



Supporting Information

for

1-Butyl-3-methylimidazolium tetrafluoroborate as suitable solvent for BF₃: the case of alkyne hydration. Chemistry vs electrochemistry

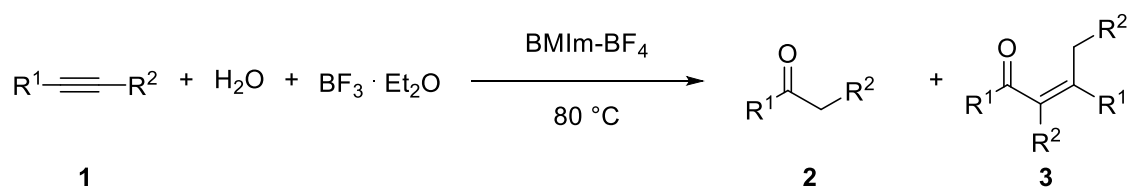
Marta David, Elisa Galli, Richard C. D. Brown, Marta Feroci, Fabrizio Vetica and Martina Bortolami

Beilstein J. Org. Chem. **2023**, *19*, 1966–1981. [doi:10.3762/bjoc.19.147](https://doi.org/10.3762/bjoc.19.147)

Additional experimental data

Table of contents

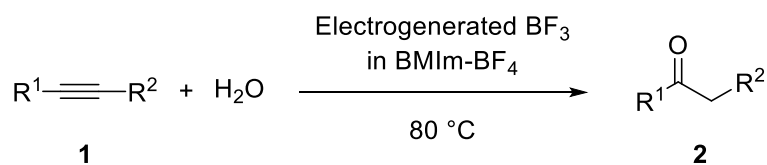
Table S1. Hydration of different alkynes catalysed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm-BF_4	S2
Table S2. Hydration of different alkynes catalysed by electrogenerated BF_3 in BMIm-BF_4	S4
Figure S1. ^{19}F -NMR spectra under neat conditions of (a) BMIm-BF_4 , (b) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm-BF_4 , (c) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and H_2O in BMIm-BF_4 , (d) anodically oxidated BMIm-BF_4 in a undivided cell, (e) anodically oxidated BMIm-BF_4 in a divided cell, (f) recycled BMIm-BF_4 after anodical oxidation in a divided cell, reaction with diphenylacetylene, ethereal extraction and solvent evaporation.....	S6
Figure S2. ^{13}C NMR spectra under neat conditions of (a) BMIm-BF_4 , (b) DIPEA (0.6 mmol) added to anodically oxidated BMIm-BF_4 (60 C) in a divided cell.....	S7
Figure S3. ^{19}F NMR spectra under neat conditions of (a) DBU and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm-BF_4 , (b) DBU (0.6 mmol) added to anodically oxidated BMIm-BF_4 (60 C) in a divided cell.....	S8
Figure S4. ^{19}F NMR spectra under neat conditions of DBU and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm-BF_4	S9
Figure S5. ^{13}C NMR spectra under neat conditions of (a) BMIm-BF_4 , (b) DBU in BMIm-BF_4 , (c) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and DBU in BMIm-BF_4 , (d) DBU (0.6 mmol) in anodically oxidated BMIm-BF_4 (60 C) in a divided cell, (e) DBU (1.2 mmol) in anodically oxidated BMIm-BF_4 (60 C) in a divided cell.....	S10
Analytical data.....	S11
^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in CDCl_3	S19
References.....	S40

Table S1. Hydration of different alkynes catalysed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm-BF_4 . ^a

Entry	Alkyne	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ ^b	Time	2 , yield ^c	3 , yield ^c	Recovered 1 ^c
1 ^d	1a	3	18 h	2a , 81%	-	11%
2	1b	3	5 h	2b , 97%	-	-
3	1b	3	18 h	2b , 100%	-	-
4	1c	3	5 h	2c , 76%	-	-
5	1d	3	5 h	2d , 32%	3d , 58%	-
6	1d	1	1 h	2d , 81%	-	-
7	1e	3	5 h	-	3e , 70%	-
8	1e	3	18 h	-	3e , 36%	-
9	1e	2	5 h	2e , 21%	3e , 74%	-
10	1e	1	1 h	2e , 61%	3e , 38%	-
11	1e	0.5	1 h	2e , 49%	3e , 31%	-
12	1f	1	1 h	2f , 43%	3f , 56%	-
13	1f	0.5	1 h	2f , 26%	-	37%
14	1g	1	1 h	2g , 81%	3g , 4%	-
15	1h	1	1 h	2h , 47%	3h , 43%	-
16	1i	1	1 h	2i , 72%	-	21%
17	1i	1	2 h	2i , 64%	3i , 29%	6%
18 ^e	1j	5 ^f	5 h	2j , 21% 2jj , 14%	-	5%

19 ^e	1j	5 ^f	18 h	2j , 13% 2jj , 14%	-	-
20 ^e	1j	3 ^f	1 h	2j , 57% 2jj , 16%	-	18%
21 ^e	1j	3 ^f	5 h	2j , 16% 2jj , 29%	-	2%
22 ^e	1j	2 ^f	1 h	2j , 56% 2jj , 22%	-	6%
23	1k	3	18 h	2k , 79%	-	-
25	1l	2	1 h	2l , 13%	-	63%
26	1l	2	18 h	2l , 62%	-	-
27	1m	5	18 h	2m , 65%	-	25%
28	1m	3	5 h	2m , 26%	-	73%
29	1n	5	18 h	2n , 47%	-	48%
30	1n	3	18 h	2n , 23%	-	68%

^a All the reactions were carried out at 80 °C in BMIm-BF₄, kept under vacuum for 16 h before each use, with 0.3 mmol of alkyne **1** and 0.3 mmol of H₂O. ^b Equivalents with respect to **1**. ^c Yields calculated from ¹H NMR spectra of the crude extracts. ^d Replicate of experiment reported in entry 9 of Table 1, for comparison. ^e 0.6 mmol of H₂O were used. ^f Equivalents with respect to one alkyne group of **1j**.

Table S2. Hydration of different alkynes catalysed by electrogenerated BF_3 in BMIm-BF_4 . ^a

Entry	Alkyne	Electrogenerated BF_3 (F/mol) ^b	Time	2 , yield ^c	Recovered 1 ^c
1	1a	4	18 h	2a , 85%	3%
2	1b	4	5 h	2b , 84%	-
3	1c	4	5 h	2c , 94%	-
4	1d	1	1 h	2d , 78%	-
5	1e	1	1 h	2e , 84% ^d	-
6	1f	1	1 h	2f , 91%	-
7	1g	1	1 h	2g , 78%	-
8	1h	1	1 h	2h , 94%	-
9	1i	1	1 h	2i , 20%	61%
10	1i	1	18 h	2i , 40%	12%
11	1i	2	18 h	2i , 79%	-
12 ^e	1j	2	1 h	2j , 39%	46%
13 ^e	1j	4	5 h	2j , 35% 2jj , 53%	3%
14	1k	1	5 h	-	54%
15	1k	2	5 h	2k , 13%	73%
16	1k	2	18 h	2k , 51%	-
17	1k	4	18 h	2k , 45%	-
18	1l	1	1 h	-	68%

19	1l	2	18 h	2l , 11%	43%
20	1l	4	18 h	2l , 23%	33%
21	1m	4	18 h	-	100%
22	1m	4 ^f	18 h	2m , 58%	40%
23	1n	4	18 h	-	100%
24	1n	8	18 h	2n , 2%	78%
25	1n	4 ^f	18 h	-	100%

^a BMIm-BF₄, kept under vacuum for 16 h before each use, was electrolyzed (galvanostatic conditions: 10 mA·cm⁻²) on platinum electrodes (rt, N₂) in divided cell configuration. At the end of electrolysis, alkyne **1** (0.3 mmol) and H₂O (0.3 mmol) were added to the anolyte. All the reactions were carried out at 80 °C for the time reported in table. ^b Amount of electrogenerated BF₃ with respect to starting alkyne, admitting a 100% current efficiency (1 mF = 96.5 C = 1 mmol of BF₃). ^c Yields calculated from ¹H NMR spectra of the crude extracts. ^d **3e**, 9%. ^e 0.6 mmol of H₂O were used. ^f The electrolysis was carried out in the presence of the alkyne (0.3 mmol) in the anodic compartment. At the end of electrolysis, H₂O (0.3 mmol) was added to the anolyte, then the reaction was carried out at 80 °C for the time reported in the table.

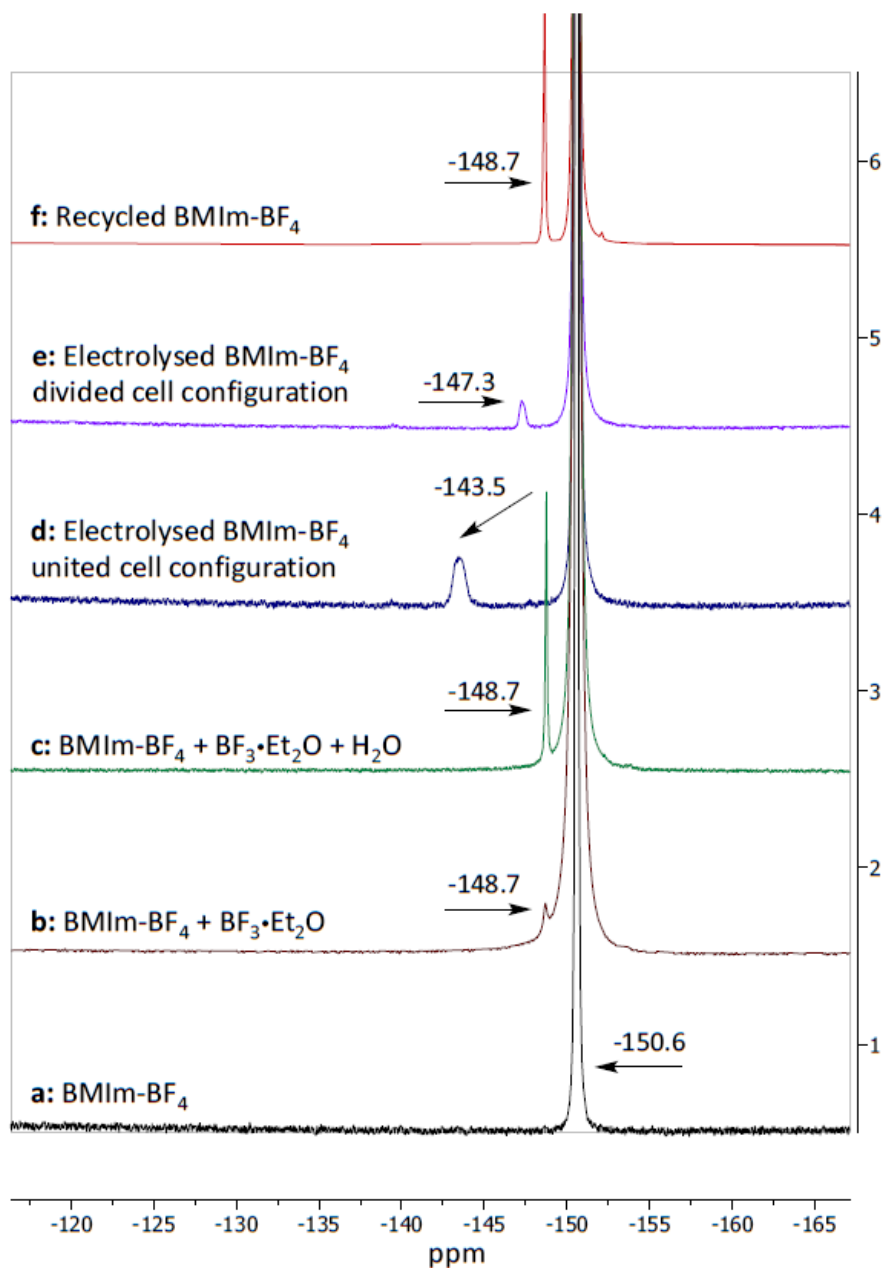


Figure S1. ^{19}F NMR spectra under neat conditions of (a) BMIm- BF_4 , (b) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm- BF_4 , (c) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and H_2O in BMIm- BF_4 , (d) anodically oxidated BMIm- BF_4 in a undivided cell, (e) anodically oxidated BMIm- BF_4 in a divided cell, (f) recycled BMIm- BF_4 after anodical oxidation in a divided cell, reaction with diphenylacetylene, etheral extraction and solvent evaporation.

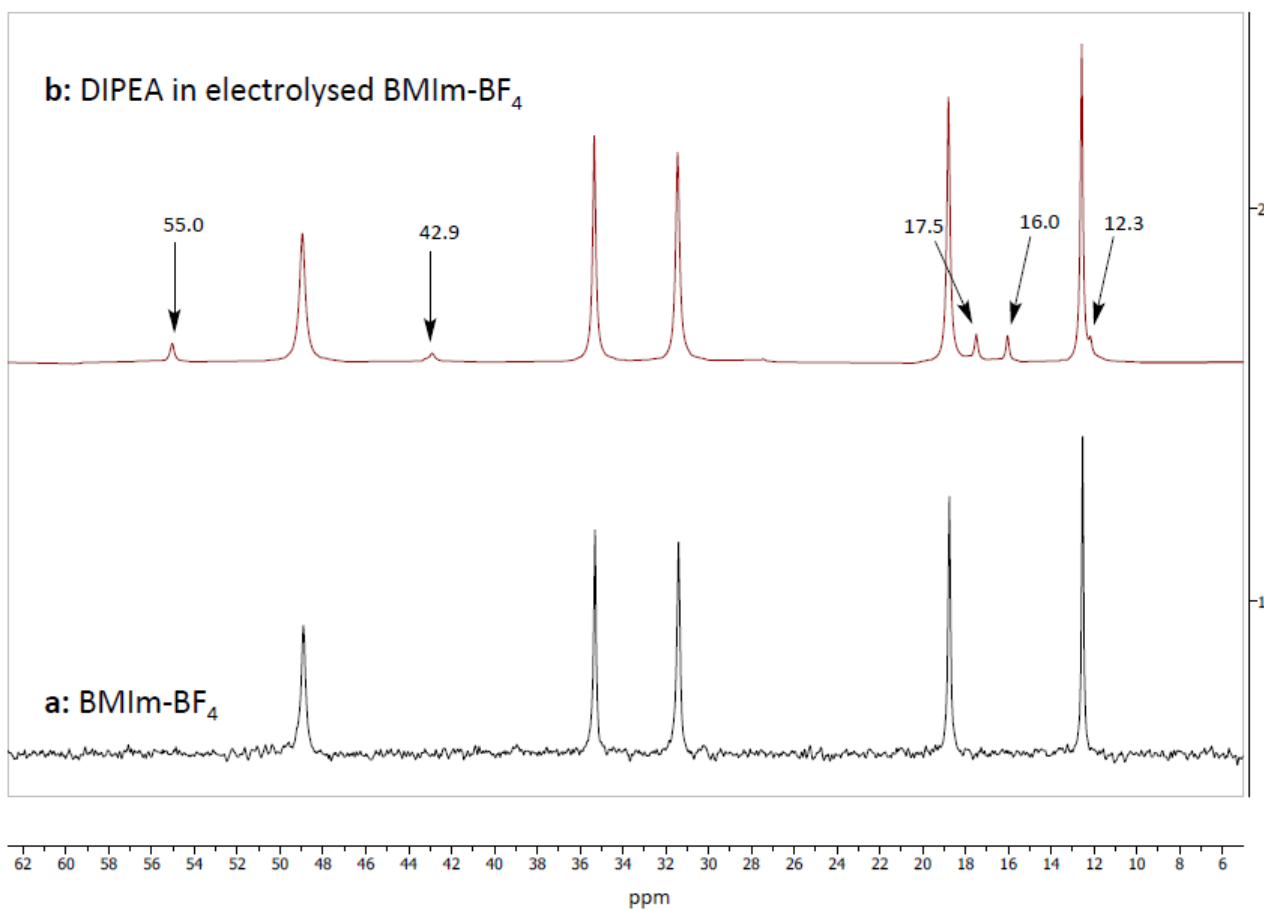


Figure S2. ^{13}C NMR spectra under neat conditions of (a) BMIm-BF₄, (b) DIPEA (0.6 mmol) added to anodically oxidated BMIm-BF₄ (60 C) in a divided cell.

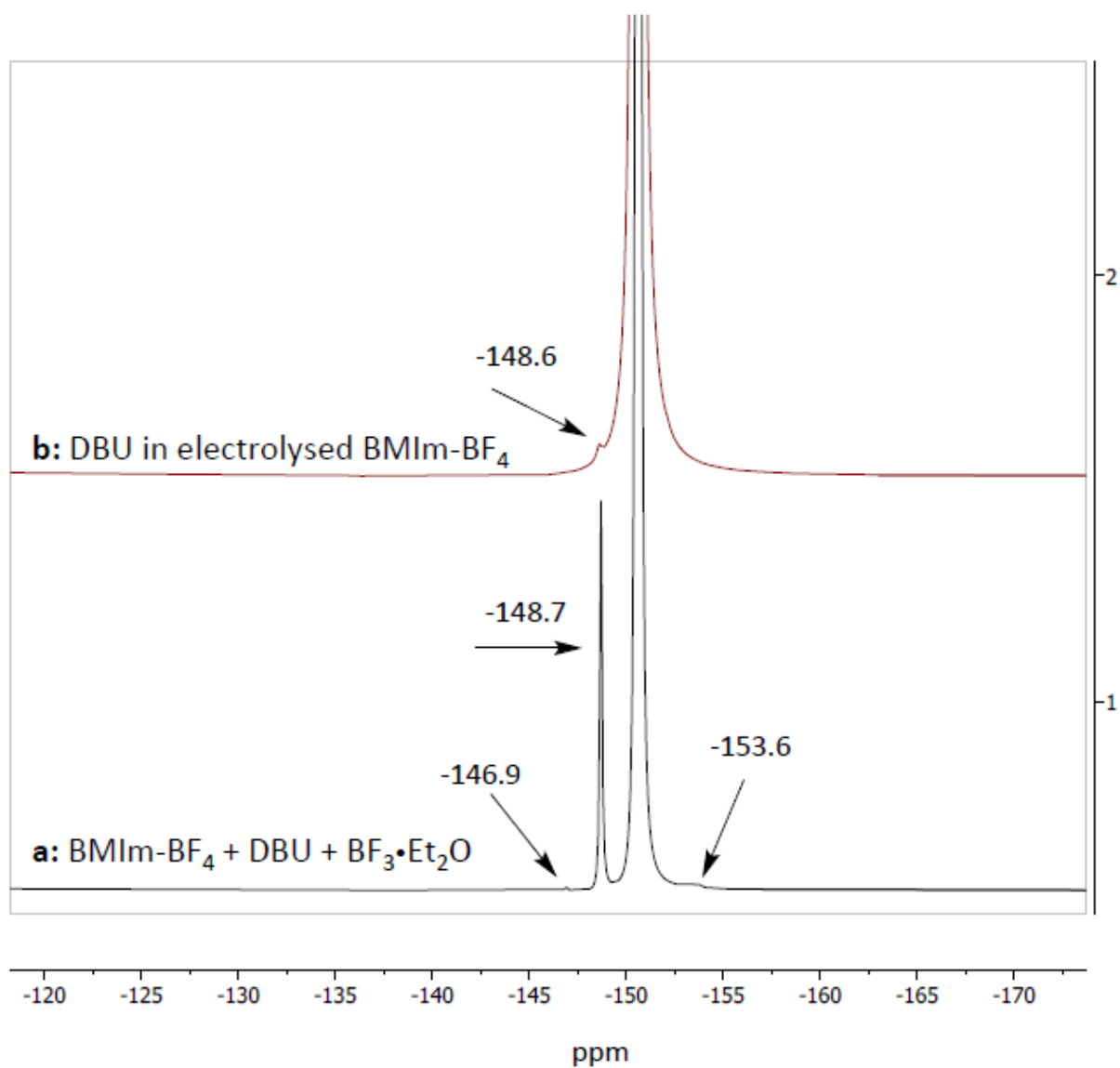


Figure S3. ^{19}F NMR spectra under neat conditions of (a) DBU and $\text{BF}_3\cdot\text{Et}_2\text{O}$ in BMIm- BF_4 , (b) DBU (0.6 mmol) added to anodically oxidated BMIm- BF_4 (60 C) in a divided cell.

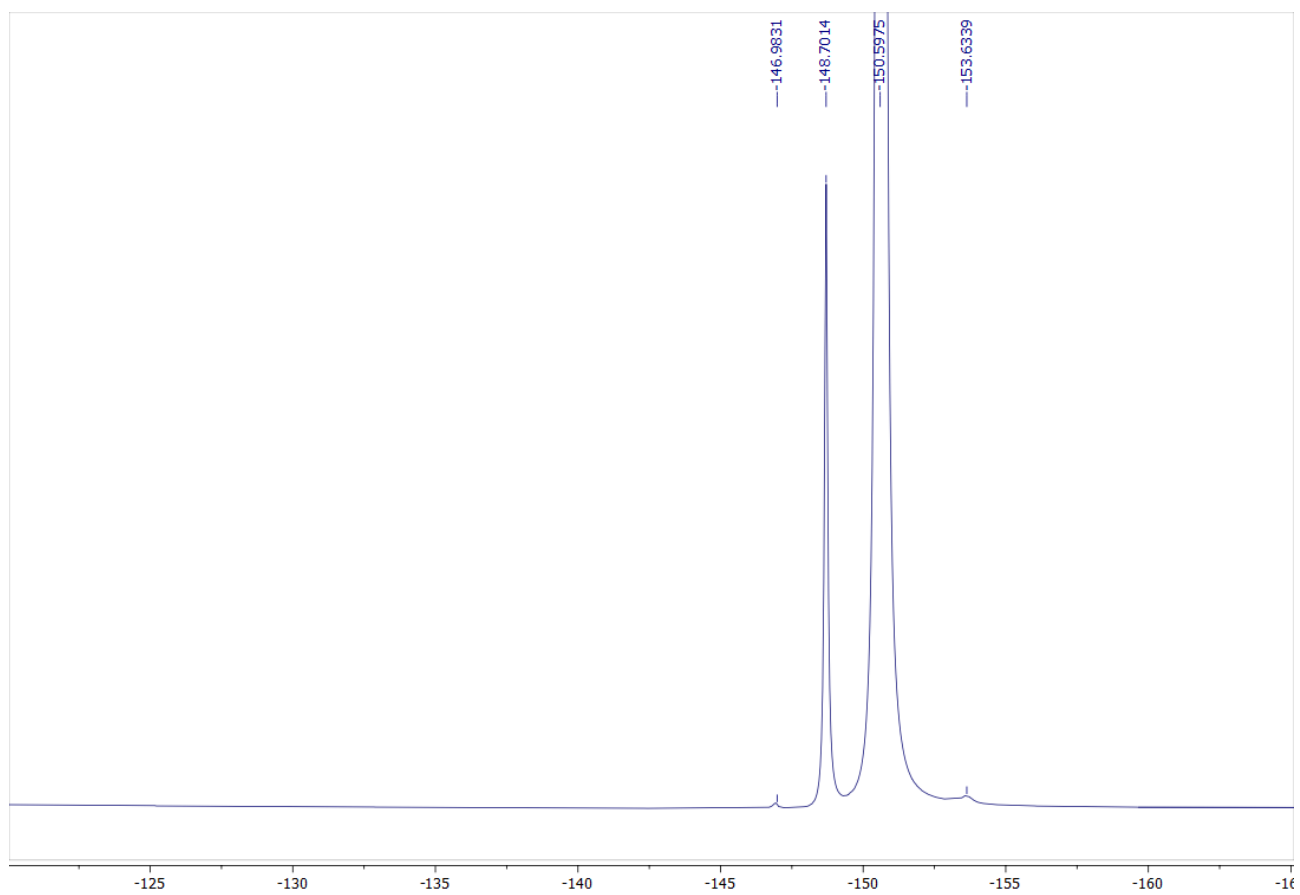


Figure S4. ^{19}F NMR spectra under neat conditions of DBU and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in BMIm- BF_4 .

