Electronic Supplementary Information

Deconstruction of Electron-Deficient Alkenes to Carbonyl Constituents by Light-Induced Hydrogen Atom Transfer

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1. General Information

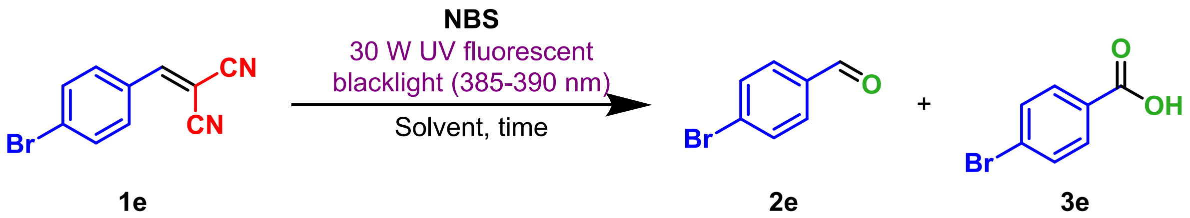
The analytical grade solvents and commercially available reagents were purchased from SDFCL, AVARICE, Fisher Scientific, MERCK, THOMAS BAKER, Spectrochem, AVRA, and LOBA Chemie. All the purchased reagents were used without further purification. Non-commercially available starting materials were synthesized by known literature procedures and their physical and spectroscopic data were compared with the reported values. Progress of the reactions was measured by thin-layer chromatography (TLC) on pre-coated aluminium backed plates. Purification of the derivatives was done by column chromatography on Silica gel (100-200 mess sizes well as 200-400 mess size). NMR spectra were acquired on a BRUKER 500 MHZ and JOEL 500 MHZ spectrometer for ^{1}H and ^{13}C respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR/ DMSO-d_6: 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR). ^{13}C NMR spectra were acquired on a broadband decoupled mode. The following abbreviations are used to describe peak patterns: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septuplet), m (multiplet), dd (doublet of doublet) br s (broad singlet). High-Resolution Mass Spectra (HRMS) were acquired on a spectrometer Bruker microTOF-Q II using electrospray (TOF-ESI+) technique and making use of the mass-works software compass data-analysis 4.0 for the formula identification. Obtained data are expressed in mass/charge (m/z) units.

Theoretical computations

All the computational calculations were executed with the help of the Orca 4.2.1 program package. Stability of the intermediates, possible interaction in the transition states, ground state geometries and electronic properties were optimized under vacuum condition by using B3LYP functional and 6-31G(d,p) basis set.

2. Experiments

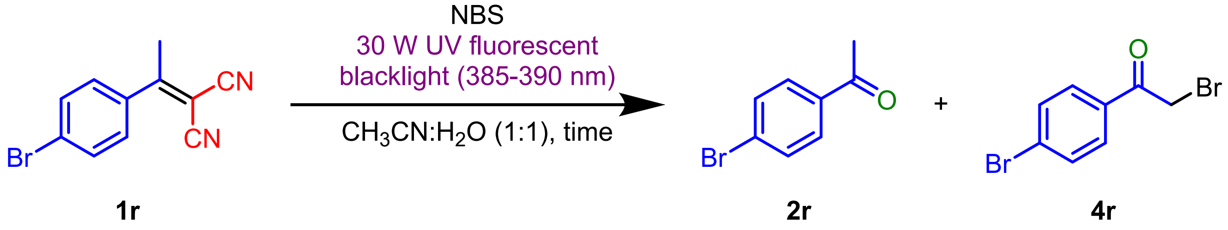
Table 1. Optimization of photoinitiated C=C cleavage.[a]



Entry	**NBS** (equiv.)	Time (h)	Solvent	Yield (%)[b]	
				2e	**3e**
1	2.5	4	H_2O	46	Trace
2	2.5	4	CH_3CN	ND	ND
3	**2.5**	**4**	**$CH_3CN:H_2O$ (1:1)**	**83**	**9**
4	2.5	4	Acetone:H_2O (1:1)	28	Trace
5	2.5	4	EtOH:H_2O (1:1)	77	Trace
6	2.5	4	THF:H_2O (1:1)	41	Trace
7	2	4	$CH_3CN:H_2O$ (1:1)	80	5
8	3	4	$CH_3CN:H_2O$ (1:1)	83	9
9	2.5	3	$CH_3CN:H_2O$ (1:1)	62	Trace
10	2.5	5	$CH_3CN:H_2O$ (1:1)	83	9
11	2.5	8	$CH_3CN:H_2O$ (1:1)	84	9
12[c]	2.5	4	$CH_3CN:H_2O$ (1:1)	Trace	ND
13[d]	2.5	4	$CH_3CN:H_2O$ (1:1)	83	9
14[e]	2.5	4	$CH_3CN:H_2O$ (1:1)	67	Trace
15[f]	2.5	4	$CH_3CN:H_2O$ (1:1)	78	Trace

[a] Reactions were performed with **1e** (0.42 mmol), NBS (1.07 mmol), $CH_3CN:H_2O$ (1:1) (4 mL), 4 h, 30 W UV fluorescent blacklight (385-390 nm). [b] Isolated yield, [c] Reaction under dark for 8 h, [d] Reaction under nitrogen atmosphere, [e] Reaction under 18 W CFL, [f] Reaction under 12 W blue LED**.** (ND: Not Detected)

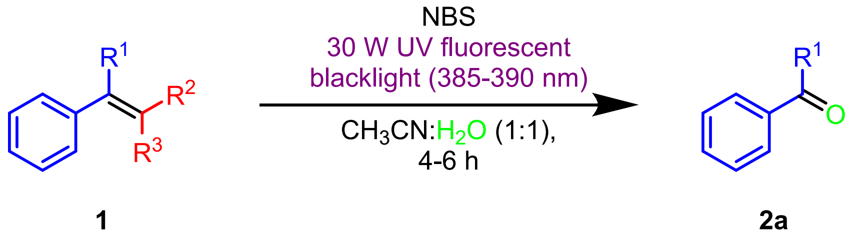
Table S1. Optimization of photoinitiated C=C Cleavage for 1-(4-bromophenyl)ethan-1-one (3q) synthesis.[a]

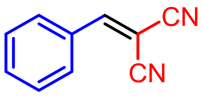
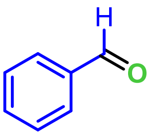
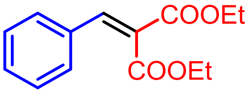
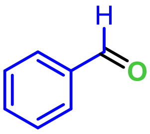
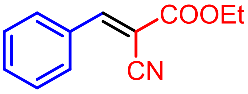
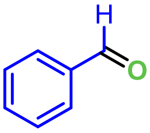


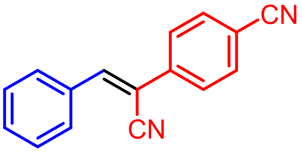
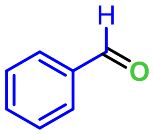
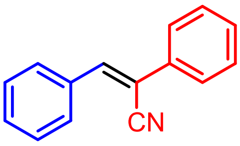
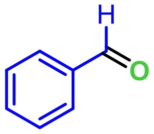
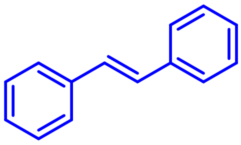
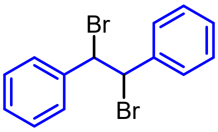
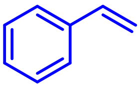
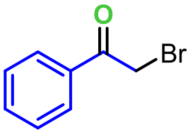
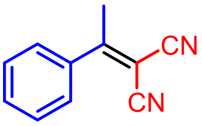
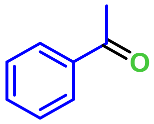
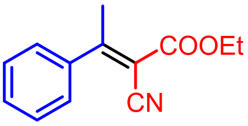
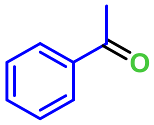
Entry	Time (h)	Yield (%)[b]	
		2r	**4r**
1	4	58	2
2	**6**	**67**	**6**
3	8	63	11

Reaction conditions: [a] **1r** (0.40 mmol), NBS (1.01 mmol), $CH_3CN:H_2O$ (1:1) (4 mL), 6 h, 30 W UV fluorescent blacklight (385-390 nm). [b] Isolated yield.

Table S2. Reaction of stilbene and styrene under standard conditions.[a]

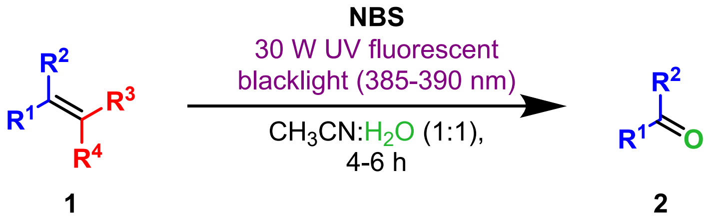


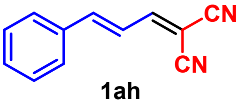
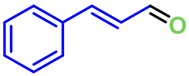
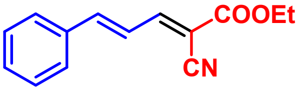
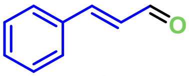
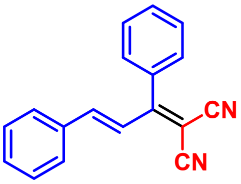
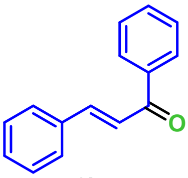
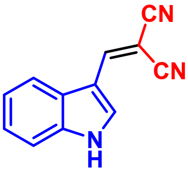
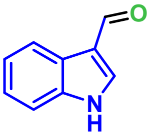
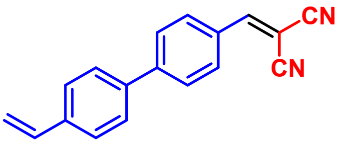
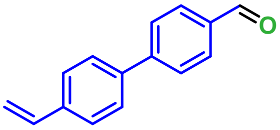
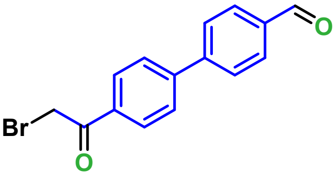
Entry	Reactant	Product	Yield (%)[b]
1	 **1aa**	 **2a**	77
2	 **1ab**	 **2a**	80
3	 **1ac**	 **2a**	76

4	 **1ad**	 **2a**	25
5	 **1ae**	 **2a**	22
6	 **1af**	 **2ae**	50
7	 **1ag**	 **2af**	81
8	 **1ba**	 **2q**	62
9	 **1bb**	 **2q**	59

Reaction Conditions: [a] Reactions were performed with **1** (0.42 mmol), **NBS** (1.07 mmol), $CH_3CN:H_2O$ (1:1) (4 mL), 4 h (**1aa-1ag**) or 6 h (**1ba-1bb**), 30 W UV fluorescent blacklight (385-390 nm). [b] Isolated yield

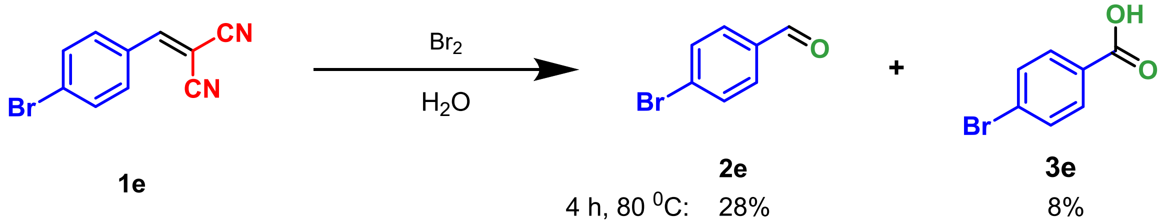
Table S3. Substrate scope for photoinitiated C=C cleavage.[a]



Entry	Reactant	Product	Yield (%)[b]
1	 **1ah**	 **2ah**	78
2	 **1ai**	 **2ai**	79
3	 **1bc**	 **2bc**	64
4	 **1aj**	 **2aj**	87
5	 **1ak**	 **2ak**	47
		 **4ak**	31

[a] Reaction Conditions: Reactions were performed with **1** (0.42 mmol), NBS (1.07 mmol), $CH_3CN:H_2O$ (1:1) (4 mL), 4 h (**1ah-1ak**) - 6 h (**1bc**), 30 W UV fluorescent blacklight (385-390 nm). [b] Isolated yield.

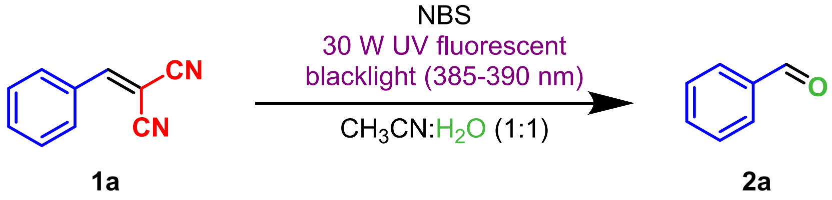
2.1. Control experiments



	2e	3e
4 h, 80 ^{0}C:	28%	8%
12 h, rt :	Trace	ND
12 h, Light:	Trace	ND

Scheme S1. Control experiments in presence of Br_2/H_2O.

2.2. Test for the production of H_2O_2



An oven-dried glass vial (**E**) was charged with 2-benzylidenemalononitrile **1a** (0.64 mmol) and **NBS** (1.62 mmol). 4 mL $CH_3CN:H_2O$ (1:1) was added to the reaction mixture and stirred under UV fluorescent black light (30 W) for 4 h. Another glass vial (**A**) was charged with NBS (1.62 mmol) followed by the addition of 4 mL $CH_3CN:H_2O$ (1:1) was added to the reaction mixture and stirred under UV fluorescent black light (30 W) for 4 h. After 4 h, both of the reaction mixture (vial **F** and **B** respectively) was diluted with 10 mL water and extracted three times in ethyl acetate. The aqueous part was kept for further experiments.

KI-glacial acetic acid test solution preparation: 0.100 g of KI dissolved in 10 mL of glacial acetic acid.

H_2O_2 generation test: 2 mL aqueous part presence in vials **F** and **B** was added to KI-glacial acetic acid test solution separately where immediate dark color appearance indicated the generation of H_2O_2 during the reaction.

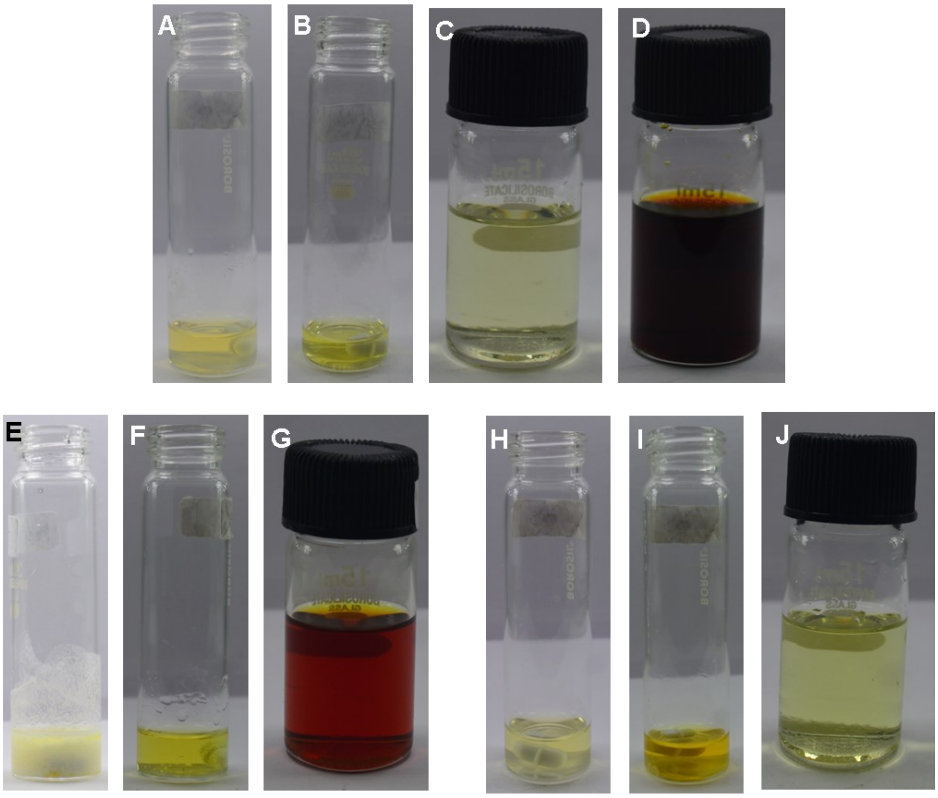
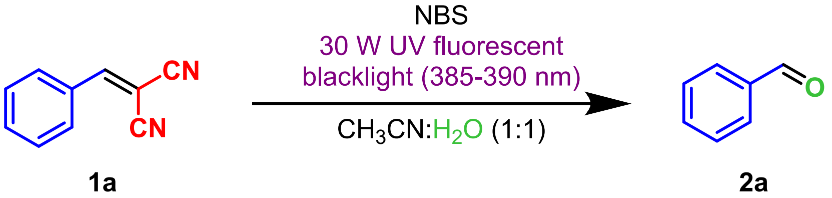


Figure S1. Test for the production of hydrogen peroxide. (A) NBS in CH_3CN:H_2O (1;1) at 0 min. (B) NBS in CH_3CN:H_2O (1:1) at 240 min. (C) KI/ AcOH. (D) Aqueous part of B added to mixture C. (E) 1a + NBS in CH_3CN:H_2O (1;1) at 0 min. (F) 1a + NBS in CH_3CN:H_2O (1;1) at 240 min. (G) Aqueous part of F added to mixture C. (H) NBS in CH_3CN (1:1) at 0 min. (I) NBS in CH_3CN (1:1) at 240 min. (J) Aqueous part of 'I' added to mixture C.

2.3. Light on-off experiment



An oven-dried glass vial was charged with 2-benzylidenemalononitrile **1a** (100 mg, 0.64 mmol) and **NBS** (288 mg, 1.62 mmol). 4 mL CH_3CN:H_2O (1:1) was added to the reaction mixture and stirred under UV fluorescent black light (30 W) for 450 min. as per the details given in Table S3.

Table S4. Light on-off experiment details.

Entry	Time	Experiment	^{1}H-NMR Conversion (%)
1	30 min.	Dark	0
2	90 min.	Light	27
3	150 min.	Dark	29
4	210 min.	Light	56
5	270 min.	Dark	58
6	330 min.	Light	83
7	390 min.	Dark	84
8	450 min.	Light	94

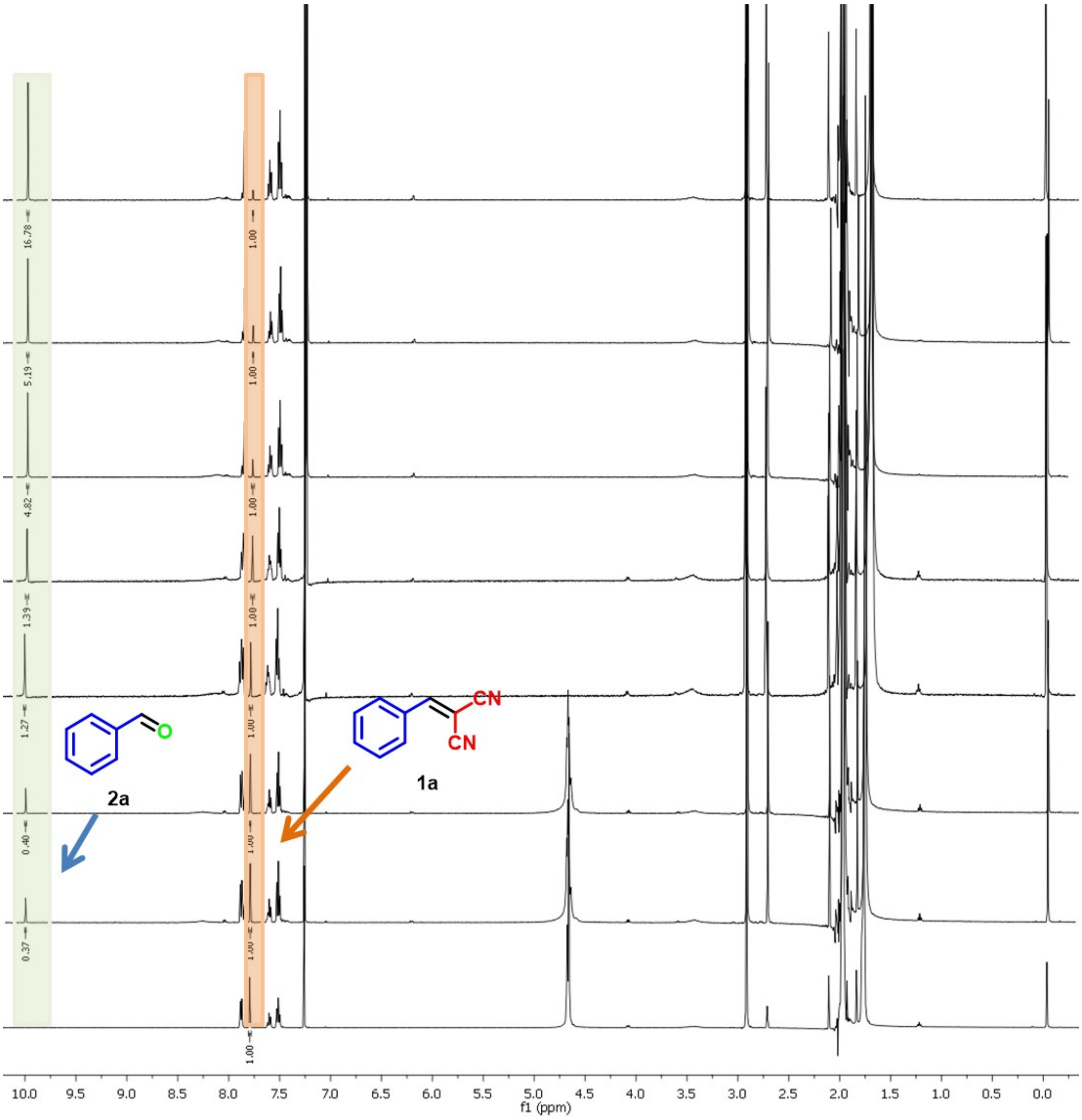


Figure S2. Crude ^{1}H-NMR for Light on-off experiment.

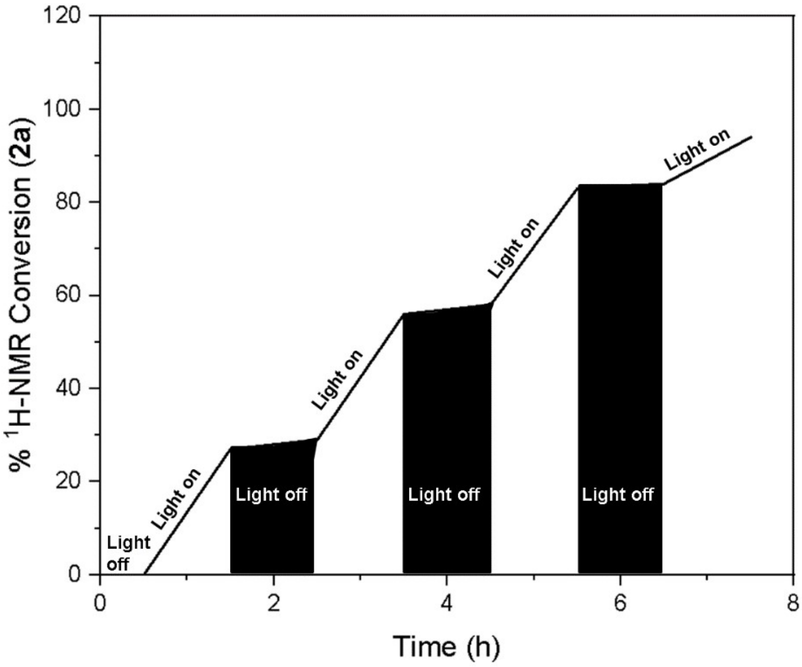


Figure S3. Light on-off experiment.

2.4. Experimental setup

Fluortronix 30 Watt (Dimensions: 23L × 18W × 4H cm) UV LED Neon Fluorescent Blacklight (220V) with a wavelength of 380-390 nm purchased from Fluortronix Innovations. The reaction was carried out in a 30 mL borosilicate glass vial with a stopper and a magnetic bar. During the reaction, the distance of fluorescent light from the borosilicate glass vials was kept at 6 cm and the room temperature was 20-25 ^{0}C for all the reactions.

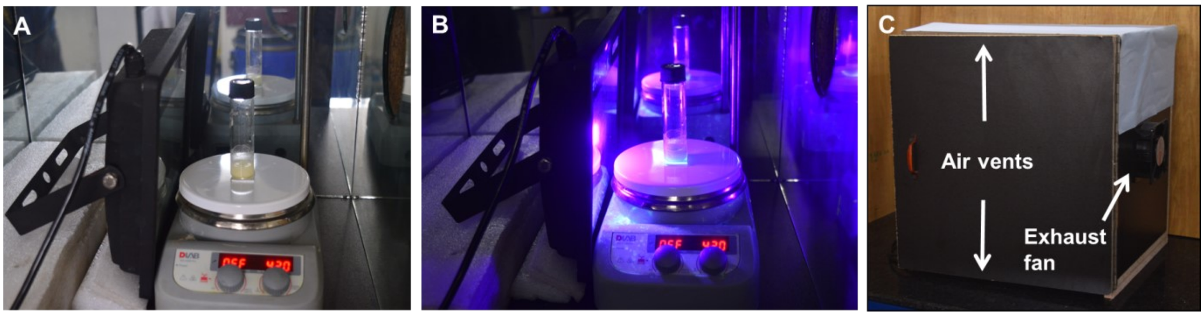
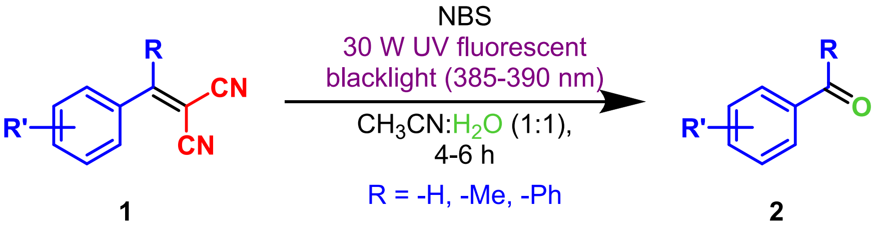


Figure S4. A typical photochemical reaction set up for photoinitiated cleavage of C=C. (A) Light off. (B) Light on. (C) Photoreactor.

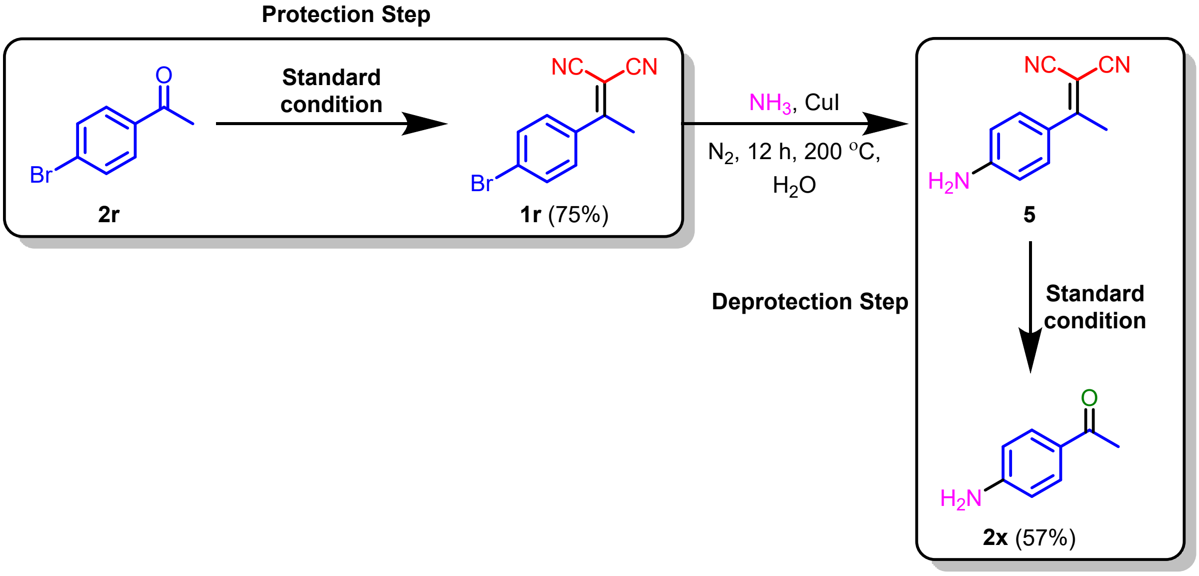
2.5. General Procedure

2.5.1 NBS photoinitiated C=C Cleavage



An oven-dried glass vial was charged with 2-(4-bromobenzylidene)malononitrile **1e** (100 mg, 0.42 mmol)/ 2-(1-(4-bromophenyl)ethylidene)malononitrile **1r** (100 mg, 0.40 mmol) and **NBS** (190 mg, 1.07 mmol/ 180 mg, 1.01 mmol). 4 mL CH_3CN:H_2O (1:1) was added to the reaction mixture and stirred it under UV fluorescent black light (30 W) for 4 h (in case of Knoevenagel products of aldehydes, **2a-2p**) or 6 h (in case of Knoevenagel products of ketones, **2q-2u**). After complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and was washed with water. The organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate = 10:1 to 4:1 as the eluent to give product **2e**/ **2r**.

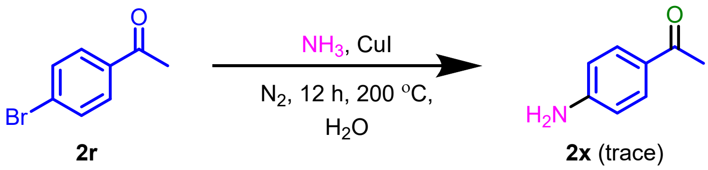
2.5.2. Synthesis of 4-aminoacetophenone (2x)



(i) An oven-dried pressure tube was charged with 2-(1-(4-bromophenyl)ethylidene)malononitrile **1r** (180 mg, 0.72 mmol) (obtained in the first step), $NH_3.H_2O$ (153 mg, 4.37 mmol), and CuI (7 mg, 0.036mmol). 3 mL distilled water was added to the reaction mixture and purging with nitrogen gas for 20 min. The pressure tube was then heated at 200 ^{0}C for 12 h.[1] The progress of the reaction was monitored by TLC. After completion of the reaction, diluted the reaction mixture with 20-30 mL chloroform and it was filtered. The filtrate was taken and extracted from water three times with chloroform (3 x 30 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to get light yellow crude of **5**. The crude **5** was directly forwarded to the next step.

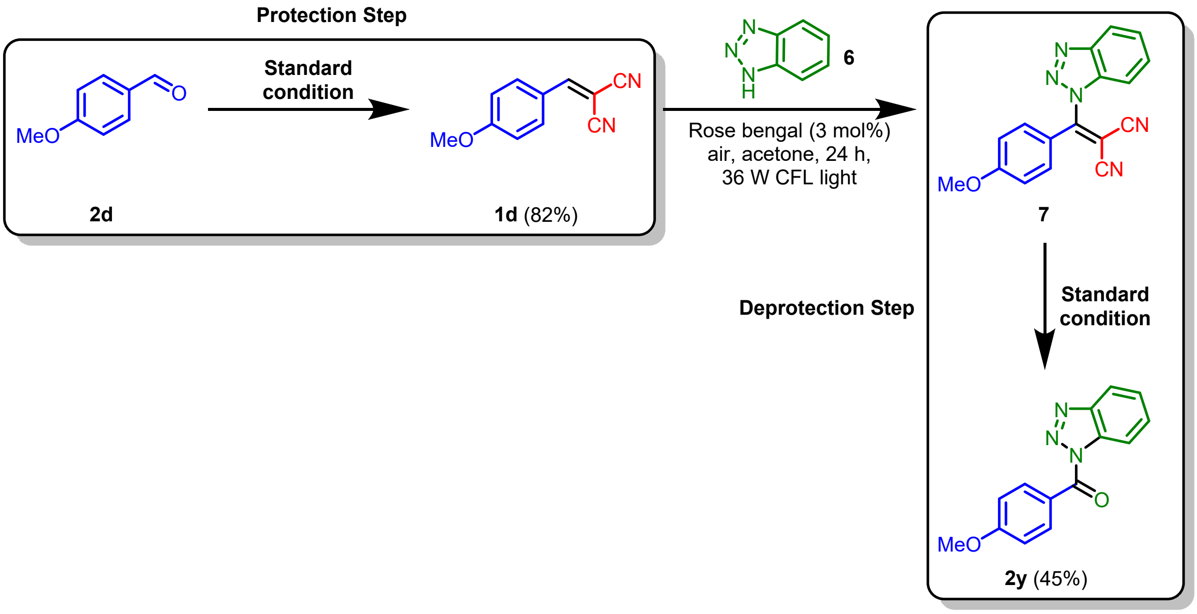
(ii) An oven-dried glass vial was charged with crude 2-(1-(4-aminophenyl)ethylidene)malononitrile **5** (considering the conversion 100%) and NBS (324 mg, 1.82 mmol). 4 mL $CH_3CN:H_2O$ (1:1) was added to the reaction mixture and stirred it under UV fluorescent black light (30 W) for 6 h. After complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and was washed with water. The organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate = 2.2:1 as the eluent to give product **2x**.

2.5.3. Synthesis of 4-aminoacetophenone (2x) from 4-bromoacetophenone (2r)



An oven-dried pressure tube was charged with 4-bromoacetophenone **2r** (200 mg, 1 mmol), $NH_3.H_2O$ (211 mg, 6 mmol), and CuI (10 mg, 0.05mmol). 3 mL distilled water was added to the reaction mixture and purging with nitrogen gas for 20 min. The pressure tube was then heated at 200 ^{0}C for 12 h. As per TLC, only a trace amount of product was detected.

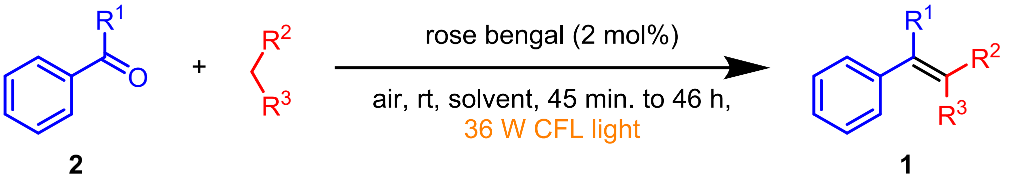
2.5.4. Synthesis of (1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methanone (2y)



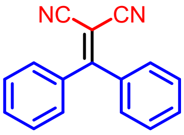
(i) An oven-dried glass vial was charged with 2-(4-methoxybenzylidene)malononitrile **1d** (200 mg, 1.08 mmol) (obtained in the first step), 1H-benzo[d][1,2,3]triazole **6** (258 mg, 2.17 mmol), and rose bengal (31 mg, 0.032 mmol). 5 mL dry acetone was added to the reaction mixture and stirred under 18 W CFL light for 24 h.[2] 20 mL water was added to the reaction mixture and extracted three times in chloroform. The combined organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to ger light-reddish color crude of **7**. The crude **7** was directly forwarded to the next step.

(ii) An oven-dried glass vial was charged with crude 2-((1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methylene)malononitrile **7** (considering the conversion 100%) and NBS (483 mg, 2.7 mmol). 4 mL CH_3CN:H_2O (1:1) was added to the reaction mixture and stirred it under UV fluorescent black light (30 W) for 6 h. After complete consumption of the starting material, the reaction mixture was diluted with ethyl acetate (10 mL) and was washed with water. The organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate = 4:1 as the eluent to give product **2y**.

2.6. Synthesis of starting materials



An oven-dried glass vial was charged with aldehyde/ketone **2** (0.94 mmol), active methylene compound (1.88 mmol), rose bengal (0.018 mmol). 4 mL distilled water/ EtOH:H_2O (1:1) was added to the reaction mixture and the glass vial was irradiated with 36 W CFL light for 45 min. (in the case of aldehydes) or 46 h (in the case of ketones). The progress of the reaction was monitored by TLC. After completion of the reaction, 10 mL of distilled water was added to the reaction mixture. In the case of aldehydes, precipitation appeared. The precipitation was filtered to get solid. It was washed several times with water and one to two times with 4:1 Water:EtOH to get pure product **1a-p**. In the case of **1q-1w**, **1ab, 1ac**. **1ad**, **1ae, 1bb**, **1ah**, **1ai**, **1bc**, **1aj**, and **1ak** 6 mL water was added to the reaction mixture and extracted three times in ethyl acetate. The combined organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate 6:1 as the eluent to give the product.

