Supporting Information

Zeolite Y Nanoparticle Assemblies with High Activity in the Direct Hydration of Terminal Alkynes

Shuling Xu,[a,b] Zhi Yun,[a]* Yu Feng,[b] Ting Tang,[b] Zhongxue Fang[b] and Tiandi Tang [b]*

[a] *College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing, Jiangsu 210009, P. R. China*

[b] *School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu 213164, P. R. China.*

1. Figures

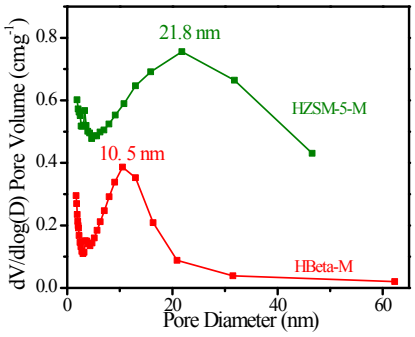


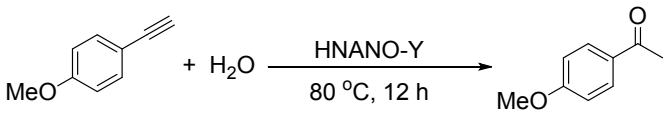
Fig. S1. Mesoporous size distributions of HBeta-M and HZSM-5-M samples.

2. Tables

Table S1. Total acidity of the zeolite catalyst samples

Sample	Acidic amounts of the catalysts (μmol·g^{-1})
HNANO-Y	830
HY	798
HBeta-M	256
HZSM-5-M	350

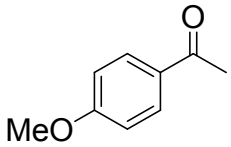
Table S2 Effect of the water content in reaction mixture on the conversion of 1-Ethynyl-4-methoxybenzene over HNANO-Y catalyst.[a]



Entry	H_2O (mmol)	Conversion	Selectivity
1	80	100	100
2	8	98	100
3	6	91	100
4	4	87	100

[a]Reaction conditions: 1-Ethynyl-4-methoxybenzene (2.0 mmol), catalyst (120 mg), 80 °C for 12 h.

3. Spectral data for products [1-3]



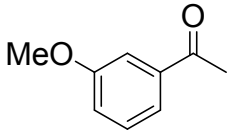
1-(4-methoxyphenyl)ethanone (**2a**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.55 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 143.7, 134.5, 129.0, 128.2, 26.3, 21.4;

HRMS (ESI) m/z calculated for $C_9H_{11}O_2$ $[M+H]^+$: 151.0759, found 151.0758.



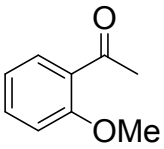
1-(3-methoxyphenyl)ethanone (**2b**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.48 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.14-7.07 (m, 1H), 3.84 (s, 3H), 2.58 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 159.7, 138.3, 129.4, 121.0, 119.5, 112.2, 55.3, 26.6;

HRMS (ESI) m/z calculated for $C_9H_{11}O_2$ $[M+H]^+$: 151.0759, found 151.0760.



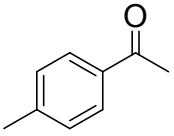
1-(2-methoxyphenyl)ethanone (**2c**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.03-6.92 (m, 2H), 3.90 (s, 3H), 2.61 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 158.8, 133.5, 130.2, 128.1, 120.4, 111.4, 55.3, 31.7;

HRMS (ESI) m/z calculated for $C_9H_{11}O_2$ $[M+H]^+$: 151.0759, found 151.0763.



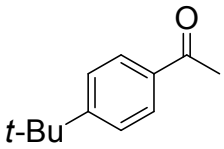
1-(p-tolyl)ethanone (**2d**)

Colorless liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 2.39 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 143.7, 134.5, 129.0, 128.2, 26.3, 21.4;

HRMS (ESI) m/z calculated for $C_9H_{11}O$ $[M+H]^+$: 135.0810, found 135.0806.



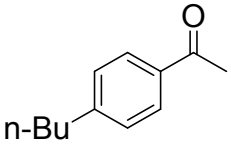
1-(4-(tert-butyl)phenyl)ethanone (**2e**)

Colorless liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H), 1.34 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 156.7, 134.5, 128.2, 125.4, 35.0, 31.0, 26.4;

HRMS (ESI) m/z calculated for $C_{12}H_{17}O$ $[M+H]^+$: 177.1279, found 177.1281.



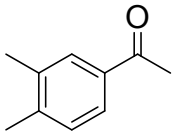
1-(4-butylphenyl)ethanone (**2f**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 1.67-1.56 (m, 2H), 1.41-1.30 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 156.7, 134.5, 128.2, 125.4, 35.0, 31.0, 26.4;

HRMS (ESI) m/z calculated for $C_{12}H_{17}O$ $[M+H]^+$: 177.1279, found 177.1282.



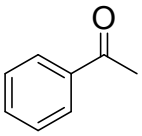
1-(3,4-dimethylphenyl)ethanone (**2g**)

Brown liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.62 (m, 2H), 7.41-7.16 (m, 1H), 2.56 (s, 3H), 2.31 (d, *J* = 6.0 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 142.5, 136.7, 135.0, 129.7, 126.0, 26.4, 19.9, 19.6;

HRMS (ESI) m/z calculated for $C_{10}H_{13}O$ $[M+H]^+$: 149.0966, found 149.0967.



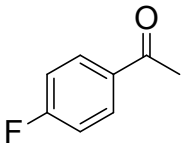
acetophenone (**2h**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.89 (m, 2H), 7.69-7.52 (m, 1H), 7.52-7.40 (m, 2H), 2.60 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 137.0, 133.0, 128.5, 128.2, 26.5;

HRMS (ESI) m/z calculated for C_8H_9O $[M+H]^+$: 121.0653, found 121.0650.



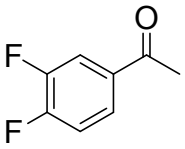
1-(4-fluorophenyl)ethanone (**2i**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-7.90 (m, 2H), 7.28-7.02 (m, 2H), 2.58 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 167.0 (d, J = 253.0 Hz), 133.6 (d, J = 2.9 Hz), 130.9 (d, J = 9.2 Hz), 115.7 (d, J = 21.8Hz), 26.5;

HRMS (ESI) m/z calculated for C_8H_8FO $[M+H]^+$: 139.0559, found 139.0560.



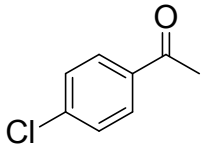
1-(3,4-difluorophenyl)ethanone (**2J**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.70 (m, 2H), 7.41-7.20 (m, 1H), 2.58 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 154.9 (q, J = 21.8, 34.6 Hz), 152.4 (q, J = 13.0, 73.3 Hz), 149.1 (d, J = 13.2 Hz), 134.2 (t, J = 39.0 Hz), 125.3 (q, J = 36.0, 74.0 Hz), 117.5 (q, J = 3.9, 17.5 Hz), 26.4;

HRMS (ESI) m/z calculated for $C_8H_7F_2O$ $[M+H]^+$: 157.0465, found 157.0466.



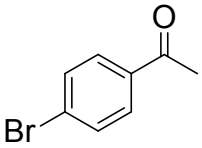
1-(4-chlorophenyl)ethanone (**2k**)

Colorless liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 2.58 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 139.5, 135.3, 129.6, 128.8, 26.4;

HRMS (ESI) m/z calculated for C_8H_8ClO $[M+H]^+$: 155.0264, found 155.0262.



1-(4-bromophenyl)ethanone (**2l**)

Colorless solid, m.p. 49-50 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.76 (m, 2H), 7.70-7.55 (m, 2H), 2.58 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 135.8, 131.8, 129.7, 128.2, 26.4;

HRMS (ESI) m/z calculated for C_8H_8BrO $[M+H]^+$: 198.9759, found 198.9750.

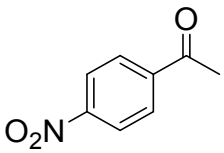
1-(2-bromophenyl)ethanone (**2m**)

White solid, m.p. 48-49 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.36 (t. *J* = 6.8 Hz, 1H), 7.32-7.25 (m, 1H), 2.63 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 141.3, 133.7, 131.7, 128.8, 127.3, 118.8, 30.2;

HRMS (ESI) m/z calculated for C_8H_8BrO $[M+H]^+$: 198.9759, found 198.9749.



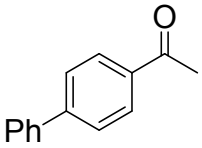
1-(4-nitrophenyl)ethanone (**2n**)

Yellow solid, m.p. 77-78 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 2.69 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 150.3, 141.3, 129.2, 123.8, 26.9;

HRMS (ESI) m/z calculated for $C_8H_8NO_3$ $[M+H]^+$: 166.0504, found 166.0503.



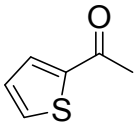
1-([1,1'-biphenyl]-4-yl)ethanone (**2o**)

White solid, m.p. 120-121 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-7.91 (m, 2H), 7.90-7.54 (m, 4H), 7.54-7.31 (m, 3H), 2.60 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 145.6, 139.6, 135.7, 128.8, 128.7, 128.1, 127.1, 127.0, 26.5;

HRMS (ESI) m/z calculated for $C_{14}H_{13}O$ $[M+H]^+$: 197.0966, found 197.0970.



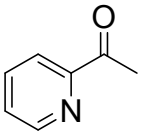
1-(thiophen-2-yl)ethanone (**2p**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 4.8 Hz, 1H), 7.64 (d, *J* = 4.8 Hz, 1H), 7.13 (t, *J* = 4.0 Hz, 1H), 2.56 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 144.4, 133.7, 132.4, 128.0, 26.8;

HRMS (ESI) m/z calculated for C_6H_7OS $[M+H]^+$: 127.0218, found 127.0224.



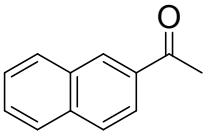
1-(pyridin-2-yl)ethanone (**2q**)

Yellow liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.88-7.79 (m, 1H), 7.51-7.44 (m, 1H), 2.73 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 153.4, 148.8, 136.7, 126.9, 121.5, 25.6;

HRMS (ESI) m/z calculated for C_7H_8NO $[M+H]^+$: 122.0606, found 122.0608.



