Visible-light-mediated oxidative C–S bond cleavage of benzyl thiols through in situ activation strategy

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Supporting Information

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1. General Information

1.1. Materials and Instruments

Reactions were performed in a well-dried flask under an oxygen atmosphere (O_2, 99.995%, 1 atm). Solvents were dried over pre-activated molecular sieves (3 Å, pellets, Alfa Aesar) in the microwave oven before using. Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar, Acros Organics, and TCI) and used without further purifications.

Flash column chromatography was performed with silica gel 60 (particle size range 230-400 mesh) using a mixture of Et_2O/hexane as the eluent. After purification of the product, the fractions were combined and concentrated under reduced pressure.

^1H and ^{13}C NMR spectra were, respectively, recorded on Bruker 400 MHz (^1H NMR), 101 MHz (^{13}C NMR) spectrometer in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference. Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet, br = broad; coupling constant(s) in Hz, integration). Infrared spectra were recorded on Agilent Cary 630 or Perkin Elmer Spectrum Two FT-IR spectrometers. The wavenumbers (ν) of recorded IR-signals are reported in cm^{-1}. UV-vis absorption spectra were recorded on Perkin Elmer Lambda 365 spectrometer. The samples were measured in QS quartz cuvettes (chamber volume 1.4 mL, path length 10 mm). Mass spectra were obtained on a Gas Chromatography Mass Spectrometer (Agilent 7890A/5975C GCMS System). X-band Continuous wave EPR spectra were recorded on Bruker EMX plus 6/1 spectrometer or JEOL JES-FA300 ESR spectrometer.

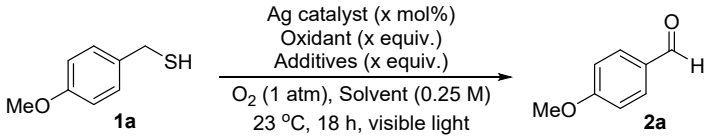
1.2. Light Sources and Photochemical Reactions Setup

Spotlight-type LED bulbs purchased from CR LIGHTING TECHNOLOGY (Model Number: CR-MR16-5W Cool White LED Bulb (λ_{max} = 450 nm, broad spectral range of 500-750 nm), CR-MR16-4W Green LED Bulb (λ_{max} = 530 nm), and CR-MR16-4W-B Blue LED Bulb (λ_{max} = 455 nm)), OSRAM 20W CFL (Model Number – Duluxstar compact 20W/865), and DAYTIME 20W EFTR20-BLB UV lamp (λ_{max} = 352 nm) were used for our study. In each case, the light source was placed around 4 cm from the reaction vessel. The reaction contents were maintained at room temperature (around 23 °C) without using additional cooling instruments.

2. Optimization of the Reaction Conditions

A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with the 4-methoxybenzylthiol **1a** (90 µL, 0.65 mmol, 1.0 equiv.). Silver catalyst, oxidant, and solvent were added (See **Table S1** for more details). The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with visible light for 18 h at room temperature. After the indicated time, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Yields are of isolated product after column chromatography (40% Et_2O in hexane).

Table S1. Optimization of the reaction conditions[a]

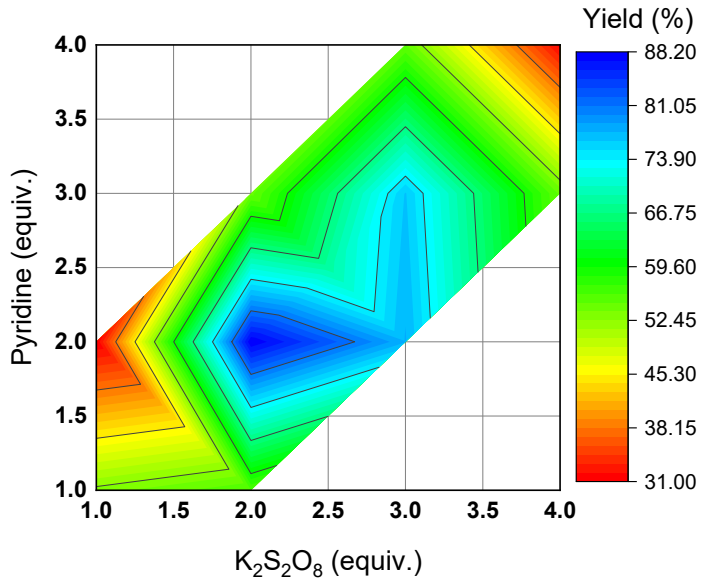


Entry	Ag catalyst (mol%)	Oxidant (equiv.)	Additives (equiv.)	Solvent	Light source	Yield (%)[b]
1	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMSO	Green LEDs (4 W)	25
2	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	THF	Green LEDs (4 W)	24
3	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	MeCN	Green LEDs (4 W)	16
4	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	Toluene	Green LEDs (4 W)	11
5	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	Benzene	Green LEDs (4 W)	14
6	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DCM	Green LEDs (4 W)	12
7	$AgNO_3$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	33
8	AgOAc (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	36
9	AgOTf (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	16
10	AgOTs (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	47
11	AgBr (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	20
12	AgF (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	45
13	$AgPF_6$ (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	49
14	Ag_2SO_4 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	41
15	Ag_2O (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	34
16	Ag_3PO_4 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	57
17	**Ag_2CO_3 (20)**	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	55
18	Ag_2CO_3 (**10**)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Green LEDs (4 W)	24
19	Ag_2CO_3 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	dark	trace
20	Ag_2CO_3 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	CFL lamp (20 W)	52
21	Ag_2CO_3 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	Blue LEDs (4 W)	52
22	Ag_2CO_3 (20)	**$K_2S_2O_8$ (3.0)**	Pyridine (3.0)	DMF	**White LEDs (5 W)**	76
23	Ag_2CO_3 (20)	$(NH_4)_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	White LEDs (5 W)	24

24†	Ag_2CO_3 (20)	$K_2S_2O_8$ (**2.0**)	Pyridine (**2.0**)	DMF	White LEDs (5 W)	88
25	Ag_2CO_3 (20)	$K_2S_2O_8$ (**2.0**)	Pyridine (**2.0**)	DMSO	White LEDs (5 W)	56
26	Ag_2CO_3 (20)	$K_2S_2O_8$ (**2.0**)	Pyridine (**2.0**)	THF	White LEDs (5 W)	24
27	Ag_2CO_3 (20)	$K_2S_2O_8$ (**2.0**)	2-Chloropyridine (**2.0**)	DMF	White LEDs (5 W)	50
28	Ag_2CO_3 (20)	$K_2S_2O_8$ (**2.0**)	2,2'-Bipyridine (**1.0**)	DMF	White LEDs (5 W)	54
29	Ag_2CO_3 (20)	$K_2S_2O_8$ (**2.0**)	2,6-Lutidine (**2.0**)	DMF	White LEDs (5 W)	67
30	Ag_2CO_3 (20)	-	Pyridine (3.0)	DMF	White LEDs (5 W)	50
31	-	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	White LEDs (5 W)	0
32[c]	Ag_2CO_3 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	White LEDs (5 W)	69
33[d]	Ag_2CO_3 (20)	$K_2S_2O_8$ (3.0)	Pyridine (3.0)	DMF	White LEDs (5 W)	0

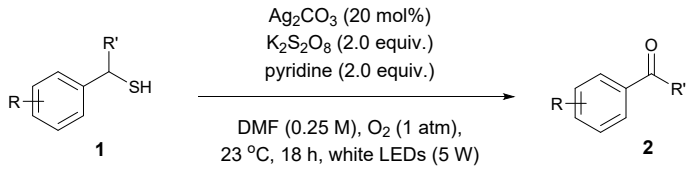
(DMSO = dimethyl sulfoxide, THF = tetrahydrofuran, MeCN = acetonitrile, DCM = dichloromethane, DMF = dimethylformamide, DIPEA = *N*,*N*-Diisopropylethylamine, DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, TEA = triethylamine)
[a]Reactions were conducted on a 0.65 mmol scale.
[b]Yields are of the isolated products after column chromatography.
[c]Under air(balloon) atmosphere
[d]Under Ar atmosphere

† Ratio of $K_2S_2O_8$ and pyridine were screened.



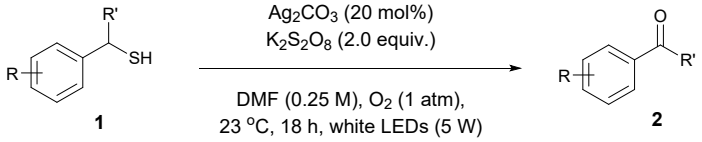
3. General Procedures for the Oxidative C-S Bond Cleavage Reactions

3.1. Condition **A**: with pyridine



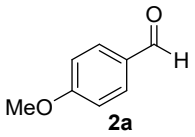
A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with the corresponding thiol (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) and pyridine (105 μL, 1.3 mmol, 2.0 equiv.) were added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (Et_2O in hexane: 5 – 60%) afforded the desired products.

3.2. Condition **B**: without pyridine



A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with the corresponding thiol (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (Et_2O in hexane: 5 –60%) afforded the desired products.

4. Physical Data for the Compounds

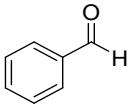


2a

4-Methoxybenzaldehyde[1] **(2a)**: Prepared according to the *general procedures* using 4-methoxybenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et_2O/hexane, R_f = 0.46) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (78 mg, 88%), *Condition **B*** (50 mg, 56%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.83 – 7.80 (m, 2H), 6.99 – 6.97 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 164.6, 131.9, 129.9, 114.3, 55.6; IR (neat) 1678, 1597, 1510, 1462, 1424, 1310, 1250, 1154, 1109, 1020, 828, 596, 515 cm^{-1}; LRMS (EI); Mass calcd for $C_8H_8O_2$ [M]$^+$: 136; found 136.

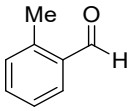


2b

Benzaldehyde[1],[2] **(2b)**: Prepared according to the *general procedures* using benzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.42) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (39 mg, 57%), *Condition **B*** (60 mg, 87%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.90 – 7.87 (m, 2H), 7.65 – 7.62 (m, 1H), 7.56 – 7.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 136.3, 134.5, 129.7, 129.0; IR (neat) 1690, 1598, 1448, 1390, 1310, 1201, 824, 740, 685, 644, 450 cm^{-1}; LRMS (EI); Mass calcd for C_7H_6O [M]$^+$: 106; found 106.

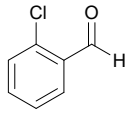


2c

2-Methylbenzaldehyde[3] **(2c)**: Prepared according to the *general procedures* using 2-methylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.67) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (trace), *Condition **B*** (65 mg, 83%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.71 (dd, J = 7.6, 1.5 Hz, 1H), 7.39 (td, J = 7.5, 1.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.19 – 7.17 (m, 1H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 140.6, 134.2, 133.6, 132.1, 131.8, 126.3, 19.6; IR (neat) 1600, 1460, 1196, 1120, 860, 750, 664, 432 cm^{-1}; LRMS (EI); Mass calcd for C_8H_8O [M]$^+$: 120; found 120.

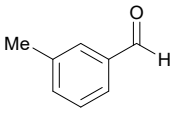


2d

2-Chlorobenzaldehyde[2],[4] **(2d)**: Prepared according to the *general procedures* using 2-chlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.53) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (trace), *Condition **B*** (72 mg, 79%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.87 – 7.85 (m, 1H), 7.50 – 7.46 (m, 1H), 7.43 – 7.38 (m, 1H), 7.35 – 7.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 137.9, 135.2, 132.4, 130.6, 129.3, 127.3; IR (neat) 1698, 1590, 1440, 1270, 1196, 1050, 825, 756, 630, 435 cm^{-1}; LRMS (EI); Mass calcd for C_7H_5ClO $[M]^+$: 140; found 140.

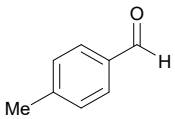


2e

3-Methylbenzaldehyde[2] **(2e)**: Prepared according to the *general procedures* using 3-methylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.63) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (60 mg, 76%), *Condition **B*** (70 mg, 89%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.69 – 7.67 (m, 2H), 7.45 – 7.40 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.2; IR (neat) 1700, 1588, 1460, 1380, 1290, 1240, 1141, 7778, 685, 430 cm^{-1}; LRMS (EI); Mass calcd for C_8H_8O $[M]^+$: 120; found 120.

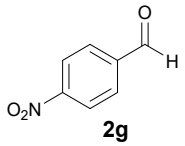


2f

4-Methylbenzaldehyde[1],[4] **(2f)**: Prepared according to the *general procedures* using 4-methylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.54) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (59 mg, 75%), *Condition **B*** (74 mg, 95%) - $AgNO_3$ (20 mol%) was used instead of Ag_2CO_3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.79 – 7.77 (m, 2H), 7.34 – 7.32 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 145.6, 134.2, 129.9, 129.7, 21.9; IR (neat) 1688, 1600, 1450, 1386, 1300, 1208, 1170, 804, 750, 600, 480 cm^{-1}; LRMS (EI); Mass calcd for C_8H_8O $[M]^+$: 120; found 120.

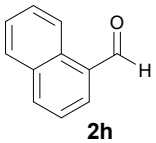


2g

4-Nitrobenzaldehyde[1] **(2g)**: Prepared according to the *general procedures* using 4-nitrobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h (*Condition **A***) or 6 h (*Condition **B***), the reaction mixture was purified by flash column chromatography (50% Et_2O/hexane, R_f = 0.46) to provide the title compound as a white solid. mp 105-107 °C (lit.[3] 101-103 °C).

Yield : *Condition **A*** (72 mg, 73%), *Condition **B*** (85 mg, 86%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.38 – 8.36 (m, 2H), 8.07 – 8.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 151.1, 140.0, 130.5, 124.3; IR (neat) 1704, 1600, 1530, 1340, 1266, 1190, 1104, 1001, 810, 734, 510, 462 cm^{-1}; LRMS (EI); Mass calcd for $C_7H_5NO_3$ $[M]^+$: 151; found 151.

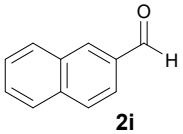


2h

1-Naphthaldehyde[5],[6] **(2h)**: Prepared according to the *general procedures* using 1-naphthalenemethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et_2O/hexane, R_f = 0.58) to provide the title compound as a pale yellow oil.

Yield : *Condition **A*** (72 mg, 70%), *Condition **B*** (64 mg, 63%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 9.26 – 9.24 (m, 1H), 8.05 – 8.03 (m, 1H), 7.93 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.69 – 7.65 (m, 1H), 7.58 – 7.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 136.6, 135.3, 133.7, 131.4, 130.5, 129.1, 128.5, 126.9, 124.9; IR (neat) 1685, 1570, 1510, 1460, 1210, 1160, 1052, 885, 768, 710, 644, 520, 402 cm^{-1}; LRMS (EI); Mass calcd for $C_{11}H_8O$ $[M]^+$: 156; found 156.



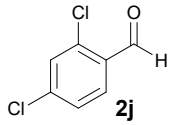
2i

2-Naphthaldehyde[2] **(2i)**: Prepared according to the *general procedures* using 2-naphthalenemethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.53) to provide the title compound as a white solid. mp 60-62 °C (lit.[19] 60-62 °C).

Yield : *Condition **A*** (86 mg, 84%), *Condition **B*** (96 mg, 95%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.27 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.92 (m, 1H), 7.89 – 7.85 (m, 2H), 7.63 – 7.59 (m, 1H), 7.57 – 7.54 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 136.3, 134.4, 134.0, 132.5, 129.4, 129.0,

129.0, 127.9, 127.0, 122.6; IR (neat) 1686, 1624, 1460, 1340, 1260, 1168, 1114, 858, 816, 740, 605, 474 cm^{-1}; LRMS (EI); Mass calcd for $C_{11}H_8O$ $[M]^+$: 156; found 156.

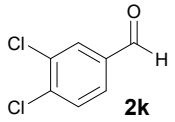


2j

2,4-Dichlorobenzaldehyde (2j)[6],[12]: Prepared according to the general procedure using 2,4-dichlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (5% Et_2O/hexane, R_f = 0.50) to provide the title compound as a white solid.

Yield : *Condition **A*** (trace), *Condition **B*** (119 mg, 68%)

^1H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.39 – 7.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 141.2, 138.6, 131.0, 130.5, 130.4, 128.0; IR (neat) 1685, 1576, 1460, 1377, 1242, 1200, 1095, 1052, 820, 760, 660, 571, 411 cm^{-1}; LRMS (EI); Mass calcd for $C_7H_4Cl_2O$ $[M]^+$: 174; found 174.

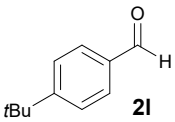


2k

3,4-Dichlorobenzaldehyde (2k)[13]: Prepared according to the general procedure using 3,4-dichlorobenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et_2O/hexane, R_f = 0.53) to provide the title compound as a white solid.

Yield : *Condition **A*** (114 mg, 65%), *Condition **B*** (140 mg, 80%)

^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.95 (d, *J* = 1.9 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.64 – 7.62 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 139.2, 135.8, 134.0, 131.3, 131.2, 128.4; IR (neat) 1698, 1580, 1460, 1362, 1258, 1190, 1133, 1031, 874, 820, 740, 551, 416 cm^{-1}; LRMS (EI); Mass calcd for $C_7H_4Cl_2O$ $[M]^+$: 174; found 174.

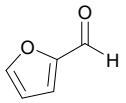


2l

4-(*tert*-Butyl)benzaldehyde (2l)[12]: Prepared according to the general procedure using 4-*tert*-butylbenzylthiol (0.65 mmol, 1.0 equiv.). After irradiation for 24 h (*condition **A***) or 18 h (*condition **B***), the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.42) to provide the title compound as a pale yellow oil.

Yield : *Condition **A*** (135 mg, 83%), *Condition **B*** (148 mg, 91%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.83 – 7.80 (m, 2H), 7.57 – 7.53 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 158.4, 134.1, 129.7, 126.0, 35.3, 31.0; IR (neat) 1692, 1603, 1465, 1362, 1310, 1265, 1218, 1172, 1104, 830, 702, 547 cm^{-1}; LRMS (EI); Mass calcd for $C_{11}H_{14}O$ $[M]^+$: 162; found 162.

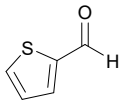


2m

Furan-2-carbaldehyde[3],[6] **(2m)**: Prepared according to the *general procedures* using 2-furanmethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h (*Condition **A***) or 12 h (*Condition **B***), the reaction mixture was purified by flash column chromatography (40% Et_2O/hexane, R_f = 0.40) to provide the title compound as a yellow oil.

Yield : *Condition **A*** (52 mg, 83%), *Condition **B*** (22 mg, 36%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.64 – 7.63 (m, 1H), 7.21 – 7.20 (m, 1H), 6.55 – 6.54 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 152.9, 148.1, 121.1, 112.6; IR (neat) 1668, 1564, 1460, 1390, 1278, 1154, 1079, 1016, 925, 882, 746, 592, 500 cm^{-1}; LRMS (EI); Mass calcd for $C_5H_4O_2$ $[M]^+$: 96; found 96.

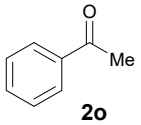


2n

Thiophene-2-carbaldehyde[1],[6] **(2n)**: Prepared according to the *general procedures* using 2-thiophenemethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (30% Et_2O/hexane, R_f = 0.40) to provide the title compound as a yellow oil.

Yield : *Condition **A*** (53 mg, 73%), *Condition **B*** (50 mg, 68%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.79 – 7.76 (m, 2H), 7.26 – 7.21 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.0, 144.1, 136.3, 135.1, 128.3; IR (neat) 1671, 1516, 1416, 1213, 1046, 729, 665 cm^{-1}; LRMS (EI); Mass calcd for C_5H_4OS $[M]^+$: 12; found 112.

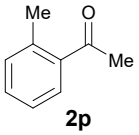


2o

Acetophenone[2],[7] **(2o)**: Prepared according to the *general procedures* using 1-phenylethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.44) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (46 mg, 59%), *Condition **B*** (55 mg, 70%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.59 – 7.55 (m, 1H), 7.49 – 7.45 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 137.2, 133.1, 128.6, 128.3, 26.6; IR (neat) 1682, 1597, 1444, 1358, 1260, 952, 759, 687, 586 cm^{-1}; LRMS (EI); Mass calcd for C_8H_8O $[M]^+$: 120; found 120.

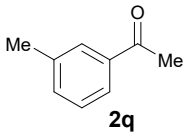


2p

1-(*o*-Tolyl)ethan-1-one[8] **(2p)**: Prepared according to the *general procedures* using 1-(*o*-tolyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 40 h, the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.45) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (trace), *Condition **B*** (69 mg, 79%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 – 7.23 (m, 2H), 2.57 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 138.4, 137.7, 132.0, 131.5, 129.4, 125.7, 29.5, 21.6; IR (neat) 1684, 1454, 1356, 1246, 1126, 1040, 952, 760, 600 cm^{-1}; LRMS (EI); Mass calcd for $C_9H_{10}O$ $[M]^+$: 134; found 134.

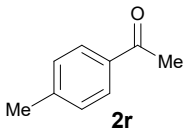


2q

1-(*m*-Tolyl)ethan-1-one[8] **(2q)**: Prepared according to the *general procedures* using 1-(*m*-tolyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.39) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (65 mg, 74%), *Condition **B*** (63 mg, 72%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 2H), 7.37 – 7.31 (m, 2H), 2.57 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 138.3, 137.2, 133.9, 128.8, 128.4, 125.6, 26.6, 21.3; IR (neat) 1680, 1590, 1424, 1355, 1272, 1190, 956, 784, 690, 586, 464 cm^{-1}; LRMS (EI); Mass calcd for $C_9H_{10}O$ $[M]^+$: 134; found 134.

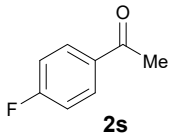


2r

1-(*p*-Tolyl)ethan-1-one[4],[9] **(2r)**: Prepared according to the *general procedures* using 1-(*p*-tolyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 24 h (*Condition **A***) or 18 h (*Condition **B***), the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.42) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (76 mg, 87%), *Condition **B*** (73 mg, 84%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.24 – 7.21 (m, 2H), 2.54 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 143.8, 134.7, 129.2, 128.4, 26.4, 21.6; IR (neat) 1680, 1606, 1356, 1270, 1182, 814, 568 cm^{-1}; LRMS (EI); Mass calcd for $C_9H_{10}O$ $[M]^+$: 134; found 134.

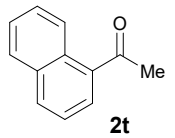


2s

1-(4-Fluorophenyl)ethan-1-one[6],[8] **(2s)**: Prepared according to the *general procedures* using 1-(4-fluorophenyl)ethane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 24 h (*Condition **A***) or 18 h (*Condition **B***), the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.43) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (79 mg, 88%), *Condition **B*** (48 mg, 53%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.12 – 7.08 (m, 2H), 2.56 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 165.7 (d, J_{cf} = 254.4 Hz), 133.6 (d, J_{cf} = 3.0 Hz), 130.9 (d, J_{cf} = 9.4 Hz), 115.6 (d, J_{cf} = 21.8 Hz), 26.4; IR (neat) 1682, 1596, 1504, 1358, 1260, 1228, 1156, 960, 838, 564, 493 cm^{-1}; LRMS (EI); Mass calcd for C_8H_7FO $[M]^+$: 138; found 138.

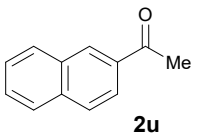


2t

1-(Naphthalen-1-yl)ethan-1-one[8] **(2t)**: Prepared according to the *general procedures* using 1-(1-naphthyl)ethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 48 h (*Condition **A***) or 18 h (*Condition **B***), the reaction mixture was purified by flash column chromatography (20% Et_2O/hexane, R_f = 0.54) to provide the title compound as a white solid. mp 30-32 °C (lit.[21] 34-34 °C).

Yield : *Condition **A*** (86 mg, 78%), *Condition **B*** (38 mg, 34%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.78 (m, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.90 (dd, J = 7.2, 1.2 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.63 – 7.58 (m, 1H), 7.54 – 7.44 (m, 2H), 2.72 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 135.4, 134.0, 133.0, 130.2, 128.8, 128.5, 128.1, 126.5, 126.1, 124.4, 29.9; IR (neat) 1670, 1504, 1350, 1236, 1190, 1124, 942, 773, 590, 490 cm^{-1}; LRMS (EI); Mass calcd for $C_{12}H_{10}O$ $[M]^+$: 170; found 170.

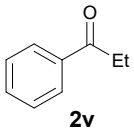


2u

1-(Naphthalen-2-yl)ethan-1-one[7],[8] **(2u)**: Prepared according to the *general procedures* using 1-(2-naphthyl)ethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 24 h (*Condition **A***) or 18 h (*Condition **B***), the reaction mixture was purified by column flash chromatography (20% Et_2O/hexane, R_f = 0.45) to provide the title compound as a pale yellow solid. mp 56-57 °C (lit.[22] 53-56 °C).

Yield : *Condition **A*** (108 mg, 98%), *Condition **B*** (59 mg, 53%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.02 – 7.99 (m, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.59 – 7.50 (m, 2H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 26.7; IR (neat) 1670, 1624, 1466, 1360, 1277, 1190, 1126, 940, 860, 816, 744, 666, 575, 475 cm^{-1}; LRMS (EI); Mass calcd for $C_{12}H_{10}O$ $[M]^+$: 170; found 170.

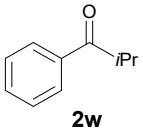


2v

Propiophenone[1],[4] **(2v)**: Prepared according to the *general procedures* using 1-phenylpropane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 36 h, the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.50) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (85 mg, 97%), *Condition **B*** (73 mg, 83%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.54 – 7.51 (m, 1H), 7.45 – 7.41 (m, 2H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 136.9, 132.8, 128.5, 127.9, 31.7, 8.2; IR (neat) 1684, 1598, 1446, 1351, 1216, 950, 740, 689, 566 cm^{-1}; LRMS (EI); Mass calcd for $C_9H_{10}O$ $[M]^+$: 134; found 134.

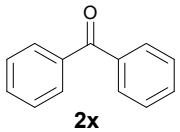


2w

2-Methyl-1-phenylpropan-1-one[4],[7] **(2w)**: Prepared according to the *general procedures* using 2-methyl-1-phenyl-propane-1-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 48 h (*Condition **A***) or 24 h (*Condition **B***), the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.50) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (64 mg, 66%), *Condition **B*** (94 mg, 97%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.54 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 3.54 (hept, *J* = 6.8 Hz, 1H), 1.20 (dd, *J* = 6.8, 0.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 136.2, 132.8, 128.6, 128.3, 35.3, 19.1; IR (neat) 1682, 1596, 1446, 1220, 1163, 978, 700 cm^{-1}; LRMS (EI); Mass calcd for $C_{10}H_{12}O$ $[M]^+$: 148; found 148.

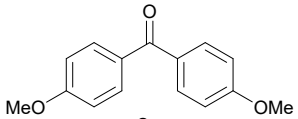


2x

Benzophenone[1],[4] **(2x)**: Prepared according to the *general procedures* using diphenylmethanethiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (10% Et_2O/hexane, R_f = 0.46) to provide the title compound as a colorless oil.

Yield : *Condition **A*** (91 mg, 77%), *Condition **B*** (59 mg, 50%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 4H), 7.48 – 7.41 (m, 2H), 7.379 – 7.30 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 137.6, 132.4, 130.0, 128.3; IR (neat) 1656, 1598, 1447, 1275, 1150, 919, 762, 694, 638 cm^{-1}; LRMS (EI); Mass calcd for $C_{13}H_{10}O$ $[M]^+$: 182; found 182.

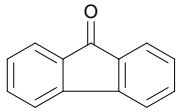


2y

Bis(4-methoxyphenyl)methanone (2y)[14],[15]: Prepared according to the general procedure using bis(4-methoxy-phenyl)methane-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash column chromatography (40% Et_2O/hexane, R_f = 0.33) to provide the title compound as a white solid.

