**Electronic Supplementary Information**

# Exploring intermolecular contacts in multi-substituted benzaldehyde derivatives: X-ray, Hirshfeld surface and Lattice energy analyses

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**Table S1.** Table showing relationship between AA-CLP, DFT total energy ($E_{tot}$) calculations and thermal strengths of the title compounds.

| Compound | $E_{Ele}$ | $E_{Pol}$ | $E_{Disp}$ | $E_{Ex-rep}$ | $E_{Tot}$ | $E_{Tot}$ [a] | $E_{Tot}$ [b] | Temp. / °C |
|---|---|---|---|---|---|---|---|---|
| **1** | -28.1 | -19.2 | -126.4 | 50.6 | -126.3 | -48.9 | -56.4 | 52 |
| **2** | -20.2 | -25.2 | -136.1 | 50.7 | -130.8 | -39.7 | -48.1 | 69 |
| **3** | -16.0 | -16.8 | -148.6 | 59.0 | -122.4 | -32.2 | -40.4 | 79 |
| **4** | -23.5 | -18.4 | -137.2 | 51.1 | -127.9 | -36.6 | -44.8 | 70 |
| **5** | -20.6 | -14.1 | -156.2 | 65.0 | -125.8 | -25.9 | -35.0 | 100 |
| **6** | -23.5 | -20.1 | -101.9 | 51.3 | -94.20 | -45.4 | -56.3 | 67 |

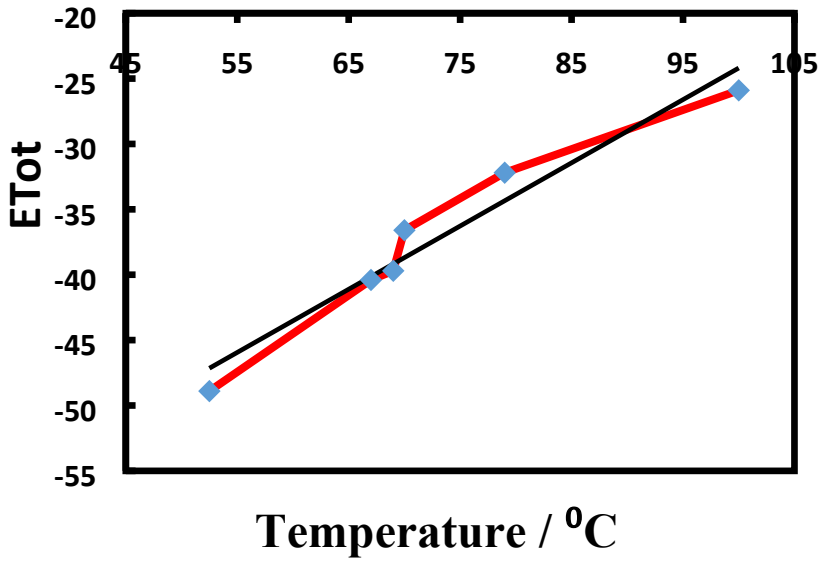


**Fig. S1.** Showing a direct relationship between DFT total energy ($E_{tot}$) calculations and thermal strengths of the title compounds

**Table S2a**. Crystal lattice energies (kJ/mol) calculated using B3LYP DFT methods for various compounds.

| | | | B3LYP | | |
|---|---|---|---|---|---|
| **Compound** | **LE (a.u)** | **LE (eV)** | **LE (eV/molecule)** | **LE (kJ/molecule)** | **LE (kJ/mole)** |
| **1** | -0.130407103 | -3.548559839 | -0.50693712 | -8.12215E-23 | -4.89E+01 |
| **2** | -0.151038133 | -4.109959052 | -0.410995905 | -6.58498E-23 | -3.97E+01 |
| **3** | -0.110461332 | -3.005807496 | -0.333978611 | -5.35101E-23 | -3.22E+01 |
| **4** | -0.111610508 | -3.037078164 | -0.37963477 | -6.08251E-23 | -3.66E+01 |
| **5** | -0.088843241 | -2.417548971 | -0.268616552 | -4.30377E-23 | -2.59E+01 |
| **6** | -0.086513102 | -2.354142624 | -0.470828525 | -7.54361E-23 | -4.54E+01 |
| **CUBNUC** | -0.2062925 | -5.613507734 | -0.701688467 | -1.12425E-22 | -6.77E+01 |
| **CUNMAZ** | -0.03223413 | -0.877135805 | -0.292378602 | -4.68449E-23 | -2.82E+01 |
| **DUTRIU** | -0.144714227 | -3.937876711 | -0.562553816 | -9.01324E-23 | -5.43E+01 |
| **DUTRIU01** | -0.130339764 | -3.546727454 | -0.506675351 | -8.11795E-23 | -4.89E+01 |
| **DUTRIU02** | -0.149801078 | -4.076297046 | -0.582328149 | -9.33006E-23 | -5.62E+01 |
| **EROHUP** | -0.233339889 | -6.349505053 | -0.705500561 | -1.13035E-22 | -6.81E+01 |
| **KERDUH** | -0.138977571 | -3.781774287 | -0.54025347 | -8.65594E-23 | -5.21E+01 |
| **IPEXEH** | -0.255785667 | -6.96028609 | -0.580023841 | -9.29314E-23 | -5.60E+01 |
| **LELQUQ** | -0.149723125 | -4.074175844 | -0.50927198 | -8.15956E-23 | -4.91E+01 |
| **LELRAX** | -0.121507167 | -3.306380115 | -0.551063353 | -8.82914E-23 | -5.32E+01 |
| **MEQLIE** | -0.068263333 | -1.857540869 | -0.61918029 | -9.92051E-23 | -5.97E+01 |
| **POMLUA** | -0.121892 | -3.316851969 | -0.473835996 | -7.5918E-23 | -4.57E+01 |
| **VOQFIS** | -0.0801145 | -2.180027705 | -0.363337951 | -5.8214E-23 | -3.51E+01 |
| **XEVROF** | -0.00036302 | -0.00987829 | -0.059269739 | -9.4962E-23 | -5.72E+01 |
| **XIMPAL** | -0.16130975 | -4.389464131 | -0.548683016 | -8.791E-23 | -5.29E+01 |