1-(naphthalen-2-yl)ethanone (**2r**)

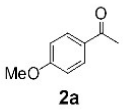
White solid, m.p. 52-53 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.05 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 8.4 Hz, 2H), 7.64-7.51 (m, 2H), 2.73 (s, 3H);

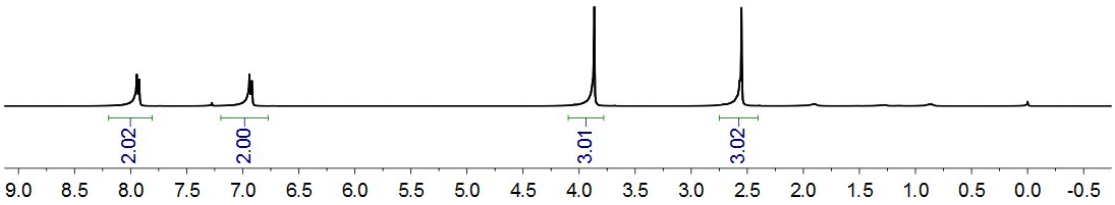
HRMS (ESI) m/z calculated for $C_{12}H_{11}O$ $[M+H]^+$: 171.0810, found 171.0807.

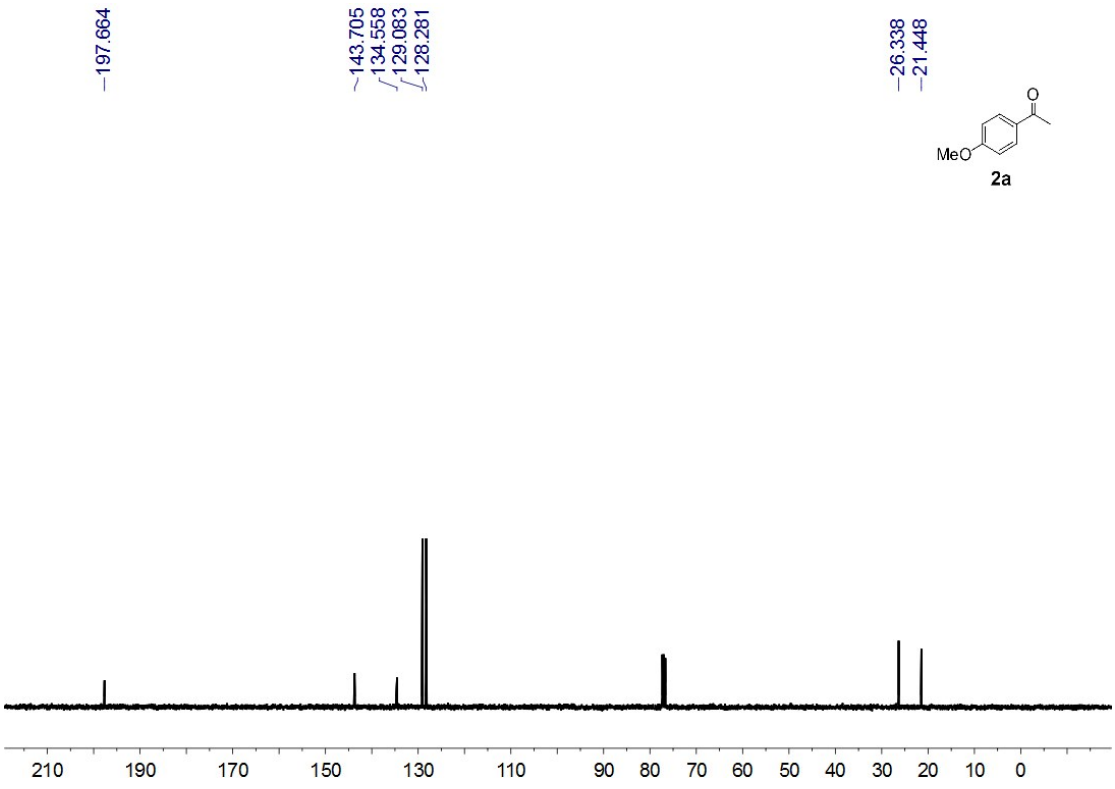
---

2. NMR spectra copes

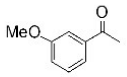


2a

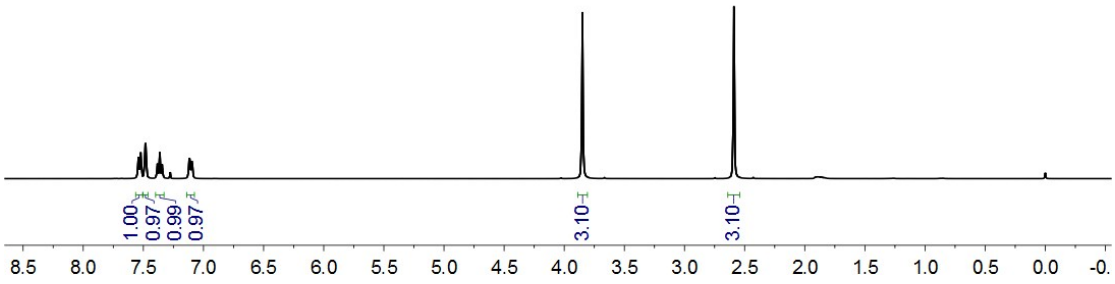


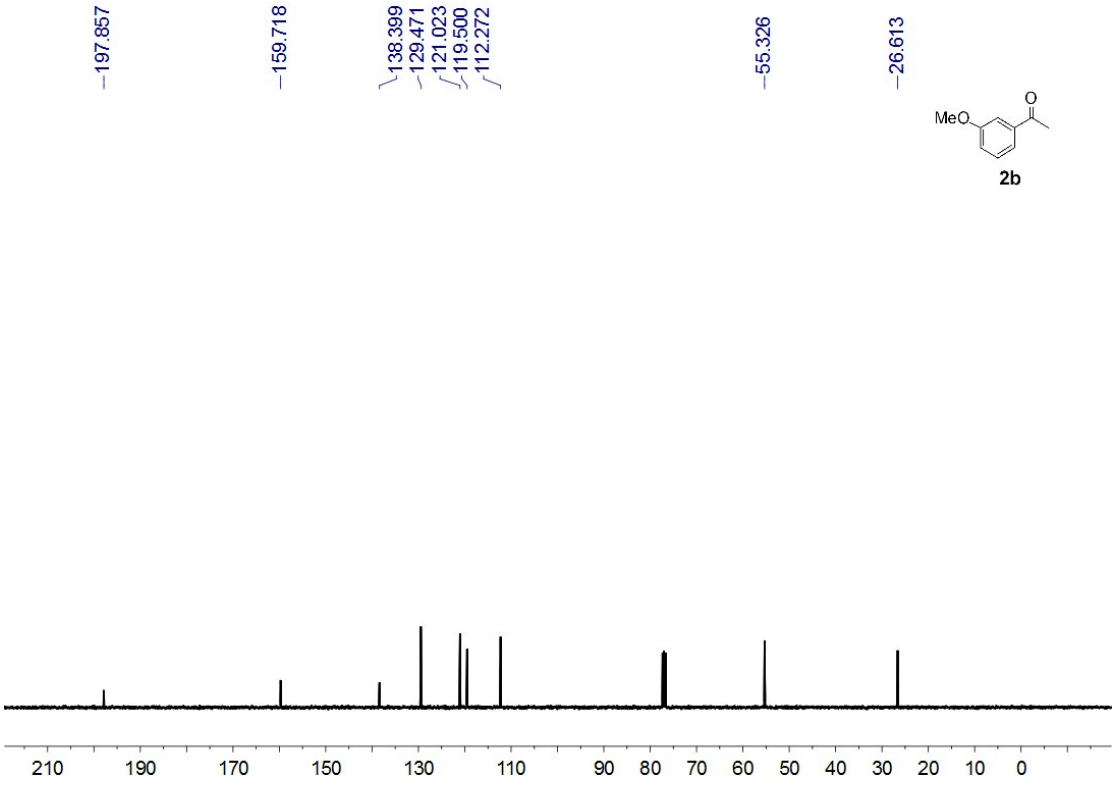


2a


MeO
O

2b


1.00
0.97
0.99
0.97
3.10
3.10
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 -0.

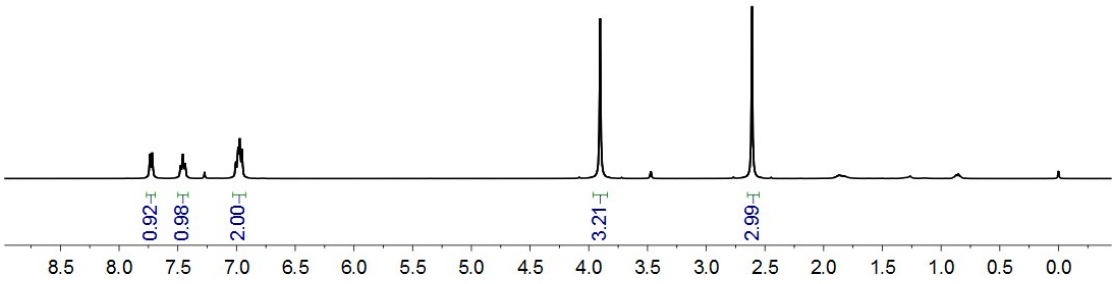

197.857
159.718
138.399
129.471
121.023
119.500
112.272
55.326
26.613
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

