Supplementary Materials



Figure S1. ¹H-NMR and ¹³C-NMR spectra of *1-adamantyl bromomethyl ketone* (1).



Figure S2. Cont.



Figure S2. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl benzoate* (2a).



Figure S3. Cont.



Figure S3. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 2-chlorobenzoate* (**2b**).



Figure S4. Cont.







Figure S4. ¹H-NMR, ¹³C-NMR and FTIR spectra of 2-(Adamantan-1-yl)-2-oxoethyl 3-chlorobenzoate (2c).



Figure S5. Cont.



Figure S5. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 4-chlorobenzoate* (**2d**).



Figure S6. Cont.





Figure S6. Cont.



Figure S6. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 2,4-dichlorobenzoate* (**2e**).



Figure S7. Cont.



Figure S7. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 2-methylbenzoate* (**2f**).



Figure S8. Cont.

2-(Adamantan-1-yl)-2-oxoethyl 3-methylbenzoate (2g)/ADA_7_1H



Figure S8. Cont.



Figure S8. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 3-methylbenzoate* (**2g**).



Figure S9. Cont.



Figure S9. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 4-methylbenzoate* (**2h**).



Figure S10. Cont.



Figure S10. Cont.



Figure S10. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 2-methoxybenzoate* (**2i**).



Figure S11. Cont.

2-(Adamantan-1-yl)-2-oxoethyl 3-methoxybenzoate (2j)/ADA_10_13C



Figure S11. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 3-methoxybenzoate* (**2j**).



Figure S12. Cont.



Figure S12. Cont.



Figure S12. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 4-methoxybenzoate* (**2k**).



Figure S13. Cont.



Figure S13. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 2-nitrobenzoate* (**2l**).



Figure S14. Cont.







Figure S14. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 3-nitrobenzoate* (**2m**).



Figure S15. Cont.



Figure S15. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 4-nitrobenzoate* (**2n**).



Figure S16. Cont.







Figure S16. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(adamantan-1-yl)-2-oxoethyl 2-aminobenzoate* (**20**).



Figure S17. Cont.



Figure S17. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(adamantan-1-yl)-2-oxoethyl 3-aminobenzoate* (**2p**).



Figure S18. Cont.



Figure S18. Cont.



Figure S18. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(adamantan-1-yl)-2-oxoethyl 4-aminobenzoate* (**2q**).



Figure S19. Cont.



Figure S19. ¹H-NMR, ¹³C-NMR and FTIR spectra of *2-(Adamantan-1-yl)-2-oxoethyl 2-pyridinecarboxylate* (**2r**).

Compound	1 (Room Temp.)	1 (100 K)
CCDC deposition number	-	-
Molecular formula	C ₁₂ H ₁₇ BrO	C ₁₂ H ₁₇ BrO
Molecular weight	257.16	257.16
Crystal system	Triclinic	Orthorhombic
Space group	$P\overline{1}$	Pbca
<i>a</i> (Å)	10.5193 (9)	9.8717 (19)
<i>b</i> (Å)	10.8581 (10)	9.8637 (19)
<i>c</i> (Å)	10.9011 (10)	21.948 (4)
α (°)	107.700 (1)	90
β (°)	90.888 (1)	90
γ (°)	104.295 (1)	90
$V(Å^3)$	1143.90 (18)	2137.1 (7)
Ζ	4	8
D_{calc} (g·cm ⁻³)	1.242	1.327
Crystal dimensions (mm)	$0.48 \times 0.36 \times 0.19$	$0.48 \times 0.36 \times 0.19$
$\mu (mm^{-1})$	3.56	3.81
T_{min}/T_{max}	0.102/0.168	0.086/ 0.155
Reflections measured	32783	11117
Ranges/indices (h, k, l)	-14, 14; -14, 14; -14, 14	-11, 13; -14, 13; -31, 19
θ limit (°)	2.0-28.7	1.9-30.3
Unique reflections	5882	3163
Observed reflections $[I > 2\sigma(I)]$	3633	2231
Parameters	253	127
Restraints	0	0
Goodness of fit on F^2	1.02	1.02
$R_1, wR_2 [I \ge 2\sigma(I)]$	0.054, 0.182	0.040, 0.099

 Table S1. Crystal data and parameters for structure refinement for 1.

