SUPPORTING INFORMATION

Mechanochemical catalytic oxidations in the solid state with in situ-generated modified IBX from 3,5-di-*tert*-butyl-2-iodobenzoic acid (DTB-IA)/Oxone

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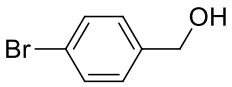
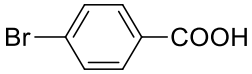
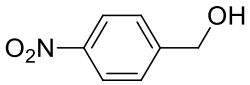
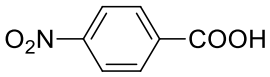
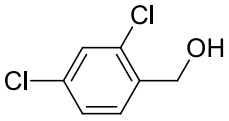
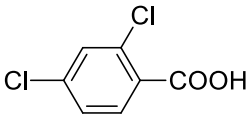
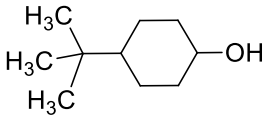
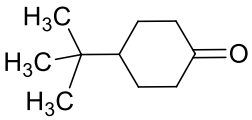
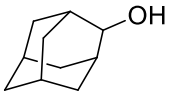
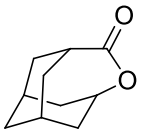
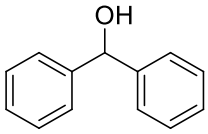
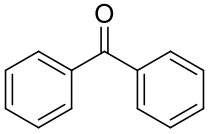
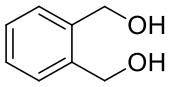
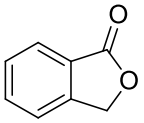
Table of Contents

Table S1. Results of oxidations of various alcohols using DTB-IA (10 mol%)/Oxone[a]

Entry	Substrate	Oxone (equiv)	Time (h)	Product (Isolated Yield, %)[a]
1		1.1	8	 (92)
2		1.1	16	 (90)
3		1.1	12	 (94)
4		1.1	24	 (59)
5		1.1	28	 (68)
6		1.1	20	 (92)
7		2.0	24	 (84)[b]

[a]All reactions were carried out on 0.10 g of the substrate in a 2 mL of CH_3CN-H_2O mixture (1:1, v/v) by employing 1.2 equiv of Oxone, unless mentioned otherwise. [b]2.0 equiv of Oxone was employed.

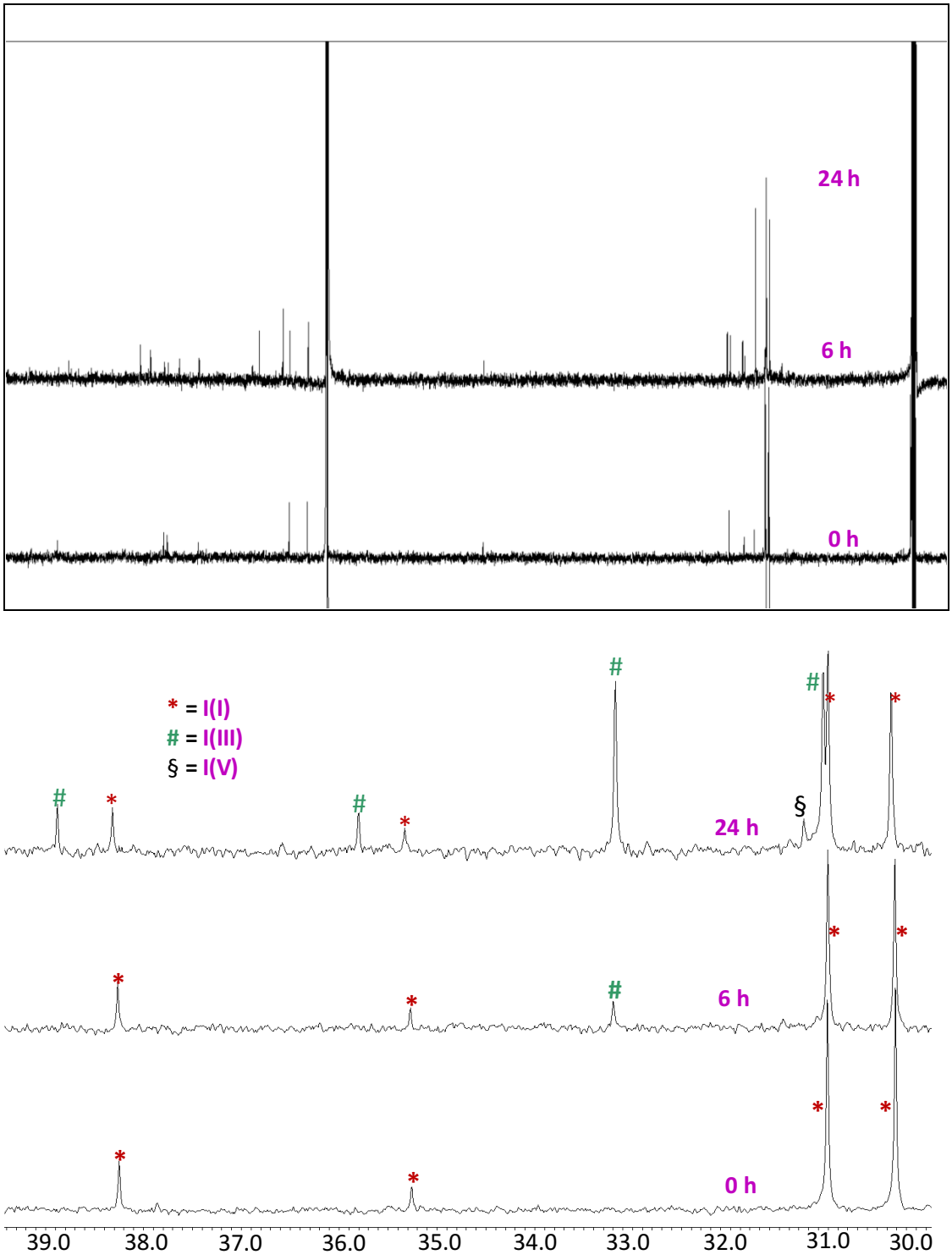


Fig. S1 Oxidation of **DTB-IA** with Oxone in CD_3CN-D_2O (1:1) mixture at rt as followed by ^{13}C NMR of the reaction mixture after 0 h, 6 h and 24 h. As can be seen, the signals due to I(III) are prominent, but those for I(V) are inadequate. This is because of very low concentration of I(V) species in the mixture, as revealed by ^{1}H NMR analysis. Otherwise, appearance of a new signal at ca. 31.2 ppm is noteworthy for the methyl group of the *tert*-butyl groups.

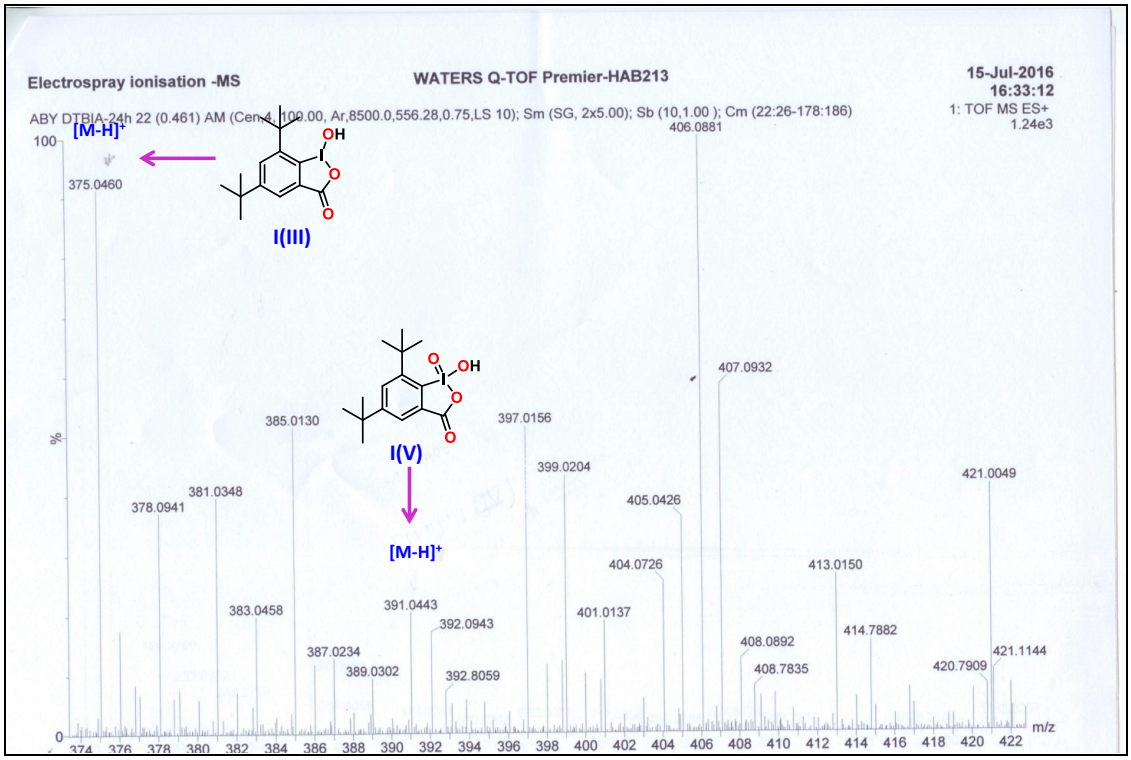


Fig. S2 ESI-MS of the reaction of **DTB-IA** with Oxone in CD_3CN-D_2O (1:1) mixture at rt after 20 h. It may be noted that the I(III) species is unambiguously established, while that of I(V) species is less clear-cut..

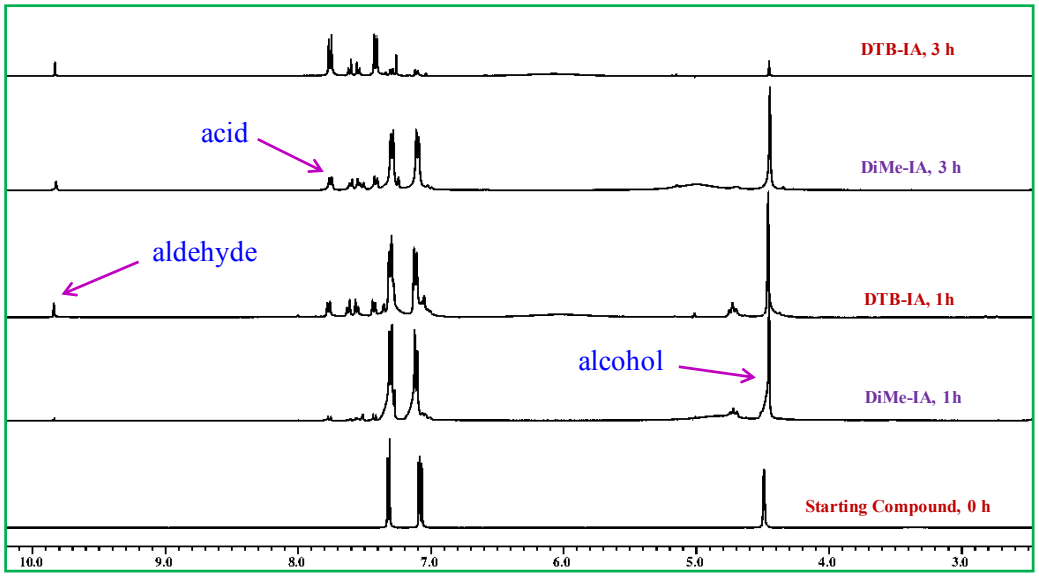


Fig. S3 Comparison of the solid state oxidation of 4-bromobenzyl alcohol with DiMe-IA and **DTB-IA** as catalysts employed in 10 mol% in the presence of 1.2 molar equivalent of Oxone. The solid reaction mixtures were removed after 1 and 3 h, and analyzed by ^{1}H NMR spectroscopy in $CDCl_3$.

Characterization data of oxidation products

Palmitic acid. Yield 85% (0.084 g); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.23–1.36 (m, 24H), 1.62 (quint, J = 7.3 Hz, 2H), 2.34 (t, J = 7.8 Hz, 2H).

4-*tert*-Butylcyclohexanone. Yield 65% (0.032 g); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (s, 9H), 1.41–1.49 (m, 3H), 2.05–2.09 (m, 2H), 2.26–2.41 (m, 4H).

4-Oxatricyclo[4.3.1.1]undecane-5-one. Yield 71% (0.077 g); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72–2.09 (m, 12H), 3.07 (t, J = 5.9 Hz, 1H), 4.46–4.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 30.9, 33.8, 35.7, 41.2, 73.1, 178.8.

Camphor. Yield 76% (0.073 g); colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (s, 3H), 0.90 (s, 3H), 0.95 (s, 3H), 1.29–1.43 (m, 3H), 1.64–1.71 (m, 1H), 1.81–1.98 (m, 1H), 2.08 (t, J = 4.6 Hz, 1H), 2.31–2.36 (m, 1H).

4-Bromobenzoic acid. Yield 90% (0.095 g) and 86% (0.172 g, Scheme 5); colorless solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H).

4-Nitrobenzoic acid. Yield 88% (0.096 g); pale yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (d, J = 9.1 Hz, 2H), 8.30 (d, J = 9.1 Hz, 2H).

4-Cyanobenzoic acid. Yield 84% (0.046 g); white solid; ^{1}H NMR (400 MHz, DMSO-d_6), δ 7.97 (d, J = 8.7 Hz, 2H), 8.07 (d, J = 8.7 Hz, 2H).

4-Chlorobenzoic acid. Yield 89% (0.097 g); white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H).

2,4-Dichlorobenzaldehyde. Yield 71% (0.07 g); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.0, 1.8 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H), 10.41 (s, 1H).

2-Nitrobenzaldehyde. Yield 72% (0.071 g); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.82 (m, 2H), 7.96 (dd, J = 7.5, 1.5 Hz, 1H), 8.12 (dd, J = 8.4, 1.8 Hz, 1H), 10.43 (s, 1H).

2,5-Dibromobenzaldehyde. Yield 79% (0.039 g); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.57 (m, 2H), 8.02 (d, J = 2.3 Hz, 1H), 10.28 (s, 1H).

4-Bromo-2,3,5,6-tetramethylbenzaldehyde. Yield 80% (0.038 g); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 6H), 2.44 (s, 6H), 10.59 (s, 1H).

4,5-Dibromo-2-mehtyl-benzaldehyde. Yield 82% (0.040 g); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 7.56 (s, 1H), 7.98 (s, 1H), 10.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.6, 122.6, 131.1, 134.2, 136.2, 136.8, 140.5, 190.3.

2-Bromo-4,5-dimethoxybenzaldehyde. Yield 73% (0.036 g); light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.96 (s, 3H), 7.05 (s, 1H), 7.41 (s, 1H), 10.18 (s, 1H).

5,7-Dibromo-1-tetralone. Yield 92% (0.045 g); light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (quintet, J = 6.8 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 2.94 (t, J = 6.4 Hz, 2H), 7.87 (d, J = 2.3 Hz, 1H), 8.12 (d, J = 2.3 Hz, 1H).

Benzophenone. Yield 97% (0.047 g) and 97% (0.096 g, Scheme 5); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 7.8 Hz, 4H), 7.59 (tt, J =7.3, 1.4 Hz, 2H), 7.80 (dd, J = 8.2, 1.3 Hz, 4H).

9-Fluorenone. Yield 94% (0.046 g) and 93% (0.074 g, Scheme 5); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (td, J = 7.1, 1.4 Hz, 2H), 7.46–7.52 (m, 4H), 7.65 (d, J = 7.3 Hz, 2H).

Benzil. Yield 86% (0.042 g); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, J = 7.4 Hz, 4H), 7.66 (t, J = 7.8Hz, 2H), 7.97 (dd, J = 8.4, 1.4 Hz, 4H).

Terephthalic acid. Yield 89% (0.106 g); colorless solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.03 (s, 4H).

2-Chloro-4-carboxybenzaldehyde. Yield 67% (0.070 g); white solid; FT-IR (KBr) cm^{-1} 3300–2500, 2963, 1696, 1265, 1124, 762; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (d, J = 7.8 Hz, 3H), 8.00–8.03 (m, 2H) 10.37 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 128.8, 130.5, 131.6, 135.3, 136.6, 137.3, 165.8, 190.0.

2-Chloroterephthalic acid. Yield 18% (0.019 g); colorless solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, J = 7.8 Hz, 1H), 7.71–7.76 (m, 1H), 7.95 (s, 1H).

2-Bromo-4-carboxybenzaldehyde. Yield 62% (0.032 g); white solid; FT-IR (KBr) cm^{-1} 3300–2500, 2960, 1671, 1255, 1124, 762; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 7.7 Hz, 1H), 8.20 (s, 1H), 10.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 125.8, 129.3, 130.9, 134.8, 136.4, 137.4, 165.8, 191.9.

2-Bromoterephthalic acid. Yield 21% (0.012 g); white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, J = 7.7 Hz, 1H), 7.97 (dd, J = 8.0, 1.8 Hz, 1H), 8.14 (d, J = 1.8 Hz, 1H).

Phthalide. Yield 93% (0.045 g); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (s, 2H), 7.48–7.56 (m, 2H), 7.68 (td, J = 7.5, 1.1 Hz, 1H), 1.92 (d, J = 7.7 Hz, 1H).

5,6-Dichlorophthalide. Yield 60% (0.029 g); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 2H), 7.63 (s, 1H), 7.99 (s, 1H).

5,6-Dibromophthalide. Yield 65% (0.031 g); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (s, 2H), 7.81 (s, 1H), 8.16 (s, 1H).