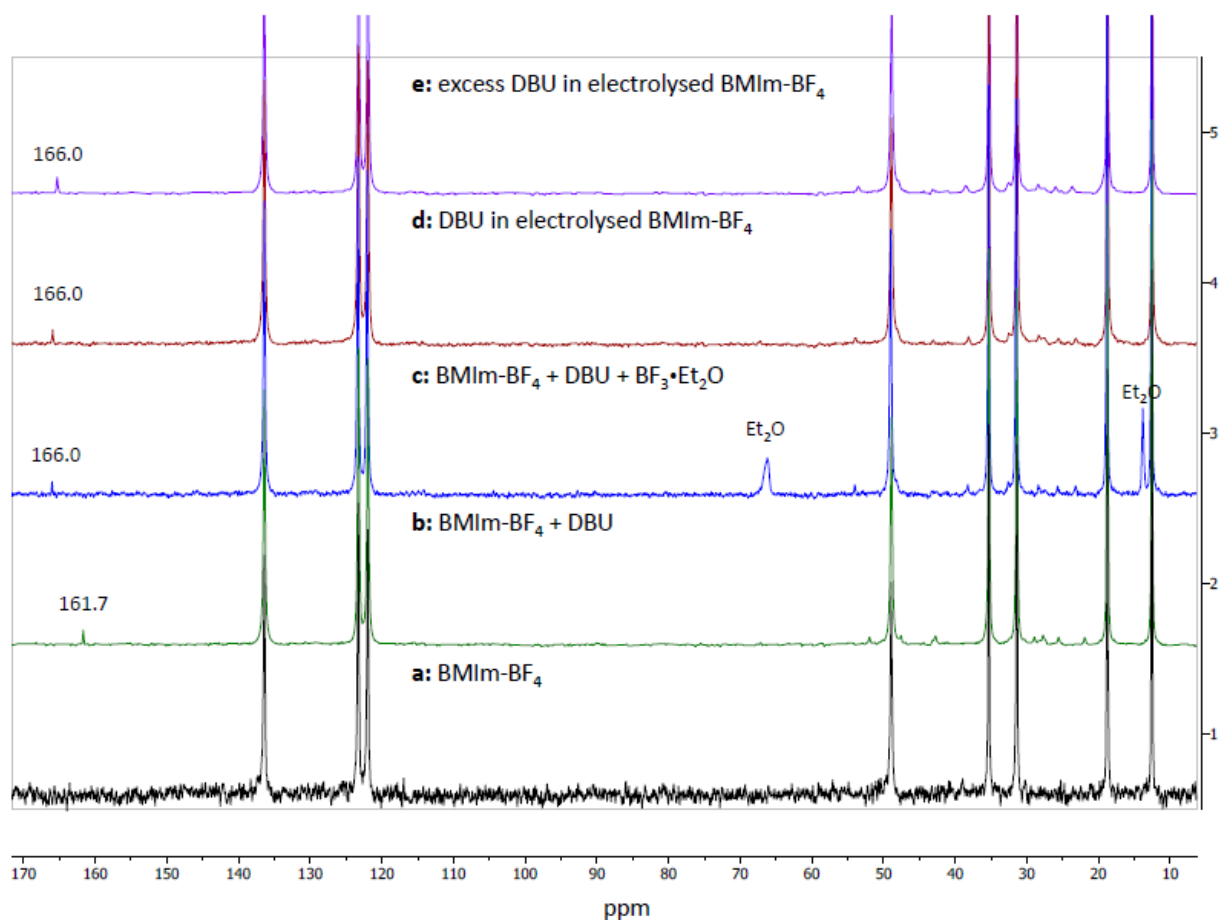
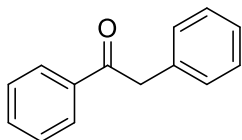


Figure S5. ^{13}C NMR spectra under neat conditions of (a) BMIm-BF₄, (b) DBU in BMIm-BF₄, (c) BF₃·Et₂O and DBU in BMIm-BF₄, (d) DBU (0.6 mmol) in anodically oxidated BMIm-BF₄ (60 C) in a divided cell, (e) DBU (1.2 mmol) in anodically oxidated BMIm-BF₄ (60 C) in a divided cell.

Analytical data

All isolated products were known and their spectral data were in accordance with those reported in the literature.

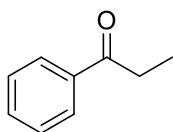


1,2-Diphenylethan-1-one (2a):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a white solid.¹

¹H NMR (400 MHz, CDCl₃) δ 8.04-8.01 (m, 2H); 7.58-7.54 (m, 1H); 7.48-7.44 (m, 2H); 7.35-7.31 (m, 2H); 7.28-7.24 (m, 3H); 4.29 (s, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 197.77; 136.75; 134.68; 133.30; 129.61; 128.81; 128.79; 128.76; 127.03; 45.64.

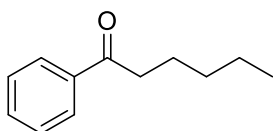


Propiophenone (2b):

The product was isolated after flash chromatography on silica gel (CH₂Cl₂/light petroleum ether 6:4) as a colourless oil.²

¹H NMR (400 MHz, CDCl₃) δ 7.98-7.96 (m, 2H); 7.57-7.53 (m, 1H); 7.48-7.44 (m, 2H); 3.01 (q, *J* = 7.24 Hz, 2H); 1.23 (t, *J* = 7.24 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 200.99; 137.07; 133.01; 128.69; 128.11; 31.92; 8.38.

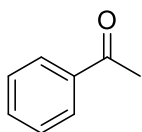


1-Phenylhexan-1-one (2c):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 97:3) as a colourless oil.³

¹H NMR (400 MHz, CDCl₃) δ 7.97-7.94 (m, 2H); 7.57-7.52 (m, 1H); 7.47-7.43 (m, 2H); 2.96 (t, *J* = 7.36 Hz, 2H); 1.78-1.70 (m, 2H); 1.40-1.34 (m, 4H); 0.93-0.89 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 200.74; 137.21; 132.97; 128.66; 128.16; 38.70; 31.67; 24.18; 22.65; 14.08.

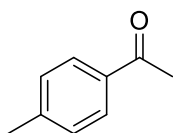


Acetophenone (2d):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a colourless oil.²

^1H NMR (400 MHz, CDCl_3) δ 7.94-7.92 (m, 2H); 7.54-7.51 (m, 1H); 7.44-7.41 (m, 2H); 2.56 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 198.07; 137.17; 133.09; 128.57; 128.30; 26.55.

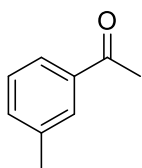


1-(p-Tolyl)ethan-1-one (2e):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a pale yellow oil.²

^1H NMR (400 MHz, CDCl_3) δ 7.85-7.82 (m, 2H); 7.24-7.22 (m, 2H); 2.55 (s, 3H); 2.38 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 197.94; 143.92; 134.73; 129.27; 128.48; 26.53; 21.64.

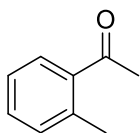


1-(m-Tolyl)ethan-1-one (2f):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a pale yellow oil.²

^1H NMR (400 MHz, CDCl_3) δ 7.77-7.74 (m, 2H); 7.38-7.32 (m, 2H); 2.59 (s, 3H); 2.41 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 198.54; 138.46; 137.27; 133.98; 128.90; 128.55; 125.70; 26.79; 21.44.

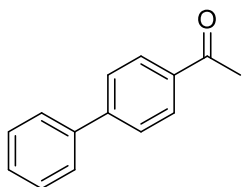


1-(o-Tolyl)ethan-1-one (2g):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a colourless oil.⁴

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.80 Hz, 1H); 7.28 (td, *J*₁ = 7.48, *J*₂ = 1.16 Hz, 1H); 7.19-7.14 (m, 2H); 2.49 (s, 3H); 2.44 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 201.80; 138.49; 137.70; 132.12; 131.60; 129.45; 125.78; 29.61; 21.67.

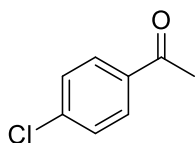


1-([1,1'-Biphenyl]-4-yl)ethan-1-one (2h):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 9:1) as a white solid.⁵

¹H NMR (400 MHz, CDCl₃) δ 8.05-8.02 (m, 2H); 7.71-7.68 (m, 2H); 7.65-7.62 (m, 2H); 7.50-7.45 (m, 2H); 7.43-7.38 (m, 1H); 2.64 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 197.89; 145.90; 139.98; 135.96; 129.08; 129.04; 128.36; 127.39; 127.34; 26.79.

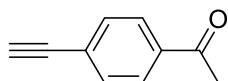


1-(4-Chlorophenyl)ethan-1-one (2i):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a colourless oil.⁴

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.56 Hz, 2H); 7.41 (d, *J* = 8.52 Hz, 2H); 2.57 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 196.90; 139.64; 135.51; 129.82; 128.97; 26.65.

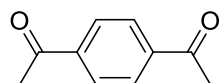


1-(4-Ethynylphenyl)ethan-1-one (2j):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 8:2) as a yellow solid.⁶

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.40 Hz, 2H); 7.55 (d, *J* = 8.40 Hz, 2H); 3.25 (s, 1H); 2.58 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 197.37; 136.84; 132.37; 128.28; 127.00; 82.84; 80.51; 26.72.

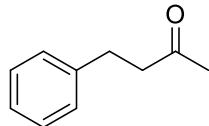


1,1'-(1,4-Phenylene)bis(ethan-1-one) (2jj):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 8:2) as a pinkish solid.⁷

¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 4H); 2.63 (s, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 197.61; 140.28; 128.61; 27.01.

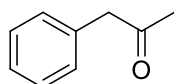


4-Phenylbutan-2-one (2k):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a colourless oil.⁴

¹H NMR (400 MHz, CDCl₃) δ 7.30-7.28 (m, 2H); 7.21-7.17 (m, 3H); 2.90 (t, *J* = 7.40 Hz, 2H); 2.76 (t, *J* = 7.40 Hz, 2H); 2.14 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 208.15; 141.13; 128.65; 128.44; 126.26; 45.34; 30.24; 29.88.

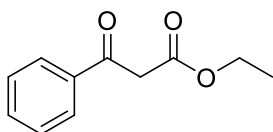


1-Phenylpropan-2-one (2l):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 9:1) as a pale yellow oil.⁴

¹H NMR (400 MHz, CDCl₃) δ 7.34-7.30 (m, 2H); 7.27-7.24 (m, 1H); 7.20-7.18 (m, 2H); 3.68 (s, 2H); 2.14 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 206.61; 134.37; 129.53; 128.90; 127.21; 51.18; 29.41.



Ethyl 3-oxo-3-phenylpropanoate (2m):

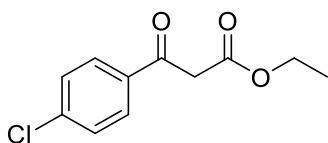
The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 9:1) as a mixture of ketone and enol forms (5:1), as a yellow oil.⁸

Ketone: ^1H NMR (400 MHz, CDCl_3) δ 7.95-7.93 (m, 2H); 7.61-7.57 (m, 1H); 7.49-7.46 (m, 2H); 4.21 (q, $J = 7.16$ Hz, 2H); 3.99 (s, 2H); 1.25 (t, $J = 7.12$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 192.65; 167.63; 131.34; 128.88; 128.61; 126.15; 61.58; 46.11; 14.17.

Enol: ^1H NMR (400 MHz, CDCl_3) δ 12.58 (s, 1H); 7.78-7.76 (m, 2H); 7.44-7.39 (m, 3H); 5.66 (s, 1H); 4.26 (q, $J = 7.16$ Hz, 2H); 1.33 (t, $J = 7.12$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.31; 171.54; 136.14; 133.84; 133.56; 128.64; 87.50; 60.43; 14.41.



Ethyl 3-(4-chlorophenyl)-3-oxopropanoate (2n):

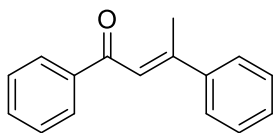
The product was isolated after flash chromatography on silica gel (CH_2Cl_2 /light petroleum ether 1:1) as a mixture of ketone and enol forms (3.8:1), as a yellow oil.⁹

Ketone: ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.60$ Hz, 2H); 7.45 (d, $J = 8.56$ Hz, 2H); 4.20 (q, $J = 7.16$ Hz, 2H); 3.95 (s, 2H); 1.25 (t, $J = 7.16$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 191.45; 167.34; 140.43; 134.46; 130.06; 129.25; 61.74; 46.08; 14.18.

Enol: ^1H NMR (400 MHz, CDCl_3) δ 12.57 (s, 1H); 7.69 (d, $J = 8.64$ Hz, 2H); 7.38 (d, $J = 8.60$ Hz, 2H); 5.63 (s, 1H); 4.26 (q, $J = 7.12$ Hz, 2H); 1.33 (t, $J = 7.12$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 173.18; 170.25; 137.42; 132.02; 128.94; 127.48; 87.79; 60.59; 14.40.

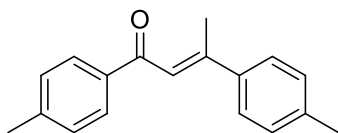


(E)-1,3-Diphenylbut-2-en-1-one (**3d**):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a pale yellow oil.¹⁰

¹H NMR (400 MHz, CDCl₃) δ 8.02-7.99 (m, 2H); 7.59-7.54 (m, 3H); 7.50-7.40 (m, 5H); 7.17 (q, *J* = 1.28 Hz, 1H); 2.60 (d, *J* = 1.28 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 192.04; 155.25; 142.93; 139.50; 132.69; 129.27; 128.75; 128.69; 128.43; 126.64; 122.27; 19.03.

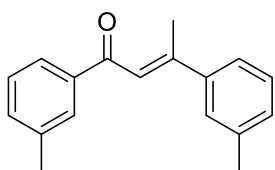


(E)-1,3-Di-*p*-tolylbut-2-en-1-one (**3e**):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 98:2) as a pale yellow solid.¹⁰

¹H NMR (400 MHz, CDCl₃) δ 7.92-7.89 (m, 2H); 7.50-7.47 (m, 2H); 7.28-7.26 (m, 2H); 7.24-7.22 (m, 2H); 7.16 (q, *J* = 1.28 Hz, 1H); 2.58 (d, *J* = 1.24 Hz, 3H); 2.42 (s, 3H); 2.40 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 191.75; 154.64; 143.32; 140.04; 139.37; 137.09; 129.42; 129.34; 128.54; 126.54; 121.61; 21.76; 21.36; 18.87.

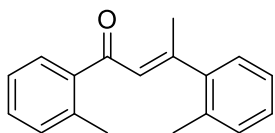


(E)-1,3-di-*m*-tolylbut-2-en-1-one (**3f**):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a pale yellow oil.¹⁰

¹H NMR (400 MHz, CDCl₃) δ 7.80-7.78 (m, 2H); 7.38-7.29 (m, 5H); 7.23-7.21 (m, 1H); 7.14 (q, *J* = 1.24 Hz, 1H); 2.58 (d, *J* = 1.28 Hz, 3H); 2.43 (s, 3H); 2.42 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 192.32; 155.22; 143.02; 139.59; 138.47; 138.38; 133.43; 129.99; 128.96; 128.64; 128.55; 127.34; 125.64; 123.78; 122.33; 21.66; 21.55; 19.08.

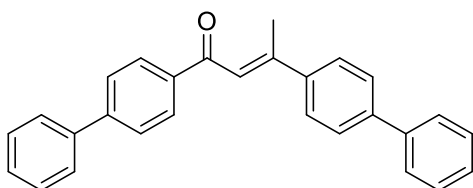


1,3-Di-o-tolylbut-2-en-1-one (*E/Z* mixture 1/0.25) (**3g**):

The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5).¹⁰

¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.76 Hz, 1H *E* isomer); 7.48-7.45 (m, 1H *Z* isomer); 7.36-7.33 (m, 1H *E* isomer); 7.26-7.06 (m, 6H *E* isomer + 6H *Z* isomer); 6.94-6.92 (m, 1H, *Z* isomer); 6.64 (d, *J* = 1.32 Hz, 1H *Z* isomer); 6.53 (d, *J* = 1.36 Hz, 1H *E* isomer); 2.54 (s, 3H *E* isomer); 2.45 (d, *J* = 1.32 Hz, 3H *E* isomer); 2.36 (s, 3H *E* isomer); 2.32 (s, 3H *Z* isomer); 2.22 (s, 3H *Z* isomer); 2.19-2.17 (m, 3H, *Z* isomer).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 196.00; 157.38; 144.41; 137.58; 134.11; 131.74; 131.31; 130.93; 130.65; 130.00; 128.60; 127.90; 127.74; 127.57; 127.41; 127.30; 126.63; 125.95; 125.77; 125.64; 125.22; 27.15; 21.62; 20.84; 20.52; 20.08; 19.54.

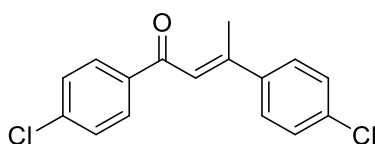


(E)-1,3-di([1,1'-biphenyl]-4-yl)but-2-en-1-one (**3h**):

The product was isolated after flash chromatography on silica gel (CH₂Cl₂/light petroleum ether 7:3) as a yellow solid.¹¹

¹H NMR (400 MHz, CDCl₃) δ 8.11-8.09 (m, 2H); 7.73-7.63 (m, 10H); 7.50-7.37 (m, 6H); 7.29 (d, *J* = 1.24 Hz, 1H); 2.66 (d, *J* = 1.16 Hz, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 190.51; 153.69; 144.42; 141.20; 140.69; 139.45; 139.18; 137.27; 128.10; 128.05; 127.30; 126.86; 126.44; 126.39; 126.22; 126.15; 121.06; 17.94.



(E)-1,3-Bis(4-chlorophenyl)but-2-en-1-one (**3i**):

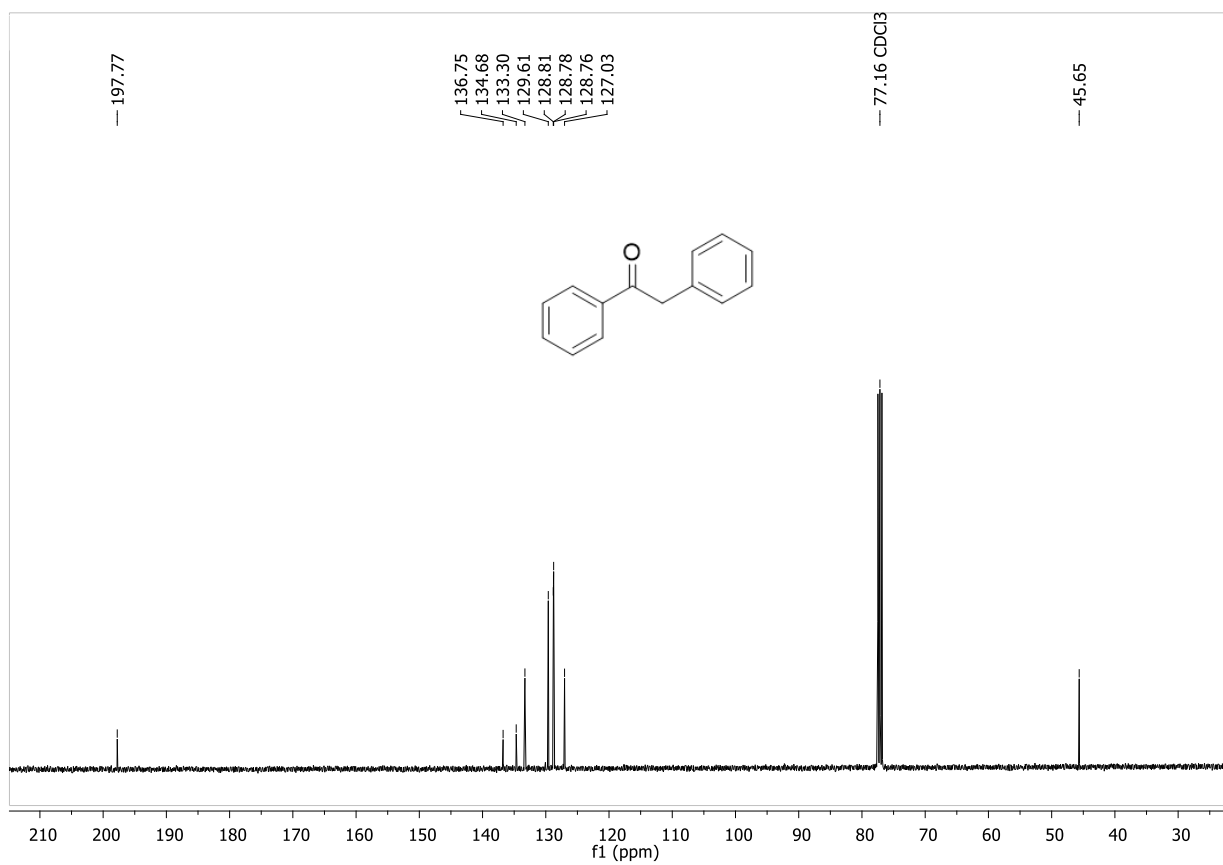
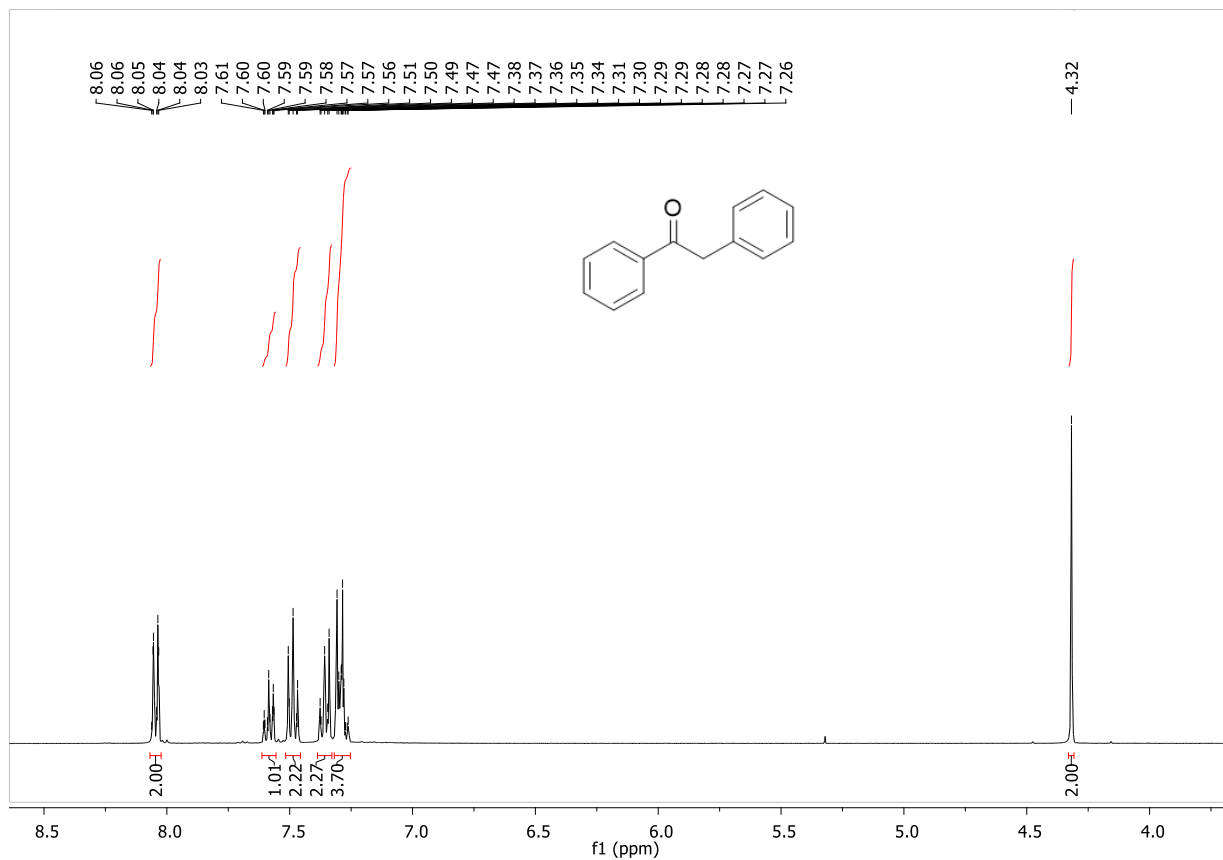
The product was isolated after flash chromatography on silica gel (light petroleum ether/EtOAc 95:5) as a pale yellow solid.¹⁰

^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.56$ Hz, 2H); 7.50 (d, $J = 8.60$ Hz, 2H); 7.45 (d, $J = 8.52$ Hz, 2H); 7.39 (d, $J = 8.60$ Hz, 2H); 7.08 (d, $J = 1.12$ Hz, 1H); 2.56 (d, $J = 1.08$ Hz, 3H).

