Supporting Information

Visible-light initiated oxidative cyclization of phenyl propiolates with sulfinic acids to coumarin derivatives under metal-free conditions

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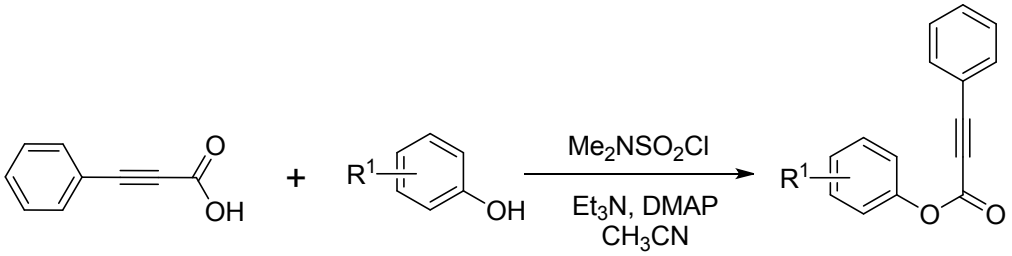
1. General considerations

All reactions were carried out under air. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) in $CDCl_3$ as solvent and recorded in ppm relative to internal standard tetramethylsilane. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectroscopic data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

2. Preparation of the starting materials

All of the starting materials, phenyl 3-phenylpropiolates were synthesized according to the literature (C. E. Song, D. Jung, S. Y. Choung, E. J. Roh and S. Lee, *Angew. Chem. Int. Ed.*, 2004, **43**, 6183).



Typical procedure for the synthesis of phenyl 3-phenylpropiolate: $Me_3N \cdot HCl$ (258 mg, 2.7 mmol) was added to a stirred solution of

phenylpropiolic acid (204.6 mg, 1.4 mmol), phenol (131.6 mg, 1.4 mmol), Et_3N (414.9 mg, 4.1 mmol), and DMAP (12.2 mg, 0.10 mmol) in CH_3CN (1.0 mL) at 0–5 ^oC under an nitrogen atmosphere, and the mixture was stirred for 10 min. Me_2NSO_2Cl (387.7 mg, 2.7 mmol) in CH_3CN (1.0 mL) was added to the mixture at 0–5 ^oC, and the mixture was stirred at that temperature for 3 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 5:1 to 7:1, V/V) to obtain the phenyl 3-phenylpropiolate as a colorless liquid.

3. Typical procedure for the synthesis of 3-sulfonated coumarin

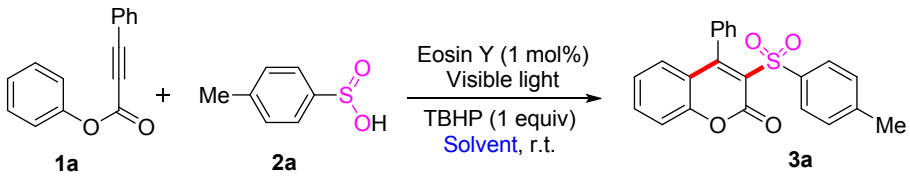
To a reaction tube equipped with a magnetic stir bar was charged with phenyl 3-phenylpropiolate (**1a**, 0.30 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.60 mmol), Eosin Y (19.4 mg, 1 mol%), TBHP (38.6 mg, 0.30 mmol), and CH_3CN/H_2O (1:1, 1.5 mL). The solution was stirred at room temperature with the irradiation of a 18 W fluorescent lamp for 12 h. After the reaction was completed, the resulting mixture was extracted with ethyl acetate (5.0 mL×3). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 5:1 to 7:1, V/V) to obtain the

desired pure product.

4. The effects of solvent on the reaction (Table S1)

The further optimization of solvent was carried out under above reaction conditions. The results are listed in Table S1 (Supporting Information). When the reaction was carried out in MeCN, DMF or THF, no desired product **3a** was detected (Table S1, entries 1−3). When the reaction was charged in H_2O and ethanol, 28% and 9% yields of **3a** were isolated, respectively (Table S1, entries 4 and 5). It was notable that the mixture of solvent could affect the reaction process. The investigation revealed that MeCN/H_2O (1:1) was the best reaction medium (Table S1, entries 6−11). Therefore, the optimized conditions were involved in Eosin Y (1 mol%), TBHP (1.0 equiv) in MeCN/H_2O (1:1) under 18 W fluorescent lamp for 12 h.

Table S1: The effects of solvent on the reaction.[a]



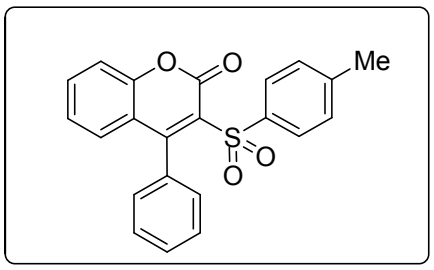
1a 2a 3a

Entry	Solvent	Yield(%)[b]
1	MeCN	Trace
2	DMF	Trace
3	THF	N.R.
4	H_2O	28
5	Ethanol	9
6	MeCN:H_2O (1:2)	42
7	MeCN:H_2O (1:3)	17
8	DCE:H_2O (1:1)	Trace
9	EtOH:H_2O (1:1)	23
10	DMF:H_2O (1:1)	12
11	DMSO:H_2O (1:1)	10

[a] Reaction conditions: phenyl 3-phenylpropiolate (**1a**, 0.30 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.60 mmol), Eosin Y (1 mol%), TBHP (0.30 mmol), solvent 1.5 mL), 18 W fluorescent lamp, at room temperature under air for 12 h. [b] Isolated yields.

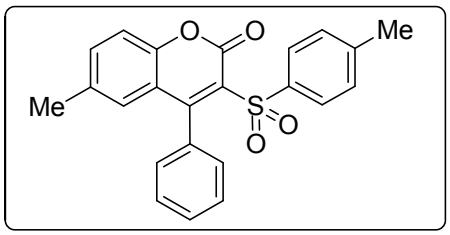
5. Characterization data for the products

4-Phenyl-3-tosyl-2*H*-chromen-2-one (3a)[1]



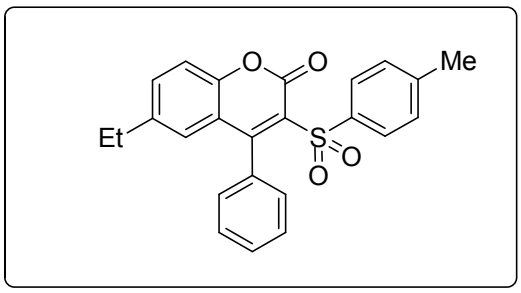
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.2 Hz, 2H), 7.61–7.57 (m, 4H), 7.36–7.29 (m, 5H), 7.21–7.17 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.03, 155.48, 153.74, 144.64, 137.21, 134.48, 132.56, 129.80, 129.17, 129.15, 129.10, 128.04, 127.38, 126.10, 124.70, 120.15, 116.65, 21.54.

6-Methyl-4-phenyl-3-tosyl-2*H*-chromen-2-one (3b)



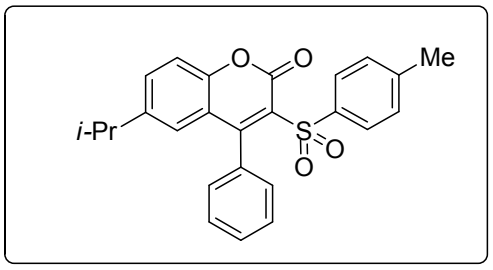
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.1 Hz, 2H), 7.58–7.56 (m, 3H), 7.34–7.32 (m, 2H), 7.30–7.28 (m, 2H), 7.13 (s, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.15, 155.75, 153.86, 146.62, 144.50, 137.41, 132.78, 129.51, 129.13, 129.08, 128.99, 127.97, 127.36, 126.05, 124.84, 117.77, 116.72, 21.75, 21.54. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{19}O_4S$: 391.1004, Found: 391.1010.

6-Ethyl-4-phenyl-3-tosyl-2*H*-chromen-2-one (3c)



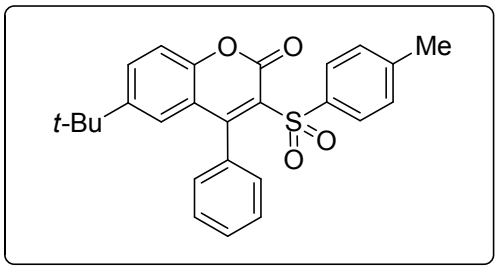
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.58–7.57 (m, 3H), 7.34–7.33 (m, 2H), 7.30–7.28 (m, 2H), 7.16 (s, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 2.73 (q, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.16, 155.80, 154.01, 152.75, 144.51, 137.34, 132.81, 129.66, 129.13, 129.09, 129.00, 127.98, 127.33, 124.90, 124.83, 117.93, 115.53, 28.90, 21.57, 14.73. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{24}H_{21}O_4S$: 405.1161, Found: 405.1160.

6-(*iso*-Propyl)-4-phenyl-3-tosyl-2*H*-chromen-2-one (3d)



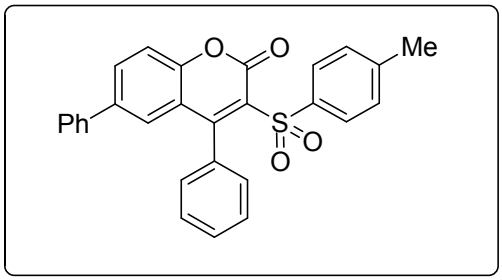
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.2 Hz, 2H), 7.58–7.56 (m, 3H), 7.35–7.33 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.19 (s, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 3.01–2.94 (m, 1H) , 2.41 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.13, 157.34, 155.80, 154.08, 144.47, 137.41, 132.83, 129.73, 129.12, 129.06, 128.99, 127.96, 127.36, 124.89, 123.56, 118.05, 114.18, 34.23, 23.27, 21.54. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{25}H_{23}O_4S$: 419.1317, Found: 419.1318.

6-(*tert*-Butyl)-4-phenyl-3-tosyl-2*H*-chromen-2-one (3e)



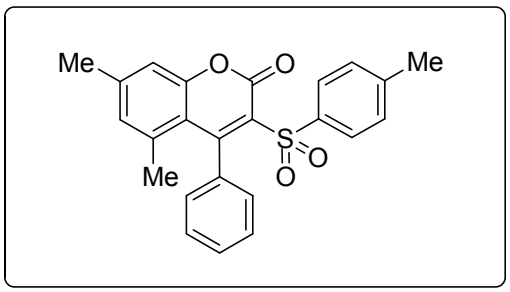
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.2 Hz, 2H), 7.58–7.56 (m, 3H), 7.35–7.33 (m, 3H), 7.30–7.28 (m, 2H), 7.23 (d, J = 8.6 Hz, 1H), 6.94 (d, J = 8.5 Hz, 1H), 2.41 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.68, 159.01, 155.87, 153.87, 144.48, 137.36, 132.81, 129.38, 129.12, 129.06, 128.98, 127.96, 127.33, 124.99, 122.40, 117.67, 113.40, 35.40, 30.70, 21.55. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{26}H_{25}O_4S$: 433.1474, Found: 433.1471.

4,6-Diphenyl-3-tosyl-2*H*-chromen-2-one (3f)



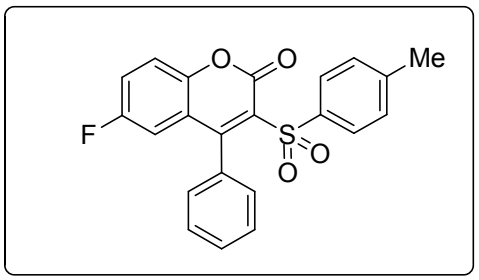
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.1 Hz, 2H), 7.61–7.60 (m, 5H), 7.56 (s, 1H), 7.50–7.42 (m, 4H), 7.39–7.37 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.84, 155.68, 154.17, 147.62, 144.61, 138.19, 137.24, 132.66, 130.17, 129.17, 129.16, 129.12, 128.07, 127.38, 127.17, 125.48, 123.46, 119.00, 114.57, 21.56. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{28}H_{21}O_4S$: 453.1161, Found: 453.1161.

5,7-Dimethyl-4-phenyl-3-tosyl-2*H*-chromen-2-one (3g)



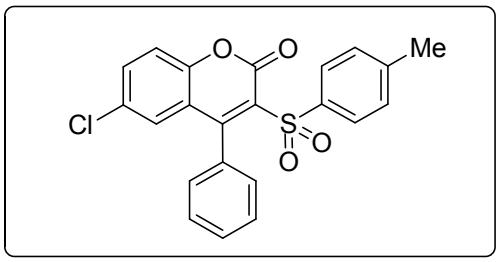
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.2 Hz, 2H), 7.58–7.57 (m, 3H), 7.34–7.32 (m, 2H), 7.30–7.28 (m, 3H), 6.61 (s, 1H), , 2.41 (s, 3H), 2.39 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.36, 155.77, 150.36, 144.47, 137.43, 137.04, 133.91, 132.96, 129.13, 129.08, 128.95, 127.92, 127.42, 127.01, 125.85, 125.55, 119.65, 21.54, 20.74, 15.17. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{21}O_4S$: 405.1161, Found: 405.1163.

6-Fluoro-4-phenyl-3-tosyl-2*H*-chromen-2-one (3i)



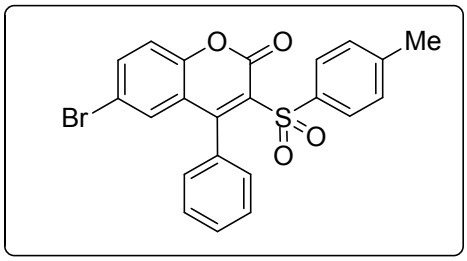
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 8.2 Hz, 2H), 7.58–7.57 (m, 3H), 7.34–7.28 (m, 4H), 7.05–7.01 (m, 2H), 6.93–6.89 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.91 (d, $J_{C\text{-}F}$ = 259.4 Hz), 158.57, 155.17, 155.08 (d, $J_{C\text{-}F}$ = 13.6 Hz), 144.75, 137.11, 132.41, 132.08 (d, $J_{C\text{-}F}$ = 10.7 Hz), 129.26, 129.21, 129.11, 128.15, 127.30, 125.09 (d, $J_{C\text{-}F}$ = 3.0 Hz), 116.98 (d, $J_{C\text{-}F}$ = 2.7 Hz), 113.11 (d, $J_{C\text{-}F}$ = 22.6 Hz), 104.12 (d, $J_{C\text{-}F}$ = 25.7 Hz), 21.54. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{22}H_{16}FO_4S$: 395.0753, Found: 395.0757.

6-Chloro-4-phenyl-3-tosyl-2*H*-chromen-2-one (3j)



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.2 Hz, 2H), 7.59–7.58 (m, 3H), 7.35–7.29 (m, 5H), 7.16 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.28, 154.92, 153.88, 144.81, 140.78, 136.98, 132.19, 130.70, 129.31, 129.22, 129.19, 128.17, 127.30, 126.06, 125.36, 118.83, 116.87, 21.55. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{16}ClO_4S$: 411.0458, Found: 411.0461.

6-Bromo-4-phenyl-3-tosyl-2*H*-chromen-2-one (3k)[1]

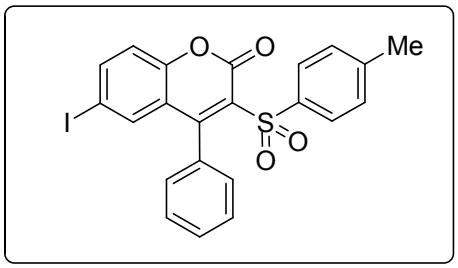


Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.1 Hz, 2H), 7.59–7.58 (m, 3H), 7.52 (s, 1H), 7.31–7.29 (m, 5H), 6.87 (d, *J* = 8.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.37, 154.87, 153.70, 144.84, 136.92, 132.13, 130.71, 129.33, 129.23, 129.20, 129.09, 128.24, 128.19, 127.29, 126.23, 119.88, 119.18, 21.57.

