Catalysis Science & Technology

Electronic Supporting Information

Conjugate addition of arylboronic acids to *α,β*-unsaturated carbonyl compounds in aqueous medium using Pd(II) complexes with dihydroxy-2,2´-bipyridine ligands: Homogeneous or heterogeneous nano-catalysis ?

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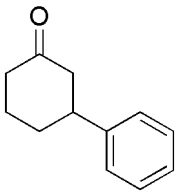
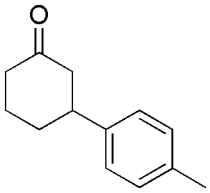
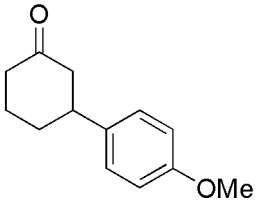
Characterization data of the 1,4-addition products 5aa-ea isolated from the reactions listed in Table 3 of the manuscript:



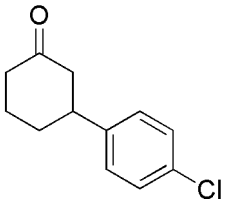
3-Phenylcyclohexanone (5aa):[1] Yellow oil. Yield: 0.075 g (86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78-1.95 (m, 2H), 2.09-2.28 (m, 2H), 2.41-2.62 (m, 4H), 2.95-3.17 (m, 1H), 7.23-7.41 (m, 5H) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 25.5, 32.8, 41.2, 44.8, 49.0, 126.6, 126.7, 128.7, 144.4, 211.0 ppm. GC-MS (EI, 70eV): *m/z* 174 (1%, M^+), 78 (17), 42 (100), 27 (82).



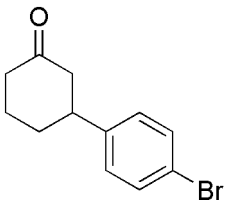
3-(4-Methylphenyl)cyclohexanone (5ab):[2] Yellow oil. Yield: 0.073 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85-1.93 (m, 2H), 2.06-2.21 (m, 2H), 2.36 (s, 3H), 2.44-2.62 (m, 4H), 2.95-3.08 (m, 1H), 7.12-7.20 (m, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 21.0, 25.6, 32.9, 41.2, 44.4, 49.1, 126.4, 129.4, 136.3, 141.4, 211.0 ppm. GC-MS (EI, 70eV): *m/z* 188 (5%, M^+), 131 (16), 91 (14), 42 (100), 27 (81).



3-(4-Methoxyphenyl)cyclohexanone (5ac):[1] Yellow oil. Yield: 0.079 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76-1.90 (m, 2H), 2.07-2.19 (m, 2H), 2.40-2.63 (m, 4H), 2.94-3.03 (m, 1H), 3.82 (s, 3H), 6.87-6.92 (m, 2H), 7.14-7.18 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 25.5, 33.0, 41.2, 44.0, 49.2, 55.3, 114.0, 127.5, 136.6, 158.3, 211.2 ppm. GC-MS (EI, 70eV): *m/z* 204 (5%, M^+), 147 (16), 134 (34), 91 (50), 42 (100).

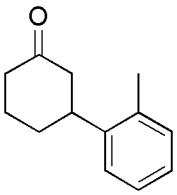


3-(4-Chlorophenyl)cyclohexanone (5ad):[3] Pale yellow oil. Yield: 0.079 g (76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76-1.91 (m, 2H), 2.07-2.27 (m, 2H), 2.36-2.64 (m, 4H), 2.95-3.11 (m, 1H), 7.15-7.22 (m, 2H), 7.30-7.38 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 25.4, 32.7, 41.1, 44.1, 48.8, 127.9, 128.8, 132.4, 142.8, 210.5 ppm. GC-MS (EI, 70eV): *m/z* 208 (1%, M^+), 138 (16), 103 (16), 77 (18), 42 (100).

