

New Journal of Chemistry

Supporting Information

The recyclable heterogeneous nanocatalyst of copper-grafted natural asphalt sulfonate (NAS@Cu): Characterization, synthesis and application in the Suzuki-Miyaura coupling reaction

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Supporting information includes Elemental mapping for NAS@Cu, SEM images of NA, Na-NAS, NAS@Cu and NAS@Cu after recovery, FT-IR spectra of natural asphalt and natural asphalt sulfonate, TEM image of NAS@Cu , selected original spectrums and Selected spectral data of the synthesized biphenyl derivatives.

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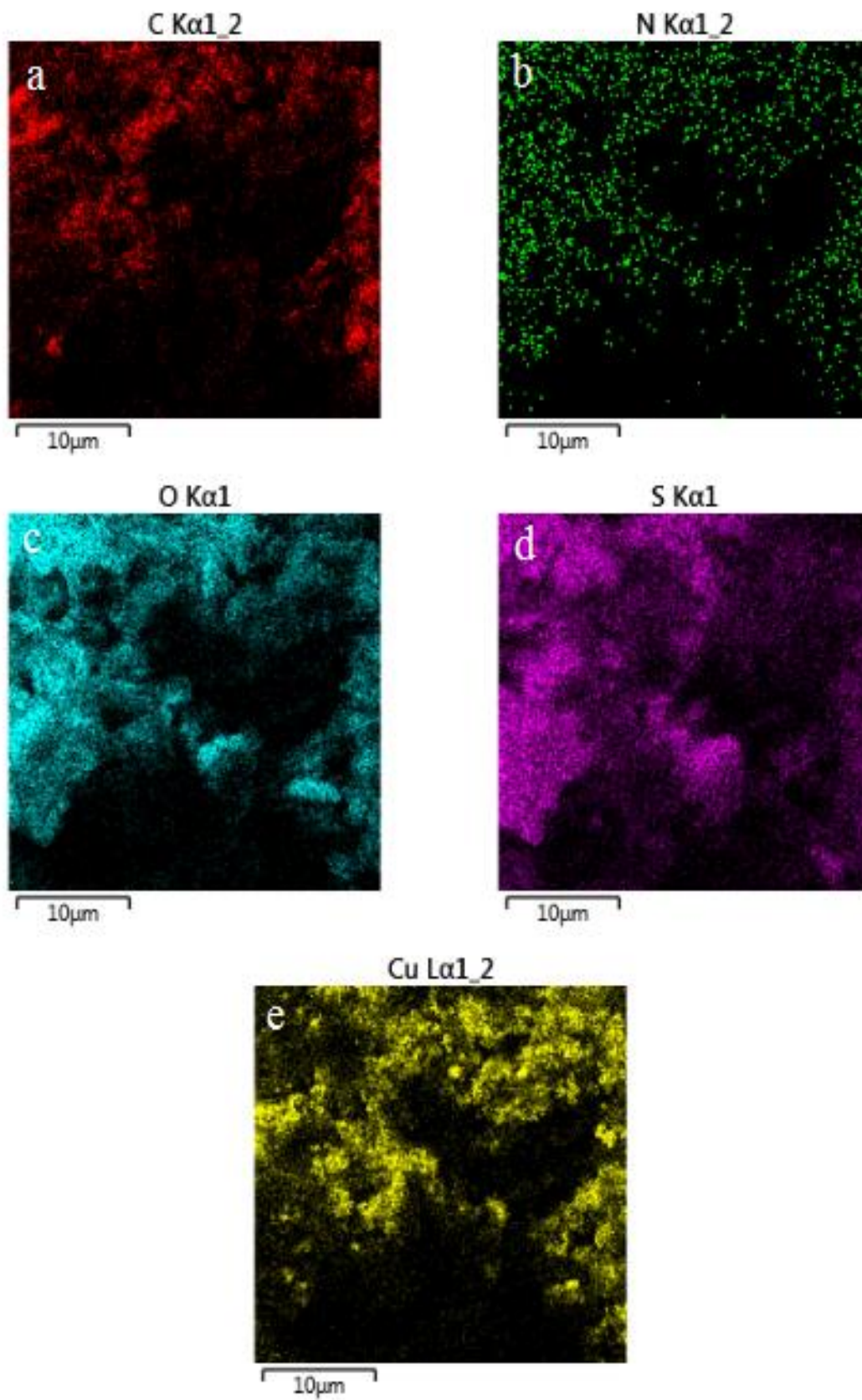


Figure S1. Elemental mapping of C (a), N (b), O (c), S (d) and Cu (e) for NAS@Cu

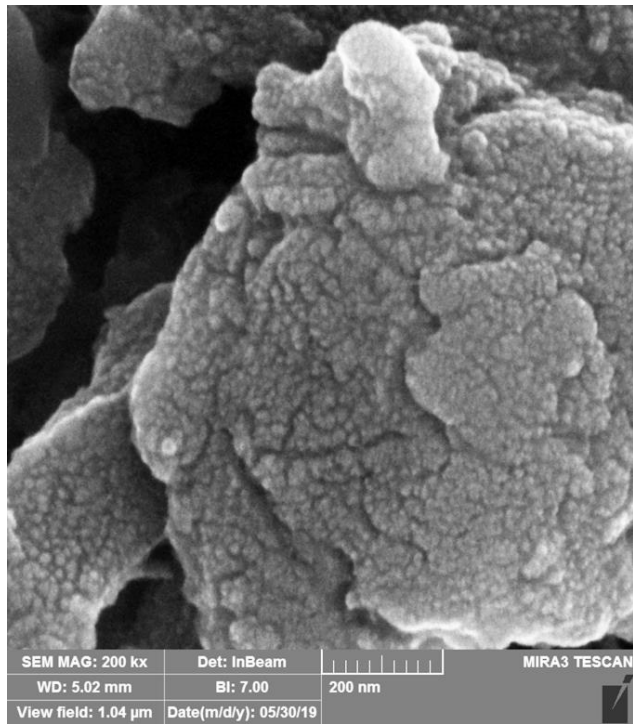
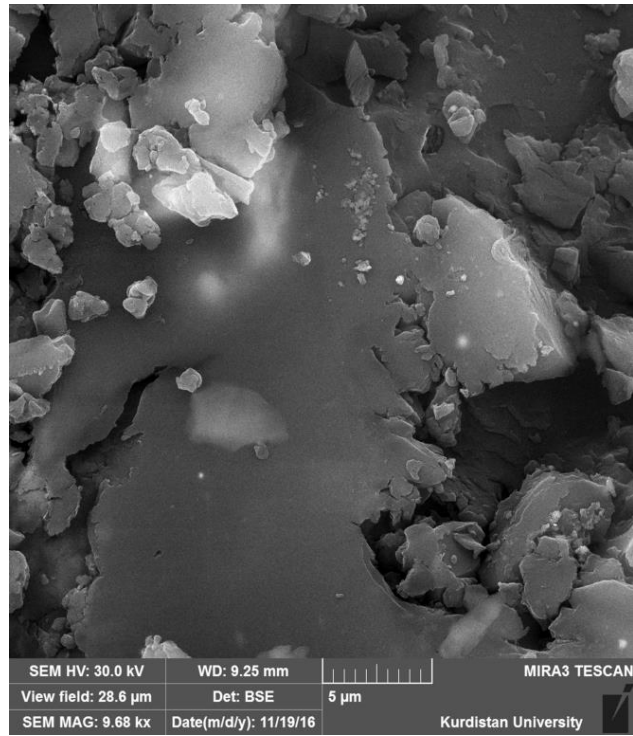


