chromatogram Peaks

Peak	Start	RT	End	Height	Area	Area %
1	6.794	6.876	7.073	28687962	39647491	100.00
2	7.172	7.254	7.468	30709790	33629464	84.82
3	7.550	7.616	7.731	7279600	7983112	20.14

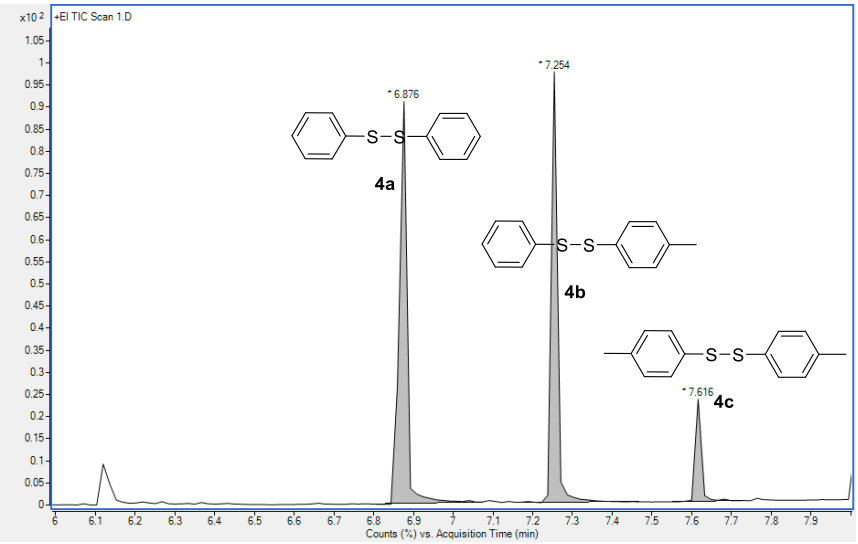
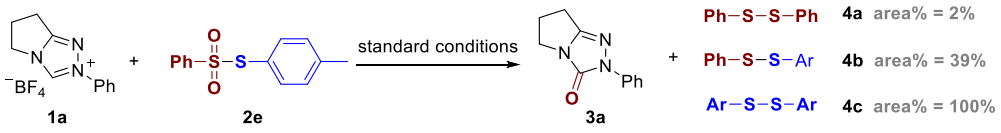


Figure 2. GCMS spectra of symmetric/asymmetric disulfides after redox reaction of **2b** with **1a**.

4.1 symmetric/asymmetric disulfides products were produced by pre-NHC 1a and sulfonates 2e.



1a 2e 3a

Chromatogram Peaks

Peak	Start	RT	End	Height	Area	Area %
1	6.827	6.876	6.925	1091356	1735061	1.76
2	7.188	7.254	7.353	35670019	37952991	38.59
3	7.550	7.632	7.797	51514785	98339909	100.00

Z

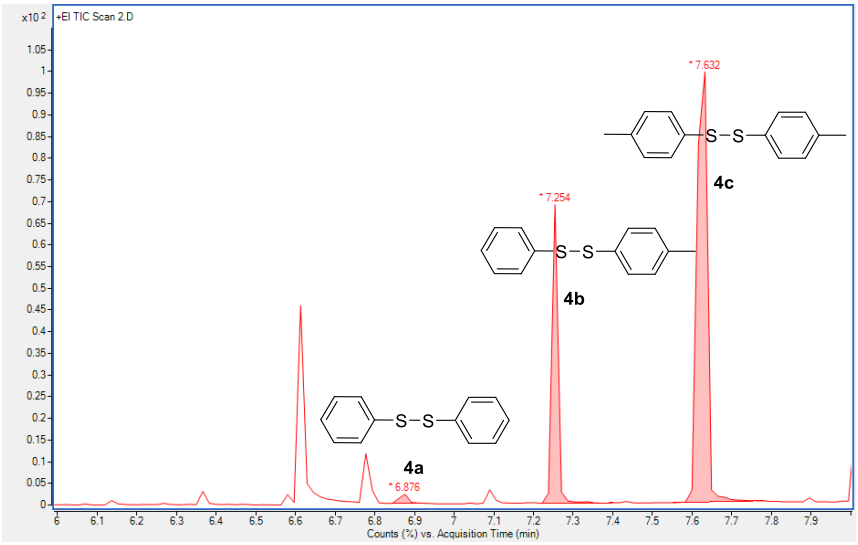
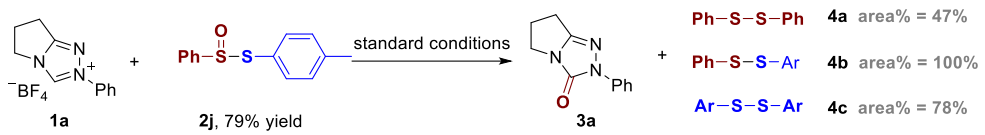


Figure 1. GCMS spectra of symmetric/asymmetric disulfides after redox reaction of **2e** with **1a**.

4.3 symmetric/asymmetric disulfides products were produced by pre-NHC 1a and sulfonates 2j.



Chromatogram Peaks

Peak	Start	RT	End	Height	Area	Area %
1	6.843	6.876	6.974	10448426	18157543	46.57
2	7.205	7.254	7.418	35621518	38986705	100.00
3	7.566	7.616	7.764	25648872	30249992	77.59

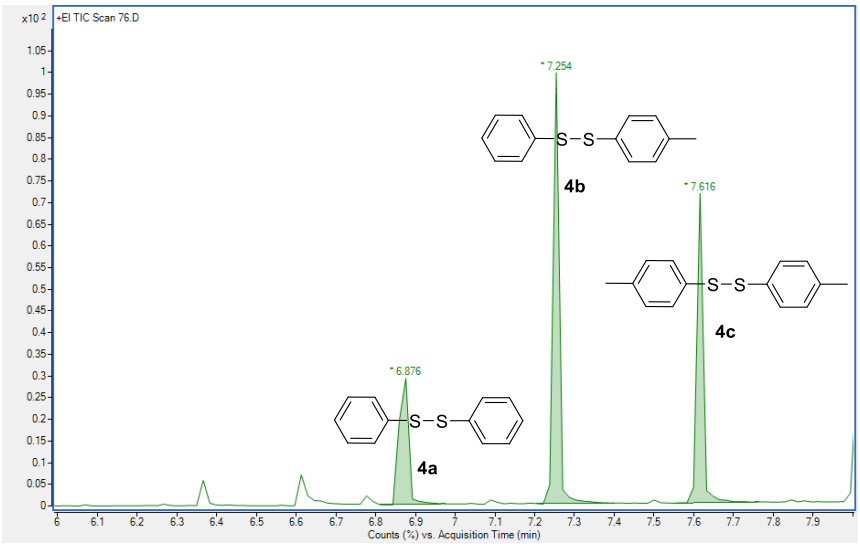
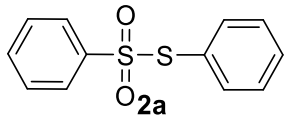


Figure 3. GCMS spectra of symmetric/asymmetric disulfides after redox reaction of **2j** with **1a**.

V. Characterizations of compounds

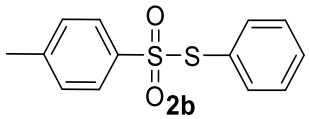
The analytical data of new compounds were as follow.

***S*-phenyl benzenesulfonothioate (2a)**



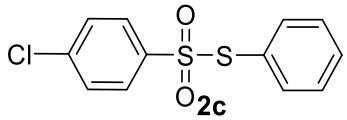
Colorless crystal, 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 3H), 7.50 – 7.44 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 – 7.30 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 136.7, 133.7, 131.5, 129.5, 128.9, 128.0, 127.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{11}O_2S_2$ 251.0200; Found 251.0209.

***S*-phenyl 4-methylbenzenesulfonothioate (2b)**



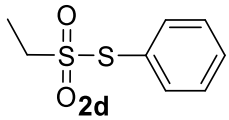
White solid, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 3H), 7.40 – 7.29 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 140.4, 136.7, 131.4, 129.5, 129.5, 128.2, 127.7, 21.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_2S_2$ 265.0357; Found 265.0353.

***S*-phenyl 4-chlorobenzenesulfonothioate (2c)**



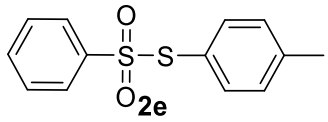
Colorless crystal, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.42 – 7.29 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 140.4, 136.7, 131.7, 129.7, 129.2, 129.1, 127.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}ClO_2S_2$ 284.9811; Found 284.9803.

***S*-phenyl ethanesulfonothioate (2d)**



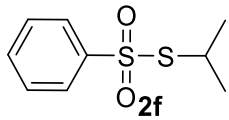
White solid, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 3.20 (q, *J* = 7.3 Hz, 2H), 1.46 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 131.6, 129.9, 128.0, 53.9, 8.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{10}O_2S_2$ 203.0195; Found 203.0195.

_S_-(p-tolyl) benzenesulfonothioate (2e)



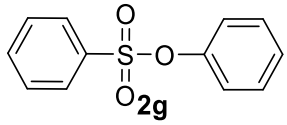
White solid. 91%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 3H), 7.47 – 7.39 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.10 (m, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 142.3, 136.6, 133.6, 130.4, 128.9, 127.7, 124.5, 21.3. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_2S_2$ 265.0357; Found 265.0353.

_S_-isopropyl benzenesulfonothioate (2f)



White solid, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.69 – 7.60 (m, 1H), 7.60 – 7.48 (m, 2H), 3.60 – 3.41 (m, 1H), 1.32 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 133.6, 129.3, 127.0, 42.8, 23.6.

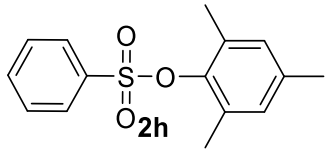
Phenyl benzenesulfonate (2g)



2g: Colorless oil, 97% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.32 – 7.24 (m, 3H), 7.03 – 6.92 (m, 2H). **^{13}C NMR** (101 MHz,

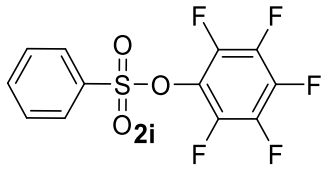
$CDCl_3$) δ 135.9, 134.6, 130.1, 129.5, 128.9, 127.6, 122.8, 115.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}O_3S$ 235.0423; Found 235.0421.

Mesityl benzenesulfonate (2h)



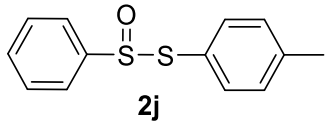
Colorless oil, 97% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 6.84 (s, 2H), 2.26 (s, 3H), 2.09 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 137.4, 136.4, 134.0, 131.7, 129.9, 129.3, 128.1, 20.7, 17.2.

Perfluorophenyl benzenesulfonate[7] **(2i)**



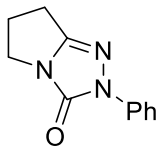
Colorless oil, 77% yield, 1.05 g. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.66 – 7.58 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 141.1, 139.2, 136.7, 135.3, 134.8, 129.6, 128.6.