Yield : *Condition **A*** (157 mg, 65%), *Condition **B*** (131 mg, 54%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 4H), 6.98 – 6.94 (m, 4H), 3.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 162.8, 132.2, 130.7, 113.4, 55.4; IR (neat) 1640, 1596, 1505, 1306, 1242, 1160, 1025, 923, 852, 768, 585 cm^{-1}; LRMS (EI); Mass calcd for $C_{15}H_{14}O_3$ $[M]^+$: 242; found 242.



2z

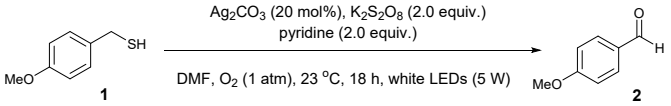
9*H*-fluoren-9-one (2z)[16]: Prepared according to the general procedure using 9*H*-fluorene-9-thiol (0.65 mmol, 1.0 equiv.). After irradiation for 18 h, the reaction mixture was purified by flash chromatography (20% Et_2O/hexane, R_f = 0.47) to provide the title compound as a yellow solid.

Yield : *Condition **A*** (166 mg, 92%), *Condition **B*** (117 mg, 65%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.45 – 7.40 (m, 4H), 7.25 – 7.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 144.3, 134.6, 134.0, 129.0, 124.2, 120.2; IR (neat) 1710, 1612, 1599, 1450, 1296, 1190, 1149, 1095, 948, 915, 811, 730, 669, 650 cm^{-1}; LRMS (EI); Mass calcd for $C_{13}H_8O$ $[M]^+$: 180; Found 180.

5. Control Experiments

Control experiments were performed to obtain further mechanistic insights into this transformation. We observed disulfide **3** and sulfide **4** during the reactions by GC-MS analysis (**Fig S1**).



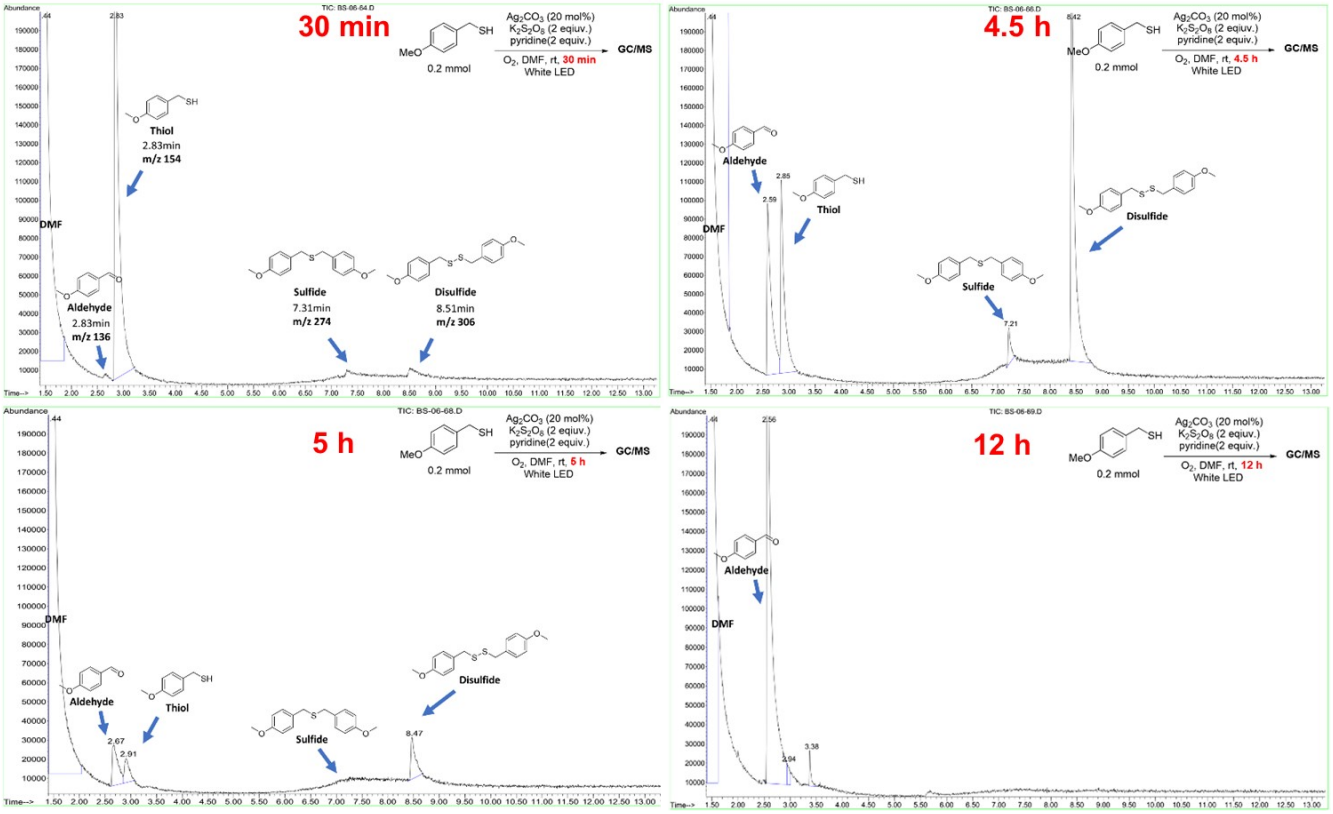
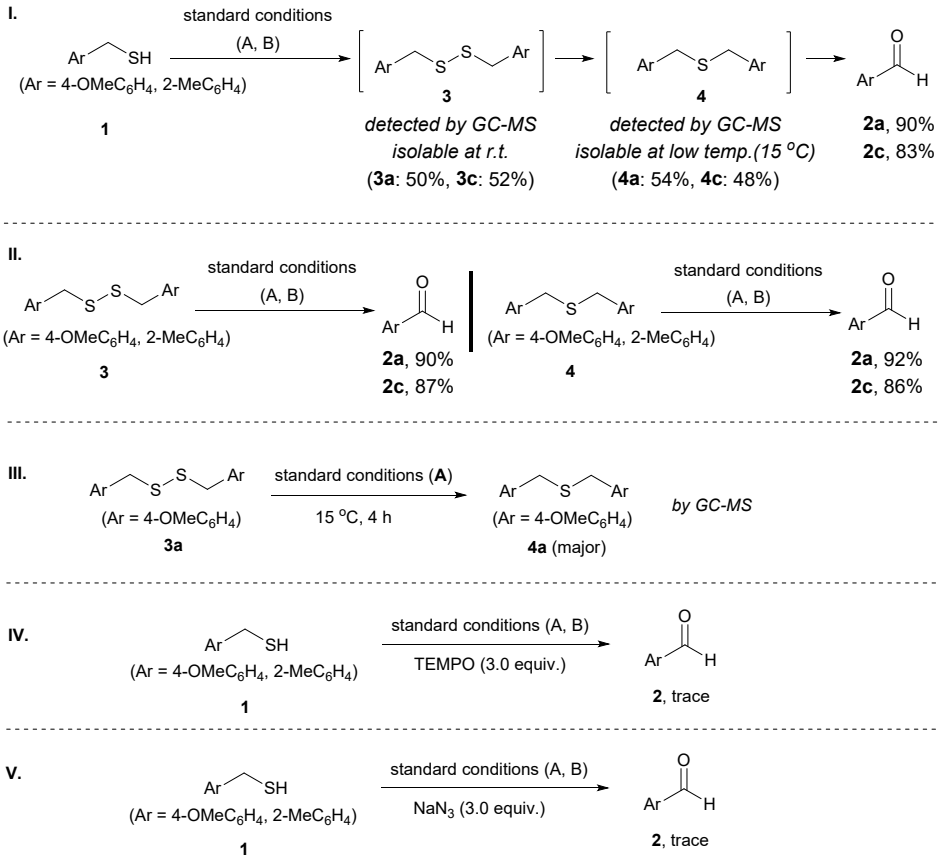


Fig S1. Reaction profile / GC-MS data

Disulfide **3** was isolable at room temperature, however, sulfide **4** was transformed to aldehyde **2** very quickly under the reaction conditions. Sulfide **4** was isolable at lower temperature (15 °C). With either disulfide **3** or sulfide **4**, the desired products were obtained under both reaction conditions (Scheme 1, II). Furthermore, disulfide **3** transformed into sulfide **4** at 15 °C under the reaction conditions (Scheme 1, III). These results indicate that disulfide **3** and sulfide **4** are intermediates in this transformation. When TEMPO was then used, only trace amounts of the desired products were obtained (Scheme 1, IV). This result indicates that the oxidative cleavage pathway includes a radical reaction. Finally, NaN_3 (a strong $^1O_2$ quencher) was added to the reaction to determine the oxygen species; no reaction was observed (Scheme 1, V).



Scheme 1. Control experiments

Experimental procedure for control experiments

1) Isolation of disulfide **3a**

A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with 4-methoxybenzylthiol (**1a**) (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) and pyridine (105 μL, 1.3 mmol, 2.0 equiv.) were added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 5 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (Et_2O in hexane: 20%) afforded the desired disulfide **3a** (50% yield).

2) Isolation of disulfide **3c**

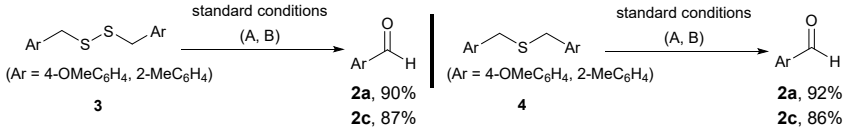
A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with *o*-tolylmethanethiolthe (**1c**) (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 5 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (DCM in hexane: 5%) afforded the desired disulfide **3c** (52% yield).

3) Isolation of sulfide **4a**

A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with 4-methoxybenzylthiol (**1a**) (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) and pyridine (105 μL, 1.3 mmol, 2.0 equiv.) were added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 4 h at 15 °C. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (Et_2O in hexane: 20%) afforded the desired sulfide **4a** (54% yield).

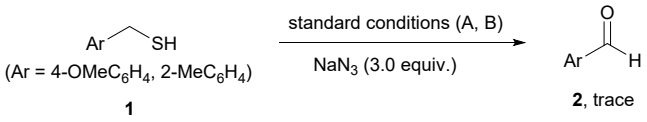
4) Isolation of sulfide **4c**

A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with *o*-tolylmethanethiolthe (**1c**) (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.) and $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 4 h at 15 °C. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (DCM in hexane: 5%) afforded the desired sulfide **4c** (48% yield).



A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with corresponding disulfide **3** or sulfide **4**, (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (71.6 mg, 0.26 mmol, 0.4 equiv.) and $K_2S_2O_8$ (702.8 mg, 2.6 mmol, 4.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. In condition A, pyridine (105 μL, 1.3 mmol, 2.0 equiv.) was also added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 5 h at room temperature. After irradiation, the crude mixture was extracted with Et_2O (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography afforded the desired products.

A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with corresponding thiols **1** (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.), $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.), TEMPO (305 mg, 1.95 mmol, 3.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. In condition A, pyridine (105 μL, 1.3 mmol, 2.0 equiv.) was also added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 h at room temperature.



A well dried 10 mL round-bottom-flask equipped with a magnetic stirring bar was charged with corresponding thiols **1** (0.65 mmol, 1.0 equiv.), Ag_2CO_3 (35.8 mg, 0.13 mmol, 0.2 equiv.), $K_2S_2O_8$ (351.4 mg, 1.3 mmol, 2.0 equiv.), NaN_3 (127 mg, 1.95 mmol, 3.0 equiv.). In the absence of light, dry DMF (0.25 M, 2.6 mL) was added. In condition A, pyridine (105 µL, 1.3 mmol, 2.0 equiv.) was also added. The resulting suspension was degassed and backfilled with O_2. The reaction mixture was stirred and irradiated with 5 W white LEDs for 18 h at room temperature.

6. Mechanistic Studies

UV-vis spectra of the benzyl thiols (**1**) were measured with the diluted concentration (0.02 M) in DMF. The absorbance for thiol substrates is limited to the UV region mostly. On the other hand, a clear red shift was observed with *in situ* generated-silver thiolate (**1a** + Ag_2CO_3), and the absorbance is expanded to the visible light region (Fig. S2).

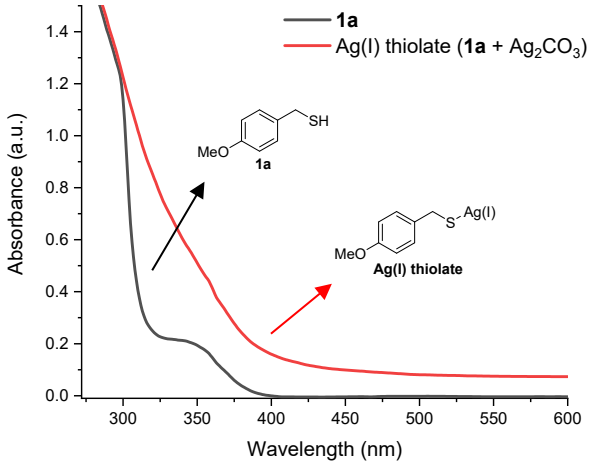


Fig S2. UV-Vis spectra of the **1a** and its *in situ* generated Ag(I) thiolate (0.02 M in DMF)

In our studies, we tested two reaction conditions, i.e., condition **A**: with pyridine and condition **B**: without pyridine. When we conducted the reaction with 4-methoxybenzyl thiol (**1a**), the addition of pyridine was found to be helpful in improving the reaction yields (Table 1). However, interestingly, some of the benzyl thiols (**1**) provided the corresponding aldehydes in better yields in the absence of pyridine. For examples, in the cases of ortho-substituted benzyl thiols such as **1c** and **1d**, the reaction did not proceed in the presence of pyridine (Table 2, **2c** and **2d**). To understand this phenomenon, we carried out additional UV-vis experiments, and interesting results were observed.

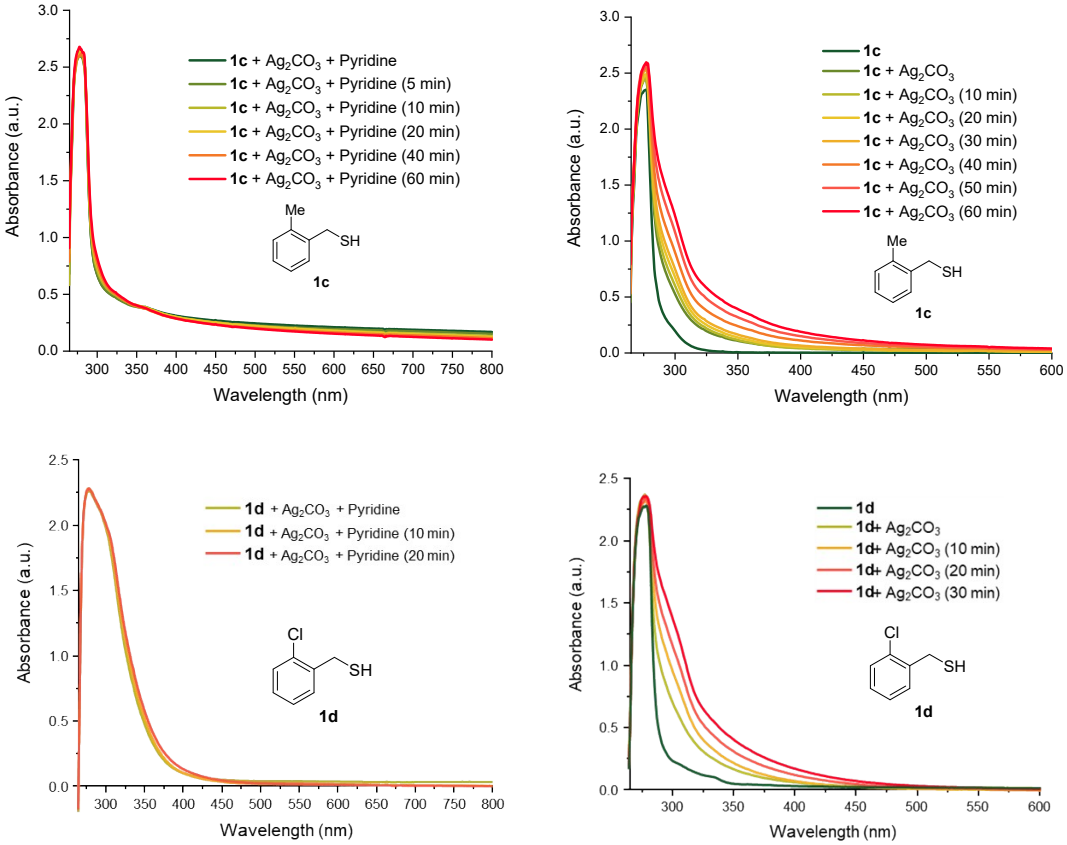
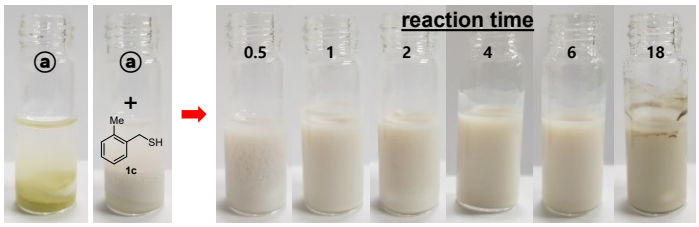


Fig S3. UV-vis absorption spectra of **1c** and **1d** under the reaction conditions (0.02 M in DMF).

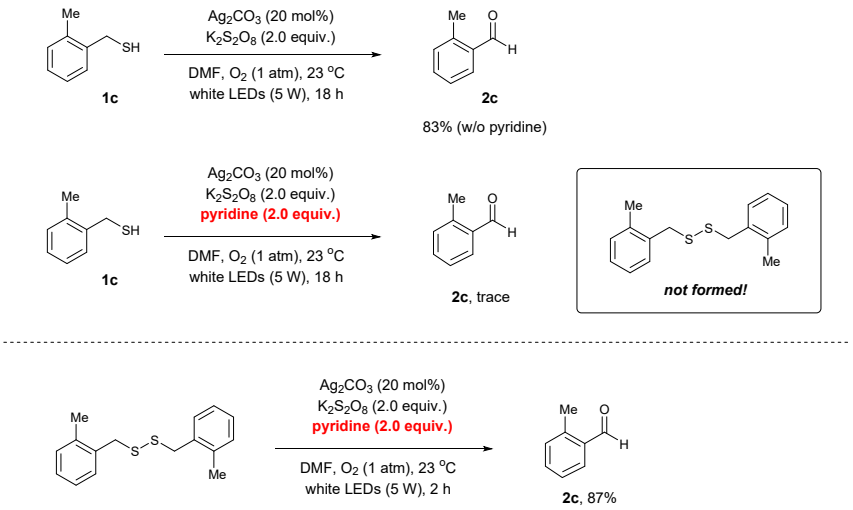
The absorbance for substrates **1c** and **1d** that resulted in the desired products in the absence of pyridine was limited to the UV region, and no red shift was observed in the presence of pyridine (**Fig S3**, left, for **1c** and **1d**). Moreover, the solution was heterogeneous, which possible affected the absorption of light (**Fig S4**). On the other hand, a clear red shift was observed in the absence of pyridine, and the absorbance was expanded to the visible light region to generate $^1O_2$ for further oxidative processes (**Fig S3**, right, for **1c** and **1d**). The results indicate that thiolates are not generated in the presence of pyridine for these substrates.



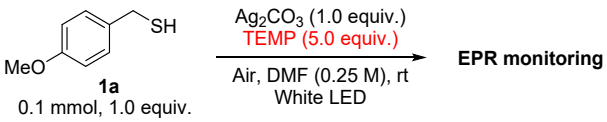
ⓐ : Ag_2CO_3 (0.1 mmol) + $K_2S_2O_8$ (1.0 mmol) + Pyridine (1.0 mmol) in DMF (2.0 mL)

Fig S4. Crude mixture of **1c** in the presence of pyridine.

Furthermore, for these substrates, we found that the addition of pyridine suppressed the formation of disulfides, key intermediates in this transformation. No disulfide or sulfide was detected during the reactions. We were curious if the reaction could be further proceeded using disulfides as the starting compounds in condition A (with pyridine). Interestingly, the desired product was obtained in this case (87% yield). We assumed that the addition of pyridine inhibited the formation of disulfides, thereby stopping further processes.



7. Determination of Singlet Oxygen Species



To determine the active species of singlet oxygen during the reaction, 2,2,6,6-tetramethylpiperidine (TEMP) was employed to trap $^1O_2$. Irradiation of air-saturated DMF solution of TEMP with *in situ* generated silver thiolate (mixed suspension of 4-methoxybenzylthiol and Ag_2CO_3 in DMF) under white LEDs resulted in the formation of a strong signal of $^1O_2$ adduct with TEMP as triplet signal (a^N = 16.0 ± 0.1 G). A series of stronger characteristic signal of $^1O_2$ were collected with prolonged irradiation time, indicating that $^1O_2$ is present during the reaction (**Fig S5**).

All EPR spectra were collected with the following experimental parameters: frequency: 9.4 GHz; power: 0.9230 mW; modulation width: 0.8 mT; amplitude: 120; time constant: 0.03 sec; sweep time: 30 sec; Number of scans: 1.

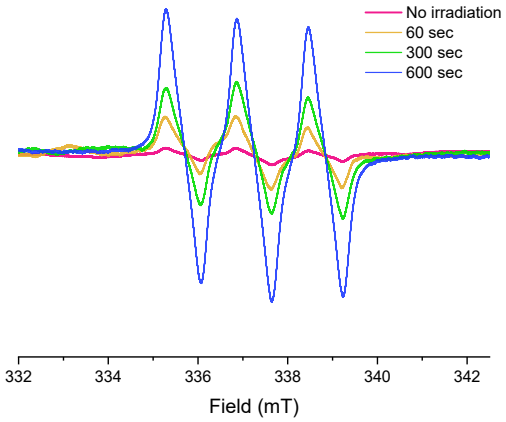
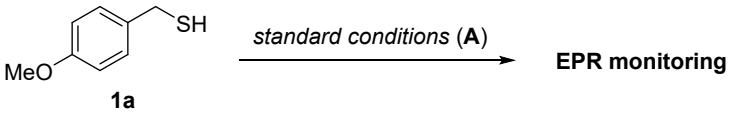


Fig S5. EPR signal of TEMPO free radical

8. Determination of Pyridine Complex



To elucidate the role of pyridine, we performed EPR studies. We observed that Ag(II) species were generated *in situ* during the reaction in the presence of pyridine. The EPR spectrum of this species is consistent with that of $[Ag(II)Py4]S_2O_8$ in terms of the *g-value* (Fig S6, red line, g_x = 2.036, g_y = 2.084, g_z = 2.142).[10],[11] The authentic sample of $[Ag(II)Py_4]S_2O_8$ was synthesized (Fig S6, blue line), and compared with our reaction sample.

All EPR spectra were collected with the following experimental parameters: frequency: 9.4 GHz; power: 0.8970 mW; modulation width: 0.8 mT; amplitude: 100; time constant: 0.03 sec; sweep time: 30 sec; Number of scans: 1.

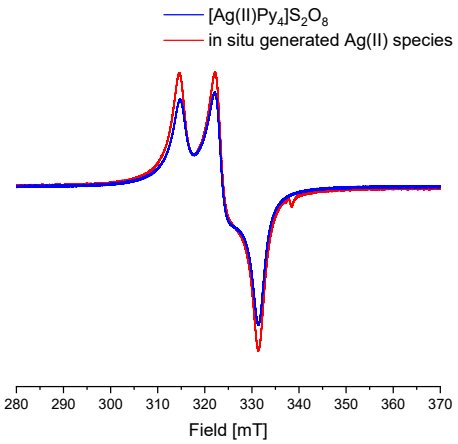
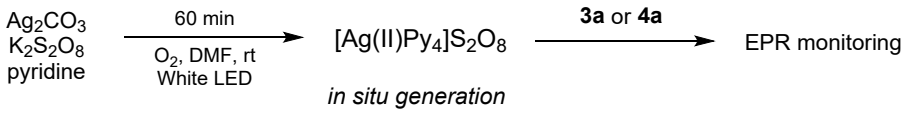


Fig S6. EPR spectra of Ag(II)-pyridine species

9. EPR Quenching Experiments



The mixture of Ag_2CO_3, $K_2S_2O_8$, and pyridine in DMF was stirred for 60 min in the presence of light, and the reaction solution was analyzed by EPR at room temperature (**Fig S7**, blue lines). Addition of bis(4-methoxybenzyl)disulfide **3a** or bis(4-methoxybenzyl)sulfide **4a** to *in situ* generated complex caused a quick quench of the Ag(II) signal (**Fig S7**, red lines).

All EPR spectra were collected with the following experimental parameters: frequency: 9.4 GHz; power: 0.9220 mW; modulation width: 0.8 mT; amplitude: 100; time constant: 0.03 sec; sweep time: 30 sec; Number of scans: 1.

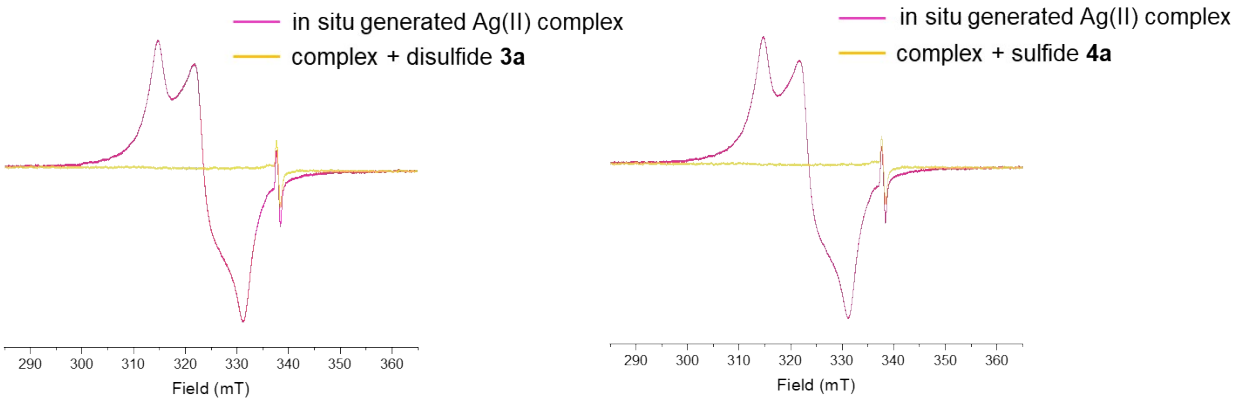


Fig S7. EPR quenching experiments

References

[1] M. Iinuma, K. Moriyama, H. Togo, *Tetrahedron.* **2013**, *69*, 2961-2970.

[2] A. Gonzalez-de-Castro, J. Xiao, *J. Am. Chem. Soc.* **2015**, 137, 8206-8218.

[3] Y. Corre, V. Rysak, F. Capet, J. P. Djukic, F. Agbossou-Niedercorn, C. Michon, *Chem. Eur. J.* **2016**, *22*, 14036-14041.

[4] K. Moriyama, M. Takemura, H. Togo, *J. Org. Chem.* **2014**, *79*, 6094-6104.

[5] L. Wang, Z. Bie, S. Shang, Y. Lv, G. Li, J. Niu, S. Gao, *RSC Adv.* **2016**, *6*, 35008-35013.

[6] G. Zhang, S. Li, J. Lei, G. Zhang, X. Xie, C. Ding, R. Liu, *Synlett.* **2016**, *27*, 956-960.

[7] M. J. Kim, Y. E. Jung, C. Y. Lee, J. Kim, *Tetrahedron Lett.* **2018**, *59*, 2722-2725.

[8] M. Yousuf, T. Das, S. Adhikari, *New. J. Chem.* **2015**, *39*, 8763-8770.

[9] S. Imai, H. Togo, *Tetrahedron.* **2016**, *72*, 6948-6954.

