Supporting Information

Visible-Light-Promoted Cascade Cyclization towards Benzo[*d*]imidazo[5,1-*b*]thiazoles under Metal- and Photocatalyst-Free Conditions

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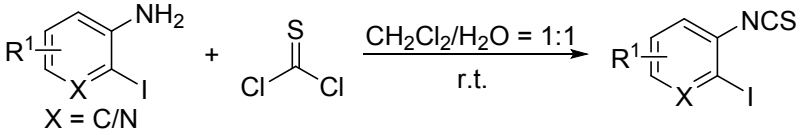
1. Experimental Section:

General Considerations. All products were prepared under argon atmosphere using standard Schlenk technique. ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm. DMSO-d_6 δ_H = 2.50 ppm, δ_C = 39.52 ppm.), respectively. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectra (HRMS) were done on Varian 7.0 T FTICR-mass spectrometer. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Aldrich, Acros, Alfa Aesar, and Energy Chemical Company and used as received without any further purification.

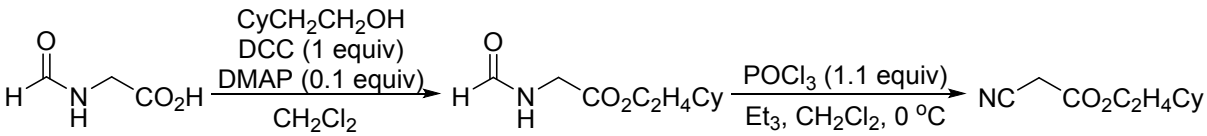
2. Synthetic Procedures

(a) General Procedure for the Preparation of 1c, 1f, 1g, 1m



A mixture of substituted *o*-iodoarylamines (5 mmol, 1.0 equiv), thiophosgene (10 mmol, 2 equiv) were weighted in a Schlenk tube equipped with a stir bar. CH_2Cl_2 (3 mL) and H_2O (3 mL) was added and the mixture was stirred at room temperature for 6 h under air. The mixture was quenched with 10 mL of water and extracted 3 times with CH_2Cl_2 (10 mL each time), the organic solutions were combined and dried with $MgSO_4$. Then, the mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether to give the corresponding *o*-iodoarylisothiocyanates (**1c, 1f, 1g, and 1m**).

(a) General Procedure for the Preparation of 2h

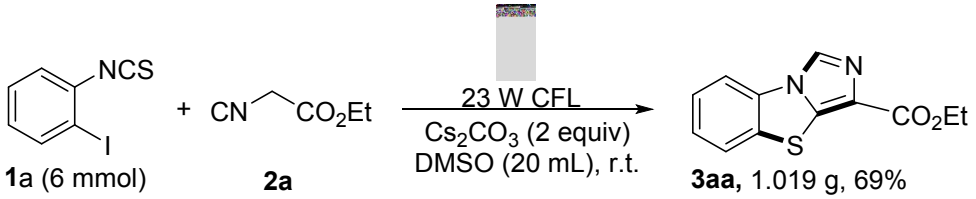


2-Cyclohexylethyl 2-cyanoacetate (**2h**) was prepared according to the previous work.[1] DCC (3.64 g, 17.6 mmol, 1.0 equiv) and DMAP (215 mg, 1.76 mmol, 0.1 equiv) were added in sequence to a stirred suspension of *N*-formyl glycine (2.00 g, 19.4 mmol, 1.1 equiv) and benzyl alcohol (1.8 mL, 1.0 eq) in CH_2Cl_2 (60 mL) at 0 °C. The reaction mixture was stirred for 16 hours at room temperature, then the solids were filtered off and solvents were evaporated. The resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether to give 2-cyclohexylethyl formylglycinate in 70% yield (2621.6 mg, 12.3 mmol). Then, $POCl_3$ (0.75 mL, 8 mmol, 1.1 equiv) was added dropwise over 20 minutes to a stirred solution of 2-cyclohexylethyl formylglycinate (7.3 mmol, 1.0 equiv) and Et_3N (2.4 mL, 17.5 mmol, 2.4 equiv) in CH_2Cl_2 (15 mL) at 0 °C. Upon addition the colorless reaction mixture became turbid and turned orange, then brown. After stirring at 0 °C for 15 minutes, saturated $NaHCO_3$ aqueous solution (10 mL) was added and the phases were separated. The aqueous layer was extracted twice with CH_2Cl_2 (15 mL), then the collected organic phases were washed with brine, dried over K_2CO_3 and filtered. the mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether to give **2h** in 83% yield (1182.3 mg, 6.06 mmol).

(c) General Procedure for the Visible-Light-Promoted Preparation of 3

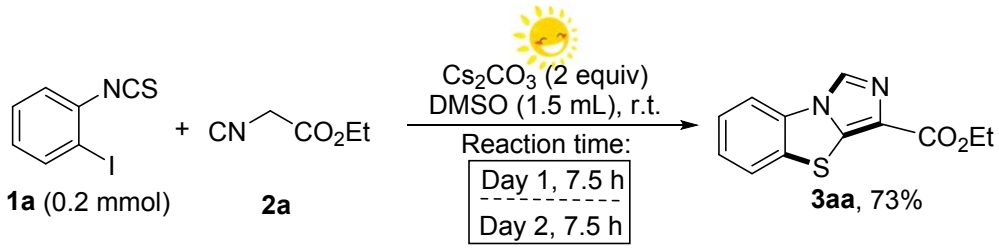
A mixture of substituted *o*-haloarylisothiocyanates (**1**) (0.2 mmol, 1.0 equiv), isocyanides (**2**) (0.3 mmol, 1.5 equiv), and Cs_2CO_3 (2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMSO (1.5 mL) was added and the mixture was stirred at room temperature with the irradiation of a 23 W compact fluorescent light (CFL) for 15 h under air. Then, the mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

(d) Gram-Scale Preparation of 3aa



A mixture of 1-iodo-2-isothiocyanatobenzene (**1a**) (1619.5 mg, 6 mmol, 1.0 equiv), ethyl 2-isocyanoacetate (**2a**) (1017.4 mg, 9 mmol, 1.5 equiv), and Cs_2CO_3 (2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMSO (20 mL) was added and the mixture was stirred at room temperature with the irradiation of a 23 W compact fluorescent light (CFL) for 15 h under air. Then, the mixture was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 69% yield (1.019 g, 4.14 mmol).

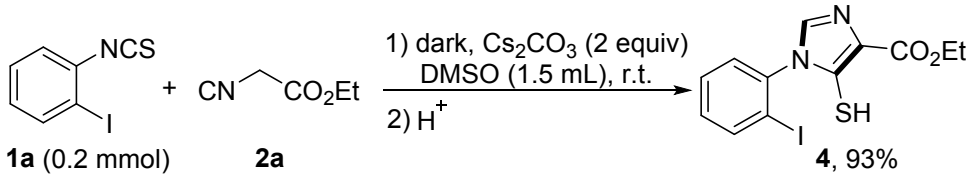
(e) Preparation of 3aa under Natural Light Irradiation



A mixture of 1-iodo-2-isothiocyanatobenzene (**1a**) (0.2 mmol, 1.0 equiv), ethyl 2-isocyanoacetate (**2a**) (0.3 mmol, 1.5 equiv), and Cs_2CO_3 (2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMSO (1.5 mL) was added and the mixture was stirred at room temperature under sunlight for 15 h under air. Then, the mixture was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 73% yield (35.9 mg, 0.146 mmol).

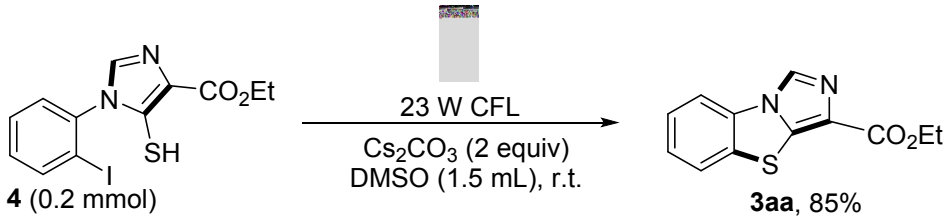
3. Mechanism Research

(a) Preparation of Intermediate 4



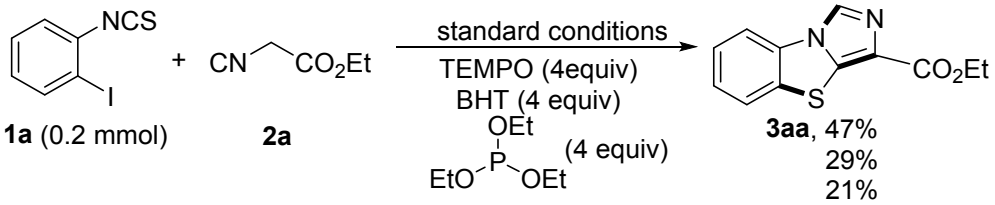
A mixture of 1-iodo-2-isothiocyanatobenzene (**1a**) (0.2 mmol, 1.0 equiv), ethyl 2-isocyanoacetate (**2a**) (0.3 mmol, 1.5 equiv), and Cs_2CO_3 (2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMSO (1.5 mL) was added and the mixture was stirred at room temperature under dark for 15 h under air. The mixture was acidified to PH = 5 with hydrochloric acid (1 M), and distributed in water and ethyl acetate. The organic layer was separated and concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the desired product **4** was affored as a yellow solid in 93% yield (69.6 mg, 0.186 mmol).

(b) The Transformation Reaction from 4 to 3aa



A mixture of ethyl 1-(2-iodophenyl)-5-mercapto-1*H*-imidazole-4-carboxylate (**4**) (0.2 mmol, 1.0 equiv) and Cs_2CO_3 (2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMSO (1.5 mL) was added and the mixture was stirred at room temperature with the irradiation of a 23 W compact fluorescent light (CFL) for 15 h under air. Then, the mixture was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 85% yield (41.8 mg, 0.17 mmol).

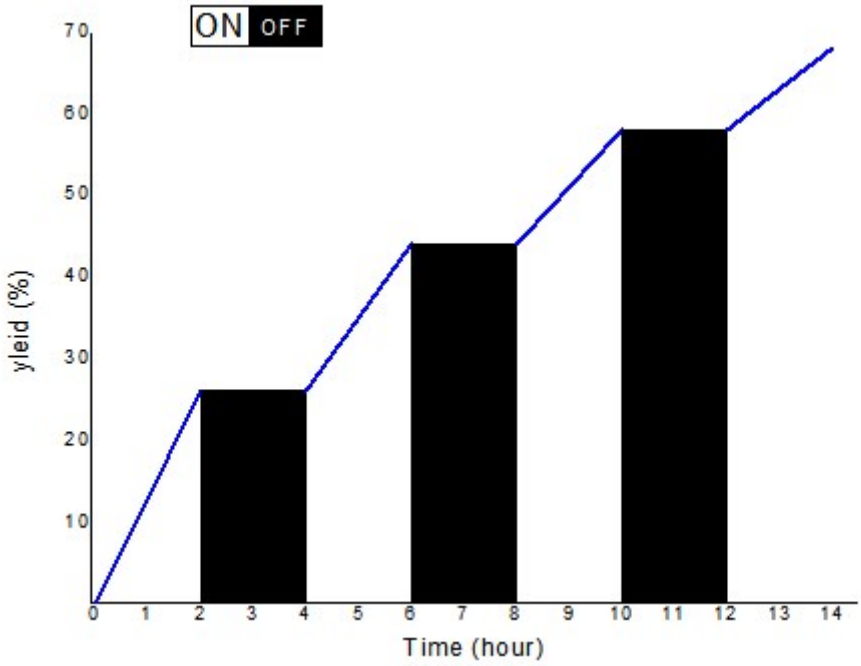
(c) Free Radical Capture Experiments



A mixture of 1-iodo-2-isothiocyanatobenzene (**1a**) (0.2 mmol, 1.0 equiv), ethyl 2-isocyanoacetate (**2a**) (0.3 mmol, 1.5 equiv), Cs_2CO_3 (2 equiv), and 4 equiv of TEMPO (or BHT or triethoxyphosphorus) were weighted in a Schlenk tube equipped with a stir bar. Dry DMSO (1.5 mL) was added and the mixture was stirred at room temperature with the irradiation of a 23 W compact fluorescent light (CFL) for 15 h under air. Then, the mixture

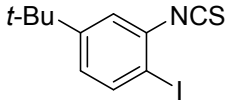
was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 47% (or 29% or 21%) yield.

(d) Visible-light Irradiation ON/OFF Experiment



The reaction between1-iodo-2-isothiocyanatobenzene (**1a**) (0.2 mmol, 1.0 equiv) and ethyl 2-isocyanoacetate (**2a**) (0.3 mmol, 1.5 equiv) was conducted under the standard conditions. The mixture was subjected to equential periods of stirring under visible light irradiation (23 W compact fluorescent light) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with chromatography column on silica gel (EtOAc:petroleum ether: 1:1) to give the corresponding products **3aa**. The yield of **3aa** was measured by weight of the product.

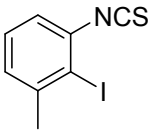
4. Characterization of Compounds 1c, 1f, 1g, 1m, 2h, 3, and 4



4-(*tert*-butyl)-1-iodo-2-isothiocyanatobenzene (1c)

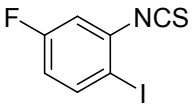
The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 82% yield (1299.6 mg, 4.1 mmol). Mp: 42 – 43 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.57 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H),

1.30 (s, 9H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 152.1, 137.1, 130.3, 128.4, 126.4, 125.4, 120.4, 34.8, 31.0. **HRMS (ESI):** Calcd for $C_{11}H_{13}INS$ $[M+H]^+$ 317.9808, found: 317.9804.



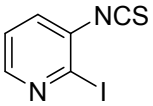
2-iodo-1-isothiocyanato-3-methylbenzene (1f)

The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 79% yield (1086.0 mg, 3.95 mmol). Mp: 66 – 67 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.20 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 2.47 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 143.9, 135.9, 135.2, 128.6, 127.9, 124.2, 100.9, 29.2. **HRMS (ESI):** Calcd for C_8H_7INS $[M+H]^+$ 275.9338, found: 275.9341.



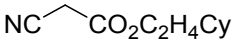
4-fluoro-1-iodo-2-isothiocyanatobenzene (1g)

The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 76% yield (1056.7 mg, 3.8 mmol). Mp: 74 – 75 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.74 – 7.72 (m, 1H), 7.00 – 6.98 (m, 1H), 6.78 – 6.74 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.7 (d, J = 250.4 Hz), 140.2 (d, J = 8.9 Hz), 138.0, 136.2 (d, J = 11.0 Hz), 116.2 (d, J = 21.8 Hz), 114.4 (d, J = 25.3 Hz), 87.7 (d, J = 3.7 Hz). **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -111.3. **HRMS (ESI):** Calcd for C_7H_4FINS $[M+H]^+$ 279.9088, found: 279.9086.



2-iodo-3-isothiocyanatopyridine (1m)

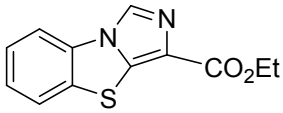
The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 71% yield (929.8 mg, 3.55 mmol). Mp: 60 – 61 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.19 – 8.19 (m, 1H), 7.43 – 7.41 (m, 1H), 7.26 – 7.26 (m, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 147.6, 139.4, 134.0, 132.8, 123.1, 117.9. **HRMS (ESI):** Calcd for $C_6H_4IN_2S$ $[M+H]^+$ 262.9134, found: 262.9131.



ethyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (2h)

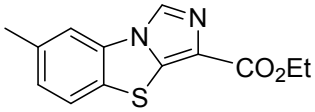
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 5/1) as a pale yellow oil in 58% total yield. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 4.24 – 4.17 (m, 4H), 1.69 – 1.59 (m, 5H), 1.53 (q, J = 6.9 Hz, 2H), 1.37 – 1.27 (m, 1H), 1.22 – 1.08 (m, 3H),

0.94 – 0.85 (m, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 163.9, 160.9, 64.8, 43.4, 35.5, 34.2, 32.8, 26.2, 25.9. **HRMS (ESI):** Calcd for $C_{11}H_{1183}NO_2$ $[M+H]^+$ 196.1332, found: 196.1335.



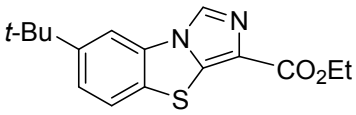
ethyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3aa)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 78% yield (38.4 mg, 0.156 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.28 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.3, 133.6, 130.9, 127.5, 126.5, 126.3, 124.6, 122.7, 113.3, 60.7, 14.4.



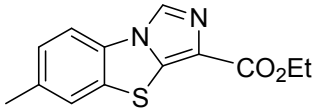
ethyl 7-methylbenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ba)[3]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 77% yield (40.0 mg, 0.154 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.27 (s, 1H), 7.63 – 7.54 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):**δ 162.4, 137.6, 137.2, 131.1, 130.4, 127.6, 127.2, 124.2, 122.6, 113.8, 60.7, 21.4, 14.5.



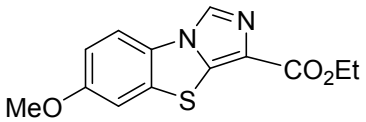
ethyl 7-(*tert*-butyl)benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ca)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 81% yield (48.9 mg, 0.162 mmol). Mp: 145 – 146 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.27 (s, 1H), 7.69 – 7.68 (m, 2H), 7.50 (d, *J* = 8.6 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.37 (s, 9H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.5, 161.2, 150.3, 133.7, 128.9, 127.3, 124.2, 122.7, 121.2, 112.8, 60.8, 35.2, 31.4, 14.5. **HRMS (ESI):** Calcd for $C_{16}H_{19}N_2O_2S$ $[M+H]^+$ 303.1162, found: 303.1158.



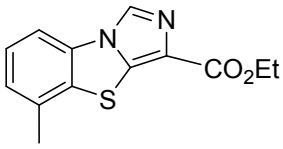
ethyl 6-methylbenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3da)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 83% yield (43.2 mg, 0.166 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.25 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 1H), 7.29 – 7.26 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.4, 137.1, 136.8, 133.7, 129.0, 127.5, 127.2, 124.6, 122.7, 112.9, 60.7, 21.3, 14.5.



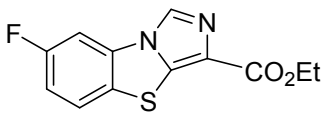
ethyl 6-methoxybenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ea)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 74% yield (40.9 mg, 0.148 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.21 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.4, 158.3, 136.9, 135.1, 127.1, 125.2, 122.9, 113.9, 113.8, 108.6, 60.7, 56.0, 14.5.



ethyl 5-methylbenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3fa)

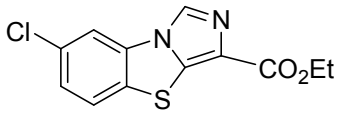
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 72% yield (37.4 mg, 0.144 mmol). Mp: 170 – 171 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.28 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.4, 134.6, 133.6, 130.8, 127.4, 126.9, 126.6, 122.7, 110.8, 60.8, 19.7, 14.5. **HRMS (ESI):** Calcd for $C_{13}H_{13}N_2O_2S$ $[M+H]^+$ 261.0692, found: 261.0690.



ethyl 7-fluorobenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ga)[2]

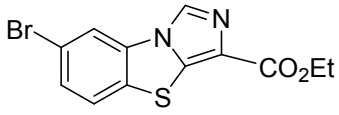
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 66% yield (34.9 mg, 0.132 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ

8.27 (s, 1H), 7.66 – 7.63 (m, 1H), 7.53 – 7.51 (m, 1H), 7.19 – 7.15 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.1, 161.3 (d, *J* = 247.7 Hz), 138.1, 131.5 (d, *J* = 11.3 Hz), 128.7 (d, *J* = 2.5 Hz), 127.4, 125.5 (d, *J* = 9.3 Hz), 122.9, 114.3 (d, *J* = 23.8 Hz), 101.6 (d, *J* = 27.9 Hz), 60.9, 14.4. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -112.7.



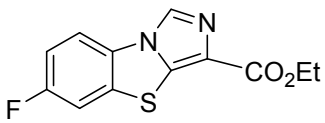
ethyl 7-chlorobenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ha)[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 70% yield (39.2 mg, 0.140 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.28 (s, 1H), 7.80 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.2, 137.5, 132.7, 132.0, 131.7, 127.4, 126.8, 125.4, 123.0, 113.9, 60.9, 14.5.



ethyl 7-bromobenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ia)

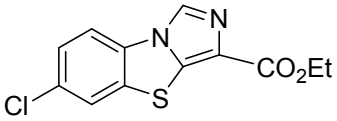
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 72% yield (46.6 mg, 0.144 mmol). Mp: 187 – 188 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.30 (s, 1H), 7.87 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.2, 136.7, 135.6, 130.1, 129.8, 127.6, 127.3, 123.1, 119.4, 114.4, 61.0, 14.5. **HRMS (ESI):** Calcd for $C_{12}H_{10}BrN_2O_2S$ $[M+H]^+$ 324.9641 and 326.9620, found: 324.9645 and 326.9624.



ethyl 6-fluorobenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ja)[3]

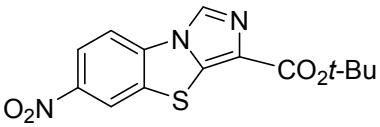
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 62% yield (32.7 mg, 0.124 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.27 (s, 1H), 7.76 – 7.73 (m, 1H), 7.46 – 7.43 (m, 1H), 7.24 – 7.20 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.2, 160.5 (d, *J* = 248.1 Hz), 137.12, 135.3 (d, *J* = 10.0 Hz), 127.7, 127.4, 123.2, 114.4 (d,

J = 25.0 Hz), 114.2 (d, J = 9.2 Hz), 111.7 (d, J = 27.4 Hz), 60.9, 14.5. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -113.4.



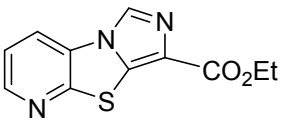
ethyl 6-chlorobenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ka)[3]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a vermeil solid in 70% yield (39.2 mg, 0.140 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.29 (s, 1H), 7.72 – 7.70 (m, 2H), 7.47 (d, J = 8.5 Hz, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.1, 136.8, 135.2, 132.1, 129.6, 127.5, 127.0, 124.3, 123.0, 114.1, 60.9, 14.4.



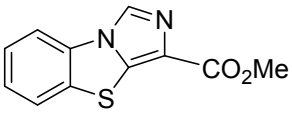
***tert*-butyl 6-nitrobenzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3le)**[2]

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 48% yield (30.6 mg, 0.096 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.66 (s, 1H), 8.46 – 8.34 (m, 2H), 7.92 (d, J = 8.8 Hz, 1H), 1.66 (s, 9H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 161.0, 145.7, 135.3, 135.0, 128.1, 128.0, 122.6, 120.7, 113.7, 82.1, 28.3.



ethyl imidazo[5',1':2,3]thiazolo[5,4-*b*]pyridine-8-carboxylate (3ma)[2]

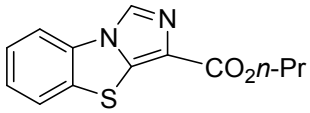
The mixture in the title were obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solids in 76% yield (37.6 mg, 0.152 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.58 (d, J = 4.5 Hz, 1H), 8.36 (s, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.46 – 7.44 (m, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.1, 156.2, 147.6, 134.5, 128.4, 126.4, 123.9, 121.6, 120.7, 120.3, 61.0, 14.5.



methyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ab)[2]

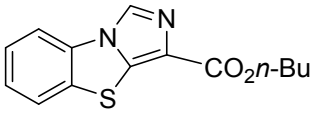
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 80% yield (37.1 mg, 0.160 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.29 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H),

7.47 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.7, 137.2, 133.6, 131.0, 127.4, 126.6, 126.4, 124.7, 122.5, 113.4, 51.9.



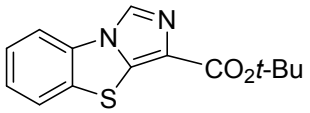
propyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ac)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 84% yield (43.7 mg, 0.168 mmol). Mp: 124 – 125 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.30 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 4.33 – 4.30 (m, 2H), 1.85 – 1.78 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.3, 136.9, 133.5, 130.9, 127.4, 126.5, 126.3, 124.5, 122.7, 113.3, 66.3, 22.1, 10.5. **HRMS (ESI):** Calcd for $C_{13}H_{13}N_2O_2S$ $[M+H]^+$ 261.0692, found: 261.0688.



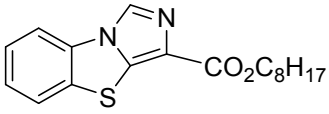
butyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ad)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 75% yield (41.1 mg, 0.150 mmol). Mp: 120 – 121 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.30 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 4.37 (t, J = 6.7 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.54 – 1.47 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.3, 137.0, 133.6, 131.0, 127.4, 126.5, 126.4, 124.6, 122.7, 113.3, 64.6, 30.8, 19.2, 13.7. **HRMS (ESI):** Calcd for $C_{14}H_{15}N_2O_2S$ $[M+H]^+$ 275.0849, found: 275.0843.



***tert*-butyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ae)**[2]

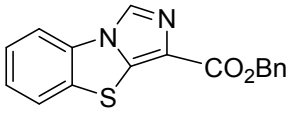
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 77% yield (42.2 mg, 0.154 mmol). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.28 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 1.64 (s, 9H).. **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 161.3, 136.2, 133.3, 130.8, 127.2, 126.2, 126.0, 124.2, 123.6, 113.2, 81.1, 28.2.



octyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3af)

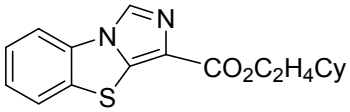
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 70% yield (46.2 mg, 0.140 mmol).

Mp: 112 – 113 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.30 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.48 – 1.41 (m, 2H), 1.34 – 1.23 (m, 8H), 0.85 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.3, 136.9, 133.6, 131.0, 127.4, 126.5, 126.4, 124.6, 122.7, 113.3, 64.9, 31.7, 29.2, 29.1, 28.8, 25.9, 22.6, 14.0. **HRMS (ESI):** Calcd for $C_{18}H_{23}N_2O_2S$ $[M+H]^+$ 331.1475, found: 331.1470.



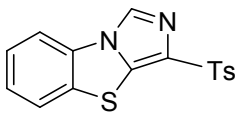
benzyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ag)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a vermeil solid in 81% yield (49.9 mg, 0.162 mmol). Mp: 188 – 189 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.30 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.41 – 7.36 (m, 3H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.41 (s, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 161.9, 137.3, 136.1, 133.5, 130.9, 128.5, 128.2, 128.1, 127.6, 126.5, 126.4, 124.6, 122.3, 113.3, 66.3. **HRMS (ESI):** Calcd for $C_{17}H_{13}N_2O_2S$ $[M+H]^+$ 309.0692, found: 309.0687.



2-cyclohexylethyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (3ah)

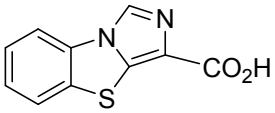
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 72% yield (47.2 mg, 0.144 mmol). Mp: 141 – 142 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.31 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.39 (t, *J* = 6.9 Hz, 2H), 1.82 – 1.60 (m, 8H), 1.51 – 1.46 (m, 1H), 1.22 – 1.10 (m, 2H), 1.00 – 0.92 (m, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 162.3, 133.6, 131.0, 127.5, 126.5, 126.4, 124.6, 122.7, 113.4, 63.0, 58.3, 36.1, 34.4, 33.1, 26.4, 26.1, 18.3. **HRMS (ESI):** Calcd for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$ 329.1318, found: 329.1313.



3-tosylbenzo[*d*]imidazo[5,1-*b*]thiazole (3ai)[3]

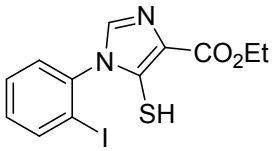
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 65% yield (42.6 mg, 0.130 mmol). **^{1}H NMR (DMSO-d_6, 500 MHz):** δ 8.96 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 7.9 Hz,

1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (DMSO-d_6, 125 MHz):** δ 144.2, 138.3, 135.2, 132.2, 130.9, 130.7, 130.0, 128.4, 127.0, 126.8, 126.8, 125.2, 114.6, 21.0.



benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylic acid (3aj)[2]

The title compound was isolated by acidification to PH 5–6 and filtration as a white solid in 61% yield (26.6 mg, 0.122 mmol). **^{1}H NMR (DMSO-d_6, 500 MHz):** δ 8.88 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR (DMSO-d_6, 125 MHz):** δ 163.2, 136.3, 132.7, 131.0, 129.4, 126.8, 126.3, 125.1, 122.4, 114.3.



