Electronic Supporting Information (ESI)

Cobalt (II) Catalyzed C(sp)-H bond Functionalization of alkynes with Phenyl hydrazines: A Facile access to Diaryl 1,2-diketones

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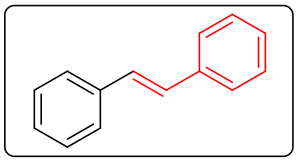
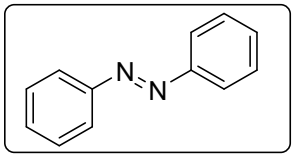
(E)-1,2-Diphenylethene (5a):[1]



Yellow solid; m.p.78-80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.0 Hz, 4H), 7.35 (t, J = 8.0 Hz, 4H), 7.25 (t, J = 8.0 Hz, 2H), 7.11 (s, 2H); ^{13}C NMR ($CDCl_3$,100 MHz): δ 137.4, 128.8, 128.7, 127.6, 126.5; IR ($CHCl_3$): ν_{max} 3437, 2922, 1621, 1597, 1577, 1495, 1451 cm^{-1}; GC-MS: *m/z* (EI) 210 (M^+, 7), 105 (100), 77 (64), 51 (17).

(E)-1,2-Diphenyldiazene (4a):[2]

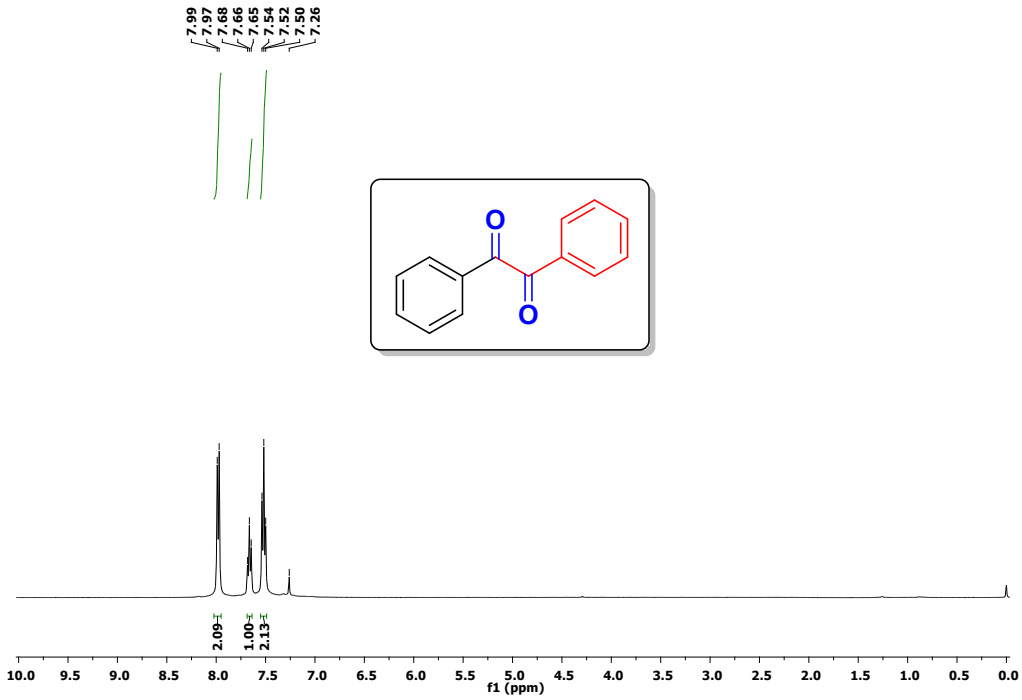


Orange solid; m.p. 67-69°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 8.0 Hz, 4H), 7.53-7.45 (m, 6H); ^{13}C NMR ($CDCl_3$,100 MHz): δ 152.7, 131.0, 129.1, 122.9; IR ($CHCl_3$): ν_{max} 3444, 1633, 1642, 1454, 1419, 1018 cm^{-1}; GC-MS: *m/z* (EI) 182 (M^+, 21), 152 (10), 105 (14), 77 (100), 51 (26).

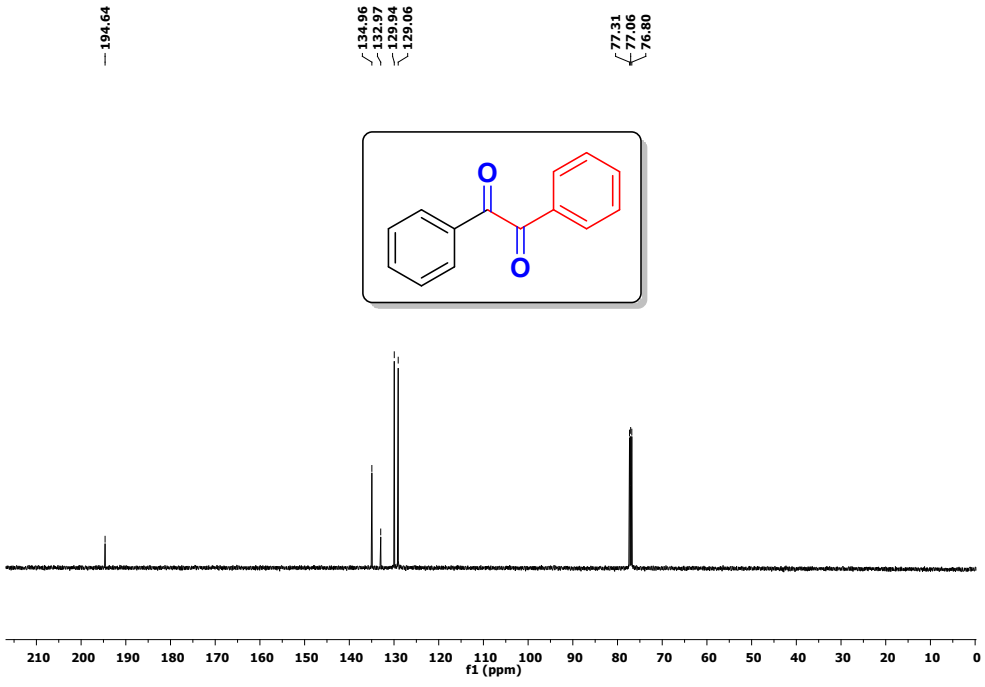
S2. Spectral data scans of 1,2-diketones (3a-3x)

S2.a. ^{1}H, ^{13}C and DEPT-135 NMR of benzil (3a):

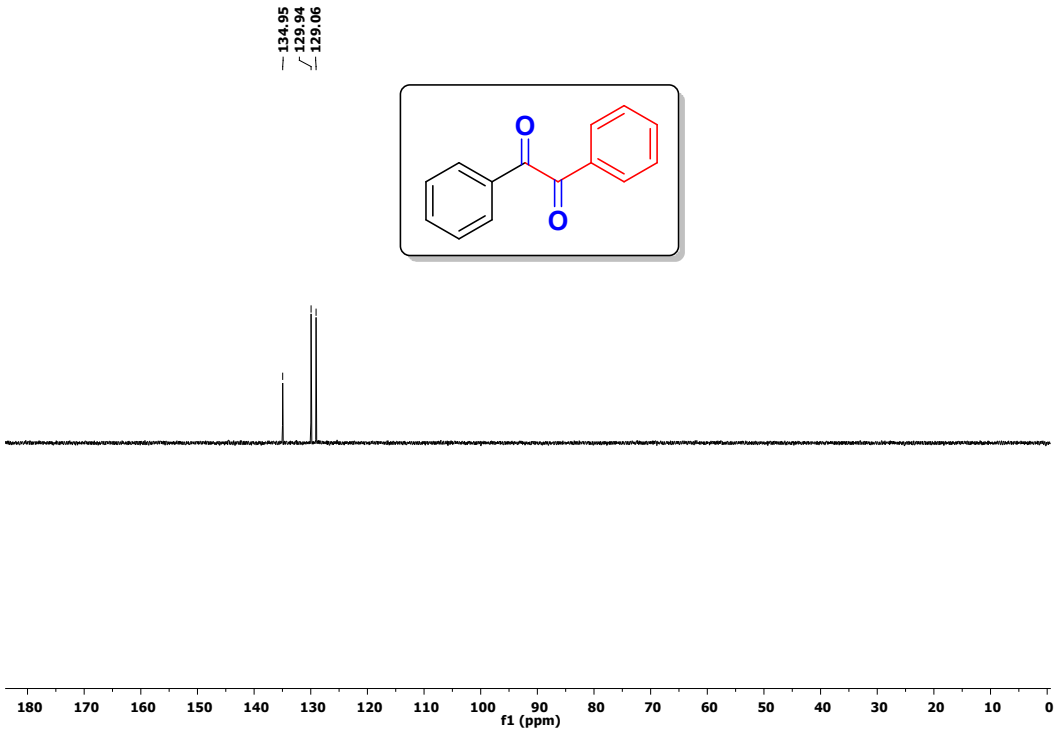
^{1}H NMR



^{13}C NMR

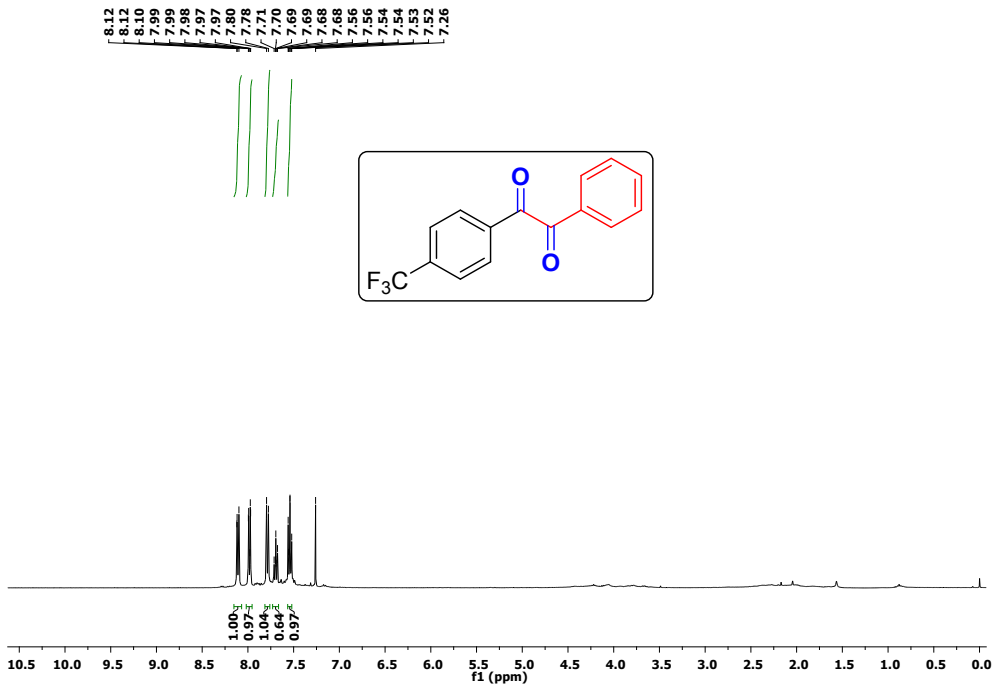


DEPT-135

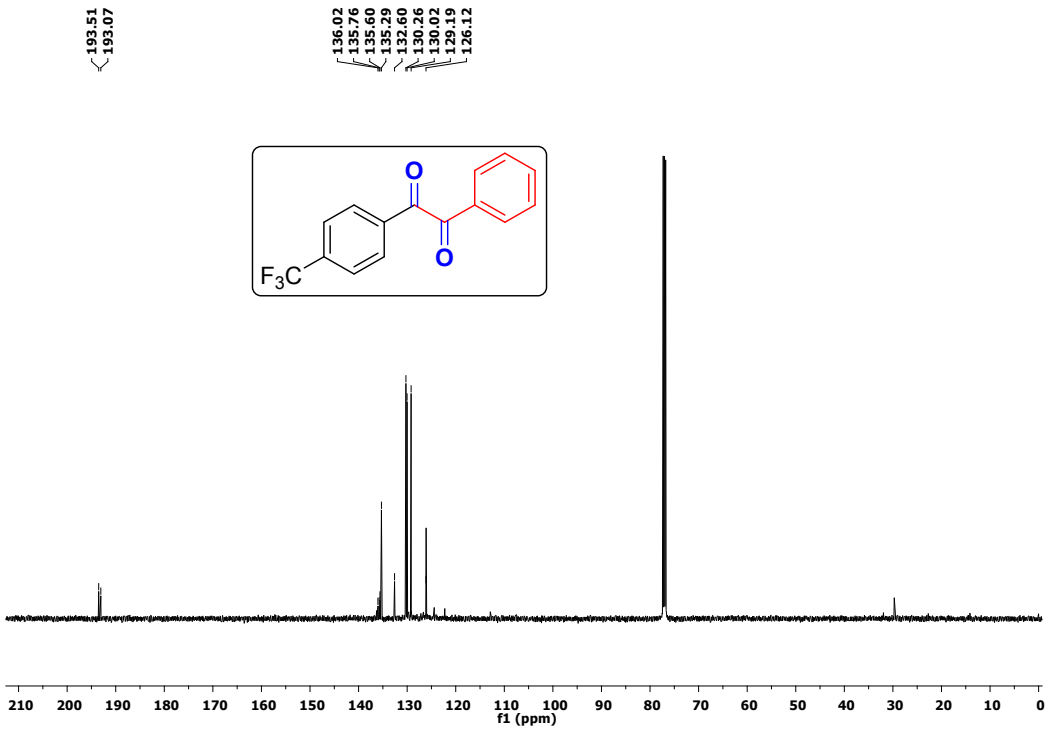

134.95
129.94
129.06
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.b. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-phenyl-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (3b):

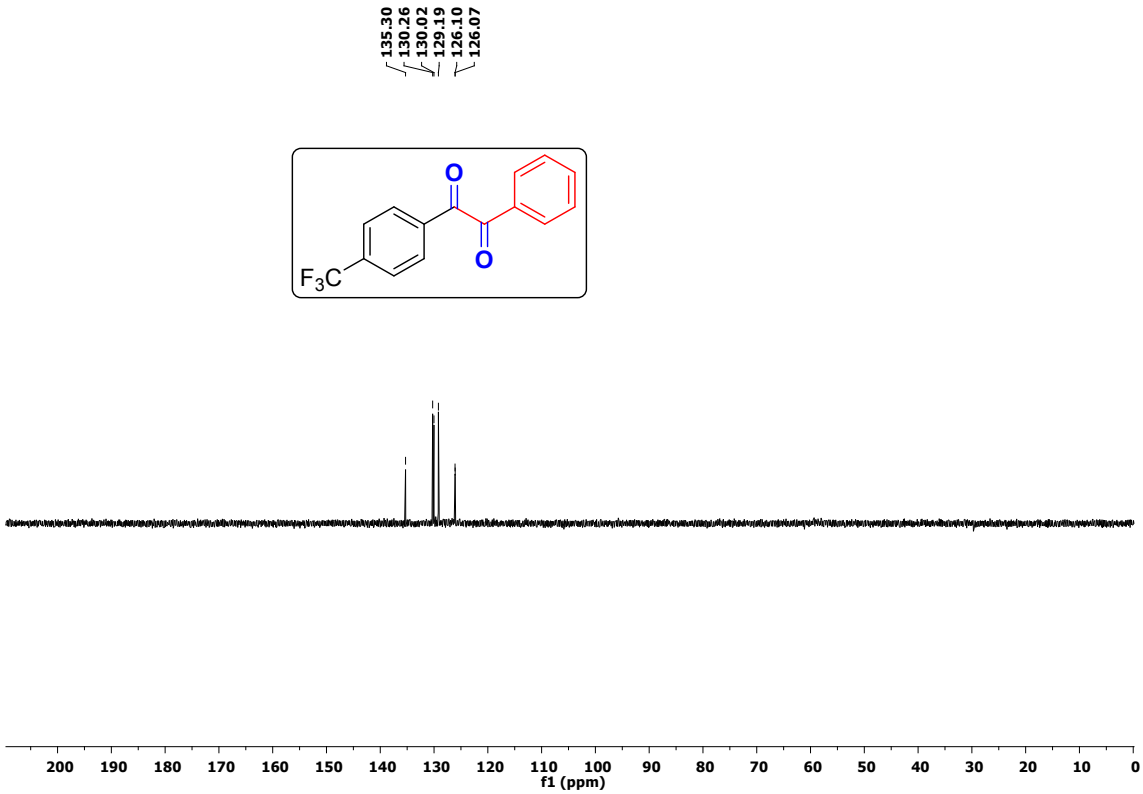
^{1}H NMR



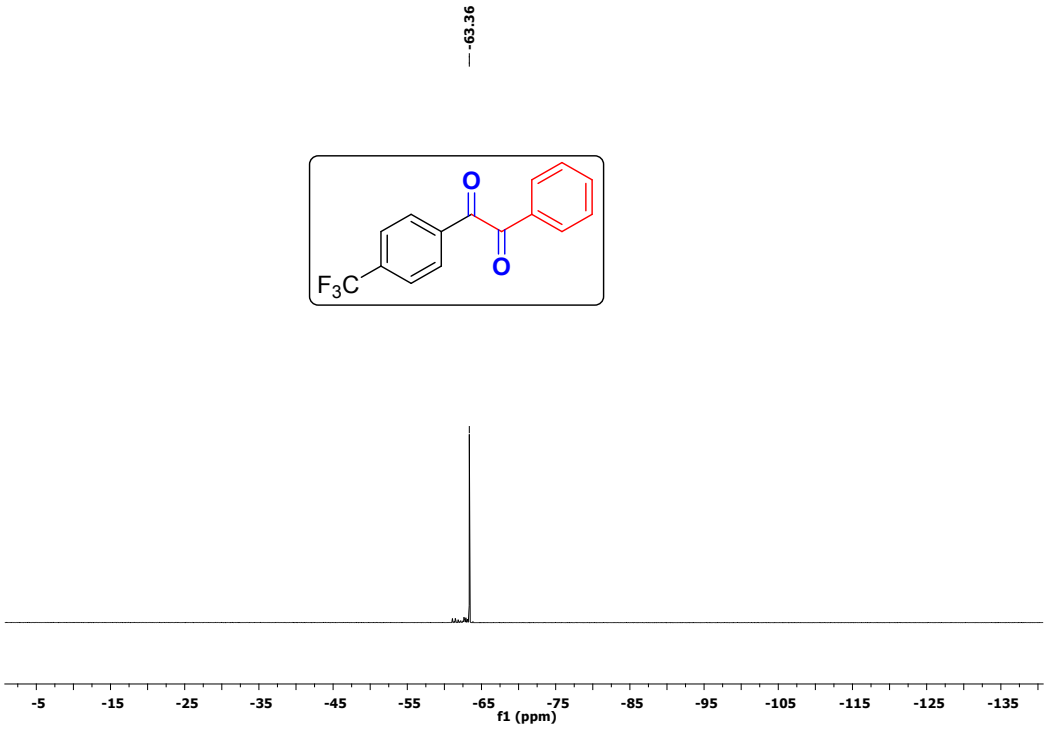
^{13}C NMR



DEPT-135

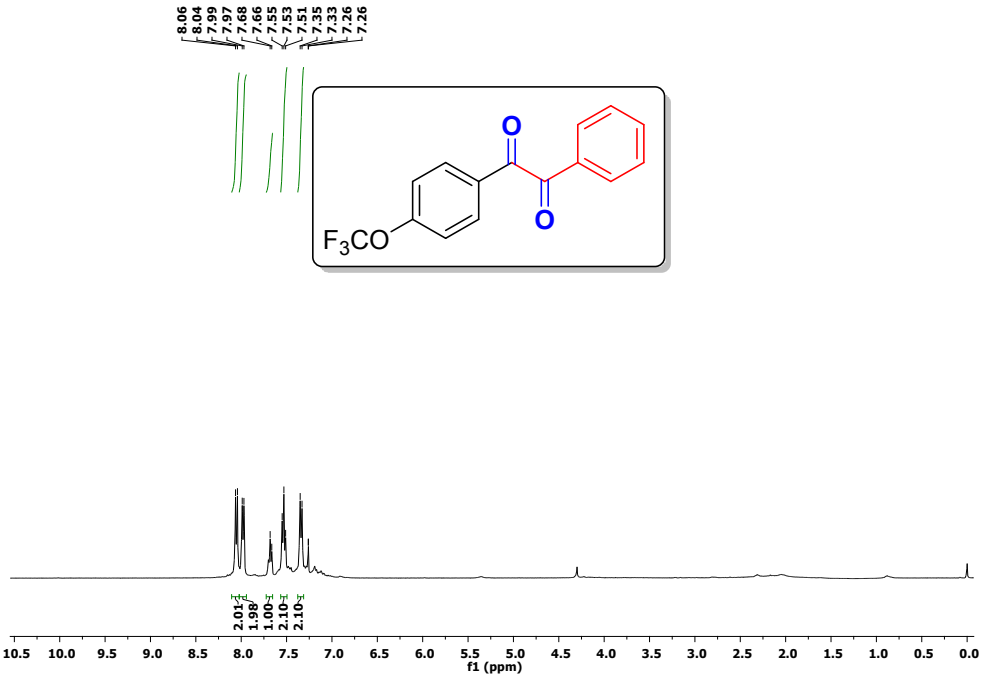


^{19}F NMR

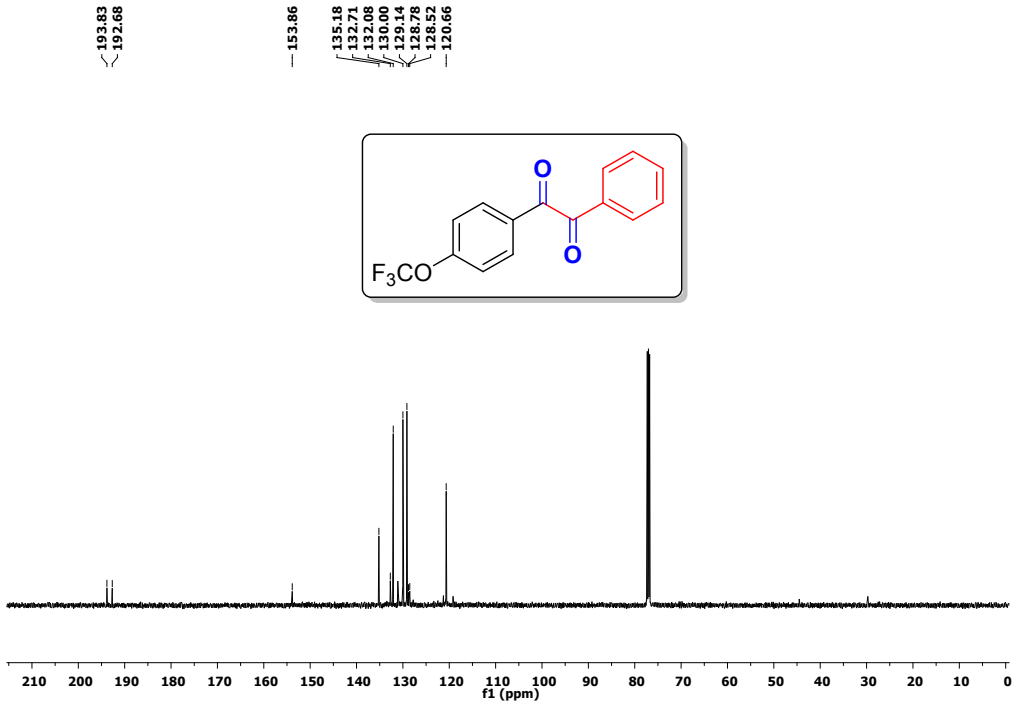


S2.c. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-phenyl-2-(4-(trifluoromethoxy) phenyl) ethane-1,2-dione (3c):

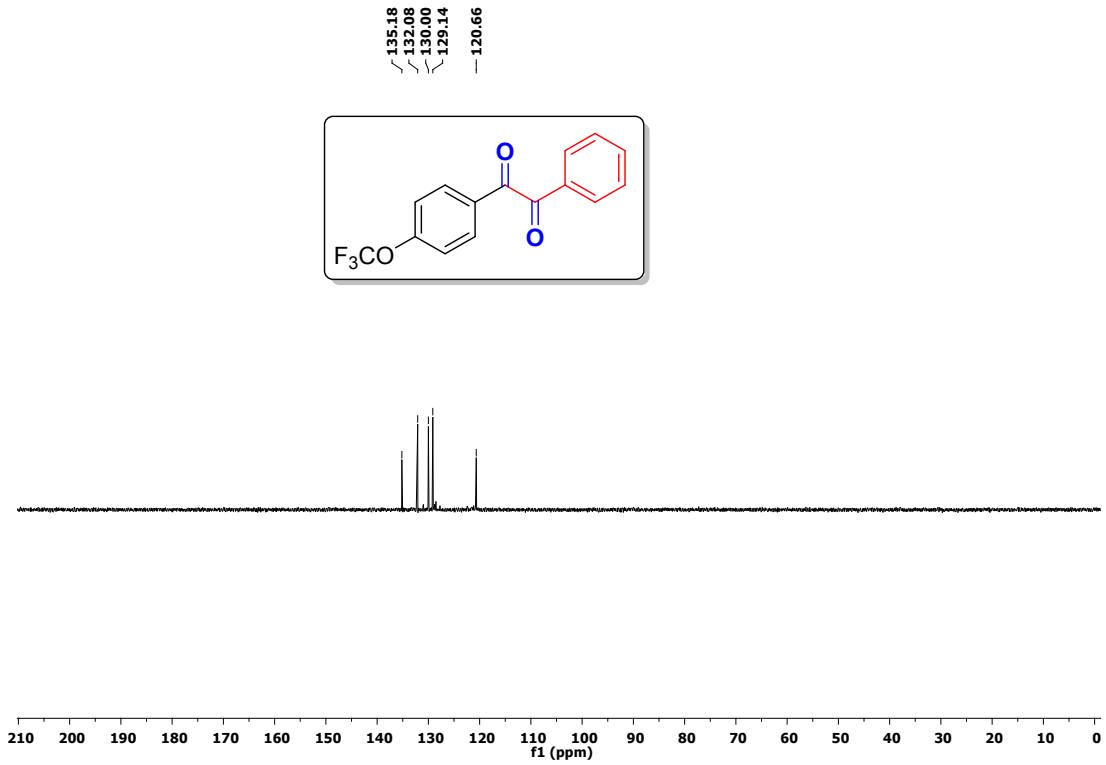
^{1}H NMR



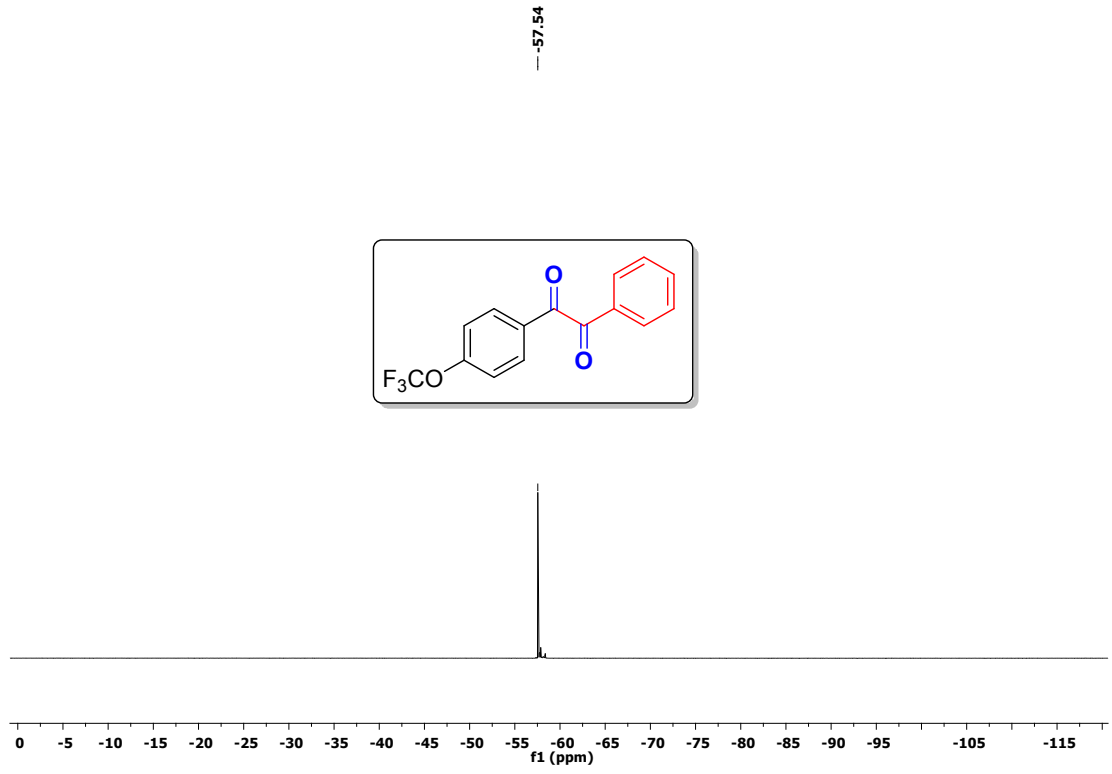
^{13}C NMR



DEPT-135

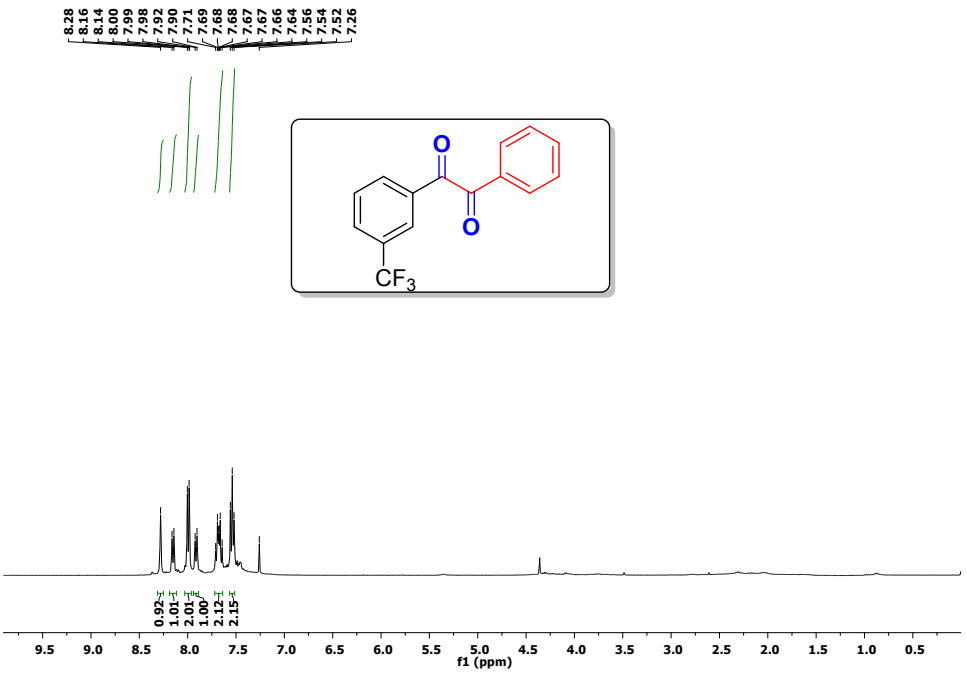


^{19}F NMR

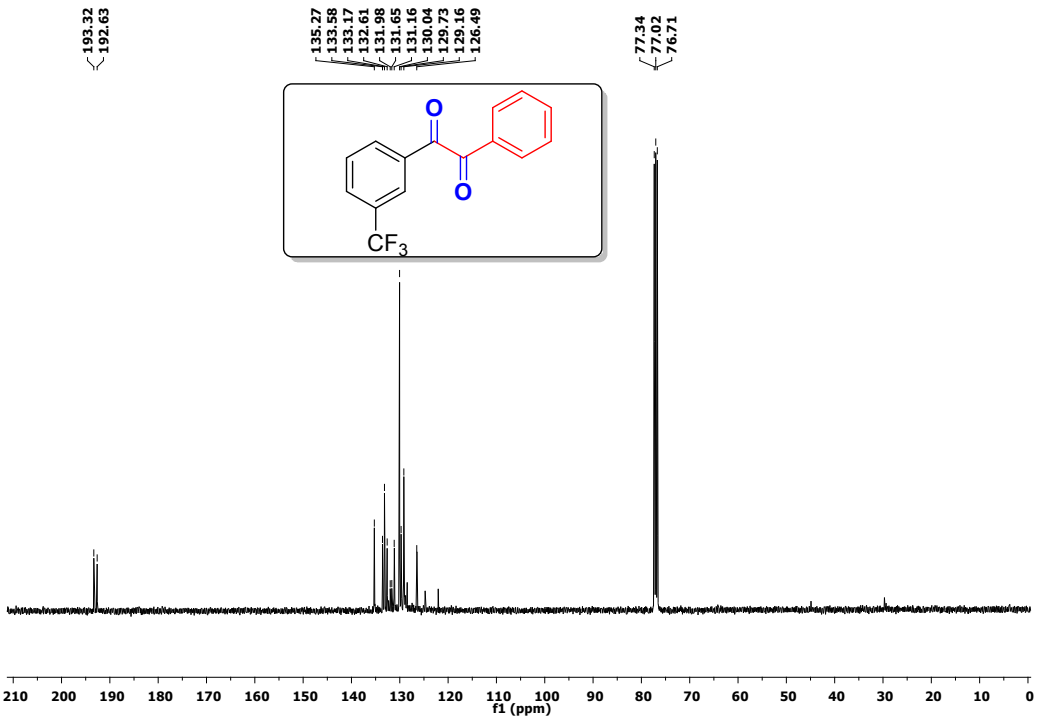


S2.d. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-phenyl-2-(3-(trifluoromethyl) phenyl) ethane-1,2-dione (3d):

