**Supplementary Data**

Direct arylation of heteroarenes by PEPPSI-type palladium–NHC complexes and representative quantum chemical calculations for the compound which the structure was determined by X-ray crystallography

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**Figure S1**. 1H and 13C{1H} NMR spectrums of **2a**.



**Figure S2**. FT-IR spectrum of **2a**.







**Figure S3**. 1H and 13C{1H} NMR spectrums of **2b**.



**Figure S4**. FT-IR spectrum of **2b**.





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**Figure S5**. 1H and 13C{1H} NMR spectrums of **2c**.



**Figure S6**. FT-IR spectrum of **2c**.





**Figure S7**. 1H and 13C{1H} NMR spectrums of **2d**.



**Figure S8**. FT-IR spectrum of **2d**.





**Figure S9**. 1H and 13C{1H} NMR spectrums of **2e**.



**Figure S10**. FT-IR spectrum of **2e**.

**Table S1.** The Second Order Perturbation Theory Analysis Results of the Fock Matrix in NBO Basis for the stable conformers of **1c** and **2c** at B3LYP/6-31+G(d,p) level in chloroform phase.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Donor(i) | EDi/e | Acceptor (j) | EDj/e | E(2)/kcalmol-1 | E(j)-E(i)/a.u | F(i.j)/a.u |
| ***1c*** |  |  |  |  |  |  |
| πC1-C2 (2) | 1.61892 | π\* C3-C4π\* C5-C6π\* N26-C28 | 0.304660.305540.49584 | 17.3417.2013.36 | 0.300.300.22 | 0.0650.0650.049 |
| π C3-C4 (2) | 1.69902 | π\* C1-C2π\* C5-C6 | 0.466970.30554 | 20.7619.09 | 0.260.28 | 0.0690.066 |
| π C5-C6 (2) | 1.70149 | π\* C1-C2π\* C3-C4 | 0.466970.30554 | 20.8618.83 | 0.260.28 | 0.0690.065 |
| π C14-C16 (2) | 1.66677 | π\* C15-C17π\* C18-C20 | 0.331640.38869 | 23.0016.78 | 0.280.27 | 0.0710.061 |
| π C15-C17 (2) | 1.70550 | π\* C14-C16π\* C18-C20 | 0.362080.38869 | 16.7220.97 | 0.290.28 | 0.0630.070 |
| π C18-C20 (2) | 1.64148 | π\* C14-C16π\* C15-C17 | 0.362080.33164 | 23.2416.99 | 0.290.28 | 0.0730.062 |
| π N26-C28 (2) | 1.89930 | π\* C1-C2 | 0.46697 | 15.61 | 0.38 | 0.076 |
| LP (1) N27 | 1.53006 | π\* C1-C2π\* N26-C28 | 0.466970.49584 | 34.7882.33 | 0.290.22 | 0.0880.122 |
| LP (2) O30 | 1.84193 | π\* C18-C20 | 0.38869 | 30.27 | 0.34 | 0.096 |
|  |  |  |  |  |  |  |
| **2c** |  |  |  |  |  |
| πC1-C2 (2) | 1.61446 | π\* C3-C4π\* C5-C6π\* N26-C28 | 0.323220.325490.44807 | 18.1918.1911.58 | 0.290.290.23 | 0.0660.0660.047 |
| π C3-C4 (2) | 1.70231 | π\* C1-C2π\* C5-C6 | 0.465150.32549 | 20.2319.09 | 0.270.28 | 0.0690.066 |
| π C5-C6 (2) | 1.70526 | π\* C1-C2π\* C3-C4 | 0.465150.32322 | 20.2518.75 | 0.270.28 | 0.0690.065 |
| π C11-N27 (2) | 1.57205 | π\* C1-C2π\* N26-C28 | 0.465150.44807 | 32.4973.93 | 0.290.24 | 0.0870.120 |
| π C15-C17 (2) | 1.70317 | π\* C14-C16π\* C18-C20 | 0.359300.39215 | 17.1821.08 | 0.290.28 | 0.0640.070 |
| π C18-C20 (2) | 1.64766 | π\* C14-C16π\* C15-C17 | 0.359300.33112 | 22.4417.00 | 0.290.29 | 0.0720.063 |
| π N26-C28 (2) | 1.88618 | π\* C1-C2 | 0.46515 | 17.05 | 0.36 | 0.077 |
| σ Pd29-Br30 (2) | 1.89069 | σ\* Pd29-Br31 LP\*(1) Pd29 | 0.157850.15236 | 4.021.20 | 0.580.65 | 0.0440.025 |
| σ Pd29-Br31 (2) | 1.89275 | σ\* Pd29-Br30  | 0.15903 | 3.89 | 0.58 | 0.043 |
| LP (3) Br30 | 1.96010 | σ\* Pd29-Br31  | 0.15785 | 4.46 | 0.97 | 0.060 |
| LP (3) Br31 | 1.96026 | σ\* Pd29-Br30 | 0.15903 | 4.31 | 0.88 | 0.057 |
| LP (2) N42 | 1.27829 | π\* C32-C34 (2)π\* C33-C36 (2) | 0.279270.27855 | 49.4049.30 | 0.240.24 | 0.1100.110 |
| LP (2) O44 | 1.84400 | π\* C18-C20 (2) | 0.39215 | 30.03 | 0.34 | 0.096 |
|  |  |  |  |  |  |  |

*\** *E(2)* means the energy of hyper conjugative interaction (stabilization energy).

**Table S2.** The Second Order Perturbation Theory Analysis Results of the Fock Matrix in NBO Basis for the **1c** and **2c** molecules at B3LYP/6-311++G(d,p) level in chloroform phase.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Donor(i) | Hybridization | EDi/e | Acceptor (j) | Hybridization | EDj/e | E(2)/ kcalmol-1 | E(j)-E(i)/ a.u | F(i.j)/ a.u |
| ***1c*** |  |  |  |  |  |  |  |  |
| πC1-C2 (2) | 0.7060p(C1)+ 0.7082p(C2) | 1.61892 | π\* C3-C4π\* C5-C6π\* N26-C28 | p(C3)- p(C4)p(C5)- p(C6)p(N26)- p(C28) | 0.304660.305540.49584 |  17.3417.2013.36 | 0.300.300.22 | 0.0650.0650.049 |
| π C3-C4 (2) | 0.7104p(C3)+ 0.7038p(C4) | 1.69902 | π\* C1-C2π\* C5-C6 | p(C1)- p(C2)p(C5)- p(C6) | 0.466970.30554 | 20.7619.09  | 0.26 0.28  | 0.0690.066 |
| π C5-C6 (2) | 0.7022p(C5)+ 0.7120p(C6) | 1.70149 | π\* C1-C2π\* C3-C4 | p(C1)- p(C2)p(C3)- p(C4) | 0.466970.30554 | 20.8618.83 | 0.260.28 | 0.0690.065 |
| π C14-C16 (2) | 0.7397p(C14)+ 0.6729p(C16) | 1.66677 | π\* C15-C17π\* C18-C20 | p(C15)- p(C17)p(C18)- p(C20) | 0.331640.38869 | 23.0016.78 | 0.280.27 | 0.0710.061 |
| π C15-C17 (2) | 0.6949p(C15)+ 0.7191p(C17) | 1.70550 | π\* C14-C16π\* C18-C20 | p(C14)- p(C16)p(C18)- p(C20) | 0.362080.38869 | 16.7220.97 | 0.290.28 | 0.0630.070 |
| π C18-C20 (2) | 0.7317p(C18)+ 0.6816p(C20) | 1.64148 | π\* C14-C16π\* C15-C17 | p(C14)- p(C16)p(C15)- p(C17) | 0.362080.33164 | 23.2416.99 | 0.290.28 | 0.0730.062 |
| π N26-C28 (2) | 0.8546p(N32)+ 0.5192p(C34) | 1.89930 | π\* C1-C2 | p(C1)- p(C2) | 0.46697 | 15.61 | 0.38 | 0.076 |
| LP (1) N27 | p | 1.53006 | π\* C1-C2π\* N26-C28 | p(C1)- p(C2)p(N26)- p(C28) | 0.466970.49584 | 34.7882.33 | 0.290.22 | 0.0880.122 |
| LP (2) O30 |  | 1.84193 | π\* C18-C20 | p(C18)- p(C20) | 0.38869 | 30.27 | 0.34 | 0.096 |
|  |  |  |  |  |  |  |  |  |
| ***2c*** |  |  |  |  |  |  |  |  |
| πC1-C2 (2) | 0.7063p(C1)+ 0.7080p(C2) | 1.61446 | π\* C3-C4π\* C5-C6π\* N26-C28 | p(C3)- p(C4)p(C5)- p(C6)p(N26)- p(C28) | 0.323220.325490.44807 | 18.1918.1911.58 | 0.290.29 0.23 | 0.0660.0660.047 |
| π C3-C4 (2) | 0.7094p(C3)+ 0.7048p(C4) | 1.70231 | π\* C1-C2π\* C5-C6 | p(C1)- p(C2)p(C5)- p(C6) | 0.465150.32549 | 20.2319.09 | 0.27 0.28 | 0.0690.066 |
| π C5-C6 (2) | 0.7031p(C5)+ 0.7111p(C6) | 1.70526 | π\* C1-C2π\* C3-C4 | p(C1)- p(C2)p(C3)- p(C4) | 0.465150.32322 | 20.2518.75 | 0.270.28 | 0.0690.065 |
| π C11-N27 (2) | 0.1284sp9.05d5.13(C11)+ 0.9917p(N27) | 1.57205 | π\* C1-C2π\* N26-C28 | p(C1)- p(C2)p(N26)- p(C28) | 0.465150.44807 | 32.4973.93 | 0.290.24 | 0.0870.120 |
| π C15-C17 (2) | 0.6954p(C15)+ 0.7186p(C17) | 1.70317 | π\* C14-C16π\* C18-C20 | p(C14)- p(C16)p(C18)- p(C20) | 0.359300.39215 | 17.1821.08 | 0.290.28 | 0.0640.070 |
| π C18-C20 (2) | 0.7313p(C18)+ 0.6820p(C20) | 1.64766 | π\* C14-C16π\* C15-C17 | p(C14)- p(C16)p(C15)- p(C17) | 0.359300.33112 | 22.4417.00 | 0.290.29 | 0.0720.063 |
| π N26-C28 (2) | 0.8762p(N32)+ 0.4820p(C34) | 1.88618 | π\* C1-C2 | p(C1)- p(C2) | 0.46515 | 17.05 | 0.36 | 0.077 |
| σ Pd29-Br30 (2) | 0.4421sp2.27d1.21(Pd29)+ 0.8970sp5.44 (Br30) | 1.89069 | σ\* Pd29-Br31 LP\*(1) Pd29 | sp2.25d1.19(Pd29)- sp5.38 (Br31)sp9.12 | 0.157850.15236 | 4.021.20 | 0.58 0.65 | 0.0440.025 |
| σ Pd29-Br31 (2) | 0.4403sp2.25d1.19(Pd29)+ 0.8978sp5.38 (Br31) | 1.89275 | σ\* Pd29-Br30  | sp2.27d1.21(Pd29)- sp5.44 (Br30) | 0.15903 |  3.89 | 0.58 | 0.043 |
| LP (3) Br30 | s | 1.96010 | σ\* Pd29-Br31  | sp2.25d1.19(Pd29)- sp5.38 (Br31) | 0.15785 | 4.46 | 0.97 | 0.060 |
| LP (3) Br31 | s | 1.96026 | σ\* Pd29-Br30 | sp2.27d1.21(Pd29)- sp5.44 (Br30) | 0.15903 | 4.31 | 0.88 | 0.057 |
| LP (2) N42 | p | 1.27829 | π\* C32-C34 (2)π\* C33-C36 (2) | p(C32)- p(C34)p(C33)- p(C36) | 0.279270.27855 | 49.4049.30 | 0.24 0.24 | 0.1100.110 |
| LP (2) O44 | p | 1.84400 | π\* C18-C20 (2) | p(C18)- p(C20) | 0.39215 | 30.03 | 0.34 | 0.096 |
|  |  |  |  |  |  |  |  |  |