Compound	2a	2b	2c	2d	2e	2f	2g	2h
CCDC deposition number	1030854	1030855	1030856	1030857	1030858	1030859	1030860	1030861
Molecular formula	$C_{19}H_{22}O_3$	$C_{19}H_{21}ClO_3$	$C_{19}H_{21}ClO_3$	$C_{19}H_{21}ClO_3$	$C_{19}H_{20}Cl_2O_3$	$C_{20}H_{24}O_3$	$C_{20}H_{24}O_3$	$C_{20}H_{24}O_3$
Molecular weight	298.37	332.81	332.81	332.81	367.25	312.39	312.39	312.39
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P\overline{1}$	$P2_{1}/n$	$P2_{1}/n$
<i>a</i> (Å)	9.7090 (9)	9.9165 (14)	15.0265 (11)	12.7776 (18)	13.5955 (10)	9.7213 (8)	14.881 (3)	8.9059 (9)
<i>b</i> (Å)	10.1224 (9)	26.0610 (4)	6.4316 (5)	6.4887 (9)	10.0877 (8)	10.0095 (8)	6.4393 (12)	6.4556 (7)
<i>c</i> (Å)	17.7587 (16)	13.6754 (19)	19.4135 (11)	19.8490 (3)	26.5950 (3)	18.9536 (13)	18.255 (3)	29.368 (3)
α (°)	77.035 (2)	90	90	90	90	75.912 (2)	90	90
β (°)	77.876 (2)	109.437 (2)	118.792 (4)	90.267 (2)	104.881 (2)	84.644 (2)	108.018 (3)	97.593 (2)
γ (°)	71.659 (2)	90	90	90	90	73.022 (1)	90	90
$V(Å^3)$	1596.0 (3)	3332.8 (8)	1644.3 (2)	1645.7 (4)	3525.1 (6)	1710.4 (2)	1663.4 (5)	1673.6 (3)
Ζ	4	8	4	4	8	4	4	4
D_{calc} (g·cm ⁻³)	1.242	1.327	1.344	1.343	1.384	1.213	1.247	1.24
Crystal dimensions (mm)	$1.42\times0.33\times0.32$	$0.51 \times 0.15 \times 0.11$	$0.60 \times 0.51 \times 0.21$	$0.48 \times 0.33 \times 0.11$	$0.66 \times 0.12 \times 0.06$	$0.57 \times 0.42 \times 0.14$	$0.32 \times 0.18 \times 0.08$	$0.64 \times 0.35 \times 0.29$
μ (mm ⁻¹)	0.08	0.24	0.25	0.25	0.38	0.08	0.08	0.08
T_{min}/T_{max}	0.892/0.974	0.888/0.974	0.866/0.950	0.891/0.975	0.788/0.978	0.956/0.989	0.974/0.993	0.958/0.988
Reflections measured	26726	45418	20743	14606	51013	27531	14965	12089
Dangas/indians (h. h.)	-12, 12; -13, 13;	-13, 13; -36, 36;	-22, 22; -9, 8;	-16, 16; -8, 8;	-15, 16; -11, 11;	-11, 11; -12, 12;	-19, 19; -8, 8:	-10, 10; -7, 7;
Ranges/matces (n, k, l)	-22, 23	-19, 19	-28, 28	-25, 25	-31, 31	-23, 23	-23, 23	-35, 36
θ limit (°)	2.4-27.4	2.4-20.2	2.4–29.1	3.2-23.3	2.5-19.0	2.2-27.8	2.9-22.0	2.8-23.6
Unique reflections	7315	9729	5669	3793	6190	6684	3801	3232
Observed reflections $[I > 2\sigma(I)]$	5306	4193	3551	2541	3574	4845	2057	2301
Parameters	561	497	208	208	433	581	209	209
Restraints	0	0	0	0	0	72	0	0
Goodness of fit on F^2	1.03	1.01	1.03	1.04	1.04	1.03	1.02	1.07
$R_1, wR_2 [I \ge 2\sigma(I)]$	0.065, 0.242	0.063, 0.216	0.050, 0.168	0.046, 0.148	0.081, 0.280	0.065, 0.218	0.045, 0.154	0.044, 0.131

 Table S2. Crystal data and parameters for structure refinement for 2(a-h).