[10] J. A. McMillan, B. Smaller, *J. Chem. Phys.* **1961**, *35*, 1698-1701.

[11] H. N. Po, *Coord. Chem. Rev.* **1976**, *20*, 171-195.

[12] N. Iqbal, E. J. Cho, *Adv. Synth. Catal.* **2015**, *357*, 2187-2192.

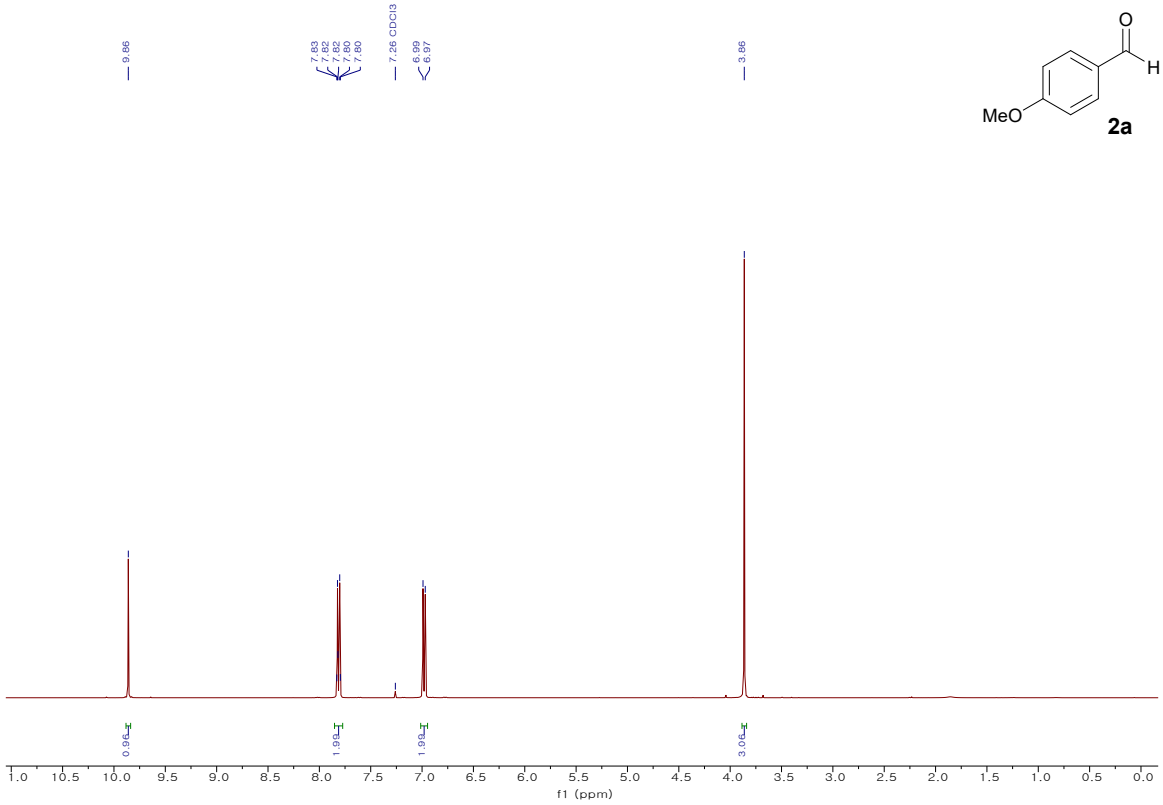
[13] M. Guan, C. Wang, J. Zhang, Y. Zhao, *RSC Adv.* **2014**, *4*, 48777-48782.

[14] H. Kim, S. Park, Y. Baek, K. Um, G. U. Han, D.-H. Jeon, S. H. Han, P. H. Lee, *J. Org. Chem.* **2018**, *83*, 3486-3496.

[15] A. Rérat, C. Michon, F. Agbossou-Niedercorn, C. Gosmini, *Eur. J. Org. Chem.* **2016**, 4554-4560.

[16] X. Zhang, X. Ji, S. Jiang, L. Liu, B. L. Weeks, Z. Zhang, *Green Chem.* **2011**, *13*, 1891-1896.

NMR Spectra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7.82
7.82
7.80
7.80
7.26 CDCl3
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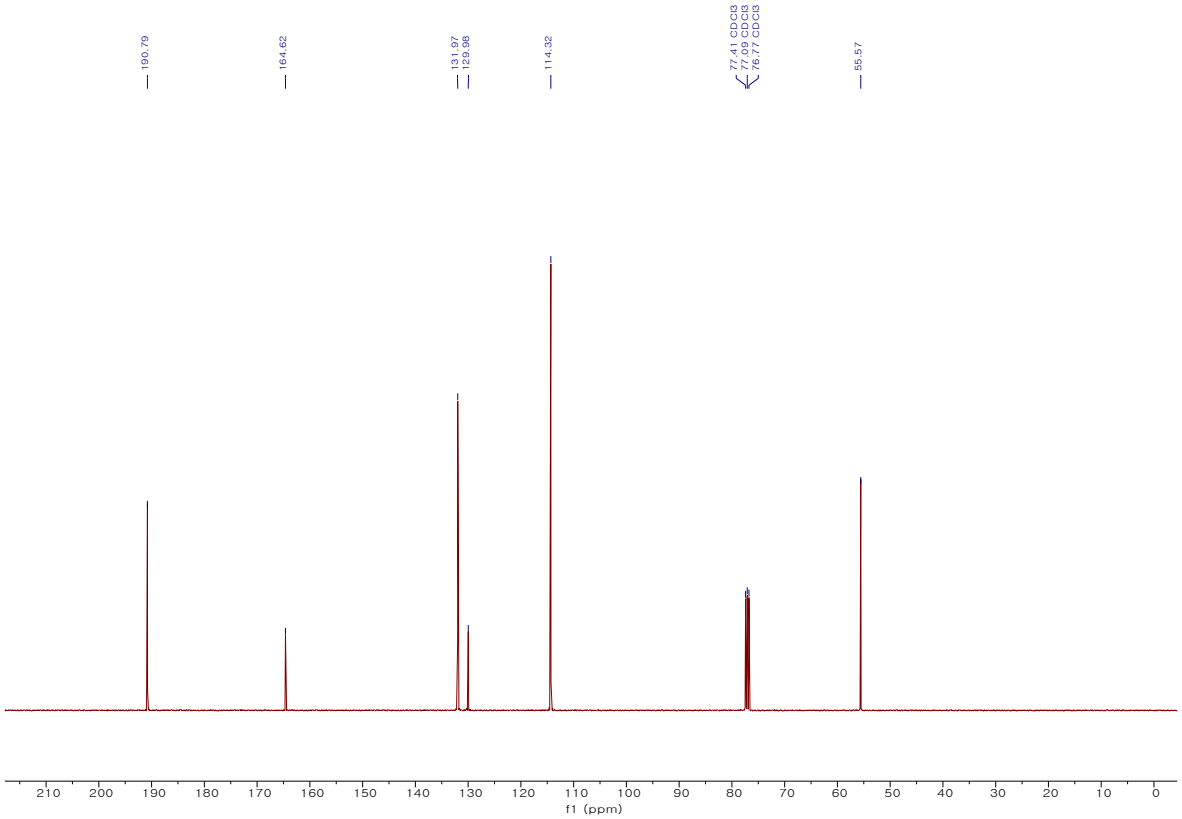
6.97
3.96
O
H
MeO
2a
0.96
1.91
1.98
3.06
f1 (ppm)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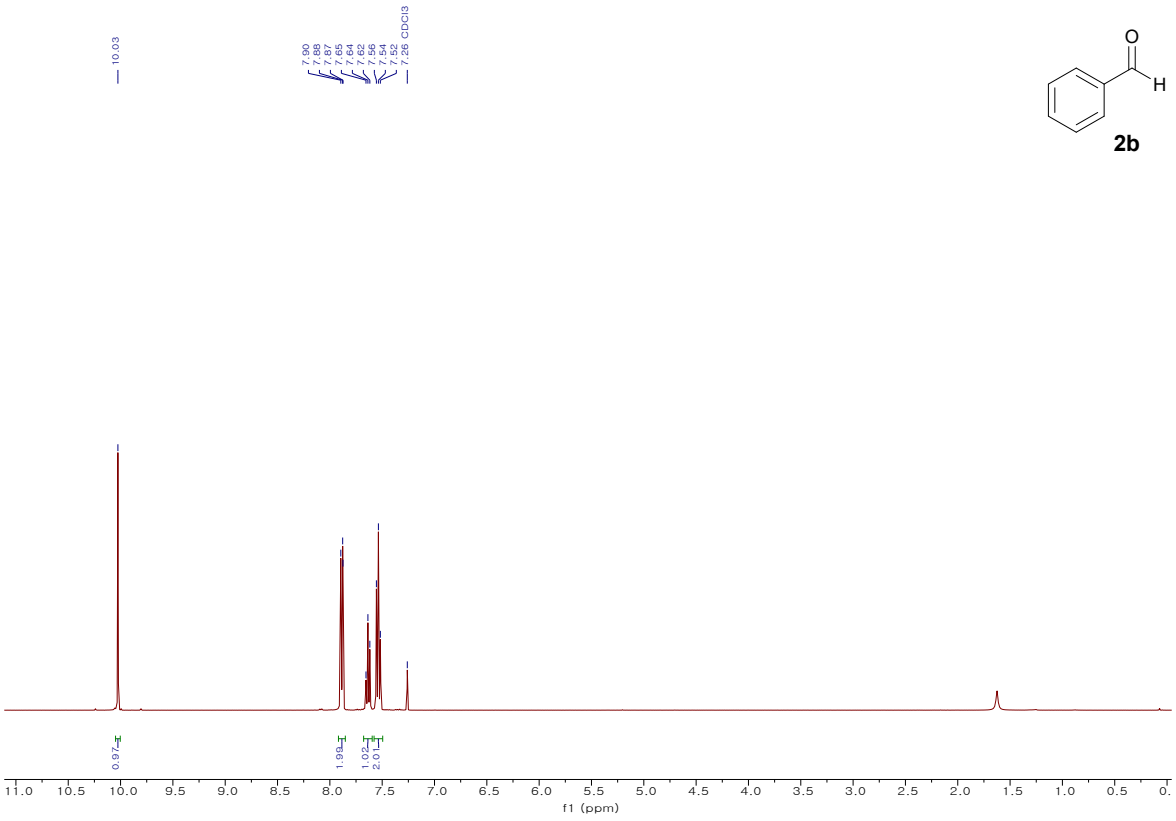
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O
H
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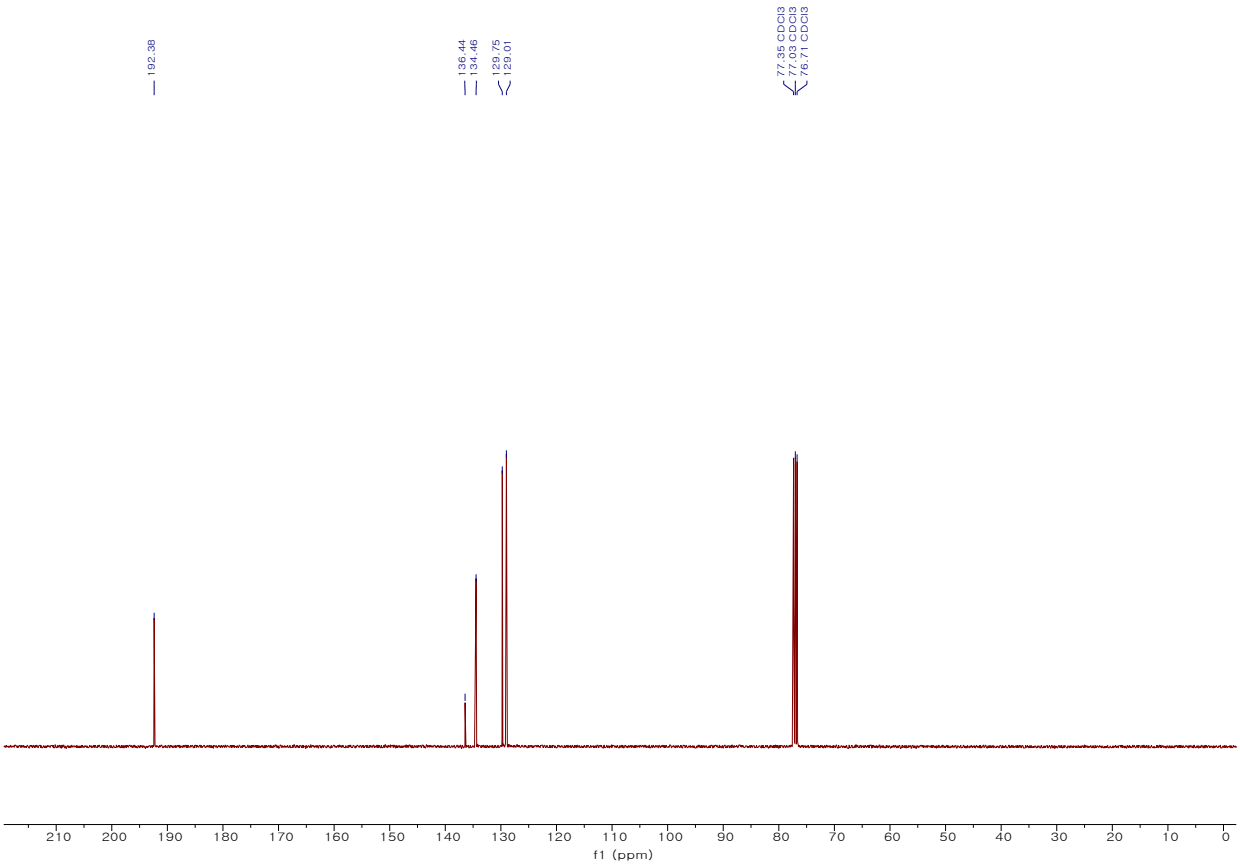
2.01
f1 (ppm)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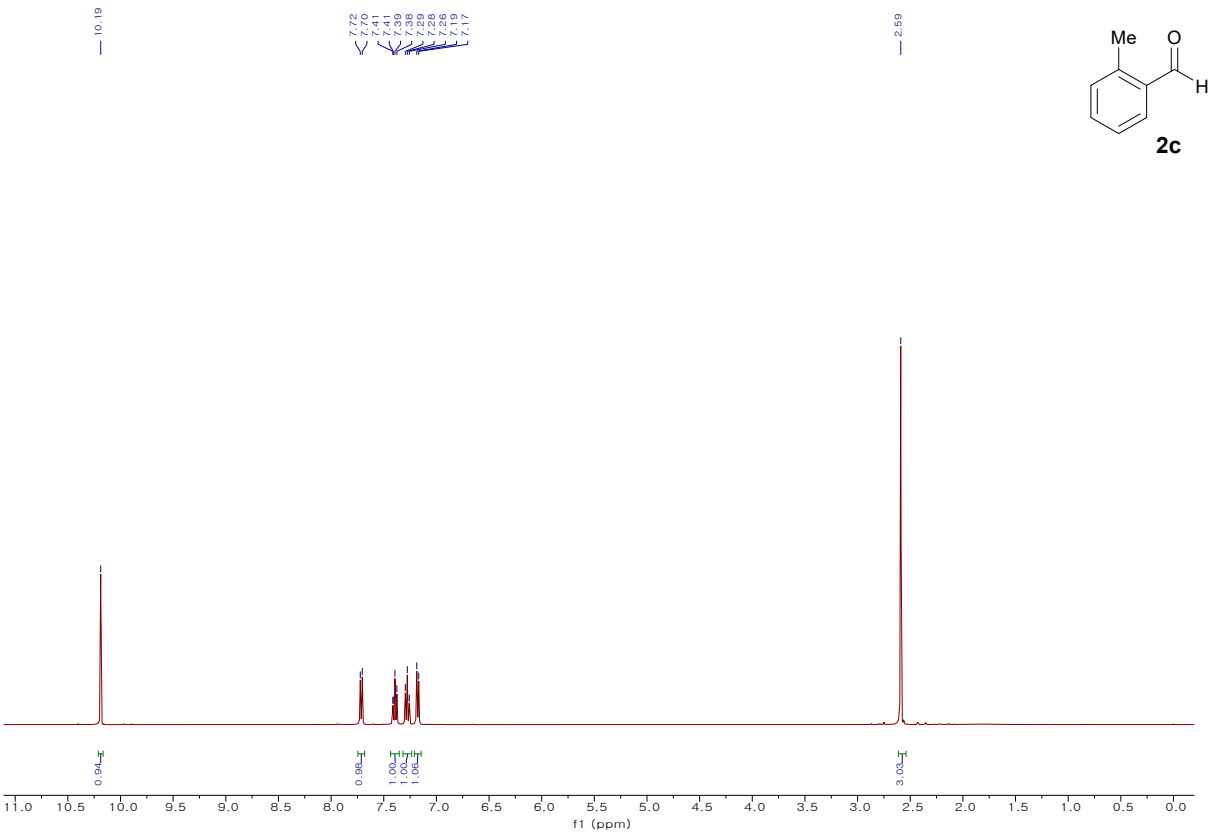
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1.00
1.00
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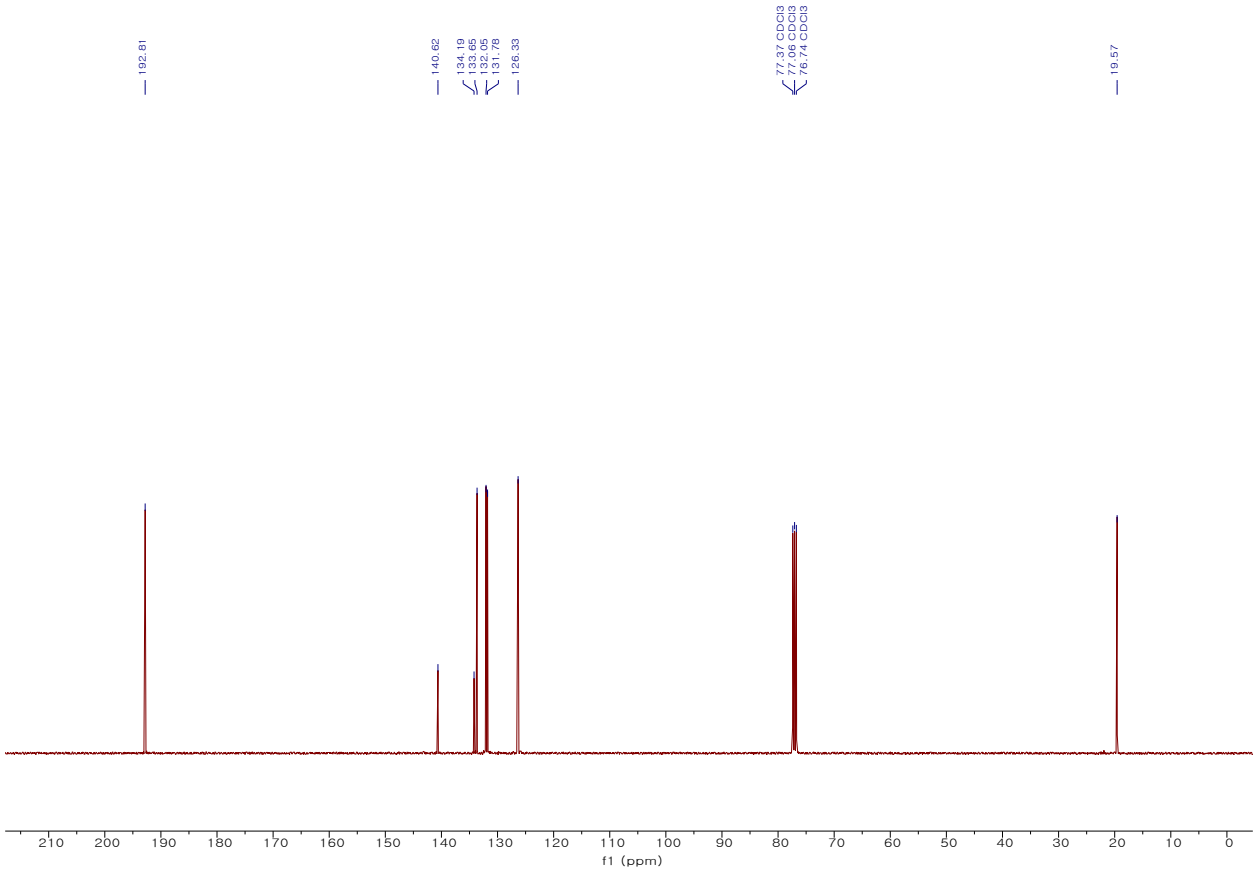
3.03
f1 (ppm)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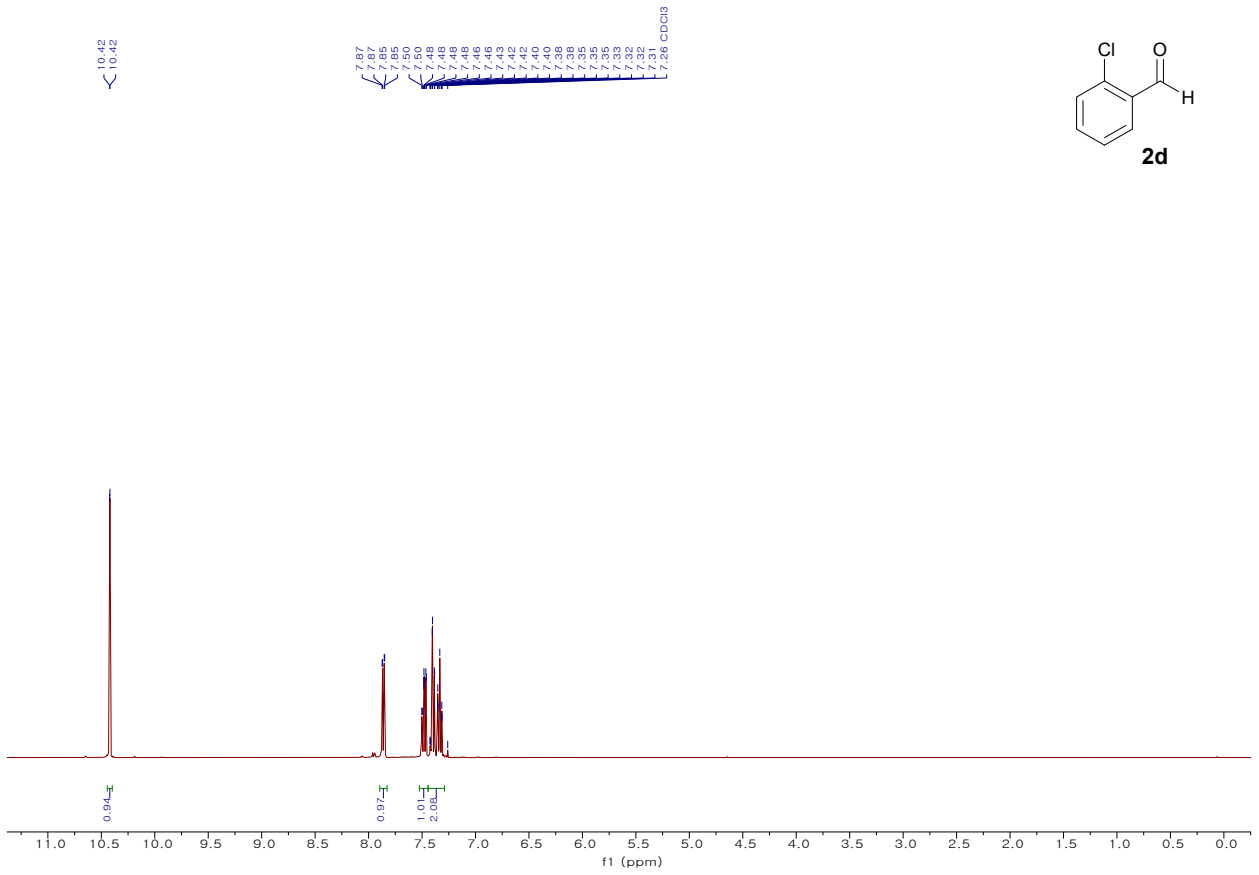
f1 (ppm)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7.35
7.35
7.35
7.33
7.32
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Cl
O
H
2d
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f1 (ppm)
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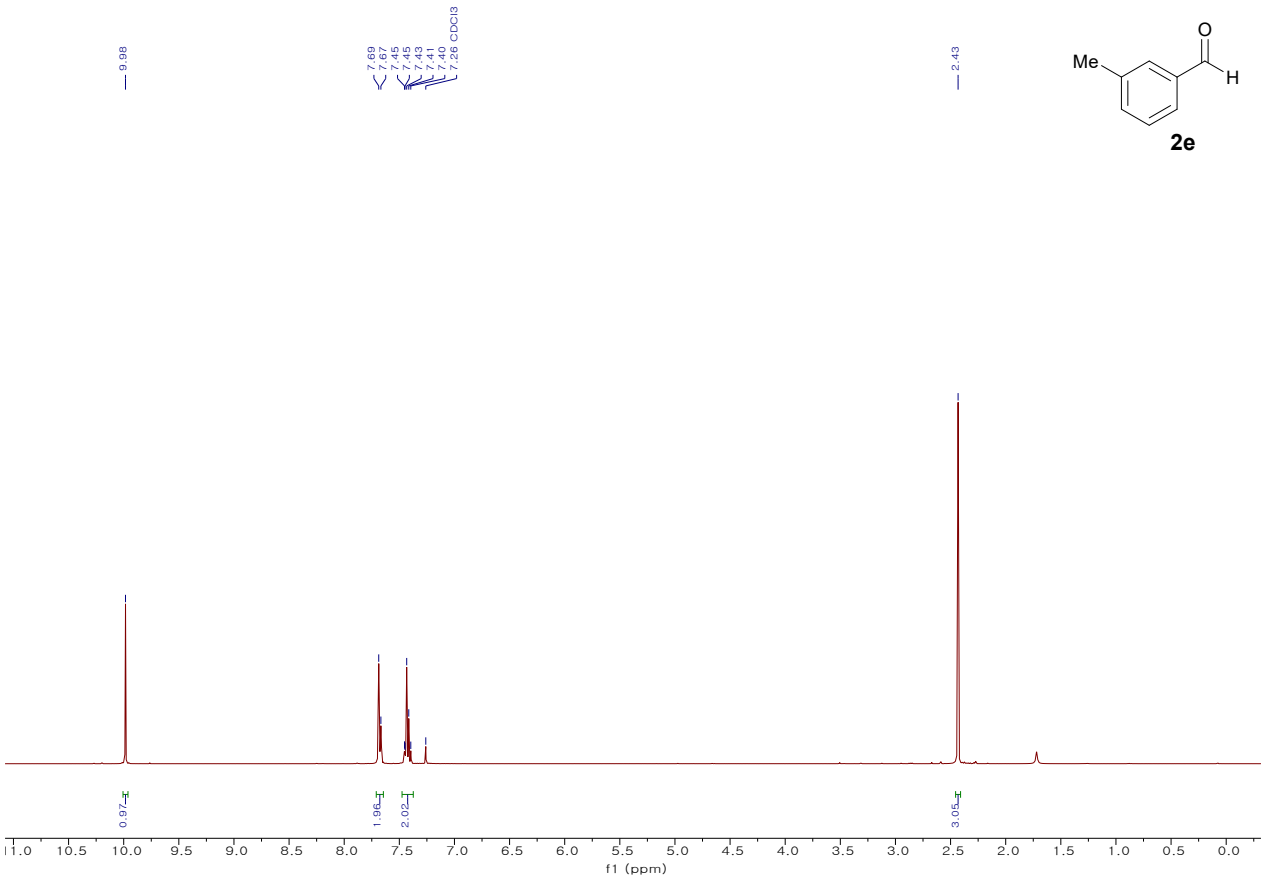
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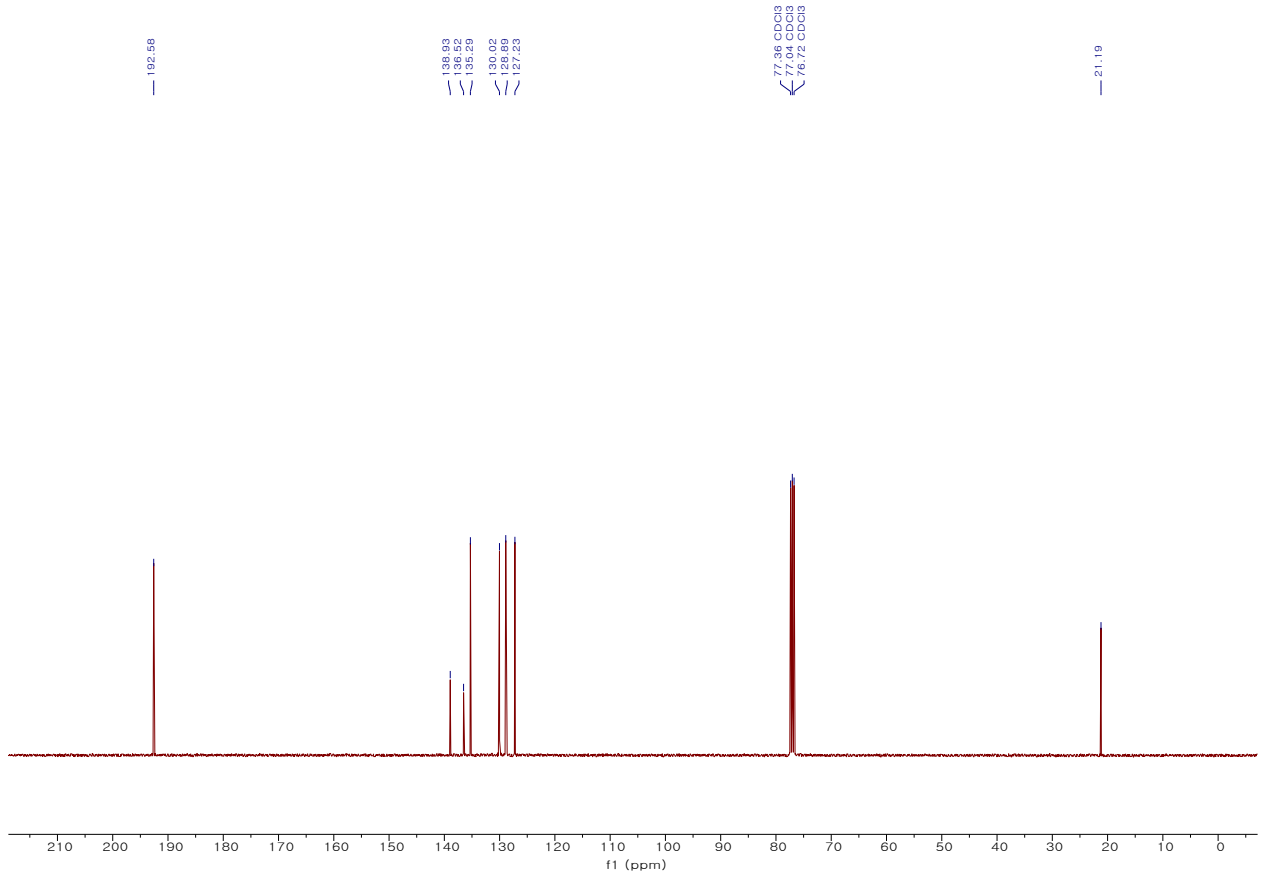
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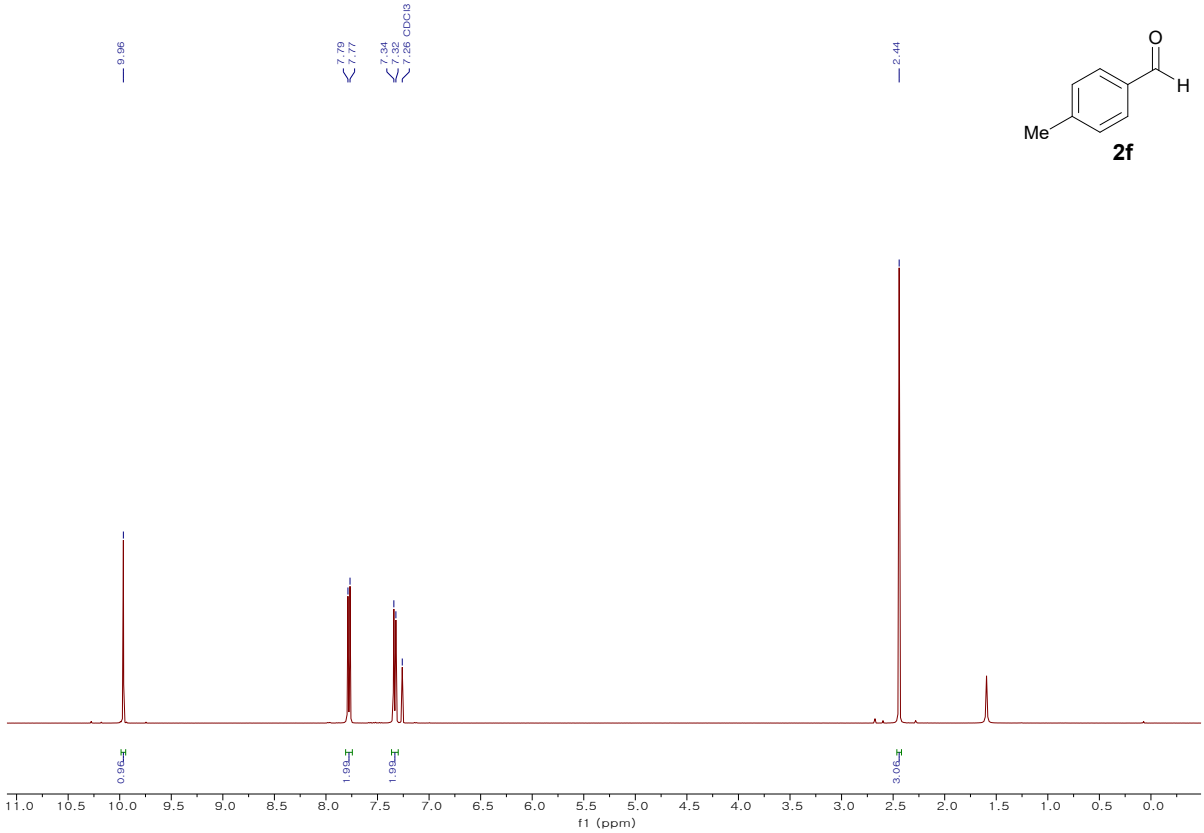
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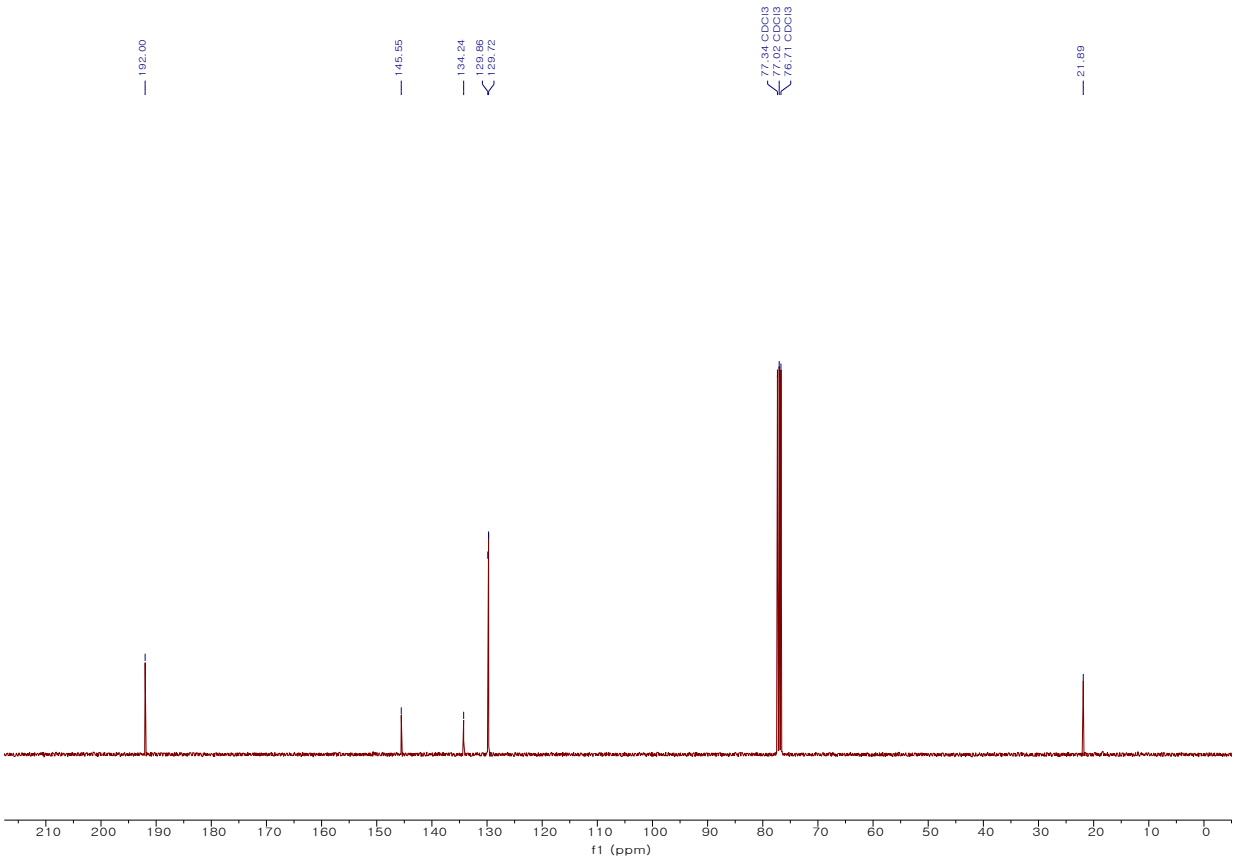
f1 (ppm)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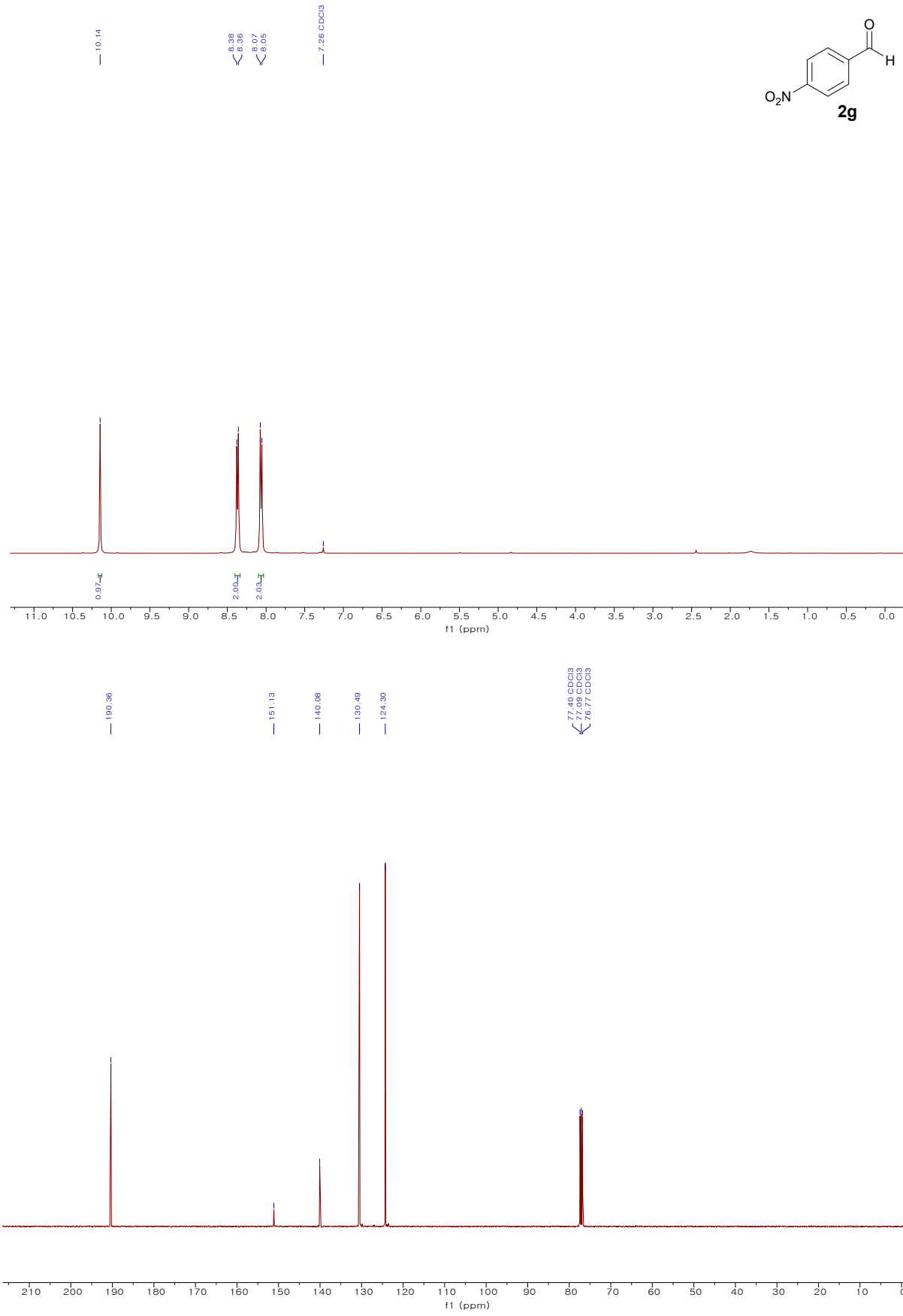
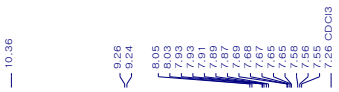
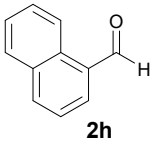
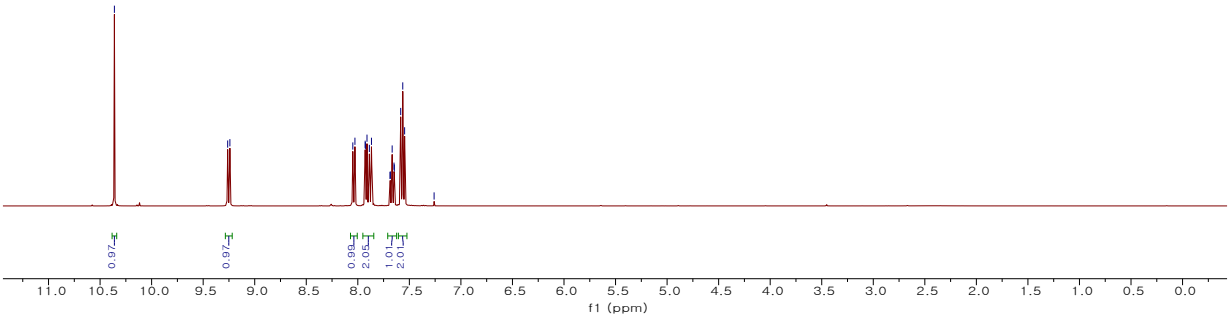
21.89
f1 (ppm)