*\** *E(2)* means the energy of hyper conjugative interaction (stabilization energy

**Table S3.** The observed and calculated vibrational frequencies (in cm-1) of **2c** and **1c** at B3LYP/6-31+G(d,p) level in the chloroform phase.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|   |  |  |  | **2c** |  |  |  | **1c** |
|  *Exp.* | *Unscal.* | *Scal.* | *IIR* | *PED %*a | *Unscal.* | *Scal.* | *IIR* | *PED %*a |
|  | 3236 | 3122 | 6 | νCH R**E** (91)  | 3335 | 3217 | 27 | νC28H (99)  |
|  | 3233 | 3119 | 5 | νasCH R**E**+ νCH R**AC** (92) | 3237 | 3123 | 2 | νCH R**A** (92) |
| 3109 | 3224 | 3110 | 3 | νasCH R**E** (97)  | 3209 | 3096 | 11 | νCH R**C** (94)  |
| 3089 | 3198 | 3086 | 2 | νasCH R**A** (94) | 3176 | 3064 | 17 | νCH R**C** (94) |
| 3070 | 3179 | 3067 | 16 | νCH R**C** (93) | 3161 | 3050 | 27 | νC31H (91) |
| 3042 | 3160 | 3049 | 26 | νC45H (89)+ νC45H3 (10) | 3156 | 3045 | 72 | νCH R**C** (99) |
|  | 3126 | 3016 | 30 | νasC23H2 (82)+ νasCH2 R**D** (12)  | 3126 | 3016 | 88 | νCH2 R**D** (85) |
| 3019 | 3121 | 3011 | 67 | νasCH2 (81)+ νC23H2 (10) | 3122 | 3012 | 5 | νasC23H2 (85)  |
|  | 3121 | 3011 | 4 | νasC11H2 (97)  | 3120 | 3010 | 7 | νasC11H2 (98) |
| 3004 | 3109 | 2999 | 32 | νasCH2 R**D** (91) | 3113 | 3003 | 32 | νasCH2 R**D** (87) |
|  | 3102 | 2993 | 22 | νasCH2 R**D** (81) | 3102 | 2993 | 24 | νasCH2 R**D** (82) |
|  | 3098 | 2989 | 41 | νasC45H2 (98) | 3100 | 2991 | 39 | νasC31H2 (100) |
| 2976 | 3079 | 2971 | 15 | νCH R**D** + νC23H2 (84) | 3072 | 2964 | 29 | νC11H2 (99)  |
|  | 3072 | 2964 | 20 | νC11H2(96) | 3070 | 2962 | 18 | νCHR**D** (83) |
|  | 3067 | 2959 | 26 | νC23H2+ νCH R**D** (86) | 3066 | 2958 | 61 | νCH2 R**D** (90) |
| 2955 | 3064 | 2956 | 60 | νCH2 R**D** (88) | 3059 | 2951 | 21 | νC23H2 (87) |
| 2929 | 3053 | 2945 | 45 | νCH2R**D** (82) | 3054 | 2947 | 22 | νCH2 R**D** (74) |
| 2880 | 3046 | 2939 | 60 | νCH2 R**D** (86) | 3049 | 2942 | 65 | νCH2R**D** (89) |
| 2864 | 3030 | 2923 | 67 | νC45H3 (99) | 3031 | 2925 | 65 | νC31H3 (91) |
| 1612 | 1658 | 1600 | 91 | νCCR**C** (56) | 1662 | 1604 | 15 | νCCR**A** (58) |
| 1605 | 1655 | 1597 | 13 | νCCR**A** (69)+ ipb HCC R**A** (10) | 1658 | 1600 | 108 | νCCR**C** (59)+ ipb HCC R**C** (14) |
|  | 1652 | 1594 | 36 | νN42C+ νCCR**E** (68)+ ipb HCC R**E** (21) | 1648 | 1590 | 10 | νCCR**A** (35) |
| 1587 | 1650 | 1592 | 0 | νCCR**A** (61) | 1624 | 1567 | 11 | νCCR**C** (62) |
|  | 1624 | 1567 | 3 | νN42C+ νCCR**E** (64) | 1600 | 1544 | 217 | ν(N26C+ N27C)(49) |
| 1514 | 1550 | 1496 | 180 | ipb HCC R**C** (50) | 1522 | 1469 | 5 | ipb HCC R**A** (62) |
| 1476 | 1521 | 1467 | 2 | ipb (H35CN42+ HCC R**E**) (62)+ ipb (CN42C+CCN42) (26) | 1518 | 1464 | 13 | ipb (HCC R**A**+ CCN26) (30)+ νCC R**A** (14) |
|  | 1518 | 1465 | 2 | ipb (HCC R**A**+ CCN26) (63) | 1513 | 1459 | 4 | σCH2 R**D** (86) |
|  | 1510 | 1457 | 11 | σCH2 R**D** (76) | 1504 | 1451 | 43 | σC31H2 (74)+ ipb HCO (16) |
| 1448 | 1503 | 1450 | 47 | σC45H2 (88) | 1493 | 1441 | 24 | σ(C11H2+C23H2) (42) |
|  | 1496 | 1443 | 40 | σC23H2 (56)+ ω(C11H2+C23H2) (10) | 1489 | 1437 | 21 | σ(C11H2+ CH2 R**D**) (78) |
|  | 1491 | 1438 | 11 | σC45H2 (79)+ ipb HCO (16) | 1486 | 1433 | 53 | σ(C11H2+ C23H2+ CH2 R**D**) (55) |
|  | 1483 | 1431 | 53 | σC11H2+ ipb HCC R**E** (56)+ νN42C(23) | 1480 | 1428 | 12 | sbC31H3(78) |
|  | 1479 | 1427 | 8 | sbC45H3(78) | 1480 | 1427 | 5 | σCH2 R**D** (87)  |
| 1416 | 1461 | 1410 | 23 | ν(CC R**C**+ N27C) (23)+ ipb HCC R**C** (15) | 1462 | 1411 | 12 | νCC R**C** (35)+ ipb HCC R**C** (23) |
| 1405 | 1446 | 1395 | 202 | ν(N26C+ N27C)+ τC23H2( (45) | 1456 | 1405 | 66 | ν(N26C+ N27C)+ σC23H2 (25) |
|  | 1442 | 1391 | 189 | ν(N26C+ N27C)+ σ(C11H2+ C23H2) (46) | 1416 | 1366 | 14 | ω(C11H2+C23H2) (22)+ ν(N26C+ N27C) (20)+ σ(C11H2+ C23H2+ CH2 R**D**) (10) |
| 1360 | 1407 | 1358 | 13 | ω(C11H2+C23H2) (18)+ σC23H2 (10) | 1400 | 1351 | 11 | ωC11H2(17)+ νCCR**A** (18) |
|  | 1399 | 1349 | 51 | ν(CC R**A**+ N26C+PdBr+NBr) (25) | 1392 | 1343 | 22 | νCC R**A** (53)+ ωC11H2 (14)+ ipb HCCR**A** (12) |
| 1342 | 1388 | 1339 | 72 | ωC11H2 (48)+ ipb HCC (15) | 1366 | 1318 | 42 | ν(N26C+ N27C) (34) |
| 1324 | 1368 | 1319 | 29 | ν(CC R**A**+ N27C)+ τC11H2 (36) | 1353 | 1306 | 56 | ipb (HCN26+ HCC R**A**) (45) |
| 1302 | 1344 | 1296 | 27 | ipb HCC R**C** (69)+ νCCR**C** (15) | 1338 | 1291 | 32 | νCCR**A** (24)+ ipb HCC R**AC** (15) |
|  | 1333 | 1286 | 61 | ipb HCC R**C**+ ωC11H2 (38) | 1316 | 1270 | 13 | ipb (HCC+ HCN26)+ τC23H2 (29)+ χ (HCCC+CCCC) R**D** (18) |
| 1274 | 1281 | 1236 | 155 | ωCH2 R**D** (27)+ ν(OC**+** νCC) (11) | 1297 | 1251 | 25 | χ (HCCC+CCCC) R**D** (26)+ ipb (HCC+ HCN26) (15) |
| 1250 | 1280 | 1235 | 276 | ν(OC**+** νCC) (33)+ ωCH2 R**D** (19)+ ipb HCC R**C** (12) | 1282 | 1237 | 428 | ν(OC**+** νCC) R**C** (48)+ β R**C** (10) |
| 1218 | 1263 | 1218 | 20 | τCH2 R**D** (38)+ τ(C11H2+ C23H2+CH2) (12) | 1268 | 1223 | 2 | ωCH2 R**D** (64) |
| 1180 | 1206 | 1163 | 75 | ipb (HCC R**C**+HCO) (70)+ νCCR**C** (12) | 1257 | 1212 | 0 | ipb HCC+ τCH2 R**D** (59)+ ρCH2 R**D** (12) |
|  | 1202 | 1160 | 2 | ipb HCO+ ipb HCC R**C** (72) | 1239 | 1195 | 24 | ipb HCC R**C**+ τC11H2 (34)+ ω(C11H2+C23H2) (10) |
|  | 1171 | 1130 | 1 | χ CHOC (82)+ σC45H2 (15) | 1236 | 1192 | 62 | ipb HCN27 (28)+ ν(N26C+ N27C)(21)+ τC11H2+ HCN26 (18) |
| 1141 | 1140 | 1100 | 16 | ipb HCC R**C** (86) | 1204 | 1161 | 6 | ipb HCO (65)+ σC31H2 (21) |
| 1116 | 1115 | 1076 | 2 | ν(C23C+ R**D**) (61) | 1190 | 1148 | 1 | ipb HCCR**A** (52) |
|  | 1096 | 1058 | 7 | νN42C(51)+ ipb HCC R**E** (10) | 1171 | 1130 | 1 | χ CHOC+ τC31H2 (83) |
| 1073 | 1095 | 1057 | 29 | ipb (CN42C+CCN42) (44)+ ipb (H35CN42+ HCC) (27) | 1142 | 1102 | 20 | ipb HCC R**C** (58)+ νCC R**C** (20) |
|  | 1054 | 1017 | 72 | νOC(78) | 1114 | 1075 | 1 | νC23C(60)  |
|  | 1039 | 1002 | 7 | νN42C+ νCCR**E** (84) | 1051 | 1014 | 71 | νOC(73) |
|  | 1031 | 995 | 23 | α R**A** (44)+ν(N26C+ N27C+ CC)(13) | 1042 | 1005 | 10 | νCC R**A** (64)  |
|  | 1019 | 984 | 0 | opb HCC R**E** (89) | 1037 | 1001 | 7 | opb HCC R**C** (56) |
|  | 974 | 940 | 1 | τCH2 R**D** (34)+ ωCH2 R**D** (21) | 979 | 944 | 1 | τCH2 R**D**+ ρC11H2+ opb HCC R**C** (59) |
|  | 957 | 923 | 1 | opb HCC R**C**+ ρC11H2 (61) | 958 | 924 | 5 | opb HCC R**C**+ ρC11H2 (66)+ χ (CCCC R**D**+HCCN27) (10) |
| 851 | 854 | 824 | 35 | νOC+ opb HCC R**C** (69) | 859 | 829 | 21 | opb (HCC R**AC+** HCN26) (71) |
| 841 | 843 | 813 | 44 | νOC+ opb HCC R**C** (41) | 846 | 816 | 21 | ipb HCBr (34) |
| 826 | 815 | 787 | 33 | ν(N26C+ N27C+ CC)(17) | 835 | 806 | 10 | opb HCC R**C** (70) |
| 802 | 810 | 781 | 9 | ν(N27C+ CC)(37) | 821 | 792 | 17 | (τ+ρ) CH2 R**D**  |
| 796 | 797 | 769 | 7 | τCH2 R**D** (12) | 790 | 762 | 14 | (τ+ρ) τCH2 R**D** (13) |
| 762 | 762 | 735 | 57 | opb (HCC R**C**+ HCN42) (59)+ χCN42C (23) | 769 | 742 | 2 | ρCH2 R**D** (19) |
| 753 | 752 | 726 | 91 | χ HCCN26 (58)+ χ (CCCC R**A**+N26CCN27) (14)+ opb HCC R**A** (13) | 756 | 729 | 118 | opb HCC R**A** (88) |
| 698 | 697 | 673 | 54 | opb HCC R**C** (72) | 743 | 717 | 1 | β R**AB** (81) |
| 681 | 688 | 664 | 10 | χ CN26CN27) (57)+ ipb CPdBr (12) | 698 | 673 | 21 | β R**C**+opb N26CN27 (12) |
| 645 | 647 | 624 | 2 | β R**C** (63) | 652 | 629 | 4 | opb CCN26 (46) |
| 598 | 593 | 572 | 7 | β R**AB**+ opb CCN26(34)+ opb HCC R**A** (10) | 646 | 623 | 8 | α R**C** (51) |
| 584 | 585 | 564 | 0 | β R**A** (59) | 593 | 572 | 23 | β R**AB**+ opb CCN26(32)+ νCCR**A** (13) |
| 540 | 546 | 527 | 26 | β R**C** (25) | 544 | 525 | 21 | opb (HCC R**C**+ COC+ CCO+ CCN26) (51) |
| 511 | 519 | 500 | 10 | χ OCCC (49)+ β R**C** (14) | 515 | 497 | 10 | opb (HCC R**C** + COC) (51) |

**a**. *I*IR, IR intensity. The abbreviations are ν,symmetric stretching; νas, asymmetric stretching; ω, wagging; τ, twisting; ρ, rocking; σ, scissoring; α, in-plan ring deformation; β, non-planar ring deformation; ipb, in-plane bending; opb, out-plane bending; sb, symmetric bending; χ, torsion; R, ring.