**Table S2b**. Crystal lattice energies (kJ/mol) calculated using M06-HF DFT methods for various compounds.

| | M06-HF | | | | |
|---|---|---|---|---|---|
| | **LE (a.u)** | **LE (eV)** | **LE (eV/molecule)** | **LE (kJ/molecule)** | **LE (kJ/mole)** |
| **1** | -0.150440454 | -4.093695378 | -0.584813625 | -9.37E-23 | -5.64E+01 |
| **2** | -0.183134529 | -4.983346922 | -0.498334692 | -7.98E-23 | -4.81E+01 |
| **3** | -0.138380373 | -3.765523691 | -0.418391521 | -6.70E-23 | -4.04E+01 |
| **4** | -0.136492018 | -3.714138885 | -0.464267361 | -7.44E-23 | -4.48E+01 |
| **5** | -0.11998112 | -3.264854249 | -0.362761583 | -5.81E-23 | -3.50E+01 |
| **6** | -0.107283796 | -2.919342286 | -0.583868457 | -9.35E-23 | -5.63E+01 |
| **CUBNUC** | -0.2309295 | -6.283914996 | -0.785489375 | -1.26E-22 | -7.58E+01 |
| **CUNMAZ** | -0.029015353 | -0.789548377 | -0.263182792 | -4.22E-23 | -2.54E+01 |
| **DUTRIU** | -0.001003586 | -0.027308989 | -0.191162923 | -1.03E-22 | -6.18E+01 |
| **DUTRIU01** | -0.000245402 | -0.006677724 | -0.046744065 | -9.35E-23 | -5.63E+01 |
| **DUTRIU02** | -0.000355113 | -0.00966313 | -0.067641907 | -8.12E-23 | -4.89E+01 |
| **EROHUP** | -0.060858333 | -1.656040452 | -0.184004495 | -2.95E-23 | -1.78E+01 |
| **KERDUH** | -0.152014714 | -4.136533196 | -0.590933314 | -9.47E-23 | -5.70E+01 |
| **IPEXEH** | -0.289101 | -7.866842951 | -0.655570246 | -1.05E-22 | -6.33E+01 |
| **LELQUQ** | -0.205798125 | -5.600055099 | -0.700006887 | -1.12E-22 | -6.75E+01 |
| **LELRAX** | -0.141651667 | -3.854540162 | -0.64242336 | -1.03E-22 | -6.20E+01 |
| **MEQLIE** | -0.025709333 | -0.699586953 | -0.233195651 | -3.74E-23 | -2.25E+01 |
| **POMLUA** | -0.122072 | -3.321750021 | -0.474535717 | -7.60E-23 | -4.58E+01 |
| **VOQFIS** | -0.085835167 | -2.335695054 | -0.389282509 | -6.24E-23 | -3.76E+01 |
| **XEVROF** | -0.000248663 | -0.00676646 | -0.04736522 | -8.42E-23 | -5.07E+01 |
| **XIMPAL** | -0.18226825 | -4.959774258 | -0.619971782 | -9.93E-23 | -5.98E+01 |

**KEY: LE = Lattice Energy**

**Table S3.** Molecular pair interaction energies partitioned into Coulombic ($E_{Coul}$), polarization ($E_{Pol}$), dispersion ($E_{Disp}$), repulsion ($E_{rep}$) and total energy ($E_{Tot}$) contributions (kJ/mol) for **1**–**6**.

| Motif | D.C. [†]/(Å) | $E_{Coul}$ | $E_{Pol}$ | $E_{Disp}$ | $E_{Rep}$ | $E_{Tot}$ | Symmetry | Important Interactions |
|---|---|---|---|---|---|---|---|---|
| | | | | **1** | | | | |
| 1 | 12.99 | -2.9 | -1.0 | -9.1 | 7.5 | -7.0 | x, -1+y, z | C23–H23···O1=C1 |
| 2 | 8.50 | -3.2 | -0.5 | -18.7 | 10.6 | -13.4 | 1/2+x, 1/2-y, z | C25–H25···O2–C2 |
| 3 | 7.96 | -11.0 | -3.2 | -20.9 | 15.6 | -22.6 | 3/2-x, -1/2+y, 1/2+z | C2–H2B···O1=C1 |
| 4 | 4.67 | -13.1 | -2.5 | -47.1 | 31.9 | -37.0 | 1-x, 1-y, -1/2+z | C12–H12···O2–C2; C26–H26···π |
| 5 | 8.86 | -9.2 | -3.1 | -12.7 | 11.9 | -15.8 | -1/2+x, 3/2-y, z | C2–H2A···O1=C1; C12–H12···O1=C1 |
| | | | | **2** | | | | |
| 1 | 4.56 | -7.6 | -3.8 | -69.1 | 39.5 | -46.7 | x, 1+y, z | C3–H3A···O3–C3; C3–H3A···π |
| 2 | 11.53 | -3.7 | -0.5 | -8.2 | 6.6 | -7.3 | 1-x, -y, 1-z | H15···H15 |
| 3 | 9.90 | -3.4 | -0.9 | -15.8 | 10.6 | -11.4 | x, 1/2-y, 1/2+z | C14–H14···π |
| 4 | 7.28 | -10.3 | -5.7 | -21.3 | 16.0 | -23.7 | 1-x, 1/2+y, 1/2-z | C1–H1···O1=C1; C2–H2A···O1=C1 |
| 5 | 10.12 | -2.5 | -0.7 | -13.8 | 10.2 | -8.9 | x, 3/2-y, 1/2+z | C23–H23···π |
| | | | | **3** | | | | |
| 1 | 7.67 | -10.9 | -3.2 | -17.7 | 18.5 | -17.9 | 3/2-x, 1/2+y, 1/2-z | C15–H15···O1=C1; C2–H2B···Br1 |
| 2 | 8.54 | -13.5 | -1.7 | -32.2 | 32.9 | -23.3 | -1/2+x, 1/2-y, 1/2+z | π···π |
| 3 | 7.91 | -8.5 | -2.2 | -18.4 | 15.0 | -17.4 | 1/2-x, 1/2+y, 1/2-z | C25–H25···Br1; C2–H2B···O1=C1 |
| 4 | 10.07 | -16.0 | -4.9 | -21.9 | 26.8 | -23.0 | -x, 1-y, 1-z | C23–H23···O1=C1; C24–H24···O1=C1 |
| 5 | 14.01 | -1.4 | -0.2 | -5.6 | 4.2 | -4.0 | -3/2+x, 1/2-y, 1/2+z | C24–H24···Br1 |
| | | | | **4** | | | | |
| 1 | 9.81 | -2.6 | -0.3 | -7.1 | 6.4 | -5.3 | 3/2+x, 1/2-y, 1/2+z | C25–H25···Cl1; C26–H26···Cl1 |
| 2 | 9.79 | -4.9 | -0.6 | -10.4 | 8.2 | -9.6 | 1/2-x, -1/2+y, 3/2-z | C25–H25···Cl1; C26–H26···Cl1 |
| 3 | 4.92 | -3.9 | -2.3 | -52.5 | 27.9 | -34.3 | 1+x, y, z | lone pair···π |
| 4 | 8.42 | -9.8 | -2.5 | -6.5 | 5.1 | -14.7 | -1/2+x, 1/2-y, 1/2+z | C15–H15···O1=C1; C16–H16···O1=C1 |
| 5 | 7.70 | -5.0 | -2.1 | -12.5 | 7.5 | -13.1 | 1/2+x, 1/2-y, 1/2+z | C2–H2A···O1=C1 |
| 6 | 6.56 | -6.0 | -1.1 | -38.8 | 25.2 | -25.4 | 1-x, 1-y, 1-z | lone pair···π [††] |
| 7 | 9.04 | -11.5 | -2.3 | -27.9 | 24.5 | -23.1 | 2-x, 1-y, 1-z | C24–H24···O1=C1 [††] |
| | | | | **5** | | | | |
| 1 | 9.79 | -7.6 | -0.2 | -8.5 | 18.2 | -4.4 | -x, 1/2+y, 3/2-z | Br1···Br2 |
| 2 | 4.10 | -23.0 | -2.7 | -75.2 | 68.3 | -49.6 | 1+x, y, z | C2–H2B···O2–C2 |
| 3 | 10.23 | -5.9 | -0.6 | -14.3 | 13.4 | -10.9 | 1/2-x, 1-y, 1/2+z | C13–H13···π |
| 4 | 9.34 | -4.5 | -0.3 | -12.1 | 10.7 | -8.9 | 1-x, 1/2+y, 3/2-z | C26–H26···Br2 |
| 5 | 7.94 | -20.2 | -4.5 | -18.0 | 21.2 | -27.2 | 1/2+x, 3/2-y, 1-z | C2–H2A···O1=C1; lone pair···lone pair |
| 6 | 10.61 | -5.1 | -0.6 | -15.6 | 14.0 | -10.8 | 3/2-x, 1-y, 1/2+z | C23–H23···Br1; C24–H24···Br2 |
| | | | | **6** | | | | |
| 1 | 4.70 | -15.4 | -3.4 | -47.6 | 32.1 | -40.4 | -x, 1-y, 1-z | C14–H14···C4≡C3 [††] |
| 2 | 7.88 | -22.9 | -5.1 | -11.2 | 24.6 | -22.6 | -x, 1-y, 2-z | C4–H4···O1=C1; C3≡C4···O1=C1[††] |
| 3 | 7.94 | -4.8 | -2.6 | -12.6 | 8.0 | -13.0 | x, 1+y, z | C3–C2···O1=C1 |
| 4 | 7.55 | -9.0 | -2.4 | -19.8 | 12.2 | -21.0 | 1-x, -y, 1-z | C5–H5C···O2–C2 [††];C5–H5C···O3–C5 [††] |
| 5 | 6.88 | -2.9 | -1.0 | -20.3 | 12.3 | -13.9 | 1-x, -y, 2-z | C2–H2A···O2–C2 [††] |
| 6 | 4.59 | -8.9 | -2.2 | -44.5 | 23.3 | -35.4 | 1-x, 1-y, 1-z | C5–H5A···O1=C1 [††] |
| 7 | 8.43 | -2.3 | -2.6 | -7.5 | 6.3 | -7.1 | 1-x, 1-y, 2-z | C1–H1···O1=C1 [††] |

