Supporting Information

Rh(III)-Catalyzed Cascade Reactions of Sulfoxonium Ylides with α-Diazocarbonyl Compounds: An Access to Highly Functionalized Naphthalenones

Xi Chen, Muhua Wang, Xinying Zhang* and Xuesen Fan*

Henan Key Laboratory of Organic Functional Molecules and Drug Innovation, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China

E-mail: xinyingzhang@htu.cn; xuesen.fan@htu.cn

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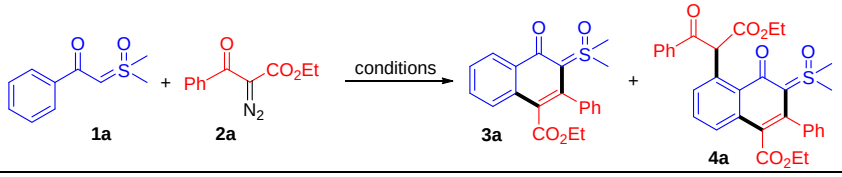
I. General experimental information

Commercial reagents were used without further purification. Benzoyl sulfoxonium ylides (**1**),[1] α-diazo carbonyl compounds (**2**),[2,3] and $[RhCp^*Cl_2]_2$[4] were prepared according to literature procedures, respectively. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Optimization Studies for the Formation of 3a or 4a

Table 1. Optimization Studies for the Formation of **3a** or **4a**[a]



Entry	Ratio of **1a**:**2a**	Catalyst	Solvent	T (°C)	Yield (%)[b]	
					3a	**4a**
1	1:1	$[RhCp^*Cl_2]_2$	DCE	80	17%	23%
2	1:1	$[RhCp^*Cl_2]_2$	dioxane	80	15%	8%
3	1:1	$[RhCp^*Cl_2]_2$	THF	80	11%	14%
4	1:1	$[RhCp^*Cl_2]_2$	CH_3CN	80	15%	10%
5	1:1	$[RhCp^*Cl_2]_2$	TFE	80	43%	trace
6	1:1	$[RhCp^*Cl_2]_2$	HFIP	80	42%	trace
7	1:1	$[RhCp^*Cl_2]_2$	toluene	80	trace	29%
8	1:1	$[RhCp^*Cl_2]_2$	PhCl	80	trace	28%
9	1:2	$[RhCp^*Cl_2]_2$	toluene	80	trace	48%
10	**1:2.2**	**$[RhCp^*Cl_2]_2$**	**toluene**	**80**	**trace**	**58%**
11	1:2.5	$[RhCp^*Cl_2]_2$	toluene	80	trace	50%
12	1.2:1	$[RhCp^*Cl_2]_2$	TFE	80	45%	trace
13	1.5:1	$[RhCp^*Cl_2]_2$	TFE	80	46%	trace
14	2.0:1	$[RhCp^*Cl_2]_2$	TFE	80	41%	trace
15	1:2.2	$[RhCp^*Cl_2]_2$	toluene	100	trace	53%
16	1:2.2	$[RhCp^*Cl_2]_2$	toluene	60	trace	43%
17	**1.2:1**	**$[RhCp^*Cl_2]_2$**	**TFE**	**100**	**51%**	**trace**
18	1.2:1	$[RhCp^*Cl_2]_2$	TFE	120	50%	trace
19[c]	1:2.2	$[RhCp^*Cl_2]_2$	TFE	80	ND	ND
20[c]	1.2:1	$[RhCp^*Cl_2]_2$	TFE	100	ND	ND
21	1:2.2	$[RhCp^*(MeCN)_3](SbF_6)_2$	toluene	80	trace	40
22	1:2.2	$[RhCp^*(OAc)_2]_2$	toluene	80	trace	32
23	1:2.2	$[Ru(cymene)_2Cl_2]_2$	toluene	80	ND	ND
24	1:2.2	$[Ir(cod)Cl_2]_2$	toluene	80	ND	ND
25	1.2:1	$[RhCp^*(MeCN)_3](SbF_6)_2$	TFE	100	36	trace
26	1.2:1	$[RhCp^*(OAc)_2]_2$	TFE	100	32	trace
27	1.2:1	$[Ru(cymene)_2Cl_2]_2$	TFE	100	ND	ND
28	1.2:1	$[Ir(cod)Cl_2]_2$	TFE	100	ND	ND

[a]Reaction conditions: **1a** (0.5 mmol for entries 1-11, 15-16, 19-22), **2a** (0.5 mmol for entries 12-14, 17-18, 23-26), catalyst (0.02 mmol, 4 mol%), $AgSbF_6$ (0.08 mmol, 16 mol%), solvent (3 mL), N_2, 24 h. [b]Isolated yield. ND: not detected. [c]In the absence of $AgSbF_6$.

III. Experimental procedures and spectroscopic data

1. General synthetic procedure and spectroscopic data of product 3

To a reaction tube equipped with a stir bar were charged with benzoyl sulfoxonium ylide (**1**, 0.6 mmol), α-diazo carbonyl compound (**2**, 0.5 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol) and TFE (3 mL). The resulting mixture was then stirred at 100 °C under N_2 for 24 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using ethyl acetate/methanol (20:1) as eluent to afford product **3**.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3a)

Eluent: ethyl acetate/methanol (20:1). White solid (94 mg, 51%), mp: 157-158°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, J = 7.2 Hz, 3H), 3.70 (s, 6H), 3.84 (q, J = 7.2Hz, 2H), 7.24-7.28 (m, 5H), 7.38 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.63 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 43.8, 60.9, 97.1, 118.0, 124.7, 124.9, 125.5, 127.2, 127.6, 129.3, 130.2, 131.1, 134.1, 137.0, 137.5, 168.8, 172.9. HRMS calcd for $C_{21}H_{21}O_4S$: 369.1155 $[M+H]^+$, found: 369.1165.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-7-methyl-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3b)

Eluent: ethyl acetate/methanol (20:1). White solid (103 mg, 54%), mp: 227-228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.79 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 3.66 (s, 6H), 3.83 (q, J = 7.2 Hz, 2H), 7.20 (d, J = 8.4 Hz, 1H), 7.23-7.27 (m, 5H), 7.38 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 22.0, 43.8, 60.8, 96.4, 117.7, 124.3, 124.7, 127.2, 127.3, 127.5, 128.3, 129.3, 134.3, 137.1, 137.5, 141.5, 168.9, 172.8. HRMS calcd for $C_{22}H_{23}O_4S$: 383.1312 $[M+H]^+$, found: 383.1306.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-7-methoxy-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3c)

Eluent: ethyl acetate/methanol (20:1). White solid (107 mg, 54%), mp: 186-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 3.68 (s, 6H), 3.79-3.84 (m, 5H), 6.97-7.02 (m, 2H), 7.23-7.28 (m, 5H), 8.23 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 44.0, 55.4, 60.8, 96.1, 105.3, 115.6, 117.4, 124.7, 126.8, 127.2, 127.5, 129.2, 136.0, 137.2, 138.7, 162.0, 168.9, 172.5. HRMS calcd for $C_{22}H_{23}O_5S$: 399.1261 $[M+H]^+$, found: 399.1263.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-6-methyl-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3d)

Eluent: ethyl acetate/methanol (20:1). White solid (111 mg, 58%), mp: 218-219°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.79 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 3.65 (s, 6H), 3.82 (q, *J* = 7.2 Hz, 2H), 7.23-7.26 (m, 5H), 7.35 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 8.10 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 21.4, 43.7, 60.8, 96.9, 117.9, 124.2, 124.9, 127.2, 127.5, 129.3, 130.2, 131.9, 132.7, 135.4, 136.5, 137.2, 168.9, 172.7. HRMS calcd for $C_{22}H_{23}O_4S$: 383.1312 $[M+H]^+$, found: 383.1311.

Ethyl 6-chloro-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3e)

Eluent: ethyl acetate. White solid (28 mg, 14%), mp: 83-84°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 6H), 3.90 (q, *J* = 7.2 Hz, 2H), 7.30-7.37 (m, 5H), 7.53 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 8.36 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 43.7, 61.0, 98.1, 117.5, 124.3, 126.7, 127.3, 127.7, 129.2, 131.2, 131.4, 131.7, 132.5, 136.7, 138.0, 168.5, 171.7. HRMS calcd for $C_{21}H_{20}ClO_4S$: 403.0765 $[M+H]^+$, found: 403.0752.

Ethyl 8-chloro-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3e')

Eluent: ethyl acetate/methanol (20:1). White solid (62 mg, 31%), mp: 118-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.90 (t, J = 7.2 Hz, 3H), 3.66 (s, 6H), 3.77 (q, J = 7.2 Hz, 2H), 7.23-7.29 (m, 6H), 7.59 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 8.31 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 43.4, 61.1, 97.9, 115.9, 124.3, 125.5, 126.9, 127.8, 129.8, 129.9, 131.5, 132.9, 133.3, 135.5, 139.0, 169.0, 171.8. HRMS calcd for $C_{21}H_{20}ClO_4S$: 403.0765 $[M+H]^+$, found: 403.0758.

Ethyl 6-bromo-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3f)

Eluent: ethyl acetate/methanol (20:1). White solid (49 mg, 22%), mp: 109-110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, J = 7.2 Hz, 3H), 3.77 (s, 6H), 3.89 (q, J = 7.2 Hz, 2H), 7.30-7.36 (m, 5H), 7.59 (d, J = 8.8 Hz, 1H), 7.66 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 8.53 (d, J = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 43.6, 61.0, 97.9, 117.4, 119.7, 126.8, 127.3, 127.5, 127.7, 129.2, 131.6, 132.8, 134.0, 136.7, 138.2, 168.4, 171.7. HRMS calcd for $C_{21}H_{20}BrO_4S$: 447.0260 $[M+H]^+$, found: 447.0250.

Ethyl 8-bromo-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3f')

Eluent: ethyl acetate/methanol (20:1). White solid (58 mg, 26%), mp: 275-276 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (t, J = 7.2 Hz, 3H), 3.73 (s, 6H), 3.84 (q, J = 7.2 Hz, 2H), 7.25-7.28 (m, 1H), 7.31-7.35 (m, 5H), 7.90 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 8.44 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.5, 43.4, 61.2, 97.9, 117.0, 119.2, 124.9, 125.9, 126.9, 127.7, 129.8, 132.9, 133.3, 135.6, 137.4, 139.4, 168.6, 171.8. HRMS calcd for $C_{21}H_{20}BrO_4S$: 447.0260 $[M+H]^+$, found: 447.0257.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-6-methoxy-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3g)

Eluent: ethyl acetate/methanol (20:1). White solid (103 mg, 52%), mp: 190-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, *J* = 7.2 Hz, 3H), 3.75 (s, 6H), 3.85-3.89 (m, 5H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.32 (s, 5H), 7.39 (t, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.9, 43.5, 56.5, 60.4, 97.7, 111.9, 115.3, 117.3, 125.4, 125.9, 126.9, 127.5, 130.0, 132.0, 135.9, 136.2, 155.0, 169.6, 171.9. HRMS calcd for $C_{22}H_{23}O_5S$: 399.1261 $[M+H]^+$, found: 399.1263.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-methyl-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3h)

Eluent: ethyl acetate/methanol (20:1). White solid (105 mg, 55%), mp: 166-167°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, *J* = 7.2 Hz, 3H), 2.89 (s, 3H), 3.69 (s, 6H), 3.83 (q, *J* = 7.2 Hz, 2H), 7.08 (d, *J*= 6.8 Hz, 1H), 7.23-7.28 (m, 5H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 24.4, 44.4, 60.9, 98.7, 119.0, 123.1, 127.2, 127.5, 128.7, 128.8, 129.3, 130.3, 135.9, 136.7 137.2, 139.4, 169.2, 175.5. HRMS calcd for $C_{22}H_{23}O_4S$: 383.1312 $[M+H]^+$, found: 383.1312.

Ethyl 5-chloro-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3i)

Eluent: ethyl acetate/methanol (20:1). White solid (107 mg, 53%), mp: 164-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 3.71 (s, 6H), 3.82 (q, *J* = 7.2 Hz, 2H), 7.21-7.28 (m, 5H), 7.32-7.34 (m, 2H), 7.48-7.50 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 44.3, 61.0, 99.6, 117.9, 124.2, 126.1, 127.3, 127.7, 128.7, 129.1, 130.4, 133.1, 136.2, 137.2, 138.6, 168.8, 173.2. HRMS calcd for $C_{21}H_{20}ClO_4S$: 403.0765 $[M+H]^+$, found: 403.0760.

Ethyl 5-bromo-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3j)

Eluent: ethyl acetate/methanol (20:1). White solid (112 mg, 50%), mp: 81-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.87 (t, *J* = 7.6 Hz, 3H), 3.77 (s, 6H), 3.89 (q, *J* = 7.2 Hz, 2H), 7.28-7.35 (m, 6H), 7.61 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.66 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 44.2, 61.0, 99.1, 117.8, 120.3, 124.9, 126.7, 127.3, 127.7, 129.1, 130.7, 132.6, 136.3, 137.1, 138.5, 168.8, 173.0. HRMS calcd for $C_{21}H_{20}BrO_4S$: 447.0260 $[M+H]^+$, found: 447.0234.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-(*p*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (3k)

Eluent: ethyl acetate/methanol (20:1). White solid (96 mg, 50%), mp: 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.84 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 3.68 (s, 6H), 3.86 (q, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.34-7.38 (m, 1H), 7.49-7.53 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 21.4, 43.7, 60.8, 97.1, 118.1, 124.7, 124.8, 125.4, 128.0, 129.1, 130.2, 131.1, 134.0, 134.1, 137.3, 137.6, 168.9, 172.9. HRMS calcd for $C_{22}H_{23}O_4S$: 383.1312 $[M+H]^+$, found: 383.1312.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-2-(4-methoxyphenyl)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (3l)

Eluent: ethyl acetate/methanol (20:1). White solid (115 mg, 58%), mp: 206-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.87 (t, *J* = 7.2 Hz, 3H), 3.67 (s, 6H), 3.74 (s, 3H), 3.88 (q, *J* = 7.2 Hz, 2H), 6.78-6.81 (m, 2H), 7.14-7.18 (m, 2H), 7.34-7.38 (m, 1H), 7.49-7.53 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 8.30 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 43.7, 55.2, 60.8, 97.3, 112.7, 118.3, 124.8, 125.4, 129.1, 130.2, 130.4, 131.1, 134.1, 137.2, 159.1, 169.0, 172.9. HRMS calcd for $C_{22}H_{22}NaO_5S$: 421.1080 $[M+Na]^+$, found: 421.1065.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalene-1-carboxylate (3m)

Eluent: ethyl acetate/methanol (20:1). White solid (83 mg, 38%), mp: 235-236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, J = 7.2 Hz, 3H), 3.81 (s, 6H), 3.92 (q, J = 7.2 Hz, 2H), 7.45-7.51 (m, 3H), 7.60-7.65 (m, 3H), 7.70-7.72 (m, 1H), 8.39 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.5, 43.7, 61.0, 96.5, 118.1, 124.1 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270.2 Hz), 124.8, 125.0, 125.9, 129.7, 129.8 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 130.3, 131.3, 134.0, 135.9, 140.9, 168.4, 172.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.44. HRMS calcd for $C_{22}H_{20}F_3O_4S$: 437.1029 $[M+H]^+$, found: 437.1023.

Ethyl 2-(4-bromophenyl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (3n)

Eluent: ethyl acetate/methanol (20:1). White solid (89 mg, 40%), mp: 177-178 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.87 (t, J = 7.2 Hz, 3H), 3.70 (s, 6H), 3.89 (q, J = 7.2 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.38-7.40 (m, 3H), 7.53 (t, J = 8.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 43.7, 61.0, 96.7, 118.1, 121.7, 124.8, 124.9, 125.7, 130.3, 130.4, 131.0, 131.2, 134.0, 136.0, 136.1, 168.6, 172.9. HRMS calcd for $C_{21}H_{20}BrO_4S$: 447.0260 $[M+H]^+$, found: 447.0255.

Ethyl 2-(3-chlorophenyl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (3o)

Eluent: ethyl acetate/methanol (20:1). White solid (91 mg, 45%), mp: 216-217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.87 (t, J = 7.2 Hz, 3H), 3.68 (s, 3H), 3.69 (s, 3H), 3.86-3.92 (m, 2H), 7.12-7.14 (m, 1H), 7.17-7.21 (m, 1H), 7.23-7.26 (m, 2H), 7.37-7.41 (m, 1H), 7.51-7.55 (m, 1H), 7.62 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 43.6, 43.7, 61.0, 96.5, 118.0, 124.8, 125.0,

125.8, 127.60, 127.62, 128.4, 129.5, 130.4, 131.2, 133.1, 134.0, 135.9, 138.8, 168.5, 172.9. HRMS calcd for $C_{21}H_{20}ClO_4S$: 403.0765 $[M+H]^+$, found: 403.0765.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-(*m*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (3p)

Eluent: ethyl acetate/methanol (20:1). White solid (97 mg, 51%), mp: 77-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.82 (t, J = 7.2 Hz, 3H), 2.29 (s, 3H), 3.69 (s, 6H), 3.85 (q, J = 7.2 Hz, 2H), 7.04-7.08 (m, 3H), 7.13-7.17 (m, 1H), 7.35-7.39 (m, 1H), 7.50-7.54 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 8.30 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 21.5, 43.7, 43.8, 60.8, 97.0, 117.9, 124.7, 124.8, 125.4, 126.5, 127.1, 128.3, 129.9, 130.2, 131.0, 134.1, 136.7, 136.9, 137.7, 168.9, 172.9. HRMS calcd for $C_{22}H_{23}O_4S$: 383.1312 $[M+H]^+$, found: 383.1313.

Ethyl 2-(3-bromophenyl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (3q)

Eluent: ethyl acetate/methanol (20:1). White solid (98 mg, 44%), mp: 192-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J = 7.2 Hz, 3H), 3.69 (s, 3H), 3.70 (s, 3H), 3.87-3.92 (m, 2H), 7.11-7.15 (m, 1H), 7.17-7.18 (m, 1H), 7.37-7.42 (m, 3H), 7.52-7.56 (m, 1H), 7.63 (d, J = 7.6 Hz, 1H), 8.31 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 43.6, 43.7, 61.0, 96.6, 118.1, 121.2, 124.8, 125.0, 125.8, 128.0, 128.7, 130.3, 130.5, 131.2, 132.3, 134.0, 135.7, 139.0, 168.4, 172.8. HRMS calcd for $C_{21}H_{20}BrO_4S$: 447.0260 $[M+H]^+$, found: 447.0255.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-2-methyl-4-oxo-3,4-dihydronaphthalene-1-carboxylate (3r)

Eluent: ethyl acetate/methanol (20:1). White solid (60 mg, 39%), mp: 167-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (t, J = 7.2 Hz, 3H), 2.42 (s, 3H), 3.78 (s, 6H), 4.38 (q, J = 7.2 Hz, 2H), 7.27-7.31 (m, 1H), 7.41-7.49 (m, 2H), 8.20 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 17.2, 43.9, 61.3, 97.3, 117.4,

124.2, 124.6, 124.9, 129.5, 130.8, 133.4, 134.5, 170.1, 173.0. HRMS calcd for $C_{16}H_{19}O_4S$: 307.0999 $[M+H]^+$, found: 307.0995.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-propyl-3,4-dihydronaphthalene-1-carboxylate (3s)

Eluent: ethyl acetate/methanol (20:1). White solid (77 mg, 46%), mp: 186-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.53-1.63 (m, 2H), 2.74-2.78 (m, 2H), 3.77 (s, 6H), 4.37 (q, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.39-7.48 (m, 2H), 8.20 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 14.5, 26.5, 32.1, 44.0, 61.2, 96.3, 117.2, 124.3, 124.5, 124.8, 129.6, 130.7, 134.6, 138.3, 170.1, 173.2. HRMS calcd for $C_{18}H_{23}O_4S$: 335.1312 $[M+H]^+$, found: 335.1316.

Methyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3t)

Eluent: ethyl acetate/methanol (20:1). White solid (85 mg, 48%), mp: 127-128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.34 (s, 3H), 3.70 (s, 6H), 7.23-7.28 (m, 5H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 43.7, 51.7, 97.4, 118.0, 124.7, 124.9, 125.6, 127.3, 127.6, 129.1, 130.1, 131.2, 134.1, 136.9, 137.7, 169.3, 172.7. HRMS calcd for $C_{20}H_{19}O_4S$: 355.0999 $[M+H]^+$, found: 355.1000.

***Tert*-butyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-2-methyl-4-oxo-3,4-dihydronaphthalene-1-carboxylate (3u)**

Eluent: ethyl acetate/methanol (20:1). White solid (75 mg, 45%), mp: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.66 (s, 9H), 2.51 (s, 3H), 3.84 (s, 6H), 7.34-7.38 (m, 1H), 7.52-7.57 (m, 2H), 8.28 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 16.9, 28.3, 43.9, 81.9, 97.1, 119.0, 124.0, 124.6, 124.7, 129.5, 130.7, 132.4, 134.6, 169.4, 172.8. HRMS calcd for $C_{18}H_{23}O_4S$: 335.1312 $[M+H]^+$, found: 335.1321.

4-Acetyl-2-(dimethyl(oxo)-λ^6-sulfanylidene)-3-methylnaphthalen-1(2H)-one (3v)

Eluent: ethyl acetate/methanol (20:1). White solid (76 mg, 55%), mp: 154-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 2.49 (s, 3H), 3.80 (s, 6H), 7.25-7.31 (m, 2H), 7.43-7.47 (m, 1H), 8.23 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.8, 33.7, 43.9, 97.0, 123.8, 124.8, 124.9, 125.3, 129.7, 130.4, 130.7, 133.9, 172.8, 208.2. HRMS calcd for $C_{15}H_{17}O_3S$: 277.0893 $[M+H]^+$, found: 277.0885.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfaneylidene)-7-fluoro-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (3w)

Eluent: ethyl acetate/methanol (20:1). White solid (85 mg, 44%), mp: 259-260 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.86 (t, *J* = 7.2 Hz, 3H), 3.76 (s, 6H), 3.89 (q, *J* = 7.2 Hz, 2H), 7.14-7.17 (m, 1H), 7.31-7.39 (m, 6H), 8.37-8.40 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 43.8, 60.9, 97.0, 109.7 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 114.3 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 117.1 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 127.1, 127.3, 127.7, 127.8 (d, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 129.1, 136.2 (d, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 136.8, 139.5, 164.6 (d, $^{1}J_{C\text{-}F}$ = 247.2 Hz), 168.4, 172.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -108.26. HRMS calcd for $C_{21}H_{20}FO_4S$: 387.1061 $[M+H]^+$, found: 387.1064.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-oxo-2-phenyl-7-(trifluoromethyl)-3,4-dihydronaphthalene-1-carboxylate (3x)

Eluent: ethyl acetate/methanol (20:1). White solid (78 mg, 36%), mp: 201-202 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.88 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 6H), 3.93 (q, *J* = 7.2 Hz, 2H), 7.31-7.37 (m, 5H), 7.63 (d, *J* = 8.4 Hz, 1H), 8.02 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 43.6, 61.1, 98.9, 117.5, 121.1 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 122.5 (q, $^{3}J_{C\text{-}F}$ = 4.4 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 271.2 Hz), 126.0, 127.4, 127.8, 129.1, 132.0, 132.5 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 133.8, 136.5, 139.5, 168.2, 172.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.63. HRMS calcd for $C_{22}H_{20}F_3O_4S$: 437.1029 $[M+H]^+$, found: 437.1048.

2. General synthetic procedure and spectroscopic data of product 4 and 5

To a reaction tube equipped with a stir bar were charged with benzoyl sulfoxonium ylide (**1**, 0.5 mmol), α-diazo carbonyl compound (**2**, 1.1 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol) and toluene (3 mL). The resulting mixture was then stirred at 80 °C under N_2 for 24 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to afford product **4** or **5**.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (4a)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (162 mg, 58%), mp: 89-90 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 3.56 (s, 3H), 3.58 (s, 3H), 3.81 (q, *J* = 7.2 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.24-7.32 (m, 7H), 7.36-7.42 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 14.3, 43.9, 44.1, 58.6, 61.0, 61.3, 99.3, 118.5, 125.3, 126.9, 127.3, 127.7, 128.5, 129.07, 129.15, 129.3, 130.3, 132.9, 133.8, 136.1, 136.5, 136.6, 137.6, 169.1, 170.4, 175.1, 195.5. HRMS calcd for $C_{32}H_{31}O_7S$: 559.1785 $[M+H]^+$, found: 559.1782.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl)-7-methoxy-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (4b)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (153 mg, 52%), mp: 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 3.57 (s, 3H), 3.59 (s, 3H), 3.71 (s, 3H), 3.80 (q, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 7.23-7.33 (m, 7H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.83 (s, 1H), 7.93-7.95 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 12.6, 13.2, 43.3,

43.4, 54.2, 57.4, 59.8, 60.2, 97.1, 104.6, 117.0, 120.5, 126.2, 126.6, 127.5, 128.0, 128.1, 128.2, 131.8, 134.8, 135.66, 135.73, 137.0, 137.5, 159.4, 168.1, 169.1, 173.7, 194.1. HRMS calcd for $C_{33}H_{33}O_8S$: 589.1891 $[M+H]^+$, found: 589.1882.

Ethyl 7-chloro-3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (4c)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (142 mg, 48%), mp: 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.79 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 3.56 (s, 3H), 3.60 (s, 3H), 3.81 (q, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 7.22-7.28 (m, 5H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.79 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.6, 14.2, 44.08, 44.10, 58.2, 61.1, 61.5, 99.9, 117.6, 124.5, 125.3, 127.4, 127.7, 127.8, 128.6, 129.0, 129.2, 133.0, 135.9, 136.2, 136.5, 136.7, 137.1, 139.1, 168.5, 169.9, 174.6, 194.6. HRMS calcd for $C_{32}H_{29}ClNaO_7S$: 615.1215 $[M+Na]^+$, found: 615.1188.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl)-6-methoxy-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (4d)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (185 mg, 63%), mp: 191-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 3.59 (s, 6H), 3.69-3.78 (m, 5H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.25-7.32 (m, 7H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.81 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.9, 14.3, 43.8, 44.0, 56.5, 58.2, 60.4, 61.1, 100.0, 111.2, 115.3, 125.9, 126.9, 127.4, 127.6, 128.2, 128.3, 128.5, 129.2, 129.8, 130.0, 132.8, 135.5, 136.5, 137.0, 154.7, 170.8, 174.5, 195.9. HRMS calcd for $C_{33}H_{33}O_8S$: 589.1891 $[M+H]^+$, found: 589.1874.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-(*p*-tolyl)propan-2-yl)-4-oxo-2-(*p*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (4e)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (176 mg, 60%), mp: 204-205 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.84 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 2.30 (s, 3H), 3.61 (s, 6H), 3.85 (q, *J* = 7.2 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.06-7.14 (m, 7H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.82-7.84 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 14.3, 21.4, 21.7, 44.0, 44.2, 58.5, 60.9, 61.2, 99.3, 118.7, 125.2, 126.8, 127.7, 128.03, 128.05, 129.0, 129.1, 129.22, 129.25, 130.2, 133.5, 133.9, 134.1, 136.1, 137.4, 137.6, 143.7, 169.2, 170.5, 175.3, 195.3. HRMS calcd for $C_{34}H_{35}O_7S$: 587.2098 $[M+H]^+$, found: 587.2085.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)-2-(4-methoxyphenyl)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4f)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (219 mg, 71%), mp: 227-228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 3.67 (s, 3H), 3.69 (s, 3H), 3.820 (s, 3H), 3.824 (s, 3H), 3.94 (q, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.82-6.89 (m, 4H), 7.15 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 7.21-7.26 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.58 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.89 (s, 1H), 7.95-7.99 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 14.3, 44.0, 44.3, 55.2, 55.4, 58.3, 60.9, 61.1, 99.5, 112.8, 113.7, 118.9, 125.1, 126.8, 127.7, 128.7, 129.5, 130.2, 130.3, 130.4, 131.5, 134.1, 136.0, 137.2, 159.2, 163.3, 169.2, 170.6, 175.4, 194.4. HRMS calcd for $C_{34}H_{34}NaO_9S$: 641.1816 $[M+Na]^+$, found: 641.1829.

Ethyl 2-(4-chlorophenyl)-5-(1-(4-chlorophenyl)-3-ethoxy-1,3-dioxopropan-2-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4g)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (163 mg, 52%), mp: 121-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, *J* = 7.6 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 3.61 (s, 3H), 3.66 (s, 3H), 3.94 (q, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 7.14 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 7.21-7.25 (m, 2H), 7.30-7.37 (m, 4H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.61 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.84 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 14.2, 43.9, 44.0, 58.4, 61.1, 61.4, 99.1, 118.8, 125.5, 126.9, 127.5, 127.7, 128.9, 130.4, 130.5, 130.6, 133.6, 133.7, 134.9, 135.2, 136.0, 136.3, 139.2, 168.8, 170.1, 174.9, 193.9. HRMS calcd for $C_{32}H_{29}Cl_2O_7S$: 627.1006 $[M+H]^+$, found:627.1014.

Ethyl 2-(4-bromophenyl)-5-(1-(4-bromophenyl)-3-ethoxy-1,3-dioxopropan-2-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4h)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (182 mg, 51%), mp: 154-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 3.56 (s, 3H), 3.61 (s, 3H), 3.87 (q, J = 7.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 7.06-7.13 (m, 3H), 7.38-7.47 (m, 5H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.75 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 14.2, 44.0, 44.1, 58.4, 61.1, 61.4, 98.9, 118.8, 121.8, 125.5, 126.9, 127.7, 128.0, 130.4, 130.45, 130.50, 130.8, 130.9, 131.8, 133.5, 135.4, 135.6, 136.0, 136.2, 168.7, 170.1, 174.9, 194.0. HRMS calcd for $C_{32}H_{29}Br_2O_7S$: 714.9995 $[M+H]^+$, found: 714.9991.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-3-(furan-2-yl)-1,3-dioxopropan-2-yl)-2-(furan-2-yl)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4i)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (161 mg, 60%), mp: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 3.71 (s, 3H), 3.73 (s, 3H), 4.12 (q, J = 7.2 Hz, 2H), 4.22-4.28 (m, 2H), 6.42-6.47 (m, 3H), 7.21 (d, J = 3.2 Hz, 1H), 7.25-7.27 (m, 1H), 7.48-7.52 (m, 3H), 7.64 (s, 1H), 7.72 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 14.2, 43.26, 43.29, 58.2, 61.3, 97.9, 109.8, 111.0, 112.2, 117.9, 119.5, 125.7, 126.1, 128.0, 128.2, 130.2, 133.3, 135.6, 142.4, 146.4, 148.2, 152.6, 168.9, 169.8, 175.0, 183.6. HRMS calcd for $C_{28}H_{26}NaO_9S$: 561.1190 $[M+H]^+$, found: 561.1189.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)-2-(4-methoxyphenyl)-7-methyl-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4j)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (158 mg, 50%), mp: 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.67 (s, 3H), 3.69 (s, 3H), 3.82 (s, 6H), 3.94 (q, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.83-6.89 (m, 4H), 6.98 (d, *J* = 1.2 Hz, 1H), 7.21-7.25 (m, 2H), 7.34 (s, 1H), 7.92 (s, 1H), 7.98 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 14.3, 21.9, 44.1, 44.4, 55.2, 55.4, 58.0, 60.9, 61.1, 98.9, 112.8, 113.7, 118.7, 124.7, 128.8, 129.4, 129.6, 130.3, 130.5, 131.5, 133.9, 136.2, 137.1, 140.5, 159.1, 163.3, 169.4, 170.6, 175.3, 194.5. HRMS calcd for $C_{35}H_{37}O_9S$: 633.2153 $[M+Na]^+$, found: 633.2159.

Ethyl 2-(4-bromophenyl)-5-(1-(4-bromophenyl)-3-ethoxy-1,3-dioxopropan-2-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-7-methyl-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4k)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (178 mg, 49%), mp: 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 3.62 (s, 3H), 3.66 (s, 3H), 3.94 (q, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 1.2 Hz, 1H), 7.14-7.19 (m, 2H), 7.37 (s, 1H), 7.44-7.48 (m, 2H), 7.51-7.55 (m, 2H), 7.85 (s, 1H), 7.87-7.90 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 14.2, 21.9, 44.0, 44.1, 58.2, 61.1, 61.4, 98.3, 118.5, 121.8, 124.8, 125.1, 127.9, 129.5, 130.4, 130.5, 130.8, 131.0, 131.8, 133.3, 135.5, 135.7, 136.2, 140.7, 168.9, 170.2, 174.8, 194.1. HRMS calcd for $C_{33}H_{31}Br_2O_7S$: 729.0152 $[M+H]^+$, found: 729.0164.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-(*m*-tolyl)propan-2-yl)-7-methyl-4-oxo-2-(*m*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (4l)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (156 mg, 52%), mp: 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.34-2.36 (m, 9H), 3.67 (s, 6H), 3.91 (q, *J* = 7.2 Hz, 2H), 4.25 (qd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 2H), 6.98 (s, 1H), 7.09-7.15 (m, 3H), 7.20-7.27 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.87 (s, 1H), 7.96 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR

(150 MHz, $CDCl_3$) δ: 13.6, 14.2, 21.4, 21.5, 21.9, 44.13, 44.15, 44.26, 44.29, 58.2, 60.8, 61.2, 98.7, 118.3, 124.8, 126.4, 126.50, 126.54, 127.1, 128.30, 128.34, 129.3, 129.5, 129.8, 130.0, 133.6, 133.7, 136.3, 136.6, 136.7, 137.7, 138.2, 140.4, 169.2, 170.6, 175.1, 195.79, 195.82. HRMS calcd for $C_{35}H_{37}O_7S$: 601.2255 $[M+H]^+$, found: 601.2263.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-3-(furan-2-yl)-1,3-dioxopropan-2-yl)-2-(furan-2-yl)-7-methyl-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4m)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (146 mg, 53%), mp: 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 3.71 (s, 3H), 3.73 (s, 3H), 4.12 (q, J = 7.2 Hz, 2H), 4.25 (qd, J_1 = 7.2 Hz, J_1 = 2.8 Hz, 2H), 6.41-6.47 (m, 3H), 7.09 (d, J = 0.8 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.47-7.53 (m, 3H), 7.68 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.1, 14.2, 21.9, 43.35, 43.40, 57.9, 61.3, 97.3, 109.7, 111.0, 112.2, 118.0, 119.3, 125.3, 126.09, 126.13, 129.8, 133.1, 135.8, 140.4, 142.3, 146.4, 148.4, 152.5, 169.1, 169.8, 174.9, 183.7. HRMS calcd for $C_{29}H_{28}NaO_9S$: 575.1346 $[M+Na]^+$, found: 575.1364.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-1,3-dioxo-3-(*p*-tolyl)propan-2-yl)-7-methoxy-4-oxo-2-(*p*-tolyl)-3,4-dihydronaphthalene-1-carboxylate (4n)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (166 mg, 54%), mp: 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.90 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 2.36 (s, 3H), 2.37 (s, 3H), 3.66 (s, 6H), 3.76 (s, 3H), 3.90 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 7.2 Hz, 2H), 6.77 (d, J = 2.4 Hz, 1H), 6.97 (d, J = 2.4 Hz, 1H), 7.14-7.22 (m, 6H), 7.89-7.91 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 14.3, 21.3, 21.6, 44.3, 44.5, 55.2, 58.3, 60.8, 61.2, 98.2, 105.6, 117.9, 118.0, 121.5, 128.00, 128.02, 129.0, 129.1, 129.21, 129.23, 133.8, 134.1, 136.0, 137.3, 138.0, 138.6, 143.6, 160.4, 169.3, 170.3, 174.9, 195.0. HRMS calcd for $C_{35}H_{36}NaO_8S$: 639.2023 $[M+Na]^+$, found: 639.2039.

Ethyl 2-(4-bromophenyl)-5-(1-(4-bromophenyl)-3-ethoxy-1,3-dioxopropan-2-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-7-methoxy-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4o)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (190 mg, 51%), mp: 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 3.60 (s, 3H), 3.65 (s, 3H), 3.79 (s, 3H), 3.92 (q, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 7.14-7.19 (m, 2H), 7.44-7.47 (m, 2H), 7.53 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 2H), 7.81 (s, 1H), 7.88 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 14.2, 44.2, 44.3, 55.3, 58.3, 61.0, 61.5, 97.8, 105.6, 118.1, 118.2, 121.5, 121.8, 128.0, 130.4, 130.5, 130.8, 130.9, 131.8, 135.6, 135.7, 137.3, 138.0, 160.5, 168.9, 169.9, 174.5, 193.7. HRMS calcd for $C_{33}H_{31}Br_2O_8S$: 745.0101 $[M+H]^+$, found: 745.0094.

Ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-ethoxy-3-(furan-2-yl)-1,3-dioxopropan-2-yl)-2-(furan-2-yl)-7-methoxy-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4p)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (133 mg, 47%), mp: 75-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 3.71 (s, 3H), 3.73 (s, 3H), 3.83 (s, 3H), 4.07-4.12 (m, 2H), 4.20-4.28 (m, 2H), 6.40-6.41 (m, 1H), 6.44-6.47 (m, 2H), 6.90 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.51-7.52 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.1, 14.2, 43.46, 43.48, 55.3, 58.1, 61.2, 61.3, 96.8, 106.0, 109.7, 111.0, 112.2, 118.0, 118.2, 118.7, 122.8, 127.2, 135.4, 137.6, 142.3, 146.4, 148.5, 152.5, 160.3, 169.1, 169.6, 174.6, 183.3. HRMS calcd for $C_{29}H_{28}NaO_{10}S$: 591.1295 $[M+Na]^+$, found: 591.1289.

Methyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-5-(1-methoxy-1,3-dioxo-3-phenylpropan-2-yl)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (4q)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (146 mg, 55%), mp: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.40 (s, 3H), 3.68 (s, 6H), 3.77 (s, 3H), 7.14 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 7.30-7.40 (m,

7H), 7.43-7.50 (m, 2H), 7.58 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.95 (s, 1H), 7.99-8.01 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 44.0, 44.1, 51.8, 52.4, 58.4, 99.4, 118.4, 125.4, 126.8, 127.3, 127.66, 127.74, 128.5, 129.0, 129.1, 130.3, 133.0, 133.7, 136.1, 136.49, 136.52, 137.9, 169.5, 170.9, 175.1, 195.5. HRMS calcd for $C_{30}H_{27}O_7S$: 531.1472 $[M+H]^+$, found: 531.1450.

Methyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-7-methoxy-5-(1-methoxy-1,3-dioxo-3-phenylpropan-2-yl)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (4r)

Eluent: petroleum ether/ethyl acetate (1:1). Yellow solid (140 mg, 50%), mp: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.36 (s, 3H), 3.66 (s, 3H), 3.67 (s, 3H), 3.77 (s, 3H), 3.78 (s, 3H), 6.77 (d, J = 2.4 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 7.27-7.40 (m, 7H), 7.50 (t, J = 7.2 Hz, 1H), 7.95 (s, 1H), 7.99-8.01 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 44.2, 44.4, 51.7, 52.5, 55.3, 58.3, 98.3, 105.7, 117.8, 118.1, 121.4, 127.3, 127.6, 128.5, 128.9, 129.0, 129.1, 133.0, 135.7, 136.5, 136.8, 138.1, 138.9, 160.5, 169.7, 170.7, 174.8, 195.2. HRMS calcd for $C_{31}H_{29}O_8S$: 561.1578 $[M+H]^+$, found: 561.1578.

Methyl 2-(4-bromophenyl)-5-(1-(4-bromophenyl)-3-methoxy-1,3-dioxopropan-2-yl)-3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4s)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (154 mg, 45%), mp: 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.46 (s, 3H), 3.66 (s, 3H), 3.69 (s, 3H), 3.77 (s, 3H), 7.12-7.18 (m, 3H), 7.46-7.59 (m, 6H), 7.86-7.88 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 44.0, 44.1, 51.9, 52.6, 58.3, 99.1, 118.6, 121.9, 125.6, 126.8, 127.8, 128.1, 130.4, 130.50, 130.53, 130.6, 130.7, 131.9, 133.4, 135.3, 135.4, 136.0, 136.5, 169.2, 170.6, 174.9, 194.0. HRMS calcd for $C_{30}H_{25}Br_2O_7S$: 686.9682 $[M+H]^+$, found: 686.9663.

Methyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-6-methoxy-5-(1-methoxy-3-(4-methoxyphenyl)-1,3-dioxo-propan-2-yl)-2-(4-methoxyphenyl)-4-oxo-3,4-dihydronaphthalene-1-carboxylate (4t)

Eluent: petroleum ether/ethyl acetate (1:1). Yellowish solid (233 mg, 75%), mp: 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.42 (s, 3H), 3.64 (s, 3H), 3.68 (s, 3H), 3.75 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 6.82-6.90 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.20-7.23 (m, 2H), 7.86 (s, 1H), 7.95 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 43.7, 44.1, 51.4, 52.3, 55.1, 55.4, 56.7, 57.9, 100.6, 111.2, 112.4, 113.7, 115.3, 126.1, 127.4, 127.7, 128.2, 128.3, 129.3, 130.8, 131.0, 131.6, 137.0, 154.5, 159.0, 163.3, 170.3, 171.4, 174.6, 194.9. HRMS calcd for $C_{33}H_{32}NaO_{10}S$: 643.1608 $[M+Na]^+$, found: 643.1586.

di-*tert*-Butyl 9-(dimethyl(oxo)-λ^6-sulfanylidene)-9a-hydroxy-2,8-dimethyl-9,9a-dihydrobenzo[*de*]chromene-3,7-dicarboxylate (5)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (98 mg, 40%), mp: 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.40 (s, 9H), 1.57 (s, 9H), 2.17 (s, 3H), 2.39 (s, 3H), 3.69 (s, 3H), 3.71 (s, 3H), 6.19 (s,1H), 7.05 (d, *J* = 6.0 Hz, 1H), 7.38-7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.5, 28.0, 28.2, 29.6, 44.36, 44.42, 63.6, 81.6, 82.0, 99.2, 119.9, 124.3, 126.2, 129.9, 132.5, 133.8, 136.3, 169.3, 169.5. HRMS calcd for $C_{26}H_{35}O_7S$: 491.2098 $[M+H]^+$, found: 491.2097.

3. Synthetic procedure and spectroscopic data of A

To a reaction tube equipped with a stir bar were charged with 2-(dimethyl(oxo)-λ6-sulfaneylidene)-1-phenylethan-1-one (98 mg, 0.5 mmol), 2-diazo-1-phenylethanone (219 mg, 1.5 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol) and TFE (3 mL). The resulting mixture was then stirred at 100 °C under N_2 for 24 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (50:1) as eluent to afford **A**.

1-Phenyl-2-(2,2,2-trifluoroethoxy)ethanone (A)

Eluent: petroleum ether/ethyl acetate (50:1). Yellow solid (111 mg, 34%), mp: 34-35 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.04 (d, J = 8.4 Hz, 2H), 4.94 (s, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 68.6 (q, $^{2}J_{C\text{-}F}$ = 3.9 Hz), 74.2, 123.9 (q, $^{1}J_{C\text{-}F}$ = 7.8 Hz), 127.7, 128.9, 134.0, 134.3, 194.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -74.20. HRMS calcd for $C_{10}H_9F_3NaO_2$: 241.0447 $[M+Na]^+$, found: 241.0464.

4. Synthetic procedure and spectroscopic data of B

To a reaction tube equipped with a stir bar were charged with 2-(dimethyl(oxo)-λ6-sulfaneylidene)-1-phenylethan-1-one (98 mg, 0.5 mmol), 2-diazo-1-phenylethanone (219 mg, 1.5 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol) and toluene (3 mL). The resulting mixture was then stirred at 80 °C under N_2 for 24 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (50:1) as eluent to afford product **B**.

1,4-Diphenylbut-2-ene-1,4-dione (B)

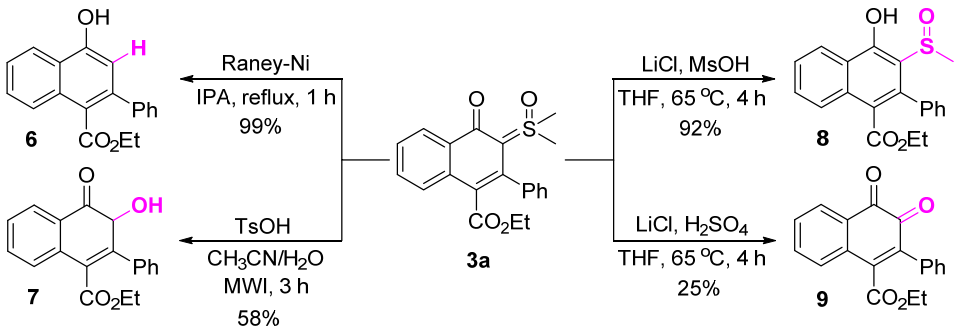
Eluent: petroleum ether/ethyl acetate (50:1). Yellow solid (24 mg, 20%), mp: 71-72 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.16 (s, 2H), 7.45 (t, J = 7.8 Hz, 4H), 7.50-7.55 (m, 4H), 7.57 (t, J = 7.2 Hz, 2H), 7.64 (t, J = 7.2 Hz, 2H), 7.93 (d, J = 7.2 Hz, 4H), 8.02 (s, 2H), 8.07 (d, J = 7.2 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 128.7, 128.8, 128.9, 129.0, 133.6, 133.9, 135.2, 135.6, 136.1, 136.9, 189.9, 192.5. HRMS calcd for $C_{16}H_{12}NaO_2$: 259.0730 $[M+Na]^+$, found: 259.0726.

5. Gram-scale preparation of 3a

To a reaction tube equipped with a stir bar were charged with 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (**1a**, 1.176 g, 6 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2a**, 1.091 g, 5 mmol),

$[Cp^*RhCl_2]_2$ (124 mg, 0.2 mmol), $AgSbF_6$ (275 mg, 0.8 mmol) and TFE (30 mL). The resulting mixture was then stirred at 100 °C under N_2 for 24 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (30 mL), and extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using ethyl acetate/methnaol (20:1) as eluent to afford ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (**3a**) in a yield of 42% (778 mg).

6. Synthetic applications of 3a



6.1. Procedure for the synthesis of 6

To a flask containing ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene -1-carboxylate (**3a**, 111 mg, 0.3 mmol) and isopropyl alcohol (7 mL) was added wet Raney nickel (341 μL of heterogeneous solution) with stirring. It was then stirred under reflux for 1 h. After being cooled to room termperature, the resulting mixture was filtered through a pad of Celite, and washed with 15 mL of isopropyl alcohol. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography using ethyl acetate as eluent to afford ethyl 4-hydroxy-2-phenyl-1-naphthoate (**6**) in a yield of 99% (87 mg).

Ethyl 4-hydroxy-2-phenyl-1-naphthoate (6)

Eluent: ethyl acetate. White solid (87 mg, 99%), mp: 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, J = 7.2 Hz, 3H), 4.04 (q, J = 7.2 Hz, 2H), 6.56 (s, 1H), 6.65 (d, J = 2.8 Hz, 1H), 7.25 (s, 5H), 7.35-7.46 (m, 2H),

7.94 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 61.4, 110.1, 122.1, 122.4, 123.4, 124.8, 125.5, 127.5, 128.1, 128.3, 128.4, 131.7, 139.9, 141.2, 153.2, 170.4. HRMS calcd for $C_{19}H_{17}O_3$: 293.1172 $[M+H]^+$, found: 293.1160.

6.2. Procedure for the synthesis of 7

To a reaction vessel equipped with a magnetic stirring bar were added ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (**3a**, 111 mg, 0.3 mmol), acetonitrile (1.5 mL), H_2O (1.5 mL) and *p*-toluenesulfonic acid (10 mg, 0.06 mmol) with stirring. The vessel was then sealed, put into the cavity of a microwave synthesis apparatus, and irradiated at 130 °C for 3 h. Upon completion, it was cooled to room temperature, quenched with saturated NH_4Cl, and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford ethyl 3-hydroxy-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (**7**) in a yield of 58% (54 mg).

Ethyl 3-hydroxy-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (7)

Eluent: petroleum ether/ethyl acetate (10:1). Orange solid (54 mg, 58%), mp: 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, J = 7.2 Hz, 3H), 3.93-4.10 (m, 2H), 4.54 (s, 1H), 6.59 (s, 1H), 7.32-7.33 (m, 3H), 7.40-7.45 (m, 3H), 7.54-7.55 (m, 2H), 8.07-8.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 63.9, 74.3, 125.7, 126.4, 128.1, 128.6, 129.0, 129.5, 129.6, 130.2, 133.3, 136.3, 142.0, 156.0, 172.7, 184.4. HRMS calcd for $C_{19}H_{17}O_4$: 309.1121 $[M+H]^+$, found: 309.1126.

6.3. Procedure for the synthesis of 8

To a flask containing ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (**3a**, 111 mg, 0.3 mmol) and THF (3 mL) were added LiCl (15 mg, 0.36 mmol) and

methanesulfonic acid (22 μL, 0.33 mmol) with stirring. The resulting mixture was stirred at 65 °C for 4 h. Upon completion, it was cooled to room temperature, quenched with saturated NH_4Cl, and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford ethyl 4-hydroxy-3-(methylsulfinyl)-2-phenyl-1-naphthoate (**8**) in a yield of 92% (98 mg).

Ethyl 4-hydroxy-3-(methylsulfinyl)-2-phenyl-1-naphthoate (8)

Eluent: petroleum ether/ethyl acetate (3:1). White solid (98 mg, 92%), mp: 144-145 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.80 (t, *J* = 7.2 Hz, 3H), 2.74 (s, 3H), 3.91-3.94 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.30-7.40 (m, 4H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 12.4 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 40.3, 61.2, 114.0, 122.7, 123.5, 125.0, 125.8, 126.4, 128.2, 128.4, 128.7, 129.5, 130.0, 130.1, 132.0, 134.9, 135.7, 159.9, 168.1. HRMS calcd for $C_{20}H_{19}O_4S$: 355.0999 $[M+H]^+$, found: 355.0990.

6.4. Procedure for the synthesis of 9

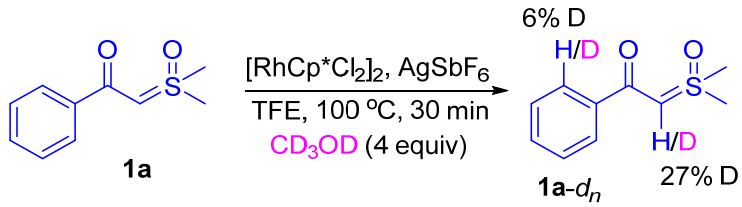
To a flask containing ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene -1-carboxylate (**3a**, 111 mg, 0.3 mmol) and THF (3 mL) were added LiCl (15 mg, 0.36 mmol) and sulfuric acid (46 μL, 0.33 mmol) with stirring. The resulting mixture was stirred at 65 °C for 4 h. Upon completion, it was cooled to room temperature, quenched with saturated NH_4Cl, and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (20:1) as eluent to afford ethyl 3,4-dioxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (**9**) in a yield of 25% (23 mg).

Ethyl 3,4-dioxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (9)

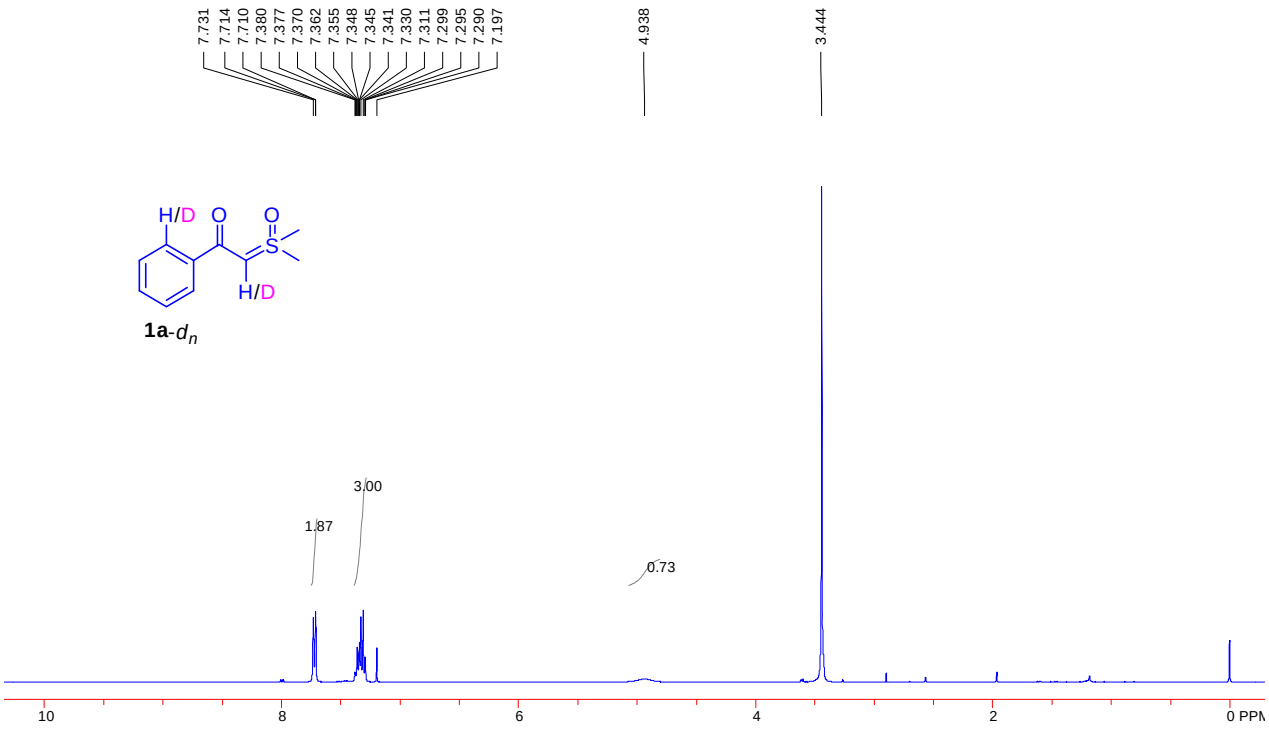
Eluent: petroleum ether/ethyl acetate (20:1). Orange solid (23 mg, 25%), mp: 74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, J = 7.2 Hz, 3H), 4.05 (q, J = 7.2 Hz, 2H), 7.21-7.23 (m, 2H), 7.30-7.34 (m, 4H), 7.47-7.51 (m, 1H), 7.59-7.63 (m, 1H), 8.12 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 62.1, 128.0, 128.3, 129.1, 129.4, 130.9, 131.0, 131.1, 132.2, 132.3, 136.0, 136.6, 144.2, 165.8, 177.8, 180.4. HRMS calcd for $C_{19}H_{15}O_4$: 307.0965 $[M+H]^+$, found: 307.0963.

IV. Mechanism studies

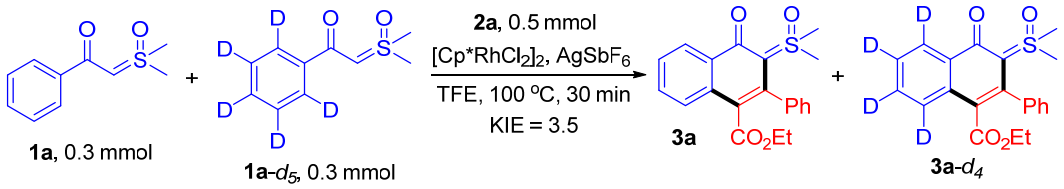
1. Reversibility of C−H bond cleavage



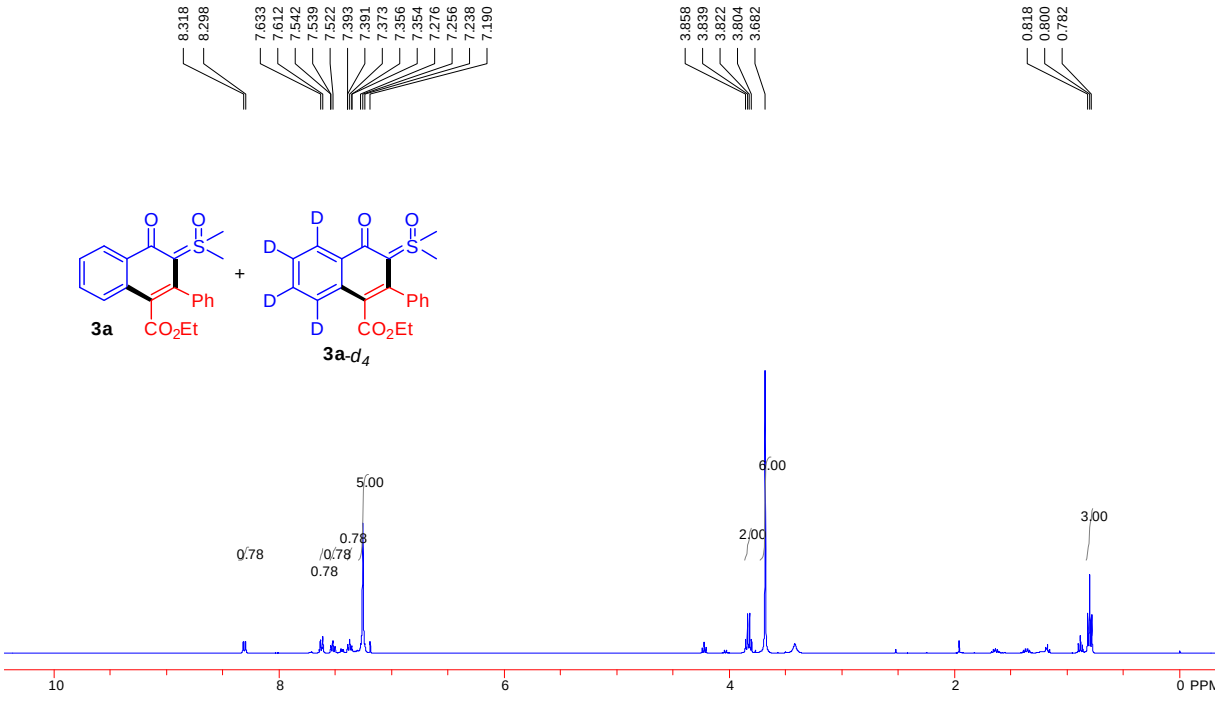
To a reaction tube equipped with a stir bar were charged with 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one (**1a**, 98 mg, 0.5 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol), CD_3OD (81 μL, 2 mmol) and TFE (3 mL). The resulting mixture was stirred at 100 °C under N_2 for 30 min. Afterwards, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using ethyl acetate as eluent to afford **1a-*d*$_n$**. ^{1}H NMR analysis revealed 6% deuteration at the *ortho*-position of phenyl ring and 27% deuteration at the α-position of the carbonyl unit. **This result indicates that the C−H bond cleavage process should be reversible.**



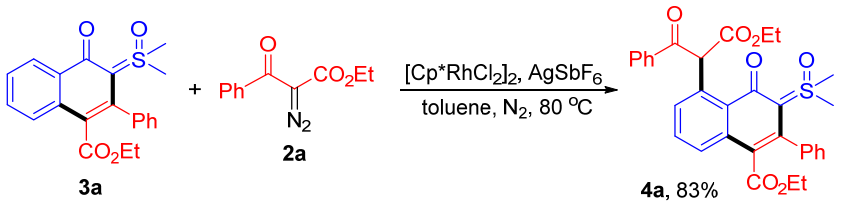
2. An intermolecular KIE experiment



To a reaction tube equipped with a stir bar were added 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenyl ethan-1-one (**1a**, 59 mg, 0.3 mmol), 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenyl-d_5-ethan-1-one (**1a-*d*$_5$**, 60 mg, 0.3 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2a**, 109 mg, 0.5 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol) and TFE (3 mL). The resulting mixture was then stirred at 100 °C under N_2 for 30 min. Afterwards, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using ethyl acetate/methanol (20:1) as eluent to afford a mixture of **3a** and **3a-*d*$_4$**. Upon analyzing the corresponding ^{1}H NMR spectrum, the intermolecular KIE (K_H/K_D) was determined as about 3.5. **This result tells that the cleavage of the *ortho*-C−H bond might be involved in the rate-limiting step of this cascade process.**

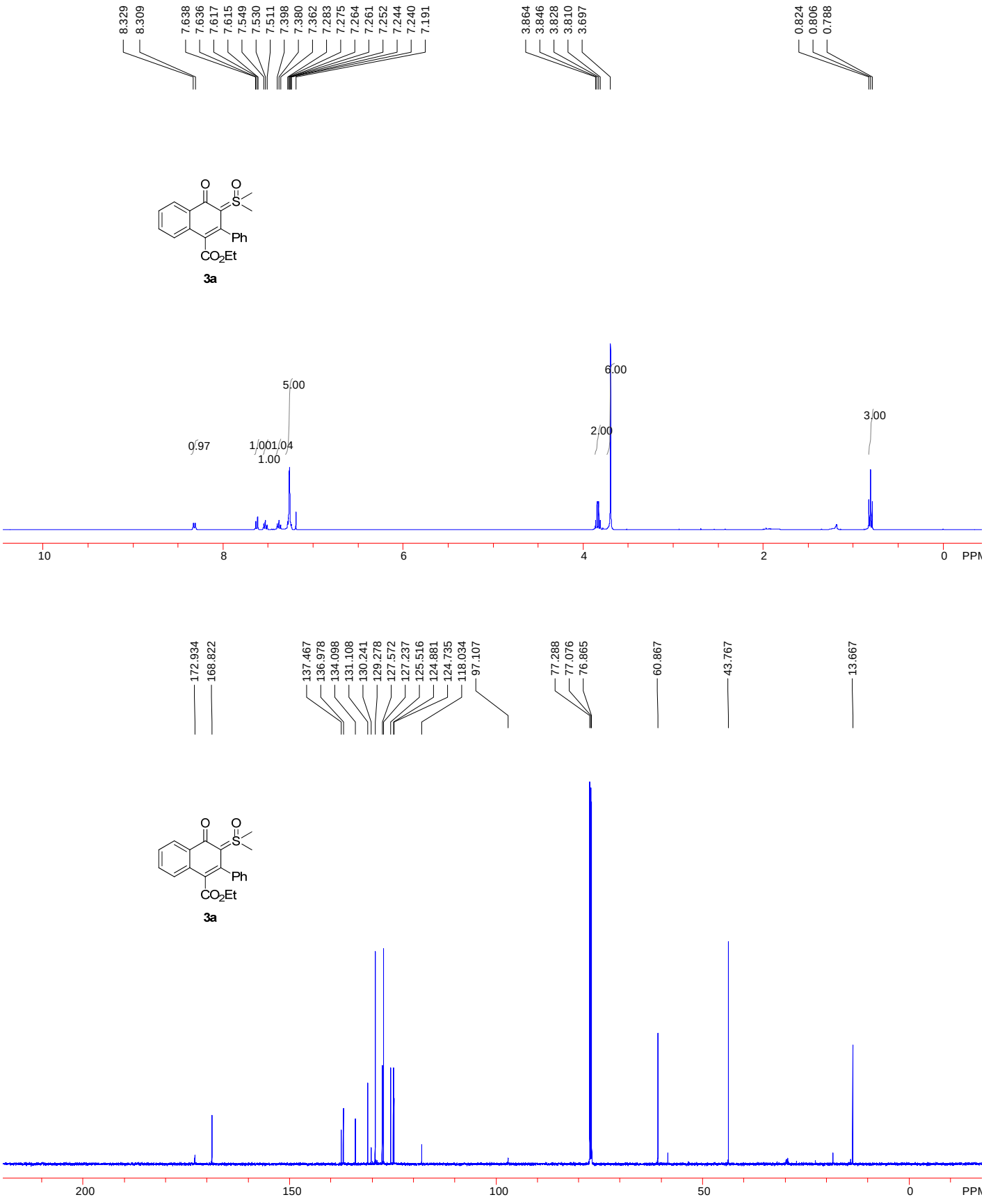


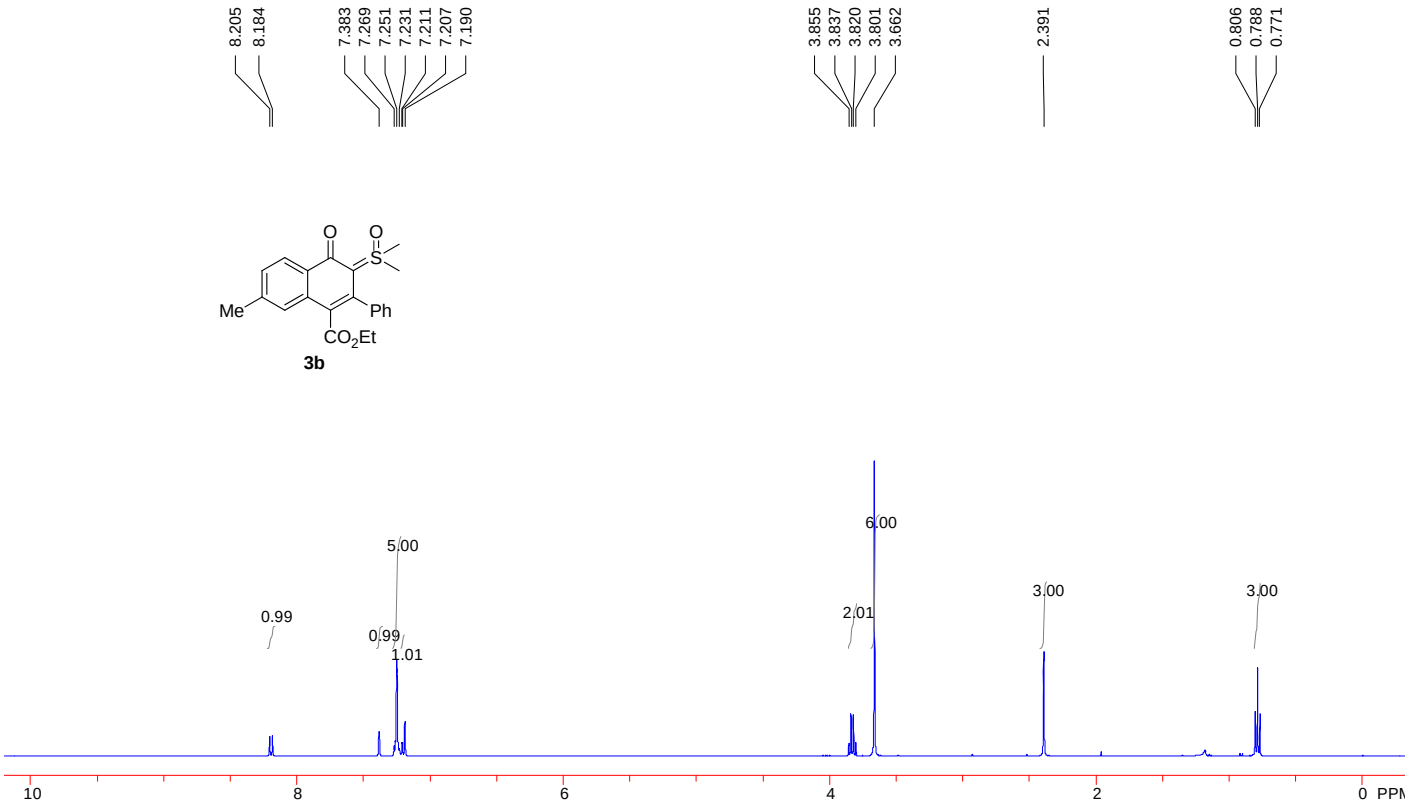
3. Control experiment



To a reaction tube equipped with a stir bar were charged with ethyl 3-(dimethyl(oxo)-λ^6-sulfanylidene)-4-oxo-2-phenyl-3,4-dihydronaphthalene-1-carboxylate (**3a**, 180 mg, 0.5 mmol), ethyl 2-diazo-3-oxo-3-phenyl propanoate (**2a**, 240 mg, 1.1 mmol), $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol), $AgSbF_6$ (28 mg, 0.08 mmol) and toluene (3 mL). The resulting mixture was stirred at 80 °C under N_2 for 24 h. Upon completion, it was cooled to room temperature, quenched with saturated brine (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1) as eluent to afford **4a** in a yield of 83% (232 mg).

V. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3x

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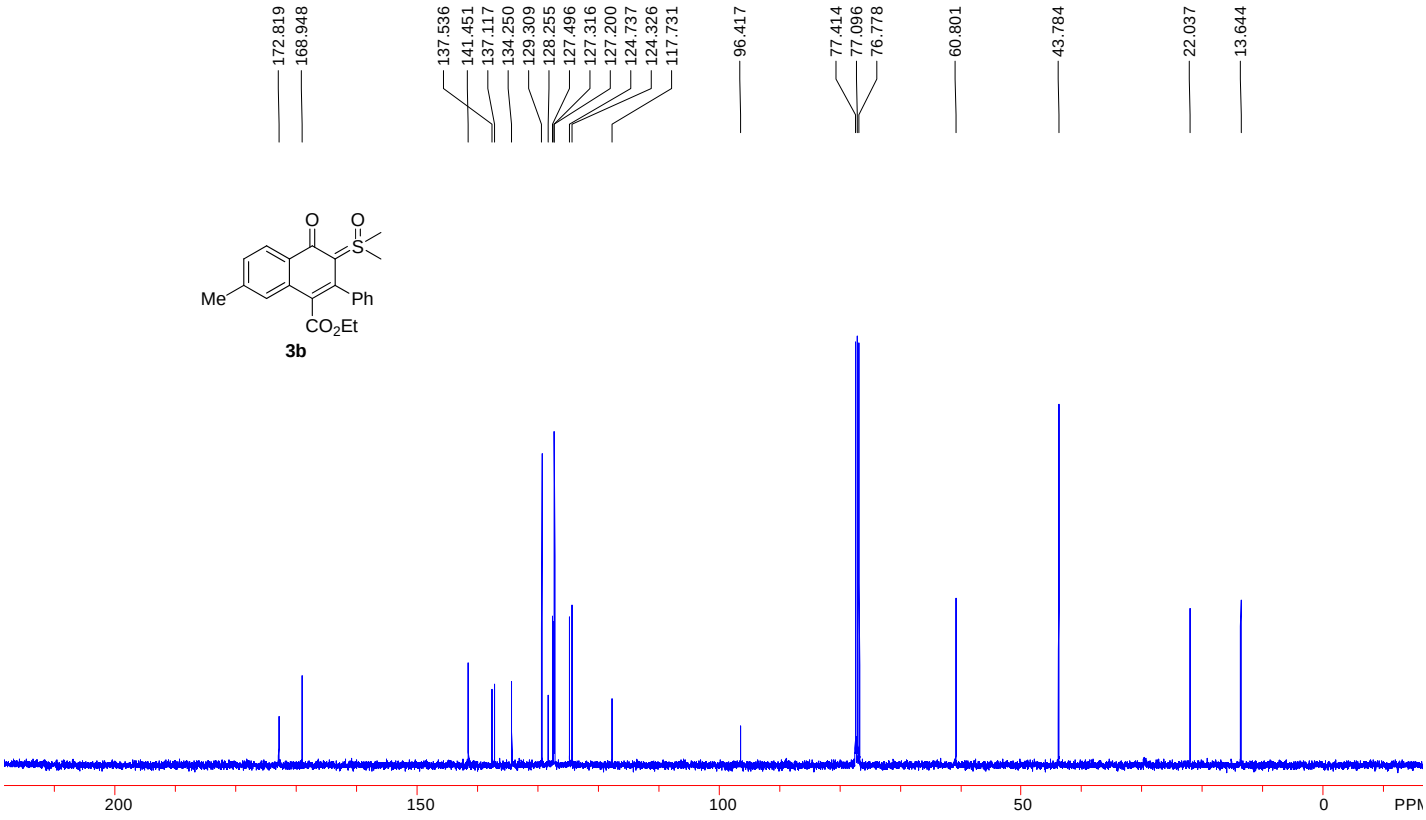
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117.731
96.417
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77.096
76.778
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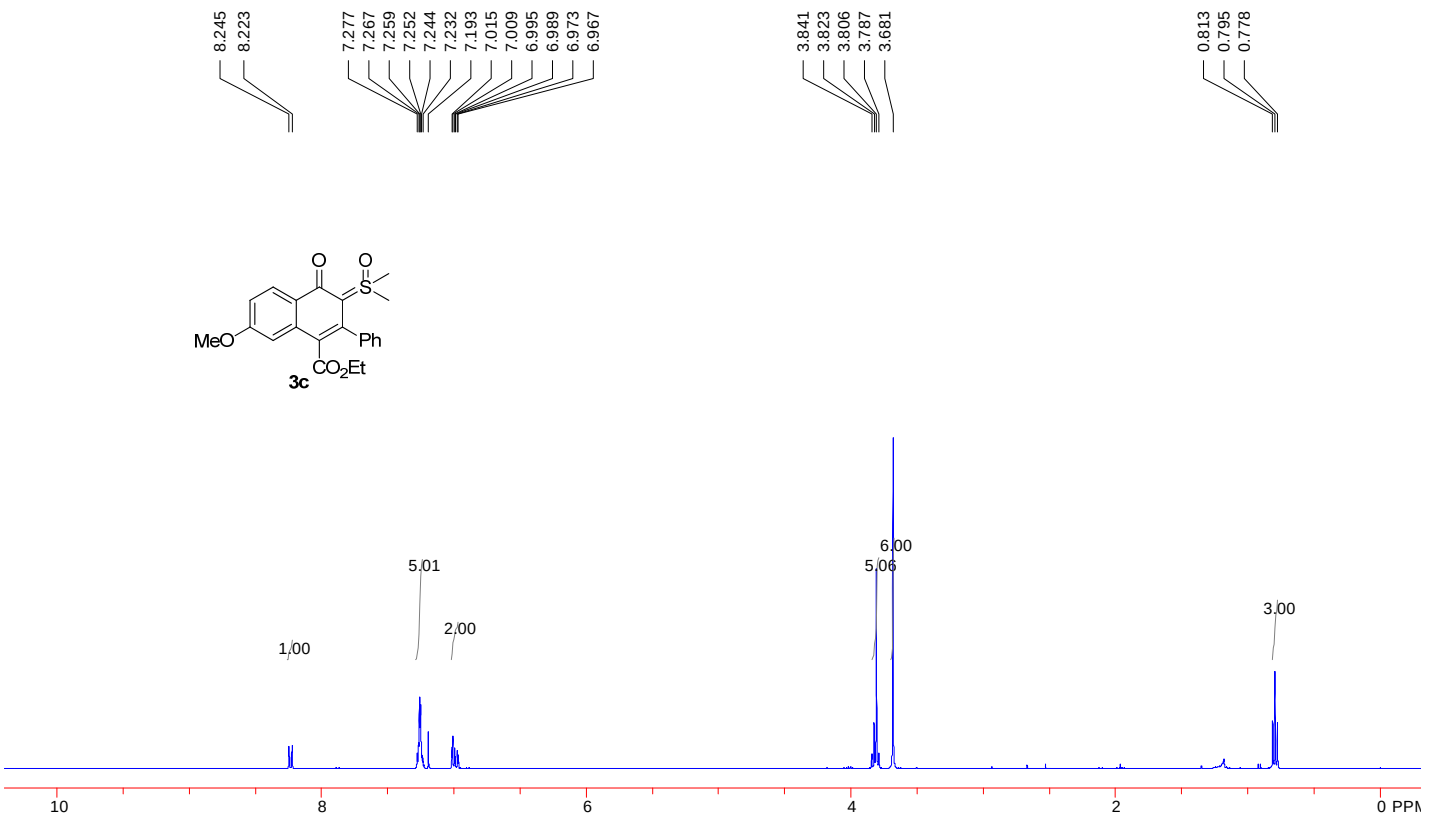
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4
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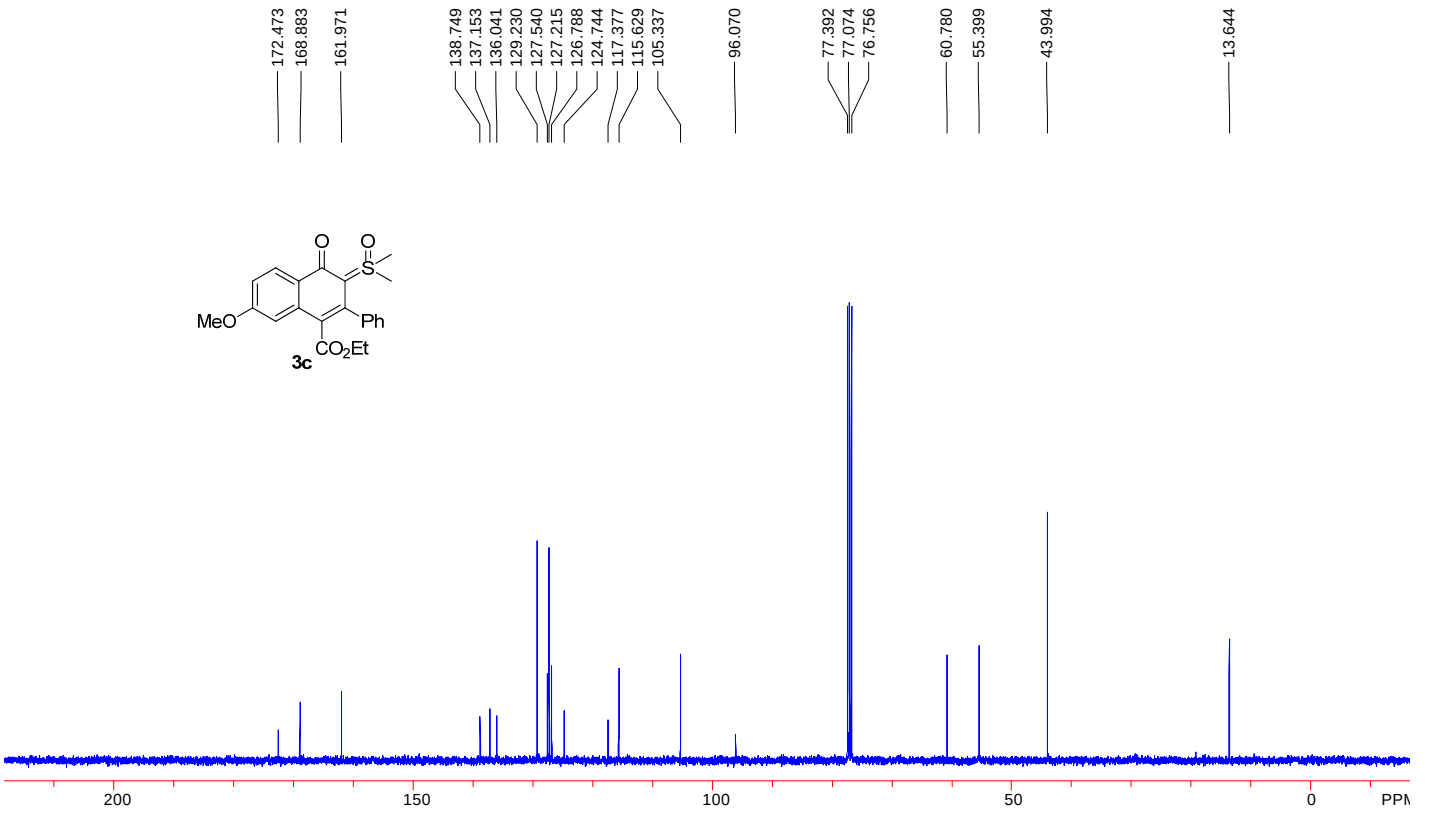
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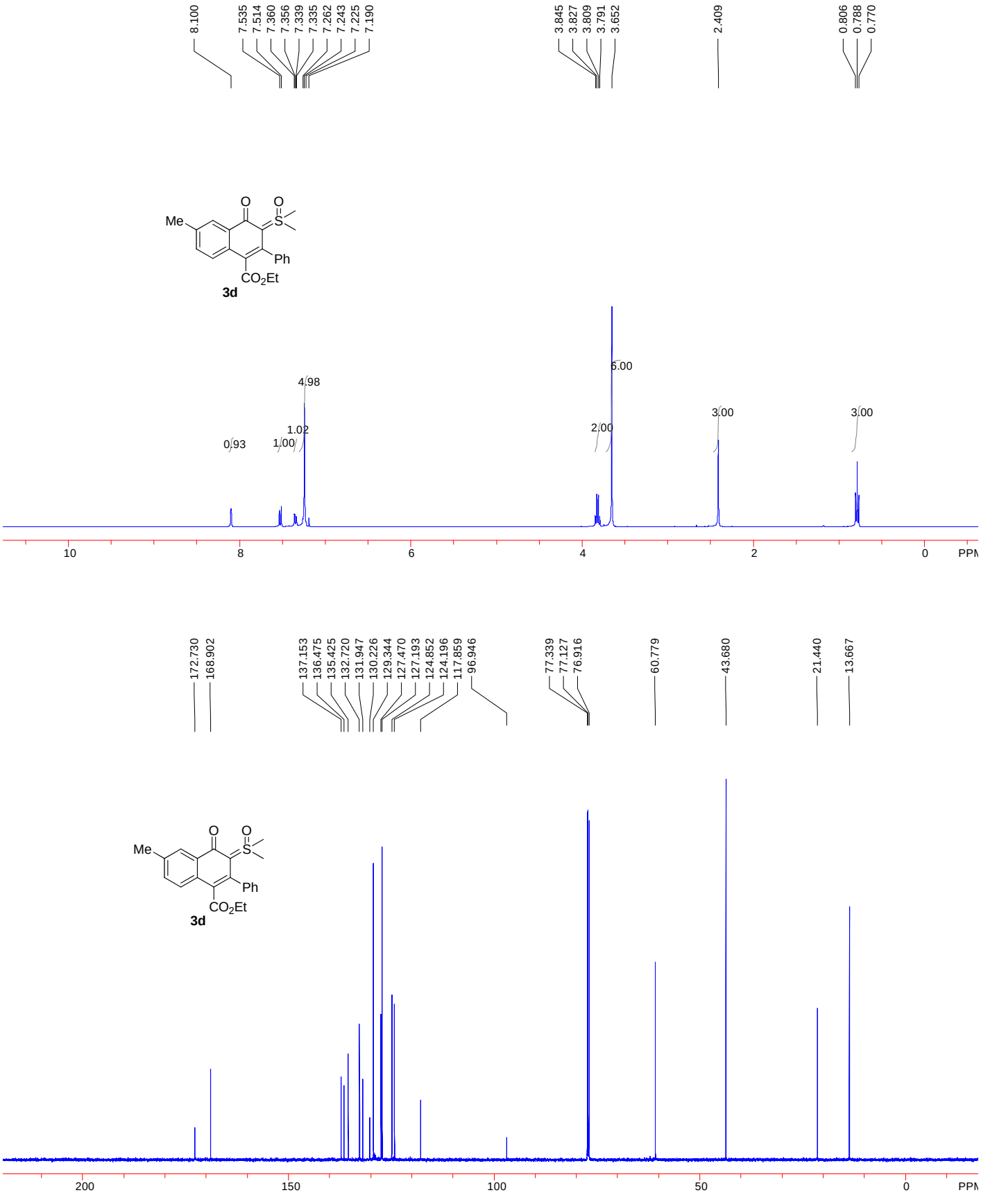
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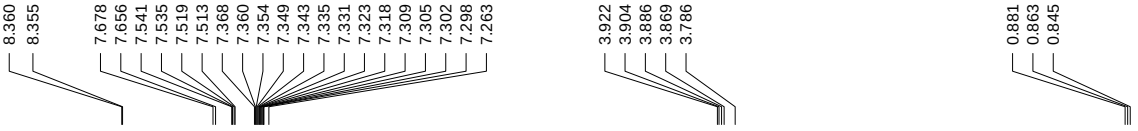
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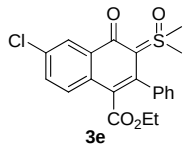
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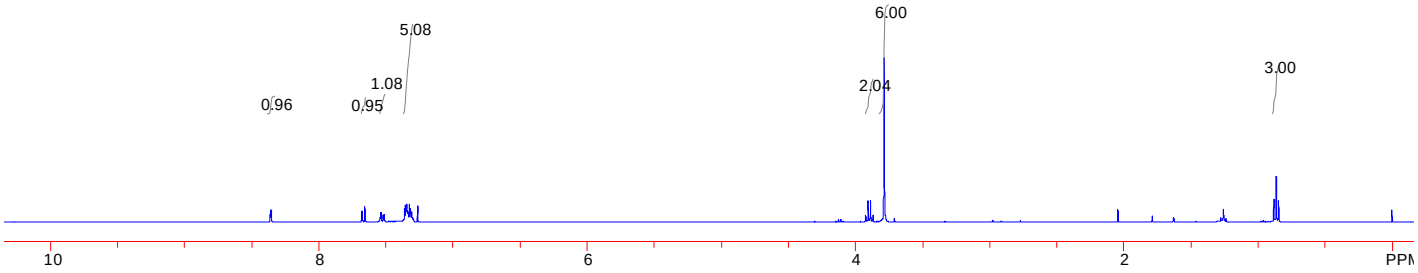
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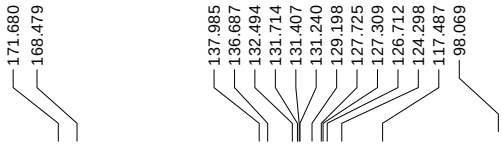
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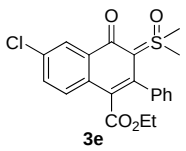
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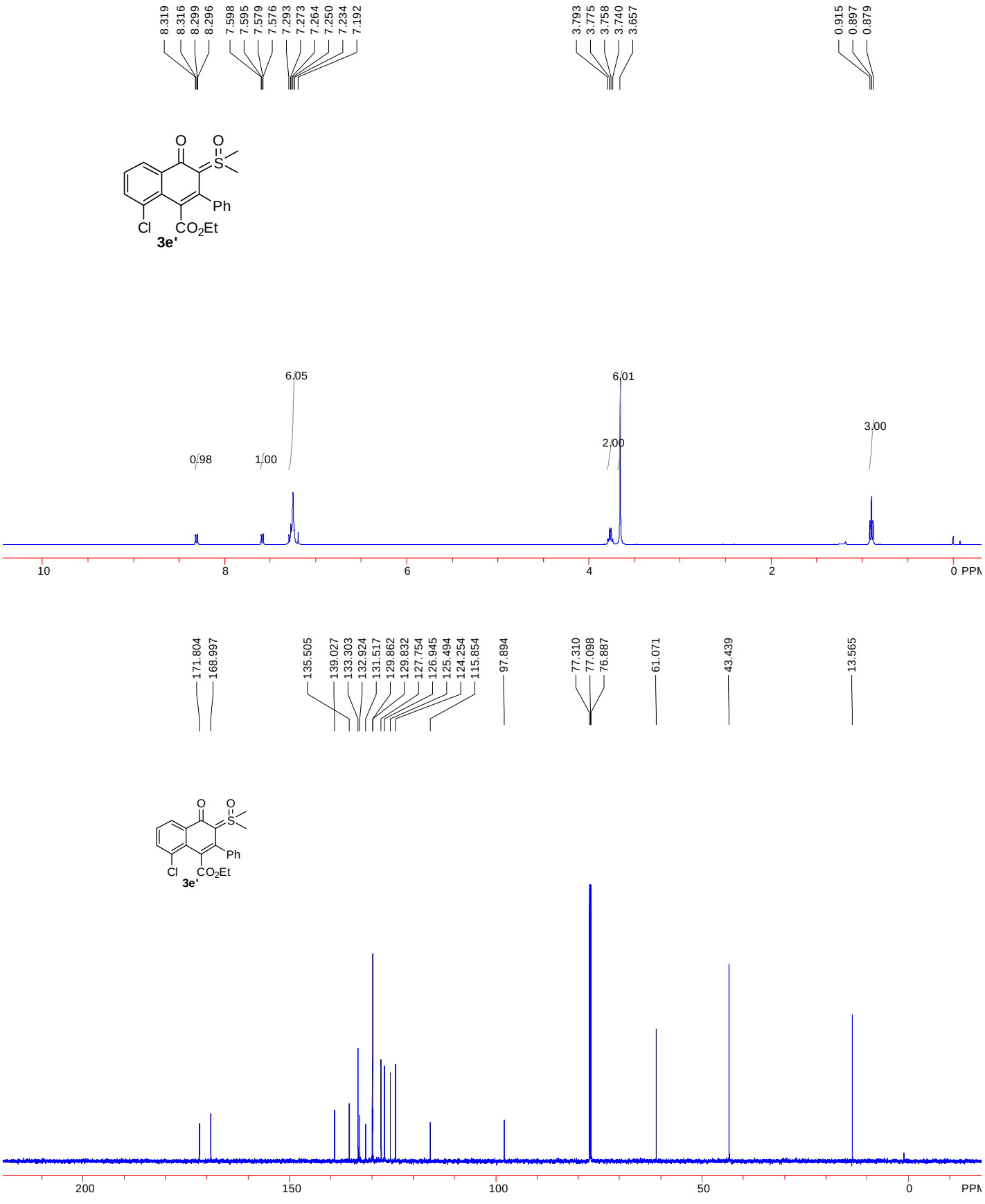
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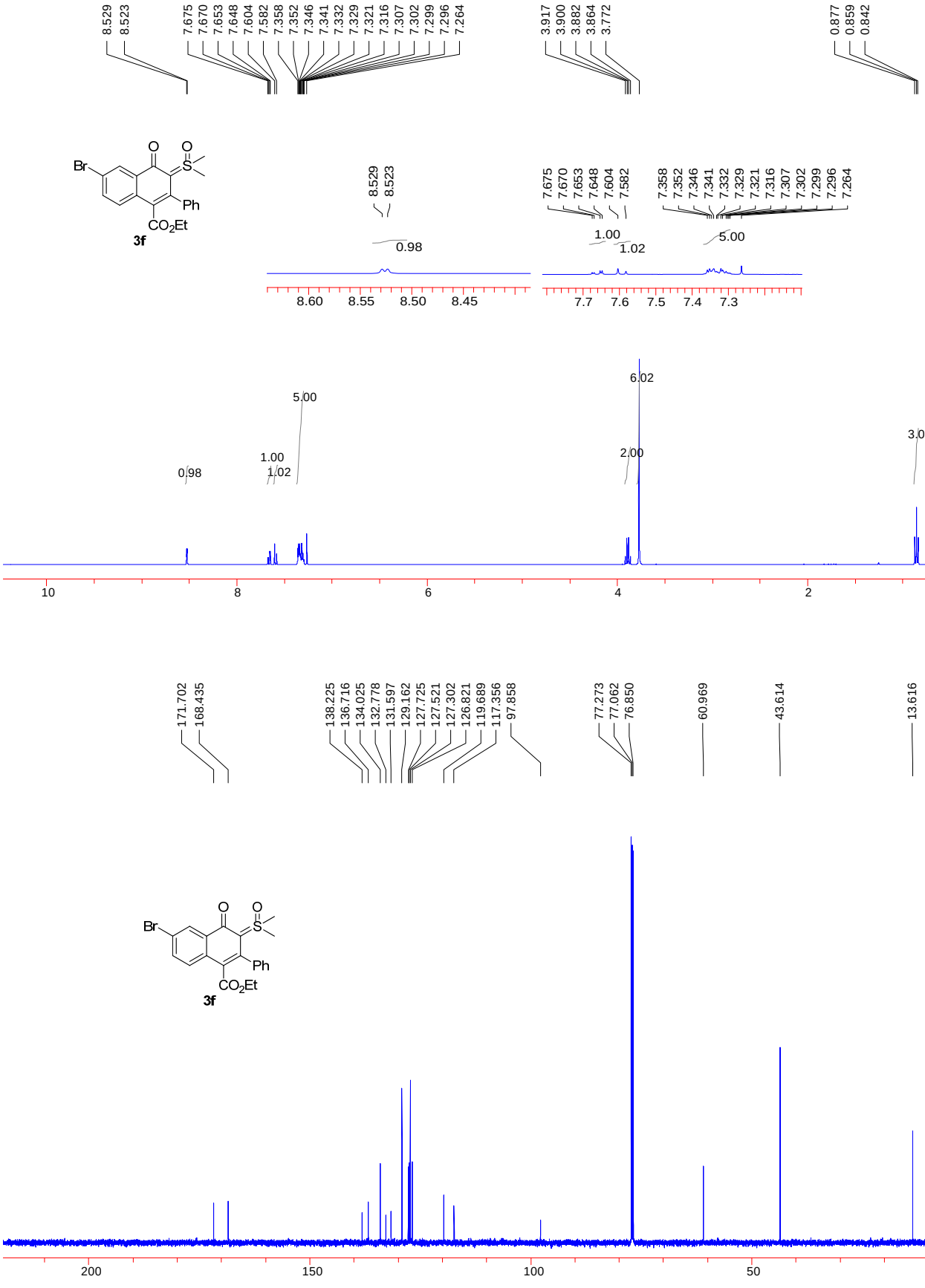
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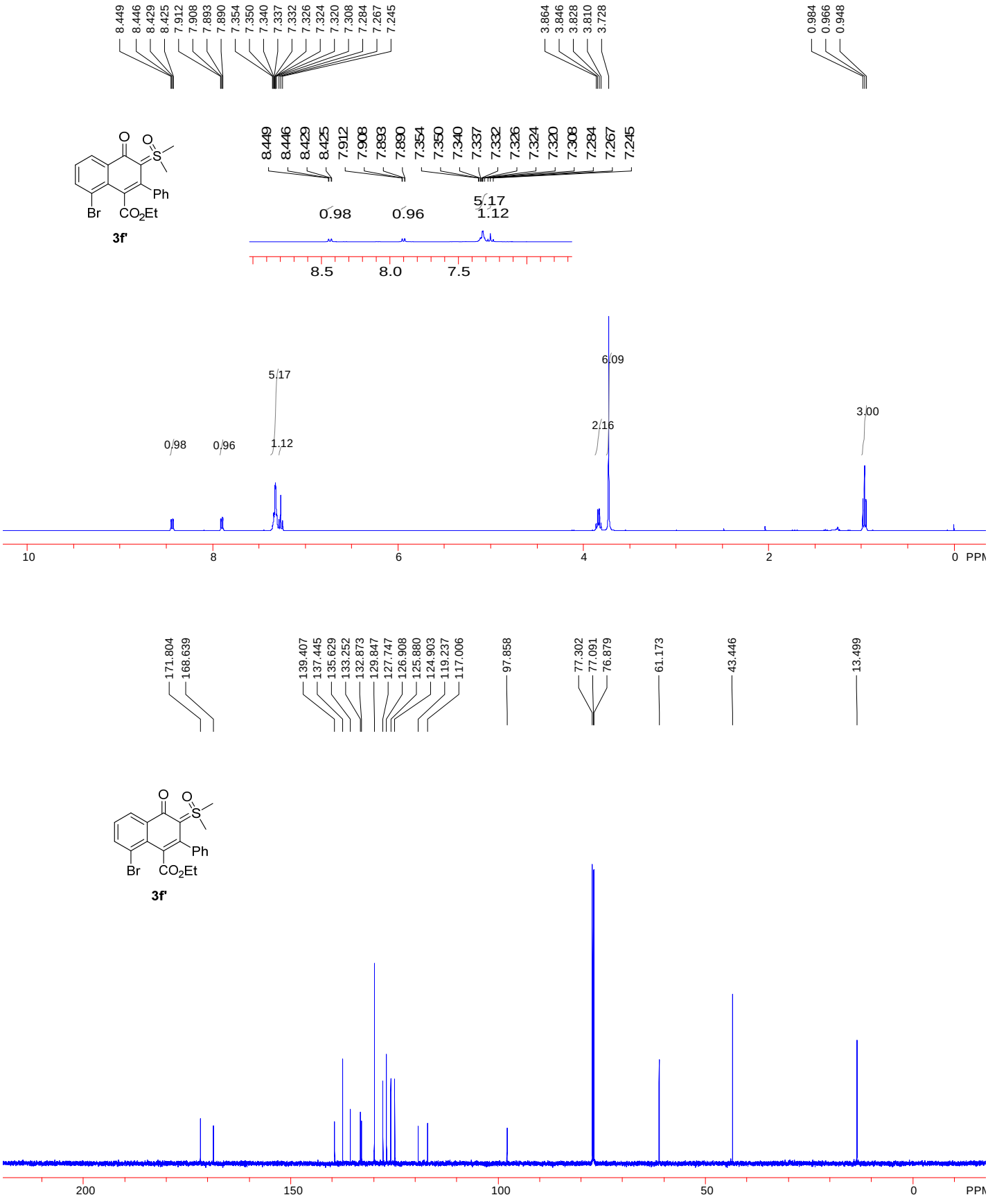
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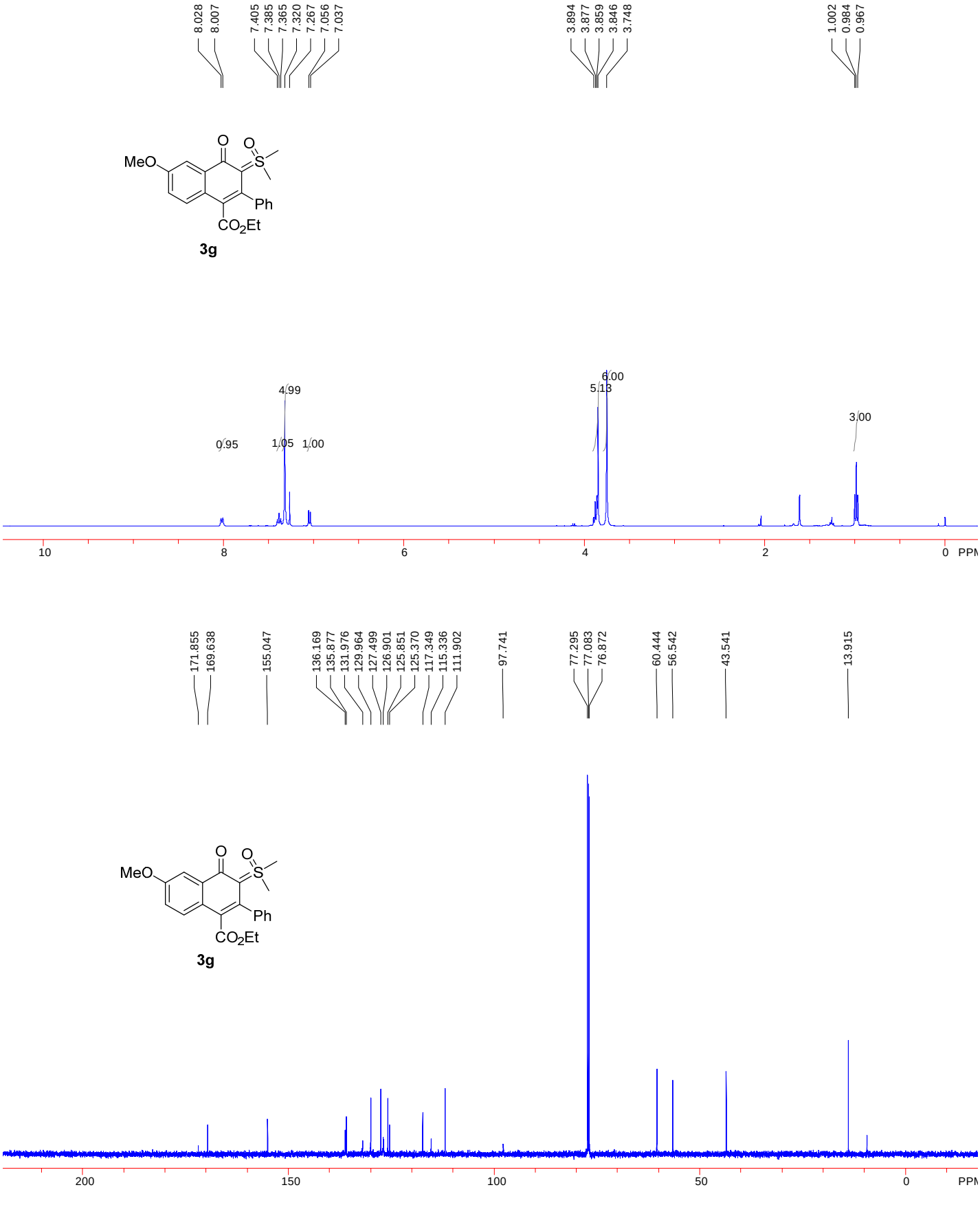
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3.00
10
8
6
4
2
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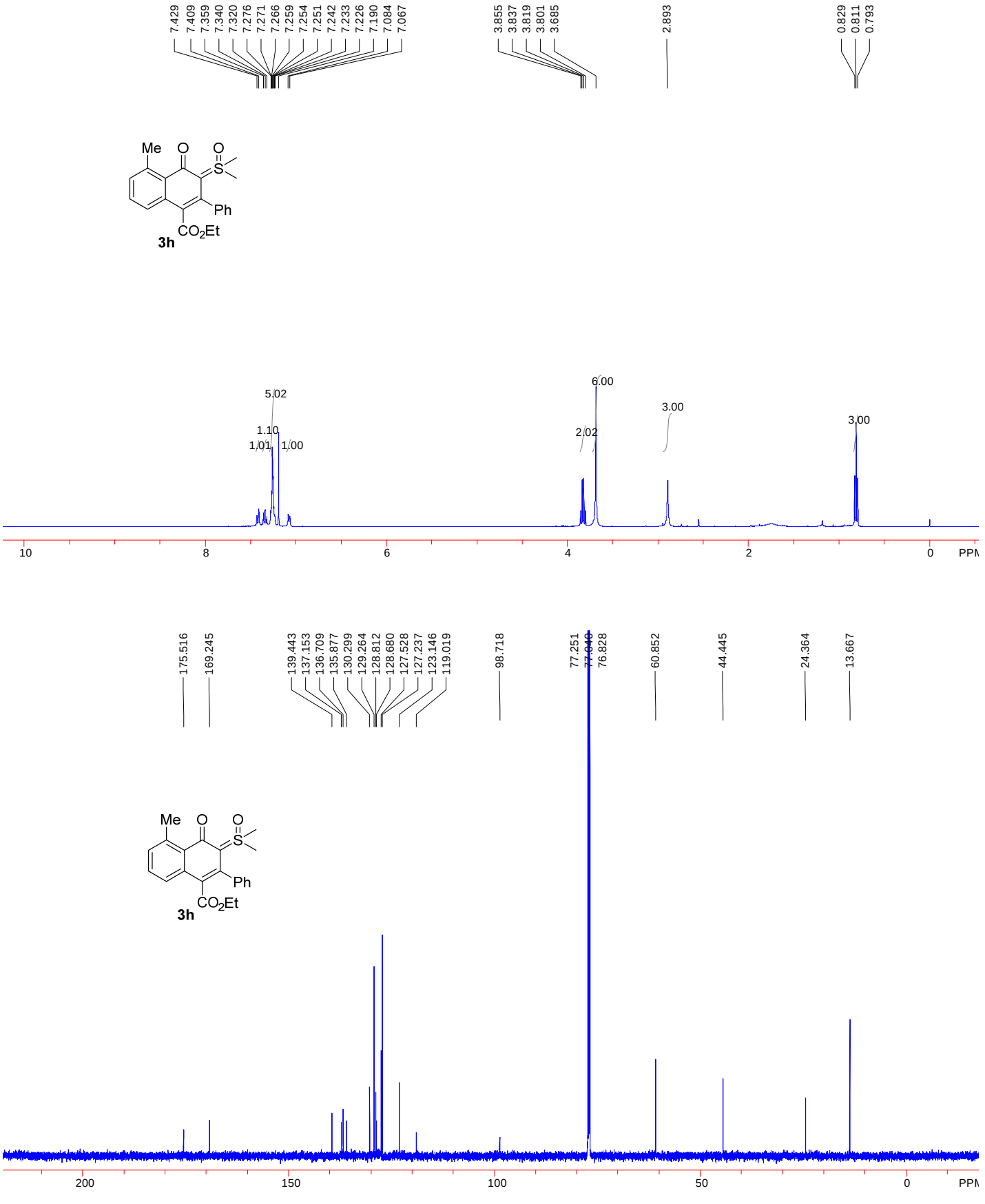
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0.811
0.793
Me
O
O
S
Ph
CO2Et
3h
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1.01
1.00
6.00
2.02
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3.00
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77.251
77.040
76.828
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O
S
Ph
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3h
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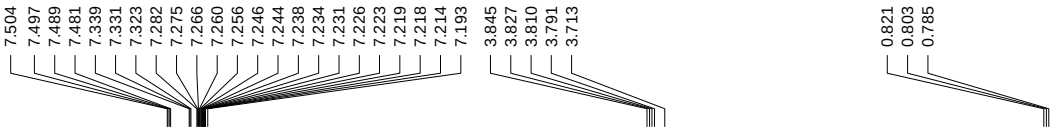
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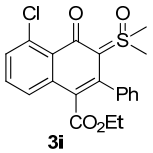
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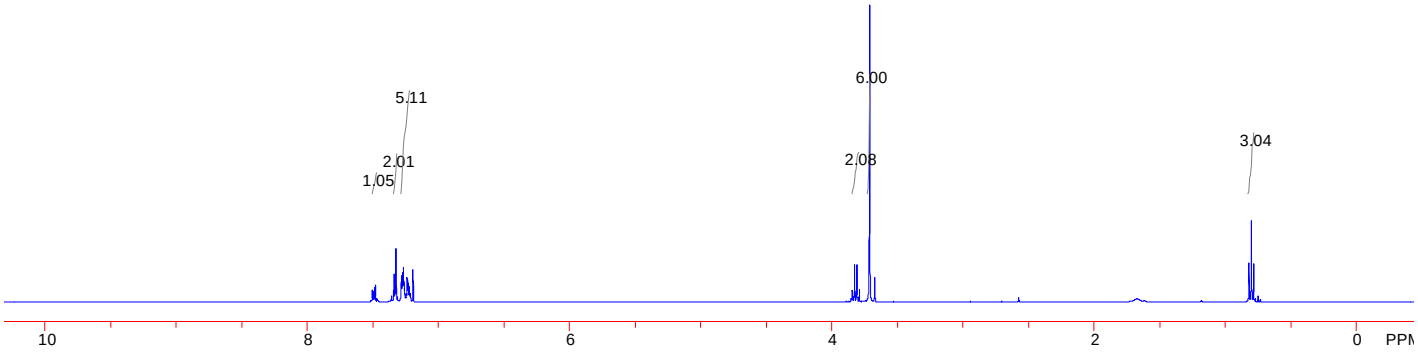
O
S
Ph
CO2Et

3i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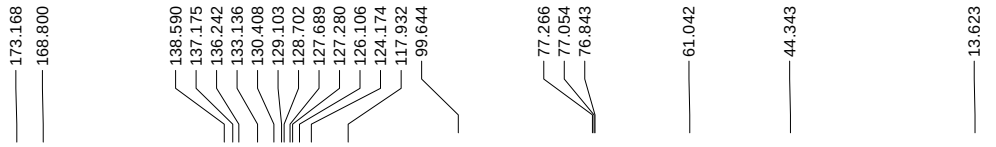
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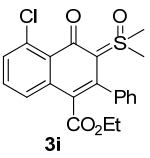
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O
O
S
Ph
CO2Et

3i

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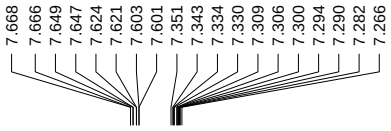
50
0
PPM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7.300
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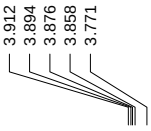
7.290
7.282
7.266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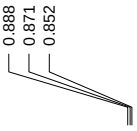
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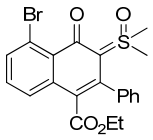
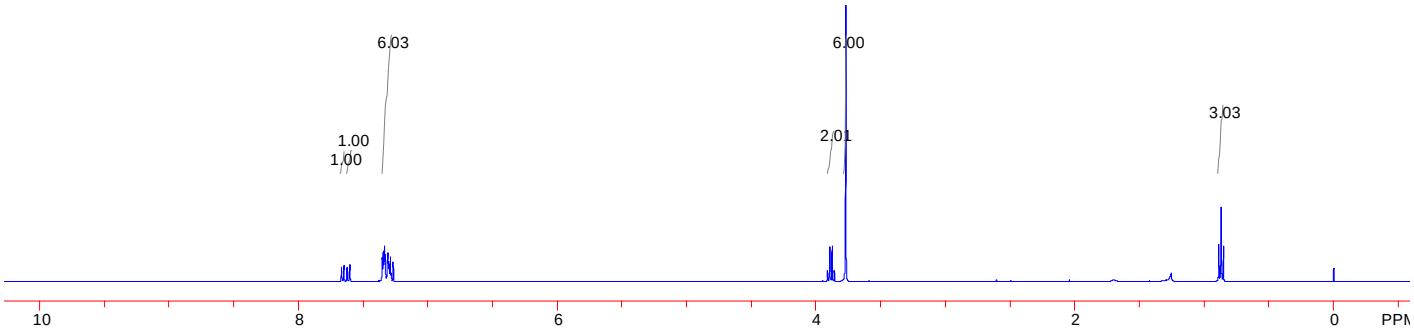

Br
O
O
S
Ph
CO2Et

3j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1.00
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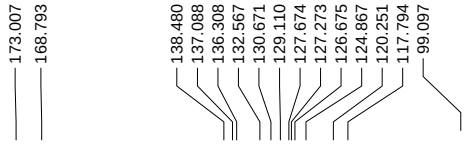
8
6
4
2
0
PPM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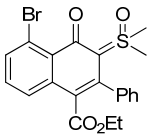
99.097


77.295
77.083
76.872

61.020

44.234


13.623


Br
O
O
S
Ph
CO2Et

3j

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150
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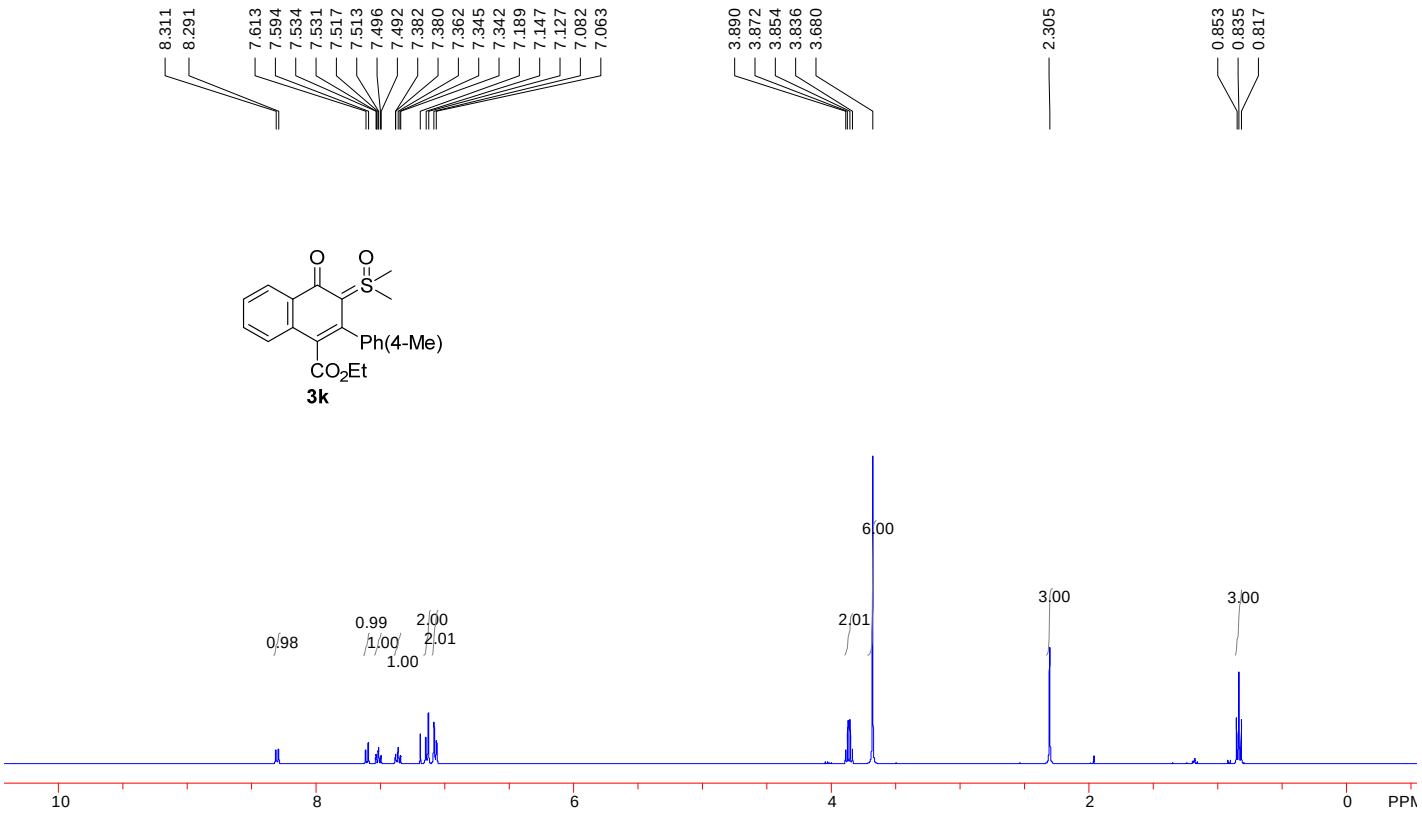
50
0
PPM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7.513
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7.492
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7.362
7.345
7.342
7.189
7.147
7.127
7.082
7.063
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3.836
3.680
2.305
0.853
0.835
0.817
Ph(4-Me)
CO2Et
3k
6.00
3.00
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2.00
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1.00
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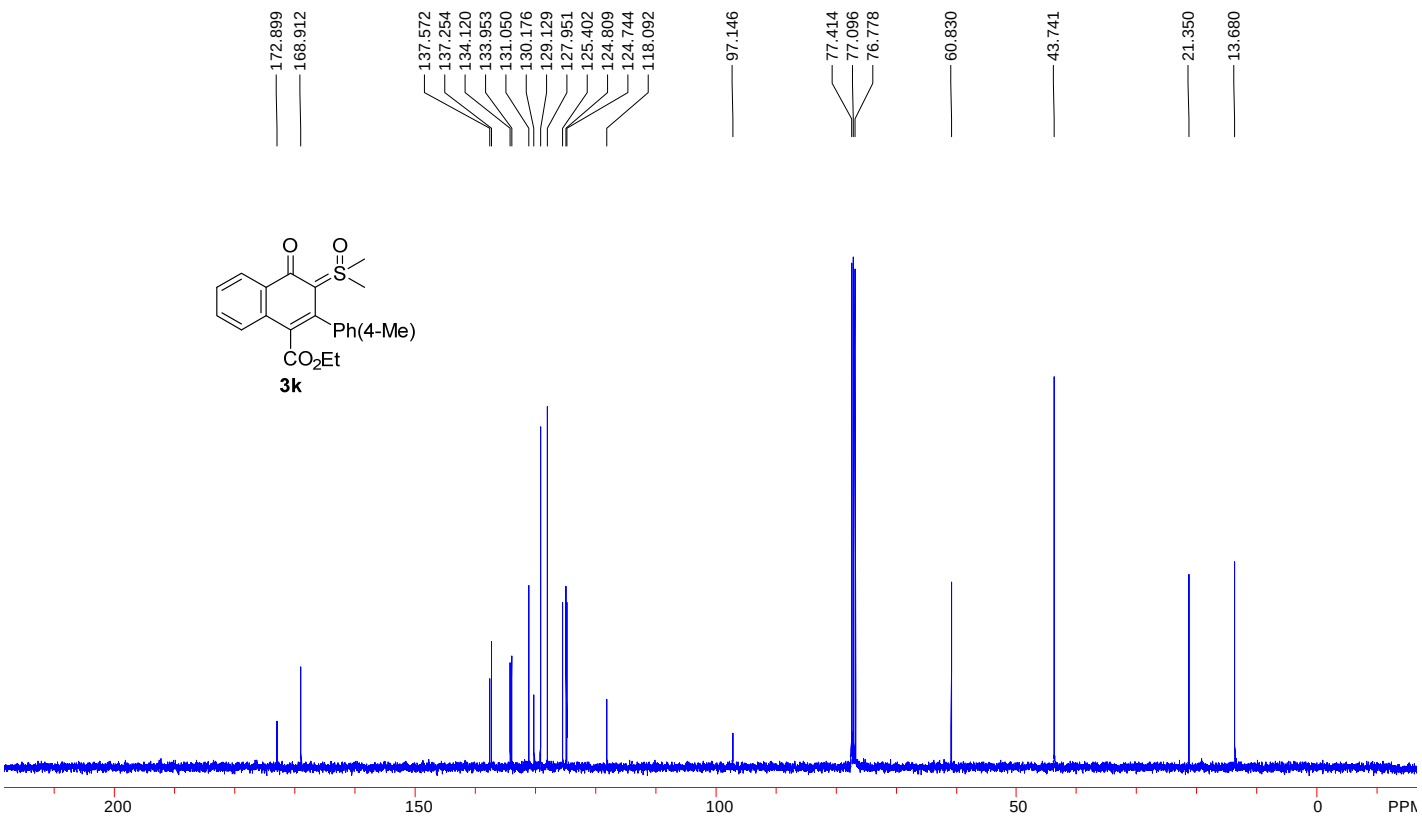
PPM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77.096
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Ph(4-Me)
CO2Et
3k
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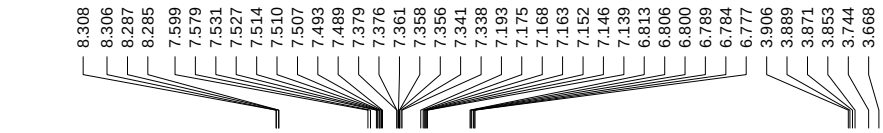
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7.489
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7.358
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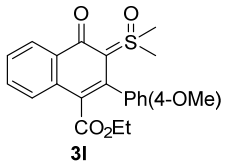
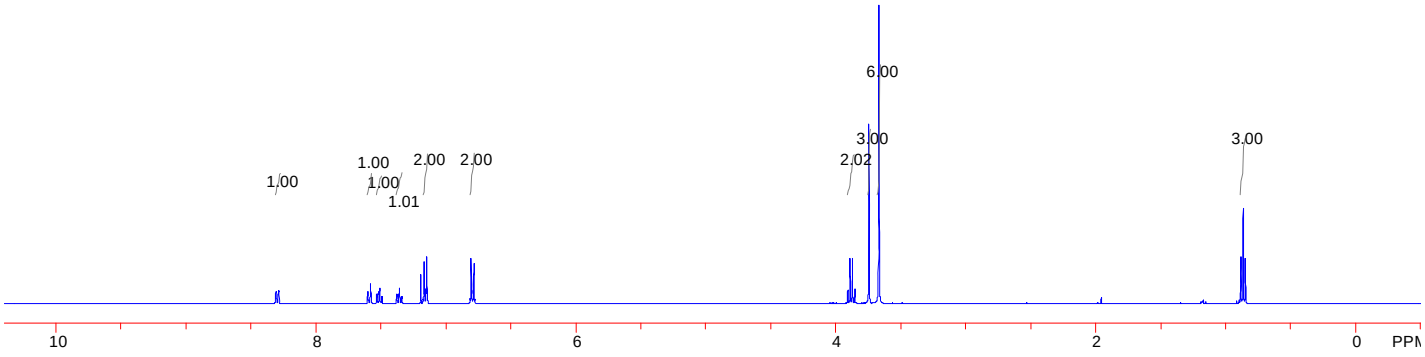
0.869
0.851


O
O
S
Ph(4-OMe)
CO2Et

3l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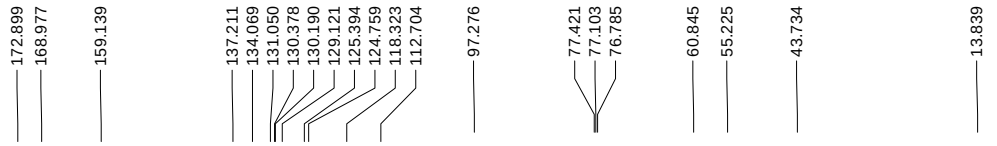
1.00
2.00
2.00
1.00
1.01
10
8
6
4
2
0
PPM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77.103
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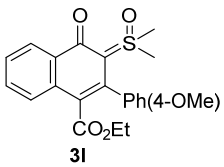
60.845
55.225
43.734
13.839