Figure S2: SEM images of NA and Na- NAS

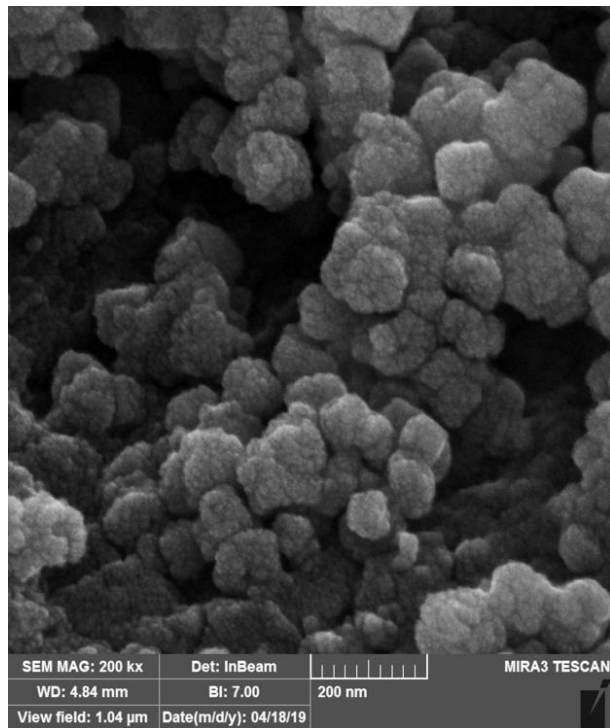
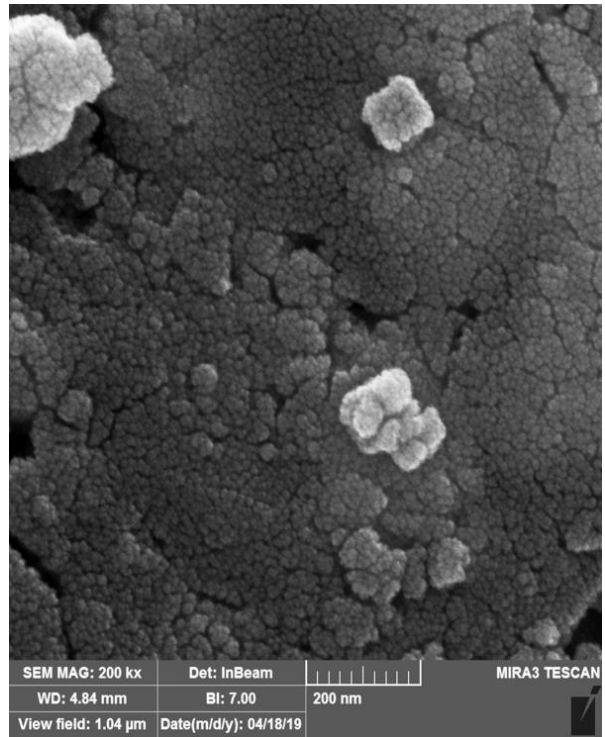


