ESI *for*

Trinuclear complexes of palladium(II) with chalcogenated *N*-heterocyclic carbenes: catalysis of selective nitrile-primary amide interconversion and Sonogashira coupling

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Table S1. Crystal data and structural refinement parameters

Compounds	**1**	**2**
Empirical formula	C40 H44 Cl6 N8 Pd3 S2	C44 H50 Cl6 N10 Pd3 Se2
Formula wt.	1232.85	1408.76
Crystal size [mm]	0.33 x 0.32 x 0.29	0.33 x 0.32 x 0.27
Crystal system	Monoclinic	Triclinic
Space group	P21/n	P-1
Unit Cell dimension	a = 11.797(3)Å b = 10.941(3)Å c = 19.404(6)Å α = 90° β = 97.804(6)° γ = 90°	a = 8.380(2))Å b = 11.721(3)Å c = 14.883(4)Å α = 67.79(2)° β = 81.88(3)° γ = 82.02(2)°
Volume [Å3]	2481.3(12)	1334.0(6)
Z	2	1
Density (Calc.) [Mg.m –3]	1.650	1.754
Absorption coeff. [mm–1]	1.520	2.706
F(000)	1224.0	692.0
θ range [°]	1.91–25.00	1.485– 24.979
Index ranges	-14<=h<=14-13<=k<= 13-23<=l<=23	-9<=h<=9-13<=k<= 13-17<=l<=17
Reflections collected	23279	12922
Independent reflections (Rint.)	4358 (0.0831)	4672 (0.1111)
Max./min. Transmission	0.646/0.610	0.495/ 0.436
Data/restraints/parameters	4353/0/271	4632/0/299
Goodnessoffit on F2	1.091	0.661
Final R indices [I >2σ(I)]	R1 = 0.0632, wR2 = 0.1383	R1 = 0.0391, wR2 = 0.0730
R indices (all data)	R1 = 0.0978, wR2 = 0.1523	R1 = 0.0499, wR2 = 0.0764
Largest diff. peak/hole [e.Å^{-3}]	0.992/-0.651	0.909/-0.980
CCDC no	1523310	1569993

Table S2. Selected bond lengths [Å] and bond angles [°]

	Bond length [Å]	Bond angle [°]
1	Pd(1)—S(1) 2.3179(19) Pd(1)—Cl(1) 2.2784(19) Pd(2)—C(9) 1.968(7) Pd(2)—Cl(2) 2.298(2) Pd(2)—Cl(3) 2.285(2) Pd(2)—N(3) 2.073(8) S(1)—C(1) 1.775(8) S(1)—C(7) 1.816(7) N(1)—C(9) 1.317(9) N(1)—C(8) 1.470(9) N(1)—C(10) 1.393(9) N(2)—C(9) 1.329(9) N(2)—C(15) 1.387(9) N(2)—C(16) 1.461(10)	Cl(1)—Pd(1)—S(1) 94.80(7) Cl(1)—Pd(1)—S(1) 85.20(7) Cl(1)—Pd(1)—Cl(1) 180.00 S(1)—Pd(1)—S(1) 180.00 Cl(2)—Pd(2)—N(3) 90.4(2) Cl(3)—Pd(2)—N(3) 93.9(2) C(9)—Pd(2)—N(3) 178.4(3) C(9)—Pd(2)—Cl(2) 88.0(2) C(9)—Pd(2)—Cl(3) 87.7(2) Cl(3)—Pd(2)—Cl(2) 175.70(9) C(1)—S(1)—Pd(1) 102.5(2) C(7)—S(1)—Pd(1) 110.7(3) N(1)—C(9)—Pd(2) 126.3(6) N(2)—C(9)—Pd(2) 123.9(6) C(9)—N(1)—C(8) 124.8(6) C(9)—N(1)—C(10) 109.1(6) C(9)—N(2)—C(15) 108.3(7) C(9)—N(2)—C(16) 126.4(7)
2	Pd(1)—Se(1) 2.4312(10) Pd(1)—Cl(1) 2.2971(12) Pd(2)—C(9) 1.952(4) Pd(2)—Cl(2) 2.2940(15) Pd(2)—Cl(3) 2.3003(15) Pd(2)—N(3) 2.079(4) Se(1)—C(1) 1.924(4) Se(1)—C(7) 1.960(4) N(1)—C(9) 1.341(5) N(1)—C(8) 1.462(5) N(1)—C(10) 1.394(5) N(2)—C(9) 1.353(5) N(2)—C(15) 1.399(5) N(2)—C(16) 1.460(5)	Cl(1)—Pd(1)—Se(1) 83.50(4) Cl(1)—Pd(1)—Se(1) 96.50(4) Cl(1)—Pd(1)—Cl(1) 180.00(1) Se(1)—Pd(1)—Se(1) 180.00(2) Cl(2)—Pd(2)—N(3) 90.16(12) Cl(3)—Pd(2)—N(3) 91.20(12) Cl(3)—Pd(2)—Cl(2) 178.64(4) C(9)—Pd(2)—N(3) 176.42(18) C(9)—Pd(2)—Cl(2) 87.67(13) C(9)—Pd(2)—Cl(3) 90.98(13) C(1)—Se(1)—Pd(1) 97.27(13) C(7)—S(1)—Pd(1) 104.83(14) N(1)—C(9)—Pd(2) 125.4(3) N(2)—C(9)—Pd(2) 127.4(3) C(9)—N(1)—C(8) 124.5(3) C(9)—N(1)—C(10) 110.2(3) C(9)—N(2)—C(15) 109.6(3) C(9)—N(2)—C(16) 125.2(4)

Table S3. Distances [Å] of inter and intra-molecular interactions for **1** and **2**

Complex 1	Complex 2
Cl1-H16 2.702	Cl1-H20A 2.925
Cl1-H14 2.939	N4-H16A 2.669

NMR Spectra of L1-L2 and 1-2

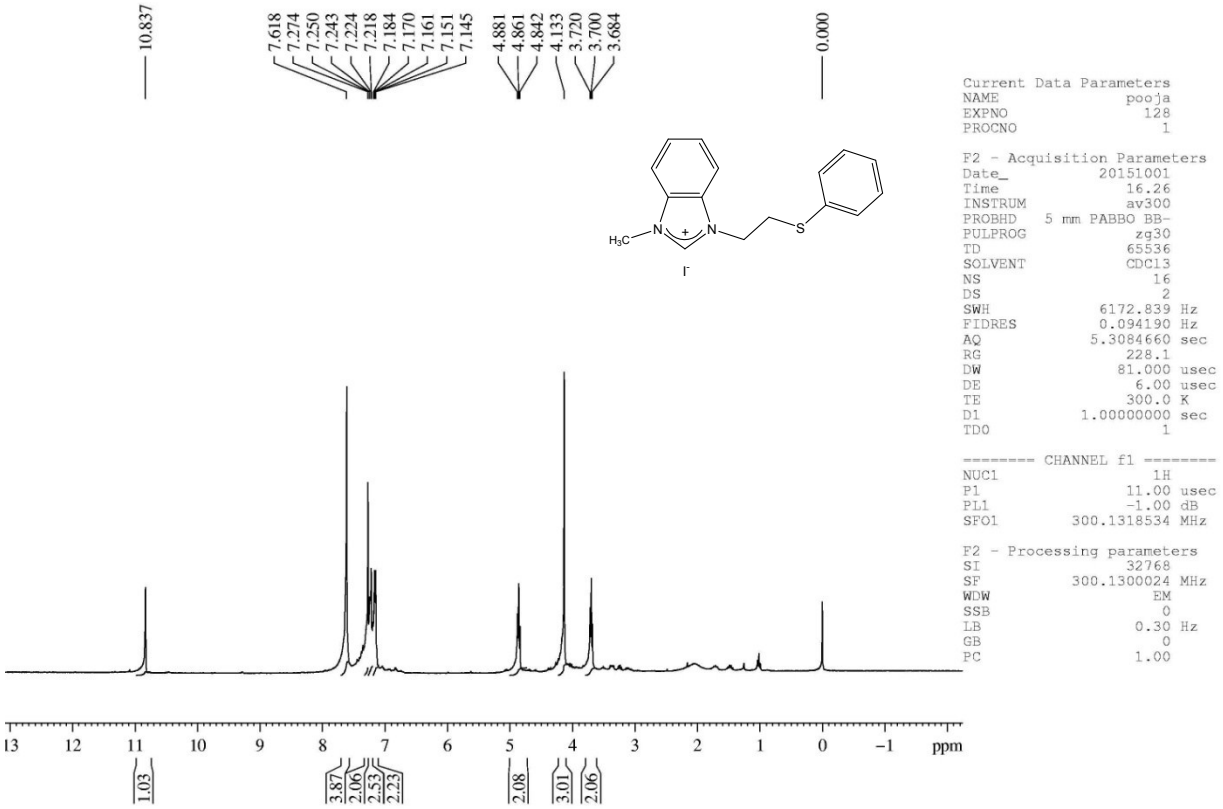


Figure S1. ^{1}H NMR of benzimidazolium salt, L1

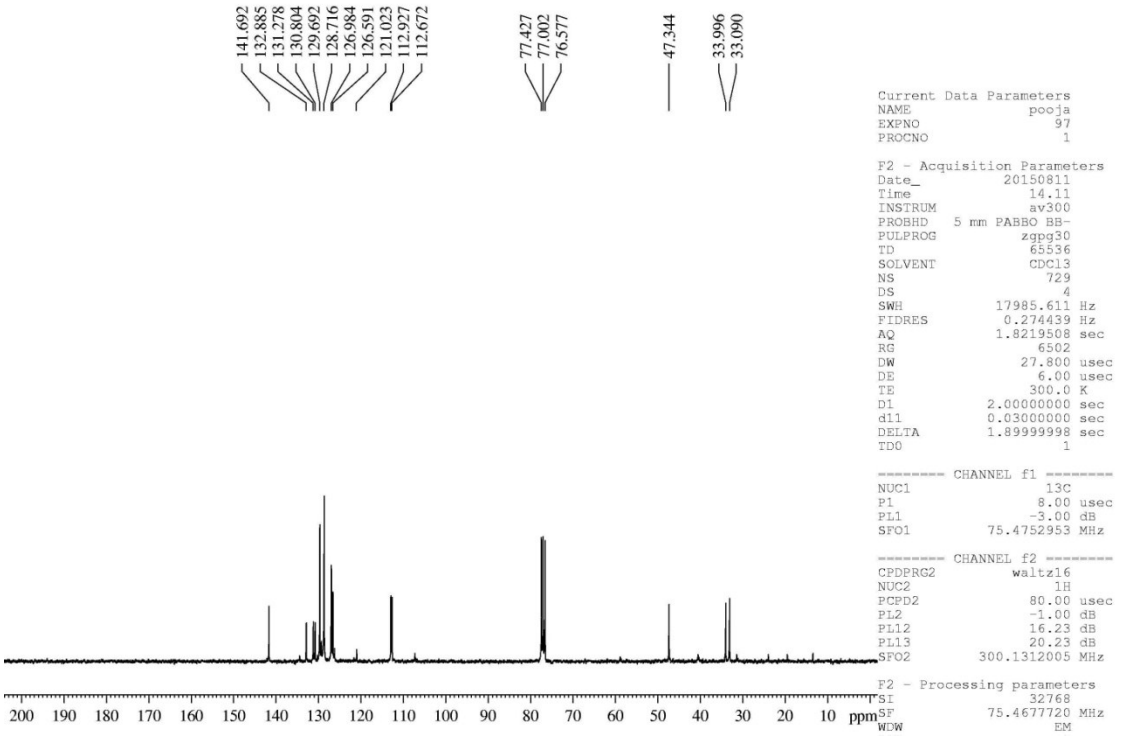


Figure S2. $^{13}C\{1H\}$ NMR of benzimidazolium salt, L1

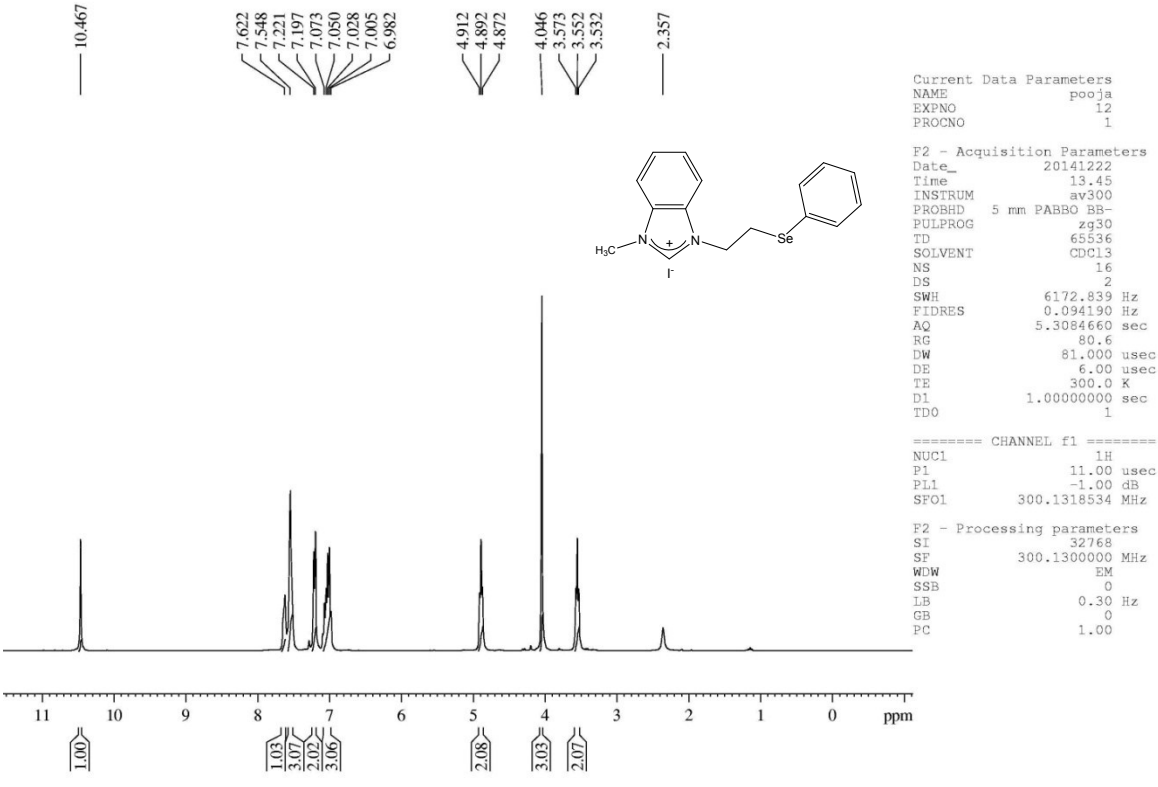


Figure S3. ^{1}H NMR of benzimidazolium salt, L2

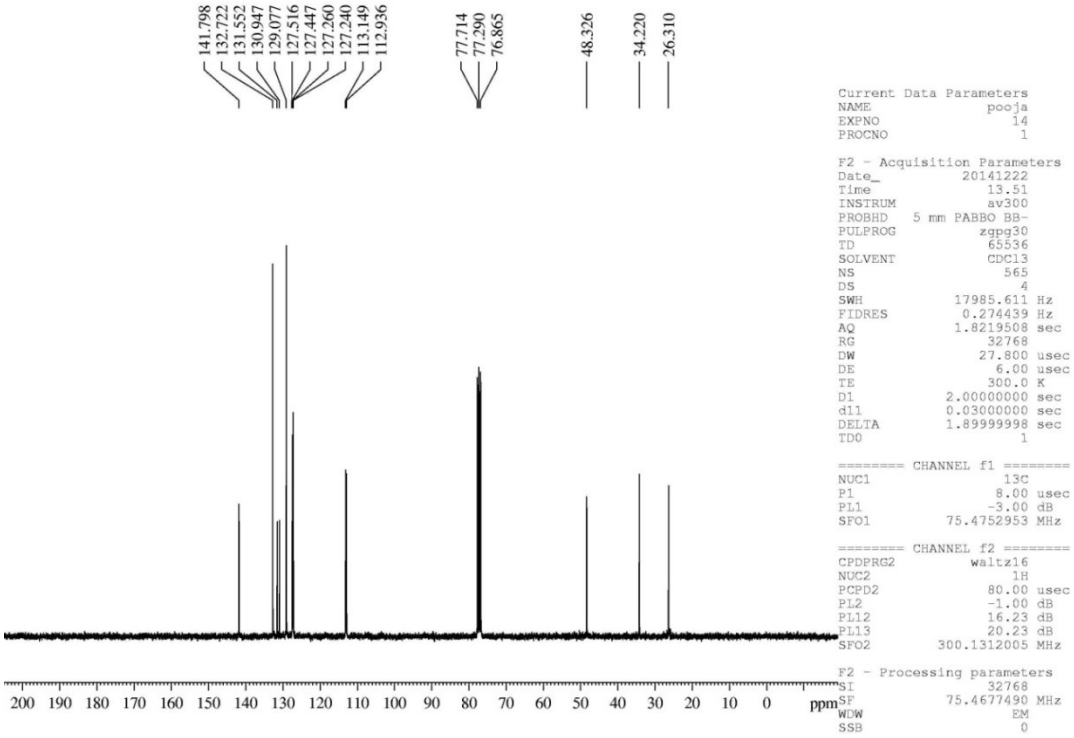


Figure S4. $^{13}C\{1H\}$ NMR of benzimidazolium salt, L2

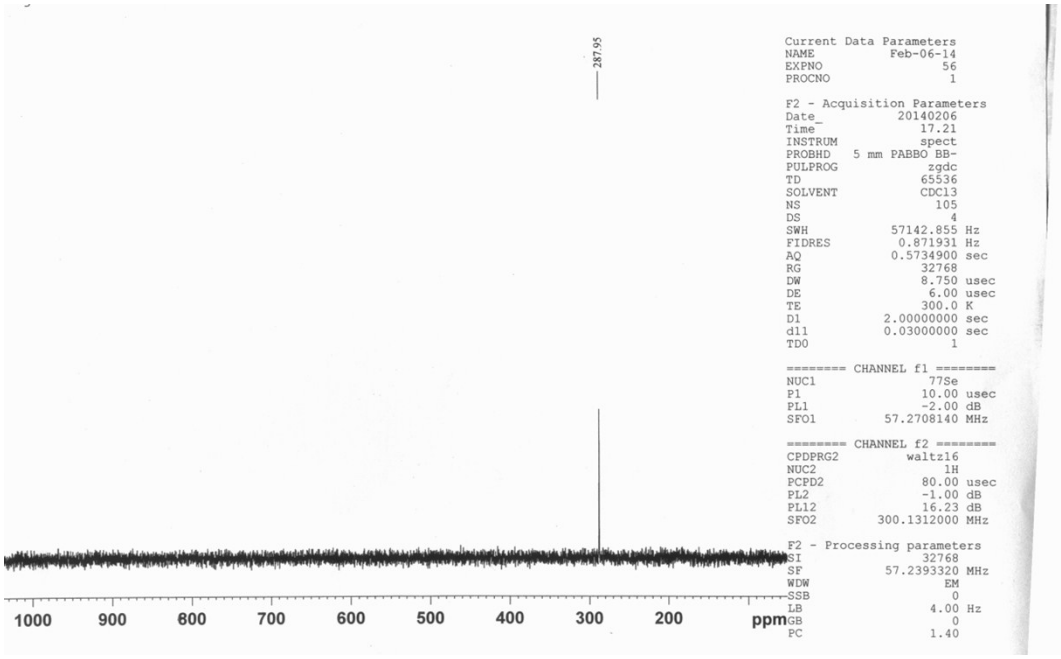


Figure S5. ^{77}Se NMR of benzimidazolium salt, L2

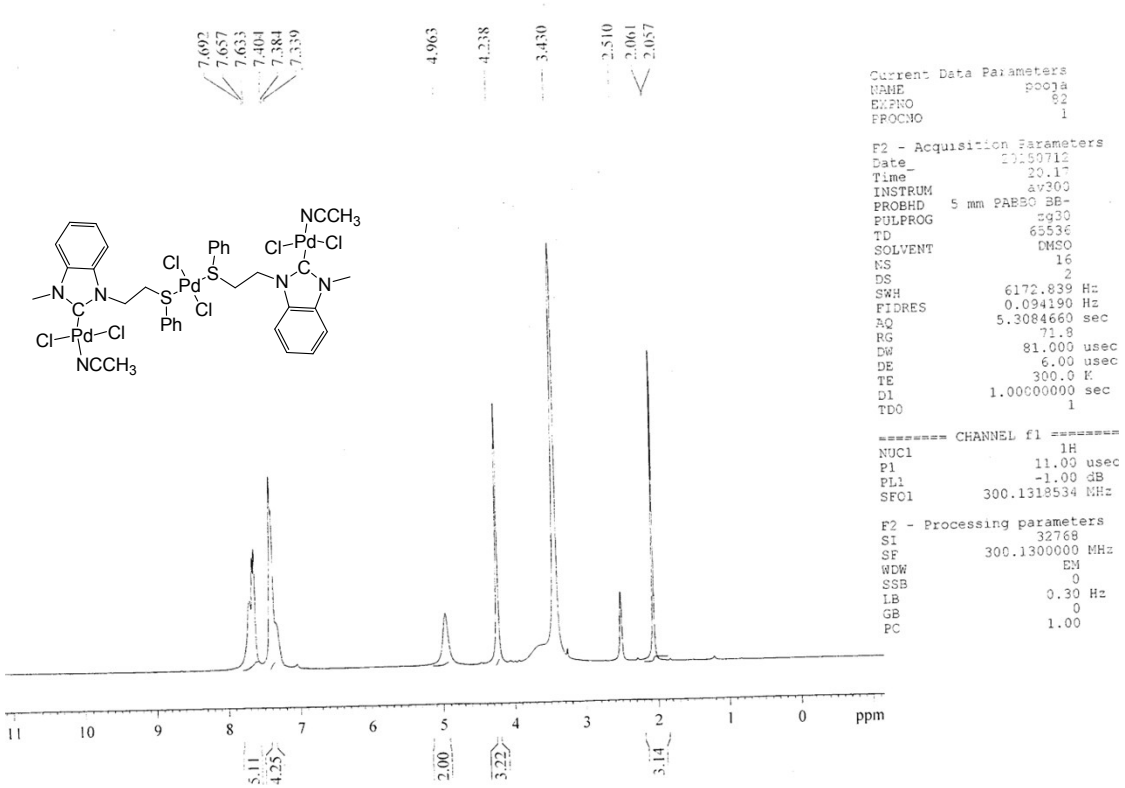


Figure S6. ^{1}H NMR of complex 1.

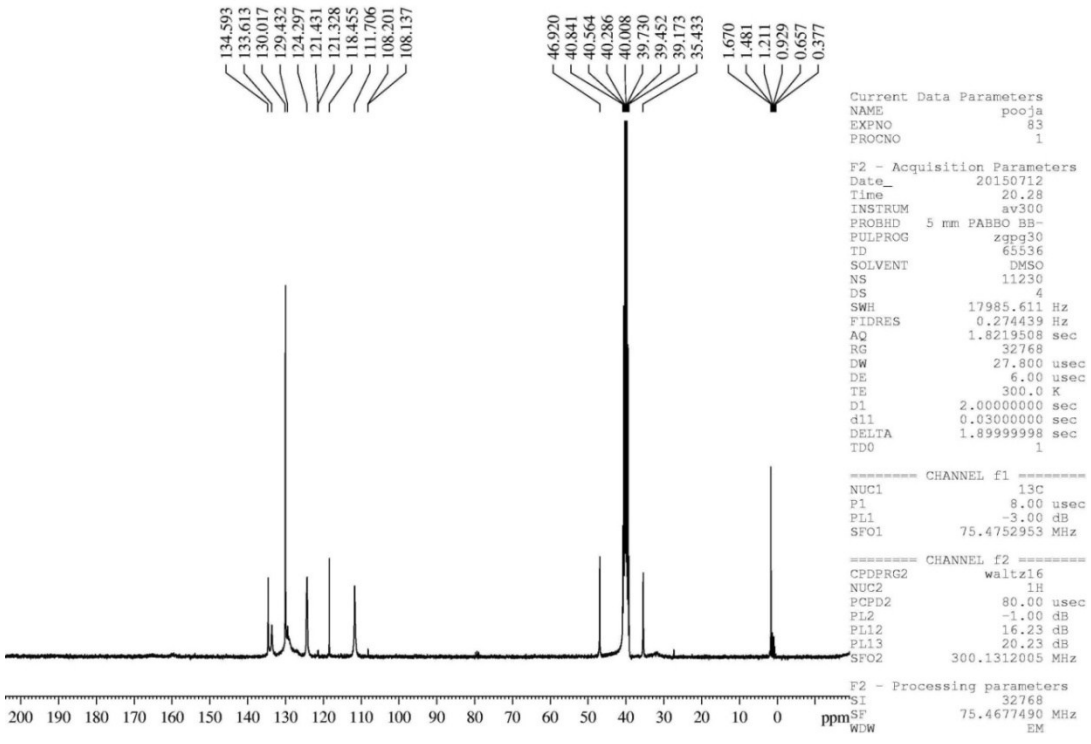


Figure S7. ^{13}C{^{1}H} NMR of complex 1

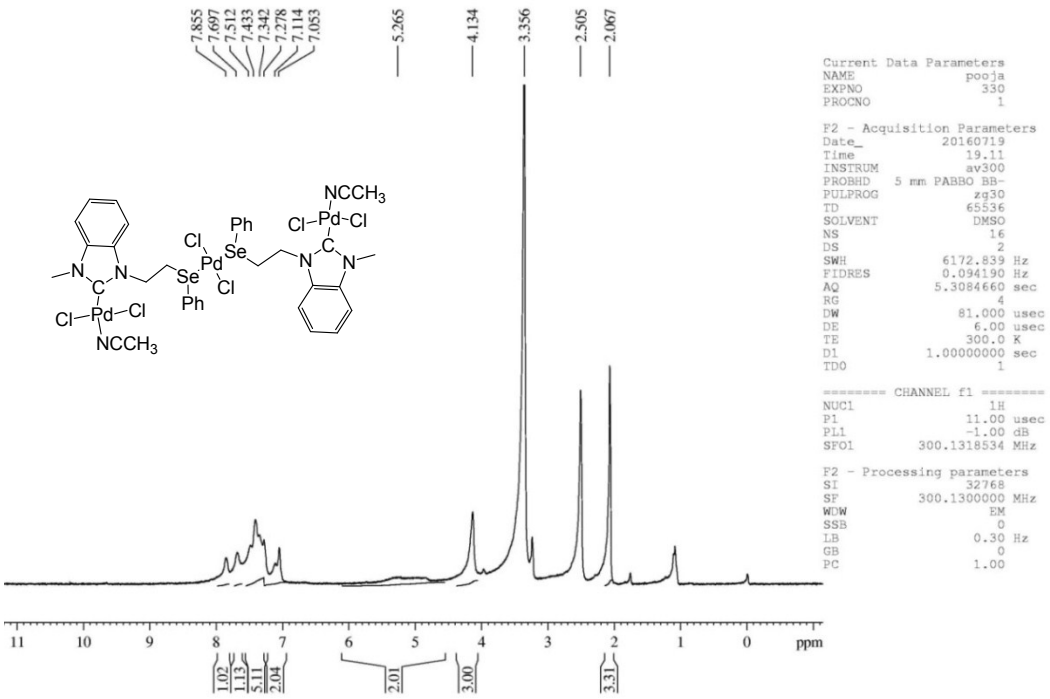


Figure S8. ^{1}H NMR of complex 2.