O
O
S
Ph(4-OMe)
CO2Et

3l

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100
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0
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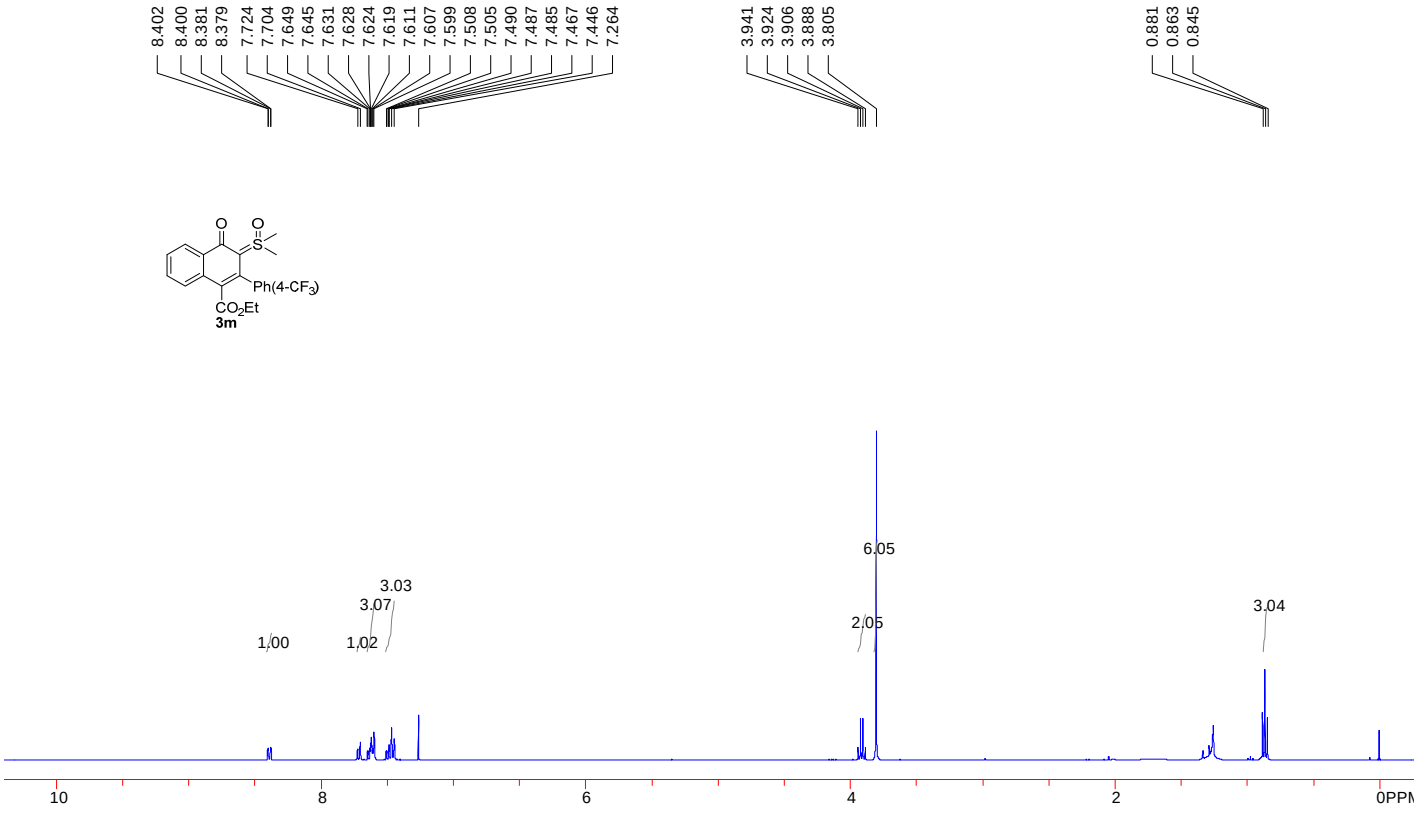
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7.628
7.624
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7.611
7.607
7.599
7.508
7.505
7.490
7.487
7.485
7.467
7.446
7.264
3.941
3.924
3.906
3.888
3.805
0.881
0.863
0.845
Ph(4-CF3)
CO2Et
3m
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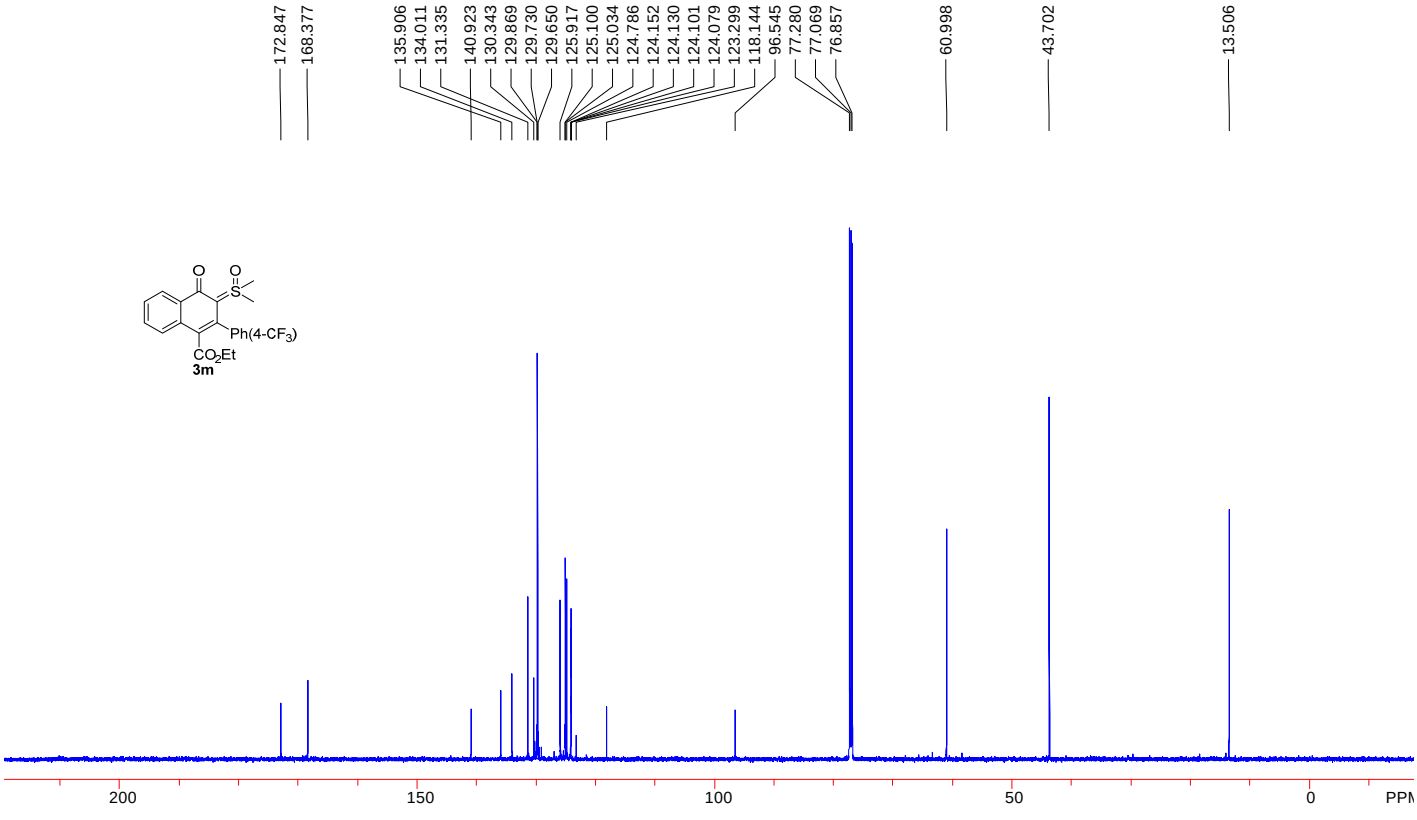
3.07
3.04
2.05
1.00
1.02
10
8
6
4
2
0PPM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124.786
124.152
124.130
124.101
124.079
123.299
118.144
96.545
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3m
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100
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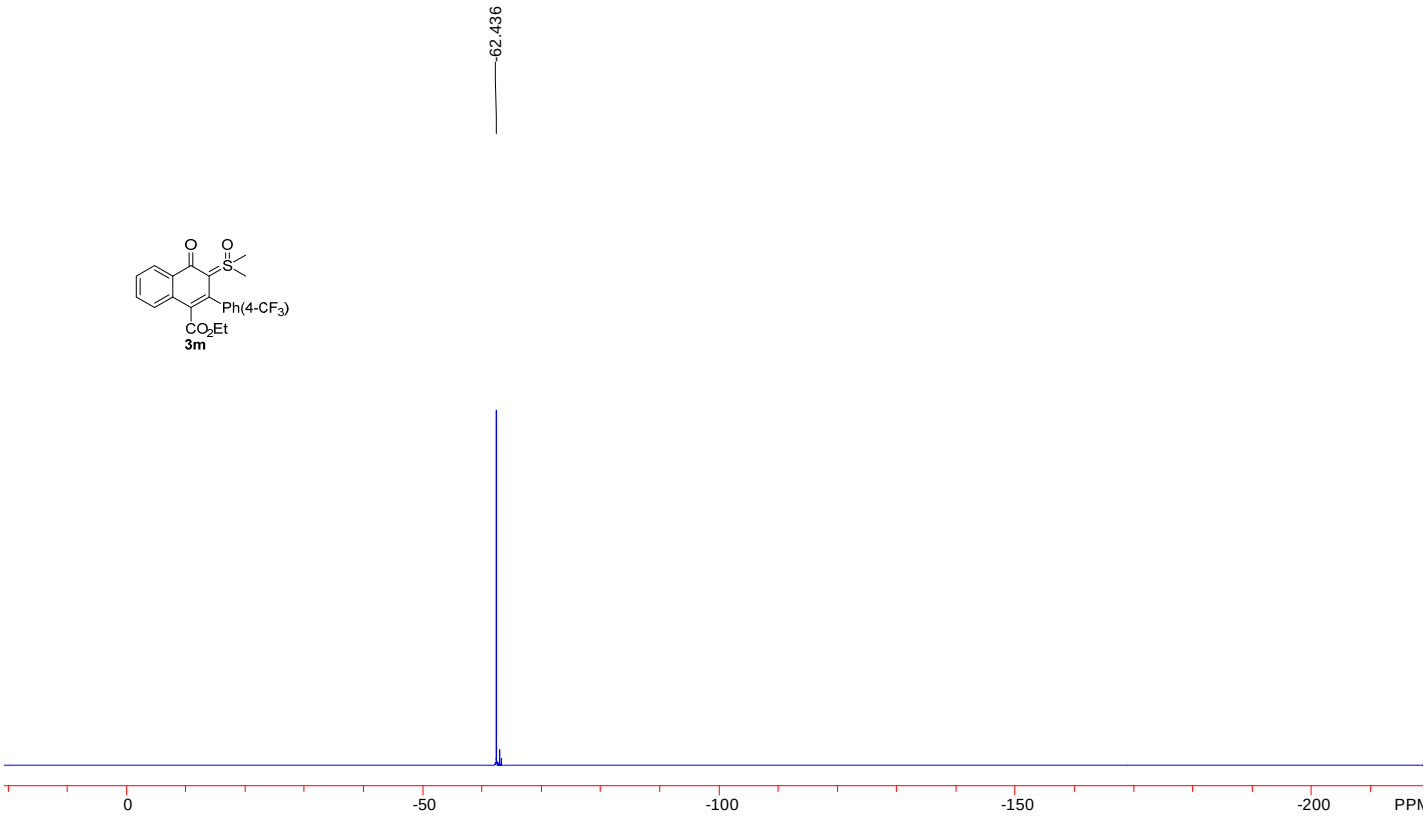
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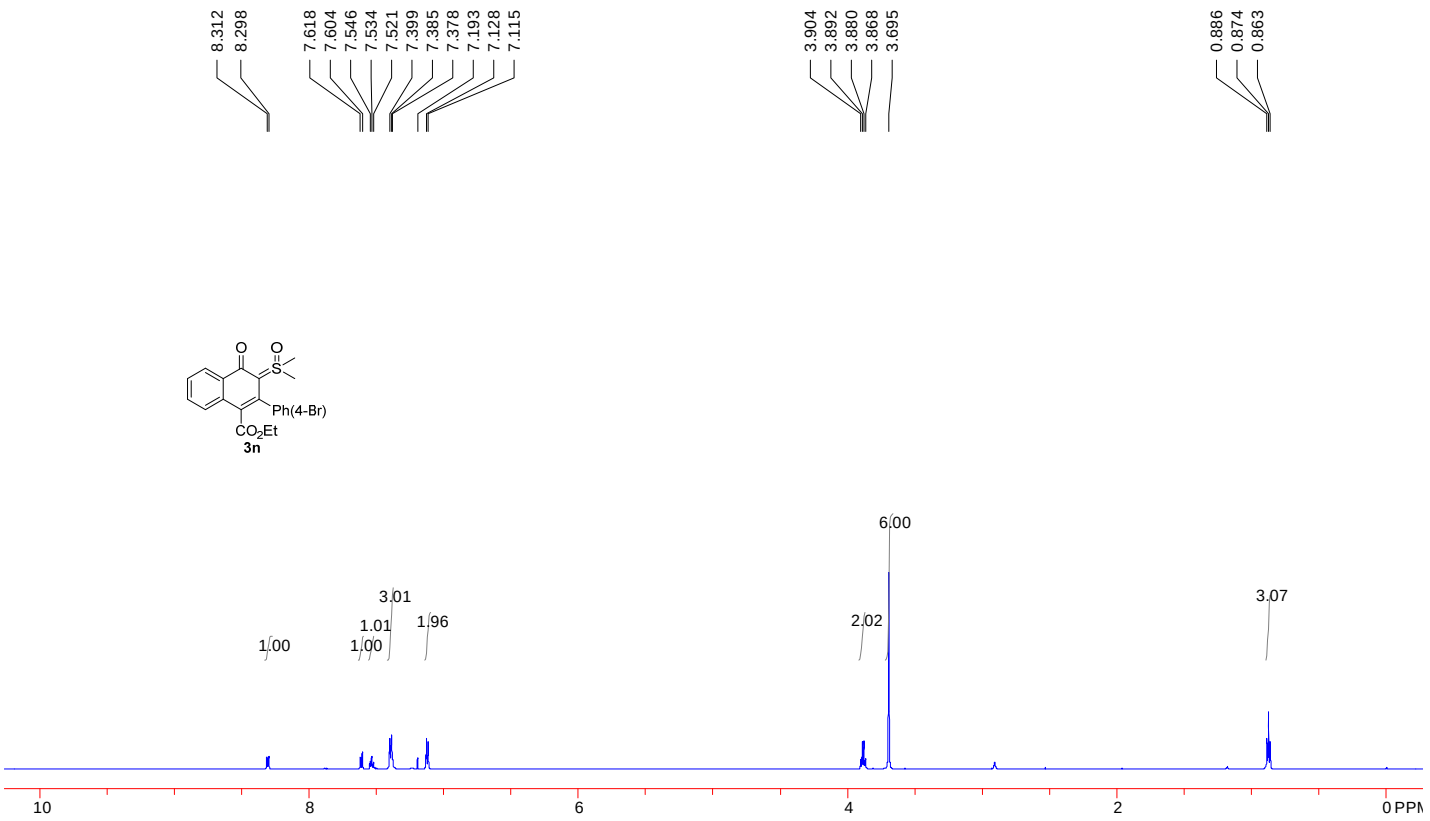
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7.193
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7.115
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3.892
3.880
3.868
3.695
0.886
0.874
0.863
Ph(4-Br)
CO2Et
3n
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1.01
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1.00
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3.07
10
8
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4
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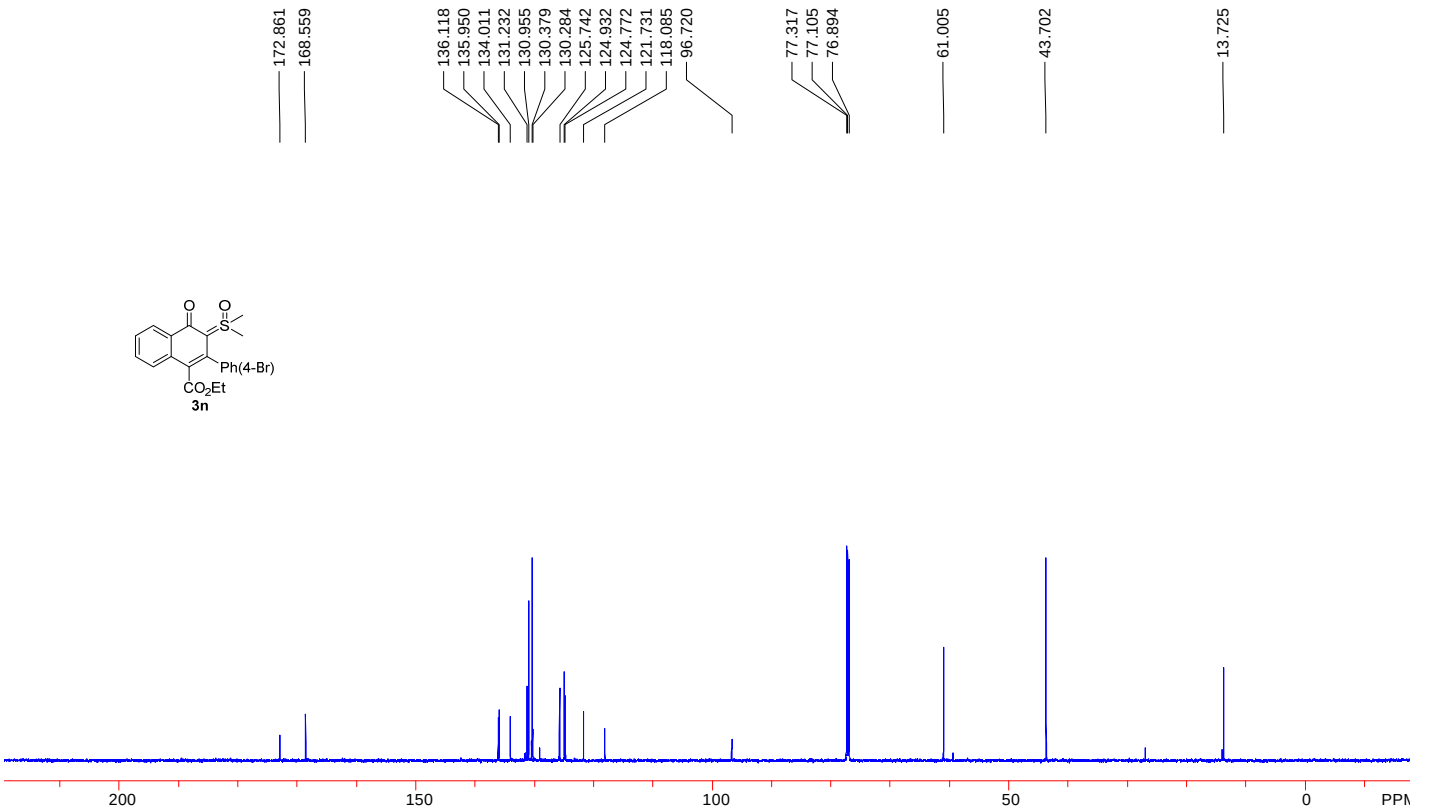
0 PPM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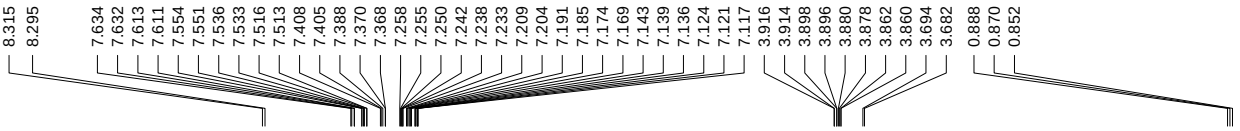
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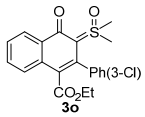
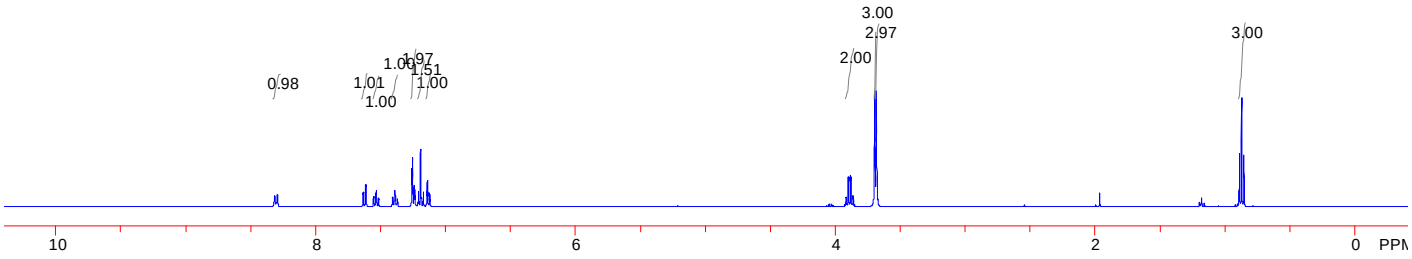

O
O
S
Ph(3-Cl)
CO2Et
3o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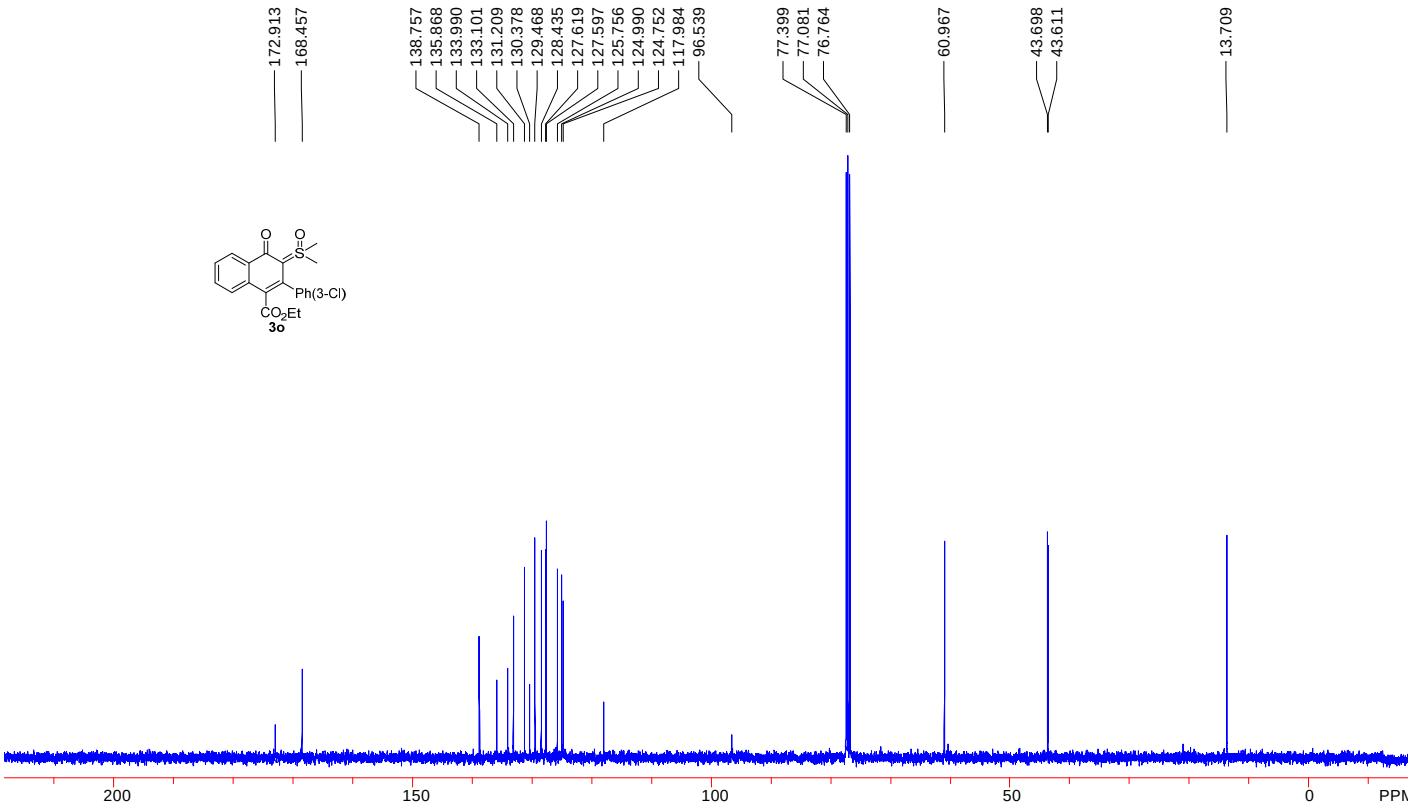
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76.764
60.967
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100
50
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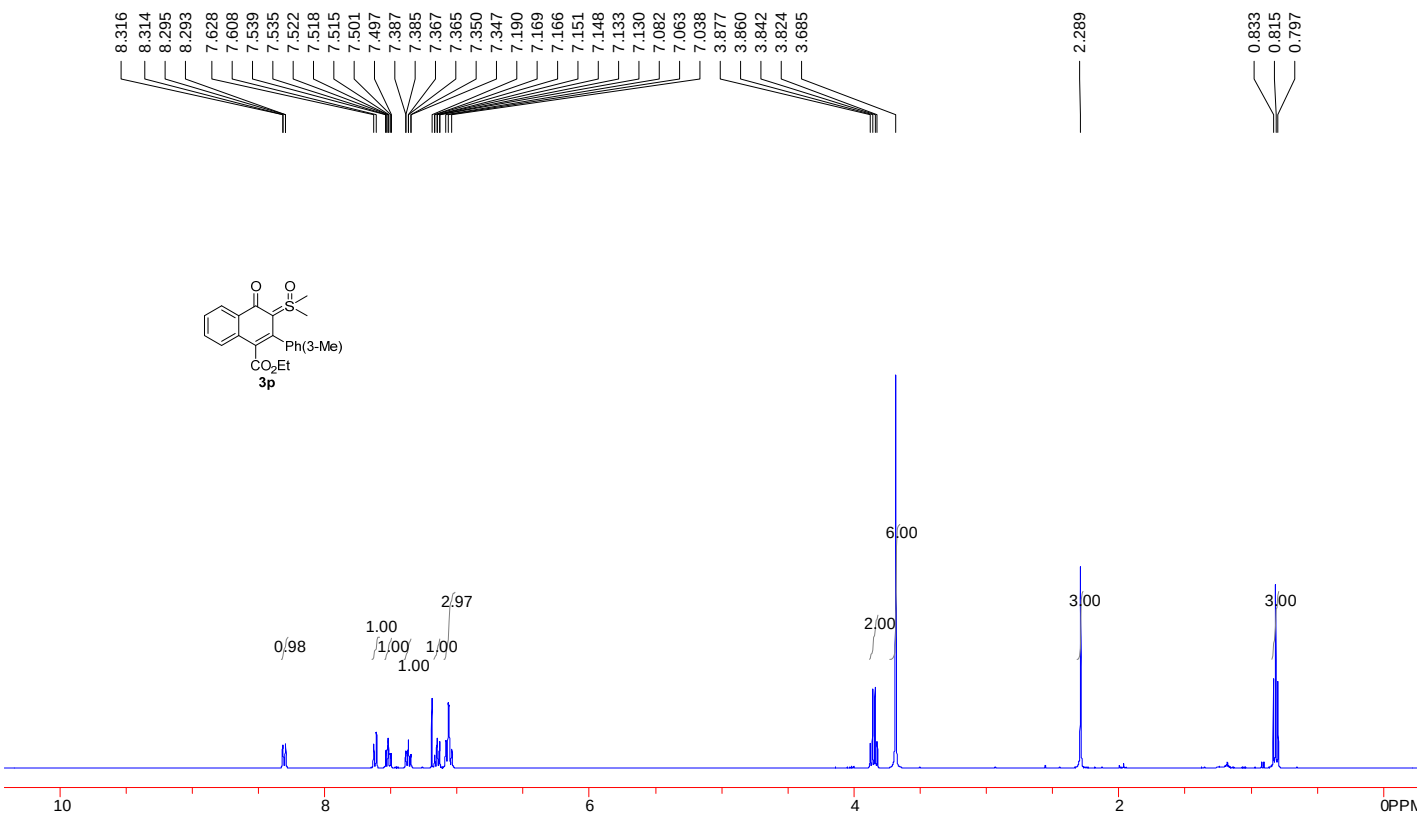
PPM

O
O
S
Ph(3-Cl)
CO2Et
3o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7.148
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7.130
7.082
7.063
7.038
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3.860
3.842
3.824
3.685
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0.815
0.797
Ph(3-Me)
CO2Et
3p
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3.00
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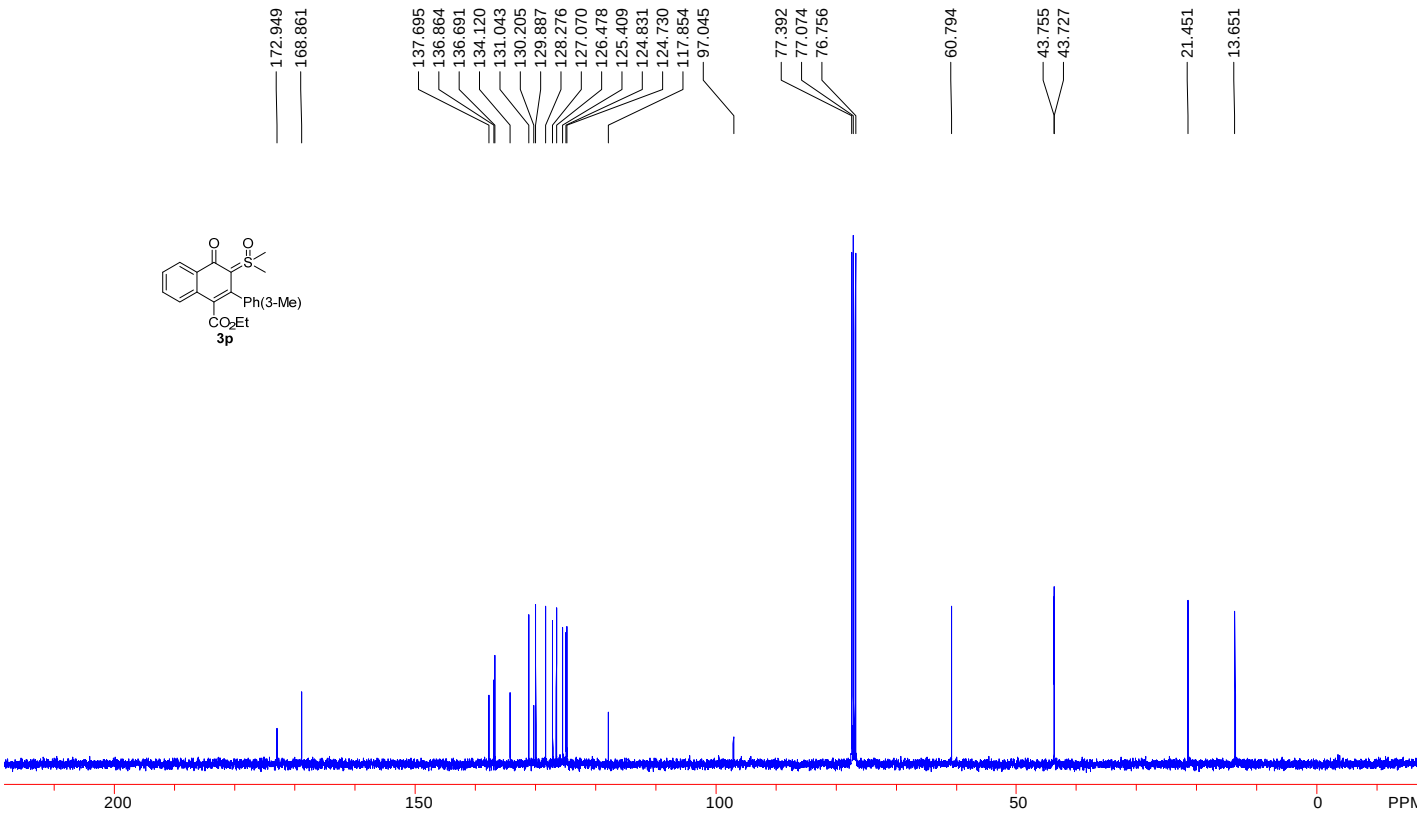
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125.409
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117.854
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77.392
77.074
76.756
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13.651
Ph(3-Me)
CO2Et
3p
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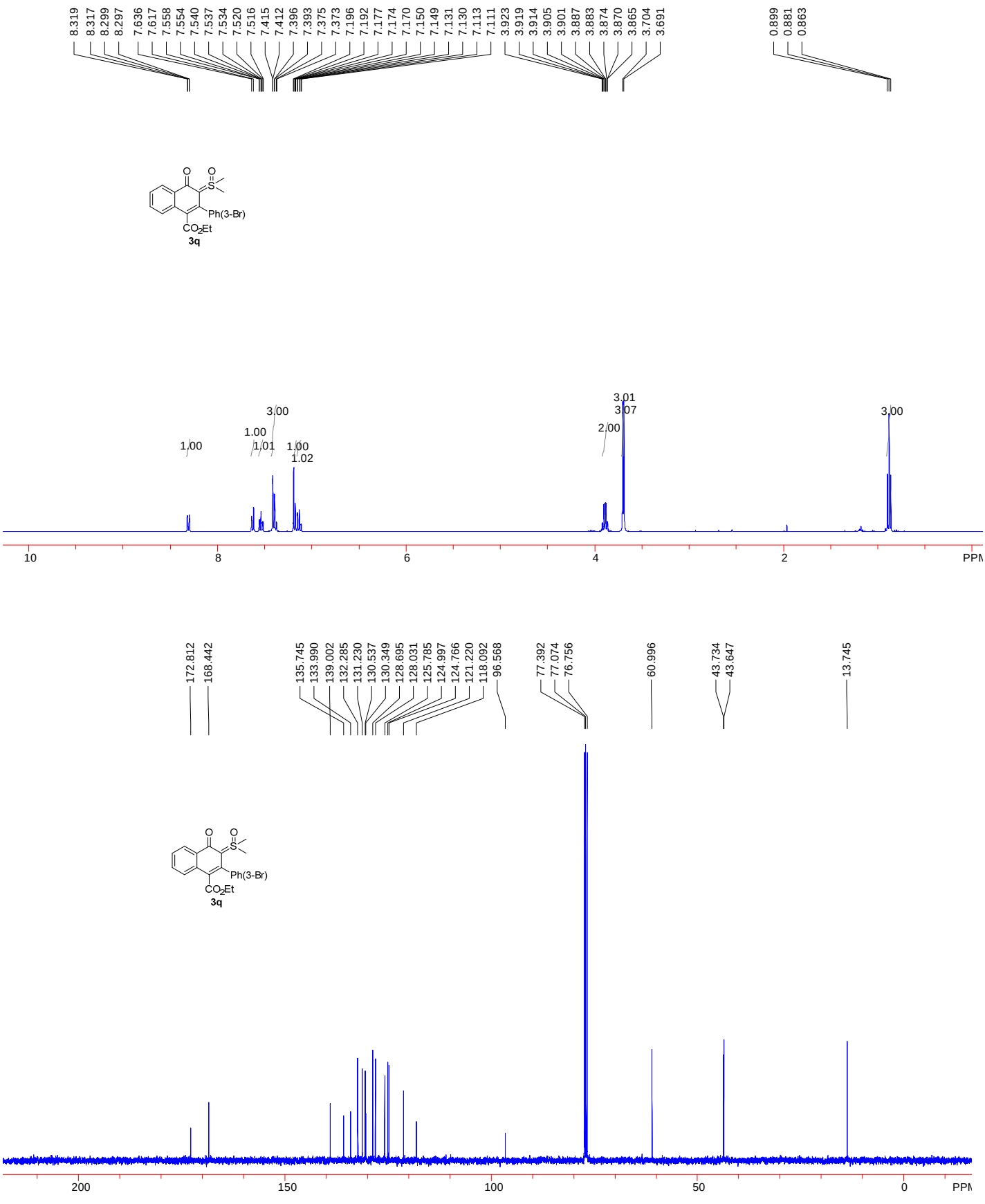
PPM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0.863
Ph(3-Br)
CO2Et
3q
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3.00
1.00
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1.00
1.02
3.01
3.07
2.00
3.00
10
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6
4
2
PPM
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125.785
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77.074
76.756
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13.745
Ph(3-Br)
CO2Et
3q
200
150
100
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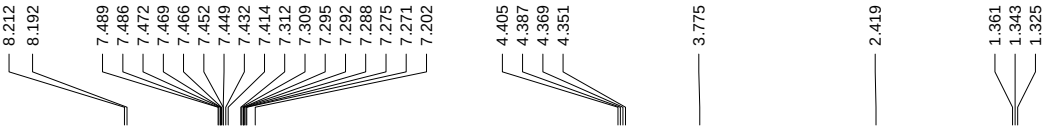
PPM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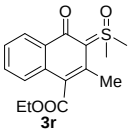
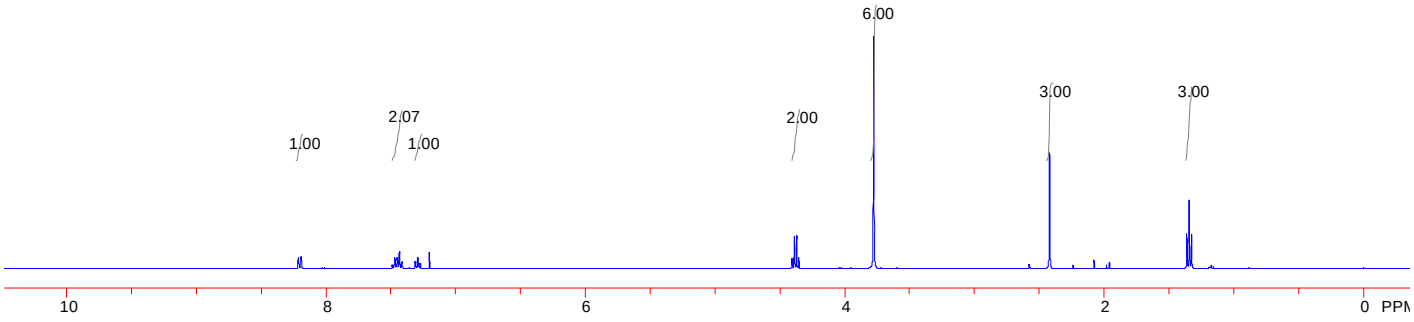
7.489
7.486
7.472
7.469
7.466
7.452
7.449
7.432
7.414
7.312
7.309
7.295
7.292
7.288
7.275
7.271
7.202
4.405
4.387
4.369
4.351
3.775
2.419
1.361
1.343
1.325


O
O
S
Me
EtOOC

3r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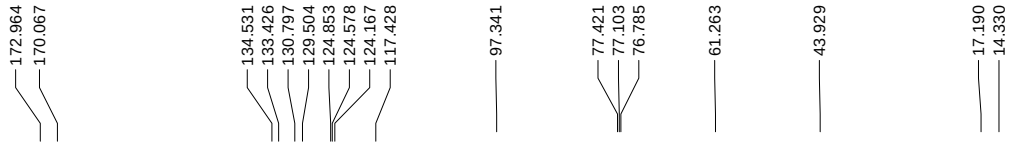
1.00
1.00
10
8
6
4
2
0
PPM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134.531
133.426
130.797
129.504
124.853
124.578
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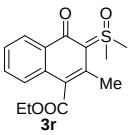
117.428
97.341
77.421
77.103
76.785
61.263
43.929
17.190
14.330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S
Me
EtOOC