[†] Centroid distance; [††] Duplicated interactions

**NMR**

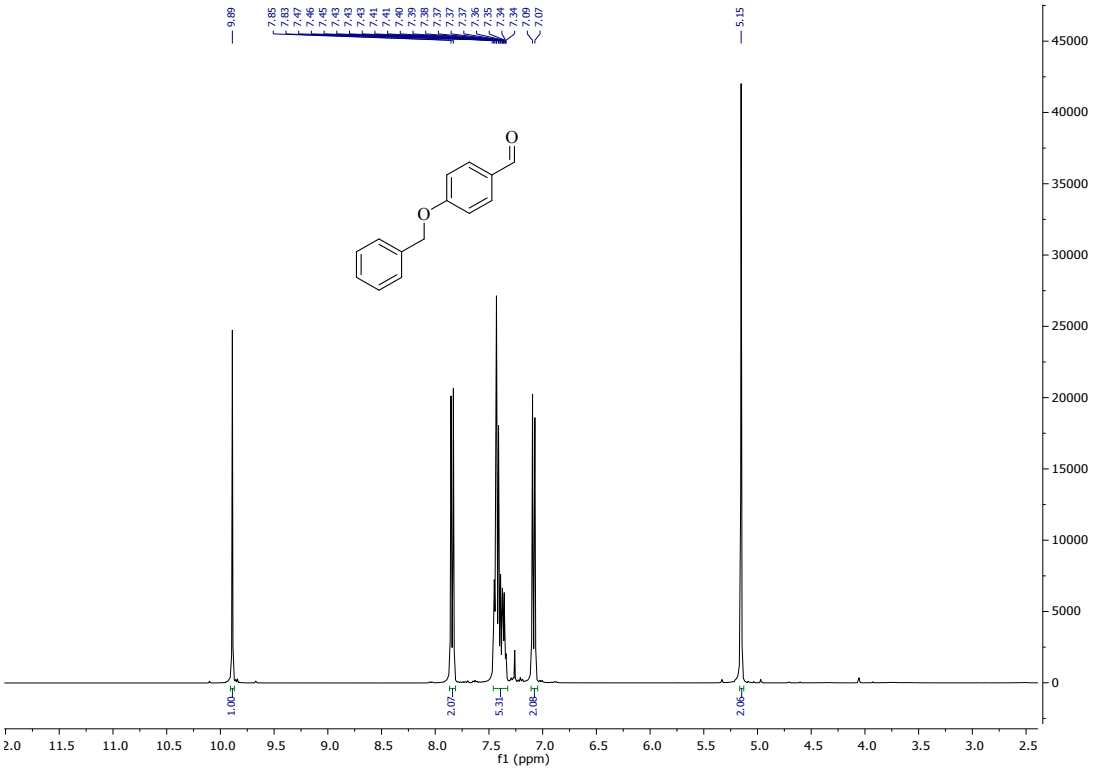


**Fig.S2a** 400 MHz $^{1}$H NMR spectrum of compound **1** in $CDCl_3$

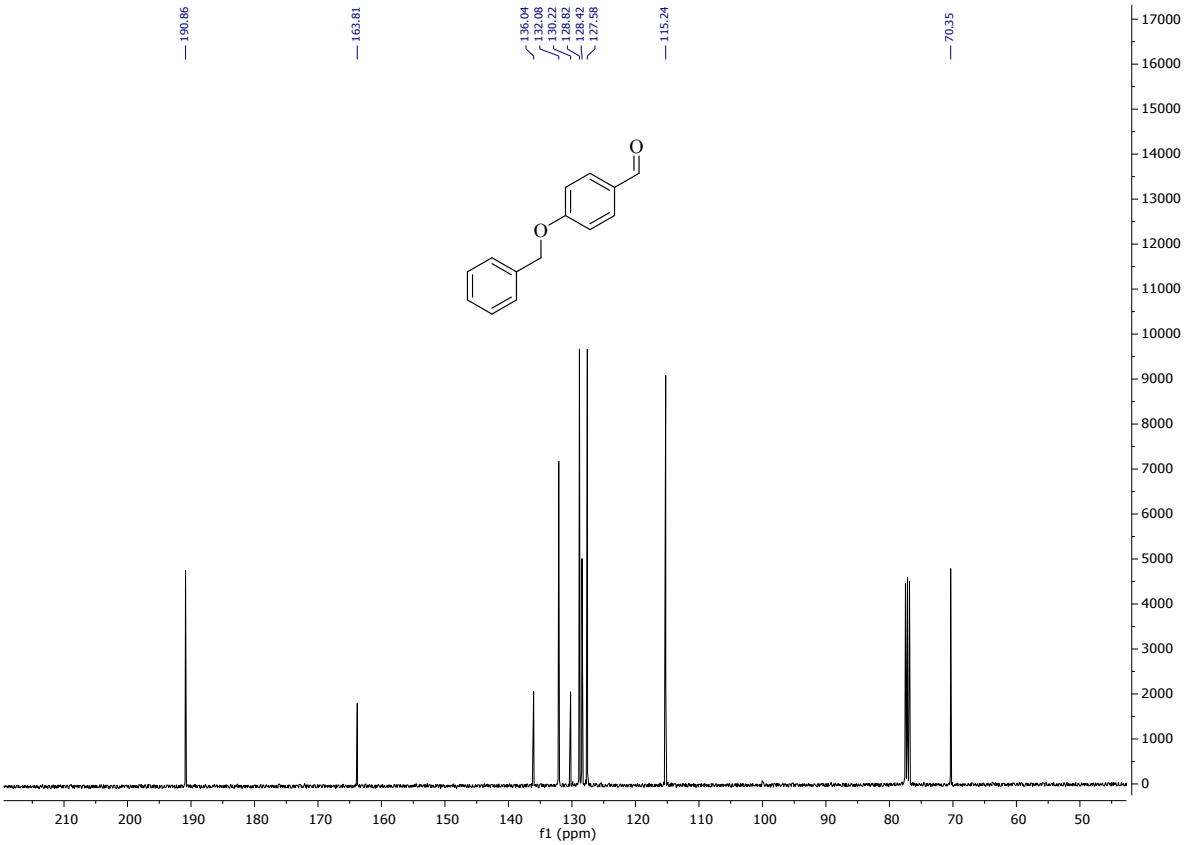


**Fig. S2b** 100 MHz $^{13}$C NMR spectrum of compound **1** in $CDCl_3$.