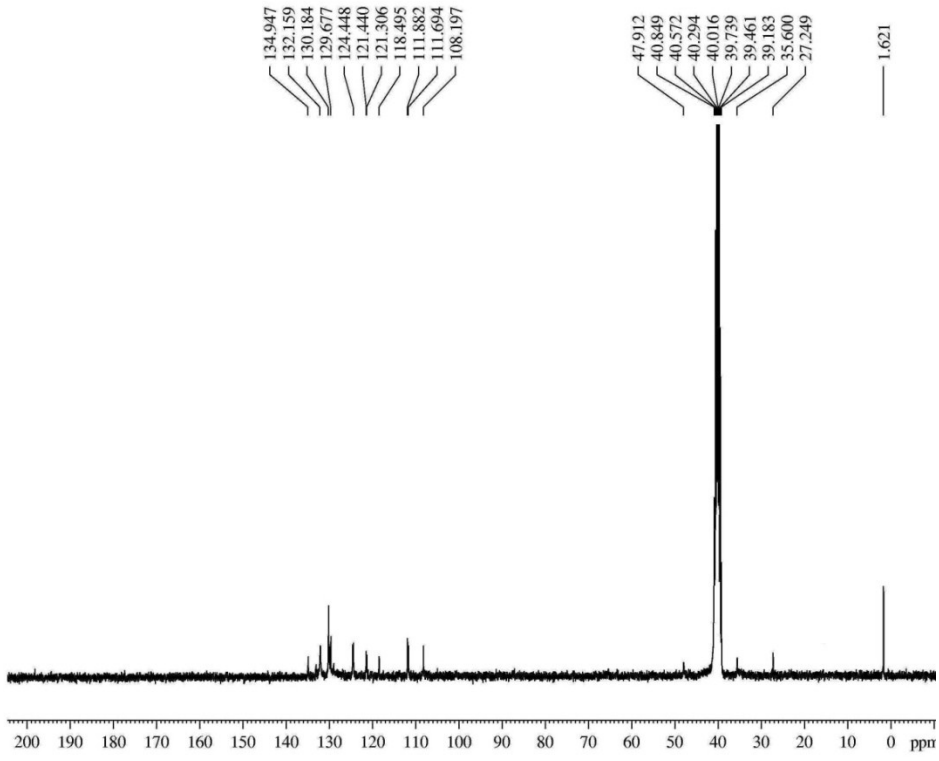


Figure S9. ^{13}C{^{1}H} NMR of complex 2 [^{13}C NMR (75 MHz, solvent d_6-DMSO)]

