

Supporting Information

Zinc Salt-Catalyzed Reduction of α -Aryl Imino Esters, Diketones and Phenylacetylenes with Water as Hydrogen Source

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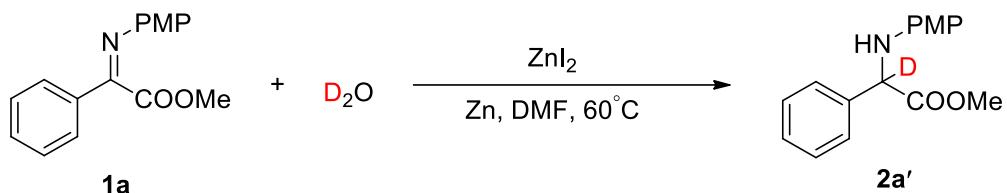
[†] *These authors contributed equally.*

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A: Procedure for the reactions

A1. Typical procedure for the transfer deuteration of α -aryl imino esters:

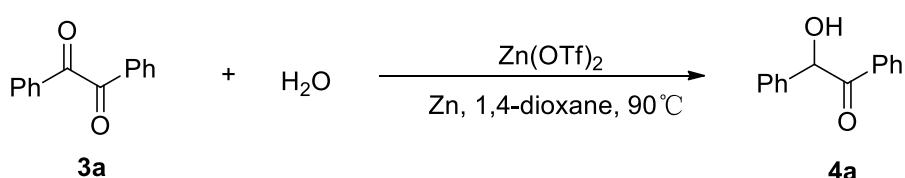


ZnI_2 (6.4 mg, 0.02 mmol), α -aryl imino esters **1a** (53.9 mg, 0.2 mmol), Zinc powder (325 mesh, 39 mg, 0.6 mmol), D_2O (20 μL , 1.0 mmol) and 2.0 mL anhydrous DMF were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 60 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified by chromatography on a silica gel column (ethyl acetate / petroleum ether, 1 / 20) to afford the desired product **2a'** (95% yield, 98% D).

Gram scale reactions:

ZnI_2 (118.4 mg, 0.371 mmol), α -aryl imino esters **1a** (1.0 g, 3.71 mmol), Zinc powder (325 mesh, 727.7 mg, 11.13 mmol), D_2O (337.3 μL , 18.55 mmol) and 36 mL anhydrous DMF were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 60 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified by chromatography on a silica gel column (ethyl acetate / petroleum ether, 1 / 20) to afford the desired product **2a'** (93% yield, 99% D).

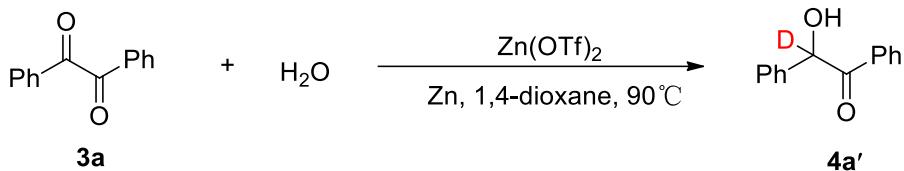
A2. Typical procedure for the transfer hydrogenation of 1, 2 - diphenylethane - 1, 2 - dione:



$Zn(OTf)_2$ (7.3 mg, 0.02 mmol), 1, 2 - diphenylethane - 1, 2 - dione **3a** (42.0 mg, 0.2 mmol), Zinc powder (325 mesh, 39 mg, 0.6 mmol), H_2O (18 μL , 1.0 mmol) and 2.0 mL anhydrous 1,4-Dioxane were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 90 °C under argon atmosphere with TLC monitoring until

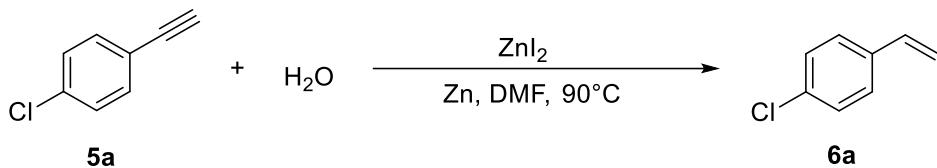
the complete consumption of **3a**. The residue was purified by chromatography on a silica gel column (ethyl acetate / petroleum ether, 1 / 5) to afford the desired product **4a** (95% yield).

A3. Typical procedure for the transfer deuteration of 1, 2 – diphenylethane – 1, 2 - dione:



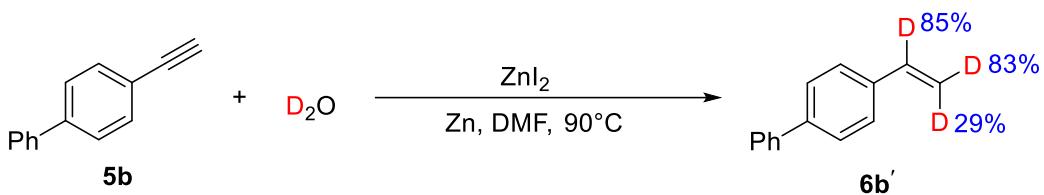
$\text{Zn}(\text{OTf})_2$ (7.3 mg, 0.02 mmol), 1, 2 - diphenylethane - 1, 2 - dione **3a** (42.0 mg, 0.2 mmol), Zinc powder (325 mesh, 39 mg, 0.6 mmol), D_2O (18 μL , 1.0 mmol) and 2.0 mL anhydrous 1,4-Dioxane were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 90°C under argon atmosphere with TLC monitoring until the complete consumption of **3a**. The residue was purified by chromatography on a silica gel column (ethyl acetate / petroleum ether, 1 / 5) to afford the desired product **4a'** (94% yield, 91% D).

A4. Typical procedure for the transfer hydrogenation of 1 – chloro – 4 – ethynyl benzene:



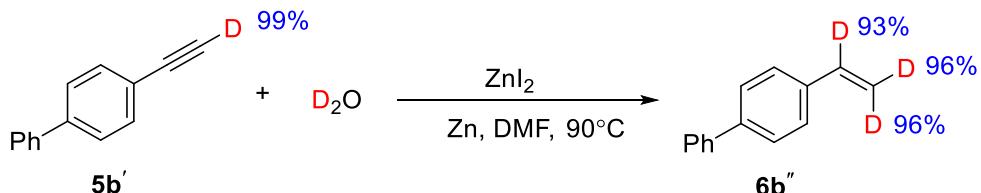
ZnI_2 (6.4 mg, 0.02 mmol), 1-chloro-4-ethynylbenzene **5a** (35.6 mg, 0.2 mmol), Zinc powder (325 mesh, 39 mg, 0.6 mmol), H_2O (18 μL , 1.0 mmol) and 2.0 mL anhydrous DMF were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 90°C under argon atmosphere with TLC monitoring until the complete consumption of **5a**. The mixture was extracted with Et_2O . The organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified by chromatography on a silica gel column (*n*-Hexane) to afford the desired product **6a** (94% yield).

A5. Typical procedure for the transfer deuteration of 4-Ethynyl-1,1'-biphenyl:



ZnI_2 (6.4 mg, 0.02 mmol), 4-Ethynyl-1,1'-biphenyl **5b** (35.6 mg, 0.2 mmol), Zinc powder (325 mesh, 39 mg, 0.6 mmol), D_2O (18 μL , 1.0 mmol) and 2.0 mL anhydrous DMF were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 90 $^\circ\text{C}$ under argon atmosphere with TLC monitoring until the complete consumption of **5b**. The mixture was extracted with Et_2O . The organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified by chromatography on a silica gel column (*n*-Hexane) to afford the desired product **6b'** (90% yield).

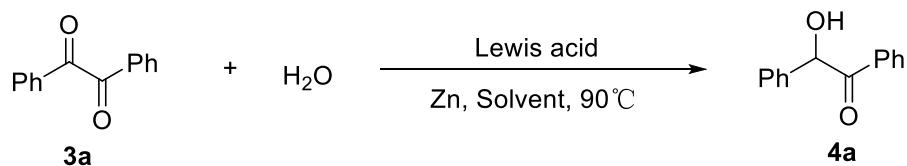
A₆. Typical procedure for the transfer deuteration of 4-Ethynyl-1,1'-biphenyl-*d*:



ZnI_2 (6.4 mg, 0.02 mmol), 4-Ethynyl-1,1'-biphenyl-*d* **5b'** (35.8 mg, 0.2 mmol), Zinc powder (325 mesh, 39 mg, 0.6 mmol), D_2O (18 μL , 1.0 mmol) and 2.0 mL anhydrous DMF were added to a Schlenk tube under argon atmosphere. The mixture was stirred at 90 $^\circ\text{C}$ under argon atmosphere with TLC monitoring until the complete consumption of **5b'**. The mixture was extracted with Et_2O . The organic layers were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified by chromatography on a silica gel column (*n*-Hexane) to afford the desired product **6b''** (95% yield).

B: Optimization Table

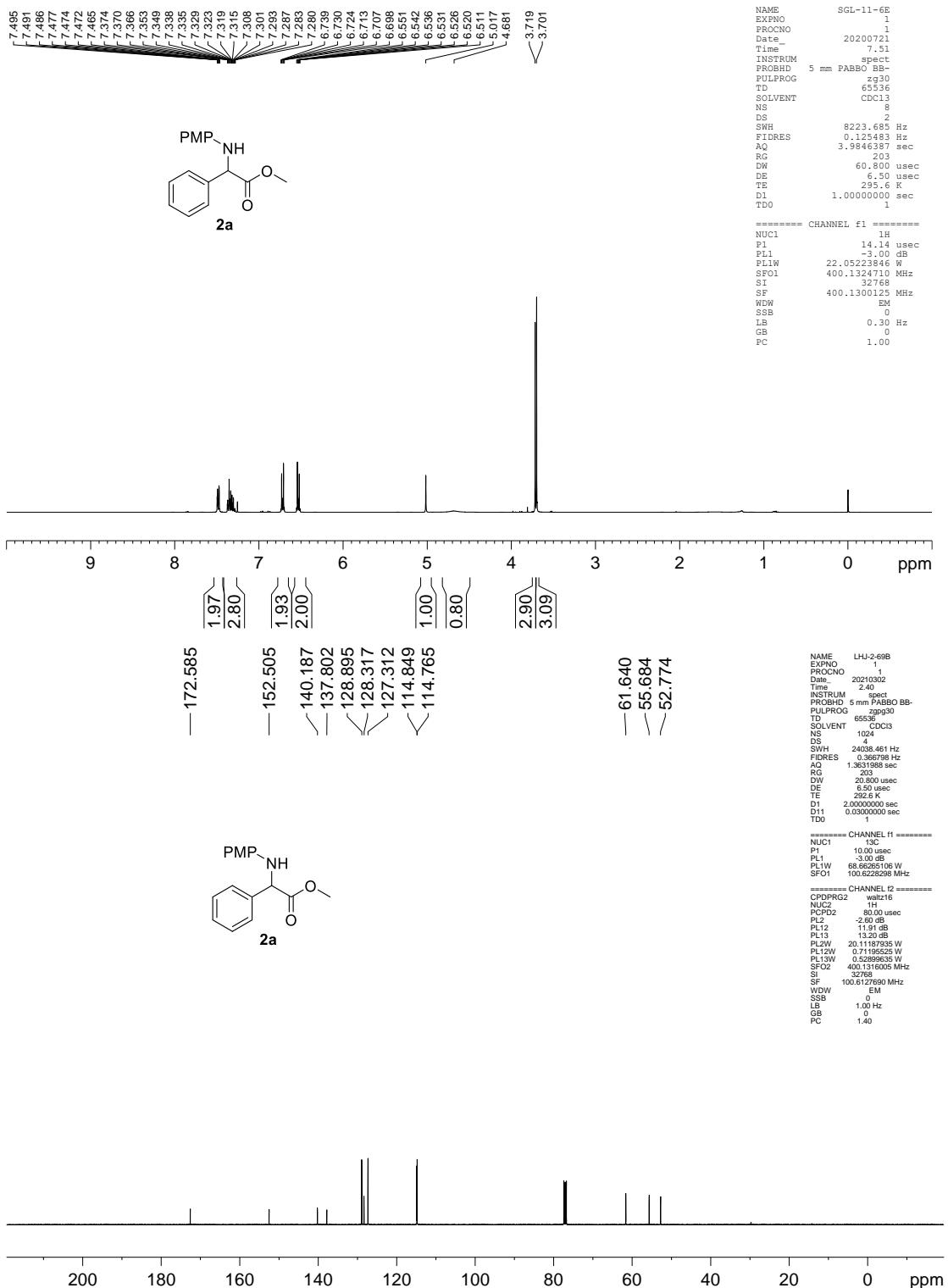
Table S1. Reaction conditions optimization for the reduction of **3a**.^a

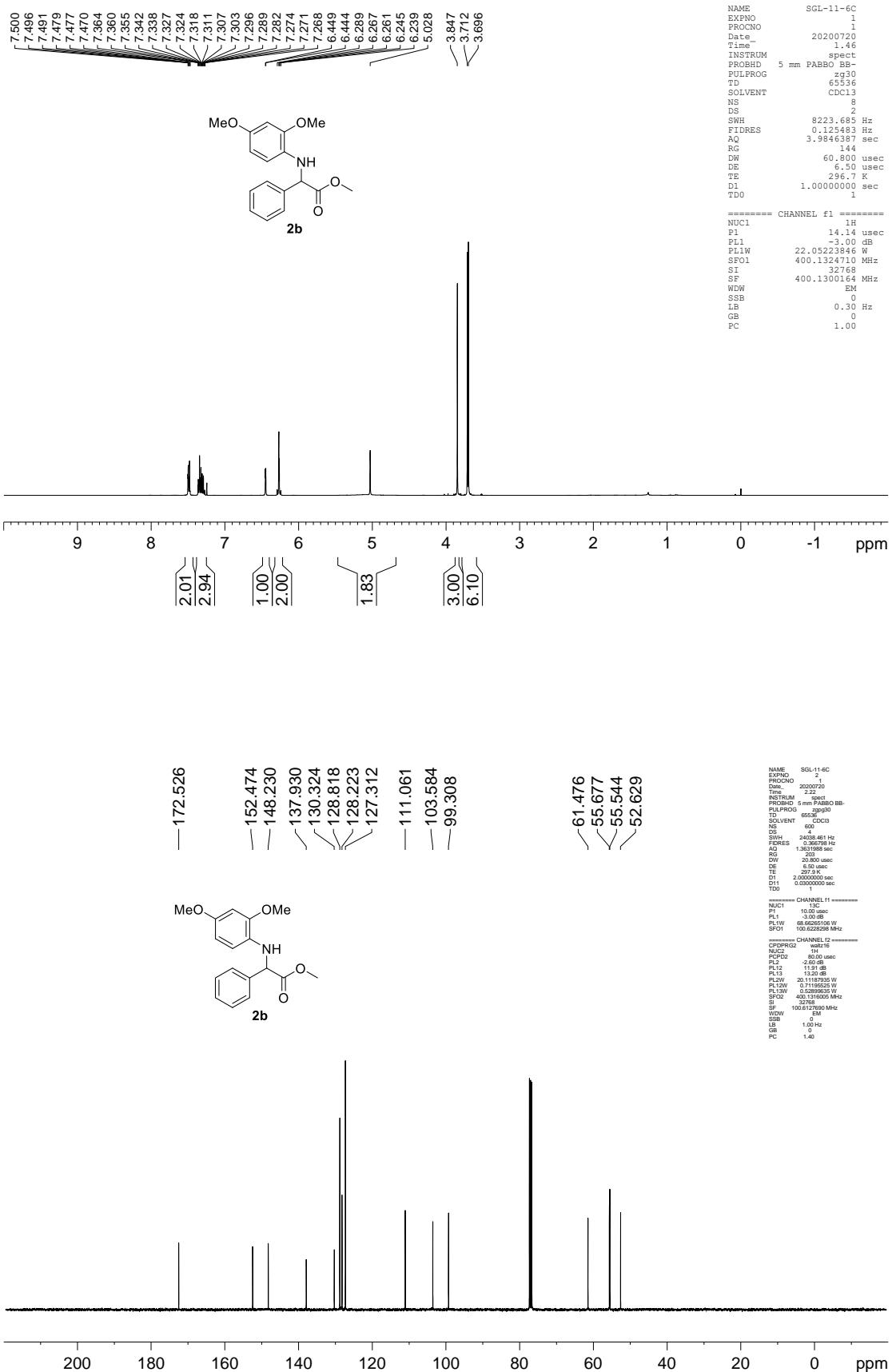


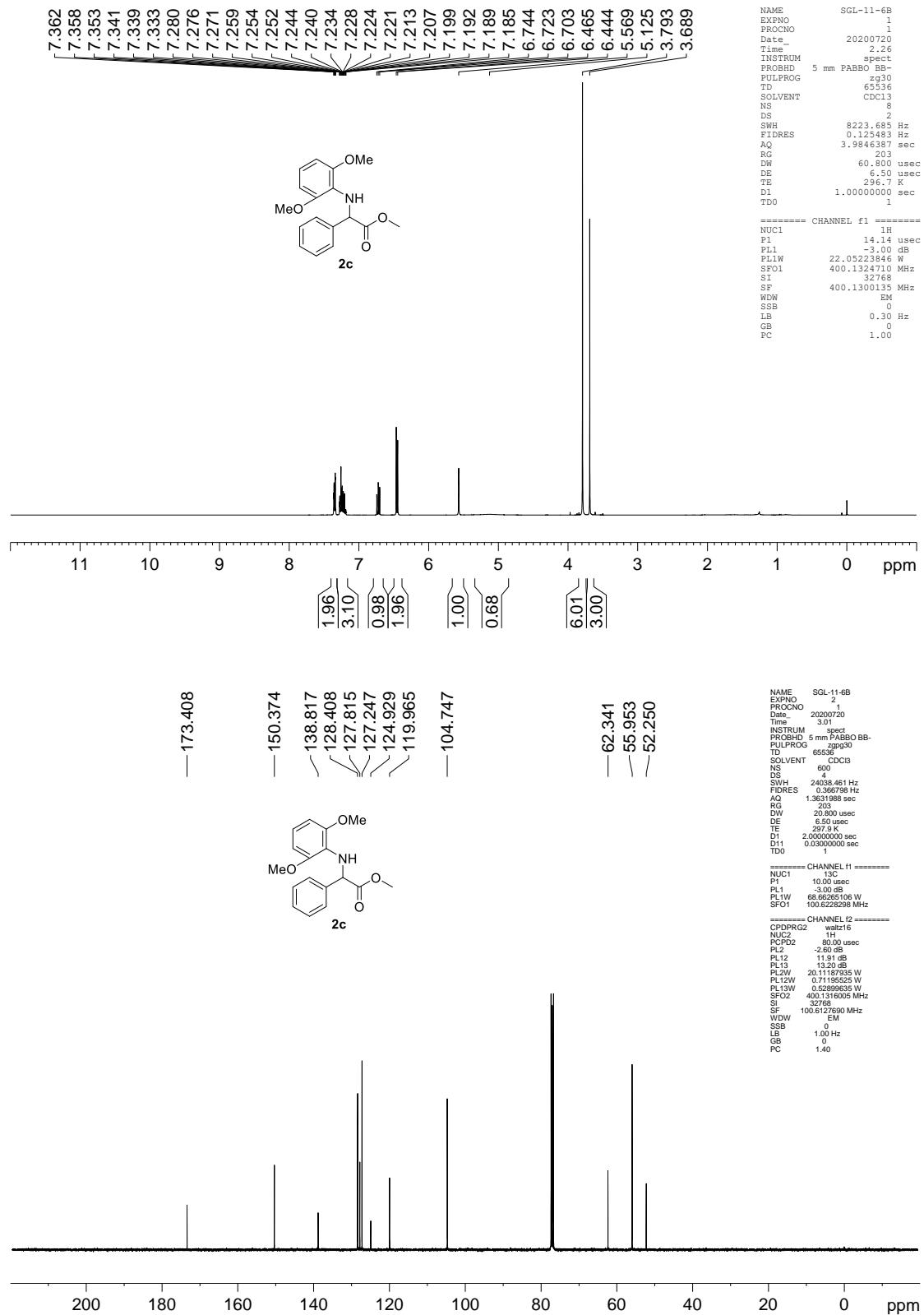
Entry	Solvent	Lewis acid	time (h)	yield (%)^b
1	1,4-dioxane	Zn(OTf) ₂	2	95
2	1,4-dioxane	AgOTf	2	90
3	1,4-dioxane	Fe(OTf) ₂	7	81
4	1,4-dioxane	Cu(OTf) ₂	7	69
5	1,4-dioxane	Yb(OTf) ₃	7	62
6	1,4-dioxane	ZnI ₂	48	95
7	1,4-dioxane	/	48	NR
8	Toluene	Zn(OTf) ₂	96	76
10	THF	Zn(OTf) ₂	2	88
11	DMF	Zn(OTf) ₂	2	88
12	DCE	Zn(OTf) ₂	96	69
13	CH ₃ CN	Zn(OTf) ₂	2	83

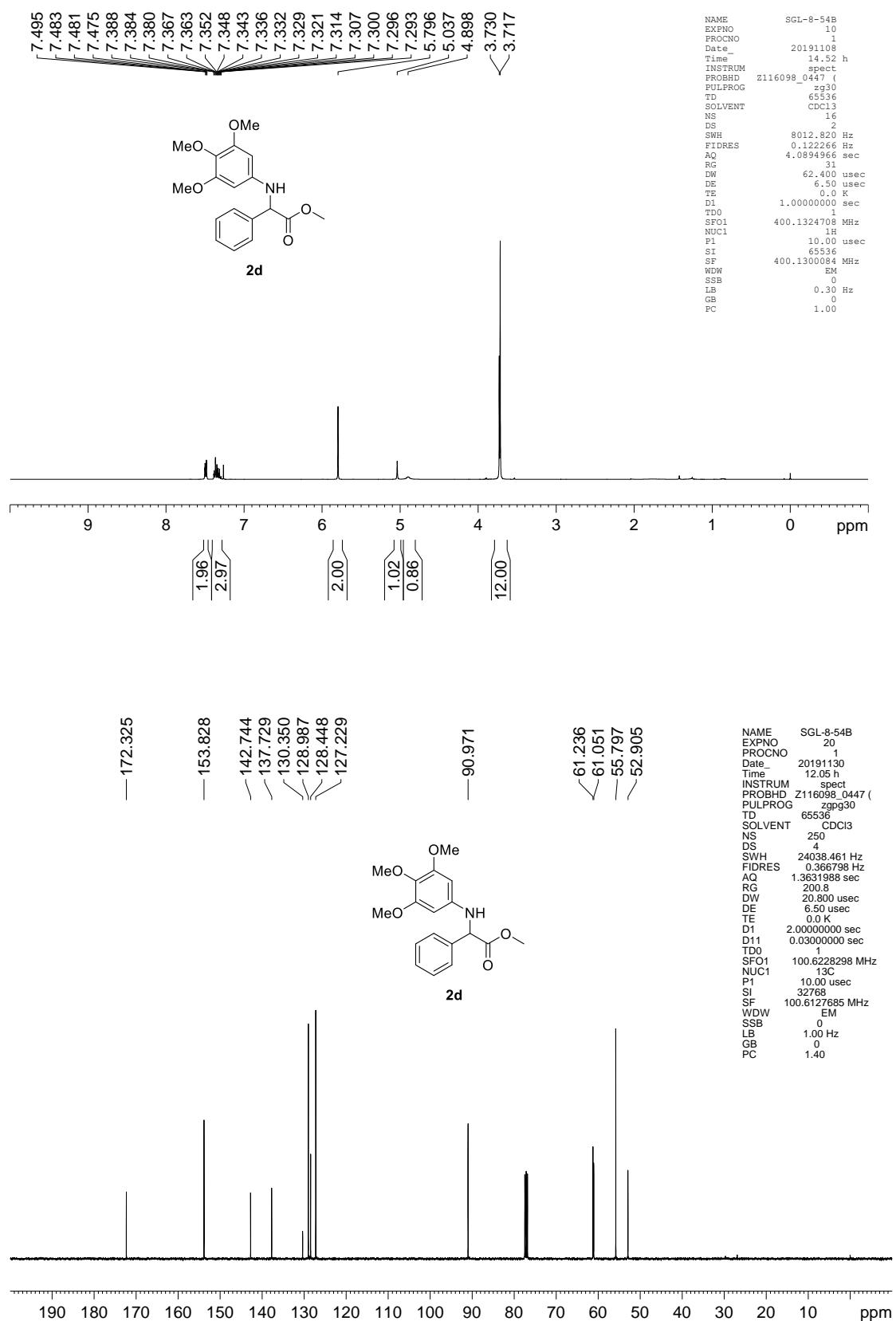
^a Reaction conditions: **3a** (0.2 mmol), H₂O (1.0 mmol), Lewis acid (0.02 mmol) and zinc powder (325 mesh, 0.6 mmol) in Solvent (2 mL) at 90 °C under an argon atmosphere. ^b Isolated yield.

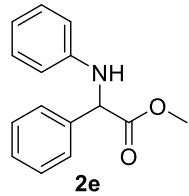
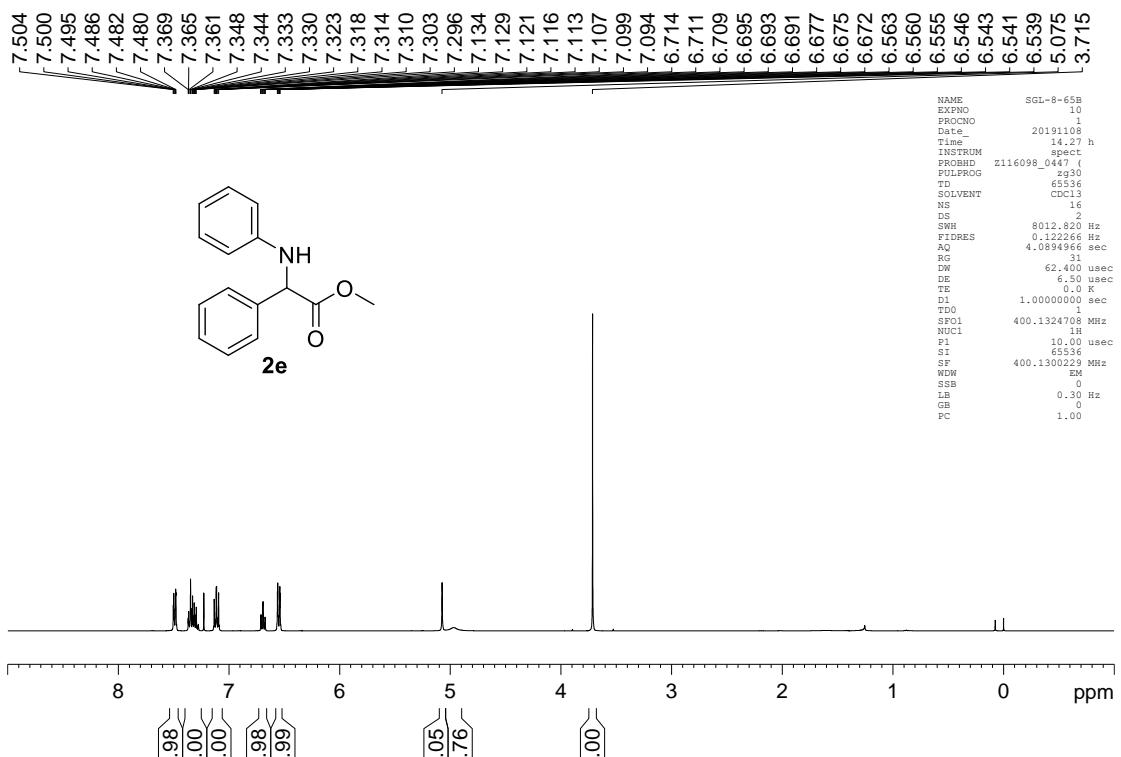
C: NMR Spectra of Products



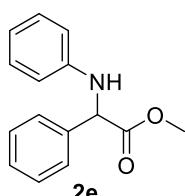
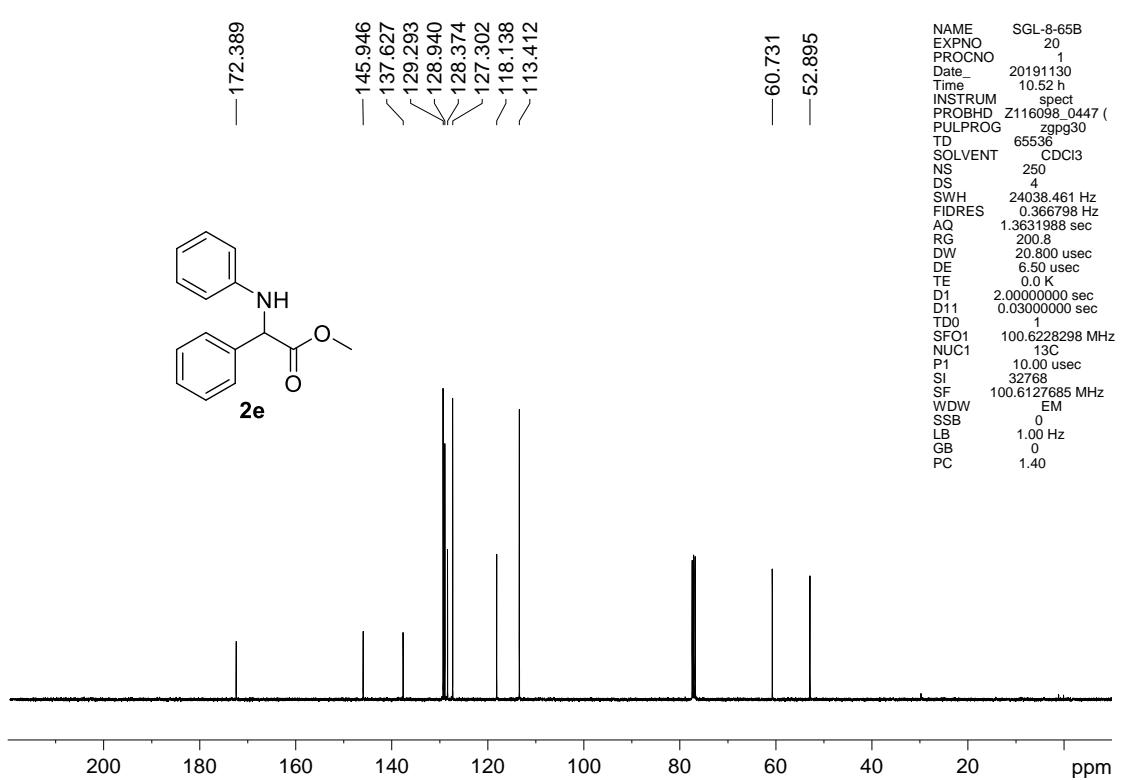