5,6-Dimethylphthalide. Yield 77% (0.037 g); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.38 (s, 3H), 5.23 (s, 2H), 7.24 (s, 1H), 7.66 (s, 1H).

Benzoic acid. Yield 89% (0.101 g); colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 7.3, 2H), 7.60–7.64 (m, 1H), 8.14 (dd, J = 8.2, 1.3 Hz, 2H).

Acetophenone. Yield 76% (0.037 g); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H), 7.45 (t, J = 7.5 Hz, 2H), 7.53-7.57 (m, 1H), 7.95 (dd, J = 8.5, 0.9 Hz, 2H).

Spectra of Products

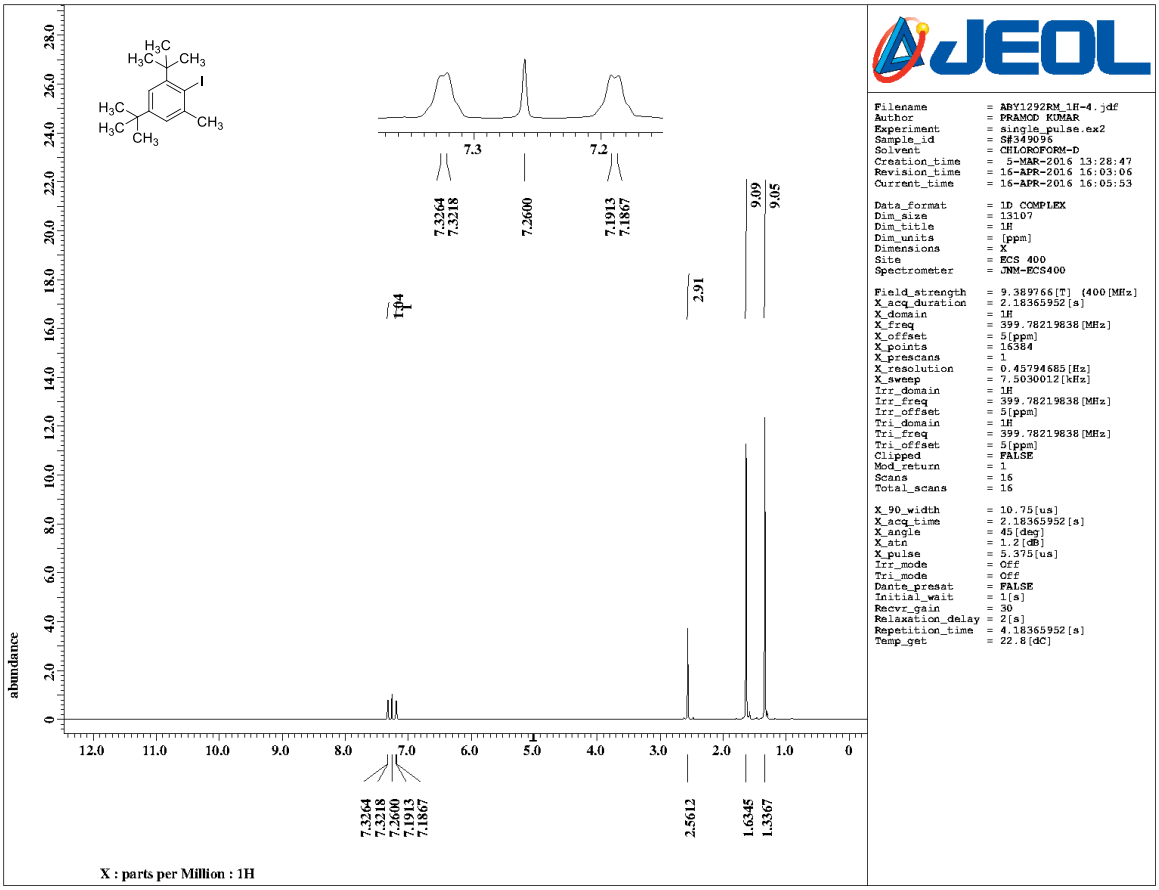


Fig. S4 ^{1}H NMR spectrum of 3,5-di-*tert*-butyl-2-iodotoluene (**DTB-IT**) in $CDCl_3$.

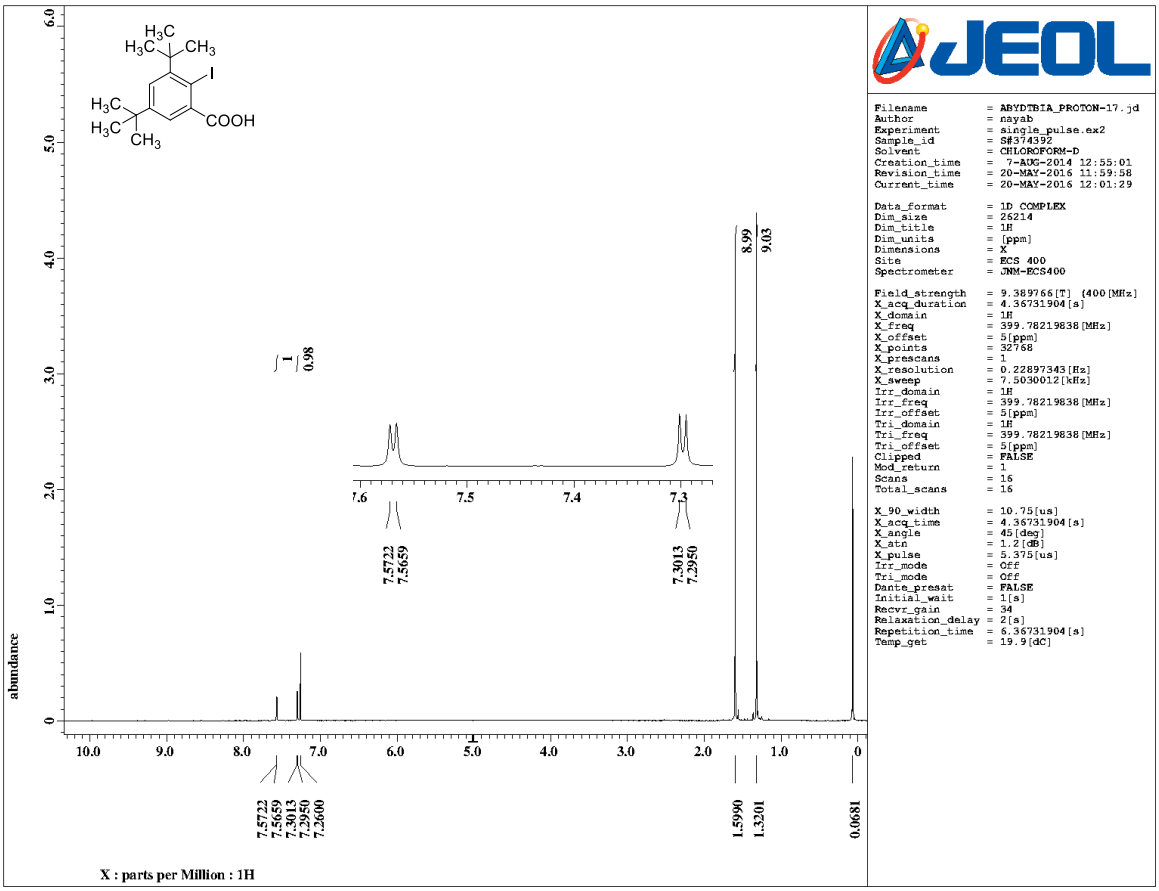


Fig. S5 ^{1}H NMR spectrum of 3,5-di-*tert*-butyl-2-iodobenzoic acid (**DTB-IA**) in $CDCl_3$.

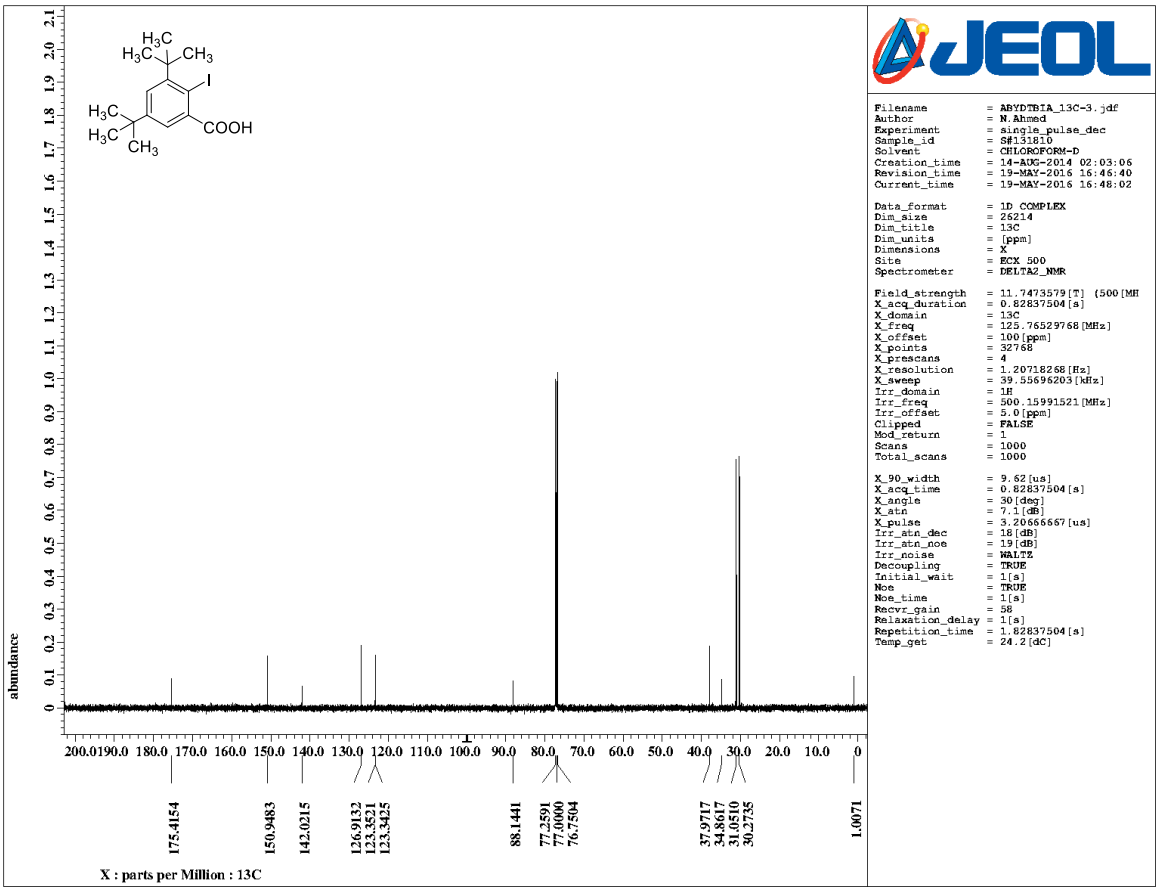


Fig. S6 ^{13}C NMR spectrum of 3,5-di-*tert*-butyl-2-iodobenzoic acid (**DTB-IA**) in $CDCl_3$.

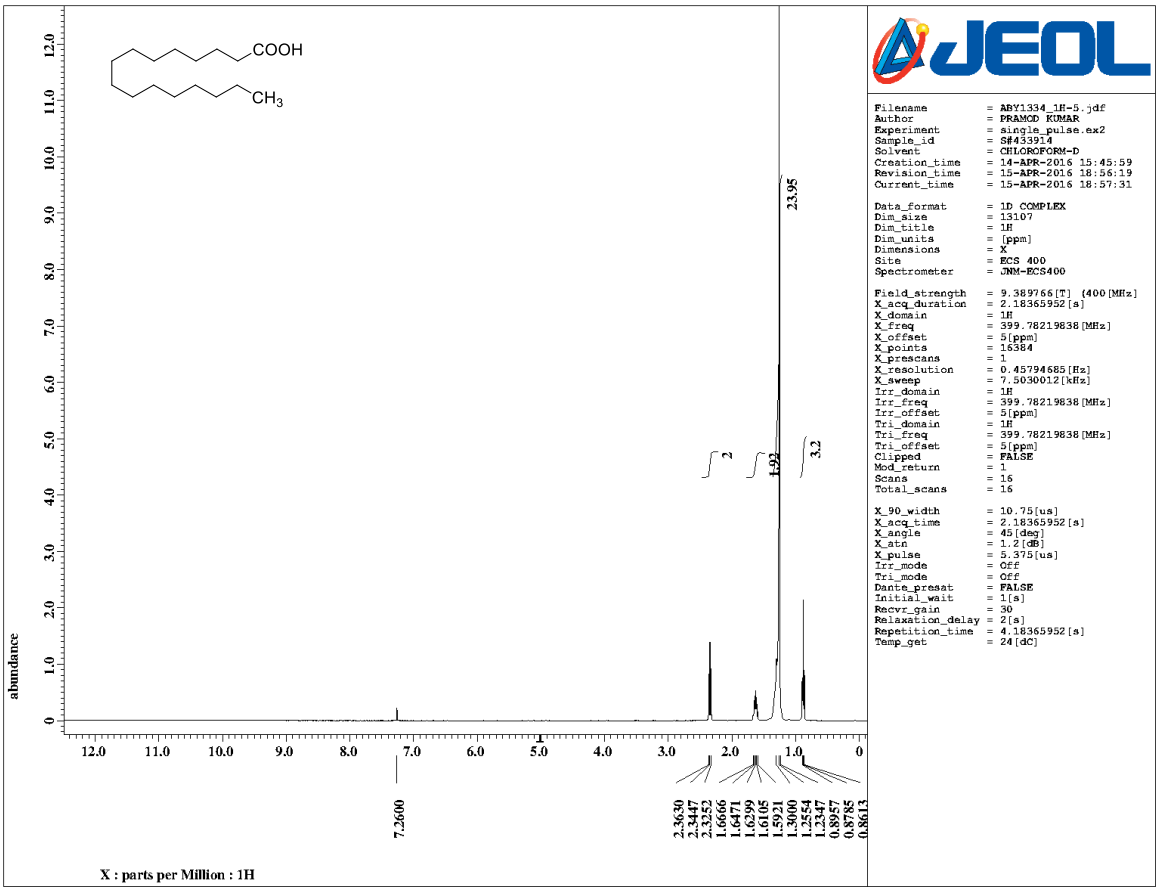


Fig. S7 ^{1}H NMR spectrum of palmitic acid in $CDCl_3$.

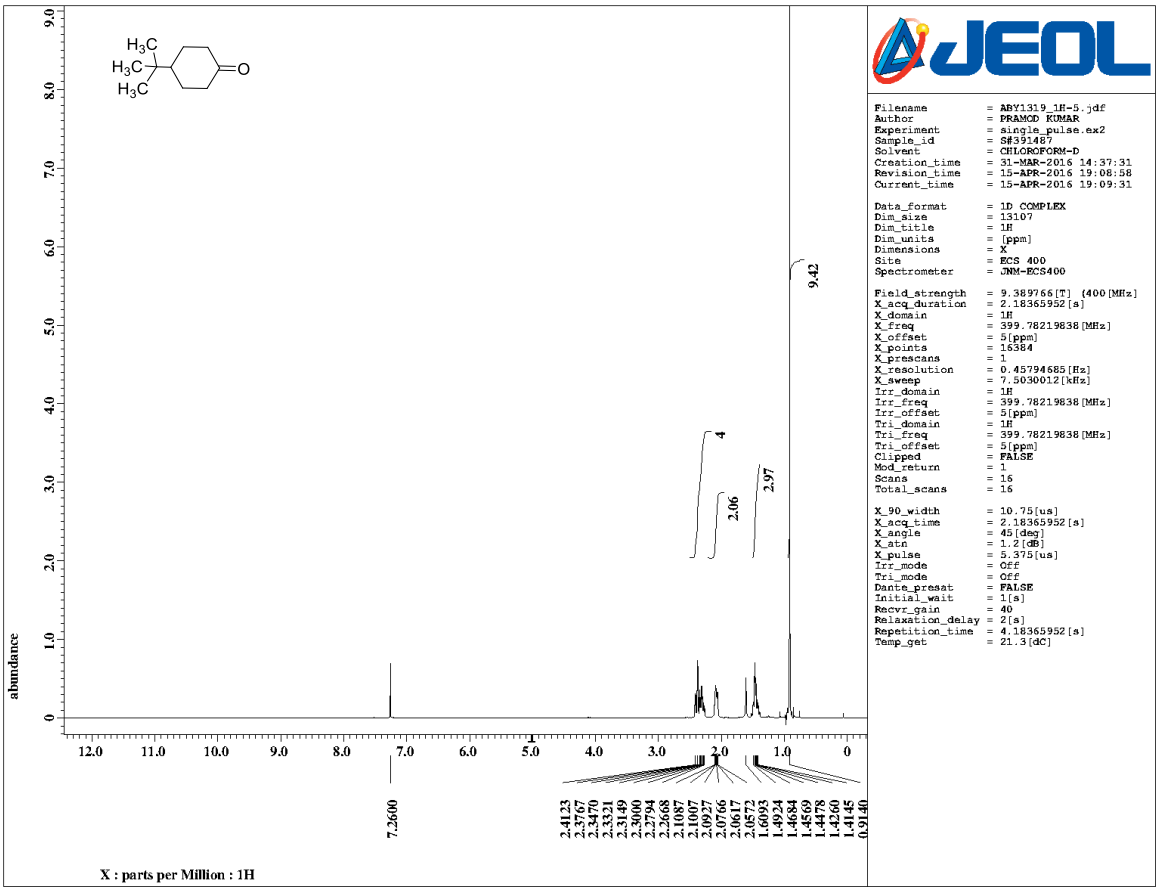


Fig. S8 ^{1}H NMR spectrum of 4-*ter*-butylcyclohexanone in $CDCl_3$.