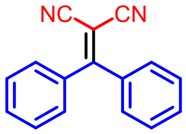


2-(Diphenylmethylene)malononitrile (1u)

2-(Diphenylmethylene)malononitrile (**1u**) was prepared according to a published procedure[3a]

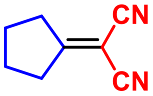
3. Spectroscopic characterization

3.1. Characterization of the starting material



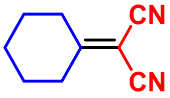
1u

2-(Diphenylmethylene)malononitrile (1u): White solid; yield: 32%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (t, J = 7.3 Hz, 2H), δ 7.49 (t, J =7.7 Hz, 4H), δ 7.44 (d, J = 7.8 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.09, 136.09, 132.76, 130.47, 128.91, 113.97, 81.63. Spectral data are in agreement with literature values.[3b]



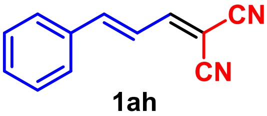
1v

2-cyclopentylidenemalononitrile (1v): Colourless liquid; yield: 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.80 (t, J = 7.2 Hz, 4H), 2.11-2.07 (m, 4H). Spectral data are in agreement with literature values.[3c]



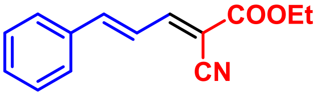
1w

2-cyclohexylidenemalononitrile (1w): Colourless liquid; yield: 82%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.66 (t, J = 6.3 Hz, 4H), 1.83-1.79 (m, 4H), 1.71-1.66 (m, 2H). Spectral data are in agreement with literature values.[3c]



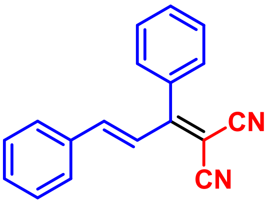
1ah

(E)-2-(3-Phenylallylidene)malononitrile (1ah): Yellow solid; yield: 85%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.59 (m, 3H), 7.47-7.45 (m, 3H), 7.29-7.26 (m, 2H). Spectral data are in agreement with literature values.[3d]



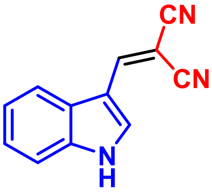
1ai

Ethyl (2E,4E)-2-cyano-5-phenylpenta-2,4-dienoate (1ai): Light yellow solid; yield: 80%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 1H), 7.60-758 (m, 2H), 7.43-7.42 (m, 3H), 7.29-7.28 (m, 2H), 4.37-4.32 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). Spectral data are in agreement with literature values.[3e]



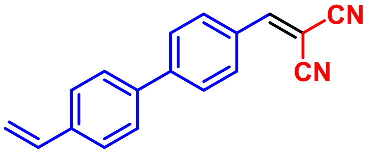
1bc

(E)-2-(1,3-Diphenylallylidene)malononitrile (1bc): Yellow solid; yield: 59%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.79 (m, 2H), 7.45-7.43 (m, 2H), 7.33-7.26 (m, 6H), 7.06 (s, 1H), 7.01 (s, 1H). Spectral data are in agreement with literature values.[3f]



1aj

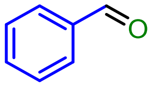
2-((1H-indol-3-yl)methylene)malononitrile (1aj): Yellow solid; yield: 86%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.72 (s, 1H), 8.53 (s, 1H), 8.04 (d, *J* = 7.1 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.32-7.26 (m, 2H). Spectral data are in agreement with literature values.[3g]



1ak

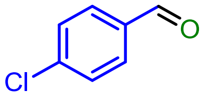
2-((4'-Vinyl-[1,1'-biphenyl]-4-yl)methylene)malononitrile (1ak): Light yellow solid; yield: 78%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.78-7.76 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 6.80-6.74 (m, 1H), 5.85 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.35 (dd, *J* = 10.9, 0.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.30, 146.91, 138.46, 138.15, 136.11, 131.58, 129.90, 127.87, 127.50, 127.12, 115.30, 114.07, 112.97, 81.95. Spectral data are in agreement with literature values.

3.2. Characterization of the Products



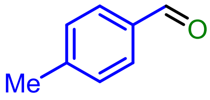
2a

Benzaldehyde (2a): Colourless liquid; yield: 77%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.03 (s, 1H), δ 7.89 (d, *J* = 7.1 Hz, 2H), δ 7.64 (t, *J* = 7.4 Hz, 1H), δ7.54 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.54, 136.50, 134.58, 129.85, 129.10. Spectral data are in agreement with literature values.[4, 5, 6b]



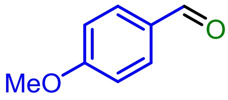
2b

4-Chlorobenzaldehyde (2b): White solid; yield: 79%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.98 (s, 1H), δ 7.82 (d, *J* = 8.4 Hz, 2H), δ 7.51 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 190.73, 140.72, 134.65, 130.79, 129.3. Spectral data are in agreement with literature values.[4b, 4c, 6b, 7]



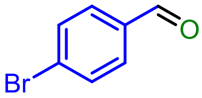
2c

4-Methylbenzaldehyde (2c): Colourless liquid; yield: 82%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.96 (s, 1H), δ 7.78 (d, *J* = 8.0 Hz, 2H), δ 7.33 (d, *J* = 7.9 Hz, 2H), δ 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 191.92, 145.48, 134.15, 129.77, 129.65, 21.77. Spectral data are in agreement with literature values.[4a, 4b, 5, 6a, 7]



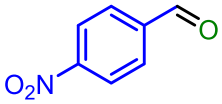
2d

4-Methoxybenzaldehyde (2d): Colourless liquid; yield: 85%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.89 (s, 1H), δ 7.84 (d, *J* =8.6 Hz, 2H), δ 7.01 (d, *J* = 8.7 Hz, 2H), δ 3.89 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 190.77, 164.58, 131.92, 129.89, 114.28, 55.52. Spectral data are in agreement with literature values.[4a, 4c, 5, 6, 7]



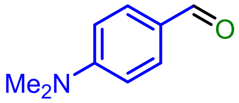
2e

4-Bromobenzaldehyde (2e): White solid; yield: 83%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.97 (s, 1H), δ 7.74 (d, *J* = 8.4 Hz, 2H), δ 7.68 (d, *J* =8.4 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 190.97, 135.00, 132.33, 130.89, 129.65. Spectral data are in agreement with literature values.[4a, 4c, 5, 6b, 7]



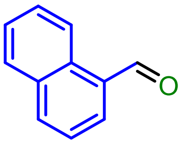
2f

4-Nitrobenzaldehyde (2f): Light brown solid; yield: 80%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), δ 8.40 (d, *J* = 8.6 Hz, 2H), δ 8.08 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.47, 151.15, 140.12, 130.56, 124.35. Spectral data are in agreement with literature values.[4a, 4c,5, 6, 7]



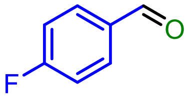
2g

4-(Dimethylamino)benzaldehyde (2g): White solid; yield: 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), δ 7.73 (d, *J* = 8.8 Hz, 2H), δ 6.70 (d, *J* = 8.8 Hz, 2H), δ 3.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.91, 154.08, 131.66, 124.76, 110.74, 39.73. Spectral data are in agreement with literature values.[5, 6a]



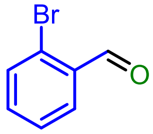
2h

1-Naphthaldehyde (2h): Colourless liquid; yield: 80%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), δ 9.26 (d, *J* = 8.6 Hz, 1H), δ 8.11 (d, *J* = 8.2 Hz, 1H), δ 8.00 (d, *J* = 7.0 Hz, 1H), δ 7.93 (d, *J* = 8.2 Hz, 1H), δ 7.70 (t, *J* = 7.7 Hz, 1H), δ 7.65-7.59 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.58, 136.71, 135.31, 133.74, 131.40, 130.53, 129.09, 128.52, 126.98, 124.90. Spectral data are in agreement with literature values.[6]



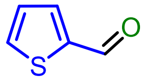
2i

4-Fluorobenzaldehyde (2i): Colourless liquid; yield: 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), δ 7.93-7.90 (m, 2H), δ 7.23-7.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.60, 167.58, 165.53, 133.01, 132.32, 132.24, 116.46, 116.28. Spectral data are in agreement with literature values.[5, 6b, 7]



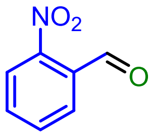
2j

2-Bromobenzaldehyde (2j): Colourless liquid; yield: 81%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), δ 7.91 (d, J = 8.7 Hz, 1H), δ 7.65 (d, J = 7.8 Hz, 1H), δ 7.47-7.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.83, 135.38, 133.92, 133.52, 129.88, 127.95, 127.14. Spectral data are in agreement with literature values.[6b, 8]



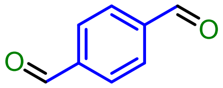
2k

Thiophene-2-carbaldehyde (2k): Yellow liquid; yield: 75%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), δ 7.79-7.76 (m, 2H), δ 7.22 (t, J = 4.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.05, 143.97, 136.46, 135.16, 128.37. Spectral data are in agreement with literature values.[9]



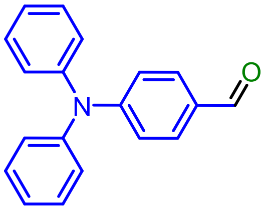
2l

2-Nitrobenzaldehyde (2l): Light brown solid: yield: 88%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), δ 8.12 (d, J = 7.9 Hz, 1H), δ 7.95 (d, J = 8.9 Hz, 1H), 7.82-7.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.23, 149.46, 134.12, 133.77, 131.24, 129.58, 124.45. Spectral data are in agreement with literature values.[6b, 10]



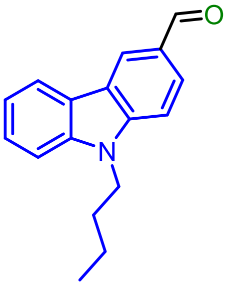
2m

Terephthalaldehyde (2m): White solid; yield: 76%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.14 (s, 2H), δ 8.06 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 191.61, 140.06, 130.18. Spectral data are in agreement with literature values.[4c, 6b, 11a]



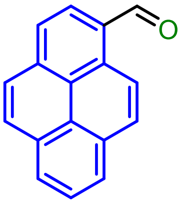
2n

4-(diphenylamino)benzaldehyde (2n): White solid; yield: 83%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.81 (s, 1H), δ 7.68 (d, J = 8.7 Hz, 2H), δ 7.34 (t, J = 7.9 Hz, 4H), δ 7.18-7.16 (m, 6H), δ 7.01 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 190.55, 153.46, 146.26, 131.42, 129.85, 129.21, 126.43, 125.23, 119.46. Spectral data are in agreement with literature values.[11b]



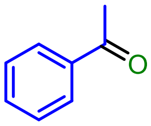
2o

9-butyl-9H-carbazole-3-carbaldehyde (2o): Yellow solid; yield: 86%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.10 (s, 1H), δ 8.60 (s, 1H), δ 8.15 (d, J = 7.6 Hz, 1H), δ 8.00 (d, J = 8.5 Hz, 1H), δ 7.55-7.45 (m, 3H), δ 7.32 (t, J = 7.1 Hz, 1H), δ 4.34 (t, J = 6.6 Hz, 2H), δ 1.91-1.85 (m, 2H), δ 1.45- 1.38 (m, 2H), δ 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 191.80, 144.07, 141.18, 128.48, 127.13, 126.73, 123.97, 123.04, 122.99, 120.74, 120.31, 109.45, 108.96, 43.16, 31.06, 20.54, 13.88. Spectral data are in agreement with literature values.[7a]



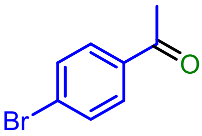
2p

pyrene-1-carbaldehyde (2p): Yellow solid; yield: 70%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.80 (s, 1H), δ 9.45 (d, *J* = 9.3 Hz, 1H), δ 8.47 (d, *J* = 7.9 Hz, 1H), δ 8.35-8.24 (m, 5H), δ 8.13-8.09 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 193.07, 135.46, 131.30, 131.00, 130.92, 130.76, 130.67, 130.38, 127.33, 127.18, 127.06, 126.85, 126.57, 124.54, 124.51, 123.99, 122.95. Spectral data are in agreement with literature values.[11c]



2q

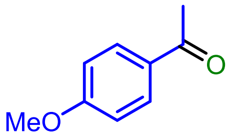
Acetophenone (2q): Colourless liquid; yield: 62%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), δ 7.57 (t, *J* = 7.4 Hz, 1H), δ 7.47, *J* = 7.7 Hz, 2H), δ 2.61 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 198.17, 137.10, 133.12, 128.57, 128.30, 26.59. Spectral data are in agreement with literature values.[12]



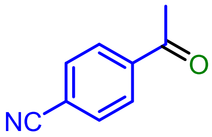
2r

1-(4-Bromophenyl)ethan-1-one (2r): White solid; yield: 67%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), δ 7.60 (d, *J* = 8.3 Hz, 2H), δ 2.58 (s, 3H); ^{13}C NMR (125 MHz,

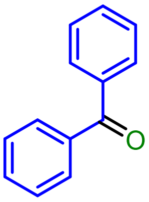
$CDCl_3$) δ 196.54, 135.55, 131.58, 129.60, 127.95, 26.27. Spectral data are in agreement with literature values.[12]


2s

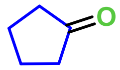
1-(4-Methoxyphenyl)ethan-1-one (2s): White solid; yield: 59%; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), δ 6.93 (d, *J* = 8.8 Hz, 2H), δ 3.87 (s, 3H), δ 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.77, 163.49, 130.57, 130.29, 113.67, 55.44, 26.30. Spectral data are in agreement with literature values.[12]


2t

4-Acetylbenzonitrile (2t): White solid; yield: 65%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), δ 7.77 (d, *J* = 8.3 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.67, 140.02, 132.61, 128.80, 118.03, 115.09, 26.86. Spectral data are in agreement with literature values.[12b, 12c]

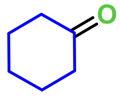

2u

Benzophenone (2u): White solid; yield: 79%; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 4H), δ 7.59 (t, *J* = 7.4 Hz, 2H), δ 7.48 (t, *J* = 7.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.66, 137.57, 132.42, 130.02, 128.28. Spectral data are in agreement with literature values.[10, 12a, 13]



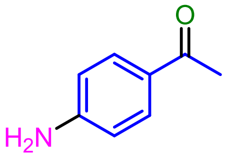
2v

Cyclopentanone (2v): Colourless liquid; yield: 61%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.17-2.14 (m, 4H), 1.97-1.93 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 220.83, 38.38, 23.26. Spectral data are in agreement with literature values.[14]



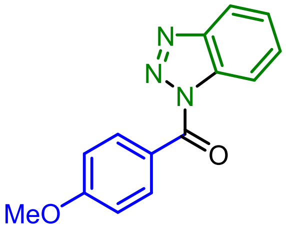
2w

Cyclohexanone (2w): Colourless liquid; yield: 64%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.35 (t, J =6.8 Hz, 4H), 1.89-1.84 (m, 4H), 1.74-1.69 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 212.53, 41.99, 27.05, 25.00. Spectral data are in agreement with literature values.[14]



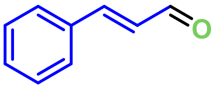
2x

1-(4-aminophenyl)ethan-1-one (2x): Light brown solid; yield: 57%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.8 (d, J = 8.5 Hz, 2H), δ 6.64 (d, J = 8.5 Hz, 2H), δ 4.15 (s, 2H), δ 2.50 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 196.72, 151.77, 130.67, 126.93, 113.45, 25.88. Spectral data are in agreement with literature values.[15]



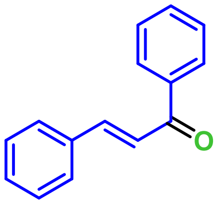
2y

(1H-benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methanone (2y): White solid; yield: 45%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.37 (d, J = 8.3 Hz, 1H), δ 8.29 (d, J = 8.9 Hz, 2H), δ 8.16 (d, J = 8.3 Hz, 1H), δ 7.69 (t, J = 7.7 Hz, 1H), δ 7.54 (t, J = 7.7 Hz, 1H), δ 7.06 (d, J = 8.9 Hz, 2H), δ 3.93 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.57, 164.14, 145.60, 134.41, 132.53, 130.13, 126.09, 123.39, 120.02, 114.81, 113.86, 55.61. Spectral data are in agreement with literature values.[16]



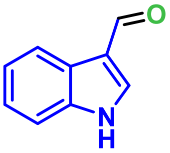
2ah/ 2ai

(E)-cinnamaldehyde (2ah/ 2ai): Colourless liquid; yield: 78%/ 79%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.71 (d, J = 7.7 Hz, 1H), 7.58-7.56 (m, 2H), 7.49 (d, J = 15.9 Hz, 1H), 7.46-7.42 (m, 3H), 6.75-6.71 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 193.89, 152.97, 134.08, 131.39, 129.20, 128.66, 128.60. Spectral data are in agreement with literature values.[17]



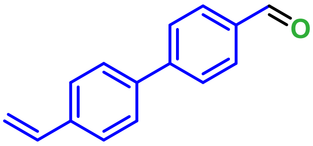
2bc

(E)-Chalcone (2bc): Light yellow solid; yield: 64%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, J = 7.9 Hz, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.66-7.64 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.56-7.50 (m, 3H), 7.43-7.42 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 190.43, 144.78, 138.17, 134.85, 132.80, 128.96, 128.63, 128.51, 128.47, 128.46, 122.02. Spectral data are in agreement with literature values.[18]



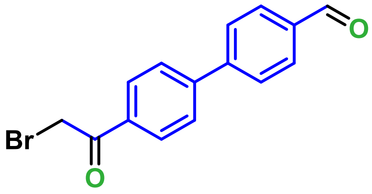
2aj

1H-indole-3-carbaldehyde (2aj): White Solid; yield: 87%; ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.13 (s, 1H), 9.89 (s, 1H), 8.26 (d, *J* = 15.4 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.24-7.16 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 185.06, 138.47, 137.19, 124.26, 123.56, 122.23, 120.98, 118.31, 112.52. Spectral data are in agreement with literature values.[19]



2ak

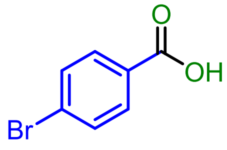
4'-vinyl-[1,1'-biphenyl]-4-carbaldehyde (2ak): White Solid; yield: 47%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.05 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.80-6.74 (m, 1H), 5.83 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.33 (dd, *J* = 10.9, 0.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.03, 146.75, 139.03, 137.92, 136.24, 135.29, 130.43, 127.61, 127.55, 126.98, 114.90. Spectral data are in agreement with literature values.[20]



4ak

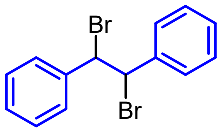
4'-(2-bromoacetyl)-[1,1'-biphenyl]-4-carbaldehyde (4ak): White Solid; yield: 31%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.09 (s, 1H), 8.10 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.81-7.75

(m, 4H), 4.48 (2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.87, 190.94, 145.47, 145.09, 136.06, 133.61, 130.48, 129.81, 128.06, 127.92, 30.86. Spectral data are in agreement with literature values.



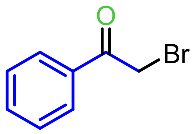
3e

4-Bromobenzoic acid (3e): White solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.92 (br s, 1H), δ 7.85 (d, *J* = 8.3 Hz, 2H), δ 7.67 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.16, 132.06, 131.73, 130.83, 127.16. Spectral data are in agreement with literature values.[12b, 21]



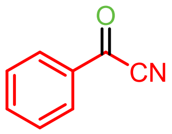
2ae

1,2-Dibromo-1,2-diphenylethane (2ae): White solid; yield: 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 4H), 7.44-7.36 (m, 6H), 5.84 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 140.17, 129.17, 128.93, 128.05, 56.22. Spectral data are in agreement with literature values.[22]



2af

2-Bromo-1-phenylethan-1-one (2af): White solid; yield: 81%. Spectral data are in agreement with literature values.[23]



8

Benzoyl cyanide (8): Yellow oil; yield: 12%. Spectral data are in agreement with literature values.[24]

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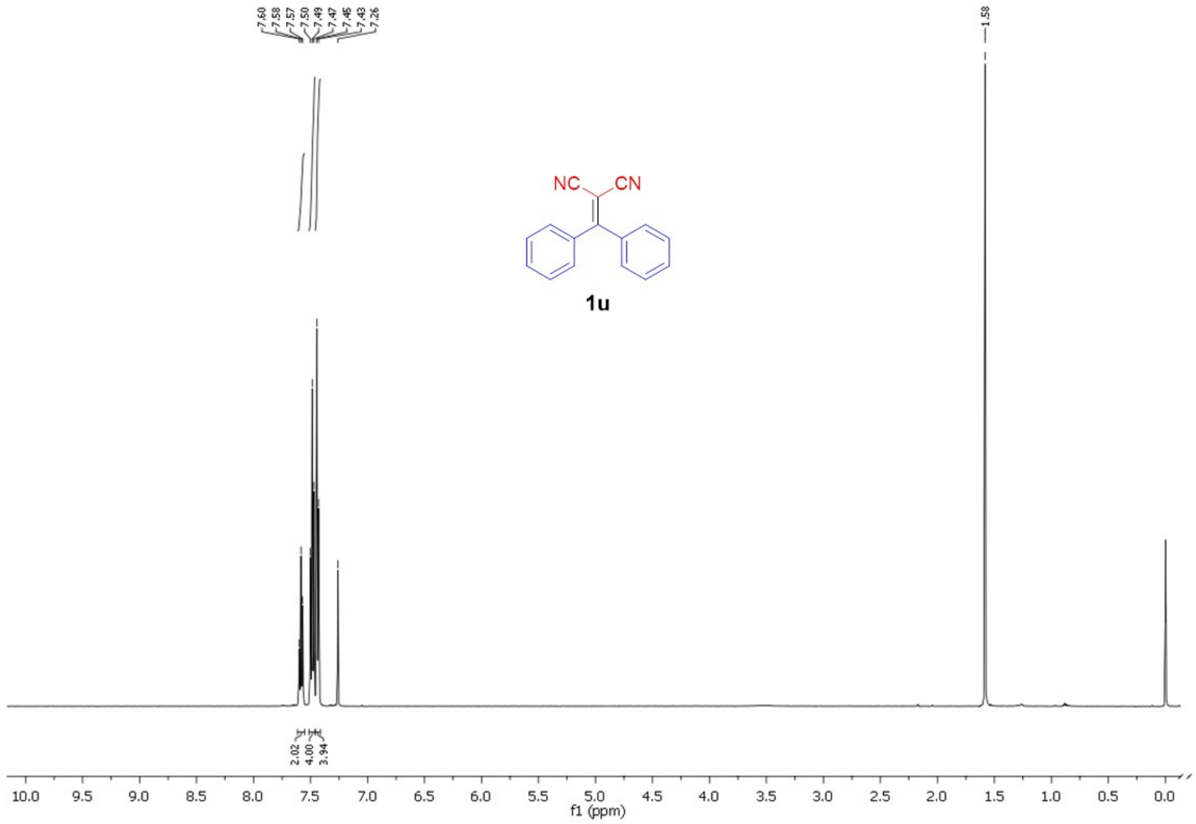
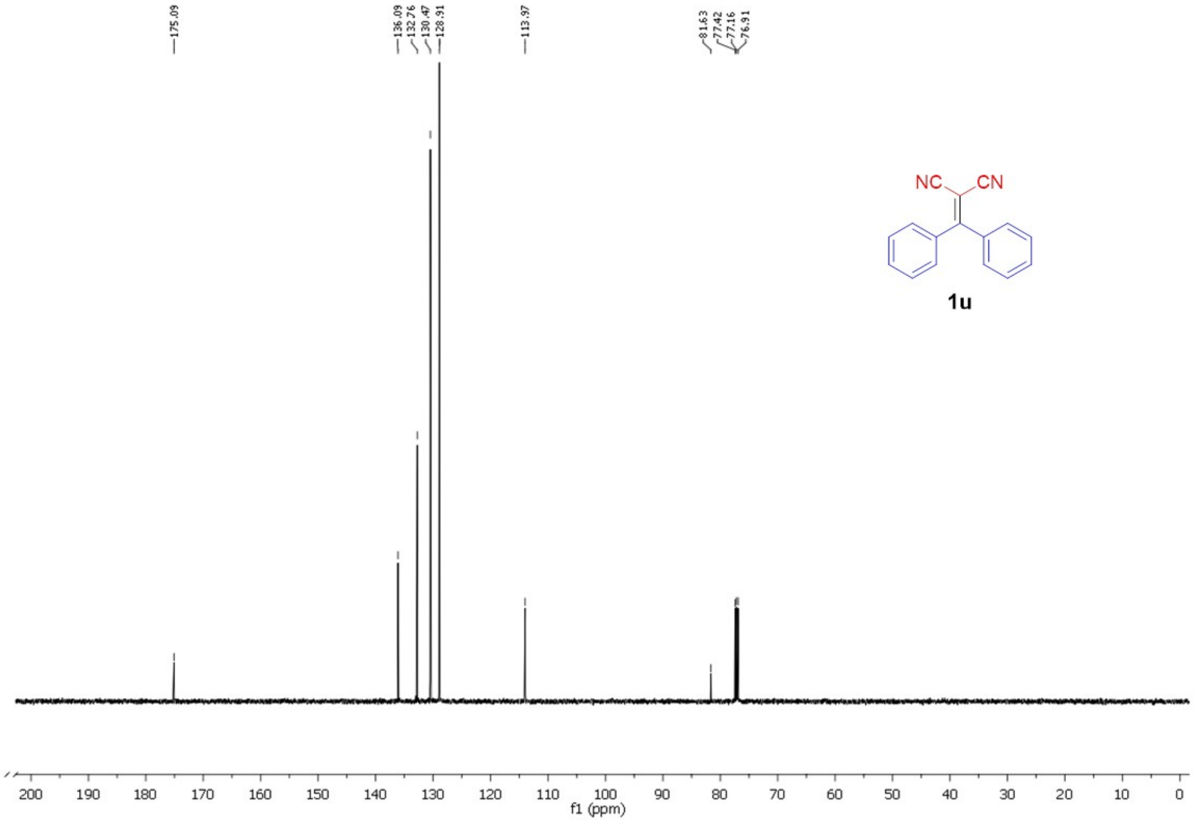
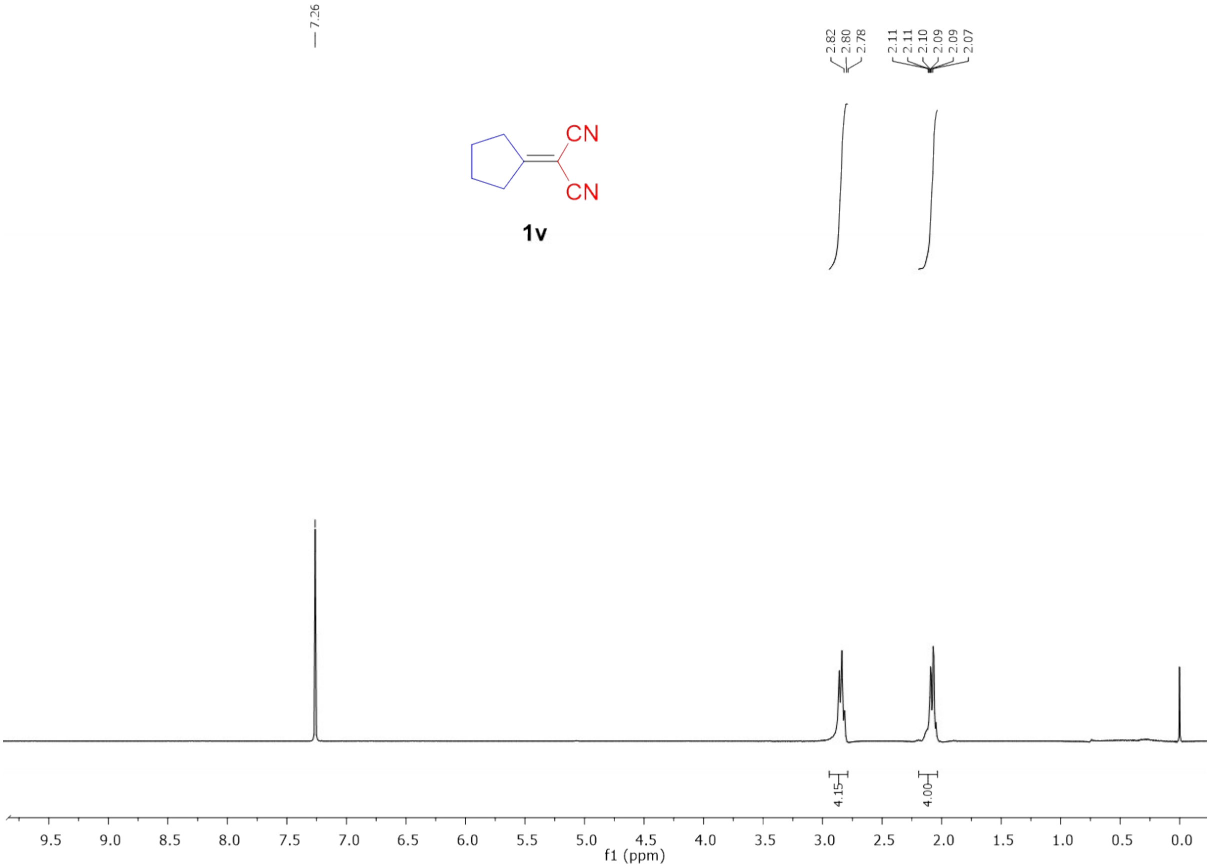
5. ^{1}H and ^{13}C NMR Spectra of the compounds



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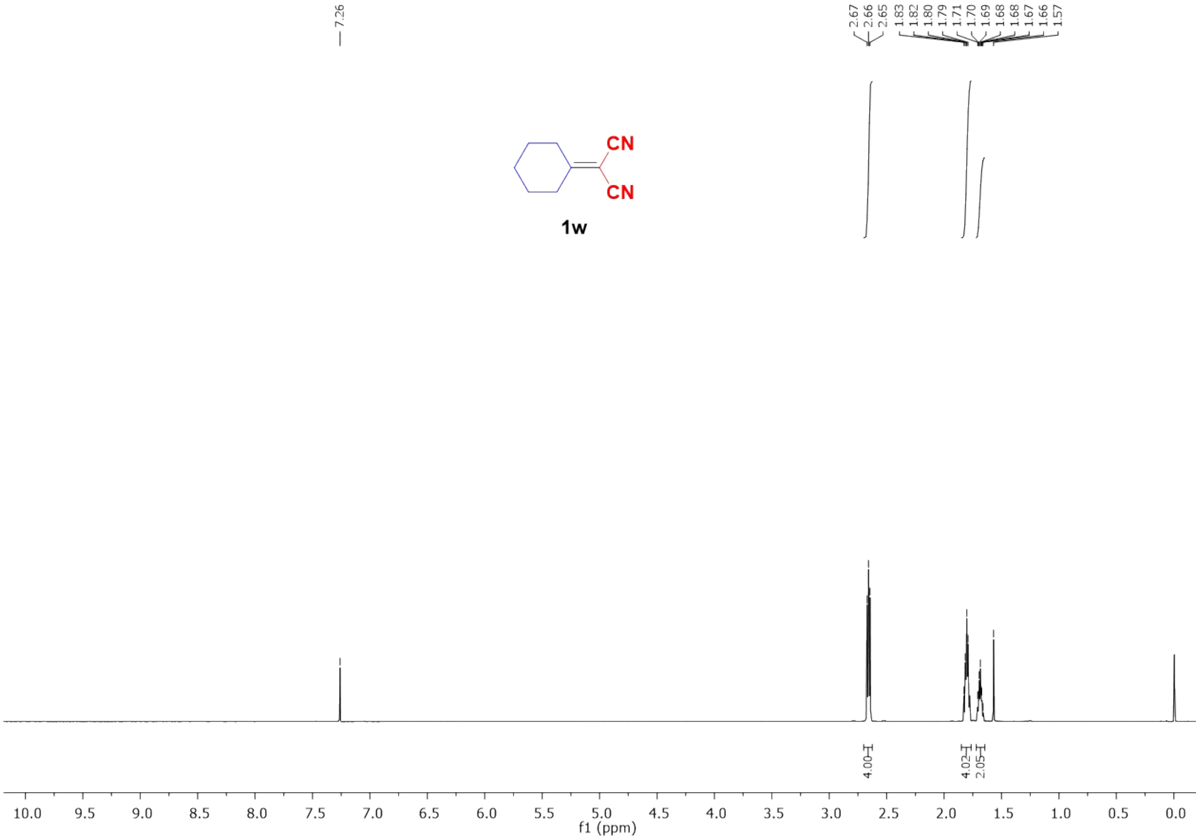
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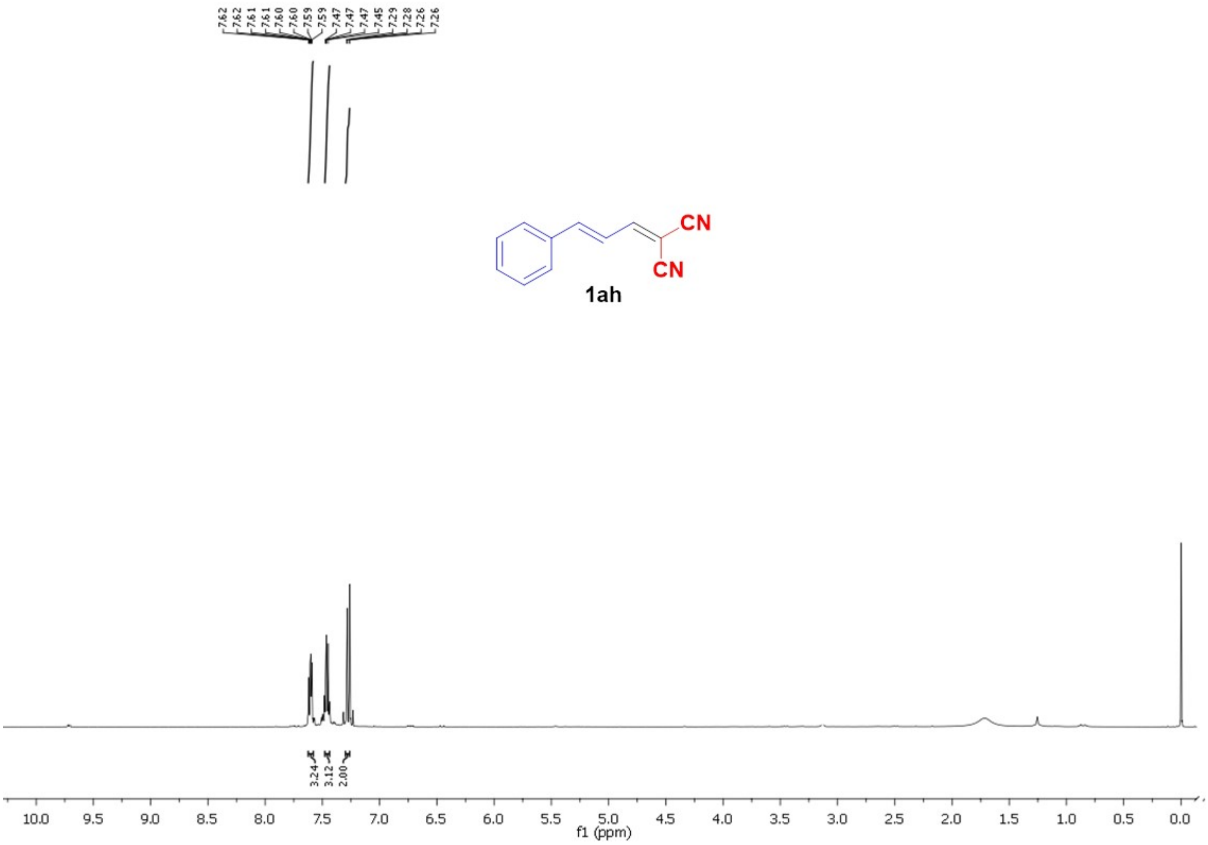
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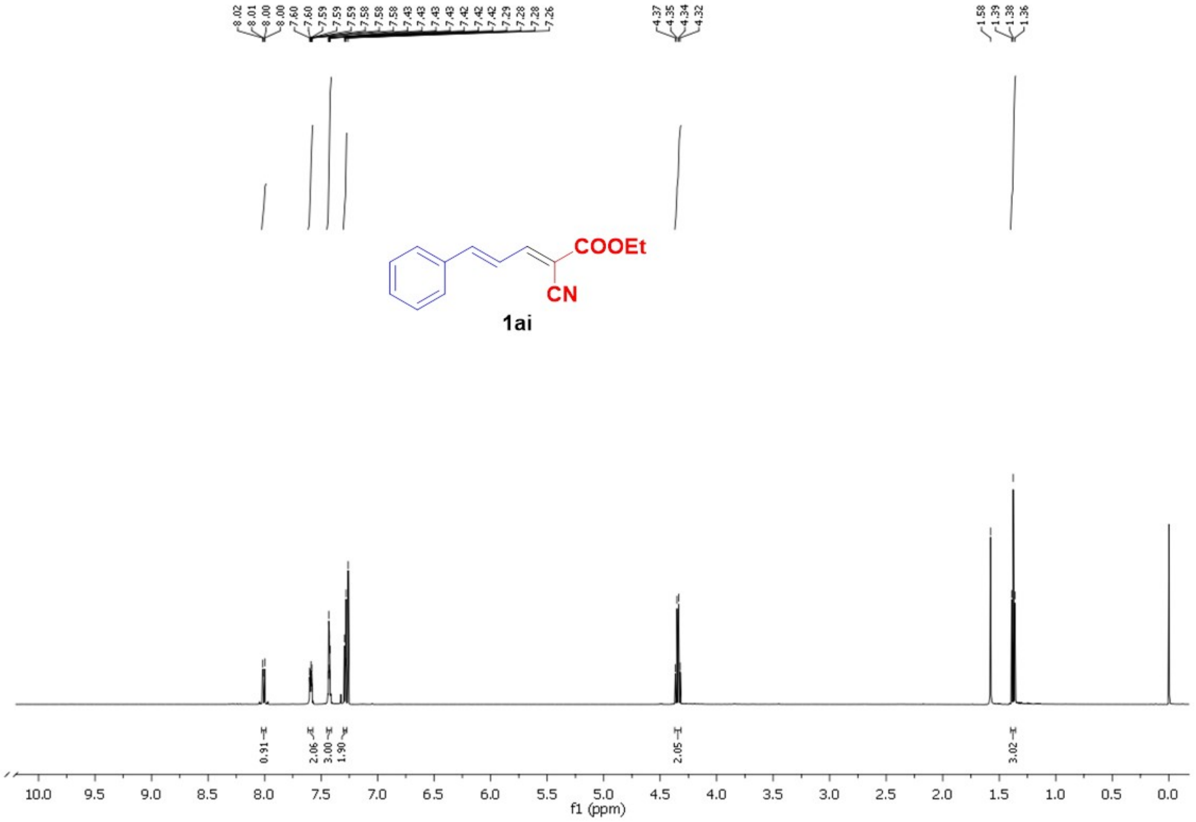
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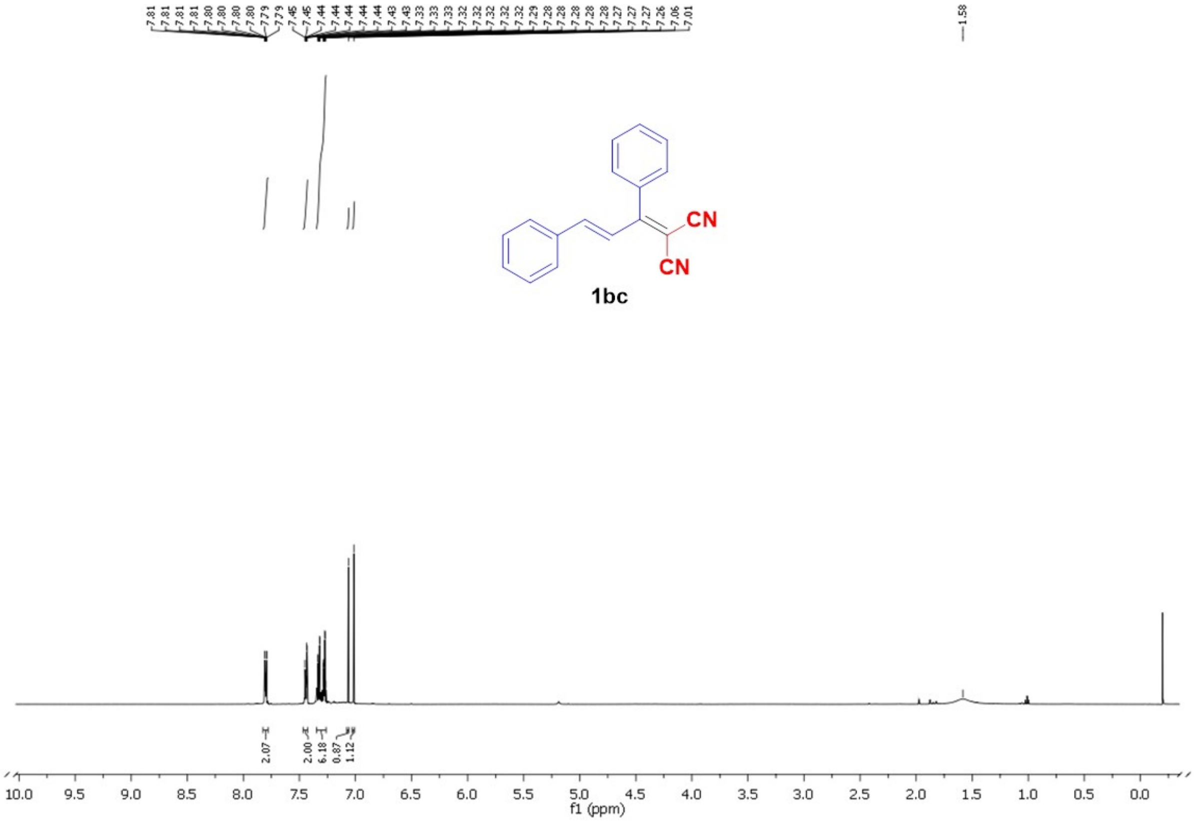