**Table S4.** The observed and calculated vibrational frequencies (in cm-1) of **2c** and **1c** molecules at B3LYP/6-31+G(d,p) level in the chloroform phase.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|   |  |  |  | **2c** |  |  |  | **1c** |
|  *Exp.* | *Unscal.* | *Scal.* | *IIR* | *PED %*a | *Unscal.* | *Scal.* | *IIR* | *PED %*a |
|  | 3236 | 3122 | 6 | νCH R**E** (91)  | 3335 | 3217 | 27 | νC28H (99)  |
|  | 3233 | 3119 | 5 | νasCH R**E**+ νCH R**AC** (92) | 3237 | 3123 | 2 | νCH R**A** (92) |
|  | 3233 | 3119 | 8 | νasCH R**C**+ νCH R**A** (82) | 3230 | 3117 | 7 | νCH R**C** (99) |
|  | 3228 | 3115 | 8 | νCH R**C** (97) | 3229 | 3115 | 5 | νCH R**A** (91) |
|  | 3226 | 3113 | 11 | νasCH R**A** (83)+ νCH R**A** (11) | 3215 | 3102 | 12 | νasCH R**A** (80)+ νCH R**A** (14) |
| 3109 | 3224 | 3110 | 3 | νasCH R**E** (97)  | 3209 | 3096 | 11 | νCH R**C** (94)  |
|  | 3220 | 3106 | 1 | νasCH R**E** (92) | 3203 | 3090 | 2 | νasCH R**A** (90) |
|  | 3211 | 3098 | 18 | νCH R**A** (83) | 3176 | 3064 | 17 | νCH R**C** (94) |
|  | 3209 | 3096 | 12 | νCH R**C** (93) | 3161 | 3050 | 27 | νC31H (91) |
|  | 3207 | 3094 | 3 | νasCH R**E** (92) | 3156 | 3045 | 72 | νCH R**C** (99) |
| 3089 | 3198 | 3086 | 2 | νasCH R**A** (94) | 3126 | 3016 | 88 | νCH2 R**D** (85) |
|  | 3190 | 3077 | 4 | νCH R**C** (97)  | 3122 | 3012 | 5 | νasC23H2 (85)  |
| 3070 | 3179 | 3067 | 16 | νCH R**C** (93) | 3120 | 3010 | 7 | νasC11H2 (98) |
| 3042 | 3160 | 3049 | 26 | νC45H (89)+ νC45H3 (10) | 3113 | 3003 | 32 | νasCH2 R**D** (87) |
|  | 3126 | 3016 | 30 | νasC23H2 (82)+ νasCH2 R**D** (12)  | 3102 | 2993 | 24 | νasCH2 R**D** (82) |
| 3019 | 3121 | 3011 | 67 | νasCH2 (81)+ νC23H2 (10) | 3100 | 2991 | 39 | νasC31H2 (100) |
|  | 3121 | 3011 | 4 | νasC11H2 (97)  | 3072 | 2964 | 29 | νC11H2 (99)  |
| 3004 | 3109 | 2999 | 32 | νasCH2 R**D** (91) | 3070 | 2962 | 18 | νCHR**D** (83) |
|  | 3102 | 2993 | 22 | νasCH2 R**D** (81) | 3066 | 2958 | 61 | νCH2 R**D** (90) |
|  | 3098 | 2989 | 41 | νasC45H2 (98) | 3059 | 2951 | 21 | νC23H2 (87) |
| 2976 | 3079 | 2971 | 15 | νCH R**D** + νC23H2 (84) | 3054 | 2947 | 22 | νCH2 R**D** (74) |
|  | 3072 | 2964 | 20 | νC11H2(96) | 3049 | 2942 | 65 | νCH2R**D** (89) |
|  | 3067 | 2959 | 26 | νC23H2+ νCH R**D** (86) | 3031 | 2925 | 65 | νC31H3 (91) |
| 2955 | 3064 | 2956 | 60 | νCH2 R**D** (88) | 1662 | 1604 | 15 | νCCR**A** (58) |
| 2929 | 3053 | 2945 | 45 | νCH2R**D** (82) | 1658 | 1600 | 108 | νCCR**C** (59)+ ipb HCC R**C** (14) |
| 2880 | 3046 | 2939 | 60 | νCH2 R**D** (86) | 1648 | 1590 | 10 | νCCR**A** (35) |
| 2864 | 3030 | 2923 | 67 | νC45H3 (99) | 1624 | 1567 | 11 | νCCR**C** (62) |
| 1612 | 1658 | 1600 | 91 | νCCR**C** (56) | 1600 | 1544 | 217 | ν(N26C+ N27C)(49) |
| 1605 | 1655 | 1597 | 13 | νCCR**A** (69)+ ipb HCC R**A** (10) | 1552 | 1498 | 153 | νCCR**C** (34) |
|  | 1652 | 1594 | 36 | νN42C+ νCCR**E** (68)+ ipb HCC R**E** (21) | 1522 | 1469 | 5 | ipb HCC R**A** (62) |
| 1587 | 1650 | 1592 | 0 | νCCR**A** (61) | 1518 | 1464 | 13 | ipb (HCC R**A**+ CCN26) (30)+ νCC R**A** (14) |
|  | 1624 | 1567 | 3 | νN42C+ νCCR**E** (64) | 1513 | 1459 | 4 | σCH2 R**D** (86) |
|  | 1624 | 1566 | 19 | νCCR**C** (59) | 1504 | 1451 | 43 | σC31H2 (74)+ ipb HCO (16) |
| 1514 | 1550 | 1496 | 180 | ipb HCC R**C** (50) | 1493 | 1441 | 9 | σC31H2 (84)+ χ CHOC+ τC31H2 (14) |
| 1476 | 1521 | 1467 | 2 | ipb (H35CN42+ HCC R**E**) (62)+ ipb (CN42C+CCN42) (26) | 1493 | 1441 | 24 | σ(C11H2+C23H2) (42) |
|  | 1518 | 1465 | 2 | ipb (HCC R**A**+ CCN26) (63) | 1489 | 1437 | 21 | σ(C11H2+ CH2 R**D**) (78) |
|  | 1513 | 1460 | 40 | ipb HCC R**A** (36)+ ipb (HCC R**A**+N26CN27) (24)+ α R**A** (16) | 1486 | 1433 | 53 | σ(C11H2+ C23H2+ CH2 R**D**) (55) |
|  | 1510 | 1457 | 11 | σCH2 R**D** (76) | 1480 | 1428 | 12 | sbC31H3(78) |
| 1448 | 1503 | 1450 | 47 | σC45H2 (88) | 1480 | 1427 | 5 | σCH2 R**D** (87)  |
|  | 1496 | 1443 | 40 | σC23H2 (56)+ ω(C11H2+C23H2) (10) | 1462 | 1411 | 12 | νCC R**C** (35)+ ipb HCC R**C** (23) |
|  | 1491 | 1438 | 11 | σC45H2 (79)+ χ CHOC (16) | 1456 | 1405 | 66 | ν(N26C+ N27C)+ σC23H2 (25) |
|  | 1485 | 1433 | 1 | σC11H2+ ipb HCC R**E** (62) | 1416 | 1366 | 14 | ω(C11H2+C23H2) (22)+ ν(N26C+ N27C)+ ωC23H2 (20)+ σ(C11H2+ C23H2+ CH2 R**D**) (10) |
|  | 1484 | 1432 | 3 | σCH2 R**D** (79) | 1400 | 1351 | 11 | ωC11H2(17)+ νCCR**A** (18) |
