Figure S2.1.1 Packing diagram illustrating C–H···Br and C–H···Cl hydrogen bonding observed in the crystal lattice of III viewed along a-axis. Hydrogen bond parameters (Å and deg): C(4)–H(4) = 0.929, H(4)···Br(1) = 3.120, C(4)···Br(1) = 3.992, C(4)–H(4)···Br(1) = 157.0; C(14)–H(14) = 0.930, H(4)···Cl(2) = 2.956, C(14)···Cl(2) = 3.992, C(14)–H(14)···Cl(2) = 160.7.
Figure S2.1.2 Packing diagram illustrating C–H⋯Br and N–H⋯Br hydrogen bonding observed in the crystal lattice of VI viewed along a-axis. Hydrogen bond parameters (Å and deg): C(6)–H(6A) = 0.950, H(6A)⋯Br(1) = 2.755, C(6)⋯Br(1) = 3.586, C(6)–H(6A)⋯Br(1) = 146.5; N(6)–H(6) = 0.880, H(6)⋯Br(1) = 2.622, N(6)⋯Br(1) = 3.393, N(6)–H(6)⋯Br(1) = 146.8; N(7)–H(7) = 0.880, H(7)⋯Br(1) = 2.839, N(7)⋯Br(1) = 3.499, N(7)–H(7)⋯Br(1) = 133.0; N(2)–H(2) = 0.880, H(2)⋯Br(2) = 2.641, N(2)⋯Br(2) = 3.441, N(2)–H(2)⋯Br(2) = 151.8; C(35)–H(35) = 0.950, H(35)⋯Br(2) = 2.655, C(35)⋯Br(2) = 3.514, C(35)–H(35)⋯Br(2) = 150.5. On one side, molecule 1 and 2 are linked by a pair of intermolecular N–H⋯Br hydrogen bonding involving Br1 and on the other side two molecules are linked by a C–H⋯Br hydrogen bonding and thus acts as a trifurcated hydrogen bond acceptor whereas Br2 is involved in intramolecular C–H⋯Br hydrogen bonding and thus acts as a bifurcated hydrogen bond acceptor.
Supporting Information

Figure S2.2.1 Packing diagram illustrating N–H···N hydrogen bonding observed in the crystal lattice of $\text{LH}_2^{2,5\text{-xylyl}}$ viewed along $a$-axis. Hydrogen bond parameters (Å and deg): N(2)–H(1) = 0.886, H(1)···N(2) = 2.135, N(2)···N(1) = 3.011, N(2)–H(1)···N(1) = 169.6.
Supporting Information

Figure S2.2.2 Packing diagram illustrating C–H···Cl and N–H···Cl hydrogen bonding observed in the crystal lattice of IX·CHCl₃ viewed along a-axis. Hydrogen bond parameters (Å and deg): C(8)–H(8B) = 0.980, H(8B)···Cl(1) = 2.762, C(8)···Cl(1) = 3.693, C(8)–H(8B)···Cl(1) = 157.0; C(33)–H(33C) = 0.980, H(33C)···Cl(2) = 2.732, C(33)···Cl(2) = 3.673, C(33)–H(33C)···Cl(2) = 161.1; C(51)–H(51) = 0.970, H(51)···Cl(2) = 2.556, C(51)···Cl(2) = 3.463, C(51)–H(51)···Cl(2) = 157.4; N(2)–H(2) = 0.880, H(2)···Cl(1) = 2.752, N(2)···Cl(1) = 3.395, N(2)–H(2)···Cl(1) = 130.9; N(5)–H(5) = 0.880, H(5)···Cl(2) = 2.747, N(5)···Cl(2) = 3.321, N(5)–H(5)···Cl(2) = 124.1. Pair of intra molecular bifurcated and solvent mediated inter and intra molecular trifurcated C–H···Cl and N–H···Cl hydrogen bonding was observed.
Figure S2.2.3 Packing diagram illustrating N–H⋯O and C–H⋯O hydrogen bonding observed in the crystal lattice of X viewed along \( a \)-axis. Hydrogen bond parameters (Å and deg): N(3)–H(3) = 0.859, H(3)⋯O(2) = 2.145, N(3)⋯O(2) = 2.870, N(3)–H(3)⋯O(2) = 141.9; C(28)–H(28) = 0.980, H(28)⋯O(2) = 2.196, C(28)⋯O(2) = 3.166, C(28)–H(28)⋯O(2) = 170.3.