6-Iodo-4-phenyl-3-tosyl-2*H*-chromen-2-one (3l)

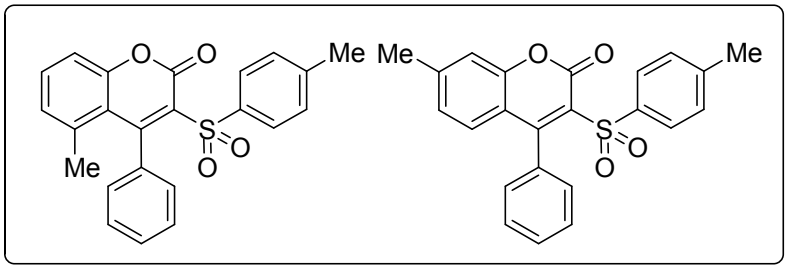
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.2 Hz, 2H),

7.72 (s, 1H), 7.59–7.58 (m, 3H), 7.51 (d, J = 8.6 Hz, 1H), 7.33–7.29 (m,



4H), 6.69 (d, J = 8.5 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.52, 154.77, 153.22, 144.83, 136.93, 134.10, 132.07, 130.49, 129.31, 129.23, 129.19, 128.18, 127.31, 126.46, 125.81, 119.70, 101.32, 21.58. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{22}H_{16}IO_4S$: 502.9814, Found: 502.9812.

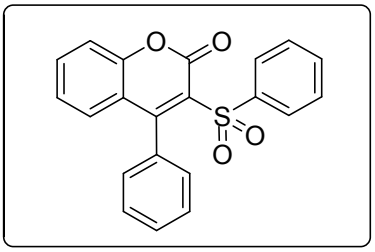
5-Methyl-4-phenyl-3-tosyl-2*H*-chromen-2-one and 7-Methyl-4-phenyl-3-tosyl-2*H*-chromen-2-one (3m and 3m’)



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91–7.88 (m, 4H), 7.59–7.56 (m, 6H), 7.46 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.35–7.33 (m, 4H), 7.30–7.28 (m, 4H), 7.23 (d, J = 8.4 Hz, 1H), 7.10–7.06 (m, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.76 (s, 1H), 2.43 (s, 3H), 2.41 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.38, 159.09, 155.69, 155.61, 152.08, 151.95, 144.58, 137.26, 135.76, 135.69, 134.61, 132.86, 132.63, 129.26, 129.16, 129.14, 129.13, 129.07, 129.01, 128.02, 127.96, 127.56, 127.41, 127.36, 126.19, 125.89, 125.65, 124.19, 119.92, 119.80, 116.42, 21.56, 20.81, 15.28, 14.10. HRMS (ESI) ([M+H]$^+$) Calcd. for

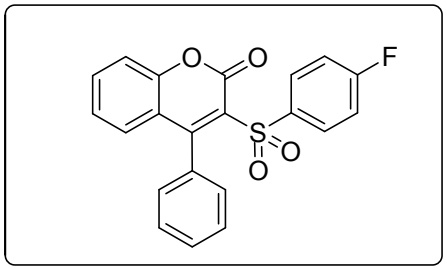
$C_{23}H_{19}O_4S$: 391.1004, Found: 391.1000.

4-Phenyl-3-(phenylsulfonyl)-2*H*-chromen-2-one (3o)[1]



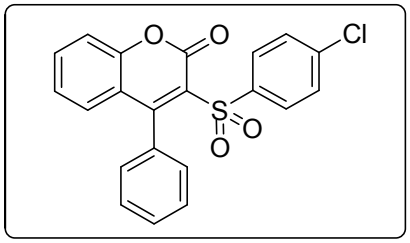
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 7.6 Hz, 2H), 7.63–7.58 (m, 5H), 7.52–7.48 (m, 2H), 7.37–7.33 (m, 3H), 7.21–7.18 (m, 1H), 7.04–7.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.46, 155.43, 153.79, 140.18, 134.62, 133.56, 132.44, 129.84, 129.17, 129.02, 128.53, 128.07, 127.38, 125.81, 124.76, 120.11, 116.69.

3-((4-Fluorophenyl)sulfonyl)-4-phenyl-2*H*-chromen-2-one (3p)[1]



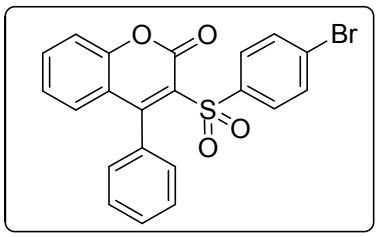
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-8.01 (m, 2H), 7.65–7.58 (m, 4H), 7.35–7.34 (m, 3H), 7.22–7.14 (m, 3H), 7.04 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.71 (d, $J_{C\text{-}F}$ = 256.4 Hz), 159.58, 155.48, 153.78, 136.14 (d, $J_{C\text{-}F}$ = 3.1 Hz), 134.76, 132.37, 132.14 (d, $J_{C\text{-}F}$ = 9.8 Hz), 129.88, 129.25, 128.12, 127.33, 125.66, 124.84, 120.05, 116.72, 115.78 (d, $J_{C\text{-}F}$ = 22.7 Hz).

3-((4-Chlorophenyl)sulfonyl)-4-phenyl-2*H*-chromen-2-one (3q)[1]



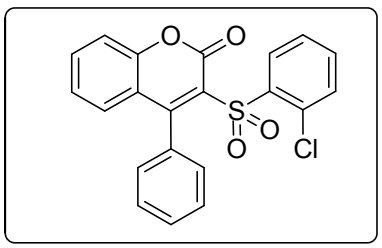
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.4 Hz, 2H), 7.65–7.59 (m, 4H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.37–7.35 (m, 3H), 7.23–7.19 (m, 1H), 7.04 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.75, 155.44, 153.81, 140.32, 138.60, 134.78, 132.27, 130.64, 129.88, 129.29, 128.82, 128.12, 127.34, 125.53, 124.84, 120.03, 116.75.

3-((4-Bromophenyl)sulfonyl)-4-phenyl-2*H*-chromen-2-one (3r)[1]



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.4 Hz, 2H), 7.64–7.58 (m, 6H), 7.35–7.33 (m, 3H), 7.23–7.19 (m, 1H), 7.04 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.82, 155.44, 153.80, 139.18, 134.85, 132.26, 131.82, 130.67, 129.89, 129.31, 128.96, 128.13, 127.35, 125.45, 124.88, 120.02, 116.75.

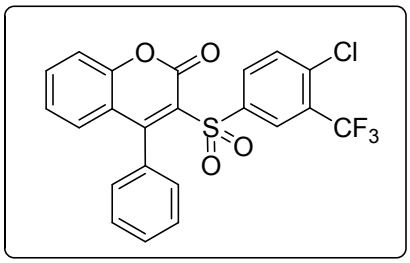
3-((2-Chlorophenyl)sulfonyl)-4-phenyl-2*H*-chromen-2-one (3s)



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, *J*= 7.6 Hz, 1H), 7.66–7.62 (m, 1H), 7.54–7.53 (m, 3H), 7.48–7.35 (m, 6H), 7.25–7.21 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.80, 155.32, 153.88, 138.58, 134.74, 134.23, 131.62, 131.58, 131.30, 131.03, 129.58, 129.54, 128.09, 128.04,

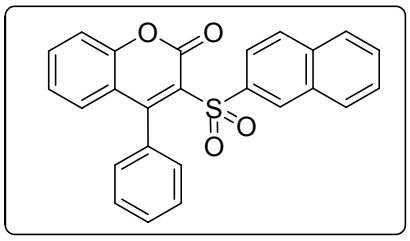
127.08, 125.14, 124.96, 119.92, 116.86. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{21}H_{14}ClO_4S$: 397.0301, Found: 397.0296.

3-((4-Chloro-3-(trifluoromethyl)phenyl)sulfonyl)-4-phenyl-2*H*-chromen-2-one (3t)



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 8.20 (dd, J = 8.4, 1.8 Hz, 1H), 7.68–7.60 (m, 5H), 7.38–7.34 (m, 3H), 7.26–7.22 (m, 1H), 7.09 (dd, J = 8.1, 0.86 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.64, 155.46, 153.88, 139.29, 138.28 (t, $J_{C\text{-}F}$ = 1.6 Hz), 135.18, 133.68, 131.97, 131.86, 129.78 (d, $J_{C\text{-}F}$ = 45.9 Hz), 128.90 (q, $J_{C\text{-}F}$ = 32.6 Hz), 128.48 (q, $J_{C\text{-}F}$ = 5.5 Hz), 128.23, 127.29, 121.89 (q, $J_{C\text{-}F}$ = 272.3 Hz), 125.04, 124.92, 119.91, 116.84. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{22}H_{13}ClF_3O_4S$: 465.0175, Found: 465.0174.

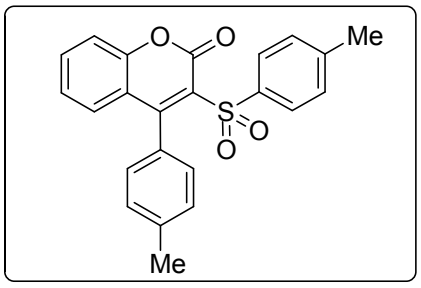
3-(Naphthalen-2-ylsulfonyl)-4-phenyl-2*H*-chromen-2-one (3u)[1]



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (s, 1H), 7.99–7.91 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.65–7.56 (m, 6H), 7.40–7.38 (m, 2H), 7.31 (d, J = 8.2 Hz, 1H), 7.20–7.16 (m, 1H), 7.04 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.44, 155.49, 153.79, 137.01, 135.26, 134.60, 132.48, 131.84,

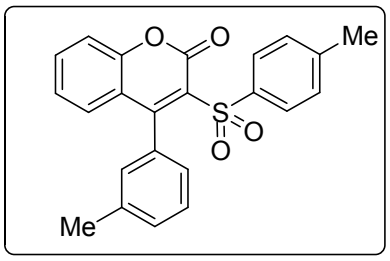
131.25, 129.82, 129.55, 129.24, 129.15, 128.63, 128.08, 127.75, 127.51, 127.27, 125.89, 124.74, 123.46, 120.12, 116.68.

4-(*p*-Tolyl)-3-tosyl-2*H*-chromen-2-one (3v)



Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.62–7.58 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.25–7.23 (m, 2H), 7.21–7.17 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 2.50 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.43, 155.56, 153.70, 144.57, 139.12, 137.22, 134.35, 129.86, 129.51, 129.15, 129.13, 128.76, 127.35, 126.07, 124.60, 120.30, 116.63, 21.56, 21.44. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{19}O_4S$: 391.1004, Found: 391.0999.

4-(*m*-Tolyl)-3-tosyl-2*H*-chromen-2-one (3w)



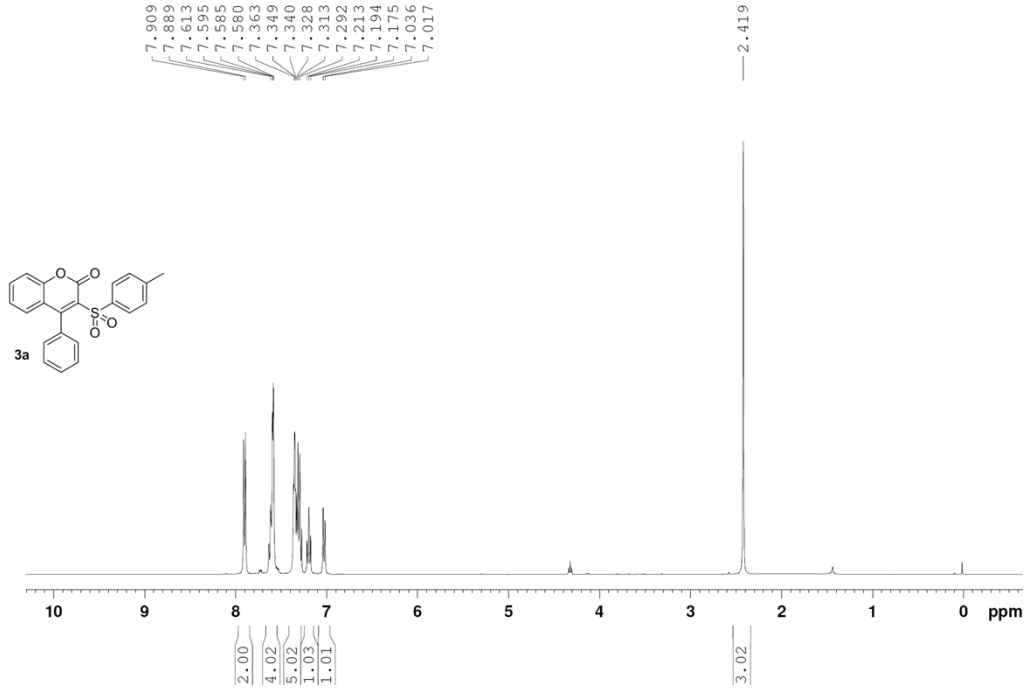
Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.1 Hz, 2H), 7.63–7.59 (m, 1H), 7.49–7.45 (m, 1H), 7.38–7.36 (m, 1H), 7.34–7.31 (m, 2H), 7.29 (s, 1H), 7.21–7.17 (m, 1H), 7.15–7.13 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 2.48 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.35, 155.56, 153.70, 144.61, 137.71, 137.24, 134.42, 132.45, 129.90, 129.88, 129.16, 129.13, 129.11,

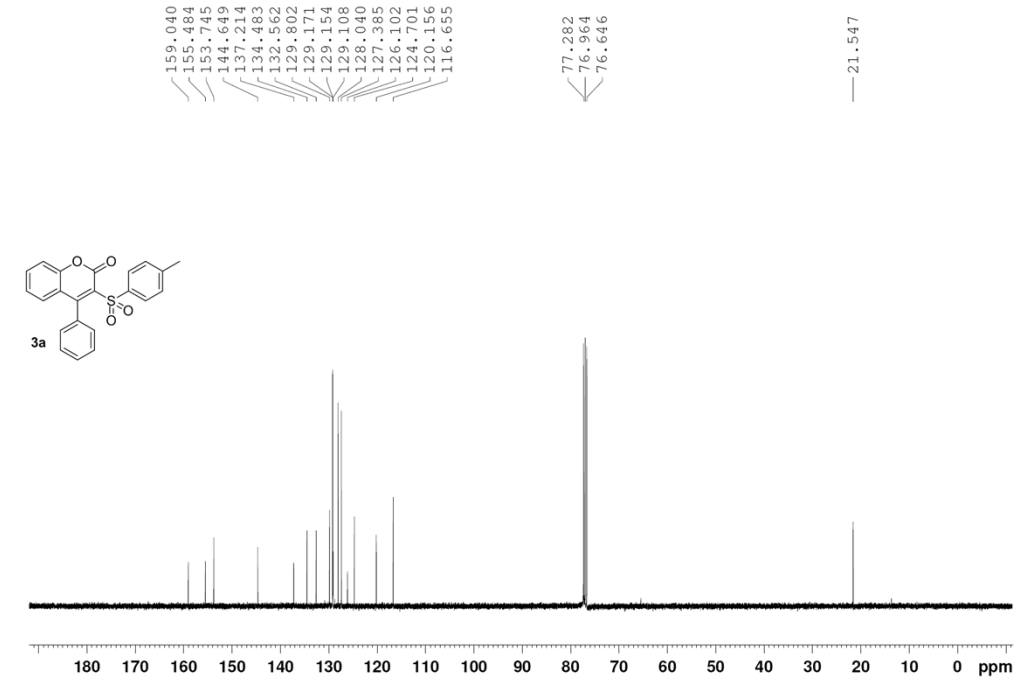
127.97, 127.91, 124.65, 124.48, 120.19, 116.61, 21.56, 21.46. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{19}O_4S$: 391.1004, Found: 391.1002.