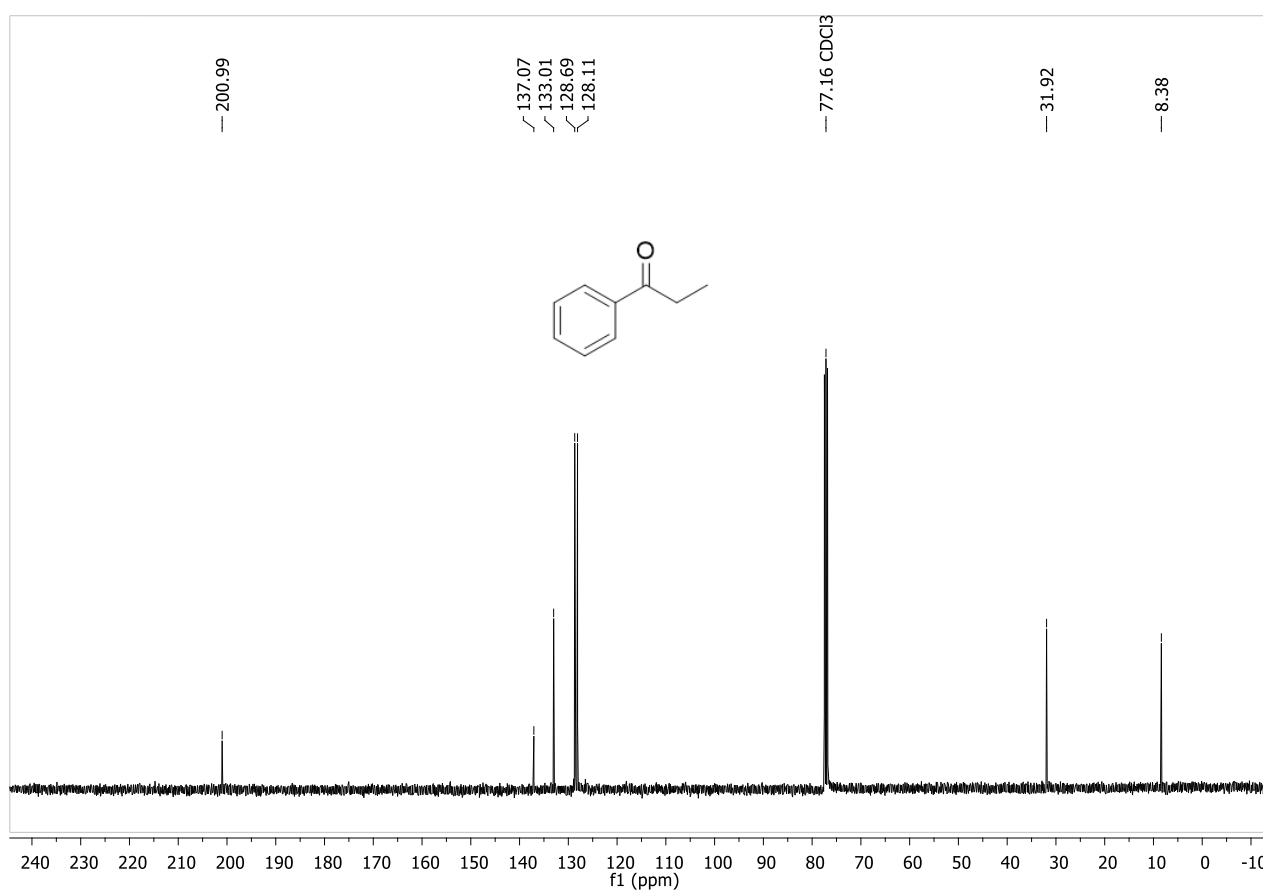
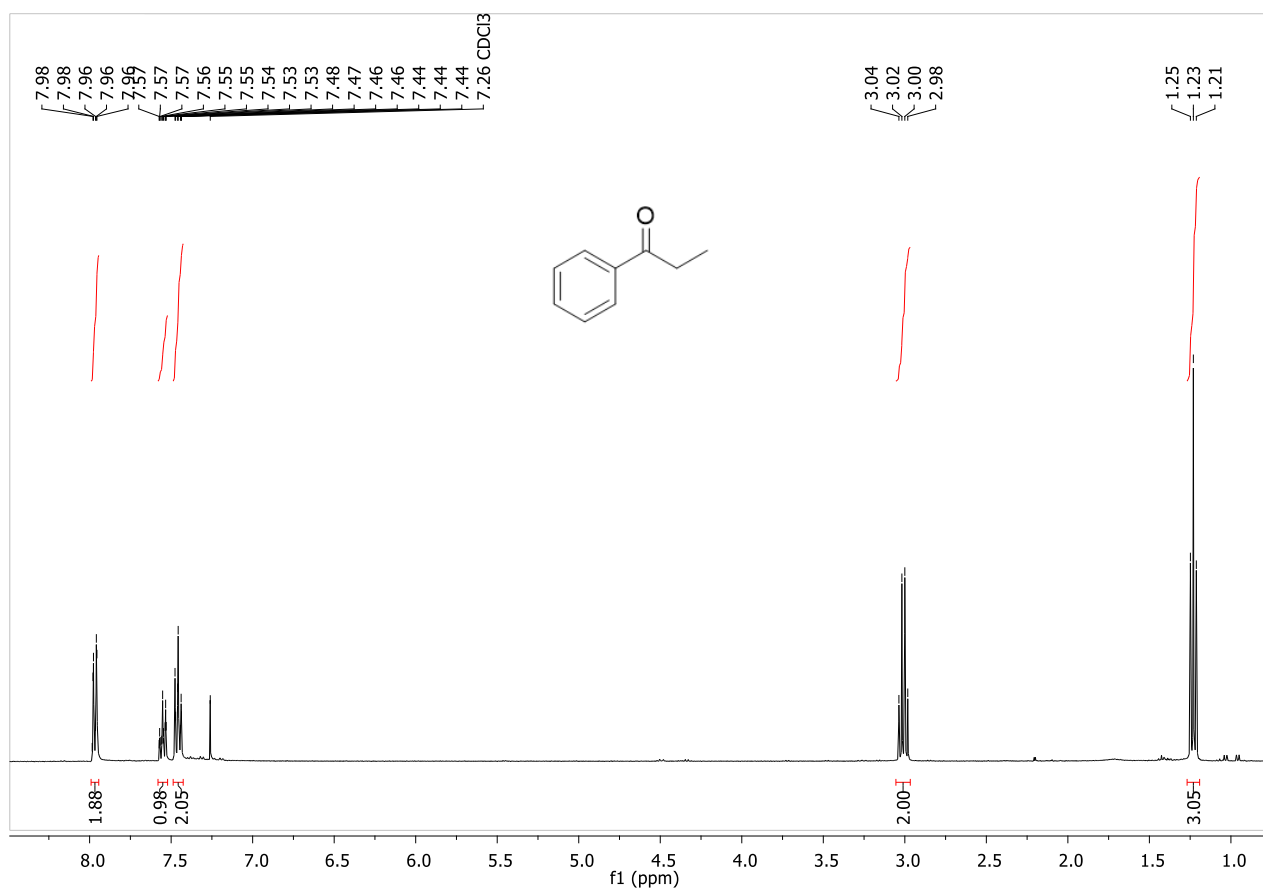
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 190.46; 154.53; 141.08; 139.22; 137.62; 135.45; 129.84; 129.04; 129.01; 127.94; 121.92; 18.99.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in CDCl_3

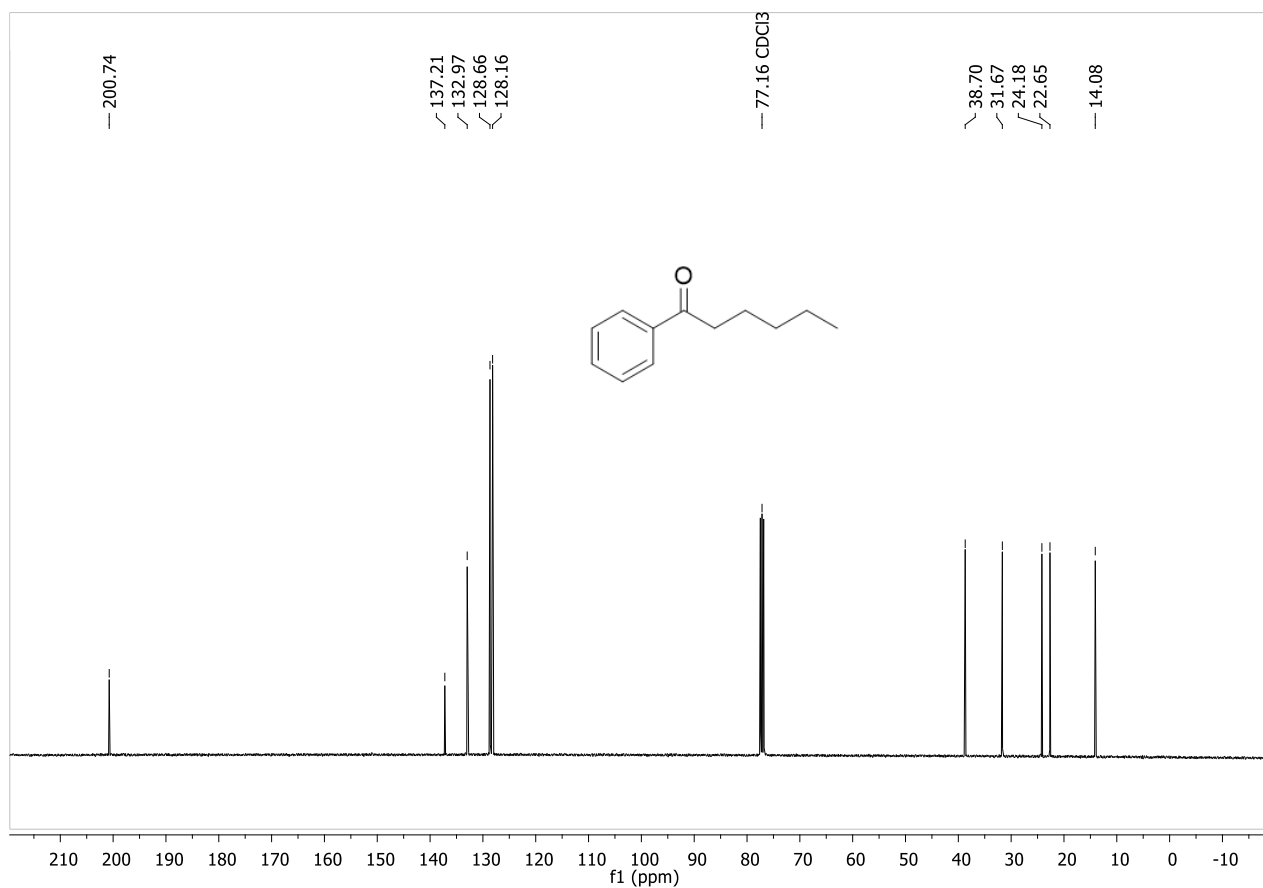
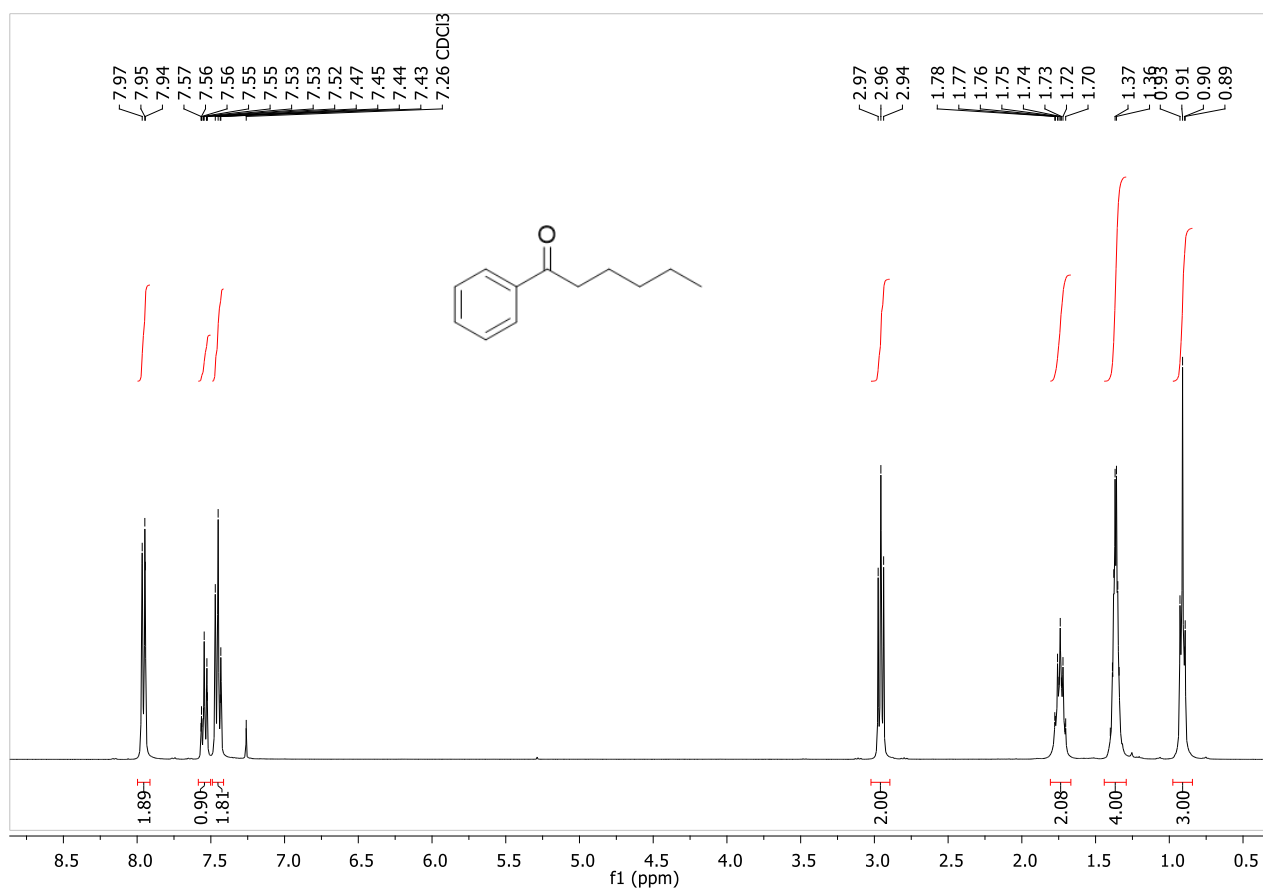
1,2-Diphenylethan-1-one (2a)



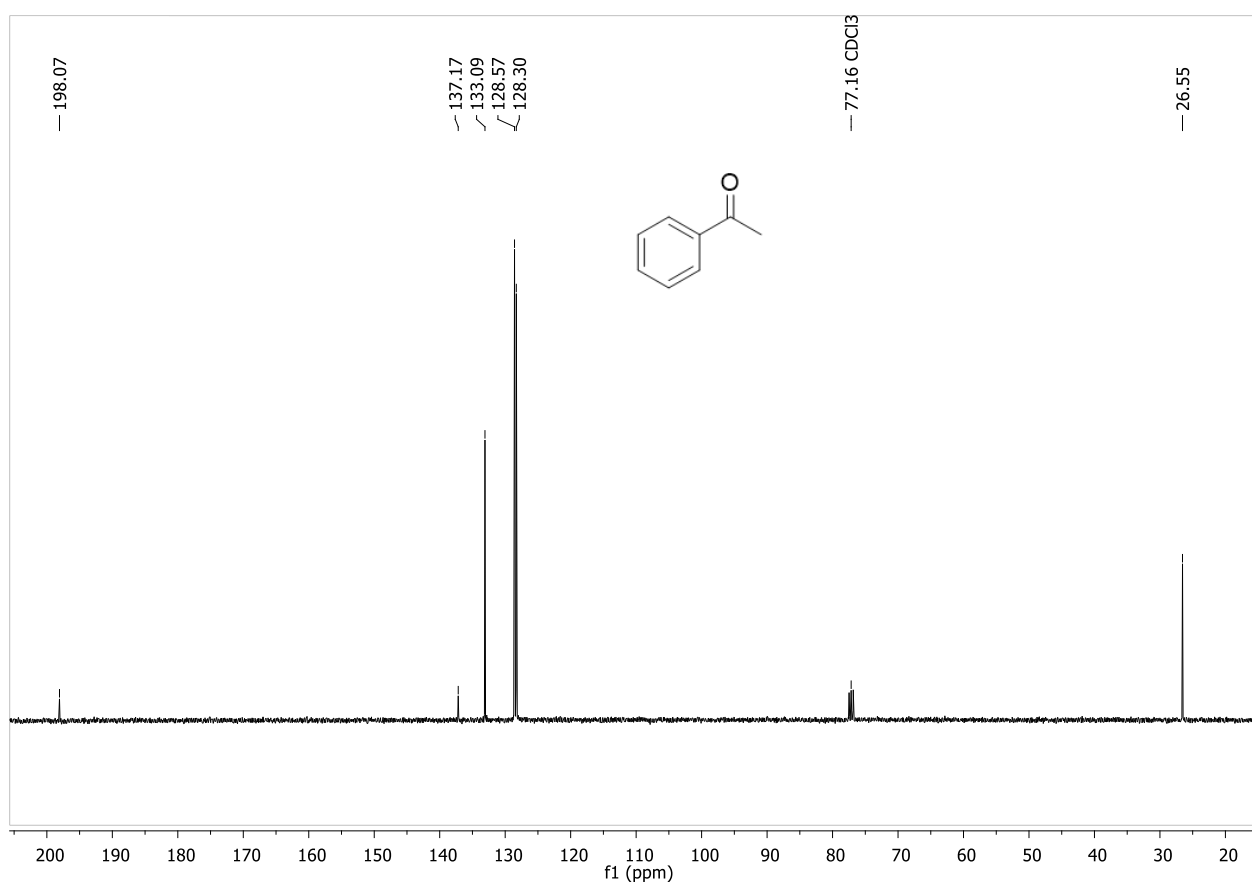
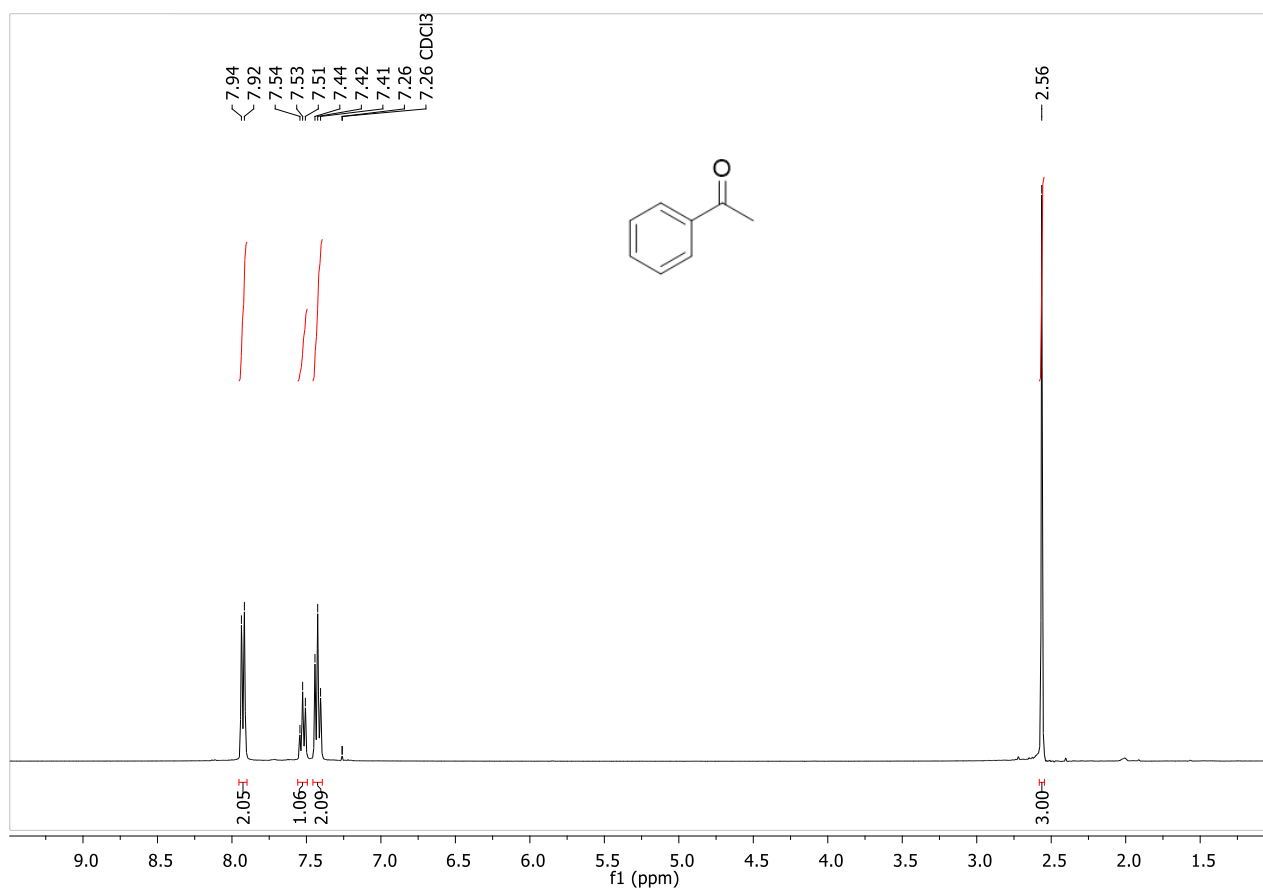
Propiophenone (2b)