10.14
8.38
8.36
8.07
8.05
7.26 CDCl3
O
H
O2N
2g
0.97
2.00
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
190.36
151.13
140.08
130.49
124.30
77.40 CDCl3
77.09 CDCl3
76.77 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.36
9.26
9.24
8.05
8.03
7.93
7.93
7.91
7.89
7.87
7.69
7.68
7.67
7.65
7.65
7.58
7.56
7.55
7.26 CDCl3


O
H

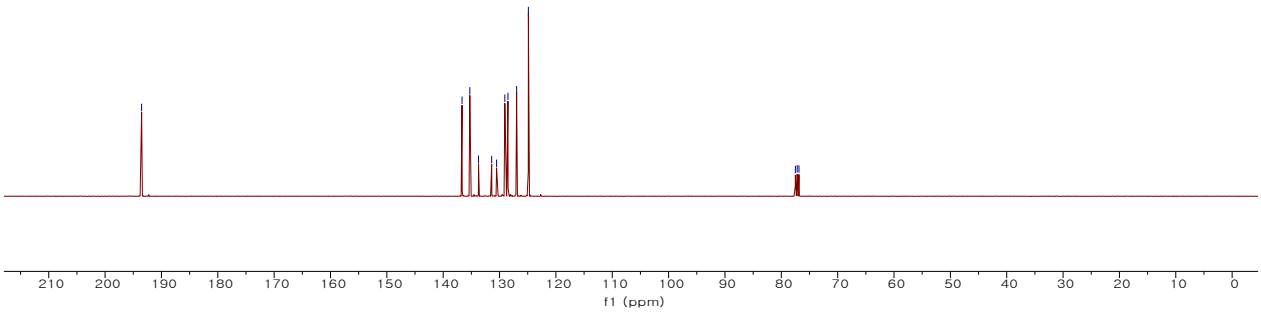
2h

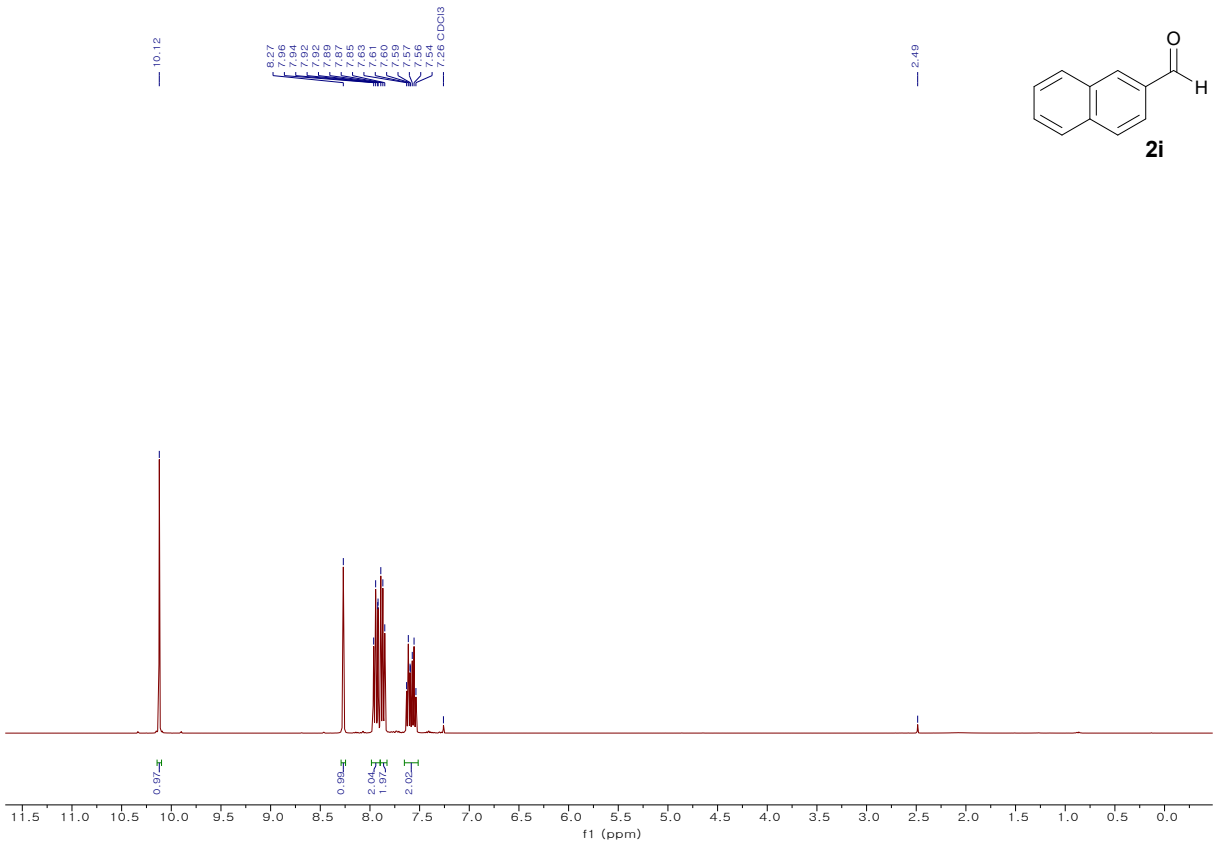

0.97
0.97
0.99
2.05
1.01
2.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

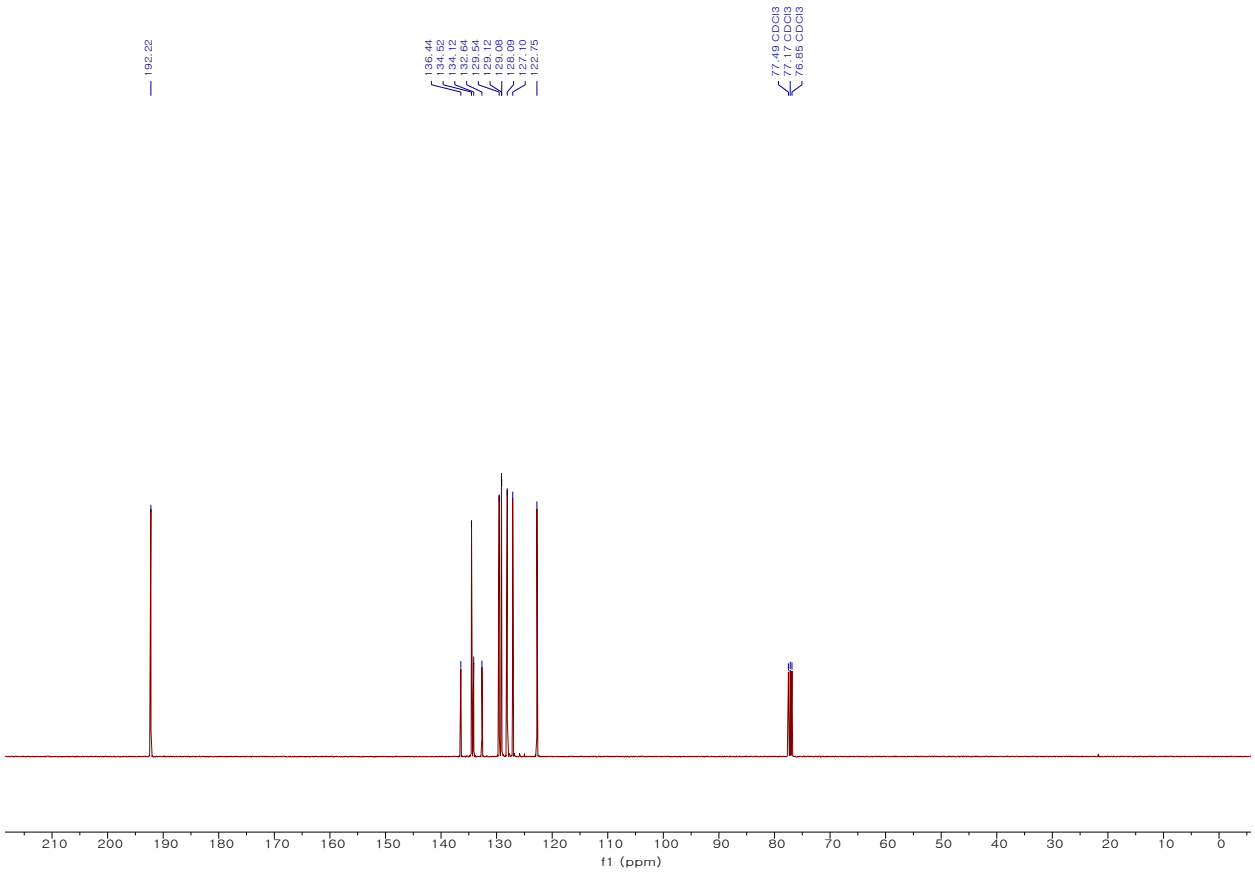

193.52

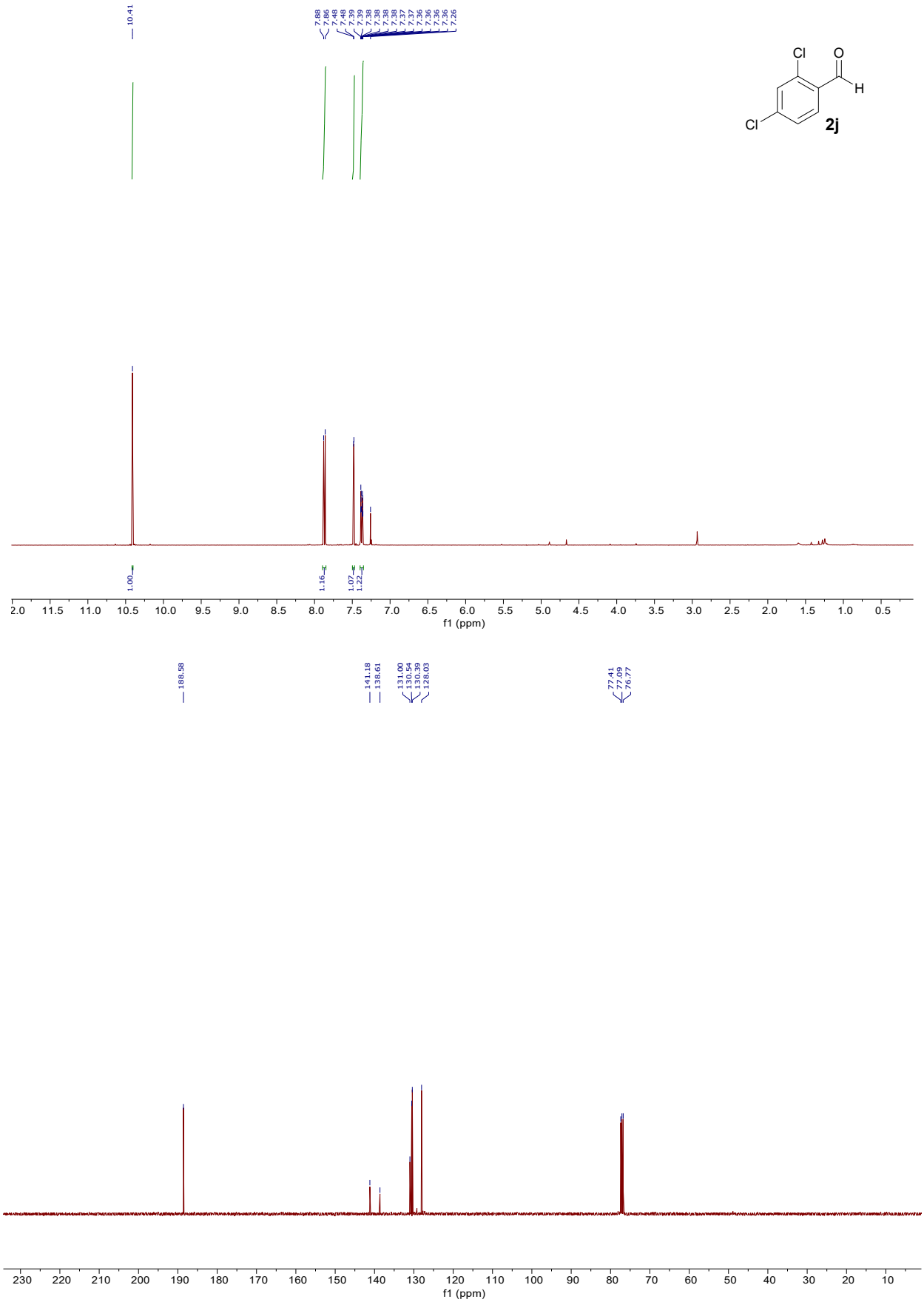
136.66
135.28
133.73
131.40
130.53
129.06
128.51
126.97
124.89