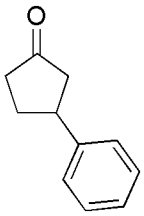


3-(4-Bromophenyl)cyclohexanone (5ae):[4] Yellow oil. Yield: 0.101 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78-1.88 (m, 2H), 2.07-2.23 (m, 2H), 2.38-2.62 (m, 4H), 2.96-3.04 (m, 1H), 7.11 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H),

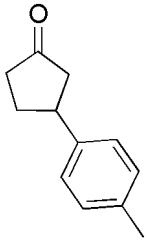
7.47 (d, $^3J_{HH}$ = 8.1 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 25.4, 32.6, 41.1, 44.2, 48.7, 120.4, 128.3, 131.8, 143.3, 210.5 ppm. GC-MS (EI, 70eV): *m/z* 254 (4%, M^+), 252 (4), 182 (19), 115 (24), 103 (26), 77 (32), 42 (100).



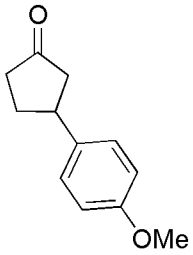
3-(2-Methylphenyl)cyclohexanone (5af):[5] Yellow oil. Yield: 0.073 g (77%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.77-1.93 (m, 2H), 2.02-2.08 (m, 1H), 2.13-2.27 (m, 1H), 2.35 (s, 3H), 2.38-2.58 (m, 4H), 3.18-3.25 (m, 1H), 7.14-7.26 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 19.3, 25.8, 32.0, 40.3, 41.3, 48.4, 125.1, 126.4, 126.5, 130.7, 135.1, 142.3, 211.3 ppm. GC-MS (EI, 70eV): *m/z* 188 (68%, M^+), 173 (17), 145 (100), 131 (85), 117 (58), 91 (33), 42 (23).



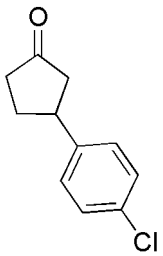
3-Phenylcyclopentanone (5ba):[3] Pale yellow oil. Yield: 0.064 g (80%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.91-2.10 (m, 1H), 2.25-2.57 (m, 4H), 2.62-2.80 (m, 1H), 3.38-3.55 (m, 1H), 7.25-7.45 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 31.2, 38.9, 42.2, 45.8, 126.7, 128.7, 143.1, 218.4 ppm. GC-MS (EI, 70eV): *m/z* 160 (7%, M^+), 104 (28), 77 (24), 42 (68), 28 (100).



3-(4-Methylphenyl)cyclopentanone (5bb):[6] Yellow oil. Yield: 0.075 g (86%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.98-2.07 (m, 1H), 2.28-2.54 (m, 4H), 2.37 (s, 3H), 2.63-2.72 (m, 1H), 3.37-3.48 (m, 1H), 7.18 (s, 4H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 21.0, 31.3, 38.9, 41.9, 45.9, 126.6, 129.3, 136.3, 140.0, 218.7 ppm. GC-MS (EI, 70eV): *m/z* 174 (55%, M^+), 118 (100), 91 (35).

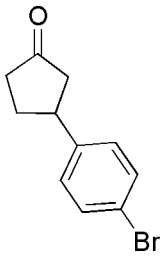


3-(4-Methoxyphenyl)cyclopentanone (5bc):[6] Yellow oil. Yield: 0.086 g (90%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.90-2.05 (m, 1H), 2.27-2.53 (m, 4H), 2.63-2.72 (m, 1H), 3.34-3.46 (m, 1H), 3.83 (s, 3H), 6.90 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.20 (d, $^3J_{HH}$ = 8.7 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 31.4, 38.9, 41.5, 46.0, 55.3, 114.0, 127.6, 135.1, 158.3, 218.7 ppm. GC-MS (EI, 70eV): *m/z* 190 (5%, M^+), 134 (14), 42 (49), 28 (66), 15 (100).