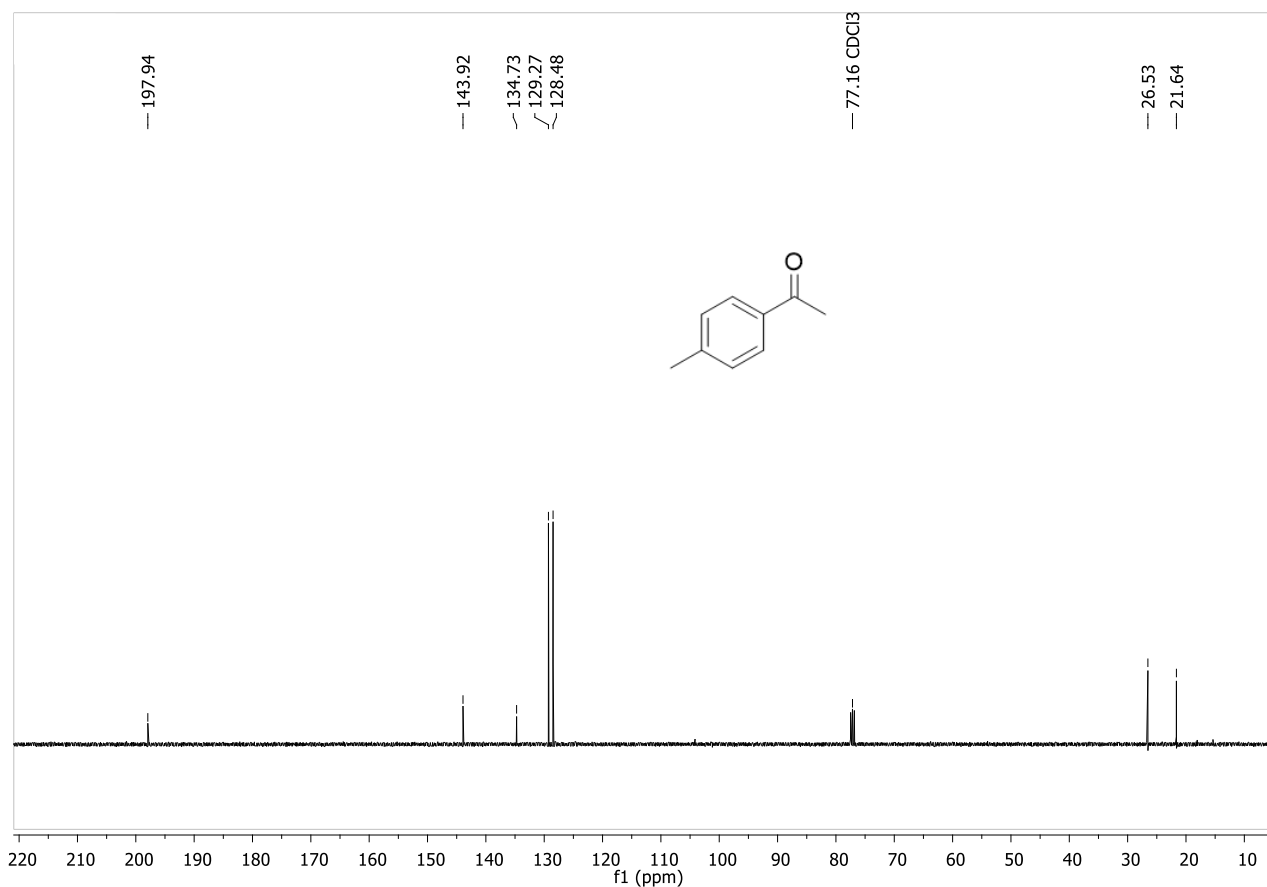
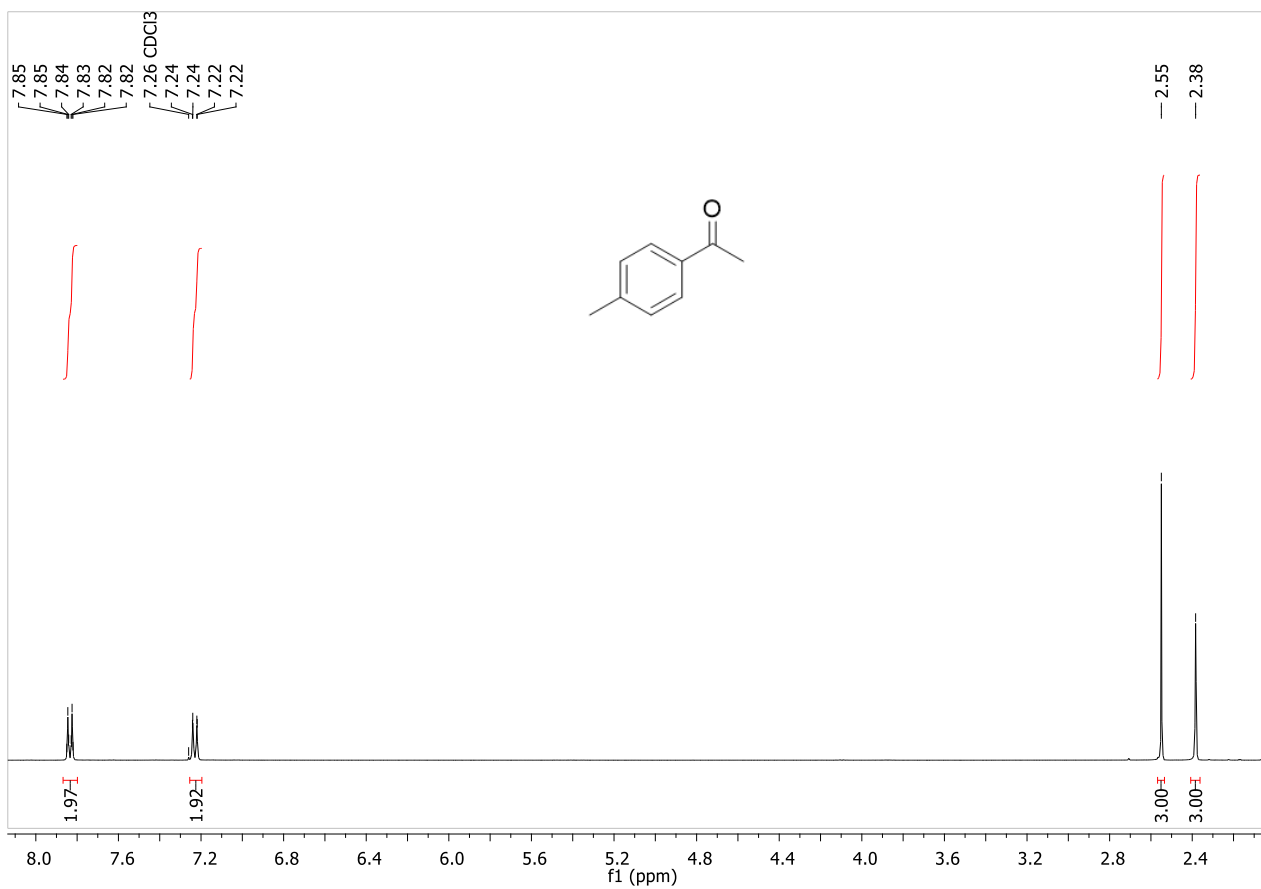
1-Phenylhexan-1-one (2c)



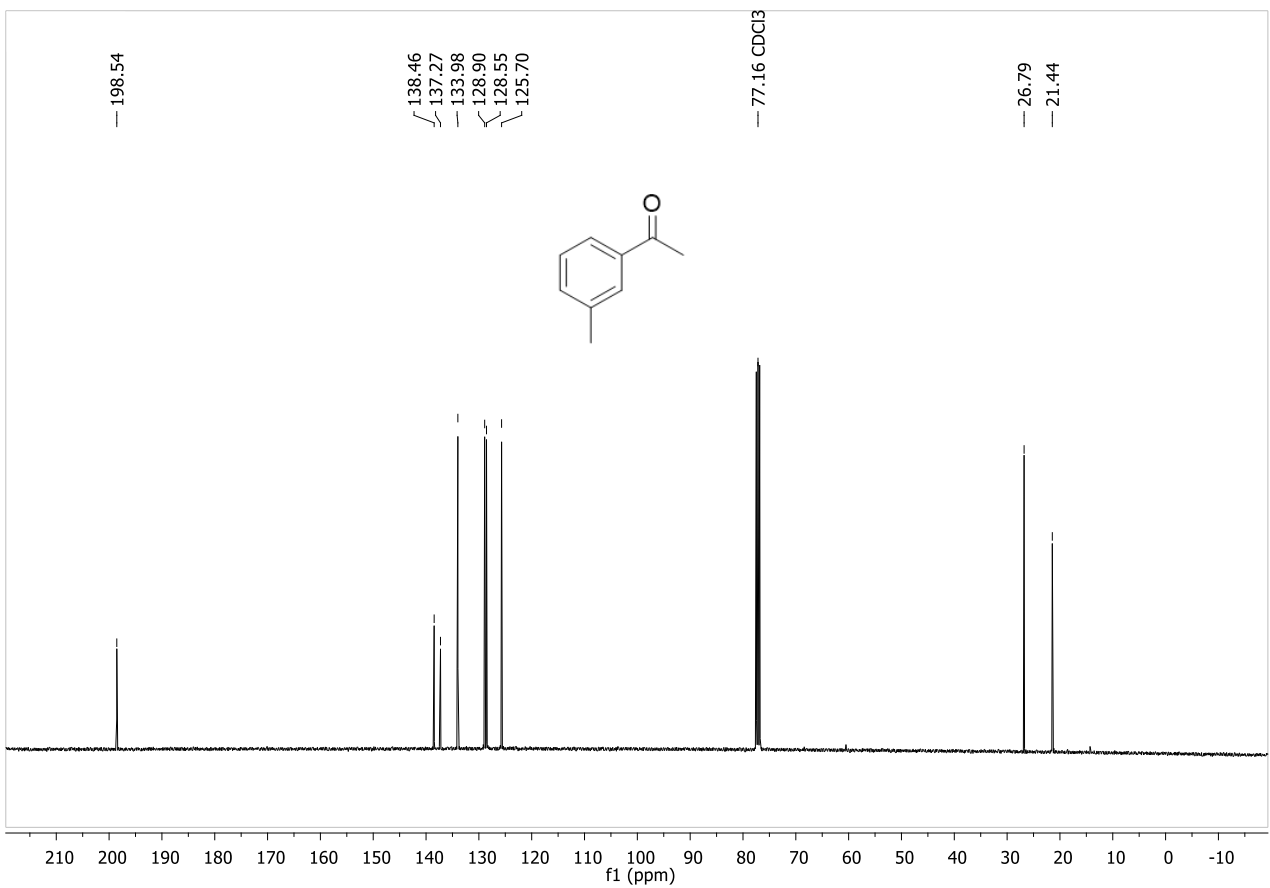
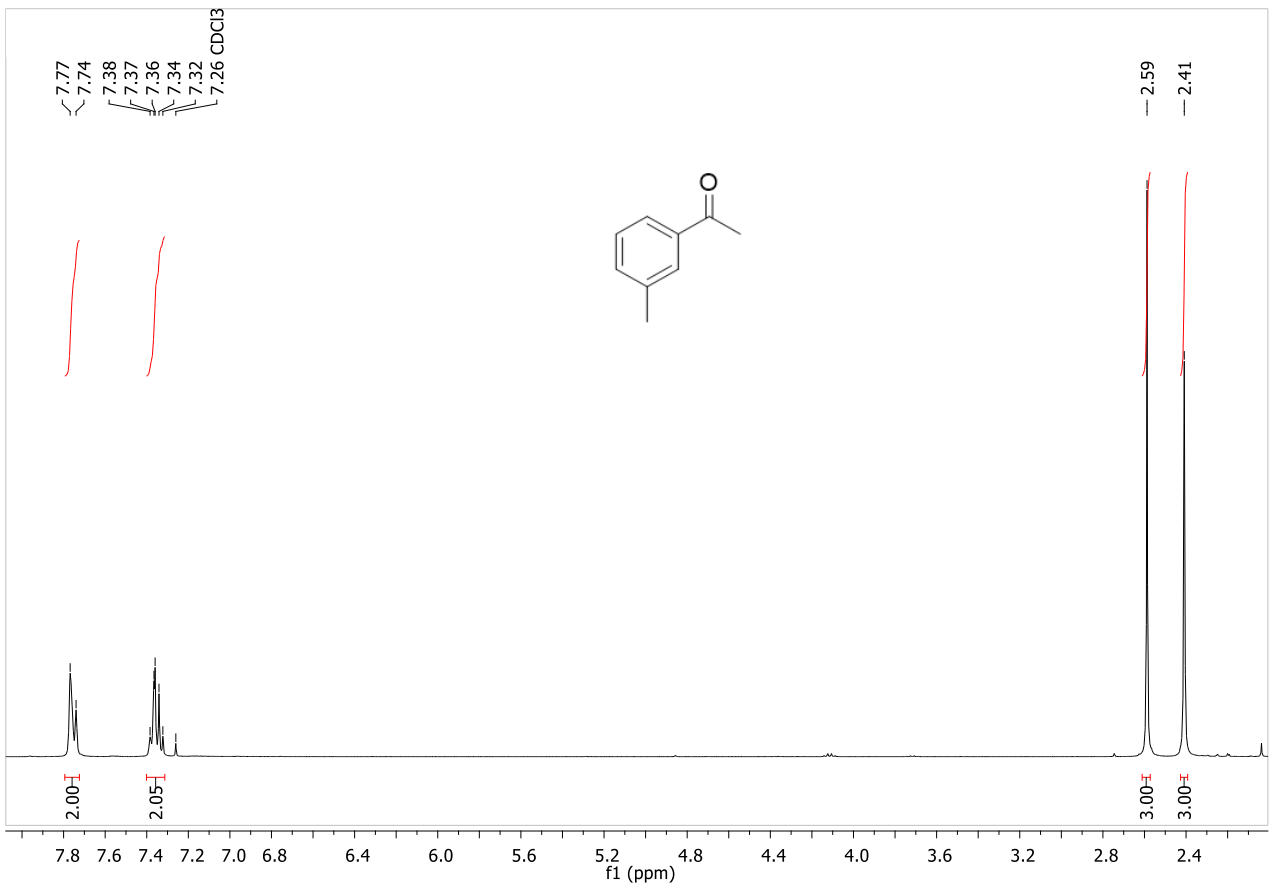
Acetophenone (2d)



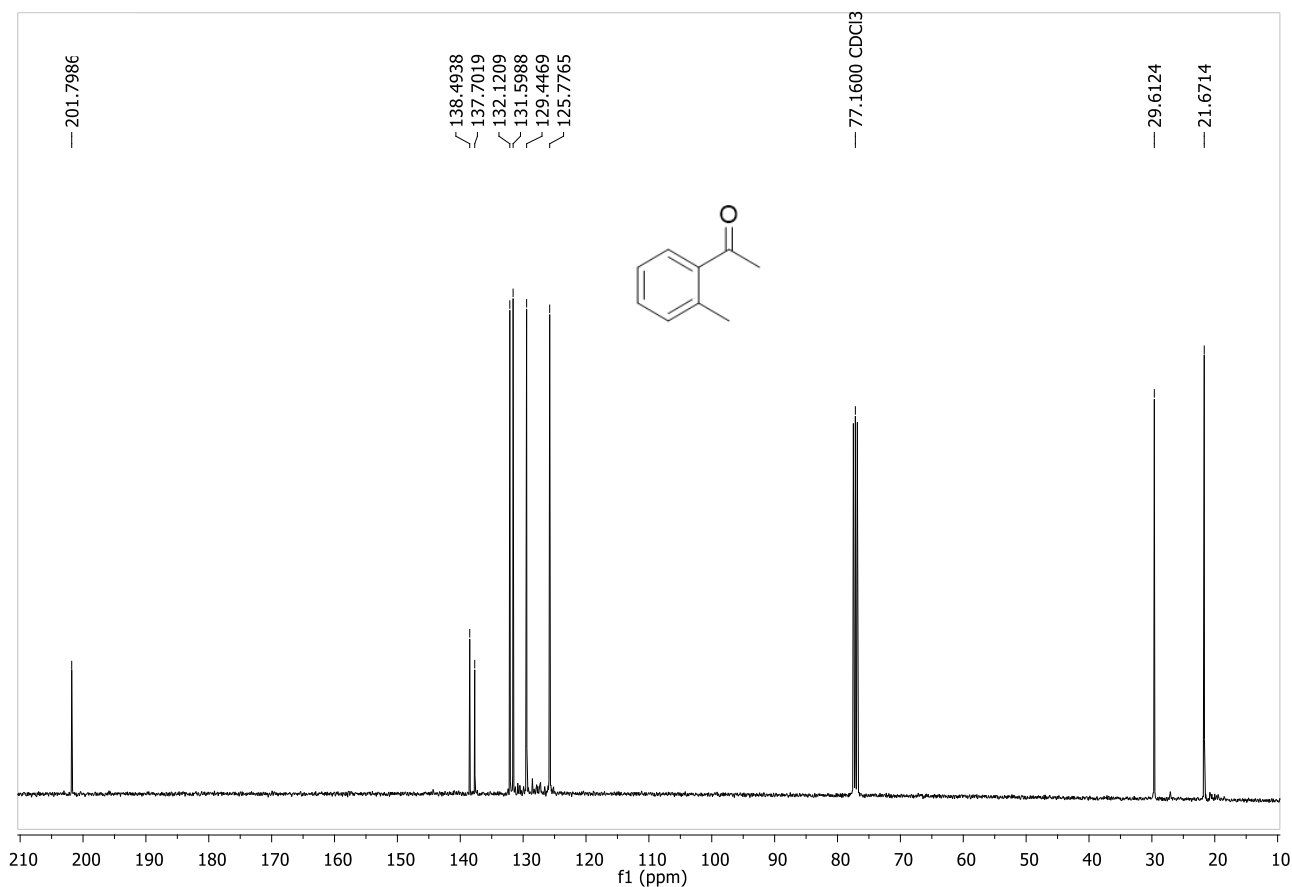
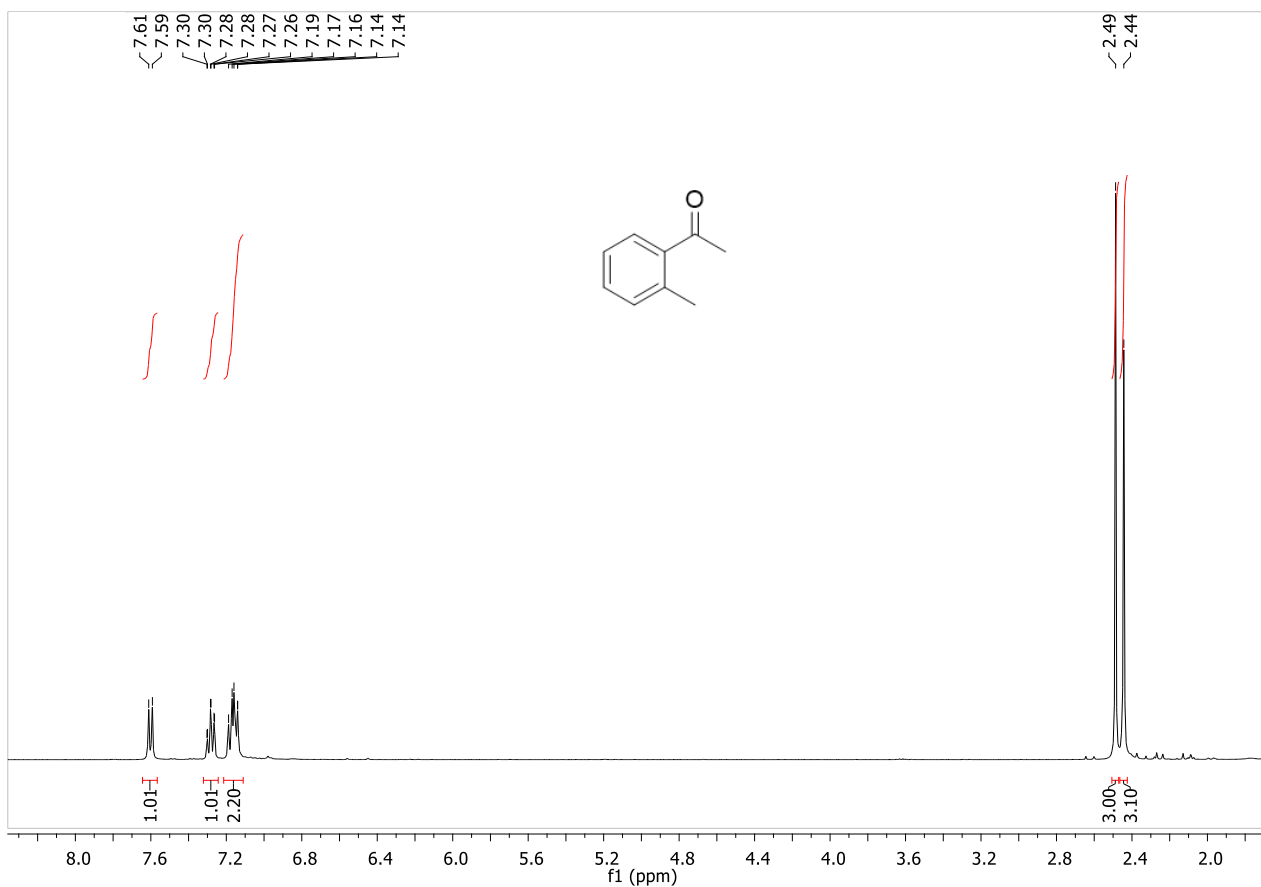
1-(*p*-Tolyl)ethan-1-one (2e)



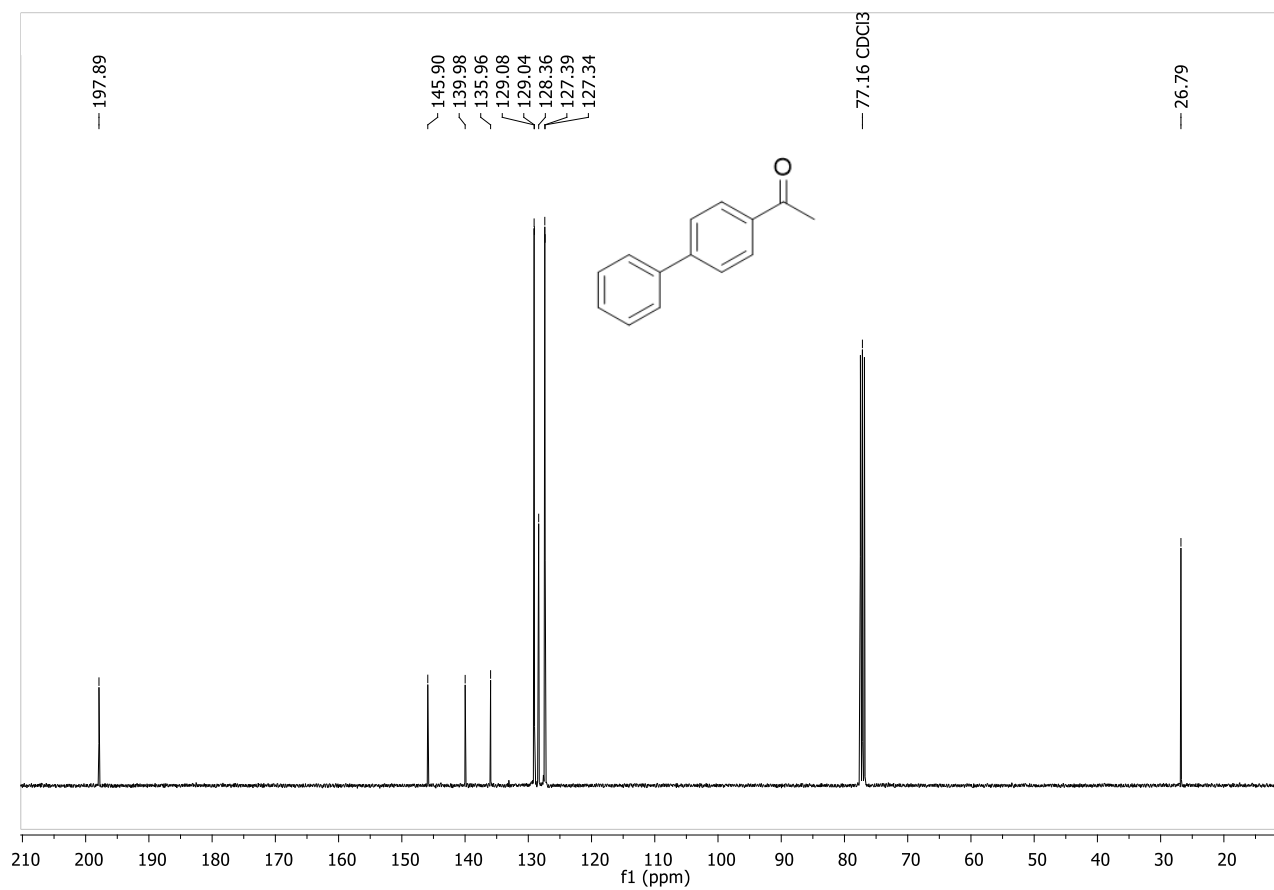
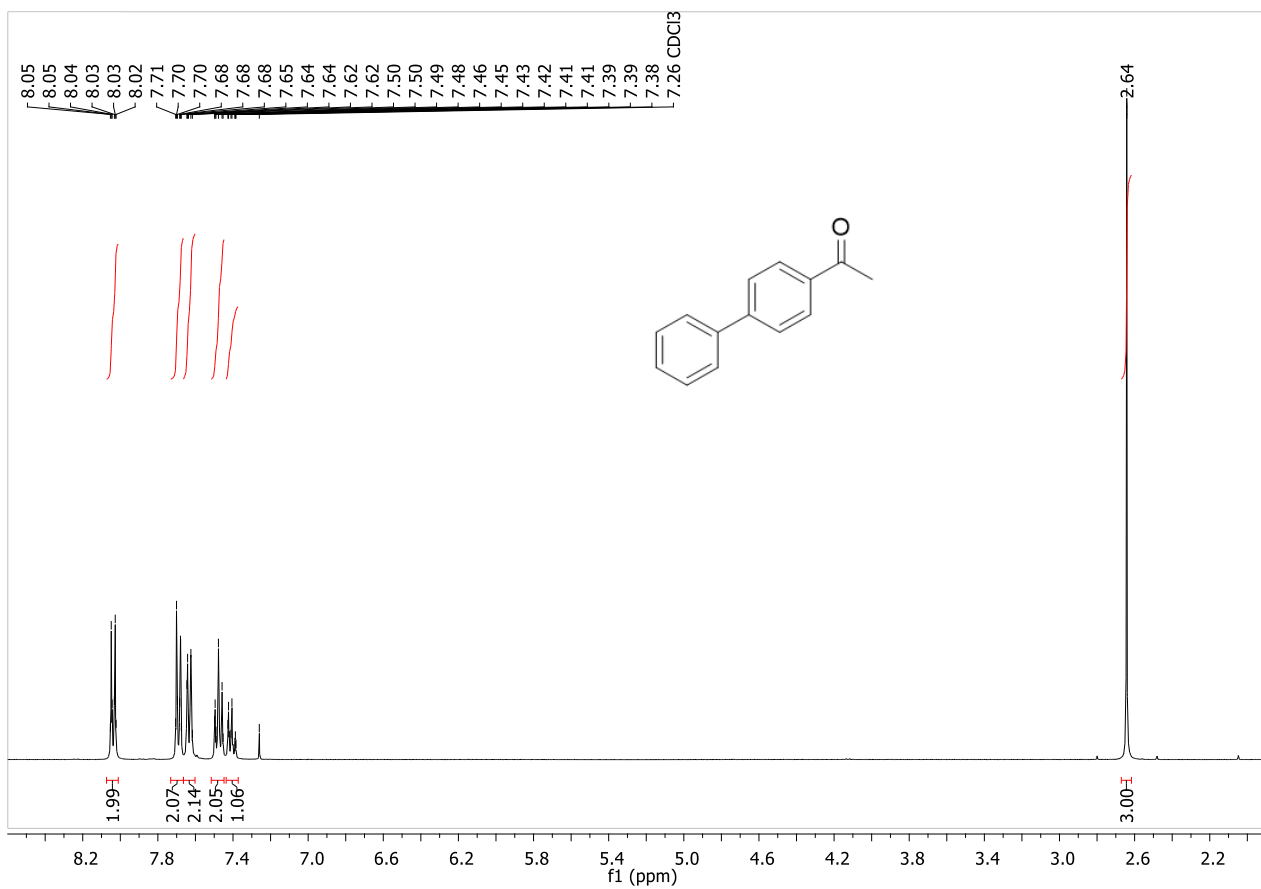
1-(*m*-Tolyl)ethan-1-one (2f)