Figure S3. SEM images of NAS@Cu and NAS@Cu after the recovery

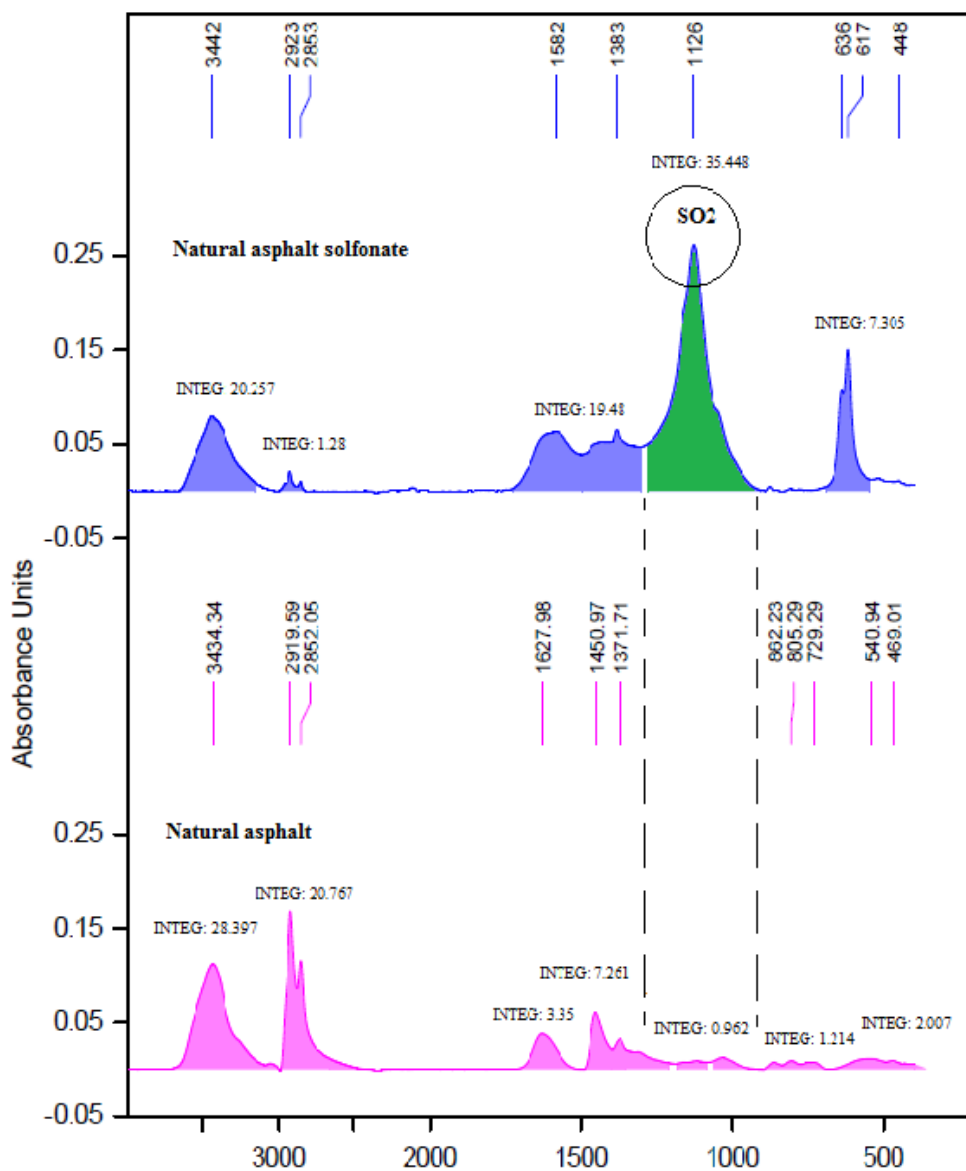


Figure S4. FT-IR spectra of natural asphalt and natural asphalt sulfonate

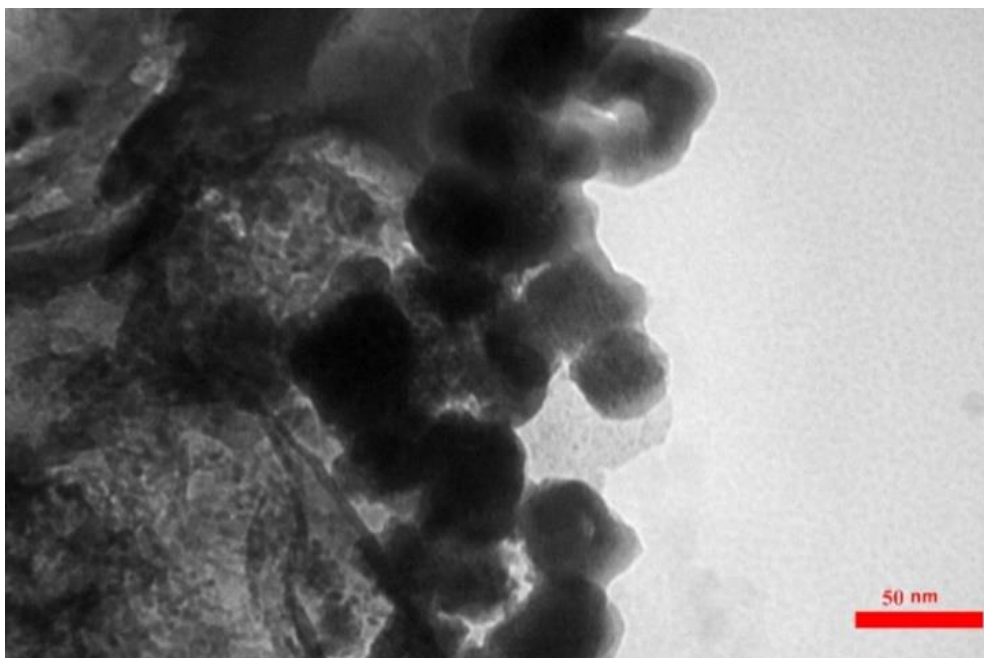


Figure S5.TEM image of NAS@Cu

¹H NMR (400 MHz, CDCl₃)

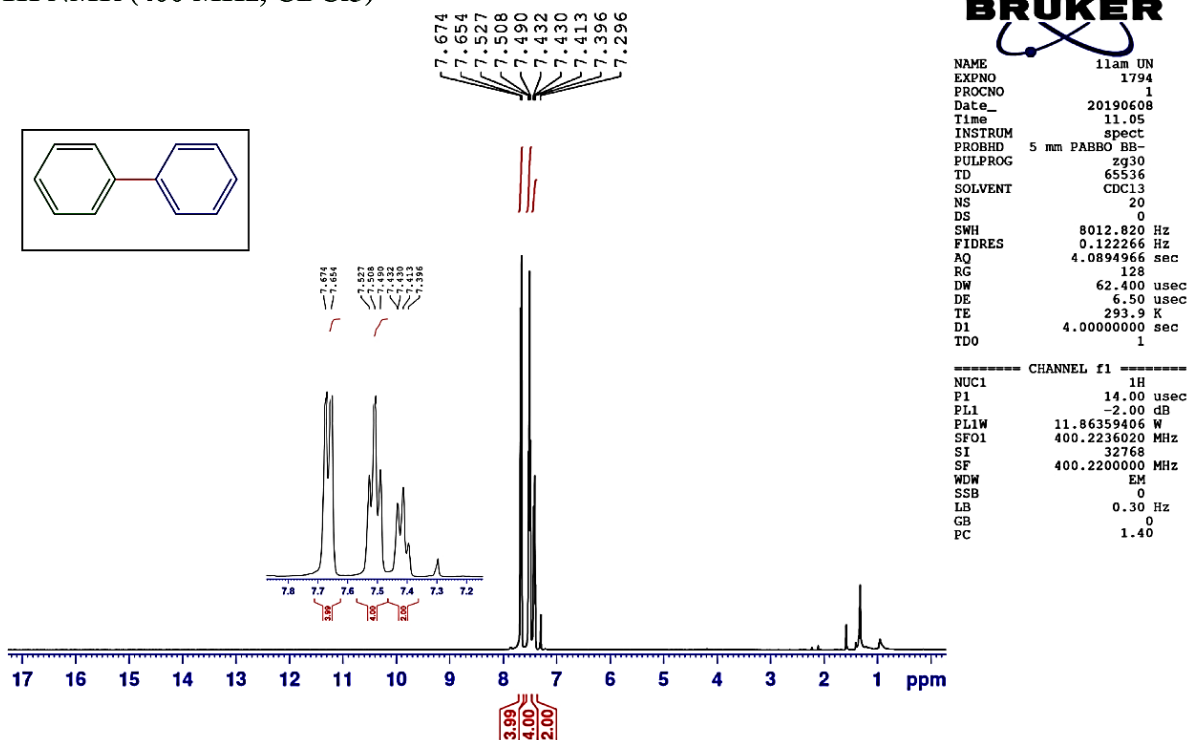
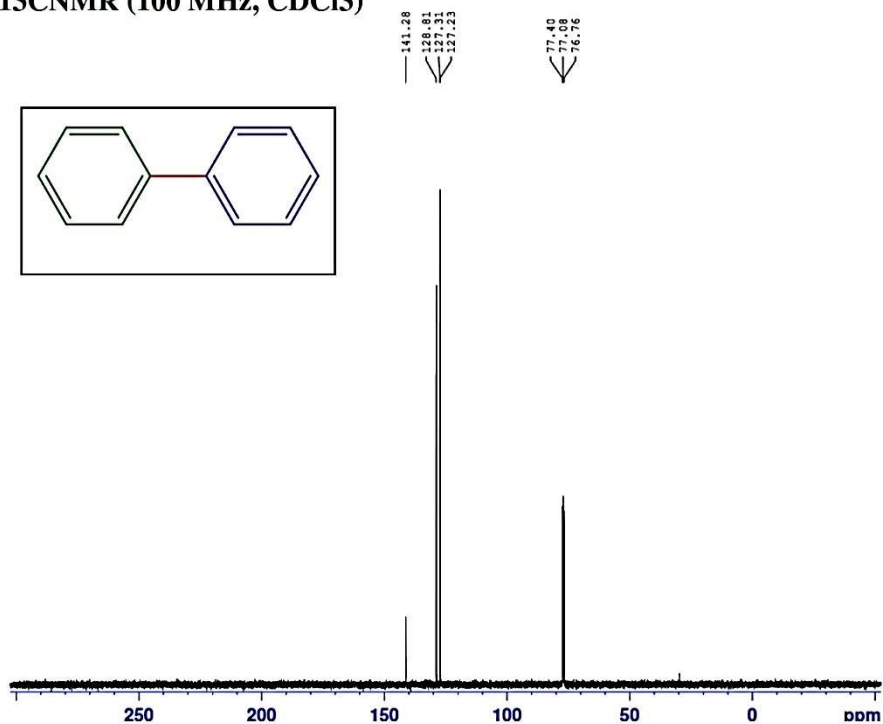
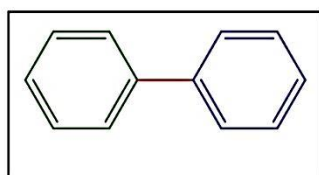