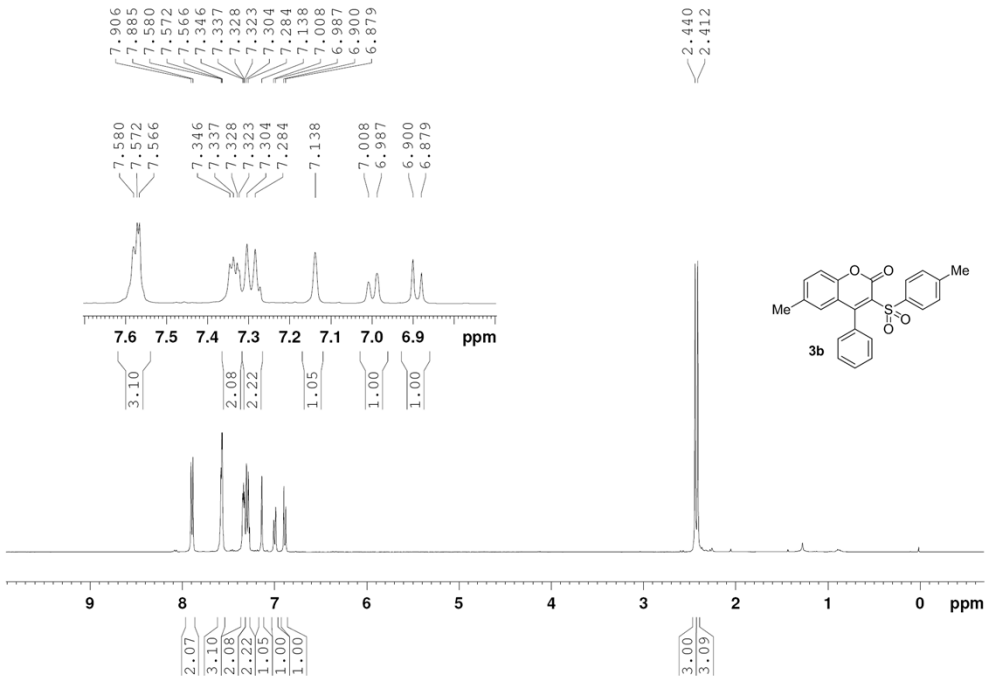
6. Reference

[1] W. Wei, J. Wen, D. Yang, M. Guo, Y. Wang, J. You and H. Wang, *Chem. Commun.*, 2015, **51**, 768.

7. ^{1}H and ^{13}C NMR spectra of the products



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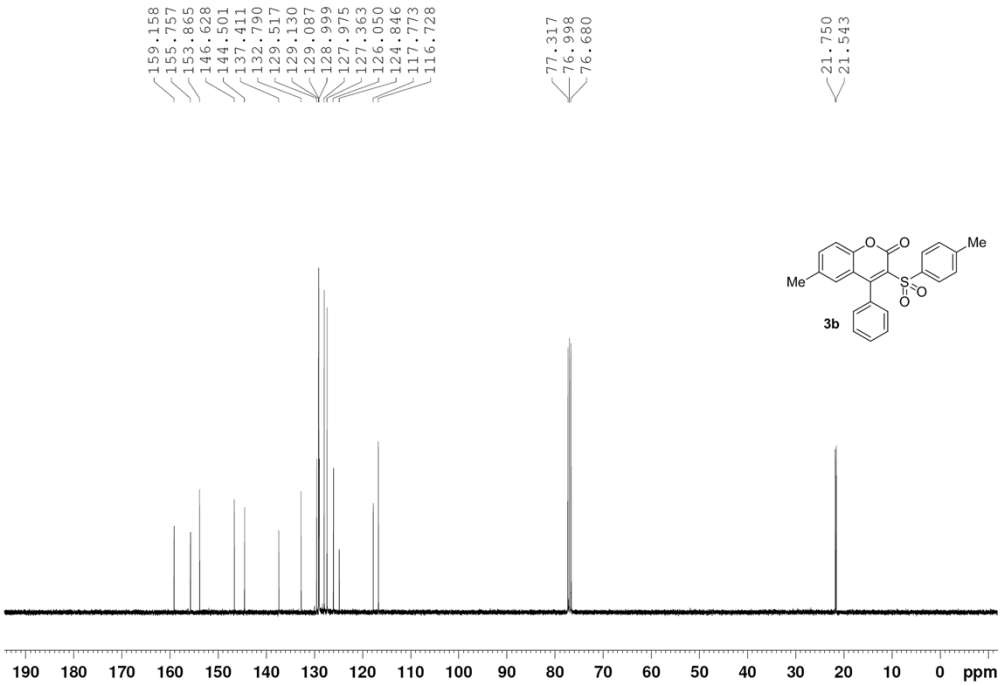
7.580
7.572
7.566
7.346
7.337
7.328
7.323
7.304
7.284
7.138
7.008
6.987
6.900
6.879
2.440
2.412
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 ppm
3.10
2.08
2.22
1.05
1.00
1.00
9 8 7 6 5 4 3 2 1 0 ppm
2.07
3.10
2.08
2.22
1.05
1.00
1.00
3.00
3.09
Me
Me
3b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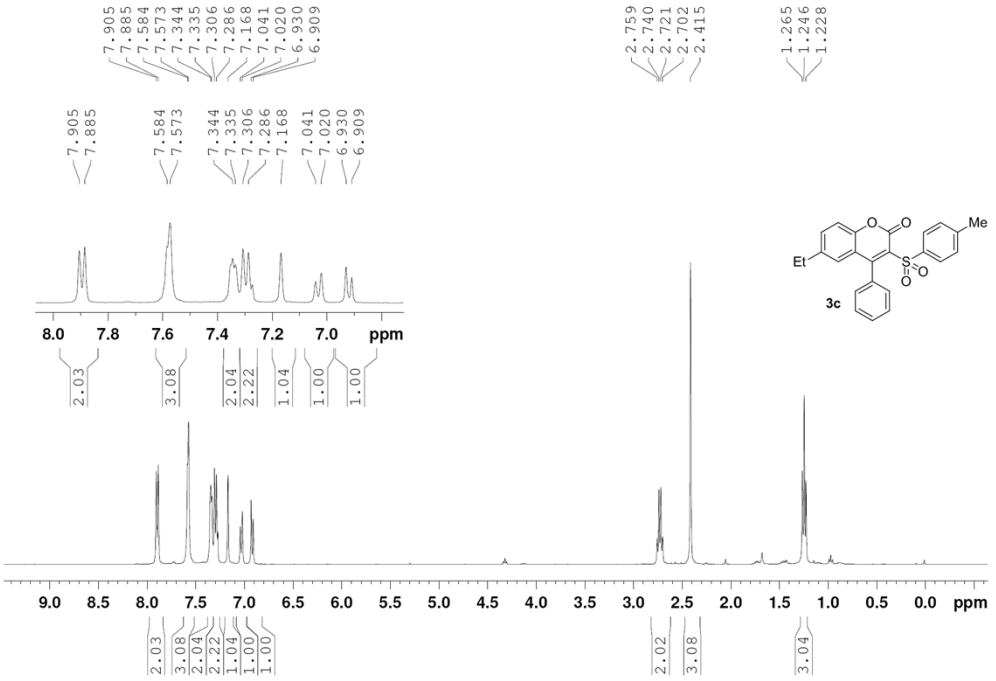
153.865
146.628
144.501
137.411
132.790
129.517
129.130
129.087
128.999
127.975
127.363
126.050
124.846
117.773
116.728
77.317
76.998
76.680
21.750
21.543
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Me
Me
3b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7.584
7.573
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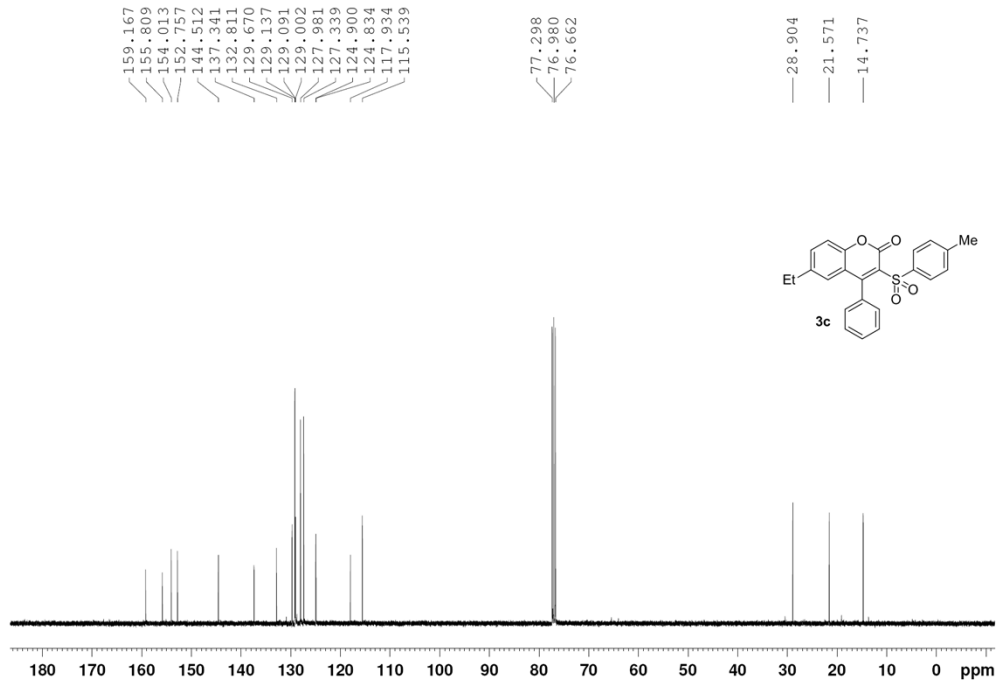
7.286
7.168
7.041
7.020
6.930
6.909
2.759
2.740
2.721
2.702
2.415
1.265
1.246
1.228
Et
Me
3c
8.0
7.8
7.6
7.4
7.2
7.0
ppm
2.03
3.08
2.04
2.22
1.04
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
3.08
2.04
2.22
1.04
1.00
1.00
2.02
3.08
3.04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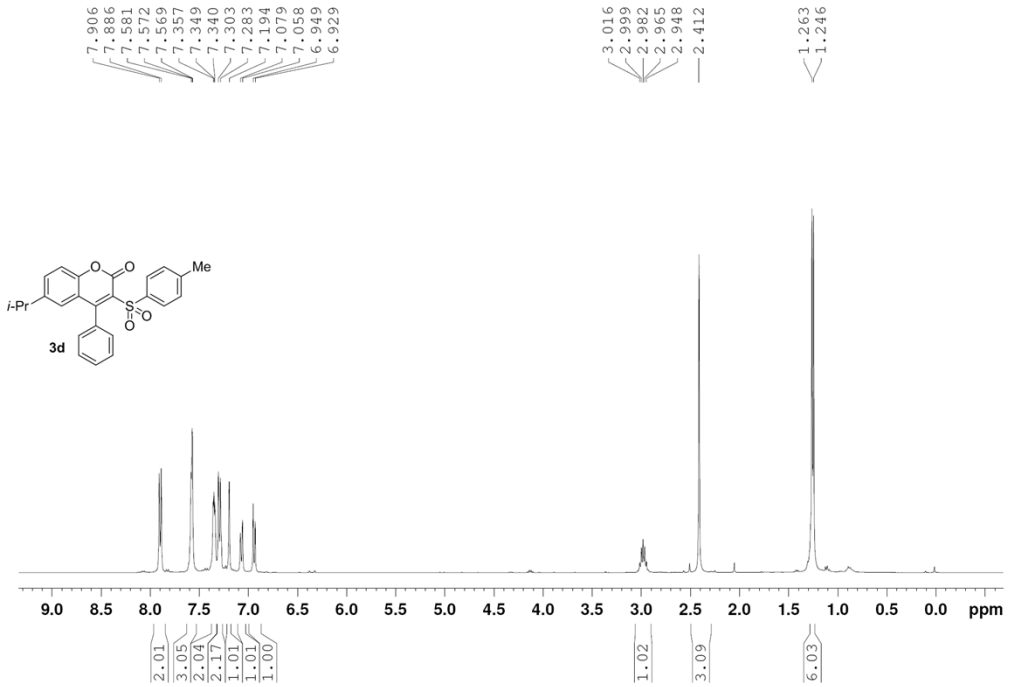
154.013
152.757
144.512
137.341
132.811
129.670
129.137
129.091
129.002
127.981
127.339
124.900
124.834
117.934
115.539
77.298
76.980
76.662
28.904
21.571
14.737
Et
Me
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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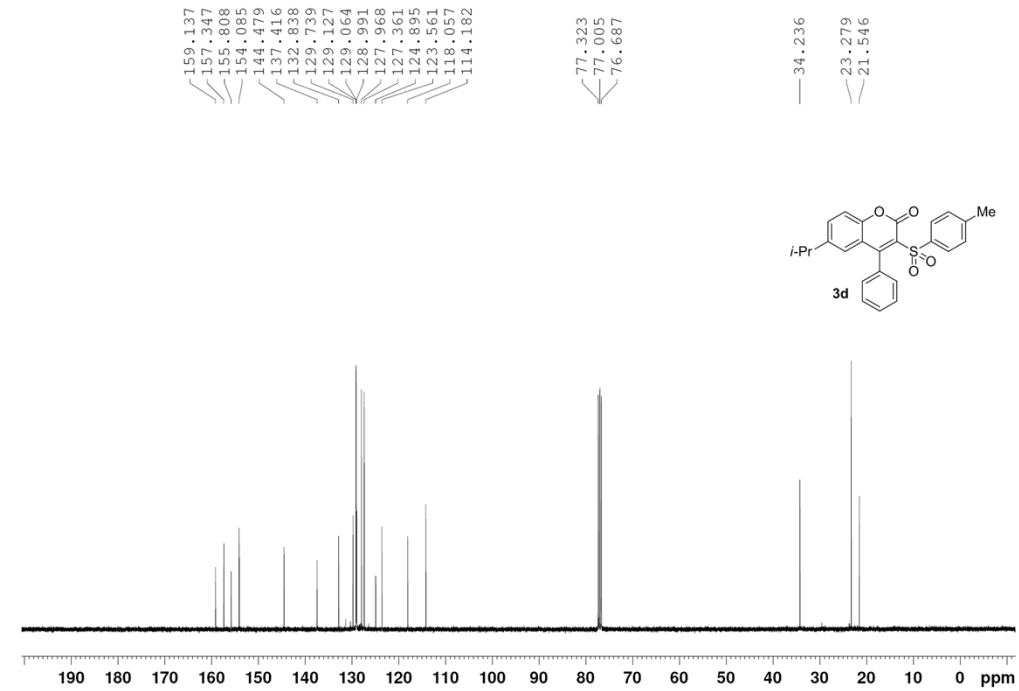
7.581
7.572
7.569
7.357
7.349
7.340
7.303
7.283
7.194
7.079
7.058
6.949
6.929
3.016
2.999
2.982
2.965
2.948
2.412
1.263
1.246
i-Pr
Me
3d
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
3.05
2.04
2.17
1.01
1.01
1.00
1.02
3.09
6.03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155.808
154.085
144.479
137.416
132.838
129.739
129.127
129.064
128.991
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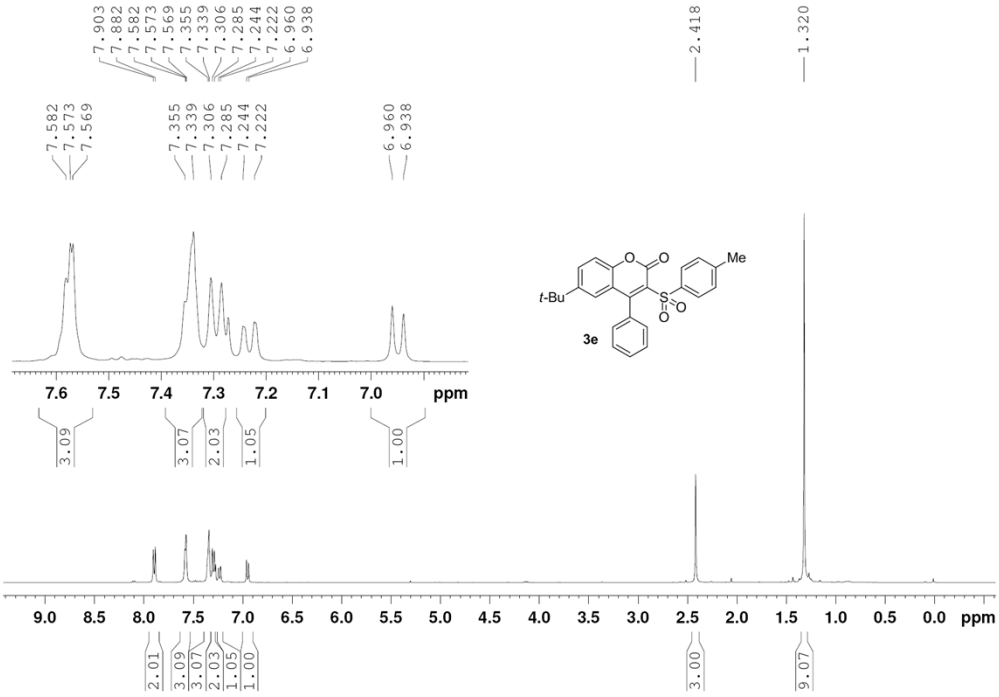
127.361
124.895
123.561
118.057
114.182
77.323
77.005
76.687
34.236
23.279
21.546
i-Pr
Me
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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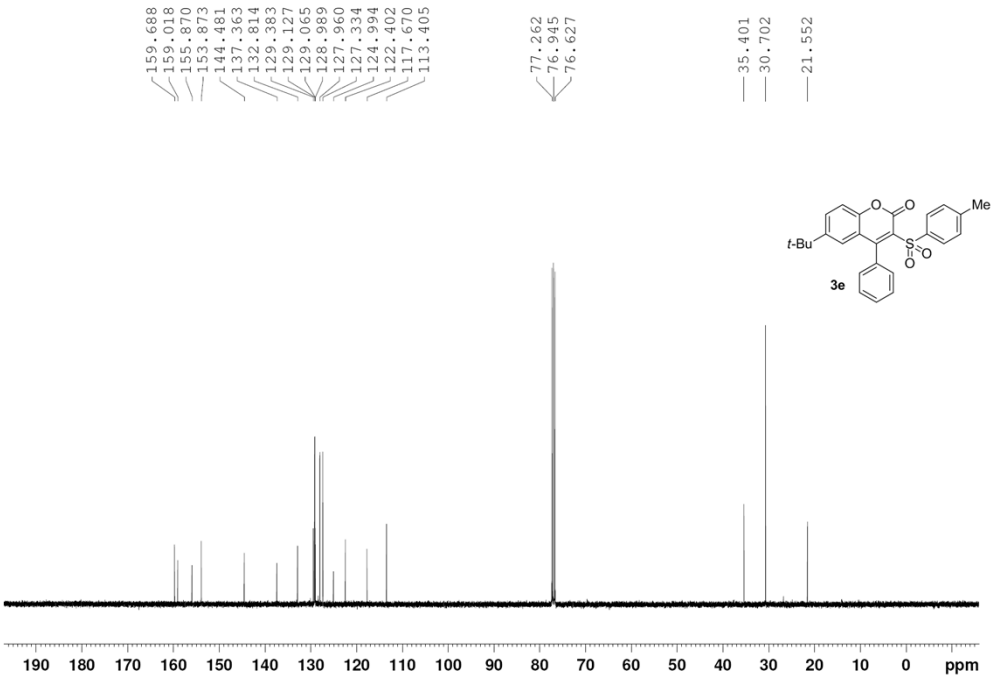
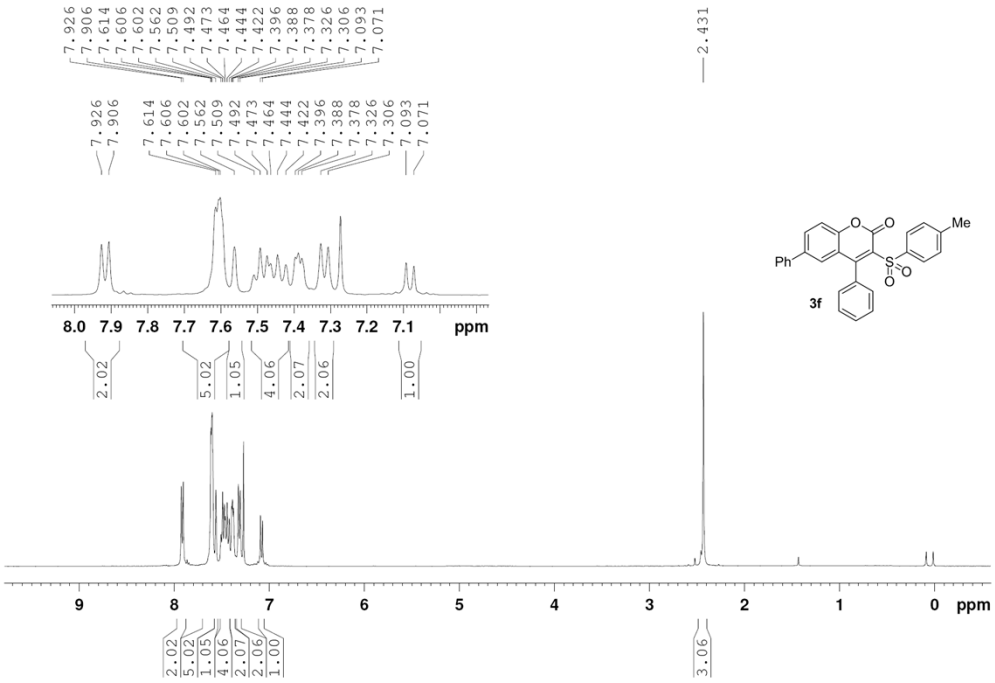
7.573
7.569
7.355
7.339
7.306
7.285
7.244
7.222
6.960
6.938
2.418
1.320
t-Bu
Me
3e
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
3.09
3.07
2.03
1.05
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
3.09
3.07
2.03
1.05
1.00
3.00
9.07