Compound	2i	2j	2k	21	2n	20	2p	2r
CCDC deposition number	1030862	1030863	1030864	1030865	1030866	1030867	1030868	1030869
Molecular formula	C20H24O4	C20H24O4	C20H24O4	C19H21NO5	C19H21NO5	C19H21NO3	C19H23NO3	C18H21NO3
Molecular weight	328.39	328.39	328.39	343.37	343.37	311.37	313.38	299.36
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\overline{1}$	$P2_{1}/n$	$P2_{1}/n$	$P\overline{1}$	$P2_{1}/c$	$P2_{1}/c$	$Pca2_1$	$P2_{1}/n$
<i>a</i> (Å)	7.9923 (4)	6.4434 (7)	9.4908 (9)	7.3004 (5)	12.8819 (9)	6.4577 (9)	10.5404 (14)	12.6664 (17)
<i>b</i> (Å)	10.6701 (6)	17.725 (2)	6.4798 (6)	10.4009 (7)	6.4845 (5)	26.664 (4)	18.371 (3)	6.6858 (9)
<i>c</i> (Å)	20.1249 (11)	14.9809 (17)	28.343 (3)	24.1685 (16)	20.0028 (13)	9.9048 (14)	8.3774 (11)	19.333 (3)
α (°)	90.813 (1)	90	90	90.137 (1)	90	90	90	90
β (°)	92.969 (1)	97.771 (2)	99.060 (2)	94.274 (1)	90.628 (1)	107.399 (3)	90	105.455 (2)
γ (°)	90.557 (1)	90	90	110.405 (1)	90	90	90	90
$V(Å^3)$	1713.65 (16)	1695.3 (3)	1721.3 (3)	1714.4 (2)	1670.8 (2)	1627.5 (4)	1622.1 (4)	1578.0 (4)
Ζ	4	4	4	4	4	4	4	4
$D_{calc} \left(\mathrm{g} \cdot \mathrm{cm}^{-3} \right)$	1.273	1.287	1.267	1.33	1.365	1.271	1.283	1.26
Crystal dimensions (mm)	$0.55 \times 0.44 \times 0.36$	$0.87 \times 0.59 \times 0.40$	$0.54 \times 0.42 \times 0.37$	$0.57 \times 0.41 \times 0.22$	$0.71 \times 0.51 \times 0.34$	$0.26 \times 0.20 \times 0.08$	$0.55 \times 0.27 \times 0.07$	$0.56 \times 0.35 \times 0.10$
μ (mm ⁻¹)	0.09	0.09	0.09	0.10	0.10	0.09	0.09	0.09
T_{min}/T_{max}	0.954/0.969	0.927/0.965	0.955/0.969	0.947/0.980	0.933/0.967	0.978/0.993	0.954/0.994	0.954/0.991
Reflections measured	47595	11481	10969	24440	22905	11958	11421	11552
	-12, 12; -16, 16;	-7, 7; -14, 21;	-11, 11; -7, 5;	-9, 8; -12, 12;	-15, 15; -8, 8;	-7, 7; -31, 31;	-13, 12; -22, 22;	-15, 15; -6, 8;
Ranges/Indices (n, κ, l)	-30, 30	-18, 18	-34, 31	-29, 29	-24, 24	-11, 11	-10, 10	-23, 23
θ limit (°)	2.7-31.0	2.7-25.5	2.2-27.6	3.0-25.8	2.6-26.0	2.6-27.4	2.2-22.1	3.3-21.8
Unique reflections	12842	3309	3359	6664	3317	2856	3191	3116
Observed reflections	7500	2555	2400	5100	2796	1720	2(02	1507
$[I > 2\sigma(I)]$	/398	2555	2499	5100	2780	1720	2602	1597
Parameters	435	300	238	489	226	245	216	399
Restraints	0	0	0	0	0	24	1	65
Goodness of fit on F^2	1.03	1.06	1.04	1.03	1.03	1.03	1.02	1.03
$R_1, wR_2 [I \ge 2\sigma(I)]$	0.060, 0.212	0.042, 0.114	0.054, 0.177	0.051, 0.172	0.042, 0.126	0.061, 0.200	0.041, 0.105	0.051, 0.188

Table S3. Crystal data and parameters for structure refinement for 2(i–l, n, o, p and r).



Figure S20. The molecular structures of 1 (polymorph a and b) with atom numbering schemes and 50% probability displacement ellipsoids.



Figure S21. The molecular structures of **2**(**a**–**h**) with atom numbering schemes and 20% probability displacement ellipsoids. Hydrogen atoms for disordered structure (**2a**, **2b** and **2f**) were omitted for clarity.



Figure S22. The molecular structures of 2(i-l, n, o, p and r) with atom numbering schemes and 20% probability displacement ellipsoids. Hydrogen atoms for disordered structure 2(j-l, o and r) were omitted for clarity.



