Supporting Information for

IBX Works Efficiently under Solvent Free Conditions in Ball milling

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EXPERIMENTAL SECTION

Methods. Unless otherwise stated, all starting materials were purchased from commercial sources and used as received. All milling experiments were performed in Retsch MM 200 high speed vibration milling instrument (21 Hz). NMR spectra were recorded on Bruker AV 400 MHz instrument and high-resolution mass spectra (HRMS) were recorded on a BrukermicroTOF-Q II, ESI TOF (time of flight) mass spectrometer. HPLC analyses were carried out in Agilent 1200 series LC with column C18 (Analytical 4.6×150 mm; 5-micron from Agilent). During ball-milling operation the progress of reaction was monitored by TLC/^{1}H NMR.*

Preparation of 2-iodoxybenzoic acid (IBX)[1]

IBX was prepared in our laboraory by following the method shown in Figure S1.

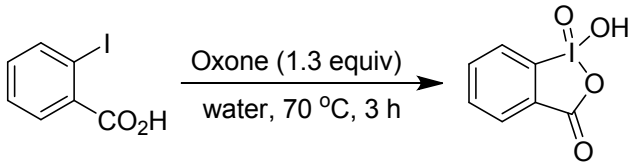
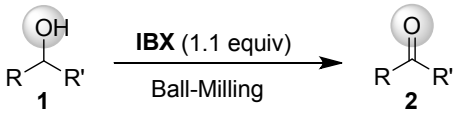
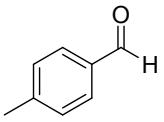


Fig. S1. Synthesis of IBX.

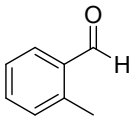
2-Iodobenzoic acid (6.0 g, 24.2 mmol) and oxone (19.9 g, 31.5 mmol) were taken in a 500 mL round bottom flask and deionized water (200 mL) was added. The suspension was placed on a preheated oil-bath (70 ºC) for 3 h, cooled to room temperature and filtered through sintered-glass funnel followed by repeatedly washing with water. After vacuum drying 5.42 g (80%) of white solid was obtained.

* The milling apparatus was stopped and small portion of sample was collected from the jar to study either proton NMR/TLC (Thin Layer Chromatography). Followed by, the reaction was started and this operation time was excluded for reporting the reaction timing.

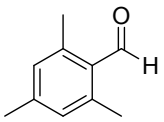




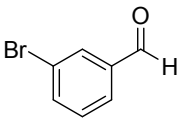
2a, 87%, 45 min



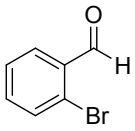
2b, 89%, 1.5 h



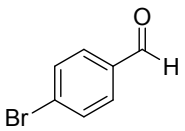
2c, 94%, 45 min



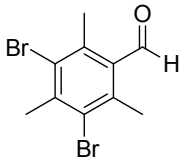
2d, 89%, 45 min



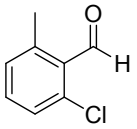
2e, 86%, 45 min



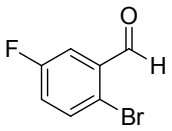
2f, 45 min, 93%



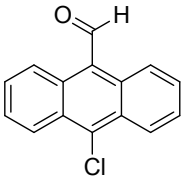
2g, 88%, 2h



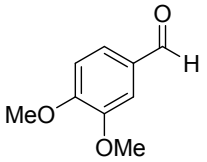
2h, 1 h, 94%



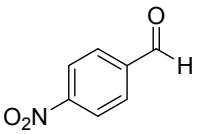
2i, 91%, 1h



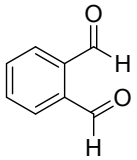
2j, 91%, 3h



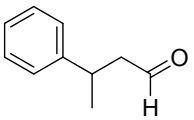
2k, 97%, 45 min



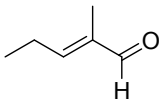
2l, 99%, 2.5 h



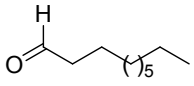
2m, 86%, 2 h



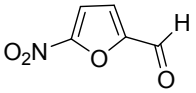
2n, 81%, 2 h



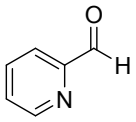
2o, 79%, 1.5 h



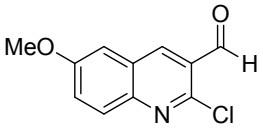
2p, 77%, 1.5 h



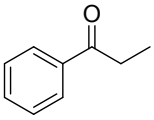
2q, 89%, 2 h



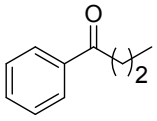
2r, 88%, 2.5 h



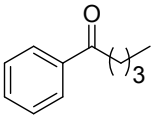
2s, 90%, 2.5 h



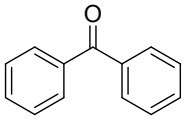
2t, 95%, 45 min



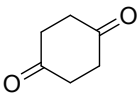
2u, 93%, 1 h



2v, 85%, 1 h



2w, 94 %, 1 h



2x, 97%, 1 h

Fig. S2. Oxidation of alcohols to the corresponding carbonyl compounds.

Reactions schemes performed under milling condition

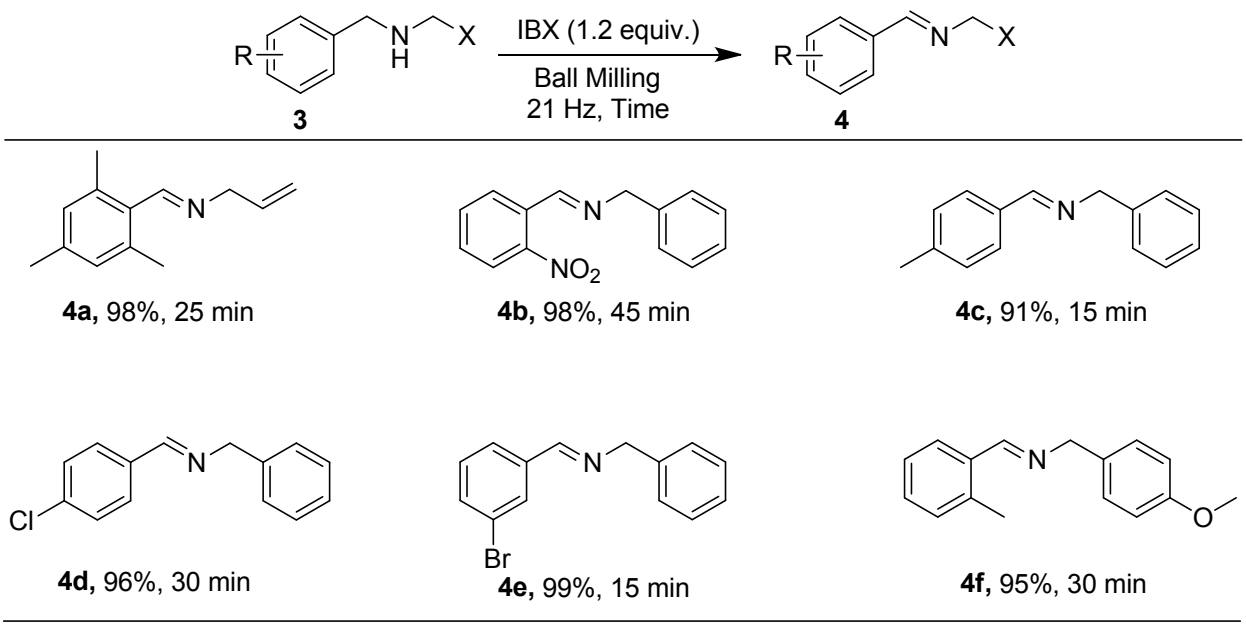


Fig. S3. Oxidation of amine to imine

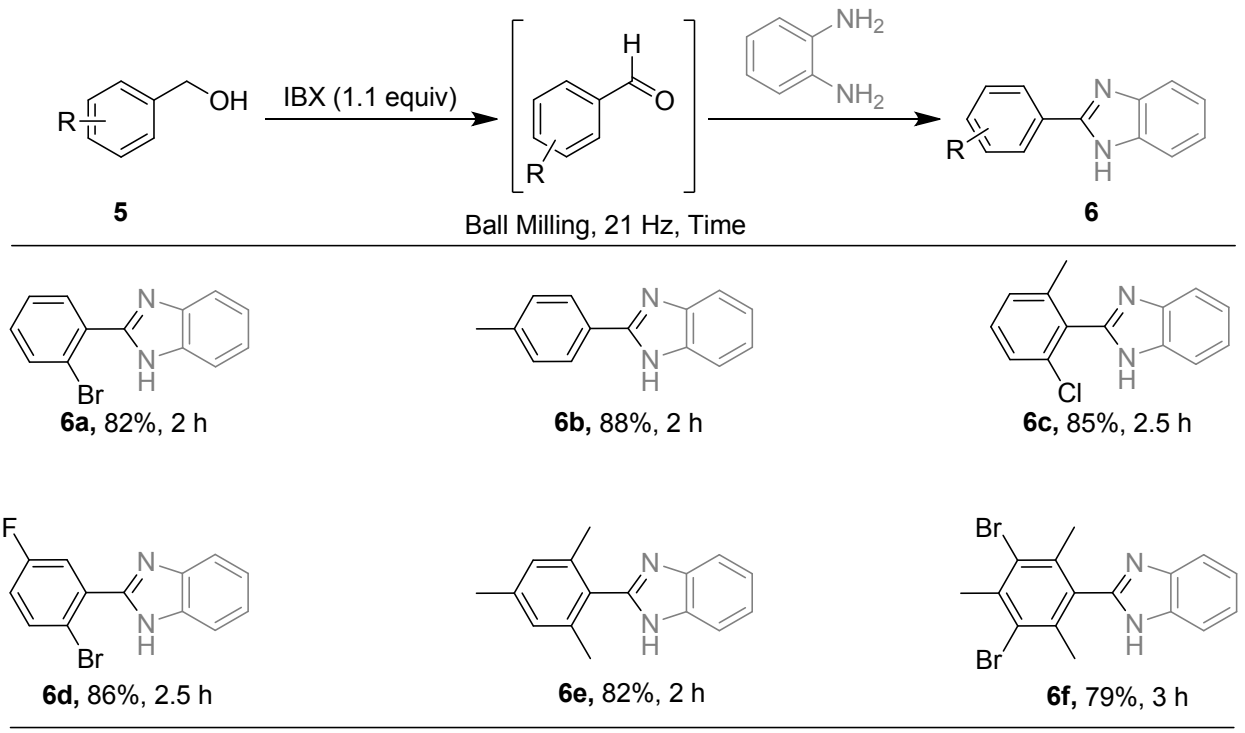


Fig. S4. One-pot Synthesis of benzimidazole

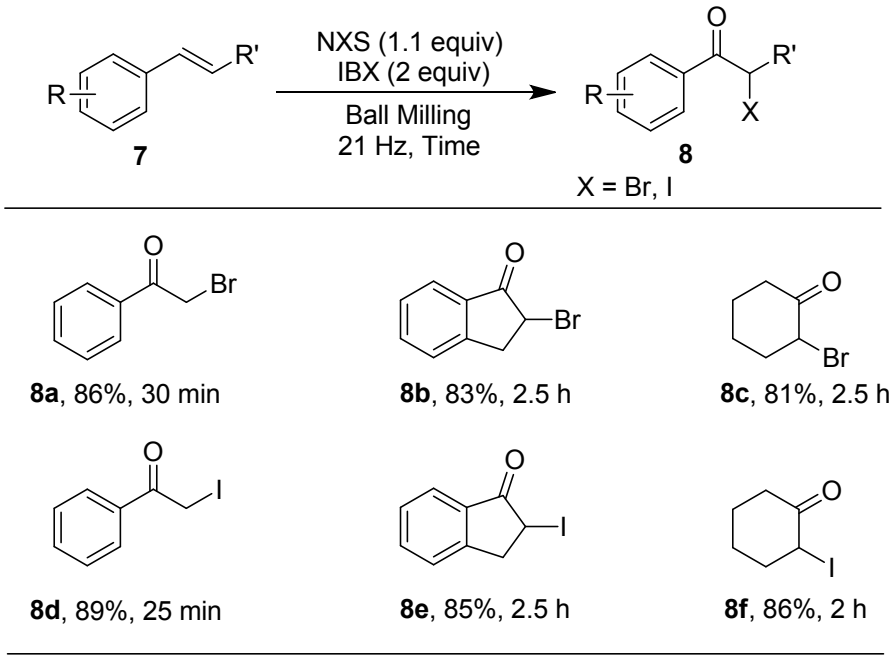


Fig. S5. Conversion of olefins to α-haloketones

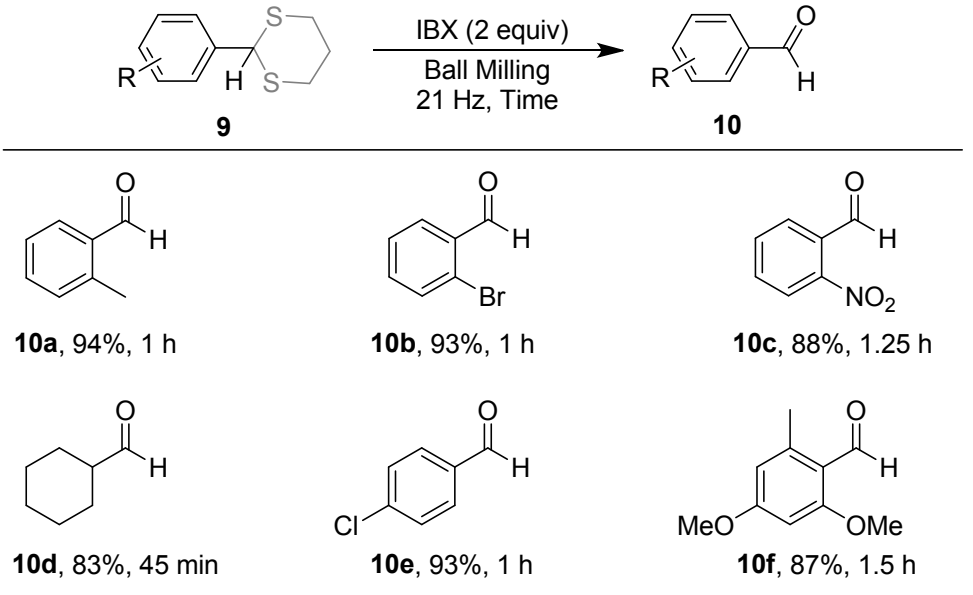


Fig. S6. Dithiane deprotection

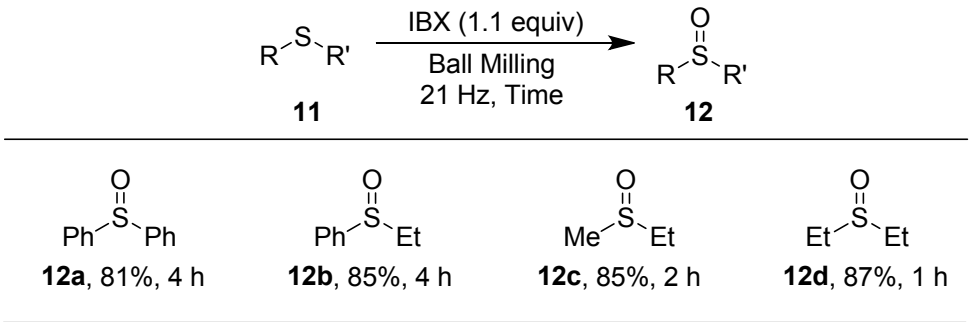


Fig. S7. Oxidation of sulfide to sulfoxide

Recycling of waste IBA by oxidative *in situ* regeneration of IBX with oxone

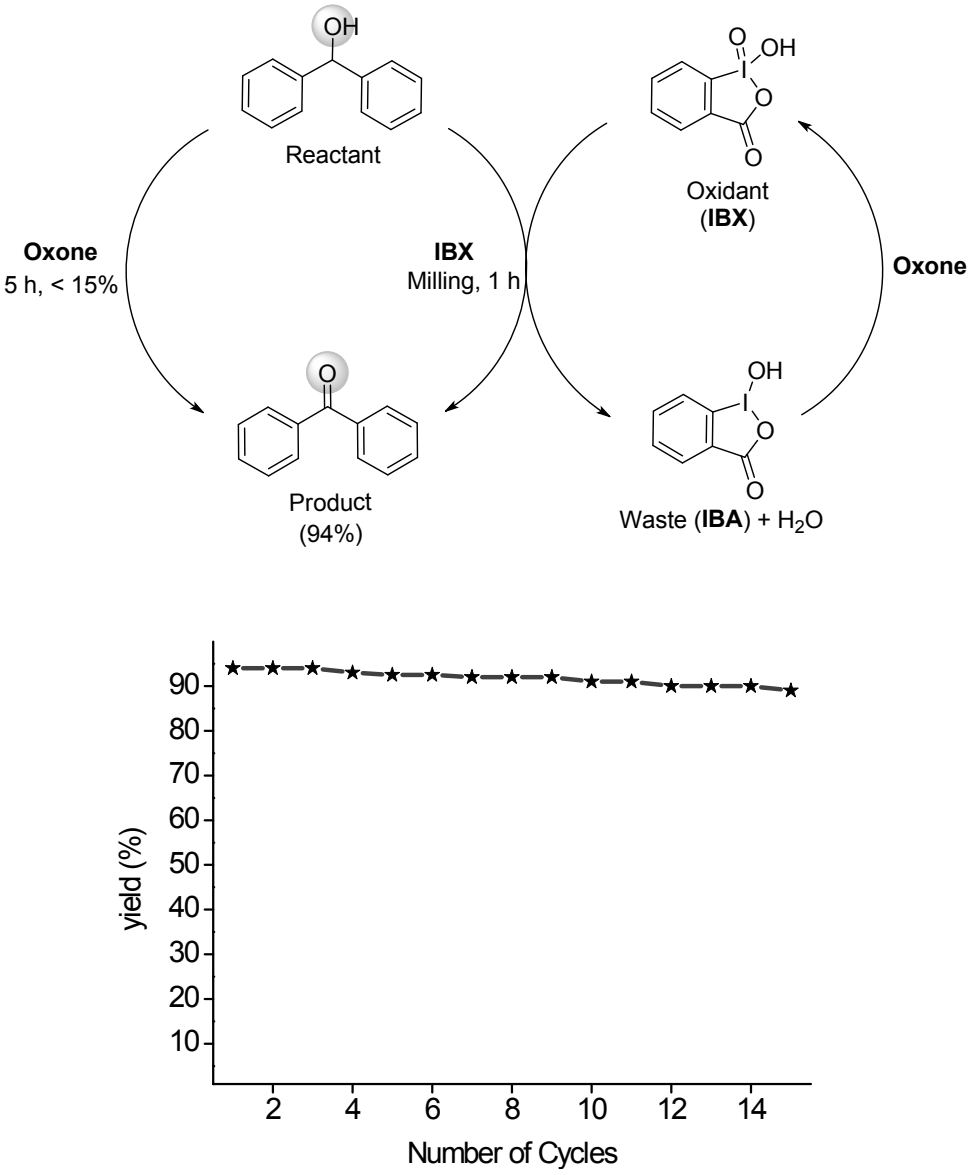
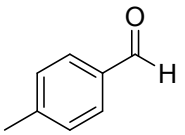


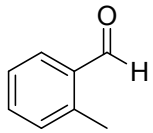
Fig. S8. Waste management via recycling of *in situ* generated IBX from IBA with Oxone

Data for commercially available compounds

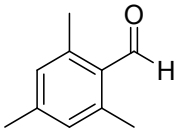
4-Methylbenzaldehyde (2a): Colourless liquid (commercially available); yield 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.77-7.75 (m, 2H), 7.33-7.31 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.12, 145.66, 134.31, 129.96, 129.82, 21.97.



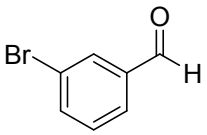
2-Methylbenzaldehyde (2b): Colourless liquid (commercially available); yield 89%; ^{1}H , $CDCl_3$): δ 10.25 (s, 1H), 7.79-7.77 (m, 1H), 7.48-36-7.33 (m, 1H), 7.25-7.24 (m, 1H), 2.66 (s, 3H); MHz, $CDCl_3$): δ 192.88, 140.68, 134.24, 133.72, 26.40, 19.64.



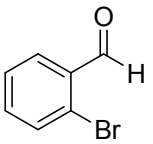
2,4,6-Trimethylbenzaldehyde (2c): Colourless liquid (commercially available); yield 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.55 (s, 1H), 6.89 (s, 2H), 2.57 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.10, 143.94, 141.59, 130.61, 130.02, 21.56, 20.60.



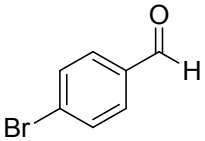
3-Bromobenzaldehyde (2d): Colourless liquid (commercially available); yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.99 (d, J = 0.4 Hz, 1H), 7.81-7.73 (m, 2H), 7.43-7.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.90, 138.05, 137.42, 132.44, 130.74, 128.50, 123.46.



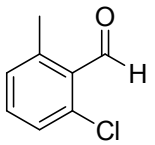
2-Bromobenzaldehyde (2e): Colourless liquid (commercially available); yield 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (s, 1H), 7.80-7.78 (m, 1H), 7.54-7.52 (m, 1H), 7.36-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.85, 135.32, 133.83, 133.39, 129.78, 127.88, 127.03.



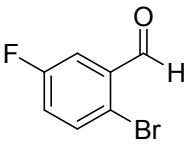
4-Bromobenzaldehyde (2f): Colourless solid; yield 93%; mp 54-56 ^{o}C (commercially available, reported 55-58 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.75-7.72 (m, 2H), 7.68-7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.23, 135.14, 132.54, 131.08, 129.89.



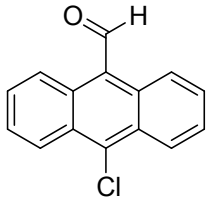
2-Chloro-6-methylbenzaldehyde (2h): Colourless solid; yield 94%; mp 37-39 ^{o}C (commercially available, reported 36-40 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.68 (s, 1H), 7.41-7.33 (m, 2H), 7.21-7.19 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.53, 142.52, 139.05, 133.54, 130.70, 128.30, 126.92, 21.25.



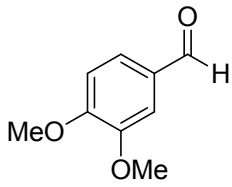
2-Bromo-5-fluorobenzaldehyde (2i): Yield 91%; mp 53-55 ^{o}C (commercially available, reported 51-56 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): 10.31 (d, J = 2.9 Hz, 1H), 7.61-7.66 (m, 2H), 7.18-7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.76, 162.15, 135.32, 134.82, 122.73, 121.17, 116.34.