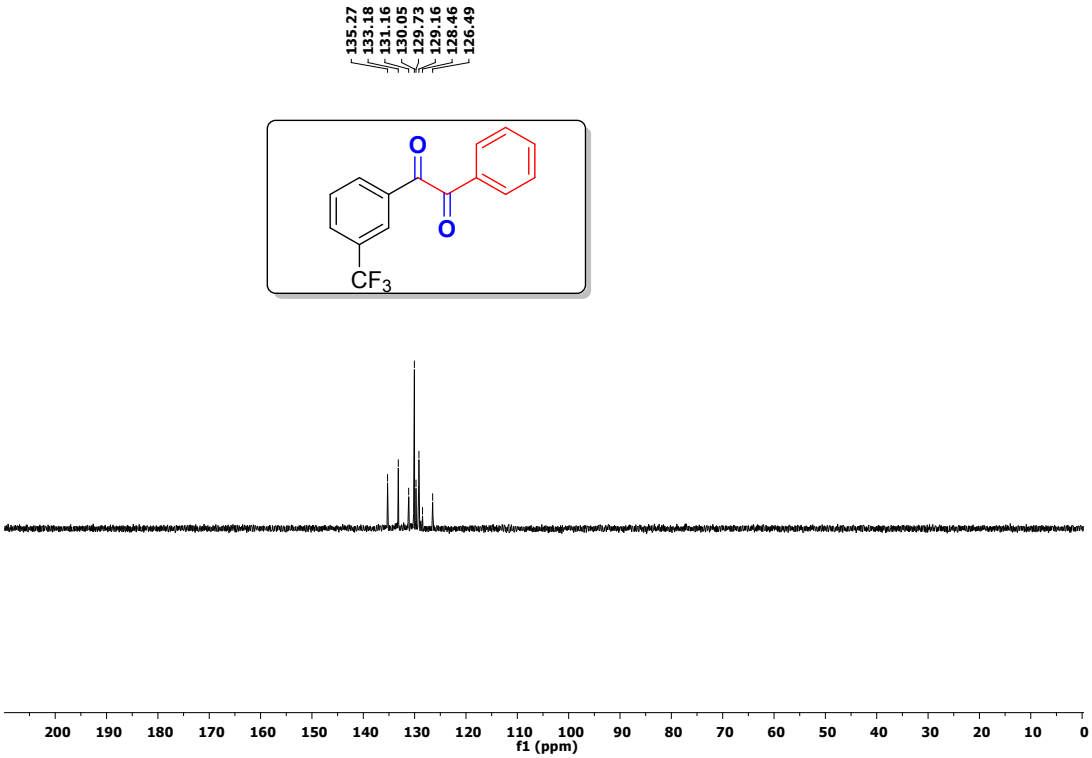
^{1}H NMR



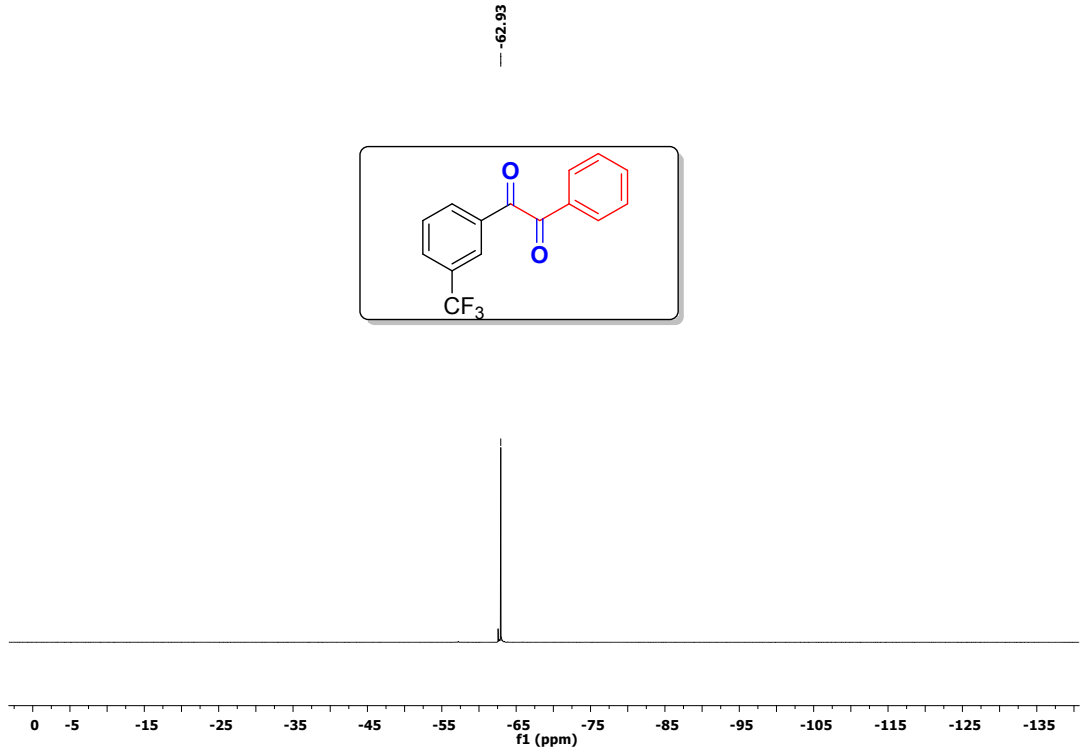
^{13}C NMR



DEPT-135

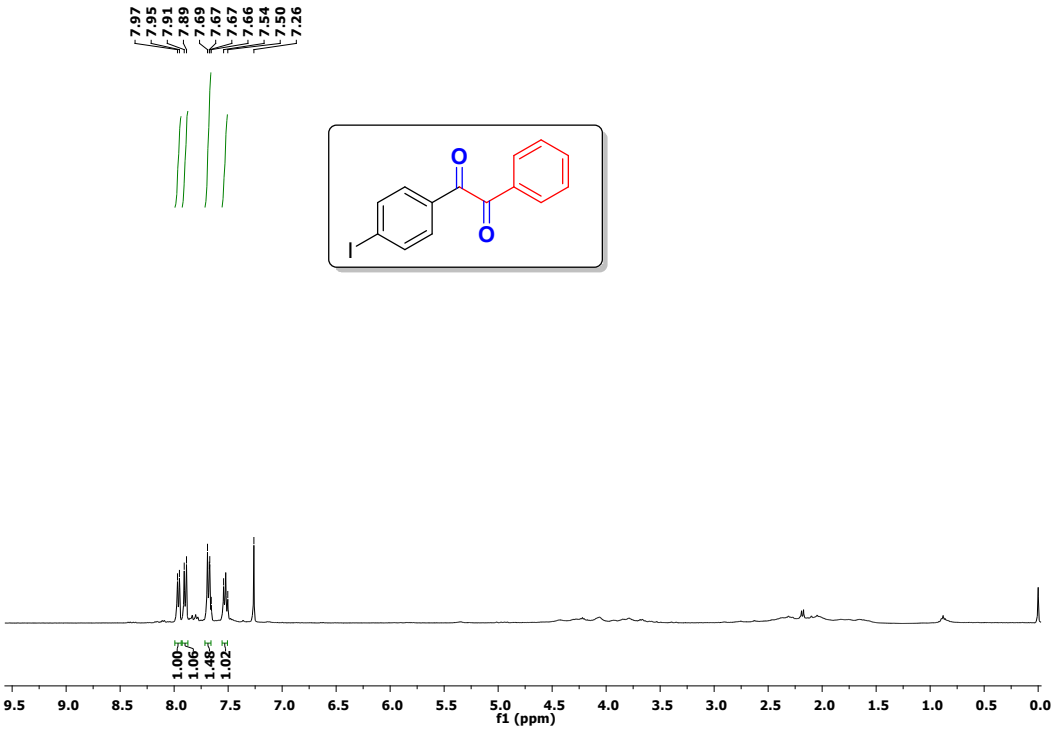


^{19}F NMR

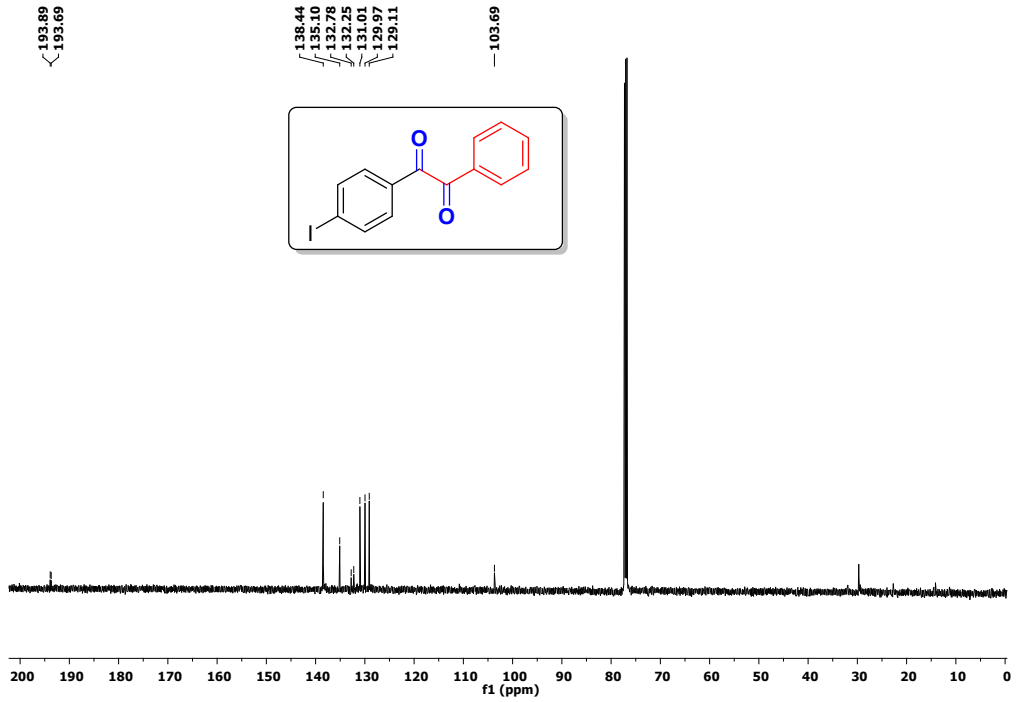


S2.e. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-iodophenyl)-2-phenylethane-1,2-dione (3e):

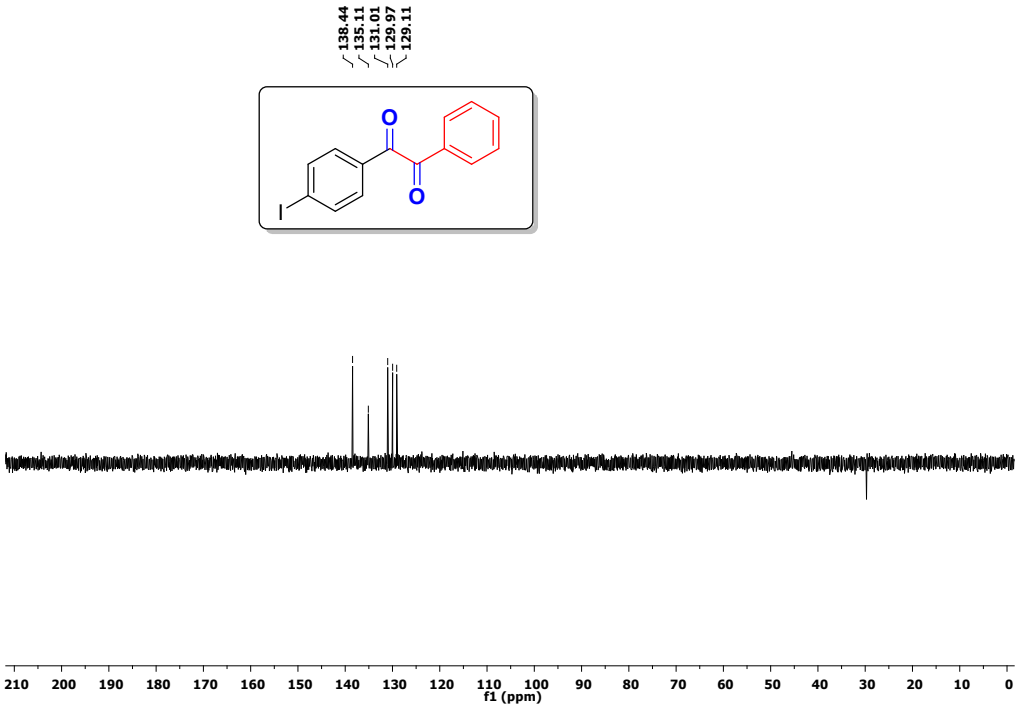
^{1}H NMR



^{13}C NMR

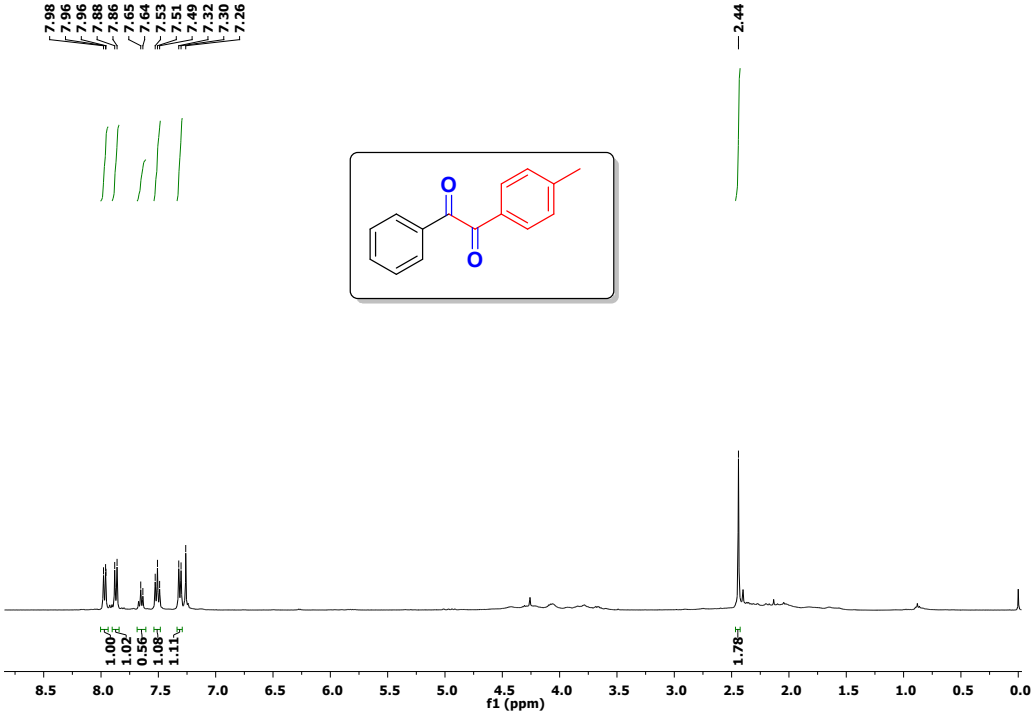


DEPT-135

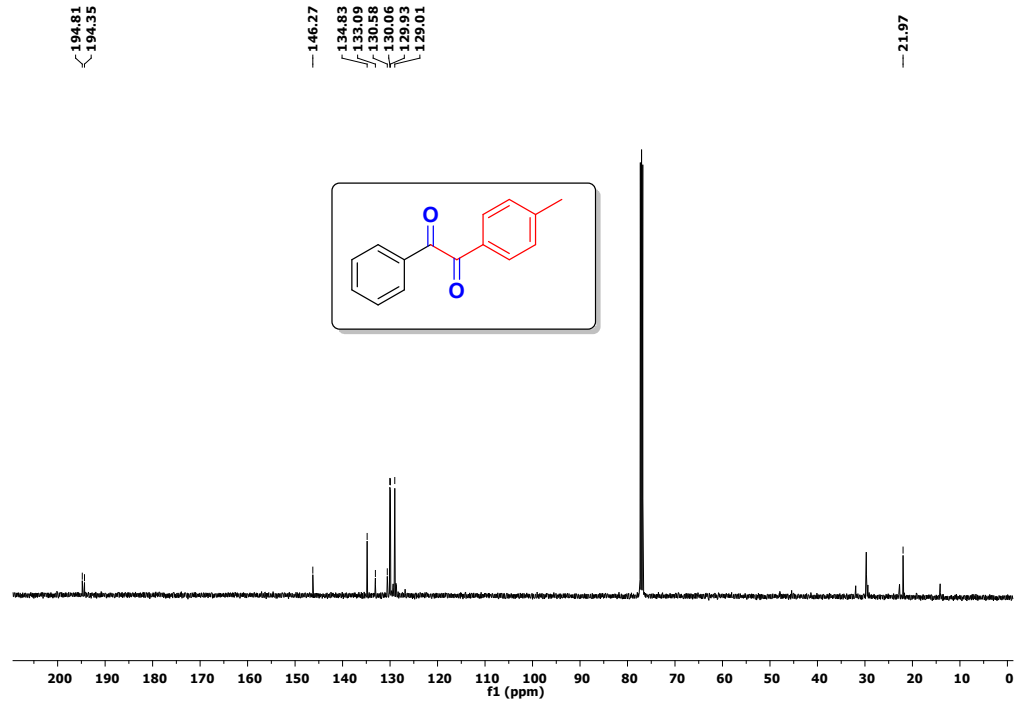

138.44
135.11
131.01
129.97
129.11
O
O
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2.f. ^{1}H, ^{13}C and DEPT-135 NMR of 1-phenyl-2-(p-tolyl)ethane-1,2-dione (3f):

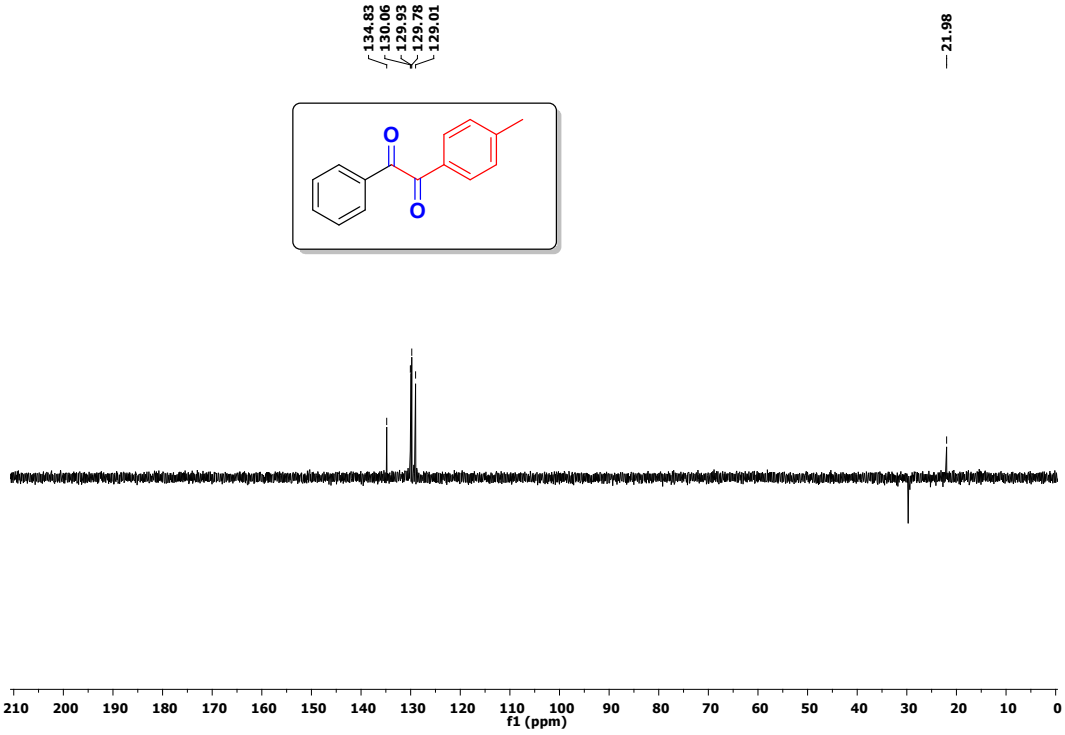
^{1}H NMR



^{13}C NMR

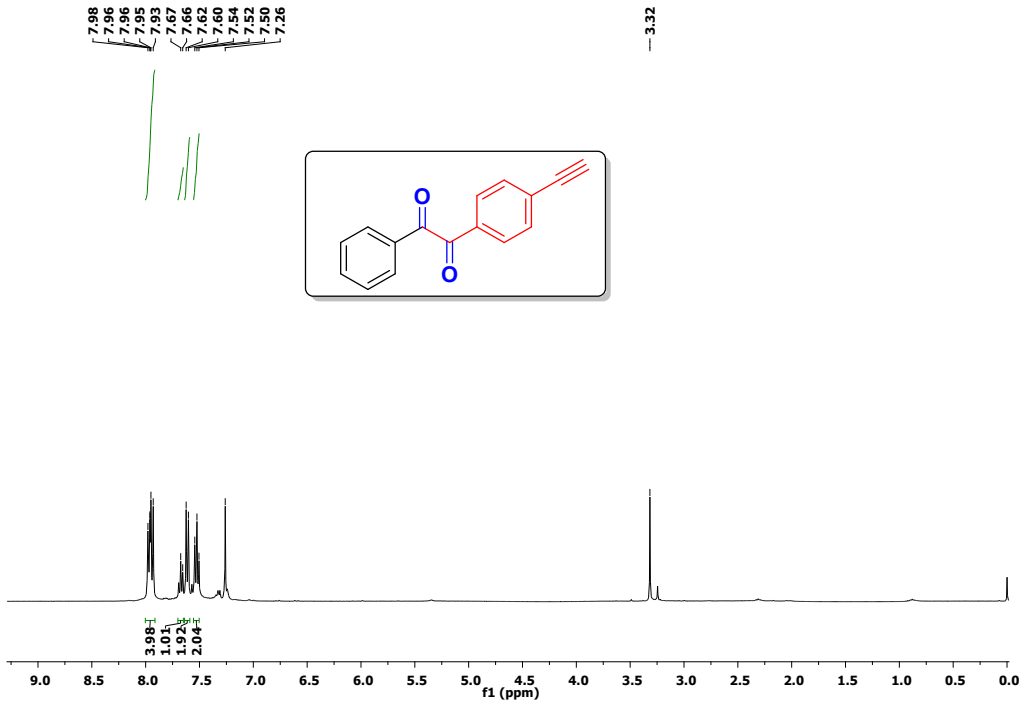


DEPT-135

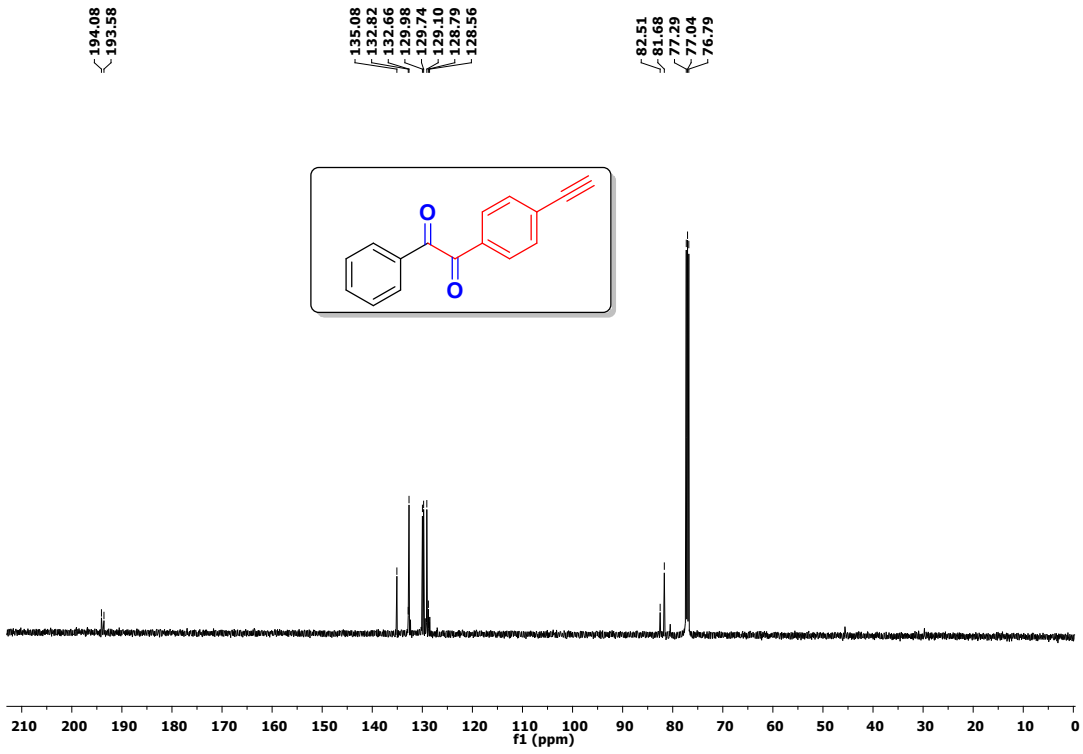

134.83
130.06
129.93
129.78
129.01
21.98
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2.g. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-ethynylphenyl)-2-phenylethane-1,2-dione (3g):

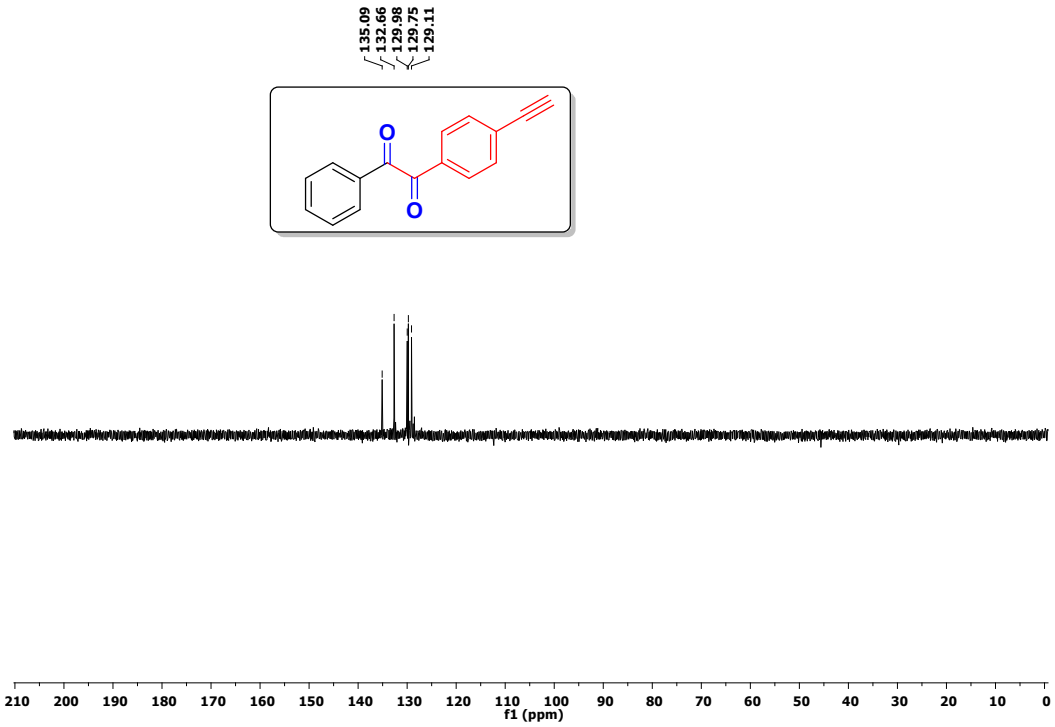
^{1}H NMR



^{13}C NMR

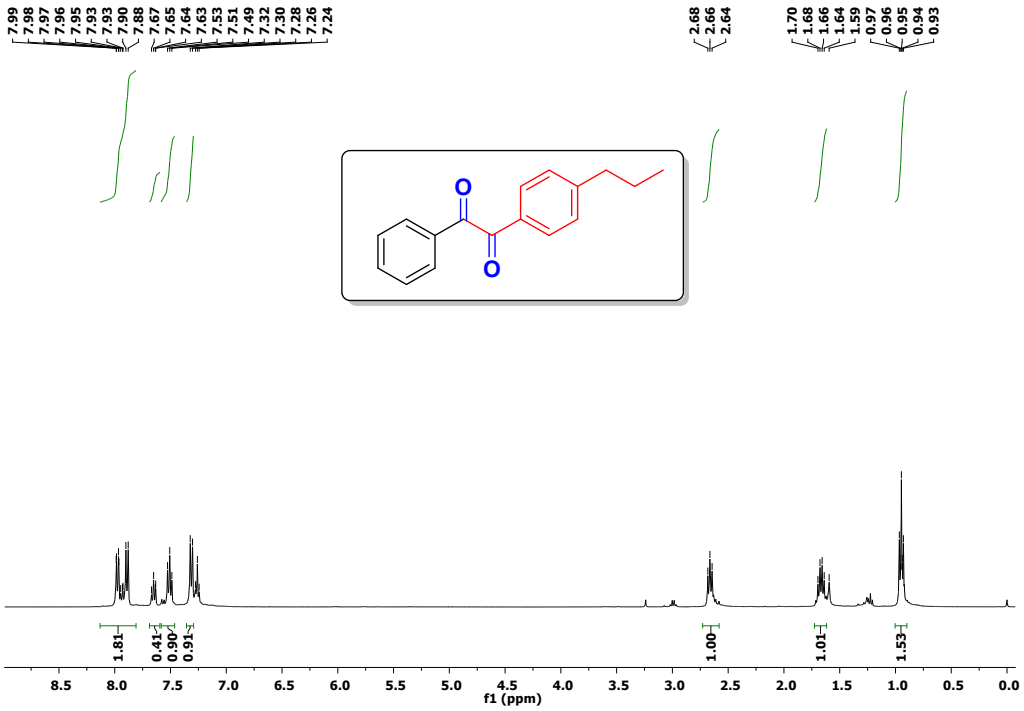


DEPT-135

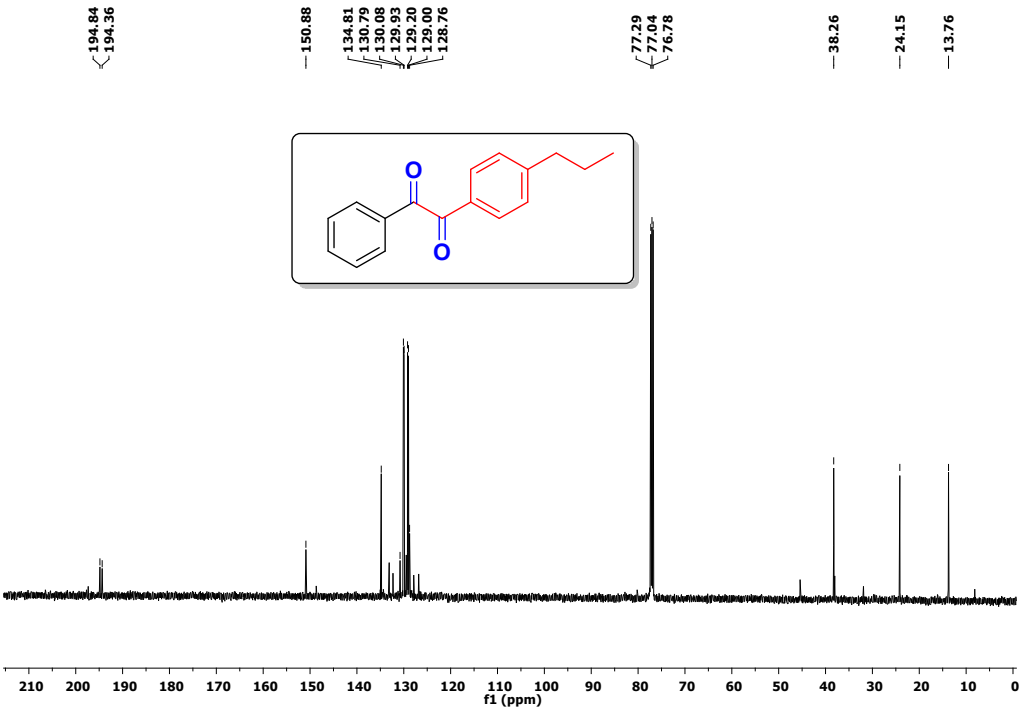

135.09
132.66
129.98
129.75
129.11
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2.h. ^{1}H, ^{13}C and DEPT-135 NMR of 1-phenyl-2-(4-propylphenyl)ethane-1,2-dione (3h):

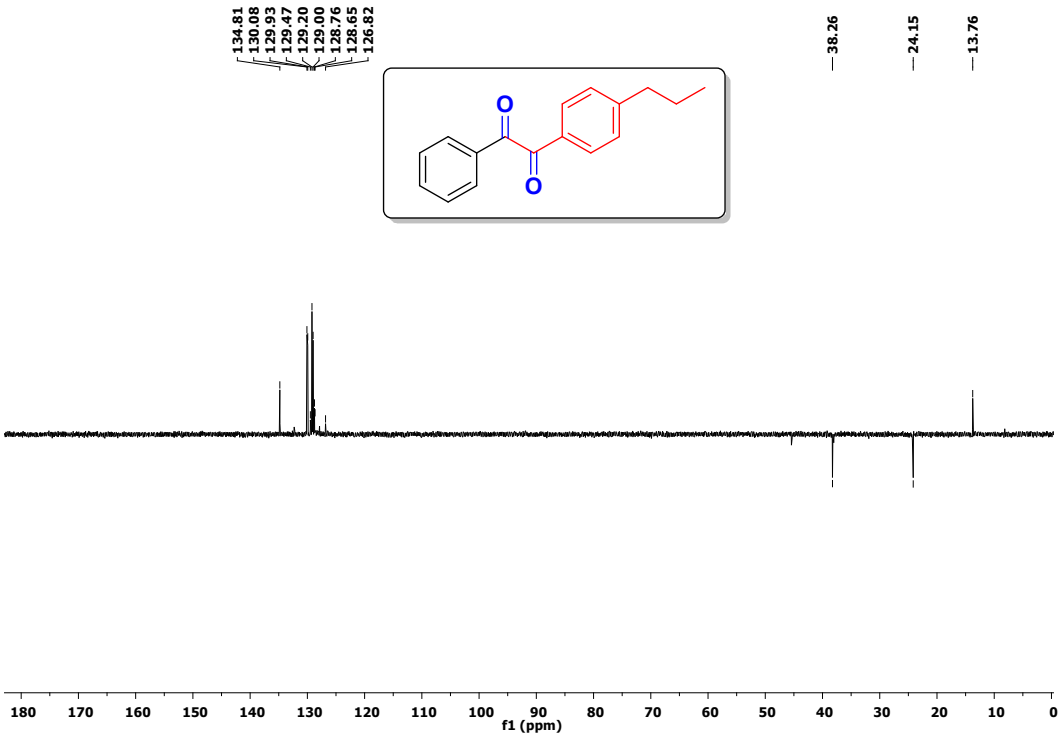
^{1}H NMR



^{13}C NMR

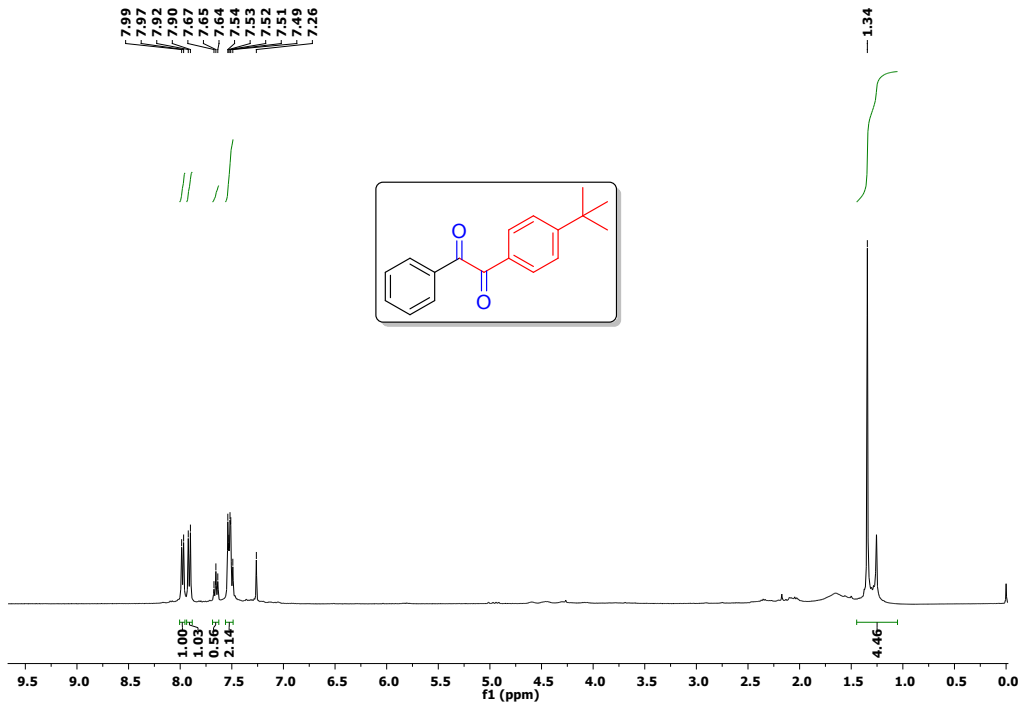


DEPT-135

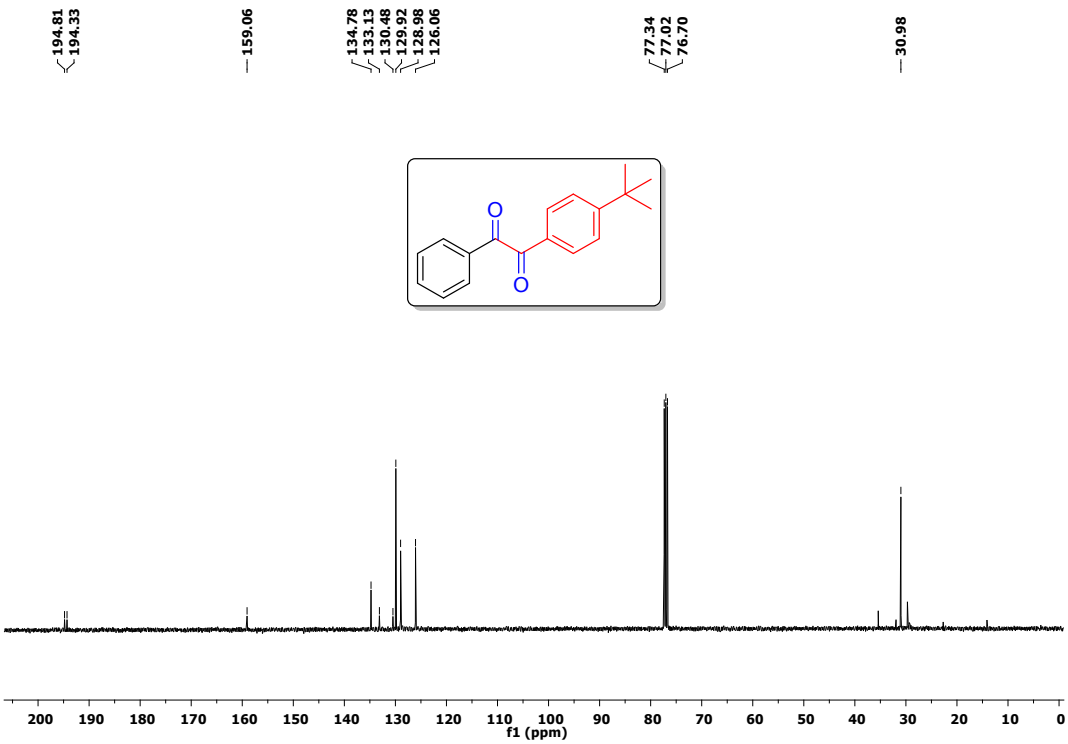

134.81
130.08
129.93
129.47
129.20
129.00
128.76
128.65
126.82
38.26
24.15
13.76
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.i. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-(tert-butyl)phenyl)-2-phenylethane-1,2-dione (3i)