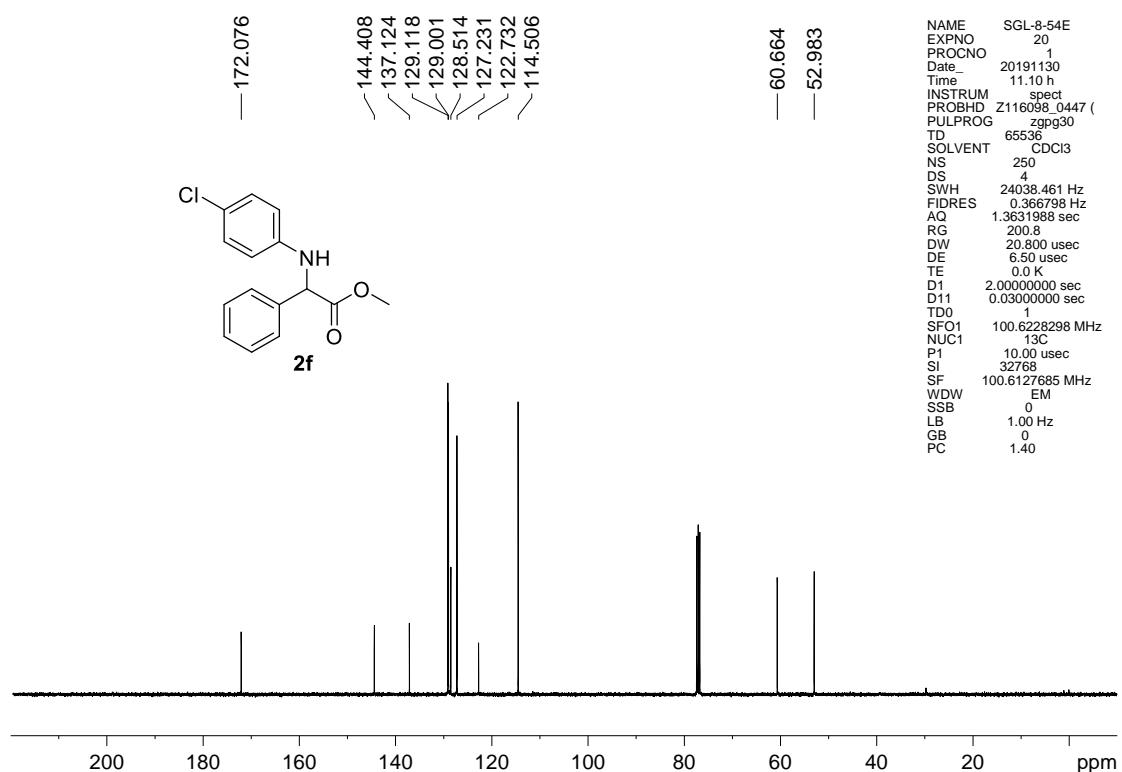
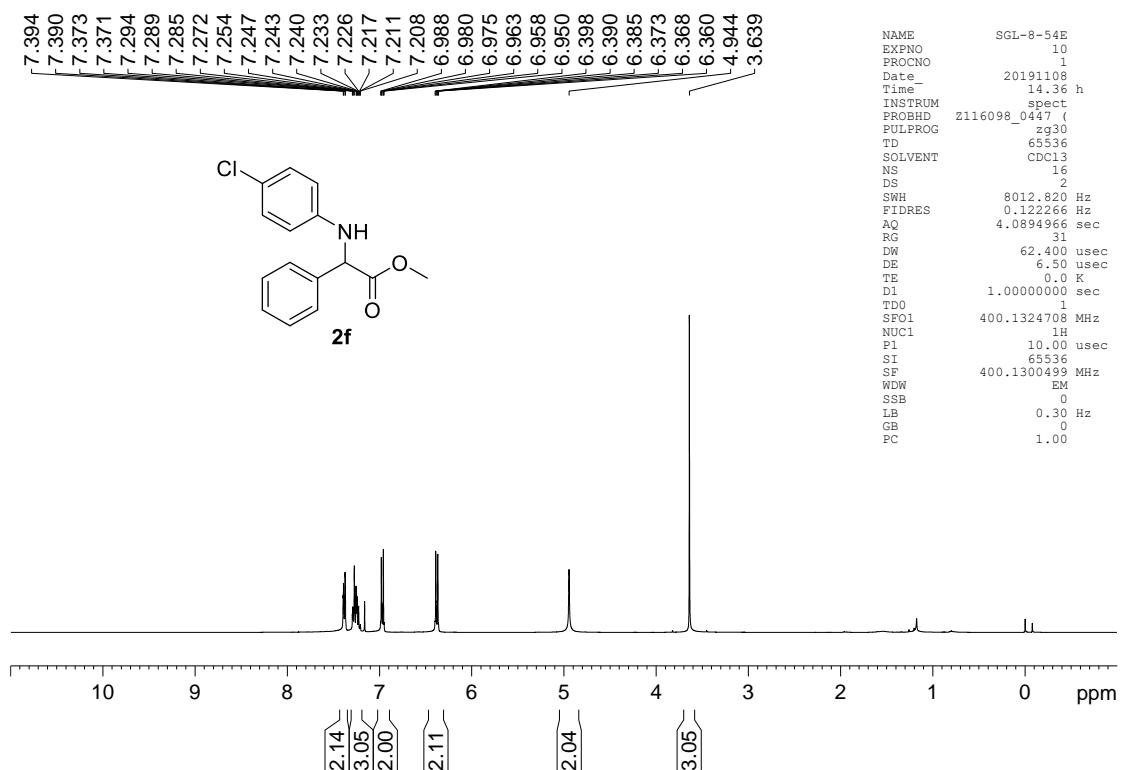


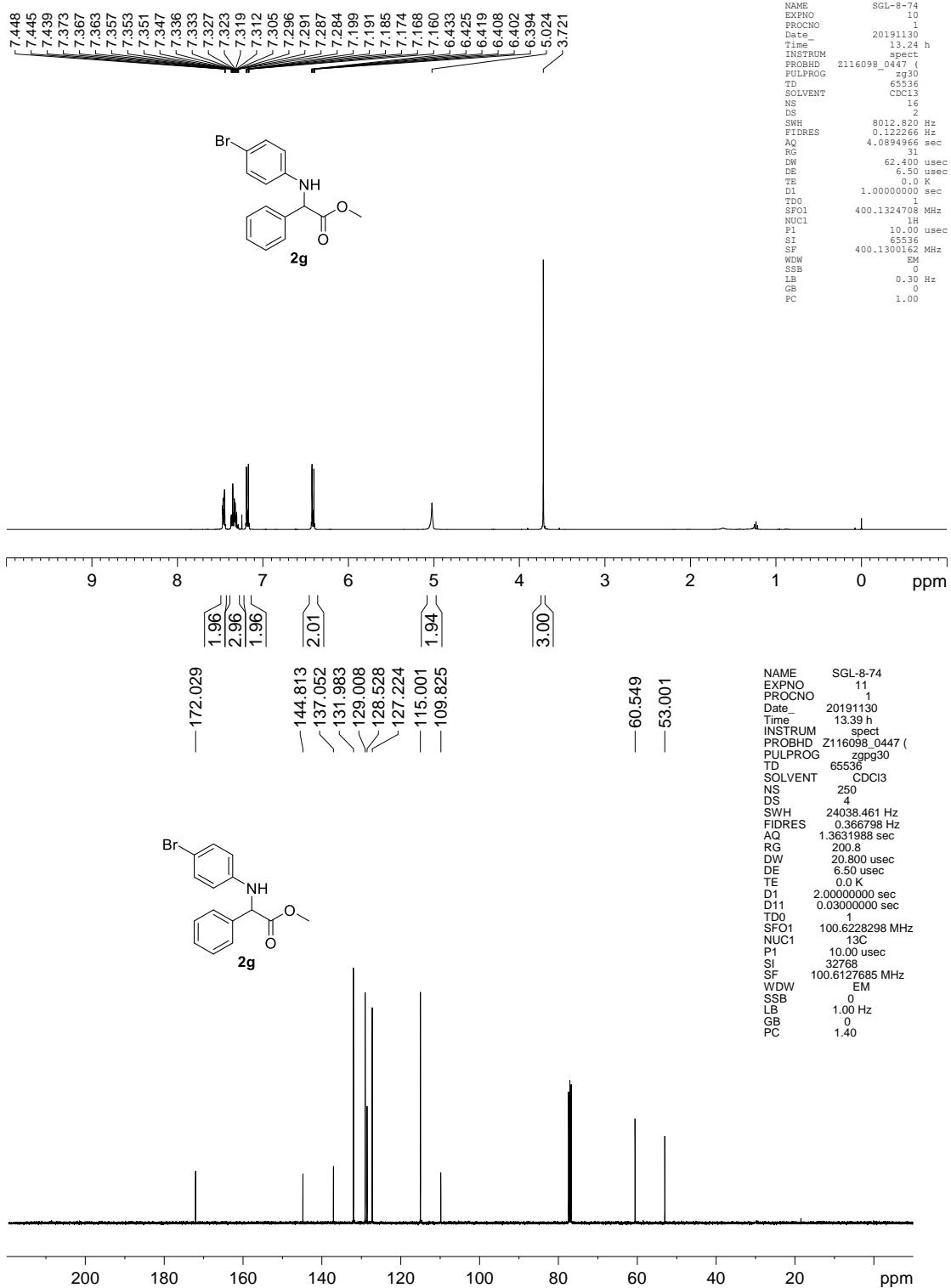
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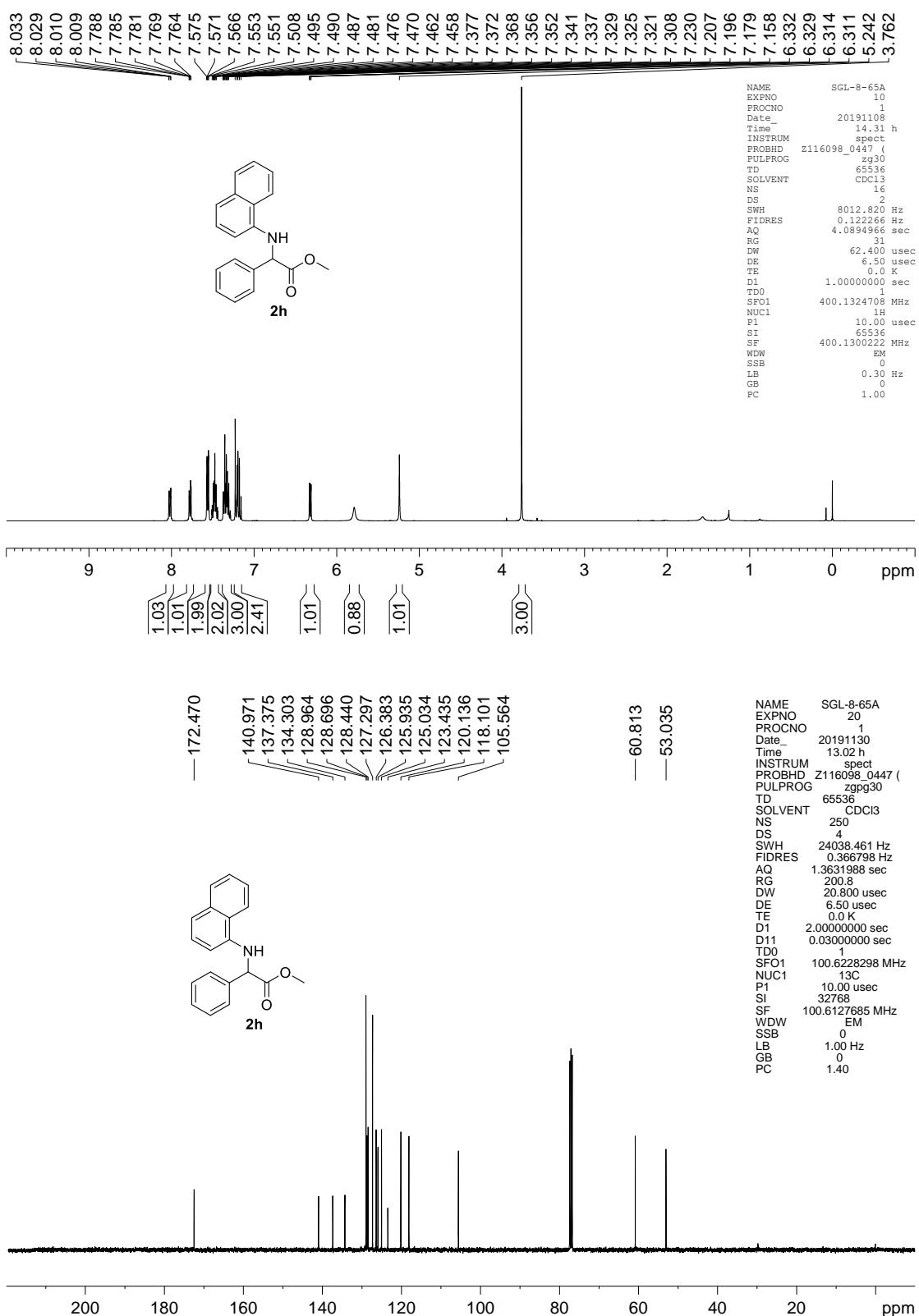


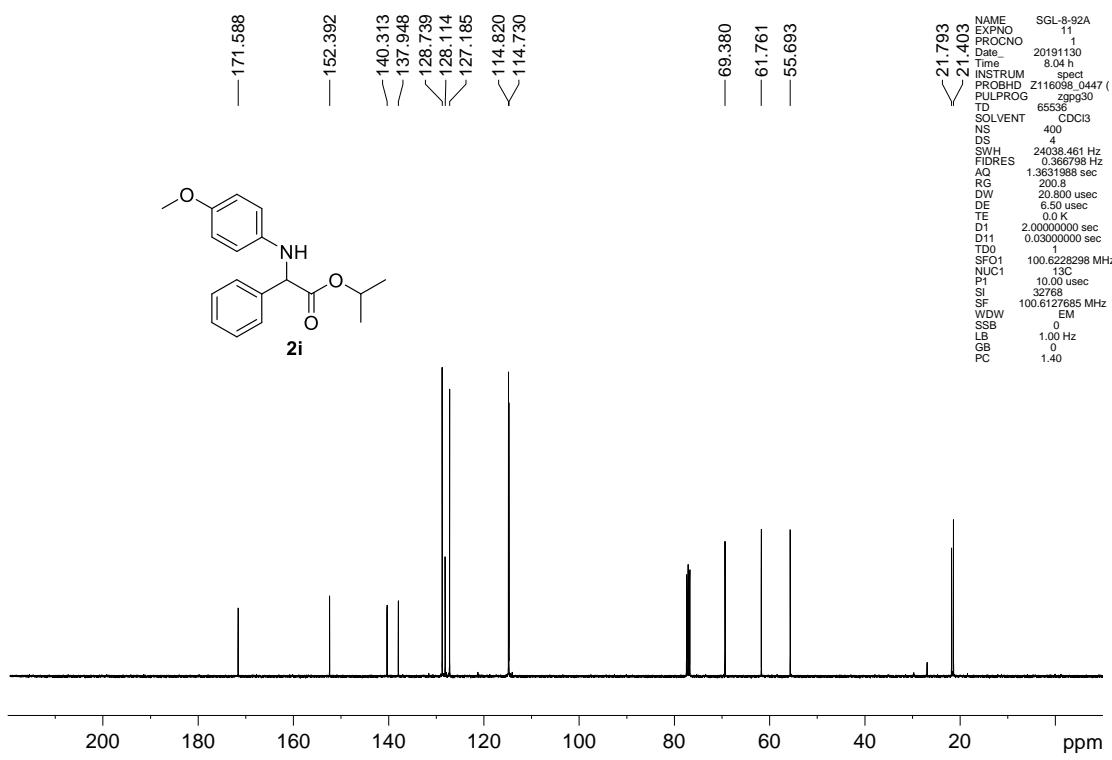
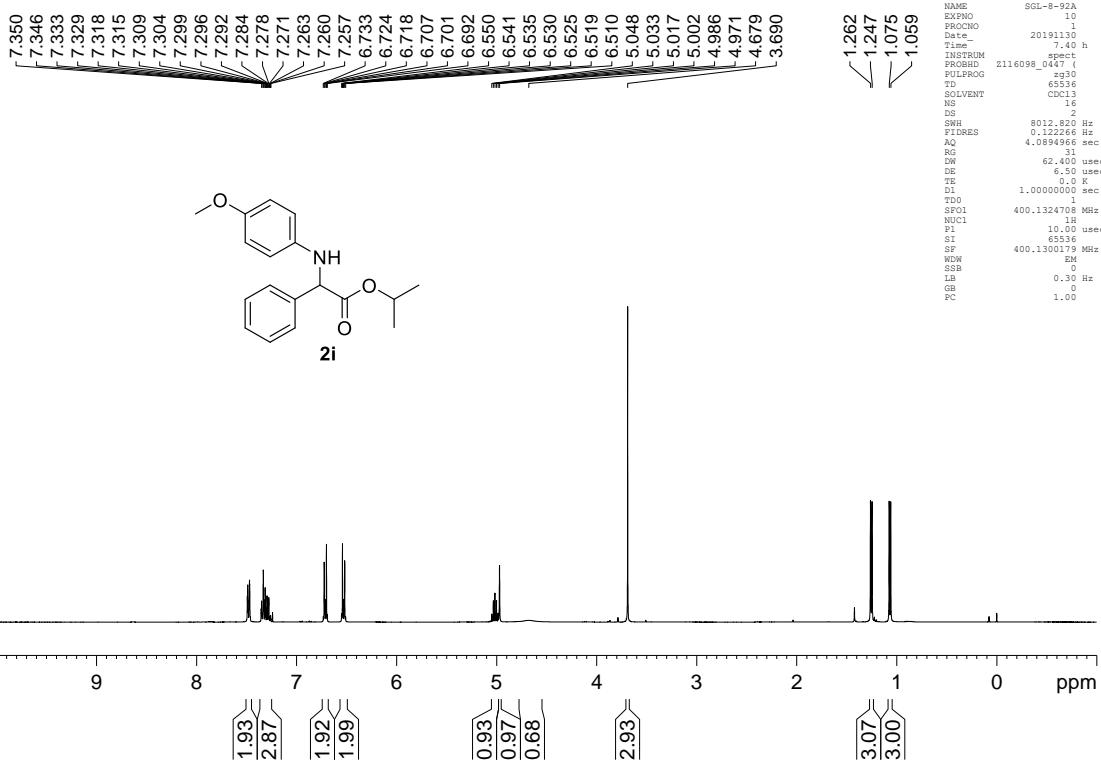
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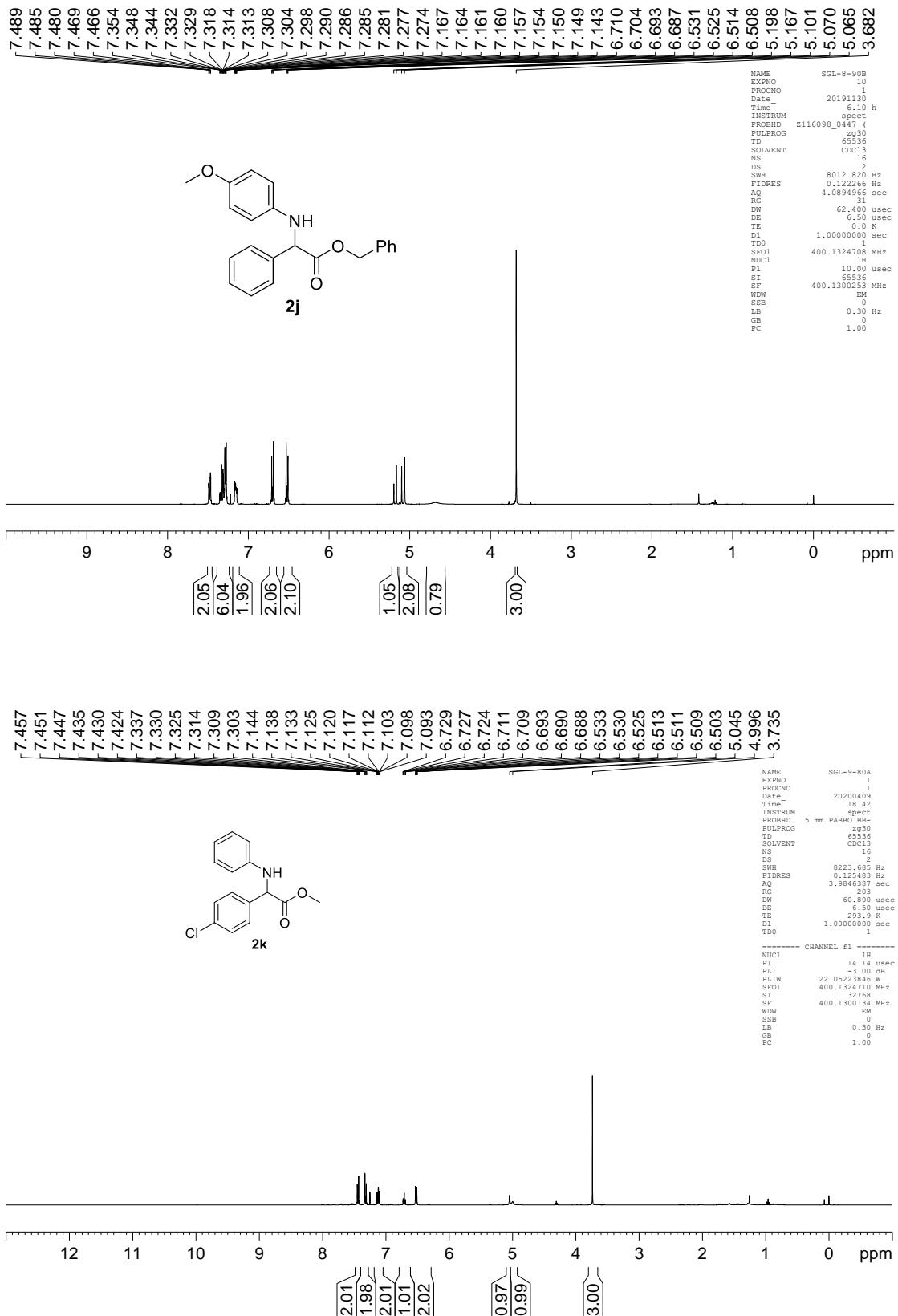
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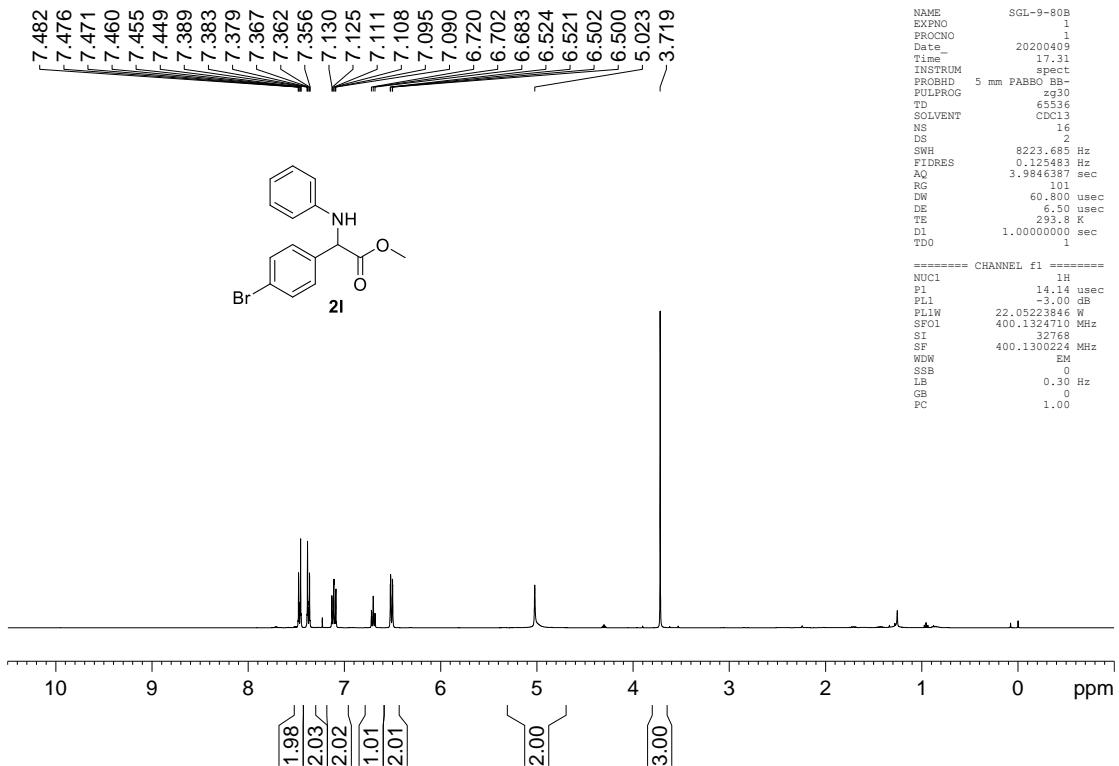
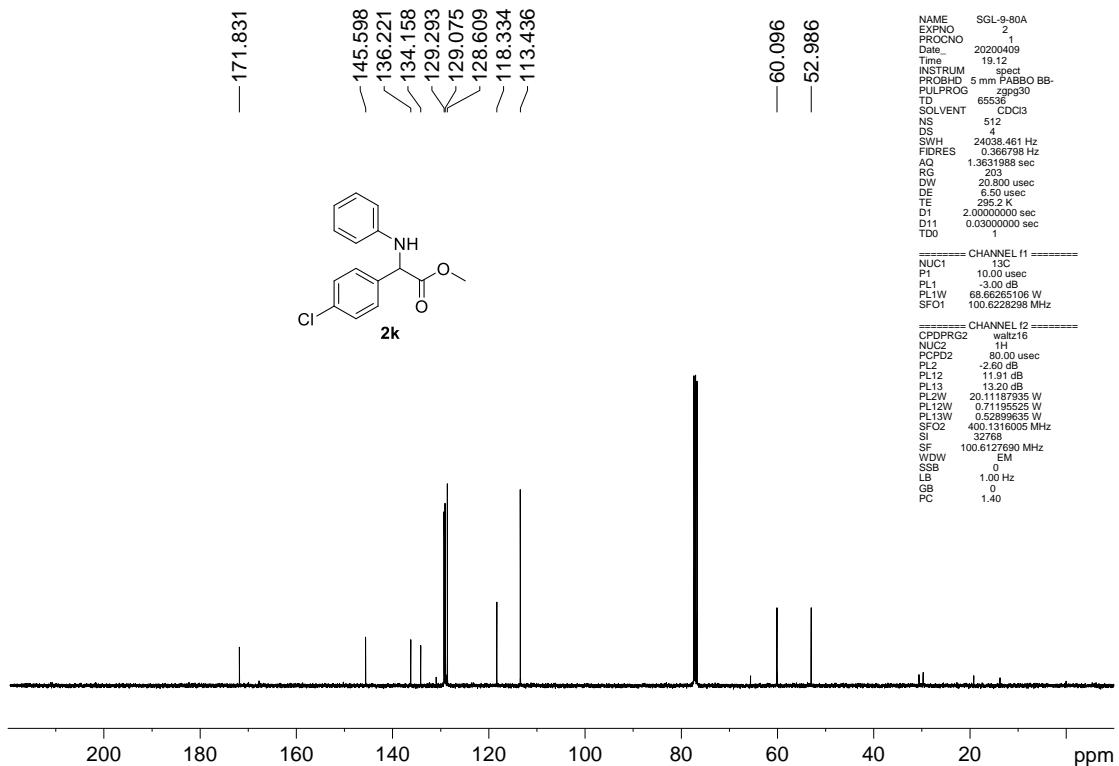


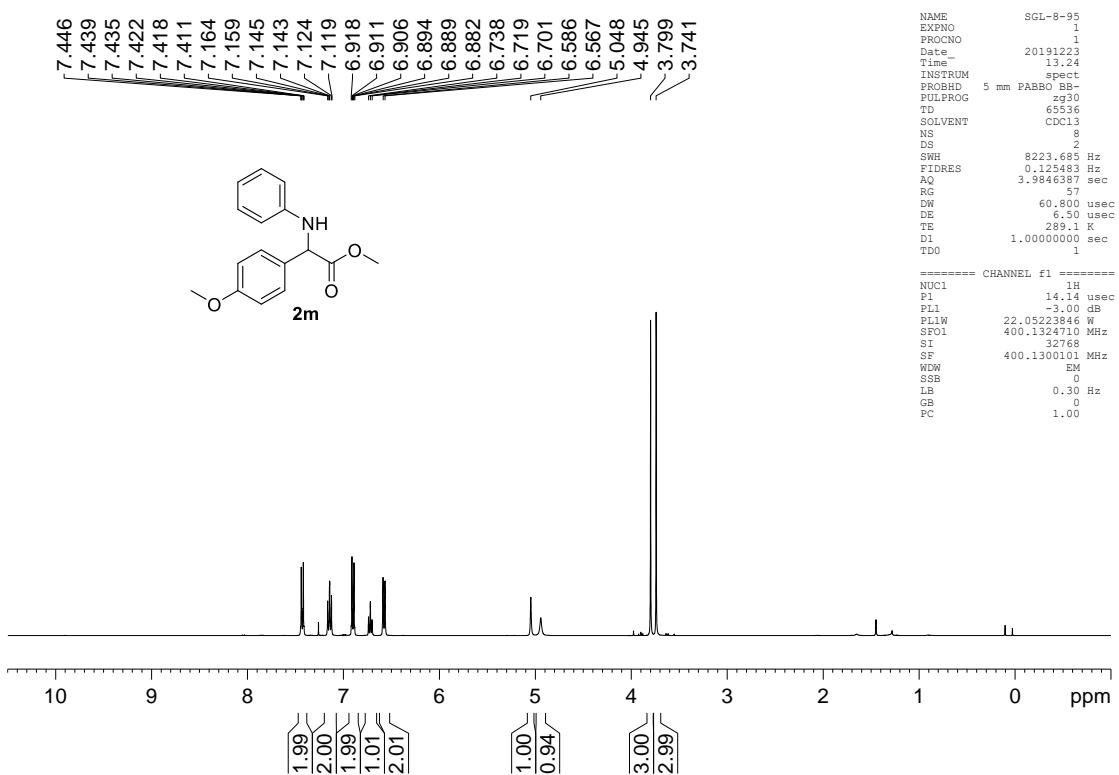
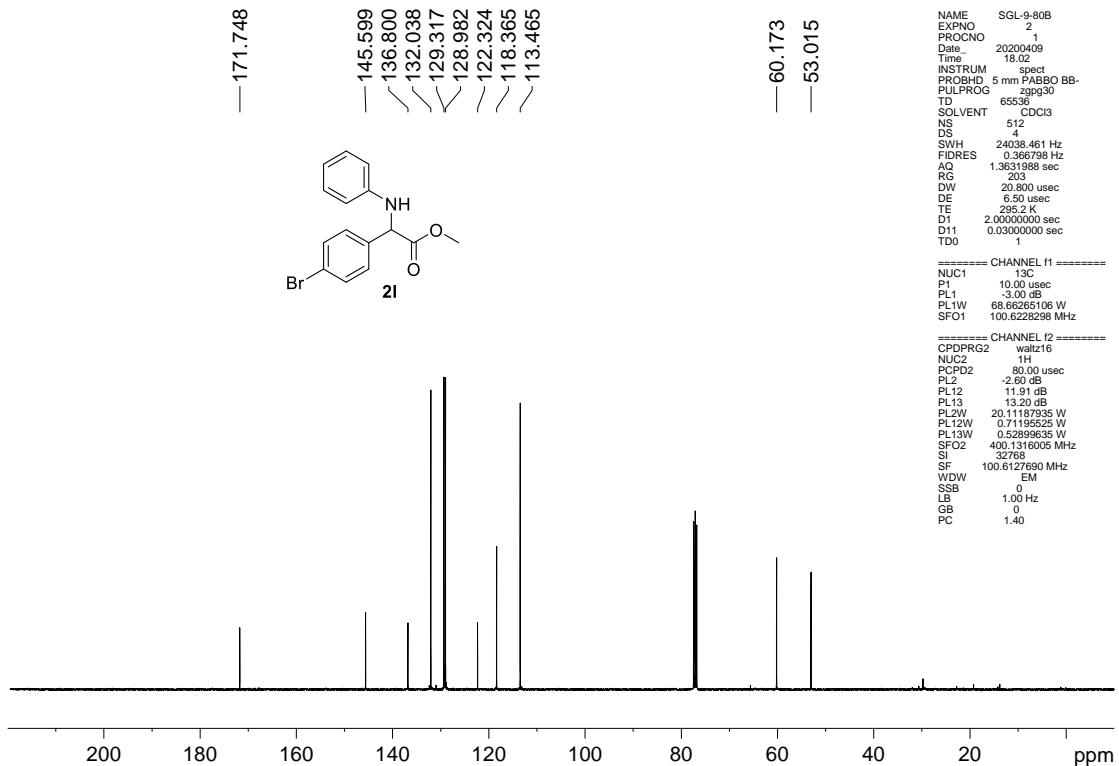