***S*-(*p*-tolyl) benzenesulfinothioate (2j)**



Yellowish solid, 65% yield, 0.32 g. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.54 – 7.45 (m, 3H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 141.0, 135.6, 131.6, 130.2, 129.0, 125.9, 124.5, 21.5.

2-Phenyl-2,5,6,7-tetrahydro-3*H*-pyrrolo[2,1-*c*][1,2,4]triazol-3-one (3a)



3a

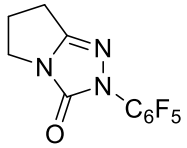
White solid, 94% yield, 18.9 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.83 (t, *J* = 7.0 Hz, 2H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.58 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 150.4, 138.7, 129.0, 125.1, 118.7, 41.8, 29.8, 26.3, 22.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{13}N_3O$ 202.0975; Found 202.0981.

2-(Perfluorophenyl)-2,5,6,7-tetrahydro-3*H*-pyrrolo[2,1-*c*][1,2,4]triazol-3-one (3b)



3b

Yellowish oil, 41% yield, 11.9 mg.

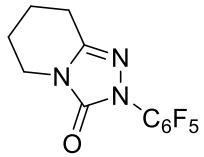
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 – 3.80 (m, 2H), 2.96 – 2.87 (m, 2H), 2.69 – 2.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 150.8, 146.2 – 145.0 (m), 143.6 – 142.1 (m), 140.1 – 138.3 (m), 137.9 – 136.3 (m), 42.2, 26.2, 22.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.4 – -144.5 (m, 2F), -152.5 (t, *J* = 21.3 Hz, 1F), -161.4 (dd, *J* = 21.2, 15.6 Hz, 2F).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_6F_5N_3O$ 292.0504; Found 292.0503.

2-(Perfluorophenyl)-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-*a*]pyridin-3(2*H*)-one (3c)



3c

Yellow solid, 47% yield, 14.3 mg.

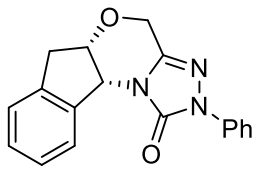
^{1}H NMR (400 MHz, $CDCl_3$) 3.71 (t, *J* = 6.1 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.01 – 1.92 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 146.9, 145.7 – 145.3 (m), 143.1 – 142.8 (m), 140.7 – 140.6 (m), 139.5 – 139.1 (m), 136.9 – 136.6 (m), δ 131.2 – 128.0 (m), 40.8, 22.8, 21.8, 19.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.7 – -144.1 (m, 2F), -152.6 (t, *J* = 21.3 Hz, 1F), -161.1 – -161.6 (m, 2F).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_8F_5N_3O$ 306.0660; Found 306.0670.

2-Phenyl-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3d)



3d

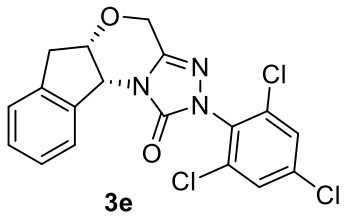
Yellowish solid, 82% yield, 25.0 mg. Melting point: 147 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.20 (m, 4H), 5.37 (d, *J* = 4.1 Hz, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.66 – 4.56 (m, 2H), 3.33 (dd, *J* = 16.8, 4.7 Hz, 1H), 3.20 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 140.8, 139.6, 138.9, 137.9, 129.1, 129.0, 127.7, 126.5, 125.5, 125.0, 118.8, 78.0, 61.1, 57.7, 37.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}N_3O_2$ 306.1237; Found 306.1234.

2-(2,4,6-Trichlorophenyl)-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3e)



3e

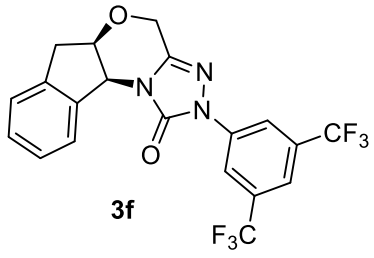
White solid, 36% yield, 14.7 mg. Melting point: 200 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 1H), 7.46 (s, 2H), 7.34 – 7.23 (m, 3H), 5.36 (d, *J* = 4.1 Hz, 1H), 4.73 (d, *J* = 15.6 Hz, 1H), 4.67 – 4.52 (m, 2H), 3.31 (dd, *J* = 16.9, 4.7 Hz, 1H), 3.17 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 142.3, 139.6, 139.0, 136.5, 136.5, 131.0, 129.0, 129.0, 127.9, 126.3, 125.0, 78.1, 61.2, 57.9, 37.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{12}Cl_3N_3O_2$ 408.0068; Found 408.0069.

2-(3,5-Bis(trifluoromethyl)phenyl)-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3f)



3f

White solid, 88% yield, 38.7 mg. Melting point: 169.5 °C

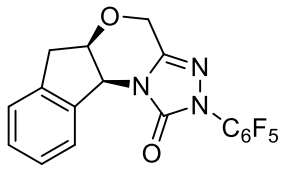
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 2H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.72 (s, 1H), 7.36 – 7.28 (m, 3H), 5.38 (d, *J* = 4.1 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H), 4.69 – 4.58 (m, 2H), 3.35 (dd, *J* = 17.0, 4.8 Hz, 1H), 3.23 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 142.2, 139.7, 139.2, 138.5, 132.6 (q, *J* = 33.6 Hz), 129.2, 127.9, 126.3, 125.1, 125.3 (q, *J* = 272.7 Hz), 118.7 – 118.2 (m), 118.0 (d, *J* = 4.3 Hz), 78.0, 60.9, 57.9, 37.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.9 (s, 6F).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{13}F_6N_3O$ 442.0985; Found 442.0986.

2-(Perfluorophenyl)-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3g)



3g

White solid, 23% yield, 9.1 mg. Melting point: 163.9 °C

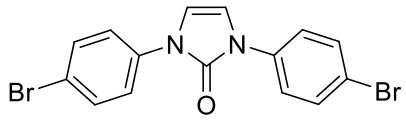
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.26 (m, 3H), 5.38 (d, *J* = 4.1 Hz, 1H), 4.77 (d, *J* = 15.8 Hz, 1H), 4.69 – 4.54 (m, 2H), 3.34 (dd, *J* = 16.9, 4.7 Hz, 1H), 3.22 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 145.6 – 145.3 (m), 143.3, 143.3 – 142.8 (m), 139.6, 141.0 – 140.9 (m), 139.6 – 139.2 (m), 138.5, 136.8 – 136.6 (m), 129.2, 129.5 – 128.5 (m), 127.9, 126.3, 125.1, 78.0, 61.0, 58.0, 37.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.6 (d, *J* = 20.2 Hz, 2F), -151.8 (t, *J* = 21.3 Hz, 1F), -161.0 (td, *J* = 22.2, 6.6 Hz, 2F).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{10}F_5N_3O_2$ 396.0766; Found 396.0767.

1,3-Bis(4-bromophenyl)-1,3-dihydro-2*H*-imidazol-2-one (3h)



3h

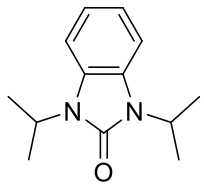
Colorless crystal, 36% yield, 14.2 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 8H), 6.71 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 132.5, 129.5, 123.4, 119.6, 110.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{10}Br_2N_2O$ 392.9233; Found 392.9234.

1,3-Diisopropyl-1,3-dihydro-2*H*-benzo[d]imidazol-2-one (3i)



3i

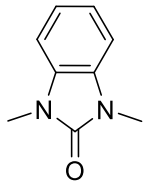
White solid, 55% yield, 12.0 mg. Melting point: 93.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.04 (dd, *J* = 5.9, 3.2 Hz, 2H), 4.74 (p, *J* = 7.0 Hz, 2H), 1.53 (d, *J* = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 128.5, 120.4, 109.1, 44.9, 20.3.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}N_2O$ 220.1514; Found 220.1525.

1,3-Dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3j)



3j

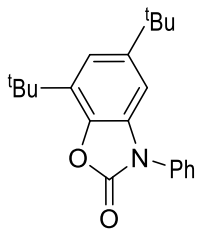
Pink solid, 59% yield, 9.6 mg. Melting point: 108.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 2H), 7.02 – 6.91 (m, 2H), 3.42 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 130.1, 121.3, 107.4, 27.2, 1.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{10}N_2O$ 163.0866; Found 163.0871.

5,7-Di-tert-butyl-3-phenylbenzo[d]oxazol-2(3*H*)-one (3k)



3k

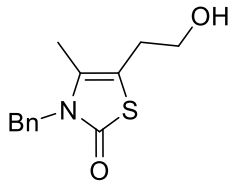
White solid, 88% yield, 28.4 g. Melting point: 138.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 72.7 Hz, 1H), 7.53 – 7.29 (m, 4H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.51 (d, *J* = 127.7 Hz, 2H), 1.48 (s, 9H), 1.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 147.9, 143.3, 141.8, 140.1, 129.8, 129.1, 127.6, 125.1, 123.5, 121.5, 35.5, 34.4, 31.4, 30.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}NO_2$ 324.1958; Found 324.1959.

3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazol-2(3*H*)-one (3l)



3l

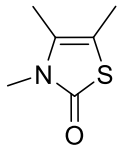
Yellowish oil, 20% yield, 5 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.59 – 7.48 (m, 3H), 7.36 – 7.26 (m, 4H), 7.21 – 7.15 (m, 2H), 4.90 (s, 2H), 4.09 (dt, *J* = 10.1, 6.3 Hz, 1H), 3.68 (dt, *J* = 10.0, 6.5 Hz, 1H), 2.77 (t, *J* = 6.4 Hz, 2H), 1.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 144.4, 136.5, 132.5, 129.2, 129.0, 127.8, 126.8, 125.3, 107.1, 63.3, 46.6, 27.7, 12.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}NO_2S$ 250.0896; Found 250.0897.

3,4,5-Trimethylthiazol-2(3*H*)-one (3m)



3m

Yellow oil, 32% yield, 4.5 mg.