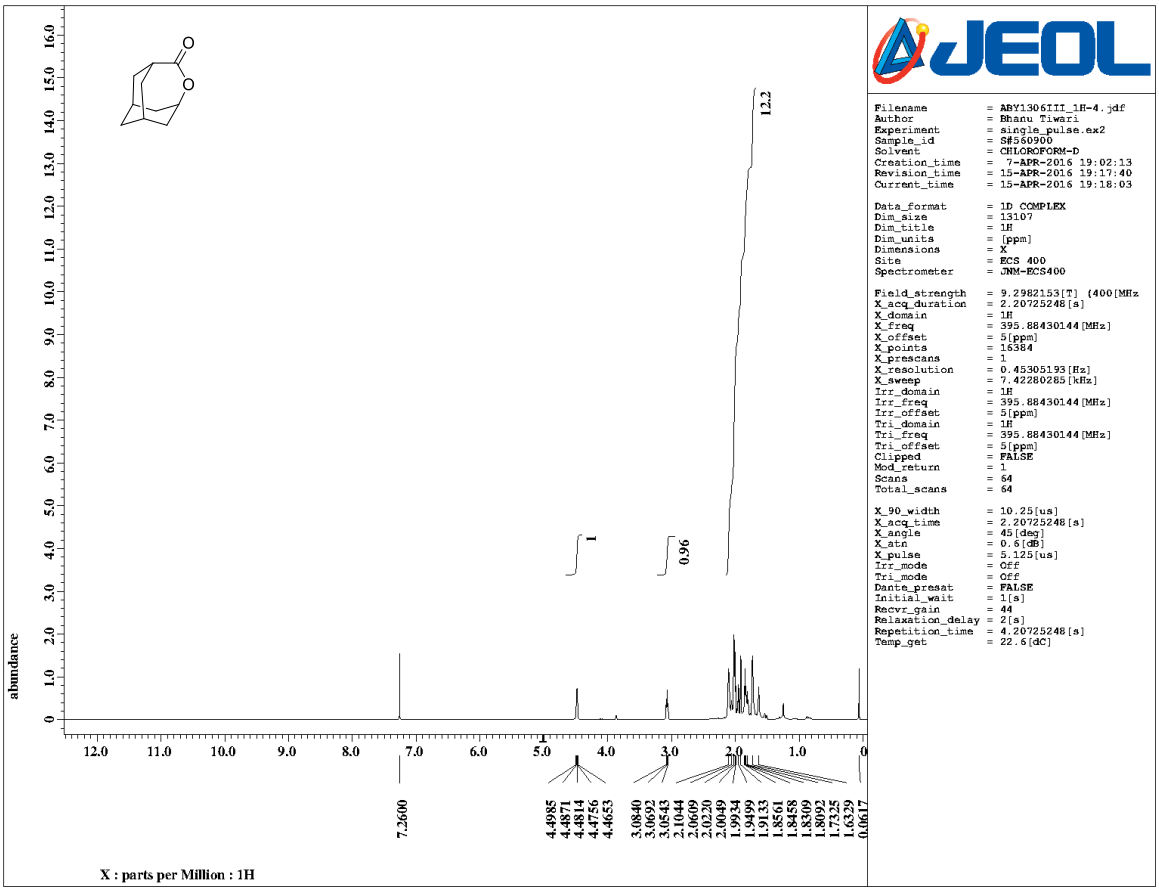


Fig. S9 ^{1}H NMR spectrum of 4-oxatricyclo[4.3.1.1]undecane-5-one in $CDCl_3$.

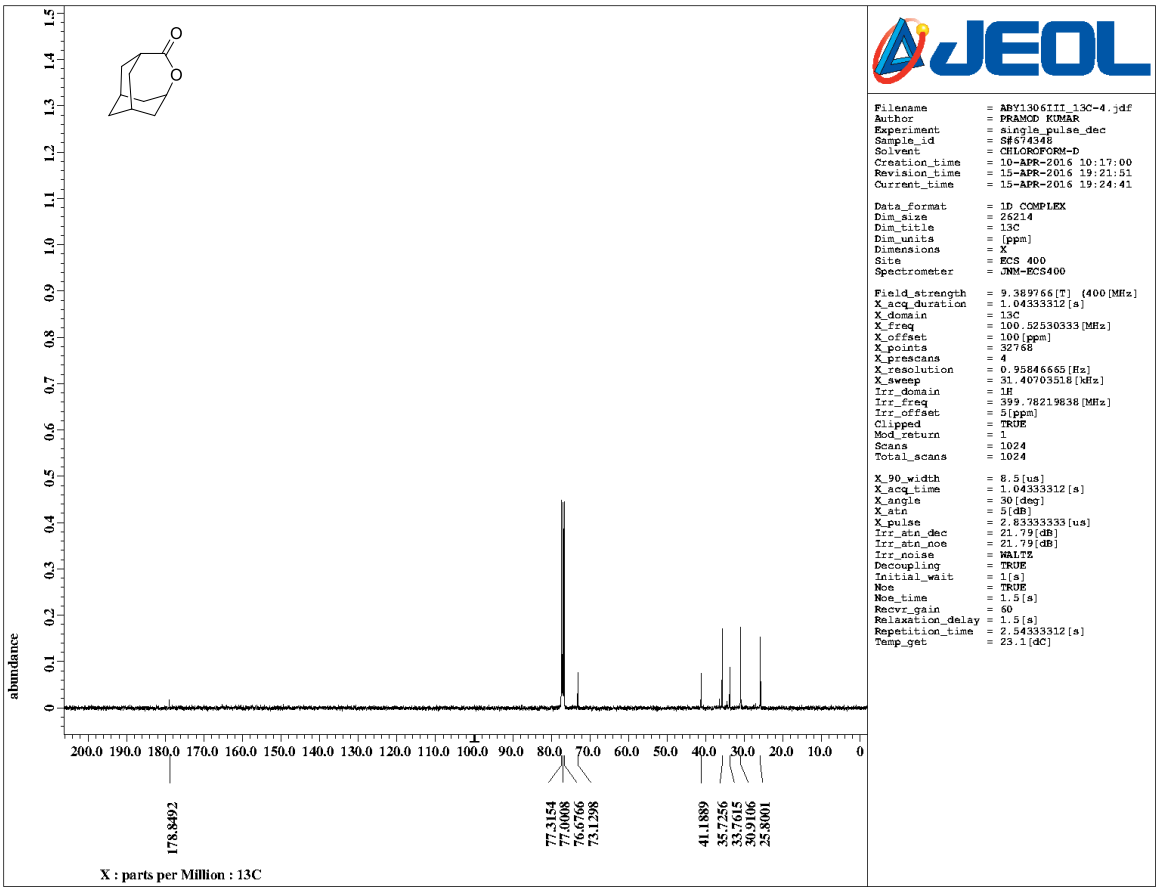


Fig. S10 ^{13}C NMR spectrum of 4-oxatricyclo[4.3.1.1]undecane-5-one in $CDCl_3$.

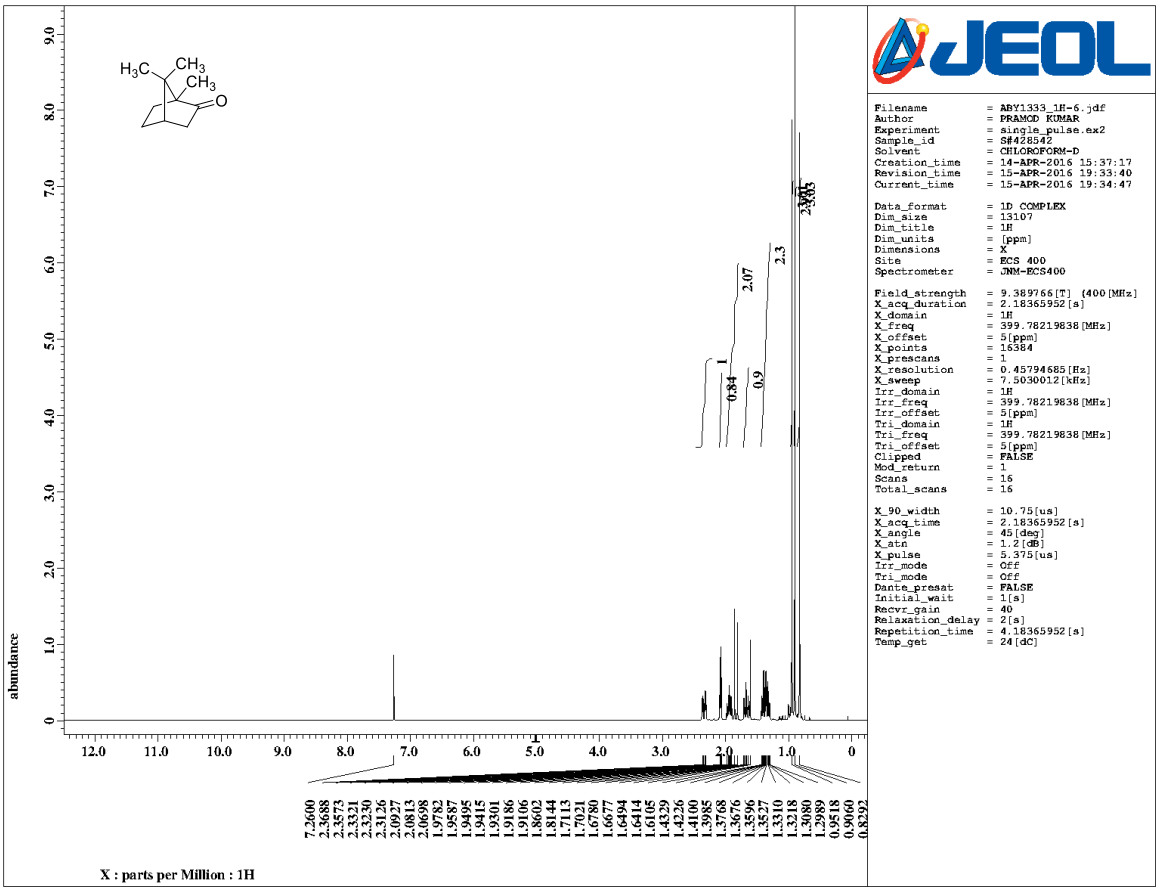


Fig. S11 ^{1}H NMR spectrum of camphor in $CDCl_3$.

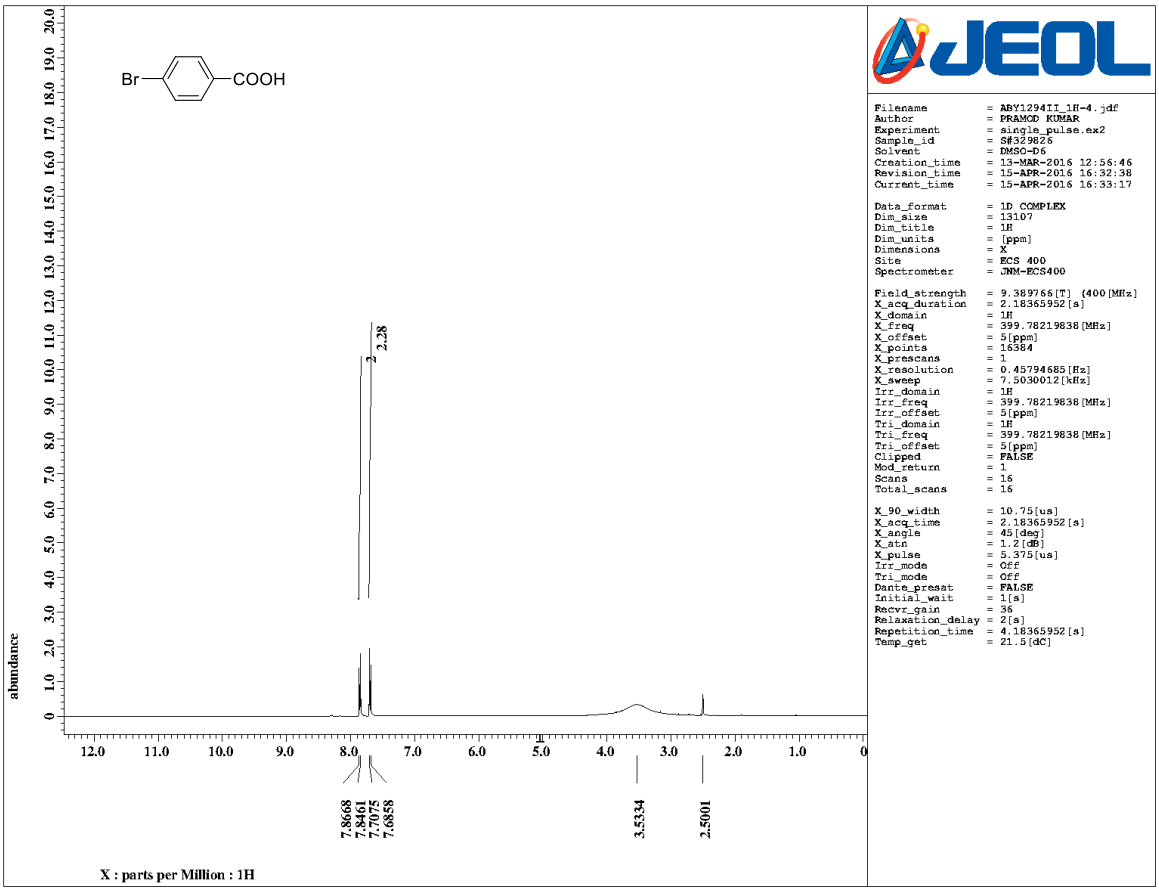


Fig. S12 ^{1}H NMR spectrum of 4-bromobenzoic acid in DMSO-d_6.

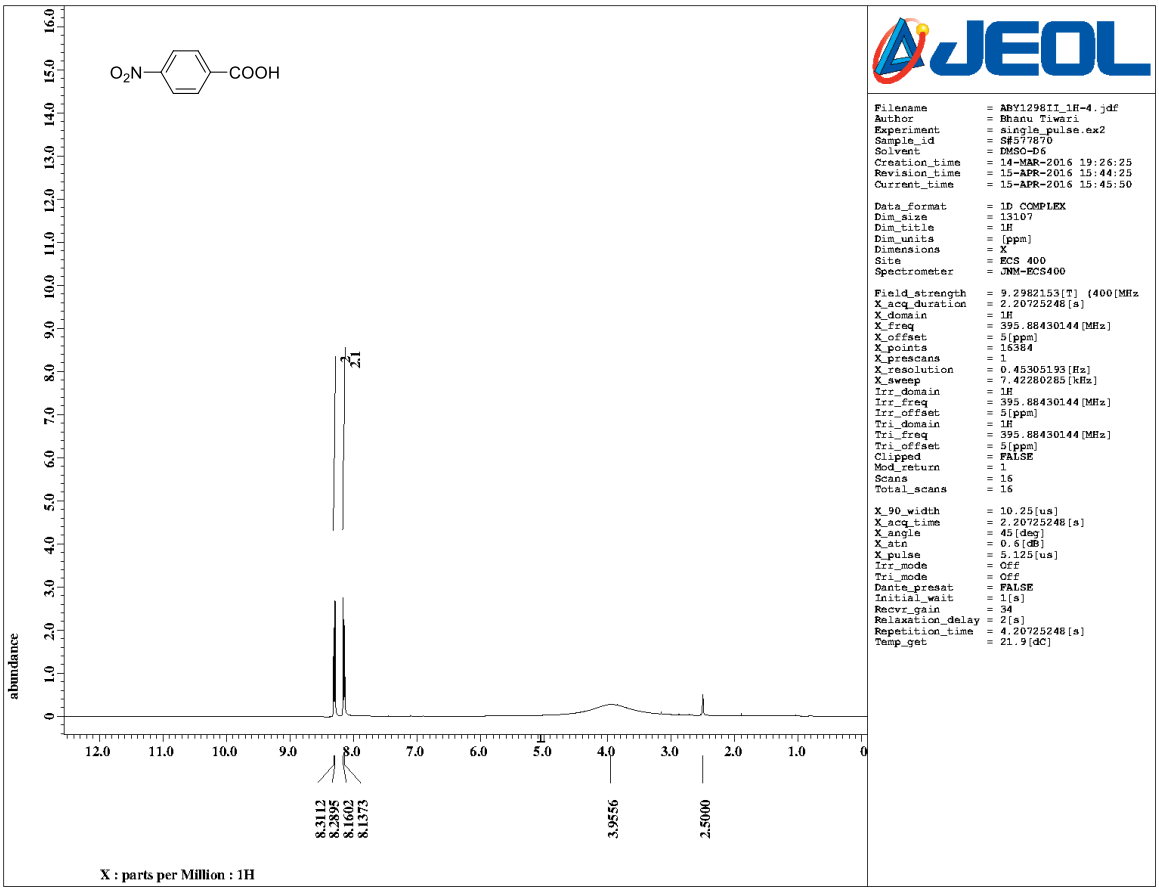


Fig. S13 ^{1}H NMR spectrum of 4-nitrobenzoic acid in DMSO-d_6.