|  | 1483 | 1431 | 53 | σC11H2+ ipb HCC R**E** (56)+ νN42C(23) | 1392 | 1343 | 22 | νCC R**A** (53)+ ωC11H2 (14)+ ipb HCCR**A** (12) |
|  | 1479 | 1427 | 8 | sbC45H3(78) | 1378 | 1329 | 2 | ipb HCC R**A** (13) |
|  | 1477 | 1425 | 3 | σCH2 R**D** (93) | 1366 | 1318 | 42 | ν(N26C+ N27C) (34) |
| 1416 | 1461 | 1410 | 23 | ν(CC R**C**+ N27C) (23)+ ipb HCC R**C** (15) | 1353 | 1306 | 56 | ipb (HCN26+ HCC R**A**) (45) |
| 1405 | 1446 | 1395 | 202 | ν(N26C+ N27C)+ τC23H2( (45) | 1349 | 1301 | 12 | ipb HCC R**C** (56)+ νCCR**C** (15) |
|  | 1442 | 1391 | 189 | ν(N26C+ N27C)+ σ(C11H2+ C23H2) (46) | 1338 | 1291 | 32 | νCCR**A** (24)+ ipb HCC R**AC** (15) |
| 1360 | 1407 | 1358 | 13 | ω(C11H2+C23H2) (18)+ σC23H2 (10) | 1316 | 1270 | 13 | ipb (HCC+ HCN26)+ τC23H2 (29)+ χ (HCCC+CCCC) R**D** (18) |
|  | 1399 | 1349 | 51 | ν(CC R**A**+ N26C+PdBr+NBr) (25) | 1297 | 1251 | 25 | χ (HCCC+CCCC) R**D** (26)+ ipb (HCC+ HCN26) (15) |
| 1342 | 1388 | 1339 | 72 | ωC11H2 (48)+ ipb HCC (15) | 1290 | 1245 | 5 | χ HCCC R**D**+ τC23H2 (24)+ ipb(HCN26+HCC) (31) |
|  | 1384 | 1335 | 5 | ipb (HCN42+ HCC) (89) | 1282 | 1237 | 428 | ν(OC**+** νCC) R**C** (48)+ β R**C** (10) |
|  | 1382 | 1334 | 11 | ipb HCC R**A** (34)+ ω(C11H2+C23H2) (20) | 1273 | 1229 | 6 | χ HCCC+ ωCH2 R**D** (40)+ τ(C23H2+CH2 R**D**) (17) |
| 1324 | 1368 | 1319 | 29 | ν(CC R**A**+ N27C)+ τC11H2 (36) | 1268 | 1223 | 2 | ωCH2 R**D** (64) |
|  | 1356 | 1308 | 37 | ωC23H2 (22)+ ν(CC R**A**+ N26C+PdBr+NBr) (20)+ ω(C11H2+C23H2) (10) | 1257 | 1212 | 0 | ipb HCC+ τCH2 R**D** (59)+ ρCH2 R**D** (12) |
| 1302 | 1344 | 1296 | 27 | ipb HCC R**C** (69)+ νCCR**C** (15) | 1239 | 1195 | 24 | ipb HCC R**C**+ τC11H2 (34)+ ω(C11H2+C23H2) (10) |
|  | 1333 | 1286 | 61 | ipb HCC R**C**+ ωC11H2 (38) | 1236 | 1192 | 62 | ipb HCN27 (28)+ ν(N26C+ N27C)(21)+ τC11H2+ HCN26 (18) |
|  | 1311 | 1265 | 2 | νCCR**E** (80)+ ipb HCC R**E** (11) | 1228 | 1185 | 1 | τ(C23H2+CH2 R**D**) (36)+ χ HCCC (10) |
|  | 1309 | 1263 | 11 | τC23H2+ ipb HCC R**AD** (38)+ ipb HCC R**A** (16) | 1220 | 1177 | 39 | τC11H2+ HCN26 (18)+ ipb HCN27 (12)+ β R**C** (10) |
|  | 1296 | 1250 | 4 | ipb HCC R**D** (29)+ ωCH2 R**D** (16)+ τCH2 R**D** (13) | 1212 | 1169 | 86 | ipb HCCR**C** (61)+ νCCR**C** (15) |
| 1274 | 1281 | 1236 | 155 | ωCH2 R**D** (27)+ ν(OC**+** νCC) (11) | 1204 | 1161 | 6 | ipb HCO (65)+ σC31H2 (21) |
| 1250 | 1280 | 1235 | 276 | ν(OC**+** νCC) (33)+ ωCH2 R**D** (19)+ ipb HCC R**C** (12) | 1203 | 1160 | 2 | χ HCCC (54) |
|  | 1265 | 1221 | 1 | ωCH2 R**D** (28)+ τCH2 R**D** (34) | 1190 | 1148 | 1 | ipb HCCR**A** (52) |
| 1218 | 1263 | 1218 | 20 | τCH2 R**D** (38)+ τ(C11H2+ C23H2+CH2) (12) | 1171 | 1130 | 1 | χ CHOC+ τC31H2 (83) |
|  | 1257 | 1213 | 0 | τCH2 R**D** (78) | 1168 | 1127 | 1 | ipb HCC R**D** (29) |
|  | 1237 | 1193 | 18 | ipb (HCC R**E**+ HCN42) (61)+ νN42C+ νCCR**E** (27) | 1154 | 1113 | 13 | ipb HCC R**A** (41) |
|  | 1233 | 1190 | 30 | τ(C11H2+ C23H2+CH2) (24) | 1146 | 1106 | 1 | ipb (CN26C+ CN27C+ N26CN27) (31)+ β R**C**+opb N26CN27 (15) |
|  | 1225 | 1182 | 4 | νC11C14 (37)+ τ(C11H2+ C23H2+CH2) (10) | 1142 | 1102 | 20 | ipb HCC R**C** (58)+ νCC R**C** (20) |
|  | 1213 | 1171 | 21 | τ(C11H2+ C23H2+CH2 R**D**) | 1114 | 1075 | 1 | νC23C(60)  |
| 1180 | 1206 | 1163 | 75 | ipb (HCC R**C**+HCO) (70)+ νCCR**C** (12) | 1064 | 1027 | 0 | νCC(36)+ χ HCN26C (10) |
|  | 1202 | 1160 | 2 | ipb HCO+ ipb HCC R**C** (72) | 1051 | 1014 | 71 | νOC(73) |
|  | 1200 | 1157 | 4 | χ HCCC R**D** (56) | 1042 | 1005 | 10 | νCC R**A** (64)  |
|  | 1192 | 1150 | 1 | ipb (HCC R**A**+N26CN27) (42) | 1037 | 1001 | 7 | opb HCC R**C** (56) |
|  | 1176 | 1135 | 4 | ipb HCC R**E** (78) | 1026 | 990 | 11 | α R**AC** (44) |
|  | 1171 | 1130 | 1 | χ CHOC (82)+ σC45H2 (15) | 1024 | 988 | 17 | α R**AC** (43) |
|  | 1170 | 1128 | 0 | ipb (HCC R**A**+N26CN27) (32) | 991 | 956 | 0 | opb HCC R**A** (86) |
|  | 1161 | 1121 | 7 | χ HCCN26 (14) | 979 | 944 | 1 | τCH2 R**D**+ ρC11H2+ opb HCC R**C** (59) |
|  | 1145 | 1105 | 5 | ipb HCC R**A** (49)+ β CCN27 (12) | 977 | 943 | 5 | χ (CCCC R**D**+HCCN27) (29)+ τCH2 R**D**+ ρC11H2+ opb HCC R**C** (12) |
| 1141 | 1140 | 1100 | 16 | ipb HCC R**C** (86) | 970 | 936 | 2 | νCCR**D** (40)+ χ (CCCC R**D**+HCCN27) (10)+ χ HCN26C (17) |