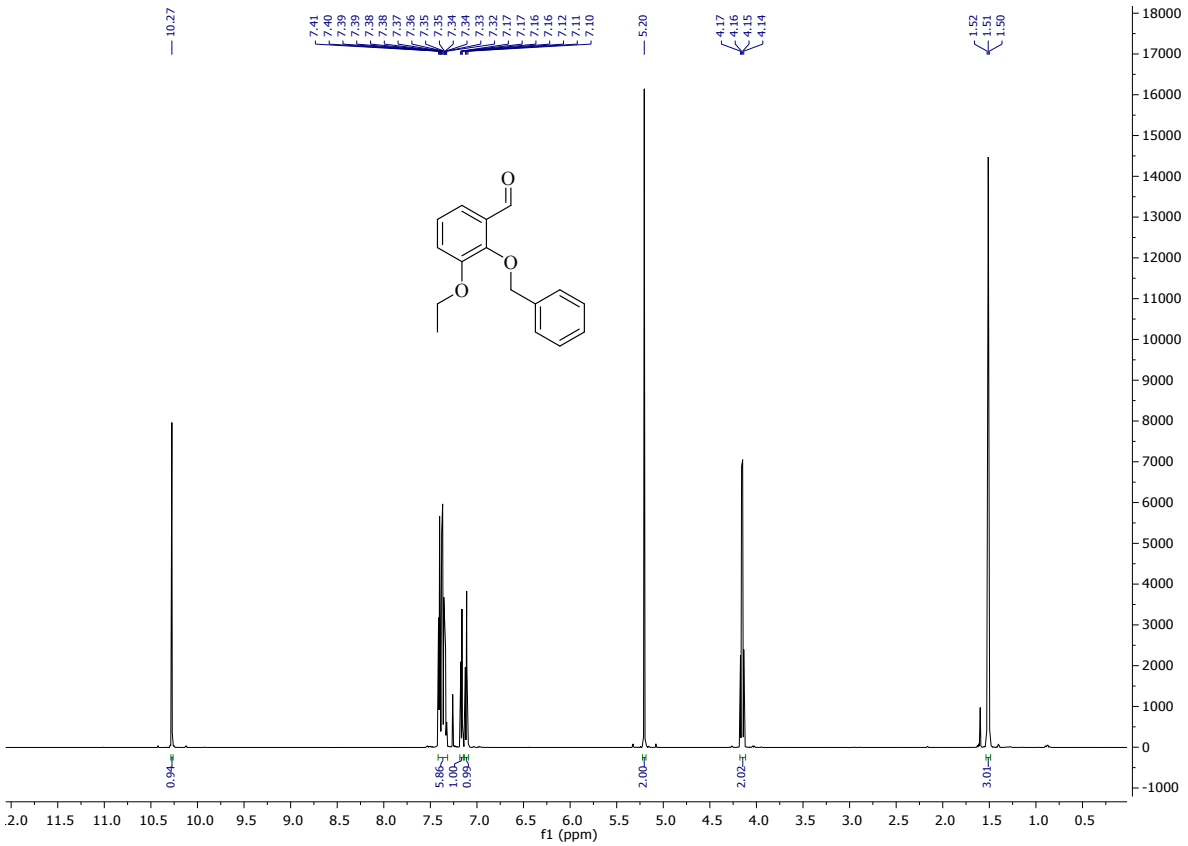


**Fig.S3a** 600 MHz $^{1}H$ NMR spectrum of compound **2** in $CDCl_3$.

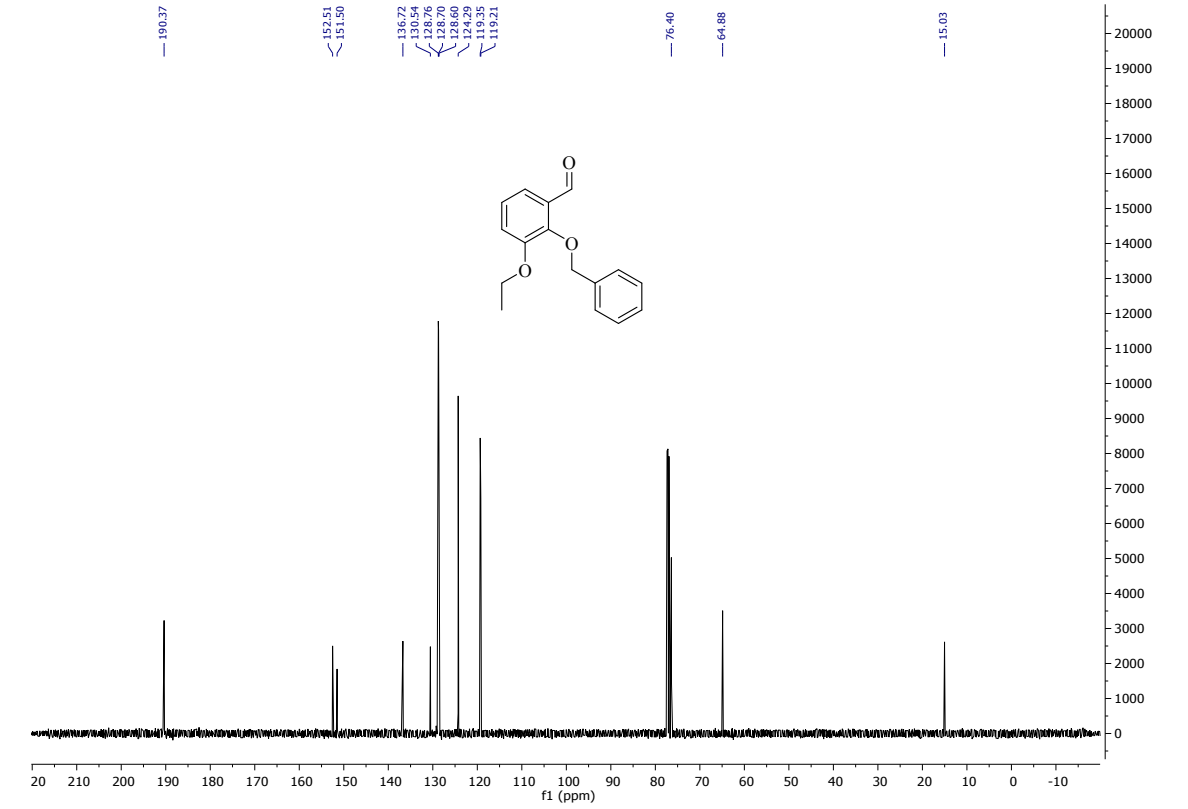


**Fig. S3b** 150 MHz $^{13}C$ NMR spectrum of compound **2** in $CDCl_3$.