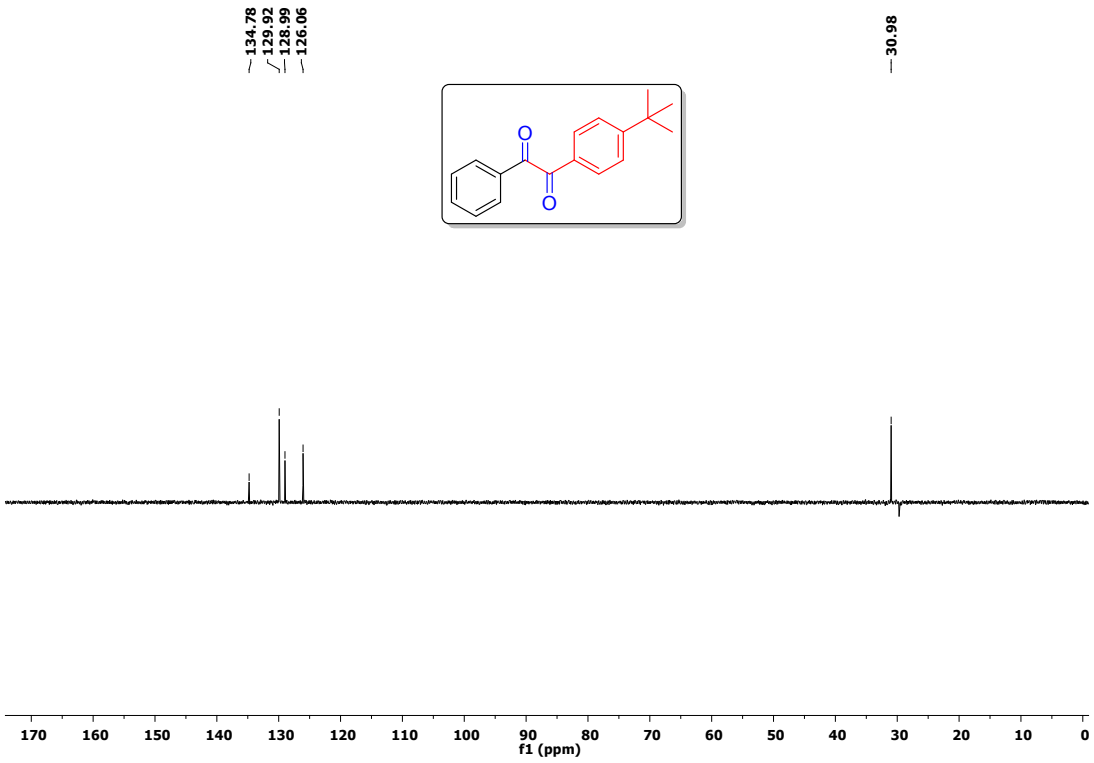
^{1}H NMR



^{13}C NMR

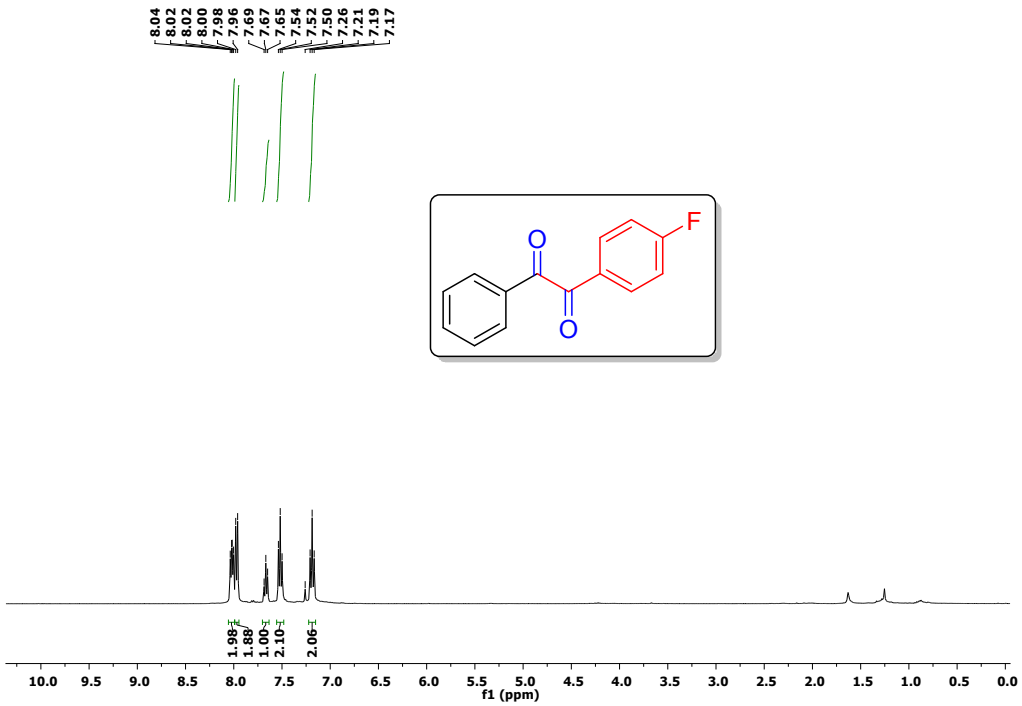


DEPT-135

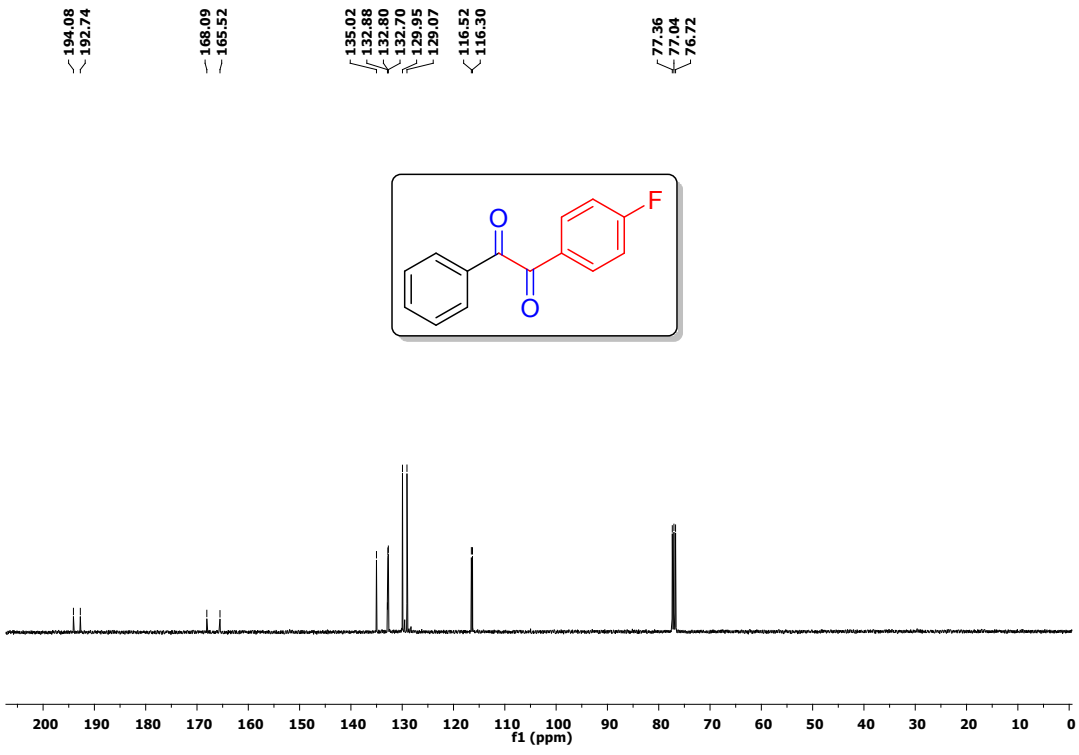

134.78
129.92
128.99
126.06
30.98
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.j. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-fluorophenyl)-2-phenylethane-1,2-dione (3j):

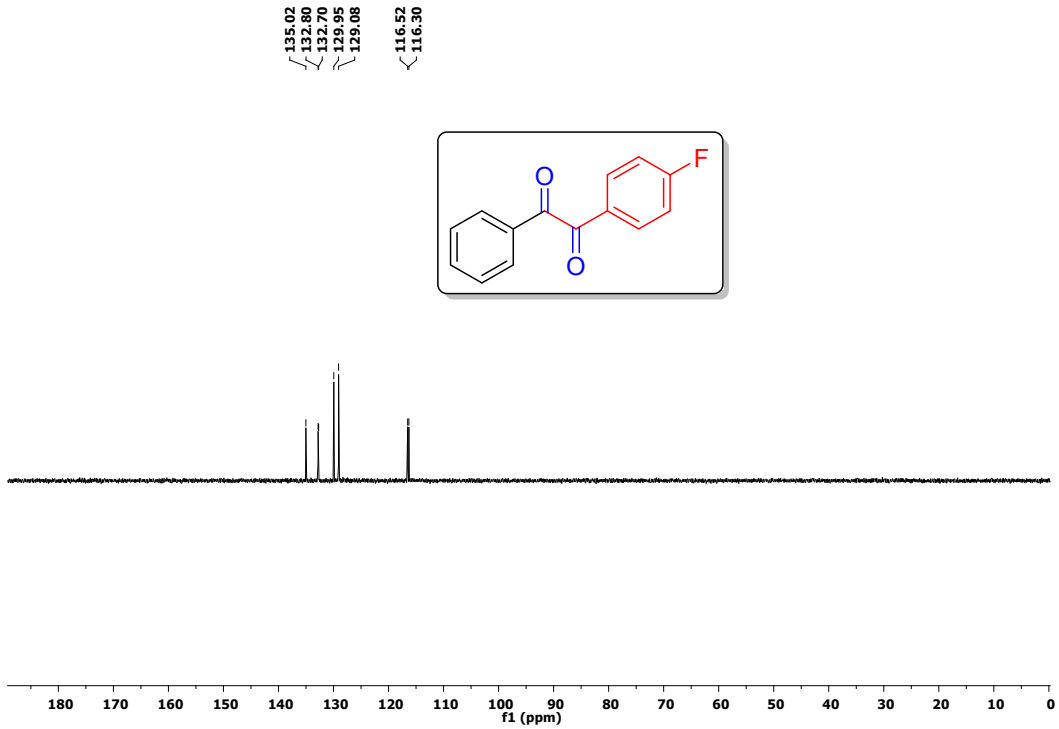
^{1}HNMR



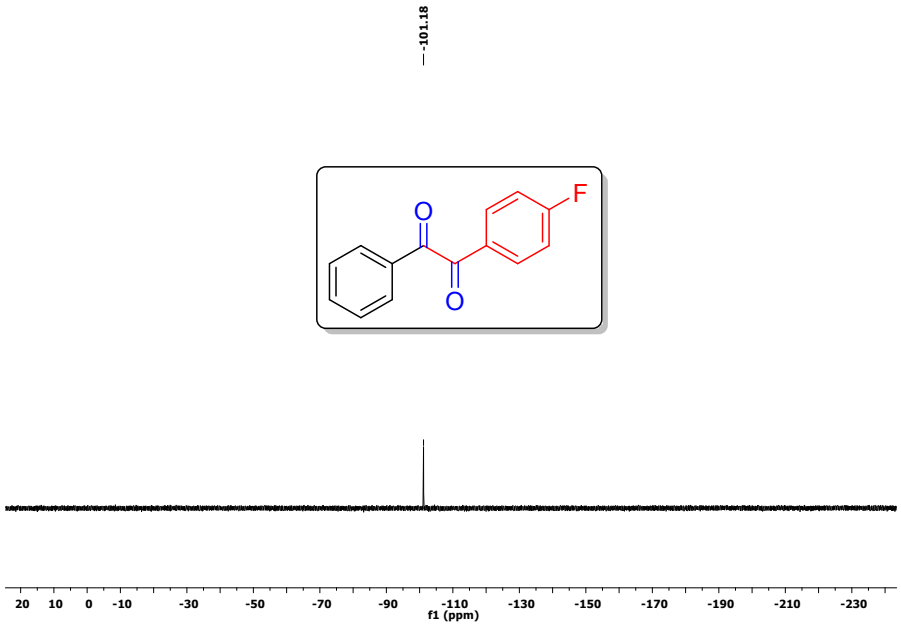
^{13}C NMR



DEPT-135

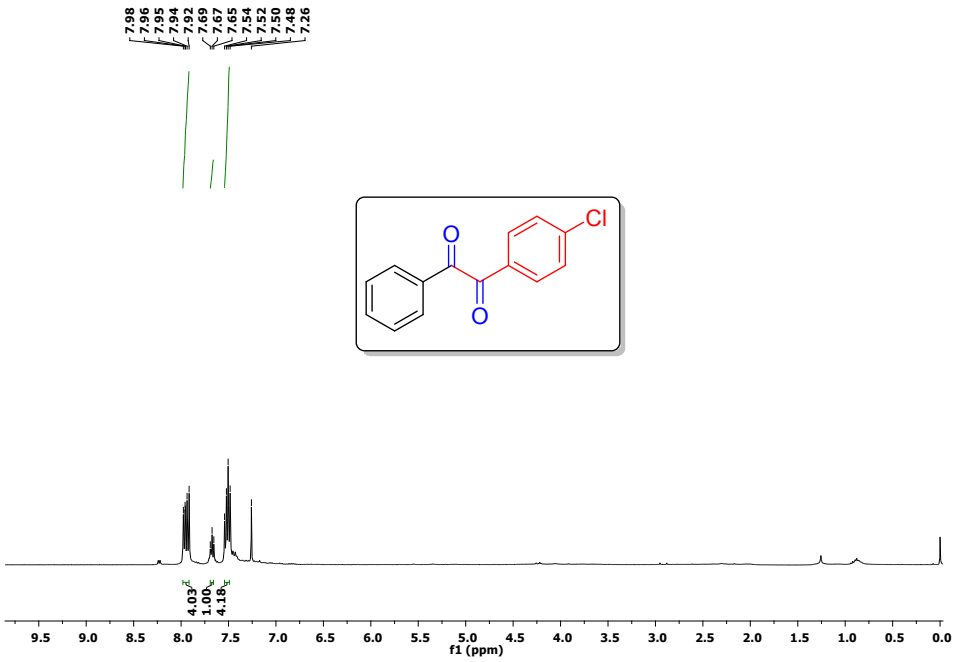


^{19}F NMR

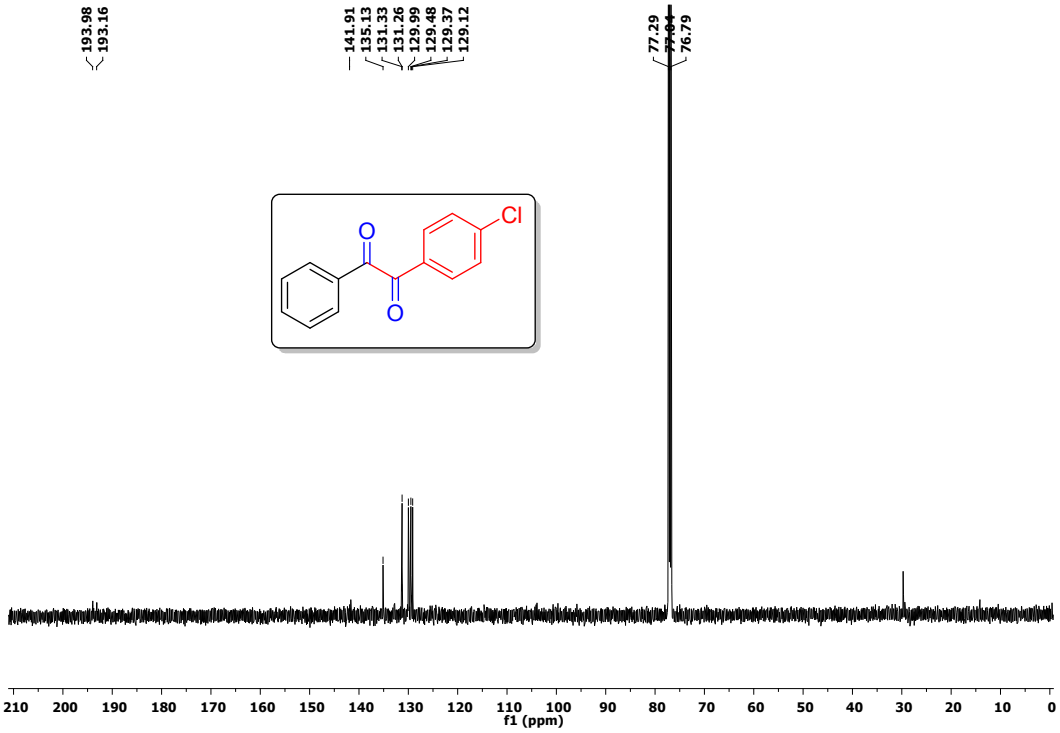


S2.k. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-chlorophenyl)-2-phenylethane-1,2-dione (3k):

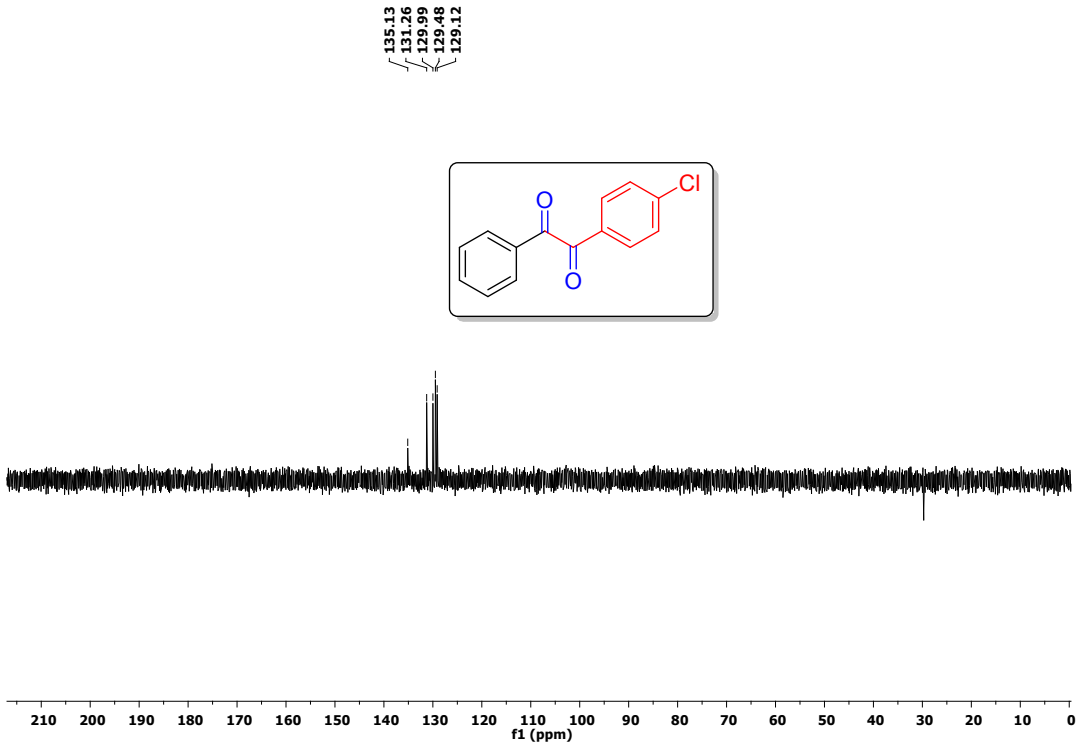
^{1}H NMR



^{13}C NMR

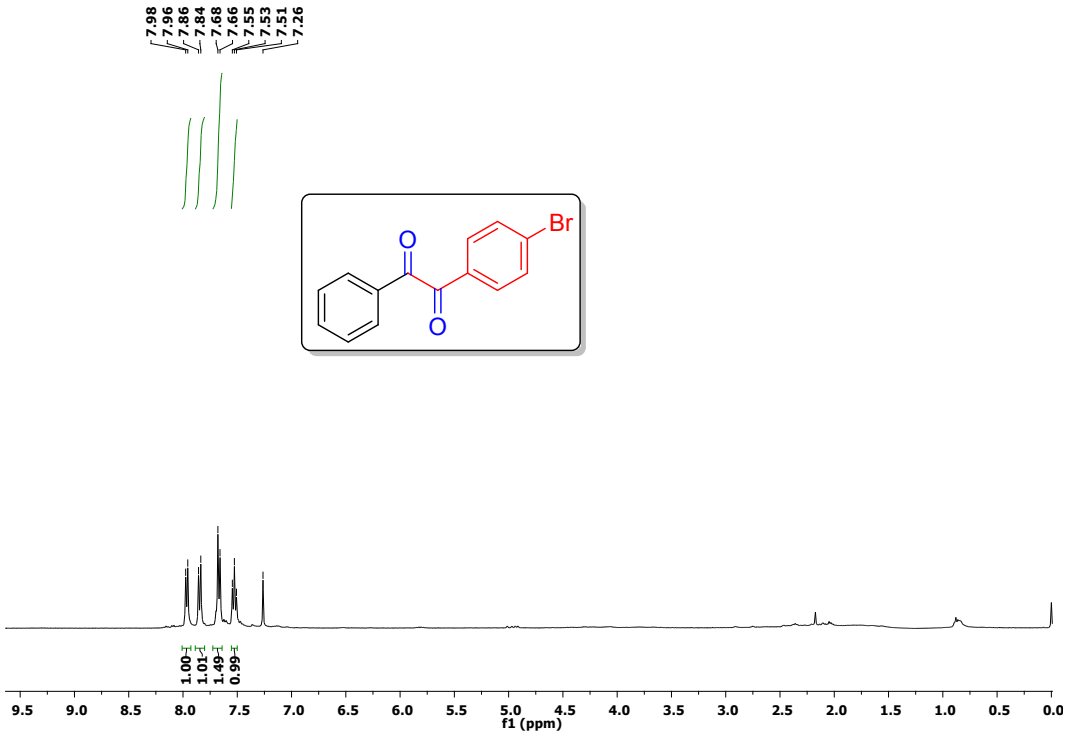


DEPT-135

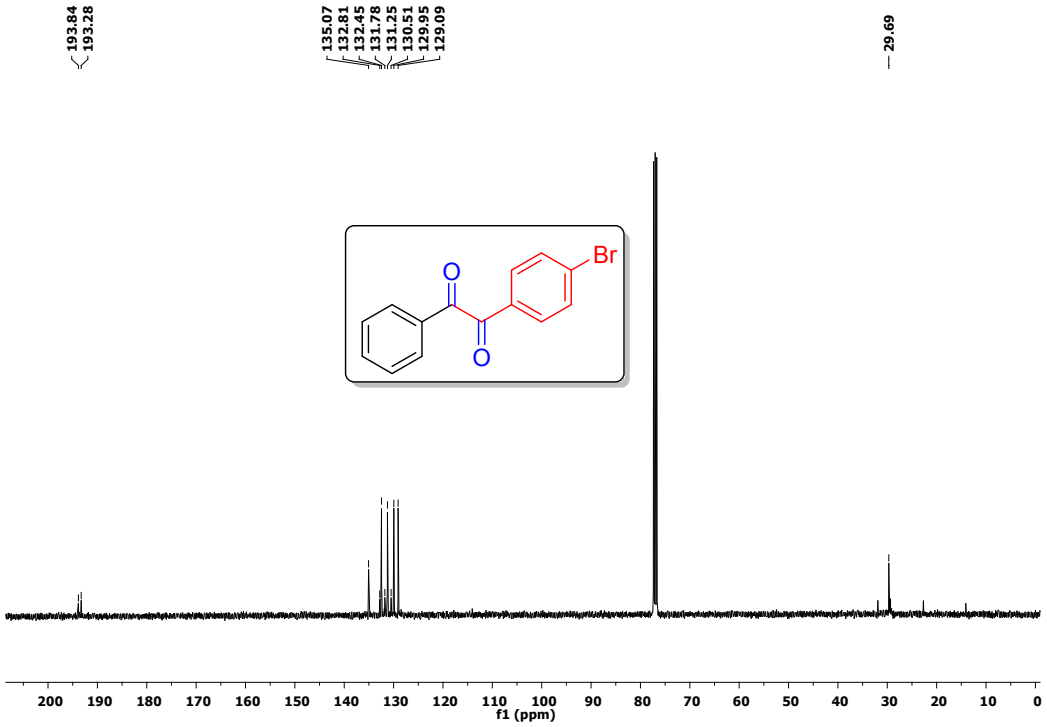

135.13
131.26
129.99
129.48
129.12
O
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2.i. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-bromophenyl)-2-phenylethane-1,2-dione (3l):

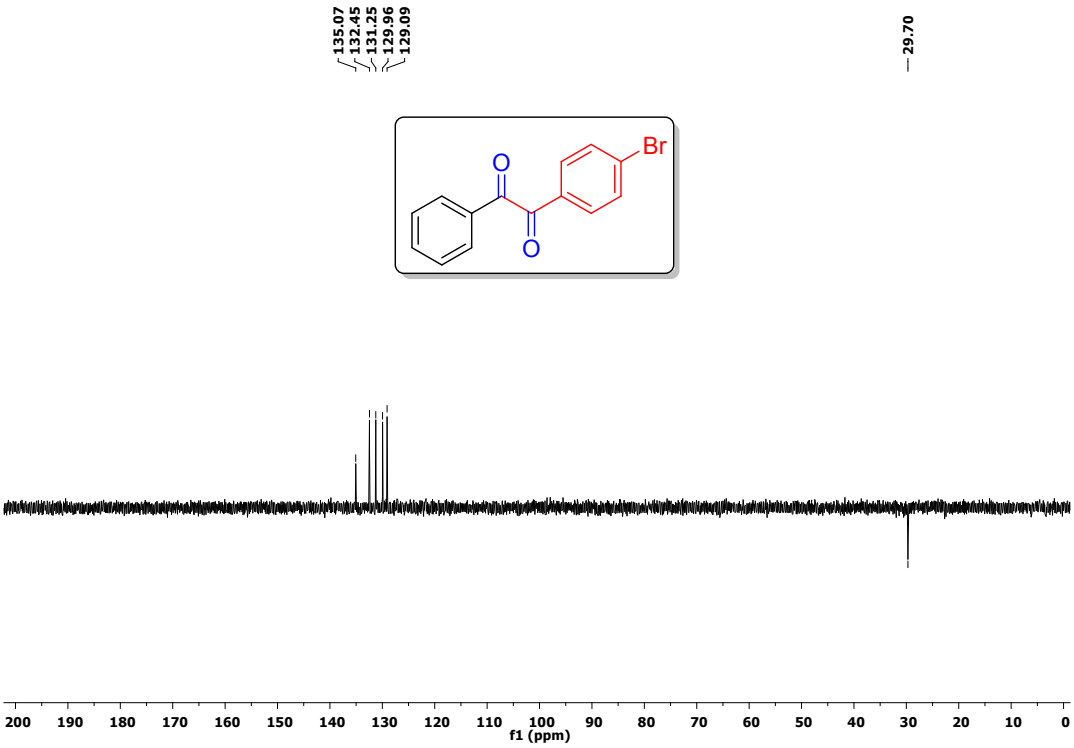
^{1}H NMR



^{13}C NMR

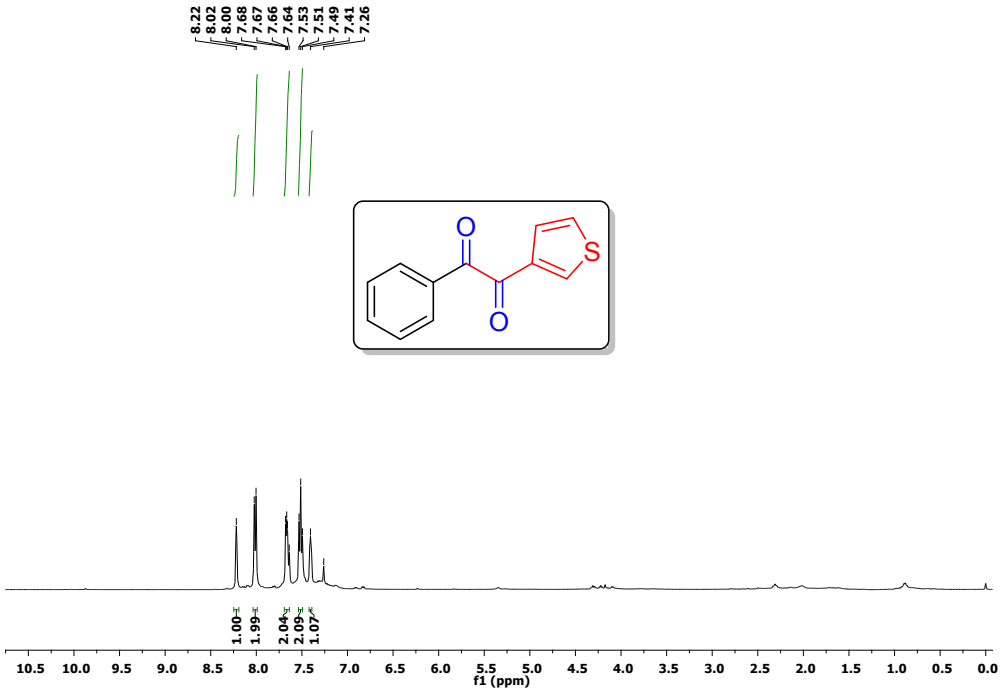


DEPT-135

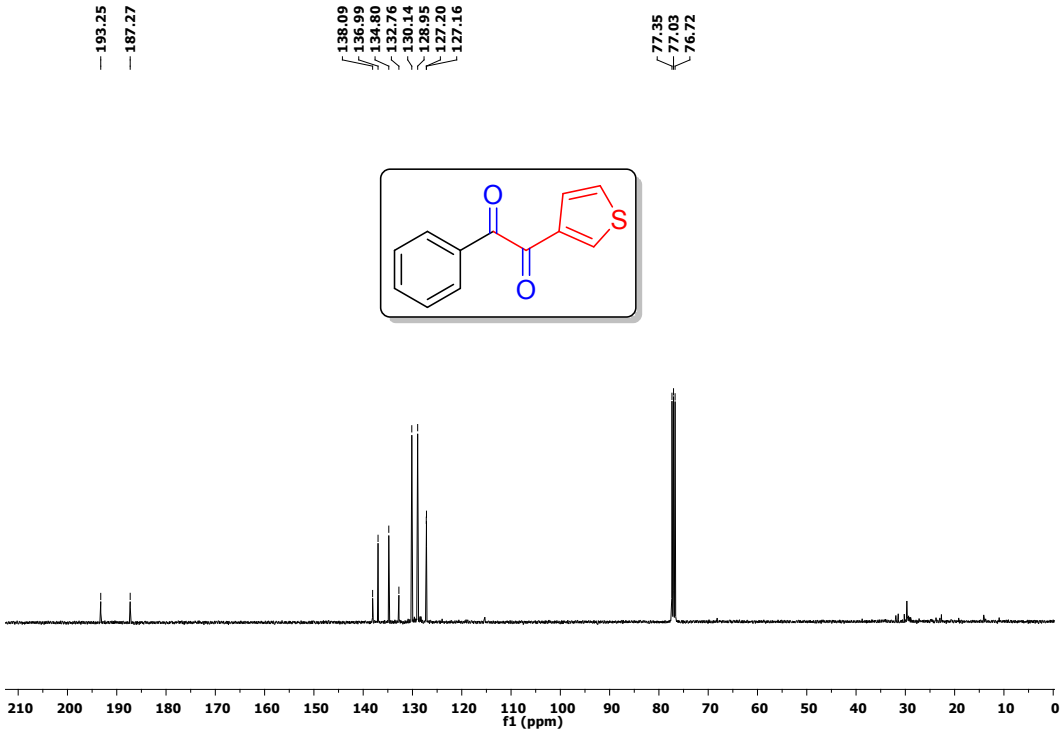

135.07
132.45
131.25
129.96
129.09
29.70
O
O
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2.m. ^{1}H, ^{13}C and DEPT-135 NMR of 1-phenyl-2-(thiophen-3-yl)ethane-1,2-dione 3(m):

