Electronic Supplementary Material (ESI) for ChemComm.

Heteroannulation Enabled by a Bimetallic Rh(III)/Ag(I) Relay Catalysis: Application in Total Synthesis of Aristolactams BII

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Support information

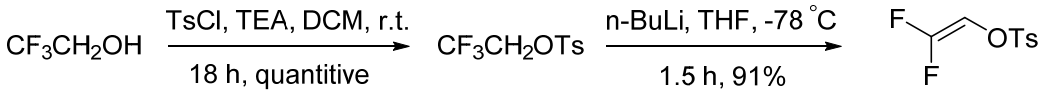
Contents

I. General considerations

Unless otherwise noted, all reactions were carried out under an air atmosphere. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: toluene (Na-benzophenone), THF (Na-benzophenone). CF_3CH_2OH, HFIP, CH_3CN, MeOH, EtOH, THF, 1,4-dioxane and CH_2Cl_2 were purchased from Acros Organics. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (200-300 mesh) by standard technique. Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, ^{19}F NMR) were recorded with Bruker AV (^{1}H at 400 MHz, ^{13}C at 101 MHz, ^{19}F at 376 MHz) unless noted. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm; d_4-MeOD: δ_H = 3.31 ppm, δ_C = 49.00 ppm, d_6-Acetone: δ_H = 2.05 ppm, δ_C = 29.84 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, J were reported in hertz unit (Hz). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

II. Preparation and characterization of starting materials

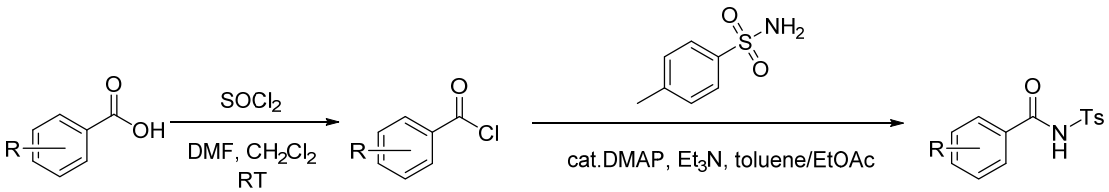
i. Preparation of 2,2-difluorovinyl tosylate 1



1

The compound **1** was prepared according to a known procedure.[1]

ii. General procedure for the preparation of *N*-tosylbenzamides 3



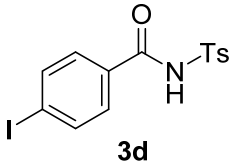
6 **19** **3**

General procedure A: To a round-bottom flask charged with carboxylic acid **6** (5 mmol) in dry dichloromethane (25 mL), were added sulfurous dichloride (0.718 g, 6.0 mmol) and DMF (0.007 g, 0.1 mmol). The reaction mixture was then stirred at room temperature and monitored by TLC. After the reaction was completed (typically 0.5-3 h), the volatile was removed under reduced pressure to give the crude acyl chloride which was used directly in the next step.[2]

To a round-bottom flask charged with *p*-toluene sulfonamide (1.0 equiv), ethyl acetate (2.0 mL/mmol), triethylamine (2.5 equiv) and DMAP (0.5 mol %), was added a toluene (0.8 mL/mmol) solution of acid chloride (1.1 equiv) via a syringe over 15 minutes under N_2. The mixture was then stirred at 55 °C for 1 h. After cooled to room temperature, the reaction was quenched with diluted hydrochloric acid. The resulting mixture was then extracted with EtOAc (3 times). The combined organic layer was dried over $MgSO_4$, filtered and evaporated. The residue was purified by passing through a pad of silica gel eluting with CH_2Cl_2.[3b]

Spectral data for **3a-3e, 3g, 3h, 3k, 3l, 3n, 3o, 3q and 3r** are consistent with the reported literatures.[3]

4-iodo-N-tosylbenzamide (3d)



3d

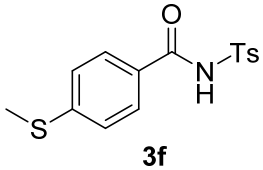
Starting from 4-iodobenzoic acid (1.0 g, 4.00 mmol), by following general procedure A, *N*-tosylbenzamide **3d** was obtained as a white solid (0.37g, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 145.6, 138.3, 135.4, 130.8, 129.8, 129.4, 128.8, 101.4, 21.9.

ESI-MS: calculated $C_{14}H_{12}INO_3S$ $[M+H]^+$, 401.9655; Found 401.9657.

4-(methylthio)-N-tosylbenzamide (3f)



3f

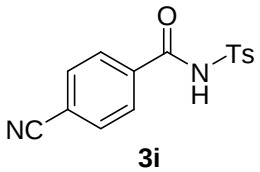
Starting from 4-(methylthio)benzoic acid (1.0 g, 6.0 mmol), by following general procedure A, *N*-tosylbenzamide **3f** was obtained as a white solid (0.45 g, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.35 – 7.86 (m, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 2.49 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 146.9, 145.3, 135.7, 129.8, 128.8, 128.2, 127.1, 125.4, 21.8, 14.9.

ESI-MS: calculated $C_{15}H_{15}NO_3S_2$ $[M+H]^+$, 322.0566; Found 322.0561.

4-cyano-N-tosylbenzamide (3i)



3i

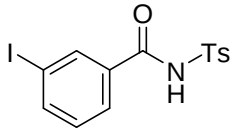
Starting from 4-cyanobenzoic acid (1.0 g, 6.8 mmol), by following general procedure A, *N*-tosylbenzamide **3i** was obtained as a white solid (0.24 g, 12% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz,$CDCl_3$) δ 162.9, 145.8, 135.3, 135.2, 132.8, 129.9, 128.9, 128.6, 117.6, 117.1, 21.9.

ESI-MS: calculated $C_{15}H_{12}N_2O_3S$ $[M+H]^+$, 301.0641; Found 301.0648.

3-iodo-N-tosylbenzamide (3m)



3m

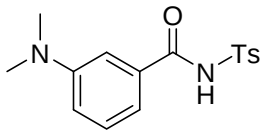
Starting from 3-iodobenzoic acid (1.0 g, 4.00 mmol), by following general procedure A, *N*-tosylbenzamide **3m** was obtained as a white solid (0.58 g, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.10 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 145.4, 142.2, 136.9, 135.3, 133.1, 130.4, 129.7, 128.7, 126.9, 94.3, 21.7.

ESI-MS: calculated $C_{14}H_{12}INO_3S$ $[M+H]^+$, 401.9655; Found 401.9648.

3-(dimethylamino)-N-tosylbenzamide (3p)



3p

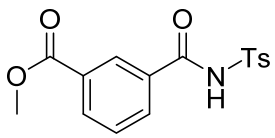
Starting from 3-(dimethylamino)benzoic acid (1.0 g, 3.75 mmol), by following general procedure A, *N*-tosylbenzamide **3p** was obtained as a white solid (0.62 g, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.09 (s, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 10.9 Hz, 1H), 2.96 (s, 6H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 150.9, 145.2, 135.8, 132.1, 129.7, 129.6, 128.8, 117.1, 114.8, 111.4, 40.5, 21.8.

ESI-MS: calculated $C_{16}H_{18}N_2O_3S$ $[M+H]^+$, 319.1111; Found 319.1107.

methyl 3-(tosylcarbamoyl)benzoate (3j)



3j

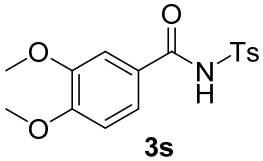
Starting from 3-(methoxycarbonyl)benzoic acid (1.0 g, 5.56 mmol), by following general procedure A, *N*-tosylbenzamide **3j** was obtained as a white solid (0.35 g, 19% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.53 (s, 1H), 8.18 (dt, *J* = 7.8, 1.4 Hz, 1H), 8.11 – 7.99 (m, 3H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.86 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.8, 145.4, 135.5, 134.2, 132.6, 131.8, 130.9, 129.7, 129.3, 128.9, 128.8, 52.6, 21.8.

ESI-MS: calculated $C_{16}H_{15}NO_5S$ $[M+H]^+$, 334.0744; Found 334.0738.

3,4-dimethoxy-N-tosylbenzamide (3s)



3s

Starting from 3,4-dimethoxybenzoic acid (1.0 g, 5.49 mmol), by following general procedure A, *N*-tosylbenzamide **3s** was obtained as a white solid (0.46 g, 25% yield).

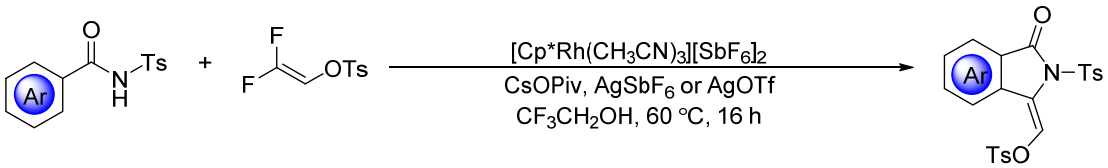
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.88 (d, *J* = 1.3 Hz, 3H), 3.82 (d, *J* = 1.3 Hz, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 153.6, 149.2, 145.2, 135.8, 129.7, 128.7, 123.6, 121.8, 110.9, 110.6, 56.2, 56.2, 21.8.

ESI-MS: calculated $C_{16}H_{17}NO_5S$ $[M+H]^+$, 336.0900; Found 336.0899.

III. Synthesis and characterization of 3-alkylidene isoindolinones and compound 5

i. Synthesis and characterization of 3-alkylidene isoindolinones

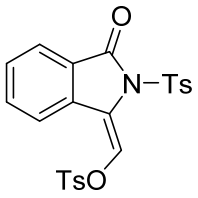


3 1 4

General procedure B: To an oven-dried Schlenk tube charged with a stirring bar, were added *N*-tosylbenzamide **3** (0.2 mmol, 1.0 equiv), 2,2-difluorovinyl tosylate **1** (70.2 mg, 0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol, 5 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) or AgOTf (10.3 mg, 0.04 mmol, 20 mol %) and CsOPiv (47.0 mg, 0.2 mmol, 1.0 equiv) in the glove box. The tube

was then moved out and 2,2,2-trifluoroethanol (TFE) (1.0 mL) was added under N_2. The mixture was stirred at 60 °C for 16 h. The reaction mixture was diluted with dichloromethane and the volatiles were removed under reduced pressure. The pure product was obtained by flash chromatography (silica gel; petroleum ether/ dichloromethane).

(E)-(3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4a)



4a

Following general procedure B using $AgSbF_6$ as additive, **4a** was obtained in 83% yield (78.1 mg, 0.167 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

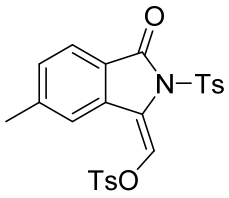
R_F (Petroleum ether/ dichloromethane 1:2): 0.18.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 4H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.65 (td, *J* = 7.7, 1.2 Hz, 1H), 7.47 (td, *J* = 7.6, 0.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 146.4, 145.9, 135.3, 134.9, 134.4, 131.9, 130.5, 130.3, 130.0, 128.4, 128.3, 127.4, 126.5, 126.3, 125.4, 124.7, 21.9, 21.9.

ESI-MS: calculated $C_{23}H_{19}NO_6S_2$ $[M+H]^+$, 470.0727; Found 470.0723.

(E)-(6-methyl-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4b)



4b

Following general procedure B using AgOTf as additive, **4b** was obtained in 72% yield (70.0 mg, 0.145 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

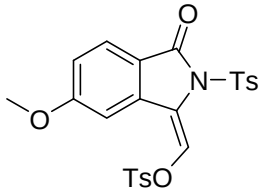
R_F (Petroleum ether/ dichloromethane 1:2): 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (t, *J* = 8.2 Hz, 4H), 7.79 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 3H), 2.45 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 146.4, 146.2, 145.8, 135.2, 134.6, 131.8, 131.5, 130.4, 129.9, 128.4, 128.2, 127.1, 126.4, 125.5, 124.5, 124.0, 22.5, 21.9, 21.8.

ESI-MS: calculated $C_{24}H_{21}NO_6S_2$ $[M+H]^+$, 484.0883; Found 484.0878.

(E)-(6-methoxy-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonatel (4c)



4c

Following general procedure B using AgOTf as additive, **4c** was obtained in 61% yield (61.4 mg, 0.123 mmol) as a white solid after column chromatography (eluent = Petroleum ether/dichloromethane 1:1 v/v).

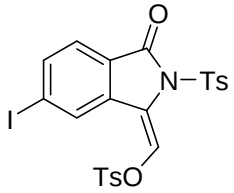
R_F (Petroleum ether/ dichloromethane 1:2): 0.50.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 (t, *J* = 8.6 Hz, 4H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.97 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.86 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 163.9, 146.5, 145.8, 136.6, 135.2, 131.8, 130.4 (2C), 129.9 (2C), 128.3 (2C), 128.1 (2C), 127.3, 126.4, 126.3, 119.0, 118.0, 108.9, 55.9, 21.9, 21.8.

ESI-MS: calculated $C_{24}H_{21}NO_7S_2$ $[M+H]^+$, 500.0832; Found 500.0834.

(E)-(6-iodo-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4d)



4d

Following general procedure B using AgOTf as additive, **4d** was obtained in 51% yield (61.1 mg, 0.102 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

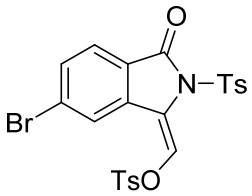
R_F (Petroleum ether/ dichloromethane 1:1): 0.20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.05 (s, 1H), 7.90 (dd, *J* = 8.4, 2.0 Hz, 4H), 7.79 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 145.5, 145.0, 138.3, 134.3, 133.8, 133.0, 130.6, 129.4, 128.9, 127.2, 127.1, 126.9, 124.6, 123.8, 101.3, 20.8, 20.7.

ESI-MS: calculated $C_{23}H_{18}INO_6S_2$ $[M+H]^{+,}$ 595.9693; Found 595.9697.

(E)-(6-bromo-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4e)



4e

Following general procedure B using AgOTf as additive, **4e** was obtained in 81% yield (88.0 mg, 0.160 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

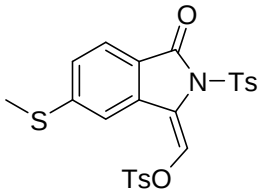
R_F (Petroleum ether/ dichloromethane 1:1): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.06 (s, 1H), 7.91 (dd, *J* = 8.4, 2.4 Hz, 4H), 7.64 – 7.55 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 146.6, 146.2, 135.6, 134.9, 133.6, 131.7, 130.6, 130.0, 129.9, 128.4, 128.3, 128.2, 128.2, 125.9, 125.2, 125.1, 21.9, 21.9.

ESI-MS: calculated $C_{23}H_{18}BrNO_6S_2$ $[M+H]^+$, 547.9832; Found 547.9828.

(E)-(6-(methylthio)-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4f)



4f

Following general procedure B using AgOTf as additive, **4f** was obtained in 35% yield (36.4 mg, 0.071 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

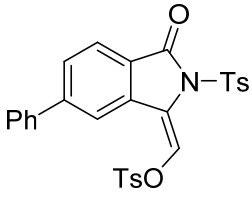
R_F (Petroleum ether/ dichloromethane 1:2): 0.19.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (dd, *J* = 8.4, 2.8 Hz, 4H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 2.52 (s, 3H), 2.47 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 148.9, 146.5, 145.9, 135.2, 135.1, 131.8, 130.5, 129.9, 128.4, 128.2, 127.4, 127.3, 126.3, 124.5, 122.6, 120.4, 21.9, 21.9, 15.1.

ESI-MS: calculated $C_{24}H_{21}NO_6S_3$ $[M+H]^+$, 516.0604; Found 516.0601.

(E)-(3-oxo-6-phenyl-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4g)



4g

Following general procedure B using AgOTf as additive, **4g** was obtained in 62% yield (68 mg, 0.125mmol) as a white

solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

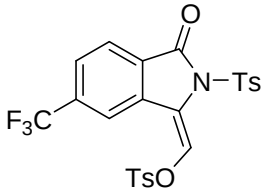
R_F (Petroleum ether/ dichloromethane 1:2): 0.38.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.4 Hz, 1H), 8.09 (s, 1H), 7.93 (dd, *J* = 14.9, 8.4 Hz, 4H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 – 7.42 (m, 5H), 7.33 (t, *J* = 8.4 Hz, 4H), 2.43 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 148.1, 146.4, 145.9, 139.5, 135.2, 135.0, 132.0, 130.4, 129.9, 129.4, 129.2, 128.8, 128.3, 128.2, 127.5, 127.3, 126.5, 125.1, 125.0, 123.7, 21.8, 21.8.

ESI-MS: calculated $C_{29}H_{23}NO_6S_2$ $[M+H]^+$, 546.1040; Found 546.1034.

(E)-(3-oxo-2-tosyl-6-(trifluoromethyl)isoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4h)



4h

Following general procedure B using AgOTf as additive, **4h** was obtained in 68% yield (73.6 mg, 0.137 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

R_F (Petroleum ether/ dichloromethane 1:1): 0.4.

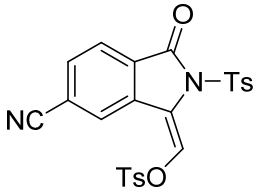
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.4 Hz, 1H), 8.14 (s, 1H), 7.99 – 7.84 (m, 5H), 7.70 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.36 (dd, *J* = 19.2, 8.1 Hz, 4H), 2.44 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 146.7, 146.4, 136.3 (q, *J* = 32.8 Hz),134.8, 134.4, 131.8, 130.5, 130.1, 129.2, 128.4, 128.4, 128.3, 127.0 (q, *J* = 3.6 Hz),125.4, 123.2 (q, *J* = 273.4 Hz), 122.3 (t, *J* = 4.1 Hz), 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94.

ESI-MS: calculated $C_{24}H_{18}F_3NO_6S_2$ $[M+H]^+$, 538.0600; Found 538.0588.

(E)-(6-cyano-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4i)



4i

Following general procedure B using $AgSbF_6$ as additive, **4i** was obtained in 62% yield (60.6 mg, 0.123 mmol) as a

white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

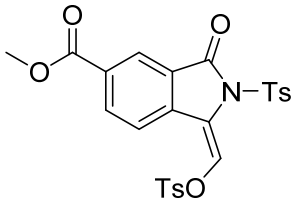
R_F (Petroleum ether/ dichloromethane 1:2): 0.25.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.15 (s, 1H), 7.93 (dd, *J* = 8.4, 3.0 Hz, 4H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.71 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 146.9, 146.5, 134.6, 134.4, 133.2, 131.6, 130.6, 130.1, 129.5, 129.1, 128.4, 128.3, 125.5, 124.4, 118.2, 117.4, 21.9, 21.9.

ESI-MS: calculated $C_{24}H_{18}N_2O_6S_2$ $[M+H]^+$, 495.0679; Found 495.0666.

(E)-3-oxo-2-tosyl-1-((tosyloxy)methylene)isoindoline-5-carboxylate (4j)



4j

Following general procedure B using $AgSbF_6$ as additive, **4j** was obtained in 66% yield (69.8 mg, 0.132 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

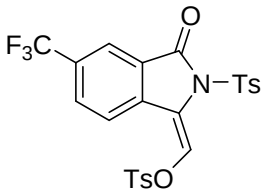
R_F (Petroleum ether/ dichloromethane 1:3): 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H), 8.29 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.16 – 8.04 (m, 2H), 7.92 (dd, *J* = 8.4, 2.1 Hz, 4H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 163.5, 146.7, 146.2, 137.5, 135.6, 134.9, 132.0, 131.7, 130.6, 130.0, 128.8, 128.4, 128.4, 126.8, 126.1, 125.5, 125.4, 52.8, 21.9, 21.9.

ESI-MS: calculated $C_{25}H_{21}NO_8S_2$ $[M+H]^+$, 528.0781; Found 528.0771.

(E)-(3-oxo-2-tosyl-5-(trifluoromethyl)isoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4k)



4k

Following general procedure B using AgOTf as additive, **4k** was obtained in 65% yield (69.4 mg, 0.129 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

R_F (Petroleum ether/ dichloromethane 1:2): 0.46.

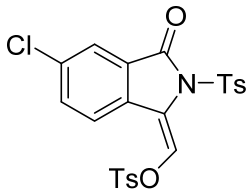
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 8.12 (s, 1H), 8.01 (d, *J* = 1.5 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 4H), 7.87 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 146.7, 146.3, 136.8, 134.6, 132.4 (q, *J* = 33.6 Hz),131.5,131.3 (q, *J* = 3.2 Hz),130.5, 129.9, 128.9, 128.3, 126.9, 125.9, 125.0, 123.1 (q, *J* = 272.8 Hz),122.0 (q, *J* = 4.0 Hz), 21.8, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84.

ESI-MS: calculated $C_{24}H_{18}F_3NO_6S_2$ $[M+H]^+$, 538.0600; Found 538.0594.

(E)-(5-chloro-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4l)



4l

Following general procedure B using $AgSbF_6$ as additive, **4l** was obtained in 65% yield (72.5 mg, 0.144 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

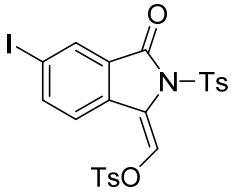
R_F (Petroleum eter/ dichloromethane 1:2): 0.56.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 4H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 146.6, 146.2, 136.6, 135.0, 134.8, 132.4, 131.6, 130.5, 130.0, 128.3, 128.3, 128.0, 127.7, 126.5, 125.5, 124.6, 21.9, 21.9.

ESI-MS: calculated $C_{23}H_{18}ClNO_6S_2$ $[M+H]^+$, 504.0337; Found 504.0324.

(E)-(5-iodo-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4m)



4m

Following general procedure B using $AgSbF_6$ as additive, **4m** was obtained in 67% yield (79.3 mg, 0.133 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

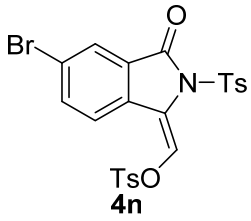
R_F (Petroleum ether/ dichloromethane 1:2): 0.38.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.90 (ddd, *J* = 11.6, 8.4, 2.4 Hz, 5H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 146.6, 146.2, 143.5, 134.8, 133.6, 133.4, 131.6, 130.5, 130.0, 128.3, 128.3, 128.1, 127.9, 126.6, 125.7, 95.7, 21.9, 21.8.

ESI-MS: calculated $C_{23}H_{18}INO_6S_2$ $[M+H]^+$, 595.9693; Found 595.9684.

(E)-(5-bromo-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4n)



4n

Following general procedure B using $AgSbF_6$ as additive, **4n** was obtained in 77% yield (84.2 mg, 0.154 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

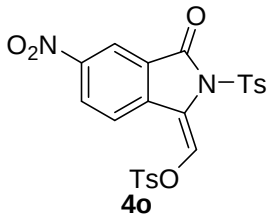
R_F (Petroleum ether/ dichloromethane 1:2): 0.61.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.95 – 7.84 (m, 6H), 7.73 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 146.6, 146.2, 137.8, 134.9, 132.9, 131.8, 130.5, 130.0, 128.3, 128.3, 128.2, 127.8, 127.6, 126.7, 125.6, 124.5, 21.9, 21.8.

ESI-MS: calculated $C_{23}H_{18}BrNO_6S_2$ $[M+H]^+$, 547.9832; Found 547.9821.

(E)-(5-nitro-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4o)



4o

Following general procedure B using $AgSbF_6$ as additive, **4o** was obtained in 51% yield (52.4 mg, 0.102 mmol) as a light yellow solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

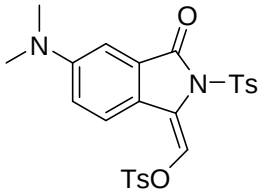
R_F (Petroleum ether/ dichloromethane 1:2): 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.1 Hz, 1H), 8.47 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.20 (d, *J* = 9.7 Hz, 2H), 7.98 – 7.88 (m, 4H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 2.48 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 148.7, 147.0, 146.6, 138.6, 134.5, 131.5, 130.7, 130.2, 130.1, 129.3, 128.5, 128.4, 127.7, 126.4, 124.6, 120.3, 22.0, 21.9.

ESI-MS: calculated $C_{23}H_{18}N_2O_8S_2$ $[M+H]^+$, 515.0577; Found 515.0570.

(E)-(5-(dimethylamino)-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4p)



4p

Following general procedure B using $AgSbF_6$ as additive, **4p** was obtained in 37% yield (37.6 mg, 0.074 mmol) as a yellow-green solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

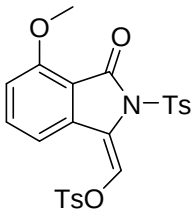
R_F (Petroleum ether/ dichloromethane 1:2): 0.27.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.74 (m, 6H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.22 (m, 2H), 6.95 – 6.80 (m, 2H), 2.99 (s, 6H), 2.44 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 151.6, 146.0, 145.6, 135.4, 132.0, 130.3, 129.8, 128.4, 128.2, 127.9, 127.4, 126.2, 124.2, 122.0, 118.6, 105.3, 40.4, 21.9, 21.8.

ESI-MS: calculated $C_{25}H_{24}N_2O_6S_2$ $[M+H]^+$, 513.1149; Found 513.1141.

(E)-(4-methoxy-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4q)



4q

Following general procedure B using $AgSbF_6$ as additive, **4q** was obtained in 32% yield (31.7 mg, 0.064 mmol) as a white solid after column chromatography (eluent = dichloromethane).

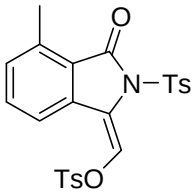
R_F (Petroleum ether/ dichloromethane 1:2): 0.10.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 4H), 7.67 – 7.49 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 158.3, 146.4, 145.7, 136.6, 136.3, 135.2, 131.8, 130.4, 129.8, 128.4, 128.4, 127.2, 125.8, 117.3, 113.5, 112.2, 56.2, 21.9, 21.8.

ESI-MS: calculated $C_{24}H_{21}NO_7S_2$ $[M+H]^+$, 500.0828; Found 500.0832.

(E)-(4-methyl-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4r)



4r

Following general procedure B using $AgSbF_6$ as additive, **4r** was obtained in 28% yield (27.5 mg, 0.056 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ dichloromethane 1:1 v/v).

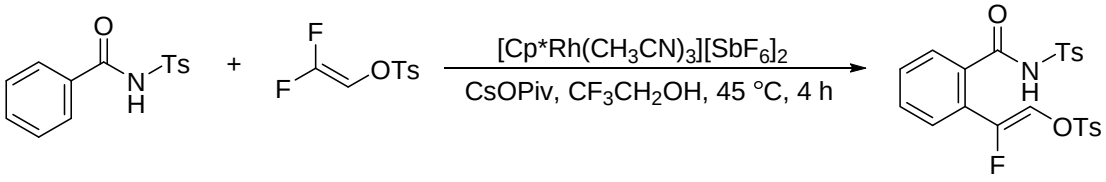
R_F (Petroleum ether/ dichloromethane 1:3): 0.41.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.89 (t, *J* = 9.3 Hz, 5H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 2.56 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 146.3, 145.8, 139.4, 135.3, 134.8, 134.3, 132.3, 131.9, 130.4, 129.9, 128.4, 128.3, 126.7, 126.0, 123.7, 122.9, 21.9, 21.9, 17.9.

ESI-MS: calculated $C_{24}H_{21}NO_6S_2$ $[M+H]^+$, 484.0883; Found 484.0872.

ii. Synthesis and characterization of compound 5

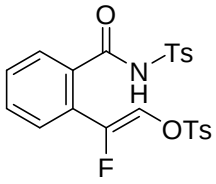


3a **1** **5**

To an oven-dried Schlenk tube charged with a stirring bar, were added *N*-tosylbenzamide **3** (0.2 mmol, 1.0 equiv), 2,2-difluorovinyl tosylate **1** (70.2 mg, 0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol, 5 mol %) and CsOPiv (47.0 mg, 0.2 mmol, 1.0 equiv) in the glove box. The tube was then moved out and 2,2,2-trifluoroethanol (TFE) (1.0 mL) was added under N_2. The mixture was stirred at 45 °C for 4 h. The reaction mixture was diluted with dichloromethane and the volatiles were removed under reduced pressure. The pure product was obtained by flash chromatography (silica gel; petroleum ether/ dichloromethane).

Compound **5** was obtained as dark red viscous oil (210.5 mg, 0.448mmol, 86%).

R_F (Petrom ether/ethyl ether /AcOH 2v/1v/1d):0.29.



5

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.86 – 7.79 (m, 2H), 7.59 – 7.23 (m, 9H), 2.46 (d, J = 2.1 Hz, 6H).

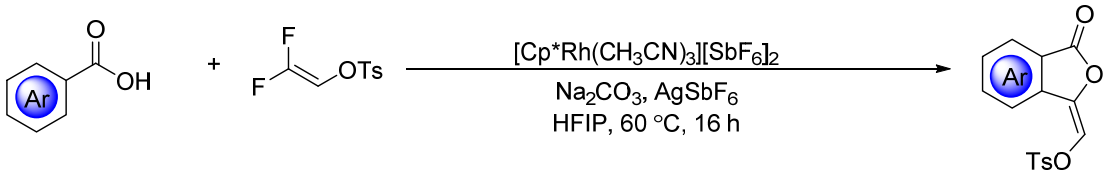
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, δ 149.8 (d, J = 258.2 Hz), 146.0, 145.5, 135.0, 132.4, δ 132.2 (d, J = 35.2 Hz), 132.1, 131.6, 130.7, 130.3, 130.2, 129.8, 129.7, 128.9 (d, J = 4.3 Hz), 128.3, 128.2, 126.4, 120.8 (d, J = 13.4 Hz), 21.9, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.45.

ESI-MS: calculated $C_{23}H_{20}FNO_6S_2$ $[M+H]^+$, 490.0789; Found 490.0801.

IV. Synthesis and characterization of 3-alkylidene isobenzofuranones and compound 8

i. Synthesis and characterization of 3-alkylidene isobenzofuranones

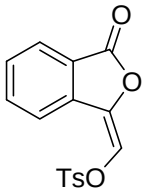


6 **1** **7**

General procedure C: To an oven-dried Schlenk tube charged with a stirring bar, were added acid **6** (0.2 mmol, 1.0 equiv), 2,2-difluorovinyl 4-methylbenzenesulfonate **1** (70.2 mg, 0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol, 5 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10 mol %) and Na_2CO_3 (21.0 mg, 0.2 mmol 1.0 equiv) in the glove box. Then the tube was then transferred out and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (1.0 mL) was added. The mixture was stirred at 60 °C for 16 h. The crude reaction was diluted with dichloromethane, the volatiles were removed and the

analytically pure product was obtained by flash chromatography (silica; petroleum ether/EtOAc).

(E)-(3-oxoisobenzofuran-1(3H)-ylidene)methyl 4-methylbenzenesulfonate (7a)



7a

Following general procedure C, **7a** was obtained in 75% yield (47.4 mg, 0.150 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

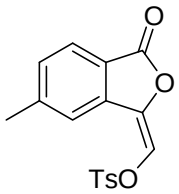
R_F (Petroleum ether/ EtOAc 8:1): 0.21.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.9, 5.0 Hz, 4H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz,2H), 7.11 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 146.4, 142.1, 136.2, 135.0, 131.5, 130.9, 130.3, 128.2, 125.6, 124.4, 123.9, 123.5, 21.7.

ESI-MS: calculated $C_{16}H_{12}O_5S$ $[M+H]^+$, 317.0478; Found 317.0471.

(E)-(6-methyl-3-oxoisobenzofuran-1(3H)-ylidene)methyl 4-methylbenzenesulfonate (7b)



7b

Following general procedure C, **7b** was obtained in 82% yield (54.0 mg, 0.164 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

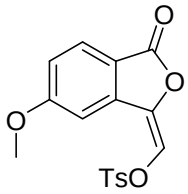
R_F (Petroleum ether/ EtOAc 8:1): 0.22.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 3H), 7.07 (s, 1H), 2.48 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 146.5, 146.4, 142.3, 136.8, 132.2, 131.7, 130.4, 128.4, 125.4, 124.2, 123.4, 122.1, 22.3, 21.9.

ESI-MS: calculated $C_{17}H_{14}O_5S$ $[M+H]^+$, 331.0635; Found 331.0638.

(E)-(6-methoxy-3-oxoisobenzofuran-1(3H)-ylidene)methyl 4-methylbenzenesulfonate (7c)



7c

Following general procedure C, **7c** was obtained in 82% yield (51.9 mg, 0.150 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

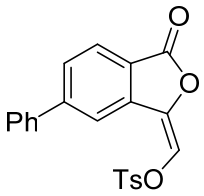
R_F (Petroleum ether/ EtOAc 4:1): 0.23.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.06 (q, *J* = 3.1, 2.1 Hz, 2H), 3.90 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 165.3, 146.5, 142.2, 138.8, 131.7, 130.4, 128.3, 127.2, 123.5, 119.0, 117.0, 107.3, 56.1, 21.9.

ESI-MS: calculated $C_{17}H_{14}O_6S$ $[M+H]^+$, 347.0584; Found 347.0578.

(E)-(3-oxo-6-phenylisobenzofuran-1(3H)-ylidene)methyl 4-methylbenzenesulfonate (7d)



7d

Following general procedure C, **7d** was obtained in 53% yield (41.2 mg, 0.106 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

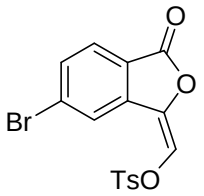
R_F (Petroleum ether/ EtOAc 8:1): 0.22.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.53 (ddd, *J* = 19.2, 13.7, 7.1 Hz, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 148.5, 146.5, 142.4, 139.3, 137.1, 131.8, 130.4, 130.2, 129.3, 129.1, 128.3, 127.7, 126.0, 123.7, 123.2, 122.3, 21.9.

ESI-MS: calculated $C_{22}H_{16}O_5S$ $[M+H]^+$, 393.0791; Found 393.0788.

(E)-(6-bromo-3-oxoisobenzofuran-1(3H)-ylidene)methyl 4-methylbenzenesulfonate (7e)



7e

Following general procedure C, **7e** was obtained in 63% yield (49.6 mg, 0.126 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

R_F (Petroleum ether/ EtOAc 8:1): 0.22 .

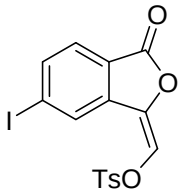
^{1}H NMR (400 MHz, $CDCl_3$ δ 7.93 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 146.7, 140.8, 137.8, 134.4, 131.6, 130.5, 130.3, 128.4, 127.0, 126.9, 124.6, 123.3, 21.9.

ESI-MS: calculated $C_{16}H_{11}BrO_5S$ $[M+H]^+$, 394.9583; Found 394.9550.

(E)-(6-iodo-3-oxoisobenzofuran-1(3H)-ylidene)methyl

4-methylbenzenesulfonate (7f)



7f

Following general procedure C, **7f** was obtained in 49% yield (43 mg, 0.098 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

R_F (Petroleum ether/ EtOAc 8:1): 0.28.

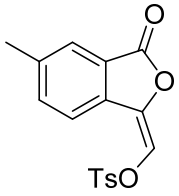
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.88 (t, *J* = 6.6 Hz, 3H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 1H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 146.7, 140.7, 140.1, 137.6, 132.9, 131.5, 130.5, 128.3, 126.7, 124.5, 123.8, 102.9, 21.9.

ESI-MS: calculated $C_{16}H_{11}IO_5S$ $[M+H]^+$, 442.9445; Found 442.9456.

(E)-(5-methyl-3-oxoisobenzofuran-1(3H)-ylidene)methyl

4-methylbenzenesulfonate (7g)



7g

Following general procedure C, **7g** was obtained in 60% yield (39.7 mg, 0.120 mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

R_F (Petroleum ether/ EtOAc 8:1): 0.21.

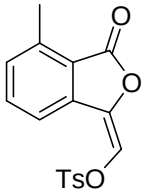
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 2.46 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 146.4, 142.5, 141.8, 136.2, 133.9, 131.7, 130.4 (2C), 128.4 (2C), 125.6, 124.8, 123.8, 122.8, 21.8, 21.7.

ESI-MS: calculated $C_{17}H_{14}O_5S$ $[M+H]^+$, 331.0635; Found 331.0631.

(E)-(4-methyl-3-oxoisobenzofuran-1(3H)-ylidene)methyl

4-methylbenzenesulfonate (7h)



7h

Following general procedure C, **7h** was obtained in 40% yield (26.4mg, 0.080mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

R_F (Petroleum ether/ EtOAc 8:1): 0.28.

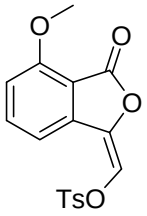
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.56 (q, *J* = 7.9 Hz, 1H), 7.34 (dt, *J* = 14.8, 7.7 Hz, 3H), 7.08 (s, 1H), 2.65 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 146.4, 142.1, 139.9, 136.7, 134.8, 132.6, 131.7, 130.4, 128.4, 123.2, 122.2, 121.6, 21.9, 17.5.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 146.4, 142.0, 139.9, 136.6, 134.7, 132.6, 131.6, 130.4, 128.3, 123.1, 122.1, 121.6, 21.9, 17.5.

ESI-MS: calculated $C_{17}H_{14}O_5S$ $[M+H]^+$, 331.0635; Found 331.0627.

(E)-(4-methoxy-3-oxoisobenzofuran-1(3H)-ylidene)methyl 4-methylbenzenesulfonate (7i)



7i

Following general procedure C, **7i** was obtained in 57% yield (39.2mg, 0.114mmol) as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 8:1 v/v).

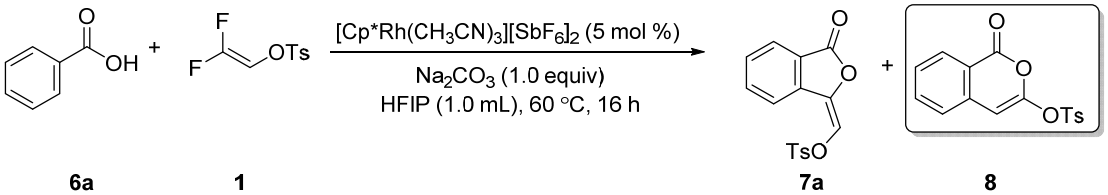
R_F (Petroleum ether/ EtOAc 2:1): 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.07 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 158.4, 146.4, 141.7, 138.4, 137.3, 131.6, 130.3, 128.3, 123.6, 115.9, 112.7, 111.7,56.3, 21.8.

ESI-MS: calculated $C_{17}H_{14}O_6S$ $[M+H]^+$, 347.0584; Found 347.0576.

ii. Synthesis and characterization of compound 8



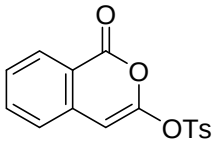
6a **1** **7a** **8**

In an oven-dried Schlenk tube with a stirring bar, acid **6a** (0.2 mmol, 1.0 equiv), 2,2-difluorovinyl 4-methylbenzenesulfonate **1** (70.2 mg, 0.3 mmol, 1.5 equiv) and $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol, 5 mol %), Na_2CO_3 (21.0 mg, 0.2

mmol 1.0 equiv) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (1.0 mL) were added under air. The mixture was stirred at 60 °C for 16 h. The crude reaction was diluted with dichloromethane, the volatiles were removed and the analytically pure product **8** was obtained by flash chromatography (silica; petroleum ether/EtOAc).

To an oven-dried Schlenk tube charged with a stirring bar, were added acid **6** (0.2 mmol, 1.0 equiv), 2,2-difluorovinyl 4-methylbenzenesulfonate **1** (70.2 mg, 0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol, 5 mol %) and Na_2CO_3 (21.0 mg, 0.2 mmol 1.0 equiv) in the glove box. Then the tube was then transferred out and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (1.0 mL) was added. The mixture was stirred at 60 °C for 16 h. The crude reaction was diluted with dichloromethane, the volatiles were removed and the analytically pure product **8** was obtained by flash chromatography (silica; petroleum ether/EtOAc).

1-oxo-1H-isochromen-3-yl 4-methylbenzenesulfonate (8)



8

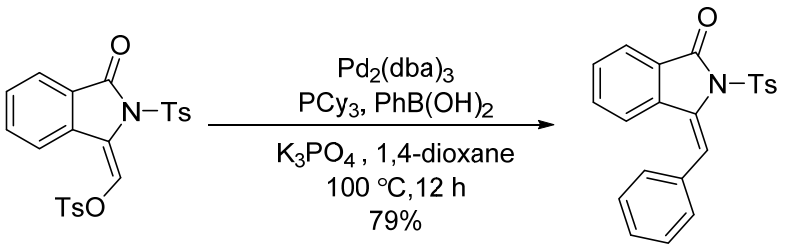
Compound **8** was obtained in 18% yield as a white solid after column chromatography (eluent = Petroleum ether/ EtOAc 16:1 v/v).

R_F (Petroleum ether/ EtOAc 8:1): 0.40.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.82 (m, 3H), 7.77 – 7.66 (m, 1H), 7.62 – 7.52 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 146.2, 137.8, 137.7, 134.9, 132.2, 130.6, 130.2, 128.3, 126.1, 124.0, 119.6, 116.7, 21.9.

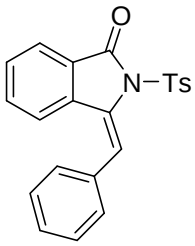
V. Derivatization of 3-alkylidene isoindolinone 4a



4a **9**

(*E*)-3-benzylidene-2-tosylisoindolin-1-one (9)[4]

To a 10.0 mL of sealed tube charged with **4a** (52.9 mg, 0.1 mmol, 1.0 equiv), were added PCy_3 (2.8 mg, 10 mmol %), (4-methoxyphenyl)boronic acid (41.4 mg, 3.0 equiv), Pd_2dba_3 (4 mg, 5 mol %) and K_3PO_4 (36 mg, 1.7 equiv) in the glove box. The tube was then removed out and and 1.6-dioxane (1.0 mL) was added under Ar. The reaction mixture was stirred at 100 °C for 12 h. After that, the resulting mixture was cooled to room temperature and concentrated in *vacuo*. The residue was purified with flash column chromatography (Petroleum ether/ EtOAc 3:1 v/v).



9

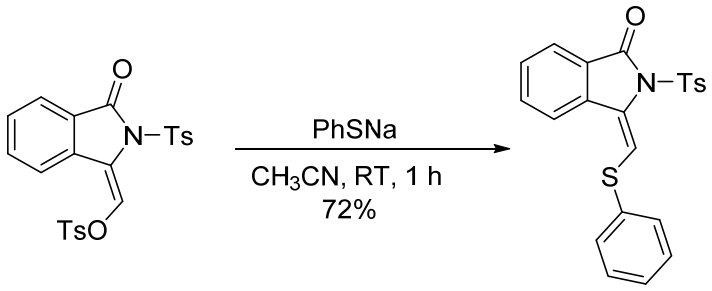
Compound **9** was obtained in 79% yield (30.0 mg, 0.079 mmol) as a white solid after column chromatography.

R_F (Petroleum ether/ EtOAc 4:1): 0.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.03 (d, *J* = 5.2 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.33 (m, 8H), 7.33 – 7.27 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 145.5, 136.4, 136.1, 135.4, 133.8, 133.5, 129.9, 129.7, 129.1, 129.1, 128.4, 128.2, 127.6, 124.5, 124.1, 118.2, 21.8.

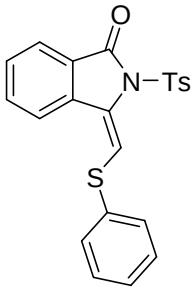
ESI-MS: calculated $C_{22}H_{17}NO_3S$ $[M+H]^+$, 376.1002; Found 376.0995.



4a **10**

(E)-3-((phenylthio)methylene)-2-tosylisoindolin-1-one (10)

To a 10.0 mL tube charged with a stirring bar, were added **4a** (15 mg, 0.032 mmol,1.0 equiv), PhSNa (10.6 mg, 0.08mmol, 2.5 equiv) and CH_3CN (1.0 mL). The vial was sealed with a PTFE lined cap and stirred at room temperature for 1 h. The solvent was then removed in *vacuo* and the residue was further purified with flash column chromatography (Petroleum ether/ EtOAc 6:1 v/v) to give the titled compound as a yellow-green solid (9.4 mg, 72%).



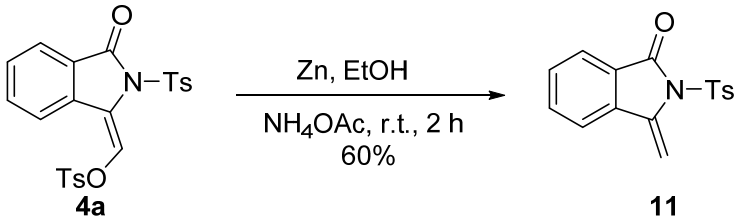
10

R_F (Petroleum ether/ EtOAc 4:1): 0.42.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.91 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 145.6, 136.1, 135.9, 134.8, 134.4, 129.9, 129.7, 129.3, 129.3, 128.3, 127.9, 126.9, 124.9, 124.8, 115.8, 21.9.

ESI-MS: calculated $C_{22}H_{17}NO_3S_2$ $[M+H]^+$, 408.0723; Found 408.0717.

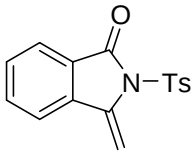


4a **11**

3-methylene-2-tosylisoindolin-1-one (11)

To a 10.0 mL tube charged with **4a** (15 mg, 0.032 mmol,1.0 equiv), Zn (56 mg, 0.896 mmol, 28.0 equiv) and EtOH (0.5 mL), was added a solution of NH_4OAc (0.3 mL, 1M). The vial was sealed with a PTFE lined cap and stirred at room

temperature for 2 h. The solvent was then removed in *vacuo* and the residue was further purified with flash column chromatography (Petroleum ether/ EtOAc 3:1 v/v) to give the titled compound as a white solid (5.7 mg, 60%).



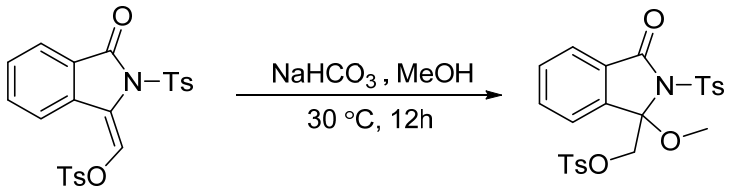
11

R_F (Petroleum ether/ EtOAc 3:1): 0.50.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.54 – 7.40 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.20 (d, *J* = 2.1 Hz, 1H), 5.54 (d, *J* = 2.2 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 145.5, 138.1, 137.6, 135.9, 134.3, 130.2, 129.9, 128.2, 126.5, 124.5, 120.2, 96.8, 21.8.

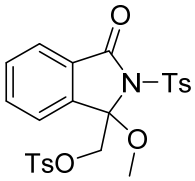
ESI-MS: calculated $C_{16}H_{13}NO_3S$ $[M+H]^+$, 300.0689; Found 300.0683



4a **12**

(1-methoxy-3-oxo-2-tosylisoindolin-1-yl)methyl 4-methylbenzenesulfonate (12)

To a 10.0 mL tube charged with **4a** (15.0 mg, 0.032 mmol,1.0 equiv), $NaHCO_3$ (21.0 mg, 0.256 mmol, 8.0 equiv), was added MeOH (1.0 mL). The tube was sealed with a PTFE lined cap and stirred at 30 °C for 12 h. The solvent was removed in *vacuo* and the residue was further purified with flash column chromatography (Petroleum ether/ EtOAc 3:1 v/v) to give the titled compound as a white solid (16.1 mg, 96%).