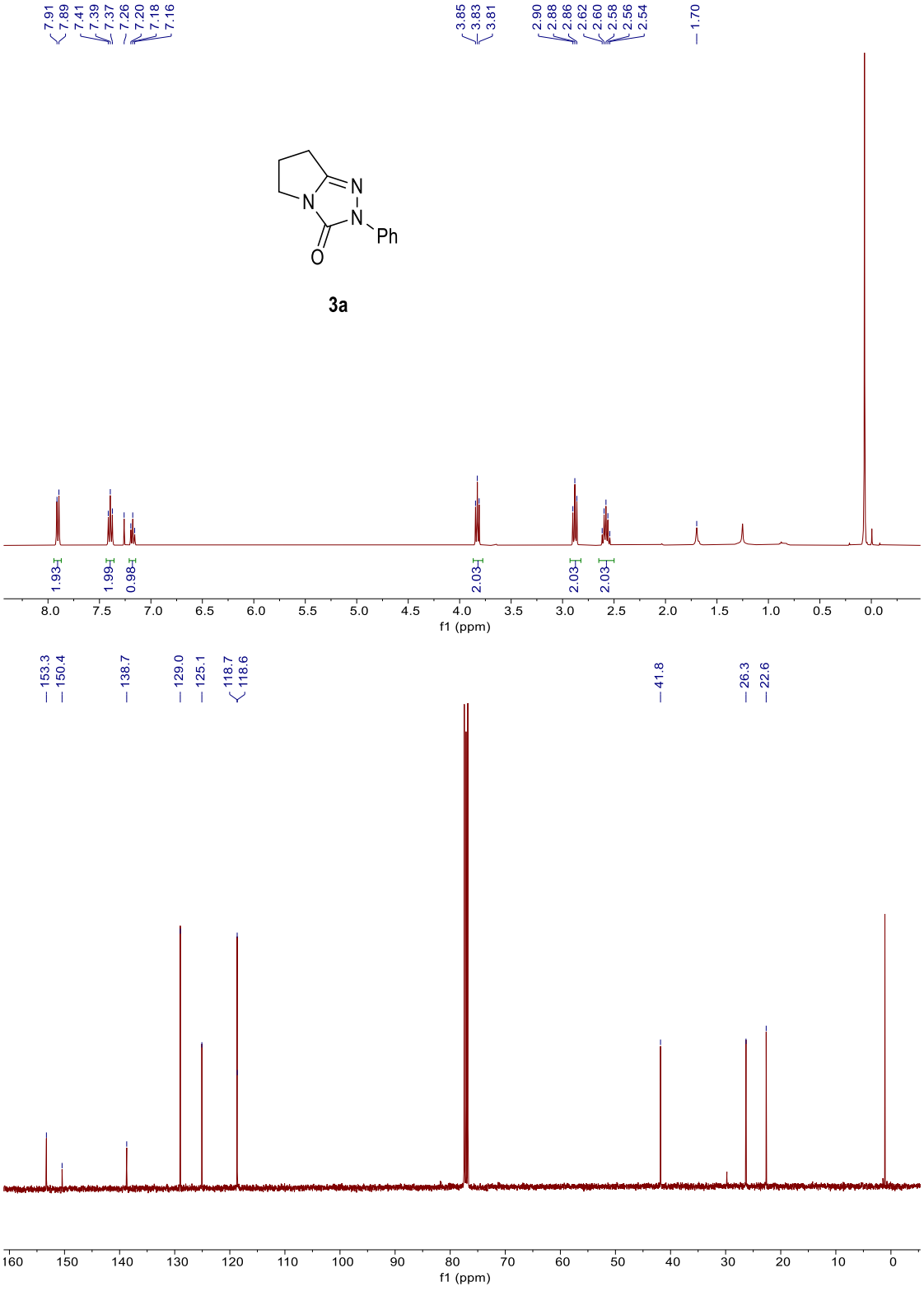
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 126.8, 106.3, 29.9, 12.1, 11.7.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for C_6H_9NOS 144.0478; Found 144.0483.

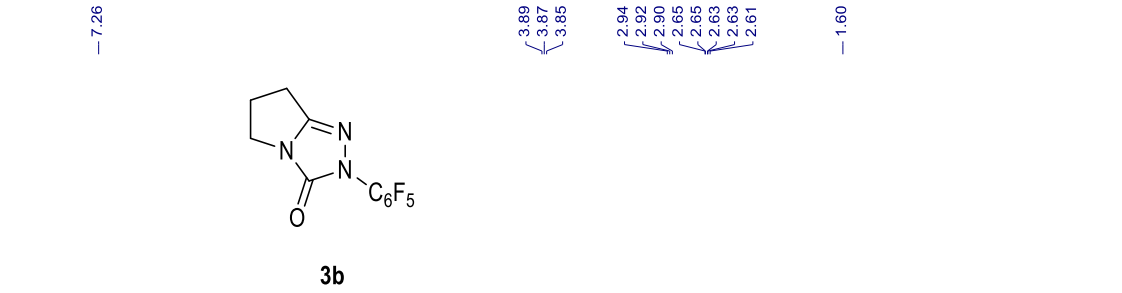
VI. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR

2-Phenyl-2,5,6,7-tetrahydro-3*H*-pyrrolo[2,1-*c*][1,2,4]triazol-3-one (3a)

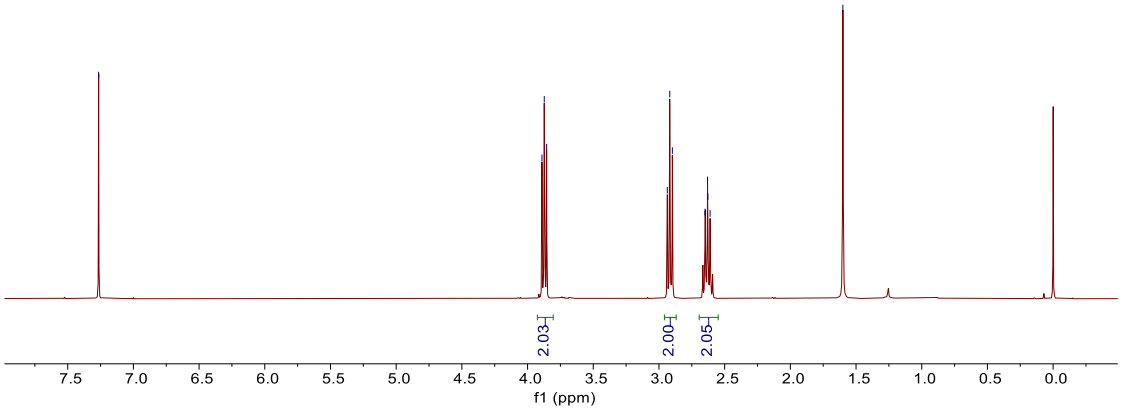


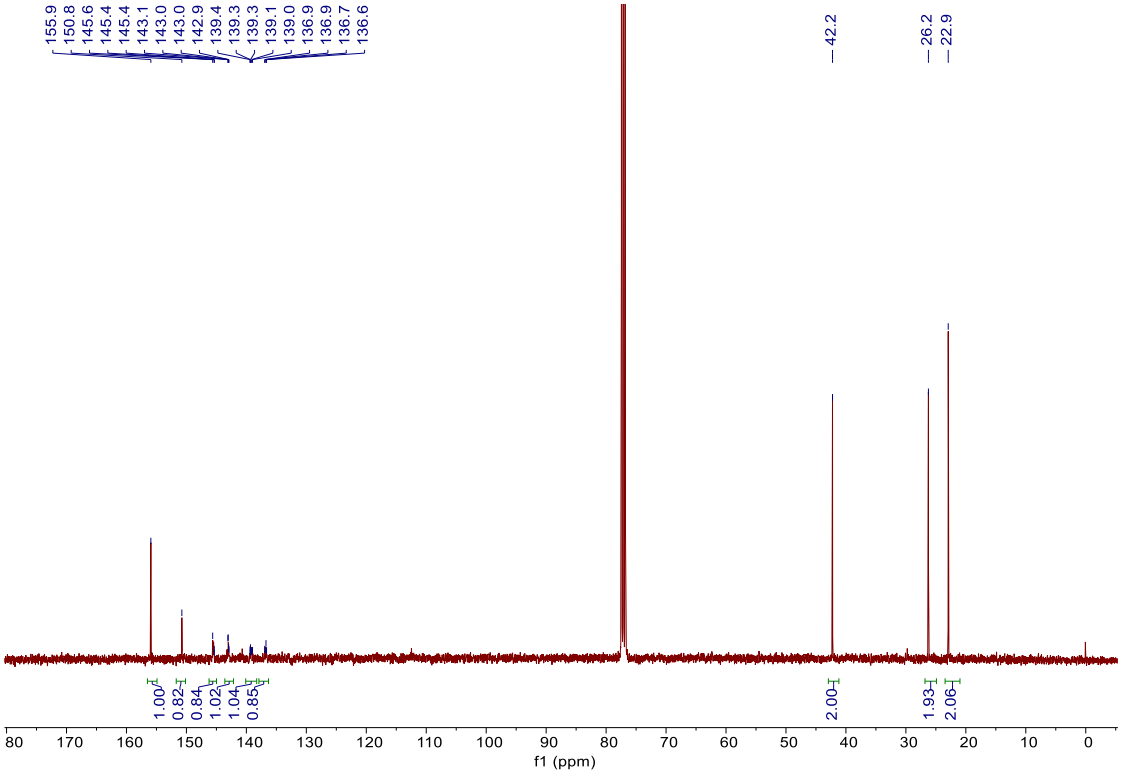
3a

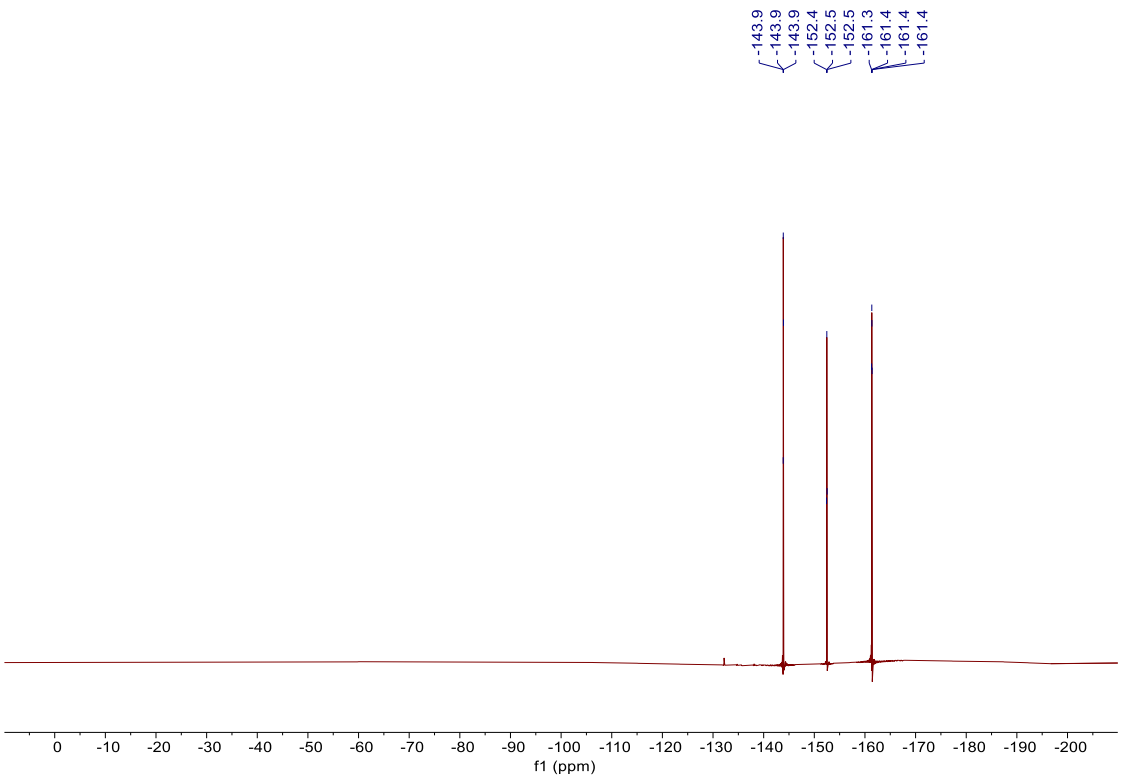
2-(Perfluorophenyl)-2,5,6,7-tetrahydro-3*H*-pyrrolo[2,1-*c*][1,2,4]triazol-3-one (3b)