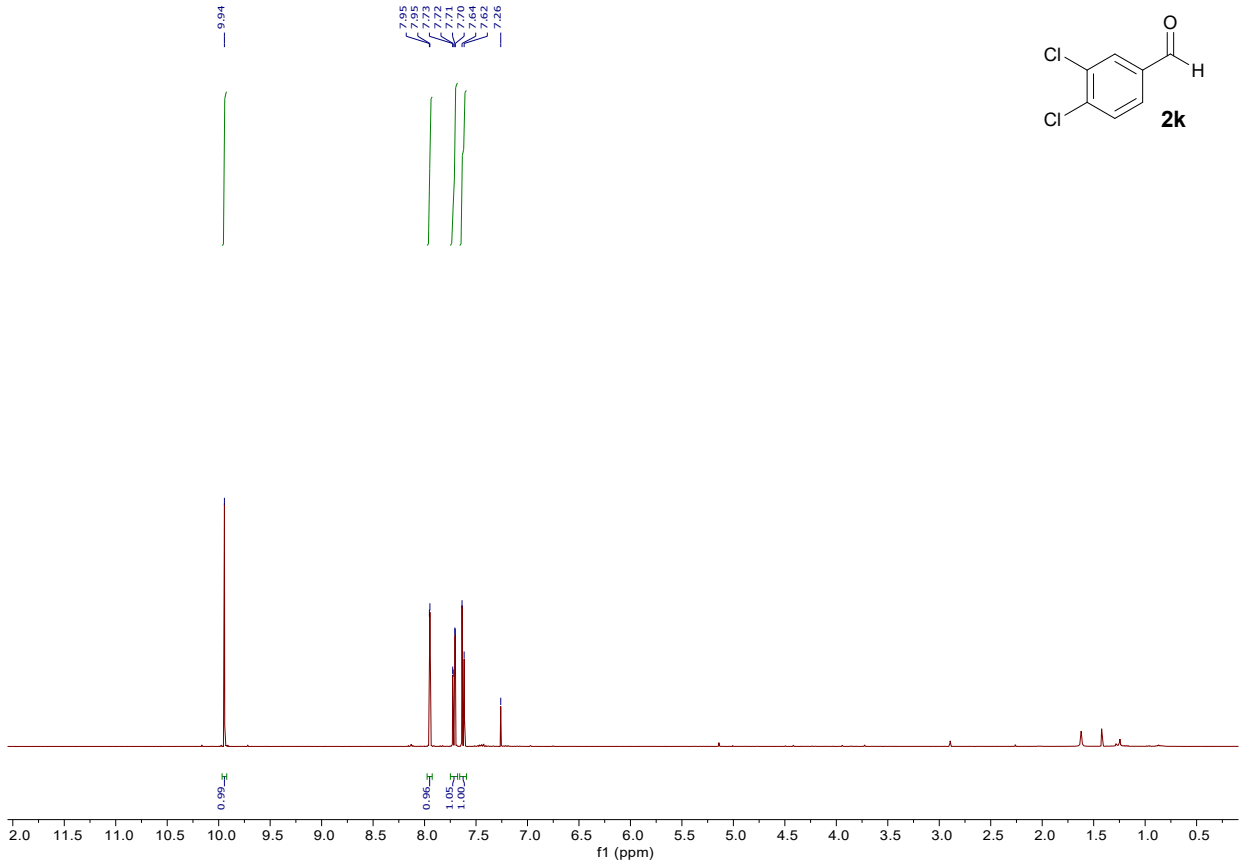

77.50 CDCl3
77.19 CDCl3
76.87 CDCl3

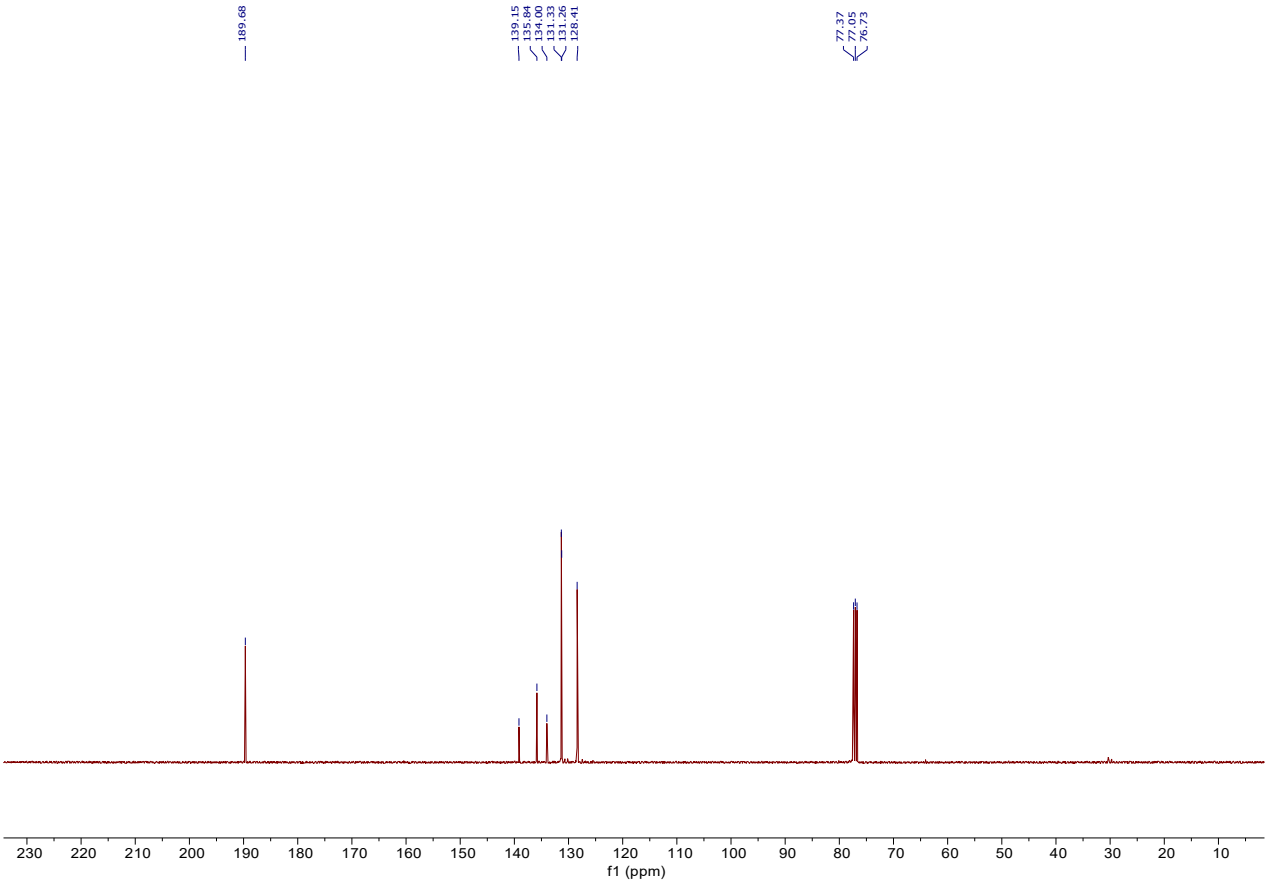

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

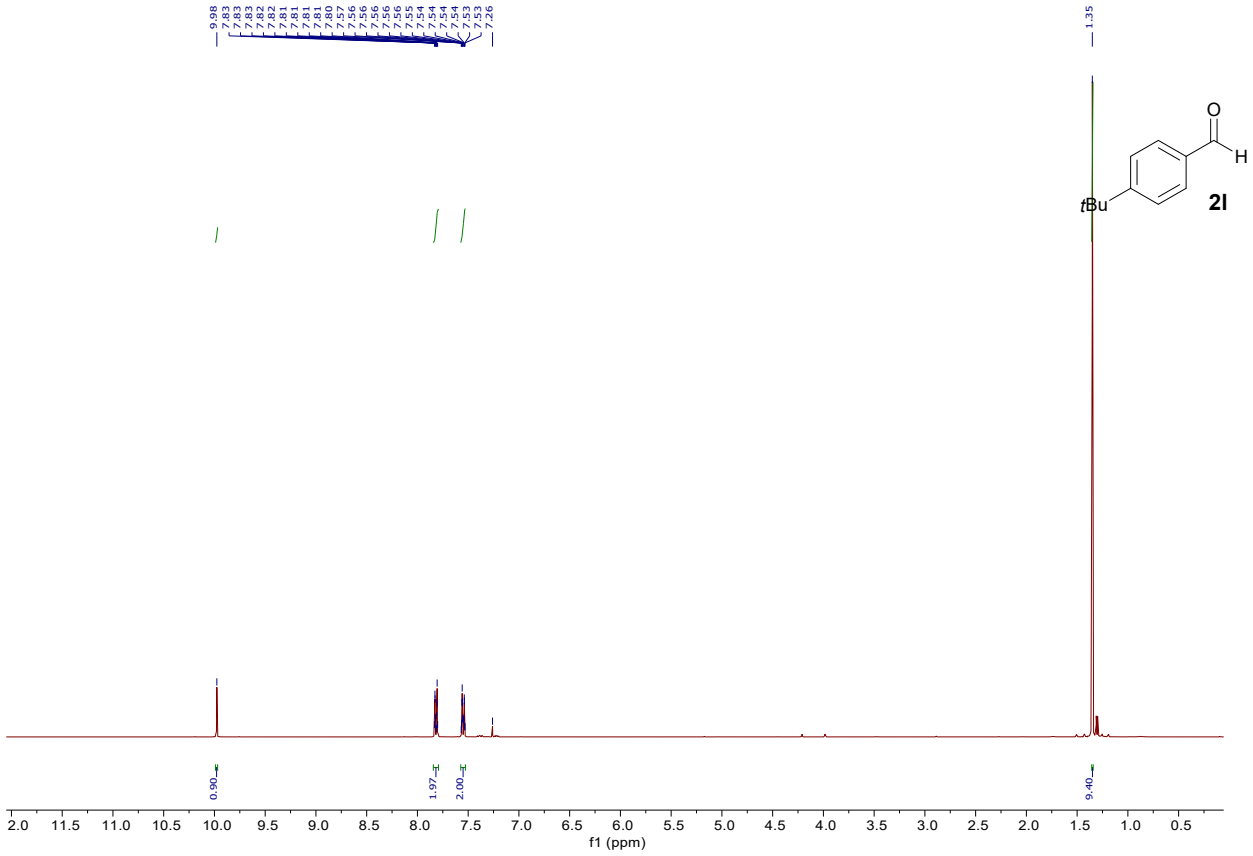

10.12
8.27
7.96
7.94
7.92
7.92
7.89
7.87
7.85
7.63
7.61
7.60
7.59
7.57
7.56
7.54
7.26 CDCl3
2.49
O
H
2i
0.97
0.99
2.04
1.97
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

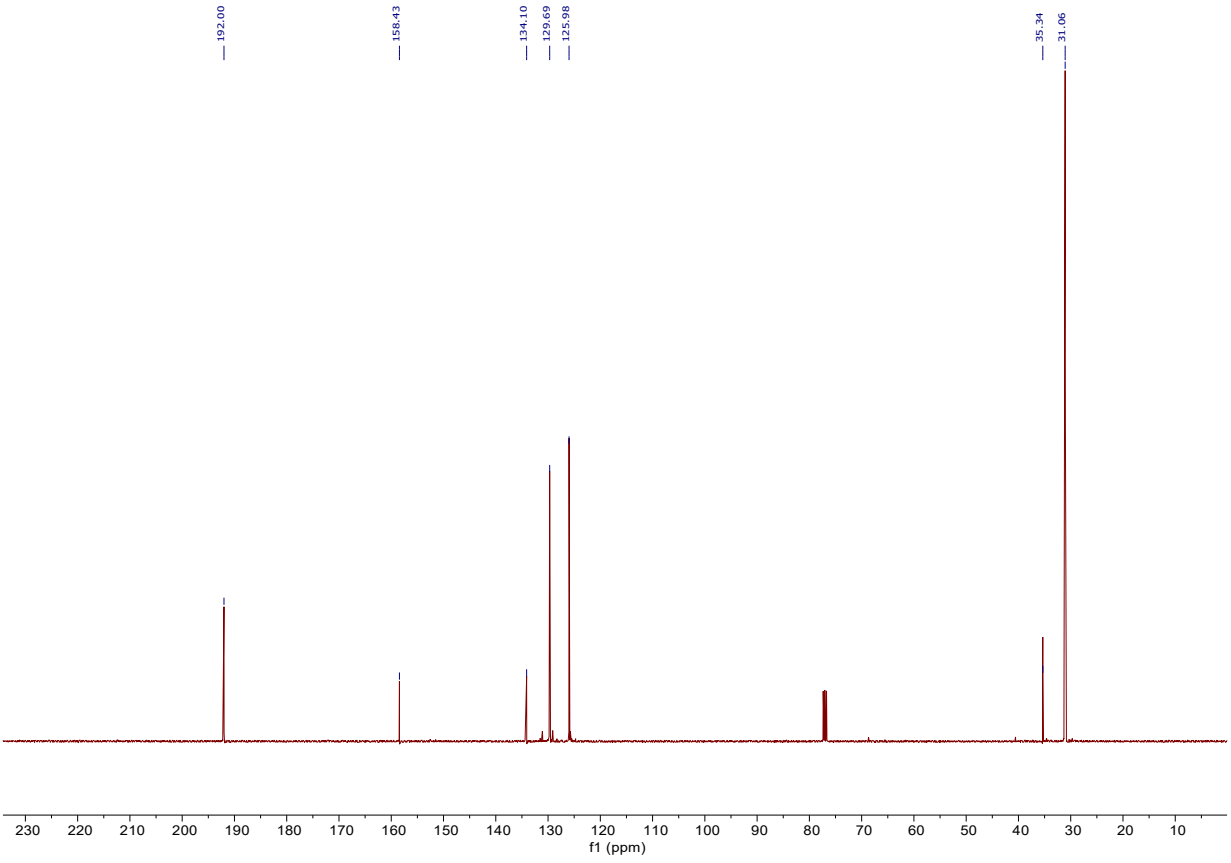

192.22
136.44
134.52
134.12
133.64
129.54
129.12
129.08
128.09
127.10
122.75
77.49 CDCl3
77.17 CDCl3
76.85 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

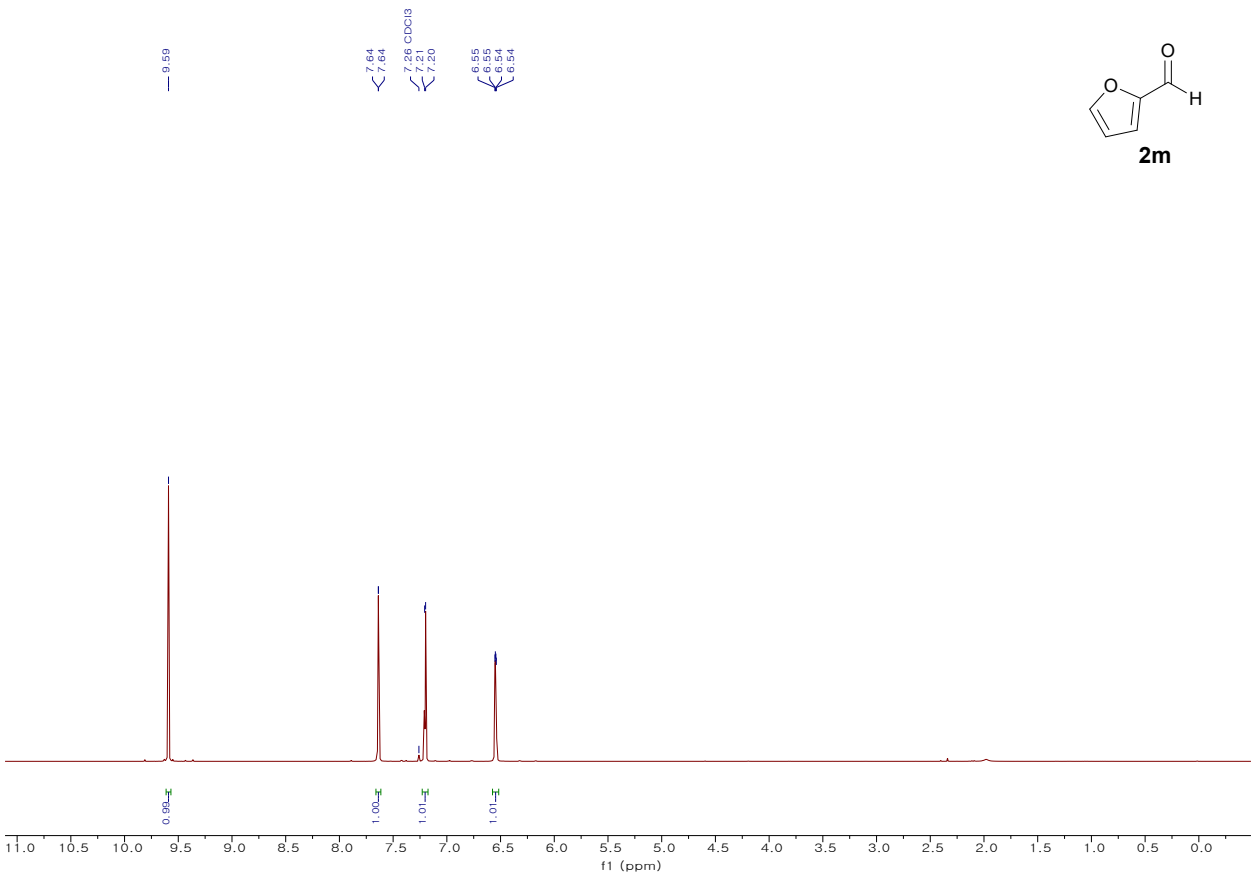

10.41
7.88
7.86
7.48
7.48
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.36
7.26
Cl
O
H
Cl
2j
1.00
1.16
1.07
1.22
f1 (ppm)
188.58
141.18
138.61
131.00
130.54
130.39
128.03
77.41
77.09
76.77
f1 (ppm)


9.94
7.95
7.95
7.73
7.72
7.71
7.70
7.64
7.62
7.26
Cl
Cl
O
H
2k
0.99
0.96
1.05
1.00
f1 (ppm)

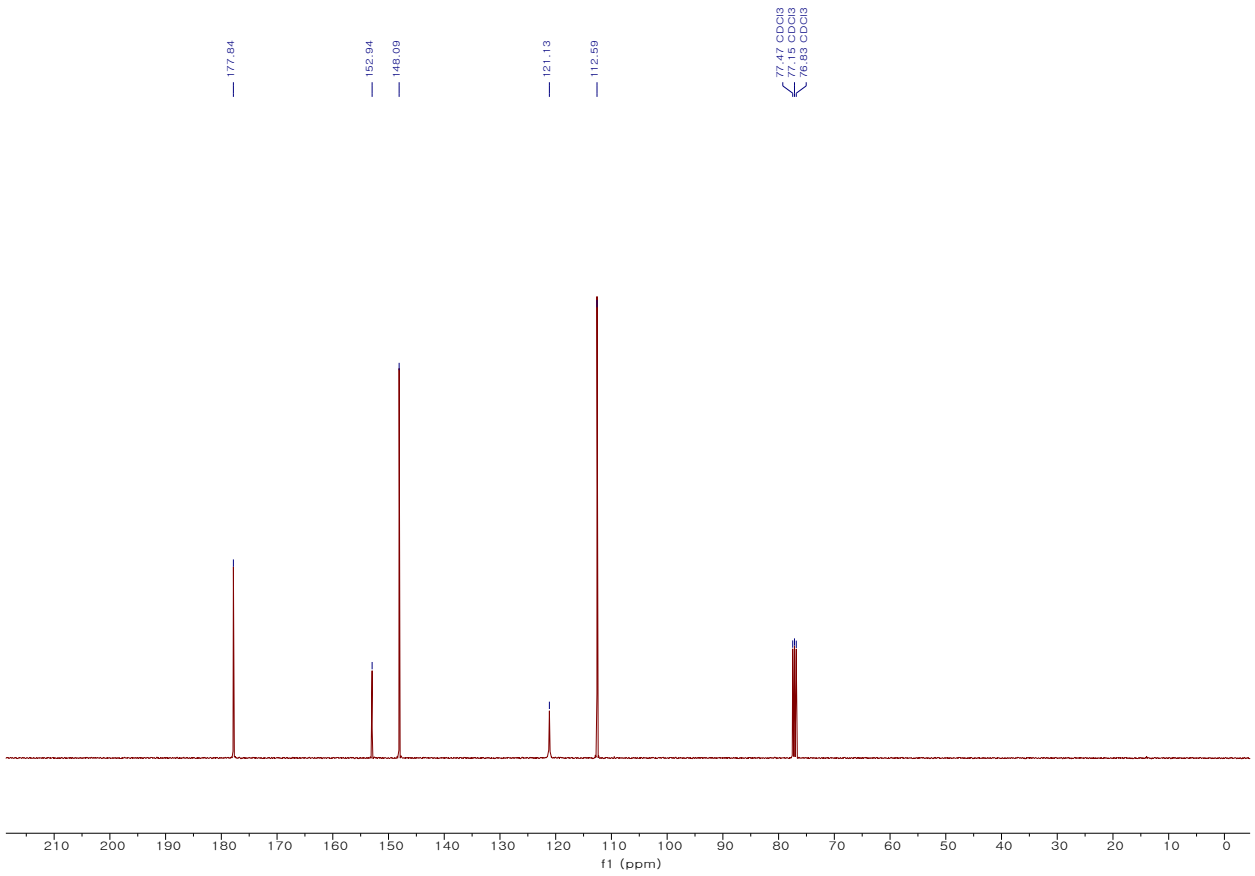

189.68
139.15
135.64
134.00
131.33
131.26
128.41
77.37
77.05
76.73
f1 (ppm)

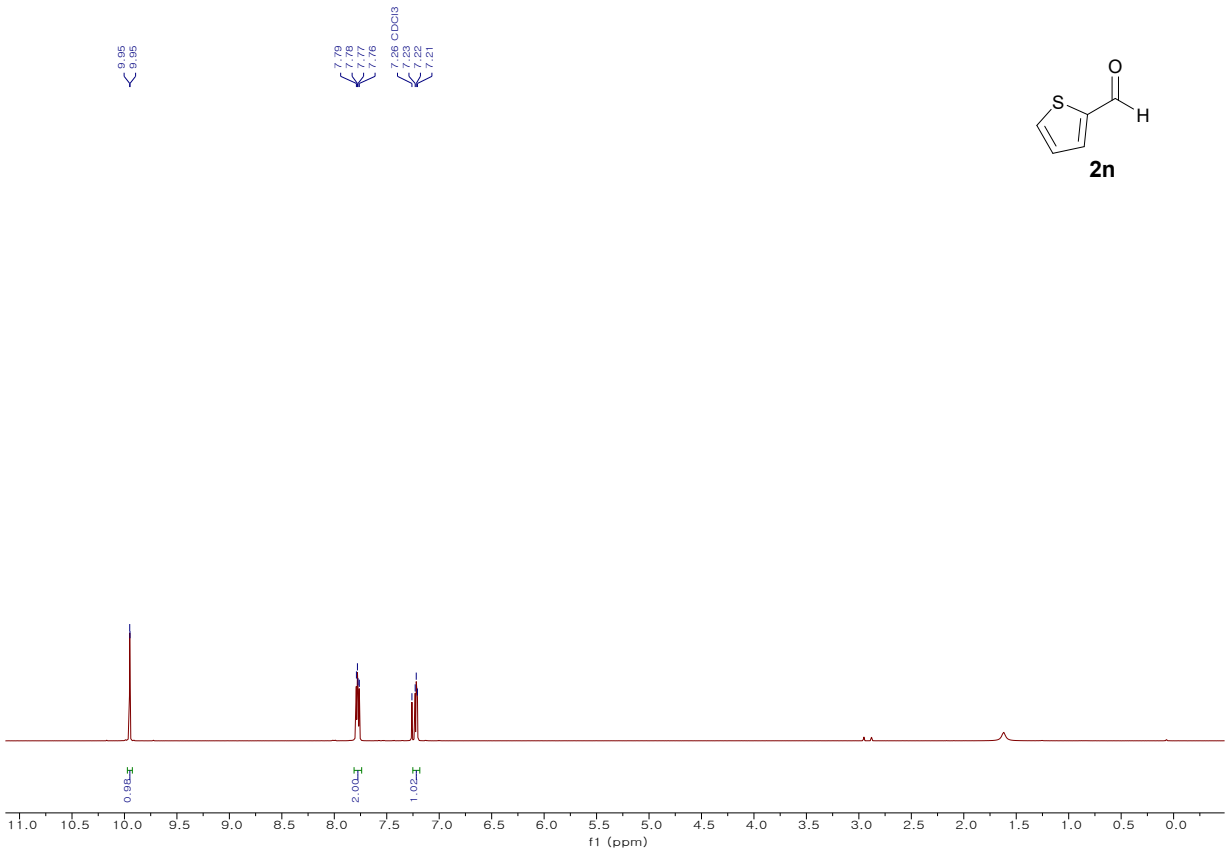

9.98
7.83
7.83
7.83
7.82
7.82
7.81
7.81
7.81
7.80
7.57
7.56
7.56
7.56
7.56
7.55
7.54
7.54
7.54
7.53
7.53
7.26
1.35
O
H
tBu
2l
0.90
1.97
2.00
9.40
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

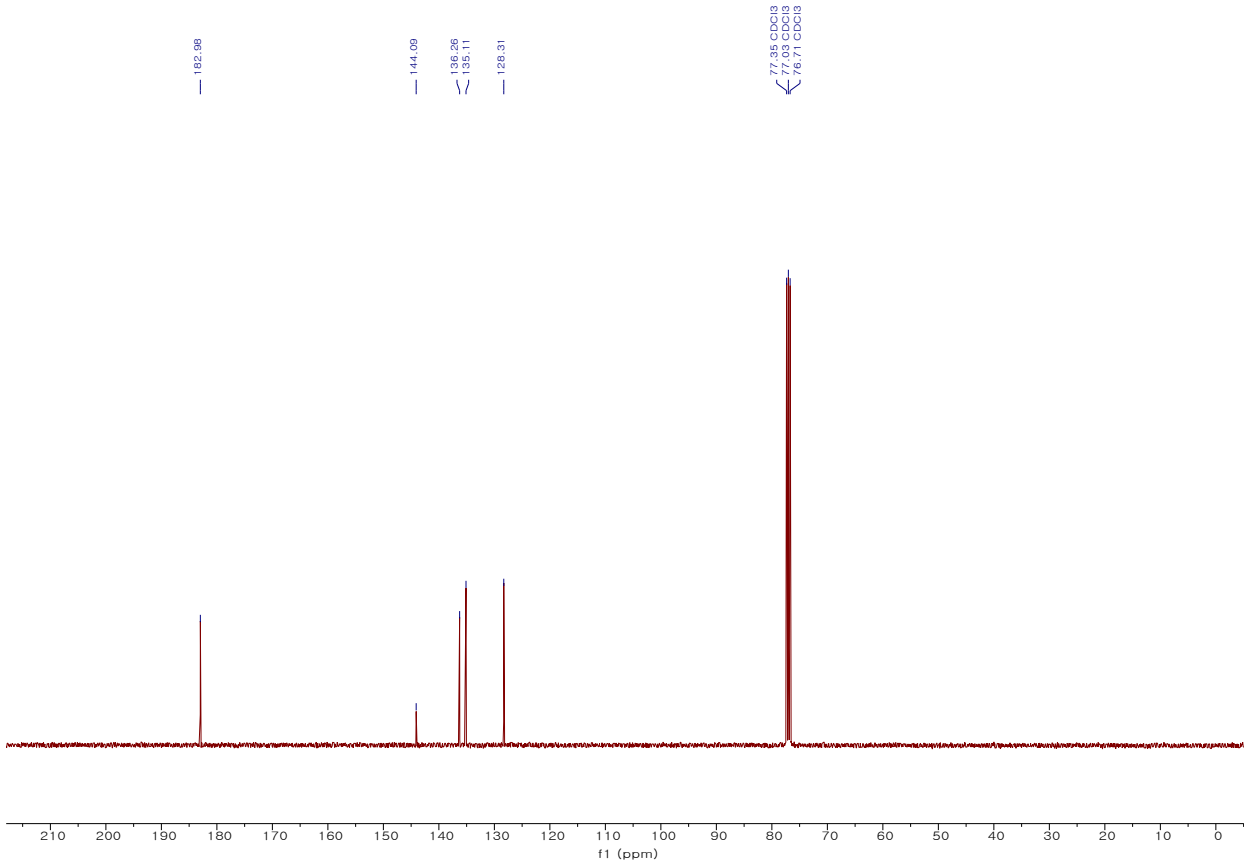

192.00
158.43
134.10
129.69
125.98
35.34
31.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