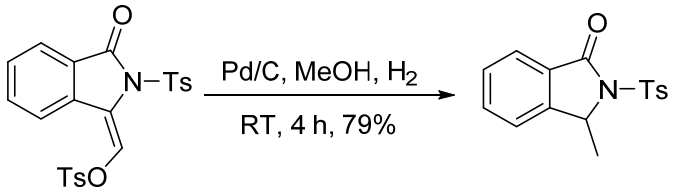
12

R_F (Petroleum ether/ EtOAc 2:1): 0.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.53 (dd, *J* = 9.7, 7.9 Hz, 3H), 7.33 (dd, *J* = 7.8, 5.7 Hz, 3H), 7.25 (d, *J* = 6.9 Hz, 2H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.74 (d, *J* = 10.1 Hz, 1H), 2.91 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 145.5, 145.3, 141.0, 135.8, 134.7, 132.3, 131.2, 130.0, 129.8, 129.5, 129.2, 128.0, 124.9, 123.1, 96.9, 69.4, 51.8, 21.9.

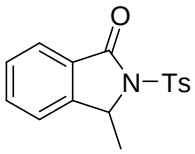
ESI-MS: calculated $C_{24}H_{23}NO_7S_2$ $[M+Na]^+$, 524.0808; Found 524.0815.



4a **13**

3-methyl-2-tosylisoindolin-1-one (13)

To a 10.0 mL tube charged with **4a** (15 mg, 0.032 mmol), were added Pd/C (3.6 mg, 0.006 mmol, 20 mol%) and MeOH (0.5 mL). The tube was evacuated and refilled with hydrogen for three times. The suspension was stirred at room temperature for 4 h and then filtered through a pad of Celite and concentrated. The residue was purified with flash column chromatography (Petroleum ether/ EtOAc 7:1 v/v) to give the titled compound as a white solid (7.6 mg, 79%).



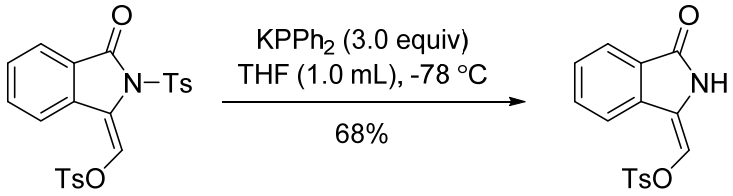
13

R_F (Petroleum ether/ EtOAc 6:1): 0.49.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.44 (q, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.30 (q, *J* = 6.6 Hz, 1H), 2.41 (s, 3H), 1.78 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 147.5, 145.1, 136.4, 134.2, 129.7, 129.0, 128.9, 128.4, 125.1, 122.6, 58.8, 21.8, 21.6.

ESI-MS: calculated $C_{16}H_{15}NO_3S$ $[M+H]^+$, 302.0845; Found 302.0849.

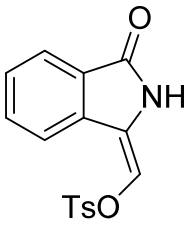


4a **14**

(E)-(3-oxoisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (14)

To a solution of (E)-(3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate **4a** (15.0 mg, 0.032 mmol,1.0 equiv) in THF (1.0 mL) was added potassium diphenylphosphide (0.50 M THF solution, 0.20 mL, 3.0 equiv) at –78 °C. The reaction mixture was stirred for 2 h at the same

temperature. Dilute hydrochloric acid (1.0 M, 0.75 mL) was then added to the reaction mixture and the temperature was raised to room temperature. The resulting mixture was stirred for 30 min. Saturated aqueous $NaHCO_3$ (10.0 mL) was added to the mixture and the mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by silica gel chromatography (hexane/EtOAc = 3:1 v/v) gave 6.8 mg (68%, 0.22 mmol) the titled compound as a white solid.



14

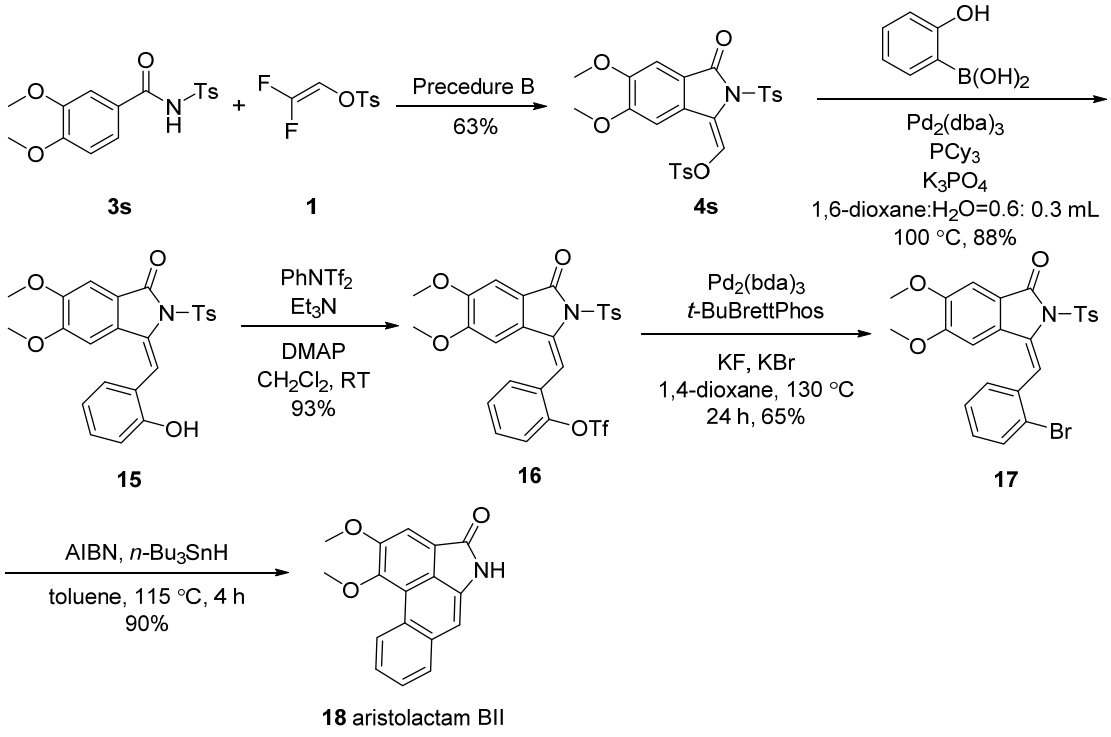
R_F (Petroleum ether/ EtOAc 3:1): 0.23.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.14 (m, 1H), 7.71 (dd, *J* = 7.5, 4.0 Hz, 3H), 7.61 – 7.48 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 1.1 Hz, 1H), 6.19 (s, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 144.9, 144.7, 135.8, 135.6, 135.2, 130.3, 130.1, 129.4, 127.7, 122.4, 120.9, 116.2, 21.7.

ESI-MS: calculated $C_{16}H_{13}NO_4S$ $[M+H]^+$, 316.0638; Found 316.0630.

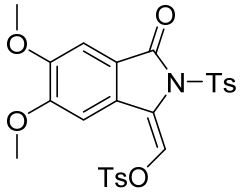
VI. Total synthesis of aristolactam BII



3s **1** **4s** **15** **16** **17**

18 aristolactam BII

(E)-(5,6-dimethoxy-3-oxo-2-tosylisoindolin-1-ylidene)methyl 4-methylbenzenesulfonate (4s)



4s

Following general procedure B, using $AgSbF_6$ as additive and HFIP (1.0 mL) as solvent, **4s** was obtained in 63% yield (66.6 mg, 0.126 mmol) as a white solid after column chromatography (eluent = dichloromethane).

R_F (Petroleum ether/ dichloromethane 1:3): 0.13.

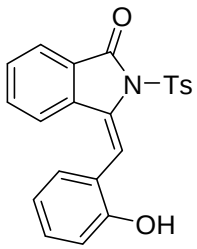
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.83 (m, 5H), 7.46 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.13 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 155.0, 151.6, 146.5, 145.7, 135.3, 131.9, 130.5, 129.9, 129.0, 128.3, 128.1, 126.9, 126.1, 119.4, 106.5, 105.1, 56.5, 56.4, 21.9, 21.8.

ESI-MS: calculated $C_{25}H_{23}NO_8S_2$ $[M+H]^+$, 530.0938; Found 530.0926.

(E)-3-(2-hydroxybenzylidene)-2-tosylisoindolin-1-one (15)[4]

To a 10.0 mL of sealed tube charged a stirring bar, were added **4s** (52.9 mg, 0.1 mmol, 1.0 equiv), PCy_3 (2.8 mg, 0.01 mmol, 10 mol %), (4-methoxyphenyl) boronic acid (41.4 mg, 3.0 equiv), and Pd_2dba_3 (4 mg, 0.005 mmol, 5 mol %). Then the tube was evacuated under reduced pressure and refilled with Ar for three times. After that, K_3PO_4 (36 mg, 1.7 equiv) dissolved in a mixed solvent (dioxane:H_2O=0.6 mL:0.3 mL) was added to the tube under Ar. The tube was sealed again and the reaction mixture was stirred at 100 °C for 12 h. The resulting mixture was cooled to room temperature and concentrated in *vacuo*. The residue was purified with flash column chromatography (Petroleum ether/ EtOAc 3:1 v/v) to give compound **15** as a white solid (40.5 mg, 88%).



15

R_F (Petroleum ether/ EtOAc 2:1):0.28.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.39 – 7.30 (m, 3H), 7.32 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H),

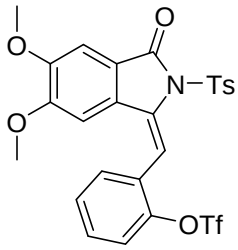
7.11 (s, 1H), 7.05 – 7.02 (m, 1H), 6.99 (td, *J* = 7.4, 1.1 Hz, 1H), 6.35 (s, 1H), 5.47 (s, 1H), 3.84 (s, 3H), 3.45 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 154.3, 153.7, 151.5, 145.5, 136.1, 135.3, 130.6, 130.5, 130.4, 129.9, 128.1, 121.7, 121.0, 120.5, 116.3, 110.0, 105.7, 104.9, 56.4, 55.8, 21.8.

ESI-MS: calculated $C_{24}H_{21}NO_6S$ $[M+H]^+$, 452.1162; Found 452.1154.

(E)-2-((5,6-dimethoxy-3-oxo-2-tosylisoindolin-1-ylidene)methyl)phenyl trifluoromethanesulfonate (16)

To a 10.0 mL tube charged with a stirring bar, were added compound **15** (68.0 mg, 0.171 mmol, 1.0 equiv), $PhNTf_2$ (90 mg, 0.240 mmol, 1.4 equiv), Et_3N (dry, 26.0 mg, 0.260 mmol, 1.5 equiv), DMAP (1.0 mg, 5 mol %) and CH_2Cl_2 (dry, 2.0 mL). The tube was stirred at room temperature for 4 h. Then the mixture was concentrated in *vacuo* and the residue was purified with flash column chromatography (Petroleum ether/ EtOAc 3:1) to give compound **16** as a white solid (92.9 mg, 93%).



16

R_F (Petroleum ether/ EtOAc 2:1):0.30.

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.80 (s, 1H), 7.77 – 7.61 (m, 4H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.16 (s, 1H), 6.23 (s, 1H), 3.88 (s, 3H), 3.41 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 165.0, 155.2, 153.0, 148.6, 146.5, 137.1, 136.5, 133.7, 131.8, 130.6, 130.5, 130.4, 130.3, 128.9, 123.3, 121.0, 108.7, 106.3, 105.6, 56.5, 55.8, 21.6.

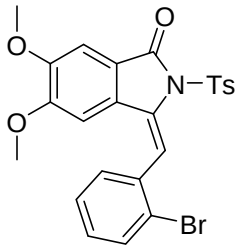
ESI-MS: calculated $C_{25}H_{20}F_3NO_8S_2$ $[M+H]^+$, 584.0655; Found 584.0645.

(E)-3-(2-bromobenzylidene)-5,6-dimethoxy-2-tosylisoindolin-1-one (17)[5]

To a sealed tube (A) equipped with a magnetic stir bar was added compound **16** (58.3 mg, 0.1 mmol, 1.0 equiv), KF (5.8 mg, 0.15 mmol, 1.5 equiv) and KBr (47.6 mg, 0.4 mmol, 4.0 equiv). The tube was sealed with a Teflon-lined septum, evacuated and backfilled with Ar (this process was repeated a total three times).

To another sealed tube (B) equipped with a magnetic stir bar was added $Pd_2(dba)_3$ (14.0 mg, 0.015 mmol, 15 mol %) and *t*-BuBrettPhos (22.0 mg, 0.045

mmol, 45 mol %). The tube was sealed with a Teflon-lined septum, evacuated and backfilled with Ar (this process was repeated a total three times). 1,4-Dioxane (1.0 mL) was added via syringe, and the mixture was heated to at 120 °C in a preheated oil bath for 3 min. After the catalyst solution was cooled to room temperature, it was added to the reaction tube (A) via syringe, followed by addition of 1,4-dioxane (3.0 mL). The resulting mixture was stirred vigorously at 130 °C in a preheated oil bath for 24 h and then cooled to room temperature and concentrated under reduced pressure. The residue was purified with flash column chromatography (Petroleum ether/ EtOAc 3:1 v/v) to give the titled compound as a light yellow solid (26.2 mg, 65%).



17

R_F (Petroleum ether/ EtOAc 3:1): 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H), 7.73 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.15 (s, 1H), 6.14 (s, 1H), 3.86 (s, 3H), 3.42 (s, 3H), 2.41 (s, 3H).

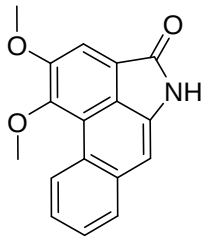
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 154.1, 151.4, 145.3, 136.5, 136.2, 133.9, 133.3, 131.5, 130.6, 129.9, 129.8, 128.2, 127.7, 124.5, 120.6, 115.4, 105.3, 105.0, 56.4, 55.8, 21.8.

ESI-MS: calculated $C_{24}H_{20}BrNO_5S$ $[M+H]^+$, 584.0655; Found 584.0645.

1,2-dimethoxydibenzo[cd,f]indol-4(5H)-one (18) [6a,6b]

To a dry 50.0 mL three-neck round-bottom flask was added compound **17** (25.0 mg, 0.049 mmol) and dry degassed toluene (30.0 mL). The flask was evacuated and filled with Ar for three times. The solution was heated at 115 °C for 20 minutes. To a 10.0 mL round bottom flask was added AIBN (12.0 mg, 1.5 equiv), *n*-Bu_3SnH (113.0 mg, 8.0 equiv) and dry degassed toluene (10.0 mL). The mixture was dropped to the reaction flash containing compound **17** via syringe in 60 minutes. Once addition finished, refluxing was kept up for a further 4 h. The toluene was evaporated under reduced pressure and the residue was further purified with (Petroleum ether/ EtOAc 2:1 v/v) to give a light yellow solid

(12.2 mg, 90%). The spectrum of the product was consistent with the literature.[7]



18

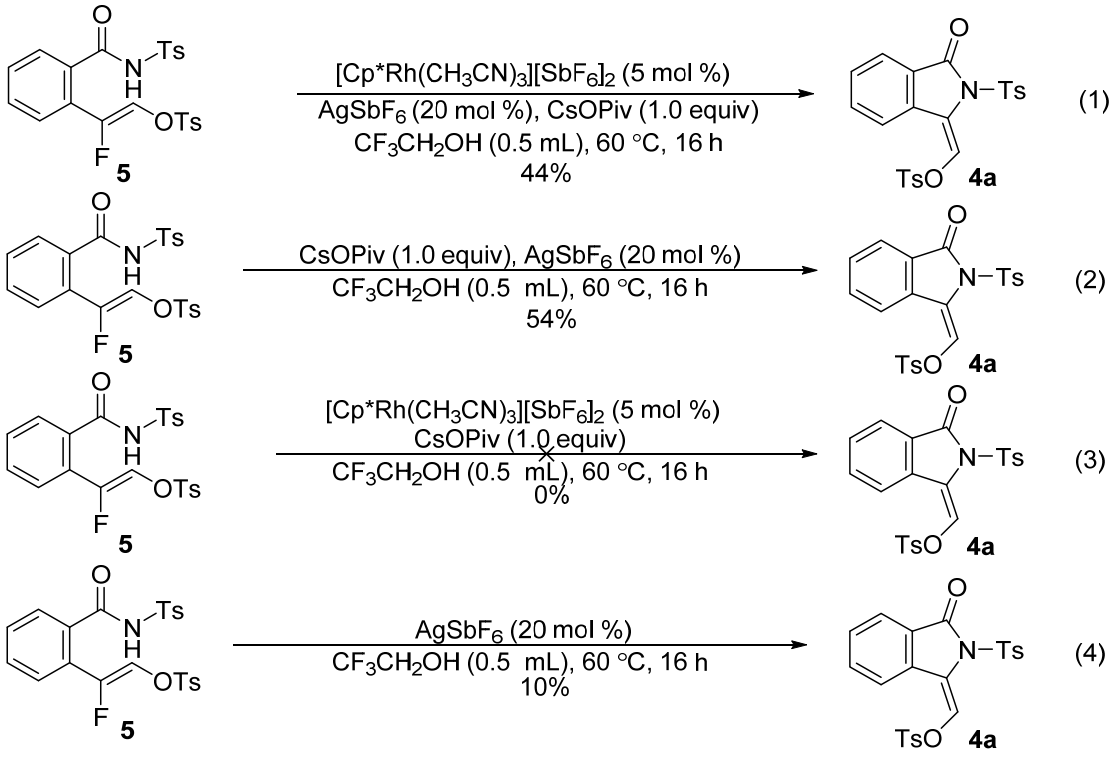
R_F (Petroleum ether/ EtOAc 1:1): 0.68.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 9.12 (dd, J = 7.8, 1.7 Hz, 1H), 7.95 (dd, J = 7.6, 1.9 Hz, 1H), 7.86 (s, 1H), 7.71 – 7.49 (m, 2H), 7.14 (s, 1H), 4.06 (s, 3H), 4.04 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 154.2, 150.4, 135.1, 134.8, 129.0, 127.5, 126.8, 125.9, 125.5, 123.3, 121.6, 119.9, 109.9, 104.6, 59.9, 57.0.

ESI-MS: calculated $C_{17}H_{13}NO_3$ $[M+H]^+$, 280.0968; Found 280.0963.

VII. Controlled experiments



To a 10.0 mL tube with a stirring bar, were added compound **5** (36.4 mg, 0.08 mmol, 1.0 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (3.3 mg, 0.004 mmol, 5 mol %) CsOPiv (18.8 mg, 0.08 mmol, 1.0 equiv) and $AgSbF_6$ (5.5 mg, 0.008 mmol, 20 mol %) in the glove-box. The tube was then moved out and TFE (0.5 mL) was added. The mixture was stirred at 60°C for 16 h. The yield was determined by ^{1}H NMR using

4-iodoanisole as an internal standard.

(1) Following the above procedure, **4a** was obtained in 44% yield

(2) Following the above procedure, with no $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ added, **4a** was obtained in 54% yield.

(3) Following the above procedure, with no $AgSbF_6$ added, no desired product **4a** was obtained.

(4) Following the above procedure, with no $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ and CsOPiv added, **4a** was obtained in 10% yield.

VIII. X-ray crystal structure data

i.X-ray structure for 4a

Single crystals of $C_{23}H_{19}N_1O_6S_2$ were colourless crystal. A suitable crystal was selected on a **Xcalibur, Onyx, Nova** diffractometer. The crystal was kept at 103(2) K during data collection. Using Olex2, the structure was solved with the XS structure solution program using Charge Flipping and refined with the XL refinement package using Gauss-Newton minimization.

Crystal Data for $C_{23}H_{19}NO_6S_2$ (M =469.54 g/mol): triclinic, space group P-1 (no. 2), a = 7.83191(19) Å, b = 12.3569(3) Å, c = 22.7654(5) Å, α = 104.4355(19)°, β = 97.8284(19)°, γ = 93.8331(19)°, V = 2102.05(9) $Å^3$, Z = 4, T = 100 K, μ(Cu Kα) = 2.668 mm^{-1}, *Dcalc* = 1.4836 g/cm^3, 16920 reflections measured (4.06° ≤ 2Θ ≤ 134.12°), 7494 unique (R_{int} = 0.0293, R_{sigma} = 0.0339) which were used in all calculations. The final R_1 was 0.0361 (I>=2u(I)) and wR_2 was 0.0979 (all data).

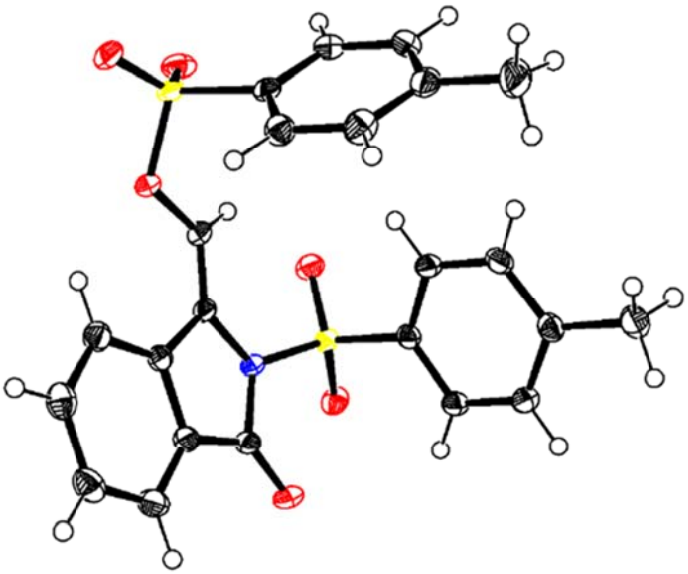


Table 1 Crystal data and structure refinement for jww_160908.

Identification code	jww_160908
Empirical formula	$C_{23}H_{19}NO_6S_2$
Formula weight	469.54
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	7.83191(19)
b/Å	12.3569(3)
c/Å	22.7654(5)
α/°	104.4355(19)
β/°	97.8284(19)
γ/°	93.8331(19)
Volume/Å^3	2102.05(9)
Z	4
ρ_{calc}g/cm^3	1.4836
μ/mm^{-1}	2.668
F(000)	981.7

Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.06 to 134.12
Index ranges	-9 ≤ h ≤ 9, -15 ≤ k ≤ 12, -28 ≤ l ≤ 27
Reflections collected	16920
Independent reflections	7494 [R_{int} = 0.0293, R_{sigma} = 0.0339]
Data/restraints/parameters	7494/0/581
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.0954
Final R indexes [all data]	R_1 = 0.0392, wR_2 = 0.0979
Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.52

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for jww_160908. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	1540.9(5)	2379.1(3)	4335.45(18)	20.63(11)
S2	422.2(6)	4892.5(4)	8310.59(19)	24.52(11)
S3	8825.6(6)	729.8(3)	7885.39(19)	22.83(11)
S4	2825.4(6)	9386.9(4)	8785.95(19)	23.25(11)
O5	473.3(17)	1336.8(11)	4091.0(6)	26.3(3)
O6	9699.0(17)	8825.3(11)	2312.2(7)	31.5(3)
O0aa	1318.2(17)	9373.8(11)	9070.7(6)	29.8(3)
O8	986.8(17)	3263.6(11)	4775.8(6)	26.9(3)
O1aa	9948.5(18)	4162.5(12)	1231.6(6)	29.7(3)
O2aa	18(2)	3660.5(11)	6927.3(6)	34.1(3)
O11	3157.5(18)	4658.1(10)	4301.0(6)	28.8(3)
O12	6623.6(19)	9687.1(11)	1426.9(6)	31.6(3)
O13	8627.3(18)	1002.4(11)	8516.1(6)	31.9(3)
O14	779.1(18)	6087.4(12)	1907.7(6)	32.5(3)
N15	693(2)	5374.0(13)	7694.5(7)	23.7(3)
N16	1828.1(19)	2882.8(12)	3728.9(6)	19.9(3)
C17	4197(2)	8398.9(15)	9658.8(8)	25.2(4)
O18	1204.5(17)	620.7(10)	2280.6(5)	23.8(3)
O19	2493.7(17)	8359(1)	8163.5(5)	24.9(3)
C20	7038(3)	1674.5(15)	7070.5(9)	27.7(4)

C21	4542(2)	8987.4(15)	9233.2(8)	22.9(4)
C22	2833(2)	2770.2(16)	2178.5(8)	25.5(4)
C23	2724(2)	7188.9(15)	6861.0(8)	22.4(4)
C24	1355(2)	5323.2(14)	6732.8(8)	20.9(4)
C25	4186(2)	1066.0(15)	4383.9(8)	24.2(4)
C26	2595(2)	2946.8(14)	2789.8(8)	20.8(4)
C27	1792(2)	2210.6(14)	3111.1(8)	19.0(3)
C28	5508(3)	1839.6(16)	6729.0(9)	33.1(5)
C29	6940(2)	919.6(14)	7426.5(8)	22.0(4)
C30	3621(3)	5308.4(16)	9010.6(8)	27.6(4)
C31	600(2)	4637.4(15)	7088.7(8)	23.4(4)
C32	4786(3)	4993.4(16)	774.1(9)	29.6(4)
C33	1099(2)	1144.8(15)	2891.4(8)	21.2(4)
C34	3622(2)	2113.2(14)	4619.7(8)	20.7(4)
C35	1946(2)	6398.6(14)	7107.5(8)	20.0(3)
C36	3151(2)	3989.4(15)	3205.5(8)	22.1(4)
C37	1526(2)	6463.3(14)	7720.5(8)	19.8(3)
C38	2895(2)	6873.9(16)	6243.2(8)	25.1(4)
C39	2762(2)	3959.3(14)	3812.5(8)	21.8(4)
C40	3132(2)	8347.5(15)	4901.2(8)	24.3(4)
C41	1710(2)	7351.5(15)	8207.9(8)	23.3(4)
C42	4433(3)	1979.8(16)	20.6(9)	29.9(4)
C43	2296(2)	5795.0(16)	5871.1(8)	25.5(4)
C44	5387(2)	335.8(16)	7446.2(9)	27.4(4)
C45	4200(3)	9150.9(15)	5373.3(8)	26.0(4)
C46	3888(3)	516.8(18)	7104.0(9)	31.8(4)
C47	1518(2)	5005.5(15)	6113.4(8)	24.3(4)
C48	4184(3)	4693.4(17)	2424.8(10)	32.0(4)
C49	3775(3)	766.4(17)	857.8(8)	29.7(4)
C50	2899(3)	3434.7(16)	8335.7(9)	30.1(4)
C51	4333(3)	6077.4(17)	988.7(9)	28.8(4)
C52	3625(3)	3650.4(17)	2006.1(9)	30.7(4)
C53	4675(2)	2942.4(15)	5076.0(8)	24.1(4)
C54	3946(2)	4869.2(16)	3033.7(9)	28.0(4)
C1	2744(3)	1787.1(17)	122.9(9)	33.2(5)
C2	2471(2)	4521.1(15)	8566.0(8)	23.8(4)
C3	3704(2)	7295.8(15)	4692.1(8)	25.7(4)
C4	2434(3)	1158.4(19)	533.0(9)	36.1(5)
C5	3927(3)	1273.0(16)	6741.5(9)	31.2(4)
C6	7730(3)	8535(2)	3622.7(11)	44.0(6)

C7	1412(3)	8607.9(17)	4616.1(9)	31.2(4)
C8	2618(3)	6393(2)	728.3(10)	38.7(5)
C9	4498(3)	3150.8(16)	8560.9(9)	32.5(4)
C10	1276(3)	2242(2)	-210.8(11)	49.0(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for jww_160908. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	24.0(2)	19.4(2)	16.6(2)	1.88(16)	2.74(16)	1.79(16)
S2	28.0(2)	24.4(2)	20.3(2)	-0.68(17)	4.45(17)	4.75(17)
S3	24.6(2)	16.4(2)	21.8(2)	2.32(16)	-2.47(16)	-2.24(16)
S4	28.8(2)	19.5(2)	18.7(2)	3.21(17)	2.26(17)	0.57(16)
O5	29.8(7)	24.3(7)	22.9(6)	-3.2(5)	3.7(5)	4.4(5)
O6	24.0(7)	20.9(6)	42.9(8)	-0.9(5)	0.2(6)	-0.2(6)
O0aa	29.0(7)	30.9(7)	26.4(7)	6.5(6)	4.5(5)	0.8(5)
O8	28.9(7)	29.7(7)	19.6(6)	8.2(5)	5.2(5)	-0.2(5)
O1aa	34.7(7)	32.0(7)	23.1(6)	6.8(6)	8.9(5)	5.4(5)
O2aa	48.8(9)	20.3(7)	30.6(7)	-3.6(6)	10.5(6)	1.2(5)
O11	37.9(8)	18.2(6)	24.0(7)	-0.6(5)	0.2(5)	-2.7(5)
O12	47.3(8)	20.6(6)	24.8(7)	2.9(6)	3.1(6)	3.5(5)
O13	41.2(8)	27.9(7)	19.8(6)	9.1(6)	-3.1(5)	-3.6(5)
O14	33.6(7)	33.9(8)	28.4(7)	-7.3(6)	3.8(6)	8.4(6)
N15	28.4(8)	21.7(8)	18.3(7)	-0.1(6)	2.5(6)	1.6(6)
N16	25.9(8)	15.9(7)	15.4(7)	2.5(6)	1.7(6)	0.4(5)
C17	28.0(9)	22.1(9)	21.5(9)	-1.3(7)	1.7(7)	0.6(7)
O18	33.0(7)	17.1(6)	17.7(6)	3.7(5)	0.0(5)	-0.3(5)
O19	32.4(7)	21.0(6)	18.0(6)	-0.2(5)	2.1(5)	0.7(5)
C20	32.2(10)	19.5(9)	28.7(10)	0.1(7)	1.9(8)	3.6(7)
C21	26.0(9)	19.4(8)	18.6(8)	1.1(7)	1.3(7)	-2.2(6)
C22	27.3(9)	26.9(9)	22.1(9)	5.2(7)	3.0(7)	5.7(7)
C23	23.3(9)	19.3(8)	22.7(9)	2.6(7)	1.6(7)	2.9(7)
C24	22.3(8)	18.7(8)	19.9(8)	3.4(7)	1.2(7)	2.7(7)
C25	33.4(10)	17.7(8)	19.4(8)	1.7(7)	2.2(7)	2.4(7)
C26	19.6(8)	19.9(8)	22.2(9)	5.6(7)	-0.0(7)	4.7(7)
C27	20.3(8)	17.8(8)	16.4(8)	4.5(6)	0.1(6)	0.9(6)
C28	49.2(12)	20.8(9)	28(1)	7.5(8)	-0.6(9)	6.7(8)
C29	25.0(9)	18.6(8)	18.8(8)	4.4(7)	1.5(7)	-1.3(7)
C30	36.8(10)	20.8(9)	22.9(9)	3.4(8)	2.7(8)	2.6(7)

C31	27.6(9)	19.6(9)	20.1(8)	2.4(7)	2.2(7)	0.5(7)
C32	35.7(11)	26.6(10)	23.5(9)	0.4(8)	1.1(8)	3.8(8)
C33	25.6(9)	19.4(8)	16.5(8)	3.2(7)	1.4(7)	1.8(7)
C34	25.9(9)	19.3(8)	17.9(8)	2.8(7)	3.9(7)	6.6(7)
C35	19.1(8)	20.1(8)	18.5(8)	5.1(7)	-0.6(6)	1.6(7)
C36	21.3(8)	19.4(8)	24.4(9)	4.0(7)	0.5(7)	4.9(7)
C37	20.1(8)	19.4(8)	19.1(8)	3.1(7)	1.1(6)	4.5(7)
C38	25.6(9)	26.8(9)	24.5(9)	4.0(7)	5.3(7)	9.0(7)
C39	22.6(9)	16.4(8)	23.9(9)	4.2(7)	-0.5(7)	2.5(7)
C40	28.4(9)	24.7(9)	22.4(9)	4.9(7)	4.4(7)	10.1(7)
C41	27.1(9)	21.8(9)	19.6(8)	1.4(7)	1.4(7)	4.5(7)
C42	40.6(11)	22.3(9)	21.7(9)	2.3(8)	-2.0(8)	0.5(7)
C43	28.4(9)	30.1(10)	18.0(8)	7.2(8)	5.3(7)	4.3(7)
C44	29.2(10)	28.9(10)	25.0(9)	2.0(8)	5.0(7)	8.4(8)
C45	35.8(10)	19.7(9)	24.0(9)	7.6(8)	5.7(8)	6.4(7)
C46	25.2(10)	36.0(11)	32.5(10)	3.1(8)	4.3(8)	5.7(8)
C47	28.4(9)	21.9(9)	19.1(8)	5.3(7)	1.9(7)	-0.7(7)
C48	29(1)	31.4(10)	40.7(11)	1.5(8)	6.7(8)	19.0(9)
C49	30.8(10)	33.6(10)	20.6(9)	-0.9(8)	5.5(7)	-0.2(8)
C50	41.9(11)	20.5(9)	25.1(9)	-1.0(8)	4.1(8)	2.5(7)
C51	38.2(11)	29.8(10)	22.7(9)	8.6(8)	9.5(8)	10.8(8)
C52	31.2(10)	37.4(11)	27.2(10)	6.8(8)	7.5(8)	12.9(8)
C53	30.6(10)	18.4(8)	21.9(9)	3.7(7)	2.8(7)	3.1(7)
C54	27.1(9)	21.5(9)	34.8(10)	1.5(7)	2.0(8)	8.1(8)
C1	35.6(11)	31(1)	22.8(9)	9.5(8)	-5.4(8)	-8.0(8)
C2	31.7(10)	20.1(9)	20.1(8)	-0.4(7)	5.2(7)	6.1(7)
C3	30.3(10)	21.6(9)	22.8(9)	-0.9(7)	0.1(7)	4.4(7)
C4	25.7(10)	47.6(13)	26.4(10)	3.2(9)	3.2(8)	-5.5(9)
C5	33.7(11)	28(1)	26.2(9)	13.5(8)	-0.9(8)	-3.1(8)
C6	41.7(13)	46.2(13)	38.4(12)	20.9(10)	-5.1(10)	2(1)
C7	31.2(10)	31.1(10)	33.4(10)	6.6(8)	2.9(8)	12.8(8)
C8	43.0(12)	43.8(12)	35.3(11)	15.4(10)	10.9(9)	15.8(10)
C9	48.3(12)	22.2(9)	28.5(10)	8.5(9)	10.5(9)	5.8(8)
C10	43.7(13)	52.3(14)	38.4(12)	18.4(11)	-12.4(10)	-4.7(11)

Table 4 Bond Lengths for jww_160908.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O5	1.4280(13)	C24	C47	1.392(2)
S1	O8	1.4225(13)	C25	C34	1.397(2)

S1	N16	1.6851(15)	C25	C45[1]	1.380(3)
S1	C34	1.7530(18)	C26	C27	1.462(3)
S2	O1aa[1]	1.4336(14)	C26	C36	1.396(2)
S2	O14[2]	1.4209(14)	C27	C33	1.335(2)
S2	N15	1.6870(16)	C28	C5	1.388(3)
S2	C2	1.7607(19)	C29	C44	1.384(3)
S3	O6[3]	1.4213(15)	C30	C32[1]	1.387(3)
S3	O13	1.4233(14)	C30	C2	1.388(3)
S3	O18[4]	1.6143(12)	C32	C51	1.394(3)
S3	C29	1.7536(18)	C34	C53	1.390(2)
S4	O0aa	1.4231(14)	C35	C37	1.461(2)
S4	O12[5]	1.4134(14)	C36	C39	1.464(3)
S4	O19	1.6268(12)	C36	C54	1.382(3)
S4	C21	1.7475(18)	C37	C41	1.336(2)
O2aa	C31	1.208(2)	C38	C43	1.400(3)
O11	C39	1.212(2)	C40	C45	1.397(3)
N15	C31	1.440(2)	C40	C3	1.394(3)
N15	C37	1.440(2)	C40	C7	1.504(3)
N16	C27	1.440(2)	C42	C1	1.389(3)
N16	C39	1.431(2)	C43	C47	1.381(3)
C17	C21	1.392(3)	C44	C46	1.381(3)
C17	C42[1]	1.388(3)	C46	C5	1.394(3)
O18	C33	1.396(2)	C48	C52	1.400(3)
O19	C41	1.384(2)	C48	C54	1.389(3)
C20	C28	1.393(3)	C49	C4	1.385(3)
C20	C29	1.385(3)	C50	C2	1.395(3)
C21	C49[1]	1.388(3)	C50	C9	1.389(3)
C22	C26	1.394(3)	C51	C8	1.508(3)
C22	C52	1.382(3)	C51	C9[1]	1.393(3)
C23	C35	1.388(3)	C53	C3[1]	1.387(3)
C23	C38	1.390(3)	C1	C4	1.390(3)
C24	C31	1.460(3)	C1	C10	1.509(3)
C24	C35	1.397(2)	C5	C6[1]	1.508(3)

[1]1-X,1-Y,1-Z; [2]-X,1-Y,1-Z; [3]2-X,1-Y,1-Z; [4]1-X,-Y,1-Z; [5]1-X,2-Y,1-Z

Table 5 Bond Angles for jww_160908.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O8	S1	O5	120.28(8)	C2	C30	C32[2]	119.30(17)

N16	S1	O5	106.03(7)	N15	C31	O2aa	125.79(17)
N16	S1	O8	106.76(8)	C24	C31	O2aa	128.94(16)
C34	S1	O5	109.08(8)	C24	C31	N15	105.27(14)
C34	S1	O8	109.31(8)	C51	C32	C30^{2}	121.18(18)
C34	S1	N16	104.13(8)	C27	C33	O18	117.24(16)
O14^{1}	S2	O1aa^{2}	120.56(8)	C25	C34	S1	119.15(13)
N15	S2	O1aa^{2}	105.98(8)	C53	C34	S1	119.59(13)
N15	S2	O14^{1}	106.57(8)	C53	C34	C25	121.26(16)
C2	S2	O1aa^{2}	108.11(8)	C24	C35	C23	119.64(16)
C2	S2	O14^{1}	109.62(9)	C37	C35	C23	131.99(16)
C2	S2	N15	104.87(8)	C37	C35	C24	108.33(16)
O13	S3	O6^{3}	121.44(8)	C39	C36	C26	109.33(16)
O18^{4}	S3	O6^{3}	108.35(7)	C54	C36	C26	122.21(17)
O18^{4}	S3	O13	102.37(7)	C54	C36	C39	128.46(16)
C29	S3	O6^{3}	109.40(9)	C35	C37	N15	106.26(14)
C29	S3	O13	110.78(8)	C41	C37	N15	124.43(16)
C29	S3	O18^{4}	102.61(7)	C41	C37	C35	129.08(17)
O12^{5}	S4	O0aa	121.61(8)	C43	C38	C23	121.72(18)
O19	S4	O0aa	107.53(7)	N16	C39	O11	124.75(17)
O19	S4	O12^{5}	102.70(7)	C36	C39	O11	129.53(17)
C21	S4	O0aa	109.43(9)	C36	C39	N16	105.69(14)
C21	S4	O12^{5}	111.07(9)	C3	C40	C45	118.49(17)
C21	S4	O19	102.51(7)	C7	C40	C45	121.17(16)
C31	N15	S2	122.50(13)	C7	C40	C3	120.33(17)
C37	N15	S2	125.07(12)	C37	C41	O19	118.36(16)
C37	N15	C31	109.99(14)	C1	C42	C17^{2}	121.04(19)
C27	N16	S1	125.32(12)	C47	C43	C38	120.33(17)
C39	N16	S1	120.93(11)	C46	C44	C29	119.06(18)
C39	N16	C27	109.98(14)	C40	C45	C25^{2}	121.37(16)
C42^{2}	C17	C21	118.82(18)	C5	C46	C44	120.86(19)
C33	O18	S3^{4}	115.57(11)	C43	C47	C24	117.75(16)
C41	O19	S4	116.41(11)	C54	C48	C52	120.07(18)
C29	C20	C28	117.82(18)	C4	C49	C21^{2}	118.61(19)
C17	C21	S4	119.63(14)	C9	C50	C2	118.83(18)
C49^{2}	C21	S4	119.10(15)	C8	C51	C32	119.94(18)
C49^{2}	C21	C17	121.23(17)	C9^{2}	C51	C32	118.43(19)
C52	C22	C26	117.97(17)	C9^{2}	C51	C8	121.63(18)
C38	C23	C35	118.23(16)	C48	C52	C22	121.96(18)
C35	C24	C31	110.09(15)	C3^{2}	C53	C34	118.71(16)
C47	C24	C31	127.59(16)	C48	C54	C36	117.93(17)

C47	C24	C35	122.33(17)	C4	C1	C42	118.72(18)
C45[2]	C25	C34	118.75(16)	C10	C1	C42	120.5(2)
C27	C26	C22	131.40(16)	C10	C1	C4	120.8(2)
C36	C26	C22	119.86(17)	C30	C2	S2	119.23(14)
C36	C26	C27	108.74(15)	C50	C2	S2	119.94(15)
C26	C27	N16	105.91(14)	C50	C2	C30	120.80(18)
C33	C27	N16	125.25(16)	C53[2]	C3	C40	121.34(17)
C33	C27	C26	128.80(16)	C1	C4	C49	121.46(19)
C5	C28	C20	121.69(19)	C46	C5	C28	118.62(18)
C20	C29	S3	119.11(14)	C6[2]	C5	C28	121.5(2)
C44	C29	S3	118.91(14)	C6[2]	C5	C46	119.9(2)
C44	C29	C20	121.95(17)	C51[2]	C9	C50	121.44(18)

[1]-X,1-Y,1-Z; [2]1-X,1-Y,1-Z; [3]2-X,1-Y,1-Z; [4]1-X,-Y,1-Z; [5]1-X,2-Y,1-Z

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for jww_160908.

Atom	*x*	*y*	*z*	U(eq)
H47	1107(2)	4270.5(15)	5865.7(8)	29.1(5)
H43	2426(2)	5604.9(16)	5449.9(8)	30.6(5)
H38	3432(2)	7404.6(16)	6069.1(8)	30.1(5)
H23	3129(2)	7925.4(15)	7107.9(8)	26.9(4)
H54	4319(2)	5572.3(16)	3323.2(9)	33.6(5)
H48	4726(3)	5281.7(17)	2292.4(10)	38.4(5)
H52	3796(3)	3544.3(17)	1591.1(9)	36.9(5)
H22	2463(2)	2066.6(16)	1889.3(8)	30.6(5)
H44	5352(2)	-182.1(16)	7691.7(9)	32.9(5)
H46	2816(3)	120.7(18)	7115.8(9)	38.2(5)
H28	5548(3)	2353.1(16)	6481.2(9)	39.7(5)
H20	8114(3)	2066.9(15)	7059.6(9)	33.2(5)
H17	3044(2)	8258.9(15)	9728.8(8)	30.3(5)
H25	3471(2)	513.8(15)	4062.5(8)	29.0(5)
H30	3321(3)	6046.3(16)	9165.8(8)	33.1(5)
H32	3989(3)	4451.8(16)	474.9(9)	35.5(5)
H33	556(2)	758.8(15)	3140.3(8)	25.4(4)
H41	1312(2)	7292.9(15)	8575.8(8)	27.9(4)
H42	4653(3)	2377.1(16)	-273.3(9)	35.8(5)
H45	3807(3)	9861.2(15)	5530.3(8)	31.2(5)
H49	3546(3)	337.9(17)	1137.1(8)	35.7(5)

H50	2110(3)	2898.7(16)	8030.2(9)	36.1(5)
H53	4292(2)	3658.4(15)	5226.0(8)	28.9(4)
H3	2968(2)	6731.0(15)	4384.4(8)	30.8(5)
H4	1277(3)	994.0(19)	591.9(9)	43.3(6)
H6a	8424(11)	9257(3)	3817(7)	66.1(9)
H6b	7454(3)	8173(14)	3941(6)	66.1(9)
H6c	8388(12)	8049(13)	3347.7(18)	66.1(9)
H7a	845(9)	9061(11)	4936.5(13)	46.8(6)
H7b	1594(3)	9028(11)	4313(5)	46.8(6)
H7c	677(8)	7905.0(18)	4413(6)	46.8(6)
H8a	2661(8)	6463(14)	311(3)	58.1(7)
H8b	1694(4)	5809(7)	717(7)	58.1(7)
H8c	2385(11)	7111(7)	988(5)	58.1(7)
H9	4801(3)	2413.9(16)	8404.4(9)	39.0(5)
H10a	843(18)	2846(12)	81(2)	73.4(10)
H10b	1693(7)	2537(15)	-533(6)	73.4(10)
H10c	338(11)	1638(5)	-397(8)	73.4(10)

ii.X-ray structure for 7a

Single crystals of $C_{16}H_{12}O_5S_1$ were colourless crystal. A suitable crystal was selected on a **Xcalibur, Onyx, Nova** diffractometer. The crystal was kept at 103(2) K during data collection. Using Olex2, the structure was solved with the XS structure solution program using Charge Flipping and refined with the XL refinement package using Gauss-Newton minimization.

Crystal Data for $C_{16}H_{12}O_5S$ (M =316.34 g/mol): monoclinic, space group P21/c (no. 14), a = 8.99567(15) Å, b = 20.3803(3) Å, c = 8.08882(13) Å, β = 102.5457(16)°, V = 1447.55(4) Å3, Z = 4, T = 100 K, μ(Cu Kα) = 2.193 mm-1, Dcalc = 1.4514 g/cm3, 6373 reflections measured (8.68° ≤ 2Θ ≤ 134°), 2570 unique (Rint = 0.0229, Rsigma = 0.0233) which were used in all calculations. The final R1 was 0.0373 (I>=2u(I)) and wR2 was 0.1046 (all data).

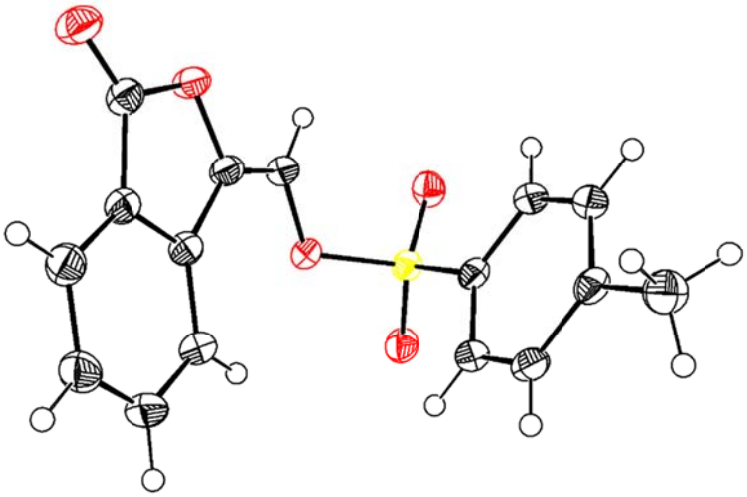


Table 1 Crystal data and structure refinement for jww_160815.