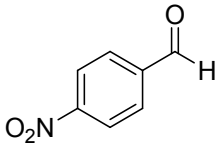
10-Chloroanthracene-9-carbaldehyde (2j): Yield 91%; mp 213-216 °C (commercially available, reported 215-218 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.45 (s, 1H), 8.91 (d, *J* = 8.8 Hz, 2H), 8.62-8.60 (m, 2H), 7.72-7.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.06, 137.16, 132.13, 129.23, 128.56, 127.14, 125.87, 124.70, 123.92.



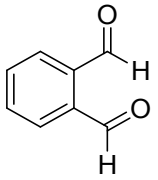
3,4-Dimethoxybenzaldehyde (2k): Yield 97%; mp 40-42 °C (commercially available, reported 40-43 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.47-7.45 (m, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 6.98 (d, *J* = 9.6 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.09, 154.66, 149.79, 130.29, 127.04, 110.54, 109.11, 56.33, 56.16.



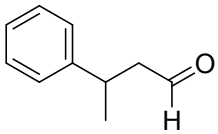
4-Nitrobenzaldehyde (2l): Yield 99%; mp 104-106 °C (commercially available, reported 103-106 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.43, 151.26, 140.17, 130.60, 124.43.



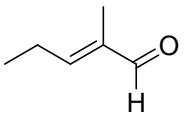
Phthalaldehyde (2m): Yield 86%; mp 53-56 °C (commercially available, reported 55-58 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.52 (s, 1H), 10.51 (s, 1H), 7.98-7.94 (m, 2H), 7.78-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.46, 136.51, 133.87, 131.21.



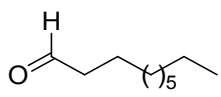
3-Phenylbutaraldehyde (2n): Colourless liquid (commercially available); yield 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.34-7.31 (m, 2H), 7.25-7.20 (m, 3H), 3.42-3.33 (m, 1H), 2.79-2.63 (m, 2H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.98, 145.52, 128.74, 126.82, 126.60, 51.77, 34.33, 22.23.



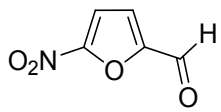
2-Methylpent-2-enal (2o): Colourless liquid (commercially available); yield 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (s, 1H), 6.45-6.41 (m, 1H), 2.35-2.28 (m, 2H), 1.68 (s, 3H), 1.08-1.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.50, 156.40, 138.82, 22.36, 12.85, 9.05.



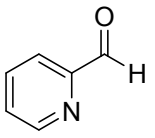
Decanal (2p): Colourless liquid (commercially available); yield 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (t, *J* = 1.8 Hz, 1H), 2.46-2.35 (m, 2H), 1.65-1.58 (m, 2H), 1.37-1.24 (m, 12H), 0.90 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.16, 101.83, 34.54, 32.02, 29.65, 29.50, 29.44, 23.70, 22.81, 14.23.



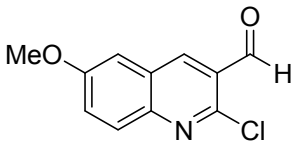
5-Nitrofuran-2-carbaldehyde (2q): Colourless solid; yield 89%; mp 38-40 °C (commercially available, reported 37-39 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.41 (d, *J* = 4 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.45, 151.09, 118.92, 111.86.



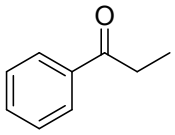
Pyridine-2-carbaldehyde (2r): Colourless liquid (commercially available); yield 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.74-8.72 (m, 1H), 7.92-7.89 (m, 1H), 7.84-7.83 (m, 1H), 7.82-7.80 (m, 1H), 7.49-7.46 (m, 1H);); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.46, 152.79, 150.24, 137.13, 127.94, 121.75.



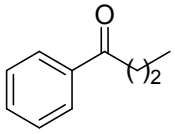
2-Chloro-6-methoxyquinoline-3-carbaldehyde (2s): Colourless solid; yield 90%; mp 150-152 ^{o}C (commercially available, reported 149-151 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.54 (s, 1H), 8.63 (s, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.52-7.49 (m, 1H), 7.18 (d, J = 2.4 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.36, 158.80, 147.63, 145.75, 138.66, 129.86, 127.76, 126.59, 126.40, 106.42, 55.77.



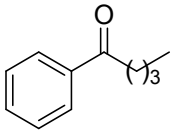
Propiophenone (2t): Colourless liquid (commercially available); yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.91 (m, 2H), 7.53-7.48 (m, 1H), 7.43-7.39 (m, 2H), 2.95 (q, $J_1 = J_2$ = 7.2 Hz, 2H), 1.19 (t, $J_1 = J_2$ = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.79, 136.90, 132.86, 128.54, 127.95, 31.75, 8.22.



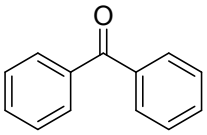
1-Phenylbutan-1-one (2u): Colourless liquid (commercially available); yield 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.53-7.49 (m, 1H), 7.44-7.39 (m, 2H), 2.93-2.89 (m, 2H), 1.79-1.70 (m, 2H), 1.00-0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.34, 137.12, 132.85, 128.54, 128.02, 40.48, 17.76, 13.88.



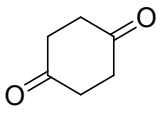
1-Phenylpentan-1-one (2v): Colourless liquid (commercially available); yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.94 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 2.96 (t, $J_1 = J_2$ = 7.2 Hz, 2H), 1.75-1.68 (m, 2H), 1.45-1.36 (m, 2H), 0.95 (t, $J_1 = J_2$ = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.74, 137.22, 132.97, 128.66, 128.17, 38.45, 26.61, 22.60, 14.05.



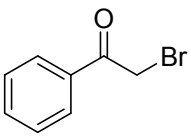
Benzophenone (2w): Colourless solid; yield 94%; mp 48-50 ^{o}C (commercially available, reported 47-51 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.89, 137.72, 132.53, 130.17, 128.39.



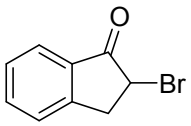
Cyclohexane-1,4-dione (2x): Colourless solid; yield 97%; mp 75-77 ^{o}C (commercially available, reported 77-78.5 ^{o}C); 1H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.51, 36.73.



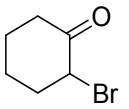
2-Bromo-1-phenylethanone (8a): Colourless solid; yield 86%; mp: 48-50 ^{o}C (commercially available, reported 48-51 ^{o}C) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 4.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.42, 134.17, 129.08, 129.00, 31.11.



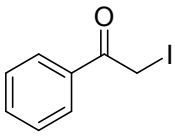
2-Bromo-2,3-dihydro-1*H*-inden-1-one (8b): Colourless liquid (commercially available); yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.81 (m, 1H), 7.69-7.64 (m, 1H), 7.46-7.40 (m, 2H), 4.65 (dd, J_1 = 7.5 Hz, J_2 = 3.2 Hz, 1H), 3.84 (dd, J_1 = 18.1 Hz, J_2 = 7.5 Hz, 1H), 3.42 (dd, J1 = 18.1 Hz, J2 = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.51, 151.16, 135.92, 133.57, 128.24, 126.48, 125.00, 44.08, 37.91.



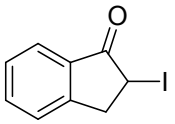
2-Bromocyclohexanone (8c): Colourless liquid (commercially available); yield 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.49-4.39 (m, 1H), 3.33-2.90 (m, 1H), 2.41-2.12 (m, 3H), 2.11-1.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.52, 53.47, 37.91, 36.72, 27.66, 22.18.



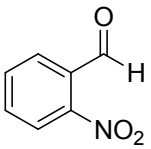
2-Iodo-1-phenylethanone (8d): Colourless liquid (commercially available); yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.91 (m, 2H), 7.59-7.43 (m, 3H), 4.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.81, 133.72, 133.48, 130.02, 128.81, 1.68.



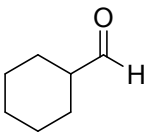
2-Iodo-2,3-dihydro-1*H*-inden-1-one (8e): Colourless liquid (commercially available); yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 4H), 4.92 (dd, J_1 = 7.5 Hz, J_2 = 3 Hz, 1H), 3.90 (dd, J_1 = 18 Hz, J_2 = 7.5 Hz, 1H), 3.45 (dd, J_1 = 18 Hz, J_2 = 3 Hz, 1H).



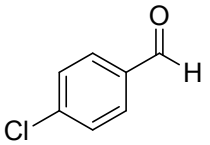
2-Nitrobenzaldehyde (10a): Yield: 88%; mp 42-44 °C (commercially available, reported 42-44 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1H), 8.12-8.10 (m, 1H), 7.95-7.93 (m, 1H), 7.81-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 188.31, 149.69, 134.22, 133.84, 131.45, 129.75, 124.62.



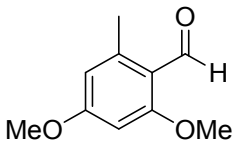
Cyclohexanecarbaldehyde (10b): Colourless liquid (commercially available); yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 2.24-2.19 (m, 1H), 1.90-1.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): 205.17, 50.07, 26.08, 26.02, 25.12.



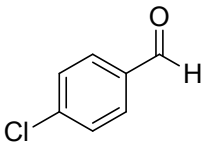
4-Chlorobenzaldehyde (10c): Colourless liquid (commercially available); yield 93%; mp 46-48°C (commercially available, reported 45-50 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.82 (d, J = 8.4, 2H), 7.51 (d, J = 8.4, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.04, 141.13, 134.85, 131.70, 131.06, 129.61, 129.03.



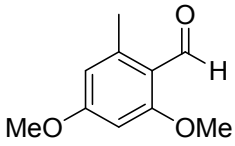
2,4-Dimethoxy-6-methylbenzaldehyde (10d): Colourless solid; yield 87%; mp 67-69 °C (commercially available, reported 65-69 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1H), 6.63 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.68, 165.30, 164.55, 144.85, 117.45, 108.87, 95.88, 55.87, 55.56, 22.46.



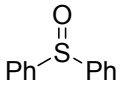
4-Chlorobenzaldehyde (10e): Colourless solid; yield 93%; mp 46-48°C (commercially available, reported 46-48 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.82 (d, *J* = 8.4, 2H), 7.51 (d, *J* = 8.4, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.04, 141.13, 134.85, 131.70, 131.06, 129.61, 129.03.



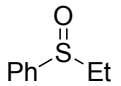
2,4-Dimethoxy-6-methylbenzaldehyde (10f): Colourless solid; yield 87%; mp 67-69 °C (commercially available, reported 67-68 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1H), 6.63 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.68, 165.30, 164.55, 144.85, 117.45, 108.87, 95.88, 55.87, 55.56, 22.46.



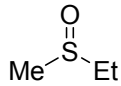
Sulfinyldibenzene (12a): Colourless liquid (commercially available); yield 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.3 Hz, 4H), 7.35-7.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.11, 130.48, 128.76, 124.05.



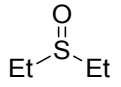
(Ethylsulfinyl)benzene (12b): Colorless liquid (commercially available); yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.51-7.49 (m, 3H), 2.95-2.86 (m, 1H), 2.80-2.71 (m, 1H), 1.18 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.94, 130.62, 128.84, 123.82, 49.90, 5.62.



(Methylsulfinyl)ethane (12c): Colorless liquid (commercially available); yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.79-2.66 (m, 2H), 2.53 (s, 3H), 1.23 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.96, 36.83, 6.53.

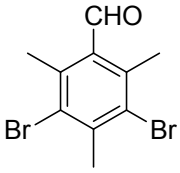


(Ethylsulfinyl)ethane (12d): Colorless liquid (commercially available); yield 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74-2.67 (m, 4H), 1.34 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.82, 6.74.

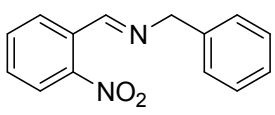


Data for literature known compounds

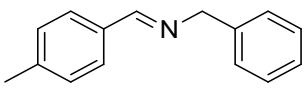
3,5-Dibromo-2,4,6-trimethylbenzaldehyde (2g): Colourless solid; yield 88%; mp 162-164 °C (lit.[2] 160 °C, decomposes); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 10.47 (s, 1H), 2.74 (s, 3H), 2.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 194.0, 142.5, 137.6, 135.0, 127.7, 26.9, 20.4.



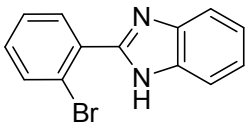
***N*-(2-nitrobenzylidene)-1-phenylmethanamine (4b):** Colourless solid; yield 98%; mp 45-46 °C (lit.[3] colorless liquid); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.12-8.10 (m, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.67-7.63 (m, 1H), 7.58-7.54 (m, 1H), 7.38-7.30 (m, 4H), 7.29-7.27 (m, 1H), 4.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.71, 148.84, 138.44, 133.43, 131.15, 130.69, 129.82, 128.56, 128.08, 127.19, 124.25, 65.20.



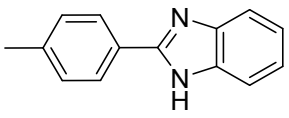
***N*-(4-methylbenzylidene)-1-phenylmethanamine (4c):** Colorless liquid;[4] yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.71 (d, J = 8 Hz, 2H), 7.37-7.24 (m, 7H), 4.83 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.04, 141.12, 139.52, 133.64, 129.42, 128.56, 128.37, 128.06, 127.02, 65.08, 21.60.



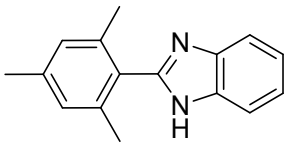
2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole (6a): Colourless solid; yield 82%; mp 242-243 °C; (lit.[5] 242 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 8.02-7.99 (m, 2H), 7.46-7.42 (m, 2H), 7.22-7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.26, 142.07, 133.60, 133.43, 132.12, 128.17, 94.83.



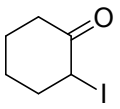
2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (6b): Colourless solid; yield 88%; mp 275 ^{o}C (lit.[6] 276 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 8.03 (d, J = 8 Hz, 1H), 7.98 (dd, J_1= J_2= 0.8 Hz, 1H), 7.88 (dd, J_1= J_2= 1.6 Hz, 1H), 7.50-7.39 (m, 2H), 7.14-7.08 (m, 2H), 6.942 (d, J = 8 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.28, 148.84, 143.36, 141.18, 137.74, 132.21, 130.91, 130.05, 128.08, 125.02, 119.70, 114.35, 94.14, 21.76.



2-Mesityl-1*H*-benzo[*d*]imidazole (6e): Colourless solid; yield 82%; mp 208 °C (lit.[7] 220 °C sublm); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.58 (m, 2H), 7.20-7.22 (m, 2H), 6.87 (s, 2H), 2.28 (s, 3H), 2.06 (s, 6H).



2-Iodocyclohexanone (8f): Colorless liquid;[8] yield 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67-4.49 (m, 1H), 3.33-3.17 (m, 1H), 2.36-2.14 (m, 2H), 2.11-1.91 (m, 4H), 1.82-1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.51, 37.48, 36. 41, 32.82, 26.66, 22.63.



References:

1. M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537-4538.
2. J. N. Moorthy, P. Mal, R. Natarajan and P. Venugopalan, *J. Org. Chem.*, 2001, **66**, 7013-7019.
3. C.-W. Chen, M.-C. Tseng, S.-K. Hsiao, W.-H. Chen and Y.-H. Chu, *Org. Biomol. Chem.*, 2011, **9**, 4188-4193.
4. J.-F. Soule, H. Miyamura and S. Kobayashi, *Chem. Commun.*, 2013, **49**, 355-357.
5. D. Saha, A. Saha and B. C. Ranu, *Green Chem.*, 2009, **11**, 733-737.
6. S. M. Inamdar, V. K. More and S. K. Mandal, *Tetrahedron Lett.*, 2013, **54**, 579-583.
7. J. N. Moorthy and I. Neogi, *Tetrahedron Lett.*, 2011, **52**, 3868-3871.
8. G. M. Rubottom and R. C. Mott, *J. Org. Chem.*, 1979, **44**, 1731-1734.

NMR Spectra of newly synthesized compounds

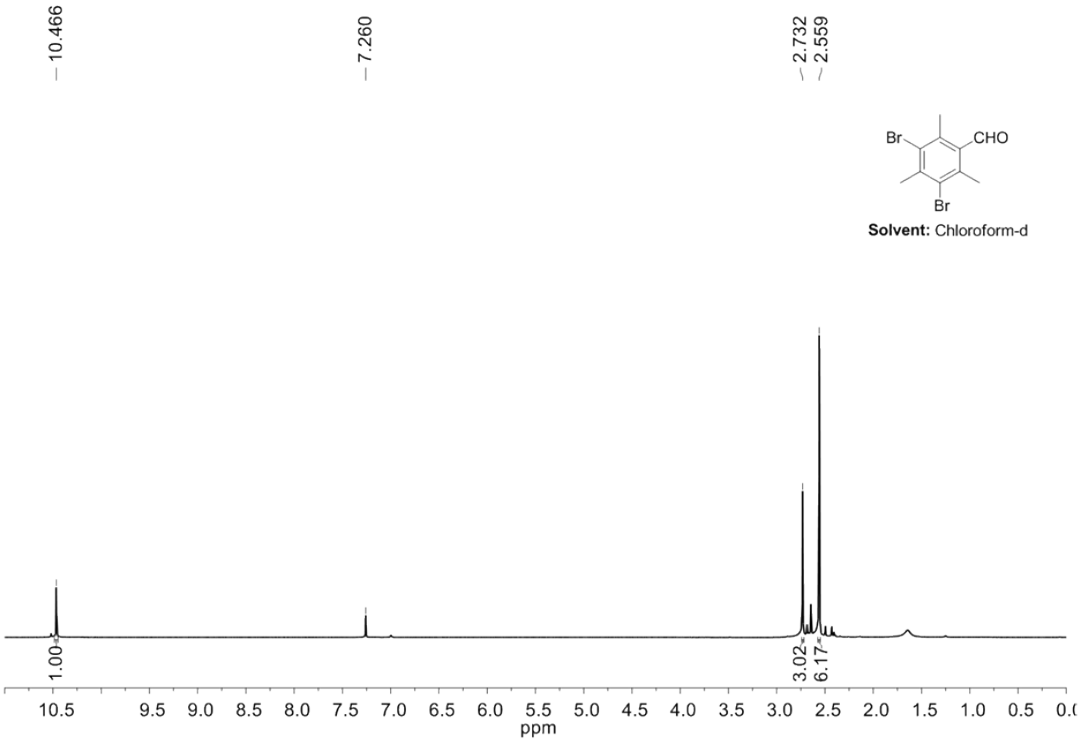


Fig. S9. ^{1}H NMR spectrum of 3,5-Dibromo-2,4,6-trimethylbenzaldehyde (**2g**).

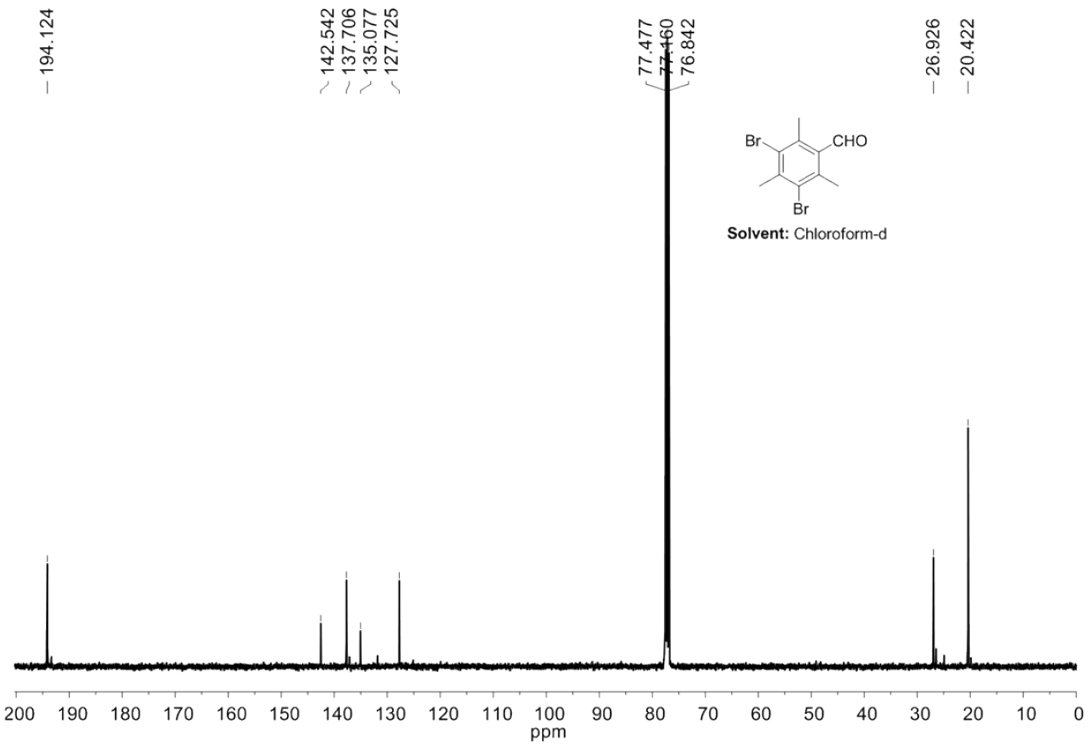


Fig. S10. ^{13}C NMR spectrum of 3,5-Dibromo-2,4,6-trimethylbenzaldehyde (**2g**).