3r

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100
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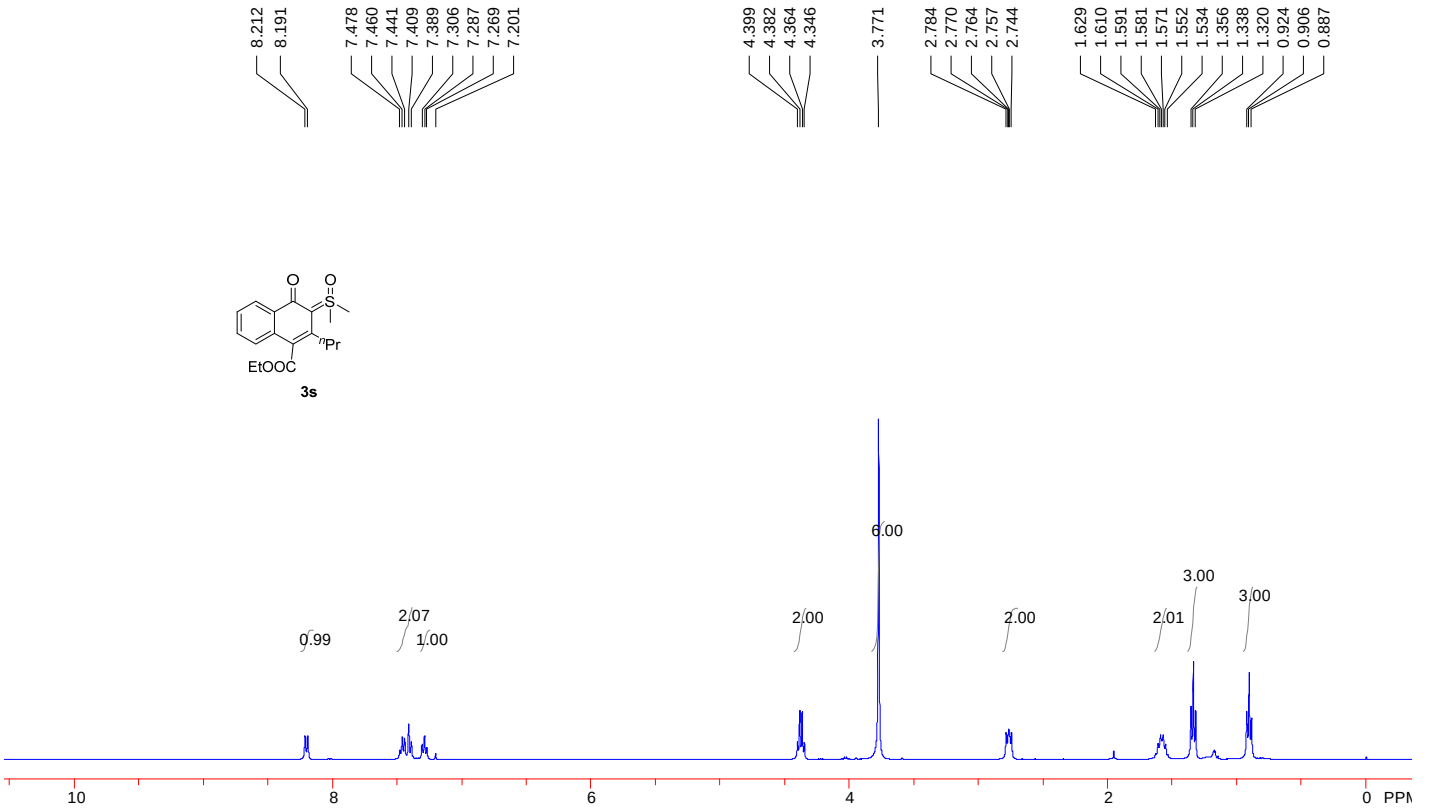
0
PPM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7.389
7.306
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4.399
4.382
4.364
4.346
3.771
2.784
2.770
2.764
2.757
2.744
1.629
1.610
1.591
1.581
1.571
1.552
1.534
1.356
1.338
1.320
0.924
0.906
0.887
EtOOC
3s
0.99
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6.00
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2.01
3.00
3.00
10
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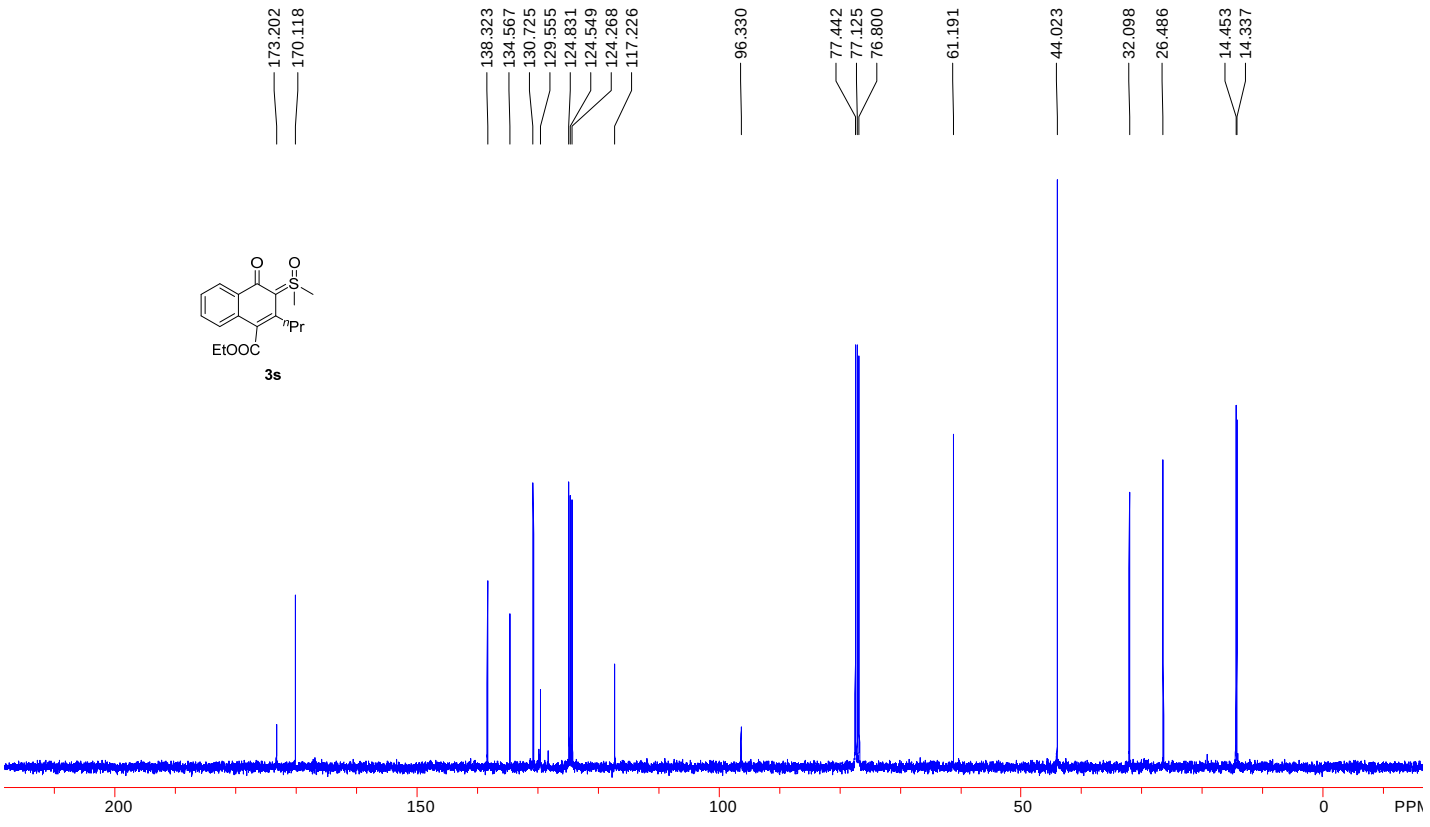
6
4
2
0
PPM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138.323
134.567
130.725
129.555
124.831
124.549
124.268
117.226
96.330
77.442
77.125
76.800
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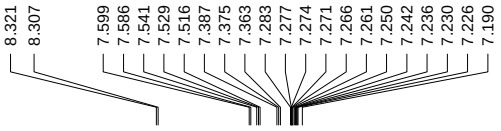
32.098
26.486
14.453
14.337
EtOOC
3s
200
150
100
50
0
PPM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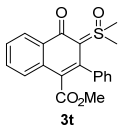
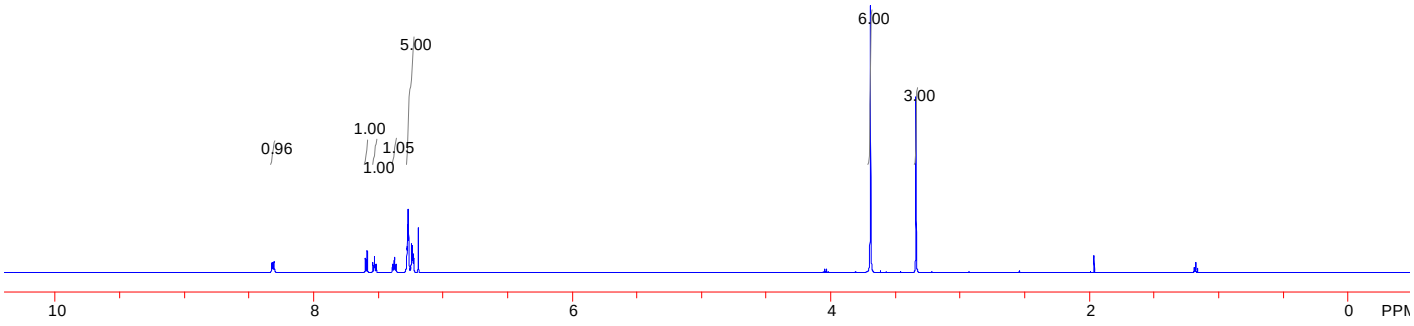
7.586
7.541
7.529
7.516
7.387
7.375
7.363
7.283
7.277
7.274
7.271
7.266
7.261
7.250
7.242
7.236
7.230
7.226
7.190


3.695
3.343


O
O
S
Ph
CO2Me

3t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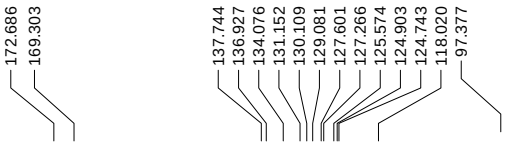
1.00
0.96
1.05
1.00
10
8
6
4
2
0
PPM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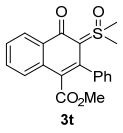
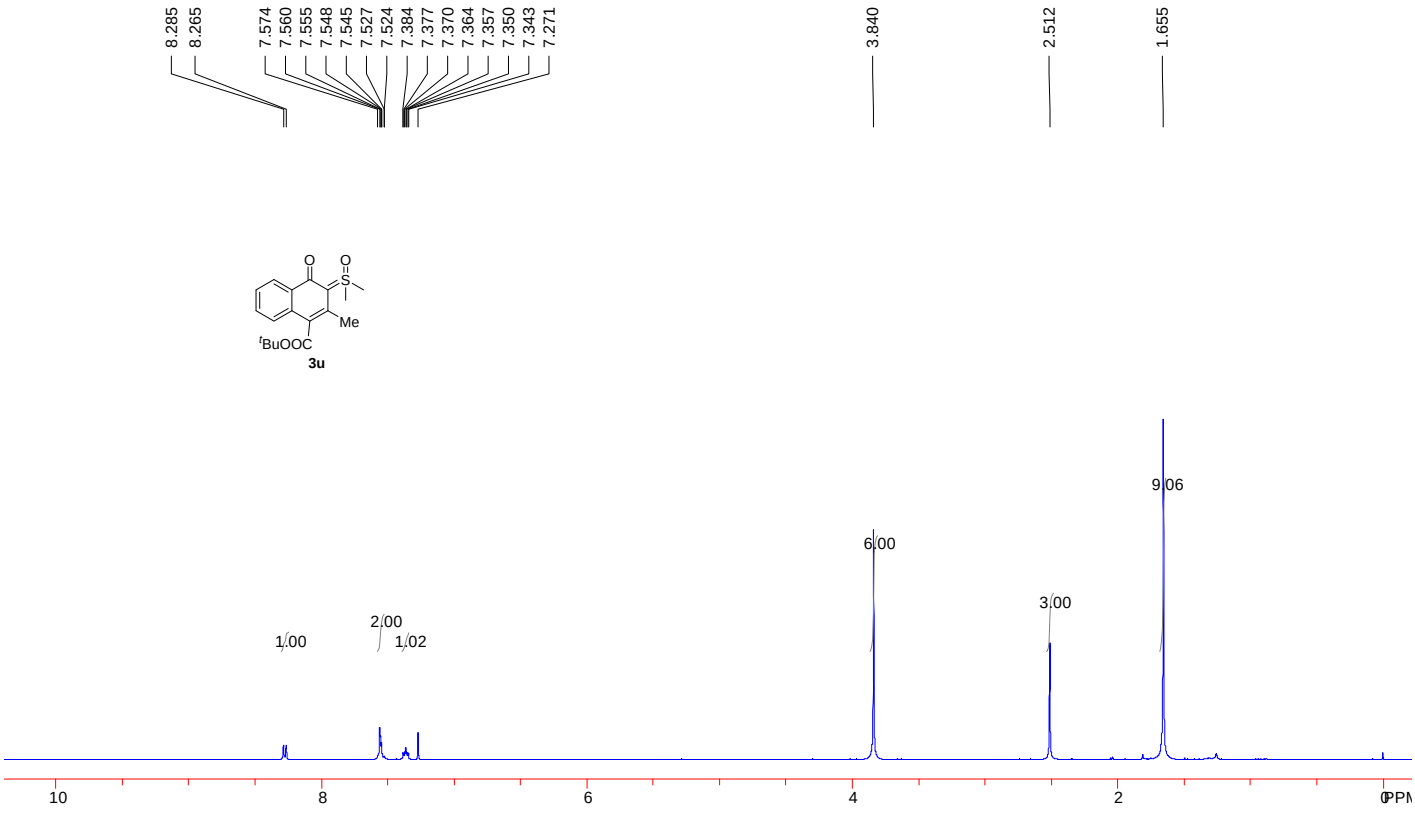
136.927
134.076
131.152
130.109
129.081
127.601
127.266
125.574
124.903
124.743
118.020
97.377
77.295
77.083
76.872
51.723
43.723


O
O
S
Ph
CO2Me

3t

200
150
100
50
0
PPM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8.265
7.574
7.560
7.555
7.548
7.545
7.527
7.524
7.384
7.377
7.370
7.364
7.357
7.350
7.343
7.271
3.840
2.512
1.655
O
O
S
Me
tBuOOC
3u
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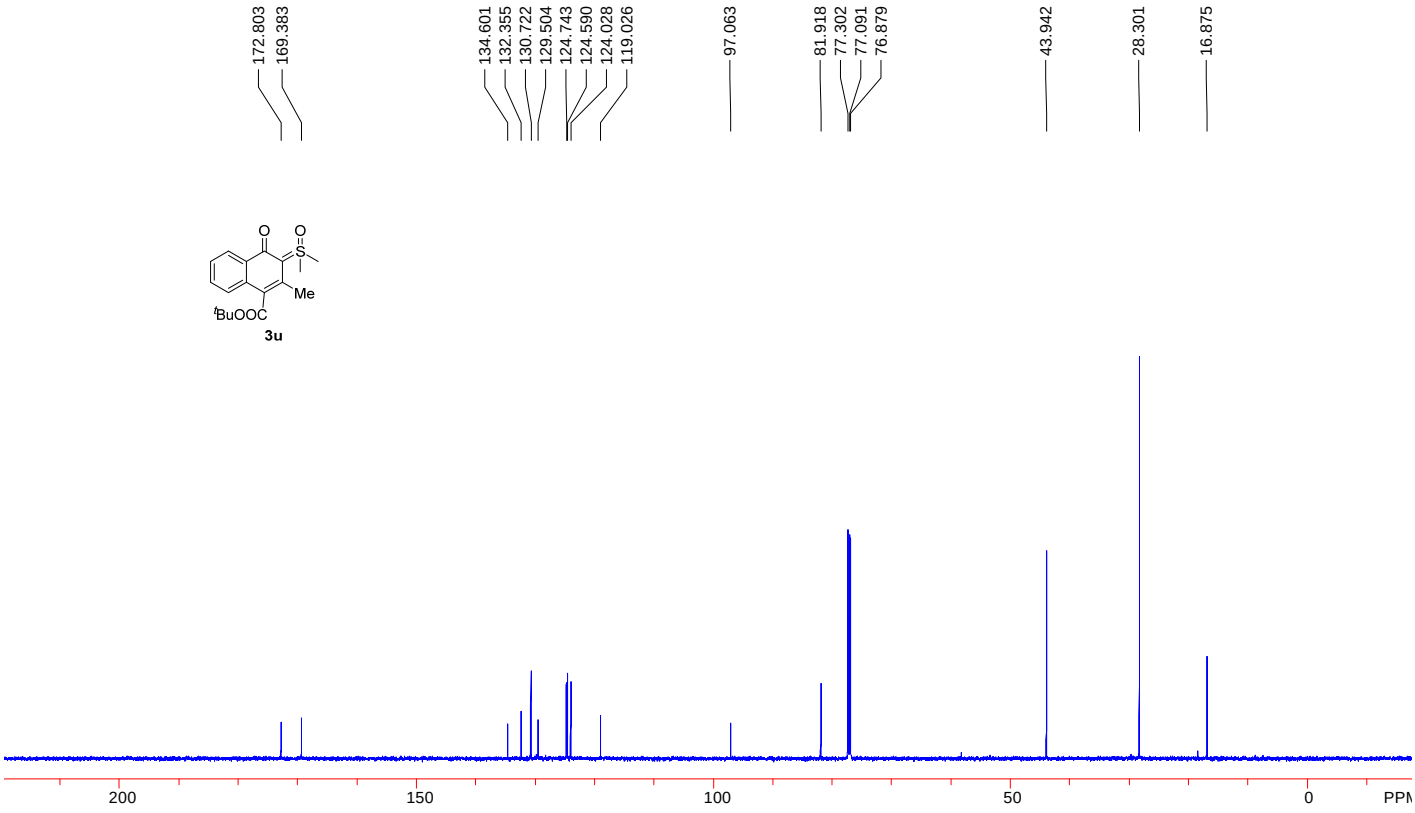
3.00
2.00
1.02
1.00
10
8
6
4
2
0
PPM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130.722
129.504
124.743
124.590
124.028
119.026
97.063
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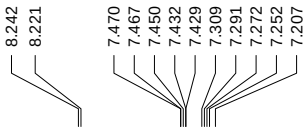
77.302
77.091
76.879
43.942
28.301
16.875
O
O
S
Me
tBuOOC
3u
200
150
100
50
0
PPM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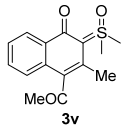
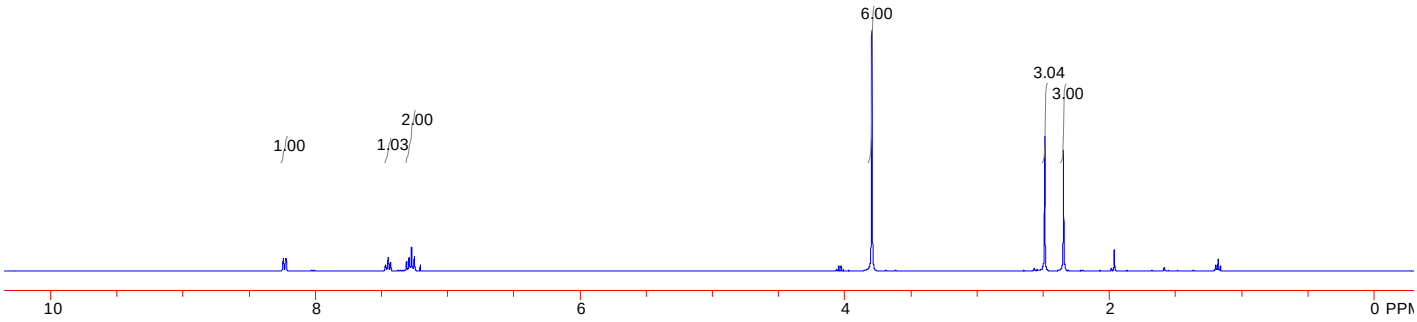
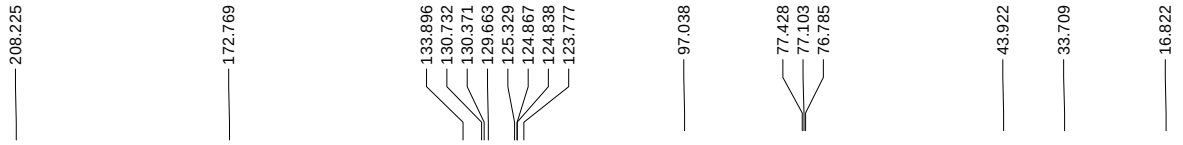
8.221
7.470
7.467
7.450
7.432
7.429
7.309
7.291
7.272
7.252
7.207
3.794
2.486
2.344


O
O
S
Me
MeOC

3v


6.00
3.04
3.00
2.00
1.00
1.03
10
8
6
4
2
0 PPM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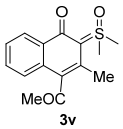
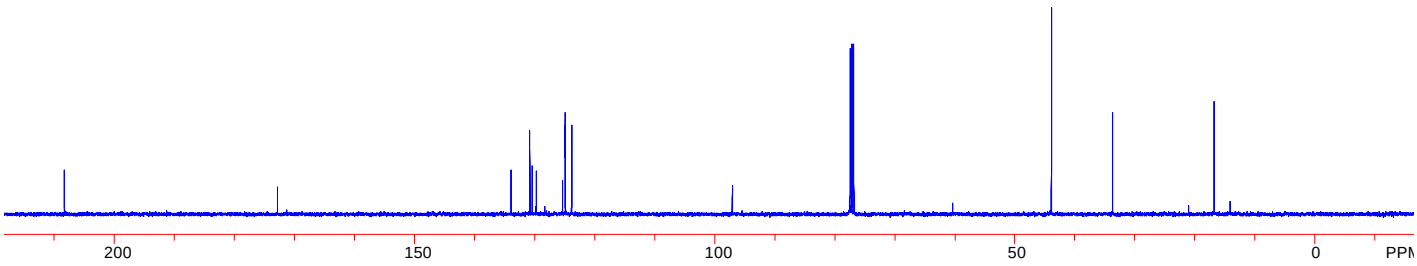
172.769
133.896
130.732
130.371
129.663
125.329
124.867
124.838
123.777
97.038
77.428
77.103
76.785
43.922
33.709
16.822


O
O
S
Me
MeOC

3v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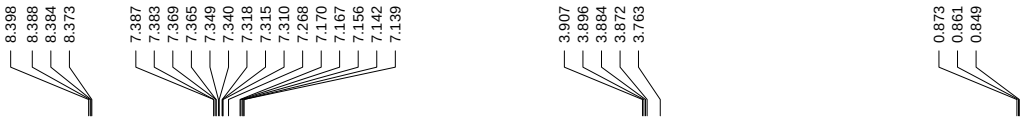
150
100
50
0
PPM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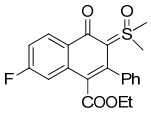
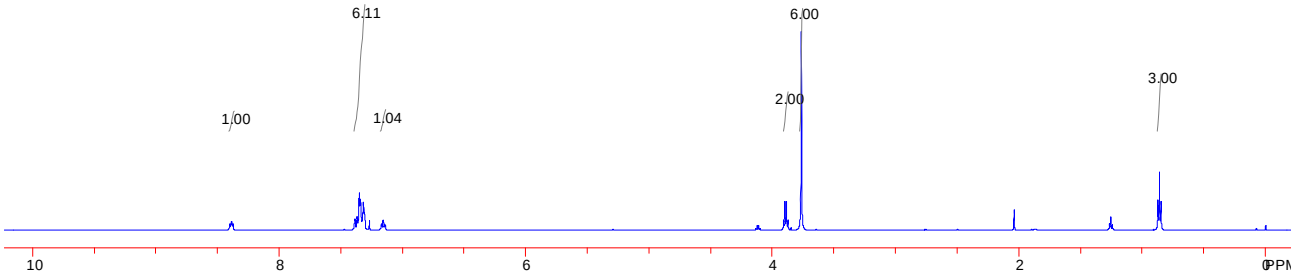
7.383
7.369
7.365
7.349
7.340
7.318
7.315
7.310
7.268
7.170
7.167
7.156
7.142
7.139
3.907
3.896
3.884
3.872
3.763
0.873
0.861
0.849


O
O
S
F
Ph
COOEt

3w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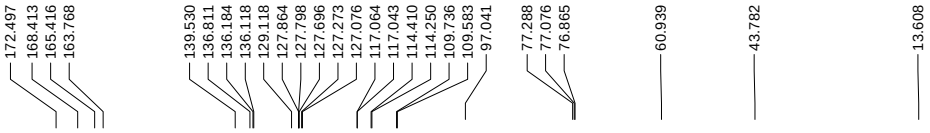
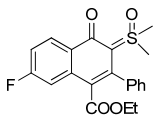
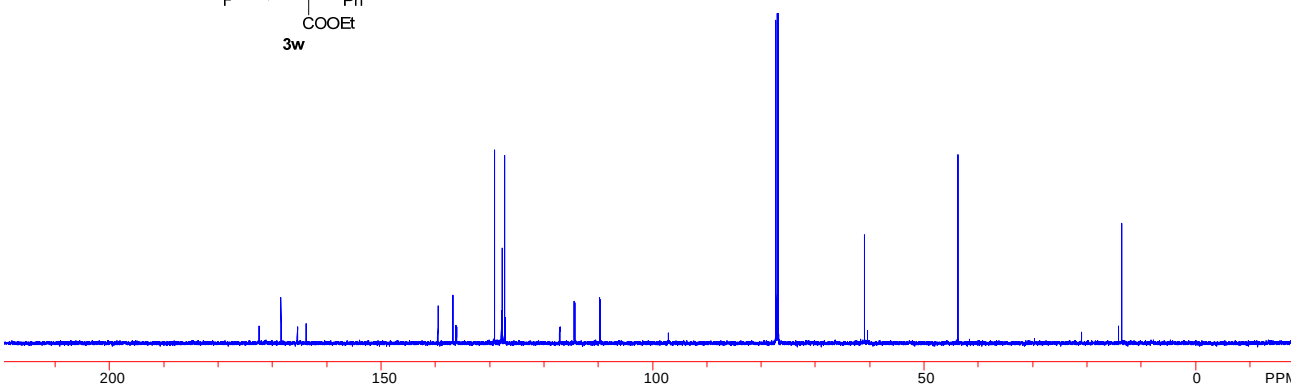
6.00
3.00
2.00
1.00
1.04
10
8
6
4
2
0
PPM


172.497
168.413
165.416
163.768
139.530
136.811
136.184
136.118
129.118
127.864
127.798
127.696
127.273
127.076
117.064
117.043
114.410
114.250
109.736
109.583
97.041
77.288
77.076
76.865
60.939
43.782
13.608


O
O
S
F
Ph
COOEt

3w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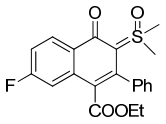
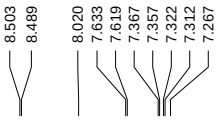
150
100
50
0
PPM



3w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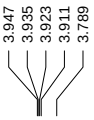
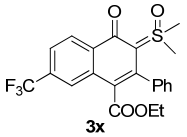
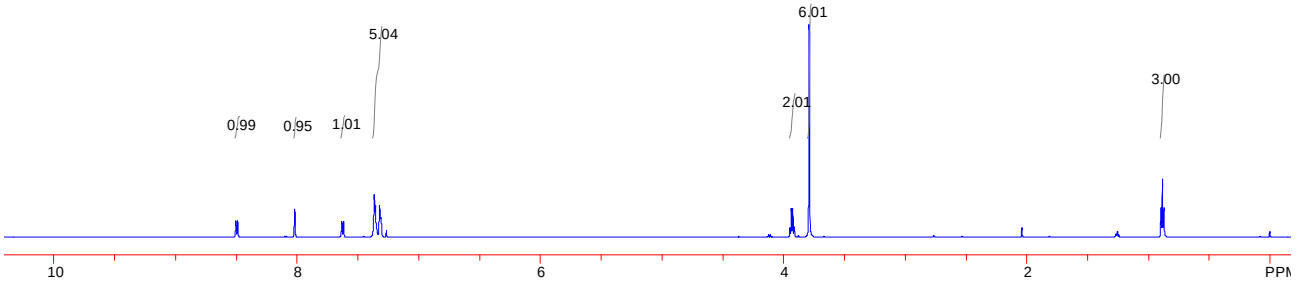
8.489
8.020
7.633
7.619
7.367
7.357
7.322
7.312
7.267

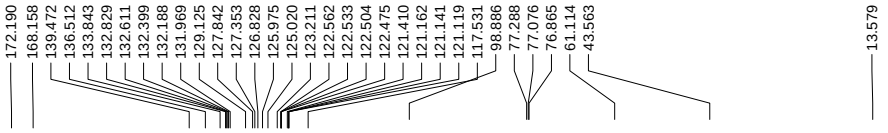

3.947
3.935
3.923
3.911
3.789

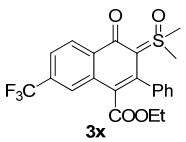

0.894
0.882
0.871


O
O
S
F3C
Ph
COOEt

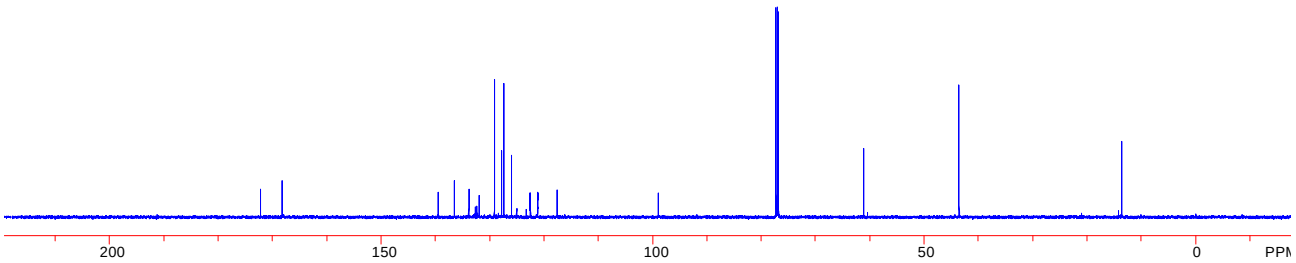
3x

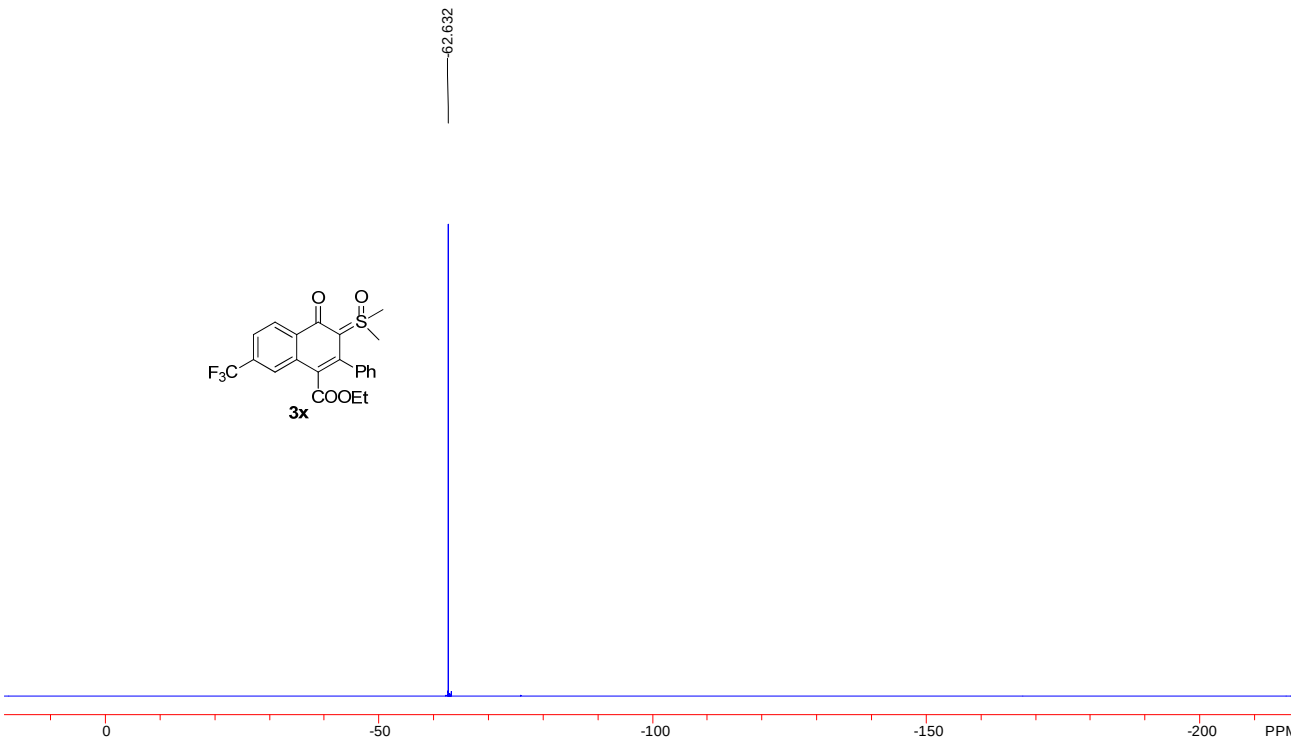

6.01
5.04
3.00
2.01
0.99
0.95
1.01
10
8
6
4
2
PPM


172.190
168.158
139.472
136.512
133.843
132.829
132.611
132.399
132.188
131.969
129.125
127.842
127.353
126.828
125.975
125.020
123.211
122.562
122.533
122.504
122.475
121.410
121.162
121.141
121.119
117.531
98.886
77.288
77.076
76.865
61.114
43.563
13.579

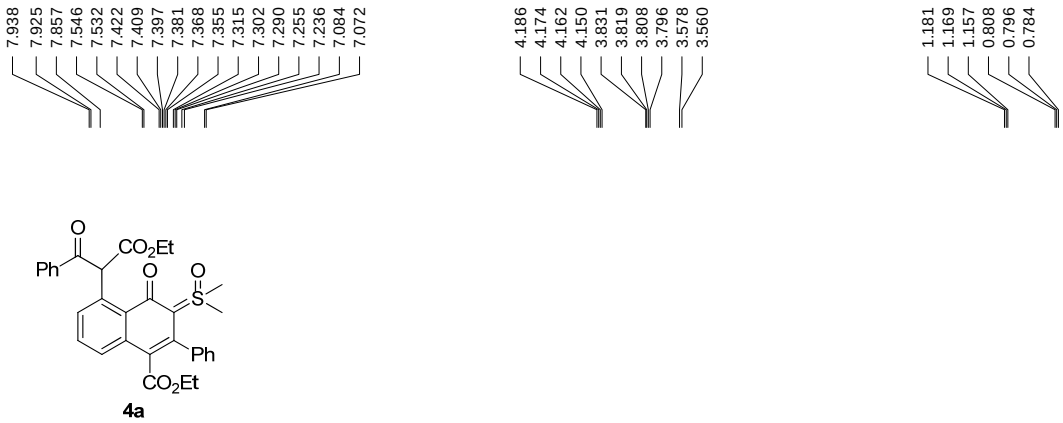

O
O
S
F3C
Ph
COOEt

3x

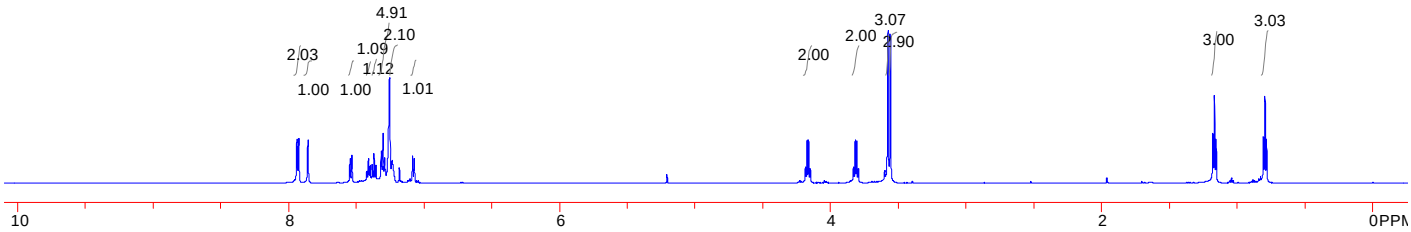

200
150
100
50
0
PPM

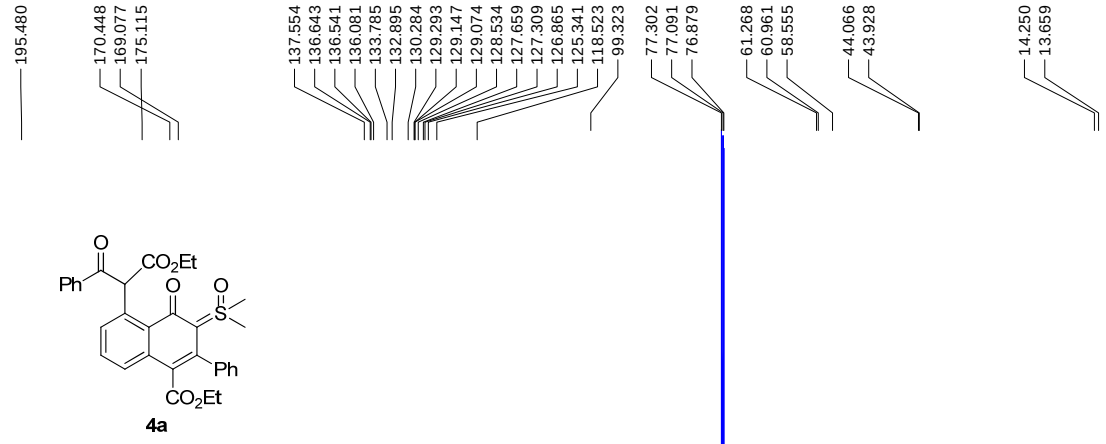

-62.632
O
O
S
F3C
Ph
COOEt
3x
0
-50
-100
-150
-200
PPM

VI. Copies of ^{1}H and ^{13}C NMR spectra of 4a-4t, 5, A. B

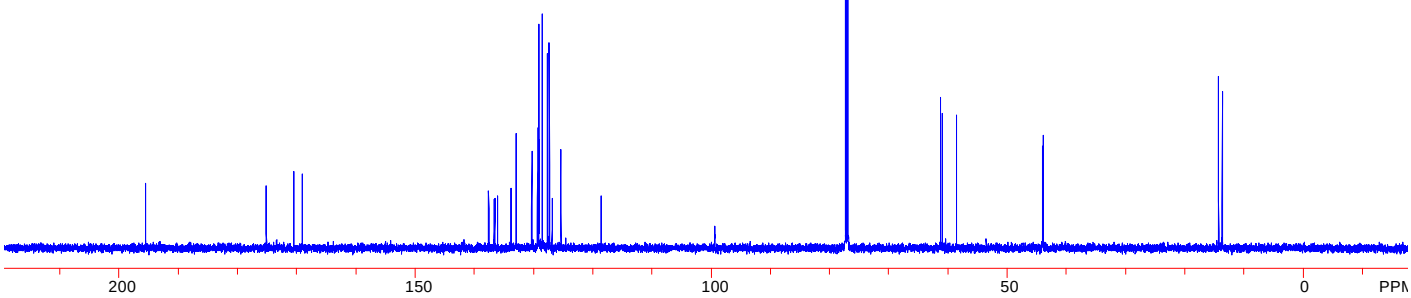


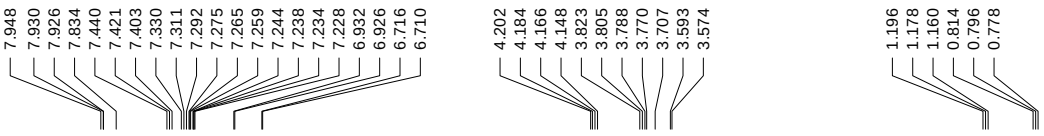
4a





4a




7.948
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7.292
7.275
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7.259
7.244
7.238
7.234
7.228
6.932
6.926
6.716
6.710
4.202
4.184
4.166
4.148
3.823
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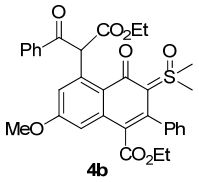
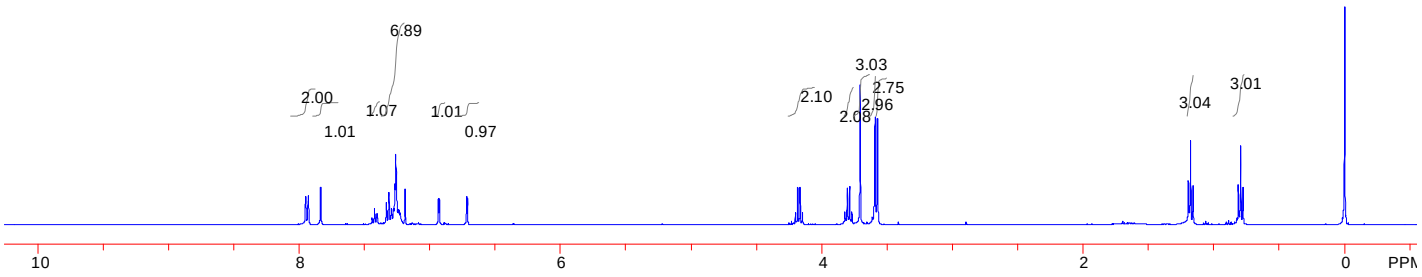
3.574
1.196
1.178
1.160
0.814
0.796
0.778