Identification code	jww_160815
Empirical formula	$C_{16}H_{12}O_5S$
Formula weight	316.34
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.99567(15)
b/Å	20.3803(3)
c/Å	8.08882(13)
α/°	90
β/°	102.5457(16)
γ/°	90
Volume/Å^3	1447.55(4)
Z	4
ρ_{calc}g/cm^3	1.4514
μ/mm^{-1}	2.193
F(000)	659.6
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	8.68 to 134
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -7 ≤ l ≤ 9
Reflections collected	6373
Independent reflections	2570 [R_{int} = 0.0229, R_{sigma} = 0.0233]
Data/restraints/parameters	2570/0/200
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.1027
Final R indexes [all data]	R_1 = 0.0395, wR_2 = 0.1046
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.44

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for jww_160815. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2588.0(5)	4945.38(19)	7948.3(5)	25.24(16)
O2	3903.4(13)	4442.0(6)	8860.8(14)	26.2(3)
O3	1551.3(15)	4922.0(6)	9044.7(16)	32.0(3)
O4	7156.0(13)	3738.6(6)	7577.1(16)	28.4(3)
O5	8710.7(14)	2906.9(6)	7224.3(18)	36.7(3)
O6	3306.7(15)	5544.3(6)	7652.9(16)	32.6(3)
C7	5212.5(19)	4395.9(8)	8202(2)	26.1(4)
C8	2165.3(19)	4815.0(9)	4544(2)	28.0(4)
C9	6146(2)	2030.5(9)	8213(2)	32.8(4)
C10	1832.3(18)	4561.2(8)	6014(2)	24.9(4)
C11	119(2)	3591.6(10)	1293(2)	36.0(4)
C12	927.6(19)	4007.4(8)	5986(2)	27.1(4)
C13	1590(2)	4498.9(9)	3026(2)	29.8(4)
C14	708.6(19)	3933.2(8)	2959(2)	27.6(4)
C15	7545.4(19)	3077.8(9)	7582(2)	28.4(4)
C16	5243.1(19)	3147.8(8)	8412(2)	26.7(4)
C17	5775.9(19)	3802.3(8)	8084(2)	25.7(4)
C18	375.1(19)	3696.3(8)	4455(2)	28.1(4)
C19	3945(2)	2929.3(9)	8921(2)	30.8(4)
C20	6317.9(19)	2705.6(9)	8083(2)	27.3(4)
C21	4844(2)	1812.6(9)	8700(2)	36.3(4)
C1	3777(2)	2254.8(10)	9056(3)	35.9(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for jww_160815. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	23.3(3)	26.1(2)	26.0(3)	1.66(15)	4.92(18)	-0.08(14)
O2	21.0(6)	29.3(6)	28.2(6)	1.4(5)	5.0(5)	1.8(5)
O3	28.1(7)	39.3(7)	29.4(7)	6.1(5)	8.0(6)	-0.5(5)
O4	22.2(6)	26.8(6)	37.9(7)	-2.0(5)	10.4(5)	0.1(5)
O5	28.7(7)	35.1(7)	49.7(8)	1.7(5)	16.1(6)	-1.6(6)
O6	35.5(7)	26.0(6)	34.4(7)	-0.8(5)	3.7(6)	-0.3(5)
C7	21.2(8)	29.1(8)	28.1(9)	-2.7(6)	5.5(7)	0.9(6)
C8	24.2(9)	29.9(9)	29.9(9)	-3.8(7)	5.7(7)	2.1(7)
C9	30.5(10)	27.9(9)	38(1)	-0.6(7)	3.2(8)	0.6(7)
C10	18.3(8)	28.8(8)	27.5(9)	1.9(6)	4.5(7)	-0.5(6)
C11	36.8(11)	38.1(10)	32.7(10)	-2.8(8)	6.6(8)	-4.0(8)
C12	22.1(8)	31.5(9)	28.7(9)	0.3(6)	7.6(7)	3.1(7)
C13	26.0(9)	37.2(10)	26.9(9)	-0.6(7)	7.6(7)	3.3(7)
C14	20.1(8)	31.6(9)	31.0(9)	4.0(7)	5.2(7)	-1.1(7)
C15	24.7(9)	27.7(9)	32.4(9)	-0.0(7)	5.2(7)	-1.6(7)
C16	23.4(9)	28.3(9)	26.7(9)	-2.3(6)	1.9(7)	1.2(6)
C17	19.8(8)	30.1(9)	27.2(9)	-2.7(6)	4.9(7)	-0.5(6)
C18	20.7(9)	28.0(8)	35.4(10)	-1.2(6)	5.6(7)	0.5(7)
C19	23.4(9)	34.8(9)	34.4(9)	-2.6(7)	6.9(7)	2.9(7)
C20	23.1(9)	28.8(9)	28.8(9)	-1.3(6)	2.8(7)	0.5(7)
C21	36.6(11)	28.4(9)	41.1(11)	-7.6(7)	2.2(8)	4.3(7)
C1	29(1)	37.9(10)	40.5(11)	-9.3(8)	7.0(8)	4.3(8)

Table 4 Bond Lengths for jww_160815.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.6181(12)	C9	C21	1.387(3)
S1	O3	1.4205(13)	C10	C12	1.389(2)
S1	O6	1.4256(13)	C11	C14	1.507(2)
S1	C10	1.7495(17)	C12	C18	1.384(2)
O2	C7	1.397(2)	C13	C14	1.394(3)
O4	C15	1.391(2)	C14	C18	1.395(2)
O4	C17	1.395(2)	C15	C20	1.467(2)
O5	C15	1.198(2)	C16	C17	1.461(2)

C7	C17	1.323(2)	C16	C19	1.393(2)
C8	C10	1.388(2)	C16	C20	1.389(2)
C8	C13	1.384(3)	C19	C1	1.390(3)
C9	C20	1.391(2)	C21	C1	1.392(3)

Table 5 Bond Angles for jww_160815.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O3	S1	O2	102.02(7)	C18	C14	C13	118.73(16)
O6	S1	O2	107.82(7)	O5	C15	O4	120.90(15)
O6	S1	O3	121.10(8)	C20	C15	O4	107.29(14)
C10	S1	O2	103.17(7)	C20	C15	O5	131.81(17)
C10	S1	O3	111.29(8)	C19	C16	C17	132.42(16)
C10	S1	O6	109.61(8)	C20	C16	C17	106.76(15)
C7	O2	S1	117.53(10)	C20	C16	C19	120.81(16)
C17	O4	C15	109.18(12)	C7	C17	O4	119.04(15)
C17	C7	O2	117.19(15)	C16	C17	O4	108.44(14)
C13	C8	C10	118.58(16)	C16	C17	C7	132.52(16)
C21	C9	C20	116.93(17)	C14	C18	C12	120.98(16)
C8	C10	S1	119.03(13)	C1	C19	C16	116.86(17)
C12	C10	S1	119.39(13)	C15	C20	C9	129.42(17)
C12	C10	C8	121.57(16)	C16	C20	C9	122.26(16)
C18	C12	C10	118.82(16)	C16	C20	C15	108.31(15)
C14	C13	C8	121.28(16)	C1	C21	C9	120.94(17)
C13	C14	C11	120.24(16)	C21	C1	C19	122.18(17)
C18	C14	C11	121.03(16)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for jww_160815.

Atom	*x*	*y*	*z*	U(eq)
H7	5678.5(19)	4774.7(8)	7854(2)	31.3(4)
H8	2774.8(19)	5197.5(9)	4579(2)	33.7(4)
H9	6885(2)	1732.5(9)	7978(2)	39.3(5)
H11b	-84(16)	3916.9(12)	380(3)	54.0(7)
H11a	883(7)	3278(5)	1082(9)	54.0(7)
H11c	-824(9)	3358(6)	1335(7)	54.0(7)
H12	692.1(19)	3844.9(8)	7000(2)	32.5(4)
H13	1801(2)	4670.7(9)	2009(2)	35.7(5)

H18	-240.4(19)	3315.8(8)	4422(2)	33.7(5)
H19	3209(2)	3227.3(9)	9164(2)	36.9(5)
H21	4679(2)	1354.9(9)	8793(2)	43.6(5)
H1	2905(2)	2090.2(10)	9403(3)	43.0(5)

IX. References

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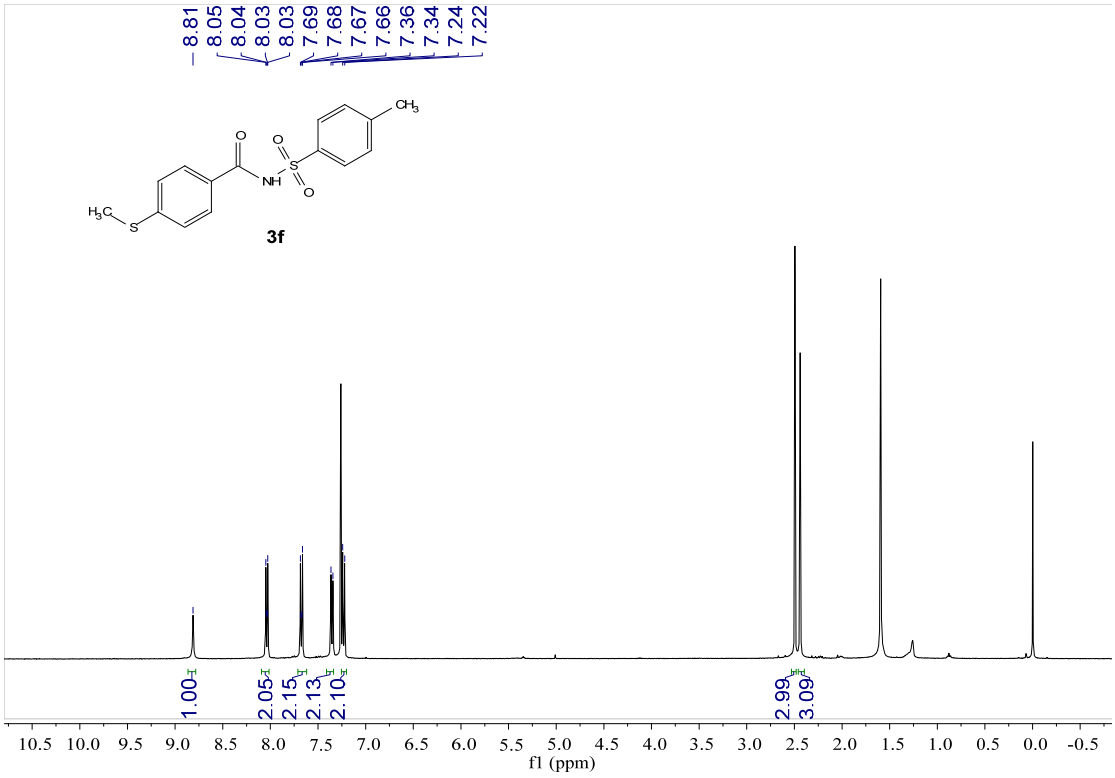
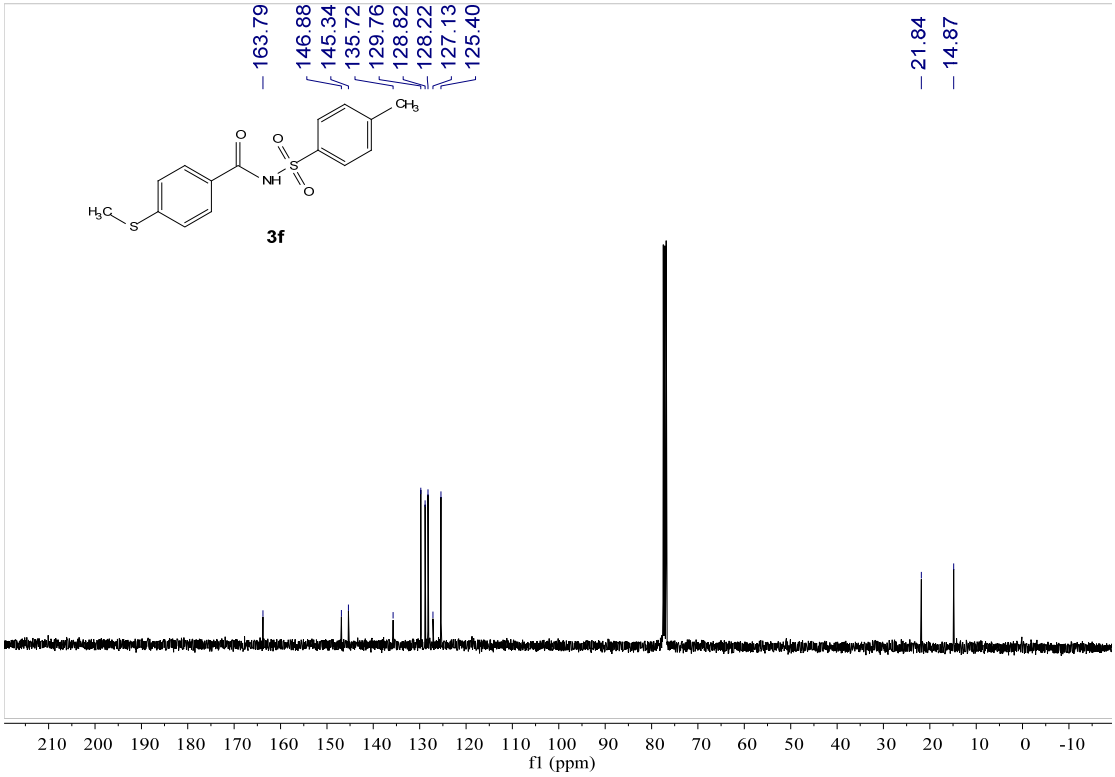
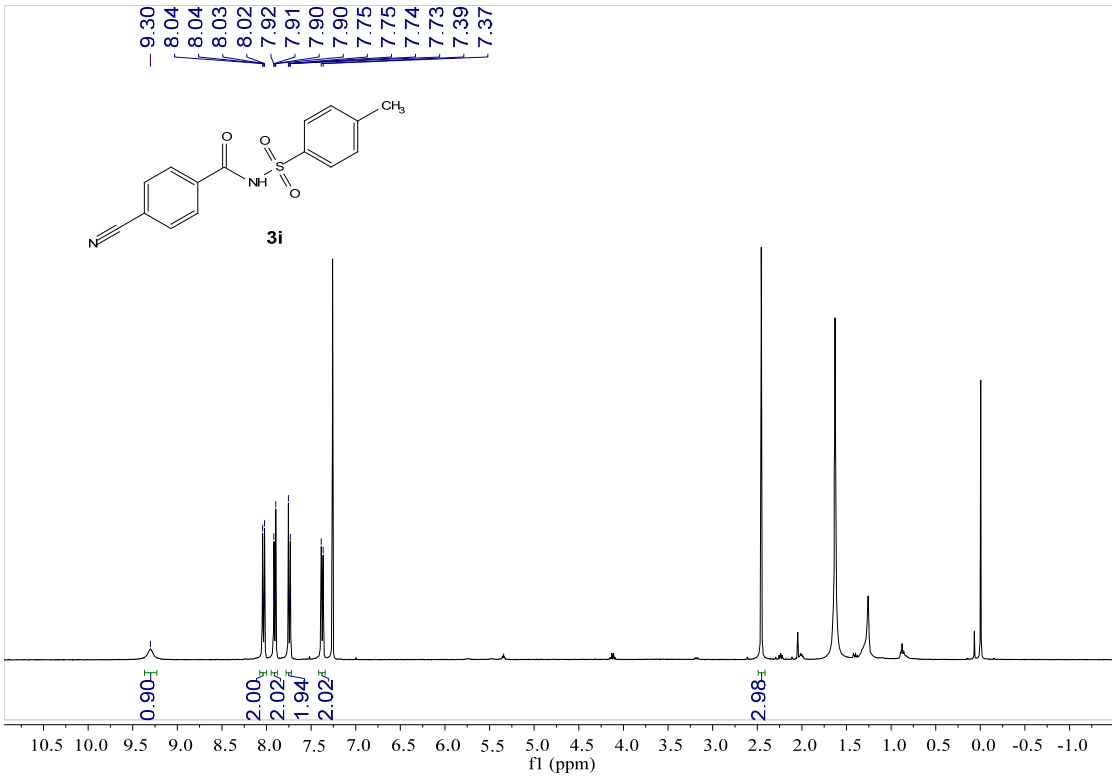
X. NMR Spectra