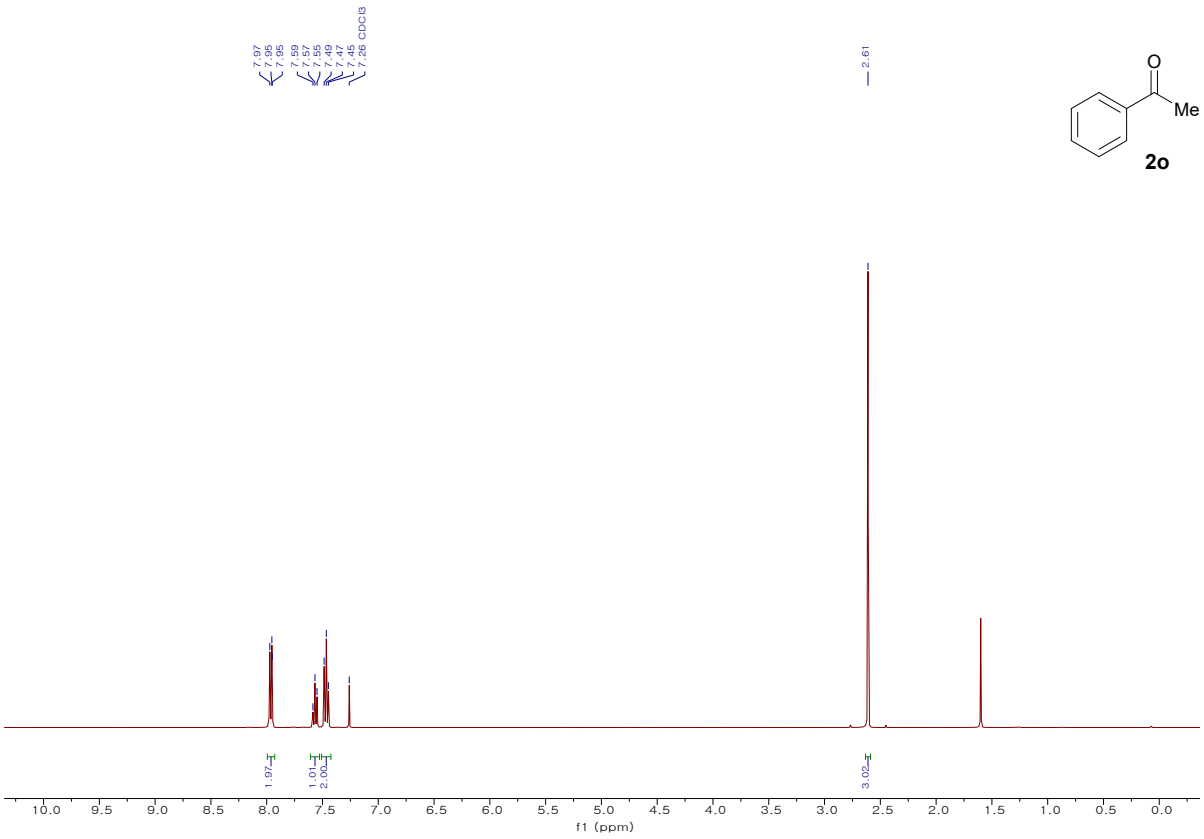

9.59
7.64
7.64
7.26 CDCl3
7.21
7.20
6.55
6.55
6.54
6.54
0.99
1.00
1.01
1.01
f1 (ppm)

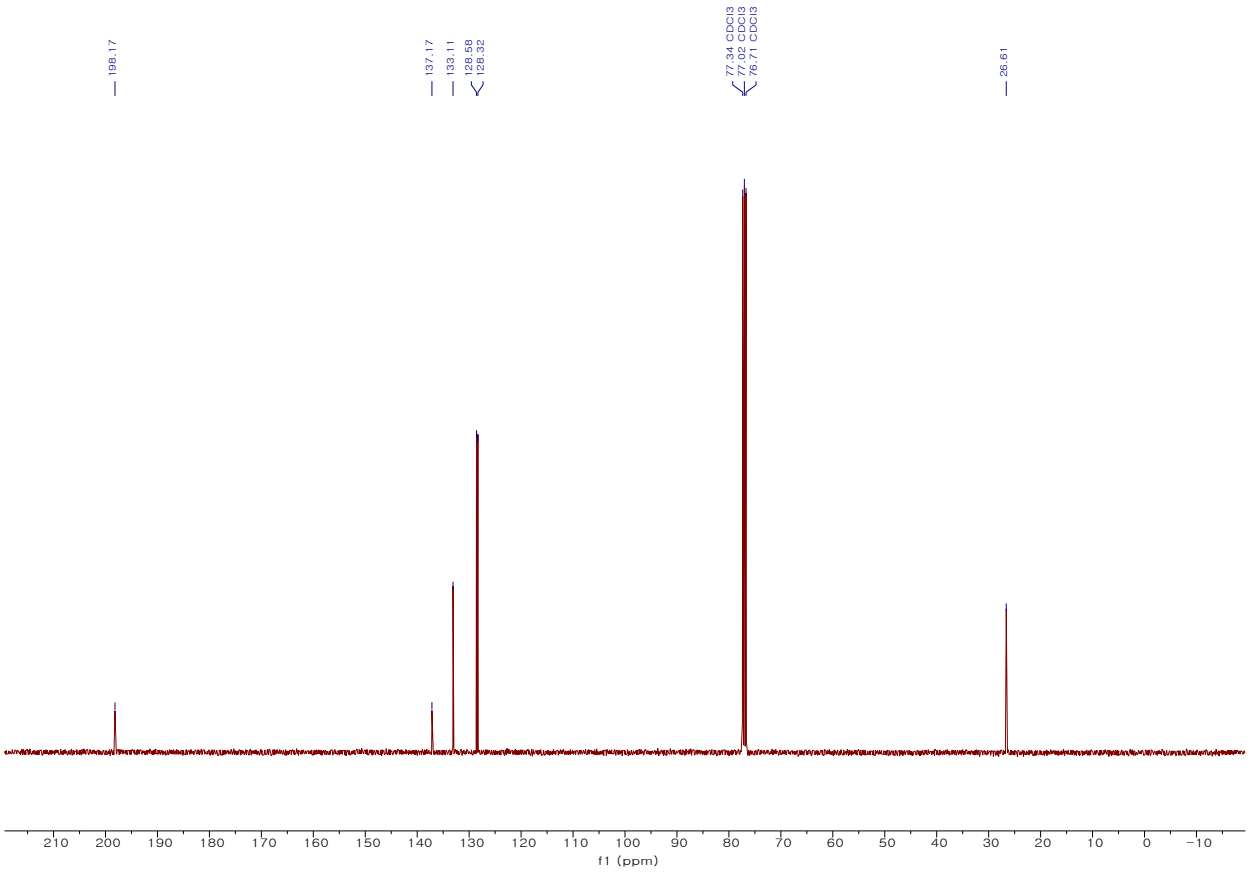
2m

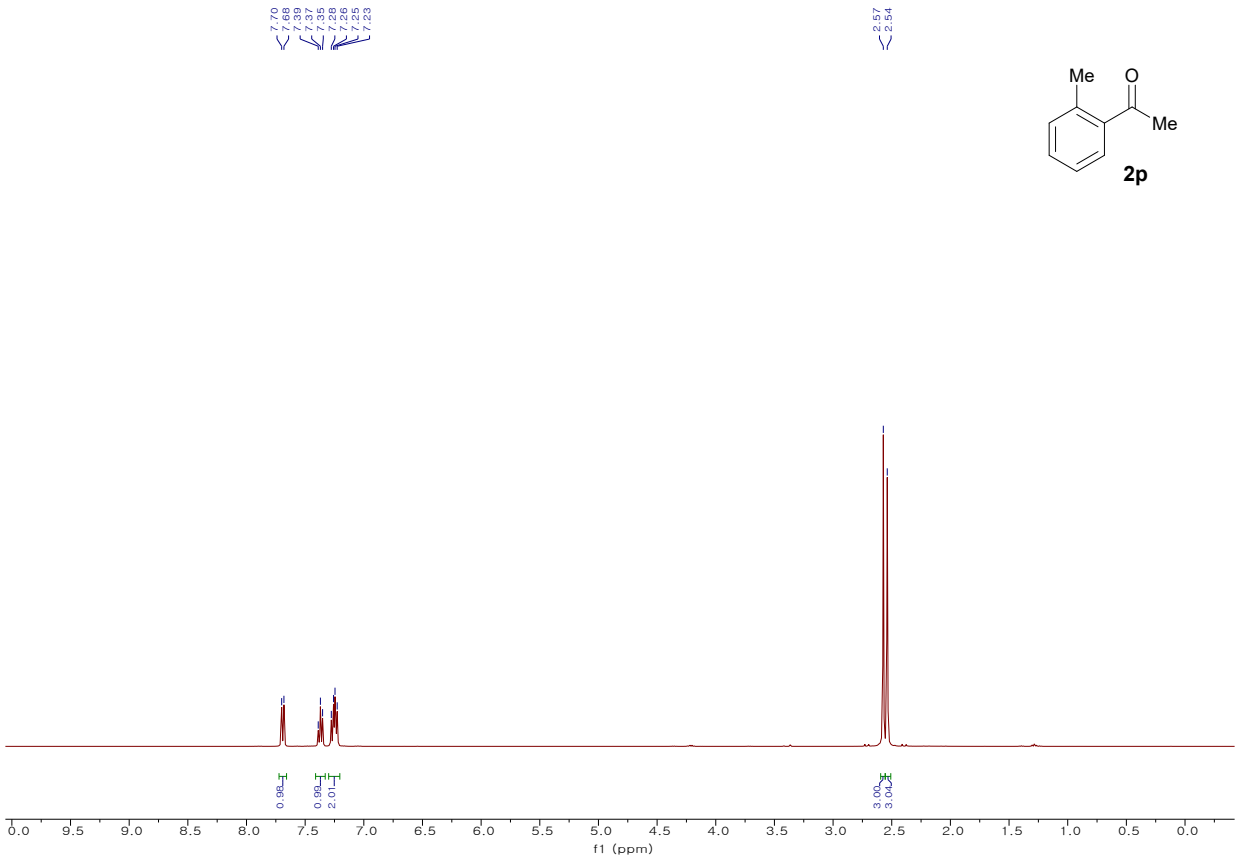

177.84
152.94
148.09
121.13
112.59
77.47 CDCl3
77.15 CDCl3
76.83 CDCl3
f1 (ppm)

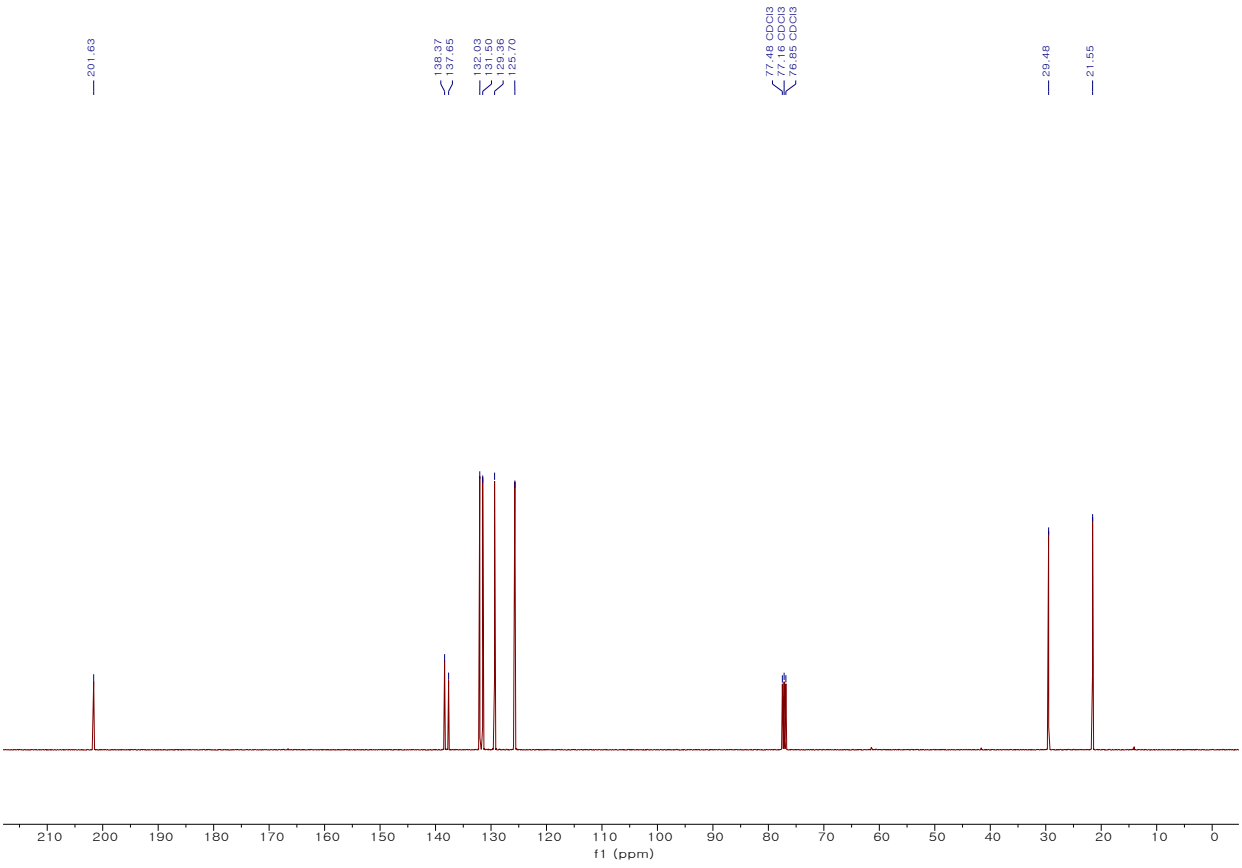

9.95
9.95
7.79
7.78
7.77
7.76
7.26 CDCl3
7.23
7.22
7.21
O
S
H
2n
0.98
2.00
1.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

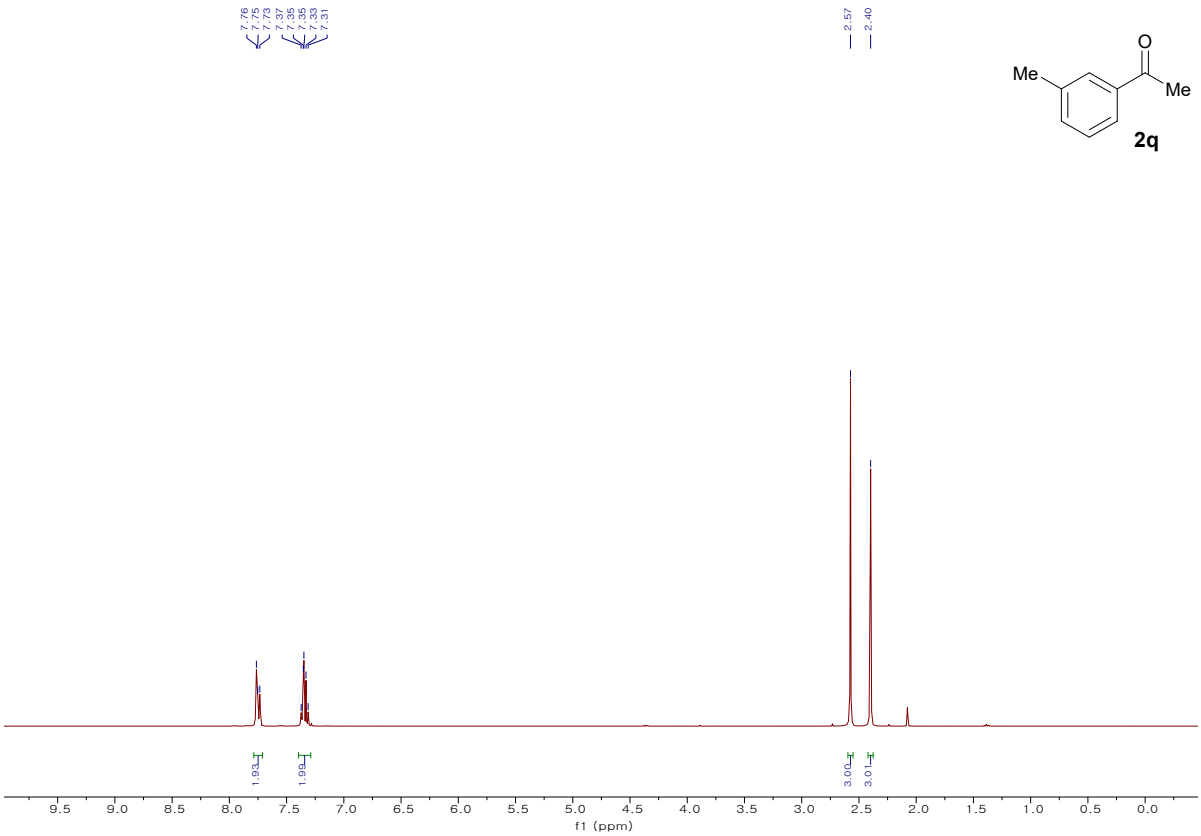

182.98
144.09
136.26
135.11
128.31
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

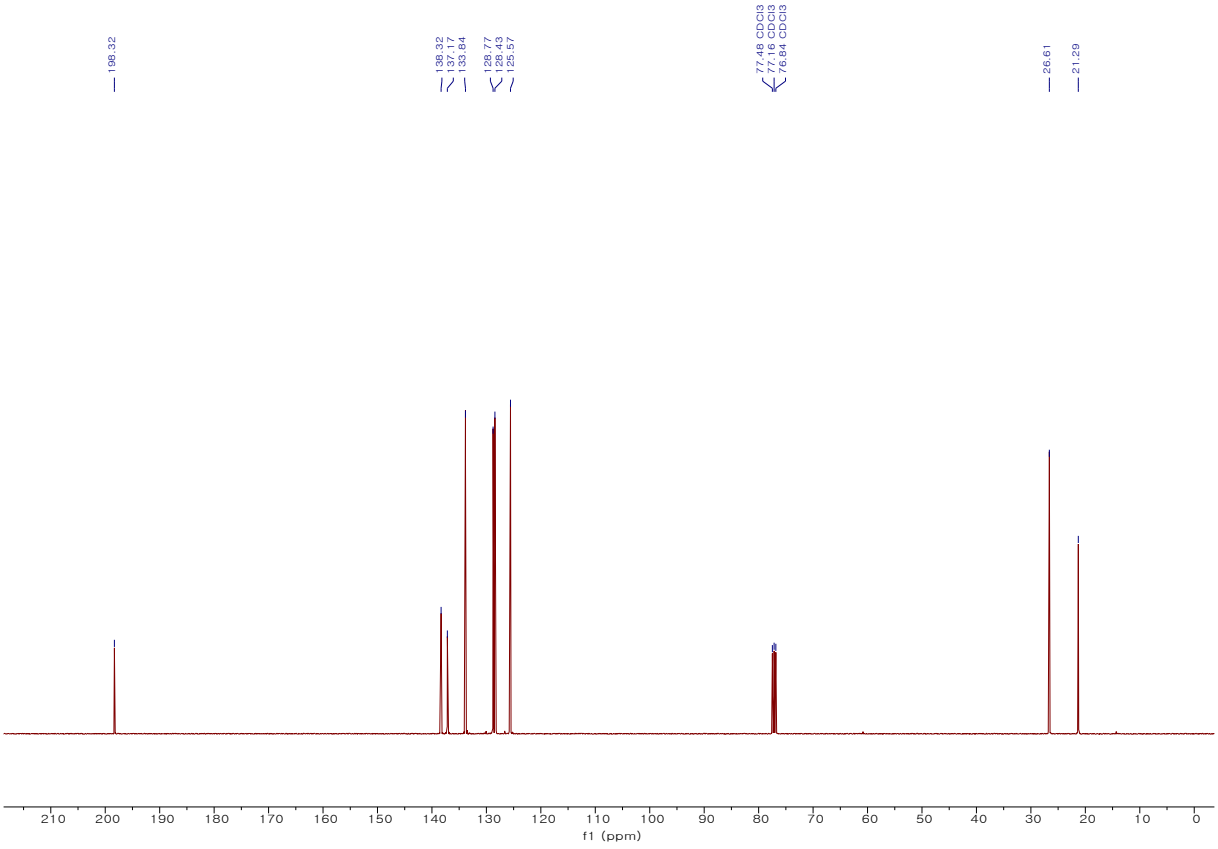

7.97
7.96
7.95
7.59
7.57
7.55
7.49
7.47
7.45
7.26 CDCl3
2.61
O
Me
2o
1.97
1.01
2.00
3.02
f1 (ppm)

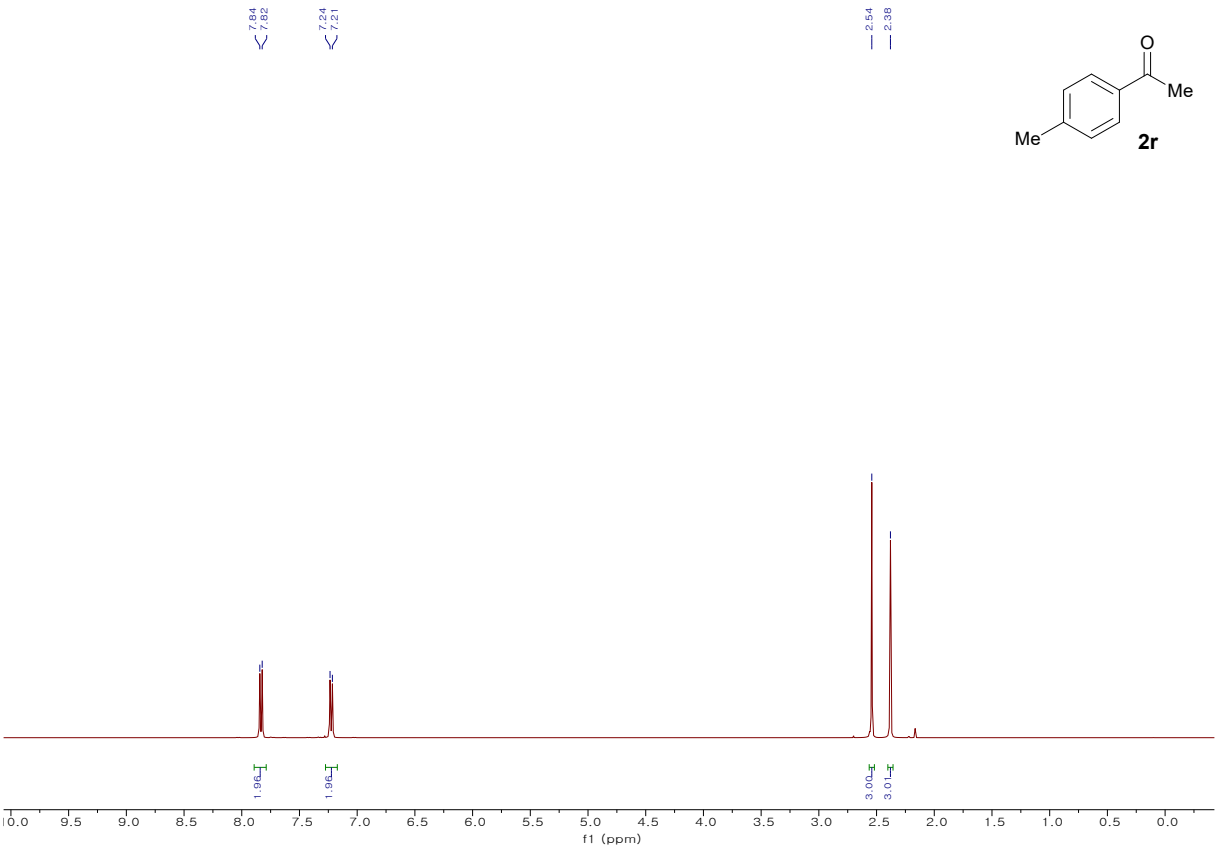

198.17
137.17
133.11
128.58
128.32
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
26.61
f1 (ppm)

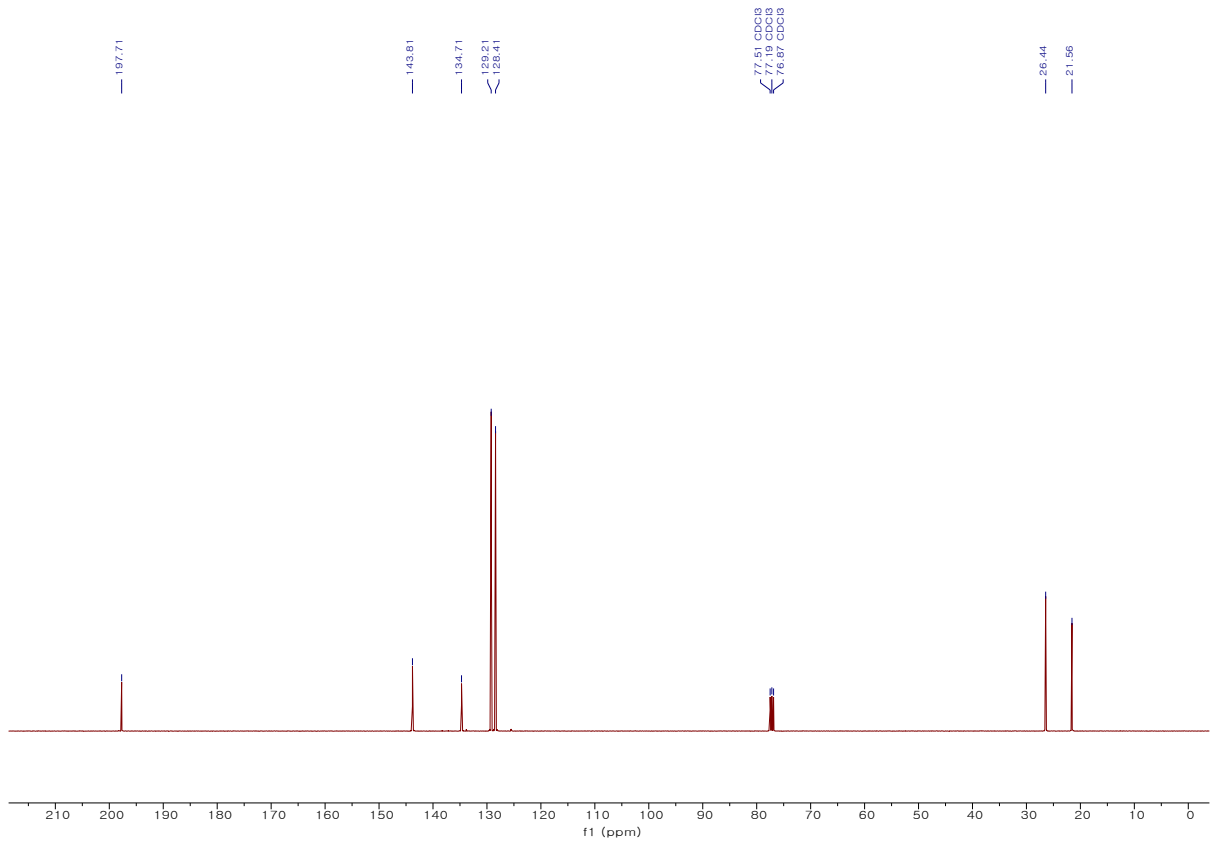

7.70
7.68
7.39
7.37
7.35
7.28
7.26
7.25
7.23
2.57
2.54
Me
O
Me
2p
0.98
0.99
2.01
3.00
3.04
f1 (ppm)