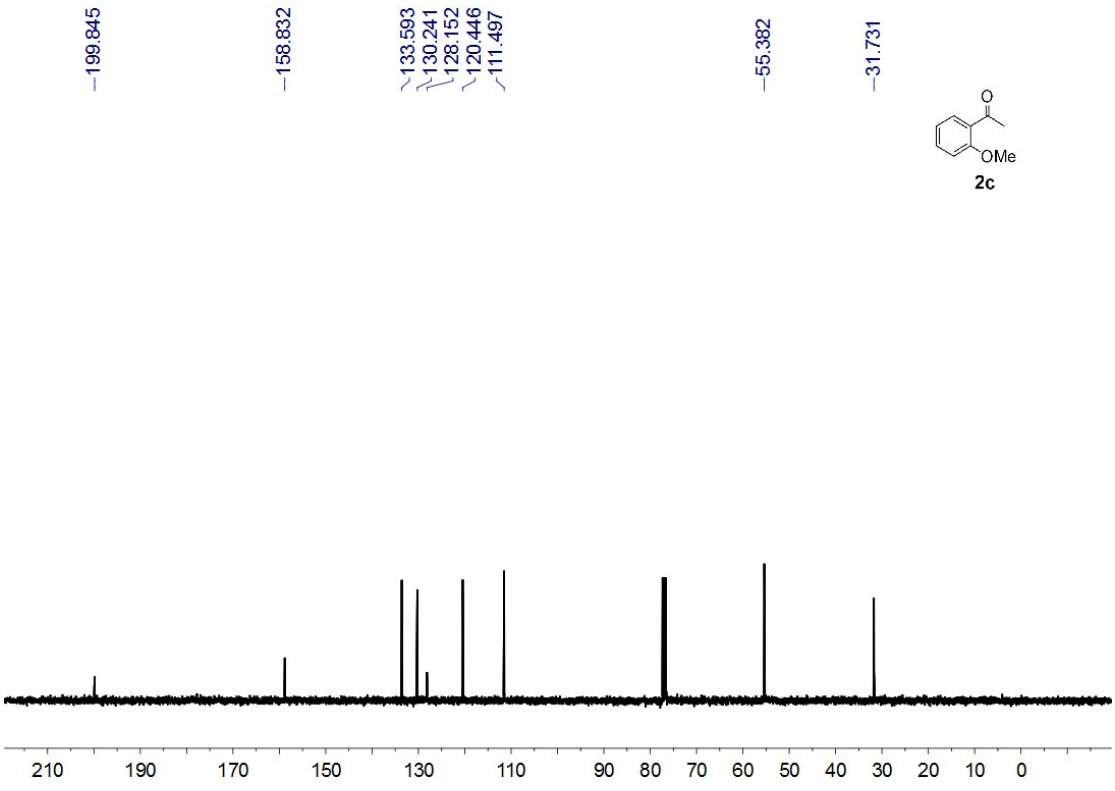
MeO
O

2b


O
OMe

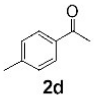
2c


0.92
0.98
2.00
3.21
2.99
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

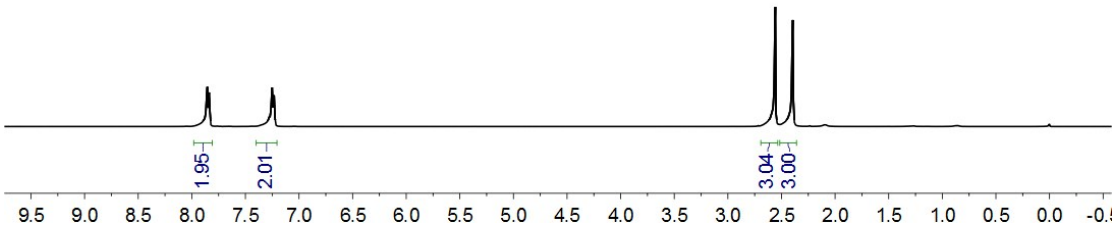

199.845
158.832
133.593
130.241
128.152
120.446
111.497
55.382
31.731
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

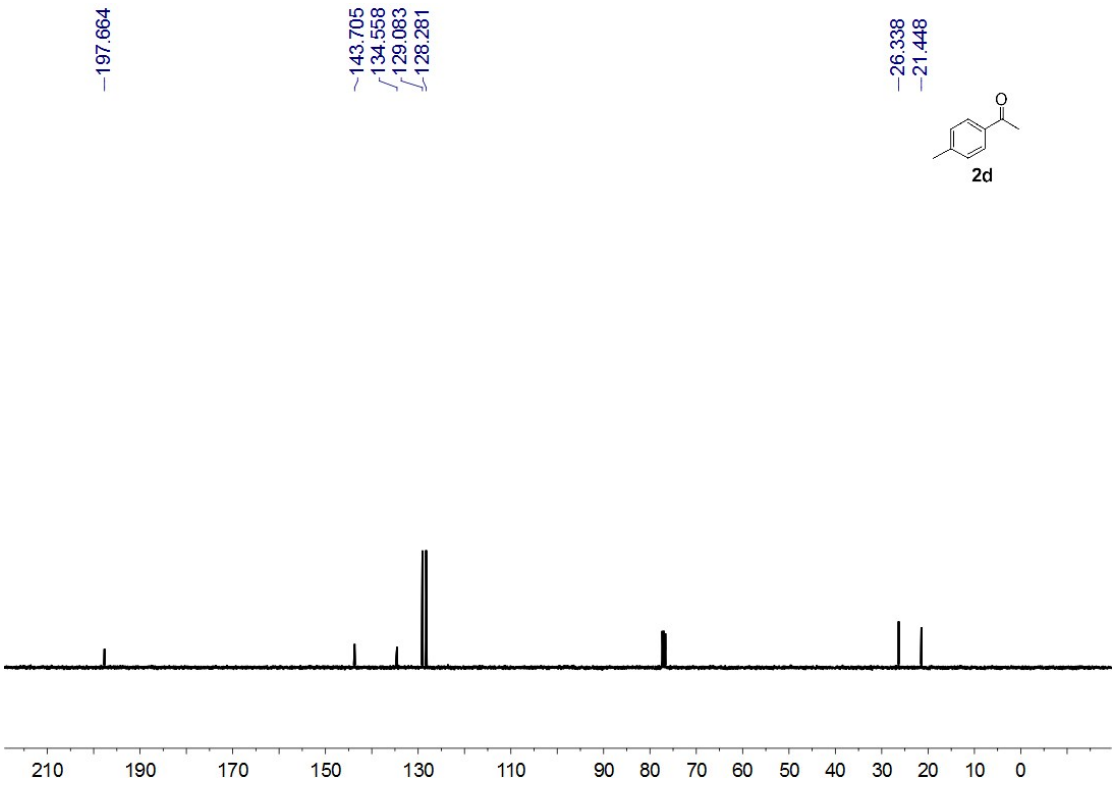
O
OMe

2c

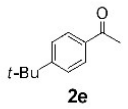


2d

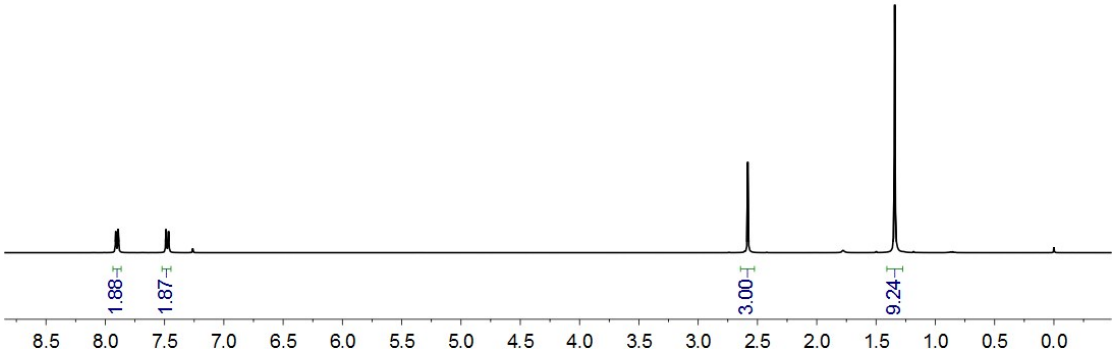

1.95
2.01
3.04
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

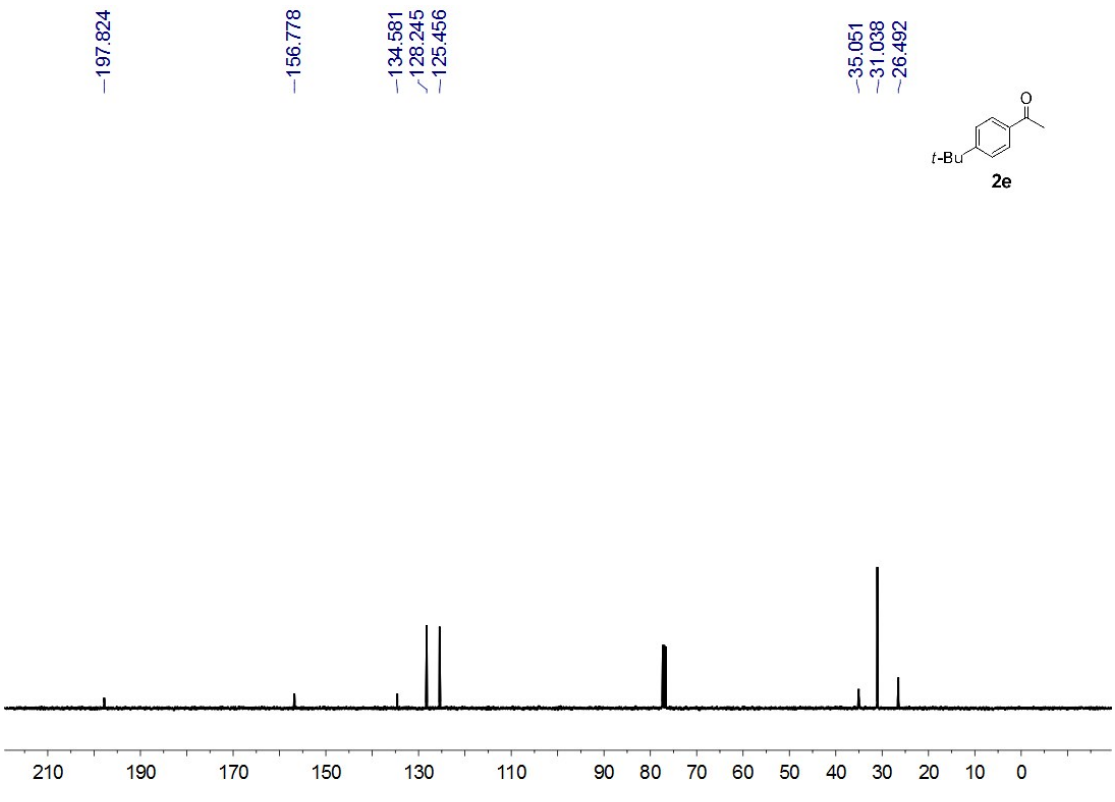

197.664
143.705
134.558
129.083
128.281
26.338
21.448
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2d