Figure S23. (a) Partial packing diagram of **2a** shows hydrogen-bonded column along *a*-axis (blue dashed lines indicated the tetramer hydrogen bonds whereas orange dashed lines indicated the hydrogen bonds that link the sets of tetramer into [100] column); (b) Partial packing diagram of **2r** view along *c*-axis. In the crystal packing of **2a**, molecules *A* and *B* are linked into tetramers via weak intermolecular C18A—H18A…O3B and C18B—H18B…O2A hydrogen bonds; these tetramers were further connected into columns along [100] direction via another weak intermolecular C12A—H12A…O2B hydrogen bond (**2a** in Figure 2). In the crystal of **2r**, molecules are linked into centrosymmetric dimers via a weak C17—H17A…O2 hydrogen bond. Similar to those one-dimensional hydrogen-bonded pattern found in compound **2a**, the dimers are also linked into columns along [010] direction via weak intermolecular C7—H7A…O3 and C18—H18A…O1 hydrogen bonds.



Figure S24. Partial packing diagram of **2b** viewed along the c-axis showing a single [100] chain. In the crystal of **2b**, molecules are connected in an alternate pattern, ...*ABAB*... pattern into infinite linear chain, running along the *a*-axis via weak intermolecular C12A—H12B····O2B and C12B—H12C···O2A hydrogen bonds.



Figure S25. Packing diagrams of (a) 2c; (b) 2d viewed along *b*-axis. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. Compounds 2c and 2d exhibit crystal packing with 2D structural similarity which parallel to *bc*-plane.



Figure S26. Partial packing diagram of **2e** showing a [010] chain (blue dashed lines indicated hydrogen bonds and short contacts are represented by violet dashed lines). There is no significant hydrogen bond observed in the crystal of **2c**. In the crystal of **2d**, the molecules are linked into centrosymmetric dimers via weak intermolecular C15—H15A···O3 hydrogen bond. In the crystal of **2e**, molecules *B* are linked into 1D chains via weak intermolecular C12B—H12C···O2B hydrogen bonds, propagating along *b*-axis, together with short intermolecular C11A···O1B contacts of 3.028(10) and 3.270(10) Å in between molecules *A* and *B*.



Figure S27. Partial packing diagram of **2f** with a *...ABAB...* pattern, viewed along the (**a**) *c*-; and (**b**) *a*-axes. In the crystal of **2f**, molecules are linked into 1D chain in a *...ABAB...* pattern along [010] via weak C12A—H12A····O2B and C12B—H12D····O2A hydrogen bonds. Atom O2A acts as a bifurcated hydrogen bond acceptor and link 1D chains into 2D (001) plane.



Figure S28. Packing diagrams of (a) 2g; (b) 2h viewed along *b*-axis. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. No significant hydrogen bonding has been observed in 2g, whereas molecules of 2h are linked into dimers by weak C18—H18A…O2 hydrogen bond.



Figure S29. Packing diagrams of **2i** viewed along *a*-axis. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. In the crystal of **2i**, molecules *A* and *B* are linked into 1D chain along *b*-axis via weak intermolecular C12A—H12A…O2B and C12B—H12C…O4A hydrogen bonds.



Figure S30. Partial packing diagram of **2j** forming a zigzag chain. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. In the crystal of **2j**, molecules are connected into infinite zigzag chains, running along [101] direction via weak intermolecular C20—H20A…O2 hydrogen bond.



Figure S31. Packing diagrams of (a) $2\mathbf{k}$ and (b) C—H··· π interaction viewed along *b*-axis. Hydrogen atoms which are not involved in hydrogen bonds were omitted for clarity. There is no significant hydrogen bond found in $2\mathbf{k}$, however, C—H··· π (C14-C19) interaction connects molecules into dimer-like motifs stacked along *b*-axis which is similar to $2\mathbf{h}$.



Figure S32. Partial packing diagram of 2l viewed along (a) *a*- and (b) *c*-axes. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. In the crystal of 2l, molecule *A* and *B* are linked into 1D chain with ...*ABAB*... pattern via weak intermolecular C18A—H18A…O2B and C12B—H12C…O2A hydrogen bonds (a). This 1D chain is linked into a 2D plane parallel to *ab*-plane through weak intermolecular C18A—H18A…O2B hydrogen bond (b).



Figure S33. A 1D chain formed in the crystal packing of **2n**. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. In the crystal of **2n**, weak C16—H16…O4 and C19—H19…O3 hydrogen bonds link the molecules into a [110] chain comprised of R_2^2 (10) dimers.