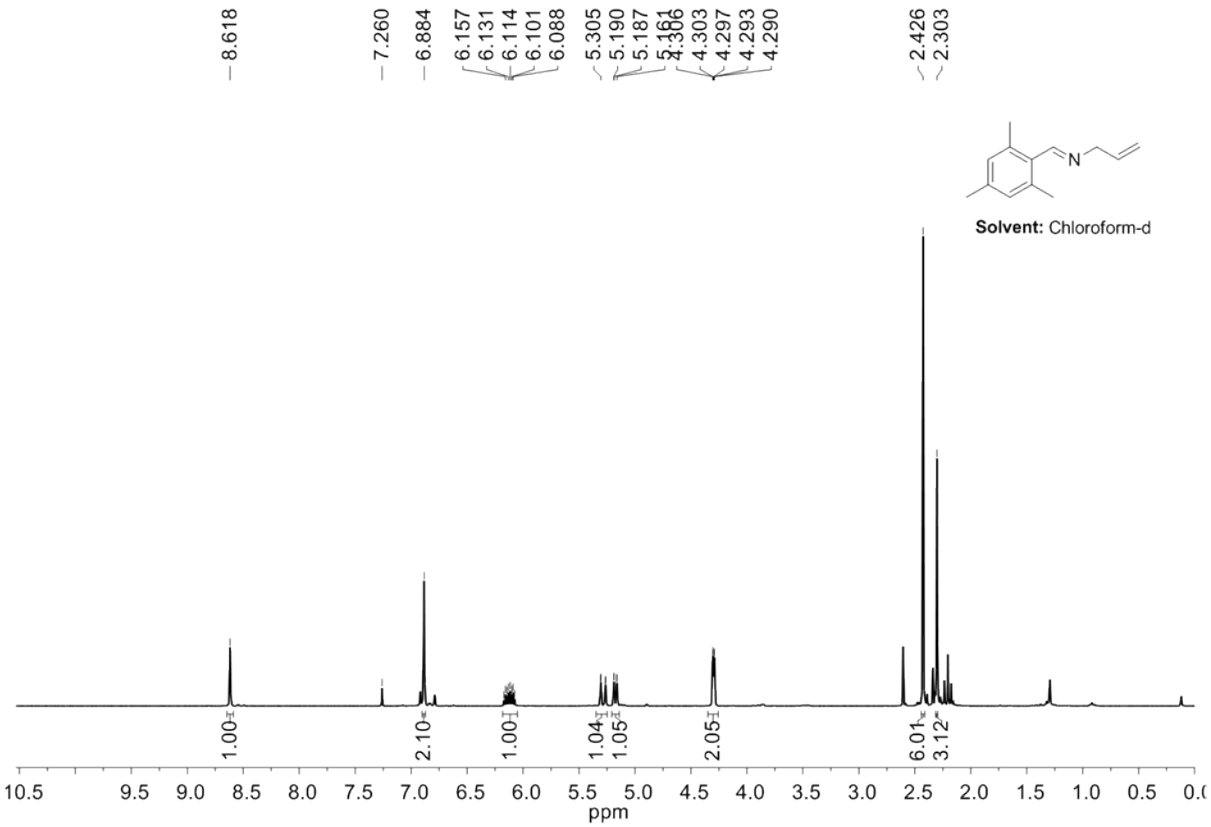


Fig. S11. [1]H NMR spectrum of *N*-(2,4,6-trimethylbenzylidene)prop-2-en-1-amine (**4a**).

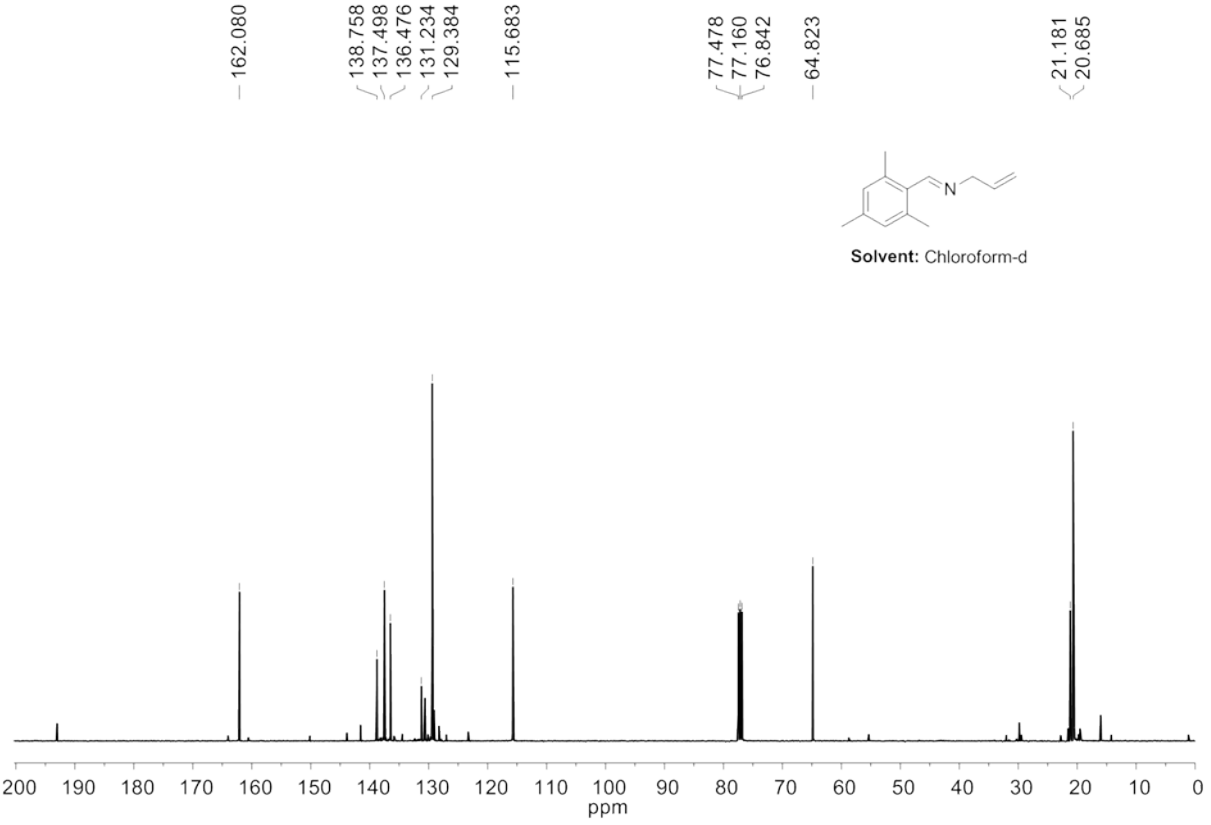


Fig. S12. [13]C NMR spectrum of *N*-(2,4,6-trimethylbenzylidene)prop-2-en-1-amine (**4a**).

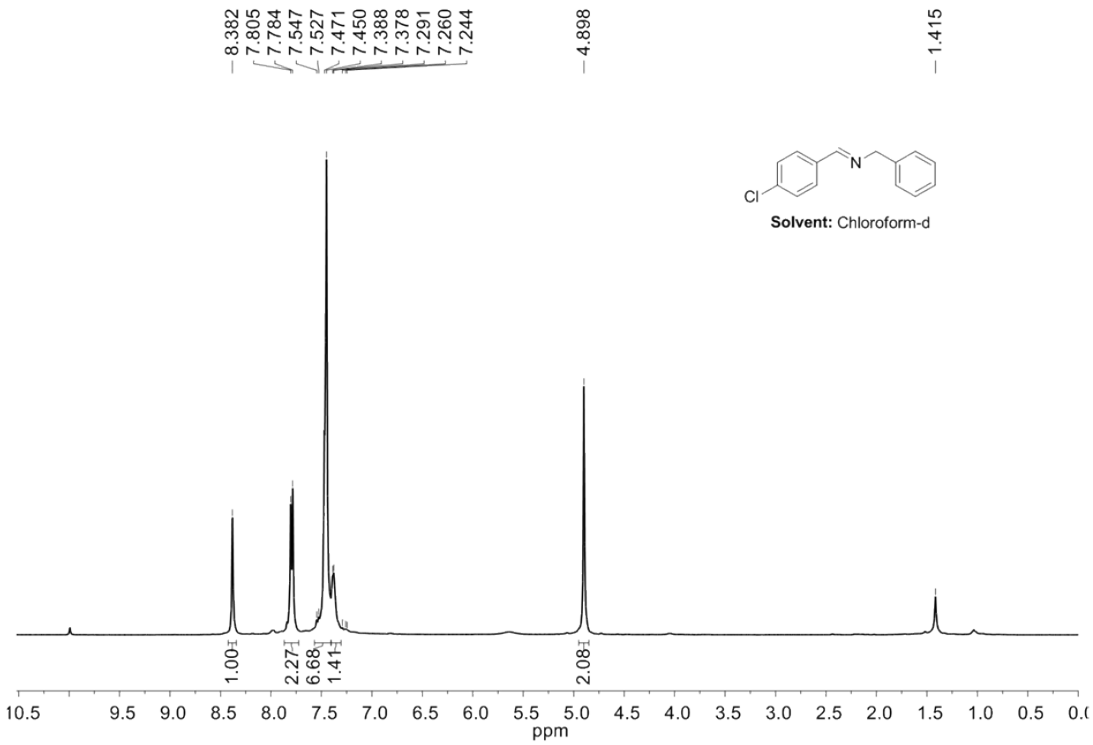


Fig. S13. [1]H NMR spectrum of (E)-N-(4-chlorobenzylidene)-1-phenylmethanamine (**4d**).

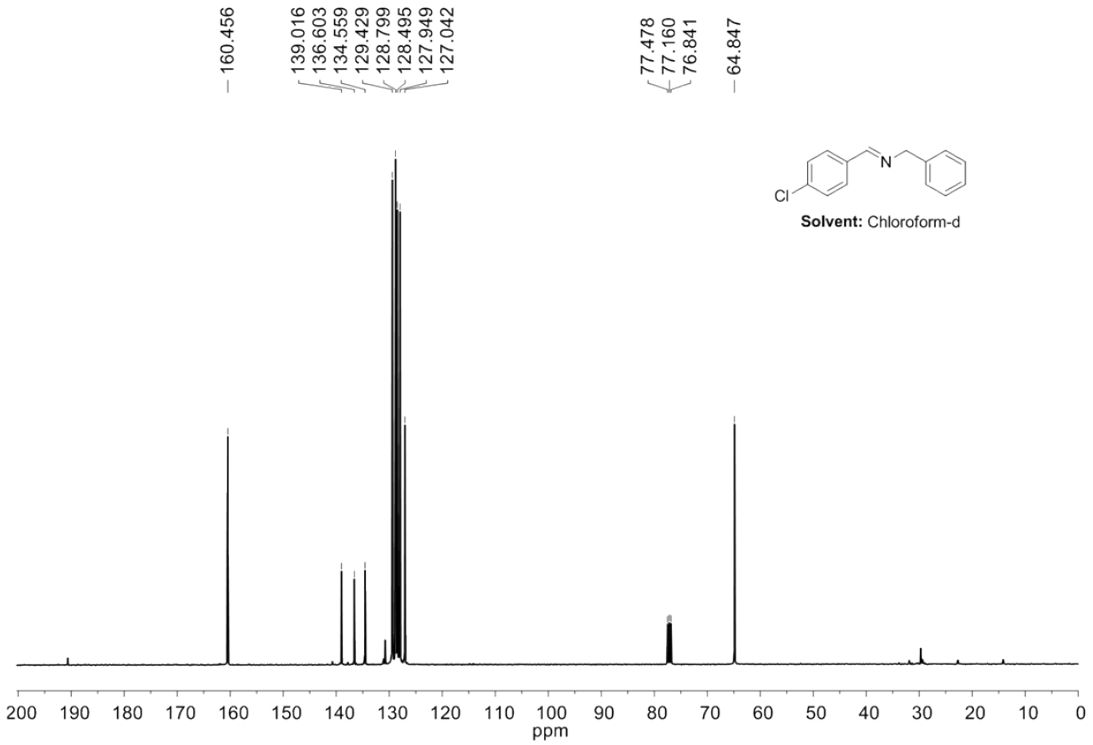


Fig. S14. [13]C NMR spectrum of (E)-N-(4-chlorobenzylidene)-1-phenylmethanamine (**4d**).

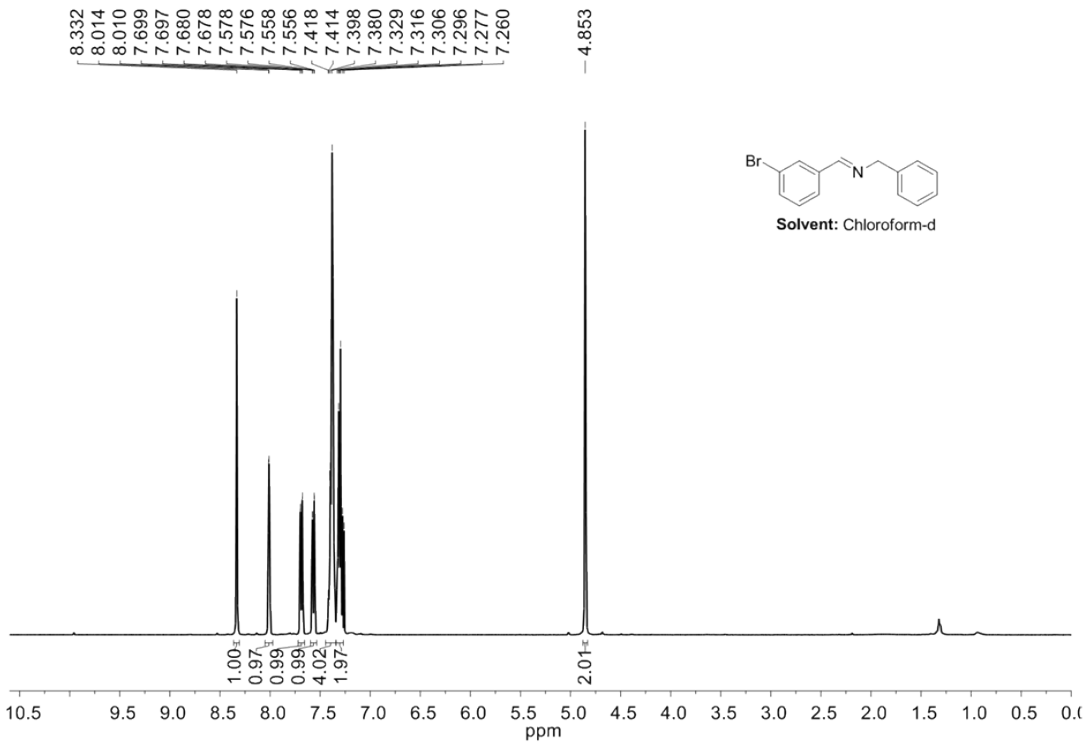


Fig. S15. [1]H NMR spectrum of *N*-(3-bromobenzylidene)-1-phenylmethanamine (**4e**).

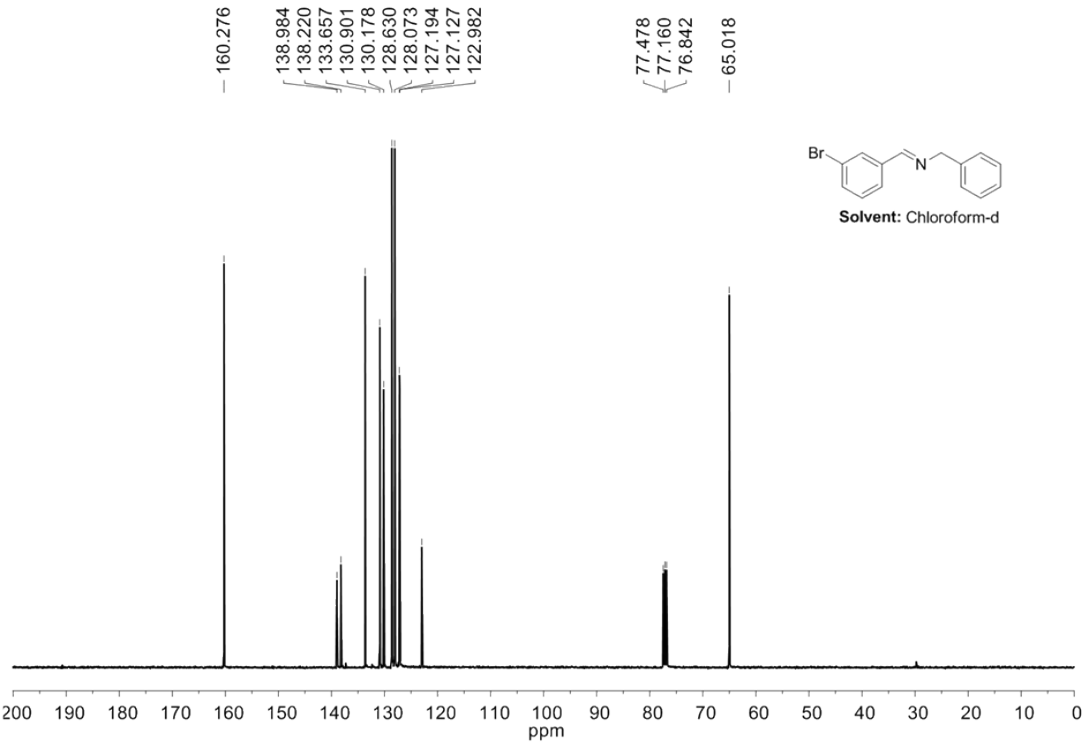


Fig. S16. [13]C NMR spectrum of *N*-(3-bromobenzylidene)-1-phenylmethanamine (**4e**).

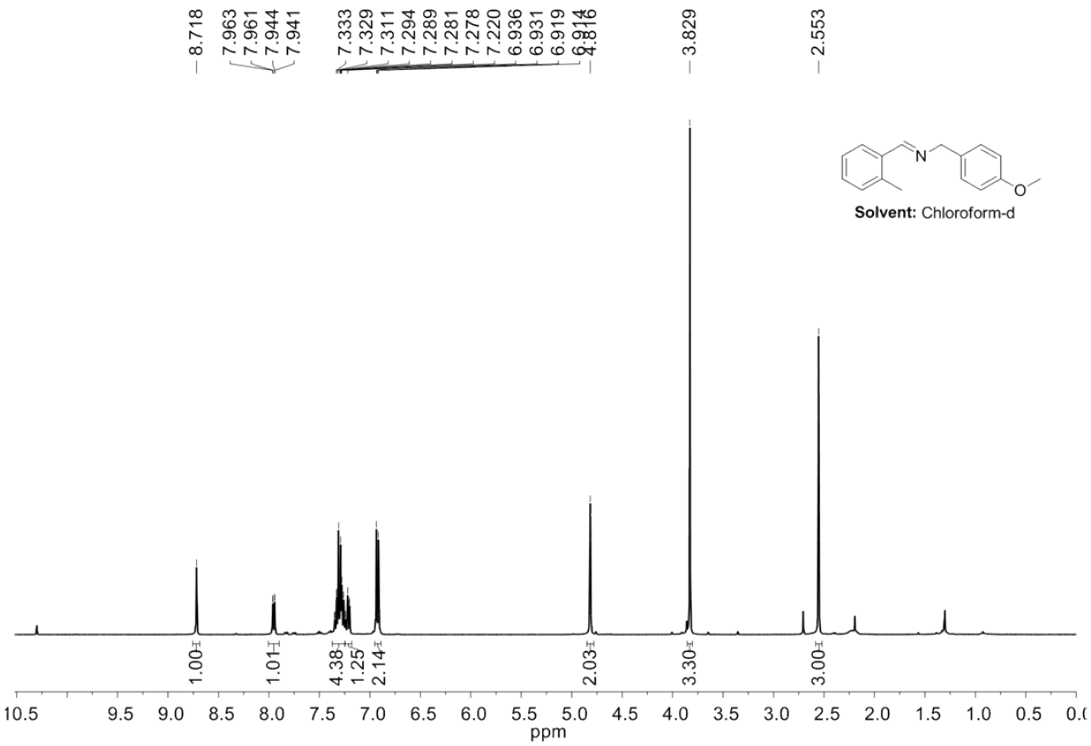


Fig. S17. [1]H NMR spectrum of 1-(4-methoxyphenyl)-*N*-(2-methylbenzylidene)methanamine (**4f**).

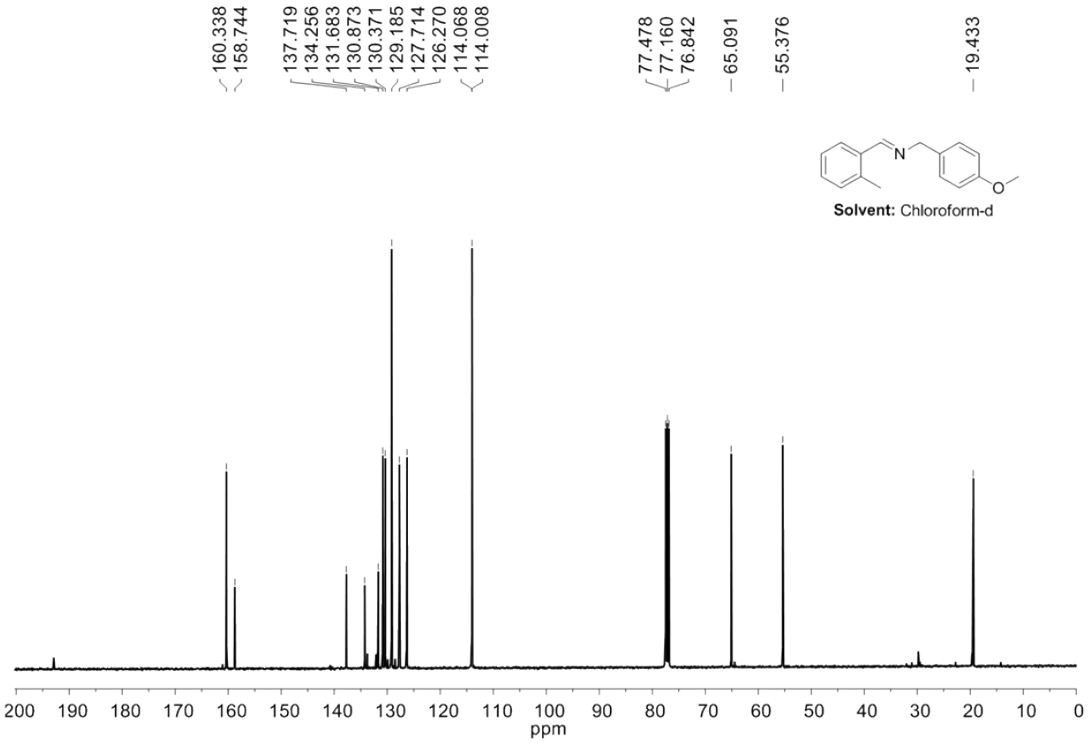


Fig. S18. [1]H NMR spectrum of 1-(4-methoxyphenyl)-*N*-(2-methylbenzylidene)methanamine (**4f**).

