Supplementary Information

Synthesis of Diaryl Ketones via a Phosphine-Free Fukuyama Reaction

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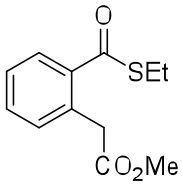
Materials and Methods

Unless otherwise stated, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen using anhydrous solvents. Tetrahydrofuran and toluene were passed through activated alumina columns. All reagents were obtained commercially and used as received. Thin-layer chromatography (TLC) was conducted with silica gel UV254 pre-coated plates (0.25mm), and visualized using UV lamps. Silica gel (particle size 40-63 μm) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra are reported relative to protiated solvent signals or tetramethylsilane. GC analysis was performed on an instrument equipped with FID detectors using a HP-5 (5%-Phenyl)-methylpolysiloxane column. High resolution mass spectra were obtained on a MicrOTOF instrument.

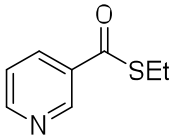
Synthesis of thioesters

General procedure for the preparation of thioesters from carboxylic acids.

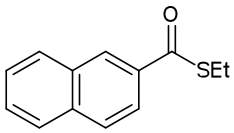
To a stirring suspension of the carboxylic acid (50 mmol), thiol (65 mmol), and dimethylaminopyridine (5 mmol) in 230 mL CH_3CN at 0 ºC was added dicyclohexylcarbodiimide (14.66 g, 52 mmol) in 3 portions. The reaction was allowed to slowly warm to 23 ºC and stirred for 4 h. After this time, the solution was pushed through a pad of Celite with the aid of DCM. The filtrate was concentrated and the residue was purified by pushing through a short pad of silica to remove residual dicyclohexylurea.



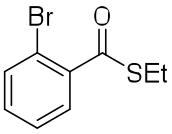
Methyl 2-(2-(ethylthiocarbonyl)phenyl)acetate, 1a. The reaction was performed according to the general procedure with 13.14 g (67.7 mmol) of 2-(2-methoxy-2-oxoethyl)benzoic acid to give 99% of the thioester (16.0 g, 67.1 mmol) as a slightly yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.23 (t, *J* = 7.6 Hz, 3H), 3.03 (q, *J* = 7.6 Hz, 2H), 3.69 (s, 3H), 3.91 (s, 2H), 7.27 (d, *J* = 7.6 Hz 1H), 7.37 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.47 (dt, *J*= 7.6, 1.2 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.2 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$): 14.9, 24.1, 39.7, 52.1, 127.7, 129.3, 132.2, 132.4, 133.0, 137.5, 171.8, 194.4; IR (DCM): 1741, 1659; HRMS (ESI): calcd for $C_{12}H_{14}O_3S$ $[M+Na]^+$: 261.0556, found 261.0560.



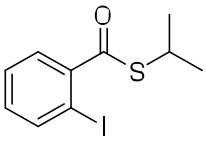
S-ethyl pyridine-3-carbothioate, 1c. The reaction was performed according to the general procedure with 6.14 g (50 mmol) of nicotinic acid to give 93% of the thioester (6.48 g, 46.5 mmol) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.34 (t, *J*= 7.40 Hz, 3H), 3.08 (q, *J*= 7.40 Hz, 2H), 7.36 (qd, *J* = 4.8, 0.8 Hz, 1H), 8.15-8.18 (m, 1H), 8.74 (dd, *J* = 4.8, 1.7, 1H), 9.13 (dd, *J* = 6.7, 0.8, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.8, 23.7, 123.6,132.9, 134.5, 148.6, 153.8, 190.7; IR (neat): 1662; HRMS (ESI): calcd for C_8H_9OS $[M+Na]^+$: 190.0297, found 190.0300.



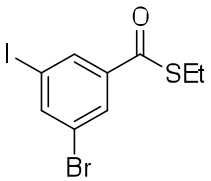
S-ethyl naphthalene-2-carbothioate, 1d. The reaction was performed according to the general procedure with 1.91 g (10.0 mmol) of 2-napthoyl chloride to give 91% of the thioester (1.96 g, 9.1 mmol) as an off white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.39 (t, *J* = 7.40 Hz, 3H), 3.13 (q, *J*= 7.40 Hz, 2H), 7.52-7.61 (m, 2H), 7.86-7.89 (m, 2H), 7.95-8.00 (m, 2H), 8.52-8.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.8, 23.6, 123.2, 126.9, 127.7, 128.3, 128.4, 128.5, 129.6, 132.5, 134.6, 135.7, 192.2; IR (DCM) 3053, 1655; HRMS (ESI): calcd for $C_{13}H_{12}OS$ $[M+Na]^+$: 239.0501, found 239.0504.



S-ethyl 2-bromobenzothioate, 1m. The reaction was performed according to the general procedure with 1.09 g (5.4 mmol) of 2-bromobenzoic acid to give 78% of the thioester (1.02 g, 4.2 mmol) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.36 (t, *J* = 7.4 Hz, 3H), 3.07 (q, *J* = 7.4 Hz, 2H), 7.27-7.36 (m, 2H), 7.59 (qd, *J* = 7.7, 1.4, 2H), ^{13}C NMR ($CDCl_3$, 100MHz): 14.6, 24.6, 118.9, 127.3, 129.2, 132.2, 134.1, 139.9, 193.2; IR (neat): 2969, 1681; HRMS (ESI): calcd for C_9H_9BrOS $[M+Na]^+$: 266.9528, found: 266.9508.

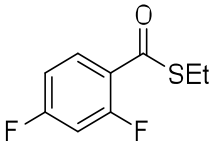


S-isopropyl 2-iodobenzothioate, 1o. The reaction was performed according to the general procedure with 6.22 g (25 mmol) of 2-iodobenzoic acid to give 88% of the thioester (6.77 g, 22.1 mmol) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.40 (d, *J* = 2.8 Hz, 6H), 3.84 (q, *J* = 6.9 Hz), 7.10 (td, *J* = 5.6, 1.6, 1H), 7.35 (td, *J* = 7.6, 1.0 Hz, 1H), 7.53 (dd, *J* = 7.5, 6.0 Hz, 1H), 7.89 (dd, *J* = 7.04, 1.0, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 22.9, 36.2, 91.4, 128.0,128.7, 132.2, 140.8, 143.2, 194.6; IR(neat):2964, 1667, 1201; HRMS (ESI): calcd for $C_{10}H_{11}OS$ $[M+Na]^+$: 328.9467, found 328.9476.

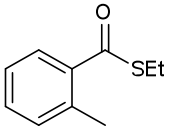


S-ethyl 3-bromo-5-iodobenzothioate, 1p. The reaction was performed according to the general procedure with 1.17 g (3.6 mmol) of 3-bromo-5-iodobenzoic acid to give 84% of the thioester (1.11 g, 3.0 mmol) as a white solid.^{1}H NMR ($CDCl_3$, 400 MHz): 1.34 (t, *J* = 7.4, 3H), 3.07 (q, *J* = 7.4, 2H), 8.01-8.02 (m, 2H), 8.167 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 14.7, 24.1, 94.5, 123.5, 129.6, 134.8, 140.1, 144, 189.5; IR (DCM): 2927, 1659, 1190; HRMS (ESI): calcd for C_9H_8BrIOS $[M+Na]^+$: 392.8416, found 392.8431.

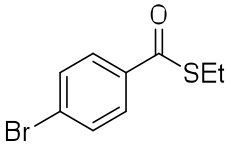
General procedure for the preparation of thioesters from acid chlorides.
To a stirring solution of thiol (50 mmol) and acid chloride (50 mmol) in 210 mL hexanes at 0 ºC is slowly added Et_3N (55 mmol) in 20 mL hexanes over 30 min. The reaction is allowed to warm to ambient temperature and stirred for 12 h. After this time, the solution was filtered with the aid of hexanes. The filtrate was concentrated and purified by column chromatography.



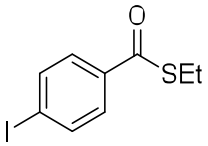
***S*-ethyl 2,4-difluorobenzothioate, 1i.** The reaction was performed according to the general procedure with 6.14 mL (50.0 mmol) of 2,4-difluorobenzoyl chloride to give 92% of the thioester (9.30 g, 46.0 mmol) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.34 (t, *J* = 7.6 Hz, 3H), 3.06 (q, *J* = 7.6 Hz, 2H), 6.85-6.96 (m, 2H), 7.86-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.6, 24.0, 105.3 (t, $J_{C\text{-}F}$ = 26 Hz), 111.9 (dd, $J_{C\text{-}F}$ = 22,4 Hz), 122.6, 131.7 (dd, $J_{C\text{-}F}$ =10, 3 Hz), 161.5 (dd, $J_{C\text{-}F}$ = 259, 12.6 Hz), 165.6 (dd, $J_{C\text{-}F}$= 255, 8 Hz); IR (DCM): 1673, 1650; HRMS (ESI): calcd for $C_9H_8F_2OS$ $[M+Na]^+$: 225.0156, found 225.0150.



S-ethyl 2-methylbenzothioate, 1j. The reaction was performed according to the general procedure with 2.6 mL (19.9 mmol) of *o*-tolyl chloride to give 36% of the thioester (1.30 g, 7.2 mmol) a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) 1.35 (t, *J* = 7.40 Hz, 3H), 2.48 (s, 3 H), 7.21-7.25 (m, 2H), 7.35-7.39 (m, 1H), 7.74 (dd, *J* = 8.3, 1.6, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): 14.8, 20.8, 23.8, 125.6, 128.8, 131.3, 137.9, 194.7; IR (neat): 1664 ; HRMS (ESI) calcd for $C_{10}H_{12}OS[M+Na]^+$: 203.0501 found 203.0501.



***S*-ethyl 4-bromobenzothioate, 1k.** The reaction was performed according to the general procedure with 5.00 g (22.8 mmol) of 4-bromobenzoyl chloride to give 95% of the thioester (5.31 g, 21.7 mmol) as a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.34 (t, *J* = 7.6 Hz, 3H), 3.07 (q, *J* = 7.6 Hz, 2H), 7.56-7.59 (m, 2H), 7.80-7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 14.9, 23.8, 128.4, 128.8, 132.0, 136.2, 191.2; IR (DCM) 1660; HRMS (ESI): calcd for C_9H_9BrOS $[M+Na]^+$: 268.9429, found 268.9434.

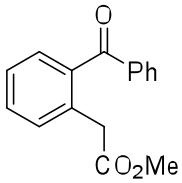


***S*-ethyl 4-iodobenzothioate, 1n.** The reaction was performed according to the general procedure with 2.00 g (7.51 mmol) of 4-iodobenzoyl chloride to give 89% of thioester (1.95 g, 6.68mmol) as a clear oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.34 (t, *J* = 7.6 Hz, 3H), 3.07 (q, *J* = 7.6 Hz, 2H), 7.64-7.68 (m, 2H), 7.78-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 14.7, 23.6, 100.9,

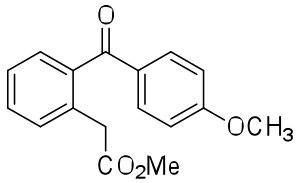
128.5, 136.6, 137.9, 191.4; IR (DCM): 1660; HRMS (ESI): calcd for C_9H_9IOS $[M+Na]^+$: 314.9311, found 314.9313.

General procedure for the preparation of arylzinc reagents.
To a stirring suspension of magnesium (1.46 g, 60.0 mmol) in 15 mL THF at 0 ºC is slowly added arylbromide (50 mmol) in 20 mL THF. The solution is allowed to warm to ambient temperature and stirred for 1 h. The Grignard solution is transferred to a stirring solution of $ZnCl_2$ (8.9 g, 68 mmol) in 40 mL THF at 0 ºC. Then the solution is stirred at ambient temperature for 1 h. After this time, the solution is taken into a glove box and filtered through a pad of Celite. The filtrate is concentrated until a concentration of 0.4-1.0 M is obtained through titration.

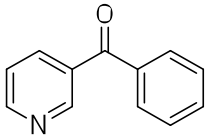
General procedure for the synthesis of biaryl ketones.
Thioester (1 mmol) in PhMe is added to $Pd(dba)_2$ (5.7 mg, 0.01 mmol) under nitrogen. To this stirring solution is added arylzinc reagent (1.2 equiv) and the solution is stirred for 1- 12 h while monitoring by GC analysis for completion. After this time, 5% HCl is added and the aqueous layer is extracted with Et_2O. The combined organic layers are dried with $MgSO_4$, concentrated and purified by flash column chromatography.



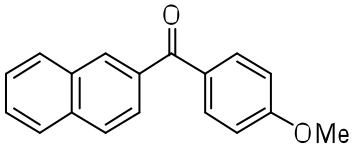
Methyl 2-(2-benzoylphenyl)acetate, 2a. The reaction is performed according to the general procedure with 238 mg (1 mmol) of methyl 2-(2-((ethylthio)carbonyl)phenyl)acetate and phenylzinc chloride (1.2 equiv) to give 85% of the product (216 mg, 0.85 mmol) as a light yellow oil. Spectroscopic data for this compound matched the previously reported literature values.[1]



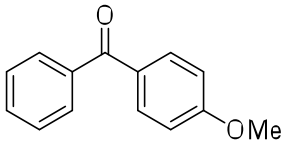
Methyl 2-(2-(4-methoxybenzoyl)phenyl)acetate, 2b. The reaction is performed according to the general procedure with 238 mg (1mmol) of methyl 2-(2-((ethylthio)carbonyl)phenyl)acetate and *p*-anisolylzinc chloride (1.2 equiv) to give 83% of the product (236 mg, 0.83 mmol) as a slightly yellow oil.^{1}H NMR ($CDCl_3$, 400 MHz): 3.54 (s, 3H), 3.84 (s, 2H), 3.87 (s, 3H), 6.92-6.95 (m, 2H), 7.32-7.38 (m, 3H), 7.43-7.47 (m, 1H), 7.78-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 38.7, 52.0, 60.6, 113.8, 126.5, 129.4, 130.4, 130.5, 131.6, 132.7, 133.4, 138.9, 163.6, 171.6, 196.6; IR (DCM): 1738, 1652; HRMS (ESI): calcd for $C_{17}H_{16}O_4$ $[M+Na]^+$: 307.0941, found 307.0935.



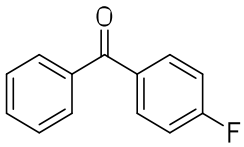
Phenyl(pyridin-3-yl)methanone, 2c. The reaction is performed according to the general procedure with 179 mg (1.0 mmol) of S-ethyl pyridine-3-carbothioate and phenylzinc chloride (1.2 equiv) to give 72% of the product (133 mg, 0.72 mmol) as a pale yellow solid that solidifies upon standing.. Spectroscopic data for this compound matched the previously reported literature values.[2]



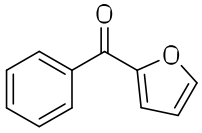
(4-methoxyphenyl)(naphthalen-2-yl)methanone, 2d. The reaction is performed according to the general procedure with 216 mg (1.0 mmol) of S-ethyl naphthalene-2-carbothioate and *p*-anisolylzinc chloride (1.2 equiv) to give 81% of the product (213 mg, 0.81 mmol) as an off-white solid. Spectroscopic data for this compound matched the previously reported literature values.[3]



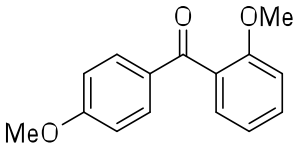
(4-methoxyphenyl)(phenyl)methanone, 2e. The reaction is performed according to the general procedure with 168 mg (1.0 mmol) of S-ethyl benzothioate and *p*-anisolylzinc chloride (1.2 equiv) to give 93% of the product (197 mg, 0.93 mmol) as a pale yellow solid. Spectroscopic data for this compound matched the previously reported literature values.[3]



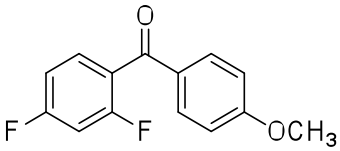
(4-fluorophenyl)(phenyl)methanone, 2f. The reaction is performed according to the general procedure with 166 mg (1.0 mmol) of S-ethyl benzothioate and (4-fluorophenyl)zinc chloride(1.2 equiv) to give 93% of the product (187 mg, 0.93 mmol) as a pale yellow oil that solidified upon standing. Spectroscopic data for this compound matched the previously reported literature values.[4]



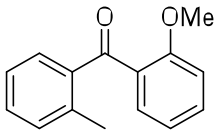
Furan-2-yl(phenyl)methanone, 2g. The reaction is performed according to the general procedure with 163 mg (1.0 mmol) of S-ethyl benzothioate and 2-furylzinc chlroide (1.2 equiv) to give 86% of the product (145.9 mg, 0.86 mmol) as a light tan oil. Spectroscopic data for this compound matched the previously reported literature values.[5]



(2-methoxyphenyl)(4-methoxyphenyl)methanone, 2h. The reaction is performed according to the general procedure with 216 mg (1.0 mmol) of S-ethyl 4-methoxybenzothioate and *o*-anisolylzinc chloride (1.2 equiv) to give 86% of the product (210 mg, 0.81 mmol) as a pale yellow solid. Spectroscopic data for this compound matched the previously reported literature values.[3]

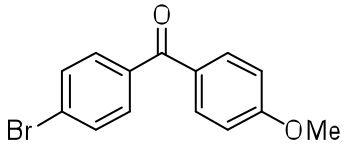


(2,4-Difluorophenyl)(4-methoxyphenyl)methanone, 2i. The reaction is performed according to the general procedure with 204 mg (1.0 mmol) of S-ethyl 2,4-difluorobenzothioate and *p*-anisolylzinc chloride (1.2 equiv) to give 82% of the product (204 mg, 0.82mmol) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.88 (s, 3H), 6.87-7.01 (m, 4H), 7.52-7.57 (m, 1H), 7.79-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 55.7, 104.7 (t, $J_{C\text{-}F}$ = 26 Hz), 111.9 (dd, $J_{C\text{-}F}$= 3, 21 Hz), 113.9, 124.0 (dd, $J_{C\text{-}F}$ = 4, 15 Hz), 130.3, 132.3 (dd, $J_{C\text{-}F}$ = 4, 10 Hz), 132.3, 160.7 (dd, $J_{C\text{-}F}$ = 12, 253 Hz), 164.1, 164.7 (dd, $J_{C\text{-}F}$ = 12, 252 Hz); IR (DCM): 1645; HRMS (ESI): calcd for $C_{14}H_{10}F_2O_2$ $[M+Na]^+$: 271.0541, found 271.0533.

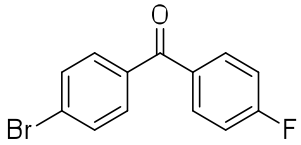


(2-methoxyphenyl)(o-tolyl)methanone, 2j. The reaction is performed according to the general procedure with 182 mg (1.0 mmol) of S-ethyl 2-methylbenzothioate and *o*-anisolylzinc chloride (1.2 equiv) to give 85% of the product (192 mg, 0.85 mmol) as a pale yellow crystalline solids. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.48 (s, 3H), 3.66 (s, 3H), 6.94 (d, J = 8.2 Hz, 1H), 6.99 (td, J = 7.5, 0.9 Hz, 1H), 7.12-7.16 (m, 1H), 7.22-7.24 (m, 1H), 7.30-7.35 (m, 2H), 7.41- 7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 20.7, 55.7, 111.8, 120.4, 125.2, 129.7, 130.1, 130.6, 130.8, 131.2, 132.7, 138.0, 139.3, 158.2, 198.3; IR (DCM): 3053, 2985, 1665; HRMS (ESI): calcd for $C_{15}H_{14}O_2$ $[M+Na]^+$: 249.0886, found 249.0873.