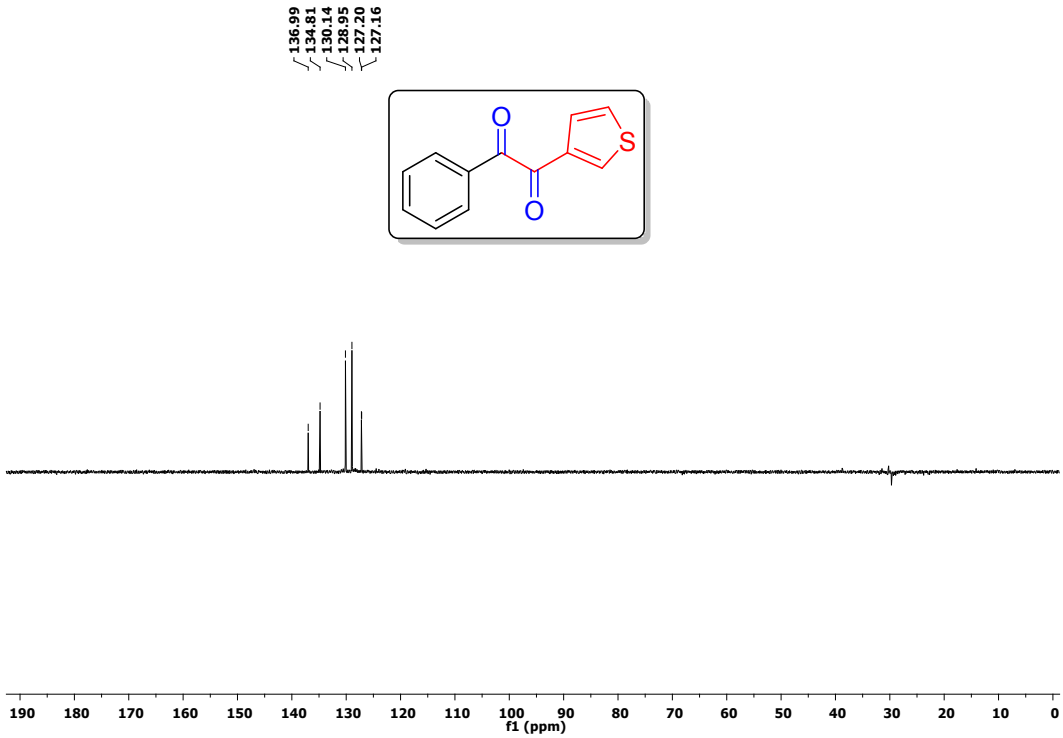
^{1}H NMR



^{13}C NMR

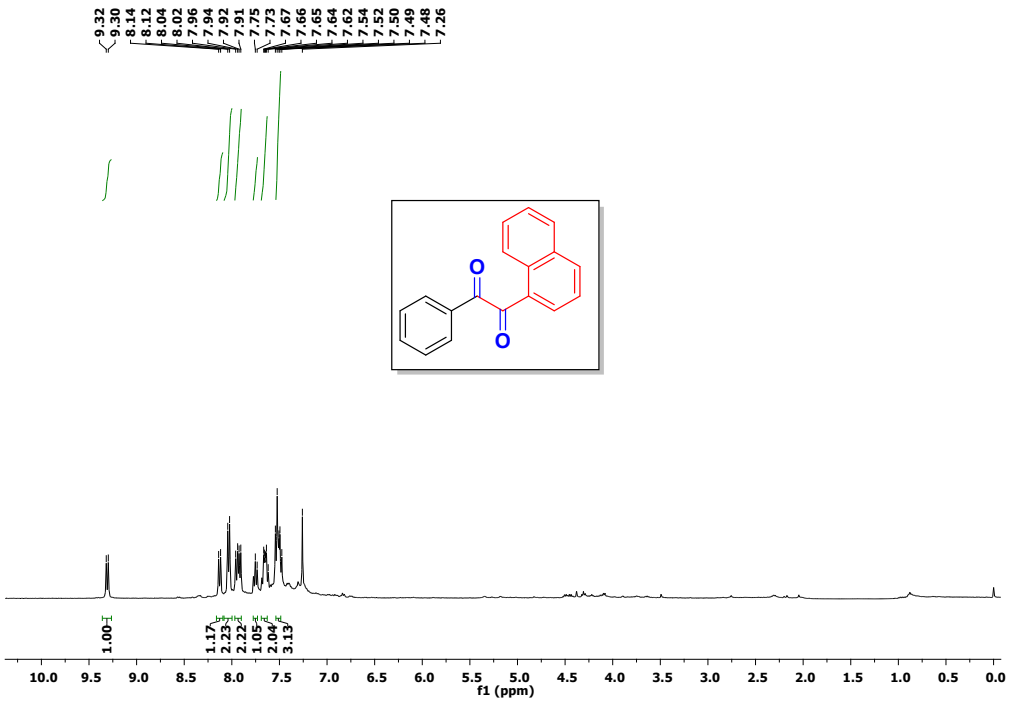


DEPT-135

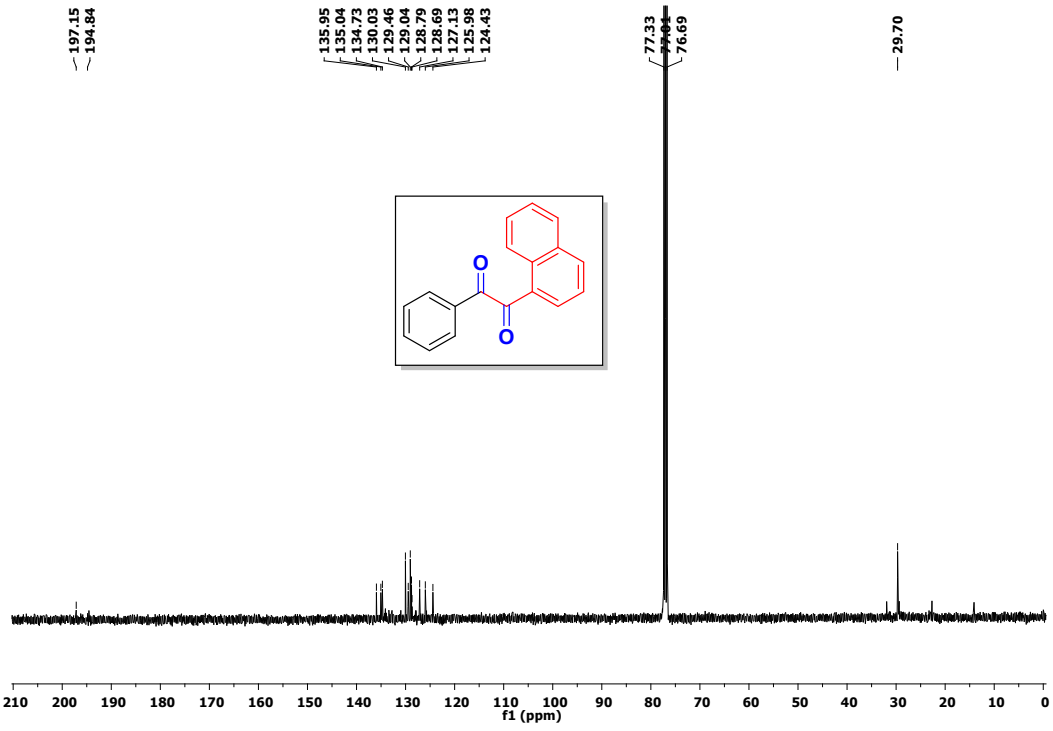

136.99
134.81
130.14
128.95
127.20
127.16
O
O
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.n. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(naphthalen-1-yl)-2-phenylethane-1,2-dione (3n):

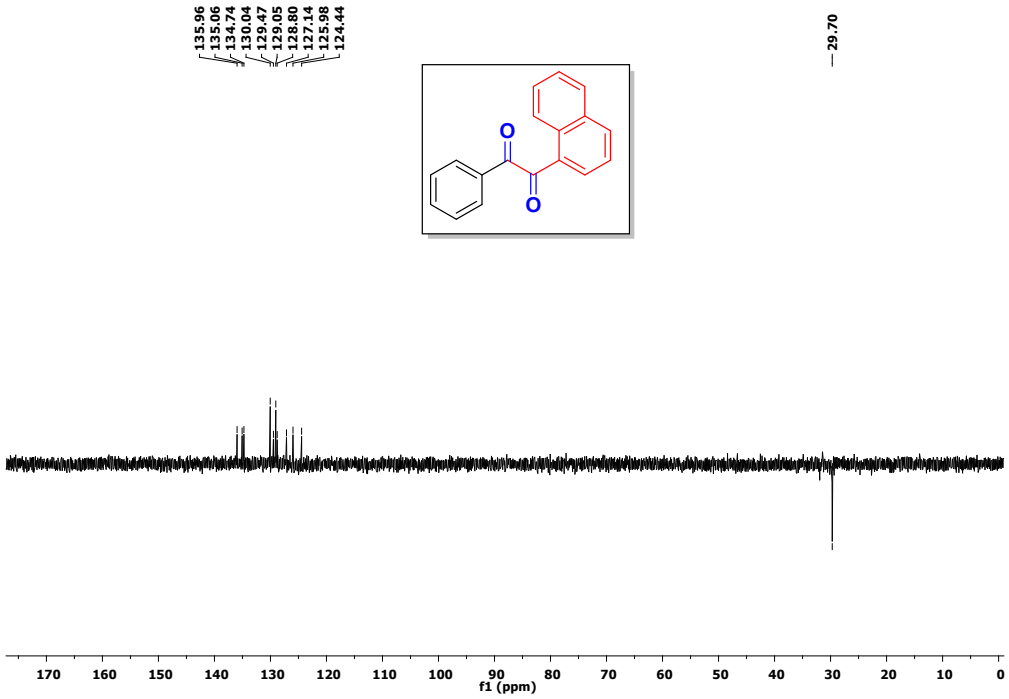
^{1}H NMR



^{13}C NMR

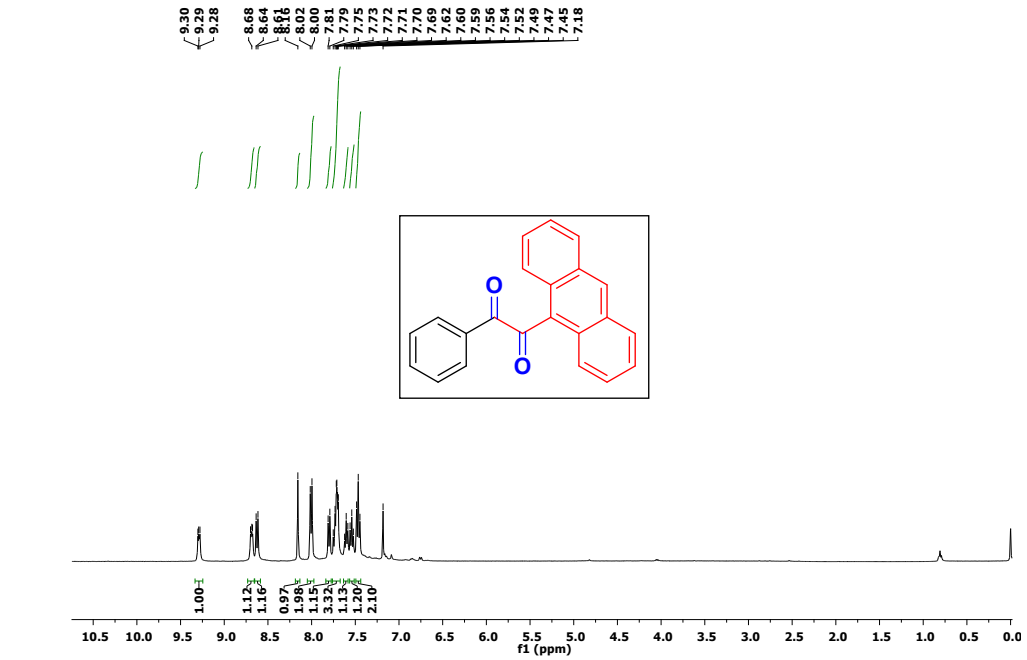


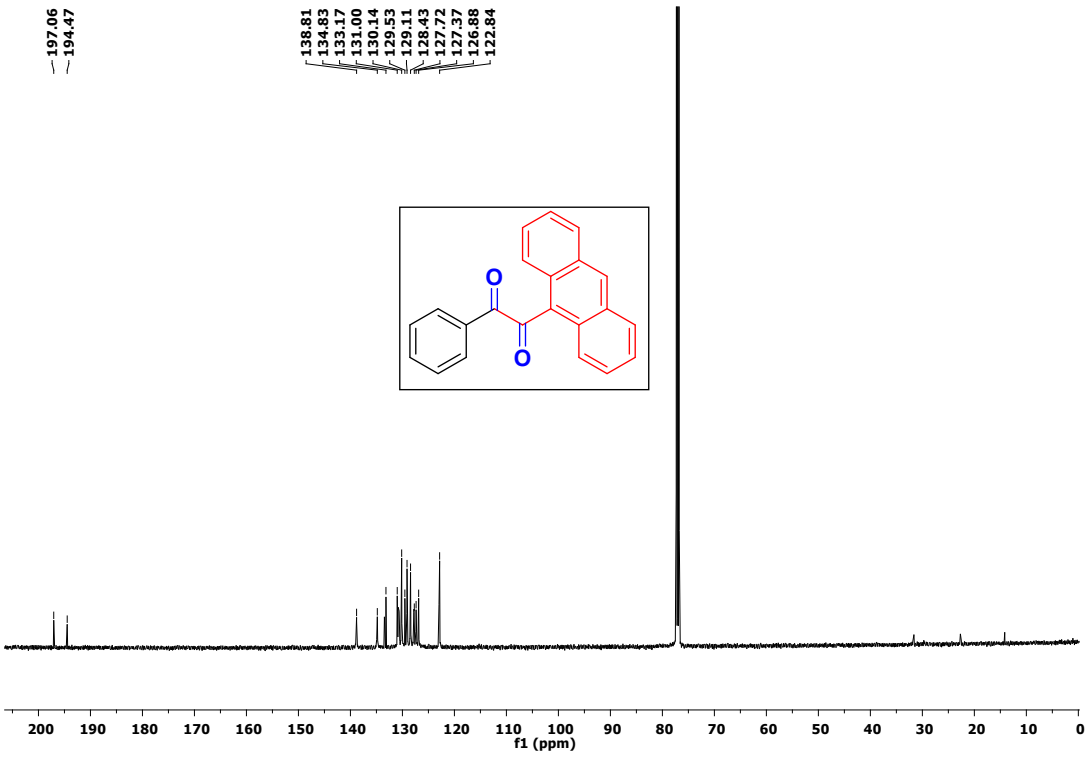
DEPT-135


135.96
135.06
134.74
130.04
129.47
129.05
128.80
127.14
125.98
124.44
29.70
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

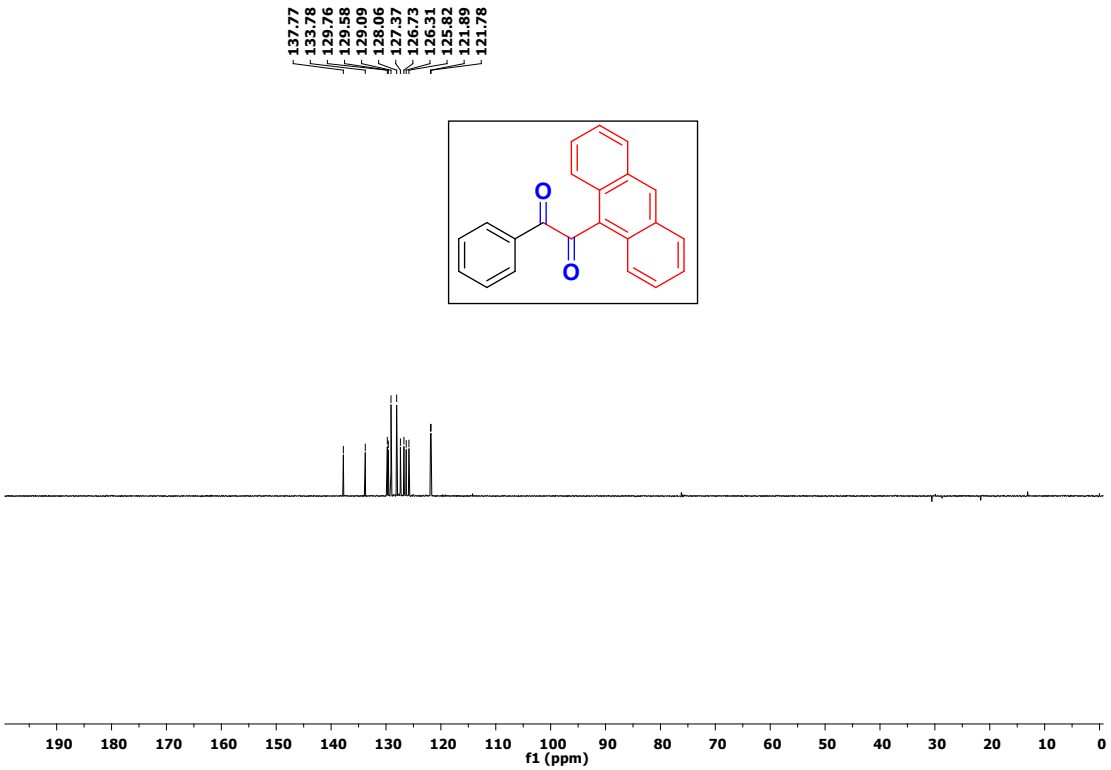
S2.o. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(anthracen-9-yl)-2-phenylethane-1,2-dione (3o):

^{1}H NMR



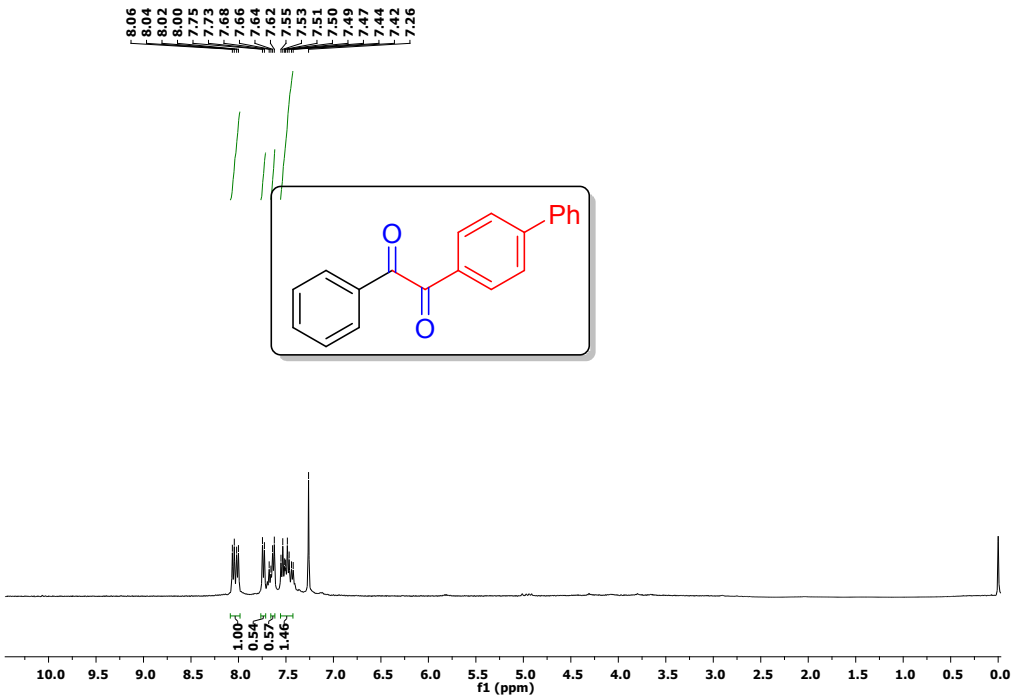


DEPT-135

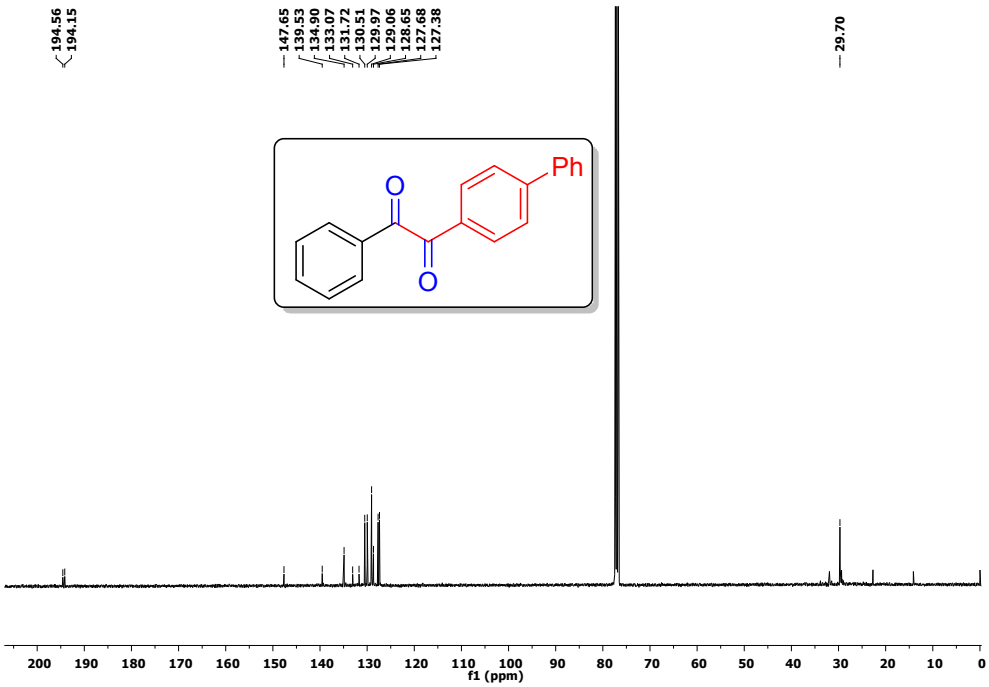

137.77
133.78
129.76
129.58
129.09
128.06
127.37
126.73
126.31
125.82
121.89
121.78
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.p. ^{1}H, ^{13}C and DEPT-135 NMR of 1-([1,1'-biphenyl]-4-yl)-2-phenylethane-1,2-dione (3p):

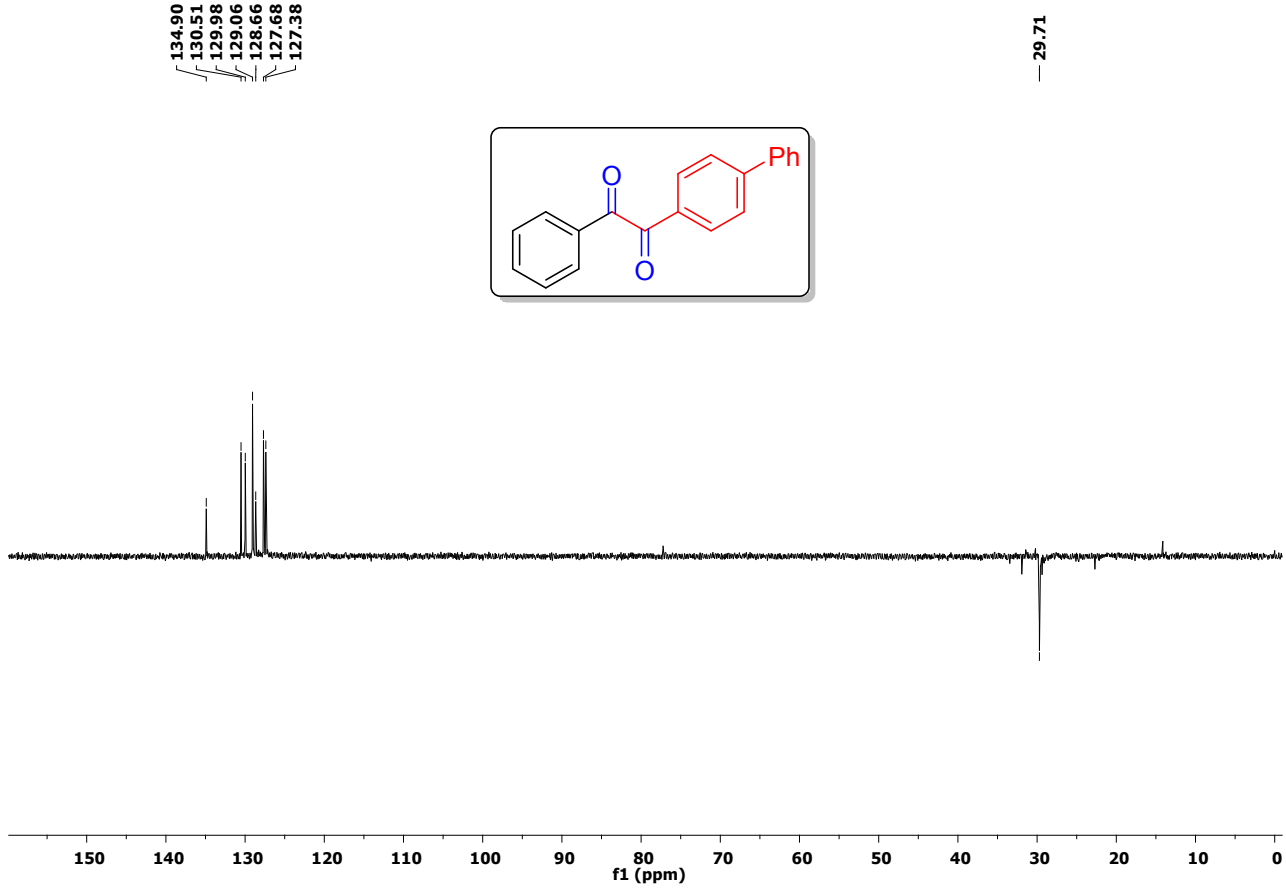
^{1}H NMR



^{13}C NMR

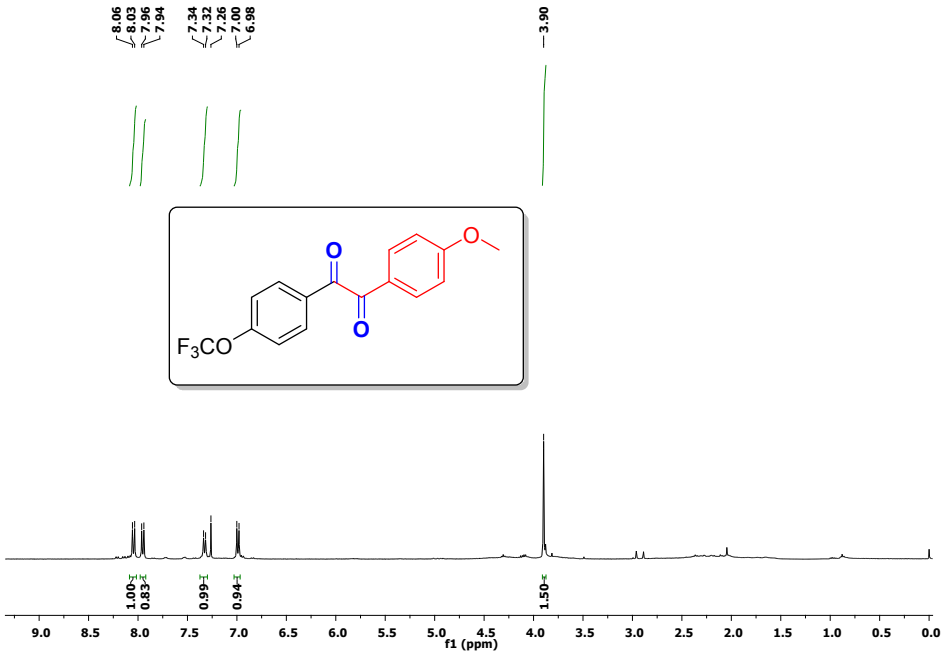


DEPT-135

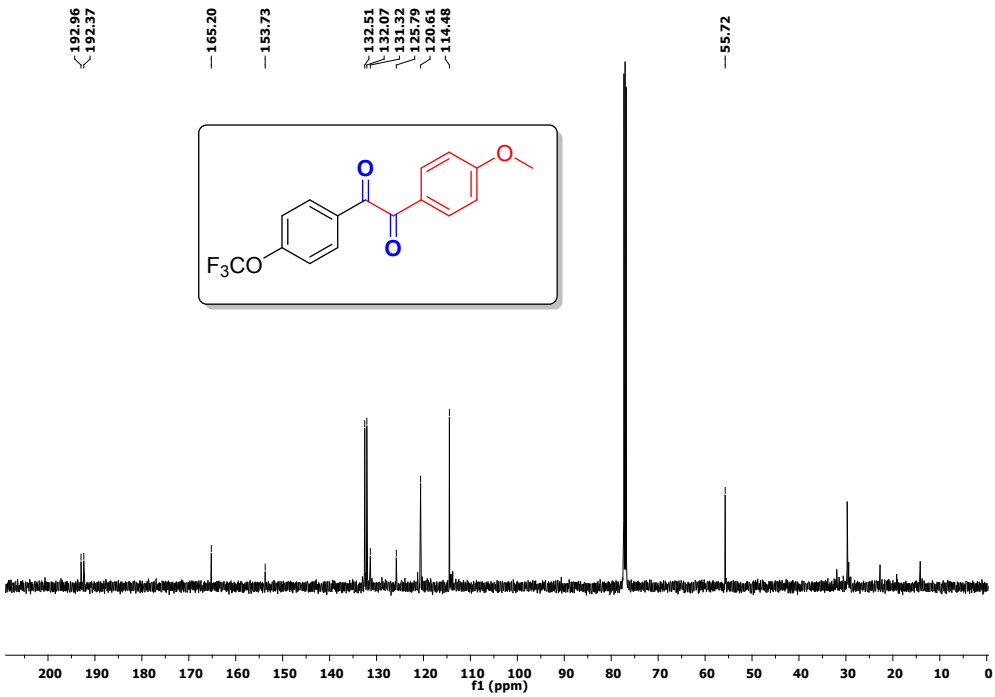

134.90
130.51
129.98
129.06
128.66
127.68
127.38
29.71
Ph
O
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.q. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-(4-methoxyphenyl)-2-(4-(trifluoromethoxy) phenyl) ethane-1,2-dione (3q):

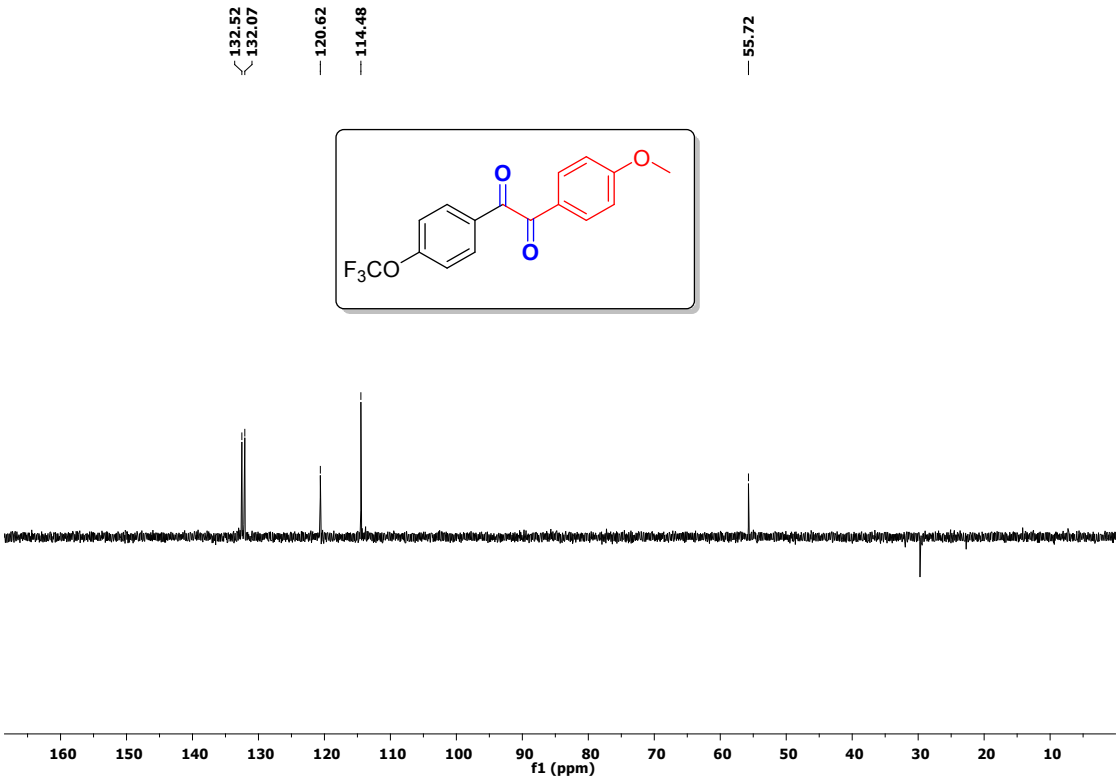
^{1}H NMR



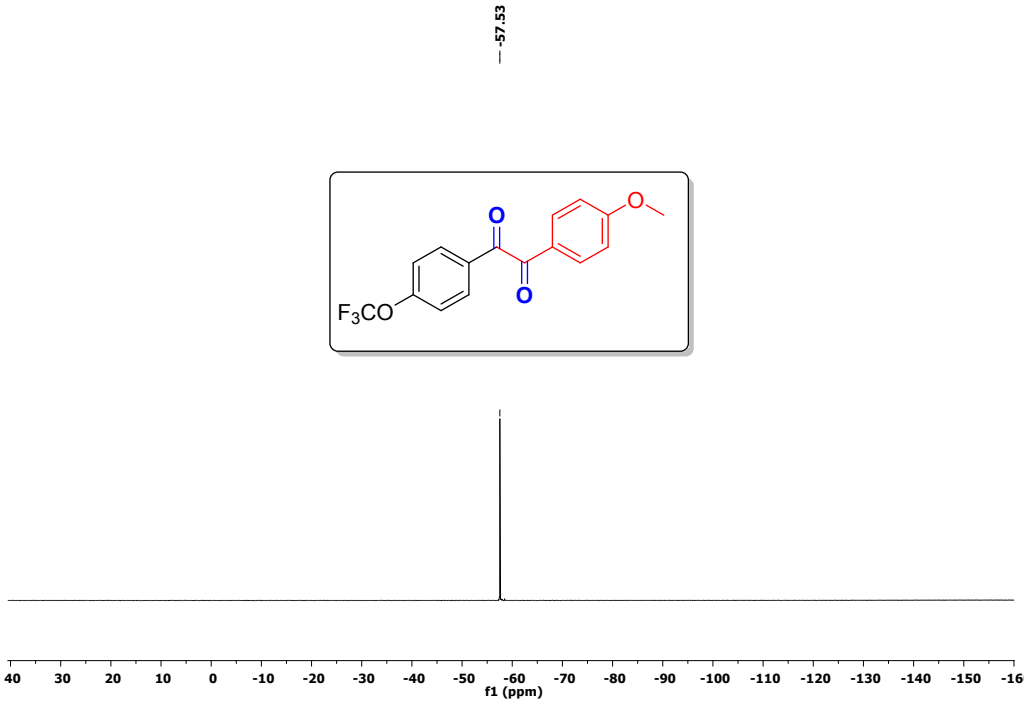
^{13}C NMR



DEPT-135

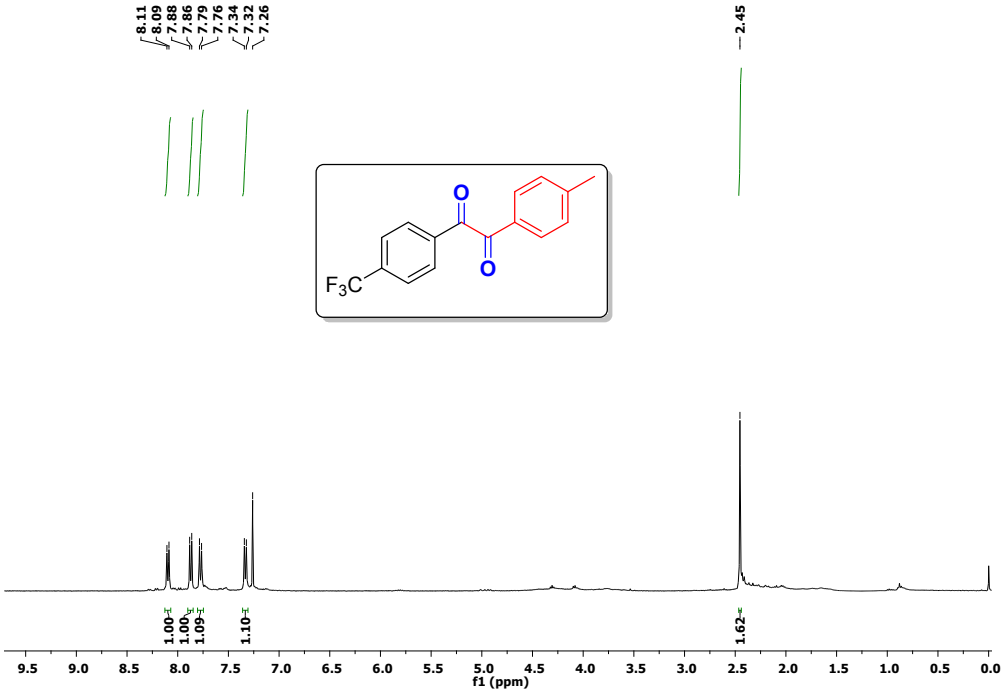


^{19}F NMR

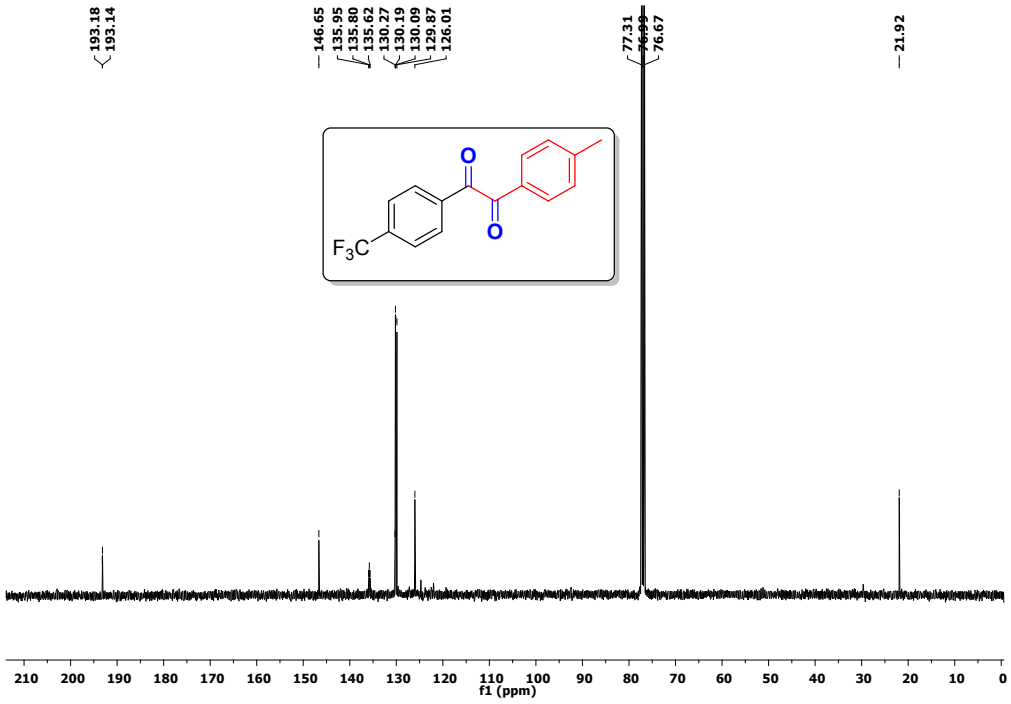


S2.r. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-(p-tolyl)-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (3r):