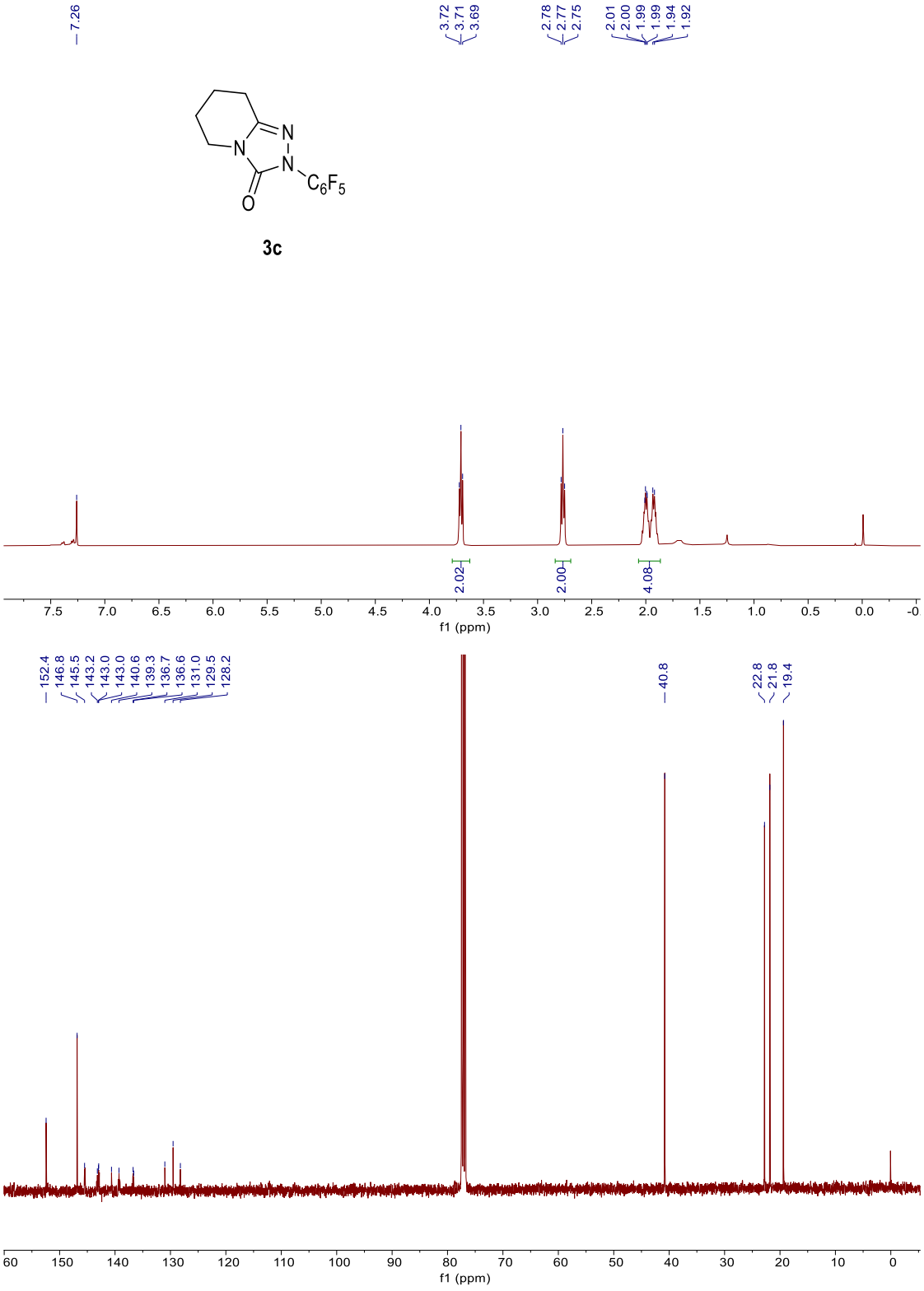
3b



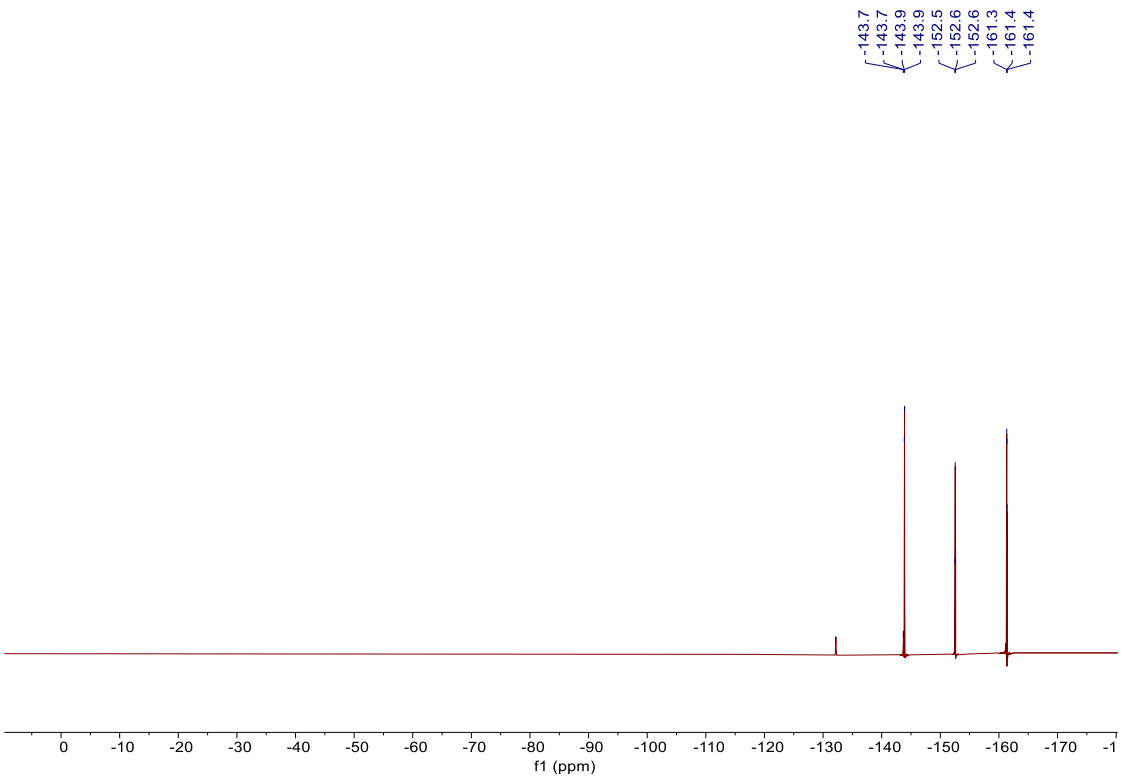



-143.9
-143.9
-143.9
-152.4
-152.5
-152.5
-161.3
-161.4
-161.4
-161.4
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

2-(Perfluorophenyl)-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-*a*]pyridin-3(2*H*)-one (3c)



3c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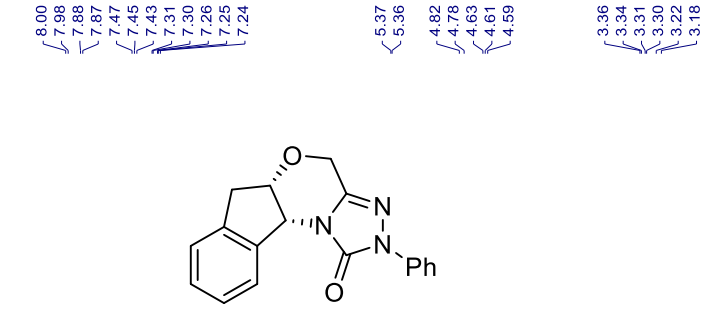
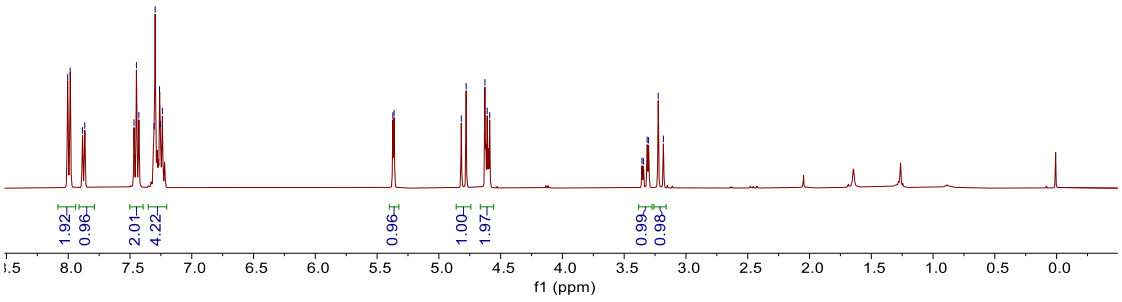
-150
-160
-170
-1
f1 (ppm)

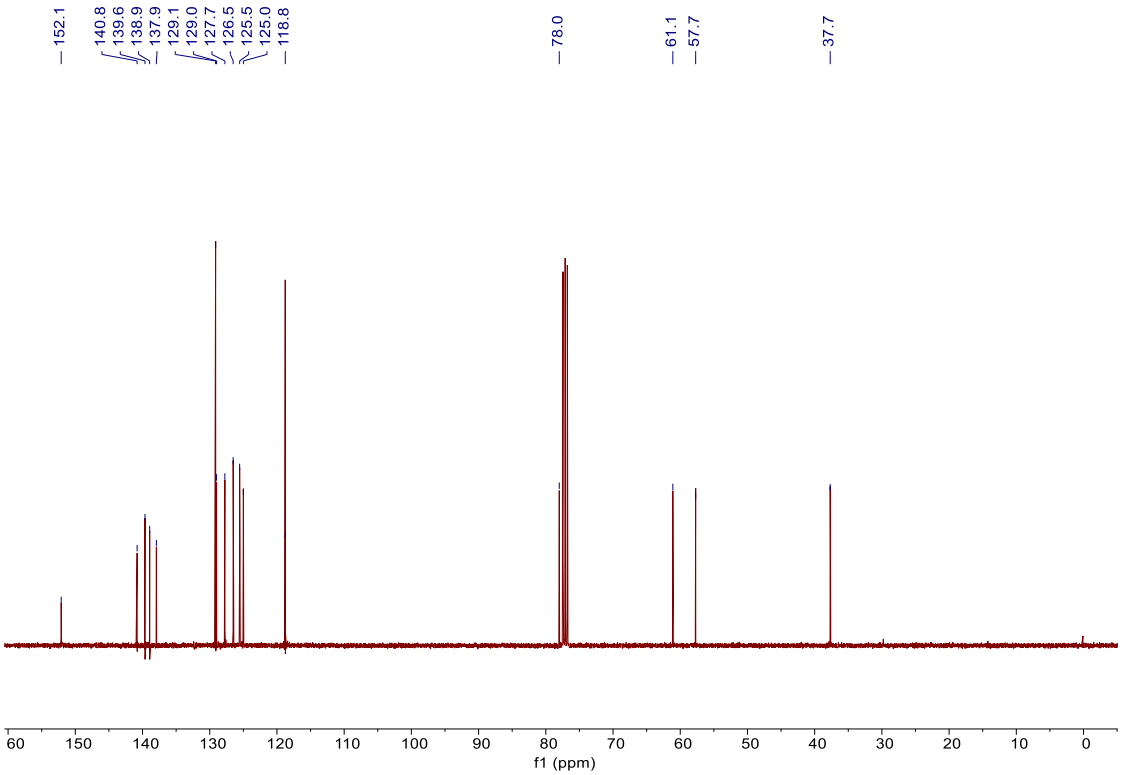
2-Phenyl-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one