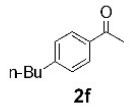

O
t-Bu

2e

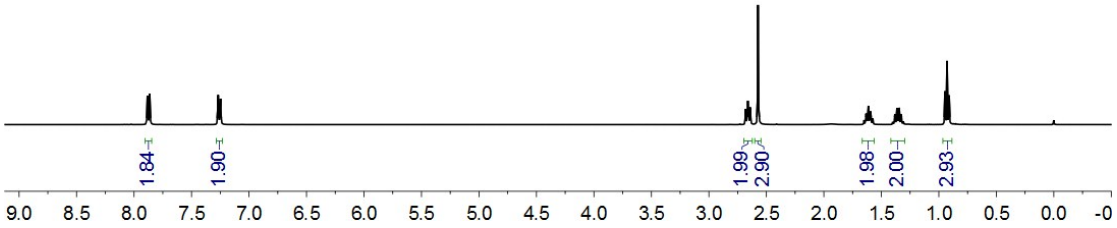

1.88
1.87
3.00
9.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

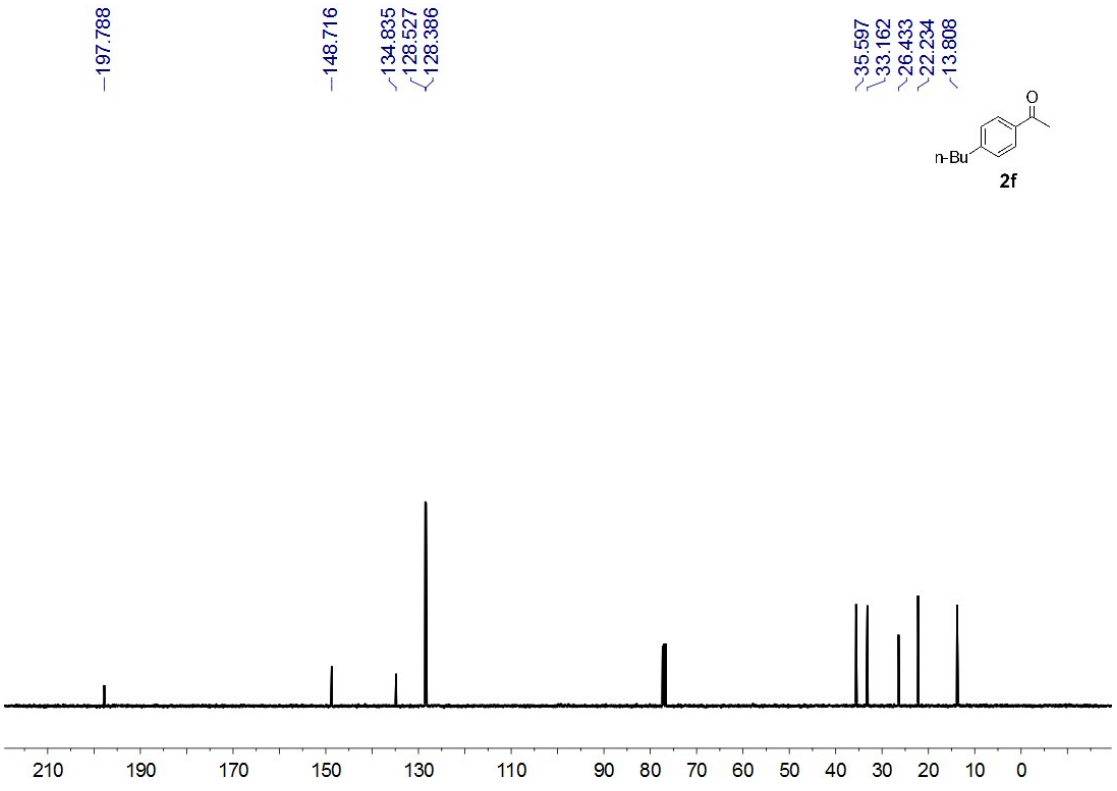

197.824
156.778
134.581
128.245
125.456
35.051
31.038
26.492
O
t-Bu
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

2e


O
n-Bu

2f

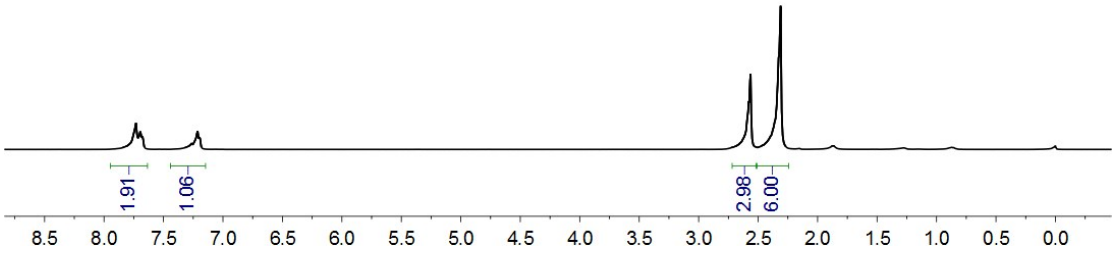

1.84
1.90
1.99
2.90
1.98
2.00
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0


197.788
148.716
134.835
128.527
128.386
35.597
33.162
26.433
22.234
13.808
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

O
n-Bu

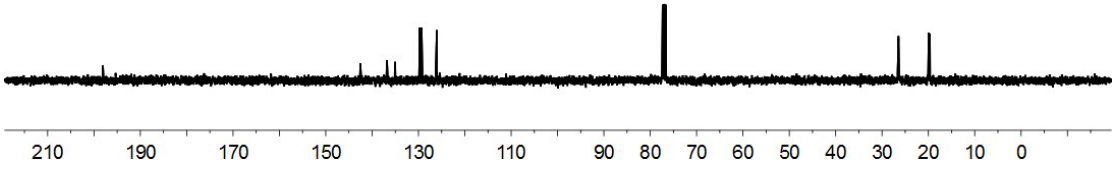
2f

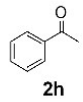
2g



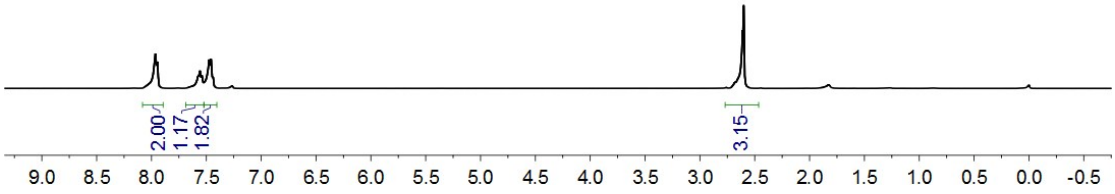
198.080
142.530
136.798
135.040
129.703
129.324
126.044
26.454
19.922
19.678