159.688
159.018
155.870
153.873
144.481
137.363
132.814
129.383
129.127
129.065
128.989
127.960
127.334
124.994
122.402
117.670
113.405
77.262
76.945
76.627
35.401
30.702
21.552
t-Bu
Me
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.614
7.606
7.602
7.562
7.509
7.492
7.473
7.464
7.444
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7.396
7.388
7.378
7.326
7.306
7.093
7.071
2.431
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
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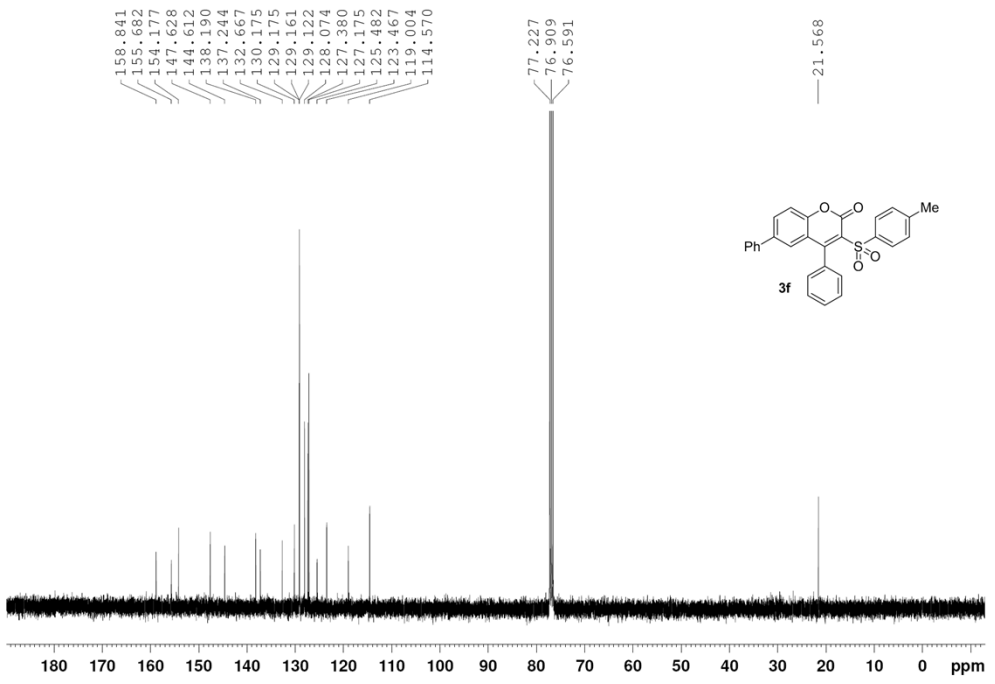
3.06
Ph
Me
3f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128.074
127.380
127.175
125.482
123.467
119.004
114.570
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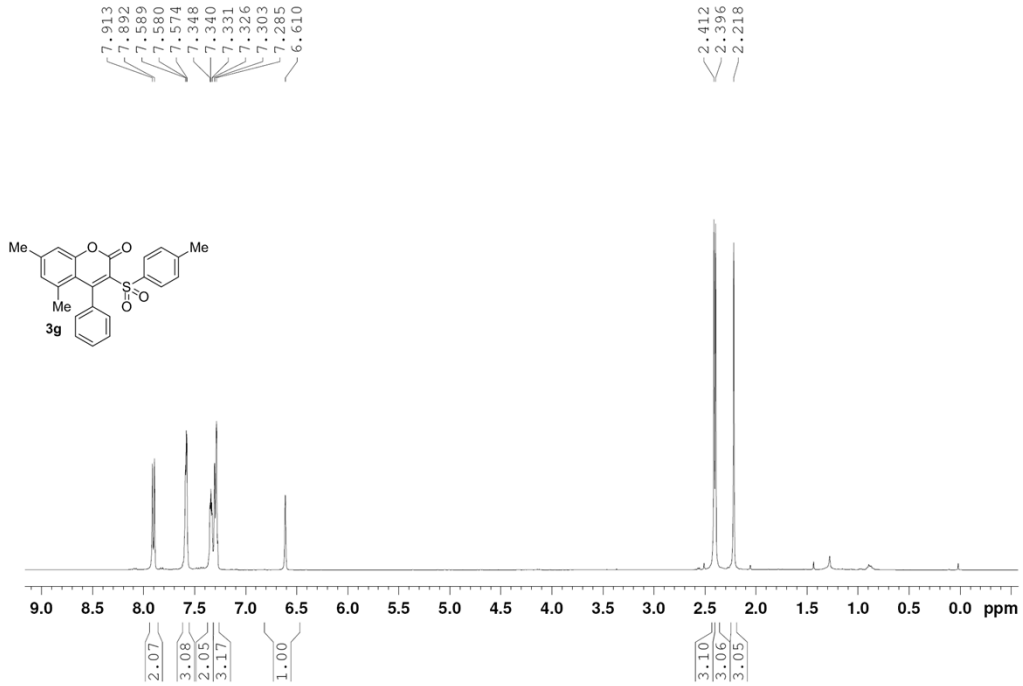
76.909
76.591
21.568
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Ph
Me
3f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7.340
7.331
7.326
7.303
7.285
6.610
2.412
2.396
2.218
Me
Me
Me
3g
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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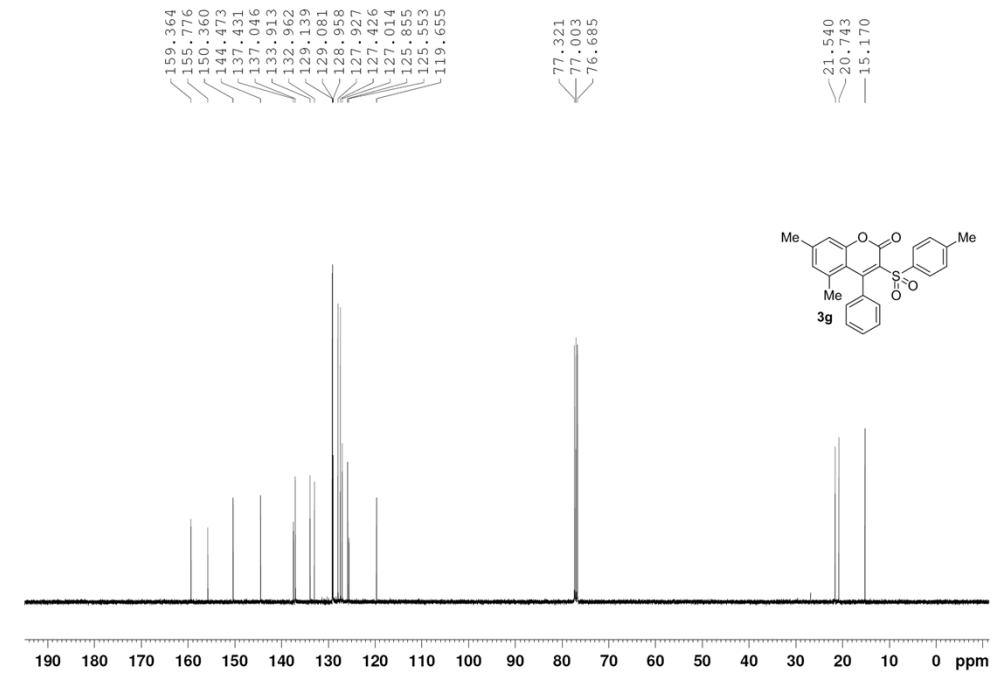
3.08
2.05
3.17
1.00
3.10
3.06
3.05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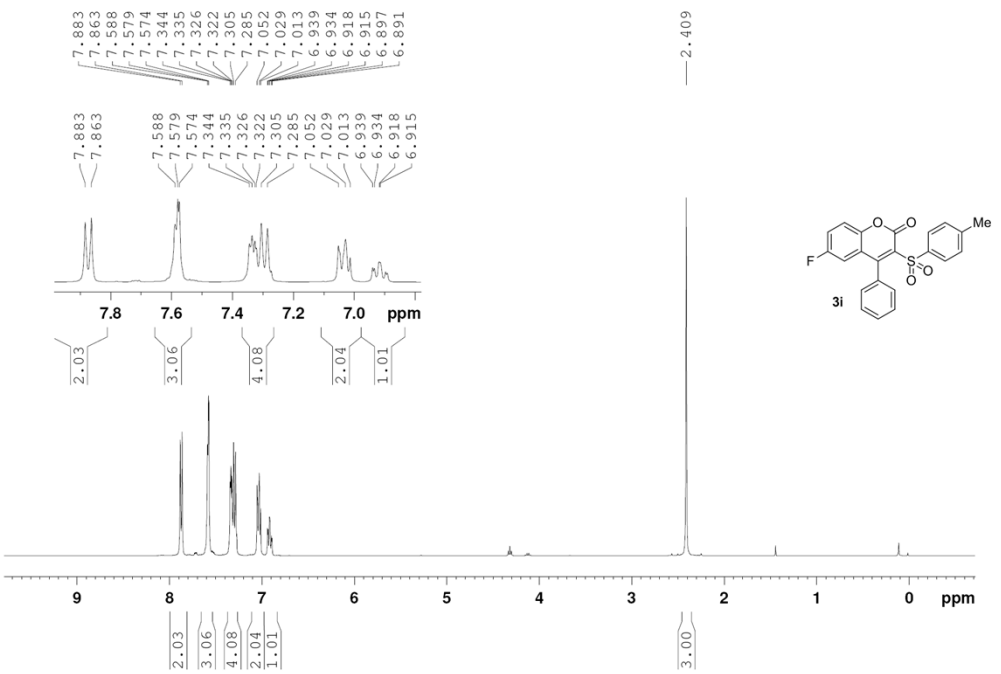
137.046
133.913
132.962
129.139
129.081
128.958
127.927
127.426
127.014
125.855
125.553
119.655
77.321
77.003
76.685
21.540
20.743
15.170
Me
Me
Me
3g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.574
7.344
7.335
7.326
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7.305
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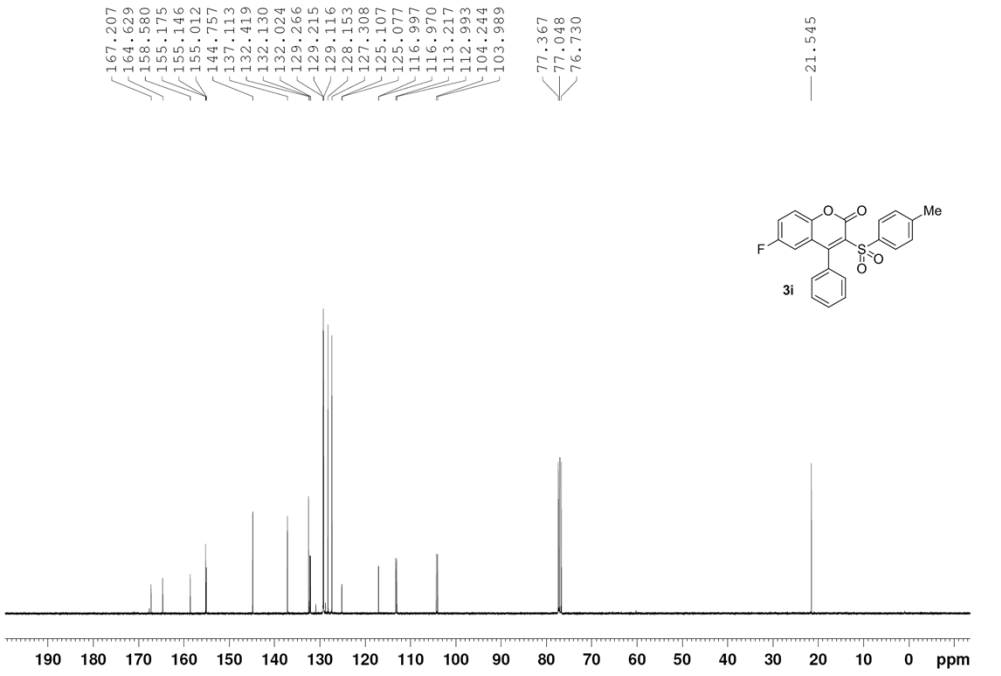
7.013
6.939
6.934
6.918
6.915
6.897
6.891
2.409
7.8
7.6
7.4
7.2
7.0
ppm
2.03
3.06
4.08
2.04
1.01
9
8
7
6
5
4
3
2
1
0
ppm
3.00
F
O
O
S
O
O
Me
3i