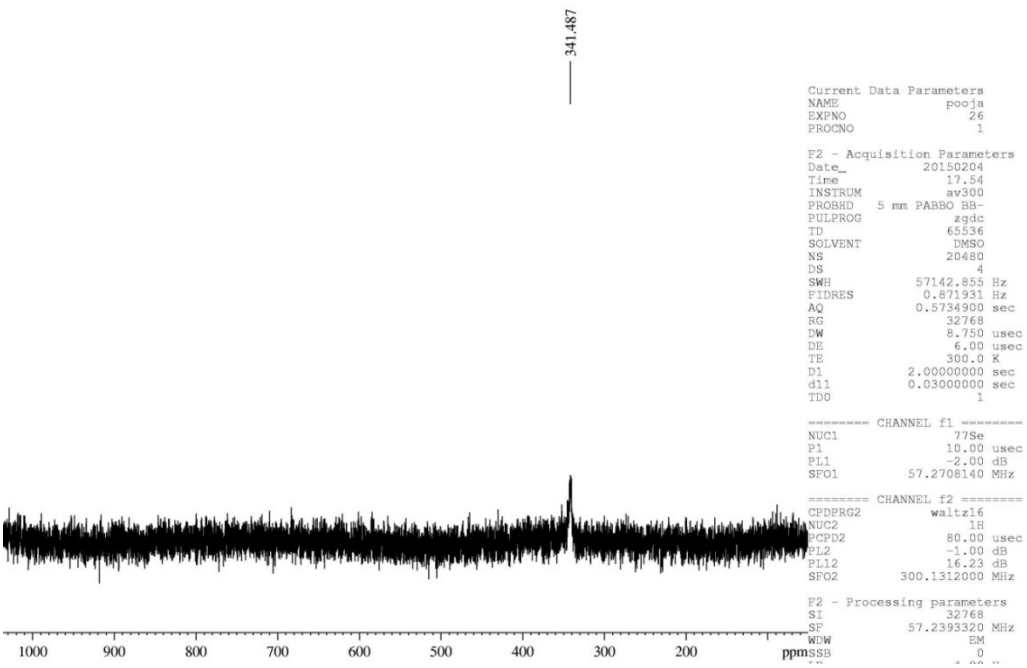


Figure S10. ^{77}Se{1H} NMR of complex 2

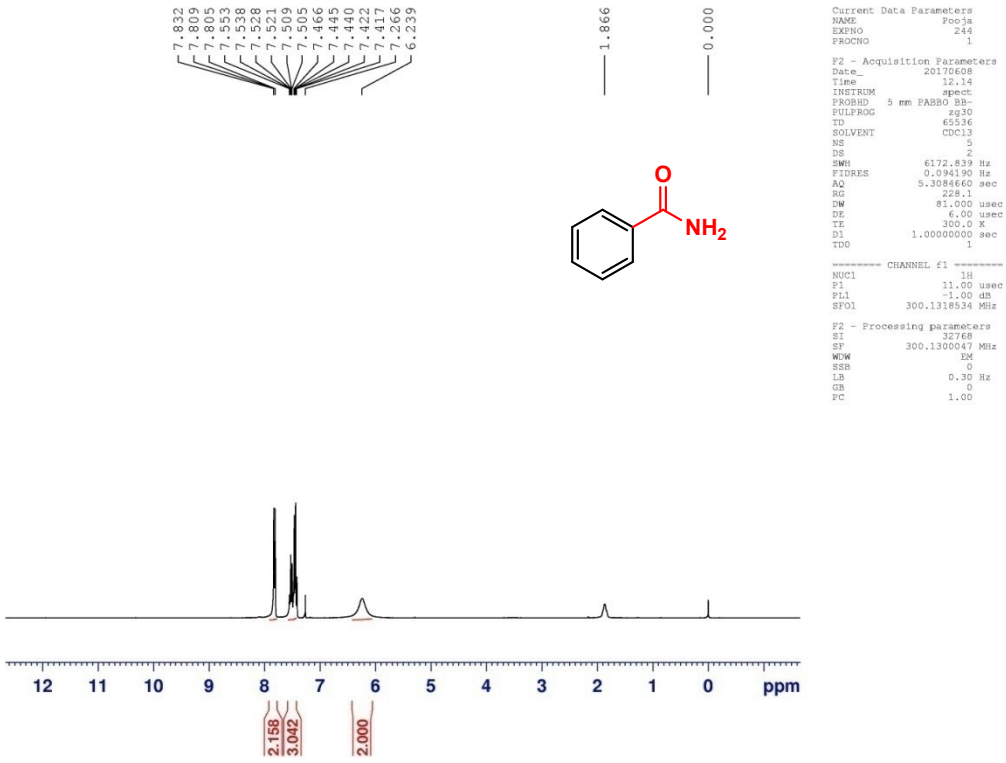


Figure S11. ^{1}H NMR of 4a

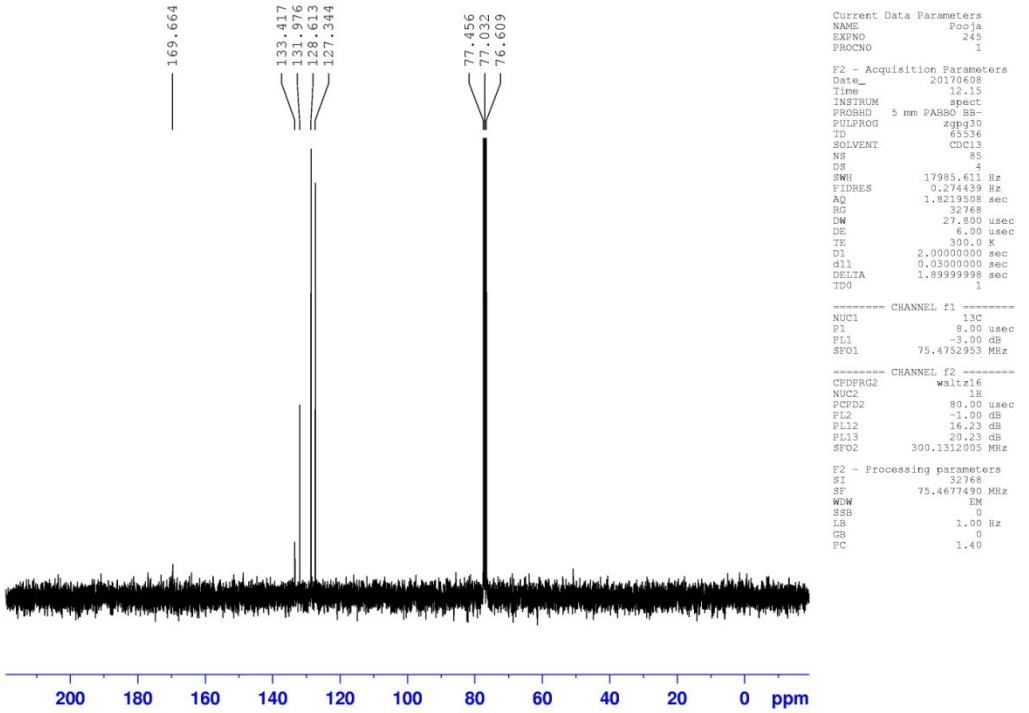


Figure S12. ^{13}C NMR of 4a

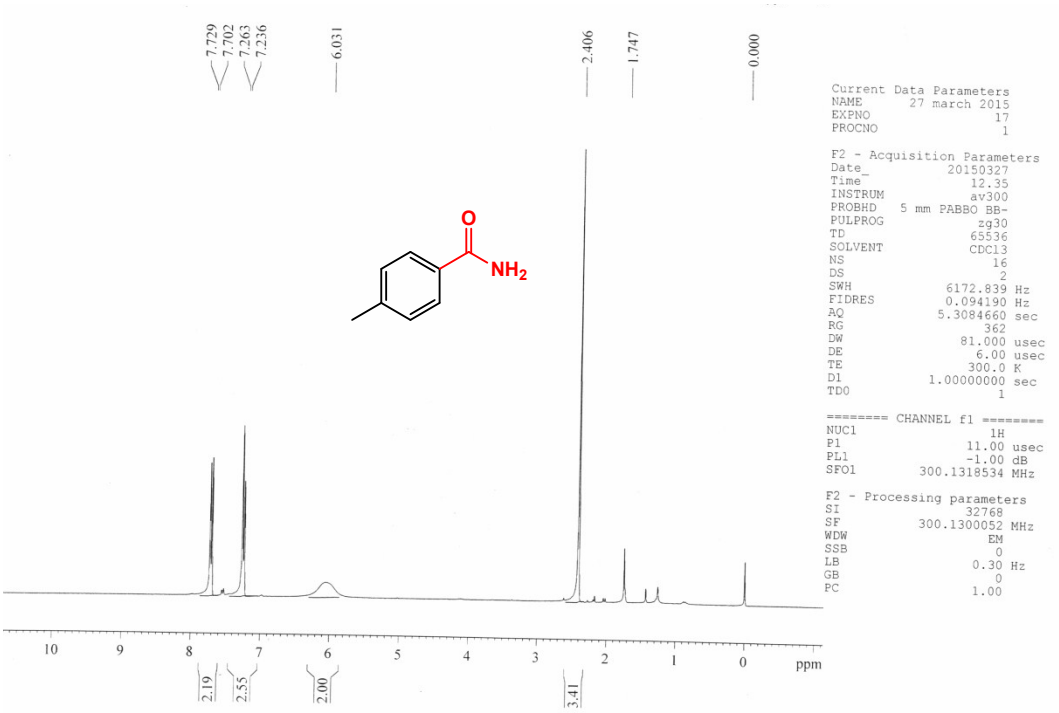


Figure S13. ^{1}H NMR of 4b

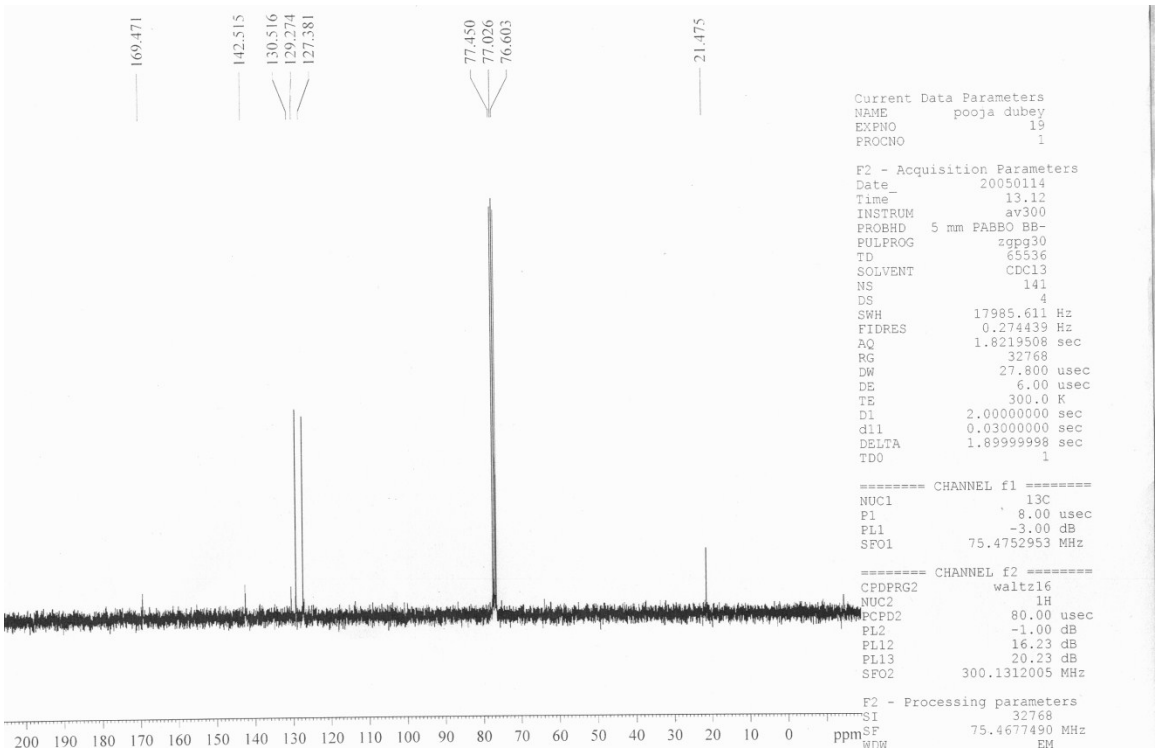


Figure S14. ^{13}C NMR of 4b

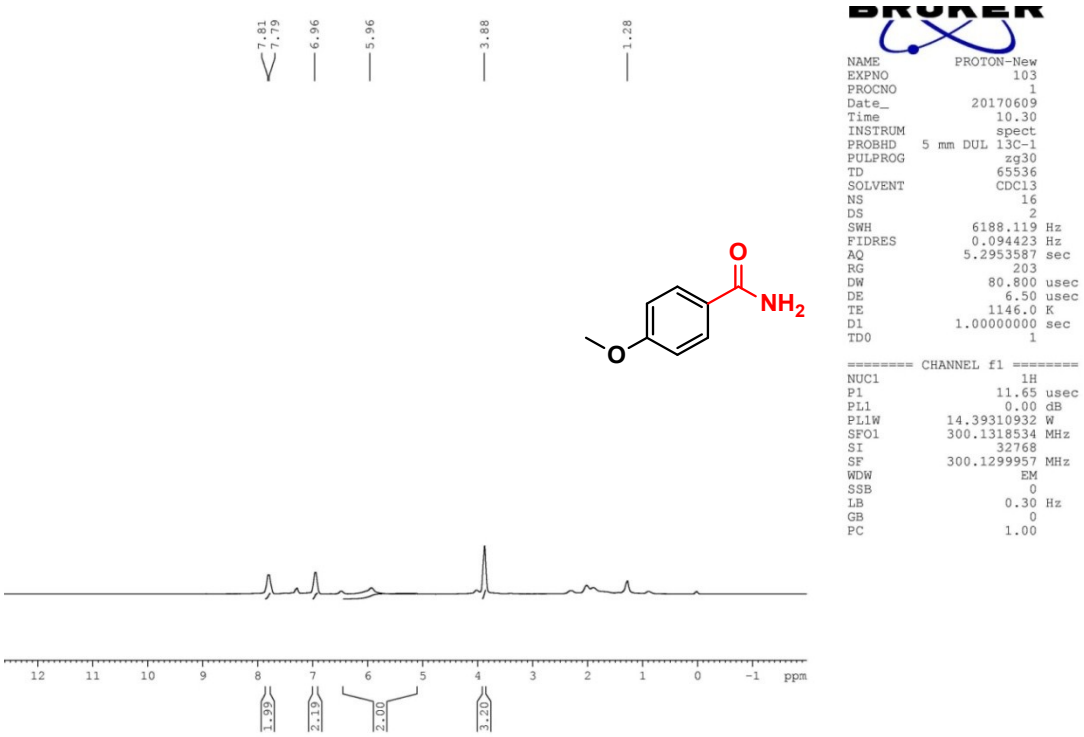


Figure S15. ^{1}H NMR of 4c

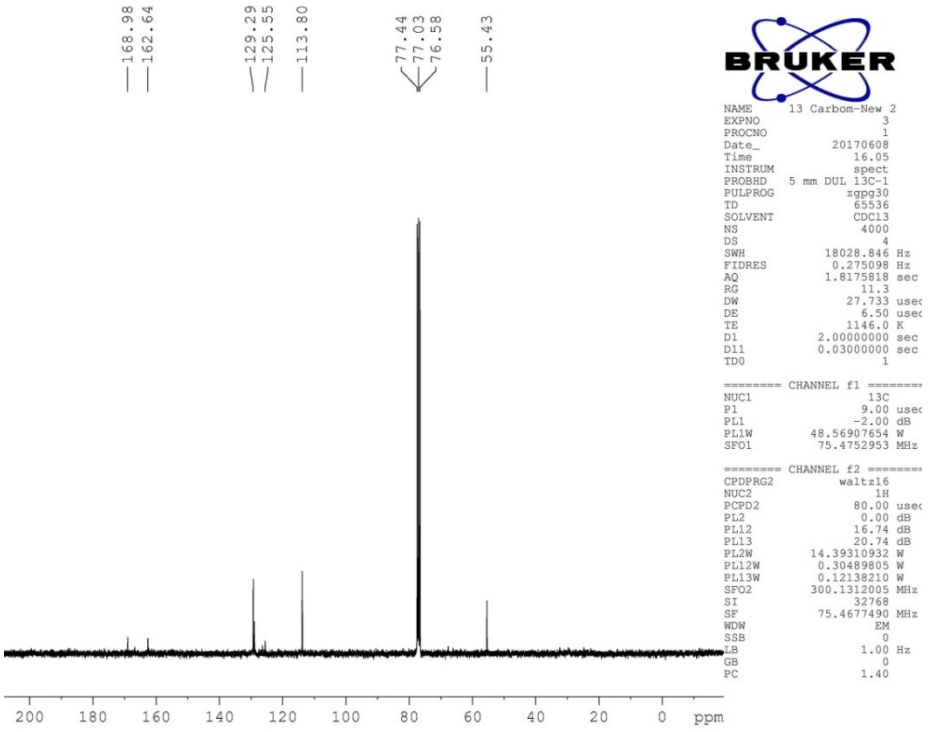


Figure S16. ^{13}C NMR of 4c

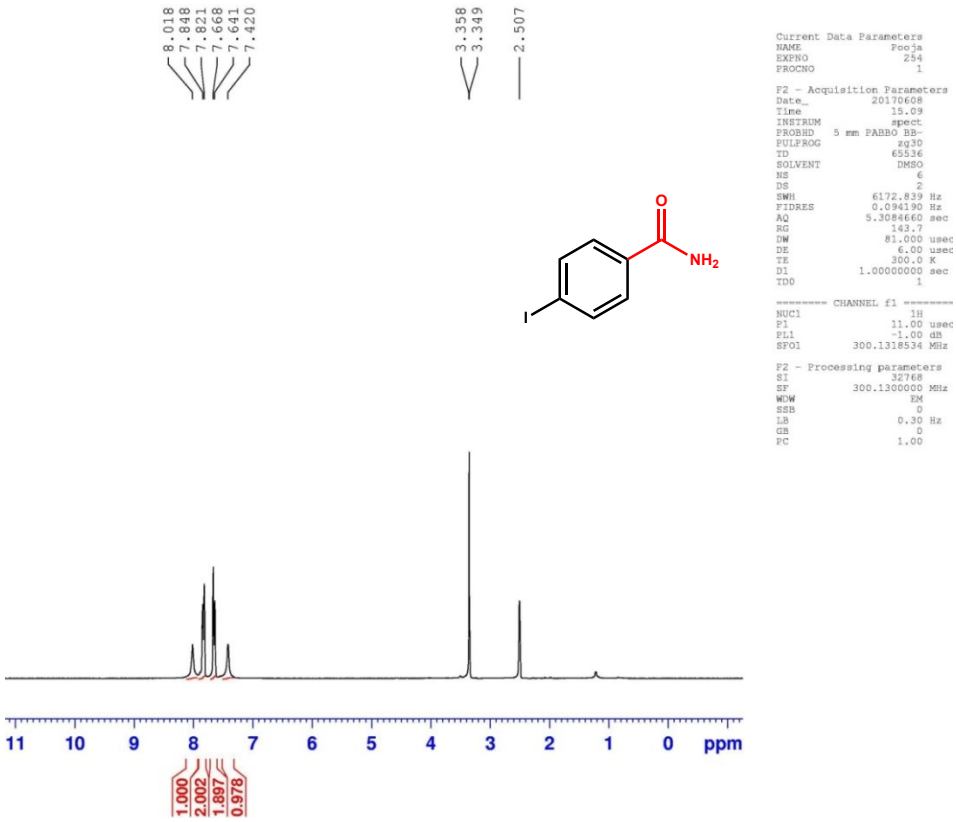


Figure S17. ^{1}H NMR of 4d

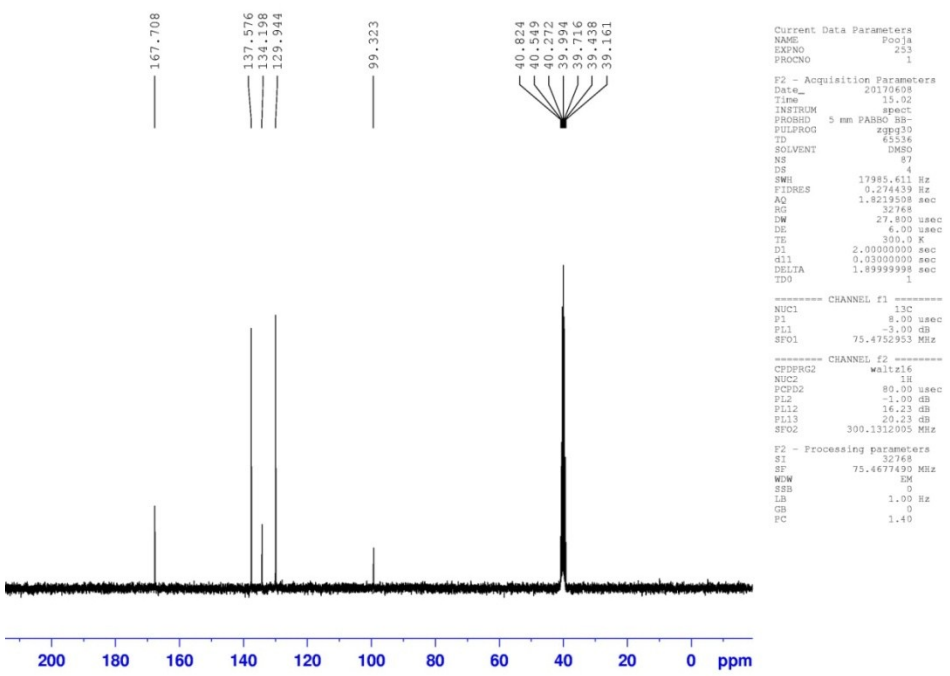


Figure S18. ^{13}C NMR of 4d

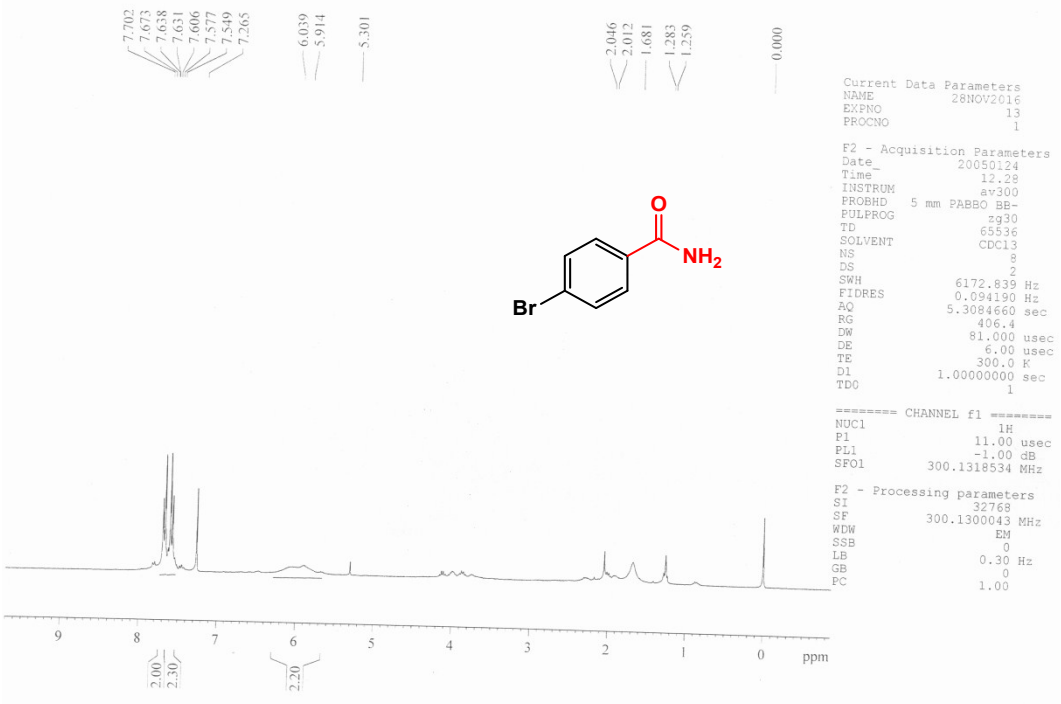


Figure S19. ^{1}H NMR of 4e

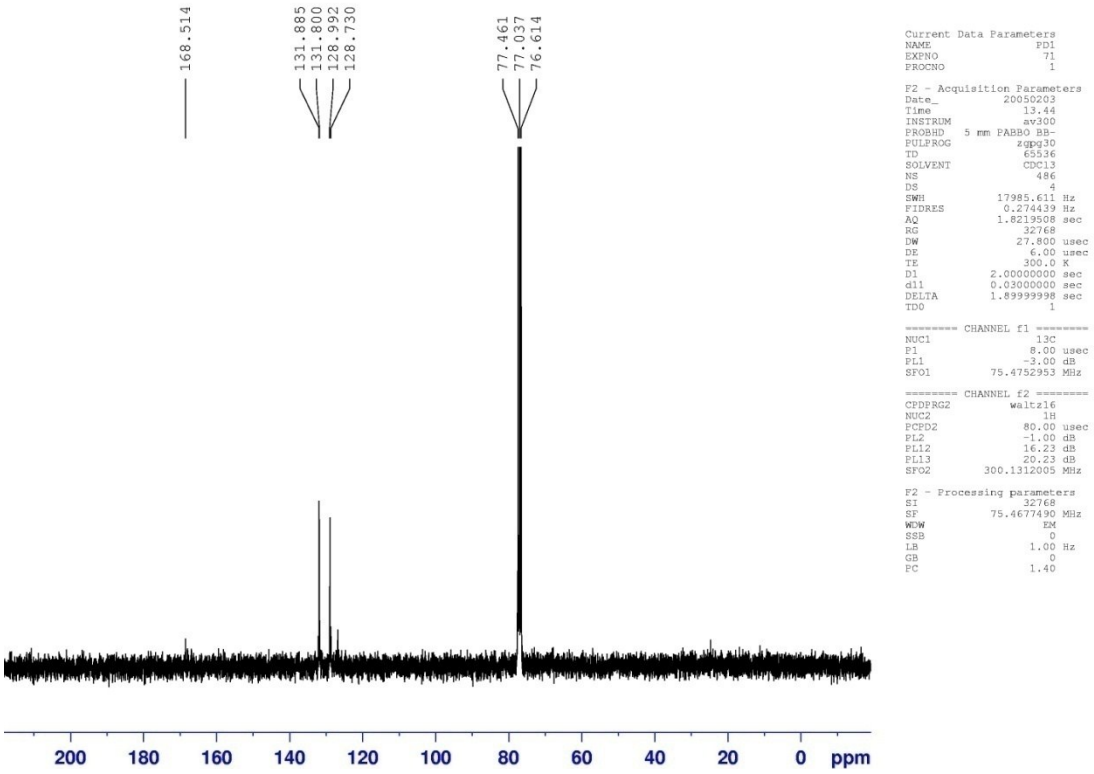


Figure S20. ^{13}C NMR of 4e

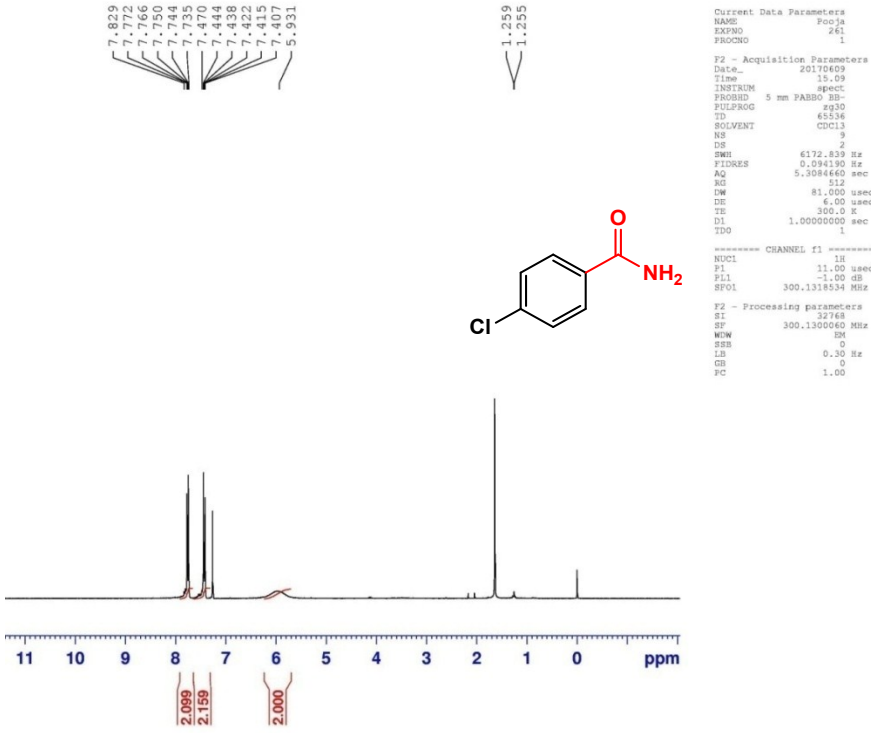


Figure S21. ^{1}H NMR of 4f

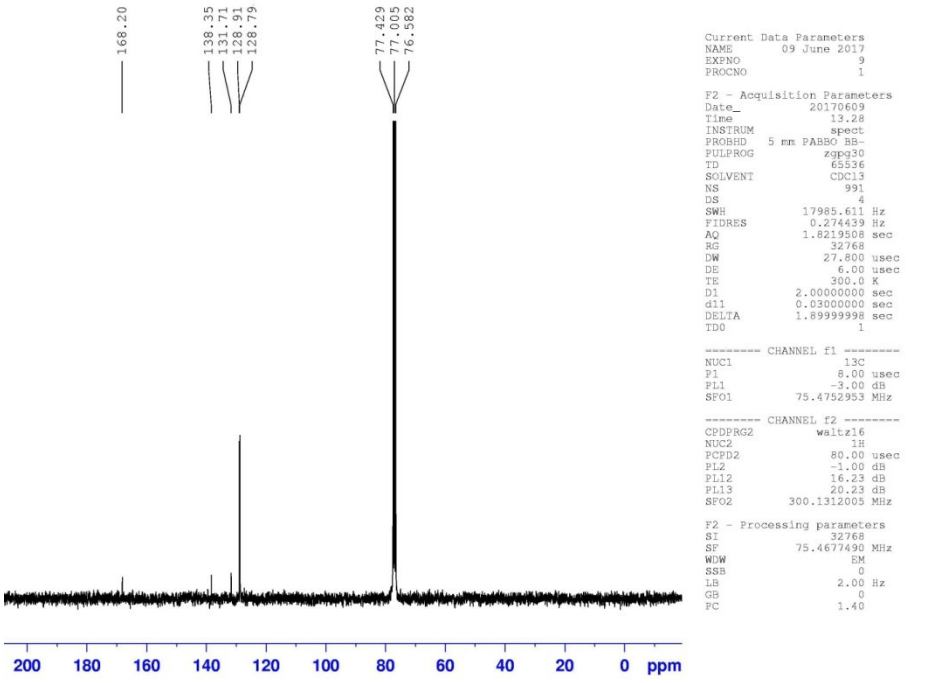


Figure S22. ^{13}C NMR of 4f

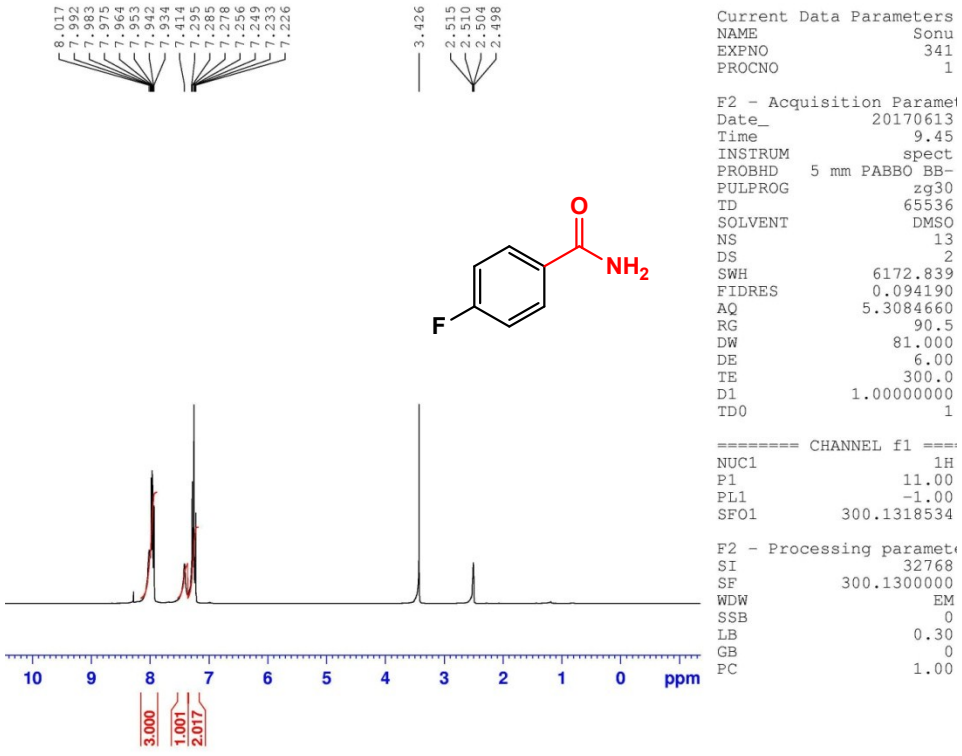


Figure S23. ^{1}H NMR of 4g

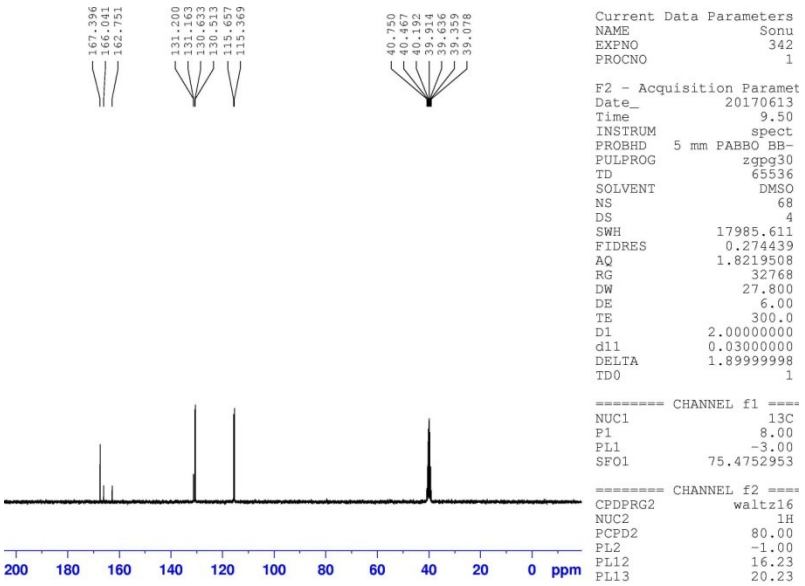


Figure S24. ^{13}C NMR of 4g

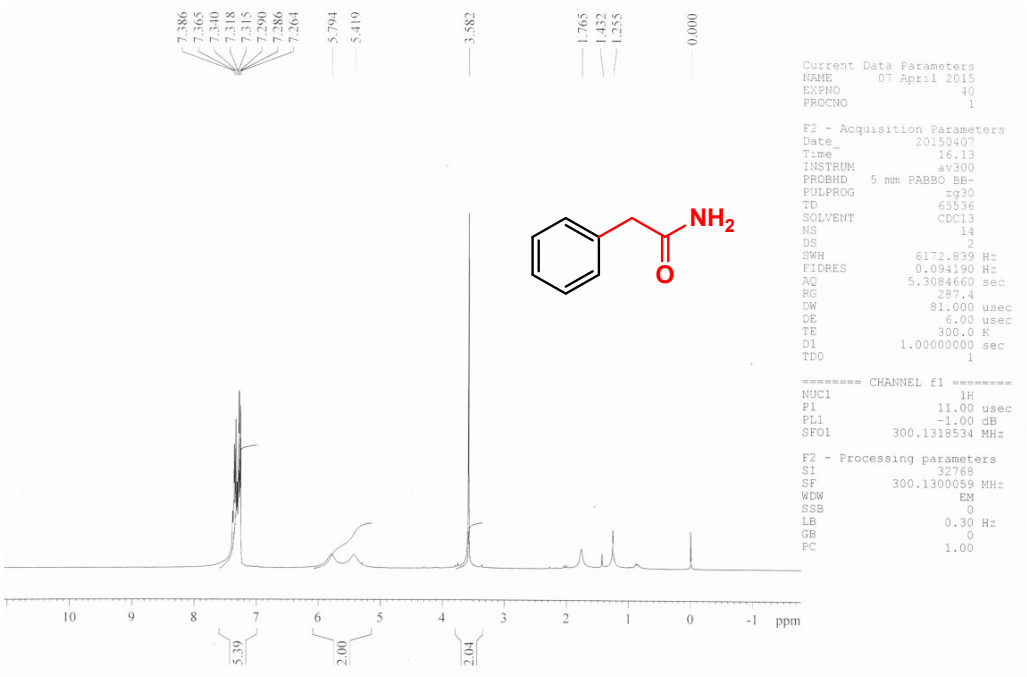


Figure S25. ^{1}H NMR of 4h

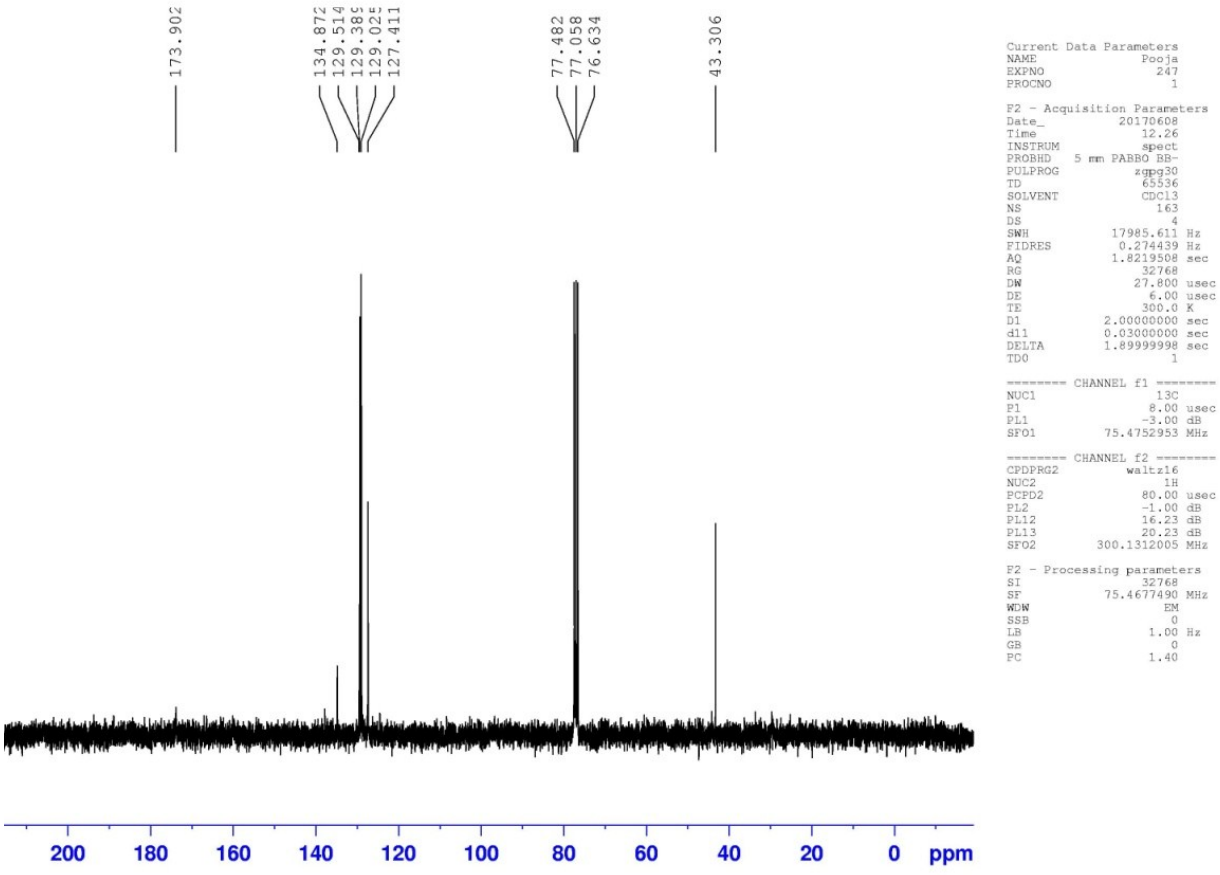


Figure S26. ^{13}C NMR of 4h

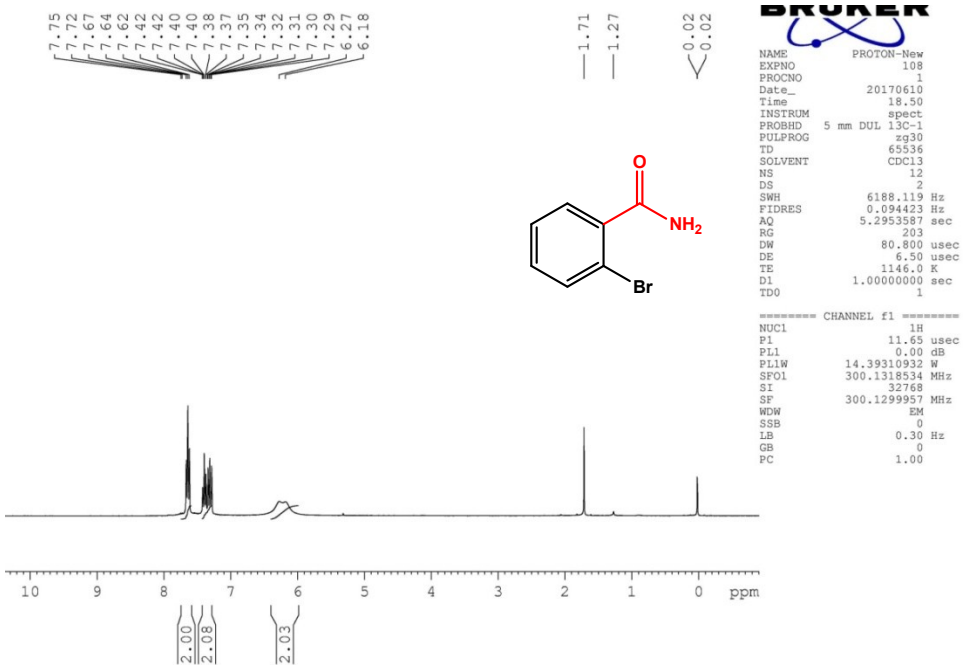


Figure S27. ^{1}H NMR of 4i

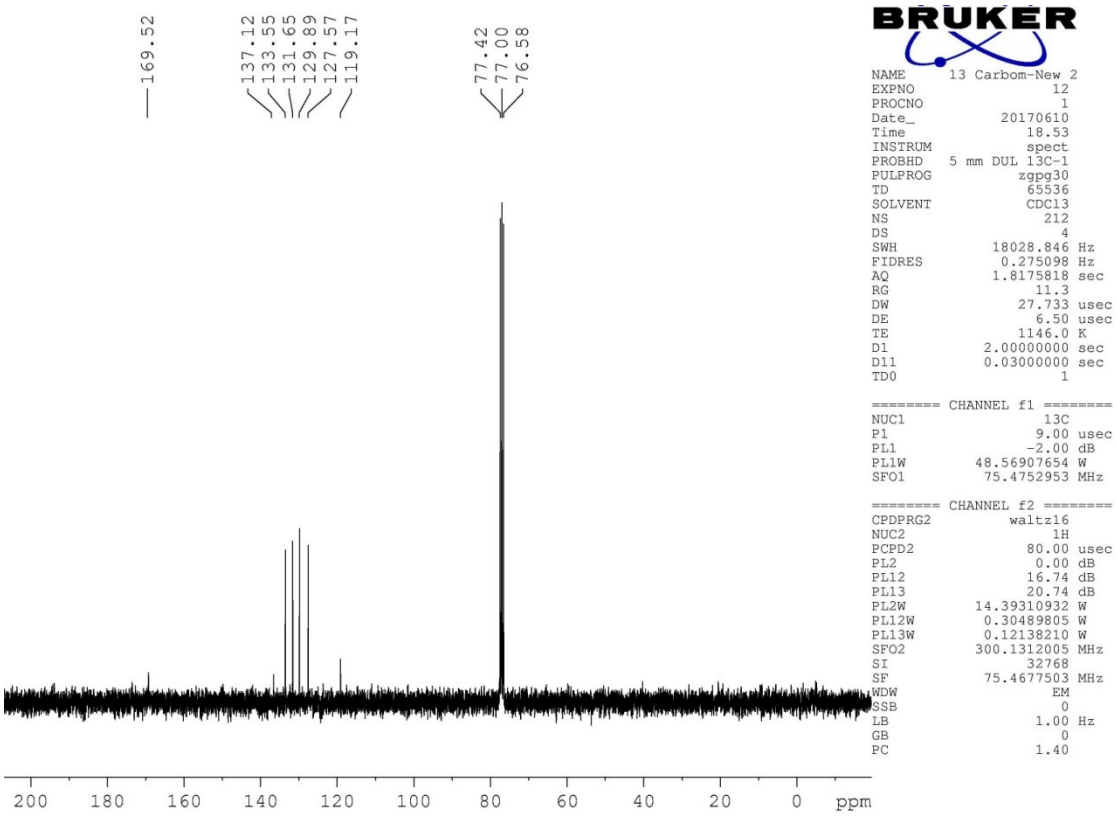


Figure S28. ^{13}C NMR of 4i

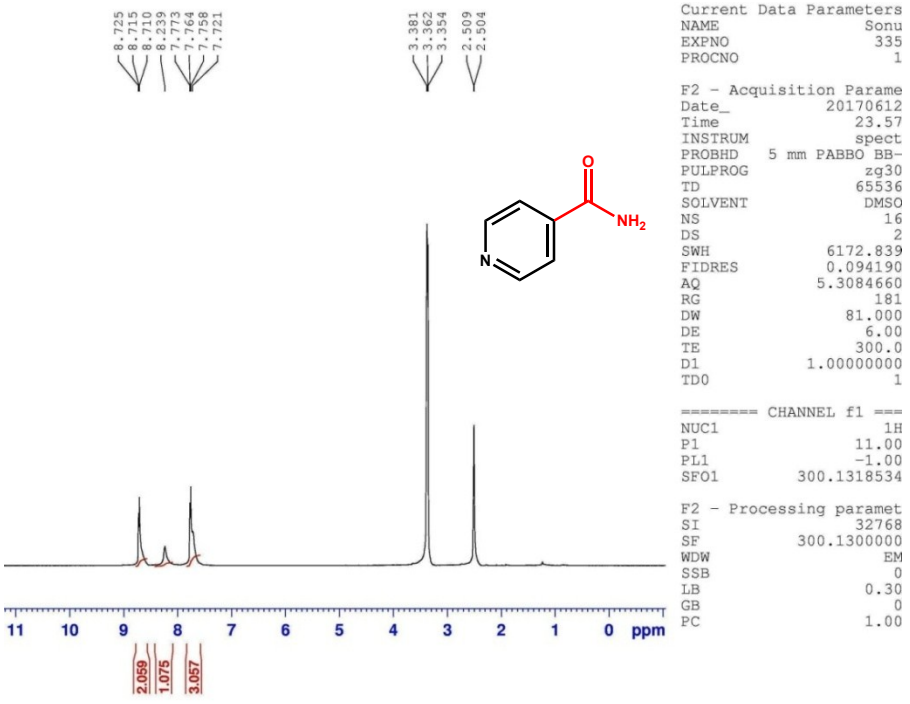


Figure S29. ^{1}H NMR of 4j

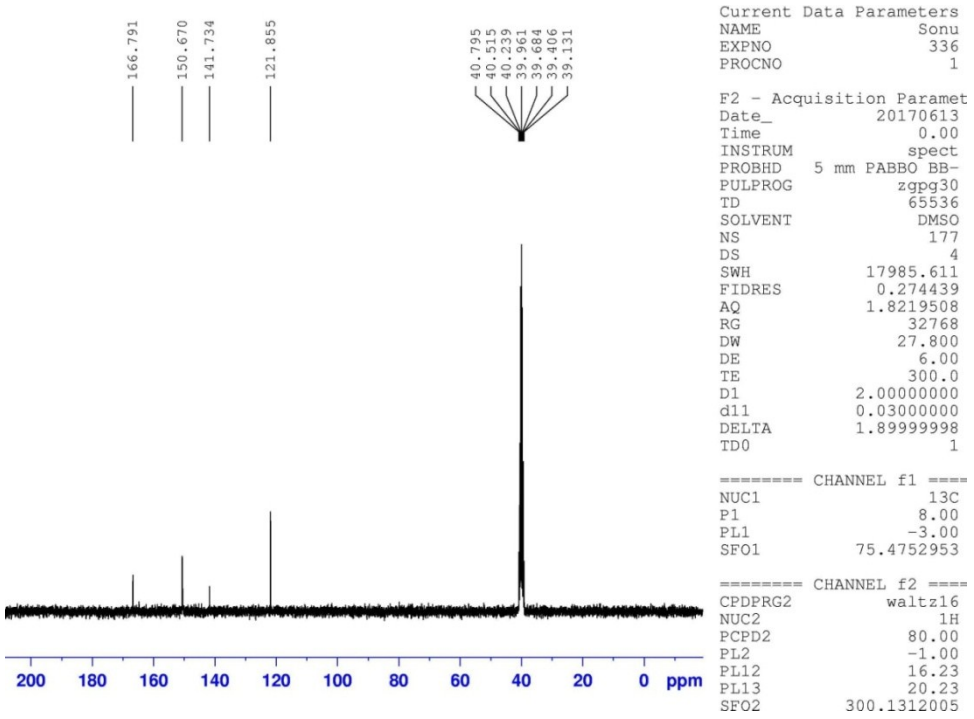


Figure S30. ^{13}C NMR of 4j

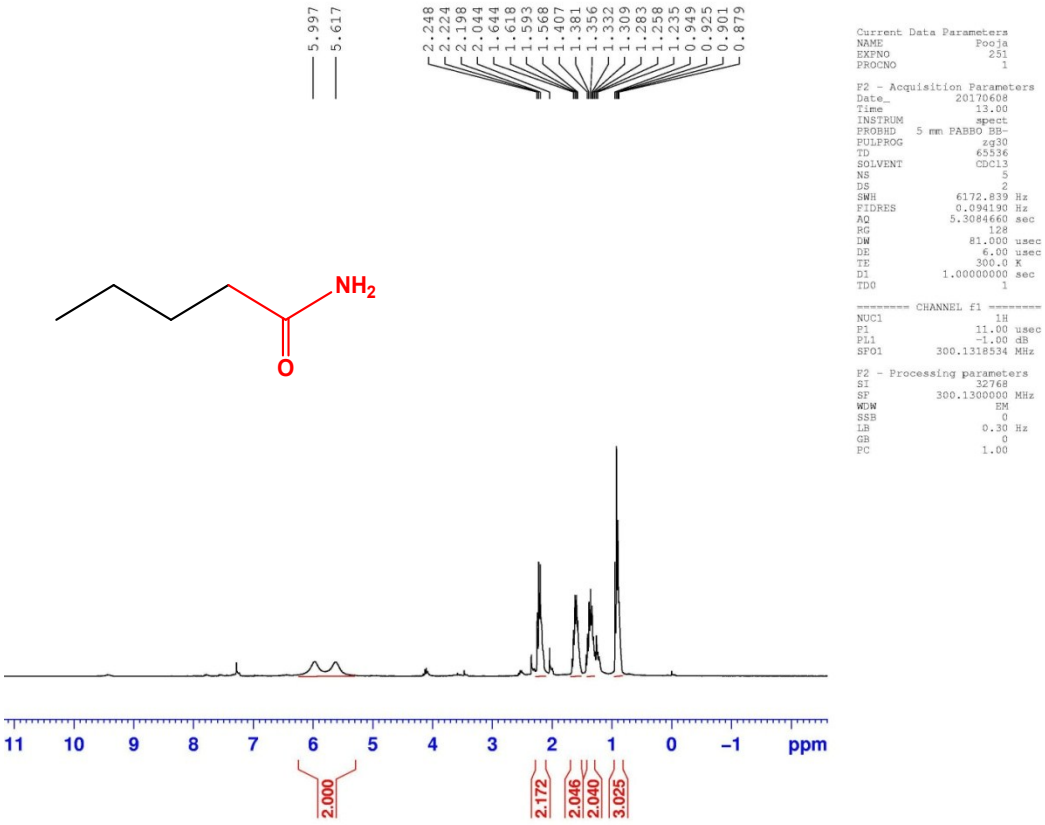
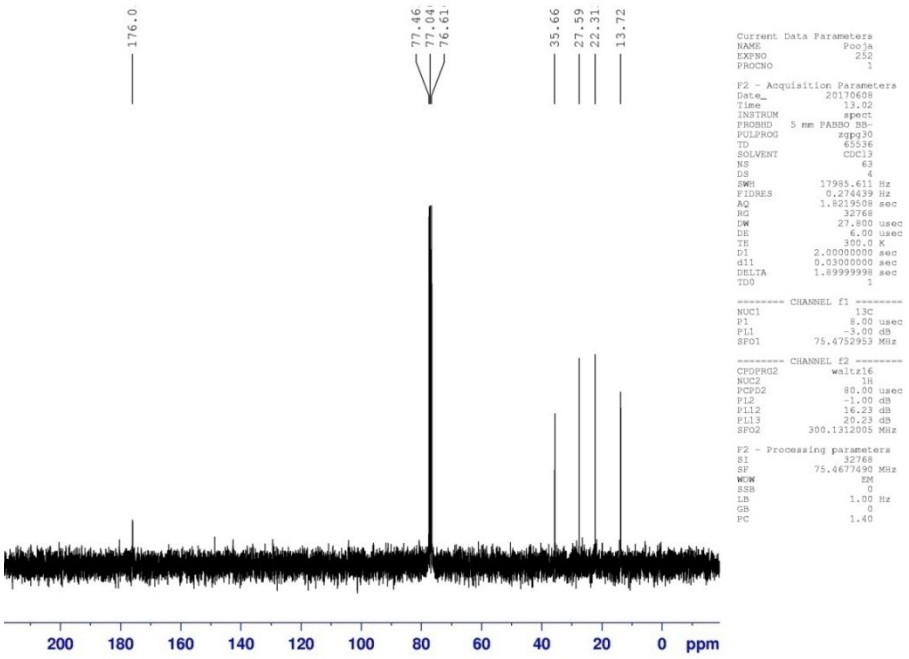


Figure S31. ^{1}H NMR of 4k



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d11 0.03000000 sec
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PL13 20.23 dB
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Figure S32. ^{13}C NMR of 4k

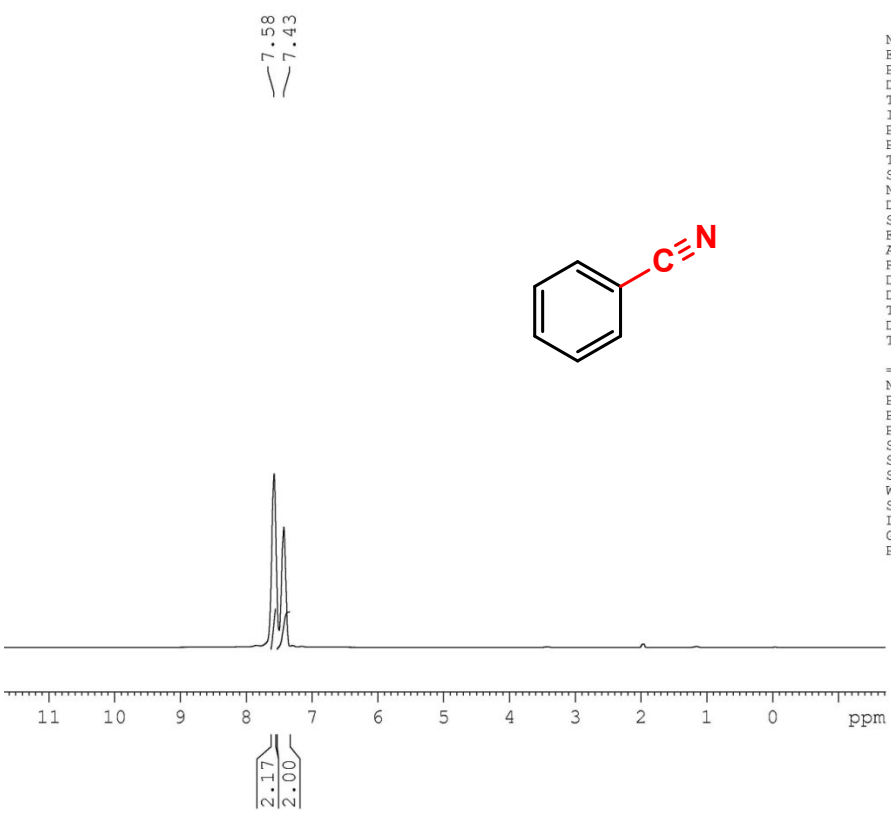

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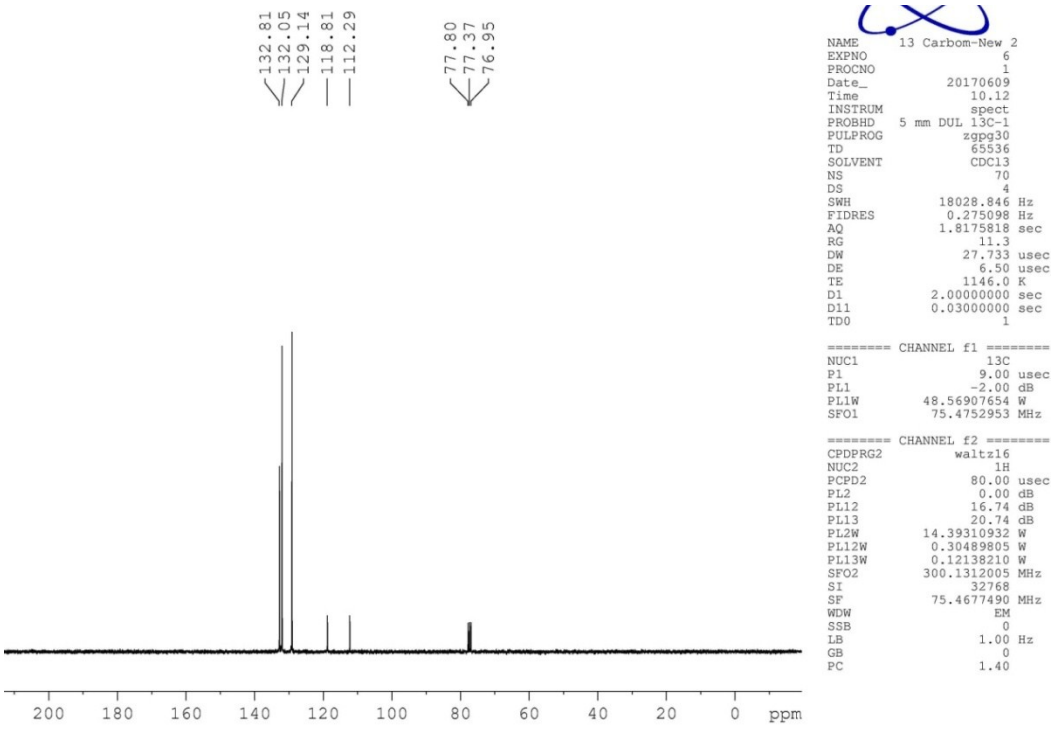
Figure S33. ^{1}H NMR of 6a

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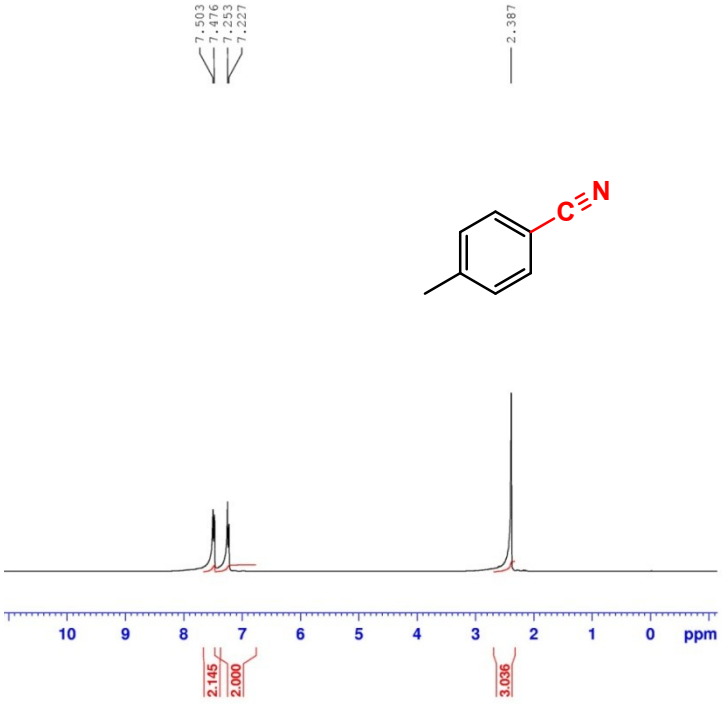
DW                       27.733 usec
DE                        6.50 usec