Fig S6. ¹H NMR spectrum of 1,1'-Biphenyl

¹³C NMR (100 MHz, CDCl₃)



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EXPNO 1795
PROCNO 1
Date_ 20190608
Time 11.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 124
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 2050
DW 14.000 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 -0.90 dB
PL1W 42.02801895 W
SFO1 100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 14.48 dB
PL13 17.90 dB
PL2W 11.86359406 W
PL12W 0.26681873 W
PL13W 0.12139934 W
SFO2 400.2216009 MHz
SI 32768
SF 100.6353990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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Fig S7. ¹³C NMR spectrum of 1,1'-Biphenyl

¹H NMR (400 MHz, CDCl₃)

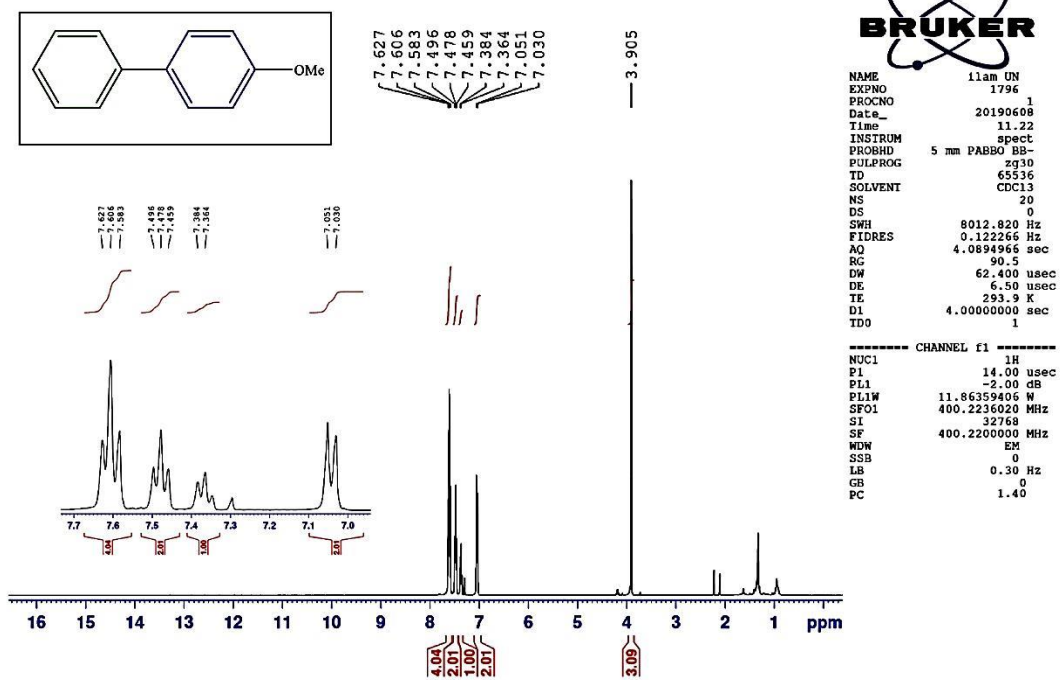
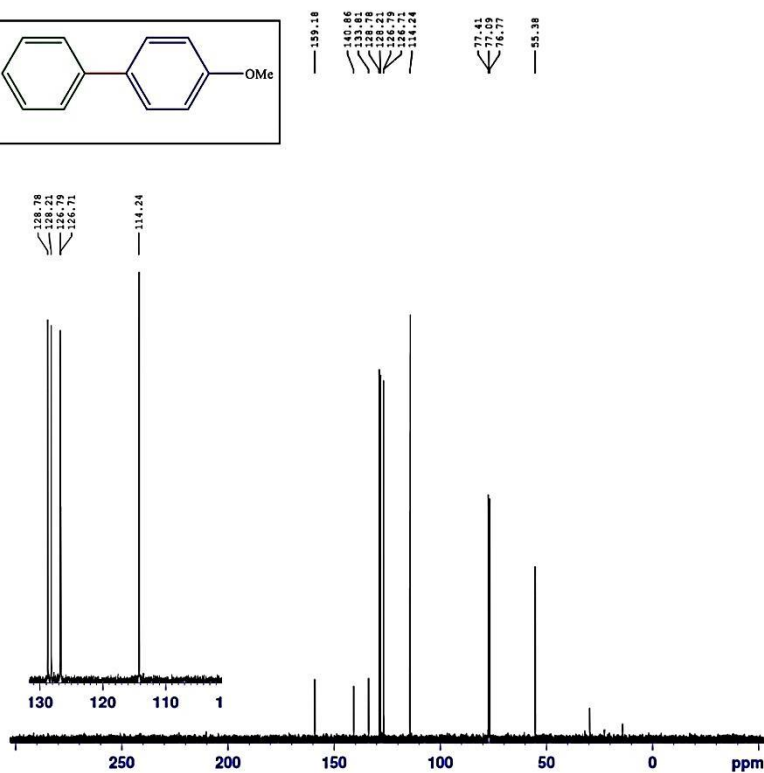
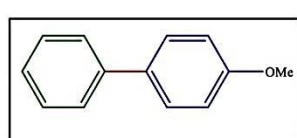