167.207
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158.580
155.175
155.146
155.012
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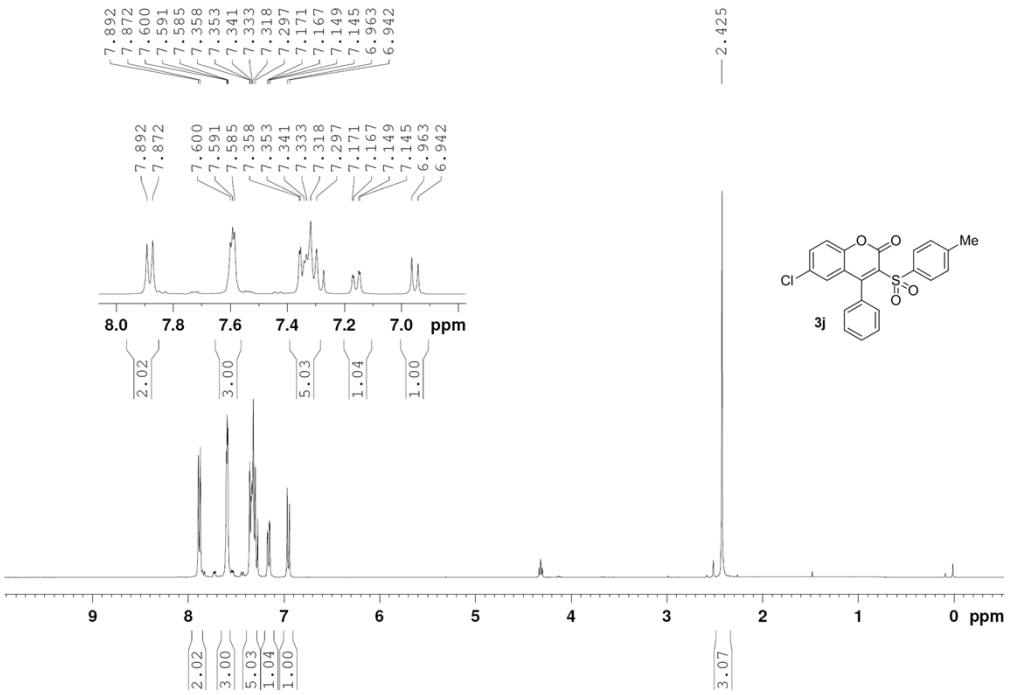
137.113
132.419
132.130
132.024
129.266
129.215
129.116
128.153
127.308
125.107
125.077
116.997
116.970
113.217
112.993
104.244
103.989
77.367
77.048
76.730
21.545
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
F
O
O
S
O
O
Me
3i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7.167
7.149
7.145
6.963
6.942
2.425
8.0
7.8
7.6
7.4
7.2
7.0
ppm
2.02
3.00
5.03
1.04
1.00
9
8
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4
3
2
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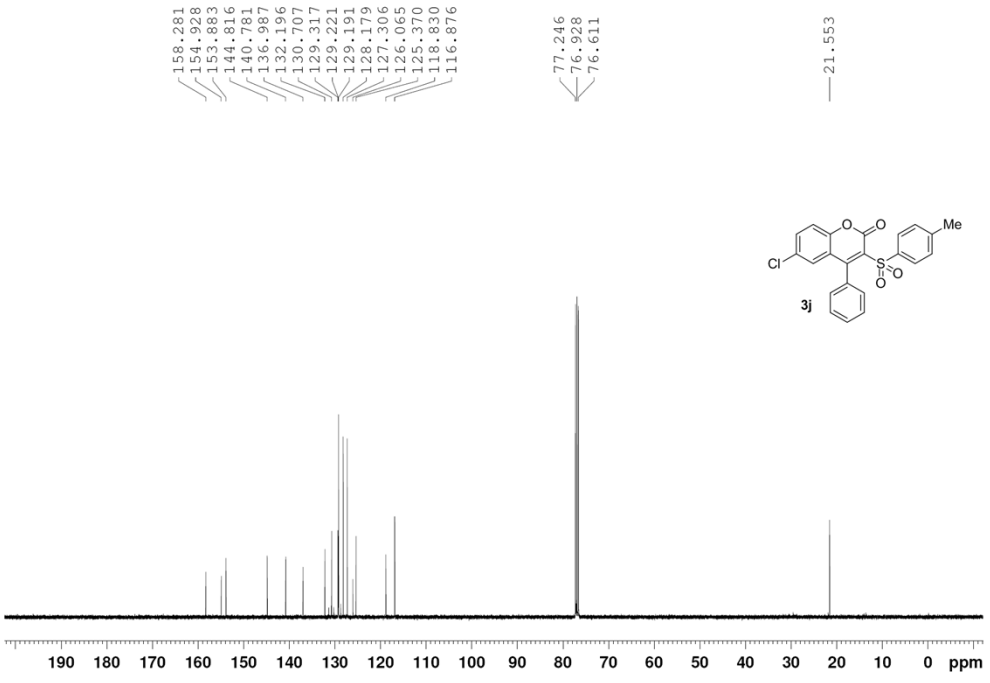
ppm
3.07
Cl
O
O
S
O
O
Me
3j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128.179
127.306
126.065
125.370
118.830
116.876
77.246
76.928
76.611
21.553
Cl
O
O
S
O
O
Me
3j
190
180
170
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140
130
120
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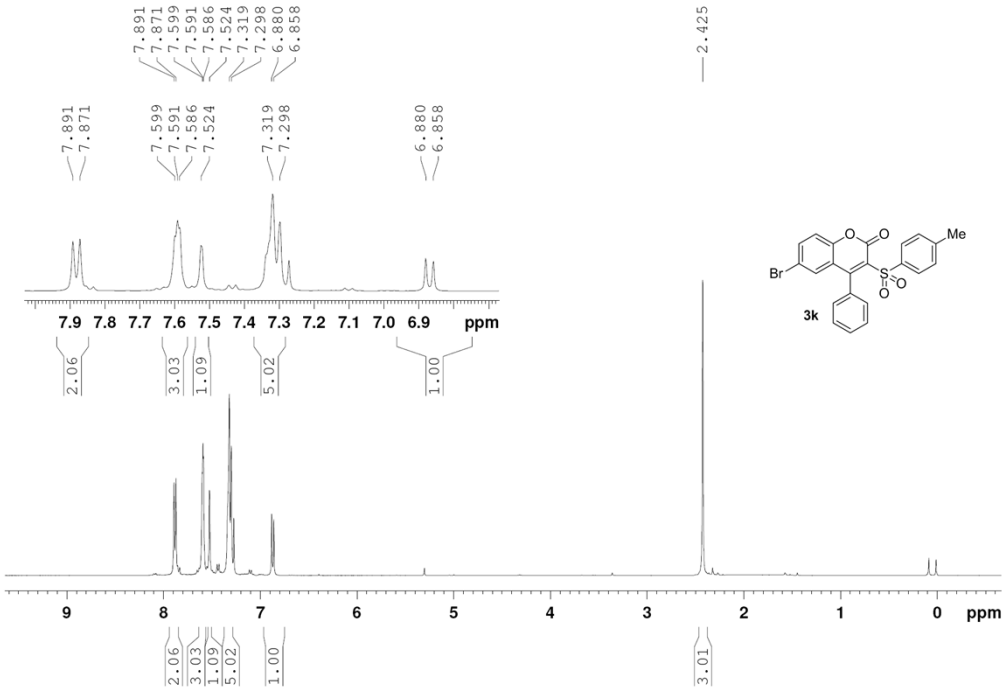
100
90
80
70
60
50
40
30
20
10
0
ppm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7.599
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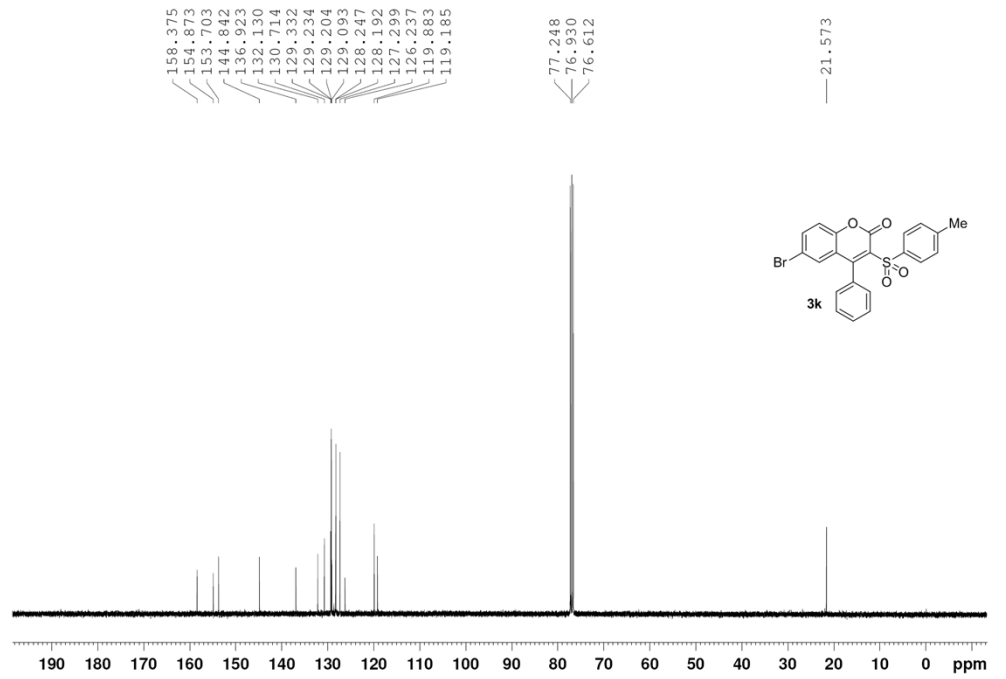
Br
Me
3k
ppm
2.06
3.03
1.09
5.02
1.00
3.01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129.332
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129.093
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126.237
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76.612
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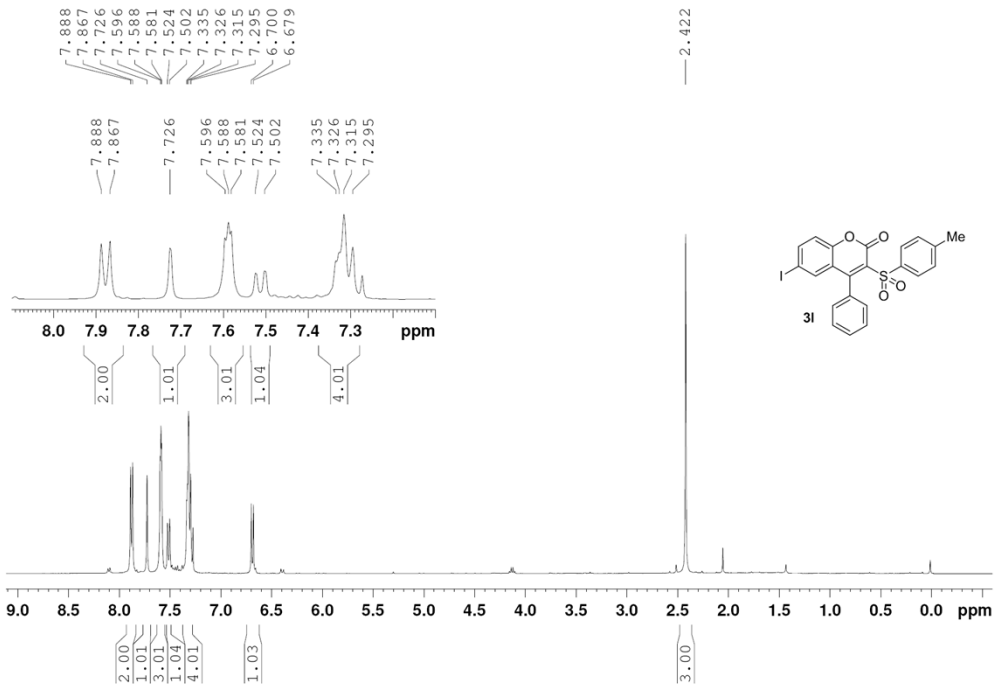
Br
Me
3k
ppm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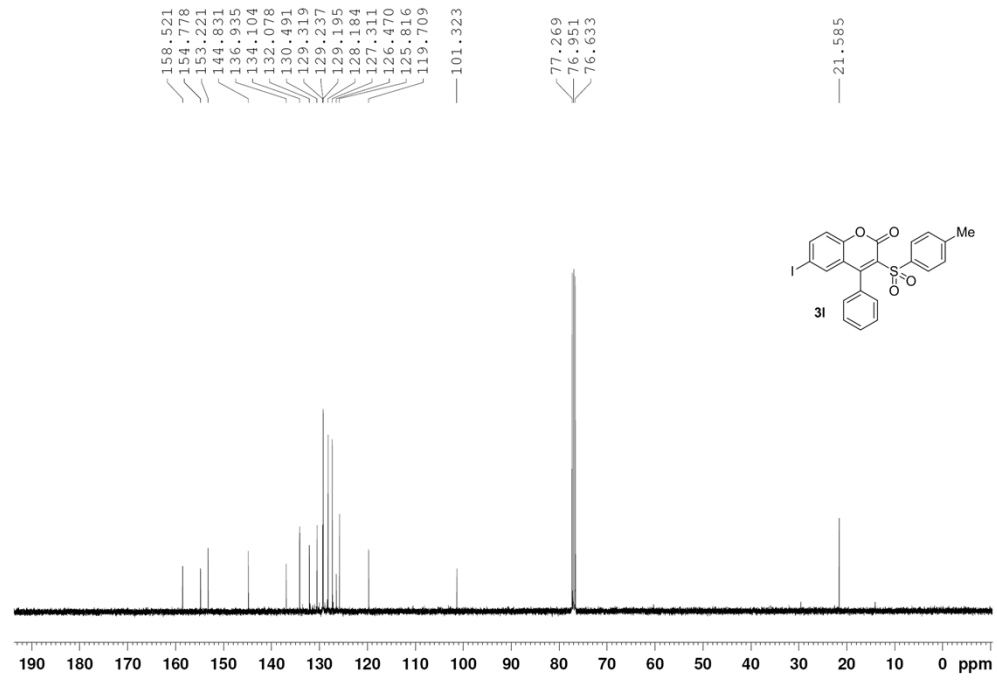
7.502
7.335
7.326
7.315
7.295
6.700
6.679
2.422
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
2.00
1.01
3.01
1.04
4.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.01
3.01
1.04
4.01
1.03
3.00
Me
I
3l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144.831
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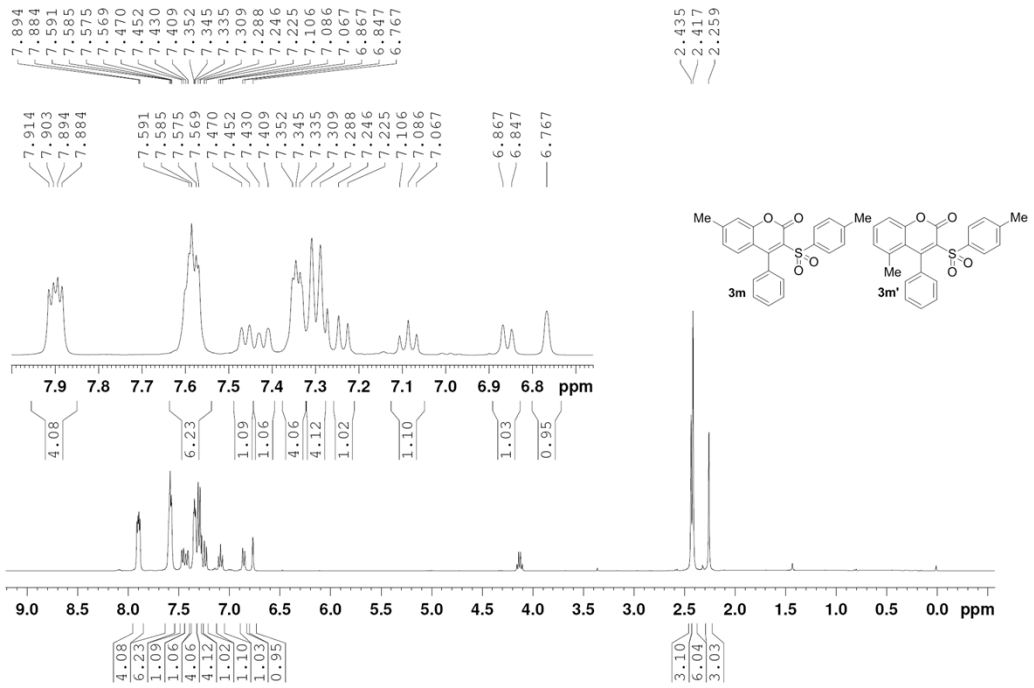
130.491
129.319
129.237
129.195