| 1116 | 1115 | 1076 | 2 | ν(C23C+ R**D**) (61) | 958 | 924 | 5 | opb HCC R**C**+ ρC11H2 (66)+ χ (CCCC R**D**+HCCN27) (10) |
|  | 1096 | 1058 | 7 | νN42C(51)+ ipb HCC R**E** (10) | 951 | 917 | 3 | opb HCC R**A** (79) |
| 1073 | 1095 | 1057 | 29 | ipb (CN42C+CCN42) (44)+ ipb (H35CN42+ HCC) (27) | 932 | 899 | 4 | νCCR**D** (81) |
|  | 1069 | 1031 | 8 | νCC R**D** (38)+ χ HCCCR**D** (12)  | 915 | 883 | 0 | χ HCN26C (31)+ ν(C23C+ R**D**) (14) |
|  | 1055 | 1018 | 3 | α R**E** + ipb CN42C (74) | 886 | 855 | 2 | ν(C23C+ R**D**) (30) |
|  | 1054 | 1017 | 72 | νOC(78) | 861 | 831 | 34 | opb (HCC R**AC+** HCN26) (55) |
|  | 1041 | 1004 | 15 | α R**A** (48) | 859 | 829 | 21 | opb (HCC R**AC+** HCN26) (71) |
|  | 1039 | 1002 | 7 | νN42C+ νCCR**E** (84) | 851 | 821 | 2 | ipb HCBr (38) |
|  | 1031 | 995 | 23 | α R**A** (44)+ν(N26C+ N27C+ CC)(13) | 846 | 816 | 21 | ipb HCBr (34) |
|  | 1025 | 989 | 3 | α R**C** (74) | 835 | 806 | 10 | opb HCC R**C** (70) |
|  | 1019 | 984 | 0 | opb HCC R**E** (89) | 821 | 792 | 17 | (τ+ρ) CH2 R**D**  |
|  | 994 | 959 | 1 | opb HCC R**E** (84) | 790 | 762 | 14 | (τ+ρ) τCH2 R**D** (13) |
|  | 994 | 959 | 4 | opb HCC R**C** (60) | 788 | 760 | 2 | ipb (CN26C+ CN27C+ N26CN27) (11)+ νCCR**A** (31)+ ipb (HCC R**A**+ CCN26) (10) |
|  | 987 | 952 | 0 | opb HCC R**A** (83) | 775 | 747 | 23 | χ CCCC R**C** (22)+ β R**C** (30)+ β R**C**+opb N26CN27 (12) |
|  | 983 | 948 | 2 | opb HCC R**C** (67) | 769 | 742 | 2 | ρCH2 R**D** (19) |
|  | 974 | 940 | 1 | τCH2 R**D** (34)+ ωCH2 R**D** (21) | 756 | 729 | 118 | opb HCC R**A** (88) |
|  | 973 | 939 | 2 | νCC R**D** (59)+ χ HCCC (12) | 743 | 717 | 1 | β R**AB** (81) |
|  | 958 | 924 | 0 | opb HCC R**E** (90) | 728 | 703 | 8 | β R**C** (30)+ χ CCCC R**C** (22) |
|  | 957 | 923 | 1 | opb HCC R**C**+ ρC11H2 (61) | 698 | 673 | 21 | β R**C**+opb N26CN27 (12) |
|  | 943 | 910 | 3 | opb HCC R**A+** χ HCCN26 (90) | 652 | 629 | 4 | opb CCN26 (46) |
|  | 932 | 899 | 3 | νCCR**D** (78)  | 646 | 623 | 8 | α R**C** (51) |
|  | 912 | 880 | 1 | χ HCCCR**D** (21)+ χ HCCN26 (10)+ τCH2 R**D** (10) | 624 | 602 | 22 | opb N26CN27 (35)+ β R**AB**+ opb CCN26(22) |
|  | 889 | 857 | 1 | νCCR**D** (34)+ τCH2 R**D+** χ (CCCH R**D**+CCCN42) (18) | 593 | 572 | 23 | β R**AB**+ opb CCN26(32)+ νCCR**A** (13) |
|  | 883 | 852 | 0 | opb HCC R**E** (56)+ opb (HCC R**C**+ HCN42) (59)+ χCN42C (18) | 577 | 556 | 2 | β R**AB**+ opb CCN26(58)+ opb (COC+ CCN26 (18) |
|  | 858 | 828 | 2 | opb HCC R**A** (90) | 563 | 543 | 5 | opb (COC+ CCN26) (29) |
| 851 | 854 | 824 | 35 | νOC+ opb HCC R**C** (69) | 548 | 529 | 10 | opb (COC+ CCN26) (43) |
| 841 | 843 | 813 | 44 | νOC+ opb HCC R**C** (41) | 544 | 525 | 21 | opb (HCC R**C**+ COC+ CCO+ CCN26) (51) |
|  | 835 | 805 | 1 | opb HCC R**C** (79) | 515 | 497 | 10 | opb (HCC R**C** + COC) (51) |
| 826 | 815 | 787 | 33 | ν(N26C+ N27C+ CC)(17) |  |  |  |  |
| 802 | 810 | 781 | 9 | ν(N27C+ CC)(37) |  |  |  |  |
| 796 | 797 | 769 | 7 | τCH2 R**D** (12) |  |  |  |  |
|  | 773 | 746 | 17 | χ (CCCC R**C**+ CCCO) (10) |  |  |  |  |
|  | 766 | 739 | 5 | τCH2 R**D+** χ (CCCH R**D**+CCCN42) (14)+ τCH2 R**D** (11) |  |  |  |  |
| 762 | 762 | 735 | 57 | opb (HCC R**C**+ HCN42) (59)+ χCN42C (23) |  |  |  |  |
|  | 755 | 728 | 14 | χ (CCCC R**A**+N26CCN27)+ opb HCC R**A** (50) |  |  |  |  |
| 753 | 752 | 726 | 91 | χ HCCN26 (58)+ χ (CCCC R**A**+N26CCN27) (14)+ opb HCC R**A** (13) |  |  |  |  |
|  | 726 | 700 | 4 | β R**C** (17)+ νC11C14 (11) |  |  |  |  |
|  | 701 | 676 | 4 | χ (CCCC R**C**+ CCCO) (39)+ χ (CCCC R**C**+ CCCO) (10)+ β R**C** (26) |  |  |  |  |
| 698 | 697 | 673 | 54 | opb HCC R**C** (72) |  |  |  |  |
| 681 | 688 | 664 | 10 | χ CN26CN27) (57)+ ipb CPdBr (12) |  |  |  |  |
|  | 663 | 639 | 0 | β R**C**+ ipb CCN42 (84)+ νCCR**C** (11) |  |  |  |  |
|  | 652 | 629 | 6 | β R**C**+ ipb CCN42 (76) |  |  |  |  |
| 645 | 647 | 624 | 2 | β R**C** (63) |  |  |  |  |
|  | 635 | 612 | 3 | β R**D** (43)+ χ HCCC R**D** (10) |  |  |  |  |
|  | 603 | 582 | 13 | β CCN27 (34)+ ipb HCC R**A** (10) |  |  |  |  |
| 598 | 593 | 572 | 7 | β R**AB**+ opb CCN26(34)+ opb HCC R**A** (10) |  |  |  |  |
| 584 | 585 | 564 | 0 | β R**A** (59) |  |  |  |  |
|  | 569 | 549 | 4 | β R**A** (39) |  |  |  |  |
| 540 | 546 | 527 | 26 | β R**C** (25) |  |  |  |  |
| 511 | 519 | 500 | 10 | χ OCCC (49)+ β R**C** (14) |  |  |  |  |