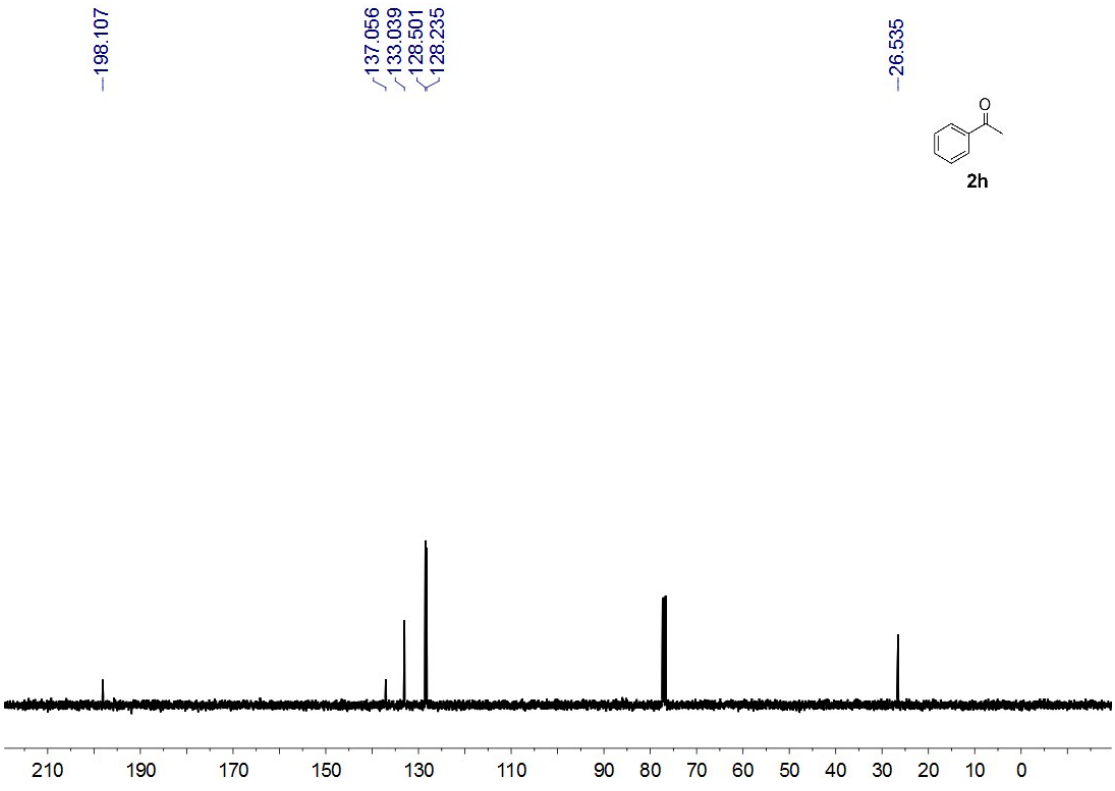
2g



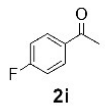


2h

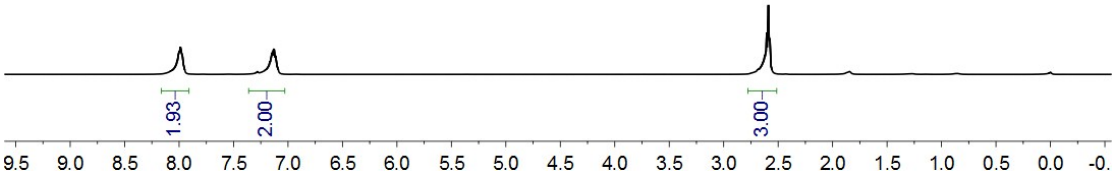

2.00
1.17
1.82
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

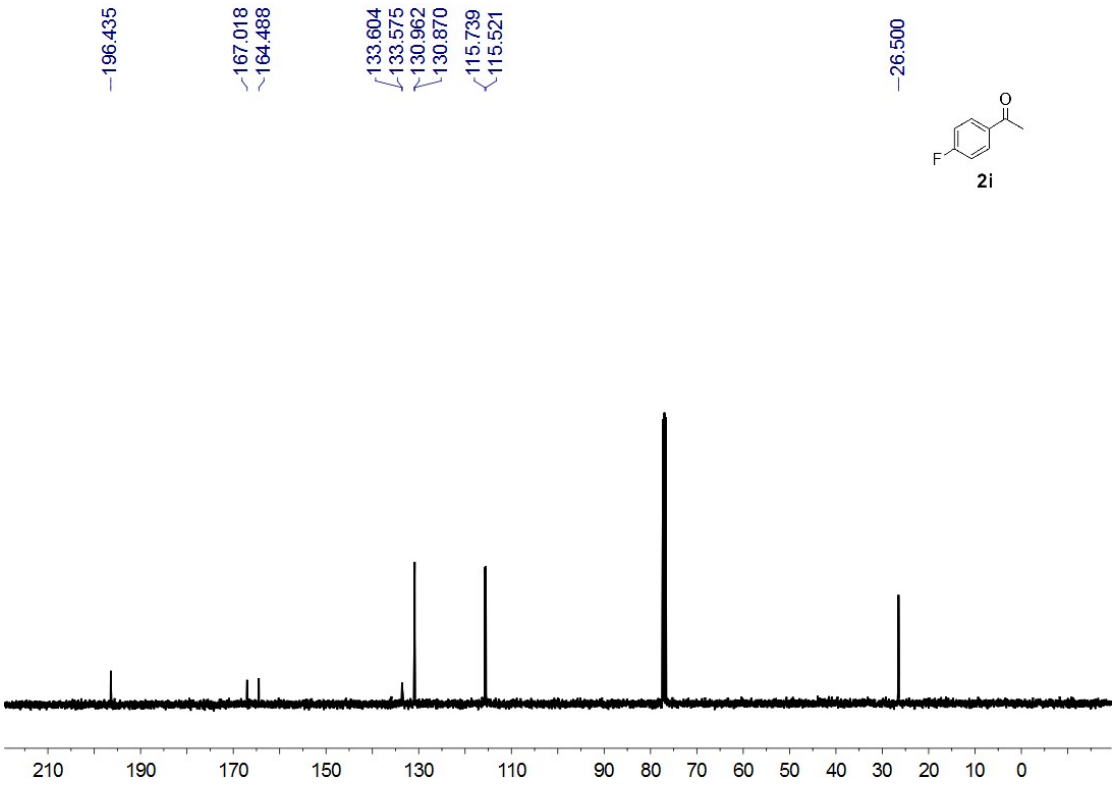

198.107
137.056
133.039
128.501
128.235
26.535
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2h

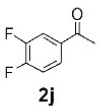

O
F

2i

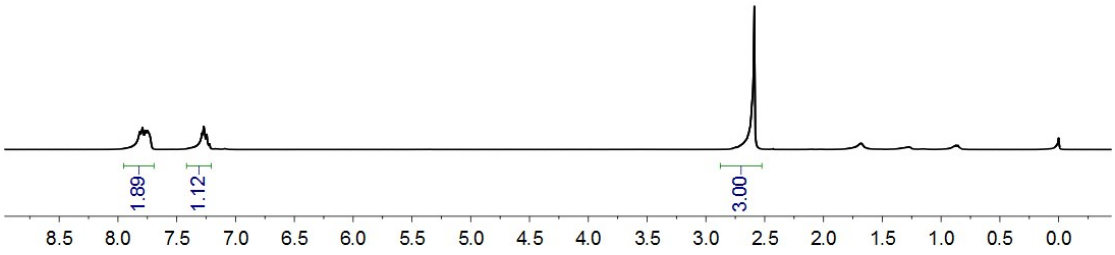

1.93
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

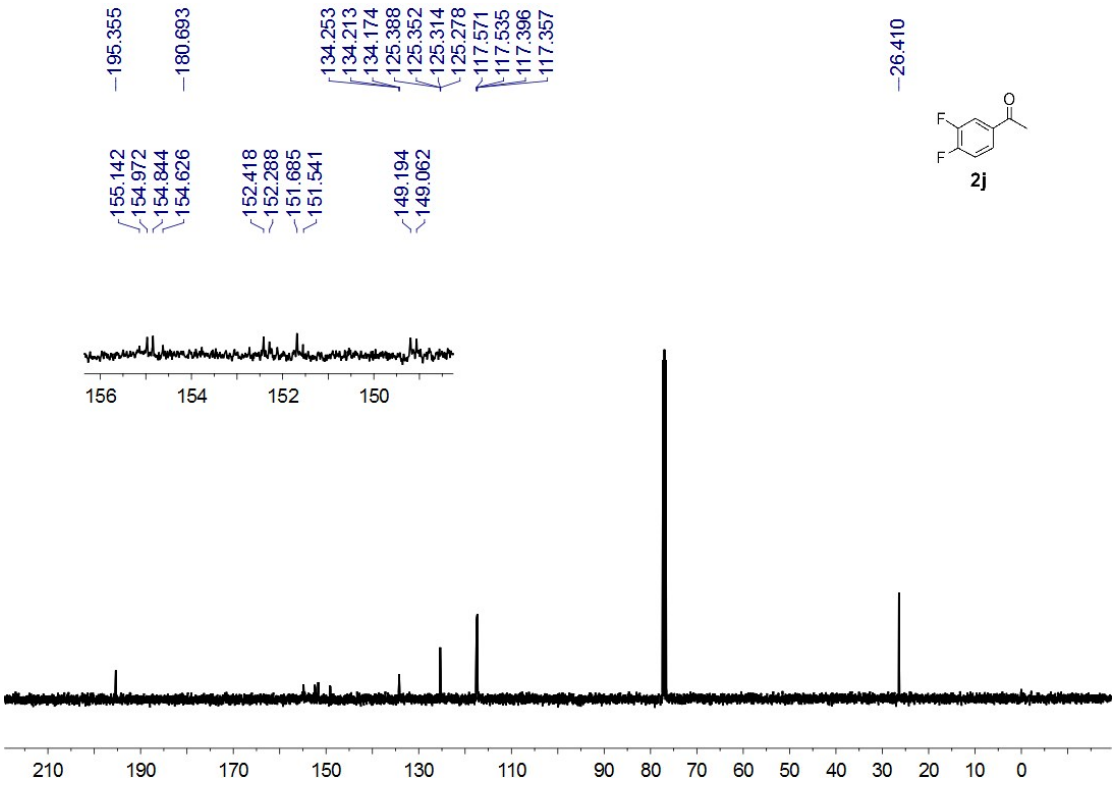

196.435
167.018
164.488
133.604
133.575
130.962
130.870
115.739
115.521
26.500
O
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2i


F
F
O

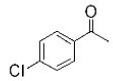
2j


1.89
1.12
3.00
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

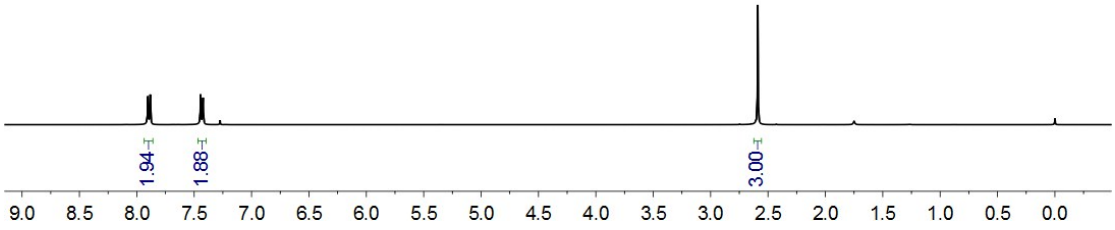

195.355
180.693
134.253
134.213
134.174
125.388
125.352
125.314
125.278
117.571
117.535
117.396
117.357
26.410
155.142
154.972
154.844
154.626
152.418
152.288
151.685
151.541
149.194
149.062
156
154
152
150
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