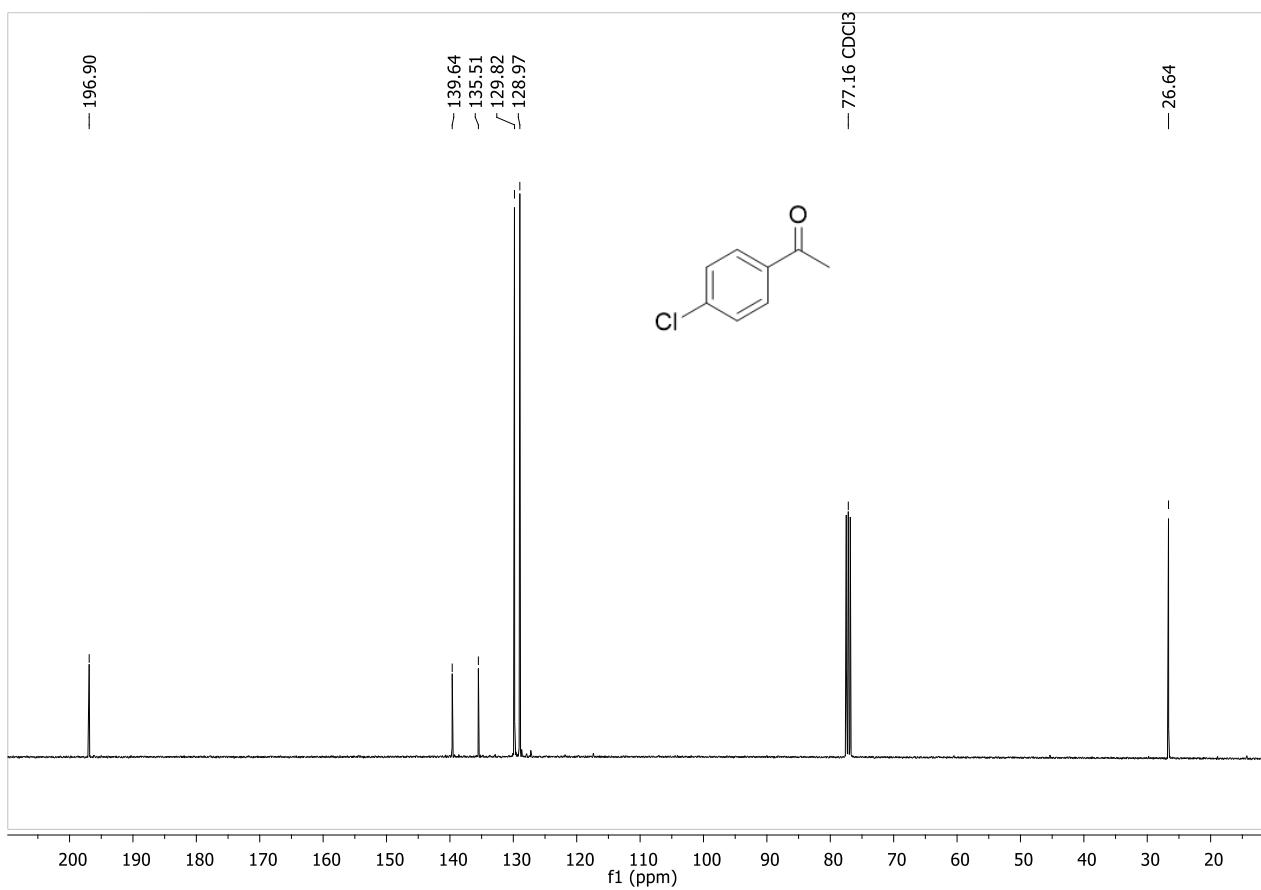
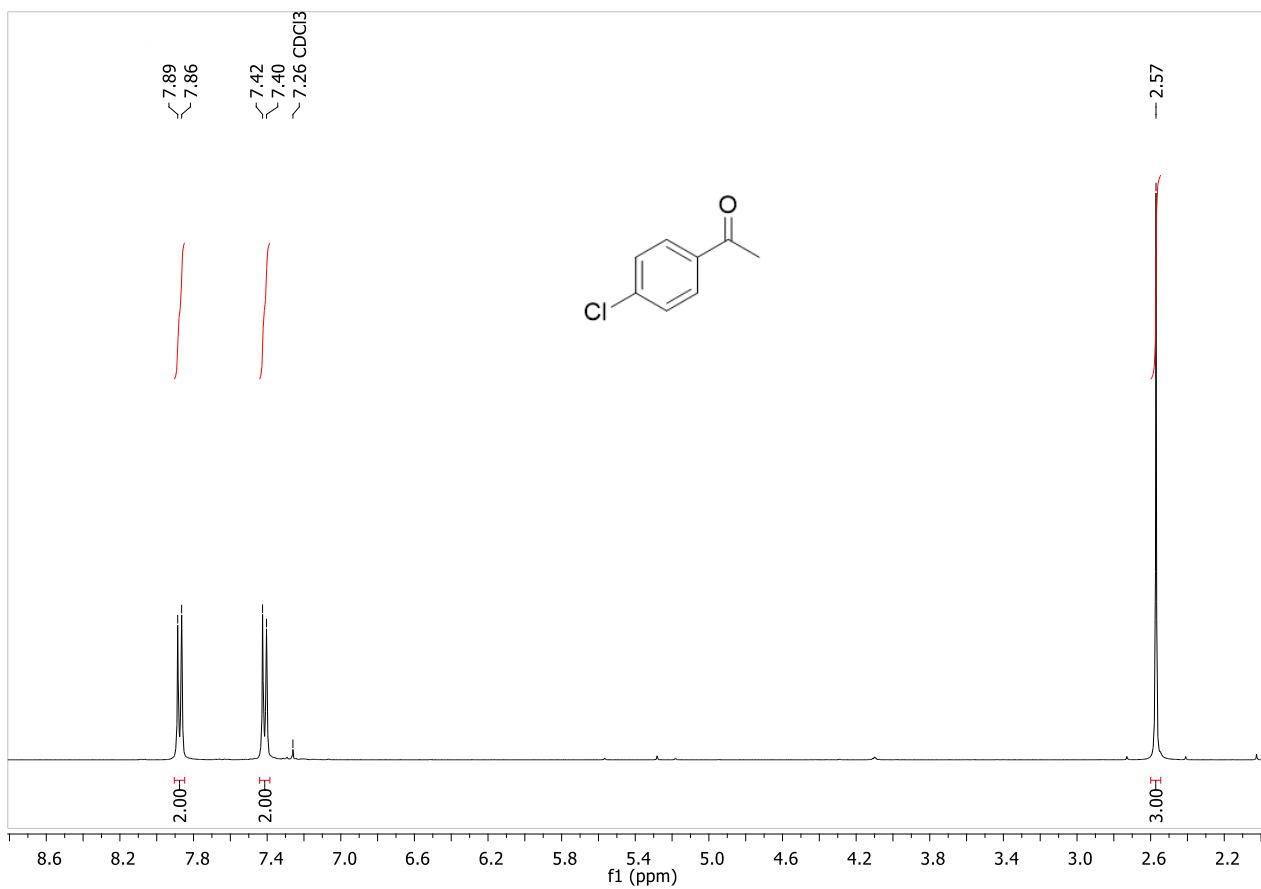
1-(*o*-Tolyl)ethan-1-one (2g)



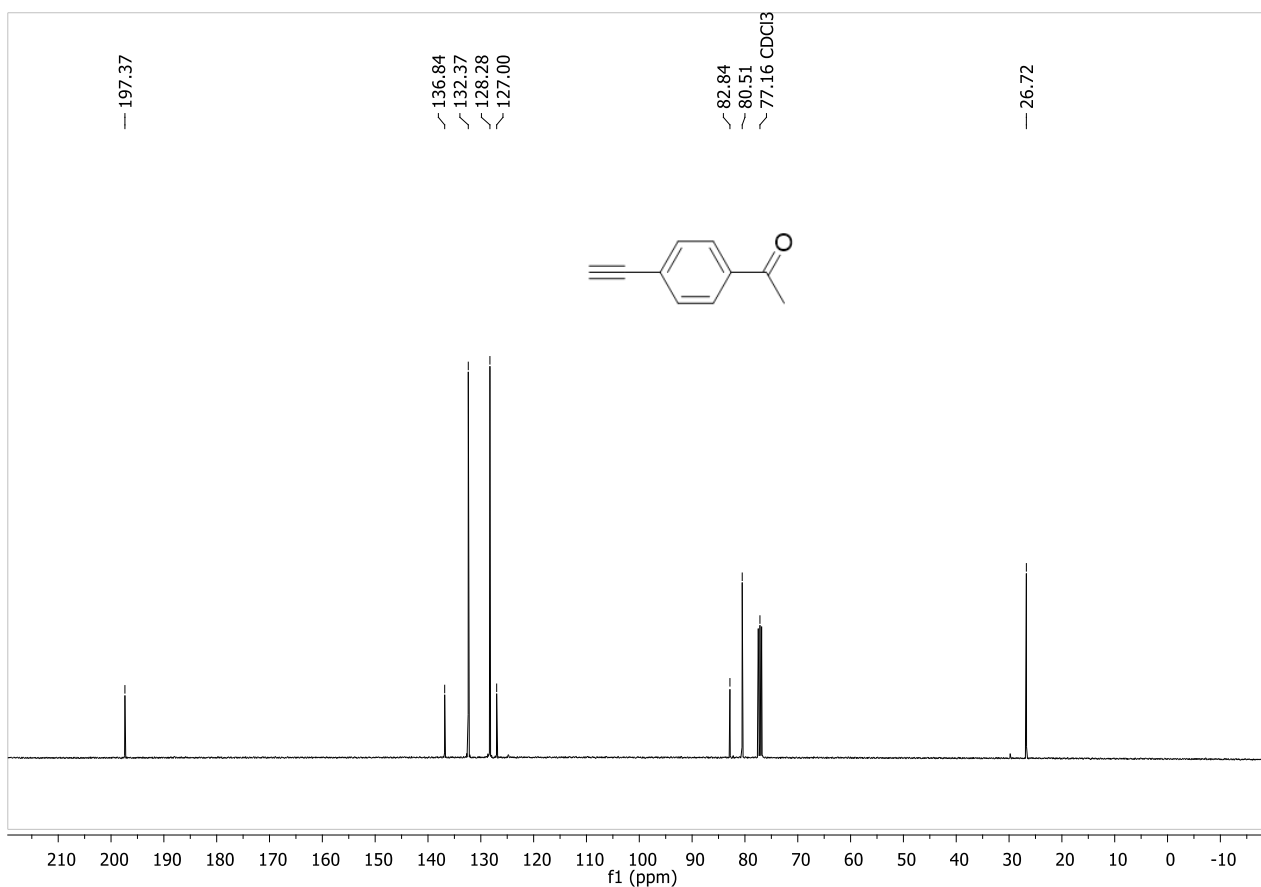
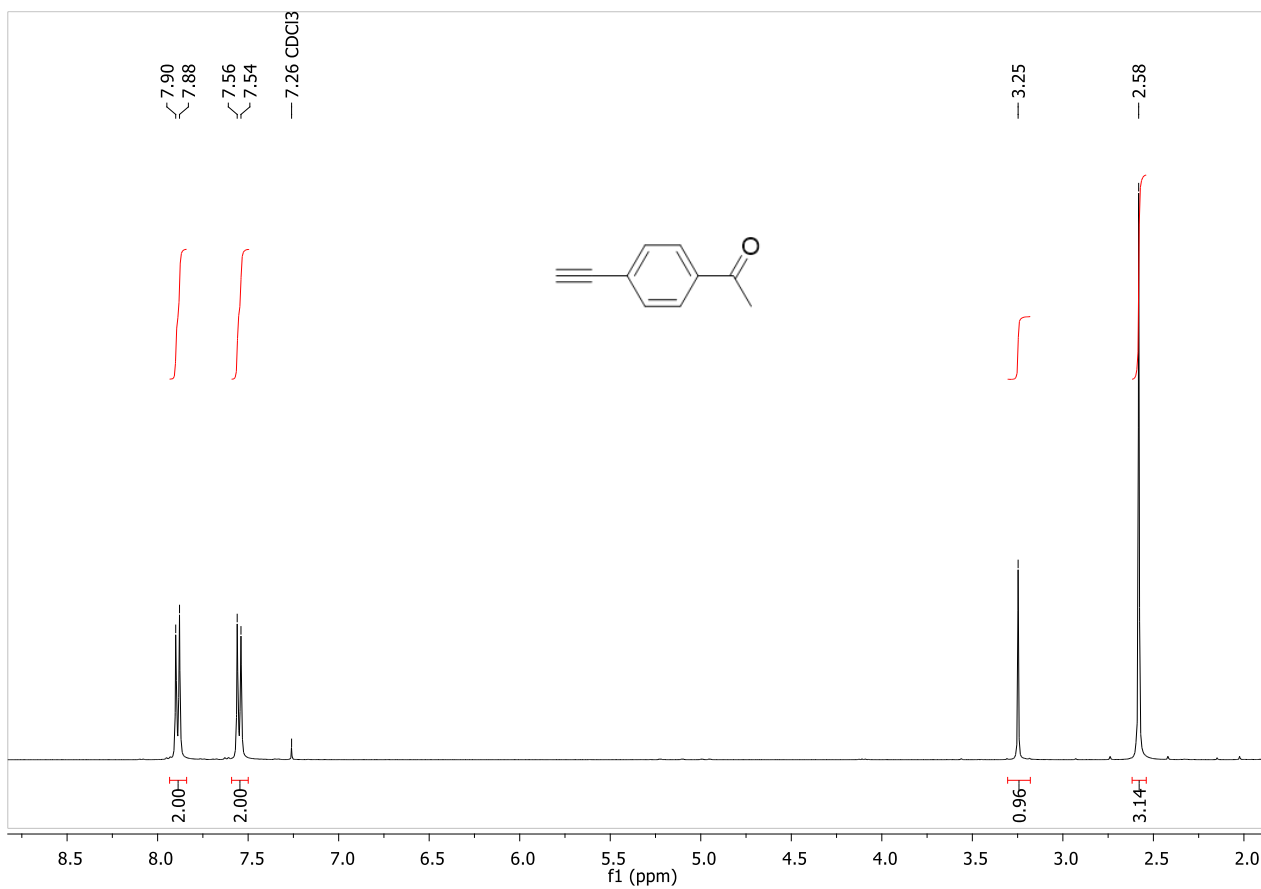
1-([1,1'-Biphenyl]-4-yl)ethan-1-one (2h)



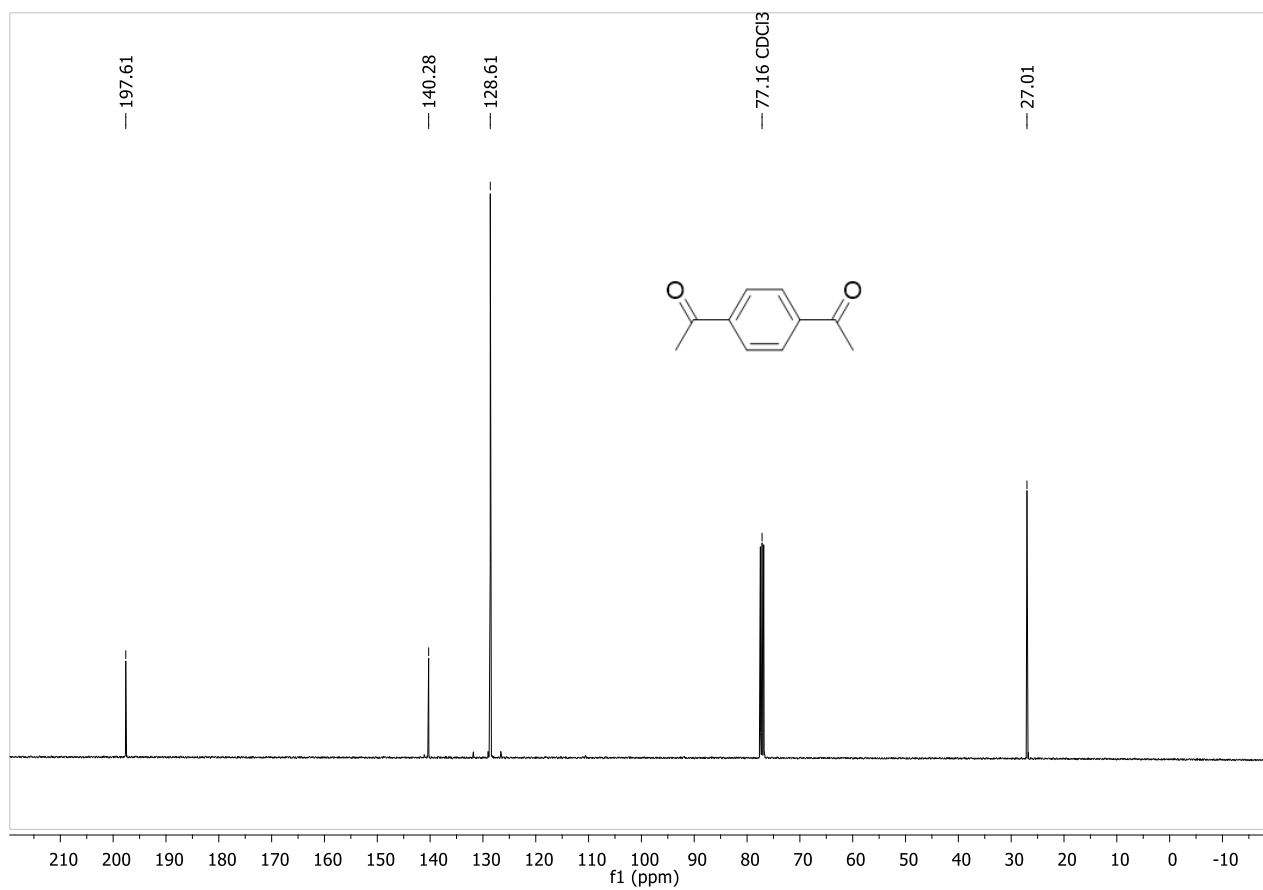
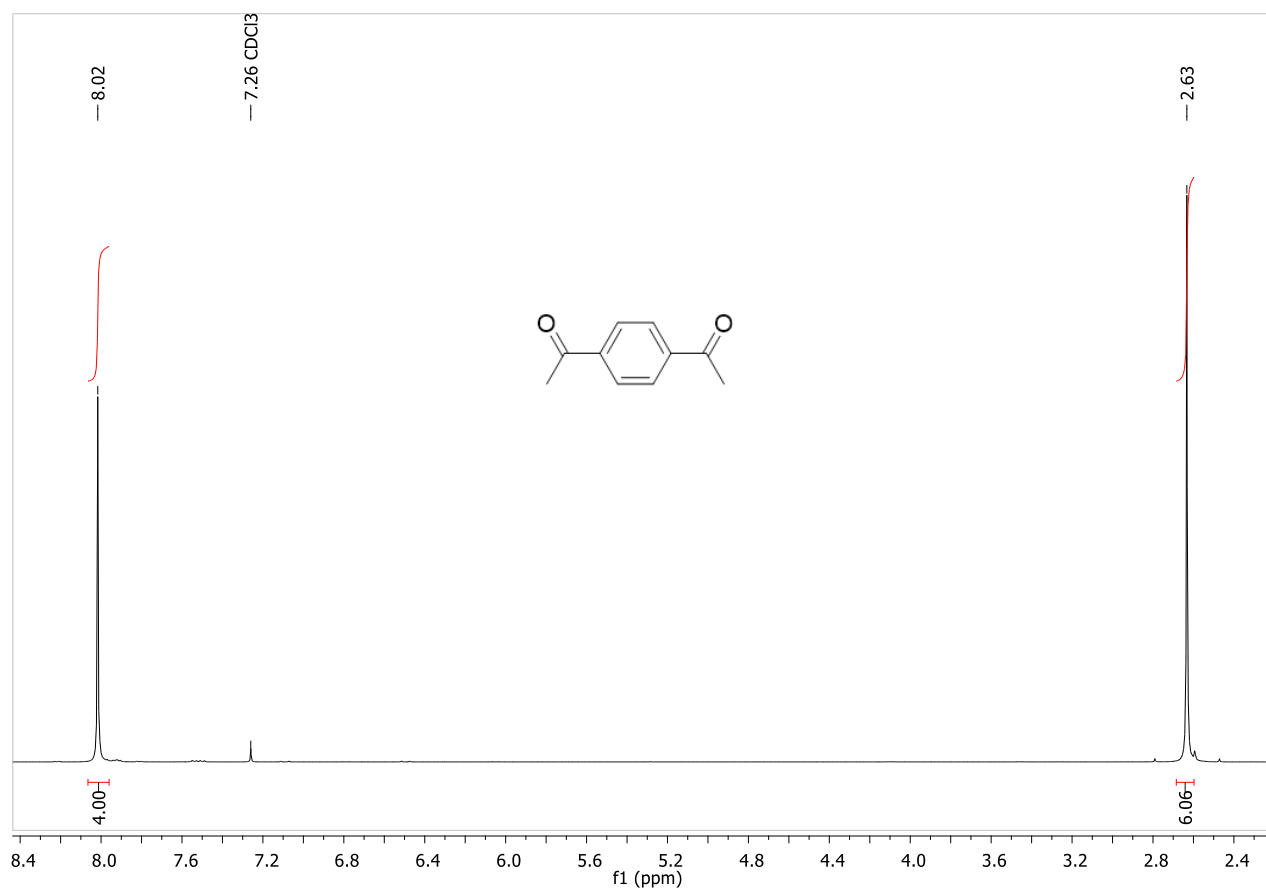
1-(4-Chlorophenyl)ethan-1-one (2i)