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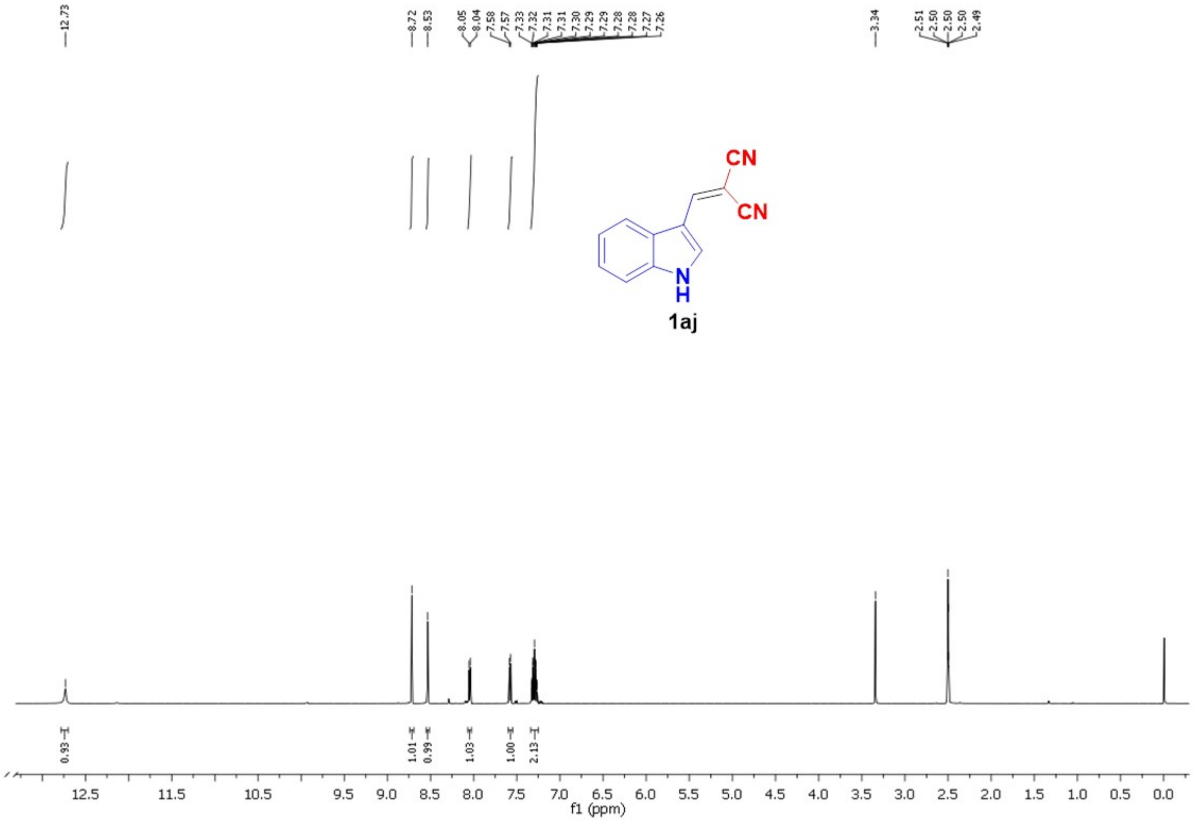
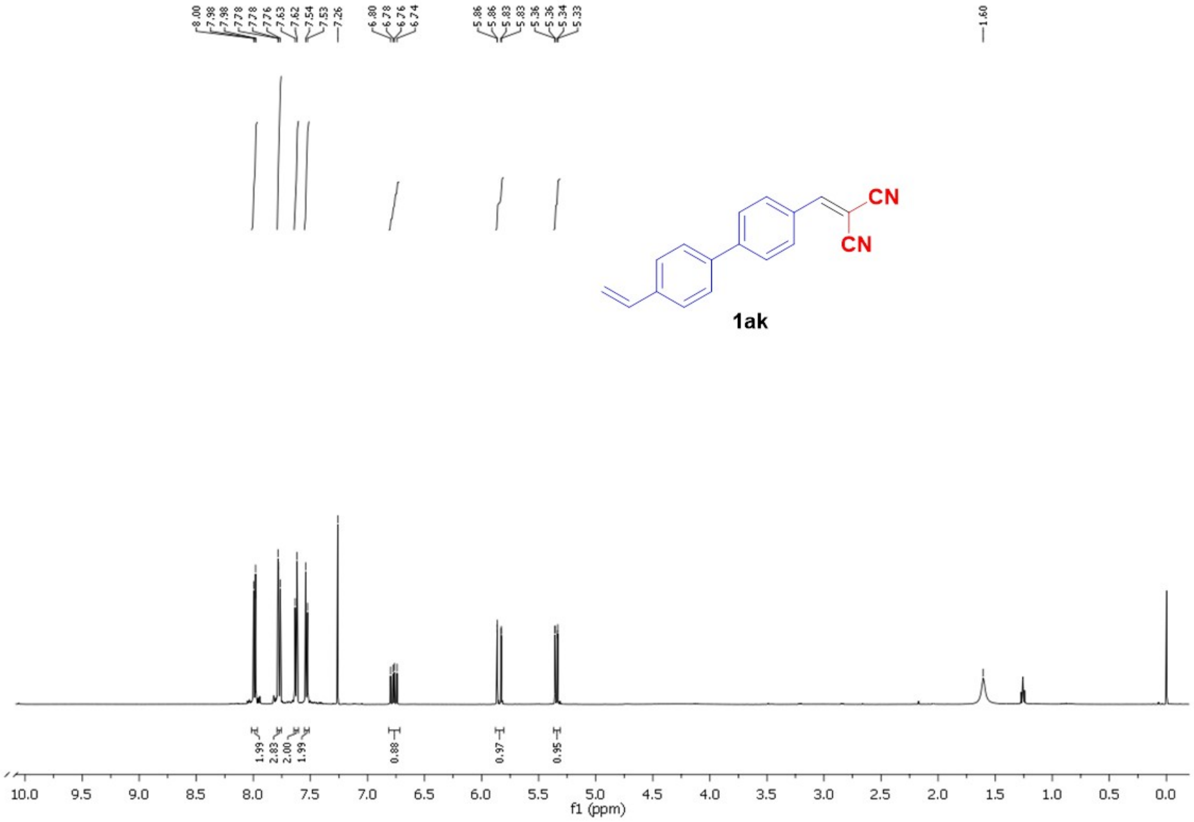
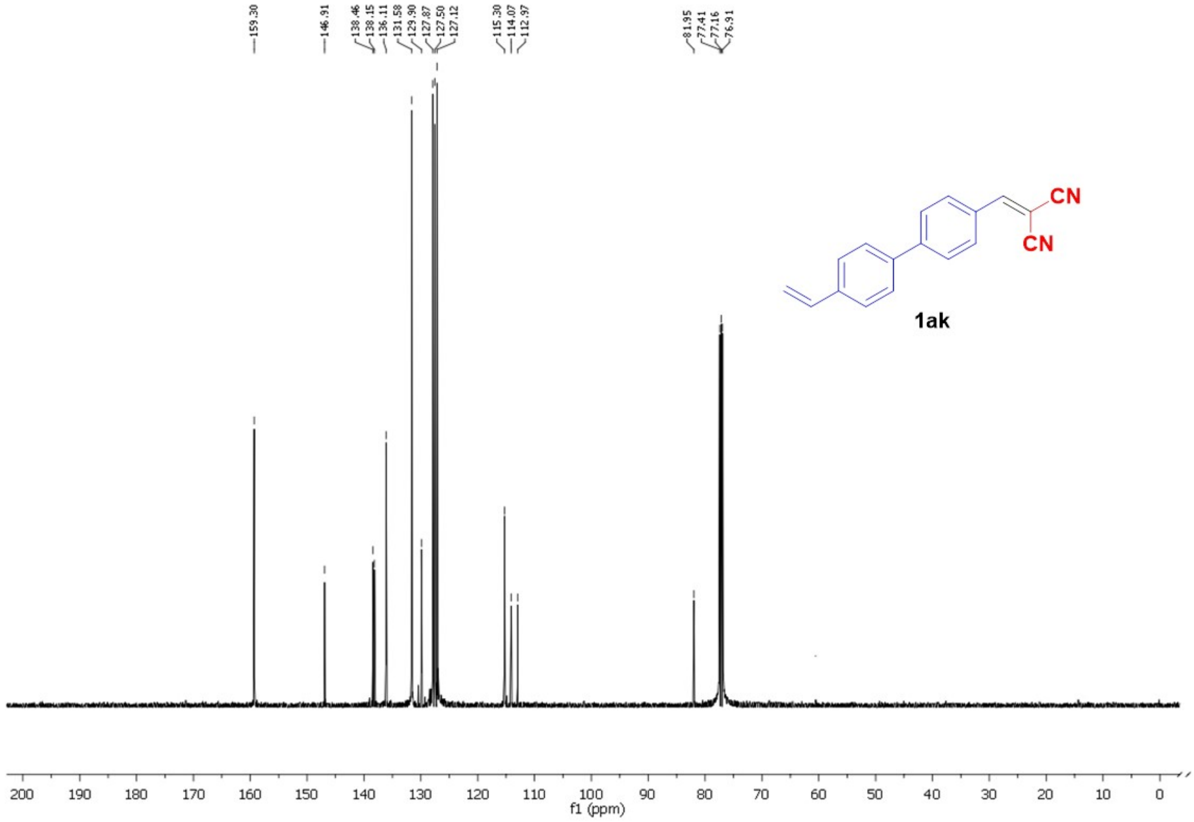
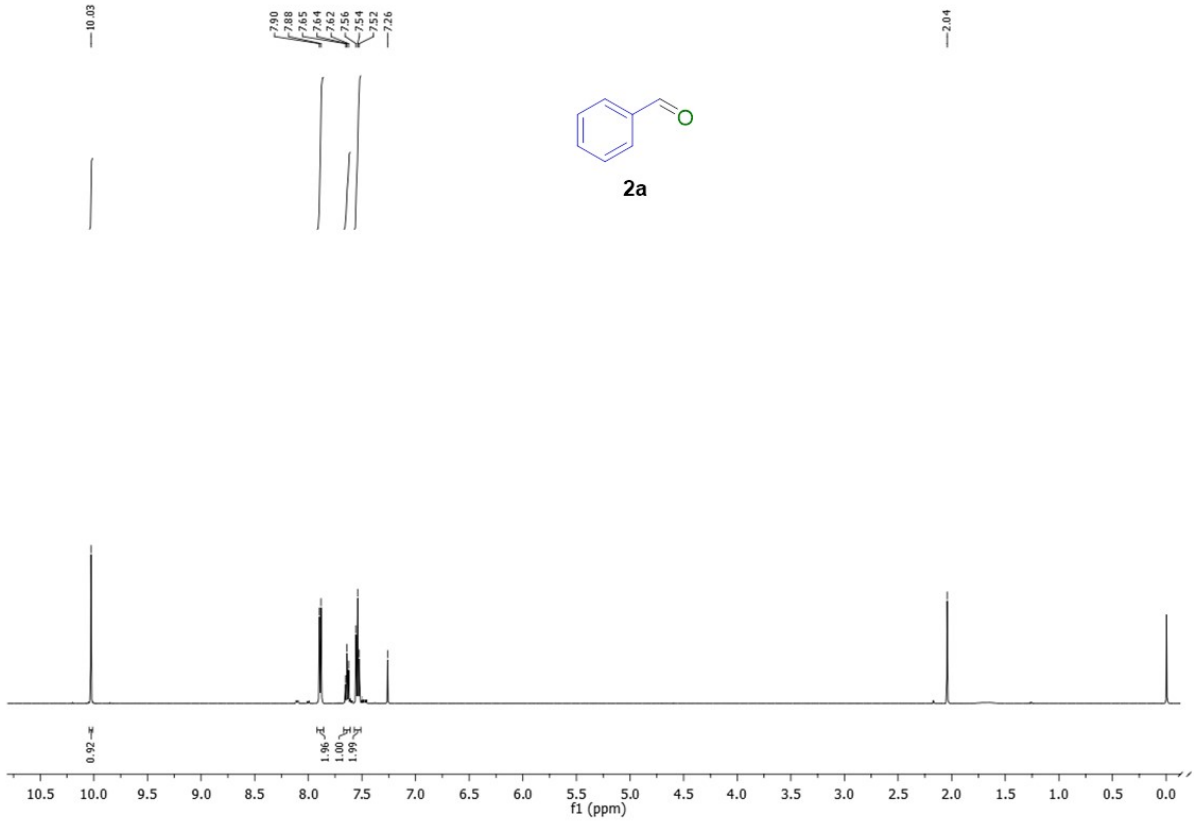


12.73
8.72
8.53
8.05
8.04
7.58
7.57
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26
3.34
2.51
2.50
2.50
2.50
2.49
CN
CN
N
H
0.93
1.01
0.99
1.03
1.00
2.13
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

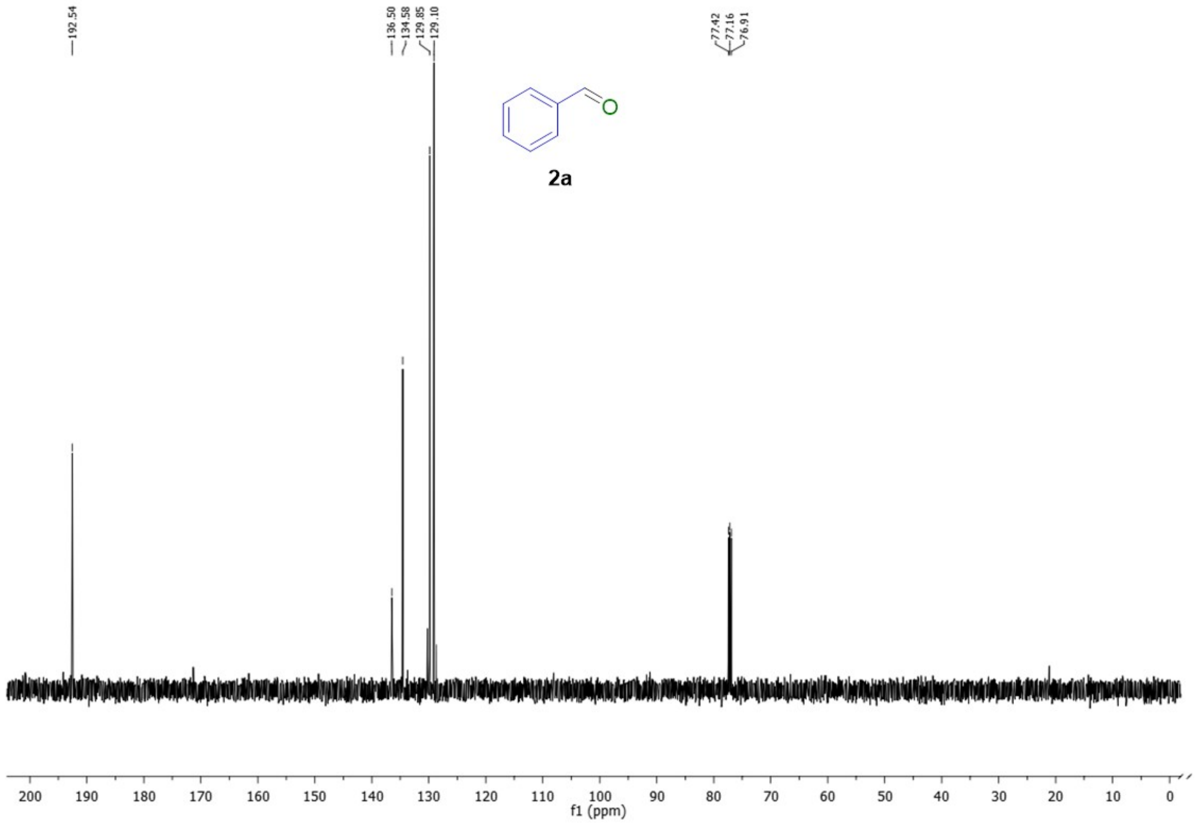
1aj


8.00
7.98
7.98
7.78
7.78
7.76
7.63
7.62
7.54
7.53
7.26
6.80
6.78
6.76
6.74
5.86
5.86
5.83
5.83
5.36
5.36
5.34
5.33
1.60
CN
CN
1ak
1.99
2.83
2.00
1.99
0.88
0.97
0.95
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)

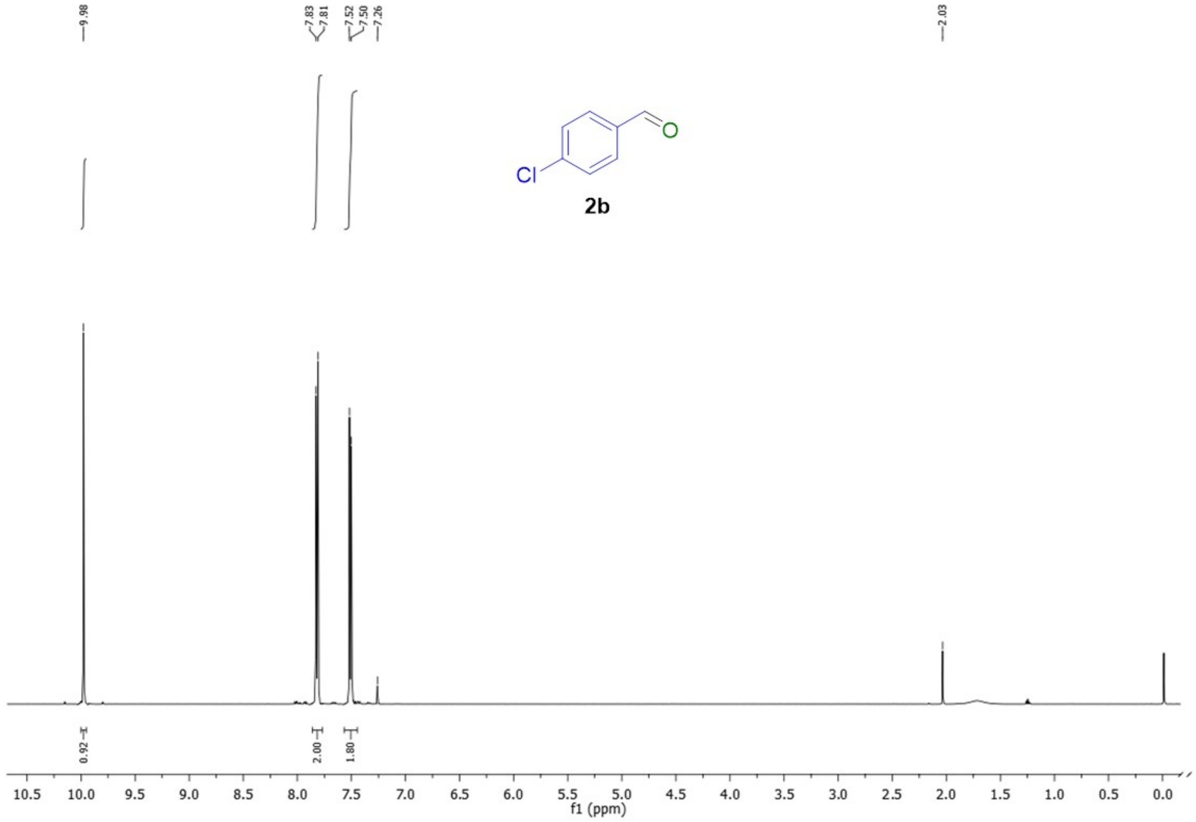

159.30
146.91
138.46
138.15
136.11
131.58
129.90
127.87
127.50
127.12
115.30
114.07
112.97
81.95
77.41
77.16
76.91
CN
CN
1ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.03
7.90
7.88
7.65
7.64
7.62
7.56
7.54
7.52
7.26
2.04
0.92
1.96
1.00
1.99
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)

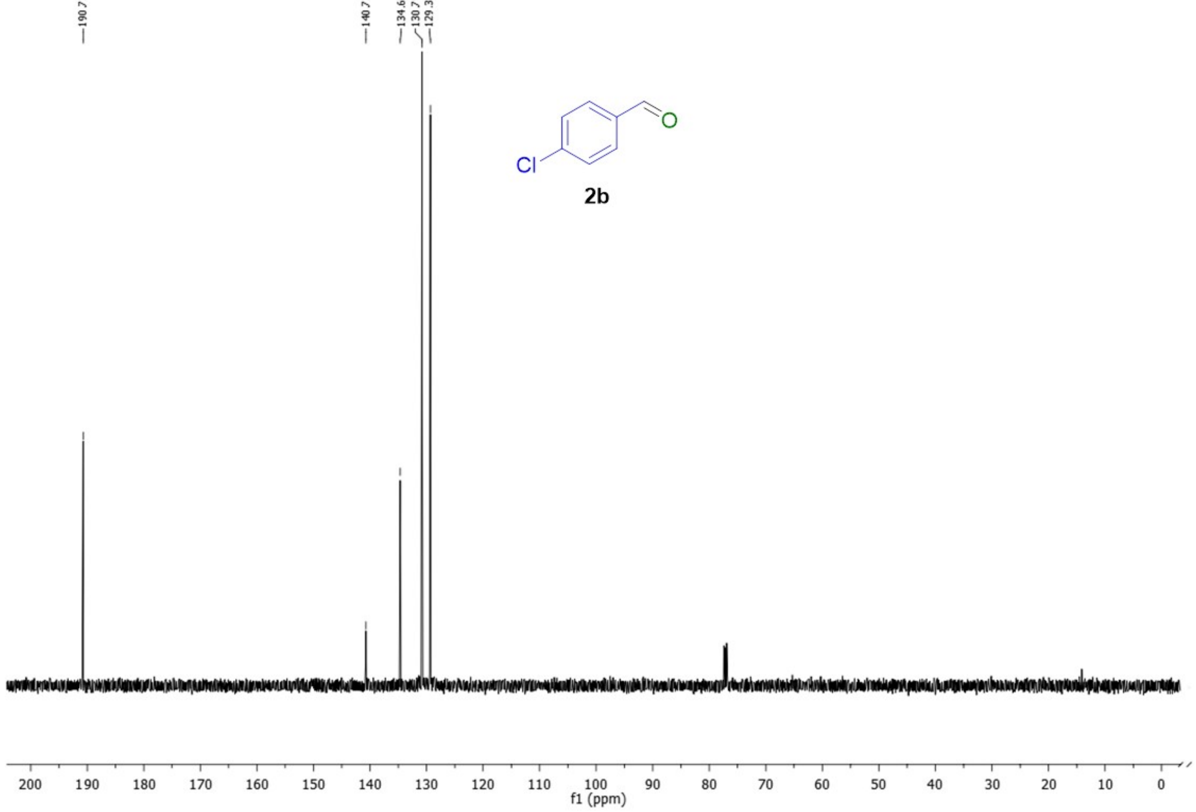
2a


192.54
136.50
134.58
129.85
129.10
77.42
77.16
76.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

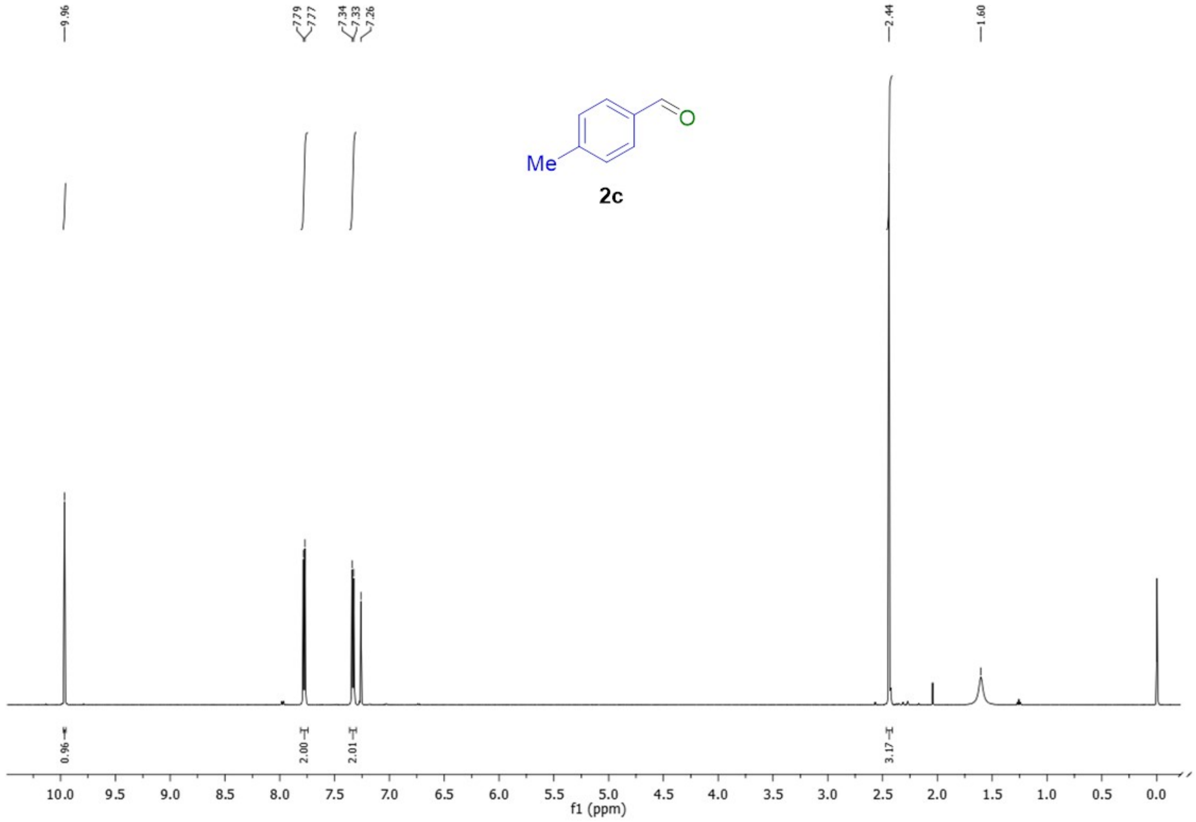
2a


9.98
7.83
7.81
7.52
7.50
7.26
2.03
Cl
O
0.92
2.00
1.80
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)

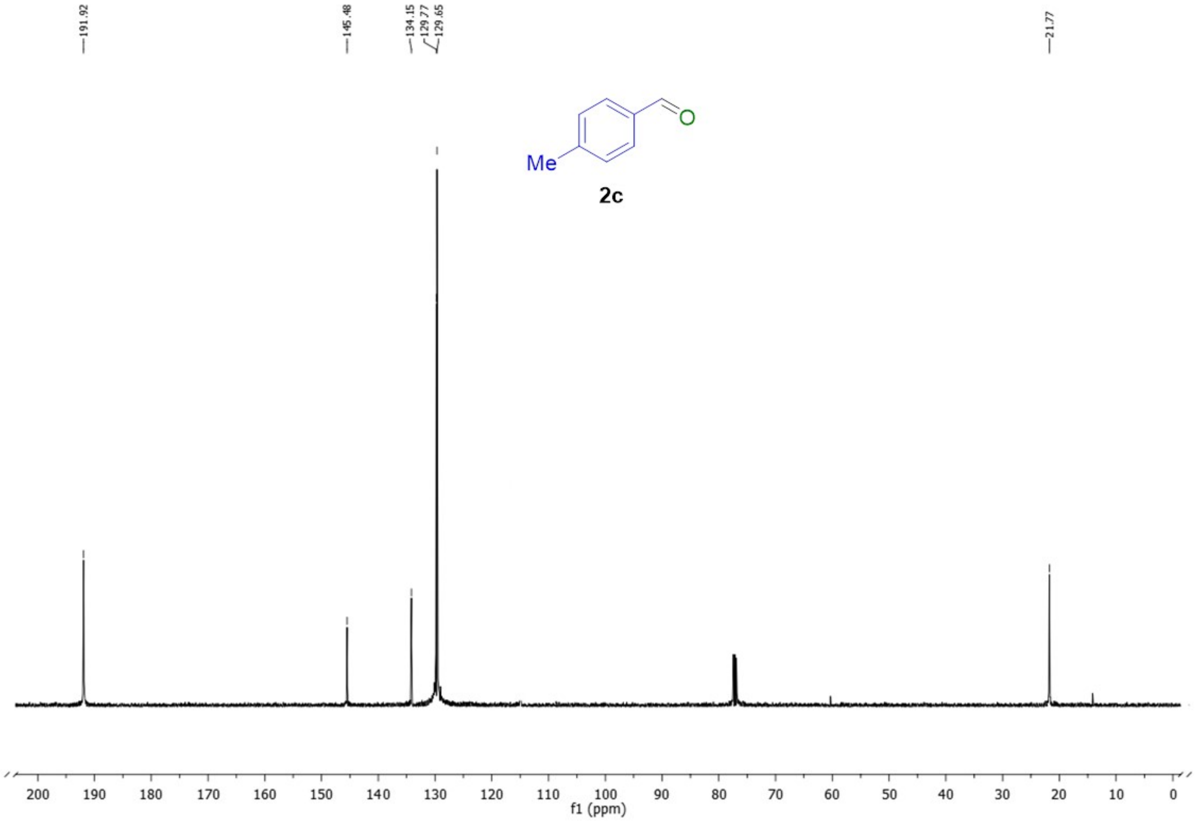
2b


190.73
140.72
134.65
130.79
129.31
Cl
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

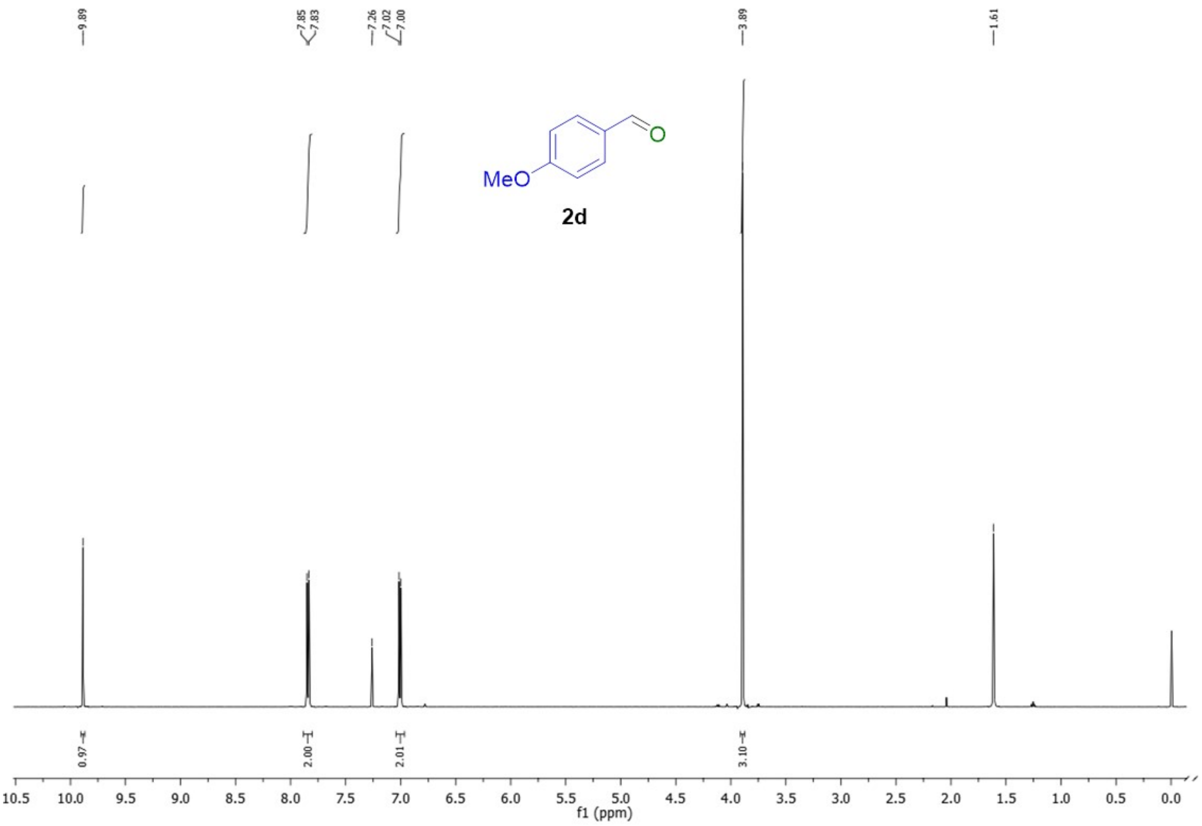
2b

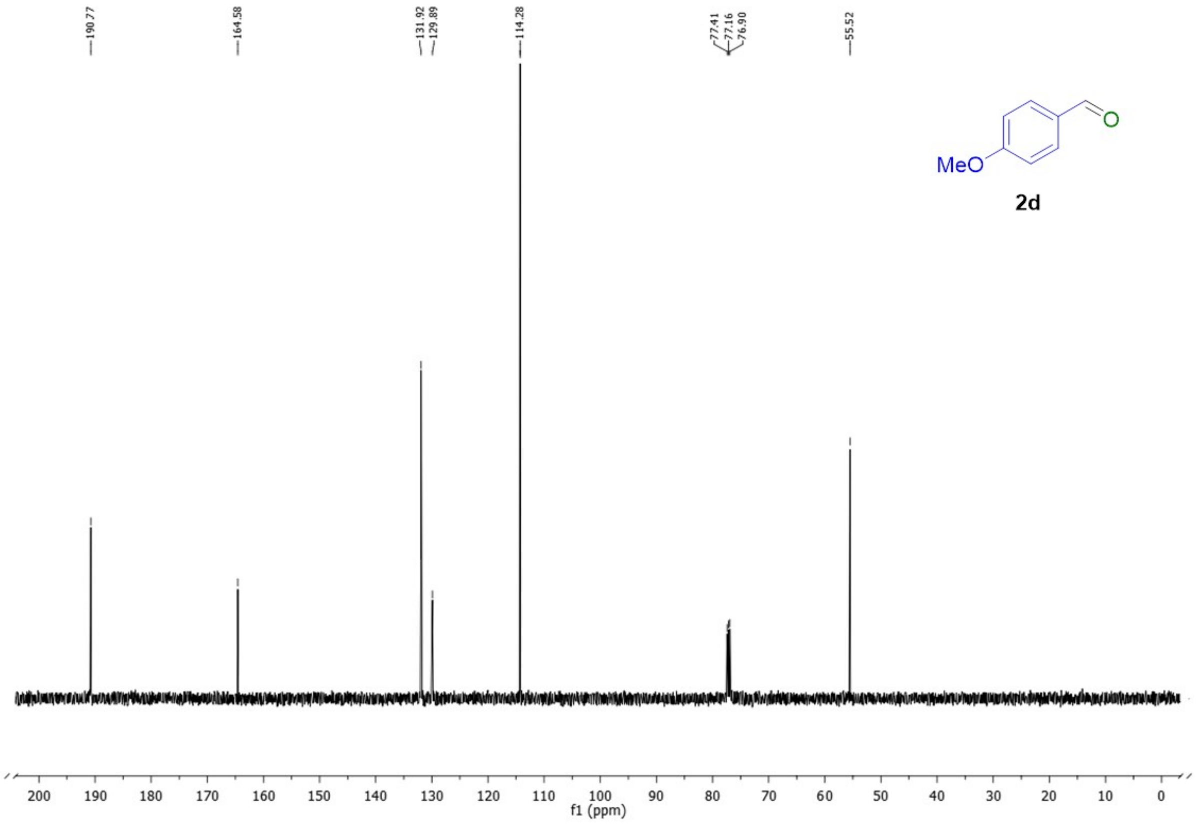

9.96
7.79
7.77
7.34
7.33
7.26
2.44
1.60
Me
O
0.96
2.00
2.01
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