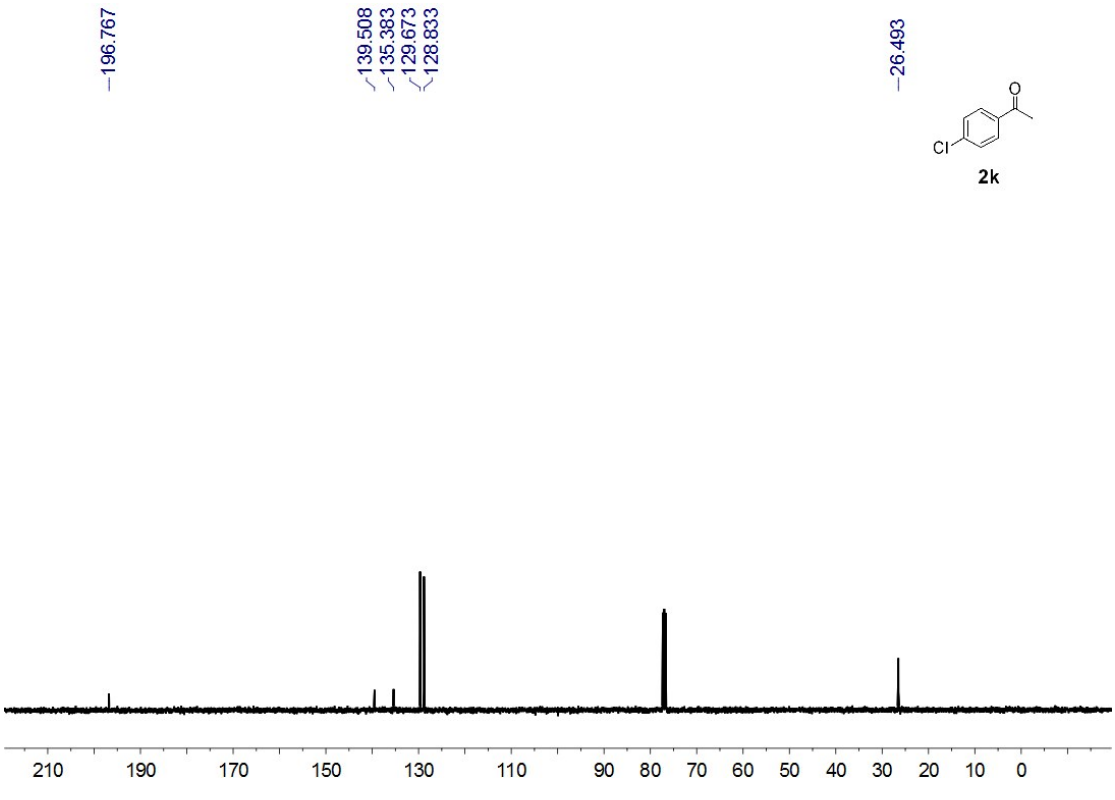
F
F
O

2j

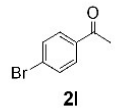

O
Cl

2k

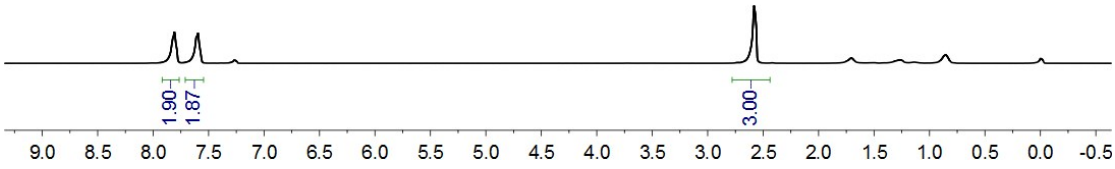

1.94
1.88
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

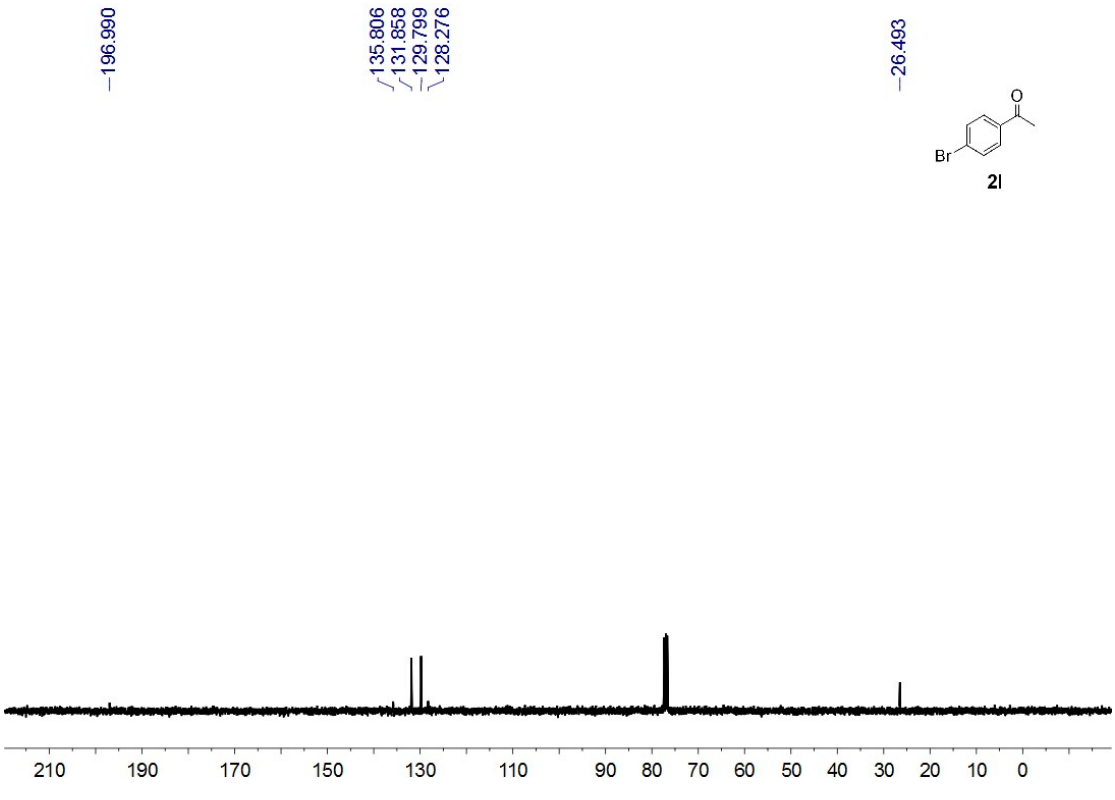

196.767
139.508
135.383
129.673
128.833
26.493
O
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2k


O
Br

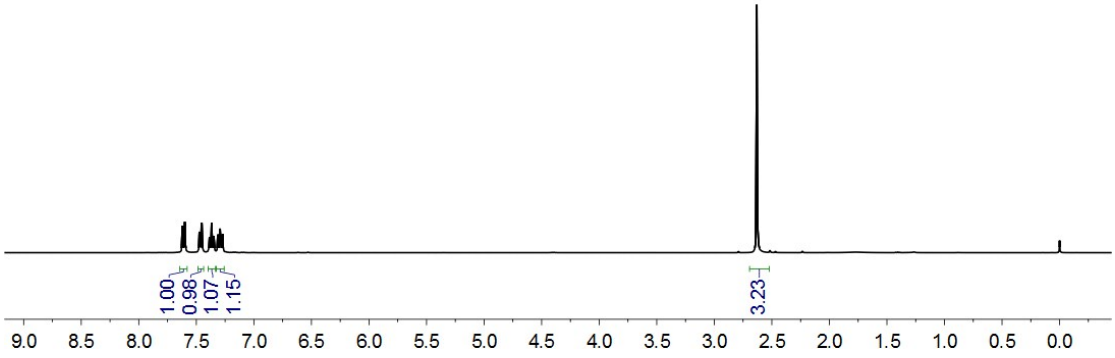
2l

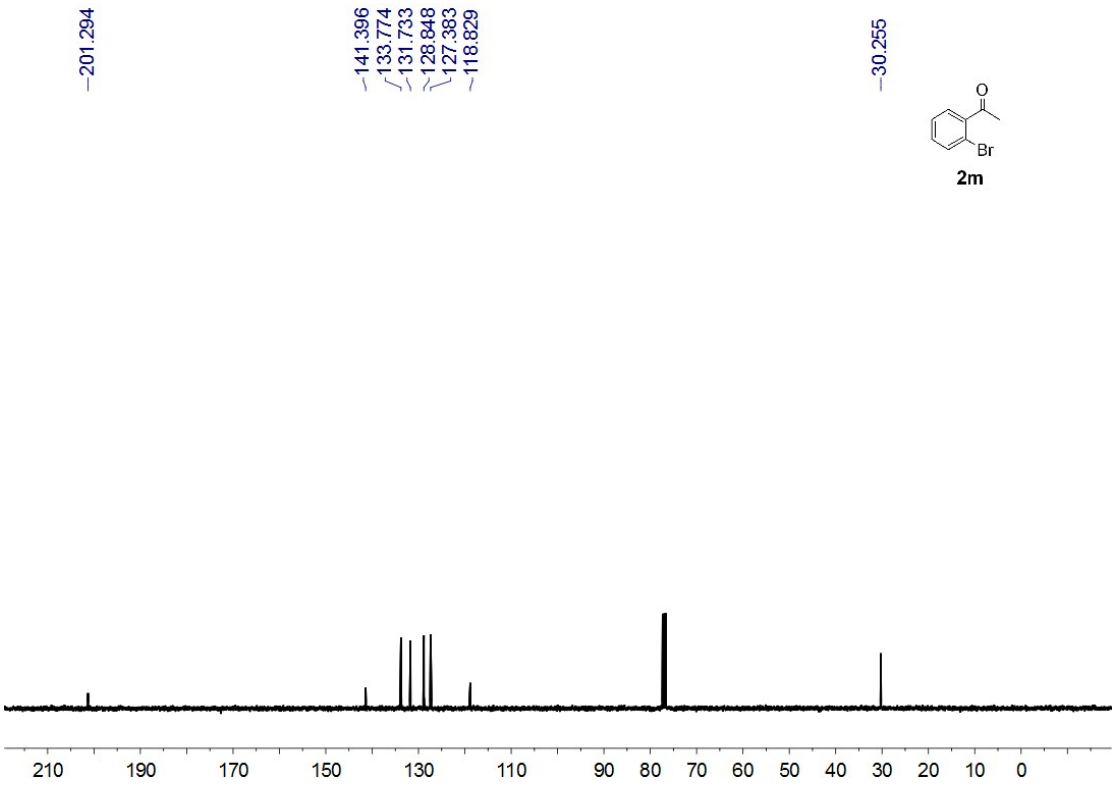

1.90
1.87
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


196.990
135.806
131.858
129.799
128.276
26.493
O
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