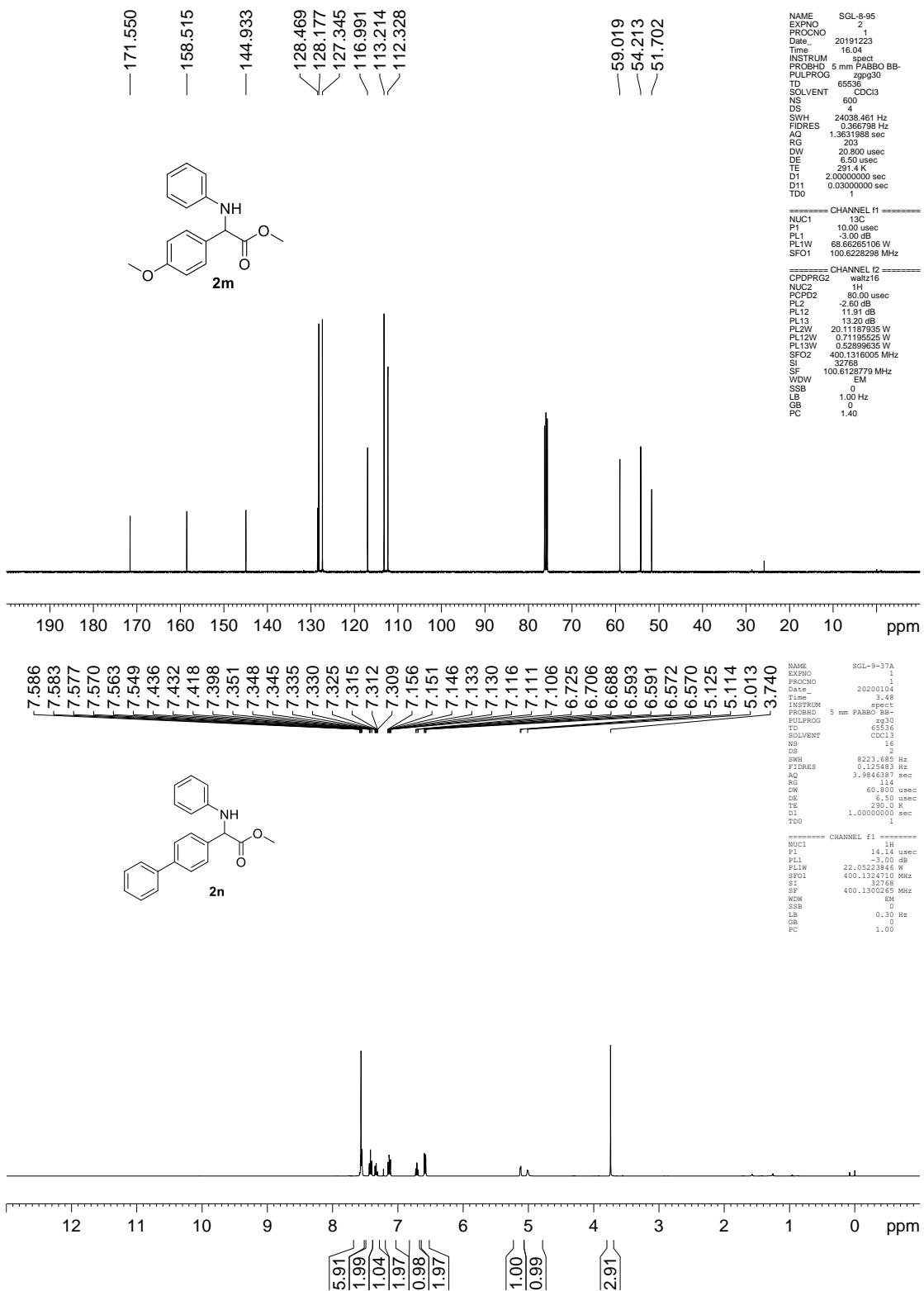


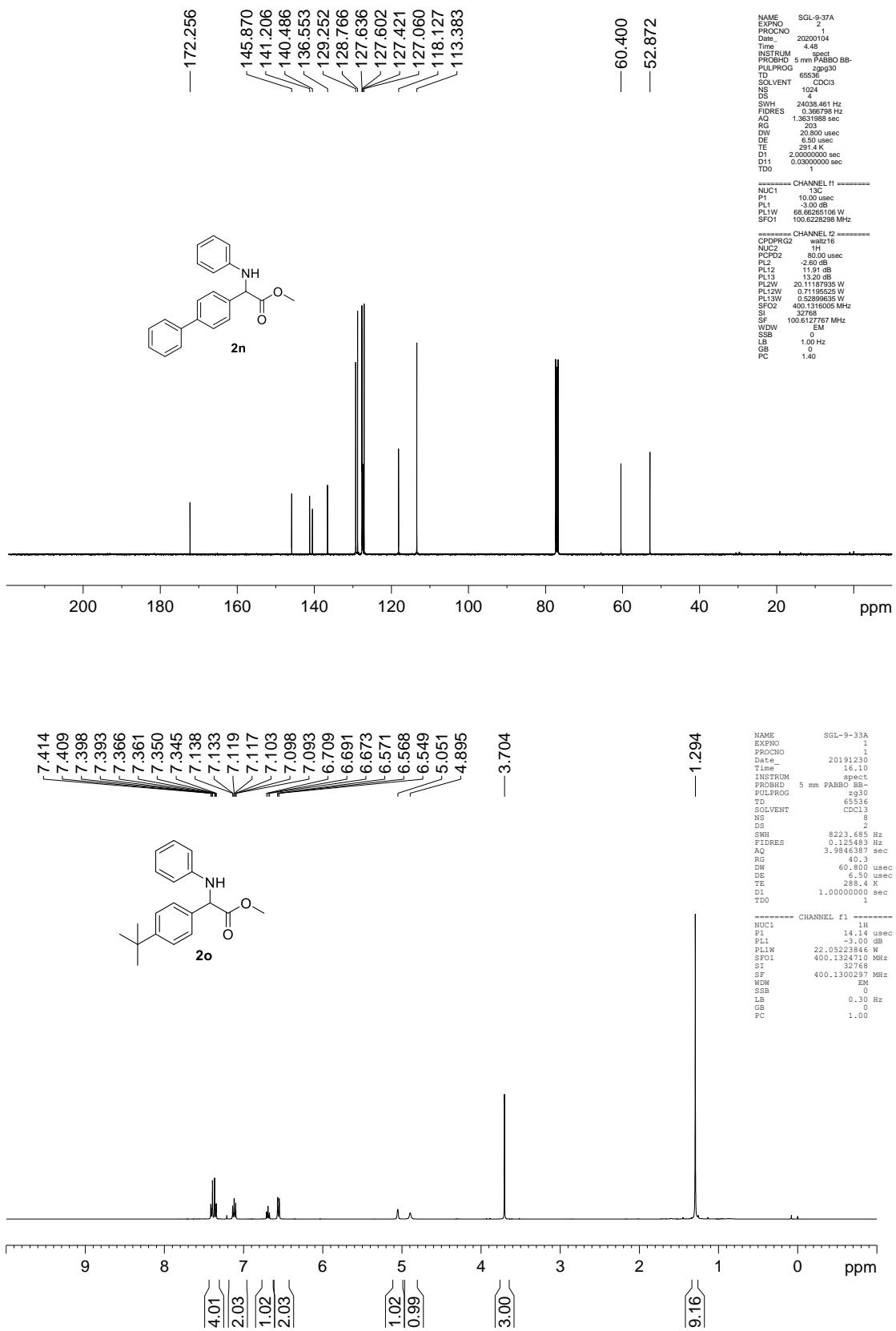


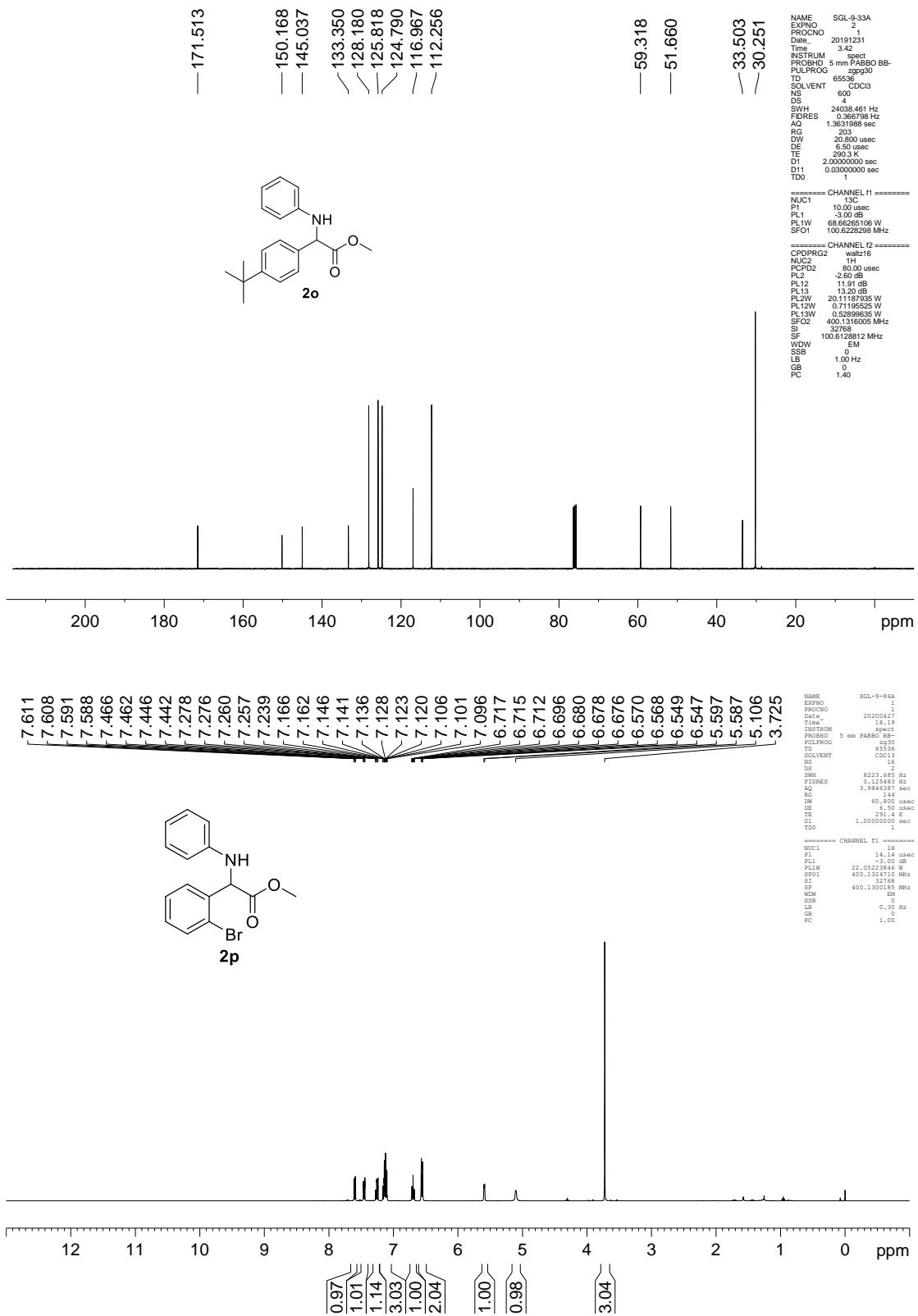


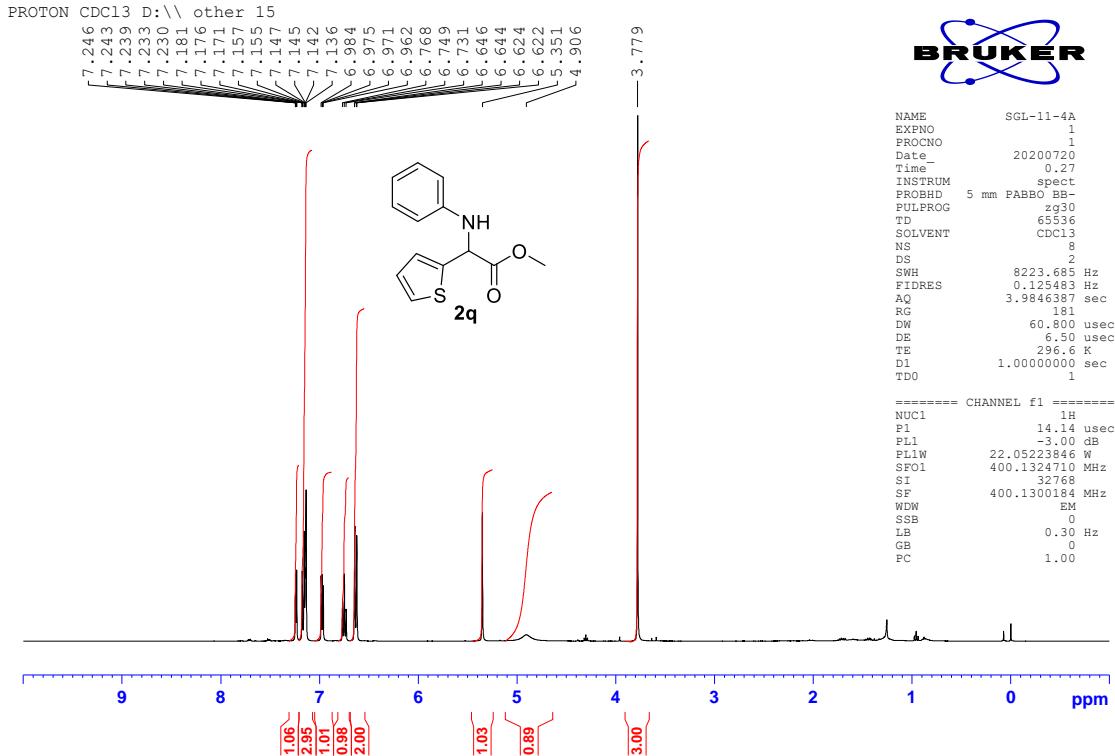
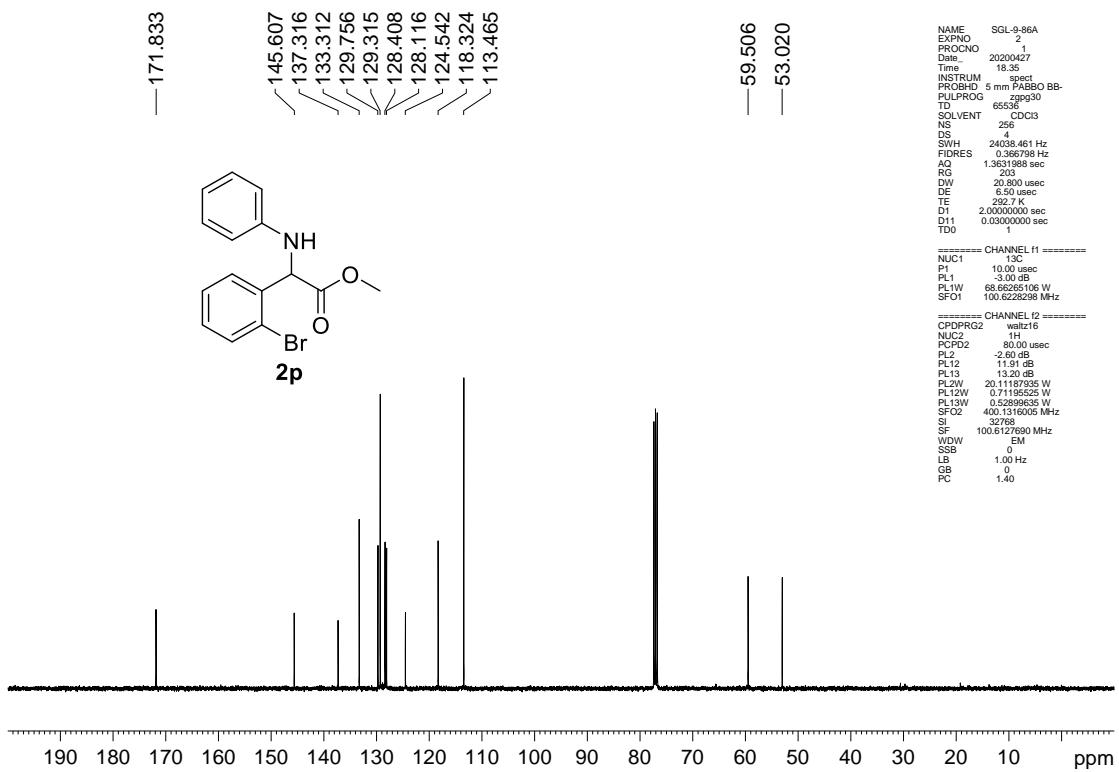


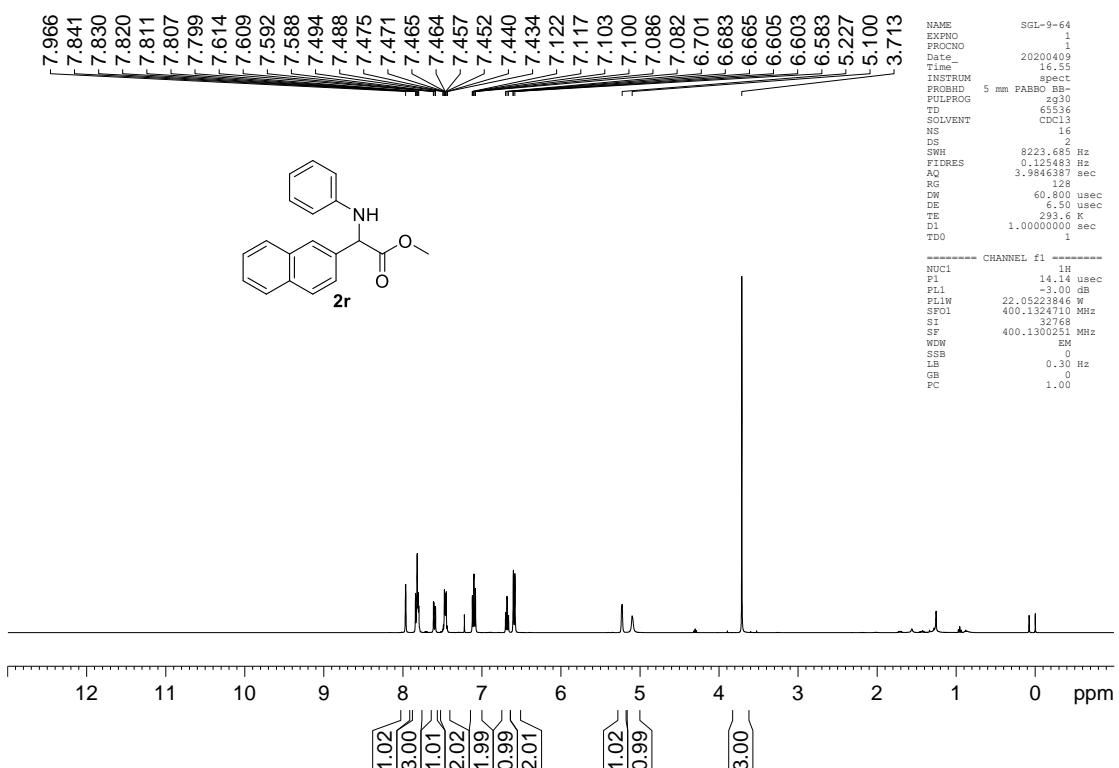
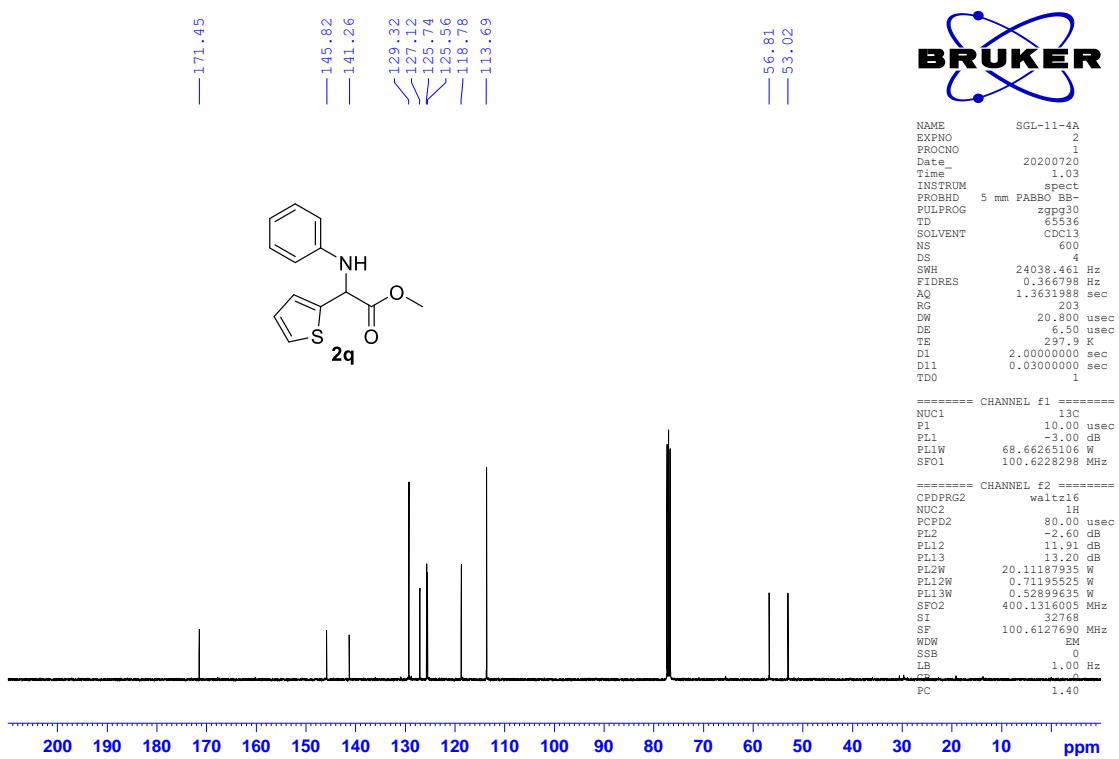


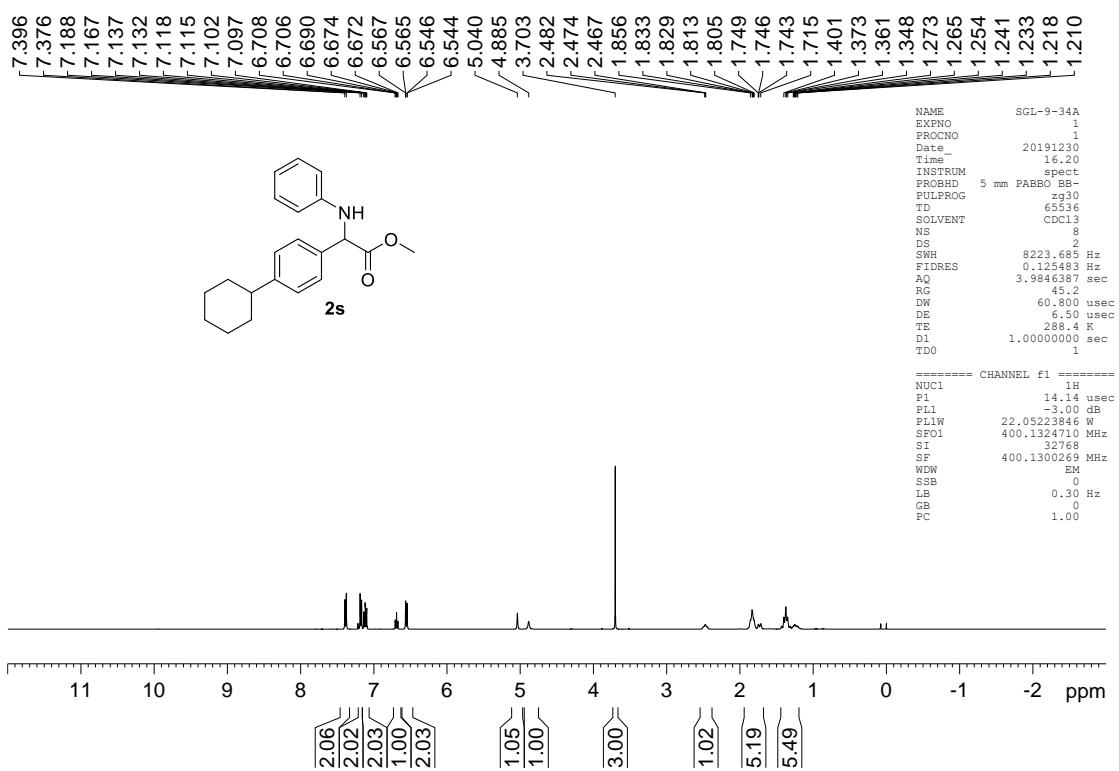
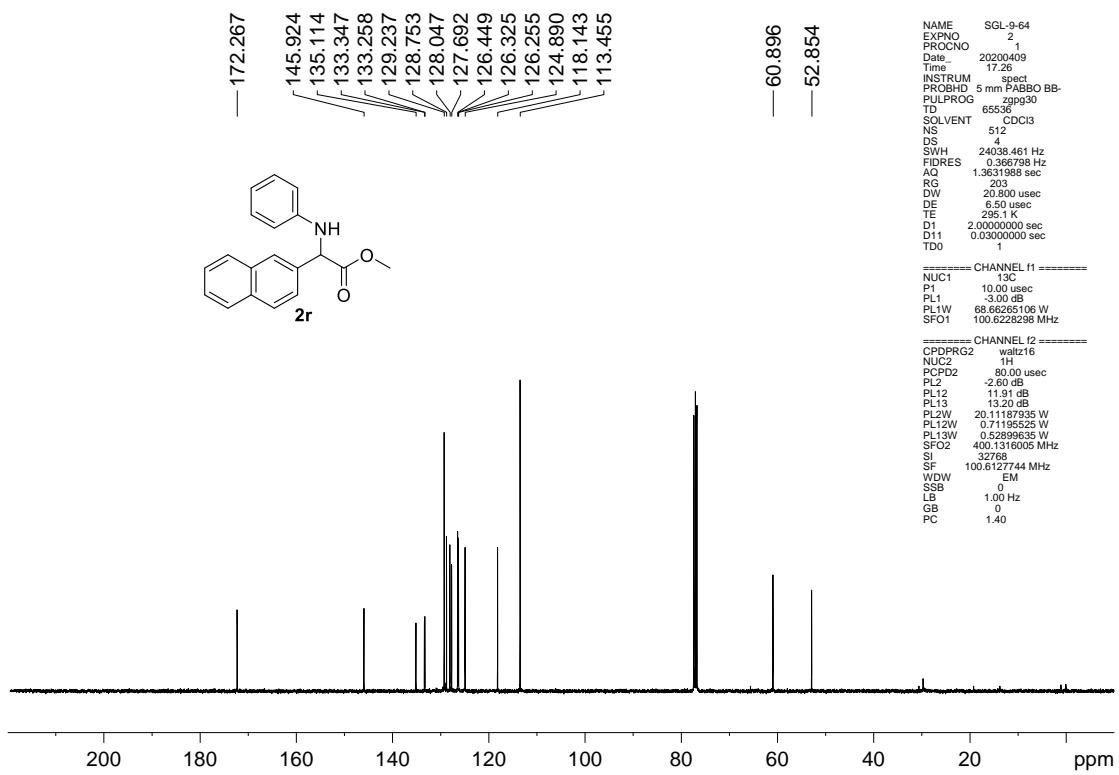


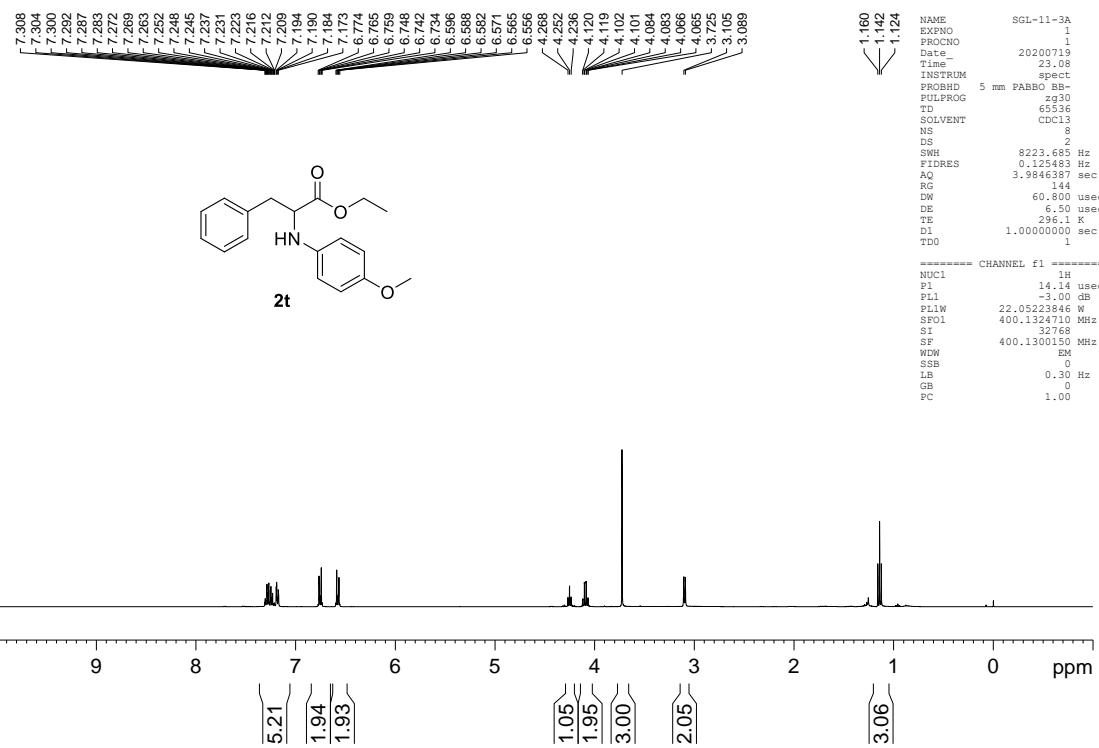
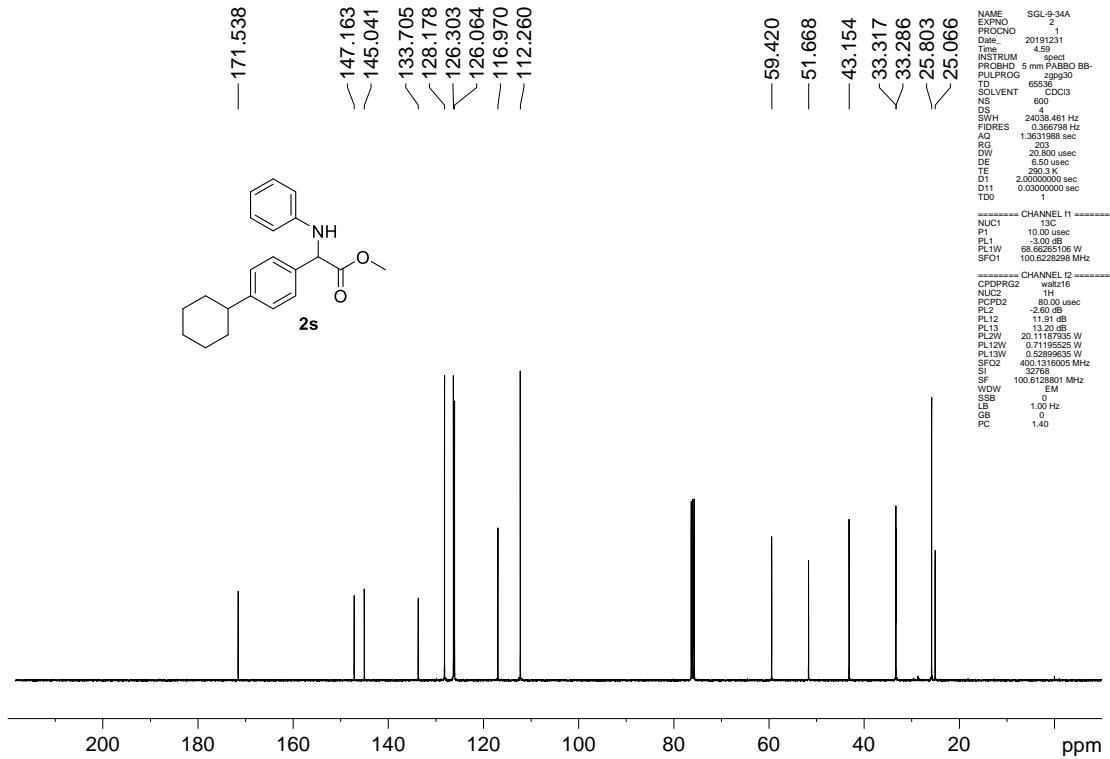