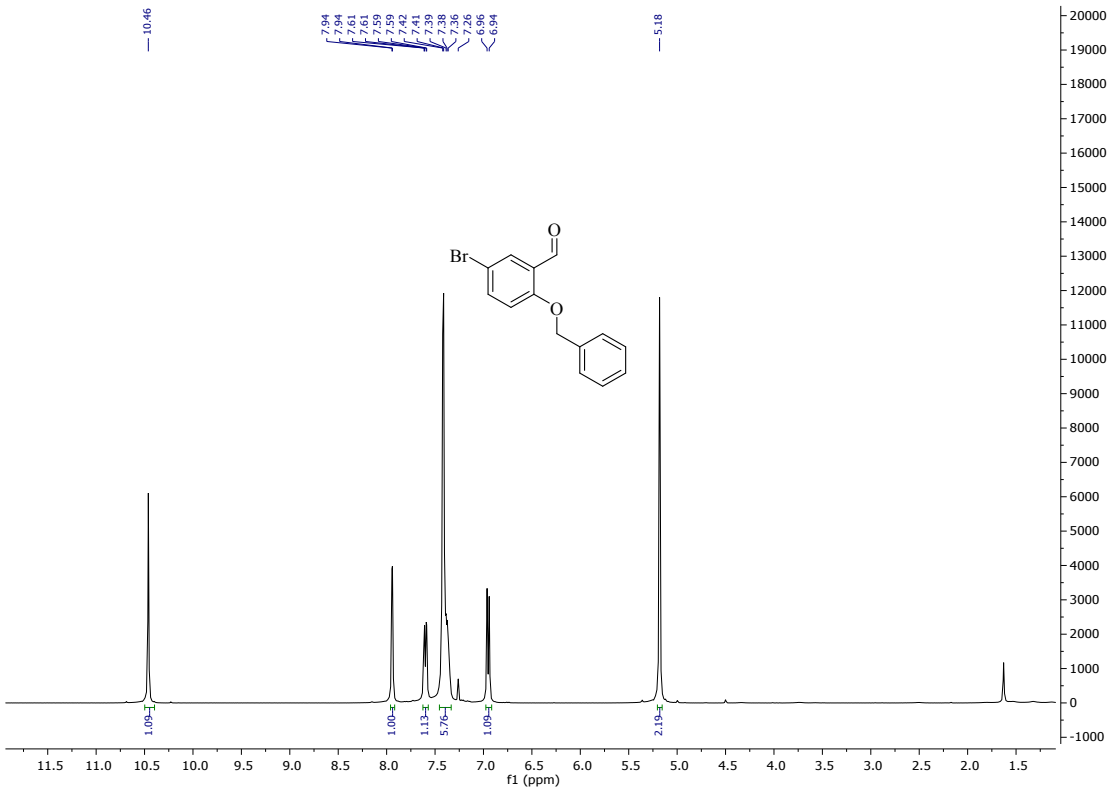


**Fig.S4a** 400 MHz $^{1}H$ NMR spectrum of compound **3** in $CDCl_3$.

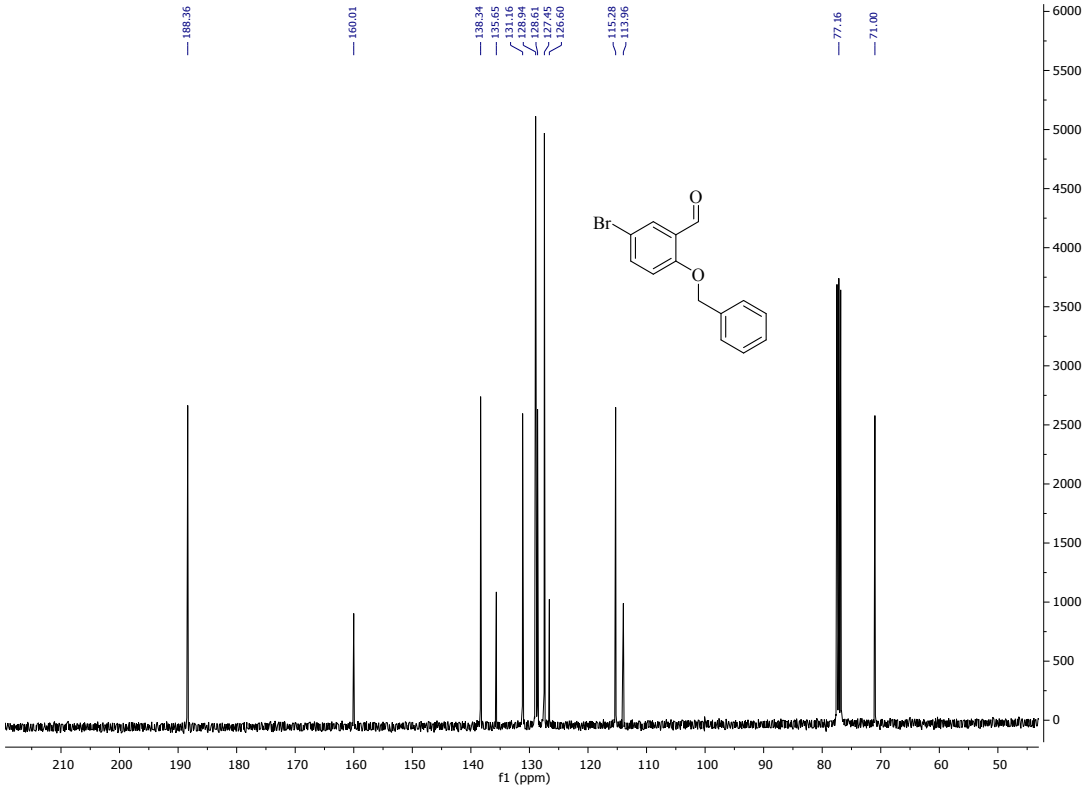


**Fig.S4b** 100 MHz $^{13}C$ NMR spectrum of compound **3** in $CDCl_3$.

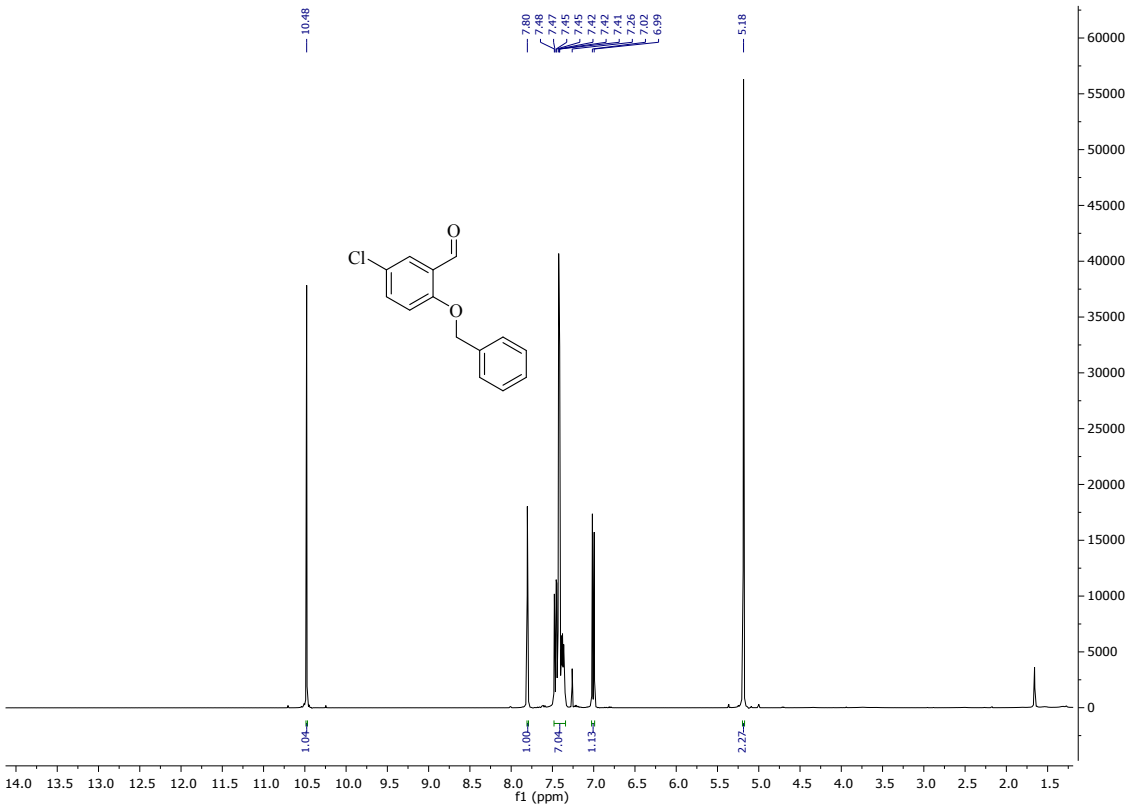