O
CO2Et
Ph
O
O
S
MeO
Ph
CO2Et

4b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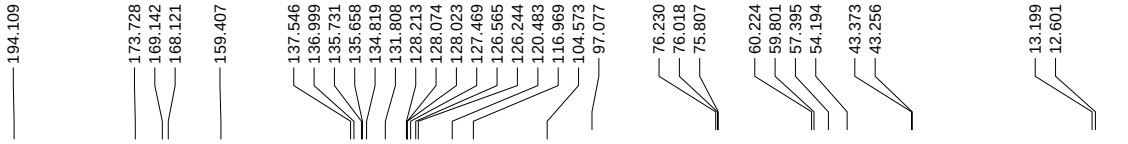
1.07
1.01
1.01
0.97
3.03
2.10
2.75
2.96
2.08
3.04
3.01
10
8
6
4
2
0
PPM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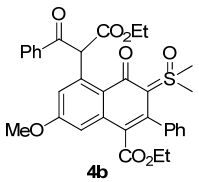
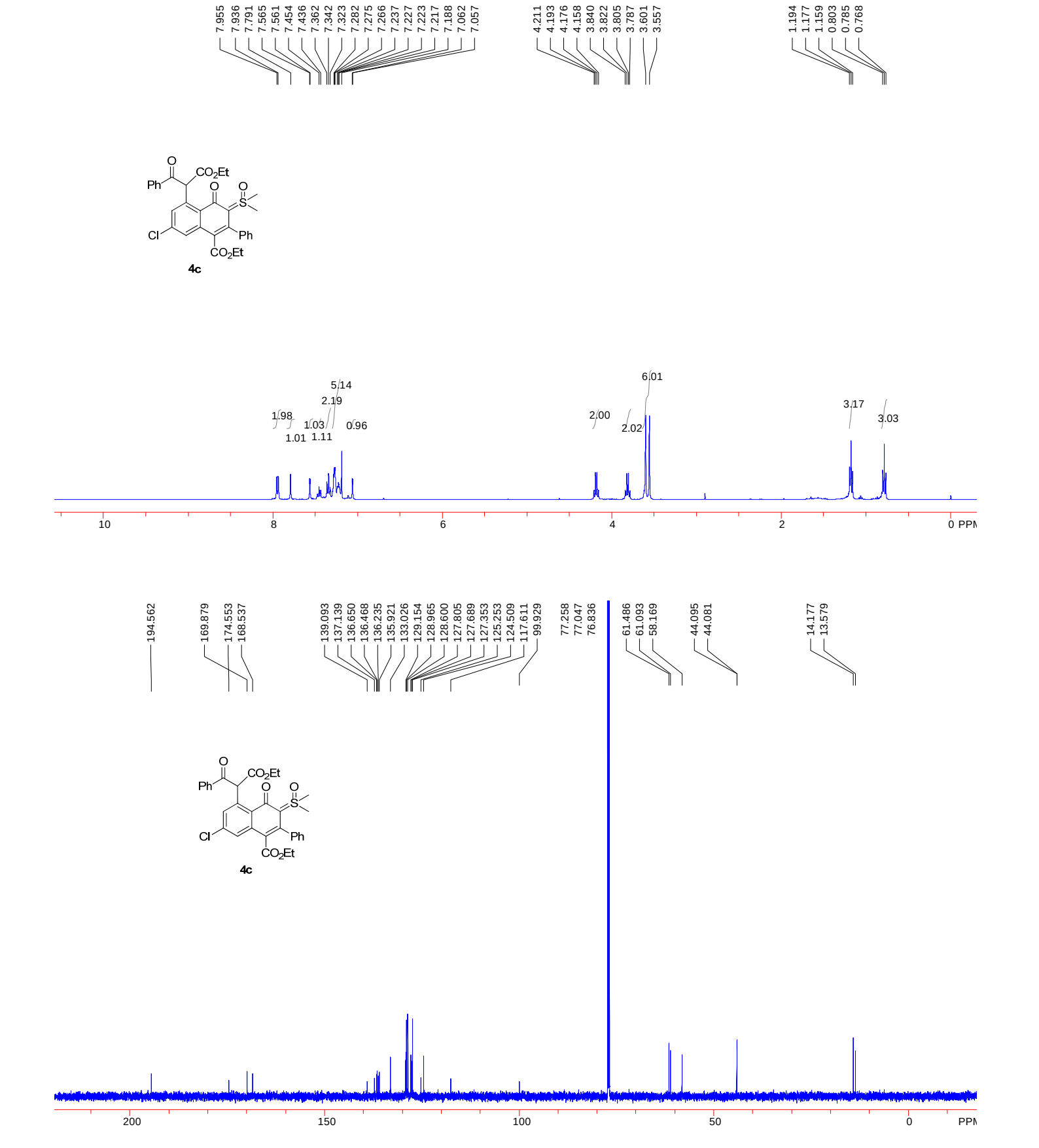
173.728
169.142
168.121
159.407
137.546
136.999
135.731
135.658
134.819
131.808
128.213
128.074
128.023
127.469
126.565
126.244
120.483
116.969
104.573
97.077
76.230
76.018
75.807
60.224
59.801
57.395
54.194
43.373
43.256
13.199
12.601


O
CO2Et
Ph
O
O
S
MeO
Ph
CO2Et

4b

200
150
100
50
0
PPM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7.454
7.436
7.362
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7.323
7.282
7.275
7.266
7.237
7.227
7.223
7.217
7.188
7.062
7.057
4.211
4.193
4.176
4.158
3.840
3.822
3.805
3.787
3.601
3.557
1.194
1.177
1.159
0.803
0.785
0.768
Ph
CO2Et
O
O
S
Cl
Ph
CO2Et
4c
5.14
2.19
1.98
1.03
1.01
1.11
0.96
2.00
2.02
6.01
3.17
3.03
10
8
6
4
2
0 PPM
194.562
169.879
174.553
168.537
139.093
137.139
136.650
136.468
136.235
135.921
133.026
129.154
128.965
128.600
127.805
127.689
127.353
125.253
124.509
117.611
99.929
77.258
77.047
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58.169
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44.081
14.177
13.579
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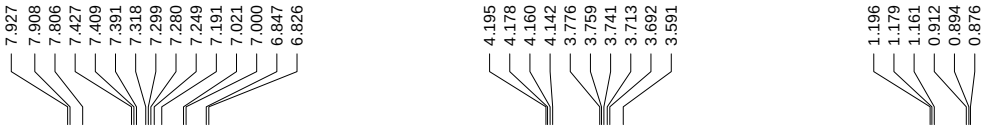
100
50
0
PPM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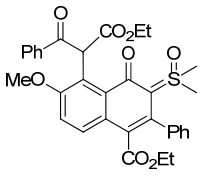
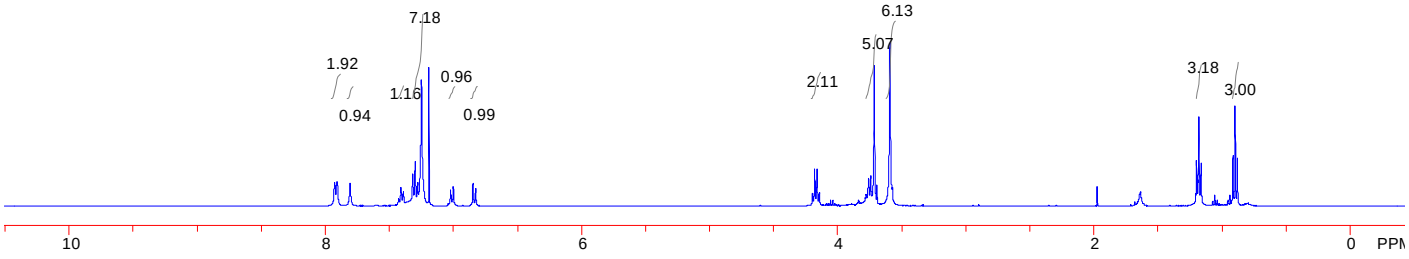
7.806
7.427
7.409
7.391
7.318
7.299
7.280
7.249
7.191
7.021
7.000
6.847
6.826
4.195
4.178
4.160
4.142
3.776
3.759
3.741
3.713
3.692
3.591
1.196
1.179
1.161
0.912
0.894
0.876


O
CO2Et
Ph
O
O
MeO
S
Ph
CO2Et

4d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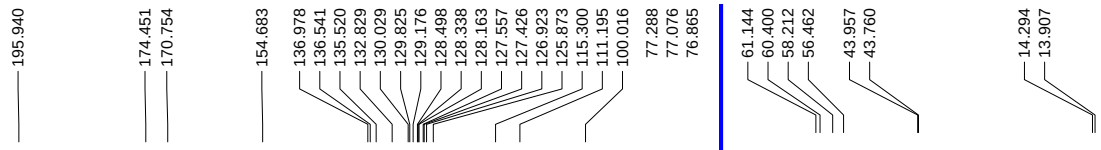
1.92
0.96
1.16
0.94
0.99
6.13
5.07
2.11
3.18
3.00
10
8
6
4
2
0
PPM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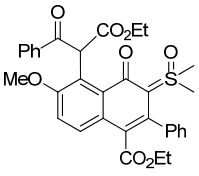
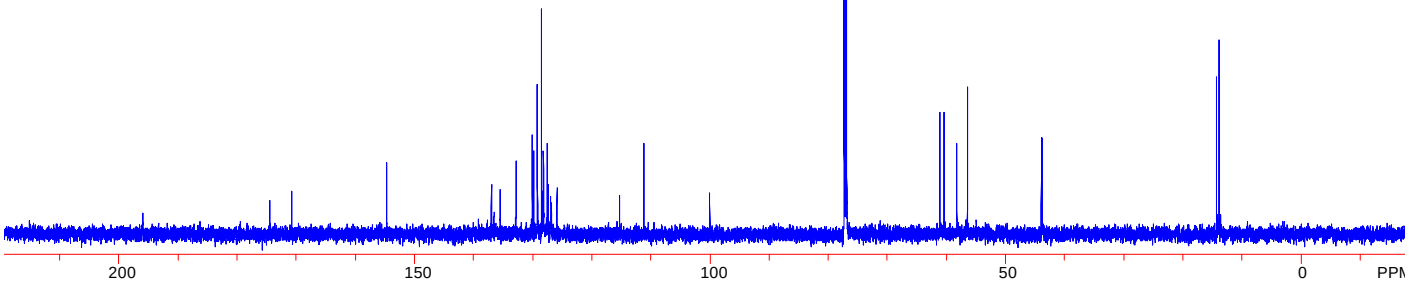
170.754
154.683
136.978
136.541
135.520
132.829
130.029
129.825
129.176
128.498
128.338
128.163
127.557
127.426
126.923
125.873
115.300
111.195
100.016
77.288
77.076
76.865
61.144
60.400
58.212
56.462
43.957
43.760
14.294
13.907


O
CO2Et
Ph
O
O
MeO
S
Ph
CO2Et

4d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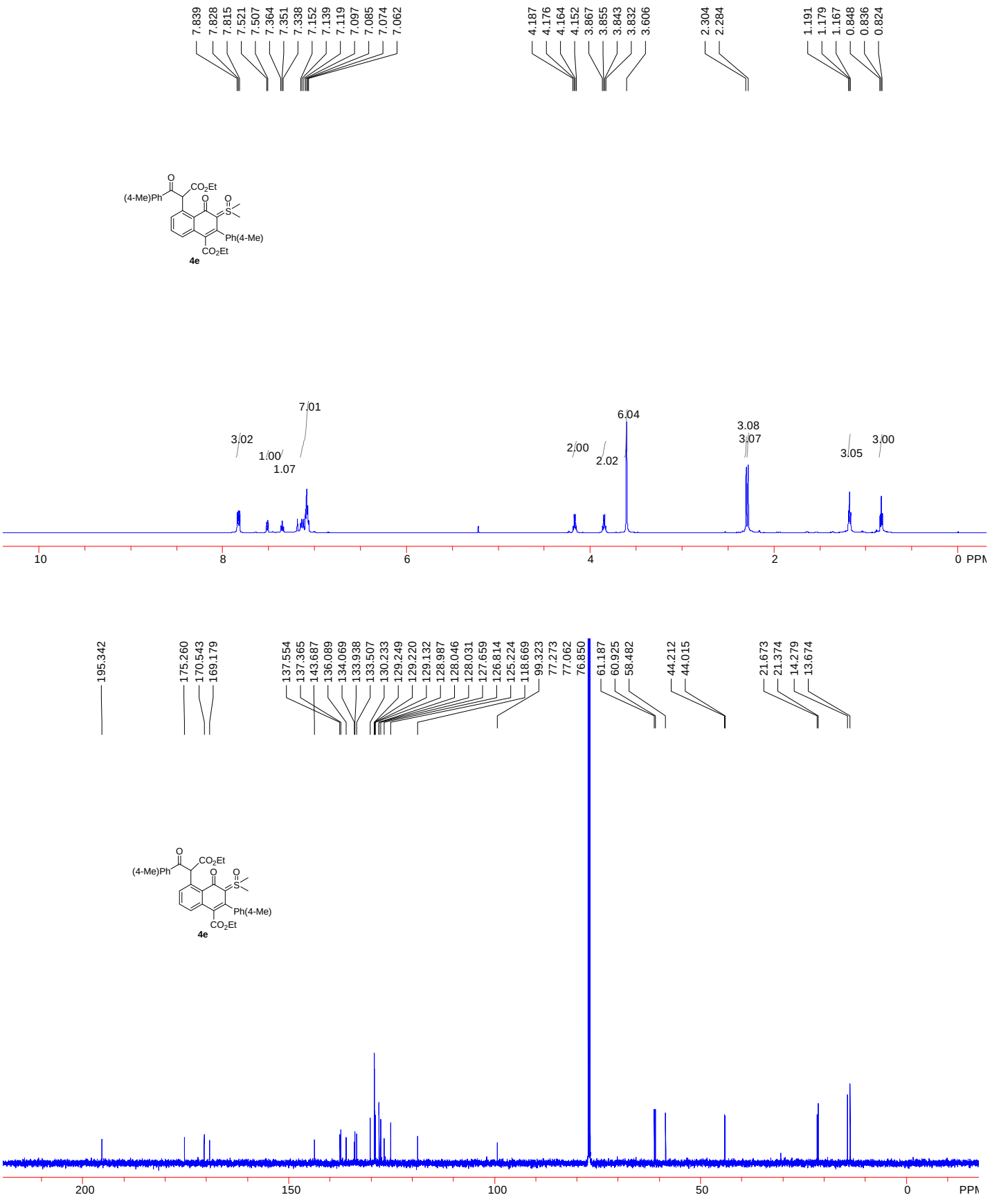
150
100
50
0
PPM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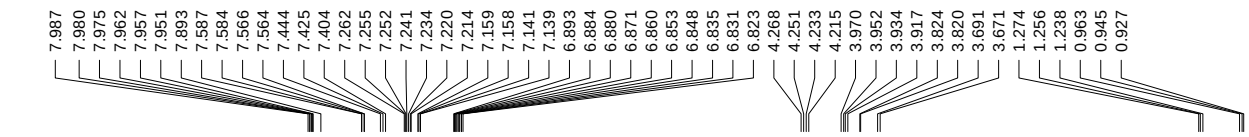
7.507
7.364
7.351
7.338
7.152
7.139
7.119
7.097
7.085
7.074
7.062
4.187
4.176
4.164
4.152
3.867
3.855
3.843
3.832
3.606
2.304
2.284
1.191
1.179
1.167
0.848
0.836
0.824
(4-Me)Ph
CO2Et
O
O
O
S
Ph(4-Me)
CO2Et
4e
3.02
1.00
1.07
7.01
2.00
2.02
6.04
3.08
3.07
3.05
3.00
10
8
6
4
2
0 PPM
195.342
175.260
170.543
169.179
137.554
137.365
143.687
136.089
134.069
133.938
133.507
130.233
129.249
129.220
129.132
128.987
128.046
128.031
127.659
126.814
125.224
118.669
99.323
77.273
77.062
76.850
61.187
60.925
58.482
44.212
44.015
21.673
21.374
14.279
13.674
(4-Me)Ph
CO2Et
O
O
O
S
Ph(4-Me)
CO2Et
4e
200
150
100
50
0
PPM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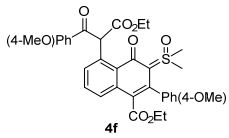
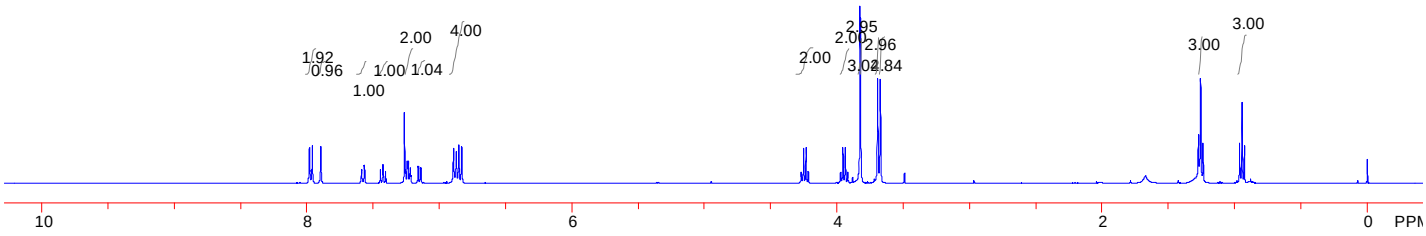
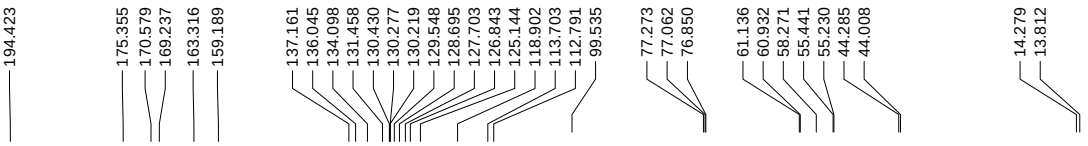
7.951
7.893
7.587
7.584
7.566
7.564
7.444
7.425
7.404
7.262
7.255
7.252
7.241
7.234
7.220
7.214
7.159
7.158
7.141
7.139
6.893
6.884
6.880
6.871
6.860
6.853
6.848
6.835
6.831
6.823
4.268
4.251
4.233
4.215
3.970
3.952
3.934
3.917
3.824
3.820
3.691
3.671
1.274
1.256
1.238
0.963
0.945
0.927


(4-MeO)Ph
CO2Et
O
O
O
S
Ph(4-OMe)
CO2Et

4f


1.92
0.96
1.00
1.00
2.00
1.04
4.00
2.00
2.00
2.95
2.96
3.02
2.84
3.00
3.00
10
8
6
4
2
0
PPM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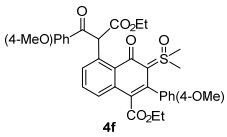
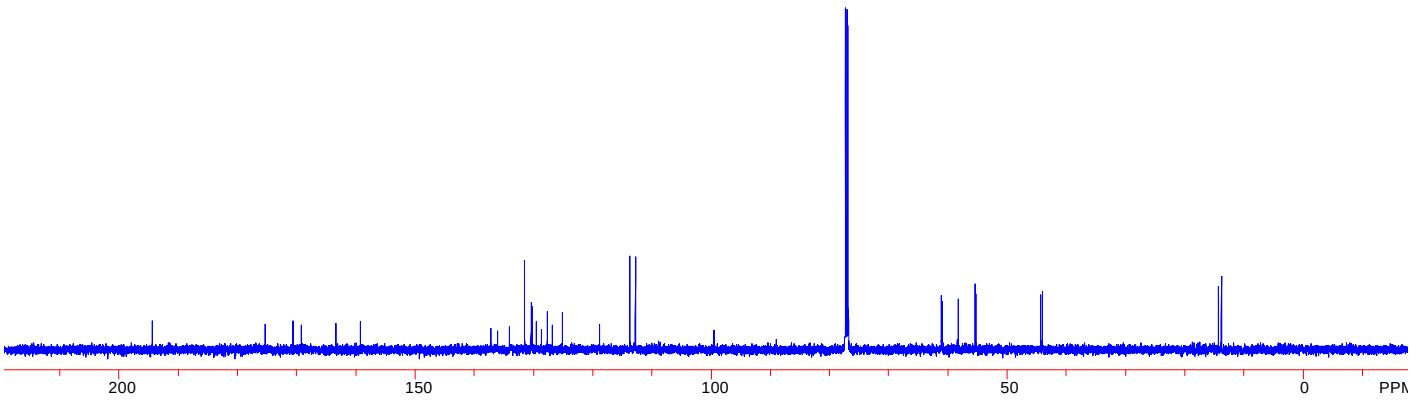
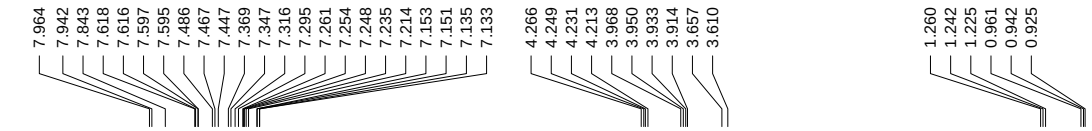
170.579
169.237
163.316
159.189
137.161
136.045
134.098
131.458
130.430
130.277
130.219
129.548
128.695
127.703
126.843
125.144
118.902
113.703
112.791
99.535
77.273
77.062
76.850
61.136
60.932
58.271
55.441
55.230
44.285
44.008
14.279
13.812


(4-MeO)Ph
CO2Et
O
O
O
S
Ph(4-OMe)
CO2Et

4f


200
150
100
50
0
PPM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7.595
7.486
7.467
7.447
7.369
7.347
7.316
7.295
7.261
7.254
7.248
7.235
7.214
7.153
7.151
7.135
7.133
4.266
4.249
4.231
4.213
3.968
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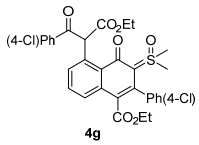
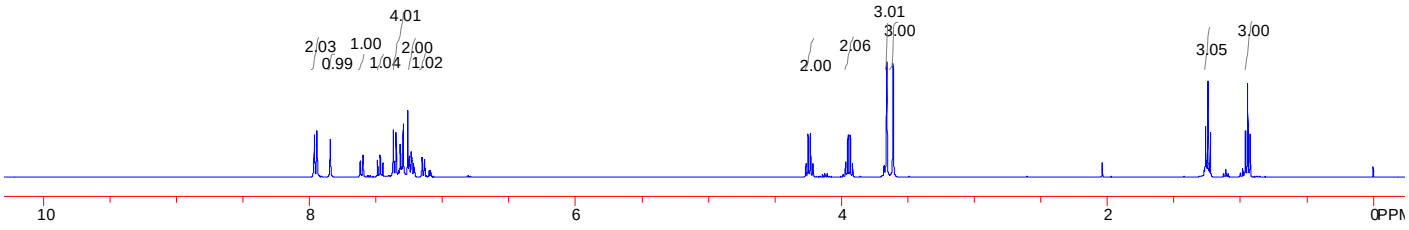
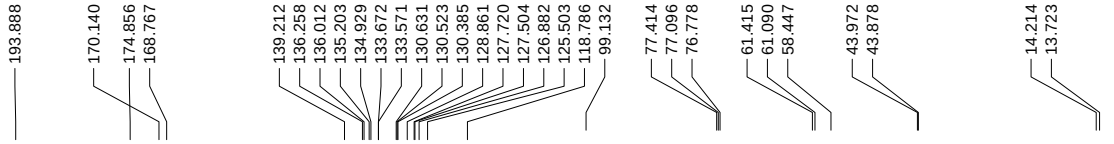
3.933
3.914
3.657
3.610
1.260
1.242
1.225
0.961
0.942
0.925


(4-Cl)Ph
CO2Et
O
O
O
S
Ph(4-Cl)
CO2Et

4g


4.01
2.03
1.00
2.00
0.99
1.04
1.02
3.01
3.00
2.06
2.00
3.05
3.00
10
8
6
4
2
0
PPM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174.856
168.767
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136.258
136.012
135.203
134.929
133.672
133.571
130.631
130.523
130.385
128.861
127.720
127.504
126.882
125.503
118.786
99.132
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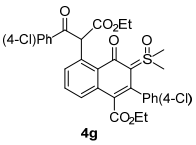
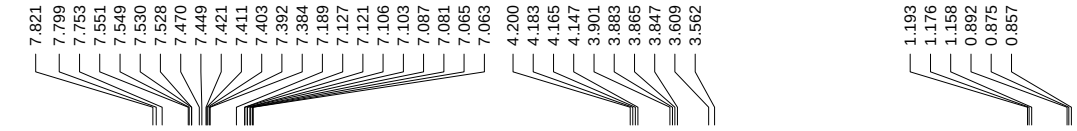
77.096
76.778
61.415
61.090
58.447
43.972
43.878
14.214
13.723


(4-Cl)Ph
CO2Et
O
O
O
S
Ph(4-Cl)
CO2Et

4g

200
150
100
50
0
PPM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7.753
7.551
7.549
7.530
7.528
7.470
7.449
7.421
7.411
7.403
7.392
7.384
7.189
7.127
7.121
7.106
7.103
7.087
7.081
7.065
7.063
4.200
4.183
4.165
4.147
3.901
3.883
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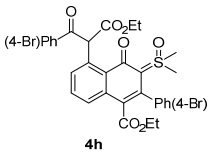
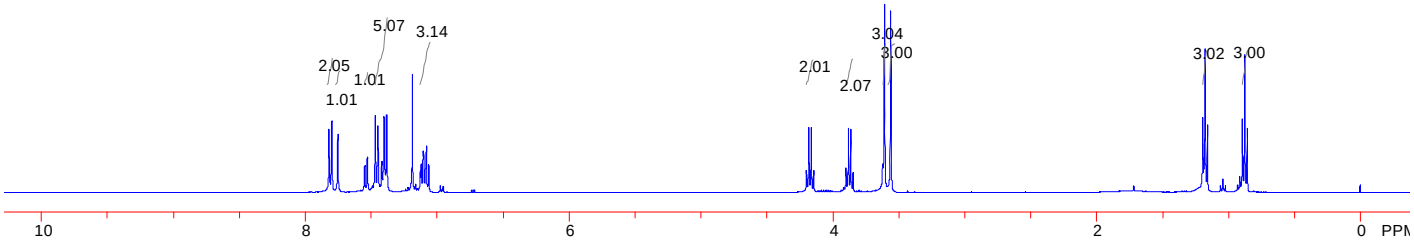
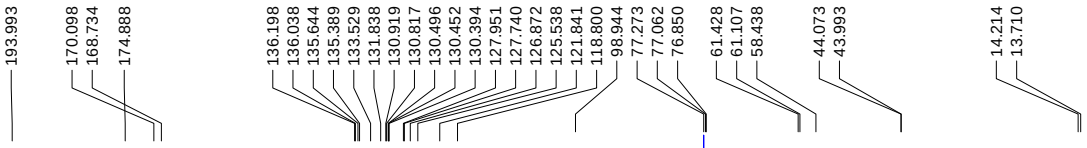
3.847
3.609
3.562
1.193
1.176
1.158
0.892
0.875
0.857


(4-Br)Ph
CO2Et
O
O
O
S
Ph(4-Br)
CO2Et

4h


5.07
3.14
2.05
1.01
1.01
2.01
2.07
3.04
3.00
3.02
3.00
10
8
6
4
2
0
PPM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174.888
136.198
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135.389
133.529
131.838
130.919
130.817
130.496
130.452
130.394
127.951
127.740
126.872
125.538
121.841
118.800
98.944
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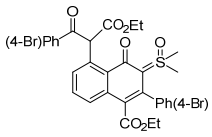
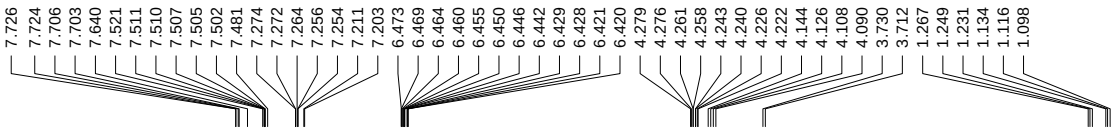
77.062
76.850
61.428
61.107
58.438
44.073
43.993
14.214
13.710


(4-Br)Ph
CO2Et
O
O
O
S
Ph(4-Br)
CO2Et

4h

200
150
100
50
0
PPM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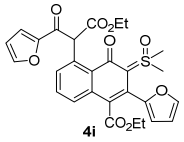
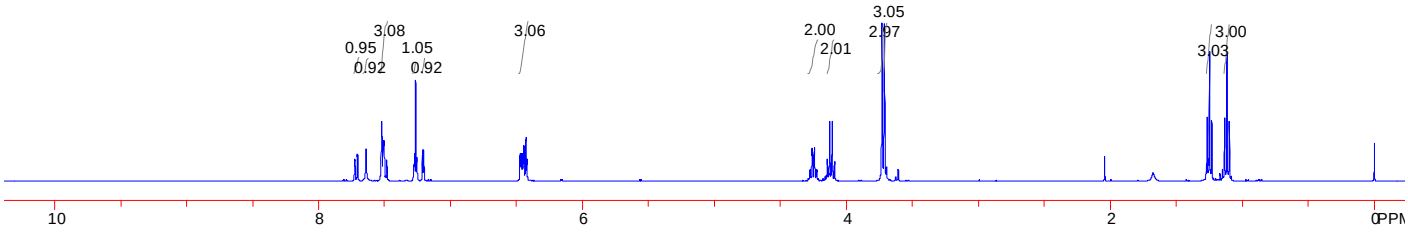
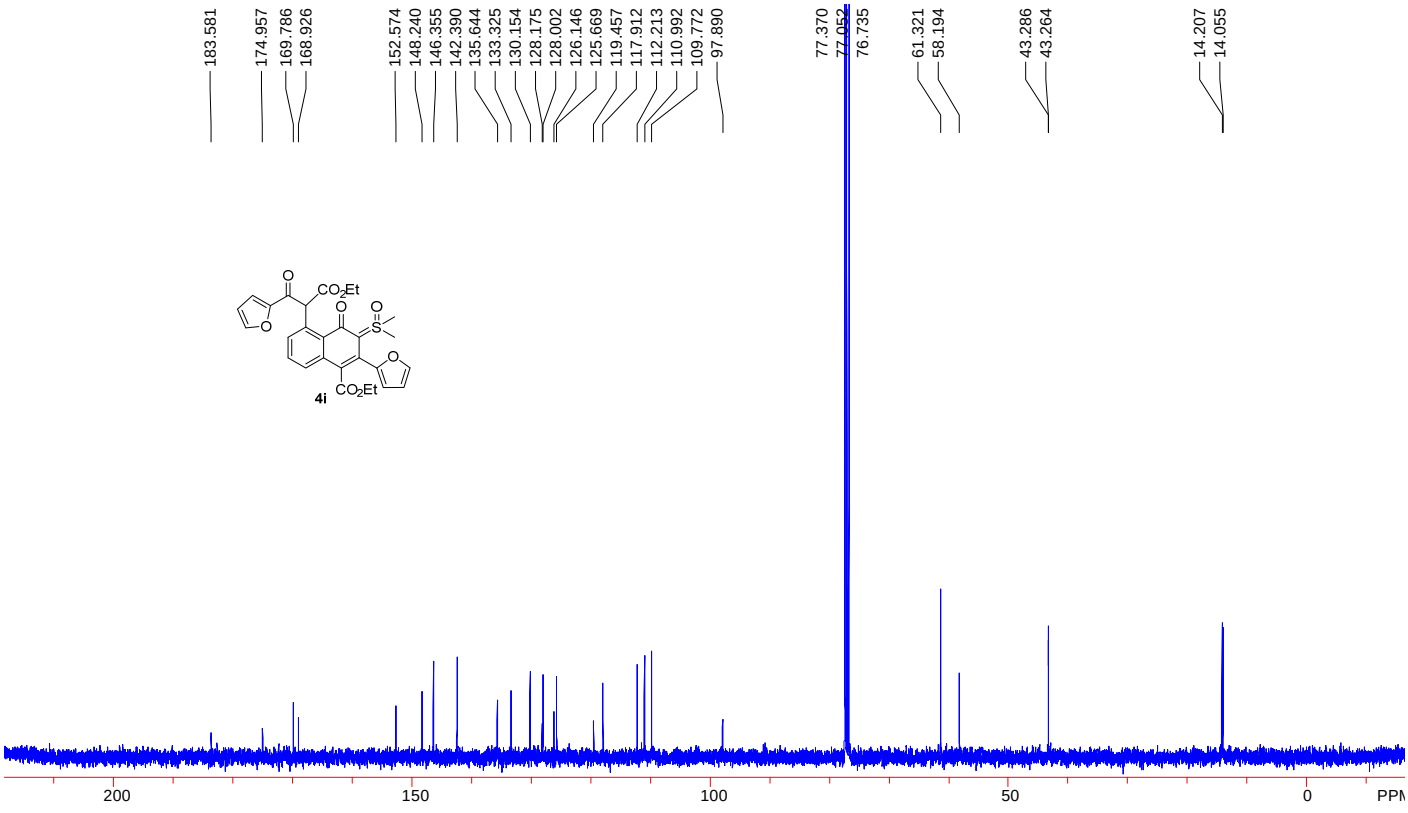
7.703
7.640
7.521
7.511
7.510
7.507
7.505
7.502
7.481
7.274
7.272
7.264
7.256
7.254
7.211
7.203
6.473
6.469
6.464
6.460
6.455
6.450
6.446
6.442
6.429
6.428
6.421
6.420
4.279
4.276
4.261
4.258
4.243
4.240
4.226
4.222
4.144
4.126
4.108
4.090
3.730
3.712
1.267
1.249
1.231
1.134
1.116
1.098


CO2Et
O
O
S
O
O
CO2Et
4i


3.08
0.95
1.05
0.92
0.92
3.06
2.00
2.01
3.05
2.97
3.00
3.03
10
8
6
4
2
0
PPM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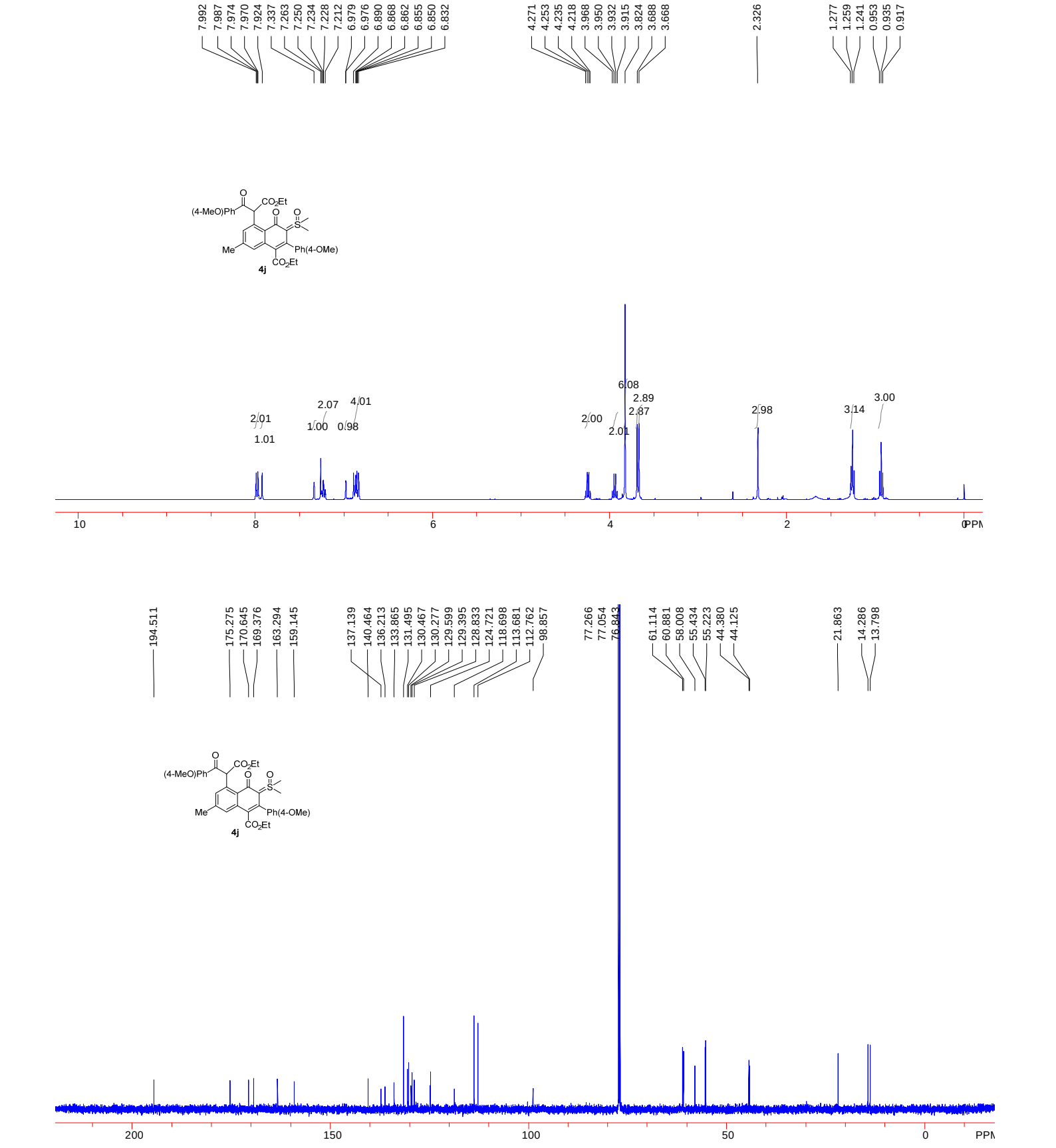
174.957
169.786
168.926
152.574
148.240
146.355
142.390
135.644
133.325
130.154
128.175
128.002
126.146
125.669
119.457
117.912
112.213
110.992
109.772
97.890
77.370
77.052
76.735
61.321
58.194
43.286
43.264
14.207
14.055
CO2Et
O
O
S
O
O
CO2Et
4i
200
150
100
50
0
PPM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4.218
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3.915
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1.259
1.241
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0.935
0.917
(4-MeO)Ph
CO2Et
O
O
S
Me
Ph(4-OMe)
CO2Et
4j
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1.01
2.07
1.00
4.01
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2.01
6.08
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3.14
3.00
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6
4
2
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136.213
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113.681
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76.843
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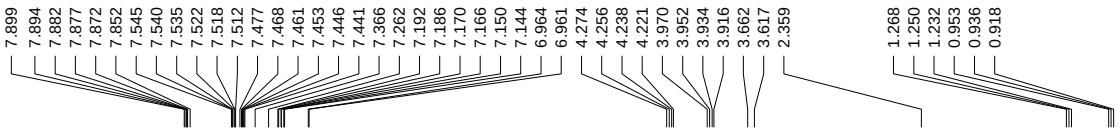
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7.150
7.144
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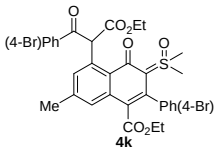
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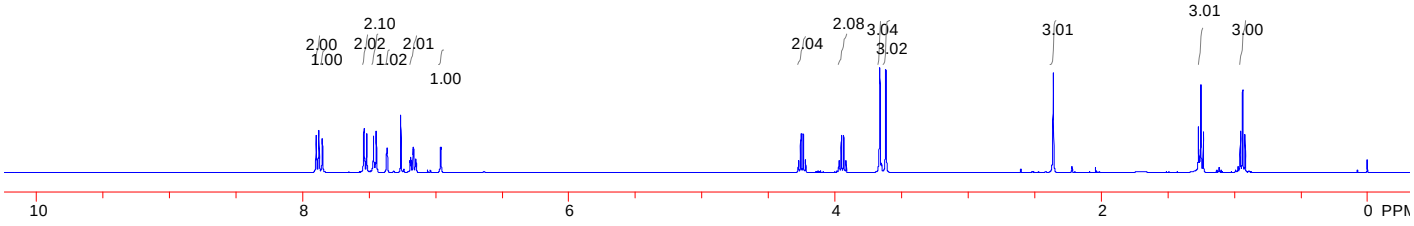
O
O
S
Me
Ph(4-Br)
CO2Et