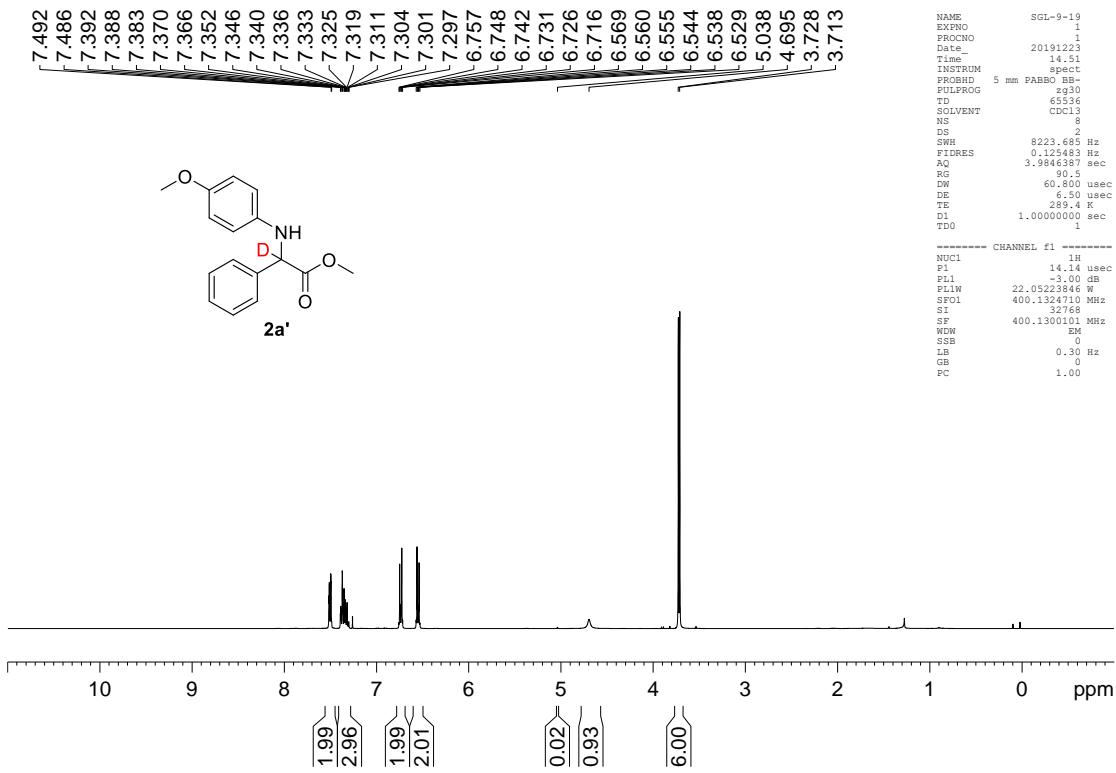
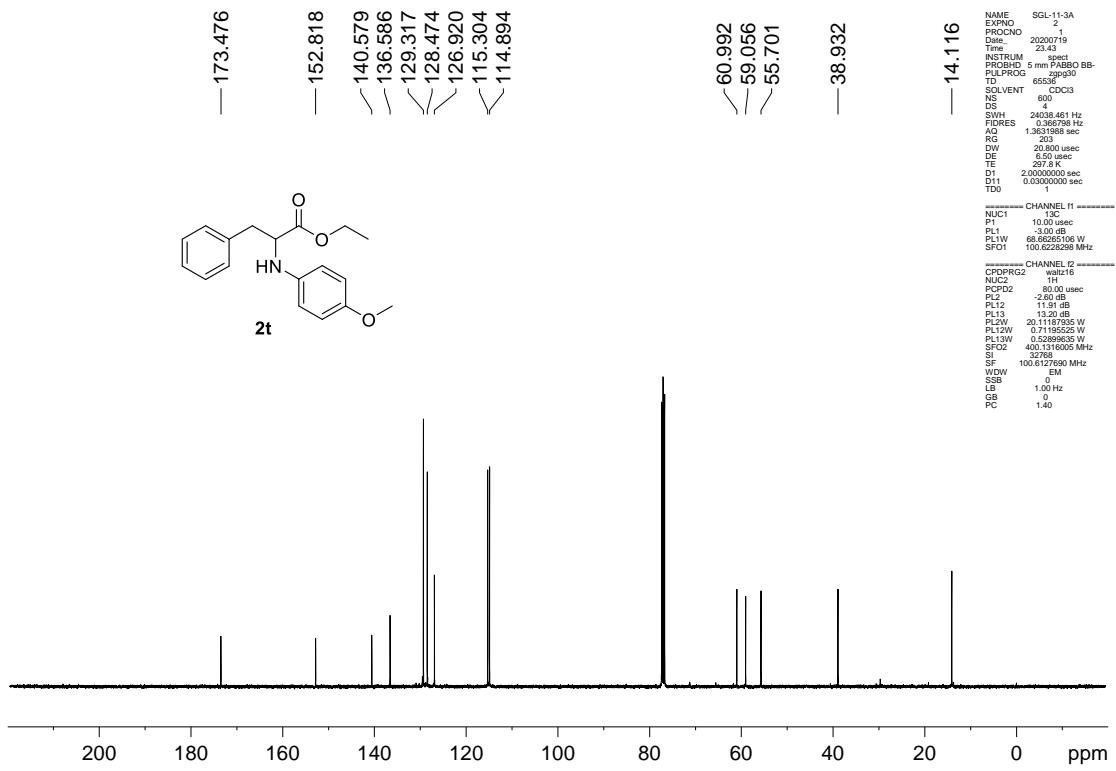


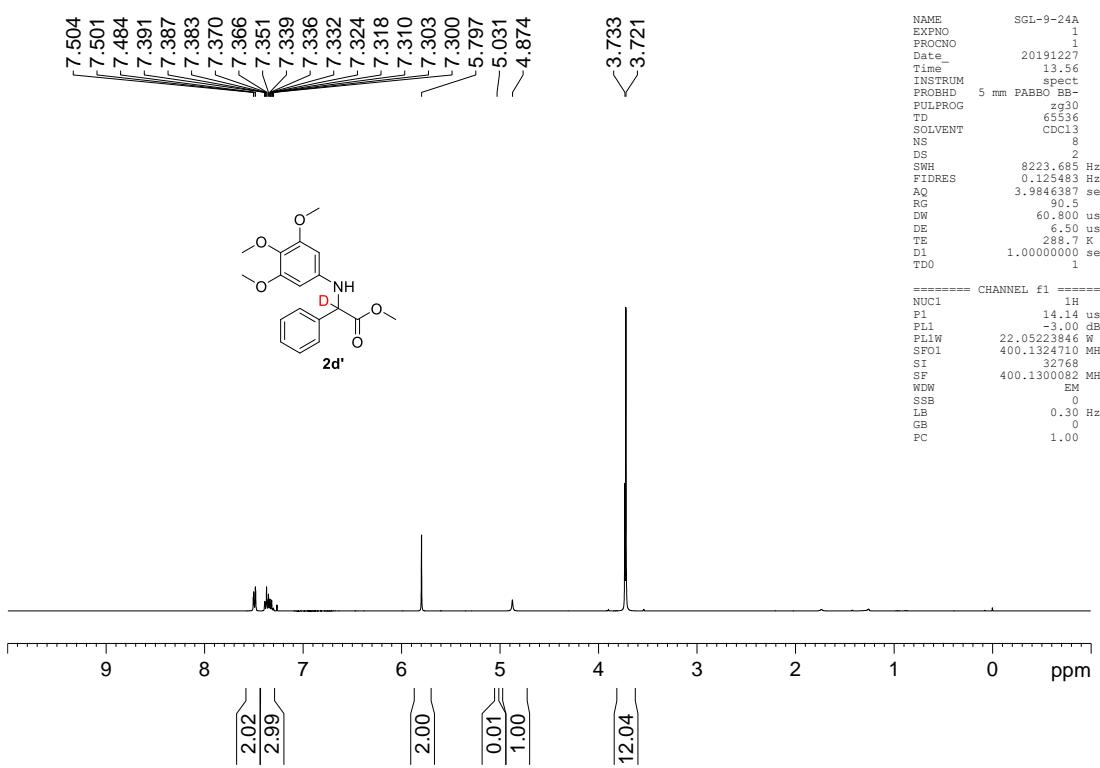
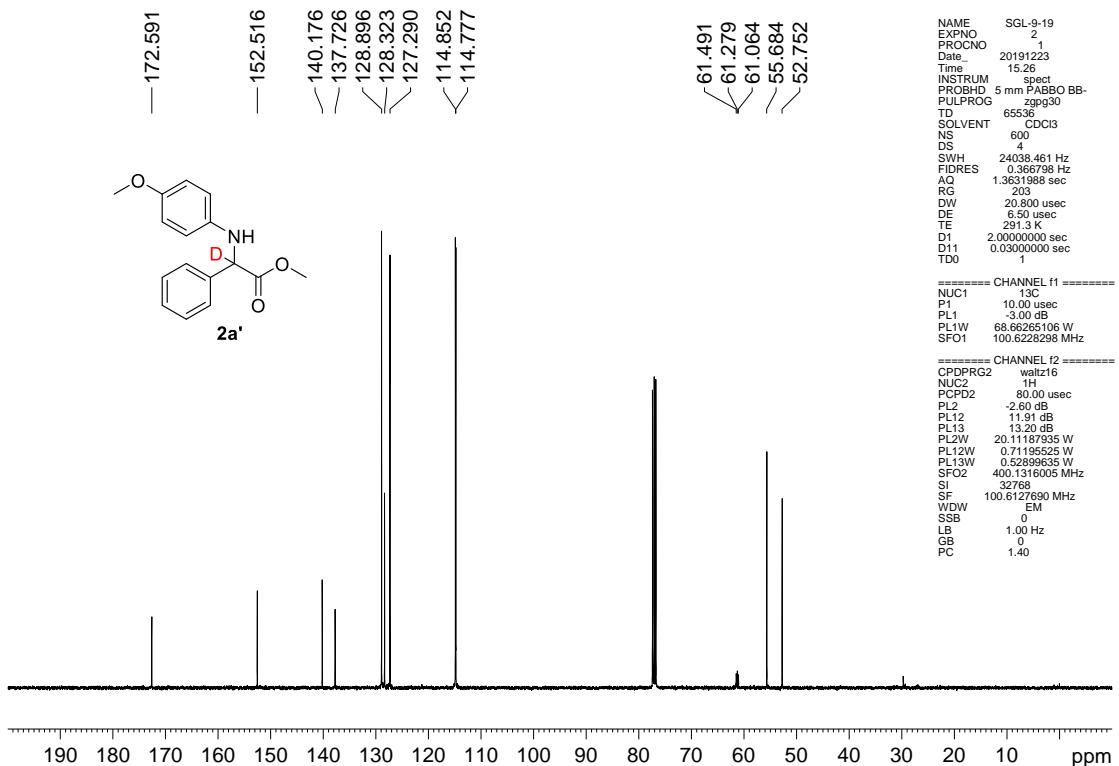


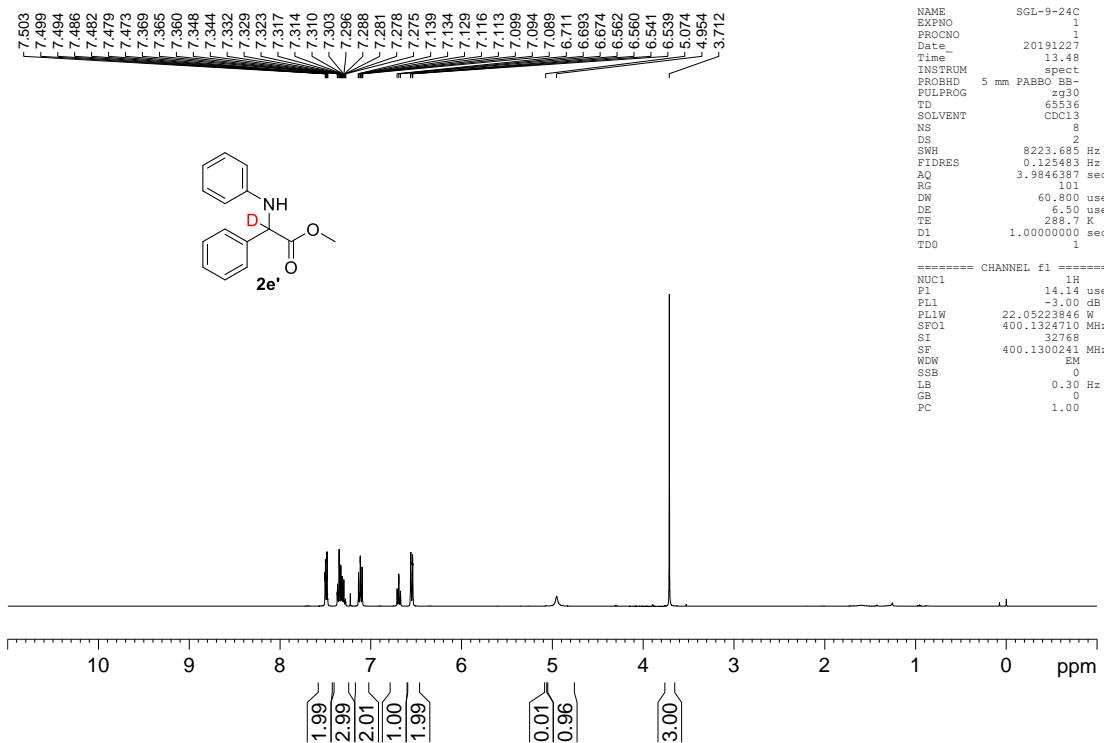
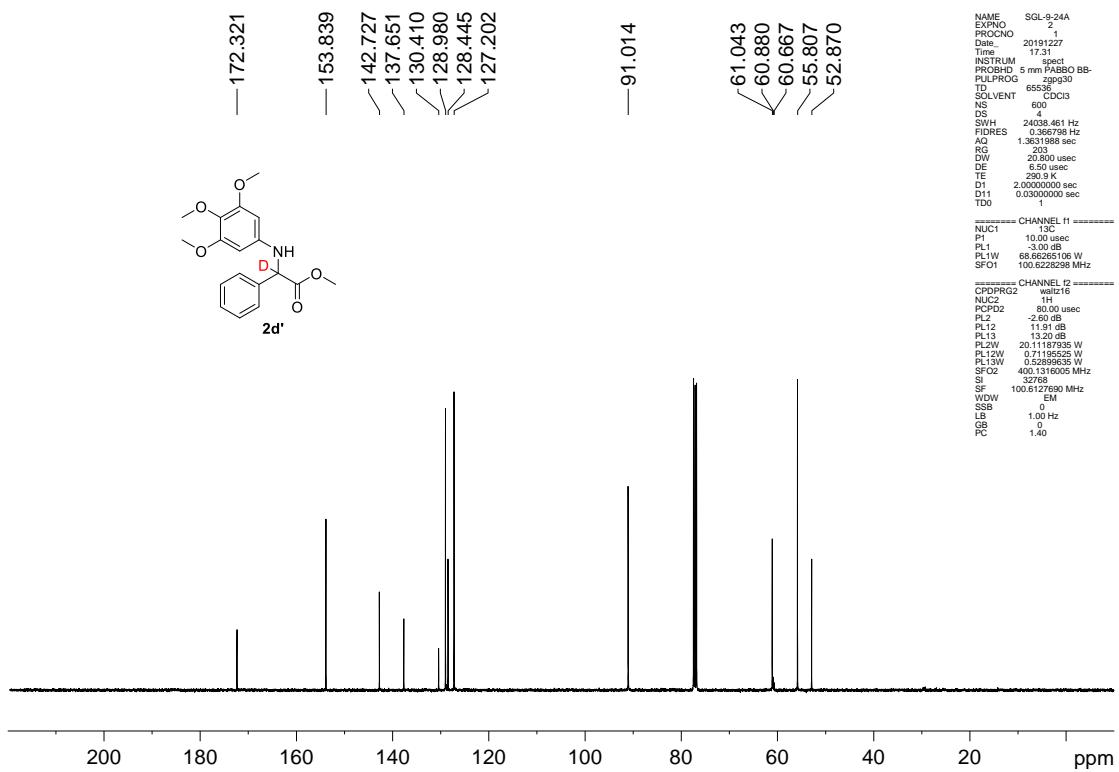


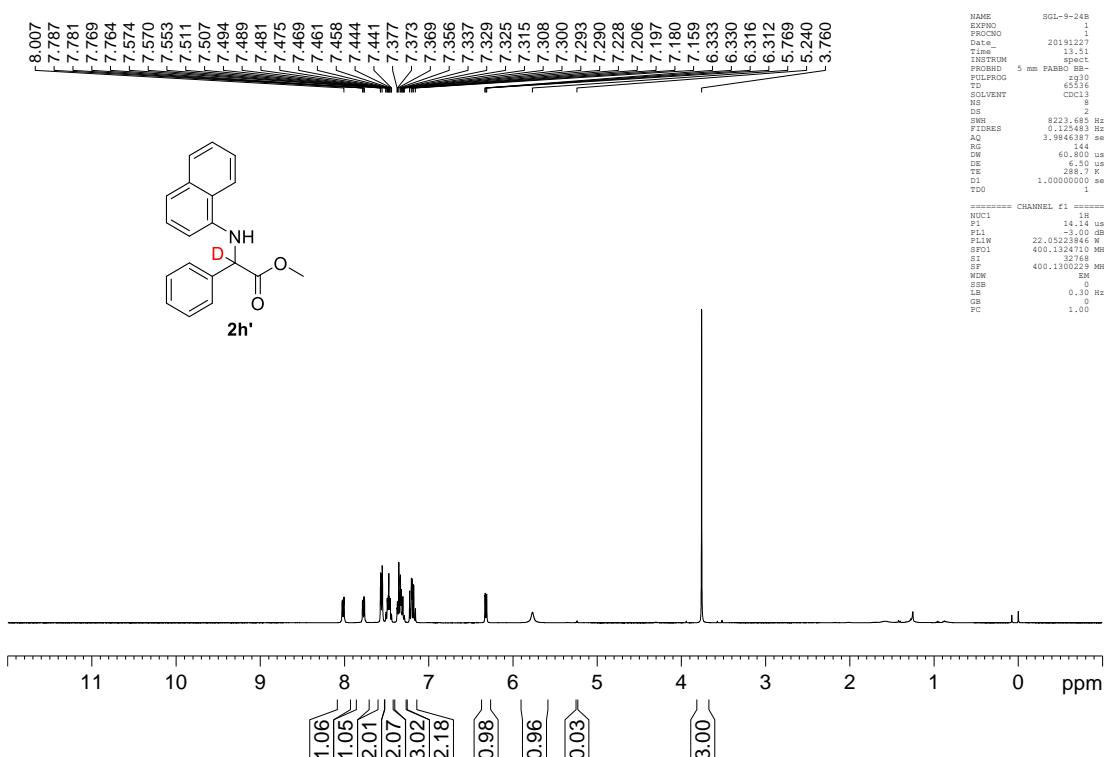
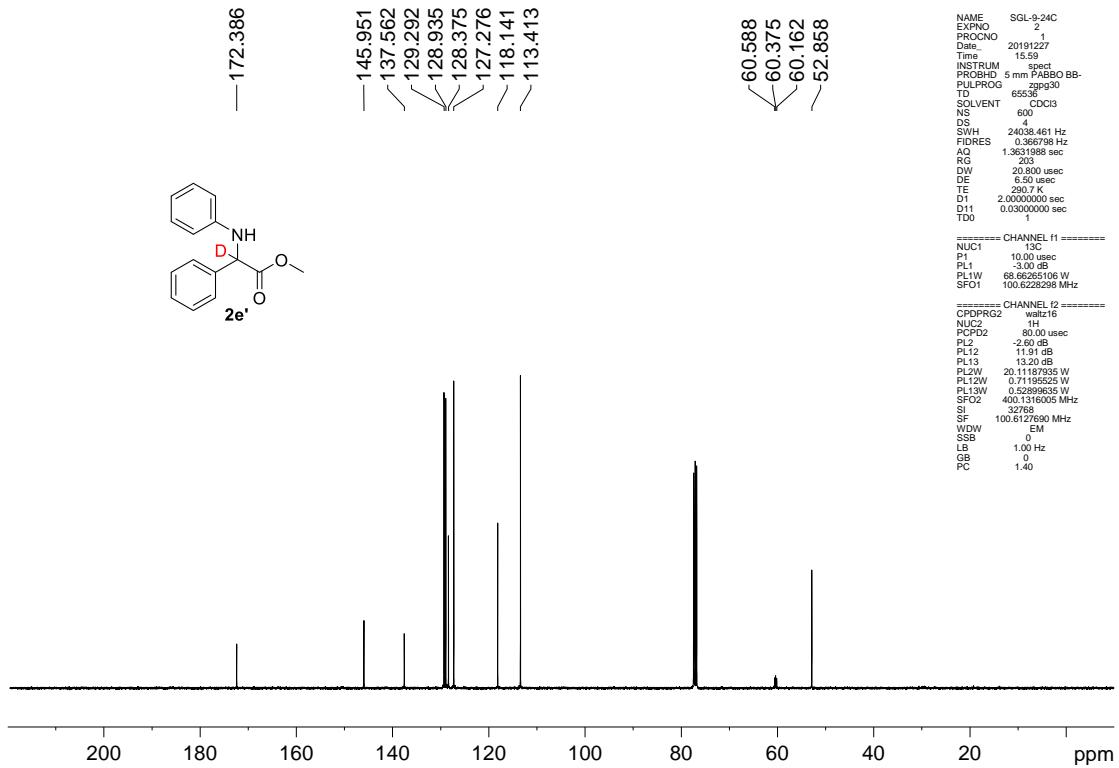


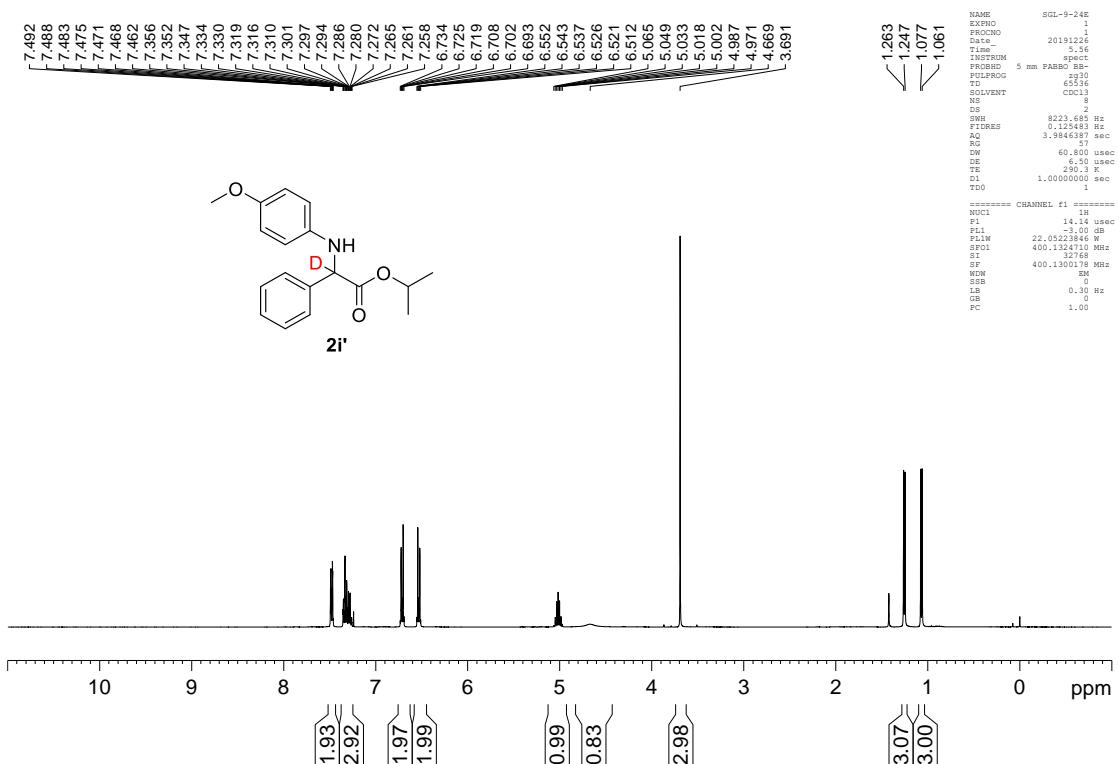
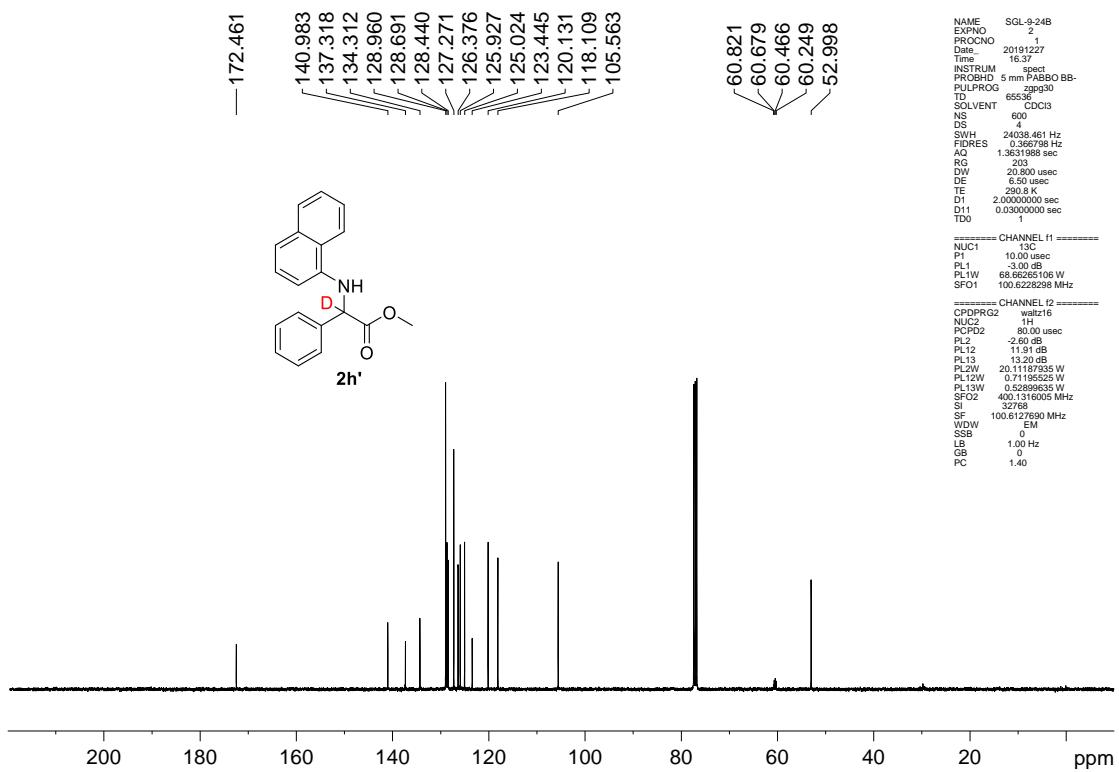


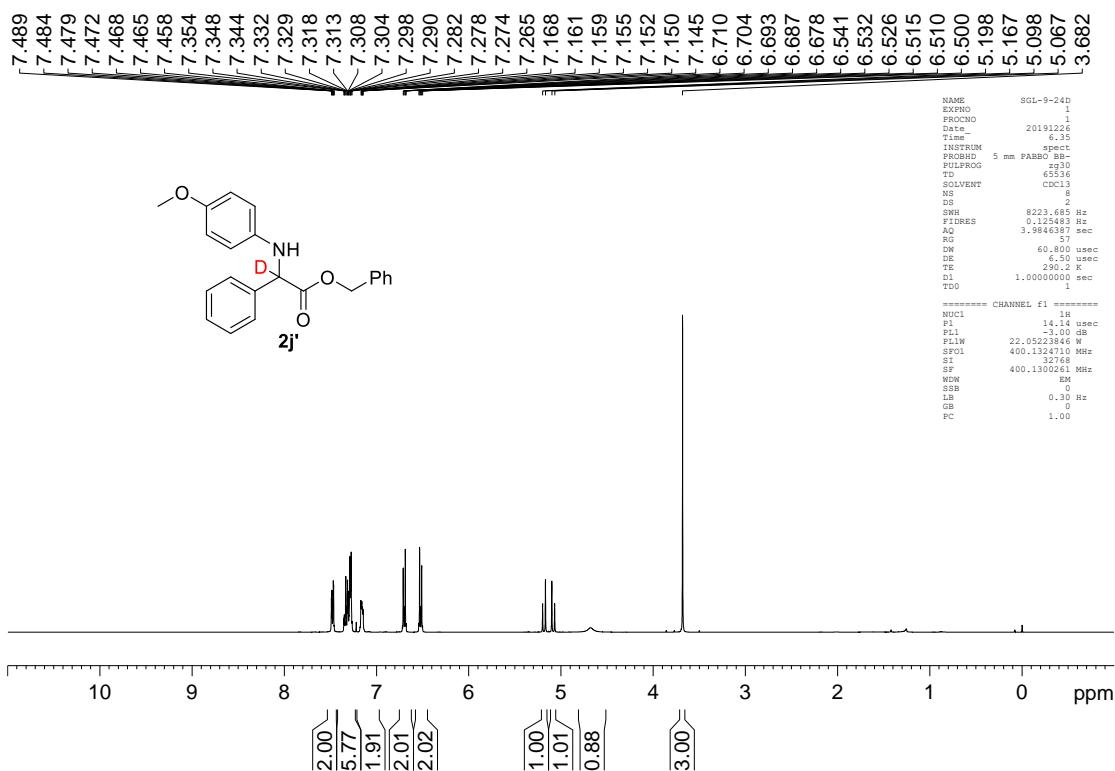
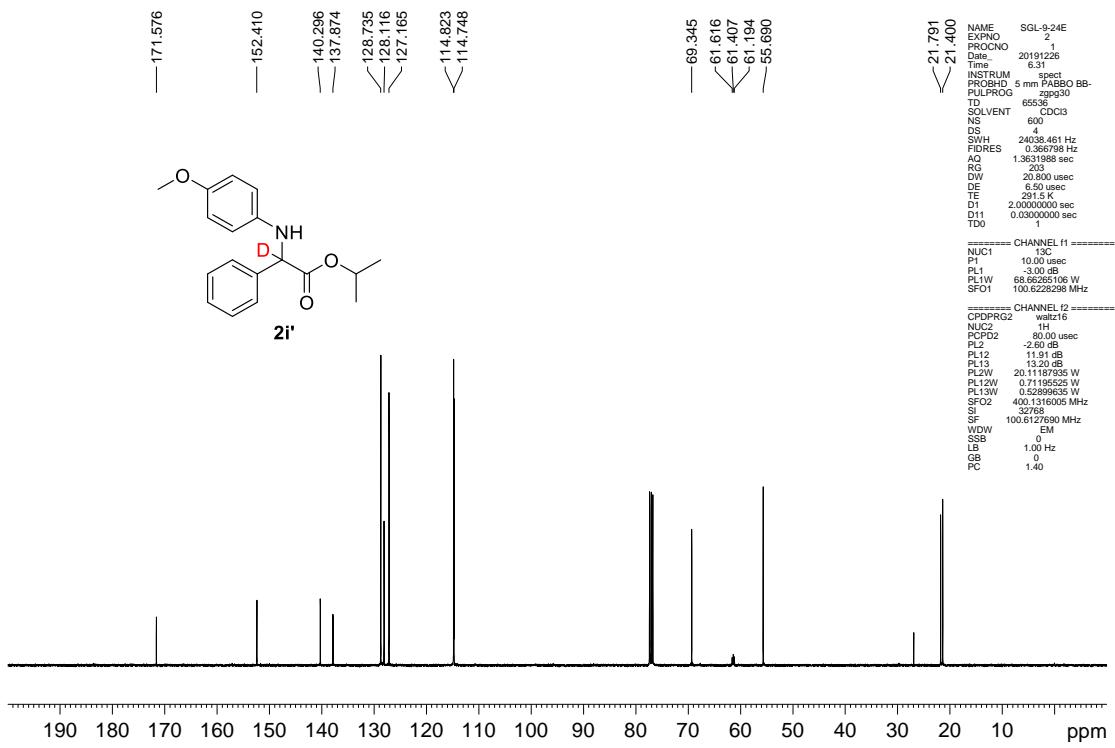