Fig S8. ¹H NMR spectrum 4-Methoxy-1,1'-biphenyl

¹³CNMR (100 MHz, CDCl₃)



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PROCNO    1
Date_     20190608
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PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         150
DS         0
SWH        35714.285 Hz
FIDRES     0.544957 Hz
AQ         0.9175540 sec
RG         2050
DW         14.000 usec
DE         6.50 usec
TE         294.3 K
D1         1.00000000 sec
D11        0.03000000 sec
TDO        1
    
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----- CHANNEL f1 -----
NUC1      13C
P1         9.00 usec
PL1        -0.90 dB
PL1W       42.02801895 W
SFO1      100.6479784 MHz
    
```

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----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -2.00 dB
PL12       14.48 dB
PL13       17.90 dB
PLW        11.86359406 W
PL12W      0.26681873 W
PL13W      0.12139934 W
SFO2      400.2215009 MHz
SI         32768
SF         100.6353990 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

Fig S9. ¹³C NMR spectrum of 4-Methoxy-1,1'-biphenyl

¹H NMR (400 MHz, CDCl₃)

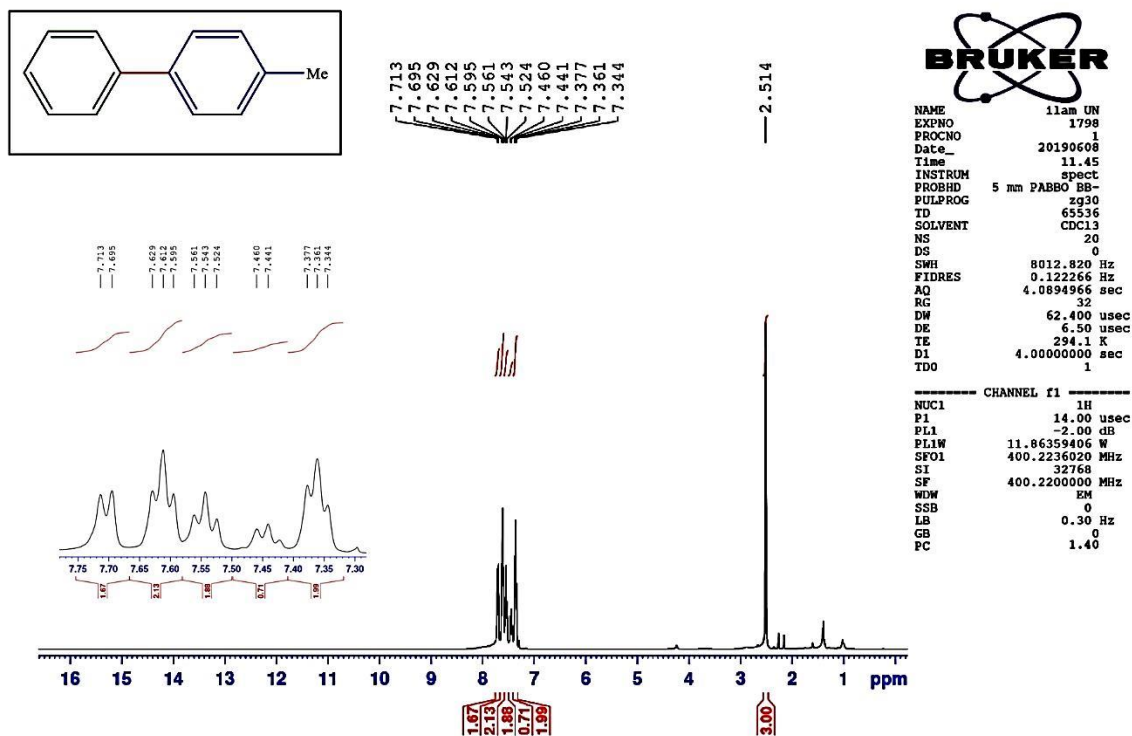


Fig S10. ¹H NMR spectrum of 4-Methyl-1,1'-biphenyl

¹³CNMR (100 MHz, CDCl₃)

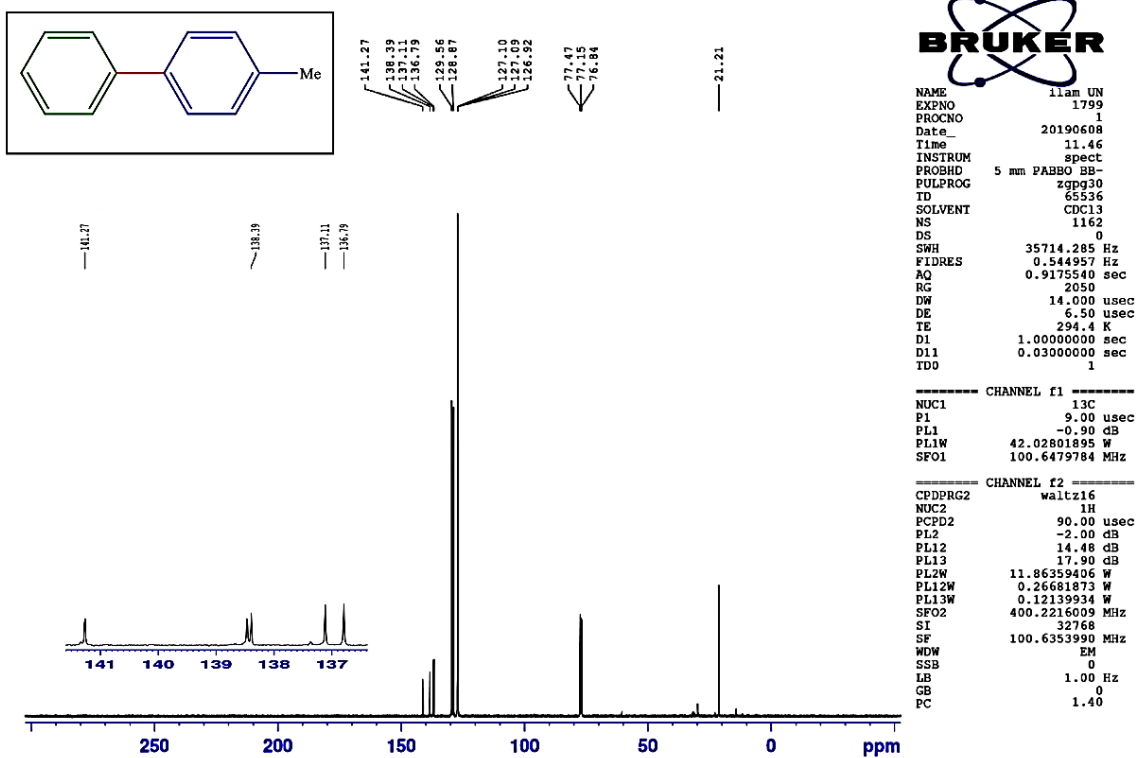


Fig S11. ¹³C NMR spectrum of 4-Methyl-1,1'-biphenyl

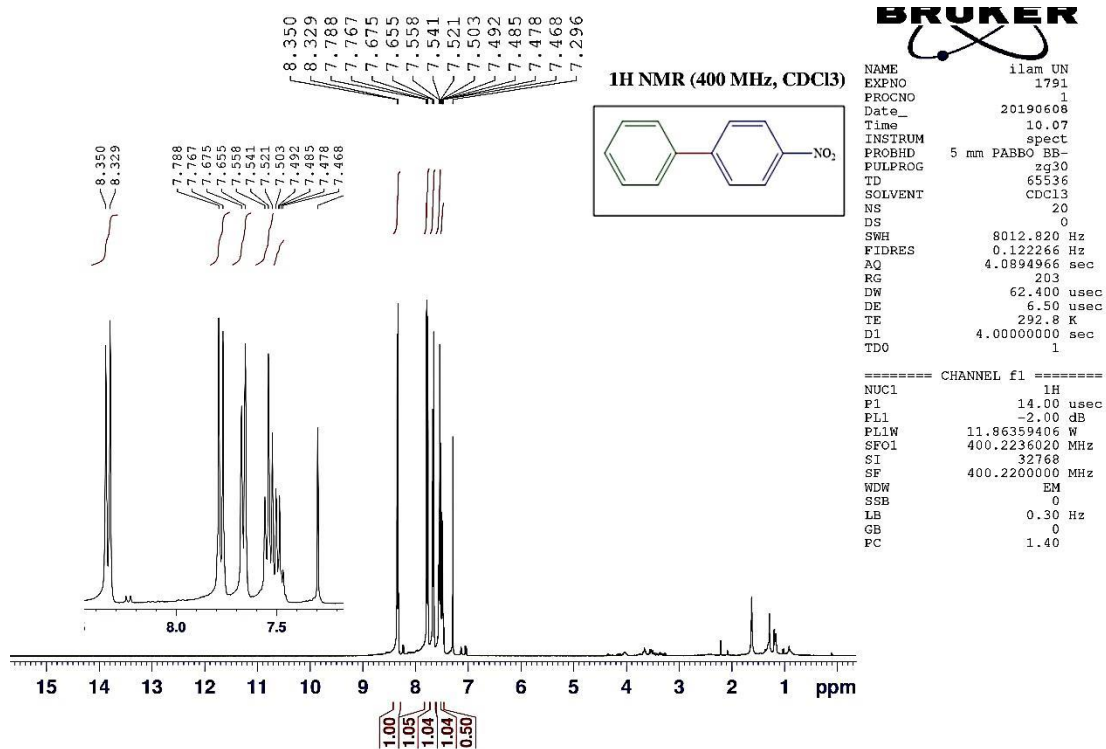


Fig S12. ¹H NMR spectrum of 4-Nitro-1,1'-biphenyl

¹³CNMR (100 MHz, CDCl₃)

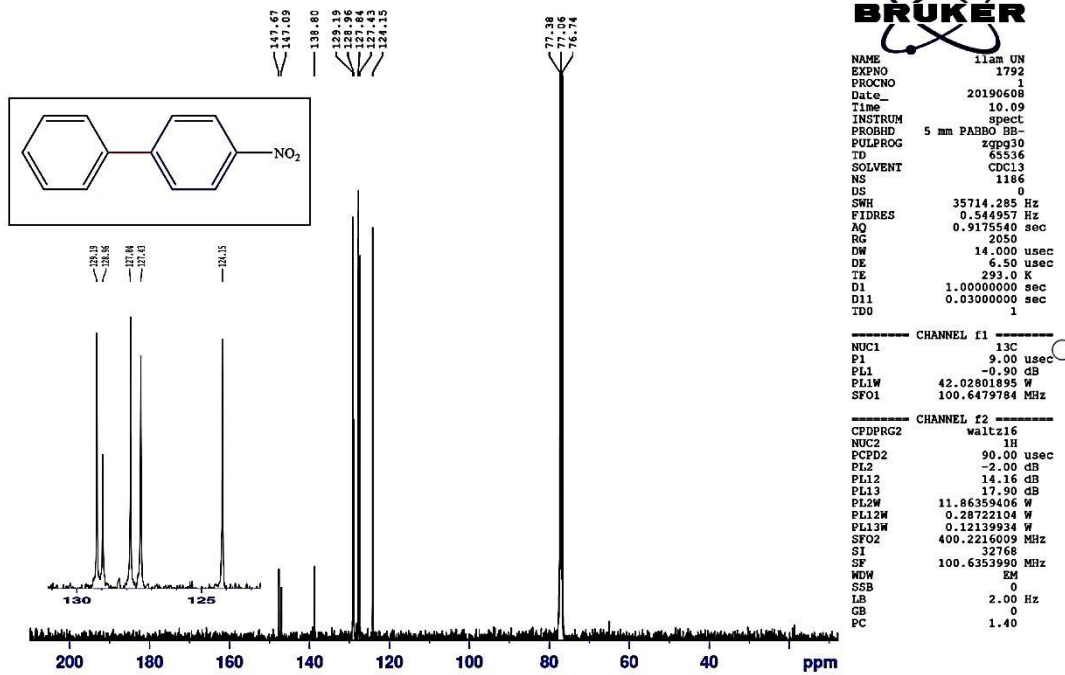
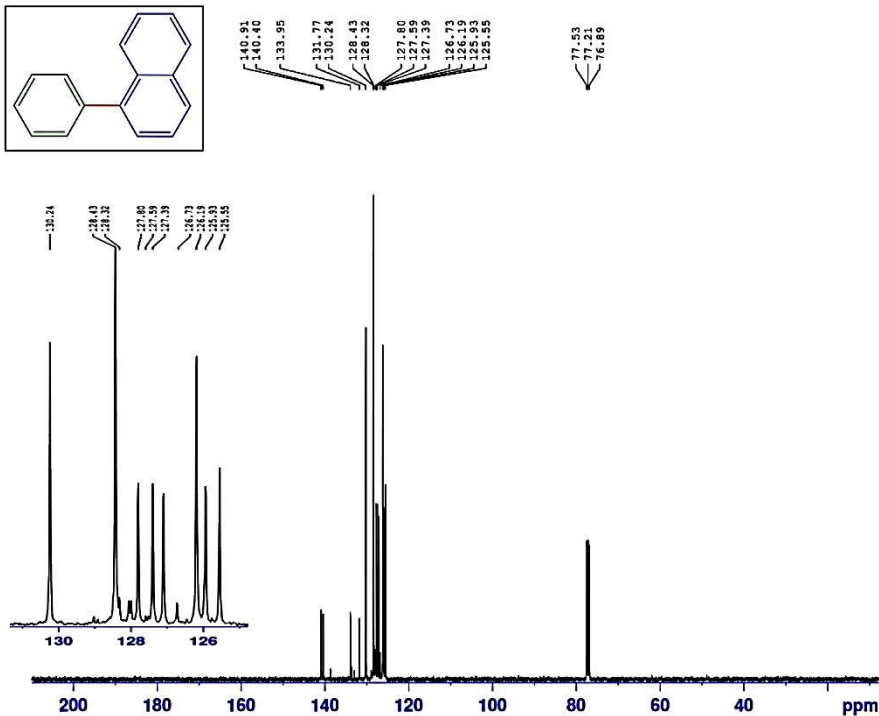
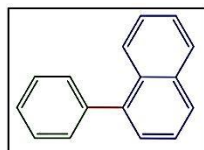


Fig S13. ¹³C NMR spectrum of 4-Nitro-1,1'-biphenyl

¹³CNMR (100 MHz, CDCl₃)



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NAME      11am UN
EXPNO     1788
PROCNO    1
Date_     20190608
Time      9.05
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         147
DS         0
SWH        35714.285 Hz
AQ         0.544957 Hz
RG         0.9175540 sec
DE         2050
DW         14.000 usec
TE         293.0 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        1

----- CHANNEL f1 -----
NUC1       13C
P1         9.00 usec
PL1        -0.90 dB
PL1W       42.02801895 W