TE                      1146.0 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.00 usec
PL1                      -2.00 dB
PL1W               48.56907654 W
SFO1                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                       0.00 dB
PL12                     16.74 dB
PL13                     20.74 dB
PL2W               14.39310932 W
PL12W               0.30489805 W
PL13W               0.12138210 W
SFO2               300.1312005 MHz
SI                        32768
SF                 75.4677490 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

Figure S34. ^{13}C NMR of 6a



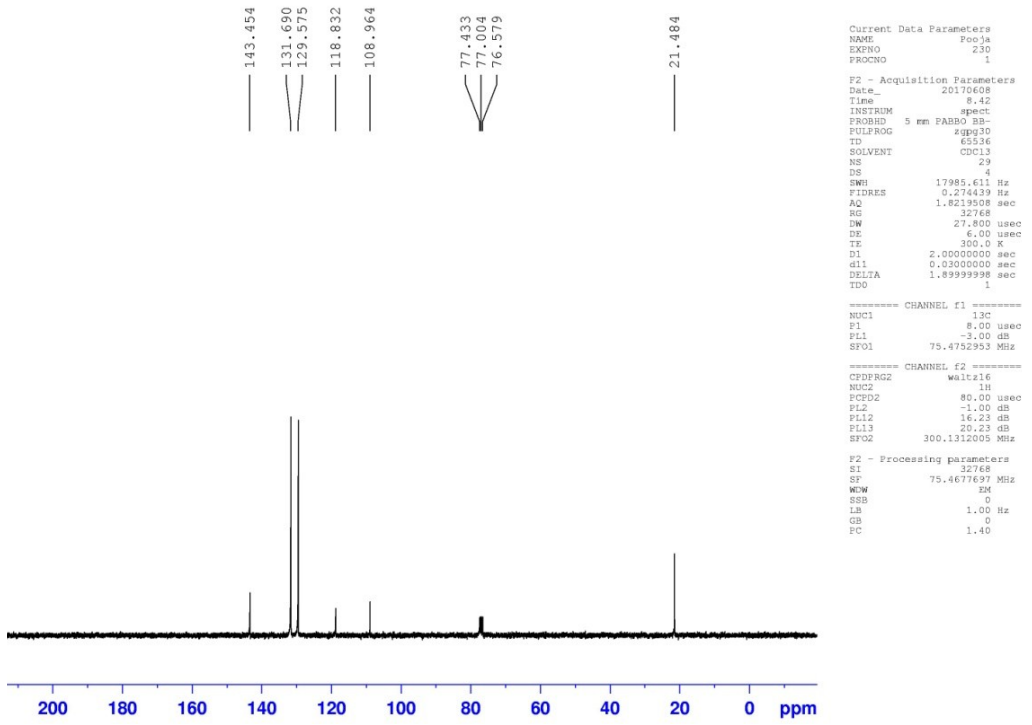

```
Current Data Parameters
NAME                     Pooja
EXPNO                      229
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20170608
Time                      8.39
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                       40.3
DW                     81.000 use
DE                      6.00 use
TE                     300.0 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                        1H
P1                      11.00 use
PL1                     -1.00 dB
SFO1               300.1318534 MHz

F2 - Processing parameters
SI                        32768
SF                 300.1300000 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

Figure S35. ^{1}H NMR of 6b



Current Data Parameters
NAME Pooja
EXPNO 230
PROCNO 1

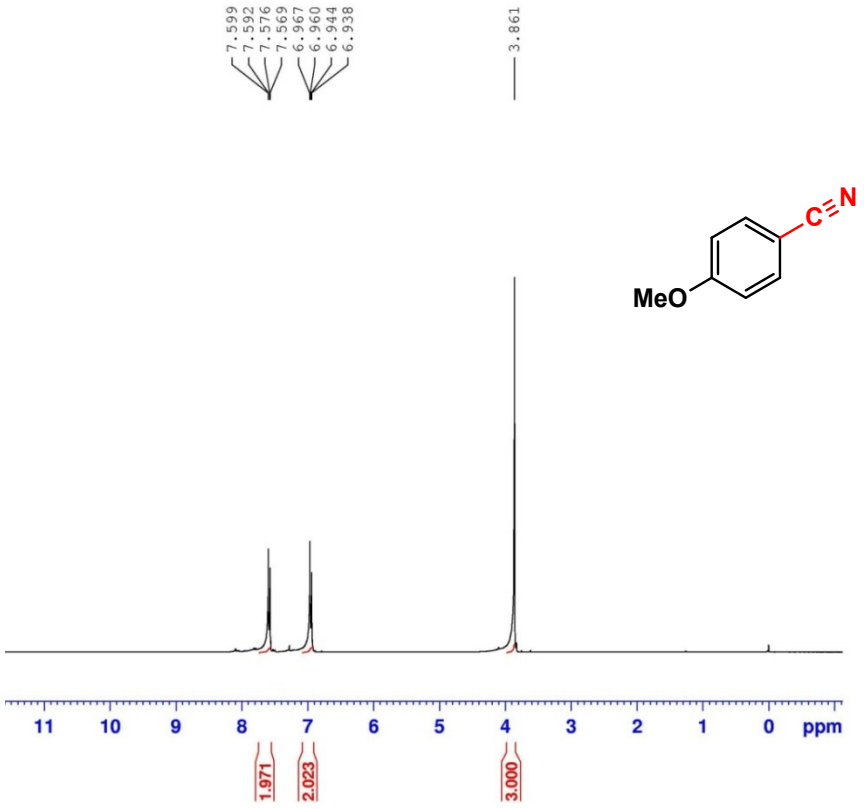
F2 - Acquisition Parameters
Date_ 20170608
Time 8.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 29
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.23 dB
PL13 20.23 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677697 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S36. ^{13}C NMR of 6b



Current Data Parameters
NAME PD1
EXPNO 27
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050119
Time 13.34
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 114
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -1.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S37. ^{1}H NMR of 6c

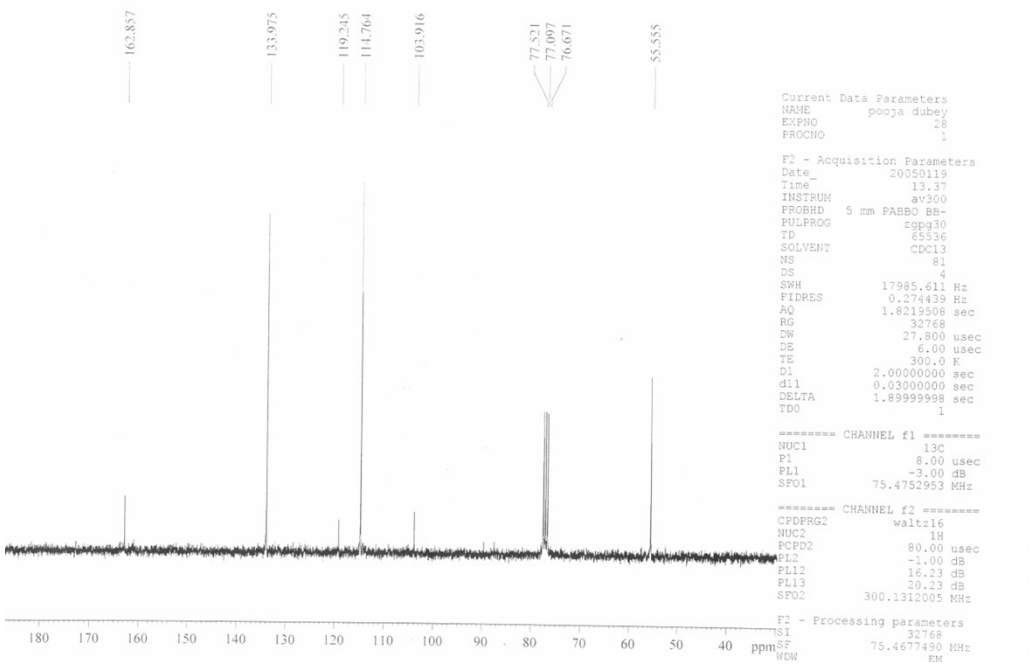


Figure S38. ^{13}C NMR of 6c

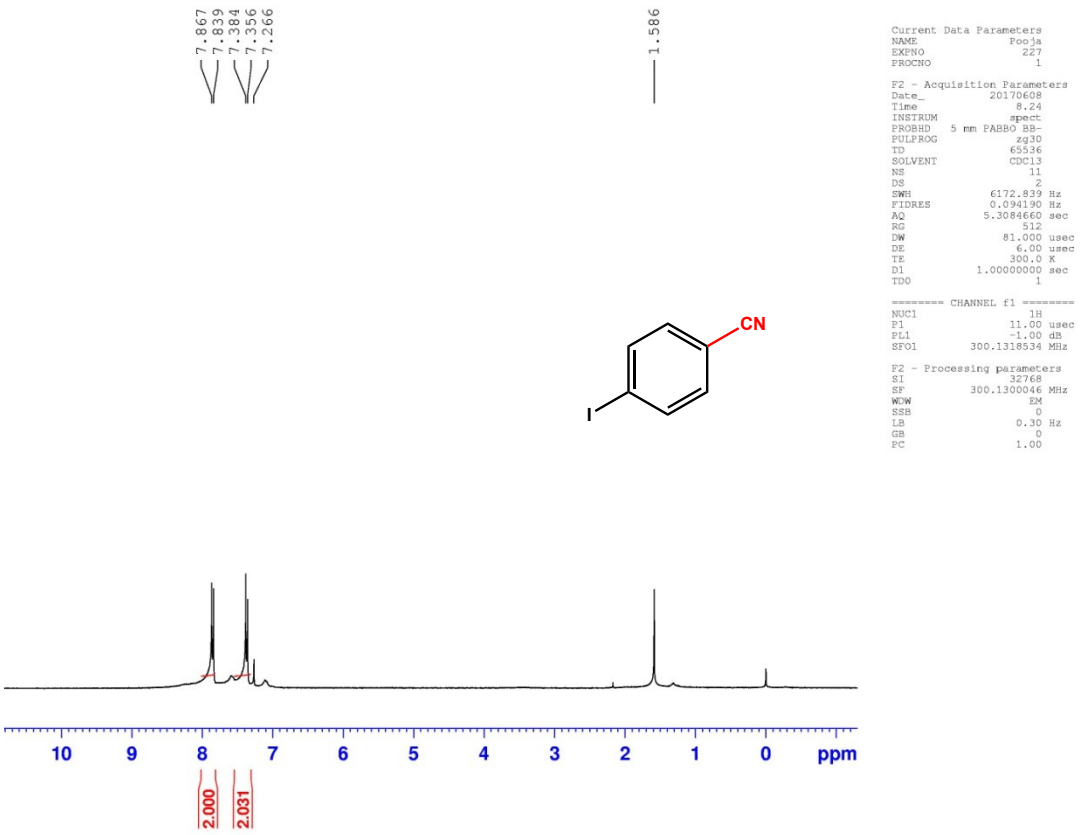
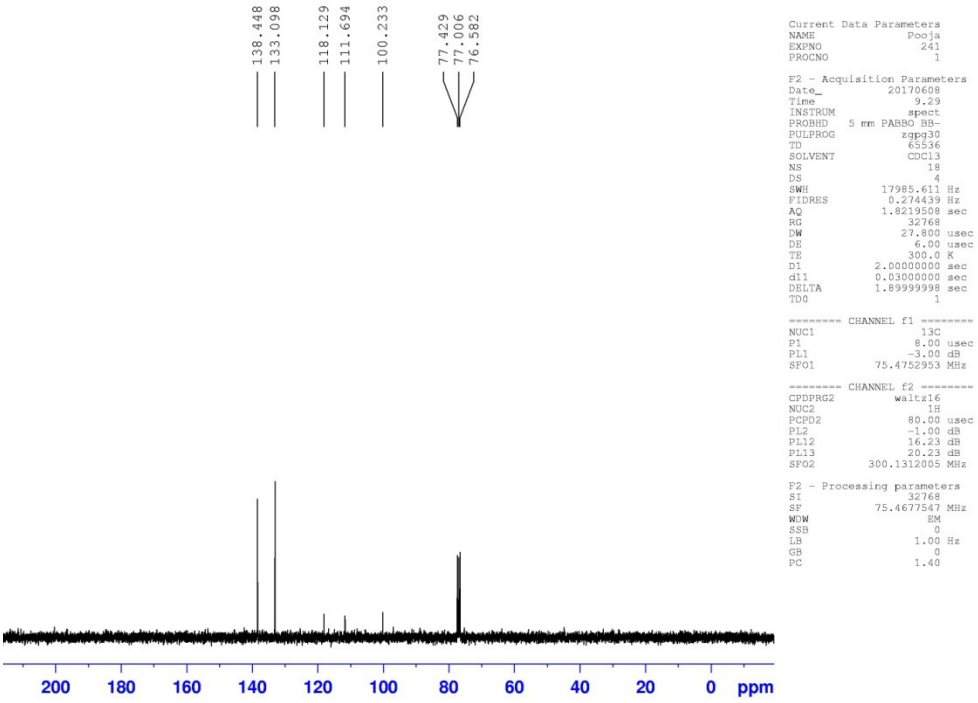


Figure S39. ^{1}H NMR of 6d