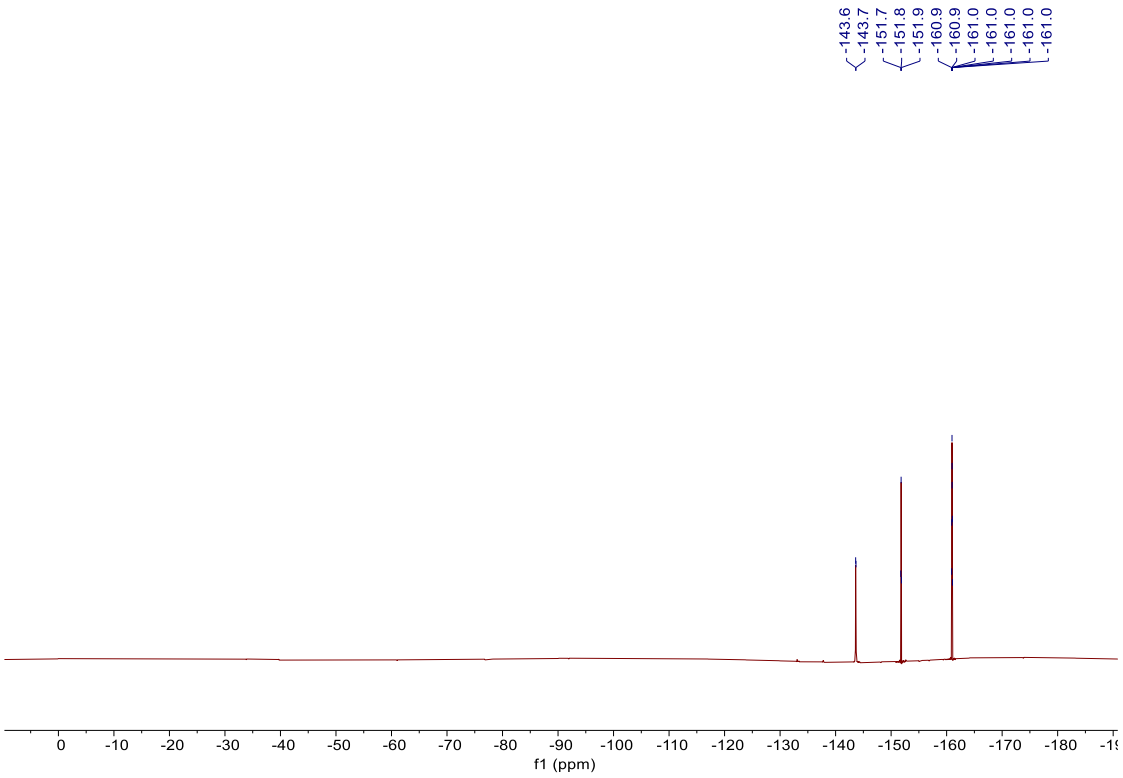
(3d)



3d






-143.6
-143.7
-151.7
-151.8
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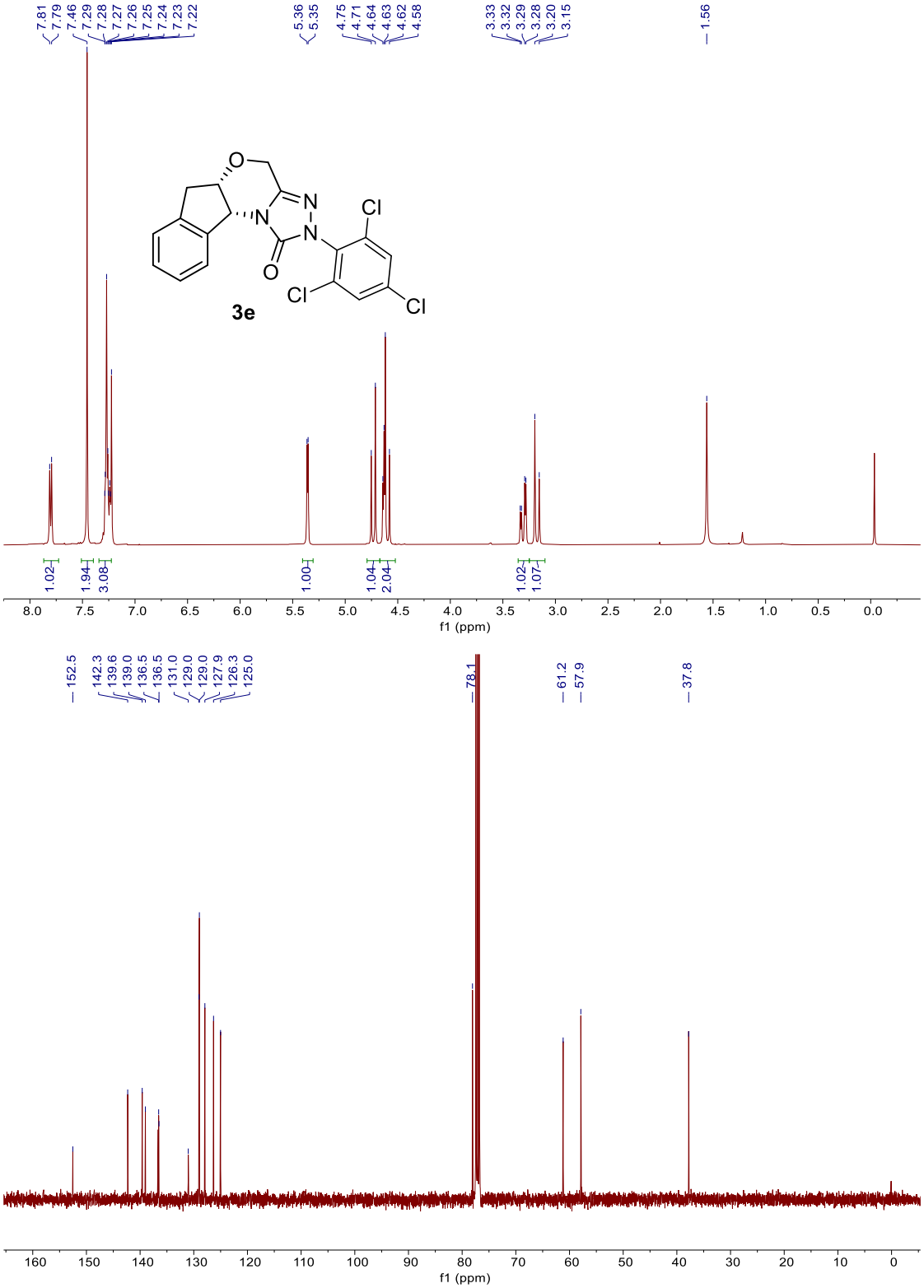
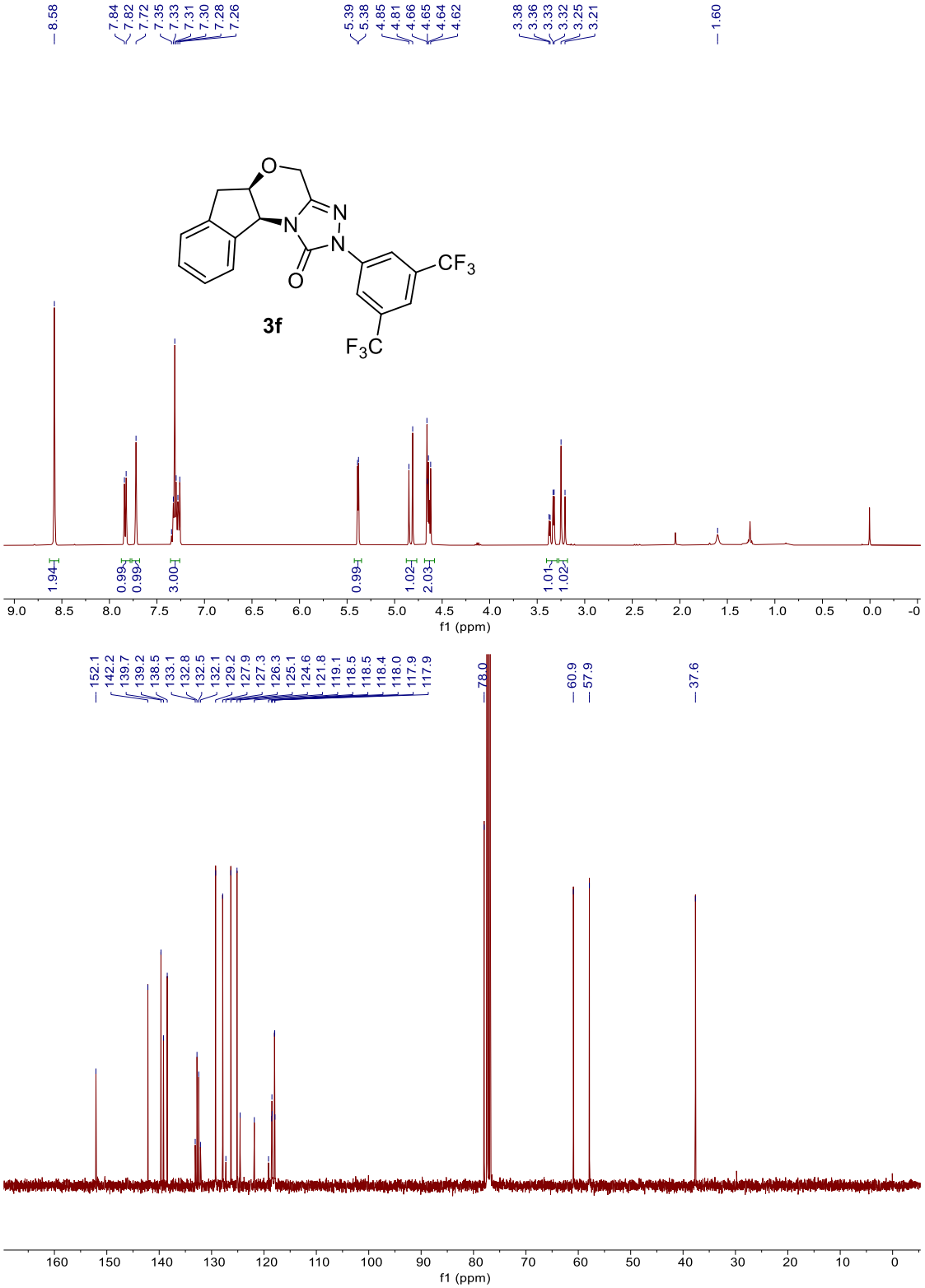
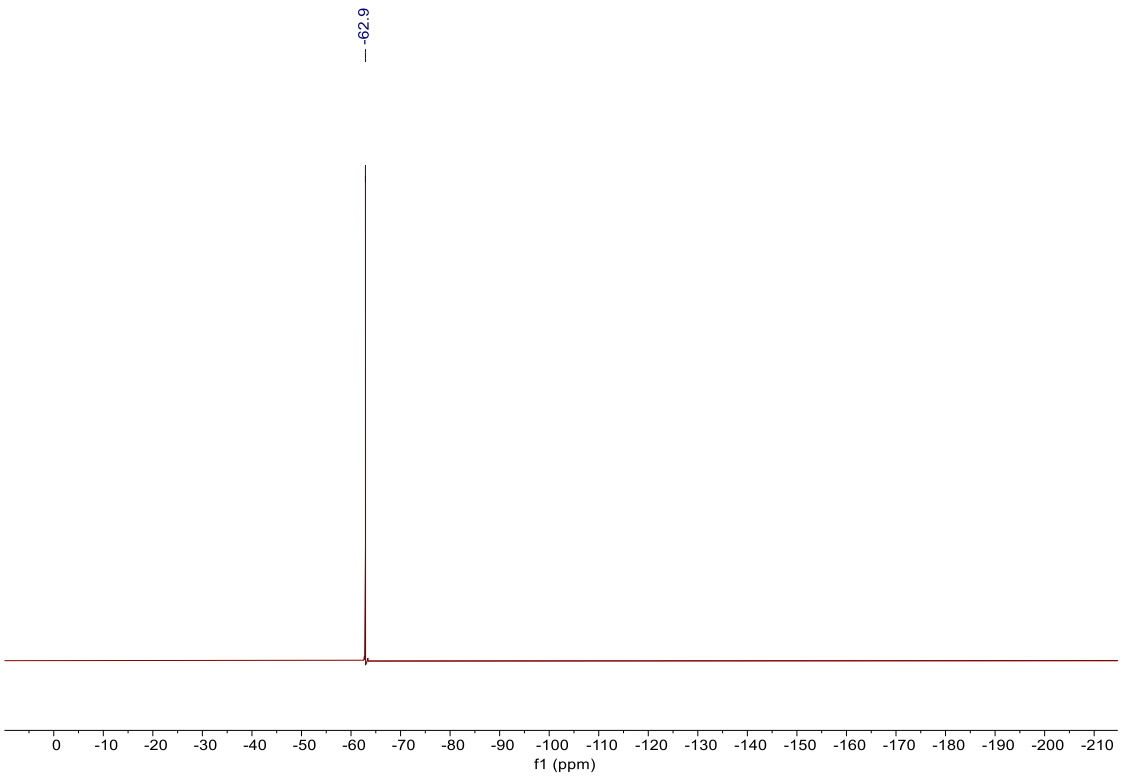
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