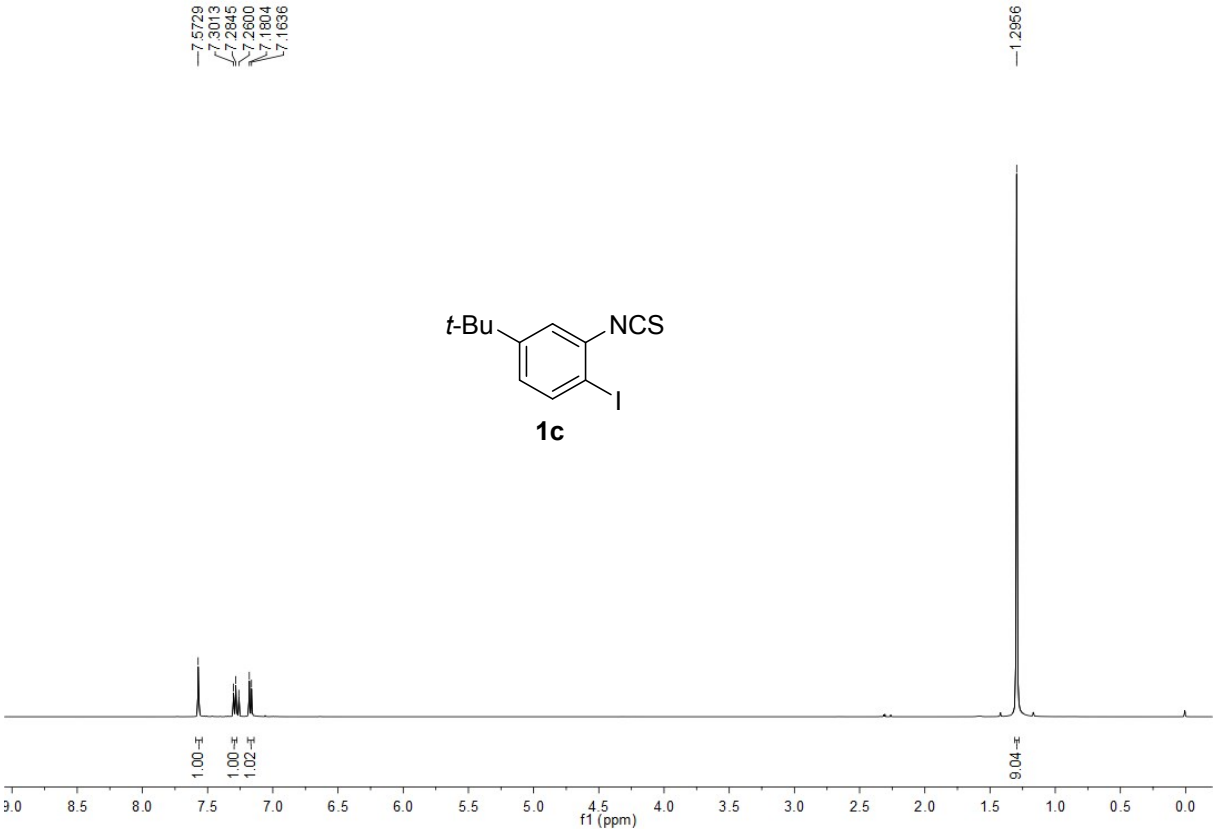
ethyl 5-mercapto-1-phenyl-1*H*-imidazole-4-carboxylate (4)

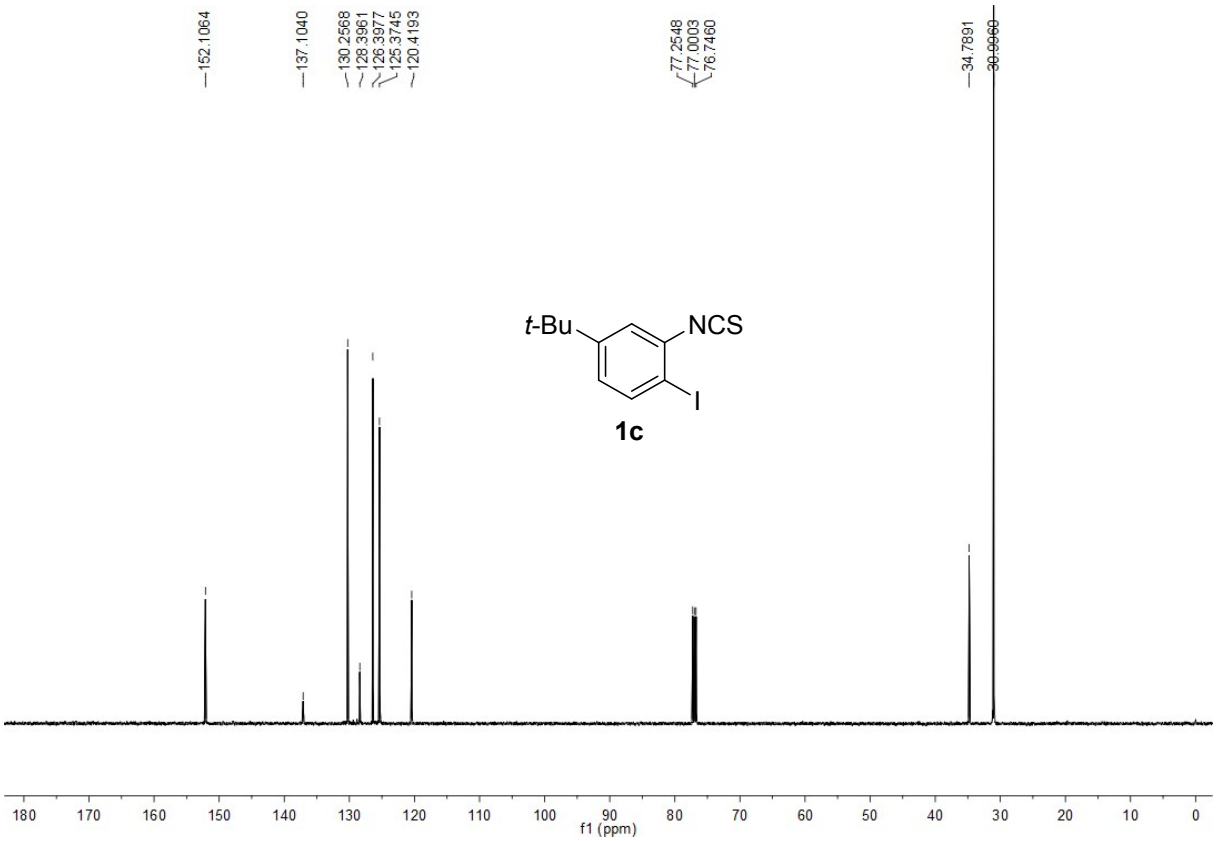
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/1) as a yellow solid in 93% yield (69.6 mg, 0.186 mmol). Mp: 126 – 127 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.85 (s, 1H), 8.00 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 4.47 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 164.8, 153.9, 141.9, 140.1, 135.6, 129.4, 125.3, 124.7, 116.9, 90.6, 61.1, 14.5. **HRMS (ESI):** Calcd for $C12H_{12}IN_2O_2S$ $[M+H]^+$ 374.9659, found: 374.9654.

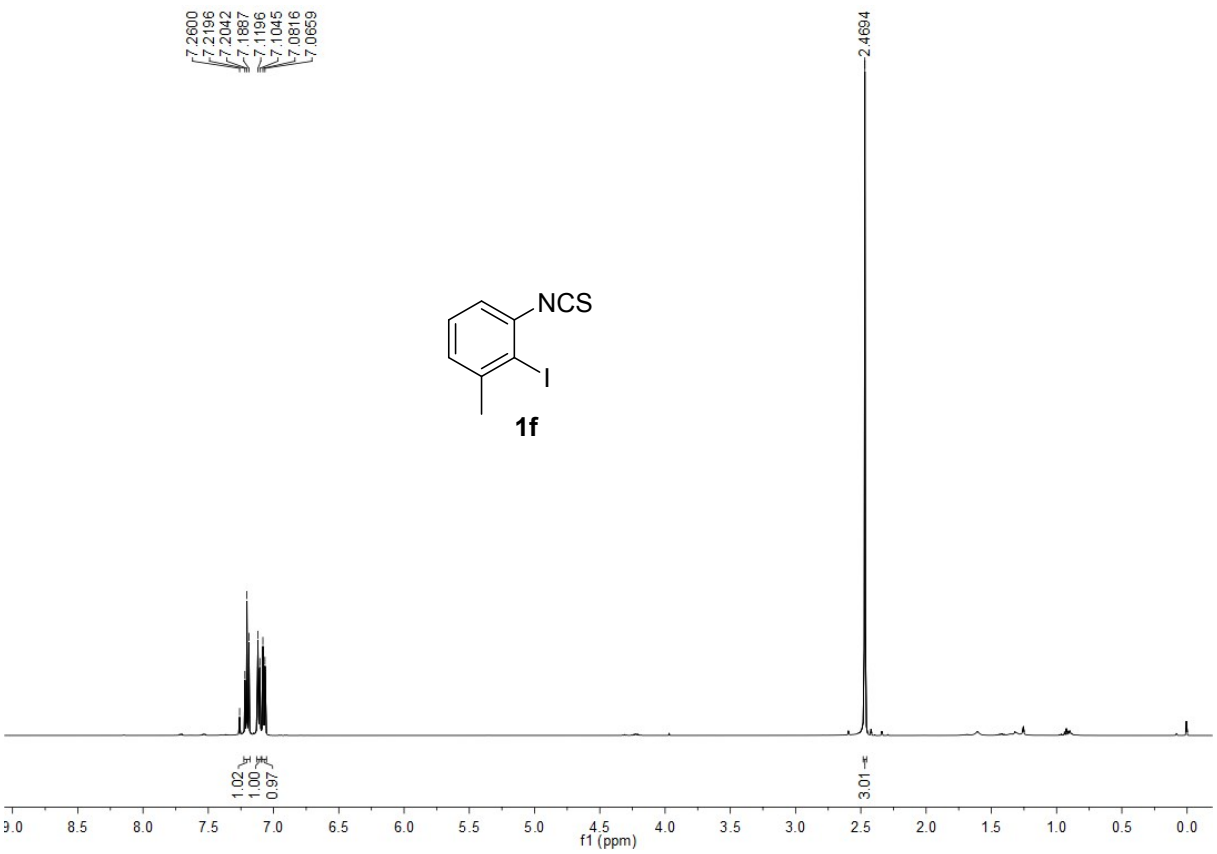
5. References:

(1) Franchino, A.; Jakubec, P.; Dixon, D. J. *Org. Biomol. Chem.* **2016**, *14*, 93–96.
(2) Yan, K.; Yang, D.; Wei, W.; Sun, P.; Lu, Y.; Wang, H. *Org. Chem. Front.* **2016**, *3*, 556–560.
(3) Hao, W.; Sang, X.; Jiang, J.; Cai, M. *Tetrahedron Letters* **2016**, *57*, 1511–1514.