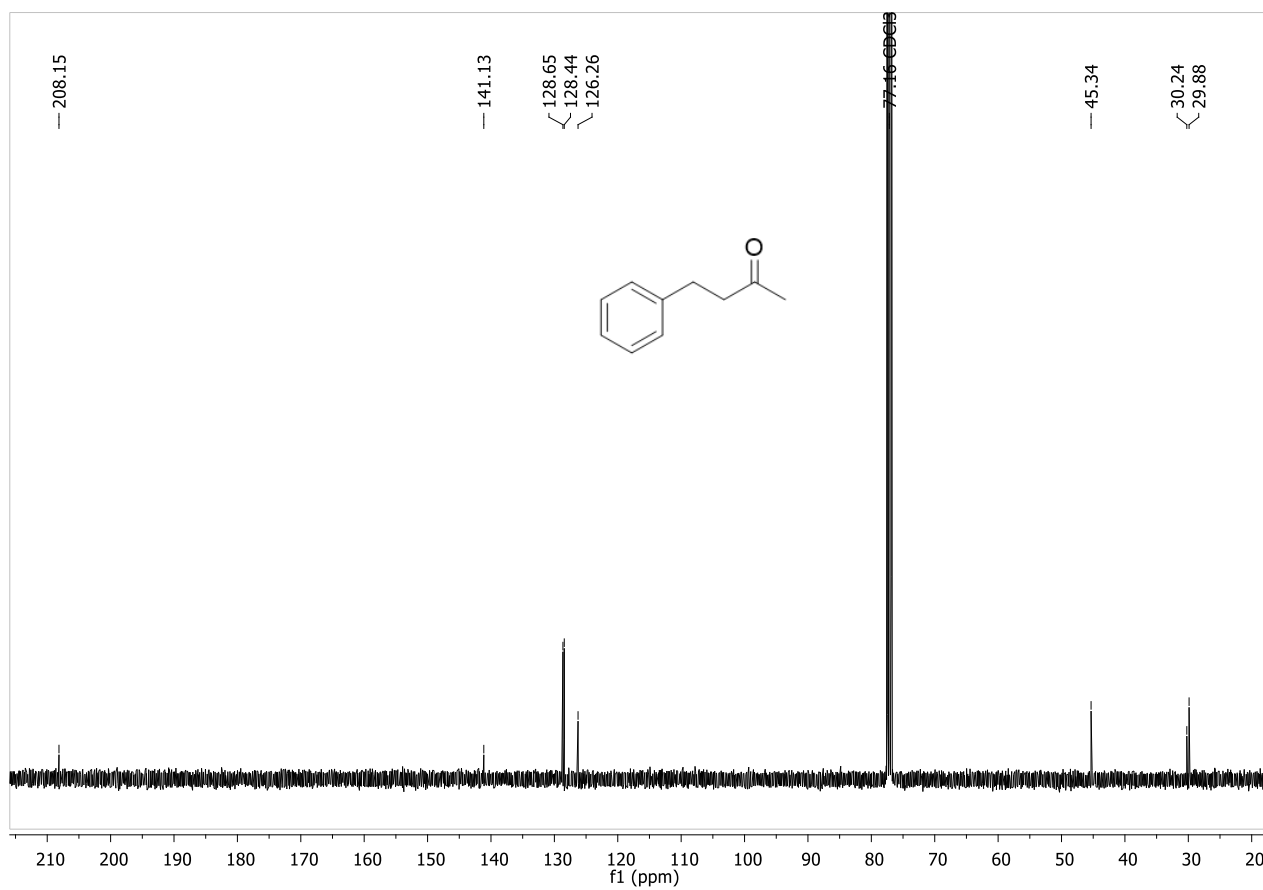
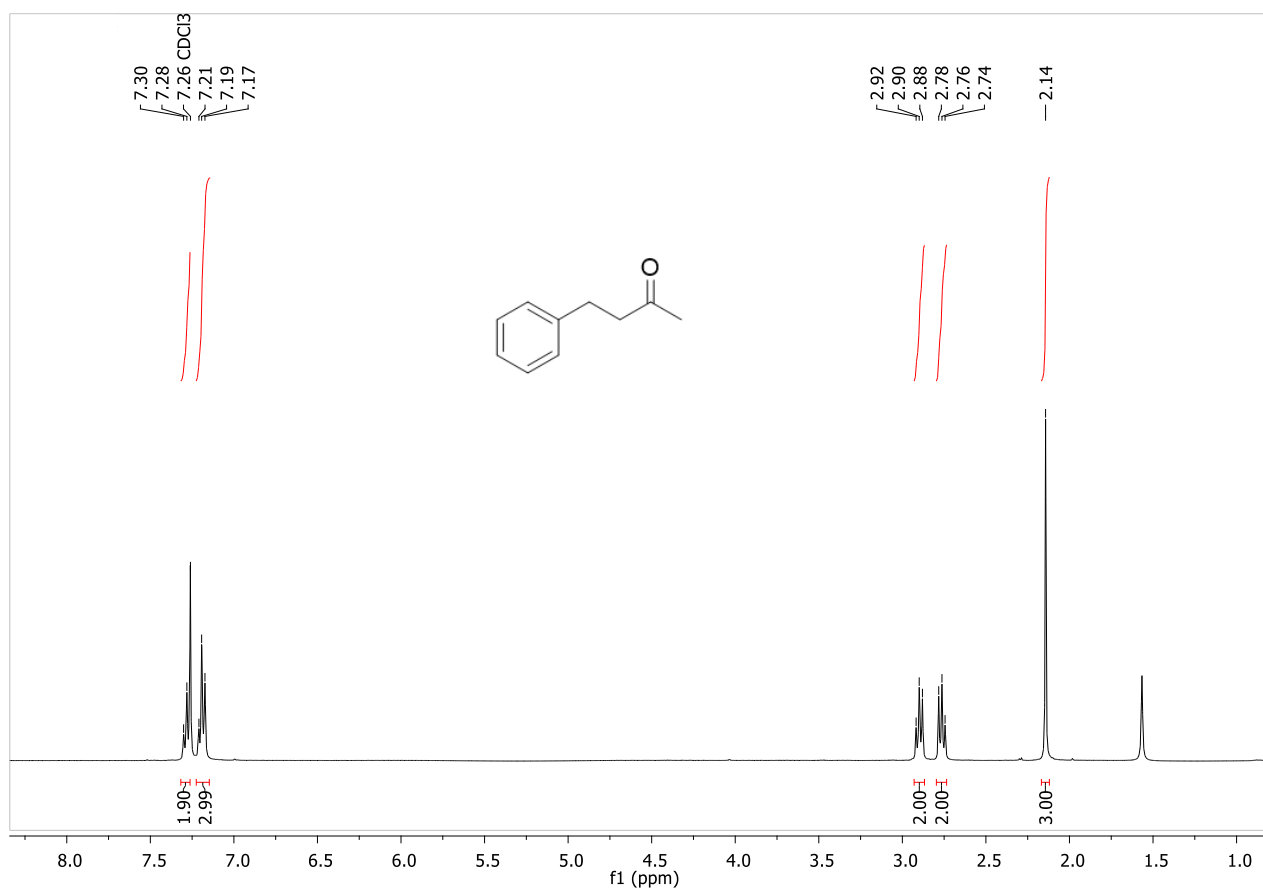
1-(4-Ethynylphenyl)ethan-1-one (2j)



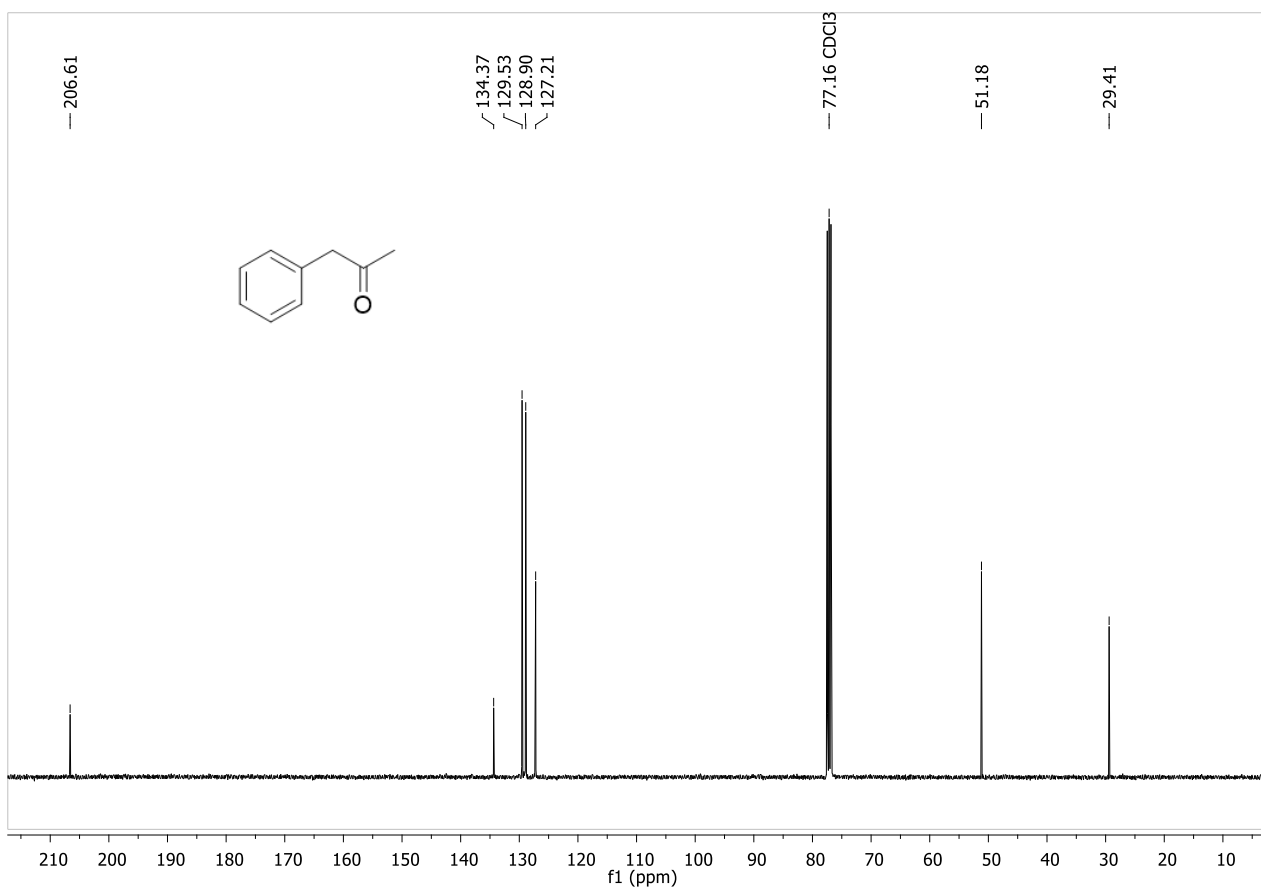
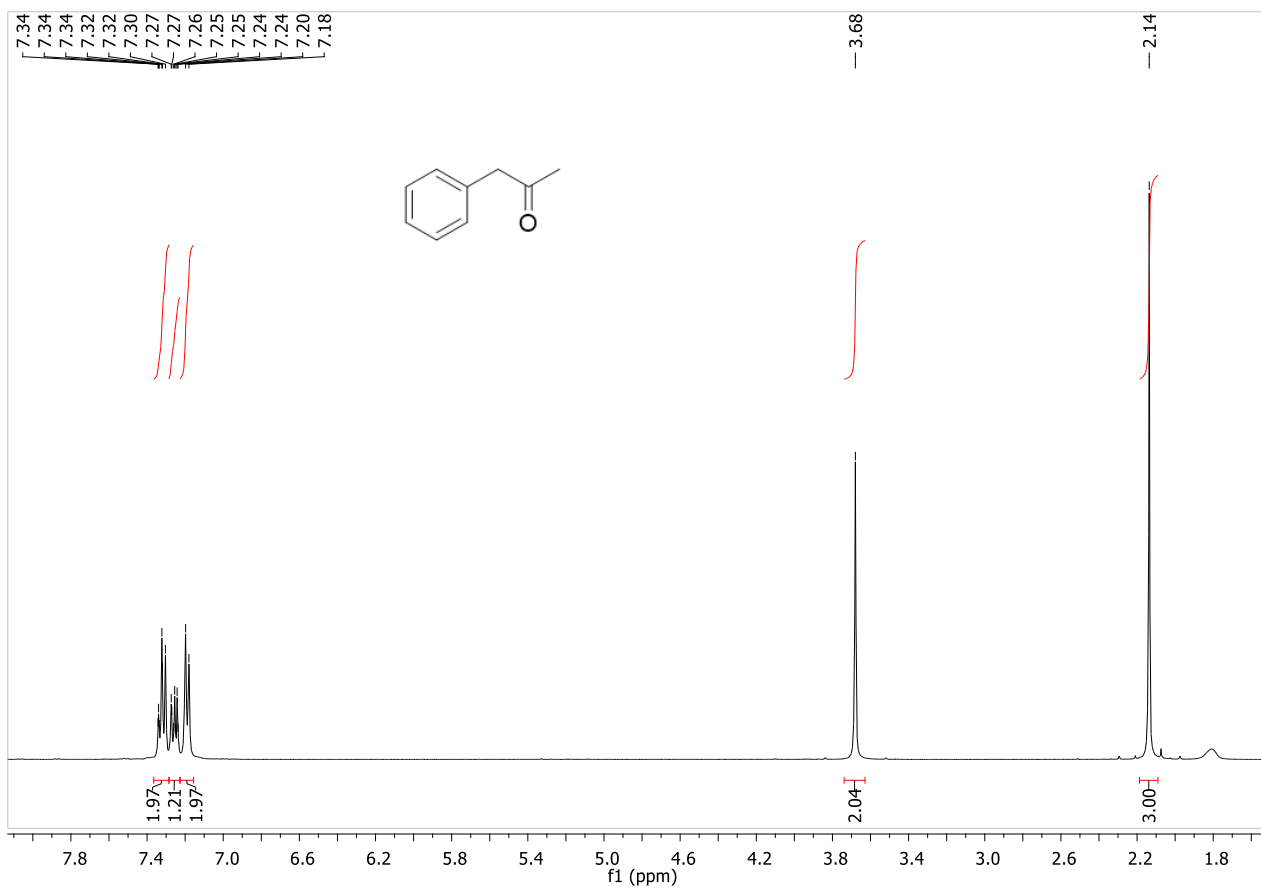
1,1'-(1,4-Phenylene)bis(ethan-1-one) (2jj)



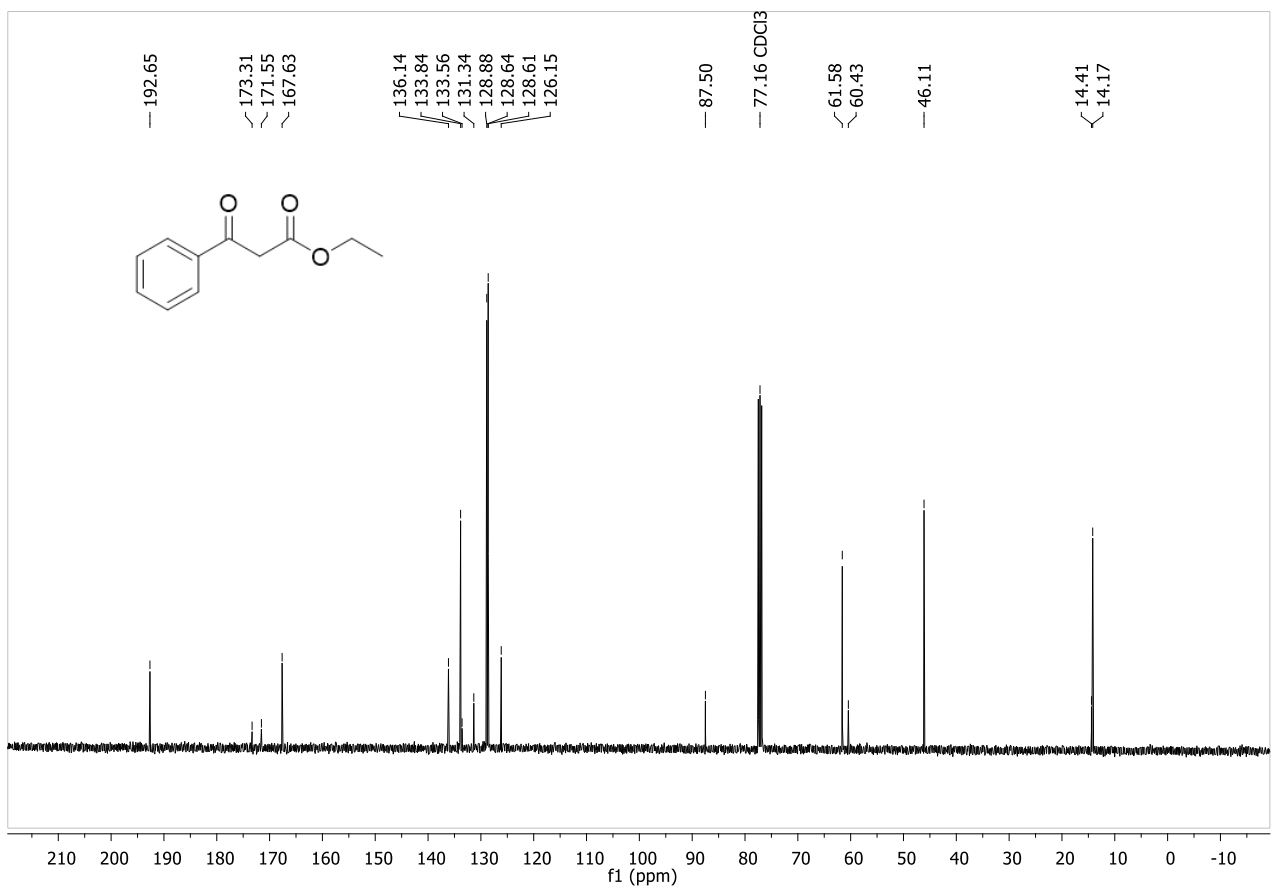
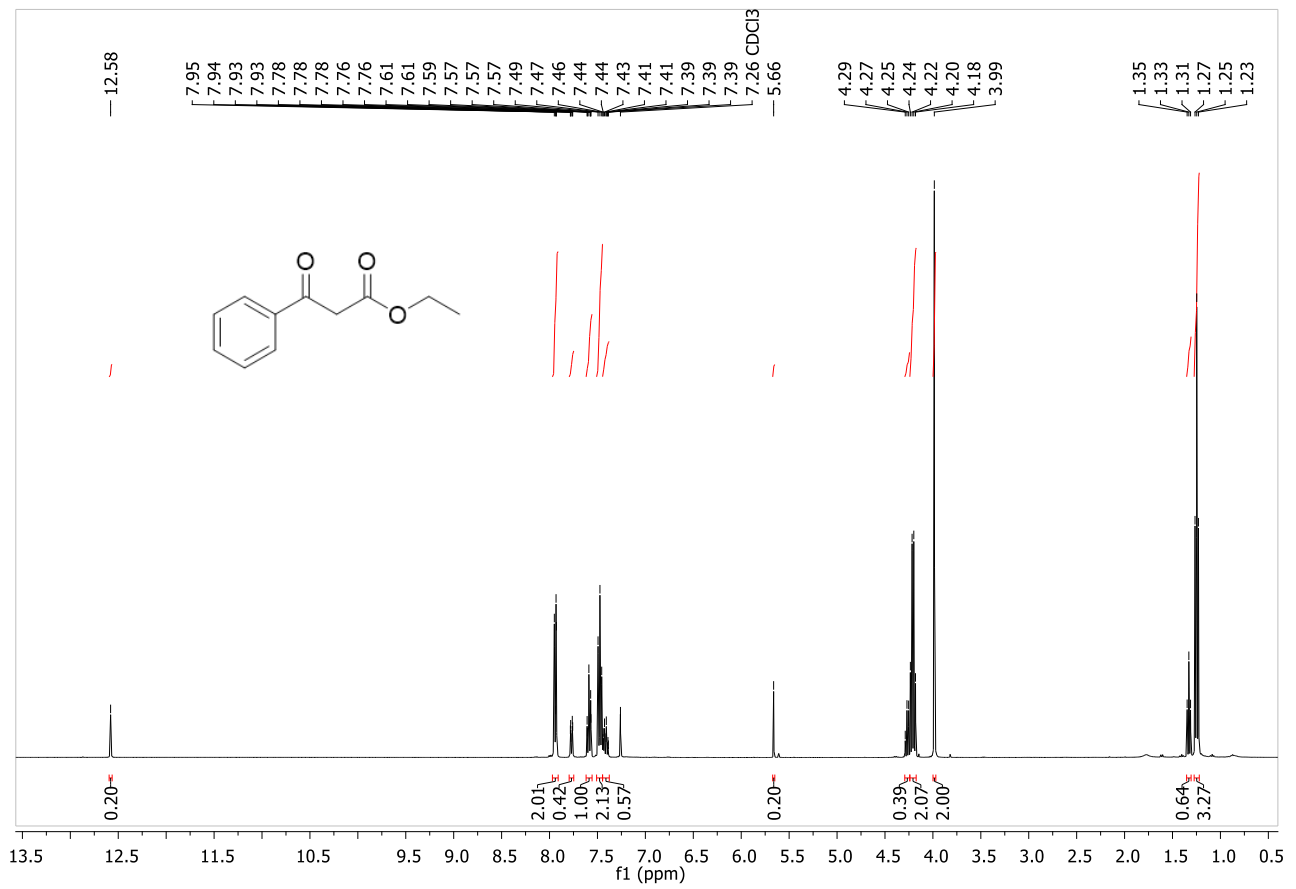
4-Phenylbutan-2-one (2k)



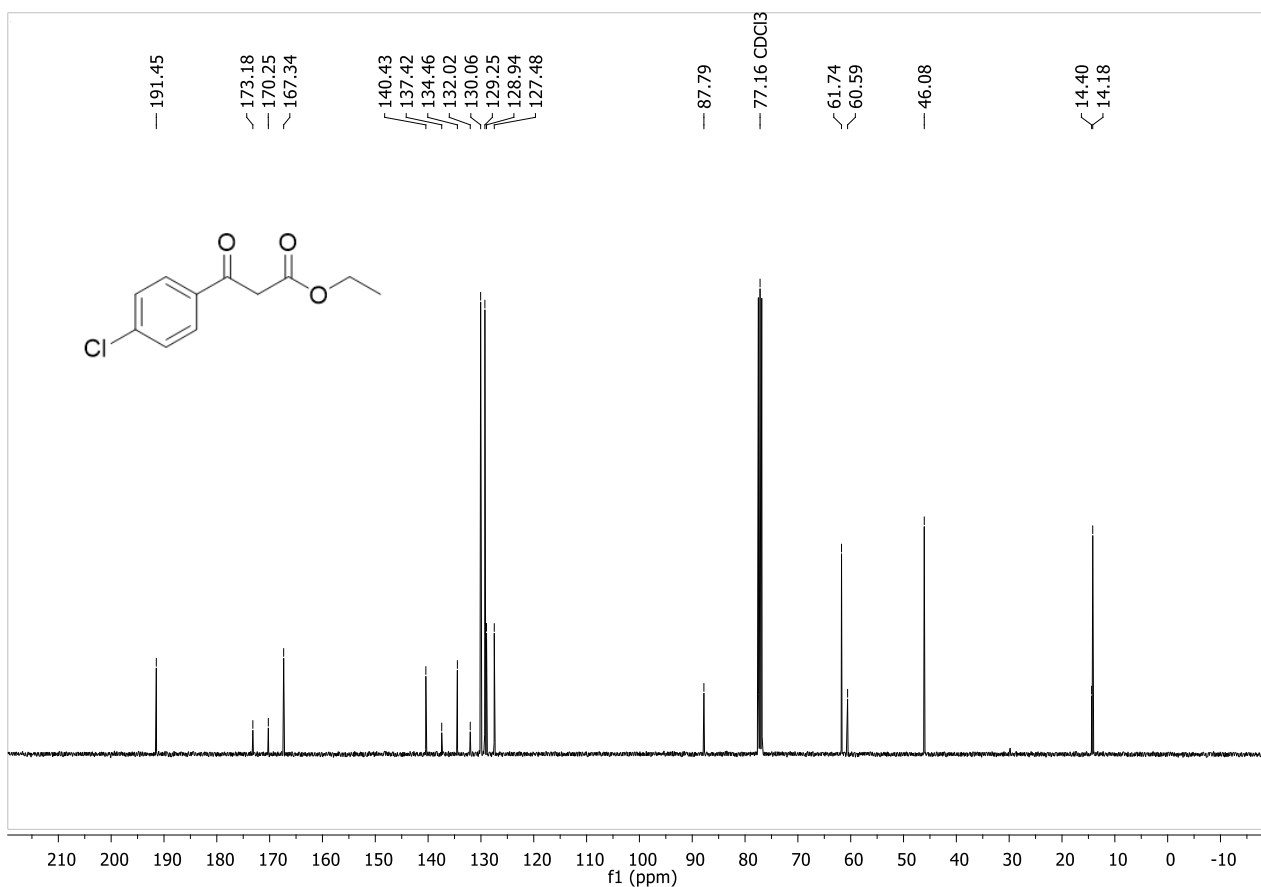
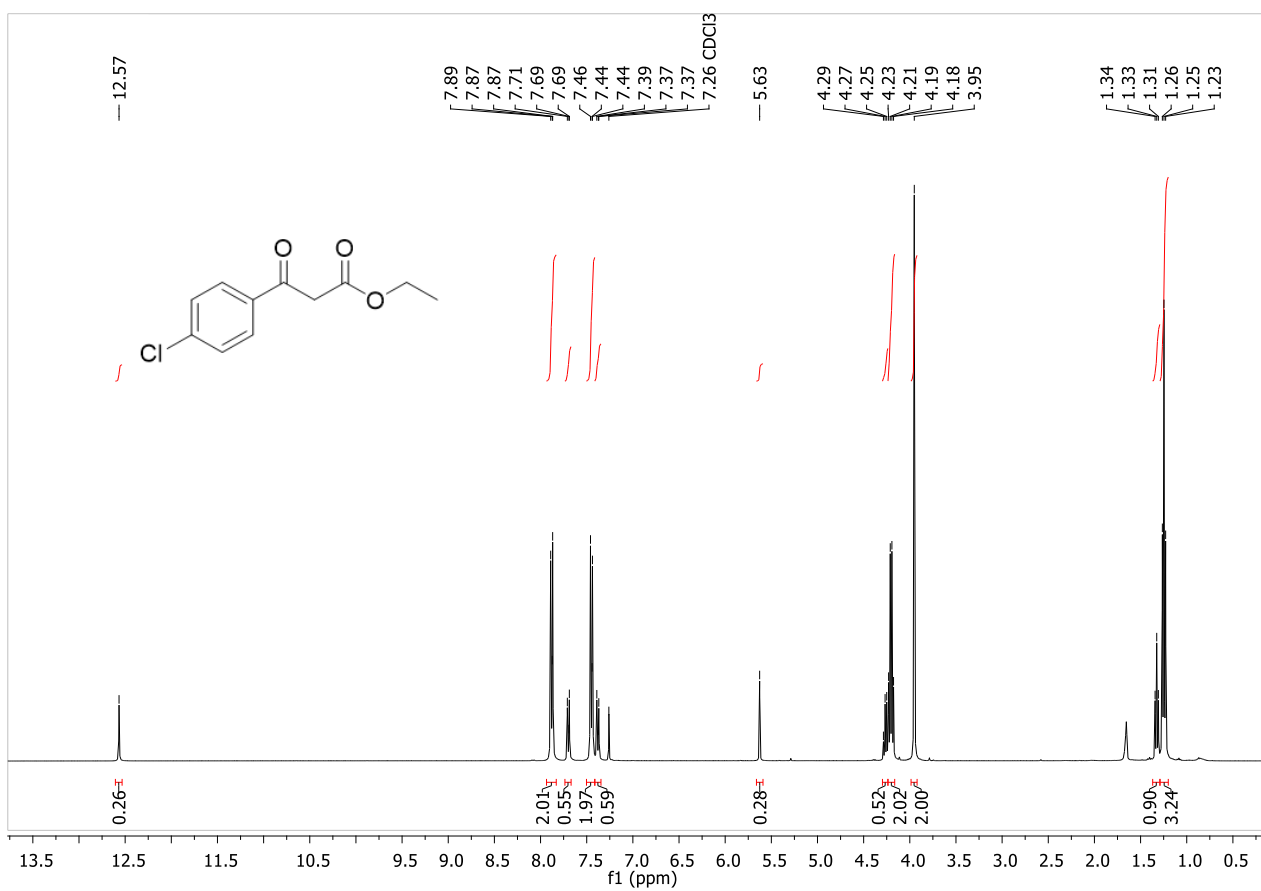
1-Phenylpropan-2-one (2l)