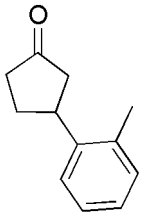


3-(4-Chlorophenyl)cyclopentanone (5bd):[6] Pale yellow oil. Yield: 0.080 g (82%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.90-1.99 (m, 1H), 2.01-2.54 (m, 4H), 2.65-2.74 (m, 1H), 3.36-3.48 (m, 1H), 7.20 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.33 (d, $^3J_{HH}$

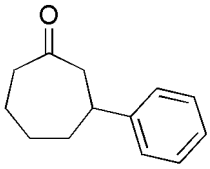
= 8.4 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 31.1, 38.8, 41.6, 45.7, 128.1, 128.8, 132.4, 141.5, 217.8 ppm. GC-MS (EI, 70eV): *m/z* 194 (3%, M^+), 138 (13), 56 (16), 42 (79), 27 (100).



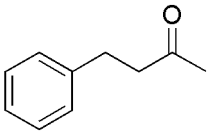
3-(4-Bromophenyl)cyclopentanone (5be):[7] Pale yellow solid. Yield: 0.087 g (73%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.90-2.05 (m, 1H), 2.26-2.54 (m, 4H), 2.63-2.72 (m, 1H), 3.37-3.46 (m, 1H), 7.15 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.48 (d, $^3J_{HH}$ = 8.4 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 31.1, 38.8, 41.7, 45.6, 120.4, 128.5, 131.8, 142.0, 217.8 ppm. GC-MS (EI, 70eV): *m/z* 240 (1%, M^+), 238 (2), 184 (6), 42 (80), 27 (100).



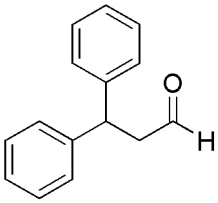
3-(2-Methylphenyl)cyclopentanone (5bf):[7] Pale yellow oil. Yield: 0.069 g (79%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.96-2.10 (m, 1H), 2.19-2.56 (m, 4H), 2.41 (s, 3H), 2.62-2.72 (m, 1H), 3.58-3.78 (m, 1H), 7.15-7.19 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 19.6, 30.1, 38.3, 38.6, 45.3, 124.7, 126.4, 126.5, 130.6, 136.0, 141.0, 218.8 ppm. GC-MS (EI, 70eV): *m/z* 174 (3%, M^+), 117 (17), 91 (11), 42 (43), 27 (100).



3-Phenylcycloheptanone (5ca):[8] Yellow oil. Yield: 0.083 g (88%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.49-1.65 (m, 1H), 1.69-1.79 (m, 2H), 2.00-2.13 (m, 3H), 2.59-2.69 (m, 3H), 2.92-2.95 (m, 2H), 7.18-7.24 (m, 3H), 7.28-7.33 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 24.2, 29.2, 39.2, 42.8, 44.0, 51.3, 126.3, 126.4, 128.6, 146.9, 213.5 ppm. GC-MS (EI, 70eV): *m/z* 188 (2%, M^+), 104 (22), 42 (88), 27 (100).



4-Phenyl-2-butanone (5da):[9] Pale yellow oil. Yield: 0.051 g (69%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H), 2.76-2.82 (m, 2H), 2.90-2.95 (m, 2H), 7.20-7.39 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 29.7, 30.1, 45.2, 126.1, 128.3, 128.5, 141.0, 208.1 ppm. GC-MS (EI, 70eV): *m/z* 148 (92%, M^+), 105 (100), 91 (70), 77 (25), 43 (57).



3,3-Diphenyl-propionaldehyde (5ea):[10] Pale yellow oil. Yield: 0.063 g (60%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.19 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.8

Hz, 2H), 4.66 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.22-7.65 (m, 10H), 9.76 (t, $^{3}J_{HH}$ = 1.8 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$): δ 45.0, 49.4, 128.6, 128.8, 129.2, 143.3, 201.2 ppm. GC-MS (EI, 70eV): *m/z* 210 (14%, M^+), 192 (14), 165 (57), 103 (45), 77 (100), 51 (73), 29 (75).