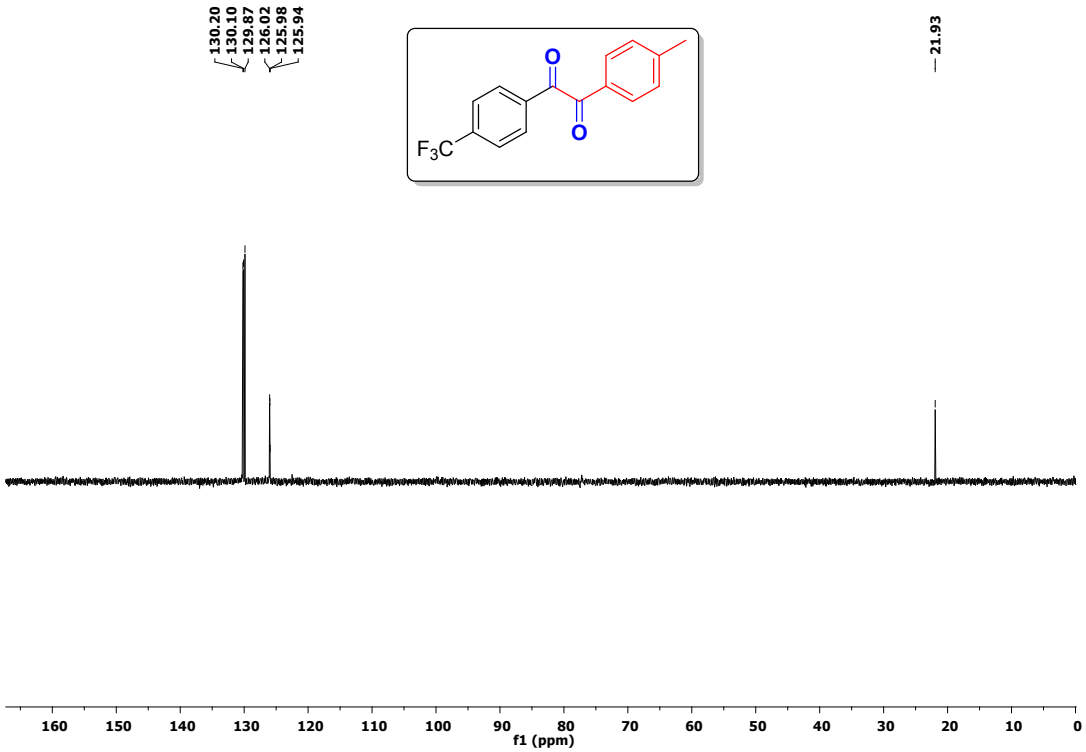
^{1}H NMR



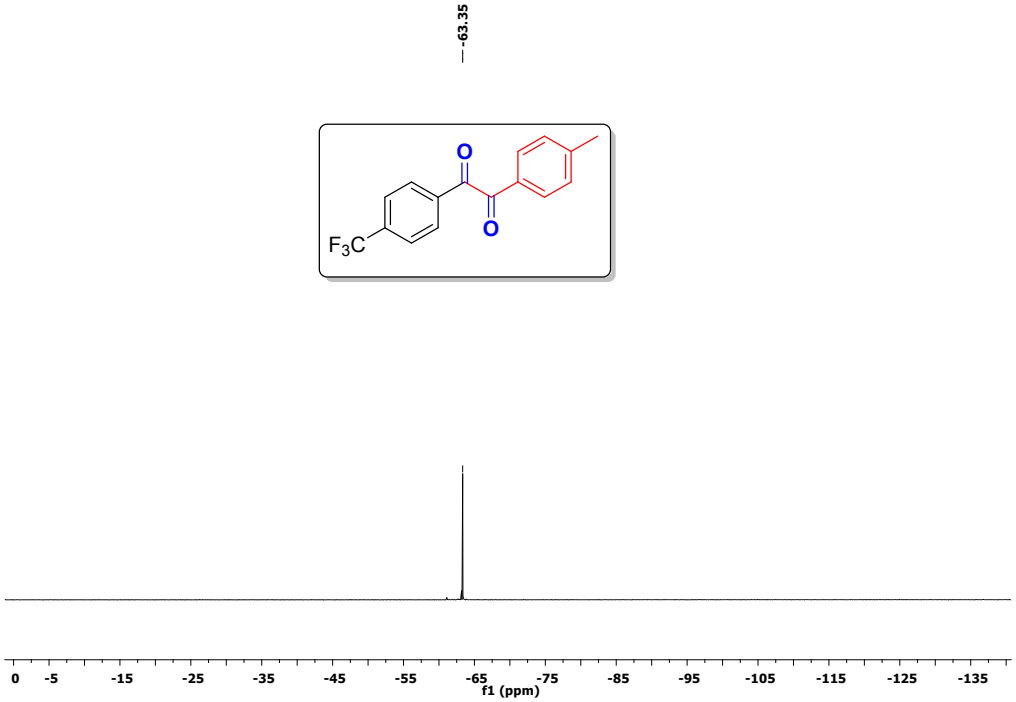
^{13}C NMR



DEPT-135

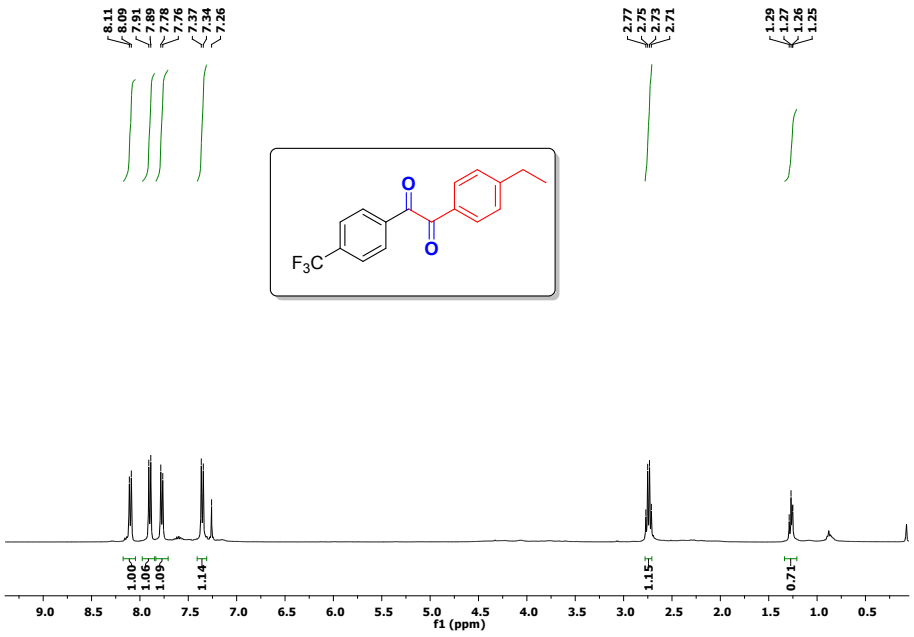


^{19}F NMR

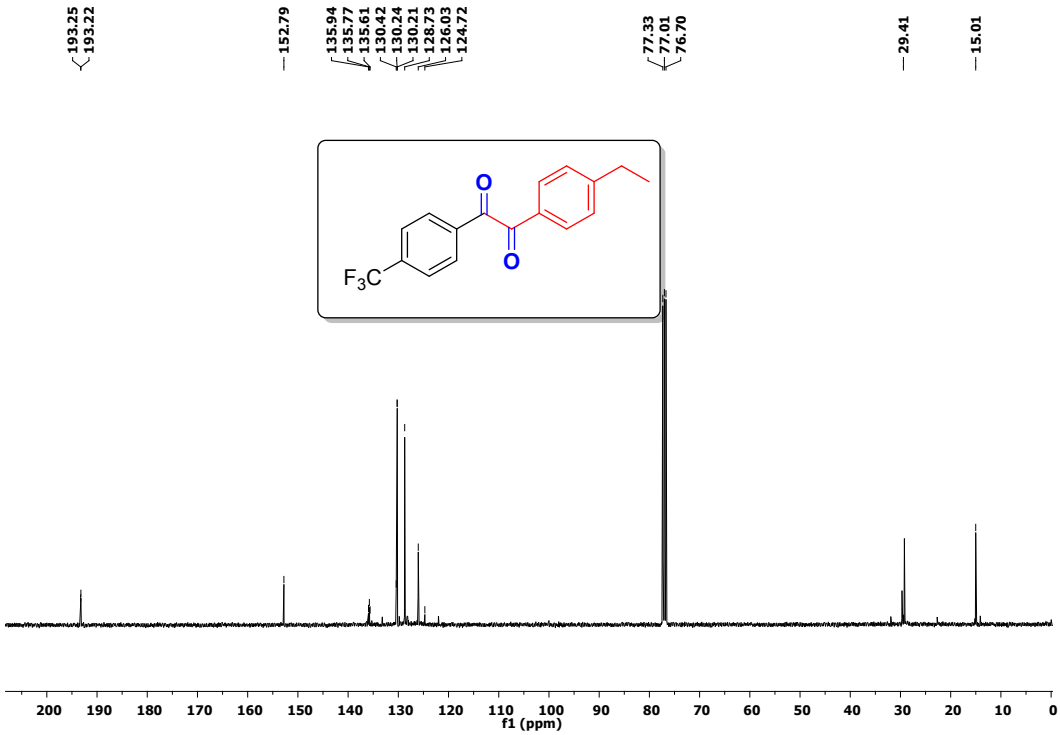


S2.s. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-(4-ethylphenyl)-2-(4-(trifluoromethyl) phenyl) ethane-1,2-dione (3s):

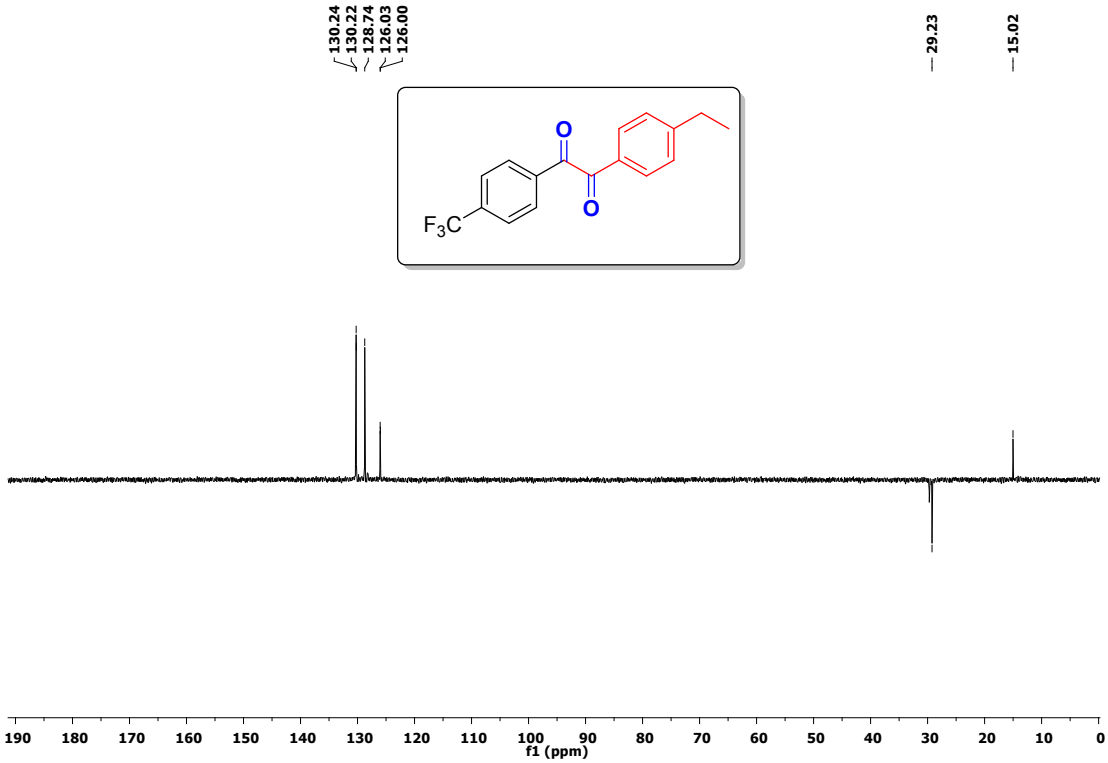
^{1}H NMR



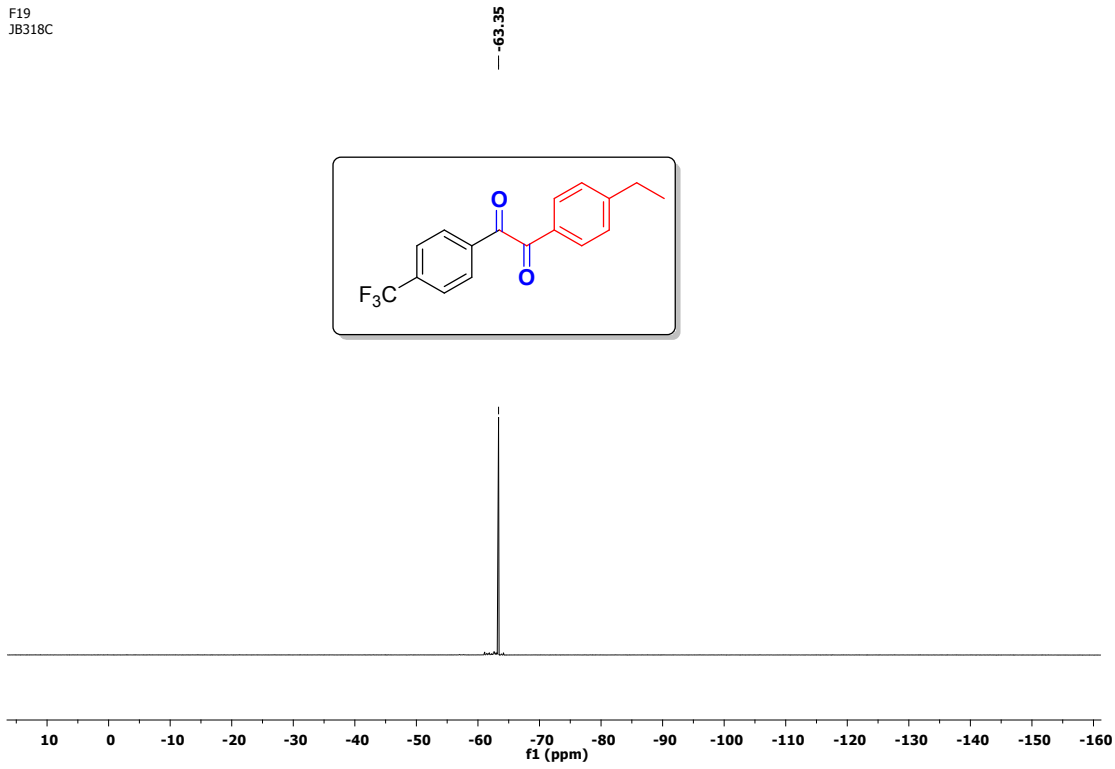
^{13}C NMR



DEPT-135

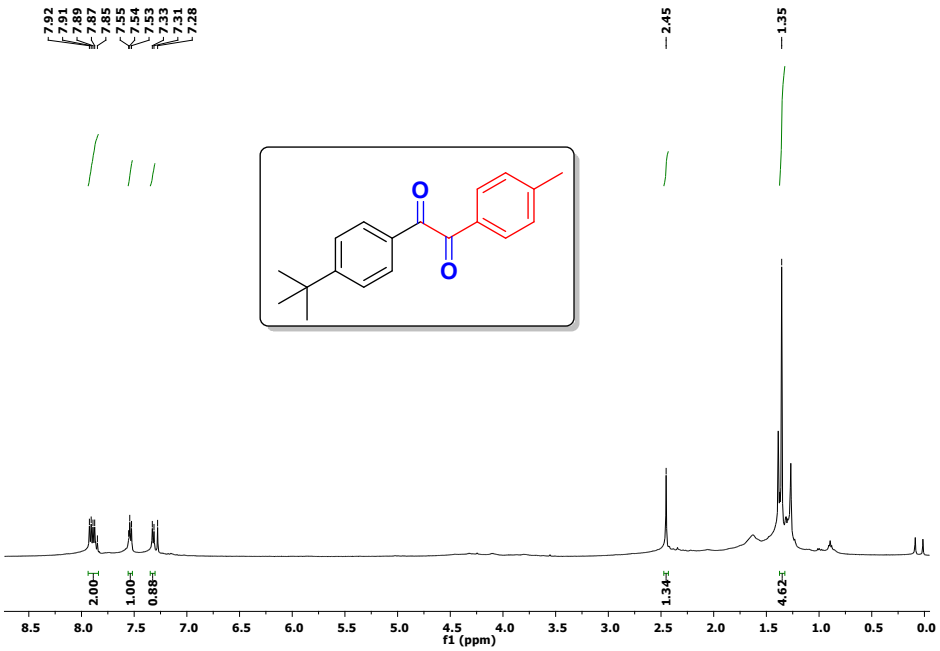


^{19}F NMR

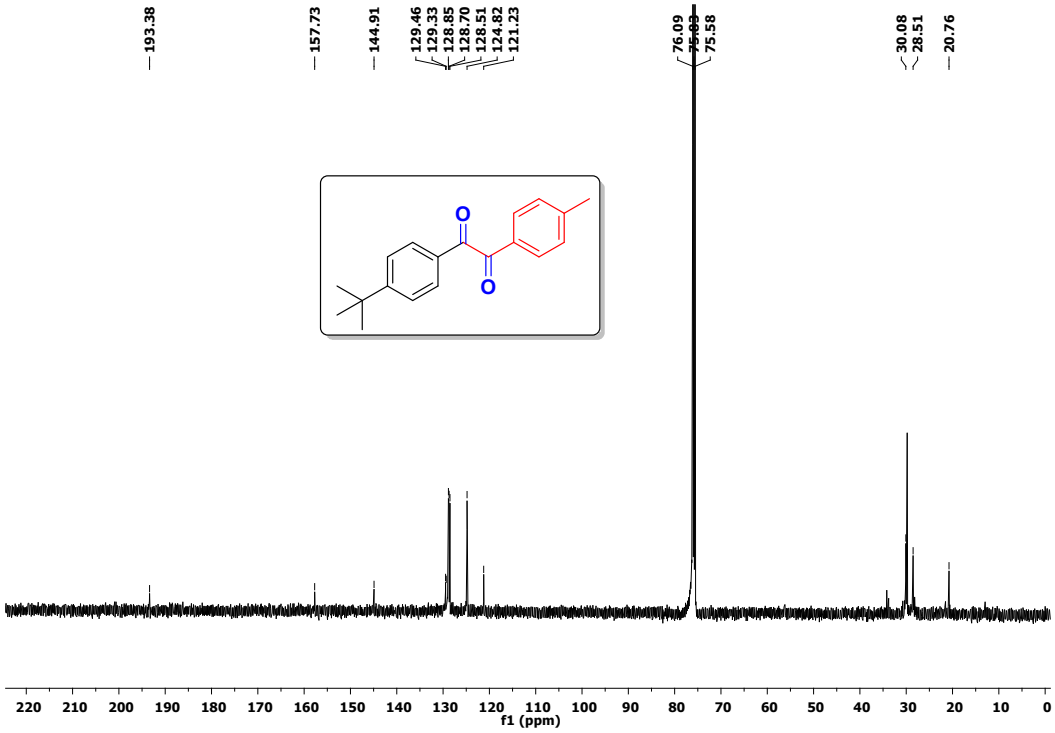


S2.t. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-(tert-butyl) phenyl)-2-(p-tolyl) ethane-1,2-dione (3t):

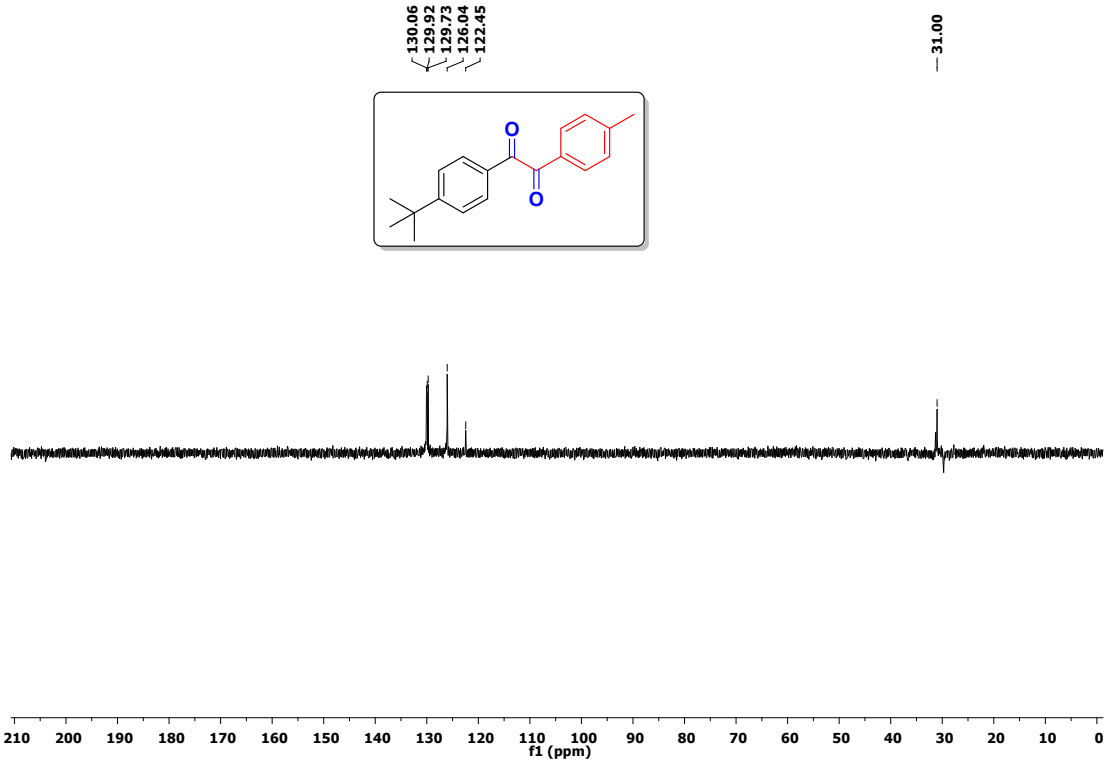
^{1}H NMR



^{13}C NMR

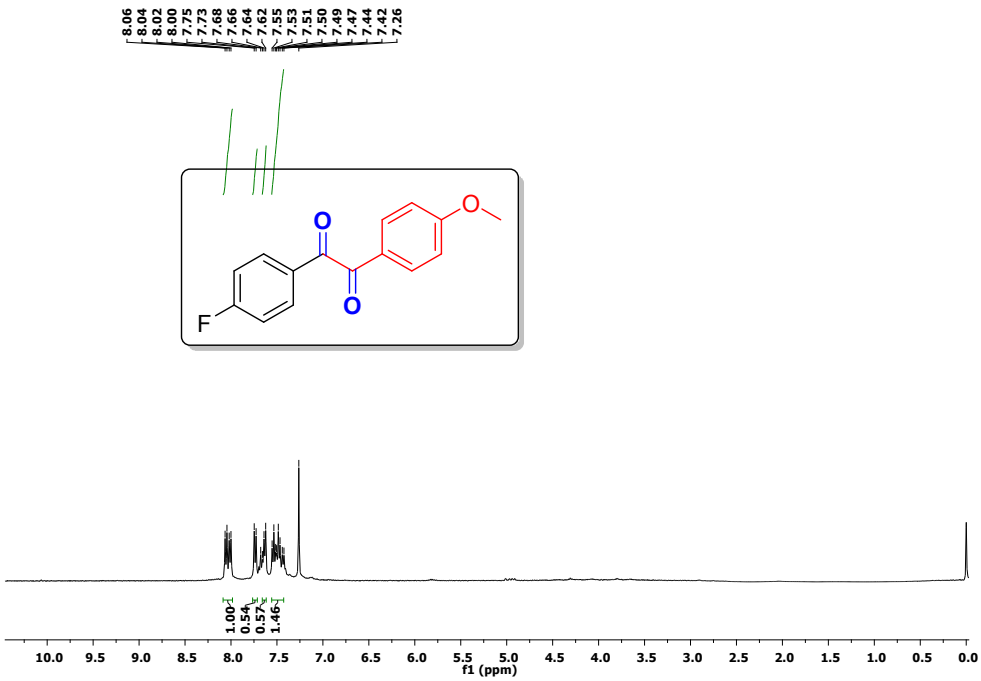


DEPT-135

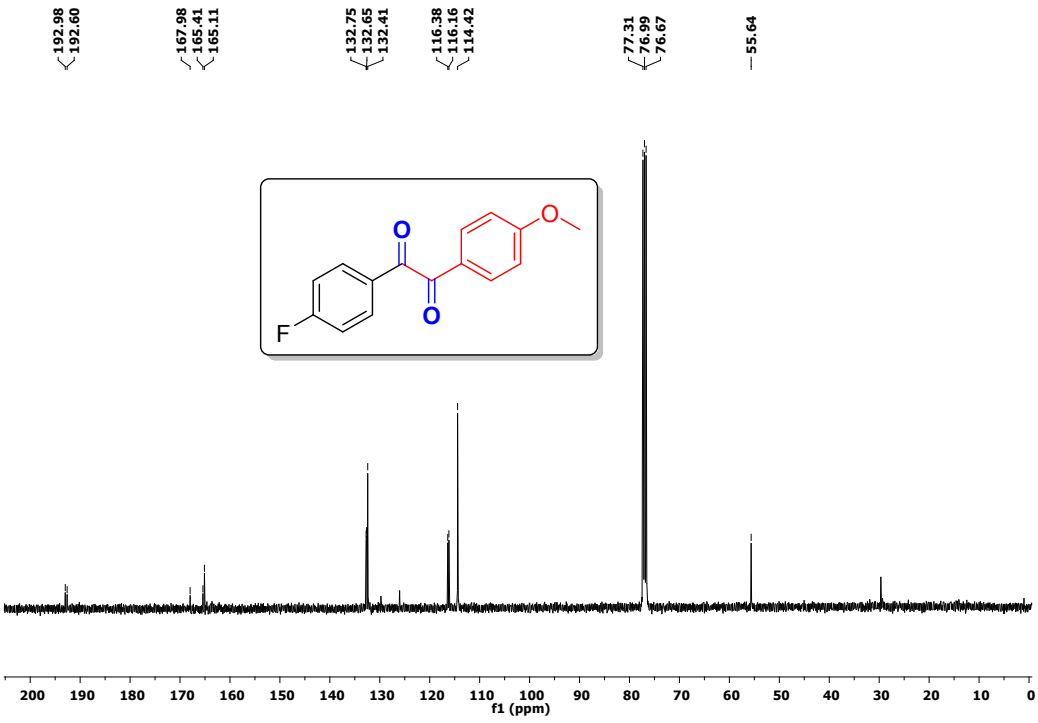

130.06
129.92
129.73
126.04
122.45
31.00
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S2.t. ^{1}H, ^{13}C, DEPT-135 and ^{19}F NMR of 1-(4-fluorophenyl)-2-(4-methoxyphenyl) ethane-1,2-dione (3u):

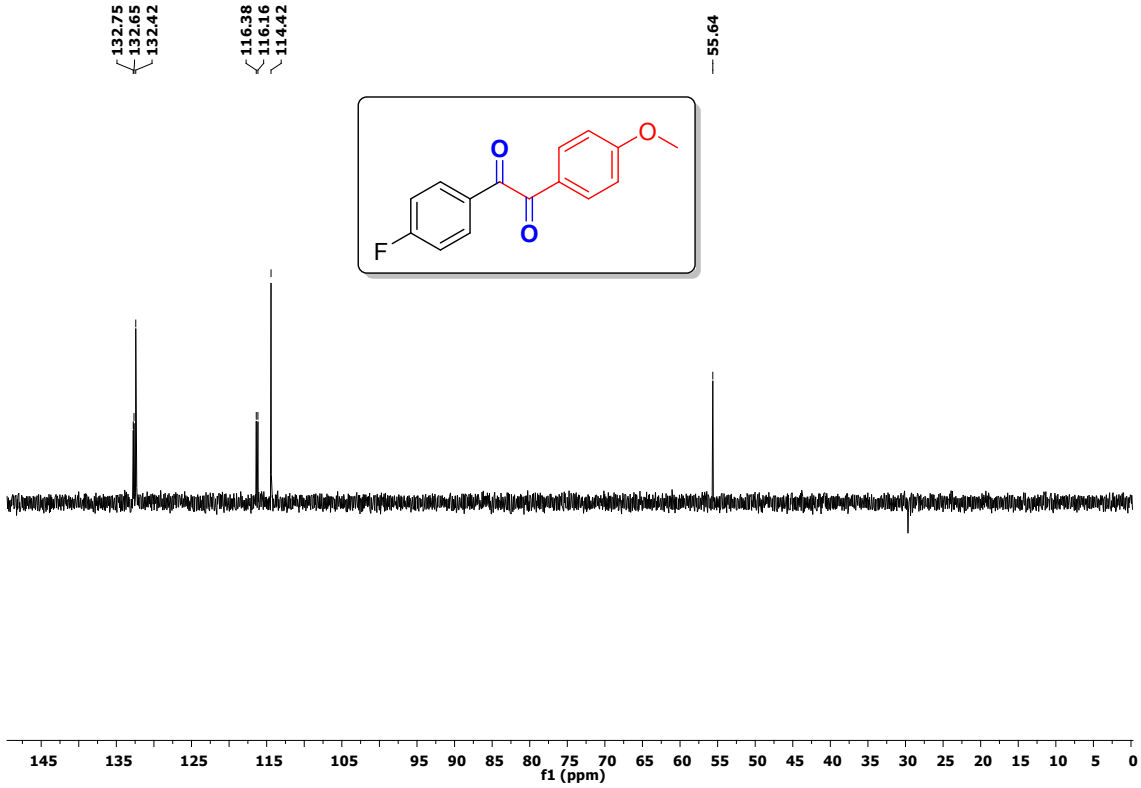
^{1}H NMR



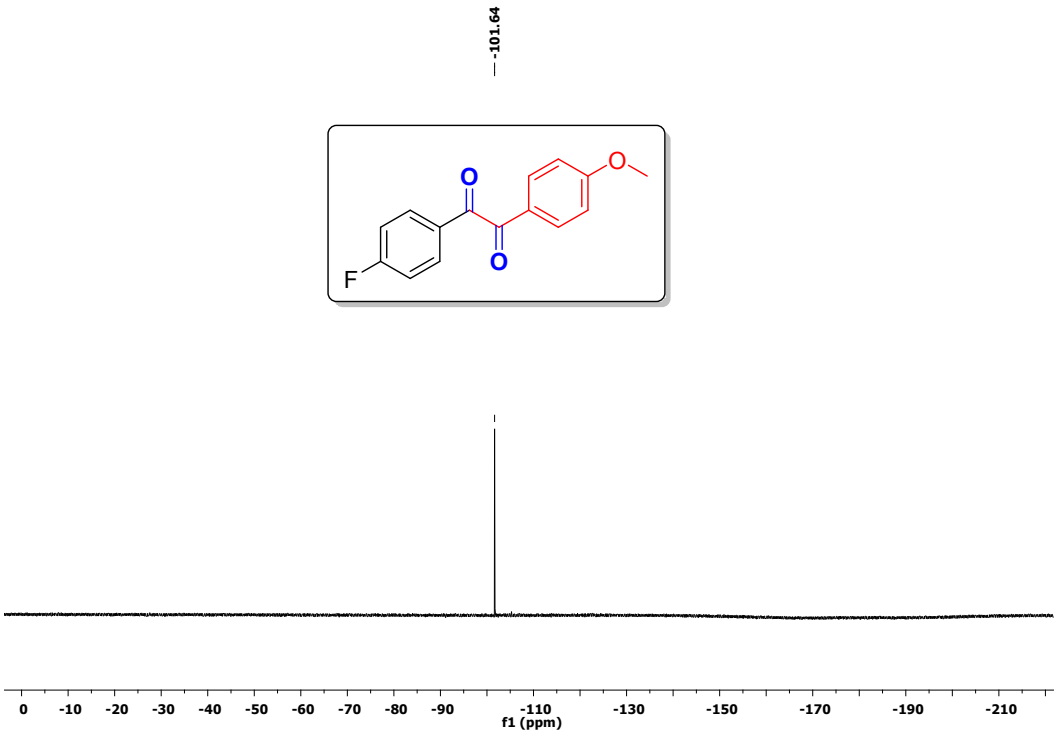
^{13}C NMR



DEPT-135

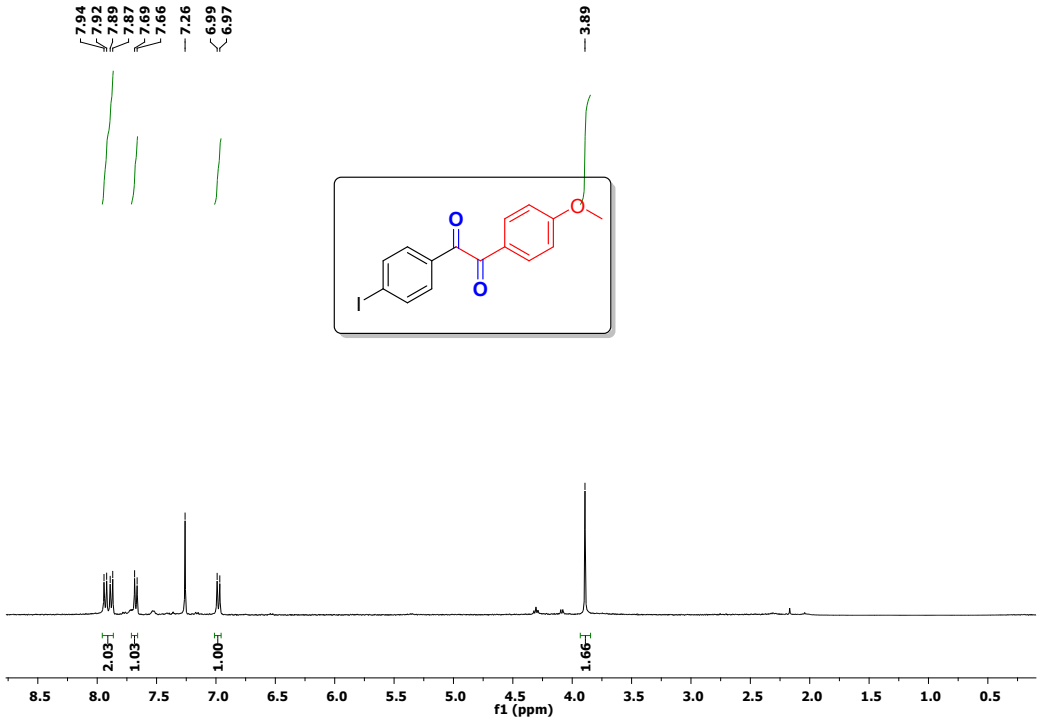


^{19}F NMR

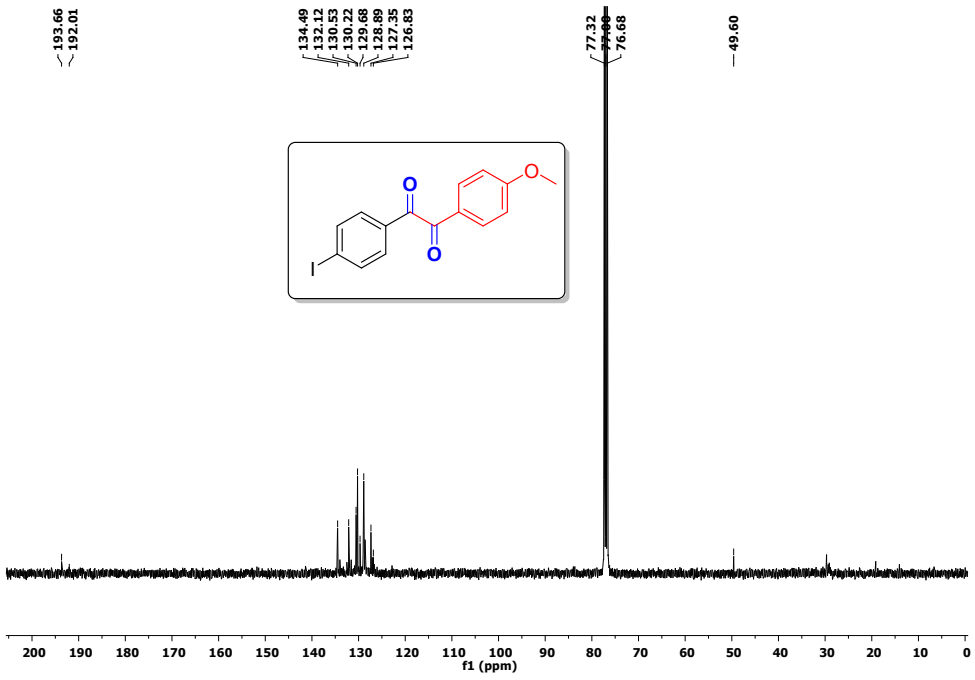


S2.v. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-iodophenyl)-2-(4-methoxyphenyl) ethane-1,2-dione (3v):