Figure S2.2.4 Packing diagram illustrating N–H···O hydrogen bonding observed in the crystal lattice of XI viewed along $a$-axis. Hydrogen bond parameters (Å and deg): N(3)–H(3) = 0.860, H(3)···O(2) = 2.008, N(3)···O(2) = 2.842, N(3)–H(3)···O(2) = 163.2.
Figure S2.2.5 Packing diagram illustrating N–H···O hydrogen bonding observed in the crystal lattice of XII viewed along $a$-axis. Hydrogen bond parameters (Å and deg): N(2)–H(2) = 0.880, H(2)···O(4) = 1.914, N(2)···O(4) = 2.761, N(2)–H(2)···O(4) = 161.00; N(5)–H(5) = 0.880, H(5)···O(2) = 1.925, N(5)···O(2) = 2.780, N(5)–H(5)···O(2) = 163.3.
Figure S2.2.6 Packing diagram illustrating N–H···O and C–H···F hydrogen bonding observed in the crystal lattice of XII viewed along \(\alpha\)-axis. Hydrogen bond parameters (Å and deg): N(2)–H(2) = 0.88, H(2)···O(2) = 2.045, N(2)···O(2) = 2.836, N(2)–H(2)···O(2) = 149.1; N(2)–H(2) = 0.88, H(2)···O(3) = 1.531, N(2)···O(3) = 1.998, N(2)–H(2)···O(3) = 108.92; C(8)–H(8C) = 0.981, H(8)···F(3) = 2.578, C(8)···F(3) = 3.531, C(8)–H(8C)···F(3) = 164.0.
Figure S2.3.1 Packing diagram illustrating C–H⋯Cl hydrogen bonding observed in the crystal lattice of XIV viewed along a-axis. Hydrogen bond parameters (Å and deg): C(6)–H(6) = 0.950, H(6)⋯Cl(1) = 2.875, C(6)⋯Cl(1) = 3.689, C(6)–H(6)⋯Cl(1) = 144.4; C(8)–H(8C) = 0.980, H(8C)⋯Cl(1) = 2.779, C(8)⋯Cl(1) = 3.529, C(8)–H(8C)⋯Cl(1) = 133.8; C(21)–H(21) = 0.950, H(21)⋯Cl(2) = 2.642, C(21)⋯Cl(2) = 3.467, C(21)–H(21)⋯Cl(2) = 145.4; C(23)–H(23B) = 0.980, H(23B)⋯Cl(2) = 2.641, C(23)⋯Cl(2) = 3.529, C(23)–H(23B)⋯Cl(2) = 120.2. The reference molecule is linked to the adjacent to the molecule related by center of symmetry by a pair of trifurcated C–H⋯Cl hydrogen bonding. The aforementioned pair is linked to the adjacent identical pair by a pair of C–H⋯Cl hydrogen bonding as illustrated in this Figure.
Figure S2.3.2 Packing diagram illustrating C–H···O hydrogen bonding observed in the crystal lattice of XIV viewed along a-axis. Hydrogen bond parameters (Å and deg): C(8)–H(8B) = 0.980, H(8B)···O(1) = 2.621, C(8)···O(1) = 3.572, C(8)–H(8B)···O(1) = 163.6; C(15)–H(15C) = 0.980, H(15C)···O(1) = 2.533, C(15)···O(1) = 3.396, C(15)–H(15C)···O(1) = 146.9. The reference molecule and the inversion related adjacent molecule are linked by a pair of acceptor bifurcated C–H···O hydrogen bonding as illustrated in this Figure.
Figure S2.3.3 Packing diagram illustrating C–H···O hydrogen bonding observed in the crystal lattice of XIV viewed along a-axis. Hydrogen bond parameters (Å and deg): C(15)–H(15C) = 0.980, H(15C)···O(1) = 2.533, C(15)···O(1) = 3.396, C(15)–H(15C)···O(1) = 146.9. The reference molecule and the inversion related adjacent molecule are linked via a pair of C–H···O hydrogen bonding as illustrated in this Figure.