Figure S34. Partial packing diagram of 20 viewed along the (a) a-; and (b) b-axes. Hydrogen atoms that are not involved in hydrogen bonds were omitted for clarity. In the crystal of 20, atom O2 acts as bifurcated acceptor and it was linked to two adjacent molecules via weak C12—H12B···O2 and N1—H1N1···O2 hydrogen bonds into 2D layers parallel to (010) plane.



Figure S35. Partial packing diagram of 2p which forms infinites linear chain along *c*-axis. Hydrogen atoms that not involved in hydrogen bonds were omitted for clarity. In the crystal of 2p, molecules are linked into 1D chains via strong intermolecular N1—H1N1…O3 hydrogen bond, propagating along the *c*-axis.

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Table S4. Hydrogen bond geometries for 2(a–l, n, o, p and r).

 $^{1}Cg1$ is the centroid of C14—C19 ring.

CCDC Reference Code	Systematic Name		
AZULUD	2-(4-Chlorophenyl)-2-oxoethyl 4-hydroxybenzoate		
CIQNEW	Benzoylmethyl 4-methoxybenzoate		
CIXVUC	2-(4-Bromophenyl)-2-oxoethyl 3-chlorobenzoate		
CIXWAJ	2-(4-Bromophenyl)-2-oxoethyl 2,4-dichlorobenzoate		
CIXWEN	2-(4-Bromophenyl)-2-oxoethyl 2-aminobenzoate		
CIXWIR	2-(4-Bromophenyl)-2-oxoethyl 3-aminobenzoate		
CIYCAQ	2-(4-Bromophenyl)-2-oxoethyl 2-nitrobenzoate		
CIYCEU	2-(4-Bromophenyl)-2-oxoethyl 3-nitrobenzoate		
CIYCIY	2-(4-Bromophenyl)-2-oxoethyl 4-nitrobenzoate		
CIYCOE	2-(4-Bromophenyl)-2-oxoethyl 4-aminobenzoate		
CIYFUN	2-(4-bromophenyl)-2-oxoethyl benzoate		
CIYGAU	2-(4-bromophenyl)-2-oxoethyl 2-chlorobenzoate		
EVAFOX	2-(4-Bromophenyl)-2-oxoethyl 4-bromobenzoate		
EVAJAN	2-(4-Chlorophenyl)-2-oxoethyl 3-(trifluoromethyl)benzoate		
EVAJIV	2-(4-Chlorophenyl)-2-oxoethyl 2,4-difluorobenzoate		
EVAZEH	2-(4-Chlorophenyl)-2-oxoethyl 2-methoxybenzoate		
EVEGIW	2-(4-Bromophenyl)-2-oxoethyl 4-chlorobenzoate		
EVEGOC	2-(4-Bromophenyl)-2-oxoethyl 2-methoxybenzoate		
EVEVEH	2-(4-Chlorophenyl)-2-oxoethyl benzoate		
GARCEJ	2-(4-Fluorophenyl)-2-oxoethyl 2-methoxybenzoate		
GITHUN	Benzoylmethyl 4-chlorobenzoate		
MANGIR	Phenacyl 5-bromo-2,3,4-trimethylbenzoate		
OBOYIP	2-(4-Bromophenyl)-2-oxoethyl 4-methylbenzoate		
OCAKUA	2-(4-Chlorophenyl)-2-oxoethyl 3,4-dimethoxybenzoate		
OCAQUG	2-(2,4-Dichlorophenyl)-2-oxoethyl 4-methoxybenzoate		
OCEFEJ	2-(4-Fluorophenyl)-2-oxoethyl 4-methoxybenzoate		
PECZAA	2-(4-Methylphenyl)-2-oxoethyl 3-bromobenzoate		
PODQIK	2-(4-chlorophenyl)-2-oxoethyl 3-methylbenzoate		
PODRAD	2-(4-chlorophenyl)-2-oxoethyl 3-nitrobenzoate		
USIWID	2-Oxo-2-phenylethyl benzoate		
USIWOJ	2-(4-Bromophenyl)-2-oxoethyl 4-methoxybenzoate		
VOBYUI	2-(4-Chlorophenyl)-2-oxoethyl 2-chlorobenzoate		
YAFWEJ	2-(4-Fluorophenyl)-2-oxoethyl 3-(trifluoromethyl)benzoate		
YAFZAI	2-(4-Bromophenyl)-2-oxoethyl 4-hydroxybenzoate		
YAHGUL	2-(4-Chlorophenyl)-2-oxoethyl 4-methylbenzoate		
YAHYOX	2-(4-Bromophenyl)-2-oxoethyl 2-methylbenzoate		

Table S5. CCDC reference code and its systematic name of reported compounds.