4k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2
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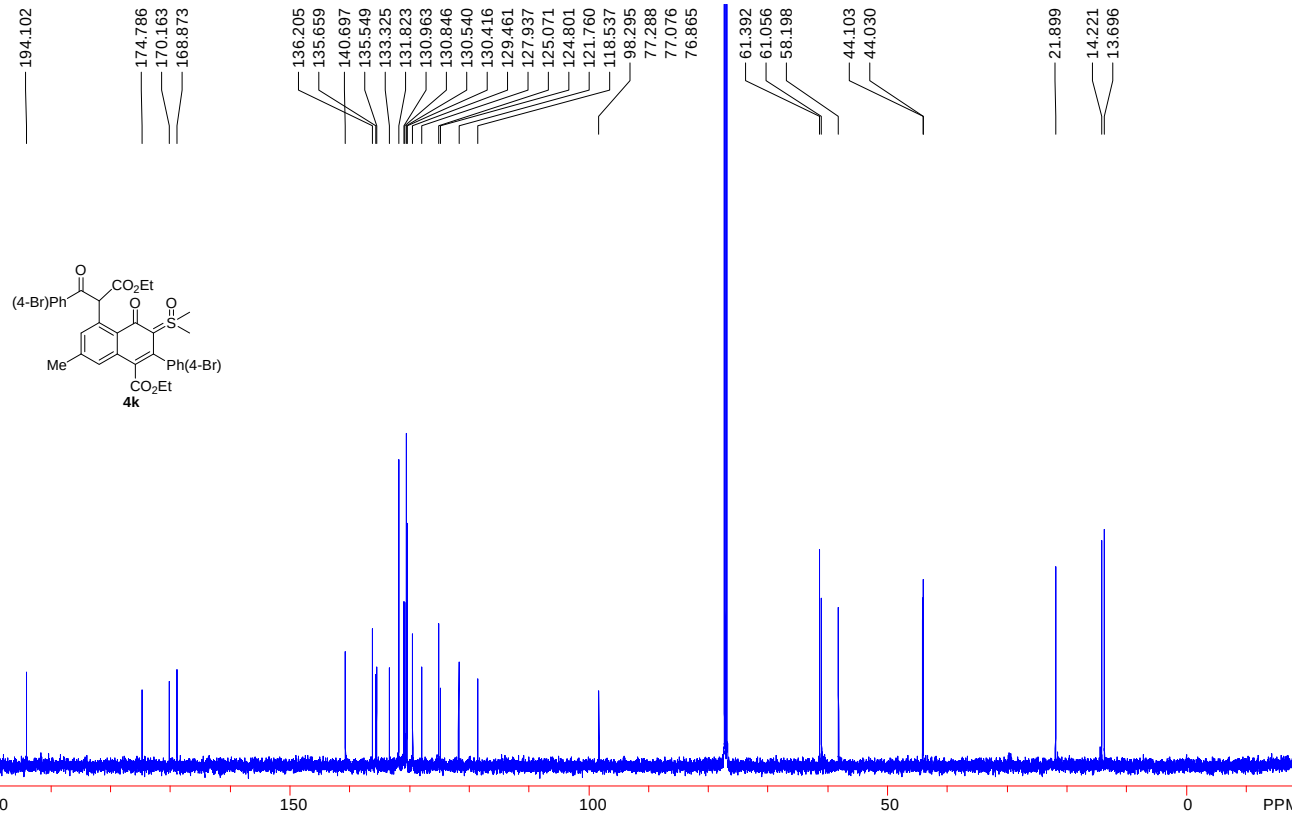
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130.416
129.461
127.937
125.071
124.801
121.760
118.537
98.295
77.288
77.076
76.865
61.392
61.056
58.198
44.103
44.030
21.899
14.221
13.696
200
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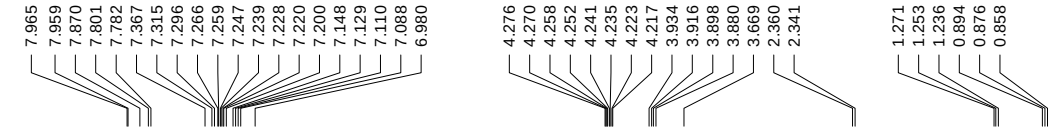
PPM

O
CO2Et
(4-Br)Ph
O
O
S
Me
Ph(4-Br)
CO2Et

4k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7.247
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7.228
7.220
7.200
7.148
7.129
7.110
7.088
6.980
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4.270
4.258
4.252
4.241
4.235
4.223
4.217
3.934
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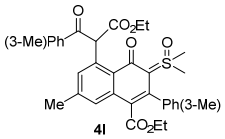
0.858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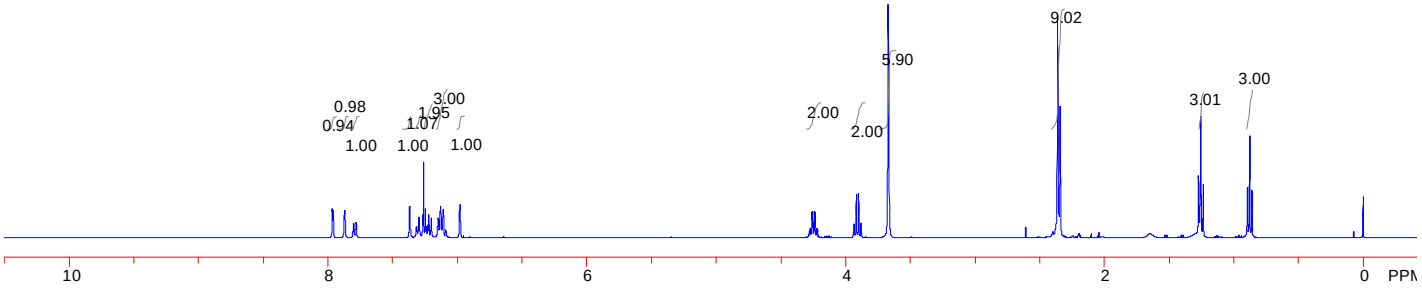
CO2Et
O
O
S
Me
Ph(3-Me)
CO2Et
4l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10
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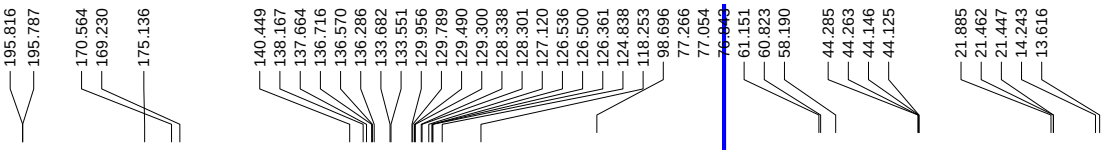
PPM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126.361
124.838
118.253
98.696
77.266
77.054
76.843
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21.447
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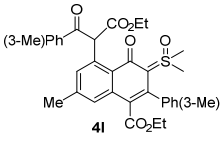
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CO2Et
O
O
S
Me
Ph(3-Me)
CO2Et
4l

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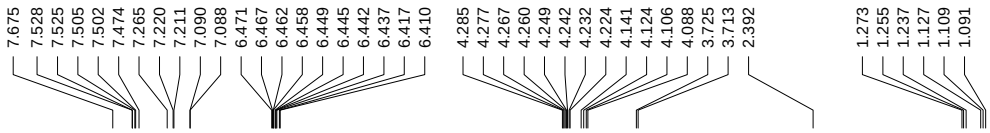
150
100
50
0
PPM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7.220
7.211
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7.088
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6.467
6.462
6.458
6.449
6.445
6.442
6.437
6.417
6.410
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4.267
4.260
4.249
4.242
4.232
4.224
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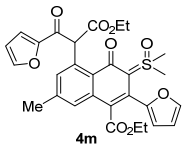
1.127
1.109
1.091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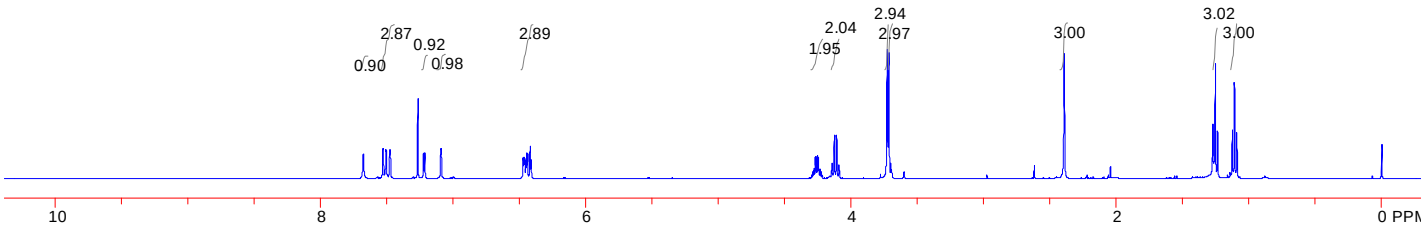
O
O
S
O
Me
O
CO2Et
4m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3.02
3.00
10
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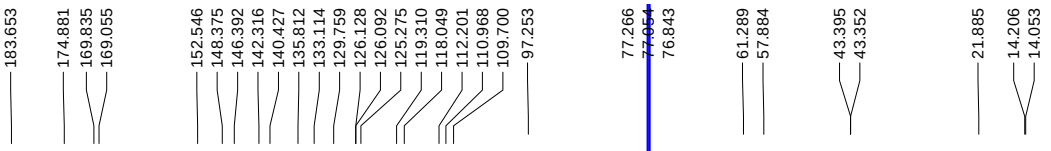
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119.310
118.049
112.201
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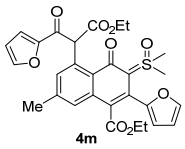
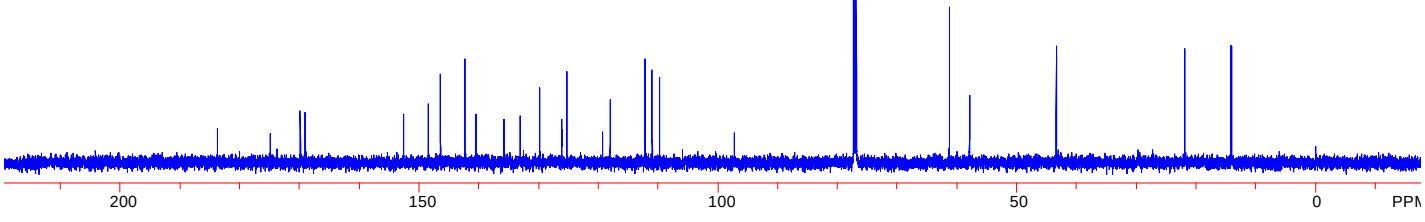
14.053


CO2Et
O
O
S
O
Me
O
CO2Et
4m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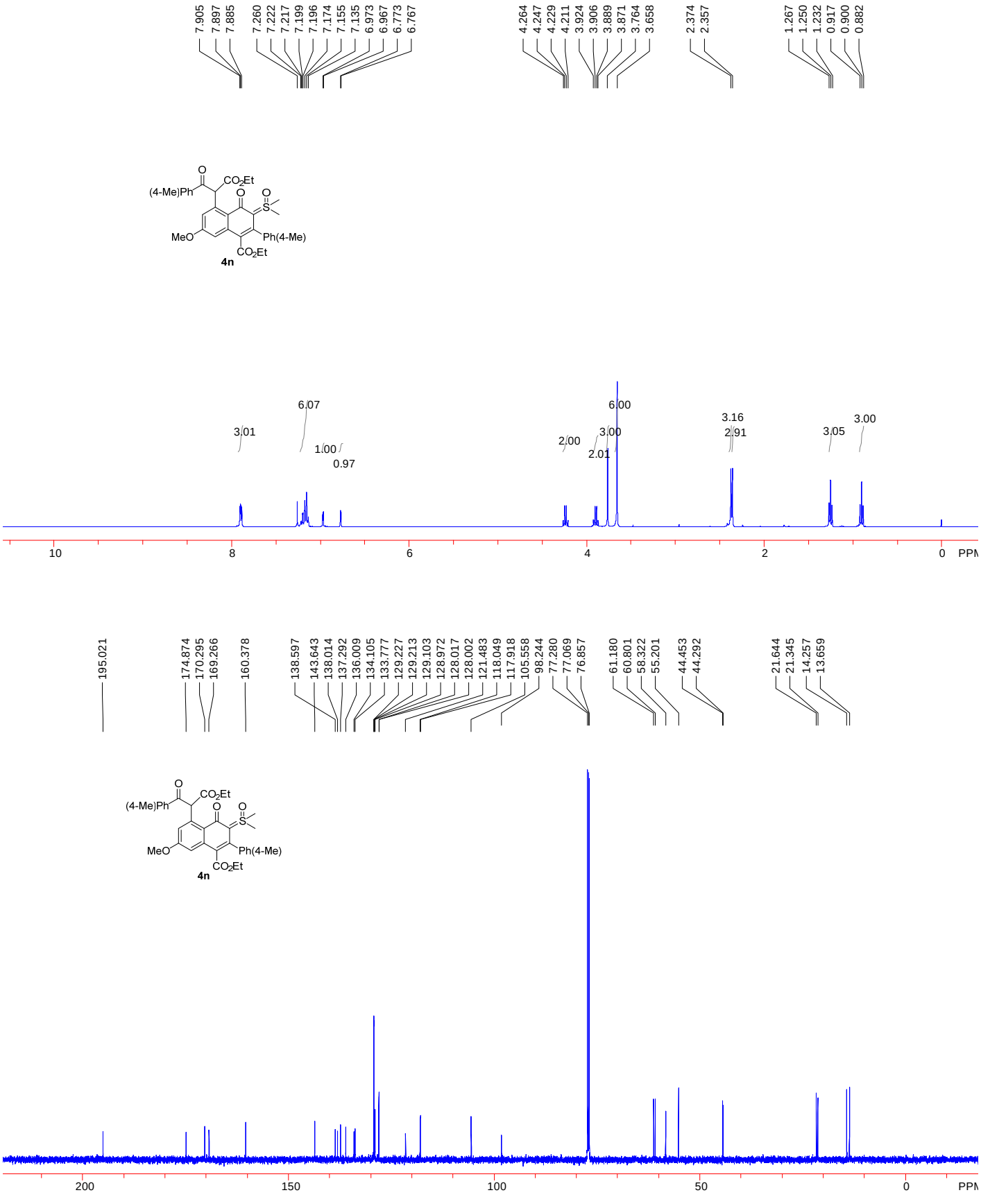
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6.773
6.767
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4.247
4.229
4.211
3.924
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3.871
3.764
3.658
2.374
2.357
1.267
1.250
1.232
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0.900
0.882
(4-Me)Ph
CO2Et
O
O
O
S
MeO
Ph(4-Me)
CO2Et
4n
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6.07
1.00
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6.00
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2.91
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10
8
6
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2
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21.345
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(4-Me)Ph
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O
O
S
MeO
Ph(4-Me)
CO2Et
4n
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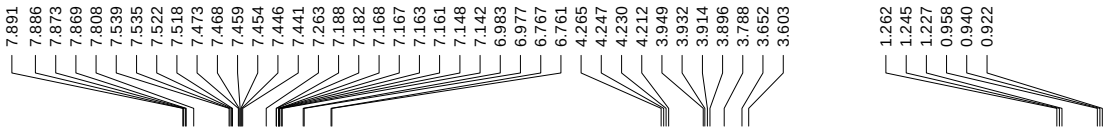
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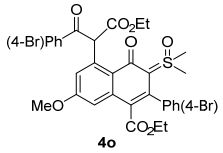
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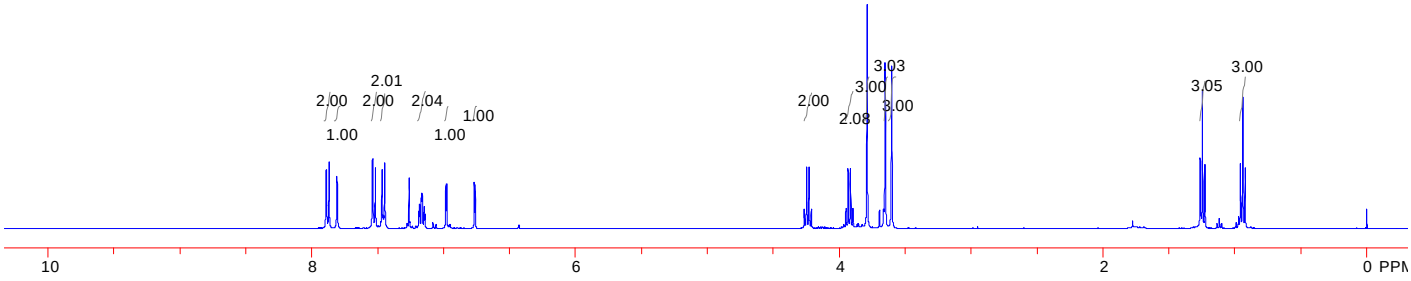
O
O
S
MeO
Ph(4-Br)
CO2Et

4o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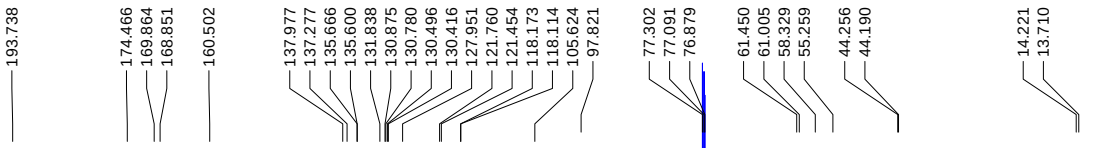
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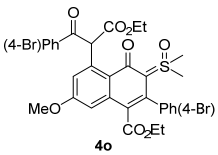
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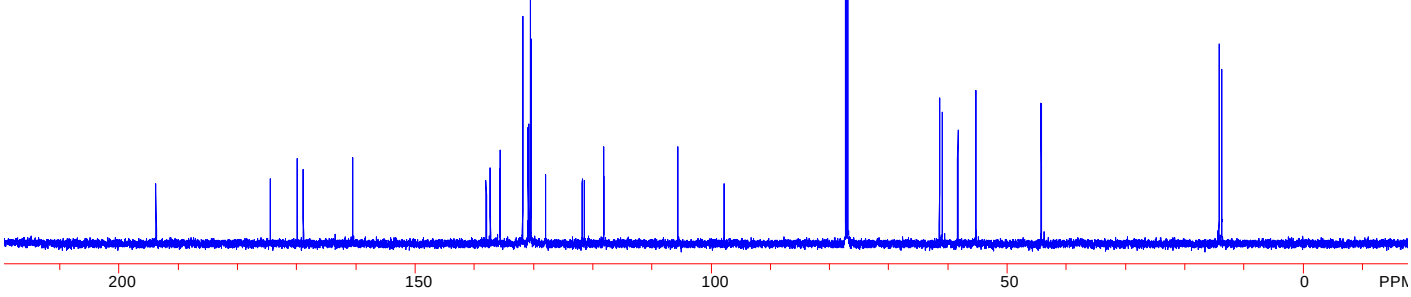
O
O
S
MeO
Ph(4-Br)
CO2Et

4o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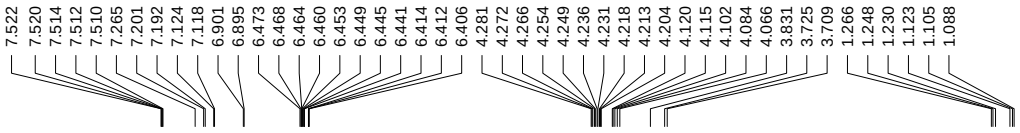
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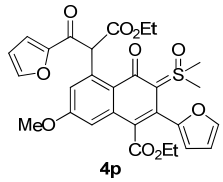
1.088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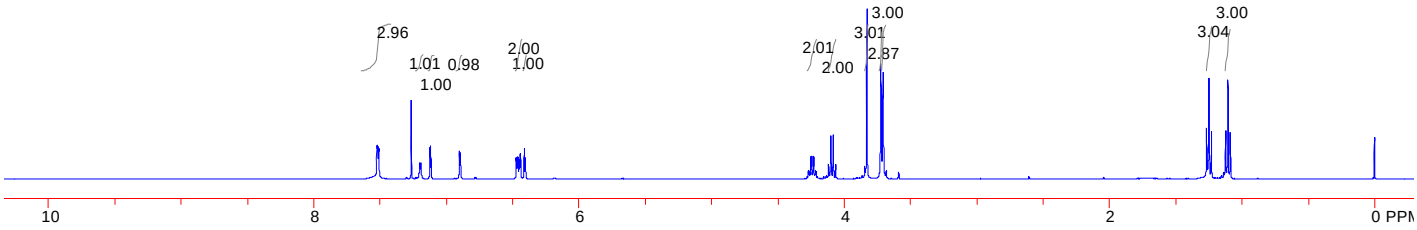
O
O
S
MeO
O
CO2Et

4p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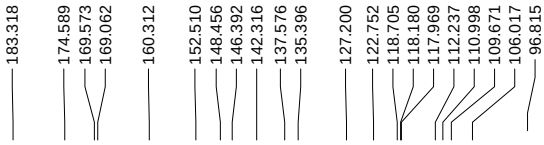
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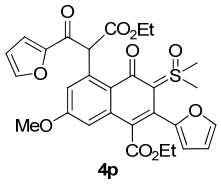
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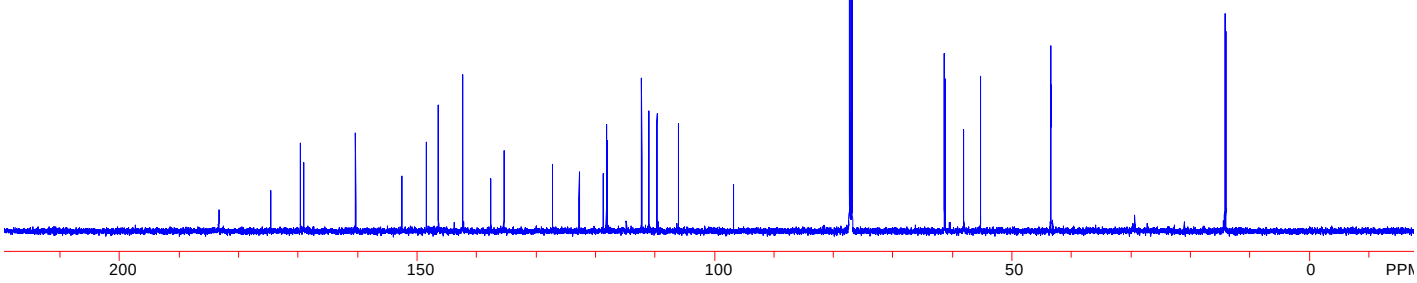
S
MeO
O
CO2Et

4p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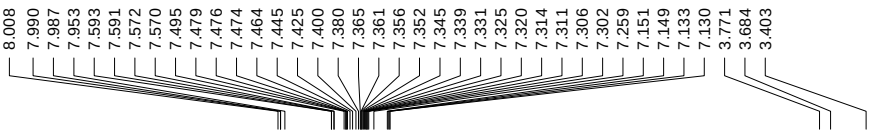
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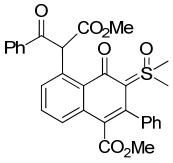
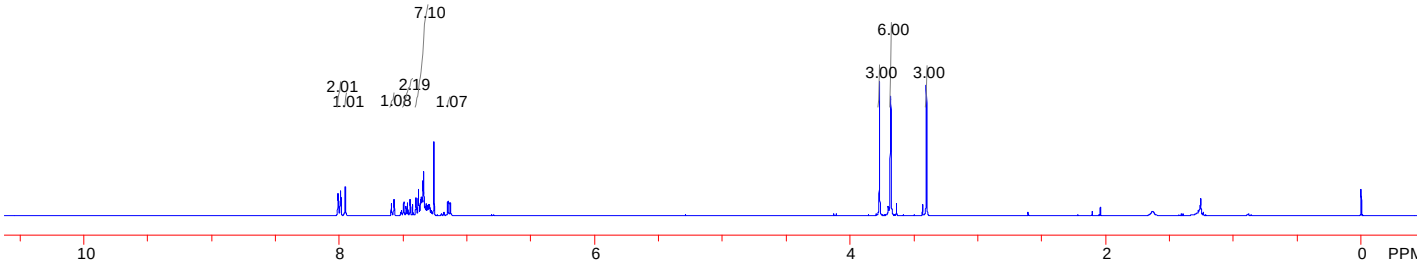

O
CO2Me
Ph
O
O
S
Ph
CO2Me

4q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1.01
2.19
1.08
1.07
10
8
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4
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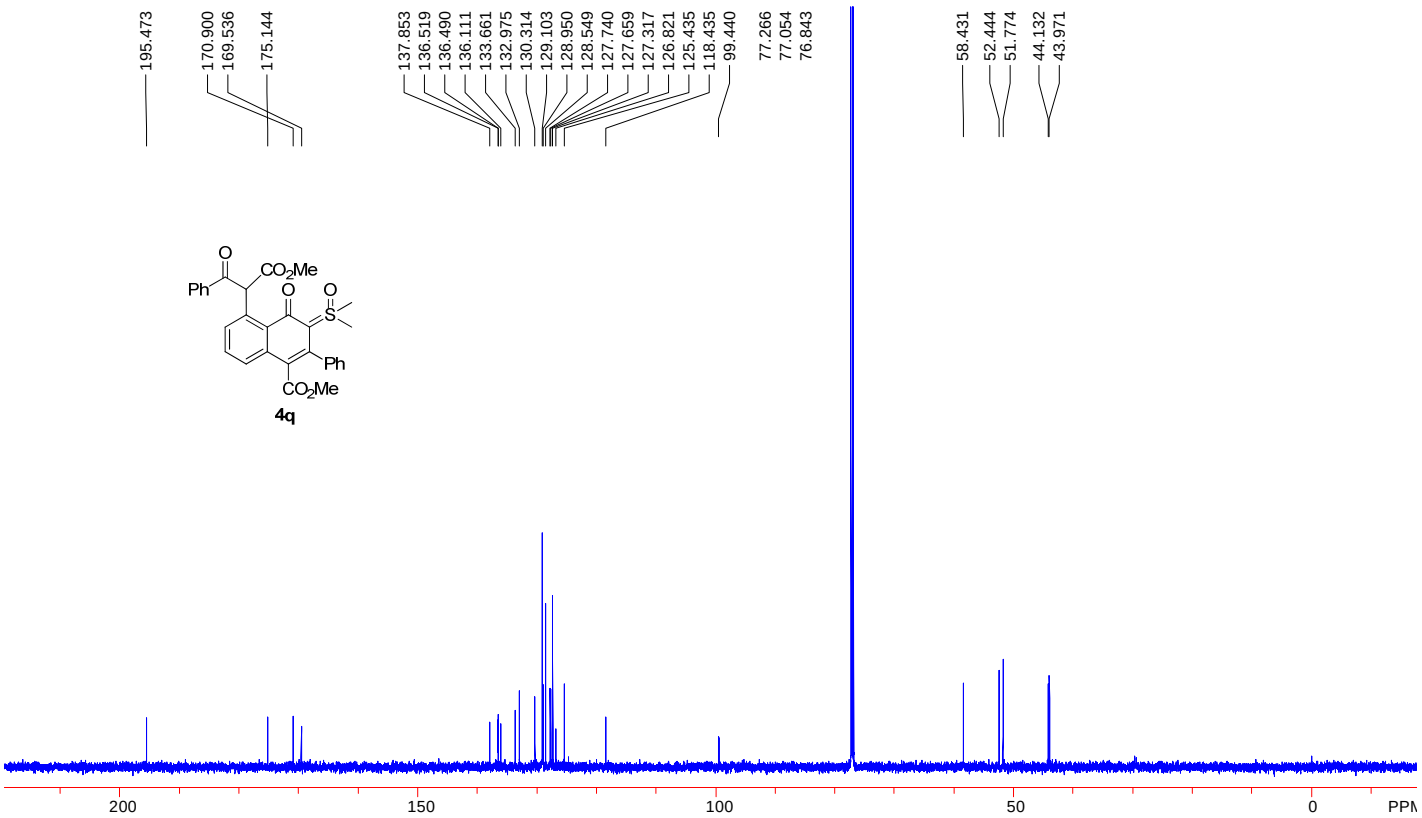
0
PPM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136.111
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132.975
130.314
129.103
128.950
128.549
127.740
127.659
127.317
126.821
125.435
118.435
99.440
77.266
77.054
76.843
58.431
52.444
51.774
44.132
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150
100
50
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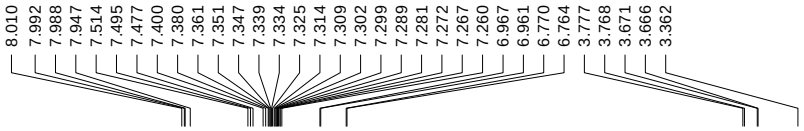
PPM

O
CO2Me
Ph
O
O
S
Ph
CO2Me

4q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7.400
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7.339
7.334
7.325
7.314
7.309
7.302
7.299
7.289
7.281
7.272
7.267
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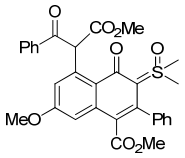
6.961
6.770
6.764
3.777
3.768
3.671
3.666
3.362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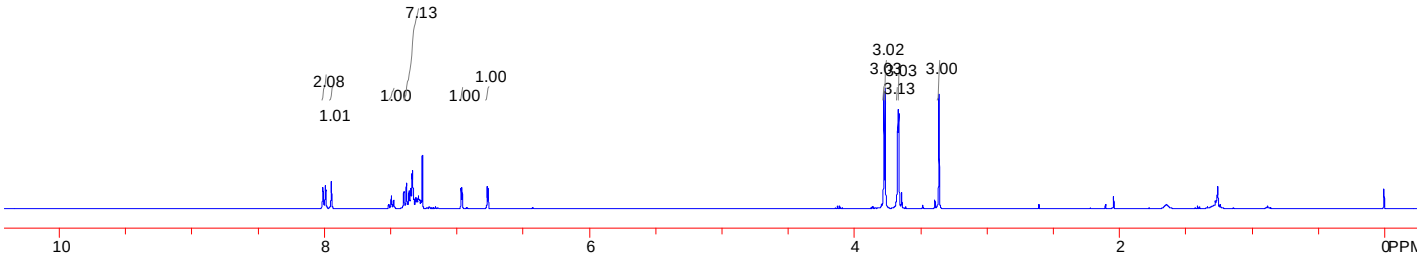
CO2Me
Ph
O
O
S
MeO
Ph
CO2Me

4r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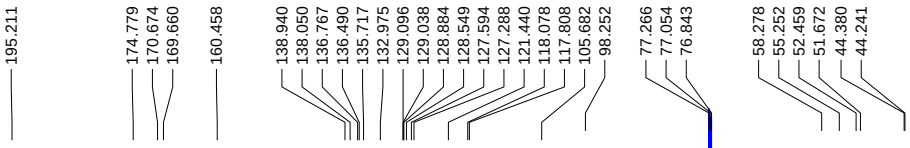
PPM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129.038
128.884
128.549
127.594
127.288
121.440
118.078
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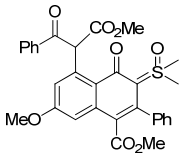
77.266
77.054
76.843
58.278
55.252
52.459
51.672
44.380
44.241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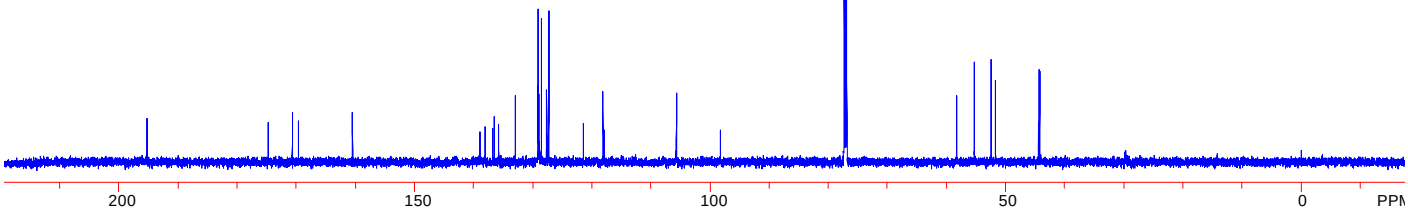
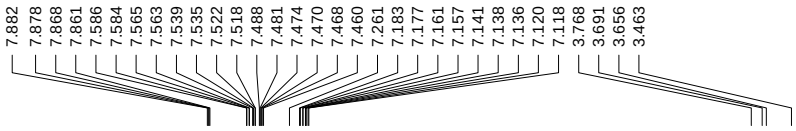
CO2Me
Ph
O
O
S
MeO
Ph
CO2Me

4r


200
150
100
50
0
PPM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7.535
7.522
7.518
7.488
7.481
7.474
7.470
7.468
7.460
7.261
7.183
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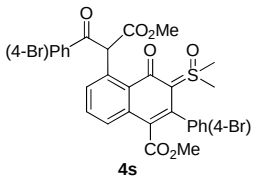
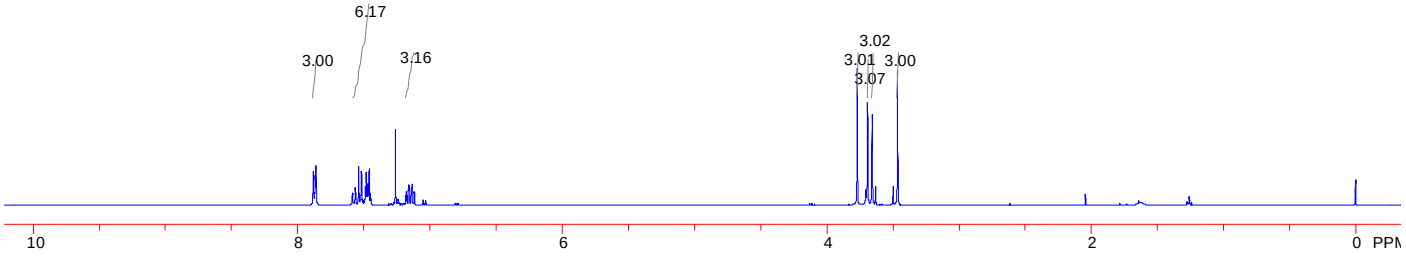
7.161
7.157
7.141
7.138
7.136
7.120
7.118
3.768
3.691
3.656
3.463


O
CO2Me
(4-Br)Ph
O
O
S
Ph(4-Br)
CO2Me

4s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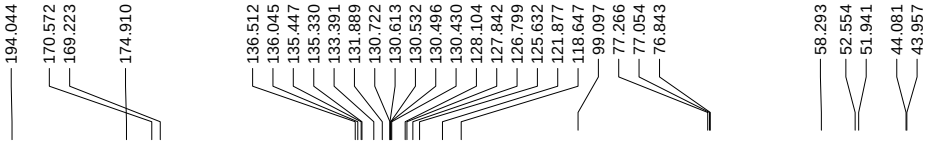
3.16
3.02
3.01
3.00
3.07
10
8
6
4
2
0
PPM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174.910
136.512
136.045
135.447
135.330
133.391
131.889
130.722
130.613
130.532
130.496
130.430
128.104
127.842
126.799
125.632
121.877
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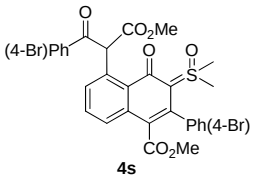
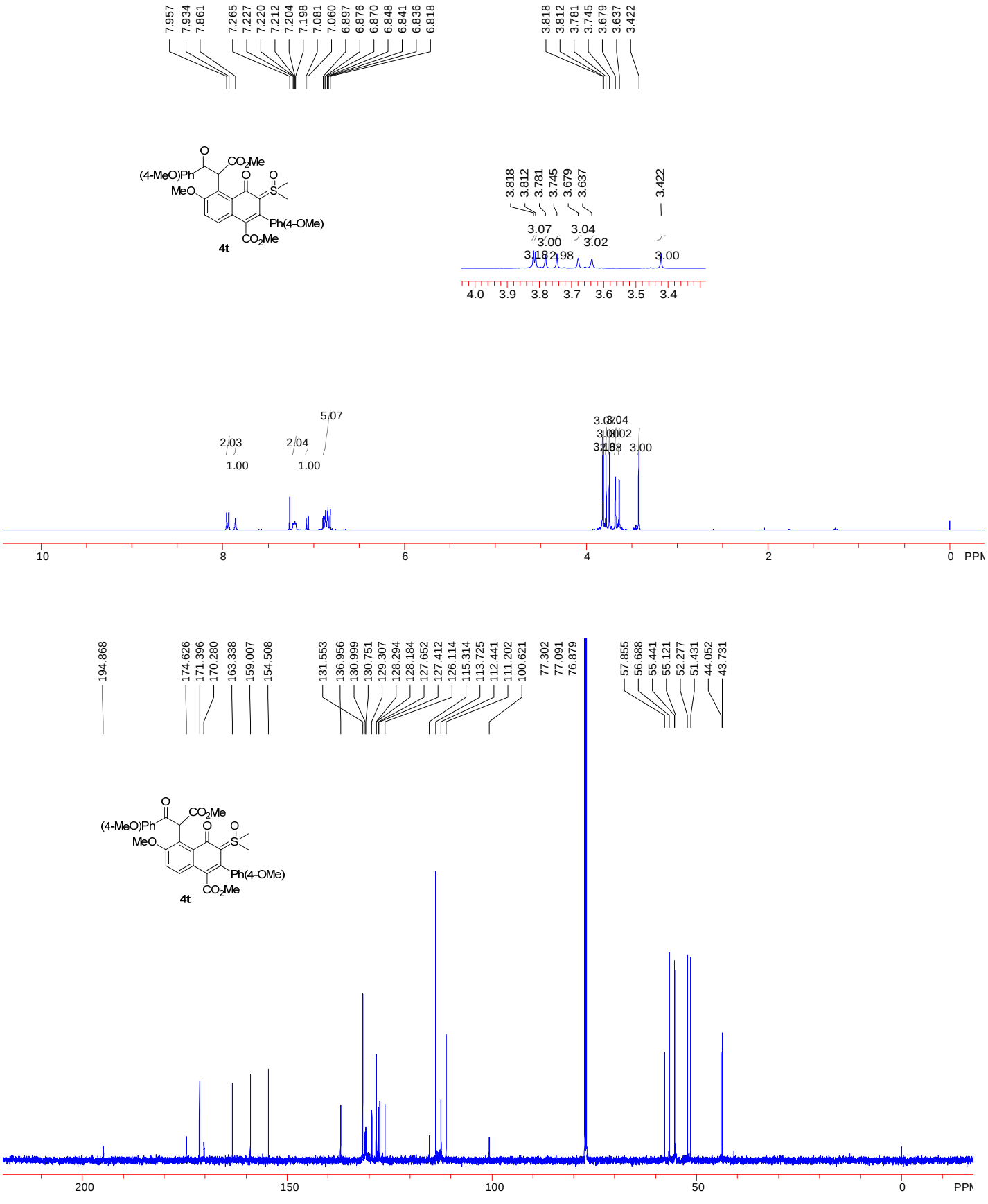
77.266
77.054
76.843
58.293
52.554
51.941
44.081
43.957