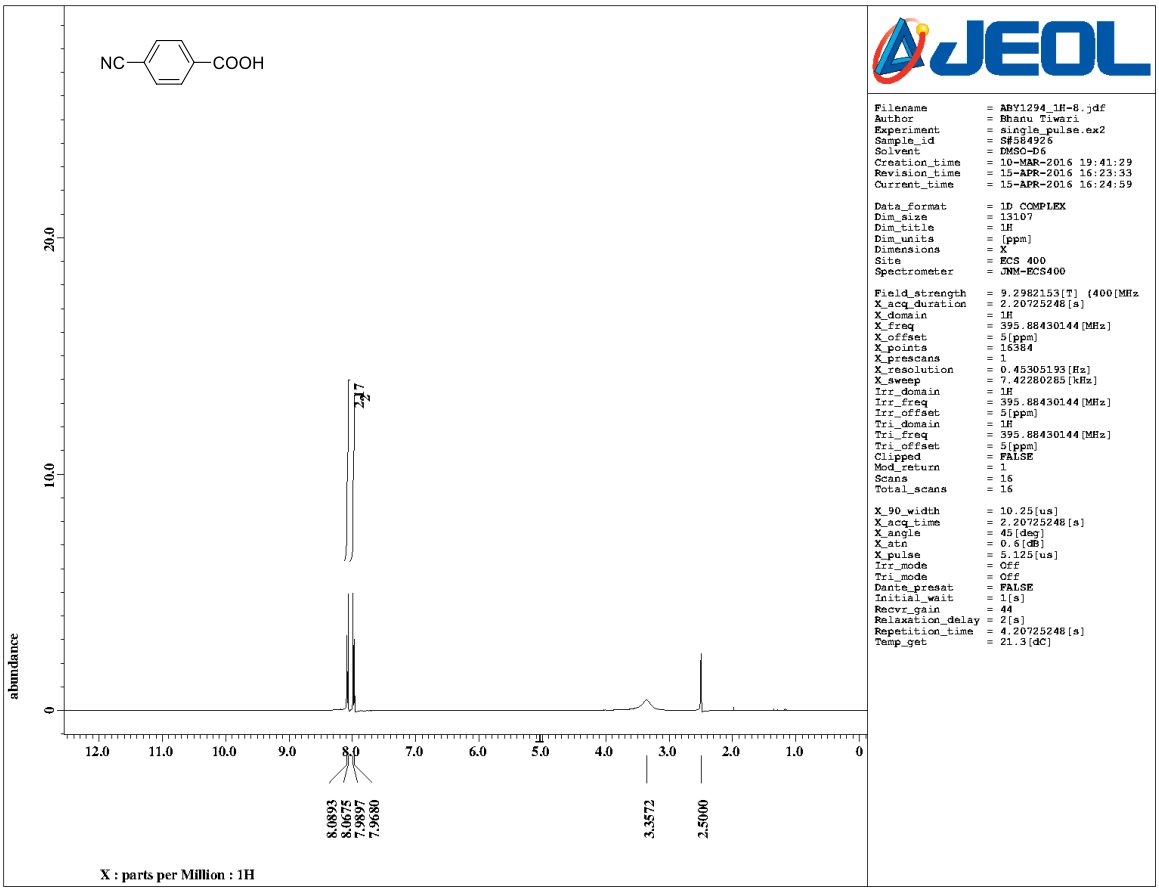


Fig. S14 ^{1}H NMR spectrum of 4-cyanobenzoic acid in DMSO-d_6.

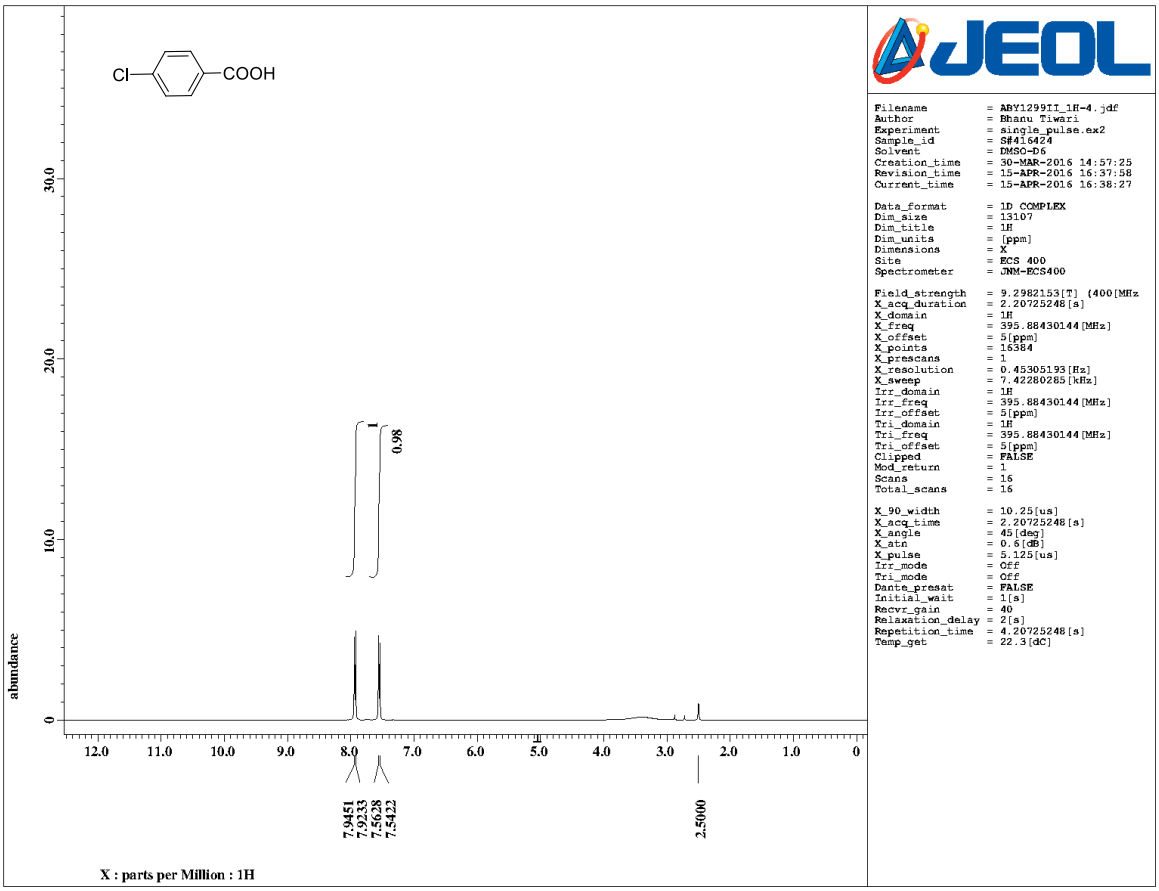


Fig. S15 ^{1}H NMR spectrum of 4-chlorobenzoic acid in DMSO-d_6.

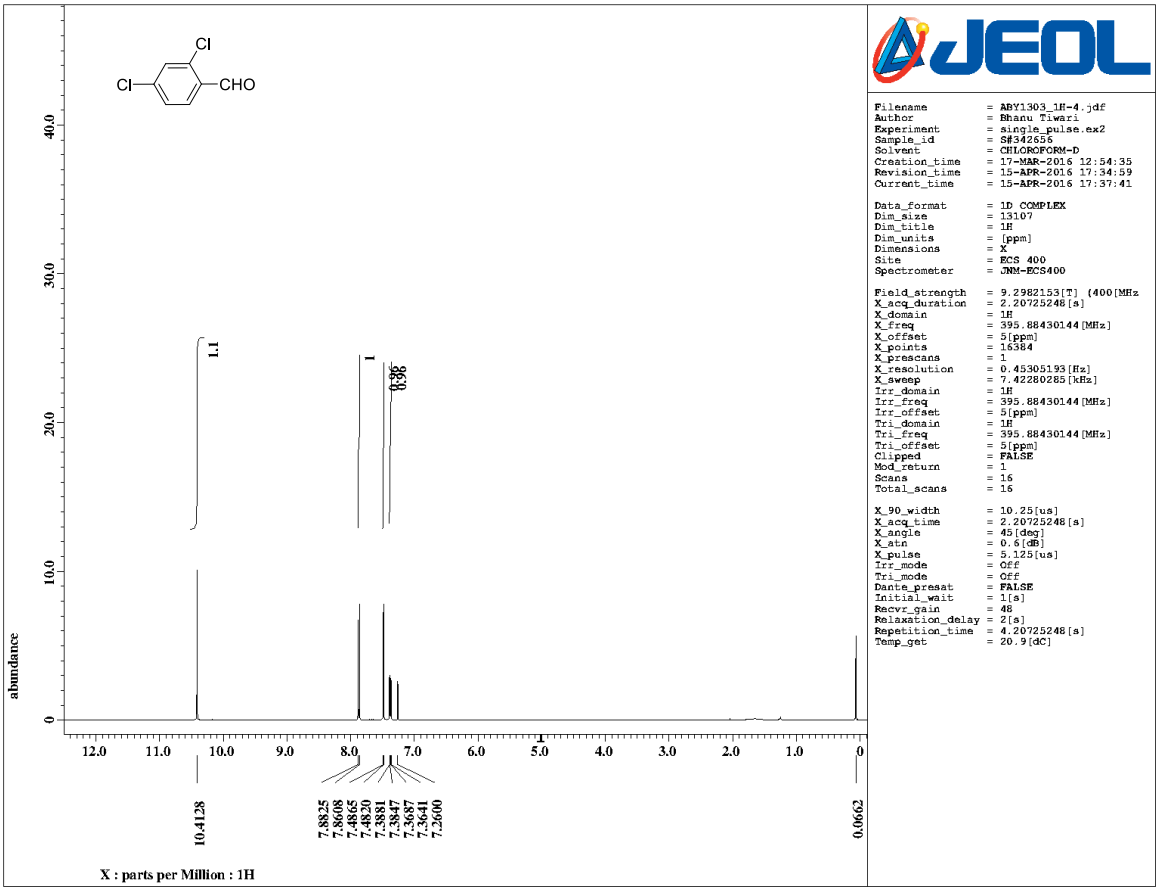


Fig. S16 ^{1}H NMR spectrum of 2,4-dichlorobenzaldehyde in $CDCl_3$.

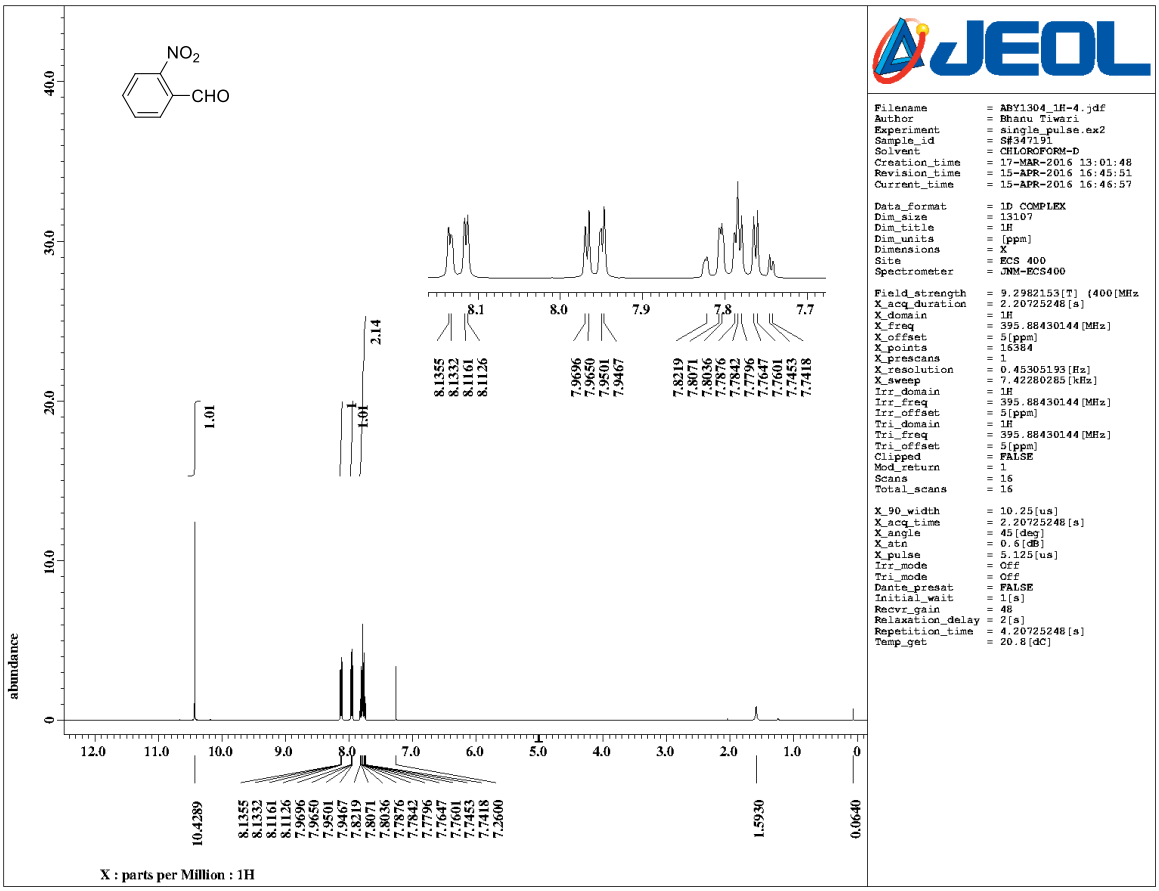


Fig. S17 ^{1}H NMR spectrum of 2-nitrobenzaldehyde in $CDCl_3$.

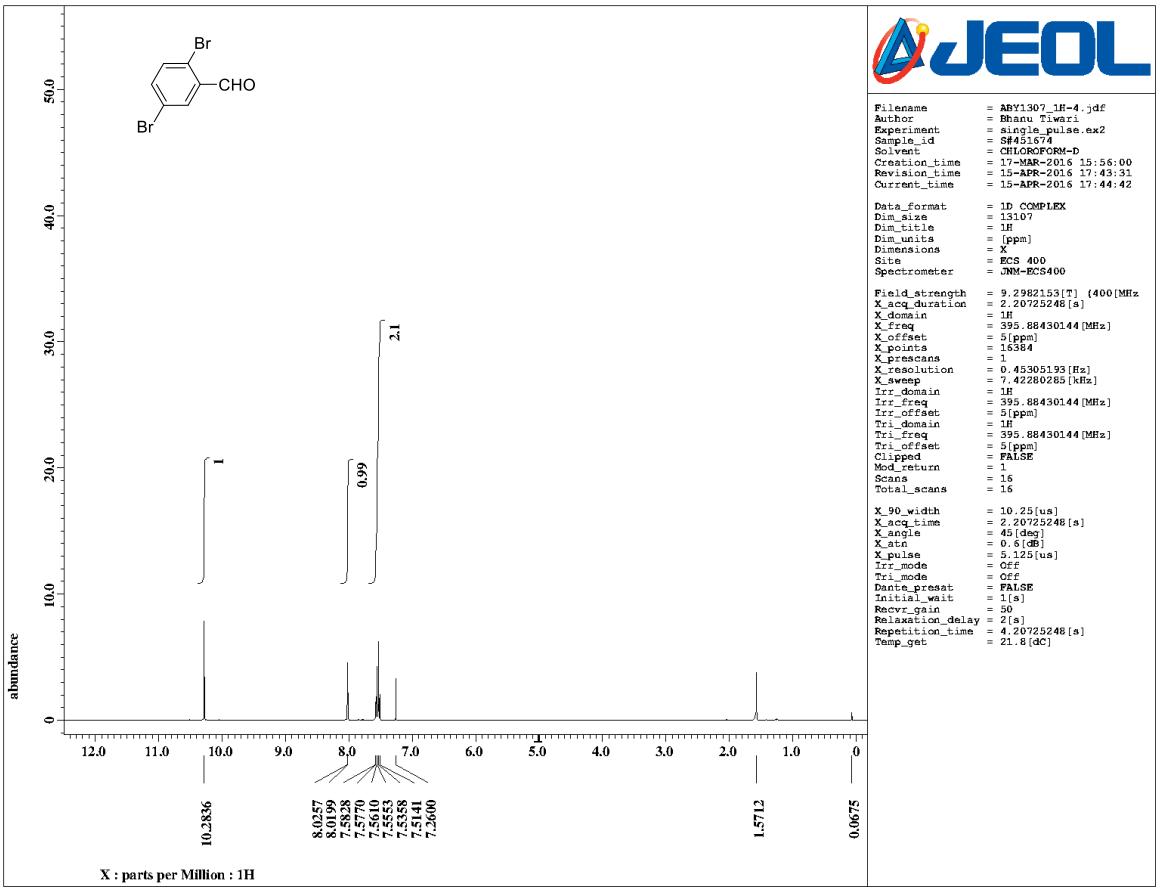


Fig. S18 ^{1}H NMR spectrum of 2,5-dibromobenzaldehyde in $CDCl_3$.