SF01       100.6479784 MHz

----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -2.00 dB
PL12       14.16 dB
PL13       17.90 dB
PL2W       11.86359406 W
PL12W     0.28722104 W
PL13W     0.12139934 W
SF02       400.2216009 MHz
SI         32768
SF         100.6353990 MHz
WDW        EM
SSB        0
LB         2.00 Hz
GB         0
PC         1.40
    
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Fig S15. ¹³C NMR spectrum of 2-Phenylnaphthalene

1H NMR (400 MHz, CDCl3)

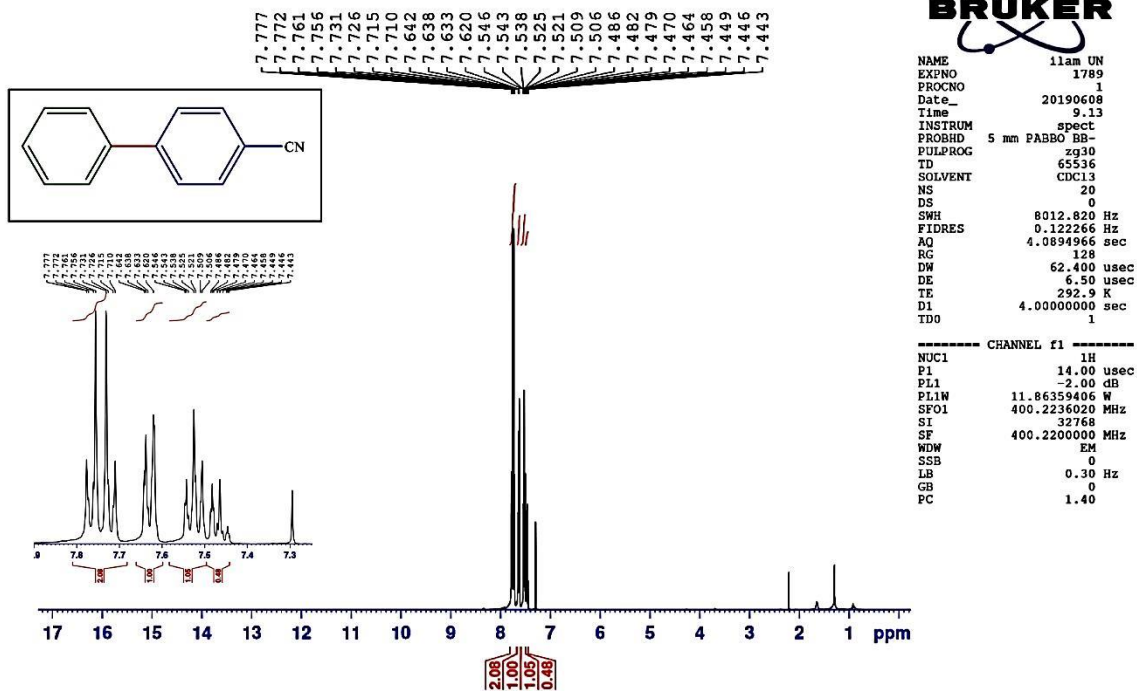
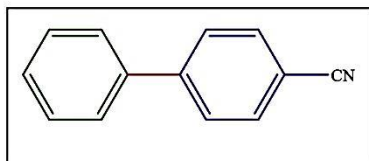
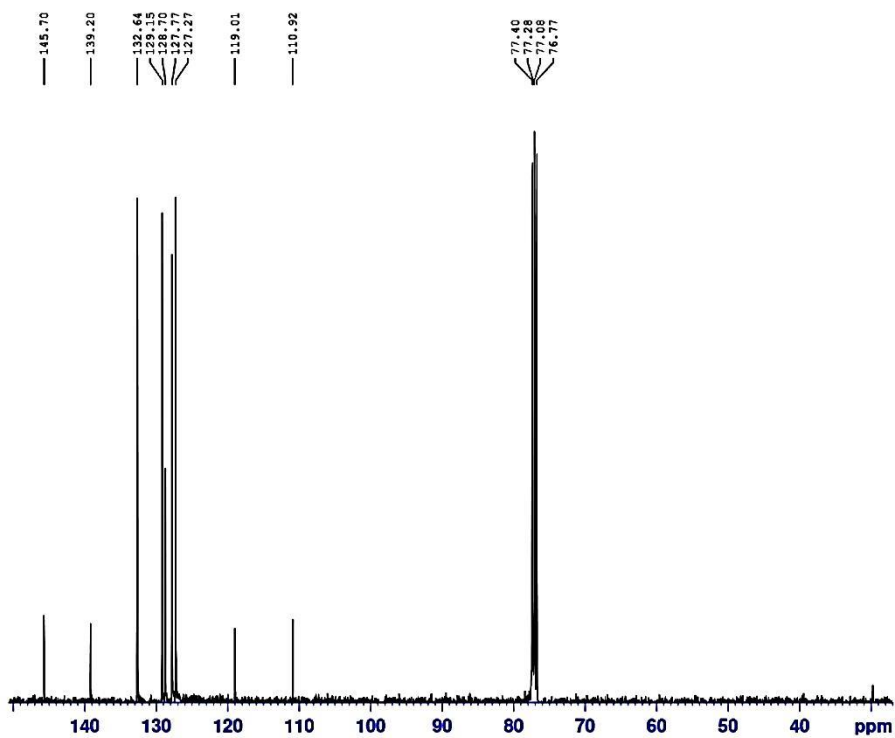


Fig S16. ¹H NMR spectrum of [1,1'-Biphenyl]-4-carbonitrile



¹³C NMR (100 MHz, CDCl₃)



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PROCNO    1
Date_     20190608
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TD        65536
SOLVENT   CDCl3
NS        549
DS        0
SWH       35714.285 Hz
FIDRES    0.544957 Hz
AQ        0.9175540 sec
RG        2050
DW        14.000 usec
DE        6.50 usec
TE        292.8 K
D1        1.00000000 sec
D11       0.03000000 sec
TD0       1
  