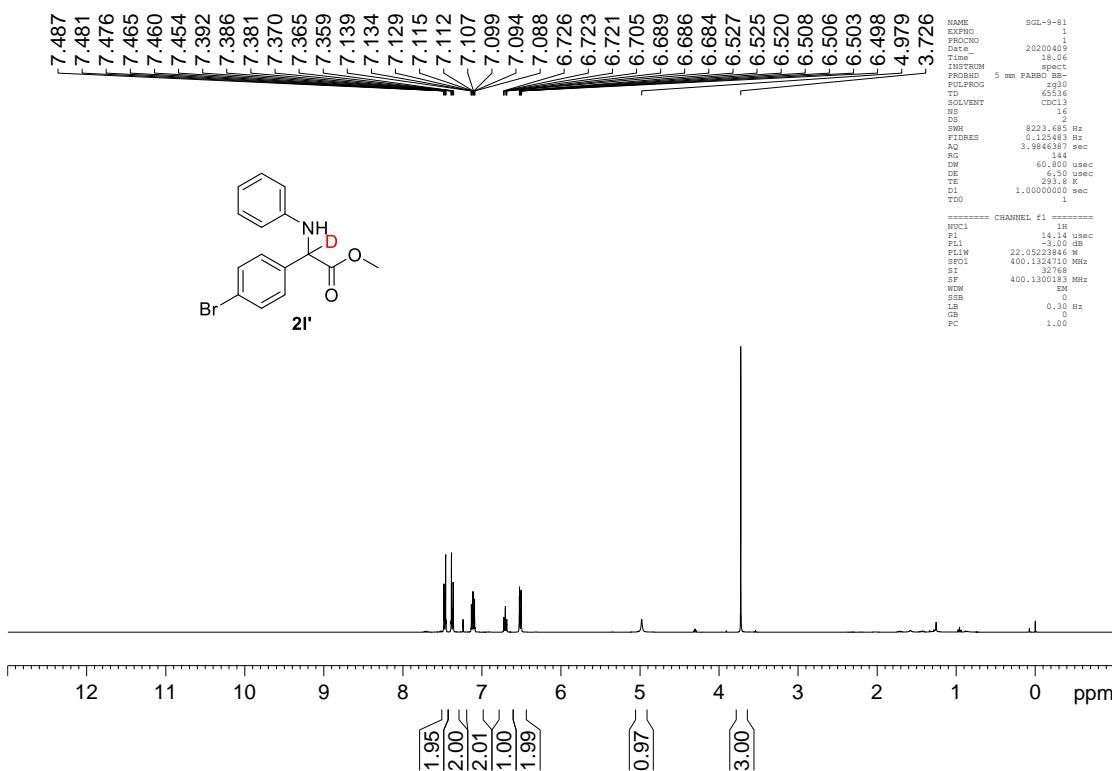
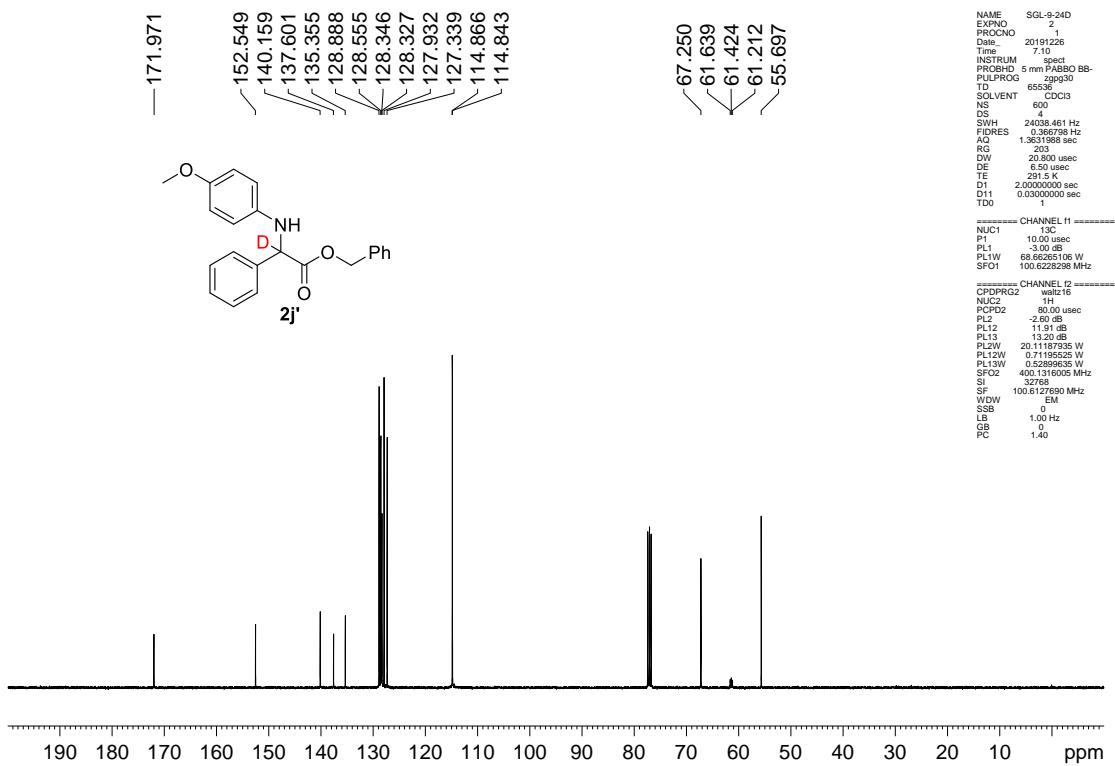


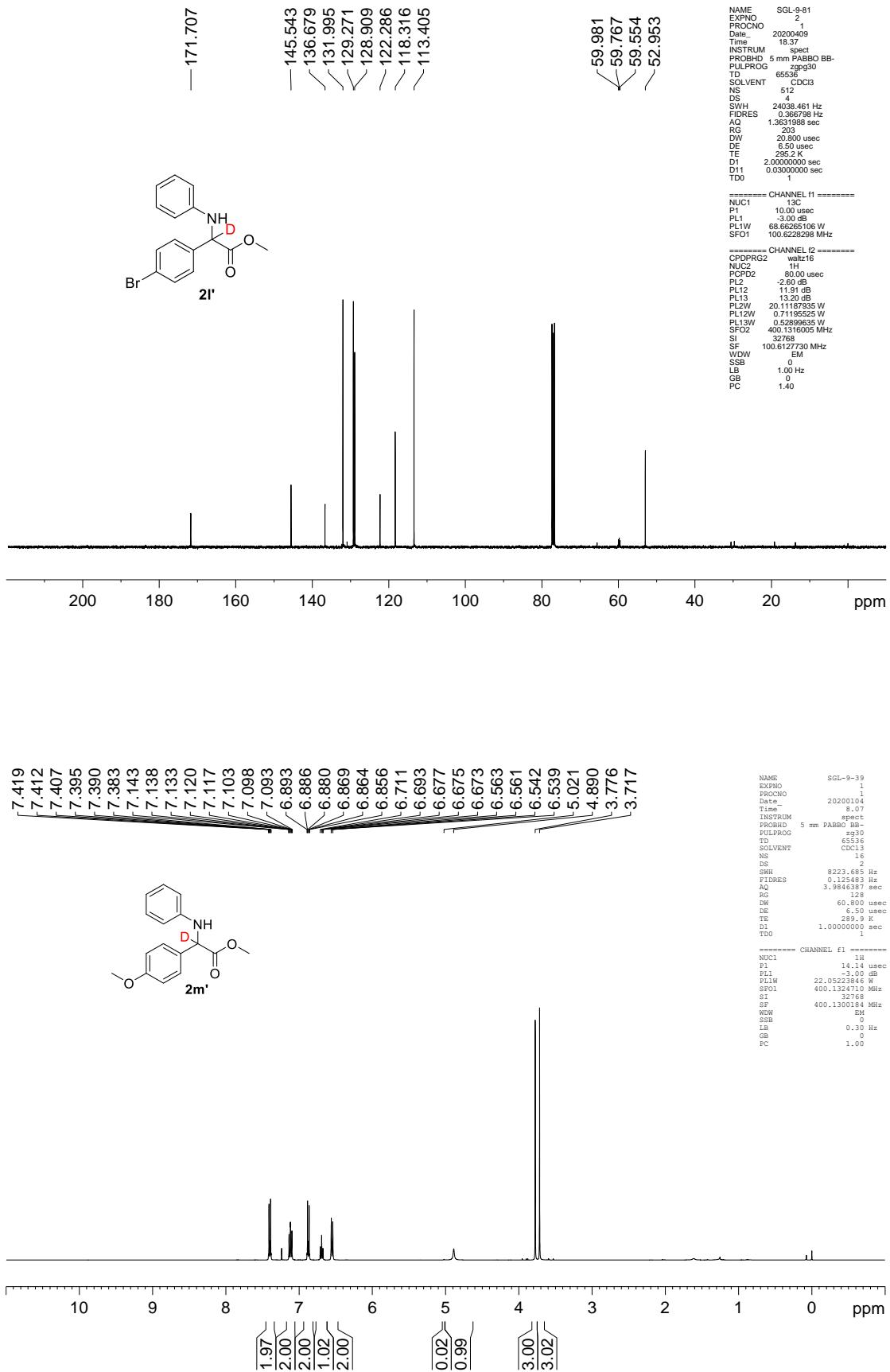


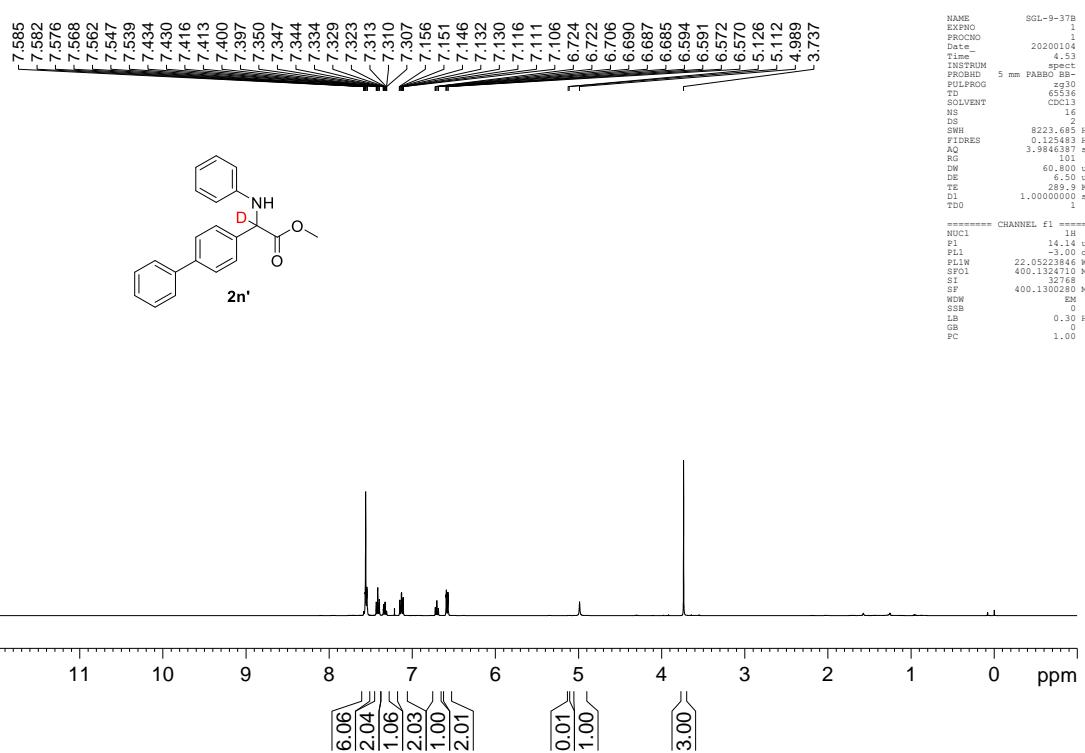
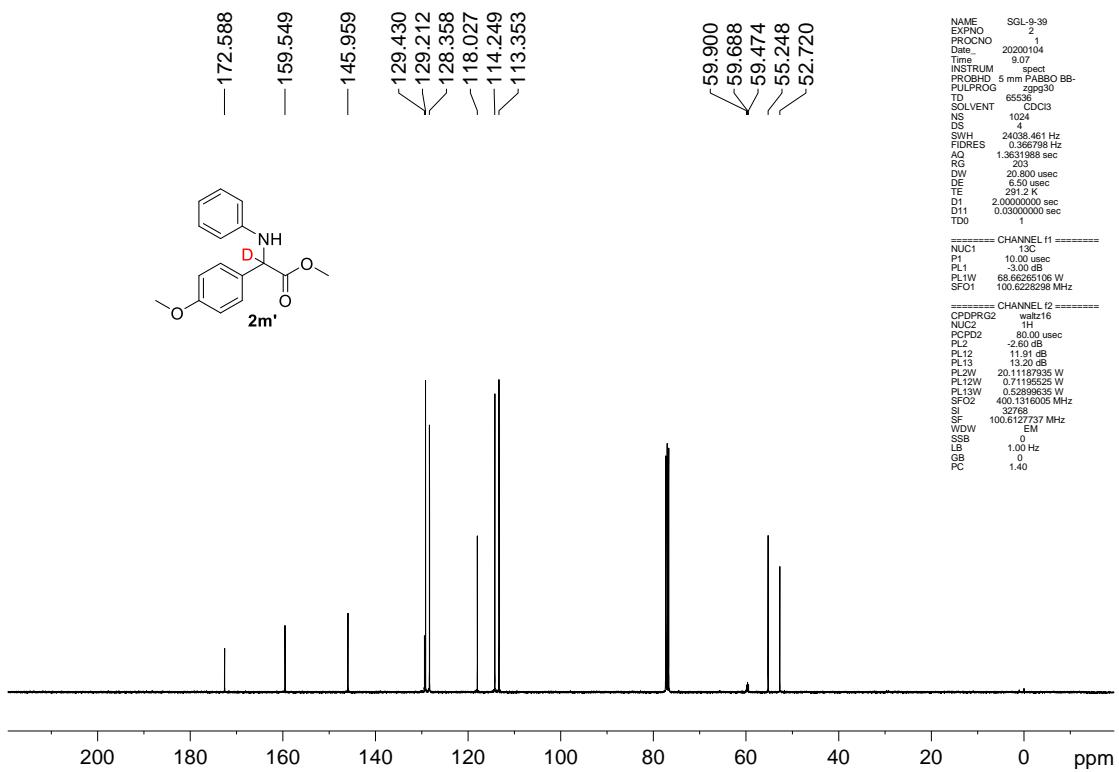


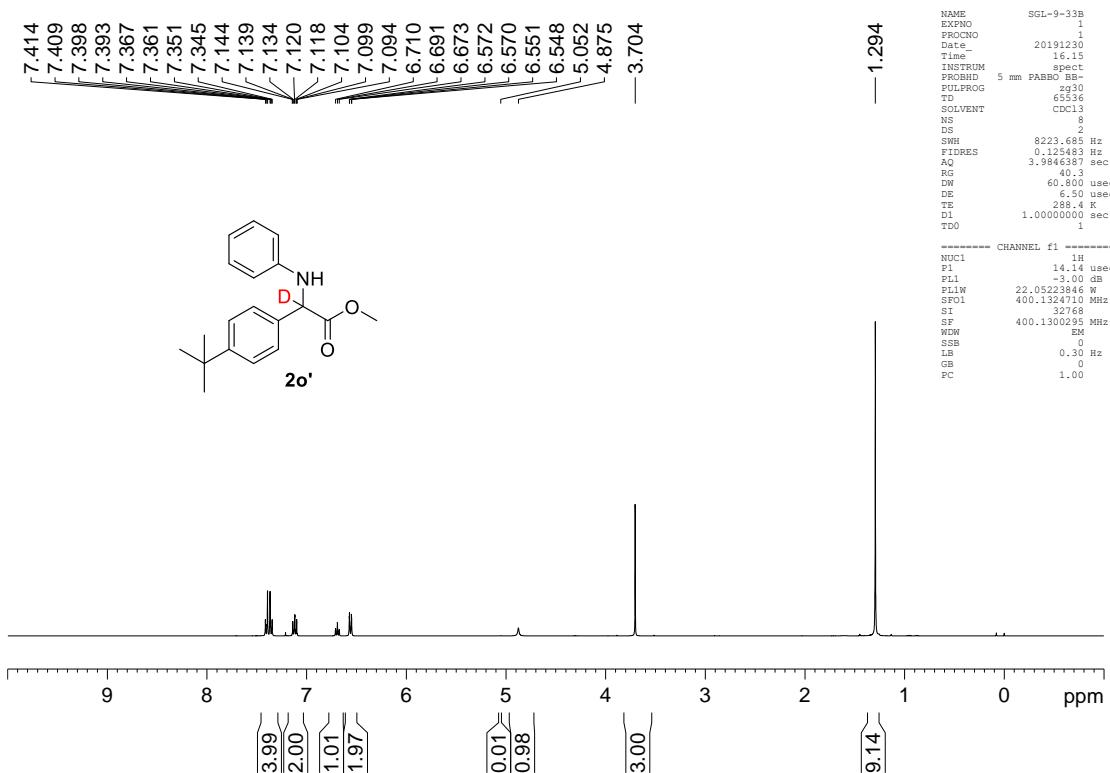
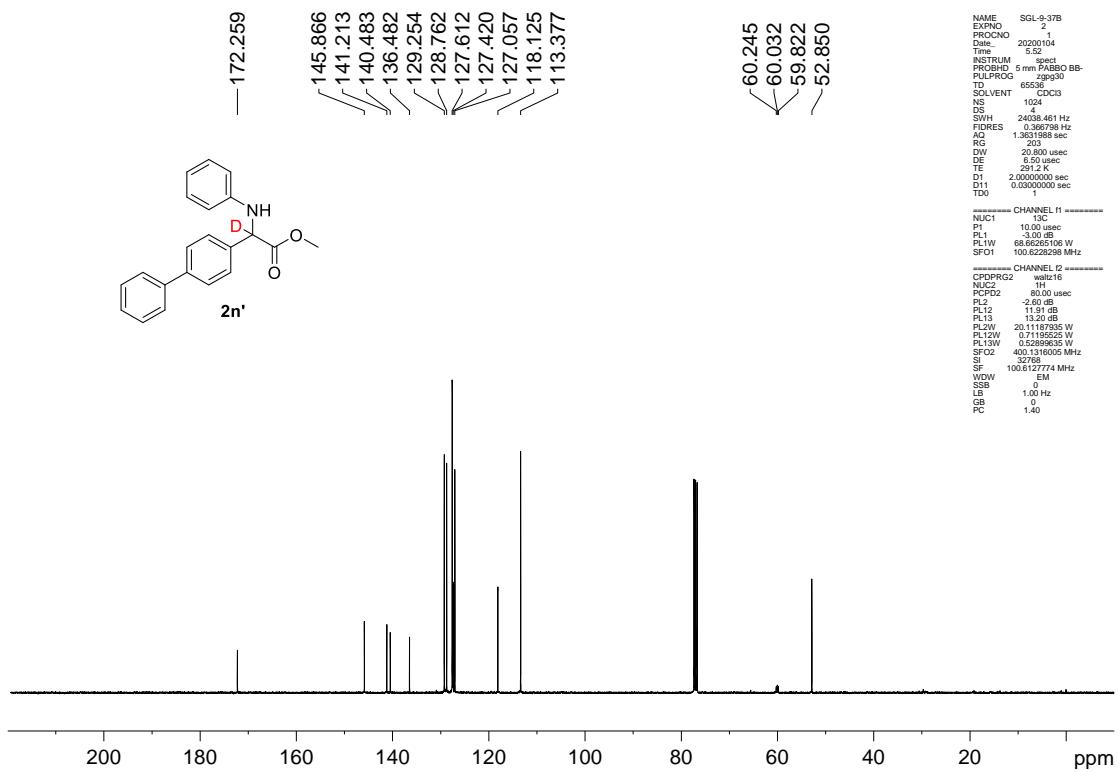


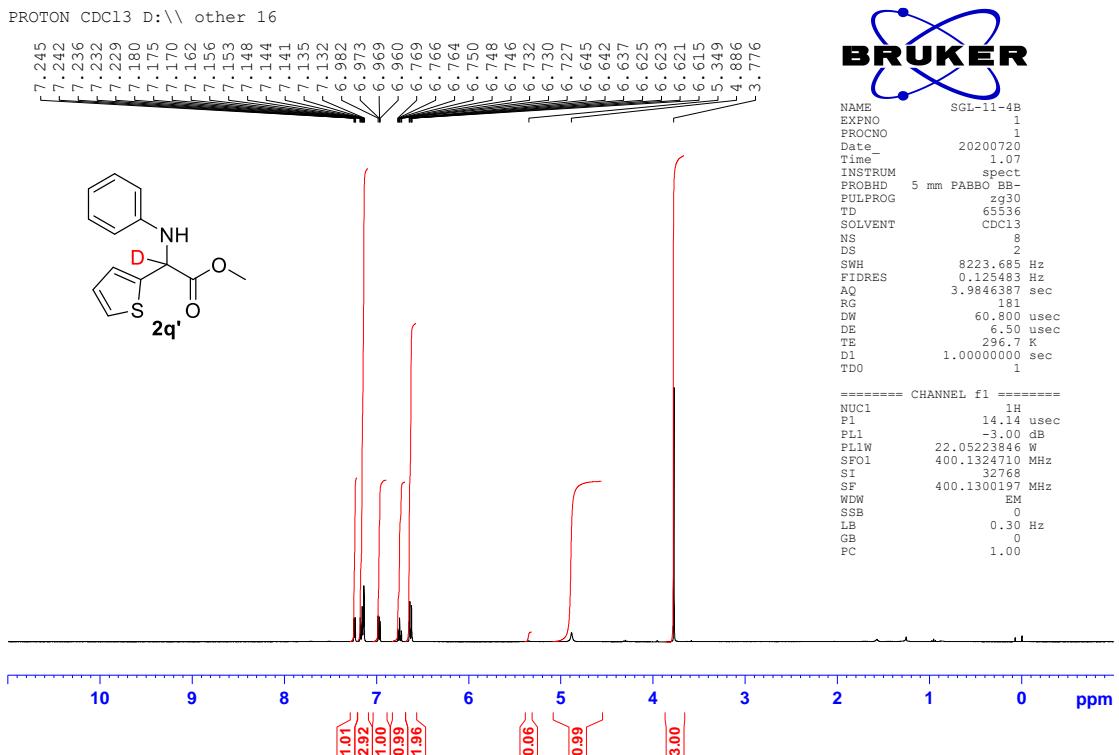
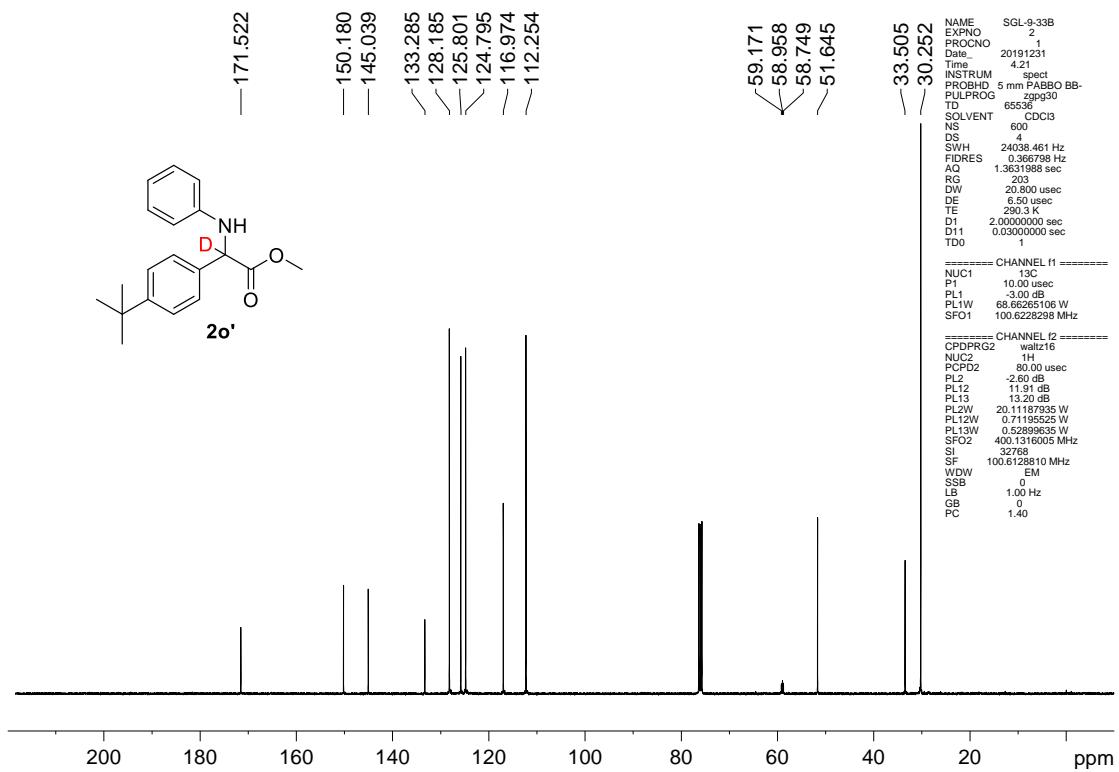










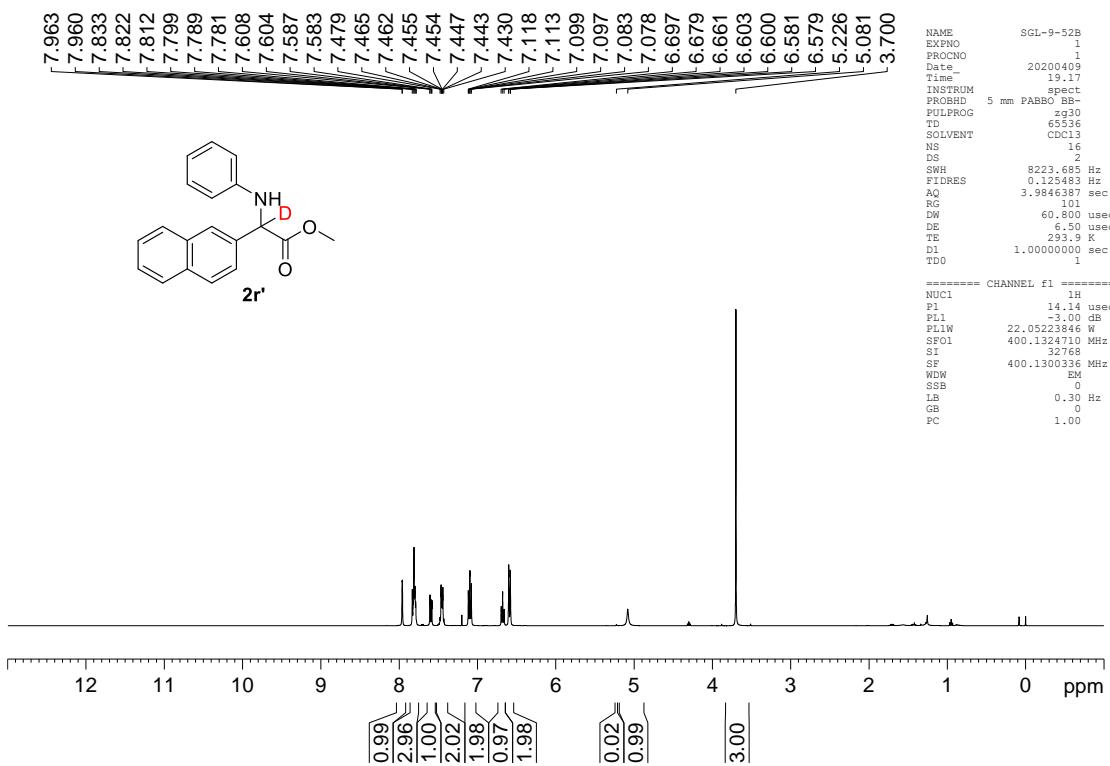
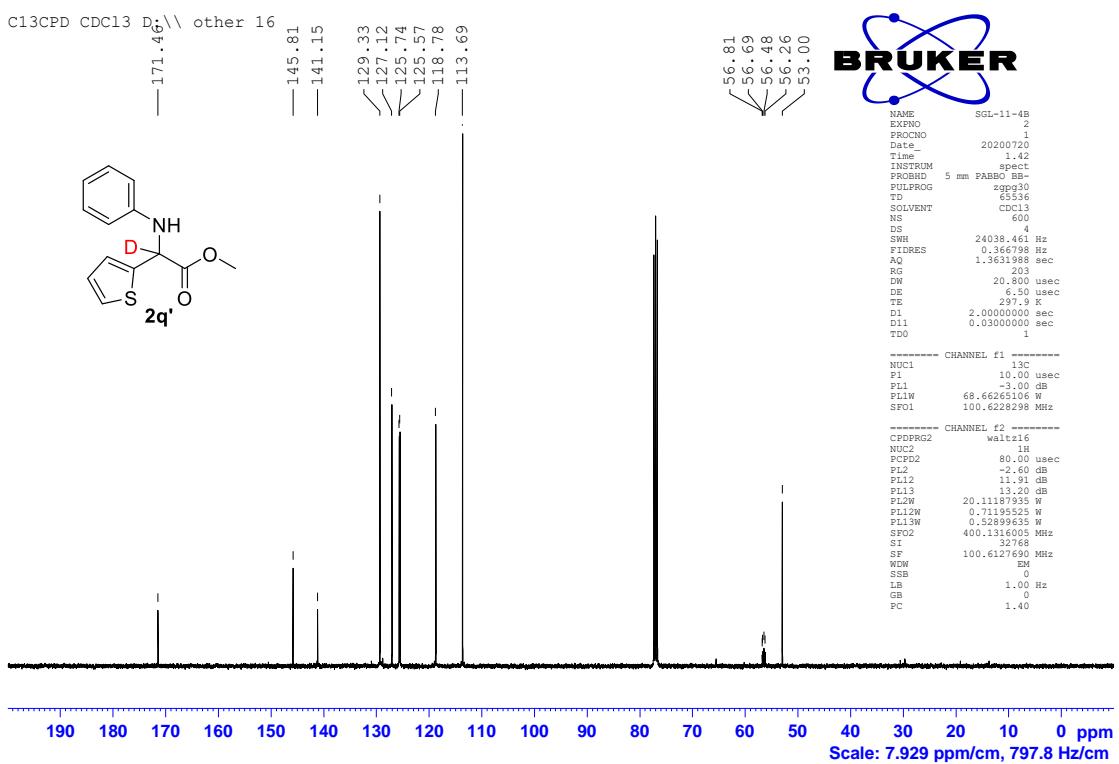


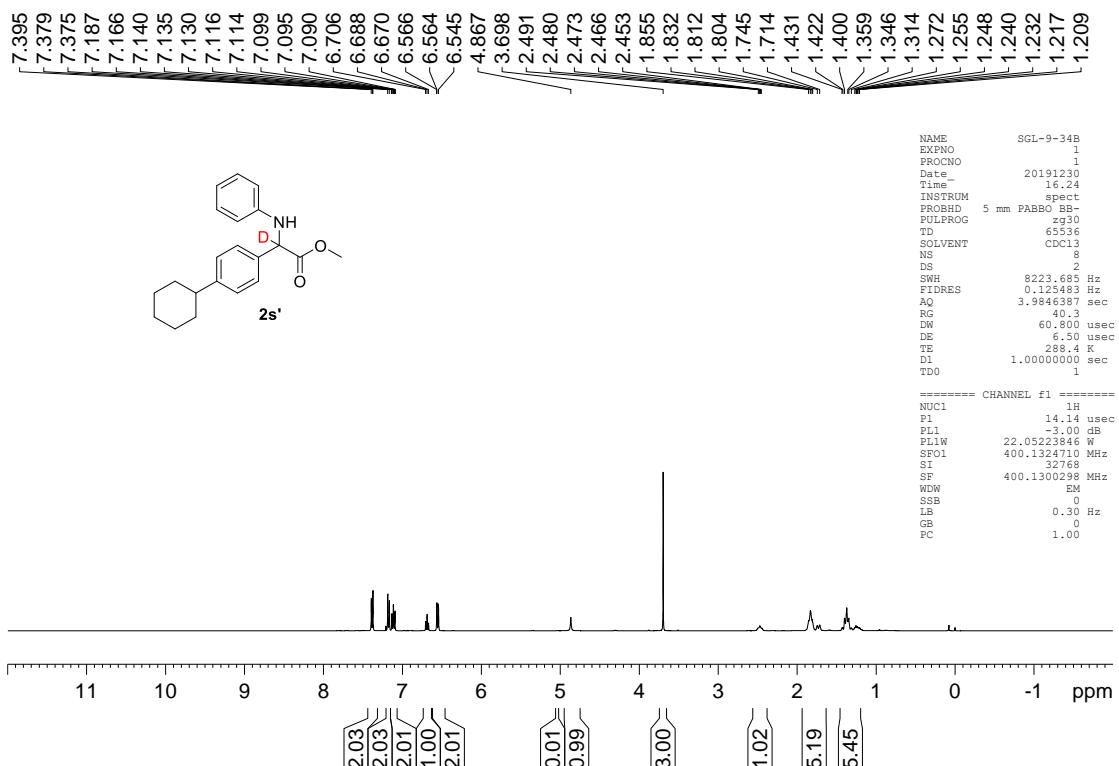
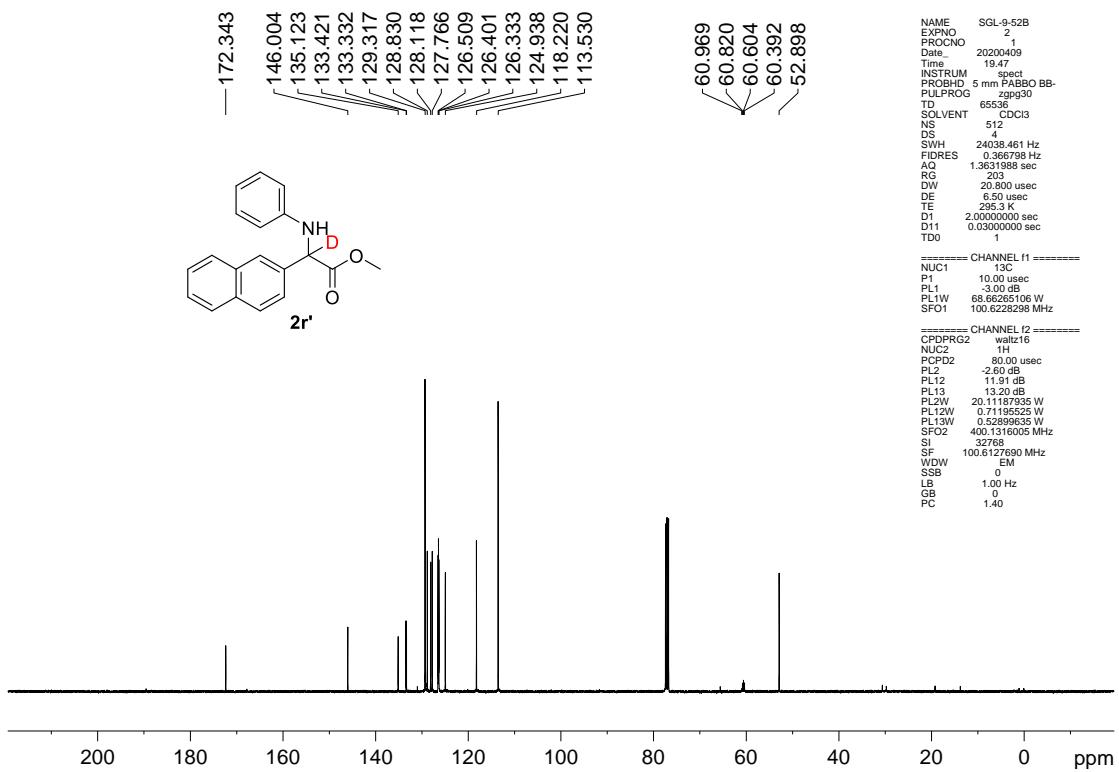
BRUKER