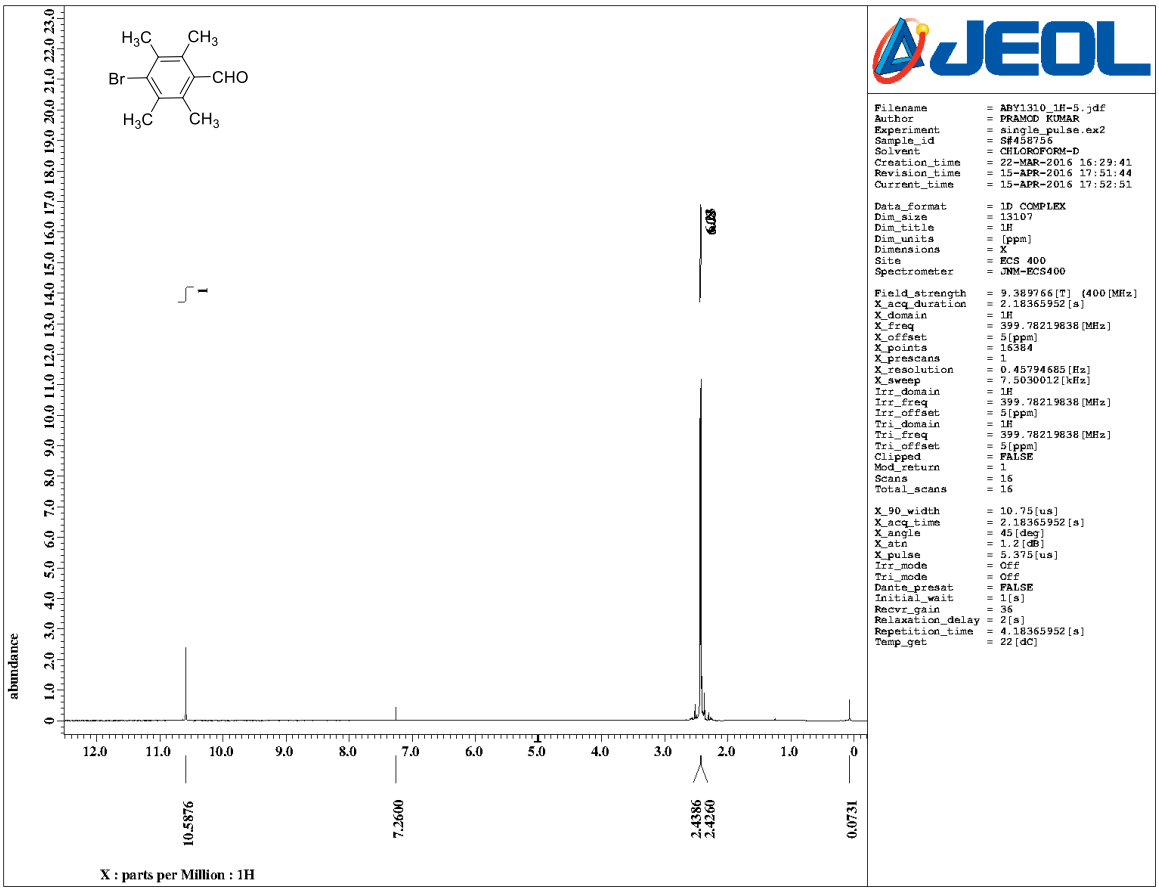


Fig. S19 ^{1}H NMR spectrum of 4-bromo-2,3,5,6-tetramethylbenzaldehyde in $CDCl_3$.

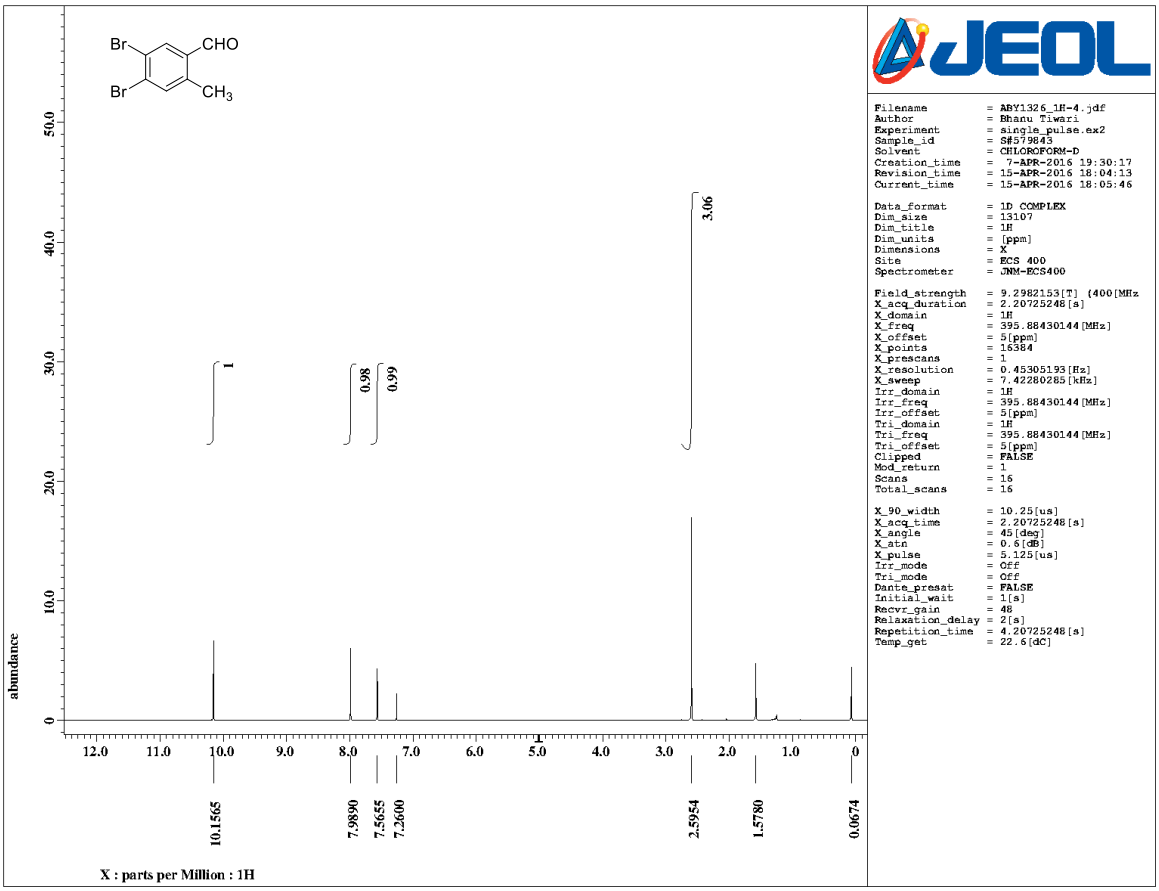


Fig. S20 ^{1}H NMR spectrum of 4,5-dibromo-2-mehtyl-benzaldehyde in $CDCl_3$.

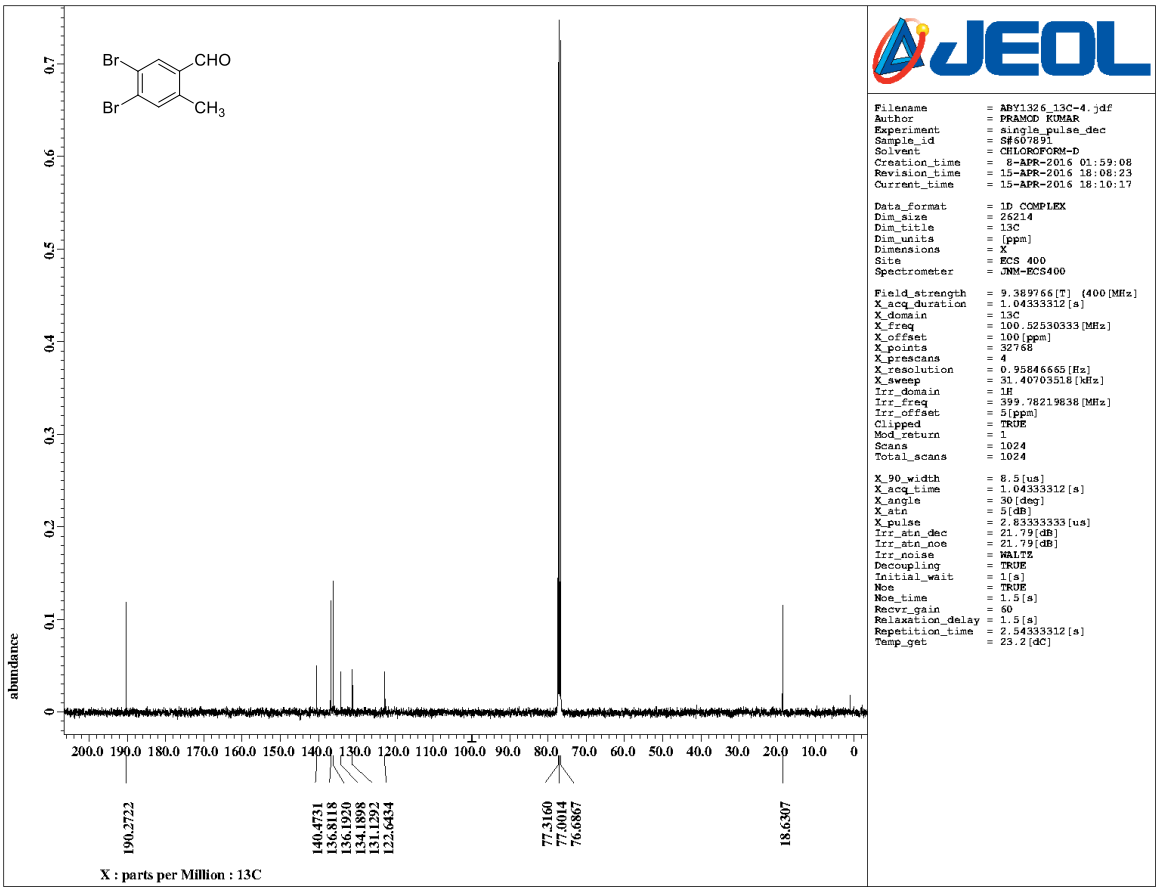


Fig. S21 ^{13}C NMR spectrum of 4,5-dibromo-2-mehtyl-benzaldehyde in $CDCl_3$.

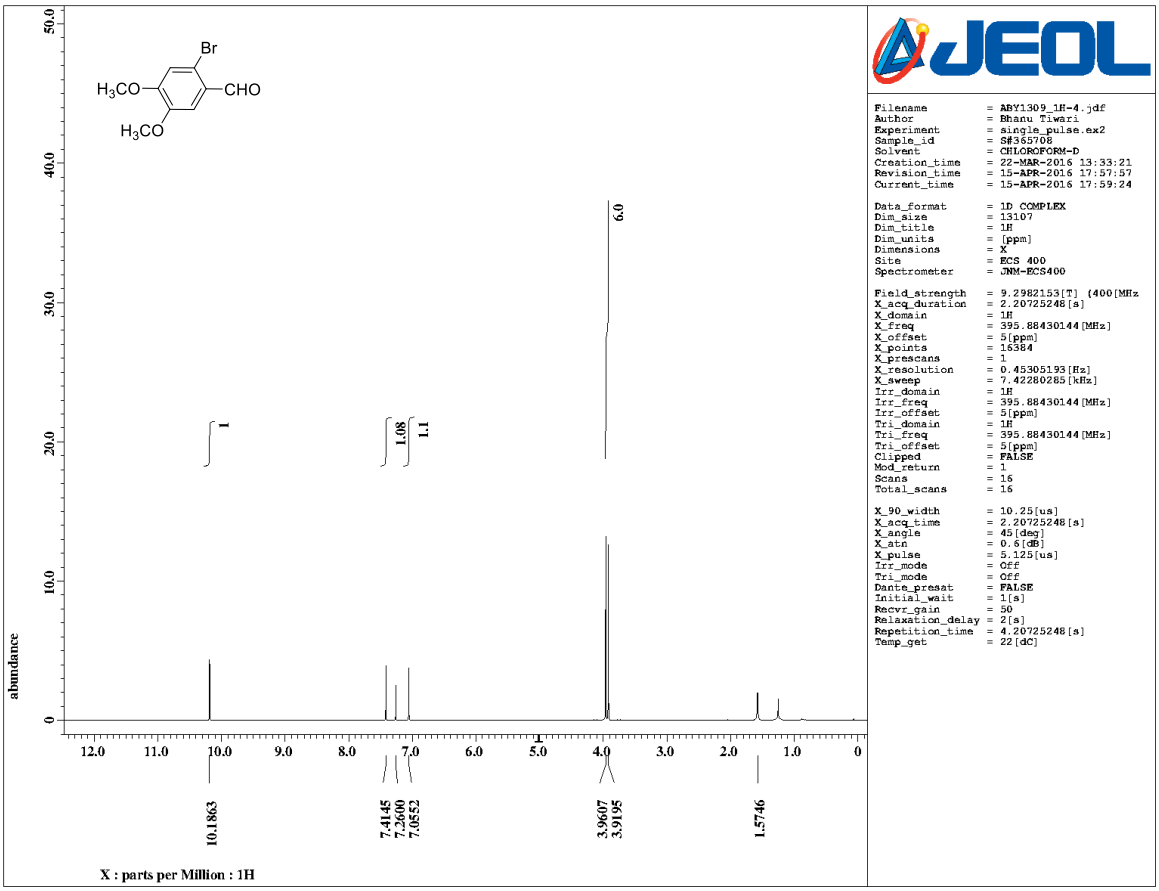


Fig. S22 ^{1}H NMR spectrum of 2-bromo-4,5-dimethoxybenzaldehyde in $CDCl_3$.

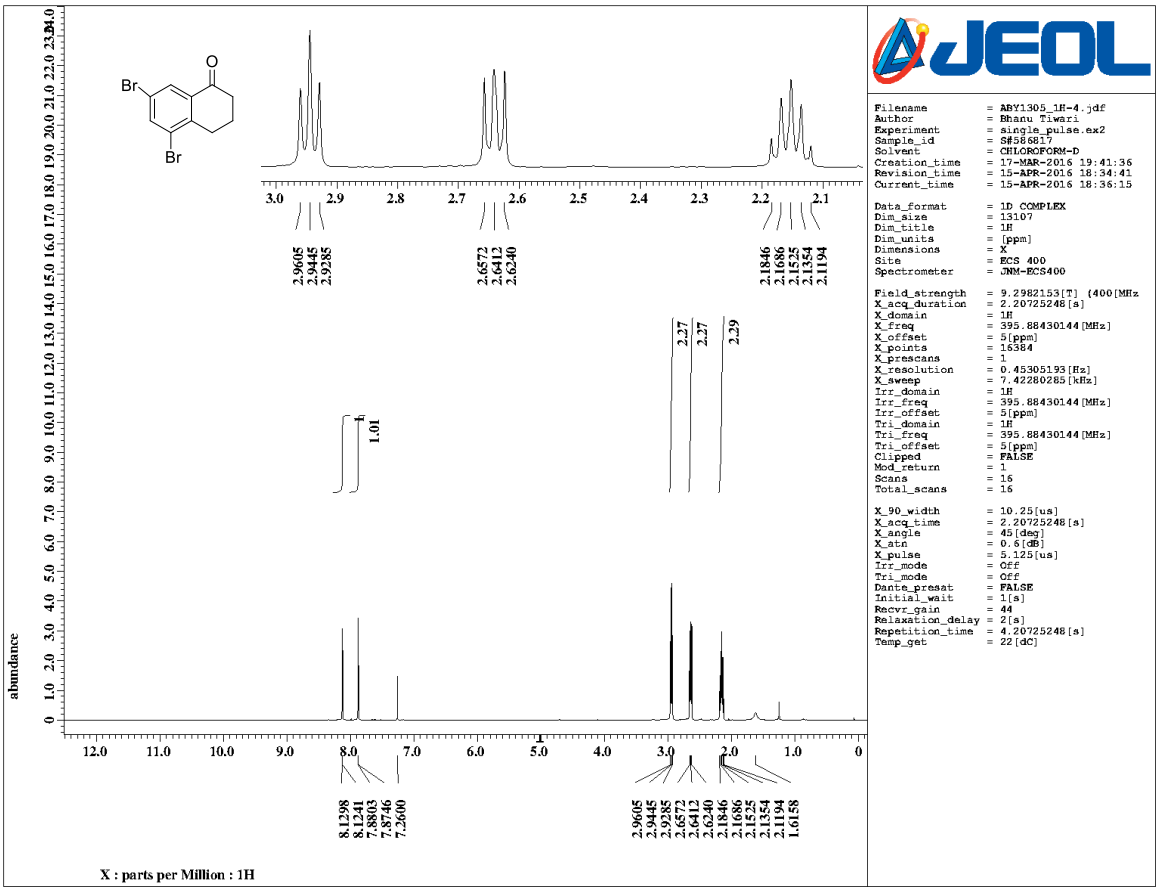


Fig. S23 ^{1}H NMR spectrum of 5,7-dibromo-1-tetralone in $CDCl_3$.