```
Current Data Parameters
NAME                  Pooja
EXPNO                   241
PROCNO                    1

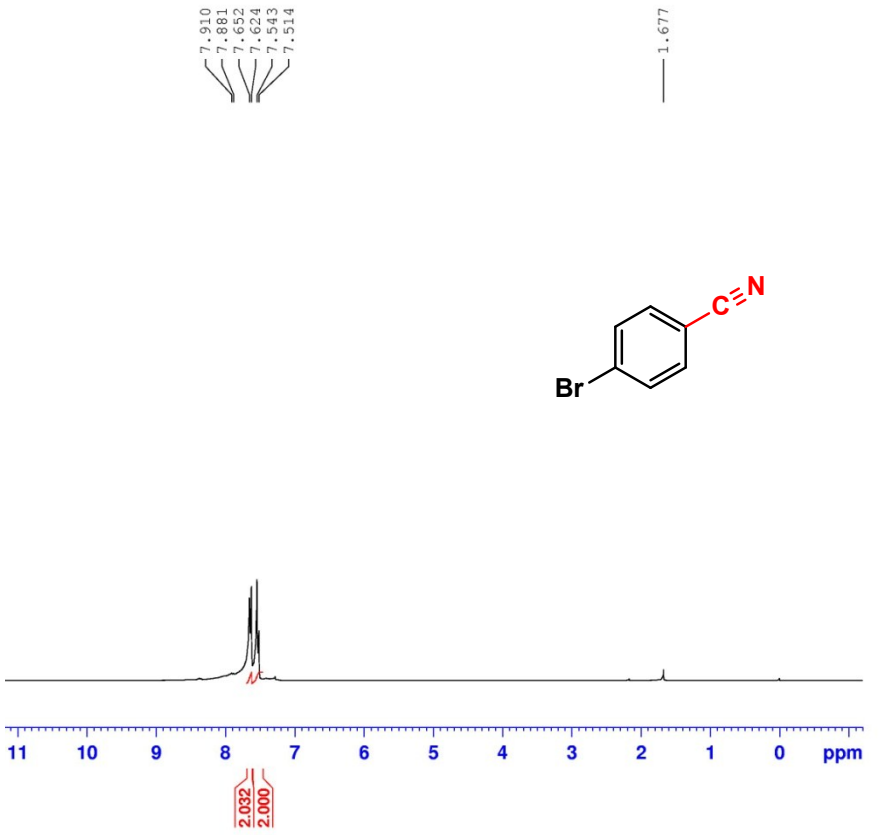
F2 - Acquisition Parameters
Date_              20170608
Time                   9.29
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       18
DS                        4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                    32768
DW                   27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.00 usec
PL1                   -3.00 dB
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 80.00 usec
PL2                   -1.00 dB
PL12                  16.23 dB
PL13                  20.23 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677547 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Figure S40. ^{13}C NMR of 6d



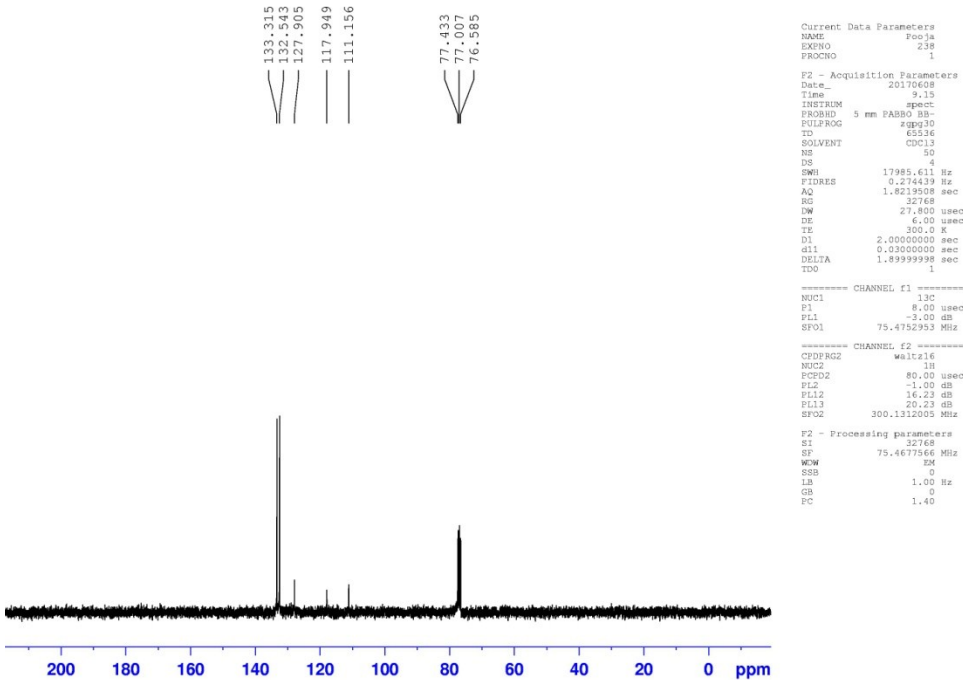

```
Current Data Parameters
NAME                  Pooja
EXPNO                   237
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170608
Time                   9.13
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                    143.7
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                    11.00 usec
PL1                   -1.00 dB
SFO1             300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF               300.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Figure S41. ^{1}H NMR of 6e



Current Data Parameters
NAME Pooja
EXPNO 238
PROCNO 1

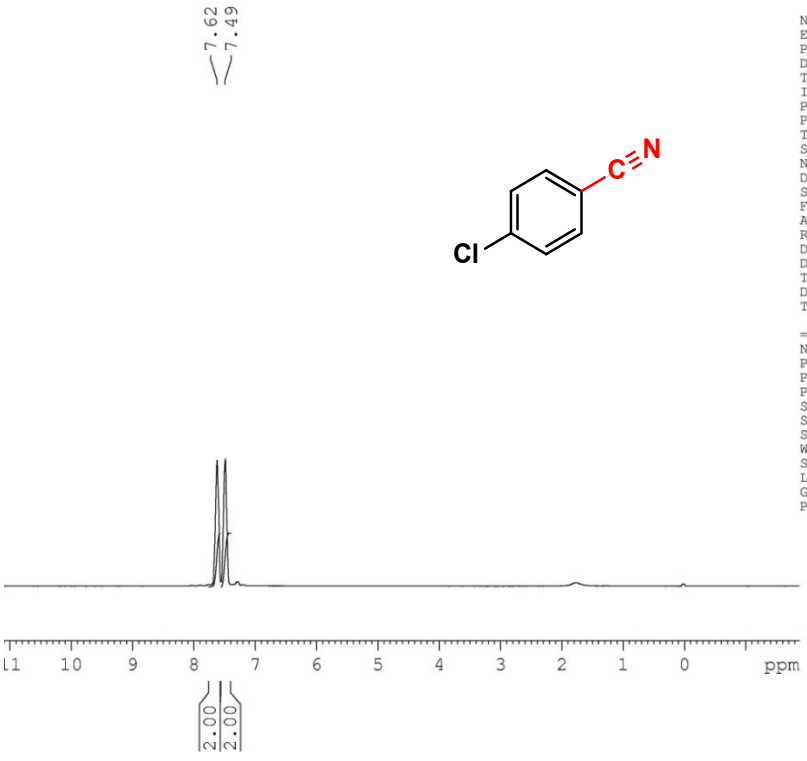
F2 - Acquisition Parameters
Date_ 20170608
Time 9.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.23 dB
PL13 20.23 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S42. ^{13}C NMR of 6e



NAME PROTON-New
EXPNO 100
PROCNO 1
Date_ 20170609
Time 10.00
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 1146.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.65 usec
PL1 0.00 dB
PL1W 14.39310932 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1299957 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S43. ^{1}H NMR of 6f

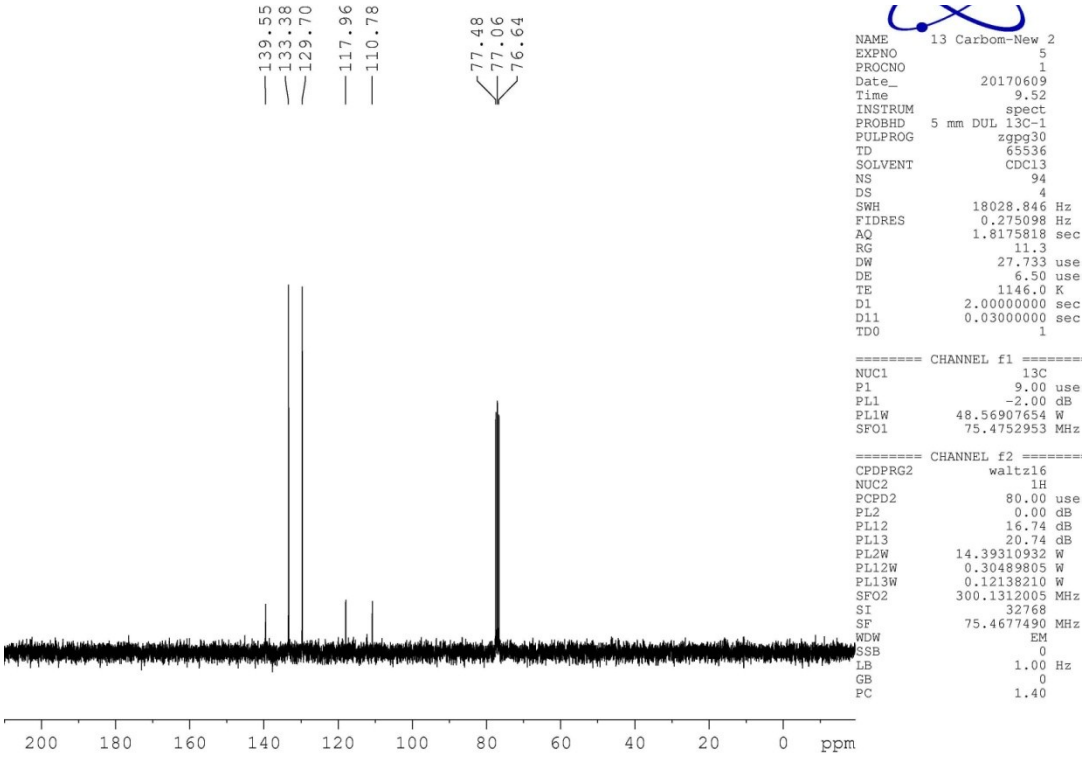


Figure S44. ^{13}C NMR of 6f

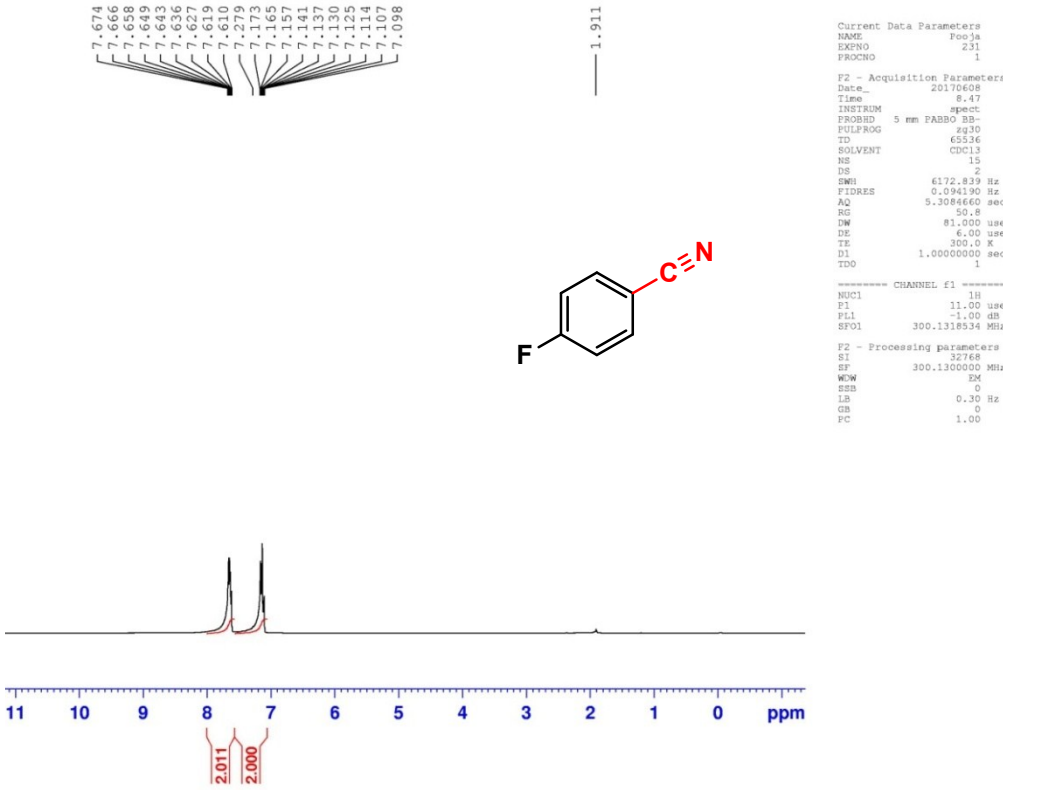
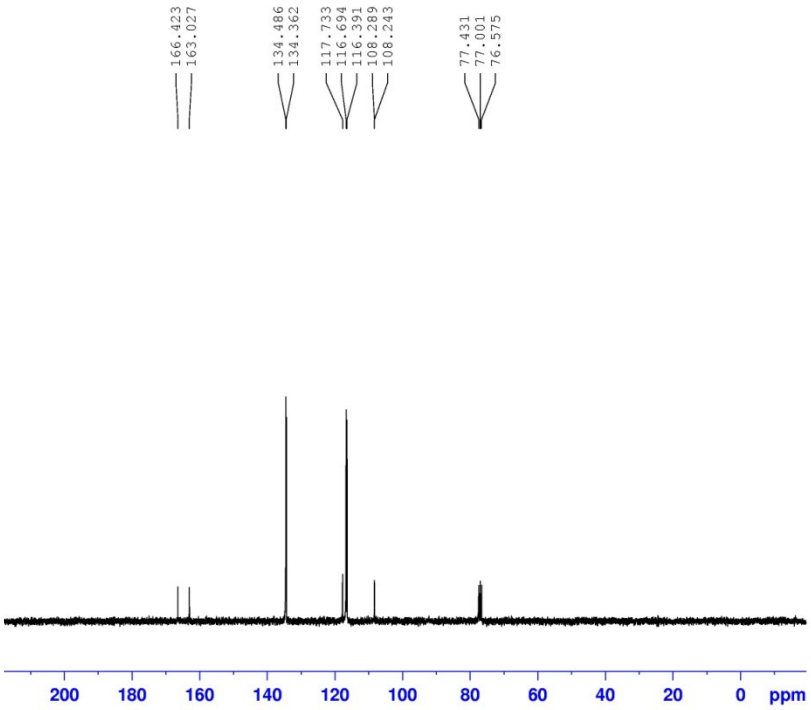


Figure S45. ^{1}H NMR of 6g




```
Current Data Parameters
NAME                  Pooja
EXPNO                   232
PROCNO                    1

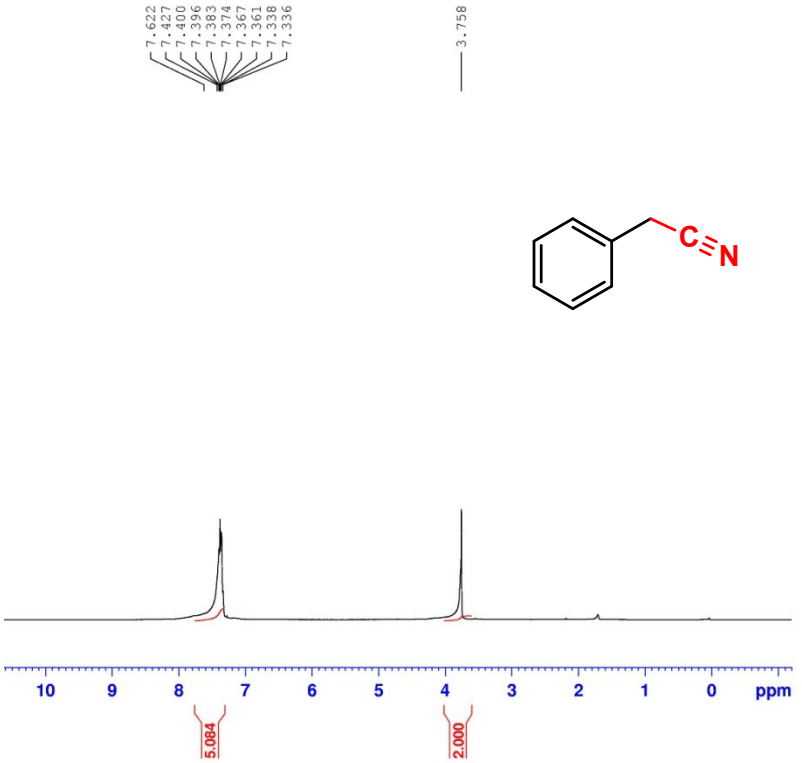
F2 - Acquisition Parameters
Date_               20170608
Time                    8.50
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       4
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1                2.00000000 sec
d11               0.03000000 sec
DELTA             1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.00 usec
PL1                   -3.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   -1.00 dB
PL12                  16.23 dB
PL13                  20.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677686 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Figure S46. ^{13}C NMR of 6g