**a**. *I*IR, IR intensity. The abbreviations are ν,symmetric stretching; νas, asymmetric stretching; ω, wagging; τ, twisting; ρ, rocking; σ, scissoring; α, in-plan ring deformation; β, non-planar ring deformation; ipb, in-plane bending; opb, out-plane bending; sb, symmetric bending; χ, torsion; R, ring.

**Table S5.** The observed and calculated *1H* and 13C{1H} NMR isotropic chemical shifts (with respect to TMS, all values in ppm) for **1c** at 6-31+G(d,p) basis set in the chloroform phase.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 13C{1H} NMR |  |  | **1H NMR** |
|  | Exp. | B3LYP | G96LYP | M06-2X | HF |  |  | Exp. | B3LYP | G96LYP | M06-2X | HF |
|  1C | 131.1 | 131.1 | 129.6 | 143.4 | 132.7 |  |  7H | 7.7 | 7.5 | 7.3 | 7.7 | 7.6 |
|  2C | 130.1 | 129.2 | 127.2 | 140.6 | 129.5 |  |  8H | 7.7 | 7.6 | 7.3 | 7.9 | 7.6 |
|  3C | 114.6 | 111.7 | 108.7 | 126.7 | 114.9 |  |  9H | 7.7 | 7.7 | 7.4 | 8.1 | 7.8 |
|  4C | 127.0 | 123.2 | 119.6 | 137.3 | 124.4 |  |  10H | 7.7 | 7.8 | 7.5 | 8.2 | 7.9 |
|  5C | 127.1 | 123.4 | 120.0 | 138.0 | 125.6 |  |  12H | 5.9 | 5.7 | 5.6 | 5.8 | 5.6 |
|  6C | 113.9 | 110.2 | 107.1 | 124.3 | 113.0 |  |  13H | 5.9 | 5.0 | 4.8 | 5.0 | 4.8 |
|  11C | 55.3 | 55.3 | 56.4 | 55.5 | 48.9 |  |  19H | 7.5 | 9.5 | 9.7 | 10.6 | 9.9 |
|  14C | 124.8 | 124.0 | 123.2 | 139.7 | 123.9 |  |  21H | 6.9 | 7.2 | 7.0 | 7.8 | 7.4 |
|  15C | 130.1 | 126.9 | 124.1 | 143.1 | 133.2 |  |  22H | 6.9 | 7.0 | 6.8 | 7.5 | 7.2 |
|  16C | 131.5 | 131.5 | 129.0 | 149.7 | 138.0 |  |  24H | 4.6 | 4.7 | 5.2 | 4.4 | 4.2 |
|  17C | 114.6 | 113.7 | 111.6 | 128.3 | 114.4 |  |  25H | 4.6 | 3.9 | 3.8 | 3.7 | 3.5 |
|  18C | 113.0 | 108.4 | 106.5 | 122.8 | 108.8 |  |  29H | 7.5 | 7.6 | 7.4 | 8.3 | 8.1 |
|  20C | 160.1 | 157.9 | 156.4 | 172.0 | 159.0 |  |  32H | 3.8 | 3.8 | 3.8 | 3.7 | 3.6 |
|  23C | 50.9 | 54.8 | 57.0 | 56.8 | 49.8 |  |  33H | 3.8 | 4.1 | 4.0 | 4.1 | 4.0 |
|  28C | 142.4 | 137.5 | 129.1 | 146.1 | 146.7 |  |  34H | 3.8 | 3.7 | 3.7 | 3.6 | 3.6 |
|  31C | 52.3 | 55.4 | 57.0 | 55.8 | 49.9 |  |  38H | 3.1 | 3.5 | 3.4 | 4.3 | 3.7 |
|  35C | 34.4 | 37.8 | 42.2 | 35.2 | 29.8 |  |  40H | 2.0 | 2.0 | 2.0 | 1.9 | 1.9 |
|  36C | 25.9 | 29.8 | 31.6 | 27.4 | 24.0 |  |  41H | 2.2 | 2.4 | 2.4 | 2.3 | 2.1 |
|  37C | 25.8 | 29.3 | 31.5 | 27.7 | 24.4 |  |  42H | 2.0 | 1.7 | 1.8 | 1.7 | 1.6 |
|  39C | 17.9 | 21.7 | 23.7 | 19.4 | 17.6 |  |  43H | 2.0 | 2.0 | 2.0 | 2.1 | 1.8 |
|  |  |  |  |  |  |  |  44H | 2.0 | 1.9 | 1.9 | 1.9 | 1.7 |
|  |  |  |  |  |  |  |  45H | 2.2 | 2.1 | 2.1 | 2.1 | 2.1 |
|  |  |  |  |  |  |  |  47H | 11.6 | 9.7 | 11.2 | 11.1 | 11.8 |