128.184
127.311
126.470
125.816
119.709
101.323
77.269
76.951
76.633
21.585
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Me
I
3l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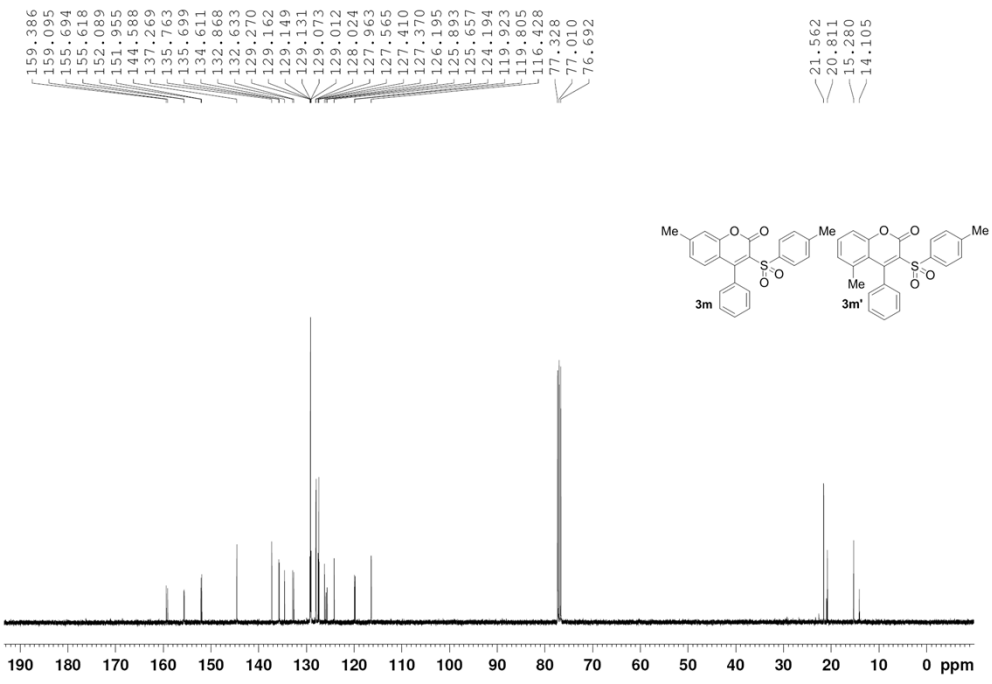
7.352
7.345
7.335
7.309
7.288
7.246
7.225
7.106
7.086
7.067
6.867
6.847
6.767
2.435
2.417
2.259
Me
Me
Me
3m
3m'
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 ppm
4.08
6.23
1.09
1.06
4.06
4.12
1.02
1.10
1.03
0.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.10
6.04
3.03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134.611
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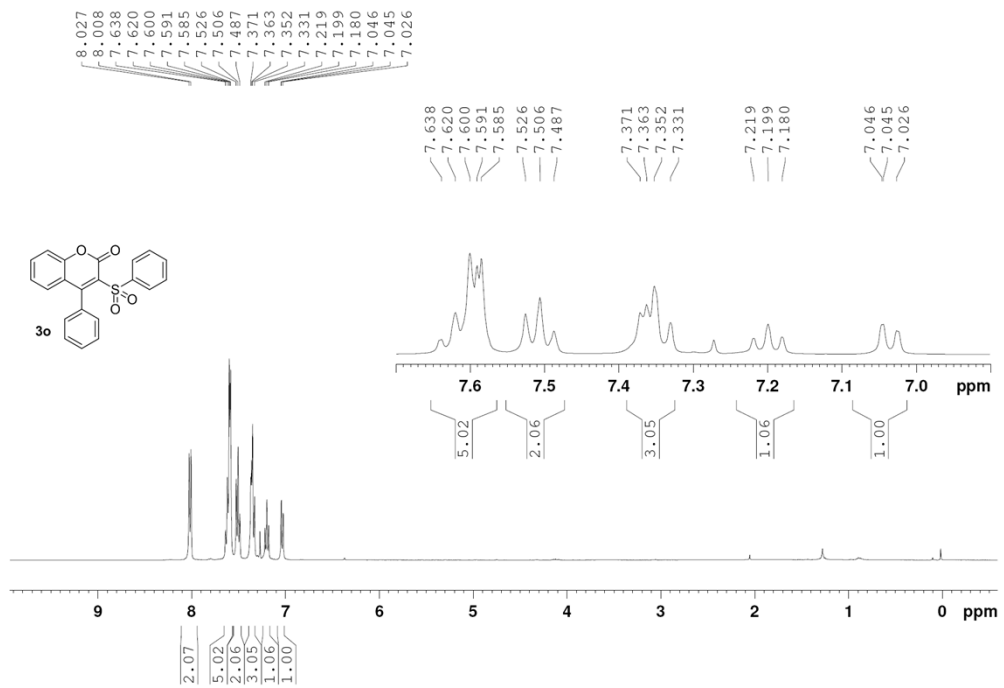
132.633
129.270
129.162
129.149
129.131
129.073
129.012
128.024
127.963
127.565
127.410
127.370
126.195
125.893
125.657
124.194
119.923
119.805
116.428
77.328
77.010
76.692
21.562
20.811
15.280
14.105
Me
Me
Me
3m
3m'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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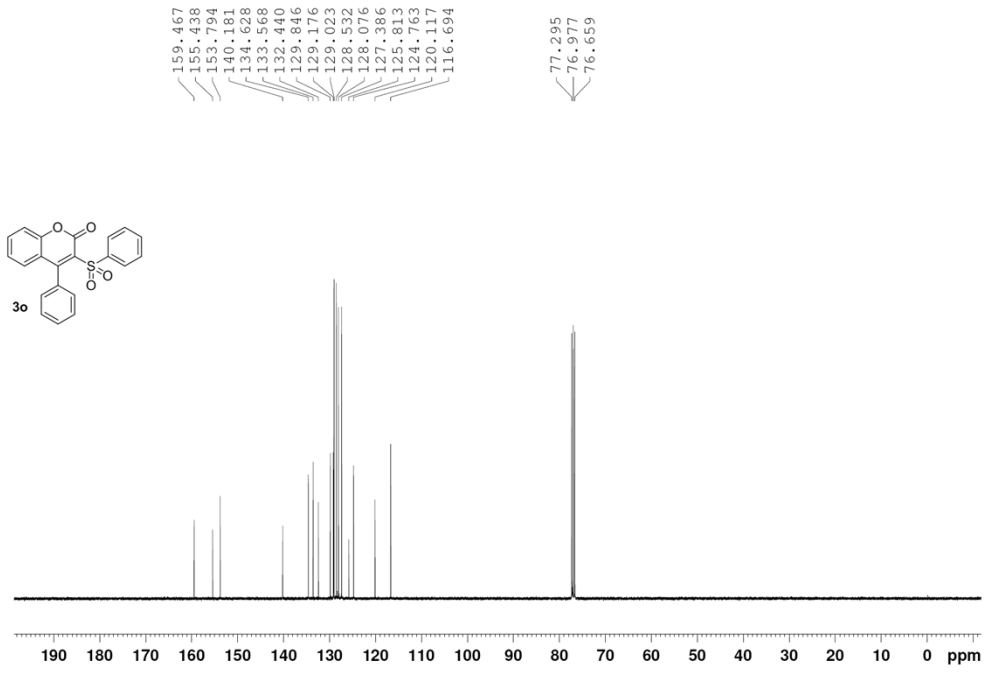
8.008
7.638
7.620
7.600
7.591
7.585
7.526
7.506
7.487
7.371
7.363
7.352
7.331
7.219
7.199
7.180
7.046
7.045
7.026
3o
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
5.02
2.06
3.05
1.06
1.00
9
8
7
6
5
4
3
2
1
0
ppm
2.07
5.02
2.06
3.05
1.06
1.00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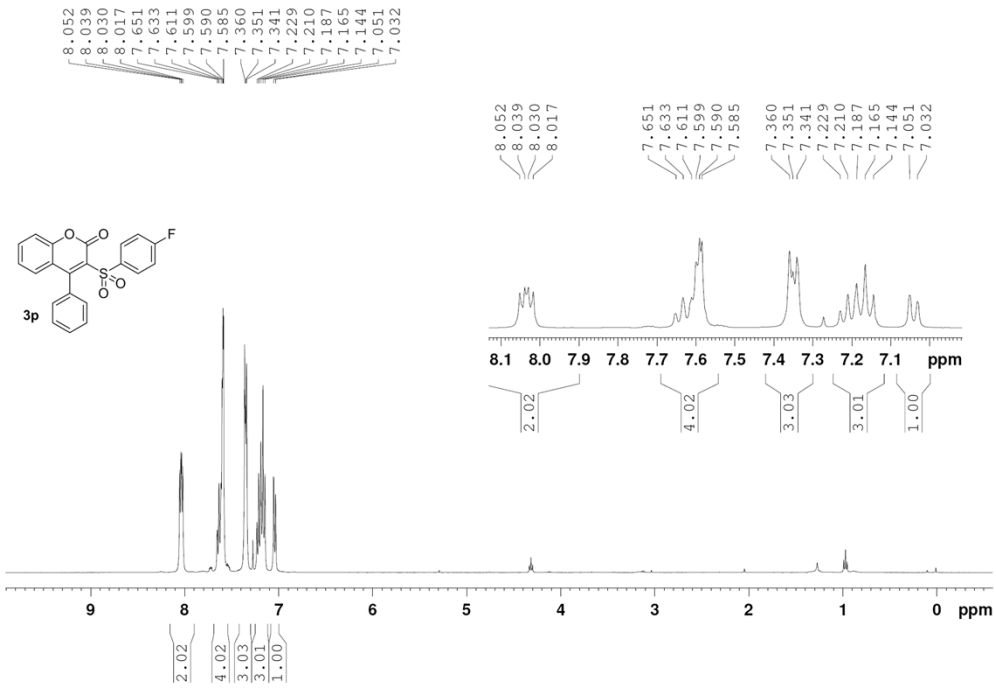
153.794
140.181
134.628
133.568
132.440
129.846
129.176
129.023
128.532
128.076
127.386
125.813
124.763
120.117
116.694
77.295
76.977
76.659
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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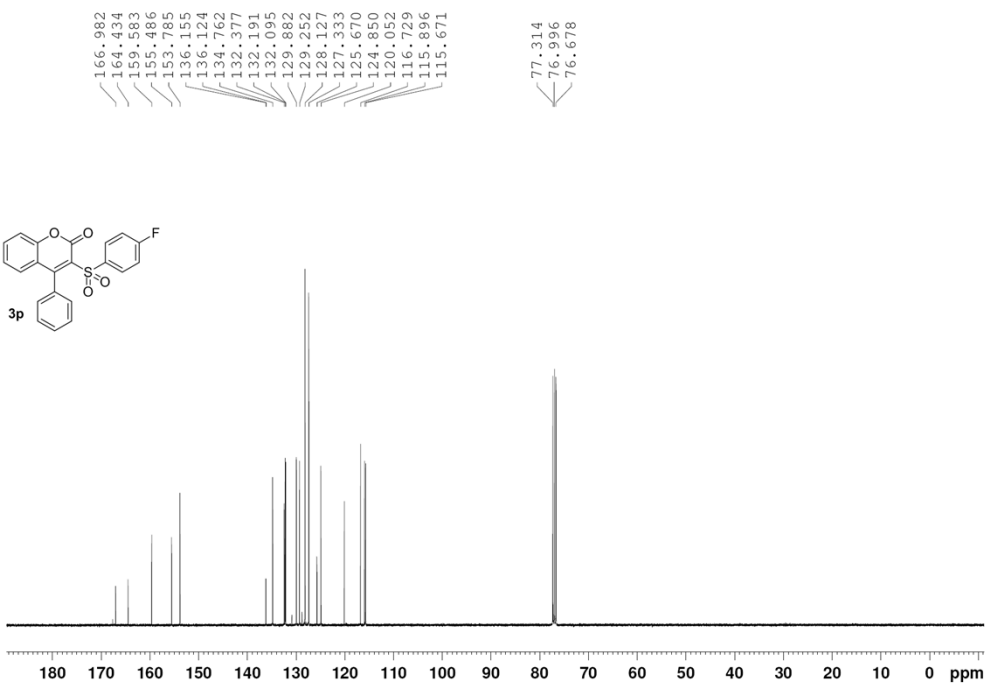
8.039
8.030
8.017
7.651
7.633
7.611
7.599
7.590
7.585
7.360
7.351
7.341
7.229
7.210
7.187
7.165
7.144
7.051
7.032
3p
F
O
S
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
2.02
4.02
3.03
3.01
1.00
9 8 7 6 5 4 3 2 1 0 ppm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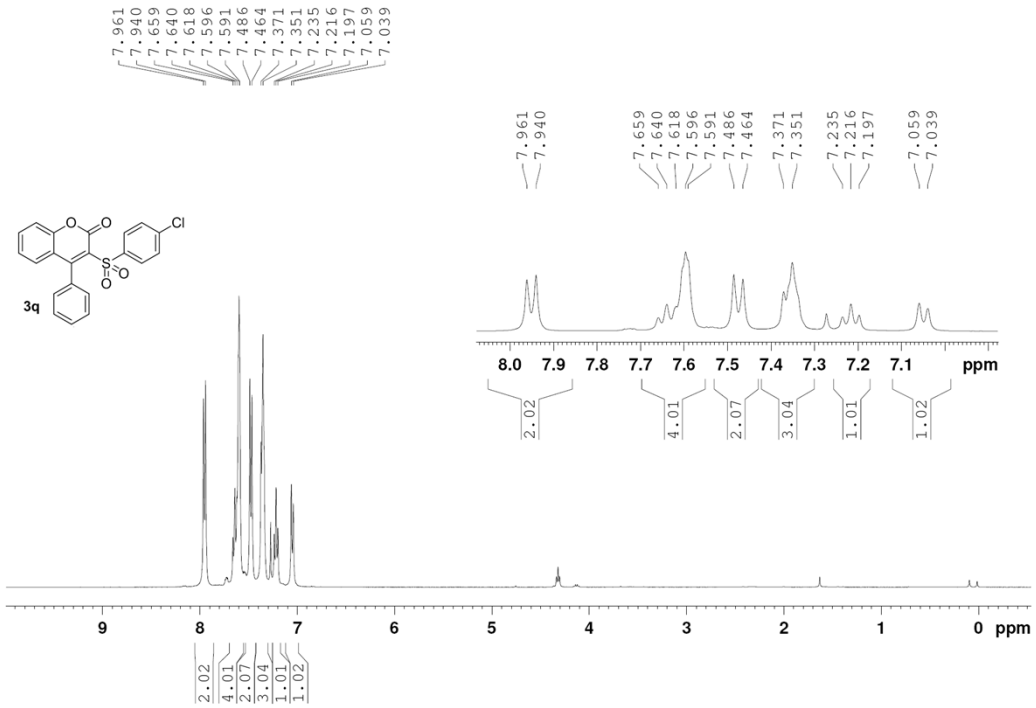
136.155
136.124
134.762
132.377
132.191
132.095
129.882
129.252
128.127
127.333
125.670
124.850
120.052
116.729
115.896
115.671
77.314
76.996
76.678
3p
F
O