**Fig.S5a** 400 MHz $^{1}H$ NMR spectrum of compound **4** in $CDCl_3$.

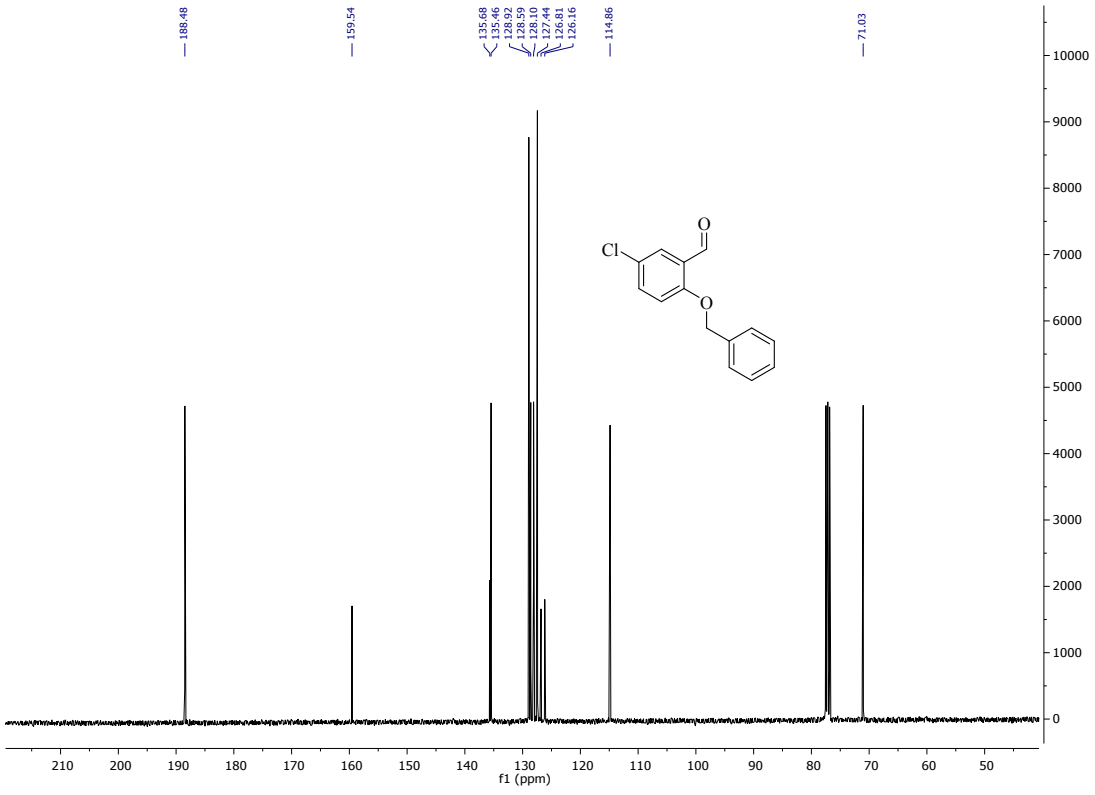


**Fig.S5b** 100 MHz $^{13}C$ NMR spectrum of compound **4** in $CDCl_3$.

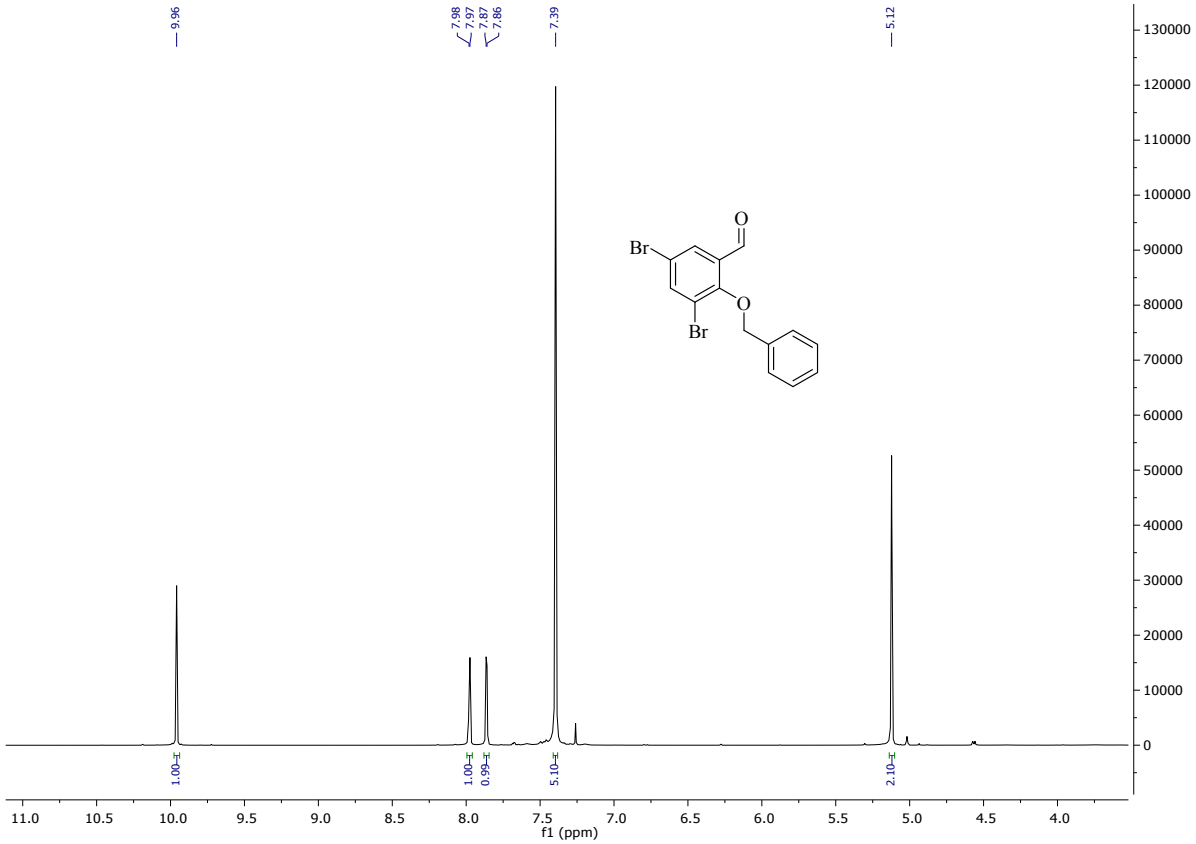