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2.02
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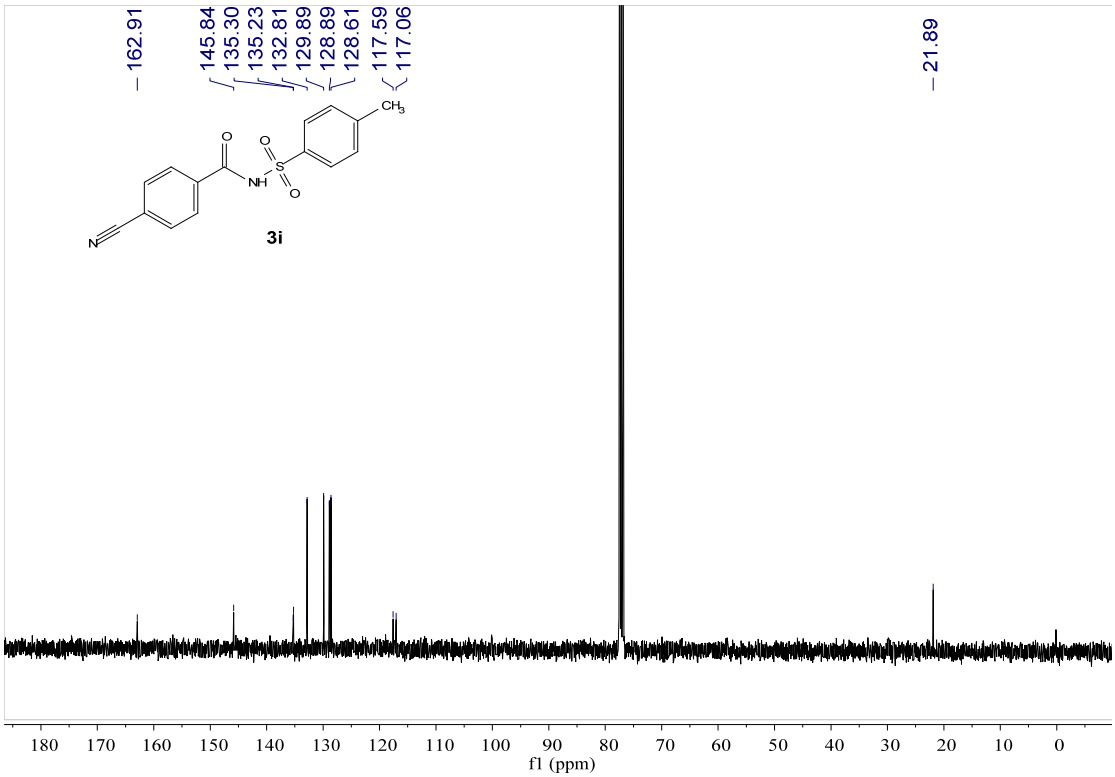
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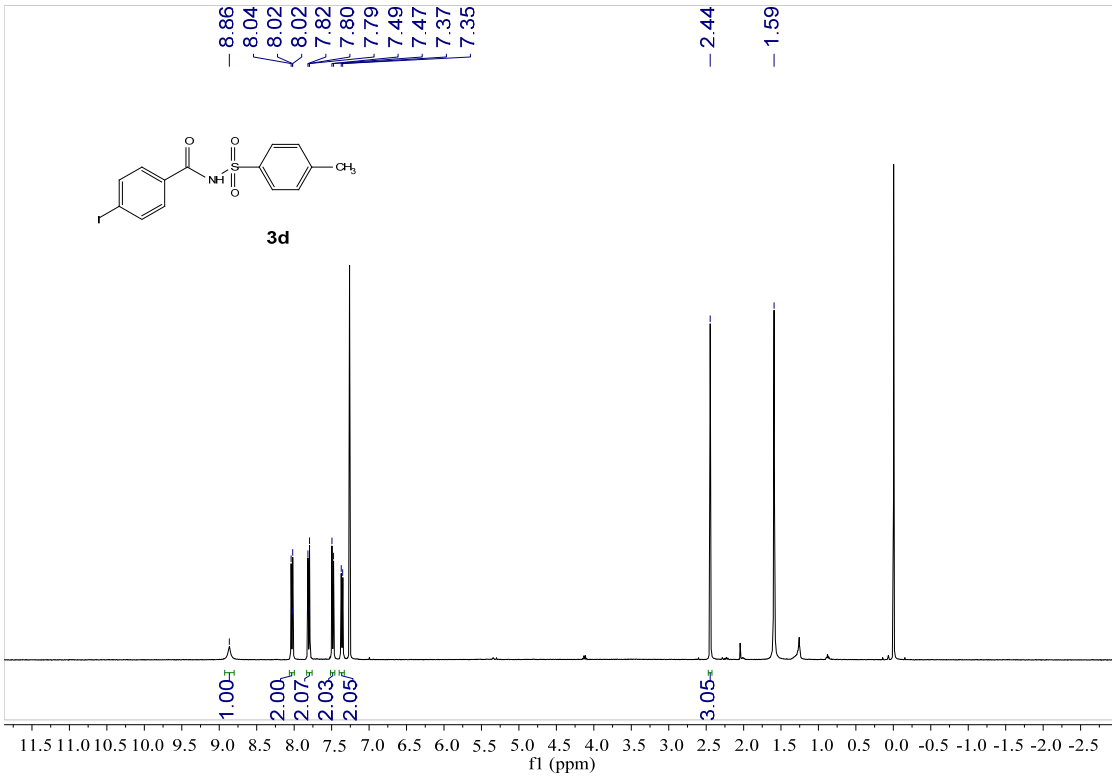
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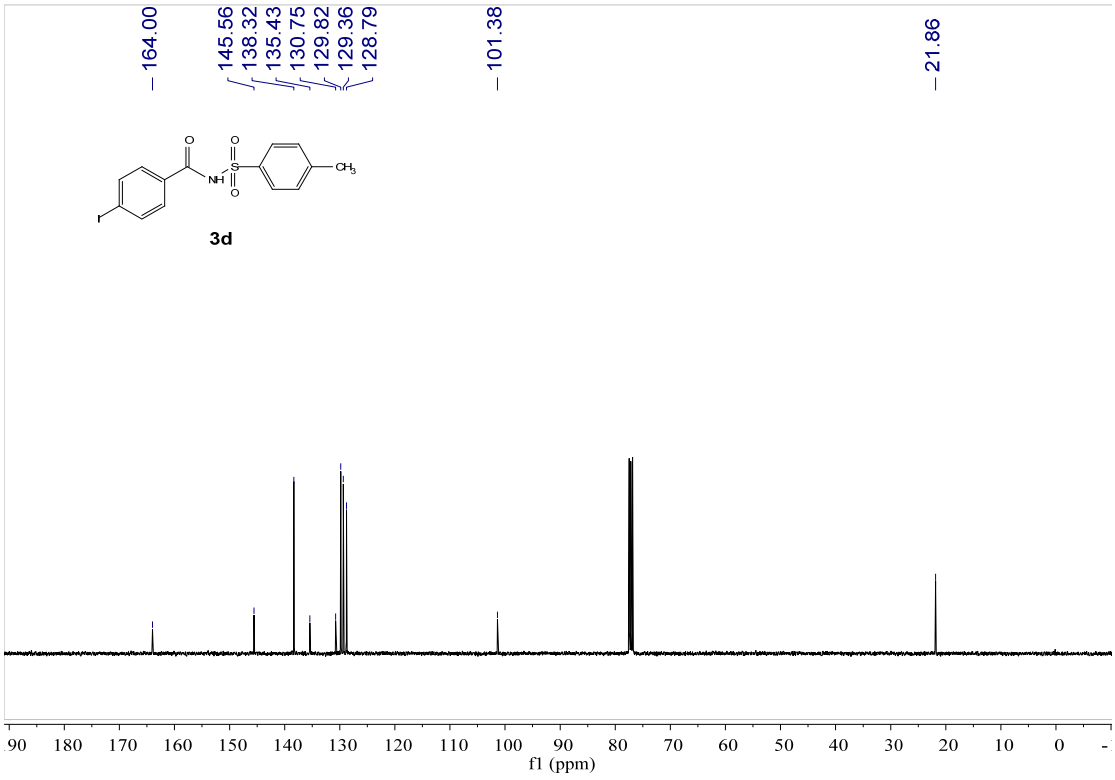
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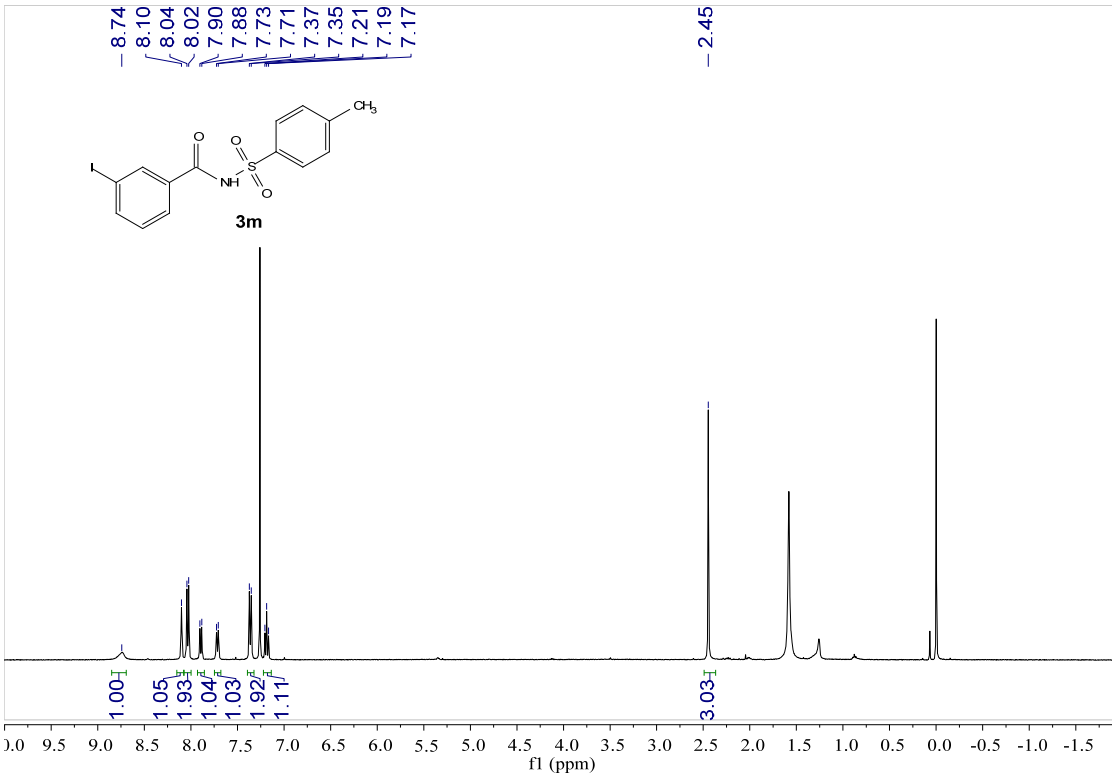
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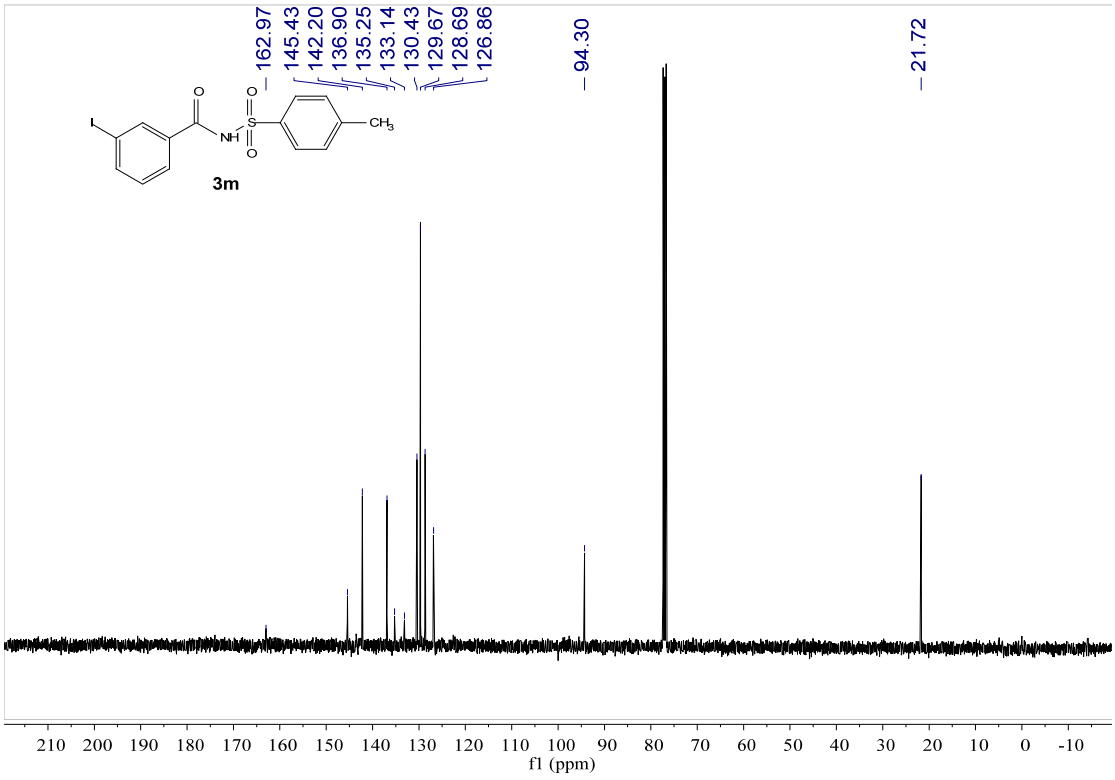
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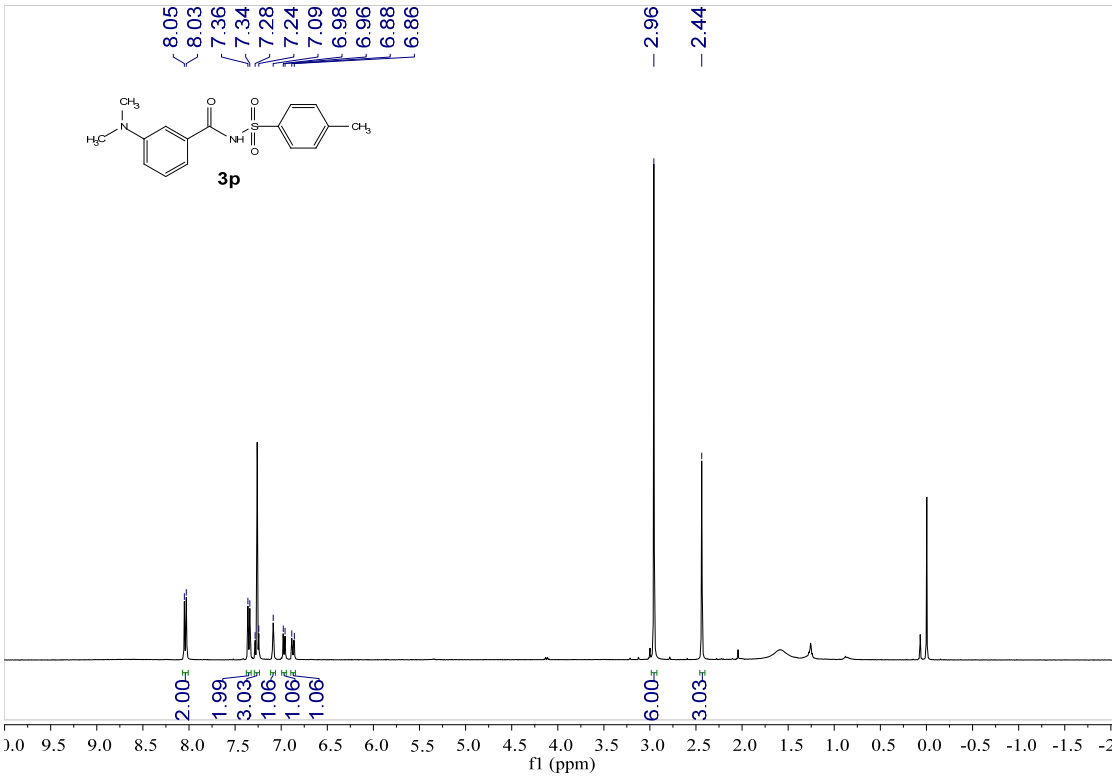
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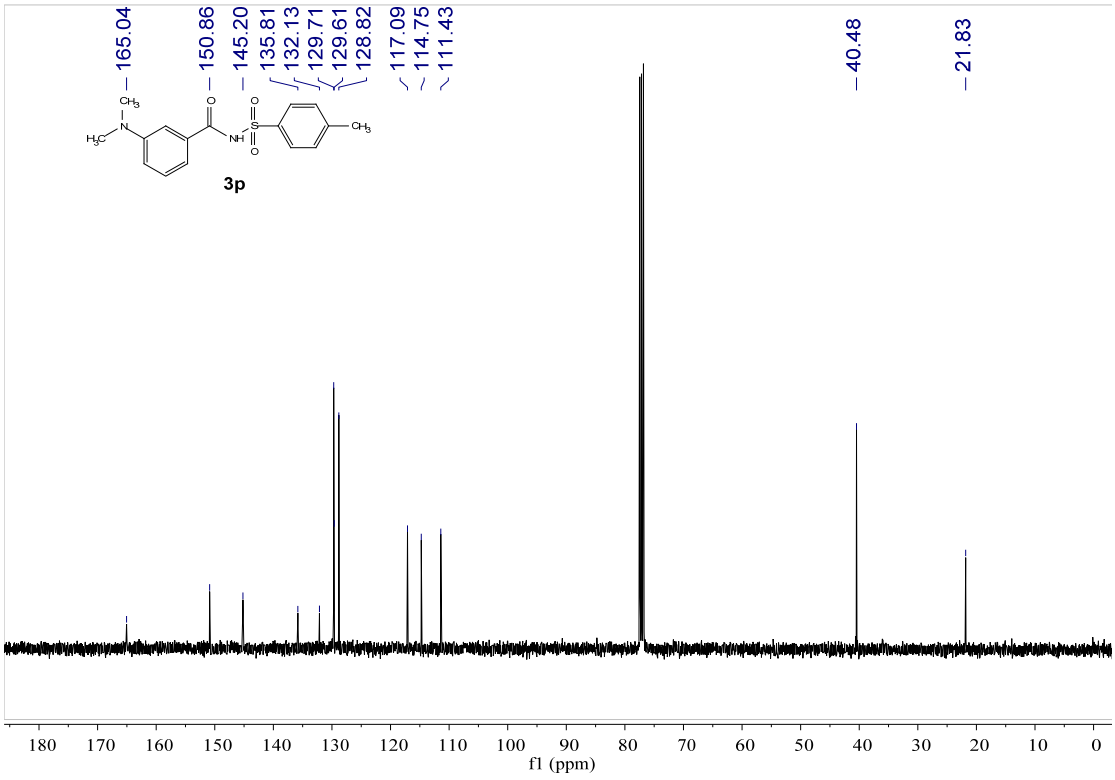
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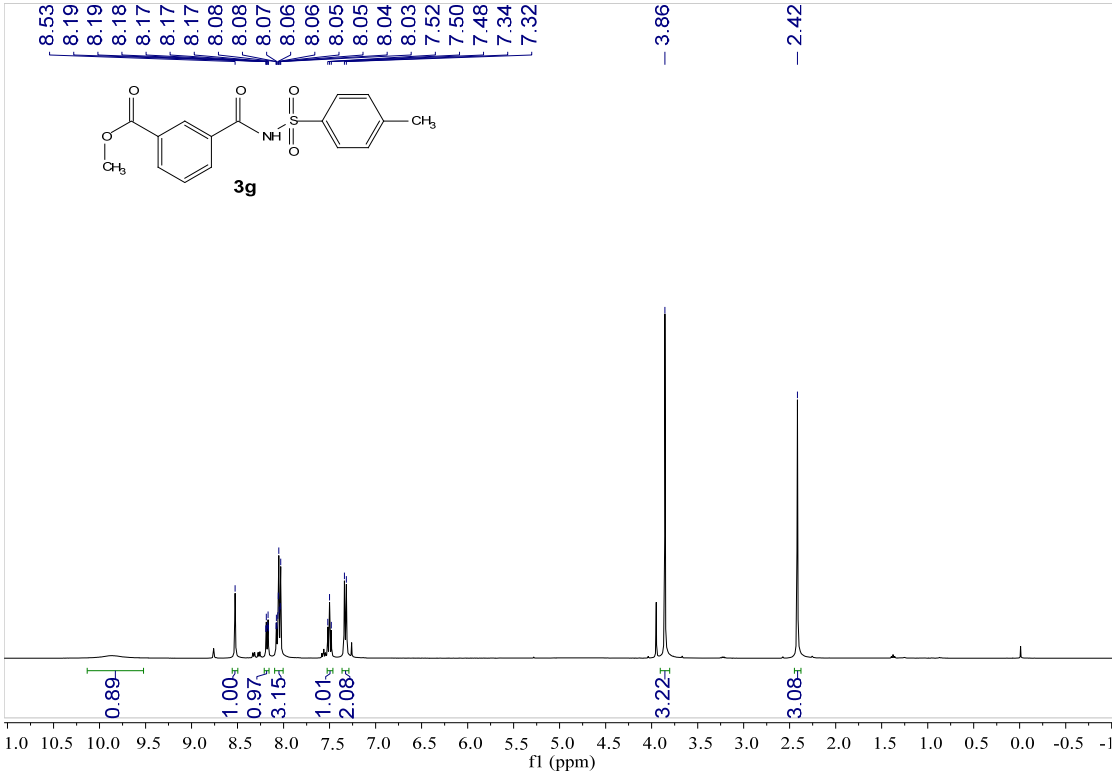
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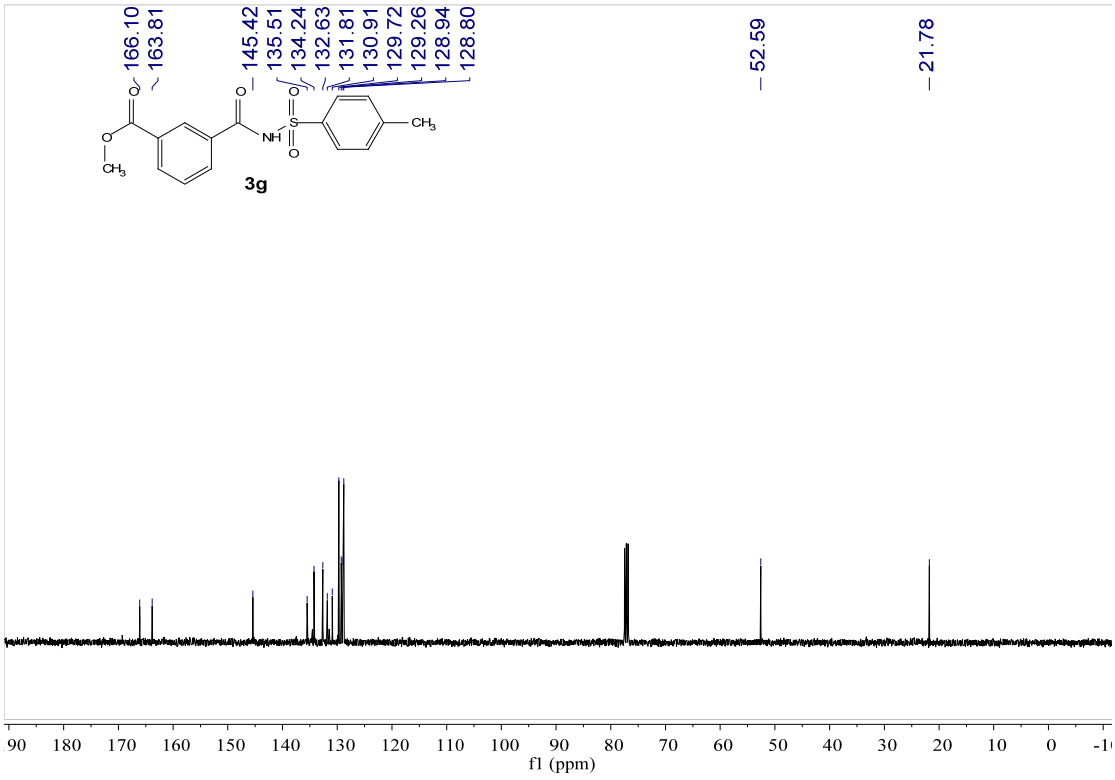
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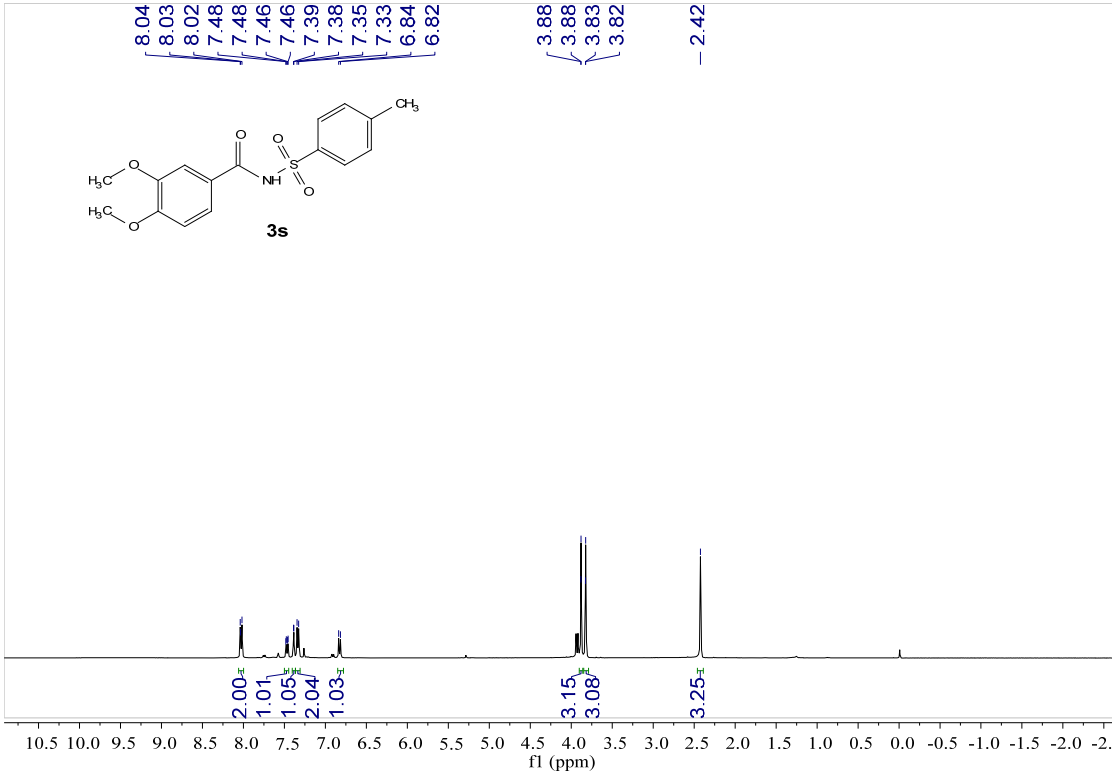
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7.38
7.35
7.33
6.84
6.82
3.88
3.88
3.83
3.82
2.42
CH3
O
S
NH
O
O
H3C
O
H3C
O
3s
2.00
1.01
1.05
2.04
1.03
3.15
3.08
3.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.
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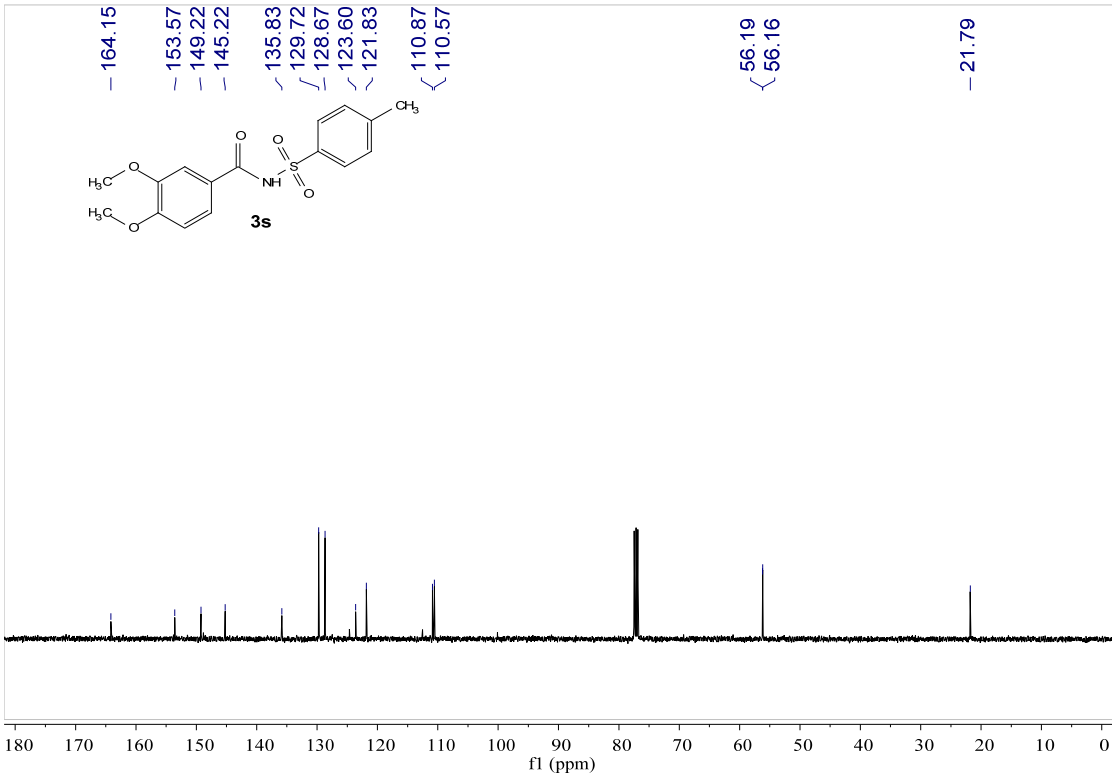
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110.57
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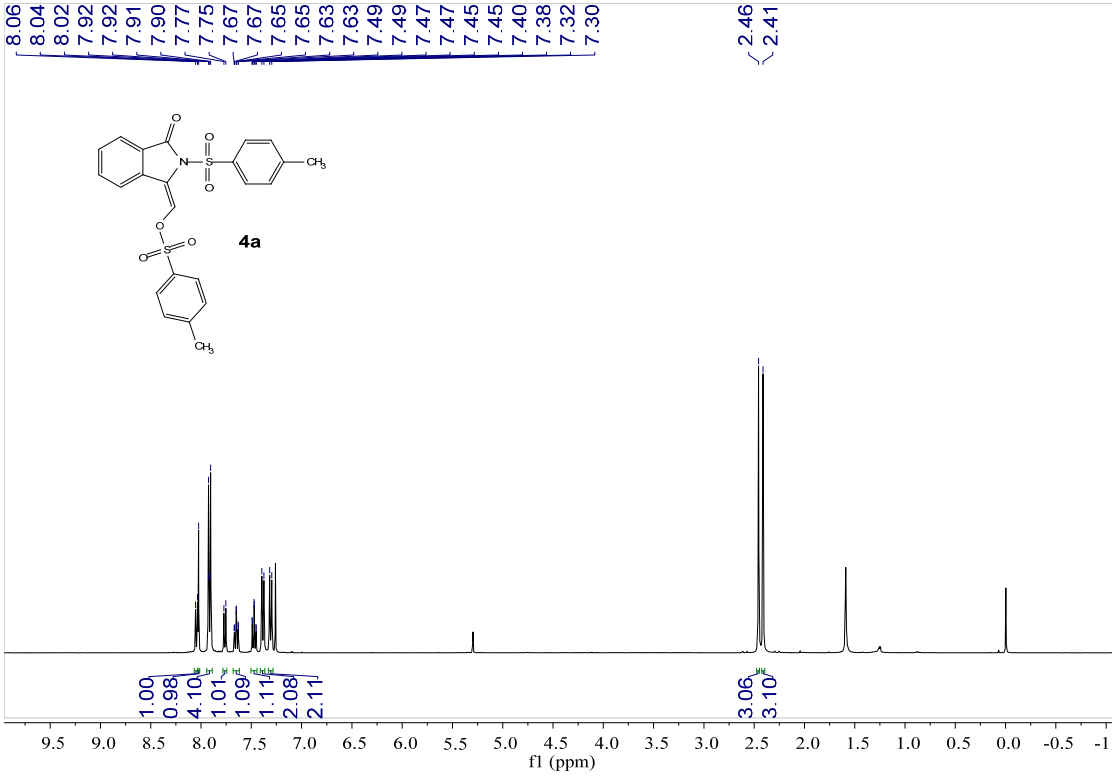
56.16
21.79
CH3
O
S
NH
O
O
H3C
O
H3C
O
3s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.63
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7.49
7.47
7.47
7.45
7.45
7.40
7.38
7.32
7.30
2.46
2.41
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1.09
1.11
2.08
2.11
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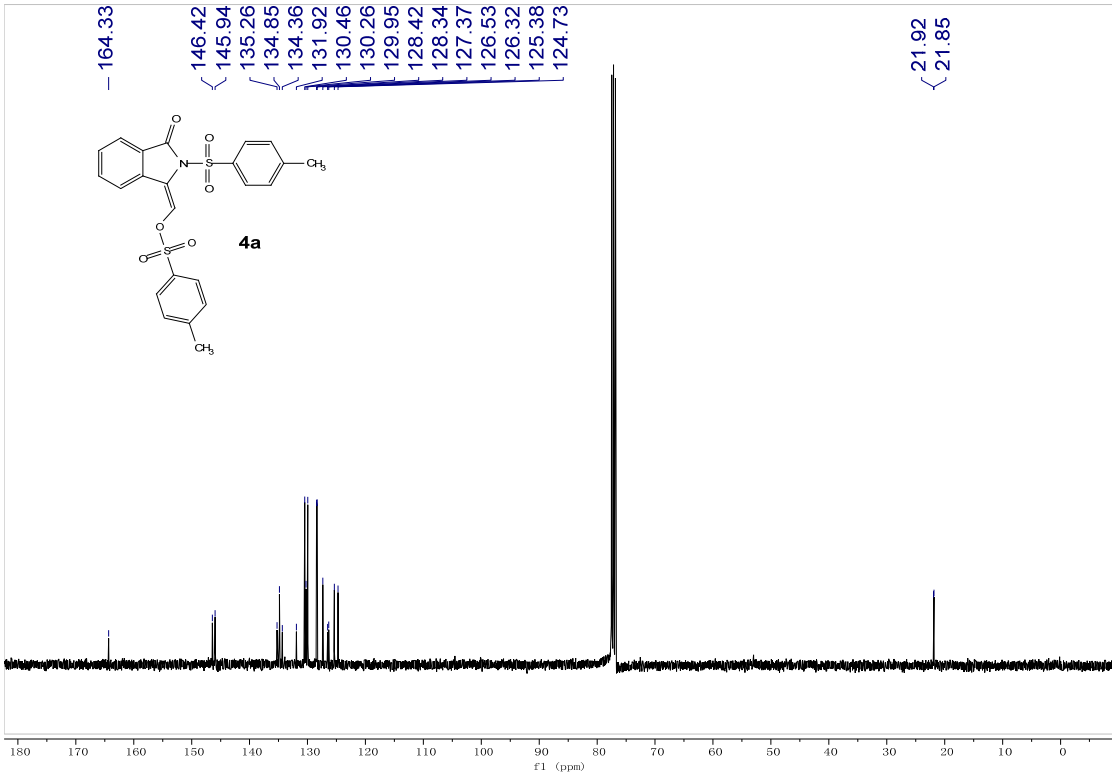
3.10
f1 (ppm)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124.73
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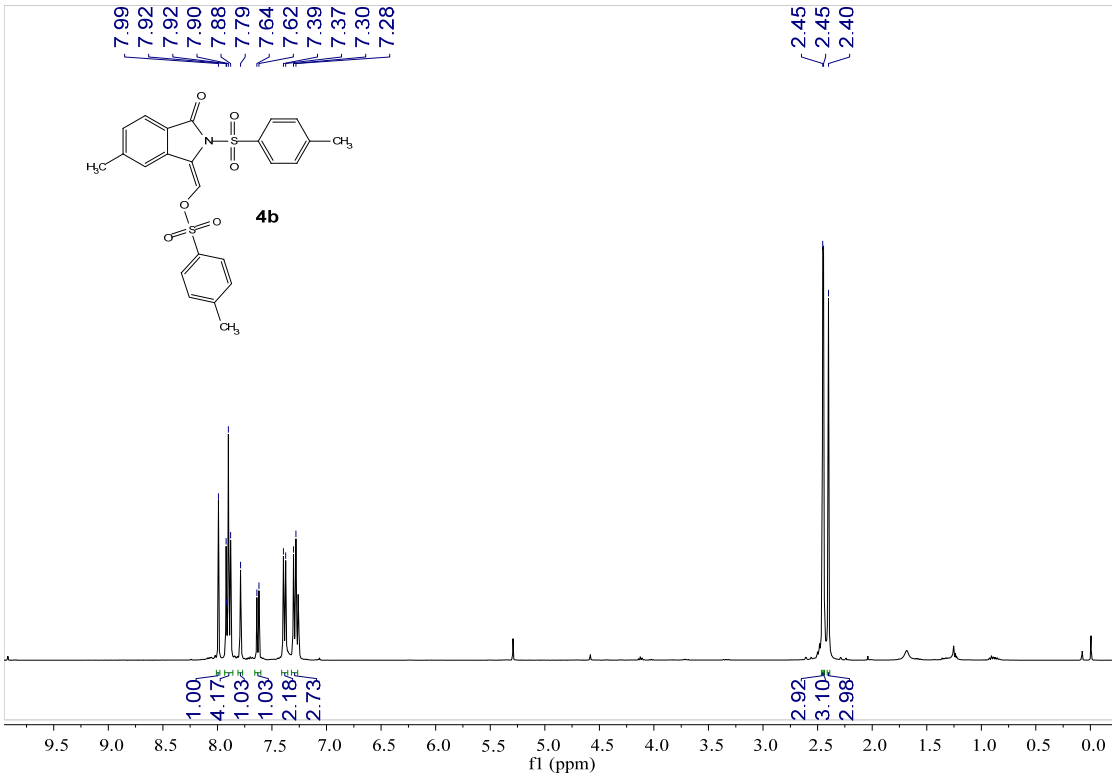
4a
f1 (ppm)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2.45
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1.03
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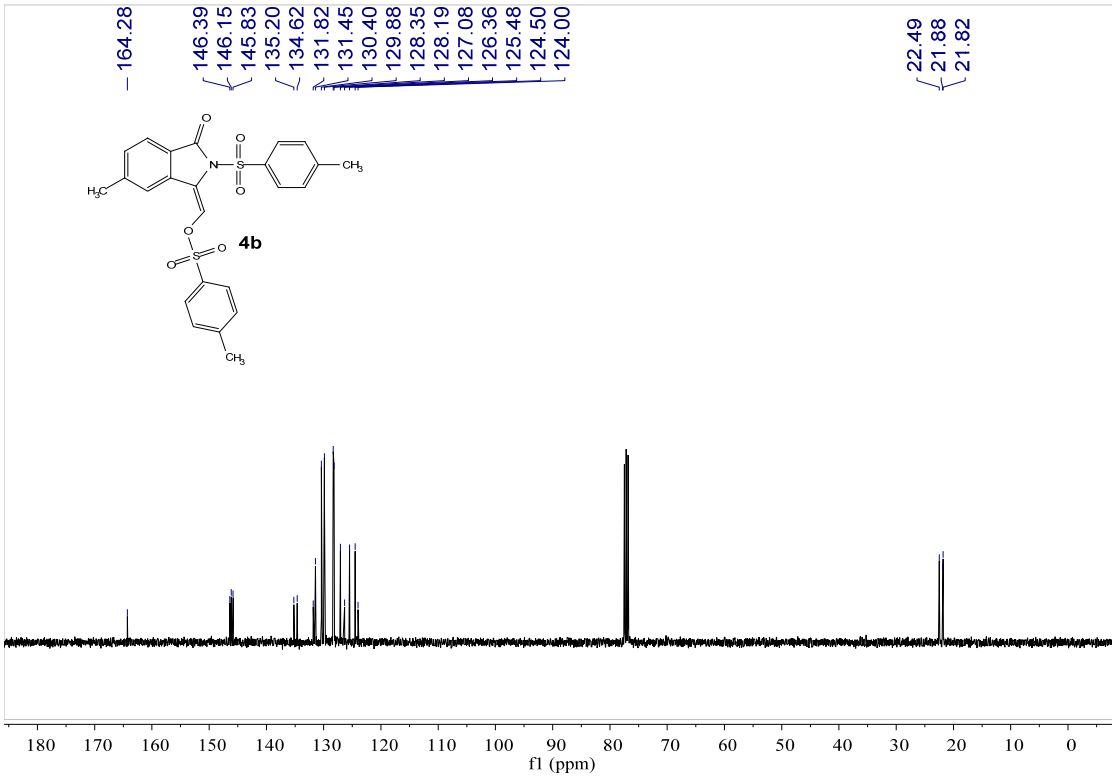
2.92
3.10
2.98
f1 (ppm)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124.00
22.49
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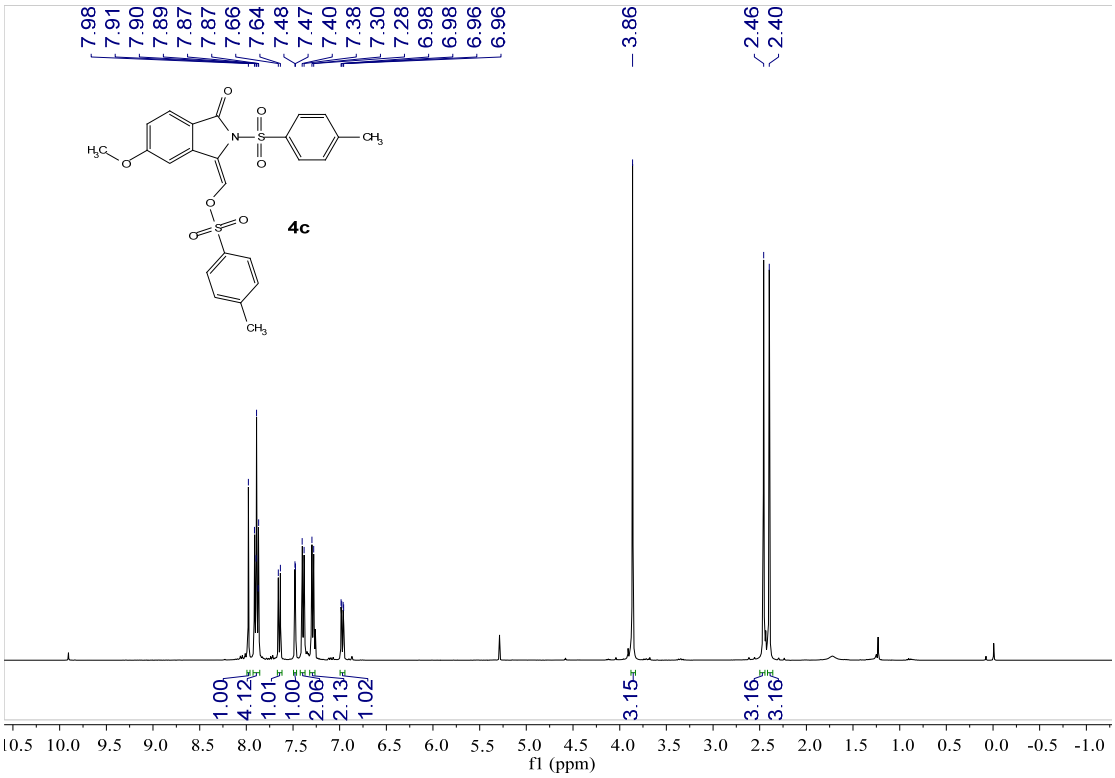
21.82
4b
f1 (ppm)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6.98
6.98
6.96
6.96
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2.40
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1.02
3.15
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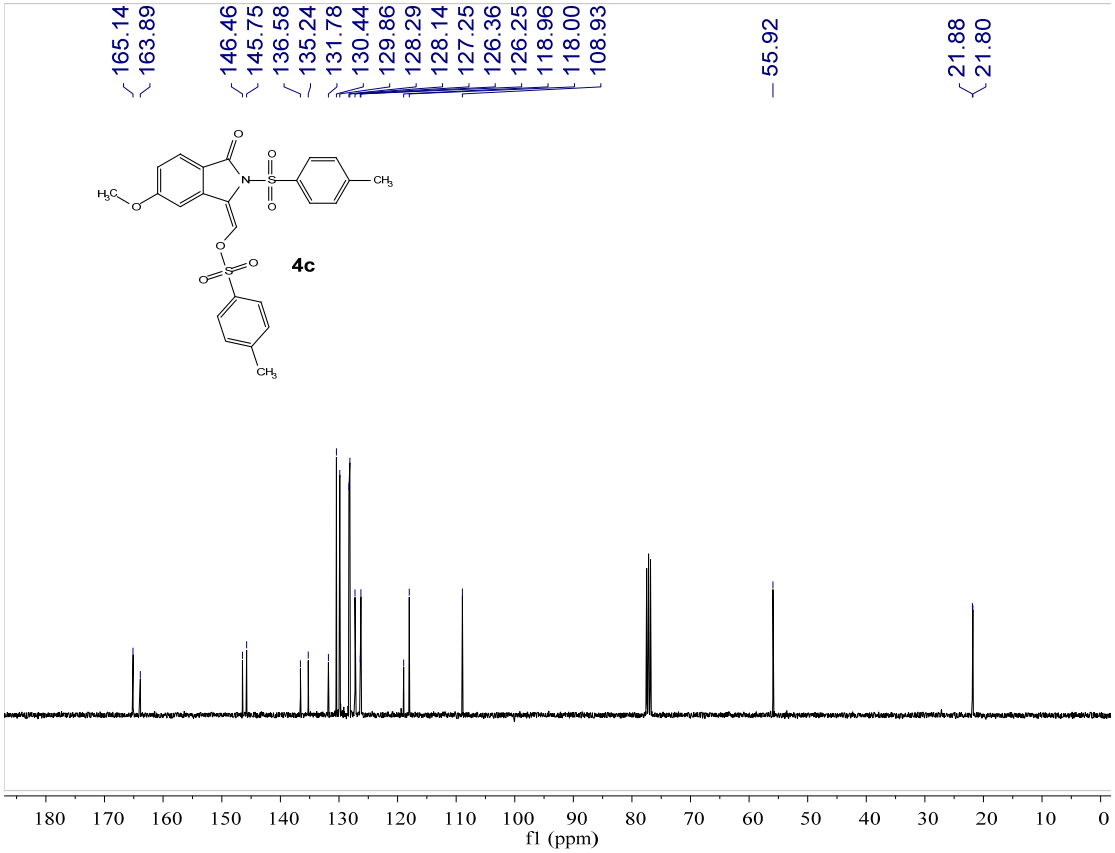
3.16
f1 (ppm)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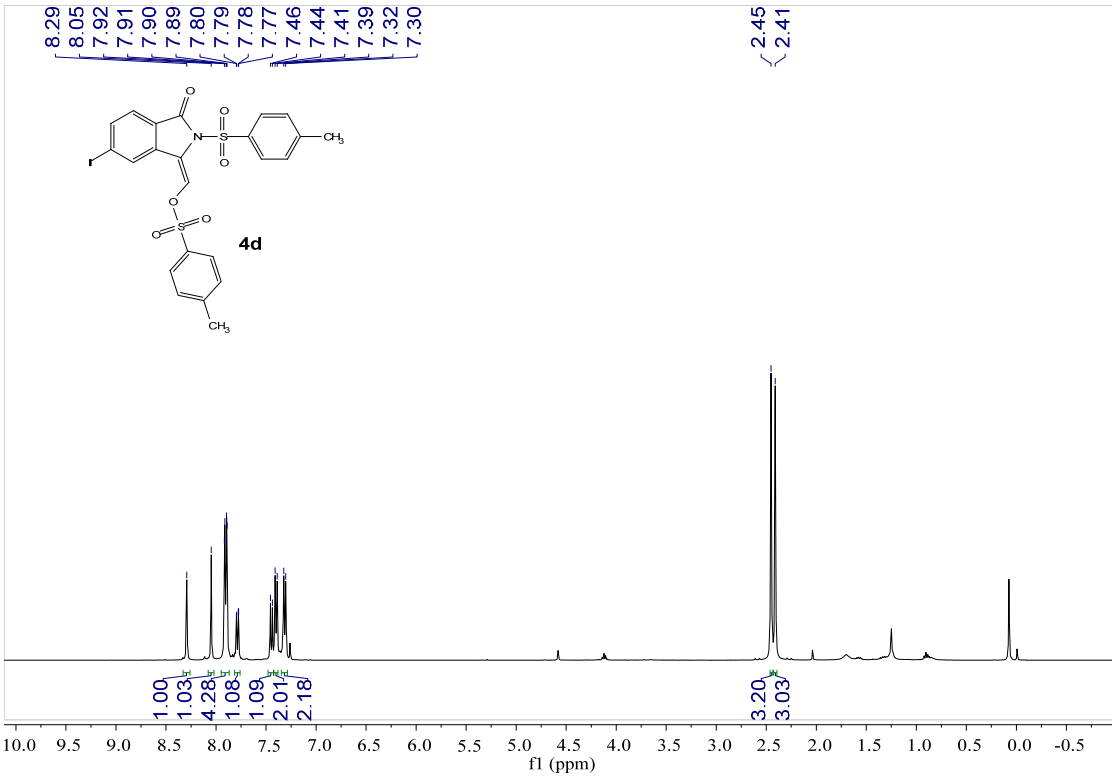
21.88
21.80
4c
f1 (ppm)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7.78
7.77
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7.41
7.39
7.32
7.30
2.45
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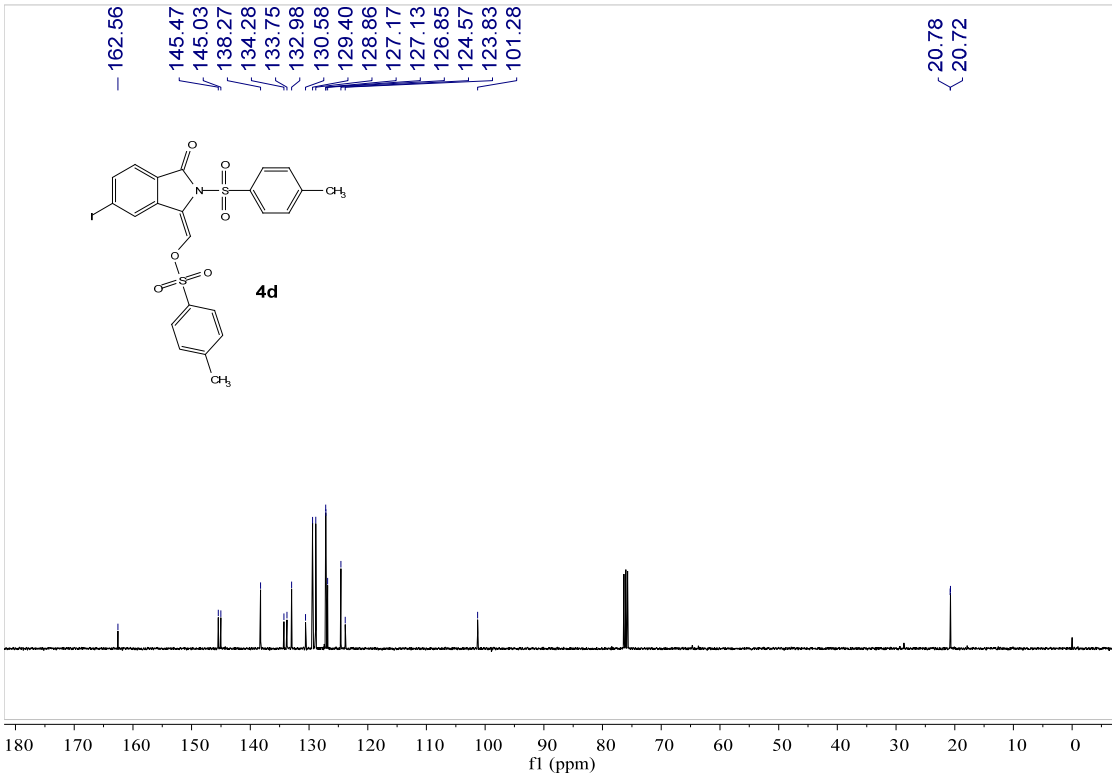
4.28
1.08
1.09
2.01
2.18
3.20
3.03
f1 (ppm)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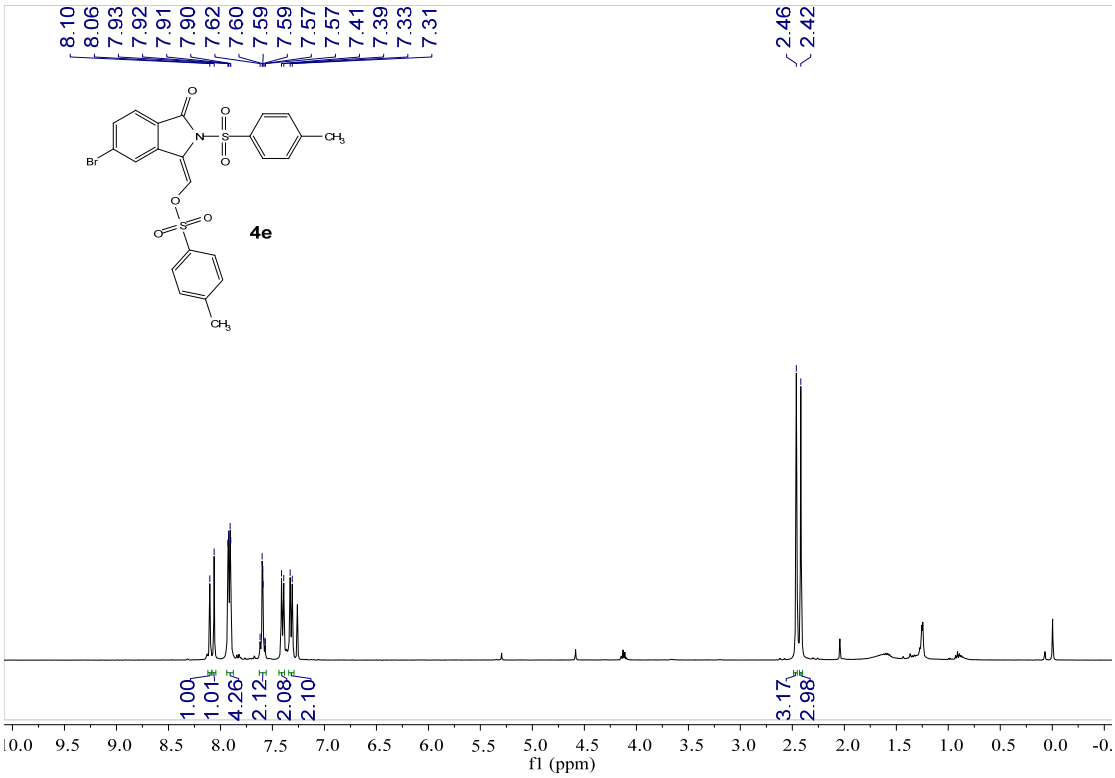
123.83
101.28
20.78
20.72
4d
f1 (ppm)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7.57
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7.41
7.39
7.33
7.31
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1.01
4.26
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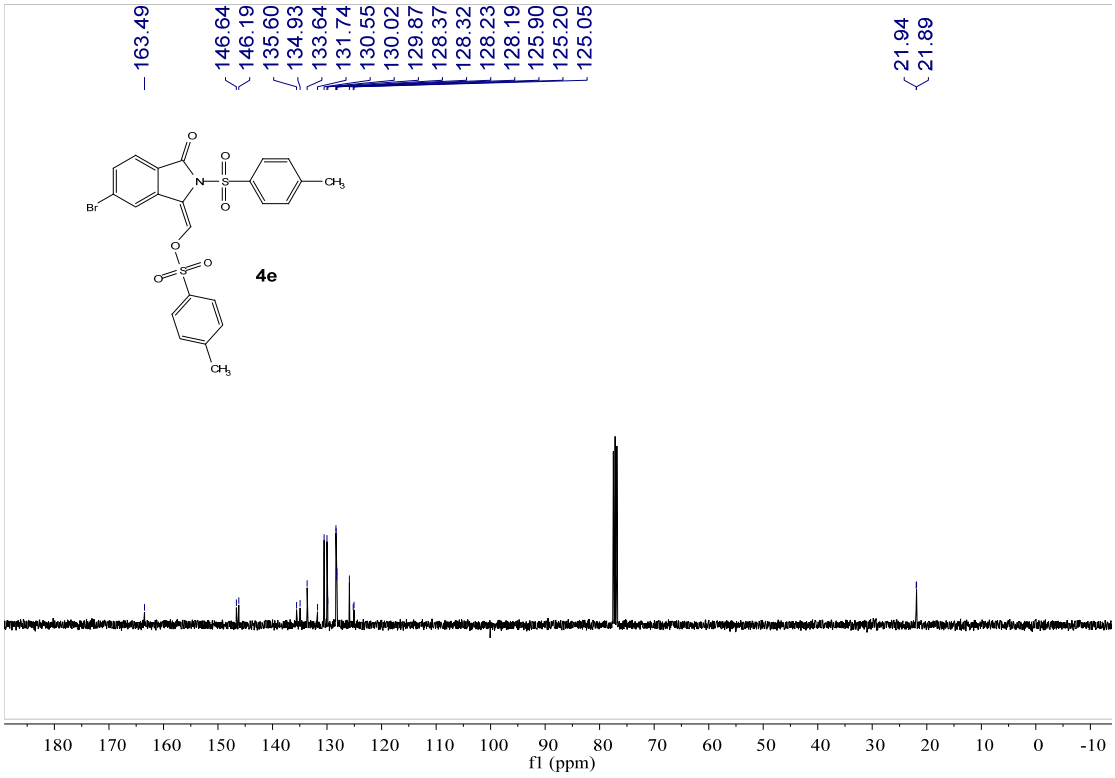
2.08
2.10
3.17
2.98
f1 (ppm)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125.05
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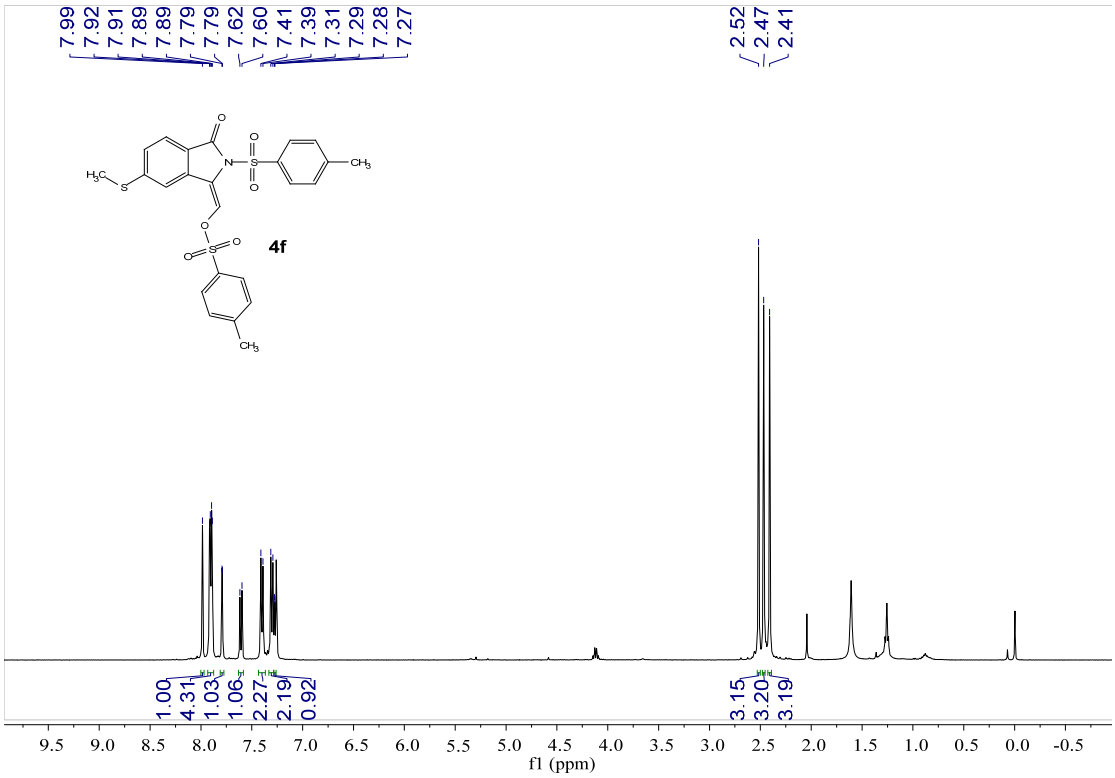
21.89
4e
f1 (ppm)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7.28
7.27
2.52
2.47
2.41
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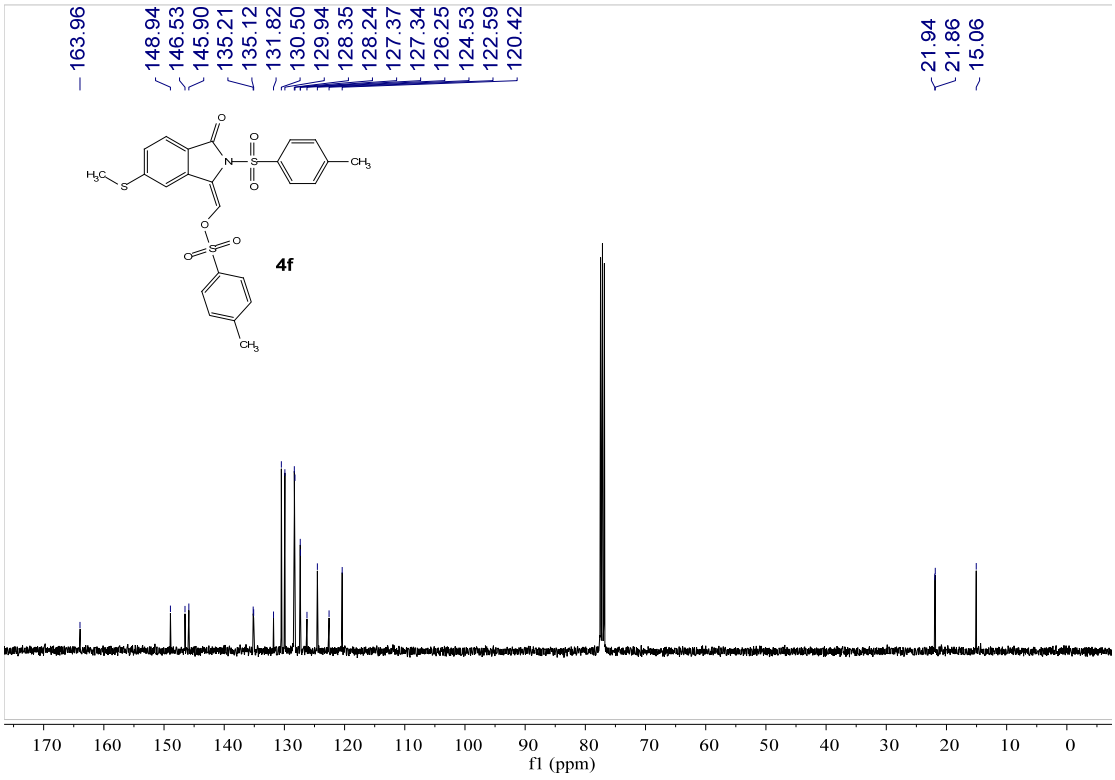
4.31
1.03
1.06
2.27
2.19
0.92
3.15
3.20
3.19
f1 (ppm)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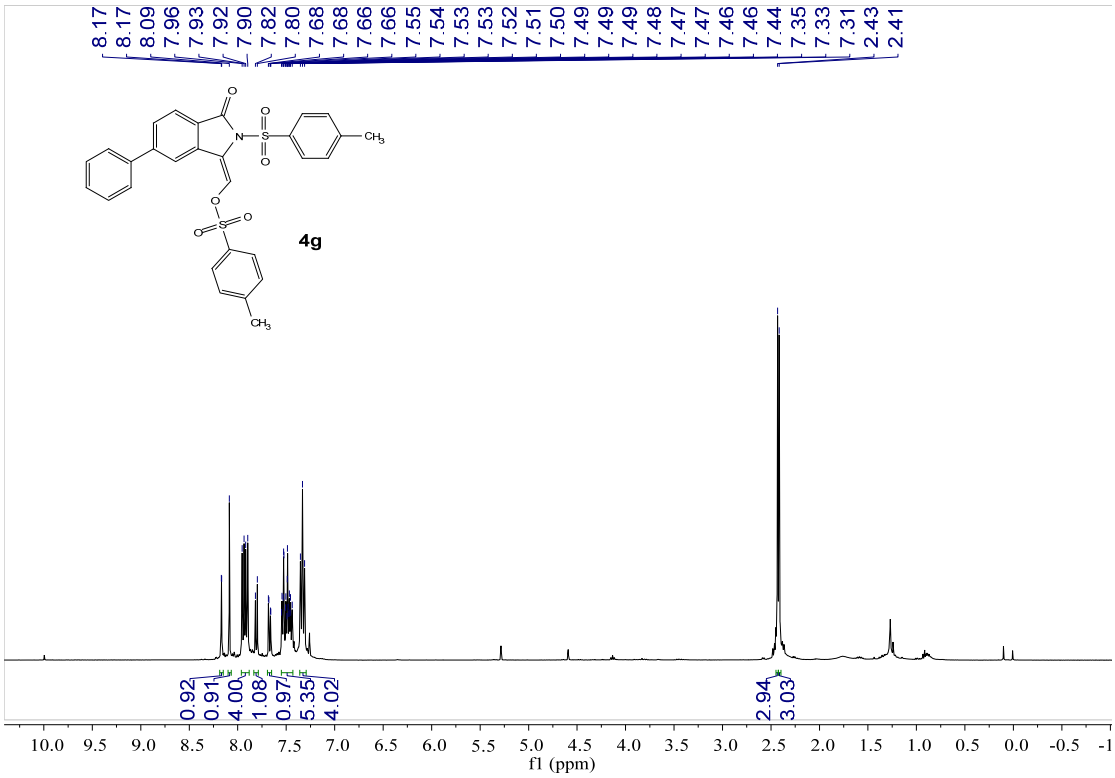
21.94
21.86
15.06
4f
f1 (ppm)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7.47
7.47
7.46
7.46
7.44
7.35
7.33
7.31
2.43
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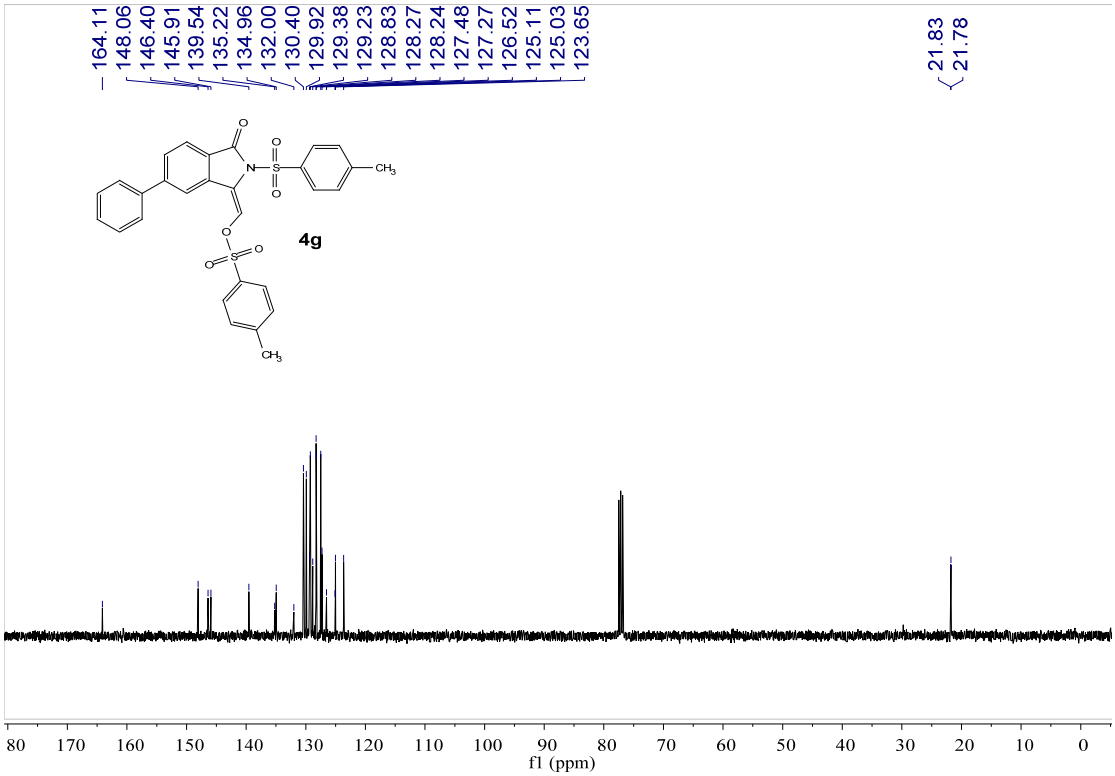
4.02
2.94
3.03
f1 (ppm)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127.27
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125.11
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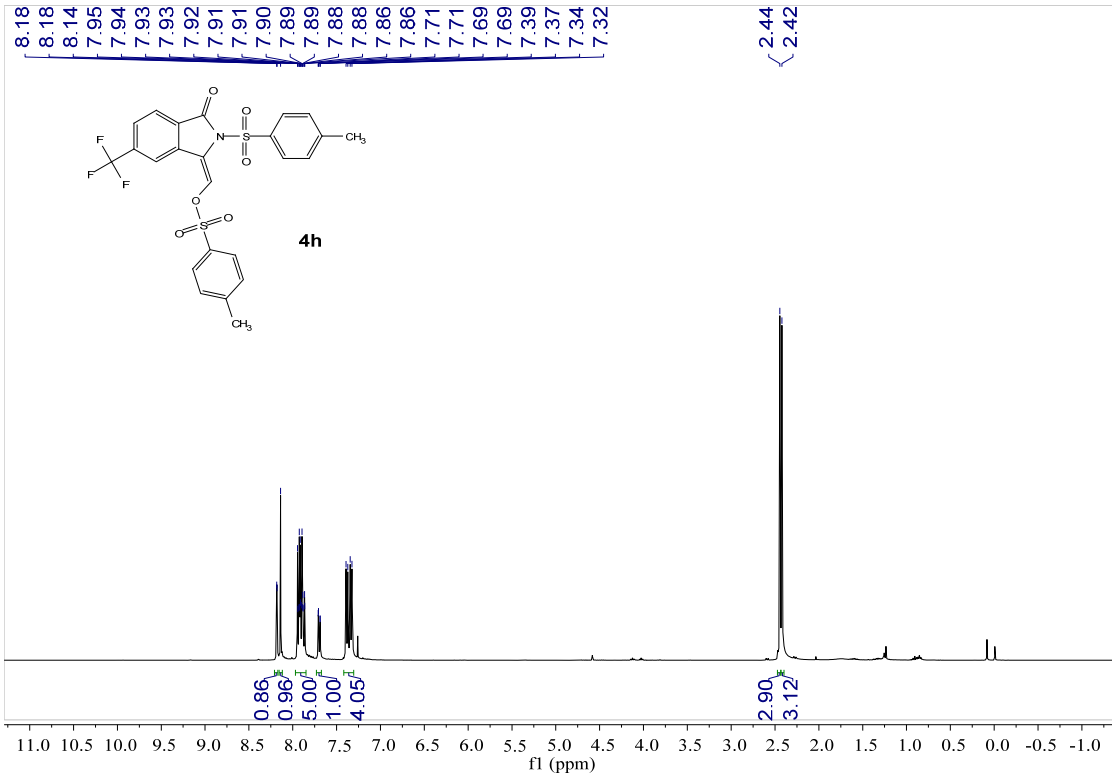
21.83
21.78
4g
f1 (ppm)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7.86
7.71
7.71
7.69
7.69
7.39
7.37
7.34
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0.96
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1.00
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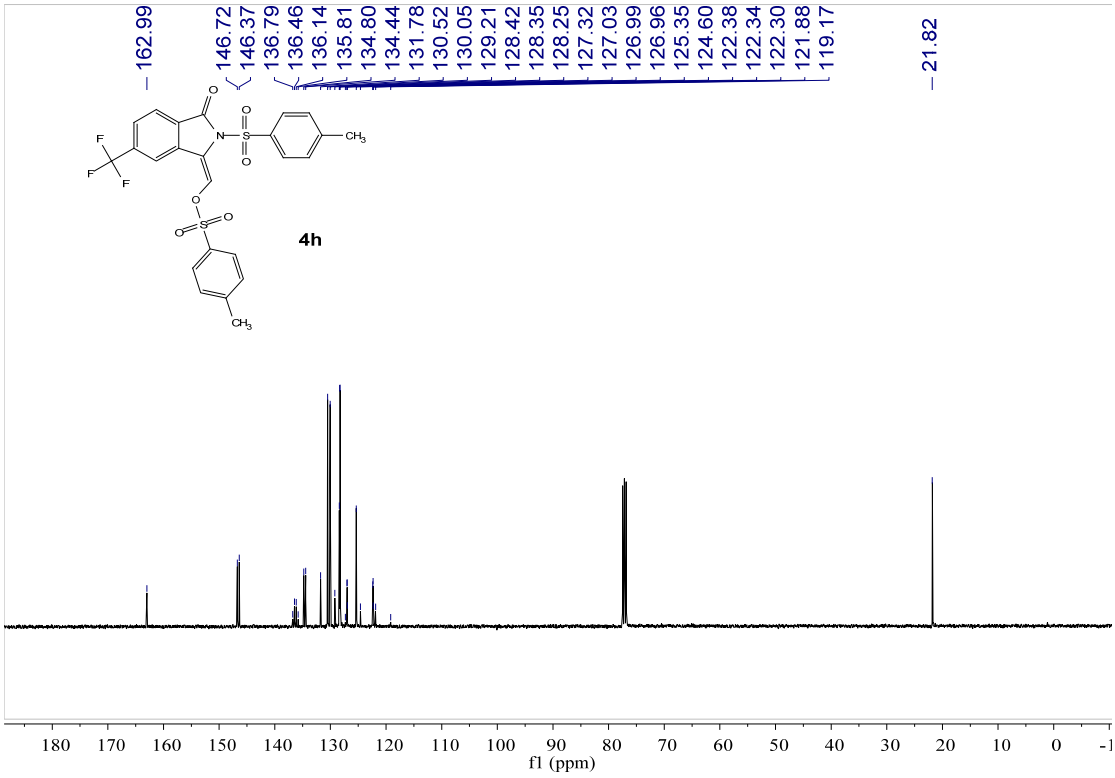
3.12
f1 (ppm)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128.25
127.32
127.03
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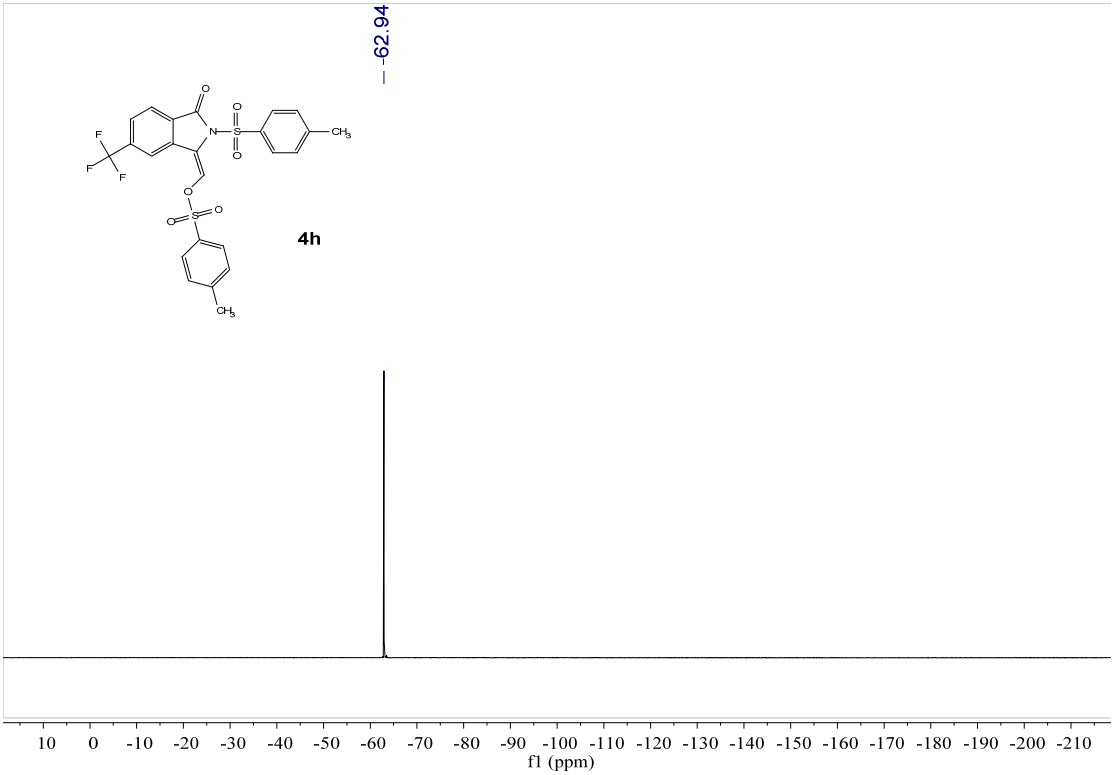