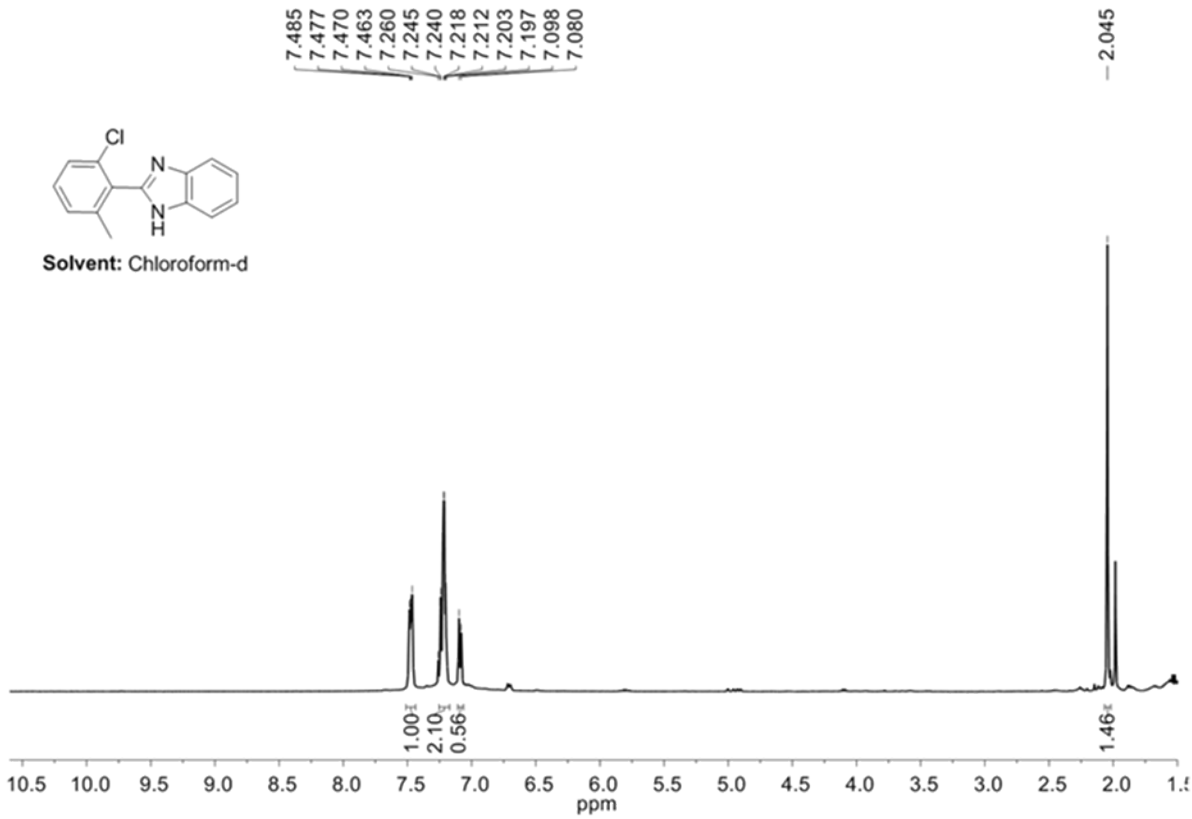


Fig. S19. [1]H NMR spectrum of 2-(2-chloro-6-methylphenyl)-1*H*-benzo[*d*]imidazole (**6c**).

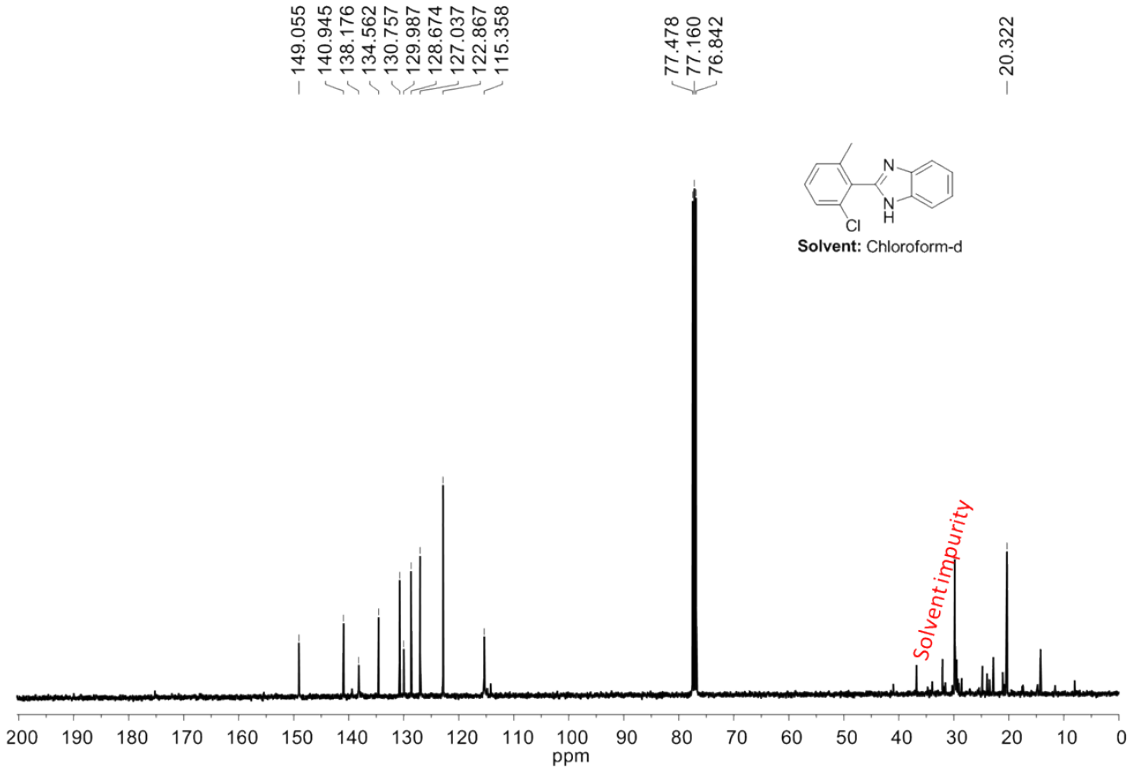


Fig. S20.[13]C NMR spectrum of 2-(2-chloro-6-methylphenyl)-1*H*-benzo[*d*]imidazole (**6c**).

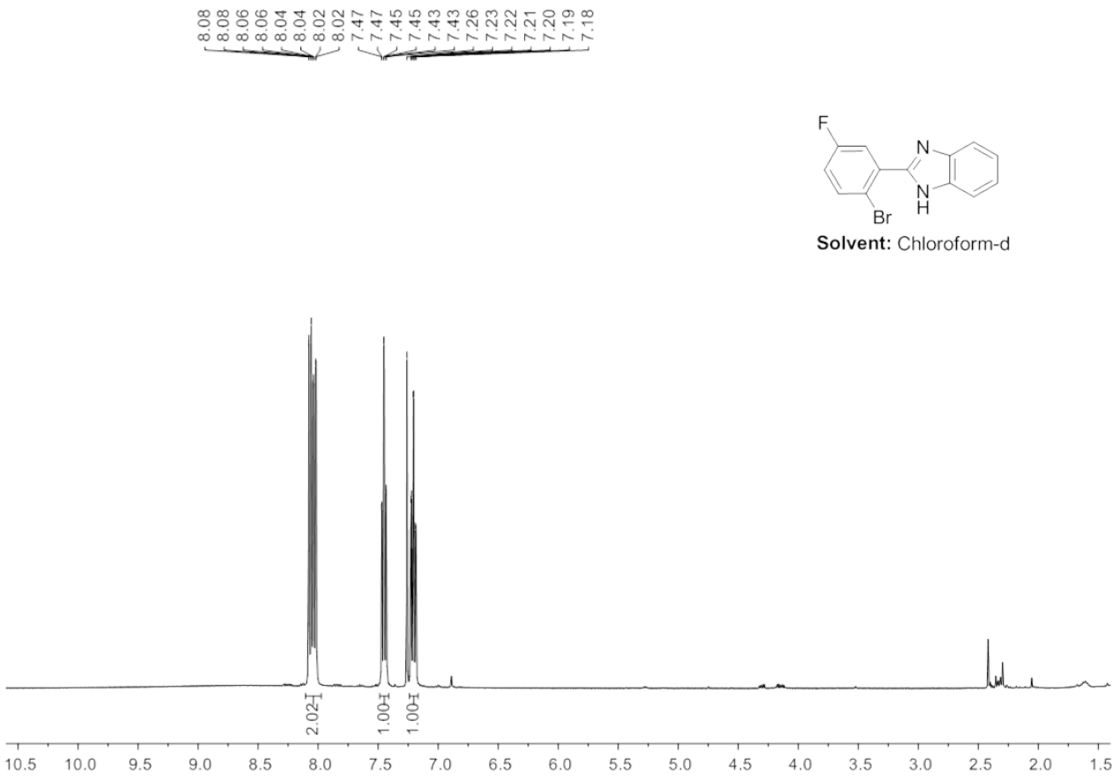


Fig. S21. [1]H NMR spectrum of 2-(2-bromo-5-fluorophenyl)-1*H*-benzo[*d*]imidazole (**6d**).

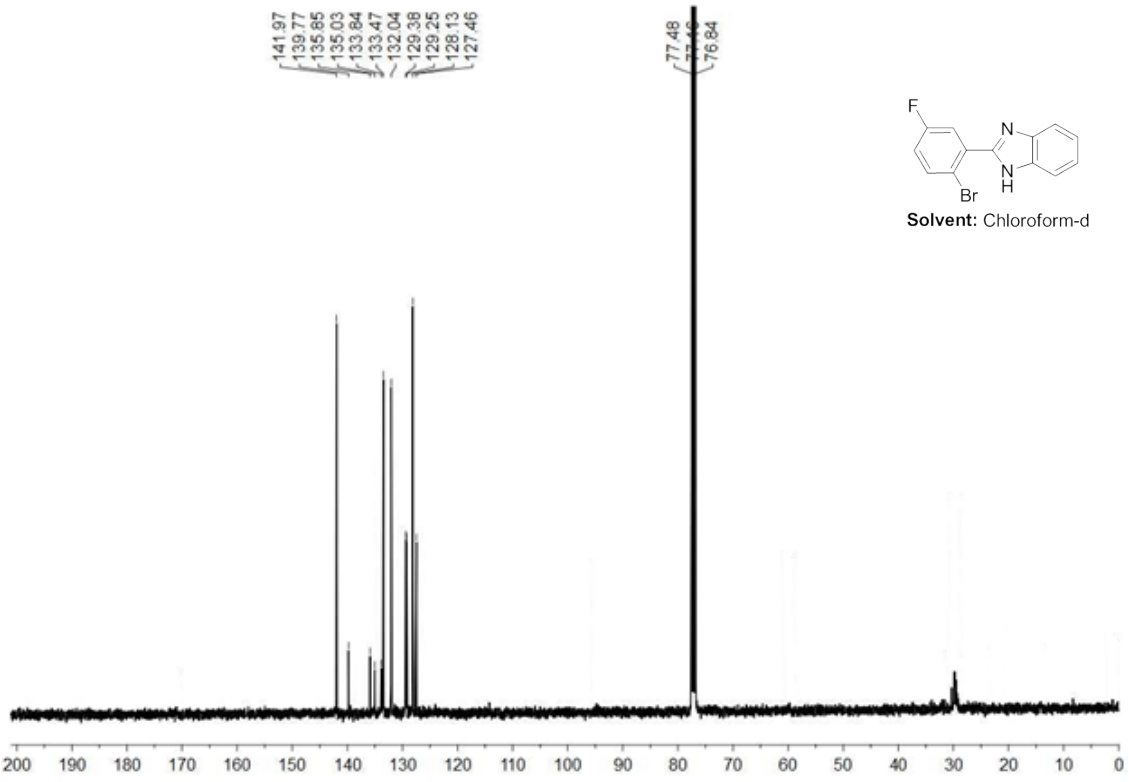


Fig. S22: [13]C NMR spectrum of 2-(2-bromo-5-fluorophenyl)-1*H*-benzo[*d*]imidazole (**6d**).

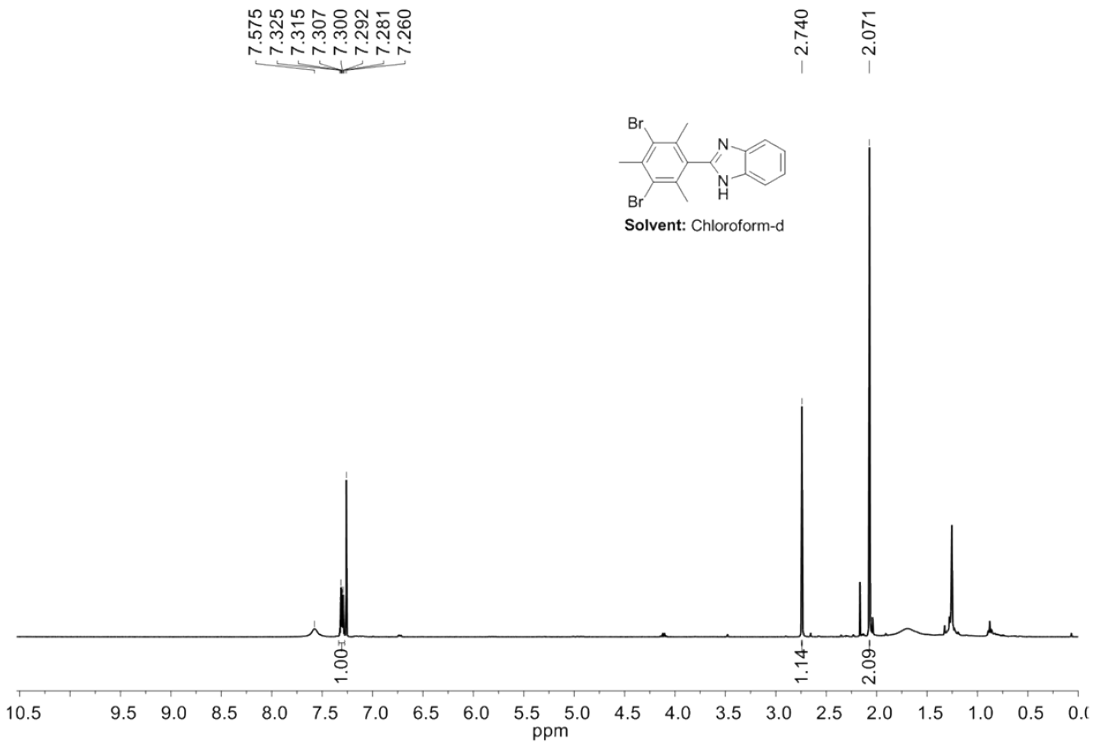


Fig. S23.[1]H NMR spectrum of 2-(3,5-dibromo-2,4,6-trimethylphenyl)-1*H*-benzo[*d*]imidazole (**6f**).

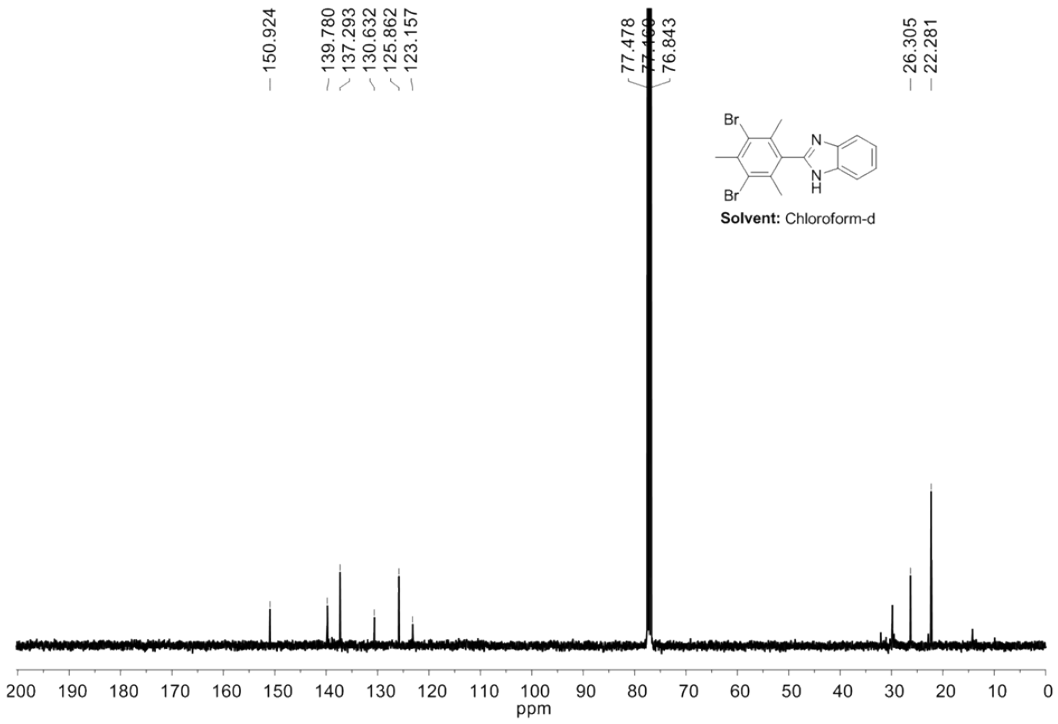


Fig. S24. [13]C NMR spectrum of 2-(3,5-dibromo-2,4,6-trimethylphenyl)-1*H*-benzo[*d*]imidazole (**6f**).

NMR Spectra of known compounds

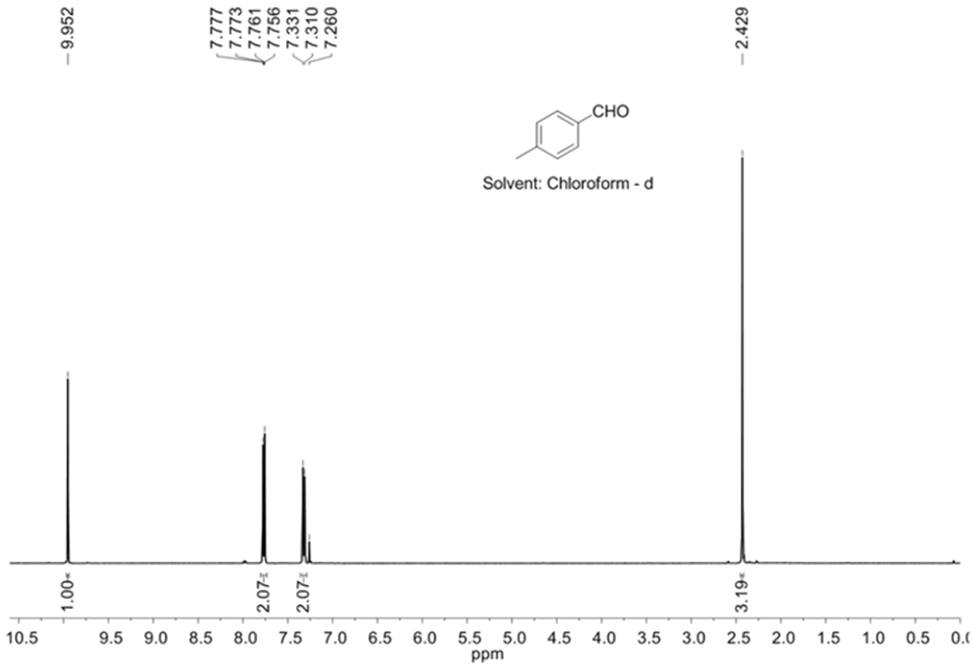


Fig. S25. ^{1}H NMR spectrum of 4-methylbenzaldehyde (**2a**).

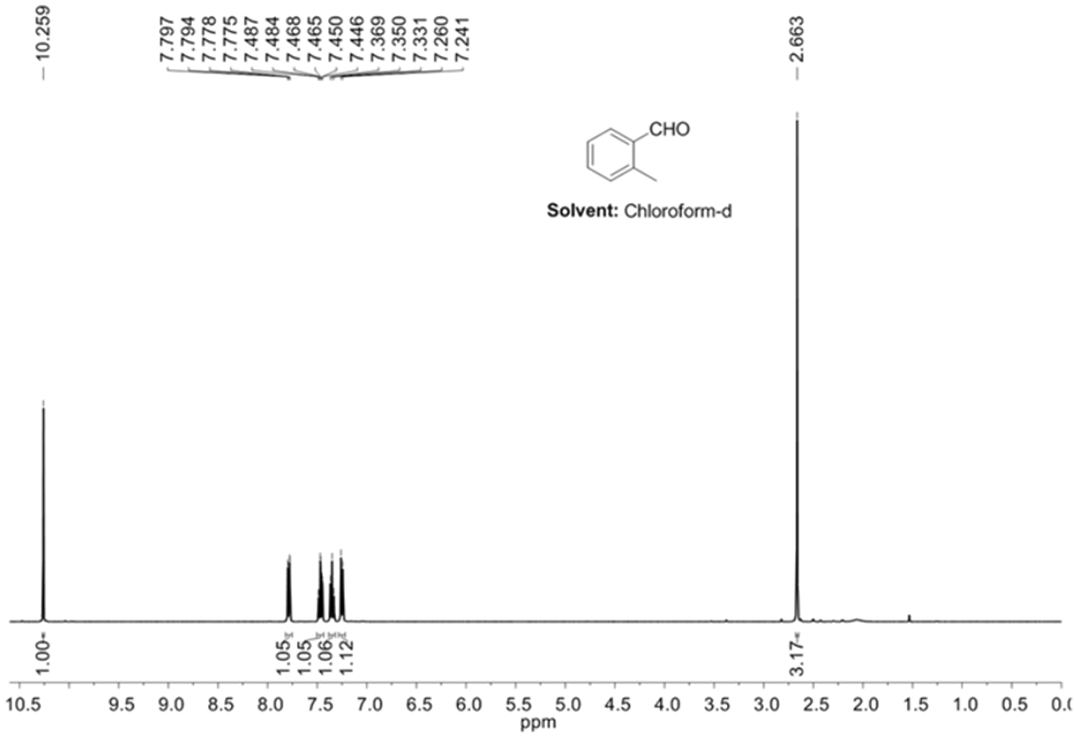


Fig. S26. ^{1}H NMR spectrum of 2-methylbenzaldehyde (**2b**).