2-(2,4,6-Trichlorophenyl)-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3e)

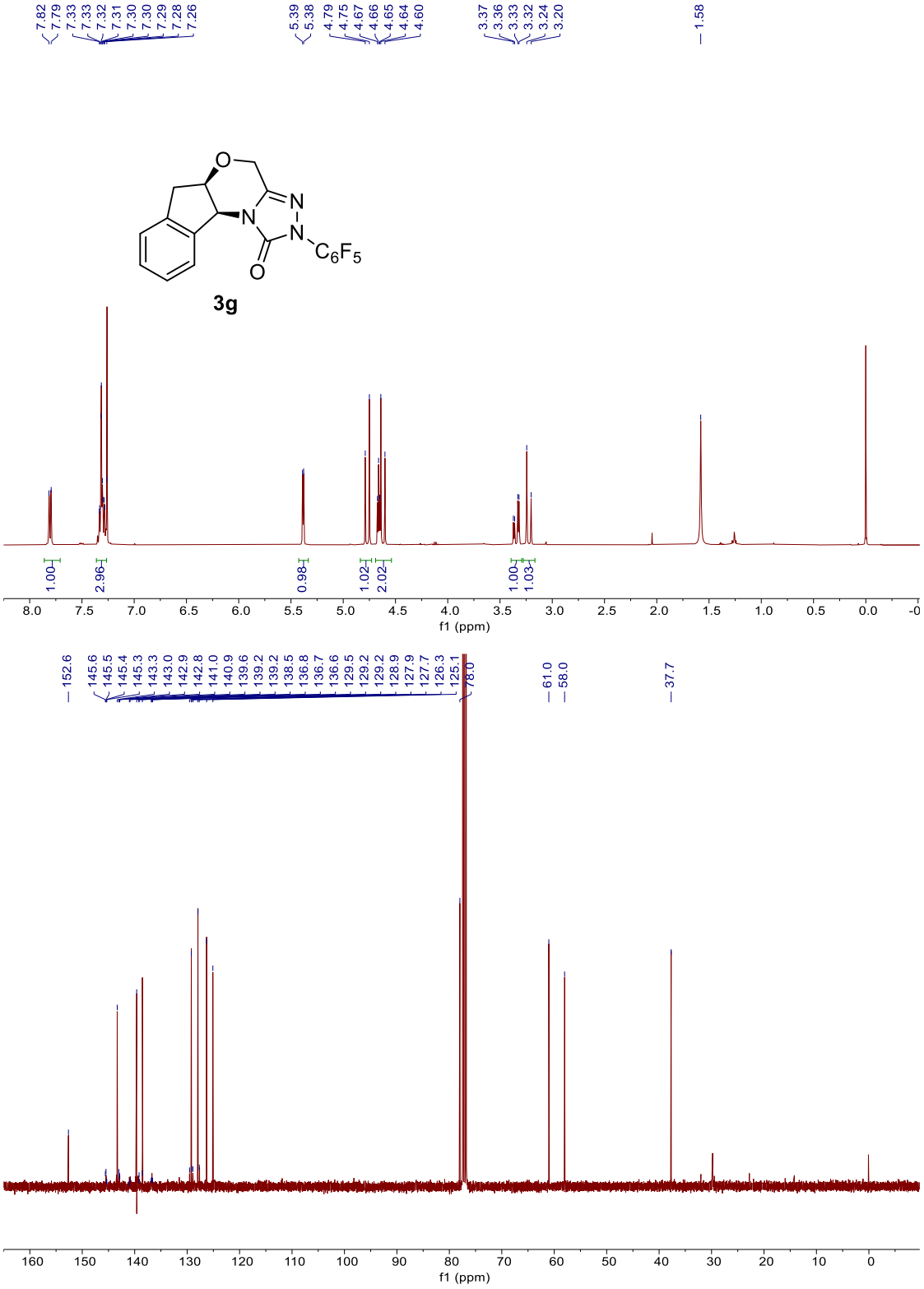


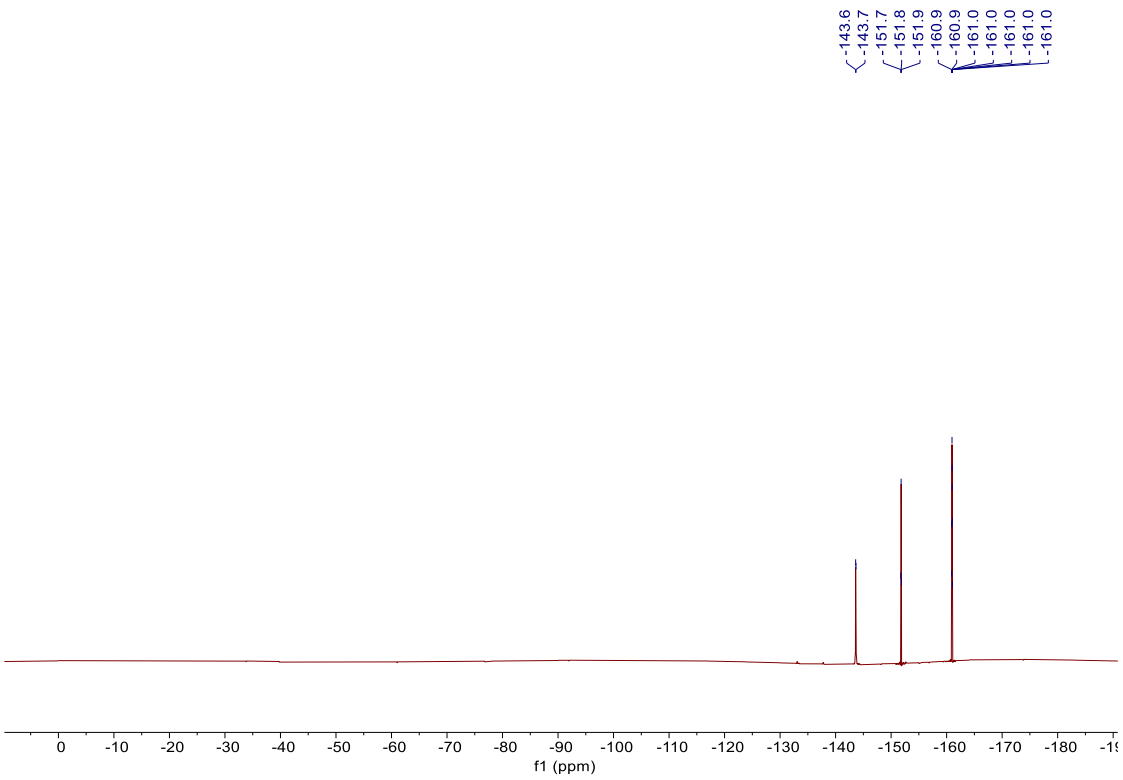
2-(3,5-Bis(trifluoromethyl)phenyl)-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3f)