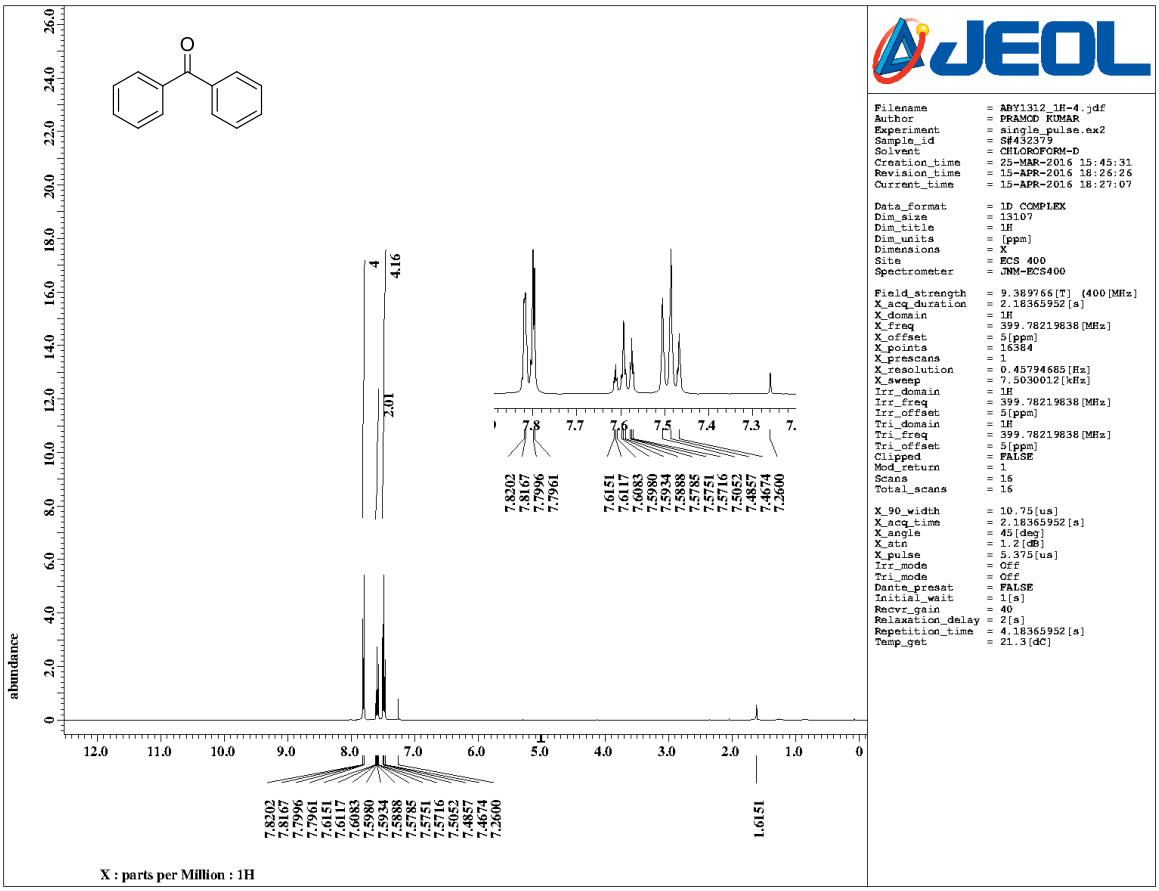


Fig. S24 ^{1}H NMR spectrum of benzophenone in $CDCl_3$.

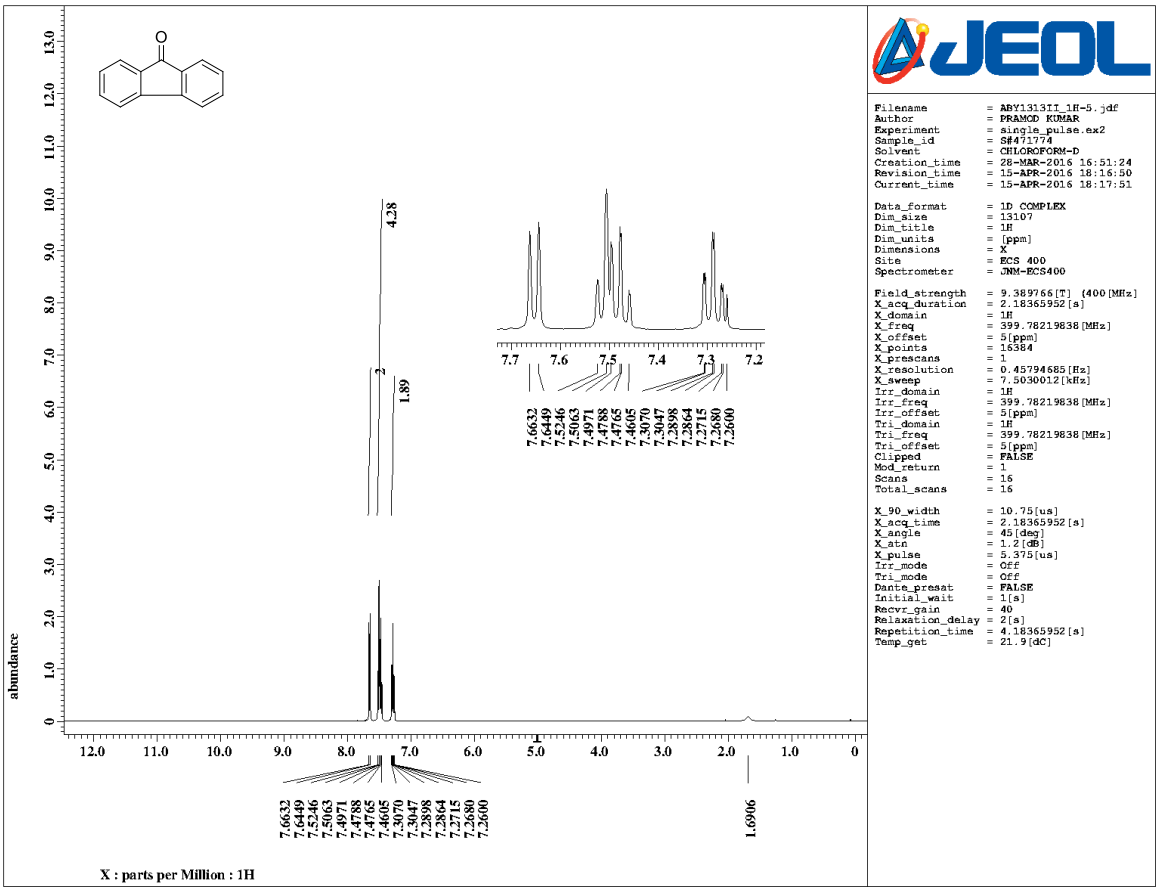


Fig. S25 ^{1}H NMR spectrum of 9-fluorenone in $CDCl_3$.

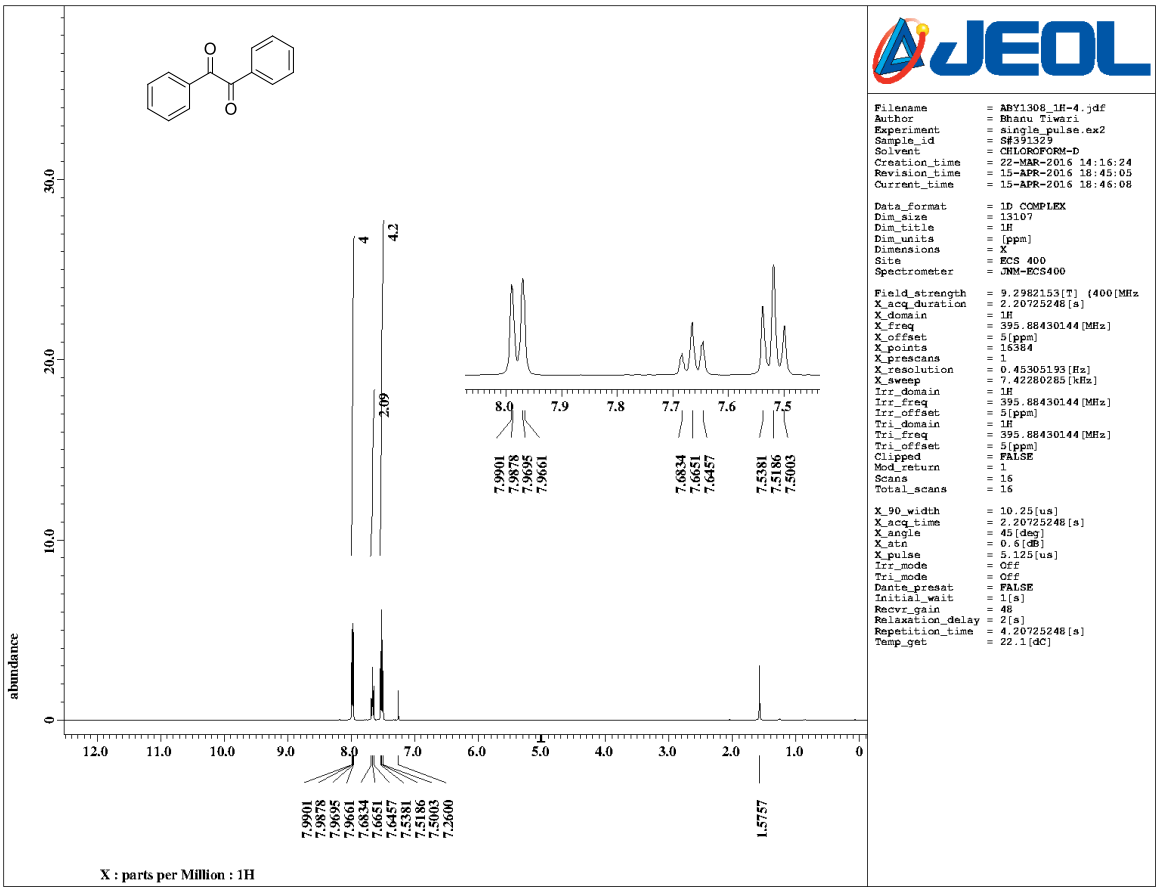


Fig. S26 ^{1}H NMR spectrum of benzil in $CDCl_3$.

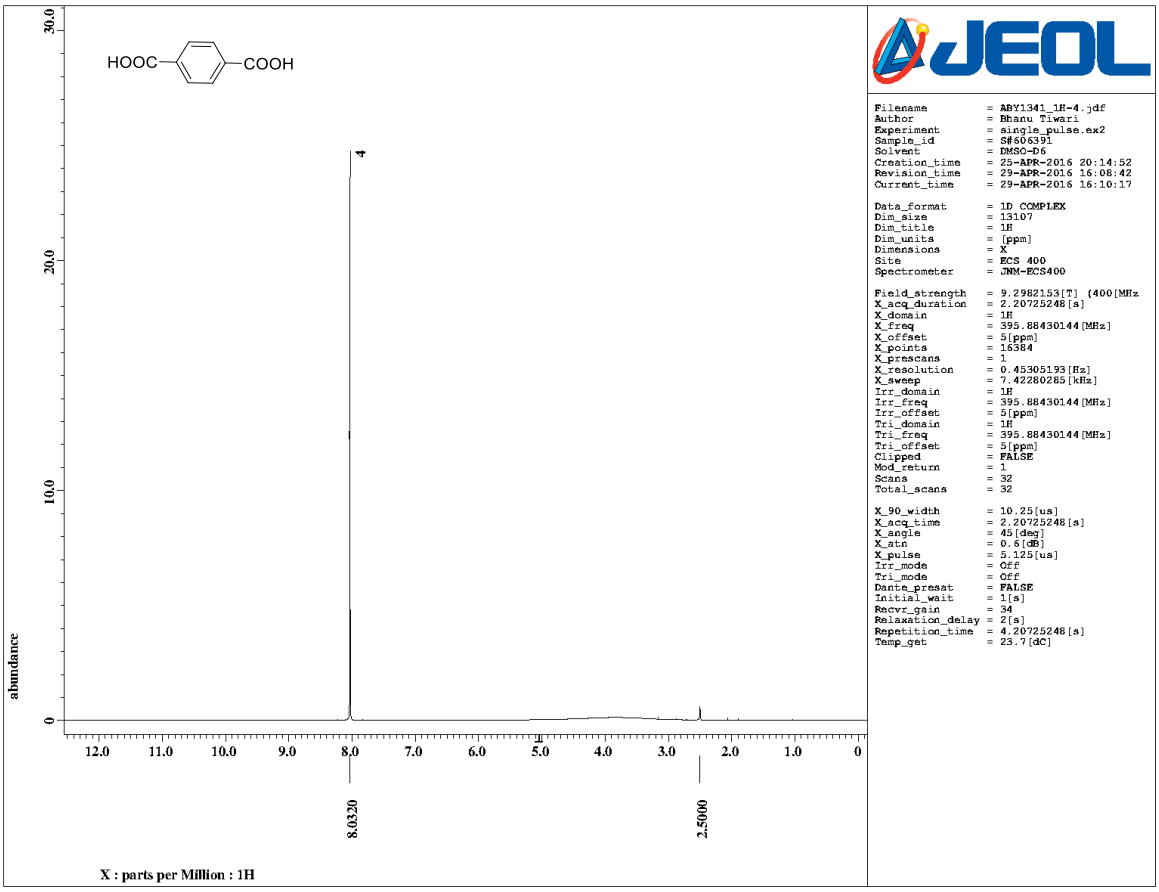


Fig. S27 ^{1}H NMR spectrum of terephthalic acid in DMSO-$d_{6.}$

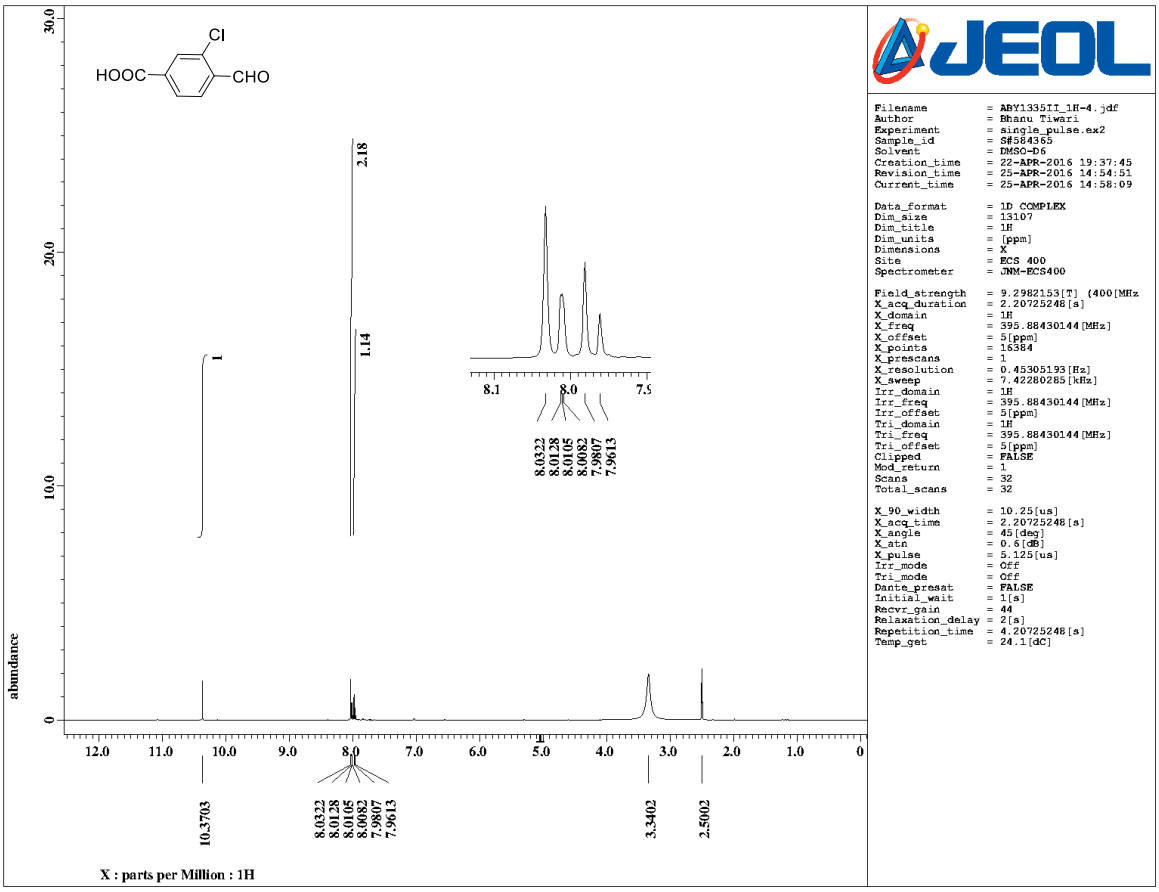


Fig. S28 ^{1}H NMR spectrum of 2-chloro-4-carboxybenzaldehyde in DMSO-d_6.

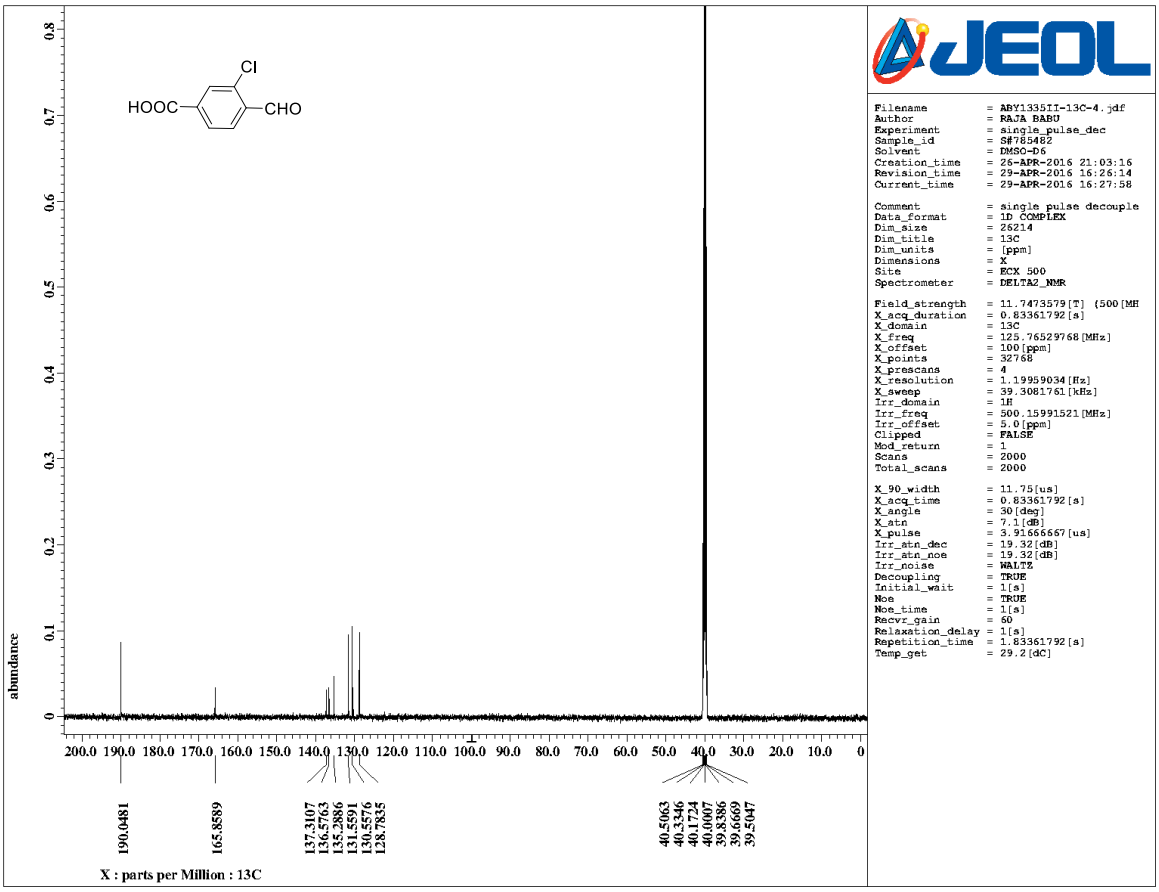


Fig. S29 ^{13}C NMR spectrum of 2-chloro-4-carboxybenzaldehyde in DMSO-d_6.