```

```

----- CHANNEL f1 -----
NUC1      13C
P1        9.00 usec
PL1       -0.90 dB
PL1W      42.02801895 W
SFO1      100.6479784 MHz
  
```

```

----- CHANNEL f2 -----
CFDPRG2   waltz16
NUC2      1H
PCPD2     90.00 usec
PL2       -2.00 dB
PL12      14.16 dB
PL13      17.90 dB
PL2W      11.86359406 W
PL12W     0.28722104 W
PL13W     0.12139934 W
SFO2      400.2216009 MHz
SI        32768
SF        100.6353990 MHz
WDW       EM
SSB       0
LB        2.00 Hz
GB        0
PC        1.40
  
```

Fig S17. ¹³C NMR spectrum of [1,1'-Biphenyl]-4-carbonitrile

Selected spectral data

1,1'-Biphenyl: White solid, Mp (°C): 63-65, ¹H NMR (400 MHz, CDCl₃): δH= 7.41 (t, J= 8Hz, 2H), ¹³CNMR (100 MHz, CDCl₃): δ = 127.2, 127.3, 129.8, 141.3.

4-Methoxy-1,1'-biphenyl: White solid, Mp (°C):83-85, ² ¹H NMR (400 MHz, CDCl₃): δH= 3.91(s, 3H), 7.03-7.05 (d, J= 8Hz, 2H), 7.47 (t, J= 8Hz, 2H), 7.60 (t, J= 8Hz, 2H) ppm. ¹³CNMR (100 MHz, CDCl₃): δ = 55.4, 114.2, 126.7, 126.8, 128.2, 128.8, 133.8, 140.9, 159.1.

4-Nitro-1,1'-biphenyl: Pale yellow solid, Mp (°C): 110-114, ¹H NMR (400 MHz, CDCl₃): δH= 7.29-7.78 (m, 5H), 7.76-7.78 (d, J= 8 Hz, 2H), 8.29-8.50 (d, J= 8Hz, 2H) ppm. ¹³CNMR (100 MHz, CDCl₃): δ = 124.15, 127.43, 127.84, 128.96, 129.19, 138.80, 147.09, 147.67.

2-Phenylnaphthalene: oil, ³ ¹H NMR (400 MHz, CDCl₃): δH= 7.54-7.58 (m,3H), 7.60-7.70 (m, 6H), 7.98-8.01 (m, 1H) ppm. ¹³CNMR (100 MHz, CDCl₃): δ = 125.55, 125.93, 126.19, 126.73, 127.39, 127.59, 127.80, 128.32, 128.43, 130.24, 131.77, 133.95, 140.40, 140.91.

[1,1'-Biphenyl]-4-carbonitrile: White solid, Mp (°C) 80-82, ¹H NMR (400 MHz, CDCl₃): δH= 7.46 (t, J= 8Hz, 1H), 7.52 (t, J= 8Hz, 2H), 7.62-7.64 (d, J= 8 Hz, 2H),7.71-7.77 (q, J= 8Hz, 4H) ppm. ¹³CNMR (100 MHz, CDCl₃): δ = 110.92, 119.01, 127.27, 127.77, 128.70, 129.15, 132.64, 139.20, 145.70.

4-Methyl-1,1'-biphenyl: White solid, Mp (°C): 44-46, ¹H NMR (400 MHz, CDCl₃): δH= 2.51(s, 3H), 7.36 (t, J= 8Hz, 2H), 7.54 (t, J= 8Hz, 2H), 7.61 (t, J= 8Hz, 2H), 7.69-7.71 (d, J= 8Hz, 2H) ppm. ¹³CNMR (100 MHz, CDCl₃): δ =21.1, 126.9, 127.1, 128.9, 129.5, 136.8, 137.1, 138.4, 141.2.

References

1. Q. Zhang, H. Su, J. Luo and Y. Wei, *Tetrahedron*. 14 (2013) 447-54.
2. J. F. Wei, J. Jiao, J. J, Feng, J. Lv, X. R. Zhang, X. Y. Shi and Z. G. Chen, *J. Org. Chem.* 74 (2009) 6283-6.
3. L. Bai and J.X. Wang, *Adv. Synth. Catal.* 25 (2008) 315-20.