122.34
122.30
121.88
119.17
21.82
4h
f1 (ppm)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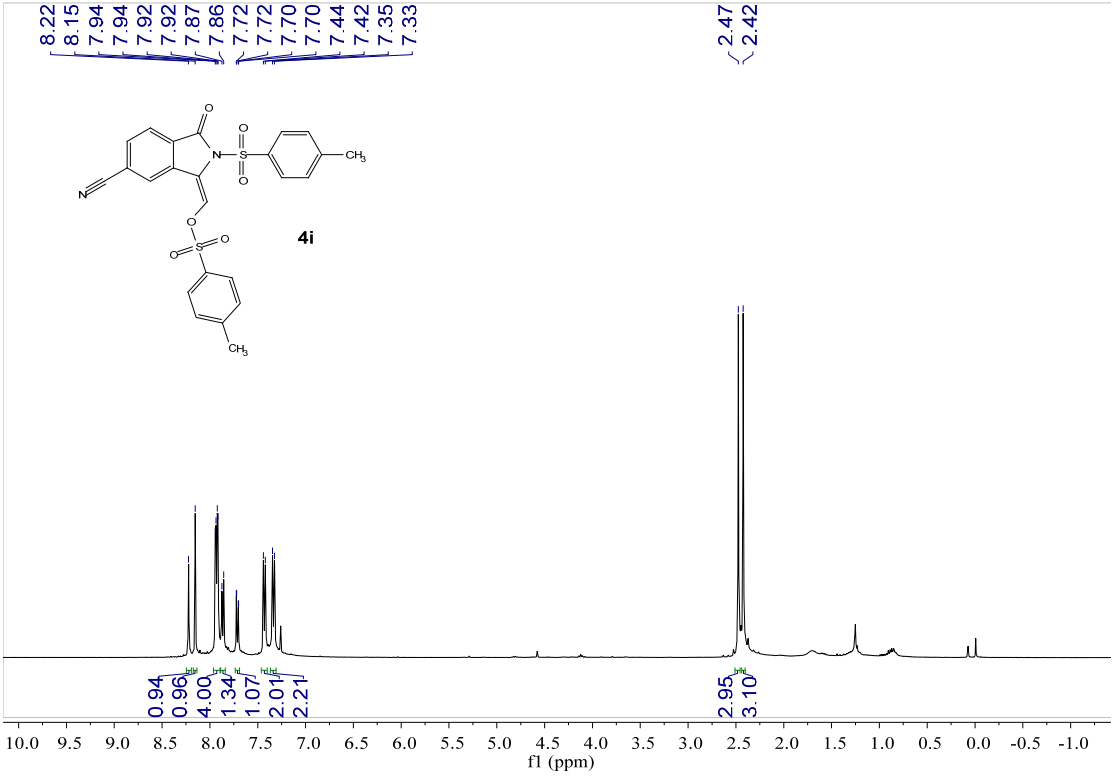
f1 (ppm)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7.70
7.44
7.42
7.35
7.33
2.47
2.42
4i
0.94
0.96
4.00
1.34
1.07
2.01
2.21
2.95
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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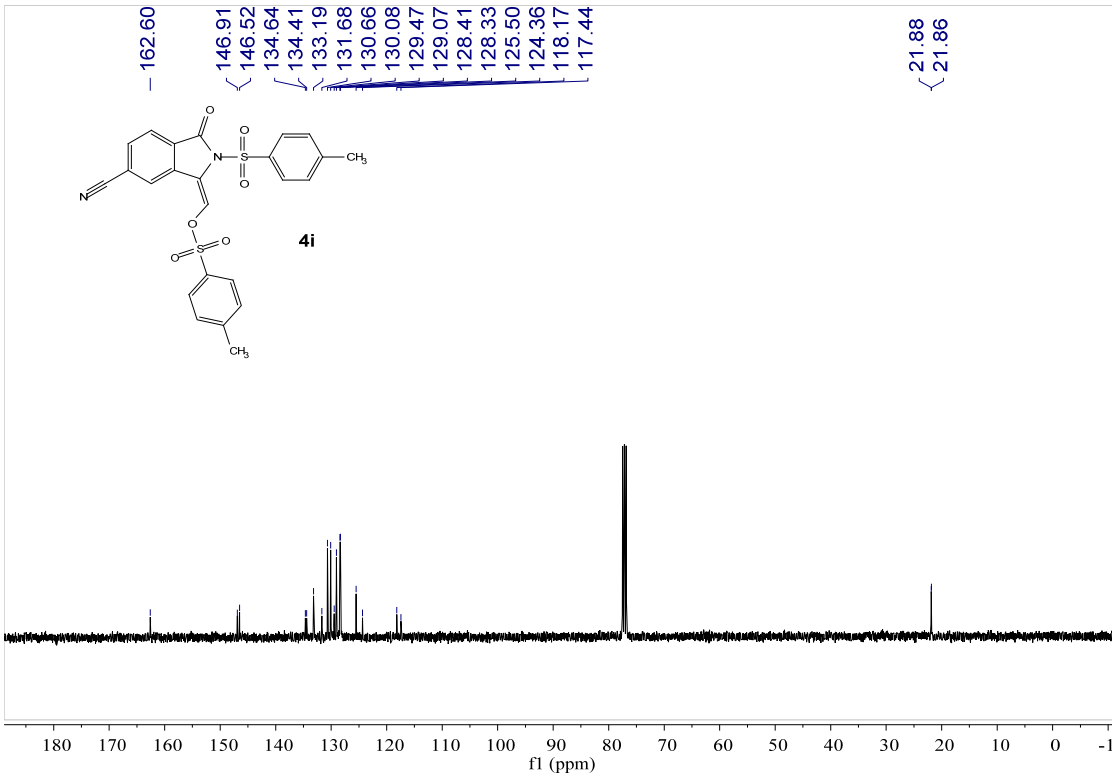
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124.36
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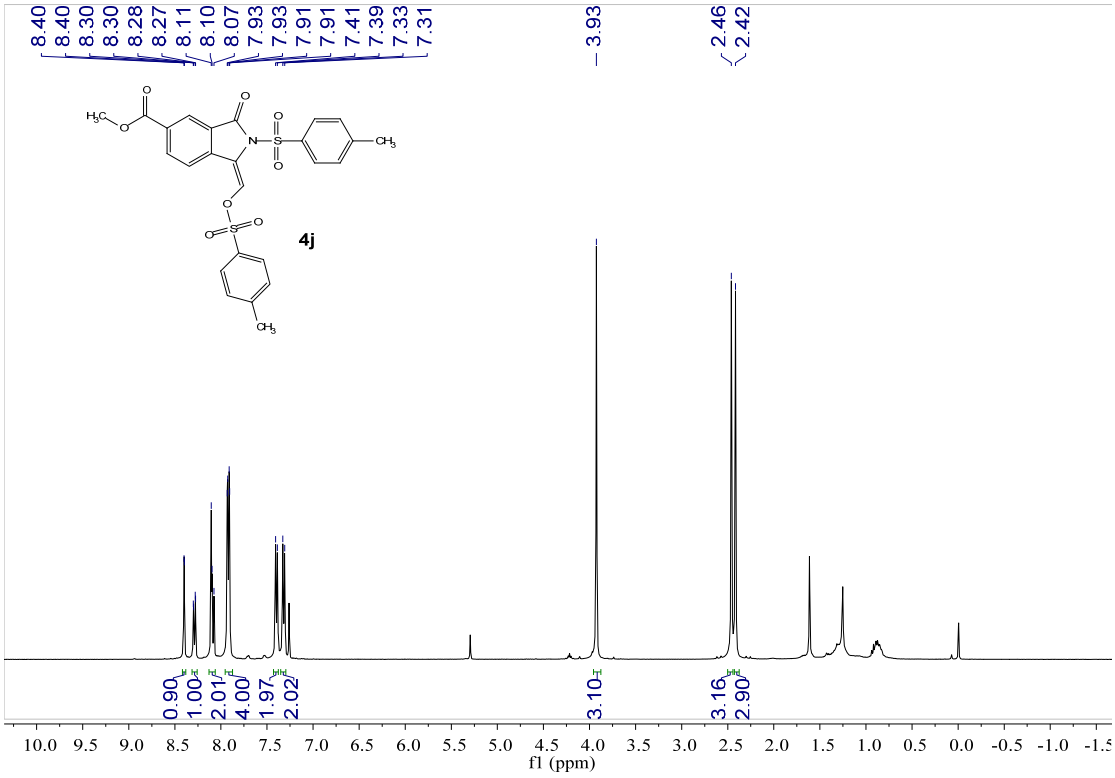
21.86
4i
f1 (ppm)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7.91
7.41
7.39
7.33
7.31
3.93
2.46
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2.01
4.00
1.97
2.02
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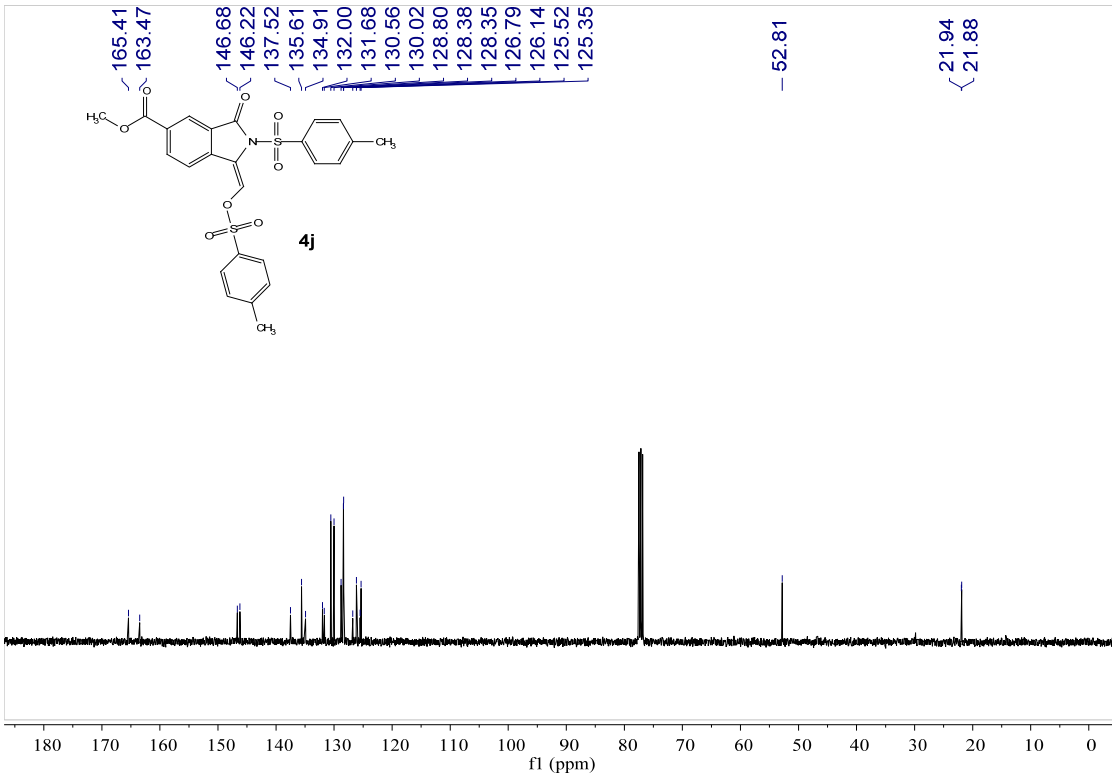
f1 (ppm)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128.35
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21.88
4j
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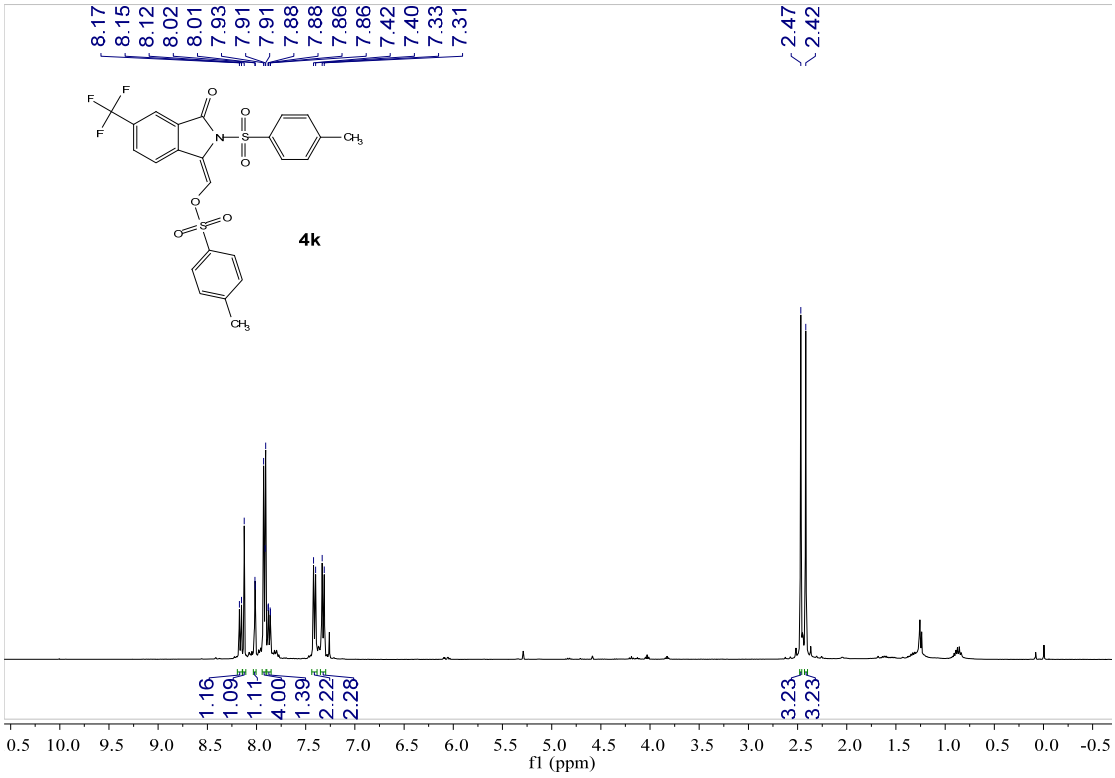
f1 (ppm)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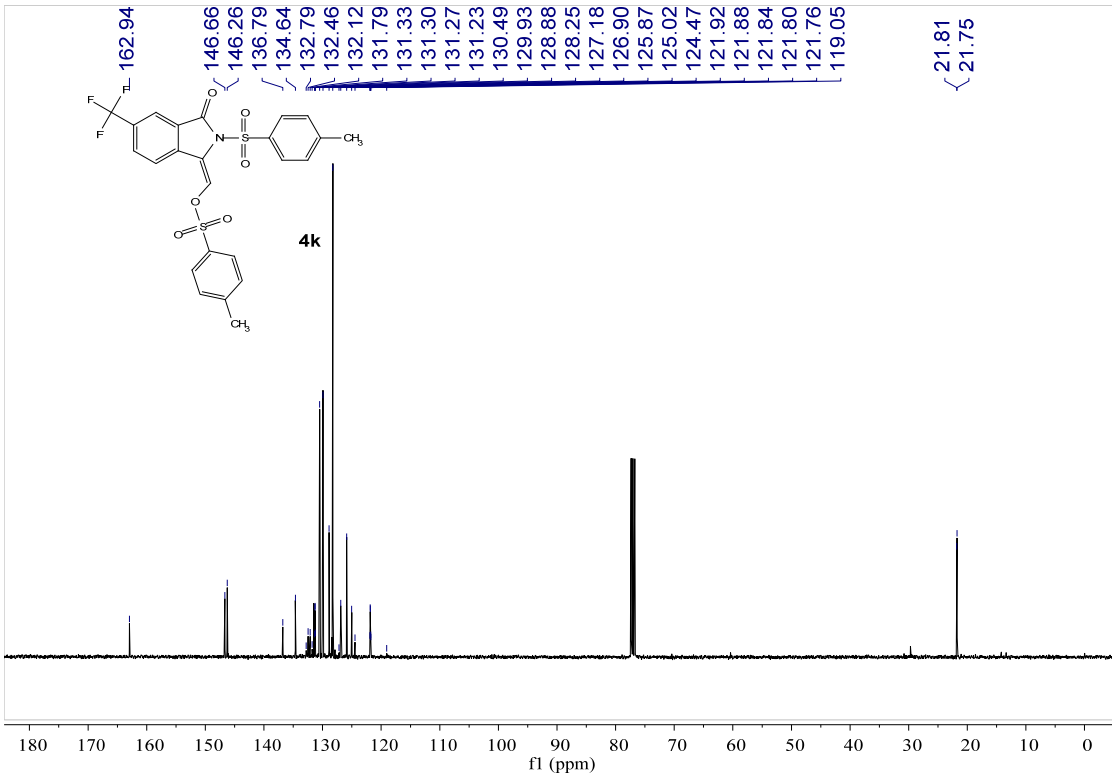
7.42
7.40
7.33
7.31
2.47
2.42
4k
1.16
1.09
1.11
4.00
1.39
2.22
2.28
3.23
3.23
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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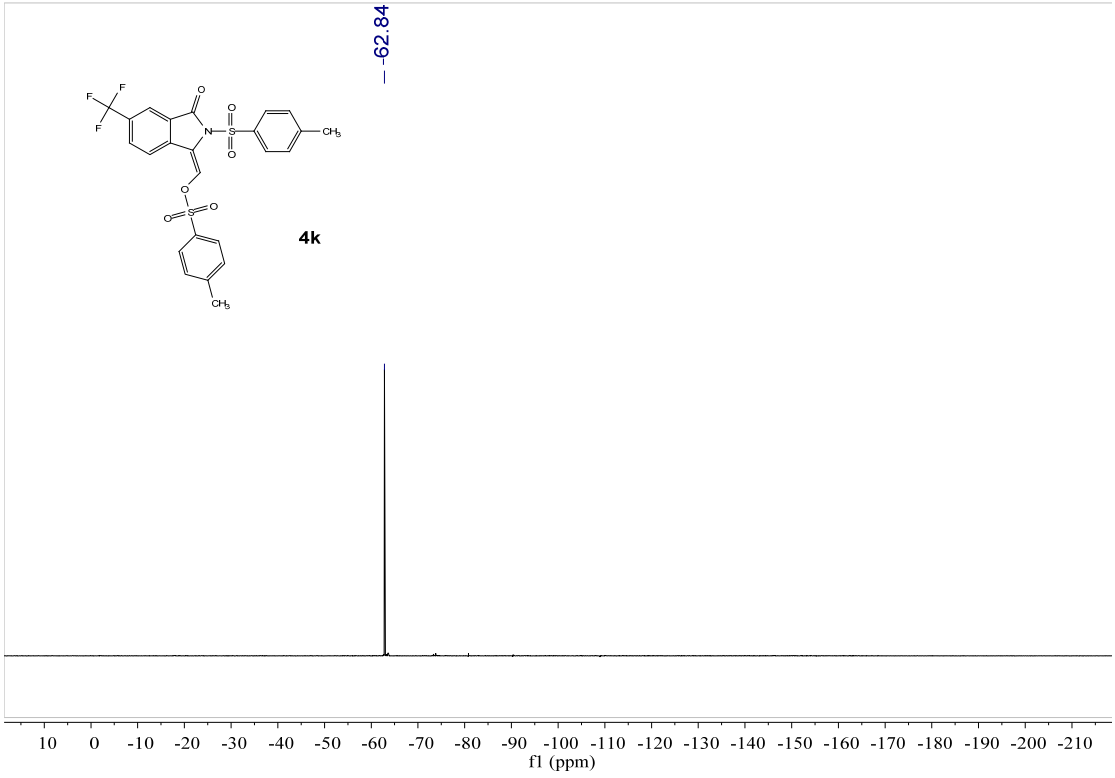
21.75
4k
f1 (ppm)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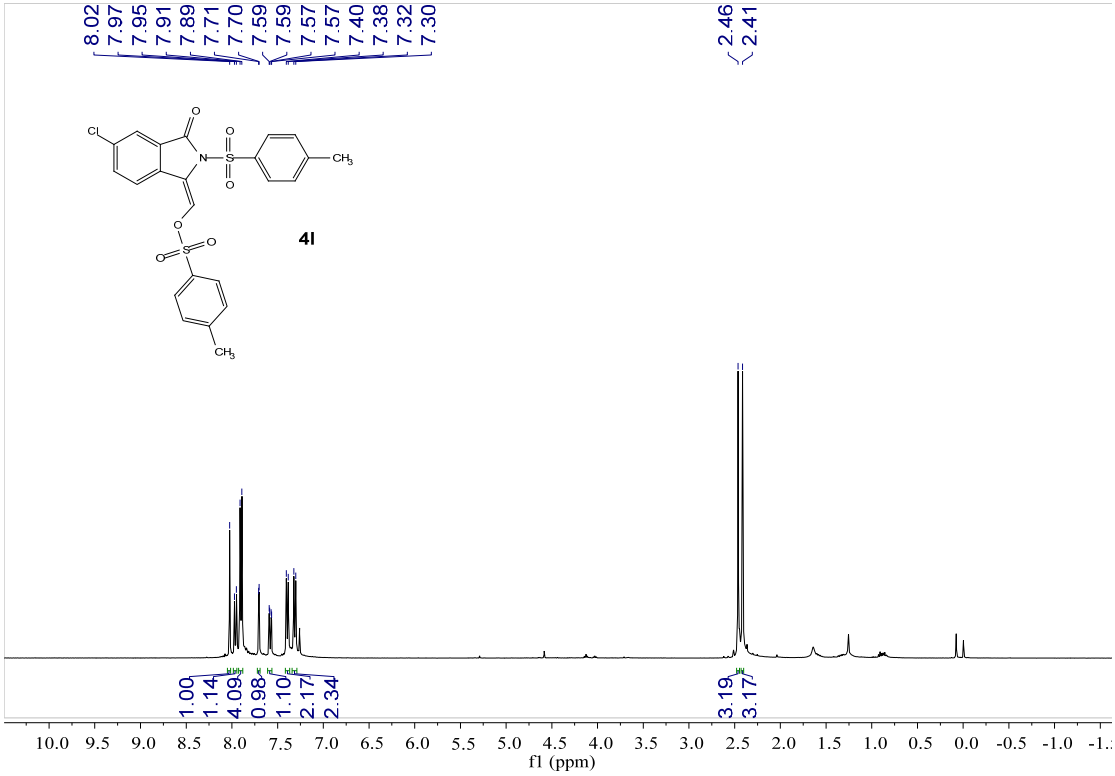
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7.38
7.32
7.30
2.46
2.41
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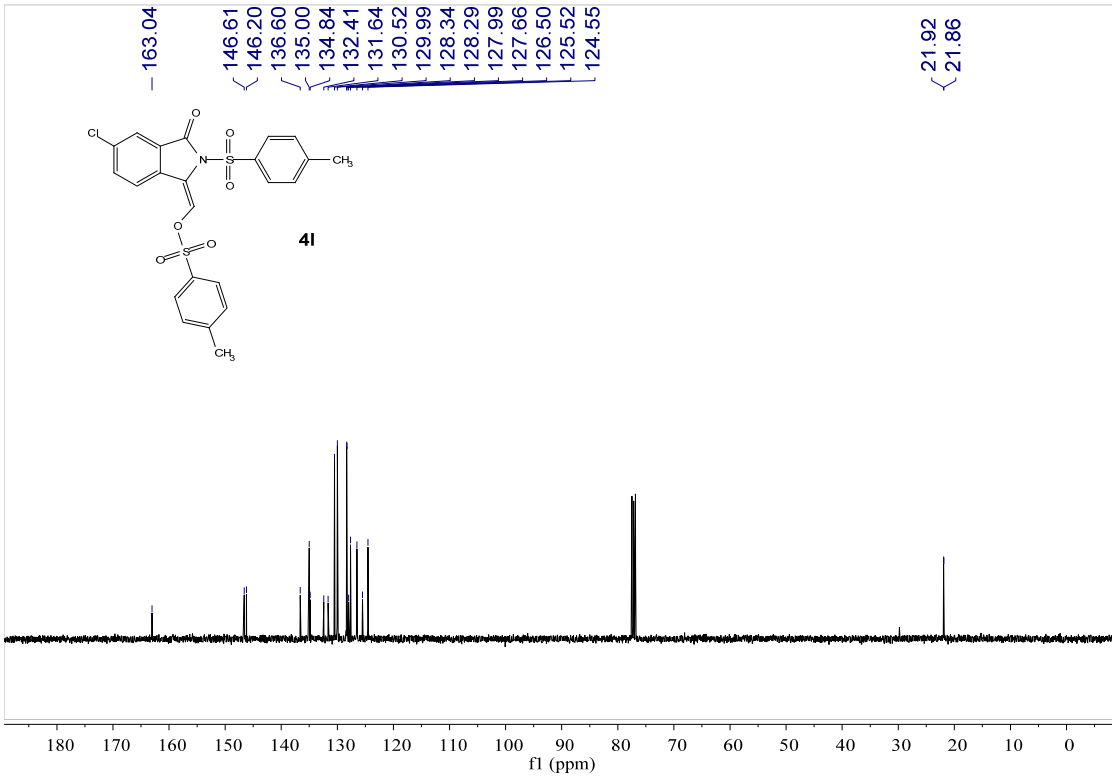
4.09
0.98
1.10
2.17
2.34
3.19
3.17
f1 (ppm)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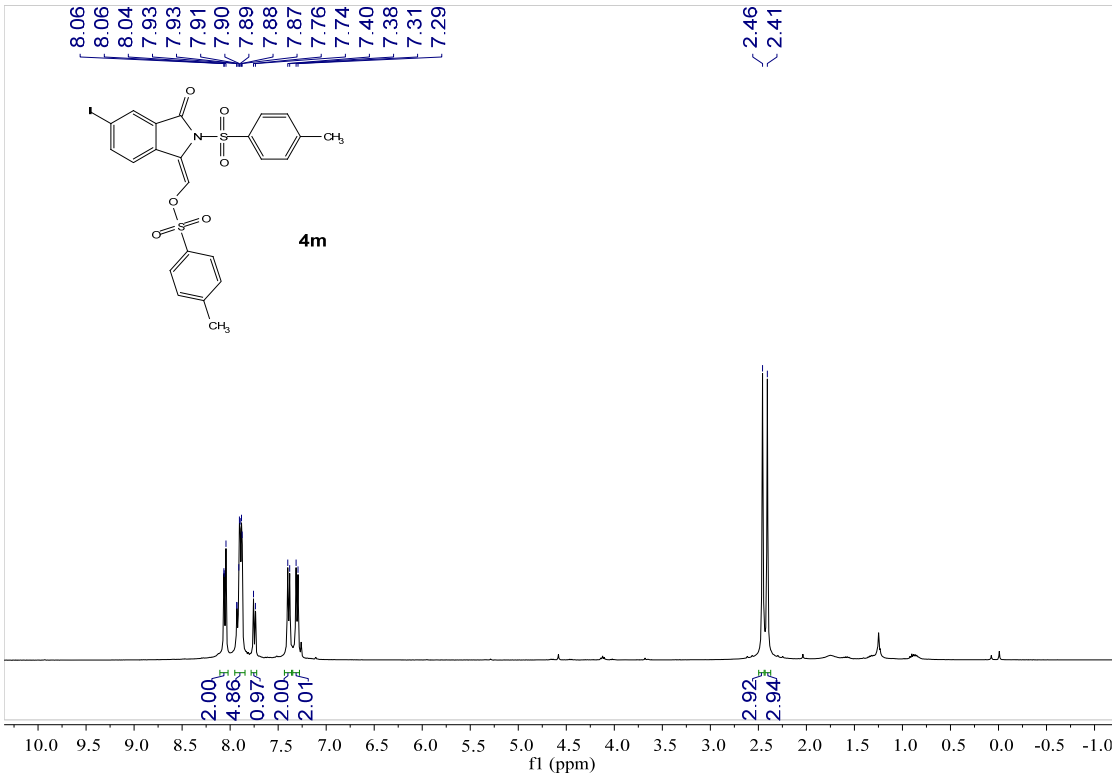
4l
f1 (ppm)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7.31
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2.00
2.01
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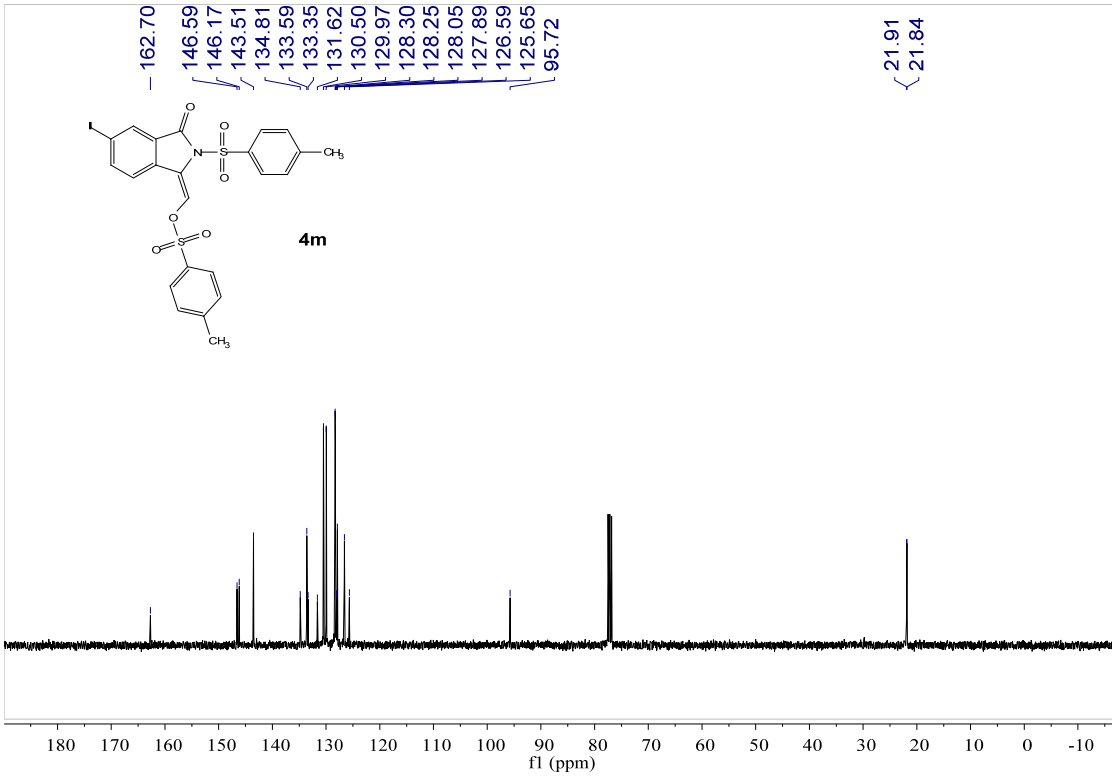
2.94
f1 (ppm)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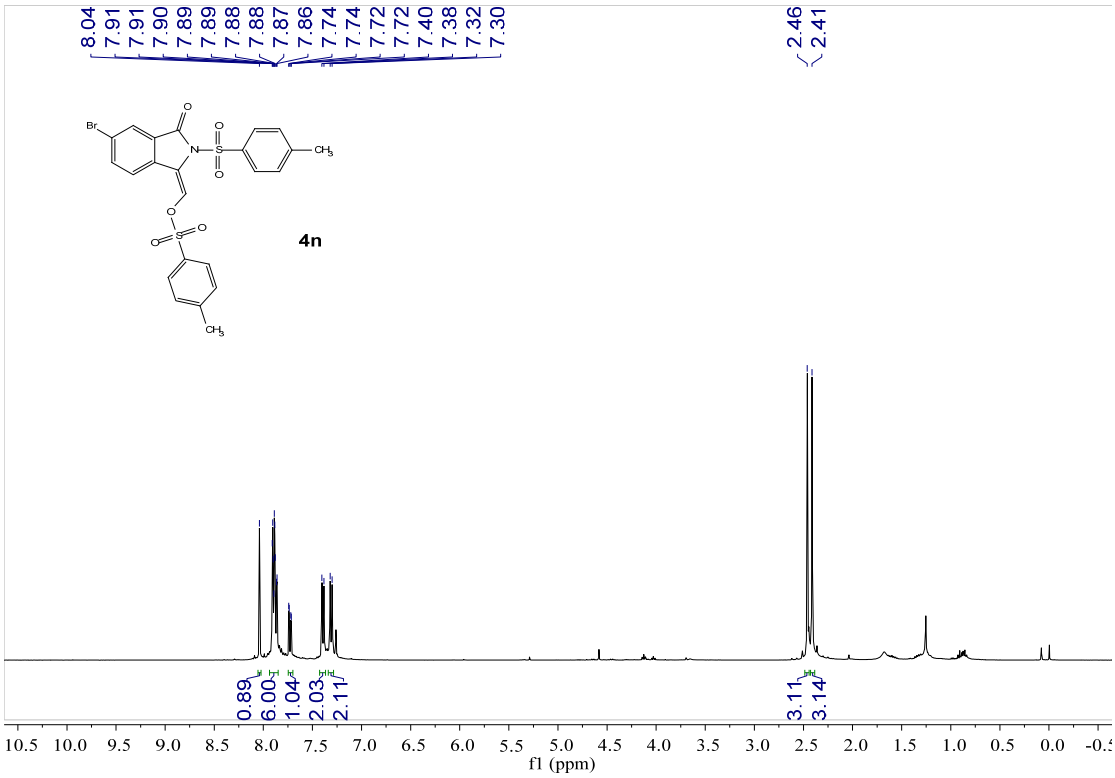
4m
f1 (ppm)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7.86
7.74
7.74
7.72
7.72
7.40
7.38
7.32
7.30
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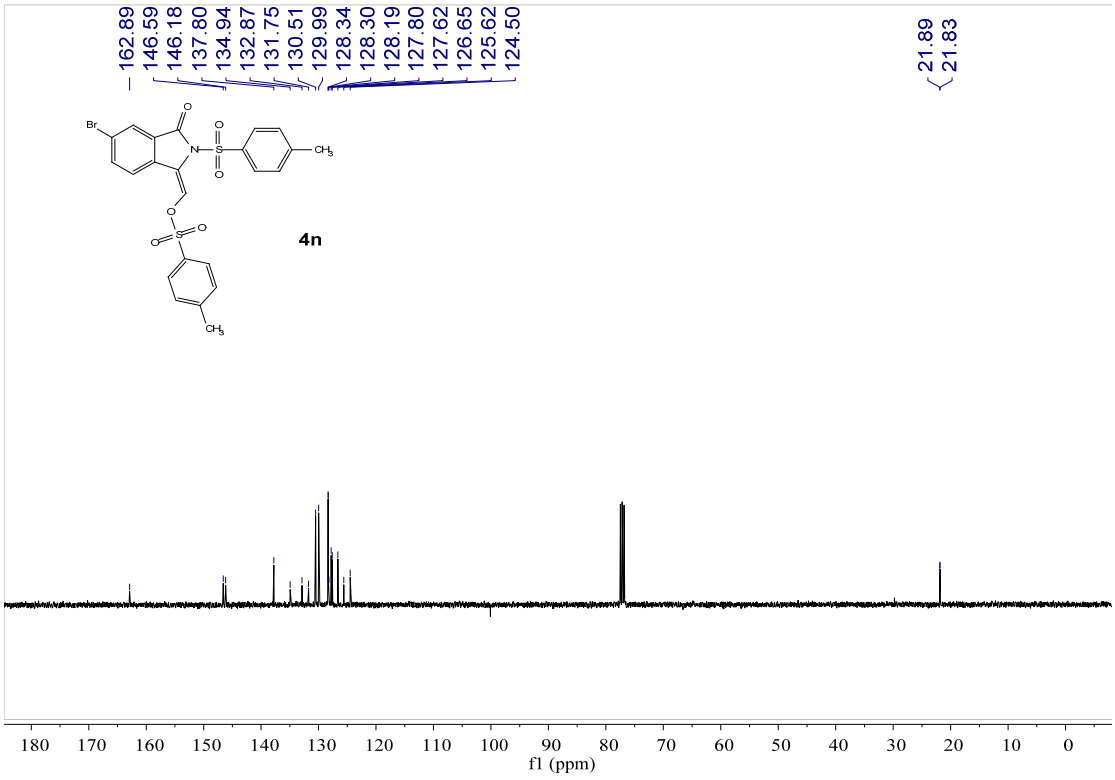
6.00
1.04
2.03
2.11
3.11
3.14
f1 (ppm)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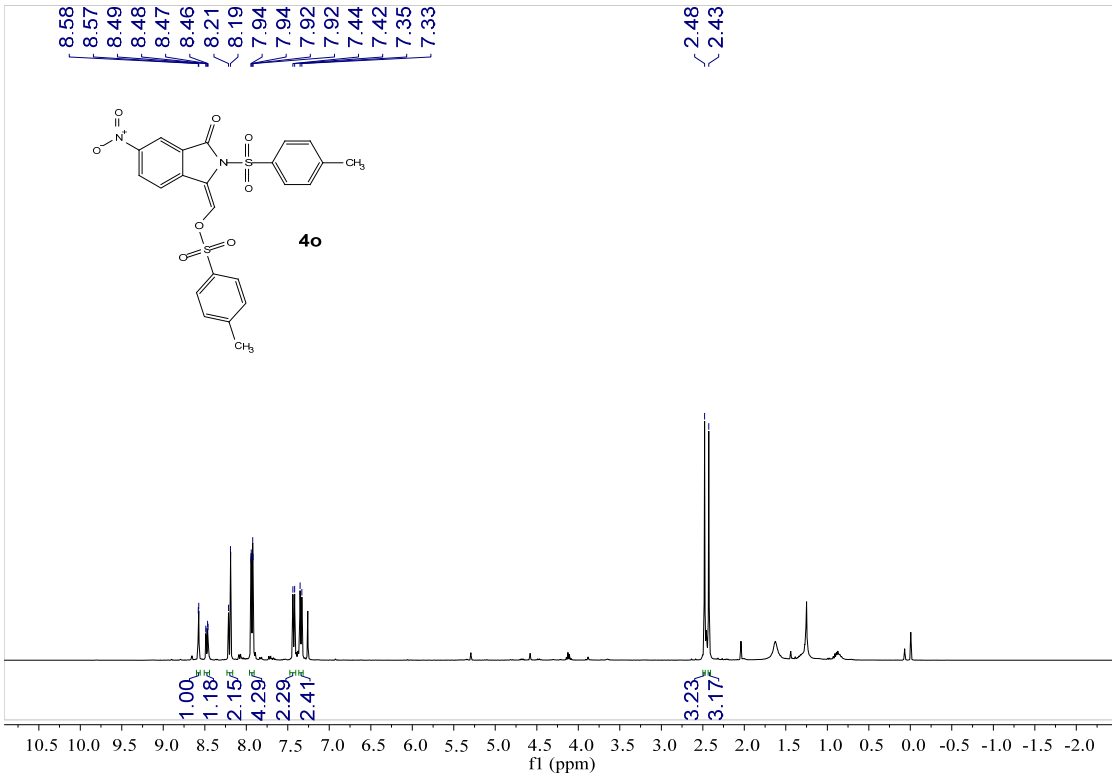
126.65
125.62
124.50
21.89
21.83
4n
f1 (ppm)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8.19
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7.94
7.92
7.92
7.44
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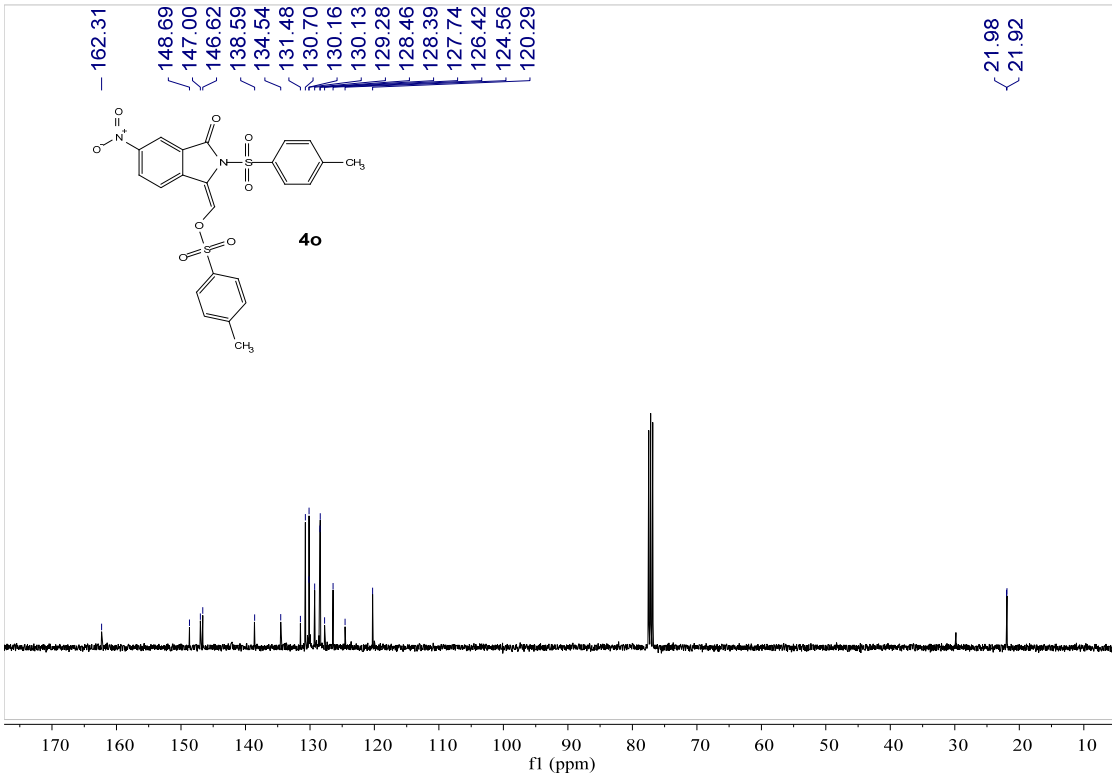
7.35
7.33
2.48
2.43
4o
1.00
1.18
2.15
4.29
2.29
2.41
3.23
3.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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128.39
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120.29
21.98
21.92
4o
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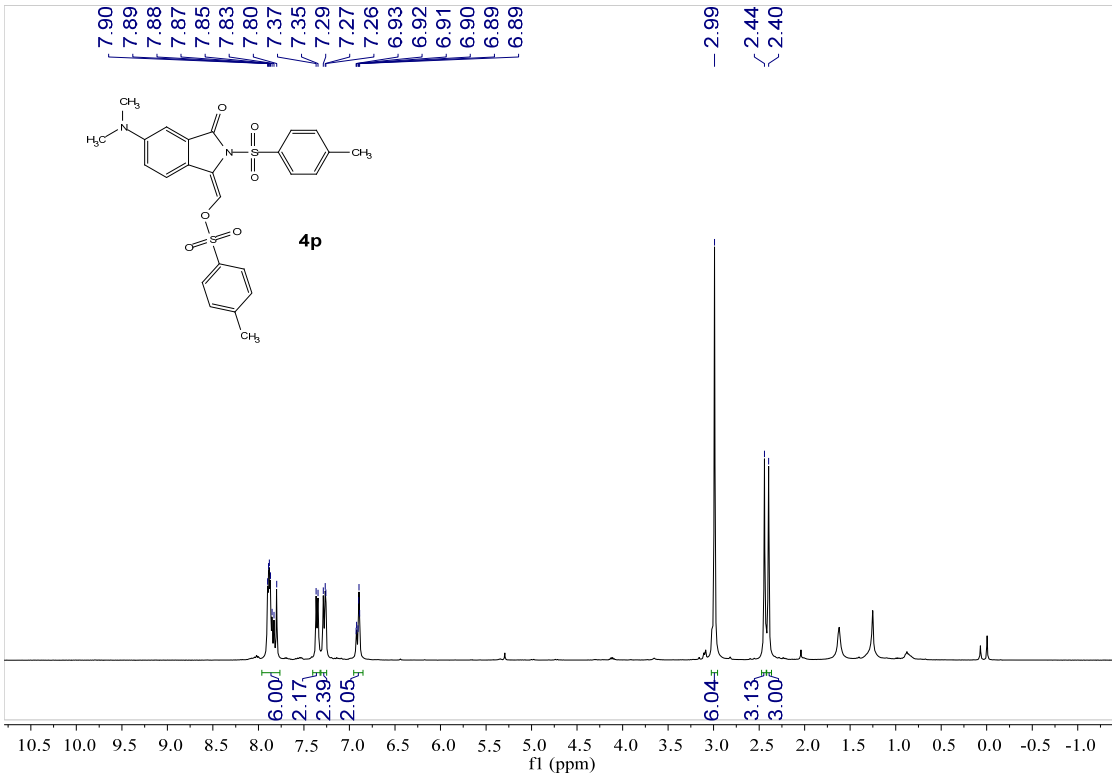
f1 (ppm)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7.37
7.35
7.29
7.27
7.26
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6.92
6.91
6.90
6.89
6.89
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2.44
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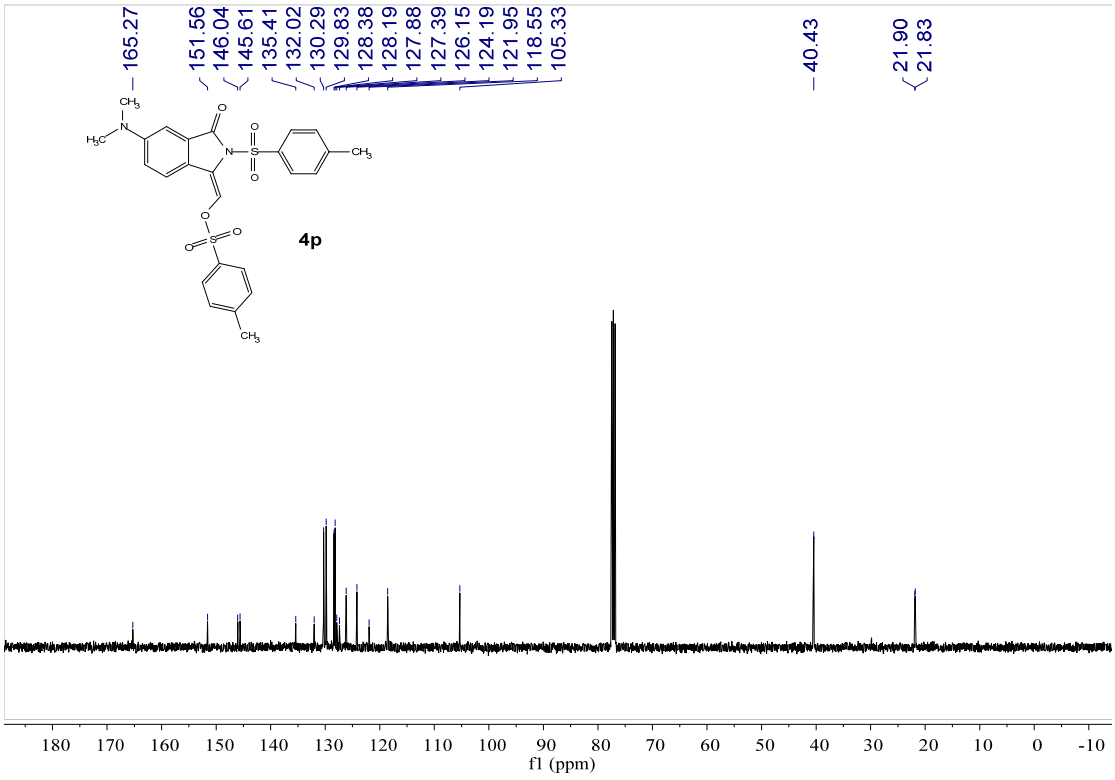
4p
6.00
2.17
2.39
2.05
6.04
3.13
3.00
f1 (ppm)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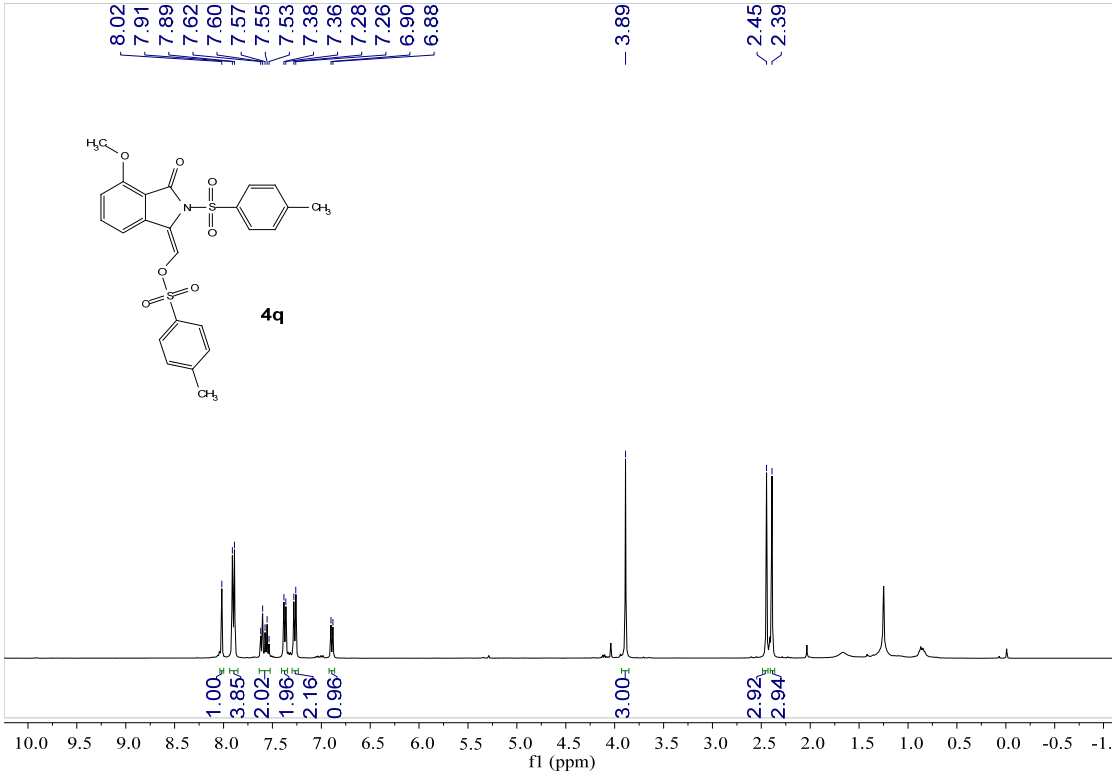
40.43
21.90
21.83
4p
f1 (ppm)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7.57
7.55
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7.38
7.36
7.28
7.26
6.90
6.88
3.89
2.45
2.39
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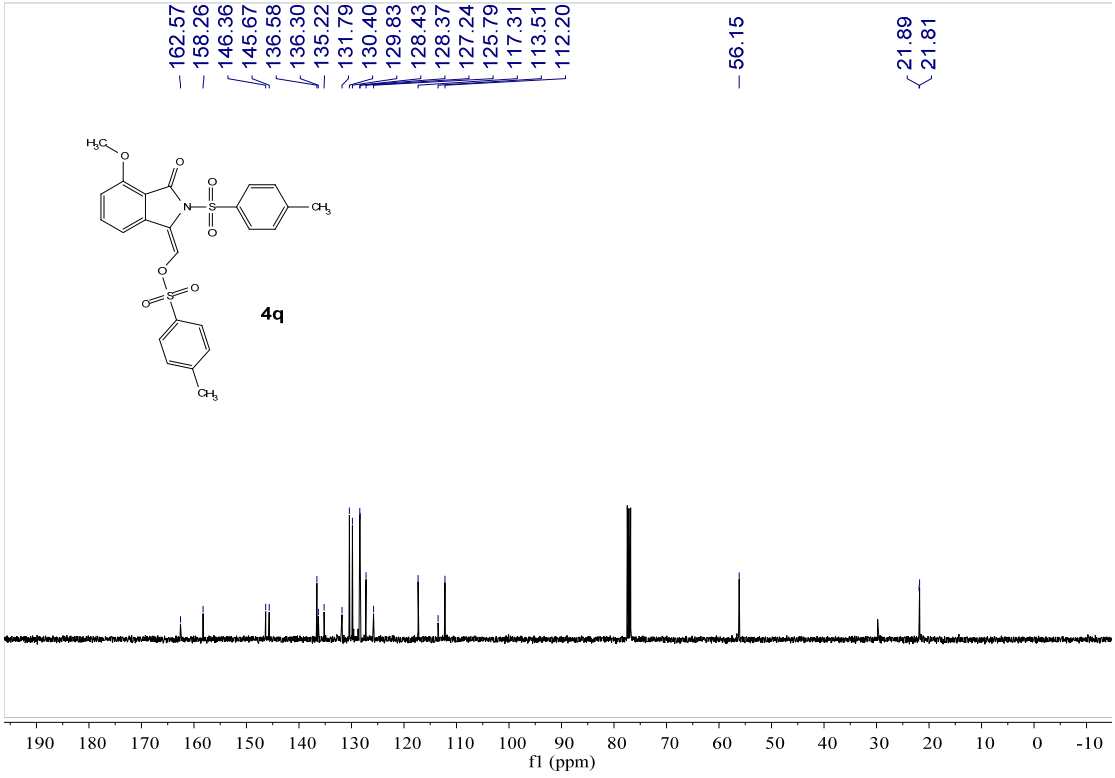
3.85
2.02
1.96
2.16
0.96
3.00
2.92
2.94
f1 (ppm)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113.51
112.20
56.15
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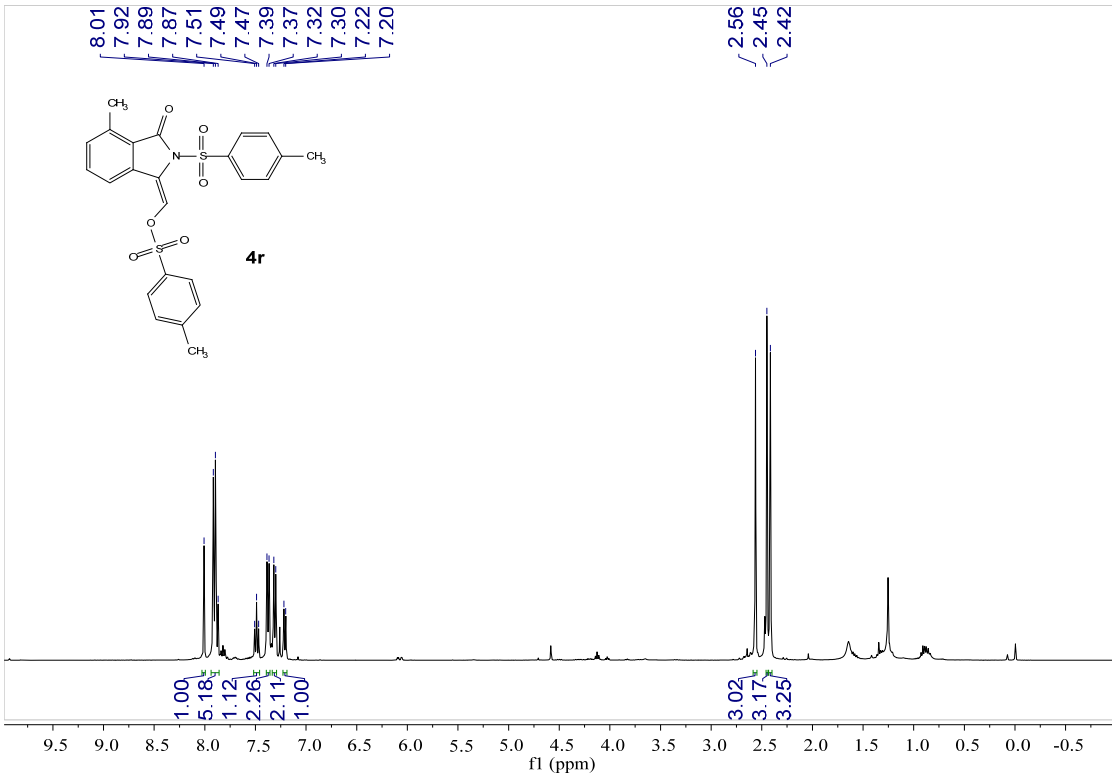
21.81
4q
f1 (ppm)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7.37
7.32
7.30
7.22
7.20
2.56
2.45
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5.18
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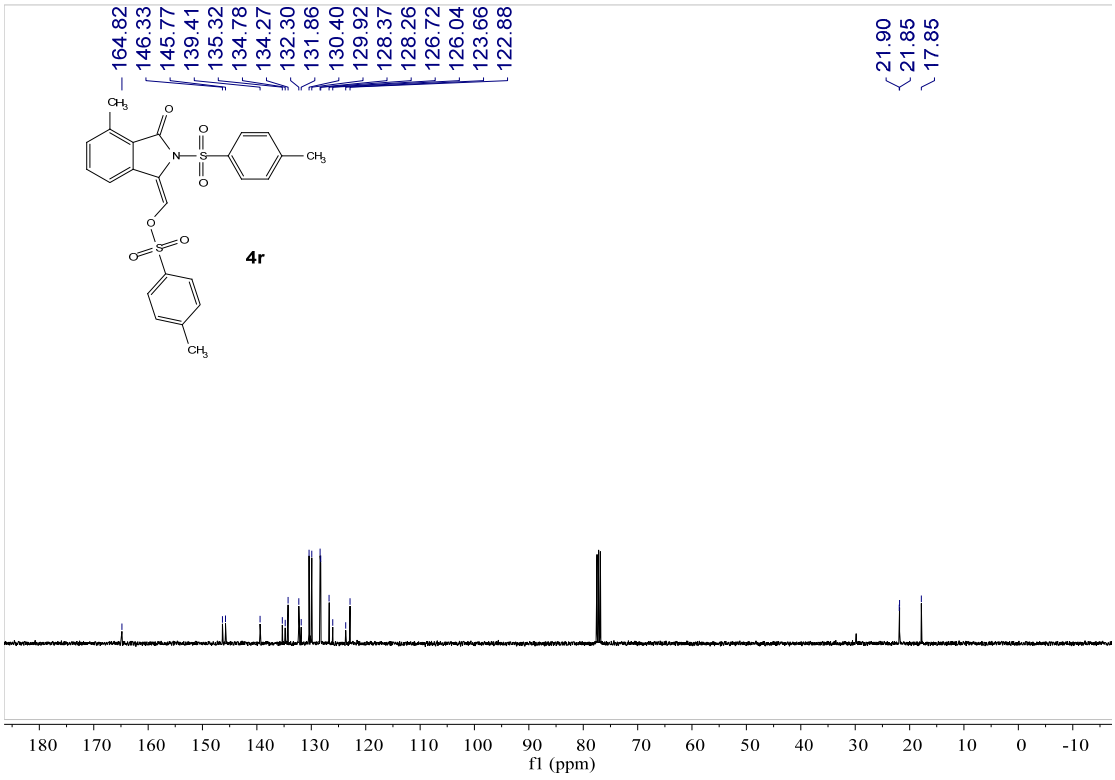
2.26
2.11
1.00
3.02
3.17
3.25
f1 (ppm)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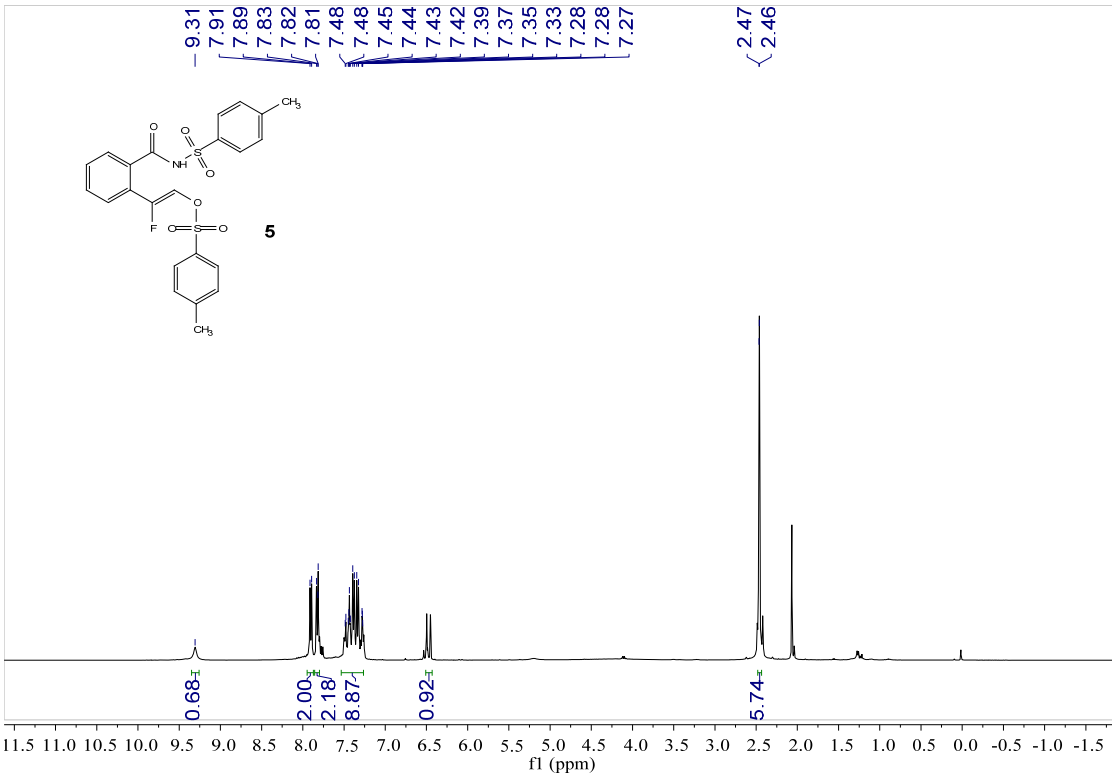
21.90
21.85
17.85
4r
f1 (ppm)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7.91
7.89
7.83
7.82
7.81
7.48
7.48
7.45
7.44
7.43
7.42
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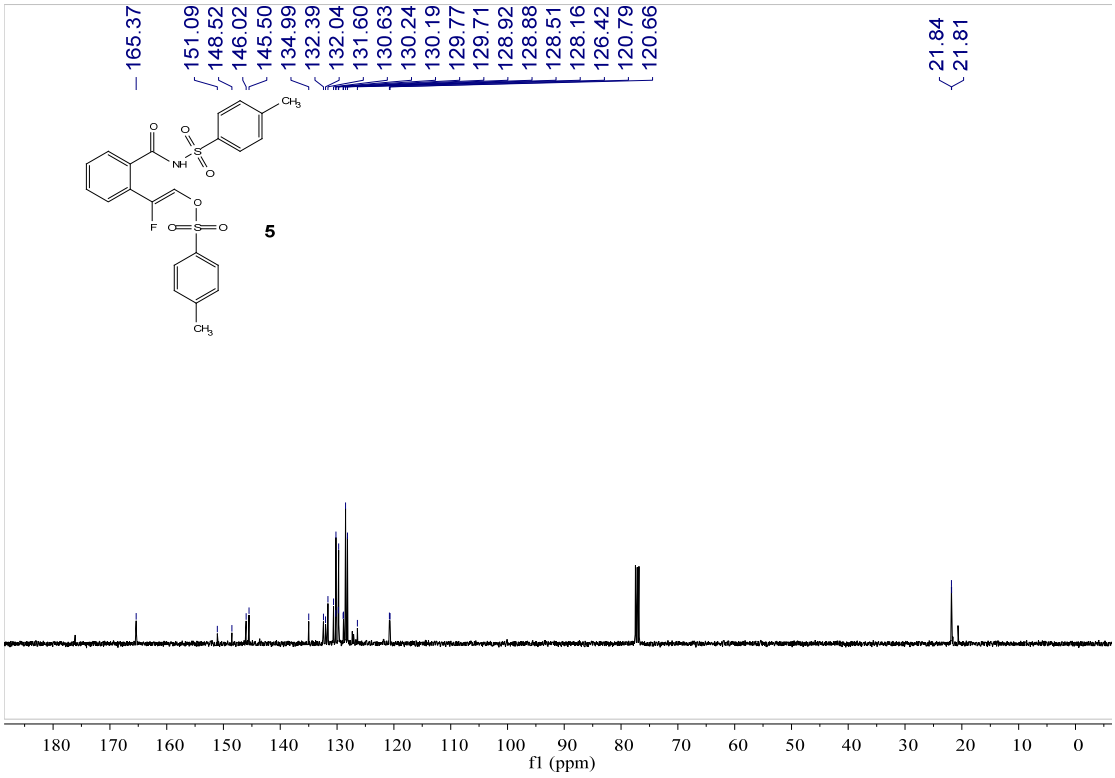
7.37
7.35
7.33
7.28
7.28
7.27
2.47
2.46
5
0.68
2.00
2.18
8.87
0.92
5.74
f1 (ppm)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129.77
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128.88
128.51
128.16
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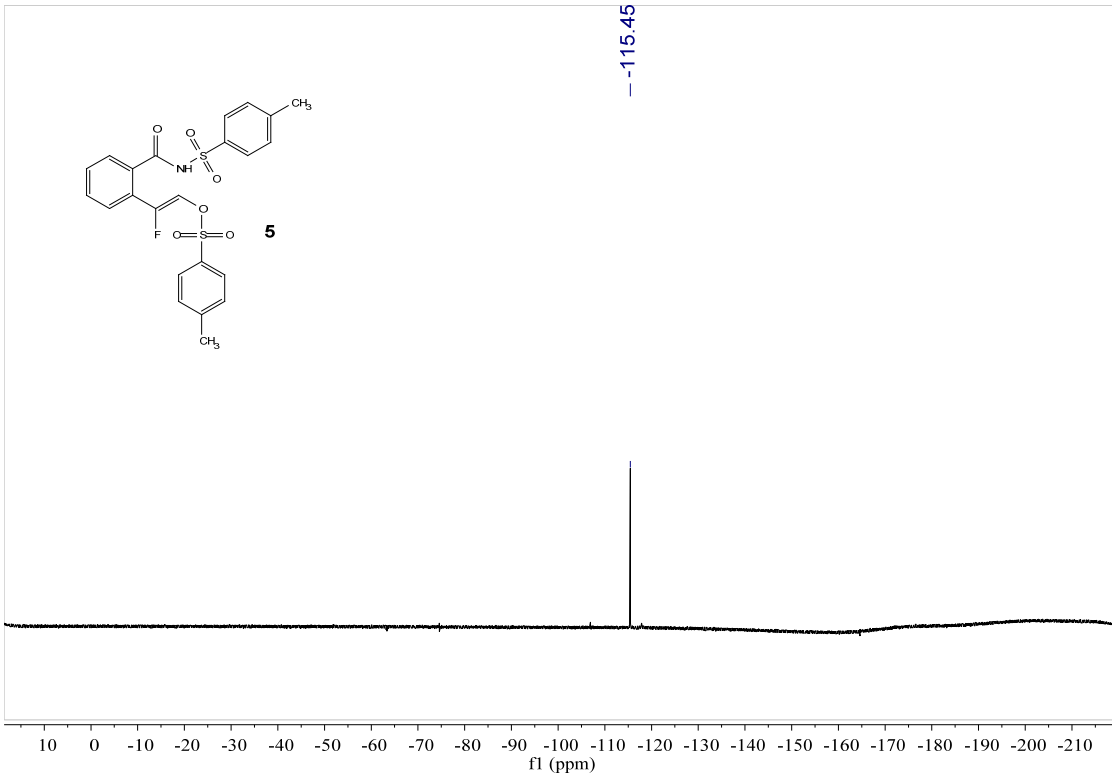
120.66
21.84
21.81
5
f1 (ppm)