**Table S6.** The observed and calculated 1H and 13C{1H} NMR isotropic chemical shifts (with respect to TMS, all values in ppm) for **2c** at 6-31+G(d,p) basis set in the chloroform phase.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 13C{1H} NMR |  |  | **1H NMR** |
|  | Exp. | B3LYP | G96LYP | M06-2X | HF |  |  | Exp. | B3LYP | G96LYP | M06-2X | HF |
|  1C | 138.0 | 134.6 | 133.2 | 148.6 | 136.4 |  |  7H | 7.0 | 7.4 | 7.2 | 7.9 | 7.4 |
|  2C | 135.5 | 132.7 | 131.2 | 145.8 | 134.5 |  |  8H | 7.1 | 7.4 | 7.2 | 7.9 | 7.5 |
|  3C | 114.2 | 109.1 | 106.8 | 123.8 | 112.9 |  |  9H | 7.3 | 7.5 | 7.3 | 8.1 | 7.6 |
|  4C | 122.9 | 119.9 | 117.5 | 135.8 | 122.9 |  |  10H | 7.3 | 7.7 | 7.5 | 8.3 | 7.9 |
|  5C | 123.0 | 120.1 | 117.6 | 136.0 | 123.5 |  |  12H | 6.0 | 7.0 | 7.0 | 7.2 | 7.3 |
|  6C | 111.6 | 108.0 | 105.7 | 121.9 | 111.4 |  |  13H | 6.0 | 5.0 | 4.9 | 5.2 | 5.1 |
|  11C | 55.3 | 56.4 | 58.3 | 57.5 | 50.0 |  |  19H | 7.4 | 8.3 | 8.1 | 9.0 | 8.1 |
|  14C | 127.1 | 126.4 | 124.7 | 141.6 | 126.6 |  |  21H | 6.8 | 7.2 | 7.1 | 7.9 | 7.6 |
|  15C | 129.5 | 127.1 | 124.4 | 143.2 | 132.5 |  |  22H | 6.8 | 6.9 | 6.7 | 7.5 | 7.1 |
|  16C | 129.5 | 127.6 | 124.7 | 144.5 | 132.7 |  |  24H | 4.8 | 5.4 | 5.3 | 5.4 | 5.5 |
|  17C | 114.3 | 114.0 | 112.1 | 129.1 | 116.0 |  |  25H | 4.8 | 4.1 | 4.1 | 4.2 | 4.0 |
|  18C | 110.5 | 107.5 | 105.9 | 122.3 | 108.7 |  |  35H | 9.0 | 8.9 | 8.8 | 9.8 | 9.2 |
|  20C | 159.4 | 157.0 | 155.8 | 171.3 | 158.1 |  |  37H | 9.0 | 8.9 | 8.7 | 9.7 | 9.1 |
|  23C | 54.2 | 56.1 | 57.7 | 56.6 | 49.9 |  |  39H | 7.5 | 7.6 | 7.5 | 8.3 | 7.7 |
| 28C | 162.7 | 190.1 | 184.1 | 209.8 | 209.6 |  |  40H | 7.5 | 7.6 | 7.5 | 8.2 | 7.6 |
|  32C | 152.7 | 148.4 | 145.8 | 166.2 | 153.9 |  |  41H | 7.7 | 8.0 | 7.8 | 8.7 | 8.5 |
|  33C | 154.4 | 148.6 | 146.1 | 166.4 | 154.0 |  |  43H | 7.0 | 7.8 | 7.6 | 8.4 | 8.2 |
|  34C | 124.6 | 122.1 | 120.6 | 137.8 | 120.9 |  |  46H | 3.7 | 3.7 | 3.8 | 3.7 | 3.6 |
|  36C | 124.6 | 122.1 | 120.6 | 137.8 | 120.9 |  |  47H | 3.7 | 4.0 | 4.0 | 4.1 | 4.0 |
|  38C | 134.3 | 134.5 | 130.9 | 153.7 | 144.9 |  |  48H | 3.7 | 3.7 | 3.7 | 3.6 | 3.5 |
|  45C | 53.4 | 54.9 | 56.5 | 55.3 | 49.7 |  |  52H | 3.5 | 3.8 | 3.8 | 4.7 | 3.7 |
|  49C | 35.5 | 41.4 | 43.7 | 39.5 | 34.2 |  |  54H | 2.2 | 2.1 | 2.2 | 2.0 | 2.2 |
|  50C | 27.2 | 29.0 | 30.9 | 27.5 | 24.2 |  |  55H | 2.2 | 2.4 | 2.4 | 2.3 | 2.5 |
|  51C | 27.3 | 32.5 | 34.1 | 28.8 | 27.1 |  |  56H | 2.0 | 2.1 | 2.1 | 1.6 | 2.0 |
|  53C | 18.4 | 21.7 | 23.4 | 18.8 | 18.0 |  |  57H | 2.0 | 1.9 | 2.0 | 1.6 | 1.7 |
|  |  |  |  |  |  |  |  58H | 1.9 | 1.9 | 1.9 | 1.8 | 1.8 |
|  |  |  |  |  |  |  |  59H | 1.9 | 2.0 | 2.0 | 2.0 | 2.0 |

**1Hand** 13C{1H} NMR **spectral analysis**

**Table S7a.** The observed and calculated 1H and 13C{1H} NMR isotropic chemical shifts (with respect to TMS, all values in ppm) for the **2c** molecule at 6-31+G(d,p)/LANL2DZ basis set in the gas phase.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 13C{1H} NMR |  |  | **1H NMR** |
|  | Exp. | B3LYP | G96LYP | M06-2X | HF |  |  | Exp. | B3LYP | G96LYP | M06-2X | HF |
|  1C |  | 134.3 | 132.7 | 148.1 | 136.1 |  |  7H |  | 7.3 | 7.1 | 7.9 | 7.3 |
|  2C |  | 132.7 | 131.0 | 145.6 | 134.4 |  |  8H |  | 7.2 | 7.1 | 7.8 | 7.3 |
|  3C |  | 108.5 | 106.0 | 123.1 | 112.6 |  |  9H |  | 7.4 | 7.2 | 7.9 | 7.5 |
|  4C |  | 118.7 | 116.2 | 134.1 | 121.9 |  |  10H |  | 7.5 | 7.3 | 8.1 | 7.7 |
|  5C |  | 118.8 | 116.3 | 134.2 | 122.5 |  |  12H |  | 7.1 | 7.1 | 7.3 | 7.3 |
|  6C |  | 106.8 | 104.2 | 120.1 | 110.2 |  |  13H |  | 4.8 | 4.7 | 5.0 | 4.8 |
|  11C |  | 56.6 | 58.3 | 57.9 | 50.5 |  |  19H |  | 8.6 | 8.3 | 9.3 | 8.5 |
|  14C |  | 125.7 | 124.0 | 140.7 | 125.8 |  |  21H |  | 7.2 | 7.0 | 7.8 | 7.5 |
|  15C |  | 125.9 | 123.1 | 141.6 | 131.5 |  |  22H |  | 6.8 | 6.6 | 7.4 | 7.0 |
|  16C |  | 128.2 | 125.1 | 145.5 | 133.7 |  |  24H |  | 5.5 | 5.5 | 5.5 | 5.5 |
|  17C |  | 113.6 | 111.6 | 128.4 | 115.7 |  |  25H |  | 3.9 | 3.8 | 3.9 | 3.8 |
|  18C |  | 106.8 | 105.0 | 121.5 | 108.2 |  |  35H |  | 9.8 | 9.6 | 10.4 | 9.4 |
|  20C |  | 156.5 | 155.1 | 170.6 | 157.7 |  |  37H |  | 9.8 | 9.6 | 10.4 | 9.3 |
|  23C |  | 56.2 | 57.5 | 56.4 | 49.6 |  |  39H |  | 7.4 | 7.2 | 8.0 | 7.4 |
| 28C |  | 191.5 | 185.5 | 211.5 | 211.7 |  |  40H |  | 7.4 | 7.2 | 8.0 | 7.4 |
|  32C |  | 149.5 | 146.9 | 165.9 | 155.6 |  |  41H |  | 7.8 | 7.6 | 8.5 | 8.3 |
|  33C |  | 149.8 | 147.2 | 166.4 | 155.8 |  |  43H |  | 7.6 | 7.4 | 8.2 | 8.0 |
|  34C |  | 119.5 | 117.8 | 136.0 | 118.1 |  |  46H |  | 3.6 | 3.6 | 3.6 | 3.6 |
|  36C |  | 119.6 | 117.9 | 135.9 | 118.1 |  |  47H |  | 4.0 | 3.9 | 4.0 | 3.9 |
|  38C |  | 132.4 | 128.5 | 150.9 | 143.3 |  |  48H |  | 3.6 | 3.6 | 3.5 | 3.5 |
|  45C |  | 53.8 | 55.2 | 54.1 | 48.7 |  |  52H |  | 4.0 | 4.0 | 4.8 | 4.0 |
|  49C |  | 40.4 | 42.7 | 38.3 | 33.3 |  |  54H |  | 2.0 | 2.0 | 1.8 | 2.0 |
|  50C |  | 28.9 | 30.6 | 27.7 | 24.1 |  |  55H |  | 2.3 | 2.3 | 2.2 | 2.4 |
|  51C |  | 32.6 | 34.1 | 28.7 | 27.1 |  |  56H |  | 1.9 | 1.9 | 1.4 | 1.9 |
|  53C |  | 21.4 | 23.1 | 18.4 | 17.8 |  |  57H |  | 2.0 | 2.0 | 1.9 | 1.7 |
|  |  |  |  |  |  |  |  58H |  | 1.8 | 1.8 | 1.7 | 1.8 |
|  |  |  |  |  |  |  |  59H |  | 2.0 | 2.0 | 1.9 | 2.0 |