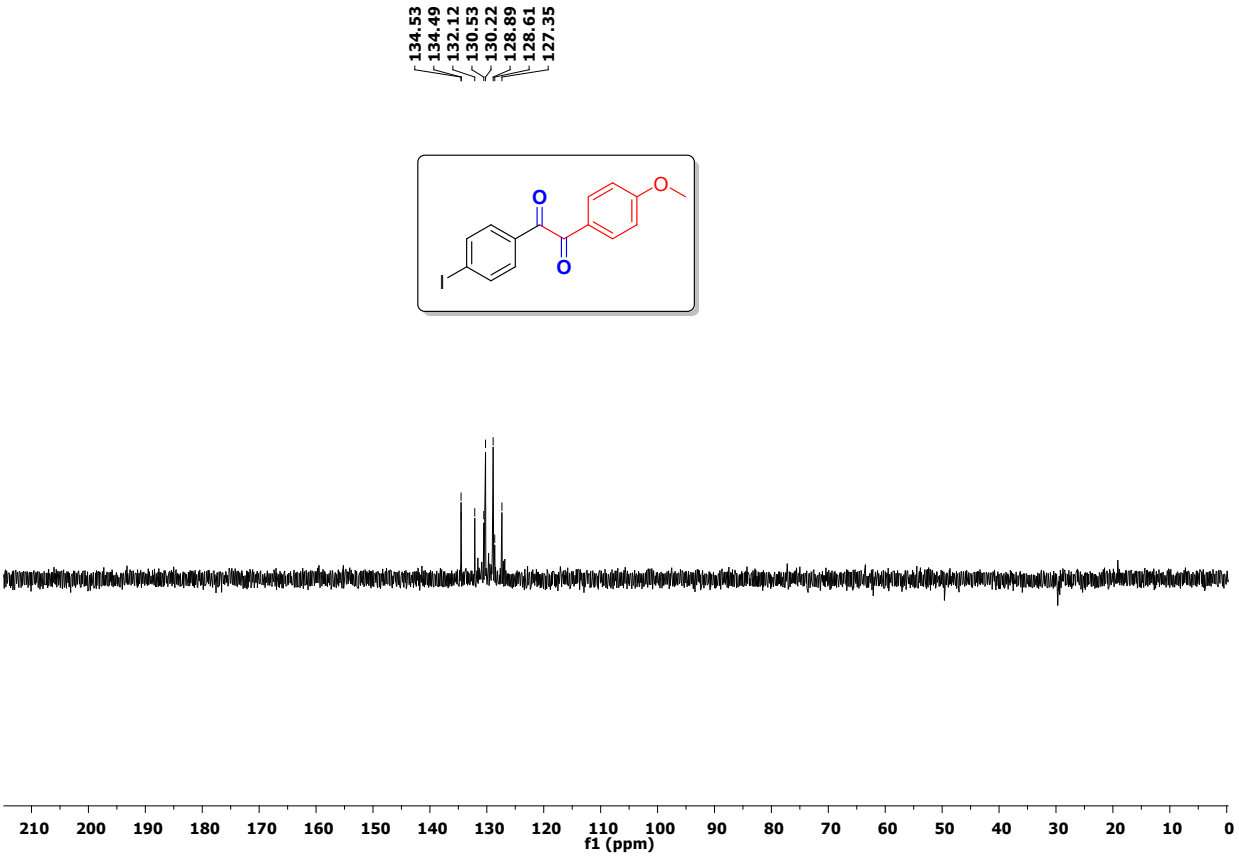
^{1}H NMR



^{13}CNMR

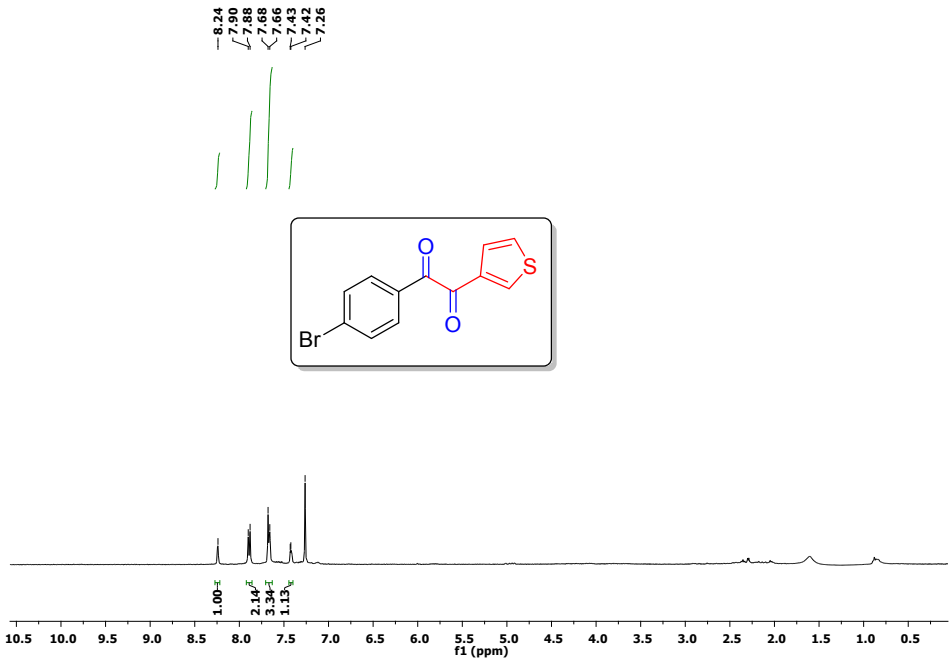


DEPT-135

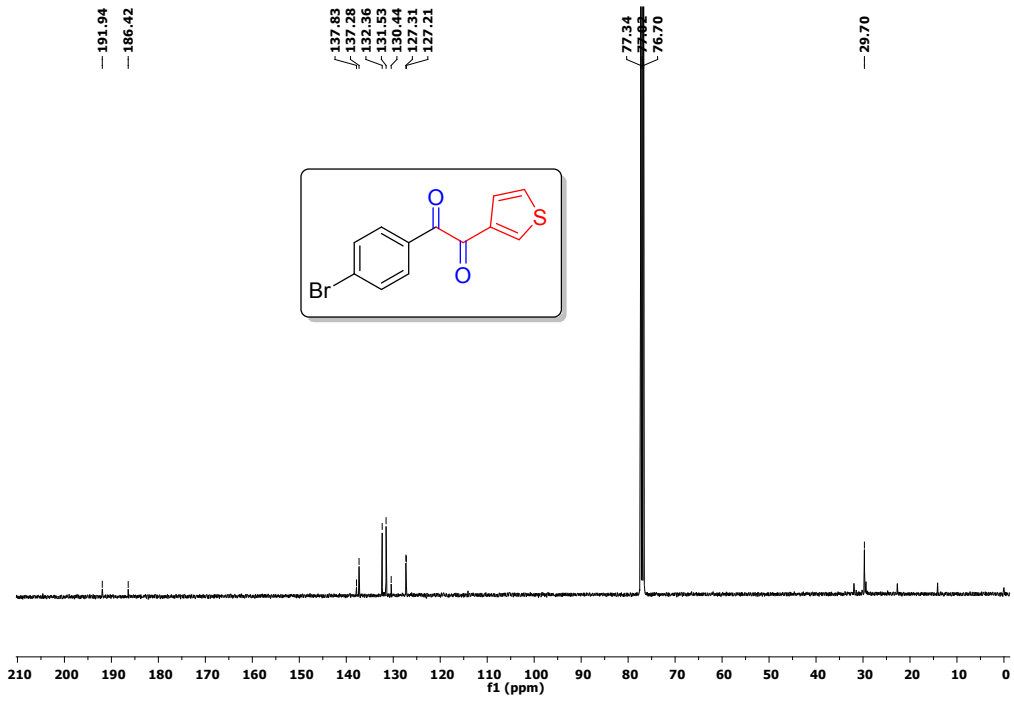

134.53
134.49
132.12
130.53
130.22
128.89
128.61
127.35
O
O
O
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.w. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-bromophenyl)-2-(thiophen-3-yl)ethane-1,2-dione (3w):

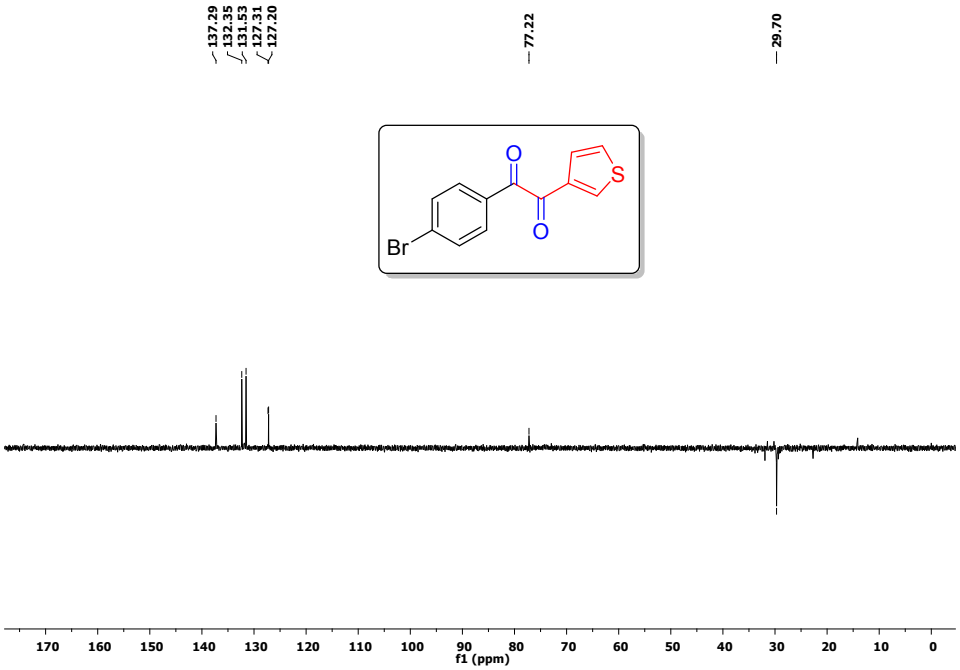
^{1}H NMR



^{13}C NMR

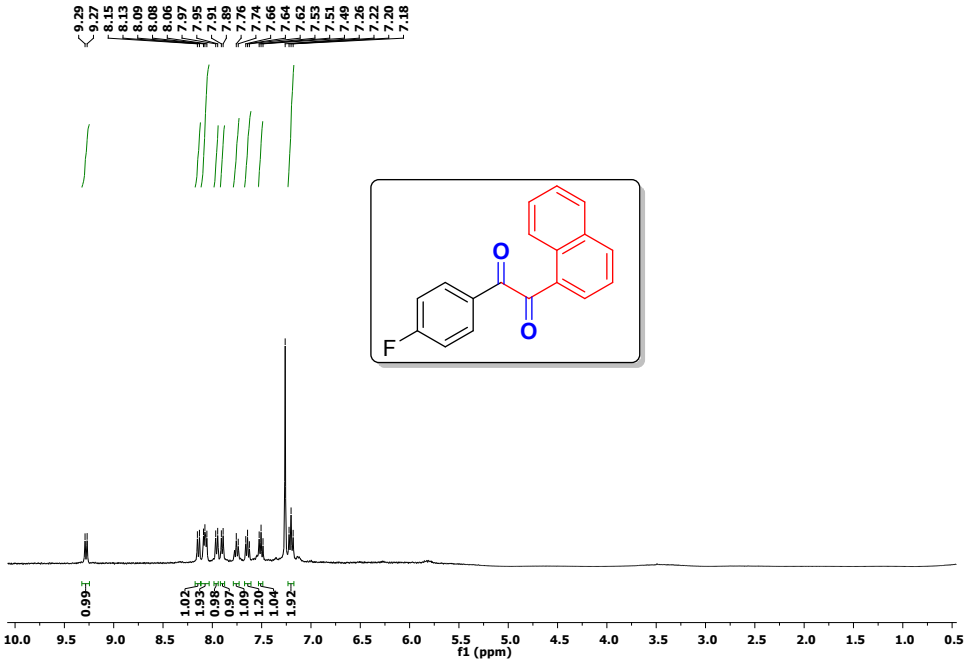


DEPT-135

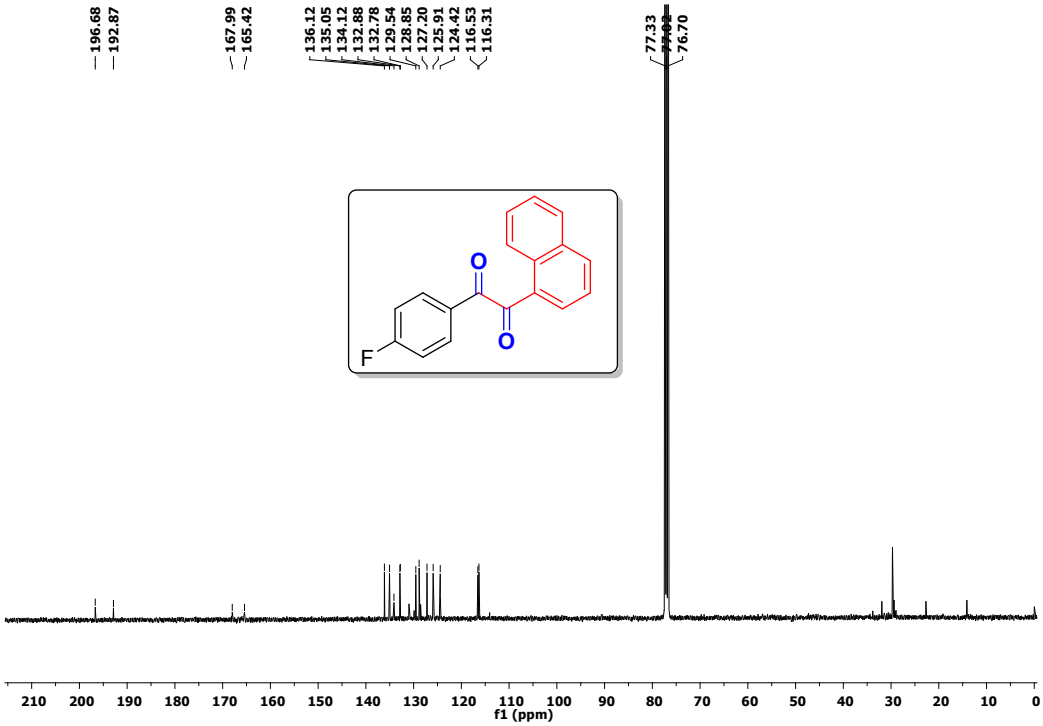

137.29
132.35
131.53
127.31
127.20
77.22
29.70
O
O
S
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S2.x. ^{1}H, ^{13}C and DEPT-135 NMR of 1-(4-fluorophenyl)-2-(naphthalen-1-yl)ethane-1,2-dione (3x):

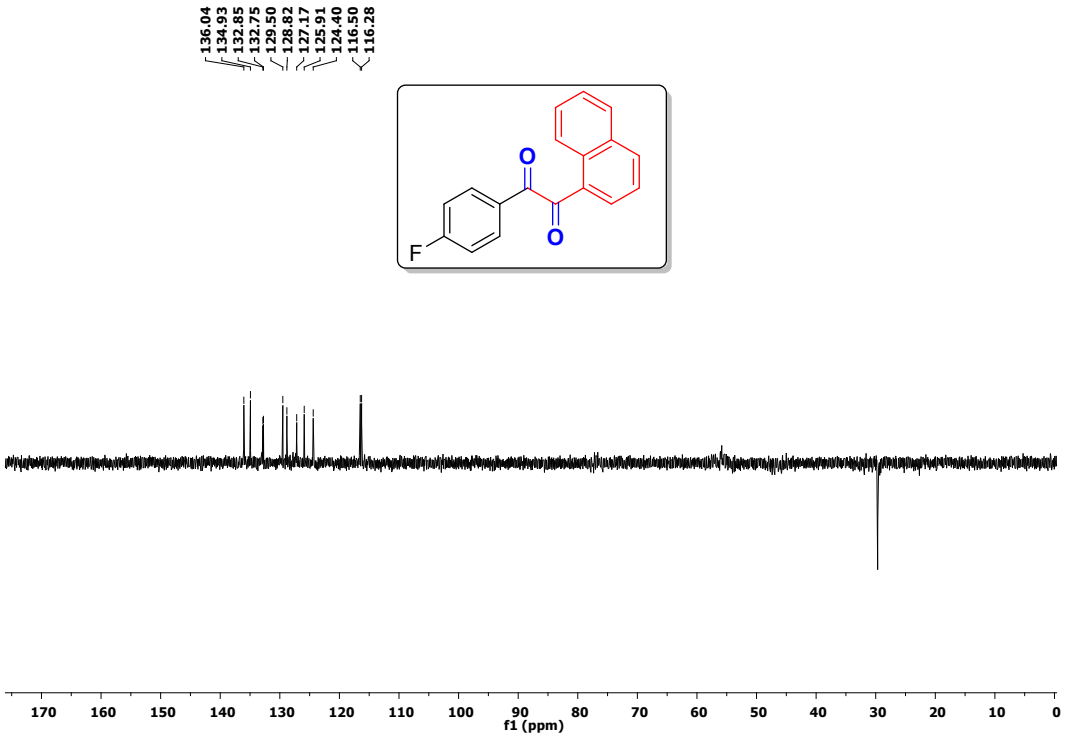
^{1}H NMR



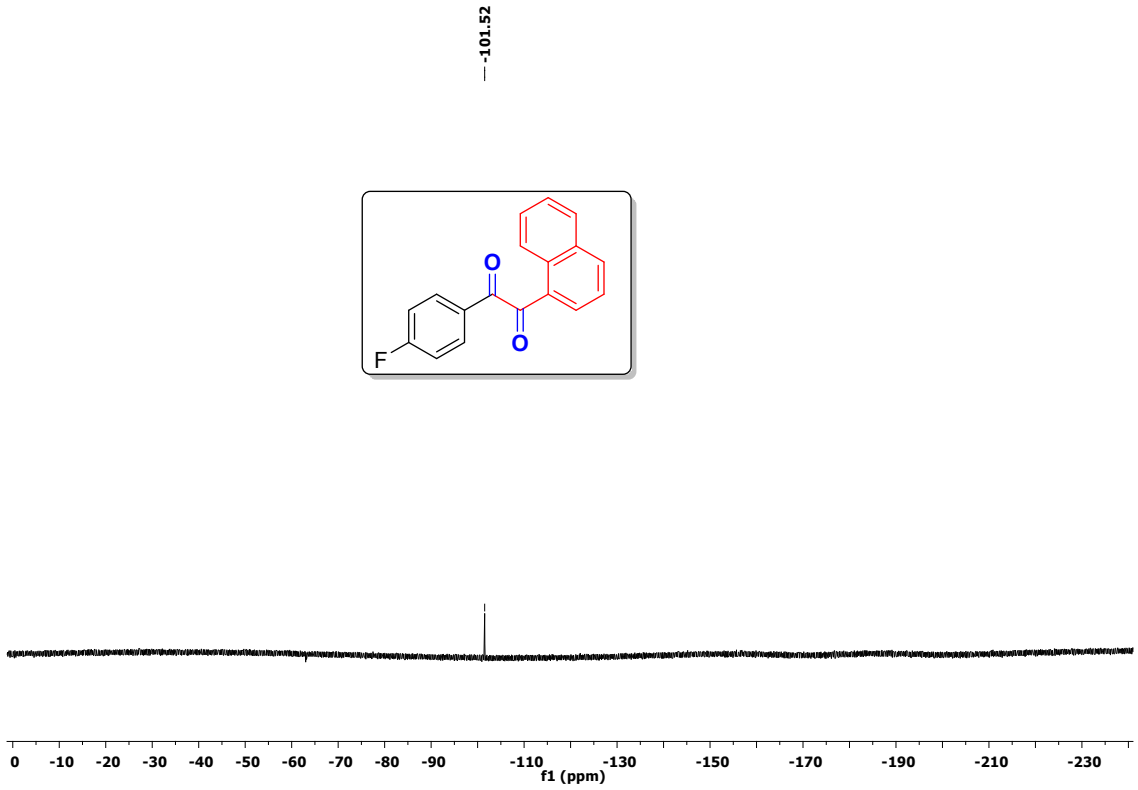
^{13}C NMR



DEPT-135



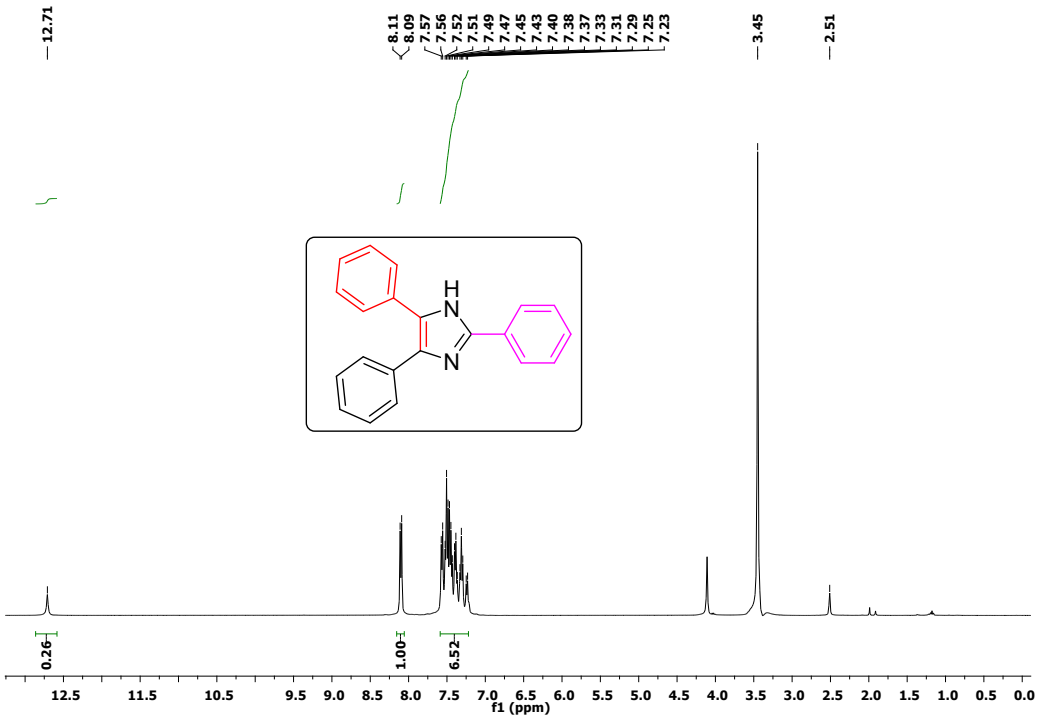
^{1}F NMR



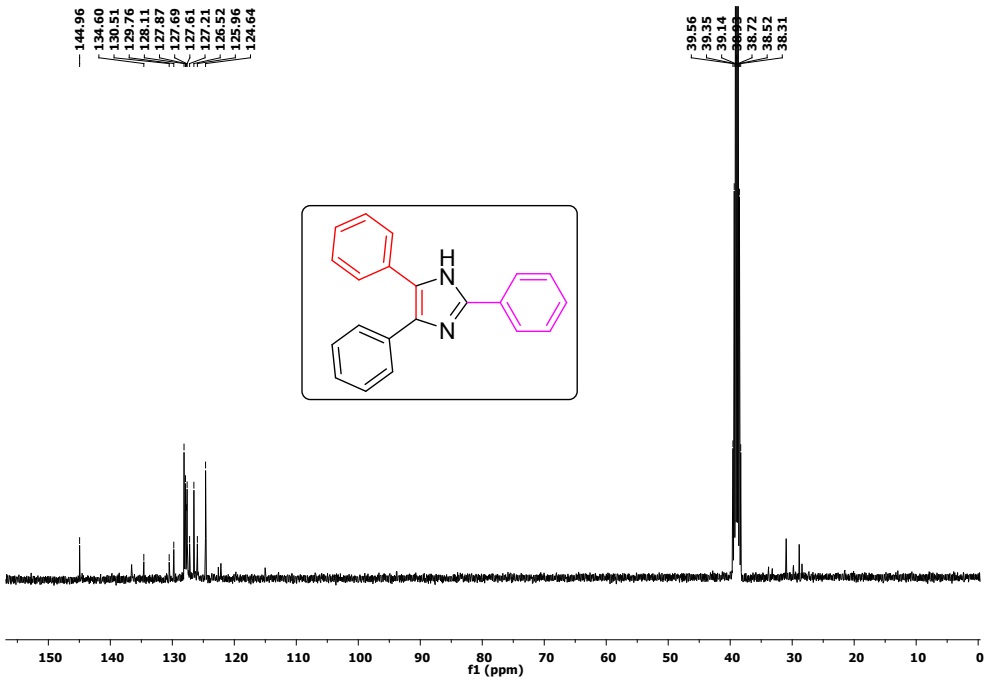
S3. Spectral data scans of imidazoles 7a-d and trifenagrel (8)

S3.a. ^{1}H, ^{13}C and DEPT-135 NMR of 2,4,5-triphenyl-1H-imidazole (7a):

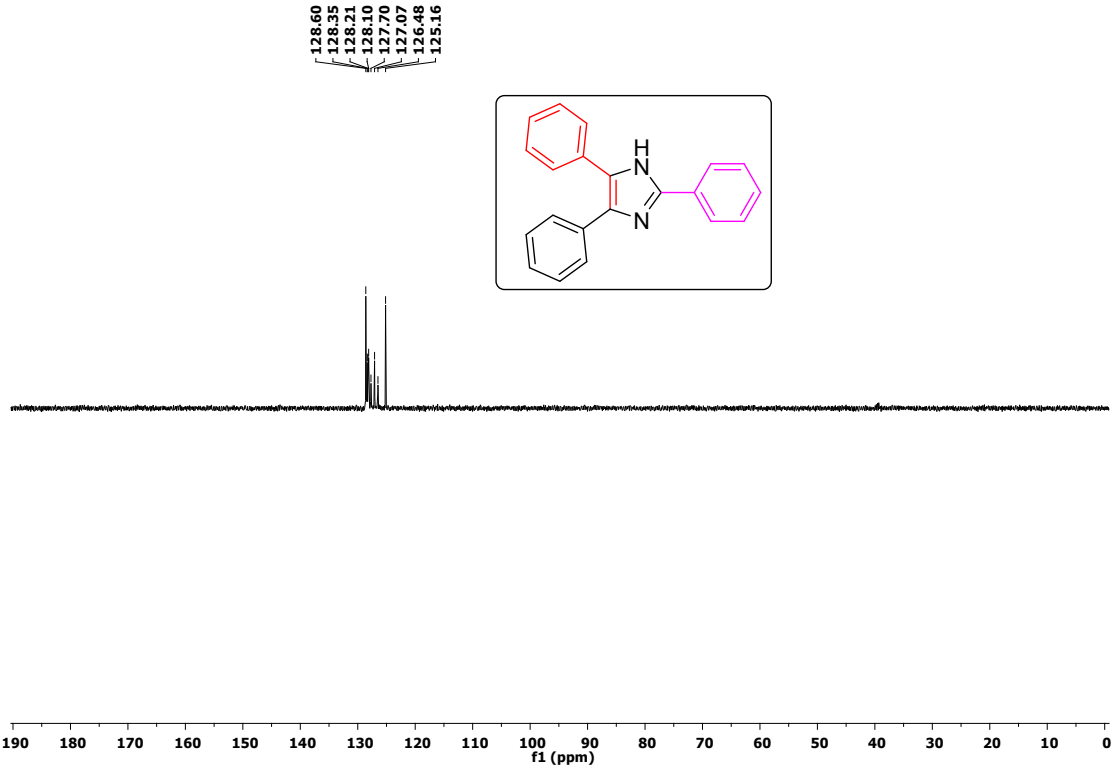
^{1}H NMR



^{13}C NMR

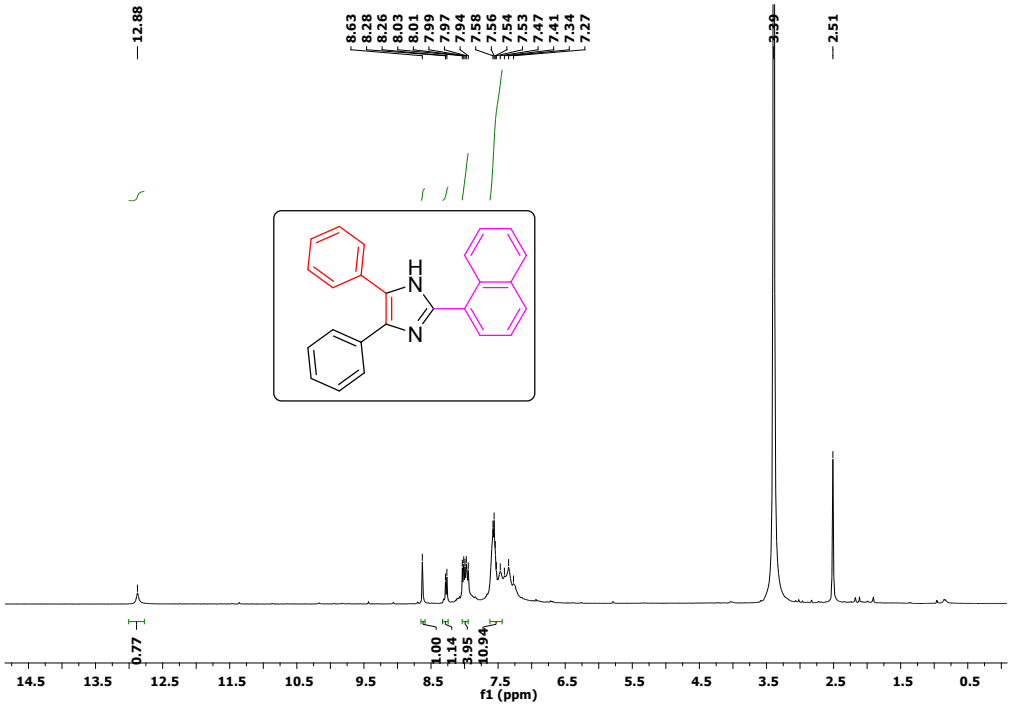


DEPT-135

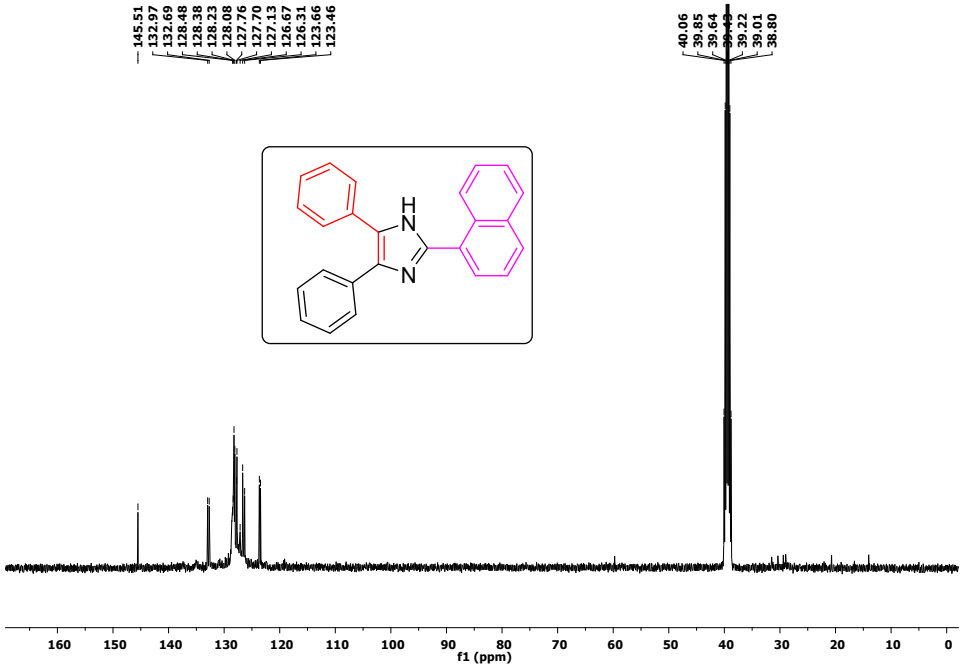

128.60
128.35
128.21
128.10
127.70
127.07
126.48
125.16
H
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S3.b. ^{1}H, ^{13}C and DEPT-135 NMR of 2-(naphthalen-1-yl)-4,5-diphenyl-1H-imidazole (7b):