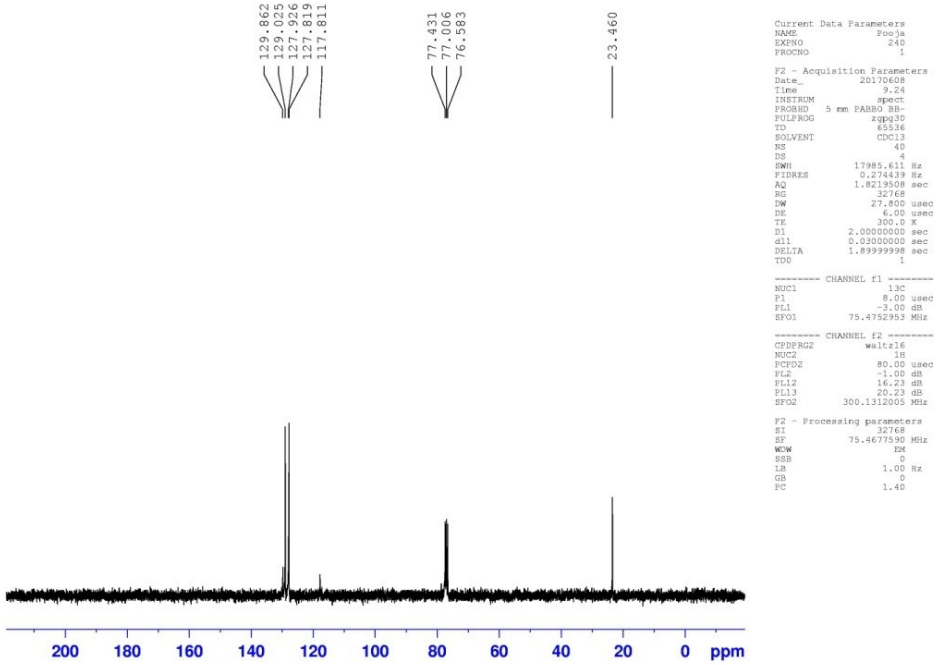

```
Current Data Parameters
NAME                  Pooja
EXPNO                   239
PROCNO                    1

F2 - Acquisition Parameters
Date_               20170608
Time                    9.21
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                   65536
SOLVENT              CDCl3
NS                      13
DS                       2
SWH                6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084660 sec
RG                      90.5
DW                  81.000 usec
DE                   6.00 usec
TE                  300.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                    11.00 usec
PL1                   -1.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF              300.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Figure S47. ^{1}H NMR of 6h



Current Data Parameters
NAME Pooja
EXPNO 240
PROCNO 1

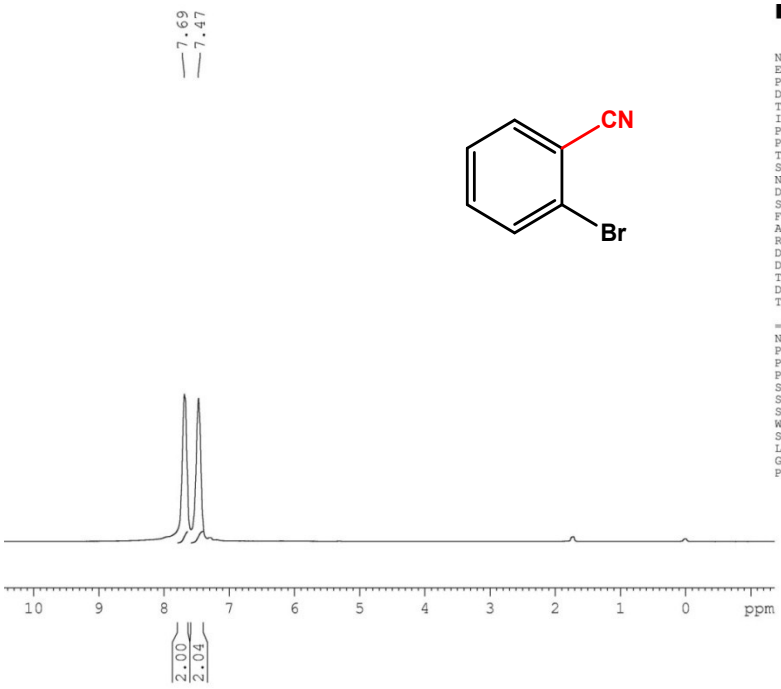
F2 - Acquisition Parameters
Date_ 20170608
Time 9.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 40
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.23 dB
PL13 20.23 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S48. ^{13}C NMR of 6h



BRUKER

NAME PROTON-New
EXPNO 105
PROCNO 1
Date_ 20170610
Time 18.34
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 1146.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 11.65 usec
PL1 0.00 dB
PL1W 14.39310932 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1299957 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S49. ^{1}H NMR of 6i

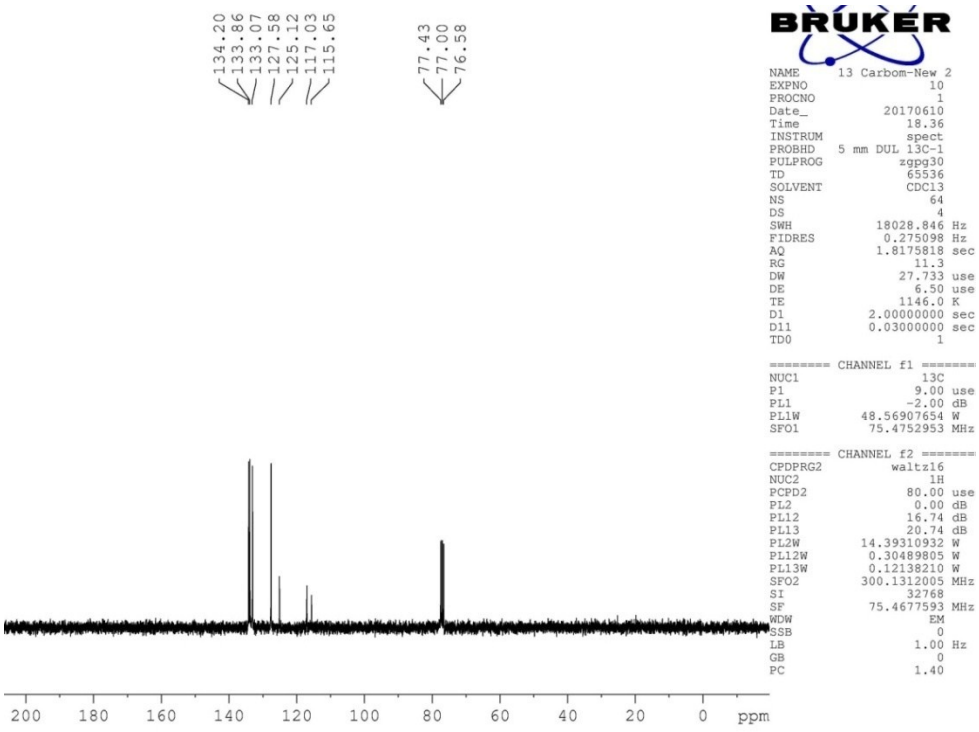


Figure S50. ^{13}C NMR of 6i

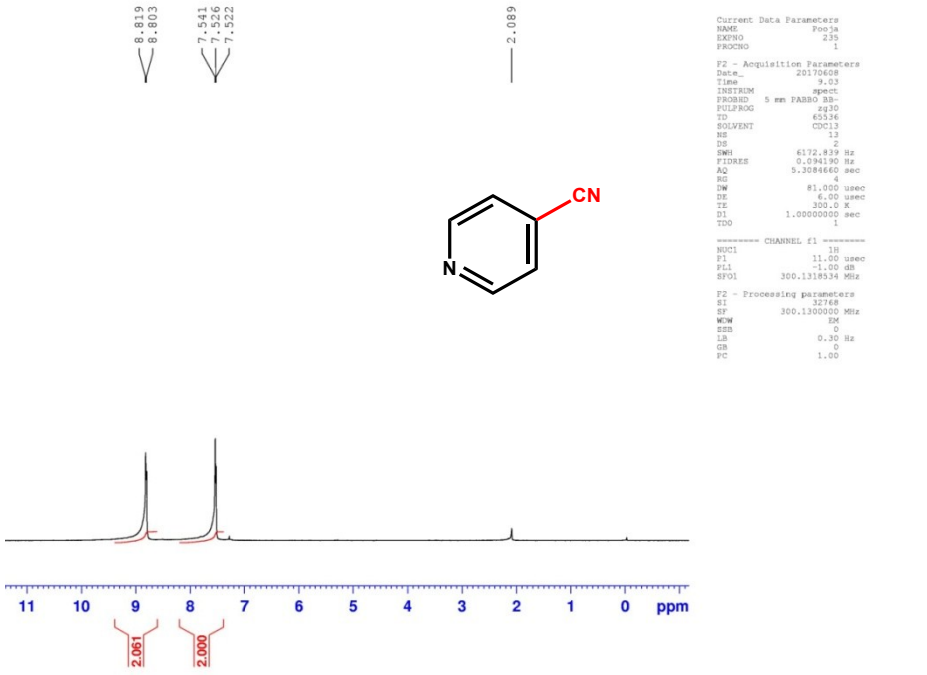
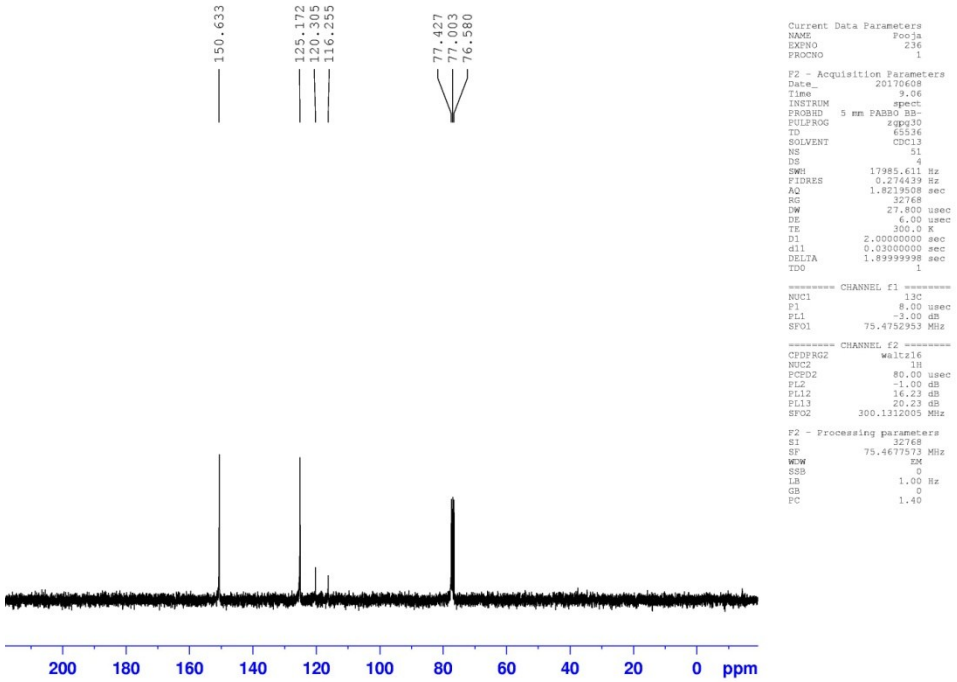


Figure S51. ^{1}H NMR of 6j



Current Data Parameters
NAME Pooja
EXPNO 236
PROCNO 1

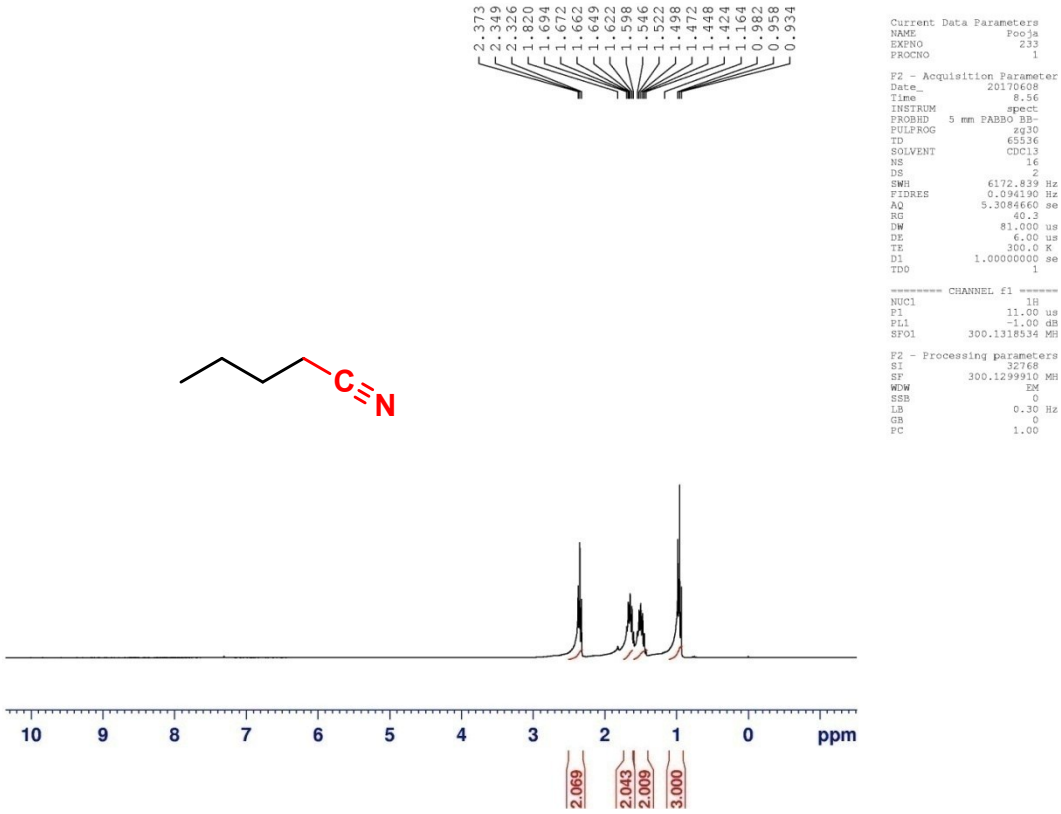
F2 - Acquisition Parameters
Date_ 20170608
Time 9.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 51
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.23 dB
PL13 20.23 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677573 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S52. ^{13}C NMR of 6j



Current Data Parameters
NAME Pooja
EXPNO 233
PROCNO 1

F2 - Acquisition Parameter
Date_ 20170608
Time 8.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 se
RG 40.3
DW 81.000 us
DE 6.00 us
TE 300.0 K
D1 1.00000000 se
TD0 1

======== CHANNEL f1 ======
NUC1 1H
P1 11.00 us
PL1 -1.00 dB
SFO1 300.1318534 MH

F2 - Processing parameters
SI 32768
SF 300.1299910 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S53. ^{1}H NMR of 6k

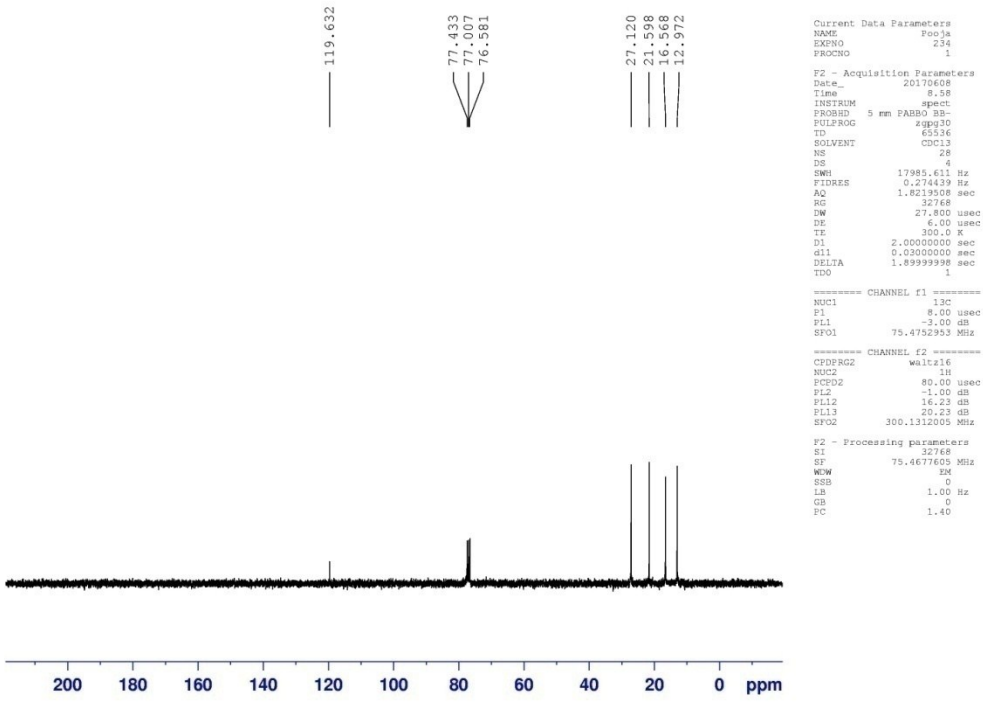


Figure S54. ^{13}C NMR of 6k

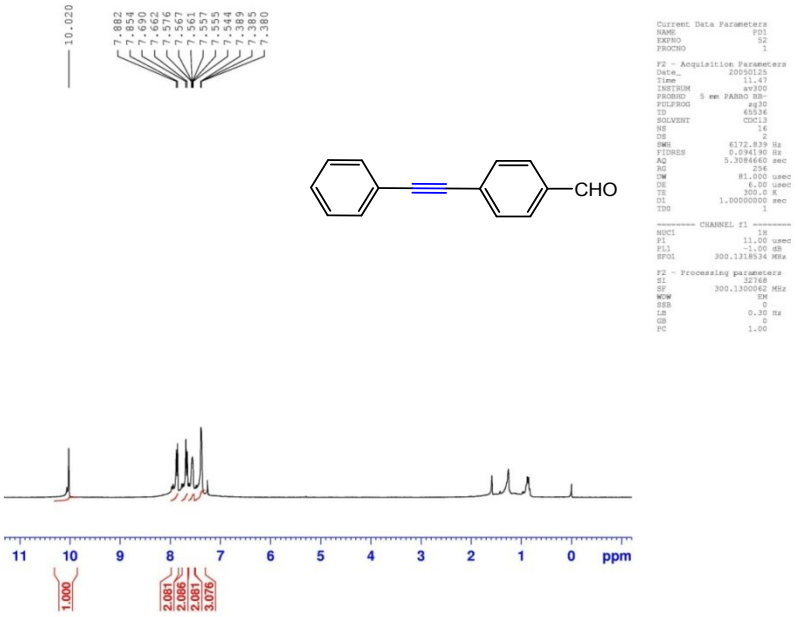


Figure S55. ^{1}H NMR of 9a

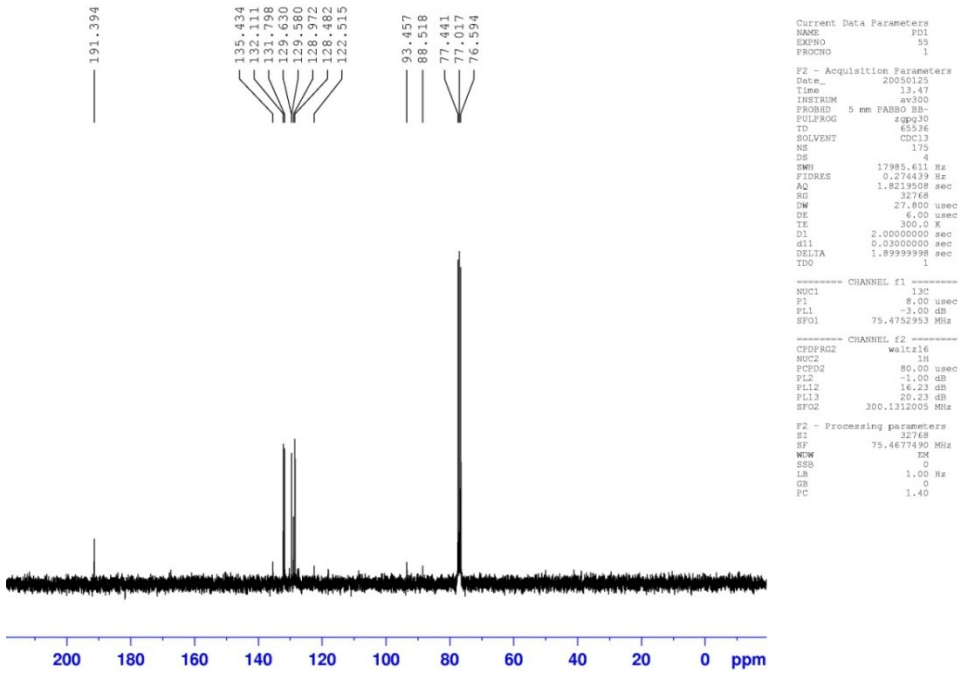


Figure S56. ^{13}C NMR of 9a

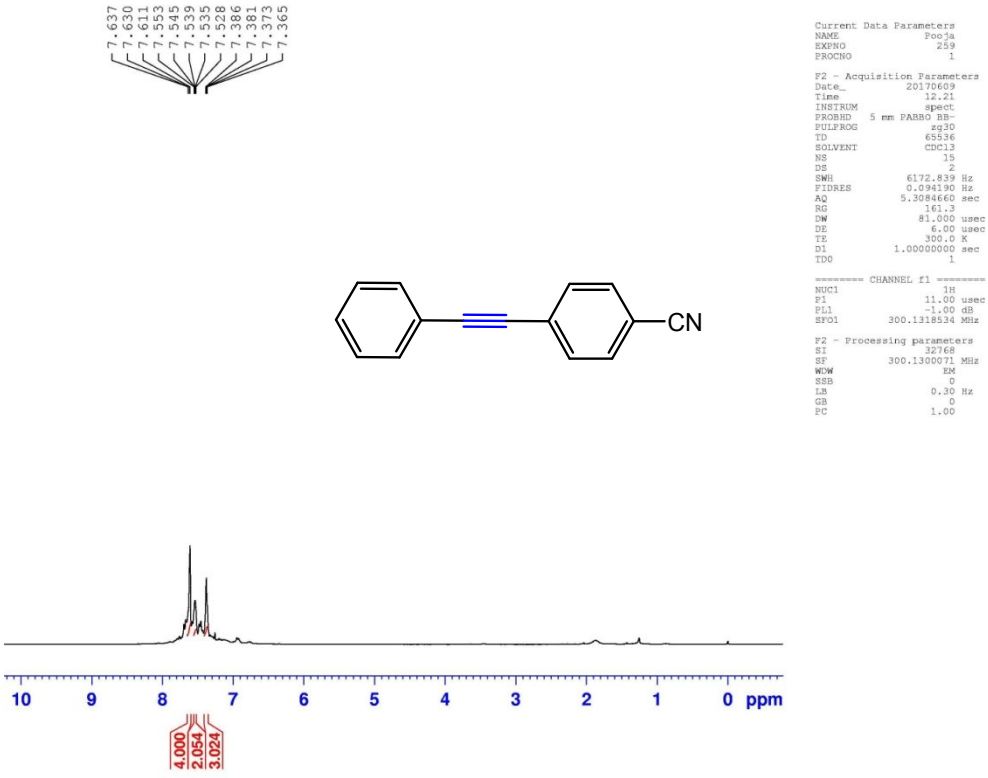
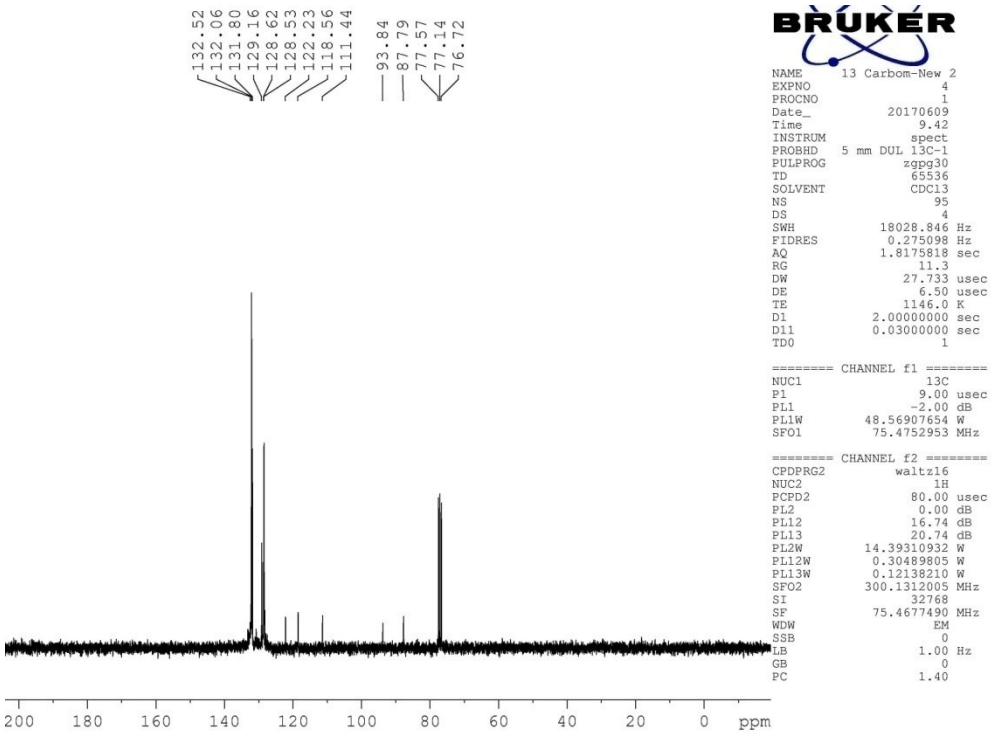


Figure S57. ^{1}H NMR of 9b

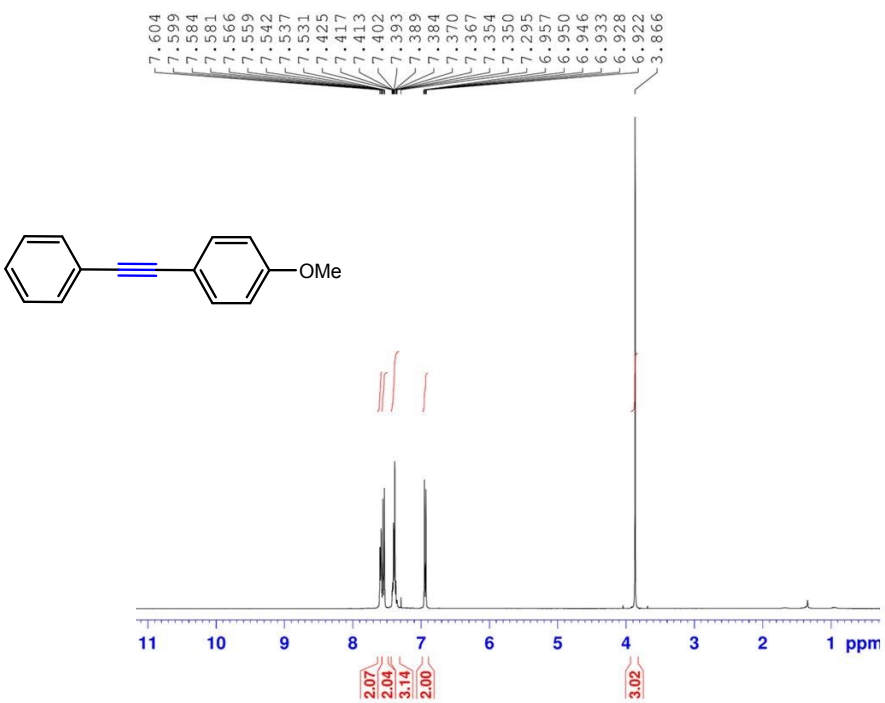