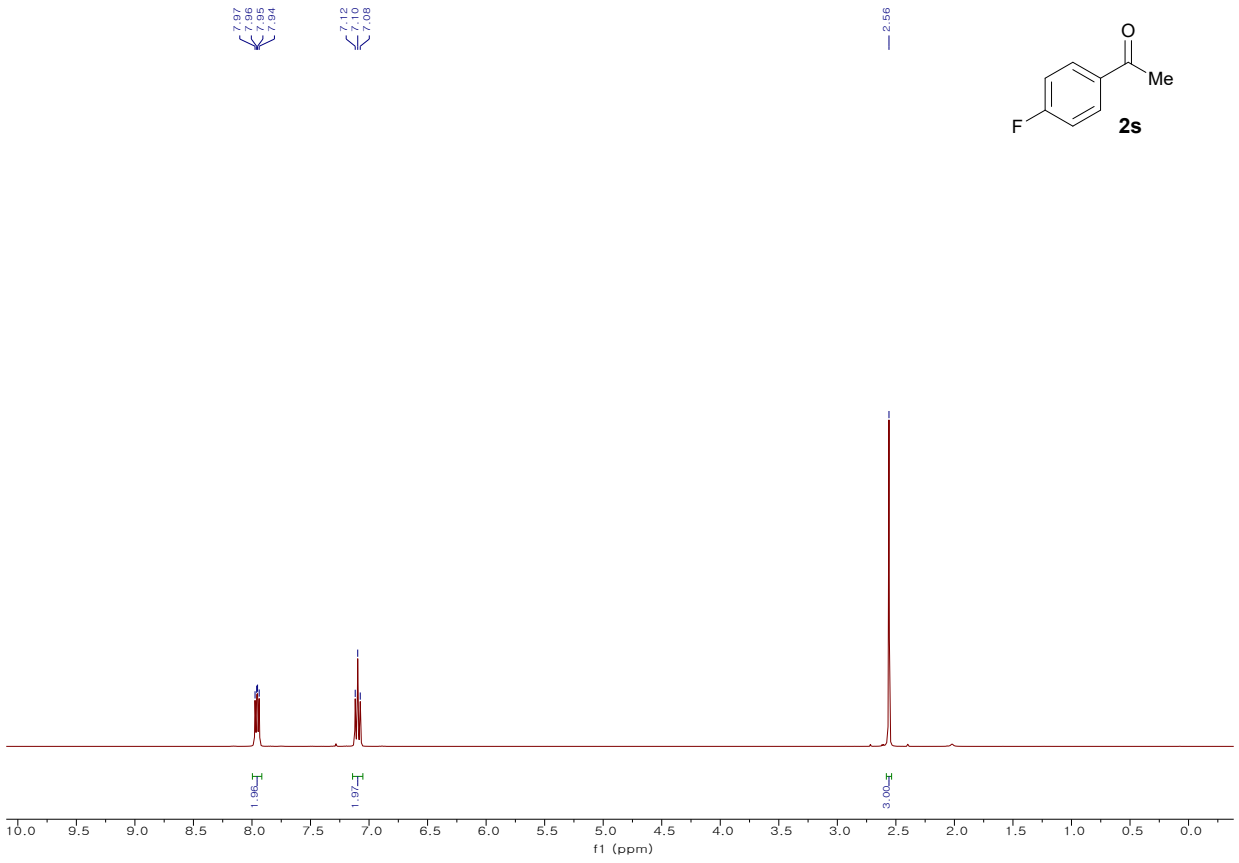

201.63
138.37
137.65
132.03
131.50
129.36
125.70
77.48 CDCl3
77.16 CDCl3
76.85 CDCl3
29.48
21.55
f1 (ppm)

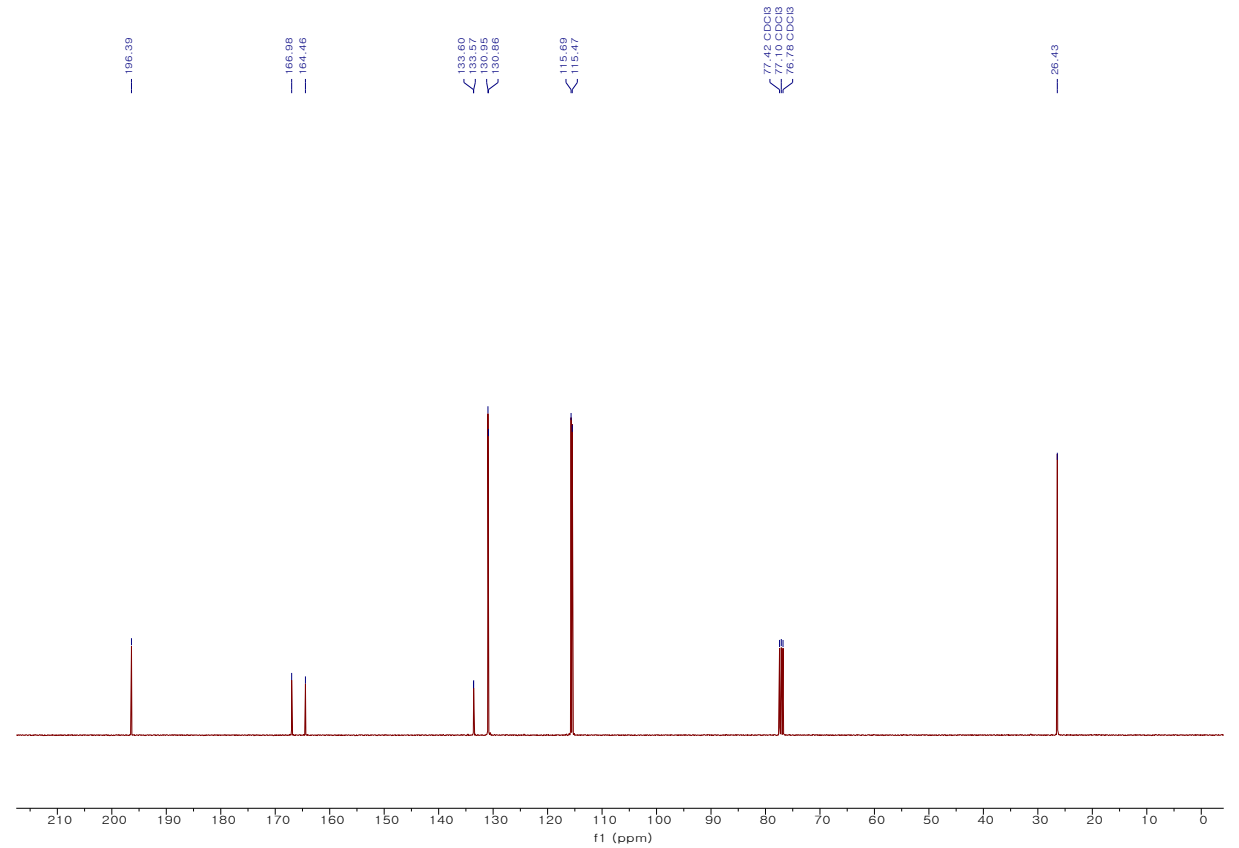

7.76
7.75
7.73
7.37
7.35
7.33
7.31
2.57
2.40
Me
Me
O
2q
1.93
1.99
3.00
3.01
f1 (ppm)

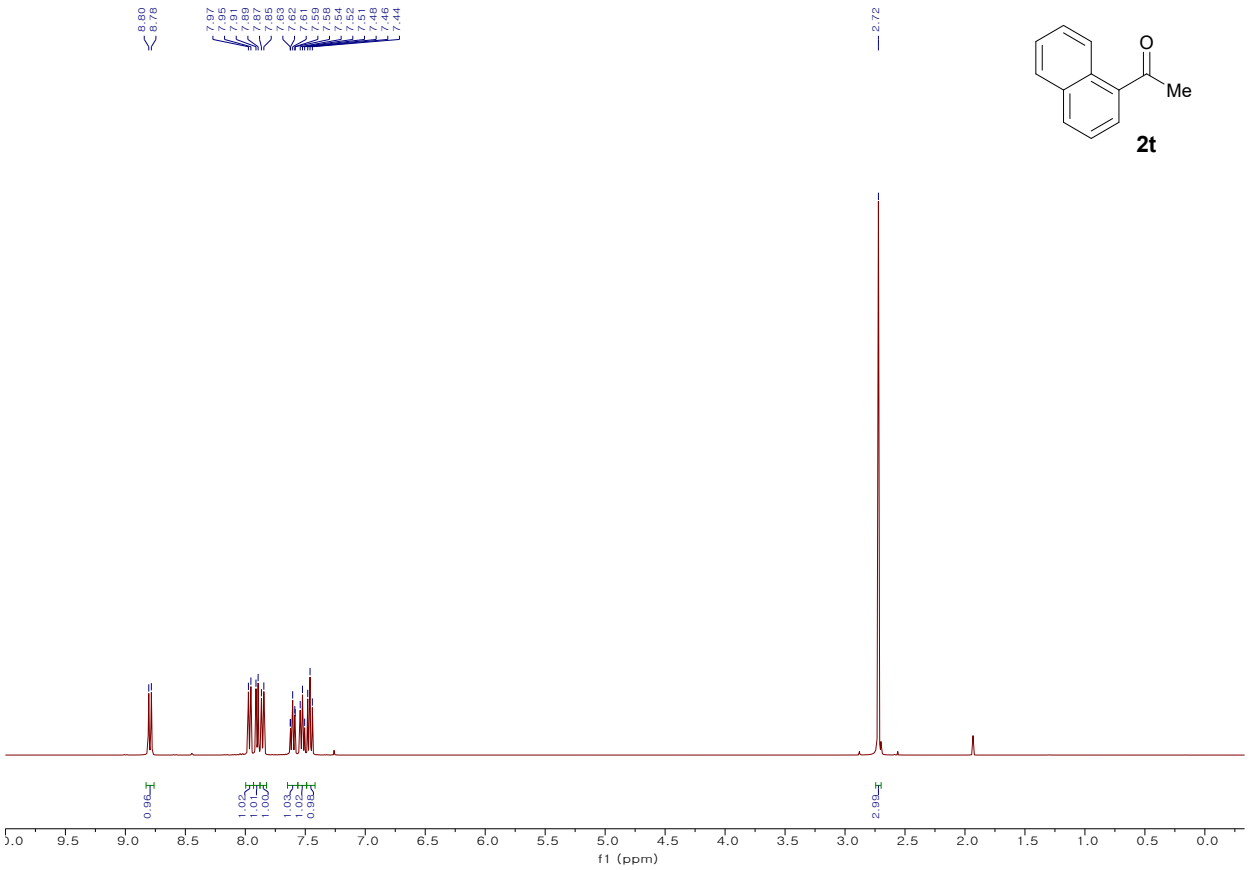

198.32
138.32
137.17
133.84
128.77
128.43
125.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
26.61
21.29
f1 (ppm)

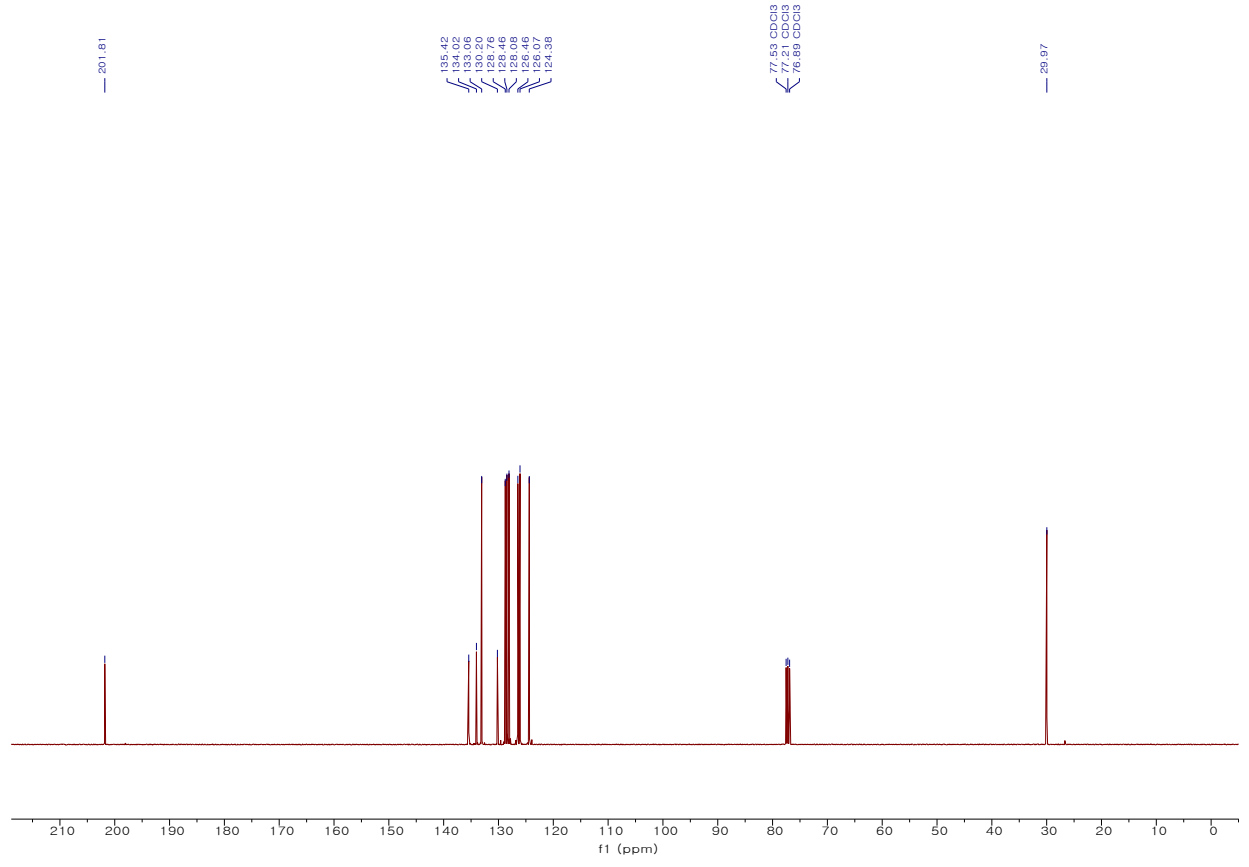

7.84
7.82
7.24
7.21
2.54
2.38
O
Me
Me
2r
1.96
1.96
3.00
3.01
f1 (ppm)

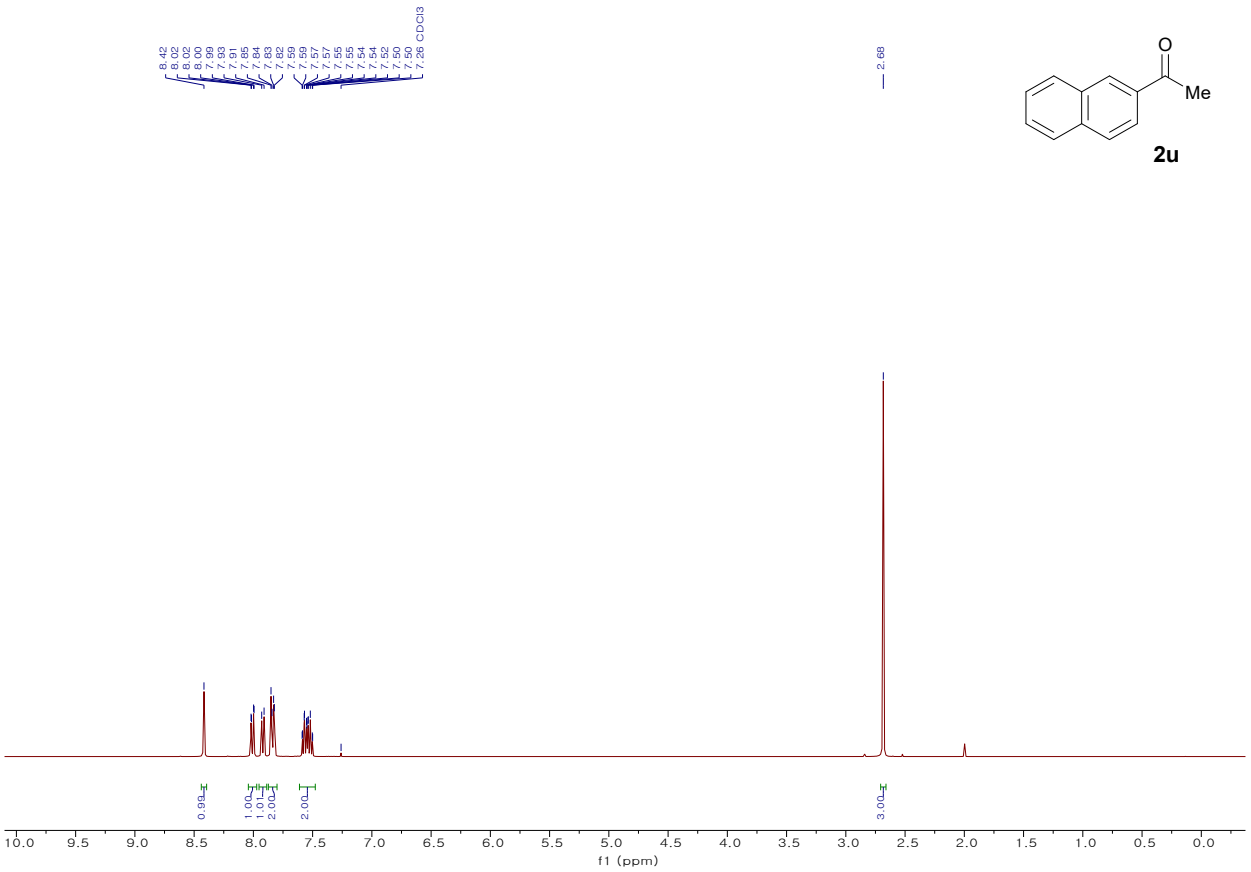

197.71
143.81
134.71
129.21
128.41
77.51 CDCl3
77.19 CDCl3
76.87 CDCl3
26.44
21.56
f1 (ppm)

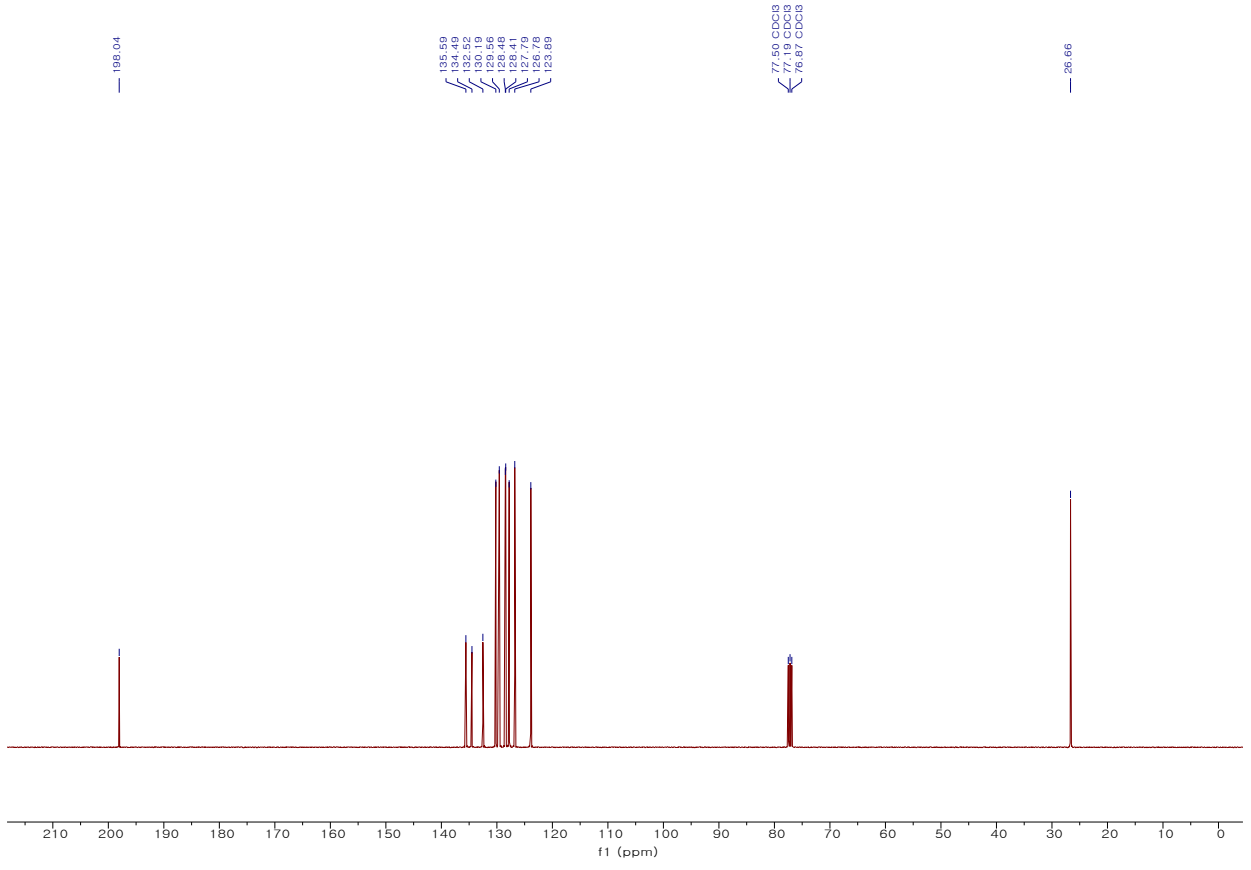

7.97
7.96
7.95
7.94
7.12
7.10
7.08
2.56
O
Me
F
2s
1.96
1.97
3.00
f1 (ppm)

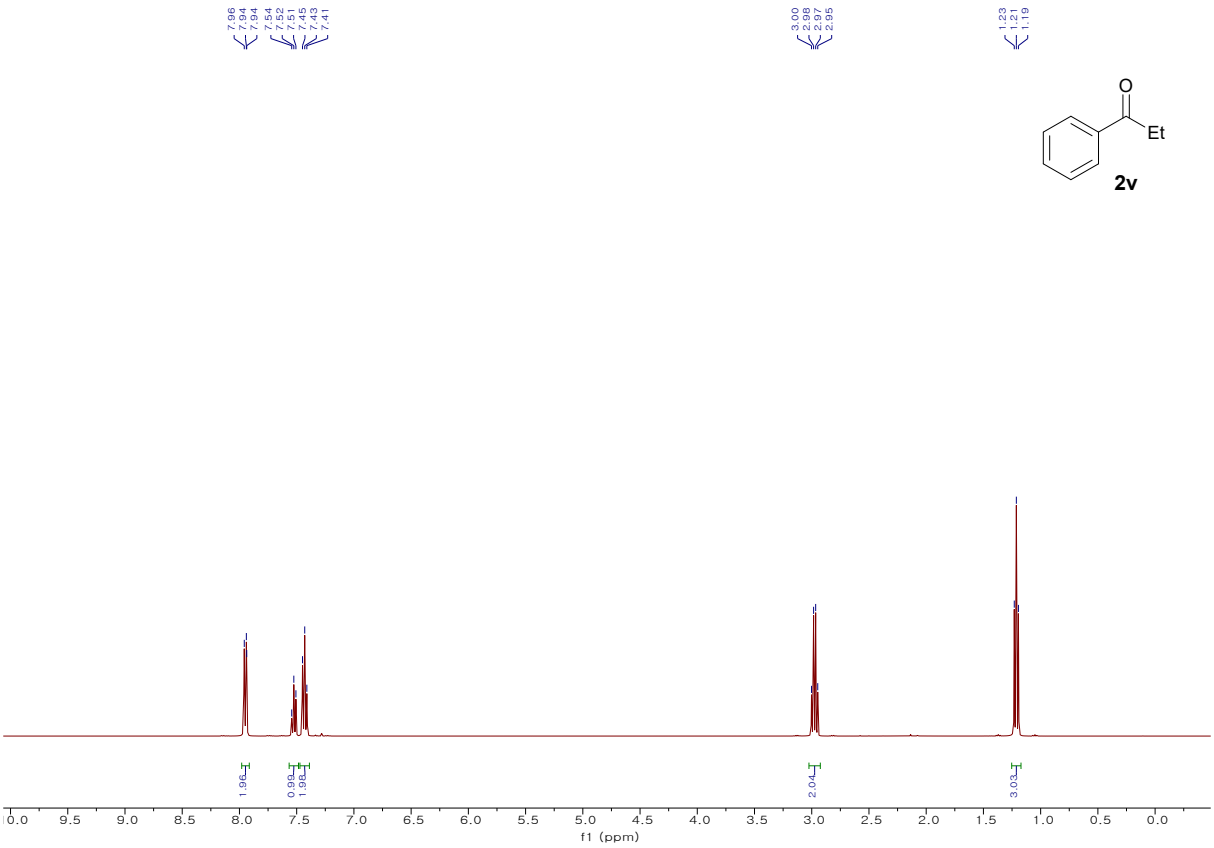

196.39
166.98
164.46
133.60
133.57
130.65
130.56
115.69
115.47
77.42 CDCl3
77.10 CDCl3
76.78 CDCl3
26.43
f1 (ppm)

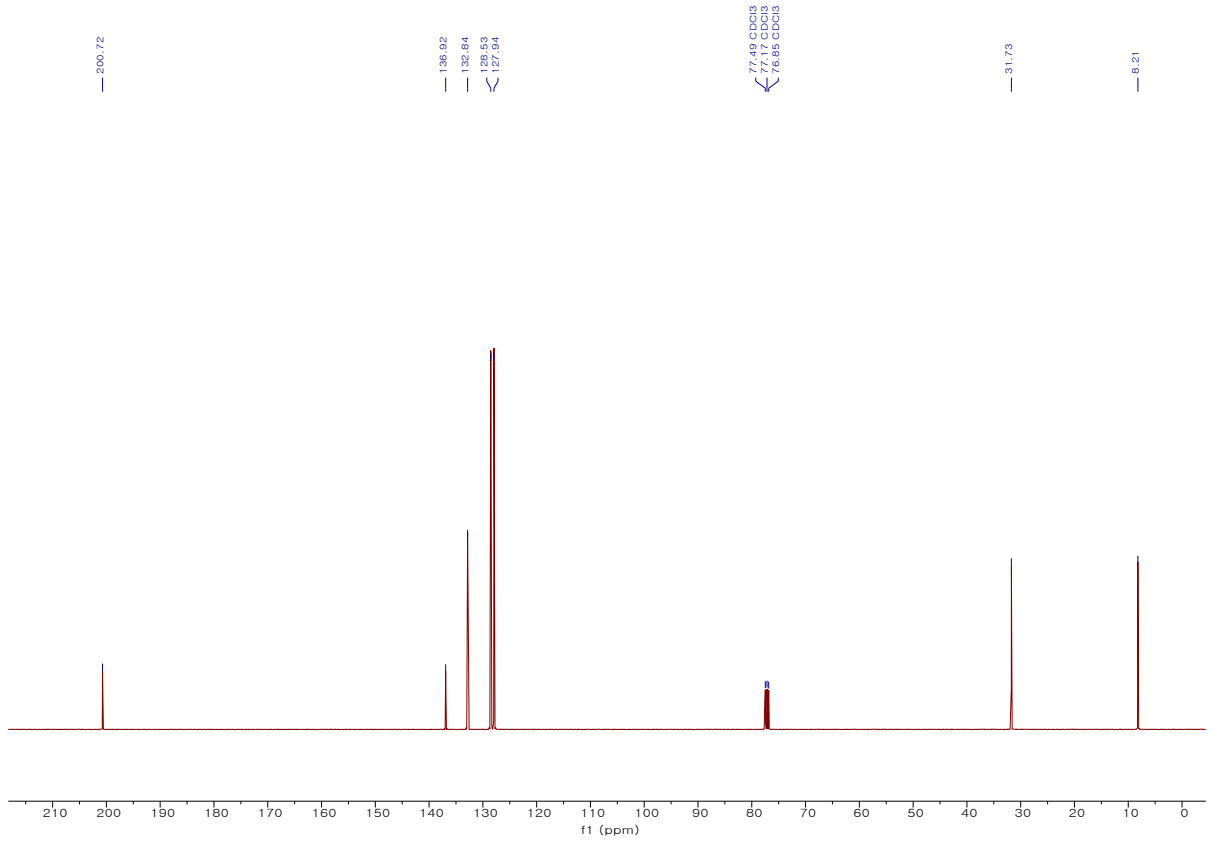

8.80
8.78
7.97
7.95
7.91
7.89
7.87
7.85
7.63
7.62
7.61
7.59
7.58
7.54
7.52
7.51
7.48
7.46
7.44
2.72
Me
O
2t
0.96
1.02
1.01
1.00
1.03
1.02
0.98
2.99
f1 (ppm)