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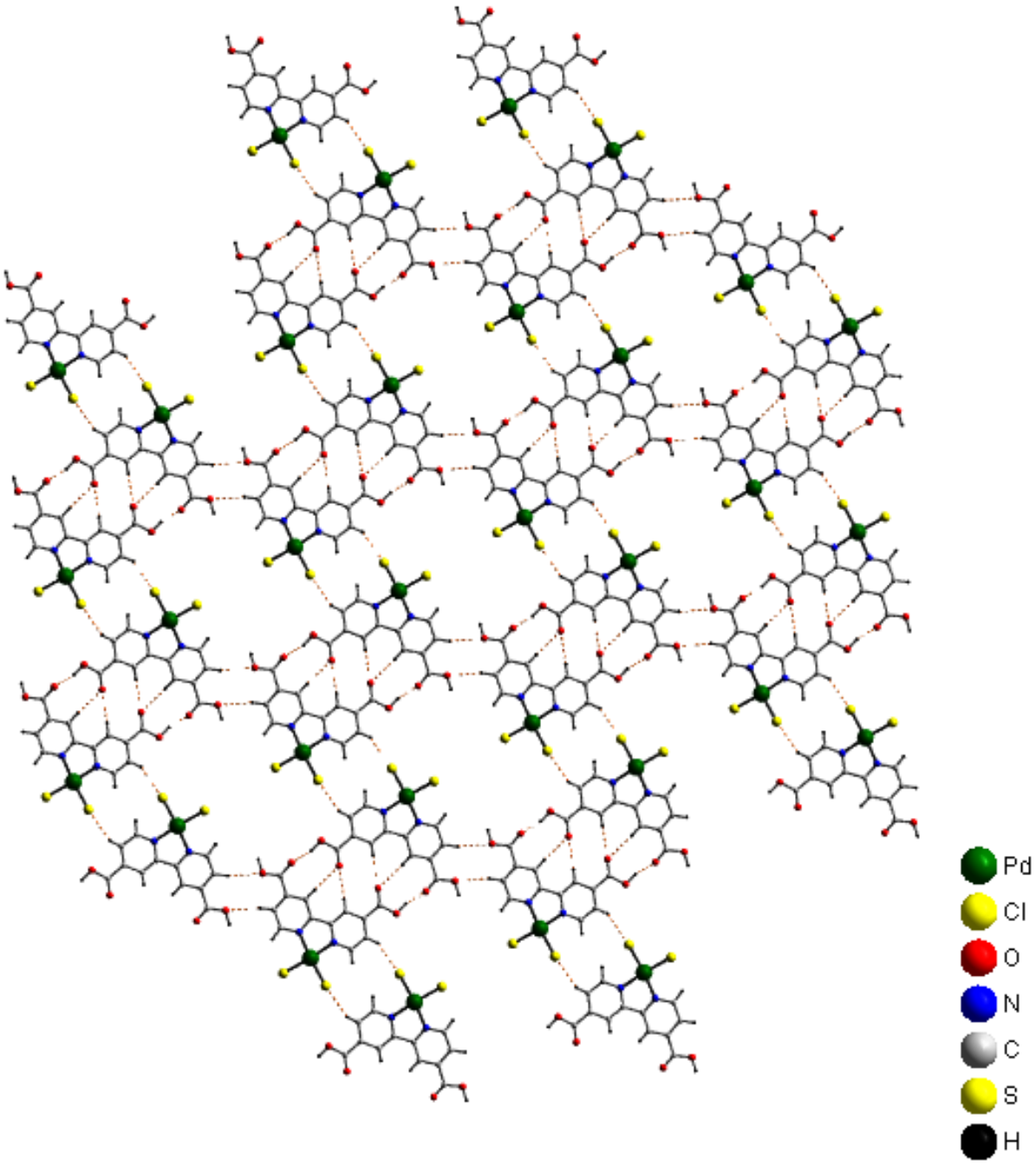

Figure S1. Packing structure of complex **14** showing the hydrogen bonding network. DMSO molecules are excluded.