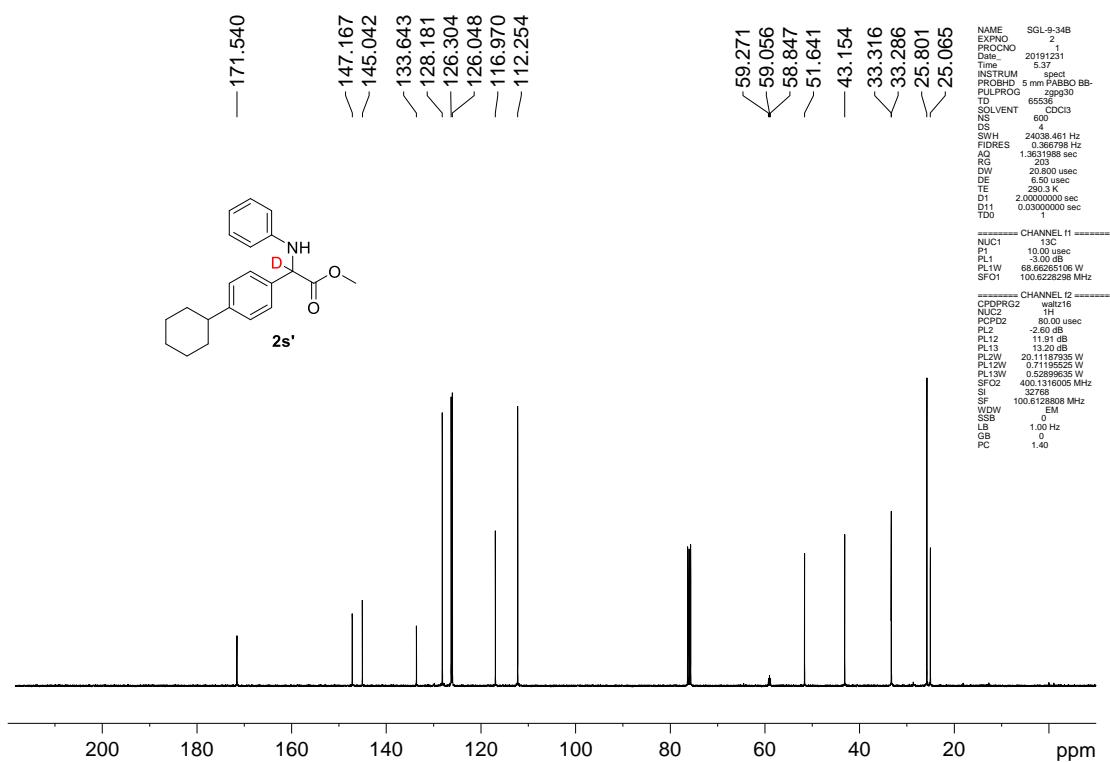
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D1        1.0000000 sec
TD0       1
===== CHANNEL f1 =====
NUC1      1H
P1        14.14 usec
PL1      -3.00 dB
PL1W    22.0522346 W
SF01    400.1324710 MHz
SF       32768
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC        1.00

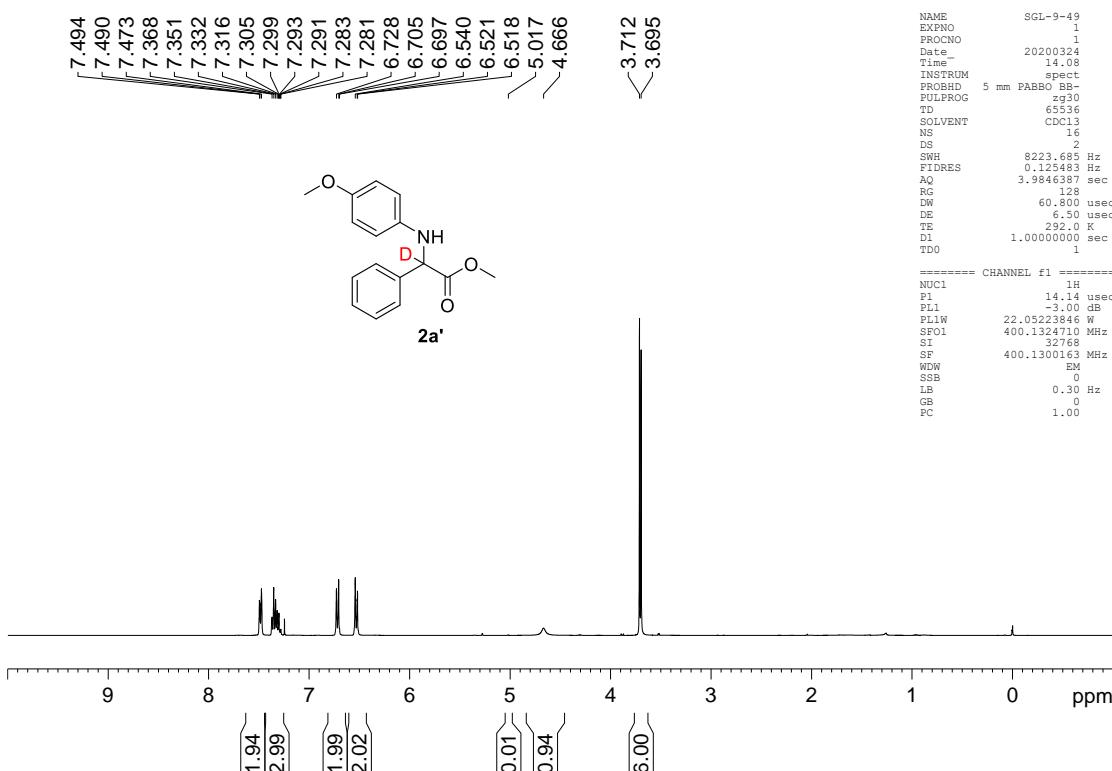
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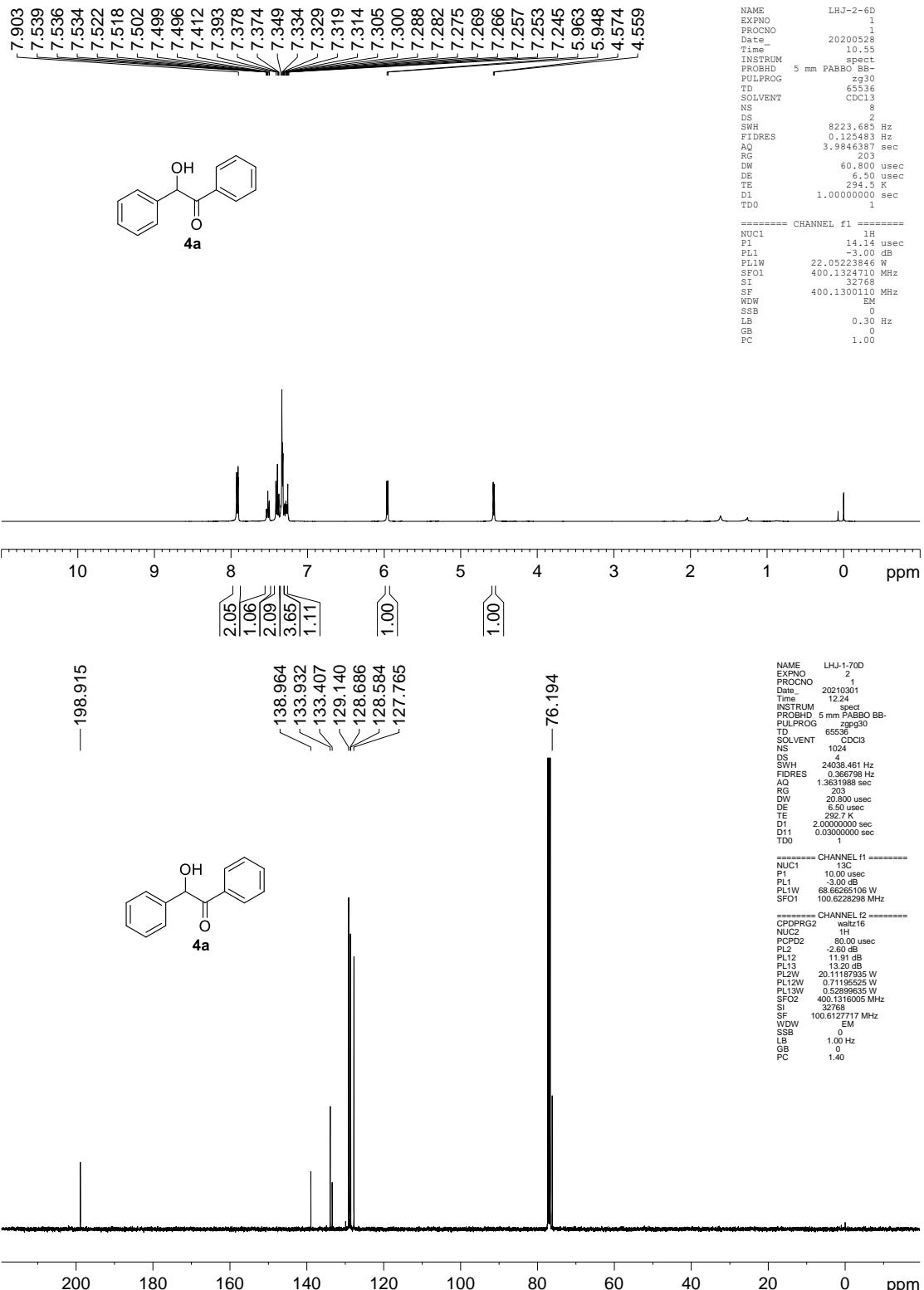


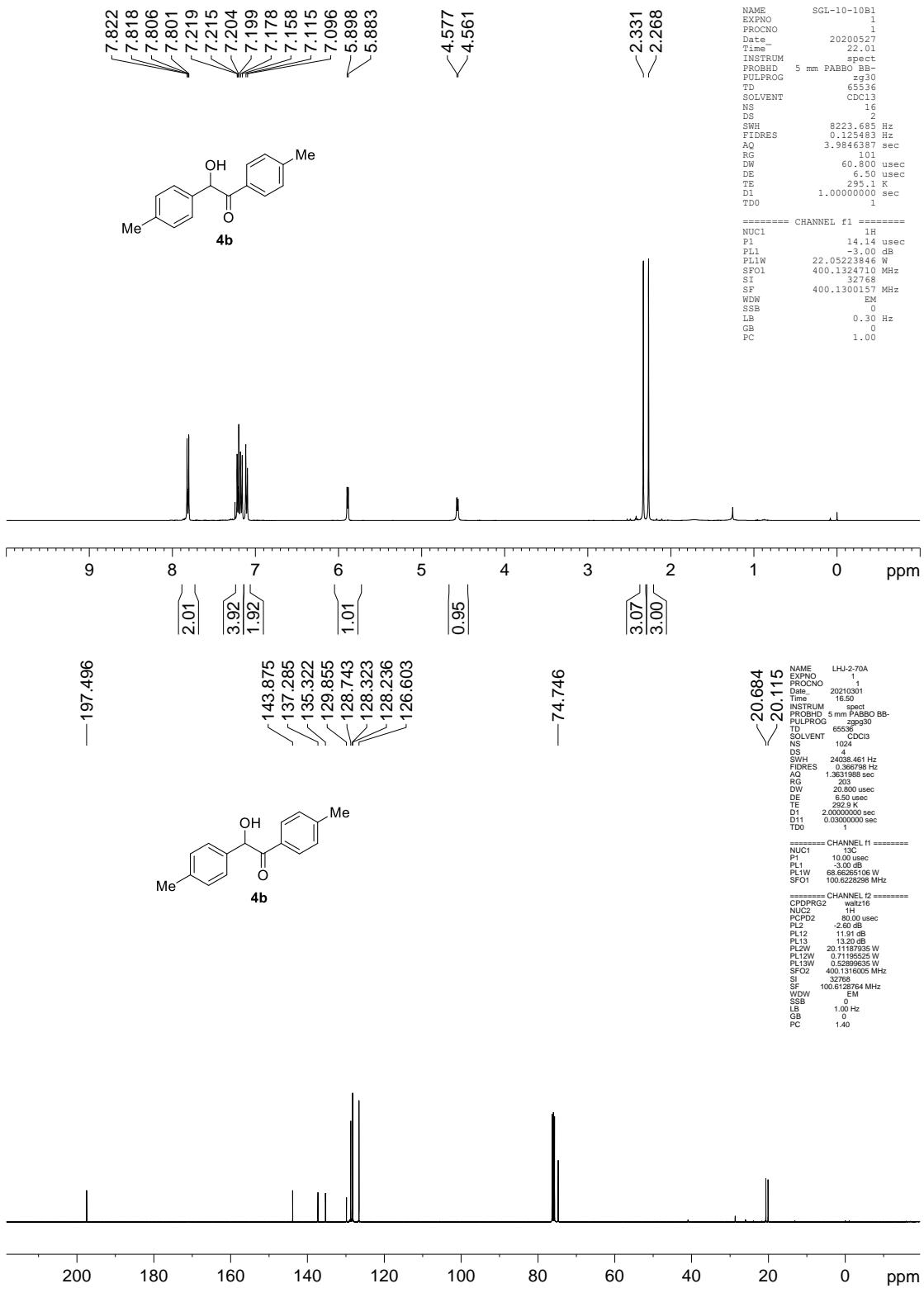


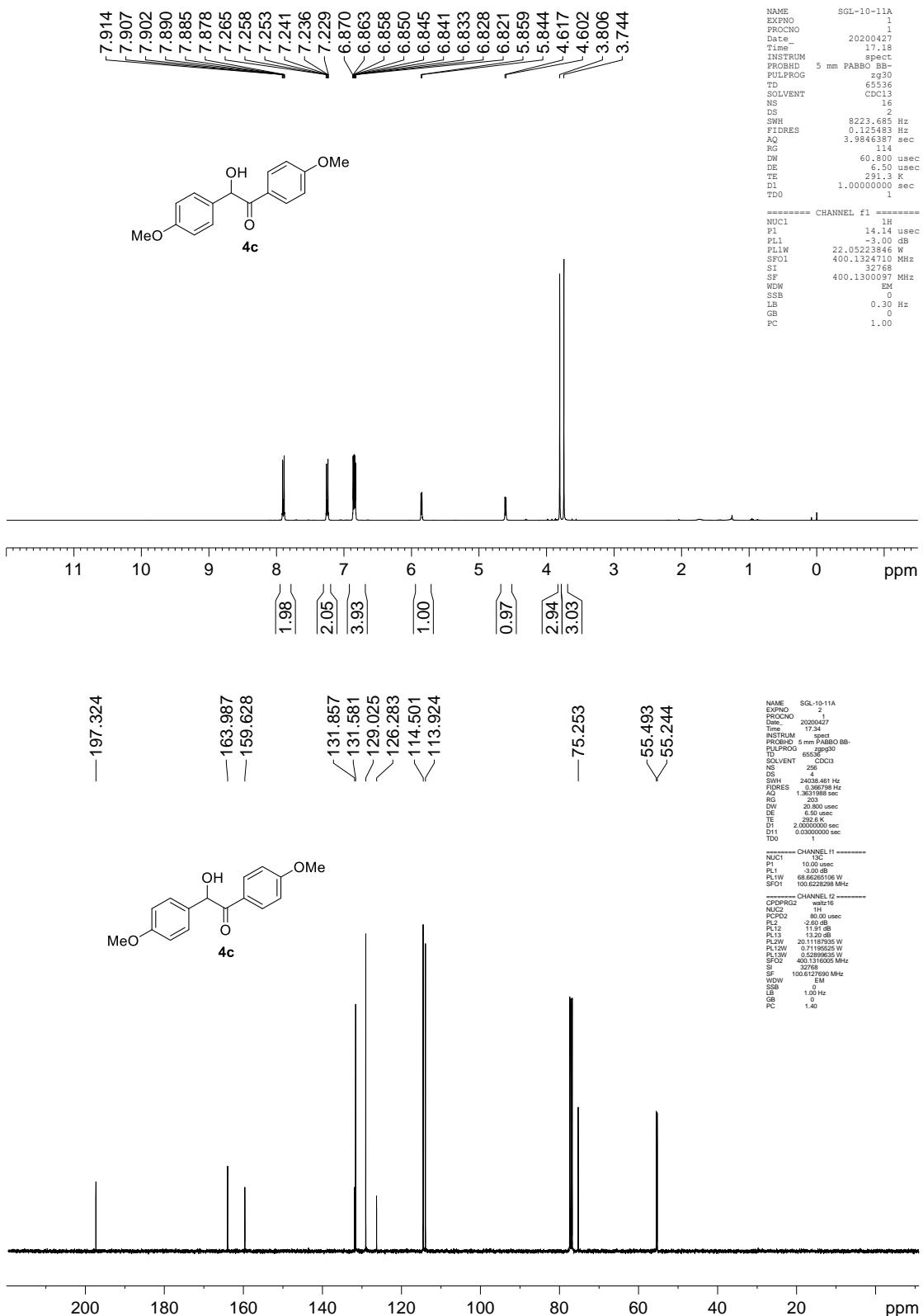


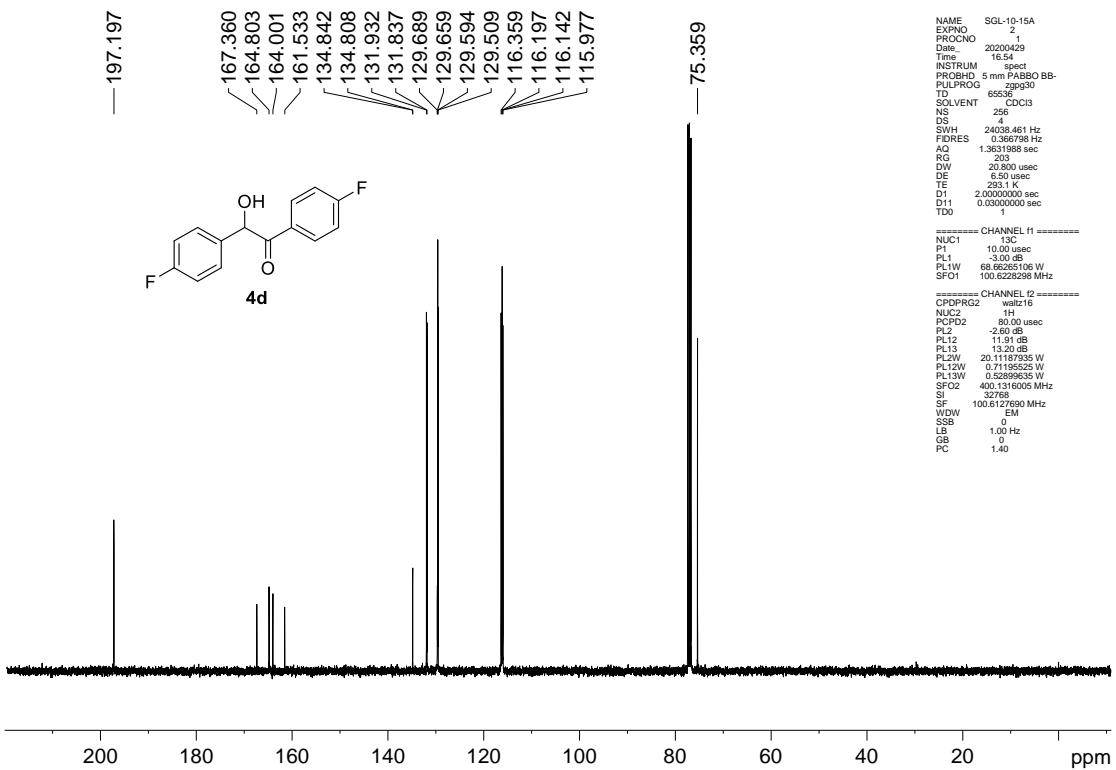
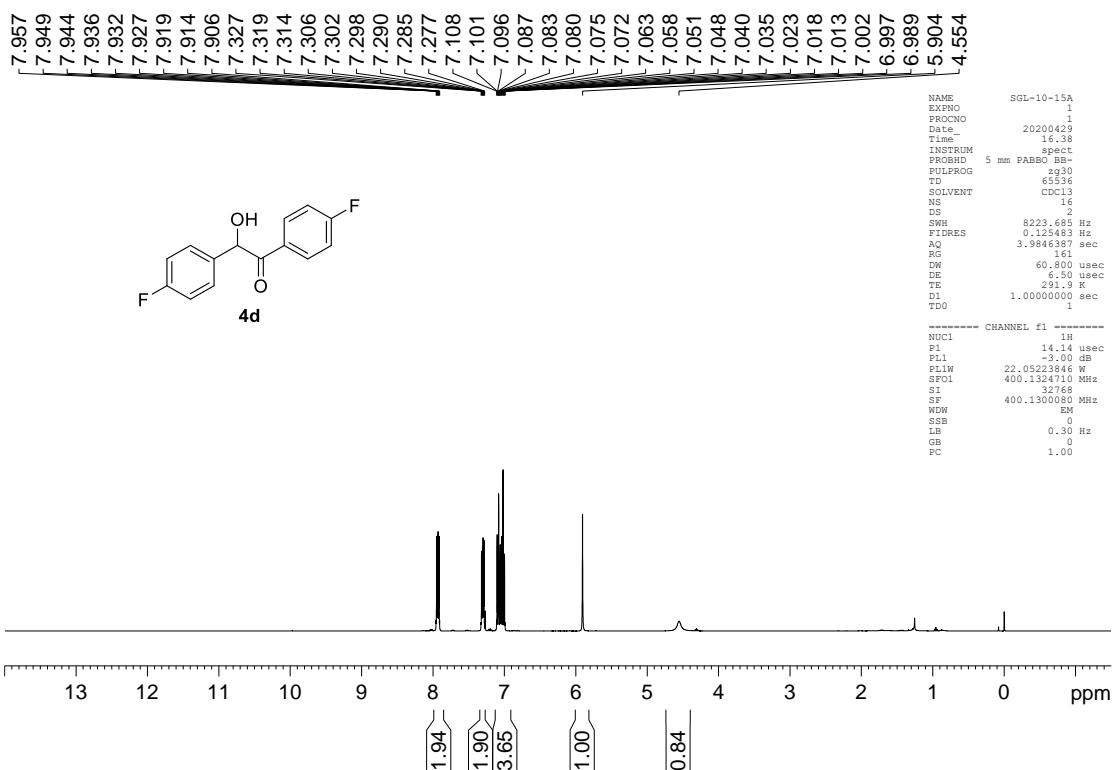
gram scale reactions



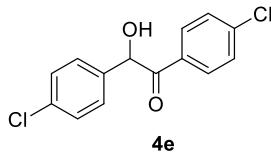








7.838
7.832
7.827
7.815
7.811
7.805
7.392
7.386
7.381
7.369
7.364
7.359
7.313
7.308
7.302
7.292
7.286
7.251
7.240
7.235
7.230
5.882
4.555
4.544



```

NAME      SGL-10-11B
EXPNO    1
PROCNO   1
Date_   20200427
Time_   17.39
INSTRUM  spect
PROBHD  5 mm PABBO BB-
PULPROG zg30
TD      65536
SOLVENT  CDCl3
NS       16
DS        2
SWH     8223.685 Hz
FIDRES  0.125000 Hz
AQ      3.9846387 sec
RG      144
DW      60.800 usec
DE      6.50 usec
TE      291.4 K
D1      1.0000000 sec
TDO      1.0000000 sec

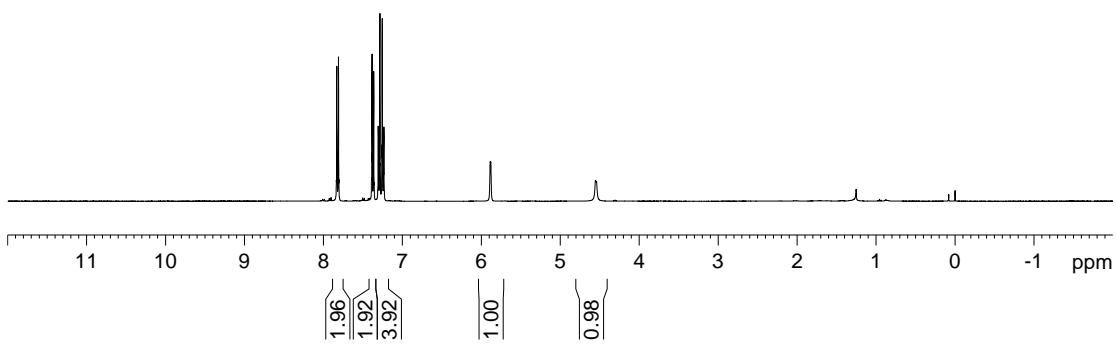
```

===== CHANNEL f1 =====

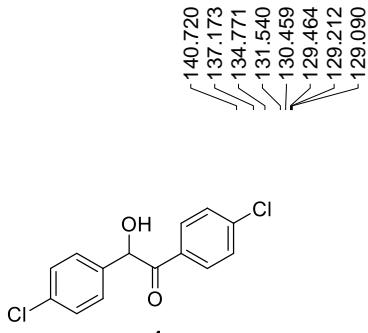
```

NUC1      1H
P1      14.14 usec
PL1     -3.00 dB
PL1W    22.052400 W
SF01    400.1324710 MHz
SI      32768
SF      400.1300091 MHz
WDW      EM
SSB      0
LB      0.30 Hz
GB      0
PC      1.00

```



— 197.478



— 75.486

```

NAME      SGL-10-11B
EXPNO    2
PROCNO   1
Date_   20200427
Time_   17.54
INSTRUM  spect
PROBHD  5 mm PABBO BB-
PULPROG zg30
TD      65536
SOLVENT  CDCl3
NS       4
DS        2
SWH     2438.4611 Hz
FIDRES  0.368738 Hz
AQ      1.3631988 sec
RG      2048
DW      20.800 usec
DE      6.50 usec
TE      291.4 K
D1      2.0000000 sec
D11     0.0000000 sec
TDO      1.0000000 sec

```

===== CHANNEL f1 =====

```

NUC1      13C
P1      19.40 usec
PL1     -3.00 dB
PL1W    68.66265106 W
SF01    100.62262698 MHz

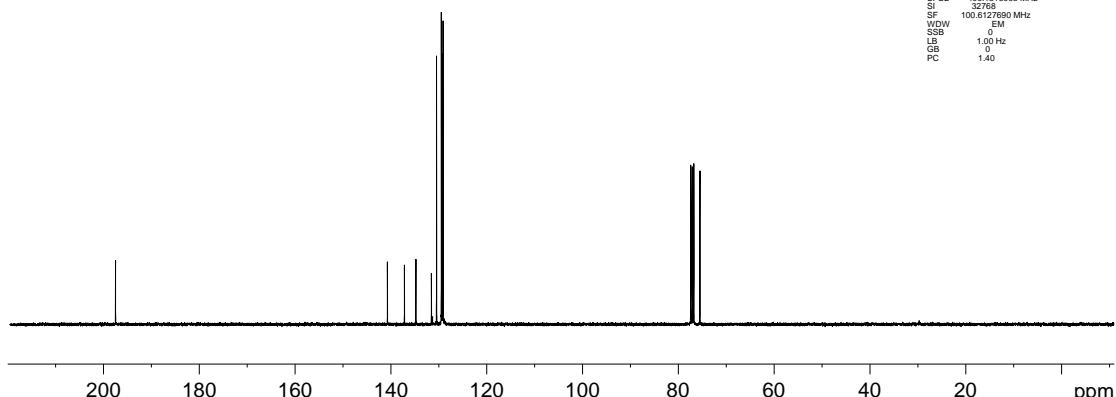
```

===== CHANNEL f1' =====

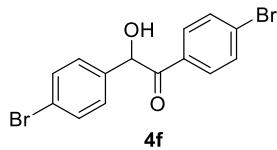
```

CPDPGR2
NUC2      1H
PDPG2    8.00 usec
PL2     -2.60 dB
PL12    11.91 dB
PL13    13.69 dB
PL2W    20.11187935 W
PL12W   10.05939632 W
PL13W   0.52899635 W
SF02    400.1316005 MHz
SI      32768
SF      100.6127690 MHz
WDW      EM
SSB      0
LB      1.00 Hz
GB      1.40
PC      1.00

```



7.744
7.723
7.552
7.531
7.458
7.437
7.190
7.169



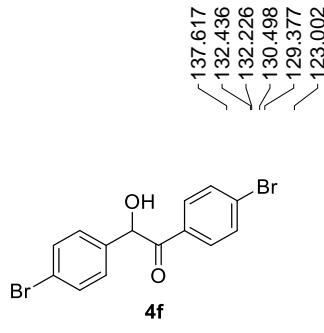
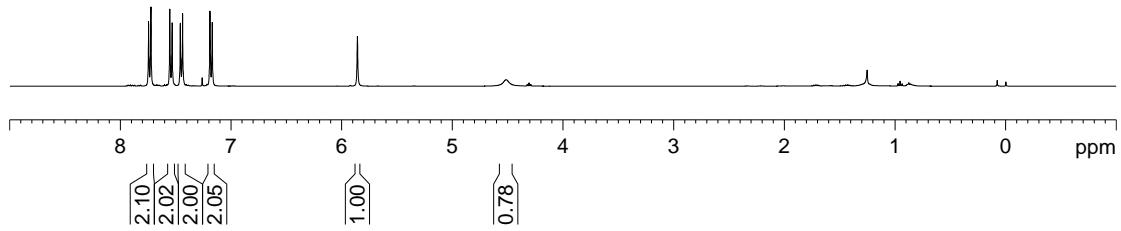
— 5.857
— 4.513

```

NAME      LHJ-2-20
EXPNO     1
PROCNO    1
Date      20200716
Time      13.35
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD        65536
SOLVENT   CDCl3
NS        16
DS        2
SWH       8223.685 Hz
FIDRES   0.125483 Hz
AQ        3.9846387 sec
RG        161
DW        60.800 usec
DE        6.50 usec
TE        293.0 K
D1        1.0000000 sec
T0        1
TD0

===== CHANNEL f1 =====
NUC1      1H
P1        14.14 usec
PL1      -3.00 dB
PL1W    22.05223846 W
SF01    400.1324710 MHz
SI        32768
SF        400.1300130 MHz
WDW      EM
SSB      0
LB        0.30 Hz
GB      0
PC        1.00