-115.45
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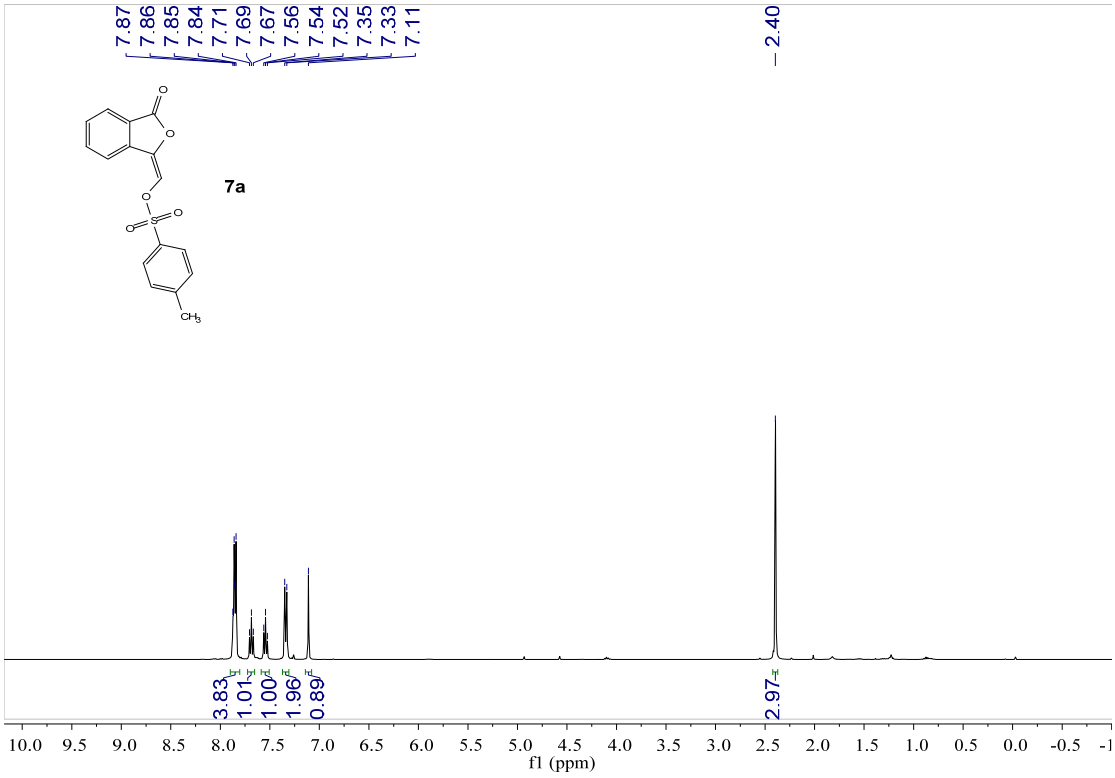
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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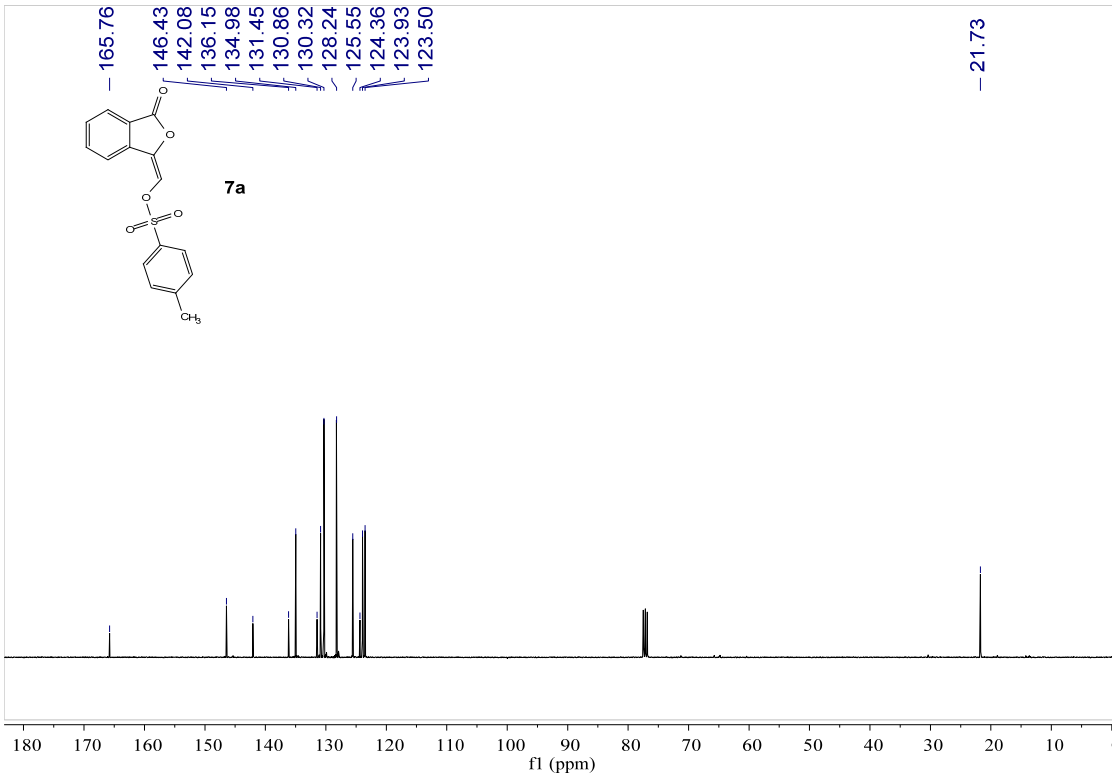
7.35
7.33
7.11
2.40
7a
3.83
1.01
1.00
1.96
0.89
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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125.55
124.36
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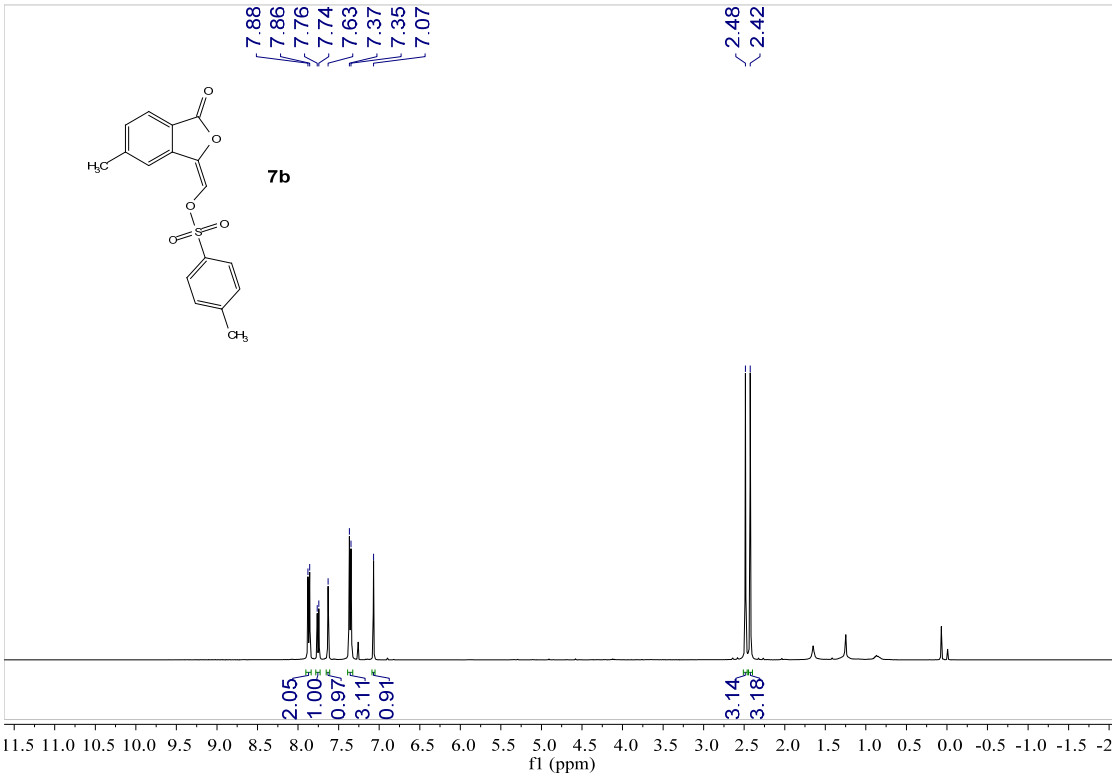
123.50
21.73
7a
f1 (ppm)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7.86
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7.37
7.35
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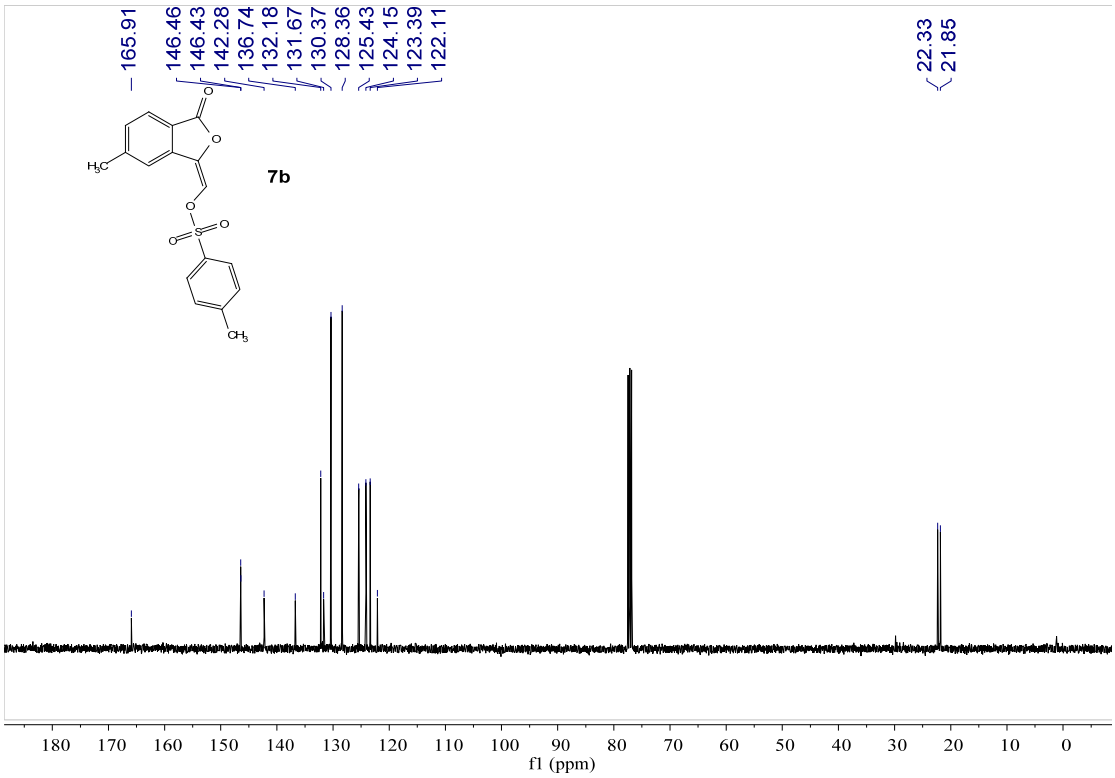
2.48
2.42
7b
2.05
1.00
0.97
3.11
0.91
3.14
3.18
f1 (ppm)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132.18
131.67
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128.36
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124.15
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122.11
22.33
21.85
7b
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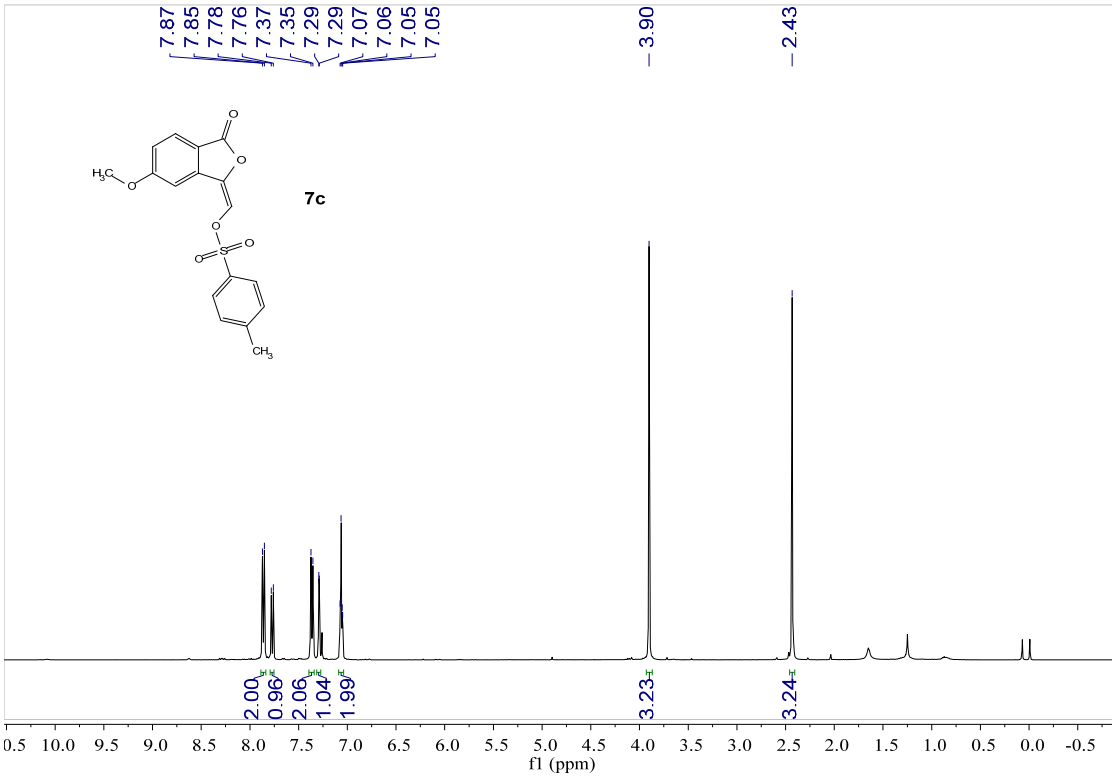
f1 (ppm)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7.85
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7.29
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7.06
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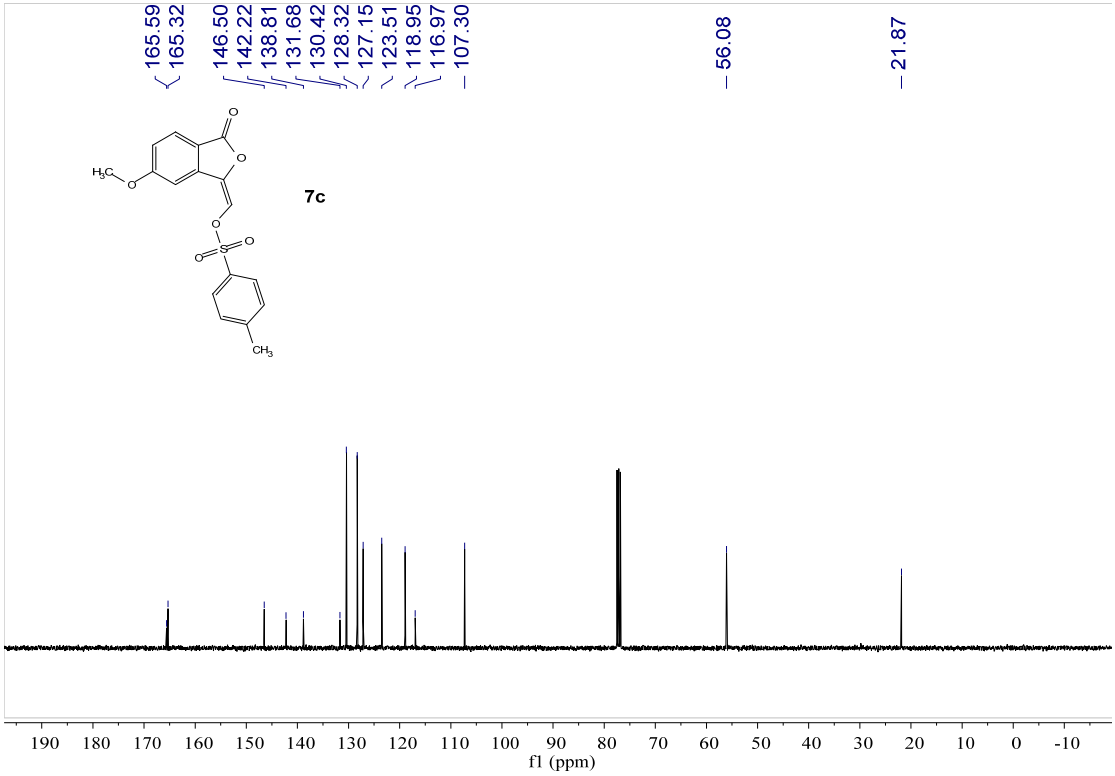
7.05
3.90
2.43
7c
2.00
0.96
2.06
1.04
1.99
3.23
3.24
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.51
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107.30
56.08
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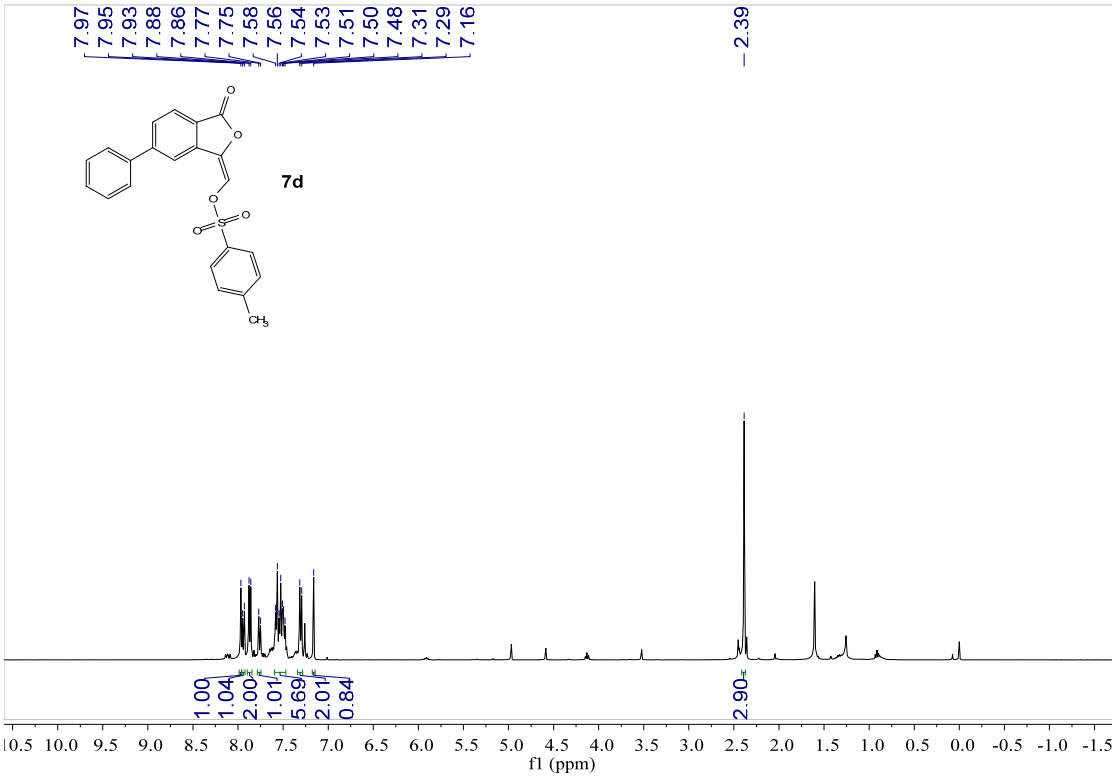
7c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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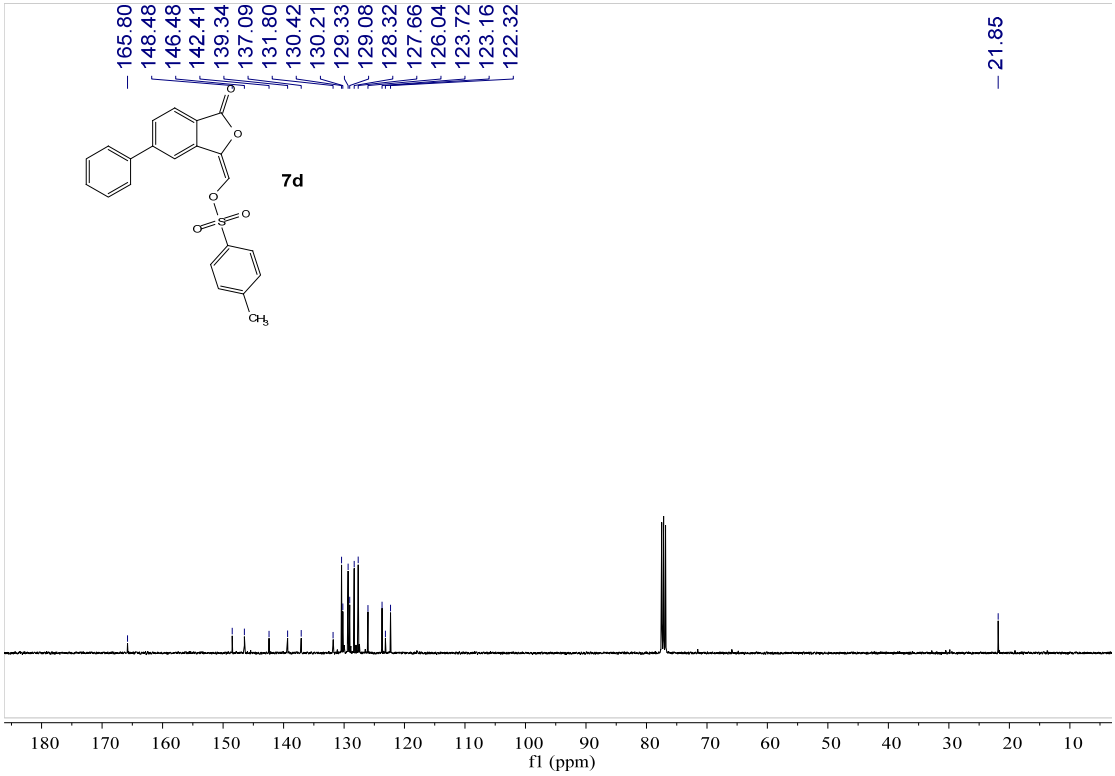
7.51
7.50
7.48
7.31
7.29
7.16
2.39
7d
1.00
1.04
2.00
1.01
5.69
2.01
0.84
2.90
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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123.16
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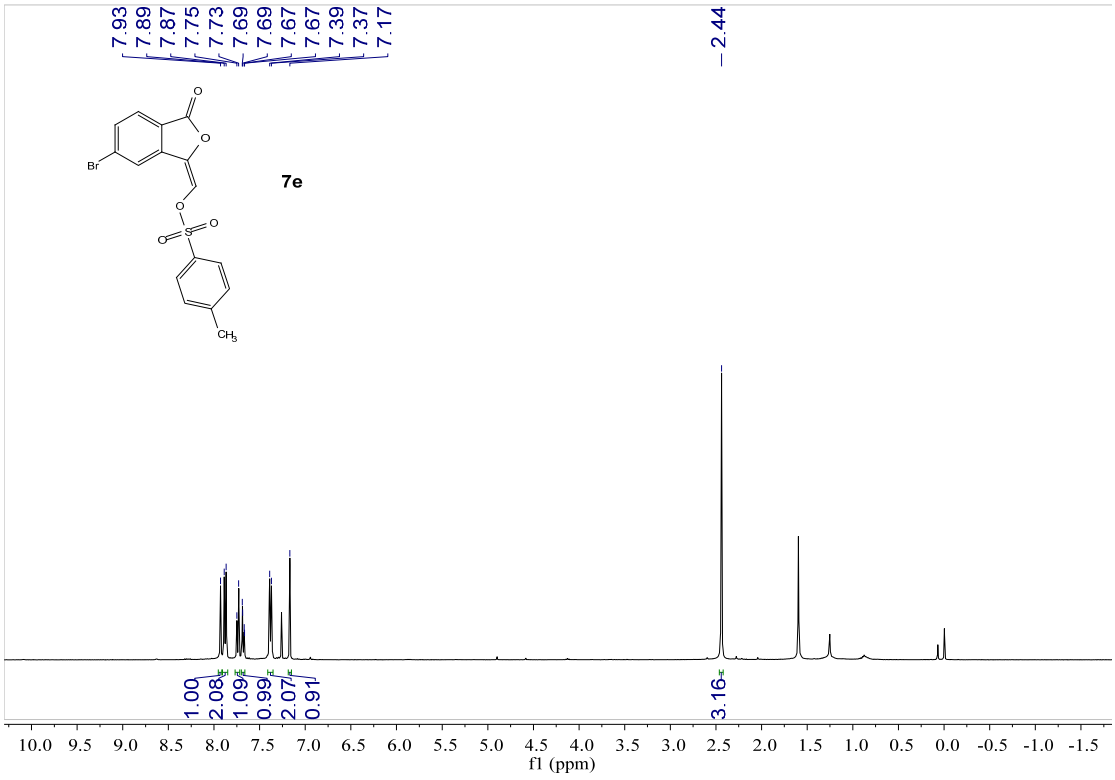
7d
f1 (ppm)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2.08
1.09
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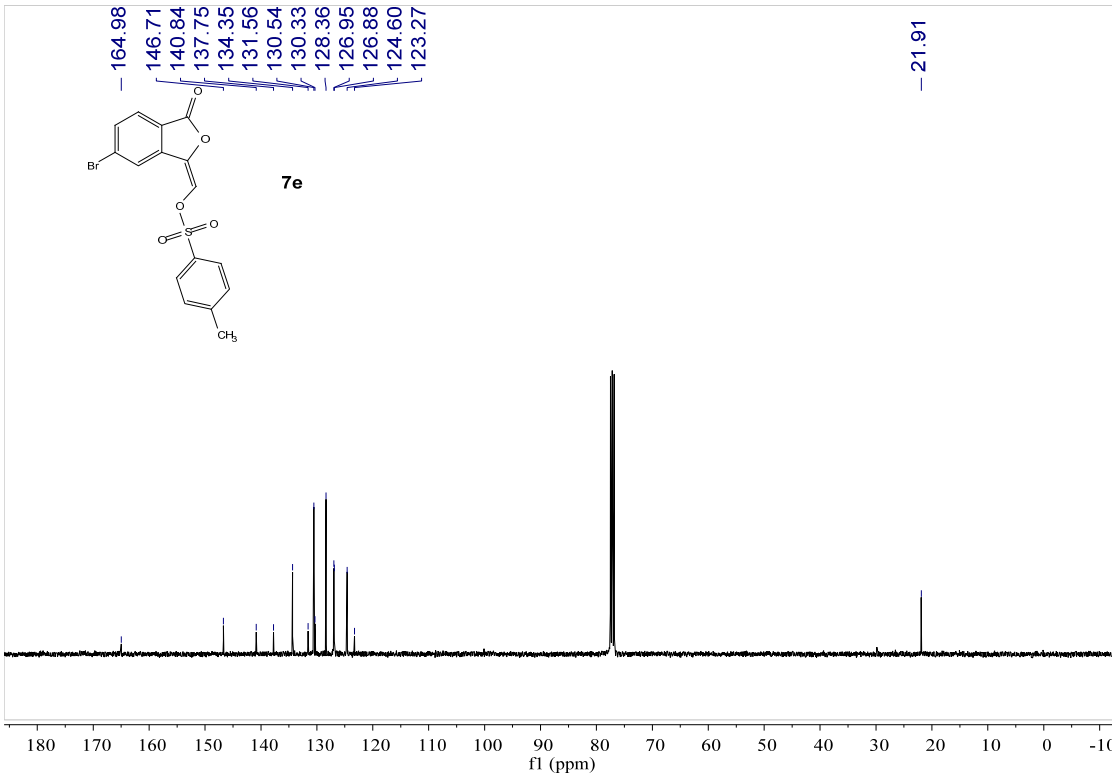
2.07
0.91
3.16
f1 (ppm)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128.36
126.95
126.88
124.60
123.27
21.91
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Br
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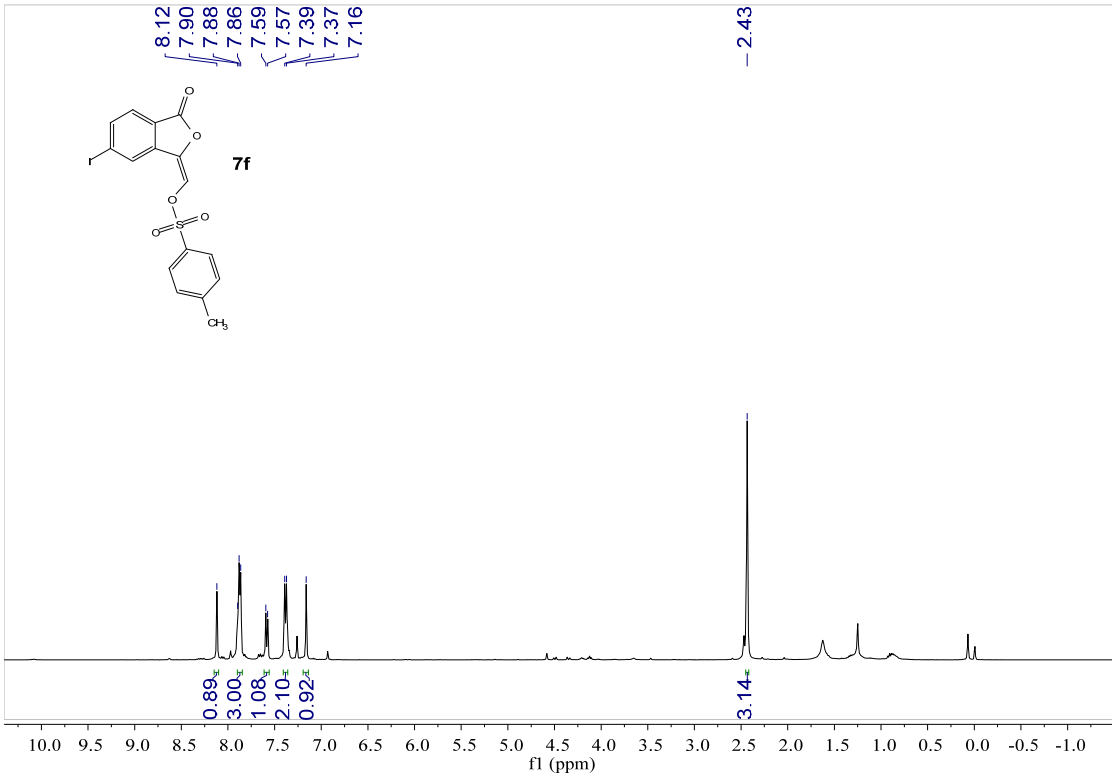
O
O
S
O
O
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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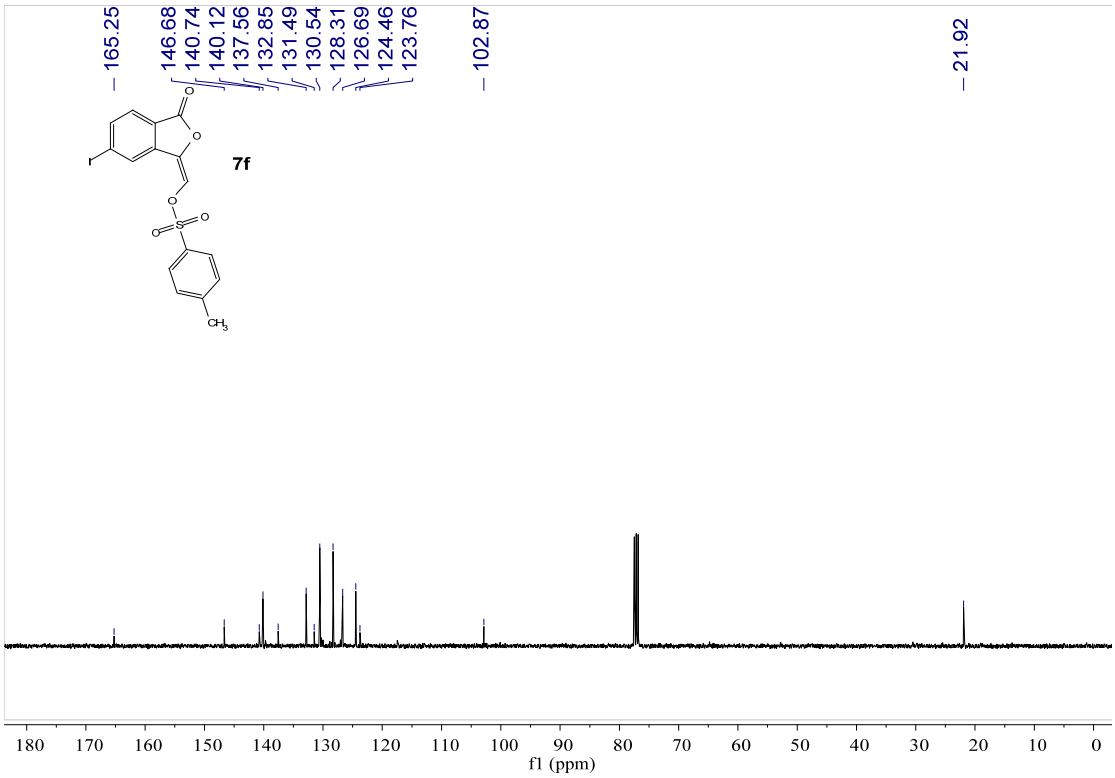
7.37
7.16
2.43
7f
I
O
O
O
S
O
O
CH3
0.89
3.00
1.08
2.10
0.92
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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21.92
7f
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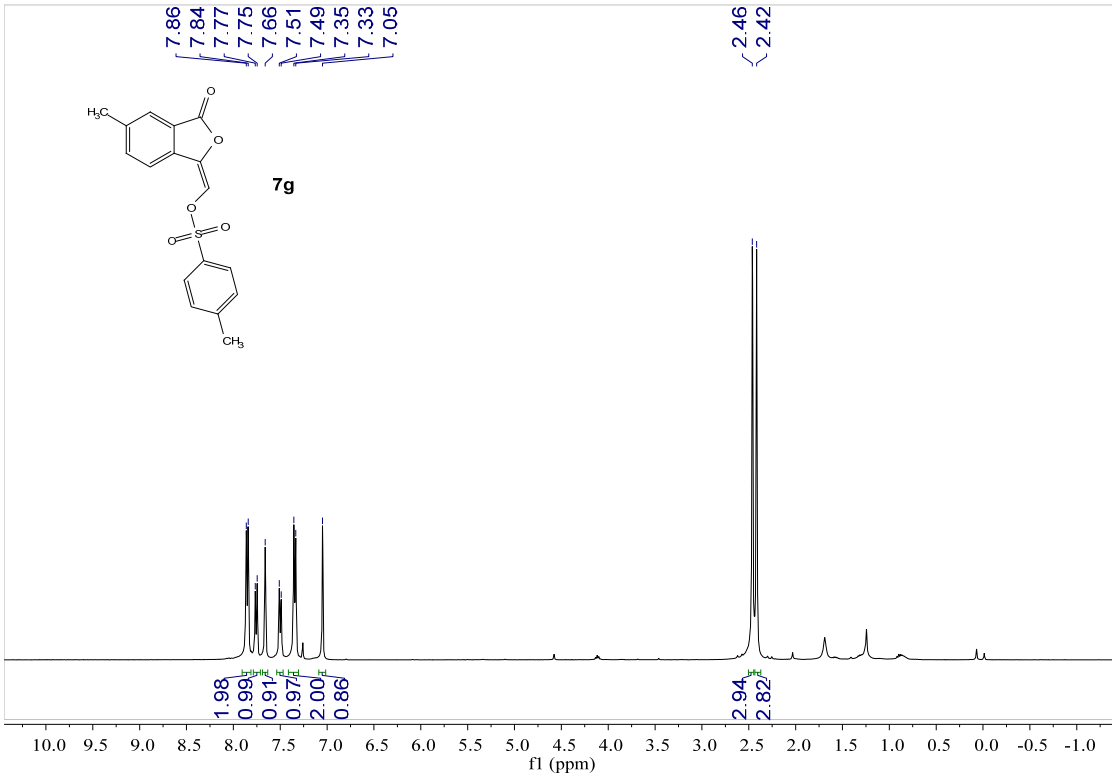
f1 (ppm)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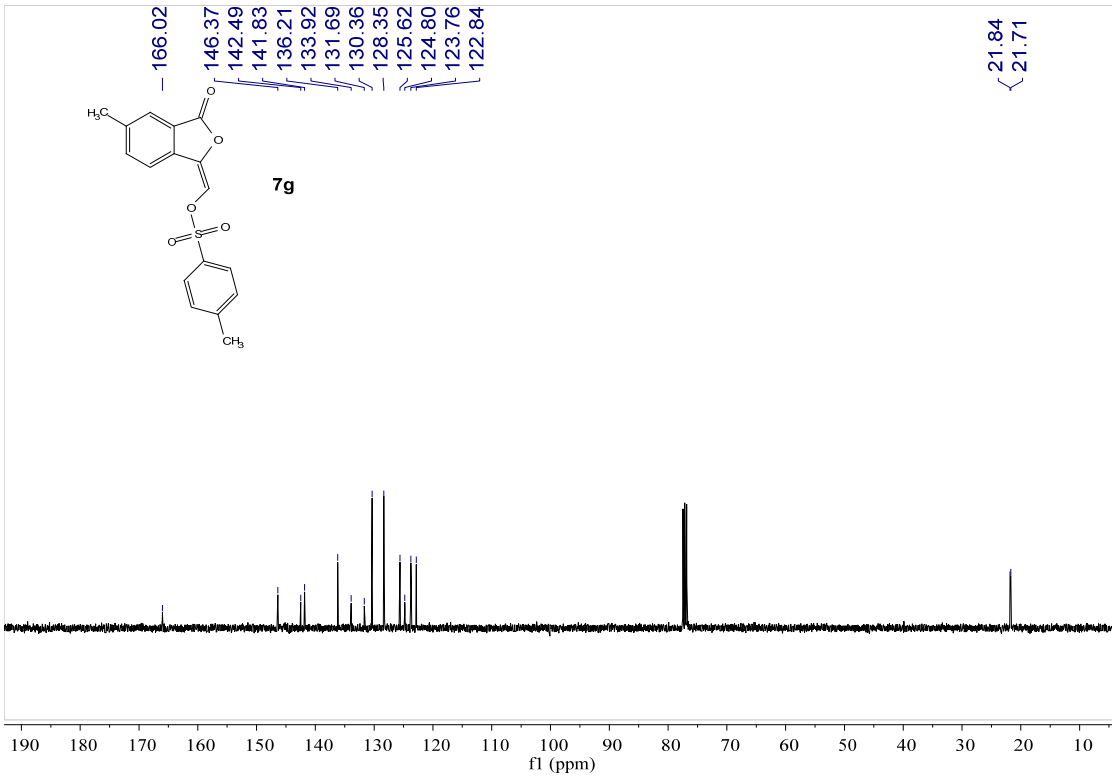
0.99
0.91
0.97
2.00
0.86
2.94
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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122.84
21.84
21.71
7g
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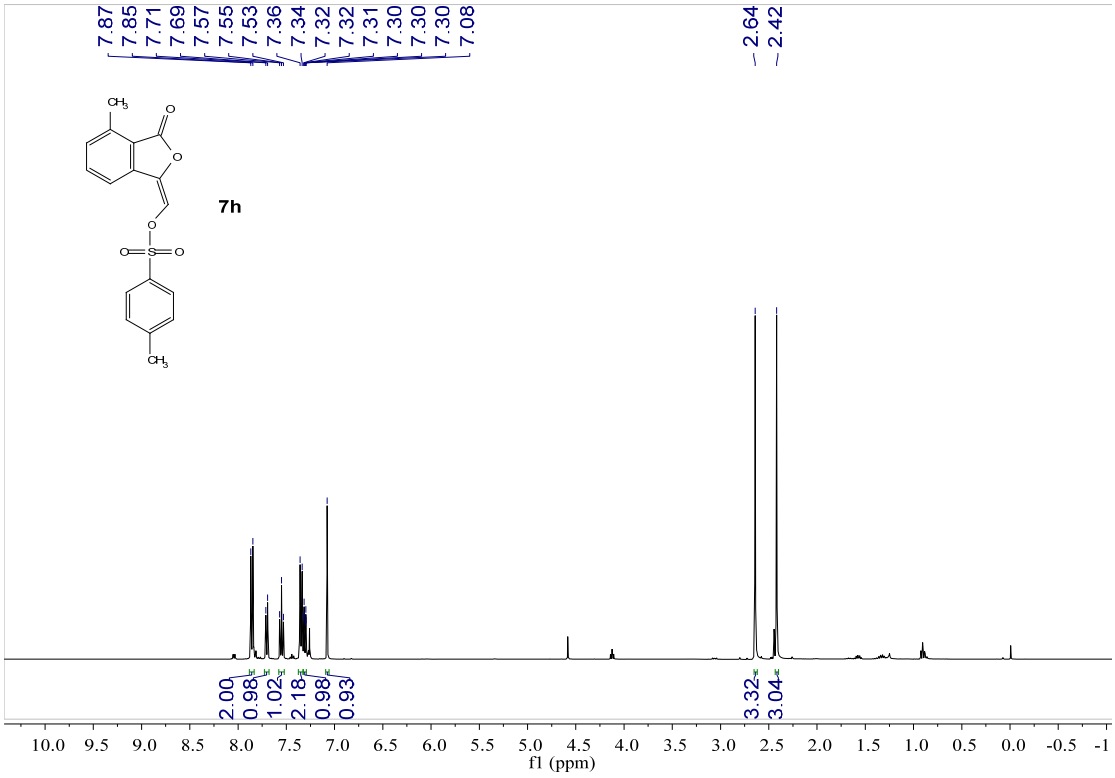
f1 (ppm)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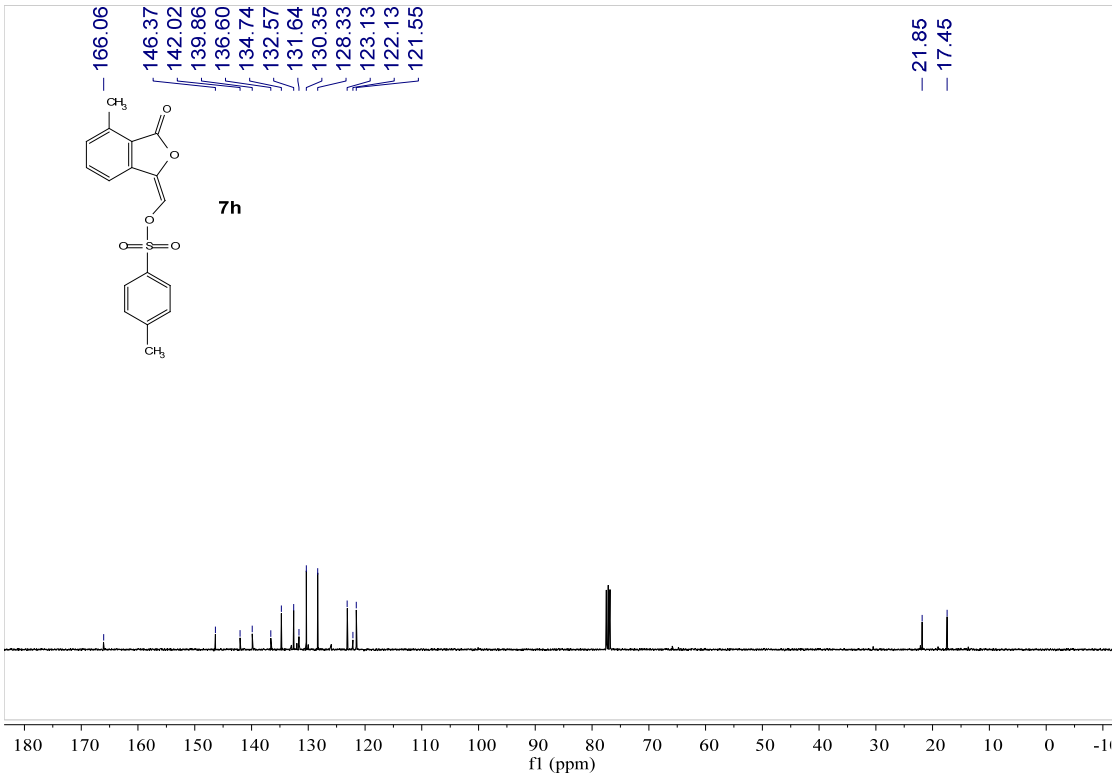
7.30
7.30
7.30
7.08
2.64
2.42
7h
2.00
0.98
1.02
2.18
0.98
0.93
3.32
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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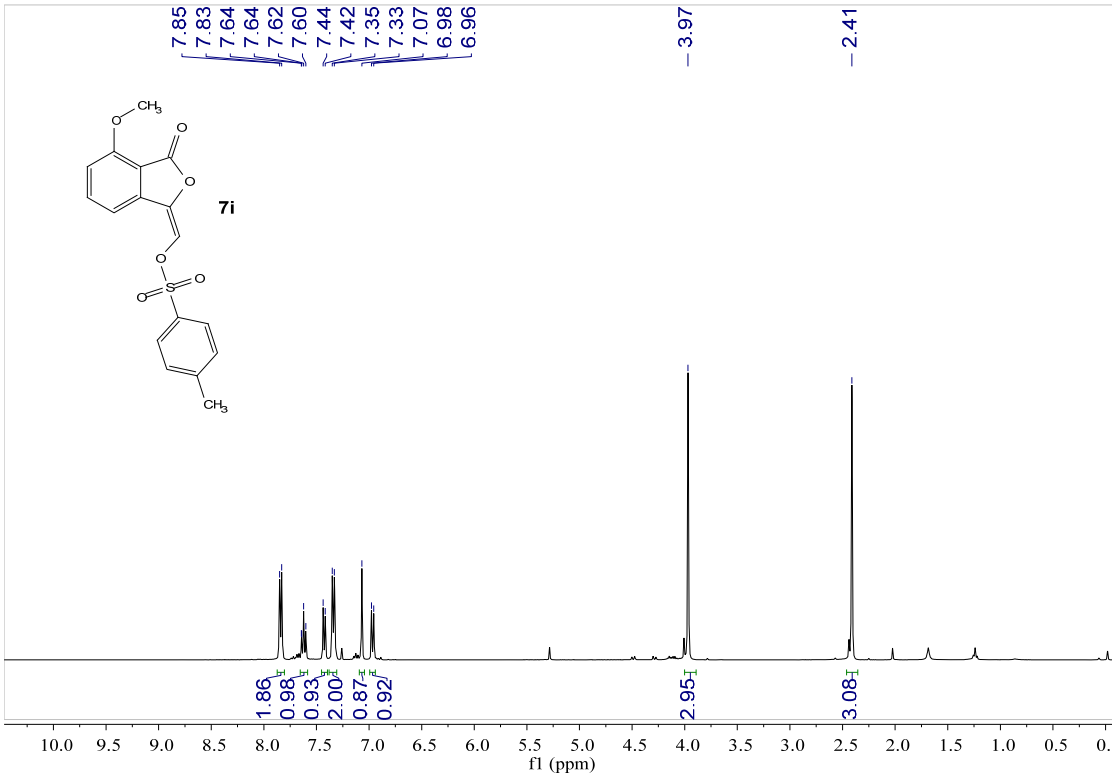
121.55
21.85
17.45
7h
f1 (ppm)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7.07
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2.41
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1.86
0.98
0.93
2.00
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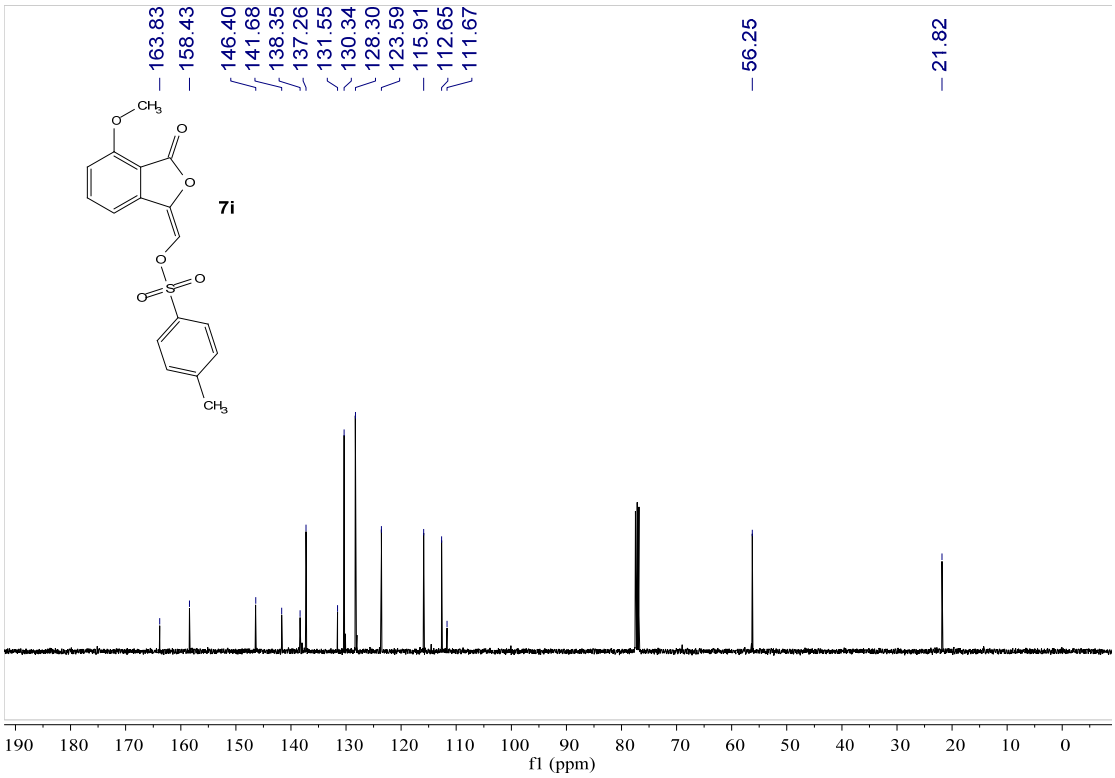
0.92
2.95
3.08
f1 (ppm)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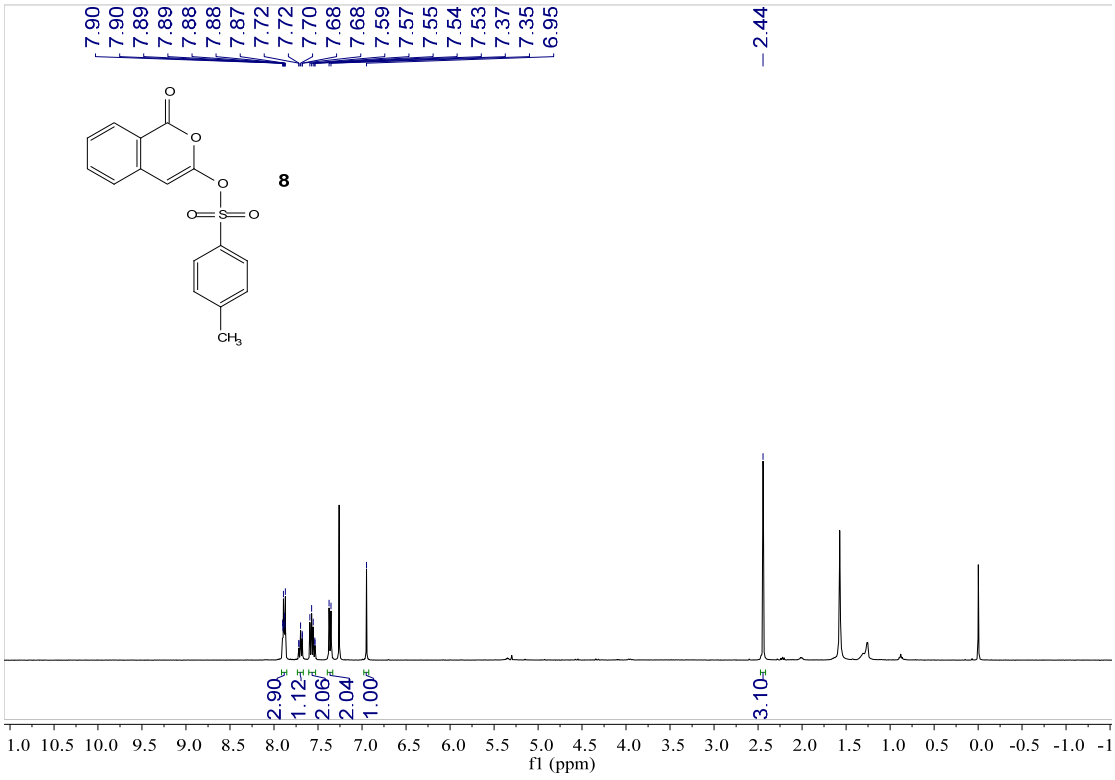
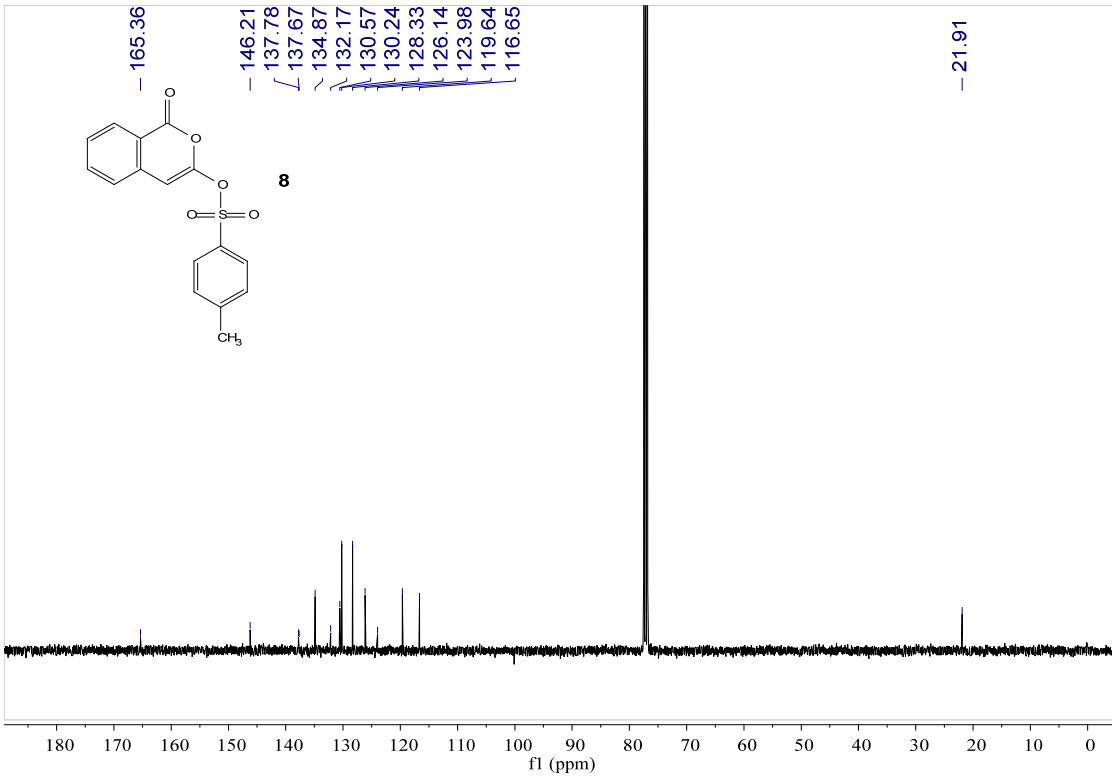
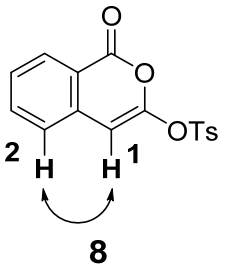
56.25
21.82
7i
f1 (ppm)