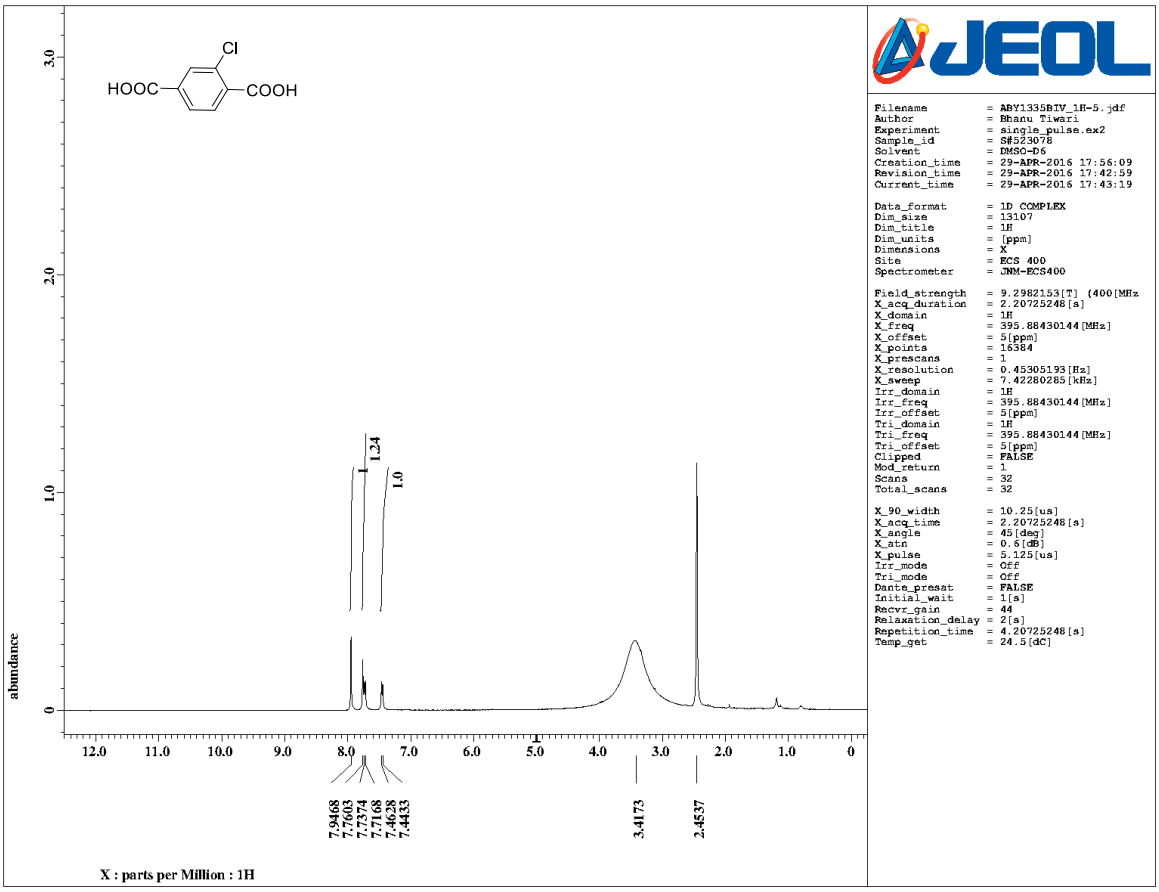


Fig. S30 ^{1}H NMR spectrum of 2-chloroterephthalic acid in DMSO-d_6.

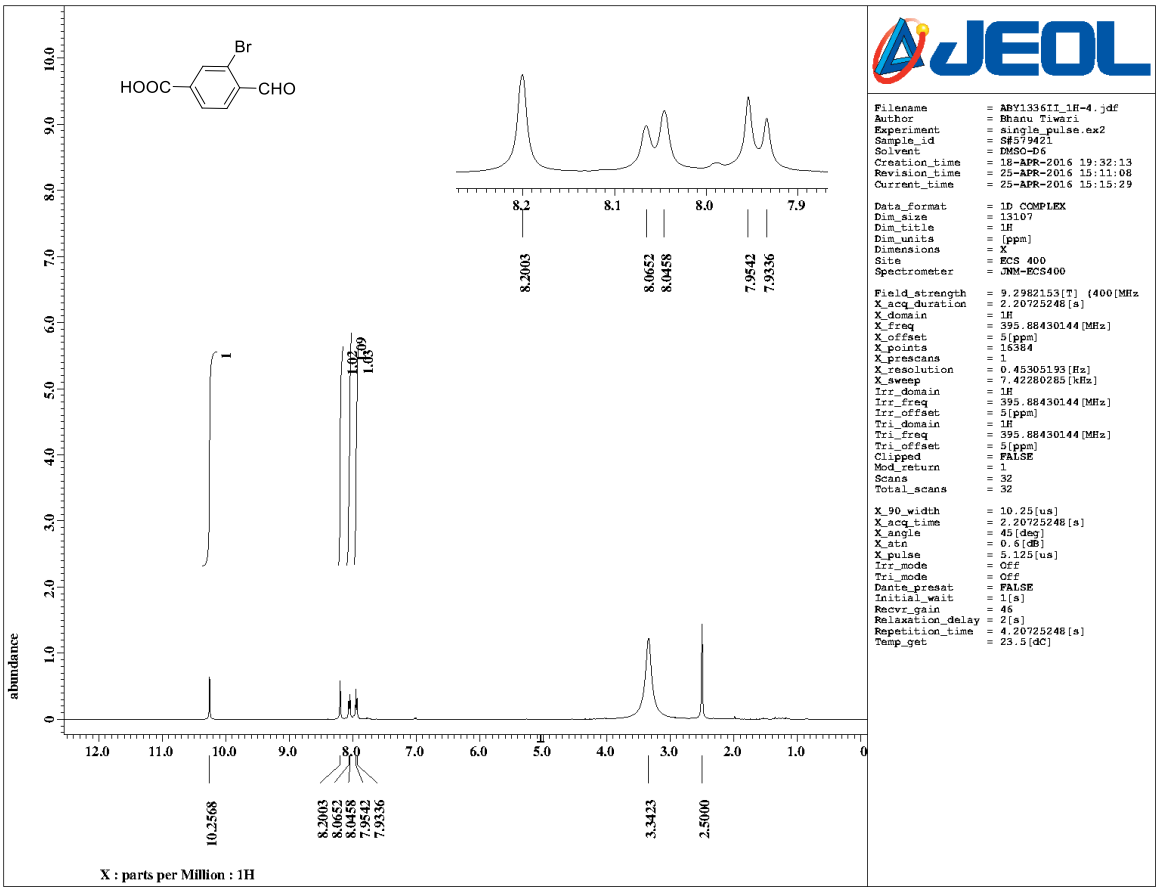


Fig. S31 ^{1}H NMR spectrum of 2-bromo-4-carboxybenzaldehyde in DMSO-d_6.

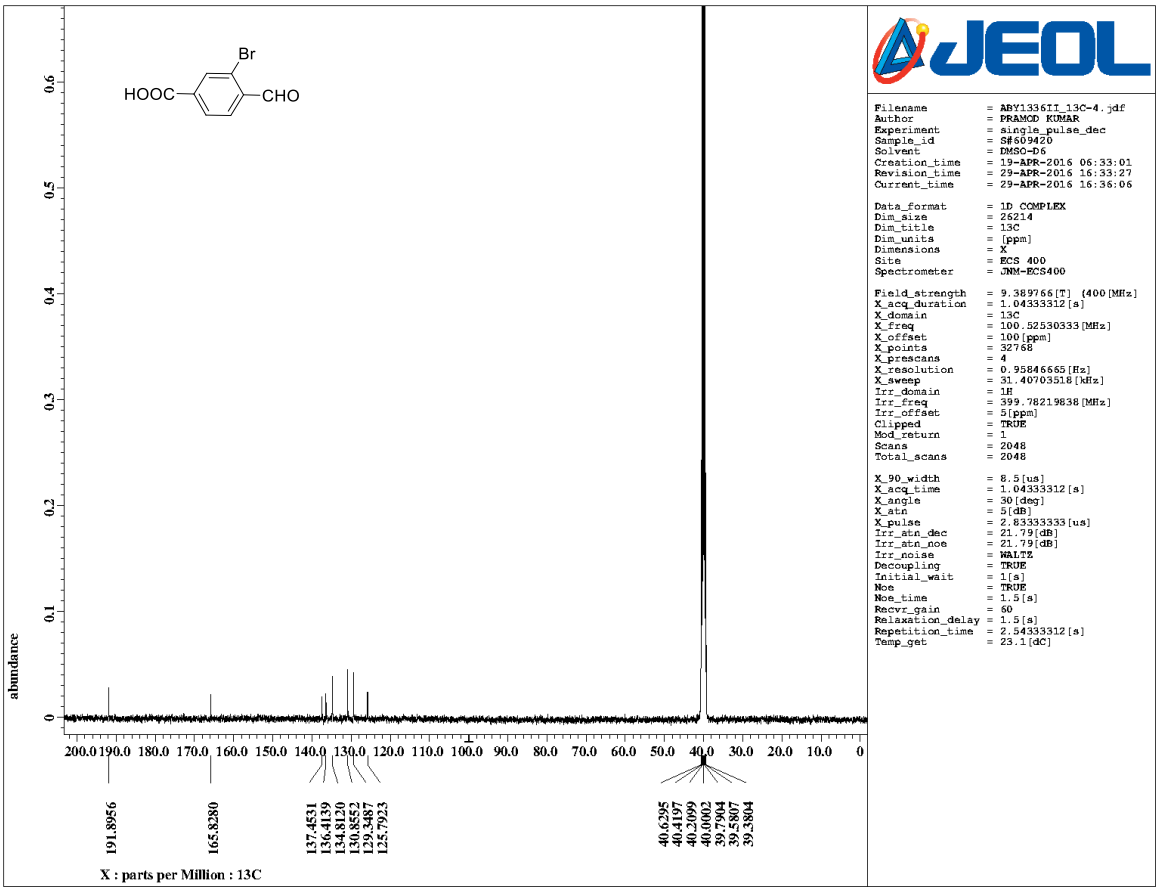


Fig. S32 ^{13}C NMR spectrum of 2-bromo-4-carboxybenzaldehyde in DMSO-d_6.

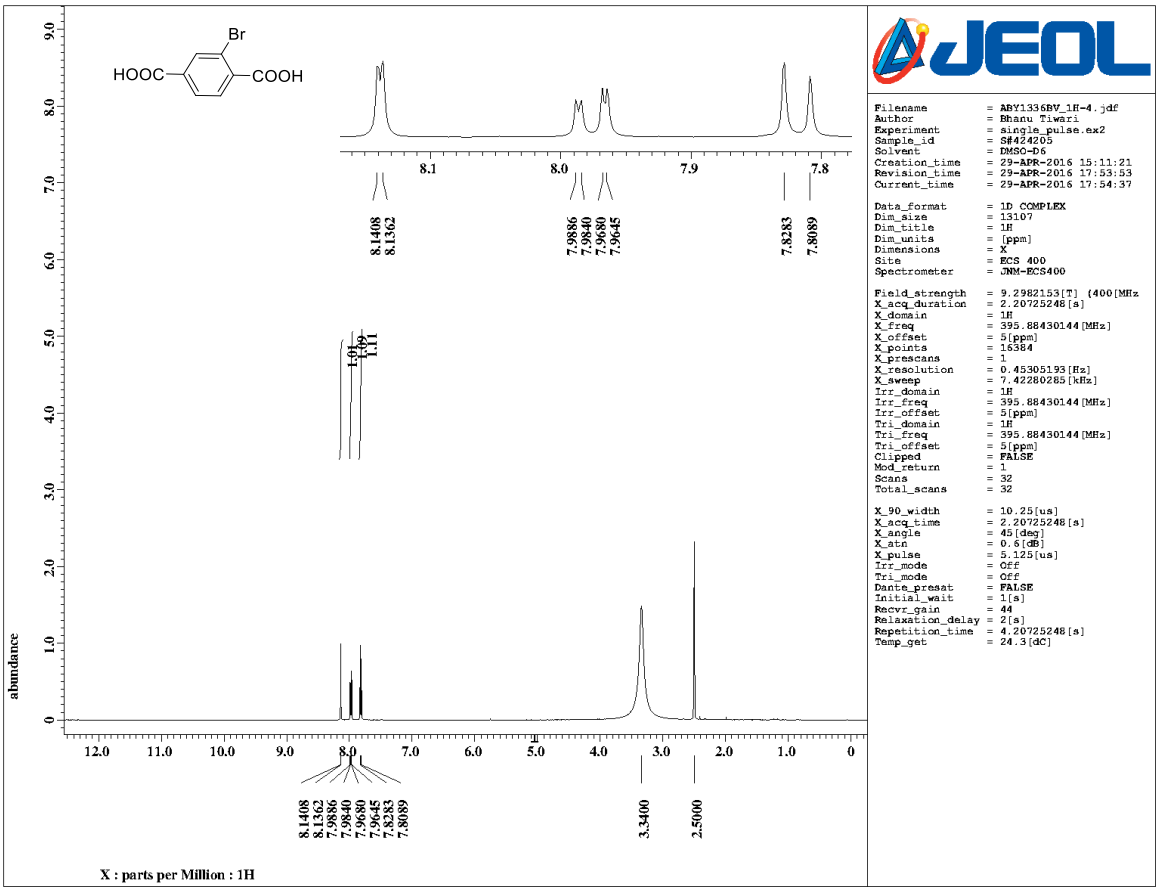


Fig. S33 ^{1}H NMR spectrum of 2-bromoterephthalic acid in DMSO-d_6.

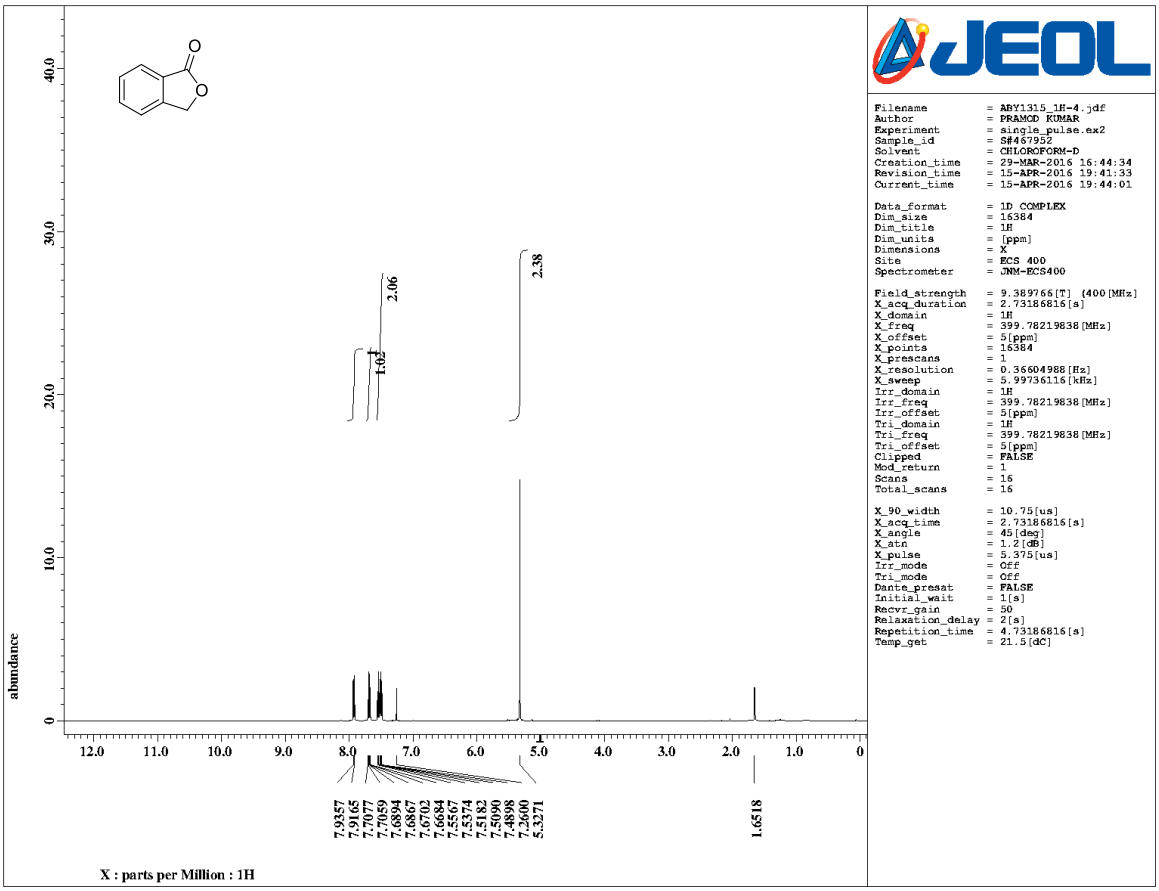


Fig. S34 ^{1}H NMR spectrum of phthalide in $CDCl_3$.