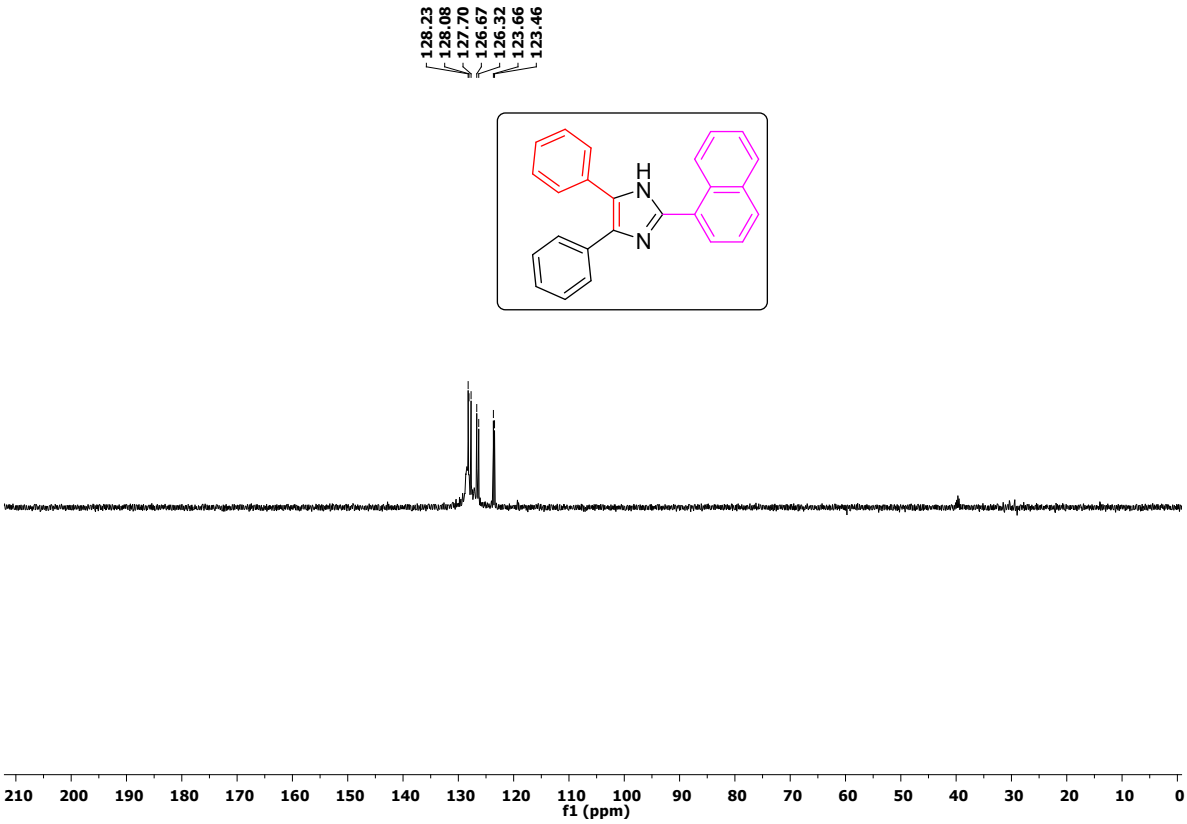
^{1}H NMR



^{13}C NMR

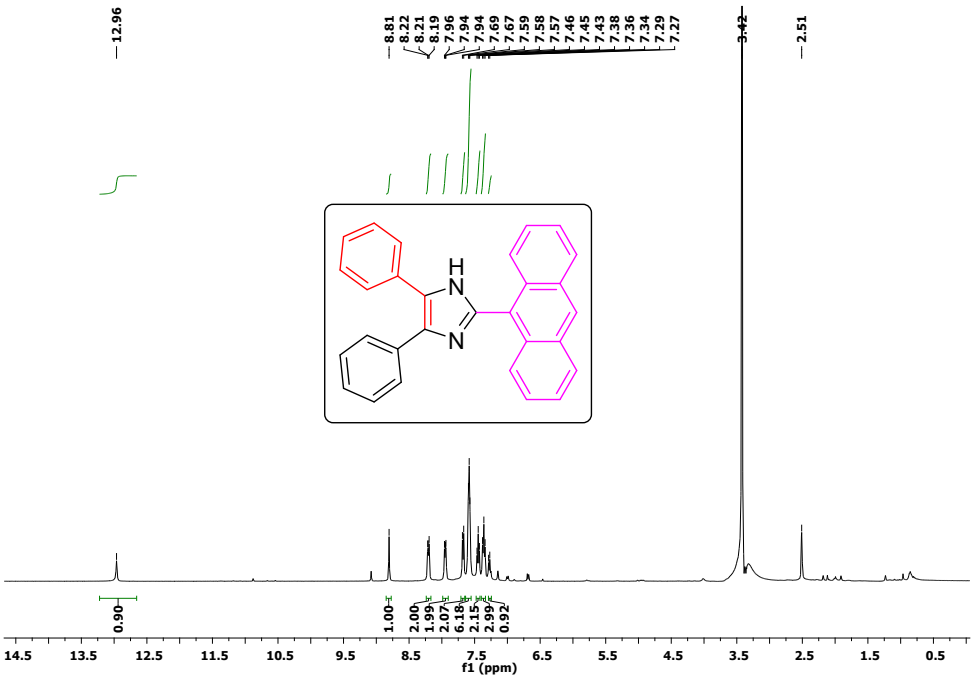


DEPT-135

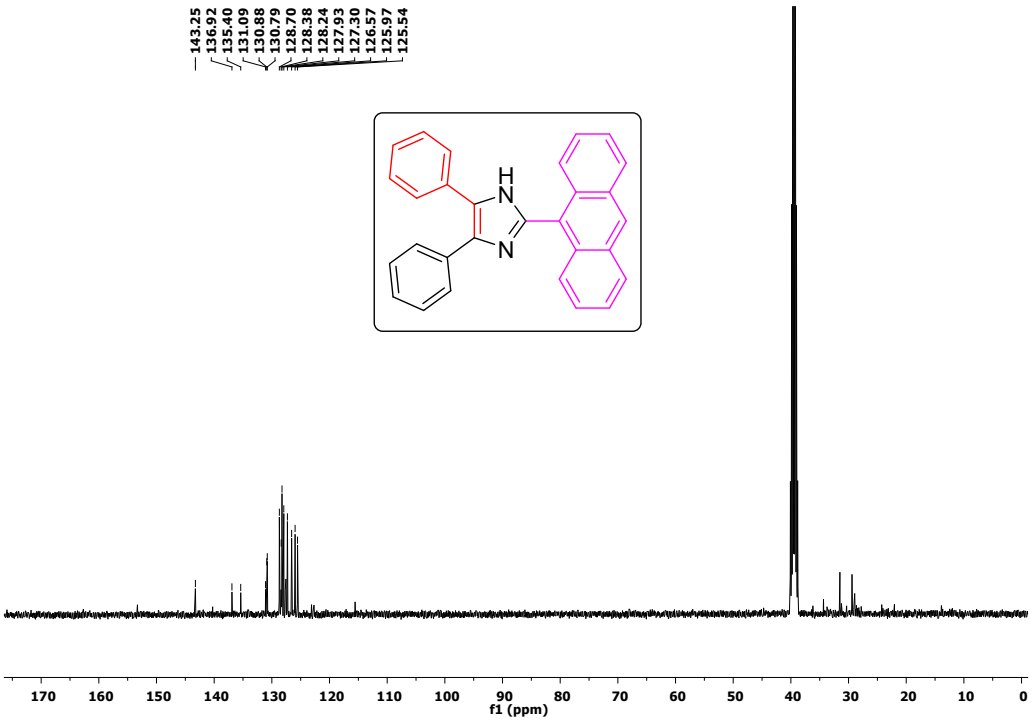

128.23
128.08
127.70
126.67
126.32
123.66
123.46
H
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S3.c. ^{1}H, ^{13}C and DEPT-135 NMR of 2-(anthracen-9-yl)-4,5-diphenyl-1H-imidazole (7c):

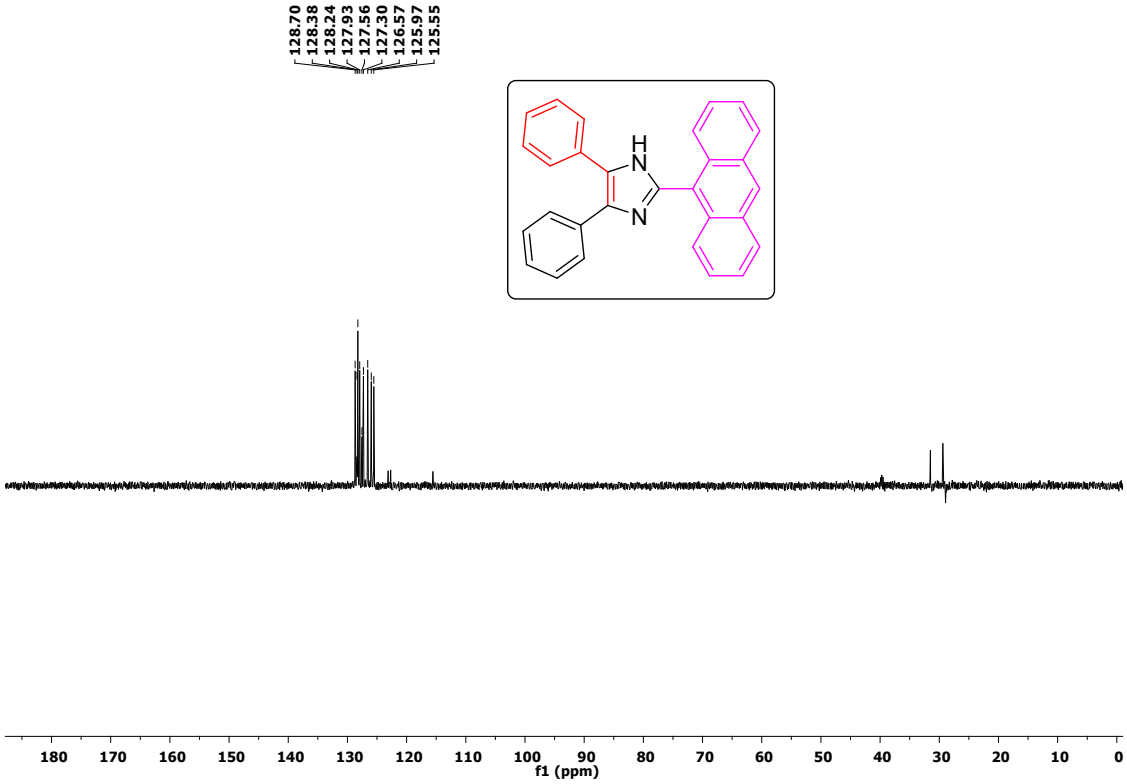
^{1}H NMR



^{13}CNMR

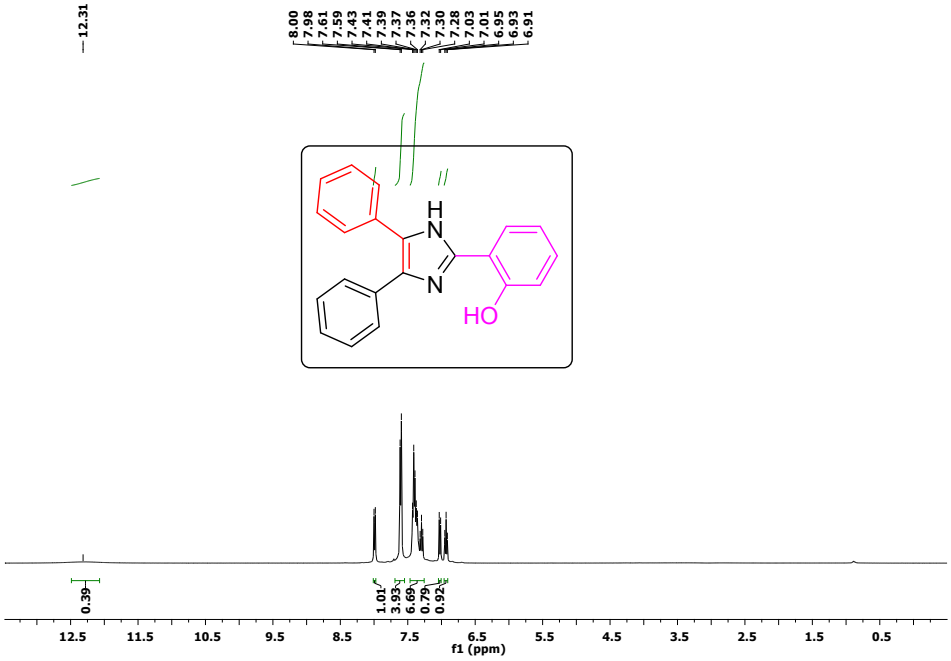


DEPT-135

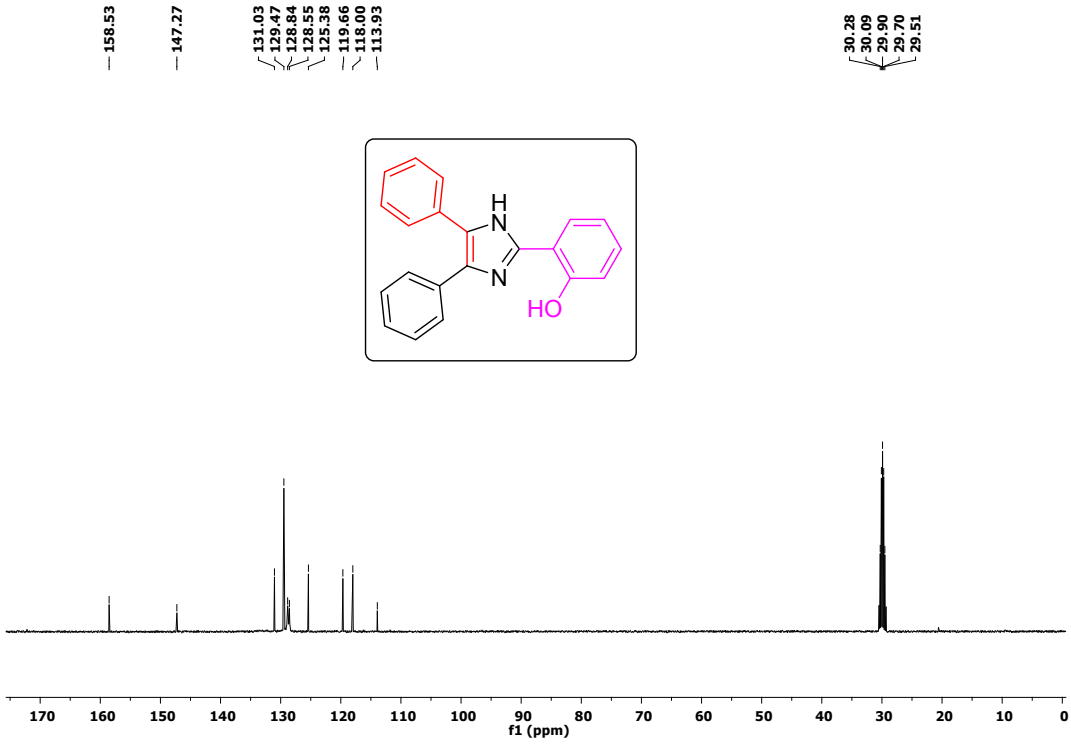

128.70
128.38
128.24
127.93
127.56
127.30
126.57
125.97
125.55
H
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S3.d. ^{1}H, ^{13}C and DEPT-135 NMR of 2-(2-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)-N,N-dimethylethan-1-amine (7d):

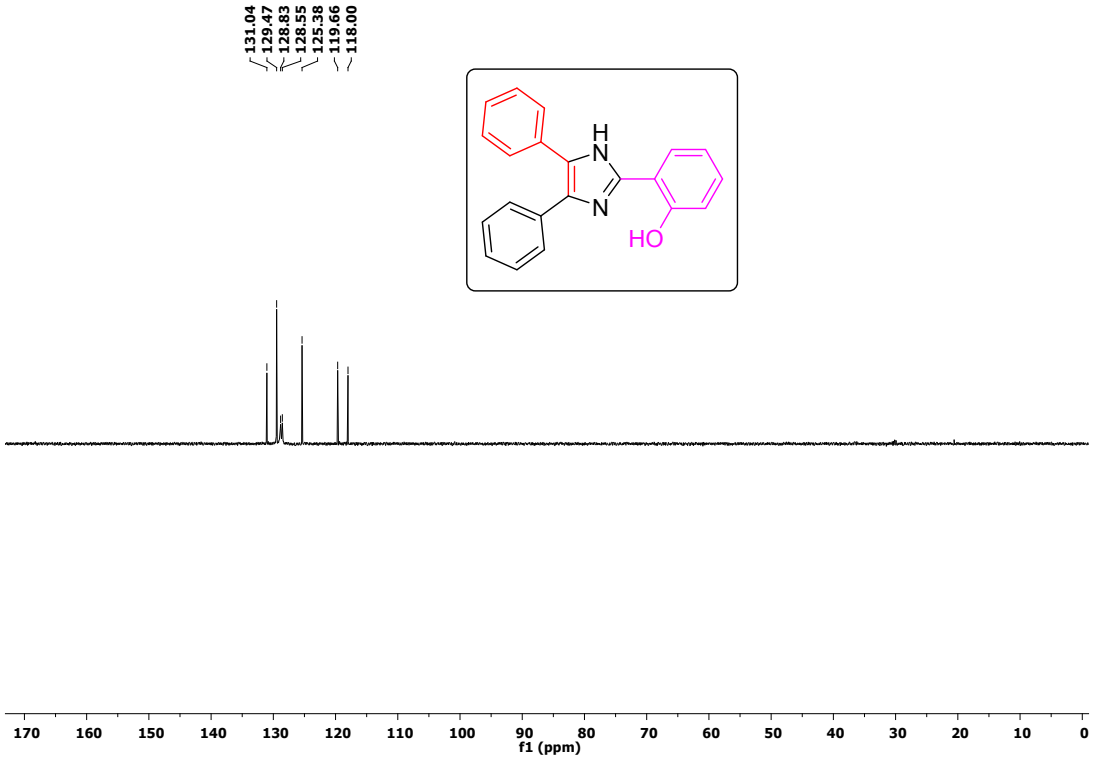
^{1}HNMR



^{13}CNMR

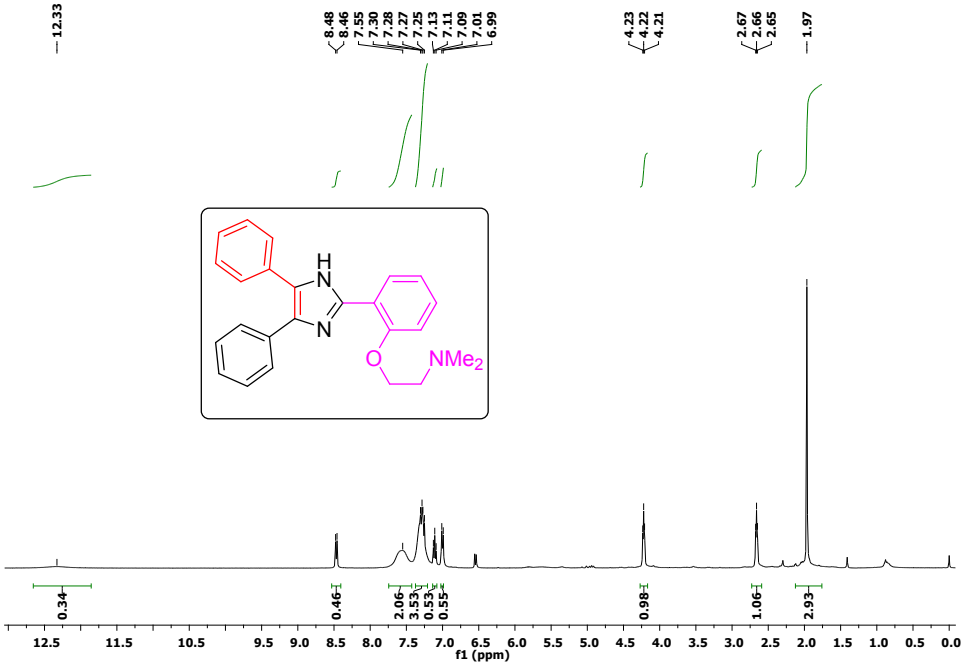


DEPT-135

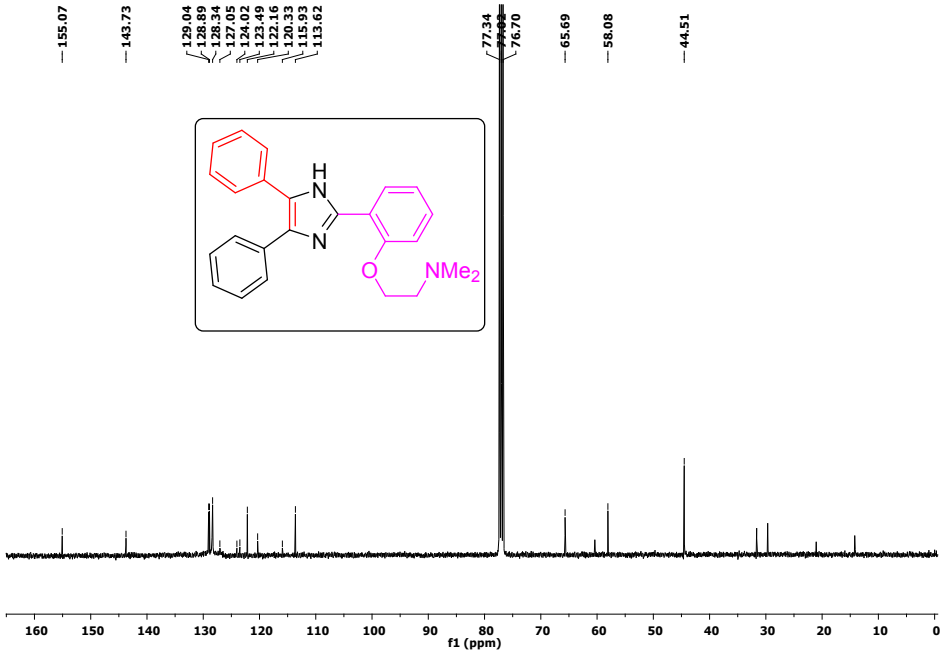

131.04
129.47
128.83
128.55
125.38
119.66
118.00
H
N
N
HO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

S3.e. ^{1}H, ^{13}C and DEPT-135 NMR of 2-(2-(4,5-diphenyl-1H-imidazol-2-yl)phenoxy)-N,N-dimethylethanamine (Trifenagrel, 8):

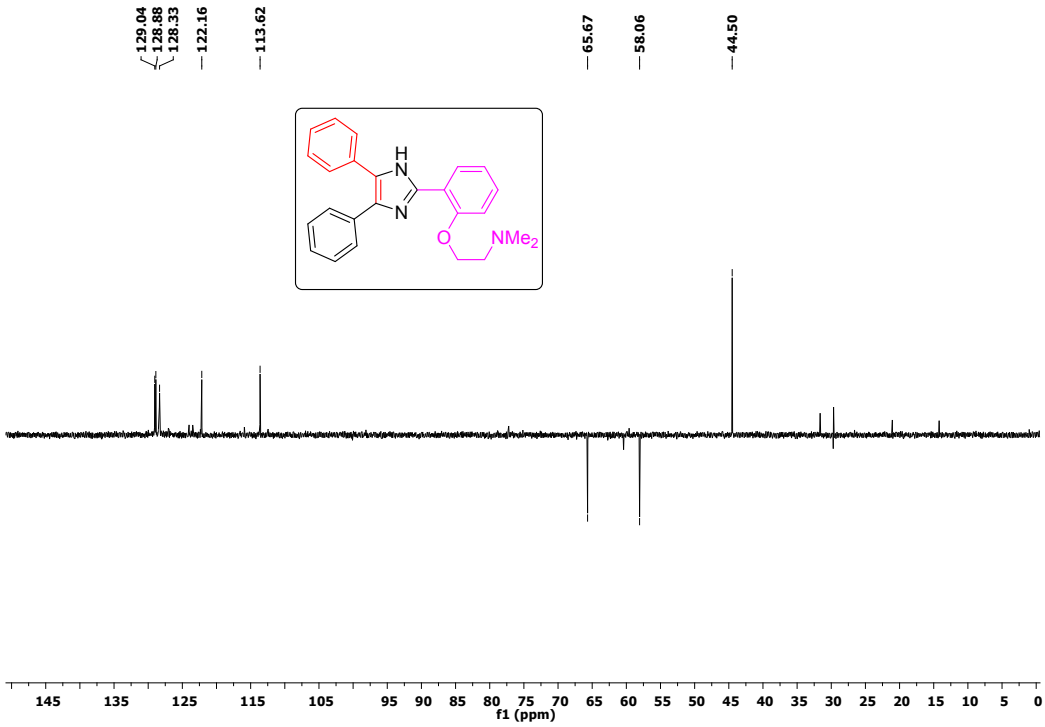
^{1}H NMR



^{13}C NMR

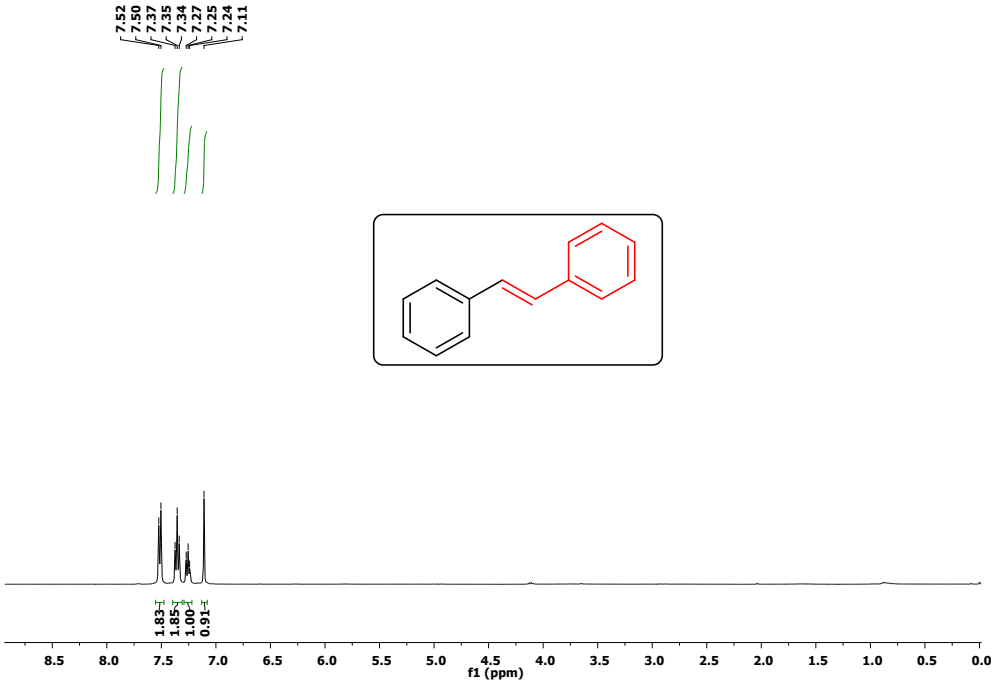


DEPT-135

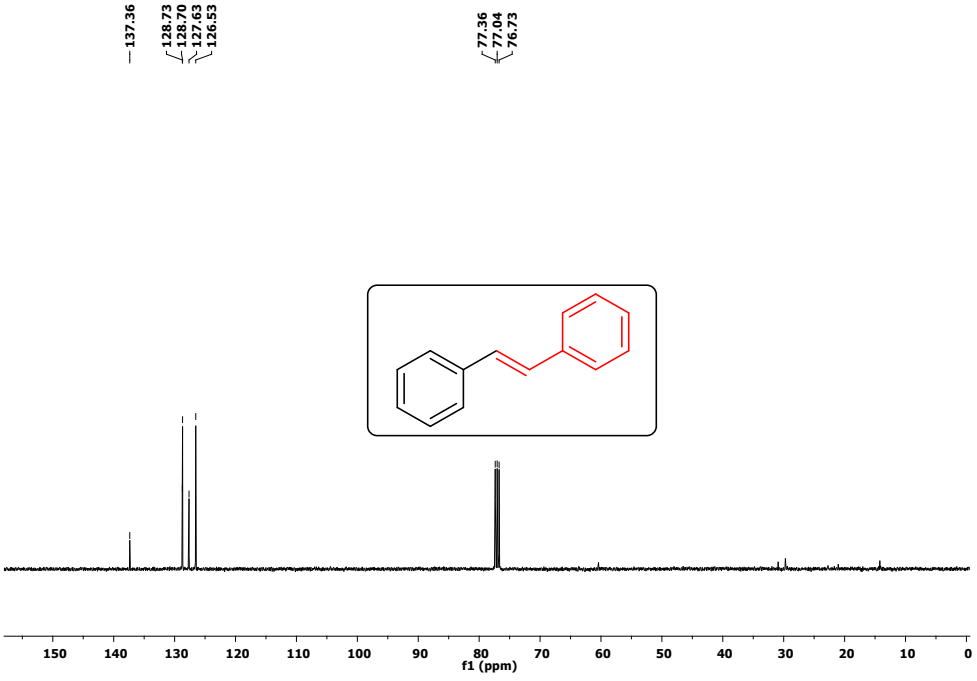

129.04
128.88
128.33
122.16
113.62
65.67
58.06
44.50
H
N
N
O
NMe2
145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

S4. ^{1}H NMR, ^{13}C NMR and DEPT-135 NMR of (E)-1,2-diphenylethene (5a):

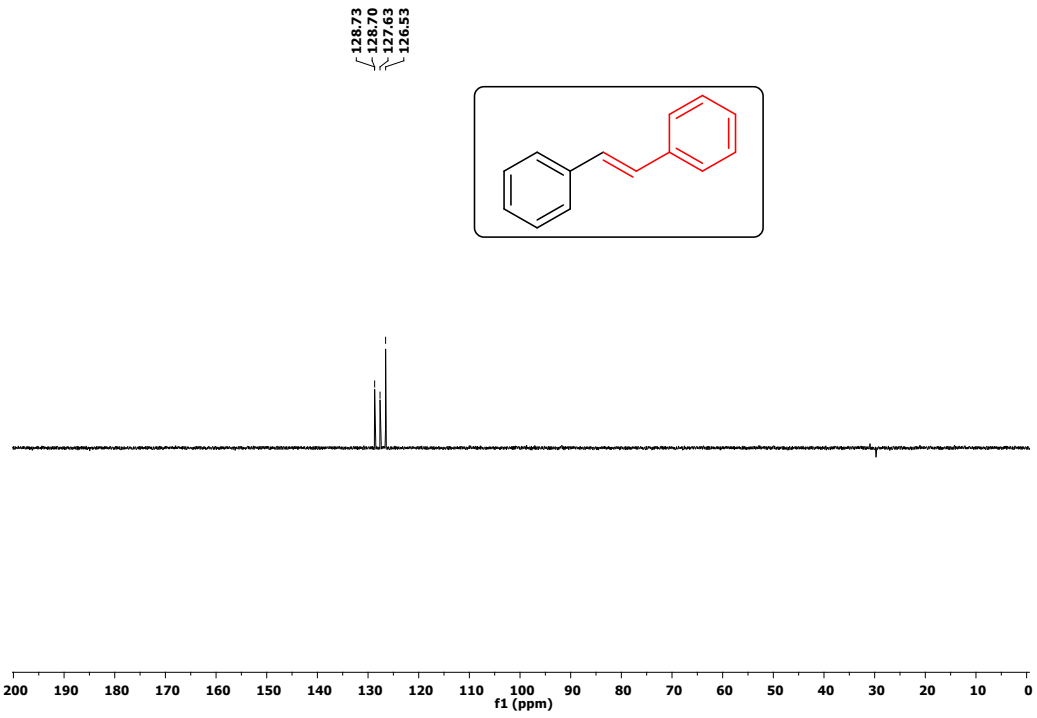
^{1}H NMR



^{13}C NMR

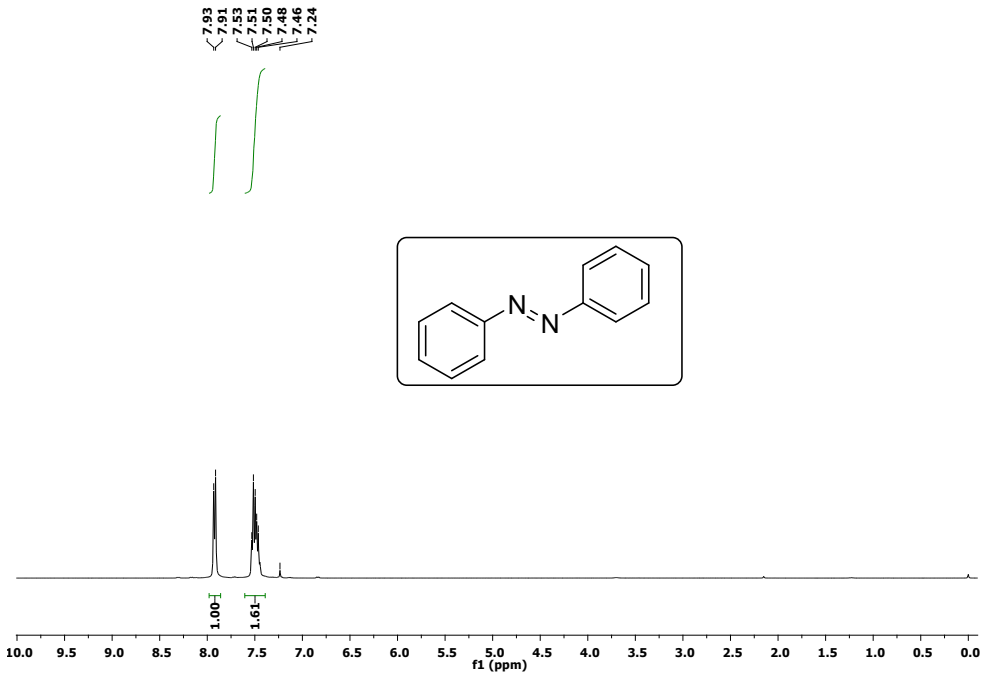


DEPT-135

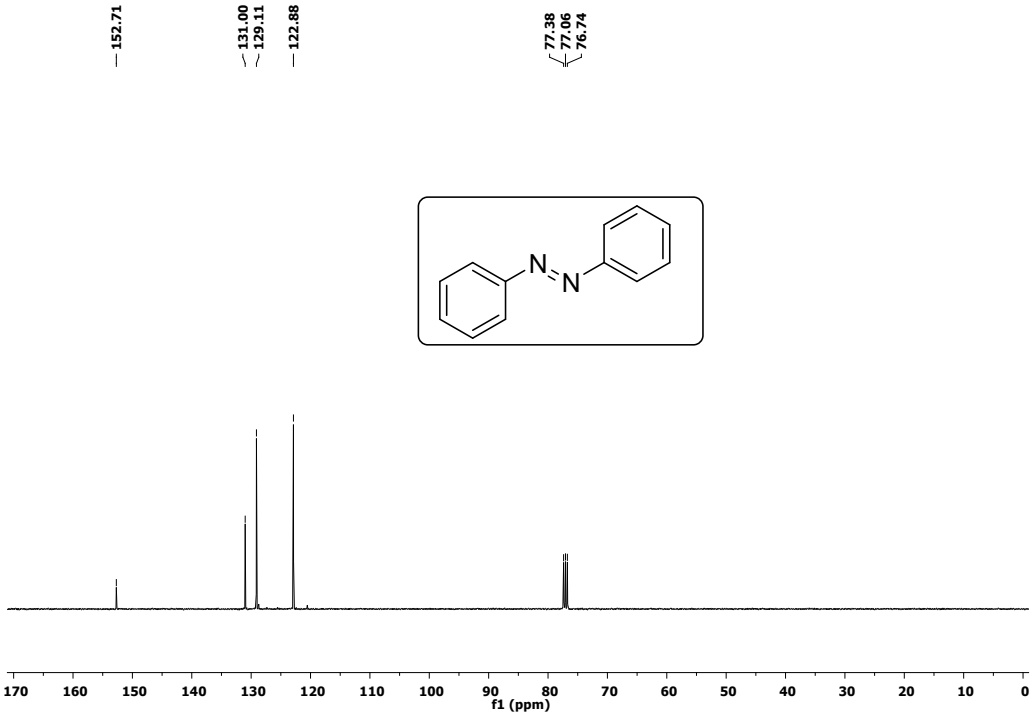

128.73
128.70
127.63
126.53
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S5. ^{1}H, ^{13}C and DEPT-135 NMR of (E)-1,2-diphenyldiazene (4a):

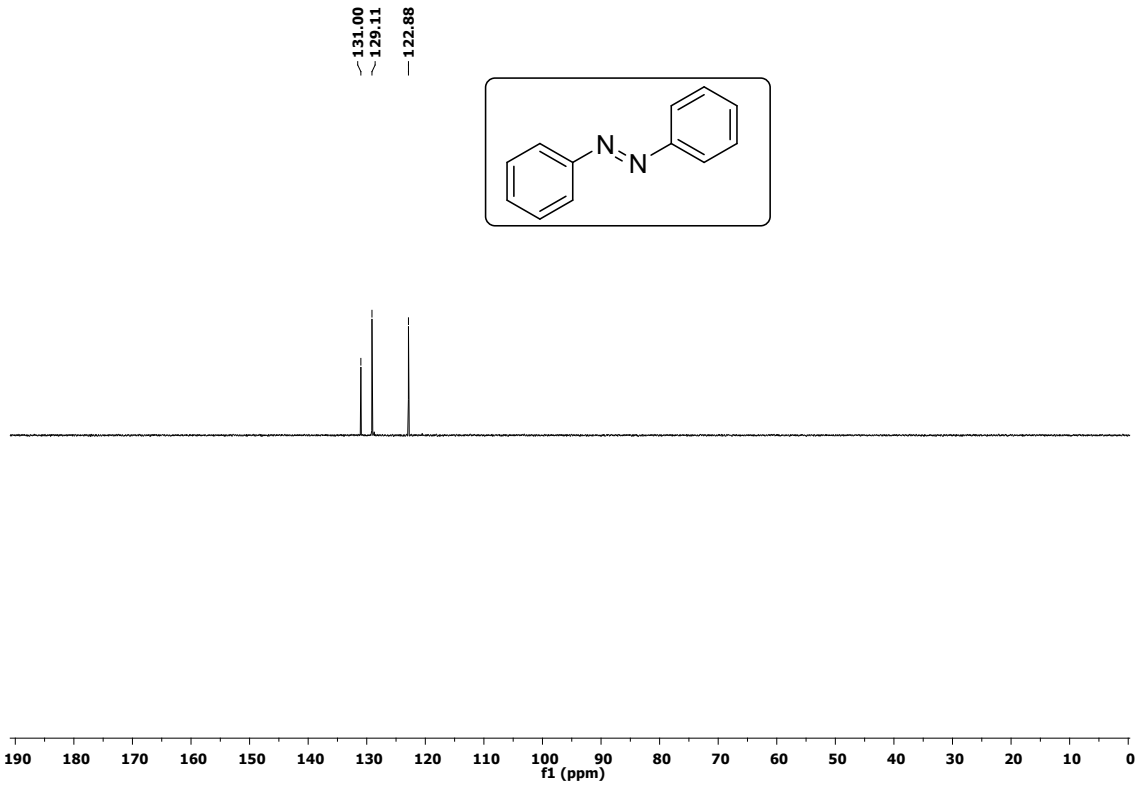
^{1}H NMR



^{13}C NMR



DEPT-135


131.00
129.11
122.88
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S6. Computational details

Absolute Free energies calculated using quantum chemical methods

The absolute free energy values of all the species involved in the proposed reaction mechanism were calculated using B3LYP/6-311+G(d,p) method and are given in Table S1. The compounds **IVb** and **V** are relatively stable in their cis configuration (w.r.t $OOH^{\cdot}$ group and $Co(acac)_2$ group) compared to its trans configuration. Hence, in the main scheme they are mentioned in cis configuration and the free energies of cis configuration are taken into consideration. The trans configurations of the compounds **IVb** and **V** are labelled as **IVb_trans** and **V_trans** and their absolute free energy values are given in Table S1. The free energy difference between the cis and trans configurations of compounds **IVb** and **V** were calculated to be 2.66 and 2.0 kcal/mol, respectively.