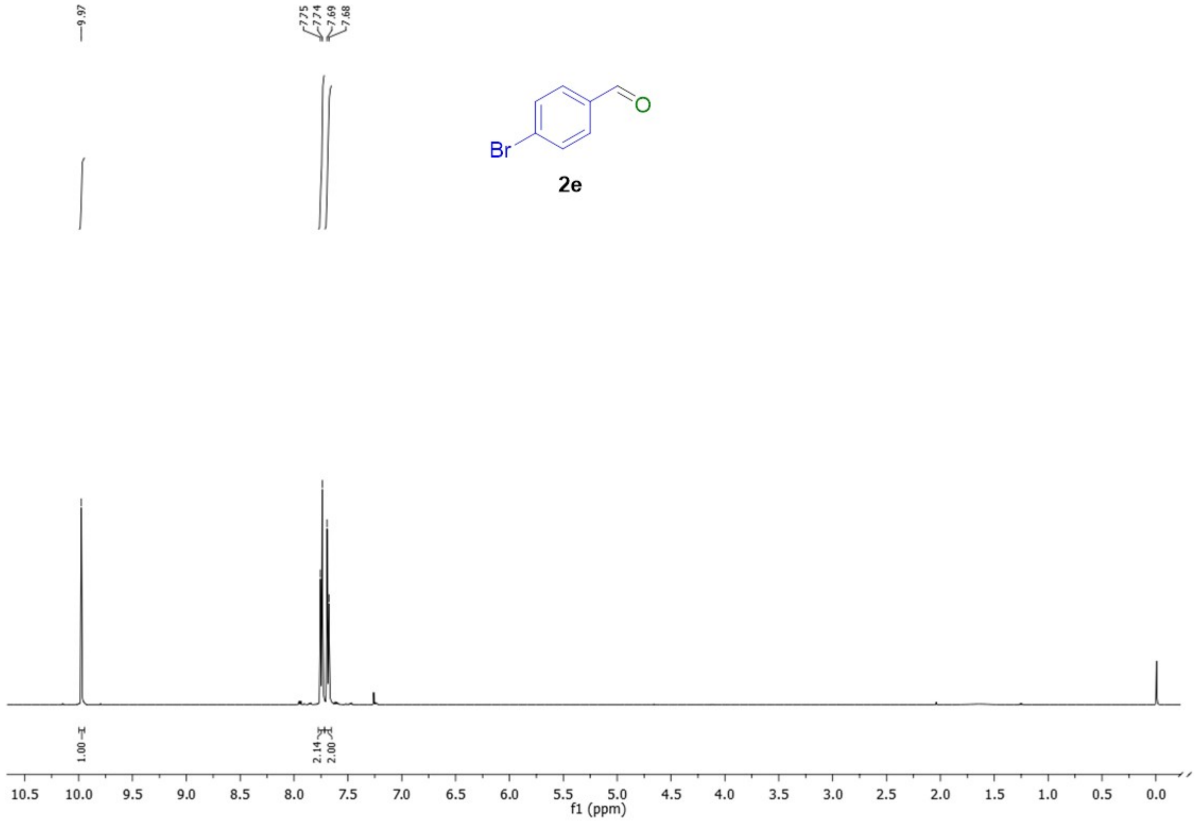
2c

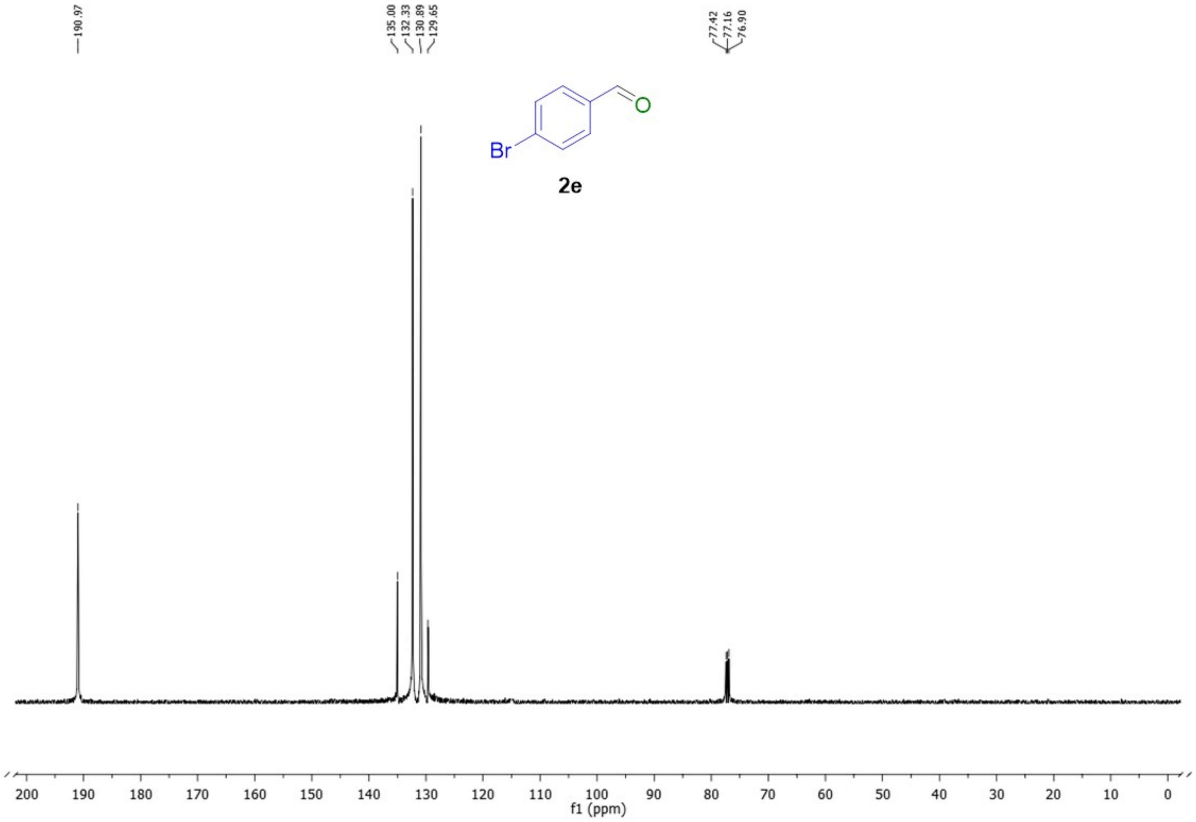

191.92
145.48
134.15
129.77
129.65
21.77
Me
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

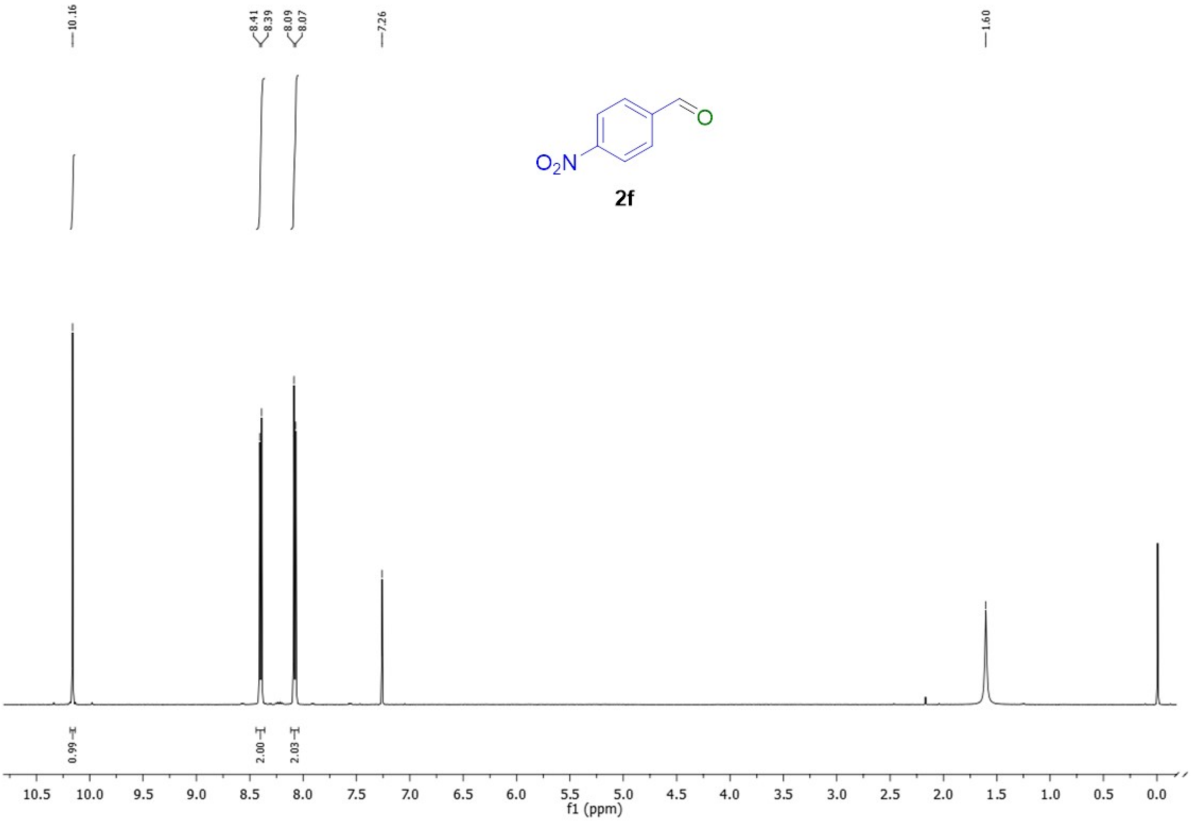
2c

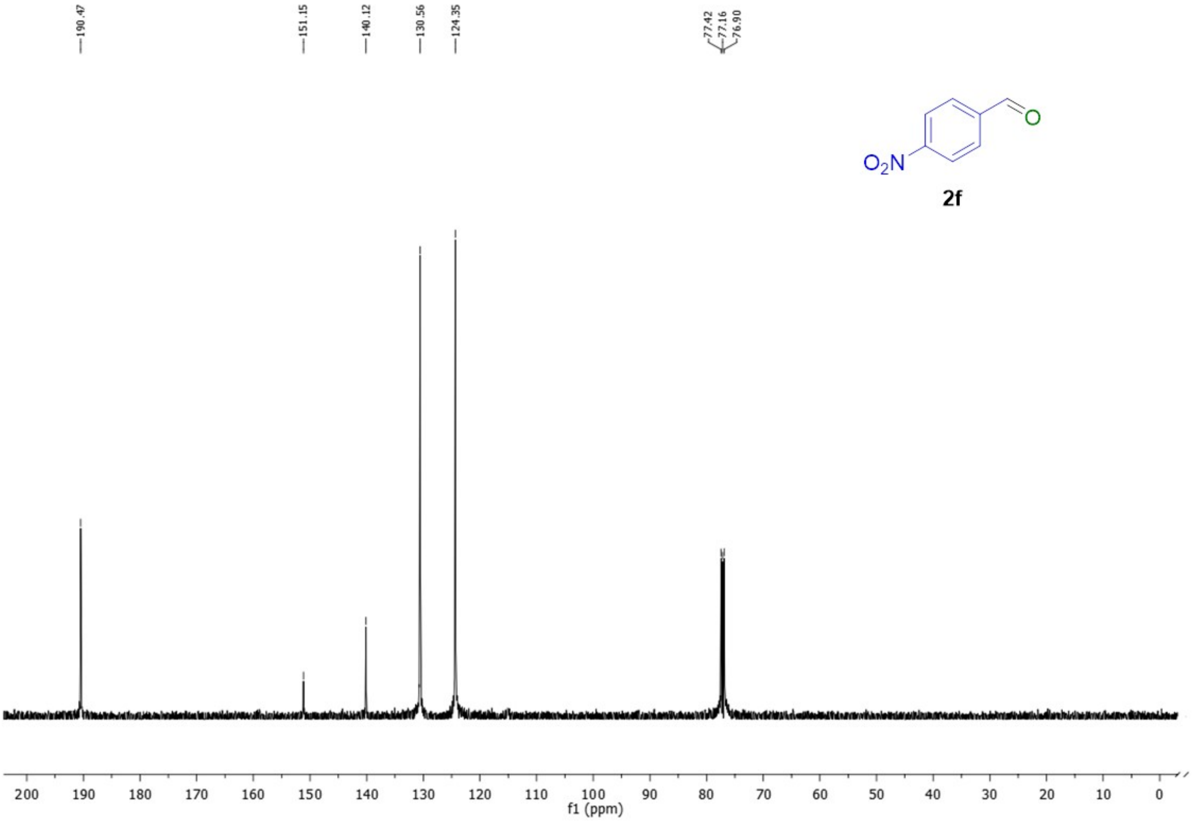

9.89
7.85
7.83
7.26
7.02
7.00
3.89
1.61
MeO
O
2d
0.97
2.00
2.01
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

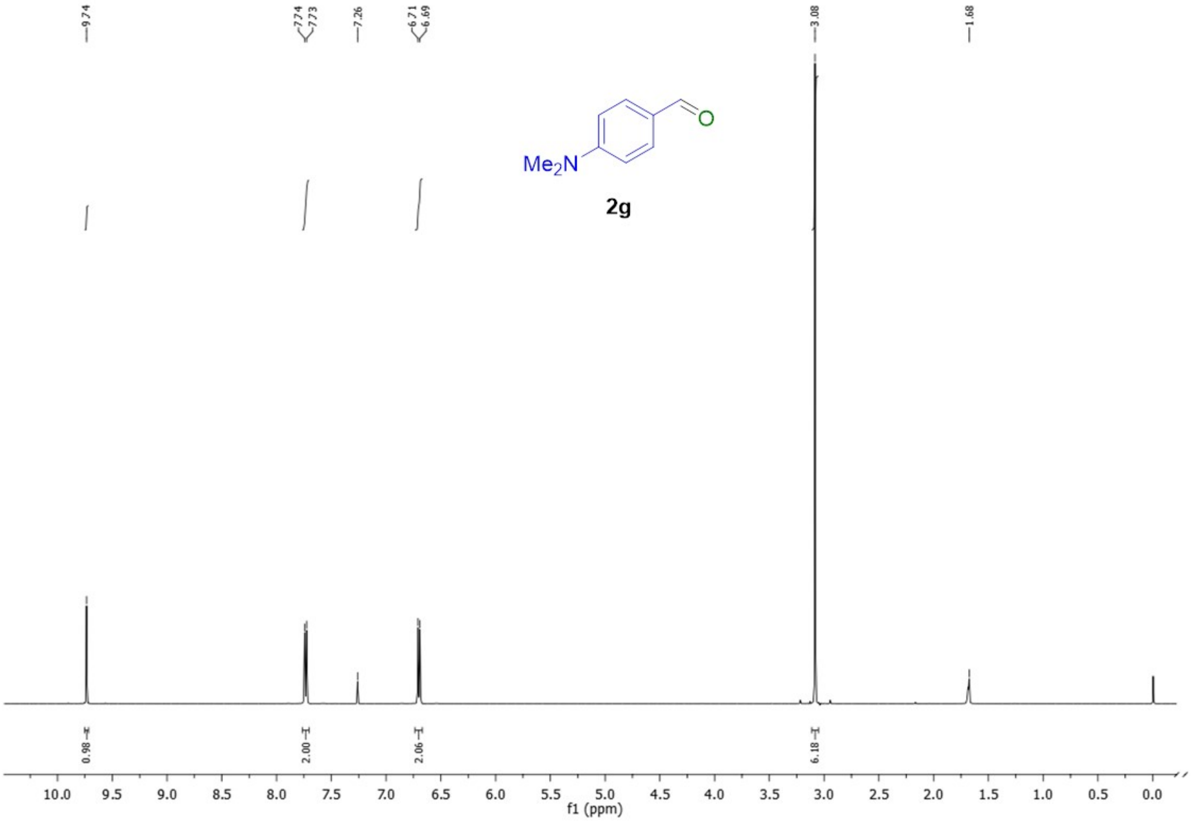

190.77
164.58
131.92
129.89
114.28
77.41
77.16
76.90
55.52
MeO
O
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.97
7.75
7.74
7.69
7.68
Br
O
2e
1.00
2.14
2.00
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)

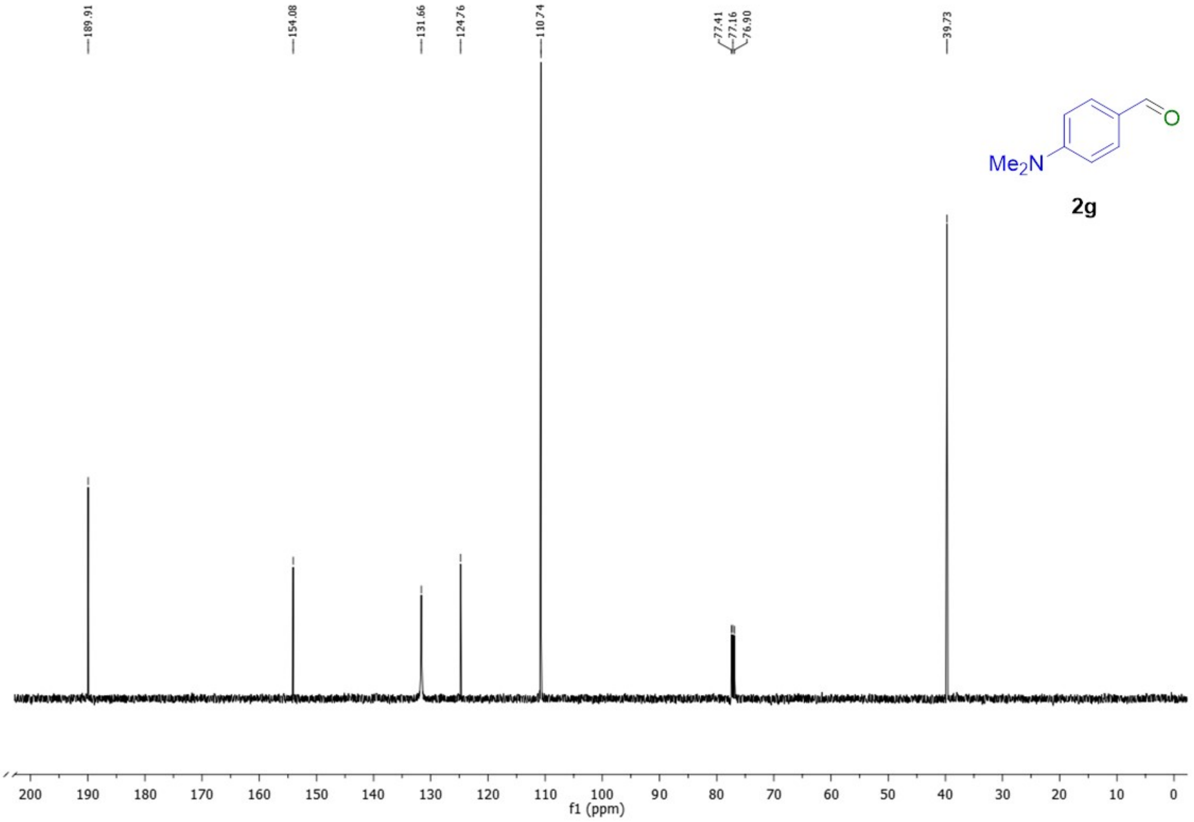

190.97
135.00
132.33
130.89
129.65
77.42
77.16
76.90
Br
O
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.16
8.41
8.39
8.09
8.07
7.26
1.60
O_2N
O
2f
0.99
2.00
2.03
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)

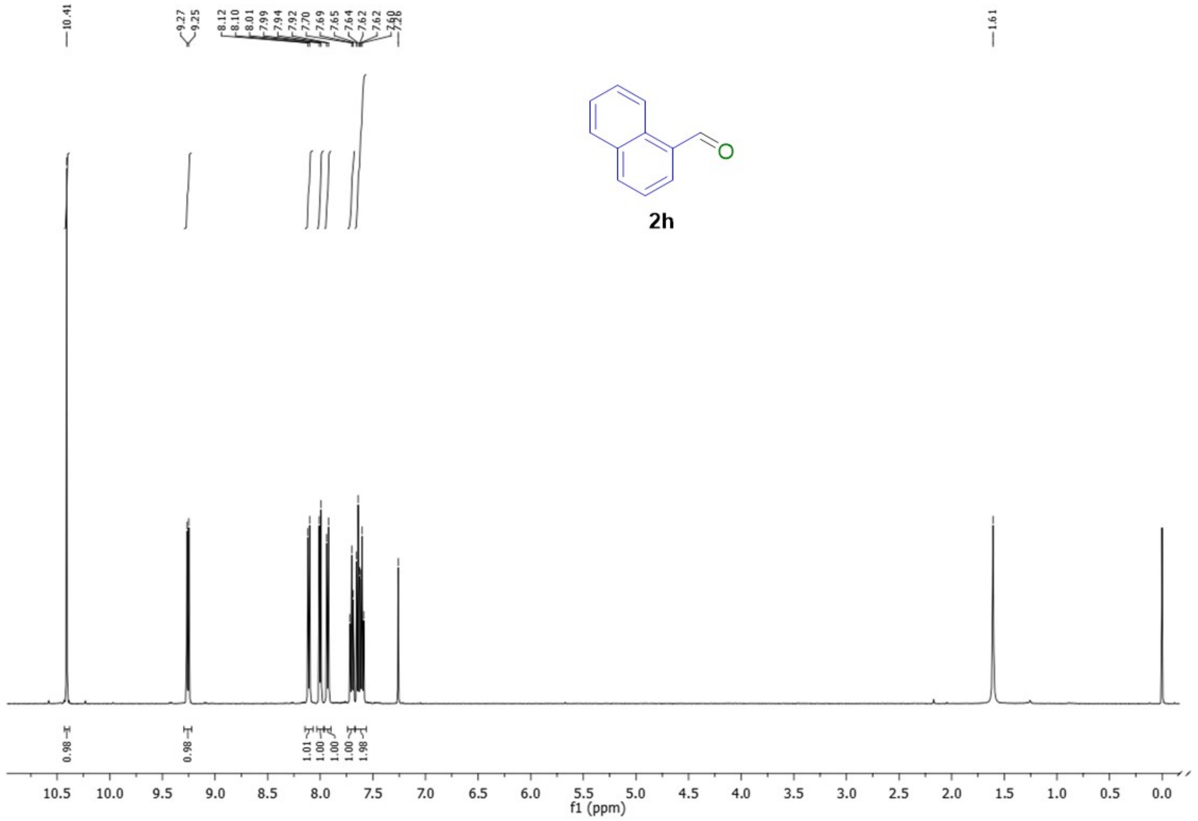

190.47
151.15
140.12
130.56
124.35
77.42
77.16
76.90
O_2N
O
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



9.74
7.74
7.73
7.26
6.71
6.69
3.08
1.68
Me$_2$N
2g
0.98
2.00
2.06
6.18
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)

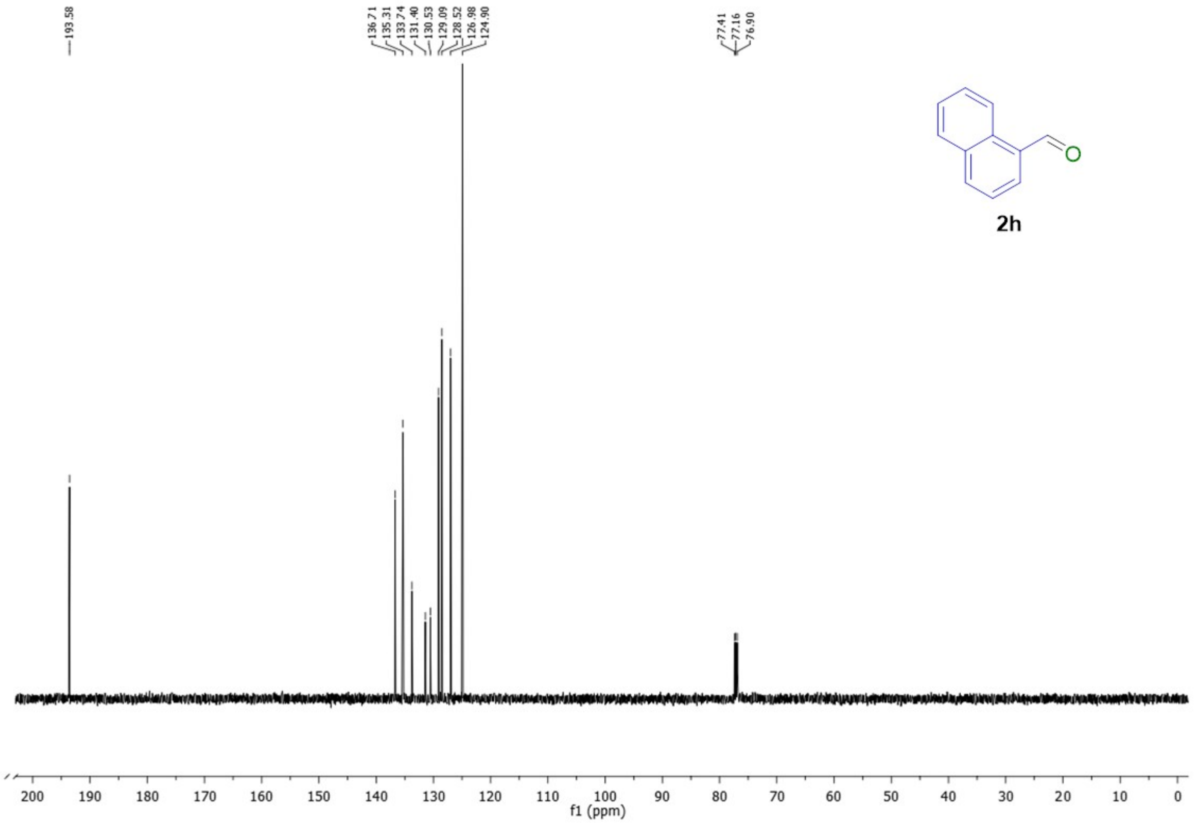


189.91
154.08
131.66
124.76
110.74
77.41
77.16
76.90
39.73
Me$_2$N
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



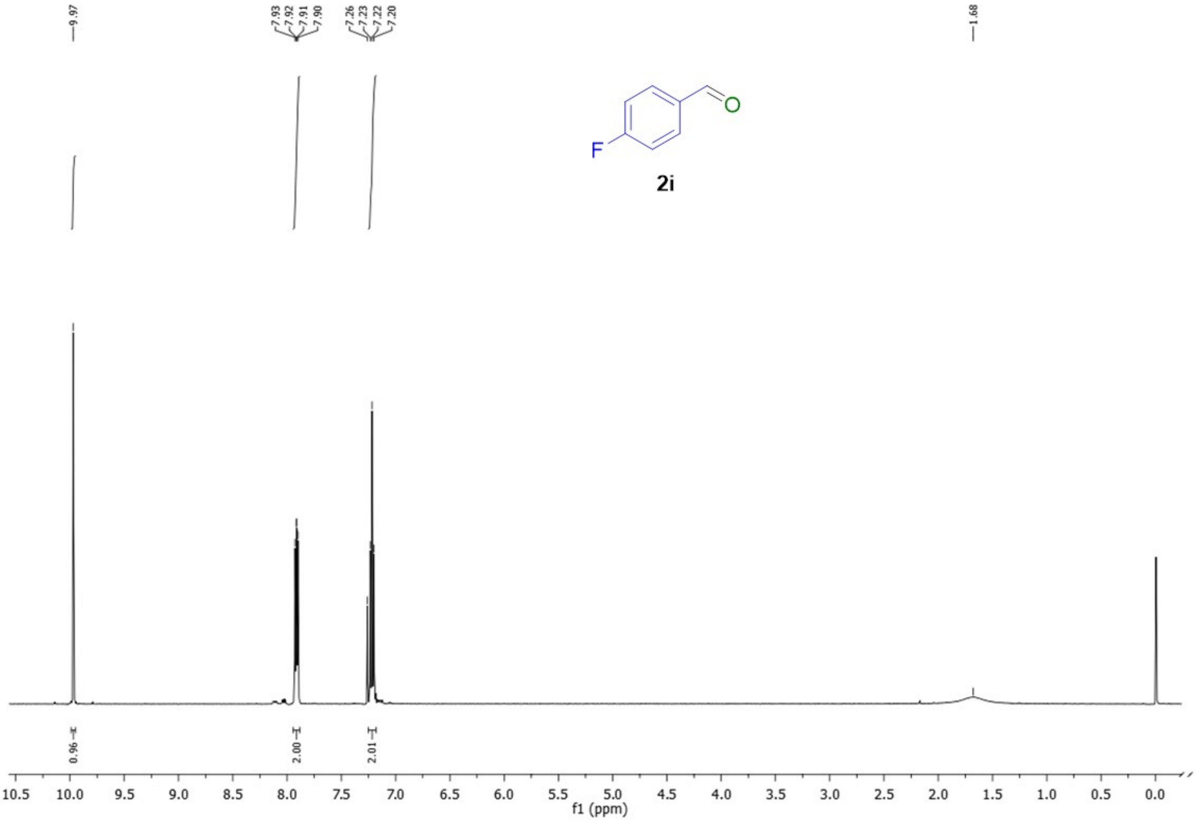
10.41
9.27
9.25
8.12
8.10
8.01
7.99
7.94
7.92
7.70
7.69
7.65
7.64
7.62
7.62
7.60
7.26
1.61
0.98
0.98
1.01
1.00
1.00
1.00
1.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O

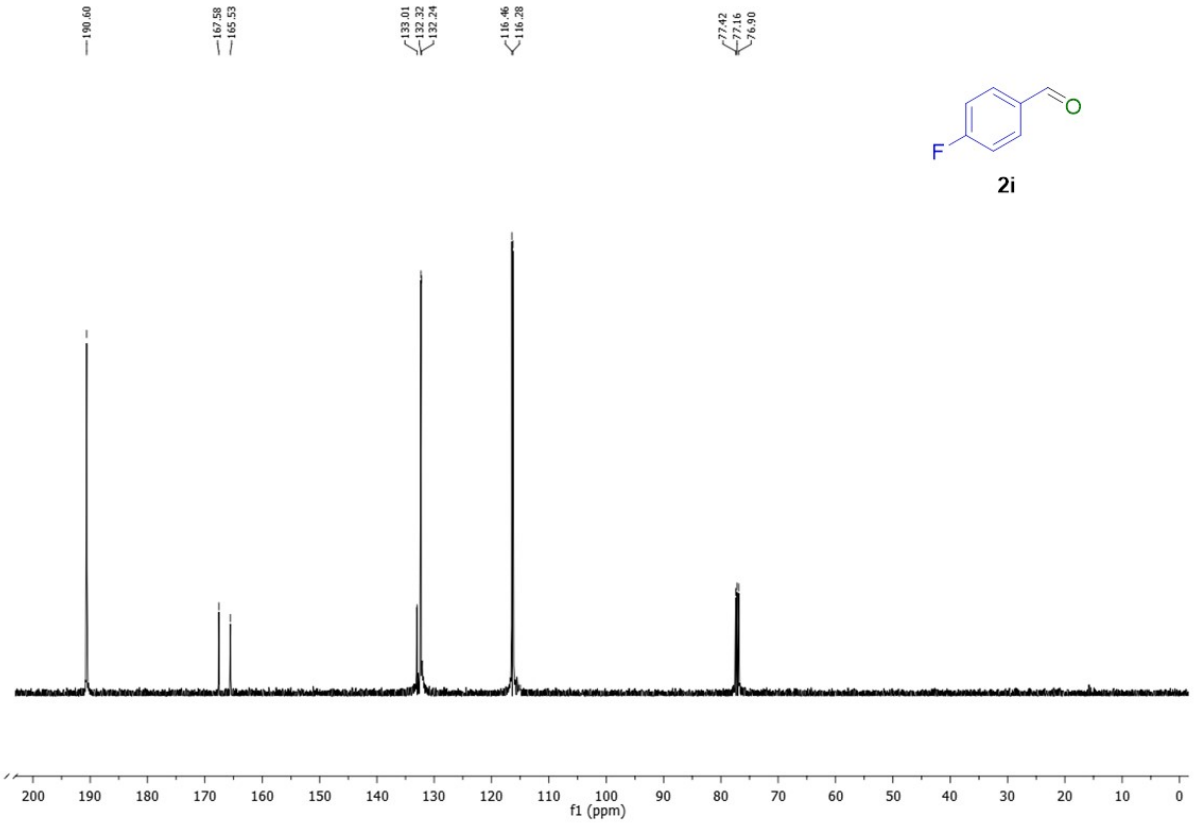
2h

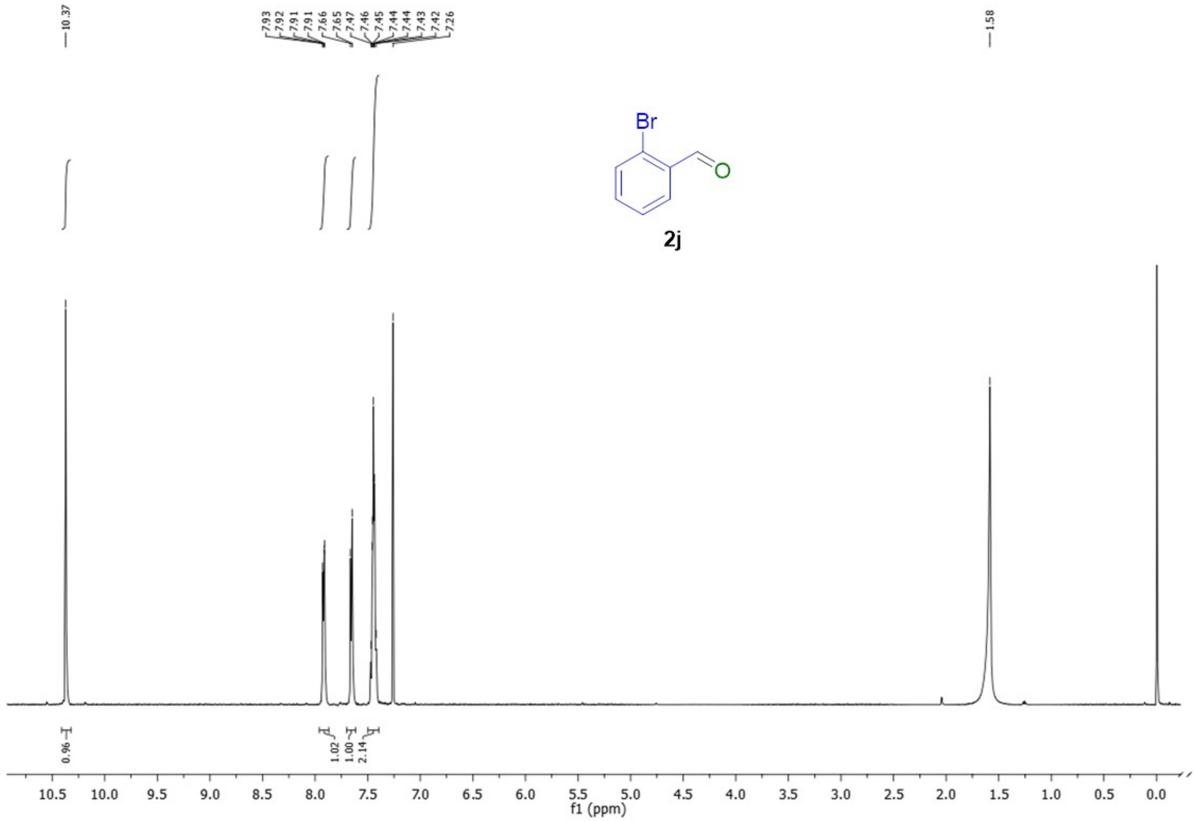


193.58
136.71
135.31
133.74
131.40
130.53
129.09
128.52
126.98
124.90
77.41
77.16
76.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O