6. Spectral Copies of ^{1}H, ^{13}C of Compounds Obtained in This Study



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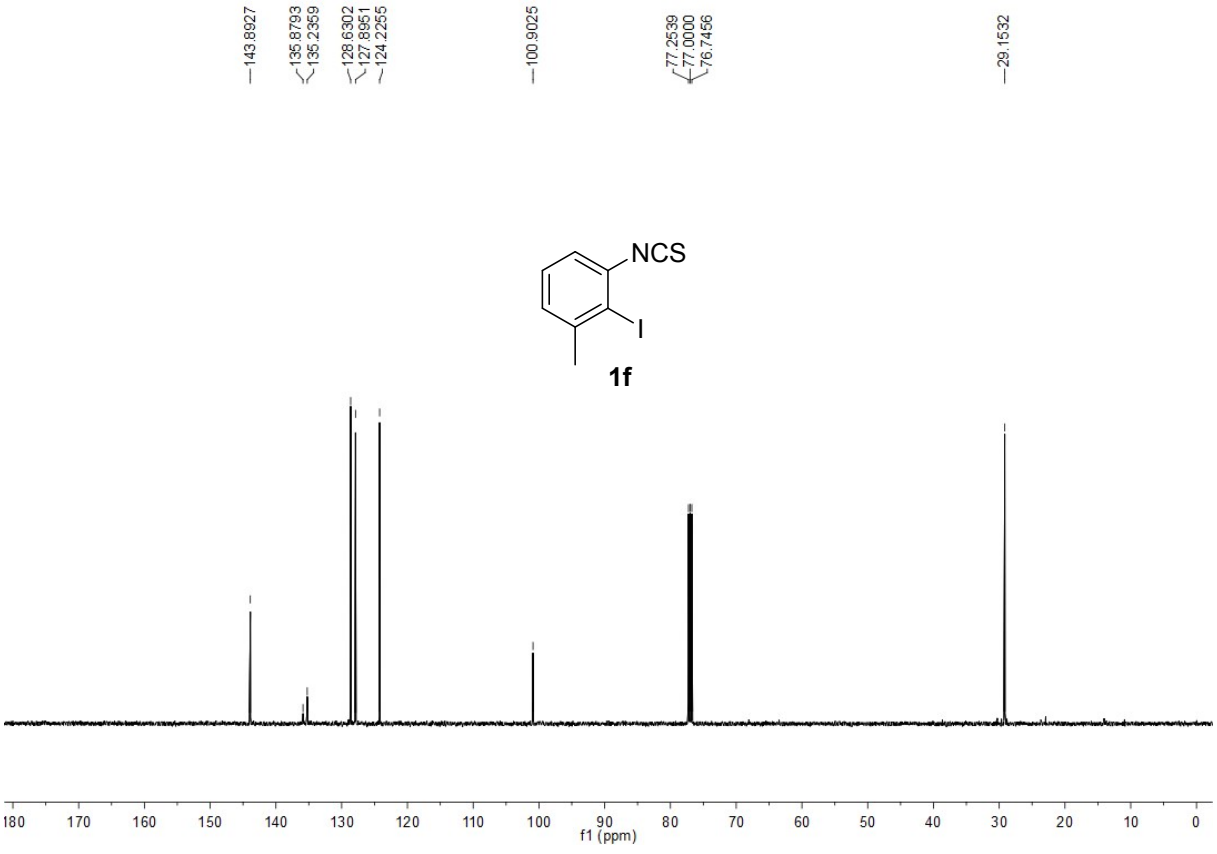
3.01
f1 (ppm)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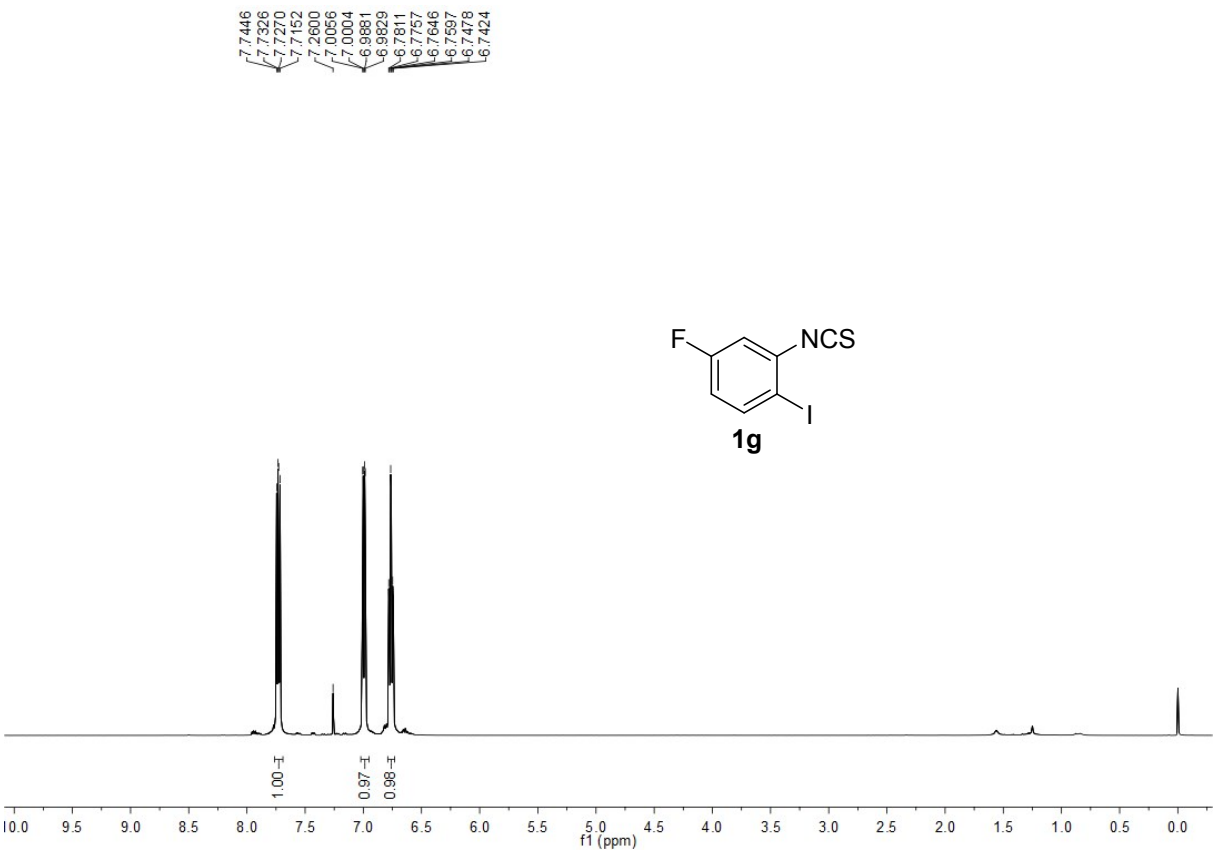
NCS
I
1f
f1 (ppm)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7.7270
7.7152
7.2600
7.0056
7.0004
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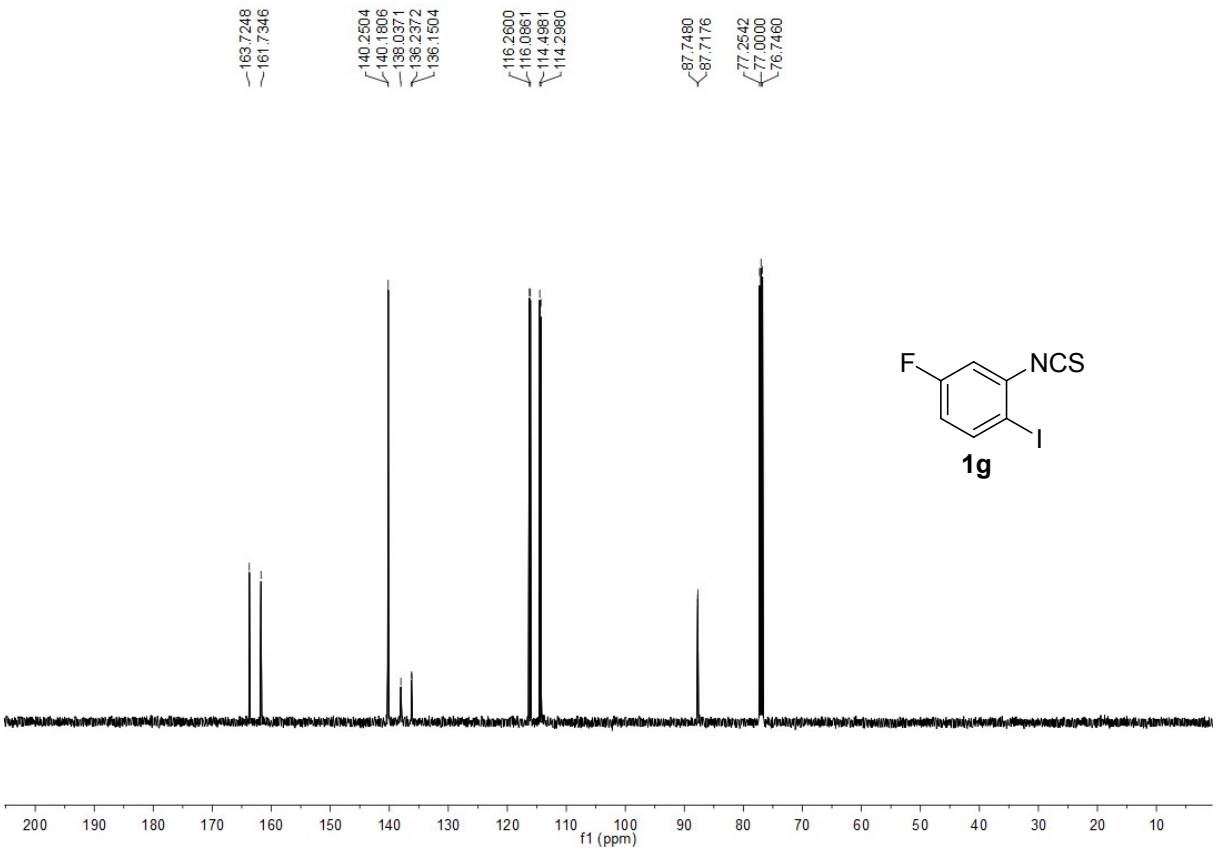
6.9829
6.7811
6.7757
6.7646
6.7597
6.7478
6.7424
F
NCS
I
1g
1.00
0.97
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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136.1504
116.2600
116.0861
114.4981
114.2980
87.7480
87.7176
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76.7460
F
NCS
I
1g
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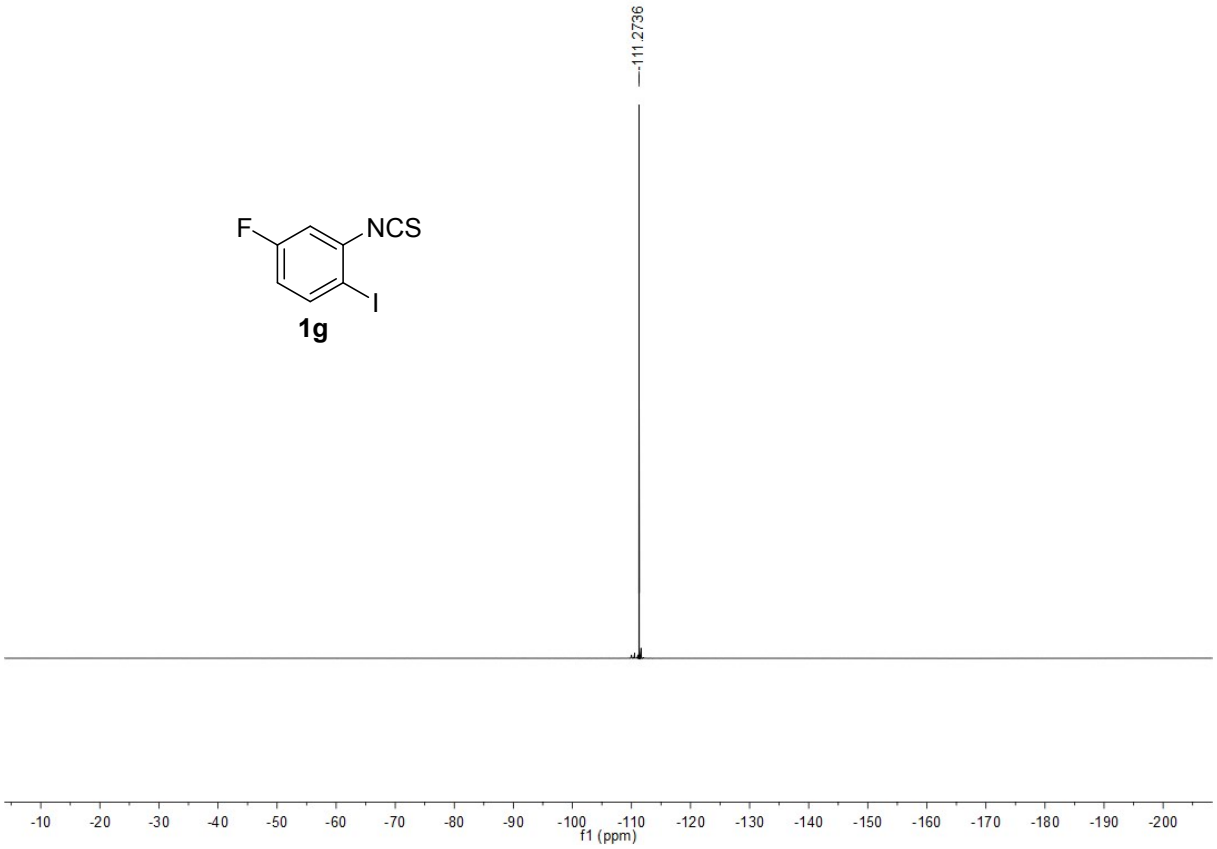
f1 (ppm)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NCS
I
1g
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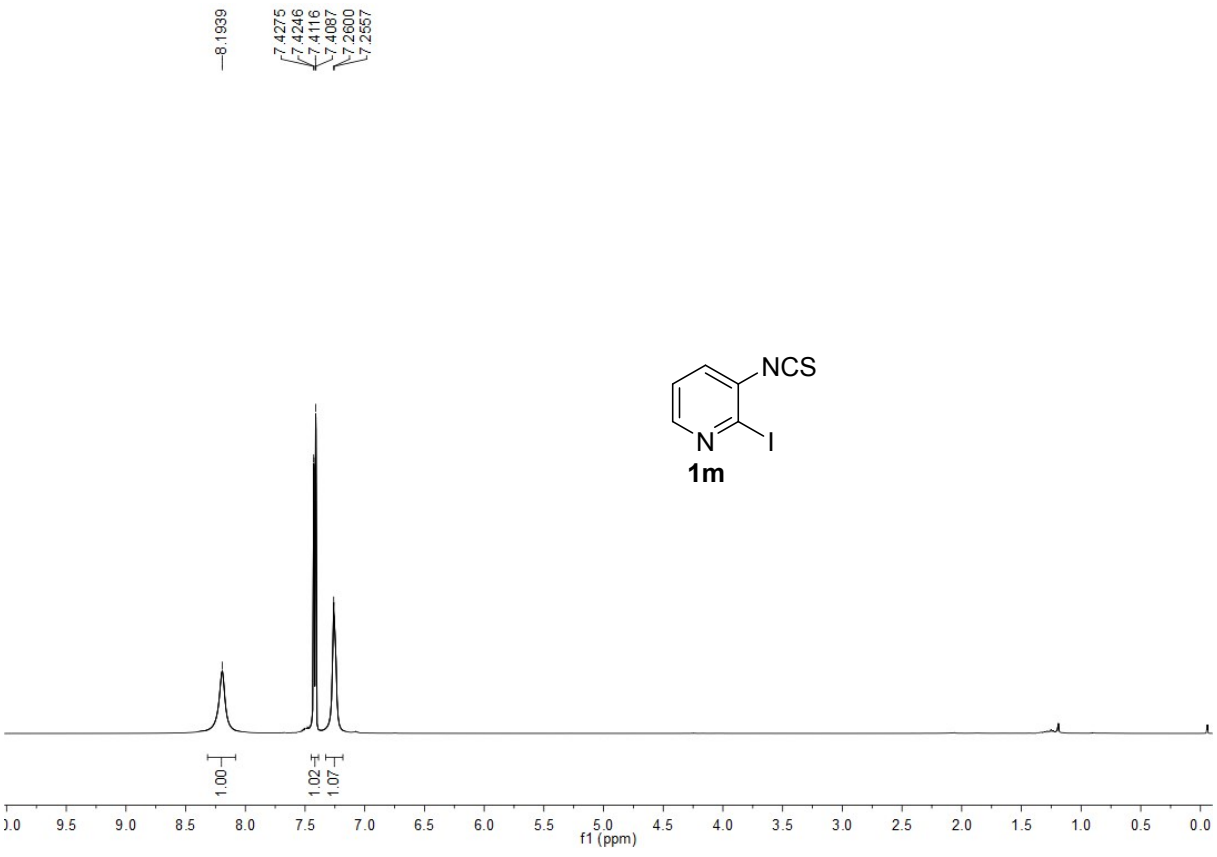
f1 (ppm)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I
1m
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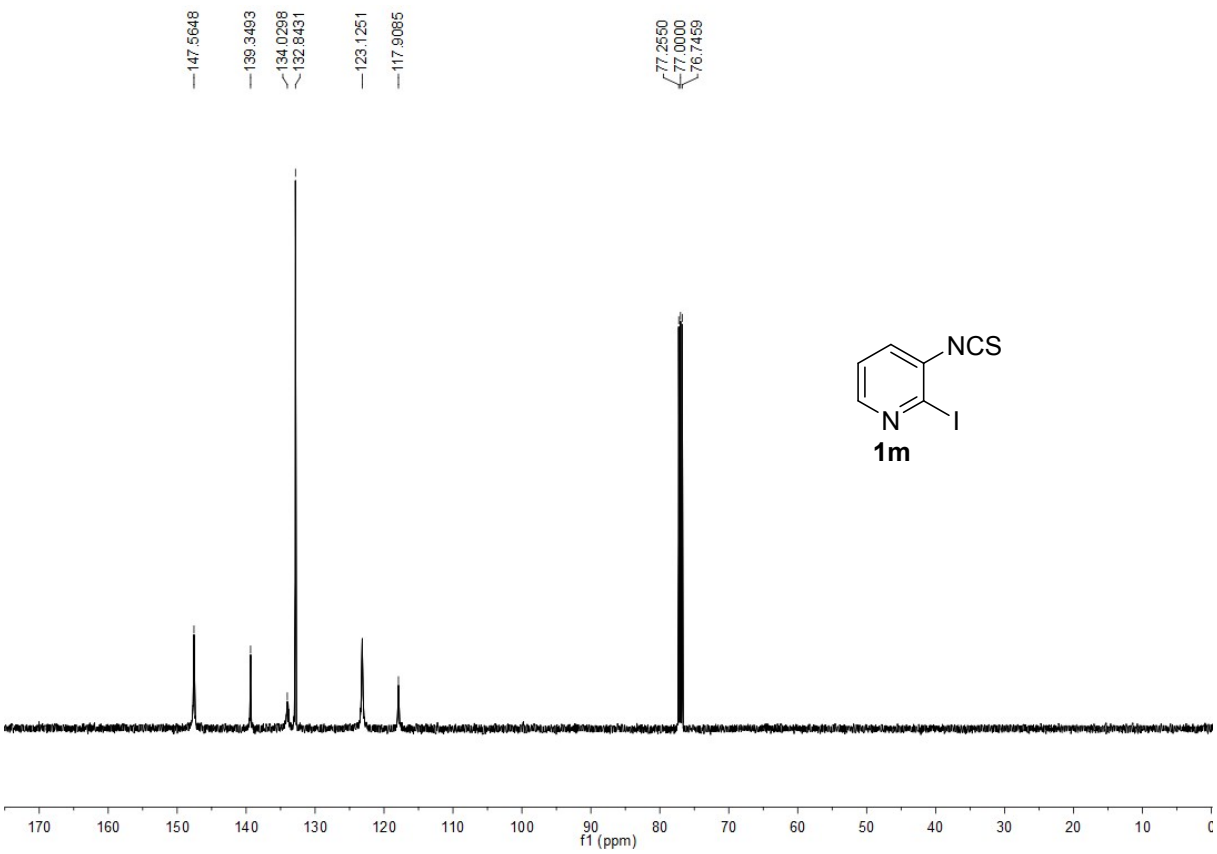
1.07
f1 (ppm)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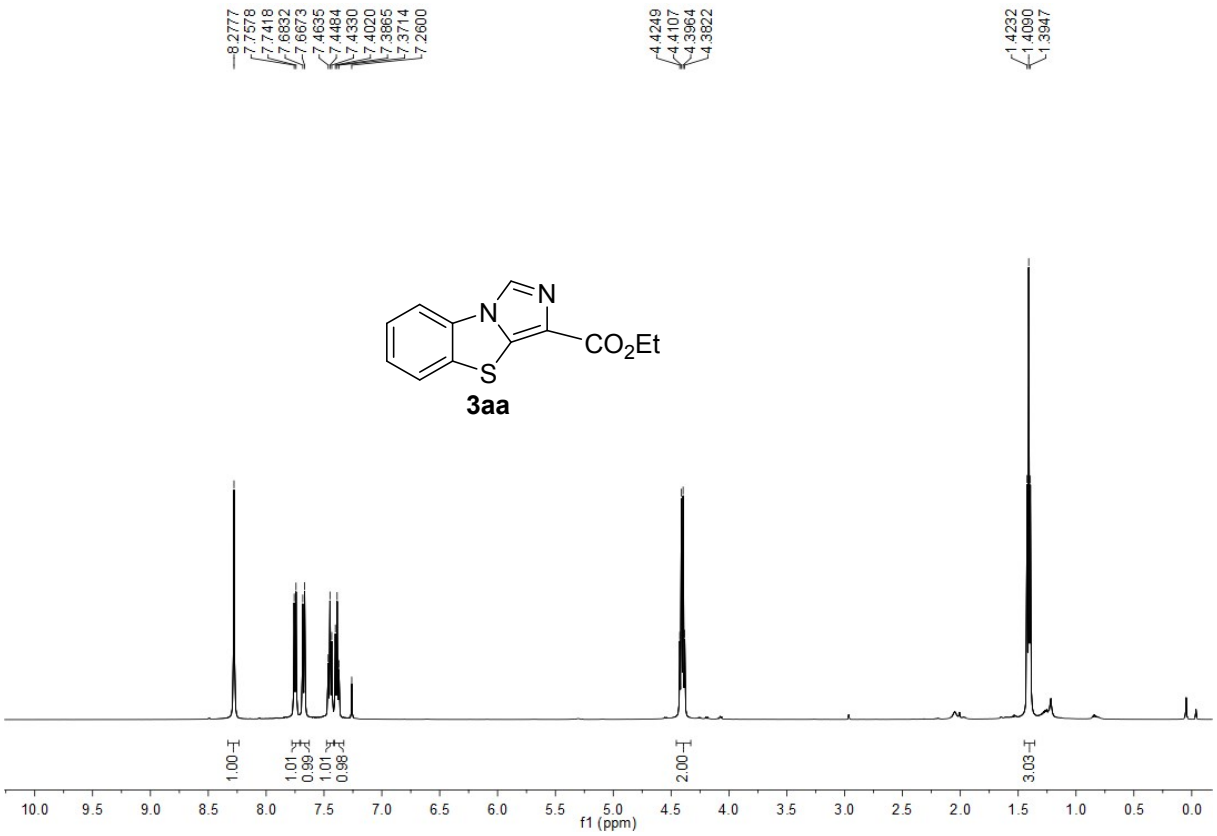
I
1m
f1 (ppm)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7.6673
7.4635
7.4484
7.4330
7.4020
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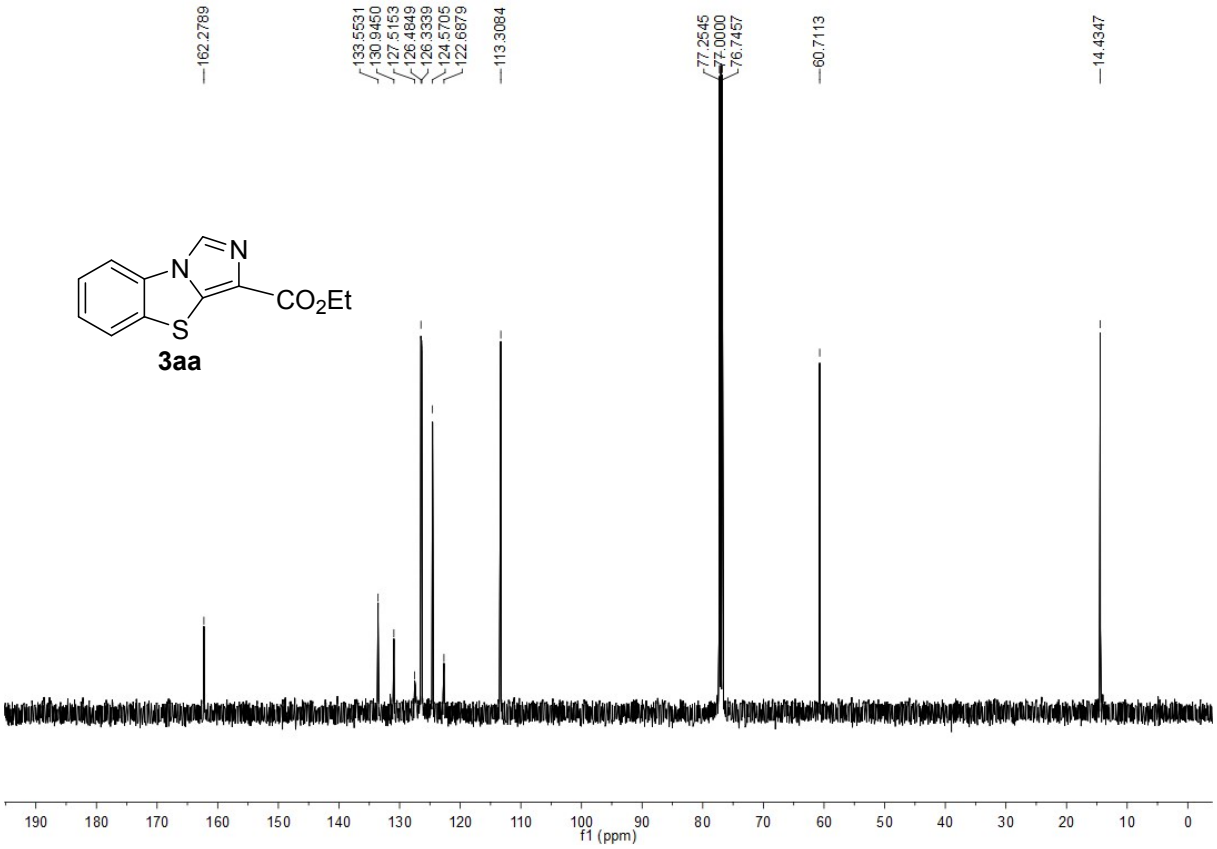
7.3714
7.2600
4.4249
4.4107
4.3964
4.3822
1.4232
1.4090
1.3947
N
N
S
CO2Et
3aa
1.00
1.01
0.99
1.01
0.98
2.00
3.03
f1 (ppm)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77.0000
76.7457
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N
N
S
CO2Et
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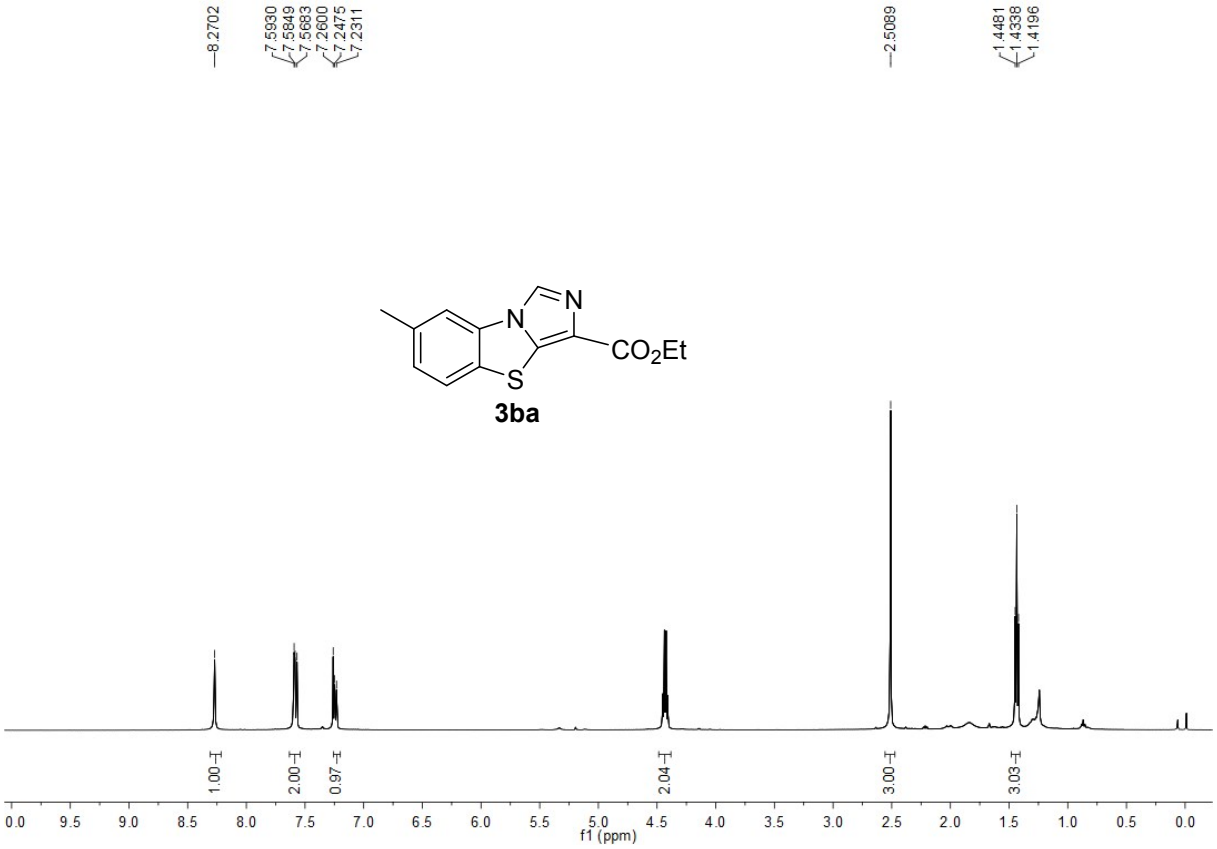
f1 (ppm)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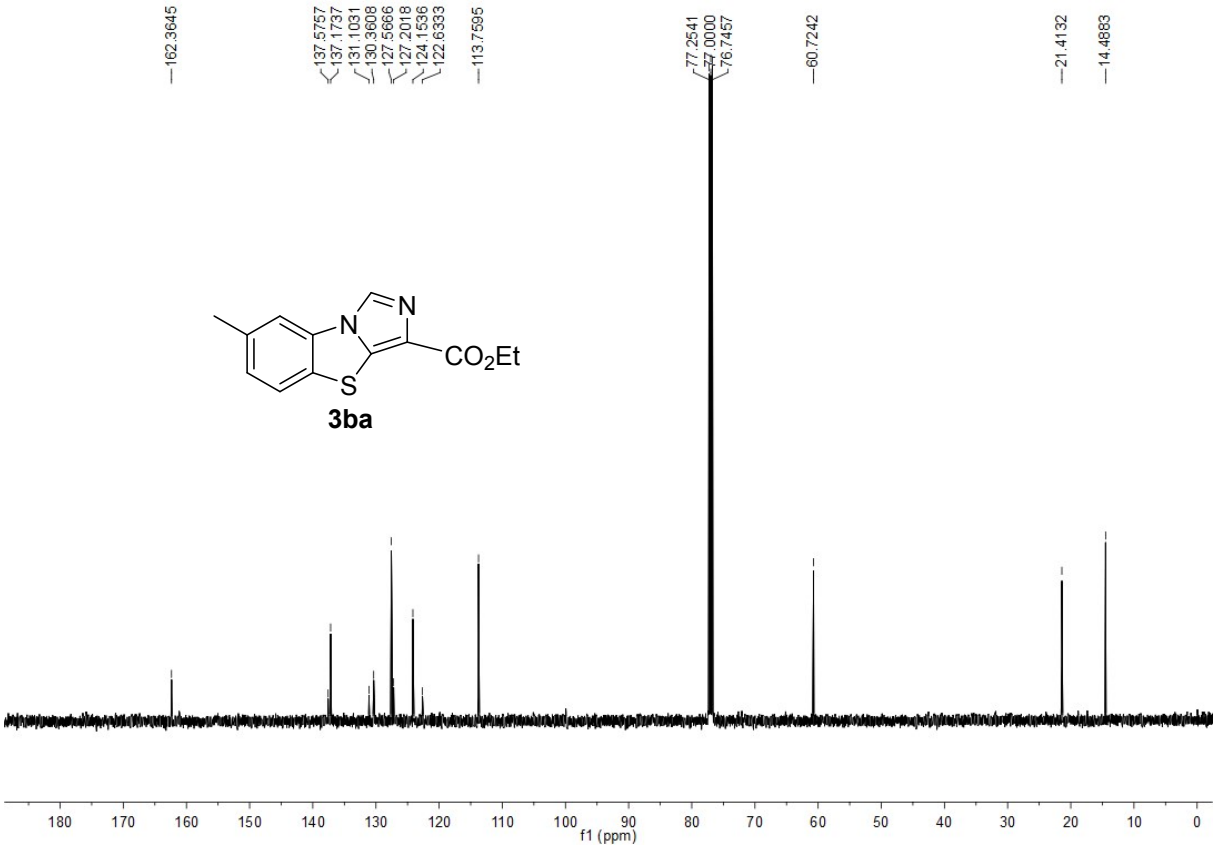
1.4338
1.4196
N
N
S
CO2Et
3ba
1.00
2.00
0.97
2.04
3.00
3.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.3608
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127.2018
124.1536
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77.0000
76.7457
60.7242
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N
S
CO2Et
3ba
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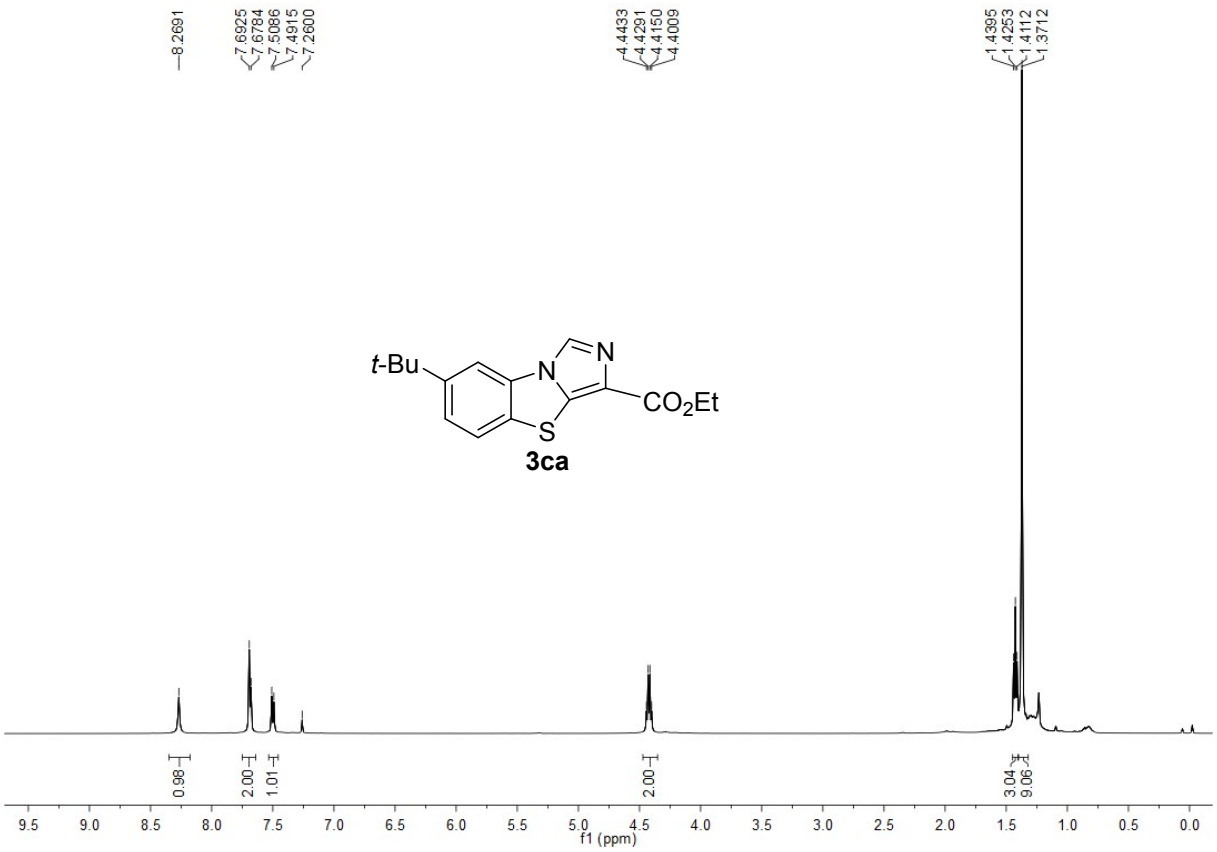
f1 (ppm)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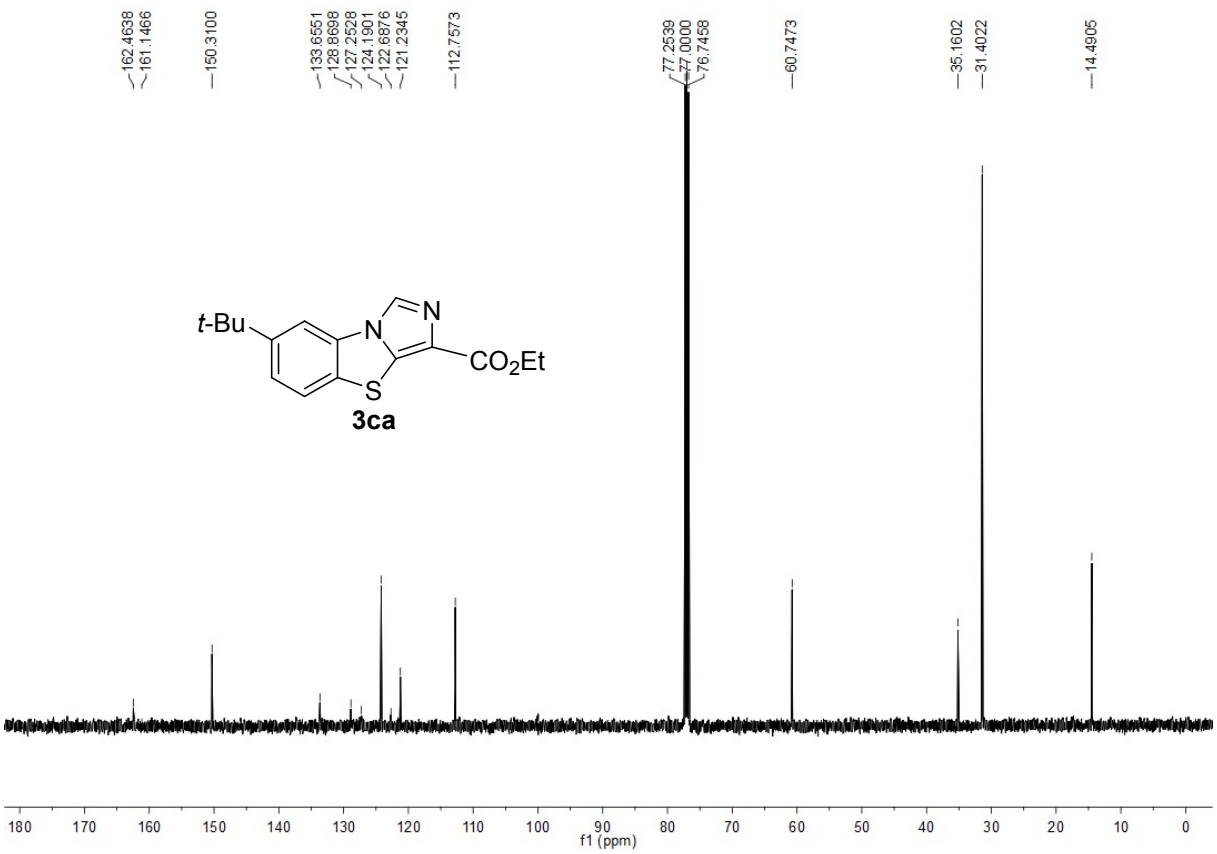
7.5086
7.4915
7.2600
4.4433
4.4291
4.4150
4.4009
1.4395
1.4253
1.4112
1.3712
t-Bu
N
N
S
CO2Et
3ca
0.98
2.00
1.01
2.00
3.04
9.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
76.7458
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35.1602
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t-Bu
N
N
S
CO2Et
3ca
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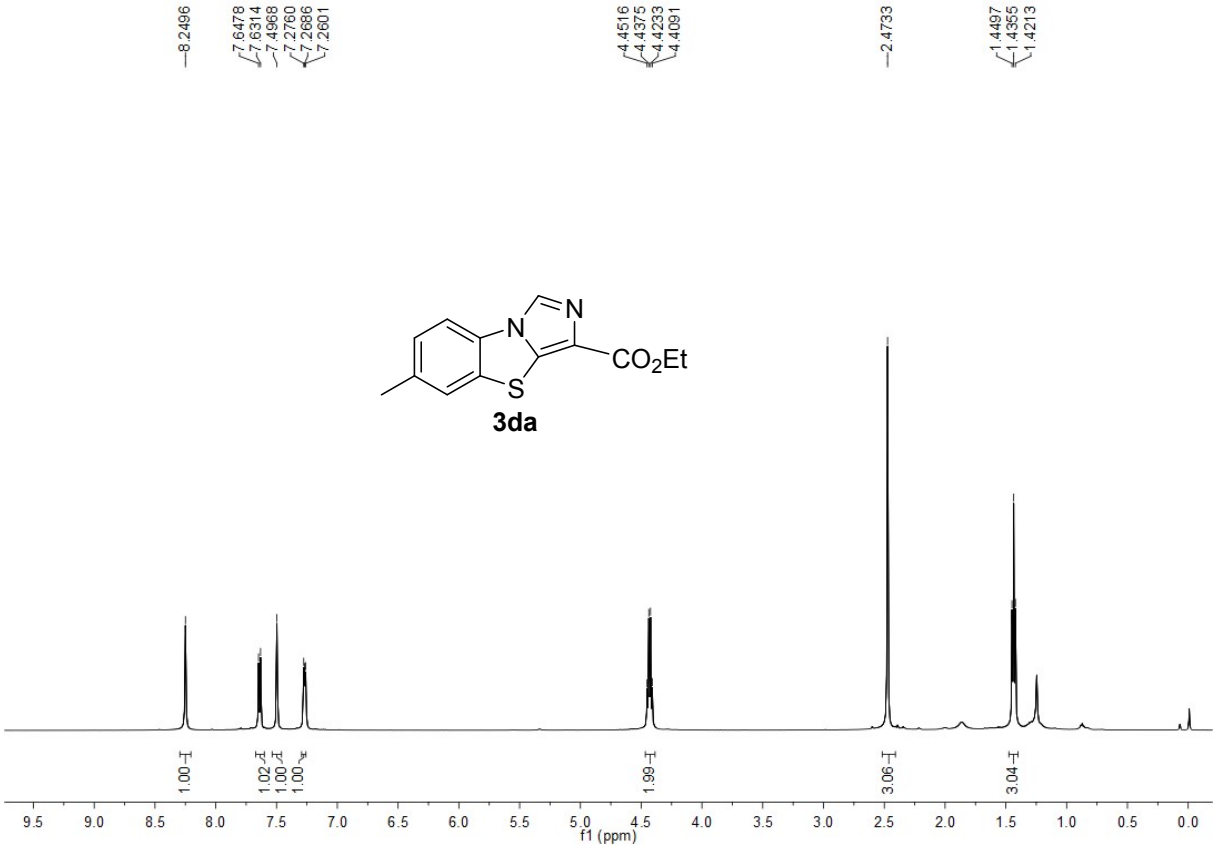
f1 (ppm)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2.4733
1.4497
1.4355
1.4213
N
N
S
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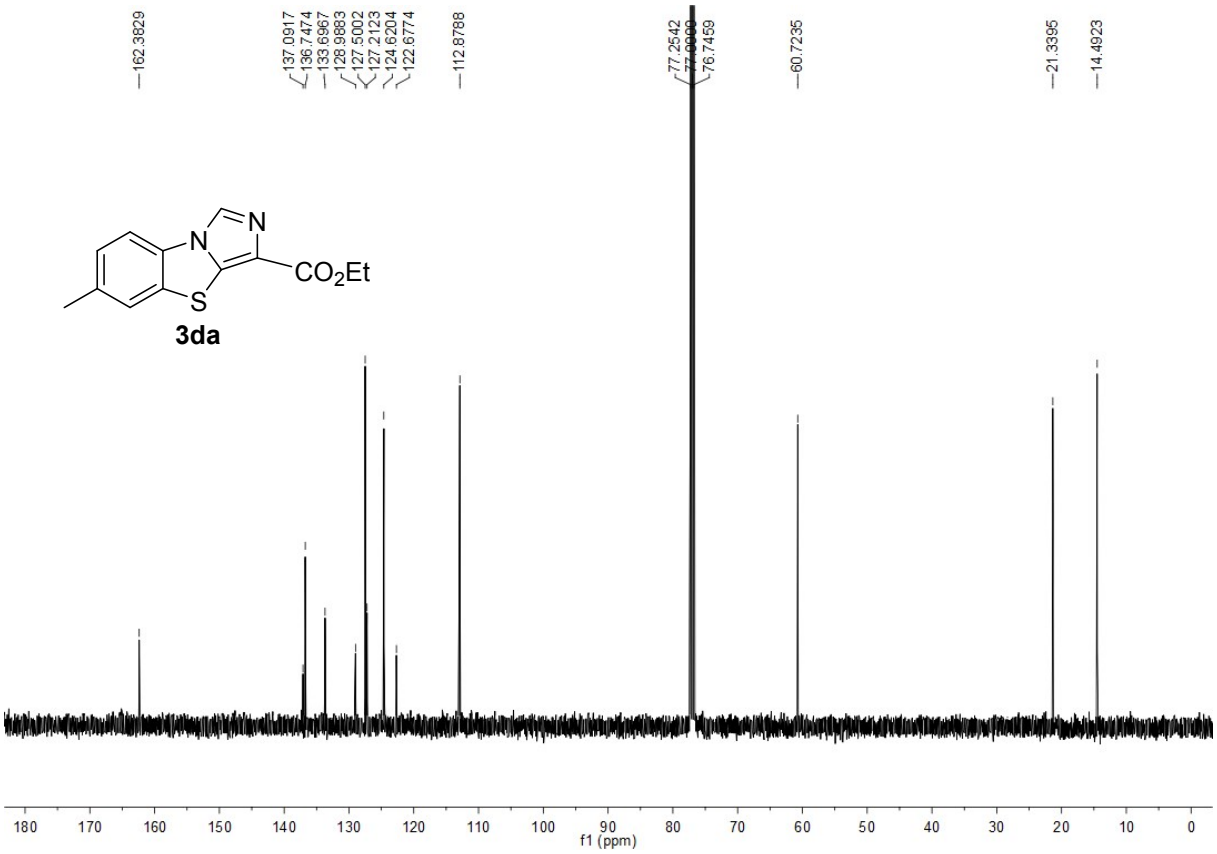
1.00
1.02
1.00
1.00
1.99
3.06