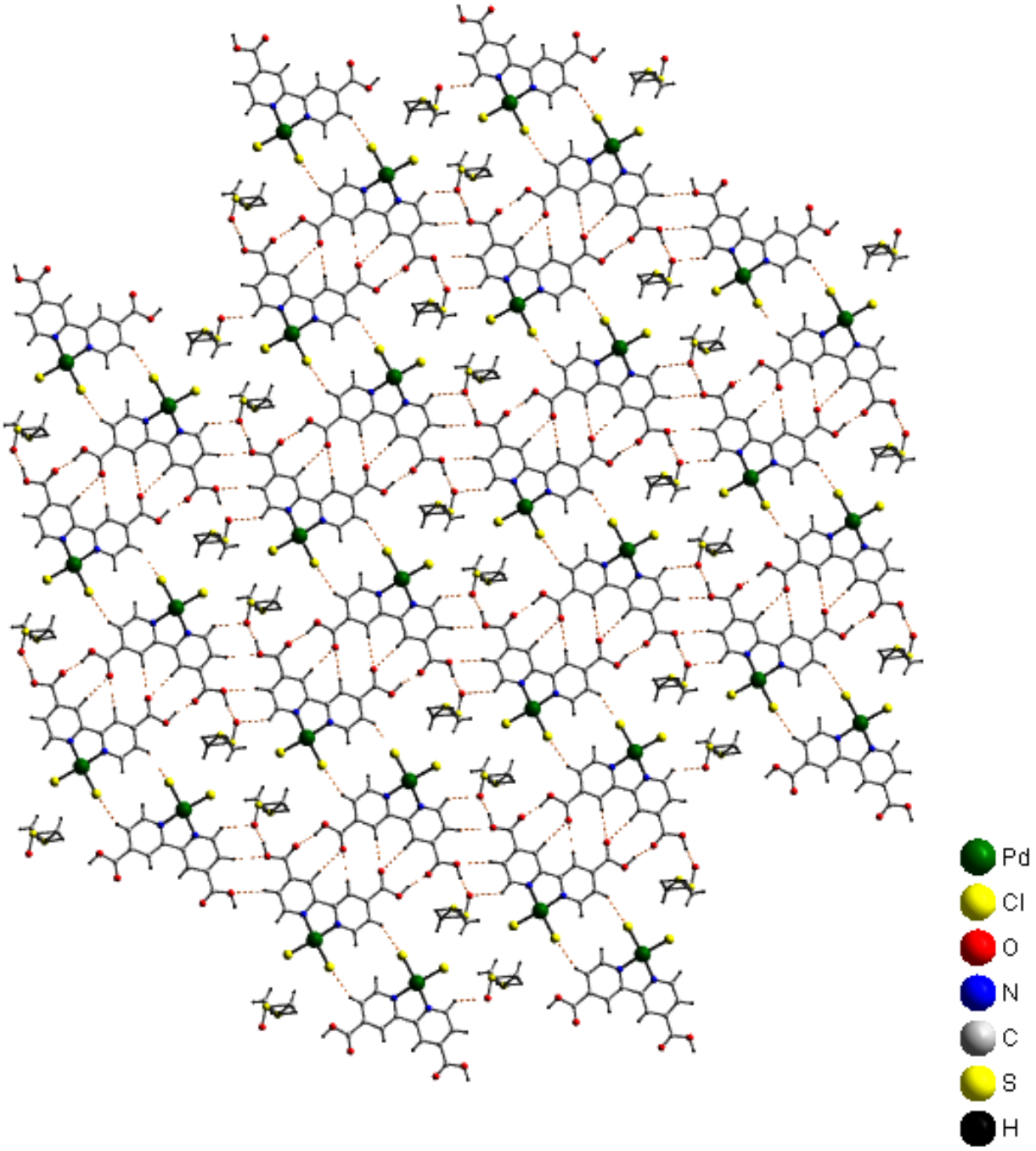

Figure S2. Packing structure of complex **14** including the disordered DMSO molecules.