Figure S2.3.4 Packing diagram illustrating C–H⋯Cl hydrogen bonding observed in the crystal lattice of XV. Hydrogen bond parameters (Å and deg). C(13)–H(13) = 0.950, H(13)⋯Cl(12) = 2.847, C(13)⋯Cl(12) = 3.731, C(13)⋯H(13)⋯Cl(12) = 155.2; C(37)–H(37) = 0.950, H(37)⋯Cl(8) = 2.850, C(37)⋯Cl(8) = 3.758, C(37)⋯H(37)⋯Cl(8) = 160.2; C(39)–H(39B) = 0.980, H(39B)⋯Cl(10) = 2.819, C(39)⋯Cl(10) = 3.456, C(39)⋯H(39B)⋯Cl(10) = 123.4; C(50)–H(50) = 1.00, H(50)⋯Cl(3) = 2.871, C(50)⋯Cl(3) = 3.630, C(50)⋯H(50)⋯Cl(3) = 133.3; C(50)–H(50) = 1.00, H(50)⋯Cl(4) = 2.519, C(50)⋯Cl(3) = 2.519, C(50)⋯H(50)⋯Cl(4) = 141.7; C(51)–H(51) = 1.001, H(51)⋯Cl(1) = 2.732, C(51)⋯Cl(1) = 3.453, C(51)⋯H(51)⋯Cl(1) = 129.2; C(51)–H(51) = 1.001, H(51)⋯Cl(2) = 2.585, C(51)⋯Cl(2) = 3.515, C(51)⋯H(51)⋯Cl(2) = 154.6.
**Figure S2.3.5** Packing diagram illustrating C–H···Cl hydrogen bonding observed in the crystal lattice of XV. Hydrogen bond parameters (Å and deg): C(51)–H(51) = 1.001, H(51)···Cl(1) = 2.732, C(51)···Cl(1) = 3.453, C(51)–H(51)···Cl(1) = 129.2; C(51)–H(51) = 1.001, H(51)···Cl(2) = 2.585, C(51)···Cl(2) = 3.515, C(51)–H(51)···Cl(2) = 154.6. Both molecules 1 and 2 are linked to two separate CHCl₃ by a C–H···Cl hydrogen bonding as illustrated in this Figure.
Figure S2.3.6 Packing diagram illustrating C–H···Cl hydrogen bonding observed in the crystal lattice of XVII. Hydrogen bond parameters (Å and deg): C(16)–H(16B) = 0.980, H(16B)···Cl(2) = 2.707, C(16)···Cl(2) = 3.574, C(16)–H(16B)···Cl(2) = 147.8; C(27)–H(27B) = 0.980, H(27B)···Cl(2) = 2.624, C(27)···Cl(2) = 3.225, C(27)···Cl(2) = 3.574, C(27)–H(27B)···Cl(2) = 119.8; C(27)–H(27C) = 0.980, H(27C)···Cl(1) = 2.687, C(27)···Cl(1) = 3.396, C(27)–H(27C)···Cl(1) = 129.6.
Figure S2.3.7 Packing diagram illustrating C–H···O hydrogen bonding observed in the crystal lattice of XVII. Hydrogen bond parameters (Å and deg): C(8)–H(8C) = 0.981, H(8C)···O(1) = 2.470, C(8)···O(1) = 3.443, C(8)–H(8C)···O(1) = 171.4. The reference molecule and the translation related adjacent molecules are linked via a pair of C–H···O hydrogen bonding as illustrated in this Figure.
Figure S2.3.8 Packing diagram illustrating C–H···O, C–H···Cl and N–H···Cl hydrogen bonding observed in the crystal lattice of XVIII. Hydrogen bond parameters (Å and deg). C(26)–H(26C) = 0.980, H(26C)···O(2) = 2.480, C(26)···O(2) = 3.321, C(26)–H(26C)···O(2) = 143.7; C(27)–H(27A) = 0.980, H(27A)···O(2) = 2.521, C(27)···O(2) = 3.348, C(27)–H(27A)···O(2) = 142.1; C(53)–H(53A) = 0.980, H(53A)···O(1) = 2.496, C(53)···O(1) = 3.313, C(53)–H(53A)···O(1) = 140.7; C(54)–H(54C) = 0.980, H(54C)···O(1) = 2.425, C(57)···O(1) = 3.289, C(54)–H(54C)···O(1) = 146.8; C(57)–H(57) = 0.950, H(57)···O(1) = 2.444, C(57)···O(1) = 3.263, C(57)–H(57)···O(1) = 144.3; C(61)–H(61) = 0.950, H(61)···O(2) = 2.594, C(61)···O(2) = 3.250, C(61)–H(61)···O(2) = 126.5; C(35)–H(35B) = 0.980, H(35B)···Cl(4) = 2.691, C(35)–H(35B)···Cl(4) = 148.1; N(2)–H(2) = 0.880, H(2)···Cl(2) = 2.396, N(2)–H(2)···Cl(2) = 148.1; N(5)–H(5A) = 0.880, H(5)···Cl(4) = 2.366, N(5)–H(5A)···Cl(4) = 149.1. Molecules 1 and 2 are linked to each other by a pair of trifurcated acceptor C–H···O hydrogen bonding wherein a pair of DMSO hydrogens and toluene hydrogen act as hydrogen bond donor. The In addition, molecule 1 is stabilised by one C–H···Cl and N–H···Cl hydrogen bonding whereas molecule 2 is also involved in similar type hydrogen bonding except that one chloride is only involved (acceptor bifurcated).