```
NAME          13 Carbom-New 2
EXPNO                      4
PROCNO                     1
Date_               20170609
Time                    9.42
INSTRUM                spect
PROBHD    5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      95
DS                       4
SWH              18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175818 sec
RG                    11.3
DW                  27.733 usec
DE                   6.50 usec
TE                 1146.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.00 usec
PL1                  -2.00 dB
PL1W          48.56907654 W
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 16.74 dB
PL13                 20.74 dB
PL2W          14.39310932 W
PL12W          0.30489805 W
PL13W          0.12138210 W
SFO2         300.1312005 MHz
SI                   32768
SF            75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Figure S58. ^{13}C NMR of 9b




```
Current Data Parameters
NAME                     PD1
EXPNO                     51
PROCNO                     1

F2 - Acquisition Parameters
Date_               20050125
Time                   11.42
INSTRUM                av300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
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FIDRES            0.094190 Hz
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RG                    456.1
DW                   81.000 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                        1

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PL1                   -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
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SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
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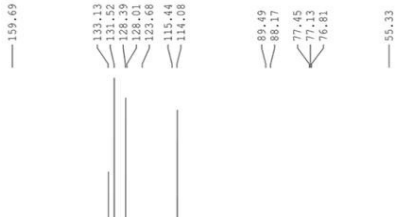
Figure S59. ^{1}H NMR of 9c

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PROCNO                     1
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TD                   65536
SOLVENT              CDCl3
NS                    4648
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FIDRES           0.275098 Hz
AQ               1.8175818 sec
RG                    11.3
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Figure S60. ^{13}C NMR of 9c

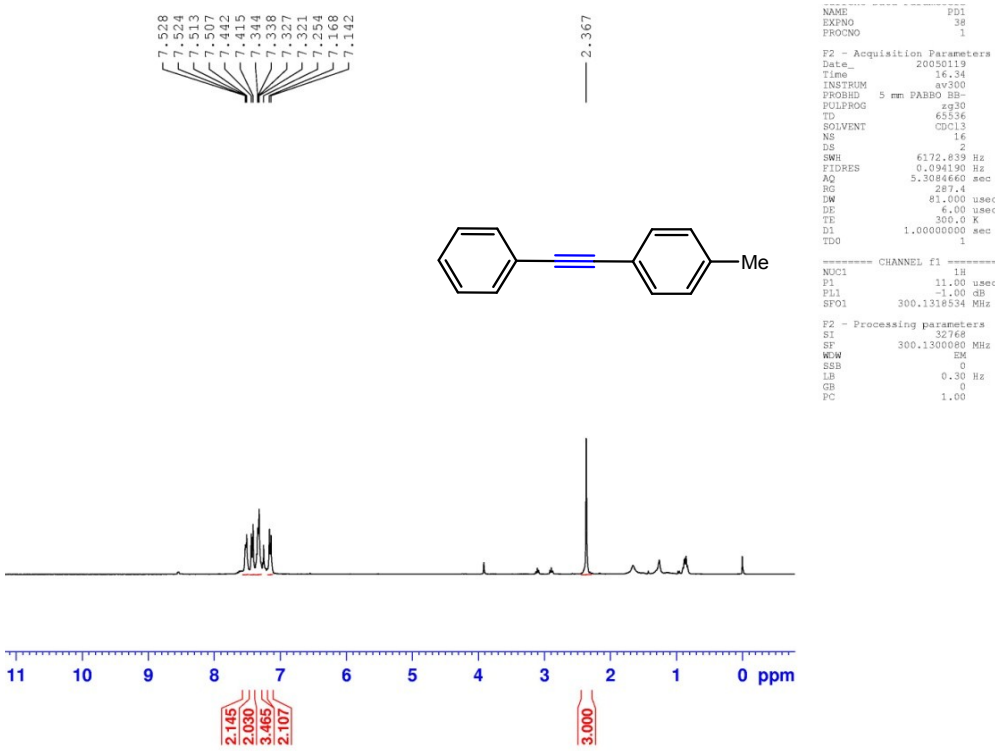


Figure S61. ^{1}H NMR of 9d

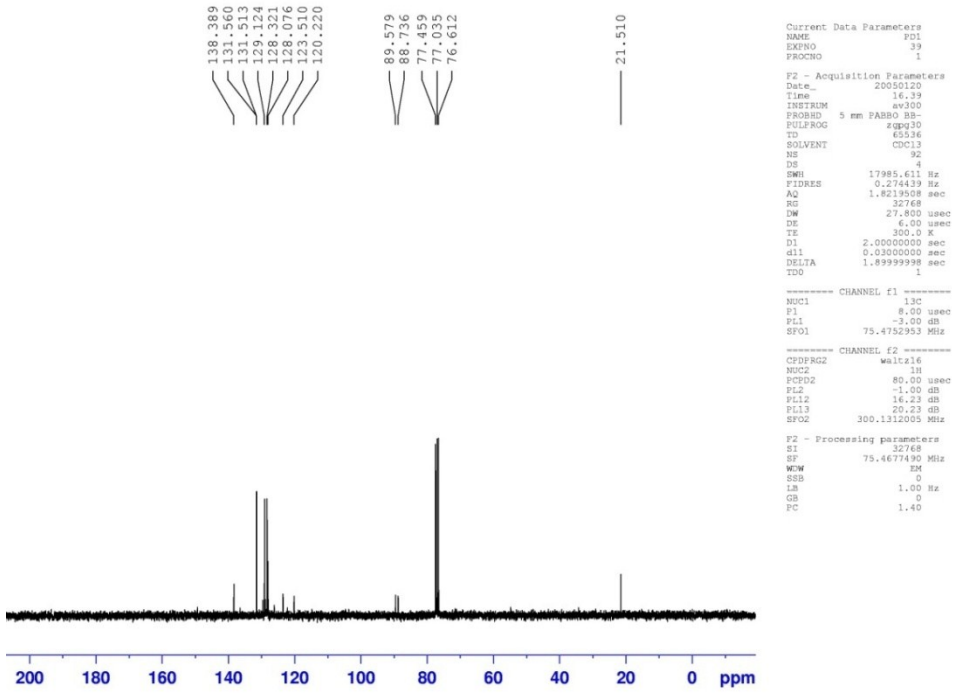


Figure S62. ^{13}C NMR of 9d

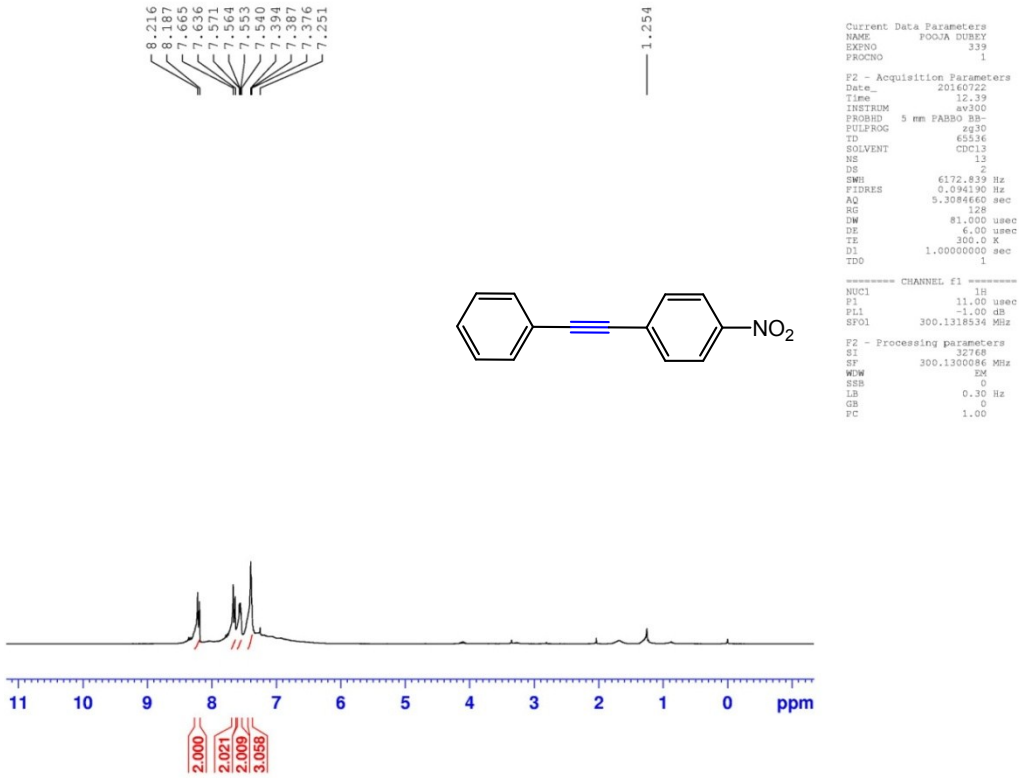


Figure S63. ^{1}H NMR of 9e

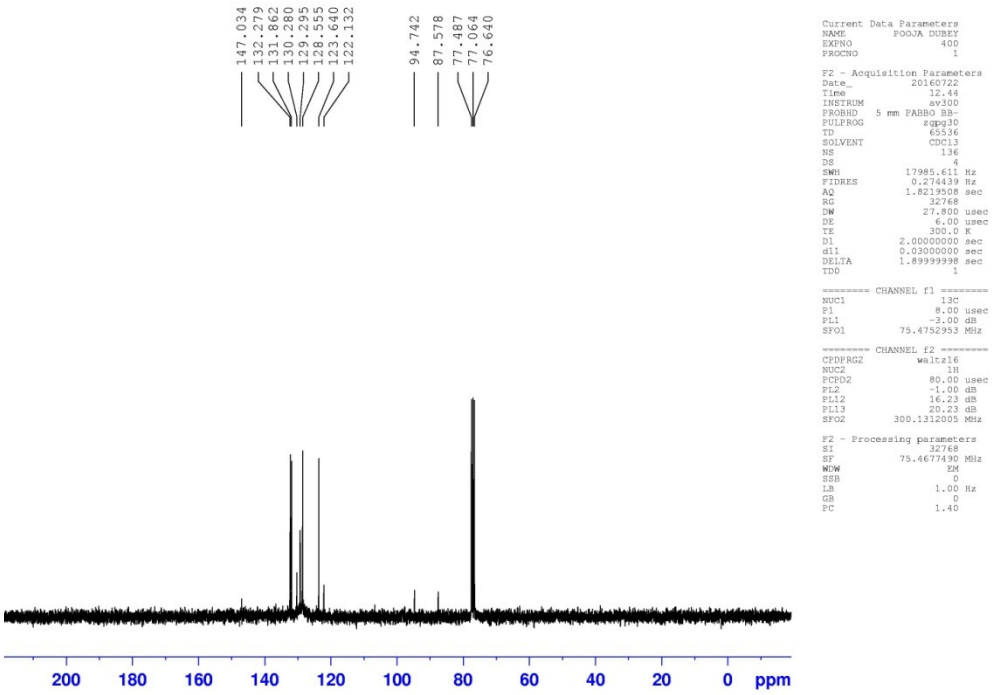


Figure S64. ^{13}C NMR of 9e

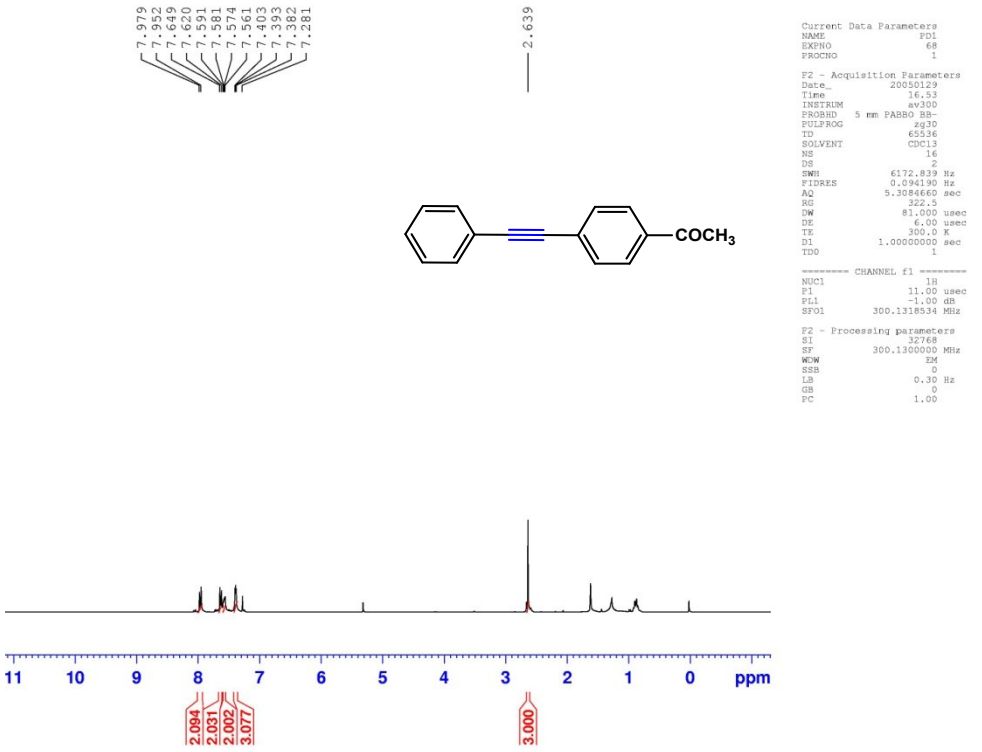
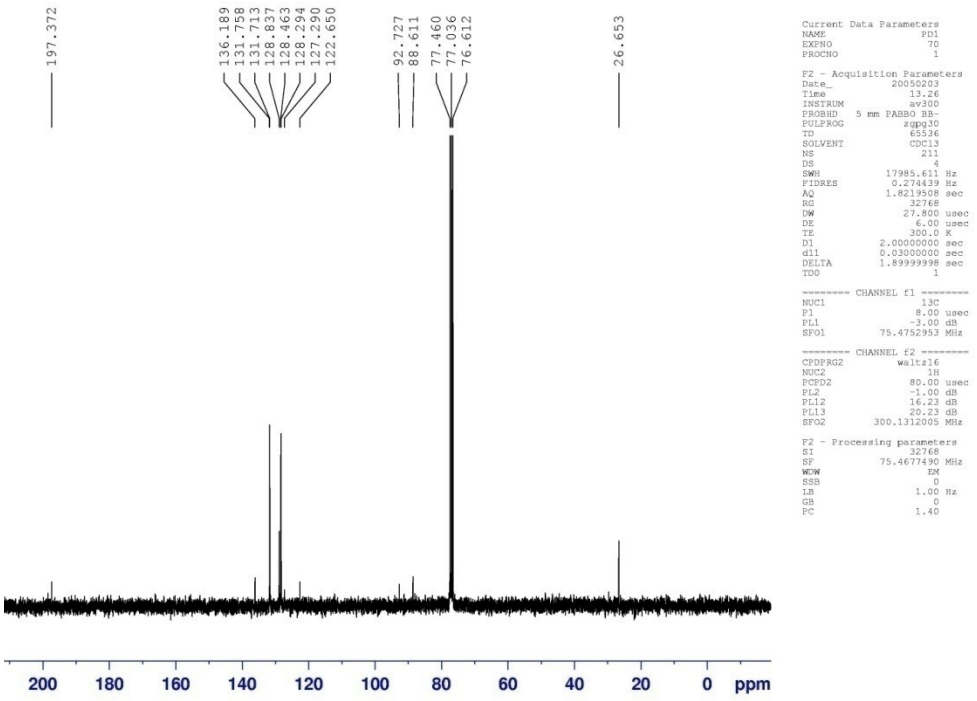


Figure S65. ^{1}H NMR of 9f

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TD                   65536
SOLVENT              CDCl3
NS                     211
DS                       4
SWH              17985.611 Hz
FIDRES           0.274439 Hz
AQ               1.8219508 sec
RG                   32768
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DE                 6.00 usec
TE                 300.0 K
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d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

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PL1               -3.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              16.23 dB
PL13              20.23 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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SSB                      0
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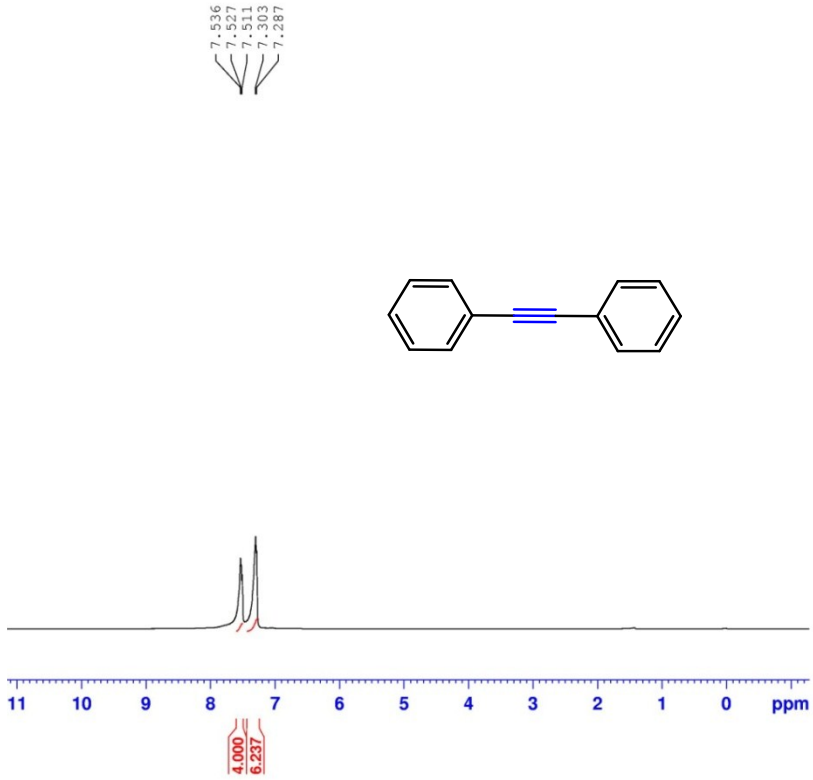
Figure S66. ^{13}C NMR of 9f

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PROCNO                  1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES           0.094190 Hz
AQ               5.3084660 sec
RG                    35.9
DW                81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                11.00 usec
PL1               -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300418 MHz
WDW                     EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                 1.00
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Figure S67. ^{1}H NMR of 9g

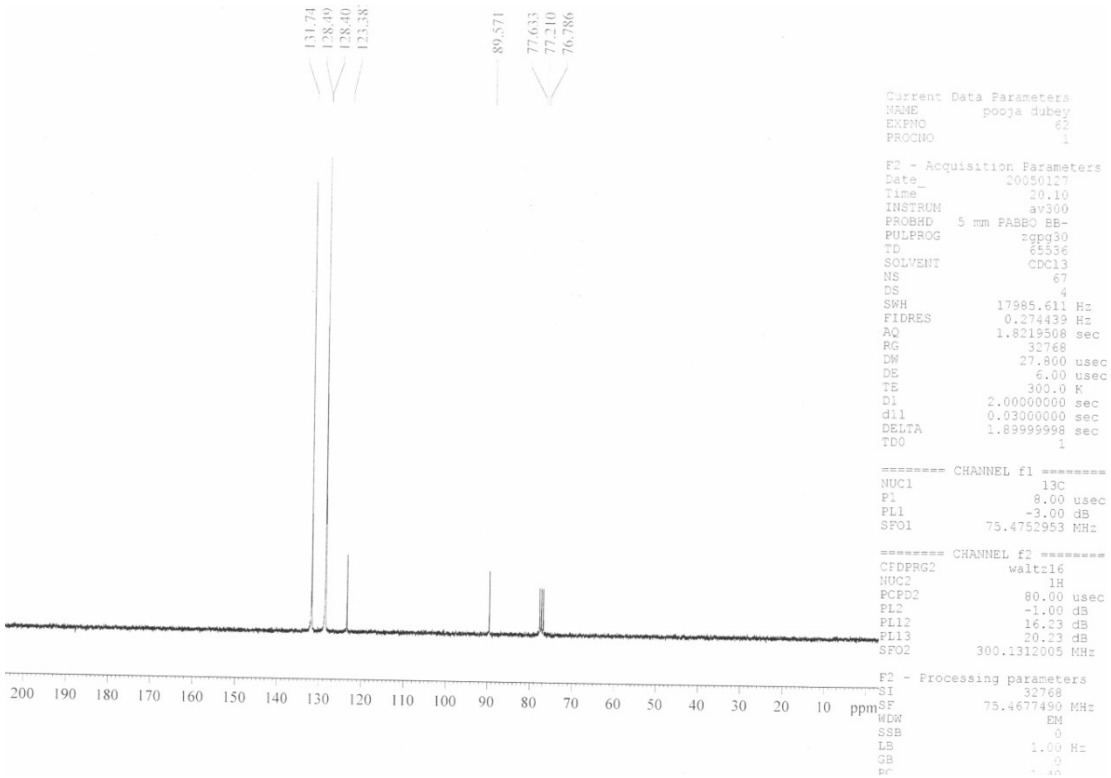


Figure S68. ^{13}C NMR of 9g

HR-MS Spectra of L1-L2 and Complexes 1-2

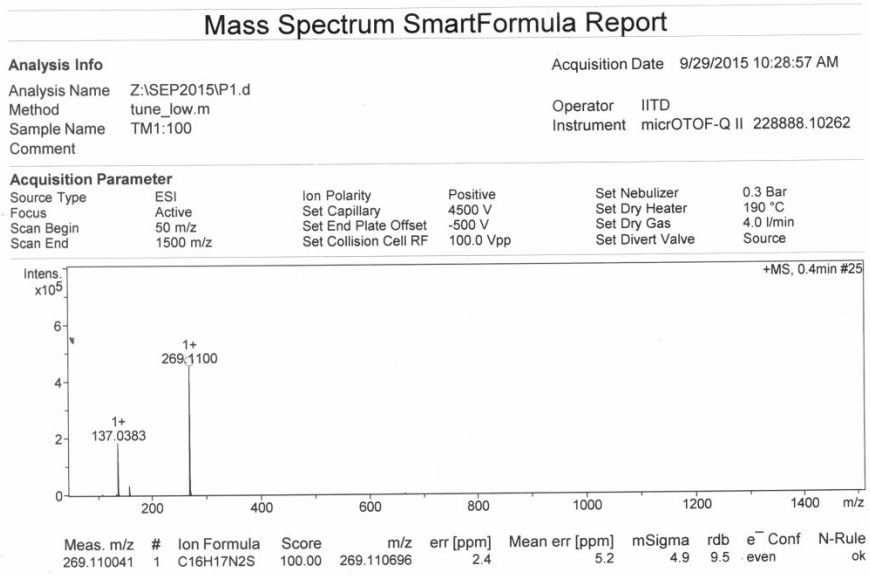


Figure S69. Mass Spectra of L1

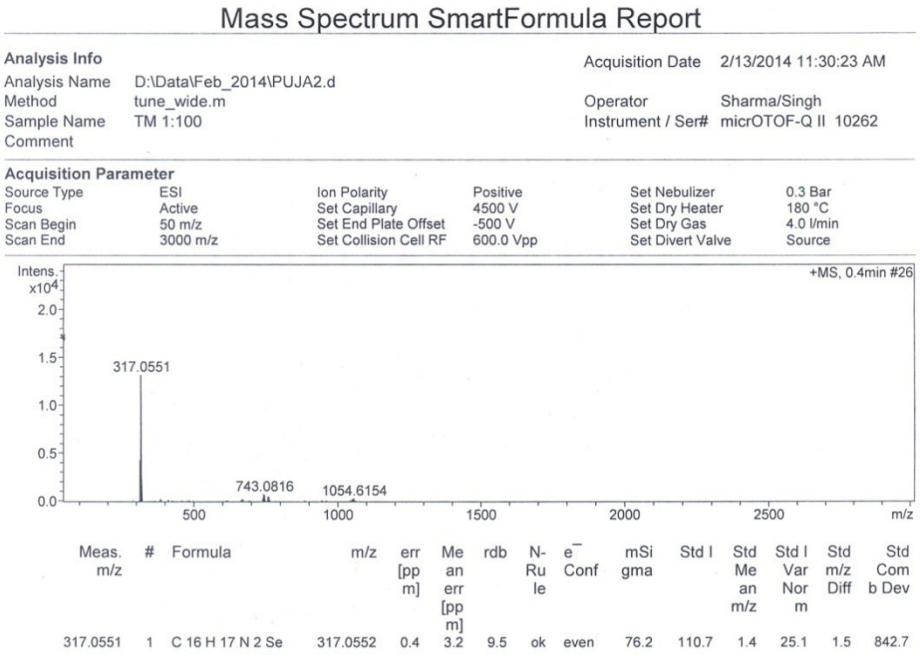
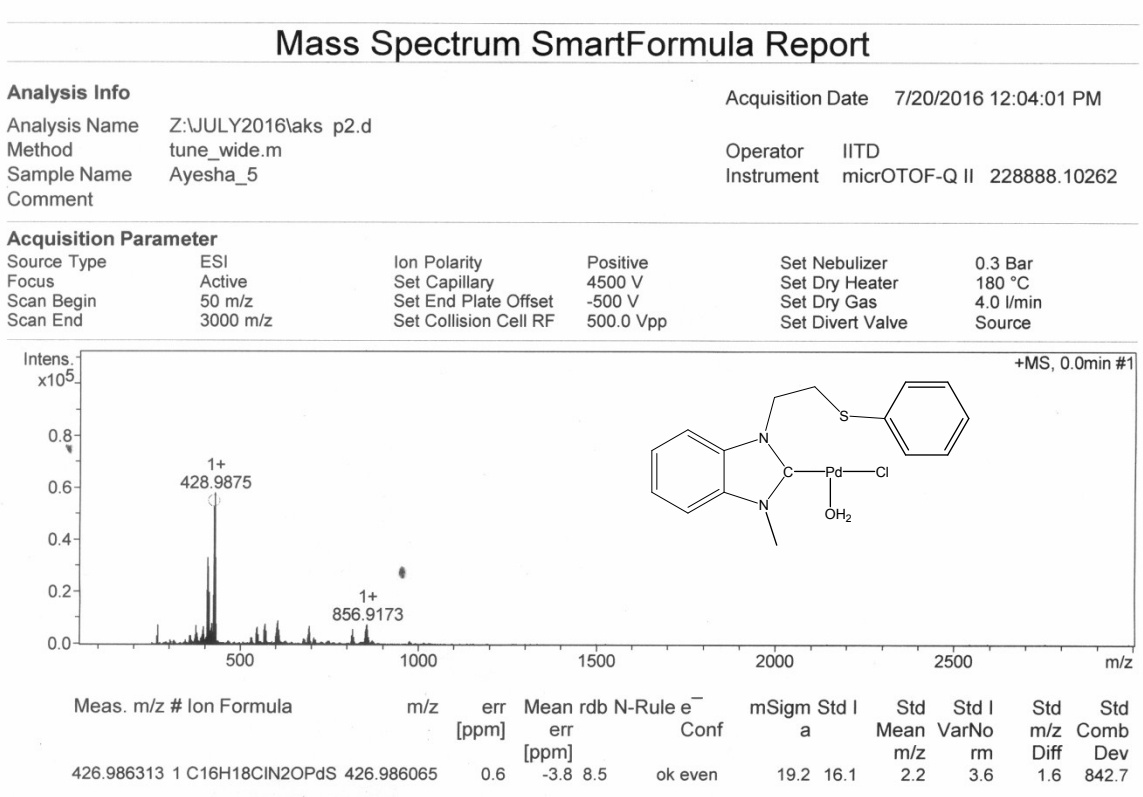


Figure S70. Mass Spectra of L2



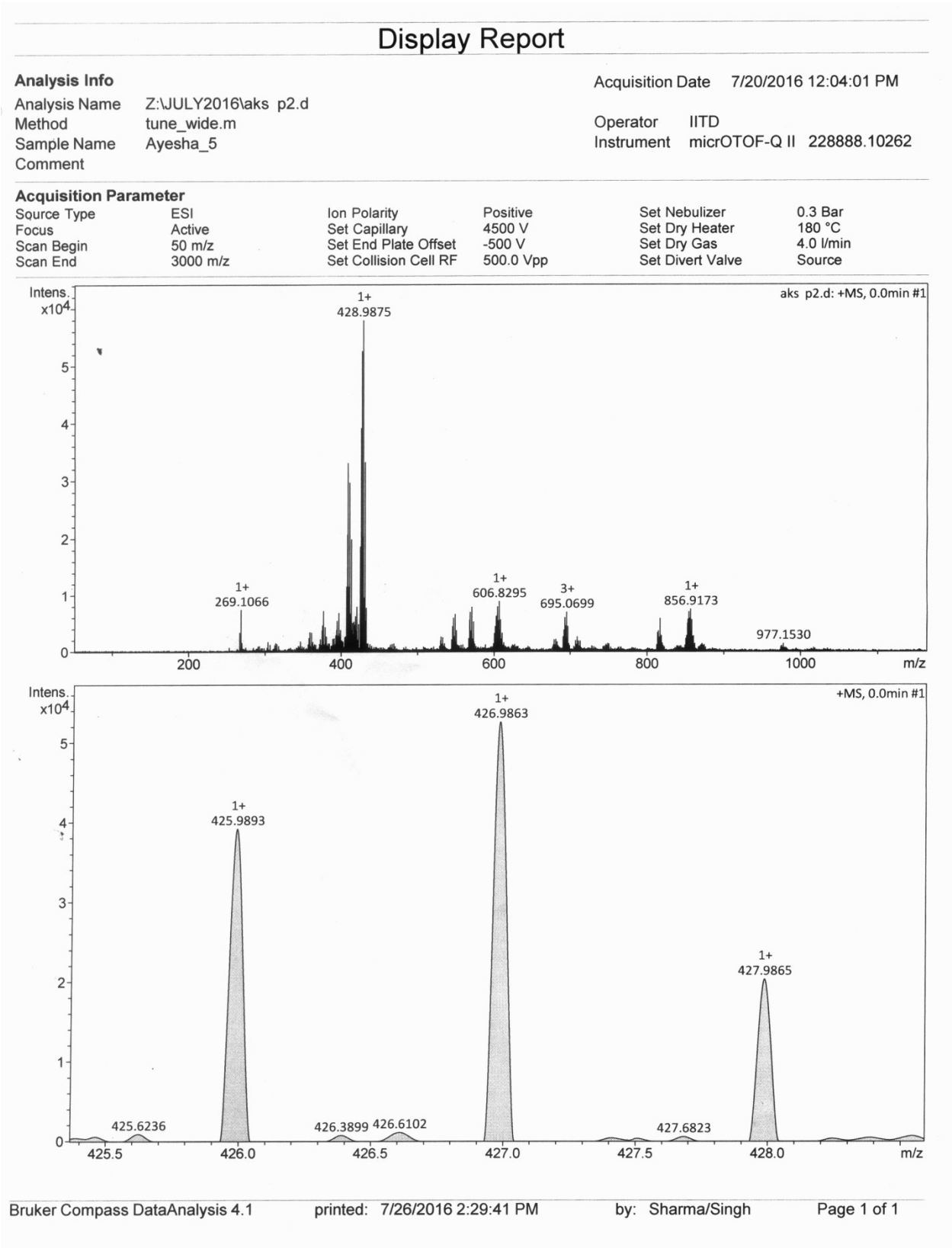


Figure S71. Mass Spectra of complex 1

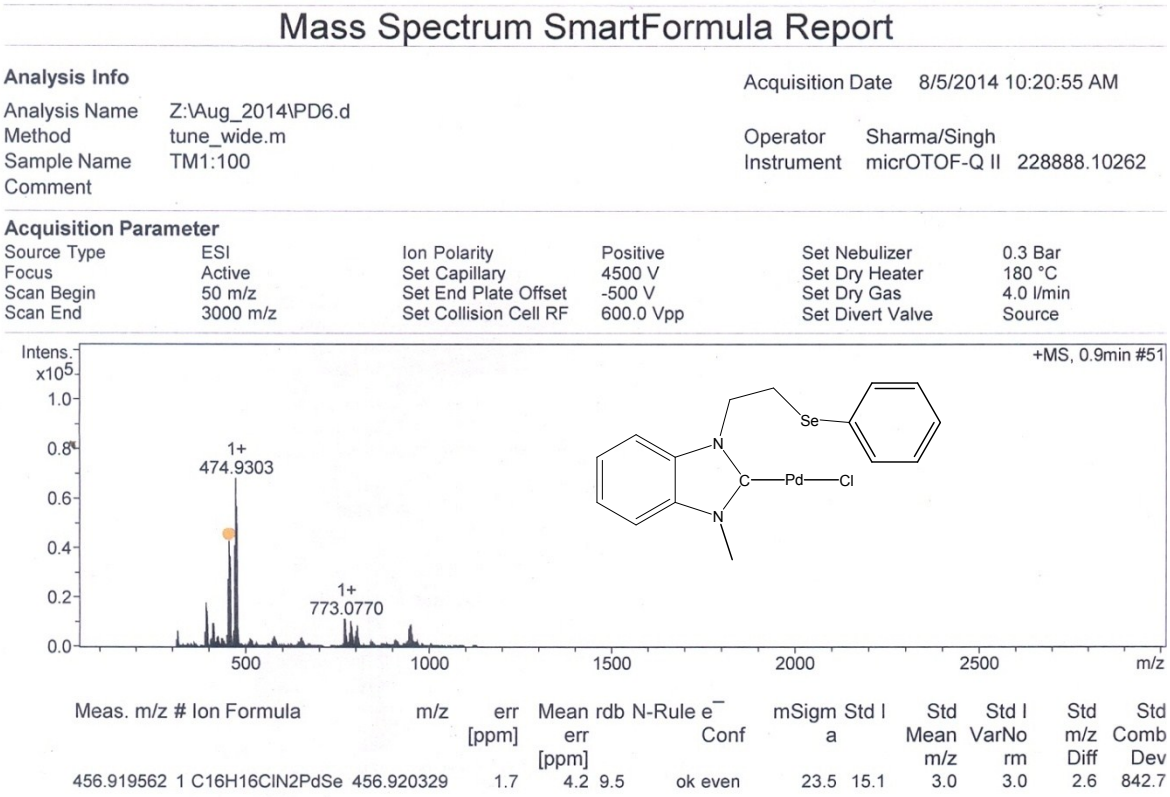


Figure S72. Mass Spectra of complex 2

The NMR spectral data of compounds found as reported in literature.[1-8]

Benzamide :[1,7] White solid. (Table 3, entry 4a), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.80-7.82 (d, *J* = 6 Hz, 2H), 7.55-7.44 (m, 3H), 6.23 (bs, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 169.6, 133.4, 131.9, 128.6, 127.3.

4-Methylbenzamide:[1,7] White solid. (Table 3, entry 4b), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.72-7.70 (d, *J* = 6 Hz, 2H), 7.26-7.23 (d, *J* = 9 Hz, 2H), 6.03 (bs, 2H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 169.4, 142.5, 130.5, 129.2, 127.3, 21.4.

4-Methoxybenzamide:[1] White solid. (Table 3, entry 4c), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.81-7.79 (d, *J* = 6 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.96 (bs, 2H), 3.88 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 168.9, 162.6, 129.2, 125.5, 113.8, 55.4.

4-Iodobenzamide.[10a] White solid. (Table 3, entry 4d), ^{1}H NMR (300 MHz, d6-DMSO): δ 8.01 (b, 1H), 7.84-7.82 (d, J = 6 Hz, 2H), 7.66-7.64 (d, J = 6 Hz, 2H), 7.42 (b, 1H). ^{13}C NMR (75 MHz, d6-DMSO): δ 167.7, 137.5, 134.1, 129.9, 99.3.

4-Bromobenzamide:[1] White solid. (Table 3, entry 4e), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.70-7.63 (d, *J* = 12 Hz, 2H), 7.60-7.54 (d, J = 9, 2H), 5.91 (bs, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 168.5, 131.8, 131.8, 128.9, 128.7.

4-Chlorobenzamide:[1] White solid. (Table 3, entry 4f), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.82-7.73 (d, *J* = 3 Hz, 2H), 7.47-7.40 (d, J = 3, 2H), 5.93 (bs, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 168.2, 138.3, 131.7, 128.9, 128.7.

4-Fluorobenzamide:[1] White solid. (Table 3, entry 4g), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.86-7.81 (m, 2H), 7.15-7.10 (t, *J* = 8.4, 2H), 5.93 (bs, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 168.3, 166.7, 129.8, 129.6, 115.8.

2-Phenylacetamide:[7] White powder. (Table 3, entry 4h), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.38 – 7.28 (m, 5H), 5.79-5.41 (m, 2H), 3.58 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 173.9, 134.8, 129.3, 129.0, 43.0

2-Bromobenzamide:[1,4] White solid. . (Table 3, entry 4i), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.49 (s, 1H), 7.75-7.62 (m, 2H), 7.42-7.29 (m, 2H), 6.27-6.18 (bs, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 169.5, 137.1, 133.5, 131.6, 129.8, 127.5, 119.1.

4-Pyridine carboxamide:[10b] White solid; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): 8.37-8.20 (2H, d, J 12), 8.05 (1H, s) δ 7.74 (2H, d J 6).