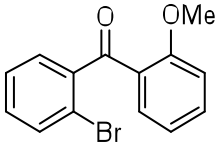
General procedure for the synthesis of biaryl ketones and biphenyl thioester.
Thioester (1 mmol) in PhMe is added to $Pd(dba)_2$ (2.9 mg, 0.005 mmol) and tri(2-furyl)phosphine under inert atmosphere. To this stirring solution is added arylzinc reagent (1.2 equiv) and the solution is stirred while monitoring by GC analysis. After this time, 5% HCl is added and the aqueous layer is extracted with Et_2O. The combined organic layers are dried with Na_2SO_4, concentrated and purified by flash column chromatography.



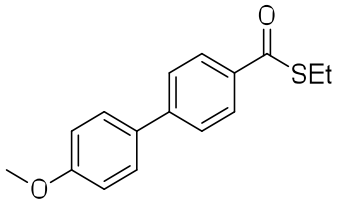
(4-Bromophenyl)(4-methoxyphenyl)methanone, 2k. The reaction was performed according to the general procedure with 246 mg (1.0 mmol) of S-ethyl 4-bromobenzothioate and *p*-anisolylzinc chloride (1.2 equiv) to give 68% of the product (197 mg, 0.68 mmol) as a white solid. Spectroscopic data for this compound matched the previously reported literature values.[6]



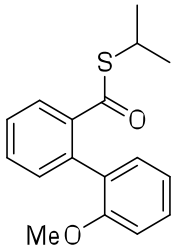
(4-bromophenyl)(4-fluorophenyl)methanone, 2l. The reaction was performed according to the general procedure using 245.0 mg (1.0 mmol) of S-ethyl 4-bromobenzothioate and *p*-fluorophenylzinc chloride (1.2 equiv) to give 72% of the product (200.0 mg, 0.72 mmol) as an off-white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.13 to 7.18 (m, 2H), 7.62 to 7.63 (m, 4H), 7.79 to 7.82 (m, 2H);^{13}C NMR ($CDCl_3$, 100 MHz): 115.7 ($J_{C\text{-}F}$= 22 Hz), 127.6, 131.6 ($J_{C\text{-}F}$= 32 Hz), 132.6 ($J_{C\text{-}F}$= 9 Hz), 133.5 ($J_{C\text{-}F}$= 3 Hz), 136.3, 164.3, 166.8, 194.1; IR (DCM): 3053, 1661; HRMS (ESI): calcd for $C_{13}H_8BrFO$ $[M+Na]^+$: 300.9635, found 300.9626.



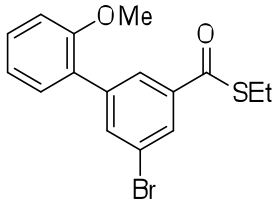
(2-bromophenyl)(2-methoxyphenyl)methanone, 2m. The reaction was performed according to the general procedure using 243.6 mg (1.0 mmol) of S-ethyl 2-bromobenzothioate and *o*-anisolylzinc chloride (1.2 equiv) to give 79% of the product (220.0 mg, 0.79 mmol) as a white solid. Spectroscopic data for this compound matched the previously reported literature values.[7]



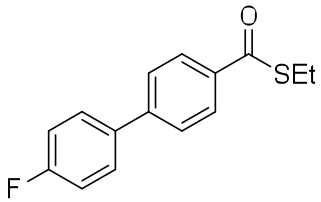
S-ethyl 4'-methoxy-[1,1'-biphenyl]-4-carbothioate, 3n. The reaction was performed according to the general procedure with 292 mg (1.00 mmol) of S-ethyl 4-iodobenzothioate and *p*-anisolylzinc chloride (1.2 equiv) to give 70% of the product (190 mg, 0.70 mmol) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.38 (t, J = 7.6 Hz, 3H), 3.10 (q, J = 7.6Hz, 2H), 3.87 (s, 3H), 6.99-7.01 (m, 2H), 7.56-7.58 (m, 2H), 7.61-7.64 (m, 2H), 8.00-8.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 15.0, 23.6, 55.5, 114.6, 126.7, 127.9, 128.5, 132.4, 135.5, 145.7, 160.1, 191.7; IR (DCM): 1643; HRMS (ESI): calcd for $C_{16}H_{16}O_2S$ $[M+Na]^+$: 295.0763, found 295.0769.



S-isopropyl 2'-methoxy-[1,1'-biphenyl]-2-carbothioate, 3o. The reaction was performed according to the general procedure with 306.2 mg (1.00 mmol) of S-isopropyl 2-iodobenzothioate and *o*-anisoylzinc chloride (1.2 equiv) to give 86% of the product (246.3 mg, 0.86 mmol) as white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): 1.27 (d *J*= 6.9 Hz, 6H), 3.61 (q, *J*= 6.9 Hz, 1H), 3.68 (s, 3H), 6.84 (d, *J*= 8.3 Hz, 1H), 6.99 (td, *J* = 7.4, 0.9 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.28-7.35 (m, 3H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): 22.6, 34.7, 54.7, 109.9, 120.4, 126.8, 127.4, 128.7, 129.3, 130.1, 130.9, 131.2, 136.4, 138.6, 155.5, 193.6; IR (DCM): 3053, 2964,1667; HRMS (ESI): calcd for $C_{17}H1_8O2S$ $[M+Na]^+$: 309.0920, found 309.0920.

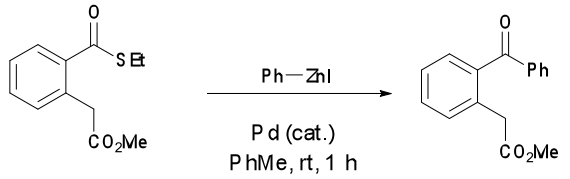


S-ethyl 5-bromo-2'-methoxy-[1,1'-biphenyl]-3-carbothioate, 3p. The reaction was performed according to the general procedure with 375.6 mg (1.00 mmol) of S-ethyl 5-bromo-2'-methoxy-[1,1'-biphenyl]-3-carbothioate and *o*-anisoylzinc chloride (1.2 equiv) to give 62% of the product (216.9 mg, 0.62 mmol) as a pale tan colored solid.^{1}H NMR ($CDCl_3$, 400 MHz): 1.35, (t, *J* = 7.4 Hz, 3H), 3.08(q, *J* = 7.4), 7.01-6.97 (m, 2H), 7.03 – 7.36 (m, 2H), 7.86 (m, 1H), 8.01 (m, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz): 22.6, 34.7, 54.7, 109.9, 120.4, 126.8, 127.4, 128.7, 129.3, 130.1, 130.9, 131.2, 136.4, 138.6, 155.5, 193.6; IR (DCM): 3053, 2964,1667; HRMS (ESI): calcd for $C_{16}H_{15}BrO_2S$ $[M+Na]^+$: 372.9898, found 372.9851



S-ethyl 4'-methoxy-[1,1'-biphenyl]-4-carbothioate, 3q. The reaction was performed according to the general procedure with 295 mg (1.00 mmol) of S-ethyl 4-iodobenzothioate and *p*-fluorophenyllzinc chloride (1.2 equiv) to give 58% of the product (150 mg, 0.58 mmol) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.36 (t, *J* = 7.64 Hz, 3H), 3.09 (q, *J* = 7.4 Hz, 2H), 3.87 (s, 3H), 7.13 (t, *J*= 8.64, 2H), 7.54-7.60 (m, 4H), 8.00 (d,*J*= 8.4, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 14.8, 23.6, 116.0 (d, J_{C-F}= 21.4 Hz), 127.1, 127.9, 129.0, (d, J_{C-F}= 8.2 Hz), 136.1, 145.0, 163.1, (d, J_{C-F}= 246.6), 191.6.IR (DCM): 2984, 1662; HRMS (ESI): calcd for $C_{15}H_{13}FOS$ $[M+Na]^+$: 283.0564, found 283.0563.

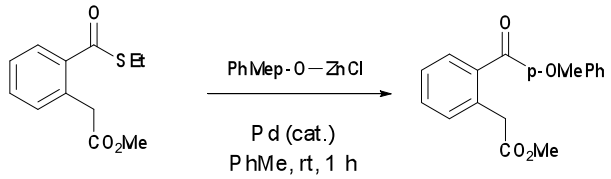
Table S1. Optimization of Diaryl ketone formation



Entry	Pd source (mol %)	Ligand (mol %)	Prod:SM [a]
1	$PdCl_2(PPh_3)_2$ (10)	--	38:62
2	$Pd[PPh_3]_4$ (6)	--	0:100
3	$Pd(dba)_2$ (9)	PPh_3	3:97
4	$Pd(dba)_2$ (13)	dppf (8)	20:80
5	$Pd(dba)_2$ (12)	P(*o*-tol)$_3$ (11)	36:64
6	$Pd(dba)_2$ (13)	TFP (15)	25:75
7	$[Pd(\mu\text{-}Br)P^tBu_3]_2$ (10)	--	95:5
8	$[Pd(\mu\text{-}Br)P^tBu_3]_2$ (0.2)	–	95:5

[a]Prod:SM ratio is the ratio of product to starting material according to ^{1}H NMR spectroscopy

Table S2: Optimization of phosphine-free Fukuyama reaction



Entry	Pd source (mol %)	Ligand (mol %)	Prod:SM [a]
1	$[Pd(\mu\text{-}Br)P^tBu_3]_2$ (0.2)	--	87:13
2	$PdCl_2(PPh_3)_2$ (0.5)	--	95:5
3	$Pd(dba)_2$ (0.5)	TFP (0.75)	85:15
4	$Pd(dba)_2$ (0.5)	PCy_3 (1.0)	95:5
5	$Pd(dba)_2$ (0.5)	P(*o*-tol)$_3$ (0.75)	87:13
6	$Pd(dba)_2$ (0.5)	CATAXium (0.75)	95:5
7	$Pd(dba)_2$ (0.5)	--	78:22
7	$Pd(dba)_2$ (1)	--	95:5

[a]Prod:SM ratio is the ratio of product to starting material according to ^{1}H NMR spectroscopy