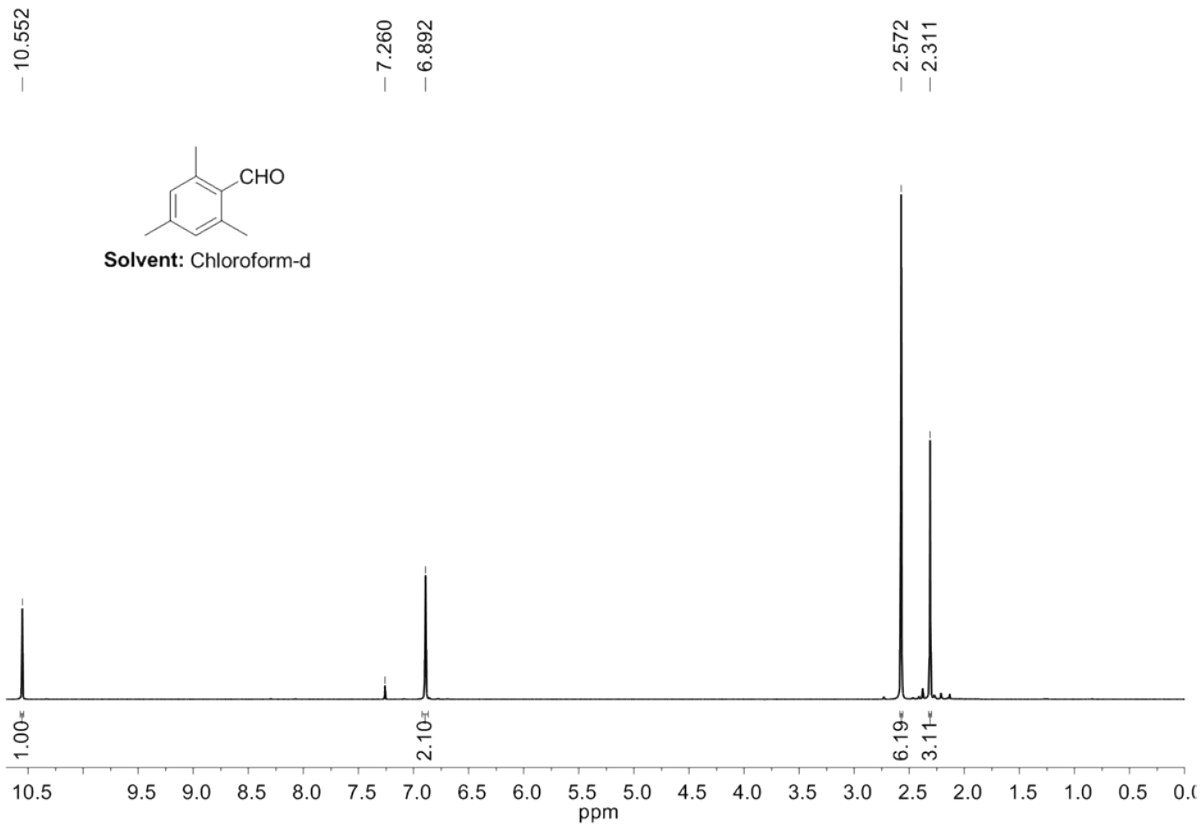


Fig. S27. [1]H NMR spectrum of 2,4,6-trimethylbenzaldehyde (**2c**).

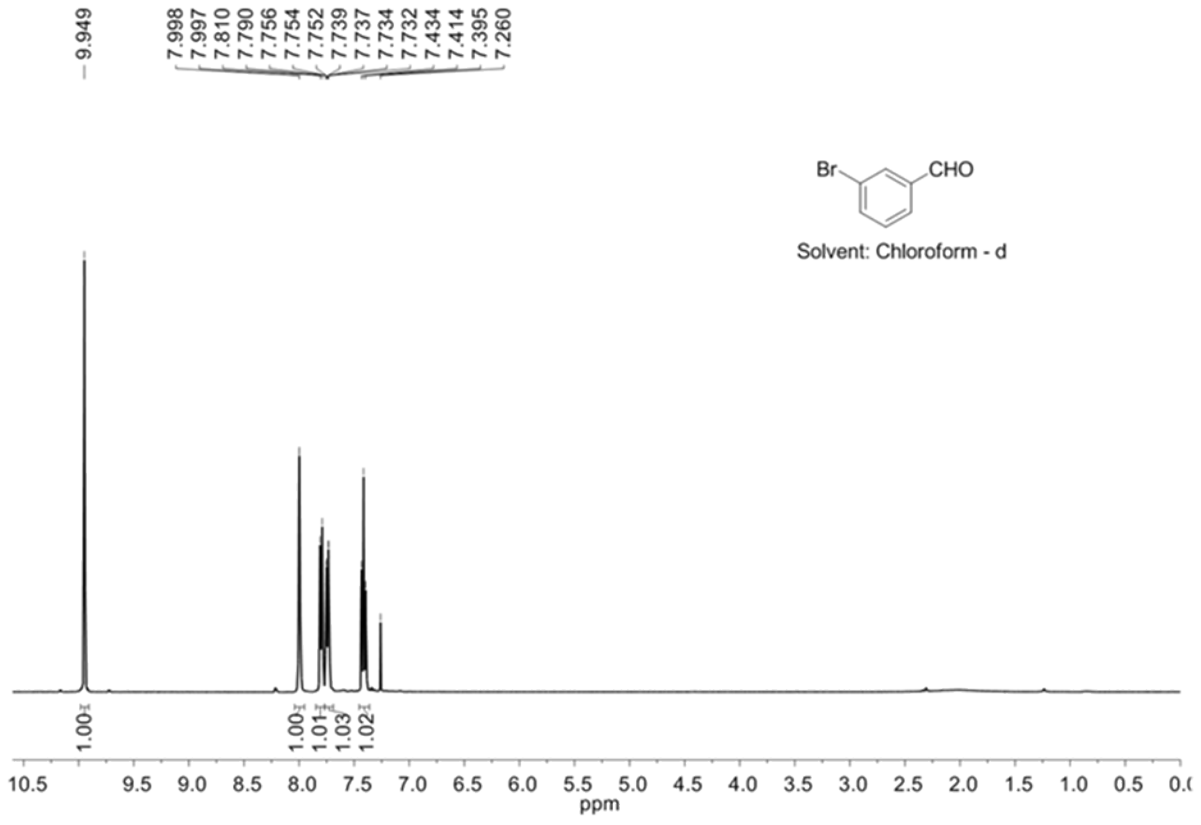


Fig. S28. [1]H NMR spectrum of 3-bromobenzaldehyde (**2d**).

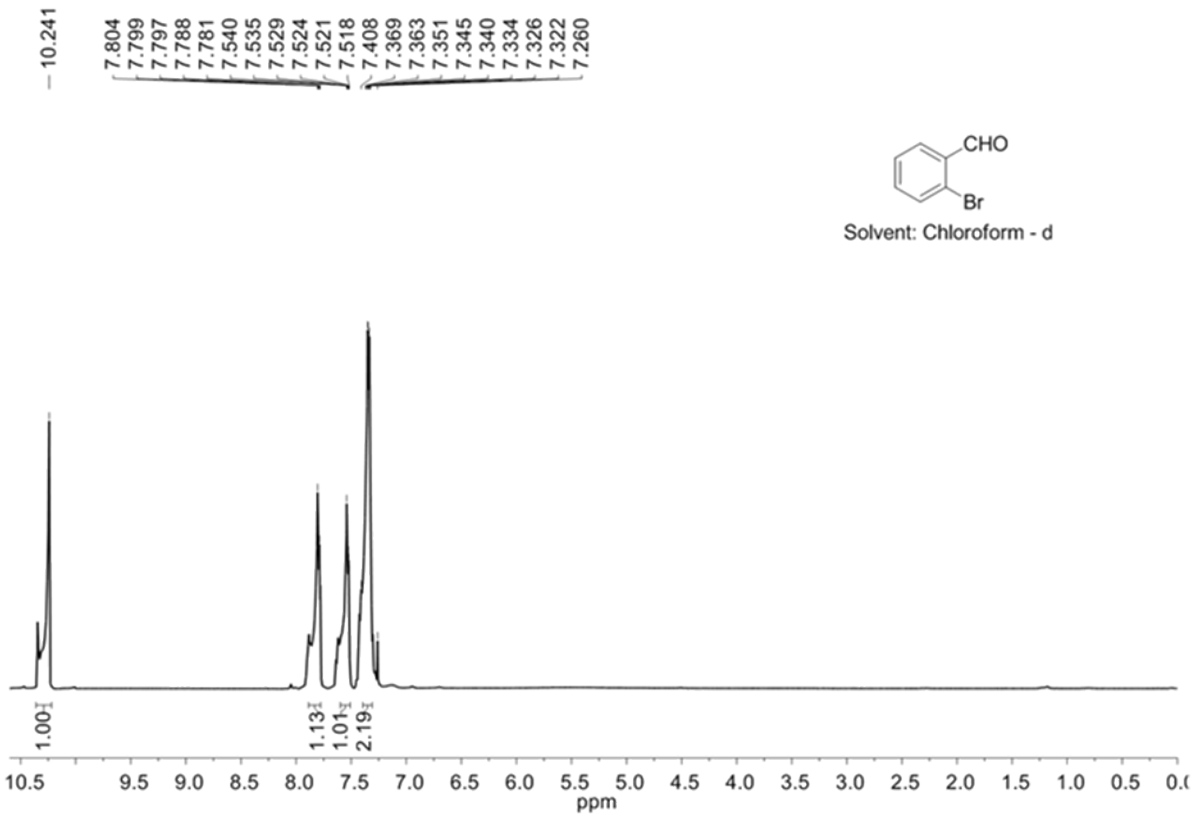


Fig. S29. [1]H NMR spectrum of 2-bromobenzaldehyde (**2e**).

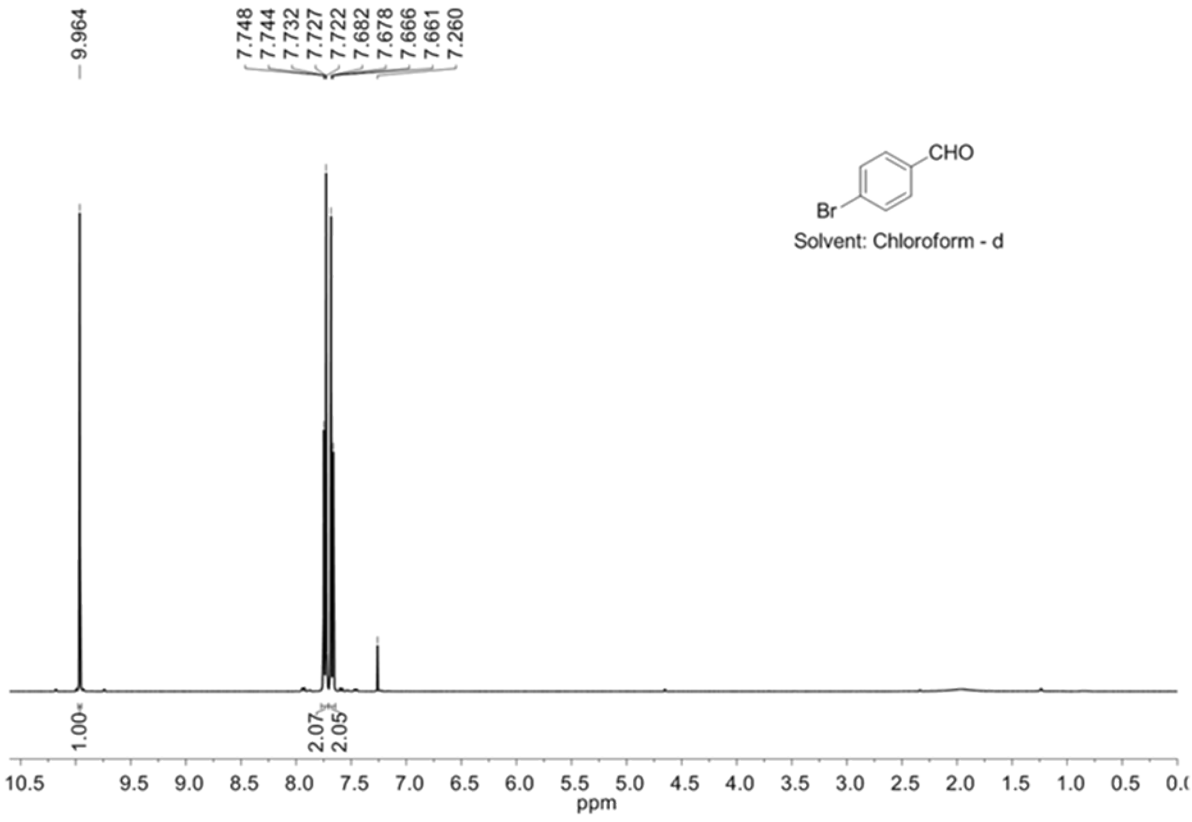


Fig. S30. [1]H NMR spectrum of 4-bromobenzaldehyde (**2f**).

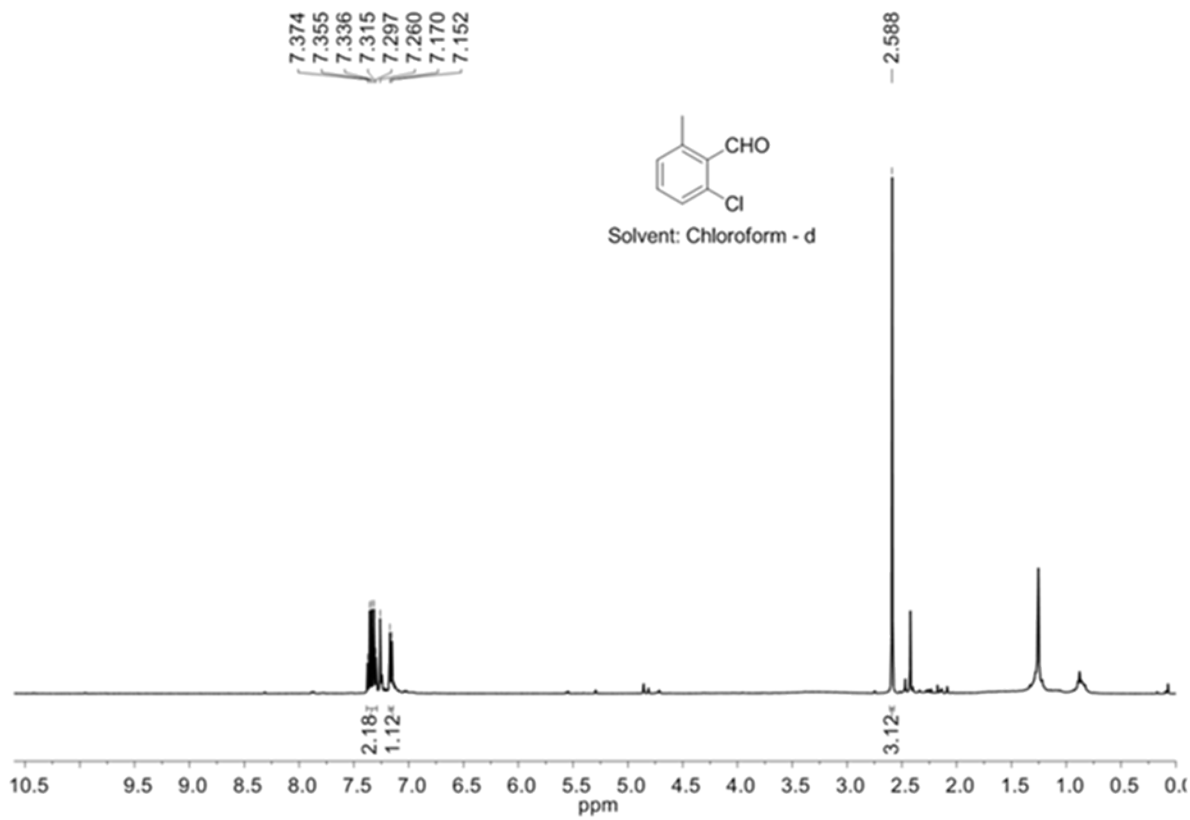


Fig. S31. [1]H NMR spectrum of 2-chloro-6-methylbenzaldehyde (**2h**).

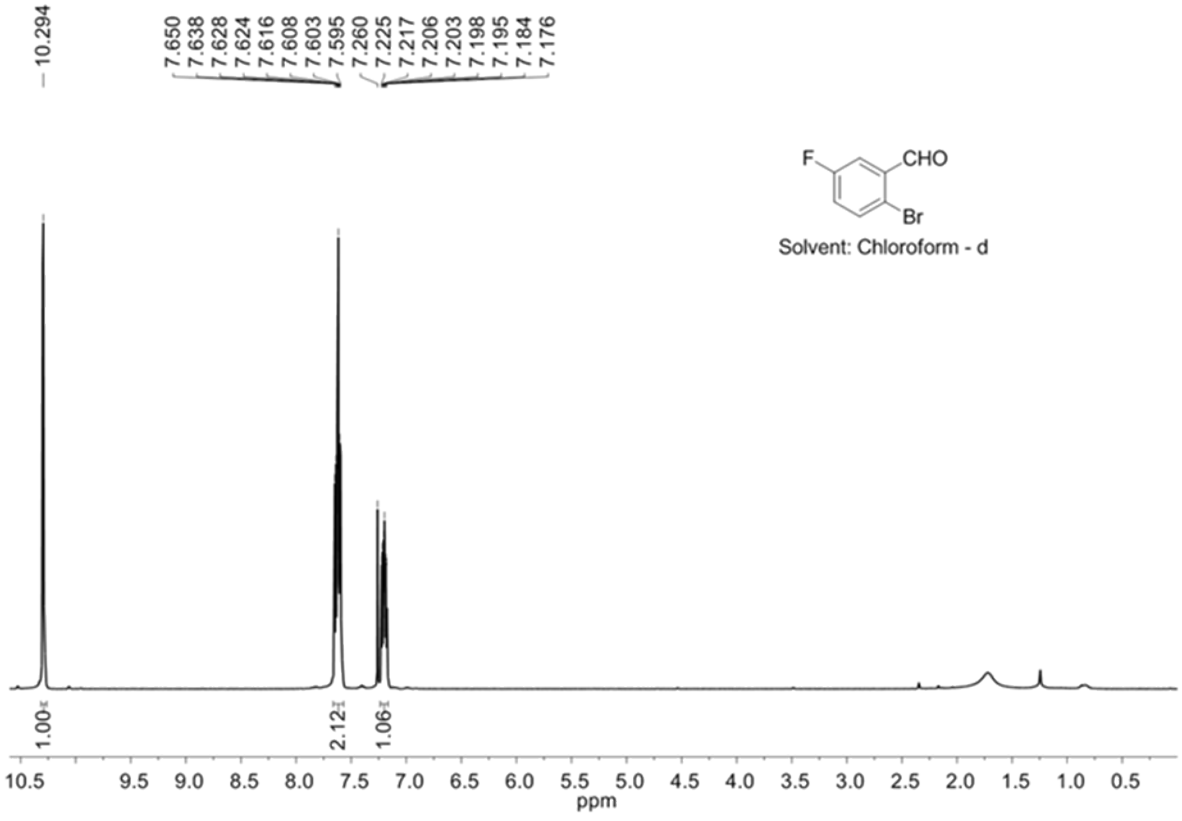


Fig. S32. [1]H NMR spectrum of 2-bromo-5-fluorobenzaldehyde **(2i).**

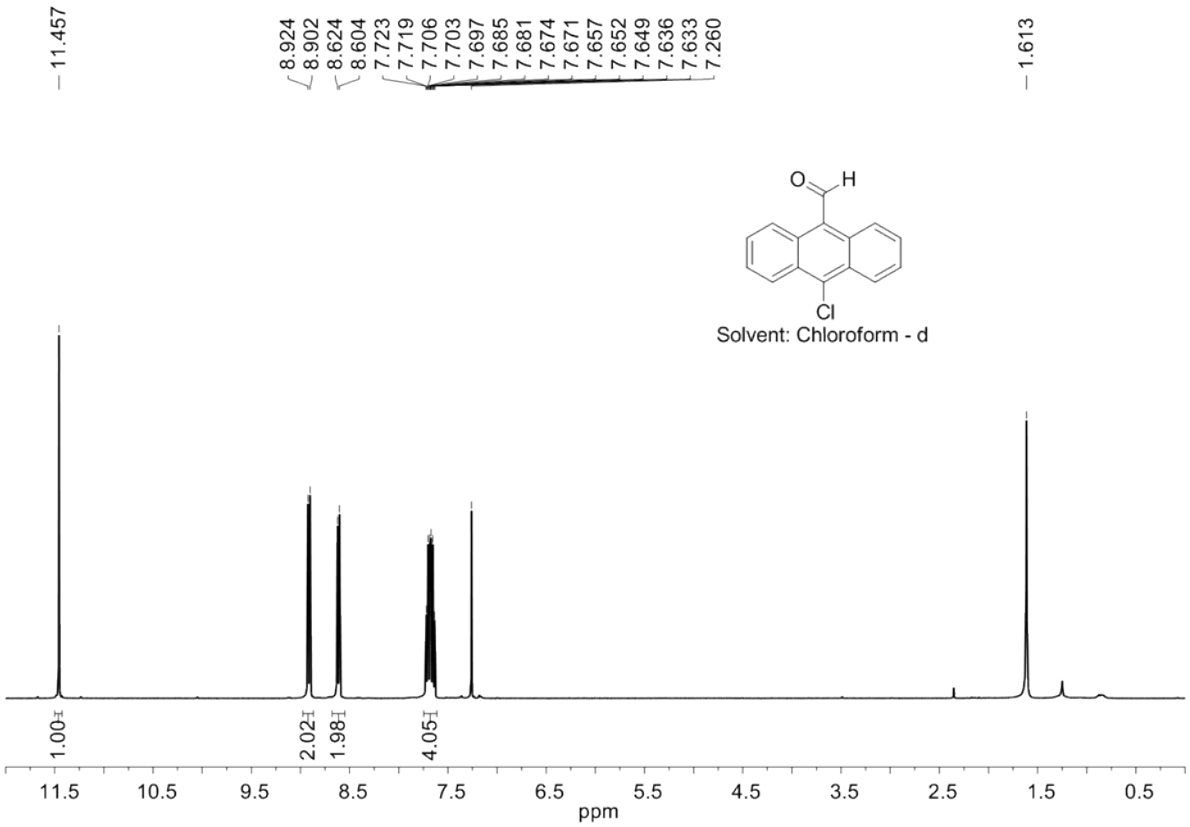


Fig. S33. [1]H NMR spectrum of 10-chloroanthracene-9-carbaldehyde (**2j**).