Figure S2.3.9 Packing diagram illustrating C–H···Cl hydrogen bonding observed in the crystal lattice of XVIII. Hydrogen bond parameters (Å and deg). C(4)–H(4) = 0.950, H(4)···Cl(3) = 2.81, C(4)···Cl(3) = 3.626, C(4)–H(4)···Cl(3) = 144.6; C(31)–H(31) = 0.950, H(31)···Cl(3) = 2.755, C(31)···Cl(1) = 3.585, C(31)–H(31)···Cl(1) = 146.1; C(35)–H(35B) = 0.980, H(35B)···Cl(4) = 2.691, C(35)···Cl(4) = 3.561, C(35)–H(35B)···Cl(4) = 148.1.
Figure S2.3.10 $^{195}$Pt-$^1$H NMR spectrum of XIV (85.5 MHz, CDCl$_3$).
Figure S2.3.10 Expansion of the $^{195}$Pt$^1$H NMR spectrum (85.5 MHz, CDCl$_3$) of XIV in –2840 to –3070 ppm region.
Figure S2.3.11 $^{195}\text{Pt}^{1}\text{H}$ NMR spectrum of XV (85.5 MHz, CDCl$_3$).
Figure S2.3.11 Expansion of the $^{195}\text{Pt}\{^{1}\text{H}\}$ NMR spectrum (85.5 MHz, CDCl$_3$) of XV in –2600 to –2860 ppm region.
Figure S2.3.12 $^{195}\text{Pt}^1\text{H}$ NMR spectrum of XVI (85.5 MHz, CDCl$_3$).
Figure S2.3.12 Expansion of the $^{195}$Pt$^{1}$H NMR spectrum (85.5 MHz, CDCl$_3$) of XVI in –2580 to –3240 ppm region.
Figure S2.3.13 $^{195}$Pt$^{11}$NMR spectrum of XVII (85.5 MHz, CDCl$_3$).
Supporting Information

Figure S2.3.13 Expansion of the $^{195}$Pt($^1$H) NMR spectrum (85.5 MHz, CDCl$_3$) of XVII in –2740 to –3170 ppm region.
Figure S2.3.14 $^{195}$Pt{$^1$H} NMR spectrum of XVIII (85.5 MHz, CDCl$_3$).
Supporting Information

**Figure S2.3.14** Expansion of the $^{195}\text{Pt}^{{}^1\text{H}}$ NMR spectrum (85.5 MHz, CDCl$_3$) of XVIII in –2780 to –3000 ppm region.
Figure S2.3.15 Packing diagram illustrating C–H···Cl hydrogen bonding observed in the crystal lattice of XX. Hydrogen bond parameters (Å and deg). C(22)–H(22A) = 0.981, H(22)···Cl(1) = 2.731, C(22)···Cl(1) = 3.677, C(22)–H(22A)···Cl(1) = 162.4; C(24)–H(24B) = 0.981, H(24B)···Cl(1) = 2.614, C(24)···Cl(1) = 3.282, C(24)–H(24B)···Cl(1) = 125.5. The reference molecule and inversion related adjacent molecule are linked by a pair of C–H···Cl hydrogen bonding wherein the chloride is a bifurcated acceptor simultaneously involved in intermolecular/intramolecular C–H···Cl hydrogen bonding as illustrated in this Figure.