Pentanamide:[1] White solid. (Table 3, entry 6k), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 0.97-0.92 (t, *J* = 7.2, 3H), 1.25-1.40 (m, 2H), 1.56-1.64 (t, *J* = 7.5 2H), 2.20-2.24 (m, 2H), 5.99 (bs, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 176.5, 35.6, 27.5, 22.3, 13.7.

Benzonitrile:[2,8] Colourless oil. (Table 4, entry 6a), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.58 (m, 3H), 7.43 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 132.8, 132.0, 129.1, 118.8, 112.9.

4-Methylbenzonitrile :[2,8] Colourless oil. (Table 4, entry 6b), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.47-7.50 (d, *J* = 9 Hz, 2H), 7.22-7,25 (d, *J* = 9 Hz, 2H), 2.38 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 143.4, 131.6, 129.5, 118.8, 108.9, 21.4.

4-Methoxybenzonitrile:[2,8] White solid. (Table 4, entry 6c), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.59-7.56 (d, *J* = 3 Hz, 2H), 6.96-6.93 (d, *J* = 3 Hz, 2H), 3.86 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 162.6, 133.2, 119.2, 114.7, 103.9, 55.5.

4-Iodobenzonitrile:[10c] White solid. (Table 4, entry 6d), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.86-7.83 (m, 2H), 7.38-7.26 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 138.4,133.0, 118.1, 111.6, 100.2.

4-Bromobenzonitrile:[2,8] White solid. (Table 4, entry 6e), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.65-7.62 (m, 2H), 7.54-7.51 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 133.3, 132.5, 127.9, 117.9, 111.1.

4-Chlorobenzonitrile:[3,8] White solid. (Table 4, entry 6f), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.62 (m, 2H), 7.49 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 139.5, 133.3, 129.7, 117.9, 110.7.

4-Fluorobenzonitrile:[4,8] White solid. (Table 4, entry 6g), ^{1}H NMR (300 MHz, DMSO-d_6 25 °C vs Me_4Si): δ 8.01-7.93 (m, 3H), 7.41 (s, 1H), 7.29-7.23 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6, 25 °C vs Me_4Si): δ 167.3, 166.0, 162.7, 131.2, 131.1, 130.6, 130.5, 115.6, 115.3.

2-Phenylacetonitrile:[8] Colourless oil. (Table 4, entry 6h), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.42 – 7.35 (m, 5H), 3.75 (s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 129.8, 129.0, 127.9, 127.8, 117.8, 23.4.

2-Bromobenzonitrile:[4,5] White solid. (Table 4, entry 6i), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 7.69 (s, 2H), 7.47 (s, 2H), 6.49 (s, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 134.0, 133.8, 133.0, 127.5, 125.1, 117.0, 115.6.

4-Cyanopyridine:[10d] White solid; (Table 4, entry 6j) ^{1}H NMR (300 MHz; DMSO-d_6) δ: 8.72-8.71 (m, 2H), 8.23 (s, 1H); 7.73-7.72 (m, 3H); ^{13}C-NMR (75 MHz, DMSO-d_6) δ: 166.7, 150.6, 141.7, 121.8.

Pentanenitrile:[6] Colourless oil. (Table 4, entry 6k), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 2.37-2.32 (t, *J* = 6, 2H), 1.69-1.62 (m, 2H), 1.59-1.42 (m, 2H), 0.93-0.98 (t, *J* =7.2, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C vs Me_4Si): δ 119.6, 27.1, 21.5, 16.5, 12.9.

Spectroscopic data of coupled products of Sonogashira cross coupling reactions[9]

4-(Phenylethynyl) benzaldehyde: Light yellow solid. . (Table 6, entry 9a), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.38 (m, 3H), 7.54-7.57 (m, 2H), 7.66-7.69 (d, 2H, *J* = 9 Hz), 7.85-7.88 (d, 2H, *J* = 9 Hz), 10.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 88.5, 93.4, 122.5, 128.4, 128.9, 129.5, 129.6, 131.7, 132.1, 135.4, 191.3.

4-(Phenylethynyl)benzonitrile: Yellow solid. (Table 2, entry 3), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.36−7.38 (m, 3H), 7.38−7.54 (m, 2H), 7.55−7.63 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 87.9, 93.8, 111.4, 118.5, 122.2, 128.5, 128.6, 129.1, 131.8, 132.0, 132.5.

1-Methoxy-4-(phenylethynyl)benzene: Light-yellow solid. (Table 6, entry 9c), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 3.87 (s, 3H), 6.96-6.92 (m, 3H), 7.43-7.35 (m, 2H), 7.60-7.53 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 55.3, 88.2, 89.5, 114.1, 115.4, 123.6, 128.0, 128.3, 133.1, 131.5, 159.6.

1-Methyl-4-(phenylethynyl)benzene: White solid. (Table 6, entry 9d), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 2.36 (s, 3H), 7.14-7.16 (d, J = 6 Hz, 2H), 7.32-7.34 (m, 3H), 7.41-7.44 (d, 2H, J = 9 Hz), 7.50-7.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 21.5, 88.7, 89.5, 120.2, 123.5, 128.0, 128.3, 129.1, 131.5, 131.5, 138.3.

1-Nitro-4-(phenylethynyl)benzene: Light-yellow solid. (Table 6, entry 9e) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 7.25-7.39 (m, 3H), 7.54-7.56 (m, 2H), 7.63-7.66 (d, J = 9, 2H), 8.18-8.21 (d, 2H, J = 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 87.5, 94.7, 121.1, 123.6, 128.5, 129.2, 130.2, 131.8, 132.2, 147.0.

4-acetyl-diphenylacetylene: White Solid. (Table 6, entry 9f), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 2.63 (s, 3H), δ = 7.38-7.40 (m, 3H), 7.56-7.59 (m, 2H), 7.62-7.64 (d, J = 6 Hz, 2H), 7.95-7.97 (d, J = 6 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3, 25 °C, TMS); *δ* (ppm): 26.6, 88.6, 92.7, 122.6, 127.2, 128.2, 128.4, 128.8, 131.7, 131.7, 136.1, 197.3.

1,2 Diphenylethyne: white solid. (Table 2, entry 7),[1]H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) : δ 7.28−7.30 (m, 6H), 7.52−7.53 (d, 4H). [13]C NMR (75 MHz, $CDCl_3$, 25 °C, TMS); *δ* (ppm): 89.5, 123.3, 128.4, 128.4, 131.7.

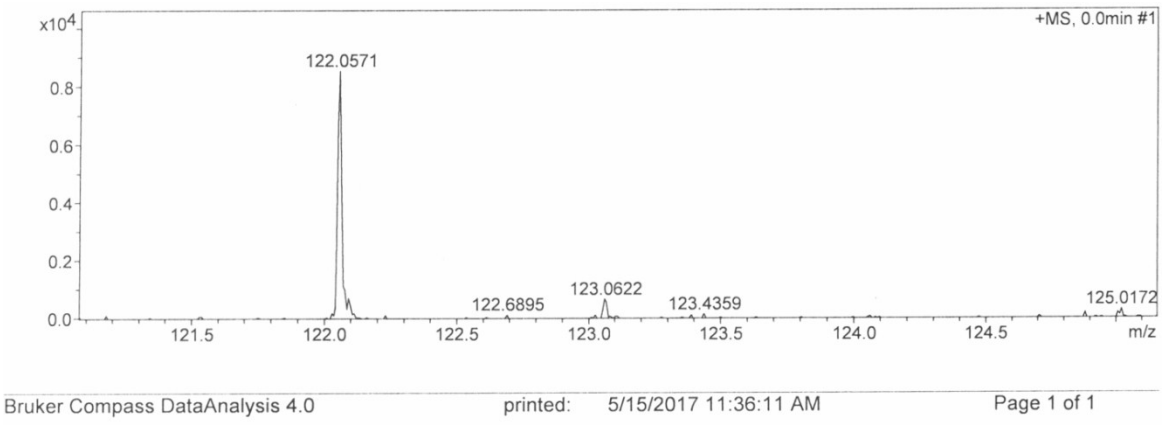


Figure S73. Mass spectra of reaction mixture

ESI-MS Data

Molecular formula	Exact mass	Mass found
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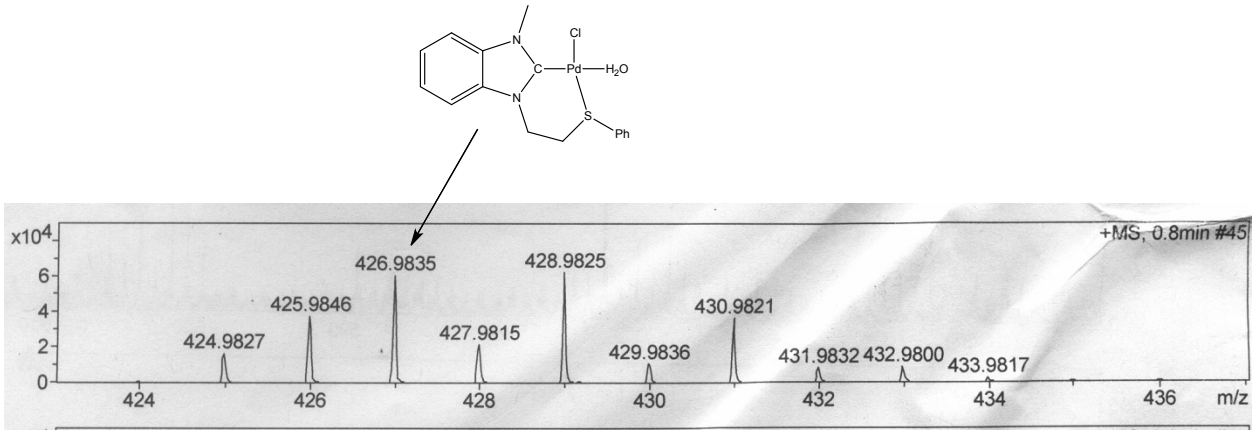

Figure S74. ESI-MS of $[Pd(II)(Cl)(L)(H_2O)]^+$

Molecular formula	Exact mass	Mass found
$C_{27}H_{30}N_5ONaPdS$	601.11	601.20

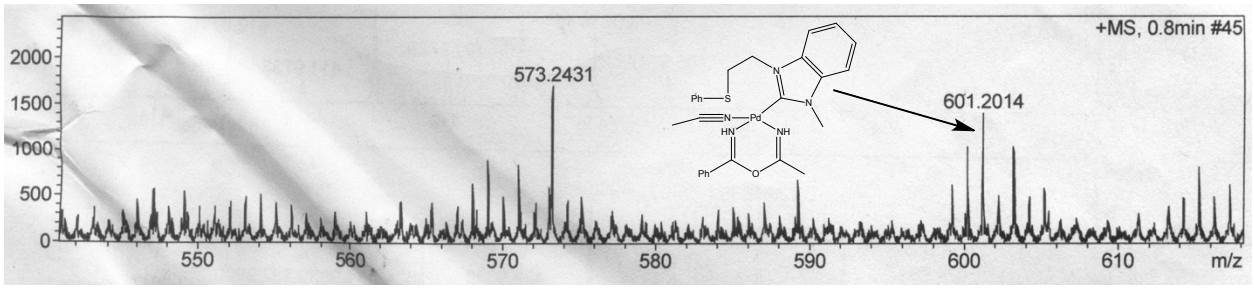

Figure S75. ESI-MS of [{Intermediate F}+Na+H]$^{2+}$

Molecular formula	Exact mass	Mass found
$C_{31}H_{27}N_2OPdS$	581.08	581.24

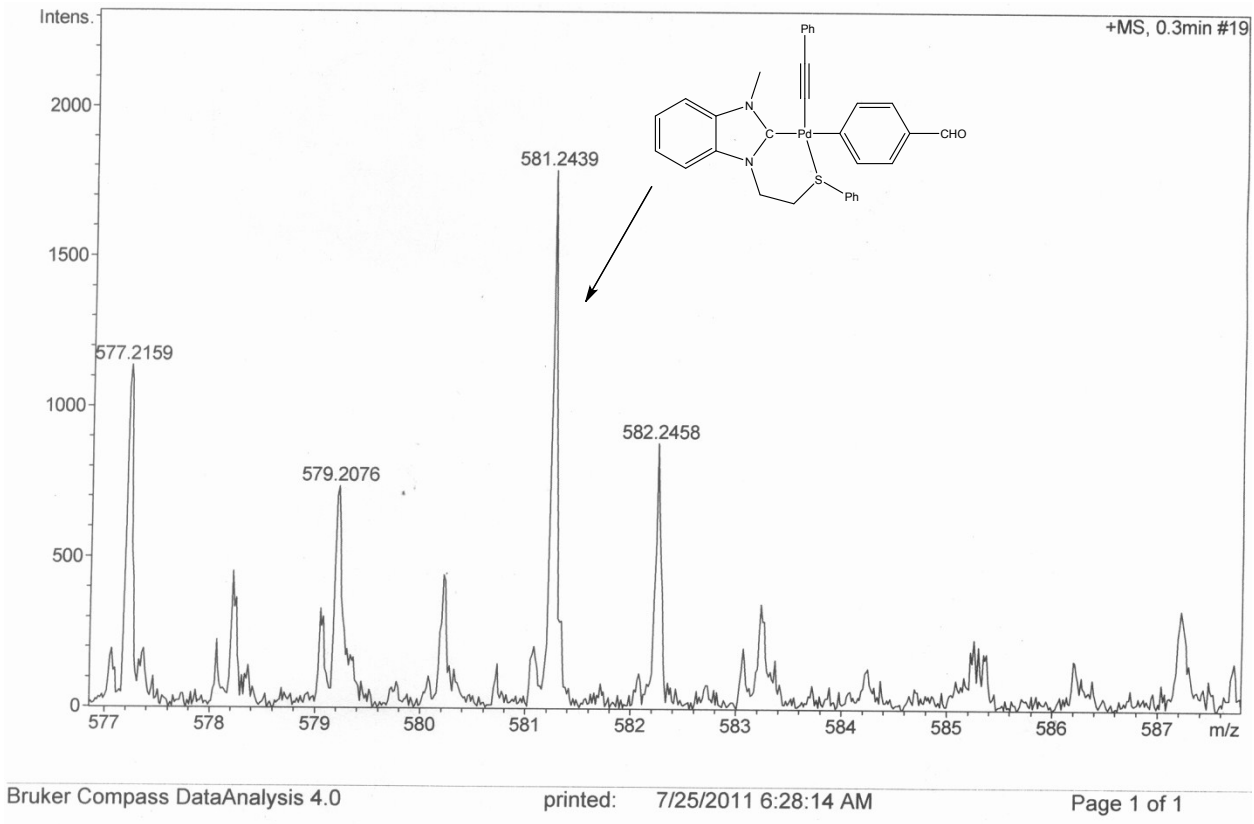

Figure S76. ESI-MS of Intermediate [{Intermediate H}+H]$^{+}$

Two-phase test

A mixture of 4-bromobenzoic acid-immobilized silica (0.20 g) (prepared by reported methods),[11] phenyl acetylene (0.224 g, 2.2 mmol), 4-bromobenzaldehyde (0.185 g, 1.0 mmol), and K_2CO_3 (0.441 g, 3.0 mmol) were heated in an inert atmosphere at 90 °C for 8 h in dry DMSO (1 mL) in the presence of 1 mol% of **1**. After completion of the reaction, the mixture was cooled and filtered through a G-4 crucible. The residue left in the crucible was washed with 20 mL of water followed by diethyl ether (2×20 mL). The filtrate and washings were collected together. The resulting mixture was extracted with 30 mL of diethyl ether. The solvent of the extract was evaporated and the residue was analyzed with ^{1}H-NMR. The yield of the cross-coupled product, 4-(phenylethynyl)benzaldehyde was ~92%. The residue in G-4 crucible was hydrolysed with KOH (1.68 g dissolved in 10 mL of EtOH + 5 mL of H_2O) at 90 °C for 3 days. The hydrolysed solution was neutralized with aqueous 20% (v/v) HCl and, extracted with dichloromethane (30 mL) followed by ethyl acetate (40 mL). The organic phases were combined together and its solvent was evaporated off. The hydrolyzed products were analyzed by ^{1}H NMR spectroscopy. Of the immobilized 4-bromobenzoic acid (as amide), nearly 77% (by ^{1}H NMR) was converted into the cross-coupled product, 4-(phenylethynyl)benzoic acid.

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