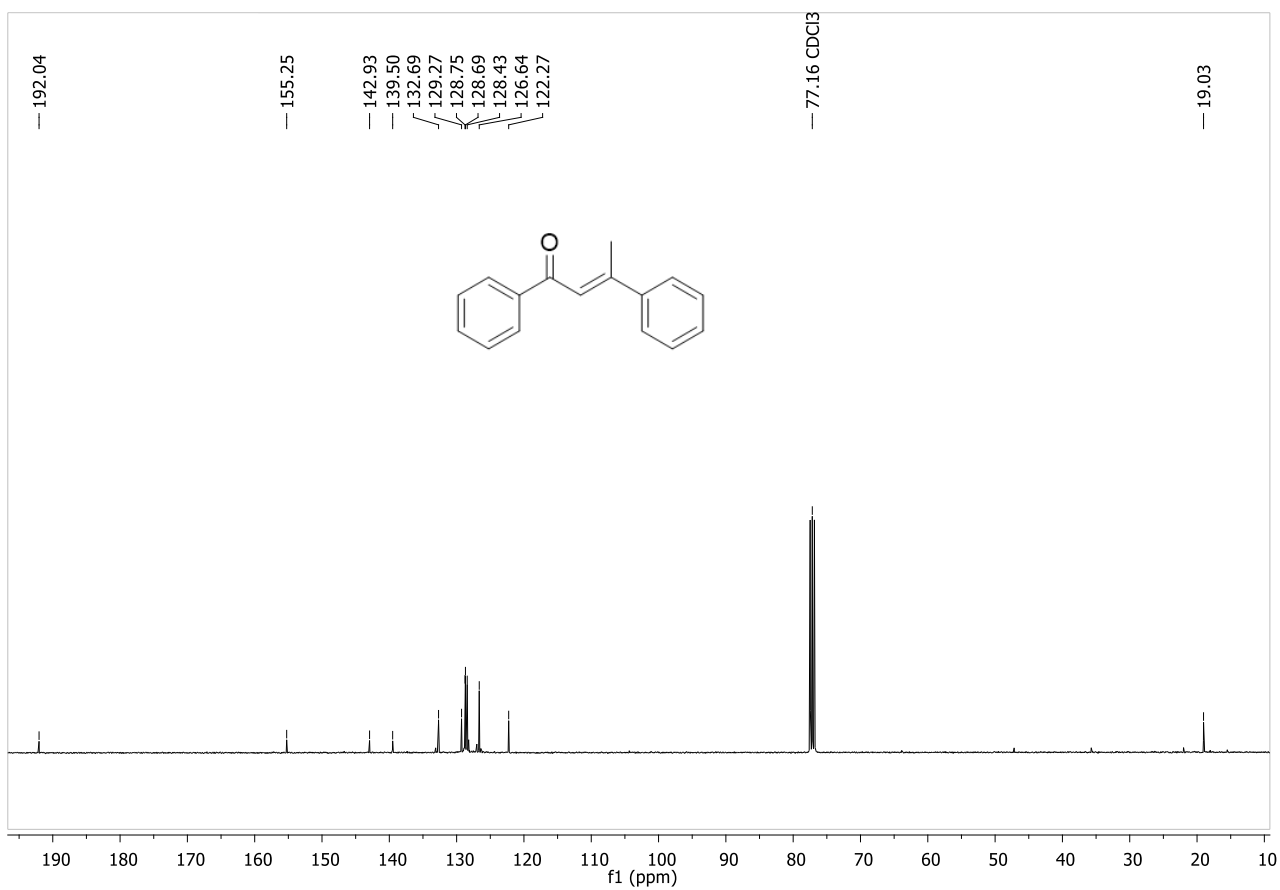
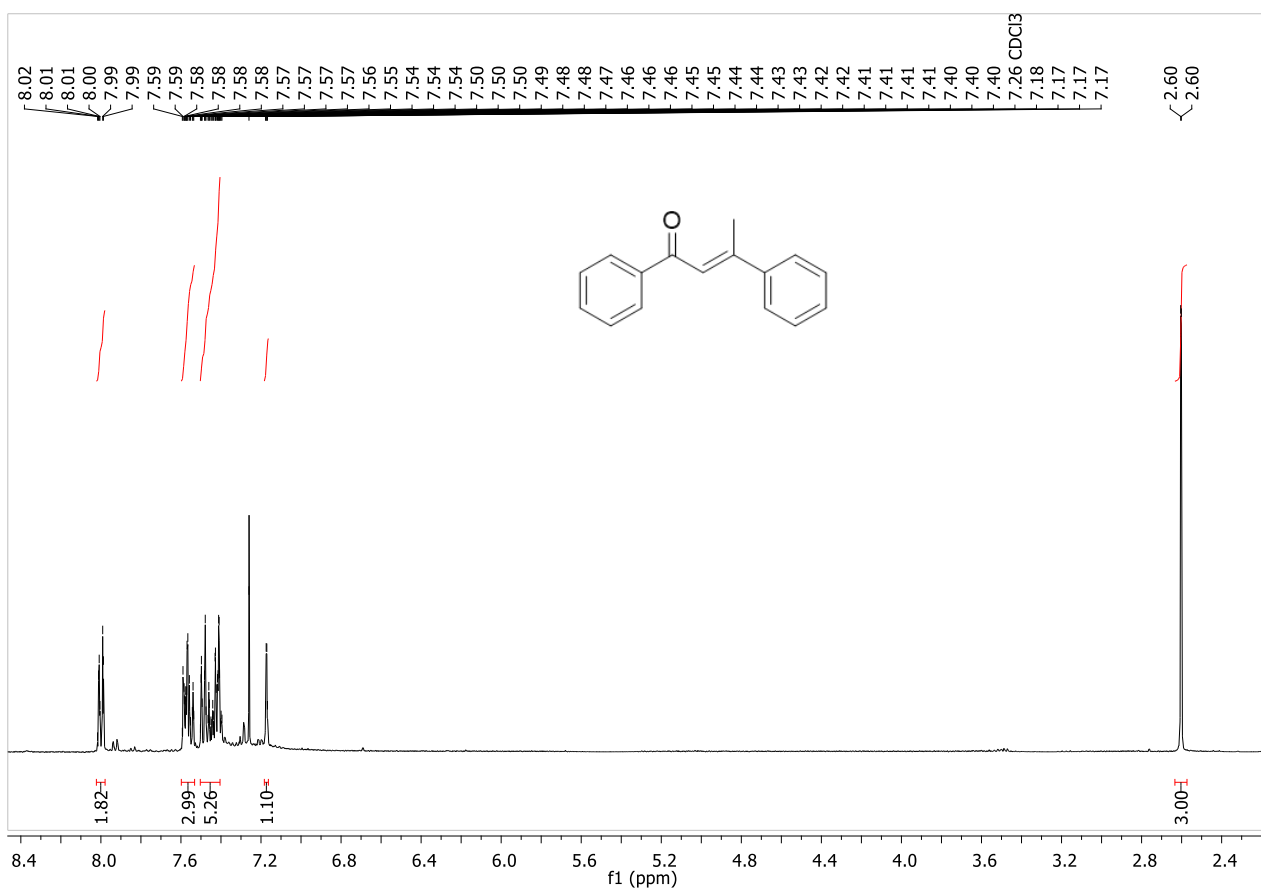
Ethyl 3-oxo-3-phenylpropanoate (2m) (keto/enol)



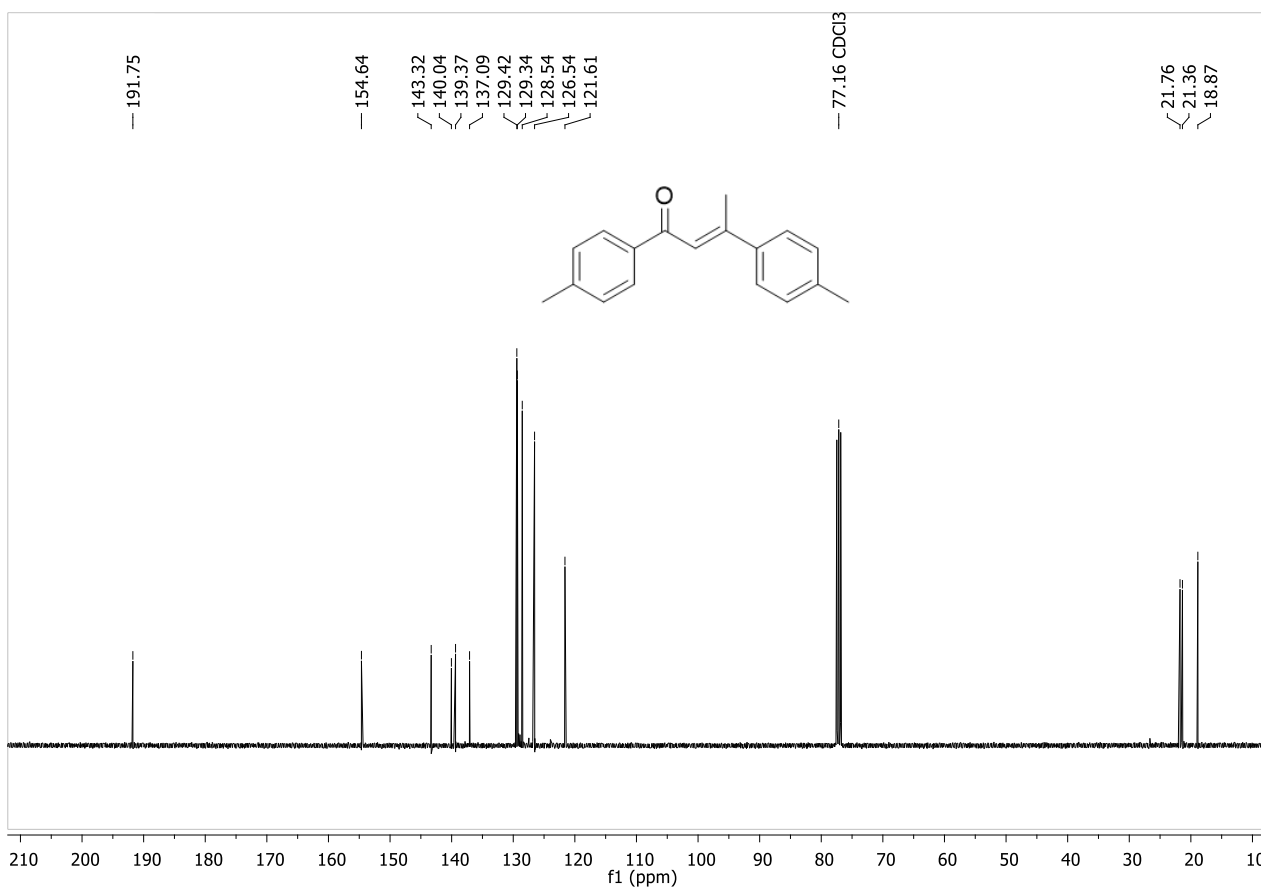
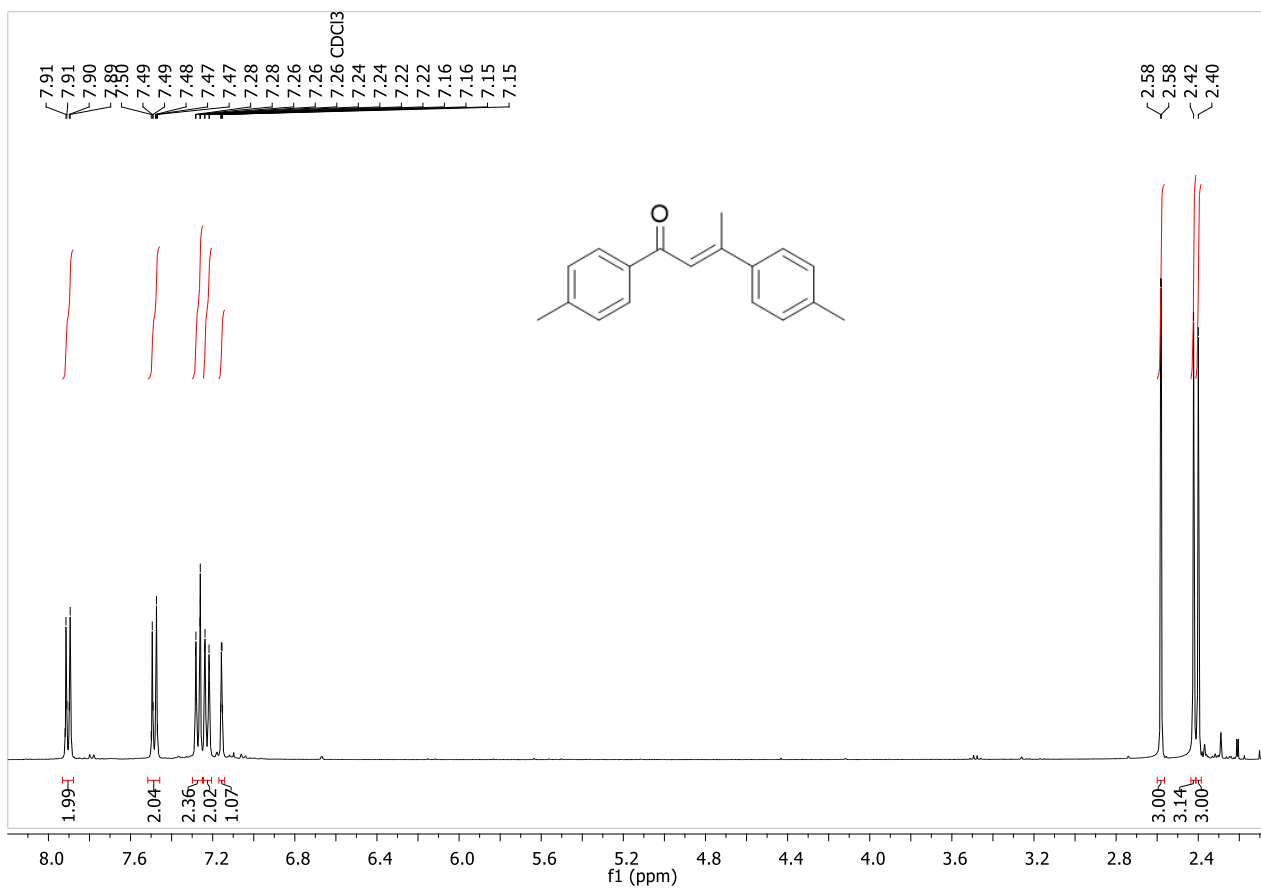
Ethyl 3-(4-chlorophenyl)-3-oxopropanoate (2n) (keto/enol)



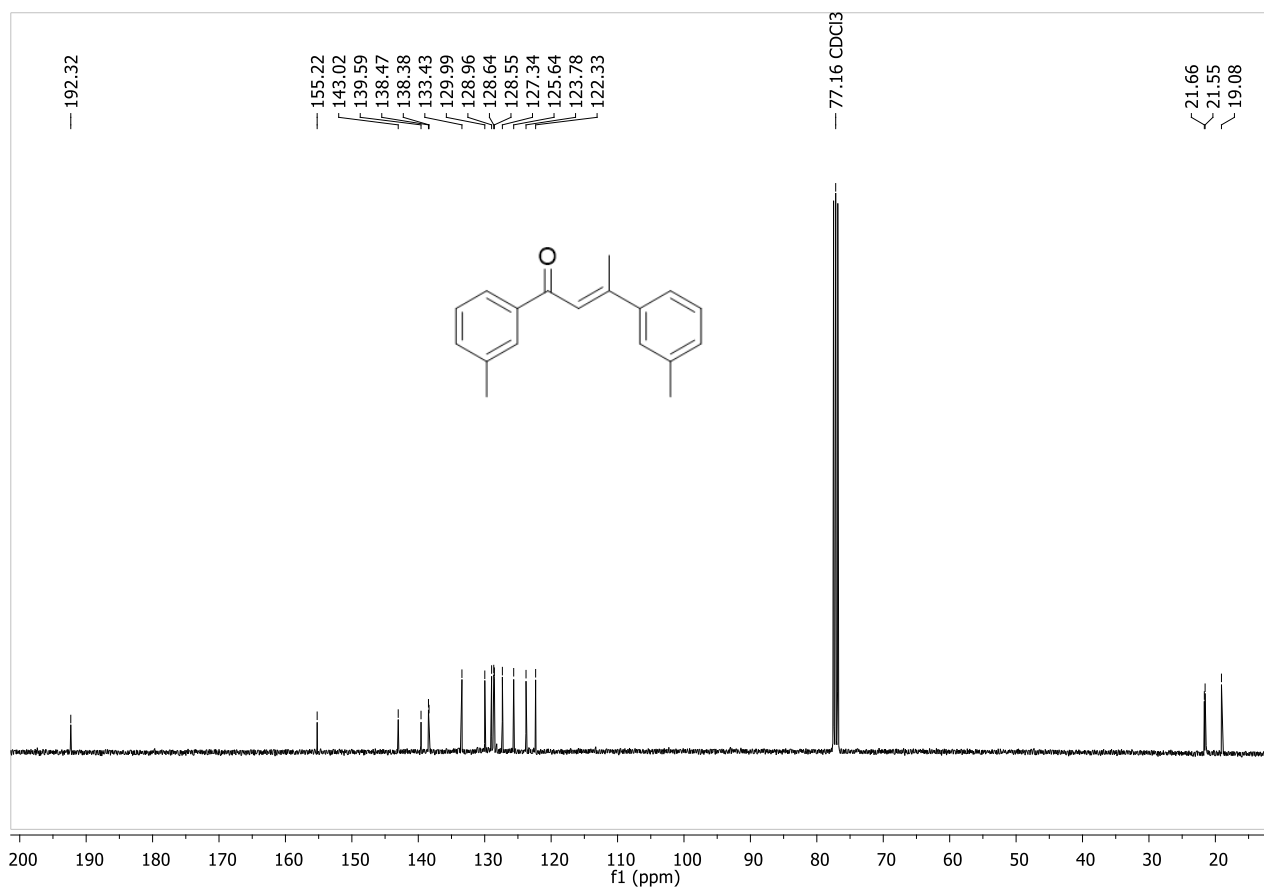
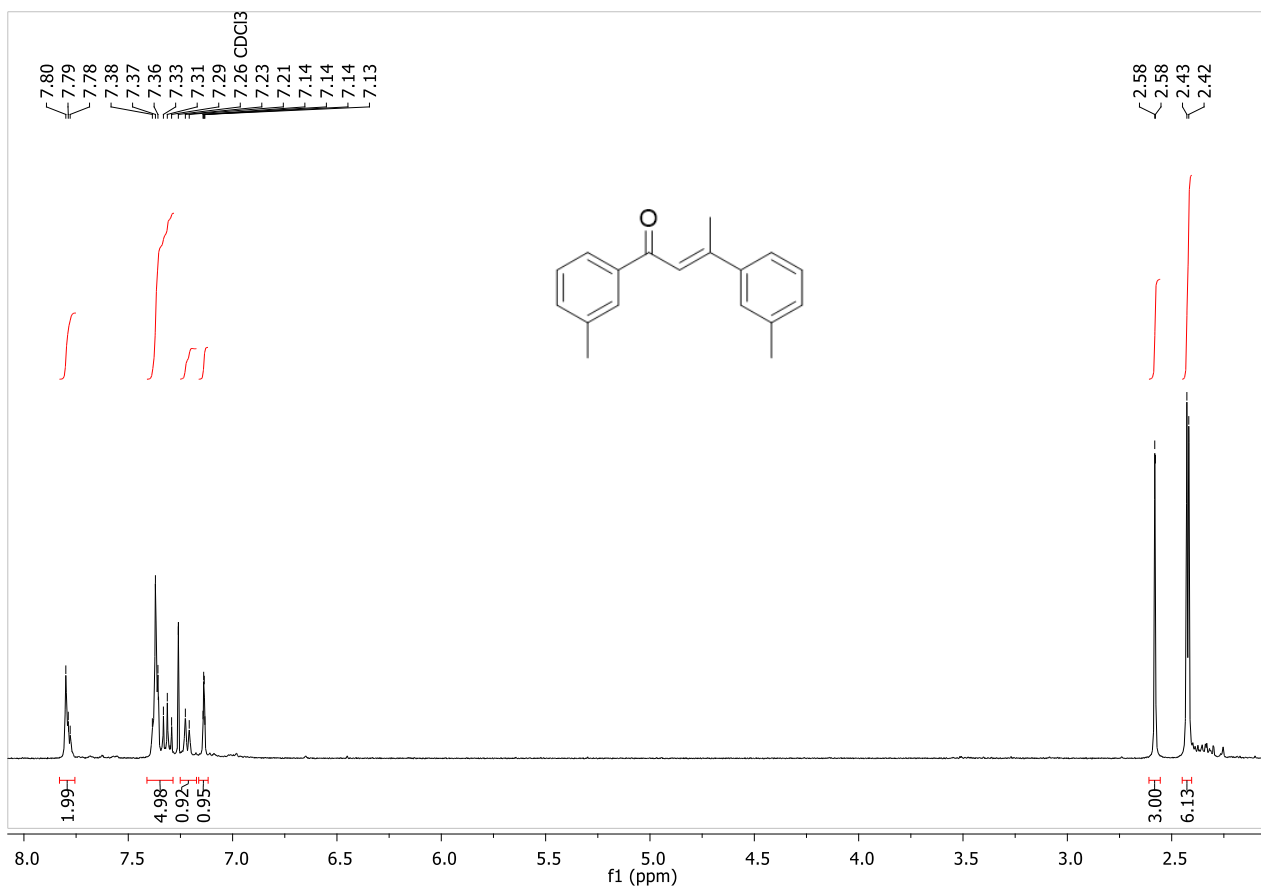
(E)-1,3-Diphenylbut-2-en-1-one (3d)