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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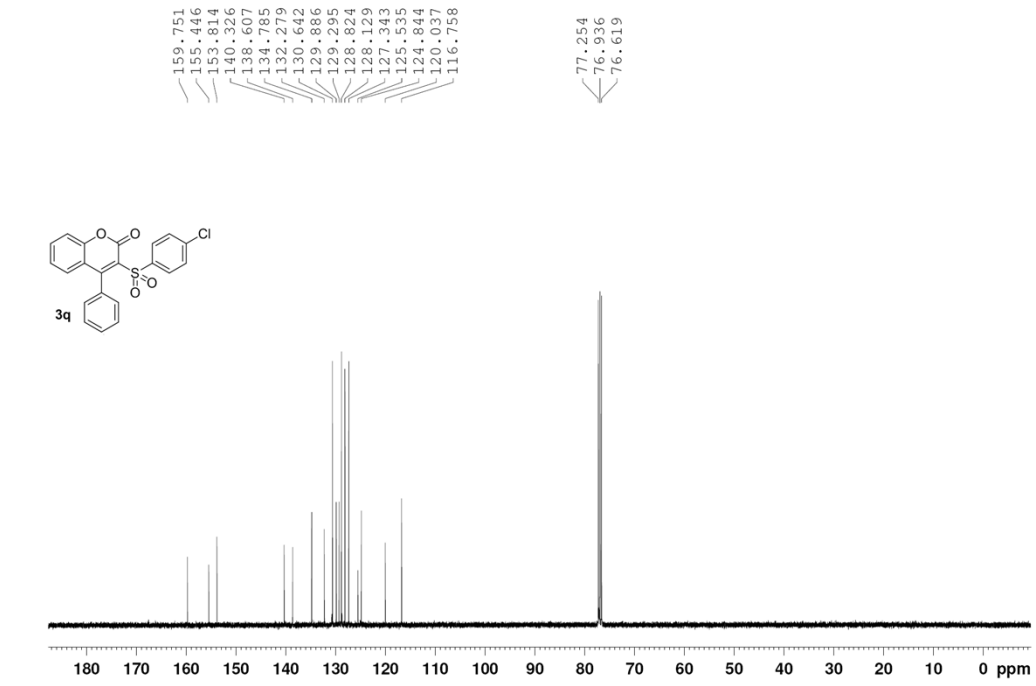
7.659
7.640
7.618
7.596
7.591
7.486
7.464
7.371
7.351
7.235
7.216
7.197
7.059
7.039
3q
Cl
O
S
O
O
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
2.02
4.01
2.07
3.04
1.01
1.02
9 8 7 6 5 4 3 2 1 0 ppm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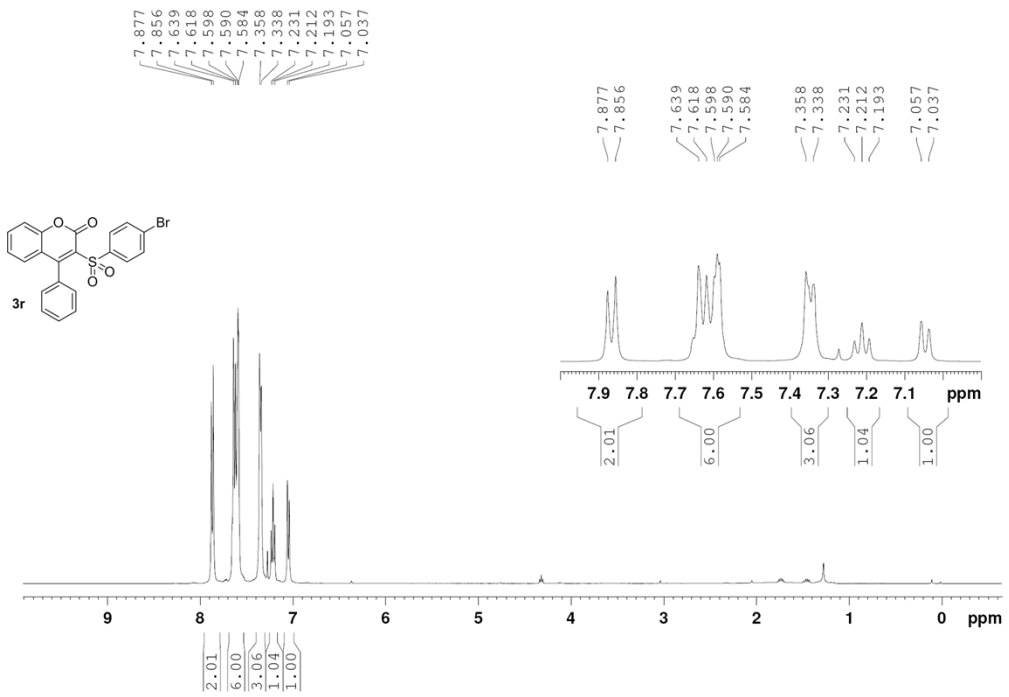
140.326
138.607
134.785
132.279
130.642
129.886
129.295
128.824
128.129
127.343
125.535
124.844
120.037
116.758
77.254
76.936
76.619
3q
Cl
O
S
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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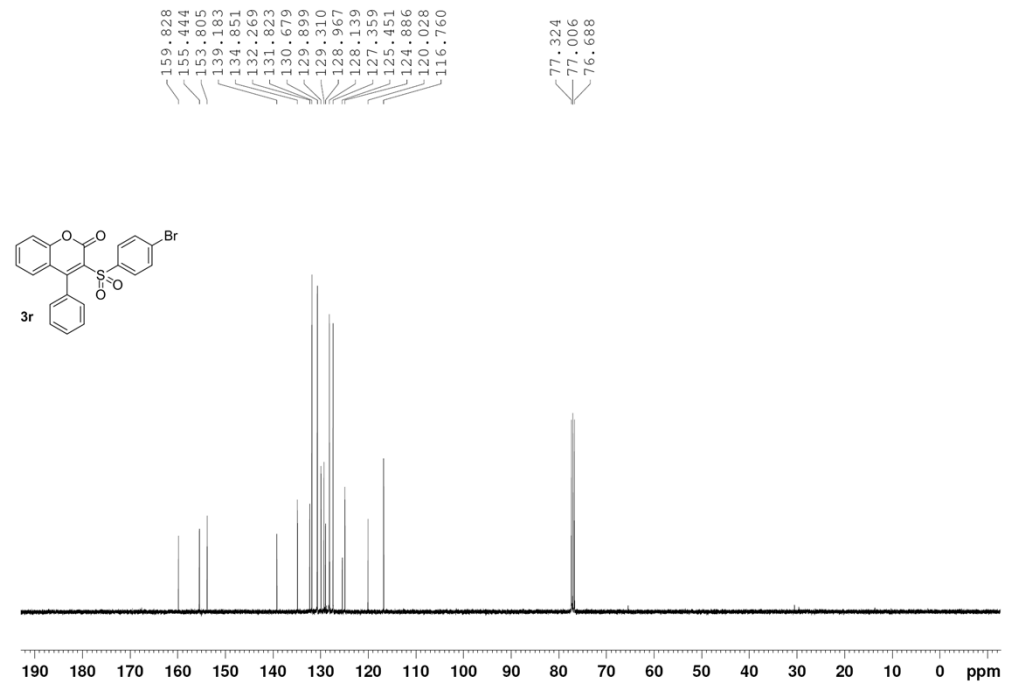
7.618
7.598
7.590
7.584
7.358
7.338
7.231
7.212
7.193
7.057
7.037
3r
Br
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
2.01
6.00
3.06
1.04
1.00
9 8 7 6 5 4 3 2 1 0 ppm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130.679
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129.310
128.967
128.139
127.359
125.451
124.886
120.028
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77.324
77.006
76.688
3r
Br
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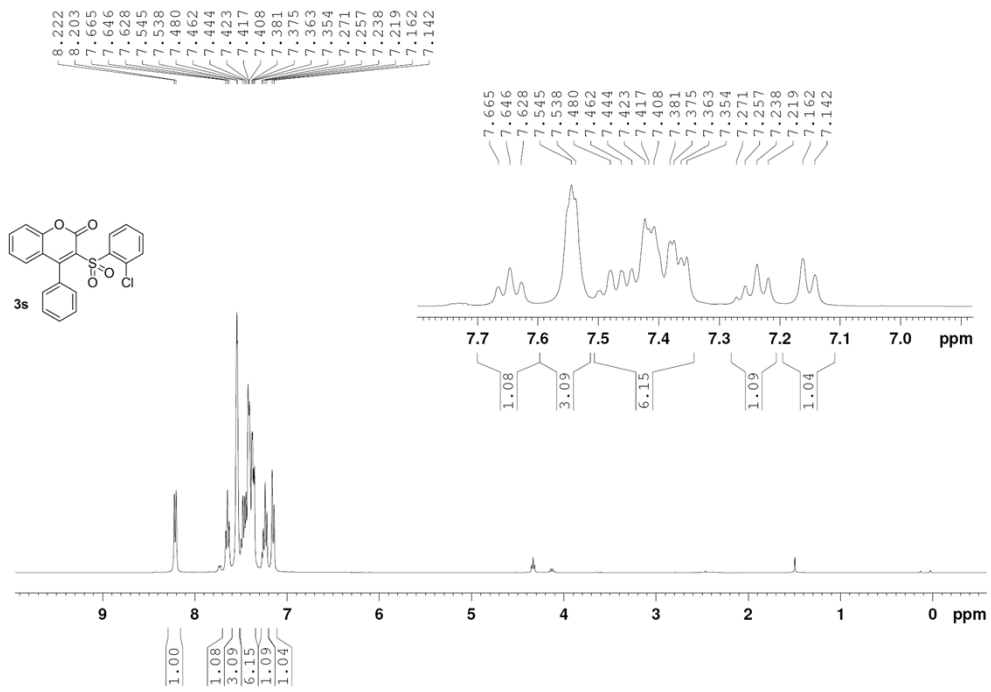
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7.665
7.646
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7.538
7.480
7.462
7.444
7.423
7.417
7.408
7.381
7.375
7.363
7.354
7.271
7.257
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7.142
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Cl
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3.09
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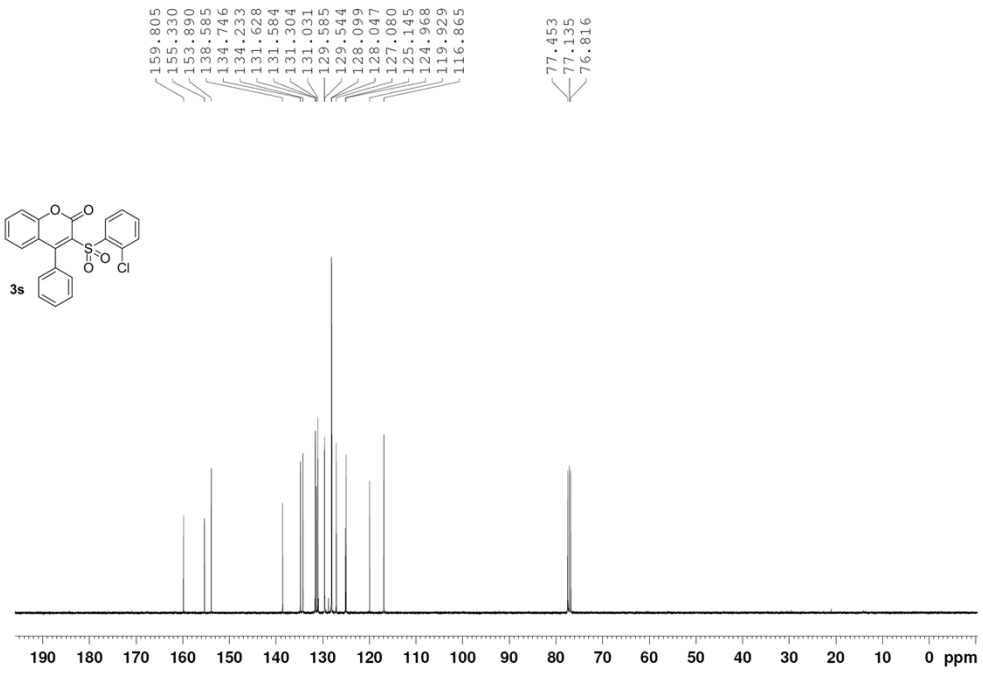
1.09
1.04
ppm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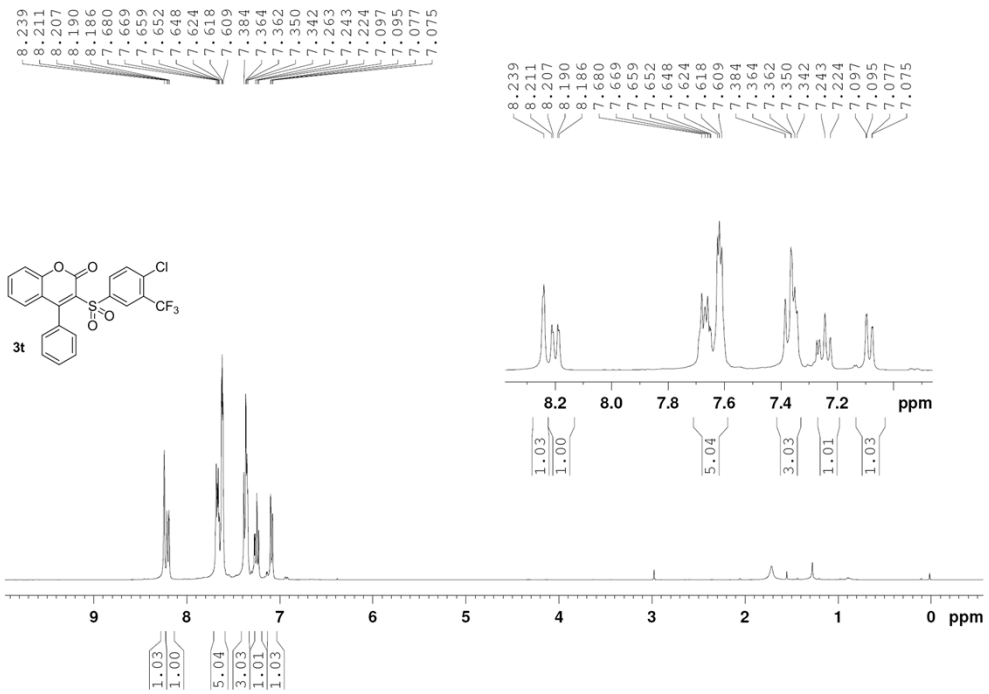
Cl
ppm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7.609
7.384
7.364
7.362
7.350
7.342
7.263
7.243
7.224
7.097
7.095
7.077
7.075
3t
8.2
8.0
7.8
7.6
7.4
7.2
ppm
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3.03
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1.03
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7