```

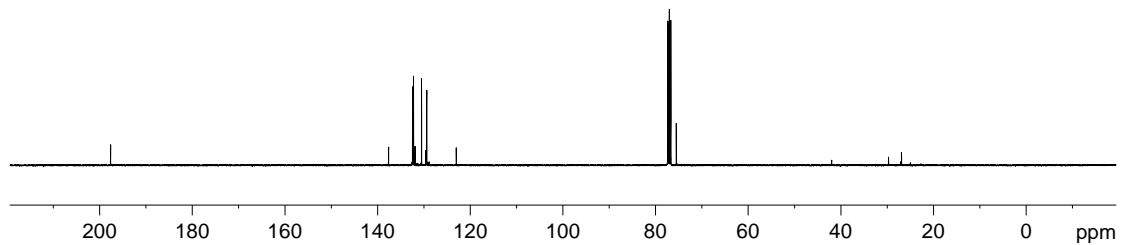


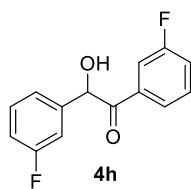
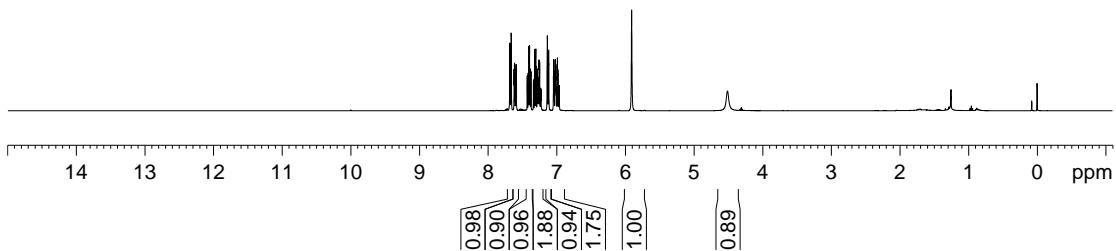
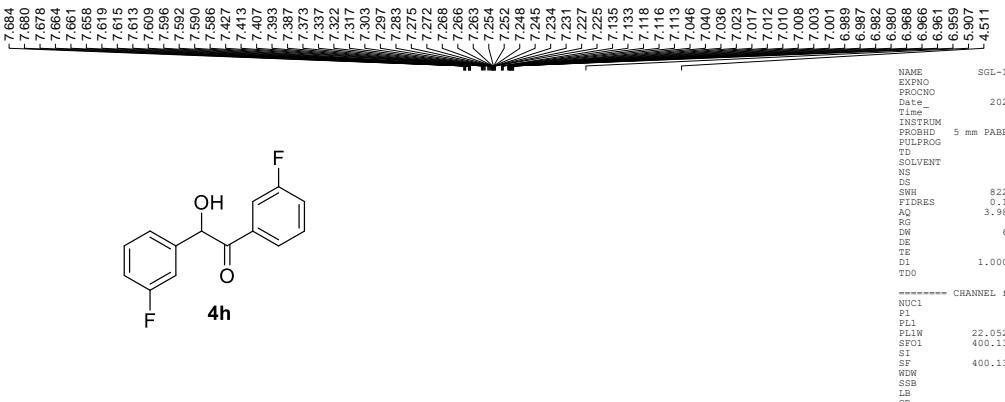
```

NAME      LHJ-2-70B
EXPNO     1
PROCNO    1
Date      20210301
Time      17.55
INSTRUM   spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT   CDCl3
NS        1024
DS        1
SWH       24038.461 Hz
FIDRES   0.366798 Hz
AQ        1.000000 sec
RG        203
DW        20.800 usec
DE        6.50 usec
TE        293.0 K
D1        2.0000000 sec
T0        1
D11      0.03000000 sec
TD0

===== CHANNEL f1 =====
NUC1      1H
P1        10.00 usec
PL1      -3.00 dB
PL1W    68.66265106 W
SF01    100.6228298 MHz
WDW      EM
SSB      0
LB        1.00 Hz
GB      0
PC        1.40

```





```

NAME      SGL-10-15B
EXPNO     2
PROCNO    1
Date: 20200429
Time: 17.00
INSTRUM spect
PROBHD  5 mm PABBO BB
PULPROG zg30
TD        65536
SOLVENT   CDCl3
NS         4
DS          2
SWH       2948.461 Hz
FIDRES   0.366798 Hz
AQ        1.3631988 sec
RG        3
DW        20.000 usec
DE        6.50 usec
TE        291.9 K
D1        2.0000000 sec
D11       0.0000000 sec
TDO      1

```

----- CHANNEL I1 -----

```

NUC1      13C
P1        10.00 usec
PL1      -3.00 dB
PL1W    68.66265106 W
SF01    100.6226298 MHz

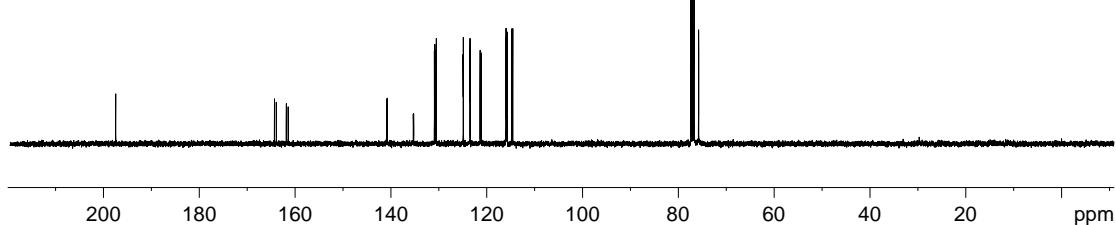
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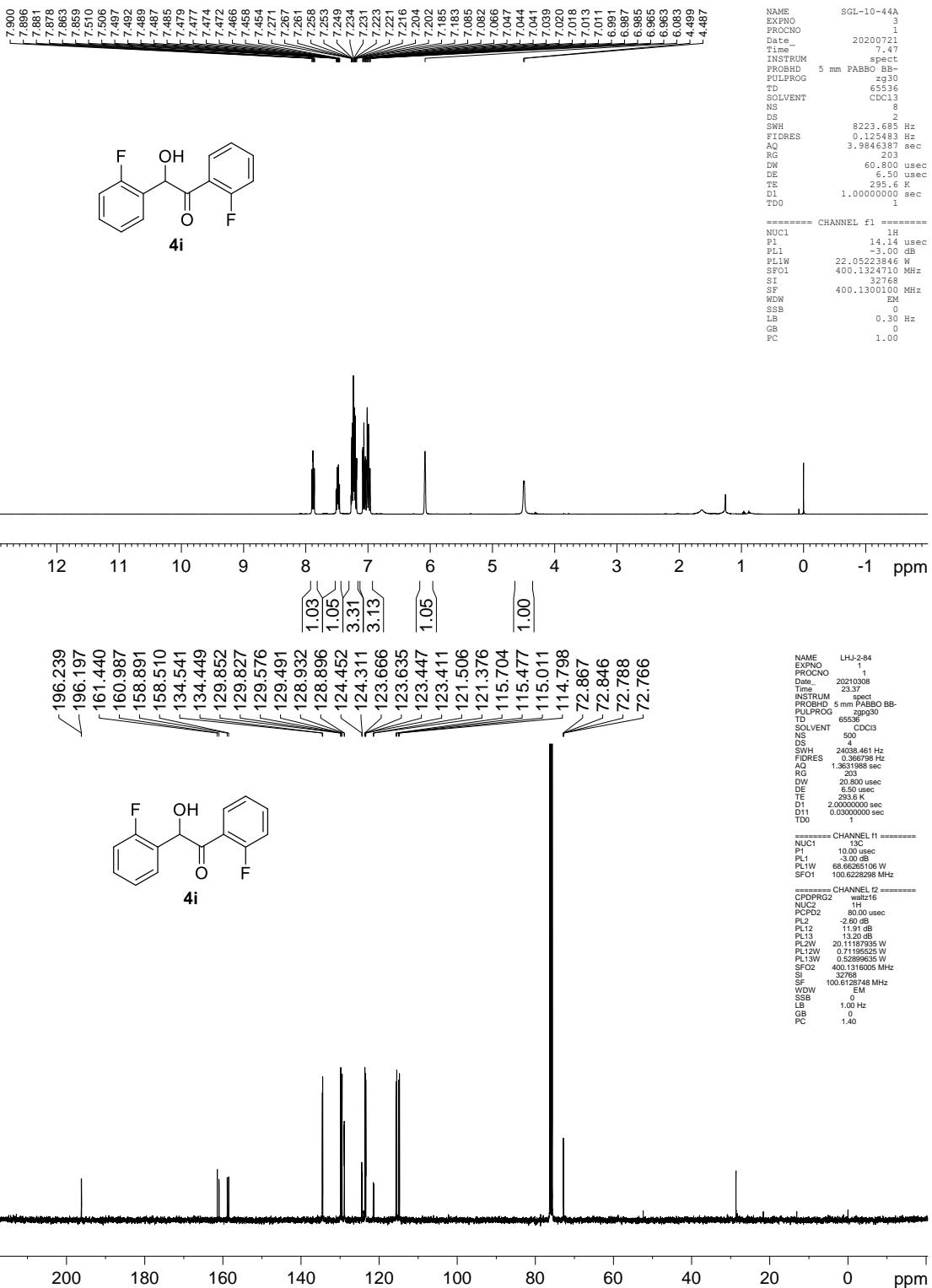
----- CHANNEL I2 -----

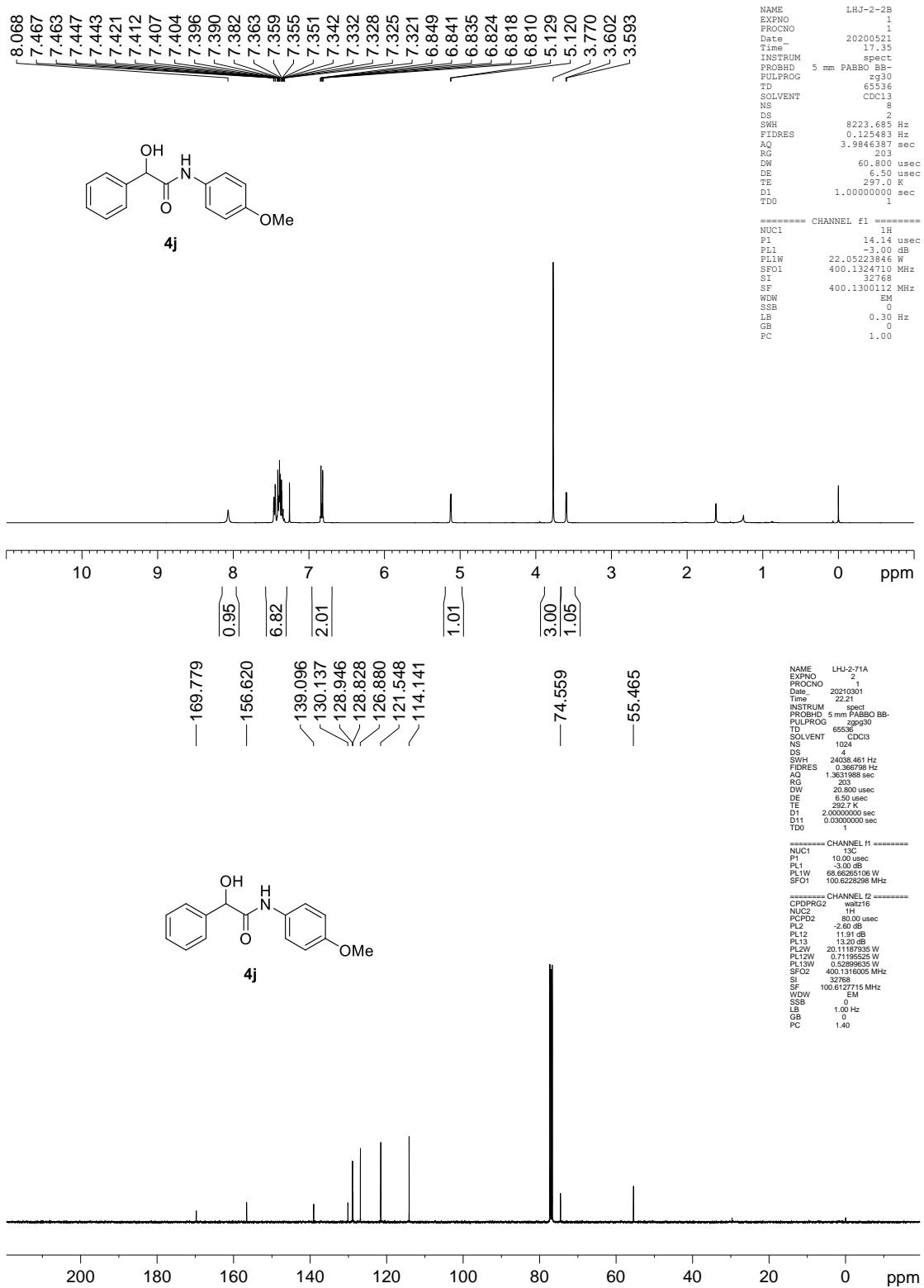
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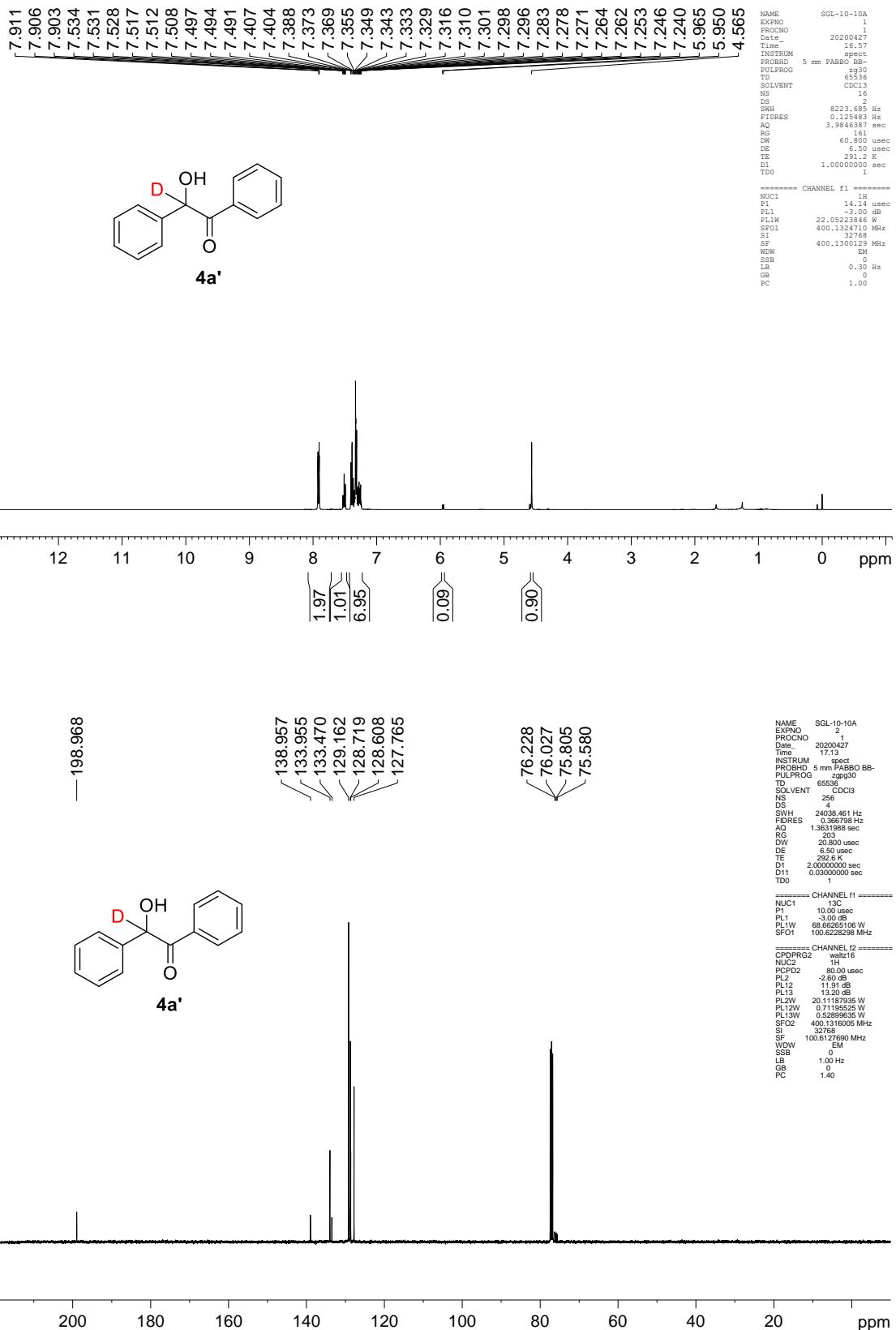
CPDPRG2  13C-1H
NUC2      1H
P1P2      1.00 usec
PL12     -2.60 dB
PL13     13.00 dB
PL2W    20.11187935 W
PL2W    0.15205525 W
PL3W    0.15205525 W
SF02    400.1316005 MHz
SI        32768
SF      100.6127690 MHz
WDW      EM
SSB      0
LB      1.00 Hz
GB      0
PC      1.40

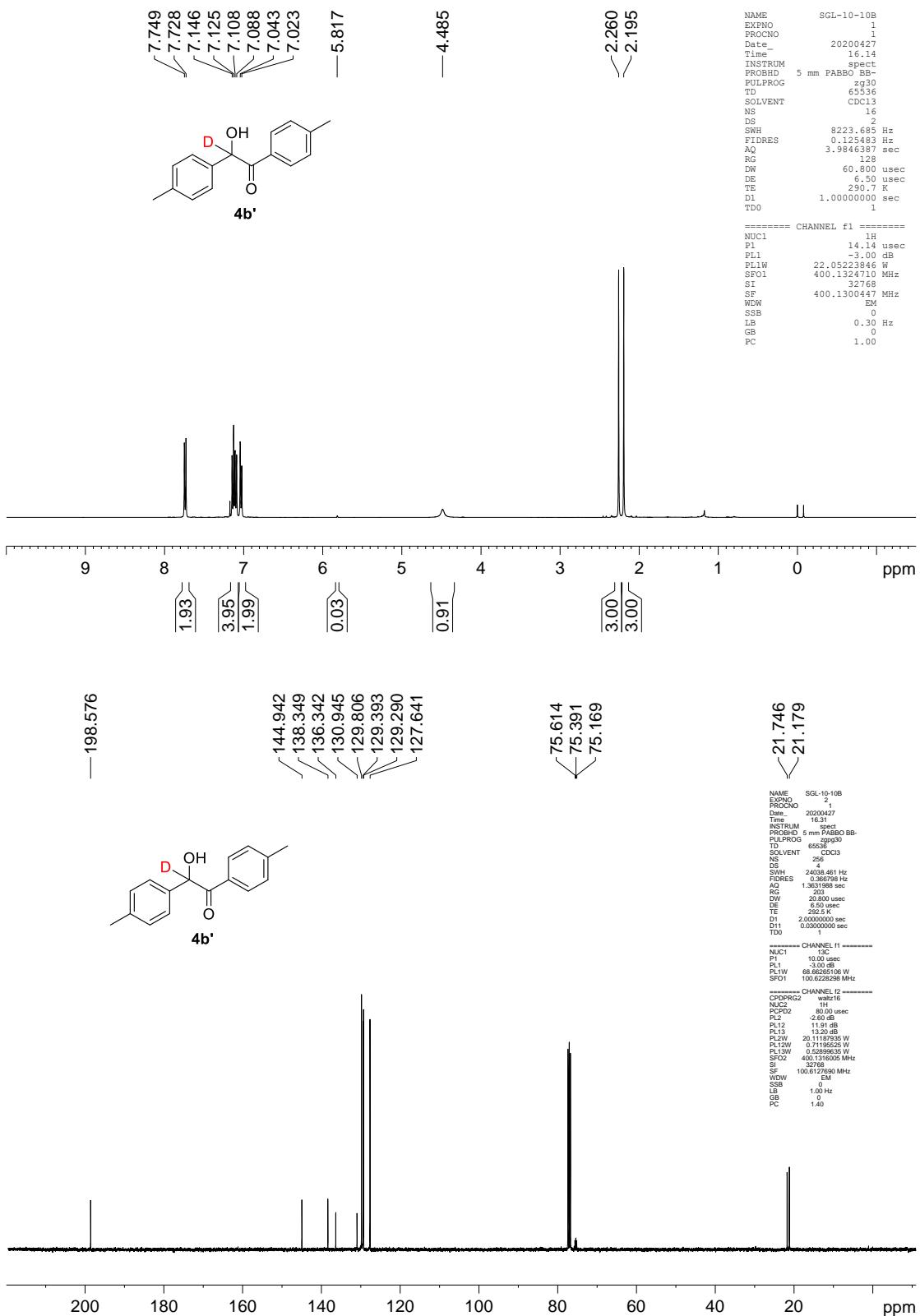
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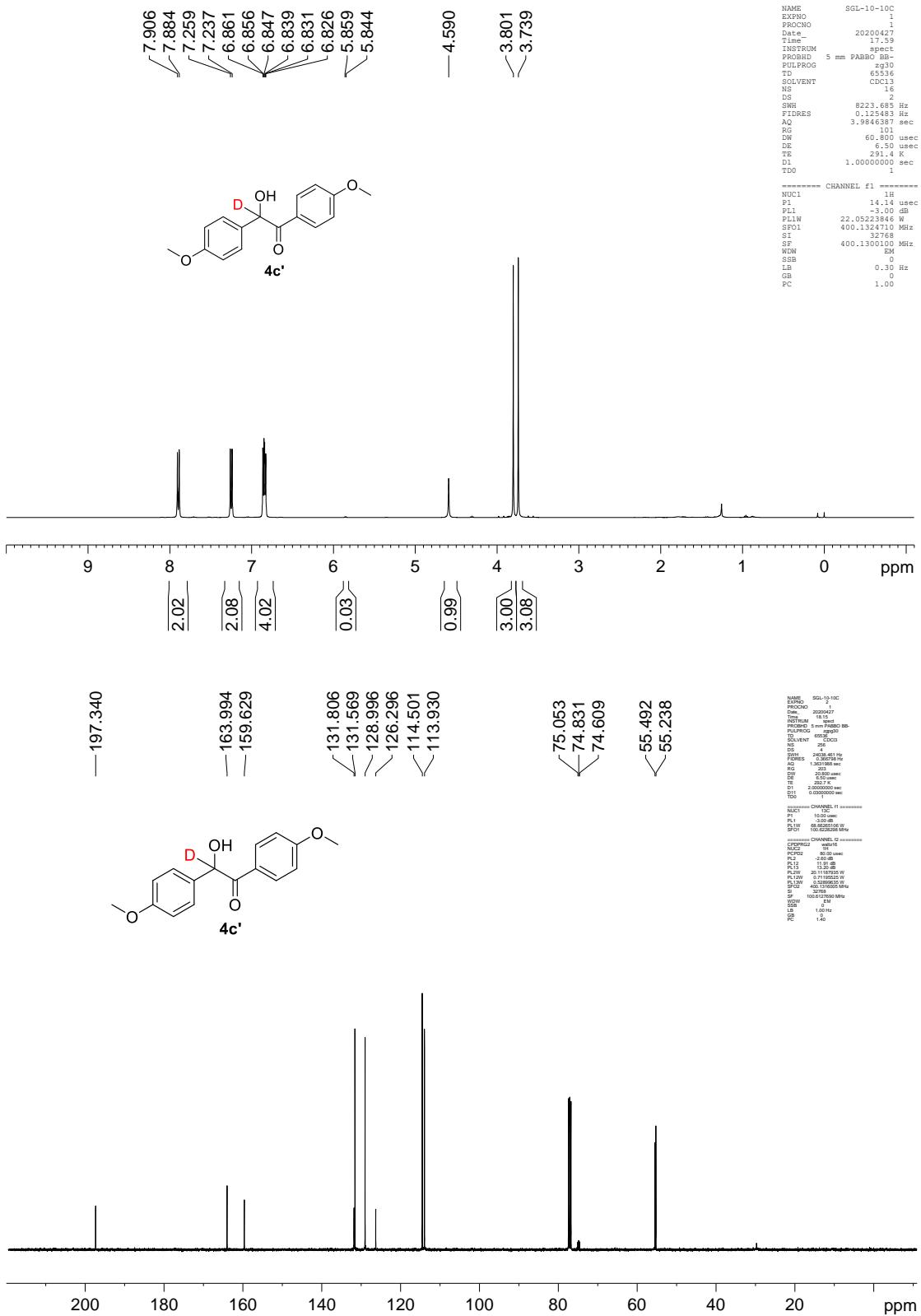


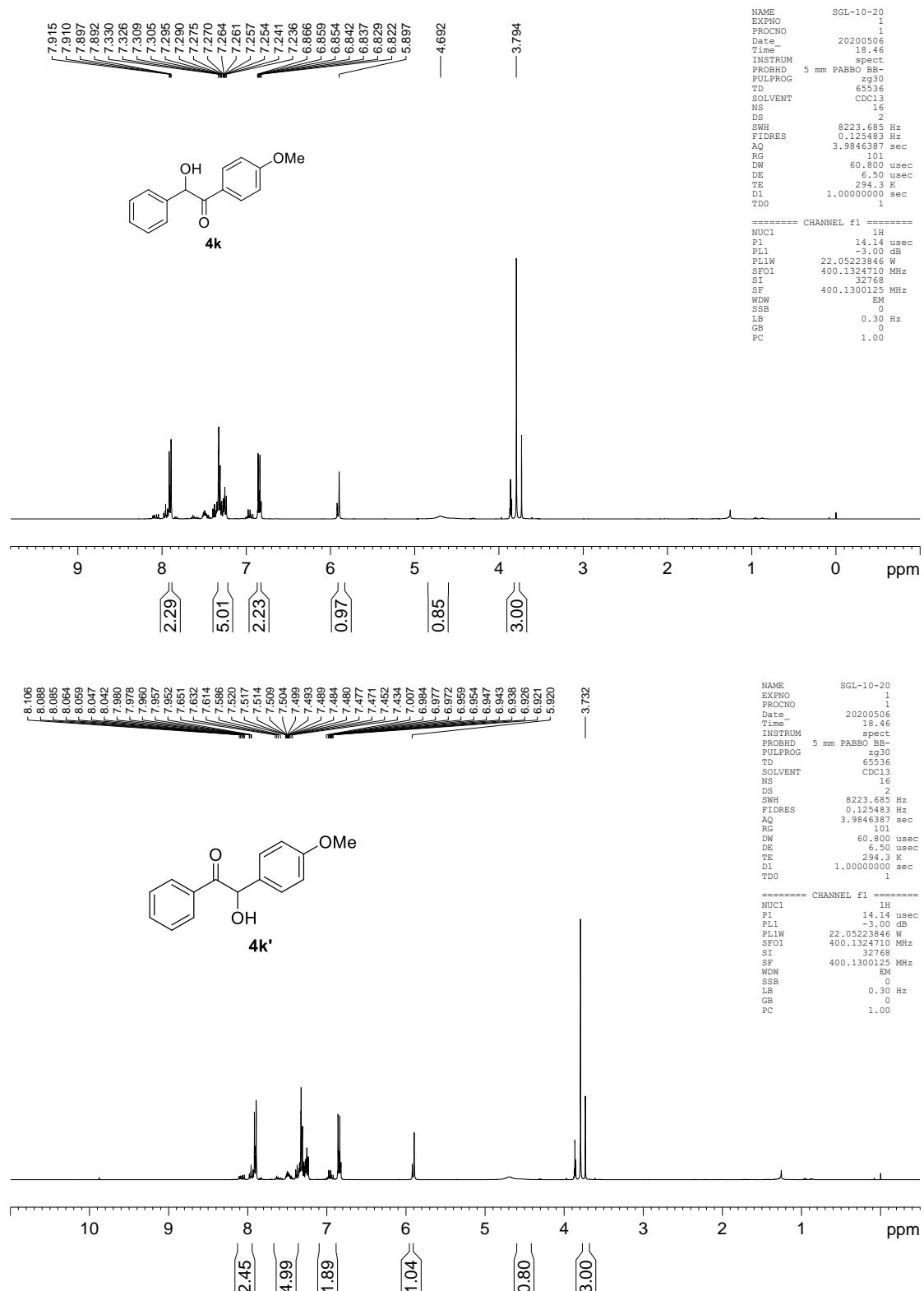


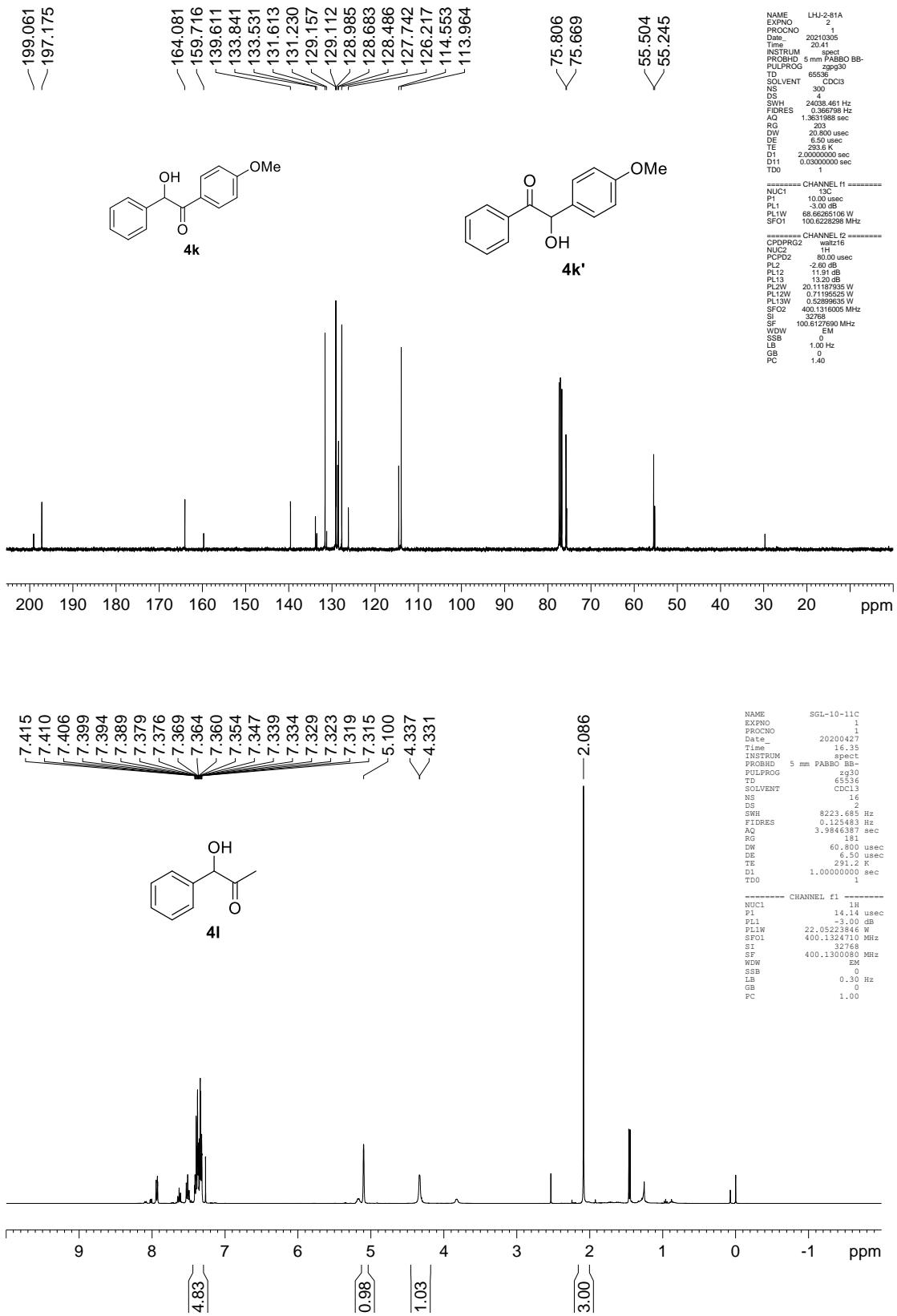


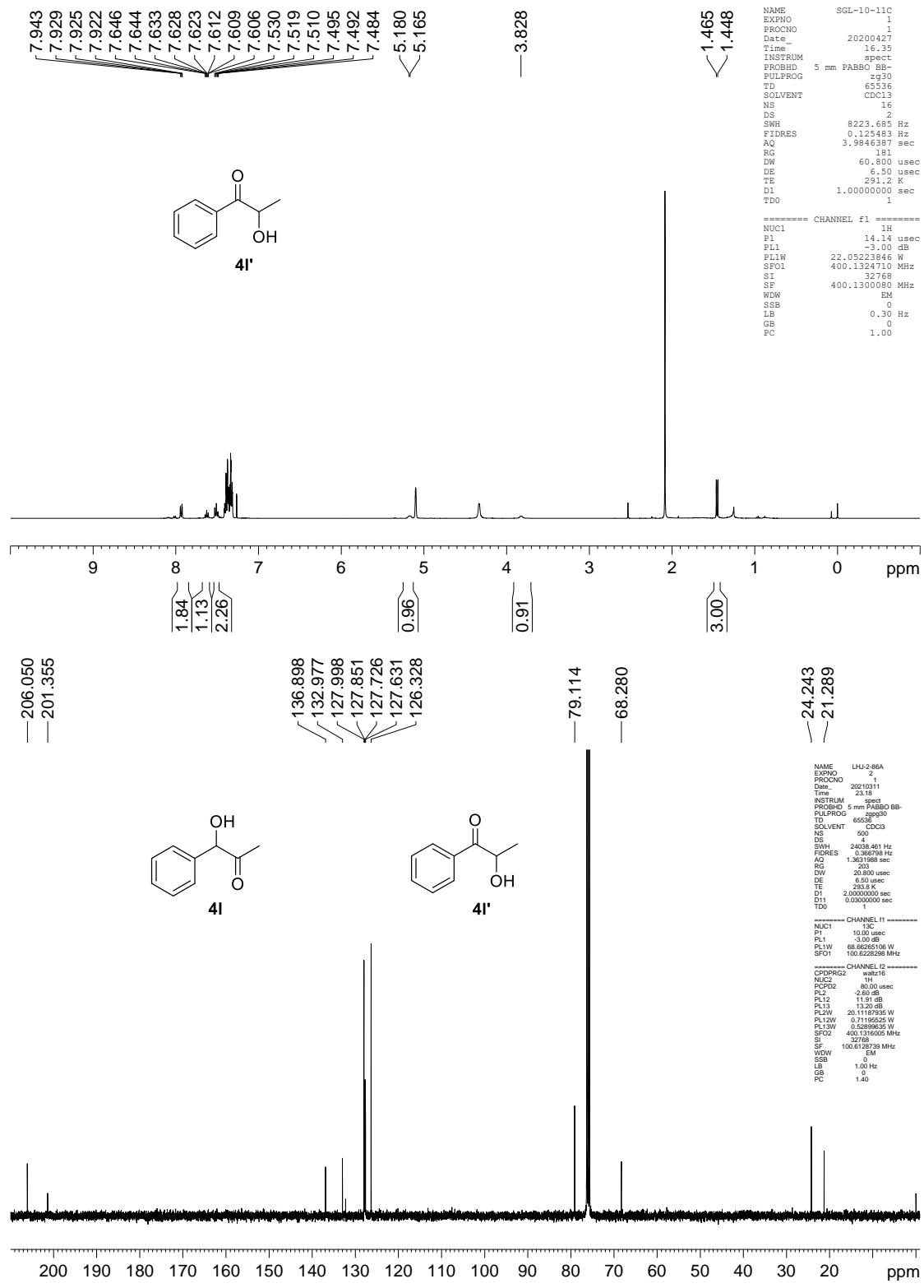


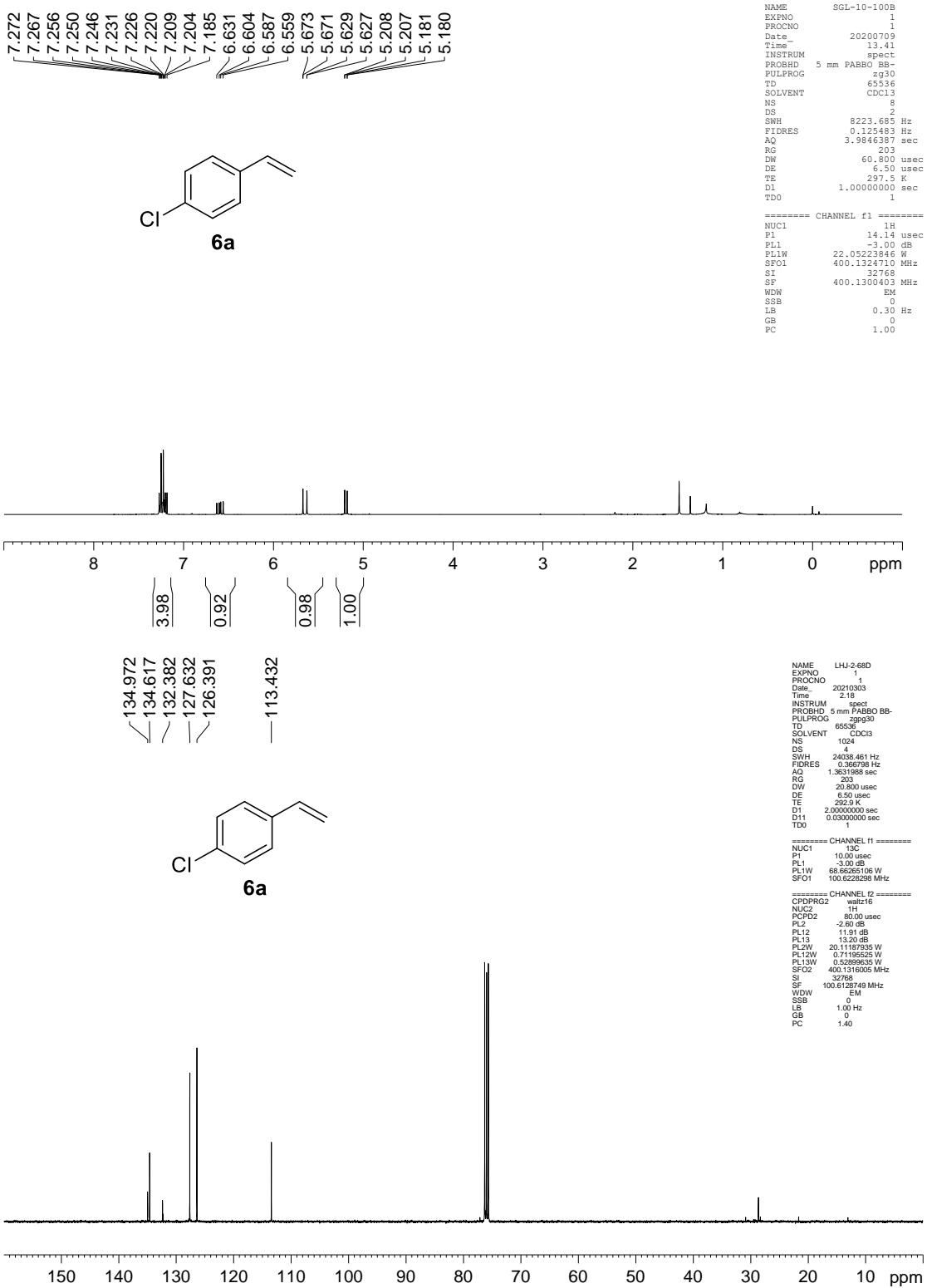










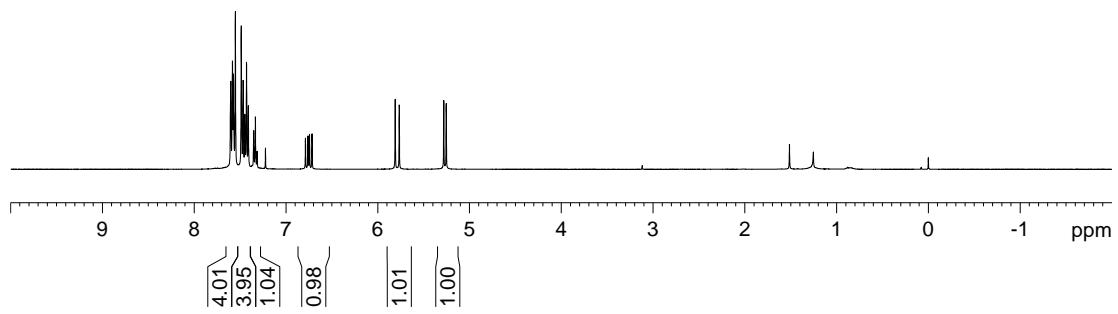




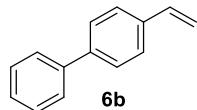
NAME SGL-10-52C
 EXPNO 1
 PROCNO 1
 Date_ 20200527
 Time 23.13
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.68 Hz
 FIDRES 0.12503 sec
 AQ 3.9846387 sec
 RG 181
 DW 60.00 usec
 DE 6.50 usec
 TE 295.3 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====

NUC1 1H
 PI 14.14 usec
 PL1 -3.00 dB
 PL1W 22.05223846 W
 SF01 400.1324710 MHz
 SI 32768
 SP 400.1300258 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



139.661
 139.515
 135.520
 < 135.339
 < 127.734
 < 126.266
 < 126.177
 < 125.910
 < 125.590
 — 112.852



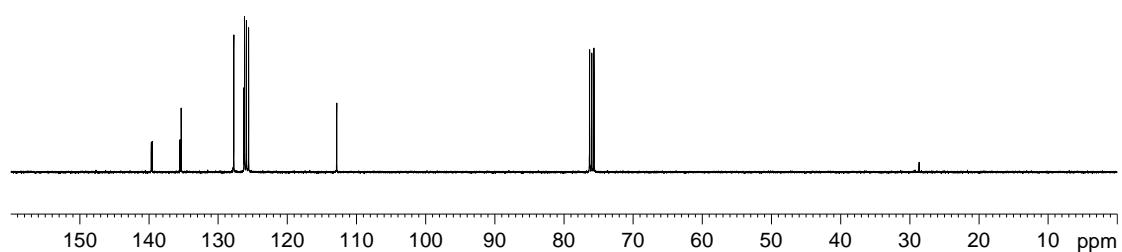
NAME LHJ-2-79A
 EXPNO 1
 PROCNO 1
 Date_ 20210304
 Time 23.47
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 300
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.366698 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 293.1 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

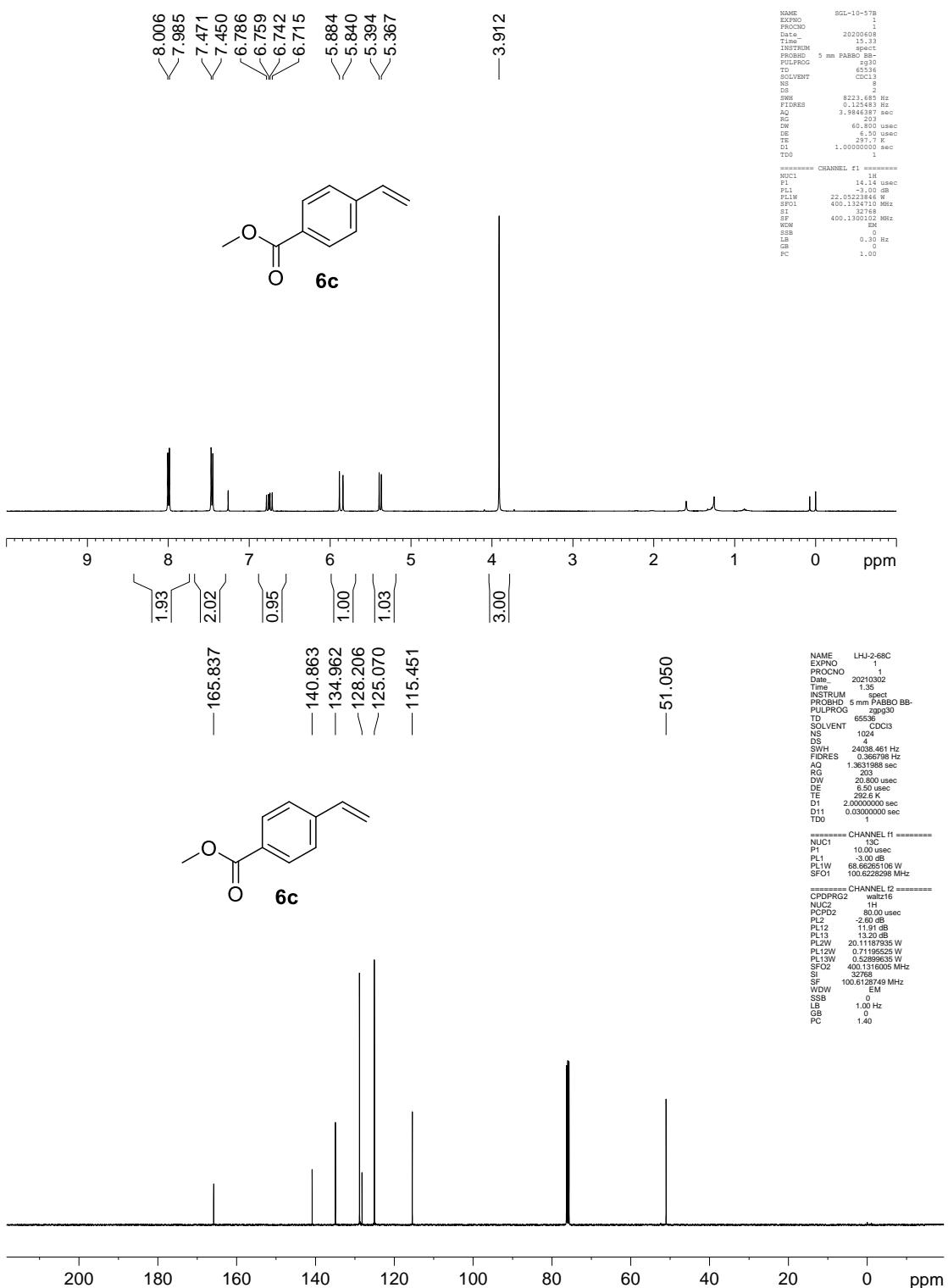
===== CHANNEL f1 =====

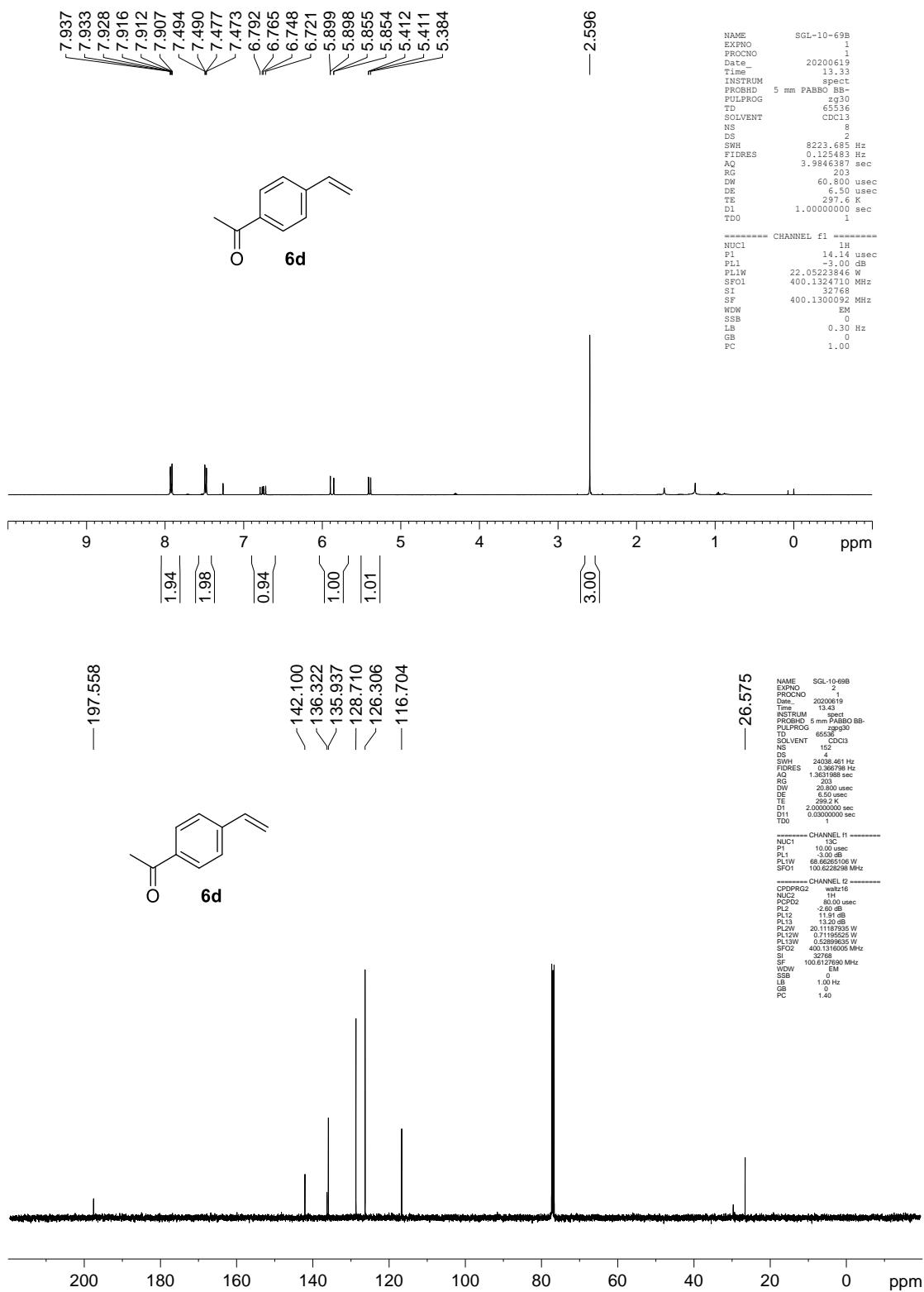
NUC1 13C
 PI 10.00 usec
 PL1 -3.00 dB
 PL1W 68.66265106 W
 SF01 100.6228298 MHz

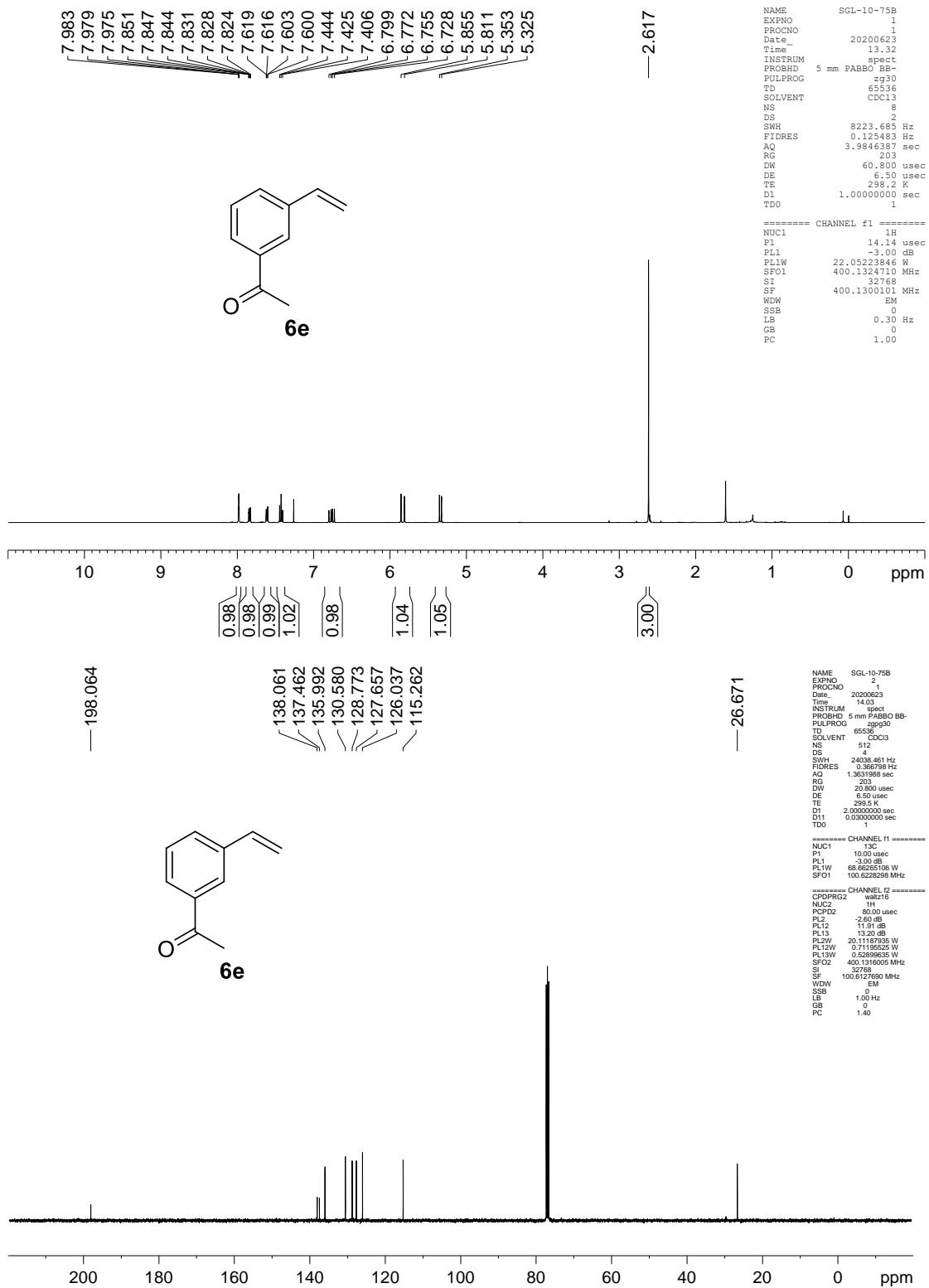
===== CHANNEL f2 =====

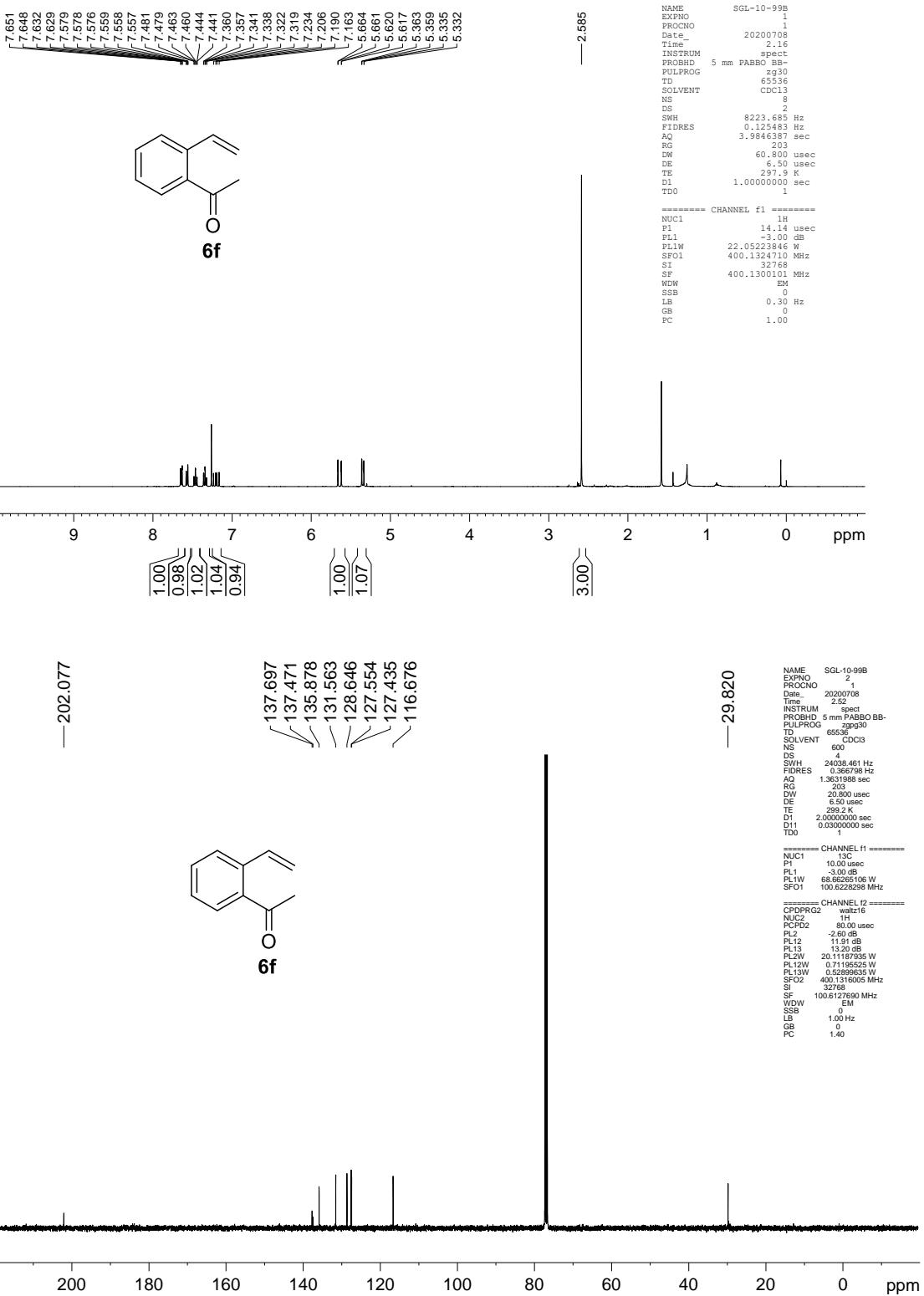
CPDPG02 13C
 PCPD2 1H
 PCPD2 80.00 usec
 PL2 -2.00 dB
 PL12 11.91 dB
 PL13 13.20 dB
 PL1W 28.000000 W
 PL12W 0.71195625 W
 PL13W 0.52899635 W
 SF02 400.1300000 MHz
 SI 32768
 SP 100.6128794 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40











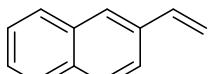
PROTON CDCl₃ D:\\ other 9



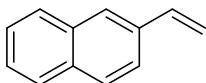
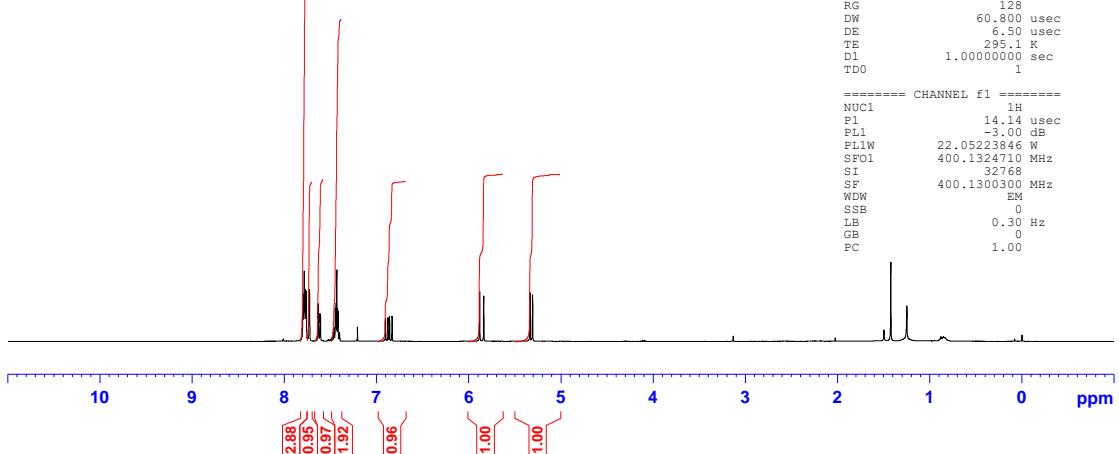
```