**Figure S2.3.16** Packing diagram illustrating N–H···O, C–H···O and C–H···Cl hydrogen bonding observed in the crystal lattice of XX. Hydrogen bond parameters (Å and deg). N(3)–H(3) = 1.06, H(3)···O(1) = 1.910, N(3)···O(1) = 2.761, N(3)–H(3)···O(1) = 134.7; C(24)–H(24C) = 0.980, H(24C)···O(1) = 2.289, C(24)···O(1) = 3.202, C(24)–H(24C)···O(1) = 154.6; C(4)–H(4) = 0.949, H(4)···Cl(1) = 2.807, C(4)···Cl(1) = 3.521, C(4)–H(4)···Cl(1) = 132.8. The pair of centrosymmetrically related molecules are related by a pair of C–H···O hydrogen bonding and this pair is connected to the adjacent identical pair by pair of C–H···Cl hydrogen bonding. The molecule is also stabilised by intramolecular N–H···O hydrogen bonding.
Figure S2.3.17 Packing diagram illustrating C–H⋯Cl hydrogen bonding observed in the crystal lattice of XXIII. Hydrogen bond parameters (Å and deg). C(22)–H(22C) = 0.980, H(22C)⋯Cl(1) = 2.824, C(22)⋯Cl(1) = 3.640, C(22)–H(22C)⋯Cl(1) = 141.3; C(23)–H(23B) = 0.980, H(23B)⋯Cl(1) = 2.824, C(23)⋯Cl(1) = 3.454, C(23)–H23B)⋯Cl(1) = 122.7; C(24)–H(24C) = 0.980, H(24)⋯Cl(1) = 2.860, C(24)⋯Cl(1) = 3.661, C(24)–H24C)⋯Cl(1) = 139.5. The reference molecule and the inversion related adjacent molecule are related by a pair of intermolecular C–H⋯Cl hydrogen bonding and one intramolecular C–H⋯Cl hydrogen bonding and in these interactions, the role of chloride is an acceptor trifurcated.
Supporting Information

**Figure S2.3.18** Packing diagram illustrating N–H···O and C–H···O hydrogen bonding observed in the crystal lattice of XXIII. Hydrogen bond parameters (Å and deg). N(3)–H(3) = 0.88, H(3)···O(3) = 2.054, N(3)···O(3) = 2.841, N(3)–H(3)···O(3) = 148.4; C(13)–H(13) = 0.950, H(13)···O(3) = 2.393, C(13)···O(3) = 3.324, C(13)–H(13)···O(3) = 166.4; C(26)–H(26A) = 0.980, H(26A)···O(4) = 2.447, C(26)···O(4) = 3.395, C(26)–H(26A)···O(4) = 162.7. The carbonyl oxygen of the acetate moiety acts as a bifurcated acceptor for intramolecular N–H···O and intermolecular C–H···O hydrogen bonding with the inversion related adjacent molecule. The reference molecule is also linked to DMSO via intermolecular C–H···O hydrogen bonding.
Figure S.3.19 $^{195}$Pt{$^1$H} NMR spectrum of XX (85.5 MHz, CDCl$_3$).
Supporting Information

Figure S2.3.19 Expansion of the $^{195}$Pt$^{('1}H)$ NMR spectrum (85.5 MHz, CDCl$_3$) of XX in $-2600$ to $-2860$ ppm region.
**Figure S2.3.20** $^{195}\text{Pt}^1\text{H}$ NMR spectrum of XXI (85.5 MHz, CDCl$_3$).
Figure S2.3.20 Expansion of the $^{195}\text{Pt} \{^1\text{H}\}$ NMR spectrum (85.5 MHz, CDCl$_3$) of XXI in –2450 to –3150 ppm region.
Figure S2.3.21 $^{195}\text{Pt}(^{1}H)$ NMR spectrum of XXII (85.5 MHz, CDCl$_3$).
Figure S2.3.21 Expansion of the $^{195}$Pt-$^{1}$H NMR spectrum (85.5 MHz, CDCl$_3$) of XXII in –1100 to –5000 ppm region.
Figure S2.3.22 $^{195}\text{Pt}^{\{1\}^1\text{H}}$ NMR spectrum of XXIII (85.5 MHz, CDCl$_3$).
Figure S2.3.22 Expansion of the $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum (85.5 MHz, CDCl$_3$) of XXIII in –2500 to –3020 ppm region.
Figure S2.3.23 $^{195}$Pt{$^1$H} NMR spectrum of XXIV (85.5 MHz, CDCl$_3$).
Figure S2.3.23 Expansion of the $^{195}\text{Pt}^{\text{1H}}$ NMR spectrum (85.5 MHz, CDCl$_3$) of XXIV in –2500 to –3500 ppm region.