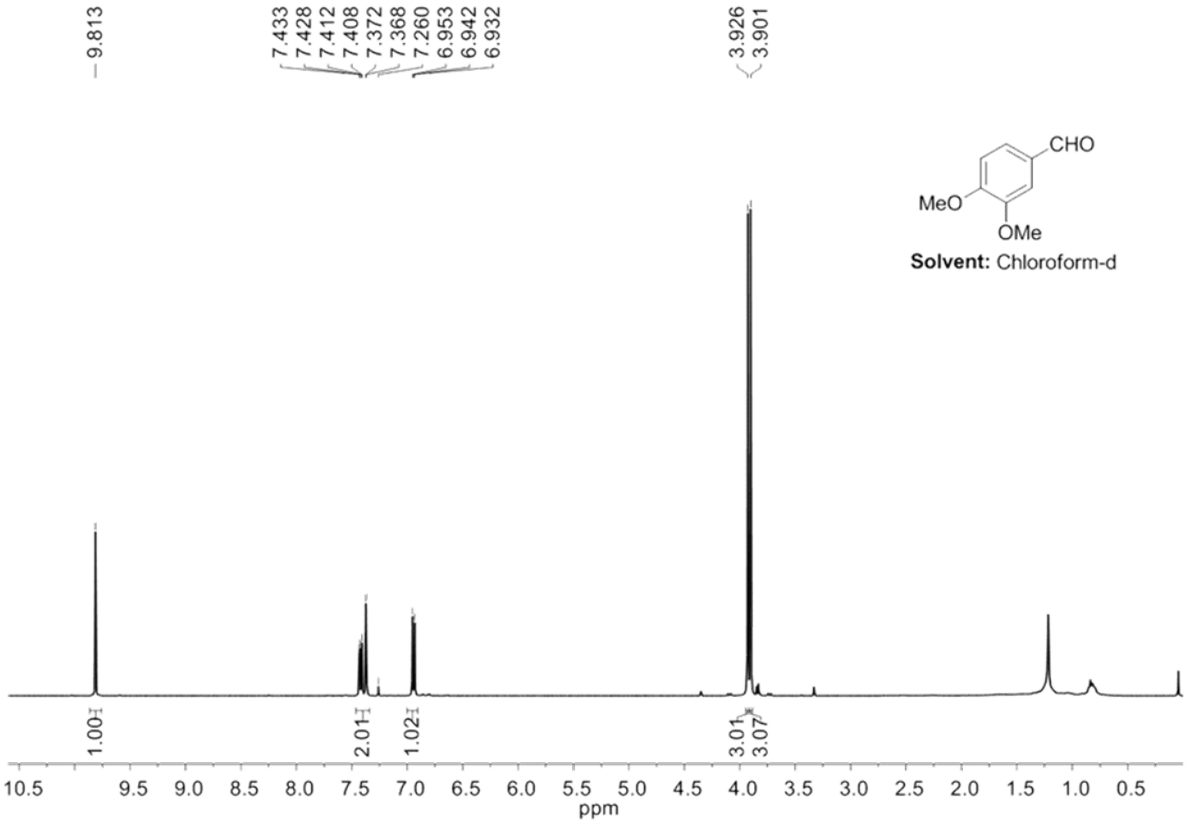


Fig. S34. [1]H NMR spectrum of 3,4-dimethoxybenzaldehyde **(2k).**

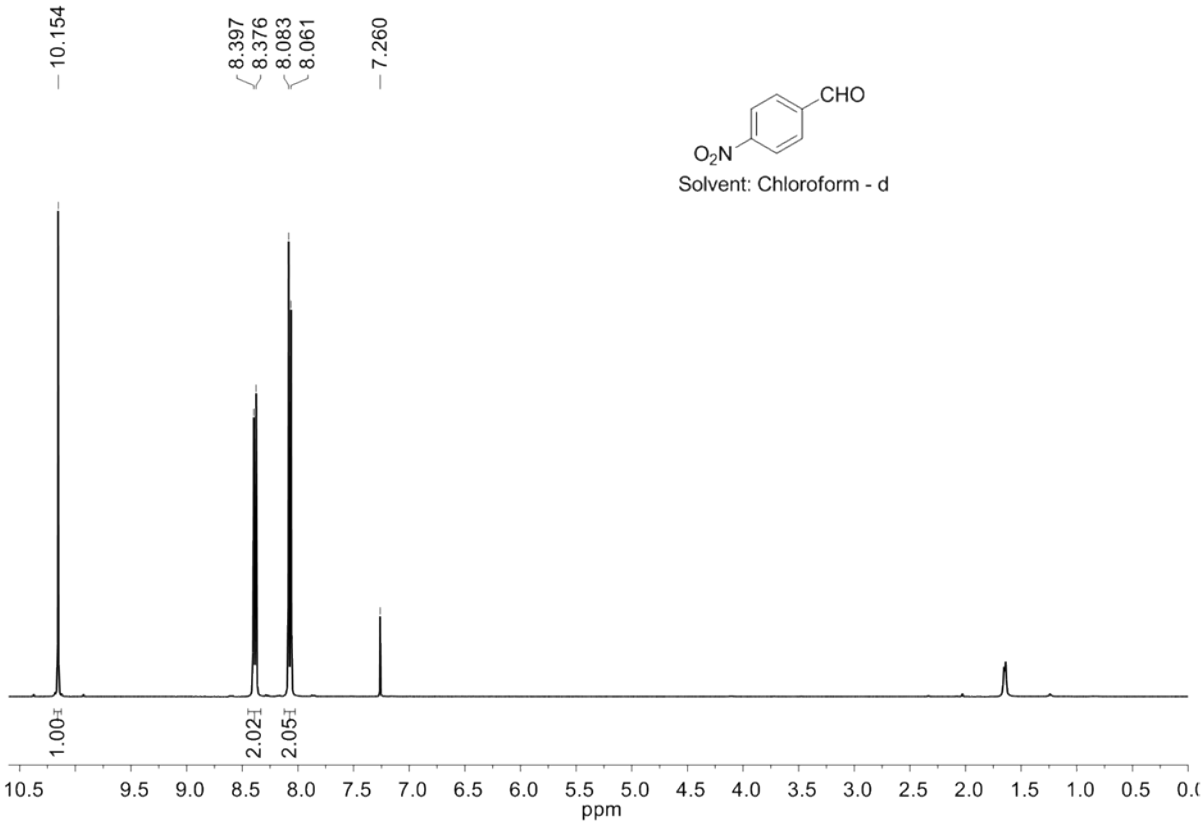


Fig. S35. [1]H NMR spectrum of 4-nitrobenzaldehyde (**2l**).

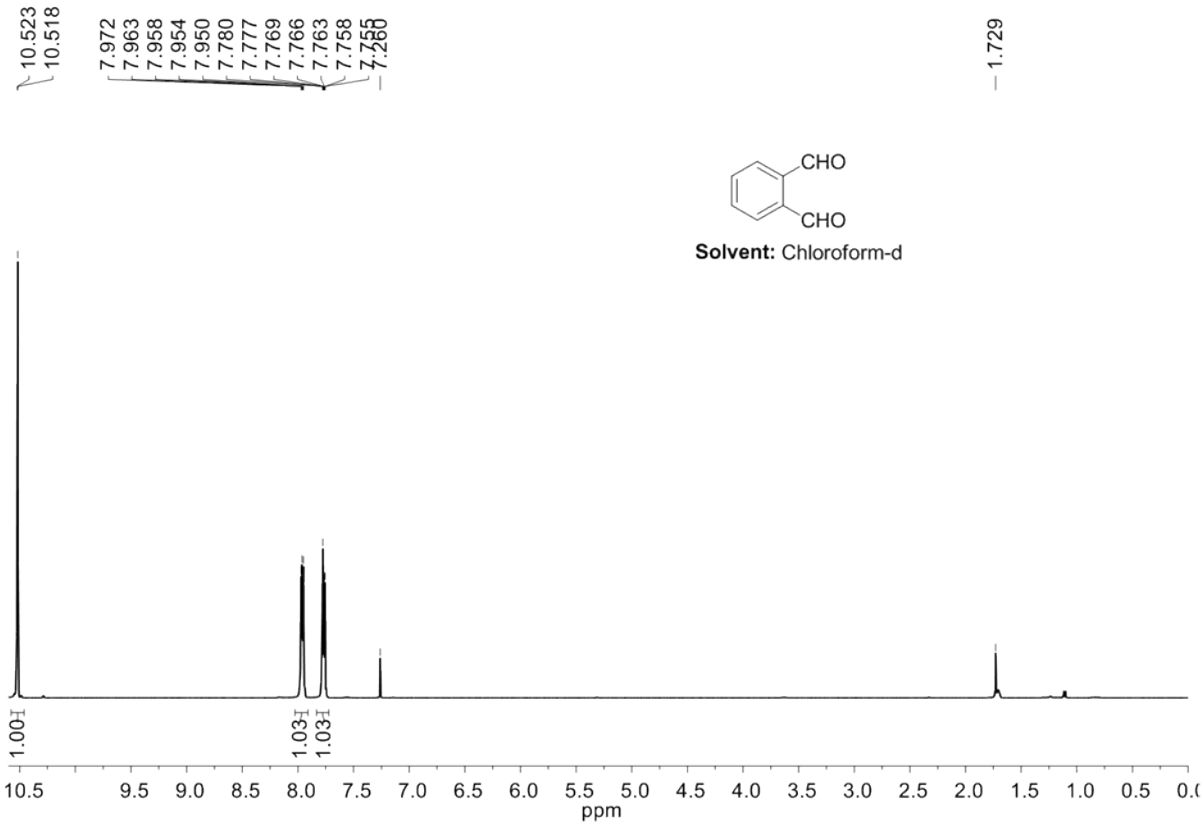


Fig. S36. [1]H NMR spectrum of phthalaldehyde (**2m**).

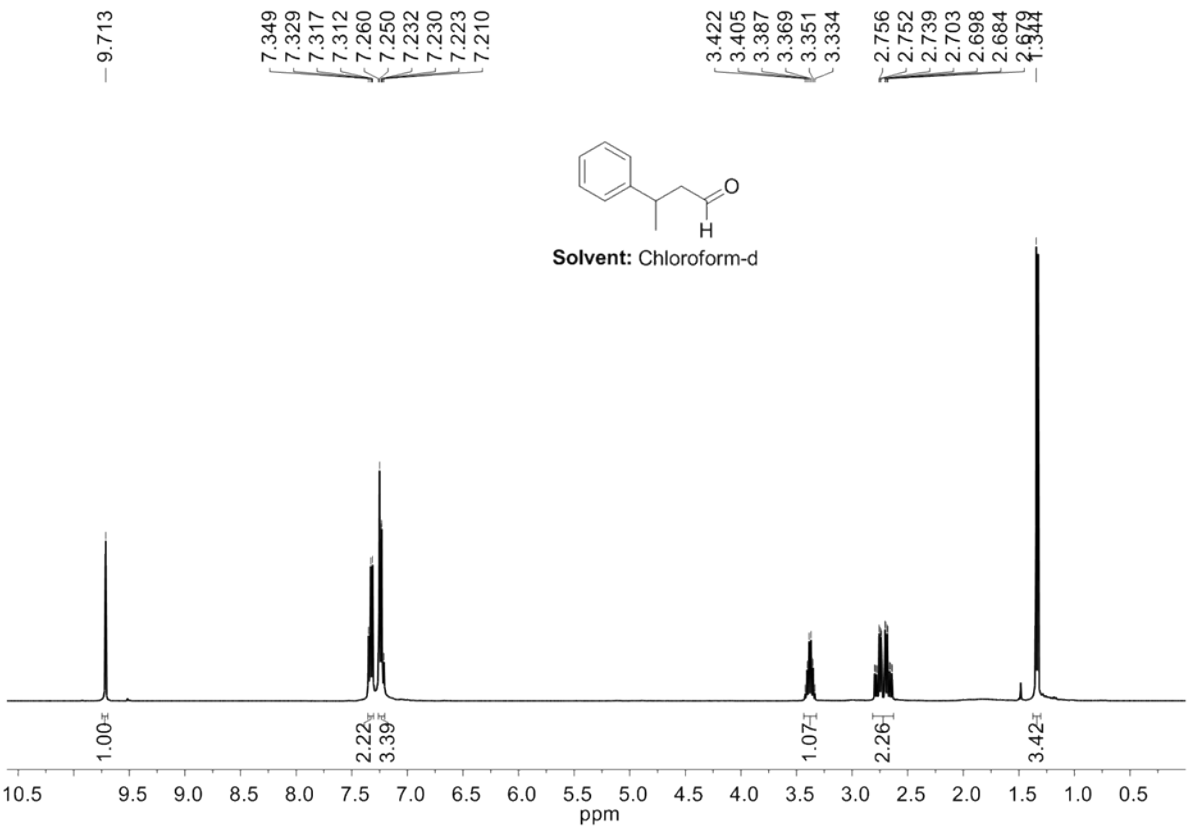


Fig. S37. [1]H NMR spectrum of 3-phenylbutanal (**2n**).

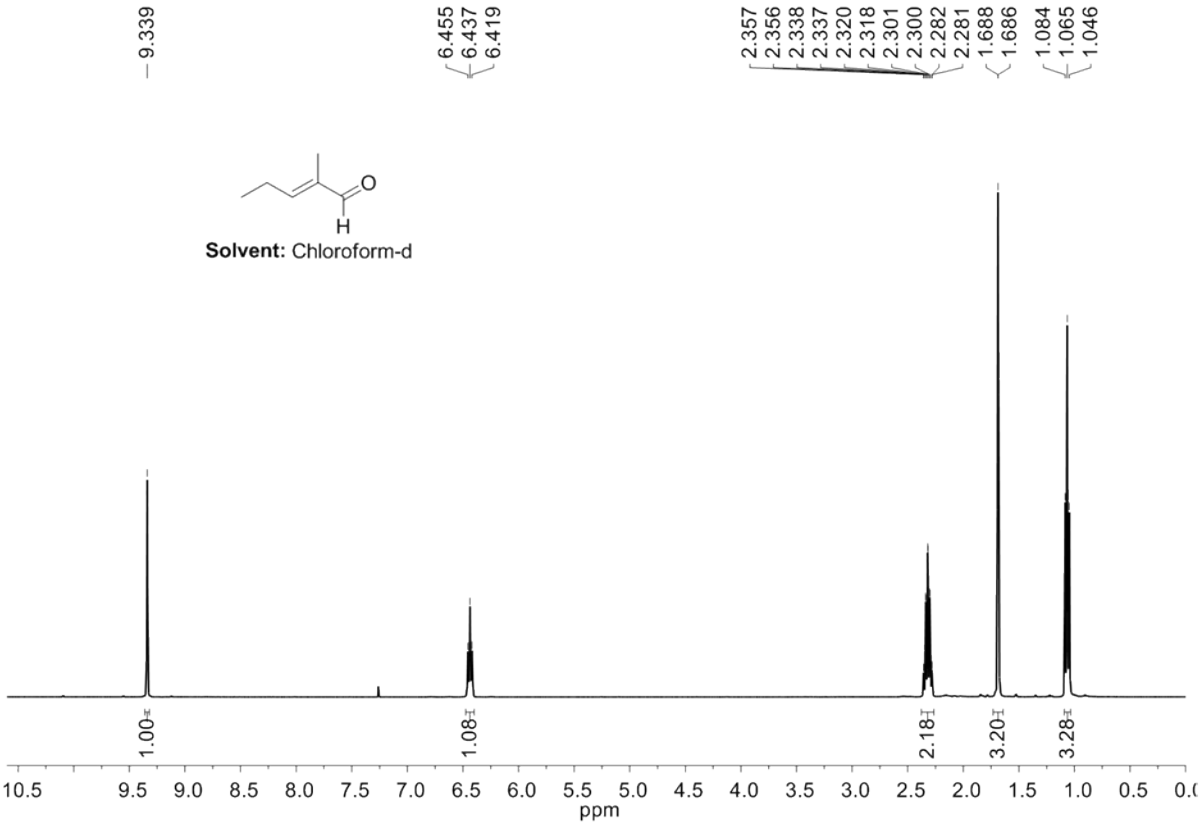


Fig. S38. [1]H NMR spectrum of 2-methylpent-2-enal (**2o**).

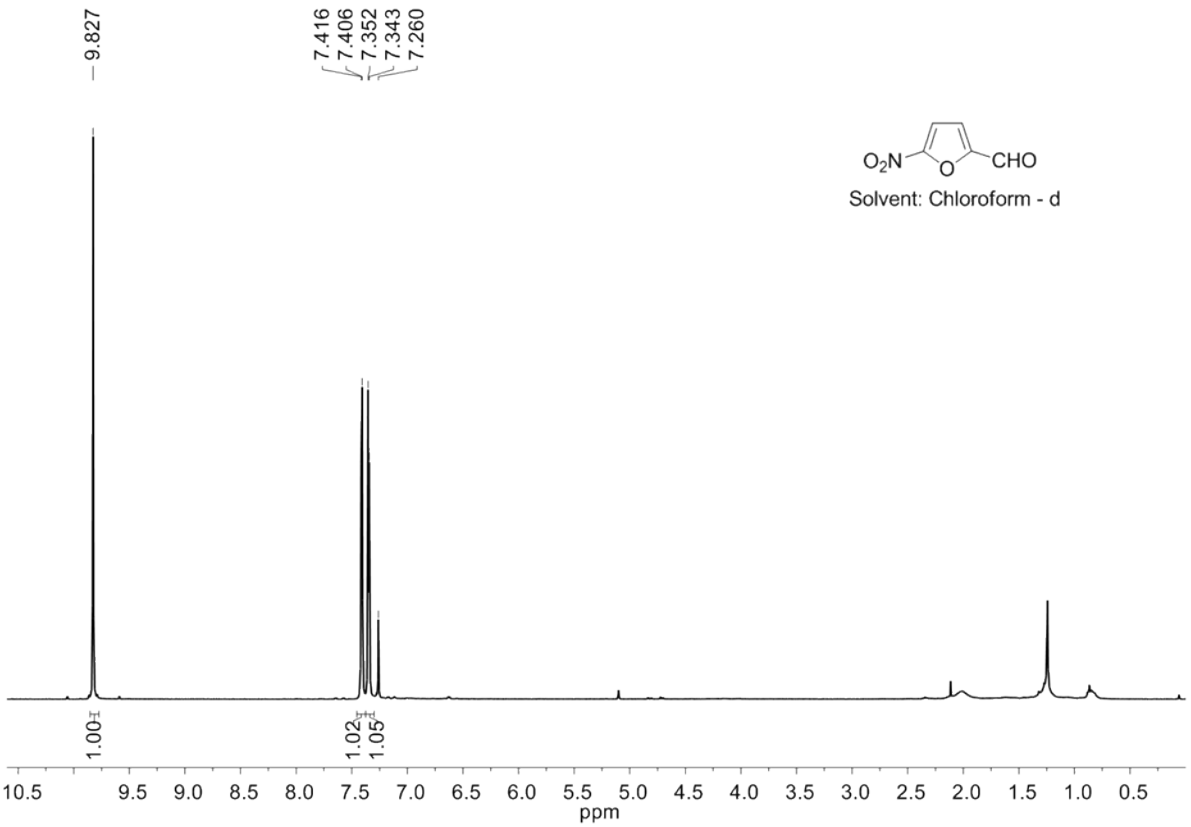


Fig. S39. [1]H NMR spectrum of 5-nitrofuran-2-carbaldehyde (**2q**).

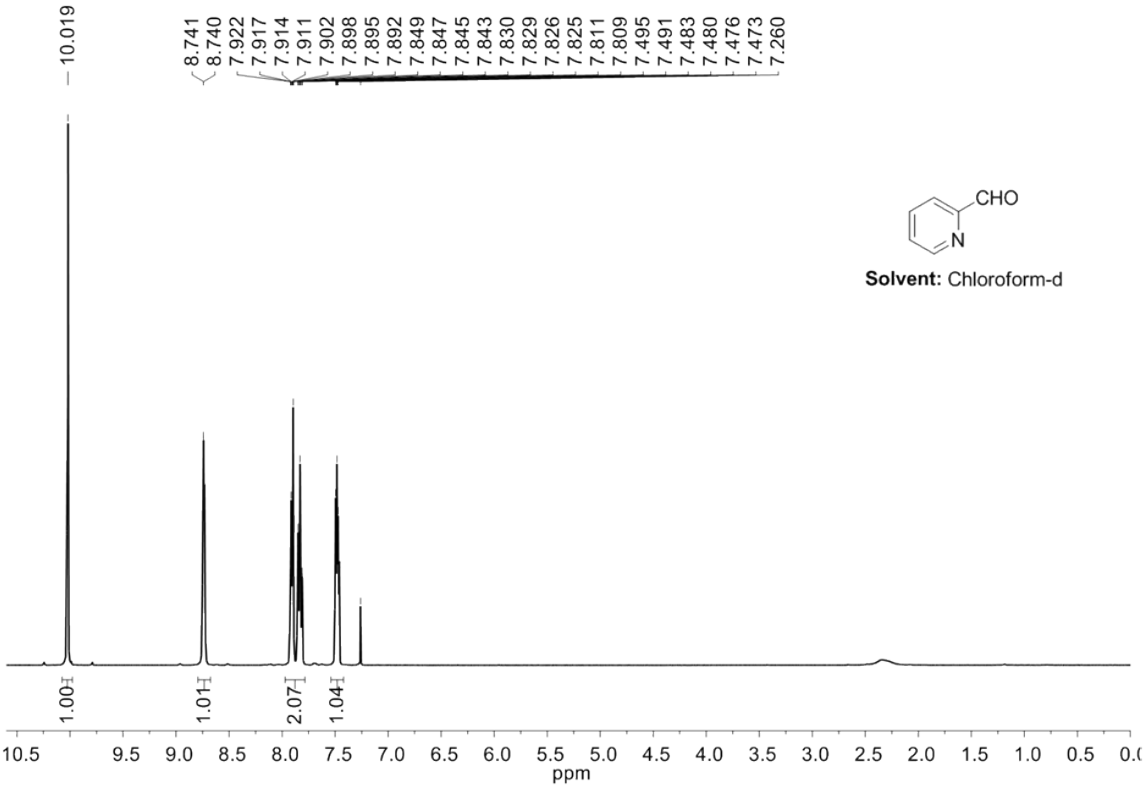


Fig. S40. [1]H NMR spectrum of pyridine-2-carbaldehyde (**2r**).