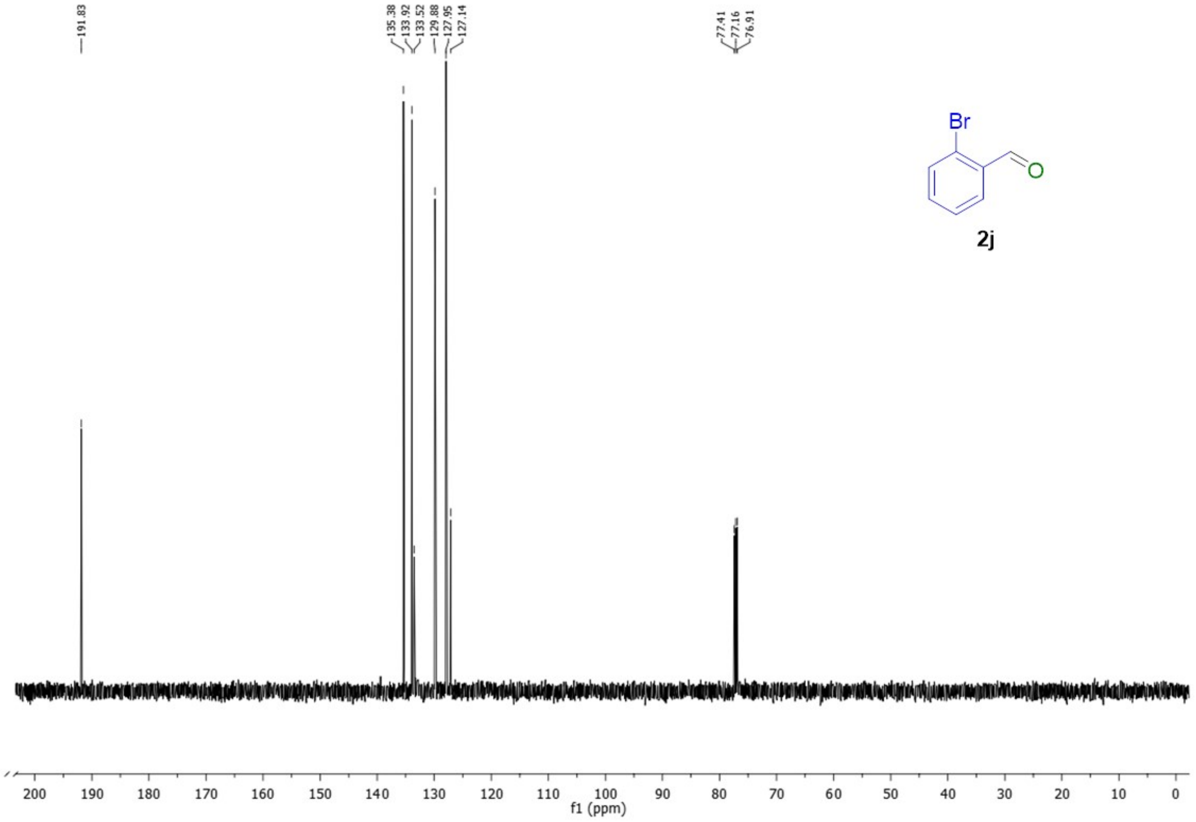
2h


9.97
7.93
7.92
7.91
7.90
7.26
7.23
7.22
7.20
1.68
F
O
2i
0.96
2.00
2.01
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)

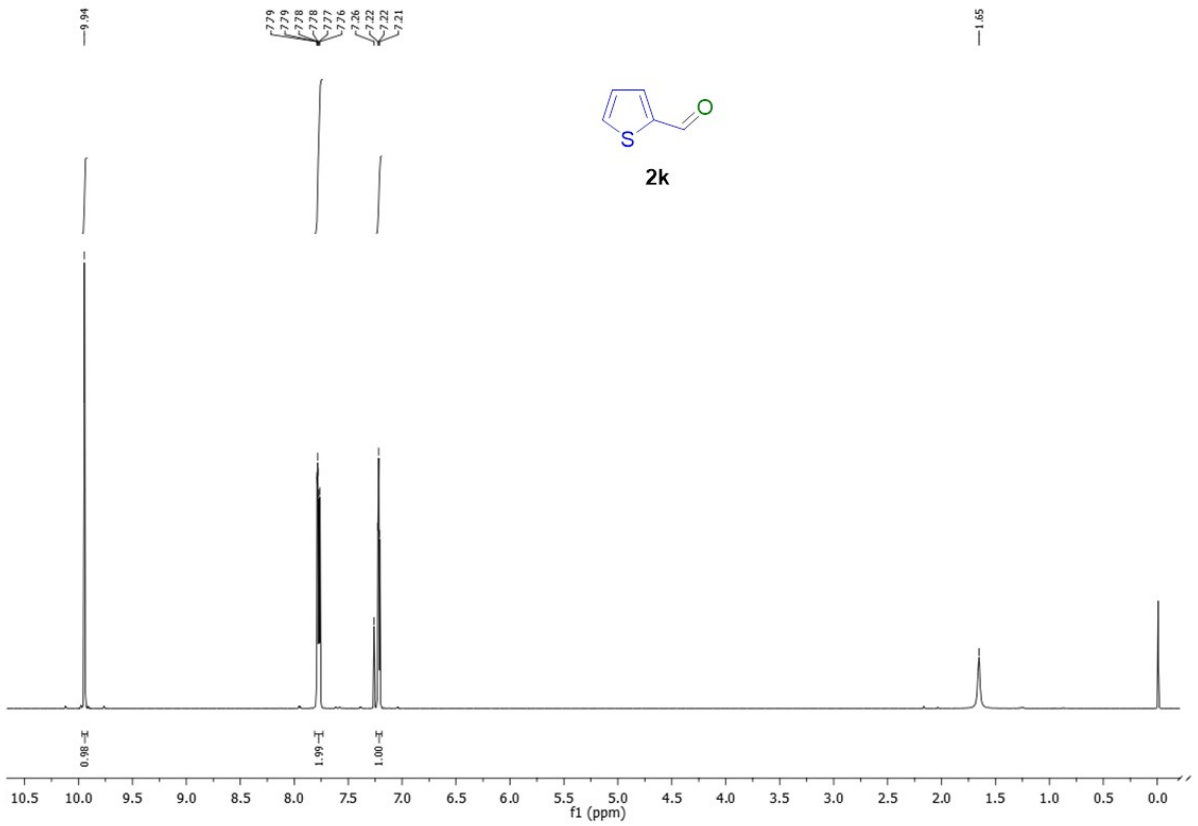

190.60
167.58
165.53
133.01
132.32
132.24
116.46
116.28
77.42
77.16
76.90
F
O
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

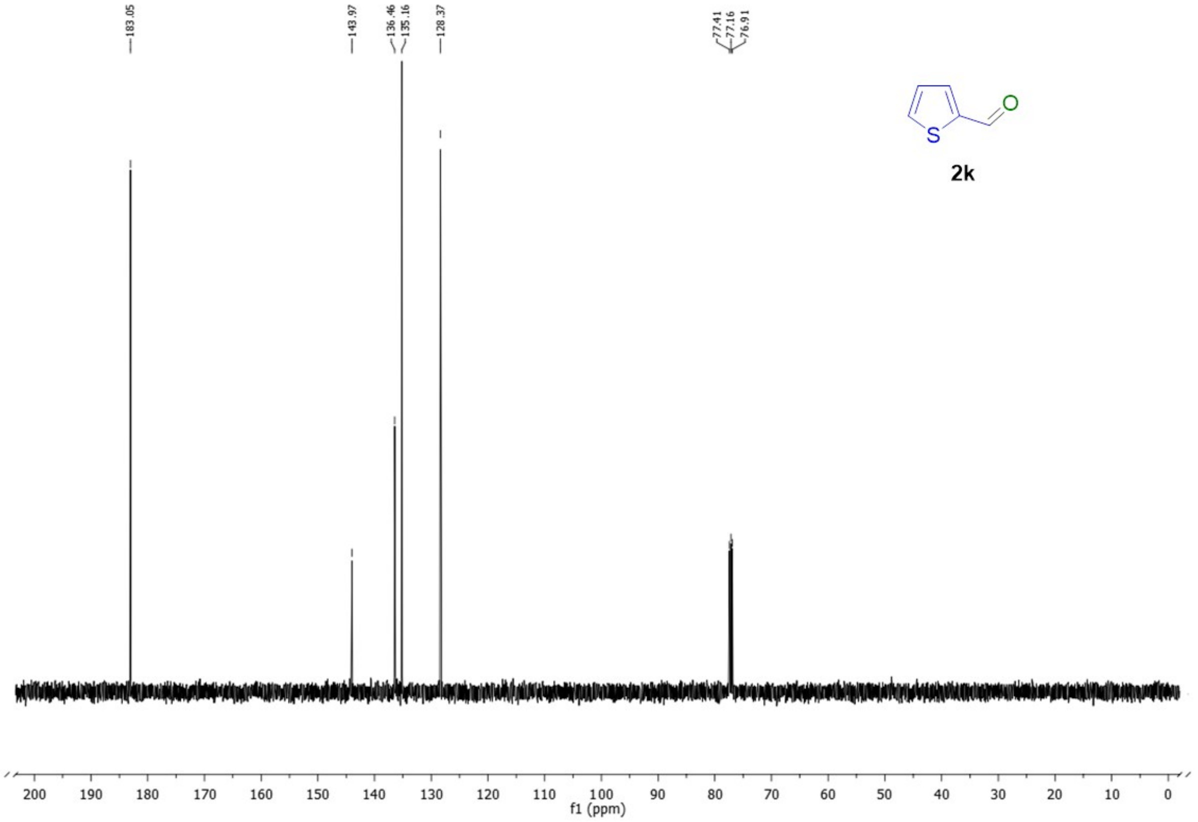

10.37
7.93
7.92
7.91
7.91
7.66
7.65
7.47
7.46
7.45
7.44
7.44
7.43
7.42
7.26
1.58
Br
O
0.96
1.02
1.00
2.14
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

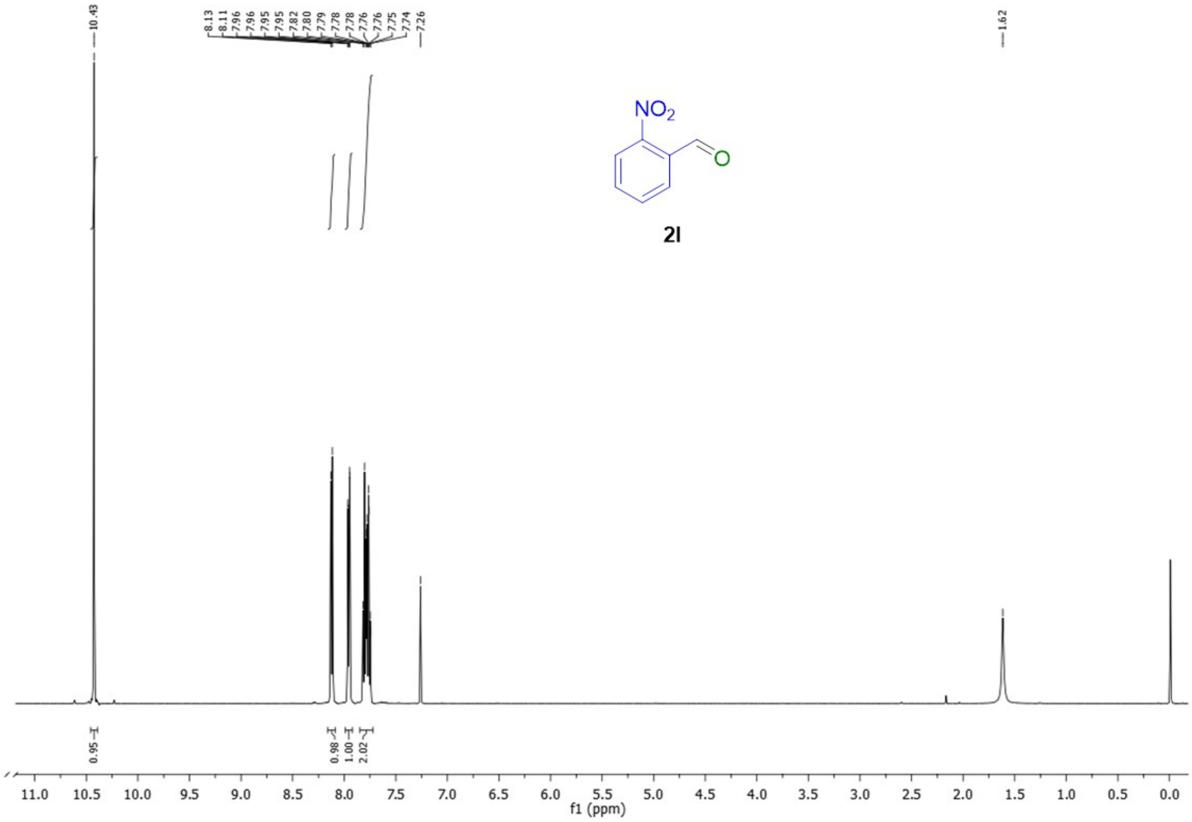
2j

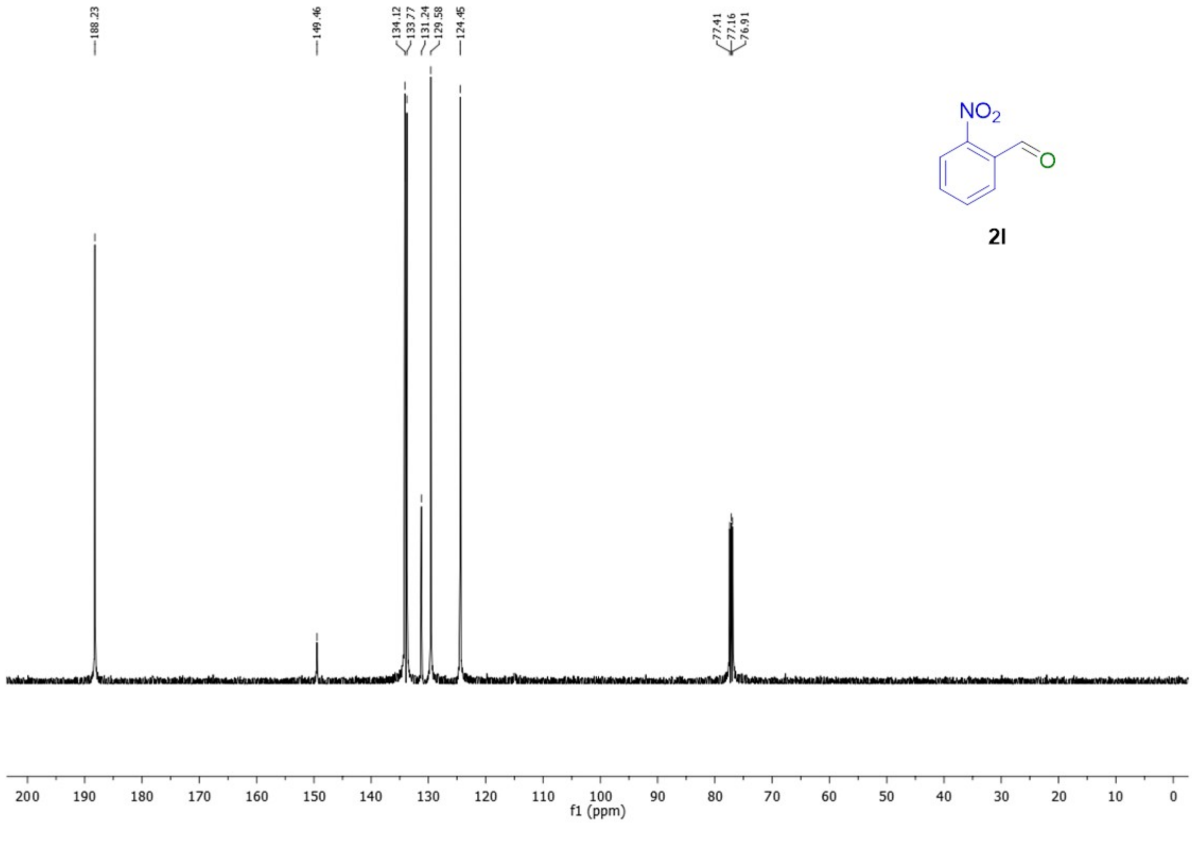

191.83
135.38
133.92
133.52
129.88
127.95
127.14
77.41
77.16
76.91
Br
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

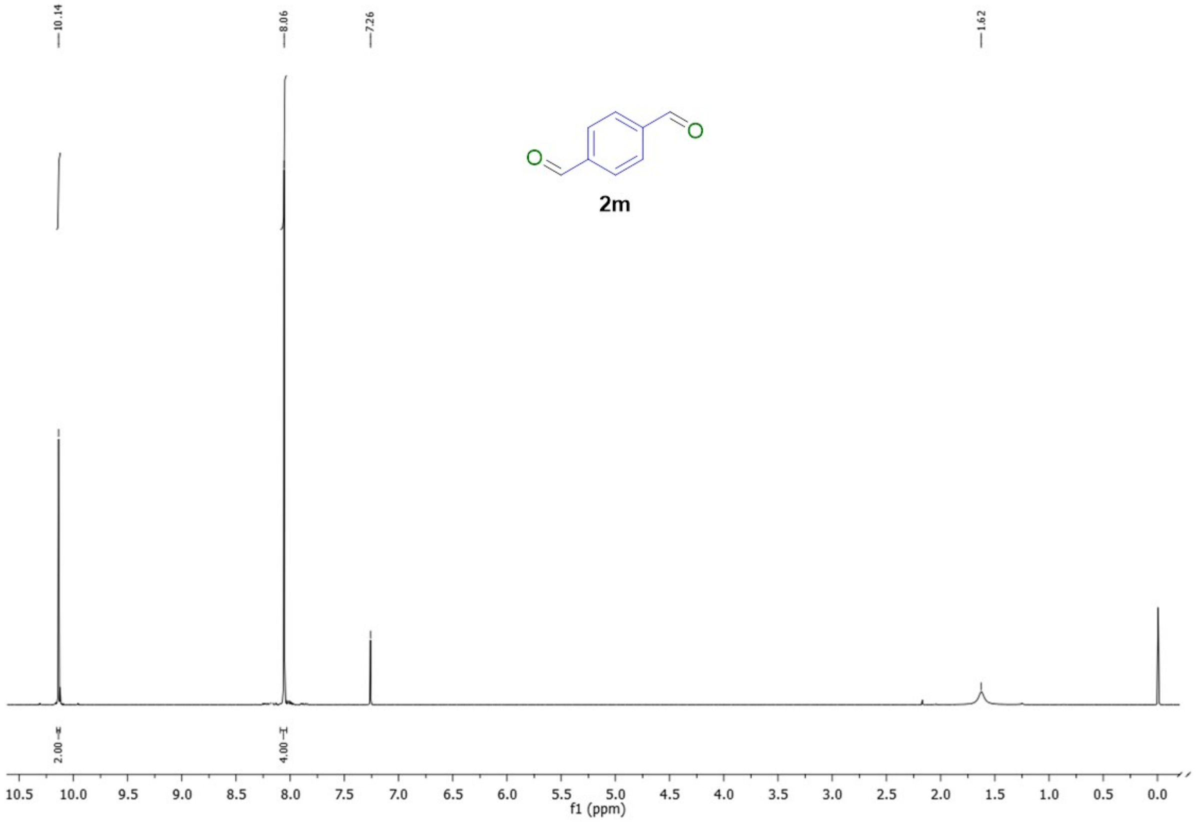
2j

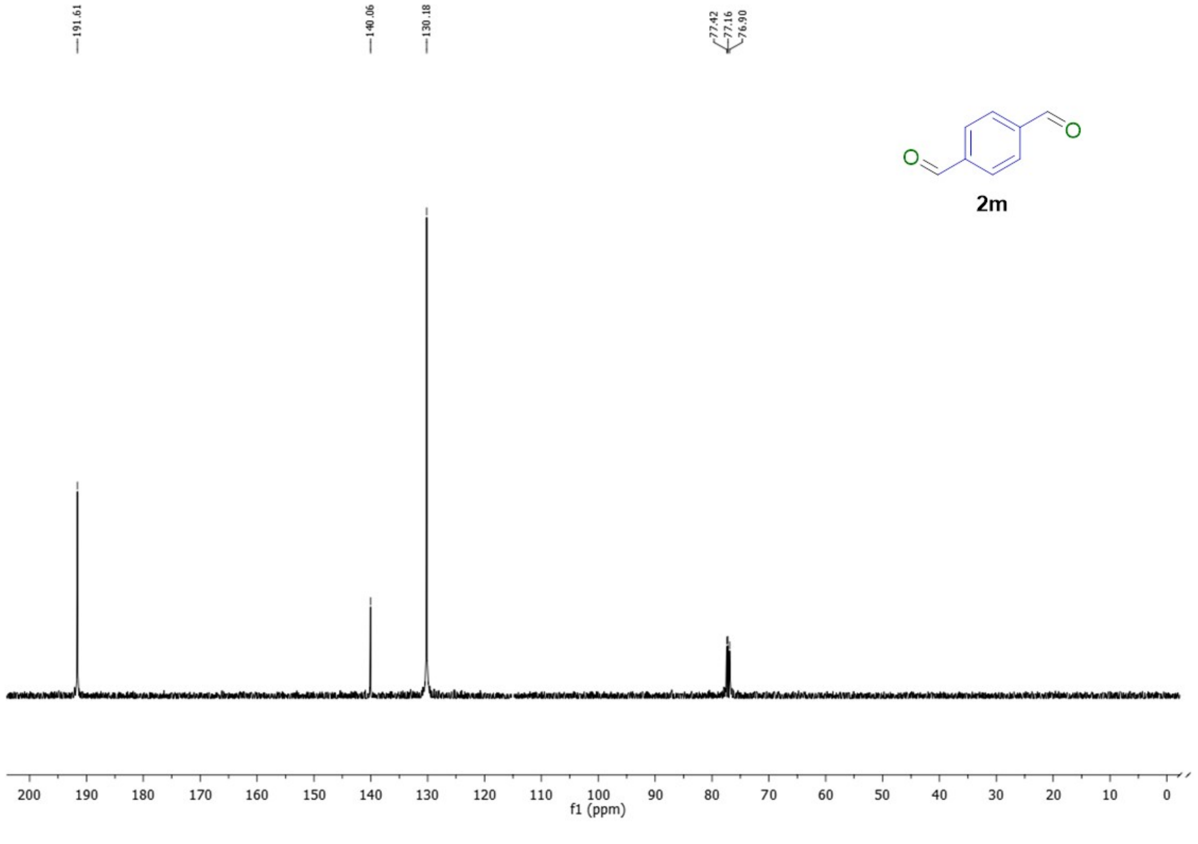

9.94
7.79
7.79
7.78
7.78
7.77
7.76
7.26
7.22
7.22
7.21
1.65
O
S
2k
0.98
1.99
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

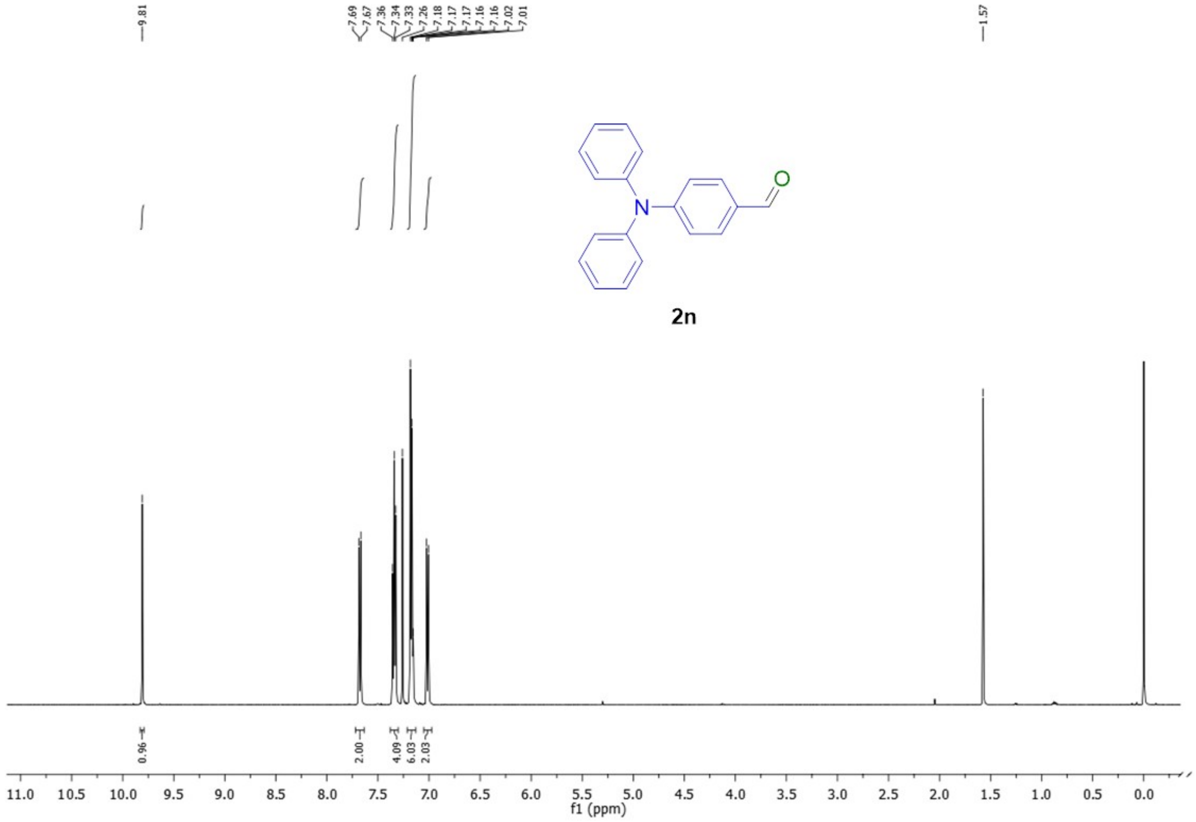

183.05
143.97
136.46
135.16
128.37
77.41
77.16
76.91
O
S
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.43
8.13
8.11
7.96
7.96
7.95
7.95
7.82
7.80
7.79
7.78
7.78
7.76
7.76
7.75
7.74
7.26
1.62
NO2
O
2l
0.95
0.98
1.00
2.02
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)

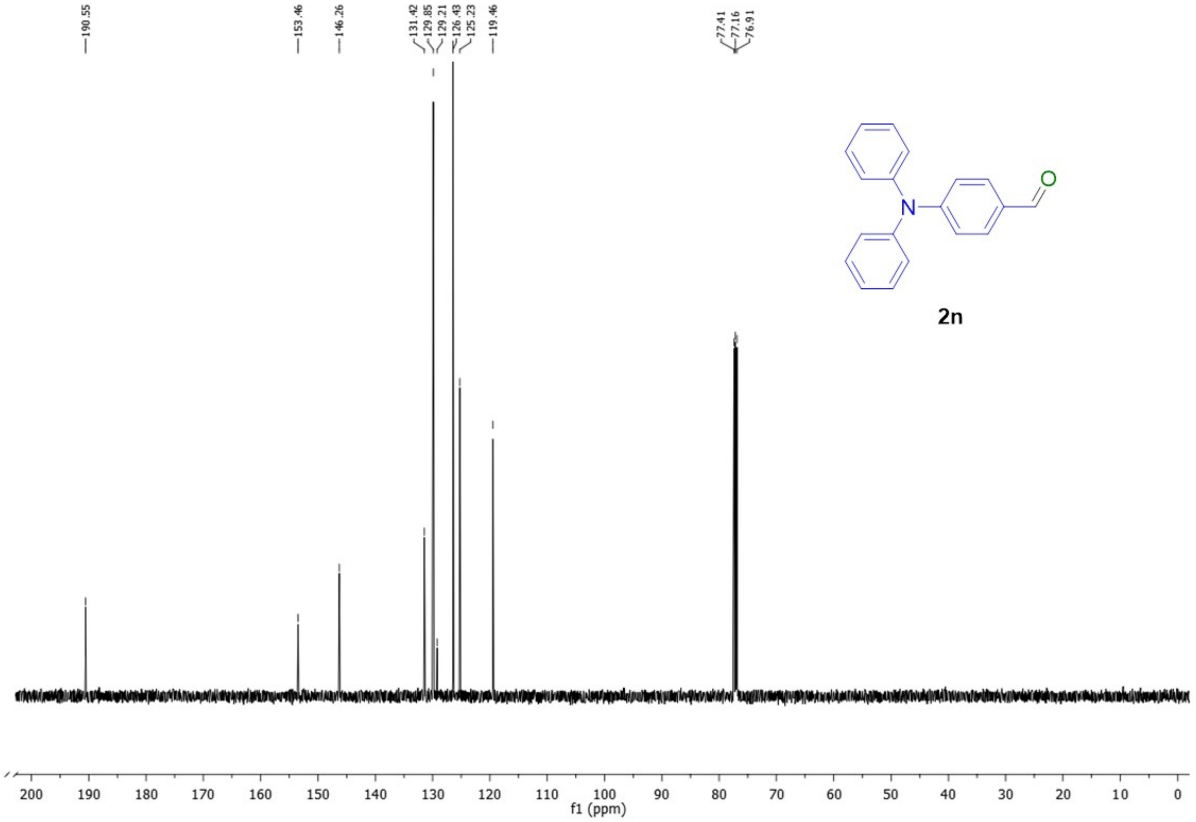

188.23
149.46
134.12
133.77
131.24
129.58
124.45
77.41
77.16
76.91
NO2
O
2l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.14
8.06
7.26
1.62
2m
2.00
4.00
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)

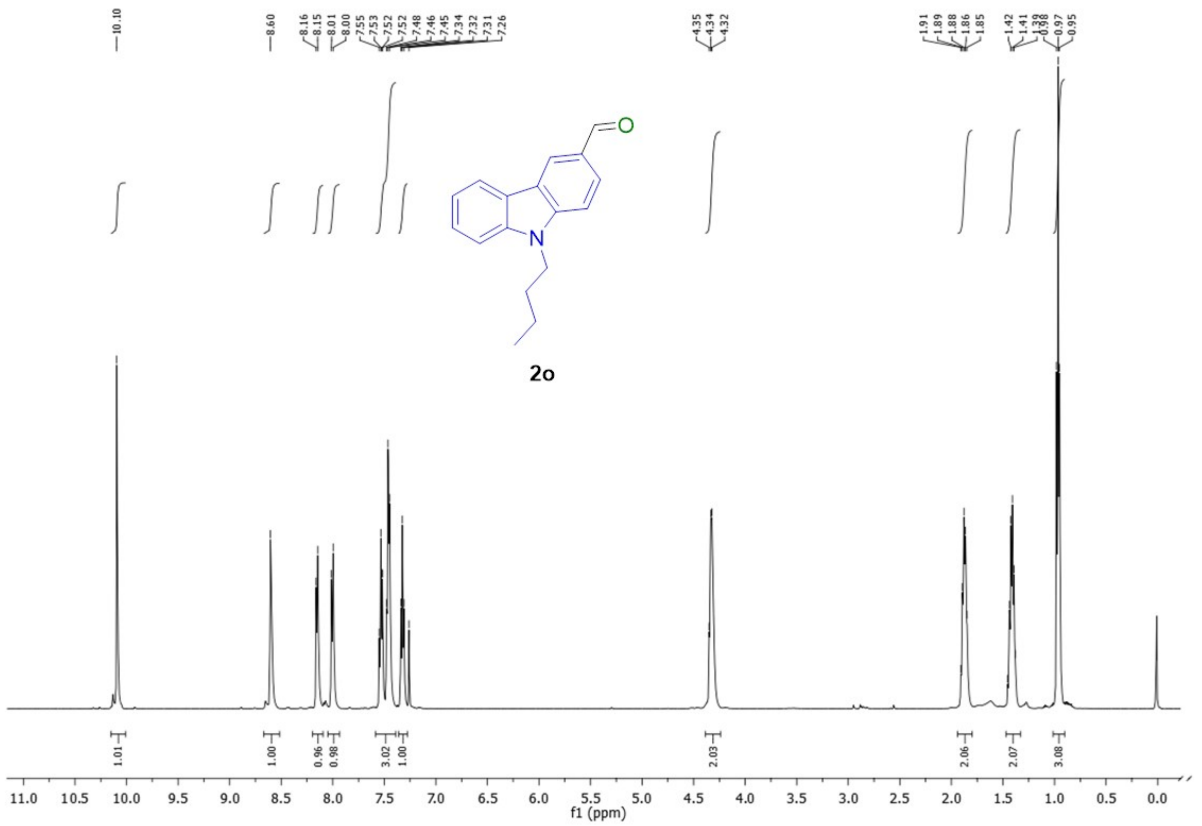

191.61
140.06
130.18
77.42
77.16
76.90
2m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

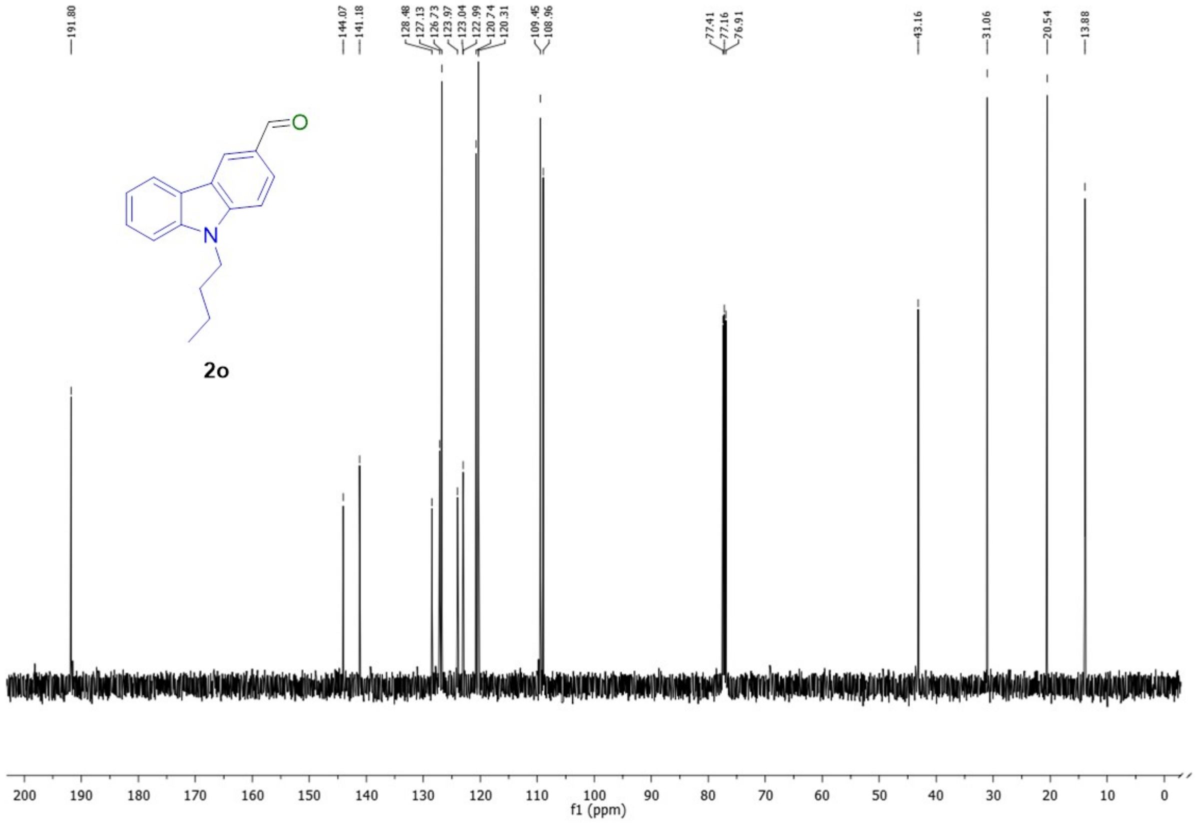

9.81
7.69
7.67
7.36
7.34
7.33
7.26
7.18
7.17
7.17
7.16
7.16
7.02
7.01
1.57
N
O
0.96
2.00
4.09
6.03
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

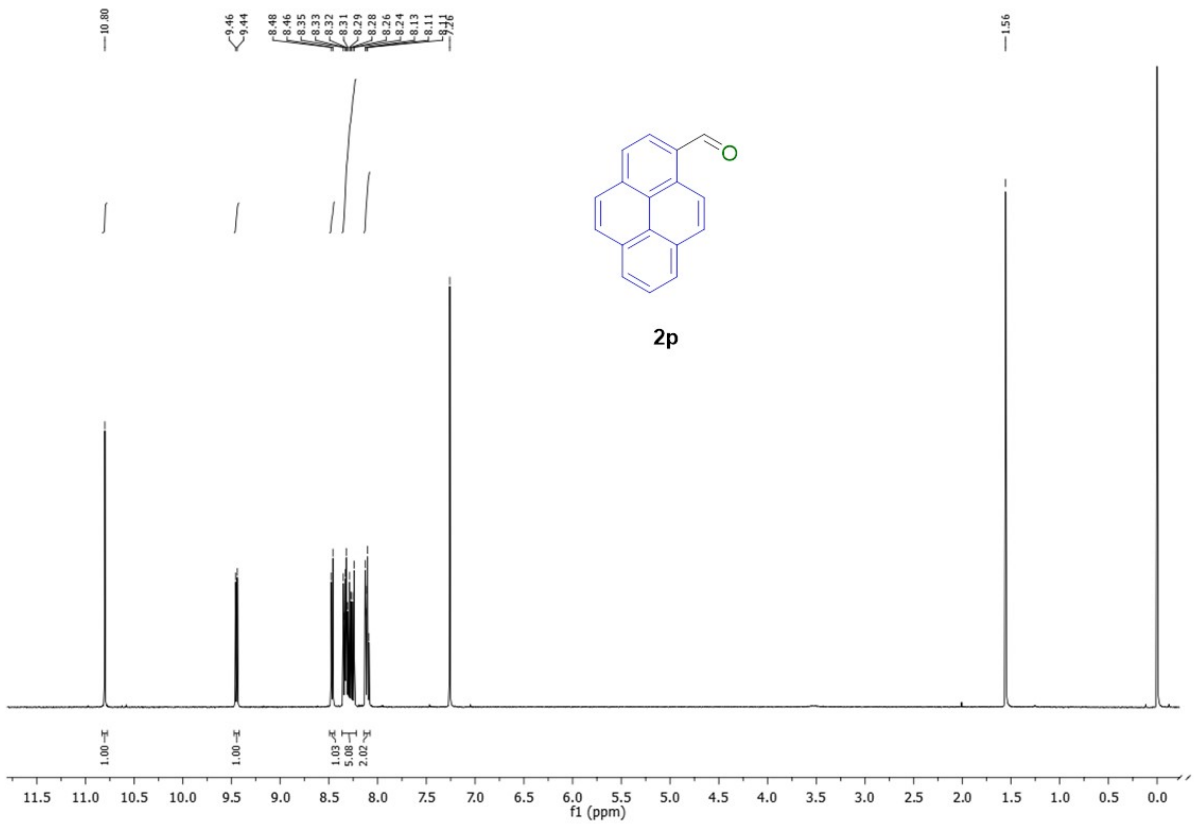
2n


190.55
153.46
146.26
131.42
129.85
129.21
126.43
125.23
119.46
77.41
77.16
76.91
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2n