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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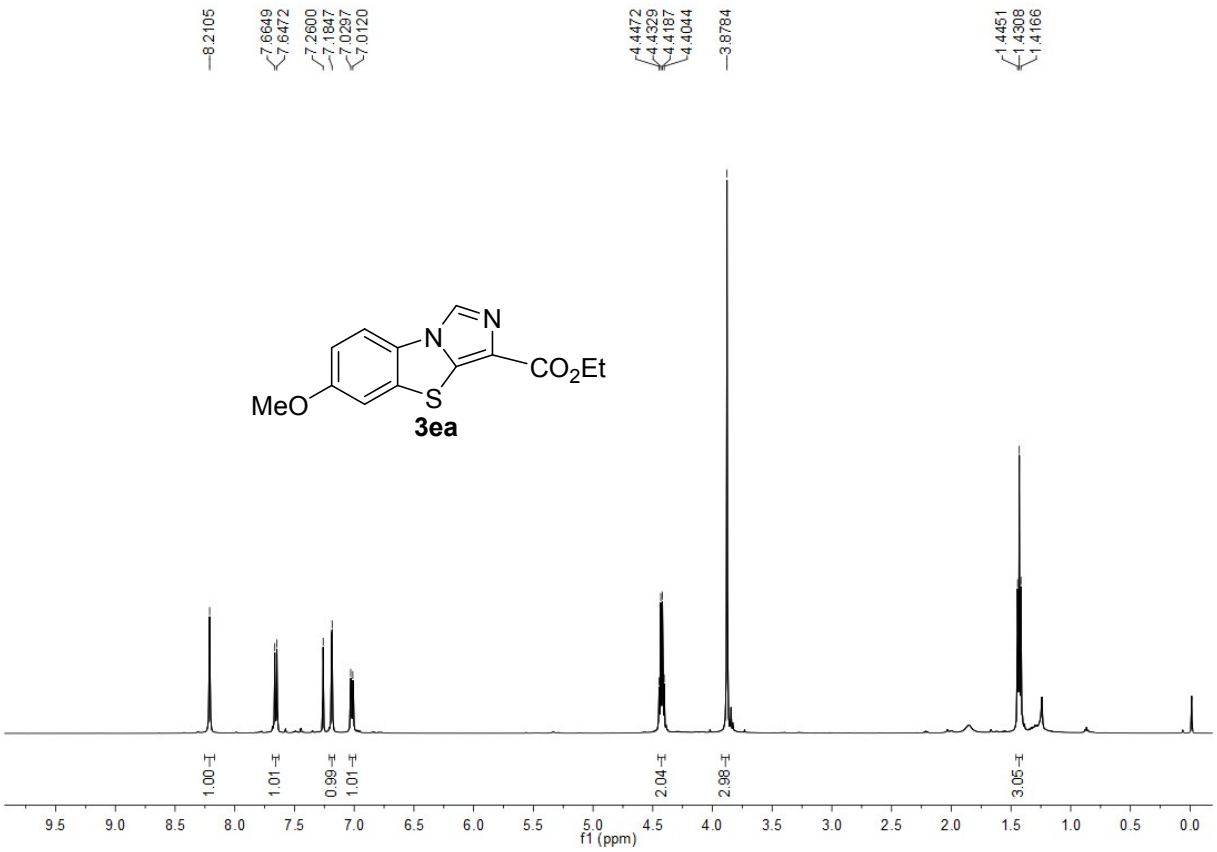
77.2542
77.0000
76.7459
60.7235
21.3395
14.4923
N
N
CO2Et
S
3da
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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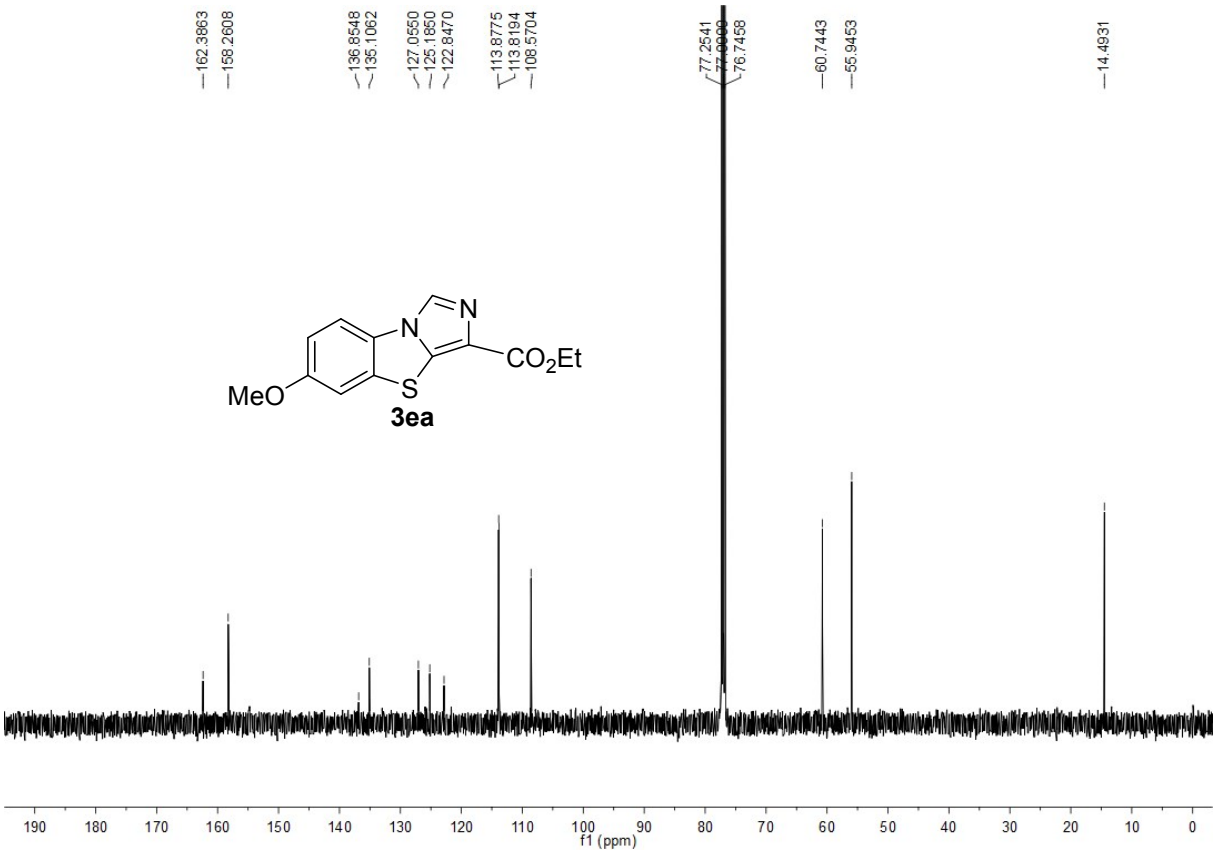
4.4044
3.8784
1.4451
1.4308
1.4166
N
N
CO2Et
MeO
S
3ea
1.00
1.01
0.99
1.01
2.04
2.98
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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N
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MeO
3ea
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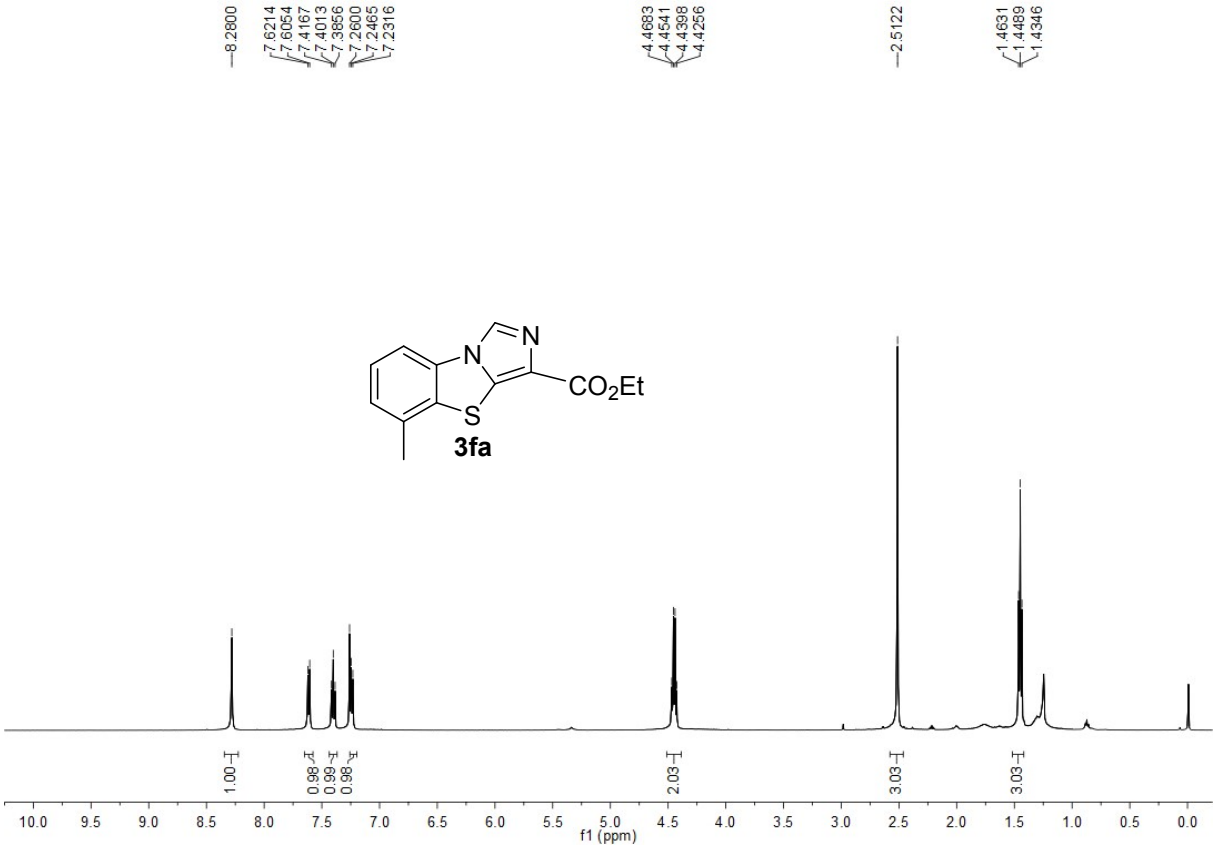
f1 (ppm)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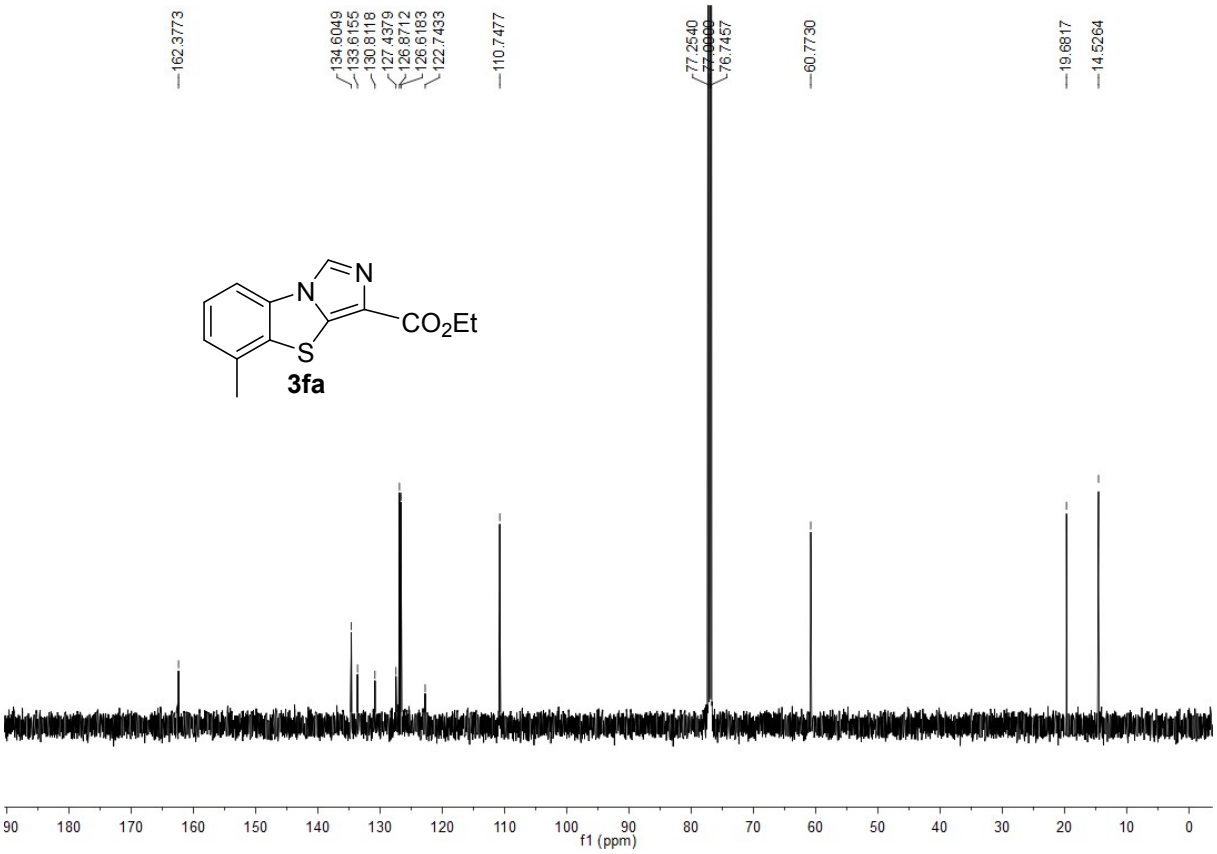
4.4398
4.4256
2.5122
1.4631
1.4489
1.4346
N
N
CO2Et
S
3fa
1.00
0.98
0.99
0.98
2.03
3.03
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
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60.7730
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N
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S
3fa
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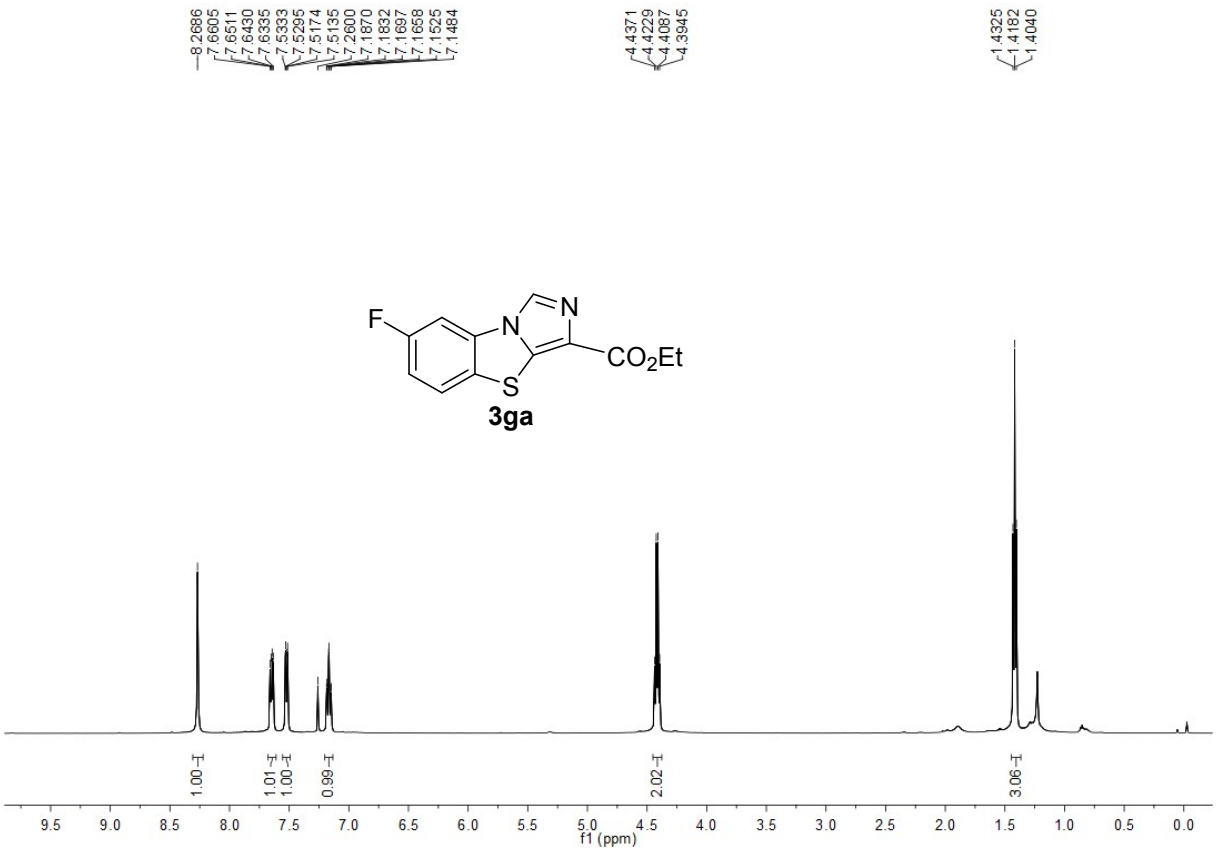
f1 (ppm)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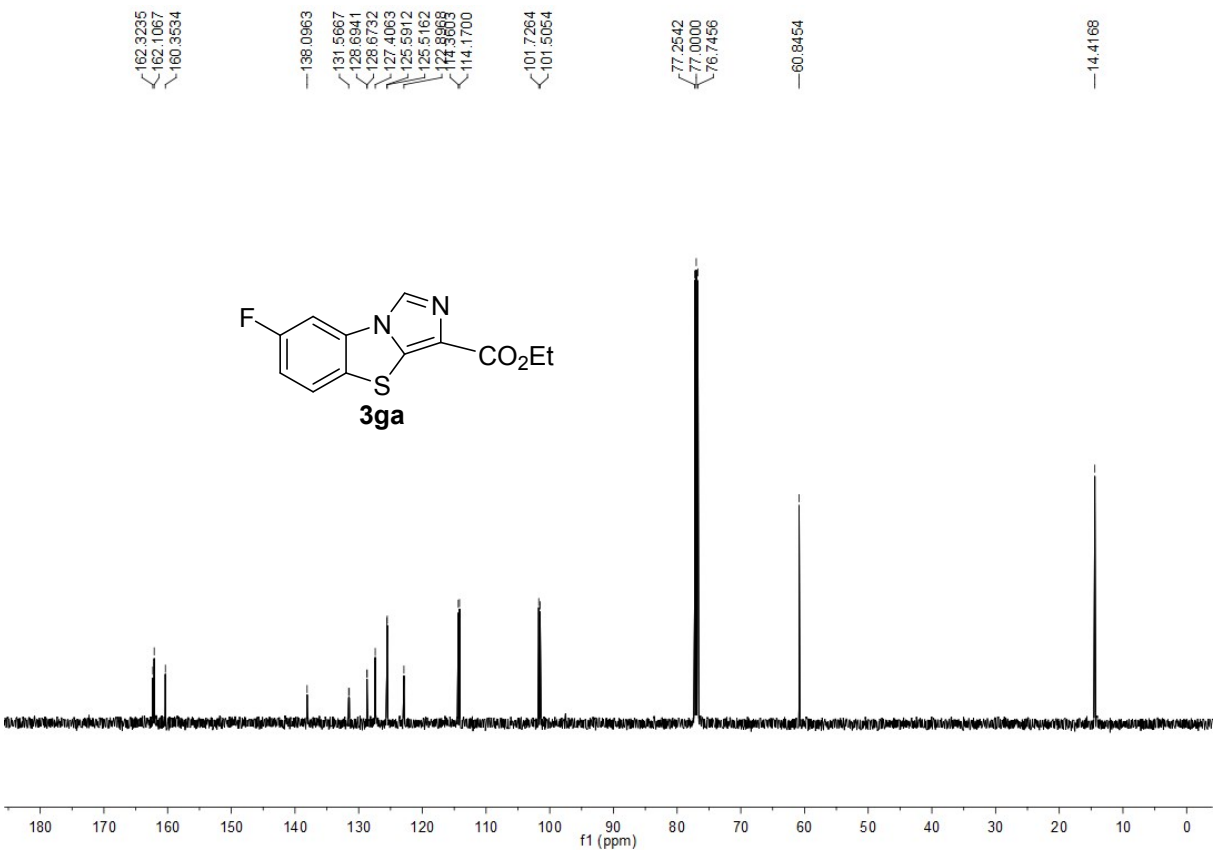
7.1832
7.1697
7.1658
7.1525
7.1484
4.4371
4.4229
4.4087
4.3945
1.4325
1.4182
1.4040
F
N
N
CO2Et
S
3ga
1.00
1.01
1.00
0.99
2.02
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0000
76.7456
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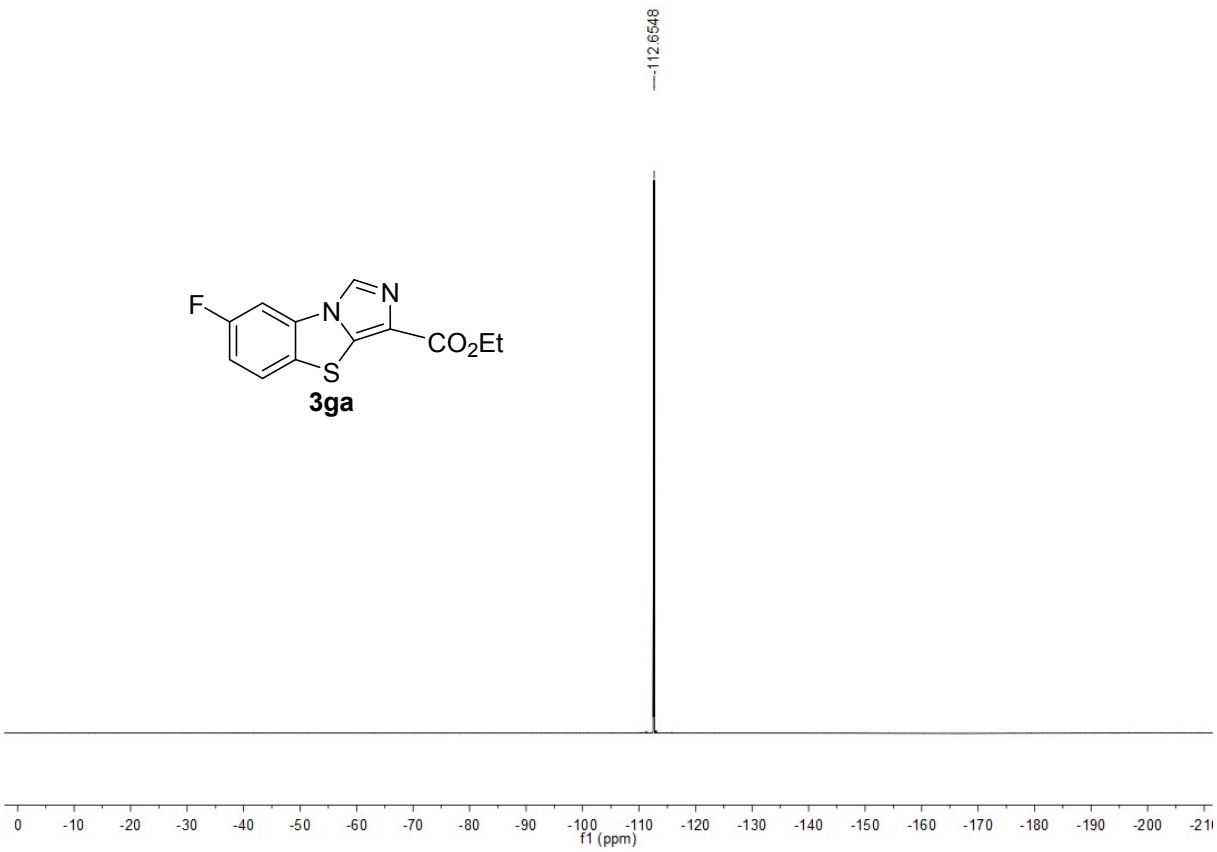
14.4168
F
N
N
S
CO2Et
3ga
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-60
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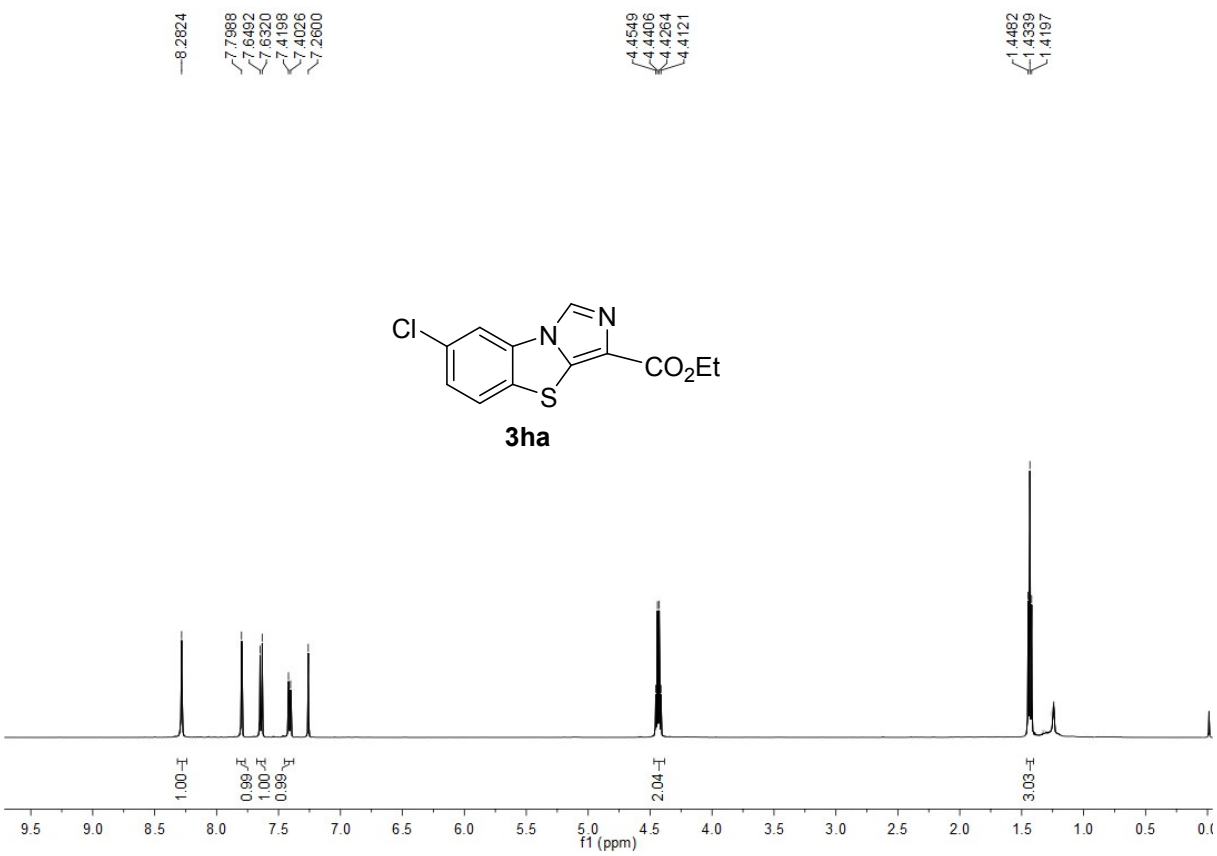
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)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1.4482
1.4339
1.4197
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S
CO2Et
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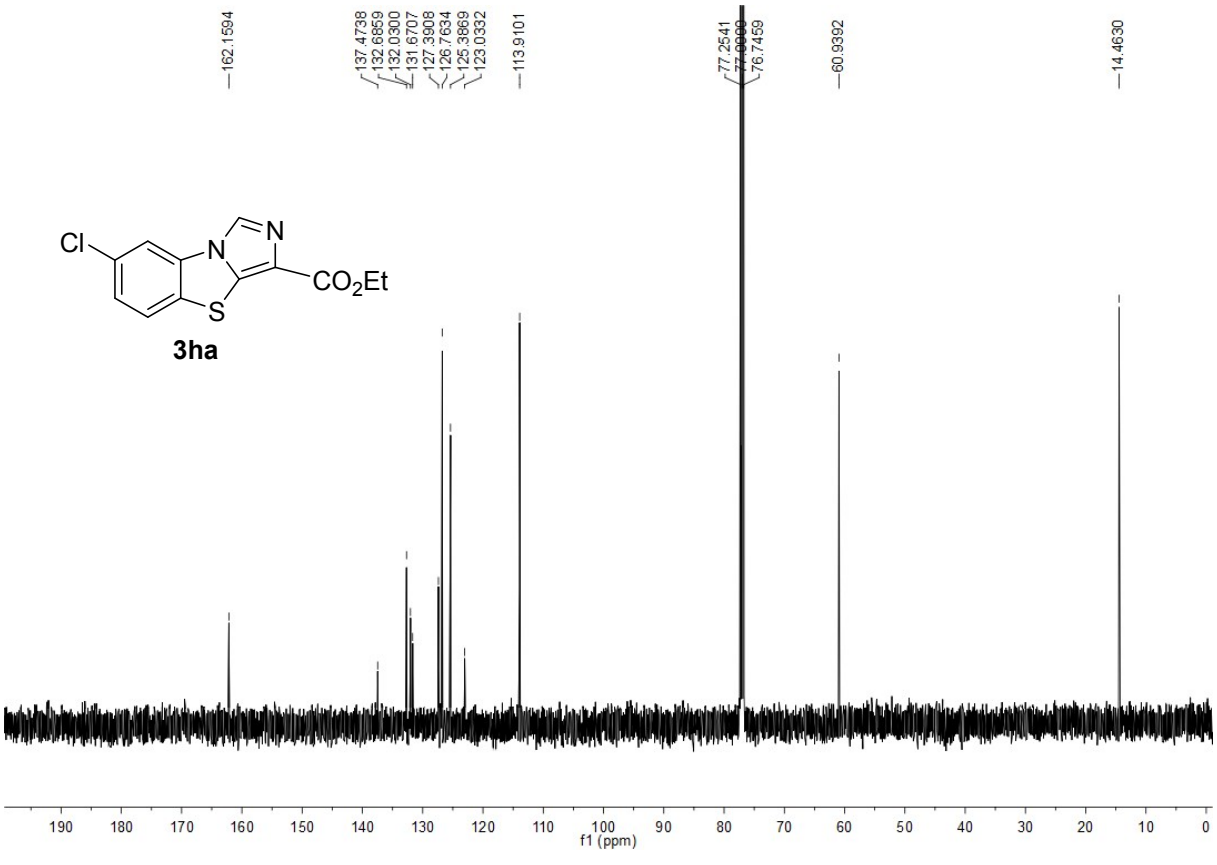
1.00
0.99
1.00
0.99
2.04
3.03
f1 (ppm)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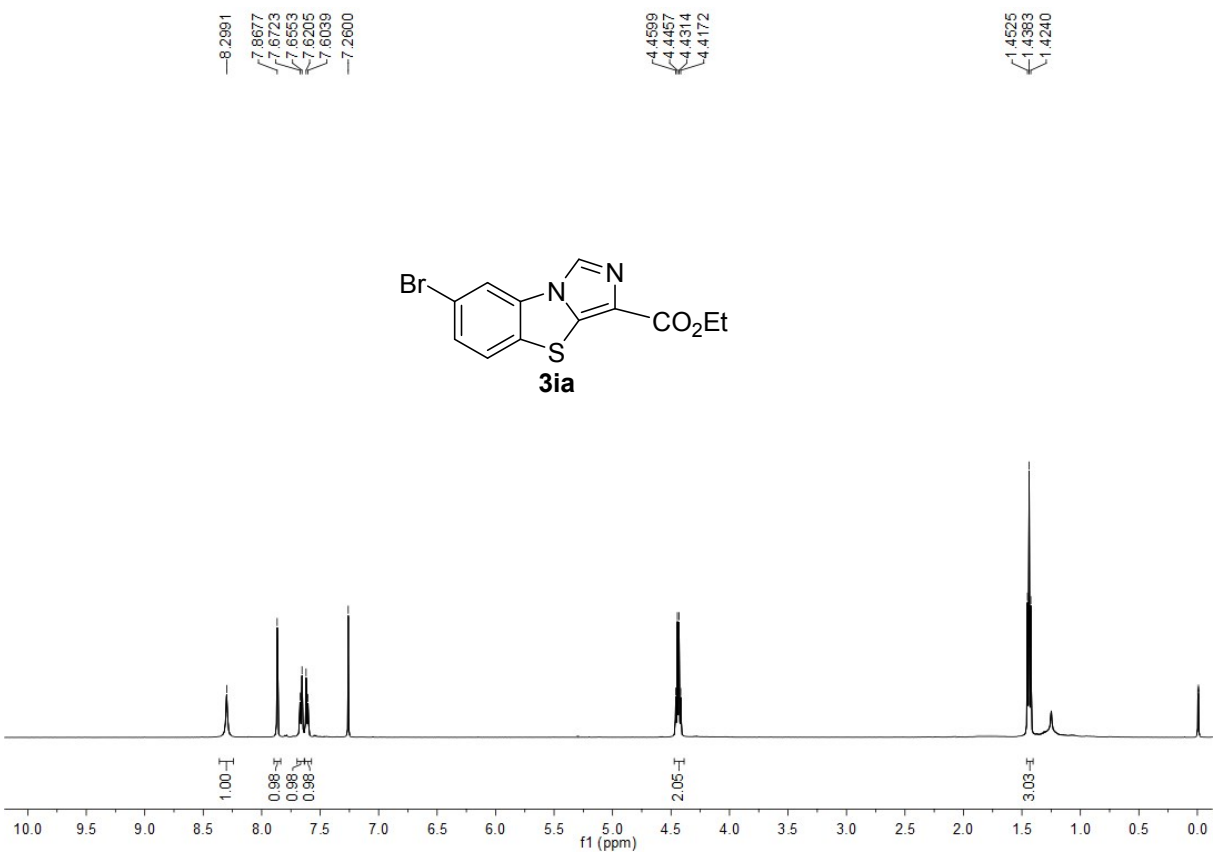
N
N
S
CO2Et
3ha
f1 (ppm)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1.4383
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S
CO2Et
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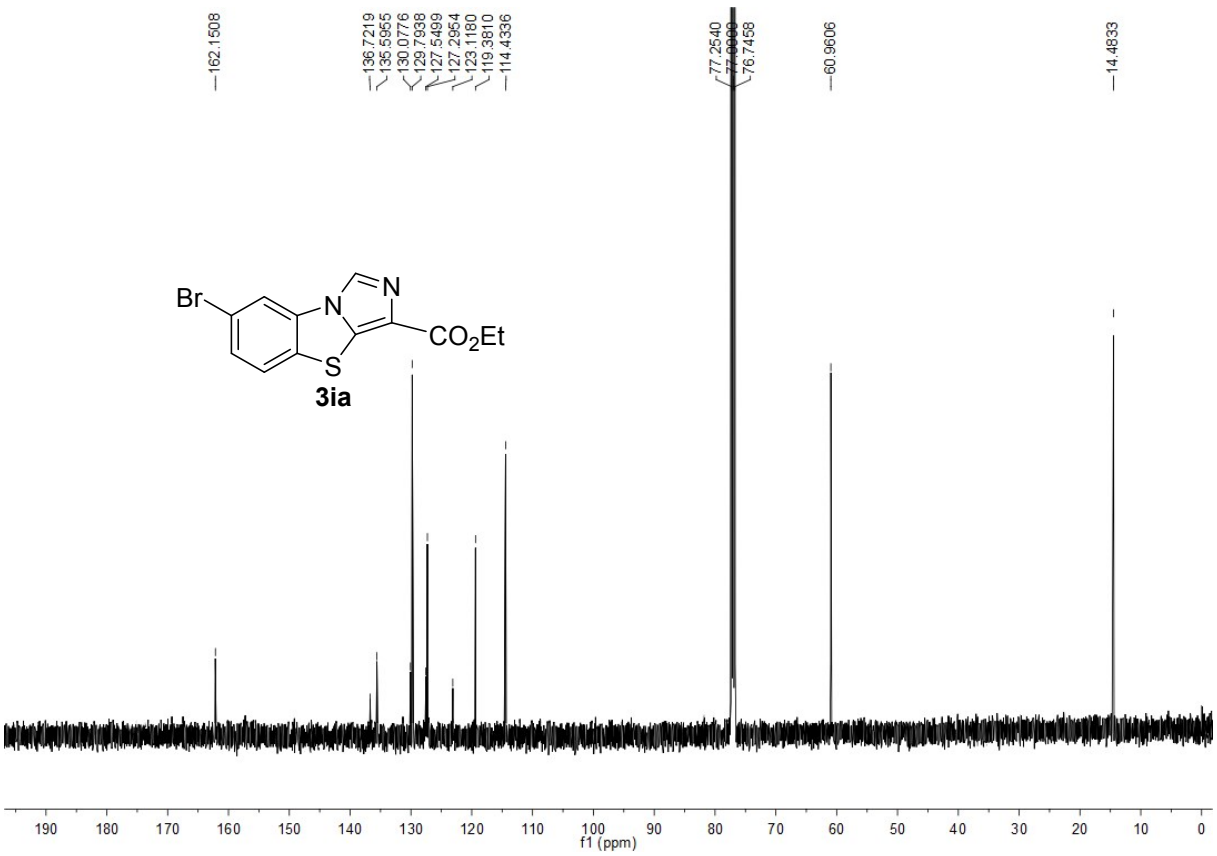
0.98
2.05
3.03
f1 (ppm)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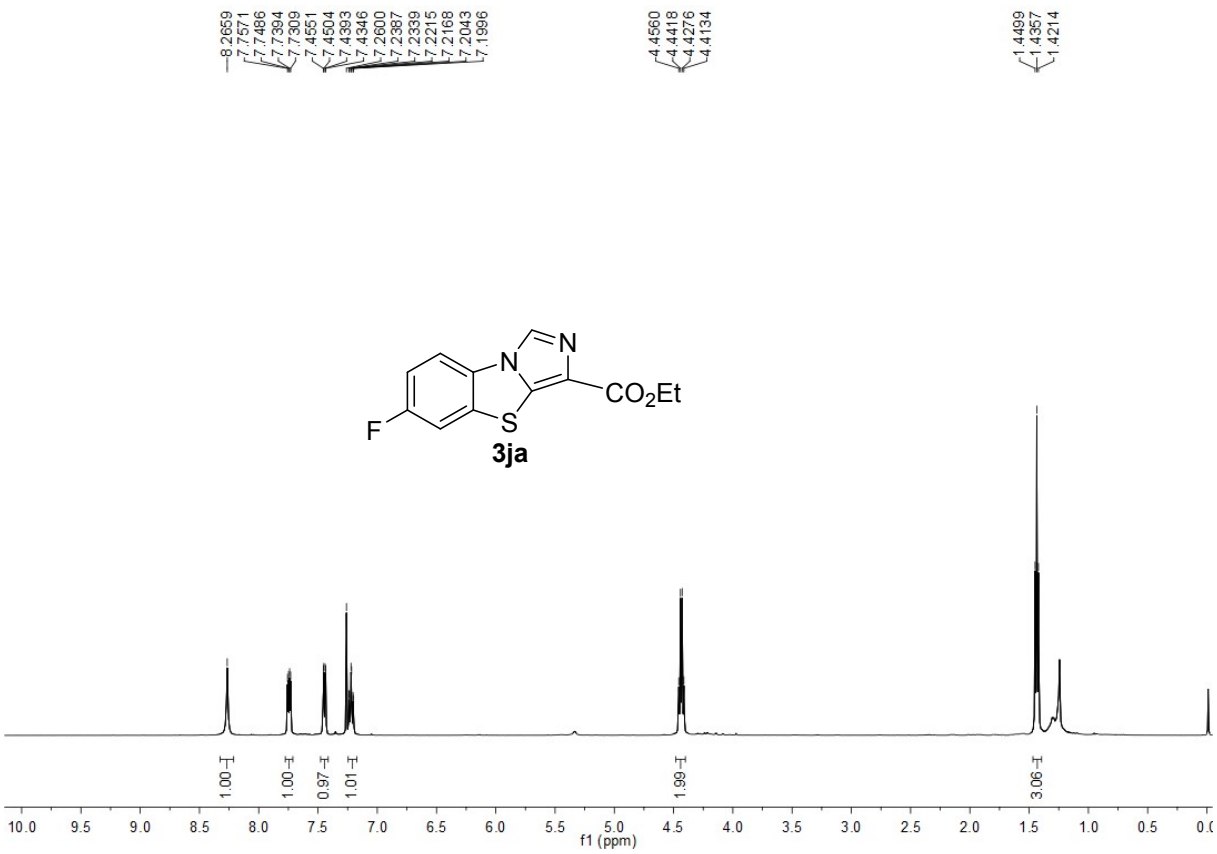
N
N
S
CO2Et
3ia
f1 (ppm)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7.2339
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7.2168
7.2043
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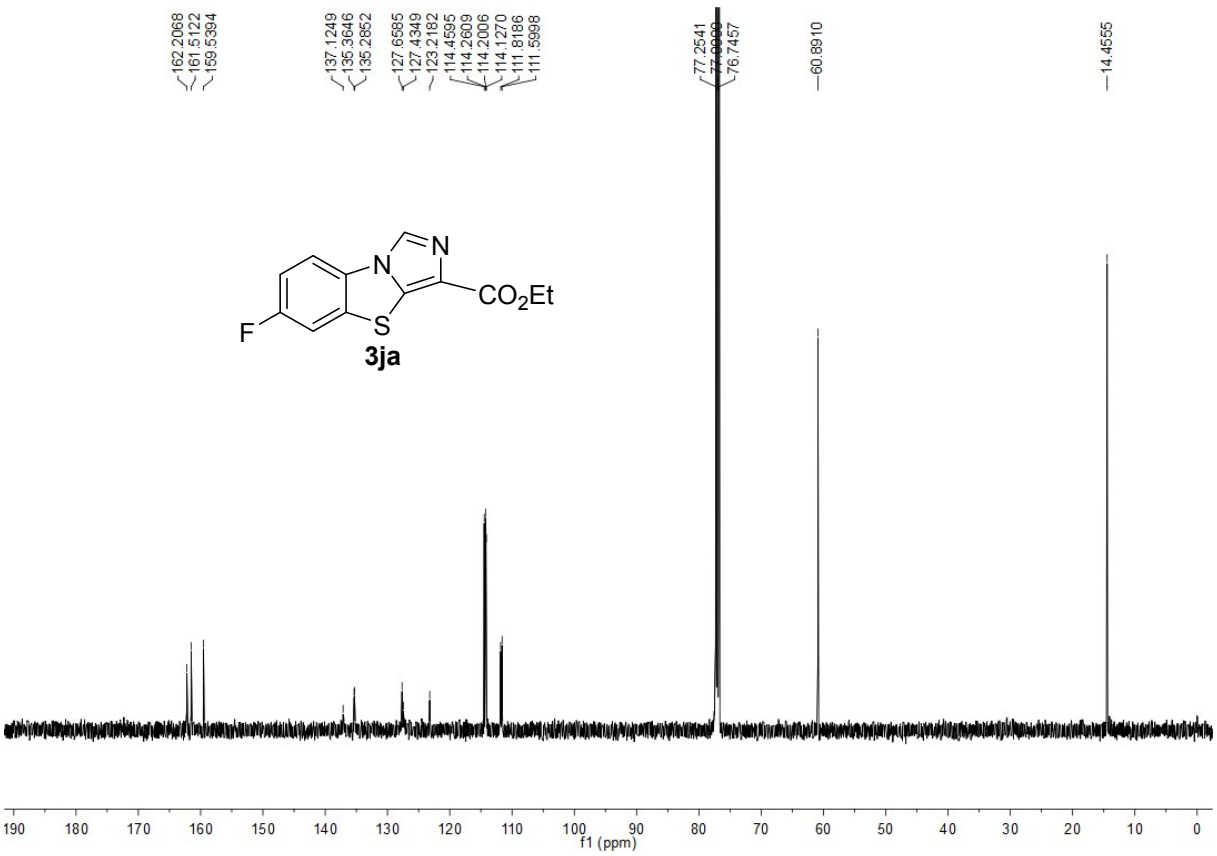
4.4418
4.4276
4.4134
1.4499
1.4357
1.4214
N
N
CO2Et
F
S
3ja
1.00
1.00
0.97
1.01
1.99
3.06
f1 (ppm)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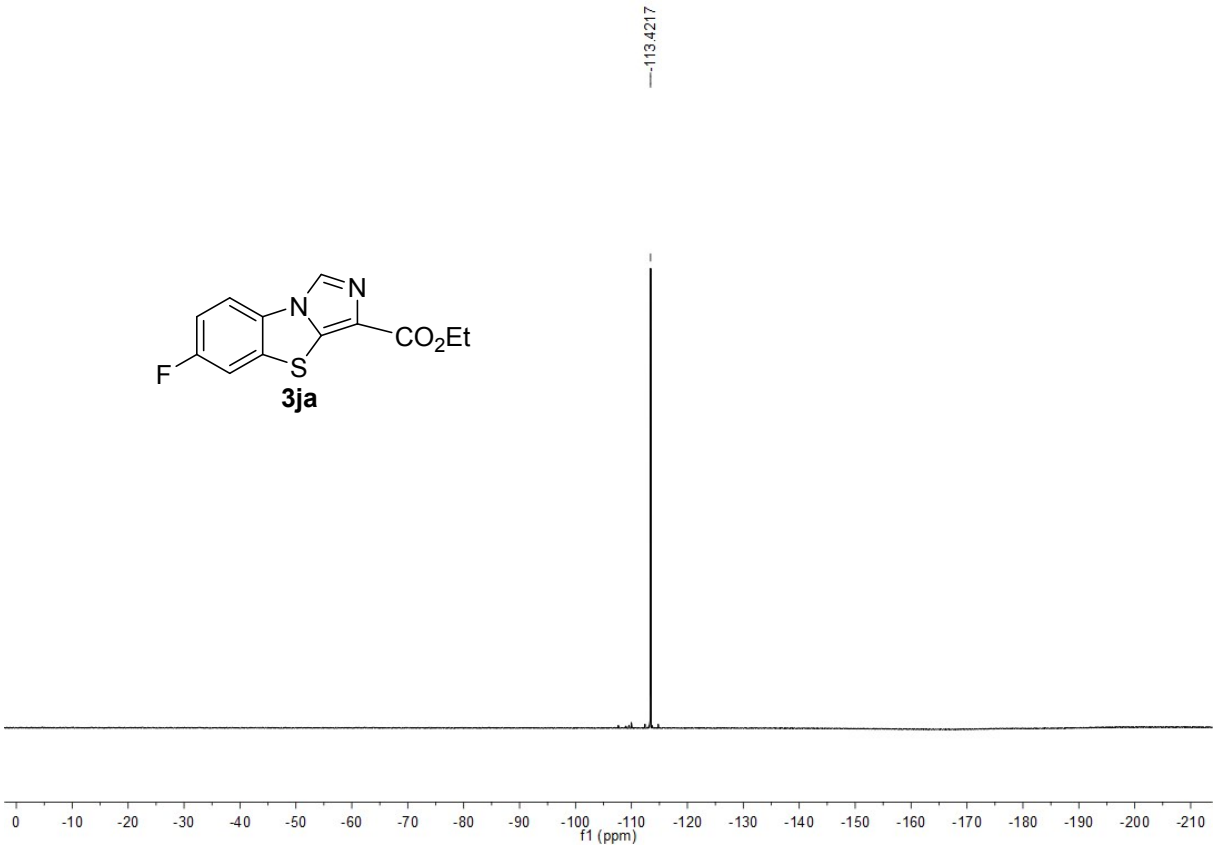
N
CO2Et
F
S
3ja
f1 (ppm)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N
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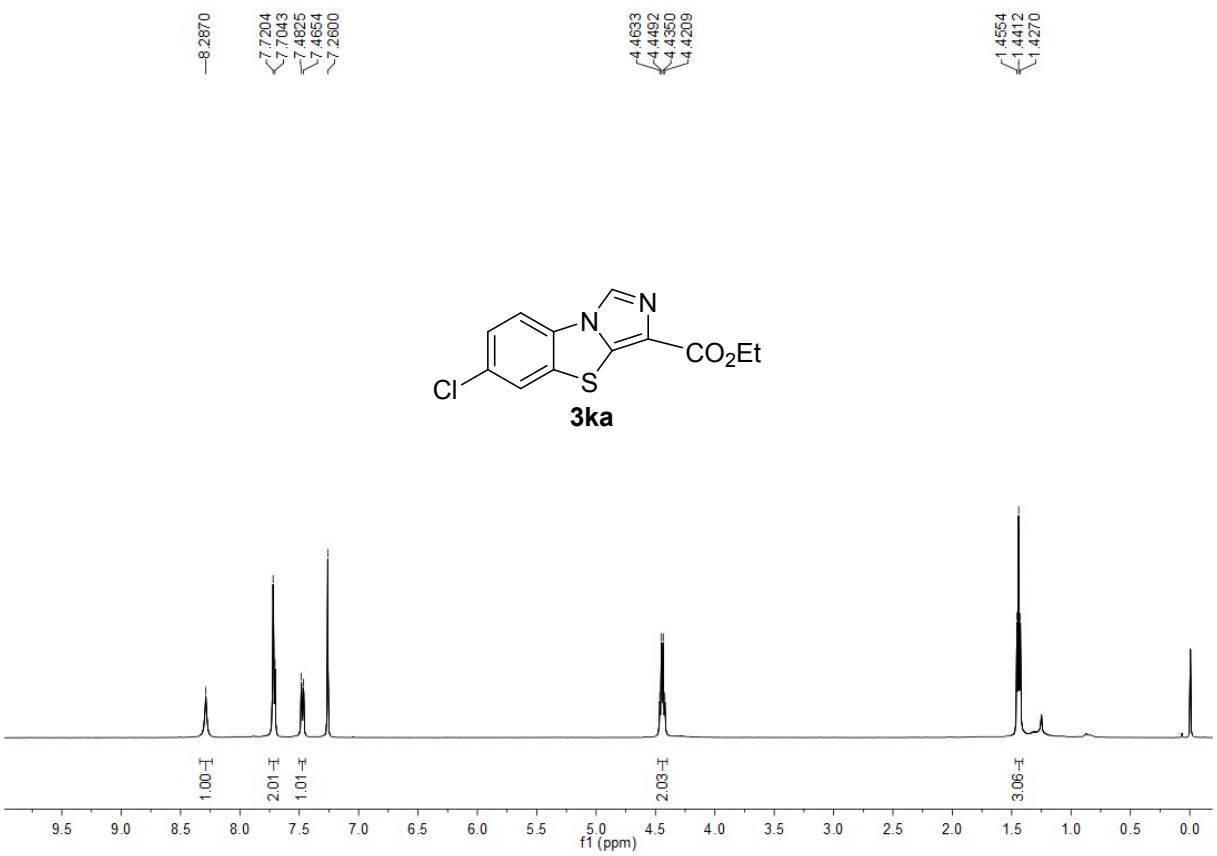
CO2Et
f1 (ppm)