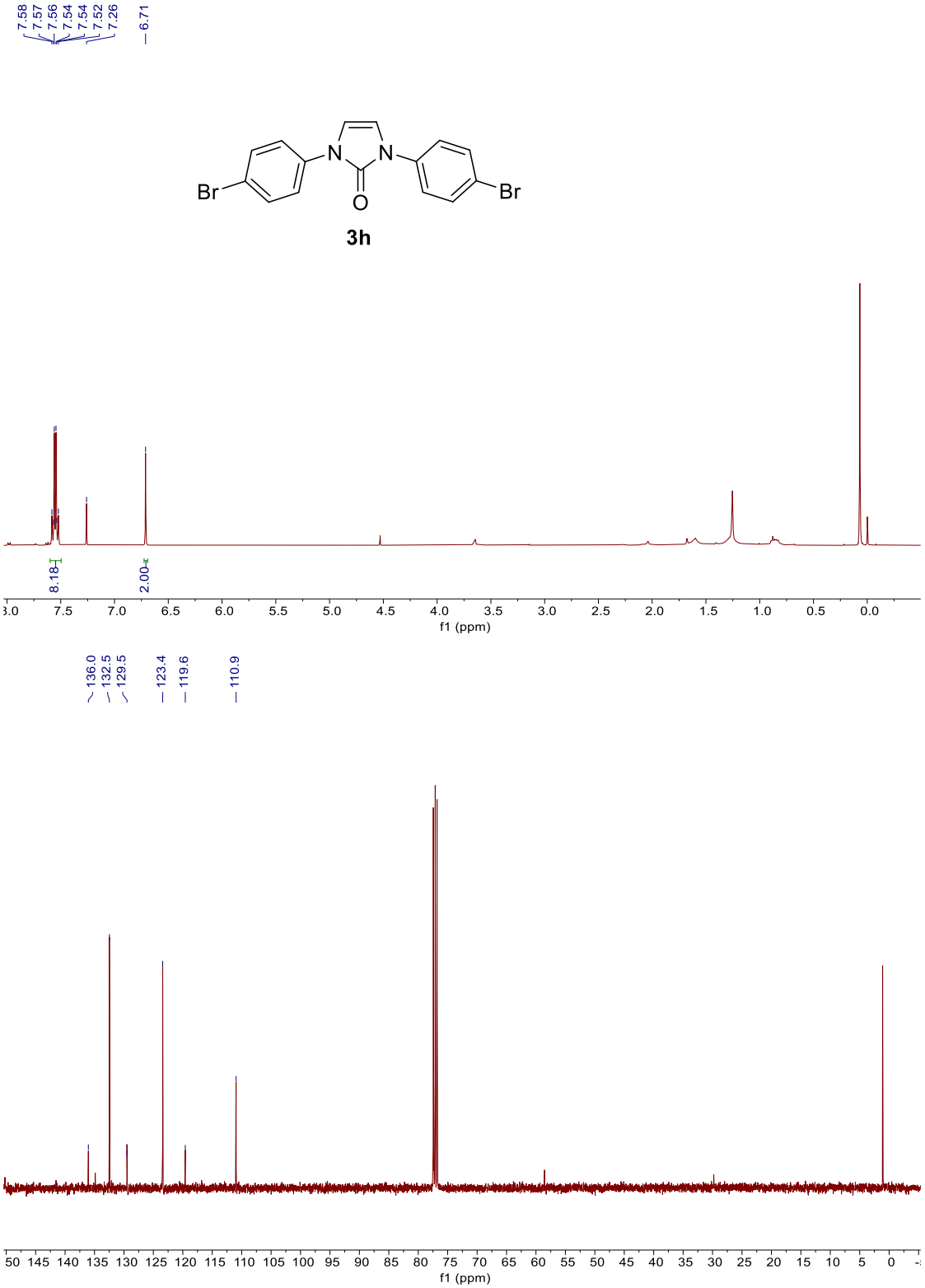

-62.9
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2-(Perfluorophenyl)-2,4,5*a*,10*b*-tetrahydro-1*H*,6*H*-indeno[2,1-*b*][1,2,4]triazolo[4,3-*d*][1,4]oxazin-1-one (3g)

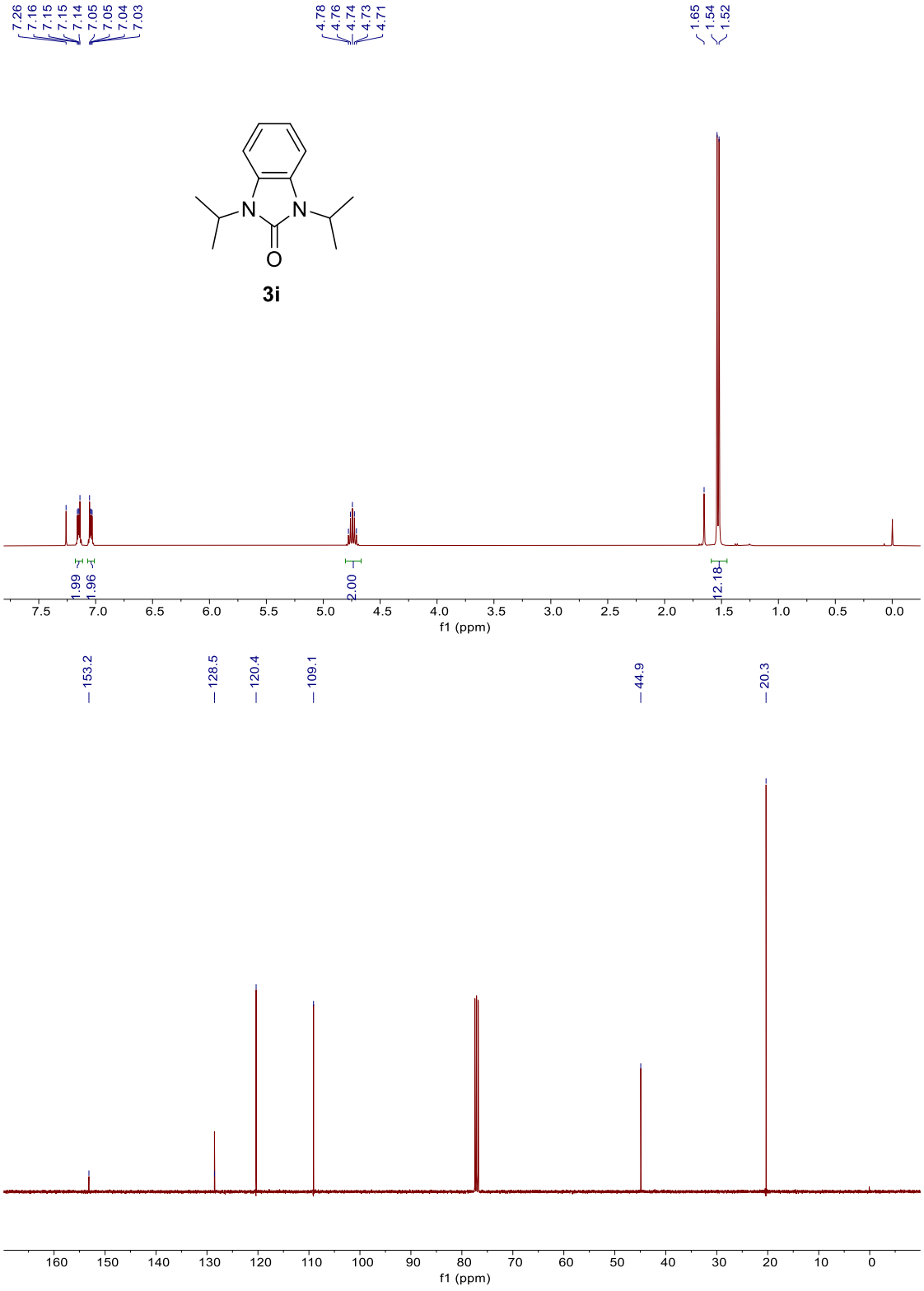



-143.6
-143.7
-151.7
-151.8
-151.9
-160.9
-160.9
-161.0
-161.0
-161.0
-161.0
-161.0
-161.0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

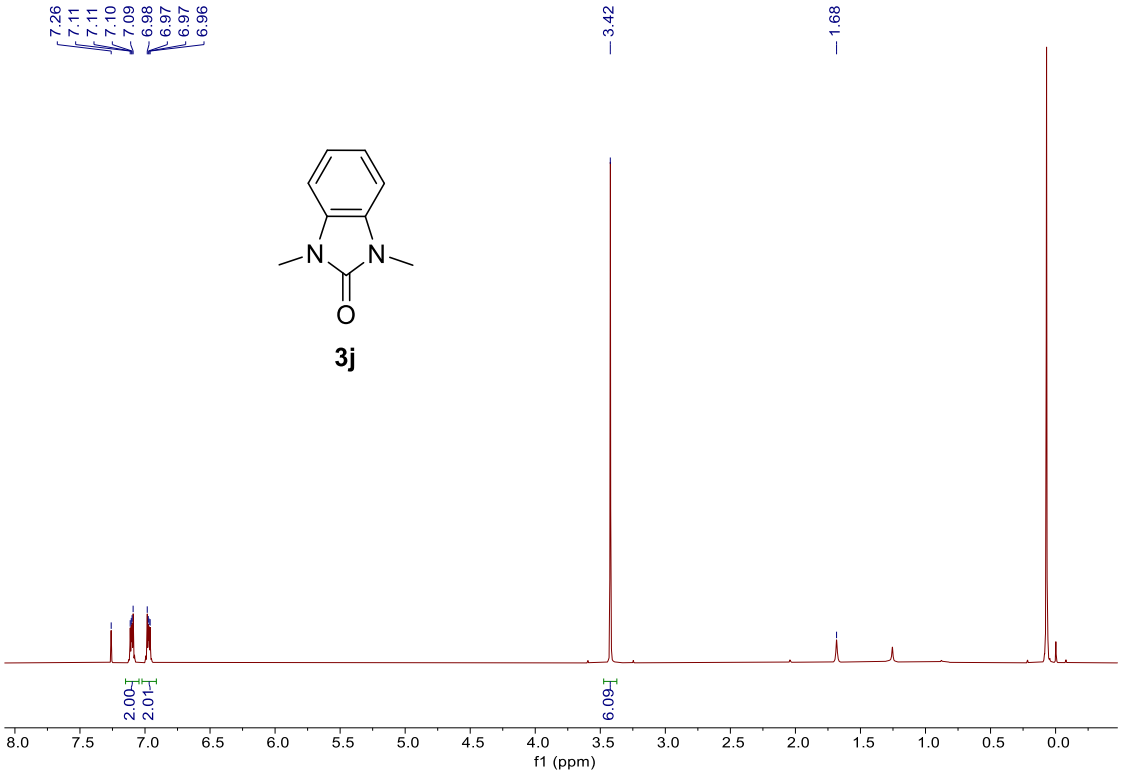
_S_-phenyl benzenesulfonothioate (3h)

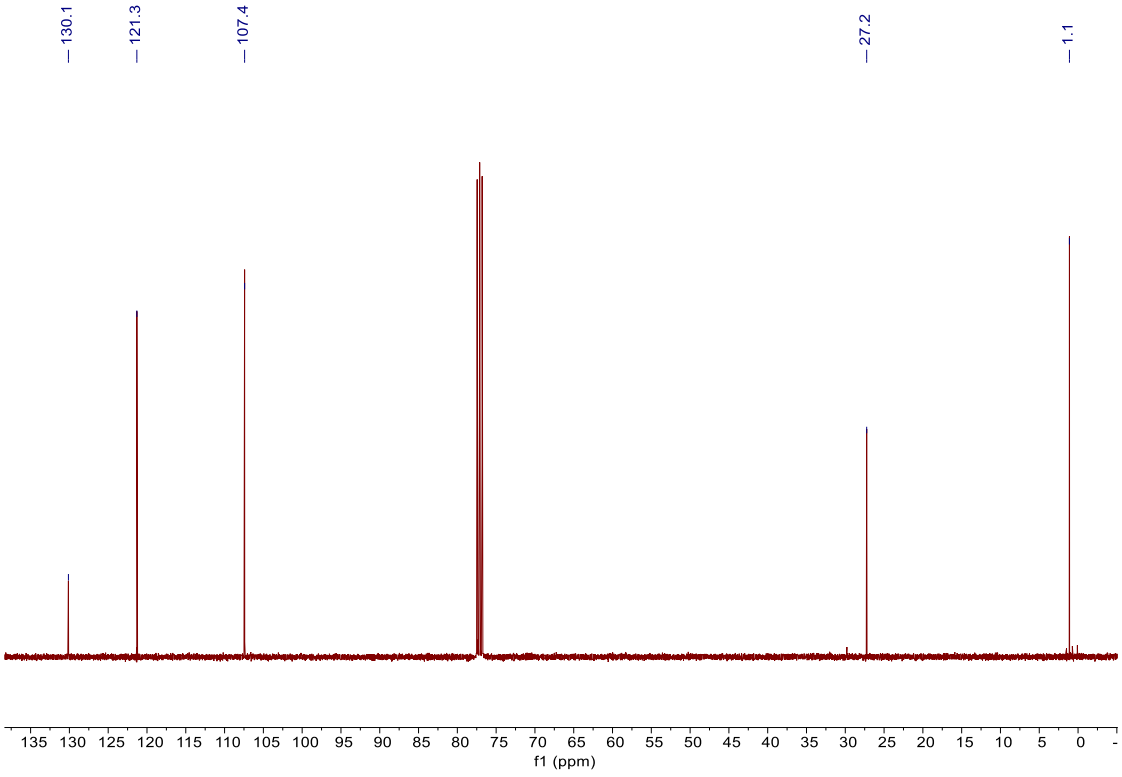


1,3-Diisopropyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3i)