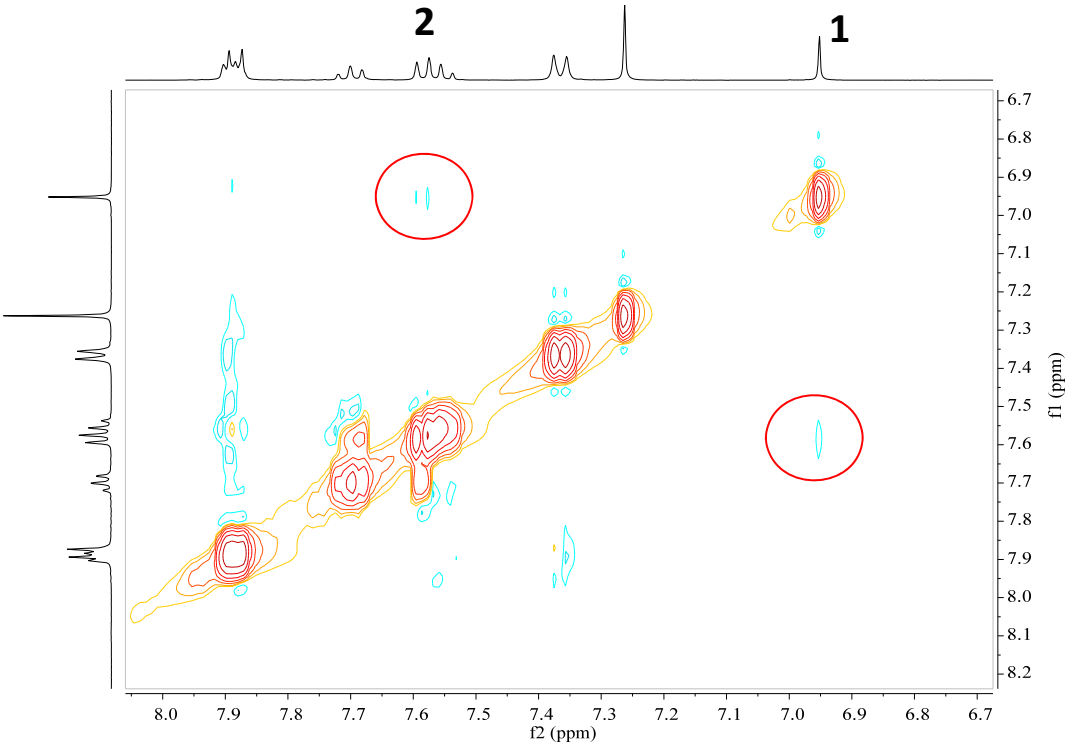

7.90
7.90
7.89
7.89
7.88
7.88
7.87
7.72
7.72
7.70
7.68
7.68
7.59
7.57
7.55
7.54
7.53
7.37
7.35
6.95
2.44
8
2.90
1.12
2.06
2.04
1.00
3.10
f1 (ppm)

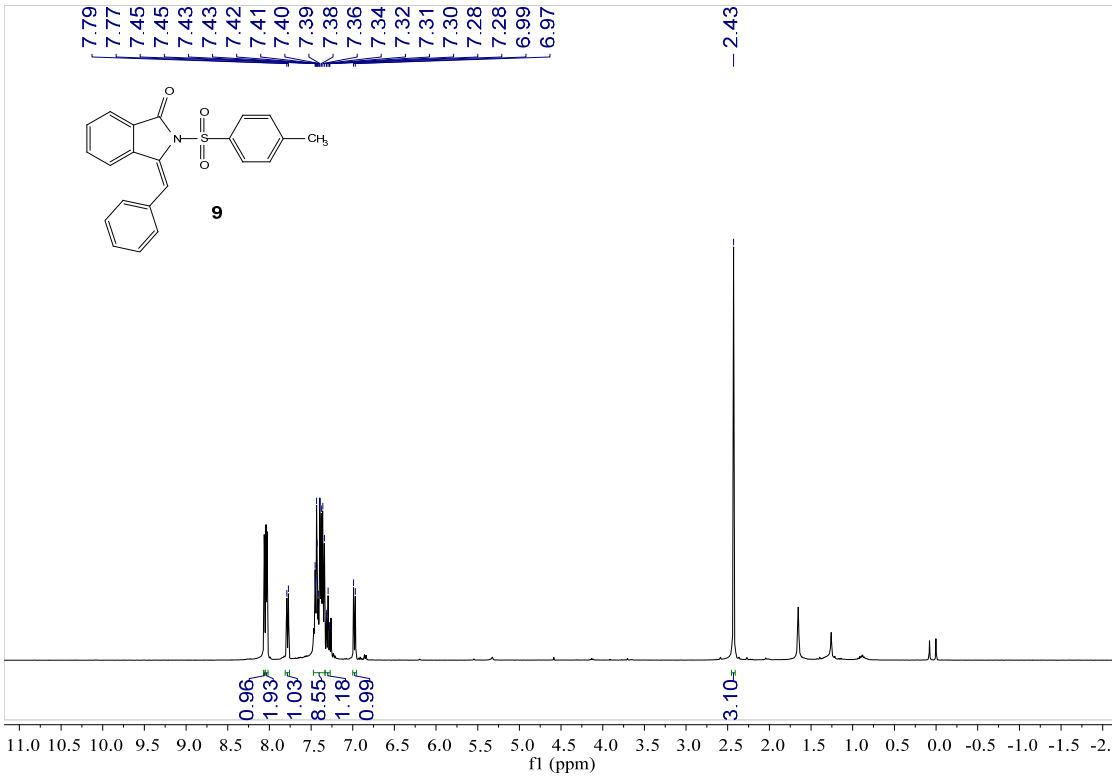

165.36
146.21
137.78
137.67
134.87
132.17
130.57
130.24
128.33
126.14
123.98
119.64
116.65
21.91
8
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

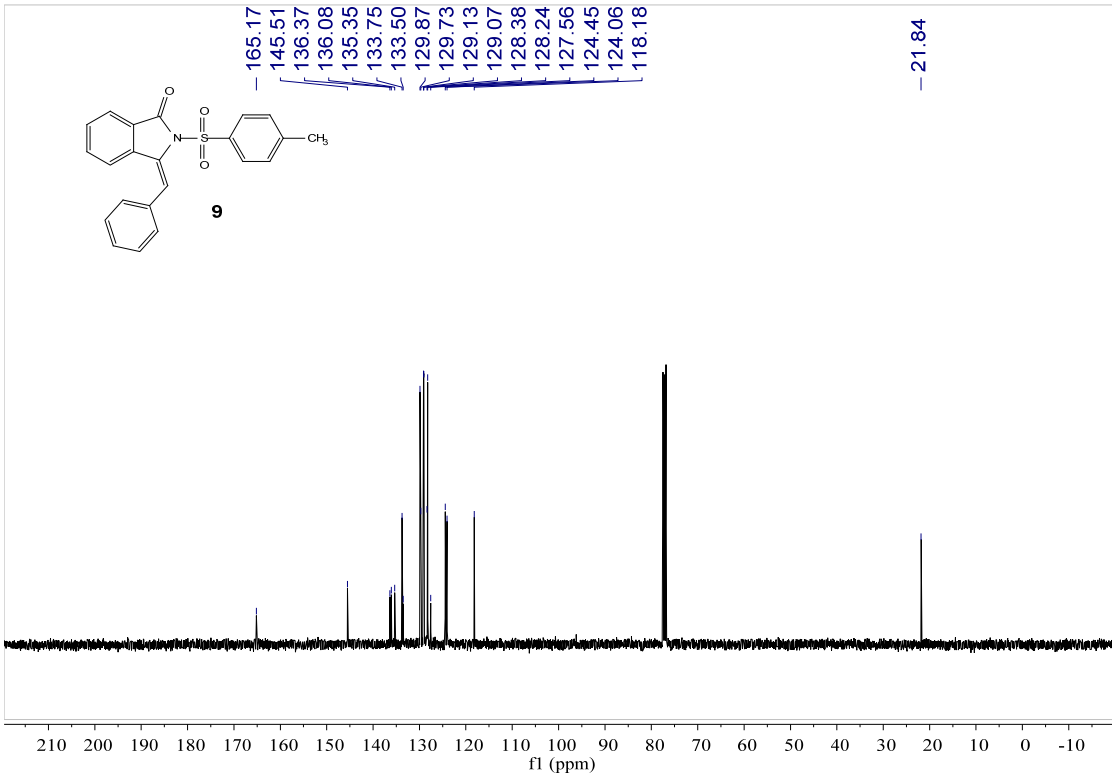
A part of the complete NOESY spectrum of compound **8** is pictured below:

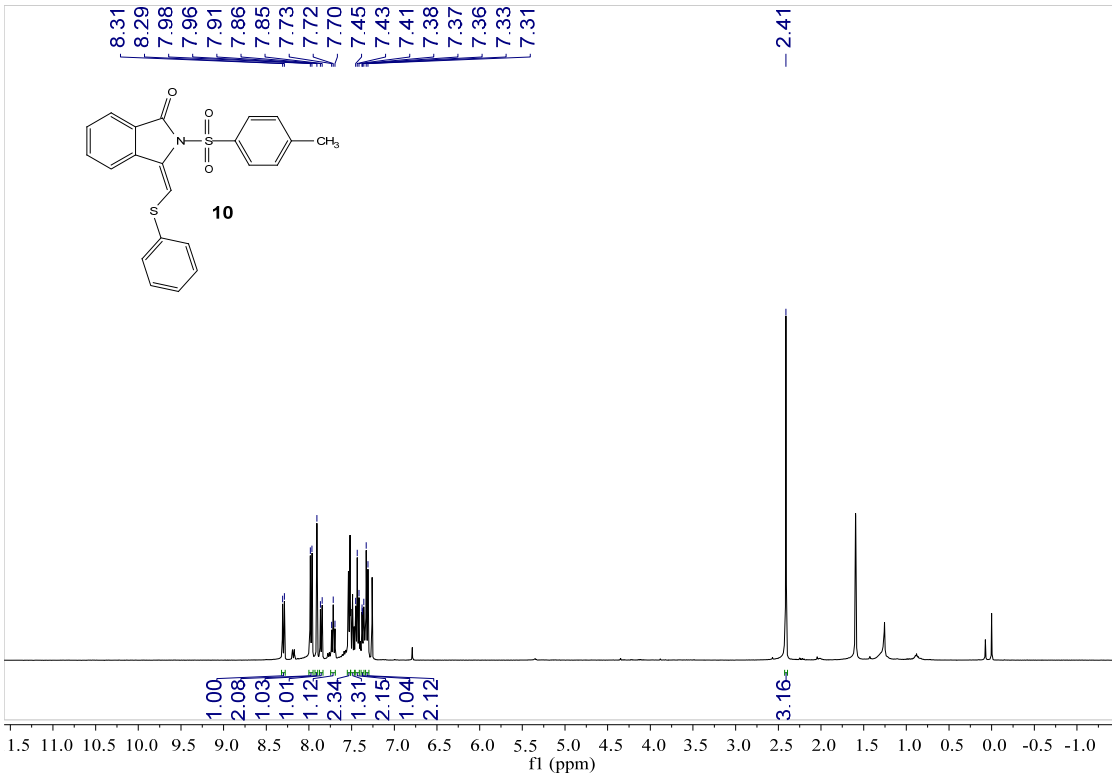


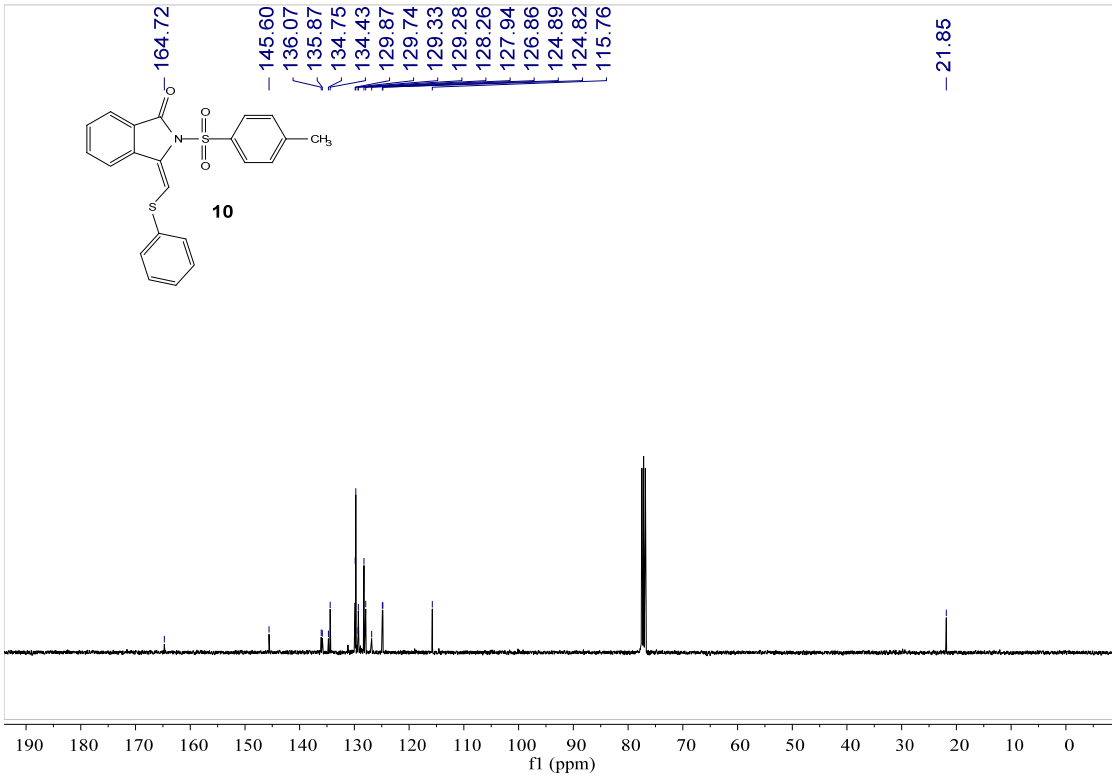
8

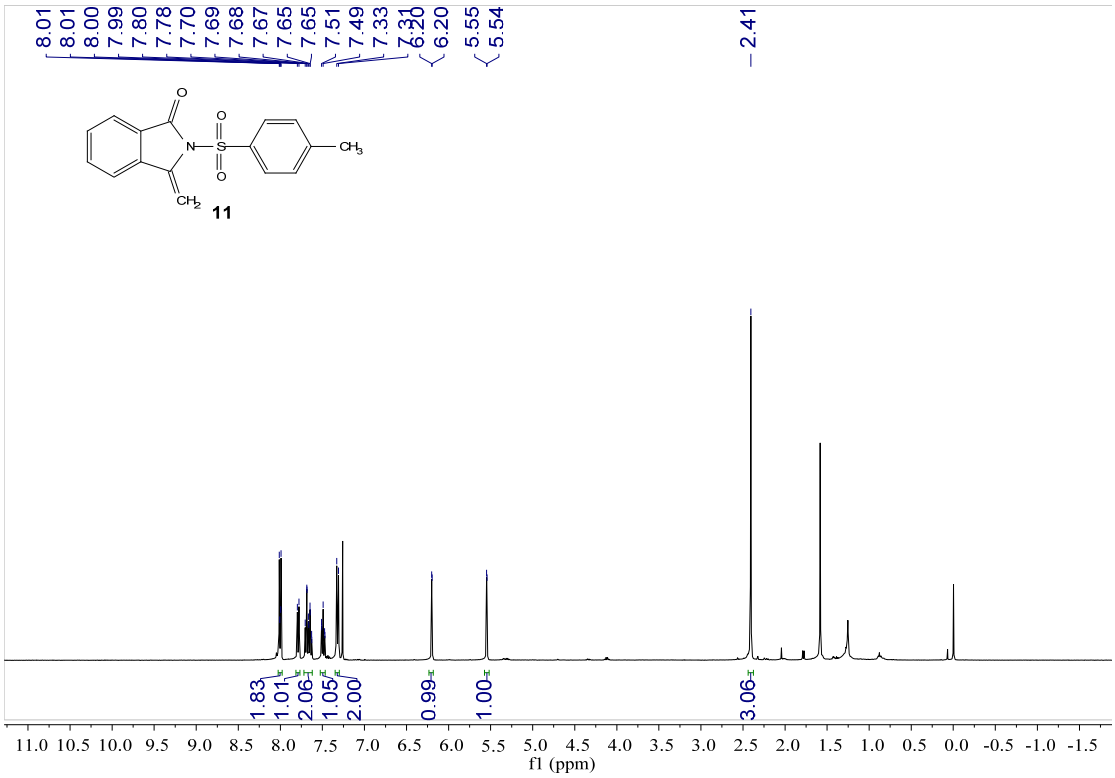


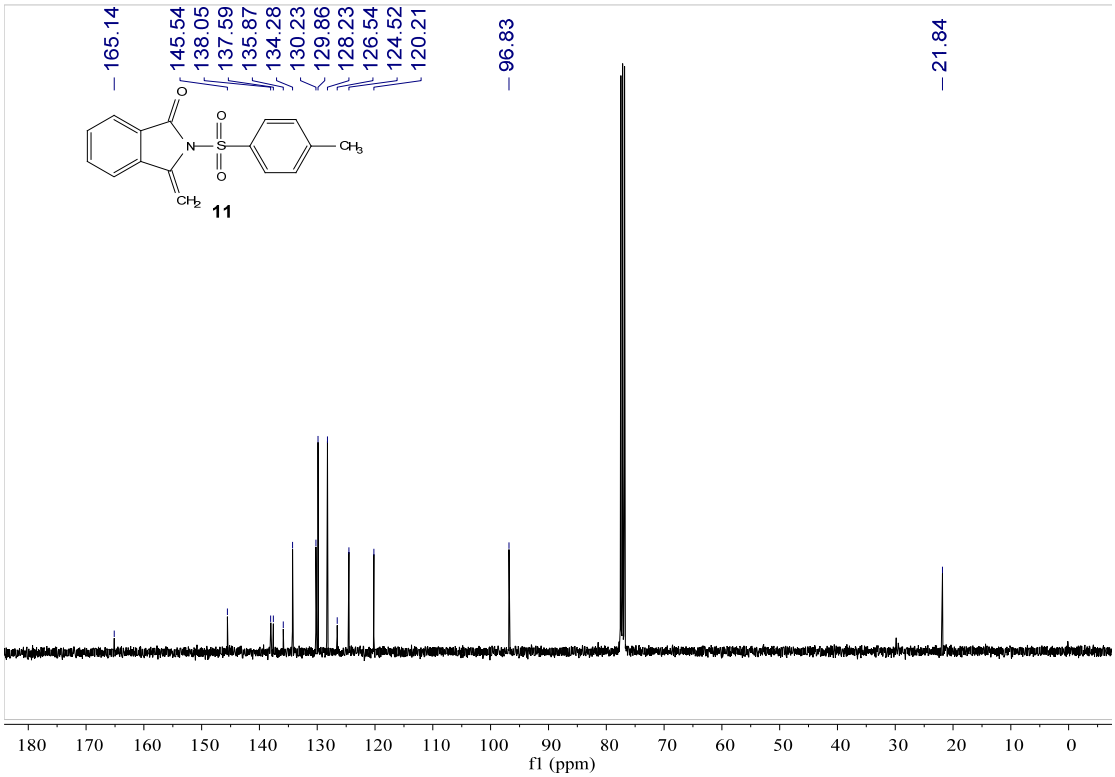

7.79
7.77
7.45
7.45
7.43
7.43
7.42
7.41
7.40
7.39
7.38
7.36
7.34
7.32
7.31
7.30
7.28
6.99
6.97
2.43
9
0.96
1.93
1.03
8.55
1.18
0.99
3.10
f1 (ppm)

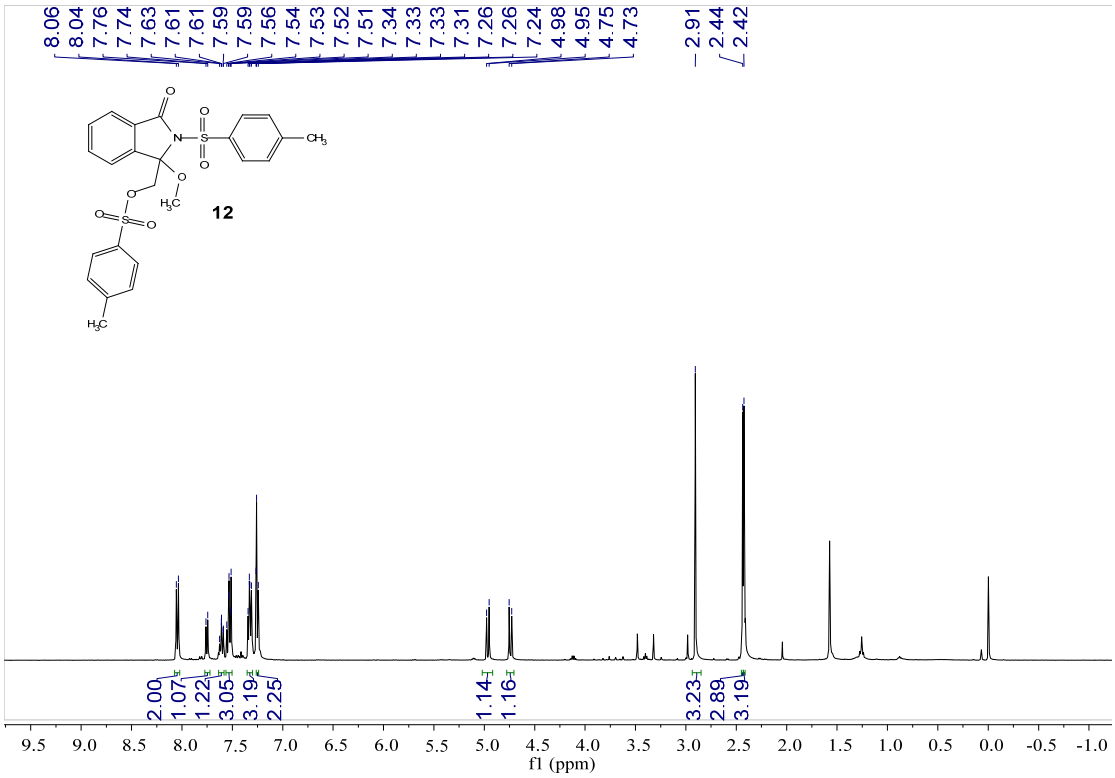

165.17
145.51
136.37
136.08
135.35
133.75
133.50
129.87
129.73
129.13
129.07
128.38
128.24
127.56
124.45
124.06
118.18
21.84
9
f1 (ppm)