References

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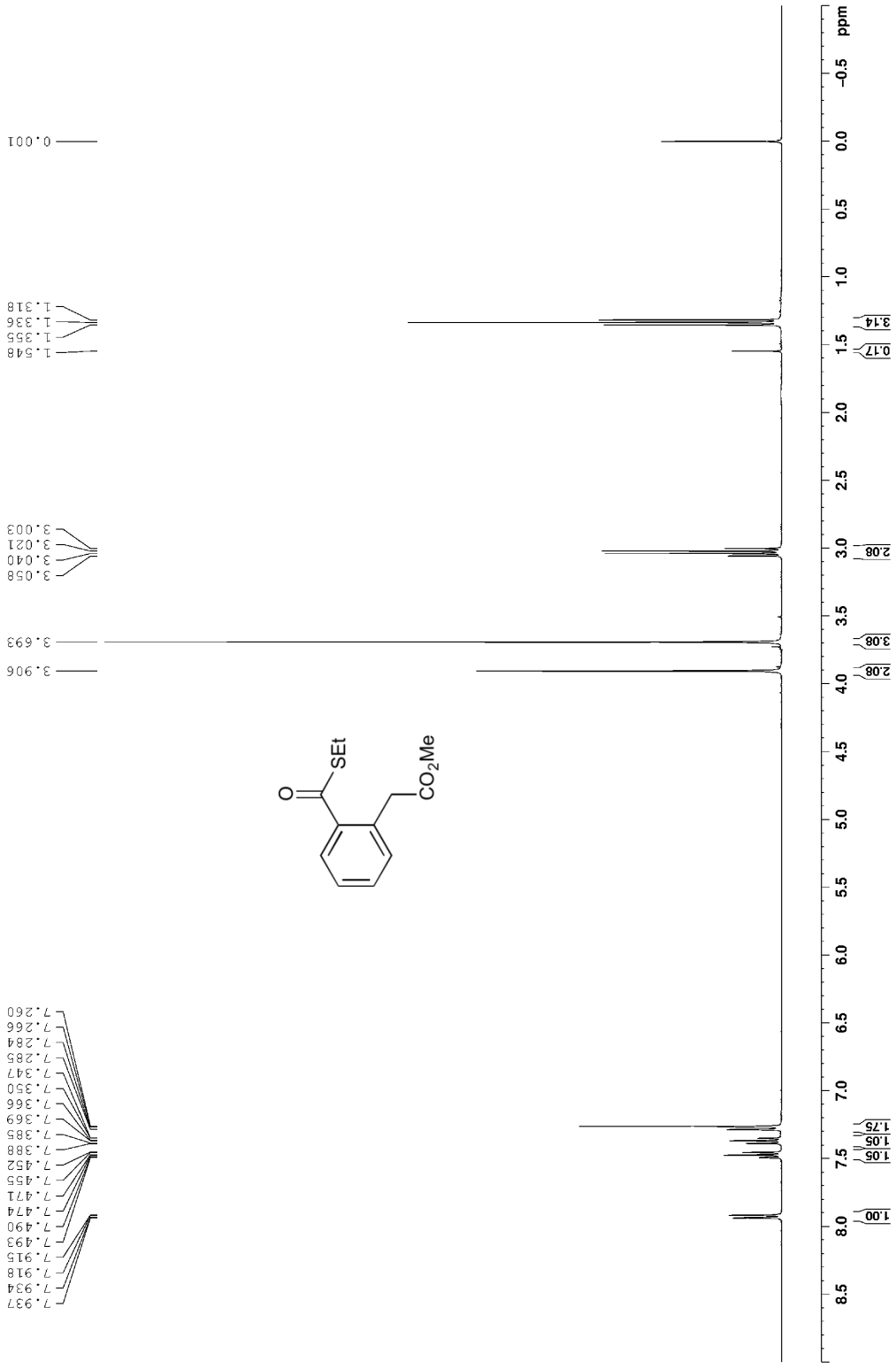
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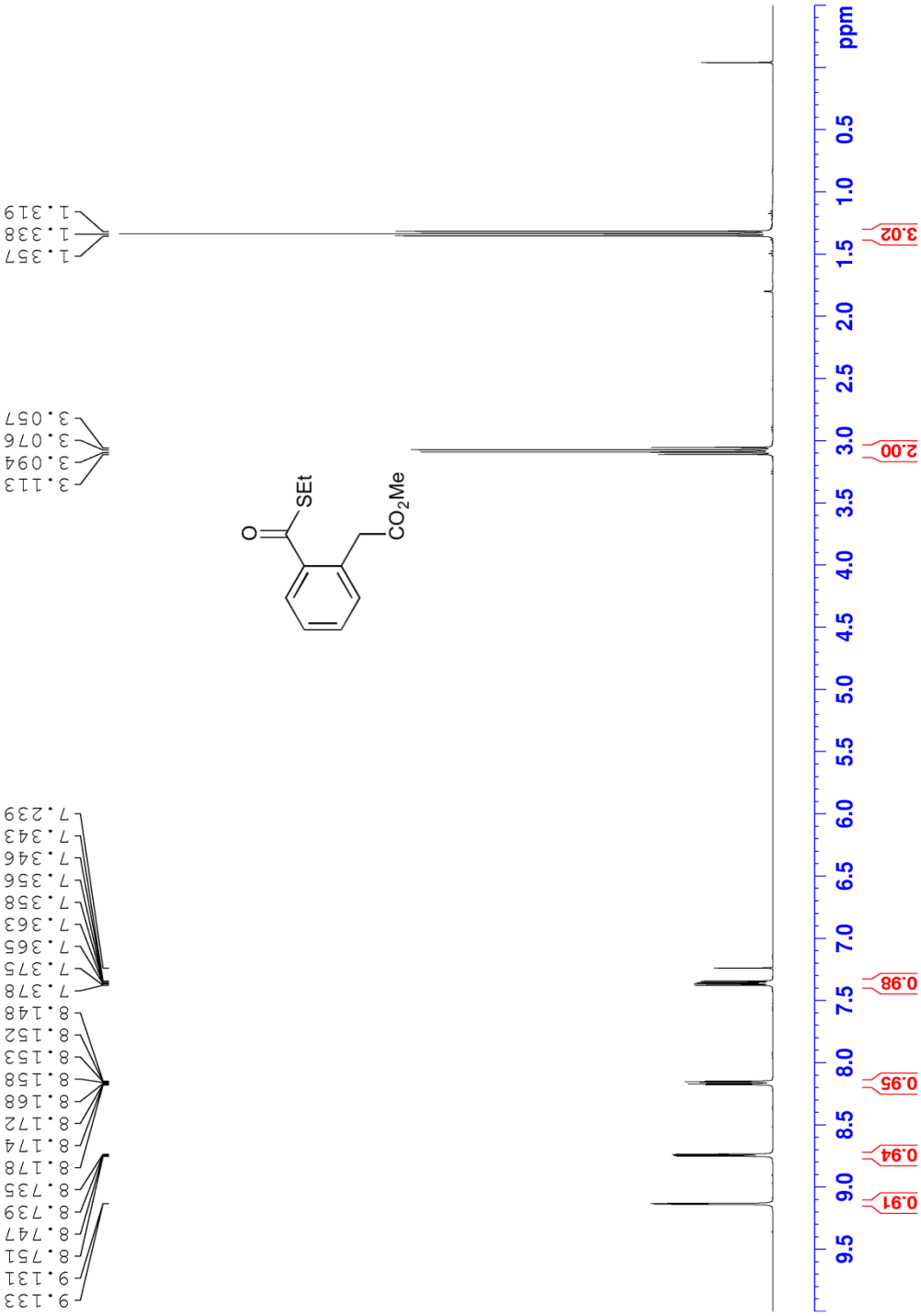
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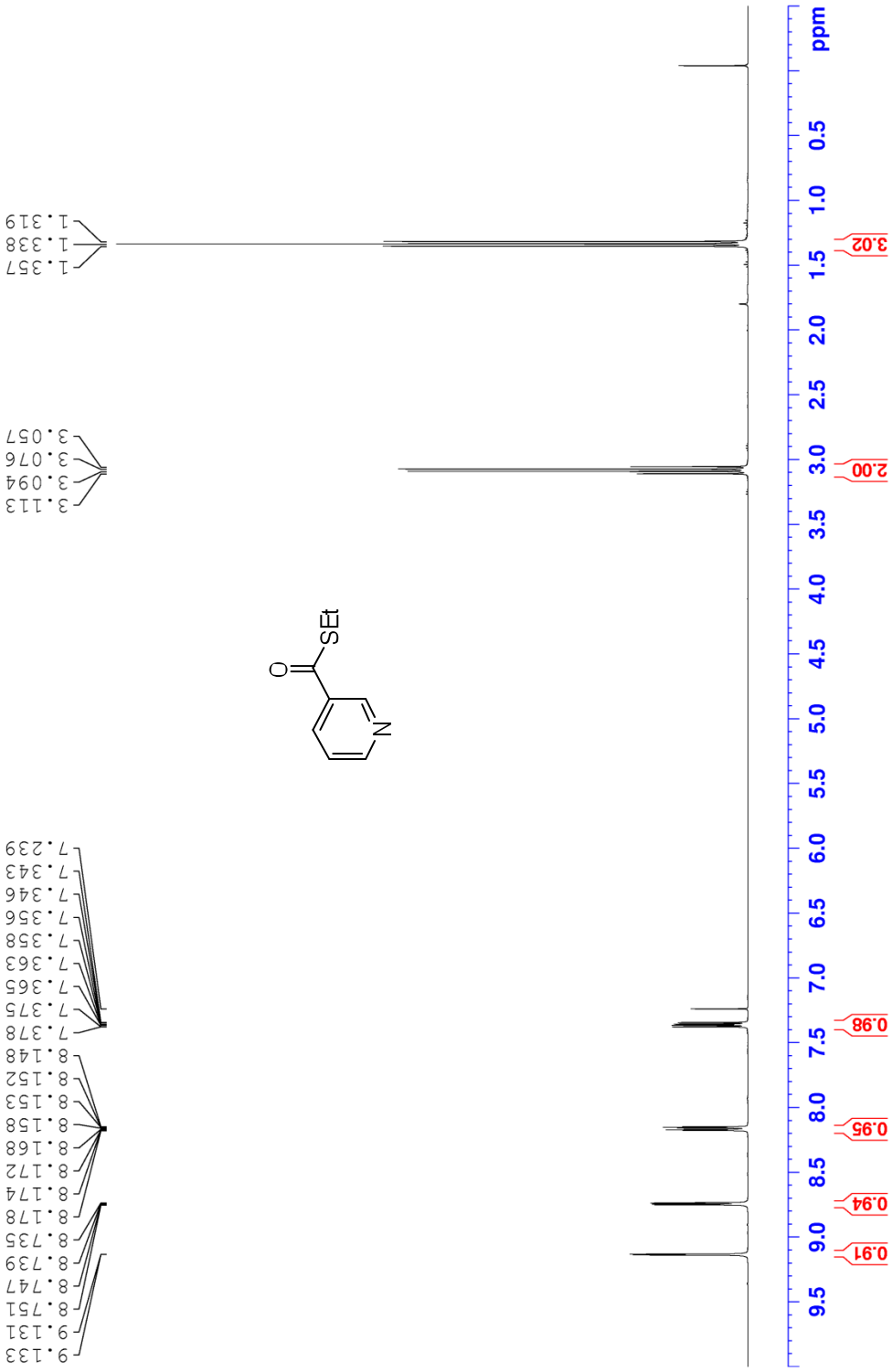
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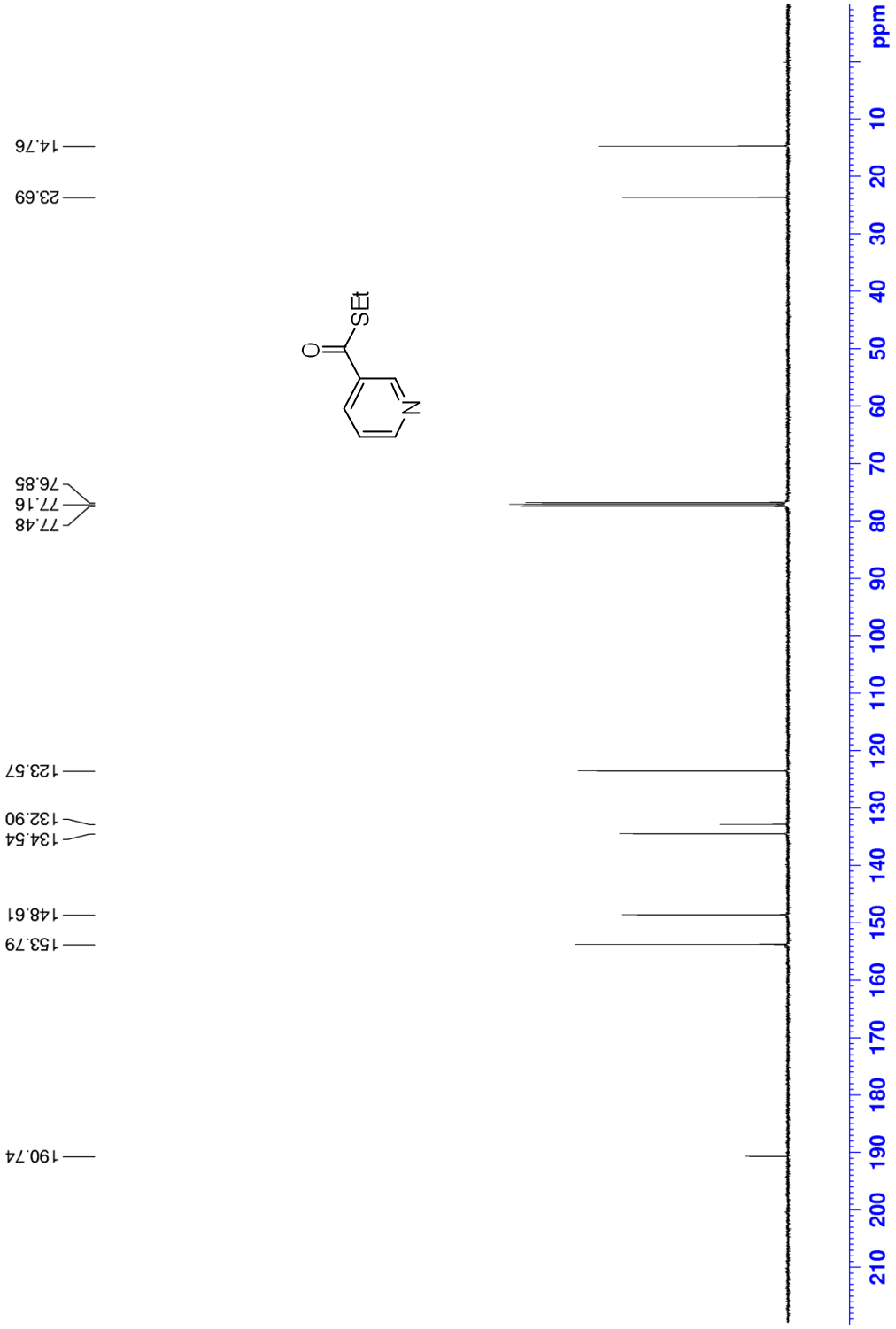
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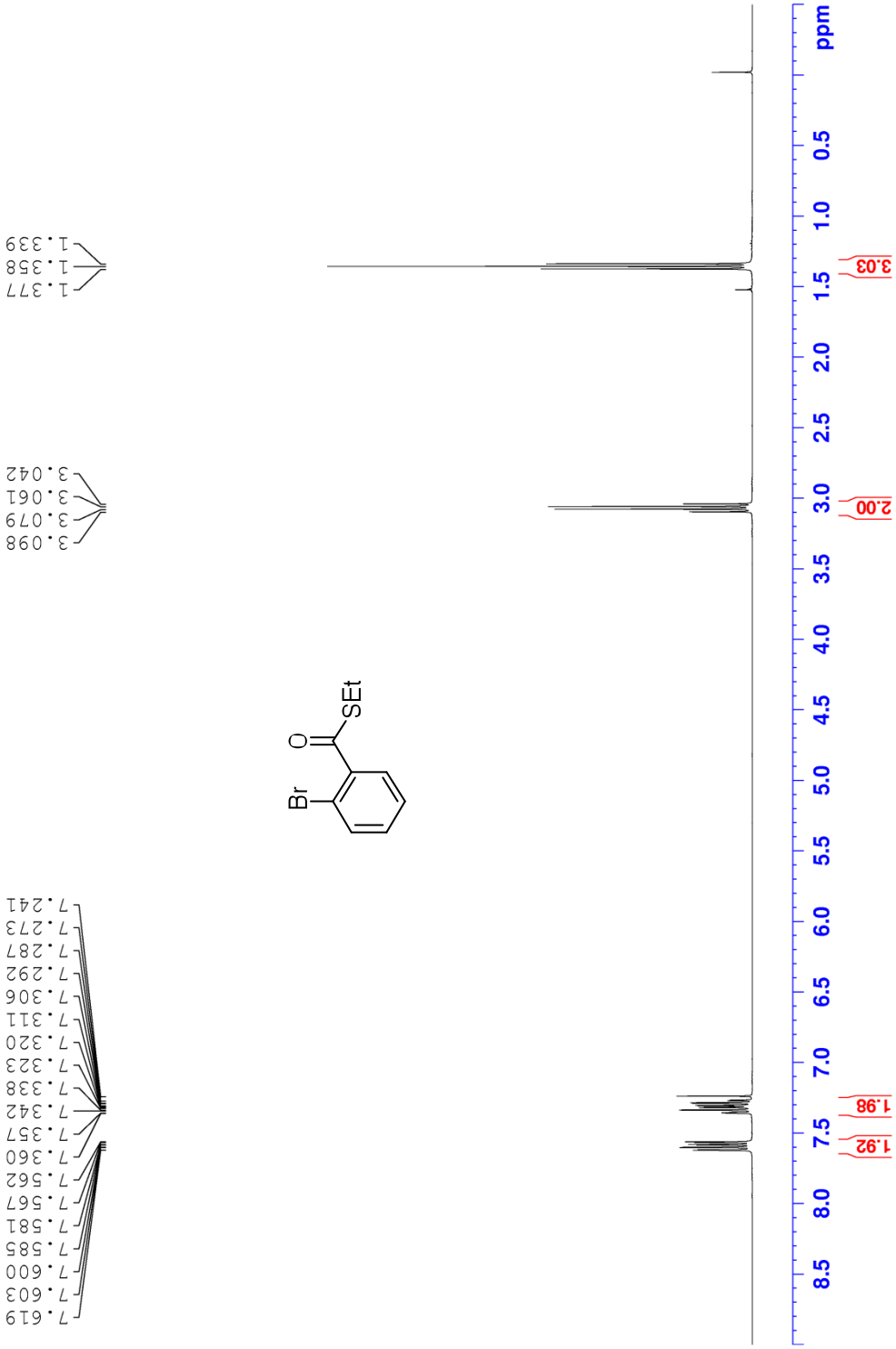
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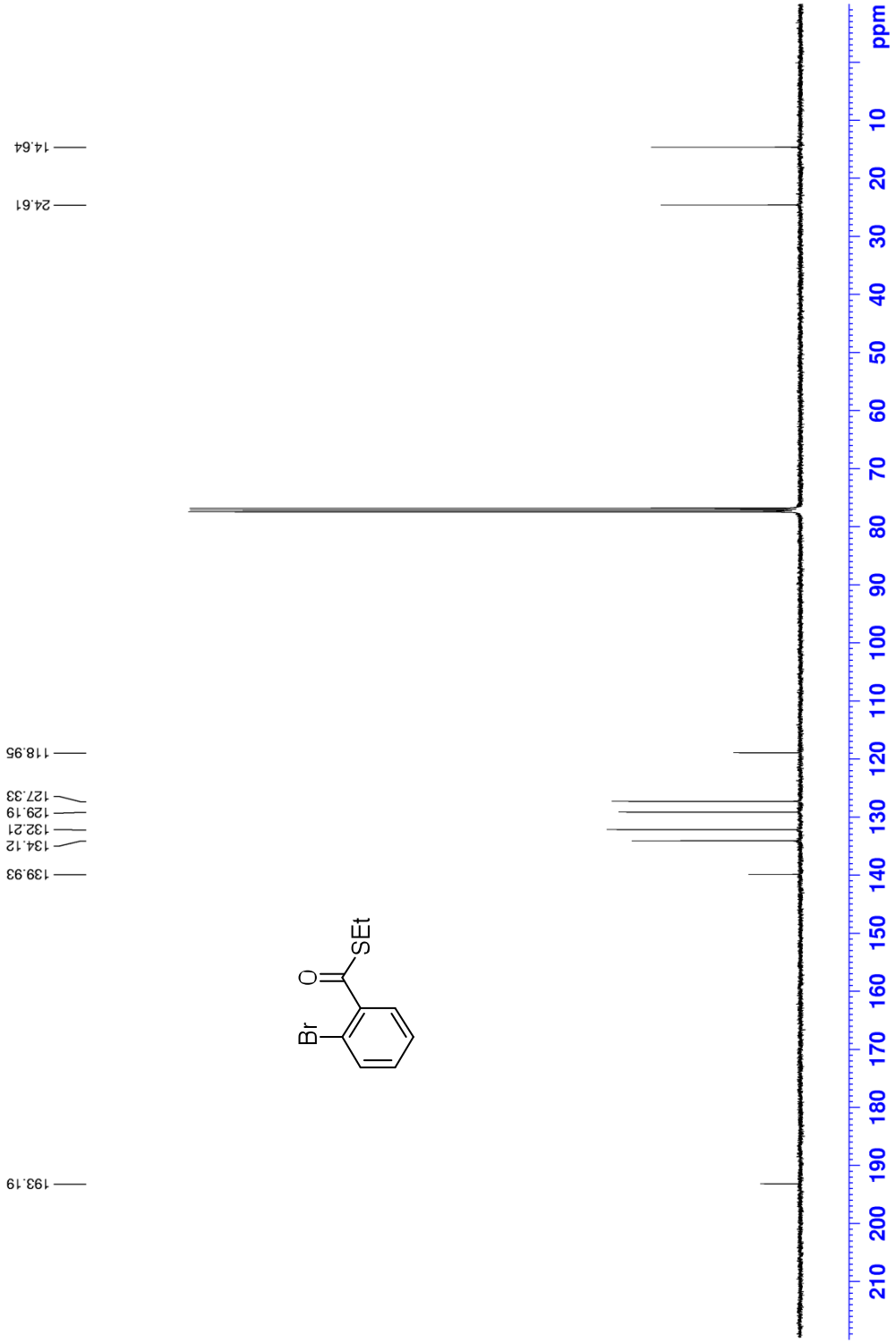
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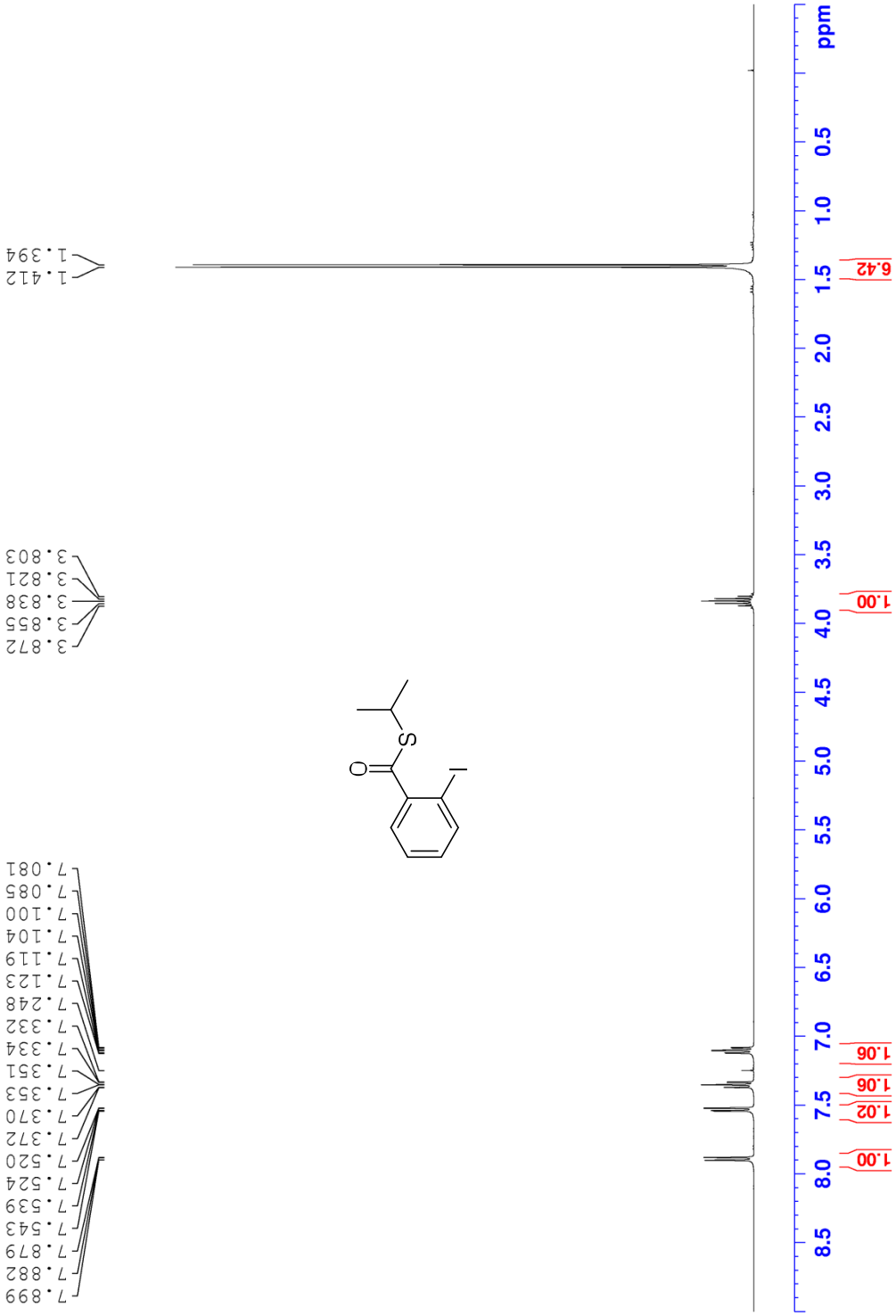
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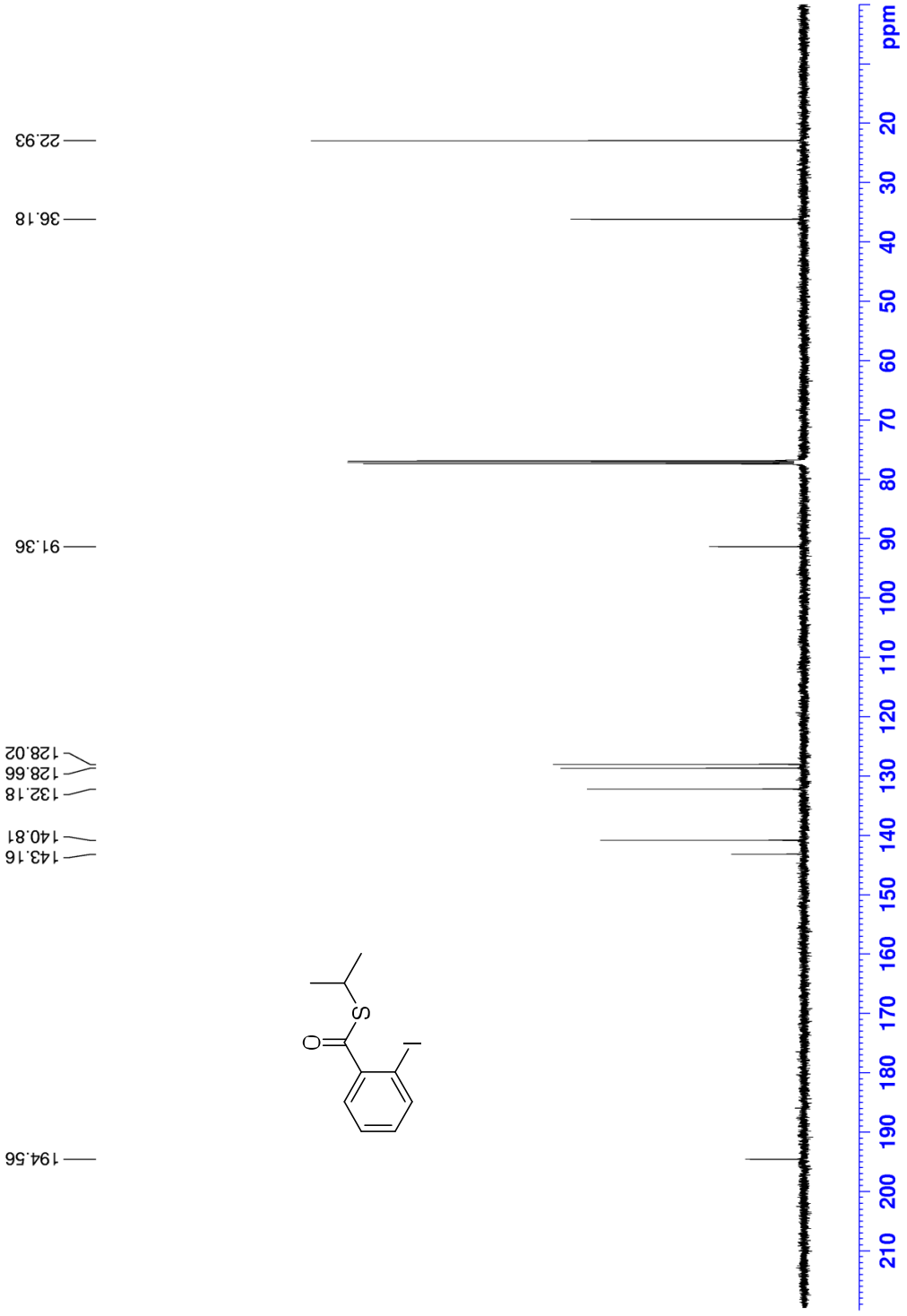
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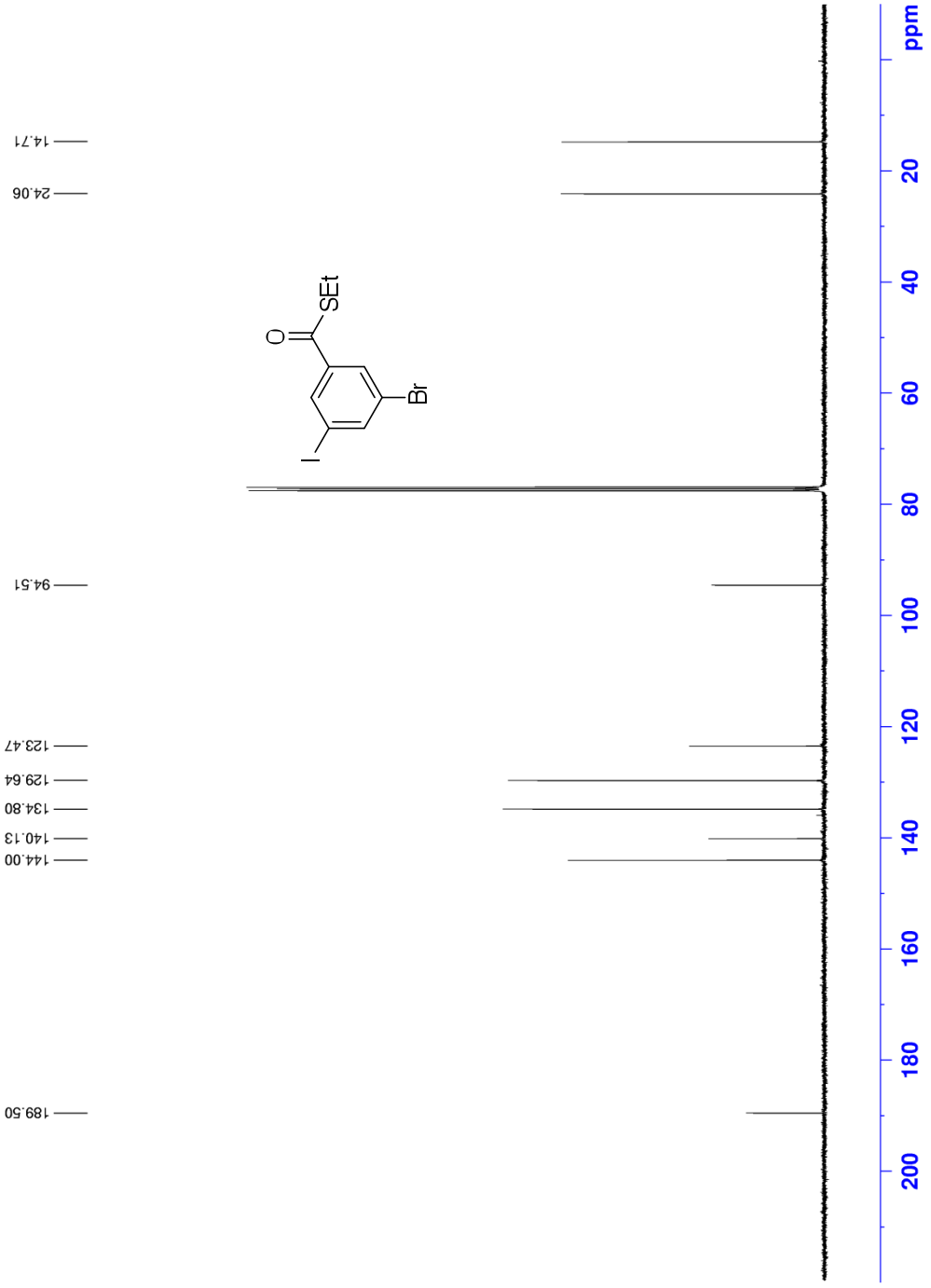
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24.06
94.51
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134.80
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144.00
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O
SEt
Br
I
ppm
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60
80
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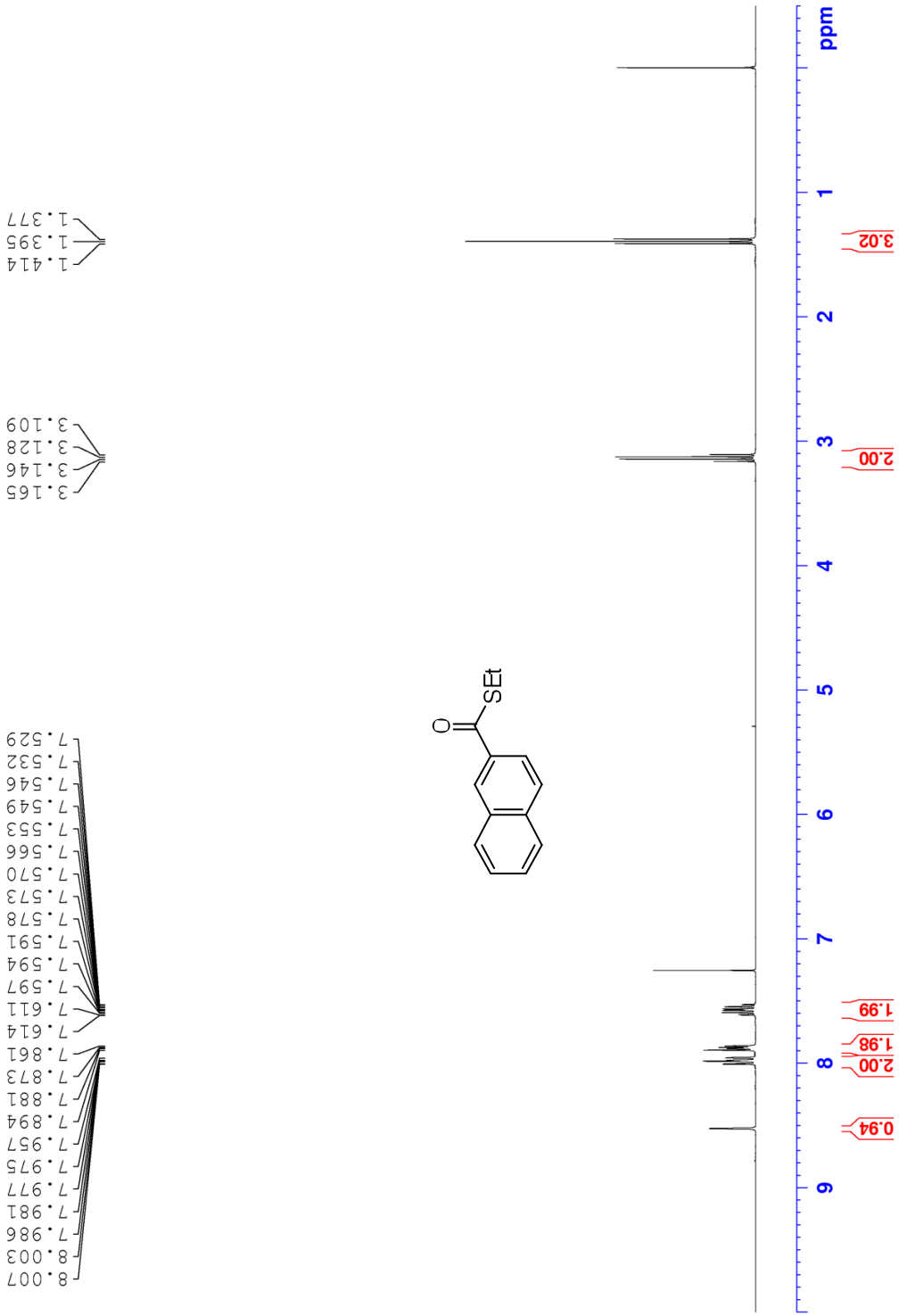
120
140
160
180
200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1.395
1.414
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3.146