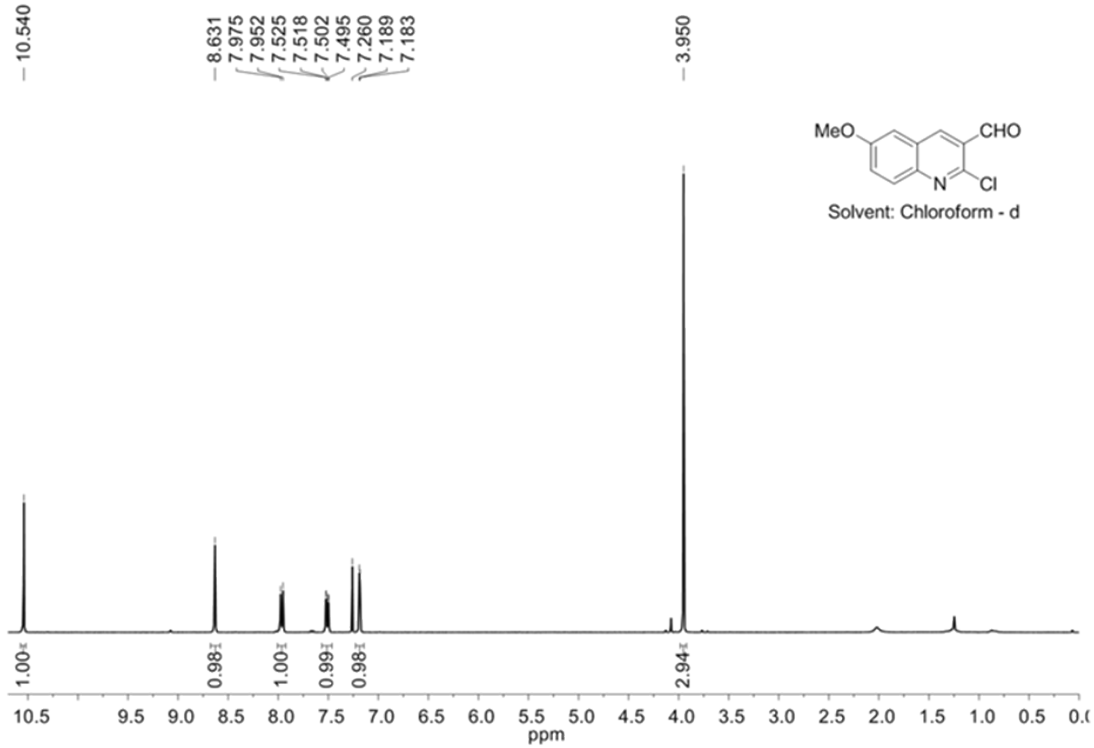


Fig. S41. [1]H NMR spectrum of 2-chloro-6-methoxy-6,7-dihydroquinoline-3-carbaldehyde **(2s)**

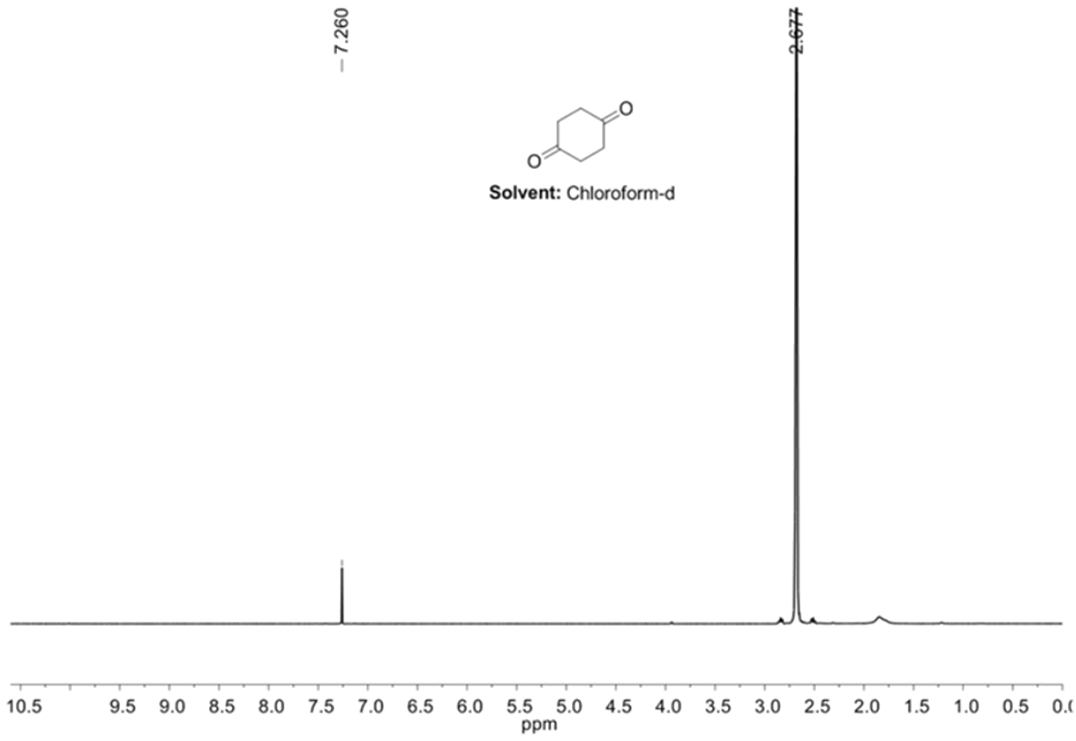


Fig. S42. [1]H NMR spectrum of cyclohexane-1,4-dione (**2t**).

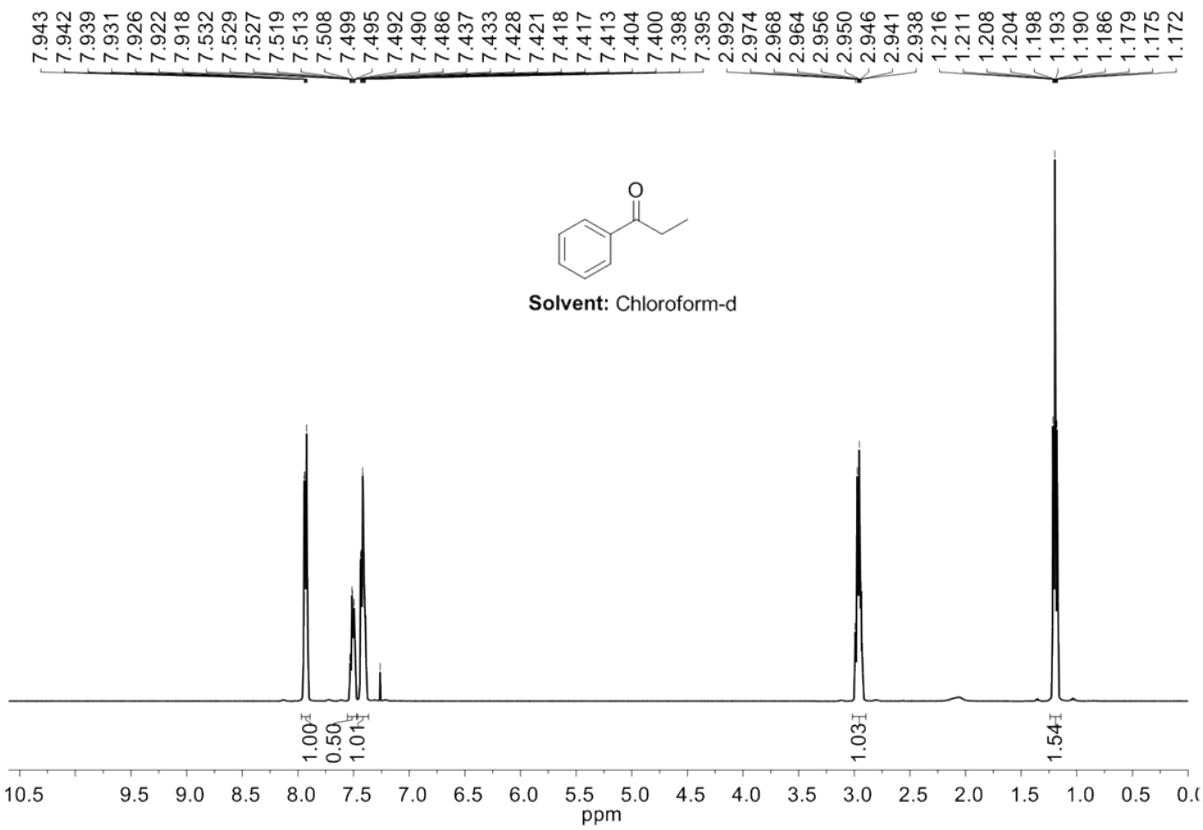


Fig. S43. [1]H NMR spectrum of propiophenone (**2u**).

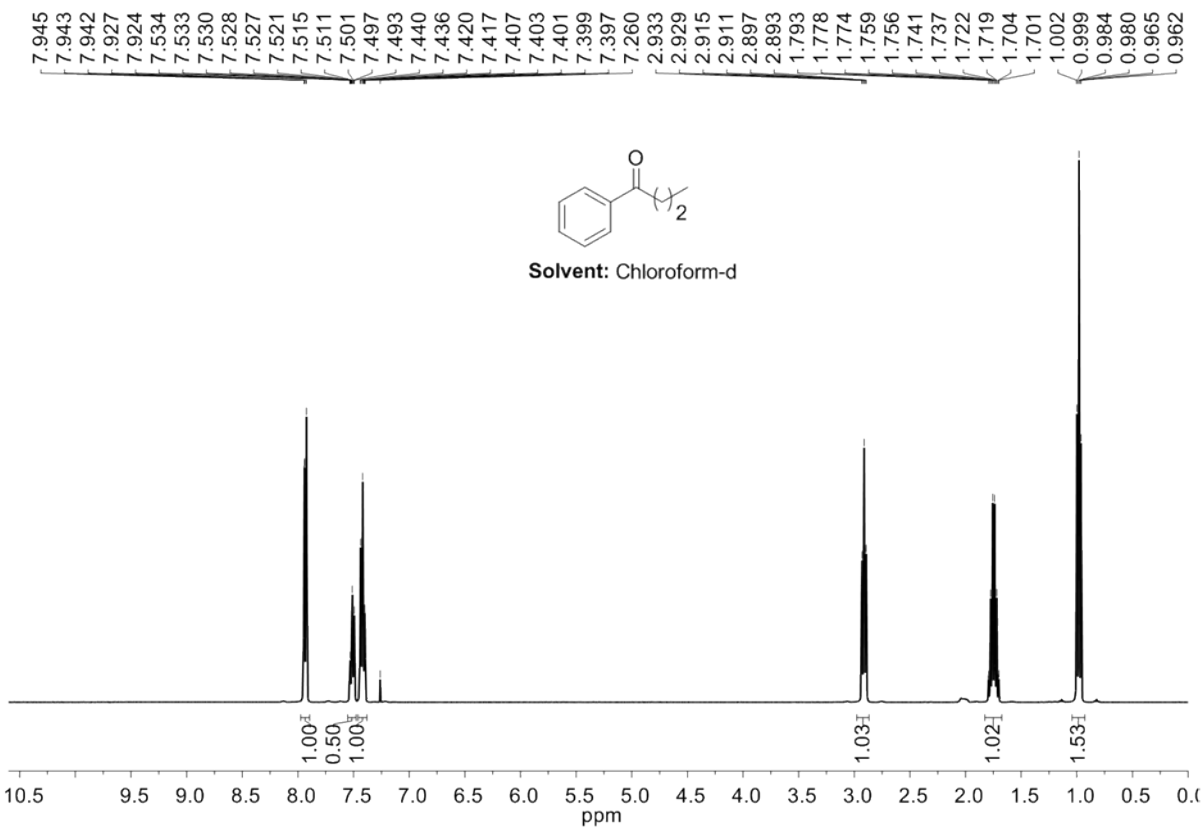


Fig. S44. [1]H NMR spectrum of 1-phenylbutan-1-one (**2v**).

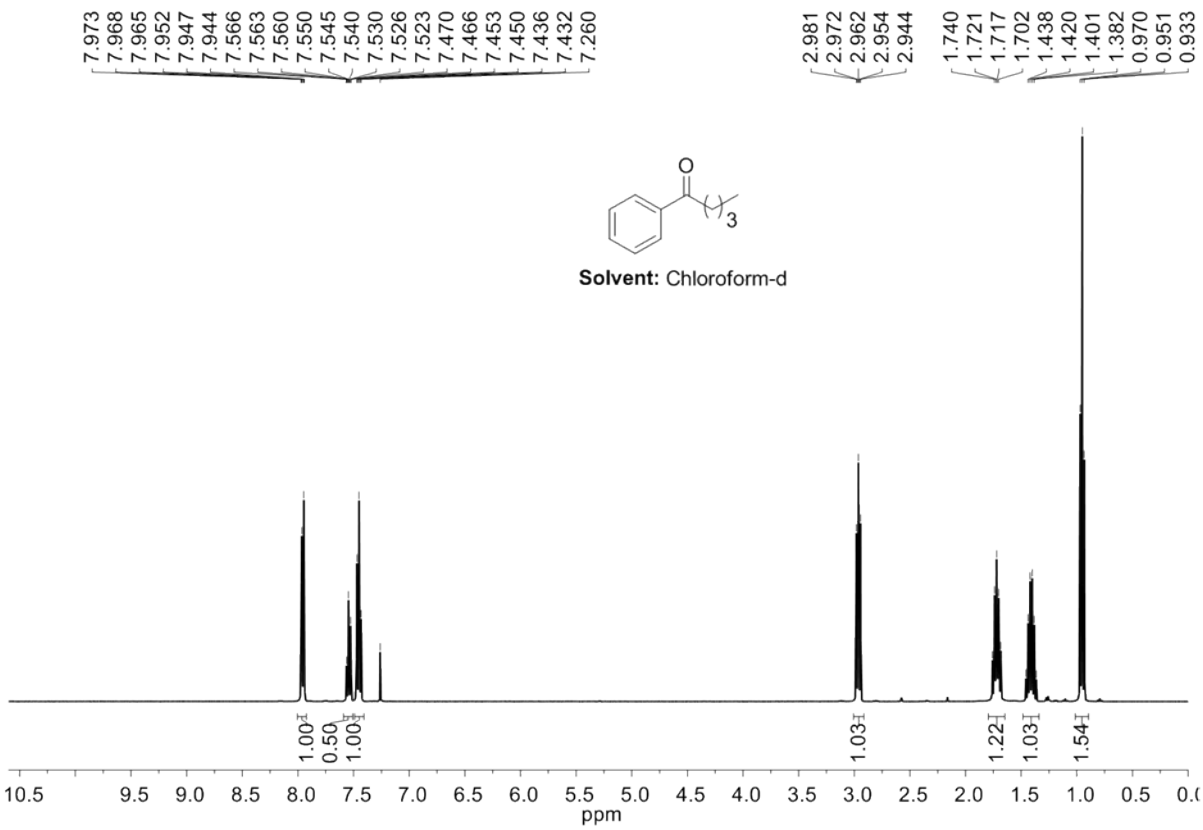


Fig. S45. [1]H NMR spectrum of 1-phenylpentan-1-one (**2w**).

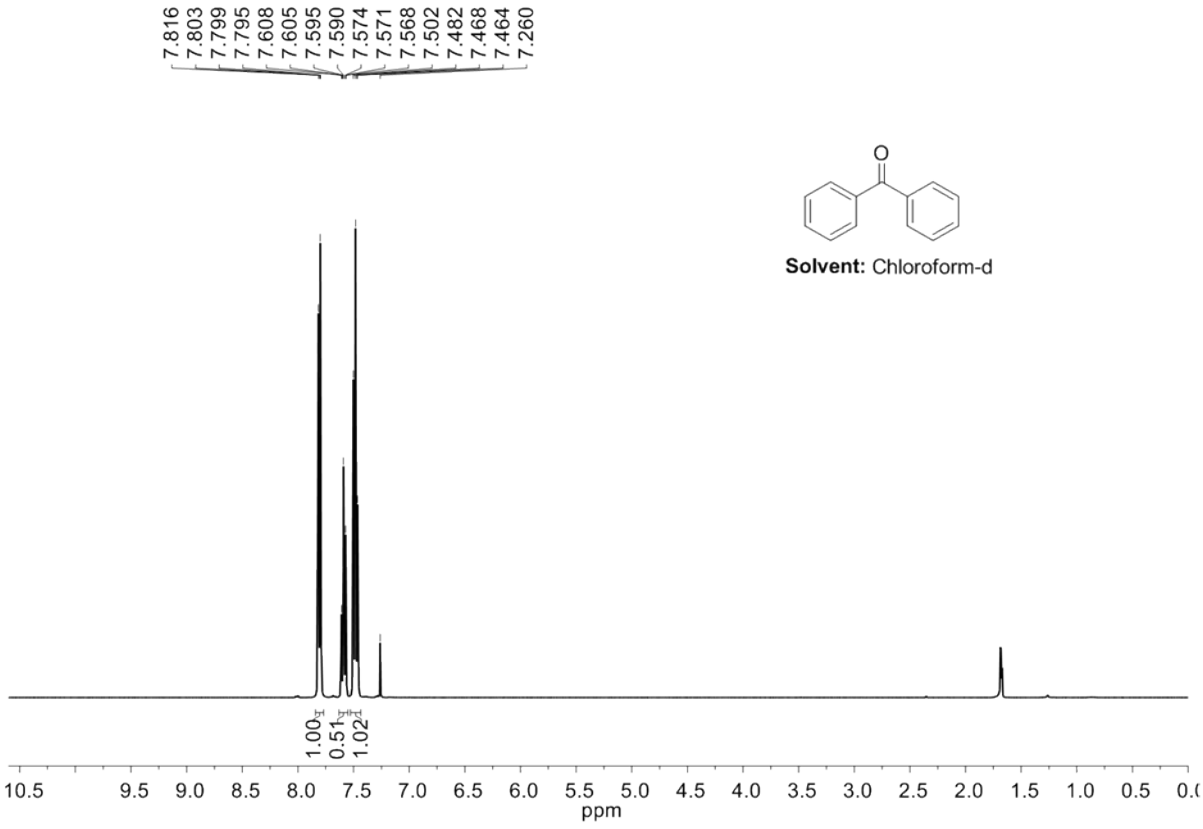


Fig. S46. [1]H NMR spectrum of benzophenone (**2x**).

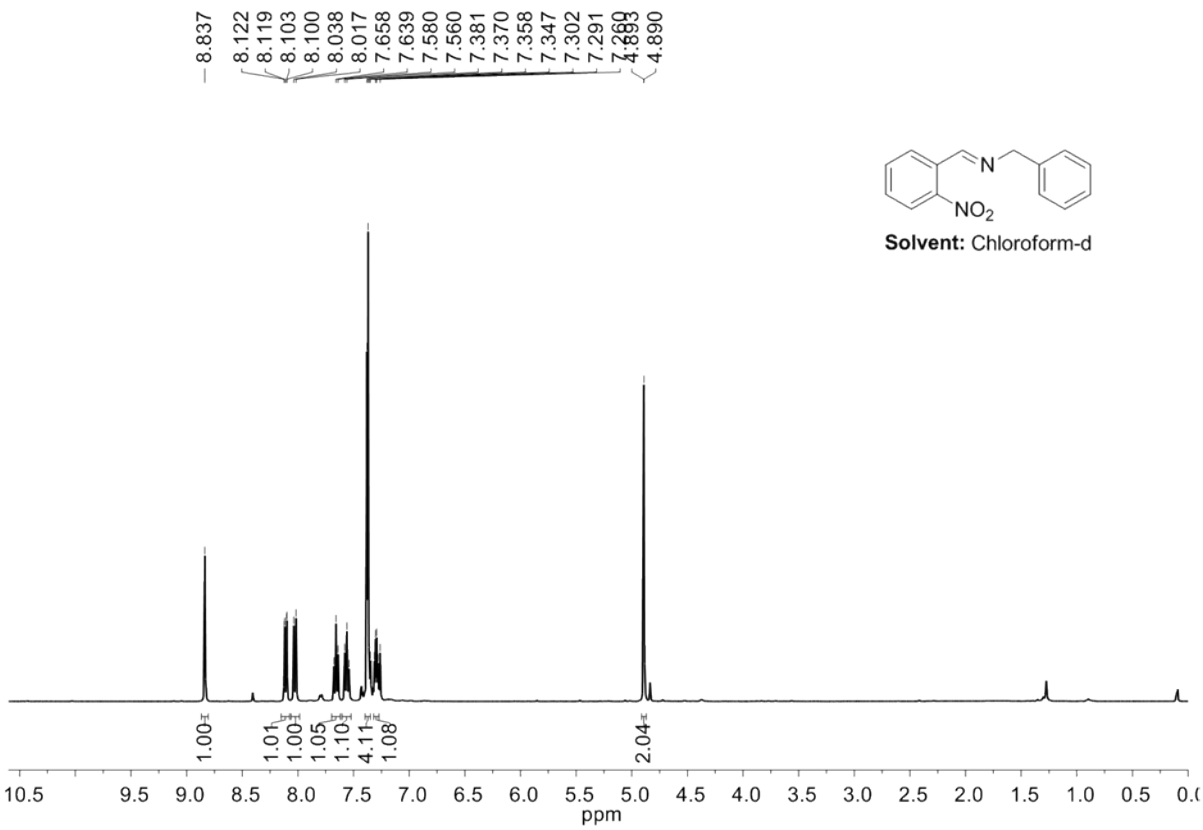


Fig. S47. [1]H NMR spectrum of N-(2-nitrobenzylidene)-1-phenylmethanamine (**4b**).

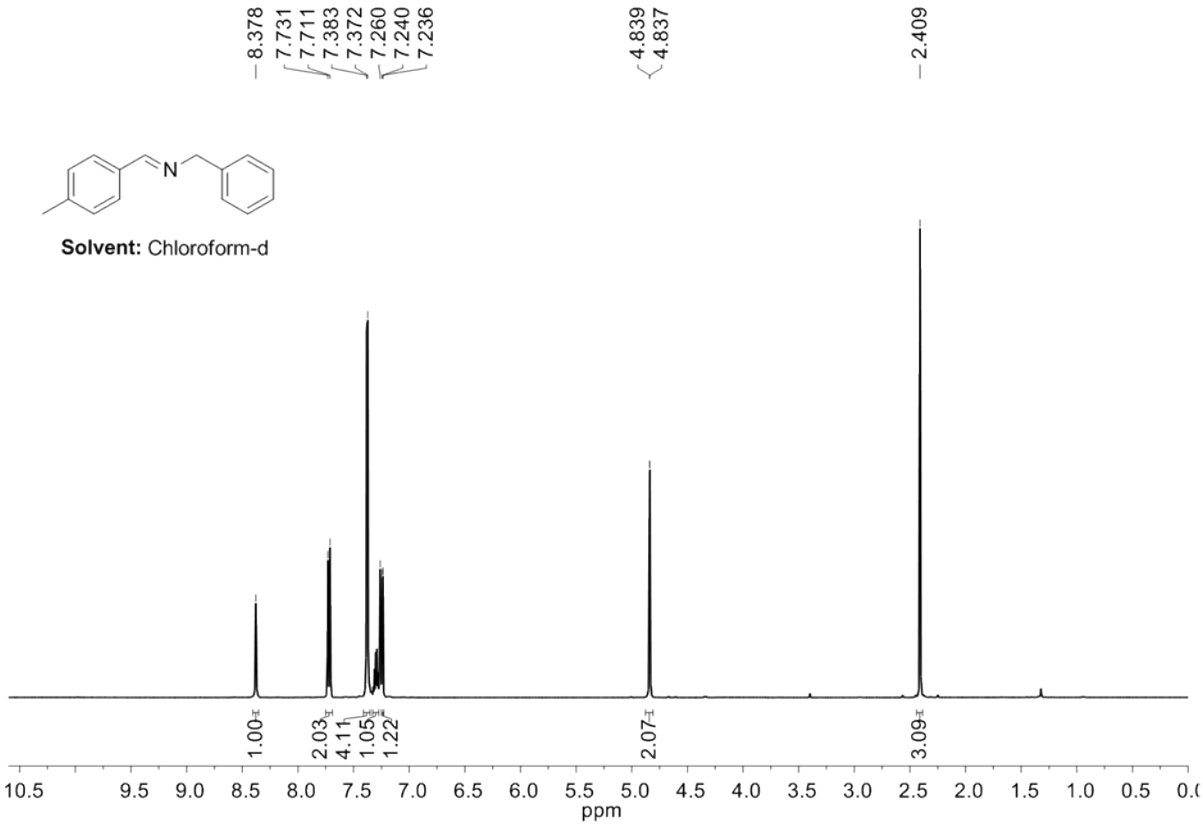


Fig. S48. [1]H NMR spectrum of N-(4-methylbenzylidene)-1-phenylmethanamine (**4c**).