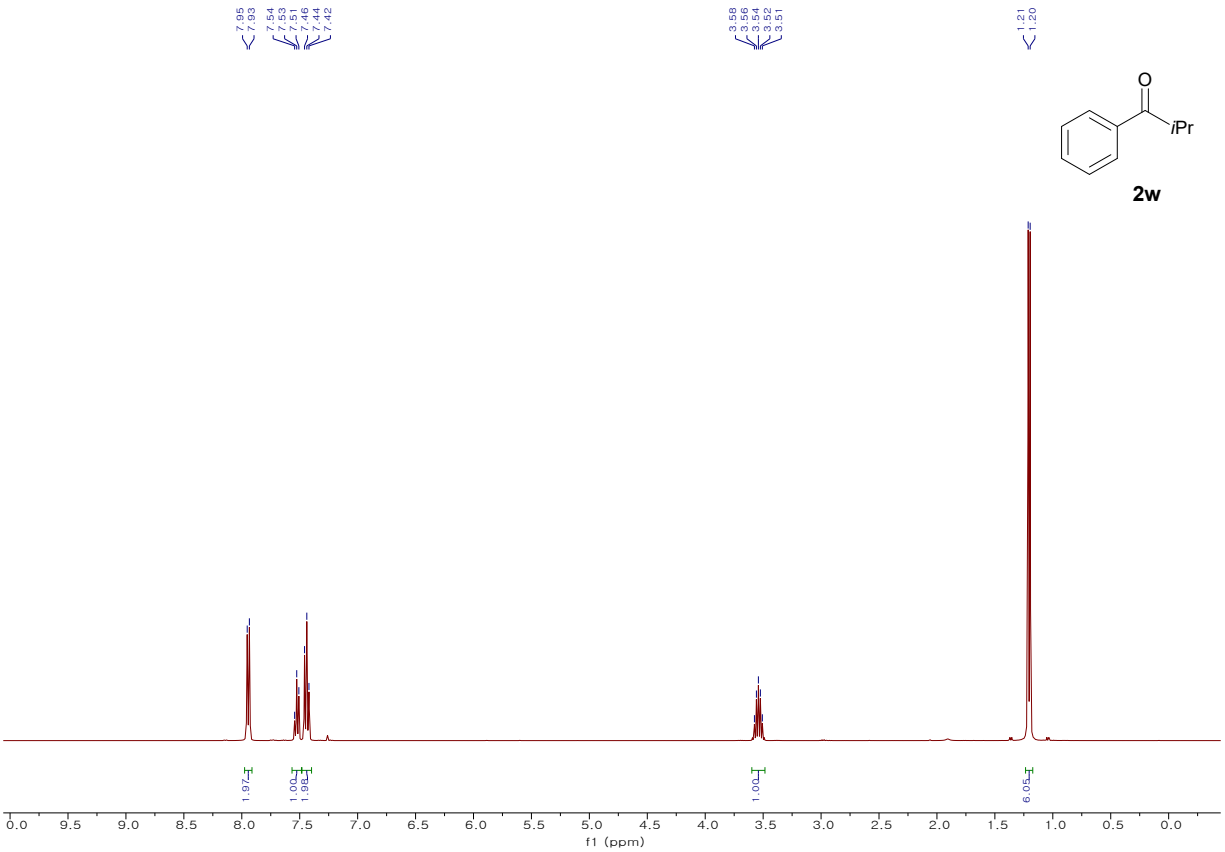

201.81
135.42
134.02
133.06
130.20
128.76
128.46
128.08
126.46
126.07
124.38
77.53 CDCl3
77.21 CDCl3
76.89 CDCl3
29.97
f1 (ppm)

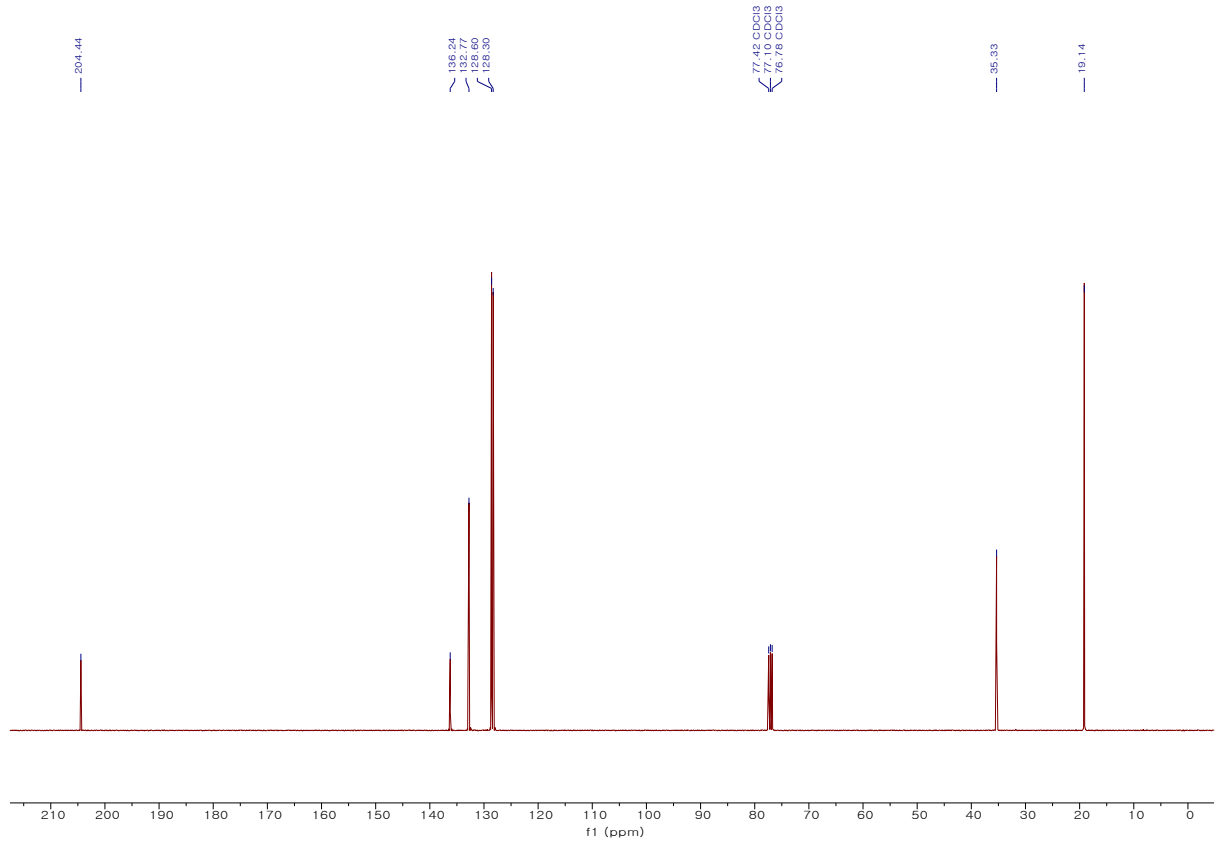

8.42
8.02
8.02
8.00
7.99
7.93
7.91
7.85
7.84
7.83
7.82
7.59
7.59
7.57
7.57
7.55
7.55
7.54
7.54
7.52
7.50
7.50
7.26 CDCl3
2.68
O
Me
2u
0.99
1.00
1.01
2.00
2.00
3.00
f1 (ppm)

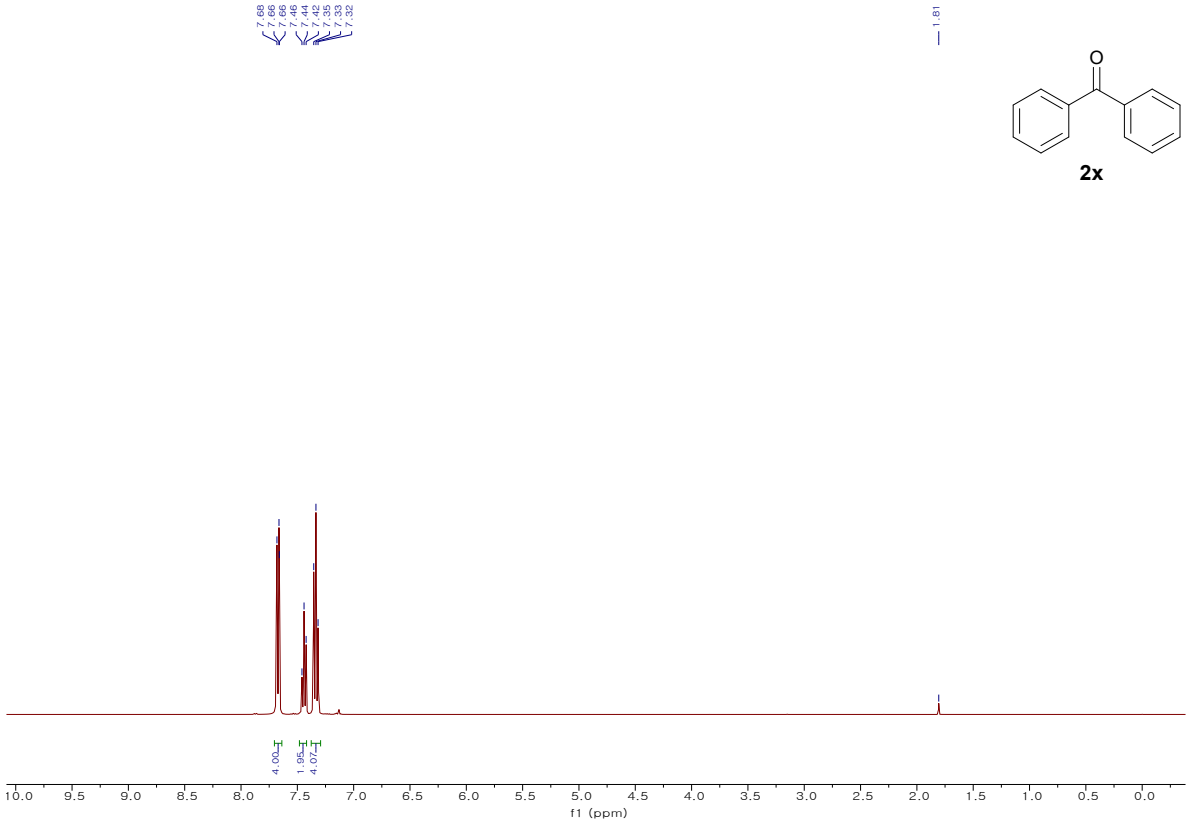

198.04
135.59
134.49
132.52
130.19
129.56
128.46
128.41
127.79
126.78
123.89
77.50 CDCl3
77.19 CDCl3
76.87 CDCl3
26.66
f1 (ppm)

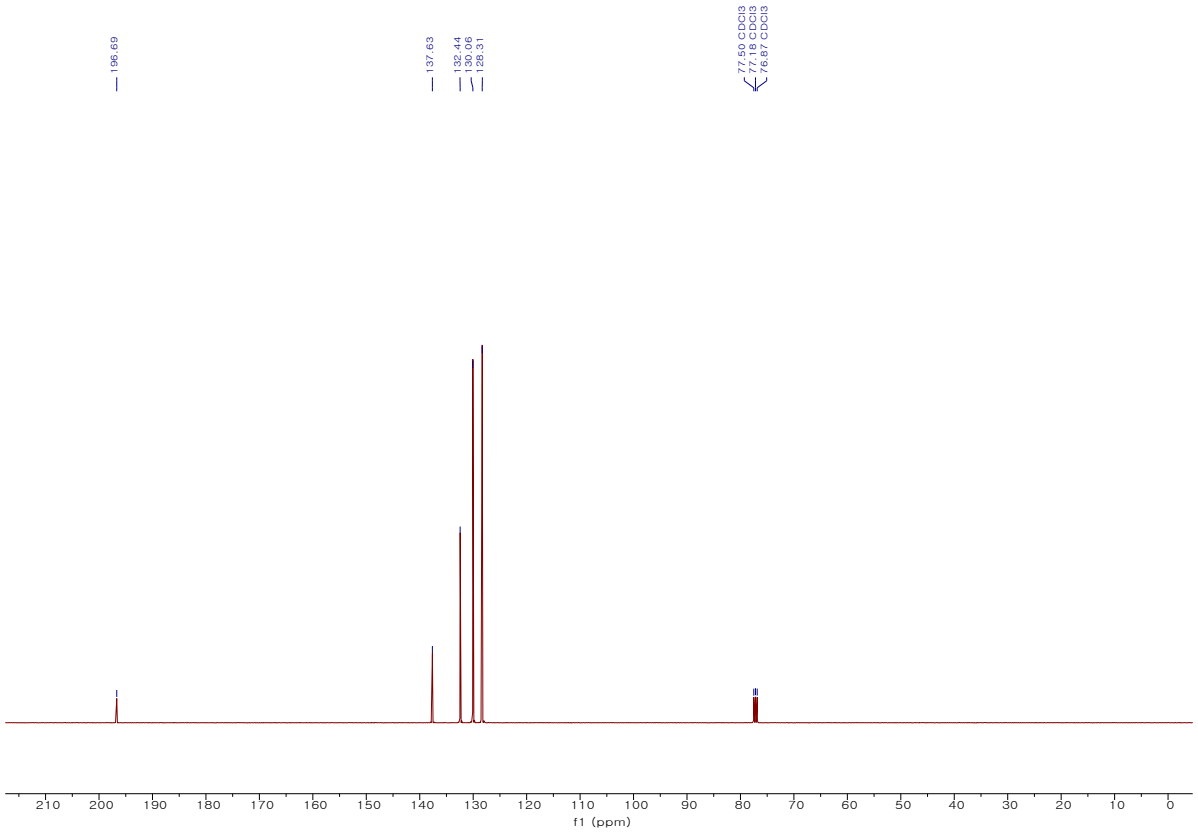

7.96
7.94
7.94
7.54
7.52
7.51
7.45
7.43
7.41
3.00
2.98
2.97
2.95
1.23
1.21
1.19
O
Et
2v
1.96
0.98
1.98
2.04
3.03
f1 (ppm)

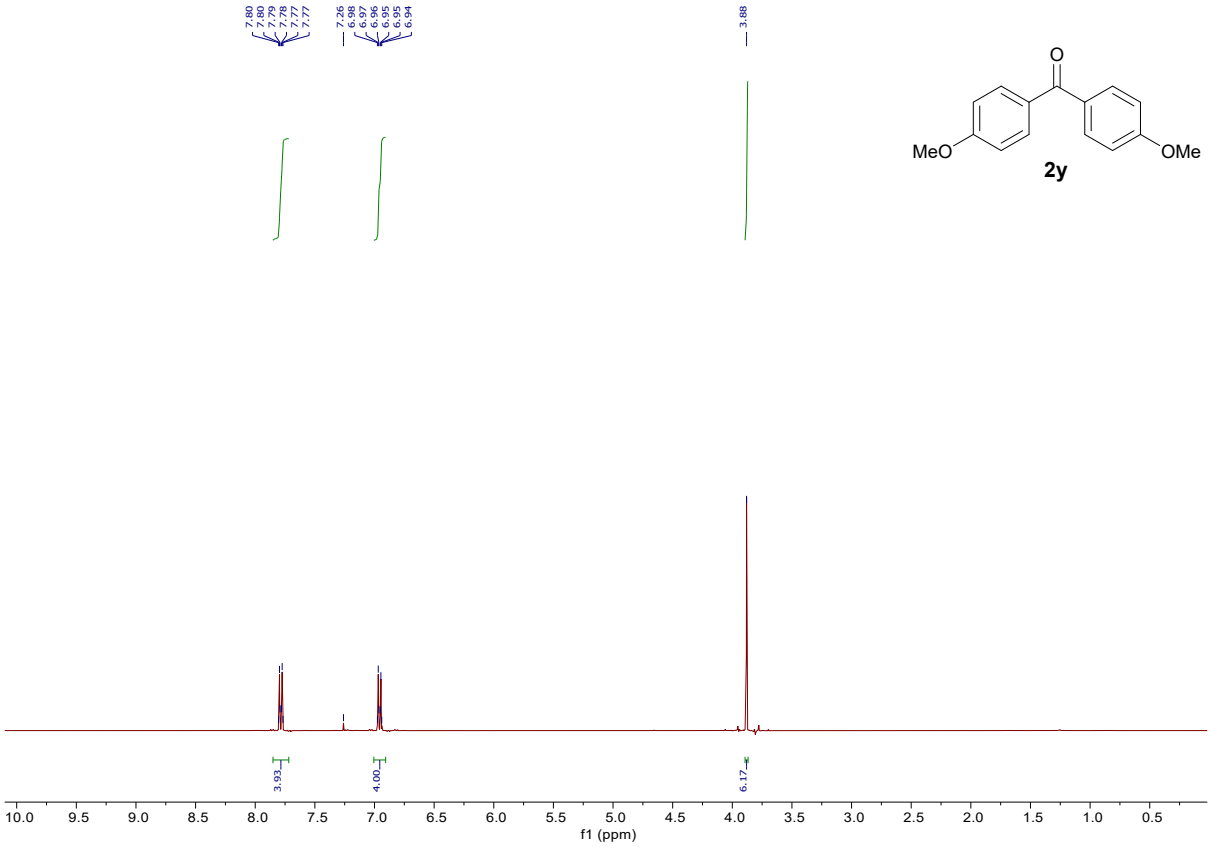

200.72
136.92
132.84
128.53
127.94
77.49 CDCl3
77.17 CDCl3
76.85 CDCl3
31.73
8.21
f1 (ppm)

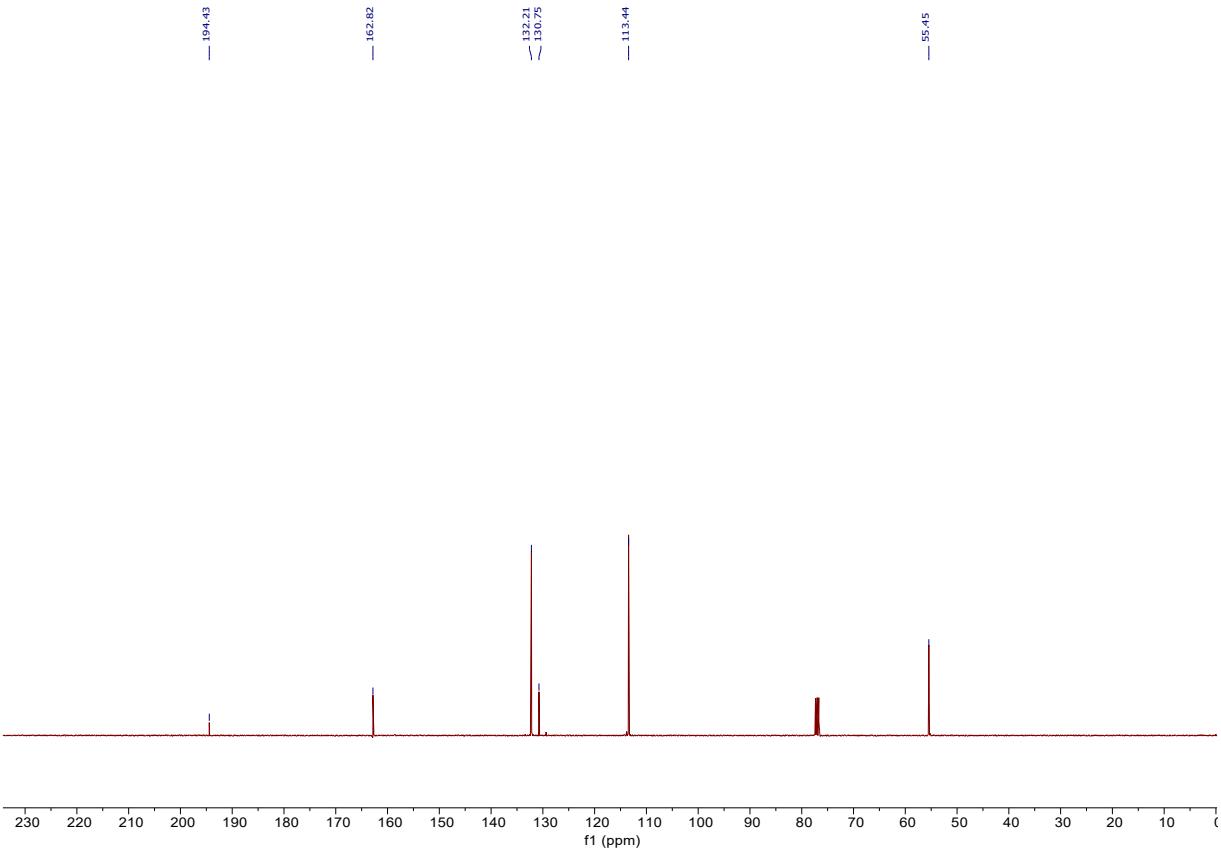

7.95
7.93
7.54
7.53
7.51
7.46
7.44
7.42
3.58
3.56
3.54
3.52
3.51
1.21
1.20
O
iPr
2w
1.97
1.00
1.98
1.00
6.05
f1 (ppm)

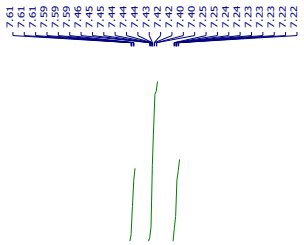

204.44
136.24
132.77
128.69
128.30
77.42 CDCl3
77.10 CDCl3
76.78 CDCl3
35.33
19.14
f1 (ppm)


7.68
7.66
7.66
7.46
7.44
7.42
7.35
7.33
7.32
1.81
O
2x
4.00
1.95
4.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.69
137.63
132.44
130.06
128.31
77.50 CDCl3
77.18 CDCl3
76.87 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.80
7.80
7.79
7.78
7.77
7.77
7.26
6.98
6.97
6.96
6.95
6.95
6.94
3.88
O
MeO
OMe
2y
3.93
4.00
6.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


194.43
162.82
132.21
130.75
113.44
55.45
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.61
7.61
7.61
7.59
7.59
7.59
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.42
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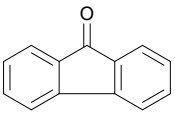
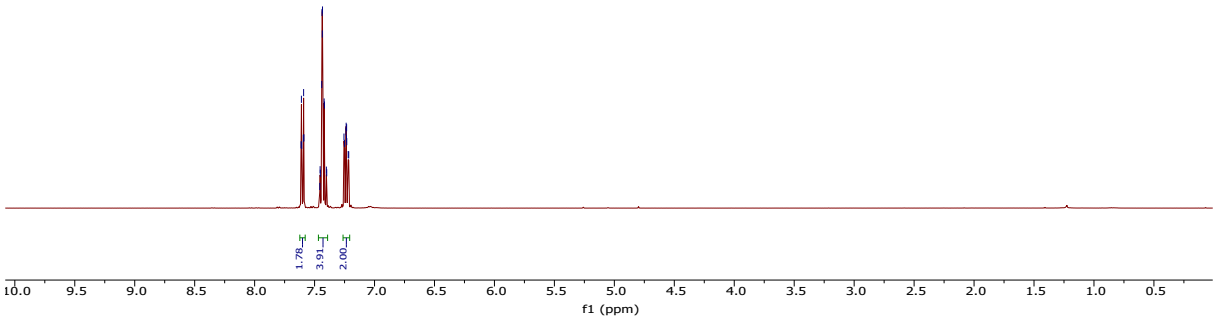
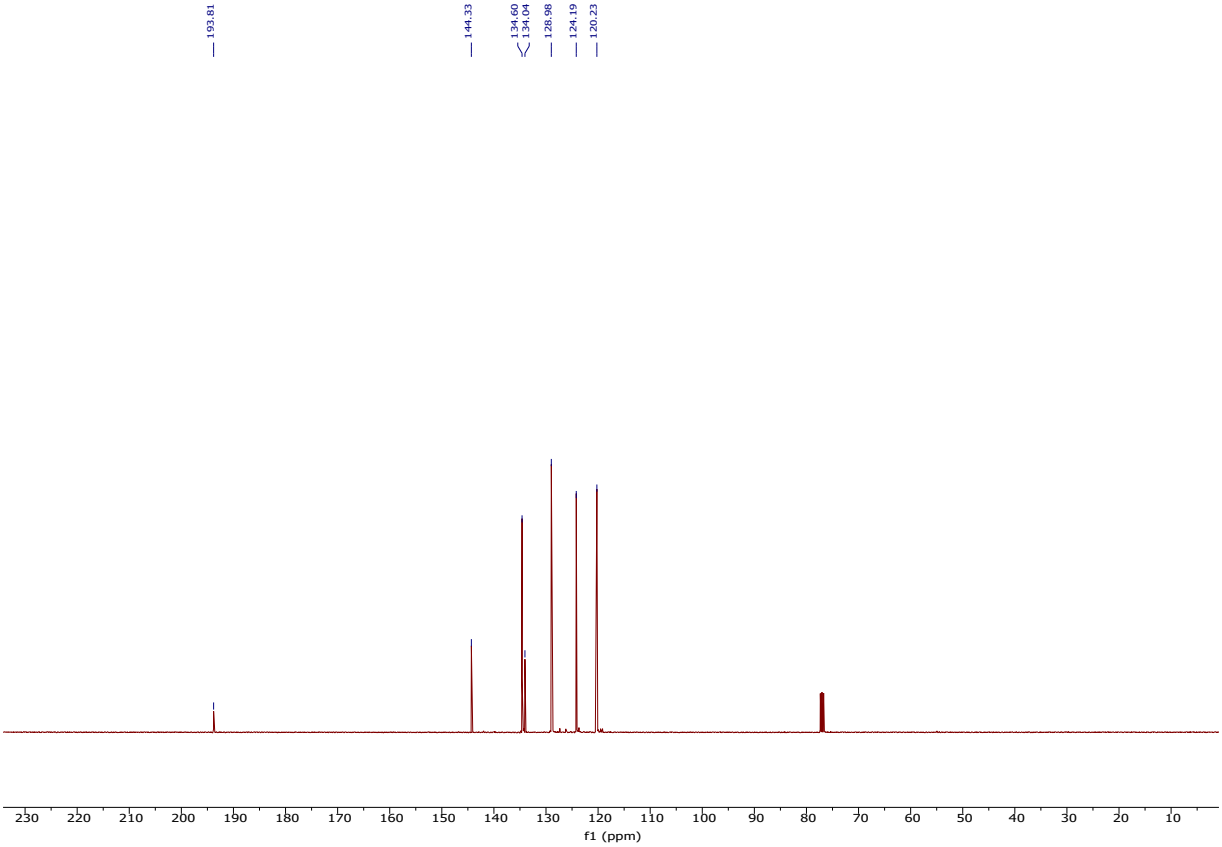
7.24
7.23
7.23
7.23
7.22
7.22


O

2z


1.78
3.91
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


193.81
144.33
134.60
134.04
128.98
124.19
120.23
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)