O
CO2Me
(4-Br)Ph
O
O
S
Ph(4-Br)
CO2Me

4s

200
150
100
50
0
PPM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7.861
7.265
7.227
7.220
7.212
7.204
7.198
7.081
7.060
6.897
6.876
6.870
6.848
6.841
6.836
6.818
3.818
3.812
3.781
3.745
3.679
3.637
3.422
(4-MeO)Ph
MeO
CO2Me
O
O
O
S
Ph(4-OMe)
CO2Me
4t
3.07
3.04
3.00
3.02
3.00
4.0
3.9
3.8
3.7
3.6
3.5
3.4
2.03
1.00
2.04
1.00
5.07
3.00
10
8
6
4
2
0
PPM
194.868
174.626
171.396
170.280
163.338
159.007
154.508
131.553
136.956
130.999
130.751
129.307
128.294
128.184
127.652
127.412
126.114
115.314
113.725
112.441
111.202
100.621
77.302
77.091
76.879
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55.441
55.121
52.277
51.431
44.052
43.731
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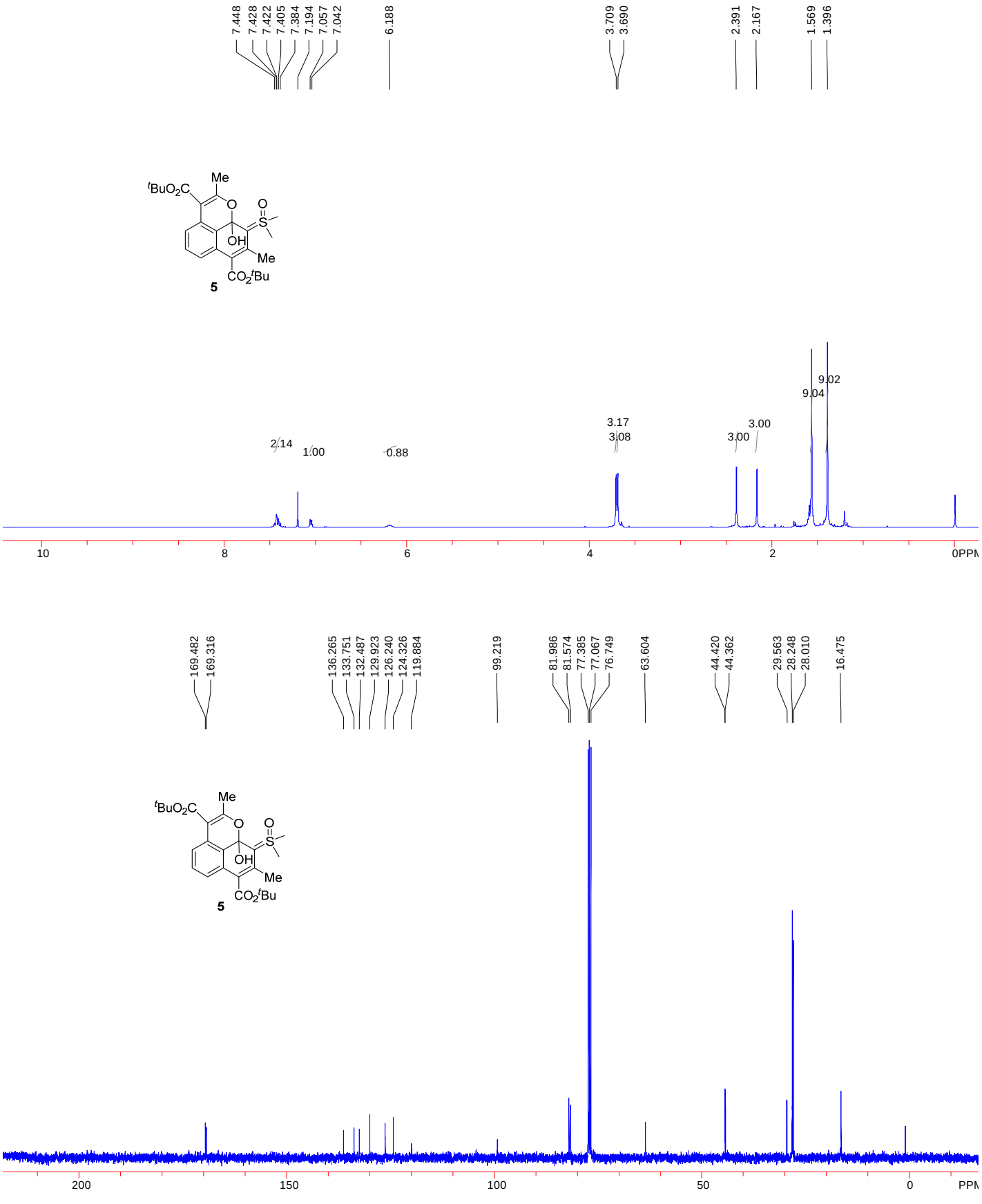
150
100
50
0
PPM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7.428
7.422
7.405
7.384
7.194
7.057
7.042
6.188
3.709
3.690
2.391
2.167
1.569
1.396
Me
tBuO2C
O
O
S
OH
Me
CO2tBu
5
2.14
1.00
0.88
3.17
3.08
3.00
3.00
9.02
9.04
10
8
6
4
2
0PPM
169.482
169.316
136.265
133.751
132.487
129.923
126.240
124.326
119.884
99.219
81.986
81.574
77.385
77.067
76.749
63.604
44.420
44.362
29.563
28.248
28.010
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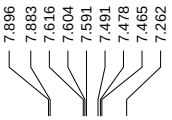
Me
tBuO2C
O
O
S
OH
Me
CO2tBu
5
200
150
100
50
0
PPM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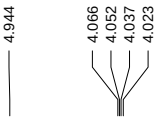
7.478
7.465
7.262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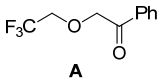
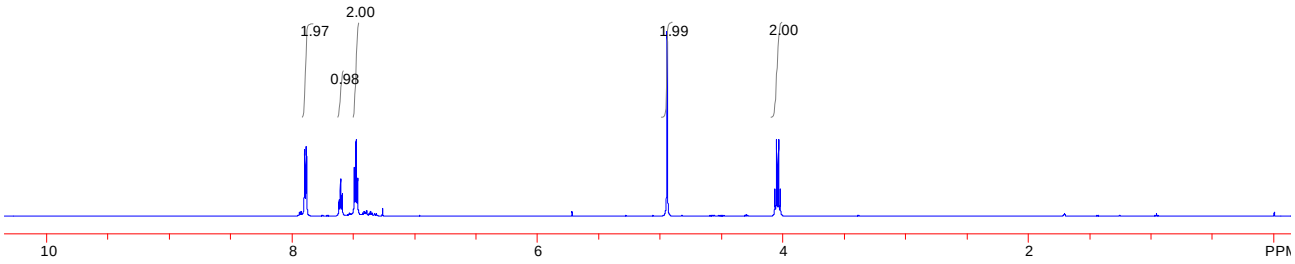
4.052
4.037
4.023


F3C
O
Ph
O

A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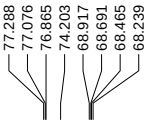
1.97
0.98
1.99
2.00
10
8
6
4
2
PPM


194.912

134.302
133.989
128.906
127.747
126.668
124.816
122.964
121.111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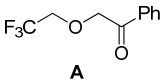
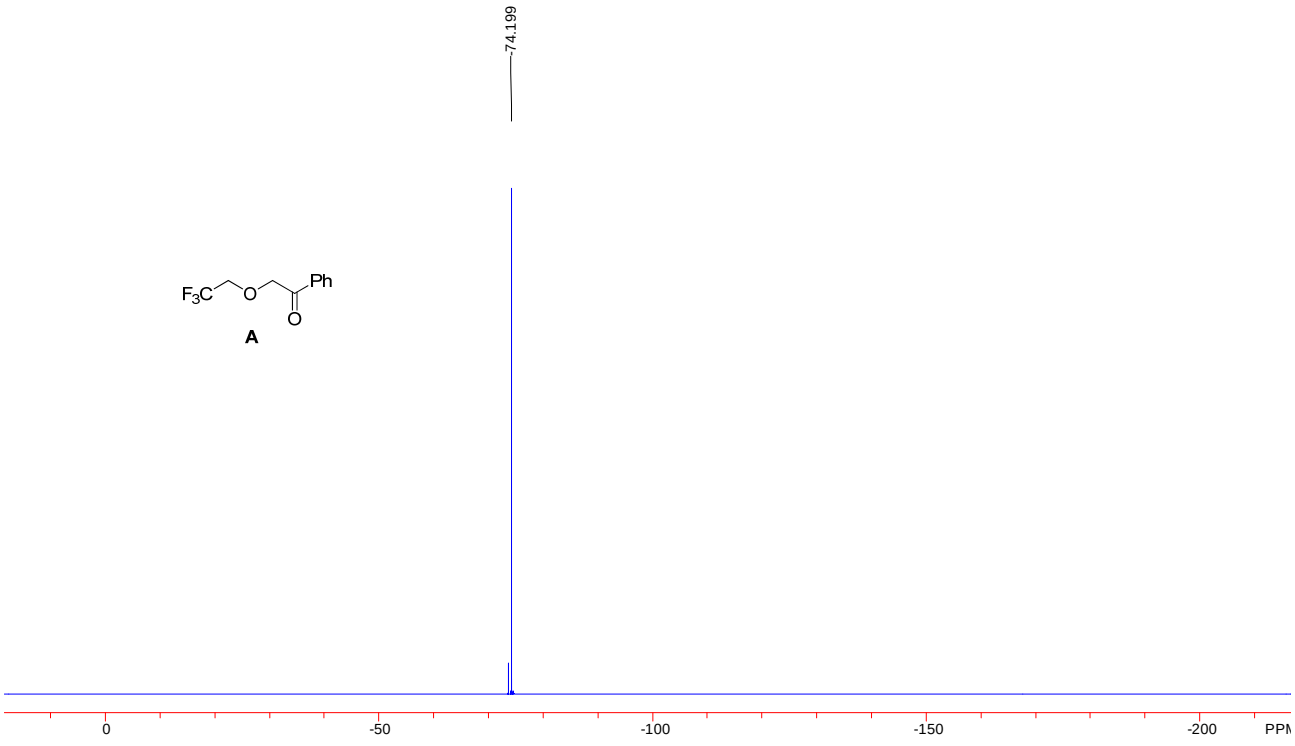
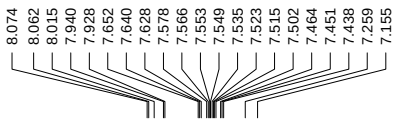
68.239


F3C
O
Ph
O

A

200
150
100
50
0
PPM


-74.199
F3C
O
Ph
O
A
0
-50
-100
-150
-200
PPM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7.940
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7.628
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7.535
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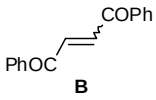
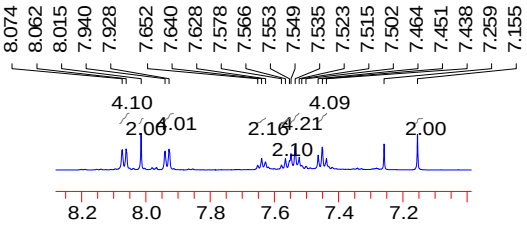
7.515
7.502
7.464
7.451
7.438
7.259
7.155


COPh
PhOC

B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8.015
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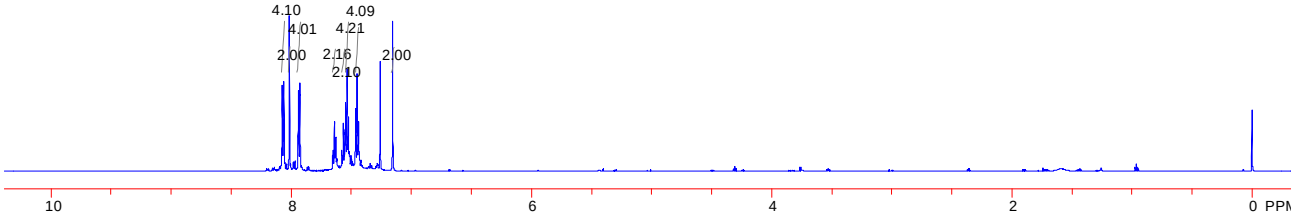
7.566
7.553
7.549
7.535
7.523
7.515
7.502
7.464
7.451
7.438
7.259
7.155
4.10
2.00
4.01
2.16
4.09
4.21
2.10
2.00
8.2
8.0
7.8
7.6
7.4
7.2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2.10
4.09
4.21
2.00
10
8
6
4
2
0
PPM


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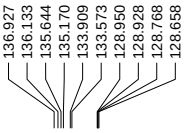
189.888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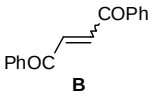
128.928
128.768
128.658

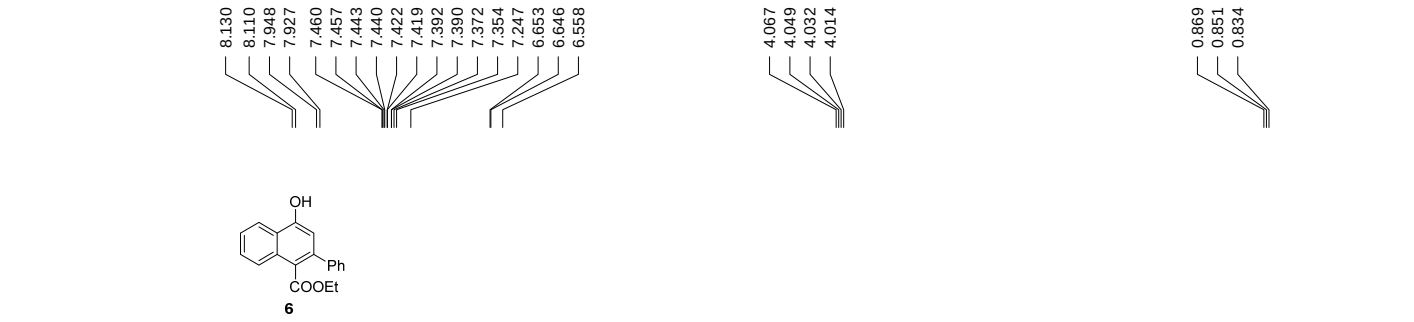

77.251
77.040
76.828


COPh
PhOC

B

200
150
100
50
0
PPM

VII. Copies of ^{1}H and ^{13}C NMR spectra 6-9



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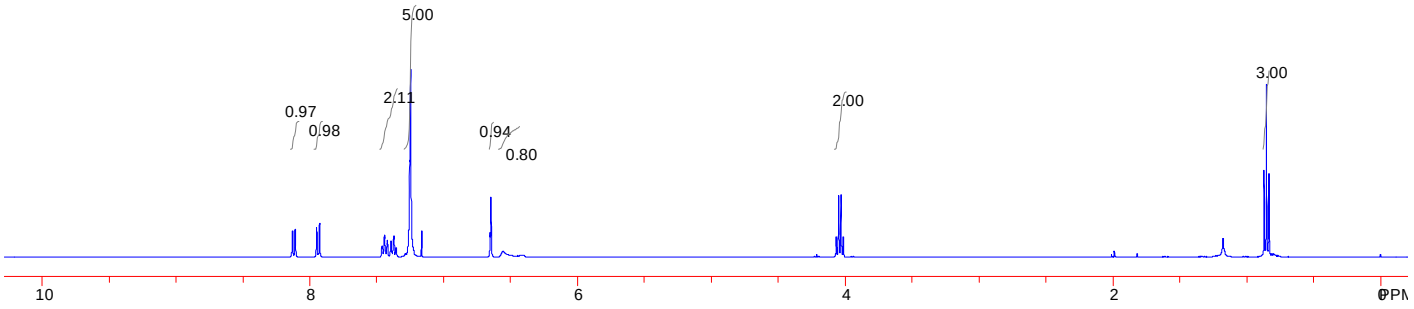

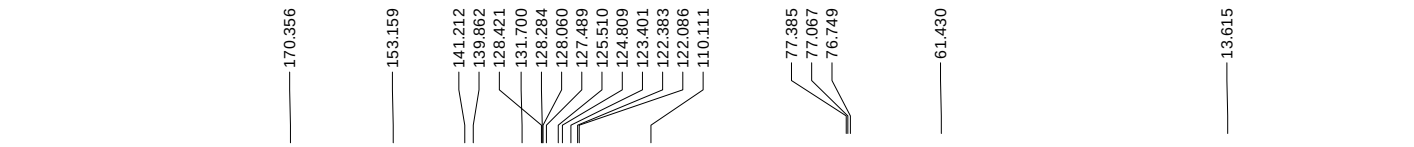

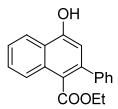

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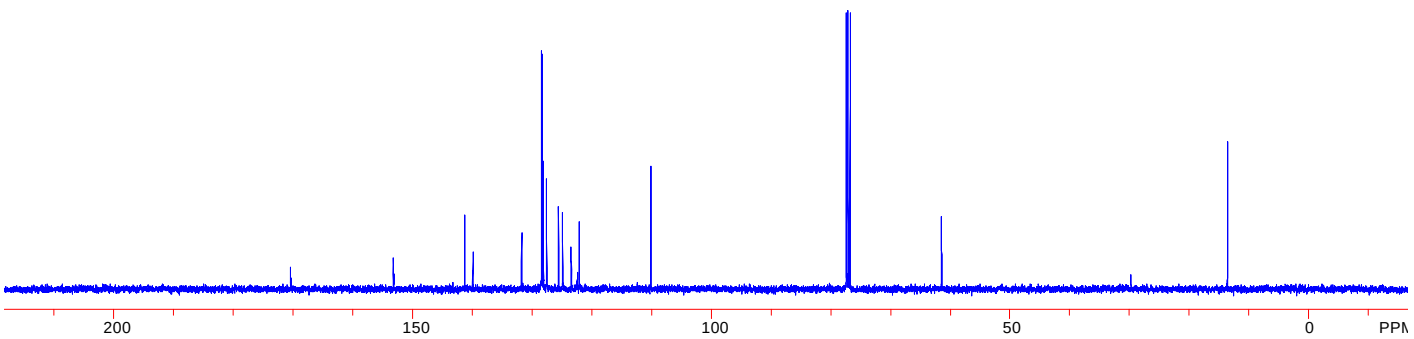

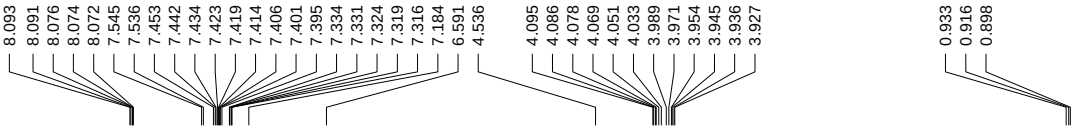
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7.406
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7.334
7.331
7.324
7.319
7.316
7.184
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4.095
4.086
4.078
4.069
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3.927
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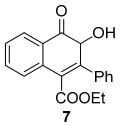
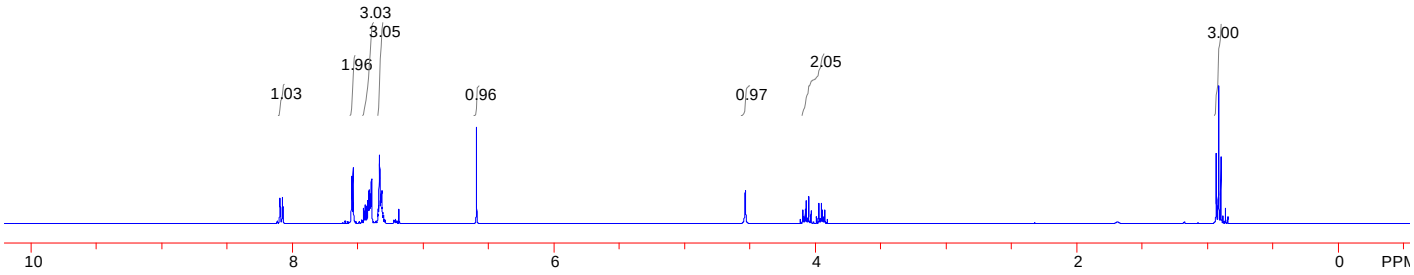
0.916
0.898


O
OH
Ph
COOEt

7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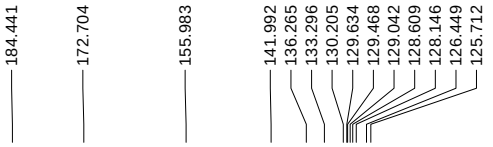
1.03
0.96
0.97
2.05
3.00
10
8
6
4
2
0
PPM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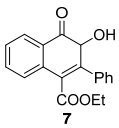
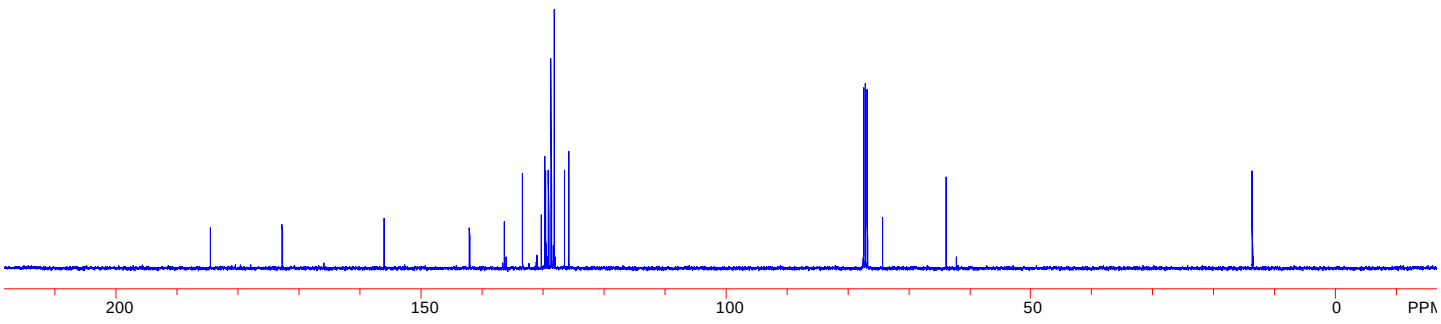
77.103
76.785
74.308
63.871
13.658


O
OH
Ph
COOEt

7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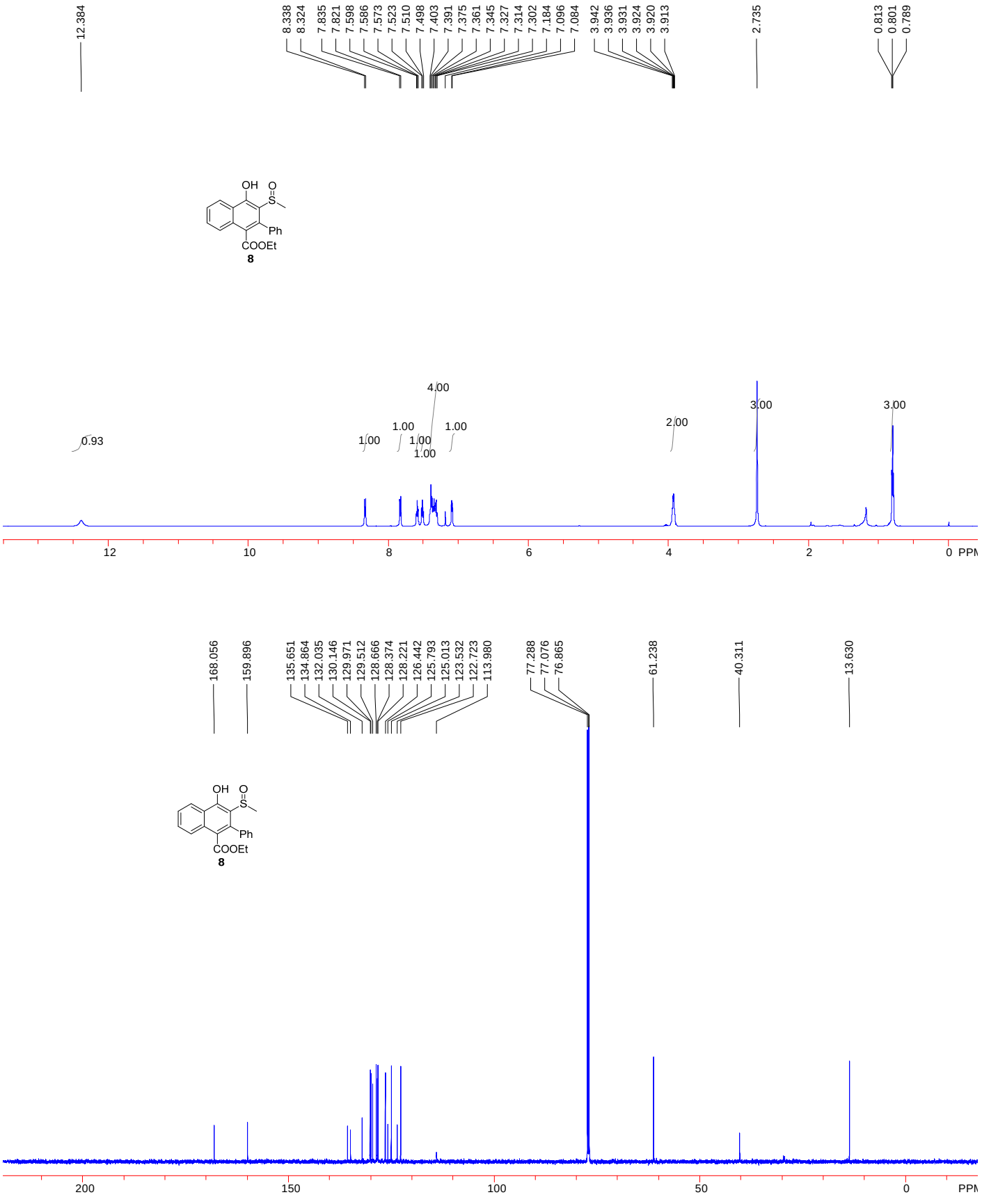
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7.391
7.375
7.361
7.345
7.327
7.314
7.302
7.184
7.096
7.084
3.942
3.936
3.931
3.924
3.920
3.913
2.735
0.813
0.801
0.789
OH
O
S
Ph
COOEt
8
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1.00
1.00
1.00
1.00
4.00
1.00
2.00
3.00
3.00
12
10
8
6
4
2
0 PPM
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159.896
135.651
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132.035
130.146
129.971
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128.374
128.221
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125.793
125.013
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113.980
77.288
77.076
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Ph
COOEt
8
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50
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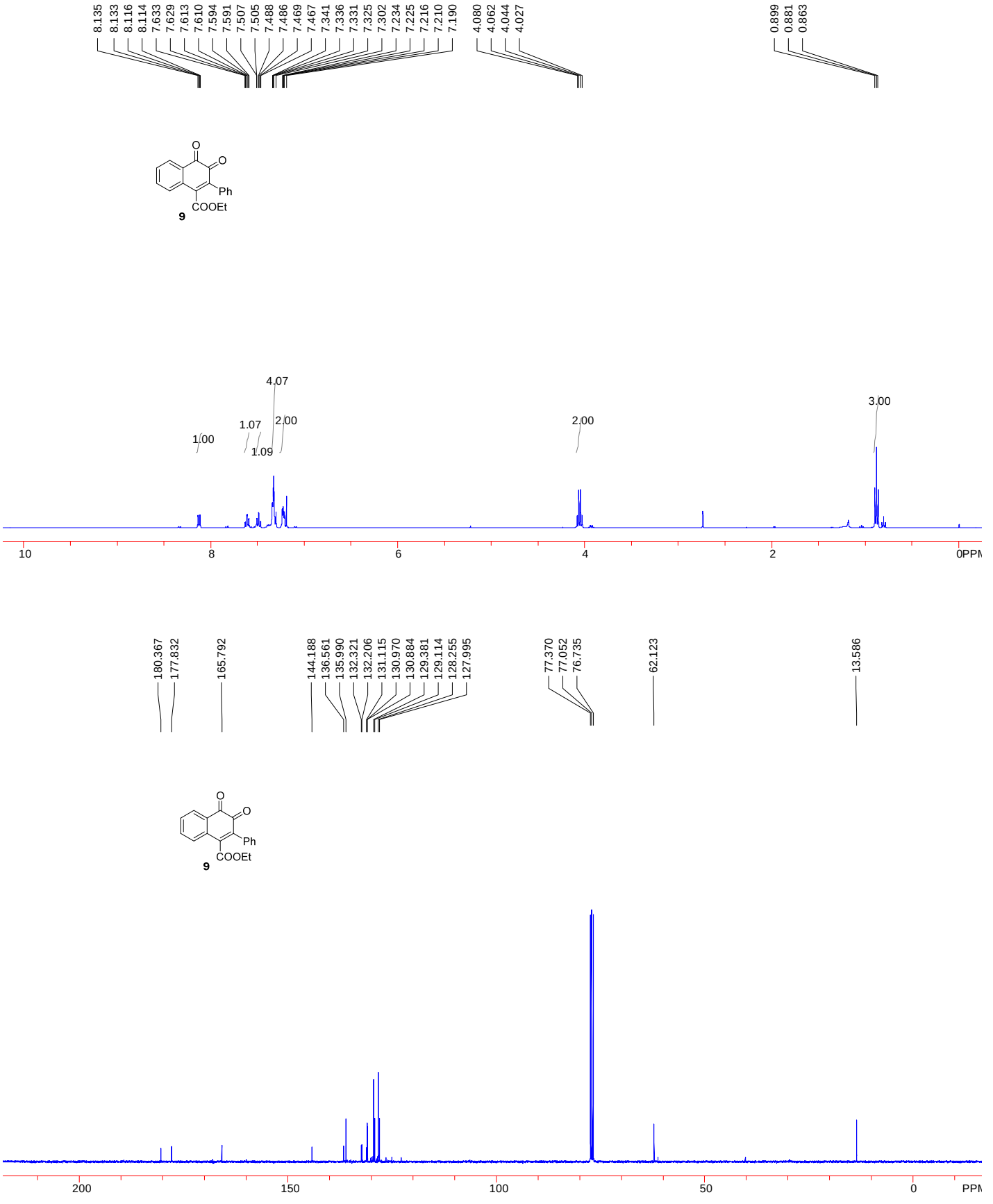
PPM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7.331
7.325
7.302
7.234
7.225
7.216
7.210
7.190
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4.062
4.044
4.027
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0.881
0.863
O
O
Ph
COOEt
9
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1.07
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1.00
1.09
2.00
3.00
10
8
6
4
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77.052
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Ph
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PPM

VIII. X-ray crystal structure and data of 3b

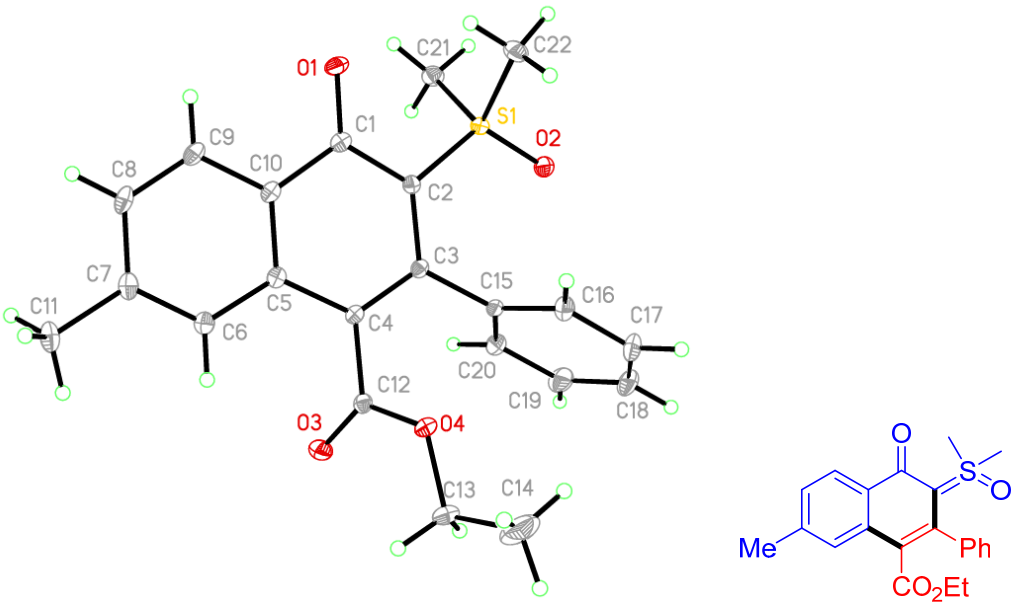

Fig. 1 X-ray structure of **3b** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an ethyl acetate solution of **3b**. Crystal data collection and refinement parameters of **3b** are summarized in Table 1. Intensity data were collected at 170 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table 2 Crystallographic data and structure refinement results of **3b**

Empirical formula	$C_{22}H_{22}O_4S$
Formula weight	382.45
Temp, K	170.00(10)
Crystal system	monoclinic
Space group	P21/c

a, Å	11.9047(4)
b, Å	8.7291(3)
c, Å	18.7097(7)
α (°)	90
β (°)	97.326(3)
γ (°)	90
Volume, Å^3	1928.39(12)
Z	4
d_{calc}, g cm^{-3}	1.317
λ, Å	0.71073
μ, mm^{-1}	0.193
No. of data collected	12904
No. of unique data	4534
R_{int}	0.0252
Goodness-of-fit on F^2	1.060
R_1, wR_2 ($I > 2\sigma(I)$)	0.0436, 0.1044
R_1, wR_2 (all data)	0.0506, 0.1085

IX. X-ray crystal structure and data of 4h

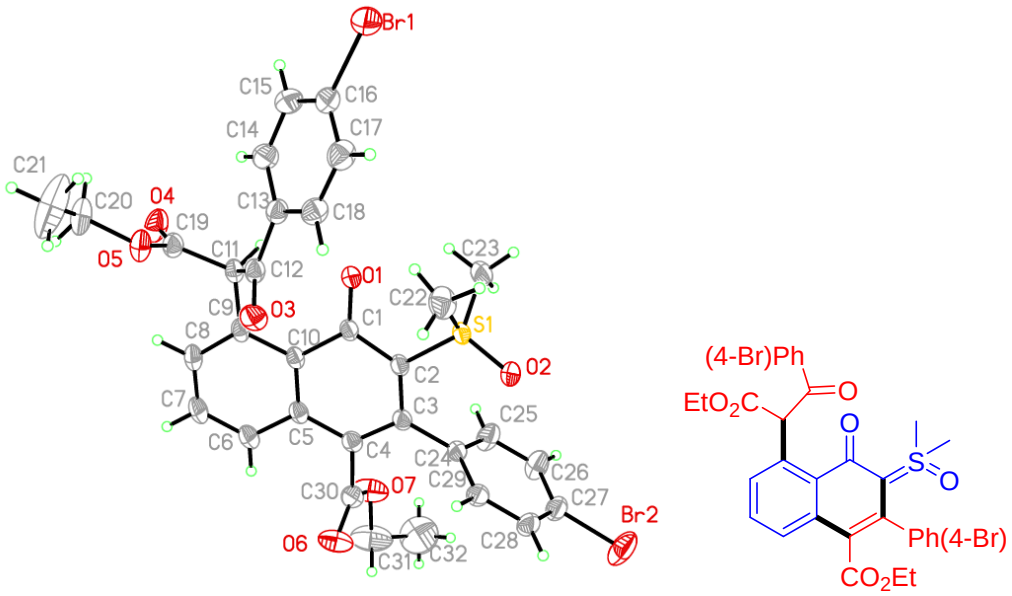

Fig. 2 X-ray structure of **4h** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a acetonitrile solution of **4h**. Crystal data collection and refinement parameters of **4i** are summarized in Table 2. Intensity data were collected at 298 K on a SuperNova Dual diffractometer using mirror-monochromated Cu Kα radiation, λ = 1.54184 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table 3 Crystallographic data and structure refinement results of **4h**

Empirical formula	$C_{32}H_{28}Br_2O_7S$
Formula weight	716.42
Temp, K	297.58(10)
Crystal system	monoclinic
Space group	I2/a
a, Å	20.3723(3)

b, Å	9.46580(10)
c, Å	32.2373(4)
α (°)	90
β (°)	96.2930(10)
γ (°)	90
Volume, Å^3	6179.19(14)
Z	8
d_{calc}, g cm^{-3}	1.540
λ, Å	1.54184
μ, mm^{-1}	4.349
No. of data collected	19605
No. of unique data	6000
R_{int}	0.0335
Goodness-of-fit on F^2	1.023
R_1, wR_2 ($I > 2\sigma(I)$)	0.0500, 0.1305
R_1, wR_2 (all data)	0.0584, 0.1361

X. X-ray crystal structure and data of 8

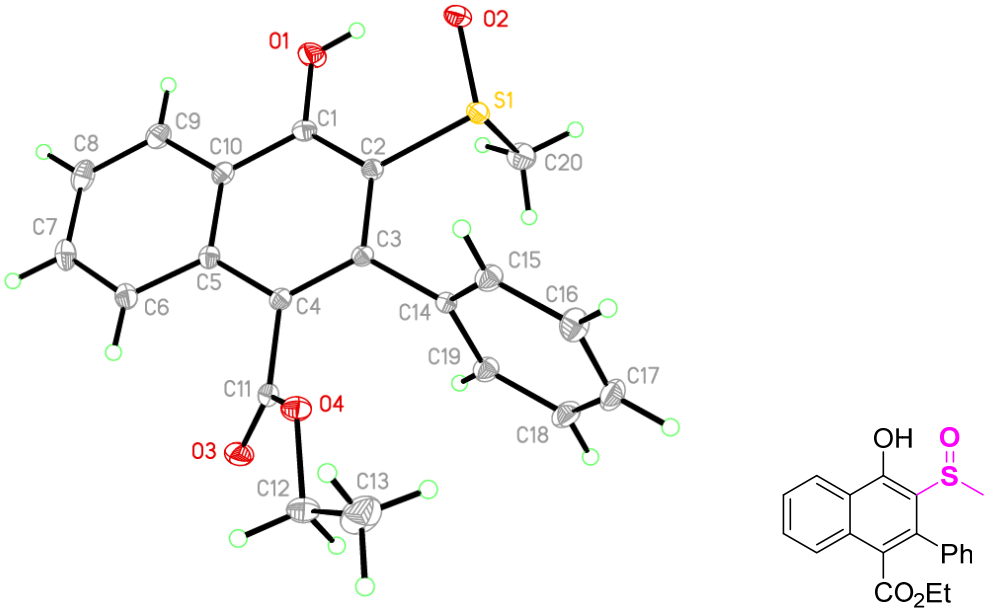

Fig. 3 X-ray structure of **8** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from an ethyl acetate solution of **8**. Crystal data collection and refinement parameters of **8** are summarized in Table 3. Intensity data were collected at 170 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table 4 Crystallographic data and structure refinement results of **8**

Empirical formula	$C_{20}H_{18}O_4S$
Formula weight	354.40
Temp, K	169.99(10)
Crystal system	monoclinic

Space group	P21/c
a, Å	9.7333(3)
b, Å	12.3673(3)
c, Å	15.0114(4)
α (°)	90
β (°)	106.850(3)
γ (°)	90
Volume, Å^3	1729.41(9)
Z	4
d_{calc}, g cm^{-3}	1.361
λ, Å	0.71073
μ, mm^{-1}	0.209
No. of data collected	11477
No. of unique data	4102
R_{int}	0.0228
Goodness-of-fit on F^2	1.059
R_1, wR_2 ($I > 2\sigma(I)$)	0.0401, 0.0949
R_1, wR_2 (all data)	0.0492, 0.0993

XI. References

(1) (a) Vaitla, J.; Bayer, A.; Hopmann, K. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 4277; (b) Xu, Y.; Yang, X.; Zhou, X.; Kong, L.; Li, X. *Org. Lett.* **2017**, *19*, 4307.

(2) Jiang, Y.; Khong, V. Z. Y; Lourdusamy, E.; Park. C.-M. *Chem. Commun*. **2012**, *48*, 3133.

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(4) Fujita, K.-i.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. *Org. Lett*. **2004**, *6*, 2785.