**Table S7b.** The observed and calculated 1H and 13C{1H} NMR isotropic chemical shifts (with respect to TMS, all values in ppm) for the **1c** molecule at 6-31+G(d,p) basis set in the gas phase.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 13C{1H} |  |  | ***1H* NMR** |
|  | Exp. | B3LYP | G96LYP | M06-2X | HF |  |  | Exp. | B3LYP | G96LYP | M06-2X | HF |
|  1C | 131.1 | 131,2 | 129,7 | 143,5 | 132,6 |  |  7H | 7.7 | 7,1 | 6,9 | 6,9 | 7,6 |
|  2C | 130.1 | 129,1 | 127,8 | 141,7 | 130,0 |  |  8H | 7.7 | 7,2 | 7,0 | 7,6 | 7,6 |
|  3C | 114.6 | 110,9 | 107,8 | 127,3 | 115,2 |  |  9H | 7.7 | 7,4 | 7,2 | 7,9 | 7,8 |
|  4C | 127.0 | 120,6 | 117,7 | 136,3 | 124,6 |  |  10H | 7.7 | 7,4 | 7,1 | 8,0 | 7,8 |
|  5C | 127.1 | 120,8 | 117,8 | 136,0 | 125,3 |  |  12H | 5.9 | 5,8 | 5,6 | 6,3 | 5,6 |
|  6C | 113.9 | 108,1 | 105,2 | 122,6 | 112,4 |  |  13H | 5.9 | 4,6 | 4,5 | 4,8 | 4,7 |
|  11C | 55.3 | 54,8 | 56,1 | 55,9 | 49,6 |  |  19H | 7.5 | 10,1 | 9,8 | 10,3 | 10,2 |
|  14C | 124.8 | 122,9 | 122,0 | 137,3 | 120,9 |  |  21H | 6.9 | 7,1 | 6,9 | 7,8 | 7,4 |
|  15C | 130.1 | 126,0 | 123,0 | 142,9 | 131,7 |  |  22H | 6.9 | 6,9 | 6,7 | 7,4 | 7,2 |
|  16C | 131.5 | 133,4 | 129,7 | 151,6 | 140,1 |  |  24H | 4.6 | 4,4 | 4,3 | 4,3 | 4,5 |
|  17C | 114.6 | 113,1 | 111,2 | 127,8 | 113,9 |  |  25H | 4.6 | 3,4 | 3,4 | 3,5 | 3,4 |
|  18C | 113.0 | 107,7 | 105,7 | 122,0 | 109,1 |  |  29H | 7.5 | 7,4 | 7,2 | 8,0 | 7,8 |
|  20C | 160.1 | 157,7 | 156,1 | 172,0 | 159,4 |  |  32H | 3.8 | 3,7 | 3,7 | 3,6 | 3,6 |
|  23C | 50.9 | 54,4 | 55,6 | 55,8 | 49,0 |  |  33H | 3.8 | 4,0 | 3,9 | 4,0 | 3,9 |
|  28C | 142.4 | 128,9 | 120,9 | 146,5 | 149,7 |  |  34H | 3.8 | 3,7 | 3,7 | 3,6 | 3,5 |
|  31C | 52.3 | 54,4 | 55,7 | 54,6 | 49,0 |  |  38H | 3.1 | 3,8 | 3,6 | 4,1 | 3,7 |
|  35C | 34.4 | 37,0 | 39,8 | 33,5 | 28,3 |  |  40H | 2.0 | 1,9 | 1,9 | 1,8 | 1,8 |
|  36C | 25.9 | 29,8 | 31,5 | 27,5 | 24,3 |  |  41H | 2.2 | 2,4 | 2,4 | 2,3 | 2,3 |
|  37C | 25.8 | 29,5 | 31,2 | 27,5 | 24,2 |  |  42H | 2.0 | 1,7 | 1,8 | 1,7 | 1,5 |
|  39C | 17.9 | 21,8 | 23,5 | 19,2 | 17,5 |  |  43H | 2.0 | 2,1 | 2,1 | 2,0 | 1,8 |
|  |  |  |  |  |  |  |  44H | 2.0 | 1,9 | 1,9 | 1,8 | 1,8 |
|  |  |  |  |  |  |  |  45H | 2.2 | 2,1 | 2,1 | 2,1 | 2,1 |
|  |  |  |  |  |  |  |  47H | 11.6 | 10,2 | 9,9 | 9,9 | 10,1 |

|  |  |
| --- | --- |
|  |  |
|  |  |

**Figure S11a.** The comparison of the experimental and calculated13C{1H} and 1H NMR isotropic chemical shifts (with respect to TMS) for **2c** molecule.

|  |  |
| --- | --- |
|  |  |
|  |  |

**Figure S11b.** The comparison of the experimental and calculated13C{1H} and 1H NMR isotropic chemical shifts (with respect to TMS) for **1c** molecule.

**Table S8.** The correlation equations between observed and calculated 1Hand 13C{1H} NMR shifts of the **2c** complex and **1c** ligand.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Phase | Method  | 13C{1H} |  | 1H |
| **2** |
| Gas phase | B3LYP | δexp= 0.9988 δcalc + 0,5811 (R2= 0.9771, S= 7.0142) |  | δexp= 0.8967 δcalc+ 0.4059 (R2= 0.9626, S= 0.4643)  |
| G96LYP | δexp= 1.0439 δcalc - 2.7735 (R2= 0.9776, S= 6.9365) |  | δexp= 0.9251 δcalc+ 0.3474 (R2= 0.9592, S= 0.4849)  |
| M06-2X | δexp= 0.8584 δcalc+ 5.9738 (R2= 0.9830, S= 6.0389) |  | δexp= 0.7962 δcalc+ 0.7325 (R2= 0.9598, S= 0.4817)  |
| HF | δexp= 0.8876 δcalc+ 11.0232(R2= 0.9611, S= 9.1326) |  | δexp= 0.8877 δcalc+ 0.4396 (R2= 0.9592, S= 0.4851) |
|  |  |  |  |  |
| Chloroform | B3LYP | δexp= 1.0025 δcalc - 0.3278 (R2= 0.9798, S= 6.5891) |  | δexp= 0.9386 δcalc+ 0.1728 (R2= 0.9717, S= 0.4042)  |
| G96LYP | δexp= 1.0482 δcalc - 3.9269 (R2= 0.9807, S= 6.4298) |  | δexp= 0.9729 δcalc+ 0.0577 (R2= 0.9712, S= 0.4080)  |
| M06-2X | δexp= 0.8589 δcalc+ 5.3016 (R2= 0.9850, S= 5.6713) |  | δexp= 0.8215 δcalc+ 0.5568 (R2= 0.9678, S= 0.4309)  |
| HF | δexp= 0.8939 δcalc+ 10.0117(R2= 0.9650, S= 8.6709) |  | δexp= 0.8944 δcalc+ 0.3495 (R2= 0.9671, S= 0.4355) |
|  |  |  |  |  |
| **1** |
| Gas phase | B3LYP | δexp= 1.0698 δcalc - 5.0643 (R2= 0.9945, S= 3.5029)  |  | δexp= 0.9648 δcalc+ 0.2998 (R2= 0.9156, S= 0.7847)  |
| G96LYP | δexp= 1.1201 δcalc – 8.4745 (R2= 0.9888, S= 5.0111)  |  | δexp= 1.0077 δcalc+ 0.2011 (R2= 0.9171, S= 0.7779)  |
| M06-2X | δexp= 0.9061 δcalc +1.8404 (R2= 0.9957, S= 3.1092)  |  | δexp= 0.9067 δcalc + 0.4596 (R2= 0.9000, S= 0.8542)  |
| HF | δexp= 0.9608 δcalc+ 4.5408 (R2= 0.9954, S= 3.2021)  |  | δexp= 0.9116 δcalc + 0.5132 (R2= 0.9186, S= 0.7706)  |
|  |  |  |  |  |
| Chloroform | B3LYP | δexp= 1.0591 δcalc - 5.1496 (R2= 0.9985, S= 1.8301)  |  | δexp= 0.9880 δcalc+ 0.1053 (R2= 0.9382, S= 0.6717)  |
| G96LYP | δexp= 1.1177 δcalc - 9.5629 (R2= 0.9949, S= 3.4013)  |  | δexp= 0.9618 δcalc+ 0.2395 (R2= 0.9494, S= 0.6074)  |
| M06-2X | δexp= 0.9090 δcalc +1.1619 (R2= 0.9961. S= 2.9753)  |  | δexp= 0.8697 δcalc + 0.4970 (R2= 0.9258, S= 0.7357)  |
| HF | δexp= 0.9678 δcalc+ 3.7830 (R2= 0.9970. S= 2.6128)  |  | δexp= 0.8802 δcalc + 0.6052 (R2= 0.9522, S= 0.5907)  |