3.165
7.529
7.532
7.546
7.549
7.553
7.566
7.570
7.573
7.578
7.591
7.594
7.597
7.611
7.614
7.861
7.873
7.881
7.894
7.957
7.975
7.977
7.981
7.986
8.003
8.007
O
SEt
ppm
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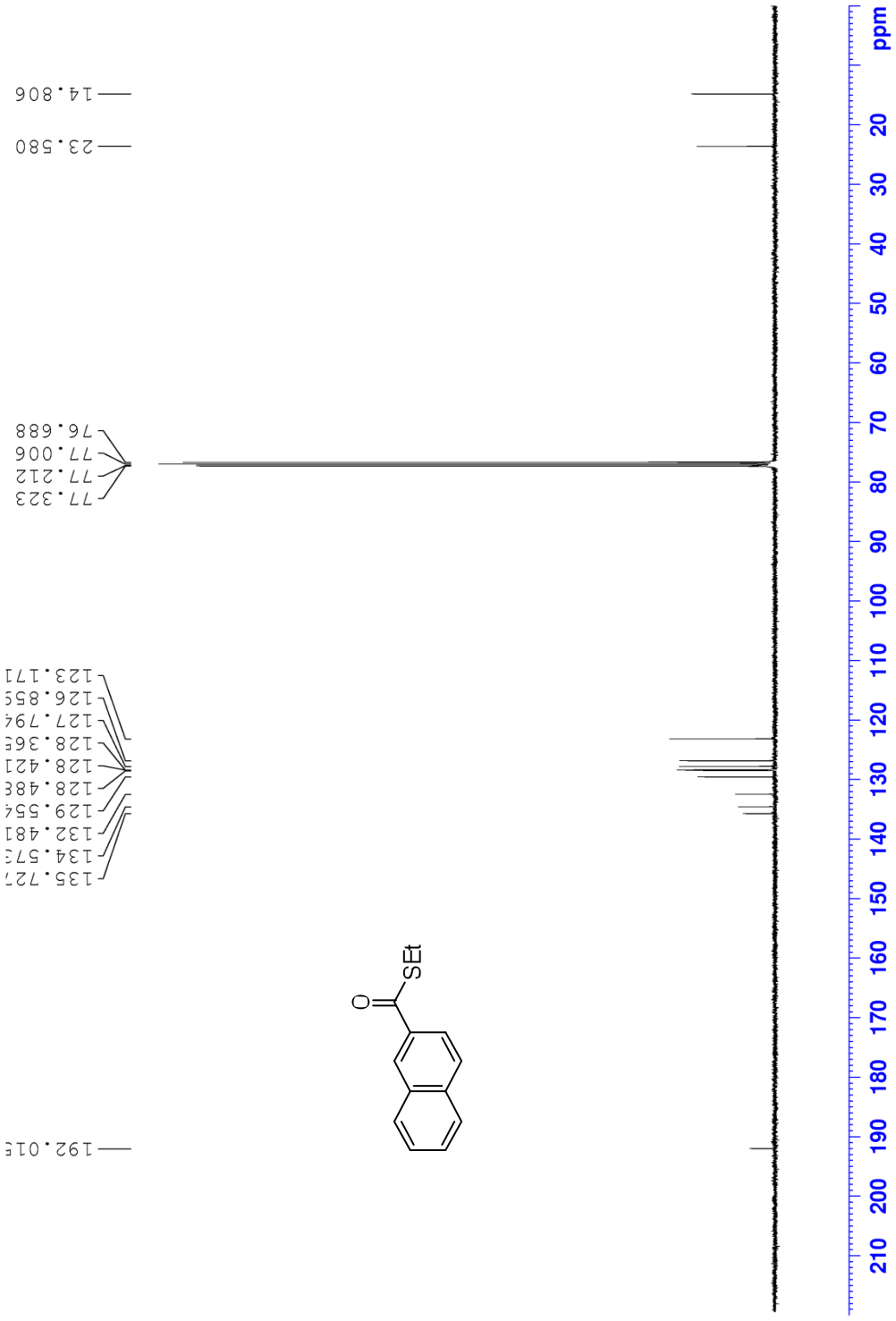
2
3
4
5
6
7
8
9
3.02
2.00
1.99
1.98
2.00
0.94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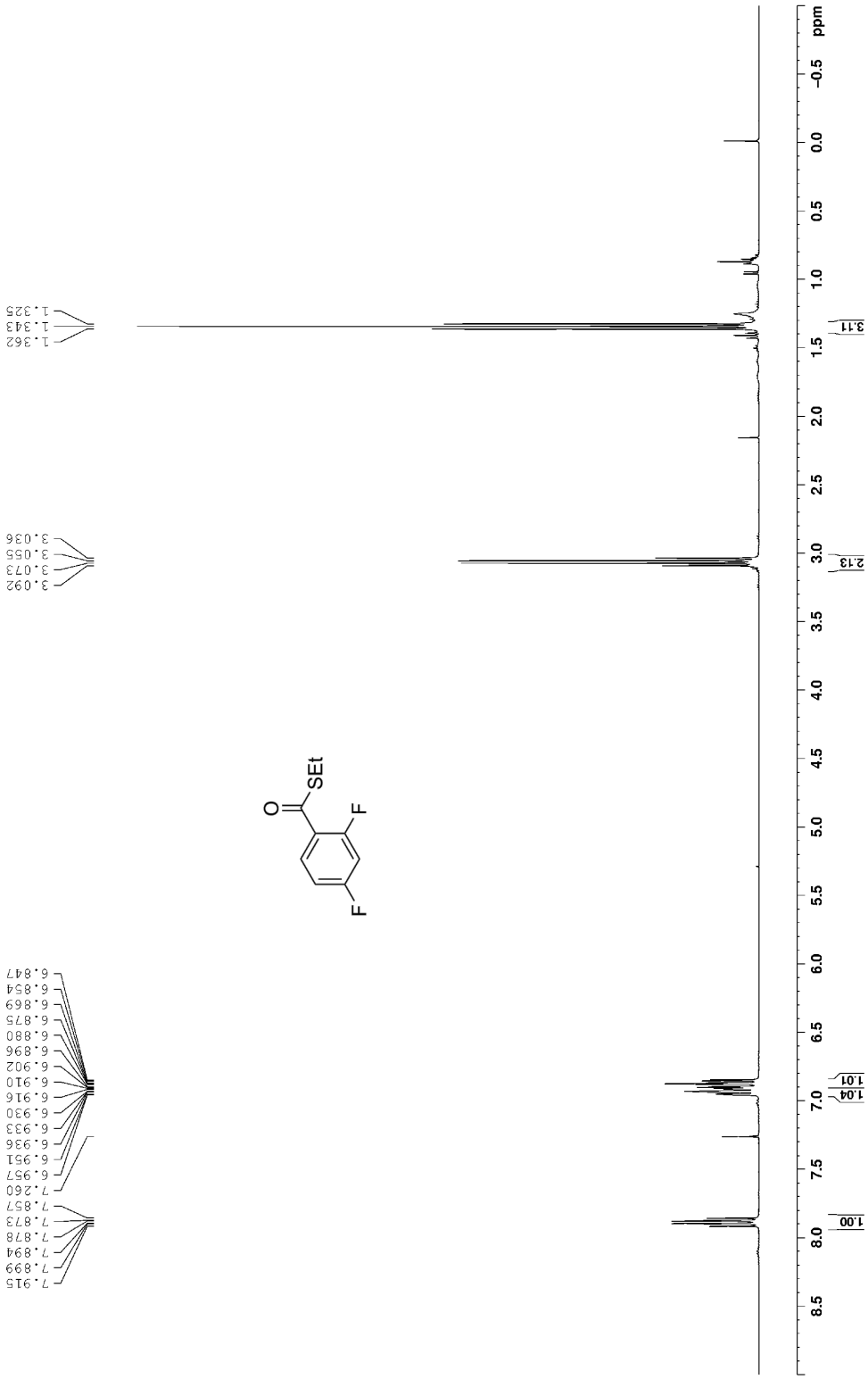
23.580
76.688
77.006
77.212
77.323
123.171
126.859
127.794
128.365
128.421
128.488
129.554
132.481
134.573
135.727
192.015
O
SEt
ppm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1.343
1.325
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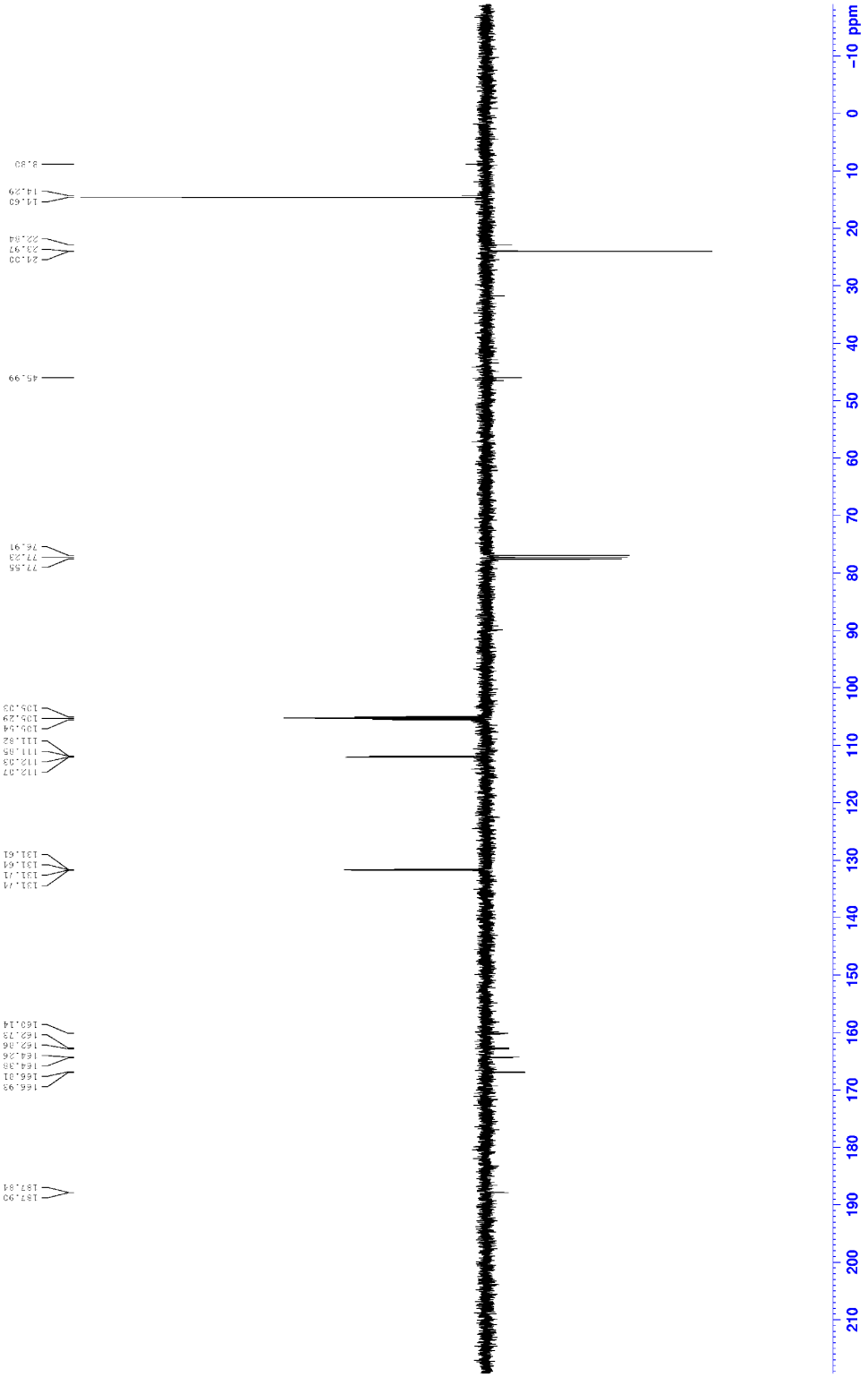
3.055
3.036
6.847
6.854
6.869
6.875
6.880
6.896
6.902
6.910
6.916
6.930
6.933
6.936
6.951
6.957
7.260
7.857
7.873
7.878
7.894
7.899
7.915
O
SEt
F
F
3.11
2.13
1.04
1.01
1.00
ppm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14.60
14.79
22.84
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24.00
45.99
76.91
77.23
77.55
105.03
105.29
105.54
111.82
111.85
112.03
112.07
131.61
131.64
131.71
131.74
160.14
162.73
162.86
164.26
164.38
166.31
166.93
187.90
187.94
ppm
-10
0
10
20
30
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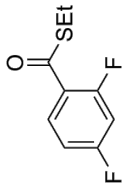
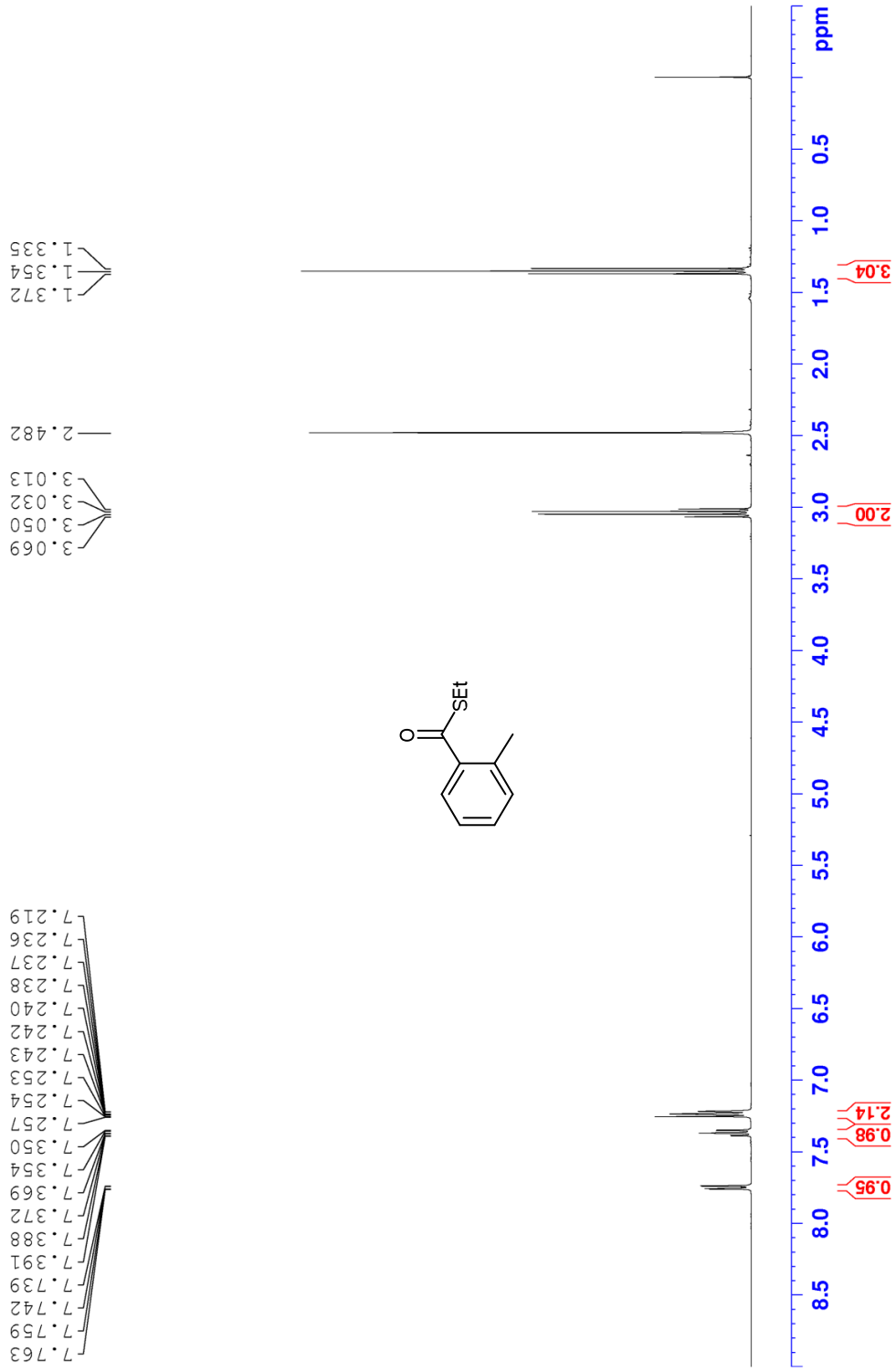
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