**Fig.S6a** 400 MHz $^{1}H$ NMR spectrum of compound **5** in $CDCl_3$.

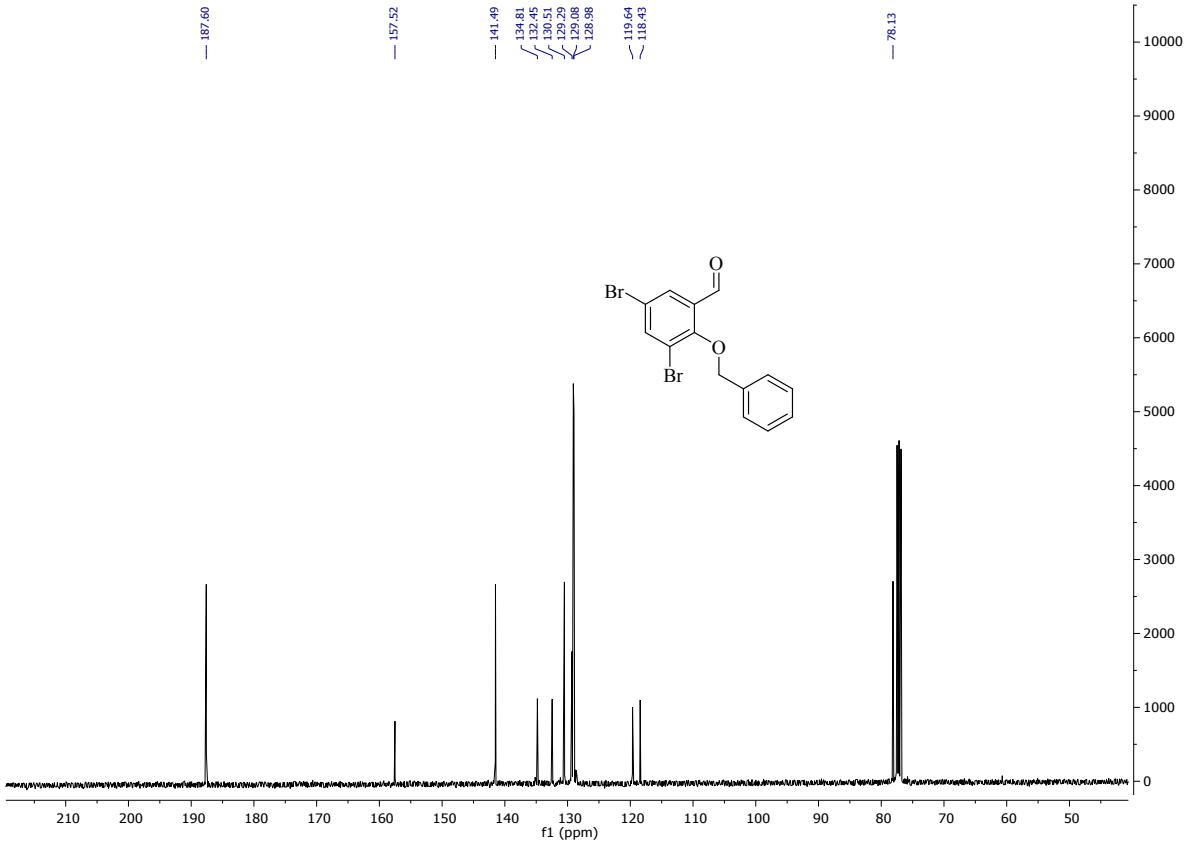


**Fig.S6b** 100 MHz $^{13}C$ NMR spectrum of compound **5** in $CDCl_3$.

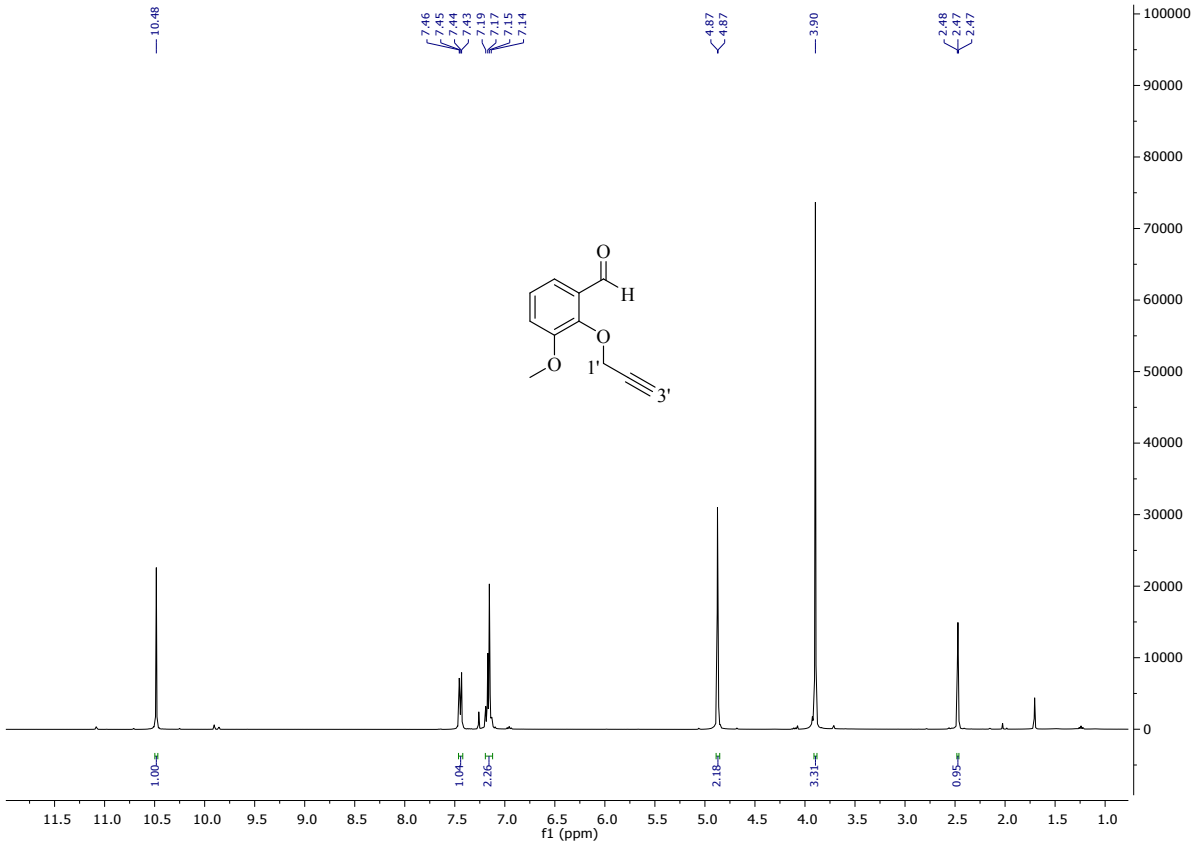