6
5
4
3
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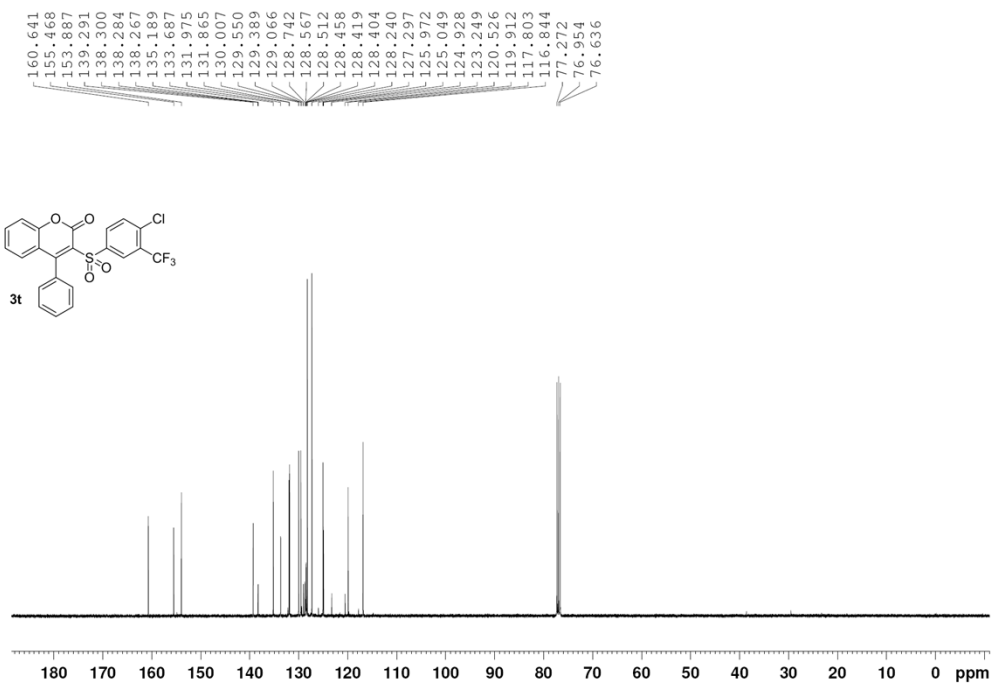
0
ppm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135.189
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129.389
129.066
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128.567
128.512
128.458
128.419
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128.240
127.297
125.972
125.049
124.928
123.249
120.526
119.912
117.803
116.844
77.272
76.954
76.636
3t
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140
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120
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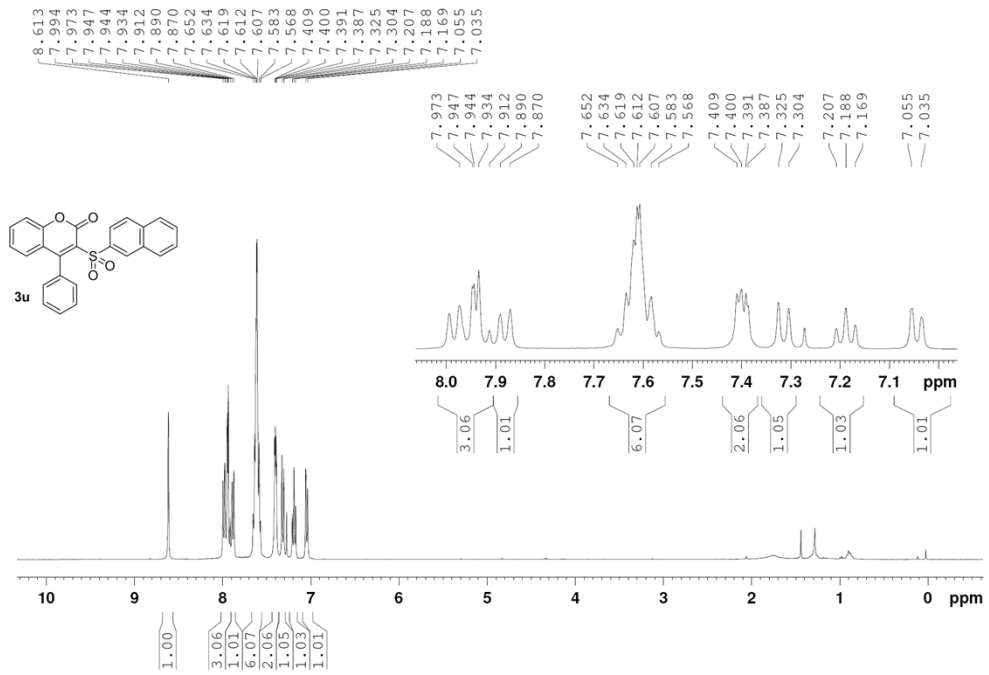
ppm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7.634
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7.612
7.607
7.583
7.568
7.409
7.400
7.391
7.387
7.325
7.304
7.207
7.188
7.169
7.055
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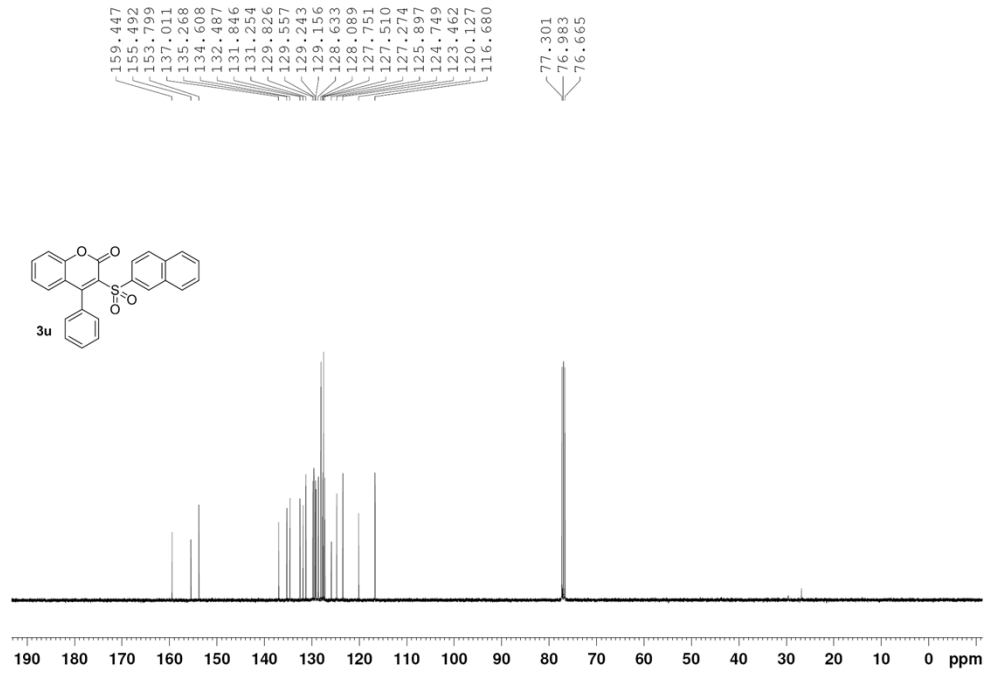
3.06
1.01
6.07
2.06
1.05
1.03
1.01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128.633
128.089
127.751
127.510
127.274
125.897
124.749
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116.680
77.301
76.983
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3u
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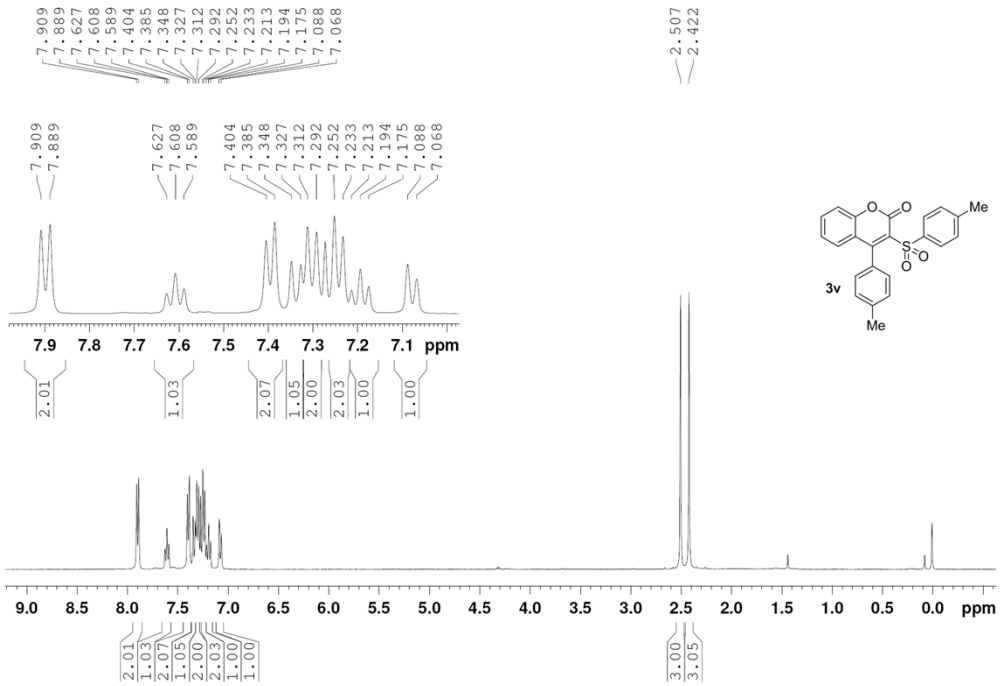
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7.292
7.252
7.233
7.213
7.194
7.175
7.088
7.068
2.507
2.422
3v
Me
Me
ppm
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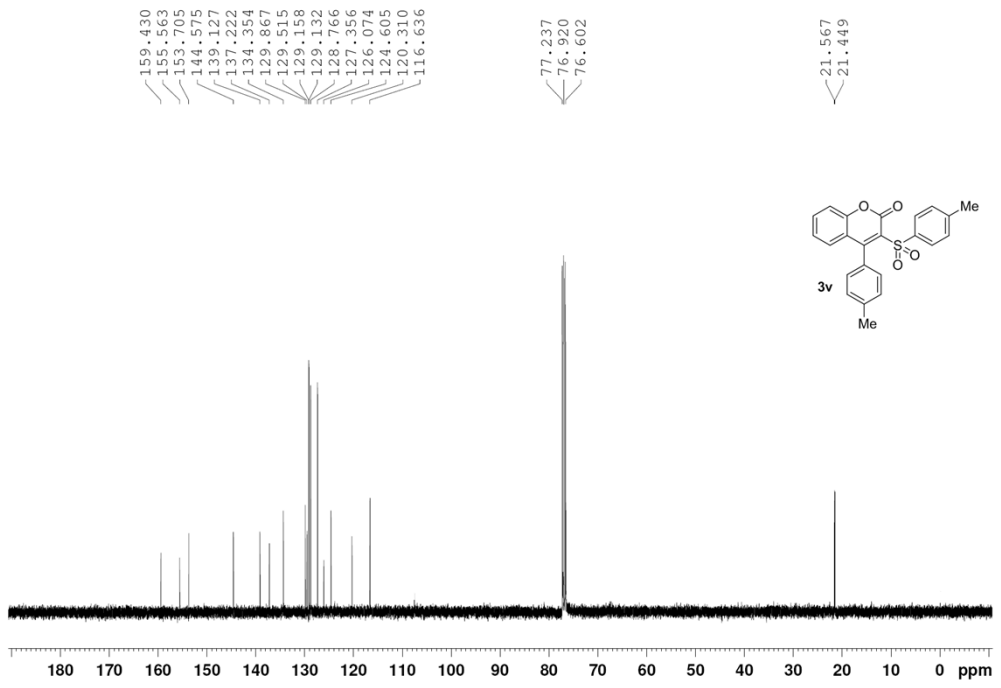
1.03
2.07
1.05
2.00
2.03
1.00
1.00
3.00
3.05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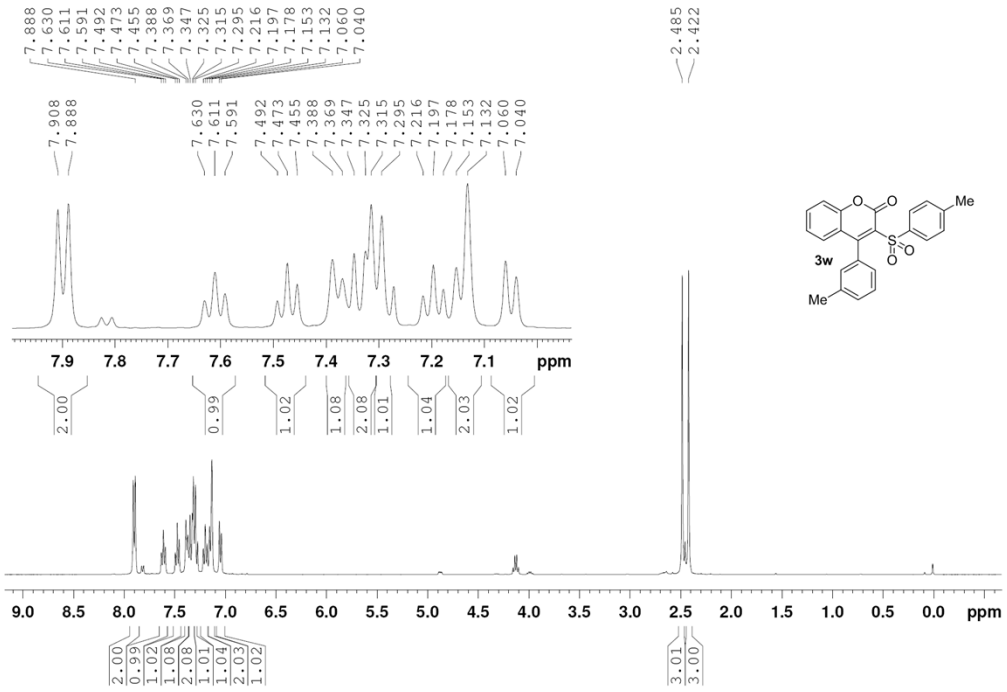
3v
Me
Me
ppm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7.295
7.216
7.197
7.178
7.153
7.132
7.060
7.040
2.485
2.422
3w
Me
Me
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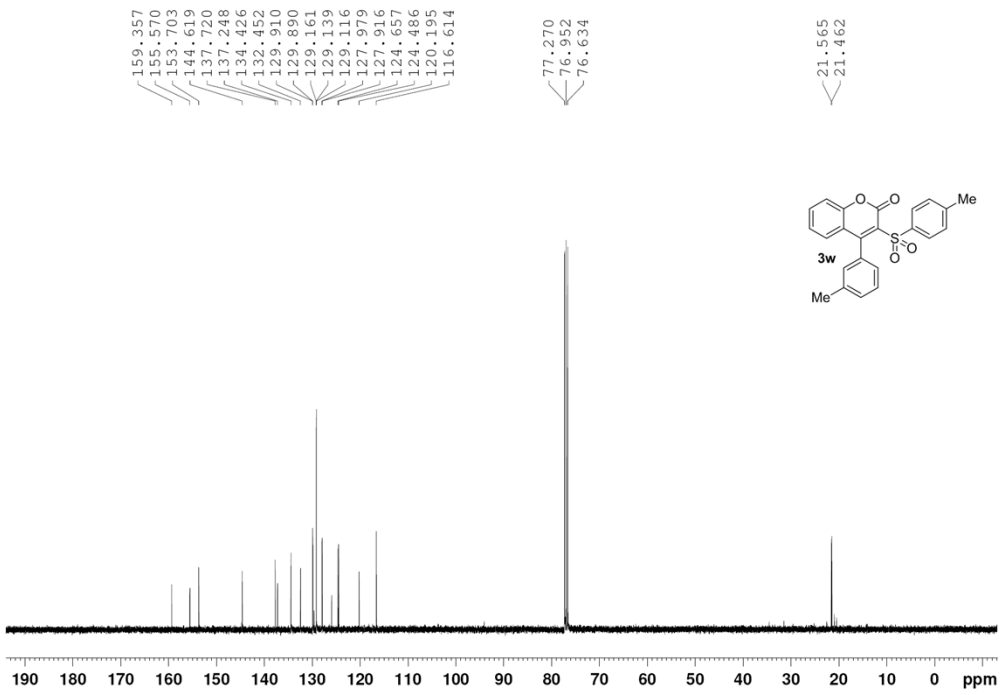
2.08
1.01
1.04
2.03
1.02
3.01
3.00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124.486
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76.952
76.634
21.565
21.462
3w
Me
Me
ppm