O
SEt
F
F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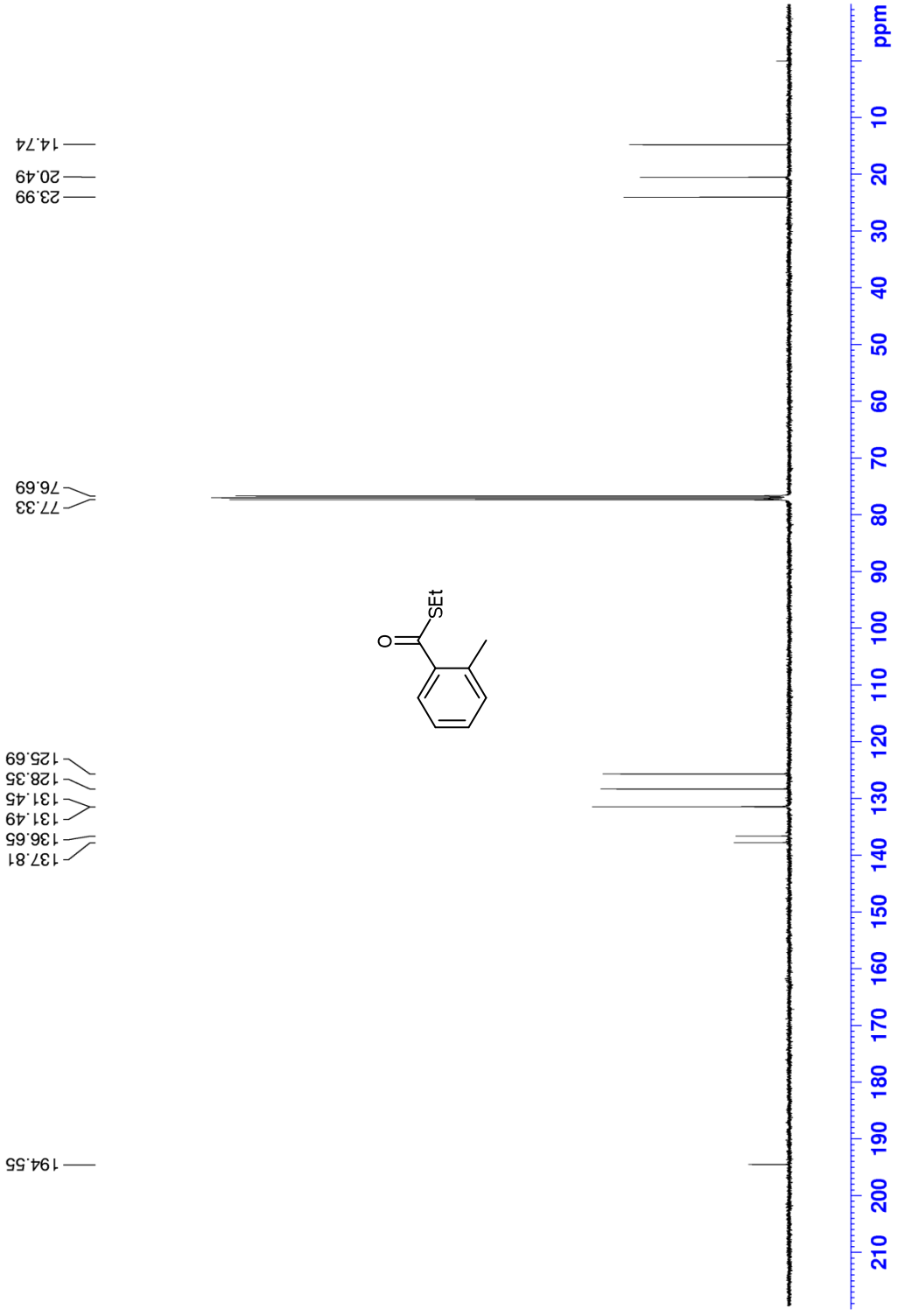
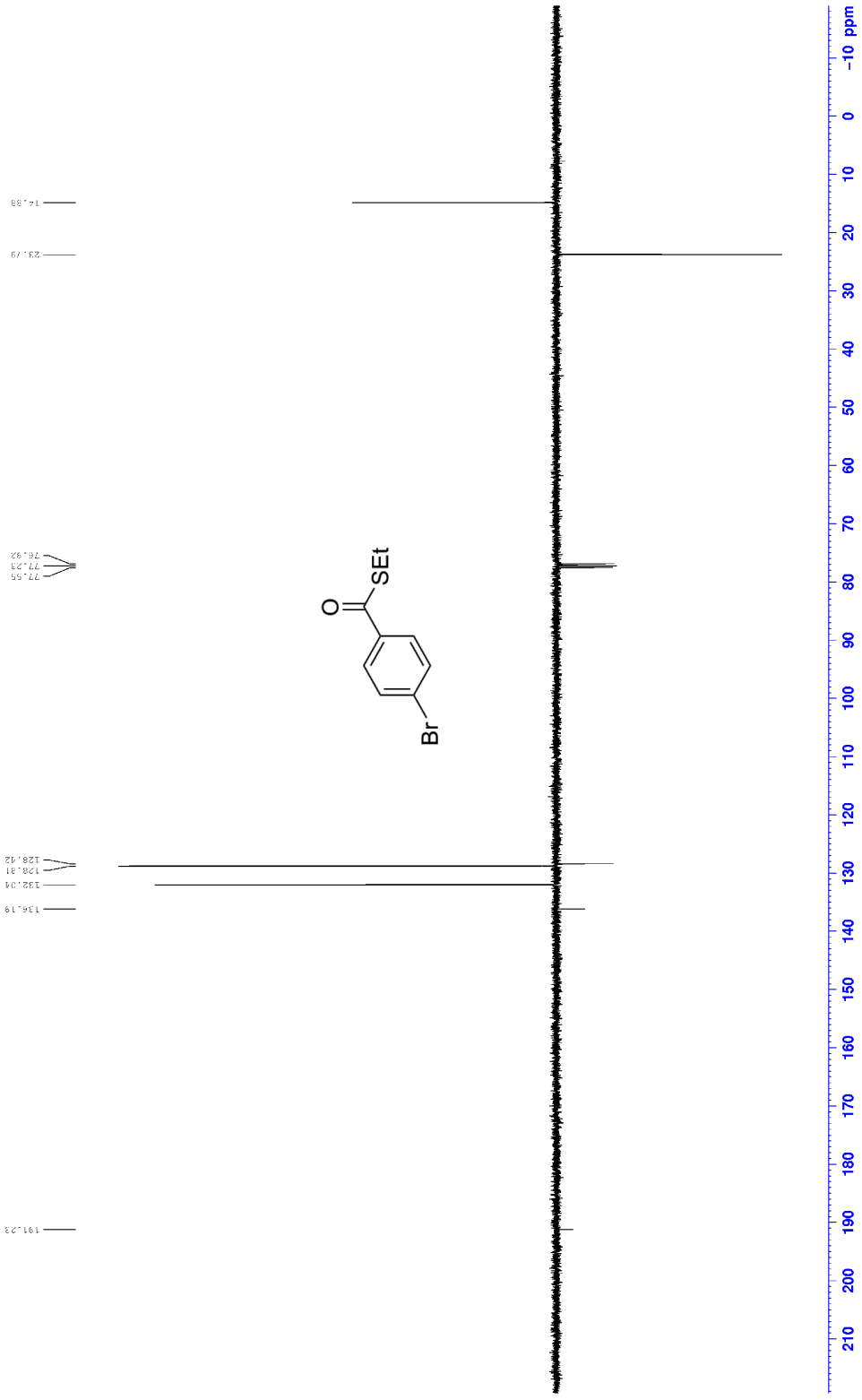
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
3.04
2.00
2.14
0.98
0.95
1.335
1.354
1.372
2.482
3.013
3.032
3.050
3.069
7.219
7.236
7.237
7.238
7.240
7.242
7.243
7.253
7.254
7.257
7.350
7.354
7.369
7.372
7.388
7.391
7.739
7.742
7.759
7.763
SEt
O