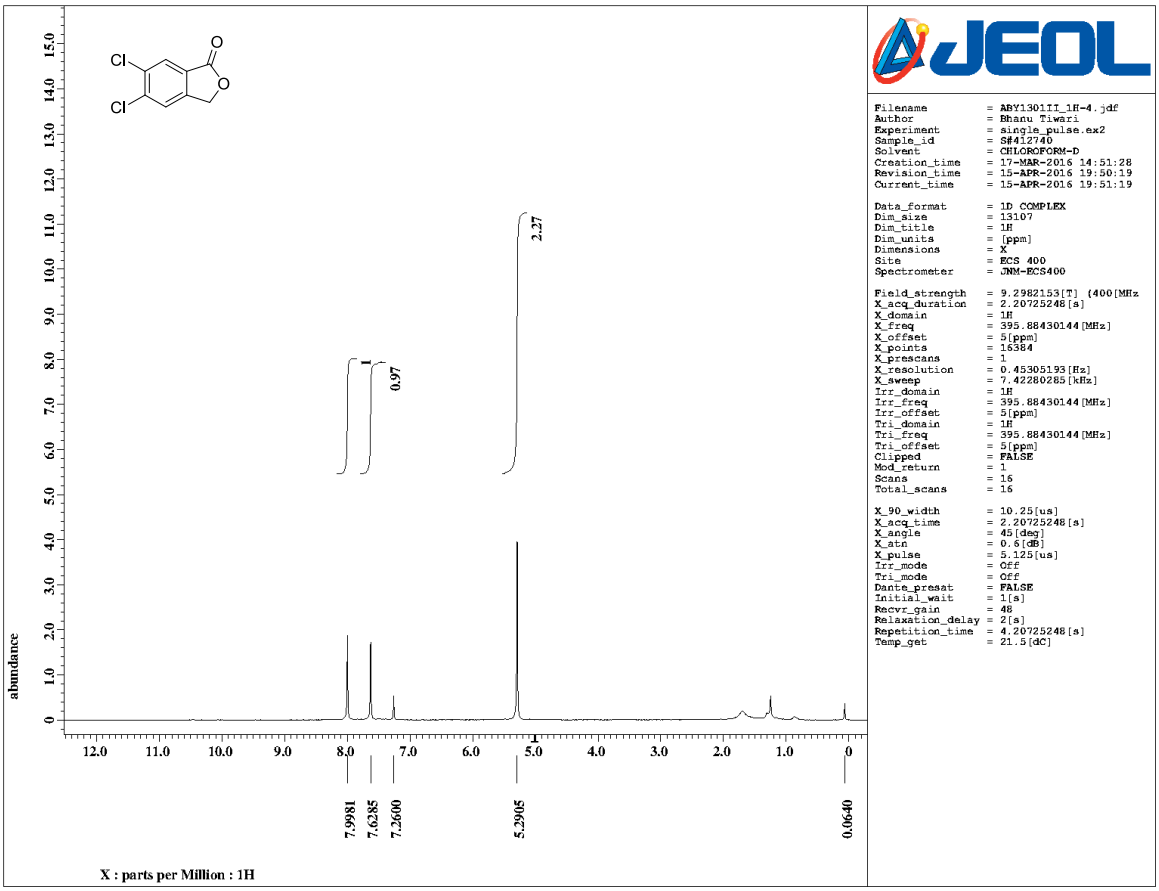


Fig. S35 ^{1}H NMR spectrum 5,6-dichlorophthalide in $CDCl_3$.

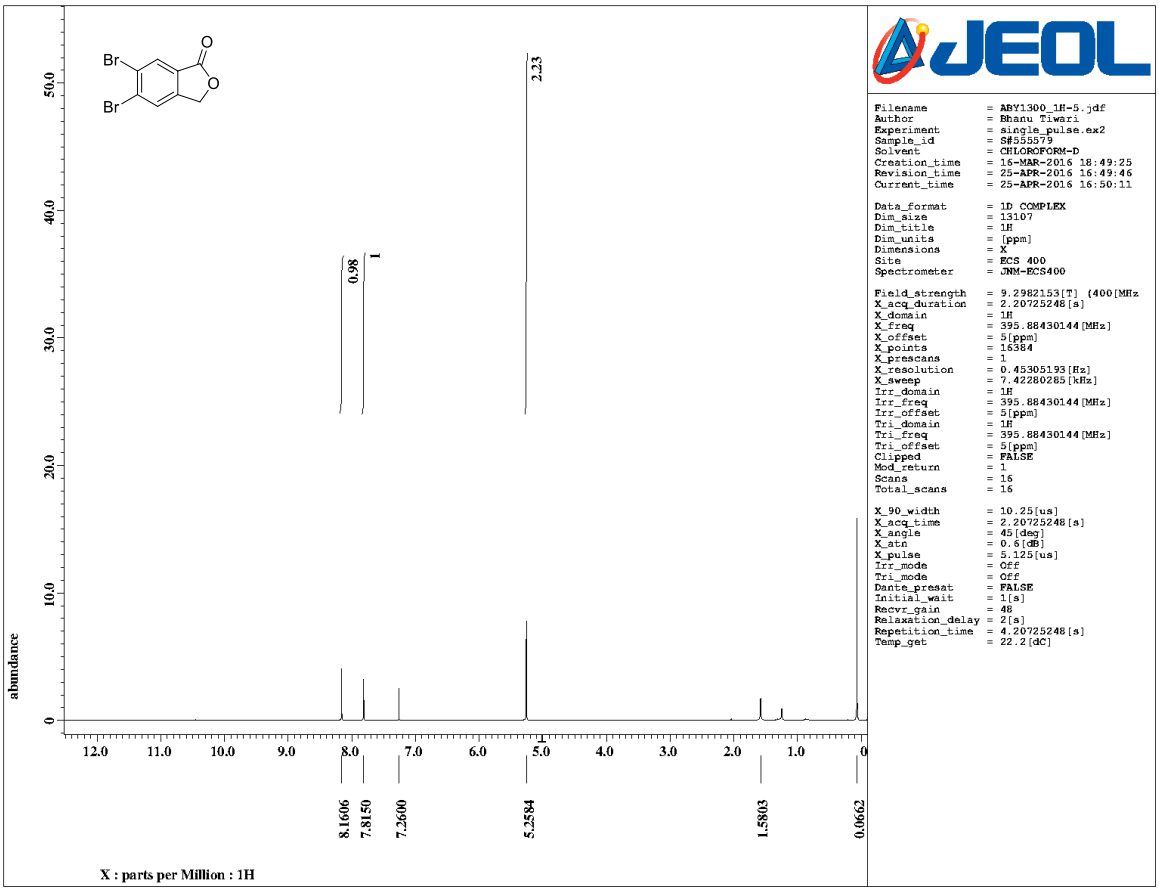


Fig. S36 ^{1}H NMR spectrum of 5,6-dibromophthalide in $CDCl_3$.

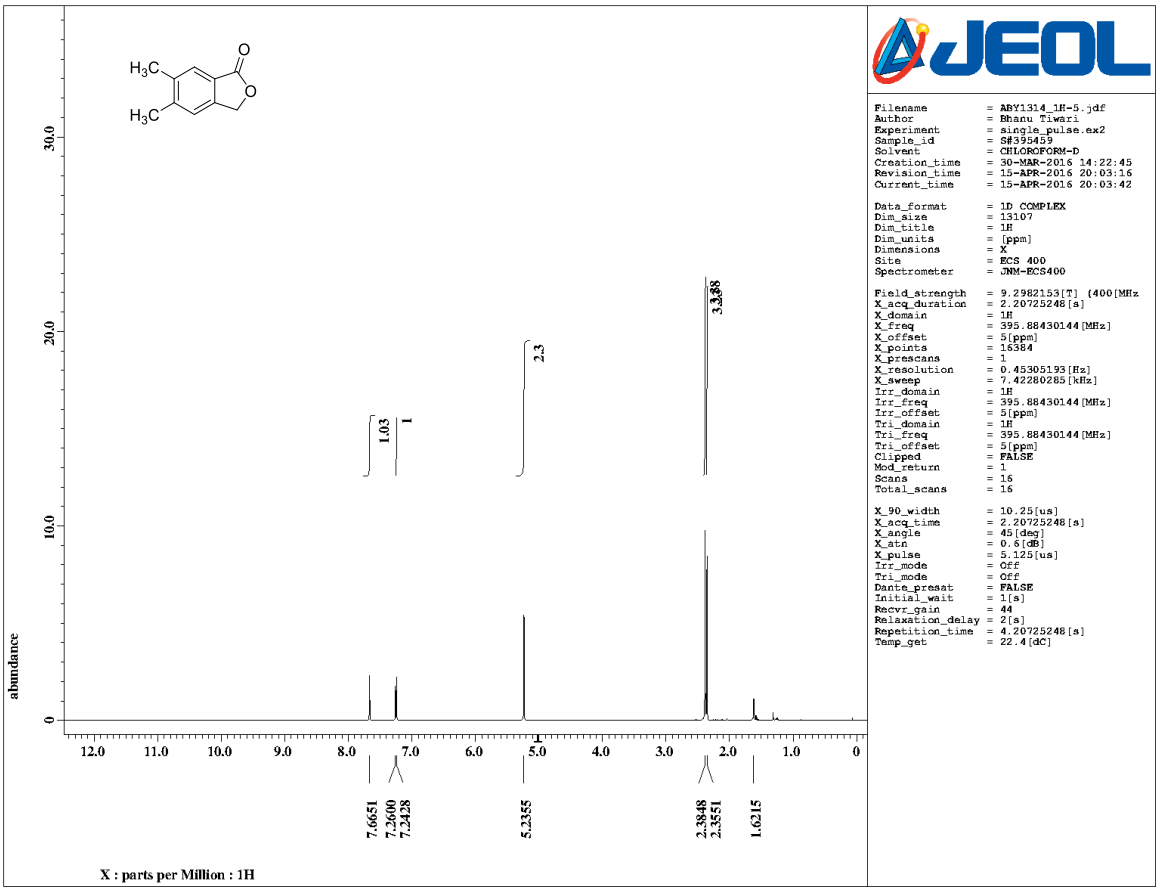


Fig. S37 ^{1}H NMR spectrum of 5,6-dimethylphthalide in $CDCl_3$.

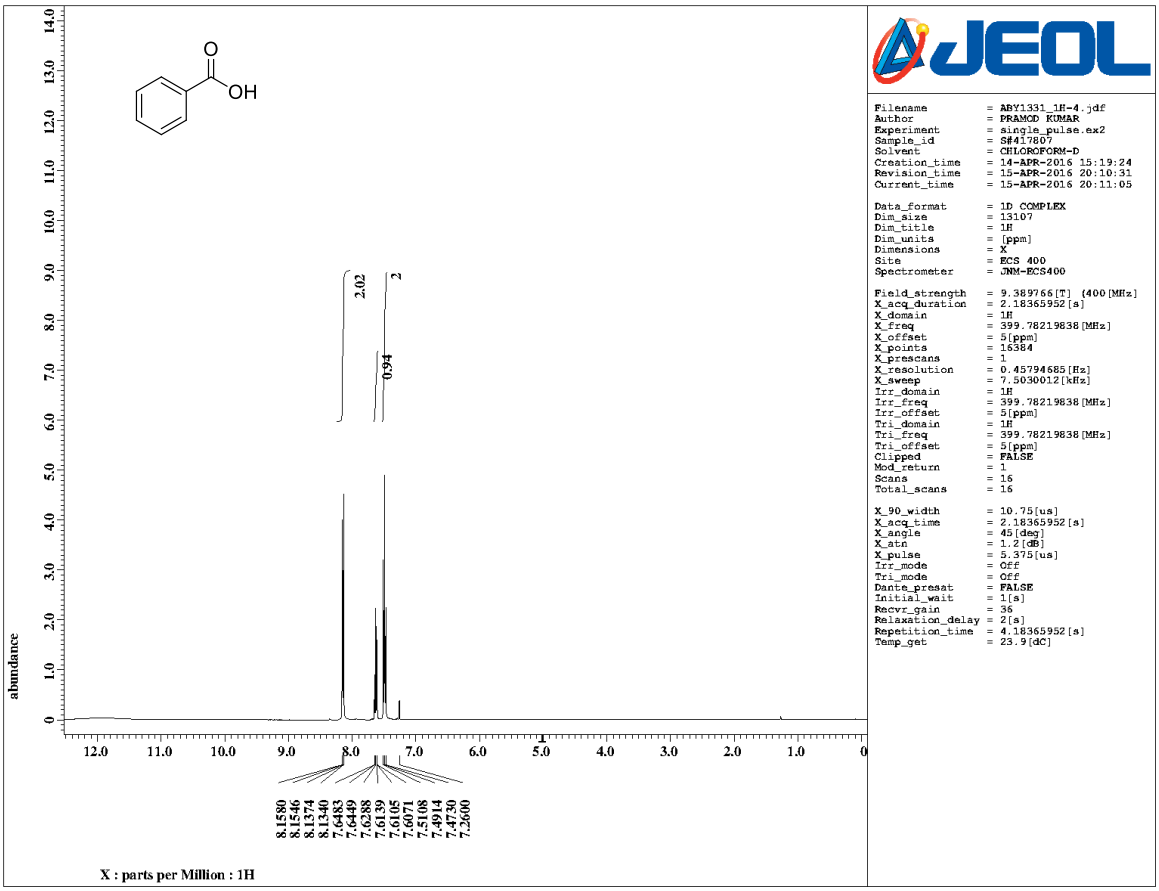


Fig. S38 ^{1}H NMR spectrum of benzoic in $CDCl_3$.

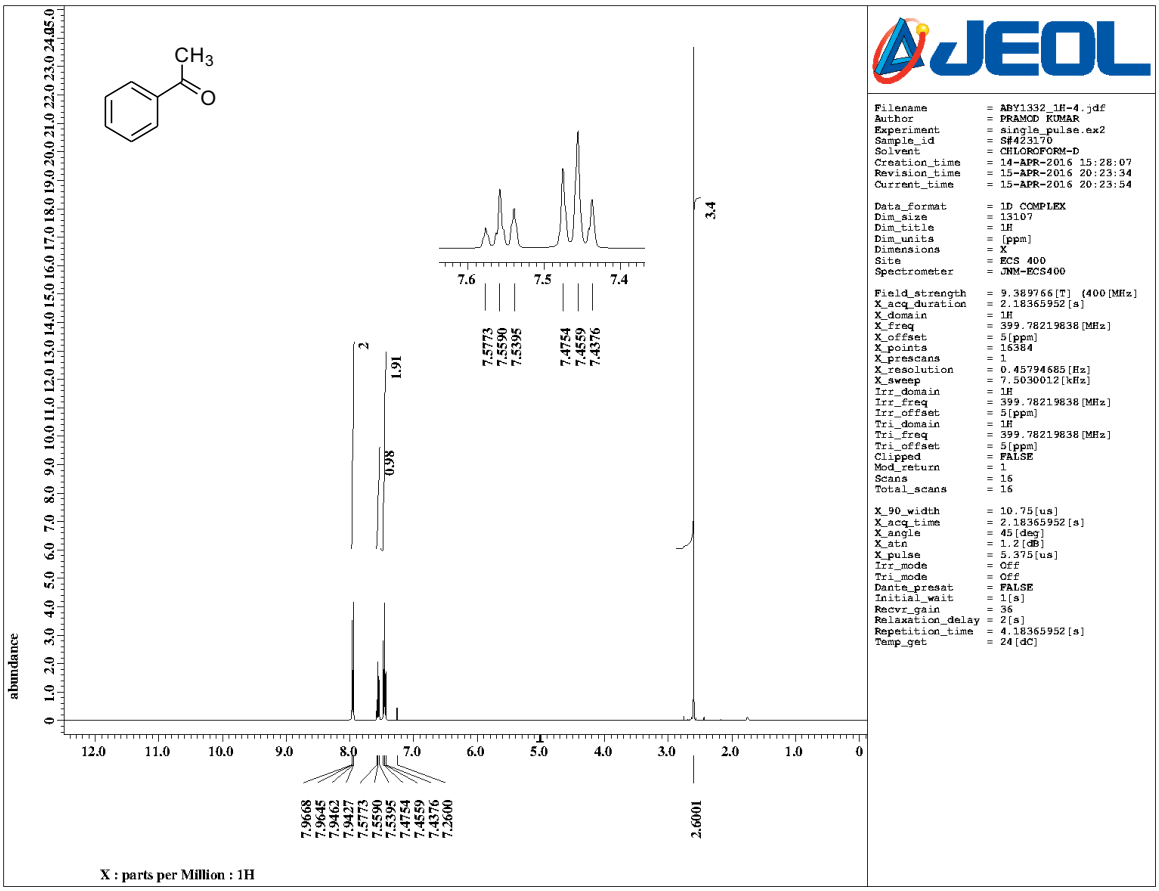


Figure S39. ^{1}H NMR spectrum of acetophenone in $CDCl_3$.