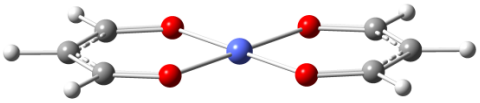
Table 1: Absolute free energy values of the species involved in the proposed reaction mechanism.

S. No.	Compound	Free Energy (kcal/mol)
1	**1a**	-342.916385
2	**2a**	-308.398494
3	**I**	-341.714712
4	**II**	-341.112554
5	**III**	-231.563402
6	**$Co(acac)_2$**	-678.354936
7	**Iva**	-986.11067
8	**IVb**	-1137.077129
9	**IVb_trans**	-1137.072883
10	**V**	-1368.758841
11	**V_trans**	-1368.75563
12	**VI**	-1513.928533
13	**VII**	-1293.012156

14	**VIII**	-1444.014675
15	**IX**	-1589.189523
14	**3a**	-689.977392
15	**N_2**	-109.572556
16	**O_2**	-150.324188
17	**HOO$^{\cdot}$**	-150.966083
18	**Ag_2O**	-366.76019
19	**AgO$^{\cdot}$**	-220.937
20	**AgOH**	-221.610543
21	**Ag$^{\cdot}$**	-145.775946
22	**H$^{\cdot}$**	-0.51281
23	**H_2O_2**	-151.597937

Cartesian coordinates of the species involved in the proposed reaction mechanism

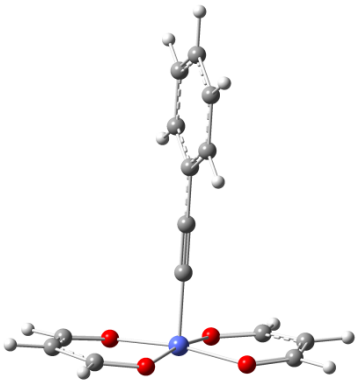
Co(acac)$_2$



```
0 2
 C                  2.55641000    1.21543600    0.00004000
 C                  3.24159800    0.00000000    0.00000500
 H                  4.32314300    0.00000000    0.00000800
 C                  2.55641000   -1.21543600   -0.00003200
 O                  1.29640000    1.37192200    0.00004100
 O                  1.29639900   -1.37192200   -0.00003800
 Co                 0.00000000    0.00000000   -0.00000100
 C                 -2.55641000    1.21543600    0.00003300
 C                 -3.24159800    0.00000000   -0.00000300
 H                 -4.32314300    0.00000000   -0.00000500
 C                 -2.55641000   -1.21543600   -0.00003900
 O                 -1.29640000    1.37192200    0.00003900
 O                 -1.29640000   -1.37192200   -0.00004300
```

H	3.13764300	-2.14356200	-0.00005900
H	3.13764400	2.14356200	0.00007000
H	-3.13764300	-2.14356200	-0.00006800
H	-3.13764300	2.14356200	0.00006100

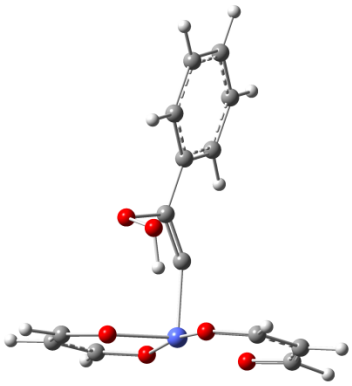
IVa



0 1

C	-1.78761700	-2.54018900	-1.21470700
C	-1.70128700	-3.21796200	0.00073100
H	-1.62131700	-4.29622200	0.00097500
C	-1.78760200	-2.53963700	1.21586300
O	-1.88303300	-1.28632000	-1.38100000
O	-1.88301800	-1.28569200	1.38158600
Co	-1.73637500	0.00000100	0.00000000
C	-1.78758400	2.53964600	-1.21586100
C	-1.70126700	3.21797100	-0.00073000
H	-1.62129500	4.29623100	-0.00097300
C	-1.78759300	2.54019700	1.21470700
O	-1.88300200	1.28570200	-1.38158500
O	-1.88301200	1.28632800	1.38100000
H	-1.80505200	-3.12660900	-2.13928600
H	-1.80502500	-3.12563600	2.14070800
H	-1.80500400	3.12564500	-2.14070700
H	-1.80502300	3.12661500	2.13928600
C	1.30715000	-0.00000800	0.00000000
C	2.73519800	-0.00000800	0.00000000
C	3.45418200	-0.00151700	-1.20883200
C	3.45418200	0.00150300	1.20883100
C	4.84520700	-0.00151100	-1.20514500
H	2.90822700	-0.00268400	-2.14468700
C	4.84520700	0.00150000	1.20514400
H	2.90822700	0.00266900	2.14468600
C	5.54749200	-0.00000400	0.00000000
H	5.38345500	-0.00268600	-2.14668200
H	5.38345400	0.00267700	2.14668100
H	6.63164600	-0.00000300	0.00000000
C	0.09538800	-0.00000800	0.00000000

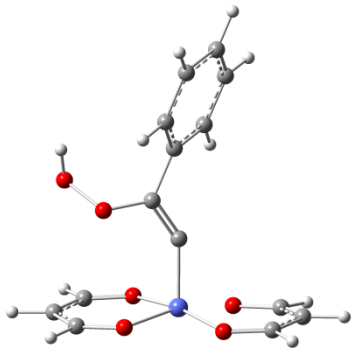
IVb



0 2

C	1.94959700	-2.52590700	0.86289600
C	2.10850800	-3.10739400	-0.39174000
H	2.18928800	-4.18307700	-0.46667600
C	2.23766400	-2.33289900	-1.54895000
O	1.83865100	-1.28591900	1.12061100
O	2.16757600	-1.07282000	-1.63238700
Co	1.71170500	0.08666100	-0.18399400
C	1.47452900	2.52654400	1.25370800
C	1.65801400	3.31030400	0.12155500
H	1.59438500	4.38566000	0.21799500
C	1.98610200	2.76101800	-1.12633000
O	1.52739000	1.25409500	1.32834400
O	2.08931600	1.53723600	-1.41105100
C	-1.22747400	-0.38372700	0.35293700
C	-2.62440400	-0.19997200	-0.08893700
C	-3.66418400	-0.29138800	0.84435500
C	-2.93031900	0.07237800	-1.43115300
C	-4.98453800	-0.10487900	0.44090300
H	-3.43033200	-0.50634900	1.87893300
C	-4.24922200	0.26233300	-1.82568900
H	-2.13260700	0.12259900	-2.16419800
C	-5.28268100	0.17476300	-0.89101700
H	-5.78185700	-0.17840400	1.17211000
H	-4.47385200	0.46965500	-2.86602100
H	-6.31148200	0.31743600	-1.20172900
C	-0.14656100	-0.05283500	-0.34254300
H	2.19551000	3.45353000	-1.95050000
H	1.28304300	3.03233300	2.20517600
H	1.93798200	-3.17567900	1.74332800
H	2.44536600	-2.84714300	-2.49400800
O	-1.02130100	-0.98770800	1.59776500
O	-0.81384200	0.04131800	2.62361300
H	0.13602800	0.22994900	2.49829700

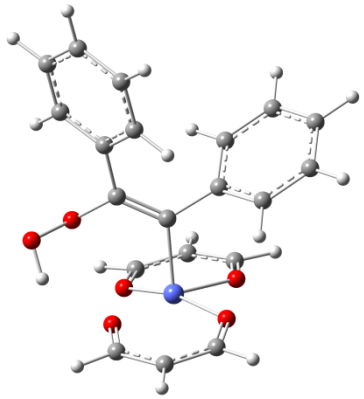
IVb_trans



0 2

C	-2.01241200	-2.45934500	-0.91408600
C	-2.02484300	-3.00496600	0.36753400
H	-2.07824700	-4.07839900	0.48369000
C	-1.97947300	-2.19835300	1.50331400
O	-1.94327500	-1.22966900	-1.22106800
O	-1.90352900	-0.93247500	1.53745200
Co	-1.74936500	0.19723200	0.01372200
C	-1.87070900	2.59671200	-1.48353500
C	-1.83732900	3.40638700	-0.34626000
H	-1.79686300	4.48032900	-0.46880900
C	-1.98008600	2.87561400	0.93866100
O	-1.92326900	1.33241500	-1.52188000
O	-2.04130300	1.65279300	1.25377100
H	-2.08734400	-3.13747700	-1.77023400
H	-2.02993100	-2.67993700	2.48563900
H	-1.88580200	3.08806400	-2.46330400
H	-2.08014200	3.57768400	1.77523900
C	1.19394700	-0.55430100	-0.22203500
C	2.56006600	-0.00711900	-0.04275900
C	3.55111300	-0.27794400	-0.99796500
C	2.87904600	0.78548000	1.06685100
C	4.83521100	0.23520500	-0.84163400
H	3.30339500	-0.87693700	-1.86737600
C	4.16129700	1.30952000	1.21073600
H	2.12085900	0.97369200	1.81779400
C	5.14326000	1.03381000	0.26059900
H	5.59426400	0.02088900	-1.58581000
H	4.39767500	1.92146900	2.07399800
H	6.14358400	1.43460000	0.37887000
C	0.10789700	0.16665400	0.01485700
O	1.06973600	-1.82426600	-0.77105000
O	1.58851400	-2.81838000	0.19896300
H	2.49449000	-2.93670500	-0.12537600

V

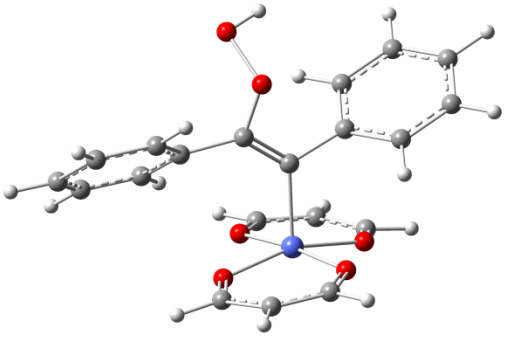


0 1

C	2.07127200	-0.34450500	-2.86525400
C	2.24740800	1.03746100	-2.96268200
H	2.33057900	1.49520200	-3.93888300
C	2.42159700	1.82011400	-1.82197900
O	1.95654100	-1.01815100	-1.79997000
O	2.35809000	1.42865600	-0.61754000
Co	1.85130400	-0.30979500	-0.04964700
C	1.90759400	-2.54155200	1.76088000
C	2.23216200	-1.75908500	2.86535600
H	2.38042200	-2.23742800	3.82378000
C	2.38234100	-0.37514700	2.76247600
O	1.71349900	-2.14626600	0.56810600
O	2.23420200	0.32965100	1.72243000
C	-0.95049200	-0.85958600	-0.40277300
C	-2.42192300	-0.82897600	-0.18882100
C	-3.26606700	-1.39713300	-1.15442000
C	-2.99522300	-0.28732000	0.96888300
C	-4.64625500	-1.39509300	-0.97832200
H	-2.82874800	-1.84544600	-2.03760300
C	-4.37563800	-0.28842600	1.14458600
H	-2.35752300	0.12778200	1.73877300
C	-5.20775200	-0.83774800	0.16980800
H	-5.28449300	-1.83430200	-1.73719600
H	-4.80179500	0.13199400	2.04882700
H	-6.28317000	-0.84017800	0.30854800
C	-0.06360700	0.08605800	-0.02761300
H	2.66298800	0.18180300	3.66453700
H	1.81326600	-3.62291100	1.91346100
H	2.05720500	-0.93558400	-3.78747700
H	2.66515100	2.88031800	-1.94801900
C	-0.43725700	1.48111800	0.26284500
C	-0.19440800	2.11972800	1.48961100
C	-1.07549900	2.22007400	-0.75202100
C	-0.59827100	3.43342600	1.70137800
H	0.31474100	1.58242900	2.27546500
C	-1.47351900	3.53555300	-0.54052400
H	-1.26583600	1.74397900	-1.70647700
C	-1.23767800	4.14904700	0.68903400

H	-0.40960300	3.90306100	2.66054800
H	-1.97142900	4.08064800	-1.33498100
H	-1.54719100	5.17459900	0.85670100
O	-0.50074700	-1.91346700	-1.16322500
O	-0.70904100	-3.19647500	-0.46355300
H	0.20717000	-3.30113100	-0.15219100

V_trans

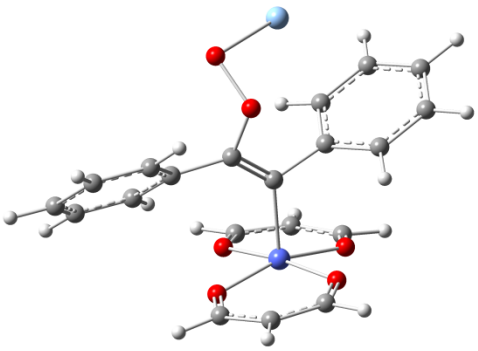


0 1

C	0.97352600	-1.54654800	-2.74550400
C	2.34705100	-1.65562000	-2.54018700
H	3.00619100	-1.70439900	-3.39618000
C	2.88635100	-1.76152200	-1.25523800
O	0.06771100	-1.49261500	-1.85743400
O	2.24953400	-1.70929600	-0.16419500
Co	0.35466300	-1.46238600	0.02720300
C	-2.13582900	-1.97578600	1.28044100
C	-1.60280100	-1.95431600	2.57010700
H	-2.25974700	-2.09177700	3.41790800
C	-0.23244100	-1.82030200	2.78230700
O	-1.49876000	-1.81791600	0.19700100
O	0.66381800	-1.66310000	1.89755800
C	-0.76646300	1.26156500	0.15603400
C	-2.18379500	1.04165000	-0.21094800
C	-3.18894900	1.58234700	0.60434200
C	-2.55240200	0.37546200	-1.38501600
C	-4.53101000	1.43327500	0.26839300
H	-2.90838100	2.12582300	1.49822400
C	-3.89525000	0.23548100	-1.72460800
H	-1.78535800	-0.04681100	-2.01890600
C	-4.88939000	0.75872900	-0.89904900
H	-5.29682100	1.85207100	0.91205400
H	-4.16538400	-0.28181600	-2.63874900
H	-5.93471100	0.65070800	-1.16730700
C	0.32582500	0.47317700	0.15671300
H	0.14103300	-1.87441500	3.81101700
H	-3.20840400	-2.16030000	1.16053800
H	0.60598400	-1.52386700	-3.77762500

H	3.96645900	-1.91782400	-1.15682100
C	1.67766500	1.05318400	0.31486800
C	2.42759200	0.93516300	1.49433100
C	2.23302800	1.76616200	-0.76198700
C	3.67854900	1.53262200	1.60073800
H	2.02558100	0.36509700	2.32041800
C	3.48980000	2.35856600	-0.65516800
H	1.67148900	1.84678800	-1.68609500
C	4.21673600	2.24597200	0.52857100
H	4.23897000	1.44026600	2.52462100
H	3.90015700	2.90658000	-1.49655000
H	5.19385900	2.70792700	0.61532800
O	-0.52528000	2.53157200	0.68896900
O	-0.77821500	3.56479800	-0.34108800
H	0.13598000	3.84727800	-0.49766800

VI



0 1

C	0.72351800	-2.04270900	2.86115200
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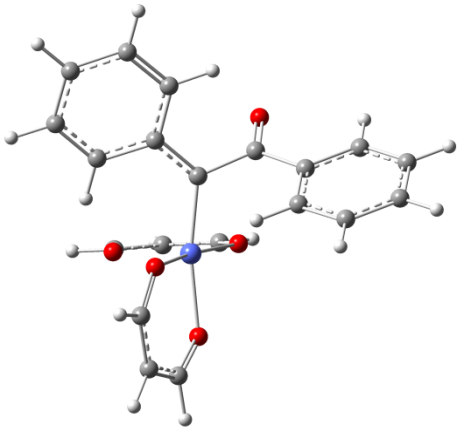
H	-0.76411400	-3.44174300	3.50669800
C	-0.53142500	-3.51403600	1.37624100
O	1.42915000	-1.46765200	1.97969100
O	-0.02608100	-3.12121500	0.28535500
Co	1.30953300	-1.74792200	0.09154800
C	3.61800800	-0.61087800	-1.08749500
C	3.27870700	-1.02158300	-2.37793700
H	3.91888300	-0.74968000	-3.20591800
C	2.16480700	-1.82426100	-2.61127500
O	2.96784700	-0.84342700	-0.02618200
O	1.32260500	-2.22952500	-1.75206400
C	0.43784200	1.06552800	-0.35412200
C	1.60943500	1.85697900	0.08366000
C	2.05638200	2.90594300	-0.73298000
C	2.24684600	1.63785800	1.30972000
C	3.13491200	3.69496500	-0.34656200
H	1.53929700	3.10226100	-1.66374500
C	3.32161600	2.43309800	1.69876200

H	1.90700300	0.83578100	1.94995400
C	3.77345000	3.46064200	0.87176000
H	3.47056800	4.50062800	-0.99052300
H	3.80488100	2.25184400	2.65282400
H	4.60854800	4.08131500	1.17845500
C	0.12338200	-0.24337900	-0.24734900
H	1.98369100	-2.17432900	-3.63382900
H	4.54326000	-0.04304800	-0.94528600
H	0.93254300	-1.73564500	3.89259200
H	-1.25542700	-4.33237500	1.28667200
C	-1.26586500	-0.68796100	-0.51332900
C	-1.70010100	-1.18390000	-1.74802000
C	-2.22023700	-0.58895600	0.52922800
C	-3.03708200	-1.51382000	-1.96220500
H	-0.97994000	-1.29998800	-2.54609700
C	-3.56980700	-0.92923200	0.31336100
H	-1.87632600	-0.34554200	1.52885000
C	-3.97982600	-1.38058500	-0.94370500
H	-3.34639900	-1.87676400	-2.93611500
H	-4.27180700	-0.89778300	1.14037600
H	-5.01647800	-1.64548600	-1.11667900
O	-0.50613100	1.78796200	-1.06621800
O	-1.09705100	2.85655500	-0.24576900
Ag	-2.91240000	1.79029500	0.24256100

VII

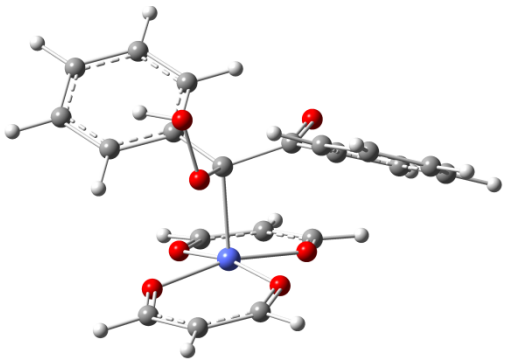


0 2

C	2.09076400	-2.85869400	-1.60256200
C	2.19702300	-2.03089200	-2.73151100
H	2.67170800	-2.42008800	-3.62262900
C	1.65768400	-0.74923300	-2.76813500
O	1.56303300	-2.55949000	-0.50114800
O	1.06728600	-0.12239300	-1.83155200
Co	0.82337700	-0.78879100	-0.01028400
C	1.07703900	-1.71558900	2.65672900

C	2.37387900	-1.22753100	2.81884100
H	2.86198000	-1.42470500	3.76522600
C	3.09764500	-0.50400300	1.85319400
O	0.30752500	-1.61458600	1.65318700
O	2.72037700	-0.16891400	0.70237100
C	-1.50050200	0.46909900	1.05937500
C	-2.60444200	-0.20668300	0.32441700
C	-3.77332100	-0.54303900	1.02008600
C	-2.50632800	-0.48586500	-1.04497000
C	-4.82824300	-1.15310900	0.35379300
H	-3.82927000	-0.32118600	2.07897700
C	-3.56859400	-1.09211700	-1.71093000
H	-1.60454600	-0.22911800	-1.59116600
C	-4.72707800	-1.42791900	-1.01240700
H	-5.72969900	-1.41848700	0.89435200
H	-3.49049700	-1.30691500	-2.77042900
H	-5.55166500	-1.90502200	-1.53043200
C	-0.20574900	0.73875100	0.36783900
H	4.11548500	-0.19707300	2.14408000
H	0.64621000	-2.26491000	3.50314200
H	2.48824900	-3.87985000	-1.68390500
H	1.72542500	-0.19882600	-3.71490600
C	0.11019000	2.09352100	0.04132400
C	1.41585300	2.43980300	-0.39360100
C	-0.86444600	3.12519700	0.13301900
C	1.72220200	3.75195200	-0.72109300
H	2.17121600	1.66895600	-0.43312800
C	-0.55290900	4.42804400	-0.21078100
H	-1.86319700	2.88781900	0.47720300
C	0.74195200	4.74226400	-0.63805900
H	2.72559600	4.00868700	-1.04005100
H	-1.30635700	5.20397000	-0.14368400
H	0.98639000	5.76605300	-0.90042100
O	-1.57870900	0.78592100	2.23689700

VIII

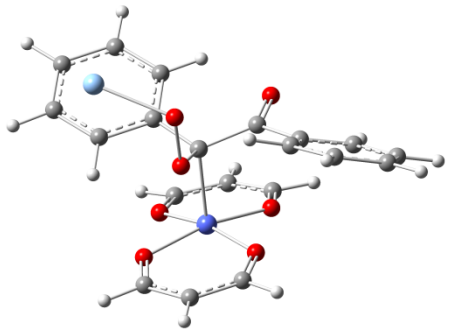


0 1

C	1.92097800	2.48974200	-0.48104100

C	1.17510600	3.23599600	-1.39468000
H	1.68763400	3.90111000	-2.07614600
C	-0.21507900	3.16062300	-1.43393900
O	1.47389500	1.68107000	0.38480700
O	-0.96145400	2.43039200	-0.71286200
Co	-0.35219100	1.23896000	0.65430100
C	-0.50342500	-0.01402800	3.19685700
C	-1.89749200	-0.01754100	3.22160600
H	-2.41009900	-0.45952900	4.06485300
C	-2.64281800	0.58653200	2.20872400
O	0.24041200	0.46534200	2.28873600
O	-2.19081100	1.13371000	1.15950100
C	0.74681700	-1.36297800	0.22343300
C	2.23172700	-1.27070000	-0.01381500
C	3.03070700	-1.44450900	1.12755800
C	2.85797900	-1.11115500	-1.25665800
C	4.41654400	-1.43027500	1.03773500
H	2.54490800	-1.57825200	2.08493600
C	4.24942400	-1.12178300	-1.34566700
H	2.27702700	-1.00956000	-2.15883000
C	5.03262600	-1.27015000	-0.20365200
H	5.01642800	-1.54782200	1.93335200
H	4.72031900	-1.01609100	-2.31688900
H	6.11457200	-1.26748300	-0.27968100
C	-0.26678100	-0.46652200	-0.50724200
H	-3.73275100	0.61904400	2.31394900
H	0.03114800	-0.44400600	4.05022400
H	3.00964200	2.60805500	-0.47796800
H	-0.74728000	3.79819900	-2.14896300
C	-1.66670700	-0.98302800	-0.73419100
C	-2.16666400	-2.18941300	-0.21989400
C	-2.51011400	-0.22349200	-1.57077700
C	-3.45305700	-2.61995500	-0.54338300
H	-1.54988900	-2.79121400	0.42811200
C	-3.78880700	-0.65923300	-1.89235300
H	-2.16491400	0.73717700	-1.92980900
C	-4.26961700	-1.86491100	-1.37987100
H	-3.81168600	-3.56020500	-0.13908100
H	-4.41695900	-0.04938700	-2.53228900
H	-5.26797900	-2.20728000	-1.62848000
O	0.34653400	-2.12634800	1.08530000
O	0.23927200	0.13783400	-1.67361300
O	0.25059300	-0.83966600	-2.78065100
H	-0.66658400	-0.78266900	-3.09564300

IX

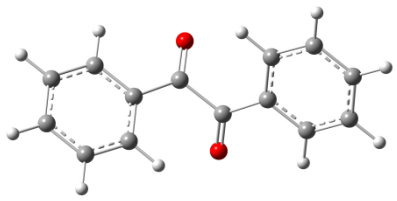


0 1

C	-2.45551500	-0.25165600	2.43923000
C	-1.51124400	-0.43423200	3.45177500
H	-1.74923700	-1.08050400	4.28556200
C	-0.27865600	0.21062600	3.42171700
O	-2.33219200	0.47228600	1.40934500
O	0.15672800	0.99024300	2.51871400
Co	-0.79425000	1.47344200	0.93307100
C	-1.61380600	3.25070200	-1.12624200
C	-0.43480300	3.99746700	-1.08689700
H	-0.31128600	4.82459700	-1.77258300
C	0.56077300	3.73731800	-0.14561300
O	-1.91500600	2.26639000	-0.38930000
O	0.56904100	2.80472000	0.71204700
C	-1.04539400	-0.20295100	-1.38070000
C	-2.27204000	-1.05939800	-1.20296900
C	-3.43889700	-0.56656000	-1.80823000
C	-2.31829900	-2.30028600	-0.55427700
C	-4.63091900	-1.27736700	-1.74365000
H	-3.39737800	0.38725000	-2.31736300
C	-3.51205700	-3.01949700	-0.51144800
H	-1.41681500	-2.71402200	-0.12486100
C	-4.67142400	-2.51077600	-1.09303800
H	-5.52657300	-0.87233100	-2.20184600
H	-3.53113200	-3.98795500	-0.02286900
H	-5.59814400	-3.07300900	-1.04716300
C	-0.00019600	-0.01443400	-0.26319200
H	1.43155100	4.40219800	-0.11569500
H	-2.38537600	3.54131400	-1.84737800
H	-3.41997300	-0.76276400	2.52797100
H	0.40463200	0.05574900	4.26465400
C	1.39597400	0.43929900	-0.64555400
C	1.80430800	0.85771400	-1.91869500
C	2.38489300	0.37723000	0.36975800
C	3.14090100	1.18001800	-2.17509400
H	1.07674500	0.92358200	-2.71150900
C	3.72106100	0.69239900	0.10375100
H	2.06619700	0.17520400	1.38466400
C	4.10682200	1.09377700	-1.17999400
H	3.42142700	1.49681700	-3.17376600
H	4.44427400	0.67380100	0.91214600

H	5.14003100	1.34765200	-1.38809700
O	-0.93145800	0.43192500	-2.41683700
O	0.05244100	-1.05143900	0.66159200
O	0.55222800	-2.26492100	-0.01101000
Ag	2.72324800	-2.11724500	0.01223400

3a

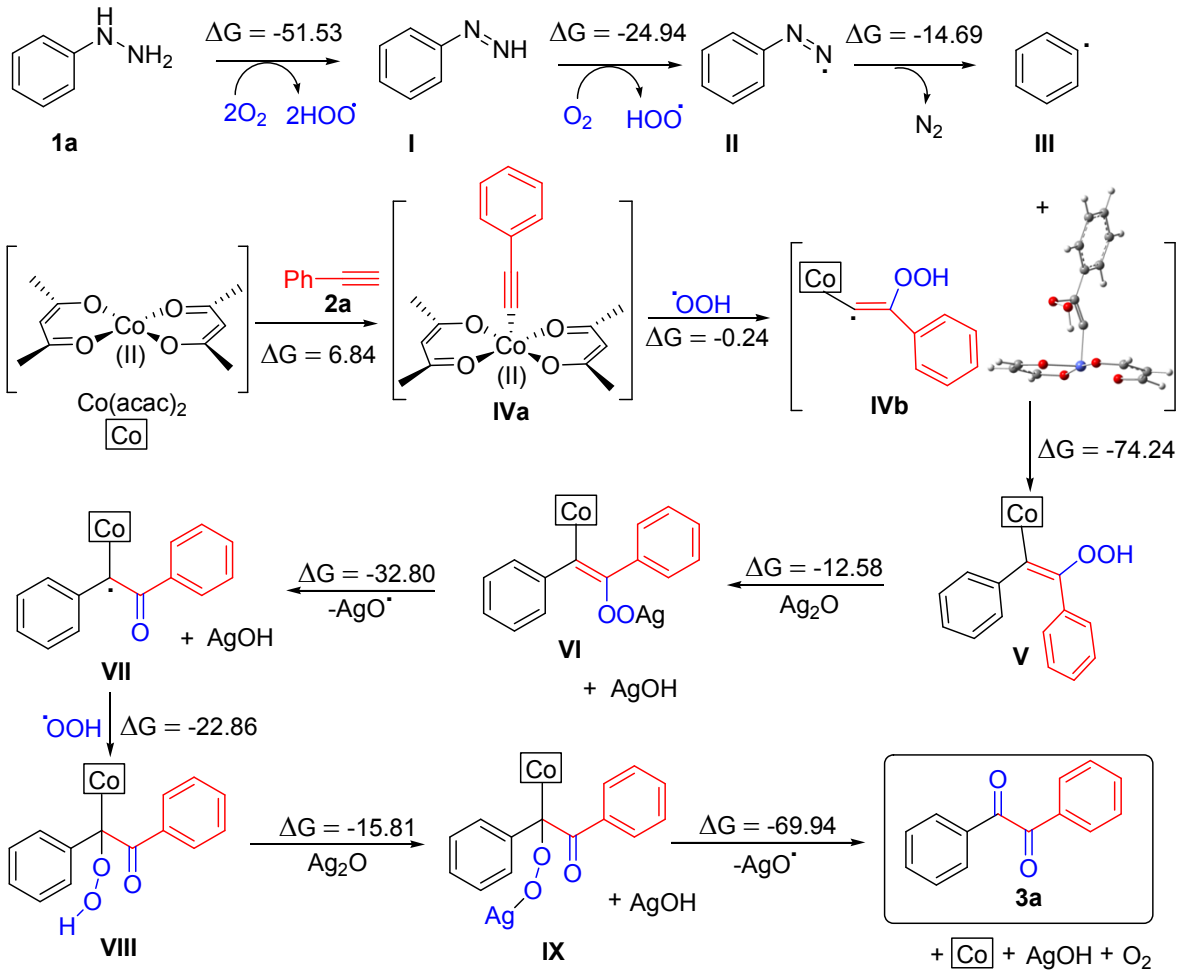


0 1

C	3.30872100	-1.31057000	-1.04363400
C	2.08084300	-1.04666700	-0.44287600
C	1.87410200	0.16658700	0.22857500
C	2.91235900	1.10884000	0.28832900
C	4.13584300	0.84075600	-0.31023900
C	4.33511700	-0.36999700	-0.97826400
H	3.46558800	-2.25136700	-1.55834900
H	1.29421100	-1.78876500	-0.48221100
H	2.73613900	2.04208700	0.80933900
H	4.93566100	1.57065600	-0.25958700
H	5.29097700	-0.57906500	-1.44566700
C	0.57105500	0.51889900	0.85244500
C	-0.57105300	-0.51888300	0.85245300
C	-1.87410100	-0.16658300	0.22857700
C	-2.08084900	1.04666600	-0.44288300
C	-2.91235300	-1.10884100	0.28833700
C	-3.30872900	1.31055700	-1.04364200
H	-1.29422200	1.78876700	-0.48222400
C	-4.13583800	-0.84076800	-0.31023200
H	-2.73612700	-2.04208400	0.80935500
C	-4.33511900	0.36997900	-0.97826600
H	-3.46560200	2.25135000	-1.55836400
H	-4.93565200	-1.57067300	-0.25957600
H	-5.29098000	0.57903800	-1.44567000
O	0.36960900	1.57598300	1.42129200
O	-0.36960600	-1.57595700	1.42131800

S6. Plausible mechanism based on thereotical calculations

On the basis of these results and previous work, we proposed a reaction mechanism for coupling of phenylacetylenes and phenyl hydrazine as depicted in Scheme 2,[3-8] and verified its feasibility using quantum chemical analysis (B3LYP/6-311+G(d,p)). The reaction possibly involves *in situ* C−H activation of terminal alkynes which proceeds via free-radical formation to give 1,2-dicarbonyl compound **3a**. Phenyl hydrazine acts as a radical source. Under oxidative condition, it leads to the formation of phenyl radical **III**.[8-13] The electron-rich phenylacetylene (**2a**) reacts with $Co(acac)_2$ to form cobalt(II)-phenyl acetylene complex **IVa**. Formation of similar complex has been earlier reported.[14] The atmospheric oxygen acts as an oxygen donor, which undergoes hydrogen peroxy radical linkage with complex **IVa** to give colbalt (II)-styryl complex **IVb**. The complex **IVb** upon coupling with phenyl radical **III** gives cobalt (II) stilbene intermediate **V**. The Ag· radical (formed from Ag_2O) couples with the peroxy radical to form cobalt (II) stilbene silver peroxy linkage **VI**. The elimination of silver oxide radical (AgO·) produces cobalt (II) 2-phenylacetophenone radical **VII**. The generated cobalt (II) 2-phenylacetophenone radical then couples with hydrogen peroxide radical to form cobalt (II) hydrogen peroxy 2-phenylacetophenone **VIII** followed by silver oxide mediated coupling to give cobalt (II) silver peroxy linkage 2-phenylacetophenone **IX**. Finally elimination of silver oxide radical (which may react with hydrogen peroxide radical to give silver hydroxide and molecular oxygen) and $Co(acac)_2$ leads to the formation of 1,2-diketone **3a**. It is interesting to note that all the steps in the above mentioned reaction mechanism are exergonic, except the formation of **IV** (which is endergonic). The possibility of free-radical mechanism was investigated by performing reaction in the presence of free-radical quencher TEMPO. Reaction performed in presence of TEMPO produced trace amounts of product **3a**. This observation clearly indicated that the reaction involves free-radical mechanism.



Scheme S1. Plausible reaction mechanism with corresponding free energy values at each step. The reaction **V** → **VI** and **VIII** → **IX** are associated with the initial conversion $Ag_2O \rightarrow Ag^{\cdot} + AgO^{\cdot}$. The $AgO^{\cdot}$ generated during **VI** → **VII** and **IX** → **3a** is expected to undergo $AgO^{\cdot} + HOO^{\cdot} \rightarrow AgOH + O_2$ reaction which is exoergic by 19.86 kcal/mol. The free energy values in the above scheme are given in kcal/mol. A model system of $Co(acac)_2$ with no methyl groups, was used for the quantum chemical calculations. The 3D structure of the optimized **IVb** is shown. On a potential energy surface, this species (**IVb**) could be identified and is stable. The Co-C=C- angle in the optimized **IVb** structure is 141˚. Hence, the angle has been elongated for **IVb** structure in scheme 2. This angle could have been even more than 141º or could have even been linear, but the intramolecular hydrogen bond interaction of –OOH and oxygens from $Co(acac)_2$ renders it to have a bent shaped structure. This intramolecular hydrogen bond gives this structure an extra stability. The absolute energy calculations and 3D coordinates are provided in the section S3 of supporting information.

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