3ja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1.4412
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Cl
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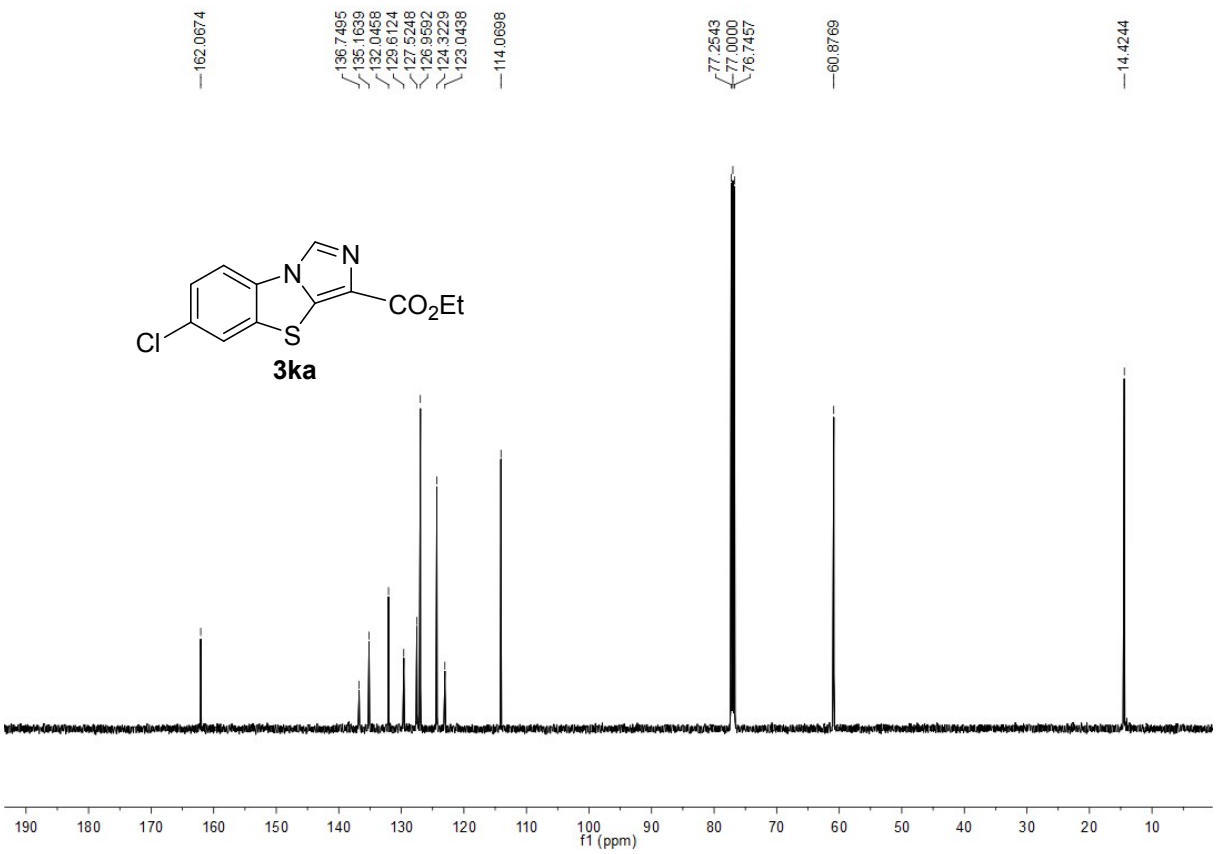
N
S
CO2Et
1.00
2.01
1.01
2.03
3.06
f1 (ppm)