NAME      SGL-10-52B
EXPNO          1
PROCNO        1
Date       20200527
Time       21.56
INSTRUM     spect
PROBHD    5 mm PABCO BB-
FULPROG   zg30
TD        65536
SOLVENT     CDC13
NS           13
DS            2
SWH       8223.680 Hz
FIDRES   0.125483 Hz
AQ        3.9846387 sec
RG           128
DW       60.800 usec
DE        6.50 usec
TE        295.1 K
D1      1.0000000 sec
TDO          1

```



6g



6g

```

NAME    LHJ-272B
EXPTNO      1
PROCNO     1
Date       20210303
Time       21.19
INSTRUMEN spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT    CDCl3
NS         500
DS          4
SWH      24038.461 Hz
FIDRES   0.363798 Hz
TE        1.33688 sec
RG        203
DW        20.800 usec
DE        6.50 usec
DM        293.2 K
D1        2.000000 sec
D11       0.03000000 sec
TDO      1

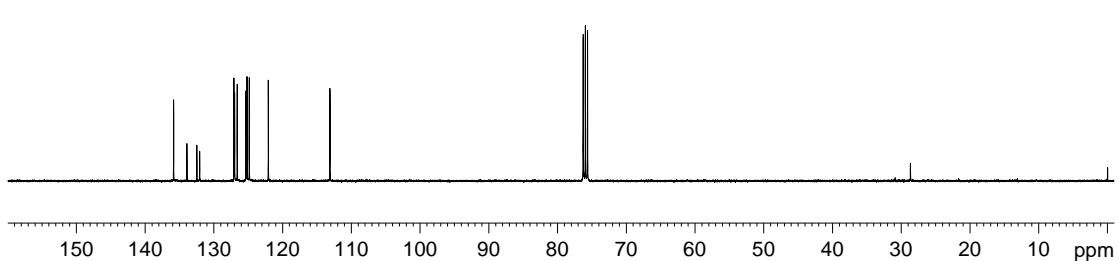
```

```

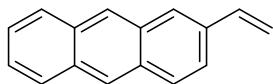
===== CHANNEL 1 =====
NUC1          13C
P1            10.00 usec
PL1           -3.00 dB
PL1W          68.665220510 W
SF01          100.622988 MHz

===== CHANNEL 2 =====
CPDPRG2      walt16z
PLC2          1H
PCPD2         80.00 usec
PL2           -2.60 dB
PL12          11.91 dB
PL13          13.20 dB
PL1W          20.000000005 W
PL12W         0.71198525 W
PL13W         0.52899635 W
SF02          401.316000 MHz
SF03          105.8128702 MHz
WDW           EM
SSS           0
GBB           1.00 Hz
BC            140

```



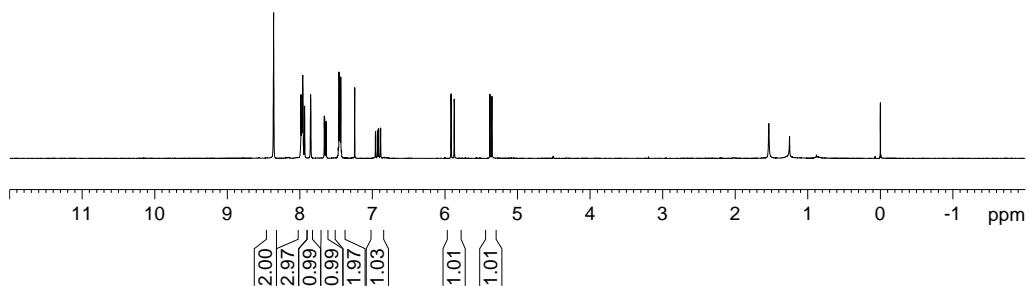
8.362
7.986
7.978
7.973
7.970
7.961
7.936
7.852
7.664
7.660
7.642
7.638
7.471
7.467
7.427
7.453
7.445
7.437
6.915
6.888
5.917
5.873
5.381
5.353



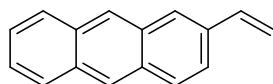
6h

NAME SGL-10-69A
EXPNO 1
PROCNO 1
Date 20200619
Time 13.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SW0 8223.685 Hz
FIDRES 0.125485 Hz
AQ 3.984657 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.1 K
D1 1.0000000 sec
TDD 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.14 usec
PL1 -3.00 dB
PL1W 22.0524710 W
SF01 400.1324710 MHz
SI 32768
SF 400.1300162 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



135.960
133.337
130.968
130.749
130.686
130.275
127.453
127.150
127.080
125.876
125.398
125.026
124.459
124.391
121.482
113.182



6h

NAME LHU-2-68F
EXPNO 1
PROCNO 1
Date 20210303
Time 3.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 3.000000 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 292.8 K
D1 2.0000000 sec
D11 0.03000000 sec
TDD 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.34 usec
PL1 -3.00 dB
PL1W 68.66265106 W
SF01 100.62262956 MHz

===== CHANNEL f2 =====
CPDPNPROG2 13C-1H
NUC2 1H
PCPD2 80.00 usec
PL2 -2.92 dB
PL12 11.91 dB
PL13 13.20 dB
PL2W 26.1195005 W
PL12W 0.71195525 W
PL13W 0.52899635 W
SF02 400.13000000 MHz
SI 32768
SF 100.6119566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