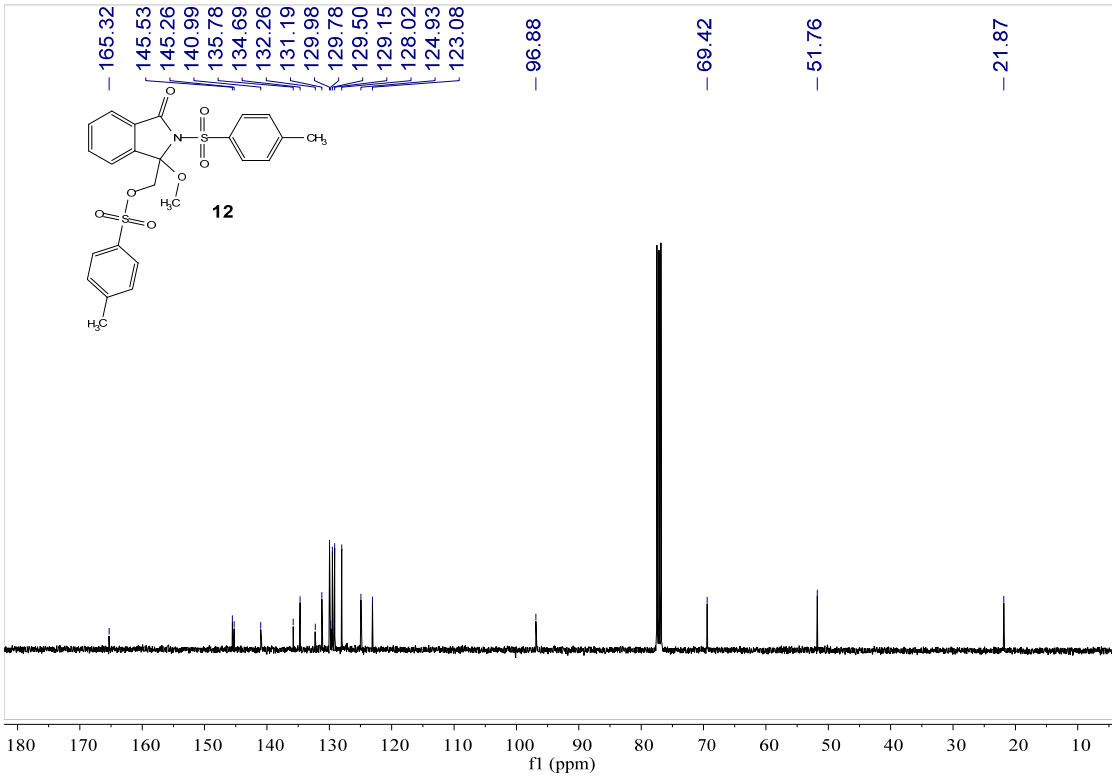

8.31
8.29
7.98
7.96
7.91
7.86
7.85
7.73
7.72
7.70
7.45
7.43
7.41
7.38
7.37
7.36
7.33
7.31
2.41
10
1.00
2.08
1.03
1.01
1.12
2.34
1.31
2.15
1.04
2.12
3.16
f1 (ppm)


164.72
145.60
136.07
135.87
134.75
134.43
129.87
129.74
129.33
129.28
128.26
127.94
126.86
124.89
124.82
115.76
21.85
10
f1 (ppm)

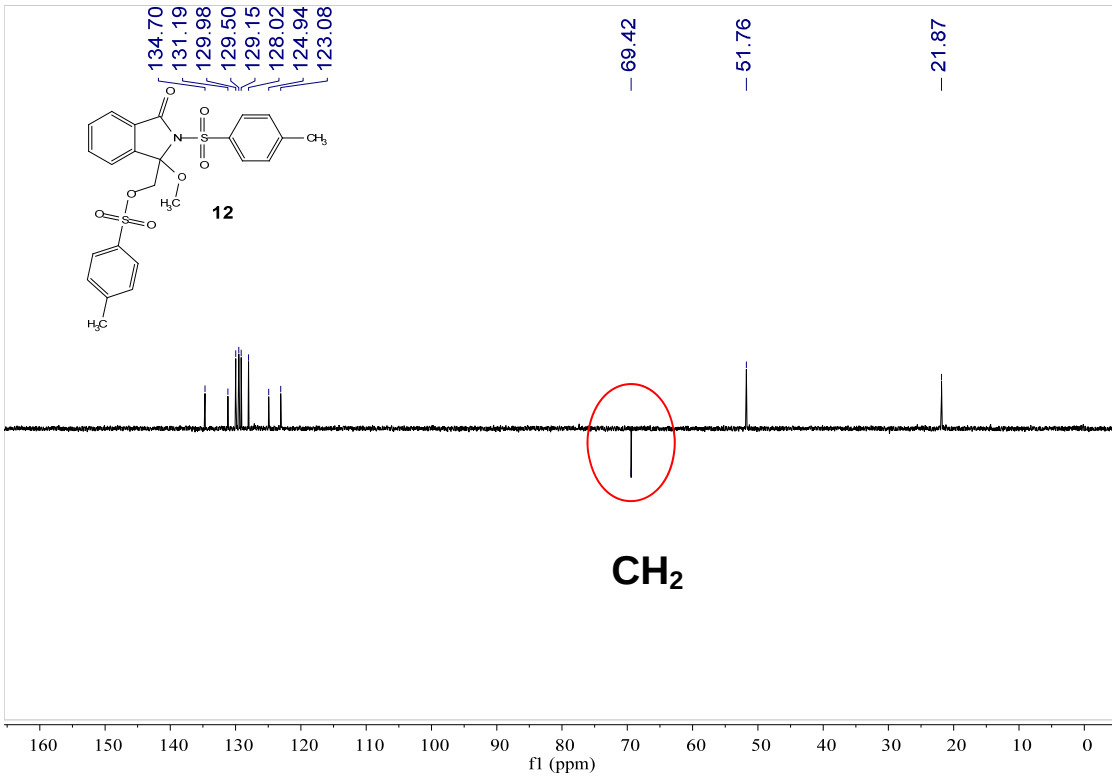

8.01
8.01
8.00
7.99
7.80
7.78
7.70
7.69
7.68
7.67
7.65
7.65
7.51
7.49
7.33
7.31
6.20
6.20
5.55
5.54
2.41
11
1.83
1.01
2.06
1.05
2.00
0.99
1.00
3.06
f1 (ppm)

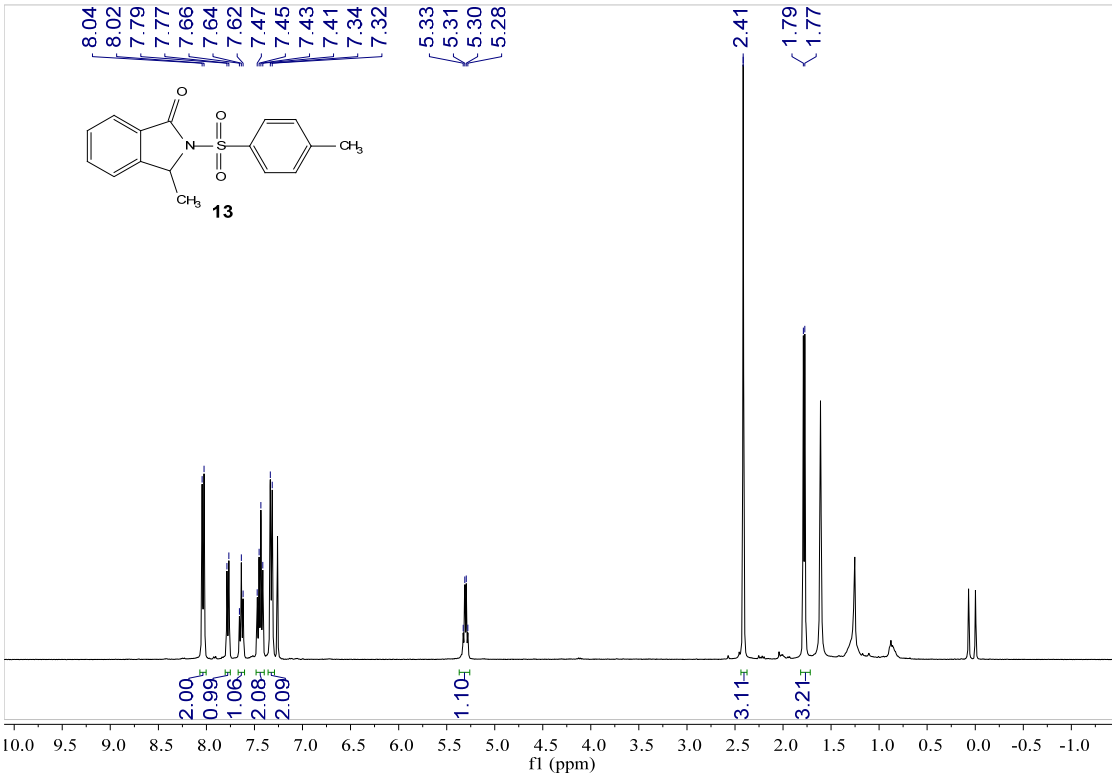

165.14
145.54
138.05
137.59
135.87
134.28
130.23
129.86
128.23
126.54
124.52
120.21
96.83
21.84
11
f1 (ppm)

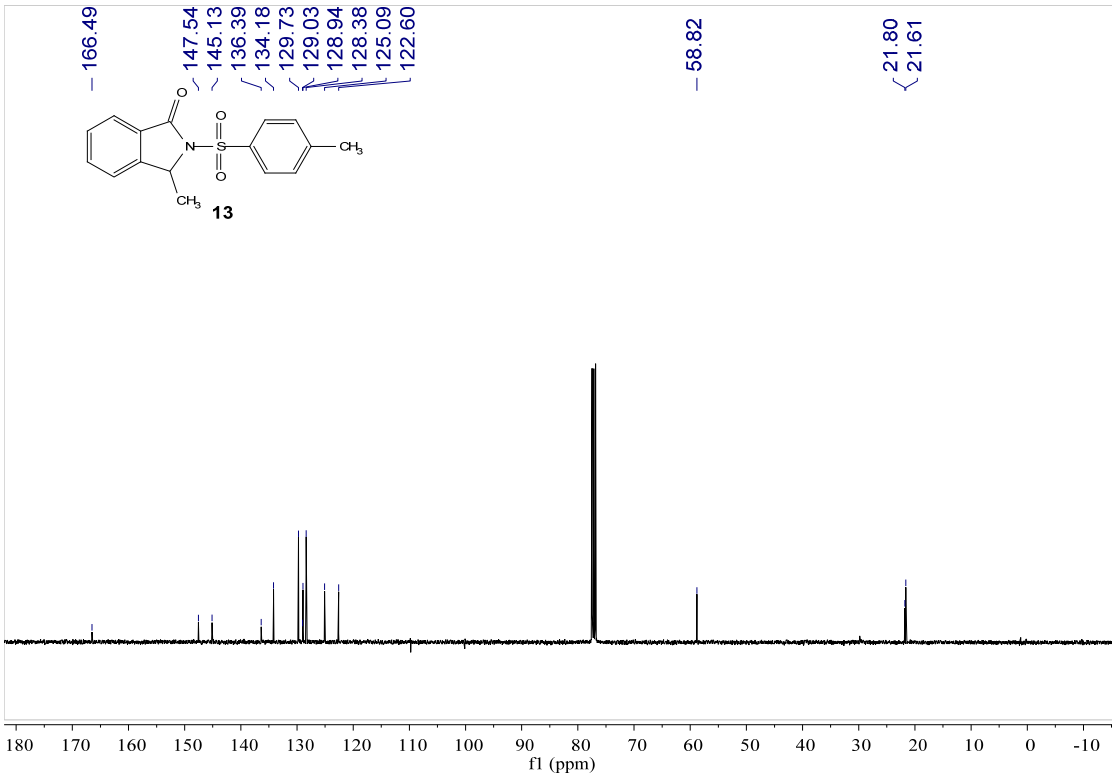


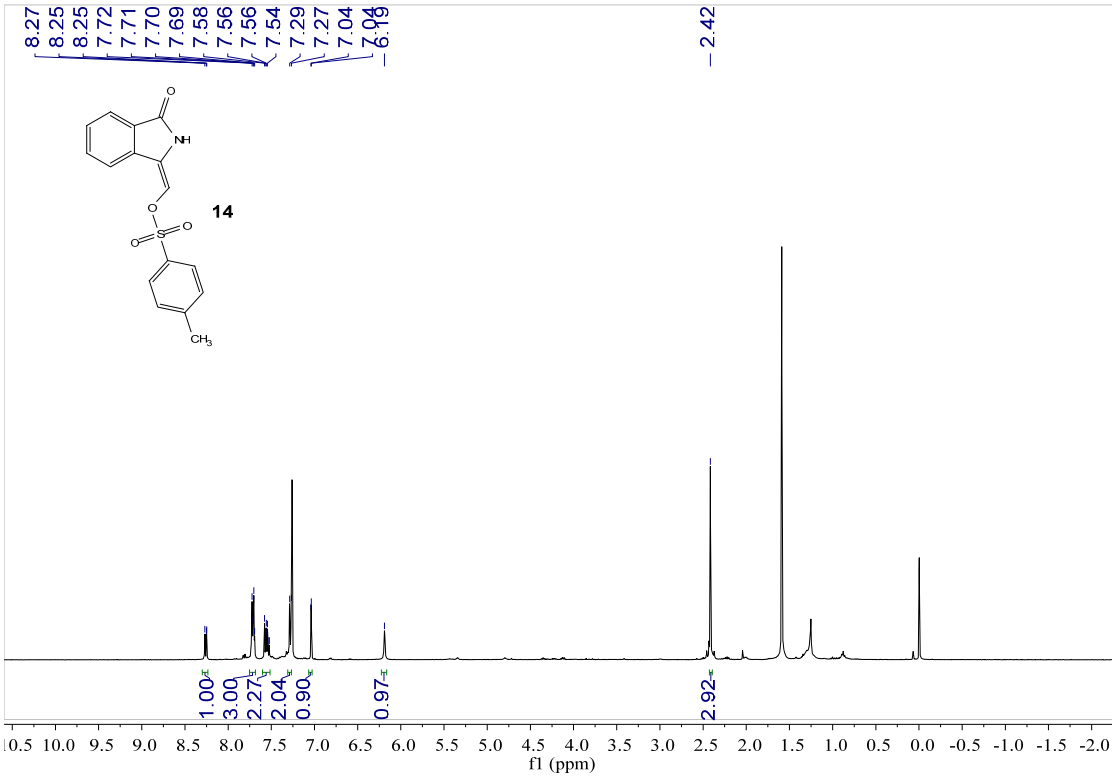


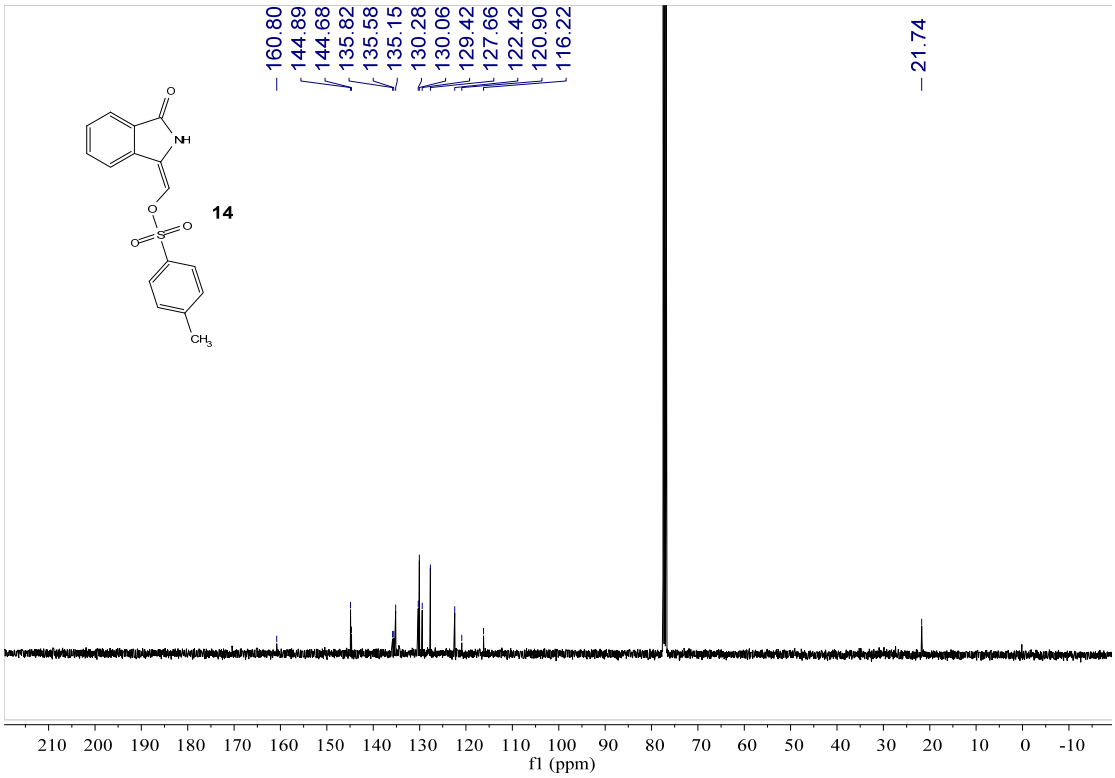
DEPT 135 spectrum is pictured below:

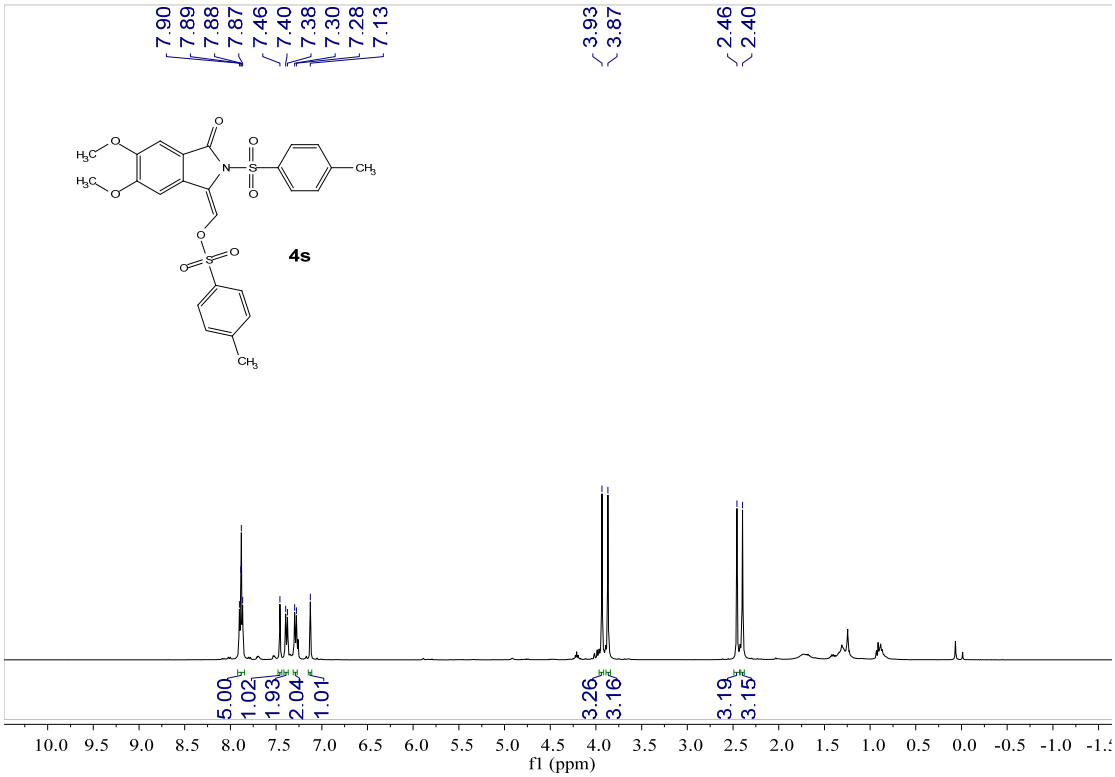

134.70
131.19
129.98
129.50
129.15
128.02
124.94
123.08
69.42
51.76
21.87
12
CH2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

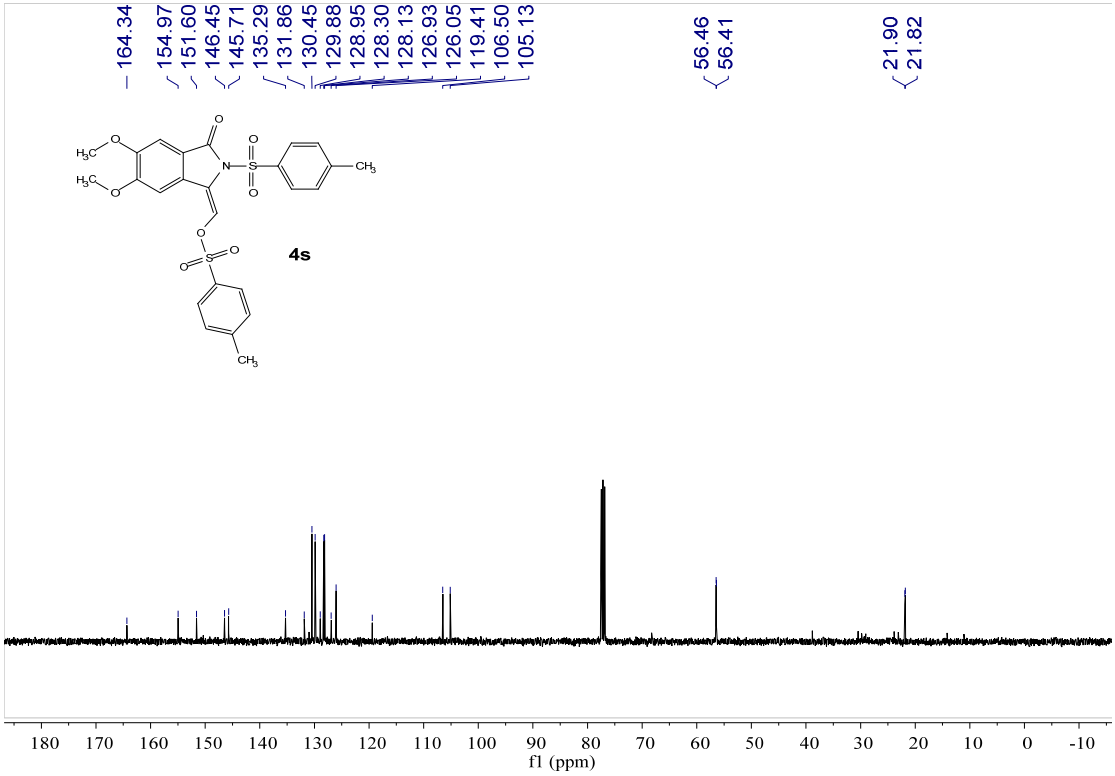

8.04
8.02
7.79
7.77
7.66
7.64
7.62
7.47
7.45
7.43
7.41
7.34
7.32
5.33
5.31
5.30
5.28
2.41
1.79
1.77
13
2.00
0.99
1.06
2.08
2.09
1.10
3.11
3.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

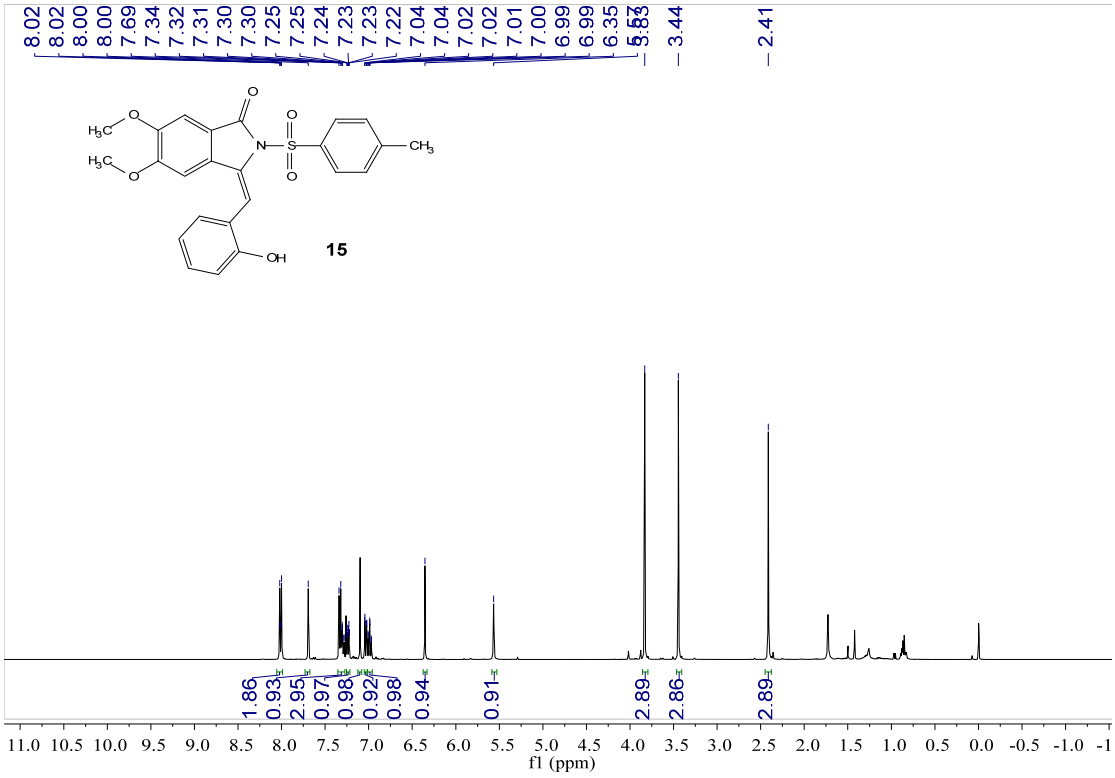

166.49
147.54
145.13
136.39
134.18
129.73
129.03
128.94
128.38
125.09
122.60
58.82
21.80
21.61
13
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

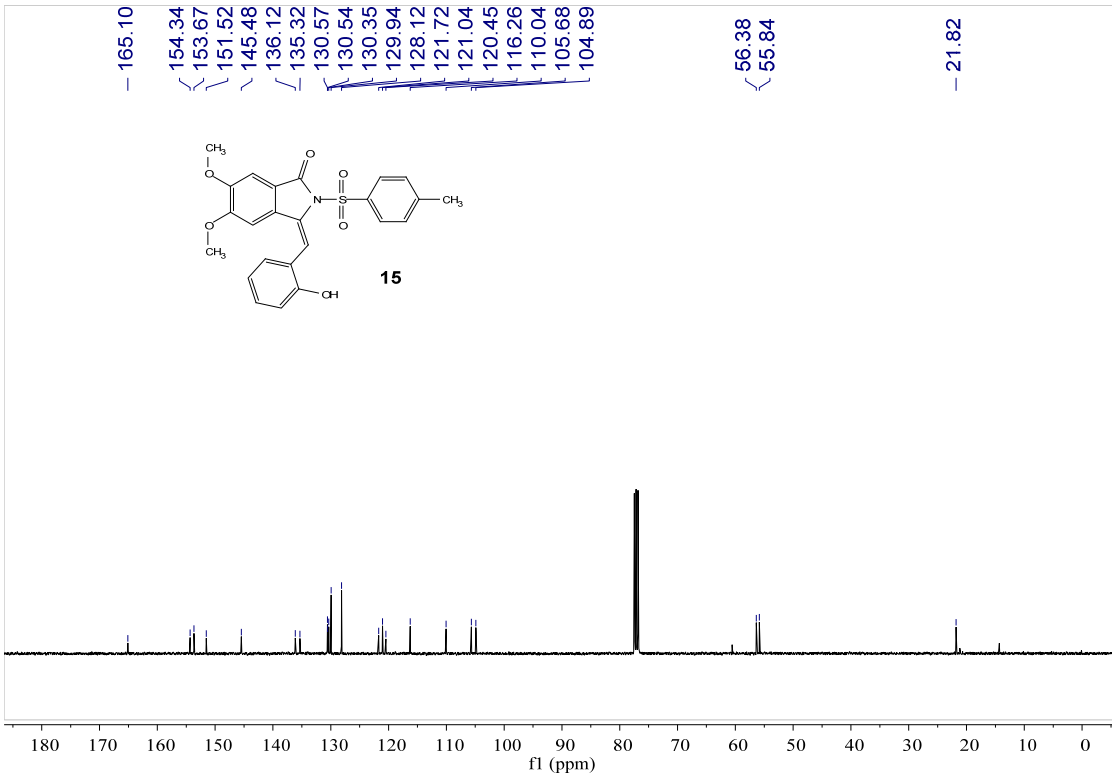

8.27
8.25
8.25
7.72
7.71
7.70
7.69
7.58
7.56
7.56
7.54
7.29
7.27
7.04
7.04
6.19
2.42
14
1.00
3.00
2.27
2.04
0.90
0.97
2.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

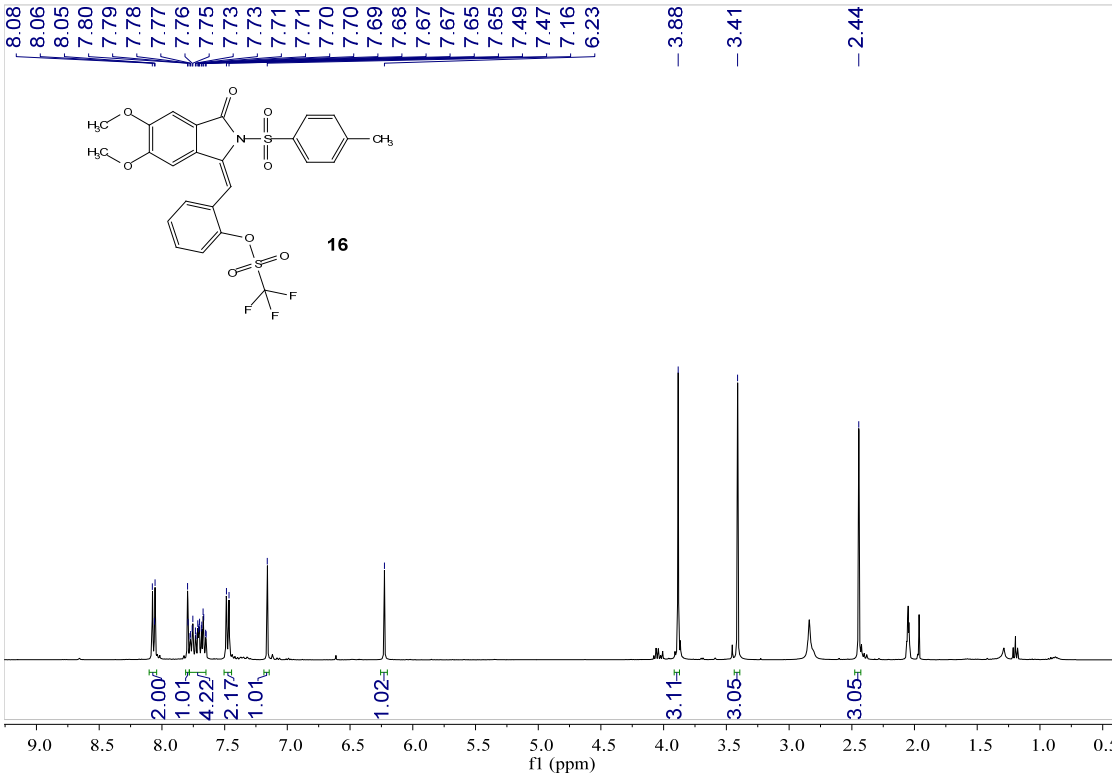

160.80
144.89
144.68
135.82
135.58
135.15
130.28
130.06
129.42
127.66
122.42
120.90
116.22
21.74
14
f1 (ppm)

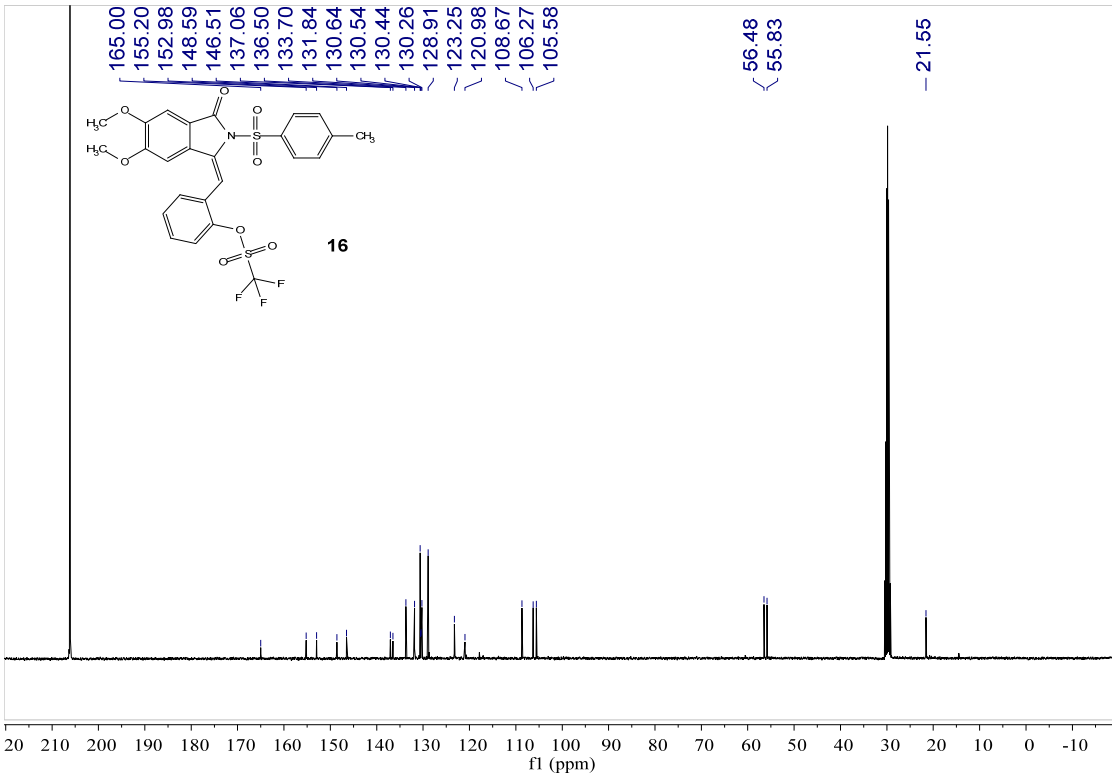

7.90
7.89
7.88
7.87
7.46
7.40
7.38
7.30
7.28
7.13
3.93
3.87
2.46
2.40
4s
5.00
1.02
1.93
2.04
1.01
3.26
3.16
3.19
3.15
f1 (ppm)

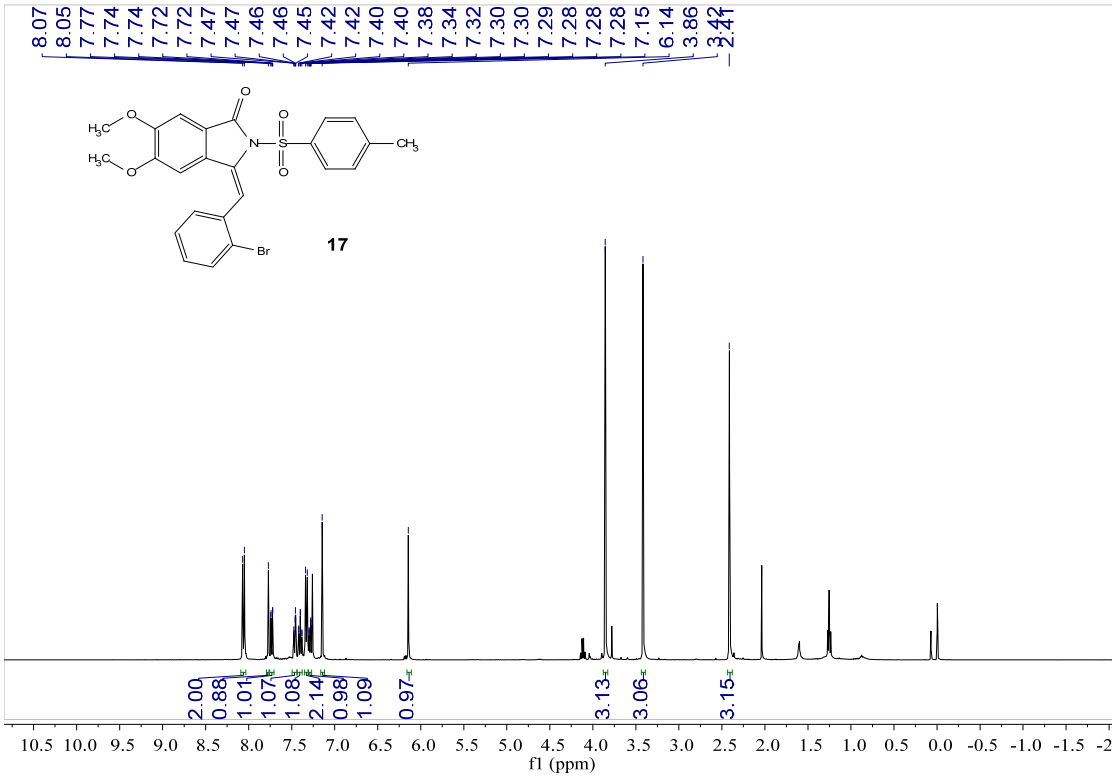

164.34
154.97
151.60
146.45
145.71
135.29
131.86
130.45
129.88
128.95
128.30
128.13
126.93
126.05
119.41
106.50
105.13
56.46
56.41
21.90
21.82
4s
f1 (ppm)

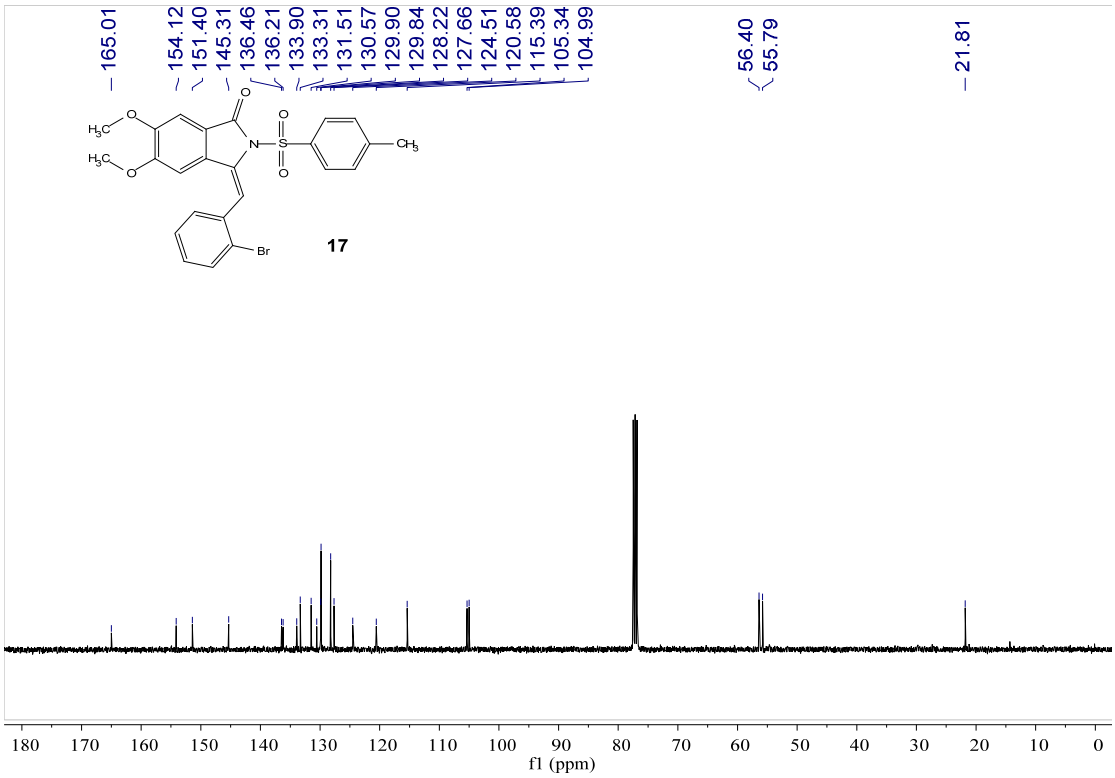

8.02
8.02
8.00
8.00
7.69
7.34
7.32
7.31
7.30
7.30
7.25
7.25
7.24
7.23
7.23
7.22
7.04
7.04
7.02
7.02
7.01
7.00
6.99
6.99
6.35
3.44
2.41
15
1.86
0.93
2.95
0.97
0.98
0.92
0.98
0.94
0.91
2.89
2.86
2.89
f1 (ppm)

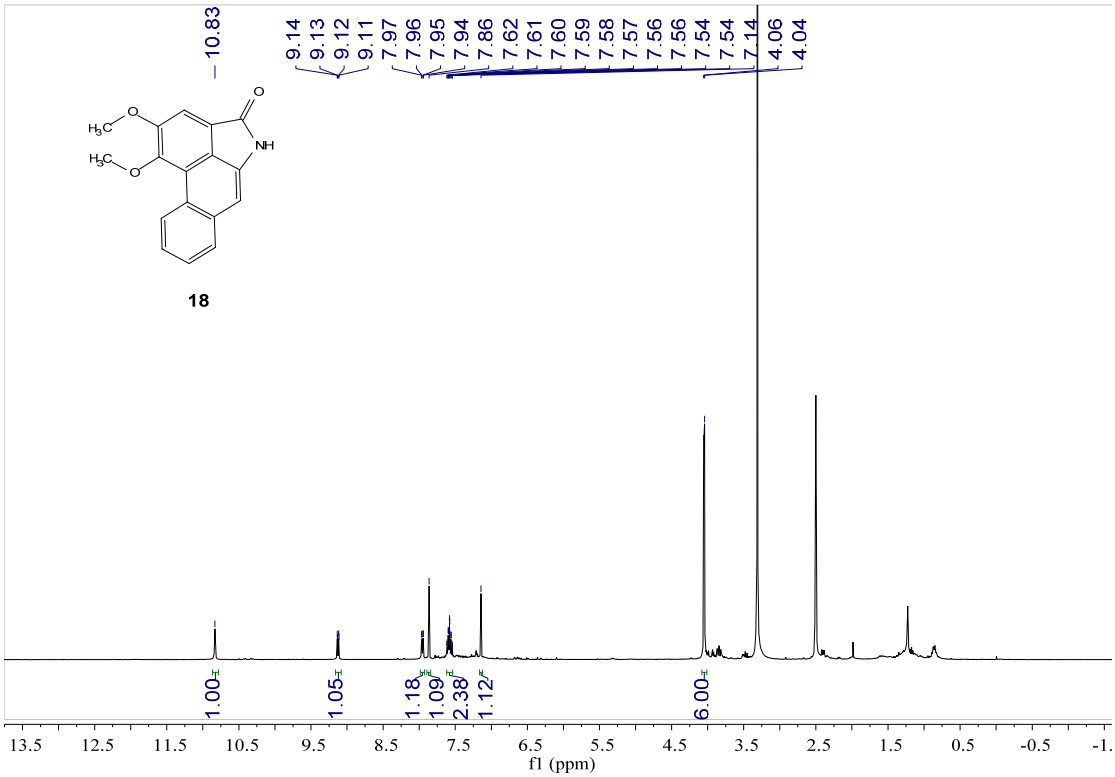

165.10
154.34
153.67
151.52
145.48
136.12
135.32
130.57
130.54
130.35
129.94
128.12
121.72
121.04
120.45
116.26
110.04
105.68
104.89
56.38
55.84
21.82
15
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

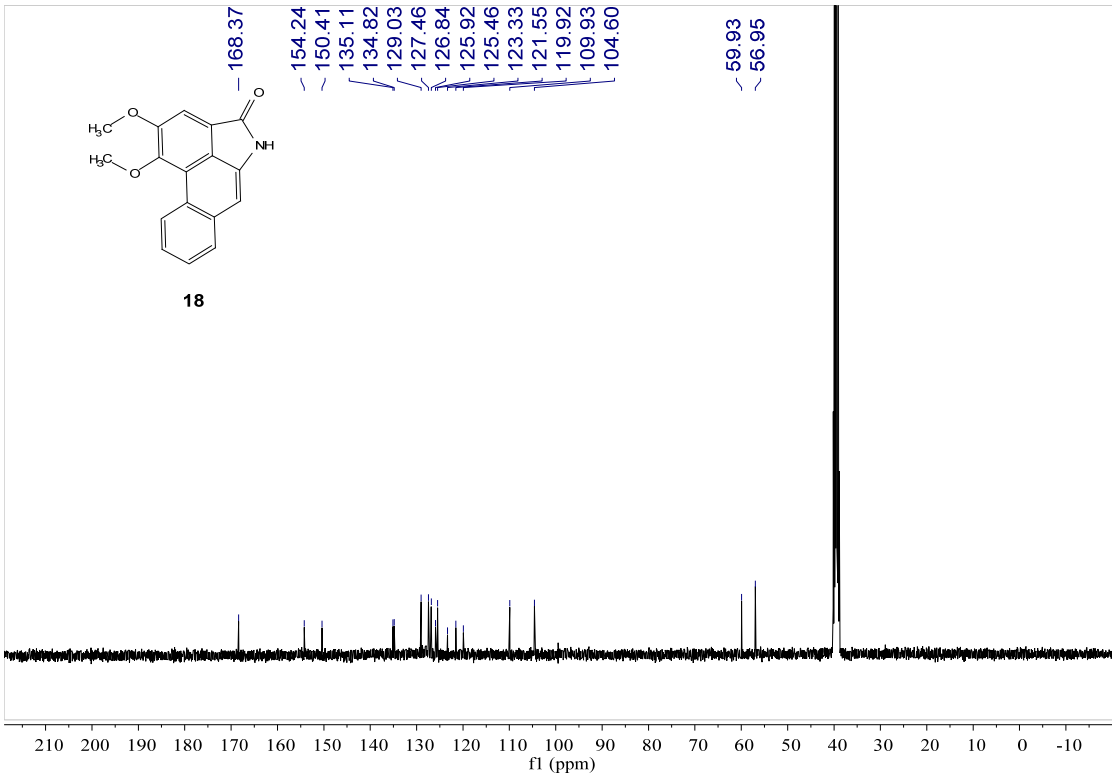

8.08
8.06
8.05
7.80
7.79
7.78
7.77
7.76
7.75
7.73
7.73
7.71
7.71
7.70
7.70
7.69
7.68
7.67
7.67
7.65
7.65
7.49
7.47
7.16
6.23
3.88
3.41
2.44
16
2.00
1.01
4.22
2.17
1.01
1.02
3.11
3.05
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


165.00
155.20
152.98
148.59
146.51
137.06
136.50
133.70
131.84
130.64
130.54
130.44
130.26
128.91
123.25
120.98
108.67
106.27
105.58
56.48
55.83
21.55
16
f1 (ppm)


8.07
8.05
7.77
7.74
7.74
7.72
7.72
7.47
7.47
7.46
7.46
7.45
7.42
7.42
7.40
7.40
7.38
7.34
7.32
7.30
7.30
7.29
7.28
7.28
7.28
7.15
6.14
3.86
3.42
2.41
17
2.00
0.88
1.01
1.07
1.08
2.14
0.98
1.09
0.97
3.13
3.06
3.15
f1 (ppm)


165.01
154.12
151.40
145.31
136.46
136.21
133.90
133.31
131.51
130.57
129.90
129.84
128.22
127.66
124.51
120.58
115.39
105.34
104.99
56.40
55.79
21.81
17
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.83
9.14
9.13
9.12
9.11
7.97
7.96
7.95
7.94
7.86
7.62
7.61
7.60
7.59
7.58
7.57
7.56
7.56
7.54
7.54
7.14
4.06
4.04
18
1.00
1.05
1.18
1.09
2.38
1.12
6.00
13.5 12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.
f1 (ppm)


168.37
154.24
150.41
135.11
134.82
129.03
127.46
126.84
125.92
125.46
123.33
121.55
119.92
109.93
104.60
59.93
56.95
O
NH
H3C
O
H3C
O
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)