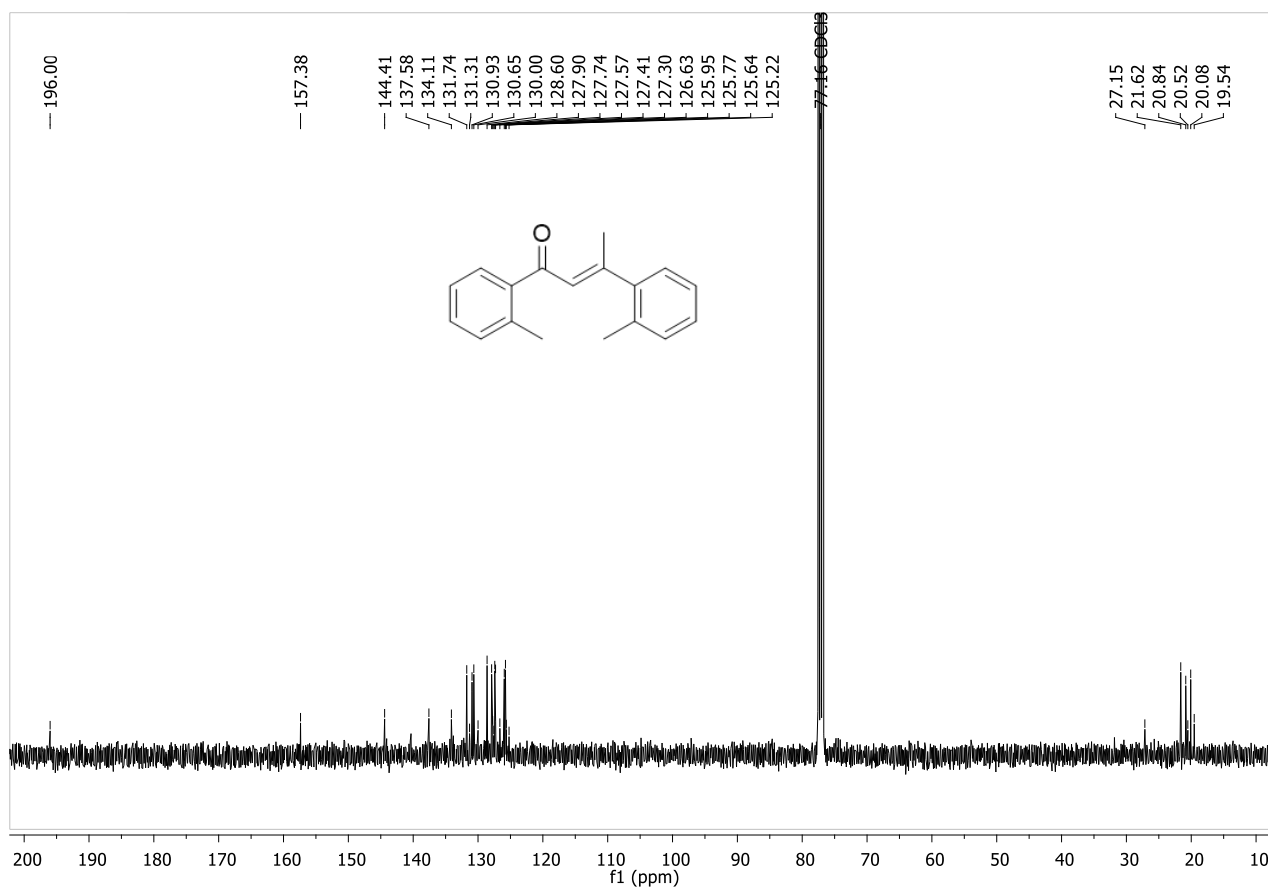
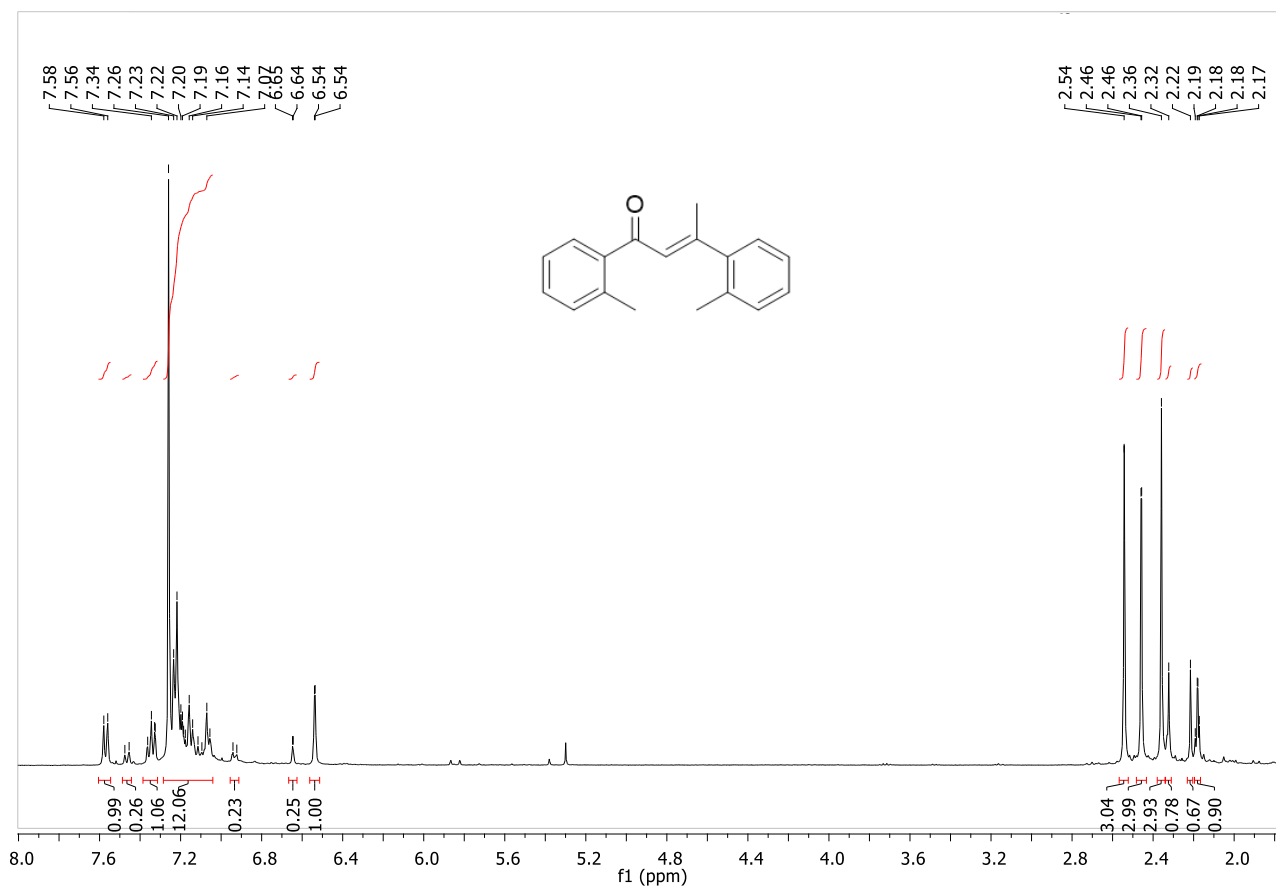
(E)-1,3-Di-*p*-tolylbut-2-en-1-one (3e)



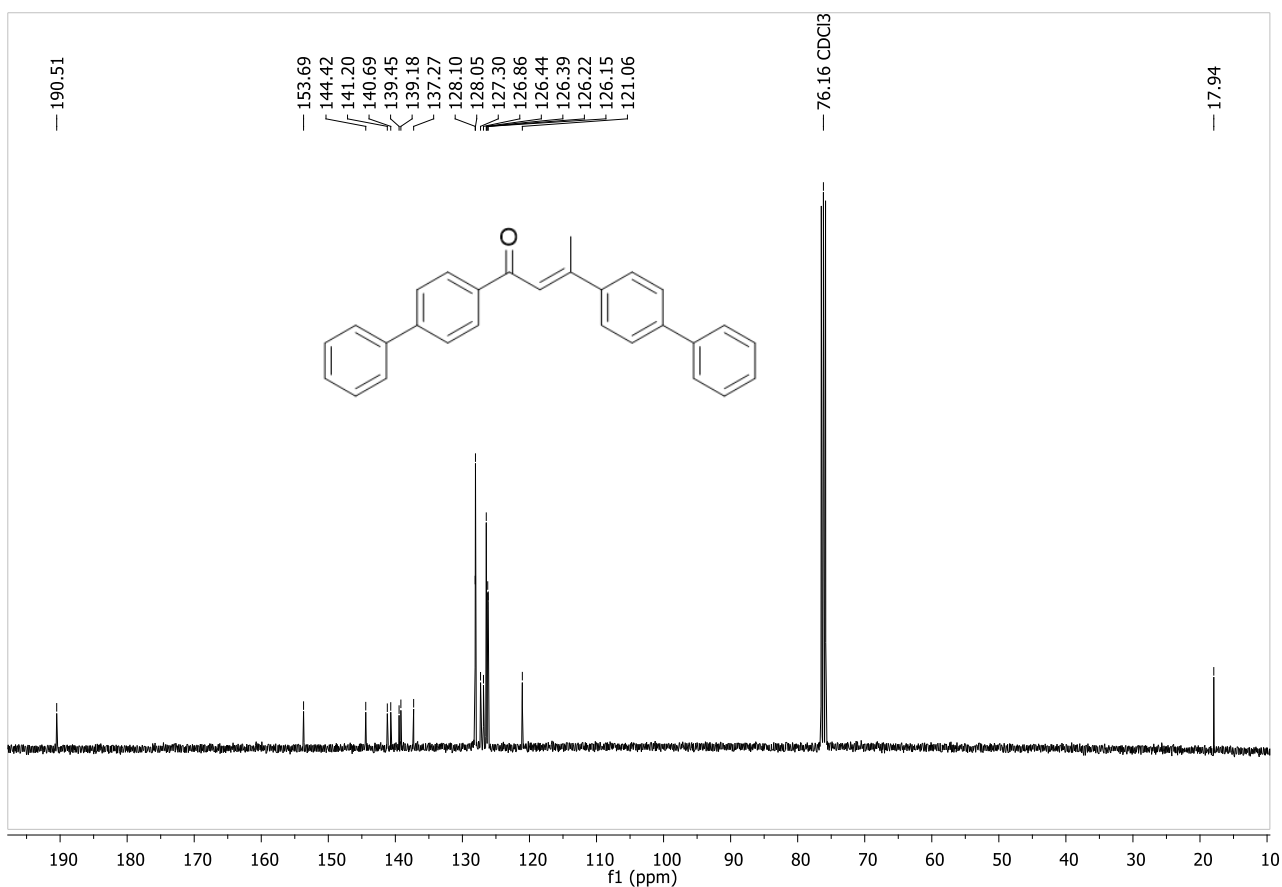
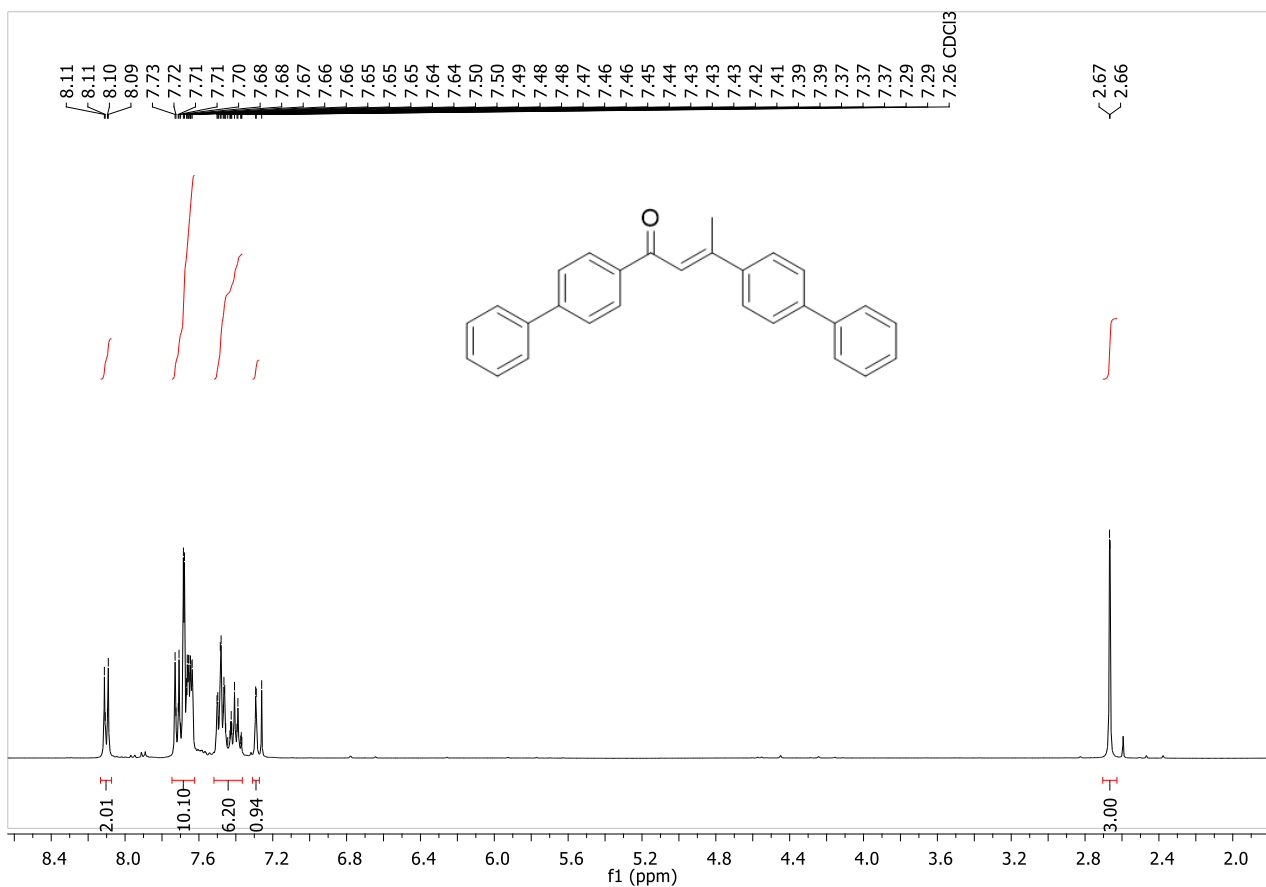
(E)-1,3-Di-*m*-tolylbut-2-en-1-one (3f)



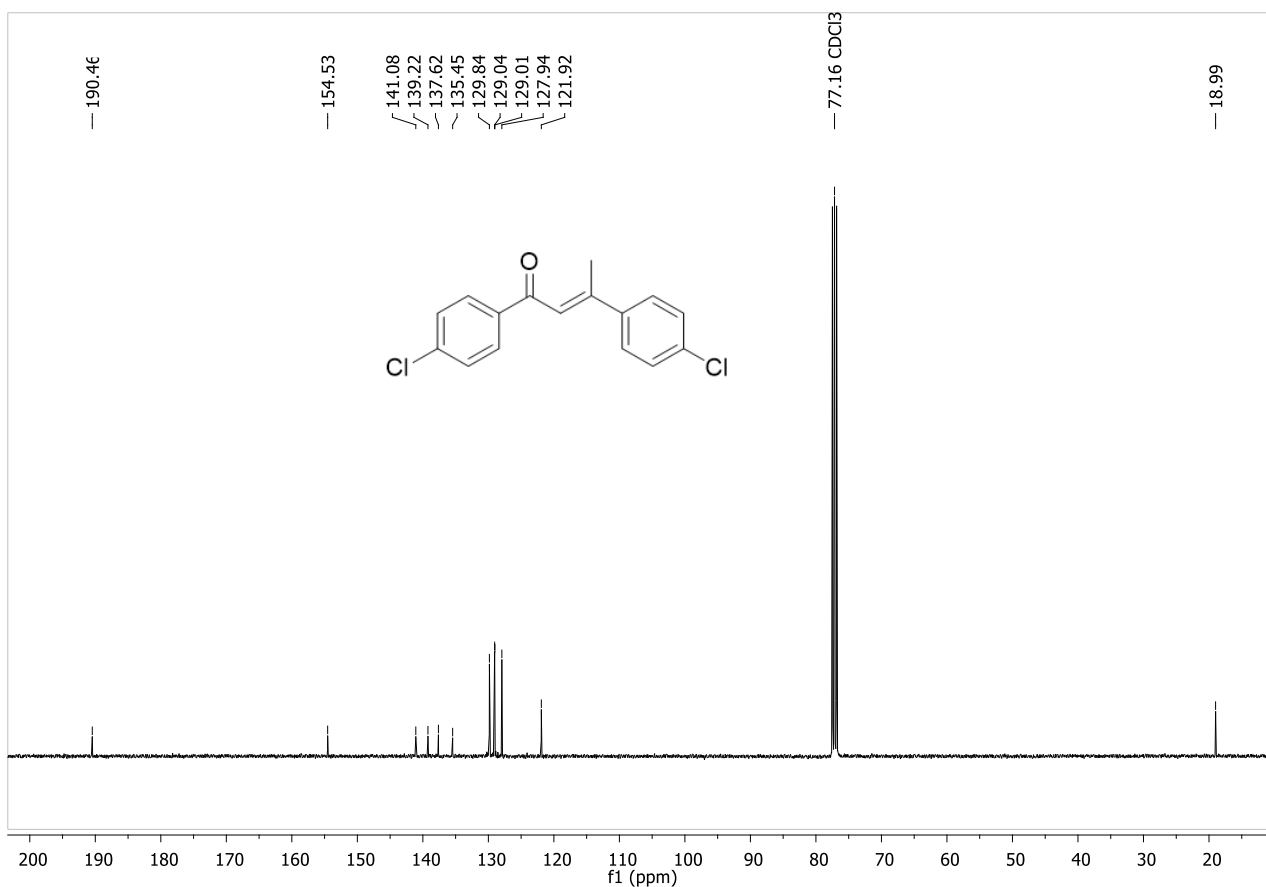
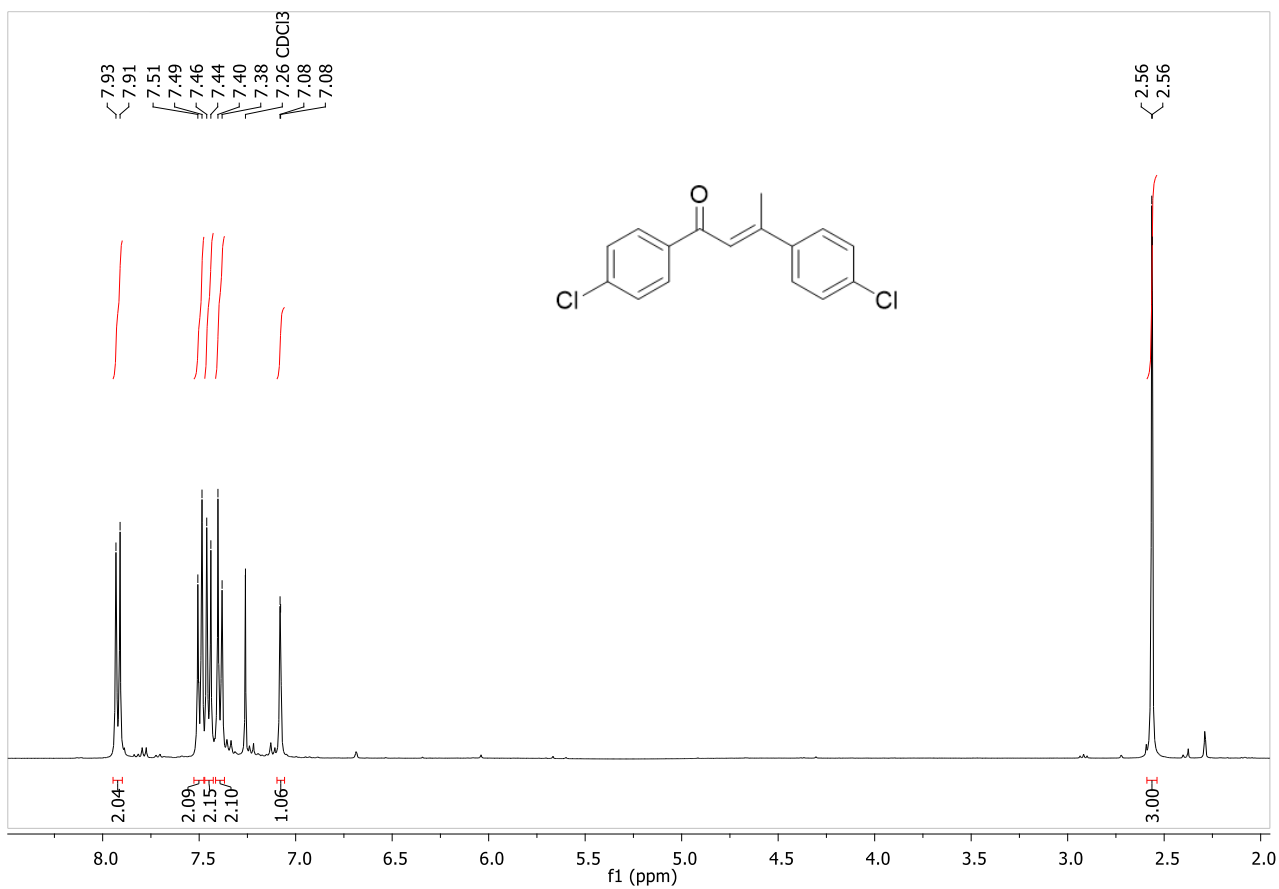
1,3-Di-*o*-tolylbut-2-en-1-one (E/Z mixture) (3g)



(E)-1,3-Di([1,1'-biphenyl]-4-yl)but-2-en-1-one (3h)



(E)-1,3-Bis(4-chlorophenyl)but-2-en-1-one (3i)



References

- 1 M. Zheng, C. Huang, J.-Z. Yan, S.-L. Xie, S.-J. Ke, H.-D. Xia and Y.-N. Duan, In Situ Hypoiodite-Catalyzed Oxidative Rearrangement of Chalcones: Scope and Mechanistic Investigation, *J Org Chem*, 2023, **88**, 1504–1514.
- 2 A. L. Sandoval, K. E. Doherty, G. P. Wadey, C. M. Schroeder and N. E. Leadbeater, Fast, easy oxidation of alcohols using an oxoammonium salt bearing the nitrate anion, *Tetrahedron Lett*, 2023, **116**, 154332.
- 3 H. Wu, S. Chen, D. Xiao, F. Li, K. Zhou, X. Yin, C. Liu, X. He and Y. Shang, Visible-Light-Mediated Deacylated Alkynylation of Unstrained Ketone, *Org Lett*, 2023, **25**, 1166–1171.
- 4 S. Zhang, J. Zhang and H. Zou, Pd-Catalyzed TBHP-Mediated Selective Wacker-Type Oxidation and Oxo-acyloxylation of Olefins Using a 2-(1 *H*-Indazol-1-yl)quinoline Ligand, *Org Lett*, 2023, **25**, 1850–1855.
- 5 J. Huang, X. Yan and Y. Xia, Directing Group-Free Formal Suzuki–Miyaura Coupling of Simple Ketones Enabled by Activation of Unstrained C–C Bonds, *Angew Chem Int Ed Engl.*, 2022, **61**, e202211080.
- 6 A. Ikeda, M. Omote, K. Kusumoto, A. Tarui, K. Sato and A. Ando, One-pot synthesis of 1,3-enynes with a CF₃ group on the terminal sp² carbon by an oxidative Sonogashira cross-coupling reaction, *Org Biomol Chem*, 2015, **13**, 8886–8892.
- 7 J. Liu, K.-F. Hu, J.-P. Qu and Y.-B. Kang, Organopromoted Selectivity-Switchable Synthesis of Polyketones, *Org Lett*, 2017, **19**, 5593–5596.
- 8 A. K. Jha, R. Kumari and S. Easwar, Synthesis of 2,2-Disubstituted Dihydro-1,4-benzothiazines from Morita–Baylis–Hillman Ketones by an Oxidative Cyclization, *J Org Chem*, 2022, **87**, 5760–5772.
- 9 L. Saney, K. E. Christensen, X. Li, M. Genov, A. Pretsch, D. Pretsch and M. G. Moloney, Tetramate Derivatives by Chemoselective Dieckmann Ring Closure of *threo*-Phenylserines and Their Antibacterial Activity, *J Org Chem*, 2022, **87**, 12240–12249.
- 10 K. Deng, Q.-Y. Huai, Z.-L. Shen, H.-J. Li, C. Liu and Y.-C. Wu, Rearrangement of Dypnones to 1,3,5-Triarylbenzenes, *Org Lett*, 2015, **17**, 1473–1476.
- 11 B.-H. Xing, X.-X. Zhao, Y.-J. Qin, P. Zhang and Z.-X. Guo, Ferric chloride-catalyzed deoxygenative chlorination of carbonyl compounds: A comparison of chlorodimethylsilane and dichloromethylsilane system, *J Chem Res*, 2020, **44**, 667–675.