3ka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N
S
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CO2Et
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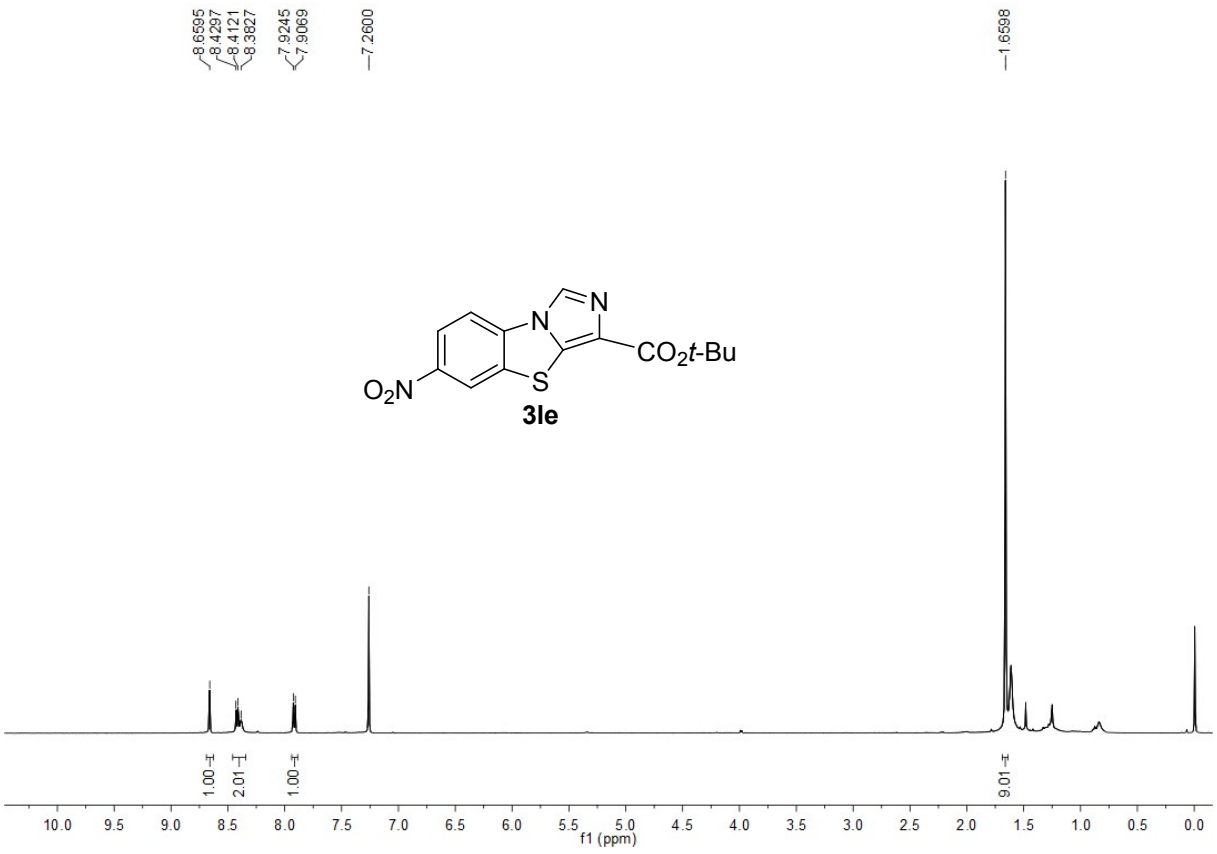
f1 (ppm)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CO2t-Bu
3le
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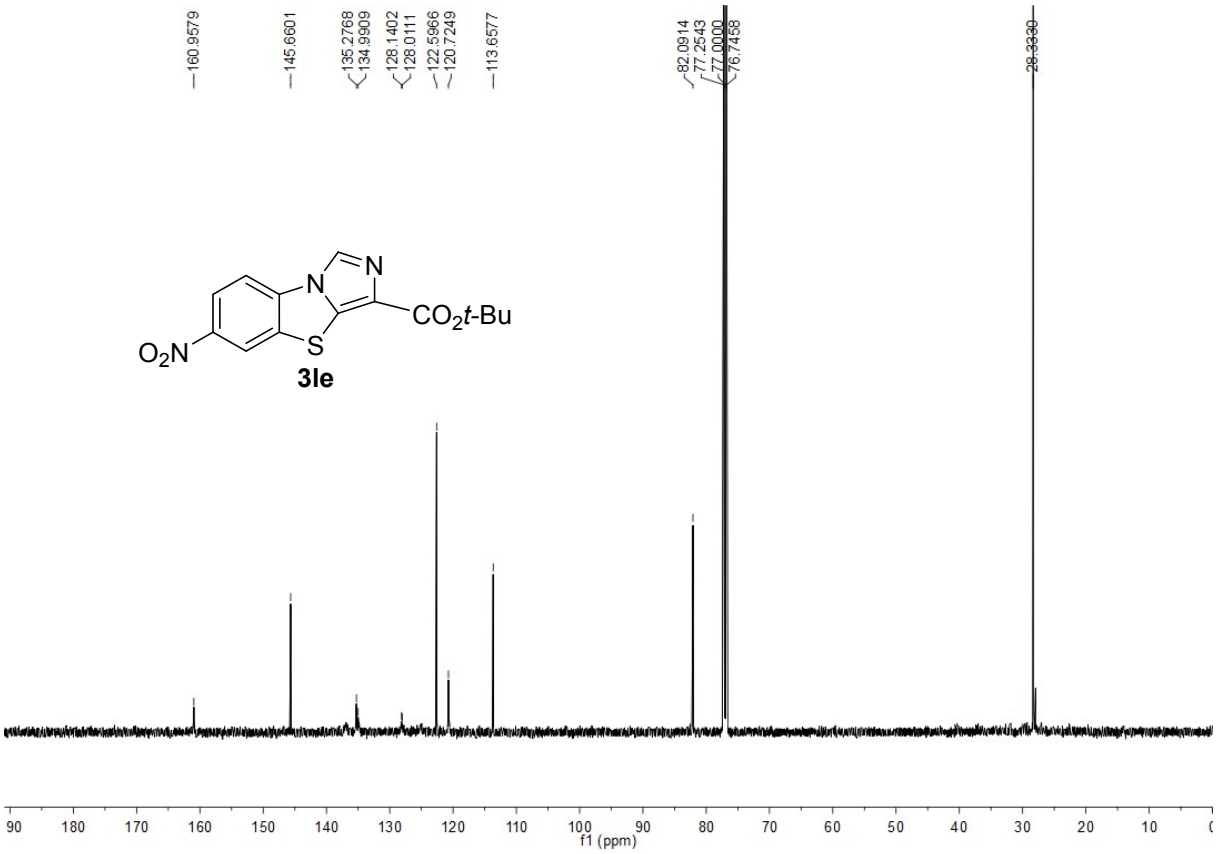
f1 (ppm)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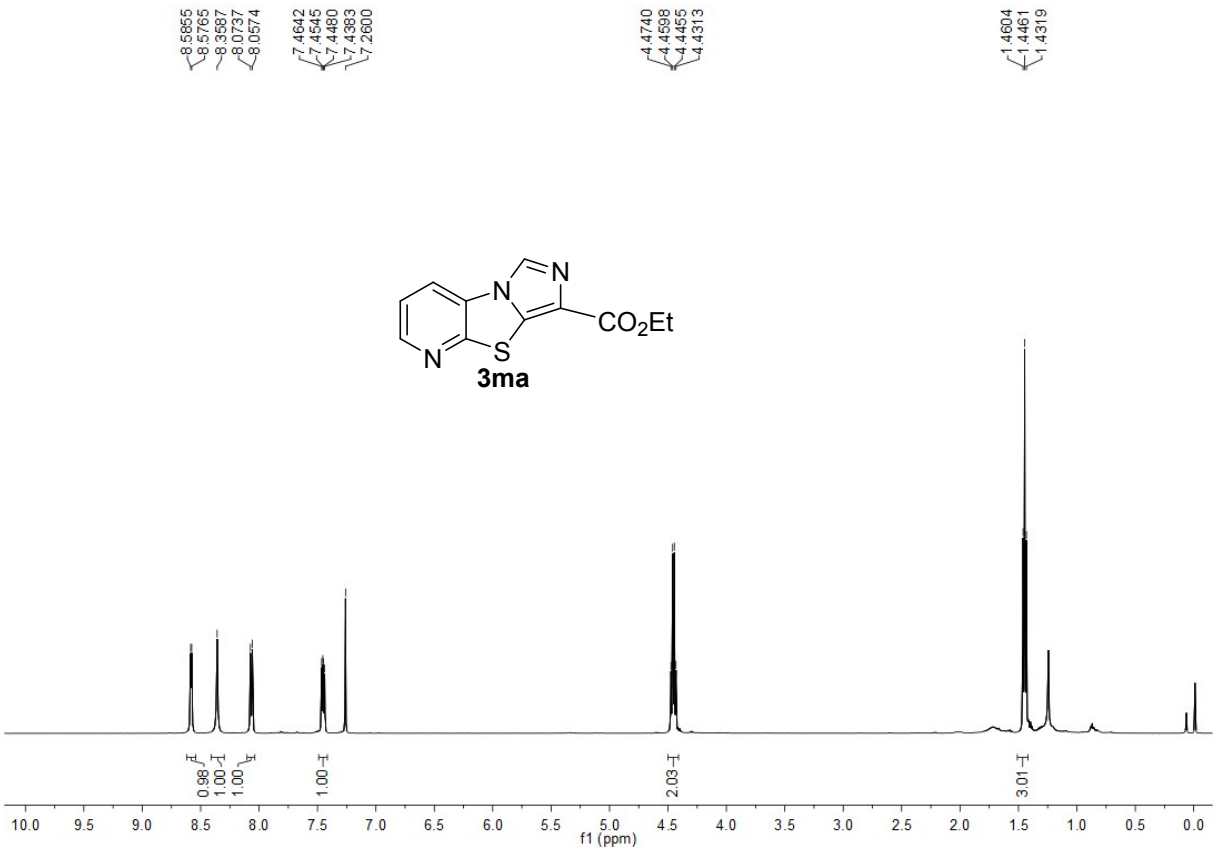
N
N
S
O2N
CO2t-Bu
3le
f1 (ppm)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4.4598
4.4455
4.4313
1.4604
1.4461
1.4319
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N
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N
CO2Et
3ma
0.98
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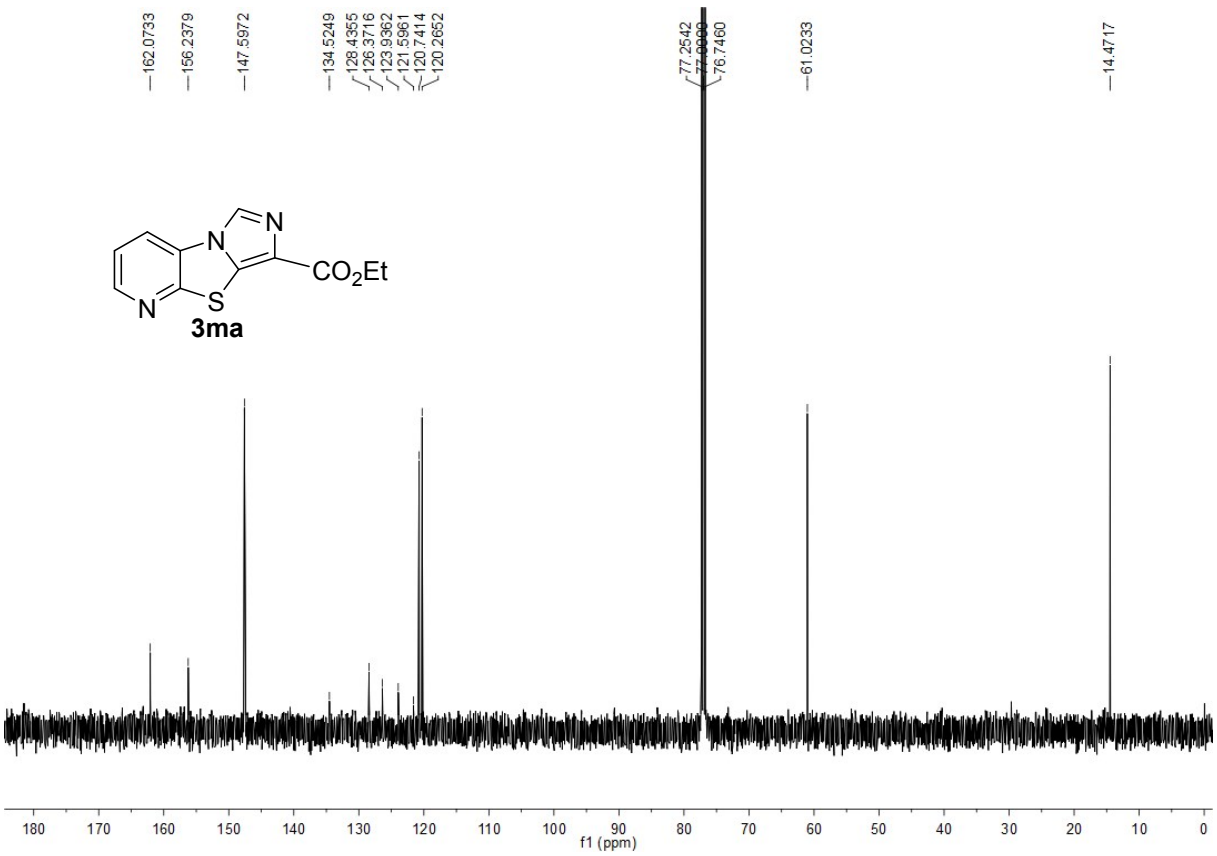
1.00
1.00
2.03
3.01
f1 (ppm)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77.0000
76.7460
61.0233
14.4717
N
N
S
N
CO2Et
3ma
180
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130
120
110
100
90
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50
40
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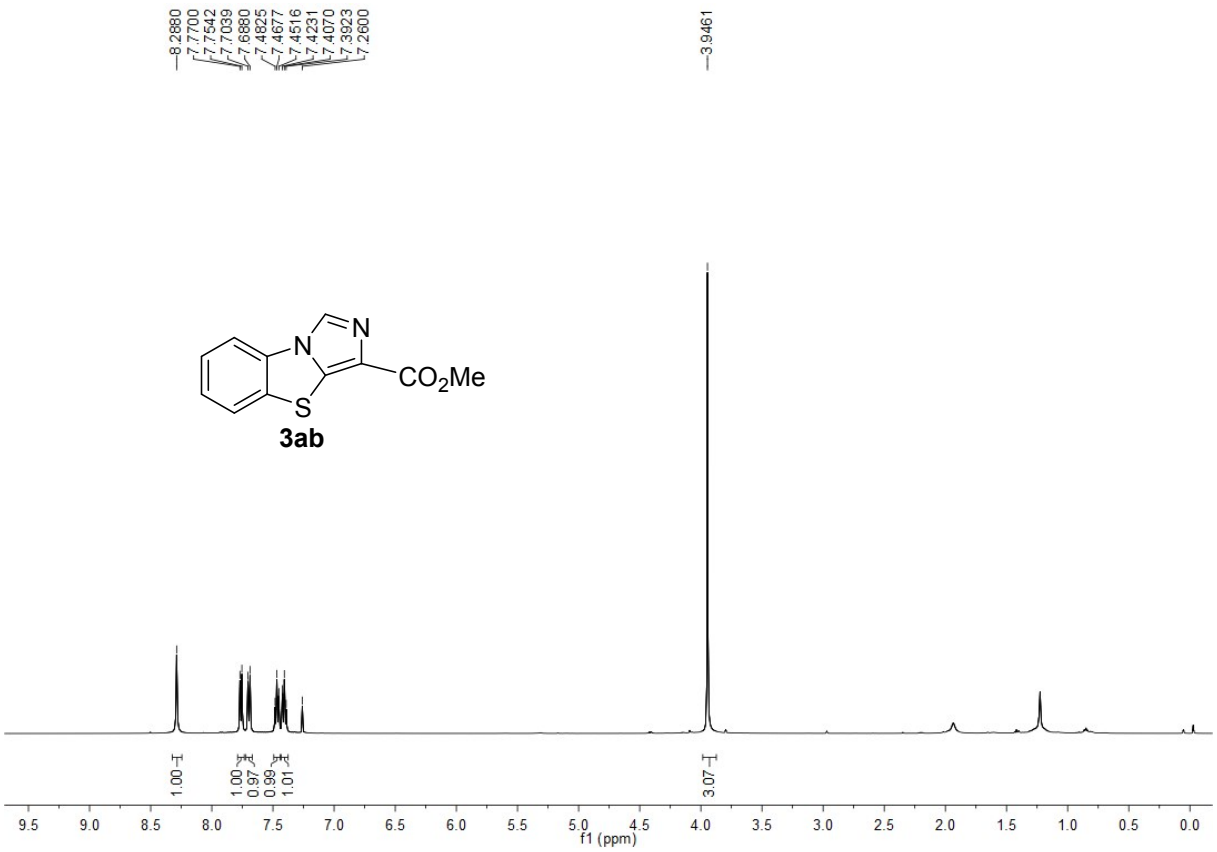
20
10
0
f1 (ppm)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7.3923
7.2600
3.9461
N
N
S
CO2Me
3ab
1.00
1.00
0.97
0.99
1.01
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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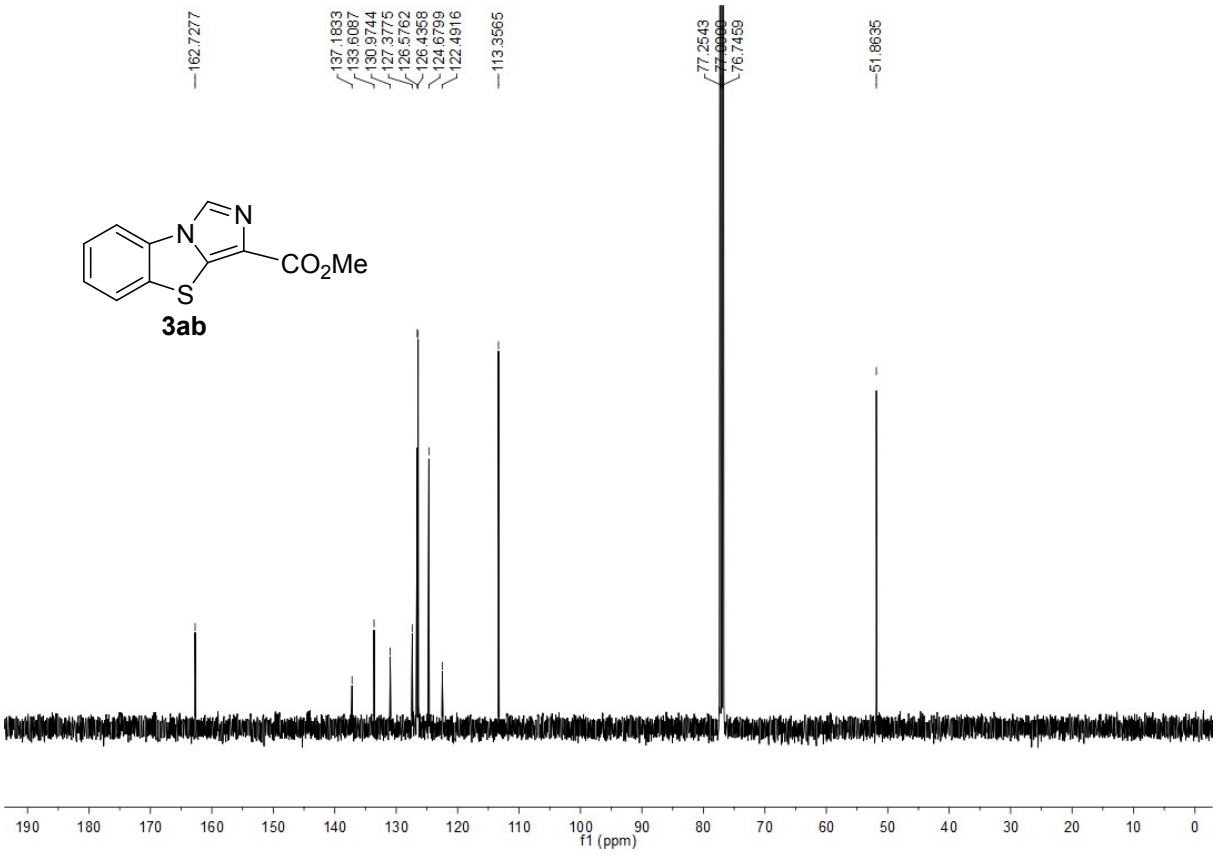
0.0
f1 (ppm)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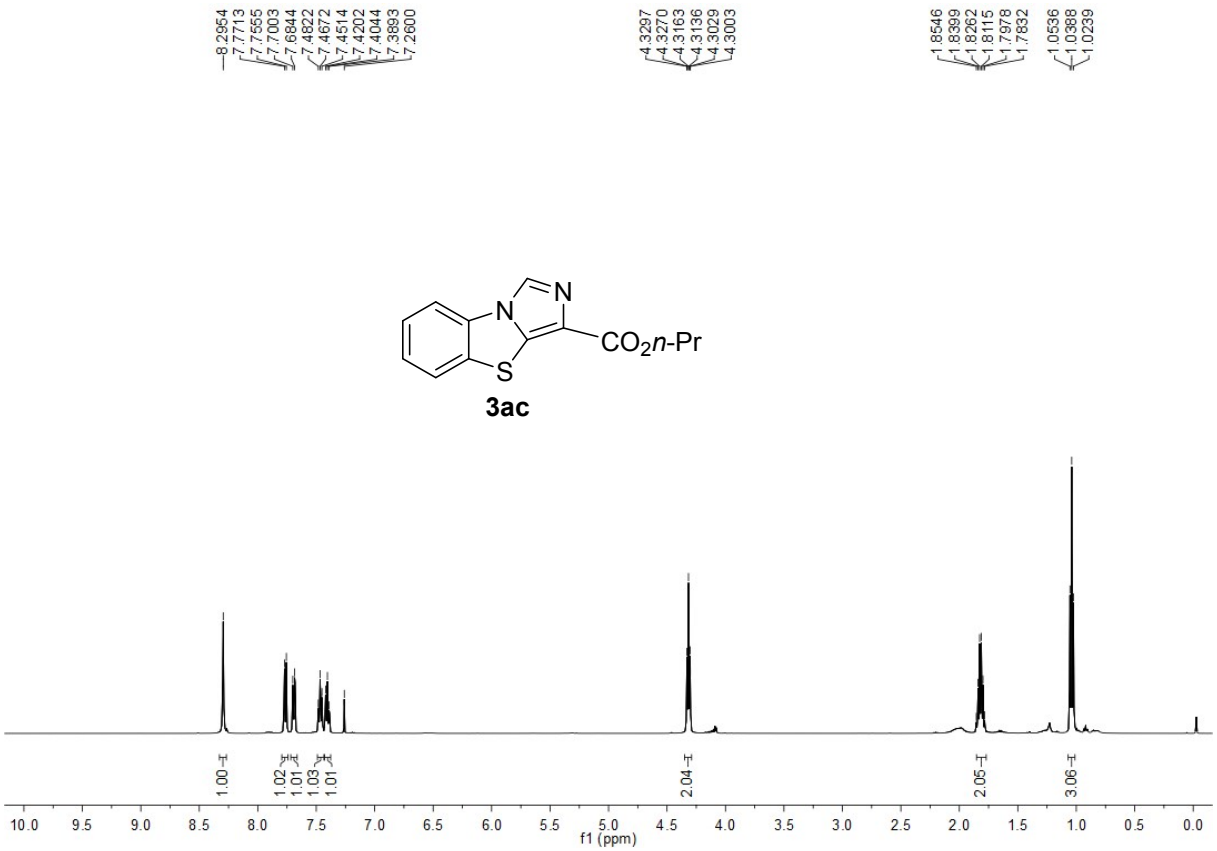
N
N
S
CO2Me
3ab
f1 (ppm)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7.2600
4.3297
4.3270
4.3163
4.3136
4.3029
4.3003
1.8546
1.8399
1.8262
1.8115
1.7978
1.7832
1.0536
1.0388
1.0239
N
N
S
CO2n-Pr
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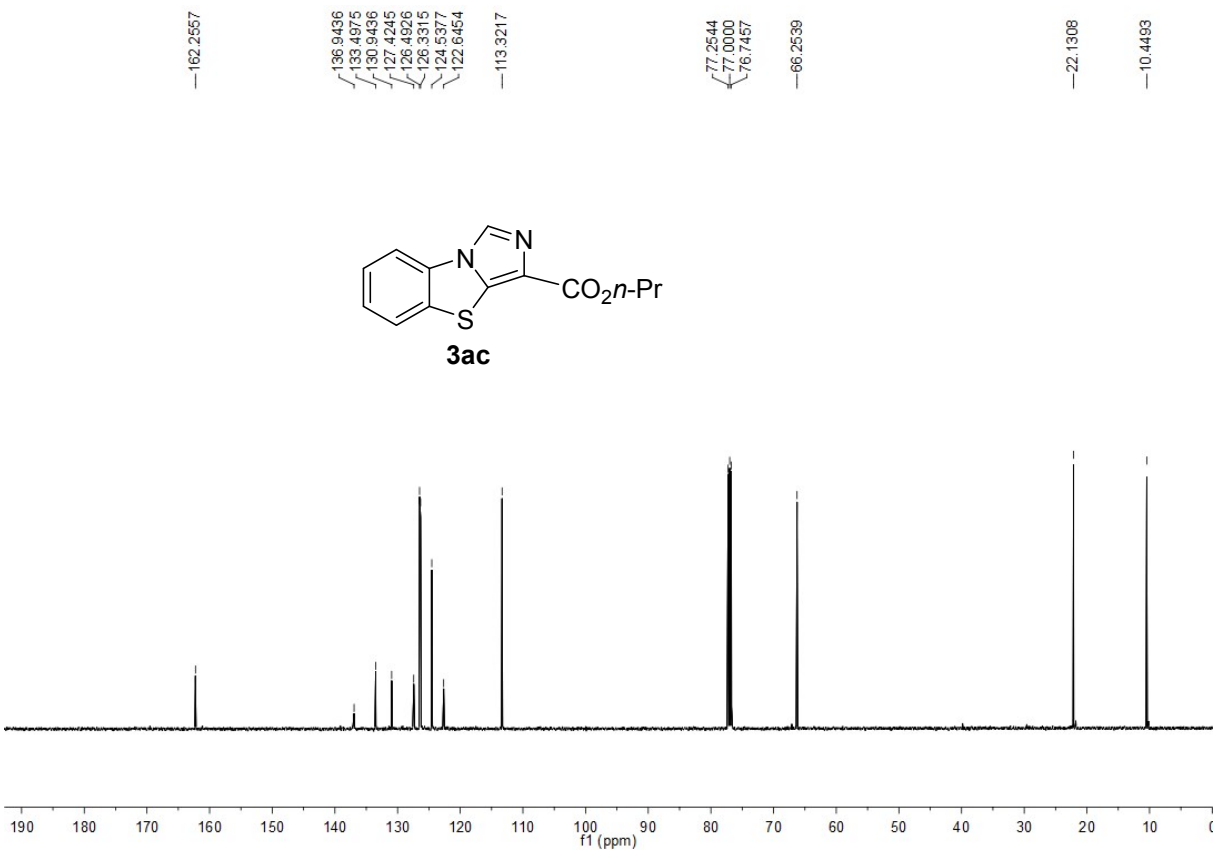
1.00
1.02
1.01
1.03
1.01
2.04
2.05
3.06
f1 (ppm)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126.3315
124.5377
122.6454
113.3217
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77.0000
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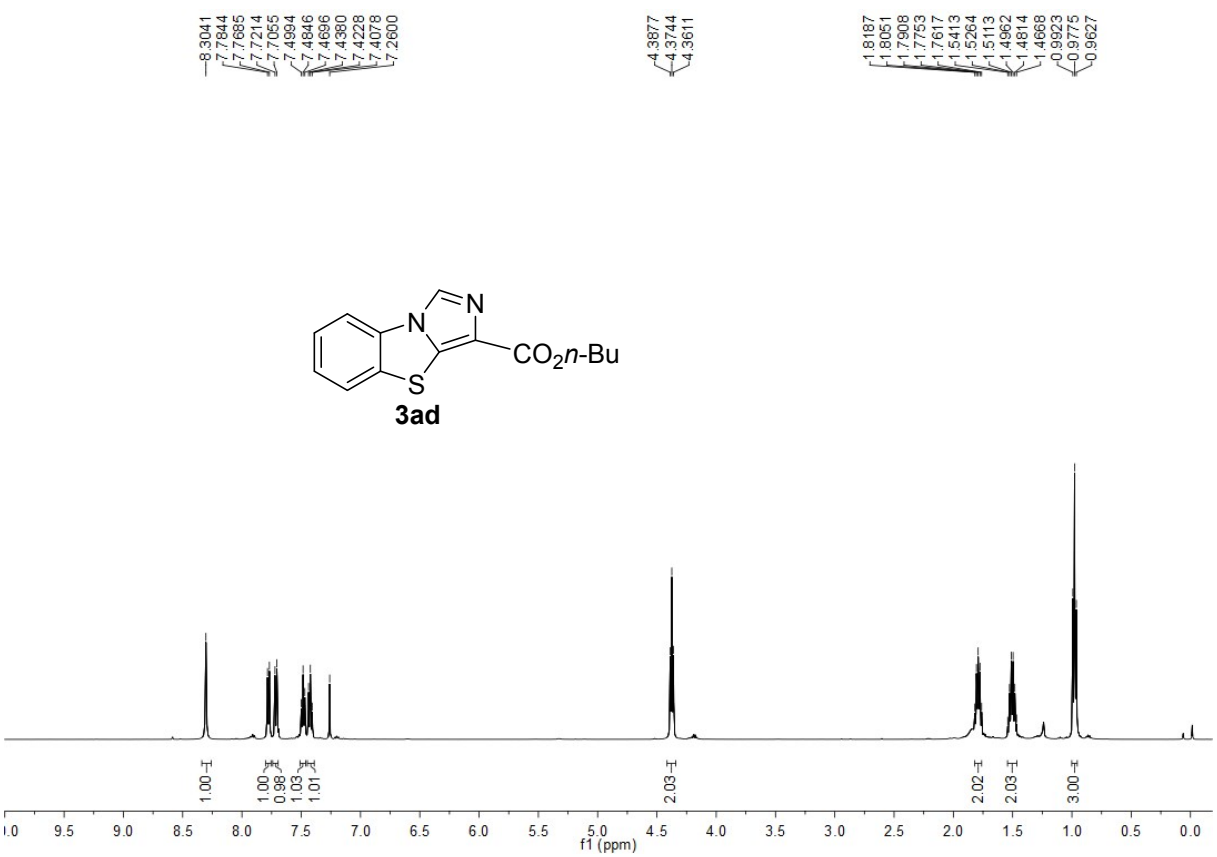
66.2539
22.1308
10.4493
N
N
S
CO2n-Pr
3ac
f1 (ppm)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7.4380
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7.2600
4.3877
4.3744
4.3611
1.8187
1.8051
1.7908
1.7753
1.7617
1.5413
1.5264
1.5113
1.4962
1.4814
1.4668
0.9923
0.9775
0.9627
N
N
S
CO2n-Bu
3ad
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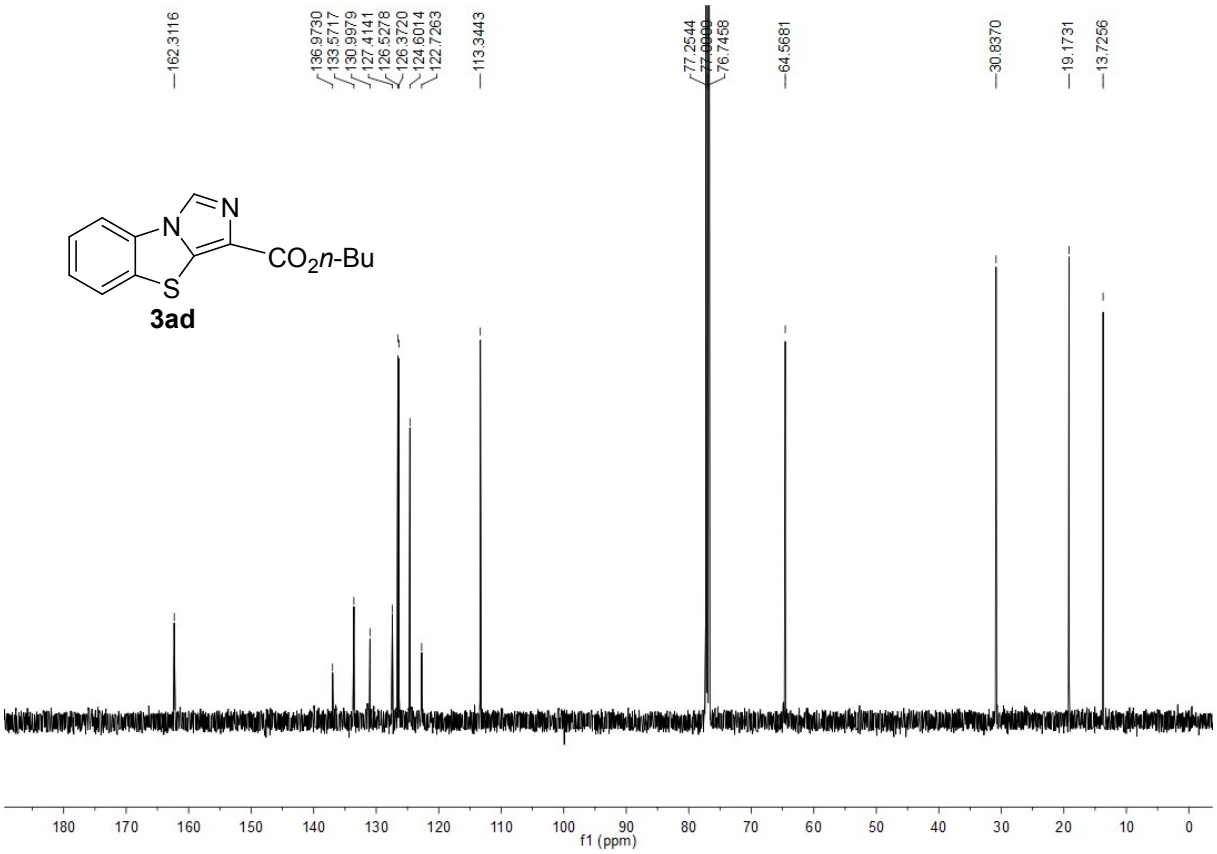
1.00
0.98
1.03
1.01
2.03
2.02
2.03
3.00
f1 (ppm)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126.3720
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77.0000
76.7458
64.5681
30.8370
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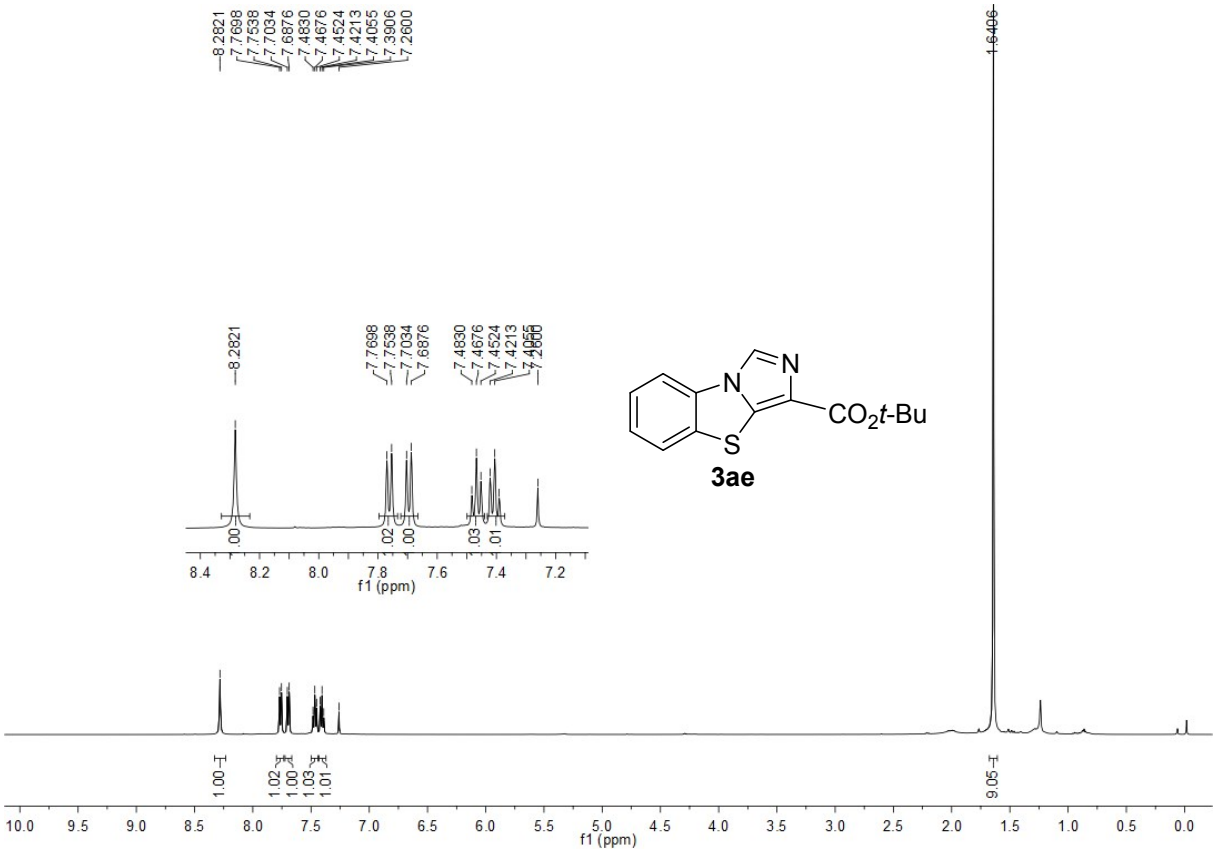
N
N
S
CO2n-Bu
3ad
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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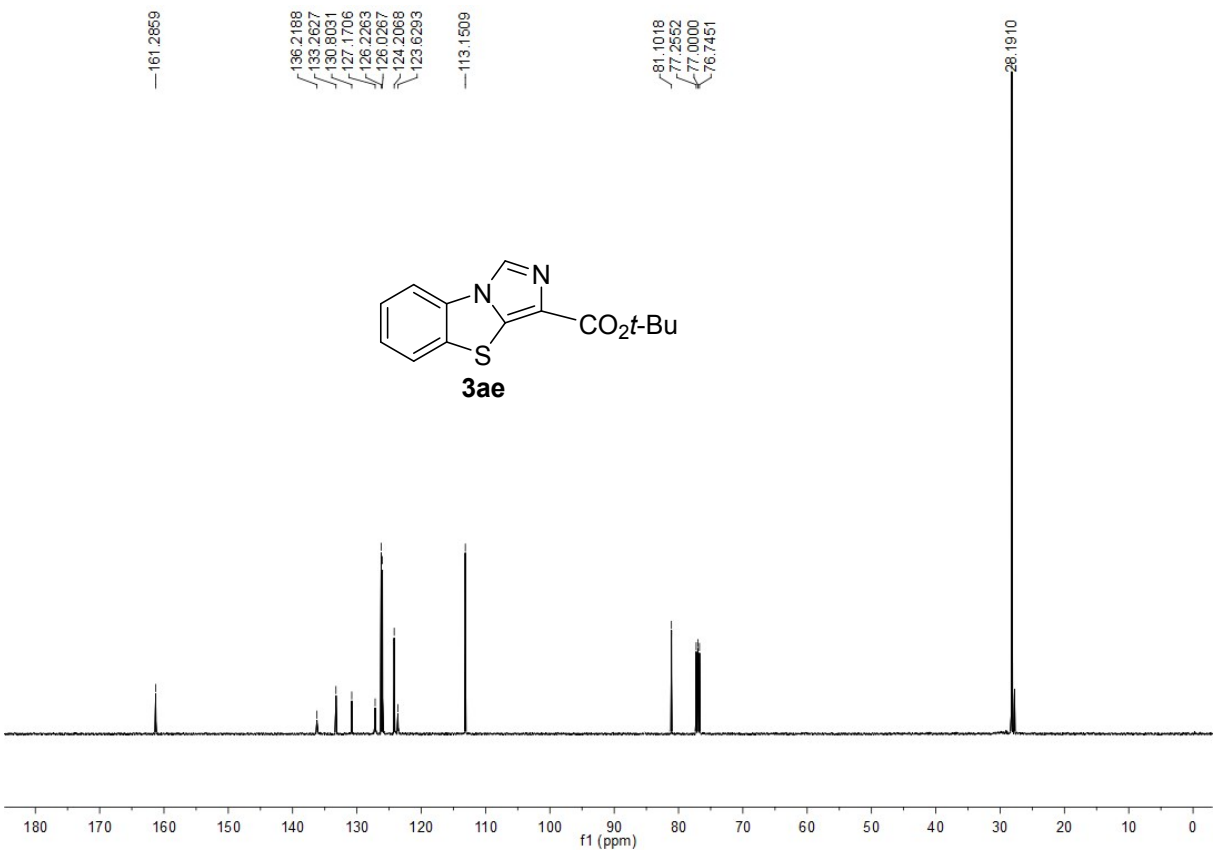
7.4055
7.3906
7.2600
1.6406
N
N
S
CO2t-Bu
3ae
1.00
1.02
1.00
1.03
1.01
9.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.6293
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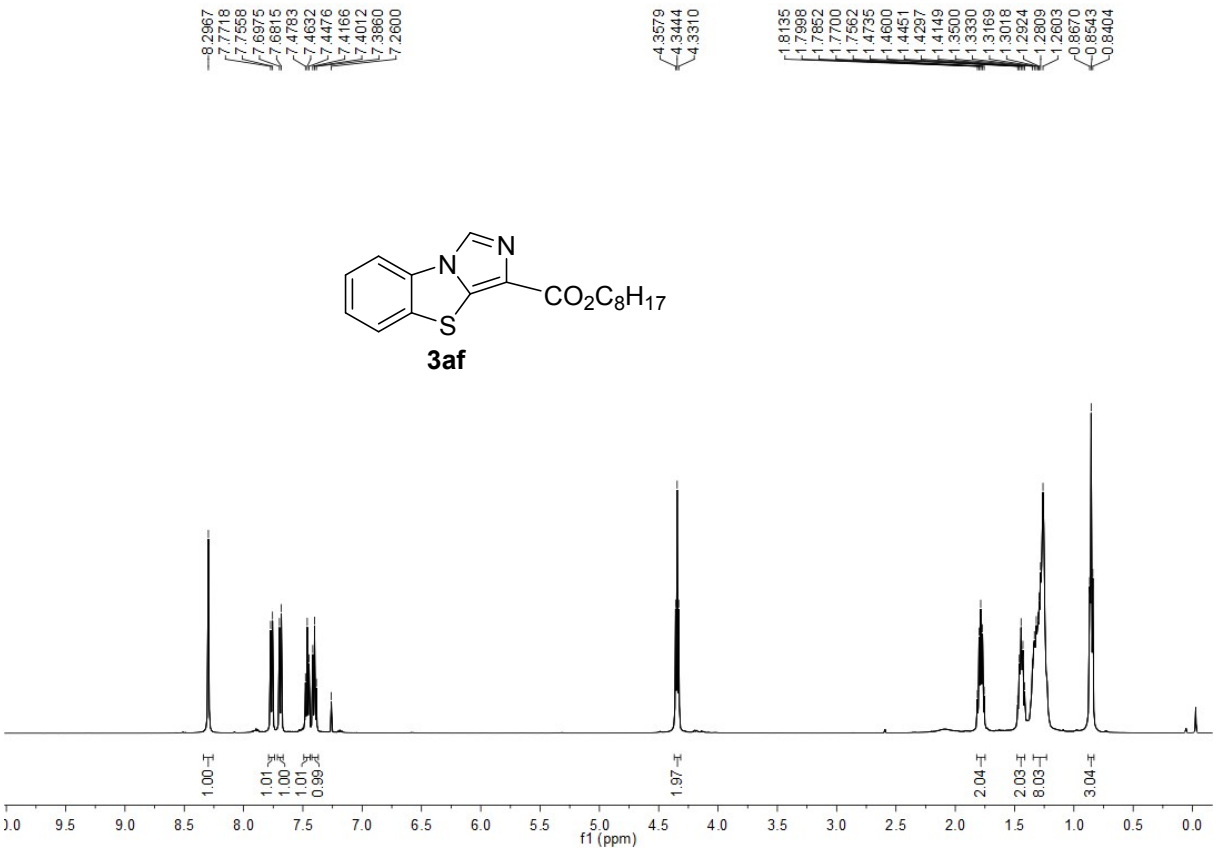
77.0000
76.7451
28.1910
N
N
S
CO2t-Bu
3ae
f1 (ppm)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7.2600
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4.3444
4.3310
1.8135
1.7998
1.7852
1.7700
1.7562
1.4735
1.4600
1.4451
1.4297
1.4149
1.3500
1.3330
1.3169
1.3018
1.2924
1.2809
1.2603
0.8670
0.8543
0.8404
N
N
S
CO2C8H17
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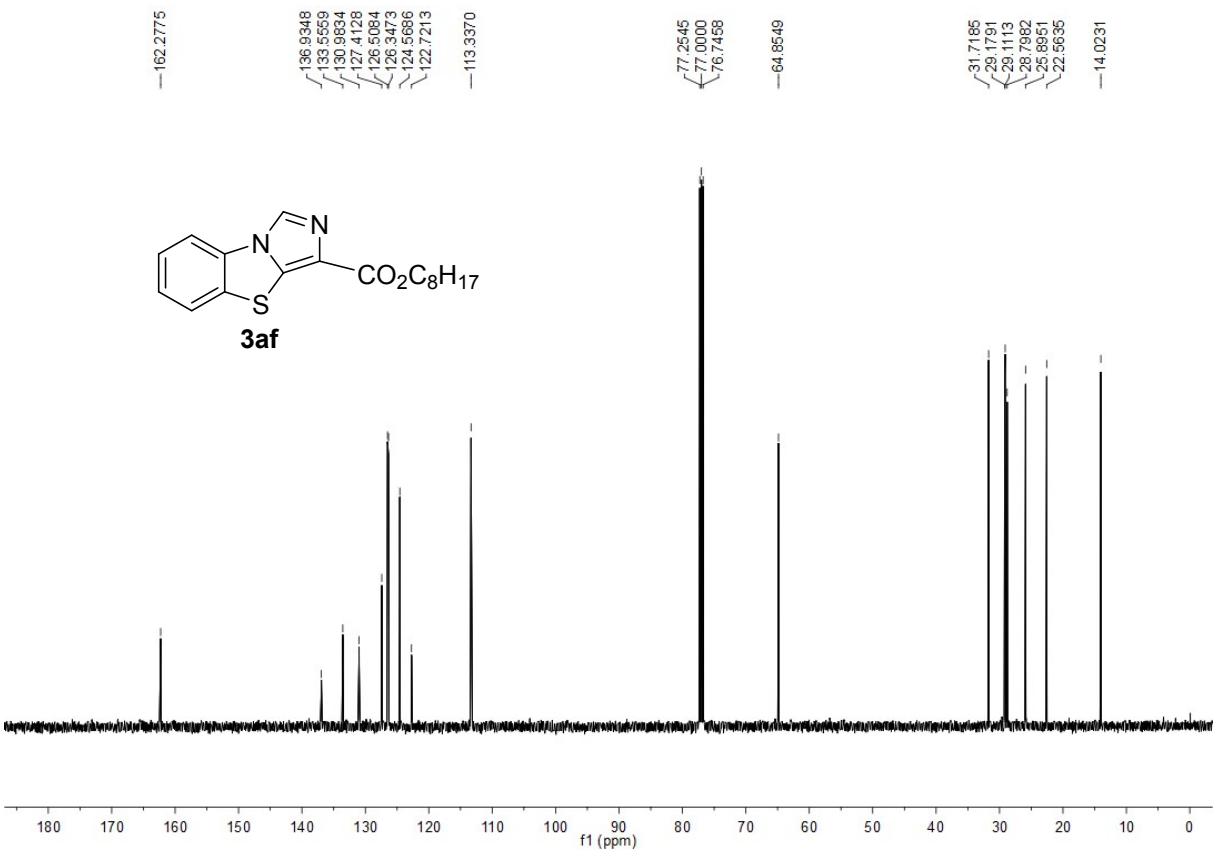
1.00
1.01
0.99
1.97
2.04
2.03
8.03
3.04
f1 (ppm)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77.2545
77.0000
76.7458
64.8549
31.7185
29.1791
29.1113
28.7982
25.8951
22.5635
14.0231
N
N
S
CO2C8H17
3af
180
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150
140
130
120
110
100
90
80
70
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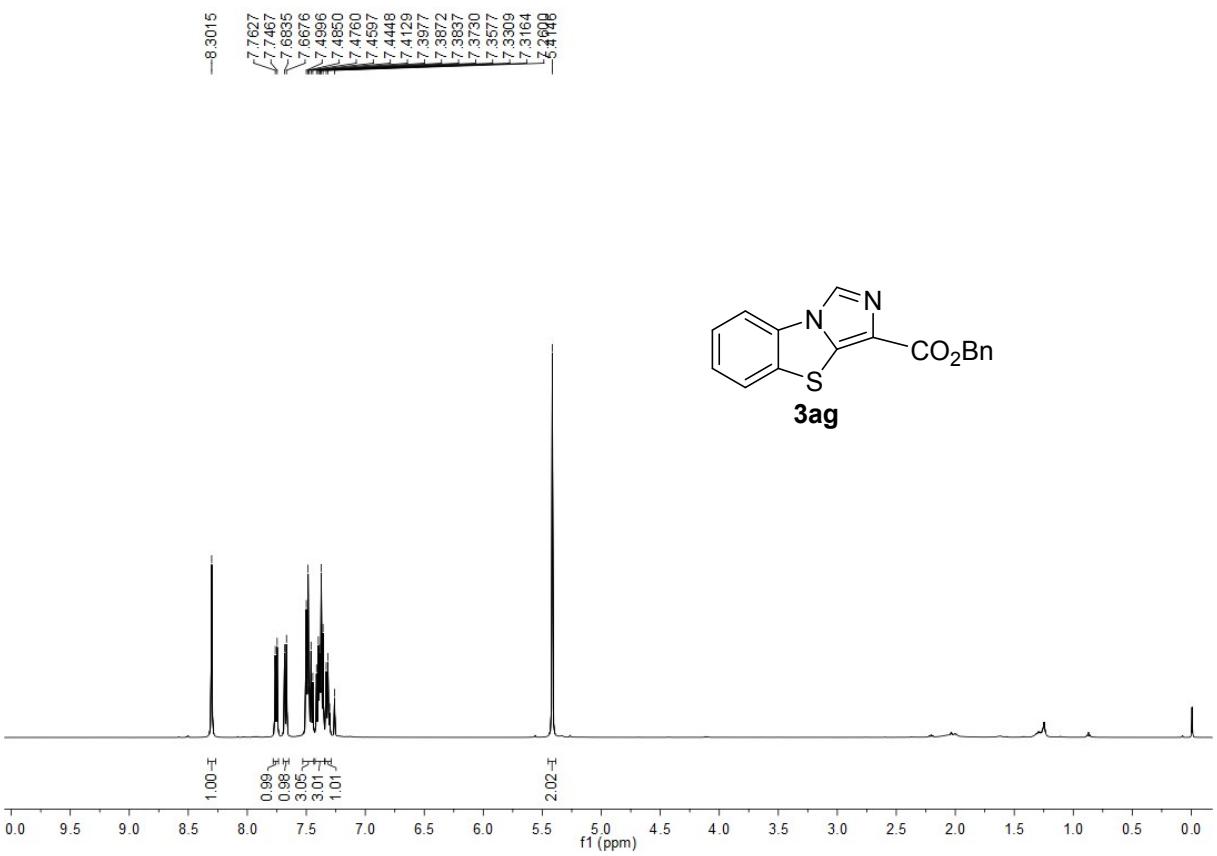
50
40
30
20
10
0
f1 (ppm)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7.3977
7.3872
7.3837
7.3730
7.3577
7.3309
7.3164
7.2600
5.4148
N
N
S
CO2Bn
3ag
1.00
0.99
0.98
3.05
3.01
1.01
2.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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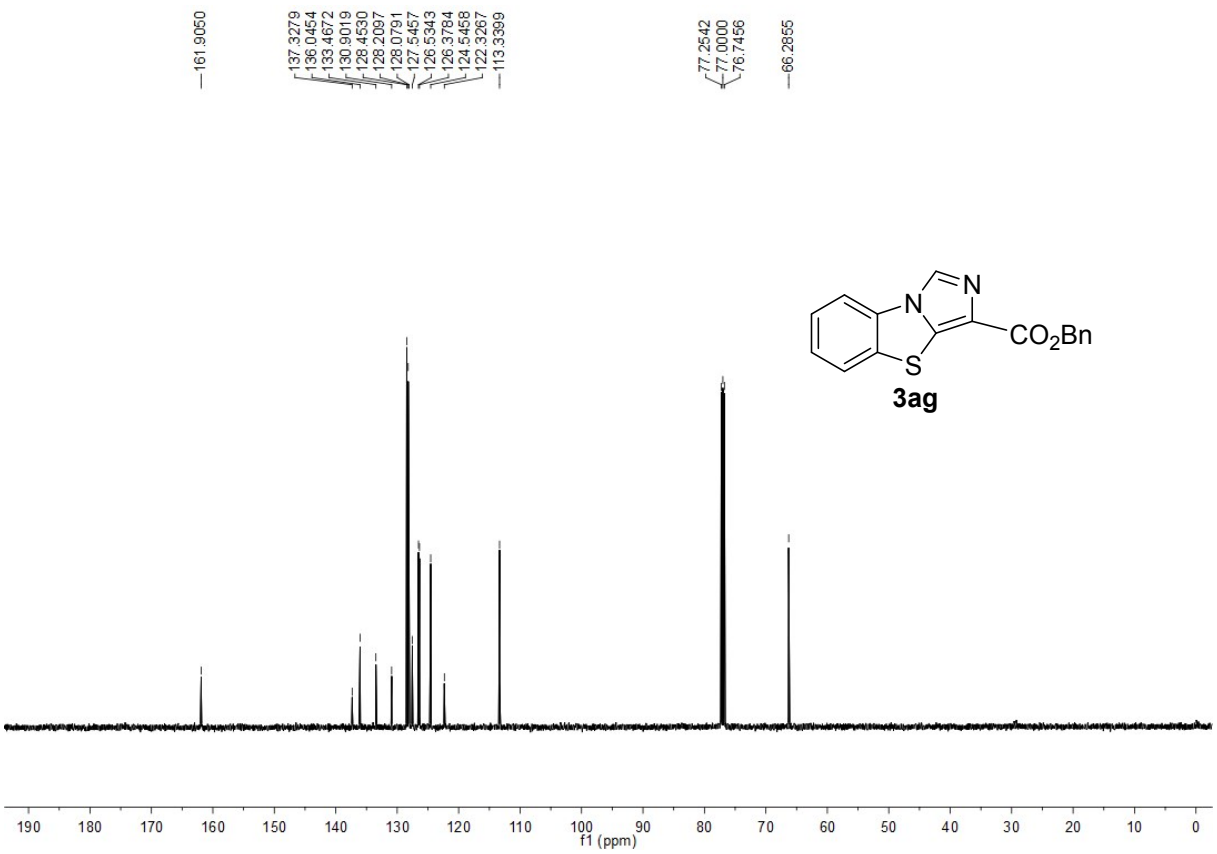
f1 (ppm)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124.5458
122.3267
113.3399
77.2542
77.0000
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N
S
CO2Bn
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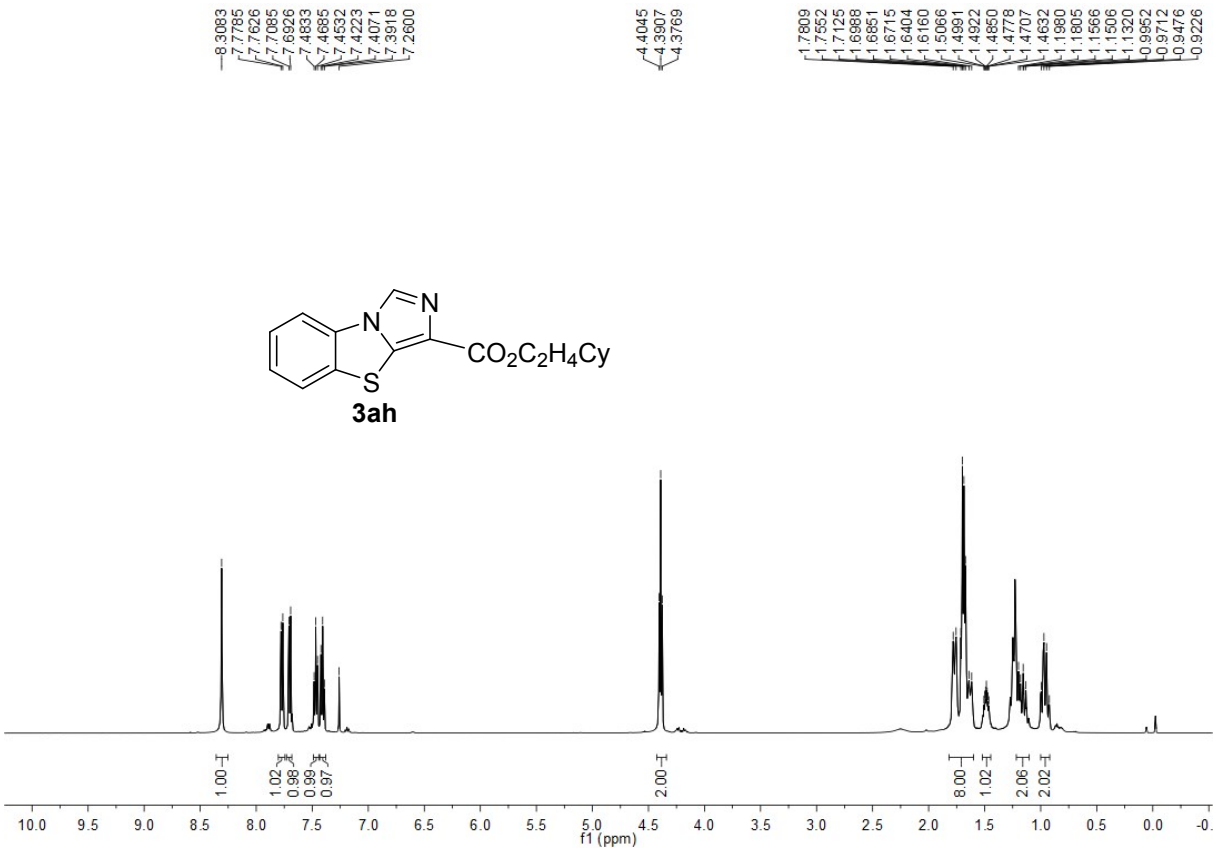
f1 (ppm)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4.4045
4.3907
4.3769
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1.7125
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1.6715
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1.6160
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1.4922
1.4850
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1.4707
1.4632
1.1980
1.1805
1.1566
1.1506
1.1320
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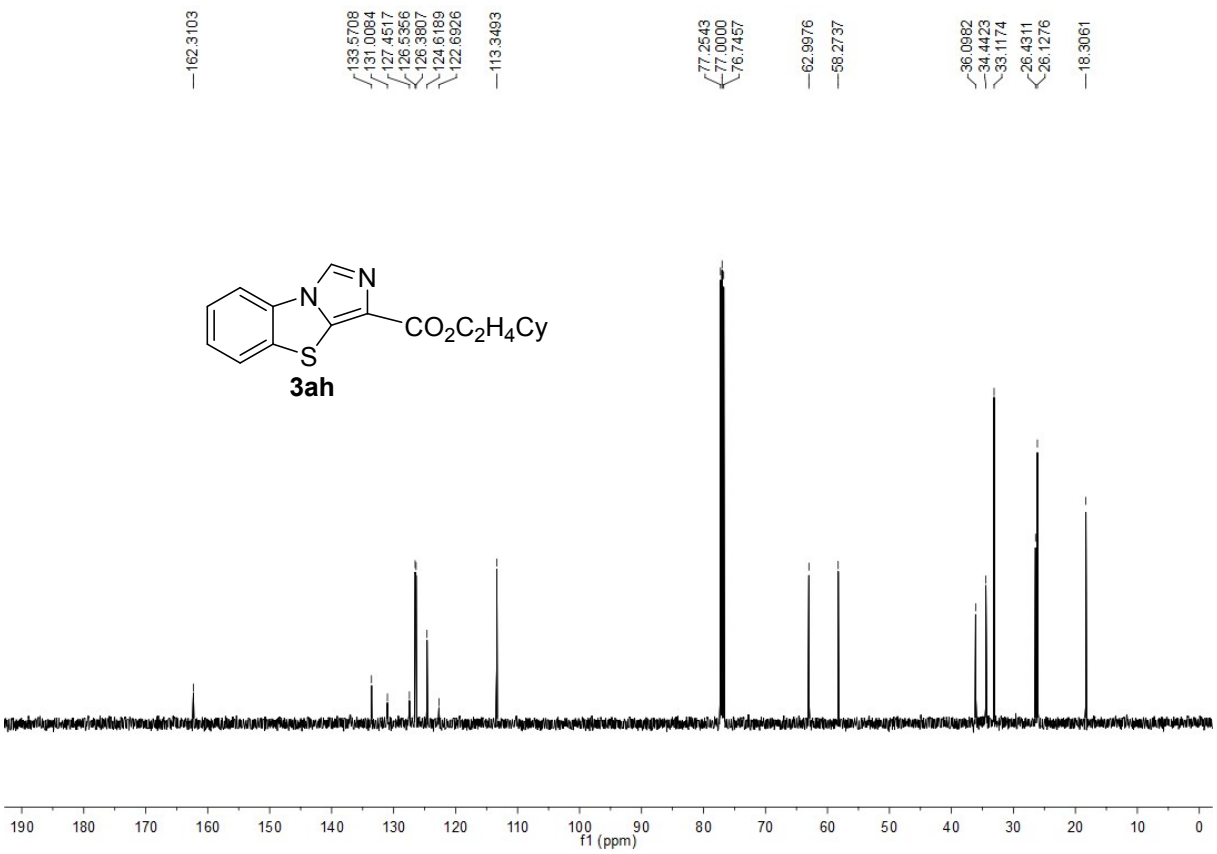
0.9712
0.9476
0.9226
N
N
S
CO2C2H4Cy
3ah
1.00
1.02
0.98
0.99
0.97
2.00
8.00
1.02
2.06
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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62.9976
58.2737
36.0982
34.4423
33.1174
26.4311
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N
S
CO2C2H4Cy
3ah
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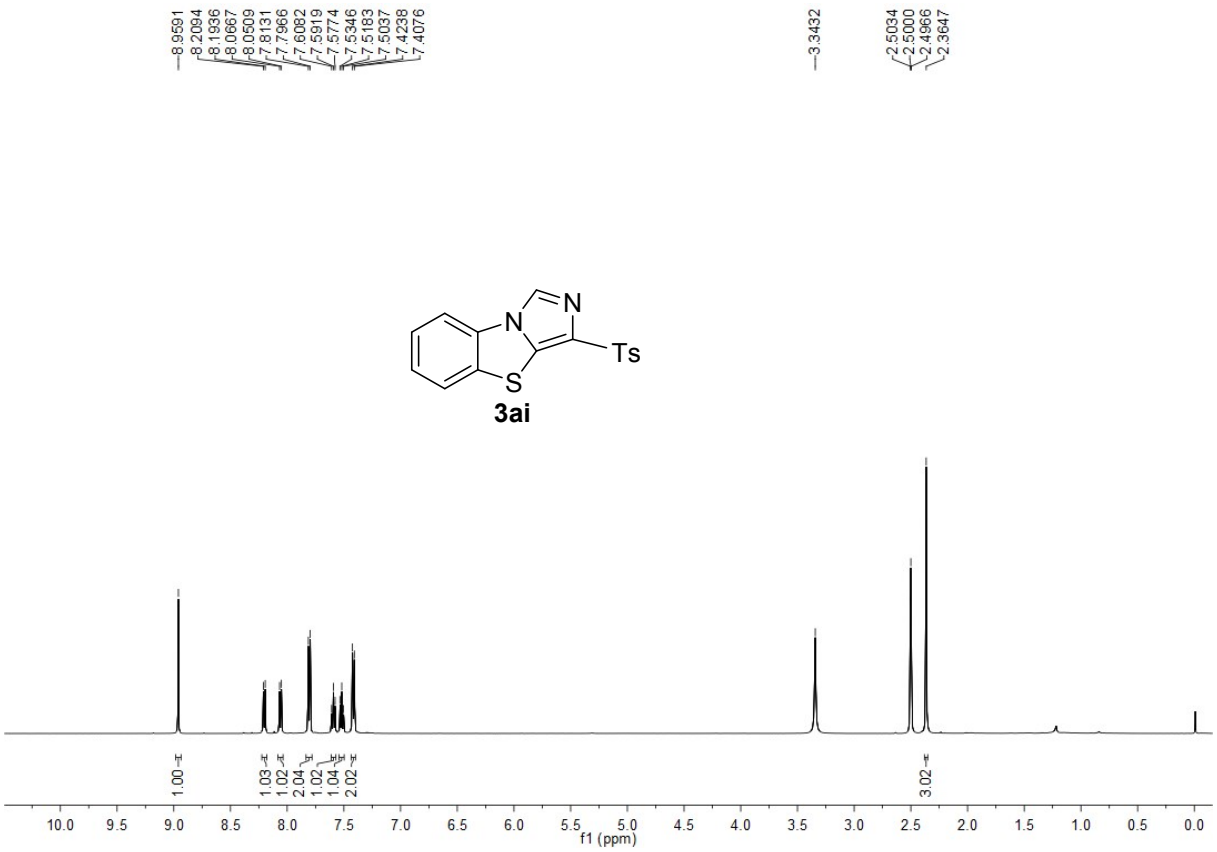
f1 (ppm)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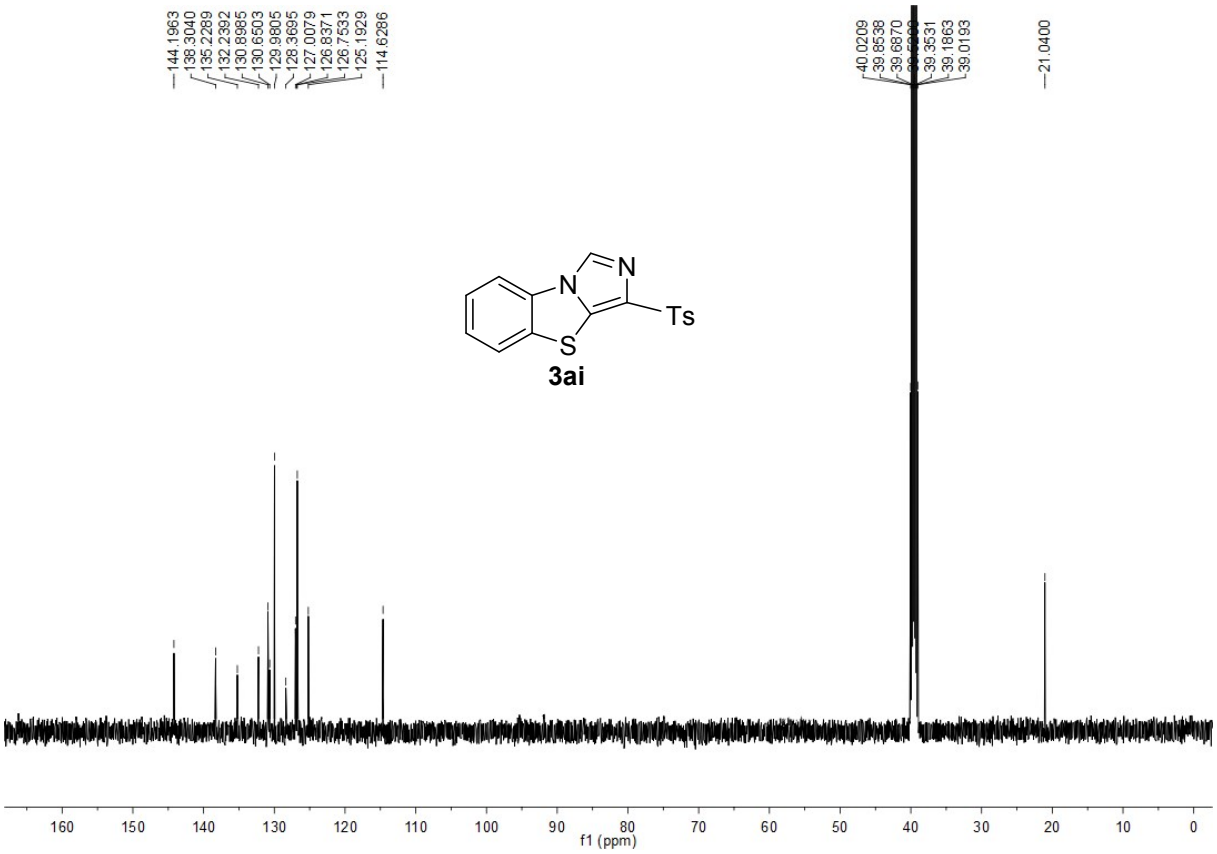
7.5183
7.5037
7.4238
7.4076
3.3432
2.5034
2.5000
2.4966
2.3647
N
N
S
Ts
3ai
1.00
1.03
1.02
2.04
1.02
1.04
2.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.1929
114.6286
40.0209
39.9538
39.6870
39.4203
39.3531
39.1863
39.0193
21.0400
N
N
S
Ts
160
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140
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120
110
100
90
80
70
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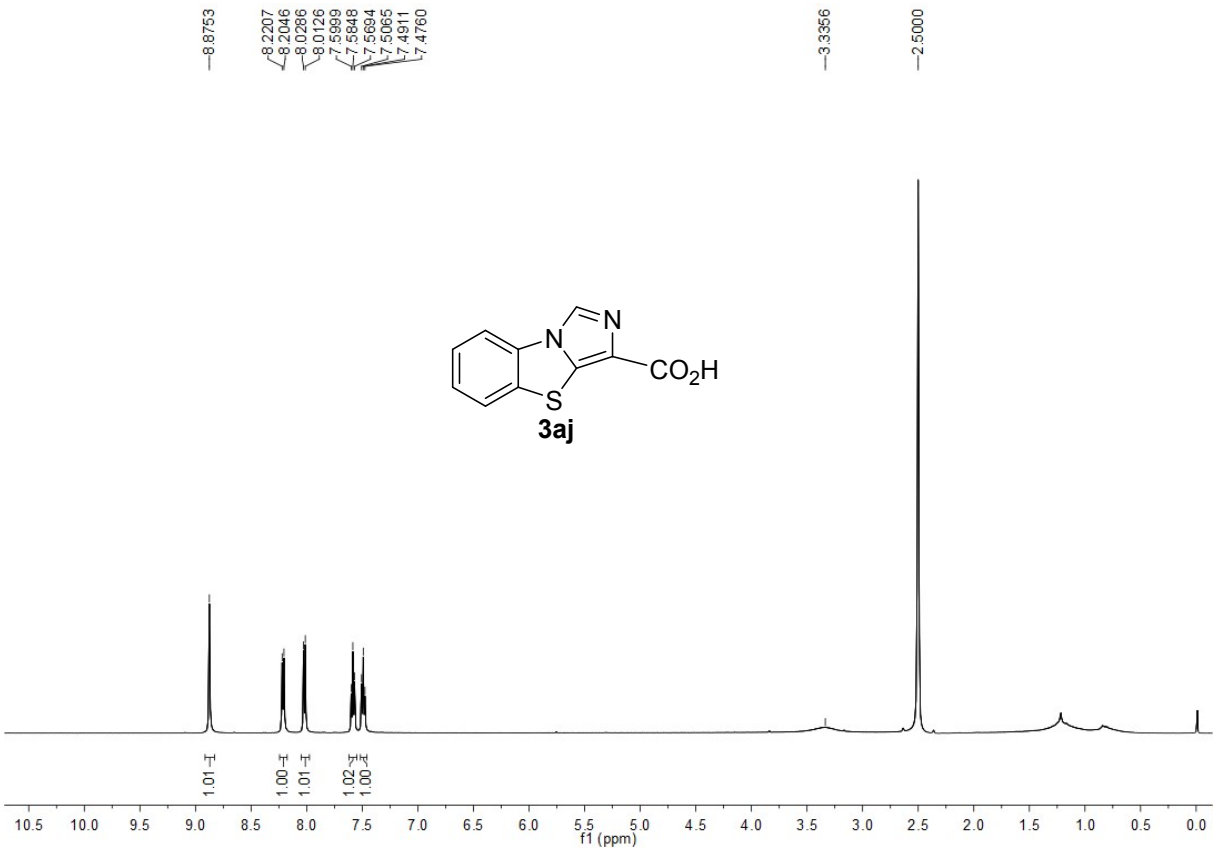
50
40
30
20
10
0
f1 (ppm)