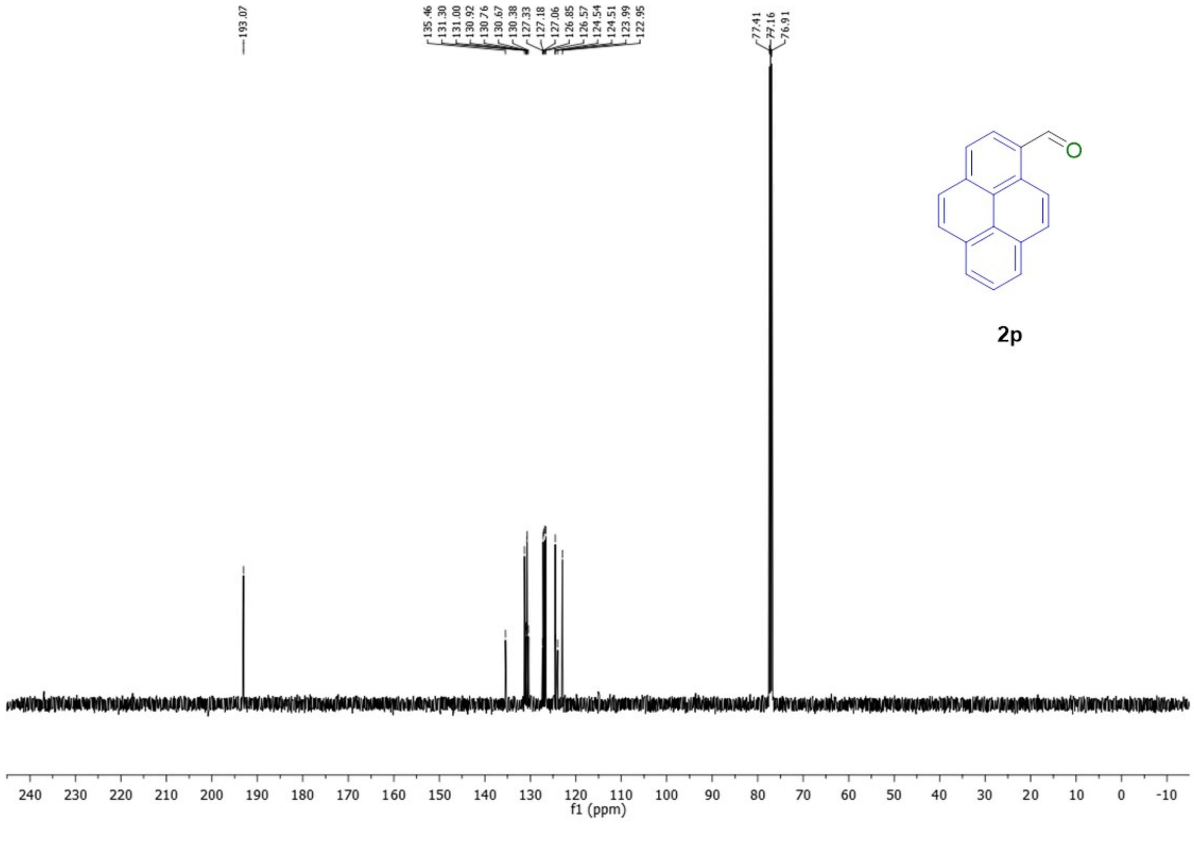

10.10
8.60
8.16
8.15
8.01
8.00
7.55
7.53
7.52
7.52
7.48
7.46
7.45
7.34
7.32
7.31
7.26
4.35
4.34
4.32
1.91
1.89
1.88
1.86
1.85
1.42
1.41
1.39
0.98
0.97
0.95
O
N
2o
1.01
1.00
0.96
0.98
3.02
1.00
2.03
2.06
2.07
3.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


191.80
144.07
141.18
128.48
127.13
126.73
123.97
123.04
122.99
120.74
120.31
109.45
108.96
77.41
77.16
76.91
43.16
31.06
20.54
13.88
O
N
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



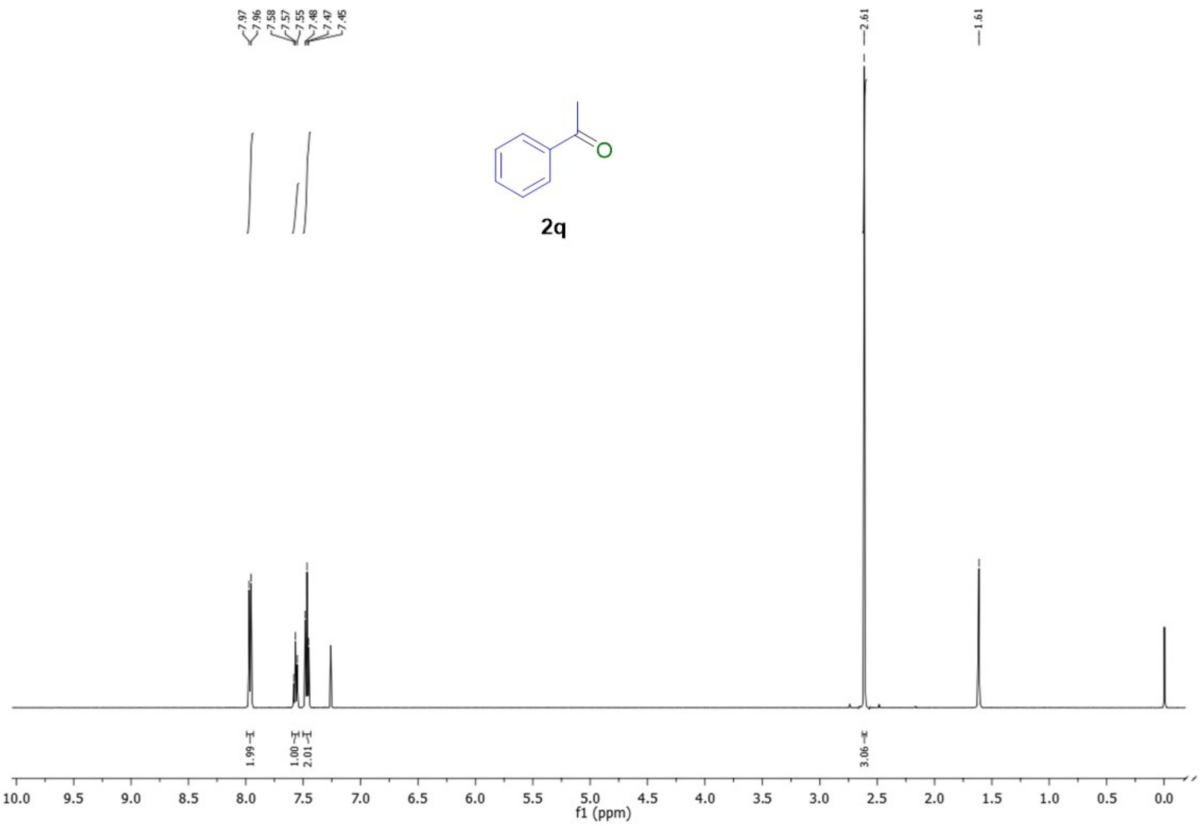
2p

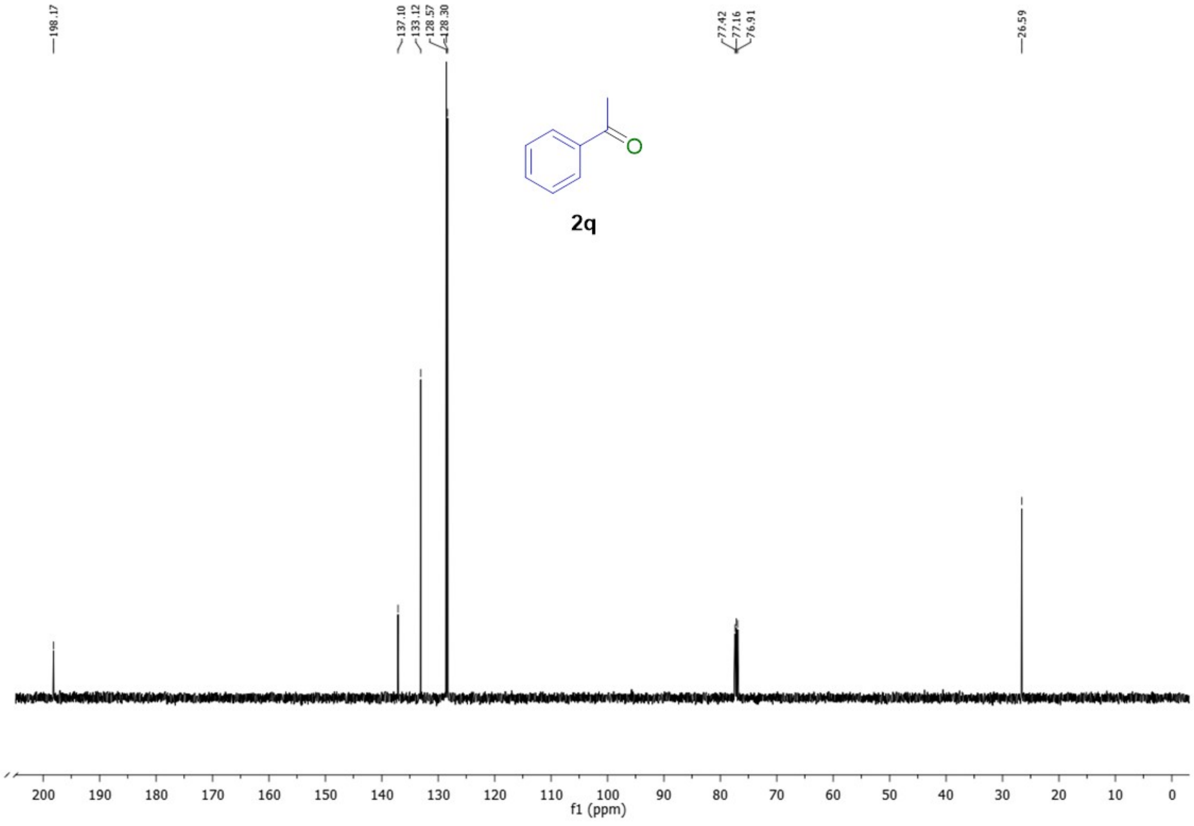
10.80
9.46
9.44
8.48
8.46
8.35
8.33
8.32
8.31
8.29
8.28
8.26
8.24
8.13
8.11
8.11
7.26
1.56
O
1.00
1.00
1.03
5.08
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

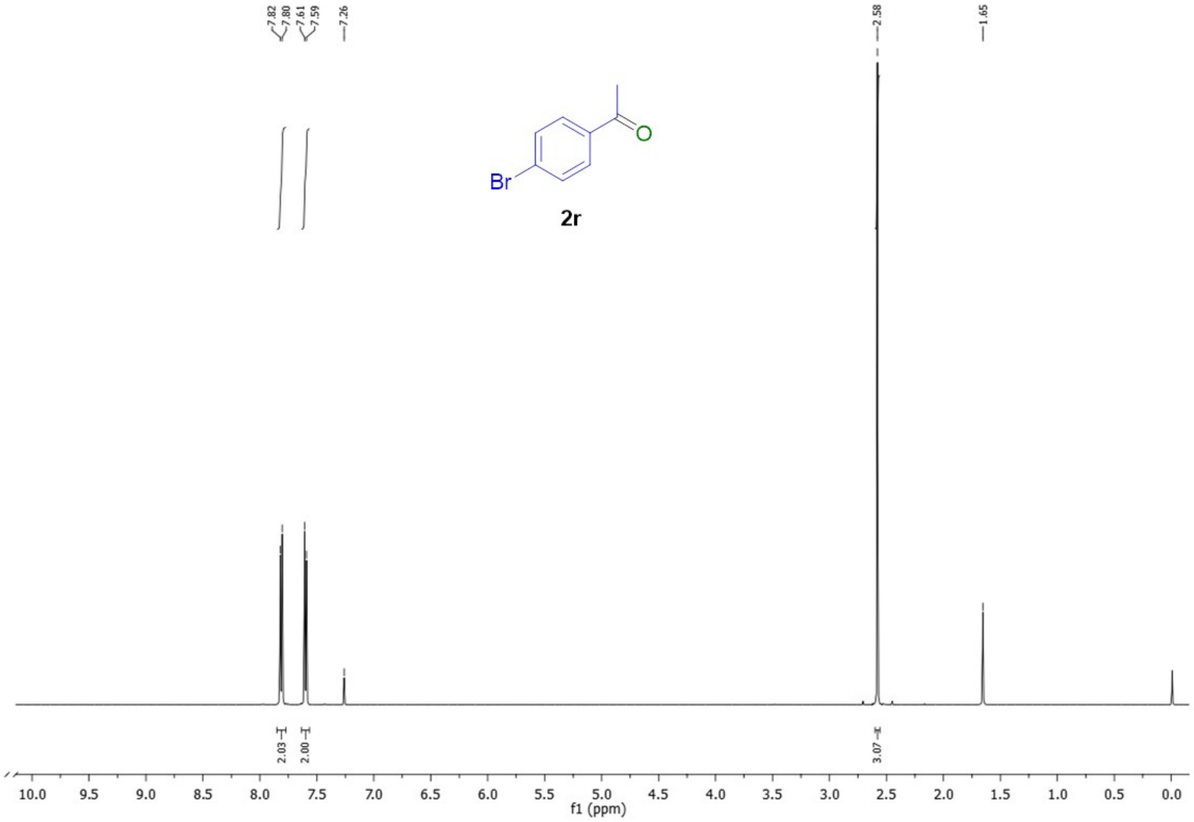


2p

193.07
135.46
131.30
131.00
130.92
130.76
130.67
130.38
127.33
127.18
127.06
126.85
126.57
124.54
124.51
123.99
122.95
77.41
77.16
76.91
O
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

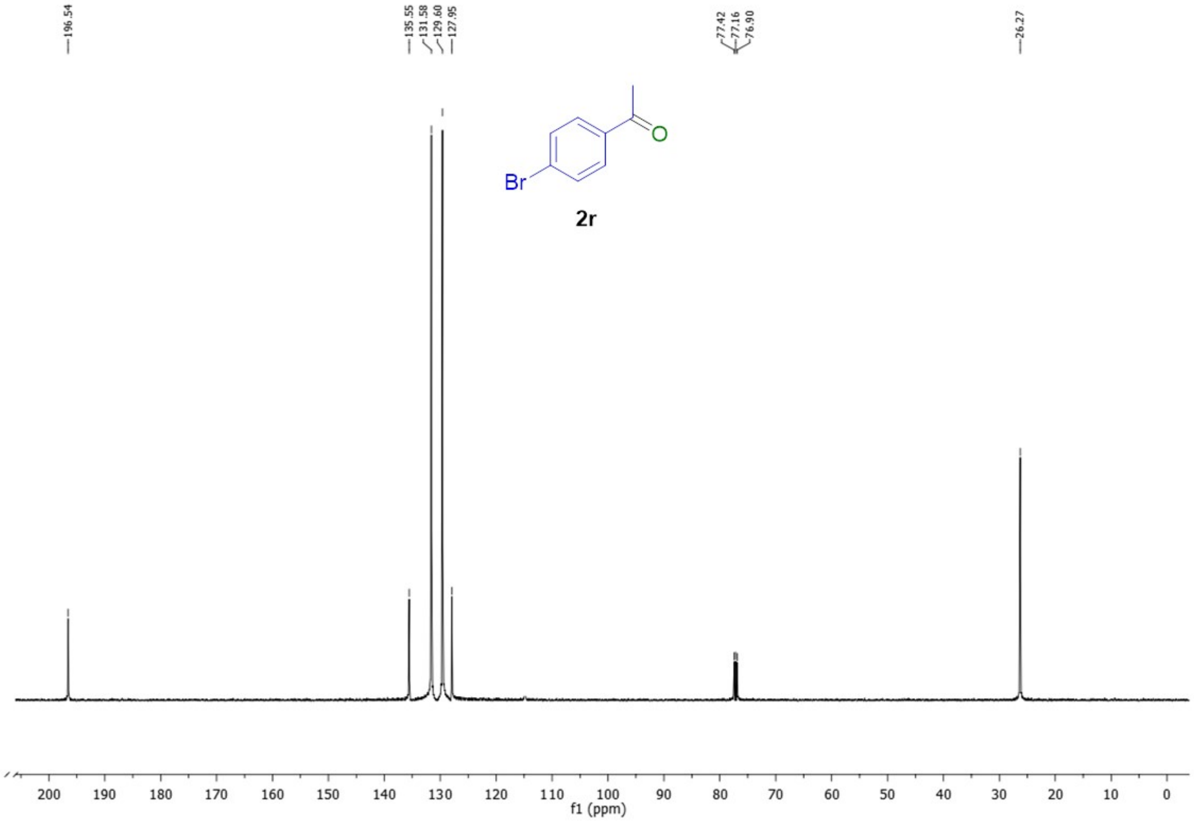

7.97
7.96
7.58
7.57
7.55
7.48
7.47
7.45
2.61
1.61
O
2q
1.99
1.00
2.01
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.17
137.10
133.12
128.57
128.30
77.42
77.16
76.91
26.59
O
2q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



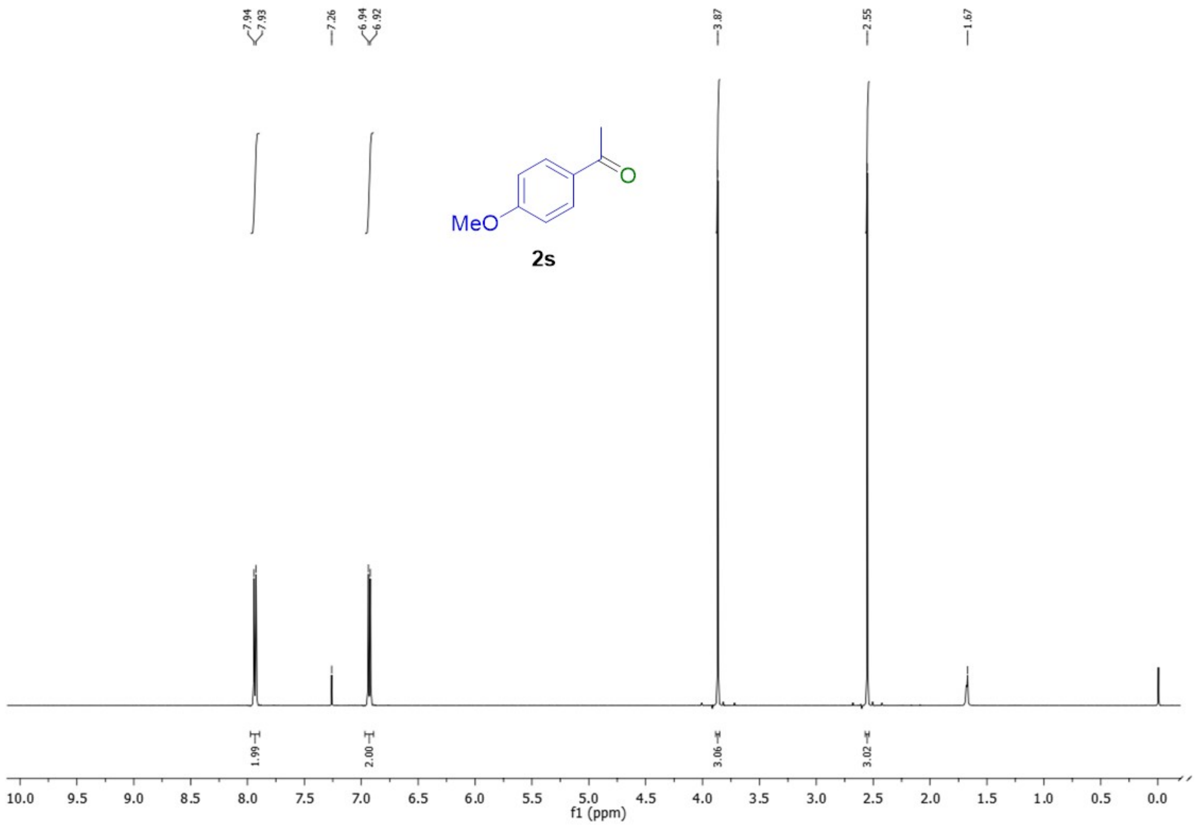
2r

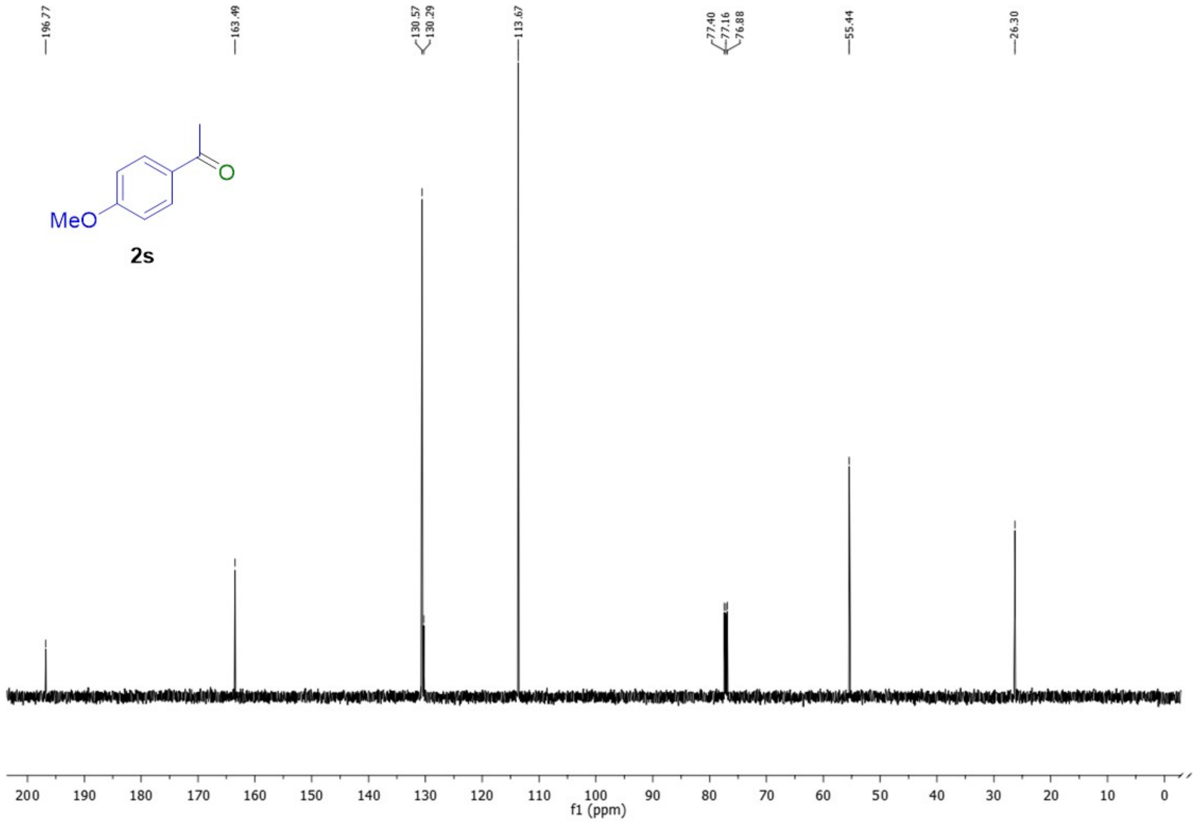
7.82
7.80
7.61
7.59
7.26
2.58
1.65
Br
O
2.03
2.00
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

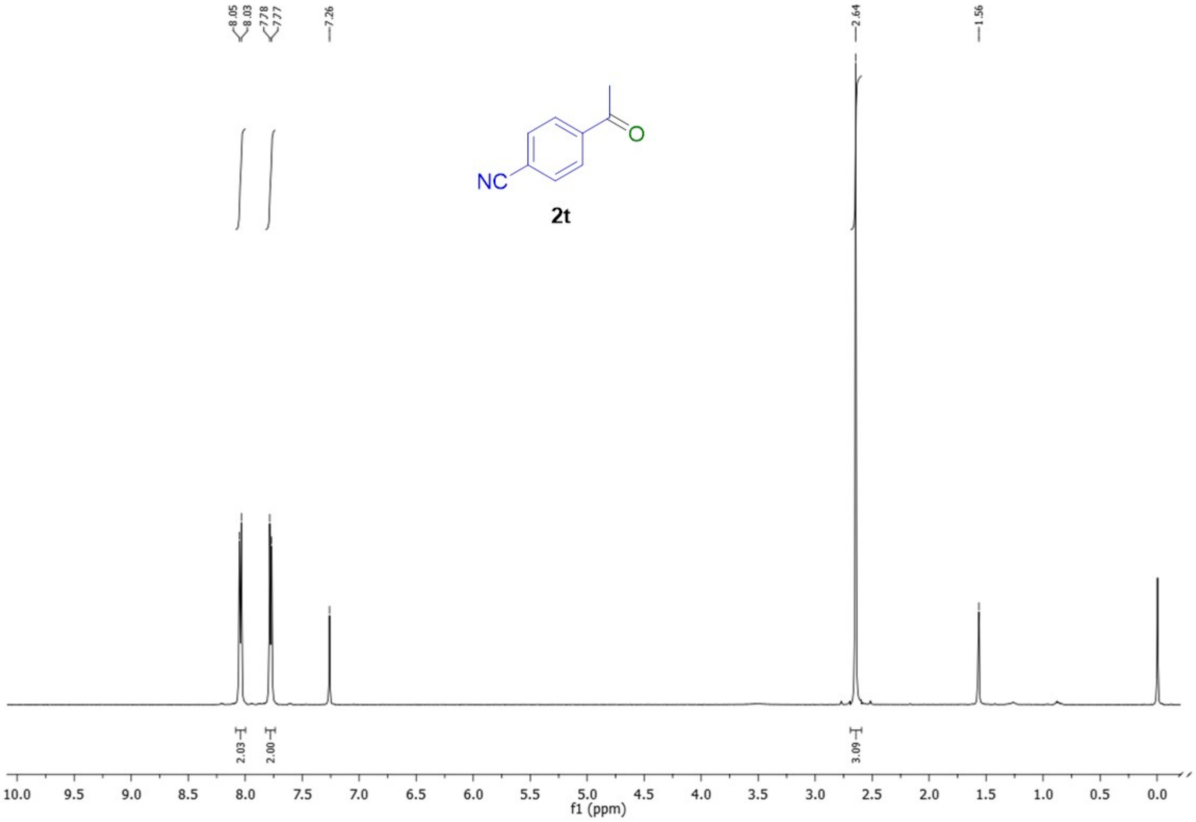


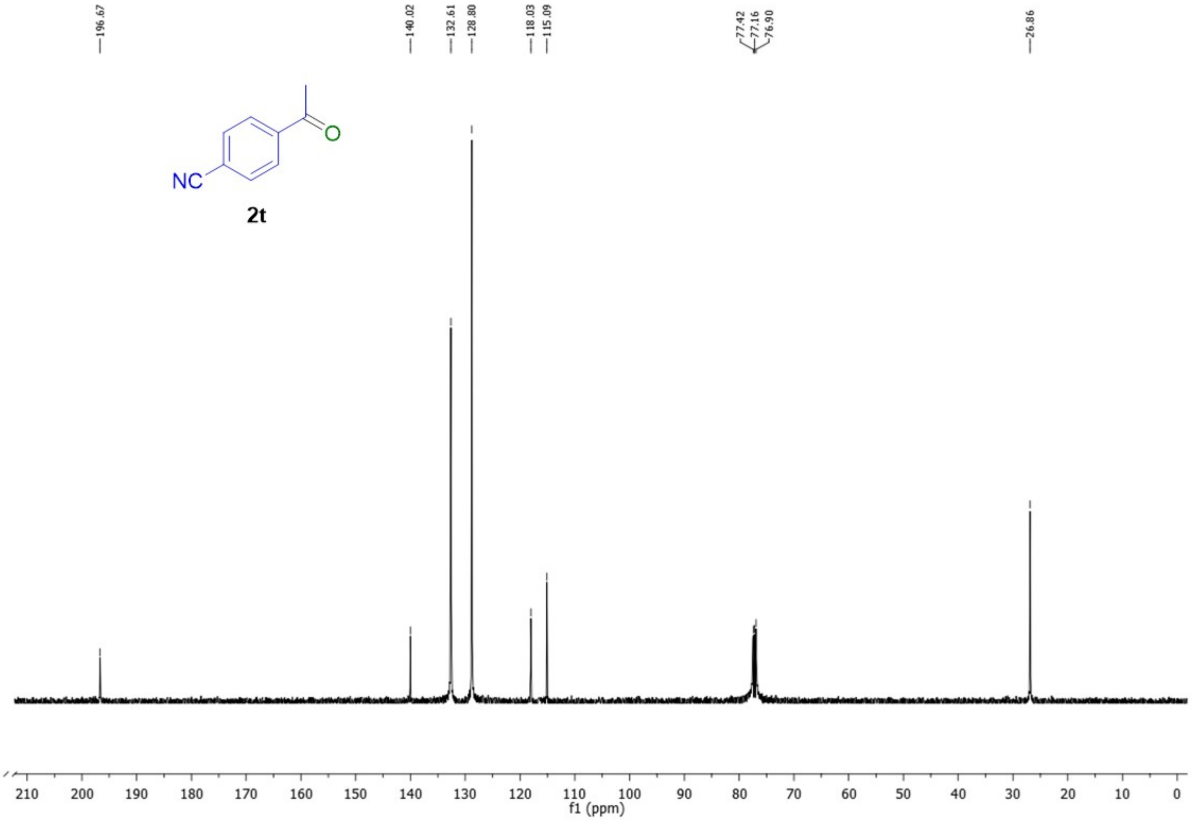
2r

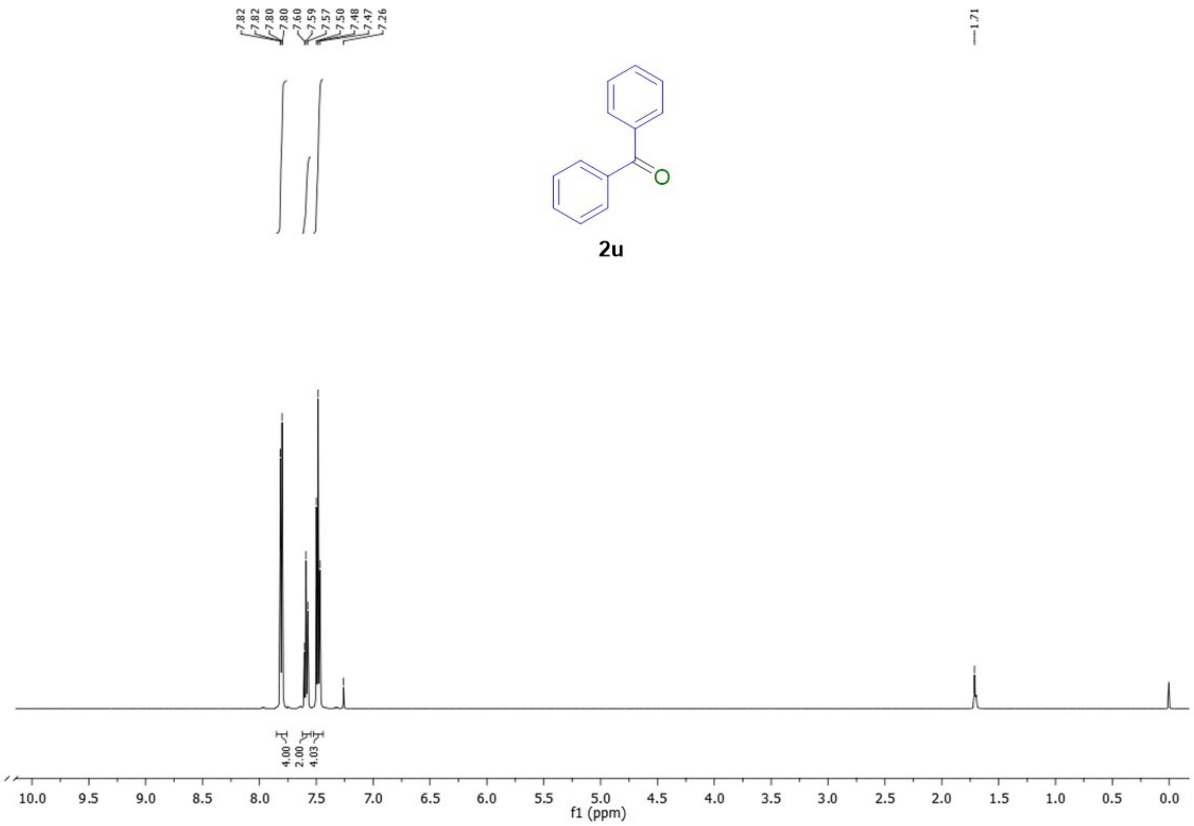
196.54
135.55
131.58
129.60
127.95
77.42
77.16
76.90
26.27
Br
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

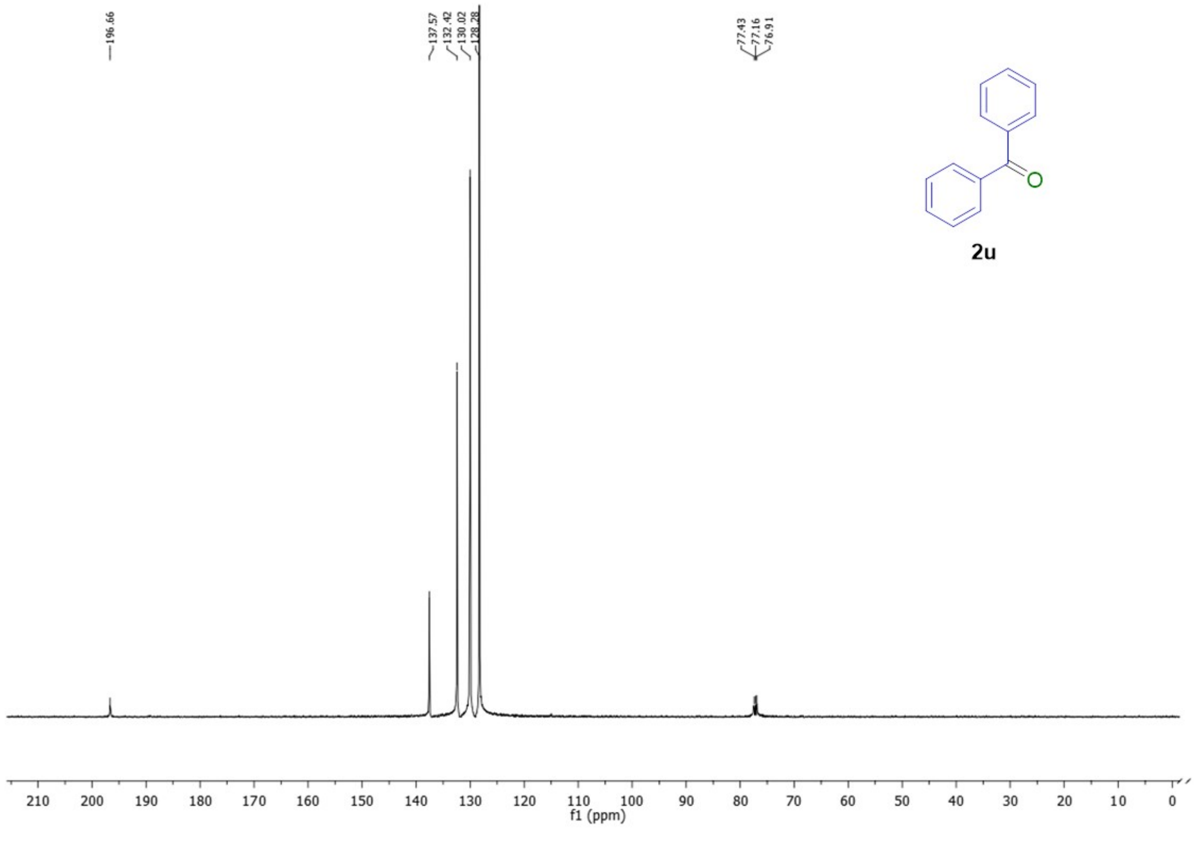

7.94
7.93
7.26
6.94
6.92
3.87
2.55
1.67
MeO
O
2s
1.99
2.00
3.06
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

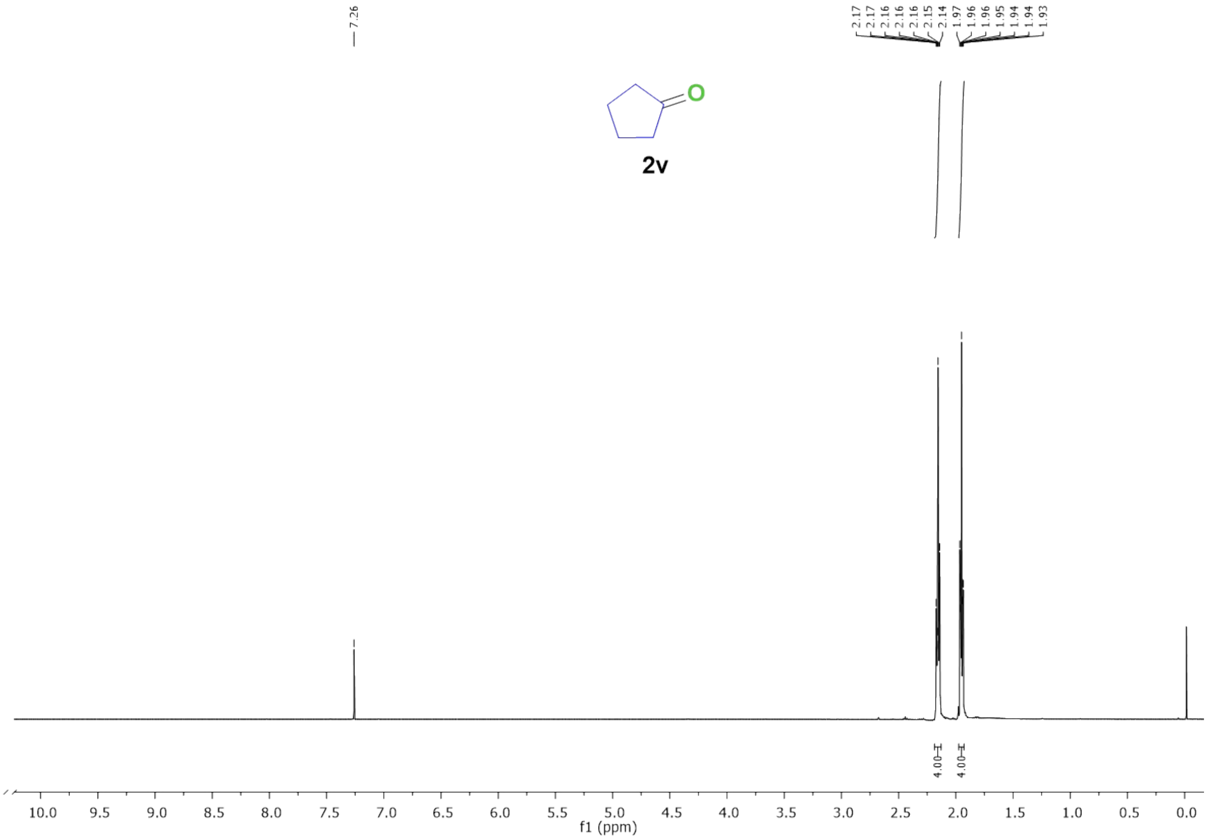

196.77
163.49
130.57
130.29
113.67
77.40
77.16
76.88
55.44
26.30
MeO
O
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