14.74
20.49
23.99
76.69
77.33
125.69
128.35
131.45
131.49
136.65
137.81
194.55
SEt
O
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


1.326
1.344
1.363
3.043
3.062
3.080
3.099
7.260
7.556
7.562
7.566
7.579
7.583
7.589
7.796
7.801
7.806
7.818
7.823
7.829
O
SEt
Br
3.06
2.03
2.02
2.00
ppm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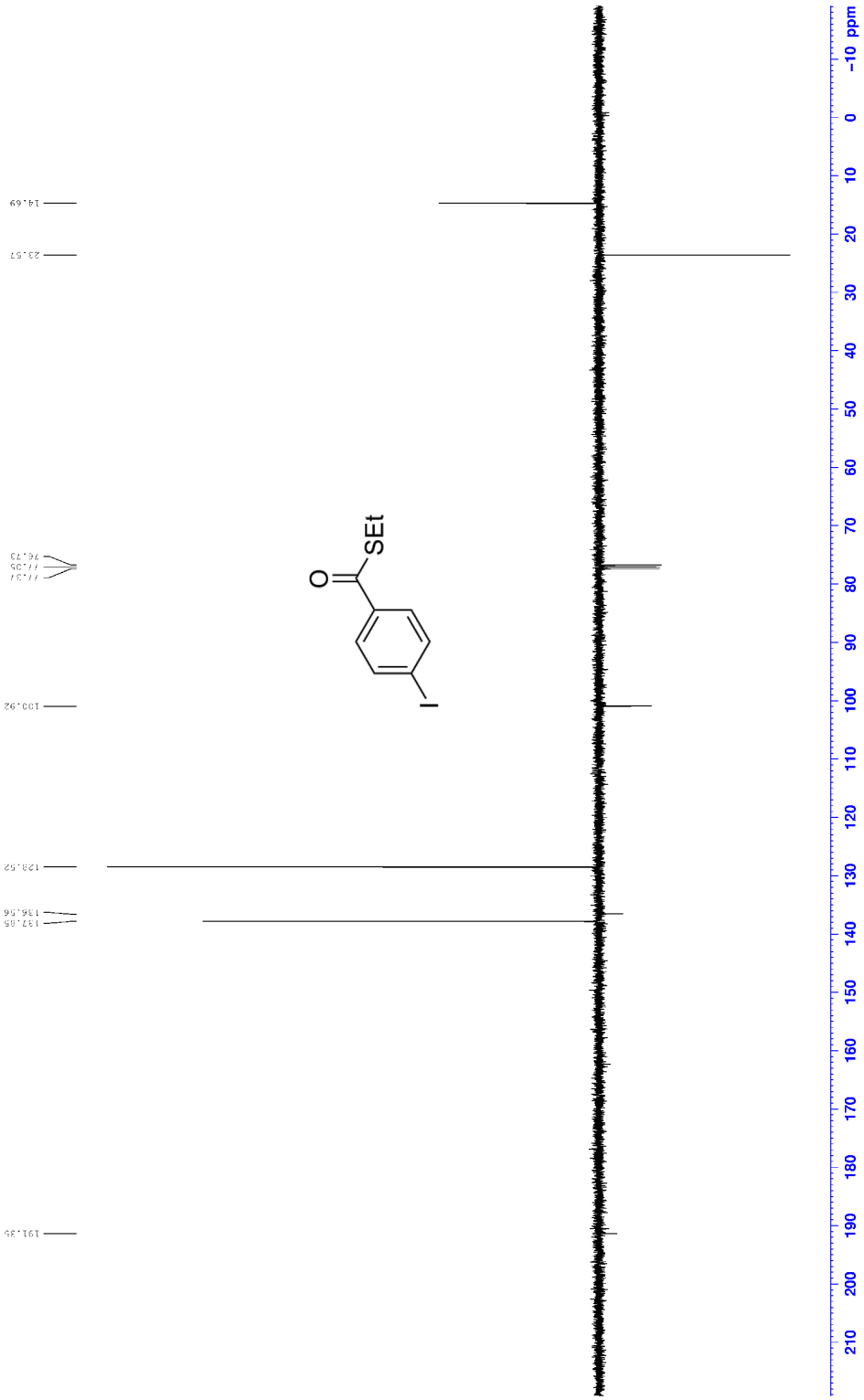
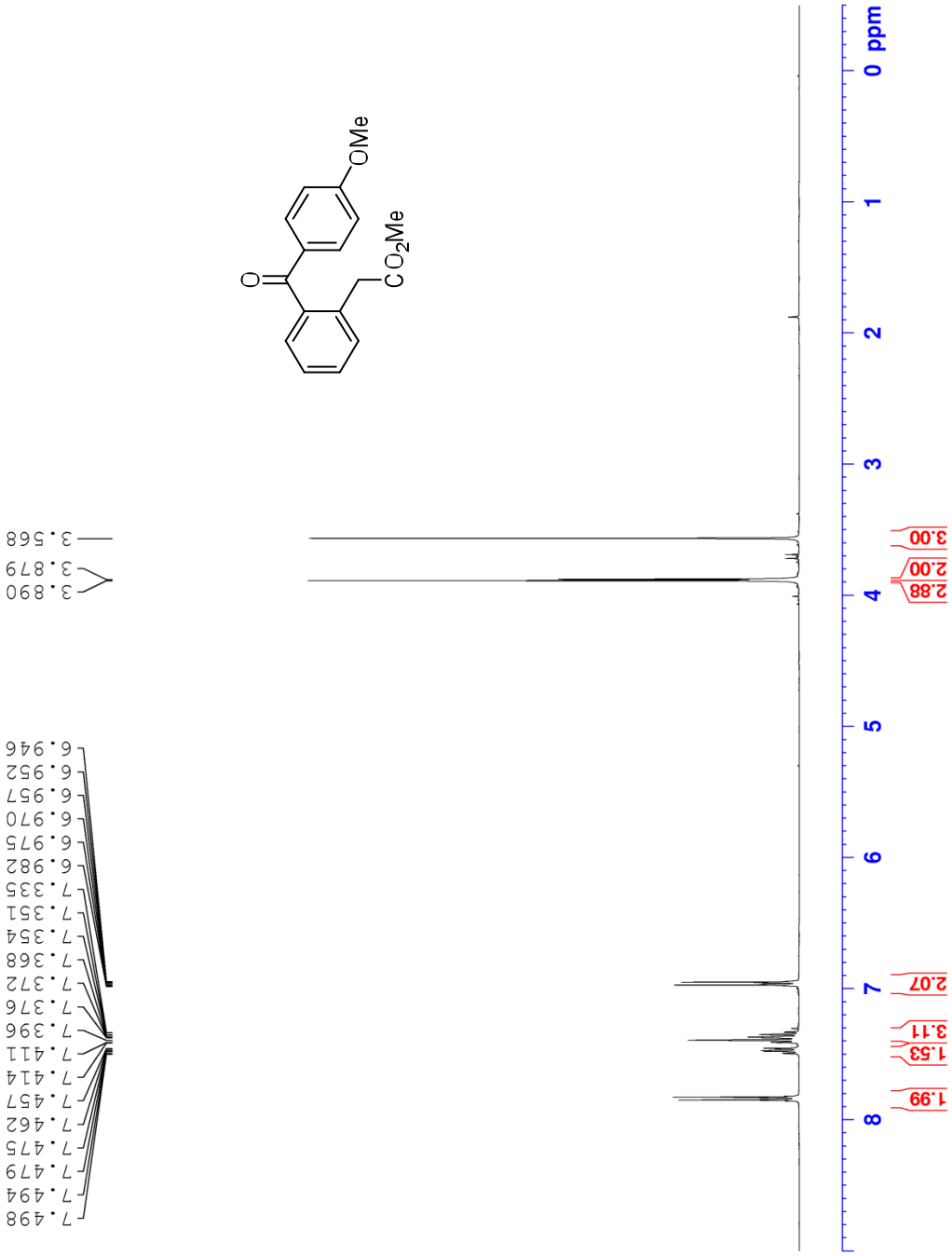
23.79
76.92
77.23
77.55
128.42
128.81
132.04
136.19
191.23
O
SEt
Br
−10 ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


1.325
1.344
1.362
3.042
3.060
3.079
3.097
7.260
7.643
7.649
7.653
7.665
7.670
7.675
7.781
7.786
7.791
7.803
7.808
7.813
SEt
O
I
3.07
2.04
2.00
2.00
ppm


14.69
23.57
76.73
77.04
77.31
100.92
128.52
132.85
136.56
191.35
SEt
O
I
-10 ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


OMe
O
CO2Me
3.568
3.879
3.890
7.498
7.494
7.479
7.475
7.462
7.457
7.414
7.411
7.396
7.376
7.372
7.368
7.354
7.351
7.335
6.982
6.975
6.970
6.957
6.952
6.946
0 ppm
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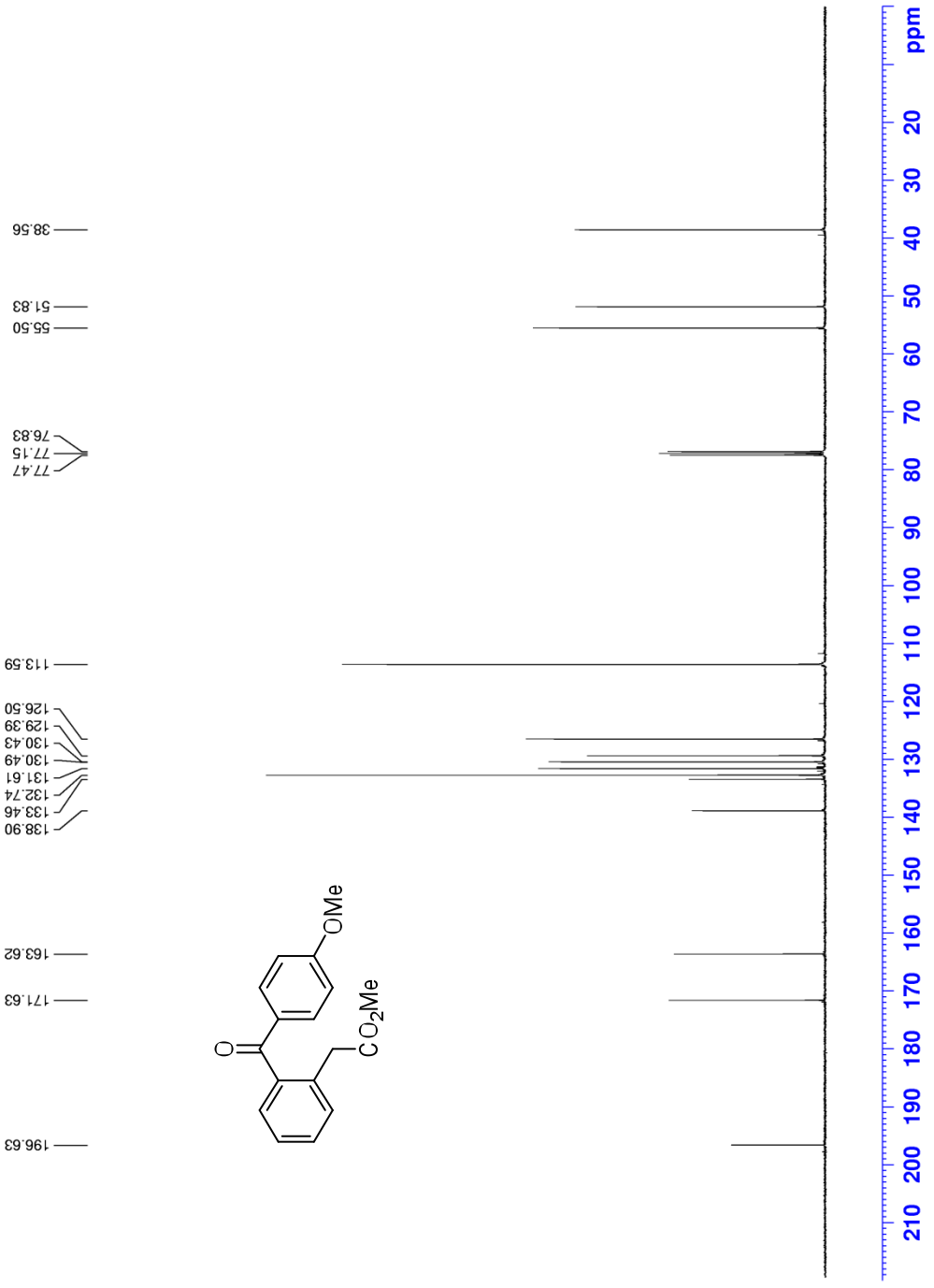
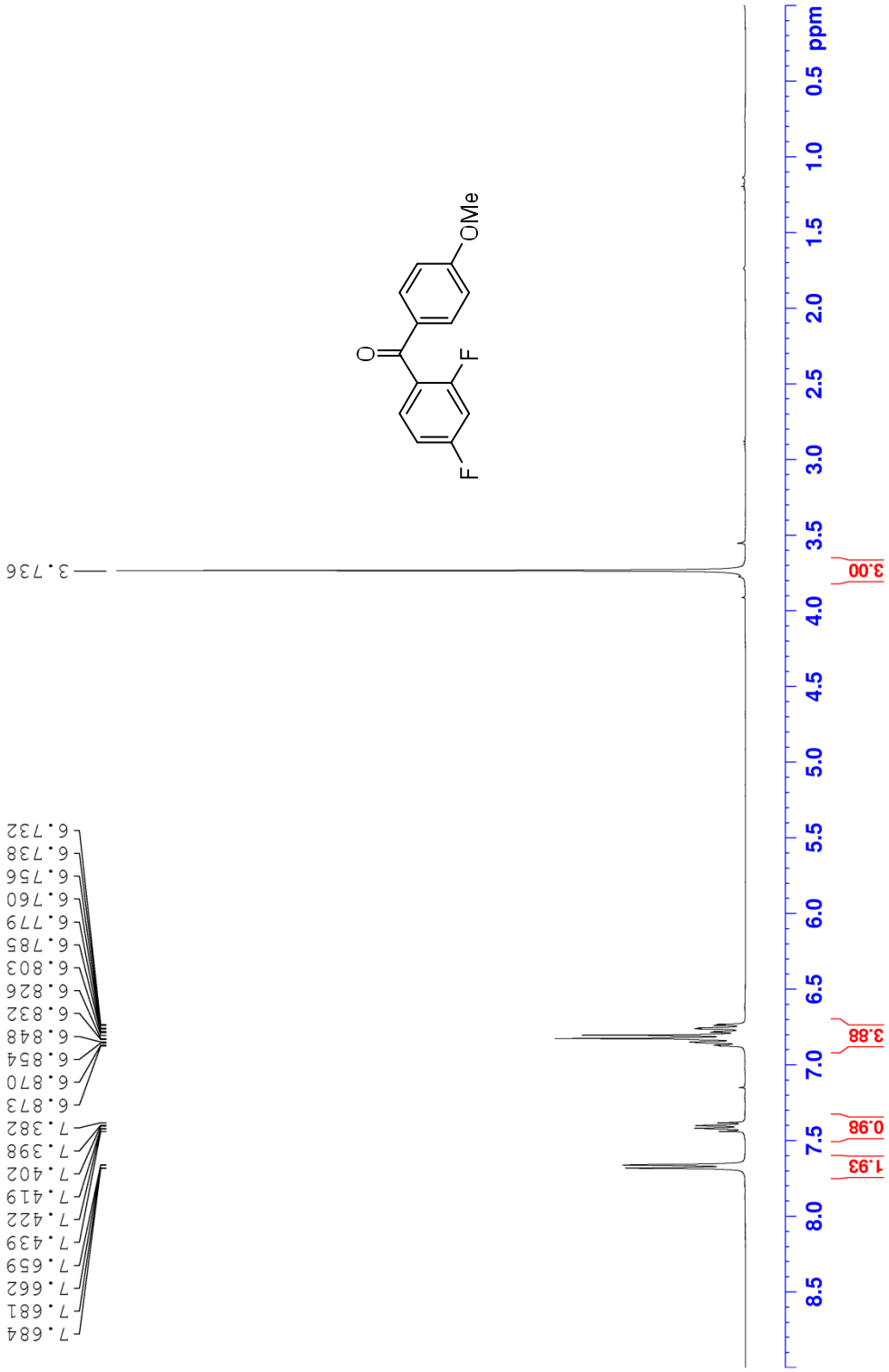
2
3
4
5
6
7
8
3.00
2.00
2.88
2.07
3.11
1.53
1.99


38.56
51.83
55.50
76.83
77.15
77.47
113.59
126.50
129.39
130.43
130.49
131.61
132.74
133.46
138.90
163.62
171.63
196.63
OMe
O
CO2Me
ppm


OMe
O
F
F
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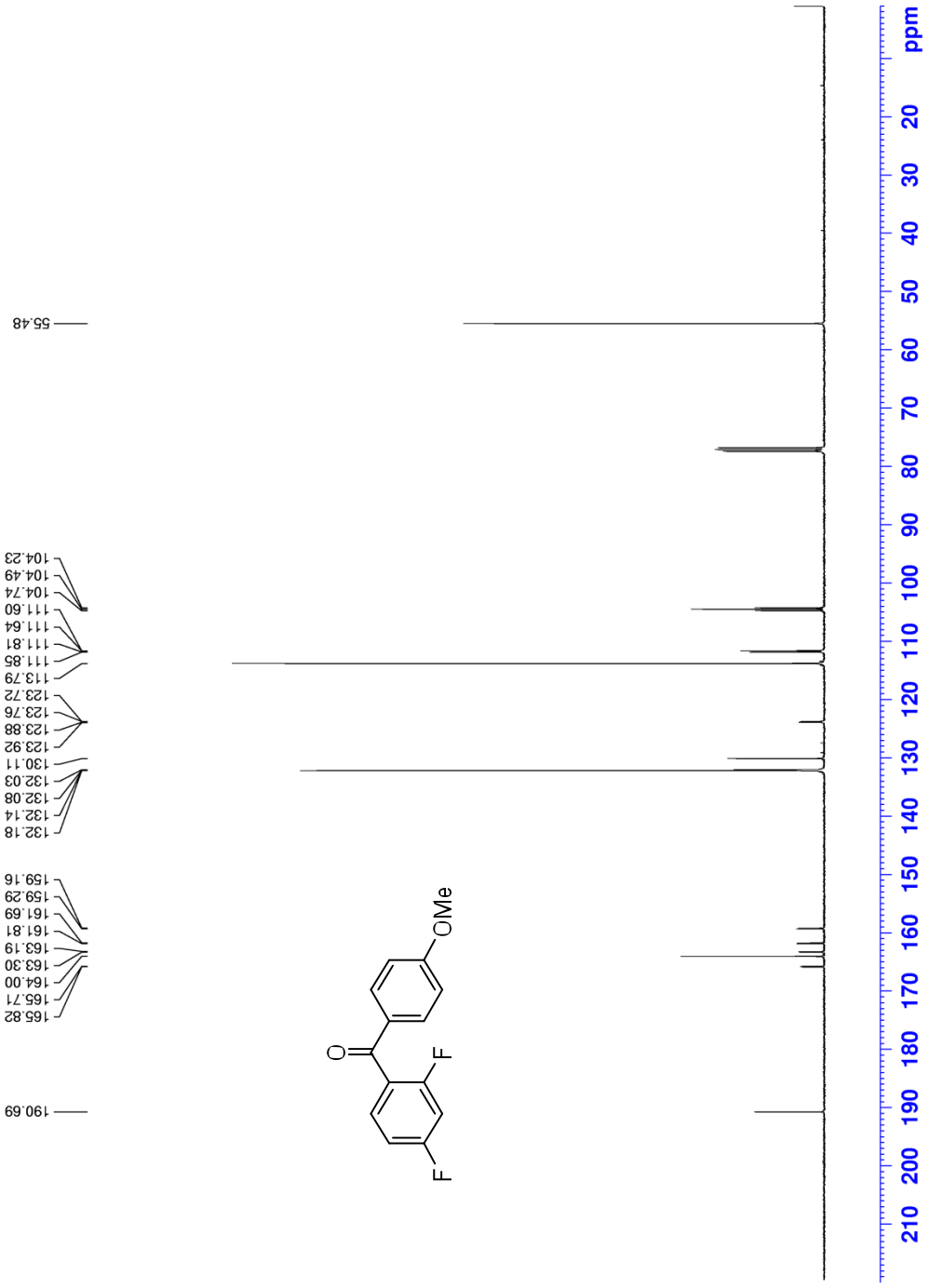
6.732
6.738
6.756
6.760
6.779
6.785
6.803
6.826
6.832
6.848
6.854
6.870
6.873
7.382
7.398
7.402
7.419
7.422
7.439
7.659
7.662
7.681
7.684
3.00
3.88
0.98
1.93
ppm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104.23
104.49
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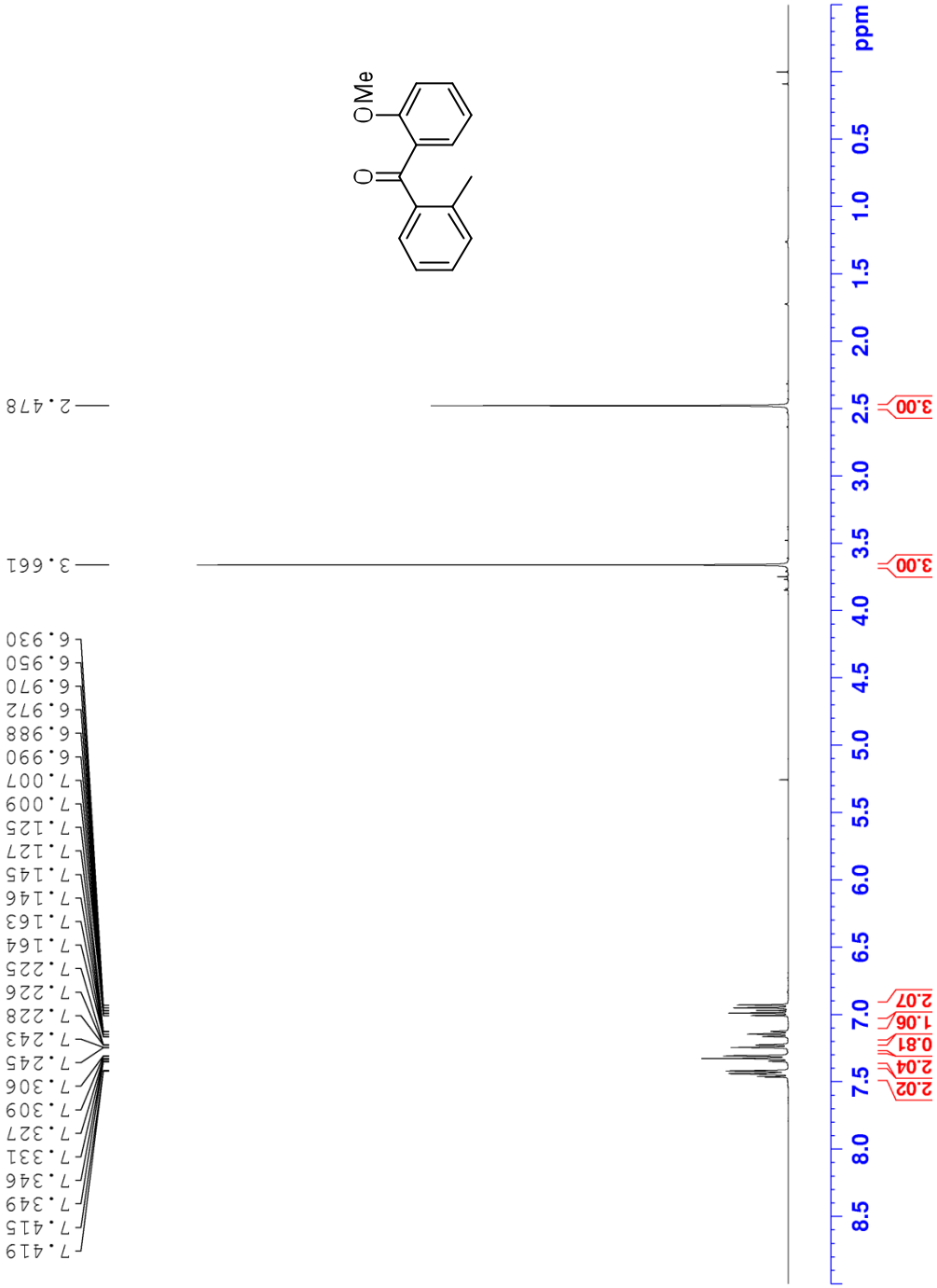
111.64
111.81
111.85
113.79
123.72
123.76
123.88
123.92
130.11
132.03
132.08
132.14
132.18
159.16
159.29
161.69
161.81
163.19
163.30
164.00
165.71
165.82
190.69
OMe
O
F
F
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