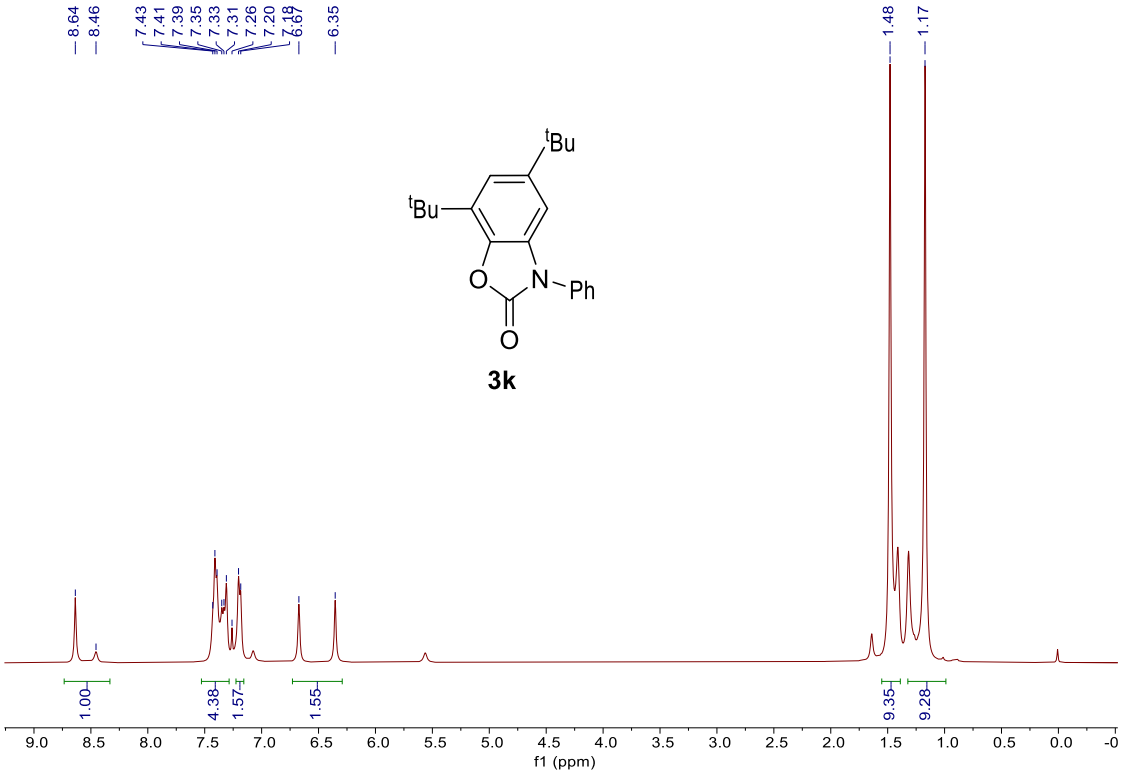


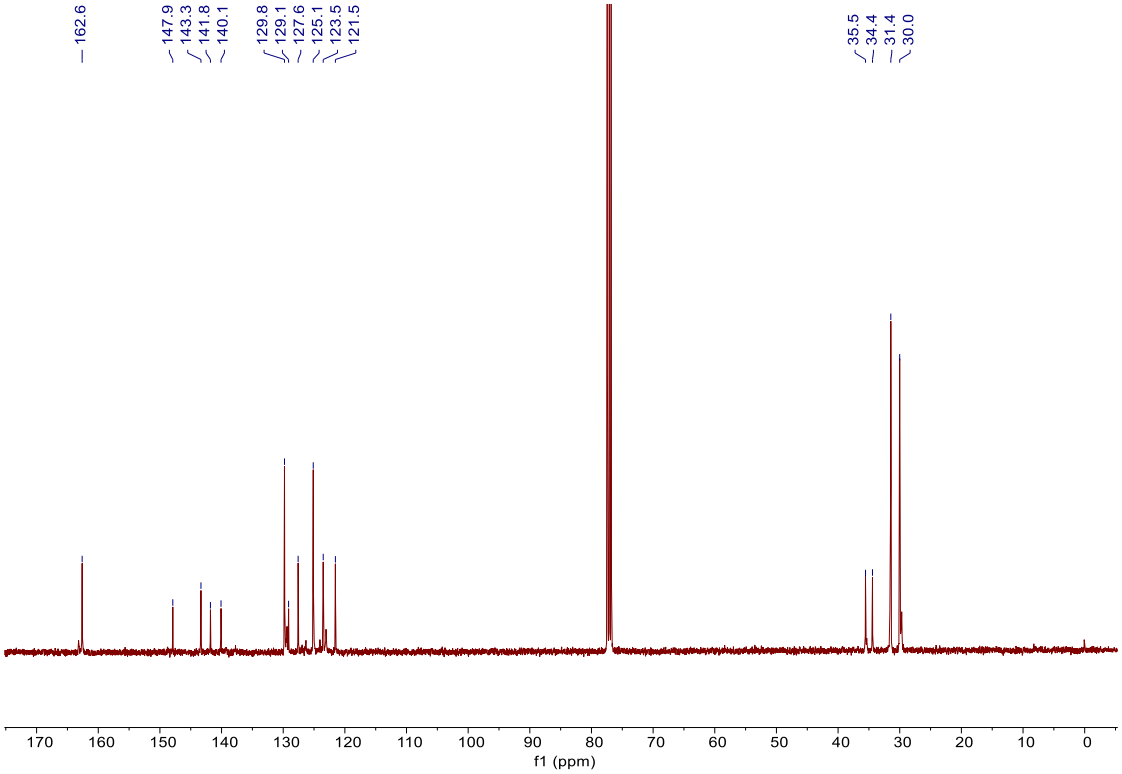
1,3-Dimethyl-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-one (3j)



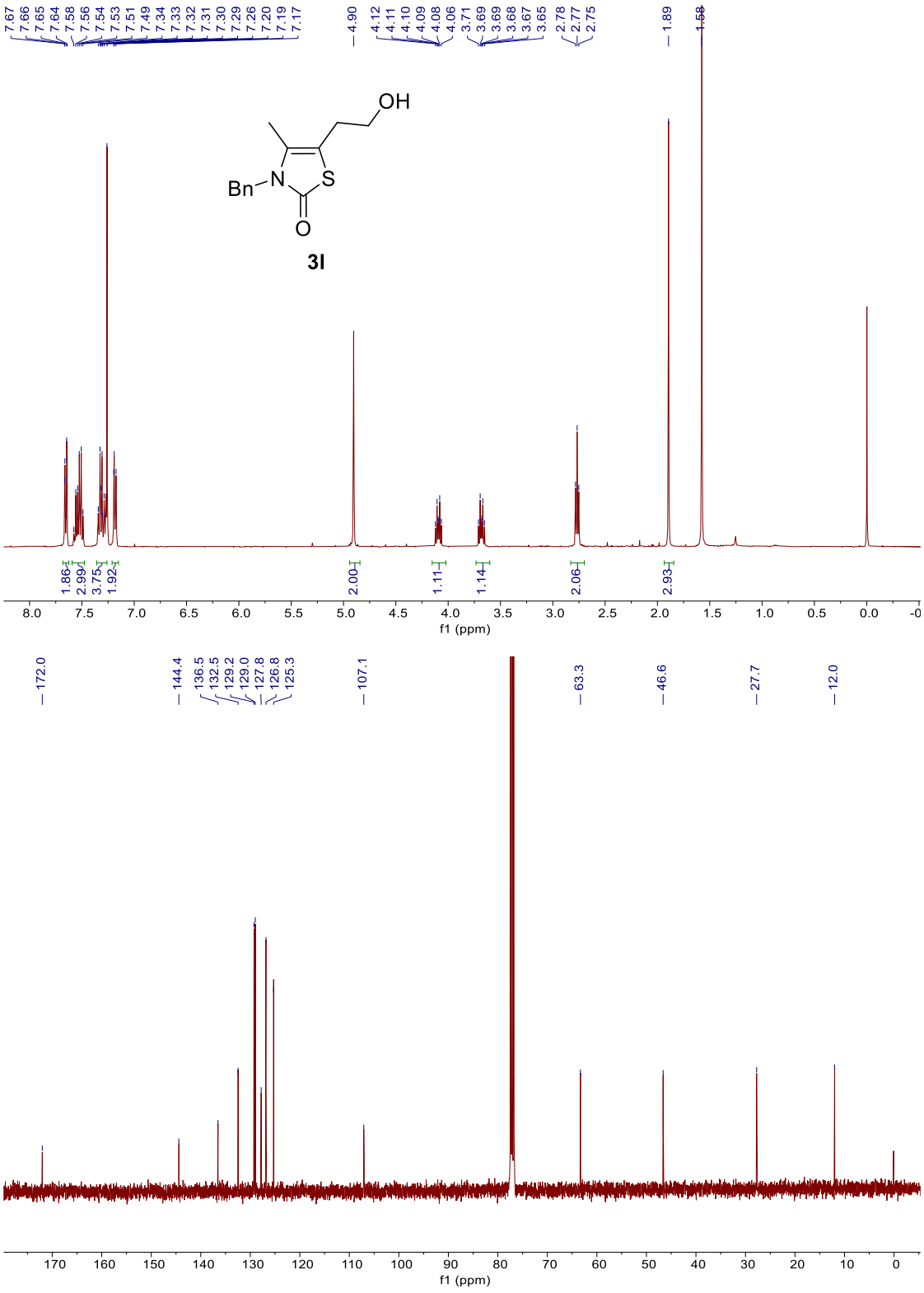


5,7-Di-tert-butyl-3-phenylbenzo[*d*]oxazol-2(3*H*)-one (3k)





3,4,5-Trimethylthiazol-2(3*H*)-one (3l)



3,4,5-Trimethylthiazol-2(3*H*)-one (3m)