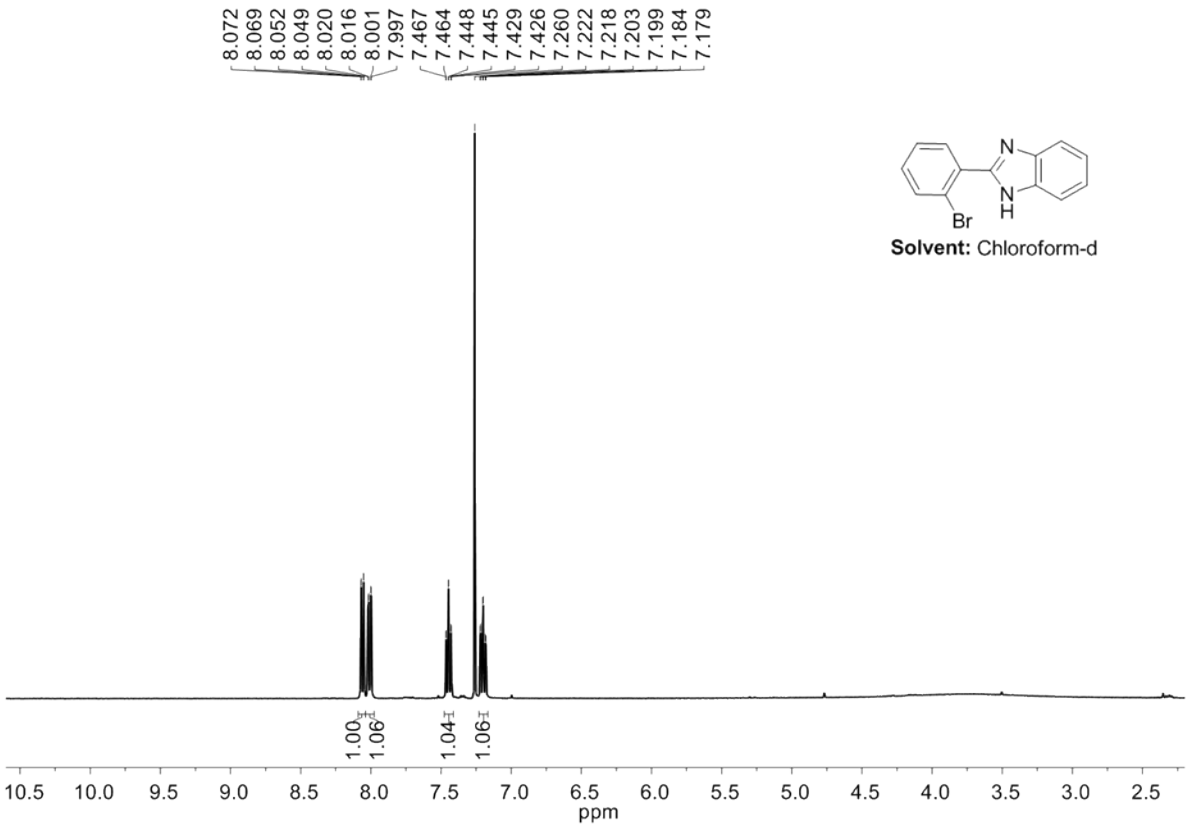


Fig. S49. [1]H NMR spectrum of 2-(2-bromophenyl)-1H-benzo[d]imidazole (**6a**).

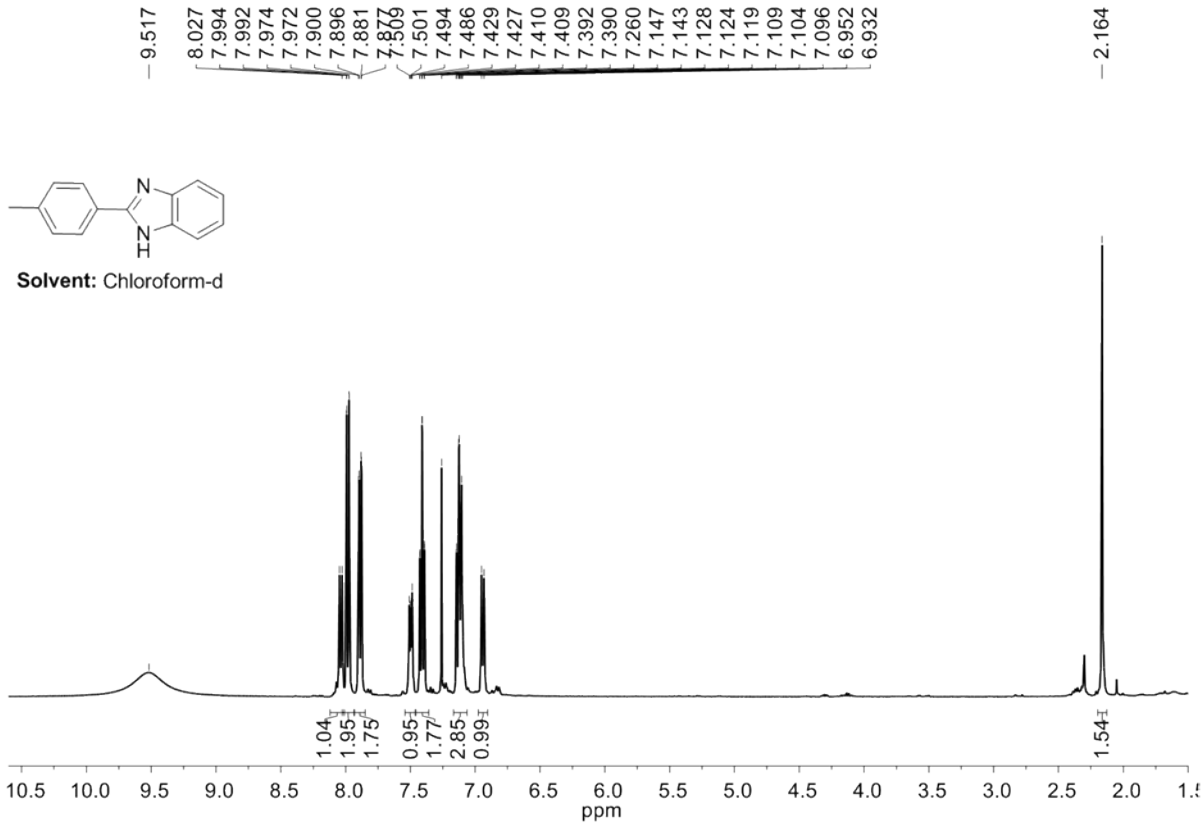


Fig. S50. [1]H NMR spectrum of 2-(p-tolyl)-1H-benzo[d]imidazole (**6b**).

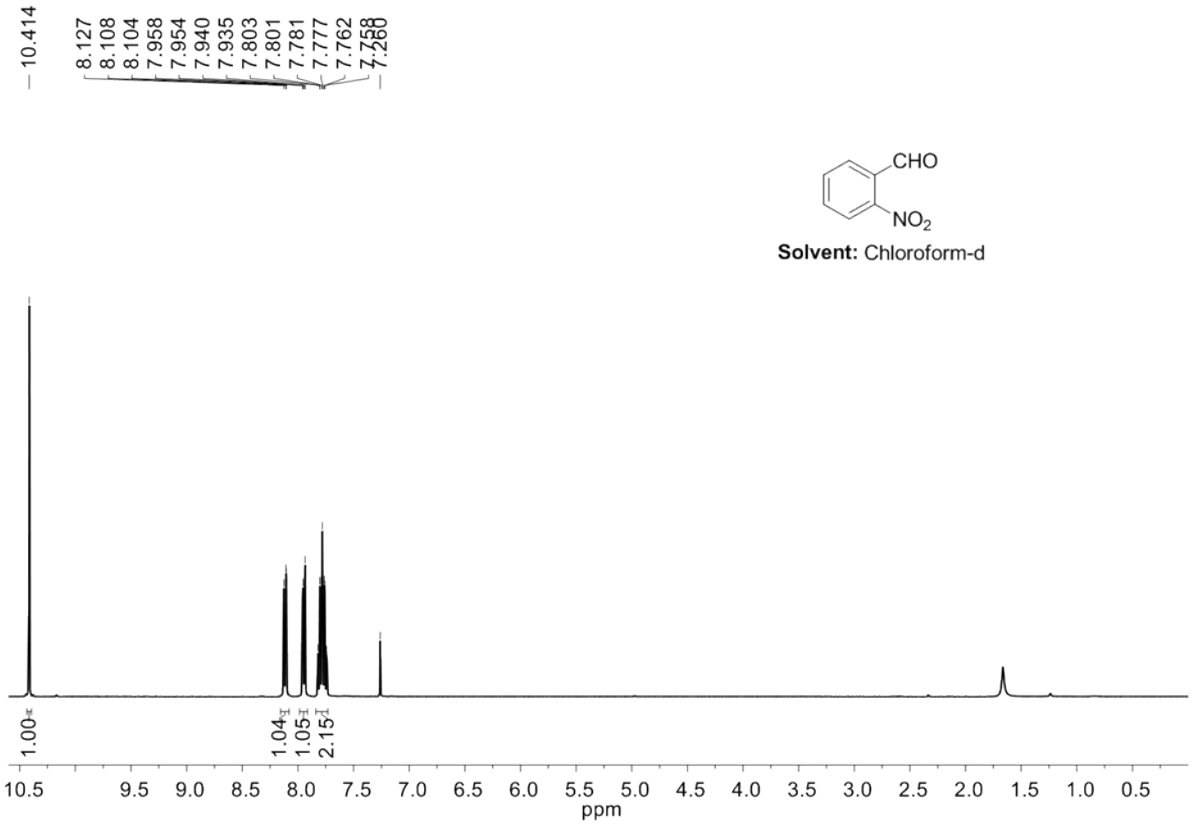


Fig. S51. [1]H NMR spectrum of 2-nitrobenzaldehyde (**10a**).

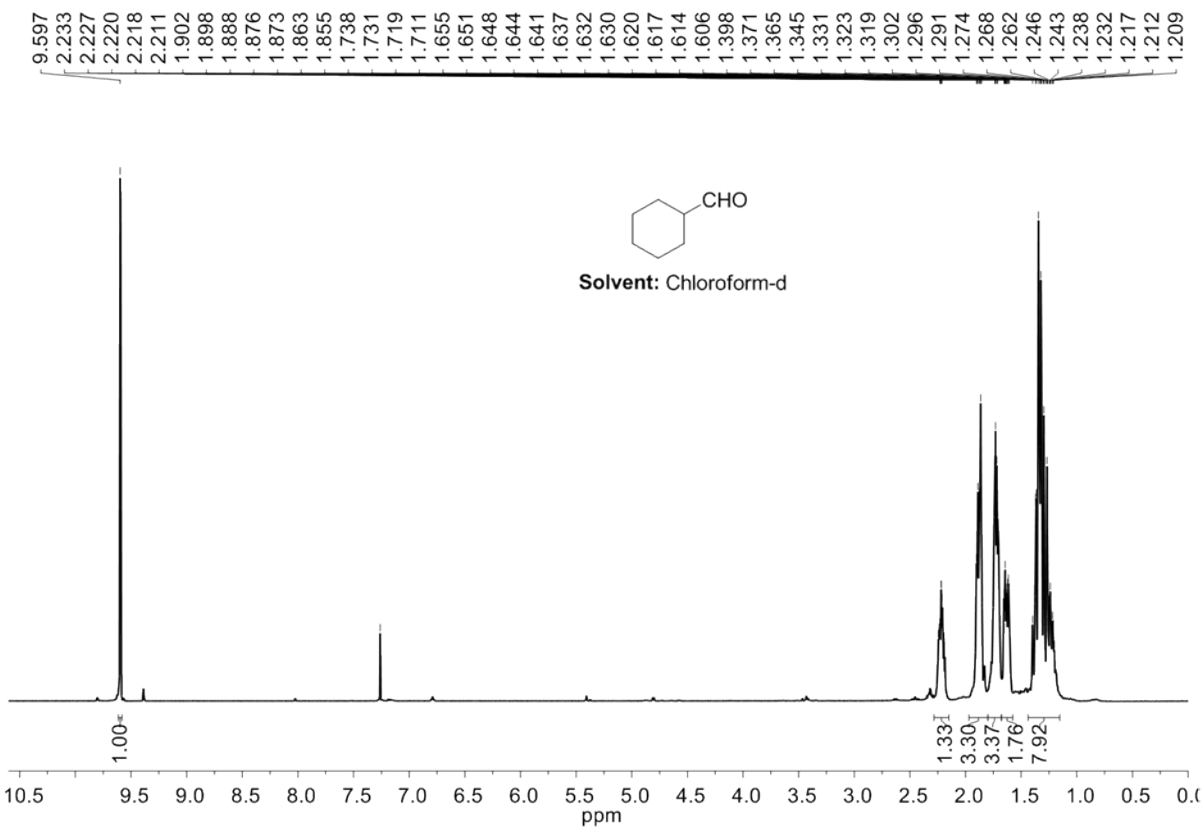


Fig. S52. [1]H NMR spectrum of cyclohexanecarbaldehyde (**10b**).

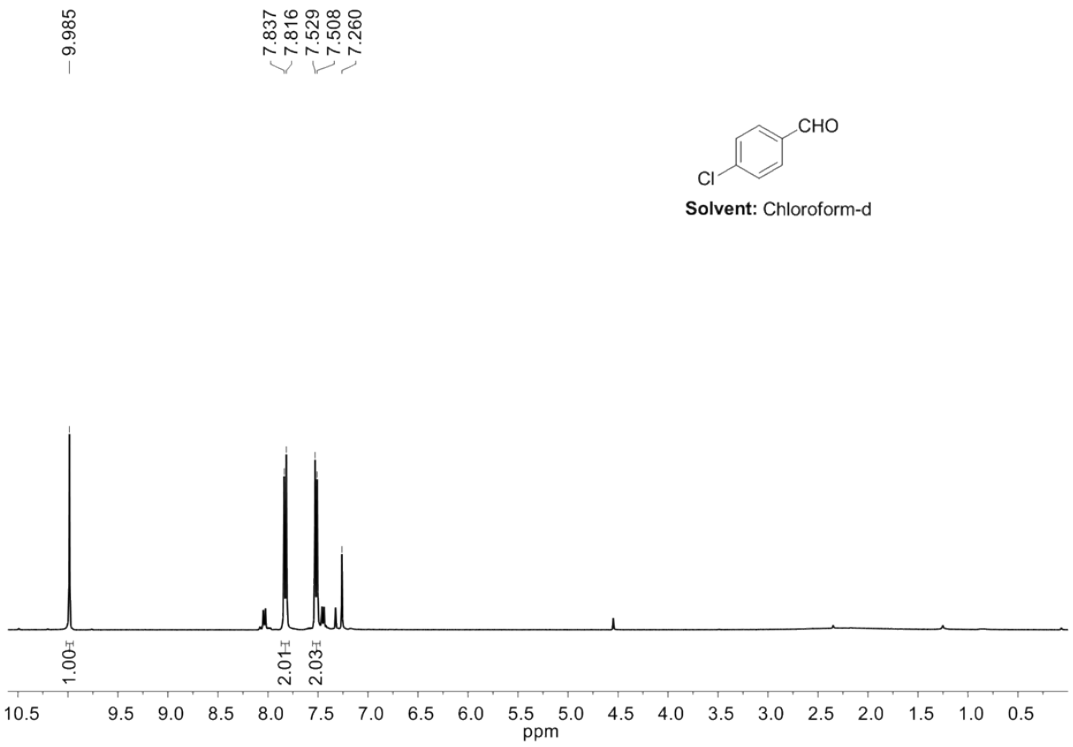


Fig. S53. [1]H NMR spectrum of 4-chlorobenzaldehyde (**10c**).

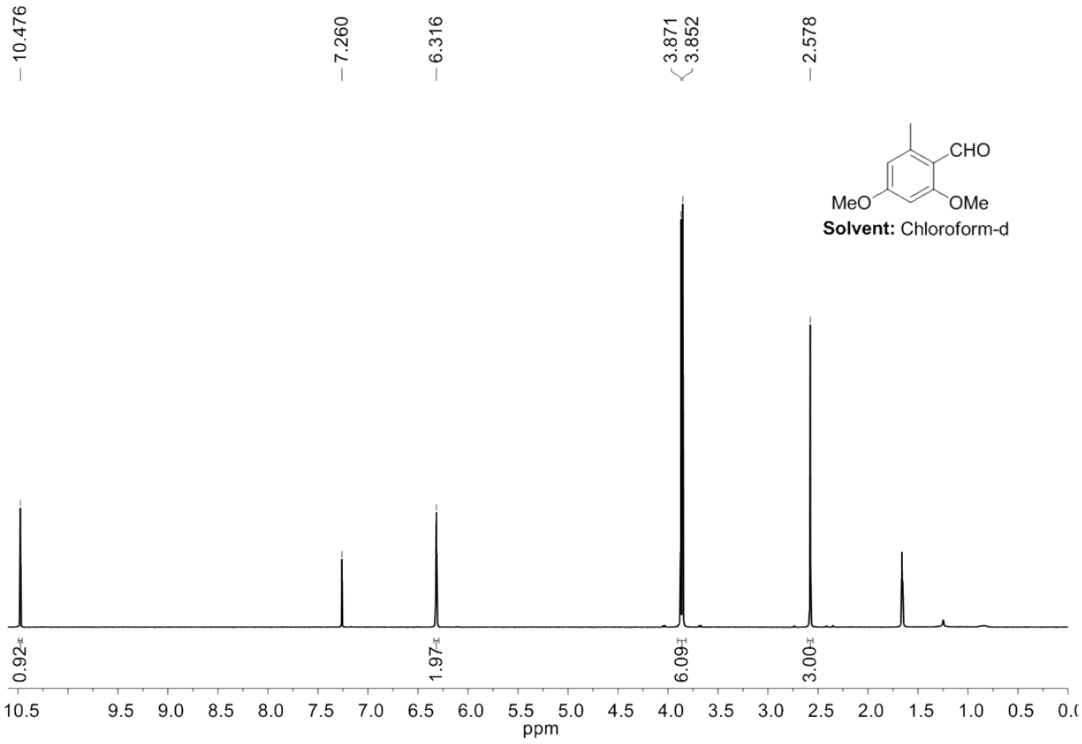


Fig. S54. [1]H NMR spectrum of 2,4-dimethoxy-6-methylbenzaldehyde (**10d**).

HPLC Analysis. HPLC analyses were performed in C18 column and using isopropanol-hexane solvent system.

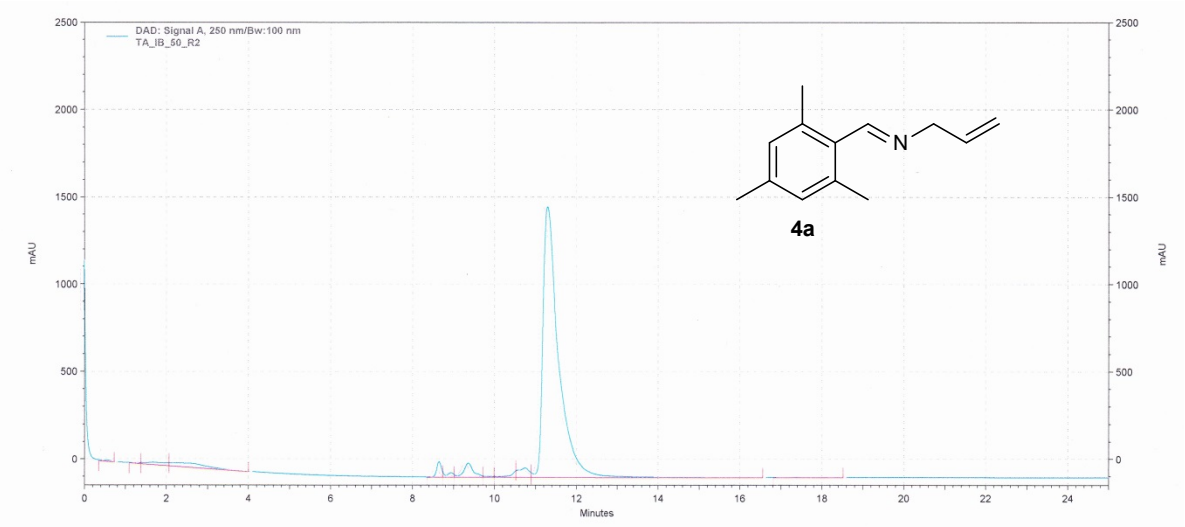


Fig. S55. HPLC chromatogram of *N*-(2,4,6-trimethylbenzylidene)prop-2-en-1-amine (**4a**).

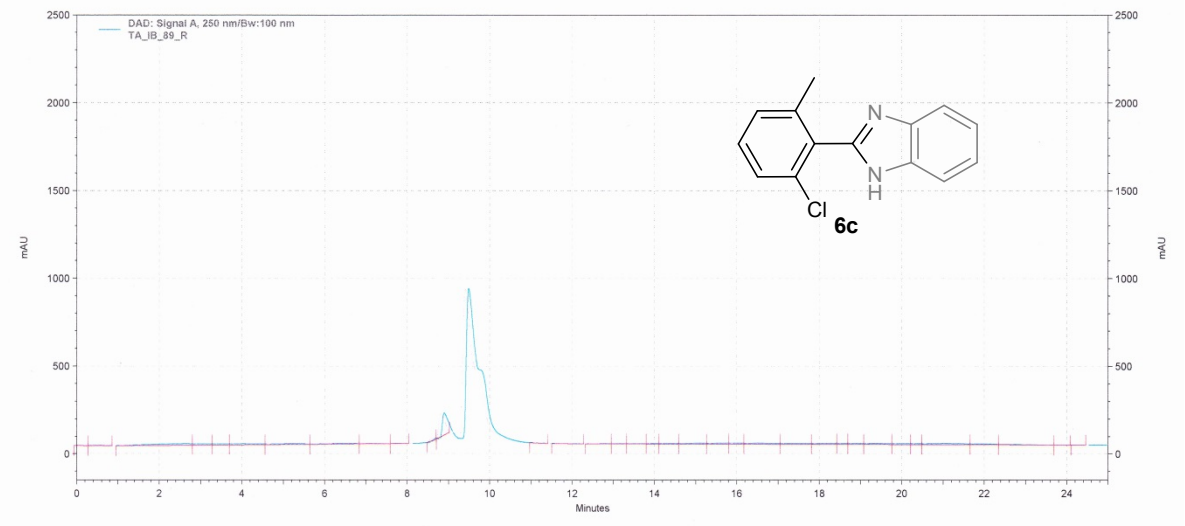


Fig. S56. HPLC chromatogram of 2-(2-chloro-6-methylphenyl)-1*H*-benzo[*d*]imidazole (**6c**).