OMe
O
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3.661
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6.950
6.970
6.972
6.988
6.990
7.007
7.009
7.125
7.127
7.145
7.146
7.163
7.164
7.225
7.226
7.228
7.243
7.245
7.306
7.309
7.327
7.331
7.346
7.349
7.415
7.419
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
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3.00
3.00
2.07
1.06
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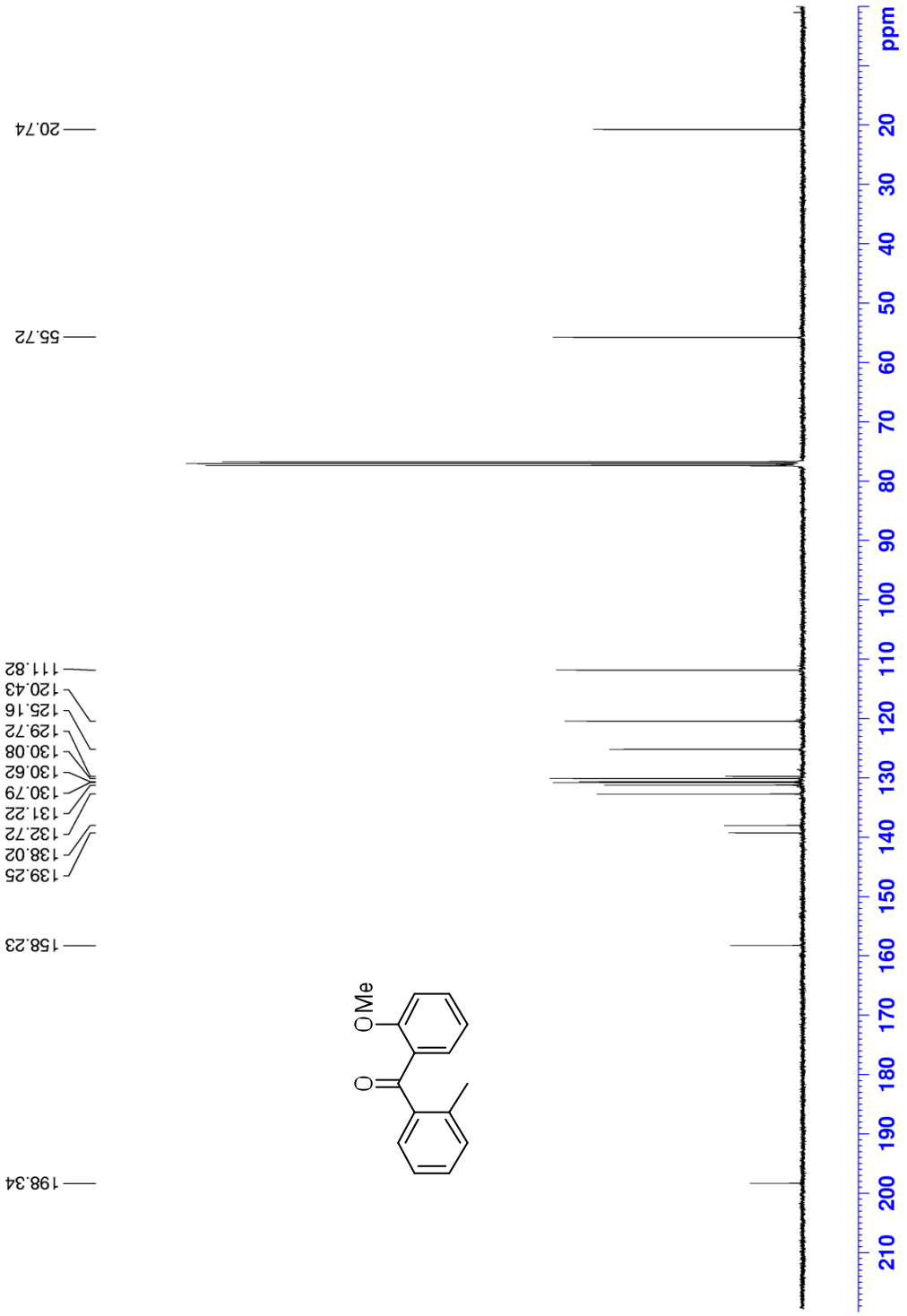
2.04
2.02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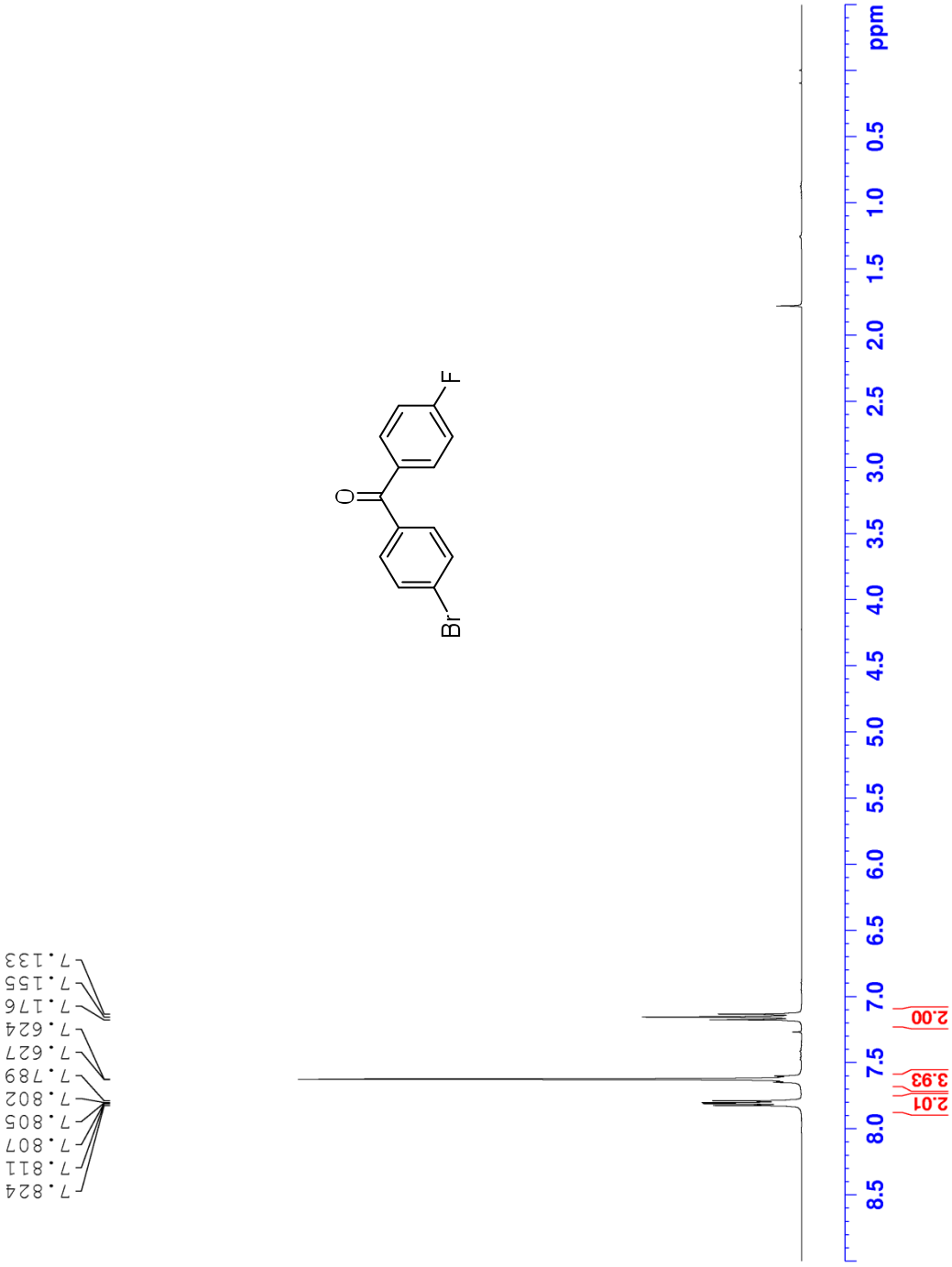
130.62
130.79
131.22
132.72
138.02
139.25
158.23
198.34
OMe
O
ppm


F
O
Br
ppm
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2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
2.00
3.93
2.01
7.824
7.811
7.807
7.805
7.802
7.789
7.627
7.624
7.176
7.155
7.133


F
O
Br
115.56
115.78
127.59
131.42
131.75
132.57
132.66
133.44
133.47
136.27
164.28
166.81
194.10
ppm
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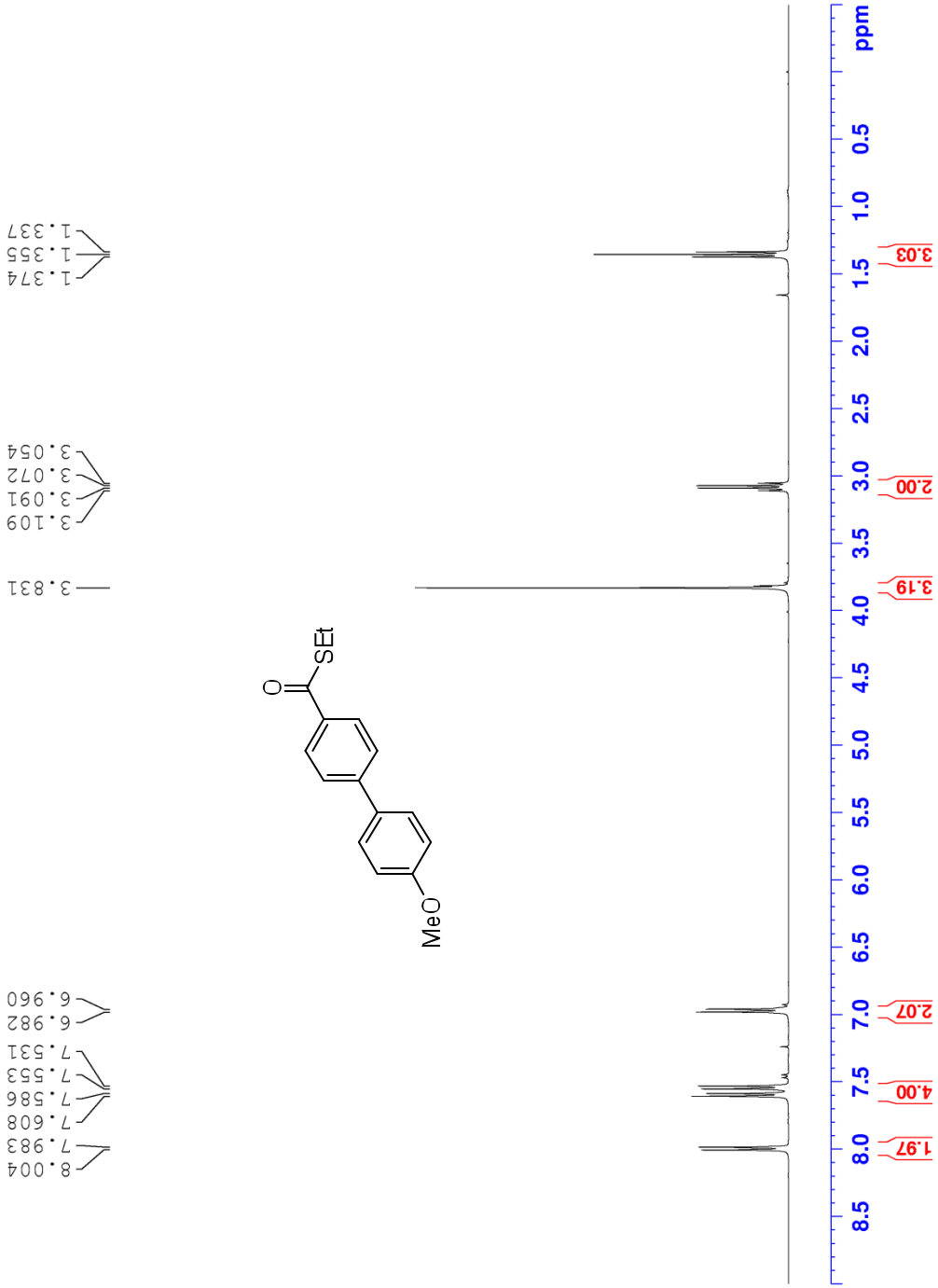
40
60
80
100
120
140
160
180
200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1.355
1.374
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3.072
3.091
3.109
3.831
6.960
6.982
7.531
7.553
7.586
7.608
7.983
8.004
O
SEt
MeO
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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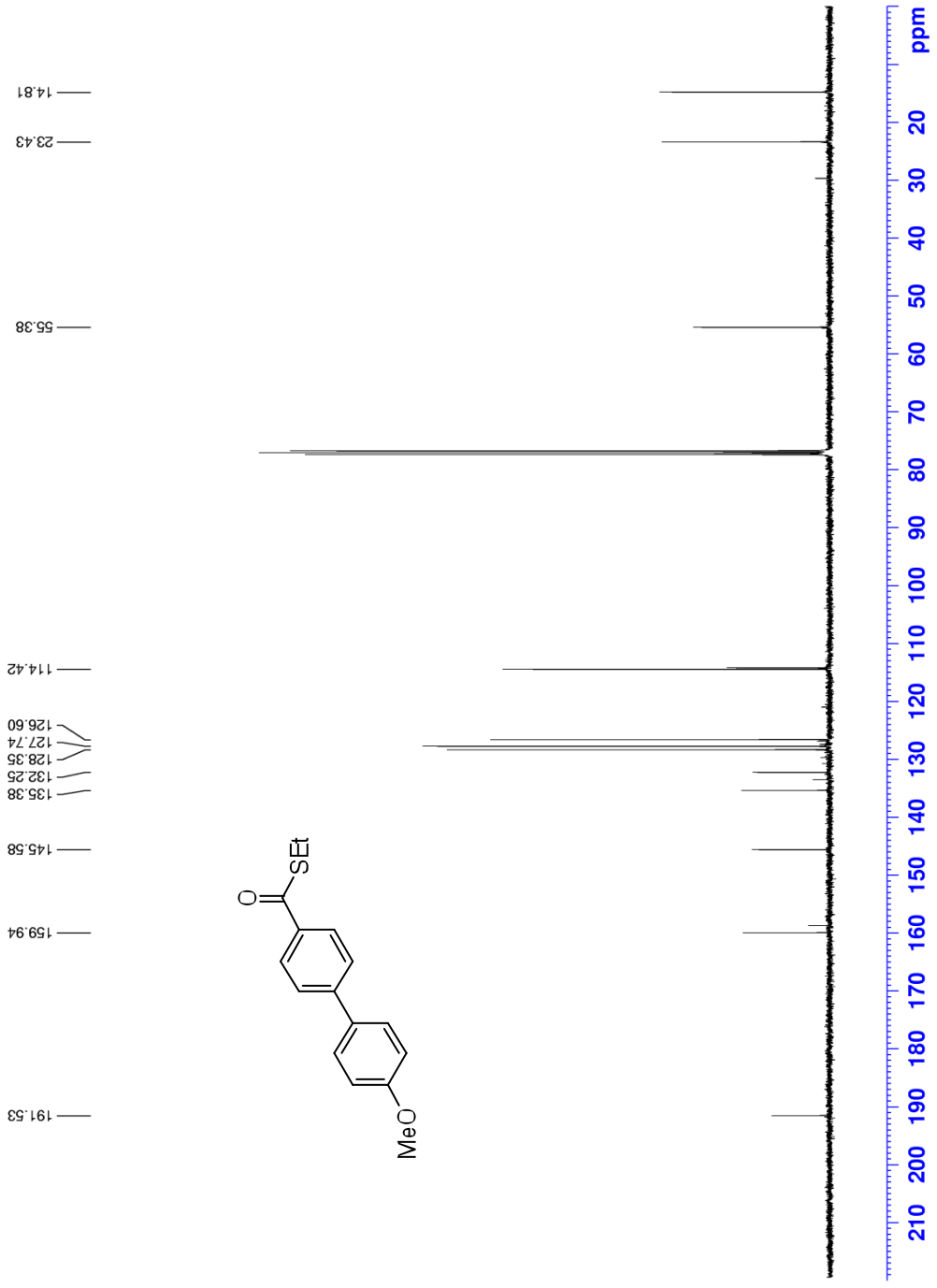
2.00
3.19
2.07
4.00
1.97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126.60
127.74
128.35
132.25
135.38
145.58
159.94
191.53
SEt
O
MeO
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
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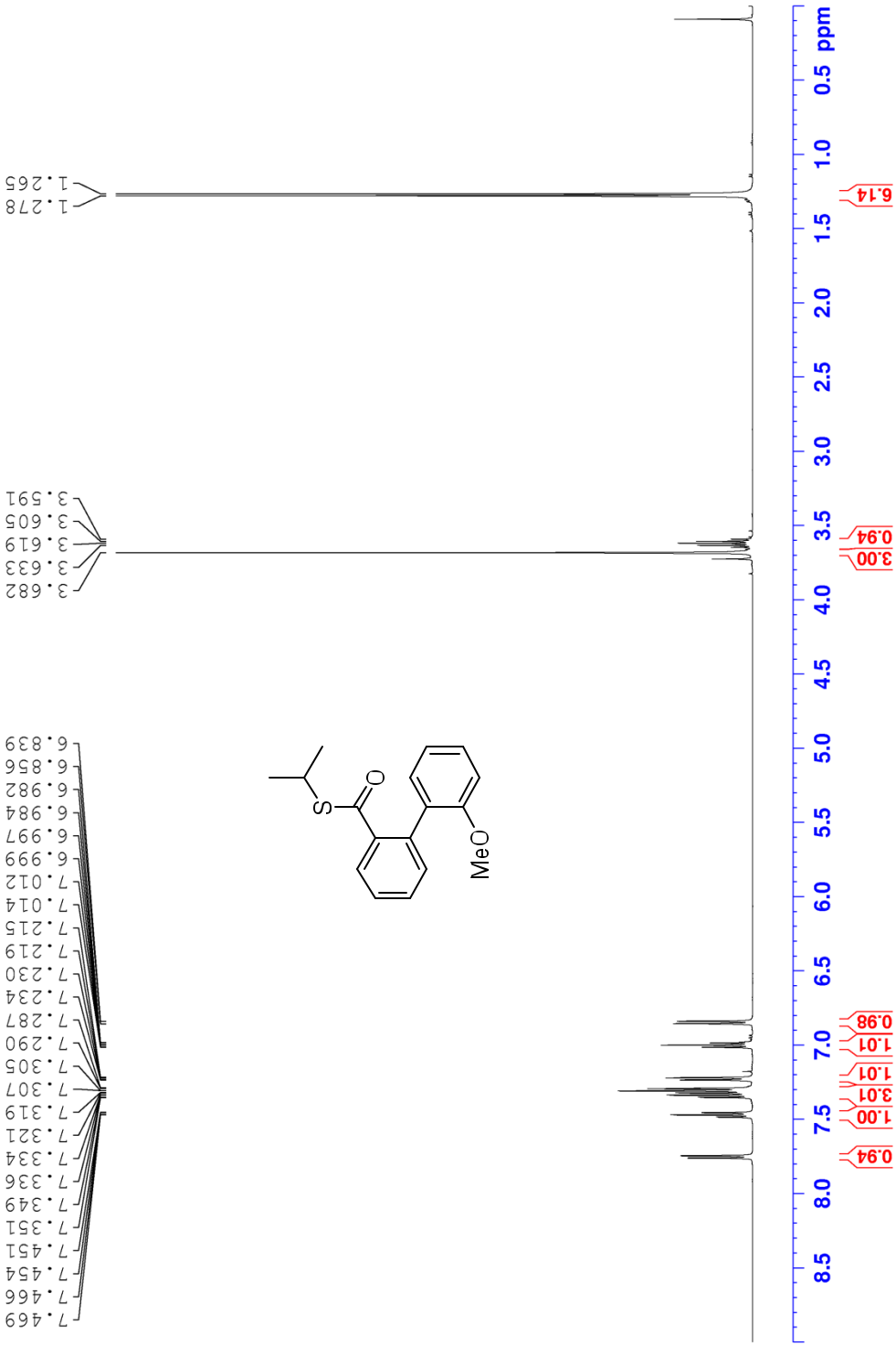
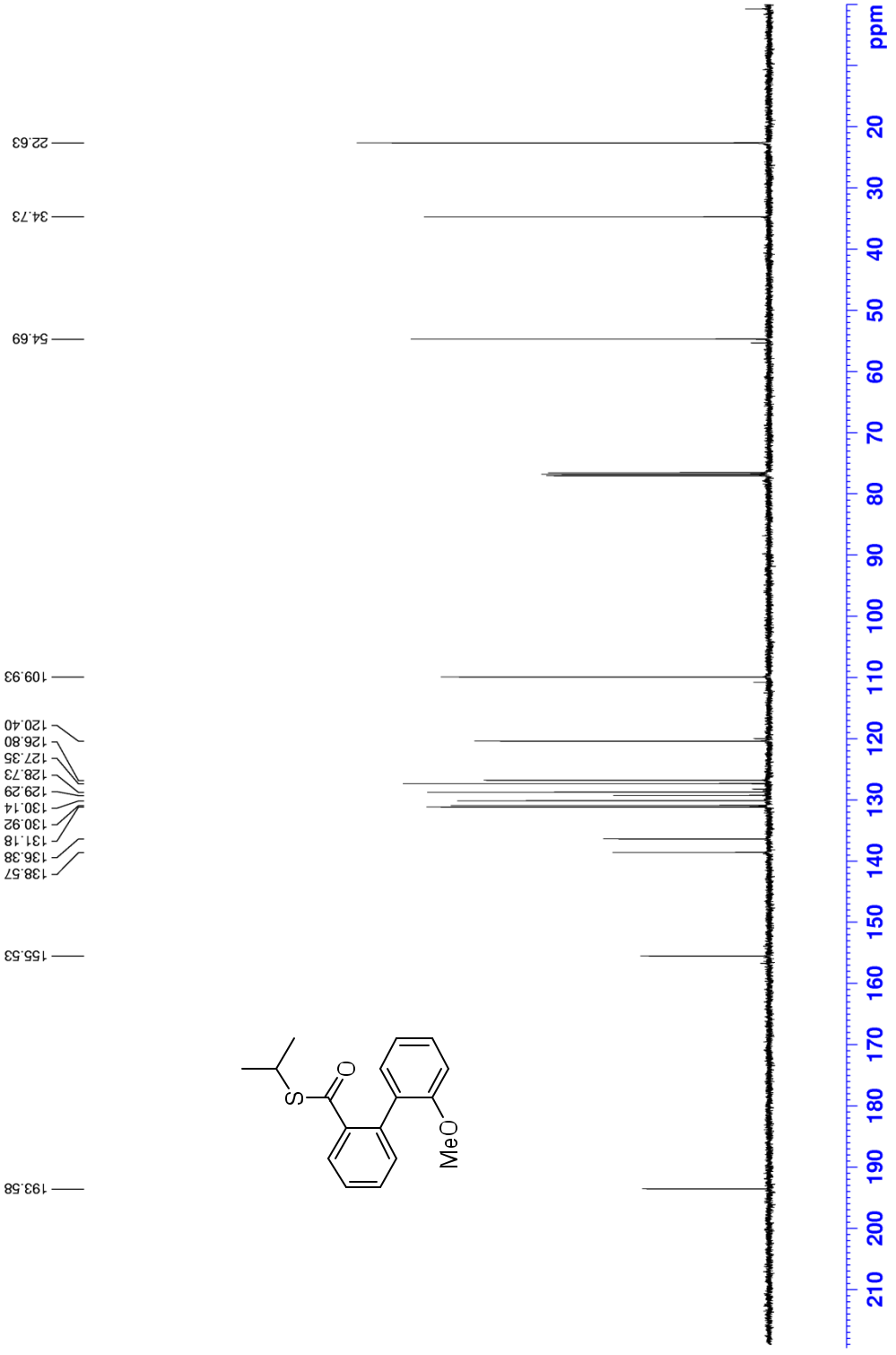
180
190
200
210