3ai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3.3356
2.5000
N
N
S
CO2H
1.01
1.00
1.01
1.02
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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2.0
1.5
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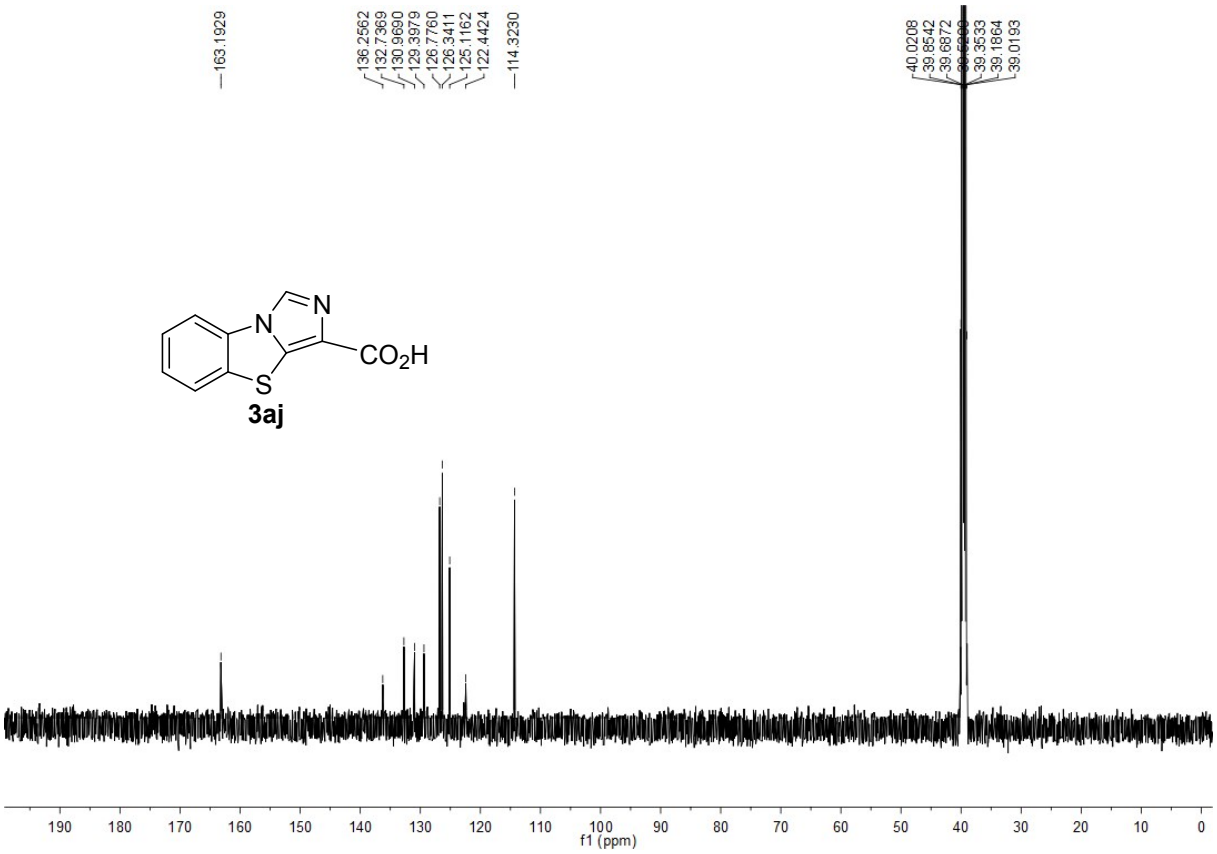
f1 (ppm)