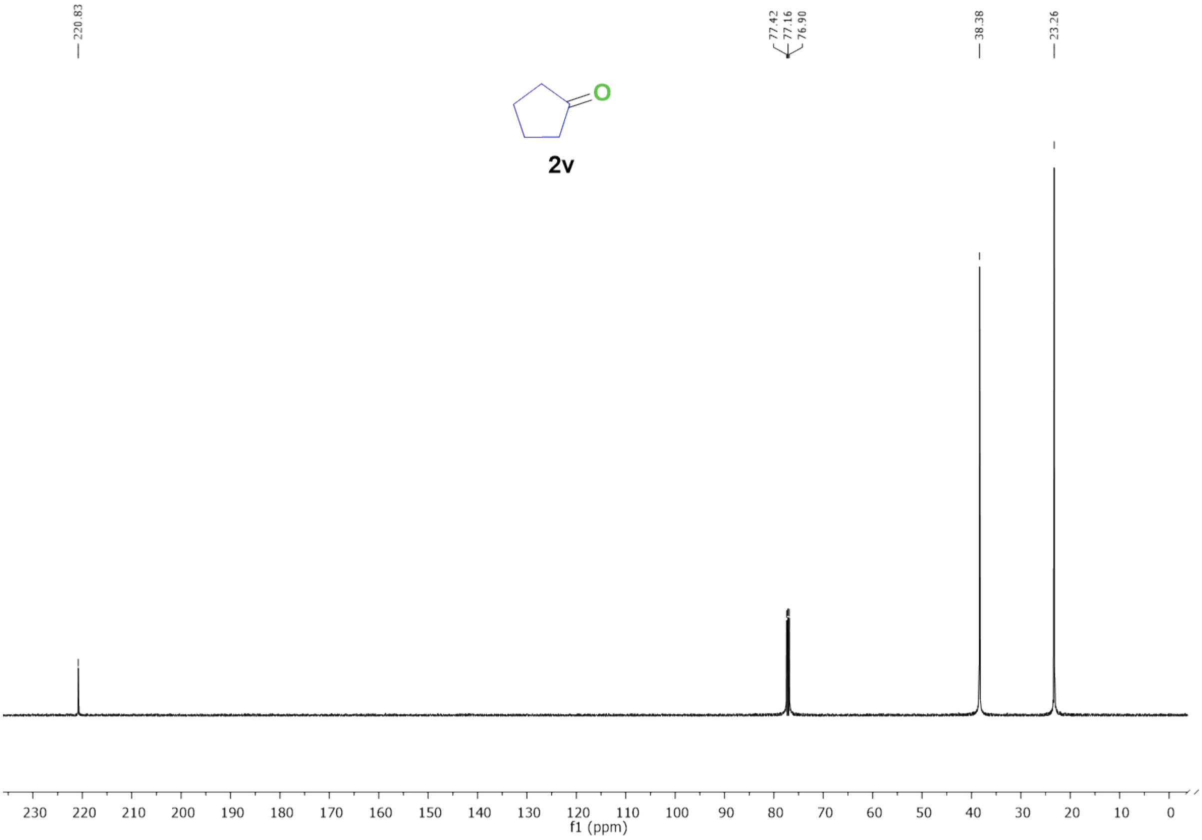

8.05
8.03
7.78
7.77
7.26
2.64
1.56
NC
O
2t
2.03
2.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

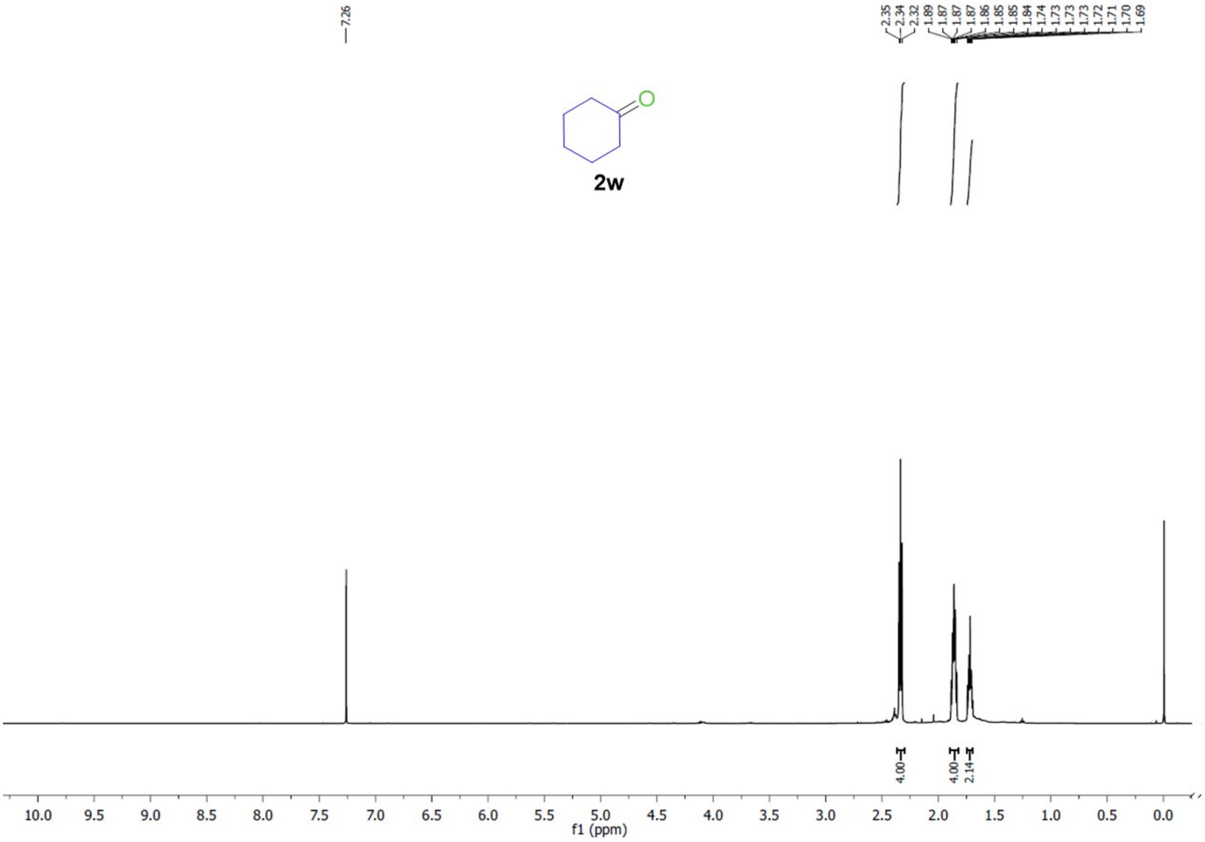

196.67
140.02
132.61
128.80
118.03
115.09
77.42
77.16
76.90
26.86
NC
O
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

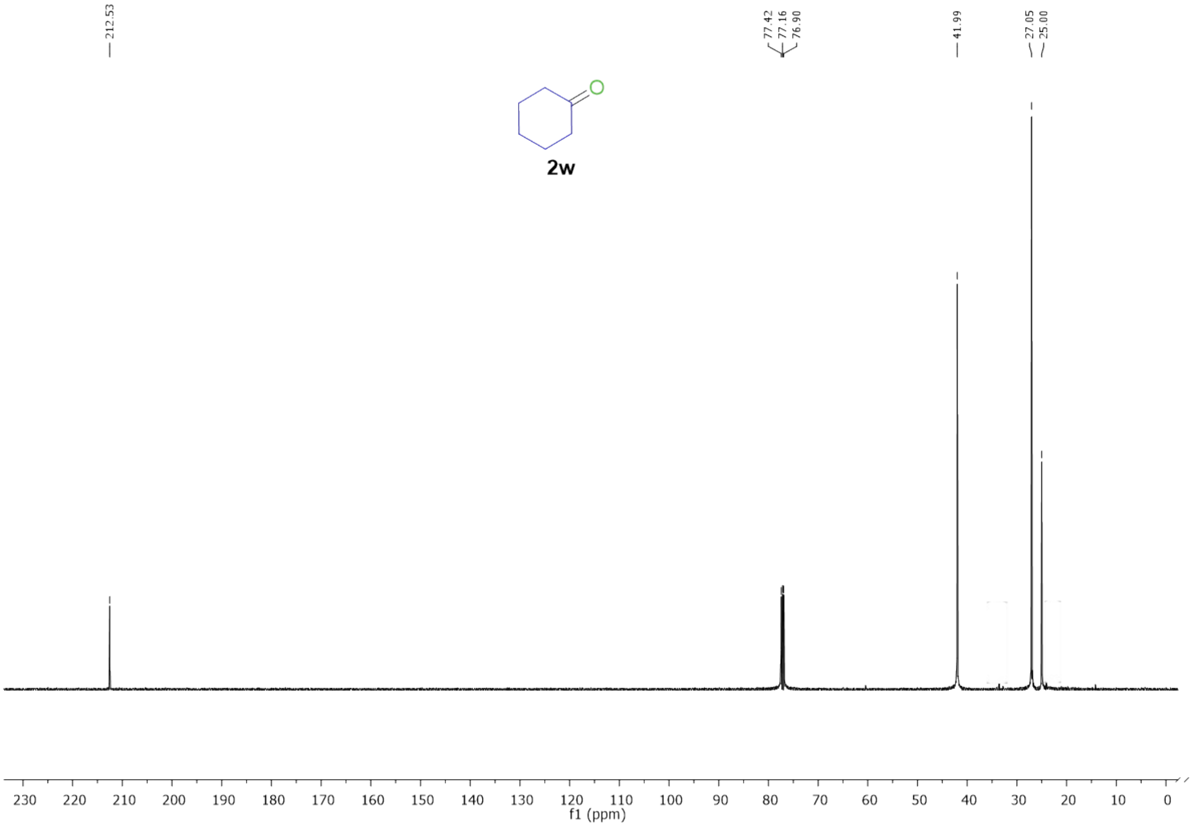

7.82
7.82
7.80
7.80
7.60
7.59
7.57
7.50
7.48
7.47
7.26
1.71
2u
4.00
2.00
4.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

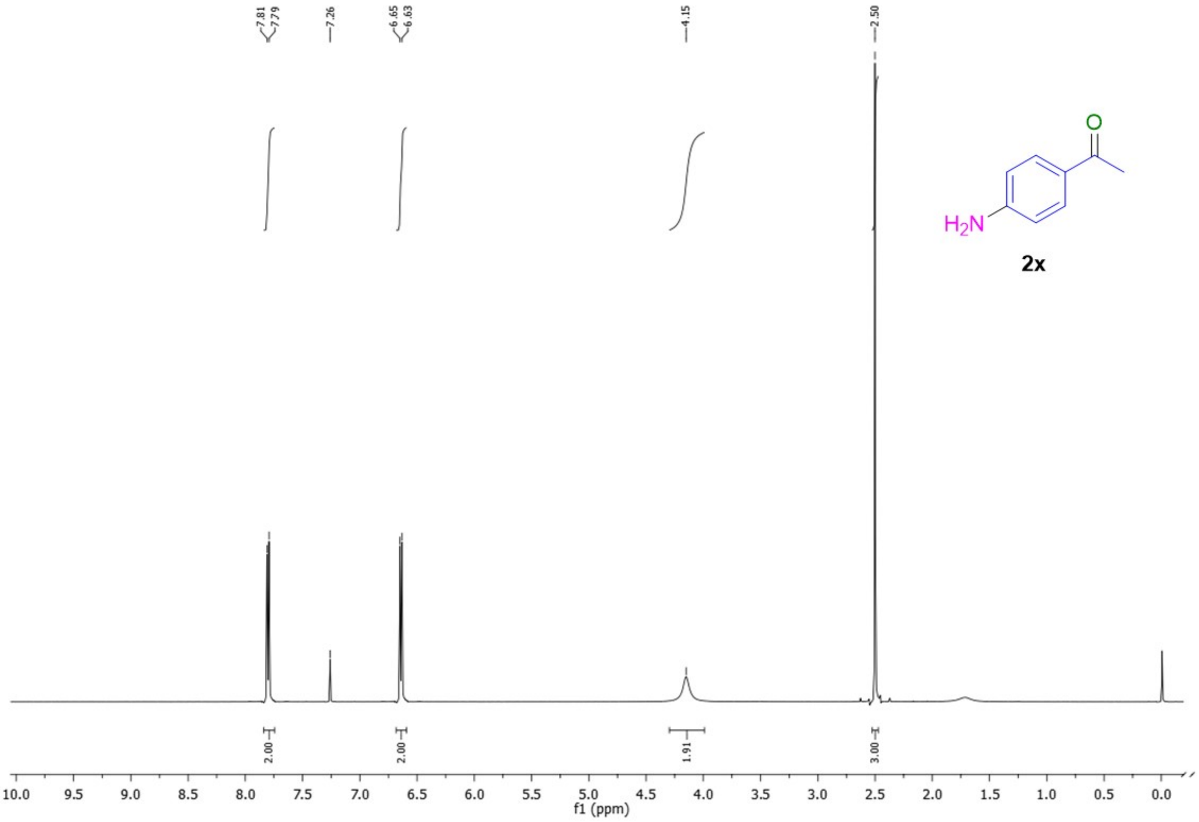

196.66
137.57
132.42
130.02
128.28
77.43
77.16
76.91
2u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
2.17
2.17
2.16
2.16
2.16
2.15
2.14
1.97
1.96
1.96
1.95
1.94
1.94
1.93
O
2v
4.00
4.00
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
0.0
f1 (ppm)

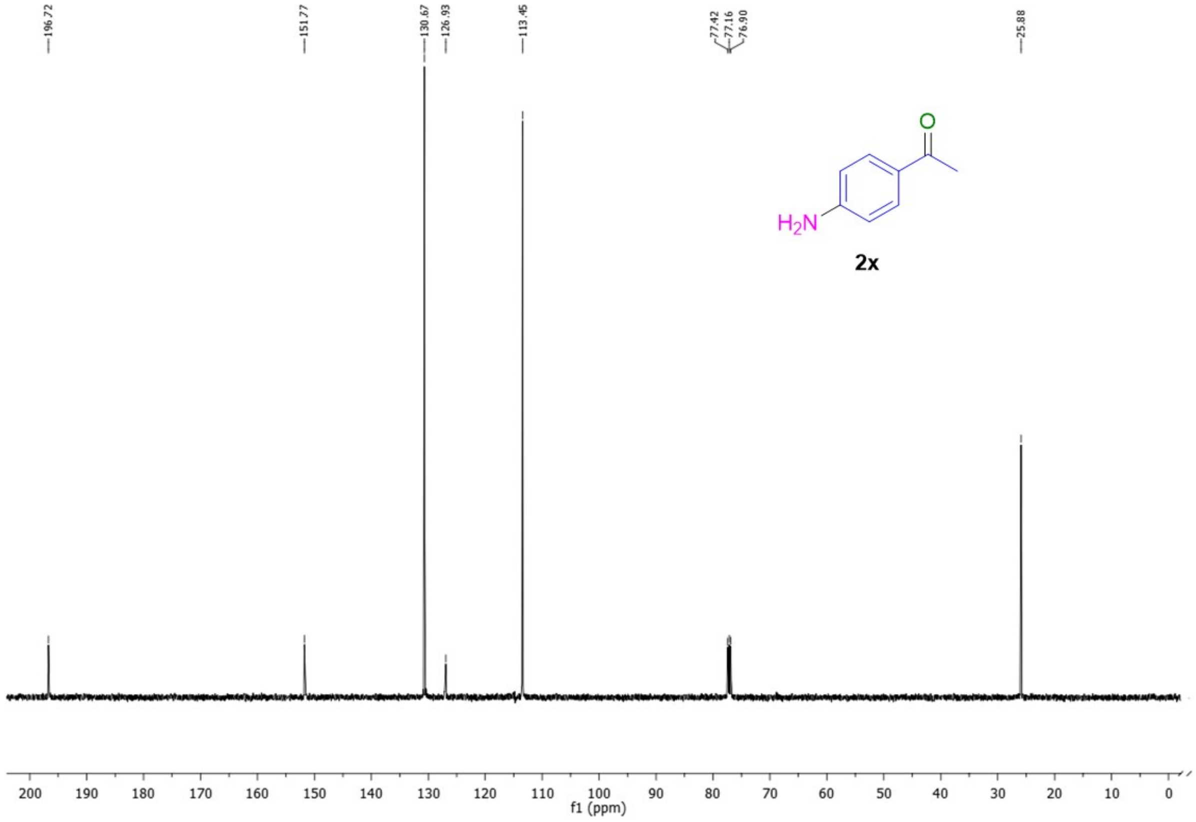

220.83
77.42
77.16
76.90
38.38
23.26
O
2v
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
2.35
2.34
2.32
1.89
1.87
1.87
1.87
1.86
1.85
1.85
1.84
1.74
1.73
1.73
1.73
1.72
1.71
1.70
1.69
2w
4.00
4.00
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

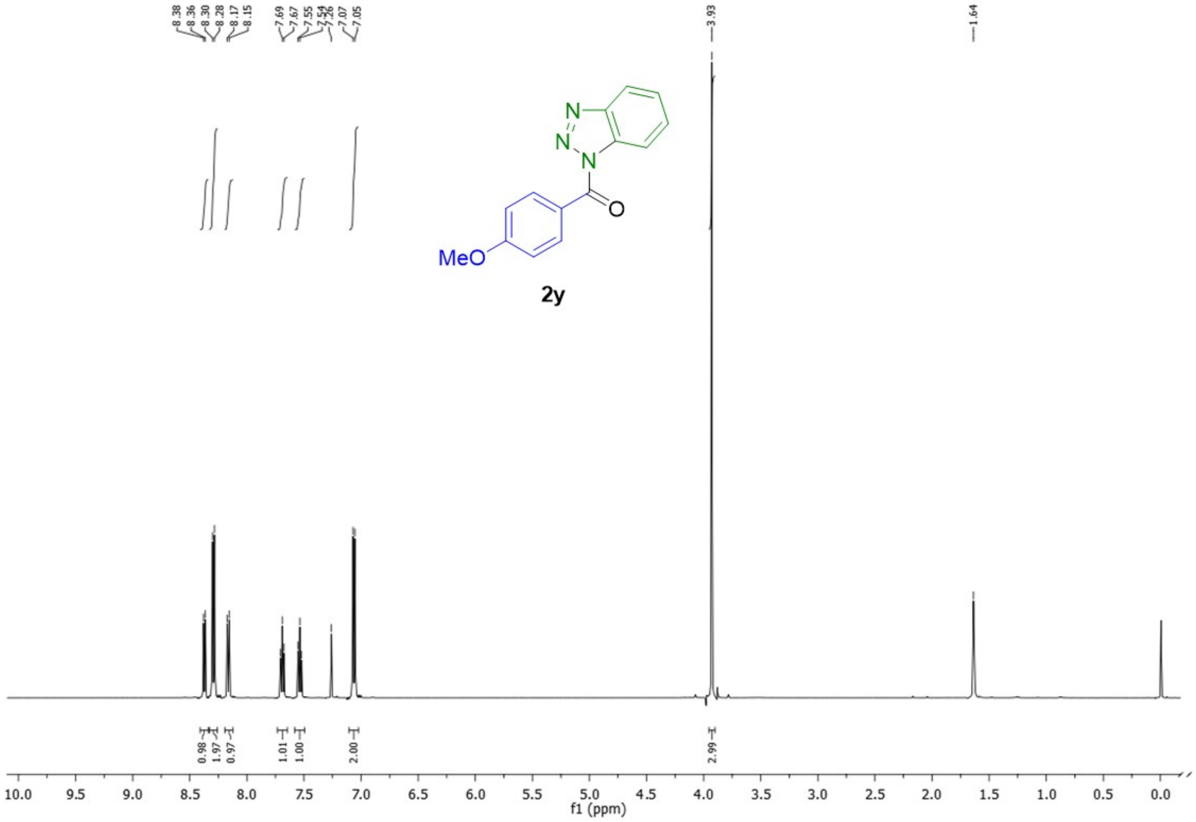

212.53
77.42
77.16
76.90
41.99
27.05
25.00
2w
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

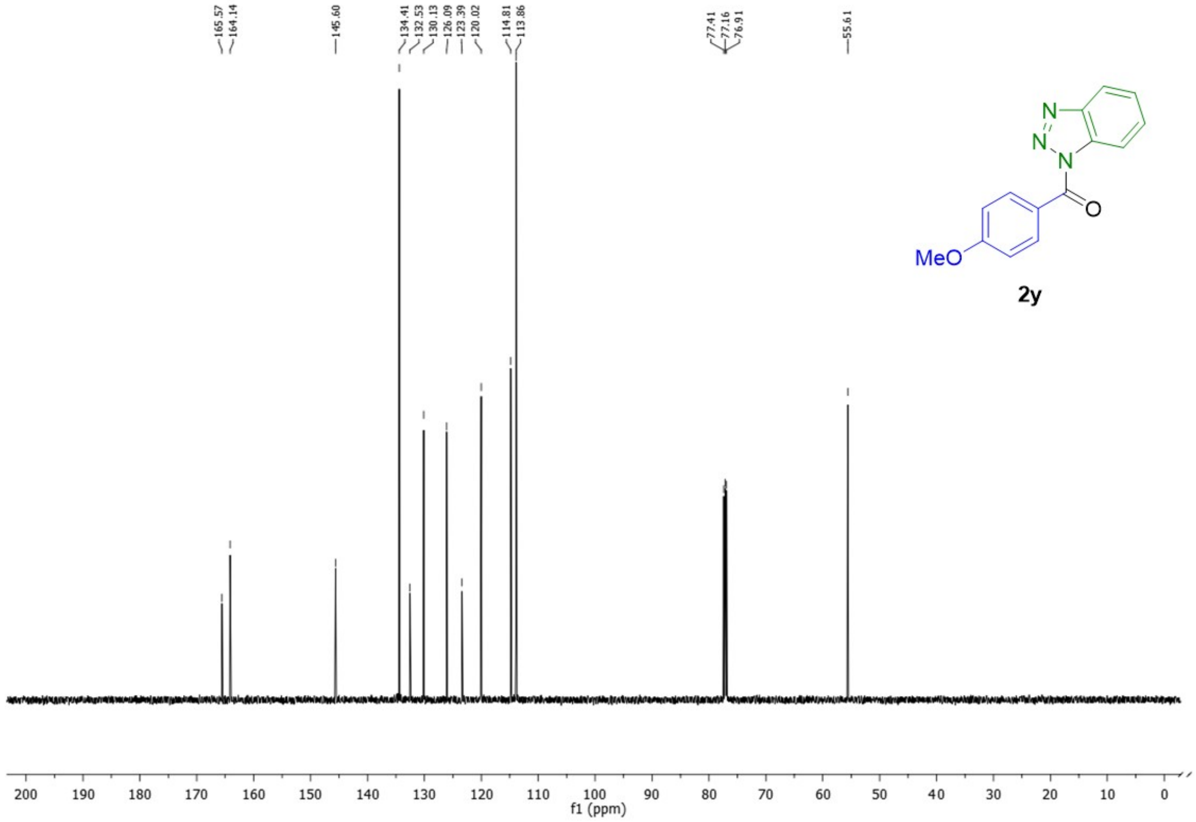


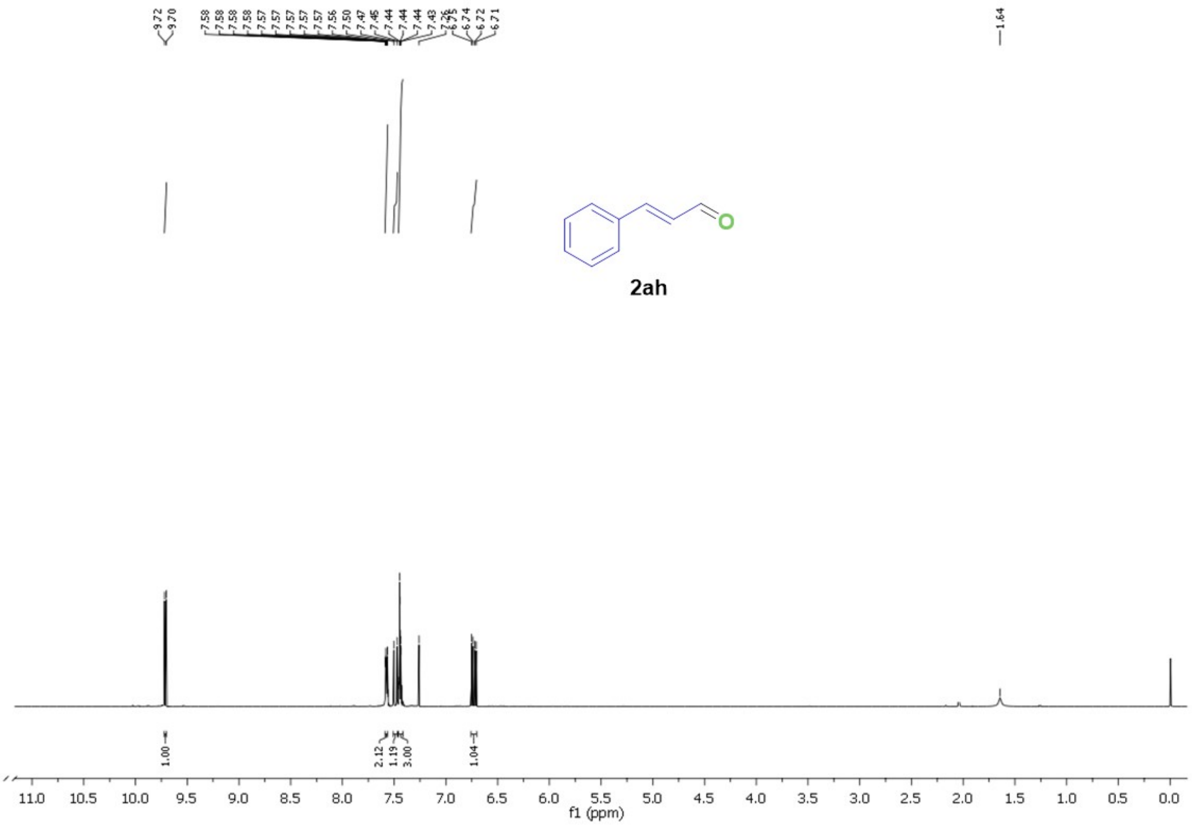
7.81
7.79
7.26
6.65
6.63
4.15
2.50
O
H2N
2x
2.00
2.00
1.91
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



196.72
151.77
130.67
126.93
113.45
77.42
77.16
76.90
25.88
O
H2N
2x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

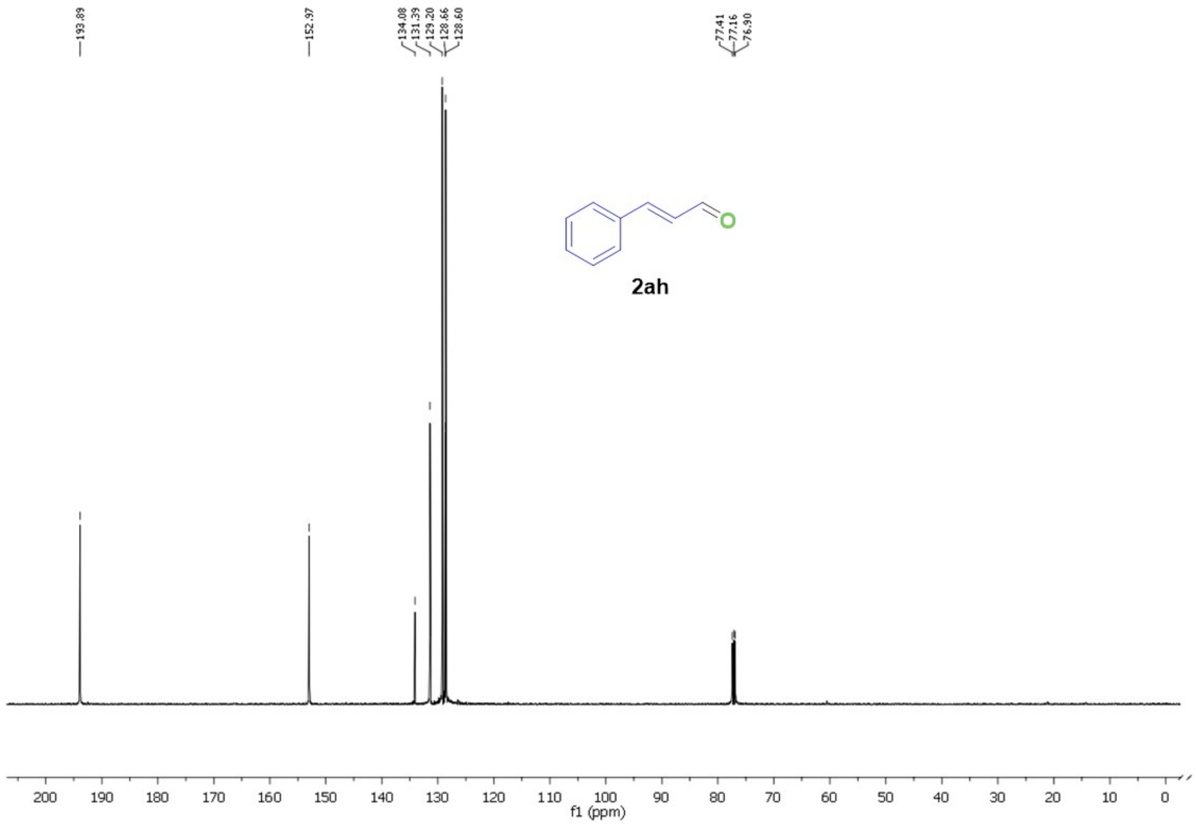

8.38
8.36
8.30
8.28
8.17
8.15
7.69
7.67
7.55
7.54
7.26
7.07
7.05
3.93
1.64
N
N
N
O
MeO
2y
0.98
1.97
0.97
1.01
1.00
2.00
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.57
164.14
145.60
134.41
132.53
130.13
126.09
123.39
120.02
114.81
113.86
77.41
77.16
76.91
55.61
N
N
N
O
MeO
2y
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



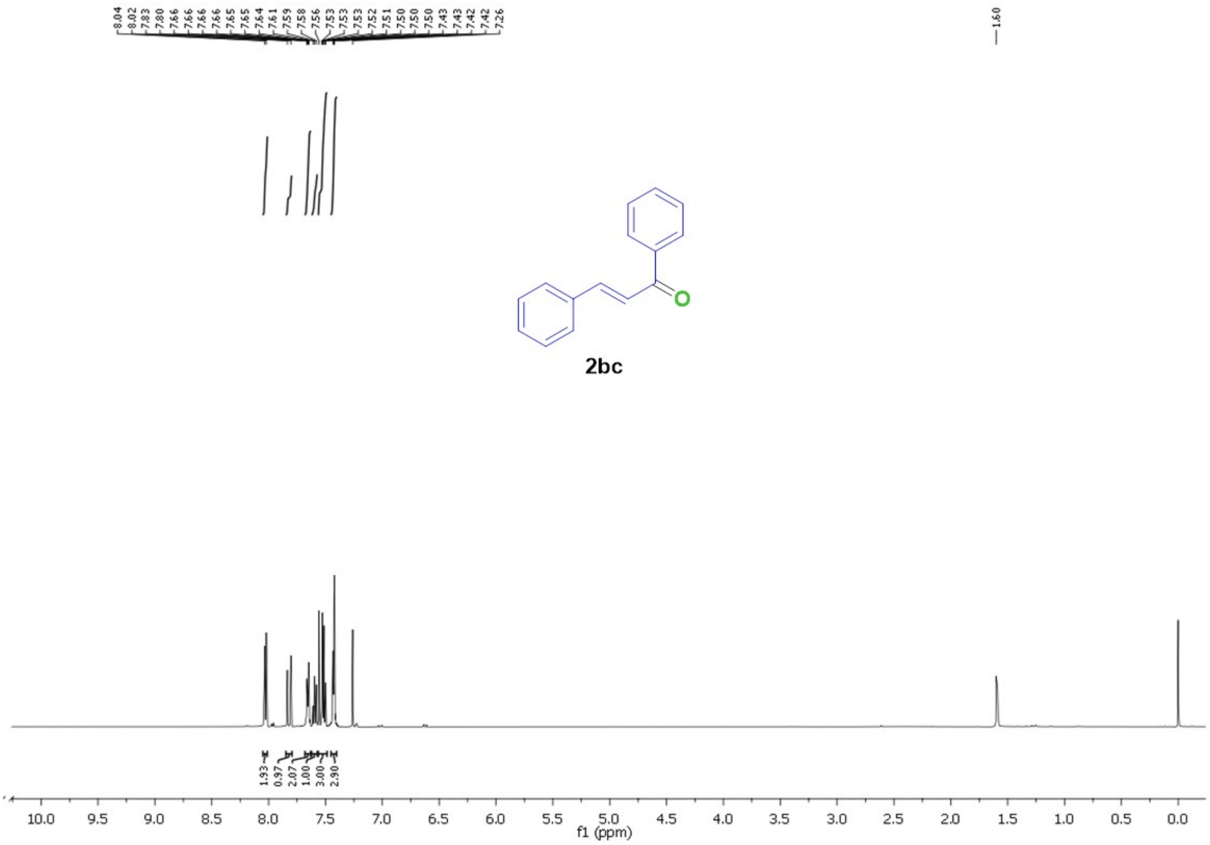
9.72
9.70
7.58
7.58
7.58
7.58
7.57
7.57
7.57
7.57
7.56
7.50
7.47
7.45
7.44
7.44
7.44
7.43
7.26
6.75
6.74
6.72
6.71
1.64
1.00
2.12
1.19
3.00
1.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2ah

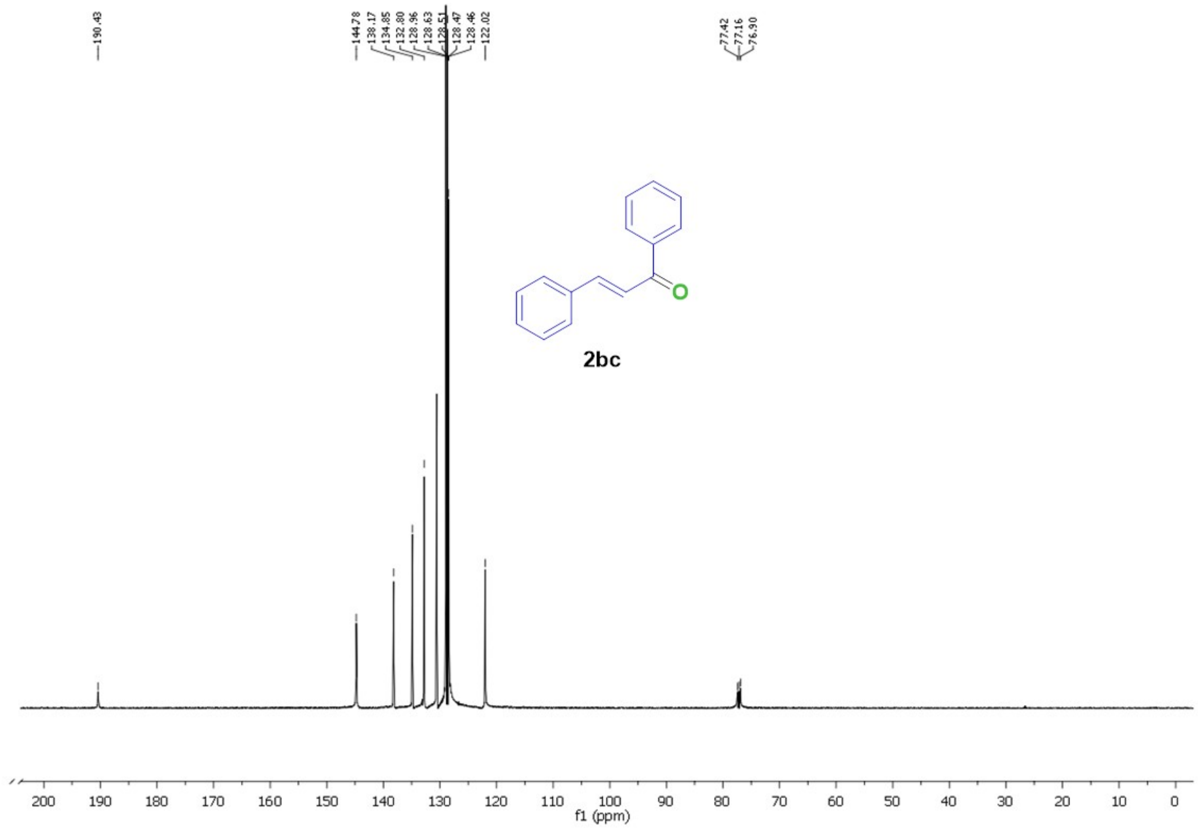


193.89
152.97
134.08
131.39
129.20
128.66
128.60
77.41
77.16
76.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