**Fig.S7a** 400 MHz $^{1}H$ NMR spectrum of compound **6** in $CDCl_3$

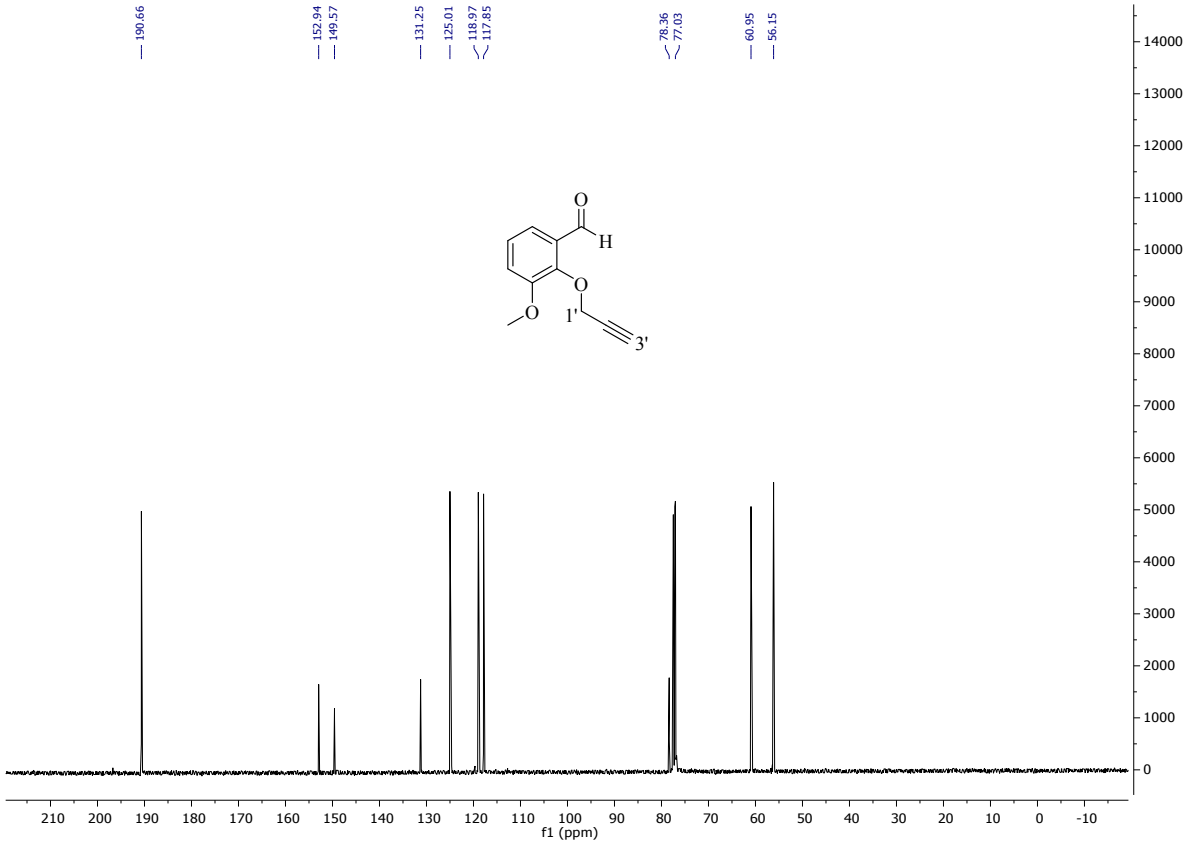


**Fig.S7b** 100 MHz $^{13}C$ NMR spectrum of compound **6** in $CDCl_3$.

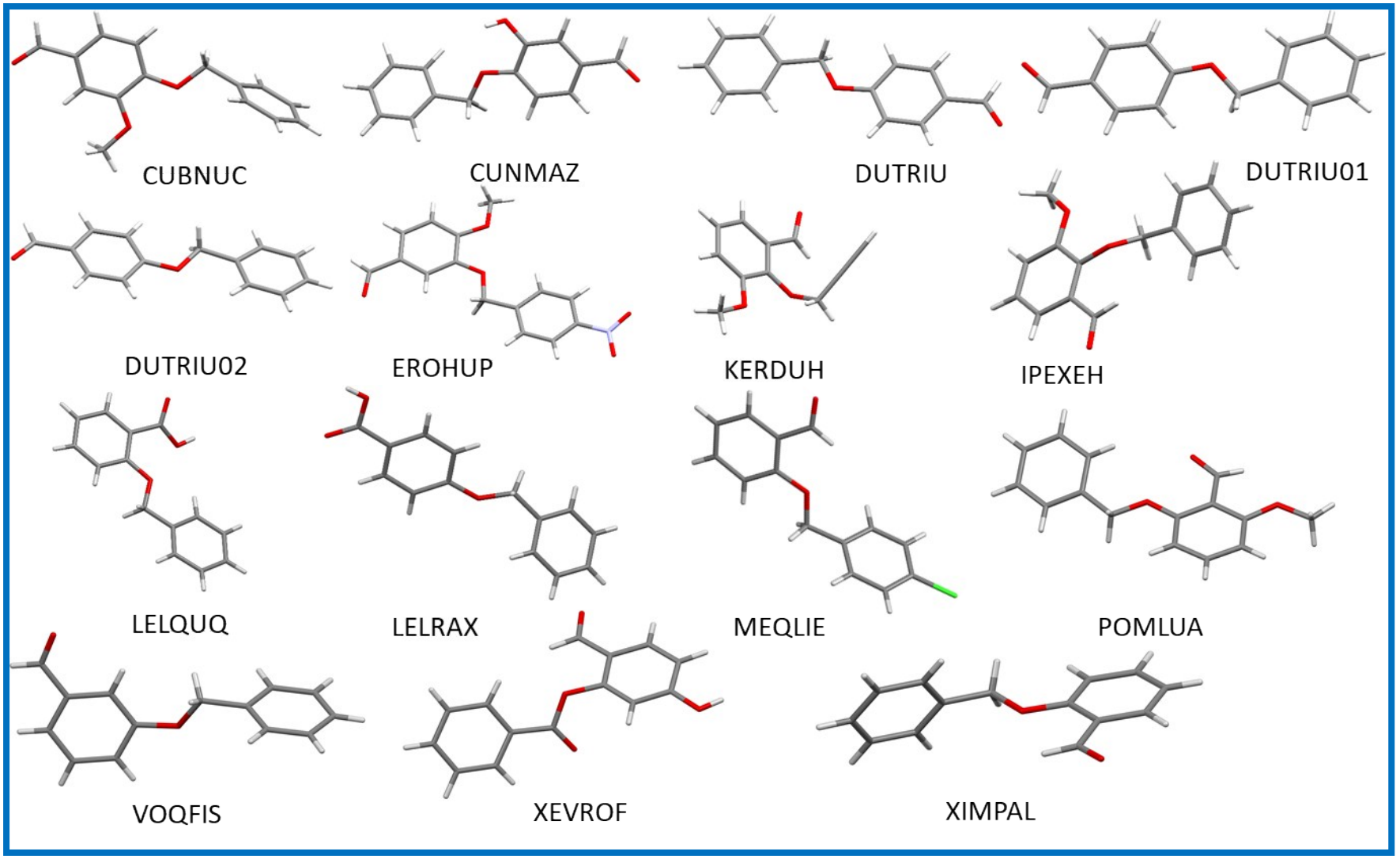


Fig. S8 Benzyloxybenzaldehydes than their analogous structures.