1.339
1.357
1.376
3.059
3.078
3.096
3.115
7.113
7.135
7.151
7.156
7.542
7.555
7.564
7.581
7.602
7.999
8.020
O
SEt
F
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
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7.0
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8.0
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3.04
2.00
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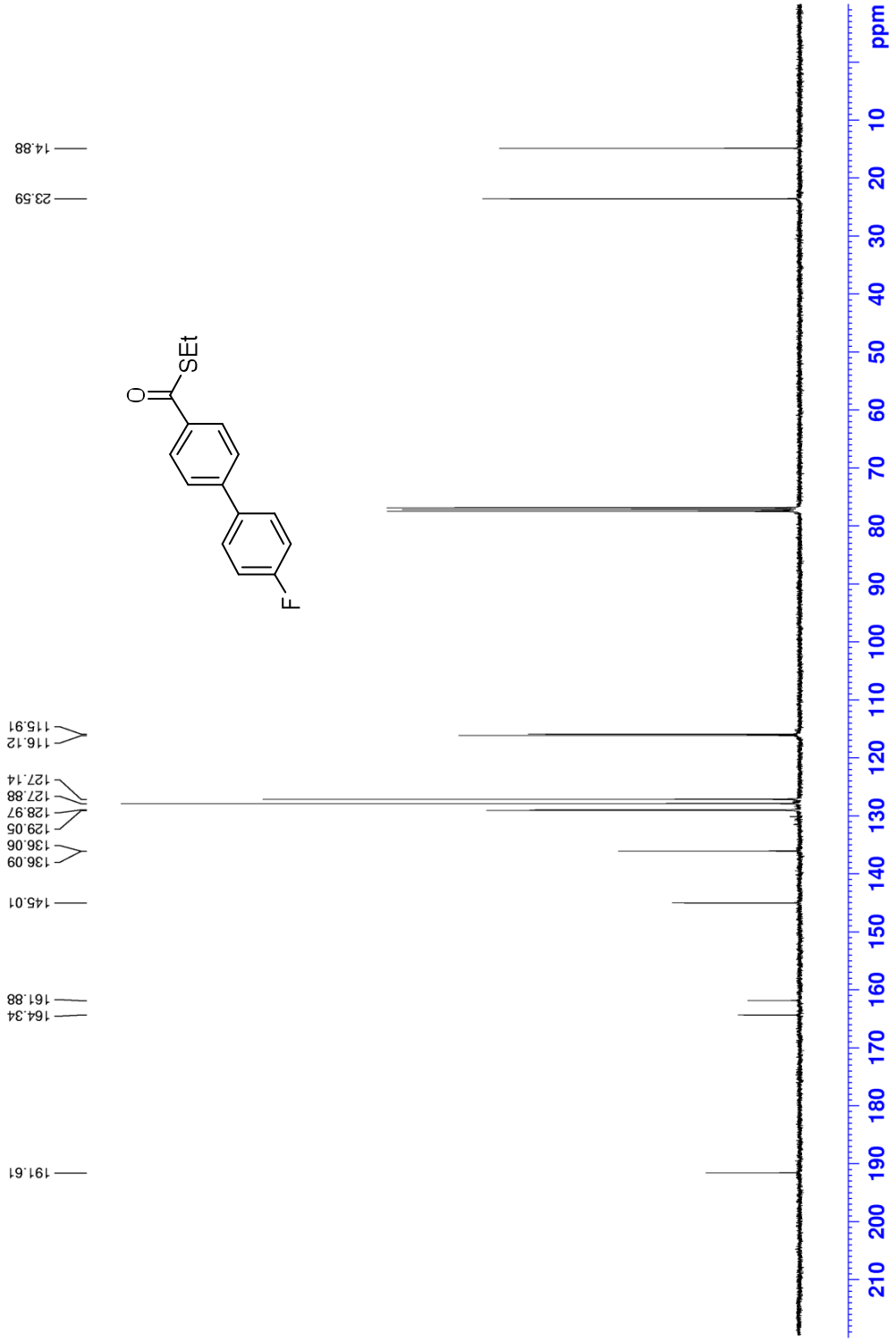
3.92
1.92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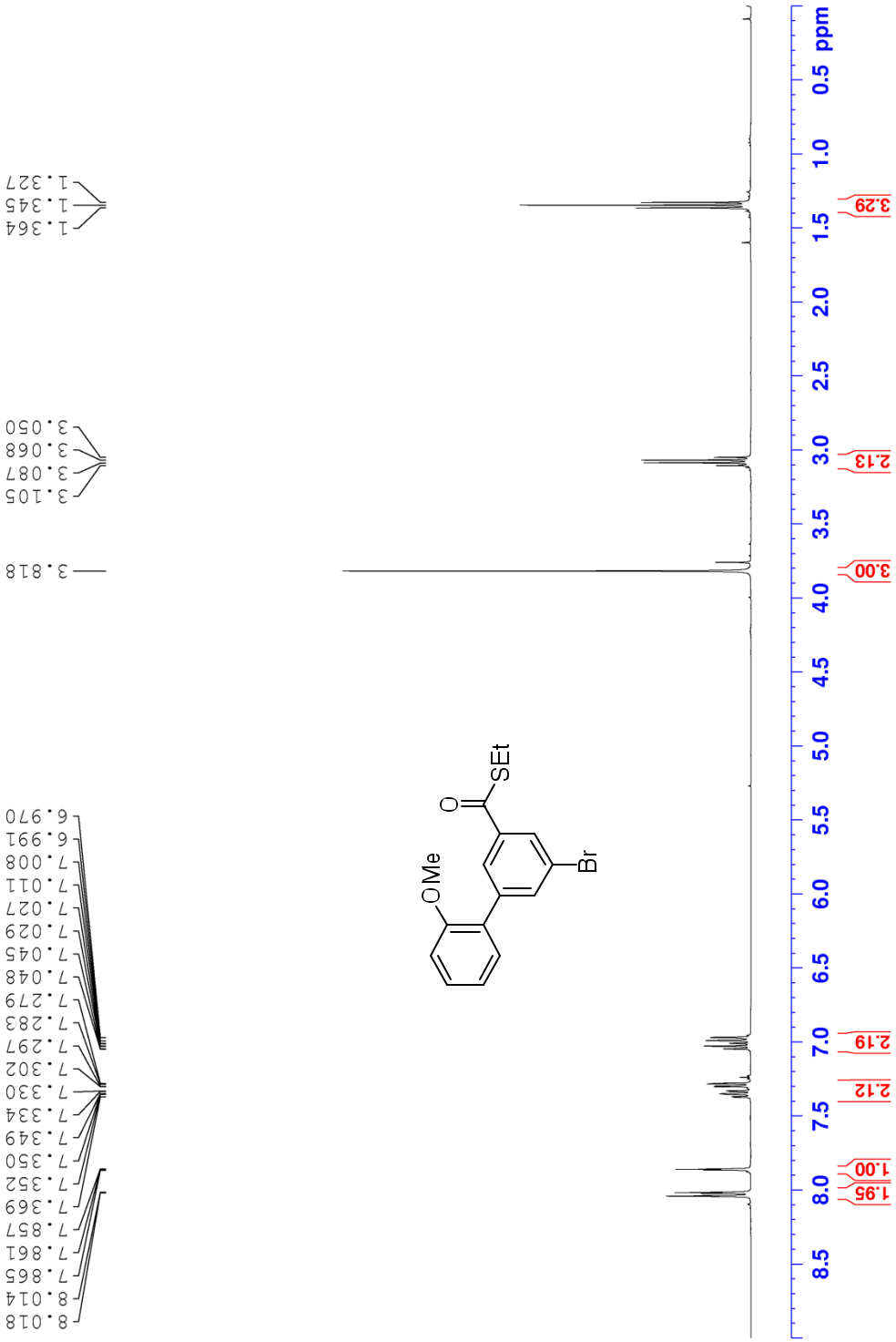
23.59
115.91
116.12
127.14
127.88
128.97
129.05
136.06
136.09
145.01
161.88
164.34
191.61
O
SEt
F
ppm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3.087
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3.818
6.970
6.991
7.008
7.011
7.027
7.029
7.045
7.048
7.279
7.283
7.297
7.302
7.330
7.334
7.349
7.350
7.352
7.369
7.857
7.861
7.865
8.014
8.018
SEt
O
OMe
Br
0.5 ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
3.29
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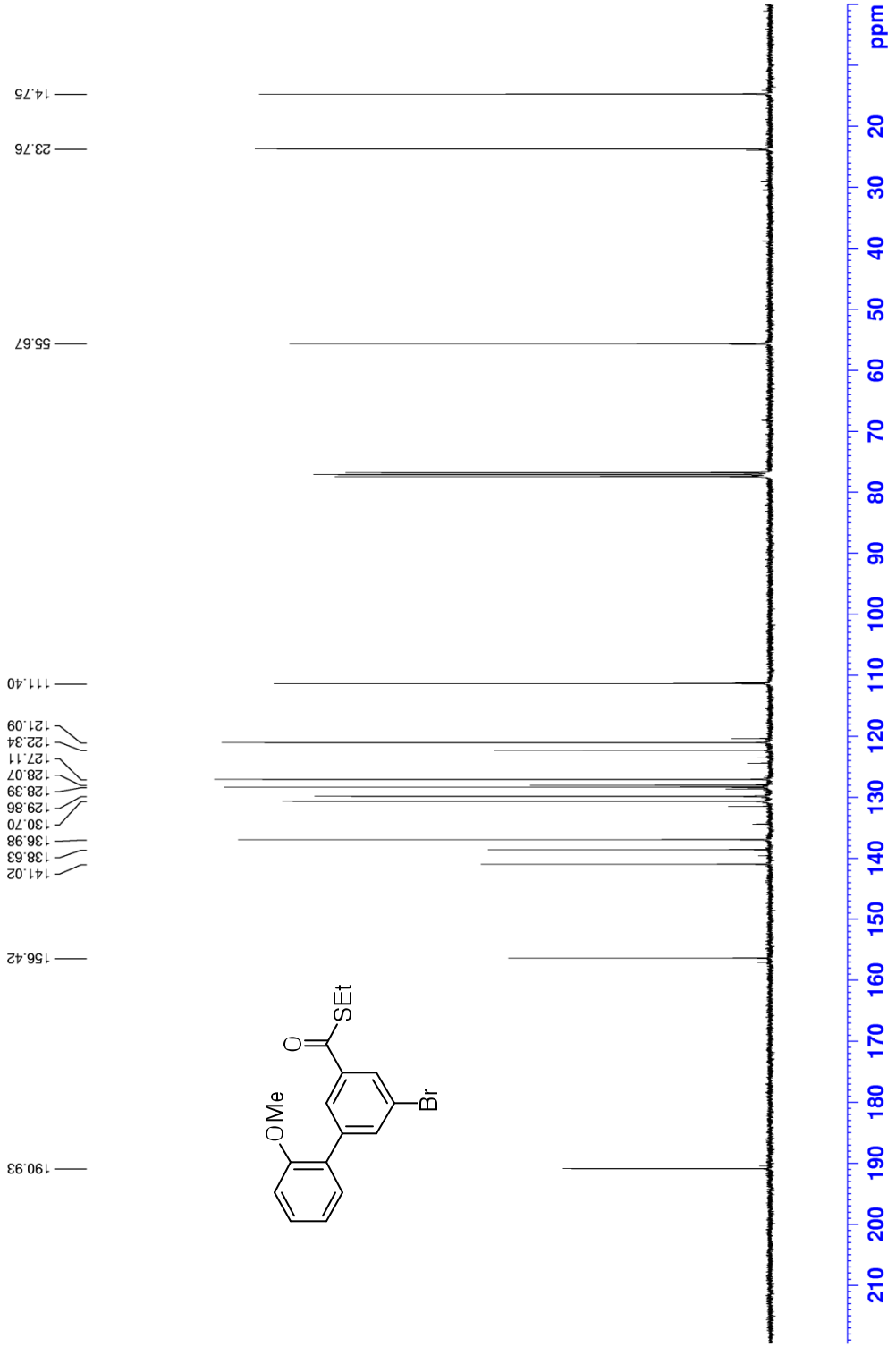
3.00
2.19
2.12
1.00
1.95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122.34
127.11
128.07
128.39
129.86
130.70
136.98
138.63
141.02
156.42
190.93
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
SEt
O
OMe
Br