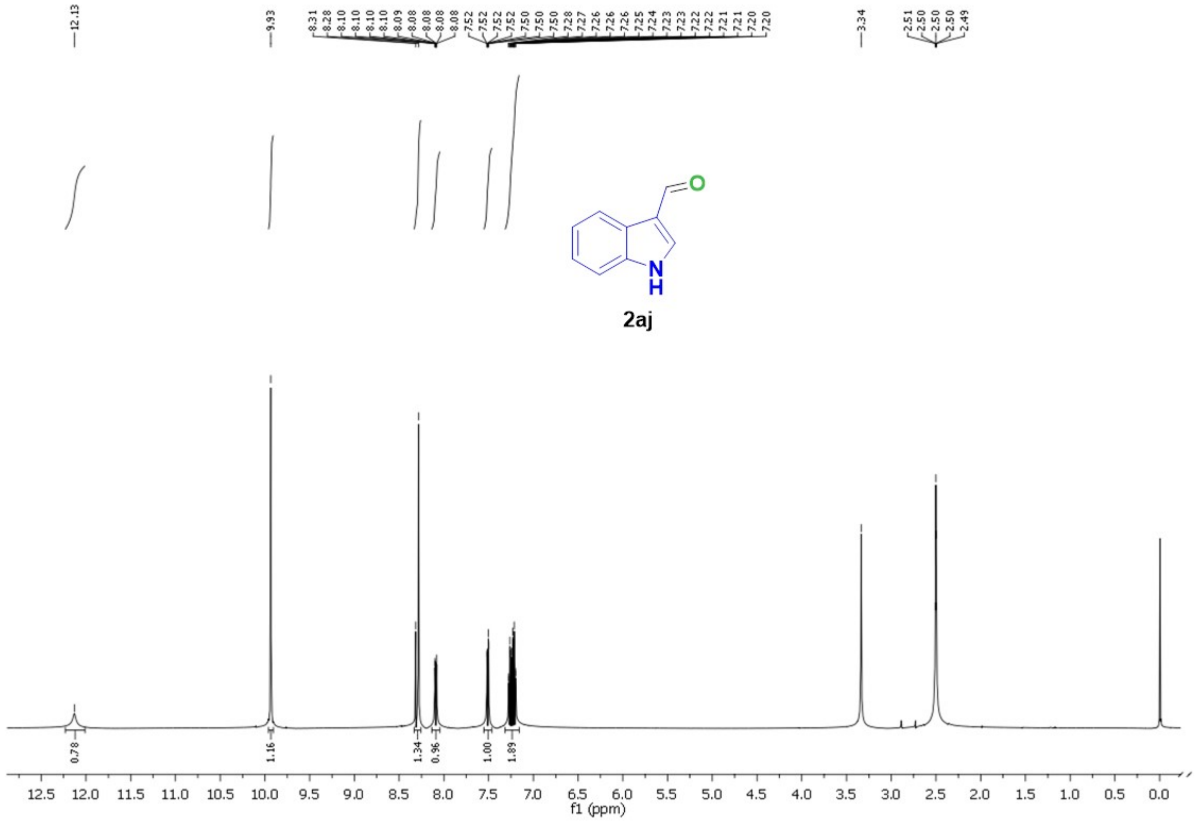
2ah

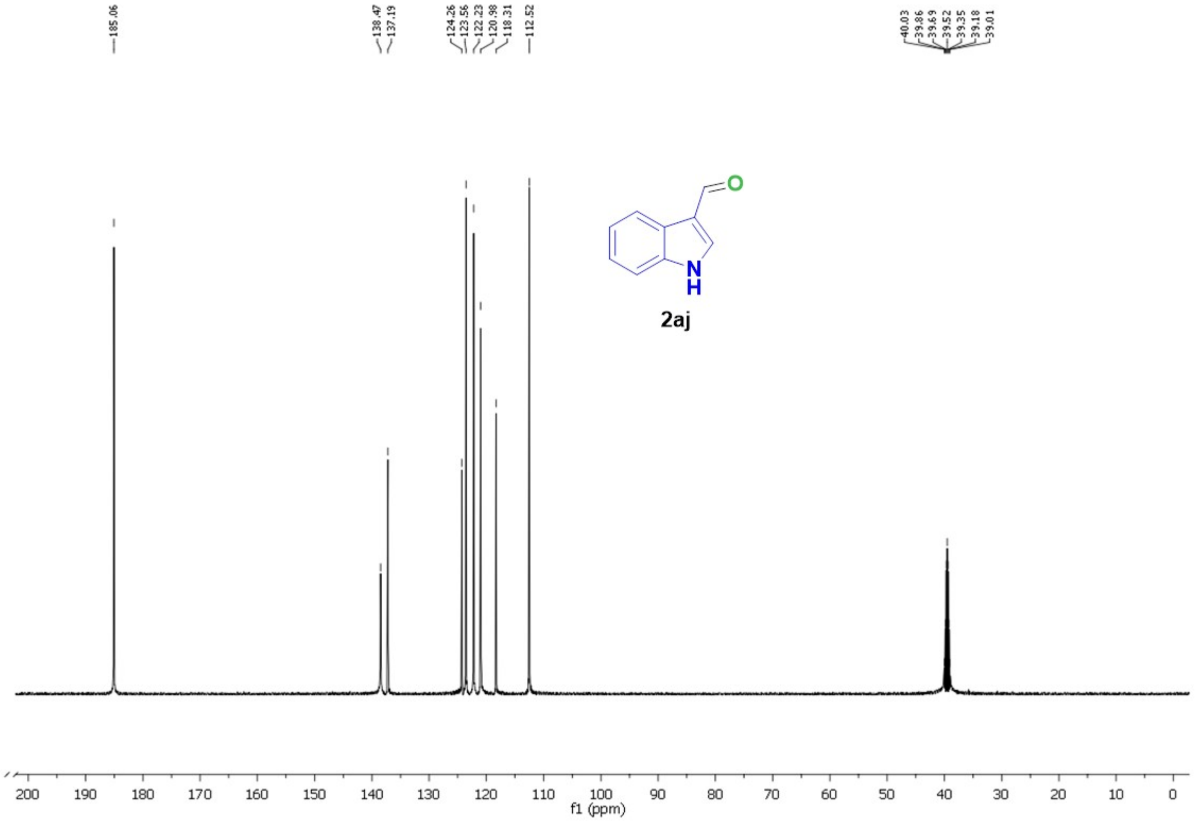

8.04
8.02
7.83
7.80
7.66
7.66
7.66
7.66
7.65
7.65
7.64
7.61
7.59
7.58
7.56
7.53
7.53
7.53
7.52
7.51
7.50
7.50
7.50
7.43
7.43
7.42
7.42
7.26
1.60
O
1.93
0.97
2.07
1.00
3.00
2.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

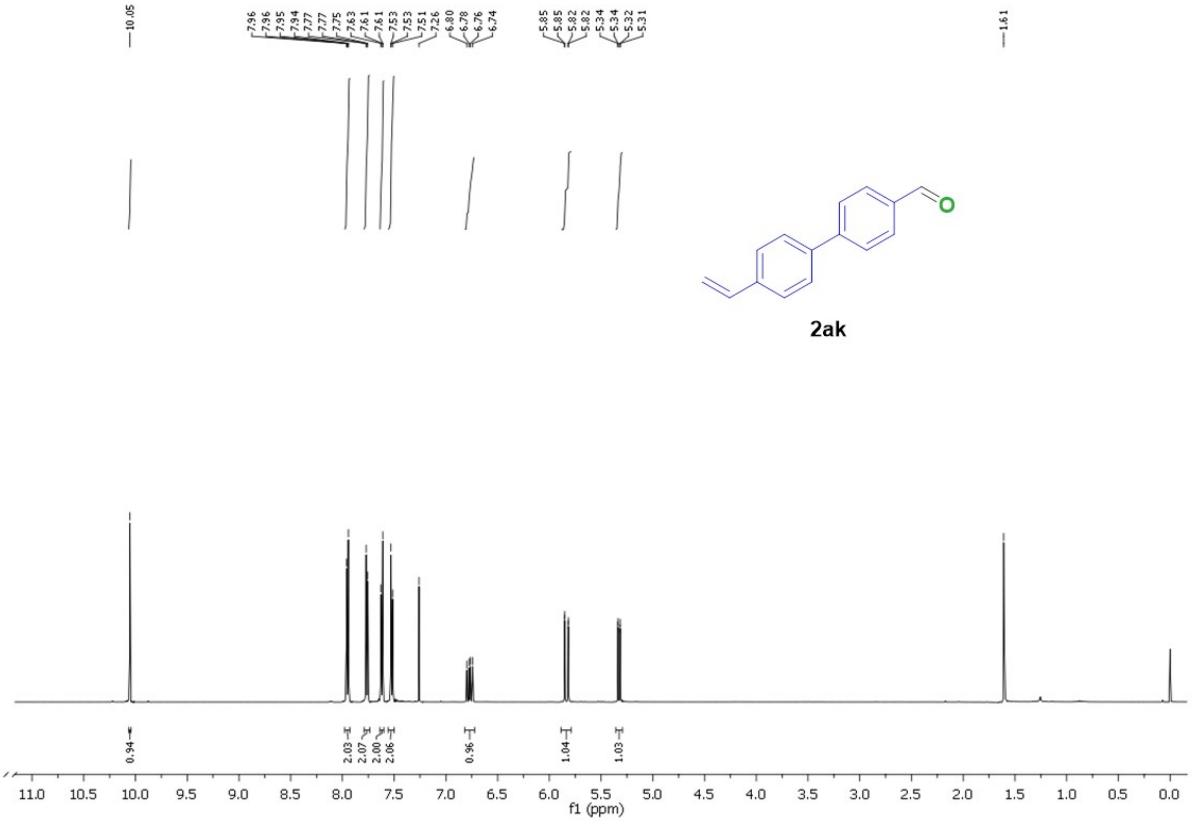
2bc


190.43
144.78
138.17
134.85
132.80
128.96
128.63
128.51
128.47
128.46
122.02
77.42
77.16
76.90
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

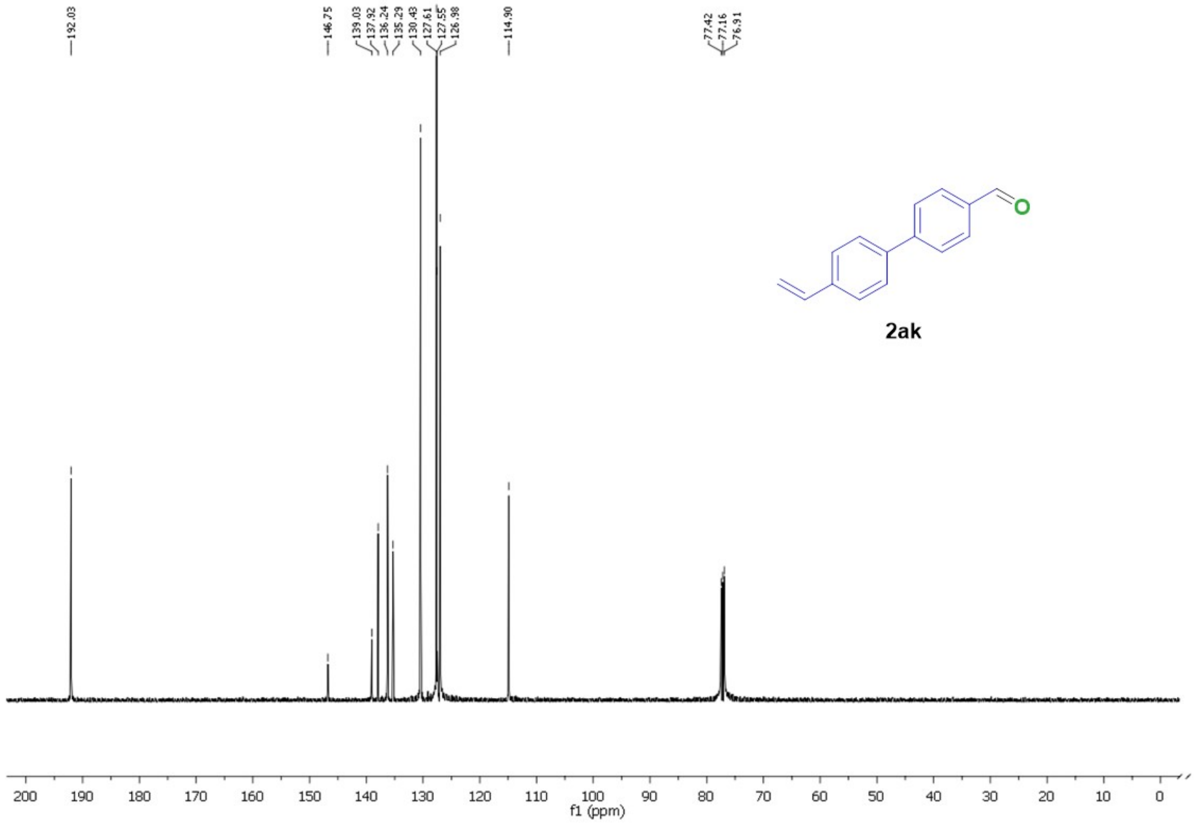
2bc


12.13
9.93
8.31
8.28
8.10
8.10
8.10
8.10
8.09
8.08
8.08
8.08
8.08
7.52
7.52
7.52
7.52
7.50
7.50
7.50
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
3.34
2.51
2.50
2.50
2.50
2.49
O
N
H
2aj
0.78
1.16
1.34
0.96
1.00
1.89
12.5 12.0 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 0.0
f1 (ppm)

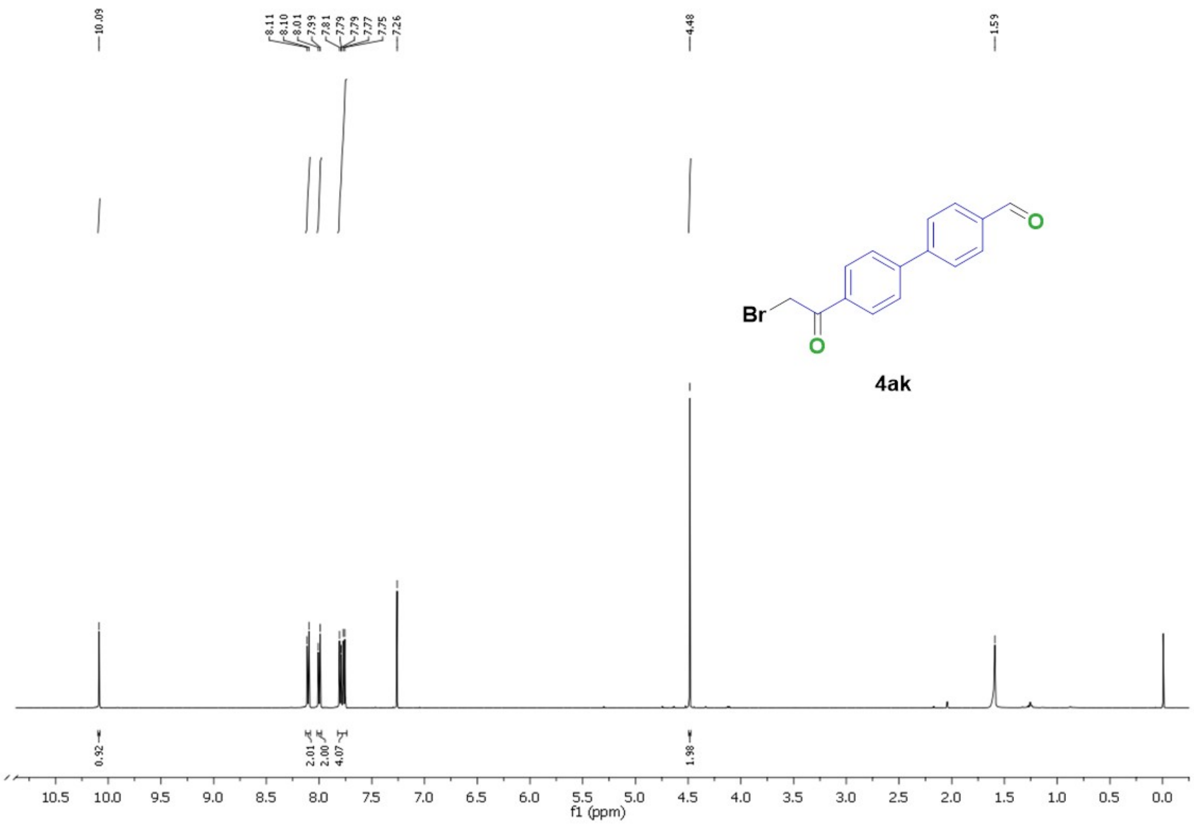

185.06
138.47
137.19
124.26
123.56
122.23
120.98
118.31
112.52
40.03
39.86
39.69
39.52
39.35
39.18
39.01
O
N
H
2aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

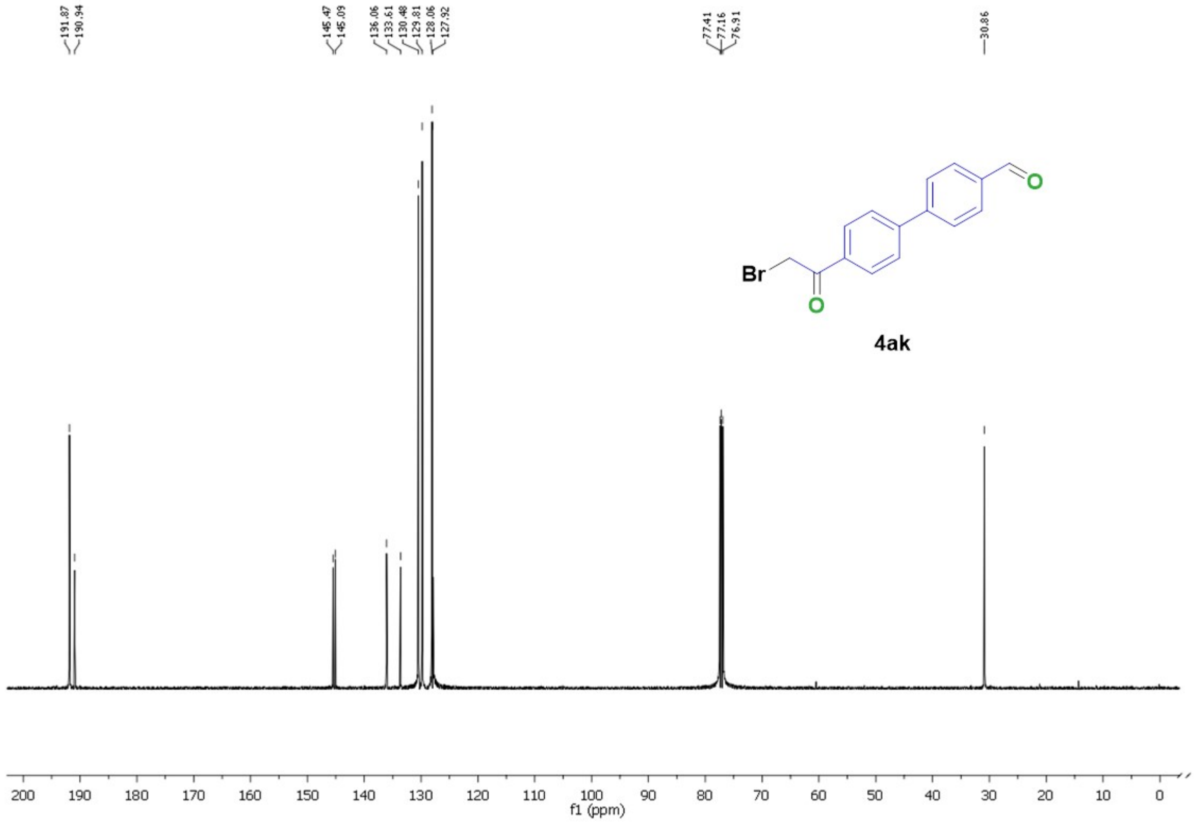

10.05
7.96
7.96
7.95
7.94
7.77
7.77
7.75
7.63
7.61
7.61
7.53
7.53
7.51
7.26
6.80
6.78
6.76
6.74
5.85
5.85
5.82
5.82
5.34
5.34
5.32
5.31
1.61
O
0.94
2.03
2.07
2.00
2.06
0.96
1.04
1.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

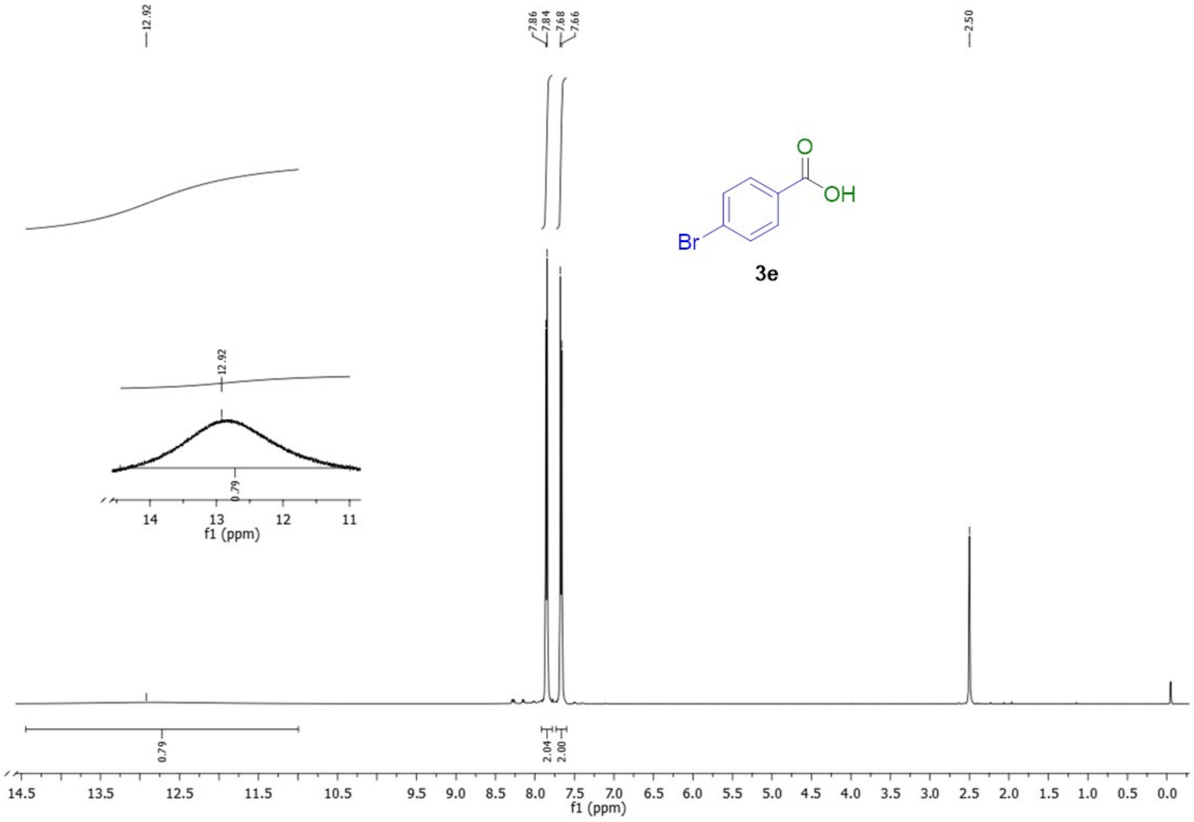
2ak

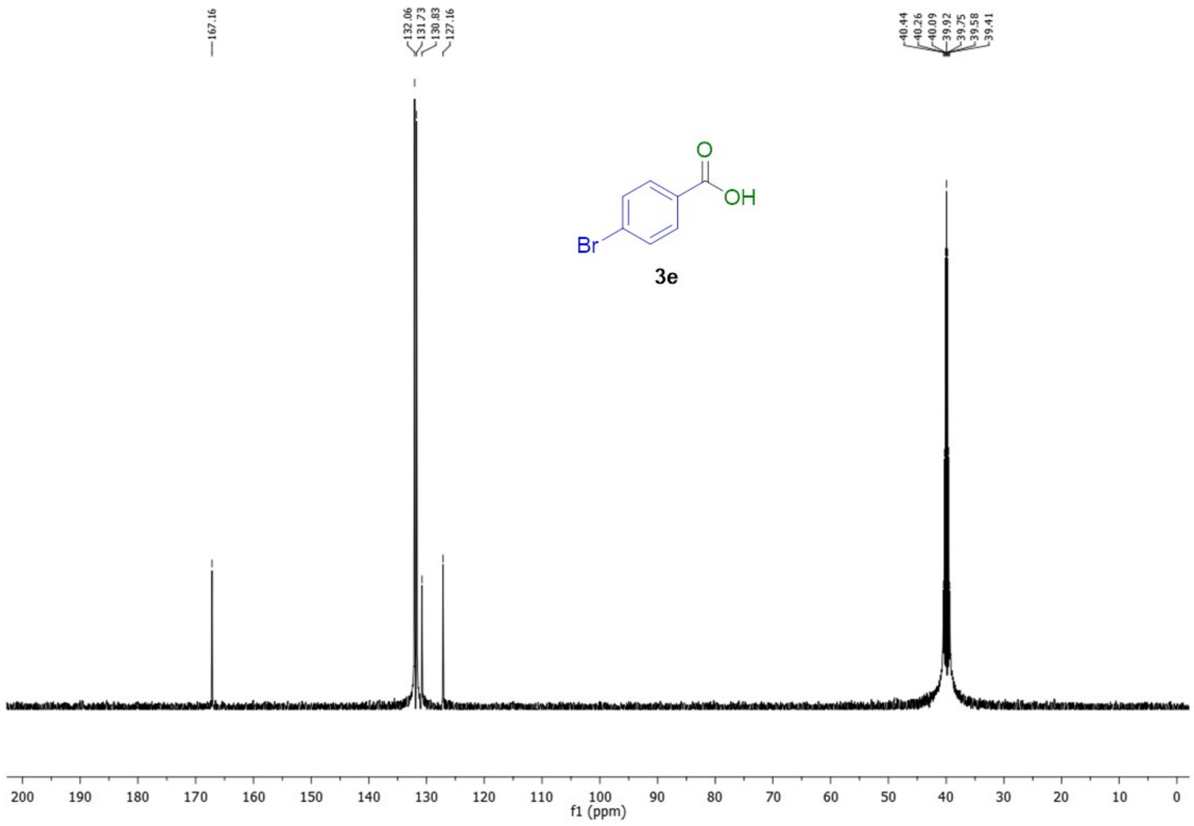

192.03
146.75
139.03
137.92
136.24
135.29
130.43
127.61
127.55
126.98
114.90
77.42
77.16
76.91
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

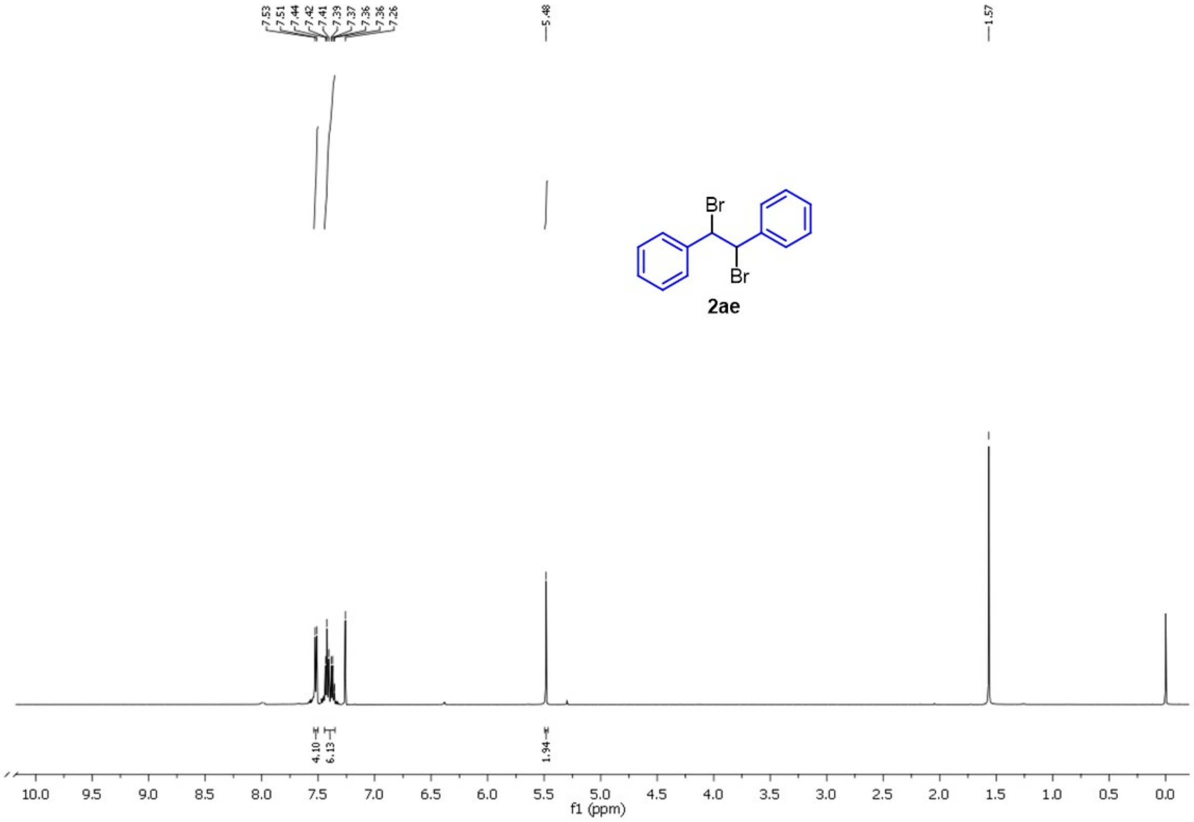
2ak

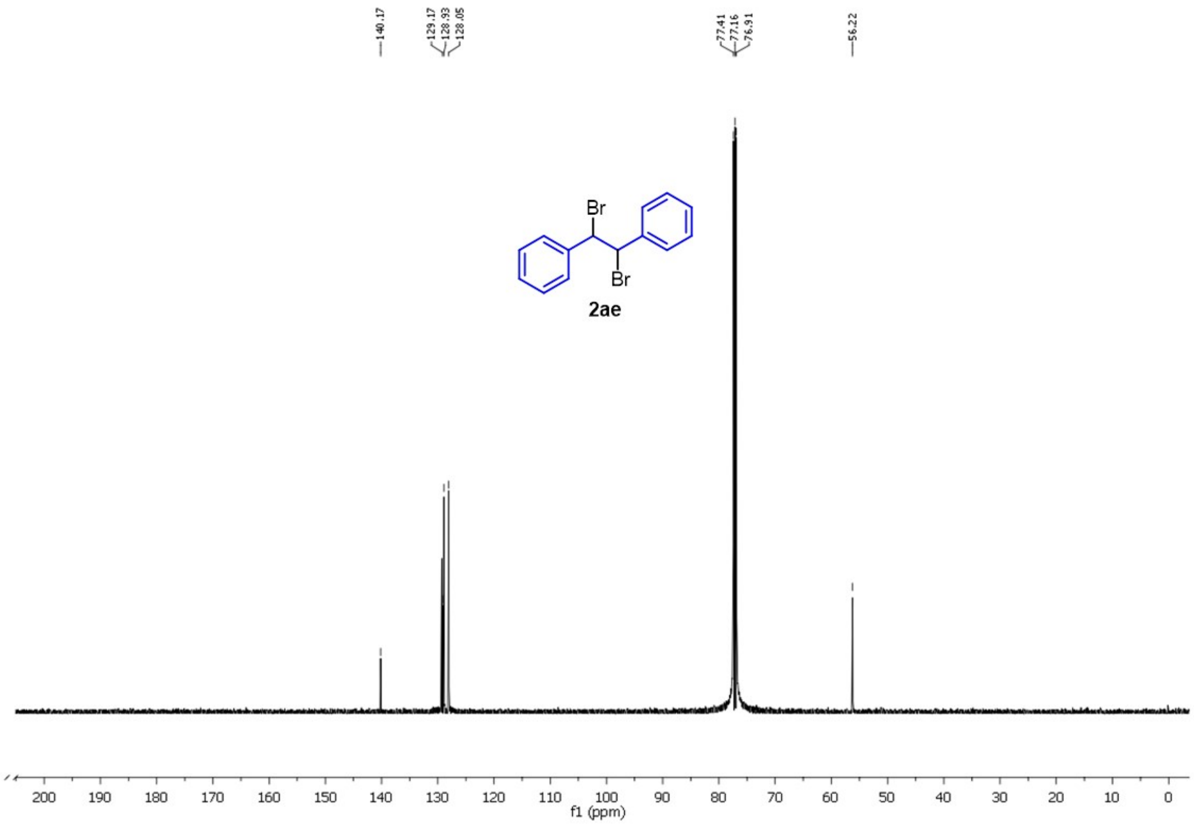

10.09
8.11
8.10
8.01
7.99
7.81
7.79
7.79
7.77
7.75
7.26
4.48
1.59
Br
O
O
4ak
0.92
2.01
2.00
4.07
1.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


191.87
190.94
145.47
145.09
136.06
133.61
130.48
129.81
128.06
127.92
77.41
77.16
76.91
30.86
Br
O
O
4ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.92
7.86
7.84
7.68
7.66
2.50
Br
O
OH
3e
12.92
0.79
14
13
12
11
f1 (ppm)
0.79
2.04
2.00
14.5
13.5
12.5
11.5
10.5
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)


167.16
132.06
131.73
130.83
127.16
40.44
40.26
40.09
39.92
39.75
39.58
39.41
Br
O
OH
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.53
7.51
7.44
7.42
7.41
7.39
7.37
7.36
7.36
7.26
5.48
1.57
Br
Br
2ae
4.10
6.13
1.94
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)


140.17
129.17
128.93
128.05
77.41
77.16
76.91
56.22
Br
Br
2ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6. HRMS spectra of TEMPO-adduct

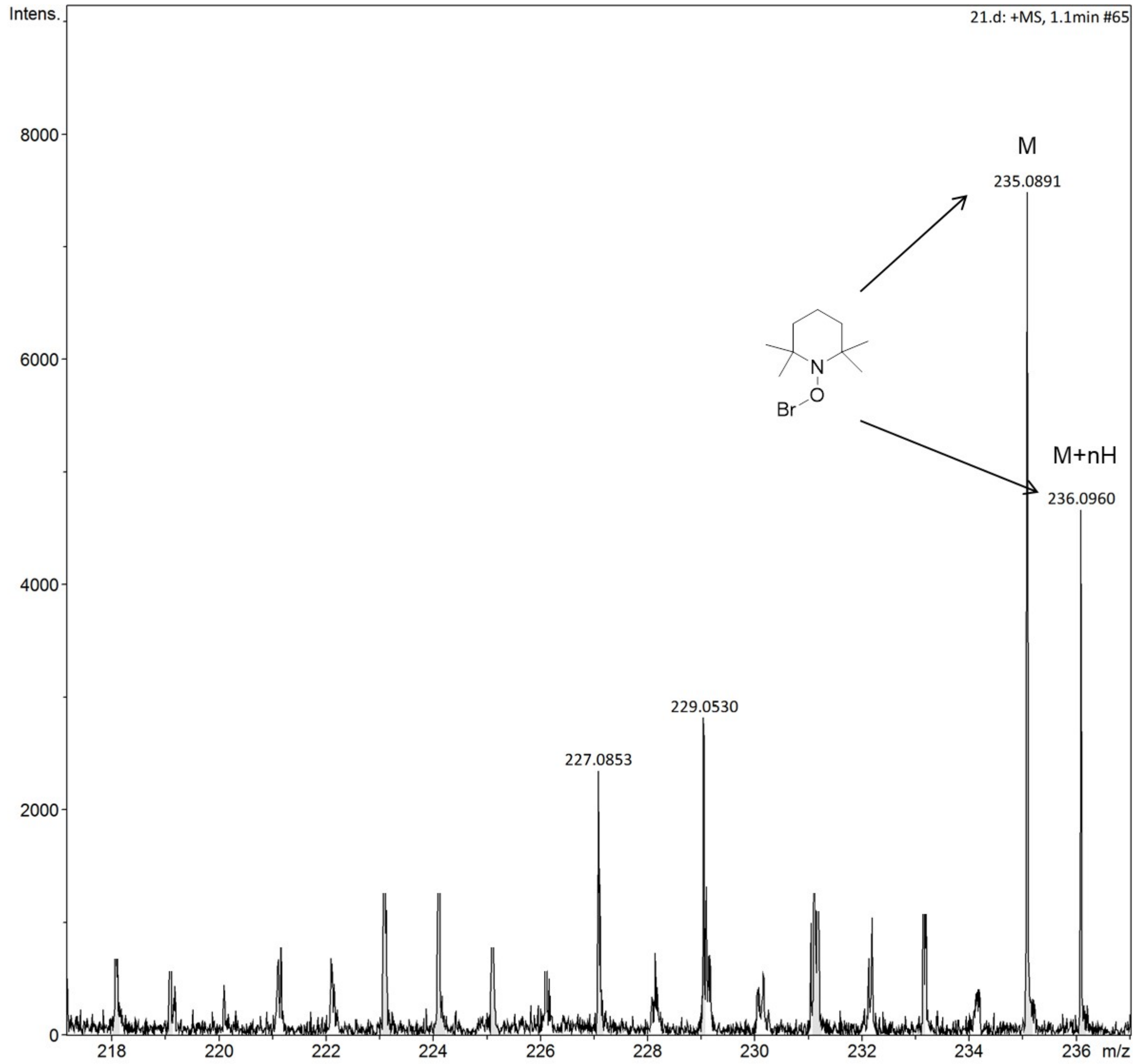


Figure S5. HRMS spectrum of TEMPO-adduct of photoinitiated C=C cleavage reaction.