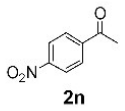
2l

2m

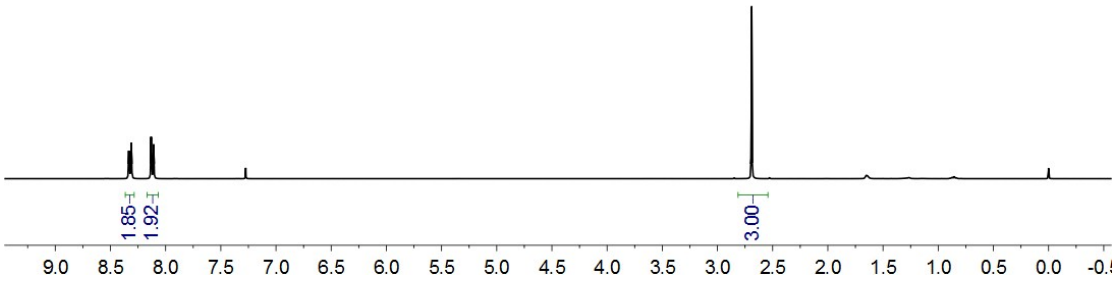

1.00
0.98
1.07
1.15
3.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

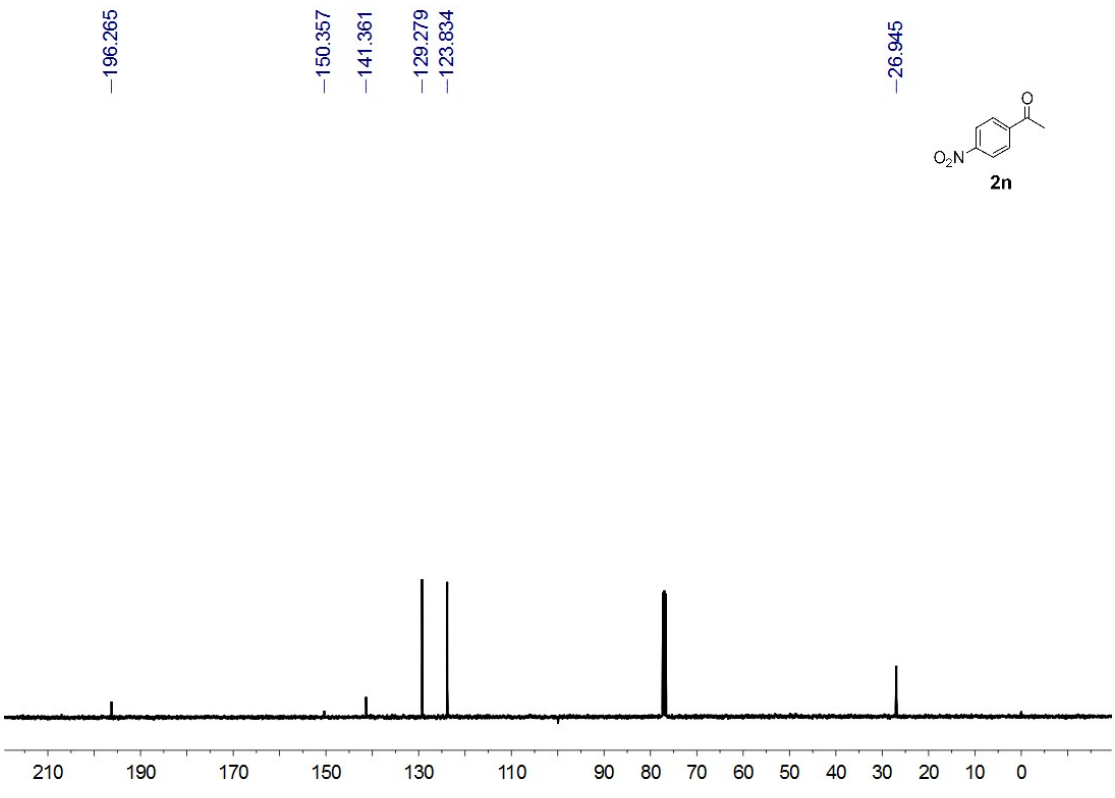

201.294
141.396
133.774
131.733
128.848
127.383
118.829
30.255
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2m

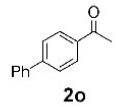


2n

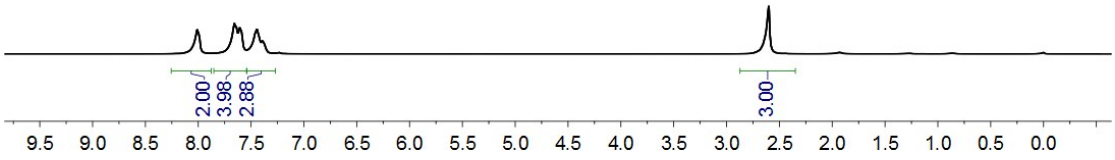

1.85
1.92
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

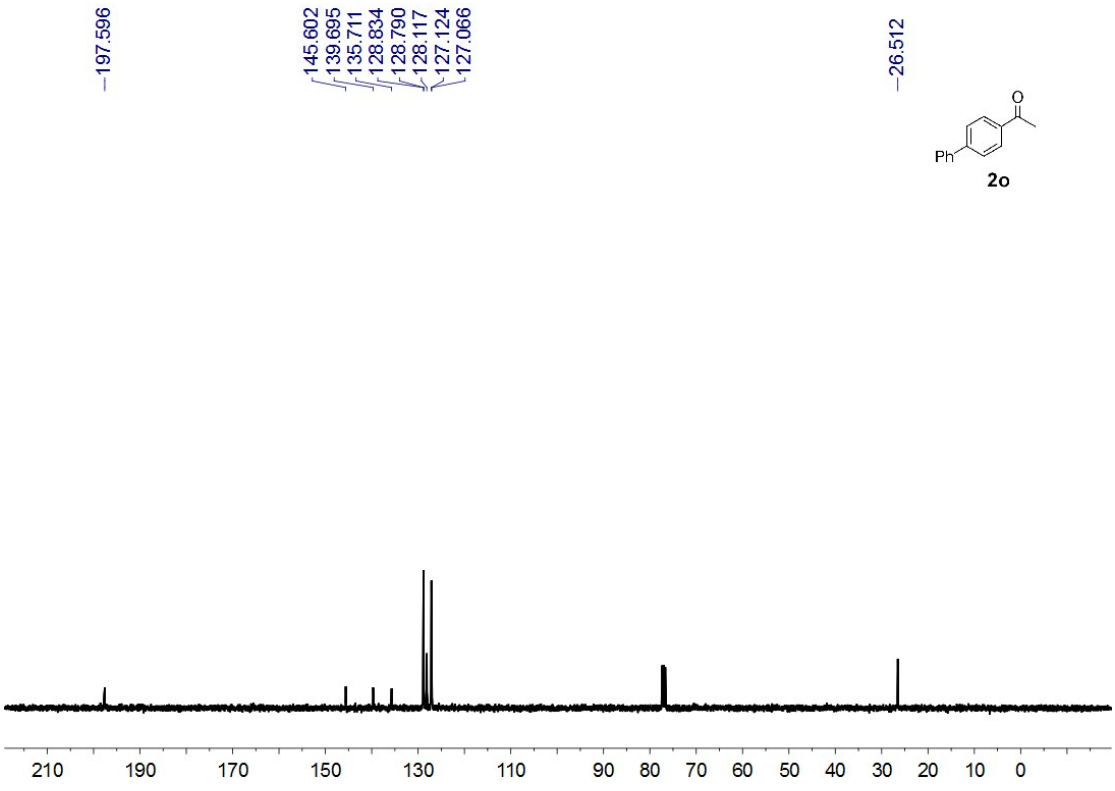

196.265
150.357
141.361
129.279
123.834
26.945
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2n