3aj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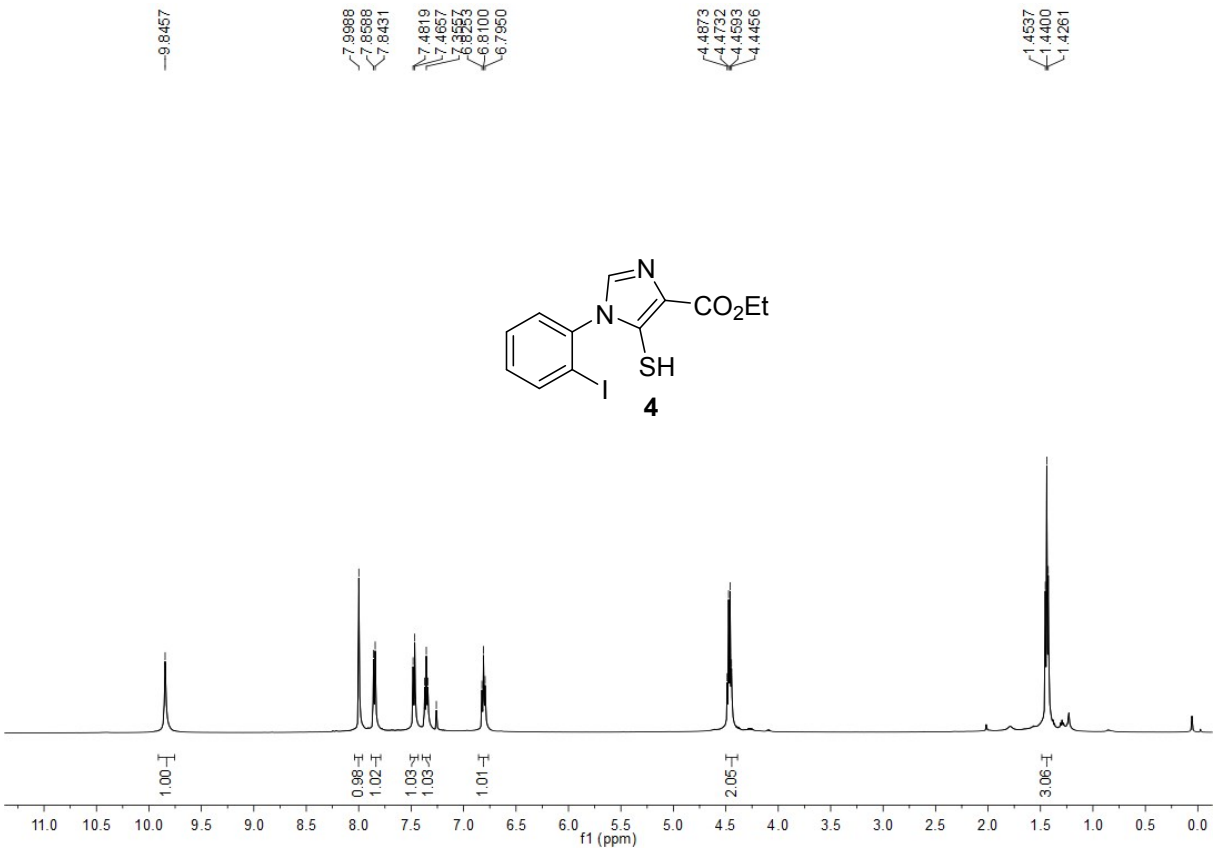
N
N
S
CO2H
3aj
f1 (ppm)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6.7950
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4.4732
4.4593
4.4456
1.4537
1.4400
1.4261
N
N
CO2Et
SH
I
4
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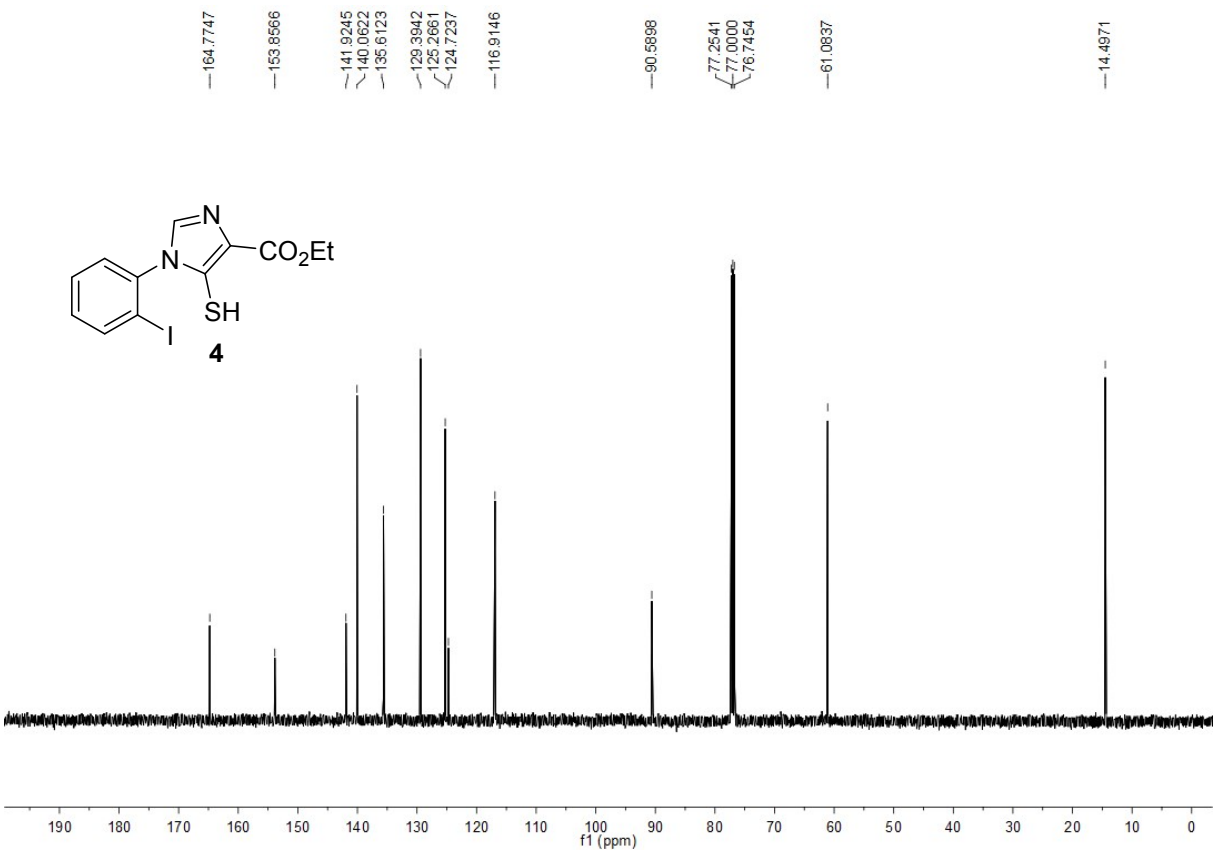
0.98
1.02
1.03
1.03
1.01
2.05
3.06
f1 (ppm)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125.2661
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116.9146
90.5898
77.2541
77.0000
76.7454
61.0837
14.4971
N
N
CO2Et
SH
I
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)