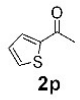

O
Ph

2o

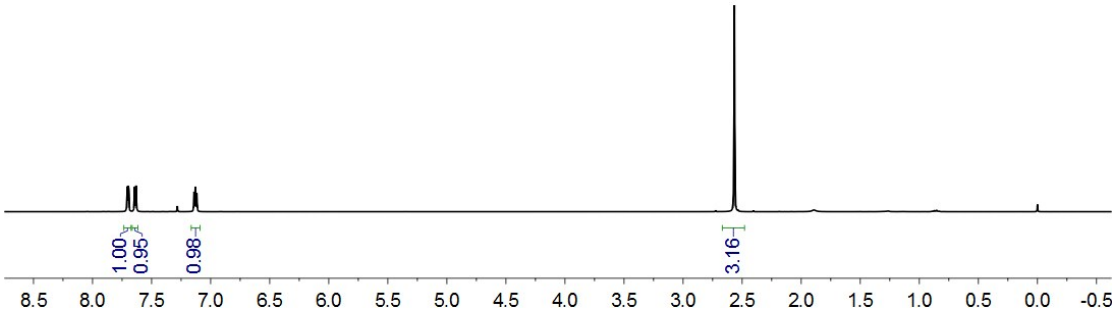

2.00
3.98
2.88
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

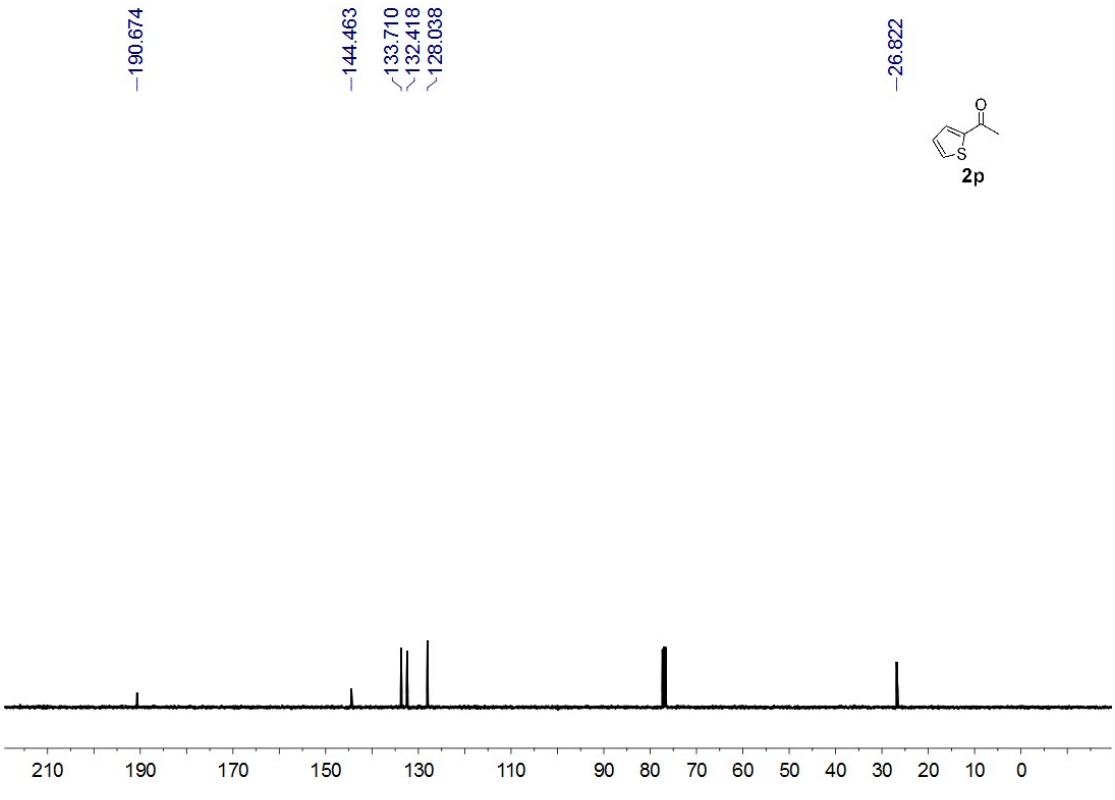

197.596
145.602
139.695
135.711
128.834
128.790
128.117
127.124
127.066
26.512
O
Ph
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2o



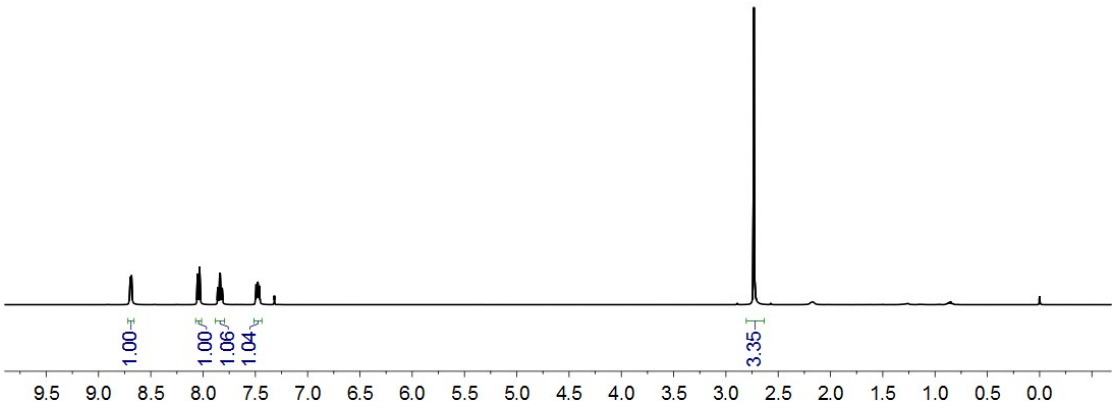
2p

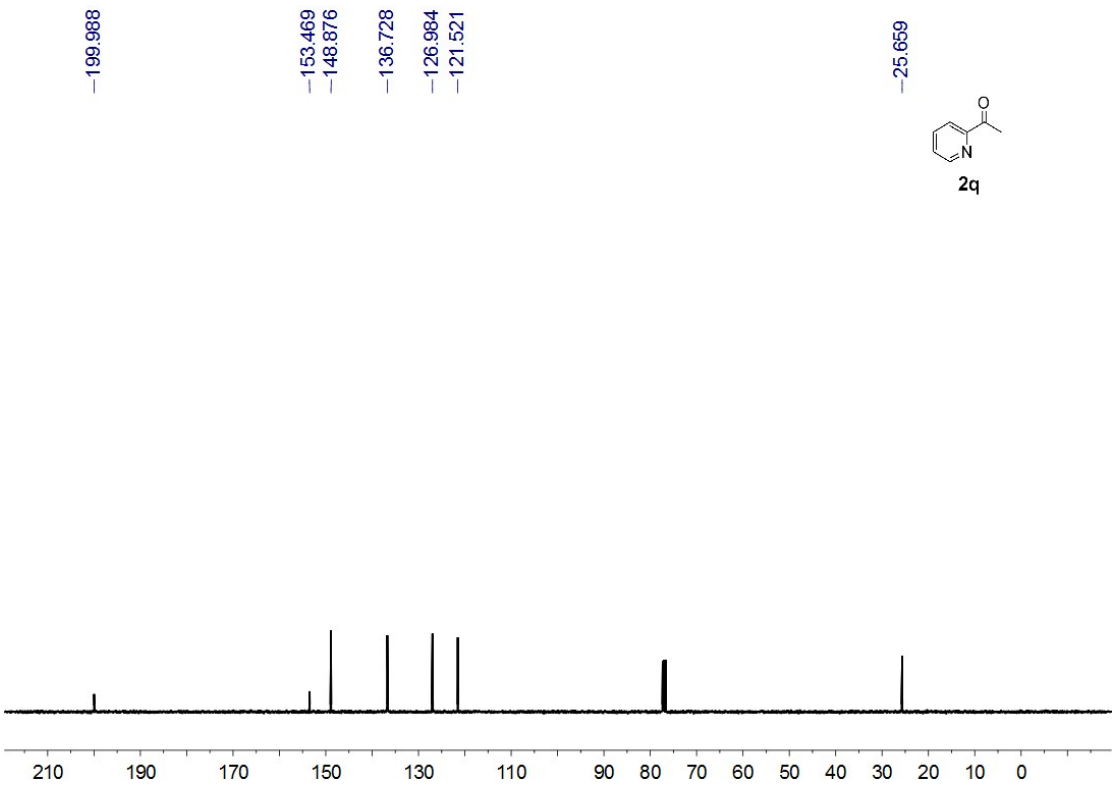

1.00
0.95
0.98
3.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


190.674
144.463
133.710
132.418
128.038
26.822
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

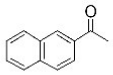
2p

2q

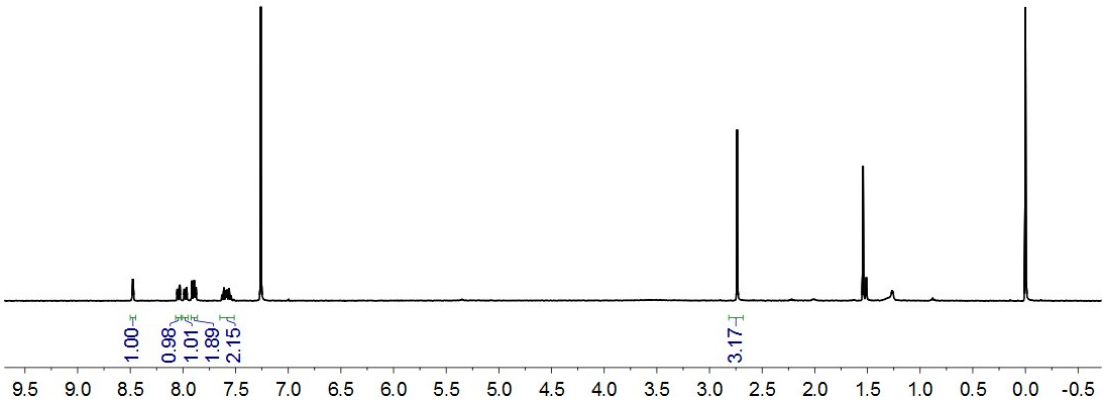

1.00
1.00
1.06
1.04
3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

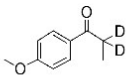

199.988
153.469
148.876
136.728
126.984
121.521
25.659
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

2q

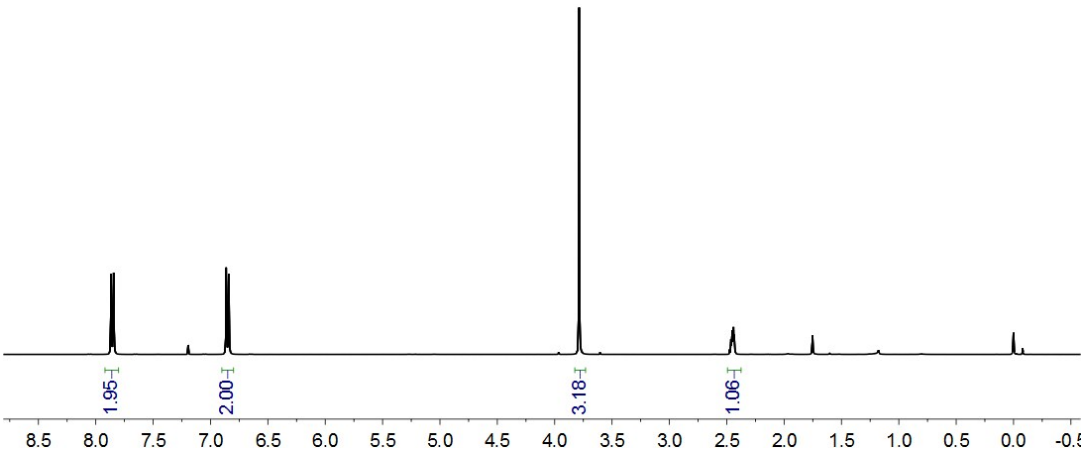


2r


1.00
0.98
1.01
1.89
2.15
3.17
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 -0.5



2a'


1.95
2.00
3.18
1.06
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

3. References

[1] J. Ruan, J. A. Iggo, N. G. Berry and J. Xiao, *J. Am. Chem. Soc.*, 2010, **132**, 16689−16699.

[2] C. Xu, W. Du, Y. Zeng, B. Dai and H. Guo, *Org. Lett.*, 2014, **16**, 948−951.

[3] S. Liang, J. Jasinski, G. B. Hammond and B. Xu, *Org. Lett.*, 2015, **17**, 162−165.